ABSTRACT

Title of Dissertation: AB INITIO MODELING OF THE SELECTIVITY AND REACTIVITY OF BOTH THERMAL AND LIGHT MEDIATED ORGANIC AND ORGANOMETALLIC TRANSFORMATIONS

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The mechanism of a reaction is the collection of events that take place that lead to the products of a chemical transformation. Though there are some events in a chemical reaction that can be observed by experiment, such long-lived intermediates, many of the events are too short lived to be measured. Due to these restrictions and the advancements in the development of moderately scaling computational tools, it is becoming commonplace to use quantum mechanical software packages to model the mechanism of a reaction. Here, I used quantum mechanical calculations alongside experimental evidence provided by multiple collaborators to understand the reactivity of both heat- and light-mediated organic transformations. In chapter 2, I investigated the role of electron donor-acceptor complexes in the generation of alkyl and acyl radicals in the presence of visible light. In addition, the pathways to the experimentally observed products, alkyl and acyl thioethers, were modeled. The lowest energy pathway to product, post-radical generation, was radical addition to the radical electron donor-acceptor complex. For a photoredox-catalyzed

method to cyclopropanes from a novel halomethyl radical precursor (Chapter 3), computations strongly supported a redox-neutral reductive radical/polar crossover mechanism over radical pathways, consistent with experimental trends. Investigation of the isomerization of cinnamyl chloride to cyclopropane via a commonly used photoredox catalyst (Chapter 4) revealed that the reaction was mediated via dexter energy transfer between photocatalyst and substrate over the more commonly proposed electron transfer, affording diastereoselective product formation. A dual nickel/photoredox-catalyzed coupling of sulfinate salts and aryl halides gave a mixture of aryl sulfide and aryl sulfone products (Chapter 5), suggesting that disproportionation of sulfone radical was leading to the formation of thiyl radical. Modeling the product determining steps indicated that the product distribution was controlled by radical addition of the thiyl radical to the nickel(II) species versus reductive elimination of the sulfone bound to the nickel(III) catalyst. A bicyclo[1.1.1]pentane diborylated with pinacolboryl groups, one at the arm and head position, was found to have reactivity only at the bridgehead position (Chapter 6). Calculations of a hydrozone coupling reaction performed by the Qin group found that the reactivity was due to the unique hybridization of the bridgehead position as well as increased steric interactions at the arm position. Finally, a sulfoxide synthesized from a sulfinate salt could be activated with Grignard reagent, affording coupling of the substituents originally bound to the sulfoxide. DFT calculations validated the role of the sulfurane intermediate acting as a mediator to the coupled product.

AB INITIO MODELING OF THE SELECTIVITY AND REACTIVITY OF BOTH THERMAL AND LIGHT MEDIATED ORGANIC AND ORGANOMETALLIC TRANSFORMATIONS

by

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Table of Contents

Acknowledgements ii
Table of Contents ii
List of Tables v
List of Figures vi
Abbreviations ix
Chapter 1: Application of Density Functional Theory to Synthetic Transformations 1
1.1 Introduction 1
1.2 Theory 2
1.2.1 Hartree-Fock Theory 2
1.2.2 Post-Hartree-Fock Methods 6
1.2.3 DFT 7
1.2.4 Time-Dependent DFT 11
1.2.5 Domain Based Local Pair Natural Orbital Coupled Cluster Theory Single, Double and Perturbative Triple Excitations 11
1.2.6 Basis Set 12
1.2.7 Implicit Solvation Models 13
1.3 Application of DFT 13
Chapter 2: Mechanism of Trifluoromethylthiolation mediated by Electron Donor-Acceptor Complex 15
2.1 Introduction 15
2.2 Methods 20
2.3 Results and Discussion 21
2.3.1 Experimental Work 21
2.3.2 Computational Work 26
2.4 Conclusion 39
Chapter 3: Elucidation of Radical/Polar Crossover Mechanism for the Redox-Neutral Photocatalyzed Cyclopropanation 40
3.1 Introduction 40
3.2 Methods 44
3.3 Results and Discussion 45
3.3.1 Pre-Computation Experimental Work 45

3.3.2 Computational Work 48
3.3.3 Post-Computation Experimental Work 53
3.4 Conclusion 56
Chapter 4: Mechanistic Investigation into the Photocatalyzed Diastereoselective Isomerization of Cinnamyl Chlorides to Cyclopropanes 57
4.1 Introduction 57
4.2 Methods 60
4.3 Results and Discussion 60
4.3.1 Pre-Calculation Experimental Work 60
4.3.2 Computational Work 62
4.3.3 Post-Calculation Experimental Work 67
4.3.4 Spectroscopy 71
4.4 Conclusion 74
Chapter 5: Origins of Product Selectivity in the Dual Ni/Photoredox Catalyzed Coupling of Sulfinate Salts and Aryl Halides 76
5.1 Introduction 76
5.2 Methods 80
5.3 Results and Discussion 80
5.3.1 Experimental Work 80
5.3.2 Computational Work 85
5.4 Conclusion 87
Chapter 6: Understanding the Reactivity of Bicyclopentane bis-Boronate via DFT 89
6.1 Introduction 89
6.2 Methods 91
6.3 Results and Discussion 92
6.3.1 Pre-Computation Experimental Work 92
6.3.2 Computational Work 93
6.3.3 Post-Computation Experimental Work 97
6.4 Conclusion 100
Chapter 7: Understanding the reactivity of Alkyl Sulfinate Mediated Cross-Coupling 102
7.1 Introduction 102
7.2 Methods 105
7.3 Results and Discussion 105
7.3.1 Experimental Work 105

7.3.2 Computational Work 107
7.4 Conclusion 110
Chapter 8: Conclusion and Future Work 111
8.1 Conclusion 111
8.2 Future Work 115
Appendix 1: Supporting Information Chapter 2 117
Appendix 2: Supporting Information Chapter 3 202
Appendix 3: Supporting Information Chapter 4 257
Appendix 4: Supporting Information Chapter 5 319
Appendix 5: Supporting Information Chapter 6 357
Appendix 6: Supporting Information Chapter 7 391
Bibliography 440

List of Tables

Table 2.1: Selected Substate Scope of Trifluoromethylthiolation via Alkyl-DHPs.....22
Table 2.2 Selected Substate Scope of Trifluoromethylthiolation via Acyl-DHPs 23
Table 2.3 Effect of the DHP Backbone on Yield 24
Table 3.1: Selected Substrate Scope of CF_3-Substituted Alkenes.....46
Table 3.2: Cyclopropanation of Diverse Olefins.....47
Table 3.3: Comparison Chloromethyl and Iodomethyl Silicates 54
Table 4.1: Initial Results by Testing Various Photocatalysts.....61
Table 4.2: Selected Substrate Scope.....69
Table 5.1: Initial Attempts at Sulfinate Cross Coupling 81
Table 5.2: Selected Substrate Scope of Diaryl Sulfonates 83
Table 6.1: Select Examples of Selective C3-Bpin functionalization of BCP Bis-boronates 99
Table 7.1: Selected Substrate Scope of Sulfone Mediated Cross-Coupling. 106

List of Figures

Figure 2.1: Envisioned decarboxylative trifluoromethylthiolation of aldehyde feedstocks; PC = photocatalyst. 16
Figure 2.2: Theory behind EDA complexes. Black and red solid lines indicate ground and excited adiabatic states while dash blue and green lines indicate diabatic states. H_{DA} = electron coupling between donor and acceptor state and λ = reorganization energy, k_B = Boltzmann's constant, T = temperature, ħ = Planks constant divided by 2π and k_{et} = rate of electron transfer. 18
Figure 2.3: Minisci byproduct formation in the presence of a terminal oxidant 25
Figure 2.4: Energetics of competing light-promoted alkyl radical formation (free energies [DLPNO-CCSD(T)/def2-TZVPP// UB3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol). Calculations performed by Ryan Dykstra. 26
Figure 2.5: Excited state potential energy surfaces of paths B and C and visualization of lowest-lying excitations. (A) Free energies of excited state molecules computed using TD-DFT, relative to free energy of ground state molecules computed using DFT [B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Wavelengths of excitations computed relative to ground state electronic structure using total energy. Bond distances are labeled in Ångstroms. Path B results in intermediate **A²** while Path C results in intermediate **D²**. Calculations performed by Ryan Dykstra. 27
Figure 2.6: Molecular orbitals of the largest contributing transitions (Transitions) and electron density difference maps (EDDMs) of lowest lying singlet excited states as indicated. Isovalues for molecular orbitals and EDDMs are 0.02 and 0.0004 e- /au3, respectively. 29
Figure 2.7: Reaction coordinate diagram to product with EDA complex. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Barrier height of D2-TS-E1 discussed in text. Calculations performed by Ryan Dykstra 30
Figure 2.8: Rearrangment from charge-separated EDA complex **F¹** to hydrogen bonding complex **G¹** and subsequent deprotonation **G¹-TS-H¹** to separated pyridine **I¹** and phthalimide **J¹**. Calculations performed by Ryan Dykstra. 31
Figure 2.9: Reaction coordinate diagram to product post dissociation of EDA complex. Calculations performed by Ryan Dykstra. 32
Figure 2.10: Energetics of radical addition of alkyl radical to sulfur dimer. Free Energies [DLPNO-CCSD(T)/def2-TZVPP// B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Calculations performed by Ryan Dykstra. 33
Figure 2.11: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra. Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra. 34
Figure 2.12: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra. 35
Figure 2.13: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical (part 2). Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-

CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra. 37
Figure 3.1: Cyclopropane containing pharmacons and trifluromethyl-substituted cyclopropanes. 40
Figure 3.2: Synthetic stratedgy to access TFCps. 42
Figure 3.3: Radical/Polar Crossover Mechanism of Cyclopropanation. 43
Figure 3.4: Influence of halogen of radical precursor on product distribution of 3 and 4. Product rations determined by 19F NMR. Sythesis performed by the Molander group. 45
Figure 3.5: Barriers and thermodynamics of S_H2 cyclization vs. E1cB of fluorine. I performed all calculations. 49
Figure 3.6: Barriers and thermodynamics of product for S_N2 cyclization vs Ec1B release of fluorine. I performed all calculations. 50
Figure 3.7: Barriers and thermodynamics of product for S_N2 cyclization vs Ec1B release of fluorine. I performed all calculations. 51
Figure 3.8: Barriers and thermodynamics of S_N2 cyclization vs radical ring opening of cyclopropane substituted olefin. I performed all calculations. Bracketing experiment performed by the Molander group. 52
Figure 3.9: Proposed mechanism for cyclopropanation 55
Figure 4.1: Classical methods to synthesize cyclopropanes. 57
Figure 4.2: Energetically uphill isomerization of acyclic compounds to strained cyclopropanes. 58
Figure 4.3: Mechanism of Energy Transfer. 59
Figure 4.4: Early studies of photochemical isomerization of allylic chlorides. 61
Figure 4.5: Proposed mechanism (and DFT calculations on dichoroine radical mechanism [UM06-2X/DGDZVP-SMD(acetonitrile)]. Pathways were mapped by Robert Martin. 63
Figure 4.6: DFT calculations on diastereoselective radical ring closure of dichoroine radical **11** [UM06-2X/DGDZVP-SMD(acetonitrile)]. Pathways were mapped by Robert Martin. 64
Figure 4.7: Lowest energy excitations to triplet states of photocatalysts and substrate (out of 10 excitations) using TD-DFT [UM062X/DGDZVP-SMD(acetonitrile)]. I computed all excited state calculations. 65
Figure 4.8: Energetics for diastereoselective photocatalytic isomerization. Free energies, in kcal/mol, are from UM06-2X/def2-TZVPP-SMD(acetonitrile) (blue) and DLPNO−CCSD(T)/def2-TZVPP-SMD(acetonitrile) (green) calculations. Geometries of MECP obtained with MECPro. I calculated the reaction coordinate diagram. 66
Figure 4.9: Reaction conditions: photocatalyst (1 mol %), cocatalyst (5 mol %), ligand (6 mol %), **1a** (0.2 mmol), MeCN (1 mL), 4 W blue LED. [a]1H NMR yields. [b]12 mol % 19 was used. Experiments run by the Tambar group. 68
Figure 4.10: Mechanistic control experiments. Experiments run by the Tambar group. 70
Figure 4.11: Proposed mechanism. Spin state of molecule indicated as superscript. 74
Figure 5.1: Sulfone containing therapeutic agents. 76
Figure 5.2: Synthetic methods to access diaryl-/heteroaryl sulfones. 77
Figure 5.3: General mechanism of dual Ni/Photoredox catalysis. SET = single electron transfer, X = halogen. 78
Figure 5.4: Envisioned mechanism of diaryl sulfone synthesis via Ni/photooredox dual catalysis via sulfonate salt radical precursors and possible fates of sulfinyl radicals. SET = single electron transfer and X = halogen. 79

Figure 5.5 A. Reaction coordinate diagram of selectivity-determining steps of diaryl sulfonate and diaryl thiyl cross coupling modeled using DFT. B. Computed barriers and experimentally determined product ratios. I performed all calculations. 86
Figure 6.1: Introduction of BCP Bis-functionalization strategy. [a]Bicyclo[1.1.1]pentanes as benzene bioisosteric 3D-surrogates in drug discovery. [b]Structure-activity relationships (SARs) analysis with BCP scaffold. [c]Programmable and orthogonal functionalization of bridge-substituted BCPs. [d]Reactivity observed with BCP bis-boronate. 90
Figure 6.2: Preliminary Chemoselectivity of BCP bis-boronates. Synthesis done by members of the Tian group. 92
Figure 6.3: Calculations on BCP bis-boronate substrate. [a]Lowest energy conformations located. [b]Relative Energies of natural bond orbitals. I performed all calculations. 94
Figure 6.4: Relative free energies of radical and anionic intermediates generated from 1 and 2 electron reactions. I performed all calculations. 95
Figure 6.5: States of C3- vs C2-addition of BCP bis-boronates in hydrazone coupling. [b]Energy decomposition analysis (EDA) of Transition States in hydrazone coupling. [c]Working hypothesis for selective BCP bis-boronates functionalizations. MC = Mulliken Charge. I performed all calculations. 96
Figure 6.6: [a]Synthesis of BCP BisBpin and [b]representative synthesis of starting material **19**. Synthesis done by the members of the Tian group. 98
Figure 7.1: A. Sulfone mediated cross-coupling via aryl alkyl sulfones. B. Previous method to access to trifluoromethylcyclopropyl substitution on aryl functionalities. 103
Figure 7.2 Isotope labeling experiment for sulfone mediated cross-coupling. 106
Figure 7.3: A. Grignard coordination and equilibrium to lowest energy sulfone Grignard complex. B. Reaction coordinate diagram of direct product formation vs. sulfurane formation. 108
Figure 7.4: Reaction coordinate diagram from sulfurane intermediate to coupled product. 109

Abbreviations

1,4-DiHydroPyridine (DHP)

1,5-CycloOctaDiene (COD)

1,10-PHENanthroline (PHEN)

1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)

(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO)

Becke, 3-parameter, Lee-Yang-Par (B3LYP)

BiCyclo[1.1.1]Pentane (BCP)

Back Electron Transfer (BET)

One carbon reagents (C1 reagents)

Continuum-like Polarizable Continuum Model (CPCM)

Coupled Cluster theory Single, Double and perturbative Triple excitations (CCSD(T))

1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide) (DABSO)

DEFault “second generation” 2 Split Valence Polarization (def2-SVP)

DEFault “second generation” 2 Triple Zeta Valence with two Polarization functions (def2-TZVPP)

Density Functional Theory (DFT)

Dimethyl Sulfoxide (DMSO)

Di-tert-Butyl Azodicarboxylate di-tert-butyl azodicarboxylate (DBAD)

Domain based Local Pair Natural Orbital-Coupled Cluster theory Single, Double and perturbative Triple excitations (DLPNO-CCSD(T))

Electron Density Difference Map (EDDM)

Electron Donor Acceptor (EDA)

Energy Decomposition Analysis (EDA)

FluoroCyclopropyl (FCp)

Generalized Gradient Approximation (GGA)

Highest Occupied Molecular Orbital (HOMO)

High-Throughput Experimentation (HTE)

Light Emitting Diode (LED)

Local Density Approximation (LDA)

Los Alamos National Laboratory 2-Double Zeta (LANL2DZ)

Lowest Unoccupied Molecular Orbital (LUMO)

Metal to Ligand Charge Transfer (MLCT)

Minimum Energy Crossing Point (MECP)

Minnesota 2006 with 2 times the HF exchange (M06-2X)

Molecular Orbital (MO)

Napthalene-1,8-DiAmino Boryl (BDAN)

Natural Bond Orbital (NBO)

Pair Natural Orbital (PNO)

Pinacolboryl (Bpin)

Pople split valence basis set with 6 Gaussians for the core atomic orbitals and the valence atomic orbitals comprising of a linear combination of 3 Gaussians and 1 primitive Gaussian (6-31G)

Pople split valence triple basis set with 6 Gaussians for the core atomic orbitals and the valence atomic orbitals comprising of a linear combination of 3 Gaussians and 2 primitive Gaussians

with diffuse functions on heavy atoms (+) with one set of d and p polarization functions (6-311+G(d,p))

Projected Atomic Orbital (PAO)

Reductive Radical/Polar Crossover (RRPC)

Single Electron Transfer (SET)

Solvation Model Density (SMD)

TetraHydroFuran (THF)

Time Dependent-Density Functional Theory (TD-DFT)

Transition State (TS)

TriFluoroacetic Acid (TFA)

TriFluoromethylCyclobutyl (TFCb)

Trifluoromethyl-substituted Cyclopropane (TFCp)

Tris(2-phenylpyridine)iridium ($Ir(ppy)_3$)

Tris(bipyridine)ruthenium(II) ($Ru(byp)_3$)

ω Becke's 1997 short range Hartree-Fock exchange "X" = ωB97X

Unrestricted = U or u in front of functional

Chapter 1: Application of Density Functional Theory to Synthetic Transformations

1.1 Introduction

Understanding the mechanism is one of the most powerful tools in which a chemist can use to tailor new synthetic transformations. Chemists will usually perform a series of mechanistic experiments to gain insight behind the reactivity as well as the physiochemical properties of the molecules in a given transformation.[1] To better understand the reasons behind the experimental observations, one often turns to modeling the dynamics of the chemical system. The dynamics of macroscopic systems are modeled using classical mechanics, where the energy varies continuously due to the large mass of the system. However, the electrons of microscopic systems are modeled using quantum mechanics due to their small mass.[2] Additional complications such as experimentally immeasurable observables, usually due to short lifetimes of crucial intermediates and transition states, make computational modeling of these transformations necessary to obtain a more complete picture of the mechanism.[1]

To understand the physical properties and reactivities of molecules in a synthetic transformation, we must be able to determine energies, bond distances, etc. of these systems. One-electron systems are solved analytically using the time independent Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}\psi}{\mathrm{d}x} + \mathrm{V(x)}\psi = \mathrm{E}\psi \qquad (1)$$

where ħ is Plank's constant, m is the mass of an electron, V(x) is the potential energy, ψ is the wavefunction and E is the total energy.[2] However, once the system contains more than one electron, the system becomes analytically unsolvable. A series of approximations must be taken to solve these systems numerically. In the following section, these approximations will be discussed.

1.2 Theory

1.2.1 Hartree-Fock Theory

In order to treat the many electron problem, a series of approximations must be taken and theorems described.[3] Originally, the wavefunction is considered to have all information about the system, including the electron and nuclear positions as well as electron spin. The Born-Oppenheimer approximation states that the nuclear and electronic components of the wavefunction can be treated separately. However, the electronic wavefunction depends on the position of the nuclei parametrically which is attributed to the slowness of the nuclei compared to that of the electrons. This makes it so the nuclei can be treated classically while the electrons are treated quantum mechanically. With this approximation, it is possible to map out a potential energy surface with respect to the nuclear coordinates of the system.

The variational method is a method to derive the solution to the time independent Schrödinger equation for a system containing more than one electron. To solve this problem, we use a trial wavefunction in combination with the variational theorem to approximately solve the system. The variational theorem is a simple inequality

$$\langle \psi | \hat{H} | \psi \rangle \geq E_0 \qquad (2)$$

stating that the expectation value of the energy of the system is always greater than or equal to the ground state where ψ is the wavefunction, $\hat{H}$ is the Hamiltonian operator and E_0 is the ground state energy.[3,4] Therefore, as long as a guess solution to the wavefunction decreases the energy, that guess is considered to be a more accurate description of the electronic ground state. The parameters of the trial wavefunction can be optimized to represent a minimum, ensuring the lowest energy solution with that trial wavefunction.[4] Overall, the variational method allows for multiple methods

to be used to find the minima of a state, so long as the method produces a wavefunction that is lower in energy.

As stated previously, the time independent Schrödinger equation cannot be solved analytically for systems containing more than one electron. The Hartree approximation[5]

$$\psi(r_1, \dots r_N) = \prod_{i=1}^{N} \chi_i(x_i), \qquad \langle \chi_i | \chi_i \rangle = 1, \tag{3}$$

describes the wavefunction as a product of normalized one electron orbitals, without describing the electron spin, where ψ is the wavefunction, x is the position of the electron, i is the number of the electron, N is the total number of electrons in the system and χ is the one-electron orbital.[3] This makes the problem numerically tractable, though this form of the wavefunction described here is not antisymmetric.

In order to treat a molecule, the one-electron atomic orbitals (χ) of the atoms in the molecule are made into molecular orbitals (ϕ) by making a linear combination of atomic orbitals[2]:

$$\phi_i = \sum_r c_{ri} \chi_r \tag{4}$$

where ϕ is the molecular orbital, c is the coefficient assigning the contribution of the atomic orbital, χ is the atomic orbital, i is number of the molecular orbitals constructed and r is the value of the atomic orbital. The total number of molecular orbitals made must be equal to the total number of atomic orbitals used to construct them.

It was not until the work by Fock[6] and Slater[7] that the indistinguishability of electrons was incorporated into the solution.[3] As electrons are fermions, the exchange of two of them must result in a wavefunction that changes sign (antisymmetric). By applying the Slater determinant,

$$\Phi(x_1, \dots x_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \phi_1(x_1) & \cdots & \phi_N(x_1) \\ \vdots & \ddots & \vdots \\ \phi_1(x_N) & \cdots & \phi_N(x_N) \end{bmatrix} \tag{5}$$

, to the matrix of one-electron orbitals, the antisymmetric wavefunction is constructed. Φ is the antisymmetric wavefunction, x is the position of the electron, N is the total number of electrons in the system and ϕ is the one-electron orbital. These orbitals are now held to be both normalized and the eigenfunctions are orthogonal to one another, as the newly found operator, discussed below for this method, is Hermitian.[2,3] Additionally, the wavefunction now also contains electron spin.

With the wavefunction described in this way, the Fock operator for a closed shell system is written to obtain the energy from the one electron orbitals:

$$\hat{F}(i) = \hat{h}(i) + \sum_{j=1}^{N/2} [2\hat{J}_j(i) - \hat{K}_j(i)] \quad (6)$$

where $\hat{h}(i)$ is the one-electron operator, $\hat{J}_j(i)$ is the coulomb operator and $\hat{K}_j(i)$ is the exchange operator. The one-electron operator

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A}^{N_{nuclei}} \sum_{i}^{N_{elec}} \frac{Z_A}{|R_A - r_i|} \quad (7)$$

contains both the kinetic energy and potential energy between the nuclei and electrons, where ∇_i^2 is the Laplace operator for the ith electron, A is the Ath nuclei, N_{nuclei} is the total number of nuclei in the system,N_{elec} is the total number of electrons in the system, Z_A is the exact charge of the Ath nuclei, R_A is the positions of the Ath nuclei and r_i is the position of the ith electron. The coulomb operator,

$$\hat{J}_j(i)\phi_i = \phi_i \int |\phi_j|^2 \frac{1}{|r_i - r_j|} dr_{j,} \quad (8)$$

, obtains the coulombic repulsion between the two electrons. ϕ_i is the one-electron molecular orbital of electron i, ϕ_j is the one-electron molecular orbital of electron j and r_i is the position of the ith electron and r_j is the position of the jth electron. The exchange operator obtains the energy due to electron exchange in the antisymmetric wavefunction:

$$\hat{K}_j(i) = \phi_j(i) \int \phi_j^*(j)\phi_i(j) \frac{1}{|r_i - r_j|} dr_j \quad (9)$$

where ϕ_i is the one-electron molecular orbital of electron i, ϕ_j is the one-electron molecular orbital of electron j, r_i is the position of the ith electron and r_j is the position of the jth electron. By adding the operator for nuclei-nuclei coulombic repulsion,

$$\hat{V}_{nn} = \sum_{A}^{N_{nuclei}} \sum_{B>A}^{N_{nuclei}} \frac{Z_A Z_B}{|R_A - R_B|} \quad (10)$$

, to the Fock operator (6), the electronic Hamiltonian is obtained, where A is the Ath nuclei, N_{nuclei} is the total number of nuclei in the system, B is the Bth nuclei, Z_A is the exact charge of the Ath nuclei, Z_B is the exact charge of the Bth nuclei R_A is the positions of the Ath nuclei and R_B is the position of the Bth nuclei. Applying the electronic Hamiltonian to the wavefunction described by the one-electron molecular orbitals delivers the energy of the system where the nuclei are held stationary.

Now that the energy can be evaluated for a molecule, a method is needed to optimize the orbitals such that they describe a minimum. An initial guess is made and optimized noting that the energy can never fall below that of the ground state based on the variational theorem discussed previously. The optimization must be performed so that the molecular orbitals remain orthogonal and normalized throughout the procedure.[8] Lagrange multipliers are utilized to ensure these conditions during the optimization. As orbitals can only be optimized in the presence of all other orbitals of the system, the calculations must be optimized iteratively. The iterative procedures are generally performed by guessing the initial coefficients of the atomic orbitals which construct the molecular orbitals (4). The Fock operator obtains the eigenvalues from the atomic orbitals to obtain the Fock matrix, which is the collection of the eigenvalues obtained from the Fock operator. The newly formed Fock matrix is then diagonalized, which gives a new set of coefficients for the atomic orbitals. The new coefficients are then used to construct a new Fock matrix. This process

is repeated until the coefficients obtained from the diagonalization of the Fock matrix are the same as the previous set of coefficients used, within a certain threshold. The process described uses the Roothan-Hall equations[9], where the Fock operator is enacted on a basis set constructed by atomic orbitals:

$$\boldsymbol{FC} = \boldsymbol{SC}\varepsilon \quad (11)$$

where $\boldsymbol{F}$ is the Fock Matrix, $\boldsymbol{C}$ is the coefficient matrix, $\boldsymbol{S}$ is the overlap matrix, and ε diagonal matrix. $\boldsymbol{F}$ contains the Fock matrix elements

$$F_{\alpha\beta} = \int \chi_{\alpha}^{*} \hat{F} \chi_{\beta} \; dr \quad (12)$$

where, $\hat{F}$ is the Fock operator, χ is an atomic orbital, α indicates alpha spin of the electron, β indicates beta spin of the electron and r indicates position. $\boldsymbol{S}$ contains the overlap matrix elements

$$S_{\alpha\beta} = \int \chi_{\alpha}^{*} \chi_{\beta} \; dr \quad (13)$$

where χ is an atomic orbital, α indicates alpha spin of the electron, β indicates beta spin of the electron and r indicates position. Finally, $\boldsymbol{C}$ is the collection of the coefficients from the atomic orbitals as can be seen in equation 4.

1.2.2 Post-Hartree-Fock Methods

Though the Hartree-Fock method is capable of solving the multielectron problem, the application of the wavefunction as a single determinant of one-electron orbitals does not treat electron correlation.[10] This results when the wavefunction is constructed as the product of single-electron orbitals, it is assumed that there is no interaction between the electrons. However, transforming the wavefunction into a Slater determinant and treating both coulomb repulsion and electron exchange results in treating the electron-electron repulsion of electrons of the same spin, as it prevents two electrons of the same spin to be found in the same location. The correlation described is called Fermi correlation. Though the exchange operator accounts for Fermi

correlation, it does not treat Coulomb correlation for electrons of opposite spins.[10,11] In addition to fermi and coulomb correlation, the electron correlation is then further broken down into static and dynamic correlation.[12,13] These types of electron correlation only arise when more than one electronic configuration is used to describe the system. Dynamic correlation, associated with the motion of electrons, is when the state of interest is predominantly described by one electronic configuration, while other electronic configurations contribute only a small amount but significantly influence the energy of the system. Static correlation is when more than one electronic configuration heavily describes the electronic state, suggesting that these electronic states are stationary. Methods such as Configuration interaction[14], Coupled cluster[15], Møller-Plesset perturbation theory[16], and Quadratic configuration interaction[17] have been developed to retrieve the missing electron correlation of the Hartree-Fock method and can be very accurate, however these methods often suffer from bad scaling with system size.[18] An alternate method that is capable of treating systems of larger size (100 – 200 atoms), which treats electron exchange and electron correlation with moderate accuracy using the electron density instead of the wavefunction, is called Density Functional Theory (DFT).

1.2.3 DFT

As stated previously, DFT is a method that determines the energy of a multi-electron system with moderate accuracy and can treat systems of moderate size. The theory behind DFT is that the energy of a system can be determined from the electron density. Simply, if the electron density is known, the number of electrons and external potential between the electrons and nuclei can be deduced. Integrating over the density, one can determine the type and number of nuclei and the charge from the peaks in the density. With this information, the Hamiltonian based on the electron

density can be constructed and therefore it must be possible to construct a functional that can determine the energy of the electron density.[18] To study how density influences the energy, the Hartree-Fock equations were made in terms of the electron density and were solved. The Hohenberg-Kohn theorem states that it must be possible to solve an equation similar to that of the Hartree-Fock equation with respect to a unique electron density to obtain a unique energy, though the exact kinetic energy term, electron exchange and correlation are unknown.[18,19] Assuming this to be true, the second theorem by Hohenberg and Kohn states that the energy obtained from these equations using a trial electron density must be greater than or equal to the actual energy obtained with the actual electron density. Therefore, minimization with the electron density using the variational methods should give the exact electron density. It was not until the work by Kohn-Sham[20] that DFT had a decent way of handling the kinetic energy. They defined the Kohn-Sham

$$\rho_{KS}(\phi_i) = \sum_{i}^{N} |\phi_i|^2 \qquad (14)$$

density

where ρ is the density, x is position, ϕ_i is the single-electron molecular orbital of the ith electron and N is the total number of electrons in the system. The single-electron molecular orbitals come from the total wavefunction which is described as a Slater determinant of single electron orbitals: where ϕ_i is the single-electron molecular orbital of the ith electron, x is position and N is the total

$$\Phi(x_1, \ldots x_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \phi_1(x_1) & \cdots & \phi_N(x_1) \\ \vdots & \ddots & \vdots \\ \phi_1(x_N) & \cdots & \phi_N(x_N) \end{bmatrix} \qquad (15)$$

number of electrons in the system. The single-electron molecular orbitals are called Kohn-Sham orbitals. They made this density equal to the real electron density, though it technically is not, to connect it to the original DFT theory. They could then solve for the kinetic energy by taking the expectation value of Kohn-Sham orbitals ϕ_i using the kinetic energy operator

$$T_s = -\frac{1}{2}\nabla^2 \quad (16)$$

. T_s is the kinetic energy operator where the subscript s indicates that the kinetic energy is obtained from the Slater determinant and ∇^2 is the Laplace operator.[8] As the Kohn-Sham density is not equal to the actual density, the portion of the kinetic energy missing from the description of the real density is clumped together with the exchange and correlation terms,

$$E_{XC}[\rho] = E_{XC}[\rho] + T[\rho] - T_s[\rho] \quad (17)$$

, where E_{XC} is the functional, dependent on ρ, which obtained the energy from the exchange (X subscript) and correlation (C subscript) functionals. T describes the total kinetic energy while T_s is the kinetic energy from the Slater determinant of the Kohn-Sham orbitals. The contribution from $T[\rho] - T_s[\rho]$ is usually very small and is often ignored. The nuclear-electron attraction functional is defined as

$$V_{eN}[\rho(r)] = -\sum_{A}^{N_{nuclei}} \rho(r)\frac{Z_A}{|R_A - r_i|}dr \quad (18)$$

where $\rho(r)$ is the density, A is the Ath nuclei, N_{nuclei} is the total number of nuclei in the system, r is the position of the electron, R is the position of the nuclei and Z is the charge of the nuclei. Finally, the electron-electron repulsion term is defined as

$$J[\rho(r)] = \frac{1}{2}\iint \frac{\rho(r_i)\rho(r_j)}{|r_j - r_i|}dr_i dr_{j,} \quad (19)$$

where ρ is the density, r is the position of the electron, i is the ith electron, and j is the jth electron. Kohn-Sham form of DFT now resembles Hartree-Fock

$$E[\rho] = V_{NN} + T_s[\rho] + V_{eN}[\rho] + J[\rho] + E_{XC}[\rho] \quad (20)$$

with the non-local exchange operator of Hartree-Fock replaced with the local exchange and correlation term, $E_{XC}[\rho]$, for DFT. All terms from left to right have been described above in equations 10, 16, 18, 19 and 17 respectively. With this description of DFT, the equation can be solved using variational methods. There is no exact form for the exchange and correlation which are constructed in several different ways, as there is not an exact solution to these functionals based

on theory. [18] In Hartree-Fock theory, the exchange and coulomb operators cancel the self-interaction. However, DFT does not have an exact way of dealing with self-interaction.[21,22]

DFT functionals are broken down by the approximations used to define the exchange and correlation.[23] Generally, these approximations are broken down into ways to construct the exchange and correlations terms for specific types of systems and consist of the local density approximation (LDA), the generalized gradient approximation (GGA), the meta-GGA approximation, and finally hybrid functionals. LDA defines the exchange-correlation functional on just the density and is used to describe systems with a uniform electron gas such as solid materials. GGA functions use both the densities and gradients of the densities to define the exchange-correlation to describe the non-uniform electron gas. Meta-GGA includes second order gradients to improve upon the original GGA functionals. Hybrid functionals incorporate a mixture of exact-exchange from the Hartree-Fock method with the exchange and correlation from GGA and meta-GGA functionals. Both hybrid and meta-hybrid GGA functionals generally give better results than GGA and LDA functionals.[23] Finally, range-separated hybrid functionals treat long and short range exchange with a mixture of Hartree-Fock and Density Functional exchange.[24] With these approximations, DFT is capable of both treating electron exchange and electron correlation, making it an improvement to Hartree-Fock, which only treats electron-exchange. Most functionals used here are either hybrid-GGA functionals (B3LYP)[25–27], hybrid-meta-GGA functionals (um06-2x)[28], and range-separated hybrid functional (ωB97x).[29]

Both Hartree-Fock and Kohn-Sham DFT struggle with describing long-range electron correlation (London dispersion).[24] Post Hartree-Fock methods use excitations (additional determinants) to obtain the long electron correlation. However, Hartree-Fock, as well as Kohn-Sham DFT, do not model excited states to retrieve the London Dispersion. As these long-range

interactions are important for modeling non-covalent interactions, dispersion corrections have been created for these methods. The empirically derived correction that we use here is the "D3" correction by Grimme.[30]

1.2.4 Time-Dependent DFT

In order to solve the time dependent-DFT (TD-DFT) equations, there must be a unique density obtained from a time dependent external potential. This was shown by Runge and Gross.[31] The kinetic energy operator as well as the time dependent external potential operator is applied to the Kohn-Sham orbitals of the ground state and is shown to give a time dependent density. By applying linear response theory, we are capable of obtaining the energies of single excitations using DFT functionals using the Tamm-Damcoff approximation[32], which decouples the excitations from the de-excitations.[33] For better performance, hybrid functionals should be used, though, even with these functionals, TD-DFT struggles with describing charge-transfer excitations.[33]

1.2.5 Domain Based Local Pair Natural Orbital Coupled Cluster Theory Single, Double and Perturbative Triple Excitations

Couple-cluster with single, double and perturbative triple excitations (CCSD(T)) is the gold standard of single determinate methods as it retrieves the majority of dynamic electron correlation missing from the Hartree-Fock method. This method is costly, with a scaling of $O(N^7)$ which is attributed to the size of the space describing the electron correlation (number of states considered). If the occupied orbitals are made to be localized, only the virtual orbitals with substantial overlap contribute to the dynamic electron correlation.[34] Therefore, if the occupied orbitals are made to be localized, the number of virtual orbitals that need to be considered to retrieve the majority of the dynamic electron correlation can be substantially reduced.[34] The domain based local pair natural

orbital coupled cluster theory single, double and perturbative triple excitations DLPNO-CCSD(T)[35,3636,37] reduces the computational scaling of the traditional CCSD(T) calculation while retaining its accuracy by using the technique described above. The occupied orbitals are localized using Foster-Boys method which are then projected to form projected atomic orbitals that span the virtual orbitals.[36] DLPNO-CCSD(T) method takes the pair natural orbitals (PNOs) which are then expanded within a set of projected atomic orbitals (PAOs) which belong to a domain of an electron pair. This results in linear scaling with system size[35] and benchmark calculations have shown to give a mean absolute deviation of ~ 0.3 kcal/mol for both the Friedrich and Hänchen and S66 sets using the Normal-PNO threshold that were used here.[38,39].

1.2.6 Basis Set

Choice of method is not the only factor that controls the accuracy of the calculation, the choice of basis set is also important. The basis set is the set of functions used to describe the one-electron orbitals. The original description of these functions were Slater-type orbitals[40], though calculation of the integrals of these orbitals was found to be difficult and replaced by the easier to integrate Gaussian type orbitals.[41] As a single Gaussian function does not match the shape of a slater type orbital, the Gaussian functions are made into the shape of the Slater orbitals by construction of the linear combination of Gaussian functions. Since this discovery, many of these types of basis sets have been created.[42] A particular category commonly used for calculation of molecular systems are split-valence basis sets, which separate the description of the core and valence electrons.[43] Typically the core electrons are described by one linear combination of Gaussians while the valence electrons are described by more than one linear combination of Gaussian functions. By increasing the number of Gaussians describing the valence electrons, one increases the quality of

the description of the system. Additional functions, called polarization functions, can be added to these basis sets to allow polarization of the electron density about an atom, which occurs during bonding.[8] Finally, diffuse functions can also be added, which attribute flexibility to the tail of the atomic orbitals, which is useful for describing loosely bound electrons, such as those in anions and excited states.[8,43] To reduce the computational cost and include relativistic effects for heavier elements, pseudopotentials can be applied[44,45]

1.2.7 Implicit Solvation Models

As the synthetic transformations are run in solvents, we must have an efficient way to model this interaction with the molecules involved in the chemical reaction, particularly when the solvent is polar, resulting in stabilization of charge. To do so, the solvent is modeled as a continuum instead of independent particles.[46] This simply means that the solvent is not considered as individual particles, but rather as an area or volume. As stated in the paper by Lange and Herbert "in the polarizable continuum model, electrostatic interactions with the continuum are modeled by charge densities at the surface of the solute cavity." Usually, the cavity is constructed by spheres around the atoms. The continuum approximation of C-PCM[47] assumes that the solvent is a perfect conductor, so that the amount of charge needed to neutralize the solute's cavity can be determined. The charge of the cavity is then stabilized by a set factor based on the permittivity of the solvent. The solute electron density (SMD) model is a more recent continuum solvation model which was parametrized against Hartree-Fock as well as multiple density functionals.[48]

1.3 Application of DFT

To obtain structures that represent a minimum on the potential energy surface, geometry optimizations are performed to obtain minima or maxima using double zeta basis sets (6-31G[49]

and def2-SVP[50]) using the Berny algorithm.[51] Forces are computed for the input structure in order to get a good trajectory to the minima or maxima. Frequency calculations are performed using the same level of theory used for the geometry optimization to ensure that true maxima and minima are obtained. Minima should have no imaginary frequencies while transition states should have only one imaginary frequency. The energies are refined by larger basis sets, such as triple zeta basis sets (6-311+G(d,p)[49] and def2-TZVPP[50]). Dispersion corrections as indicated previously, are used to correct for long-range electron correlation. Pseudopotentials are used for heavier atoms.

The frequency calculation gives a set of corrections that are used to obtain the thermal energy, enthalpy and free energy from the energy obtained from the calculation performed (Hartree-Fock, DFT…). The thermal correction energy is calculated by adding together the energies from translational motion, vibrational motion, rotational and electronic motion. The enthalpy correction is simply just the thermal correction plus the Boltzmann's constant times temperature. Finally, the free energy correction is obtained by taking the entropy correction and subtracting the total entropy of the system times the temperature. The total entropy is obtained by the sum of the translational, rotational, and vibrational motion of the molecule plus the entropy of the electronic motion. Each entropy term is determined by the partition function of each motion.

Chapter 2: Mechanism of Trifluoromethylthiolation mediated by Electron Donor-Acceptor Complex

Excerpts from this chapter were published in: Lipp, A[#].; Badir, S. O[#].; **Dykstra, R.**[#]; Gutierrez, O.*; Molander, G. A.* Catalyst-Free Decarbonylative Trifluoromethylthiolation Enabled by Electron Donor-Acceptor Complex Photoactivation. *Advanced Synthesis & Catalysis* **2021**, *363*, 3507–3520.

2.1 Introduction

Fluorinated functional groups have long captured the attention of the synthetic community because of the distinct characteristics that they impart onto bioactive subunits. Fluorine incorporation has direct effects on a molecule's chemical, physical, and biological properties, such as its pK_a, dipole moment, and molecular conformation. These effects, in combination, have enormous implications in their applications to the pharmaceutical industry, where the optimization of pharmacokinetics as well as adsorption, distribution, metabolism, and excretion (ADME) properties have witnessed a renaissance following the rise of fluorinated small molecules.[52] As a consequence of these factors, fluorinated motifs are embedded in more than 25% of commercialized drug products.[53] As an important representative, the trifluoromethyl thioether (SCF_3) group is known to exhibit high electronegativity and lipophilicity (Hansch parameter π_R= 1.43), leading to enhanced metabolic stability and transmembrane permeability in drug candidates (Figure 2.1A).[54–57] In this vein, the development of synthetic strategies for trifluoromethylthiolation employing diverse feedstocks has gained considerable momentum.[54,55,55–68] Owing to their widespread availability, aldehydes are attractive commodity chemicals that have been harnessed in deoxygenative and α-C-H trifluoromethylthiolation.[69–73]

Recently, photoredox- mediated hydrogen atom transfer (HAT) catalysis has been utilized to generate acyl radicals from aldehydes to access trifluoromethyl thioesters (Figure 2.1B).[74–90] In this context, the use of aldehydes as selective alkyl radical precursors for the decarbonylative

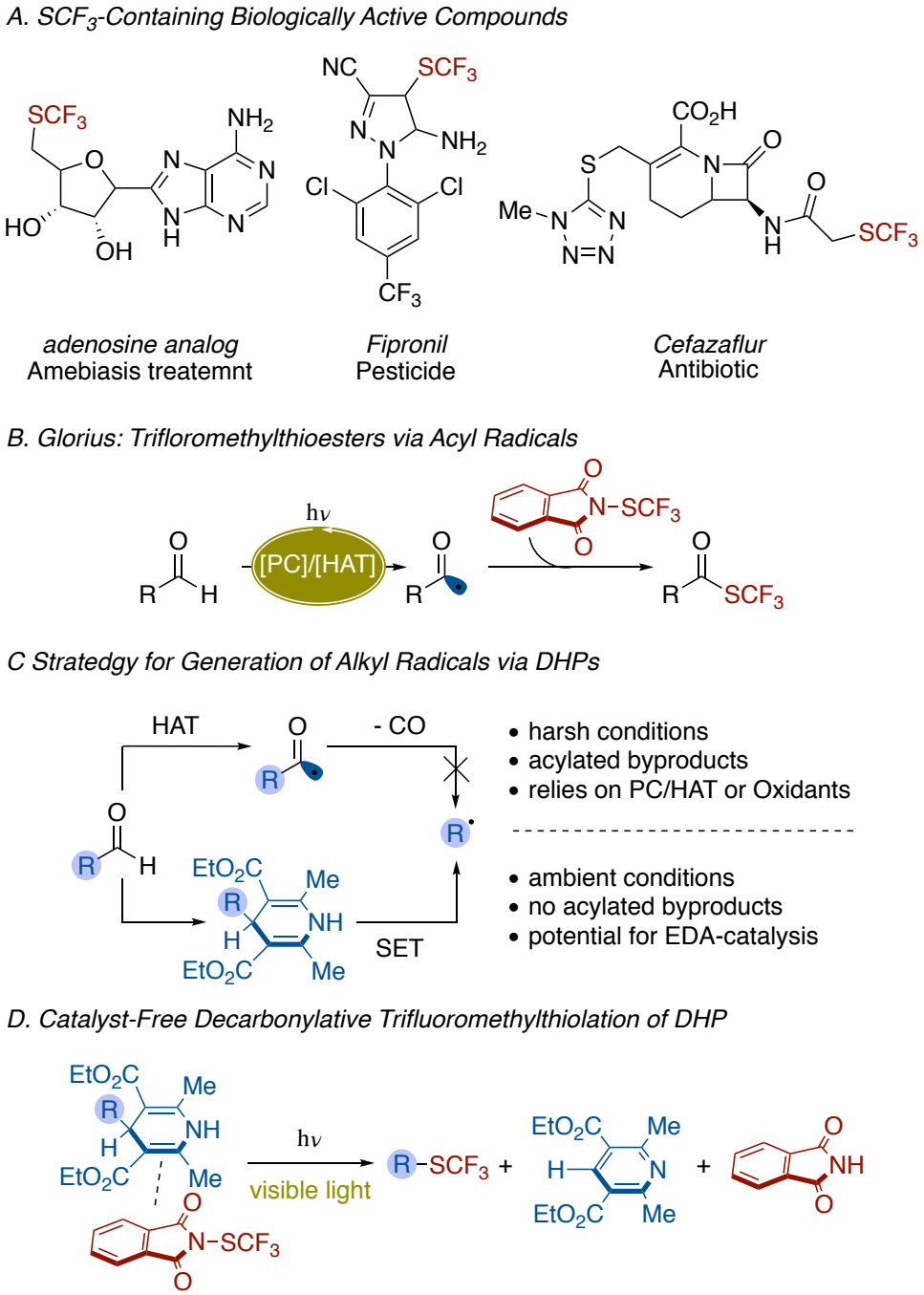


Figure 2.1: Envisioned decarboxylative trifluoromethylthiolation of aldehyde feedstocks; PC = photocatalyst.

construction of C(sp3)-SCF_3 bonds would represent a complementary strategy. In particular, the

development of selective trifluoromethylthiolation processes for late-stage functionalization of complex targets under redox-neutral and additive-free conditions is of great significance in medicinal chemistry.

Recently, visible-light photocatalysis has been enlisted to facilitate the construction of challenging structural motifs with high functional group tolerance.[91–99] Through single electron transfer (SET) paradigms, a photoexcited catalyst undergoes oxidative or reductive quenching pathways with a radical precursor to yield reactive carbon- or heteroatom-based radicals that engage in subsequent synthetic operations. However, the majority of these processes rely on the redox potentials of expensive transition-metal complexes, largely based on ruthenium and iridium. These manifolds are further complicated by the oxidation/reduction steps of the photocatalyst.

An alternative approach, circumventing the need for exogenous photoredox catalysts, exploits the association of electron-donor/electron-acceptor pairs to form new molecular aggregates in the ground state, exhibiting red-shifted absorption bands.[100–117] Typically, the energy of this transition lies within the visible light region. Direct photoexcitation of such electron donor-acceptor (EDA) complexes induces an intermolecular single electron transfer (SET) event, generating a radical ion pair. An inherent challenge in EDA photochemistry stems from competitive back electron transfer (BET) events that restore the ground state of the complex. To overcome this complication and facilitate the otherwise improbable cage escape, the acceptor typically carries a suitable leaving group, enabling elimination of excess charge by rapid bond scission. The photoactivation of EDA complexes has allowed the introduction of new synthetic frameworks to tackle major synthetic challenges not addressed in conventional photoinduced pathways (e.g., high redox potentials, oxygen- and water-sensitivity, site-selectivity in oxidation- and reduction-labile systems, etc.).[100–117]

In previous synthetic studies, the Molander group demonstrated that 1,4-dihydropyridines (DHPs) undergo oxidative, homolytic fragmentation under classical photoredox conditions.[118–122] DHPs are readily accessible from commercially available aldehydes in one step and are known to engage in radical-mediated alkylation.[118–122] Specifically, DHPs function as masked aldehydes to deliver alkyl radicals selectively, circumventing the formation of undesired, acylated byproducts as well as the need for elevated temperatures required for efficient CO extrusion in decarbonylative pathways (Figure 2.1C).[123–129] Recent methods based on photochemical and persulfate-mediated oxidation of DHPs to enable carbon-carbon bond-forming processes illustrate the potential of these building blocks to undergo functionalization through strategies that are unavailable to the parent aldehydes.[118–123] Inspired by these efforts, the Molander group envisioned the use of DHPs in conjunction with electron-deficient N-(trifluoromethylthio)phthalimide[130,131] to form electron donor-acceptor complexes that facilitate the generation of open-shell reactive species in the

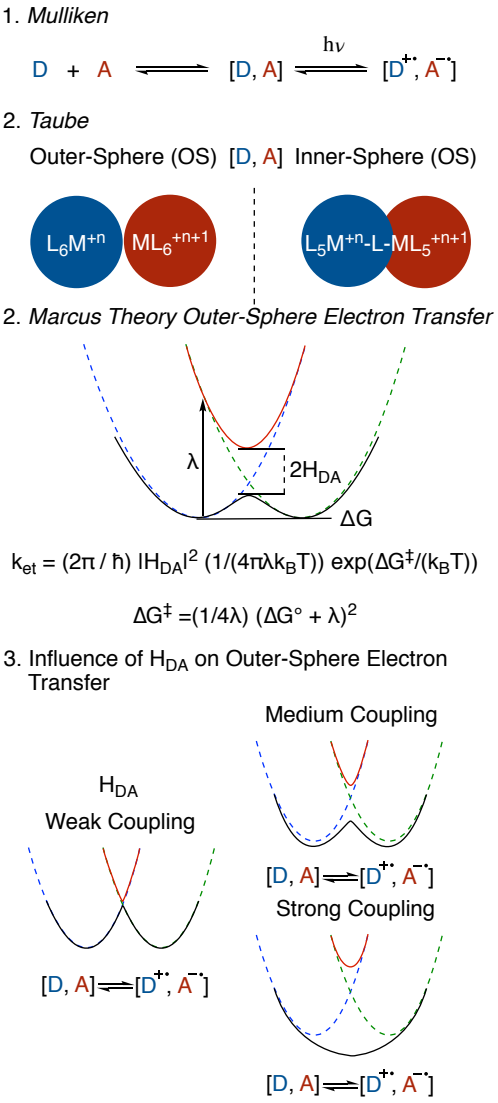


Figure 2.2: Theory behind EDA complexes. Black and red solid lines indicate ground and excited adiabatic states while dash blue and green lines indicate diabatic states. H_{DA} = electron coupling between donor and acceptor state and λ = reorganization energy, k_B = Boltzmann's constant, T = temperature, ħ = Planks constant divided by 2π and k_{et} = rate of electron transfer.

absence of precious transition- metal-based complexes. Herein, they harnessed the synthetic utility of EDA photochemistry to enable a catalyst- and additive-free decarbonylative trifluoromethylthiolation of aldehyde feedstocks under open-air and ambient reaction conditions (Figure 2.1D).

In the 1950s, Mulliken derived a quantum description of EDA complexes to "explain the chemical binding" (Figure 2.2A) .[132–134] Since these initial descriptions, much progress has been made in defining the formation of these complexes by Taube[135,136], Marcus[137,138] and Hush[139,140] describing inner- vs. outer-sphere electron transfer, the description of non-adiabatic, and adiabatic outer-sphere electron transfer respectfully.[141,142] By considering the free energy of electron transfer $\Delta G°$ and the reorganization energy of the participating molecules and solvent λ, one can determine the rate of electron transfer for non-adiabatic system (Figure 2.2B) using where electronic coupling $J = 0$. If there is electronic coupling between the donor and acceptor, via orbital overlap, the adiabatic scenario can be modeled with $J > 0$. Using Marcus-Hush theory, the strength and tightness of the complex can be attributed to the type of potential energy surface the complex has, either weak, medium and strong electronic coupling between the neutral and charged states of the system (Figure 2.2C).[141,142] Though the theoretical aspects of the formation of these EDA complexes are well understood, it was not until recently that EDA complexes have been utilized to mediate radical chemistry in the presence of visible light.[100–117] Though previous DFT/TD-DFT calculations have been performed on other EDA mediated transformations[143–151] where there is strong experimental evidence for the intermediacy of radical species, the mechanisms of these transformations are still not well understood. In recognition of the growing utility of organic reactions promoted by EDA complex photoactivation,[100–117] I performed quantum calculations on this transformation to investigate the mechanism, electronic properties, and dynamics to gain a

deeper understanding of the underlying charge transfer processes.

2.2 Methods

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3)/def2-SVP level of the theory in implicit dimethyl sulfoxide (DMSO) solvent (DMSO) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, except were indicated otherwise. [30,47,50,152–155] Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Though DFT has been used to describe donor and acceptor interaction energies,[156–158] DFT is known to struggle at accurately describing these interactions due to overstabilization of the virtual molecular orbitals.[159,160] DLPNO-CCSD(T) calculations were performed to accurately model the EDA interaction. To evaluate the accuracy of the interaction energies from the DFT calculations, benchmark calculations of a series of functionals including B3LYP, B3LYP-D3, M06-2X and the ωB97X, against the DLPNO-CCSD(T) method, revealing that all DFT calculations underestimate the complexation free energy by at least 1.8 kcal/mol. In addition, B3LYP-D3 geometries are similar to those obtained using ωB97X, shown to be acceptable for describing the ground state of these EDA complexes by Brédas et al, but give free energies of complexation much closer to those obtained from DLPNO-CCSD(T). All DLPO-CCSD(T) calculations were corrected using solvation energy corrections obtained from B3LYP-D3/def2-TZVPP-CPCM(DMSO). 20 excitations were calculated on DFT optimized structures using TD-DFT single points with the same method, basis set, and solvation model used for optimizations to generate UV/vis spectra.

TD-DFT optimization were performed with the same method stated previously but using 3 excitations above the excitation of interest. To see how it would influence the energetics of key pathways, single point calculations were run using both DFT and TDDFT with acetone set as the implicit solvent, which gave almost identical energetics as obtained using DMSO (see Appendix). Where indicated, single point energy calculations in implicit solvent using and B3LYP-D3/def2-TZVPP-CPCM(DMSO) were also performed and presented with DLPNO energies for reference. All 3-D structures were generated using CYLview[161] and all electron density difference plots were generated using GaussView 5.[162] For simplicity, the discussion is largely limited to the alkyl-DHP systems for which a bathochromic shift was observed experimentally. For acyl counterparts, a brief summary of key findings is presented here, and the full details are provided in the see Appendix.

2.3 Results and Discussion

2.3.1 Experimental Work

This part of the work was performed by Alexander Lipp and Shorouk O. Badir

From the outset of the experimental investigation, performed by the Molander group, the key role of solvent was recognized in the proposed trifluoromethylthiolation, as in these types of charge transfer processes, the solvent cage heavily affects the molecular assembly and formation of EDA complexes.[163] Under the optimized reaction conditions, experiments were carried under blue Kessil irradiation (λ_{max}= 456 nm) in acetone.[164] No product formation was detected in the absence of light, validating the photochemical nature of this transformation. In contrast to radical-mediated alkylation catalyzed by an external photocatalyst, this EDA paradigm circumvents side reactions in the presence of oxygen that would result from triplet energy transfer.

The scope of this transformation was examined, using DHPs featuring diverse alkyl substituents at the C4-position (Table 2.1). Both cyclic and acyclic derivatives delivered the desired trifluoromethylthiolated products in excellent yields. Of note, alkene (**3f**, **3h**) and halide (**3c** and **3l**) functional handles are accommodated, providing linchpins that have the potential to drive molecular complexity. The scope was further extended to stabilized primary and secondary α-oxy systems. Destabilized primary- and aryl radicals cannot be generated from the corresponding DHPs because of competitive C-H bond scission.[118–122] The use of structurally related 4-acyl-1,4-DHPs[165] provided access to the corresponding trifluoromethyl thioesters under

Table 2.1: Selected Substate Scope of Trifluoromethylthiolation via Alkyl-DHPs

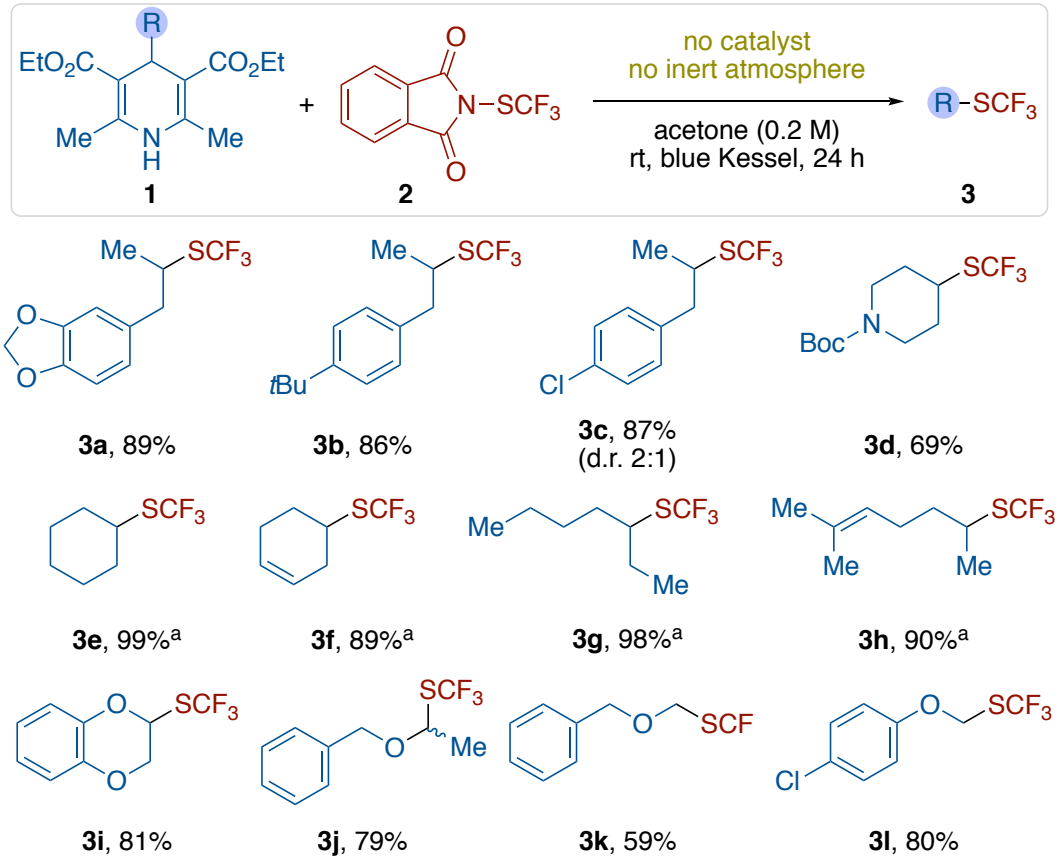


Table 2.1: Selected scope of the developed trifluoromethylthiolation. Reaction conditions: N-(trifluoromethylthio)phthalimide (**2**, 0.5 mmol, 1.0 equiv.), alkyl- (**1a–l**, 24 h reaction time) in acetone (2.5 mL, 0.2 M) under blue light irradiation (Kessil lamp, λ_{max} = 456 nm). Yields correspond to isolated products after chromatographic purification. [a]Product volatile, yield was determined via ^{1}H NMR with 5-bromopyrimidine (0.25 mmol) as internal standard (IS). Synthesis performed by Molander group.

a similar photochemical paradigm (Table 2.2). In general, both electron-donating and electron-withdrawing substitution patterns are amenable. The introduction of heteroaryl (**5f**) as well as aliphatic (**5h**) frameworks was equally fruitful. Notably, in the case of **5h**, competitive C(sp^3)-SCF_3 bond formation stemming from decarbonylation of the intermediate aliphatic acyl radical was not observed.

To probe the formation of charge-transfer complexes, UV/vis absorption studies were performed, see paper for spectra.[164] Although a solution of *N*-(trifluoromethylthio)-phthalimide (**2**) in acetone (0.2M, reflecting the actual reaction concentration) displays no absorbance in the visible light region, a mixture with 4-alkyl-1,4-DHP **1a** exhibits a significant bathochromic shift. Upon mixing, a yellow color appears, accompanied by an absorption band tailing into the

Table 2.2 Selected Substate Scope of Trifluoromethylthiolation via Acyl-DHPs

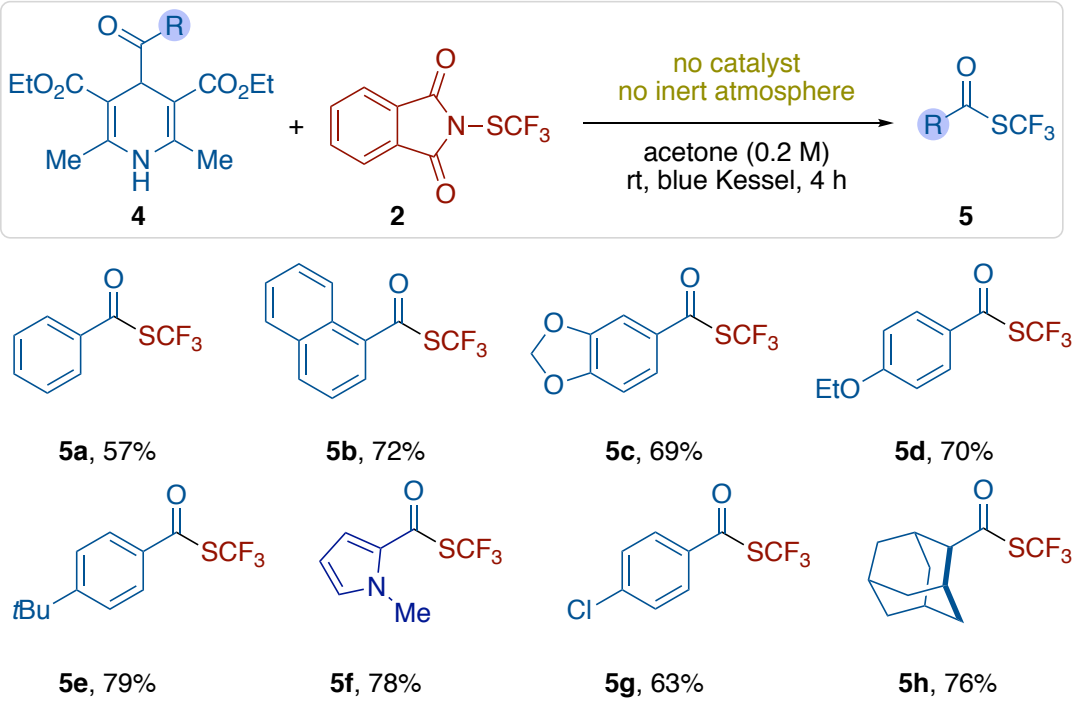


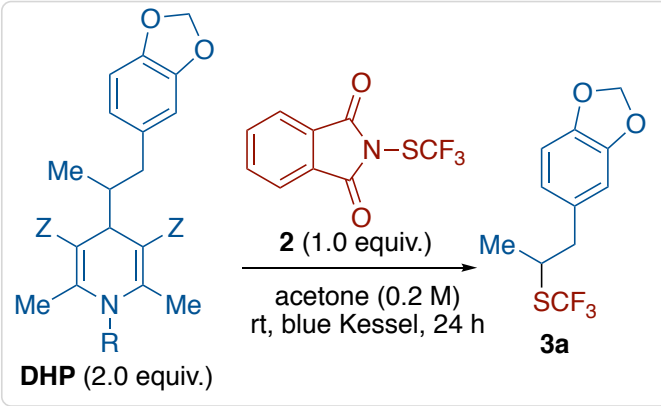
Table 2.2: Selected scope of the developed trifluoromethylthiolation. Reaction conditions: N-(trifluoromethylthio)phthalimide (**2**, 0.5 mmol, 1.0 equiv.), acyl-DHP (**4a**–**f**, 4 h reaction time) (each 1.0 mmol, 2.0 equiv.) in acetone (2.5 mL, 0.2 M) under blue light irradiation (Kessil lamp, λ_{max} = 456 nm). Yields correspond to isolated products after chromatographic purification. [a]Product volatile, yield was determined via ^{1}H NMR with 5-bromopyrimidine (0.25 mmol) as internal standard (IS). Synthesis performed by Molander group.

wavelength region of blue Kessil irradiation. A Job plot revealed a 1:1 stoichiometry of the corresponding EDA complex. Further studies using the Benesi-Hildebrand[166] method revealed an association constant (k_{EDA}) of 0.6 M^{-1} of DHP and *N*-(trifluoromethylthio)phthalimide.[164]

Furthermore, the intermediacy of alkyl radicals was validated through TEMPO trapping experiments.[164] In the case of 4-acyl-1,4-DHP **4a**, no bathochromic shift was detected, suggesting a plausible mechanistic scenario involving direct photoexcitation of these species (*vide infra*) to generate acyl radicals *via* homolytic fragmentation.[164,165]

Once the viability of DHPs as an alkylating agent was established in charge-transfer processes, the influence of the 1,4-dihydropyridine backbone on the outcome of the developed trifluoromethylthiolation was investigated (Table 2.3). At the outset, reaction with *N*-methyl-DHP **6** did not result in product formation, highlighting the importance of the N-H motif for reaction efficiency. This is likely due to the proton transfer step from the N-H group to the developing phthalimide anion facilitates the generation of the neutral species (phthalimide and pyridine).

Table 2.3 Effect of the DHP Backbone on Yield



DHP	R	Z	Yield
6	Me	CO_2Et	0%
7	H	CN	traces
1a	H	CO_2Et	89%
8	H	CO_2Me	80%[a]
9	H	$CO_2{}^iPr$	92%
10	H	$CO_2{}^tBu$	87%

Table 2.3: [a]In acetone/DMSO = 5/1. Synthesis performed by Molander group.

Further, cyano-substitution at the C3 and C5 positions (**7**; Table 2.3) led to trace product formation, which was rationalized by competitive C-H bond scission yielding 4-alkylpyridine

derivatives selectively. With respect to the ester substitution pattern, no significant impact on the reactivity was detected (note that the slightly reduced yield for methyl ester derivative **8** results from limited solubility in acetone, see Appendix). This is in contrast to previously reported C-H alkylation protocols in which a correlation between the steric bulk of the ester substituents at C3 and C5 and the reactivity of the corresponding DHPs was observed in the presence of persulfate as a terminal oxidant (Figure 2.3).[123] The enhanced reaction efficiency was attributed to increased steric hindrance at the C4-position of the pyridine byproduct generated upon homolytic fragmentation. This could limit competitive rebound of the alkyl radical, which, followed by an oxidative rearomatization event, yields the corresponding Minisci byproduct (*vide infra*). In the developed catalyst-free EDA paradigm, this detrimental side reaction is circumvented because of the absence of a terminal oxidant.

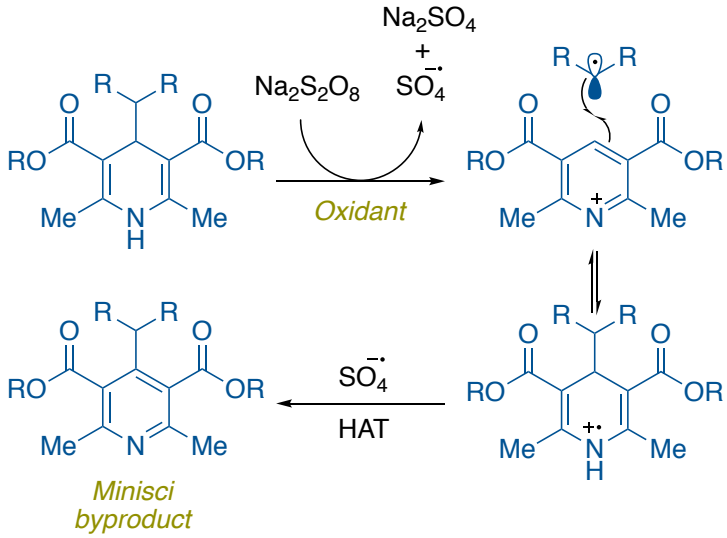


Figure 2.3: Minisci byproduct formation in the presence of a terminal oxidant

Finally, monitoring the reaction progress *via* ^{19}F NMR analysis revealed the intermediacy of disulfide **16** [$S_2(CF_3)_2$] (Figure 2.5) in the trifluoromethylthiolation of both 4-alkyl- and 4-acyl-1,4-DHPs (see the Appendix). In separate experiments, this intermediate was prepared independently and subsequently converted to product in the presence of excess **1a** or **4a**. In these cases, alkyl or acyl radicals were presumably generated through homolytic cleavage of the corresponding photoexcited DHPs (*vide infra*).[165,167] For 4-acyl-DHPs, this fragmentation occurs rapidly, reflecting their high absorption coefficients in the blue wavelength region. In contrast,

without *N*-(trifluoromethylthio)phthalimide (**2**) as electron acceptor, the fragmentation of 4-alkyl-DHPs is slow under blue Kessil irradiation (only ~ 5% of **1a** fragments upon irradiation of a 0.4 M solution of this DHP in acetone using the standard setup, 24h). Although sufficient to validate the intermediacy of disulfide **16**, it is evident that in the presence of **2** as an acceptor species, the major pathway for alkyl radical formation is photoexcitation of the corresponding EDA complex followed by a charge-transfer event (see the computational investigation).

2.3.2 Computational Work

This part of the work was performed by Ryan Dykstra

I started the computational investigation by modeling the thermodynamics of the potential

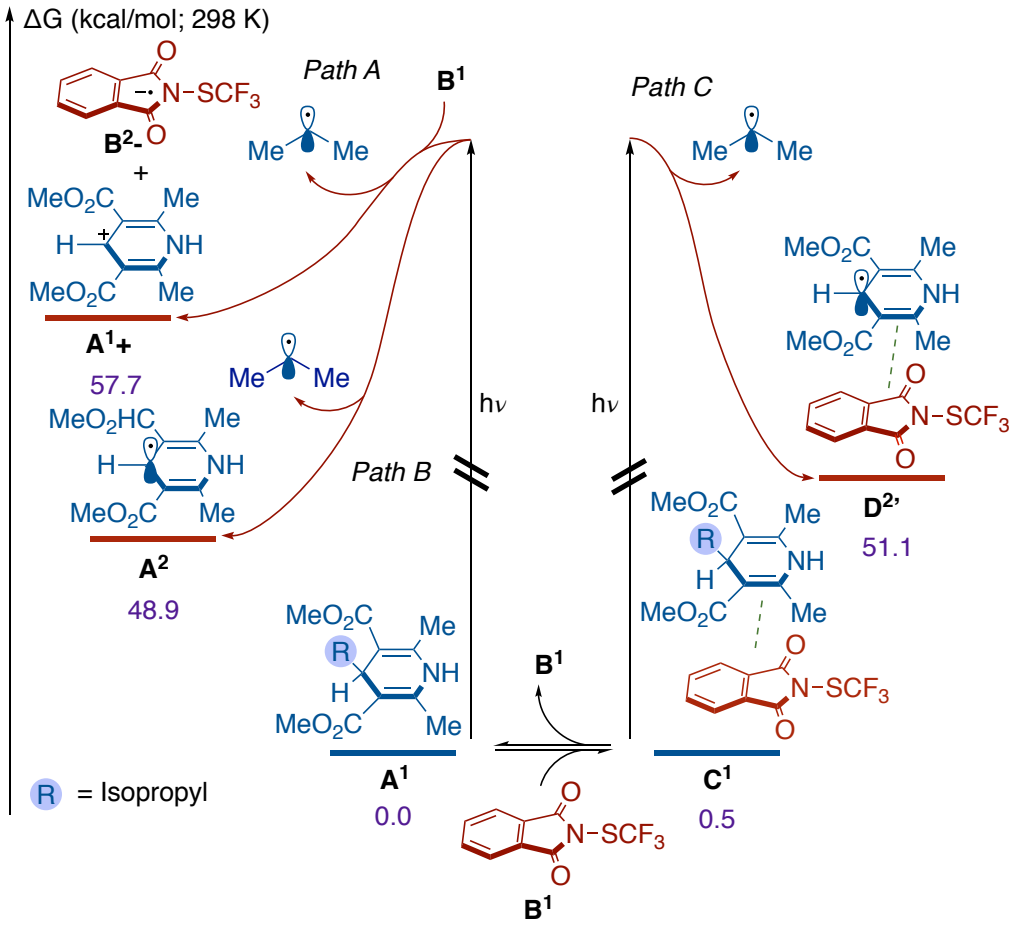


Figure 2.4: Energetics of competing light-promoted alkyl radical formation (free energies [DLPNO-CCSD(T)/def2-TZVPP// UB3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol). Calculations performed by Ryan Dykstra.

competing photochemical pathways that could lead to the formation of the putative alkyl radical intermediate were explored (Figure 2.4). In particular, alkyl radical formation as a result of direct excitation of the dihydropyridine scaffold **A**[1] followed by single electron transfer (SET) with phthalimide **B**[1] (**Path A**)[168–173] or direct homolytic cleavage (**Path B**) was envisioned.

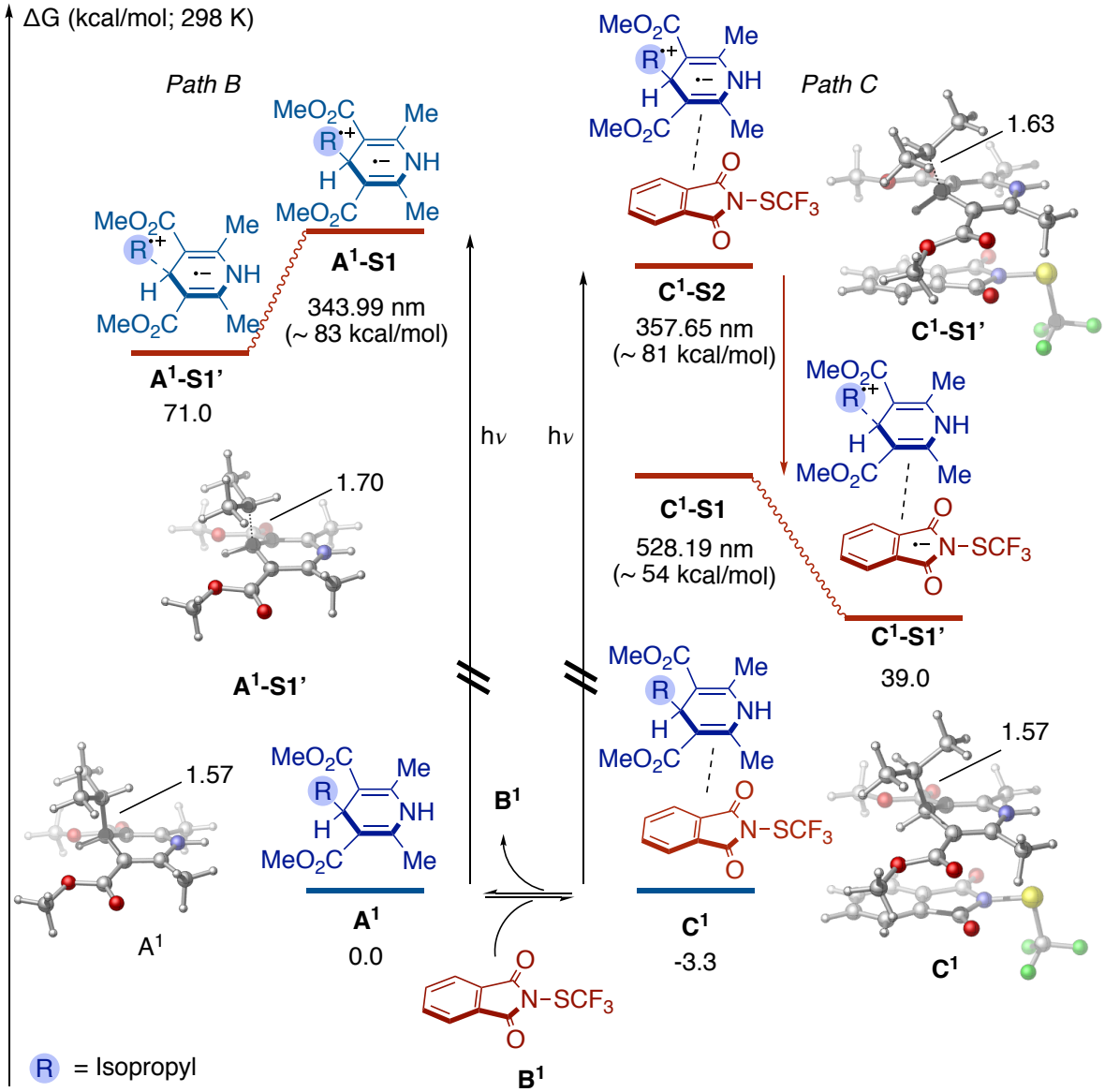


Figure 2.5: Excited state potential energy surfaces of paths B and C and visualization of lowest-lying excitations. (A) Free energies of excited state molecules computed using TD-DFT, relative to free energy of ground state molecules computed using DFT [B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Wavelengths of excitations computed relative to ground state electronic structure using total energy. Bond distances are labeled in Ångstroms. Path B results in intermediate **A**[2] while Path C results in intermediate **D**[2]. Calculations performed by Ryan Dykstra.

Alternatively, dihydropyridine $\mathbf{A^1}$ and phthalimide $\mathbf{B^1}$ could first associate to form electron donor-acceptor (EDA) complex $\mathbf{C^1}$, then undergo excitation to generate the alkyl radical with concomitant formation of radical EDA complex $\mathbf{D^{2'}}$ (**Path C**).[174,175] In turn, photoexcitation of $\mathbf{C^1}$ could lead to alkyl radical and intermediate $\mathbf{D^{2'}}$ (**Path C**) which is found slightly uphill in comparison to **Path B** (by ~2kcal/mol). Overall, these results suggest that alkyl radical formation from either direct photoexcitation of $\mathbf{A^1}$ or EDA complex $\mathbf{C^1}$ (**Path B** and **C**, respectively) are both energetically feasible, while alkyl radical formation *via* SET (**Path A**) is less likely due to the formation of unstable charge-separated species. Direct excitation of $\mathbf{A^1}$ followed by SET (**Path A**) is uphill in energy by 57.7 kcal/mol, while alkyl radical formation *via* homolytic C-C bond cleavage (**Path B**) is thermodynamically more favorable by ~ 9 kcal/mol. On the other hand, EDA complexation to form $\mathbf{C^1}$ is nearly isoenergetic to the separated species.

Next, TD-DFT calculations were used to investigate the energetic feasibility of the electronic transitions leading to alkyl radical formation (Figure 2.5).[146] Consistent with experiment, computations show that the excitation of DHP $\mathbf{A^1}$ has its lowest lying singlet excited state **S1** with λ_{max} ~ 344 nm and a tail that goes out to ~ 466 nm (see the Appendix for computed UV/vis spectra). On the other hand, EDA complex $\mathbf{C^1}$ shows the lowest lying singlet excited state with the significant absorbance owing to **S2**, with λ_{max} ~ 357 nm, and a tail extending to ~ 495 nm. These results suggest that EDA complexation should result in bathochromic shifting as observed experimentally. Also, in agreement with experiment, DHP alone shows very little absorbance at 450 nm, highlighting the crucial role of EDA complexation for efficient formation of alkyl radicals. Even though scenarios **A**, **B**, and **C** are all thermodynamically feasible (Figure 2.6), excitation of EDA complex $\mathbf{C^1}$ is the major pathway for alkyl radical generation.

Closer inspection of the molecular orbitals (MOs) corresponding to the strongest electronic transitions of DHP **A**[1] and EDA complex **C**[1] (Figure 2.6) reveals complete charge transfer from the DHP to the phthalimide core *via* internal conversion from excited states **C**[1]**-S2** to **C**[1]**-S1** that allows the formation of a more stable intermediate **C**[1]**-S1'**, which then undergoes C-C bond cleavage, liberating the alkyl radical. In particular, both singlet excited states responsible for absorbance, **A**[1]**-S1** and **C**[1]**-S2**, (see the Appendix for details) have maximum absorption at wavelengths corresponding to ~ 83 and ~ 81 kcal/mol, respectively. In contrast, the lowest lying singlet excited state for the EDA complex, **C**[1]**-S**[1], is found to have a lambda max much lower in energy (~ 54 kcal/ mol). Moreover, the singlet excitation of the DHP (**A**[1]**- S1**) could be described as primarily a transition from the HOMO containing the C-C σ-bond between the isopropyl group and the DHP scaffold to the π* LUMO on the DHP. The second singlet excited state of the EDA complex **C**[1]**-**

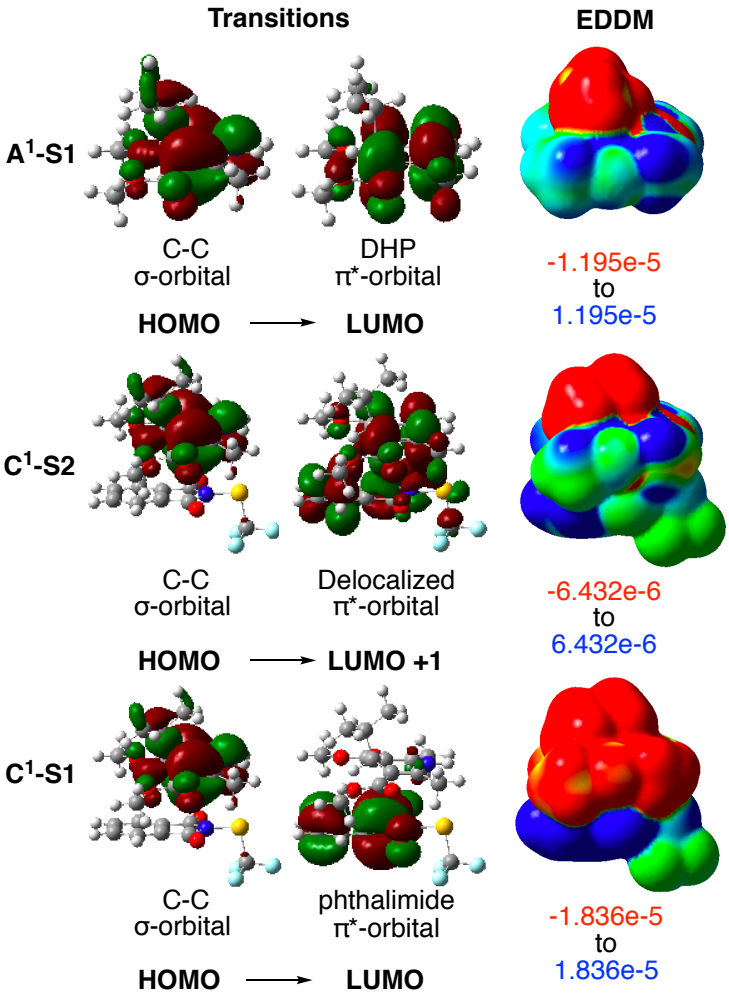


Figure 2.6: Molecular orbitals of the largest contributing transitions (Transitions) and electron density difference maps (EDDMs) of lowest lying singlet excited states as indicated. Isovalues for molecular orbitals and EDDMs are 0.02 and 0.0004 e- /au3, respectively.

S2 is of a similar nature to **A**[1]**-S1** with the only difference being the inclusion of the π* orbitals on

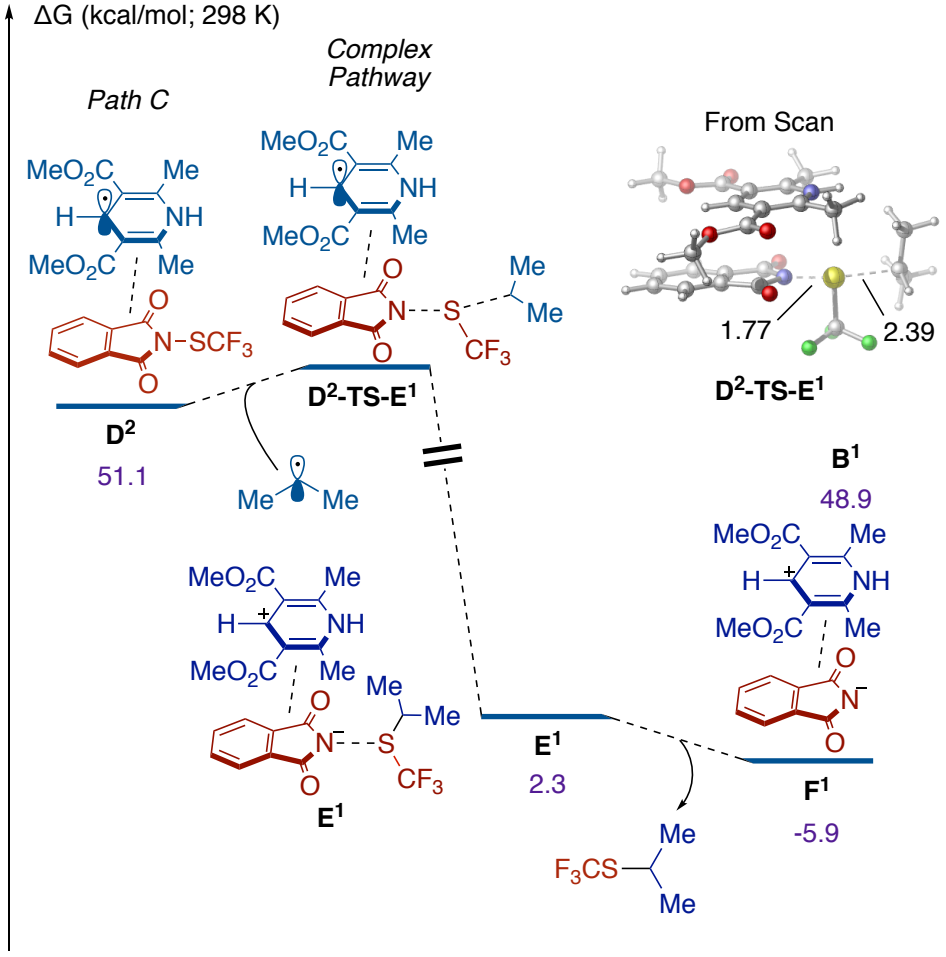


Figure 2.7: Reaction coordinate diagram to product with EDA complex. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Barrier height of D2-TS-E1 discussed in text. Calculations performed by Ryan Dykstra

the phthalimide moiety. Overall, as both excitations are transitions centered about the dihydro-pyridine, little to no difference in energy is observed between them. On the other hand, excitation **C**[1]**-S1** is a transition from the HOMO on the DHP to the π* LUMO on the phthalimide, ascribed to a charge transfer event.

The similarities between **A**[1]**-S1** and **C**[1]**-S2** and the differences of **C**[1]**-S1** are further emphasized by the electron density difference maps (EDDMs) illustrated in Figure 2.6. EDDMs are used to show the change in electron density of the excitation of interest with respect to the ground state

electron density. Red indicates a decrease in electron density while blue indicates an increase in electron density. As can be seen from the EDDMs of **A^1-S1** and **C^1-S2**, electron density is reduced from the isopropyl moiety and the nitrogen in the DHP ring, while electron density increases about the methyl groups and the esters on the DHP. An increase in electron density is found to occur on the aryl portion of the phthalimide **C^1-S2**, which is expected when compared to the major electronic transition of this excited state. On the other hand, excited state **C^1-S1** shows complete electron density depletion from the DHP moiety, and similarly an increase in electron density occurs about the entire π system of the phthalimide. Furthermore, as shown in Figure 2.5, optimization of the **A^1-S1** excited state of the DHP leads to **A^1-S1'**, is associated with substantial elongation of the C-C σ-bond between the alkyl moiety and the DHP core (from 1.57 to 1.70 Å). Subsequent C-C bond

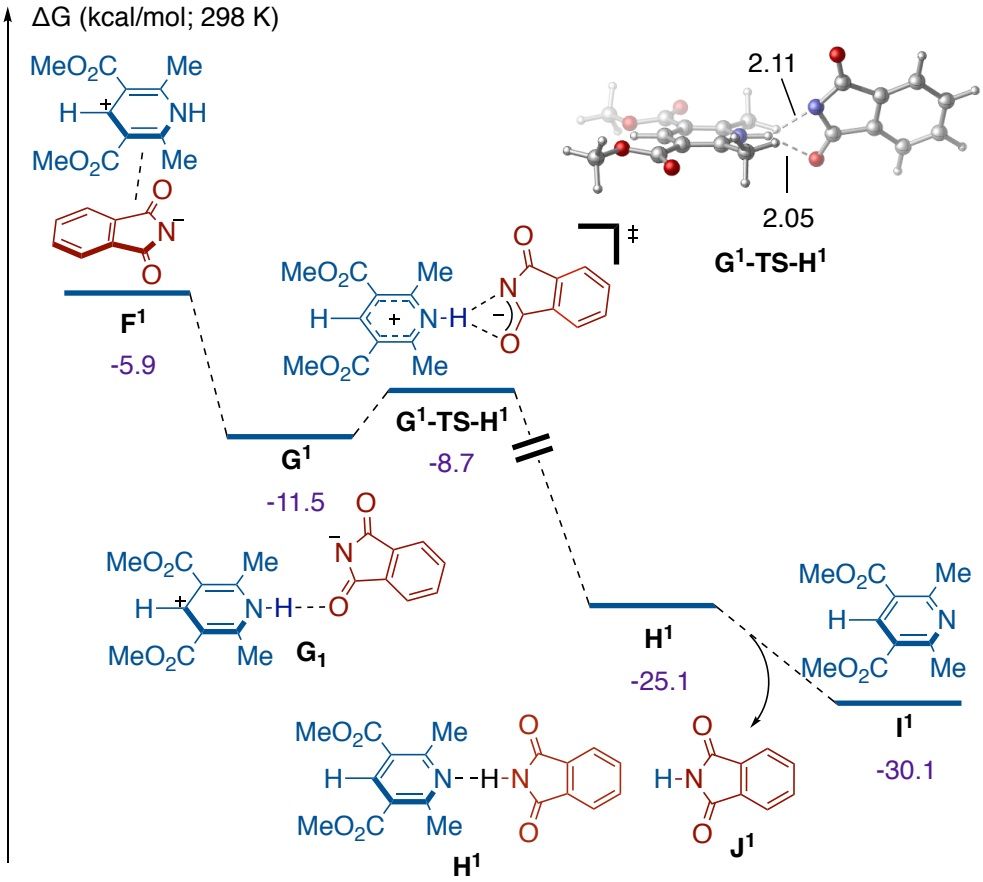


Figure 2.8: Rearrangment from charge-separated EDA complex **F^1** to hydrogen bonding complex **G^1** and subsequent deprotonation **G^1-TS-H^1** to separated pyridine **I^1** and phthalimide **J^1**. Calculations performed by Ryan Dykstra.

cleavage can then lead to the formation of the corresponding isopropyl radical and **A**^{2} (see the Appendix for full pathway). On the other hand, optimization of **C**^{1}**-S1**, from rapid internal conversion of **C**^{1}**-S2**, leads to **C**^{1}**-S1'** with significant bond elongation between the alkyl and DHP moieties (1.57 to 1.63 Å). Interestingly, no elongation of the N-S σ-bond was observed upon optimization of excitation **C**^{1}**-S1**, suggesting that SCF_3 radical dissociation is less likely to occur upon relaxation of the lowest lying excited state.

Following the computational investigation of photoexcitation and formation of alkyl radicals, I then explored the thermodynamic feasibility of three potential pathways to product formation.

(1) As shown in Figure 2.7, from the dissociated isopropyl radical and the corresponding radical EDA complex **D**^{2} (**Path C**, *Complex Pathway*), product can be formed *via* S_H2 addition of the isopropyl radical to the SCF_3 moiety bound to the phthalimide core (**D**^{2}**-TS-E**^{1}). Despite numerous attempts, transition state **D**^{2}**-TS-E**^{1} could not be located. However, scans of this potential

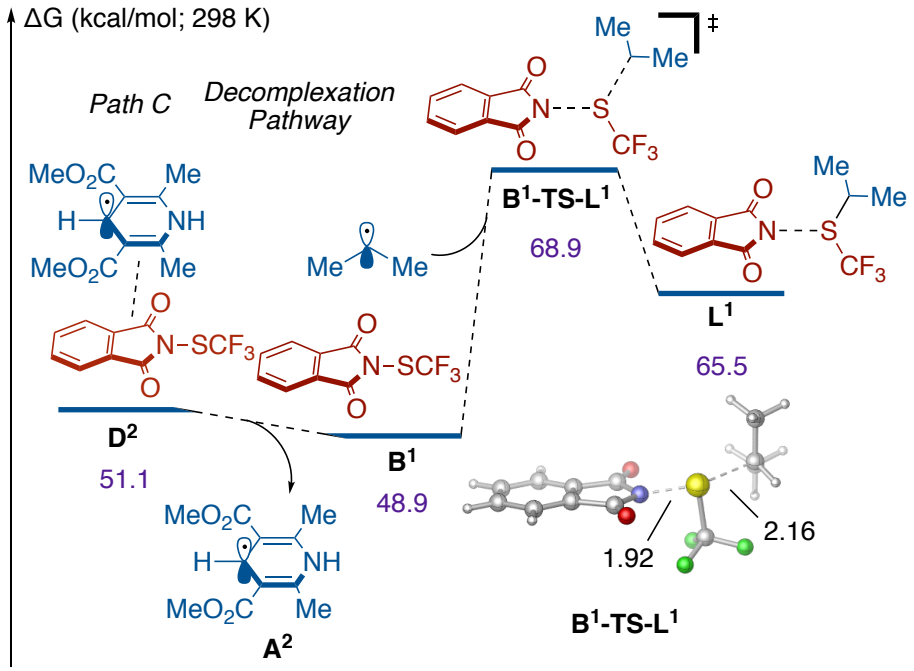


Figure 2.9: Reaction coordinate diagram to product post dissociation of EDA complex. Calculations performed by Ryan Dykstra.

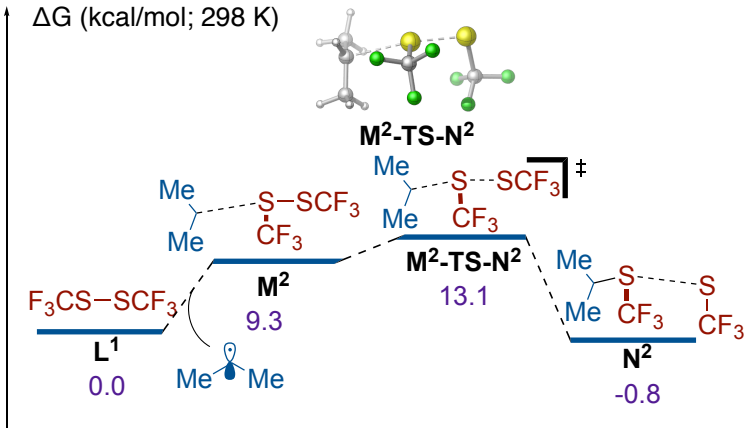


Figure 2.10: Energetics of radical addition of alkyl radical to sulfur dimer. Free Energies [DLPNO-CCSD(T)/def2-TZVPP// B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Calculations performed by Ryan Dykstra.

energy surface revealed the process to be essentially barrierless (i.e., a barrier height of 0.8 kcal/ mol with respect to **D²** in terms of total energy) and to be associated with a charge transfer event (see the Appendix for details). The resulting complex **E¹**, exergonic by 48.8 kcal/mol from **D²**, could then undergo dissociation of the desired S-C coupled product to form complex **F¹** (overall downhill in energy by 8.2 kcal/mol). In turn, reorganization of the π-stacked complex **F¹** to the hydrogen bonded complex **G¹** (Figure 2.8) is energetically favorable by 5.6 kcal/mol. Finally, proton transfer *via* tautomeric transition state **G¹-TS-H¹a** with a small barrier of 2.8 kcal/mol allows dissociation of the pyridine and phthalimide molecules.

(2) Decomplexation of **D²** (**Path C**, Figure 2.9), where dissociation of DHP radical **A²** liberates *N*-(trifluoromethylthio)phthalimide (**B¹**), is slightly exergonic by 2.2 kcal/mol. Addition of the isopropyl radical to phthalimide *via* **B¹-TS-K²** has a barrier of 20.0 kcal/mol. This implies that EDA complexation is not only required for efficient formation of alkyl radicals but also beneficial for C-S bond formation.

(3) The experimental observation of disulfide **16** (presumably generated through recombination of the corresponding thiyl radicals) and its validation as an intermediate for product formation prompted computation of the barrier for S_H2 reaction of alkyl radicals with disulfide **16** (Figure 2.10) as well as exploration of routes that lead to the generation of thiyl radicals (Figure 2.11-1.13). Complexation of alkyl radical with the sulfur dimer **M²** (Figure 2.10) occurs with a cost

of 9.3 kcal/mol with regards to the separated species **L**[1]. The following S_H2 transition state (**M**[2]-**TS-N**[2]) has a barrier of 13.1 kcal/mol and gives intermediate **N**[2], which is essentially isoenergetic to **L**[1]. These results reinforce the notion that the sulfur dimer can serve as an intermediate leading to product formation.

Turning to the exploration of potential pathways leading to thiyl radical formation, I initially sought to compute the thermodynamics of SCF_3 radical generation initiated by SET between *N*-(trifluoromethylthio)phthalimide (**B**[1]) and photoexcited DHP **A**[1] as done previously for alkyl radical (**Path A**, Figure 2.4). The free energy of the anionic intermediate formed (**B**[1·-]) post homolytic cleavage of SCF_3 from radical anion **B**[2·-] (see in the Appendix) was found to be 60.5 kcal/mol, which is higher than alkyl radical formation by 2.8 kcal/mol, suggesting that the single electron transfer pathway is unlikely the major pathway to thiyl radical. As phthalimide was shown

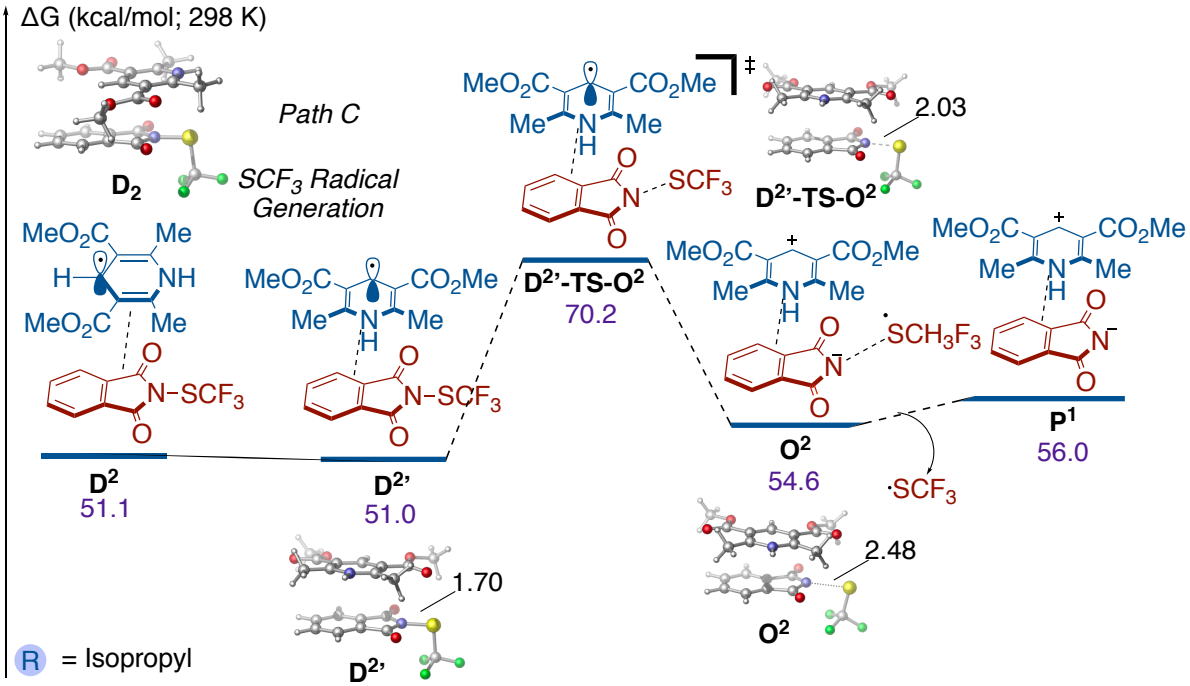


Figure 2.11: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra. Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra.

experimentally to have little to no absorbance from 405 nm and above, I did not explore excited state pathways of phthalimide leading to thiyl radical (similar to **Path B** in Figure 2.4 and 2.5). Furthermore, the TD-DFT calculations clearly suggest that photoexcitation of the EDA complex does not result in N-S bond cleavage and that C-C bond scission occurs instead (Figure 2.5, **Path C**). Therefore, two potential pathways leading to SCF_3 radical from intermediate $\mathbf{D^2}$ were explored (Figures 2.11-2.13). Interestingly, thiyl radical dissociation was only obtained *via* intermediate $\mathbf{D^{2'}}$ and was not isolated from $\mathbf{D^2}$. Homolytic cleavage of the SCF_3 functional group ($\mathbf{D^{2'}}$**-TS-**$\mathbf{O^2}$) was found to have a barrier of 19.2 kcal/mol relative to $\mathbf{D^{2'}}$, leading to intermediate $\mathbf{O^2}$, a process that is endergonic by 3.6 kcal/mol. Upon inspection of the Mulliken charges of intermediates $\mathbf{D^{2'}}$ and

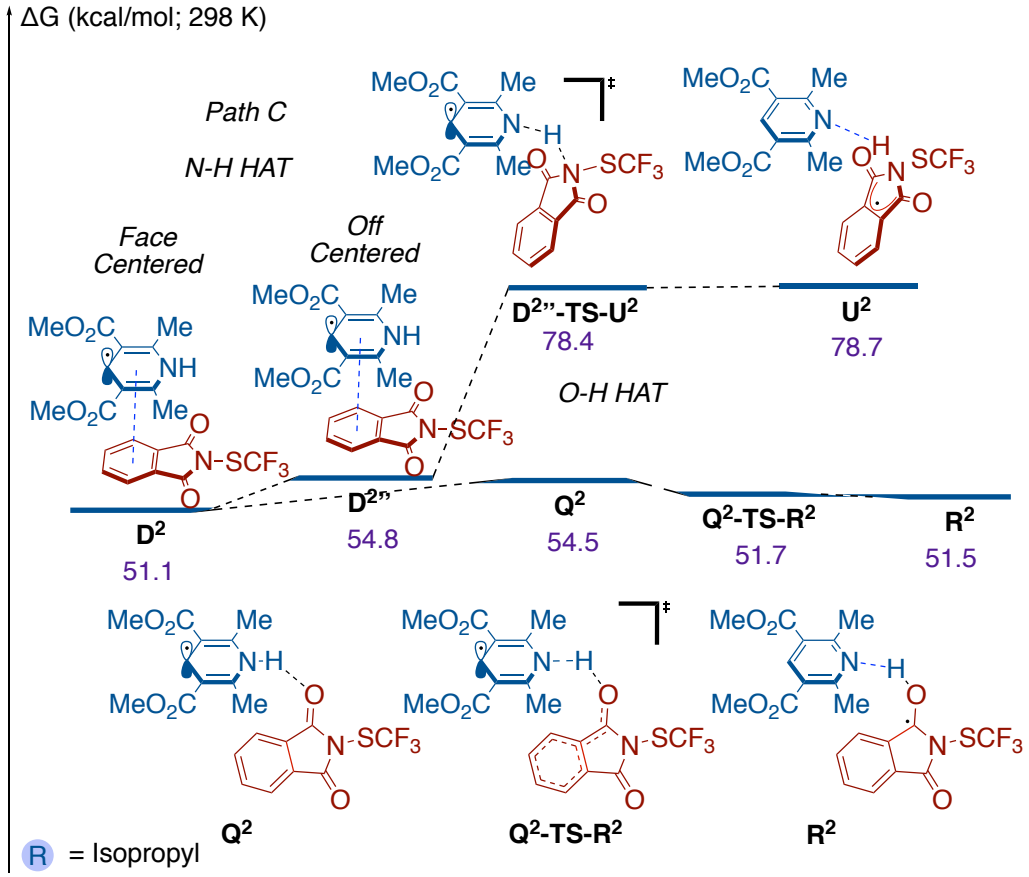


Figure 2.12: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical. Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra.

O², it was found that dissociation of the SCF_3 radical occurs in concert with charge transfer from the DHP radical to the phthalimide core, forming charge transfer complex **O²** (see the Appendix). Release of the SCF_3 radical to form **P¹** was found to be slightly higher in free energy than **O²** (by 1.4 kcal/ mol). Pyridine and phthalimide, the two side products formed in this transformation, are then liberated from complex **P¹** upon proton transfer (same as Figure 2.8).

Because of the relatively large barrier of radical dissociation directly from **D²** (19.1 kcal/mol, Figure 2.11), hydrogen atom transfer (HAT) pathways (Figures 2.12 and 2.13). Rearrangement of **D²** to the O-H hydrogen-bonded complex **Q²** is found to be 3.4 kcal/mol higher in energy. Subsequent HAT occurs *via* a barrierless transition state (**Q²-TS-R²**) to complex **R²**, which is essentially identical in energy to **D²**. As indicated in Figure 2.14, the free energy of **Q²-TS-R²** was found to be lower than that of intermediate **Q²** (by 2.8 kcal/mol).

A similar result was obtained for **D²"-TS-U²**, which also has a free energy 0.3 kcal/mol lower than its following intermediate **U²**. However, the total energies were found and have barriers of 0.8 and 1.0 kcal/mol with respect to **U²** and **R²** using B3LYP-D3 with def2-TZVPP as the basis set, though the free energies of these transition states corresponding intermediates by 0.6 and 0.8 kcal/mol, respectively. Each transition state also has a single imaginary frequency corresponding to the indicated HAT event. Dissociation of pyridine **I¹** gives **S²** and is endergonic by 1.7 kcal/mol. SCF_3 radical dissociation *via* **S²-TS-T²** has a barrier of 18.0 kcal/mol with respect to **R²** and gives intermediate **T²**, which is overall endergonic by 3.2 kcal/mol with respect to **D²**. Exploration of the N-H HAT (**D²"-TS-U²**) revealed a prohibitively large barrier of 27.3 kcal/mol when compared to **D²**. Intermediate **U²** was found to be essentially isoenergetic to the preceding transition state. Dissociation of pyridine **I¹** costs 1.5 kcal/mol and gives intermediate **V²**. Homolytic cleavage of the SCF_3 radical (**V²-TS-W²**) has a barrier of 4.9 kcal/mol relative to **V²** and gives complex **W²**,

which is exergonic by 22.7 kcal/ mol with respect to **D**[2].

For the acyl-DHP system, potential pathways for radical generation were explored using similar computations as for their alkyl counterparts (see the Appendix). TD-DFT calculations revealed that the lone acyl-DHP's lowest lying singlet excited state (Figure S12, **A**[1]**-S1**) absorbs at 433 nm and, upon optimization (Figure S12, **A**[1]**-S1'**), shows bond elongation of the acyl-DHP's C-C σ-bond (1.55 to 1.65 Å). This suggests that EDA complexation is not required for the generation of acyl radicals under these conditions. However, the free energy of EDA complexation between acyl-DHP and *N*-(trifluoromethylthio)phthalimide was found to be exergonic by 1.2 kcal/mol when computed using DLPNO-CCSD(T) (Figure S19). TD-DFT calculations on the corresponding EDA complex (Figure S14, **C**[1]) suggest hypsochromic shifting of the absorption

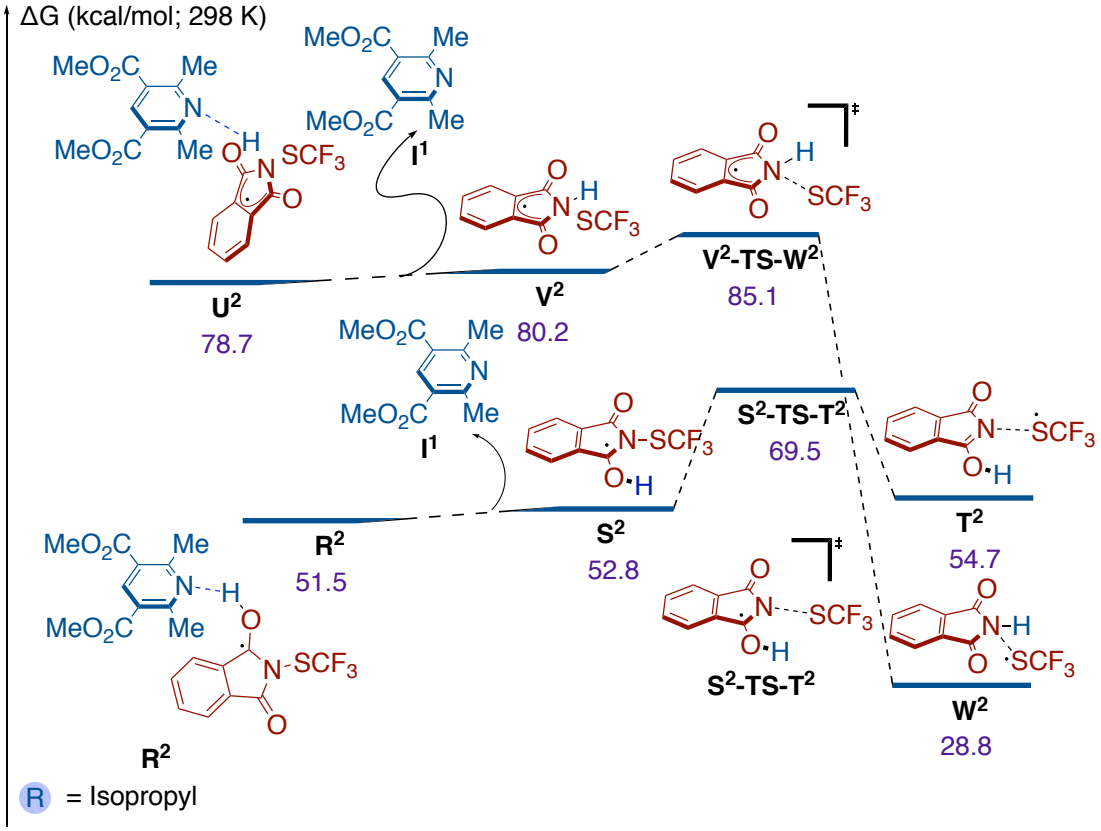


Figure 2.13: Energetics of ground state intermediates from light-mediated pathways to SCF_3 radical (part 2). Free Energies [DLPNO-CCSD (T)/def2-TZVPP//B3LYP-D3/def2-SVP-CPCM(DMSO)] in kcal/mol. Distances are reported in Ångstroms. Calculations performed by Ryan Dykstra.

spectrum from 433 to 418 nm – when comparing the lowest lying singlet excited states with significant absorbance of the noncomplexed acyl-DHP (**A^1-S1**) to that of the EDA complex (**C^1-S2**). Fast internal conversion to **C^1-S1** and relaxation of this excited state also results in bond elongation of the acyl-DHP's C-C σ-bond from 1.55 to 1.63 Å. In combination, these results indicate that photoexcitation of both the individual DHP and the EDA complex are viable pathways for acyl radical generation. However, given the large absorption coefficient of the acyl-DHPs under blue light (note the difference to their alkyl counterparts), it appears likely that direct photoexcitation of the acyl-DHPs might predominate.

Overall, computational investigations were performed to elucidate both light-mediated generation of alkyl radicals (Figure 2.5 and 2.6) and subsequent ground state pathways to product formation (Figures 2.7 - 2.10). In line with the experimental efforts, these calculations highlight the necessity of EDA-complexation for efficient alkyl radical formation. Upon photoexcitation, charge-transfer is followed by homolytic C-C bond cleavage, which delivers the alkyl radical. The subsequently formed radical complex **D^2** plays a crucial role in the two thermodynamically favorable pathways to product formation: (1) S_H2 reaction of **D^2** with alkyl radicals, although the latter represents a reaction of two transient species and might hence be less dominant than (2) S_H2 reaction of alkyl radicals with disulfide **16** (**L^1**, Figure 2.10),[83,176] which was validated experimentally. Formation of **16** occurs *via* combination of the corresponding thiyl radicals, which are generated upon completion of charge transfer in **D^2** (Figure 2.11). An alternative mechanistic scenario involving S_H2 reaction of alkyl radicals with *N*-(trifluoromethylthio)phthalimide (**B^1**, Figure 2.9) was found to be both kinetically and thermodynamically less favorable, but probably represents a co-existing pathway that might even be dominant in an early phase of the reaction, before sufficient levels of disulfide **16** are accumulated.

2.4 Conclusion

In summary, the Molander group has developed a catalyst- and additive-free decarbonylative trifluoromethylthiolation of aldehydes under open-air conditions. This abundant feedstock has not been previously employed as a source of alkyl radicals to construct C(sp^3)-SCF_3 and C(sp^3)-SCN bonds, thus providing a complementary approach to help increase chemical space. This photochemical strategy is driven by selective excitation of electron donor-acceptor (EDA) complexes, stemming from the association of 1,4-dihydropyridines with *N*-(trifluoromethylthio)phthalimide, to trigger intermolecular SET events that deliver reactive radical species under ambient conditions. The synthetic utility is further demonstrated through visible light-promoted radical thiocyanation, thioesterification, and conjunctive 1,3-difunctionalization of [1.1.1]propellane. The necessity for EDA complexation of the dihydropyridine donor and phthalimide acceptor for efficient alkyl radical generation was elucidated through a combination of spectroscopic measurements performed by the Molander group and high-level quantum mechanical calculations [dispersion-corrected (U)DFT, DLPNO-CCSD(T), and TD-DFT], which I performed. Specifically, computation of subsequent ground state pathways revealed that S_H2 addition of the alkyl radical to the intermediate radical EDA complex $\mathbf{D^2}$ is extremely exergonic and results in a charge transfer event, yielding intermediates poised to undergo facile deprotonation. Alternatively, product formation can occur through S_H2 reaction of alkyl radicals with disulfide **16**, which was observed experimentally, or with *N*-(trifluoromethylthio)phthalimide. This comprehensive case study provides a deeper understanding of photoactive EDA paradigms involving phthalimide- as well as DHP-systems and exemplifies how such EDA manifolds can be treated computationally.

Chapter 3: Elucidation of Radical/Polar Crossover Mechanism for the Redox-Neutral Photocatalyzed Cyclopropanation

Excerpts from this chapter were published in: Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; **Dykstra, R.**; Gutierrez, O.*; Molander, G. A.* Redox-Neutral Photocatalytic Cyclopropanation via Radical/Polar Crossover. *J. Am. Chem. Soc.* **2018**, *140*, 8037–8047.

3.1 Introduction

The cyclopropyl group is a common motif found in many pharmaceutical products[177,178] and secondary metabolites.[179] It is employed to increase metabolic stability, enhance potency, and decrease plasma clearance.[177] Consequently, cyclopropane rings appear in 10 of the top 200 highest grossing pharmaceutical products from 2011.[178] Furthermore, the substitution pattern of these rings can impart bioisosteric properties. Trifluoromethyl-substituted cyclopropanes (TFCps) are salient examples of the unique bioisosterism possible with cyclopropanes; TFCps are tert-butyl

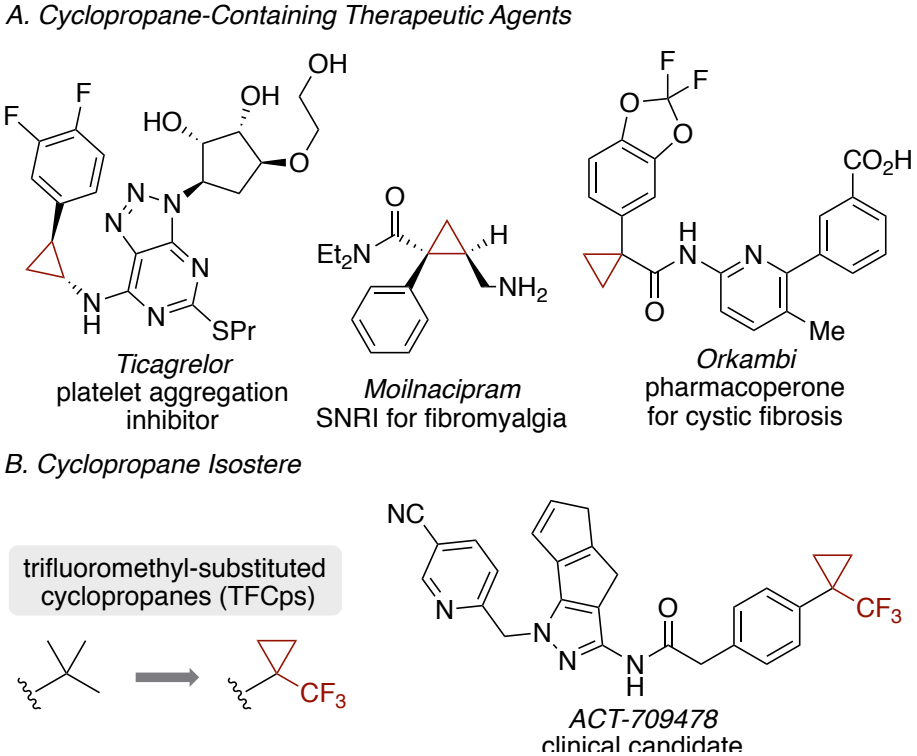


Figure 3.1: Cyclopropane containing pharmacons and trifluromethyl-substituted cyclopropanes.

isosteres that improve in vitro and in vivo stability while retaining biological activity.[180–188] A TFCp was utilized in the development of a selective, brain-penetrating T-type calcium channel blocker (ACT-709478) with a safety profile suitable for advancement into Phase I clinical trials (Figure 3.1B).[183] Among the more popular strategies for cyclopropane assembly are [2 + 1]-type reactions with olefins. Some examples include the use of carbenoids generated from diethylzinc and halomethanes (Simmons−Smith),[189–195] or via diazo compounds.[196,197] In some cases, a two-step process (Michael-type addition followed by intramolecular nucleophilic displacement) can be employed for the direct cyclopropanation of certain olefins (e.g., sulfur ylides with enones in the Corey−Chaykovsky reaction).[197–199] Although these routes are well-established in the literature, they are often lacking in broad functional group tolerance or operational simplicity, and rarely employ mild conditions. Specifically, state-of-the-art methods for TFCp synthesis by cyclopropanation rely on multistep sequences involving treatment of the corresponding trifluoromethyl alkene with diazomethane followed by a retro-[3 + 2]-cycloaddition in refluxing xylenes (Figure 3.2A).[180,184,185] Alternate strategies that do not rely on cyclopropanation of CF_3-substituted olefins do exist (e.g., cationic ring closure,[186,187] Minisci-type alkylation[188]), but their scope is constrained by inherent mechanistic limitations.

Single-electron approaches for the cyclopropanation of alkenes are much less well-developed. Leading methods rely on the use of diazo compounds,[200–204] prefunctionalized substrates,[205,206] or methods that require large excesses of reagents and multiple additives.[207,208] Thus, these methods are not easily employed in late-stage functionalization of complex molecules. Photoredox catalysis has enabled the operationally simple generation of radicals while maintaining the broad functional group tolerance and orthogonality to acidic or basic residues that is associated with processes proceeding through open shell intermediates.[92–94,209,210] These catalysts are chromophores, that

have long lived excited states which, when excited with visible light, have unique redox potentials (Figure 3.2B). After excitation, these catalysts undergoes either oxidative or reductive quenching

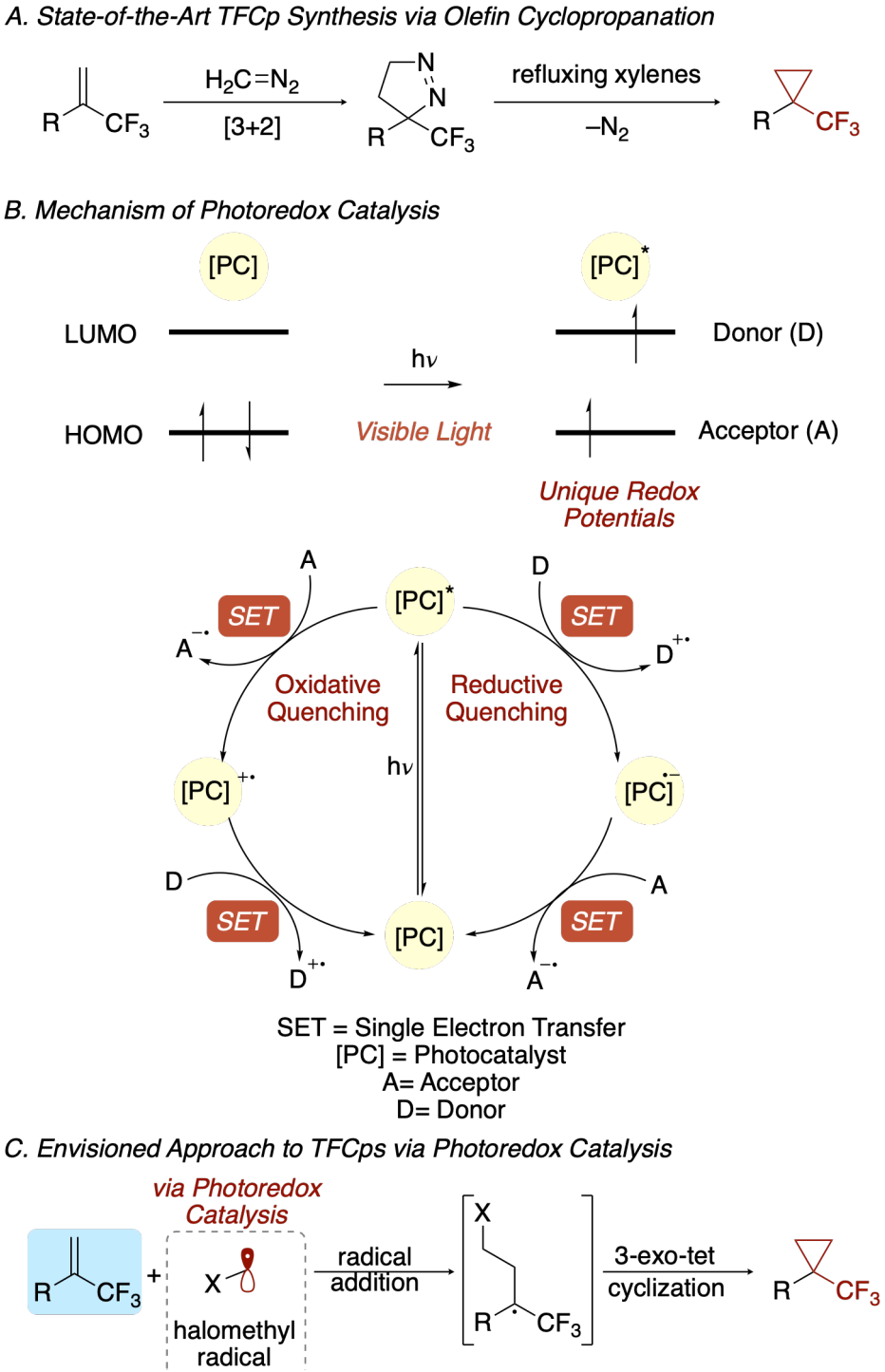


Figure 3.2: Synthetic stratedgy to access TFCps.

cycles with donor or acceptor substrates. One of these donor or acceptor substrates generate reactive radicals upon oxidation or reduction, coined radical precursors (RPs), to generate catalytic quantities of radicals. Though numerous radical precursors have been made since the application of photoredox in synthetic organic chemistry,[93,94,211,212] no photooxidizable C1 reagent for radical cyclopropanation is described in the literature. The Molander group thus directed their efforts toward designing such a species to fill this gap. They envisioned that a reagent furnishing a halomethyl radical could operate as a cyclopropanating reagent where, following radical addition to an olefin, a 3-exo-tet cyclization would forge the second C–C bond required for cyclopropanation (Figure 3.2C). In addition to serving as an effective cyclopropanating reagent, successful design of a reagent furnishing a halomethyl radical would allow the properties of this

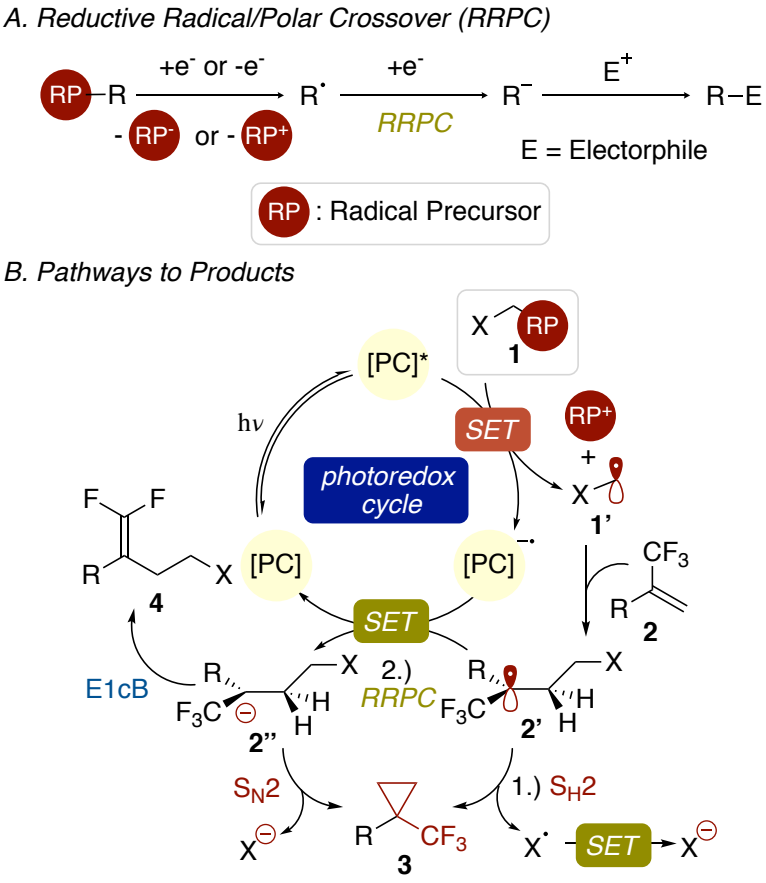


Figure 3.3: Radical/Polar Crossover Mechanism of Cyclopropanation.

reactive odd-electron intermediate to be probed.[213–216] Reductive radical/polar crossover (RRPC) reactions (Figure 3.3A), discovered in the 1990s,[217,218] where a stable radical intermediate is converted to an anion via SET from an electron source, was revived in 2017 due to the ability of a photoredox catalyst to undergo two electron transfer events to generate both the radical and anionic intermediate in one catalytic cycle.[219] With this in mind, the envisioned cyclopropanation (Figure 3.3B) could follow two pathways to product: 1) direct S_H2 cyclization from the radical intermediate **2'** where the resulting halogen radical is reduced by the photocatalyst or 2.) the photocatalyst undergoes RRPC with **2'** to generate the anion **2''** which can undergo S_N2 cyclization to product. To discern which pathway is responsible for product formation, quantum calculations were performed, as the nature of the cyclization cannot be decerned experimentally. Additional calculations were performed on the E1cB fluorine elimination pathways, on cyclization's from non-trifluoromethyl substituted olefins and on a single electron transfer bracketing experiment.

3.2 Methods

Calculations were initially performed at the UM06-2X/DGDZVP level of theory in implicit solvent.[28] Further, to assess the influence of dynamic correlation, open-shell, domain-based local pair, and natural orbital Coupled-Cluster calculations using single and double with perturbative triple excitations (DLPNO−CCSD(T)) using def2-TZVPP basis using ORCA were also performed.[35,37] This latter method provides accurate energies (within 3 kJ/mol) with the computational cost comparable to DFT calculations.[220,221] Single point energy calculations in implicit solvent using B3LYP-D3BJ/def2-TZVPP and UM06-2X/def2-TZVPP were performed in parallel for comparison, which revealed identical trends and very similar energetic profiles as the

DLPNO−CCSD(T) method (see Appendix).[222] For simplicity, only DLPNO−CCSD(T) free energies are presented and discussed explicitly in the text. All 3D structures were generated using CYLview.[161]

3.3 Results and Discussion

3.3.1 Pre-Computation Experimental Work

This part of the work was performed by members of the Molander group.

The Molander group synthesized α-halomethyl bis(catecholato)silicates[223] (α-chloro **1a**, α-bromo **1b**, and α-iodo **1c**) from commercially available chloromethyl-trimethoxysilane (~$0.26 per mmol)[223] to serve as radical precursor of a halomethyl radical. Application of this novel radical precursor in the presence of trifluoromethyl-substituted alkene **2** under the photoredox conditions outlined in Figure 3.4 gave the cyclopropane product **3** and fluorine elimination byproduct **4**. It was noted that the halogen on the radical precursor influence the product distribution, where iodine gave predominant formation of TFCps **3** while bromine and chlorine pushed the product distribution towards byproduct **4**.

The substrate scope of this transformation showed generally good yields and with excellent functional group compatibility[223] with some examples shown in Table 3.1. Multiple arenes (**3a**−**h**) reacted efficiently to provide the desired products. The reaction was not limited to α-styryl

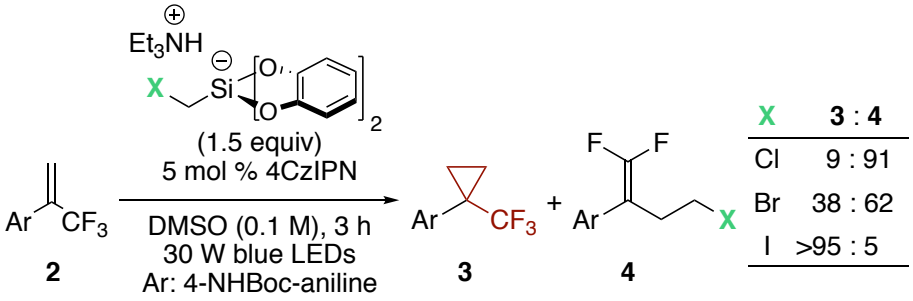


Figure 3.4: Influence of halogen of radical precursor on product distribution of 3 and 4. Product rations determined by 19F NMR. Sythesis performed by the Molander group.

trifluoromethyl-substituted alkenes. A representative trifluoromethyl-substituted aliphatic alkene (**3i**) also efficiently underwent cyclopropanation, albeit at an extended reaction time and with higher silicate loading.

Table 3.1: Selected Substrate Scope of CF_3-Substituted Alkenes

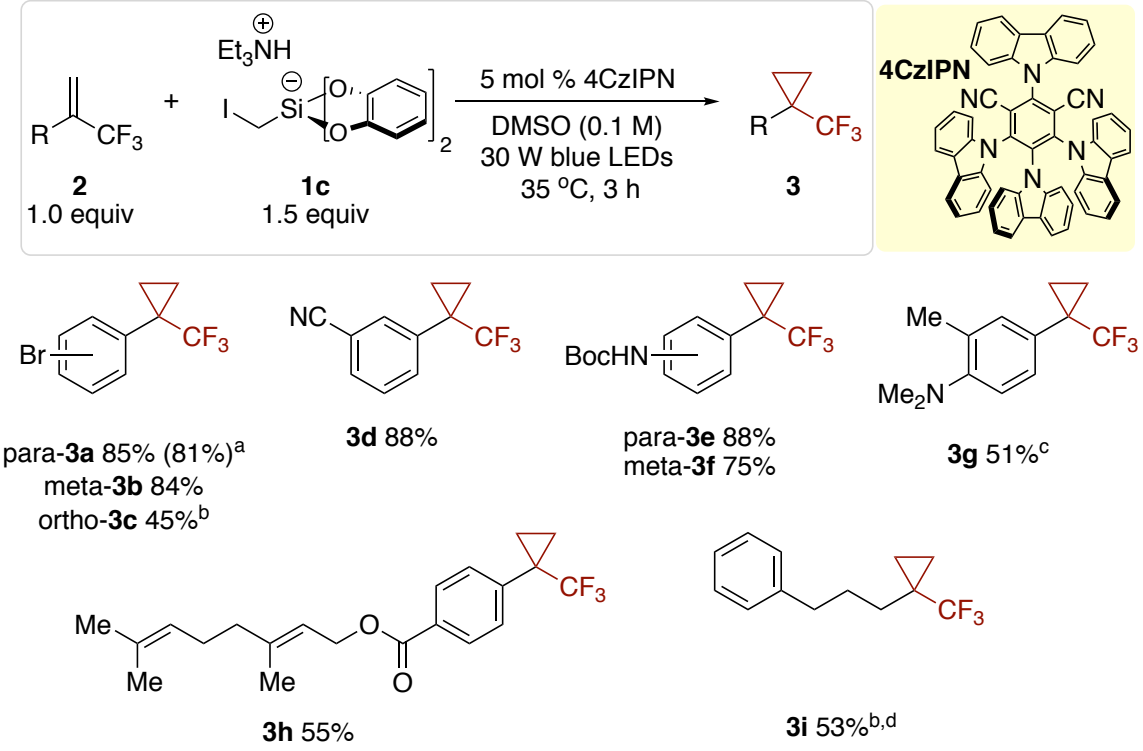
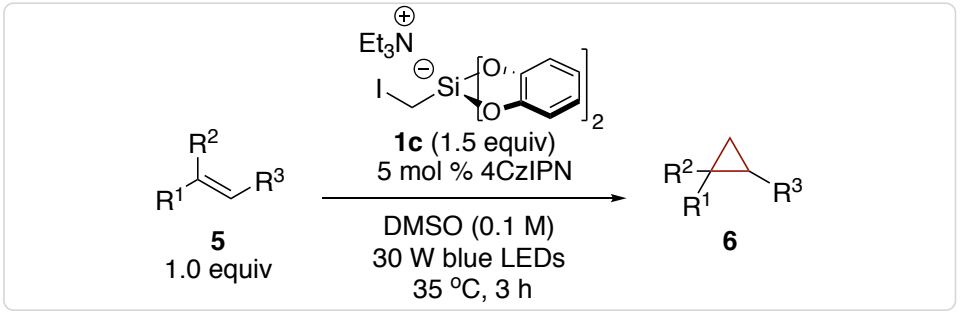


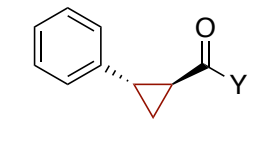
Table 3.1: All values indicate yield of the isolated product. pin = 2,3-dimethylbutane-2,3-diol. General reaction conditions: iodosilicate (1.5 equiv, 0.75 mmol), alkene (1.0 equiv, 0.50 mmol), 4CzIPN (5 mol %, 0.025 mmol), DMSO (0.1 M), 3 h, irradiating with blue LEDs (30 W). [a]Isolated yield on 5 mmol scale. [b]Conducted using 2.0 equiv of silicate. [c]Conducted using 1.75 equiv of silicate. [d]Reaction run for 24 h. Reactions performed by the Molander group.

The generality of this transformation was then explored by applying it to an array of stereoelectronically diverse olefins. Overall, various electronically distinct olefins were amenable to cyclopropanation, and the functional group tolerance matched that observed with trifluoromethyl-substituted alkenes (some examples shown in Table 3.2). α,β-Unsaturated ester and amides (**5a**–**5d**) readily underwent the cyclopropanation to give the corresponding trans products (Table 3.2). Several alkenes bearing 1,1-disubstitution (**5e**) and 1,1-diarylethylenes **5f**–**5h**) were readily cyclopropanated.

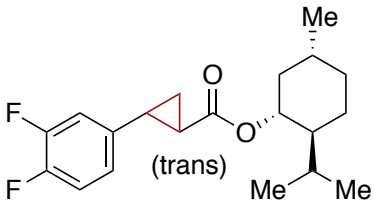
Table 3.2: Cyclopropanation of Diverse Olefins

Cyclopropanation of Stereoelectronically Diverse Olefins

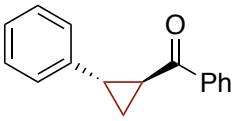




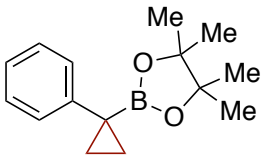
(±)-**6a** Y = OMe, 65%
(±)-**6a**' Y = OEt, 75%
(±)-**6b** Y = NHEt, 53%[a]



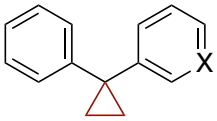
1:1 dr
6c 59%



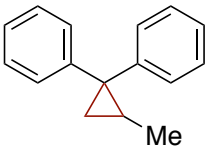
(±)-**6d** 45%



6e 71%



6f X = CH 98%[c]
6g X = N 44%[c]



6h 73%[a,b,c]

Table 3.2: All values indicate yield of the isolated product. General reaction conditions: iodosilicate (1.5 equiv, 0.75 mmol), alkene (1.0 equiv, 0.50 mmol), 4CzIPN (5 mol %, 0.025 mmol), DMSO (0.1 M), 3 h, irradiating with blue LEDs (30 W). [a]Conducted using 2.0 equiv of silicate.[b]Reaction run for 18 h. [c]Product isolated as a 94:6 mixture of product and starting material. Reactions performed by the Molander group.

Mechanistic experiments were then performed to determine whether the proposed 3-exo-tet cyclization proceeded via an anionic (S_N2) or radical (S_H2) pathway. These experiments were inconclusive to which pathway led to product as iodine is both more prone to nucleophilic and radical displacement. Experiments on the electronics on product distribution did not show substantial change in the distribution.[223] Interestingly, the reaction could also be conducted in the presence of 3 equivalents of trifluoroacetic acid (TFA) without any change in ratio or reaction conversion, suggesting cyclization must be faster than protonation or hydrogen atom transfer of

the corresponding anionic or radical intermediate formed. Although intriguing, these results were not sufficient to preclude one of the two cyclization pathways.

3.3.2 Computational Work

This part of the work was performed by Ryan Dykstra.

I began quantum mechanical calculations to evaluate these mechanistic postulates more conclusively. Specifically, I sought to determine which of the two mechanisms more accurately described the observed results (i.e., α-halomethyl radical influence on product selectivity, 3.4). The barriers of radical 3-exo-tet cyclization were initially modeled. In this pathway (Figure 3.5), radical intermediate **2′** presumably arises from Giese-type addition[224–228] of the halomethyl radical **1′** to the alkene **2**, which can undergo ring-closure via an S_H2 mechanism to deliver the desired TFCp **2**'. Note that energetics of the initial radical addition to the alkene show regioselective formation of α-radical **INT-I**, implying that α-radical formation is both kinetically and thermodynamically favored over β-radical formation (see the Appendix for additional details). Except for the iodo system (22.0 kcal/mol barrier of cyclization from **INT-I**), the barriers for the radical cyclization (S_H2-type pathway, **TS-II** and **TS-III**, respectively) are not feasible under experimental conditions (barriers are 27.6 kcal/mol and 34.5 kcal/mol). All other methods predicted similar barriers (see Appendix). This was surprising given that formation of cyclopropane was observed with all halomethyl silicates. Even more surprising was the fact that, in all cases, the reactions are net endergonic. Notably, the barriers and (endergonic) reaction energies are consistent with the strength of the C−X bond (C−X bond dissociation energies for C−I, C−Br, and C−Cl are ∼57, ∼71, and ∼85 kcal/mol, respectively).[229] The computed barriers for a possible radical-mediated fluoride elimination to give the gem-difluoroalkene (not shown)

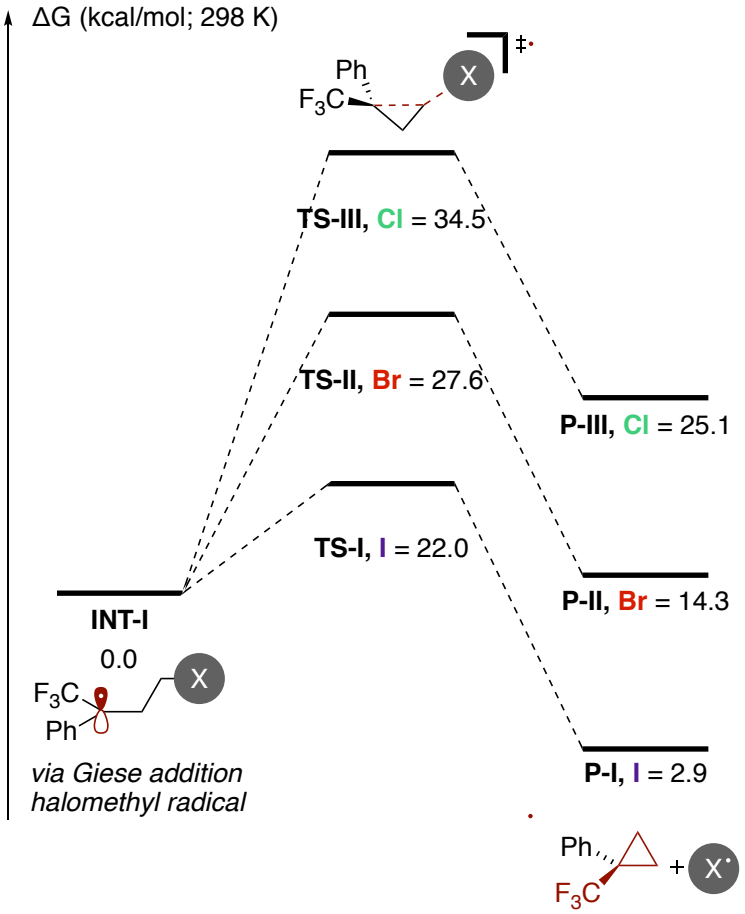


Figure 3.5: Barriers and thermodynamics of S_H2 cyclization vs. E1cB of fluorine. I performed all calculations.

were too high to be feasible and were universally highly endergonic (~63 kcal/mol between all adducts of halomethyl addition).

The energetic inconsistency of the radical cyclization pathway with the experimental observations led us next to investigate whether anionic pathways might be operative for both cyclization and gem-difluoroalkene formation (Figure 3.6). In excellent agreement with experiment, the computed barriers for the anionic pathway: (1) are feasible under experimental conditions (~4−9 kcal/mol) and exergonic (~ −4 to −43 kcal/mol), and (2) qualitatively and quantitatively replicate the experimental trends (Figure 2.4B). Further, although the barriers for the S_N2-type cyclization increase with the leaving group ability (I > Br > Cl), the barriers for the elimination (E1cB pathway) remained relatively unchanged for all halo systems (6.7-7.5

kcal/mol). Therefore, for the iodo-system, cyclopropane formation **P−IV** (via S_N2-type transition state) is kinetically favored by 2.8 kcal/mol over the alkene product (**P−VII**). However, for the bromo system, the energy difference between these two competing pathways decreases ($\Delta\Delta G^{\ddagger}$ is

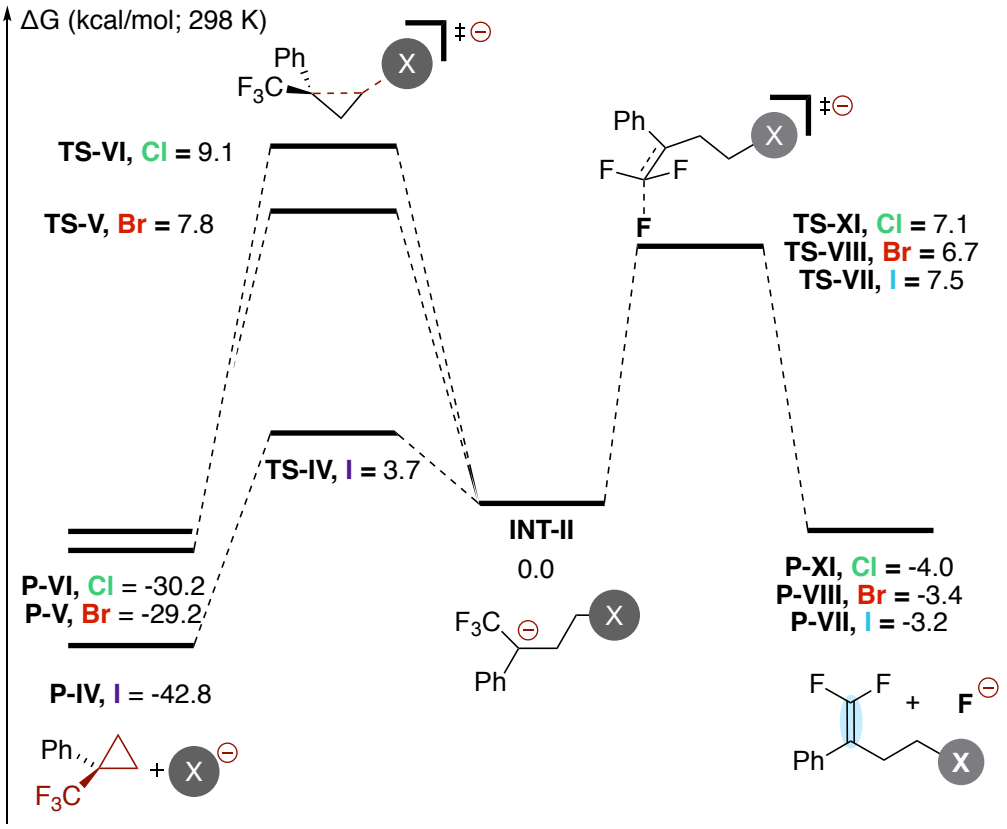


Figure 3.6: Barriers and thermodynamics of product for S_N2 cyclization vs Ec1B release of fluorine. I performed all calculations.

1.1 kcal/mol for **TS-V** versus **TS-VIII**) in favor of gem-difluoroalkene formation. Finally, in the chloro-system, the elimination transition state (**TS-IX**) is favored by 2 kcal/mol over the substitution pathway (via **TS-VI**), thus further favoring the formation of the alkene.

Not only do the barriers for cyclization explain the observed selectivity (and, because of their less energy-demanding nature, rule out the S_H2-type pathway), but they agree with the experimentally observed results. Both pathways rule against intermolecular (bimolecular) protonation as a viable reaction outcome because the reaction is likely proceeding at catalytic concentrations of anionic and radical intermediates, and the barriers for intramolecular cyclization

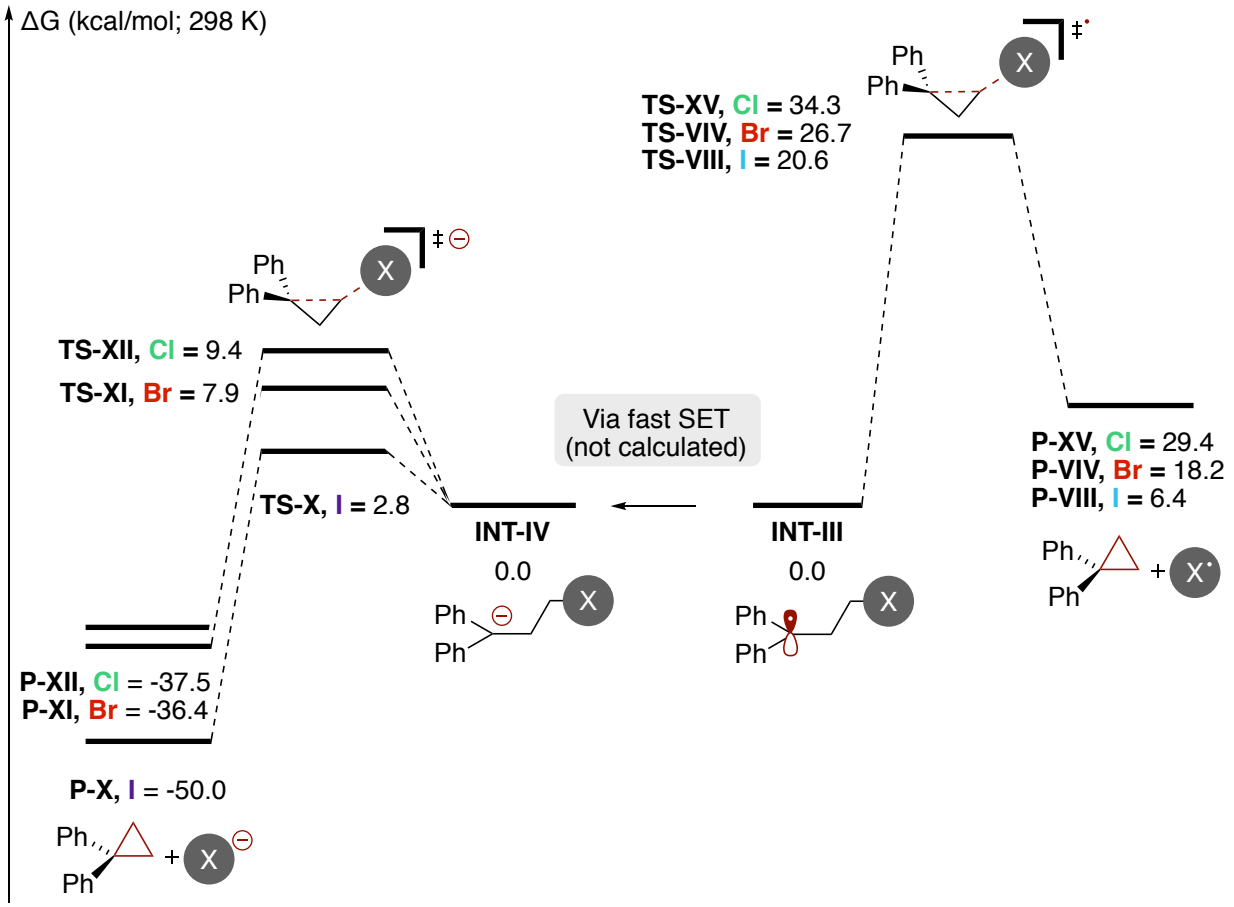


Figure 3.7: Barriers and thermodynamics of product for S_N2 cyclization vs Ec1B release of fluorine. I performed all calculations.

and elimination are low (<9 kcal/mol). This rationalizes how this reaction can operate in the presence of a highly acidic species such as TFA This same insensitivity toward acid likely rules out the formation of an iodomethyl anion (and thus the formation of carbene). Moreover, it explains how gem-difluoroalkene formation is the predominant pathway when using non-bifunctional radicals, rather than traditional Giese-type hydro-alkylation.[230,231] Finally, the very low barrier for cyclization from the iodomethyl-derived anion (Figure 3.6, **TS-IV**) explains the relative insensitivity to varying electronics of the arene, see publication for .

Next, I wondered whether the mechanistic findings would translate to the nontrifluoromethylated systems using **1c**. More specifically, the possibility of a mechanistic spectrum where the electronics of an α-substituent would control whether the cyclization proceeds

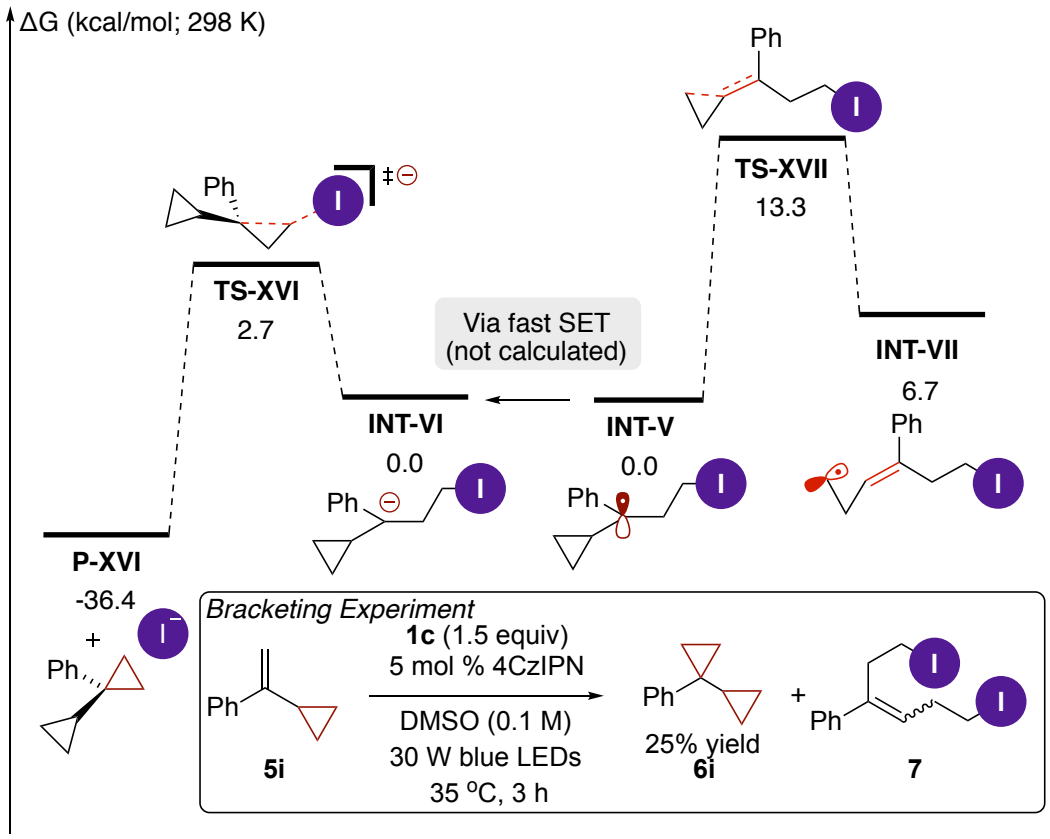


Figure 3.8: Barriers and thermodynamics of S_N2 cyclization vs radical ring opening of cyclopropane substituted olefin. I performed all calculations. Bracketing experiment performed by the Molander group.

through a radical or anionic pathway. Whereas photoredox Giese-type processes are established for α-carbonyl[232–234] and α-boryl[235–240] olefins, similar reactivity in more electron-rich olefins is not established. Thus, the energetics of anionic and radical ring closure for a representative system, 1,1-diphenyl-ethylene were evaluated (Figure 3.7). The result of this set of calculations rules out a mechanistic spectrum; the energetic trends are similar to the α-trifluoromethyl systems. That is, the barrier for radical cyclization is ~20 kcal/mol (via **TS-XIII**) from the corresponding 1,1-diphenyl-3-iodopropyl radical, while the barrier for the cyclization from the corresponding 1,1-diphenyl-3-iodopropyl anion is virtually barrierless (~3 kcal/mol; via **TS-X**). Importantly, the anionic mechanism is contingent on a rather fast (and favorable) SET reduction of the intermediate radical. Other halomethyl radical additions show similar trends.

To computationally bracket the rate of electron transfer, calculations were performed on anionic cyclization and radical ring opening from both anionic and radical intermediates generated post Giese addition to a cyclopropane substituted olefin. As the barrier of cyclization is found to be substantially lower than radical ring opening (Figure 2.8), the rate of electron transfer controls which product is observed.

3.3.3 Post-Computation Experimental Work

This part of the work was performed by members of the Molander group.

The transition states for the reaction of the 1,1-diphenyl-ethylene with various halomethyl radicals (Figure 3.7) are suggestive that, if an anionic pathway is indeed operative, cyclization should be feasible under experimental conditions with even the less reactive chloromethyl radical as fluorine elimination is not possible. To probe this prediction, the cyclopropanation of various non-trifluoromethyl substituted olefins using chloromethylsilicate **1a** was attempted under the conditions optimized for **1c** (Table 3.3), resulting in varying levels of success. Overall, the isolated yields were lower when using **1a**, reflective of the higher barrier to cyclization onto an alkyl chloride versus alkyl iodide. Seemingly less-stabilized anions were more likely to engage in appreciable cyclization. Substrates that proceed through stabilized enolate anions (**5a′**, **5d)** provide no cyclized product. Additionally, some substrates preferentially underwent protonation to give the uncyclized, alkyl chloride Giese-type addition product (**5g**). Overall, the observations here are consistent with the proposed anionic cyclization pathway.

The experimental results are again borne out in the computational model (Figure 3.8). The calculated ring opening process for this system shows that the barrier for SET reduction must be lower than the calculated barrier for ring-opening (13.3 kcal/mol). This agrees with the bracketing

experiment (Figure 3.8, Bracketing Experiment) where only cyclopropane product is observed. To bracket the rate of radical reduction experimentally, **5p** was prepared and subjected to cyclopropanation. Surprisingly, the major product was bis-cyclopropane **6p**, albeit in low isolated yield. Giese-type adduct **7** was not observed (Figure 3.8). This implies that SET reduction exceeds the known rate constant of ring opening for the related α-cyclopropyl benzyl radical of 1.1×10^4 s^{-1}, which corresponds to a barrier of ~11.1 kcal/mol at 298 K.[241]

Table 3.3: Comparison Chloromethyl and Iodomethyl Silicates

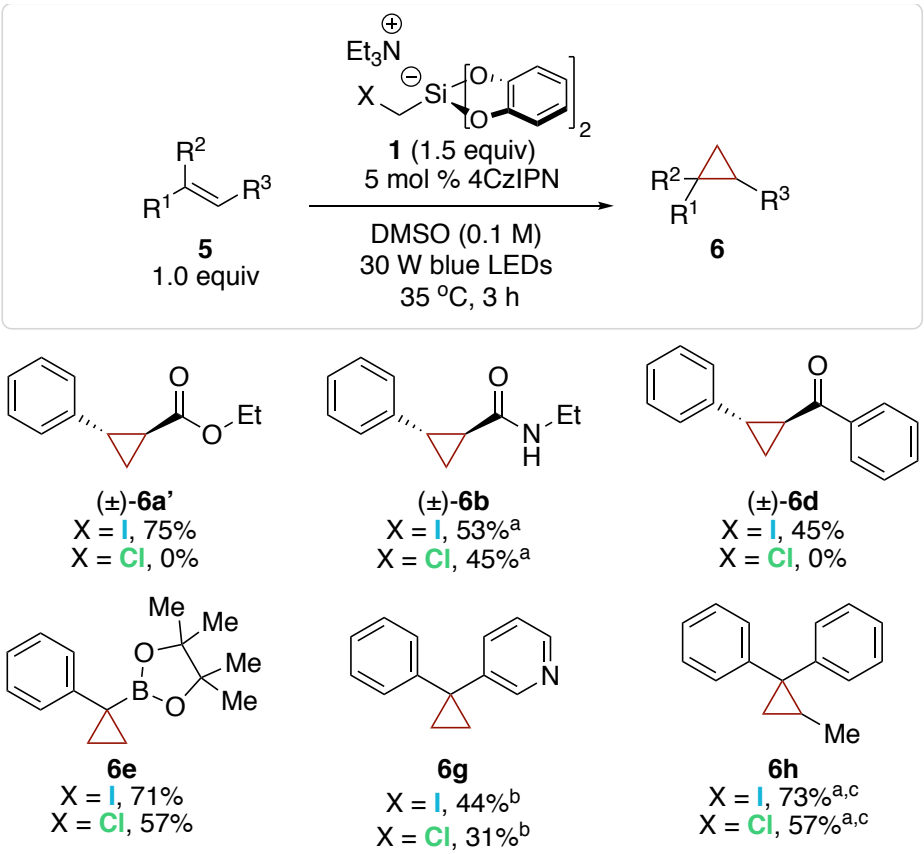


Table 3.3: All values indicate yield of the isolated product. General reaction conditions: iodosilicate (1.5 equiv, 0.75 mmol), alkene (1.0 equiv, 0.50 mmol), 4CzIPN (5 mol %, 0.025 mmol), DMSO (0.1 M), 3 h, irradiating with blue LEDs (30 W). [a]Conducted using 2.0 equiv of silicate.[b]Conducted using 1.75 equiv of silicate. [c]Reaction run for 18 h.e[g]Isolated product contained 2% yield of non-cyclized Giese-type addition product. [f]Isolated 60% yield of non-cyclized Giese-type addition product. Reactions performed by the Molander group.

With all these data in hand, the following order of events as the operative mechanism are proposed (Figure 3.9 under the developed reaction conditions: 1) Visible light-mediated photoexcitation of 4CzIPN to its excited state. 2) Reductive quenching of 4CzIPN* by halomethyl

silicate **1**. This mode of quenching is supported by Stern−Volmer emission quenching experiments (see Appendix) and also by the generally low, favorable oxidation potentials of silicates (E1/2 = +0.4−0.7 vs SCE) and the high, unfavorable reduction potentials of primary iodides (e.g., E1/2 = −1.44 V vs SCE for CH_2I_2).[207] Subsequent fragmentation of oxidized b furnishes halomethyl radical **1′**. (3) After radical generation, Giese-type addition by the halomethyl radical generates adducts **2′** or **5′**. (4) SET reduction of these adducts by the reduced state of 4CzIPN gives anions **2″** or **5″** and returns 4CzIPN to its original ground state. (5) Anionic cyclization of **2″** or **5″** furnishes cyclopropanes **3** or **1.** Ultimately, this process is a closed cycle and does not appear to operate by a chain mechanism. The quantum yield of this process was determined to be 0.066, implying that an assisted chain process is not operative.

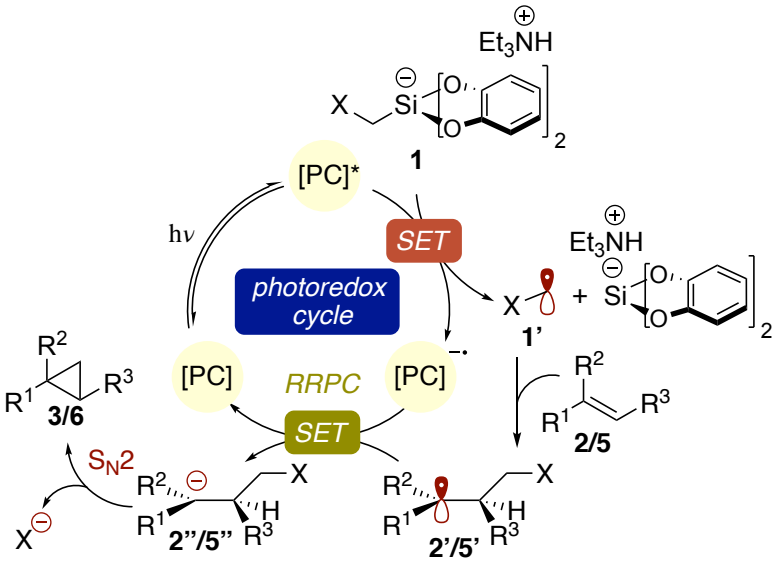


Figure 3.9: Proposed mechanism for cyclopropanation

In cases where the olefin is 1,2-disubstituted or trisubstituted, stereoconvergence is observed. Stereoconvergence likely arises from rapid equilibration of Giese-adduct 2/5 to the most stable conformation followed by stereoretentive reduction and rapid ring closure (see Appendix for calculations supporting this hypothesis). Alternatively, because photochemical isomerization of the starting olefin is possible, a dynamic kinetic resolution-type scenario may arise. Experimental comparisons between this work and the previous method by Suero and co-workers can be seen in the publication of this work. [164]

3.4 Conclusion

Herein, the successful development of a new reagent for the redox-neutral cyclopropanation of olefins under mild, photo- catalytic conditions is disclosed. This reagent has not only resulted in the generation of a suite of TFCps, but also enabled radical/polar crossover cyclopropanation of a diverse range of olefins to be accomplished with ease and excellent functional group on reaction likely proceeds via a photooxidatively generated iodomethyl radical addition to an olefin followed by radical SET reduction, culminating in an anionic 3-exo-tet ring closure. Further applications for this reagent are under development and will be reported in due course. More generally, the findings disclosed here not only enable facile access to halomethyl radicals, but also begin to shed light on the unique capabilities of these C1 synthons.

Chapter 4: Mechanistic Investigation into the Photocatalyzed Diastereoselective Isomerization of Cinnamyl Chlorides to Cyclopropanes

Excerpts from this chapter were published in: Xu, B.; Troian-Gautier, L.; **Dykstra, R.**; Martin, R. T.; Gutierrez, O.*; Tambar, U. K.* Photocatalyzed Diastereoselective Isomerization of Cinnamyl Chlorides to Cyclopropanes. *J. Am. Chem. Soc.* **2020**, *142*, 6206–6215.

4.1 Introduction

Molecules incorporating cyclopropanes have fascinated organic chemists for decades. The cyclopropyl group is a common motif found in many pharmaceutical products and secondary metabolites.[242,243] This privileged functional group is employed to increase metabolic stability, enhance potency, and decrease plasma clearance in druglike molecules.[177,179]

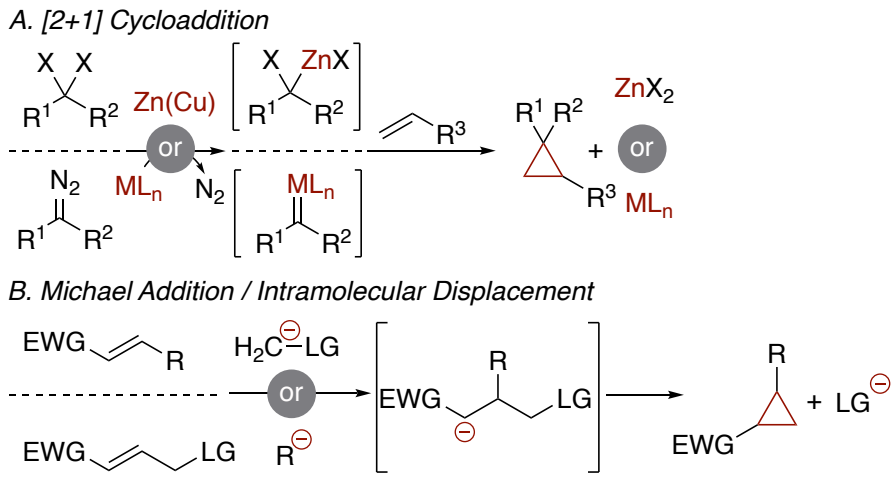


Figure 4.1: Classical methods to synthesize cyclopropanes.

The strain associated with the cyclopropane ring system (approximately 27 kcal/ mol), along with the electronic character of its bent carbon−carbon bonds, has been the subject of many seminal discoveries in chemical structure and bonding.[244,245] Moreover, the unique reactivity of cyclopropanes has been exploited for the synthesis of several distinct classes of products.[197,246–248] Given the general intrigue and practical utility of cyclopropanes, synthetic chemists have developed elegant strategies for the assembly of these three-membered ring systems. To date most

approaches are based on the reaction of stable substrates with high energy reagents that provide the potential energy necessary for generating strained cyclopropanes (Figure 5.1). Popular strategies for cyclopropane synthesis include [2 + 1]-type cycloadditions between alkenes and reactive reagents, such as carbene equivalents generated from diethylzinc and dihalomethanes (Simmons–Smith reaction)[190,213,249] or metal carbenes generated from diazo compounds (Figure 4.1A).[250,251] In some cases (Figure 4.1B), a two-step process (Michael-type or Giese addition followed by intramolecular displacement) can be employed for the cyclopropanation of activated alkenes (e.g., sulfur ylides with enones in the Corey–Chaykovsky reaction or alkyl radicals in radical-polar crossover cyclopropanations).[252] Although these routes are well-established in the literature, they are often lacking in broad functional group tolerance and operational simplicity and rarely employ mild conditions. More recently, photoreducible and photooxidizable C1 reagents and olefins, in combination with a photoredox catalyst, have been developed by Suero,[207,208,253,254] Molander,[223,255,256] Aggarwal,[257] and others.[258–262]

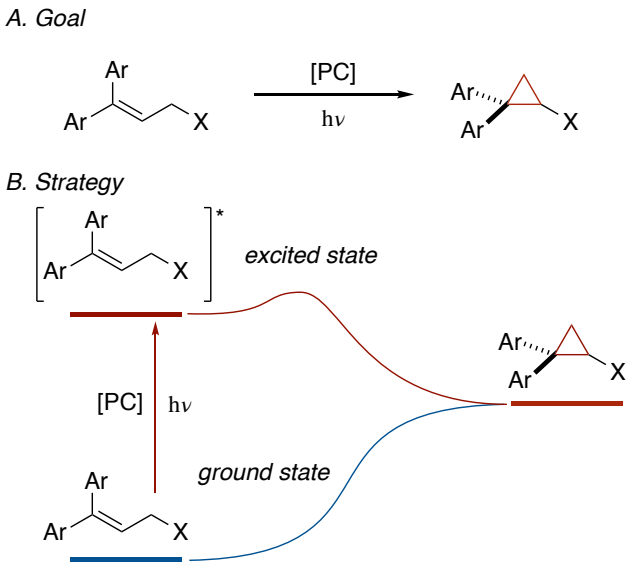


Figure 4.2: Energetically uphill isomerization of acyclic compounds to strained cyclopropanes.

The Tambar group was interested in developing a different strategy to access strained cyclopropanes via the photocatalytic unimolecular isomerization of their low energy acyclic precursors (Figure 4.2A). If successful, this novel approach would be a more atom-economic and direct synthesis of cyclopropanes. However, the thermal isomerization from a low energy substrate to a high energy strained product is an energetically endergonic process ($\Delta G_{rxn} > 0$) and, hence,

represents an extremely challenging "uphill" transformation.

Though photoredox catalysts traditionally mediate substrate reactivity through a series of electron transfer events, as discussed in chapters 1 and 2, these photocatalysts are also capable of activating substrates through alternate mechanisms, called energy transfer (Figure 4.3). Energy transfer occurs under two mechanisms: A.) the excited state donor (photocatalyst) induces a dipole in the acceptor (substrate), transferring the energy from the donor to the acceptor (Försters energy transfer) or B.) orbital overlap between the donor and acceptor results in an exchange of respective excited and ground state electrons between them (Dexter energy transfer).[263] As Försters energy transfer cannot mediate the transfer of a photocatalysts triplet state to a substrate, due to Wigners spin conservation rule,[264] Dexter energy transfer the only means by which triplet excited states can be transferred. These alternate mechanisms have been utilized as an alternative strategy for mediating energetically endergonic isomerizations.[265] In this context, elegant photocatalytic processes have recently been reported for the isomerization of trans-alkenes to cis-alkenes[266–276] and of cyclic alcohols to acyclic carbonyl compounds.[277] A selective and high-yielding photocatalytic isomerization of acyclic compounds to strained cyclopropanes is unprecedented, and it represents a unique challenge to the concept of controlling energetically endergonic isomerizations (Figure 4.2B). Herein, a photocatalytic system for the diastereoselective synthesis of anti-chlorocyclopropanes from their acyclic cinnamyl chloride

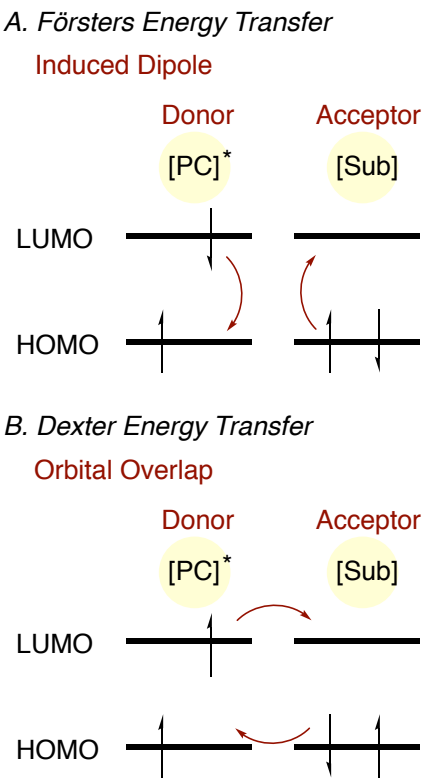


Figure 4.3: Mechanism of Energy Transfer.

precursors is presented. In addition to exploring the scope and synthetic utility of this general transformation, experimental and computational studies were performed to gain insight into the overall mechanism. Quantum calculations revealed that the RRPC mechanism, discussed in chapter 2, was not responsible for the observed reactivity. Excited state calculations of photocatalysts and substrates alongside mapping of the reaction coordinate diagram of the excited substrate revealed that Dexter energy transfer mechanism is responsible for the diastereoselective isomerization of cinnamyl chlorides to anti-chlorocyclopropanes.

4.2 Methods

All structures were optimized using unrestricted DFT with M06-2X functional and a DGDZVP basis set in acetonitrile (SMD solvation model) as implemented in Gausian09. To refine energetics, I performed subsequent single point calculations with a def2-TZVPP basis set (UM062X/def2-TZVPP-SMD(acetonitrile)//UM06-2X/DGDZVPSMD(acetonitrile)). For comparison, I also performed single point energy calculations using DLPNO−CCSD(T) (with solvent corrections from (UM06-2X/def2-TZVPP-SMD(acetonitrile) single point calculations) and the def2-TZVPP basis set using ORCA software version 4.1.2.9a. 10 excited states were calculated on optimized structures using TD-DFT single points with the same method, basis set, and solvation model used for optimizations. For simplicity, only UM06-2X singlet point calculations will be discussed. Minimum energy crossing points were found using the MECPro version 1.0.3.[278] Structures were visualized using CYLview version 1.0.[161] See the for further details.

4.3 Results and Discussion

4.3.1 Pre-Calculation Experimental Work

This part of the work was performed by the members of the Tambar group.

Allylic chlorides were selected as an initial starting point to develop an energetically endergonic isomerization of acyclic compounds to strained cyclopropanes. Early studies with this

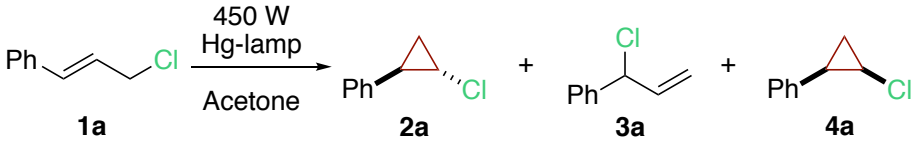
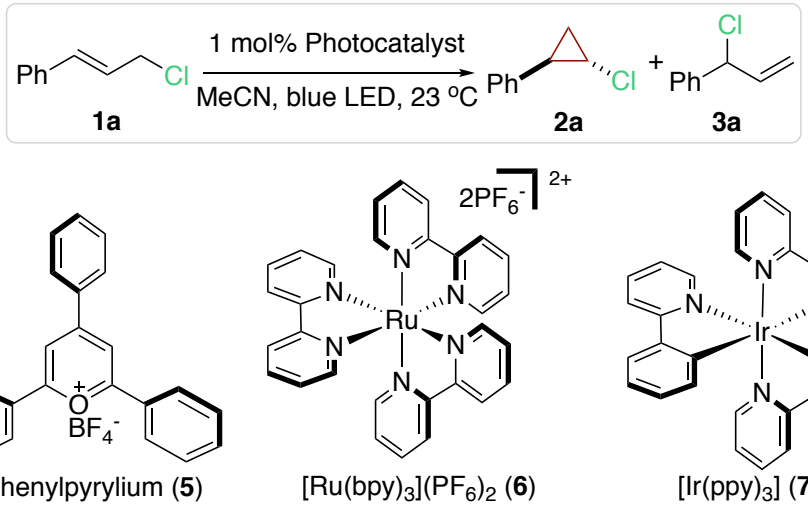


Figure 4.4: Early studies of photochemical isomerization of allylic chlorides.

class of substrates suggested that the photochemical isomerization of allylic chlorides could furnish cyclopropane products. UV irradiation of allylic chlorides such as **1a** with organic photosensitizers led to a mixture of rearranged products, including chlorocyclopropanes **2a** and **4a** as well as acyclic allylic chloride **3a**, albeit in low yields and poor product selectivity (Figure 4.4).

Despite the potential utility of these transformations, their synthetic applicability remains severely

Table 4.1: Initial Results by Testing Various Photocatalysts



Entry[a]	Photocatalyst	Time	Ratio of **1a** / **2a** / **3** / **4**[a]
1	**5**	24 hours	100%, 0%, 0%, 0%
2	**6**	24 hours	100%, 0%, 0%, 0%
3	**7**	24 hours	60%, 20%, 10%, 0%

Table 4.1: Reaction conditions: photocatalyst (1 mol %), **1a** (0.2 mmol), MeCN (1 mL), 4 W blue LED. [a]^{1}H NMR yields based on 1,3,5-tribromobenzene as an internal standard. Experiments run by the Tambar group.

limited, and their mechanism is poorly defined. Based on these results and recent efforts on endergonic photocatalytic reactions, it was hypothesized that the use of a photoredox catalyst and visible light, along with a deeper mechanistic understanding of this photochemical isomerization, could lead to a more efficient and functional group tolerant strategy for generating a broad range of strained chlorocyclopropanes.[93,95,279–281]

To commence our studies, cinnamyl chloride **1a** was subjected to different photocatalysts under blue LED light irradiation (Table 4.1). 2,4,6-triphenylpyrylium tetrafluoroborate (**5**), a typical organophotocatalyst, did not catalyze any conversion of cinnamyl chloride **1a** (entry 1). The ruthenium-centered photocatalyst, $[Ru(bpy)_3](PF_6)_2$ (**6**), did not activate the cinnamyl chloride **1a** either (entry 2). To our delight, iridium-centered photocatalyst $Ir(ppy)_3$ (**7**) partially converted linear substrate **1a** to the desired cyclopropane product **2a**, with a significant amount of undesired branched allylic chloride **3a** as byproduct (entry 3). Interestingly, while early examples of photochemical isomerization of allylic chlorides in the presence of UV light yielded diastereomers **2a** and **4a** in a 2:1 ratio (Figure 4.4),[282–285] under our mild visible-light mediated photocatalyzed conditions, chlorocyclopropane **2a** was formed as the only diastereomer. Previous mechanistic studies on similar systems supported triplet−triplet energy transfer leading to an excited triplet state as the first intermediate in these photosensitized isomerizations.[282–285] However, the nature of subsequent steps remain poorly understood (i.e., homolytic or heterolytic C−Cl bond breaking, zwitterionic or singlet/triplet diradical intermediates, radical-cage recombination/cyclization, etc.).

4.3.2 Computational Work

This part of the work was performed by Robert Martin.

In an effort to optimize the conversion of acyclic allylic chloride **1a** to cyclopropane **2a** and gain insights into the mechanism of formation of byproduct **3a**, Robert and I performed quantum

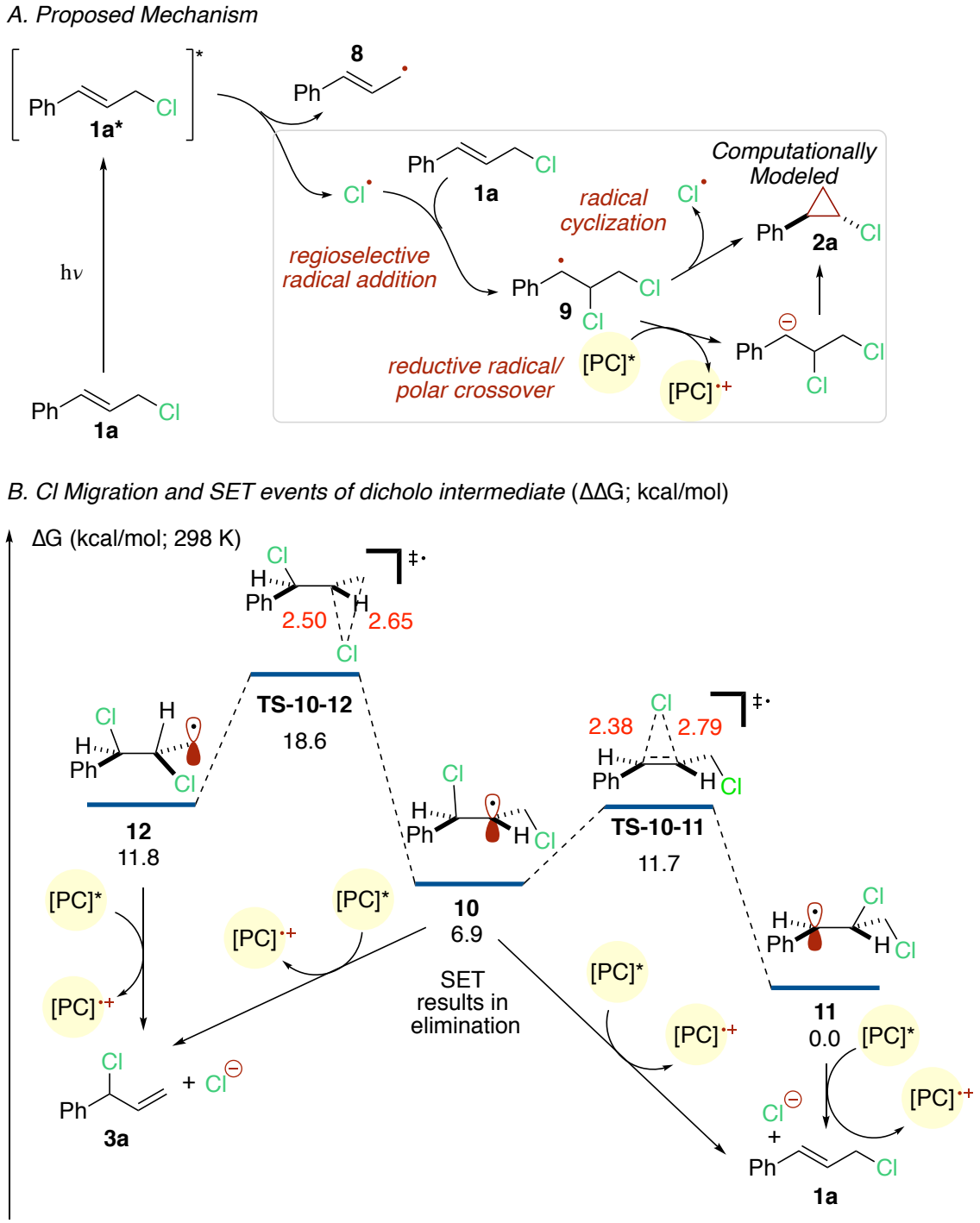


Figure 4.5: Proposed mechanism (and DFT calculations on dichoroine radical mechanism [UM06-2X/DGDZVP-SMD(acetonitrile)]. Pathways were mapped by Robert Martin.

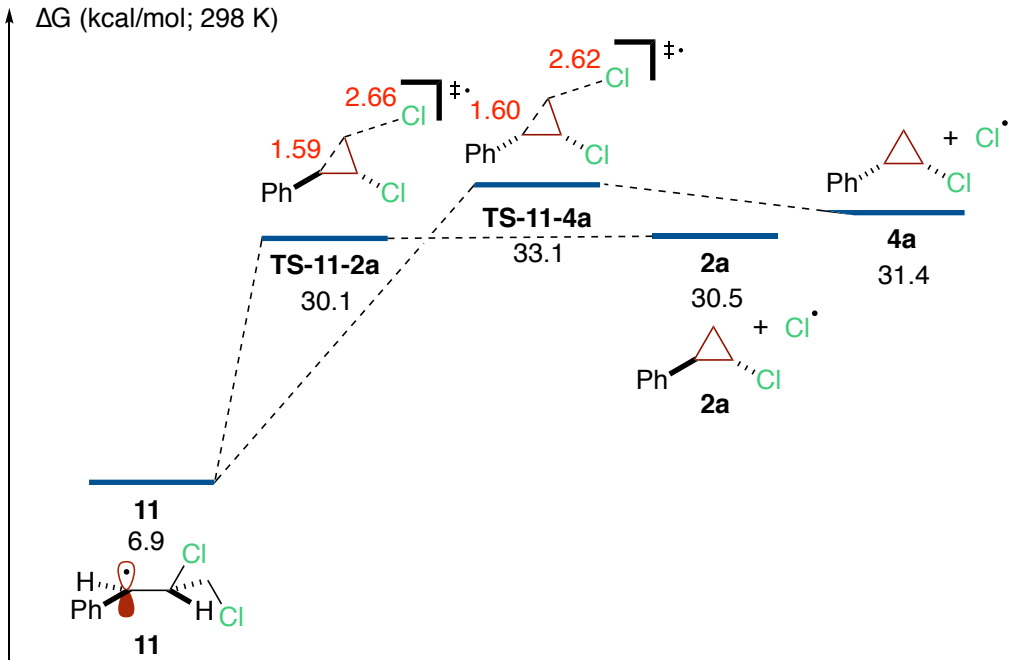


Figure 4.6: DFT calculations on diastereoselective radical ring closure of dichoroine radical **11** [UM06-2X/DGDZVP-SMD(acetonitrile)]. Pathways were mapped by Robert Martin.

mechanical calculations. Akin to my recent calculations on photoredox cyclopropanation studies, discussed in chapter 2,[223] Robert Martin initially hypothesized that a photochemically generated chlorine atom could undergo regioselective Giese addition to cinnamyl chloride **1a** leading to the formation of 1,2-dichloro radical intermediate **11** (Figure 4.5A). Equilibration of the radical dichloro intermediate to **11**, **12**, and **13** and reductive radical/polar crossover results in elimination of chloride, resulting in products **1a** and **3a** (Figure 4.5B). Diastereoselective ring-closing of **11** to form the desired products **2a** and **4a** (Figure 4.6). Thus, quantum mechanical calculations ruled against formation of dichlororadical or anionic species as key intermediates in the photochemical isomerization (see the Appendix for further details).

This part of the work was performed by Ryan Dykstra.

Next, I focused on examining cyclopropanation via a triplet spin state surface. TD-DFT calculations on cinnamyl chloride **1a** revealed that the lowest lying singlet excitation, 4.86 eV, is inaccessible directly by blue LED irradiation, which is consistent with the experimentally

determined UV/vis absorption spectrum of substrate **1a** (See Appendix).[286] I then suspected that triplet−triplet energy transfer may allow for excitation of the cinnamyl chloride to its triplet state.[282–285] As shown in Figure 4.6, the triplet excited state of cinnamyl chloride **1a** is inaccessible via ruthenium (**6**) and triphenylpyrylium (**5**) triplet excited states. Notably, Ir-based photocatalyst **7** has the energy requirements to promote triplet−triplet energy transfer and is thus able to activate the allylic chloride substrate. Additional TD-DFT calculations affirm that excitation of the product **2a** and byproduct **3a** is not possible under these conditions (Figure 4.7), making this transformation photochemically irreversible and allowing for a productive endergonic isomerization. Assuming facile triplet−triplet energy transfer from the excited state of the photocatalyst **7** to the cinnamyl chloride $\mathbf{1a}^{1\prime\prime}$, the triplet intermediate $\mathbf{1a}^{3\prime}$ can then undergo homolytic carbon-chlorine bond dissociation (via $\mathbf{TS\text{-}1a}^{3\prime}\mathbf{\text{-}14}^{3\prime}$) to form isoenergetic triplet radical pair $\mathbf{13}^{3\prime}$ with an overall barrier

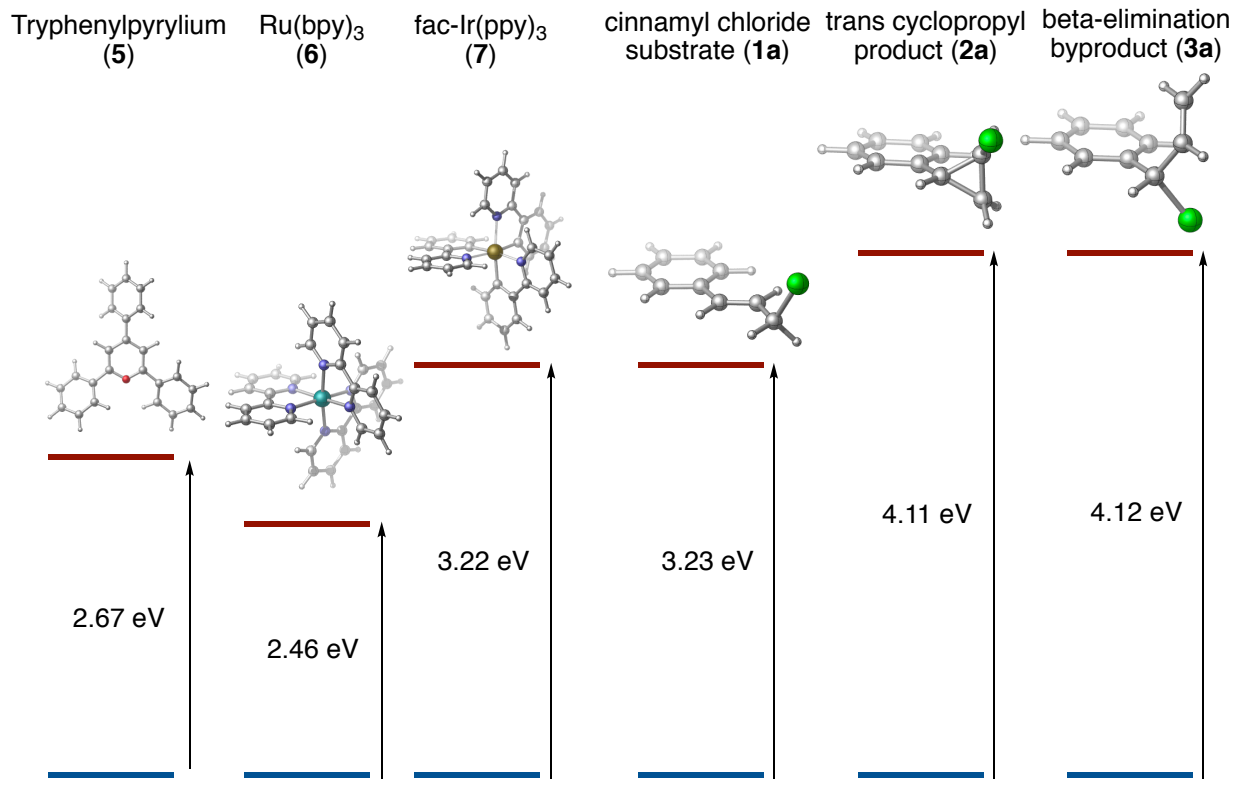
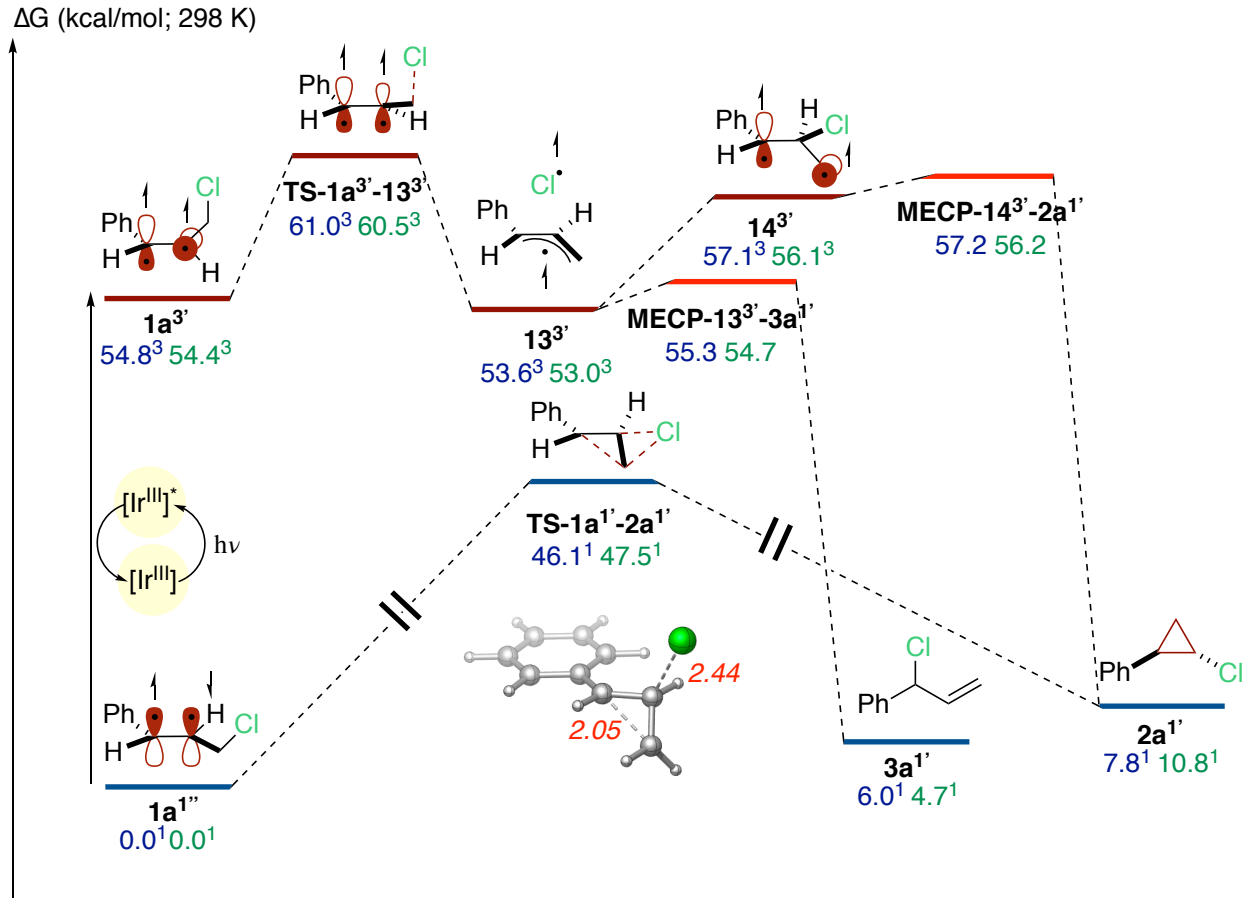


Figure 4.7: Lowest energy excitations to triplet states of photocatalysts and substrate (out of 10 excitations) using TD-DFT [UM062X/DGDZVP-SMD(acetonitrile)]. I computed all excited state calculations.

of only ~6 kcal/mol from **1a$^{3'}$** (Figure 4.8A). This intermediate, albeit lower in energy, could undergo C−Cl bond formation to form 1,3-diradical triplet intermediate **13$^{3'}$** via an almost

A. Energy Transfer Reaction Coordinate Diagram



B. Geometries Minimum Energy Crossing Points

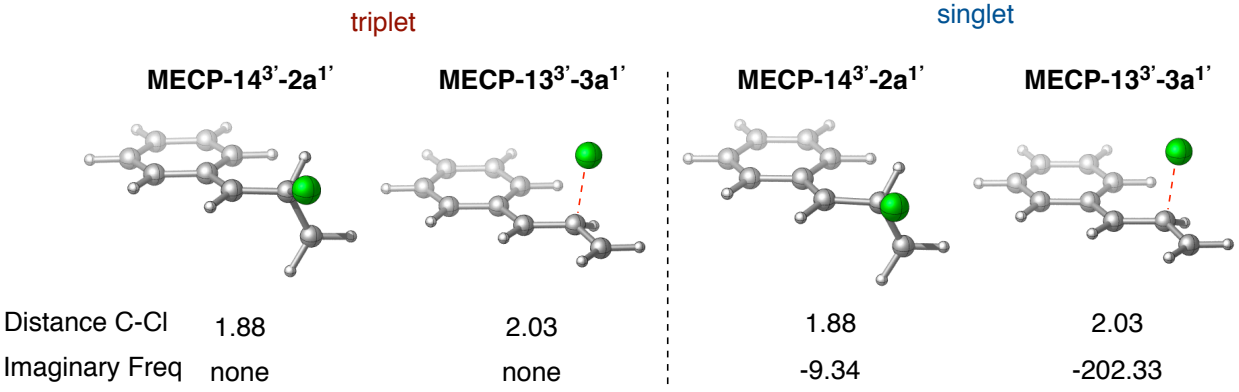


Figure 4.8: Energetics for diastereoselective photocatalytic isomerization. Free energies, in kcal/mol, are from UM06-2X/def2-TZVPP-SMD(acetonitrile) (blue) and DLPNO−CCSD(T)/def2-TZVPP-SMD(acetonitrile) (green) calculations. Geometries of MECP obtained with MECPro. I calculated the reaction coordinate diagram.

barrierless (∼4.0 kcal/mol via ultrafine scan) Cl radical recombination (Appendix S3B). A triplet transition state ring-closing from **$14^{3\prime}$** to form the desired cyclopropane in the triplet spin state was located (not shown), but this process was ruled out because it has an insurmountable kinetic barrier (>40 kcal/ mol) and it is endergonic by more than 35 kcal/mol from **$13^{3\prime}$** (Appendix S3). Importantly, from the two triplet diradical intermediates **$13^{3\prime}$** and **$14^{3\prime}$**, I located the corresponding minimum energy crossing points (**MECP-$13^{3\prime}$-$3a^{1\prime}$** and **MECP-$14^{3\prime}$-$2a^{1\prime}$**) that will form the experimentally observed branched allylic chloride and cyclopropane products **$3a^{1\prime}$** and **$2a^{1\prime}$**, respectively, after intersystem crossing. All singlet MECP had a single imaginary frequency (Figure 4.8B) which, upon visualization, represented the desired motions that lead to products **$3a^{1\prime}$** and **$2a^{1\prime}$**. The Triplet MECP did not give imaginary frequencies, providing additional support that intersystem crossing to the singlet potential energy surface leads to the observed products. Notably, the barriers for these two minimum energy crossing points differ by only 1.9 kcal/mol, which is consistent with the formation of both products (entries 5 and 6, Table 1). Further, consistent with our initial hypothesis, these two products are thermally endergonic in energy compared to the substrate by ∼6−8 kcal/mol. Overall, since the rearranged products **$3a^{1\prime}$** and **$2a^{1\prime}$** are higher in energy than the linear allylic chloride and the energy to undergo triplet−triplet energy transfer is much higher (4.11 and 4.12 eV; Figure 4.7), our DFT calculations suggest that this process is a result of a photochemical transformation rather than a photoinduced chain reaction. Finally, the thermal concerted 1,2-sigmatropic shift/ring-closing transition state (**TS-$1a^{1\prime}$-$2a^{1\prime}$**) was also located that leads to product **$2a^{1\prime}$**, which has a barrier of ∼46 kcal/mol. However, this pathway was ruled out based on unfavorable ground state thermodynamics and kinetics.

4.3.3 Post-Calculation Experimental Work

This part of the work was performed by the members of the Tambar group.

To improve the efficiency of the photocatalyzed cyclopropanation, it was hypothesized that a cocatalyst could be introduced to the reaction to recycle branched allylic chloride byproduct **3a** back into the catalytic cycle (Figure 4.9A). One potential strategy would be to isomerize byproduct **3a** back to substrate **1a** with a cocatalyst that can generate metal-allyl complex **16**, such as $Pd_2(dba)_3$, $[Ir(COD)Cl]_2$, or $Ni(COD)_2$.[287–296] The use of dual catalyst systems based on photocatalysts and transition metal complexes is an emerging area of research, with several proposed roles of the transition metal complexes in light mediated processes.[91,210,297] The Tambar group found that the $Ni(COD)_2$ catalyst with 2,2'-bioxazoline ligand alongside further

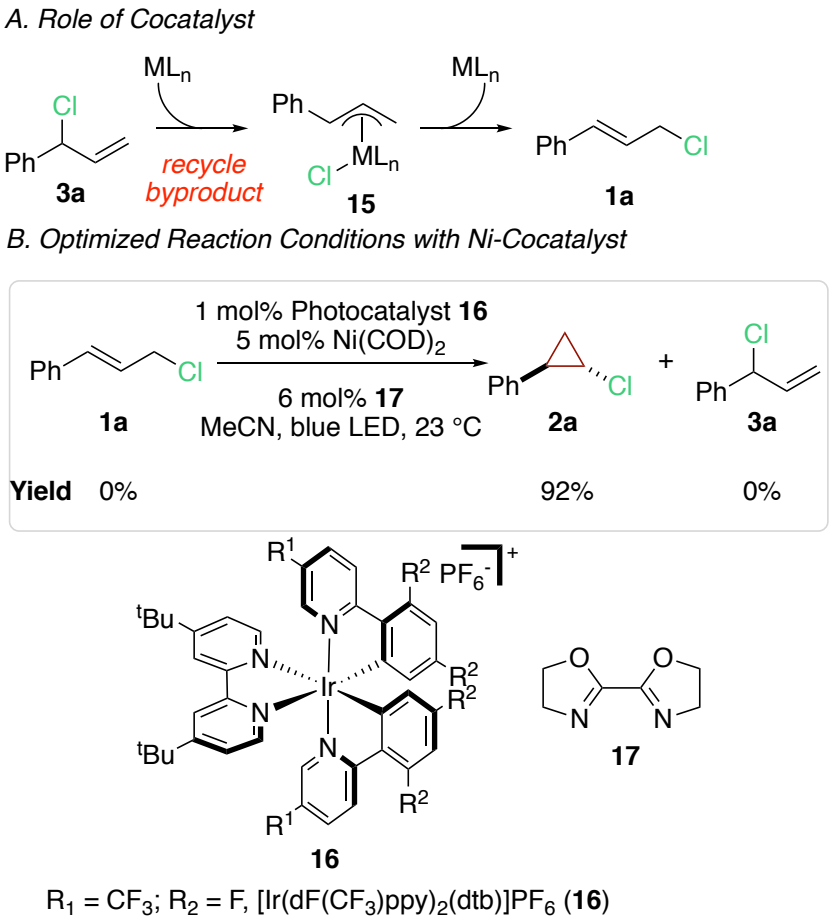


Figure 4.9: Reaction conditions: photocatalyst (1 mol %), cocatalyst (5 mol %), ligand (6 mol %), **1a** (0.2 mmol), MeCN (1 mL), 4 W blue LED. [a]1H NMR yields. [b]12 mol % 19 was used. Experiments run by the Tambar group.

optimization of the photocatalyst give a yield of 92% of **2a** over 4 hours (Figure 4.9B). Evaluation of the scope of the reaction exhibited great tolerance to aromatic systems with a broad range of substituents. On the para position, electron-donating groups (MeO, **2b**), alkyl substitution (Me, **2c**), aromatic rings (Ph, **2d**), halogens (F, Cl, Br; **2e−g**), and electron-withdrawing groups (CF3, CO2Me, C(O)Me**; 2h−j**) all provided the desired cyclopropanation products with high anti-selectivity (>95:5) and yields (up to 92%). Similar functional group compatibility was exhibited among the substituents on the meta- and ortho-positions (**2k− n**). Multi-substituted (**2o**) and fused aromatic rings (**2p** and **2q**) also afforded satisfying results. To our delight, this reaction showed tolerance to heterocycles, for example pyridine (**2q**). 1,1-Diaryl-substituted allylic chlorides were

Table 4.2: Selected Substrate Scope

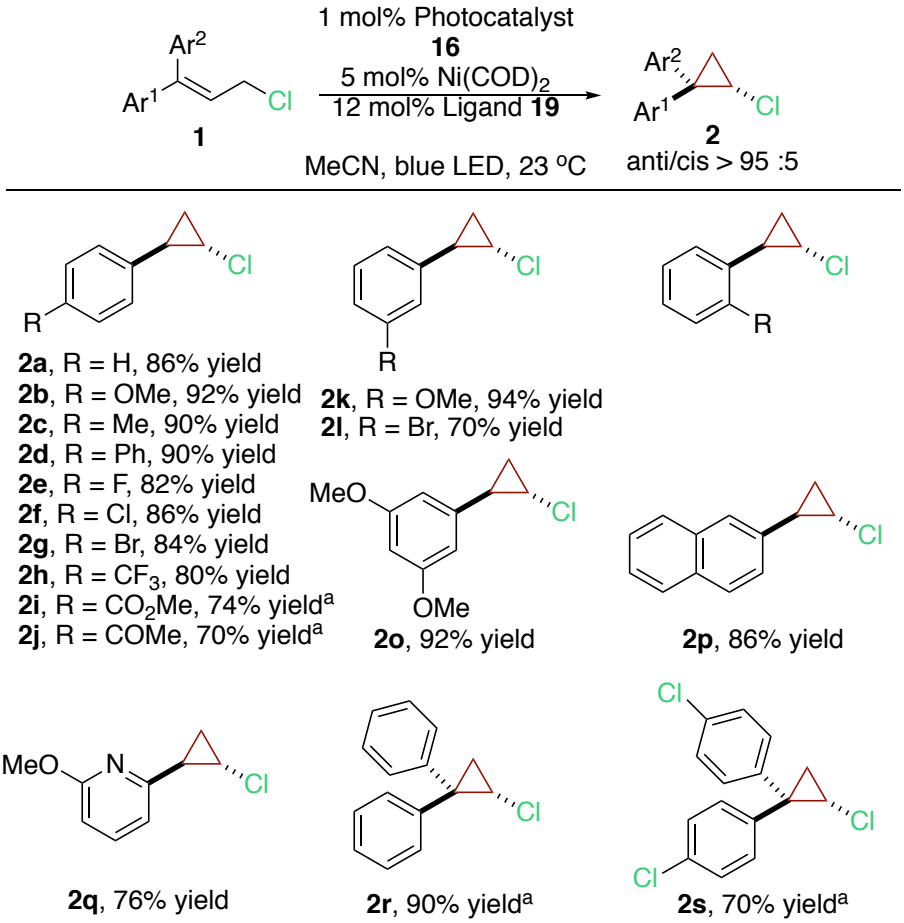


Table 4.2: Reaction conditions: photocatalyst (1 mol %), cocatalyst (5 mol %), ligand (12 mol %), **1a** (0.2 mmol), MeCN (1 mL), 4 W blue LED, 4 h, isolated yields. [a]48 h. Experiments run by the Tambar group.

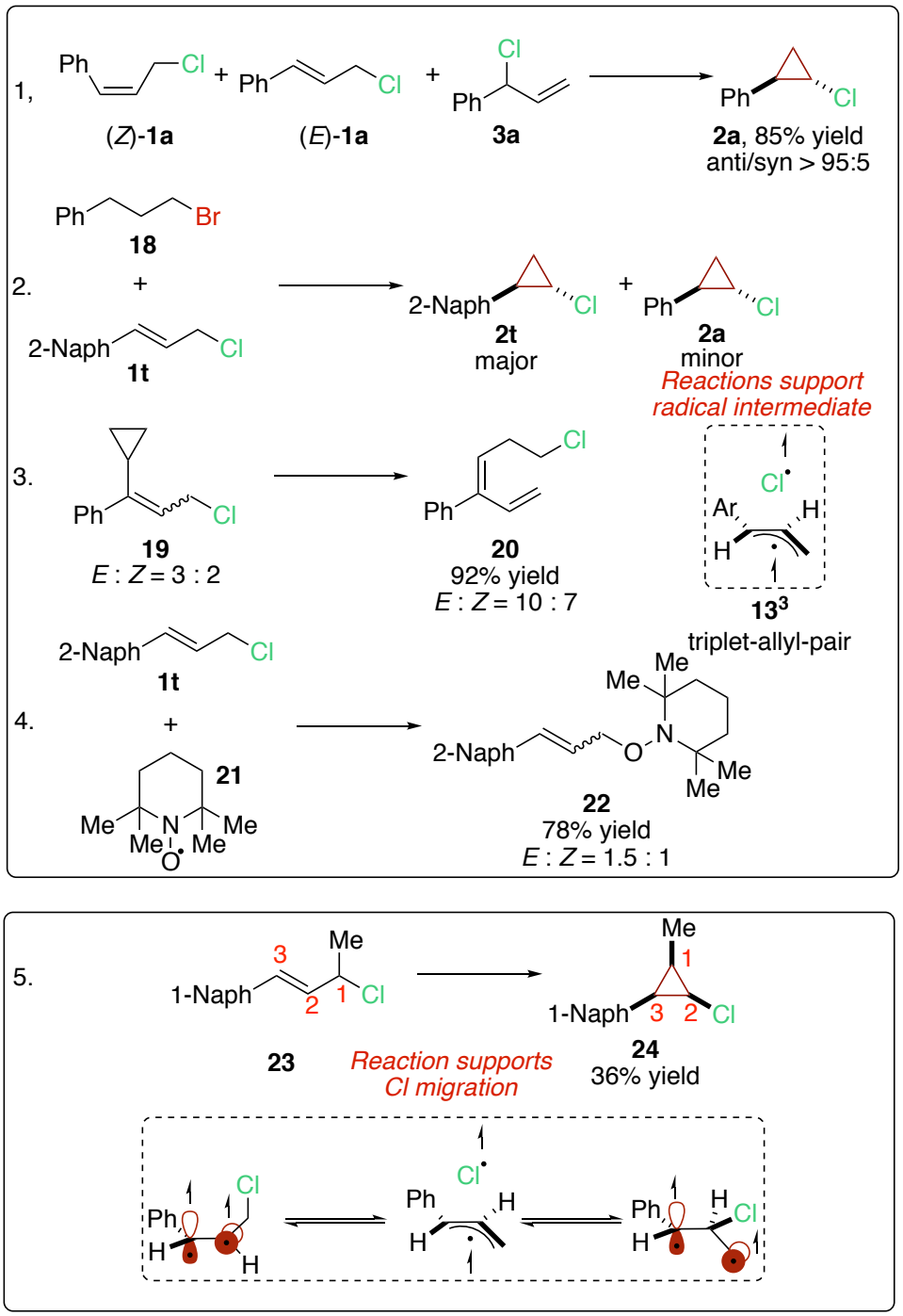


Figure 4.10: Mechanistic control experiments. Experiments run by the Tambar group.

also examined. The corresponding cyclopropane products were obtained with high yields (**2r** and **2s**).

The Tambar group then carried out a series of control experiments to gain insight into the

mechanism of dual nickel/photocatalyzed cyclopropanation (Figure 4.8). First, a mixture of allylic chlorides (Z)-**1a**, (E)-**1a**, and **3a** cleanly furnished anti-cyclopropane **2a** with similarly high diastereoselectivity (eq 1), which suggests that the mechanism involves a common intermediate that can be accessed by either linear Z- or E-allylic chloride substrates as well as branched allylic chloride byproduct **3a**, such as triplet-allyl pair **13a**^{3}. This observation represents a practical advantage to the method, as a mixture of alkene isomers of the starting material leads to the anti-chlorocyclopropane product **2a** through a stereoconvergent mechanism. In addition, under the optimal reaction conditions, cinnamyl bromide **18** did not provide any cyclopropanation product. In a crossover experiment of cinnamyl bromide **18** and 2-naphthyl substituted cinnamyl chloride **1t**, the crossover product **2a** was observed (eq 2). In line with prior computational work, this experiment implies dissociation of the C−Cl bond and bimolecular recombination during the reaction process. A radical clock experiment with substrate **19** (eq 3) and radical-trapping experiment with TEMPO (eq 4) both support the involvement of free radical intermediates in the cyclopropanation mechanism. Interestingly, by using compound **23** as substrate, cyclopropane **24** was obtained instead of the expected cyclopropane **24** (eq 5), which is consistent with Cl migration during the reaction.

4.3.4 Spectroscopy

This part of the work was performed by the members of the Ludovic Troian-Gautier.

Steady-state and time-resolved absorption and photoluminescence spectroscopies were used to seek additional mechanistic information on the role of the iridium photoredox catalyst. The iridium photosensitizer **9** exhibits properties that are typical of compounds with low-lying metal-to-ligand charge transfer (^{3}MLCT) excited states.[298–301] Room temperature photoluminescence centered at

470 nm was observed with an excited-state lifetime of 2.26 ± 0.20 μs.[301] Both the steady-state as well as the time-resolved photoluminescence were efficiently quenched by various cinnamyl chloride derivatives used in the photocatalytic reactions. The quenching data was well described by the Stern−Volmer model that provided quenching rate constants, kq that ranged from 0.47 × 109 M^{-1} s^{-1} (**1p**) to 2.06 × 109 M^{-1} s^{-1} (**1i**).[301] Stern−Volmer plots using ratios of the steady-state time-resolved (τ_0/τ) photoluminescence were linear and coincident under the conditions used.[302,303] This observation ruled out static quenching through the formation of a ground-state adduct but rather indicated that the excited-state quenching mechanism was solely dynamic, i.e., that the excited-state iridium photosensitizer and the cinnamyl chloride derivative must diffuse to form an encounter complex leading to excited-state reactivity. Control Stern−Volmer experiments with (Z)-**1a** and **2a** were nonlinear with concentration, an observation most consistent with the formation of a less emissive adduct.[301] At low concentration, the Stern−Volmer slope for excited-state quenching by (Z)-**1a** was slightly steeper than with the corresponding (E)-**1a** isomer.

Excited-state mechanistic investigations were performed using nanosecond transient absorption spectroscopy with pulsed 420 nm light excitation. First, key spectra such as the excited-state absorption spectra as well as the one-electron reduced and one-electron oxidized absorption spectra of **9** were determined.[301,304] These spectra are of paramount importance as they inform on the oxidation state of the iridium photosensitizer during photoredox catalysis. The excited-state absorption spectrum was characterized by an increased ΔAbs between 440 and 550 nm with a maximum centered at 480 nm. The monoreduced species exhibited a maximum at 530 nm (orange), whereas the singly oxidized species exhibited weak absorption features between 440 and 550 nm as well as above 750 nm.

Interestingly, nanosecond transient absorption spectroscopy performed in the presence of

cinnamyl chlorides **1a** or **1i** led to a drastic excited-state quenching, with an excited-state lifetime that decreased from 2.32 μs to ∼10 ns. This confirmed the excited-state quenching data quantified by Stern−Volmer experiments but did not provide evidence for the products of the quenching reactions. Had oxidative or reductive quenching of the excited state occurred in the presence of cinnamyl chlorides with cage escape yields greater than 5%, the Ir complex would have reported on the redox chemistry, contrary to what was observed. The inability to observe redox products implies either electron transfer with rapid recombination or energy transfer. Note that the photoinduced trans−cis isomerization of cinnamic acid derivatives with an iridium photosensitizer was recently reported to occur via triplet−triplet energy transfer.[305]

The excited-state reactivity of photocatalyst **9** with a cinnamyl amine **28** was investigated to distinguish between electron transfer and energy transfer.[301] This cinnamyl amine derivative was suspected to undergo facile electron transfer with photoredox catalysts. A quenching rate constant ($kq = 7.23 \times 109\ M^{-1}\ s^{-1}$) was determined by Stern−Volmer analysis. Furthermore, nanosecond transient absorption spectroscopy provided undisputable evidence for electron transfer between photocatalyst **9** and cinnamyl amine **28**, with a spectral signature corresponding to both the oxidized amine and the monoreduced iridium sensitizer. Hence, the lack of spectroscopic signature observed for cinnamyl chloride **1a** or **1i** in the presence of photoexcited catalyst **9** is more consistent with an excited-state quenching mechanism that involves energy transfer from the excited-state Ir* to cinnamyl chloride derivatives.

On the basis of these experimental investigations and DFT calculations, the mechanism depicted in Figure 4.12 was proposed. Cinnamyl chloride $\mathbf{1a^1}$ is activated to the excited state $\mathbf{1a^3}$ after energy transfer from irradiated $Ir^{(III)}$ photocatalyst $\mathbf{9^3}$. Subsequently, a triplet-allyl-pair ($\mathbf{13^3}$)

containing chlorine radical is formed from the excited complex **1a**^{3}. There are two pathways for intermediate **13**^{3}. One path involves a direct intersystem crossing, which provides the undesired branched byproduct **3a**^{1}. The other path proceeds through triplet-β-Cl intermediate **14**^{3}, which then provides the desired cyclopropanation product **2a** after an intersystem crossing. Based on the increase in yields of **2a**^{1}, byproduct **3a**^{1} can be recycled into the catalytic cycle via oxidative addition with $Ni^{(0)}$ complex **23** to form nickel allyl complex **24** and subsequent reductive elimination to provide starting material **1a**^{1}. At this time, we cannot rule out the possibility that cinnamyl chloride **1a** undergoes an oxidative addition with nickel catalyst **29** to form allyl-$Ni^{(II)}$ complex **30**, which is then activated to the excited state **30*** via energy transfer from irritated $Ir^{(III)}$ photocatalyst **9***.[47,48,209] We are currently conducting mechanistic studies to examine the role of photoexcited nickel−allyl complexes.

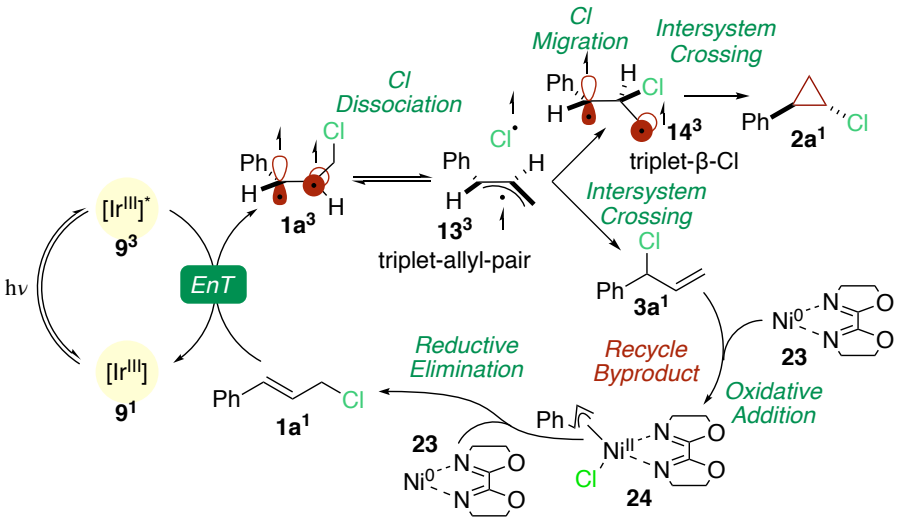


Figure 4.11: Proposed mechanism. Spin state of molecule indicated as superscript.

Figure 4.11: Proposed mechanism. Spin state of molecule indicated as superscript.

4.4 Conclusion

In summary, a dual catalyst system for the efficient photocatalytic isomerization of acyclic cinnamyl chlorides that is highly diastereoselective for the formation of anti-chlorocyclopropanes has been developed. Synthetic work and control experiments were performed by the Tambar

group. I performed all quantum calculations on the photocatalytic isomerization pathways while both Robert Martin and I mapped out the previously explored RRPC pathways. Ludovic Troian-Grautier ran and analyzed all steady-state and time resolved absorption and photoluminescence spectroscopies. Both experimental and computational evidence for the energy transfer from an iridium photocatalyst to the allylic chloride substrates, followed by a cycloisomerization to the strained cyclopropane products. The reaction demonstrates broad functional group compatibility, which can be attributed to the mildness of activation with visible light. Computational studies provided insight into the mechanism of the reaction and guided the development of a more efficient process by addition of a nickel cocatalyst. A novel role for the nickel catalyst is proposed to recycle a byproduct generated during the reaction. It is anticipated that the combination of photoactivation of substrates via photocatalysis and recycling of the byproducts by transition metal catalysis will provide unique opportunities for the discovery of novel reactivity.

Chapter 5: Origins of Product Selectivity in the Dual Ni/Photoredox Catalyzed Coupling of Sulfinate Salts and Aryl Halides

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5.1 Introduction

Sulfones are prominent motifs that are of particular relevance to both the medicinal chemistry and agrochemical communities (Figure 5.1).[306,307] Aryl- and heteroaryl sulfones are excellent electronic modifiers, a property that has been exploited in drug design, various synthetic methods, as well as in the material sciences (e.g., polymer synthesis).[308] Various tactics can be used to install this valuable functional group (Figure 5.2), although the most commonly employed strategy is the exhaustive oxidation of the corresponding sulfide (Figure 5.2A).[309,310] The most apparent limitations of this approach are the notable sensitivity of a variety of functional groups to the strongly oxidizing conditions necessary for sulfone formation and the possibility of incomplete oxidation (affording the sulfoxide). More generally, this approach requires the C–S bond to be forged[311,312] prior to sulfone formation and thus has the added drawback of using odious, more toxic thiols as part of the synthetic sequence. Alternatively, nucleophilic aromatic substitution processes using sulfonate salts (easily prepared, bench-top stable, non-odorous solids) does allow

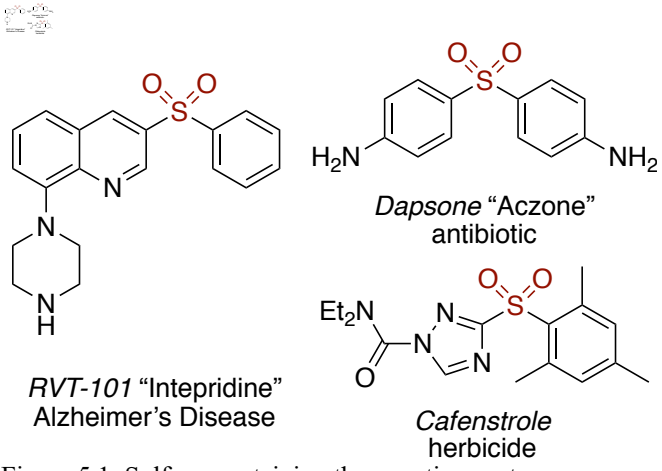


Figure 5.1: Sulfone containing therapeutic agents.

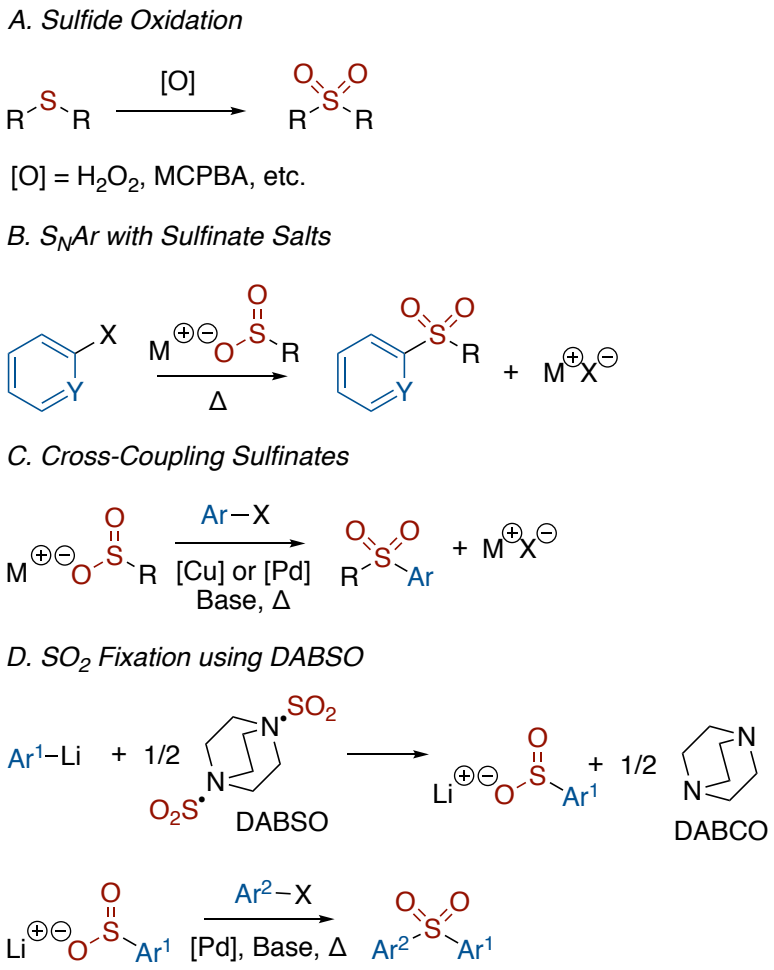


Figure 5.2: Synthetic methods to access diaryl-/heteroaryl sulfones.

direct access to diaryl- or heteroaryl sulfones (Figure 5.2B).[313,314] However, this route is limited by the inherent restrictions of S_NAr chemistry (electron-deficient arenes with specific substitution patterns and elevated temperatures).

In light of the limitations of both of these classical methods, transition metal-catalyzed cross-coupling processes have emerged as an alternate means of assembling these types of sulfones (Figure 5.2C).[315–322] Indeed, in these reactions, sulfonate salts can be cross-coupled with an array of electrophilic partners and even with organoboron species using either copper- or palladium-based catalysts. Unfortunately, these approaches are dependent on strongly alkaline conditions and high temperature to facilitate $ArSO_2–C_{sp2}$ bond formation. Willis and co-workers have employed

DABSO {1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct} as a SO_2 surrogate to construct sulfones de novo from two distinct aryl halides, thus proffering an elegant means to construct unsymmetrical sulfones (Figure 5.2D).[320–322] However, to do so, main group organometallics and/or elevated temperatures/strong bases must be employed. Thus, this approach does not overcome the existing limitation on functional group compatibility and sulfonate scope.

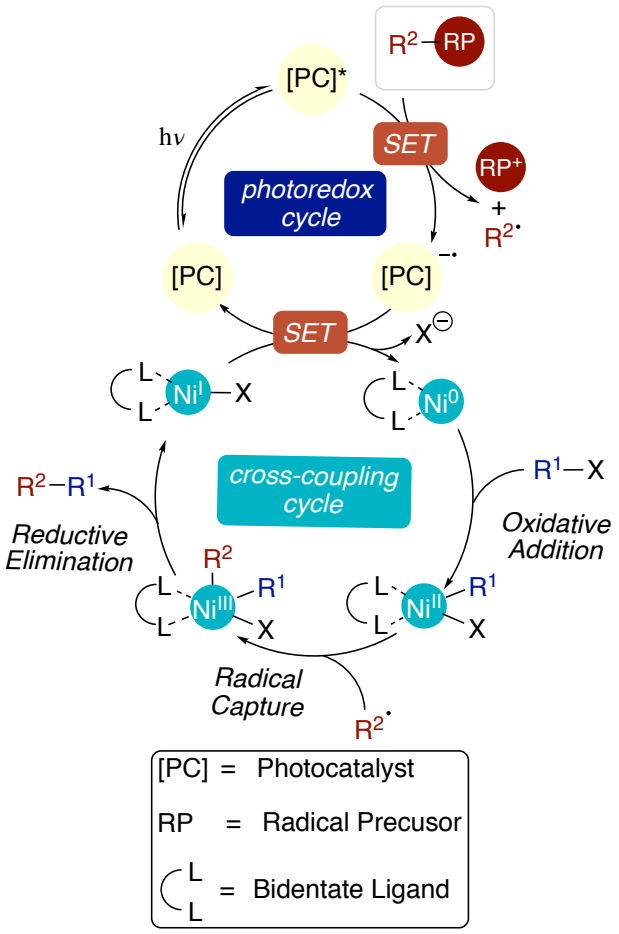


Figure 5.3: General mechanism of dual Ni/Photoredox catalysis. SET = single electron transfer, X = halogen.

Given that, to the best of our knowledge, analogous Ni-based processes were not documented in the literature nor were there general conditions established for executing this type of coupling under mild conditions, the Molander group considered whether Ni/photoredox dual catalysis[91,92,209,323–326] might be uniquely poised for facile $ArSO_2$–C_{sp2} bond formation (Figure 5.2E). In this process, radicals are generated by photoredox-mediated SET events and subsequently undergo facile single electron transmetalation (labeled *radical capture)* with transition metal catalysts (Figure 5.3). Ultimately, this allows myriad Y–C_{sp2} bonds (Y = C_{sp3}, N, O, S, and P) to be forged under remarkably mild conditions using an array of functional group-rich electrophiles (aryl/alkenyl halides, aryl/alkenyl sulfonate esters, and acyl chlorides).[91,92,209,325,326] During the course of this work and while this

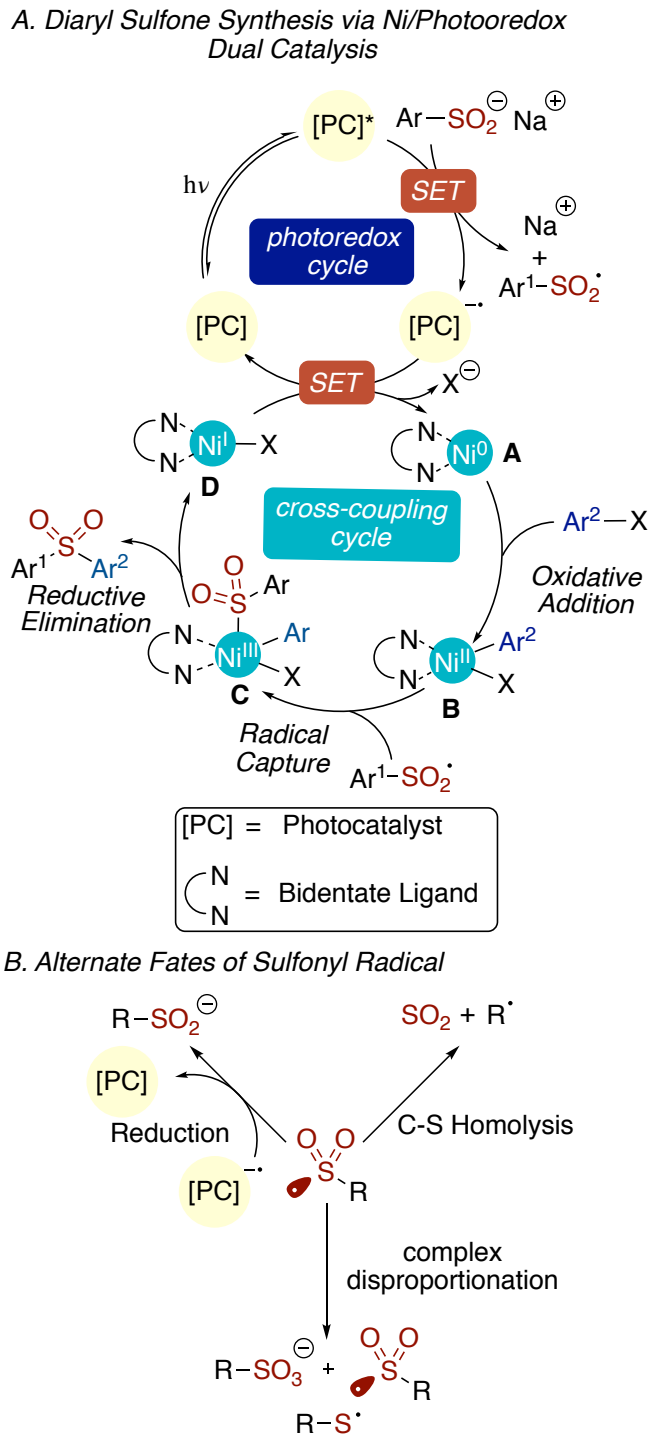


Figure 5.4: Envisioned mechanism of diaryl sulfone synthesis via Ni/photooredox dual catalysis via sulfonate salt radical precursors and possible fates of sulfinyl radicals. SET = single electron transfer and X = halogen.

work was under review, two papers detailing similar transformations using Ni/photoredox dual catalysis were reported by Rueping and Manolikakes, respectively.[327,328]

In our consideration of this approach, the Molander group envisioned that aryl sulfonate salts that have low redox potentials (e.g., $E_{1/2}$ = -0.37 V vs. SCE for **2a**)[329] could undergo SET oxidation by the appropriate photocatalyst to furnish sulfonyl radicals (Figure 5.4A). The ultimate fate of these S-centered radicals does vary (Figure 5.4B). Whereas certain alkyl sulfonates can undergo C–S bond dissociation to give alkyl radicals and SO_2 evolution at this point,[330,331] aryl sulfonyl radicals are much less prone to C–S scission.[332] Thus, these types of radicals could be intercepted by Ni^0 species **A** to generate a Ni^I–SO_2Ar species **B**.[333] Subsequent oxidative addition to an aryl halide would yield a Ni^{III} complex **C**. Reductive elimination at this point would forge the $ArSO_2$–

C_{sp2} bond and yield a Ni^{I} species **D**, which could undergo SET reduction by the reduced state of the appropriate photocatalyst to regenerate **A**.[334,335] The sulfinate cross coupling delivered two products, the desired diaryl sulfone as well as the diaryl thioether,. To gain insight into the product distribution, I performed DFT calculations on the product determining steps proposed based on previous calculations[333], which were able to describe the electronic effects of the aryl halide on the product distribution as well as bracket the rate of complex disproportionation leading to the diaryl thioether.

5.2 Methods

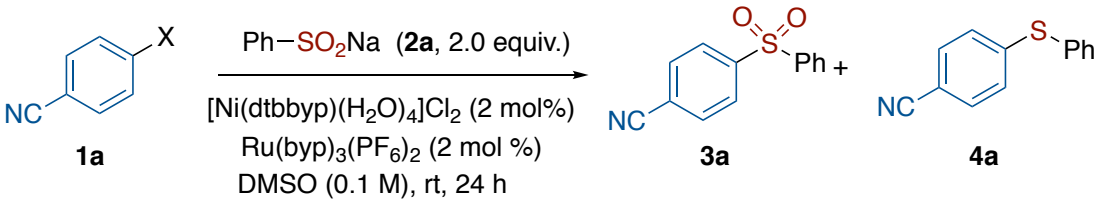
All optimizations of intermediates and transition states were calculated without constraints using unrestricted B3LYP/6-31G(d)-LANL2DZ(Br, S, and Ni) with the "guess=mix" keyword as implemented in Gaussian09. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). To refine the energies calculated, single point energy calculations using UM06/6-311+G(d,p)-SDD(Br, S, and Ni) in THF using SMD as the solvation model were run. Similar methods have been used before to rationalize selectivity and reactivity on related systems.[1,336] All structural figures were generated using CYLview.[161] Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

5.3 Results and Discussion

5.3.1 Experimental Work

This part of the work was performed by members of the Molander group.

Table 5.1: Initial Attempts at Sulfinate Cross Coupling



Entree	Deviation from initial conditions	3a/IS Ratio	4a/IS Ratio
1	None	3.37	0.26
2	No light	n.d.	n.d.
3	No Ru photocatalyst	n.d.	n.d.
4	No Ni catalyst	n.d.	n.d.
5	No Ni or Ru photocatalyst	n.d.	n.d.
6	MeOH, acetone, dioxane, or MeCN	n.d.	n.d.
7	DMA	2.73	0.23
8	DMF	3.10	0.30
9	DMF/H_2O (9:1)	2.57	n.d.

Table 5.1: Optimization reactions performed using 0.1 mmol of **1a** in the presence of 4,4'-di-*tertt*-butylbiphenyl as internal standard (IS) (0.01 mmol) for 24 h at 27 °C. Ratios of **3a** or **4a** to IS is determined by HPLC analysis of crude reaction mixture; n.d. = not detected, 4CzIPN: 2,4,5,6-tetra-9*H*-carbazol-9-yl-1,3-benzenedicarbonitrile. Experiments performed by the Molander group.

Model studies focused on the cross-coupling of aryl bromide **1a** and sodium sulfinate **2a**. Using a slight modification of conditions previously optimized for alkylsilicates and 2 equiv. of **2a**, the desired cross-coupling was initially realized (Table 5.1, entry 1). Control studies confirmed that this was indeed a dual catalytic process (entries 2–5) and that all the components of the reaction were necessary to ensure cross-coupling. Early screens assessing the role of solvent and photocatalyst revealed that $Ru(bpy)_3(PF_6)$ (E_{ox} [RuII/RuI] = 0.77 V vs. SCE) in conjunction with highly polar solvents such as DMSO, DMF, or DMA were ideal for the generation of sulfone **3a**. Surprisingly, a major by-product of this reaction was the corresponding aryl sulfide **4a**, which may arise from disproportionation of sulfonyl radicals to give thiols/thiolates or thiyl radicals (Figure 5.4B).[327,337–339] Such species are known to engage in cross-coupling under Ni/photoredox

conditions.[340–342] Higher temperatures appeared to increase sulfide formation and diminish overall conversion.[343] To improve conversion and minimize formation of this byproduct, High-Throughput Experimentation (HTE) screening of an array of Ni sources and ligands was employed.[343] Ultimately, a combination of 1,10-phenanthroline (phen) with $Ni(py)_4Cl_2$ was identified as an appropriate cross-coupling system. The bench-top stable performed Ni complex $[Ni(phen)•(H_2O)_4]Cl_2$ in place of $Ni(py)_4Cl_2$/phen gave virtually identical results. Ultimately, Ni loading was reduced by half without compromising yield or drastically increasing reaction time. Control experiments under these optimized conditions confirmed that this was indeed a dual catalytic process; no reaction occurred in the absence of irradiation, photocatalyst, or Ni.[343] Analysis of these conditions over time indicated that the relative ratio of sulfide to sulfone did not appreciably change over extended reaction time.[343]

With suitable conditions in hand, the scope of the transformation was explored next (Table 5.2). An evaluation of the reaction in the context of various aryl halide coupling partners was first conducted. Gratifyingly, the scope of the transformation was quite broad, and the yields were moderate to good. In practically all cases, small amounts of the undesired thioether byproduct were formed but were easily removed *via* column chromatography. Generally, both aryl iodides and aryl bromides performed well, with aryl iodides proving to be superior when electron-rich substituents were present or when significant amounts of the thioether byproduct was observed. Indeed, Ni(phen)-type species have been shown to be more competent catalysts when using aryl iodides under Ni/ photoredox conditions.[344] The reaction tolerates an array of functional groups, including nitrogen-based heterocycles, amides, lactones, phenols, and species that may be prone to H-atom abstraction events. Many of these systems would not be amenable to the classical approaches for sulfone construction or even those that employ transition metal catalysts. Indeed, systems such as

3h would give an alternate product under SNAr-type conditions, and systems such as **3c** would likely undergo off-target oxidation under the conditions required for oxidative sulfone synthesis from thioethers. The reaction was electrophile-specific, enabling a selective functionalization of bifunctional electrophiles (e.g., **3h**, **3n**, **3o**). In addition, the process described here tolerates functional group-rich medicinal chemistry intermediates.[343]

After surveying a broad range of electrophilic partners, a variety of aryl sulfinate salts were

Table 5.2: Selected Substrate Scope of Diaryl Sulfonates

next assessed. Although some are commercially available, these salts are readily accessed from commodity chemicals (sulfonyl chlorides and sodium sulfite) in a single chemical step and are

Table 5.2: Selected Substrate Scope of Diaryl Sulfonates

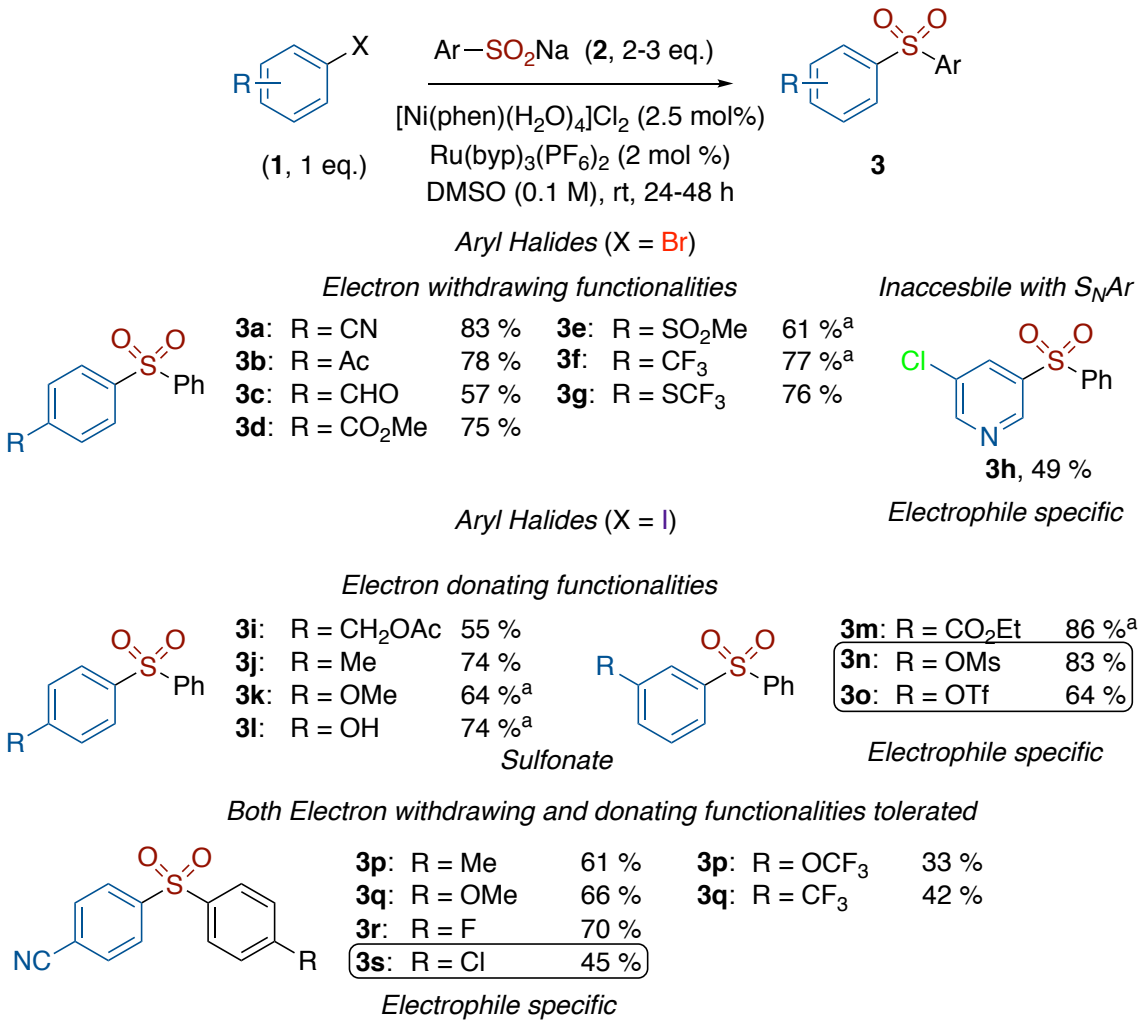


Table 5.2: Unless otherwise noted reactions were performed using aryl halide (1.0 equiv, 0.5 mmol), sulfinate salt (2 equiv), $[Ni(phen)(H_2O)_4]Cl_2$ (2.5 mol %) and $Ru(bpy)_3(PF6)_2$ (2 mol %) in DMSO (0.1 M) at rt with irradiation with blue LEDs. All yields are isolated yields after purification. [a]3 equiv of sulfinate salt were used. Experiments performed by Molander group. Experiments performed by Molander group.

bench-top stable, crystalline solids.[345,346] An array of sulfinate salts readily succumbed to cross-coupling. Both electron-rich and electron-poor sulfinates were compatible, as were heterocyclic and polycyclic sulfinates. In addition, chemoselective cross-coupling ensured **3s** and **3t** retained their functional handles for further diversification. Sulfonate esters, especially electron-deficient aryl triflates, readily undergo Ni/photoredox C_{sp3}–C_{sp2} cross coupling with alkylsilicates.[209] Thus,

3o represents an ideal substrate for rapid diversification, although sulfonate ester-bearing sulfones are not explicitly known to engage in Ni/photoredox cross-coupling.

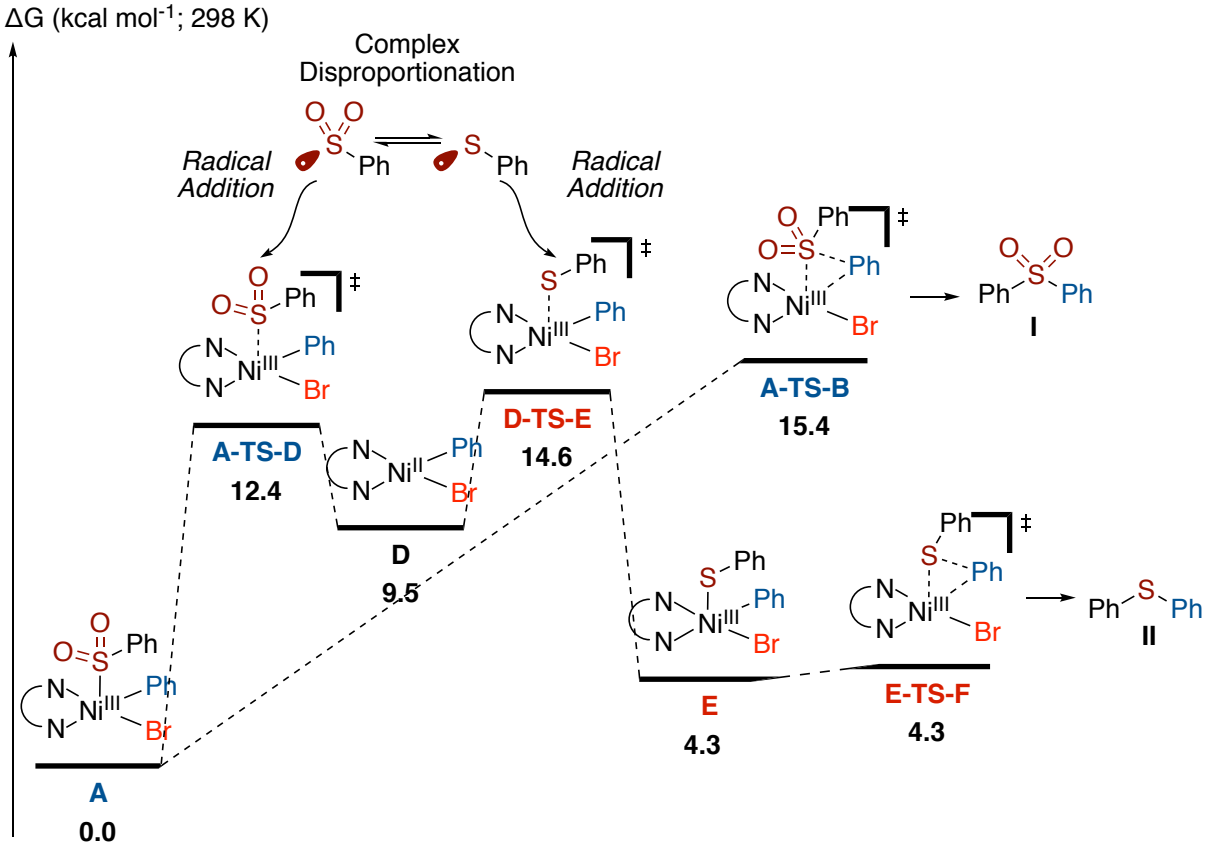
5.3.2 Computational Work

This part of the work was performed by Ryan Dykstra.

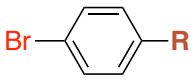
To gain insight into the mechanism and origin of product selectivity, I turned to quantum mechanical calculations. A previous publication by Dr. Gutierrez demonstrated that dual Ni/photoredox cross-coupling reactions involving radicals converged to an alkyl– Ni^{III} intermediate that can undergo reversible radical dissociation prior to reductive elimination.[333] Similarly, DFT calculations (Figure 5.5) in the current system support formation of Ni^{III} intermediate **C** (Figure 5.4 via $Ni^0/Ni^I/Ni^{III}$ or $Ni^0/Ni^{II}/Ni^{III}$ pathway; not calculated) and reversible radical dissociation (12.4 kcal/mol via **A-TS-D**) to form Ni^{II} **D** and $^{\bullet}SO_2Ph$ species prior to reductive elimination. Reductive elimination of Ni^{III} intermediate **A** (via **A-TS-B**) will generate sulfone product **3** (Figure 5.5A; **I**) and Ni^{I} **D** (Figure 5.5A). Alternatively, prior to reductive elimination, the $^{\bullet}$SO2Ph radical can undergo a complex disproportionation (not calculated) to generate $^{\bullet}$SPh radical, which can engage with the Ni^{II} intermediate **D** (via **D-TS-E**) to go on to form the sulfide adduct **4** (Figure 5.5A **II**), after reductive elimination of **E** (via **E-TS-F**). Based on experiments, competition between reductive elimination (via **A-TS-B**) and complex disproportionation, presumably via Ni/PC-promoted pathway, are the product determining steps (vide infra). Overall, the highest barrier for sulfone formation is the reductive elimination (13.4 kcal/mol via **A-TS-B**; Figure 5.5 A), while thiyl radical addition to the Ni complex (14.6 kcal/mol

via **D-TS-E**) is the highest barrier for sulfide **4** formation pathway (Figure 5.5A). If disproportionation of ˙SO2Ph to ˙SPh radical is fast (vide infra), the latter pathway is favored by

A. Reactioon Coordinate Diagram of Sulfonyl Cross Coupling from Ni^{II} Species



B. Computed Barriers Governing Selectivity and Ratios Product Distribution via ^{1}HNMR



			R = —CN	—H	—Me	—OMe
$\Delta G^{‡}$ (radical addition)	**D-TS-E**	**A-TS-D**	**11.0** 8.6	**14.6** 12.4	**15.0** 12.5	**15.2** 13.0
$\Delta G^{‡}$ (reductive elimination)	**E-TS-F**	**A-TS-B**	2.9 **13.4**	4.3 **15.4**	11.1 **15.1**	11.3 **15.2**
Experimental ratios **I/II**			**9.1/1**		**1.7/1**	**1.1/1**

ca. 1 kcal/mol, which will lead to sulfide as major product. These results are not consistent with the observed results, in which the sulfone is the major product. Given that formation of sulfone **3** was accompanied by significant sulfide by-product **4** for a series of aryl bromides (Figure 5.5B),

Figure 5.5 A. Reaction coordinate diagram of selectivity-determining steps of diaryl sulfonate and diaryl thiyl cross coupling modeled using DFT. B. Computed barriers and experimentally determined product ratios. I performed all calculations.

at this level of theory, I estimate that the barrier for the rate limiting step of disproportionation is ca. 16 kcal/mol. If the barriers for reductive elimination (**A** to **B**) are ~16 kcal/mol, it will therefore be in competition with •SO2Ar radical disproportionation. In turn, the •SAr will compete for addition to Ni^{II} to form Ni^{III}–SAr intermediate which will quickly undergo reductive elimination to form thioether **4**. Consistent with experiment, the formation of sulfone is only slightly favored for R = H, OMe, and Me, in which the reductive elimination barriers are estimated to be >15 kcal/mol (Figure 5.5B; bold, RED). However, in the presence of electron deficient aryl bromides (e.g., R = CN; Figure 5.5B) the reductive elimination barrier leading to sulfone is much lower (12.4 kcal/mol) than this complex disproportionation threshold, leading to a higher sulfone to sulfide ratio. In this regard, a linear correlation (R^2 = 0.85) between sulfone/sulfide ratio and Hammett σ_p for a series of para-substituted aryl bromides was found (see Appendix).

Notably, DFT calculations rule against generation of •SPh from •SO2Ph radical prior to formation of Ni^{II} phenyl bromide intermediate. In this scenario, and in contrast to experiment, DFT calculations predict Ph–S–Ar **4** as the major product for a variety of aryl bromides because the overall barriers for sulfide formation (Figure 5.5, bold, BLUE) are lower than sulfone formation (Figure 5.5, bold, RED). Further, DFT calculations rule against rapid equilibration between •SAr and •SO2Ar. If so, the equilibrium will strongly tilt toward formation of Ph–S–Ar **4** for all systems.

5.4 Conclusion

In summary, Ni/photoredox dual catalysis enables the construction of aryl- and heteroaryl sulfones from aryl halides and sulfonate salts. The base-free, room-temperature reaction conditions described here permit a wide array of functional groups to be tolerated. The broad tolerance and mild nature of the described reaction will likely translate to its use in the preparation of sulfones

with biological relevance (e.g., in bioconjugation, drug substance synthesis, etc.) as demonstrated in the synthesis of drug-like compounds or their precursors. A mechanistic manifold consistent with experimental and computational data is presented. Computations on the product determine steps allow for bracketing of the complex disproportionation of the sulfinyl radical which capture the experimental trends observed with product distribution and substrate electronic effects. These results will aid in rational reaction design and provides a holistic understanding of the reaction that is currently absent in the literature. Finally, sequential functionalization using the process outlined here and existing Ni/photoredox methods allows an array of diverse scaffolds to be assembled from bifunctional electrophiles.

Chapter 6: Understanding the Reactivity of Bicyclopentane bis-Boronate via DFT

Excerpts from this chapter are submitted for publication: Yang, Y.; Tsien, J.; **Dykstra, R.**; Chen, S.-J.; Wang, J. B.; Merchant, R. R.; Hughes, J. M. E.; Peters, B. K.; Gutierrez, O.*; Qin, T.* Exploring Uncharted Chemical Space: Orthogonal Late-Stage Functionalization of Bridge-substituted BCP bis-Boronates. Submitted

6.1 Introduction

Infinite chemical space provides boundless opportunities for medicinal chemists, within which three-dimensional scaffolds with drug-like properties are particularly sought after[347,348] The past decade has witnessed growing interests in novel chemical space of bicyclo[1.1.1]pentane (BCP), a class of medicinally relevant motifs as a three-dimensional bioisosteric replacement of aromatic moieties (Figure 6.1A).[182,349–357] Such consideration was driven by its potential to improve physicochemical, pharmacological, and toxicological properties of drug candidates,[182,354,355] with bridgehead (C_1 and C_3)-substituted BCPs widely recognized as saturated bioisosteres for mono- and *para*-substituted benzenes and analogously in synthetic chemistry.[358–371]Analogously, it has been hypothesized that C_1, C_2-disubstituted BCPs could represent bioisosteres of *ortho*- and *meta*-substituted benzenes.[182,372–374] However, despite the recent reports from Baran,[374] Ma,[375,376] our group[377] and others,[378–380] efficient preparation of bridge-substituted BCPs still proves challenging and the practical applications of such BCPs in medicinal chemistry remain heavily constrained. Compared with C(sp^2) cross-coupling chemistry enabling rapid diversification of arenes,[381] yet derivatization of the C(sp^3)-rich bioisostere BCPs requires multi-step *de novo* synthesis.[377] Such constraints represent the biggest bottleneck to access and evaluate these promising compounds in structure-activity-relationship (SARs) studies. Thus, development of a modular and programmable

strategy to access C_1, C_2-disubstituted and C_1, C_2, C_3-trisubstituted BCPs should enable more comprehensive SAR campaigns and chemical space exploration.

The inert C-H bond within BCPs not only provide metabolic stability for this three-dimensional scaffold,[36-38] but also create the synthetic hurdles to generally access bridge(C_2)-substituted derivatives via C-H functionalization.[373] Despite our earlier success in multi-substituted BCP syntheses via intramolecular cyclization strategy,[377] the installation of the bridge-

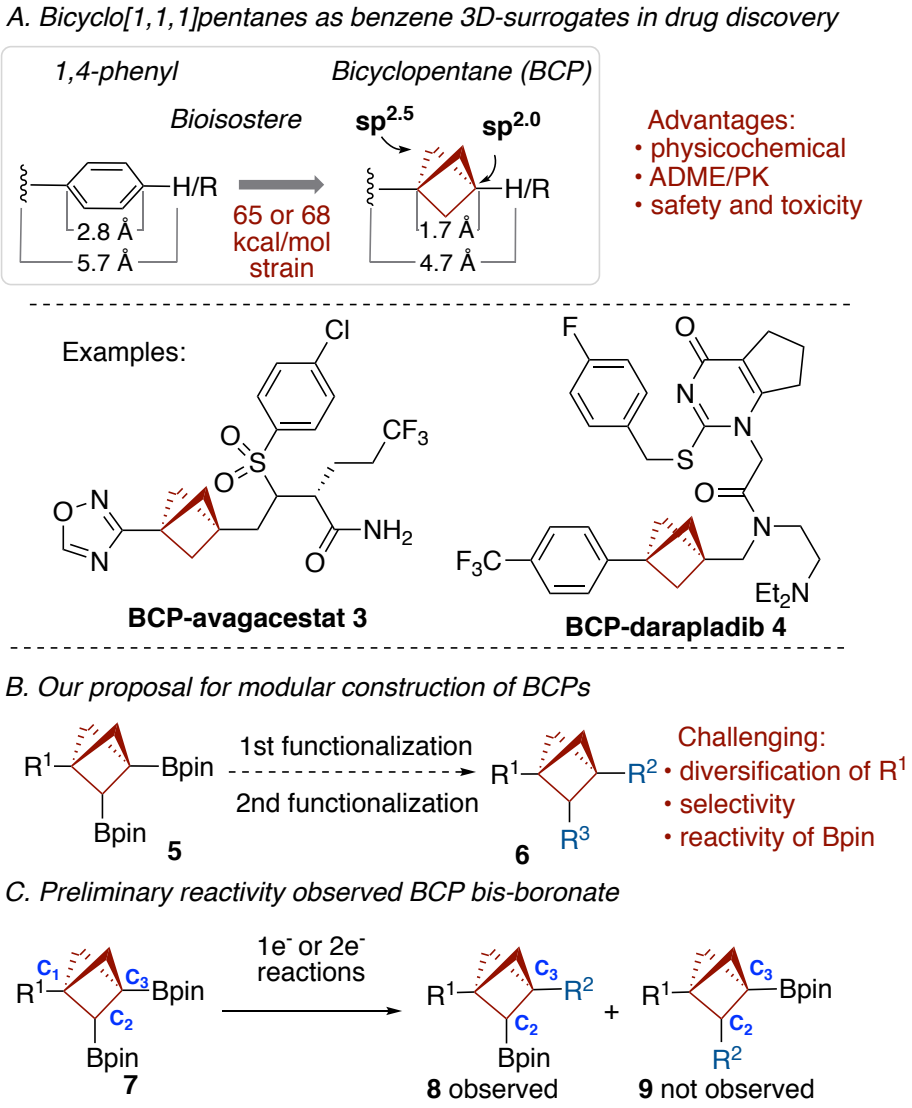


Figure 6.1: Introduction of BCP Bis-functionalization strategy. [a]Bicyclo[1.1.1]pentanes as benzene bioisosteric 3D-surrogates in drug discovery. [b]Structure-activity relationships (SARs) analysis with BCP scaffold. [c]Programmable and orthogonal functionalization of bridge-substituted BCPs. [d]Reactivity observed with BCP bis-boronate.

substitution group prior to the cyclization substantially increased the synthetic steps required to access each analog. To address these issues, our goal was to identify a late-stage BCP intermediate with two functional handles that could be selectively and rapidly modified to pursue divergent SARs exploration. To that end, our group previously reported[377] the preparation of two C_1-alkyl BCPs bearing Bpin substitutents at both C_2 and C_3. Inspired by breakthrough reports by Morken,[1–3] Aggarwal,[382,383] and others,[384,385] we postulated that these BCP bis-boronates could be selectively and sequentially functionalized (Figure 6.1C) and this synthetic method would provide a rapid access to novel bridge-substituted C_1, C_2-di- and C_1, C_2, C_3-tri-substituted BCPs. The first 1 and 2 electron functionalizations performed using the BCP bis-boronates revealed regioselective reactivity at the bridghehead (C_3) Bpin (Figure 6.1D). To understand the origin of the observed selectivity, DFT calculations were run on the substrate (BCP bis-boronate) and on the hydrazone coupling reaction. The reactivity of the modeled chemical transformation is found to be a controlled by a concerted transition state from reactants to products, dissimilar to the previously proposed stepwise mechanisms of the original hydrazone coupling reported.

6.2 Methods

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3)/def2-SVP level of the theory in implicit solvent (PhCl) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, Revision C.01. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Single point energy calculations in implicit solvent using and B3LYP-D3/def2-

TZVPP-CPCM(DMSO) were also performed. All energy decomposition analysis (EDA) was done using the second-generation absolutely-localized molecular orbital EDA available in Q-Chem version 5.3.

These calculations were performed at the same level of theory used for single point energy calculations but in the gas phase. All 3-D structures were generated using CYLview20. NBO analysis was performed using NBO version 3.1 as available in the Gaussian software package. Orbitals visualized using GaussView 6. Non-covalent interaction (NCI) analysis was performed using the Multiwfn software with the isosurfaces visualized using VMD and colored scatter plots made with Multiwfn scripts and gnuplot 5.4.

6.3 Results and Discussion

6.3.1 Pre-Computation Experimental Work

This part of the work was performed by members of the Qin group.

The striking reactivity difference, obtained by the Qin group, between C_2-Bpin and C_3-Bpin units was initially observed in the boronate ligand exchange reaction with BCP **10** (Figure 6.2). Under treatment of naphthalene-1,8-diamine in toluene, selective formation of C_3-Bdan-

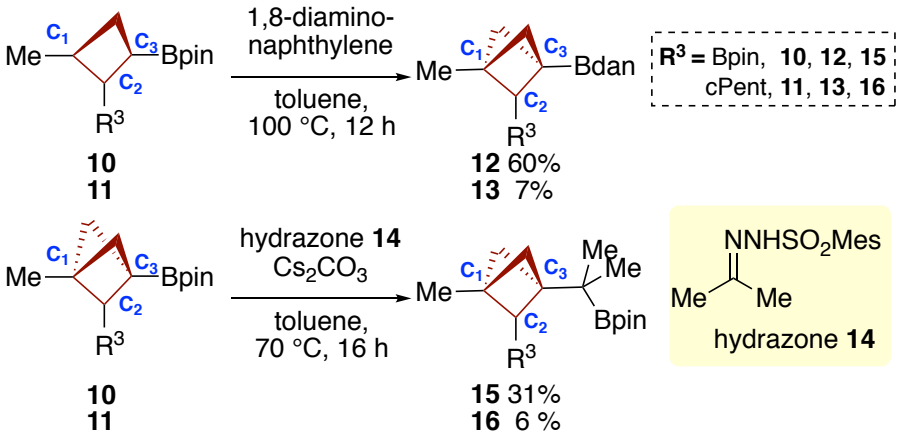


Figure 6.2: Preliminary Chemoselectivity of BCP bis-boronates. Synthesis done by members of the Tian group.

substituted product **12** was identified by NMR analysis and confirmed by single-crystal X-ray diffraction. In comparison, the C_2-cyclopentyl-substituted BCP **11** afforded significantly lower yield of the corresponding product (**13**, 7%). In a similar vein, this chemoselectivity was also observed in the hydrazone coupling[41.] The bridgehead C_3-Bpin in BCP bis-boronates presented an activated reactivity and underwent coupling with sulfonyl hydrazone while C_2-Bpin in bis-boronates and BCP **11** remained mostly intact (Figure 6.2). We initially hypothesized that, as noted by Morken,[386,387] and others,[382–385] selective activation at the C_3 position in this bis-boronate system is likely due to intramolecular coordination (e.g., oxygen lone pair-boron interaction) of the Bpin at the C_2 position. However, careful analysis of B_3–C_3–C_1 angles of these BCPs X-ray crystal structures revealed no obvious initial interaction between the two adjacent Bpin groups in the BCP scaffolds, presumably because the strained bicyclic scaffold restricts the spatial orientations of these groups (Figure 6.2).

6.3.2 Computational Work

This part of the work was performed by Ryan Dykstra.

To gain further insights into the selective reactivity of BCP bis-boronates, we turned to quantum mechanical calculations. First, analysis of the lowest energy conformations of BCP bis-boronate **13** found no apparent Bpin-Bpin noncovalent interactions, consistent with the crystal structures (Figure 6.3A) and natural bond orbital (NBO) analysis (see Appendix). To determine if the observed reactivity was correlated with the difference in Lewis acidity of the two Bpin moieties and as the empty p-orbital of the Bpins share the same canonical orbital, the energies of the Bpin natural bond orbitals (NBOs) were compared for the two lowest energy conformations. As can be seen in Figure 6.3B, the arm Bpin is computed to be a stronger Lewis acid when in the lowest

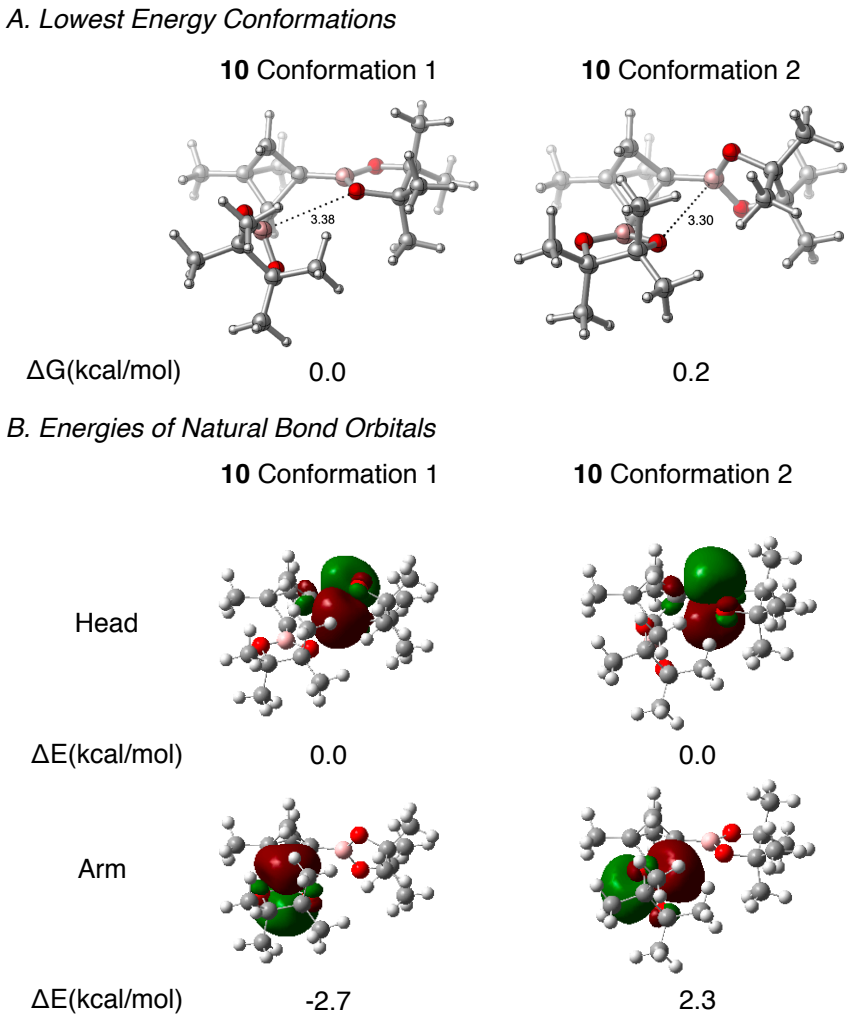


Figure 6.3: Calculations on BCP bis-boronate substrate. [a]Lowest energy conformations located. [b]Relative Energies of natural bond orbitals. I performed all calculations.

energy conformation by 2.7 kcal/mol while the head Bpin was the stronger Lewis acid by 2.3 kcal/mol while in the second lowest energy conformation; making it hard to assign which Bpin is the stronger Lewis acid. Comparison between the putative anionic intermediates generated revealed a ~10 folds thermodynamic preference for the C_3 (bridgehead) 3o anionic intermediate ($\Delta\Delta G_{rel}$ $\mathbf{13}^{\mathbf{C2^-/C3^-}}$ = +1.8 kcal/mol, Figure 6.4). In contrast, DFT calculations show an energetic preference for the formation of the 2o alkyl radical, which might occur via C_2-Bpin homolysis ($\Delta\Delta G_{rel}$ $\mathbf{13}^{\mathbf{C2^\bullet/C3^\bullet}}$ = –3.0 kcal/mol, Figure 2B). Such results can be rationalized by the higher s-character of C_3 carbon (behaved as $sp^{2.0}$) than C_2 carbon ($sp^{2.5}$),[356,388] leading to a higher

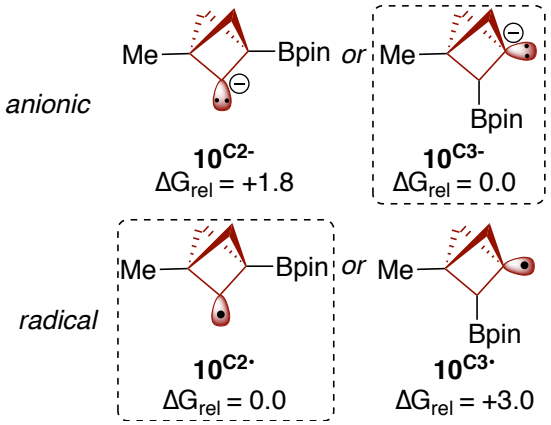


Figure 6.4: Relative free energies of radical and anionic intermediates generated from 1 and 2 electron reactions. I performed all calculations.

electronegativity at the bridgehead position and an increased Lewis acidity of the attached Bpin. Given that exclusive reactivity at the bridgehead position was observed for all transformations *(vide infra)*, these calculations support an anion-mediated *C-B activation* pathway. (Figure 2C). Further study probed into the bond-forming step, where the hydrazone coupling reaction[389] between bis-boronate **10** and a diazo compound presumably generated from the corresponding sulfonyl hydrozone under basic conditions (Figure 6.5A). In agreement with the synthetic outcomes (Figure 6.2), these calculations highlighted a strong preference for activation and functionalization of the C_3 carbon versus C_2-Bpin functionalization. Specifically, DFT calculations identified an energetically much lower concerted addition/migration/N_2 extrusion transition state that will lead to the corresponding C-C coupling at the C_3- than at the C_2-carbon (**10-TS^{C3}** vs. **10-TS^{C2}**, $\Delta\Delta G_{rel}$ = +6.0 kcal/mol). Moreover, the resulting C_3-product is also more thermodynamically favorable than the C_2-coupling product by similar energy (See Appendix). Inspection of the Mulliken charges (MC) of the transition states (Figure 2C) revealed a greater buildup of negative charge in **10-TS^{C2}** (MC C_2 = –0.181, MC C_3 = –0.045). Additional energy decomposition analysis (EDA) of **10-TS^{C2}** and **10-TS^{C3}** (Figure 6.5B) suggested that despite greater non-covalent electrostatic, orbital, and dispersion stabilizing interactions in **10-TS^{C2}**, much more significant steric interactions in **10-TS^{C2}** ($\Delta\Delta E_{steric}$ **10-TS^{C2}** = +310.3 kcal/mol, $\Delta\Delta E_{steric}$ **10-TS^{C3}** = +268.1 kcal/mol) were observed, overall resulting in a higher barrier via the C_2 transition state ($\Delta\Delta E_{rel}$ = +11.0 kcal/mol, Figure 2C). Overall, I attributed the selectivity to 1) greater buildup

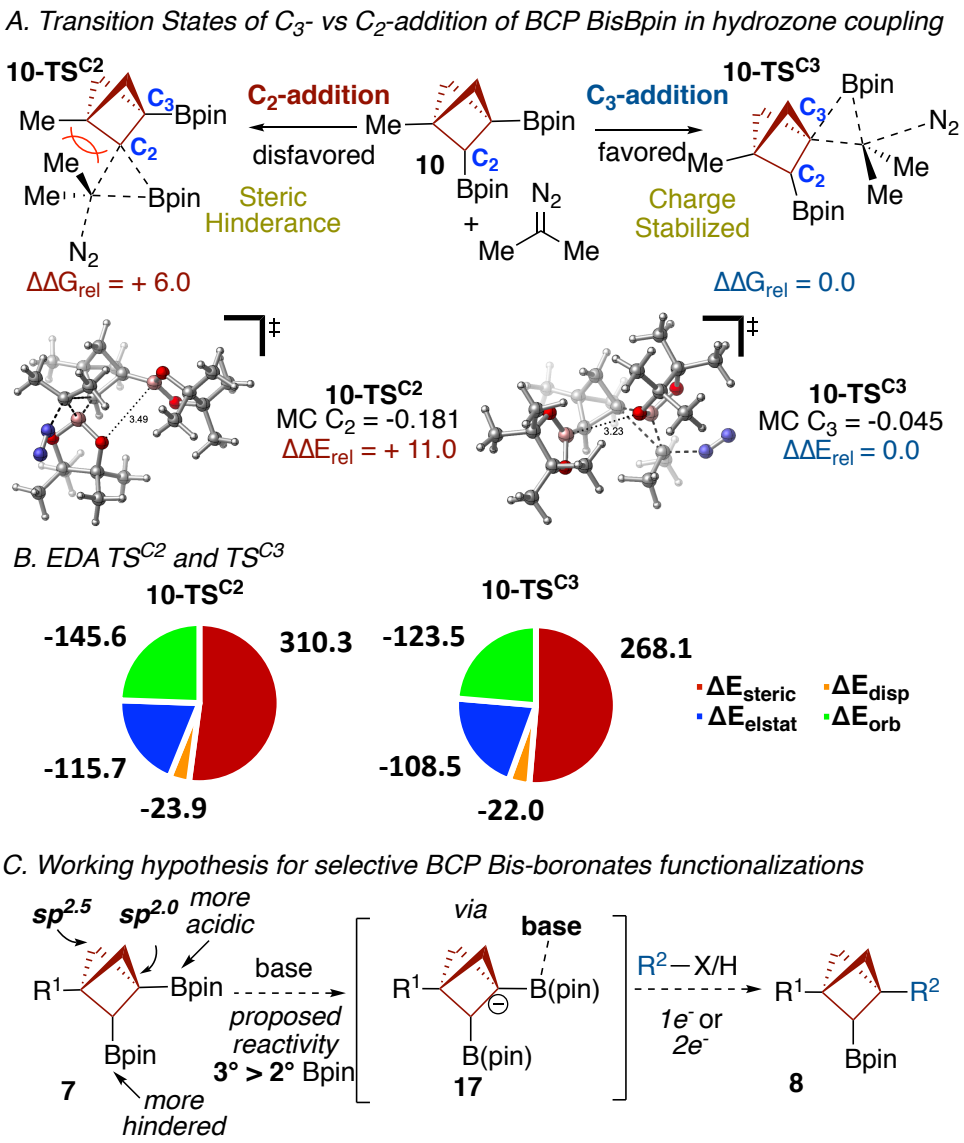


Figure 6.5: States of C3- vs C2-addition of BCP bis-boronates in hydrazone coupling. [b]Energy decomposition analysis (EDA) of Transition States in hydrazone coupling. [c]Working hypothesis for selective BCP bis-boronates functionalizations. MC = Mulliken Charge. I performed all calculations.

of negative charge and 2) less destabilizing steric interactions between the BCP scaffold and pinacol ligand in the transition states at the C_3 position (See Appendix for further details). Additional calculations comparing the barriers of the hydrozone coupling of the BCP bis-boronate to those of model isopropyl Bpin and isopropyl boronic acid can be found in the appendix. Taking advantage of the higher reactivity of C_3-, a sequential functionalization protocol of BCP bis-boronates was envisioned, where C_3- and C_2- Bpin can be transformed into multiple functional

groups and access divergent C_1, C_2, C_3-tri- substituted BCPs (Figure 6.5C).

6.3.3 Post-Computation Experimental Work

This part of the work was performed by members of the Qin group.

In the Tian groups previous work,[377] the alkyl substituted BCP bis-boronate (**10**) was synthesized from readily accessible aldehyde via diborylation of its derived sulfonyl hydrazones[390] and intramolecular coupling[377] on gram scale and in moderate yield. BCP **20** and **21** were prepared via similar routes (Figure 6.6A). However, the carboxylate ester, trifluoromethyl and aryl substituted BCP bis-boronates were found incompetent by the challenging access to germinal bisBpin precursors (yield < 5%) and the diminished yield in intramolecular cyclization. These BCPs (**19**, **22**, **27**3 were successfully accessed (Figure 6.6A) through crucial modifications including the diborylation of germinal dibromo compounds[391] and intramolecular cyclization under "dry" conditions (pre-preparation of sulfonyl hydrazone, dry solvent and base). As an example, synthesis of ester C_1-substituted BCP **19** (Figure 6.6B) starts from an affordable cyclobutyl diester **24**. The cyclobutyl sulfonyl hydrazone **27** was generated in high yields through a sequence of DIBAL-H reduction, dibromination and diborylation. The following cyclization mediated by anhydrous Cs_2CO_3 robustly afforded **19** on 40-gram scale in a single pass without deterioration of yield. Notably, all the synthesized BCP bis-boronates are stable crystalline solids and can be stored at -20 °C without any noticeable degradation for several months.

Consistent with theoretical modelling, BCP bis-boronates underwent selective alkylation at the bridgehead (C_3) Bpin with sulfonylhydrazones[377] (Table 6.1A, **28, 29**), leaving the resultant alkyl Bpins intact. It is worth noting that other non-BCP alkyl Bpins were generally incompatible with

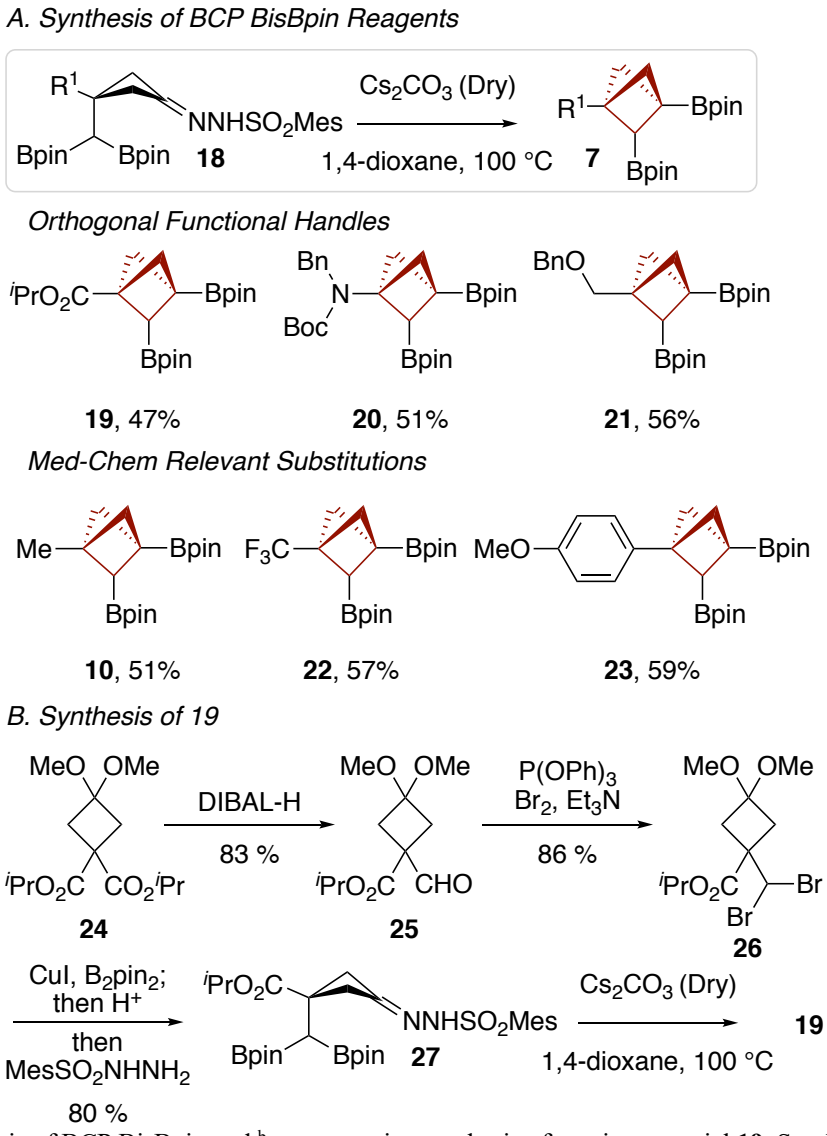
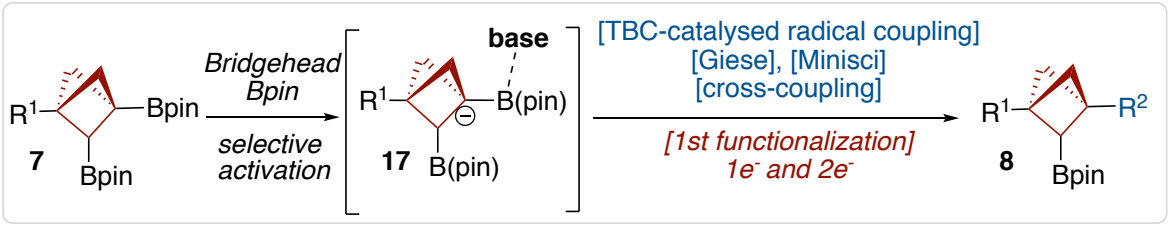


Figure 6.6: [a]Synthesis of BCP BisBpin and [b]representative synthesis of starting material **19**. Synthesis done by the members of the Tian group.

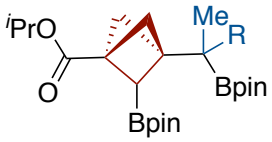
this hydrazone coupling.[392] The Tian group then sought to investigate selective additional C3-Bpin deborylative functionalization strategies. C_3-protodeborylation of BCP bis-boronates to afford C_2-Bpin substituted BCPs, which provides a modular tool to access a library of diverse 1,2-disubstituted BCPs (Table 6.1B), a class of potential bioisosteres for *ortho*- and *meta*-disubstituted arenes. Inspired by Renaud's studies,[393,394] BCP bis-boronates underwent effective protodeborylation with tert-butyl catechol (TBC) upon heating under argon atmosphere and C_2-Bpin disubstituted BCPs were afforded with good yields (**30**). Enabled by the TBC strategy, the

C_3-centered radicals formed *in situ* can also react with tosyl cyanide (TsCN), $PhSO_2SPh$, and di-

Table 6.1: Select Examples of Selective C3-Bpin functionalization of BCP Bis-boronates

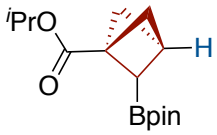


A. [Hydrazone Alkylation][a]
sulfonyl hydrazone, toluene, Cs_2CO_3, 70 °C



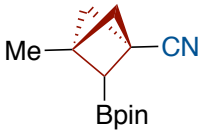
R = Me, **28**, 62%[i]
CH_2CH_2Ph, **29**, 57%[ii]

B. [Protodeborylation][b]
TBC, toluene, 100 °C



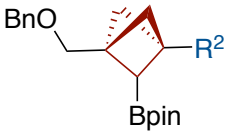
30, 72%

C. [Cyanation][d]
TBC, TsCN, toluene, 70 °C

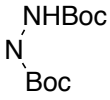


31, 50%

D. [C-S & C-N Formation][e]
TBC, $PhSO_2SPh$ or DBAD, toluene, 100 °C

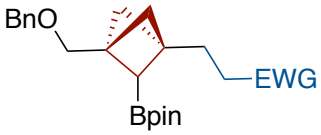


R^2 = SPh, **32**, 57%



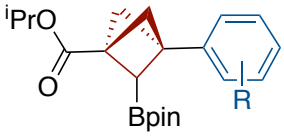
33, 50%

E. [Giese Alkylation][f]
Michael Acceptors, DMAP [Ir], acetone/MeOH, hv



EWG = COMe, **34**, 70%
CO_2Et, **35**, 39%
CN, **36**, 55%

F. [Cross-Coupling][g]
ArBr, [Ni], $Zn(OTf)_2$, DMAP, 4-CzIPN, DMA, rt, hv



R = 4-CO_2Et, **37**, 35%
4-COMe, **38**, 32%
4-CN, **39**, 39%
4-OMe, **40**, 33%
3,5-diOMe, **41**, 34%

[a]Structure determined by X-ray. [b]Dr = 1:1.

Table 6.1: Examples of selective C3-Bpin functionalization of BCP Bis-boronates. Reaction conditions with BCP BisBpin as the limiting reagent at 0.05-0.2 mmol scale: [a]sulfonyl hydrazone (2.0 equiv.), Cs2CO3 (2.0 equiv.), toluene (0.2 M), 70 °C, 18-48 h; [b]TBC (2.5 equiv.), toluene (0.2 M), Ar or air atmosphere, 100 °C, 2-12 h; [c]4-CzlPn (5 mol%), MeOBcat (30 mol%), acetone/MeOH (1:1, 0.1 M), blue LED, r.t., 2 h; [d]TsCN (2.0 equiv.), TBC (20 mol%), toluene (0.2 M), 18 h; [e]PhSO2SPh or DBAD (2.0 equiv.), TBC (20 mol%), toluene (0.2 M), 70 °C, 18-24 h; [f][Ir] (5 mol%), DMAP (30 mol%), Michael acceptor (2.0 equiv.), acetone/MeOH (1:1, 0.1 M), blue LED, r.t., 24 h. Synthesis done by members of the Tian group.

tert-butyl azodicarboxylate (DBAD) to afford nitrile- (**31**), thioether- (**32**) and hydrazide- (**33**) containing BCPs in moderate yields (Table 6.1C and 6.1D). C_3-selective Giese alkylation of BCPs (**34, 45** and **36**) was achieved with Ley's conditions[395,396] via the bridgehead C_3 radical from photoinduced oxidation of a Bpin-DMAP ate complex (Table 6.1E). Assessment of Ni-catalyzed

cross-coupling started with aryl bromides, an abundant class of building blocks, yet all the previously reported conditions failed to afford the desirable product.[323,333,397–399].Extensive screening efforts identified a photosensitized method with 4-CzlPn as the photosensitizer and $Zn(OTf)_2$ as a key Lewis acid additive, where aryl bromides with diverse electronic properties were well tolerated (**37-41**, Figure 4F). Additional reactions were explored to both determine synthetic strategies which are amenable to late-stage functionalization of the BCP bis-boronates and to expand the previously unexplored chemical space of the C_1, C_2, C_3-trisubstituted (not discussed here).

6.4 Conclusion

Initial reactions on the BCP bis-boronate substrate revealed preferential reactivity at the bridgehead (C_3) Bpin over the arm (C_2) Bpin. Additionally, both one electron and two electron reactions performed resulted in preferential reactivity at the bridgehead (C_3) position. To understand the observed selectivity, we analyzed the canonical orbitals of the BCP bis boronate and its intermediate stability at both positions from one and two electron pathways. The stability of the anionic intermediates agrees with the observed reactivity, suggesting an anionic *B-C activation* pathway is likely responsible for the observed reactivity. Additional DFT calculations on the C_{sp3}-C_{sp3} hydrazone coupling resulted in location of a concerted transition states at both the bridgehead and arm positions which lead to product. The barriers at the bridgehead position were substantially lower in energy than those at the arm position, revealing that these reactions are kinetically controlled. Energy decomposition analysis of the concerted transition states indicated that a large increase in steric interactions through the arm (C_2) transition states are responsible for the observed regioselectivity. As all other 1st functionalization resulted in preferential reactivity at

the bridgehead carbon, we propose that a combination of stabilization of negative charge at the C_3 position and increased steric interactions at the C_2 position is responsible for the observed reactivity of the BCP bis boronate.

Chapter 7: Understanding the reactivity of Alkyl Sulfinate Mediated Cross-Coupling

Excerpts from this chapter are submitted for publication: Zhou, M.; Tsien, J.; **Dykstra, R.**; Hughes, J. M. E.; Peters, B. K.; Merchant, R. R.; Gutierrez, O.*; Qin, T.* Alkyl Sulfinates as Cross-Coupling Partners: Programmable and Stereospecific Installation of C(sp^3) Bioisosteres. *Submitted.*

7.1 Introduction

Traditionally, "flat structures" featuring biaryl moieties have dominated the practice of medicinal chemistry. However, in recent years, the need to improve receptor complementarity and pharmacokinetic properties have compelled medicinal chemists to venture into chemical space with increasing saturation.[347,348] As a consequence of this, a variety of cycloalkyl groups with quaternary carbons have emerged as promising bioisosteres for aromatics and other functionalities.[354,400–403] The cyclopropyl- and cyclobutyl trifluoromethyl groups are illustrative examples, as these building blocks are found to confer desirable properties to drug-like molecules.[180,182,183] Nevertheless, modular installation of these coveted fragments remains an unsolved synthetic challenge.[186,223,404–408]

Baran and co-workers have pioneered the development of a series of alkyl sulfinate reagents, bearing pharmaceutically relevant alkyl bioisosteres.[409–415] These reagents serve as radical precursors via single sequential electron oxidation and loss of sulfur dioxide (SO_2) and generation of alkyl radical (Figure 7.1A).[188] Although this work has enabled functionalization of various heterocycles, the innate reactivity of this transformation (Minisci-type) poses limitations in achieving programmable and stereospecific functionalization of any aromatic or heterocycle. Prior

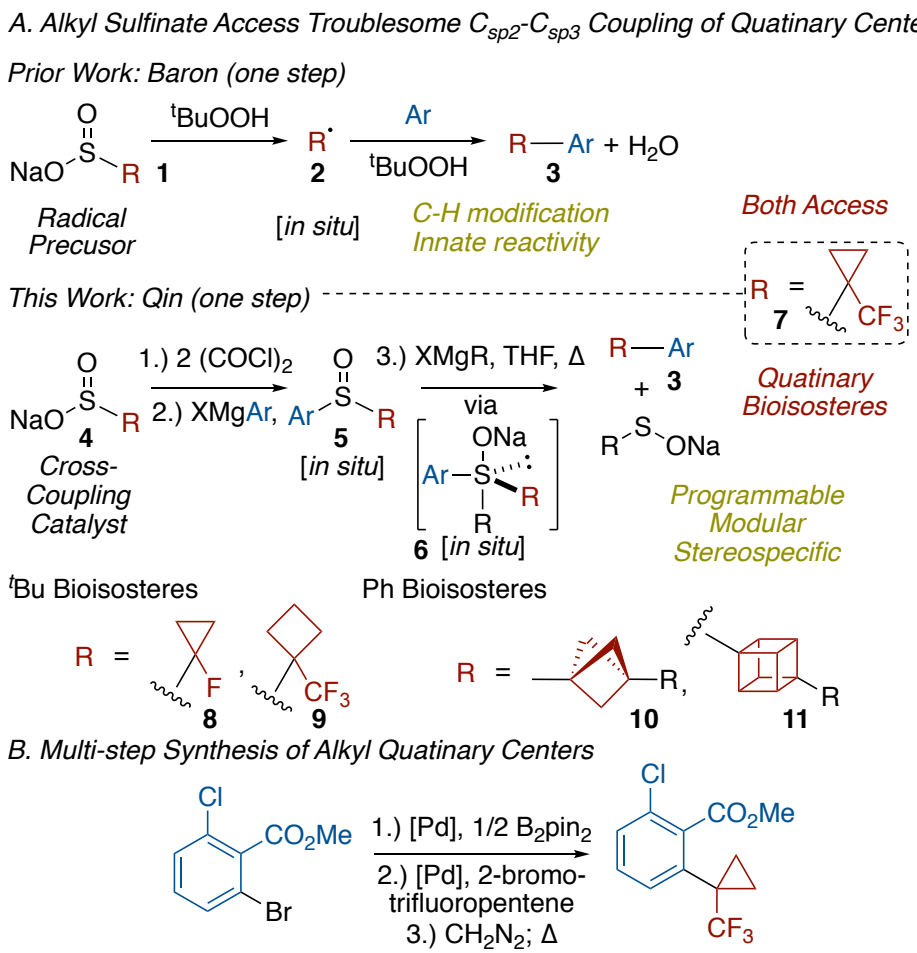


Figure 7.1: A. Sulfone mediated cross-coupling via aryl alkyl sulfones. B. Previous method to access to trifluoromethylcyclopropyl substitution on aryl functionalities.

work has shown that sulfoxide can participate in sulfurane cross-coupling via electrophilic activation.[416–418] Therefore, we envisaged that in contrast to extrusion of SO_2 during the radical process, the alkyl sulfinates could serve as stereospecific and programmable coupling partners in sulfur mediated cross-coupling instead.

Multi-carbon linked sulfuranes have been considered unstable species which could be ideal to facilitate the bond formation between two attached ligands.[419] As demonstrated by Furukawa and Oae, the addition of organometallic nucleophiles to sulfoxides led to the formation of the varied ligand coupled products presumably from oxy-sulfurane intermediates.[420–428] In recent years, there have been multiple reports by Stockman,[429] Procter,[430] McGarrigle,[431] Kano,[432] Peng,[433] Hoye[434]

and our group[435] on C(sp^2)–C(sp^2) or C(sp^2)-benzyl cross-couplings via sulfurane intermediates. Despite these reports, there is no general method for the use of sulfurane intermediates in C(sp^2)–C(sp^3) cross-coupling[436], in particular for the installation of sterically hindered and electronic-unique alkyl bioisosteric groups. Since strained cycloalkyls possess more sp^2 character than typical unstrained aliphatic moieties, we surmised that this modality of sulfur-mediated coupling may be amendable to programmable construction of C-C bonds between arenes and cycloalkyl groups, particularly those containing quaternary carbons such as the cyclopropyl trifluoromethyl motif. This sulfurane-mediated C(sp^3)–C(sp^2) formation would facilitate installation of several medicinal chemistry relevant alkyl groups, such as the trifluoromethyl-cyclopropyl (TFCp),[188,408,437,438] fluorocyclopropyl (FCp)[439–444] and trifluoromethylcyclobutyl (TFCb) groups, which all continue to be challenging motifs to incorporate into structures of therapeutic interest (Figure 7.1A). Traditionally, such alkyl-substituted arenes require *de novo* preparation over multiple steps. These multi-step routes are necessitated due to the lack of reactivity of these sterically hindered C(sp^3)-rich scaffolds as traditional cross- coupling partners. For instance, the preparation of medicinal chemistry relevant motif compound **5** requires multistep *de novo* synthesis from the aromatic bromide (Figure 1B).[445] Herein, the Qin group describes a novel approach for the construction of hindered C(sp^2)–C(sp^3) bond via sulfurane intermediates starting from bench-stable and in many instances, commercially available alkyl sulfinates[446–449] (Figure 7.1A; Bottom). This two-electron strategy not only provides a general and modular means to install these hindered bioisosteric alkyl groups, but also a route to install the alkyl group with complete stereochemical fidelity.[450,451] Due to the inability to experimentally isolate the proposed sulfurane intermediate (Figure 7.1A; This Work), I performed DFT calculations to determine if this intermediate is responsible for the observed reactivity.

7.2 Methods

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3BJ)/def2-SVP level of the theory in implicit solvent (THF) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, Revision C.01. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Single point energy calculations in implicit solvent using and B3LYP-D3BJ/def2-TZVPP-CPCM(DMSO) were also performed. All 3-D structures were generated using CYLview20.

7.3 Results and Discussion

7.3.1 Experimental Work

This part of the work was performed by members of the Qin Group.

Success of the proposed reaction hinged upon our hypothesis that tertiary cycloalkyl groups are a relatively electron-rich alkyl moieties that would drive the pseudo rotation equilibrium towards that will place the two reacting ligands orthogonal to each other prior to undergoing C-C bond formation. As a result, this would bring the two coupling partners in closer proximity and enable preferred tertiary cycloalkyl group coupling with the heteroaryl- or aryl partner. In addition, taking inspiration from Furukawa, Oae,[420–422] and Stockman's[429] studies on aryl–benzyl coupling, the alkyl group originally attached on sulfoxide was surmised as superior ligand coupling partner probably owning to kinetically favored sulfurane intermediate.

Table 7.1: Selected Substrate Scope of Sulfone Mediated Cross-Coupling.

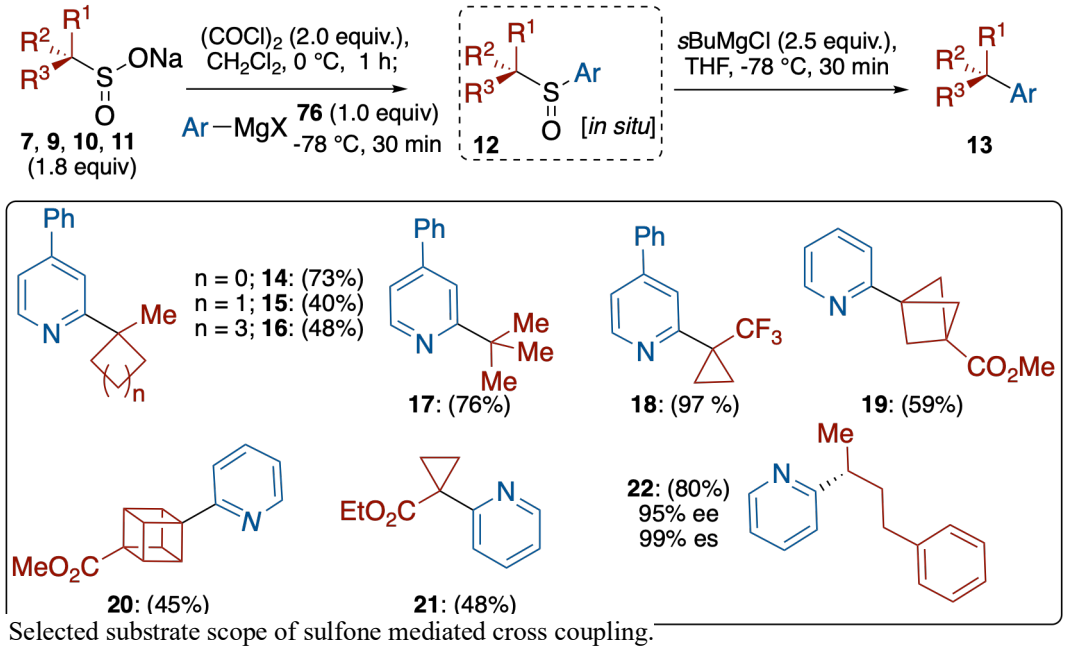


Table 7.1: Selected substrate scope of sulfone mediated cross coupling.

The sulfurane mediated C(sp^2)-C(sp^3) coupling also allows for the installation of multiple bioisosteric quaternary alkyls. As illustrated in Table 7.1, the tertiary cyclopropyl groups (**14**, **18**, **21**) cyclic tertiary groups (**15**, **16**), *tert*-butyl (**17**), bicylo[1.1.1]pentane (**19**) and cubanes (**20**) were smoothly coupled under the current protocol. Several enantioenriched alkyl sulfinates were prepared[449] and the sulfurane-mediate coupling demonstrated high stereochemical fidelity (>99%

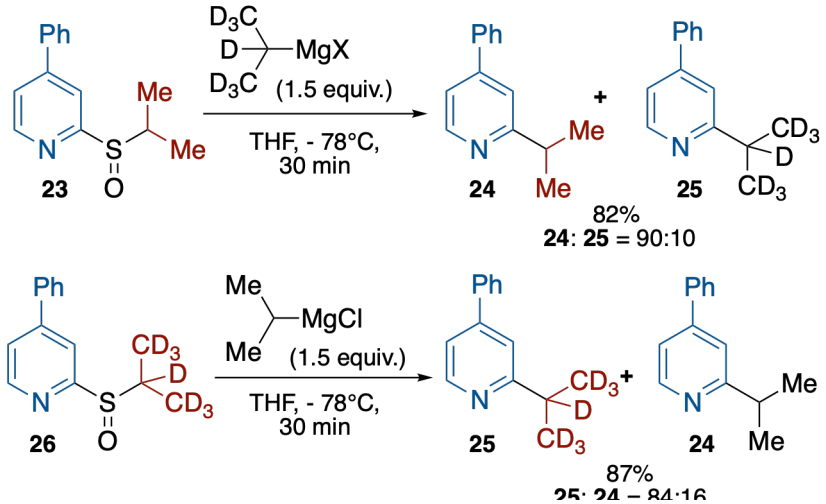


Figure 7.2 Isotope labeling experiment for sulfone mediated cross-coupling.

es, **22**). In contrast to the Minisci-type radical reactions, the coupling described herein completely retains the C(sp^3) partner stereochemistry of the C(sp^3) coupling partner. The synthetic impact of this methodology was highlighted by its modular and rapid synthesis of real-life medicinal chemistry intermediates, which can be seen in the manuscript.[452]

The alkyl coupling trend was preliminarily studied in Figure 7.2. In order to probe the coupling tendency of the initial ligands on sulfoxides and additional ligand, the sulfoxide **23** and its deuterated isotope **26** were prepared (Figure 7.2). Under the coupling conditions, similar yields were observed, with a higher ratio of **24** and **25** in each respective control study suggesting that the ligands originally attached on sulfoxide were preferred to couple. This could arise from the kinetically formed sulfurane intermediate in which pyridine and initial ligand are perpendicular to each other.[423]

7.3.2 Computational Work

This part of the work was performed by Ryan Dykstra.

Unfortunately, additional experimental mechanistic experiments failed to observe the sulfurane intermediate presumably due to the high instability of these intermediates. To probe the mechanism and intermediacy of sulfurane intermediates, we turned to dispersion-DFT calculations (Figure 7.3 and 7.4). To avoid the complexity of Grignard reactivity,[453,454] we initially modeled this transformation using the monomer of the chloroalkyl Grignard. Notably, calculations revealed that the THF solvent plays a crucial role in stabilizing the sulfurane intermediate. Specifically, complexation between the haloalkyl Grignard and the sulfoxide and concomitant release of a THF molecule to form **B** is 1.7 kcal/mol downhill in free energy (Figure 7.3). Rotation of the pyridine functionality to chelate to Mg further stabilizes this complex leading to either **C**, -3.9 and -3.6

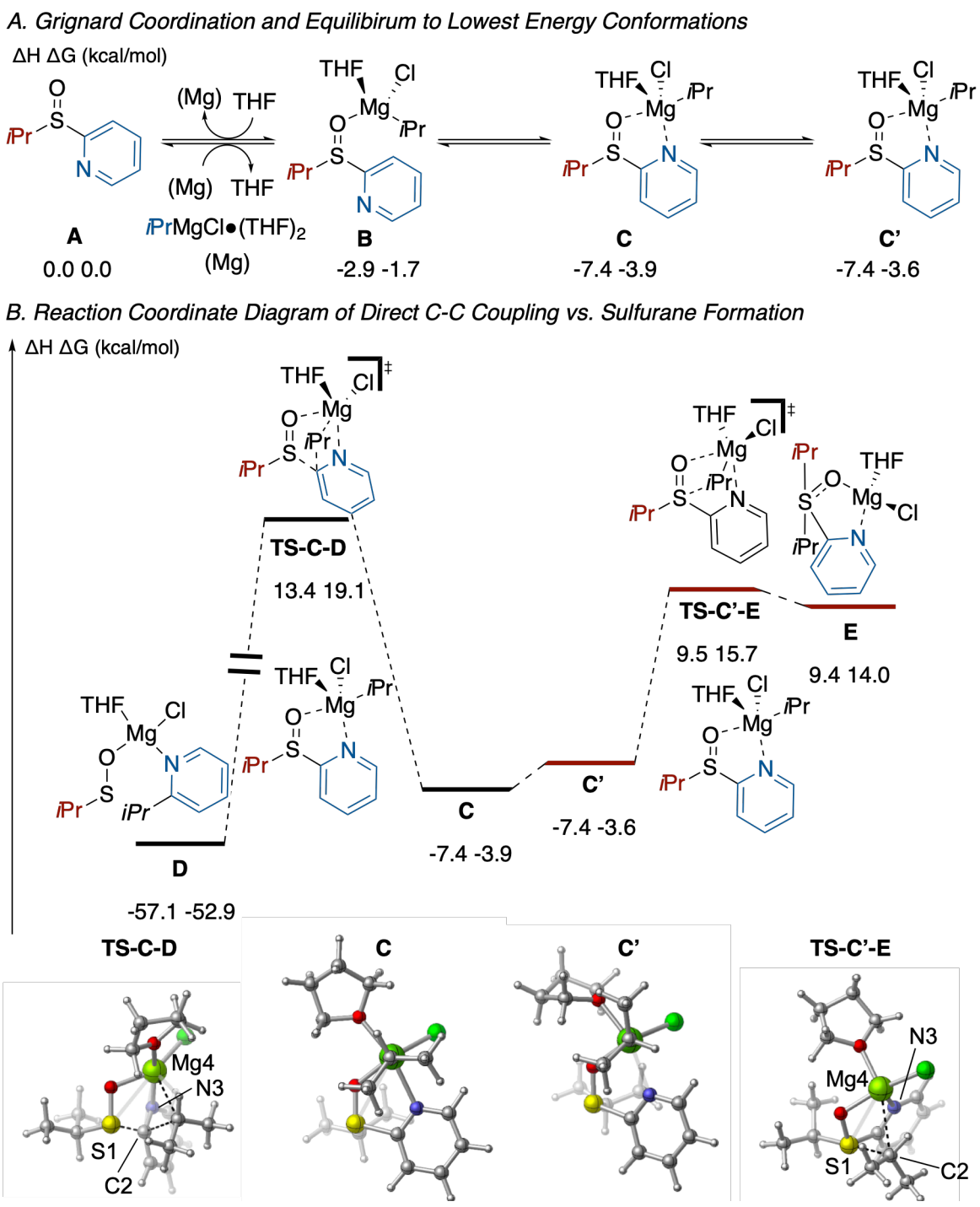


Figure 7.3: A. Grignard coordination and equilibrium to lowest energy sulfone Grignard complex. B. Reaction coordinate diagram of direct product formation vs. sulfurane formation.

kcal/mol lower in energy respectively. Calculations show that conformation **C** is predisposed to go direct C(sp^2)-C(sp^3) bond formation with the alkyl group of the Grignard reagent via **TS-C-D**

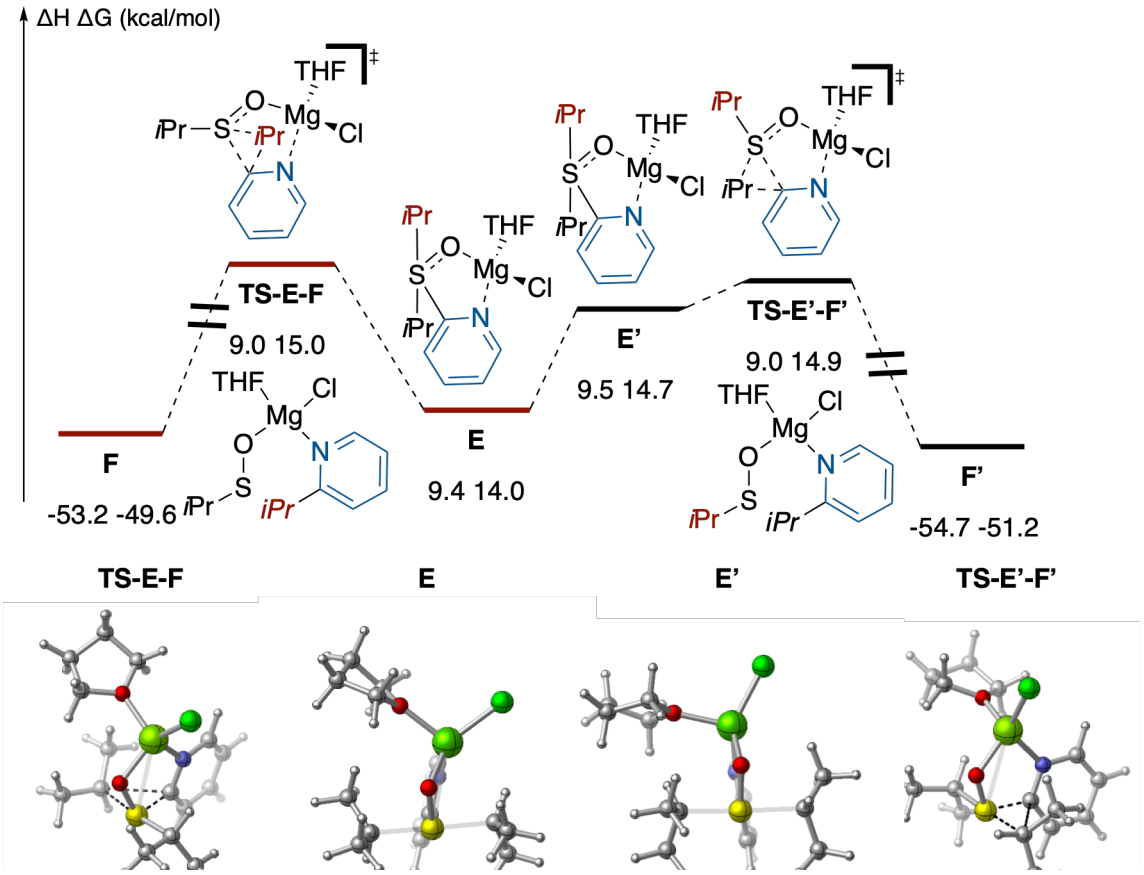


Figure 7.4: Reaction coordinate diagram from sulfurane intermediate to coupled product.

with an overall barrier of 23.0 kcal/mol while **C'** favors alkyl addition to the sulfur atom (**TS-C'-E**) to form sulfurane intermediate **E** with a barrier of 19.3 kcal/mol. The difference in barrier can be correlated with the deviation of the dihedral angle S1-C2-N3-Mg4 of **TS-C'-E** and **TS-C-D** with respect to their corresponding intermediates **C'** and **C**. **TS-C-D** undergoes more distortion (35.93°) than that of **TS-C'-E** (4.16°), resulting in the higher barrier. In addition, the THF molecule is found to be coordinated *trans* of the migrating isopropyl group through **TS-C'-E**, mediating alkyl migration as previously shown by Nova and Cascella.[453,454] Overall, these calculations show a ~5 kcal/mol preference formation of highly kinetically unstable (*vide infra*) sulfurane intermediate versus direct C-C bond formation from chelated intermediates (**C** or **C'**). Finally, from sulfurane intermediate **E** (Figure 7.4), C-C bond formation can occur form the alkyl

originally from the Grignard reagent or the sulfoxide. As the lowest energy barriers to each product differ only by 0.1 kcal/mol, the selectivity of this reaction is likely controlled by the equilibrium (i.e., relative concentration) between the rotamers **E** and **E'** connected to the transition states but given the relative flat potential energy surfaces selectivity is likely to arise from dynamic effects.[78] Nonetheless, both intermediates result in low barriers for irreversible $C(sp^2)$-$C(sp^3)$ bond formation (<1 kcal/mol) leading to the desired products downhill in free energy by ~50 kcal/mol.

7.4 Conclusion

In conclusion, we have developed a general approach to utilize the stable and accessible alkyl sulfinates as programmable $C(sp^2)$-$C(sp^3)$ coupling reagents. In contrast of SO_2 extrusion in sulfinate chemistry, this chemoselective method utilizes the sulfur(IV) atom as the key linchpin, which enables rapid and modular preparation of a variety of synthetically challenging isosteric alkyl groups, TFCp, FCp and TFCb in particular. DFT calculations supported the role of the sulfurane intermediate in product formation, as it is the lowest energy pathway to product. Though these calculations do explain the experimental results, it is likely that the selectivity of these reactions are due to dynamics due to the flatness of the potential energy surface.

Chapter 8: Conclusion and Future Work

8.1 Conclusion

The mechanisms of a series of novel synthetic transformations, discovered by our collaborators, which access compounds of medicinal relevance, were explored using DFT, DLPNO-CCSD(T) and TD-DFT. The calculations I performed, corroborated by experimental evidence obtained by our collaborators, unveiled unique pathways to product for each system studied.

In chapter 2, a novel catalyst-free method to access both trifluoromethyl thioethers and thioesters via an EDA complex between both alkyl and acyl-DHPS and SCF_3 substituted phthalimides was discovered by the Molander group. As the strategy of applying EDA complexes to generate radicals is more recent, a thorough computational investigation of the mechanism was performed, particularly to understand the role of the EDA complex in product formation post-radical generation. TD-DFT calculations supported that the EDA complex was responsible for radical generation for the alkyl-DHP systems through a light-mediated charge transfer event from the DHP to the phthalimide. Mapping the reaction coordinate diagram, via DFT and DLPNO-CCSD(T), post-radical generation, found that the lowest energy pathway to product is via radical addition to the radical EDA complex. Additionally, it was found that SCF_3 radical generation occurs via a completion of charge transfer from the DHP to the phthalimide of the radical EDA complex, which can go on to form the observed SCF_3 dimer. The dimer can serve as an alternate, yet higher energy pathway to product.

The Molander group found a photoredox catalyzed method, chapter 3, to access cyclopropanes using photoredox catalysis and a novel halomethyl radical precursor, bis(catecholato)silicate. This

method was able to access the medicinally relevant trifluoromethyl substituted cyclopropanes under mild reaction conditions. It was experimentally observed that, for trifluoromethyl substituted cyclopropane, the product distribution varied from favoring cyclopropane product to fluorine elimination byproduct upon varying the halogen from iodine, to bromine, to chlorine. To discern if a reductive radical/polar crossover mechanism was responsible for the observed distribution of products, the barriers of both radical and anionic cyclization were computed alongside fluorine elimination pathways. Anionic pathways to both cyclopropane and byproduct were found to reproduce the product distribution observed, indicating that a reductive radical/polar crossover was responsible for product formation. Additional calculations on non-trifluoromethyl substituted systems predicted that less expensive chlorine atom could be used instead of iodine which was confirmed experimentally. This work is the first computational interrogation of these reductive radical/polar crossover reactions, which strongly support the necessity of this step in enhancing the reactivity with the electrophiles in the reaction.

An uphill isomerization of cinnamyl chlorides, chapter 4, was shown to access the diastereoselective formation of chlorine substituted cyclopropanes by the Tambar group. As photoredox catalysts were utilized, it was suspected that a reductive radical/polar crossover was, once again, responsible for the observed reactivity. However, modeling the vertical excitations from the ground state to the triplet excited states of the photoredox catalysts revealed that the iridium photoredox catalyst had identical triplet excited state energies as the cinnamyl chloride. This result suggested that the substrate was being activated by the photoredox catalyst via Dexter energy transfer instead of the commonly proposed single electron transfer events associated with photoredox catalysis. The triplet reaction coordinate diagram of the cinnamyl chloride was modeled, where it was found that chlorine dissociation led to a triplet allyl pair. Intersystem

crossing from this intermediate lead to the observed byproduct, while radical rebound of the chlorine radical beta to the phenyl group resulted in an uphill in energy triplet diradical, which undergoes intersystem crossing to form the chlorine substituted cyclopropane.

As discussed in chapter 5, aryl sulfones are important electronic modifiers used in medicinal chemistry, however, the most common method employed in accessing these functionalities is the oxidation of sulfides. The Molander group created a method to access diaryl sulfones that utilized dual Ni/photoredox catalysis, which utilizes visible light and mild reaction conditions using sulfinate salts and aryl halides to access these functionalities. It is known that the sulfonyl radical can undergo complex disproportionation to form thiyl radical, which can deliver a diaryl thioether byproduct. It was found experimentally that, as the aryl halides are made more electron rich, the formation of the diaryl thioether byproduct increases. To explain the origin of the product distribution, the product determining steps were modeled using DFT, assuming complex disproportionation formed by sulfonyl and thiyl radical. It was found that radical addition of the thiyl radical was in competition with the reductive elimination step of the sulfone with the phenyl group, where increasing the electron donation resulted in a smaller difference between the barrier of the two transition states.

The bicyclopentanes, modeled in chapter 6, have become a recent interest in medicinal chemistry due to their unique biophysical properties and their three-dimensional character. Though there are multiple methods to functionalize the bridgehead positions of bicyclopentanes, synthetic methods to access functionalization of the arm positions are challenging. In order to address this issue, the Qin group as well as our collaborators at Merck developed a method to synthesize difunctionalized bicyclopentanes with Bpins at both the bridgehead and arm positions. However, when both one and two electron reactions were performed, all reactivity was observed to go

through the bridgehead position. To understand the observed reactivity, the boron insertion reaction performed by the Qin group was modeled using DFT. A concerted transition state from product to reactants was located at both the bridgehead and arm positions. Energy decomposition analysis revealed that reactivity at the bridgehead position was favored due to charge stabilization through the transition state, while steric hindrance was responsible for the decreased reactivity at the arm positions.

Finally, in chapter 7, the Qin group described a novel approach for the construction of hindered $C(sp^2)$–$C(sp^3)$ bonds, via sulfurane intermediates formed from reacting aryl alkyl sulfoxides and alkyl Grignards. Using this transformation, they were able to couple quaternary alkyl centers with aryl groups, which is pharmaceutically relevant as several cycloalkyl groups with quaternary carbons have shown to have promising bioisosteric properties. Though sulfurane intermediates were proposed as the inspiration for this transformation, these intermediates could not be observed experimentally. DFT calculations were performed to determine if these intermediates were responsible for the observed reactivity and to determine why the alkyl originally bound to the sulfoxide is predominantly found in the product over the alkyl from the alkyl Grignard additive. It was found that sulfurane formation is lower in energy than direct coupling between the complexed alkyl Grignard reagent. Barriers from the sulfurane intermediate, back to reactant or to product, are very low, explaining why this intermediate could not be isolated or observed experimentally. The observed alkyl selectivity could be explained by the difference in energy of the conformations of the lowest energy pathways to product from the sulfurane intermediate. Due to the flatness of the potential energy surface, dynamics calculations are likely needed to understand the selectivity.

8.2 Future Work

Though a thorough investigation of the role of the EDA complex in chapter 2 was performed using DFT, there were some issues locating the following transition states: homolytic cleavages of the S-N bond via the phthalimide radical anion and more importantly the product forming transition state from the EDA complex. Fine scans of the reaction coordinate of these transition states resulted in sudden jumps in energy, indicating sudden changes in electronic structure. This is likely due to DFT's inability to treat the multireference nature of this reaction coordinate, as the Kohn-Sham formalism used here are single-reference methods.[19,455,456] As the purpose of this work was to investigate the radical reactivity of these transformations, multi-reference calculations should be performed on the transition state-like geometries obtained from scans to more accurately evaluate the energetics and electronic nature of this transformation. These calculations should also be run on the EDA complex to see if substantial differences are observed in electronic structure, binding, and energy of complexation.

By performing calculations on the barriers of both radical and anionic cyclization, I strongly supported a reductive radical/polar crossover mechanism for the photoredox transformation reported in chapter 3. However, this was determined without modeling the barriers of electron transfer. One of the major issues in photoredox catalysis is selecting a catalyst that will undergo fast electron transfer events to give the desired reactivity. Traditionally, the photocatalyst is selected based on experimentally determined redox potentials of these catalysts,[94] which commonly does not lead to the desired reactivity due to the existence of the inverted region[457], where favorable free energies of reaction result in high barriers of electron transfer. To address this issue, the barriers of the SET events of these transformations can be modeled with various photocatalysts using an approximate form of Marcus theory to provide a quantum mechanical

means of photocatalyst selection. Assuming that these events are described by diabatic states, these electron transfer events can be modeled using DFT alongside the Nelson 4-point method to approximate the rates of SET for these reactions.[458] By comparing the barriers of electron transfer to product distribution, the reliability of this method at determining the barriers of electron transfer can be determined.

To better understand the role of the nickel co-catalyst used in Chapter 4, DFT calculations on the transformation should be performed. Additional DFT/TD-DFT calculations should also be performed on cinnamyl bromide and iodide to better understand the reason why neither of these substrates led to product. Calculations on the excited states of these structures revealed that both of these structures had similar excited states energies to that of the iridium photocatalyst modeled with deviations of 0.07 eV (~ 1.6 kcal/mol) and 0.17 eV (~ 4.0 kcal/mol) of cinnamyl bromide and iodide with respect to the fac-$Ir(ppy)_3$ photocatalyst (See Appendix).

As stated previously in Chapter 6 , the hydrazone coupling reaction typically does not proceed with alkyl Bpins[392] but works in the presence of alkyl boronic acid. Preliminary calculations suggested that this is due to steric interactions at the Bpin ligand (see Appendix) as well as the hybridization of the alkyl group. Additional calculations should be performed to tailor a chiral ligand that affords enantioselective coupling.

The pathways to determine the alkyl selectivity from the sulfurane intermediate, calculated in chapter 7, are quite flat, making it hard to determine if the reaction coordinate diagram mapped is responsible for the observed selectivity. The motion of the molecule along the potential energy surface likely plays a crucial role in the observed selectivity. Additional dynamics calculations should be performed to address these issues.

Appendix 1: Supporting Information Chapter 2

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3)/def2-SVP level of the theory in implicit solvent (DMSO) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, except were indicated otherwise. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). 20 excitations were calculated on DFT optimized structures using TD-DFT single points with the same method, basis set, and solvation model used for optimizations to generate UV-Vis spectra. TD-DFT optimization were performed with the same method stated previously but using 3 excitations above the excitation of interest. Further, to assess the influence of dynamic correlation, open-shell domain-based local pair natural orbital Coupled-Cluster calculations using single and double excitations with perturbative triple excitations (DLPNO-CCSD(T)), with def2-TZVPP basis, were performed using ORCA software which were corrected using solvation energy corrections obtained from B3LYP-D3/def2-TZVPP-CPCM(DMSO). Where indicated, single point energy calculations in implicit solvent using and B3LYP-D3/def2-TZVPP-CPCM(DMSO) were also performed and presented with DLPNO energies for reference. All 3-D structures were generated using CYLview and all electron density difference plots were generated using GaussView 5. Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

Full Reference of Gaussian 16 software:

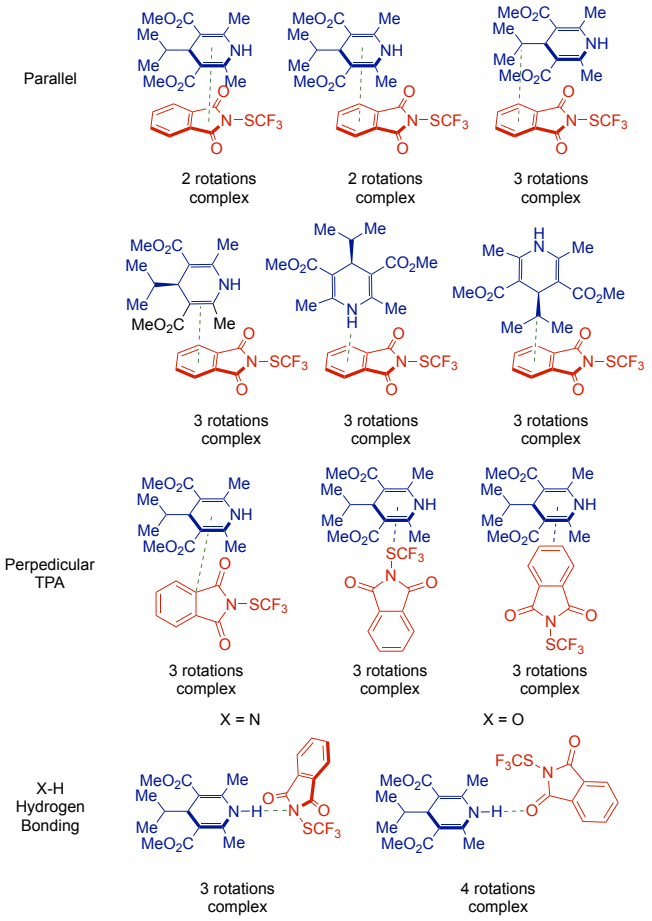
Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

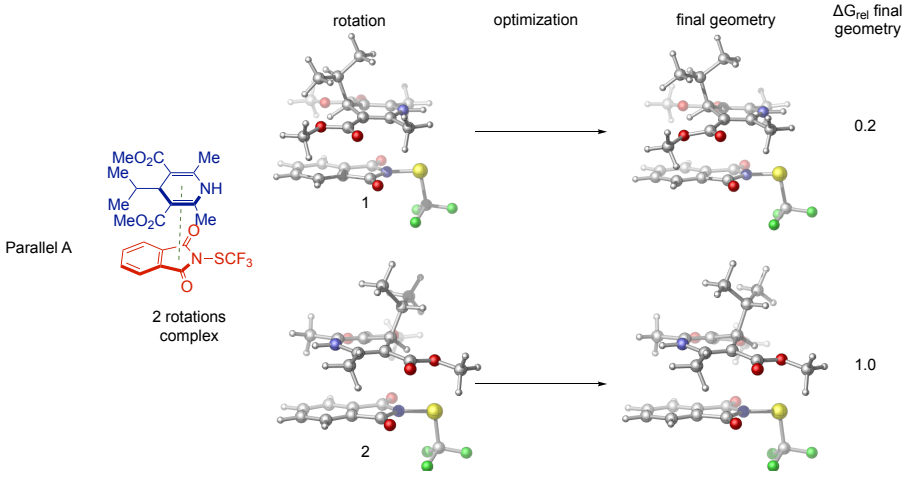
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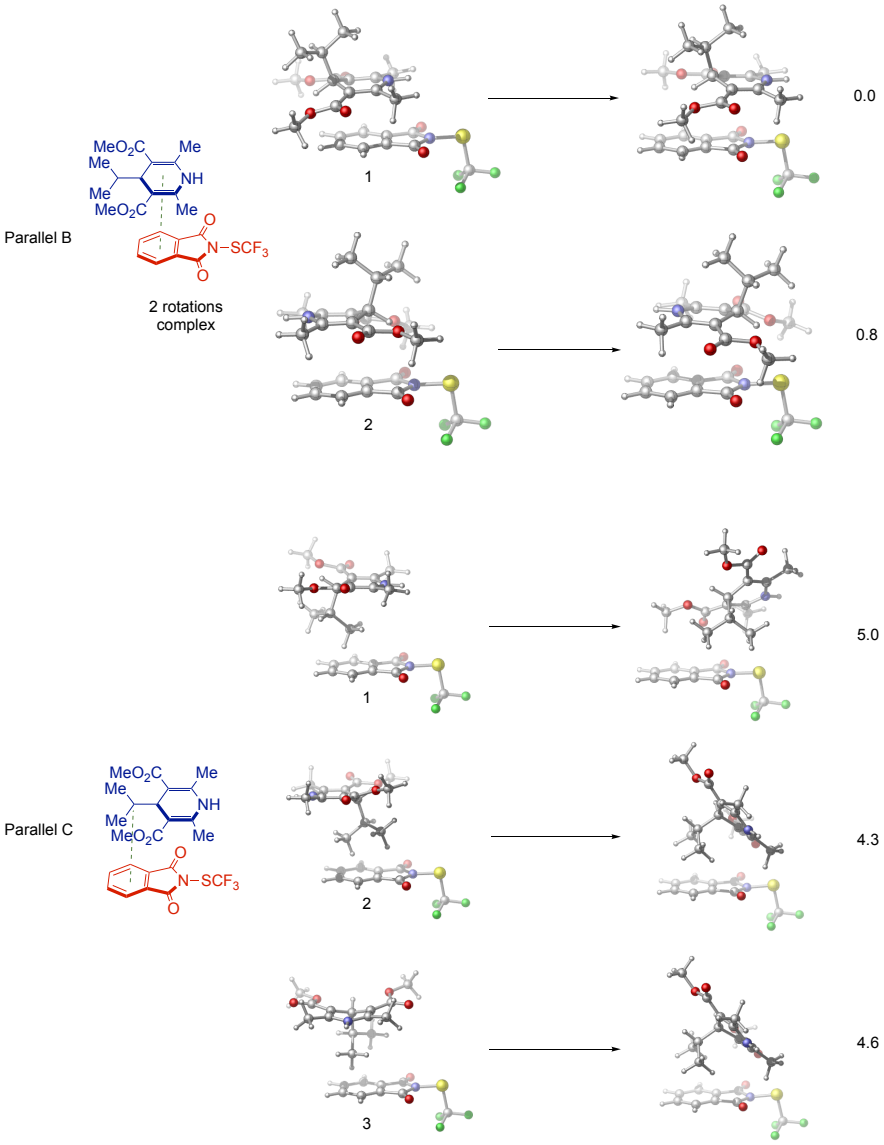
Dennington, R., Keith, T. and Millam, J. (2009) Gauss View, Version 5. Semichem Inc., Shawnee Mission.

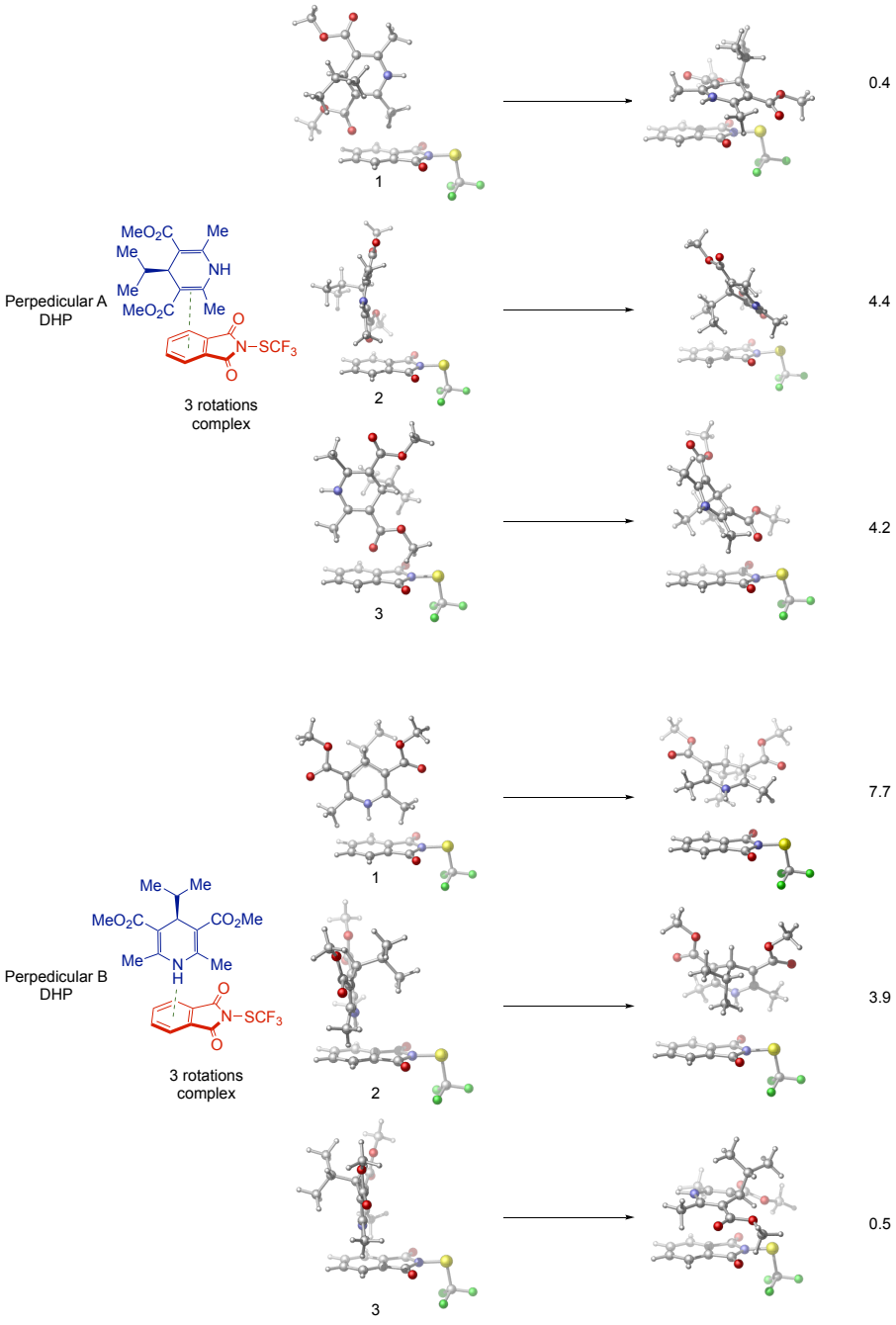
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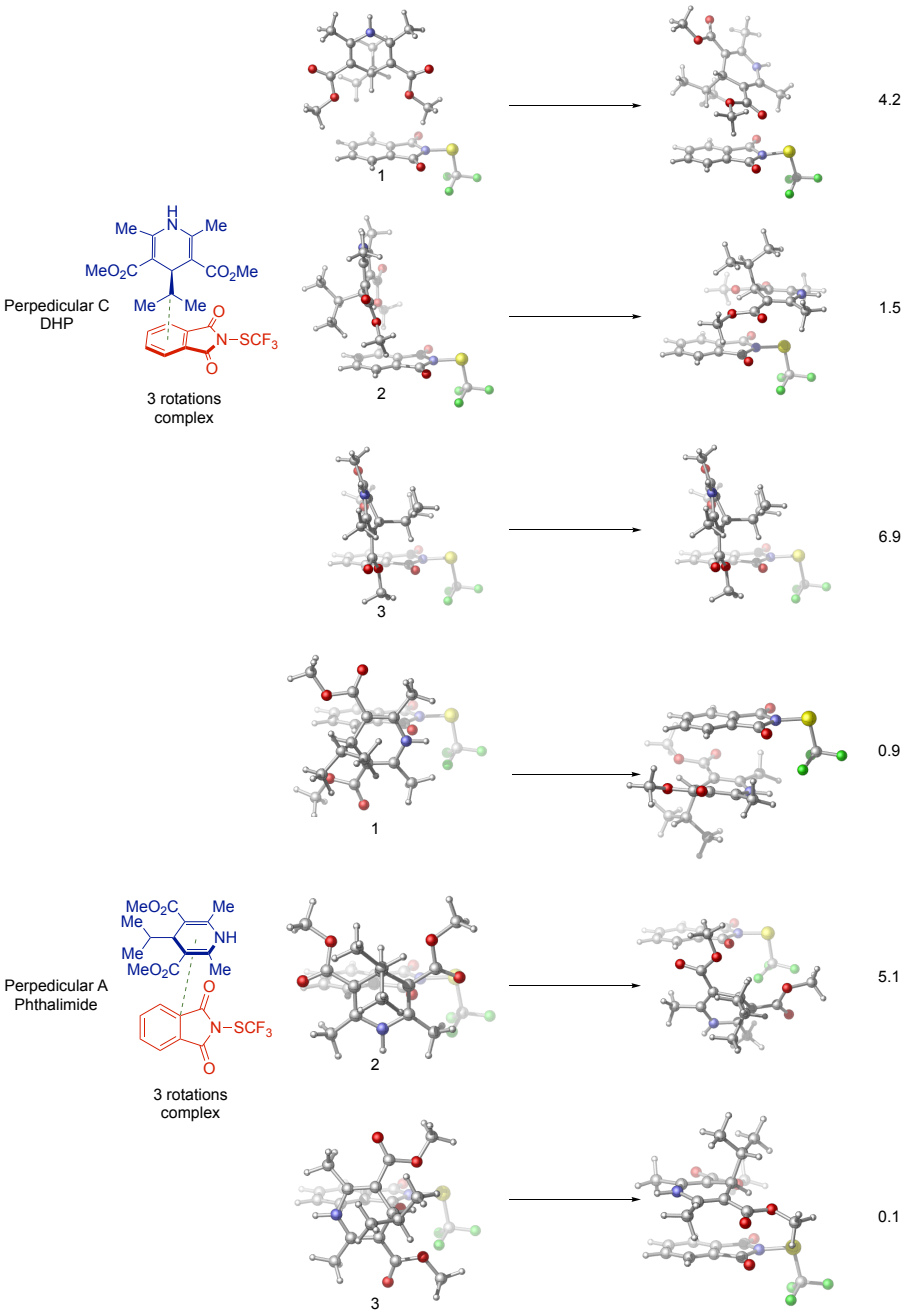
Legault, C. Y.; *CYLview,* rev 1.0b; Université de Sherbrooke, 2009 http://www.cylview.org.

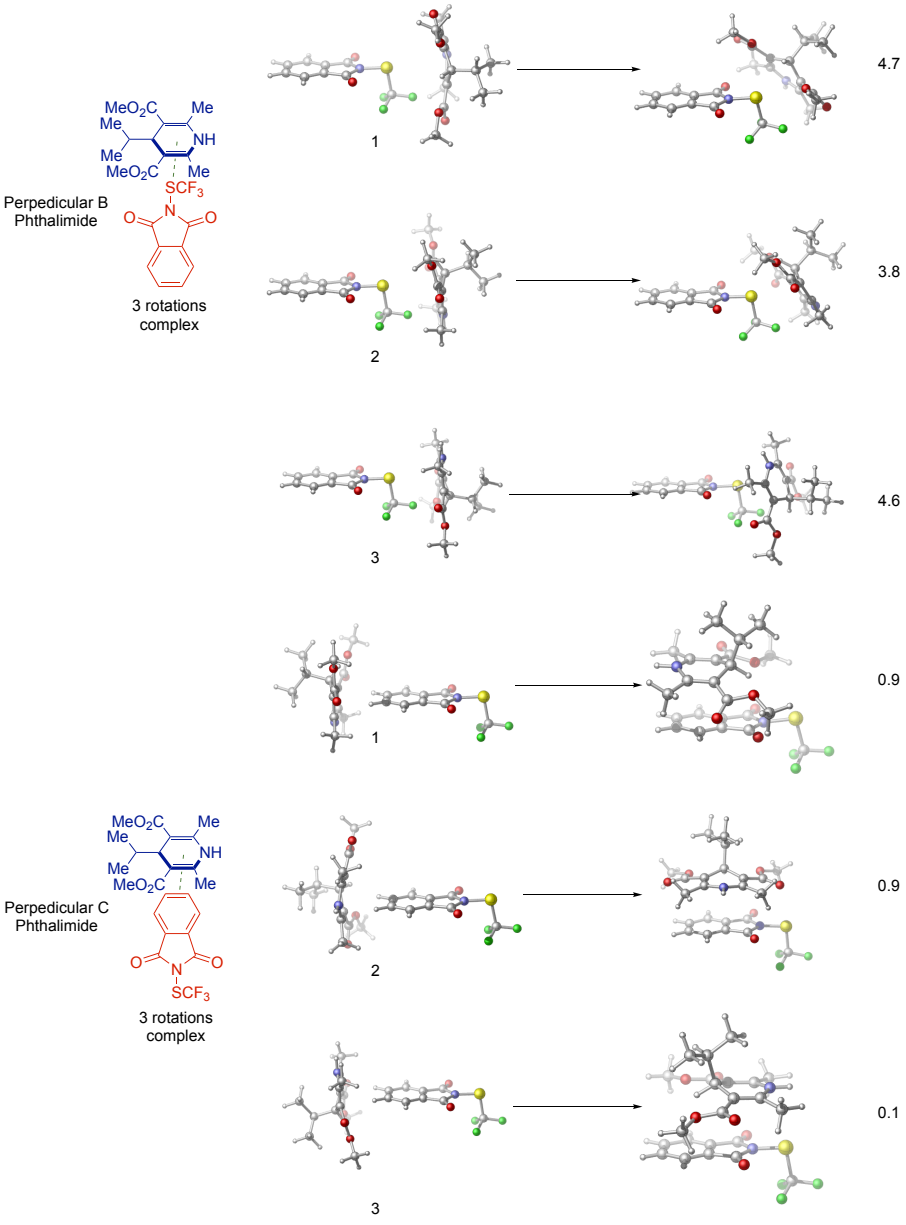





Parallel B
2 rotations complex
1
2
0.0
0.8
Parallel C
1
2
3
5.0
4.3
4.6


Perpedicular A DHP
3 rotations complex
1
2
3
0.4
4.4
4.2
Perpedicular B DHP
3 rotations complex
1
2
3
7.7
3.9
0.5


Perpedicular C
DHP
3 rotations
complex
Perpedicular A
Phthalimide
3 rotations
complex
1
2
3
1
2
3
4.2
1.5
6.9
0.9
5.1
0.1


Perpedicular B Phthalimide
3 rotations complex
1
2
3
4.7
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0.9
Perpedicular C Phthalimide
3 rotations complex
1
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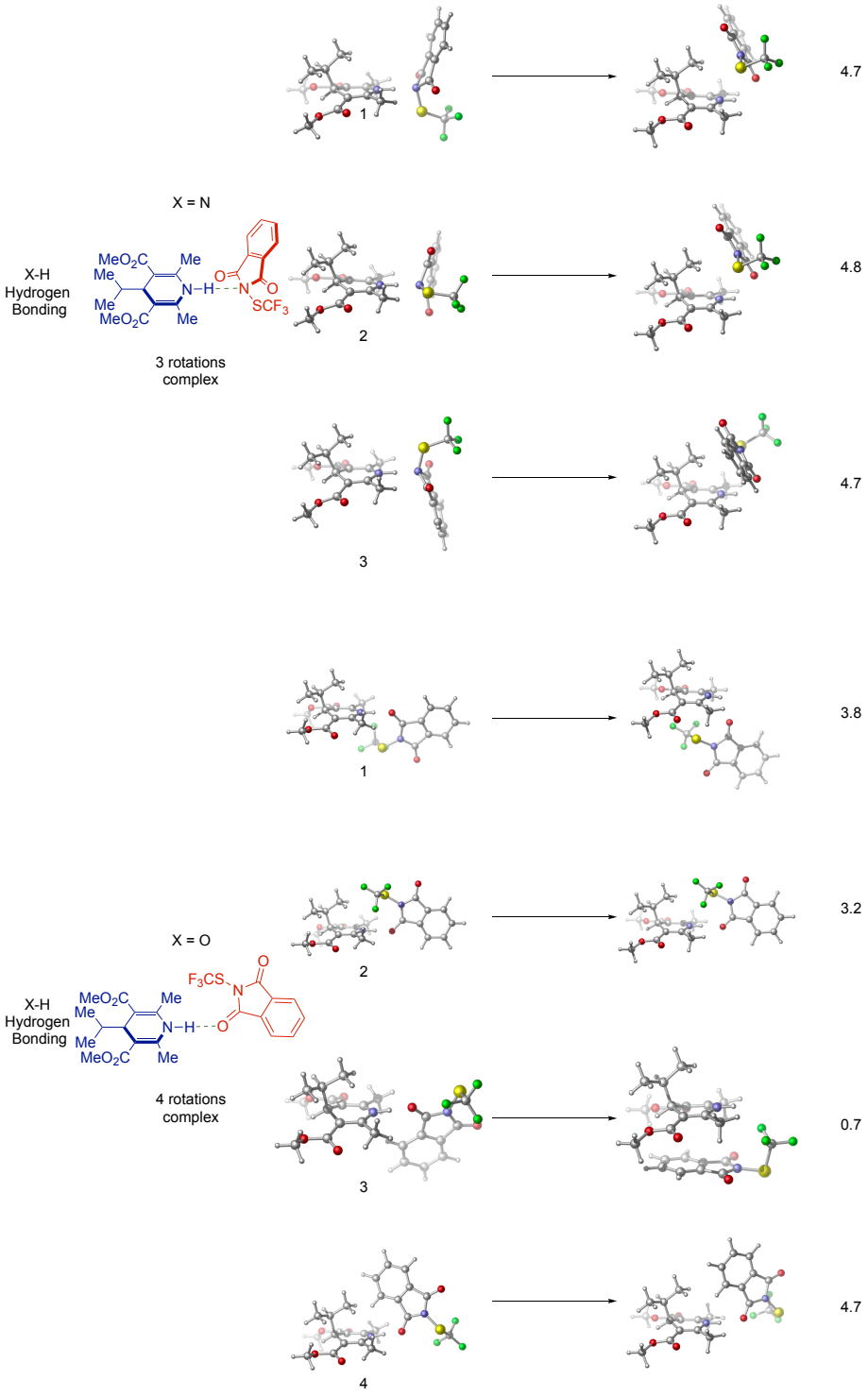


Figure A1.1: Various starting points (labeled rotation) and final geometries obtained with UB3LYP/def2-SVP-CPCM(DMSO) of EDA complex **C**[1]. Free energies made relative to lowest

energy geometry obtained of the complex from the UB3LYP/def2-SVP-CPCM(DMSO) optimizations and frequency calculations.

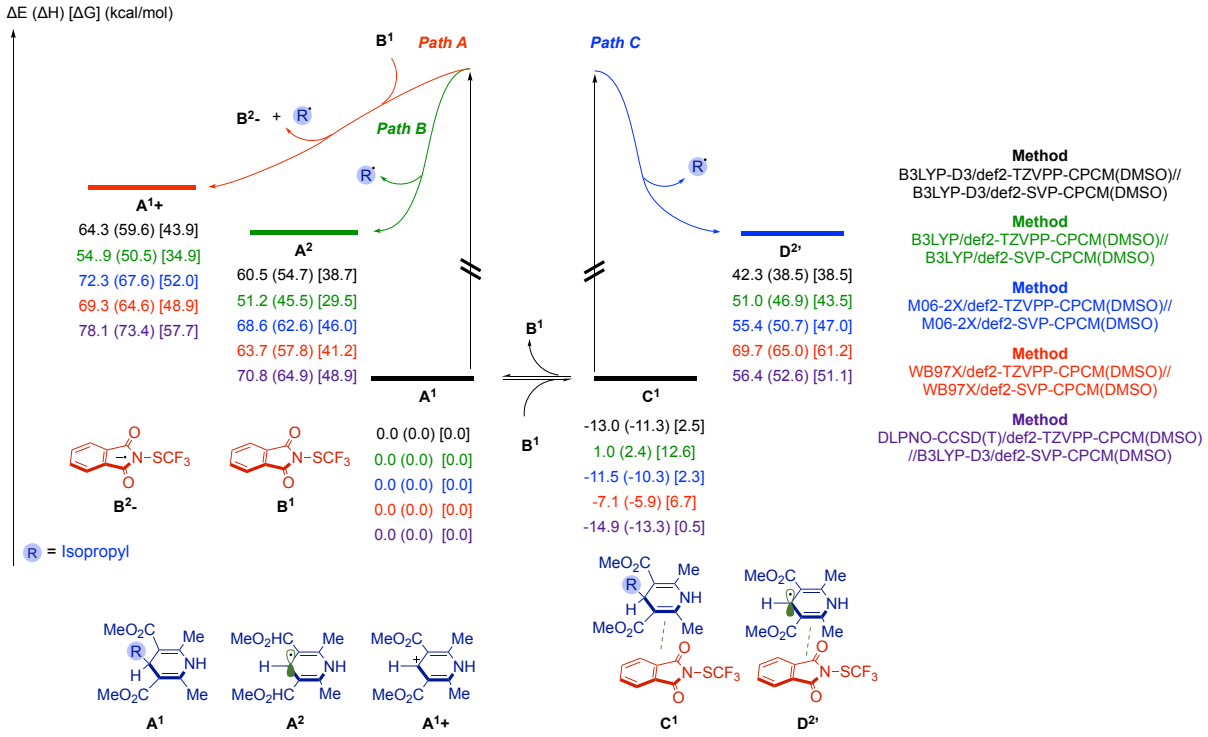


Figure A1.2: Relative total energy, enthalpy and free energy of intermediates, accessible via photochemical excitation via alkyl-DHP $\mathbf{A^1}$ or alkyl-EDA complex $\mathbf{C^1}$, optimized with various DFT functionals with varying amounts and treatments of HF exchange. In addition, dispersion corrected B3LYP (B3LYP-D3) was also used as a reference. Energies were refined by performing SP calculations with the same method, with the exception of the DLPNO-CCSD(T) singlet point calculation, using def2-TZVPP basis set.

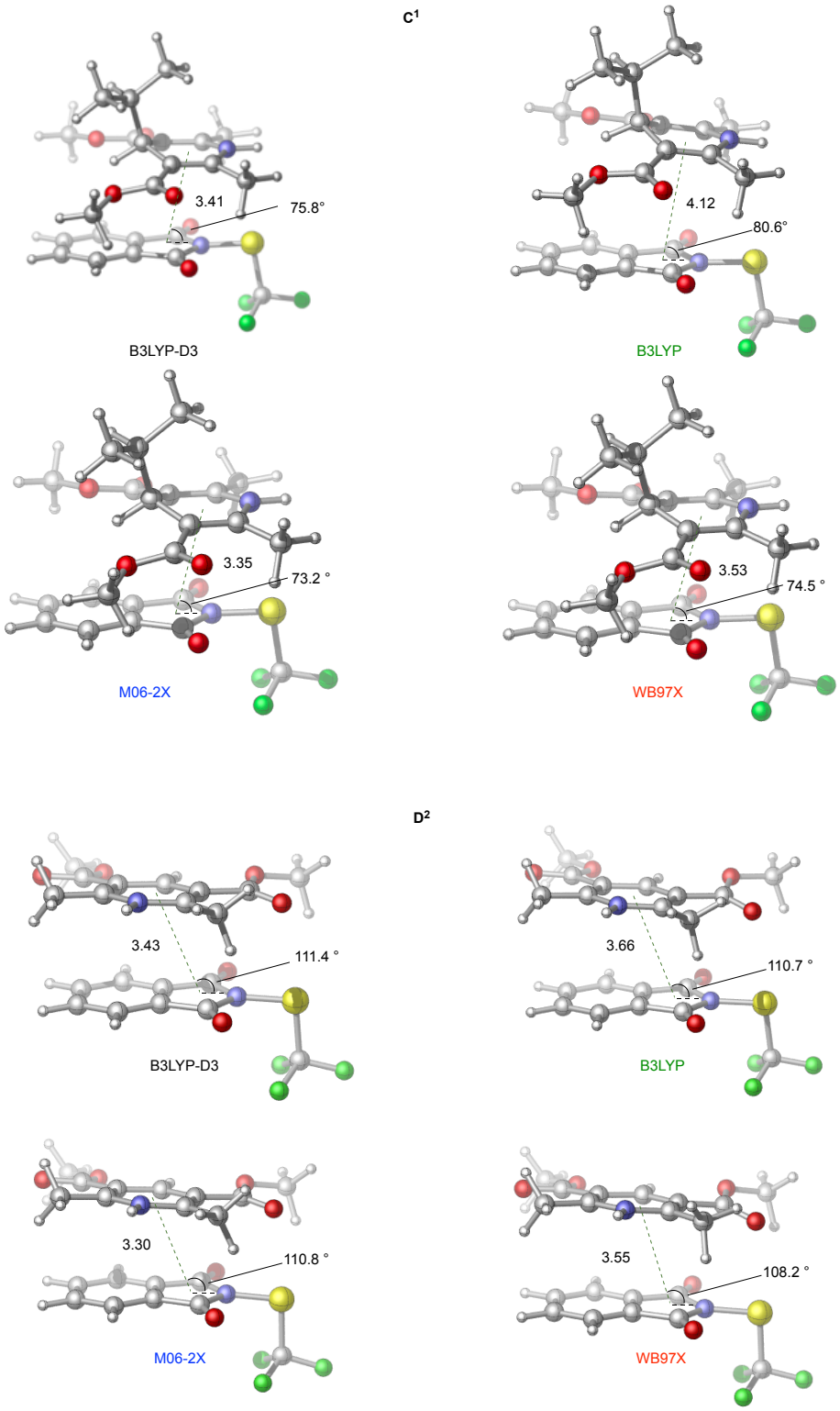


Figure A1.3: Geometries of EDA complex **C**[1] and **D**[2] obtained with the DFT functionals used in Figure A1.2. Distance between the center of the 6-membered DHP ring and the center of the 5-

membered ring phthalimide (in green) reported in Ångstroms. Angle between the center of the 6- and 5-membered rings of the DHP and phthalimide as well as the nitrogen on the phthalimide reported in degrees.

We decided to investigate the ability of DFT, particularly B3LYP-D3, to predict both the energetics (**Figure A1.2**) and geometries (**Figure A1.3**) of the EDA complex **C1**, as well as other key intermediates proposed, as DFT has been found to fail to accurately describe these complexes without appropriate treatment of dispersion.[28] Energetically, B3LYP-D3 was found to give a much lower energy for EDA complexation than the non-dispersion corrected B3LYP. M06-2X, which has a larger amount of HF exchange than B3LYP, was found to give energies of EDA complexation closer to that of B3LYP-D3. WB97X gives an energy in between that predicted by M06-2X and B3LYP-D3 and B3LYP. The energetic differences of the complex **C1** are reflected in the distances between the two molecules in the complex. The methods that give a lower energy for EDA complexation are found to result in a tighter complex (distances of 3.30 and 3.41 Ångstrosm between the two molecules) while methods that give higher energies have a larger distance between the two molecules (3.54 and 4.12 Angstroms). As EDA complexation is observed experimentally (via UV-Vis), these results suggests that B3LYP-D3 accurately describes the scenario where EDA complex **C1** is in equilibrium with the separated molecules of the complex **A1** and **B1**.

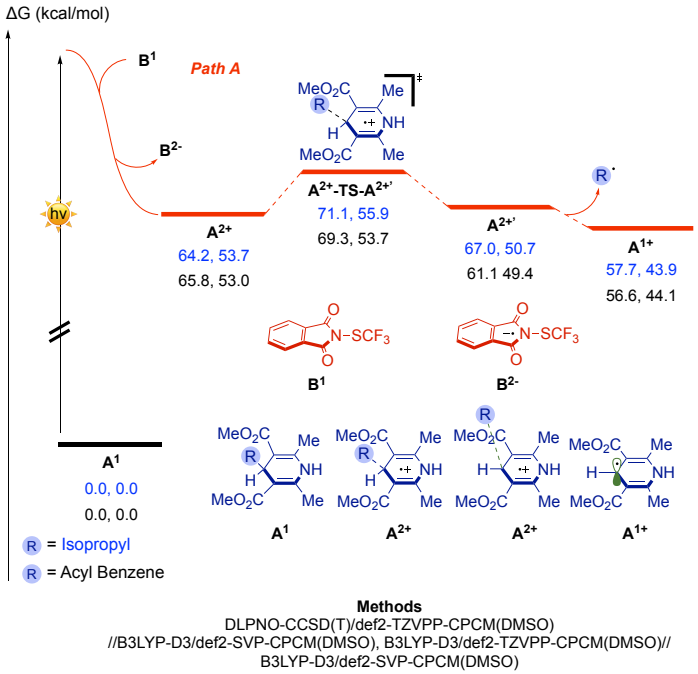


Figure A1.4: Potential energy surface of radical generation of both the isopropyl and acyl benzene radical from radical cation $\mathbf{A^2}$+ which could be formed from light mediated electron transfer between phthalimide $\mathbf{B^1}$ and DHP $\mathbf{A^1}$.

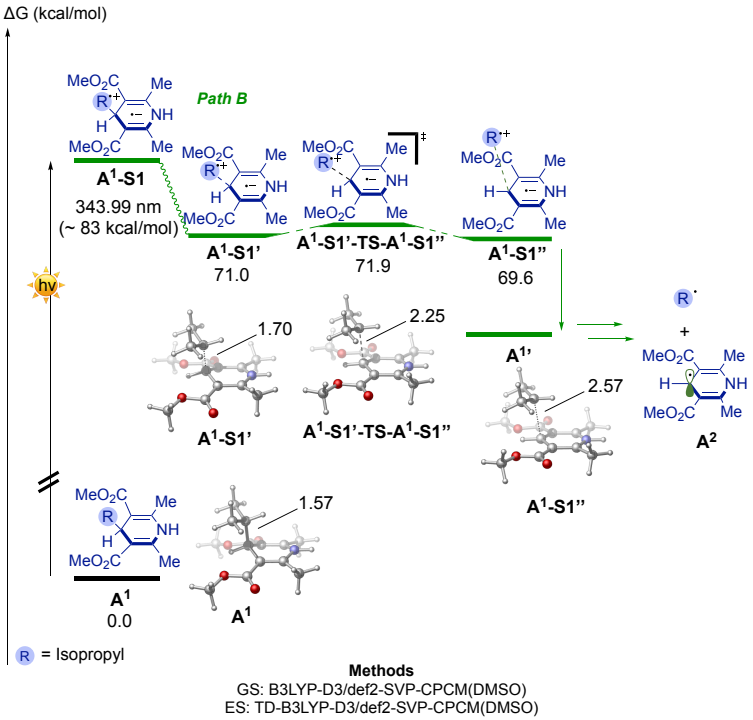


Figure A1.5: Excited State Potential energy surface of radical generation of the isopropyl radical from the lowest lying singlet excited state of alkyl-DHP **A[1]**. Labeled bond lengths in Ångstroms.

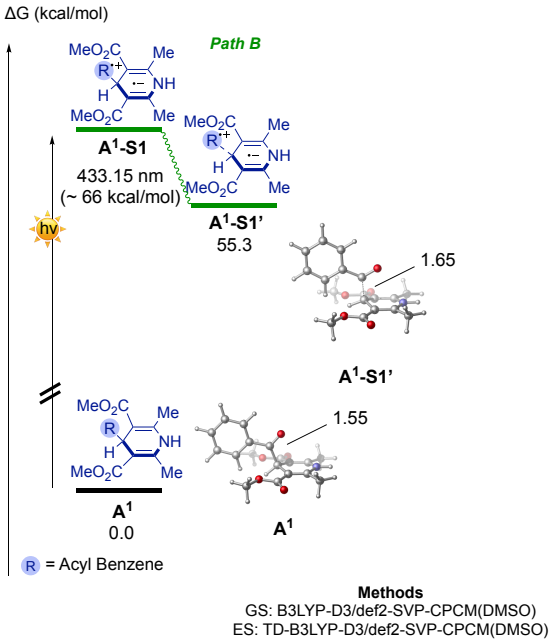


Figure A1.6: Excited State Potential energy surface of radical generation of the acyl benzene radical from the lowest lying singlet excited state of acyl-DHP **A[1]**. Labeled bond lengths in Ångstroms.

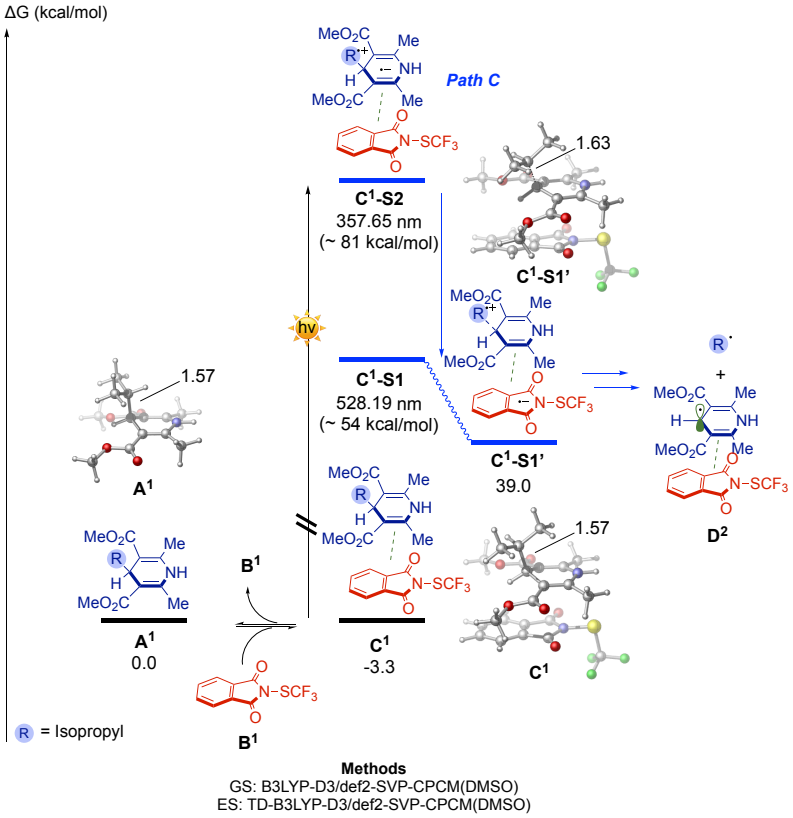


Figure A1.7: Excited State Potential energy surface of radical generation of the isopropyl radical from the lowest lying singlet excited states of alkyl-EDA complex $\mathbf{C^1}$. Labeled bond lengths in Ångstroms.

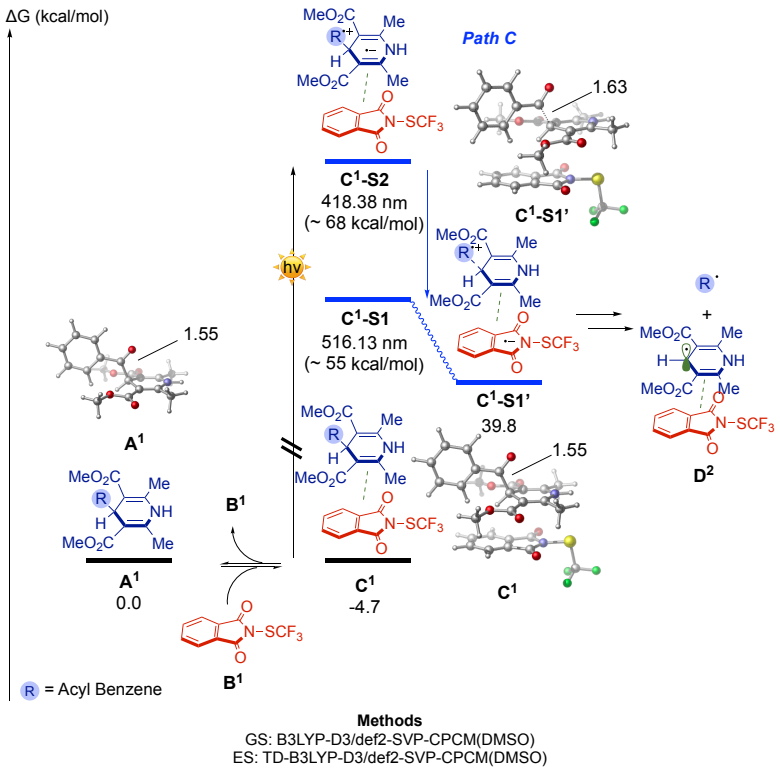


Figure A1.8: Excited State Potential energy surface of radical generation of the acyl benzene radical from the lowest lying singlet excited states of acyl-EDA complex $\mathbf{C^1}$. Labeled bond lengths in Ångstroms.

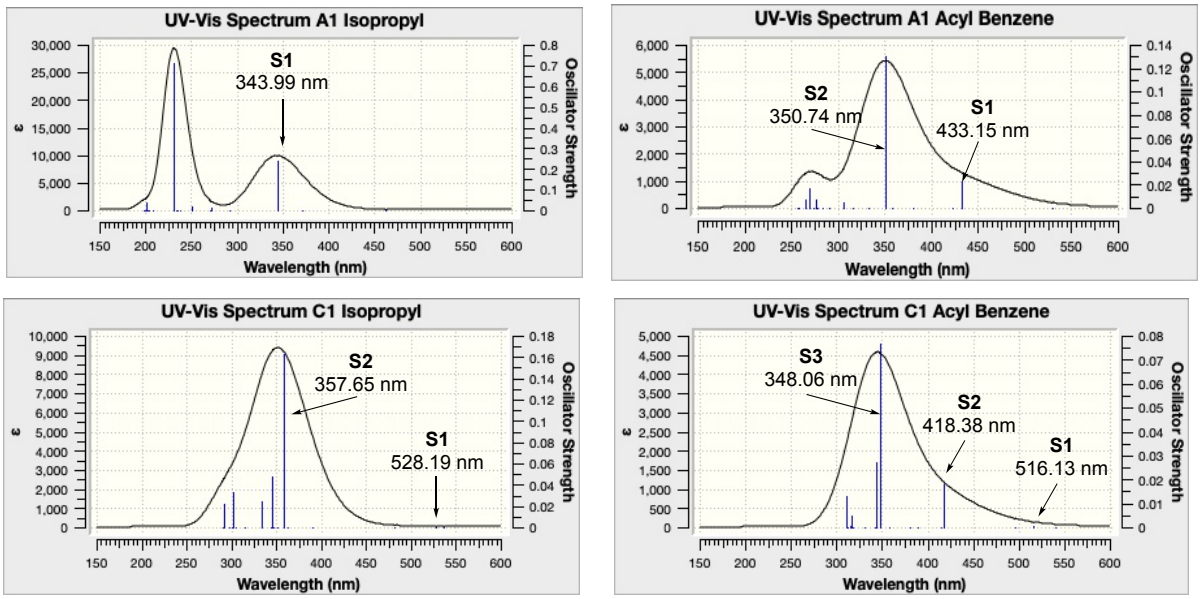


Figure A1.9: TD-DFT Computed UV-Vis of isopropyl and acyl benzene DHP **A[1]** and isopropyl and acyl benzene EDA complex **C[1]** using UB3LYP-D3/def2-SVP-CPCM(DMSO). 20 Excitations were calculated to generate the UV-Vis spectra.

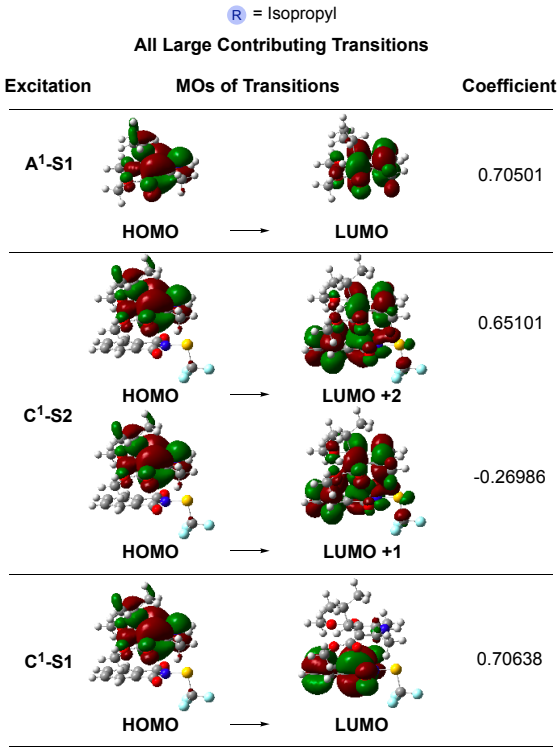


Figure A1.10: Canonical molecular orbitals of the electronic transitions involved in the indicated excitations of both isopropyl DHP **A[1]** and EDA complex **C[1]** calculated using TD-DFT calculations at UB3LYP-D3/def2-SVP-CPCM(DMSO). The coefficient of the transitions is included next to each transition. Isovalue of MOs set to 0.02 e^-/au^3.

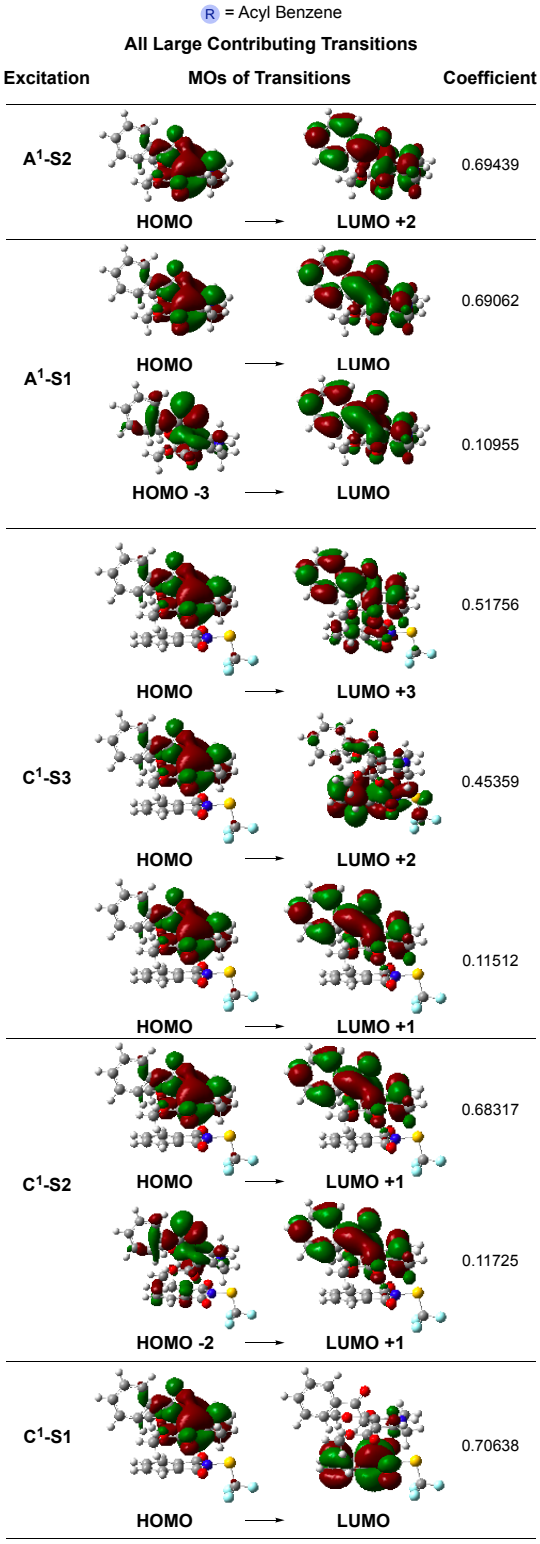


Figure A1.11: Canonical molecular orbitals of the electronic transitions involved in the indicated excitations of both acyl benzene DHP $\mathbf{A^1}$ and EDA complex $\mathbf{C^1}$ calculated using TD-DFT

calculations at UB3LYP-D3/def2-SVP-CPCM(DMSO). The coefficient of the transitions are included next to each transition. Isovalue of MOs set to 0.02 e^-/au^3.

In addition to the isopropyl system presented in the Thesis, the excited states of a DHP substituted with Acyl Benzene was also probed as a model for the acyl systems. It was found that EDA complexation is not required for these systems, as the uncompleted acyl-DHP **A1** has an electronic transition at 433.15 (**Figure A1.6**) which allows the tail to go out to 550 nm (**Figure A1.9**). Swapping the isopropyl for acyl benzene causes this shift in absorbance, which as be seen by comparing the canonical orbitals of the electronic transitions of the alkyl-DHP to that of the acyl-DHP (**Figures A1.10 and A1.11**). TD-DFT calculations of the EDA complex acyl-**C1** also show that is not a significant difference between the UV-Vis of the complex versus that of the acyl-DHP **A1**, which is observed experimentally. In addition, DFT calculations suggest that EDA complexation is even lower in energy for the acyl systems than for the alkyl systems (**Figure A1.13** for refined energetics of both the isopropyl and acyl benzene complexes).

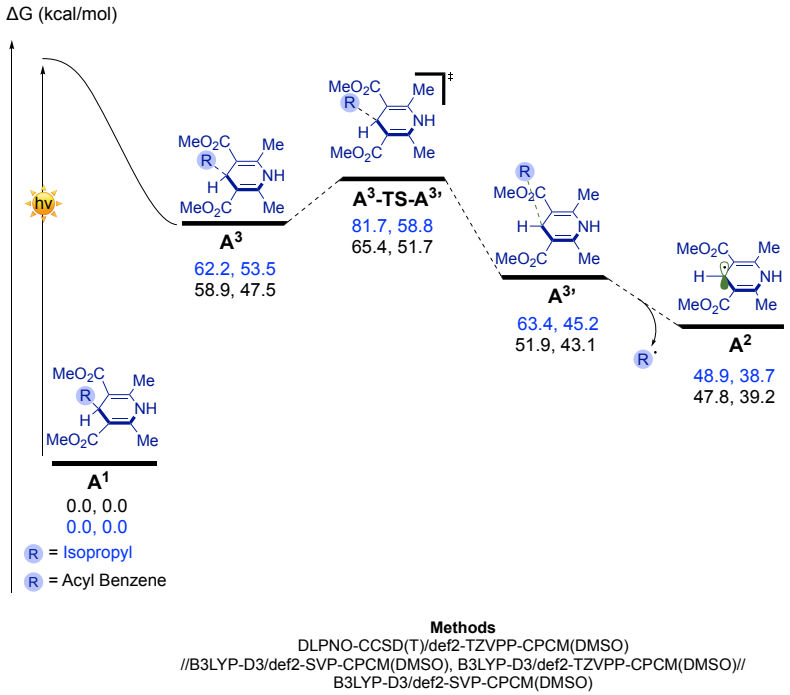


Figure A1.12: Triplet potential energy surface leading to both isopropyl and acyl benzene radical which could be accessed via excitation of DHP **A**[1].

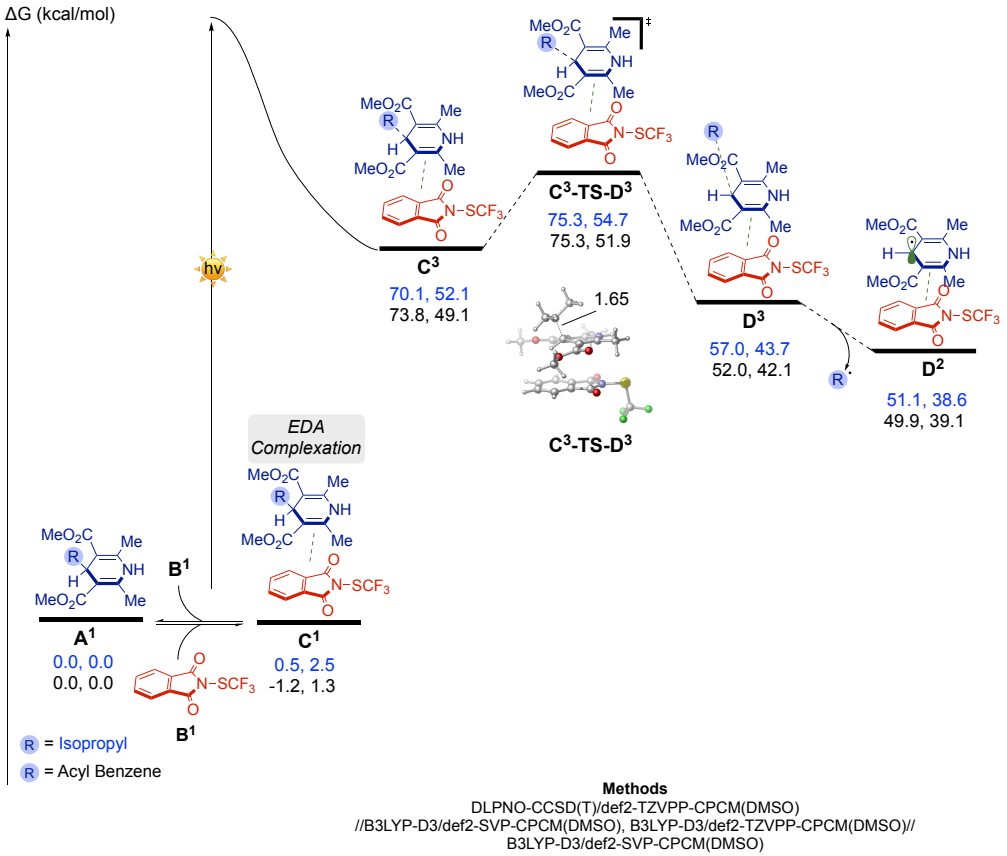


Figure A1.13: Triplet potential energy surface leading to both isopropyl and acyl benzene radical which could be accessed via excitation of EDA complex **C**[1]. Labeled bond lengths in Ångstroms.

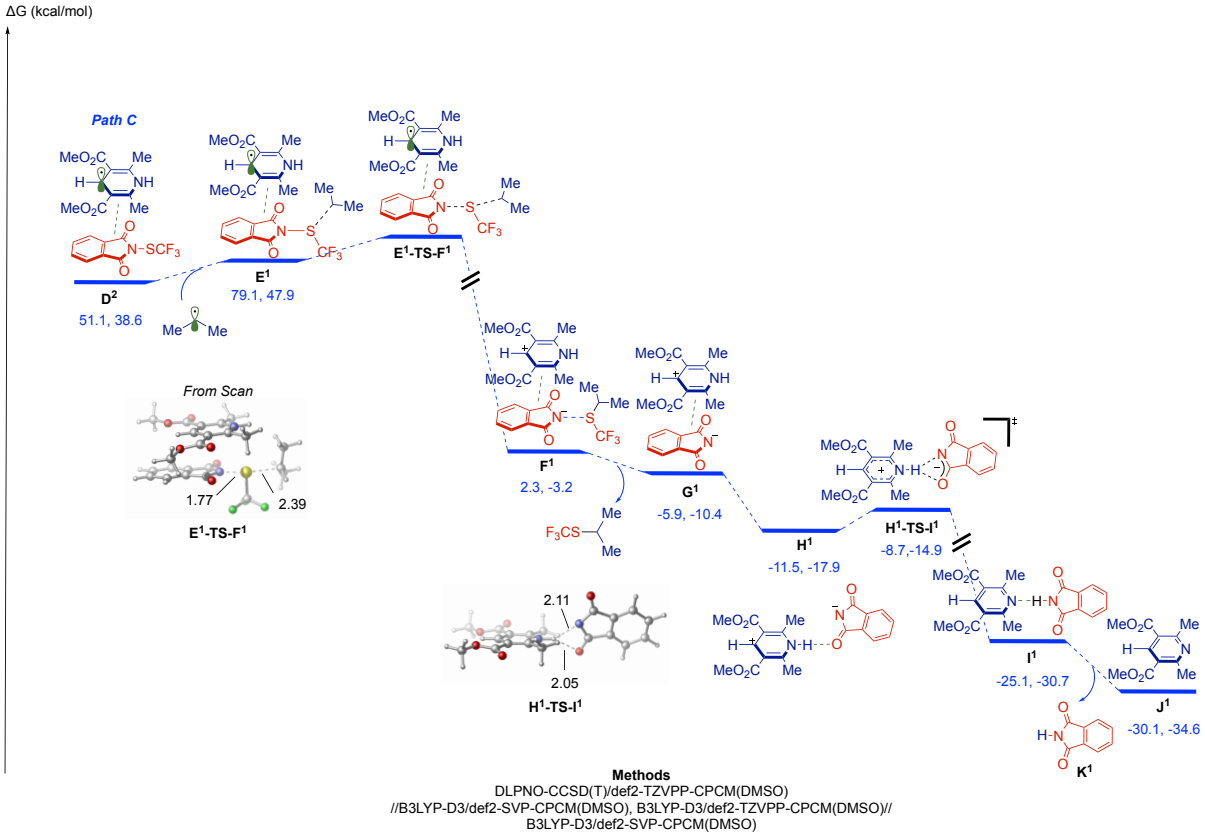


Figure A1.14: Full potential energy surface (**E¹** omitted in Thesis) of S-C coupling of isopropyl radical and SCF_3 moiety, via S_H2 transition state like geometry **E¹-TS-F¹**, from complex **D²** and subsequent deprotonation to observed byproducts **K¹** and **J¹**. Labeled bond lengths in Ångstroms.

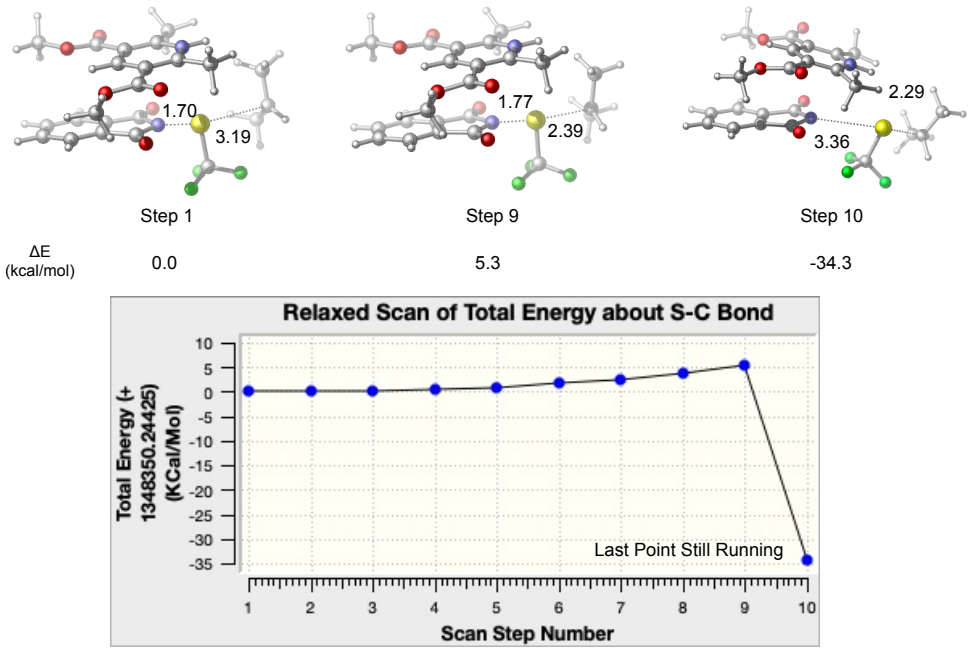


Figure A1.15: Scan of S-C bond starting from complex **E**[1]. The y-axis was made relative to the first point of the scan.

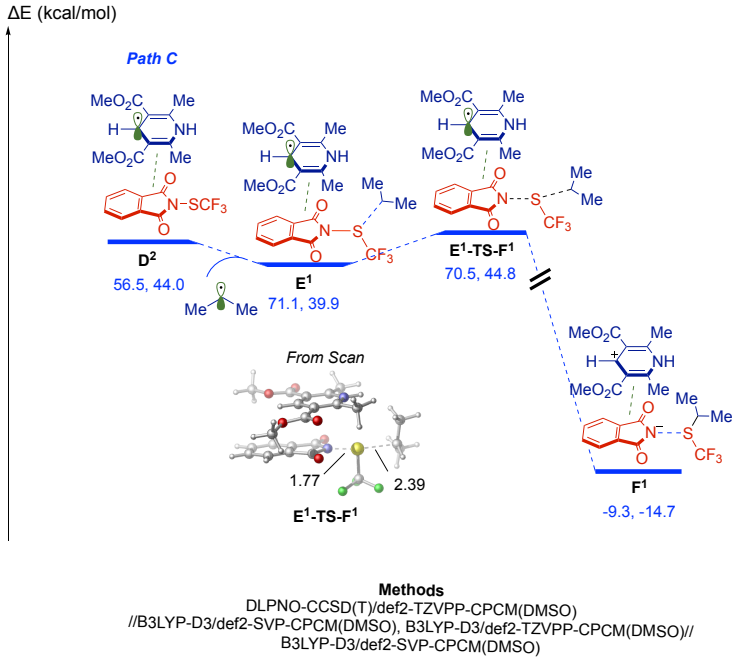
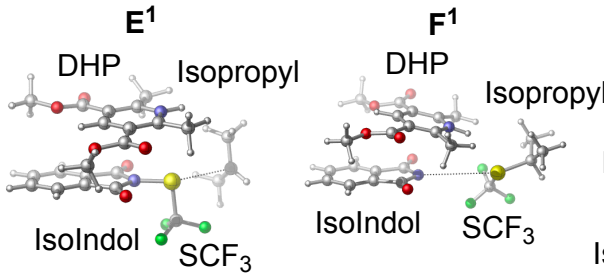


Figure A1.16: Potential energy surface, in total energy, of S-C coupling of isopropyl radical and SCF_3 moiety, via S_H2 transition state like geometry **E**[1]**-TS-F**[1], from complex **D**[2] to complex **F**[1].

Labeled bond lengths in Ångstroms.



	E^1		F^1	
Frag	Charge	Spin	Charge	Spin
DHP	0.40	0.55	0.86	0.00
IsoIndol	-0.41	0.44	-0.90	0.00
SCF_3	0.00	-0.02	-0.17	0.00
Isopropyl	0.01	-0.97	0.20	0.00

Figure A1.17: Mulliken charges and spin densities of fragments indicated of complexes $\mathbf{E^1}$ and $\mathbf{F^1}$. DHP indicates the whole dihydropyridine moiety, including the ester functionalities while IsoIndol indicates whole isondoline-1,3-dione.

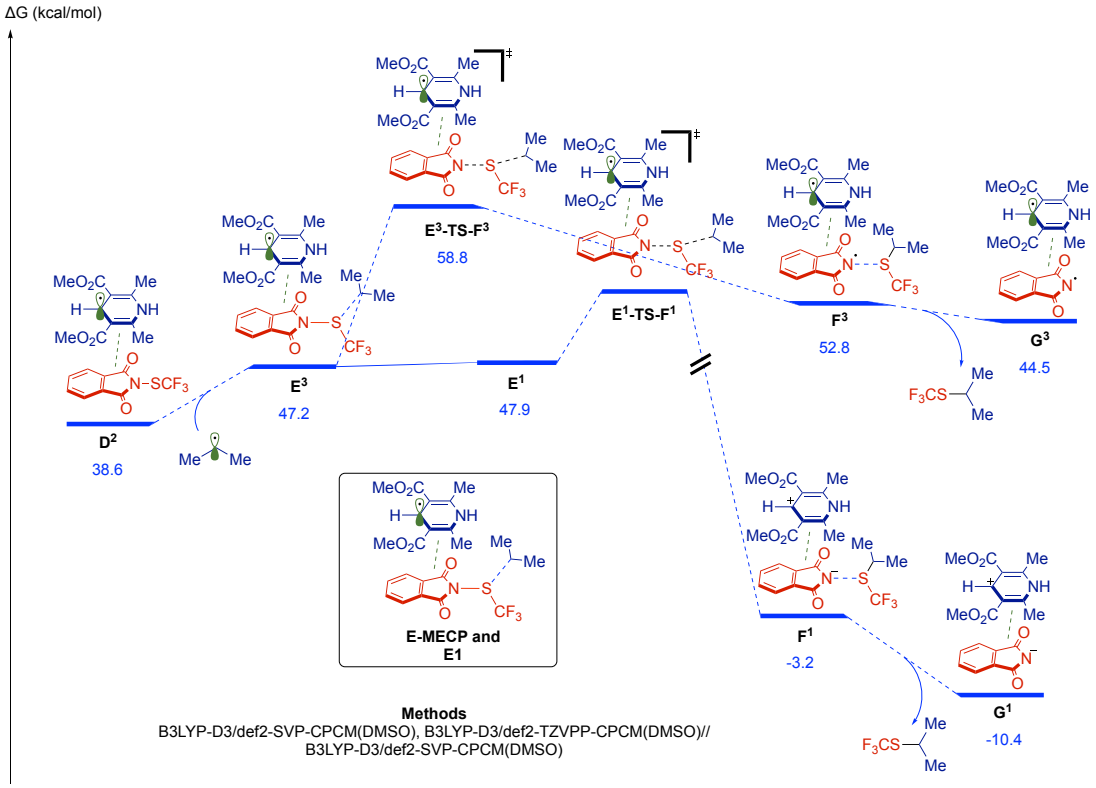


Figure A1.18: Triplet potential energy surface leading to S-C coupling from complex $\mathbf{D^2}$.

After multiple attempts to isolate **E1-TS-F1** (**Figure A1.13**), we decided to perform a relaxed scan about the C-S bond using **E1** as a starting point (**Figure A1.14**). The highest point of the scan

(**Figure A1.15**; **Step 9**) was used as a starting point of a transition state optimization but still could not be isolated. We then decided to take the Step 9 (Labeled **E1-TS-F1** in **Figure A1.16**) and run single point calculations using B3LYP-D3 and DLPNO-CCSD(T) and compare the total energy obtained from these two methods to that of isolated intermediates **D2**, **E1** and **F1** (**Figure A1.16**). Using B3LYP-D3, the relative total energy (ΔE) converted into kcal/mol of **E1-TS-F1** was found to be only 0.8 kcal/mol higher in energy than intermediate **D2** while being only ~5.0 kcal/mol higher in energy than intermediate **E1** with intermediate **F1** being extremely exergonic. The energies predicted with DLPNO-CCSD(T) suggest that going from **D2** to **E1** is uphill in energy by 14.6 kcal/mol with **E1-TS-F1** being slightly lower in energy than E1. Upon inspection of the DLPNO-CCSD(T) calculations, the T1 diagnostic of **E1** was found to be greater than 0.02, suggesting that the energies of **E1** cannot be trusted from DLPNO-CCSD(T) and suggesting that multireference calculations may be needed in order to obtain accurate energetics for **E1** as well as to isolate the actual transition state **E1-TS-F1**. In the Thesis, we report the results obtained from the B3LYP-D3 single points reported in **Figure A1.16**. As a side note, **E1** was found to be isoenergetic with **E3** when using B3LYP-D3 (**Figure A1.18; E1 and E3**)

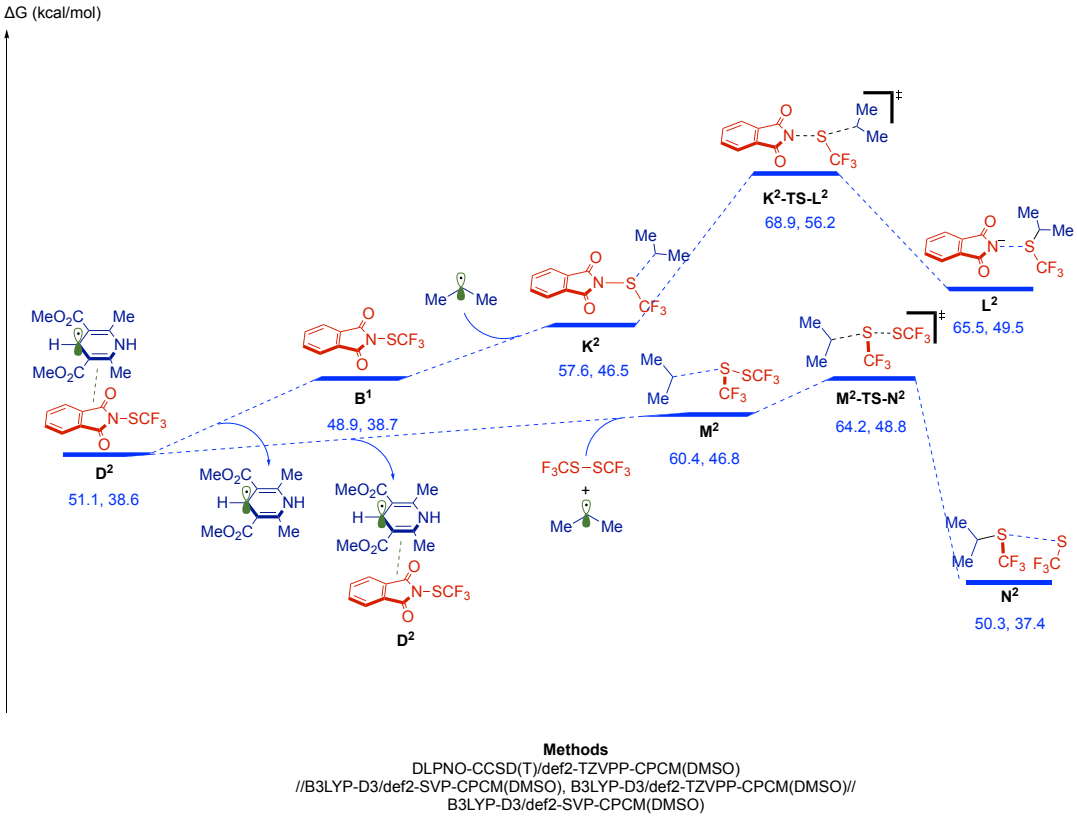


Figure A1.19: All alternate pathways computed leading to S-C coupling from alkyl radical, including S-C coupling from SCF_3 dimer.

In addition to Path C proposed in the Thesis, we also probed a series of alternate pathways leading to the SCF_3-Isoporopyl product (**Figure A1.17** and **A1.18**). The triplet potential energy surface to product was found to have a barrier of 20.2 kcal/mol (**D2** to **F3; Figure A1.18**), making it an unlikely pathway to product. In addition, dissociation of **D2**, **Figure A1.19**, and subsequent radical addition of the isopropyl radical to **B1** has a barrier of 17.6 kcal/mol with respect to **D2**. As the SCF_3 dimer was observed experimentally, we want to also consider the possibility of the dimer acting as an intermediate in the reaction. An S_H2 radical addition of the isopropyl radical to the SCF_3 dimer (**M2-TS-N2; Figure A1.19**) was found have a barrier of only ~10 kcal/mol with respect to **D2** and is overall exergonic with respect to **D2**, making this a viable pathway for product formation.

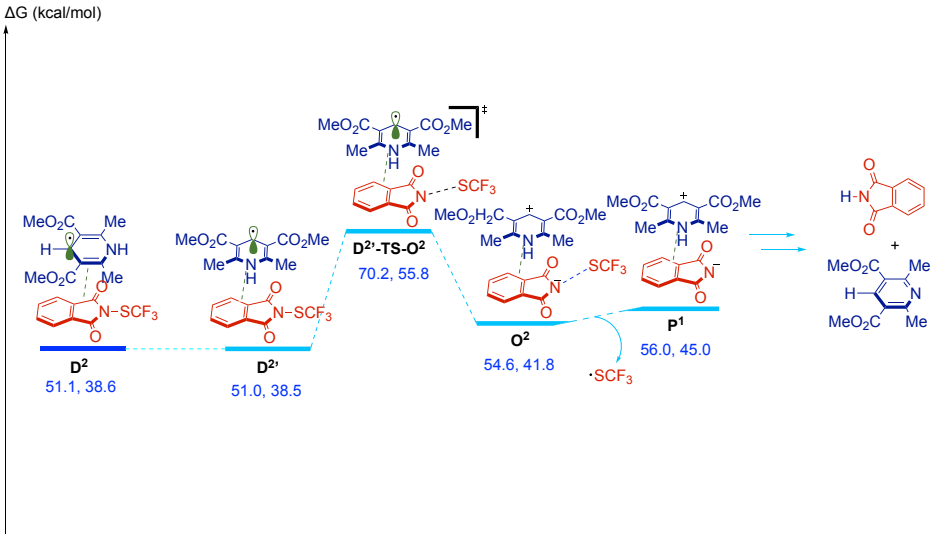
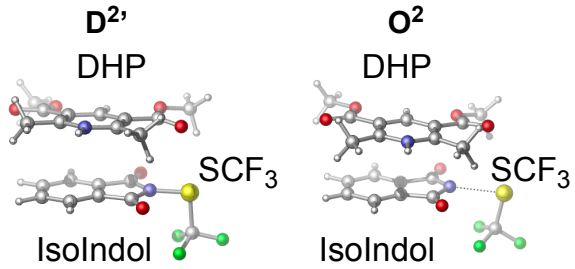


Figure A1.20: Potential energy surface for SCF_3 radical formation from complex $\mathbf{D^2}$.



	D²'		O²	
Frag	Charge	Spin	Charge	Spin
DHP	0.46	0.56	0.91	0.00
IsoIndol	-0.47	0.49	-0.58	0.28
SCF_3	-0.01	0.00	-0.33	0.72

Figure A1.21: Mulliken charges and spin densities of fragments indicated of complexes $\mathbf{D^{2'}}$ and $\mathbf{Q^2}$. DHP indicates the whole dihydropyridine moiety, including the ester functionalities while IsoIndol indicates whole isoindoline-1,3-dione.

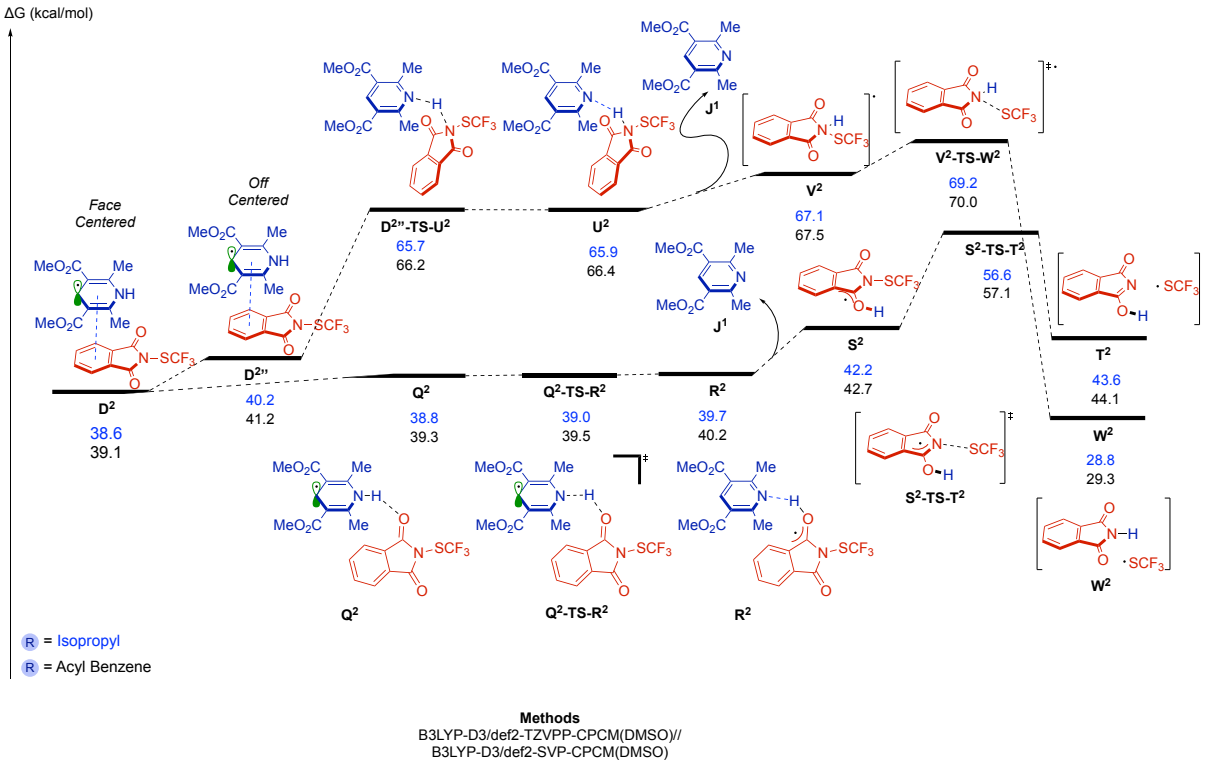


Figure A1.22: Potential energy surface of SCF_3 radical formation from HAT transfer.

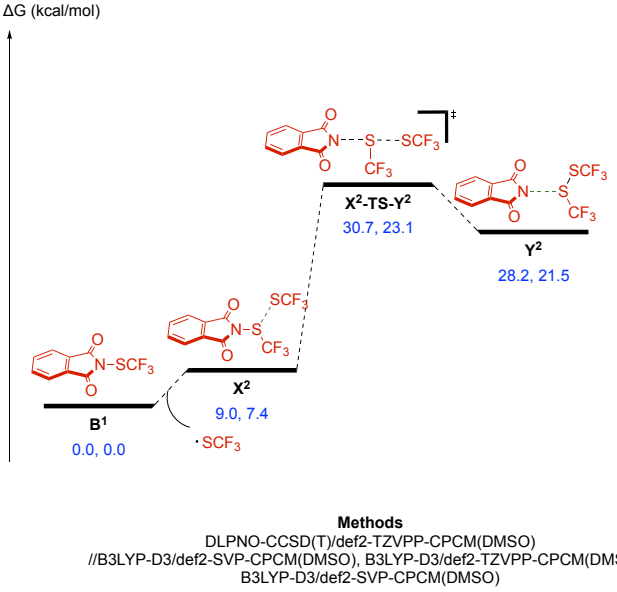


Figure A1.23: Potential energy surfaces leading to SCF_3 dimer and S-C product from phthalimide $\mathbf{B^1}$.

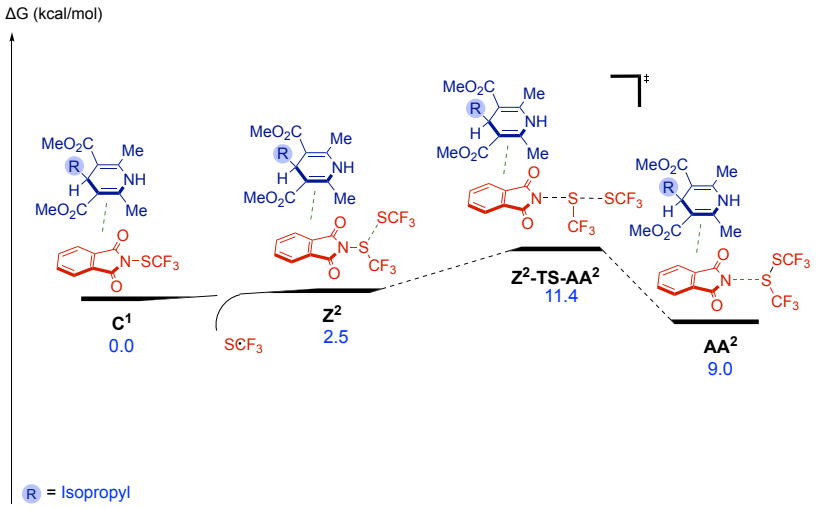


Figure A1.24: Potential energy surfaces leading to SCF_3 dimer from alkyl EDA complex **C[1]**.

Due to the experimental observation of the formation of the SCF_3 dimer, we wanted to see if we could determine a mechanistic explanation for its formation. We proposed a series of pathways in which an SCF_3 radical could be formed either directly from complex D2 (**Figure A1.20**) or from other hydrogen atom transfer pathways from D2 (**Figure A1.22**). The proposed SCF_3 dimer formation via direct S_H2 like reaction with either phthalimide **B1** (**Figure A1.23**) or EDA complex **C1** (**Figure A1.24**). All pathways proposed for SCF_3 radical formation had a barrier of ~20 kcal/mol with respect to **D2**, making them unlikely pathways to lead to dimer formation.

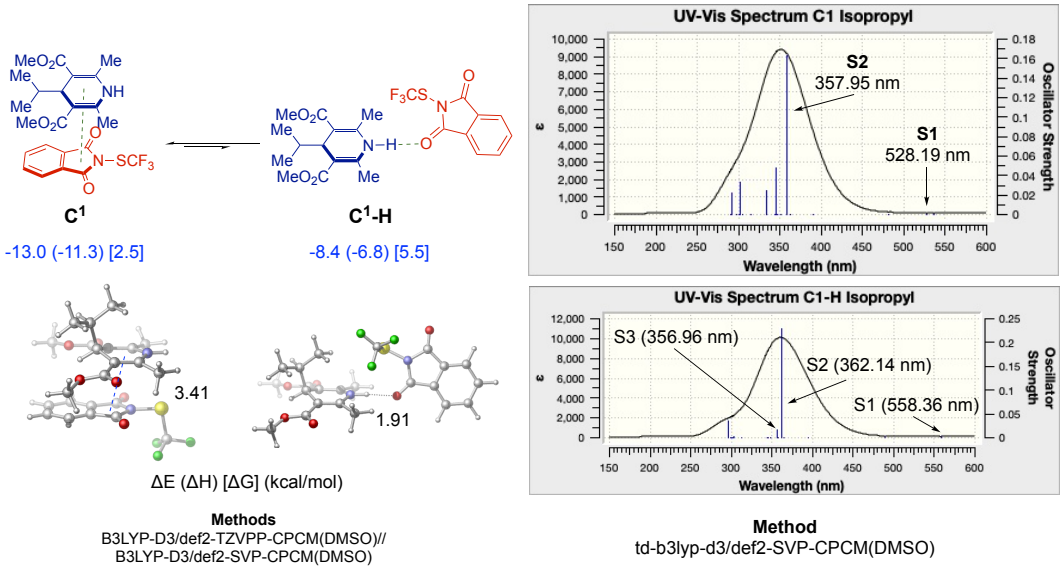


Figure A1.25: Ground state energies of Complexes **C^1** and **C^1-H** (left) and UV-Vis spectra (right) calculated with 20 excited states using TD-DFT. Distance between complexes labeled in Angstroms. Distance of **C^1** labeled between the center of the 6- and 5-membered rings of DHP and the phthalimide of while the distance of **C^1-H** labeled is of the hydrogen bond between the carbonyl oxygen and the hydrogen bound to the nitrogen.

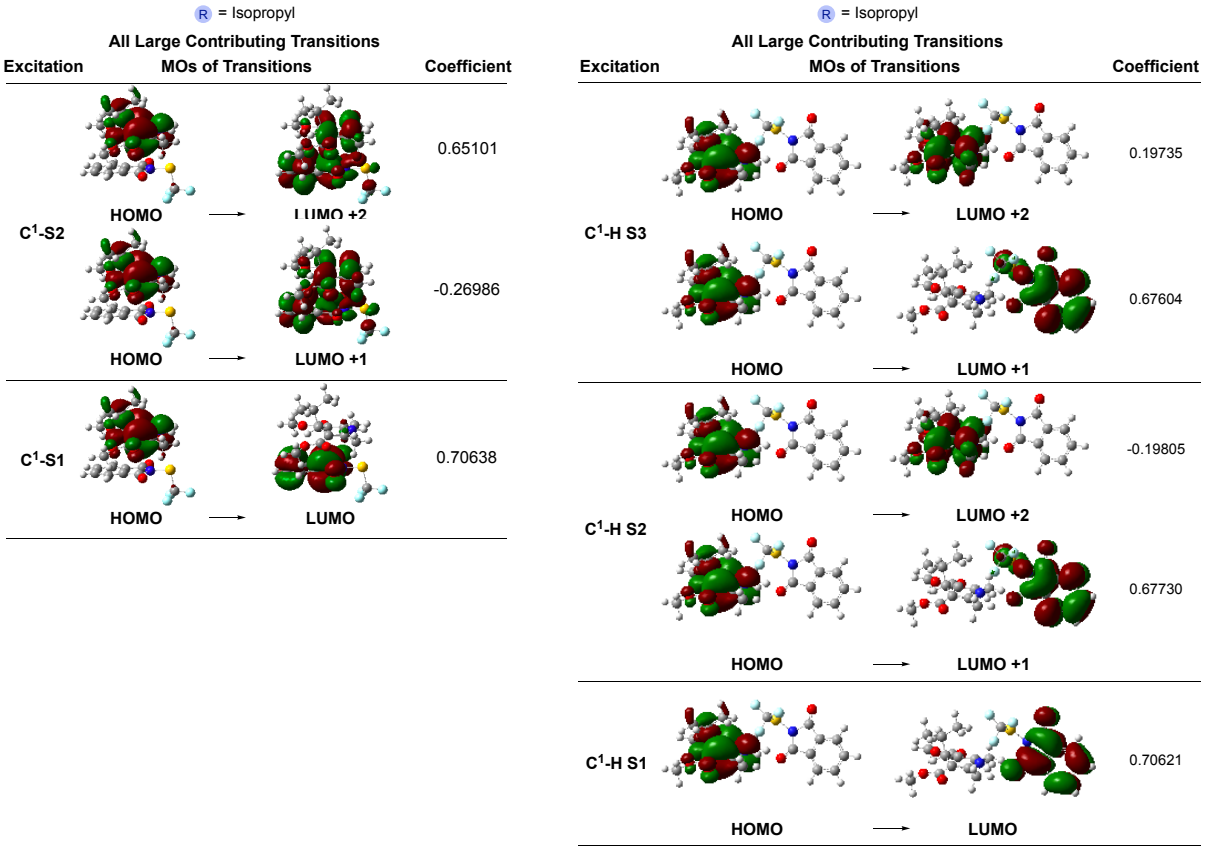


Figure A1.26: Canonical molecular orbitals of the electronic transitions involved in the indicated excitations of both isopropyl EDA complex **C^1** and **C^1-H** calculated using TD-DFT calculations at UB3LYP-D3/def2-SVP-CPCM(DMSO). The coefficient of the transitions is included next to each transition. Isovalue of MOs set to 0.02 e^-/au^3.

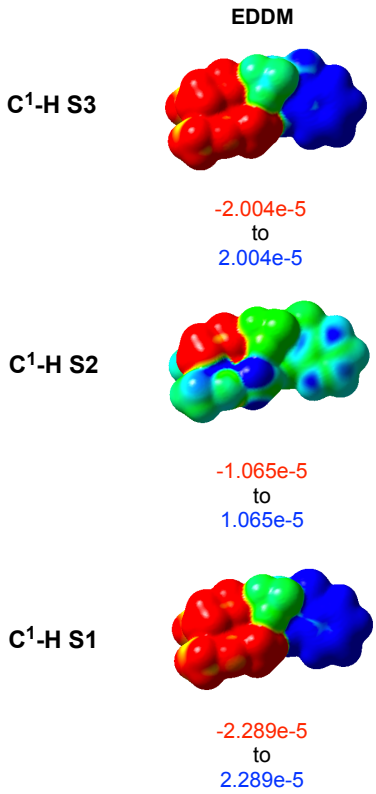


Figure A1.27: Electron density difference maps (EDDMs) of lowest lying singlet excited states are indicated. Isovalue of EDDMs 0.0004 e^-/au^3.

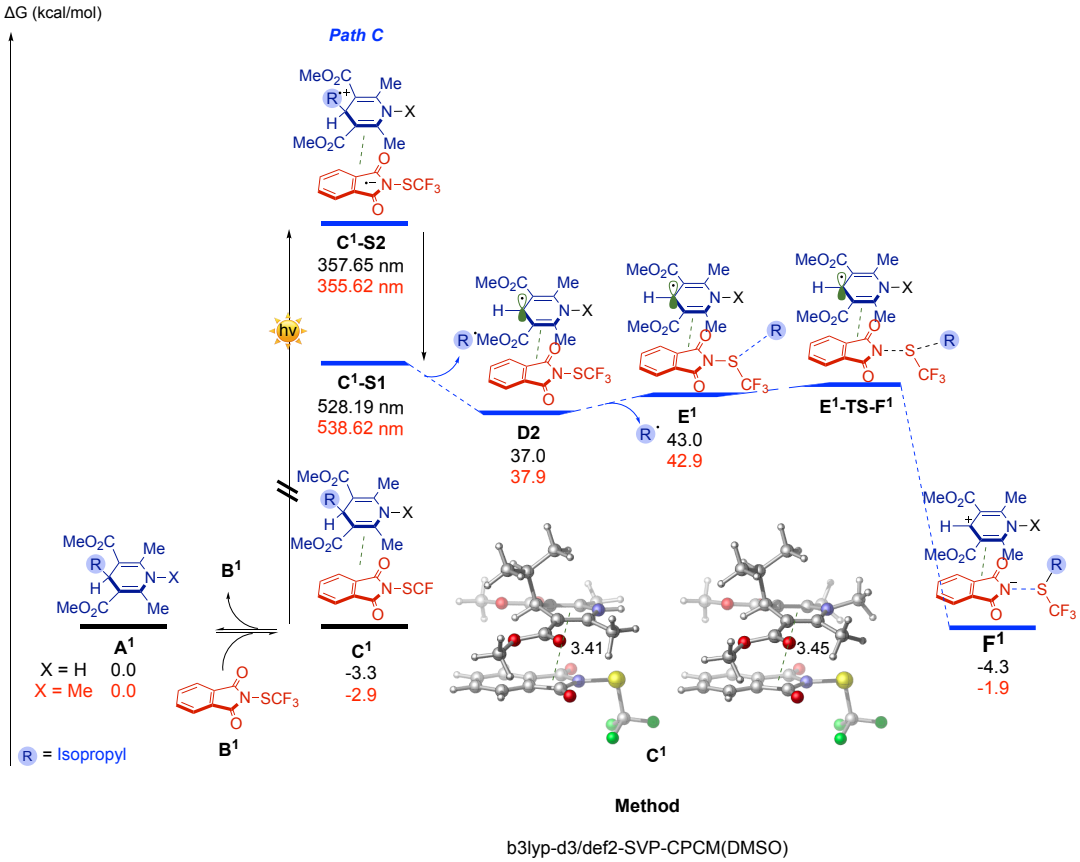


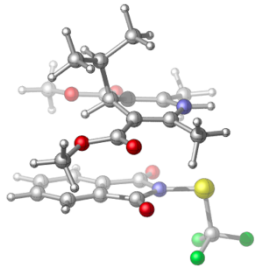
Figure A1.28: Potential energy surface of EDA complex

As it was found experimentally that N-H of the pyridine is crucial for this reaction to proceed, we probed the excited states of the hydrogen bonded complex **C1-H** to see if there would be significant differences in the excitations and UV-Vis of these complexes (**Figure A1.25**). It was found that complex **C1-H** was uphill in energy by 2.0 kcal/mol with respect to **C1** based on DFT calculations using B3LYP-D3. In addition, the computed UV-Vis spectra of **C1-H** was found to be similar in nature to that of **C1**. Both had a second singlet excitation (S2) at ~360 nm and a lowest lying singlet excited state (S1) past 500 nm. Comparing the canonical molecular orbitals and electron density difference maps of the S2 and S1 excited state transitions were of a similar nature with the S2 excitation being a mixture of a DHP localized transition and charge transfer transition from the DHP to the phthalimide while the S1 excitation being a clean change transfer from the DHP to the phthalimide. Finally, to see if methyl substitution would significantly change the energetics of the main pathway proposed in the Thesis, we substituted the N-H with N-Me on the DHP (**Scheme A1.28**). Overall, the relative energies and excitations remained the same, suggesting that there

alternate mechanistic complications (such as explicit solvent interactions) with this mechanism which are not captured in these computation

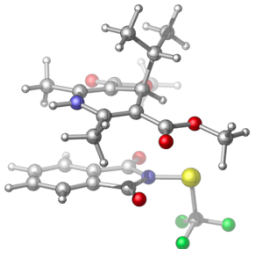
Energies and Coordinates

A1 = A1.1-Parallel-A-rotation-1



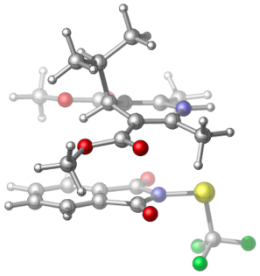
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459887 (Hartree/Particle)
Thermal correction to Energy= 0.495433
Thermal correction to Enthalpy= 0.496377
Thermal correction to Gibbs Free Energy= 0.390974
Sum of electronic and zero-point Energies= -2148.358610
Sum of electronic and thermal Energies= -2148.323064
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Sum of electronic and thermal Free Energies= -2148.427523

A1 = A1.1-Parallel-A-rotation-2



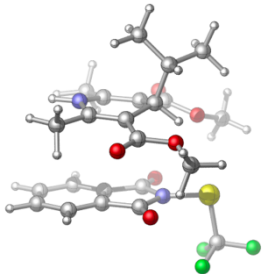
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460036 (Hartree/Particle)
Thermal correction to Energy= 0.495512
Thermal correction to Enthalpy= 0.496456
Thermal correction to Gibbs Free Energy= 0.390457
Sum of electronic and zero-point Energies= -2148.356739
Sum of electronic and thermal Energies= -2148.321263
Sum of electronic and thermal Enthalpies= -2148.320319
Sum of electronic and thermal Free Energies= -2148.426319

A1 = A1.1-Parallel-B-rotation-1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459751 (Hartree/Particle)
Thermal correction to Energy= 0.495385
Thermal correction to Enthalpy= 0.496329
Thermal correction to Gibbs Free Energy= 0.390614
Sum of electronic and zero-point Energies= -2148.358750
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Sum of electronic and thermal Enthalpies= -2148.322172
Sum of electronic and thermal Free Energies= -2148.427887

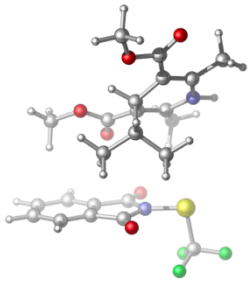
A1 = A1.1-Parallel-B-rotation-2



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Thermal correction to Energy= 0.495500
Thermal correction to Enthalpy= 0.496445

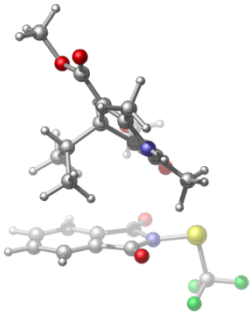
Thermal correction to Gibbs Free Energy= 0.390709
Sum of electronic and zero-point Energies= -2148.357380
Sum of electronic and thermal Energies= -2148.321796
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Sum of electronic and thermal Free Energies= -2148.426588

A1 = A1.1-Parallel-C-rotation-1



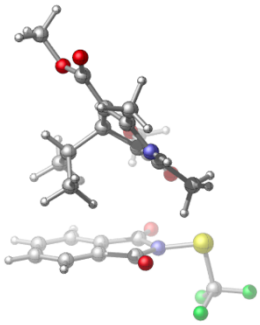
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459538 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.496386
Thermal correction to Gibbs Free Energy= 0.388785
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Sum of electronic and thermal Energies= -2148.313294
Sum of electronic and thermal Enthalpies= -2148.312349
Sum of electronic and thermal Free Energies= -2148.419951

A1 = A1.1-Parallel-C-rotation-2



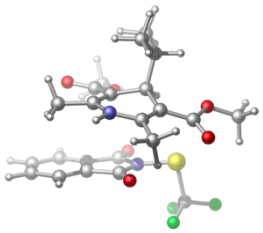
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459849 (Hartree/Particle)
Thermal correction to Energy= 0.495571
Thermal correction to Enthalpy= 0.496515
Thermal correction to Gibbs Free Energy= 0.389527
Sum of electronic and zero-point Energies= -2148.350689
Sum of electronic and thermal Energies= -2148.314967
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Sum of electronic and thermal Free Energies= -2148.421010

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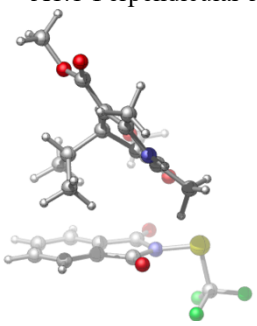
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Zero-point correction= 0.459982 (Hartree/Particle)
Thermal correction to Energy= 0.495639
Thermal correction to Enthalpy= 0.496583
Thermal correction to Gibbs Free Energy= 0.389957
Sum of electronic and zero-point Energies= -2148.350569
Sum of electronic and thermal Energies= -2148.314912
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Sum of electronic and thermal Free Energies= -2148.420594

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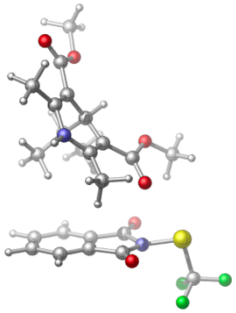


B3LYP-D3/def2-SVP-CPCM(DMSO)
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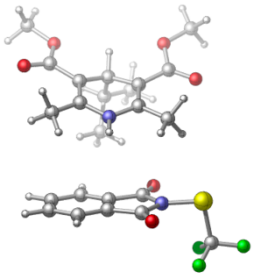
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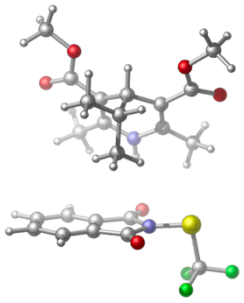
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Zero-point correction= 0.459963 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.496582
Thermal correction to Gibbs Free Energy= 0.389733
Sum of electronic and zero-point Energies= -2148.350597
Sum of electronic and thermal Energies= -2148.314923
Sum of electronic and thermal Enthalpies= -2148.313978
Sum of electronic and thermal Free Energies= -2148.420828
A1 = A1.1-Perpendicular-A-DHP-rotation-3



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459959 (Hartree/Particle)
Thermal correction to Energy= 0.495671
Thermal correction to Enthalpy= 0.496615
Thermal correction to Gibbs Free Energy= 0.389312
Sum of electronic and zero-point Energies= -2148.350605
Sum of electronic and thermal Energies= -2148.314893
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Sum of electronic and thermal Free Energies= -2148.421251
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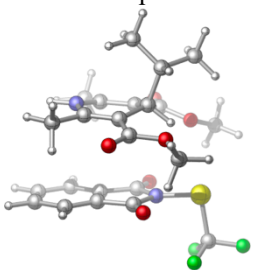


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Thermal correction to Gibbs Free Energy= 0.388279
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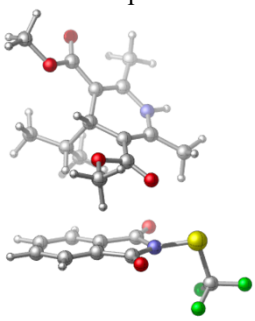


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Thermal correction to Enthalpy= 0.496479
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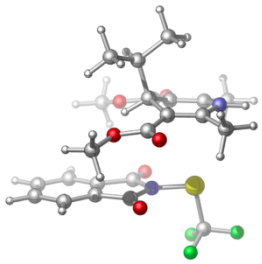


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Zero-point correction= 0.459862 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.496413
Thermal correction to Gibbs Free Energy= 0.390266
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Sum of electronic and thermal Energies= -2148.321821
Sum of electronic and thermal Enthalpies= -2148.320877
Sum of electronic and thermal Free Energies= -2148.427023
A1 = A1.1-Perpendicular-C-DHP-rotation-1

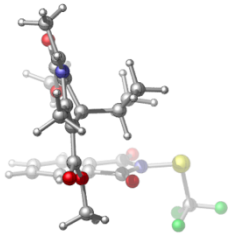


B3LYP-D3/def2-SVP-CPCM(DMSO)

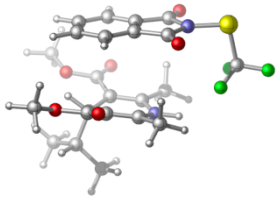
A1 = A1.1-Perpendicular-C-DHP-rotation-2



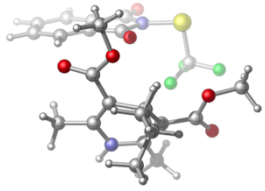
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459947 (Hartree/Particle)
Thermal correction to Energy= 0.495676
Thermal correction to Enthalpy= 0.496620
Thermal correction to Gibbs Free Energy= 0.389343
Sum of electronic and zero-point Energies= -2148.350584
Sum of electronic and thermal Energies= -2148.314856
Sum of electronic and thermal Enthalpies= -2148.313912
Sum of electronic and thermal Free Energies= -2148.421189
A1 = A1.1-Perpendicular-C-DHP-rotation-3



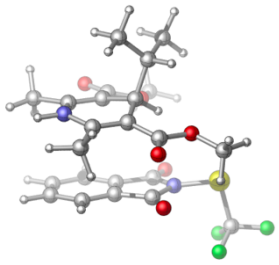
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460164 (Hartree/Particle)
Thermal correction to Energy= 0.495568
Thermal correction to Enthalpy= 0.496512
Thermal correction to Gibbs Free Energy= 0.391273
Sum of electronic and zero-point Energies= -2148.356625
Sum of electronic and thermal Energies= -2148.321222
Sum of electronic and thermal Enthalpies= -2148.320278
Sum of electronic and thermal Free Energies= -2148.425517
A1 = A1.1-Perpendicular-A-Phthalimide-rotation-1



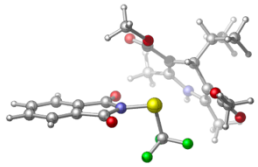
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460227
(Hartree/Particle)
Thermal correction to Energy= 0.495671
Thermal correction to Enthalpy=
0.496615
Thermal correction to Gibbs Free Energy=
0.391864
Sum of electronic and zero-point Energies= -
2148.358085
Sum of electronic and thermal Energies= -
2148.322641
Sum of electronic and thermal Enthalpies= -
2148.321697
Sum of electronic and thermal Free Energies= -
2148.426447
A1 = A1.1-Perpendicular-A-Phthalimide-rotation-2



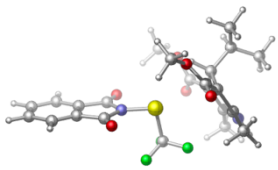
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459458
(Hartree/Particle)
Thermal correction to Energy= 0.495316
Thermal correction to Enthalpy=
0.496260
Thermal correction to Gibbs Free Energy=
0.388593
Sum of electronic and zero-point Energies= -
2148.348965
Sum of electronic and thermal Energies= -
2148.313107
Sum of electronic and thermal Enthalpies= -
2148.312163
Sum of electronic and thermal Free Energies= -
2148.419830
A1 = A1.1-Perpendicular-A-Phthalimide-rotation-3



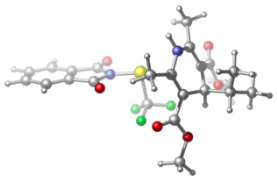
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459570
(Hartree/Particle)
Thermal correction to Energy= 0.495350
Thermal correction to Enthalpy=
0.496295
Thermal correction to Gibbs Free Energy=
0.388930
Sum of electronic and zero-point Energies= -
2148.357044
Sum of electronic and thermal Energies= -
2148.321263
Sum of electronic and thermal Enthalpies= -
2148.320319
Sum of electronic and thermal Free Energies= -
2148.427683
A1 = A1.1-Perpendicular-B-Phthalimide-rotation-1



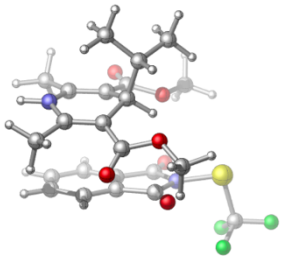
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459144
(Hartree/Particle)
Thermal correction to Energy= 0.495141
Thermal correction to Enthalpy=
0.496085
Thermal correction to Gibbs Free Energy=
0.388279
Sum of electronic and zero-point Energies= -
2148.349487
Sum of electronic and thermal Energies= -
2148.313491
Sum of electronic and thermal Enthalpies= -
2148.312547
Sum of electronic and thermal Free Energies= -
2148.420352
A1 = A1.1-Perpendicular-B-Phthalimide-rotation-2



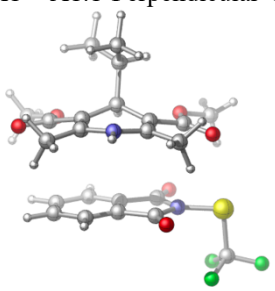
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459349
(Hartree/Particle)
Thermal correction to Energy= 0.495306
Thermal correction to Enthalpy=
0.496250
Thermal correction to Gibbs Free Energy=
0.387884
Sum of electronic and zero-point Energies= -
2148.350342
Sum of electronic and thermal Energies= -
2148.314386
Sum of electronic and thermal Enthalpies= -
2148.313441
Sum of electronic and thermal Free Energies= -
2148.421808
A1 = A1.1-Perpendicular-B-Phthalimide-rotation-3



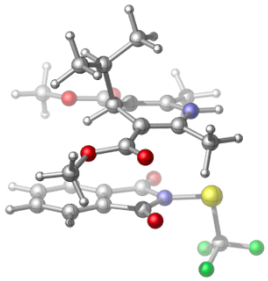
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459418
(Hartree/Particle)
Thermal correction to Energy= 0.495308
Thermal correction to Enthalpy=
0.496252
Thermal correction to Gibbs Free Energy=
0.388650
Sum of electronic and zero-point Energies= -
2148.349752
Sum of electronic and thermal Energies= -
2148.313862
Sum of electronic and thermal Enthalpies= -
2148.312918
Sum of electronic and thermal Free Energies= -
2148.420520
A1 = A1.1-Perpendicular-C-Phthalimide-rotation-1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460005
(Hartree/Particle)
Thermal correction to Energy= 0.495593
Thermal correction to Enthalpy=
0.496537
Thermal correction to Gibbs Free Energy=
0.390054
Sum of electronic and zero-point Energies= -
2148.356445
Sum of electronic and thermal Energies= -
2148.320857
Sum of electronic and thermal Enthalpies= -
2148.319913
Sum of electronic and thermal Free Energies= -
2148.426395
A1 = A1.1-Perpendicular-C-Phthalimide-rotation-2

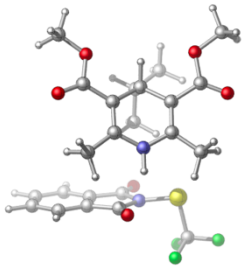


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459964
(Hartree/Particle)
Thermal correction to Energy= 0.495496
Thermal correction to Enthalpy=
0.496440
Thermal correction to Gibbs Free Energy=
0.391012
Sum of electronic and zero-point Energies= -
2148.357485
Sum of electronic and thermal Energies= -
2148.321953
Sum of electronic and thermal Enthalpies= -
2148.321009
Sum of electronic and thermal Free Energies= -
2148.426437
A1 = A1.1-Perpendicular-C-Phthalimide-rotation-3



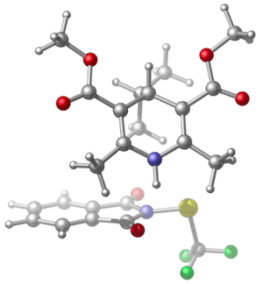
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459927 (Hartree/Particle)
Thermal correction to Energy= 0.495504
Thermal correction to Enthalpy= 0.496448
Thermal correction to Gibbs Free Energy= 0.390763
Sum of electronic and zero-point Energies= -2148.358567
Sum of electronic and thermal Energies= -2148.322991
Sum of electronic and thermal Enthalpies= -2148.322046
Sum of electronic and thermal Free Energies= -2148.427731

A1 = A1.1-N-H-Hydrogen-Bonding-rotation-1



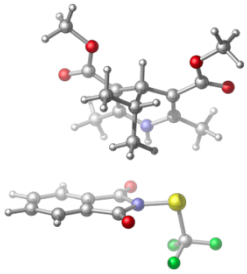
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459631 (Hartree/Particle)
Thermal correction to Energy= 0.495510
Thermal correction to Enthalpy= 0.496454
Thermal correction to Gibbs Free Energy= 0.387949
Sum of electronic and zero-point Energies= -2148.348347
Sum of electronic and thermal Energies= -2148.312468
Sum of electronic and thermal Enthalpies= -2148.311524
Sum of electronic and thermal Free Energies= -2148.420029

A1 = A1.1-N-H-Hydrogen-Bonding-rotation-2



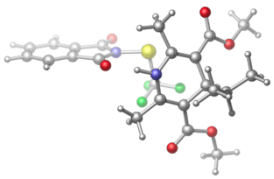
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459677 (Hartree/Particle)
Thermal correction to Energy= 0.495529
Thermal correction to Enthalpy= 0.496473
Thermal correction to Gibbs Free Energy= 0.388124
Sum of electronic and zero-point Energies= -2148.348283
Sum of electronic and thermal Energies= -2148.312431
Sum of electronic and thermal Enthalpies= -2148.311486
Sum of electronic and thermal Free Energies= -2148.419836

A1 = A1.1-N-H-Hydrogen-Bonding-rotation-3

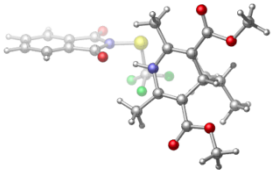


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459669 (Hartree/Particle)
Thermal correction to Energy= 0.495547
Thermal correction to Enthalpy= 0.496491
Thermal correction to Gibbs Free Energy= 0.387998
Sum of electronic and zero-point Energies= -2148.348377
Sum of electronic and thermal Energies= -2148.312500
Sum of electronic and thermal Enthalpies= -2148.311555
Sum of electronic and thermal Free Energies= -2148.420048

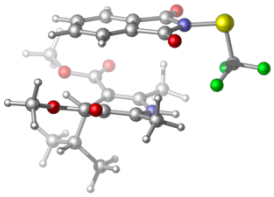
A1 = A1.1-O-H-Hydrogen-Bonding-rotation-1



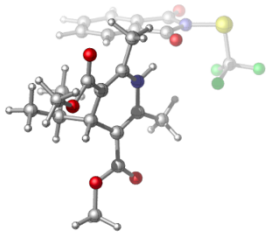
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459256 (Hartree/Particle)
Thermal correction to Energy= 0.495233
Thermal correction to Enthalpy= 0.496177
Thermal correction to Gibbs Free Energy= 0.387728
Sum of electronic and zero-point Energies= -2148.349869
Sum of electronic and thermal Energies= -2148.313892
Sum of electronic and thermal Enthalpies= -2148.312948
Sum of electronic and thermal Free Energies= -2148.421397
A1 = A1.1-O-H-Hydrogen-Bonding-rotation-2



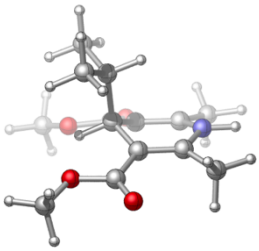
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459567 (Hartree/Particle)
Thermal correction to Energy= 0.495404
Thermal correction to Enthalpy= 0.496348
Thermal correction to Gibbs Free Energy= 0.388493
Sum of electronic and zero-point Energies= -2148.351429
Sum of electronic and thermal Energies= -2148.315593
Sum of electronic and thermal Enthalpies= -2148.314648
Sum of electronic and thermal Free Energies= -2148.422503
A1 = A1.1-O-H-Hydrogen-Bonding-rotation-3



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460279 (Hartree/Particle)
Thermal correction to Energy= 0.495694
Thermal correction to Enthalpy= 0.496638
Thermal correction to Gibbs Free Energy= 0.391988
Sum of electronic and zero-point Energies= -2148.358038
Sum of electronic and thermal Energies= -2148.322623
Sum of electronic and thermal Enthalpies= -2148.321679
Sum of electronic and thermal Free Energies= -2148.426329
A1 = A1.1-O-H-Hydrogen-Bonding-rotation-4



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459797 (Hartree/Particle)
Thermal correction to Energy= 0.495610
Thermal correction to Enthalpy= 0.496554
Thermal correction to Gibbs Free Energy= 0.387387
Sum of electronic and zero-point Energies= -2148.347600
Sum of electronic and thermal Energies= -2148.311787
Sum of electronic and thermal Enthalpies= -2148.310843
Sum of electronic and thermal Free Energies= -2148.420010
Thesis = A1, A1 = A1.2-A1-B3LYP-D3, A1.4-A1, A1.5-A1, A1.7-A1-Isopropyl, A1.9-A1-Isopropyl, A1.10-A1, A1.11-A1-Isopropyl, A1.12-A1-Isopropyl, A1.26-A1



B3LYP-D3/def2-SVP-CPCM(DMSO)

Zero-point correction= 0.336308 (Hartree/Particle)
Thermal correction to Energy= 0.357433
Thermal correction to Enthalpy= 0.358377
Thermal correction to Gibbs Free Energy= 0.286627
Sum of electronic and zero-point Energies= -900.869620
Sum of electronic and thermal Energies= -900.848495
Sum of electronic and thermal Enthalpies= -900.847551
Sum of electronic and thermal Free Energies= -900.919301
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.334054484072
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -902.2088374
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -902.2088374
TD- B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -901.20513869
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.6782 eV 462.94 nm f=0.0000 <S**2>=2.000
71A -> 74A -0.12928
72A -> 73A 0.68759
71B -> 74B 0.12928
72B -> 73B -0.68759

Excited state symmetry could not be determined.
Excited State 2: 3.000-?Sym 3.3422 eV 370.96 nm f=0.0000 <S**2>=2.000
70A -> 73A -0.17709
71A -> 73A 0.57997
72A -> 74A -0.34232
70B -> 73B 0.17709
71B -> 73B -0.57997
72B -> 74B 0.34232

Excited state symmetry could not be determined.
Excited State 3: 1.000-?Sym 3.6042 eV 343.99 nm f=0.2415 <S**2>=0.000
72A -> 73A 0.70501
72B -> 73B 0.70501
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -901.073474103
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 4.2558 eV 291.33 nm f=0.0000 <S**2>=2.000
69A -> 74A 0.12472
70A -> 73A 0.27476
71A -> 73A 0.37399
72A -> 74A 0.50731
69B -> 74B -0.12472
70B -> 73B -0.27476
71B -> 73B -0.37399
72B -> 74B -0.50731

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 4.5643 eV 271.64 nm f=0.0000 <S**2>=2.000
69A -> 73A 0.60927
70A -> 74A 0.21372
71A -> 74A 0.24811
69B -> 73B -0.60927
70B -> 74B -0.21372
71B -> 74B -0.24811

Excited state symmetry could not be determined.
Excited State 6: 1.000-?Sym 4.5684 eV 271.40 nm f=0.0115 <S**2>=0.000
69A -> 74A 0.12342
70A -> 73A 0.30605
71A -> 73A 0.56524
72A -> 74A 0.25970
69B -> 74B 0.12342
70B -> 73B 0.30605
71B -> 73B 0.56524
72B -> 74B 0.25970

Excited state symmetry could not be determined.
Excited State 7: 3.000-?Sym 4.5797 eV 270.73 nm f=0.0000 <S**2>=2.000
69A -> 74A 0.19846
70A -> 73A 0.57239
72A -> 74A -0.34029
69B -> 74B -0.19846
70B -> 73B -0.57239
72B -> 74B 0.34029

Excited state symmetry could not be determined.
Excited State 8: 1.000-?Sym 4.9363 eV 251.17 nm f=0.0185 <S**2>=0.000
69A -> 73A 0.65409
70A -> 74A 0.19964

71A -> 74A 0.14976
69B -> 73B 0.65409
70B -> 74B 0.19964
71B -> 74B 0.14976

Excited state symmetry could not be determined.
Excited State 9: 1.000-?Sym 4.9443 eV 250.76 nm f=0.0126 <S**2>=0.000
69A -> 74A 0.11712
70A -> 73A 0.51226
72A -> 74A -0.45868
69B -> 74B 0.11712
70B -> 73B 0.51226
72B -> 74B -0.45868

Excited state symmetry could not be determined.
Excited State 10: 3.000-?Sym 5.1992 eV 238.47 nm f=0.0000 <S**2>=2.000
67A -> 73A -0.40933
68A -> 74A -0.19082
69A -> 73A -0.13863
70A -> 74A -0.18576
71A -> 74A 0.44056
72A -> 73A 0.11778
67B -> 73B 0.40933
68B -> 74B 0.19082
69B -> 73B 0.13863
70B -> 74B 0.18576
71B -> 74B -0.44056
72B -> 73B -0.11778

Excited state symmetry could not be determined.
Excited State 11: 3.000-?Sym 5.2633 eV 235.56 nm f=0.0000 <S**2>=2.000
67A -> 74A 0.27097
68A -> 73A 0.61153
67B -> 74B -0.27097
68B -> 73B -0.61153

Excited state symmetry could not be determined.
Excited State 12: 3.000-?Sym 5.3181 eV 233.13 nm f=0.0000 <S**2>=2.000
67A -> 73A 0.45412
68A -> 74A 0.19642
69A -> 73A -0.11527
70A -> 74A -0.13233
71A -> 74A 0.41447
67B -> 73B -0.45412
68B -> 74B -0.19642
69B -> 73B 0.11527
70B -> 74B 0.13233
71B -> 74B -0.41447

Excited state symmetry could not be determined.
Excited State 13: 1.000-?Sym 5.3629 eV 231.19 nm f=0.7135 <S**2>=0.000
70A -> 73A 0.31818
71A -> 73A -0.40093
72A -> 74A 0.46144
70B -> 73B 0.31818
71B -> 73B -0.40093
72B -> 74B 0.46144

Excited state symmetry could not be determined.
Excited State 14: 1.000-?Sym 5.9490 eV 208.41 nm f=0.0007 <S**2>=0.000
66A -> 73A -0.10897
69A -> 73A -0.18936
71A -> 74A 0.65253
66B -> 73B -0.10896
69B -> 73B -0.18936
71B -> 74B 0.65253

Excited state symmetry could not be determined.
Excited State 15: 3.000-?Sym 6.1001 eV 203.25 nm f=0.0000 <S**2>=2.000
66A -> 73A -0.40928
69A -> 73A -0.25303
70A -> 74A 0.45694
71A -> 74A 0.15224
66B -> 73B 0.40928
69B -> 73B 0.25303
70B -> 74B -0.45694
71B -> 74B -0.15224

Excited state symmetry could not be determined.
Excited State 16: 3.000-?Sym 6.1415 eV 201.88 nm f=0.0000 <S**2>=2.000
72A -> 75A 0.62939
72A -> 76A -0.12699
72A -> 78A 0.23451
72B -> 75B -0.62939
72B -> 76B 0.12699
72B -> 78B -0.23451

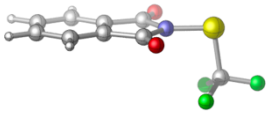
Excited state symmetry could not be determined.
Excited State 17: 1.000-?Sym 6.1821 eV 200.55 nm f=0.0392 <S**2>=0.000
68A -> 73A 0.69565
68B -> 73B 0.69565

Excited state symmetry could not be determined.
Excited State 18: 1.000-?Sym 6.1877 eV 200.37 nm f=0.0004 <S**2>=0.000
67A -> 73A 0.68962
67B -> 73B 0.68962

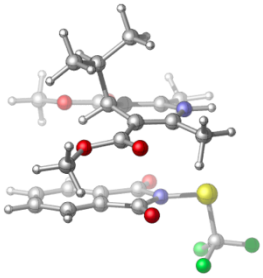
Excited state symmetry could not be determined.

Excited State 19: 3.000-?Sym 6.1975 eV 200.06 nm f=0.0000 <S**2>=2.000
65A -> 73A -0.19661
69A -> 74A 0.49840
70A -> 73A -0.17622
70A -> 79A 0.12147
71A -> 73A -0.10952
72A -> 75A -0.17746
72A -> 78A 0.28423
65B -> 73B 0.19661
69B -> 74B -0.49840
70B -> 73B 0.17622
70B -> 79B -0.12147
71B -> 73B 0.10952
72B -> 75B 0.17746
72B -> 78B -0.28423

Excited state symmetry could not be determined.
Excited State 20: 1.000-?Sym 6.2541 eV 198.24 nm f=0.0014 <S**2>=0.000
72A -> 75A 0.69352
72A -> 76A -0.11200
72B -> 75B 0.69352
72B -> 76B -0.11200
Thesis = B1, A1 = A1.2-B1-B3LYP-D3, A1.7-B1, A1.8-B1, S29-B1, A1.26-B1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.121381 (Hartree/Particle)
Thermal correction to Energy= 0.134428
Thermal correction to Enthalpy= 0.135372
Thermal correction to Gibbs Free Energy= 0.079715
Sum of electronic and zero-point Energies= -1247.461290
Sum of electronic and thermal Energies= -1247.448244
Sum of electronic and thermal Enthalpies= -1247.447300
Sum of electronic and thermal Free Energies= -1247.502957
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1246.619210958789
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -1248.7037384
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -1248.6925959
Thesis = C1, A1 = A1.2-C1-B3LYP-D3, A1.3-B3LYP-D3, A1.7-C1, A1.9-C1, A1.10-C1, A1.11-C1, A1.12-C1, A1.23-C1, A1.24-C1, A1.25-C1, A1.26-C2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459887 (Hartree/Particle)
Thermal correction to Energy= 0.495433
Thermal correction to Enthalpy= 0.496377
Thermal correction to Gibbs Free Energy= 0.390974
Sum of electronic and zero-point Energies= -2148.358610
Sum of electronic and thermal Energies= -2148.323064
Sum of electronic and thermal Enthalpies= -2148.322120
Sum of electronic and thermal Free Energies= -2148.427523
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.979284187807
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF= -2150.9458349
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.9242687
TD- B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.8184971
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.3108 eV 536.54 nm f=0.0000 <S**2>=2.000
134A ->135A -0.68593
134A ->136A -0.12105
134A ->137A 0.10192
134B ->135B 0.68594
134B ->136B 0.12105

134B ->137B -0.10192

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.3473 eV 528.19 nm f=0.0010 <S**2>=0.000
134A ->135A 0.70638
134B ->135B 0.70637
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2148.73223403
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.5721 eV 482.03 nm f=0.0000 <S**2>=2.000
134A ->135A 0.16178
134A ->136A -0.51903
134A ->137A 0.42930
134B ->135B -0.16178
134B ->136B 0.51903
134B ->137B -0.42930

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.1819 eV 389.65 nm f=0.0000 <S**2>=2.000
124A ->135A -0.12758
129A ->135A 0.39271
129A ->136A -0.11969
129A ->137A -0.11715
130A ->135A 0.44284
130A ->136A 0.11373
130A ->137A 0.13998
131A ->135A -0.10139
133A ->135A 0.10450
124B ->135B 0.12758
129B ->135B -0.39271
129B ->136B 0.11969
129B ->137B 0.11715
130B ->135B -0.44284
130B ->136B -0.11374
130B ->137B -0.13998
131B ->135B 0.10139
133B ->135B -0.10450

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.4151 eV 363.05 nm f=0.0000 <S**2>=2.000
132A ->136A 0.17577
132A ->137A -0.14251
133A ->135A -0.22594
133A ->136A -0.37355
133A ->137A 0.32001
134A ->139A 0.33928
132B ->136B -0.17577
132B ->137B 0.14251
133B ->135B 0.22594
133B ->136B 0.37355
133B ->137B -0.32001
134B ->139B -0.33928

Excited state symmetry could not be determined.
Excited State 6: 1.000-?Sym 3.4667 eV 357.65 nm f=0.1633 <S**2>=0.000
134A ->136A 0.65101
134A ->137A -0.26986
134B ->136B 0.65101
134B ->137B -0.26987

Excited state symmetry could not be determined.
Excited State 7: 3.000-?Sym 3.5321 eV 351.02 nm f=0.0000 <S**2>=2.000
130A ->135A 0.15517
134A ->136A 0.42748
134A ->137A 0.51367
130B ->135B -0.15517
134B ->136B -0.42747
134B ->137B -0.51365

Excited state symmetry could not be determined.
Excited State 8: 3.000-?Sym 3.5715 eV 347.15 nm f=0.0000 <S**2>=2.000
126A ->135A -0.12650
127A ->135A -0.35077
128A ->135A 0.55938
126B ->135B 0.12650
127B ->135B 0.35077
128B ->135B -0.55938

Excited state symmetry could not be determined.
Excited State 9: 1.000-?Sym 3.5844 eV 345.90 nm f=0.0481 <S**2>=0.000
134A ->136A 0.26981
134A ->137A 0.64979
134B ->136B 0.26982
134B ->137B 0.64980

Excited state symmetry could not be determined.
Excited State 10: 3.000-?Sym 3.6016 eV 344.24 nm f=0.0000 <S**2>=2.000
125A ->135A -0.11696
129A ->135A -0.44155
130A ->135A 0.39442
132A ->135A 0.23952
133A ->135A 0.15846
134A ->136A -0.10858
134A ->137A -0.12739

125B ->135B 0.11696
129B ->135B 0.44155
130B ->135B -0.39443
132B ->135B -0.23953
133B ->135B -0.15846
134B ->136B 0.10859
134B ->137B 0.12740

Excited state symmetry could not be determined.
Excited State 11: 3.000-?Sym 3.7162 eV 333.63 nm f=0.0000 <S**2>=2.000
130A ->135A 0.14010
133A ->135A -0.63459
133A ->136A 0.11737
133A ->137A -0.10423
134A ->139A -0.13563
130B ->135B -0.14012
133B ->135B 0.63523
133B ->136B -0.11737
133B ->137B 0.10424
134B ->139B 0.13565

Excited state symmetry could not be determined.
Excited State 12: 1.000-?Sym 3.7176 eV 333.51 nm f=0.0249 <S**2>=0.000
133A ->135A 0.70228
133B ->135B 0.70171

Excited state symmetry could not be determined.
Excited State 13: 1.000-?Sym 3.9447 eV 314.30 nm f=0.0005 <S**2>=0.000
126A ->135A -0.10686
127A ->135A -0.28638
128A ->135A 0.61778
126B ->135B -0.10686
127B ->135B -0.28638
128B ->135B 0.61779

Excited state symmetry could not be determined.
Excited State 14: 3.000-?Sym 4.0681 eV 304.77 nm f=0.0000 <S**2>=2.000
124A ->135A 0.46741
126A ->135A -0.10545
129A ->135A 0.25965
130A ->136A -0.11240
130A ->137A -0.11247
132A ->135A 0.31881
124B ->135B -0.46740
126B ->135B 0.10545
129B ->135B -0.25965
130B ->136B 0.11240
130B ->137B 0.11247
132B ->135B -0.31883

Excited state symmetry could not be determined.
Excited State 15: 1.000-?Sym 4.1097 eV 301.69 nm f=0.0330 <S**2>=0.000
132A ->135A 0.69778
132B ->135B 0.69777

Excited state symmetry could not be determined.
Excited State 16: 3.000-?Sym 4.1334 eV 299.95 nm f=0.0000 <S**2>=2.000
124A ->135A -0.11236
129A ->136A -0.16520
129A ->137A -0.19336
130A ->135A -0.24639
130A ->136A 0.17168
130A ->137A 0.20007
132A ->135A 0.48451
132A ->136A 0.13266
124B ->135B 0.11236
129B ->136B 0.16520
129B ->137B 0.19336
130B ->135B 0.24640
130B ->136B -0.17168
130B ->137B -0.20007
132B ->135B -0.48451
132B ->136B -0.13266

Excited state symmetry could not be determined.
Excited State 17: 3.000-?Sym 4.1753 eV 296.95 nm f=0.0000 <S**2>=2.000
123A ->135A 0.43586
124A ->135A -0.27030
128A ->136A -0.10992
128A ->137A -0.10985
129A ->135A 0.14607
129A ->136A 0.13112
129A ->137A 0.14375
130A ->136A -0.15200
130A ->137A -0.16131
132A ->135A 0.16445
132A ->137A -0.10321
123B ->135B -0.43586
124B ->135B 0.27030
128B ->136B 0.10992
128B ->137B 0.10985
129B ->135B -0.14607
129B ->136B -0.13112
129B ->137B -0.14375
130B ->136B 0.15200
130B ->137B 0.16131
132B ->135B -0.16444
132B ->137B 0.10321

Excited state symmetry could not be determined.

Excited State 18: 3.000-?Sym 4.2426 eV 292.24 nm f=0.0000 <S**2>=2.000

123A ->135A	-0.45837
124A ->135A	-0.30971
129A ->136A	0.10067
129A ->137A	0.10465
130A ->136A	-0.12274
130A ->137A	-0.12195
131A ->135A	-0.22298
132A ->135A	0.14307
132A ->137A	-0.11238
123B ->135B	0.45837
124B ->135B	0.30971
129B ->136B	-0.10067
129B ->137B	-0.10465
130B ->136B	0.12274
130B ->137B	0.12196
131B ->135B	0.22297
132B ->135B	-0.14306
132B ->137B	0.11238

Excited state symmetry could not be determined.

Excited State 19: 1.000-?Sym 4.2565 eV 291.28 nm f=0.0220 <S**2>=0.000

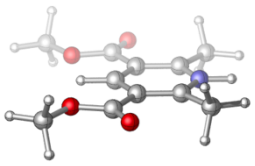
124A ->135A	-0.13730
129A ->135A	-0.32306
130A ->135A	-0.39374
131A ->135A	0.45134
124B ->135B	-0.13729
129B ->135B	-0.32306
130B ->135B	-0.39373
131B ->135B	0.45136

Excited state symmetry could not be determined.

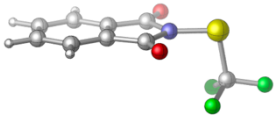
Excited State 20: 3.000-?Sym 4.2764 eV 289.93 nm f=0.0000 <S**2>=2.000

123A ->135A	0.11838
124A ->135A	0.11663
129A ->135A	-0.15726
131A ->135A	-0.56761
132A ->135A	-0.16179
132A ->136A	0.11109
133A ->137A	-0.11497
134A ->139A	0.17095
123B ->135B	-0.11839
124B ->135B	-0.11662
129B ->135B	0.15728
131B ->135B	0.56765
132B ->135B	0.16179
132B ->136B	-0.11109
133B ->137B	0.11497
134B ->139B	-0.17095

Thesis = A1+, A1 = A1.2-A1+, A1.4-A1+, A1.11-A1+

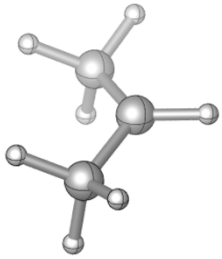


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.242851 (Hartree/Particle)
Thermal correction to Energy= 0.259327
Thermal correction to Enthalpy= 0.260272
Thermal correction to Gibbs Free Energy= 0.197770
Sum of electronic and zero-point Energies= -782.345251
Sum of electronic and thermal Energies= -782.328774
Sum of electronic and thermal Enthalpies= -782.327830
Sum of electronic and thermal Free Energies= -782.390331
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -781.796479918326
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-783.4708634
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-783.3959284
Mauscript = B2-, A1 = A1.2-(B2-)-B3LYP-D3, A1.4-B2-

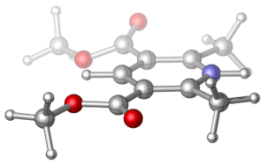


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.118749 (Hartree/Particle)
Thermal correction to Energy= 0.131936
Thermal correction to Enthalpy= 0.132880
Thermal correction to Gibbs Free Energy= 0.076144
Sum of electronic and zero-point Energies= -1247.570646
Sum of electronic and thermal Energies= -1247.557459
Sum of electronic and thermal Enthalpies= -1247.556515
Sum of electronic and thermal Free Energies= -1247.613251

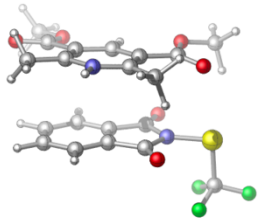
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1246.658022864678
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1248.8191762
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1248.7434442
Thesis =Isopropyl Radical, A1 = A1.2-Isopropyl-Radical-B3LYP-D3, A1.3-Isopropyl-Radical, A1.4 Isopropyl Radical, A1.11-Isopropyl Radical, A1.13-Isopropyl Radical, S24-Isopropyl Radical, A1.21-Isopropyl Radical,



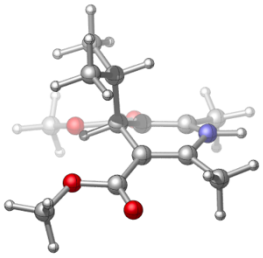
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.087112 (Hartree/Particle)
Thermal correction to Energy= 0.092248
Thermal correction to Enthalpy= 0.093192
Thermal correction to Gibbs Free Energy= 0.059988
Sum of electronic and zero-point Energies= -118.309350
Sum of electronic and thermal Energies= -118.304214
Sum of electronic and thermal Enthalpies= -118.303269
Sum of electronic and thermal Free Energies= -118.336473
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -118.246817328885
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-118.5326876
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-118.5321478
Thesis = A2, A1 = A1.2-A2-B3LYP-D3,



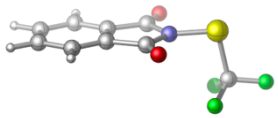
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.237815 (Hartree/Particle)
Thermal correction to Energy= 0.254943
Thermal correction to Enthalpy= 0.255887
Thermal correction to Gibbs Free Energy= 0.191867
Sum of electronic and zero-point Energies= -782.468236
Sum of electronic and thermal Energies= -782.451108
Sum of electronic and thermal Enthalpies= -782.450164
Sum of electronic and thermal Free Energies= -782.514184
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -781.973610728724
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-783.5922778
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
F=-783.5793983
Thesis = D2', A1 = A1.2-D2-B3LYP-D3, A1.3-B3LYP-D3, A1.19-D2'



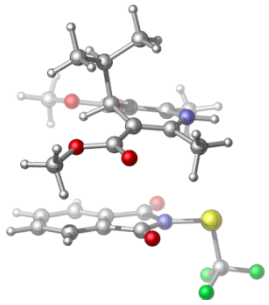
B3LYP-D3/def2-SVP-CPCM(DMSO)
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2028.614893037425
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3225523
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
-2032.2976613
A1 = A1.2-A1-B3LYP



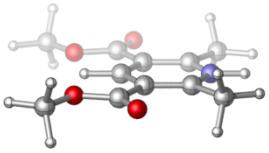
B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.335670 (Hartree/Particle)
Thermal correction to Energy= 0.357043
Thermal correction to Enthalpy= 0.357987
Thermal correction to Gibbs Free Energy= 0.285592
Sum of electronic and zero-point Energies= -900.825228
Sum of electronic and thermal Energies= -900.803855
Sum of electronic and thermal Enthalpies= -900.802910
Sum of electronic and thermal Free Energies= -900.875306
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-902.1765068
Thesis = B1, A1 = A1.2-B1-B3LYP



B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.121387 (Hartree/Particle)
Thermal correction to Energy= 0.134443
Thermal correction to Enthalpy= 0.135388
Thermal correction to Gibbs Free Energy= 0.079626
Sum of electronic and zero-point Energies= -1247.443788
Sum of electronic and thermal Energies= -1247.430732
Sum of electronic and thermal Enthalpies= -1247.429788
Sum of electronic and thermal Free Energies= -1247.485549
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-1248.6864273
A1 = A1.2-C1-B3LYP, A1.3-B3LYP

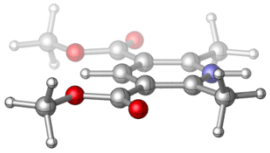


B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.457888 (Hartree/Particle)
Thermal correction to Energy= 0.494534
Thermal correction to Enthalpy= 0.495478
Thermal correction to Gibbs Free Energy= 0.383622
Sum of electronic and zero-point Energies= -2148.270973
Sum of electronic and thermal Energies= -2148.234326
Sum of electronic and thermal Enthalpies= -2148.233382
Sum of electronic and thermal Free Energies= -2148.345239
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-2150.8612774
A1 = A1.2-A1+-B3LYP



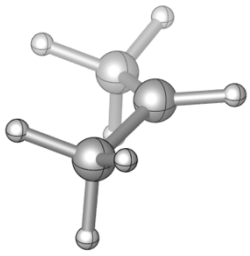
B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.242564 (Hartree/Particle)
Thermal correction to Energy= 0.259235
Thermal correction to Enthalpy= 0.260179
Thermal correction to Gibbs Free Energy= 0.197194
Sum of electronic and zero-point Energies= -782.318583
Sum of electronic and thermal Energies= -782.301912
Sum of electronic and thermal Enthalpies= -782.300968
Sum of electronic and thermal Free Energies= -782.363953
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-783.4439735

A1 = A1.2-(B2-)-B3LYP



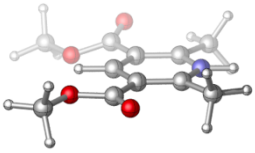
B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.118777 (Hartree/Particle)
Thermal correction to Energy= 0.131953
Thermal correction to Enthalpy= 0.132897
Thermal correction to Gibbs Free Energy= 0.076261
Sum of electronic and zero-point Energies= -1247.553216
Sum of electronic and thermal Energies= -1247.540040
Sum of electronic and thermal Enthalpies= -1247.539096
Sum of electronic and thermal Free Energies= -1247.595732
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-1248.8019645

A1 = A1.2-Isopropyl Radical-B3LYP



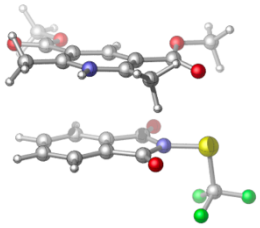
B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.087115 (Hartree/Particle)
Thermal correction to Energy= 0.092269
Thermal correction to Enthalpy= 0.093213
Thermal correction to Gibbs Free Energy= 0.059947
Sum of electronic and zero-point Energies= -118.306149
Sum of electronic and thermal Energies= -118.300995
Sum of electronic and thermal Enthalpies= -118.300051
Sum of electronic and thermal Free Energies= -118.333317
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-118.5294857

A1 = A1.2-A2-B3LYP



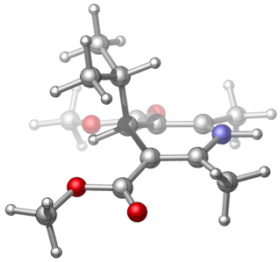
B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.237445 (Hartree/Particle)
Thermal correction to Energy= 0.254770
Thermal correction to Enthalpy= 0.255714
Thermal correction to Gibbs Free Energy= 0.191018
Sum of electronic and zero-point Energies= -782.441837
Sum of electronic and thermal Energies= -782.424513
Sum of electronic and thermal Enthalpies= -782.423569
Sum of electronic and thermal Free Energies= -782.488264
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-783.5654287

A1 = A1.2-D2-B3LYP, A1.3-B3LYP

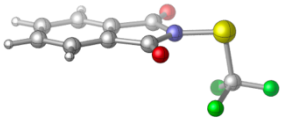


B3LYP/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.360696 (Hartree/Particle)
Thermal correction to Energy= 0.392718
Thermal correction to Enthalpy= 0.393662
Thermal correction to Gibbs Free Energy= 0.293400
Sum of electronic and zero-point Energies= -2029.890542
Sum of electronic and thermal Energies= -2029.858520
Sum of electronic and thermal Enthalpies= -2029.857576
Sum of electronic and thermal Free Energies= -2029.957838
B3LYP/def2-TZVPP-CPCM(DMSO)//B3LYP/def2-SVP-CPCM(DMSO)
HF=-2032.2522472

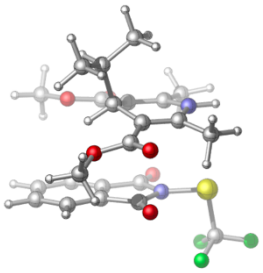
A1 = A1.2-A1-UM06-2X



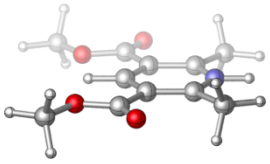
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.339983 (Hartree/Particle)
Thermal correction to Energy= 0.360915
Thermal correction to Enthalpy= 0.361859
Thermal correction to Gibbs Free Energy= 0.290679
Sum of electronic and zero-point Energies= -900.427361
Sum of electronic and thermal Energies= -900.406429
Sum of electronic and thermal Enthalpies= -900.405485
Sum of electronic and thermal Free Energies= -900.476665
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
-901.7972515
A1 = A1.2-B1-UM06-2X



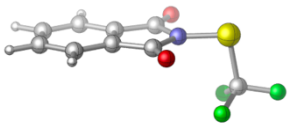
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.123531 (Hartree/Particle)
Thermal correction to Energy= 0.136443
Thermal correction to Enthalpy= 0.137387
Thermal correction to Gibbs Free Energy= 0.082005
Sum of electronic and zero-point Energies= -1247.108721
Sum of electronic and thermal Energies= -1247.095809
Sum of electronic and thermal Enthalpies= -1247.094865
Sum of electronic and thermal Free Energies= -1247.150247
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-1248.3511884
A1 = A1.2-C1-UM06-2X, A1.3-UM06-2X



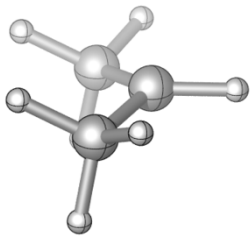
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.465528 (Hartree/Particle)
Thermal correction to Energy= 0.500517
Thermal correction to Enthalpy= 0.501461
Thermal correction to Gibbs Free Energy= 0.398684
Sum of electronic and zero-point Energies= -2147.561091
Sum of electronic and thermal Energies= -2147.526102
Sum of electronic and thermal Enthalpies= -2147.525158
Sum of electronic and thermal Free Energies= -2147.627935
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-2150.166719
A1 = A1.2-A1+-UM06-2X



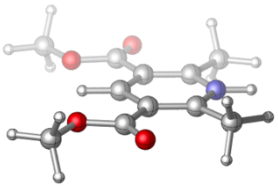
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.245834 (Hartree/Particle)
Thermal correction to Energy= 0.262202
Thermal correction to Enthalpy= 0.263146
Thermal correction to Gibbs Free Energy= 0.201015
Sum of electronic and zero-point Energies= -781.977773
Sum of electronic and thermal Energies= -781.961405
Sum of electronic and thermal Enthalpies= -781.960460
Sum of electronic and thermal Free Energies= -782.022591
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-783.1170545
A1 = A1.2-(B2-)-UM06-2X



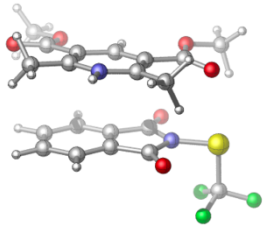
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.121145 (Hartree/Particle)
Thermal correction to Energy= 0.134100
Thermal correction to Enthalpy= 0.135045
Thermal correction to Gibbs Free Energy= 0.079141
Sum of electronic and zero-point Energies= -1247.218968
Sum of electronic and thermal Energies= -1247.206013
Sum of electronic and thermal Enthalpies= -1247.205068
Sum of electronic and thermal Free Energies= -1247.260972
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-1248.4666236
A1 = A1.2-Isopropyl Radicala-UM06-2X



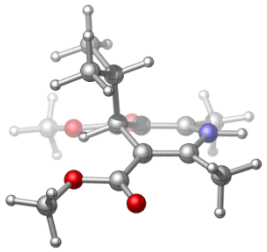
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.088123 (Hartree/Particle)
Thermal correction to Energy= 0.093228
Thermal correction to Enthalpy= 0.094172
Thermal correction to Gibbs Free Energy= 0.061089
Sum of electronic and zero-point Energies= -118.222543
Sum of electronic and thermal Energies= -118.217438
Sum of electronic and thermal Enthalpies= -118.216494
Sum of electronic and thermal Free Energies= -118.249577
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-118.4494895
A1 = A1.2-A2-UM06-2X



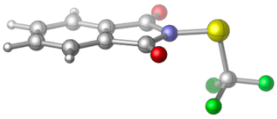
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.240426 (Hartree/Particle)
Thermal correction to Energy= 0.257582
Thermal correction to Enthalpy= 0.258526
Thermal correction to Gibbs Free Energy= 0.194072
Sum of electronic and zero-point Energies= -782.101703
Sum of electronic and thermal Energies= -782.084547
Sum of electronic and thermal Enthalpies= -782.083603
Sum of electronic and thermal Free Energies= -782.148057
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-783.2384511
A1 = A1.2-D2-UM06-2X, A1.3-UM06-2X



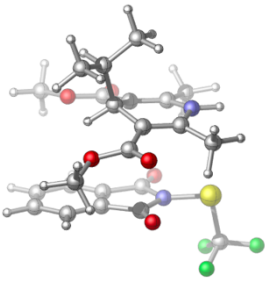
UM06-2X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.366684 (Hartree/Particle)
Thermal correction to Energy= 0.397534
Thermal correction to Enthalpy= 0.398478
Thermal correction to Gibbs Free Energy= 0.303390
Sum of electronic and zero-point Energies= -2029.237985
Sum of electronic and thermal Energies= -2029.207135
Sum of electronic and thermal Enthalpies= -2029.206191
Sum of electronic and thermal Free Energies= -2029.301280
UM06-2X/def2-TZVPP-CPCM(DMSO)// UM06-2X/def2-SVP-CPCM(DMSO)
HF=-2031.6106623
A1 = A1.2-A1-WB97X



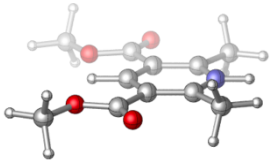
WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.341296 (Hartree/Particle)
Thermal correction to Energy= 0.362267
Thermal correction to Enthalpy= 0.363211
Thermal correction to Gibbs Free Energy= 0.291766
Sum of electronic and zero-point Energies= -900.610712
Sum of electronic and thermal Energies= -900.589741
Sum of electronic and thermal Enthalpies= -900.588797
Sum of electronic and thermal Free Energies= -900.660241
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-901.9464238
A1 = A1.2-B1-WB97X



WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.123928 (Hartree/Particle)
Thermal correction to Energy= 0.136753
Thermal correction to Enthalpy= 0.137697
Thermal correction to Gibbs Free Energy= 0.082576
Sum of electronic and zero-point Energies= -1247.231280
Sum of electronic and thermal Energies= -1247.218456
Sum of electronic and thermal Enthalpies= -1247.217511
Sum of electronic and thermal Free Energies= -1247.272632
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-1248.4639119
A1 = A1.2-C1-WB97X, A1.3-WB97X

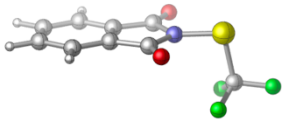


WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.466284 (Hartree/Particle)
Thermal correction to Energy= 0.501867
Thermal correction to Enthalpy= 0.502812
Thermal correction to Gibbs Free Energy= 0.396343
Sum of electronic and zero-point Energies= -2147.858909
Sum of electronic and thermal Energies= -2147.823326
Sum of electronic and thermal Enthalpies= -2147.822382
Sum of electronic and thermal Free Energies= -2147.928851
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-2150.4216097
A1 = A1.2-A1+-WB97X

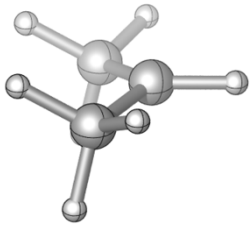


WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.246369 (Hartree/Particle)
Thermal correction to Energy= 0.262795
Thermal correction to Enthalpy= 0.263739
Thermal correction to Gibbs Free Energy= 0.201483
Sum of electronic and zero-point Energies= -782.123064
Sum of electronic and thermal Energies= -782.106638
Sum of electronic and thermal Enthalpies= -782.105694
Sum of electronic and thermal Free Energies= -782.167950
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-783.2377736

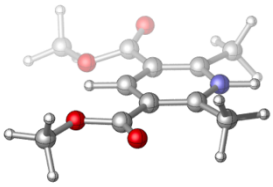
A1 = A1.2-(B2-)-WB97X



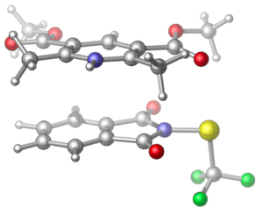
WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.121452 (Hartree/Particle)
Thermal correction to Energy= 0.134351
Thermal correction to Enthalpy= 0.135295
Thermal correction to Gibbs Free Energy= 0.079426
Sum of electronic and zero-point Energies= -1247.338845
Sum of electronic and thermal Energies= -1247.325946
Sum of electronic and thermal Enthalpies= -1247.325002
Sum of electronic and thermal Free Energies= -1247.380871
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-1248.5759505
A1 = A1.2-Isopropyl Radical-WB97X



WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.088250 (Hartree/Particle)
Thermal correction to Energy= 0.093449
Thermal correction to Enthalpy= 0.094393
Thermal correction to Gibbs Free Energy= 0.060953
Sum of electronic and zero-point Energies= -118.267761
Sum of electronic and thermal Energies= -118.262561
Sum of electronic and thermal Enthalpies= -118.261617
Sum of electronic and thermal Free Energies= -118.295057
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-118.4862457
A1 = A1.2-A2-WB97X

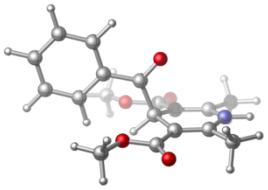


WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.241202 (Hartree/Particle)
Thermal correction to Energy= 0.258398
Thermal correction to Enthalpy= 0.259342
Thermal correction to Gibbs Free Energy= 0.194811
Sum of electronic and zero-point Energies= -782.247394
Sum of electronic and thermal Energies= -782.230199
Sum of electronic and thermal Enthalpies= -782.229255
Sum of electronic and thermal Free Energies= -782.293785
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-783.3585918
A1 = A1.2-D2-WB97X, A1.3-WB97X



WB97X/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.366366 (Hartree/Particle)
Thermal correction to Energy= 0.398133
Thermal correction to Enthalpy= 0.399077
Thermal correction to Gibbs Free Energy= 0.299965
Sum of electronic and zero-point Energies= -2029.495308
Sum of electronic and thermal Energies= -2029.463540
Sum of electronic and thermal Enthalpies= -2029.462596
Sum of electronic and thermal Free Energies= -2029.561709
WB97X/def2-TZVPP-CPCM(DMSO)//WB97X/def2-SVP-CPCM(DMSO)
HF=-2031.8130767

A1 = A1.4-A1-Acyl Benzene, A1.7-A1-Acyl Benzene, A1.8-A1, A1.9-A1-Acyl Benzene, A1.11-A1, A1.11-A1-Acyl Benzene, A1.12-A1-Acyl Benzene



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.343249 (Hartree/Particle)
Thermal correction to Energy= 0.366798
Thermal correction to Enthalpy= 0.367742
Thermal correction to Gibbs Free Energy= 0.288191
Sum of electronic and zero-point Energies= -1127.148444
Sum of electronic and thermal Energies= -1127.124896
Sum of electronic and thermal Enthalpies= -1127.123952
Sum of electronic and thermal Free Energies= -1127.203502
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.393868440500
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.7534366
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.7361313
TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1127.4916935
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.3410 eV 529.62 nm f=0.0000 <S**2>=2.000
87A -> 88A 0.62111
87A -> 89A 0.30634
87B -> 88B -0.62111
87B -> 89B -0.30634

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.8624 eV 433.15 nm f=0.0234 <S**2>=0.000
84A -> 88A 0.10955
87A -> 88A 0.69062
84B -> 88B 0.10955
87B -> 88B 0.69062
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1127.38650261
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.9336 eV 422.64 nm f=0.0000 <S**2>=2.000
84A -> 88A -0.29796
87A -> 88A -0.25740
87A -> 89A 0.56491
84B -> 88B 0.29796
87B -> 88B 0.25740
87B -> 89B -0.56491

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.2609 eV 380.21 nm f=0.0000 <S**2>=2.000
82A -> 89A -0.13997
83A -> 89A -0.10967
85A -> 88A -0.12375
85A -> 90A -0.22227
86A -> 88A 0.52439
86A -> 89A -0.29084
82B -> 89B 0.13997
83B -> 89B 0.10967
85B -> 88B 0.12375
85B -> 90B 0.22227
86B -> 88B -0.52439
86B -> 89B 0.29084

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.4586 eV 358.48 nm f=0.0000 <S**2>=2.000
82A -> 88A 0.24278
82A -> 89A 0.16196
83A -> 88A 0.34492
83A -> 89A 0.26341
85A -> 88A 0.11946
85A -> 89A 0.12969
86A -> 89A -0.21801
87A -> 91A 0.34529
82B -> 88B -0.24278
82B -> 89B -0.16196
83B -> 88B -0.34492
83B -> 89B -0.26341
85B -> 88B -0.11946
85B -> 89B -0.12969
86B -> 89B 0.21801
87B -> 91B -0.34529

Excited state symmetry could not be determined.
Excited State 6: 1.000-?Sym 3.5350 eV 350.74 nm f=0.1307 <S**2>=0.000
87A -> 89A 0.69439
87B -> 89B 0.69439

Excited state symmetry could not be determined.
Excited State 7: 3.000-?Sym 3.7181 eV 333.46 nm f=0.0000 <S**2>=2.000
84A -> 88A 0.58041
84A -> 89A -0.18934
84A -> 92A -0.12391
87A -> 88A -0.19271
87A -> 89A 0.26365
84B -> 88B -0.58041
84B -> 89B 0.18934
84B -> 92B 0.12391
87B -> 88B 0.19271
87B -> 89B -0.26365

Excited state symmetry could not be determined.
Excited State 8: 3.000-?Sym 3.9203 eV 316.26 nm f=0.0000 <S**2>=2.000
83A -> 88A -0.18854
83A -> 89A 0.12518
85A -> 88A 0.55135
85A -> 89A -0.31330
86A -> 88A 0.13072
83B -> 88B 0.18854
83B -> 89B -0.12518
85B -> 88B -0.55135
85B -> 89B 0.31330
86B -> 88B -0.13072

Excited state symmetry could not be determined.
Excited State 9: 1.000-?Sym 4.0501 eV 306.13 nm f=0.0046 <S**2>=0.000
84A -> 88A 0.65572
84A -> 89A -0.18799
84A -> 92A -0.10213
87A -> 88A -0.11222
84B -> 88B 0.65572
84B -> 89B -0.18799
84B -> 92B -0.10213
87B -> 88B -0.11222

Excited state symmetry could not be determined.
Excited State 10: 3.000-?Sym 4.2600 eV 291.04 nm f=0.0000 <S**2>=2.000
81A -> 91A -0.18032
82A -> 88A -0.30269
82A -> 89A -0.21541
83A -> 88A 0.35928
83A -> 89A 0.21405
85A -> 88A 0.16195
85A -> 89A 0.17221
86A -> 88A 0.14480
86A -> 89A 0.14162
87A -> 91A -0.19707
81B -> 91B 0.18032
82B -> 88B 0.30269
82B -> 89B 0.21541
83B -> 88B -0.35928
83B -> 89B -0.21405
85B -> 88B -0.16195
85B -> 89B -0.17221
86B -> 88B -0.14480
86B -> 89B -0.14162
87B -> 91B 0.19707

Excited state symmetry could not be determined.
Excited State 11: 3.000-?Sym 4.3624 eV 284.21 nm f=0.0000 <S**2>=2.000
82A -> 88A -0.11000
83A -> 88A -0.11399
83A -> 90A -0.16532
85A -> 90A 0.41434
86A -> 88A 0.29883
87A -> 91A 0.37514
82B -> 88B 0.11000
83B -> 88B 0.11399
83B -> 90B 0.16532
85B -> 90B -0.41434
86B -> 88B -0.29883
87B -> 91B -0.37514

Excited state symmetry could not be determined.
Excited State 12: 3.000-?Sym 4.4689 eV 277.44 nm f=0.0000 <S**2>=2.000
82A -> 88A -0.28852
82A -> 89A -0.12018
83A -> 88A -0.11887
83A -> 90A 0.15041
85A -> 90A -0.38708
86A -> 89A 0.19022
87A -> 91A 0.39250
82B -> 88B 0.28852
82B -> 89B 0.12018
83B -> 88B 0.11887
83B -> 90B -0.15041
85B -> 90B 0.38708
86B -> 89B -0.19022
87B -> 91B -0.39250

Excited state symmetry could not be determined.
Excited State 13: 1.000-?Sym 4.4768 eV 276.95 nm f=0.0070 <S**2>=0.000

81A -> 91A -0.10757
82A -> 88A -0.23005
82A -> 89A -0.16074
83A -> 88A 0.29505
83A -> 89A 0.15452
85A -> 88A 0.46470
86A -> 88A 0.24361
81B -> 91B -0.10757
82B -> 88B -0.23005
82B -> 89B -0.16074
83B -> 88B 0.29505
83B -> 89B 0.15452
85B -> 88B 0.46470
86B -> 88B 0.24361

Excited state symmetry could not be determined.
Excited State 14: 3.000-?Sym 4.5287 eV 273.77 nm f=0.0000 <S**2>=2.000
81A -> 88A 0.50503
81A -> 89A 0.39417
82A -> 91A 0.17612
83A -> 91A -0.16500
81B -> 88B -0.50503
81B -> 89B -0.39417
82B -> 91B -0.17612
83B -> 91B 0.16500

Excited state symmetry could not be determined.
Excited State 15: 1.000-?Sym 4.5929 eV 269.95 nm f=0.0174 <S**2>=0.000
82A -> 88A -0.18606
83A -> 88A 0.43522
85A -> 88A -0.42808
85A -> 89A 0.18033
86A -> 90A -0.16407
82B -> 88B -0.18606
83B -> 88B 0.43522
85B -> 88B -0.42808
85B -> 89B 0.18033
86B -> 90B -0.16407

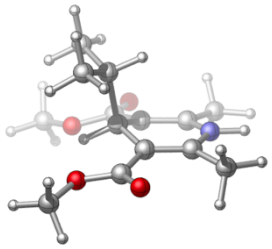
Excited state symmetry could not be determined.
Excited State 16: 1.000-?Sym 4.6629 eV 265.89 nm f=0.0078 <S**2>=0.000
82A -> 88A -0.17812
83A -> 88A -0.26798
85A -> 88A -0.21924
86A -> 88A 0.53691
87A -> 91A 0.20177
82B -> 88B -0.17812
83B -> 88B -0.26798
85B -> 88B -0.21924
86B -> 88B 0.53691
87B -> 91B 0.20177

Excited state symmetry could not be determined.
Excited State 17: 3.000-?Sym 4.6719 eV 265.38 nm f=0.0000 <S**2>=2.000
87A -> 90A 0.70389
87B -> 90B -0.70388

Excited state symmetry could not be determined.
Excited State 18: 1.000-?Sym 4.6806 eV 264.89 nm f=0.0000 <S**2>=0.000
87A -> 90A 0.70453
87B -> 90B 0.70453

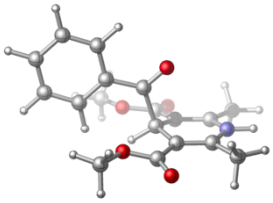
Excited state symmetry could not be determined.
Excited State 19: 1.000-?Sym 4.8063 eV 257.96 nm f=0.0004 <S**2>=0.000
81A -> 88A 0.59149
81A -> 89A 0.30835
82A -> 91A 0.12623
83A -> 91A -0.10493
84A -> 89A -0.11747
81B -> 88B 0.59149
81B -> 89B 0.30835
82B -> 91B 0.12623
83B -> 91B -0.10493
84B -> 89B -0.11747

Excited state symmetry could not be determined.
Excited State 20: 3.000-?Sym 4.8158 eV 257.45 nm f=0.0000 <S**2>=2.000
84A -> 88A 0.21680
84A -> 89A 0.65460
84B -> 88B -0.21680
84B -> 89B -0.65460
A1 = A1.4-A2+-Isopropyl

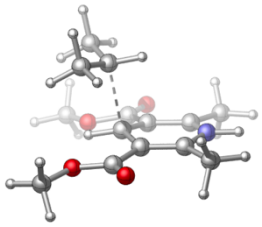


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.336315 (Hartree/Particle)
Thermal correction to Energy= 0.357311
Thermal correction to Enthalpy= 0.358255
Thermal correction to Gibbs Free Energy= 0.286359
Sum of electronic and zero-point Energies= -900.668395

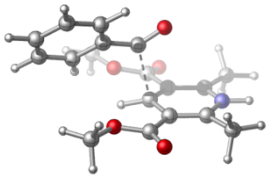
Sum of electronic and thermal Energies= -900.647399
Sum of electronic and thermal Enthalpies= -900.646455
Sum of electronic and thermal Free Energies= -900.718351
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.066022601206
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.0164986
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.9454705
A1 = S1-A2+-Acyl Benzene



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.342636 (Hartree/Particle)
Thermal correction to Energy= 0.366226
Thermal correction to Enthalpy= 0.367171
Thermal correction to Gibbs Free Energy= 0.287094
Sum of electronic and zero-point Energies= -1126.948194
Sum of electronic and thermal Energies= -1126.924604
Sum of electronic and thermal Enthalpies= -1126.923660
Sum of electronic and thermal Free Energies= -1127.003737
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.128566024180
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.5487959
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.4790695
A1 = A1.4-A2+-TS-A2+'-Isopropyl

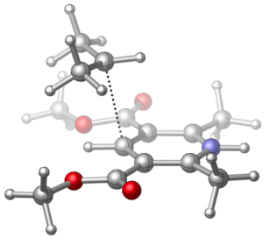


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.333841 (Hartree/Particle)
Thermal correction to Energy= 0.355102
Thermal correction to Enthalpy= 0.356046
Thermal correction to Gibbs Free Energy= 0.283369
Sum of electronic and zero-point Energies= -900.661841
Sum of electronic and thermal Energies= -900.640581
Sum of electronic and thermal Enthalpies= -900.639636
Sum of electronic and thermal Free Energies= -900.712313
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.051676127886
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.010025
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.9395089
A1 = A1.4- A2+-TS-A2+'-Acyl

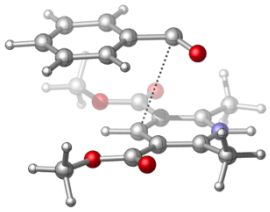


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.341220 (Hartree/Particle)
Thermal correction to Energy= 0.365025
Thermal correction to Enthalpy= 0.365969
Thermal correction to Gibbs Free Energy= 0.284825
Sum of electronic and zero-point Energies= -1126.942654
Sum of electronic and thermal Energies= -1126.918850

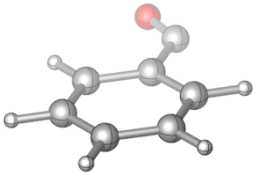
Sum of electronic and thermal Enthalpies= -1126.917905
Sum of electronic and thermal Free Energies= -1126.999049
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.122202700034
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.545419
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.4772365
A1 = A1.4- A2+'-Isopropyl



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.332347 (Hartree/Particle)
Thermal correction to Energy= 0.355189
Thermal correction to Enthalpy= 0.356133
Thermal correction to Gibbs Free Energy= 0.278221
Sum of electronic and zero-point Energies= -900.665127
Sum of electronic and thermal Energies= -900.642285
Sum of electronic and thermal Enthalpies= -900.641341
Sum of electronic and thermal Free Energies= -900.719254
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.053306488526
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.0131087
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.9419462
A1 = A1.4- A2+'-Acyl Benzene

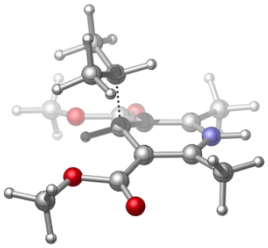


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.341815 (Hartree/Particle)
Thermal correction to Energy= 0.366506
Thermal correction to Enthalpy= 0.367450
Thermal correction to Gibbs Free Energy= 0.283877
Sum of electronic and zero-point Energies= -1126.947424
Sum of electronic and thermal Energies= -1126.922733
Sum of electronic and thermal Enthalpies= -1126.921789
Sum of electronic and thermal Free Energies= -1127.005363
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.131429970146
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.551442
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.4802767
A1 = A1.4-Acyl Benzene radical



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.097726 (Hartree/Particle)
Thermal correction to Energy= 0.104001
Thermal correction to Enthalpy= 0.104945
Thermal correction to Gibbs Free Energy= 0.066530
Sum of electronic and zero-point Energies= -344.586586
Sum of electronic and thermal Energies= -344.580311
Sum of electronic and thermal Enthalpies= -344.579367

Sum of electronic and thermal Free Energies= -344.617782
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -344.313628136075
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-345.0689374
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-345.0638187
A1 = A1.5-A1-S1'



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.1883466
Zero-point correction= 0.331995 (Hartree/Particle)
Thermal correction to Energy= 0.353674
Thermal correction to Enthalpy= 0.354619
Thermal correction to Gibbs Free Energy= 0.281806
Sum of electronic and zero-point Energies= -900.755923
Sum of electronic and thermal Energies= -900.734244
Sum of electronic and thermal Enthalpies= -900.733300
Sum of electronic and thermal Free Energies= -900.806113
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 1.8243 eV 679.62 nm f=0.0000 <S**2>=2.000
71A -> 74A 0.10127
72A -> 73A 0.69957
71B -> 74B -0.10127
72B -> 73B -0.69957

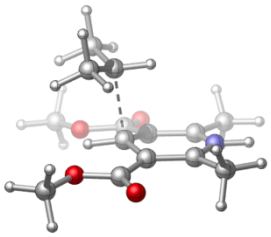
Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.7328 eV 453.69 nm f=0.1558 <S**2>=0.000
72A -> 73A 0.70655
72B -> 73B 0.70655

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -901.087918857
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.8931 eV 428.55 nm f=0.0000 <S**2>=2.000
70A -> 73A 0.16242
71A -> 73A 0.60184
72A -> 74A 0.32020
70B -> 73B -0.16242
71B -> 73B -0.60184
72B -> 74B -0.32020

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.8854 eV 319.10 nm f=0.0000 <S**2>=2.000
70A -> 73A 0.25278
71A -> 73A -0.35121
72A -> 74A 0.54355
70B -> 73B -0.25278
71B -> 73B 0.35121
72B -> 74B -0.54355

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 4.1678 eV 297.48 nm f=0.0000 <S**2>=2.000
69A -> 74A 0.16676
70A -> 73A 0.60448
72A -> 74A -0.30823
69B -> 74B -0.16676
70B -> 73B -0.60448
72B -> 74B 0.30823
A1 = A1.5-A1-S1'-TS- A1-S1''



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.1335116
Zero-point correction= 0.330460 (Hartree/Particle)
Thermal correction to Energy= 0.352252
Thermal correction to Enthalpy= 0.353197
Thermal correction to Gibbs Free Energy= 0.279656

Sum of electronic and zero-point Energies= -900.753949
Sum of electronic and thermal Energies= -900.732157
Sum of electronic and thermal Enthalpies= -900.731212
Sum of electronic and thermal Free Energies= -900.804753
Excitation energies and oscillator strengths:

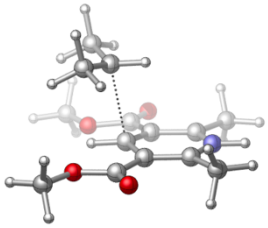
Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 1.8403 eV 673.71 nm f=0.0000 <S**2>=2.000
72A -> 73A -0.69937
72B -> 73B 0.69938

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.4227 eV 511.77 nm f=0.0620 <S**2>=0.000
72A -> 73A 0.70655
72B -> 73B 0.70654
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -901.067758526
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.5306 eV 489.93 nm f=0.0000 <S**2>=2.000
71A -> 73A -0.13147
72A -> 74A -0.56148
72A -> 75A 0.39729
71B -> 73B 0.13147
72B -> 74B 0.56148
72B -> 75B -0.39729

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.3630 eV 368.67 nm f=0.0000 <S**2>=2.000
70A -> 73A -0.17400
71A -> 73A -0.36239
72A -> 74A -0.26317
72A -> 75A -0.49566
70B -> 73B 0.17400
71B -> 73B 0.36238
72B -> 74B 0.26318
72B -> 75B 0.49566

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.9644 eV 312.74 nm f=0.0000 <S**2>=2.000
71A -> 73A -0.54480
72A -> 74A 0.33080
72A -> 75A 0.26204
71B -> 73B 0.54481
72B -> 74B -0.33087
72B -> 75B -0.26206
A1 = A1.5-A1-S1''



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-901.1103778
Zero-point correction= 0.330034 (Hartree/Particle)
Thermal correction to Energy= 0.353060
Thermal correction to Enthalpy= 0.354004
Thermal correction to Gibbs Free Energy= 0.276287
Sum of electronic and zero-point Energies= -900.754591
Sum of electronic and thermal Energies= -900.731566
Sum of electronic and thermal Enthalpies= -900.730622
Sum of electronic and thermal Free Energies= -900.808339
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym -0.9336 eV -1328.09 nm f=-0.0000 <S**2>=2.000
72A -> 74A -0.72670
72B -> 74B 0.72670
72A <- 74A -0.19949
72B <- 74B 0.19949

Excited state symmetry could not be determined.
Excited State 2: 3.000-?Sym 0.1430 eV 8667.45 nm f=0.0000 <S**2>=2.000
72A -> 73A -0.84957
72B -> 73B 0.84957
72A <- 73A -0.47405
72B <- 73B 0.47405

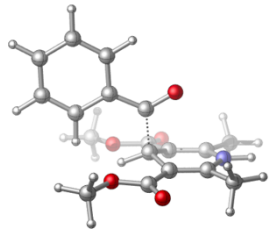
Excited state symmetry could not be determined.
Excited State 3: 1.000-?Sym 0.6488 eV 1911.04 nm f=0.0044 <S**2>=0.000
72A -> 73A 0.71217
72B -> 73B 0.71217

This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -901.084619635
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 2.1826 eV 568.05 nm f=0.0000 <S**2>=2.000
71A -> 73A 0.19854
72A -> 75A -0.67426
71B -> 73B -0.19854
72B -> 75B 0.67426

Excited state symmetry could not be determined.
Excited State 5: 1.000-?Sym 2.6223 eV 472.82 nm f=0.5061 <S**2>=0.000
72A -> 74A 0.69596
72A -> 75A 0.17485
72B -> 74B 0.69596
72B -> 75B 0.17485
72A <- 74A -0.15562
72B <- 74B -0.15562

Excited state symmetry could not be determined.
Excited State 6: 1.000-?Sym 2.7616 eV 448.95 nm f=0.0836 <S**2>=0.000
72A -> 74A -0.18476
72A -> 75A 0.67962
72B -> 74B -0.18476
72B -> 75B 0.67962
A1 = A1.6-A1-S1'



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1127.4754066
Zero-point correction= 0.340048 (Hartree/Particle)
Thermal correction to Energy= 0.363732
Thermal correction to Enthalpy= 0.364676
Thermal correction to Gibbs Free Energy= 0.286066
Sum of electronic and zero-point Energies= -1127.061419
Sum of electronic and thermal Energies= -1127.037735
Sum of electronic and thermal Enthalpies= -1127.036791
Sum of electronic and thermal Free Energies= -1127.115402
Excitation energies and oscillator strengths:

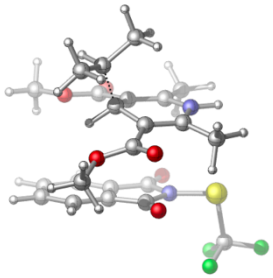
Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.3410 eV 529.62 nm f=0.0000 <S**2>=2.000
87A -> 88A 0.62111
87A -> 89A 0.30634
87B -> 88B -0.62111
87B -> 89B -0.30634

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.8516 eV 434.78 nm f=0.0345 <S**2>=0.000
84A -> 88A 0.10506
87A -> 88A 0.69321
84B -> 88B 0.10506
87B -> 88B 0.69321
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -1127.38689775
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.9336 eV 422.64 nm f=0.0000 <S**2>=2.000
84A -> 88A -0.29797
87A -> 88A -0.25740
87A -> 89A 0.56490
84B -> 88B 0.29797
87B -> 88B 0.25740
87B -> 89B -0.56490

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.2609 eV 380.21 nm f=0.0000 <S**2>=2.000
82A -> 89A -0.13996
83A -> 89A -0.10967
85A -> 88A -0.12375
85A -> 90A -0.22227
86A -> 88A 0.52439
86A -> 89A -0.29084
82B -> 89B 0.13996
83B -> 89B 0.10967
85B -> 88B 0.12375
85B -> 90B 0.22227
86B -> 88B -0.52439
86B -> 89B 0.29084

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.4586 eV 358.48 nm f=0.0000 <S**2>=2.000
82A -> 88A 0.24278
82A -> 89A 0.16196
83A -> 88A 0.34492
83A -> 89A 0.26341
85A -> 88A 0.11946
85A -> 89A 0.12969
86A -> 89A -0.21801
87A -> 91A 0.34529
82B -> 88B -0.24278
82B -> 89B -0.16196
83B -> 88B -0.34492
83B -> 89B -0.26341
85B -> 88B -0.11946
85B -> 89B -0.12969
86B -> 89B 0.21801
87B -> 91B -0.34529
A1 = A1.7-C1-S1'



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.8008882
Zero-point correction= 0.457921 (Hartree/Particle)
Thermal correction to Energy= 0.493576
Thermal correction to Enthalpy= 0.494521
Thermal correction to Gibbs Free Energy= 0.388667
Sum of electronic and zero-point Energies= -2148.290788
Sum of electronic and thermal Energies= -2148.255132
Sum of electronic and thermal Enthalpies= -2148.254188
Sum of electronic and thermal Free Energies= -2148.360042
Excitation energies and oscillator strengths:

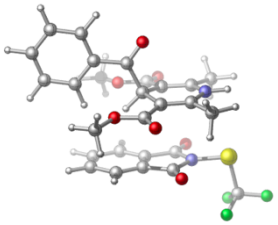
Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 1.3943 eV 889.22 nm f=0.0000 <S**2>=2.000
134A ->135A 0.70589
134B ->135B -0.70588

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 1.4201 eV 873.05 nm f=0.0018 <S**2>=0.000
134A ->135A 0.70672
134B ->135B 0.70673
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2148.74870825
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.2812 eV 543.51 nm f=0.0000 <S**2>=2.000
134A ->137A -0.69211
134B ->137B 0.69211

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 2.6835 eV 462.02 nm f=0.0000 <S**2>=2.000
124A ->135A 0.18361
128A ->136A 0.15397
130A ->135A -0.53001
130A ->140A -0.10319
131A ->135A 0.15393
132A ->135A 0.13169
133A ->135A -0.30474
124B ->135B -0.18360
128B ->136B -0.15397
130B ->135B 0.53001
130B ->140B 0.10319
131B ->135B -0.15393
132B ->135B -0.13169
133B ->135B 0.30474

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.0092 eV 412.02 nm f=0.0000 <S**2>=2.000
130A ->135A 0.22257
133A ->135A -0.24442
134A ->136A -0.61551
130B ->135B -0.22257
133B ->135B 0.24442
134B ->136B 0.61552
A1 = A1.8-C1, A1.9-C1-Acyl Benzene, A1.10-C1, A1.11-C1-Acyl Benzene, A1.12-C1-Acyl Benzene, S29- C1-Acyl Benzene



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.466369 (Hartree/Particle)
Thermal correction to Energy= 0.504630
Thermal correction to Enthalpy= 0.505574
Thermal correction to Gibbs Free Energy= 0.391966
Sum of electronic and zero-point Energies= -2374.639625
Sum of electronic and thermal Energies= -2374.601364
Sum of electronic and thermal Enthalpies= -2374.600420
Sum of electronic and thermal Free Energies= -2374.714028
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2373.040057354060
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.4792021
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.4517922
TD- B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2375.105994
Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.2927 eV 540.79 nm f=0.0000 <S**2>=2.000
149A ->150A -0.54706
149A ->151A 0.38481
149A ->153A 0.19185
149B ->150B 0.54706
149B ->151B -0.38480
149B ->153B -0.19185

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.4022 eV 516.13 nm f=0.0005 <S**2>=0.000
149A ->150A 0.70512
149B ->150B 0.70512

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.5018 eV 495.58 nm f=0.0000 <S**2>=2.000
149A ->150A 0.44228
149A ->151A 0.49983
149A ->153A 0.18921
149B ->150B -0.44227
149B ->151B -0.49983
149B ->153B -0.18921

Excited state symmetry could not be determined.
Excited State 4: 1.000-?Sym 2.9634 eV 418.38 nm f=0.0182 <S**2>=0.000
146A ->151A 0.11725
149A ->151A 0.68317
146B ->151B 0.11724
149B ->151B 0.68317
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2374.99708940
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 2.9842 eV 415.47 nm f=0.0000 <S**2>=2.000
146A ->151A -0.31217
146A ->153A 0.10514
149A ->151A -0.22562
149A ->152A 0.19836
149A ->153A 0.52312
146B ->151B 0.31217
146B ->153B -0.10514
149B ->151B 0.22564
149B ->152B -0.19836
149B ->153B -0.52312

Excited state symmetry could not be determined.
Excited State 6: 3.000-?Sym 3.1806 eV 389.82 nm f=0.0000 <S**2>=2.000
136A ->150A 0.12914
140A ->152A 0.13790
141A ->150A 0.40133
142A ->150A -0.36351
142A ->152A 0.14619
143A ->150A 0.13222
144A ->152A 0.10302
146A ->150A 0.24044
136B ->150B -0.12914
140B ->152B -0.13789
141B ->150B -0.40131
142B ->150B 0.36353
142B ->152B -0.14619
143B ->150B -0.13222

144B ->152B -0.10302
146B ->150B -0.24044

Excited state symmetry could not be determined.
Excited State 7: 3.000-?Sym 3.2580 eV 380.55 nm f=0.0000 <S**2>=2.000
144A ->153A -0.10943
147A ->151A -0.19646
147A ->153A 0.12504
147A ->155A 0.22333
148A ->151A 0.47776
148A ->152A -0.11888
148A ->153A -0.31449
144B ->153B 0.10943
147B ->151B 0.19646
147B ->153B -0.12504
147B ->155B -0.22333
148B ->151B -0.47776
148B ->152B 0.11888
148B ->153B 0.31449

Excited state symmetry could not be determined.
Excited State 8: 3.000-?Sym 3.4698 eV 357.33 nm f=0.0000 <S**2>=2.000
144A ->150A 0.16273
144A ->151A -0.28454
144A ->153A -0.18809
145A ->150A -0.16175
145A ->151A 0.28934
145A ->153A 0.21512
148A ->153A 0.12790
149A ->156A 0.33037
144B ->150B -0.16273
144B ->151B 0.28454
144B ->153B 0.18809
145B ->150B 0.16175
145B ->151B -0.28934
145B ->153B -0.21512
148B ->153B -0.12790
149B ->156B -0.33037

Excited state symmetry could not be determined.
Excited State 9: 3.000-?Sym 3.5586 eV 348.40 nm f=0.0000 <S**2>=2.000
139A ->150A -0.30625
140A ->150A 0.33320
141A ->150A -0.23415
142A ->150A -0.18451
149A ->152A 0.39793
149A ->153A -0.14120
139B ->150B 0.30625
140B ->150B -0.33321
141B ->150B 0.23415
142B ->150B 0.18448
149B ->152B -0.39784
149B ->153B 0.14127

Excited state symmetry could not be determined.
Excited State 10: 1.000-?Sym 3.5622 eV 348.06 nm f=0.0768 <S**2>=0.000
149A ->151A 0.11512
149A ->152A 0.45359
149A ->153A 0.51756
149B ->151B 0.11512
149B ->152B 0.45359
149B ->153B 0.51756

Excited state symmetry could not be determined.
Excited State 11: 3.000-?Sym 3.5679 eV 347.49 nm f=0.0000 <S**2>=2.000
139A ->150A -0.23313
140A ->150A 0.34028
141A ->150A -0.13025
144A ->150A 0.10123
149A ->152A -0.50335
149A ->153A 0.17846
139B ->150B 0.23313
140B ->150B -0.34028
141B ->150B 0.13024
144B ->150B -0.10124
149B ->152B 0.50338
149B ->153B -0.17837

Excited state symmetry could not be determined.
Excited State 12: 1.000-?Sym 3.6074 eV 343.70 nm f=0.0271 <S**2>=0.000
149A ->152A 0.53793
149A ->153A -0.45350
149B ->152B 0.53796
149B ->153B -0.45351

Excited state symmetry could not be determined.
Excited State 13: 3.000-?Sym 3.6218 eV 342.32 nm f=0.0000 <S**2>=2.000
137A ->150A 0.11466
140A ->150A 0.31533
141A ->150A 0.28661
142A ->150A 0.39783
144A ->150A 0.30505
149A ->152A 0.15739
137B ->150B -0.11466
140B ->150B -0.31531
141B ->150B -0.28664
142B ->150B -0.39782
144B ->150B -0.30505
149B ->152B -0.15742

Excited state symmetry could not be determined.

Excited State 14: 3.000-?Sym 3.7527 eV 330.38 nm f=0.0000 <S**2>=2.000

146A ->151A	0.54028
146A ->153A	-0.19455
146A ->159A	-0.11384
149A ->151A	-0.19406
149A ->153A	0.28712
146B ->151B	-0.54028
146B ->153B	0.19455
146B ->159B	0.11384
149B ->151B	0.19406
149B ->153B	-0.28712

Excited state symmetry could not be determined.

Excited State 15: 3.000-?Sym 3.9029 eV 317.67 nm f=0.0000 <S**2>=2.000

144A ->150A	0.10580
147A ->151A	0.22625
147A ->153A	-0.11926
148A ->150A	-0.61515
144B ->150B	-0.10584
147B ->151B	-0.22625
147B ->153B	0.11926
148B ->150B	0.61533

Excited state symmetry could not be determined.

Excited State 16: 1.000-?Sym 3.9084 eV 317.23 nm f=0.0047 <S**2>=0.000

144A ->150A	-0.14780
148A ->150A	0.68226
144B ->150B	-0.14780
148B ->150B	0.68231

Excited state symmetry could not be determined.

Excited State 17: 3.000-?Sym 3.9094 eV 317.15 nm f=0.0000 <S**2>=2.000

145A ->151A	-0.12764
147A ->151A	-0.46898
147A ->152A	0.11633
147A ->153A	0.30920
148A ->150A	-0.28122
148A ->151A	-0.18333
148A ->153A	0.11104
145B ->151B	0.12763
147B ->151B	0.46898
147B ->152B	-0.11634
147B ->153B	-0.30919
148B ->150B	0.28072
148B ->151B	0.18334
148B ->153B	-0.11103

Excited state symmetry could not be determined.

Excited State 18: 1.000-?Sym 3.9311 eV 315.39 nm f=0.0004 <S**2>=0.000

139A ->150A	-0.30205
140A ->150A	0.47409
141A ->150A	-0.30970
142A ->150A	-0.20889
145A ->150A	-0.11419
147A ->150A	0.10191
139B ->150B	-0.30206
140B ->150B	0.47410
141B ->150B	-0.30970
142B ->150B	-0.20886
145B ->150B	-0.11419
147B ->150B	0.10191

Excited state symmetry could not be determined.

Excited State 19: 3.000-?Sym 3.9675 eV 312.50 nm f=0.0000 <S**2>=2.000

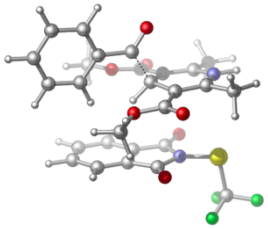
145A ->150A	0.43404
147A ->150A	-0.50229
149A ->156A	0.12442
145B ->150B	-0.43411
147B ->150B	0.50238
149B ->156B	-0.12442

Excited state symmetry could not be determined.

Excited State 20: 1.000-?Sym 3.9789 eV 311.61 nm f=0.0128 <S**2>=0.000

140A ->150A	-0.10220
145A ->150A	-0.39032
147A ->150A	0.55266
140B ->150B	-0.10220
145B ->150B	-0.39024
147B ->150B	0.55257

A1 = A1.8-C1-S1’



TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2375.0863201
Zero-point correction= 0.464203 (Hartree/Particle)
Thermal correction to Energy= 0.502240
Thermal correction to Enthalpy= 0.503184
Thermal correction to Gibbs Free Energy= 0.391342
Sum of electronic and zero-point Energies= -2374.570100
Sum of electronic and thermal Energies= -2374.532064

Sum of electronic and thermal Enthalpies= -2374.531119
Sum of electronic and thermal Free Energies= -2374.642961
Excitation energies and oscillator strengths:

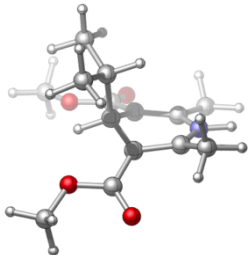
Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 1.3883 eV 893.08 nm f=0.0000 <S**2>=2.000
149A ->150A 0.70226
149B ->150B -0.70223

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 1.4154 eV 875.94 nm f=0.0007 <S**2>=0.000
149A ->150A 0.70651
149B ->150B 0.70654
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2375.03430353
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

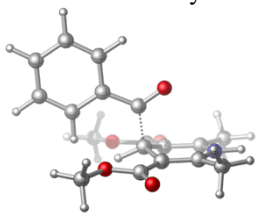
Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.0810 eV 595.79 nm f=0.0000 <S**2>=2.000
149A ->151A 0.58135
149A ->152A -0.22494
149A ->153A -0.30192
149B ->151B -0.58135
149B ->152B 0.22494
149B ->153B 0.30192

Excited state symmetry could not be determined.
Excited State 4: 1.000-?Sym 2.5670 eV 482.99 nm f=0.0161 <S**2>=0.000
149A ->151A 0.68558
149A ->152A -0.11811
149B ->151B 0.68558
149B ->152B -0.11811

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 2.6280 eV 471.78 nm f=0.0000 <S**2>=2.000
145A ->151A 0.15539
149A ->151A 0.33546
149A ->152A 0.13121
149A ->153A 0.56235
145B ->151B -0.15539
149B ->151B -0.33546
149B ->152B -0.13121
149B ->153B -0.56235
A1 = A1.11-A3-Isopropyl

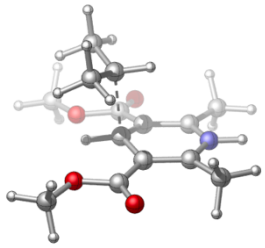


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.333272 (Hartree/Particle)
Thermal correction to Energy= 0.354846
Thermal correction to Enthalpy= 0.355791
Thermal correction to Gibbs Free Energy= 0.282085
Sum of electronic and zero-point Energies= -900.783616
Sum of electronic and thermal Energies= -900.762041
Sum of electronic and thermal Enthalpies= -900.761097
Sum of electronic and thermal Free Energies= -900.834803
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.229414669041
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1315237
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1179405
A1 = A1.11-A3-Acyl Benzene

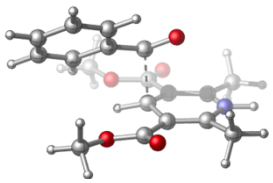


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.339649 (Hartree/Particle)
Thermal correction to Energy= 0.363528
Thermal correction to Enthalpy= 0.364472
Thermal correction to Gibbs Free Energy= 0.283510
Sum of electronic and zero-point Energies= -1127.072295
Sum of electronic and thermal Energies= -1127.048416

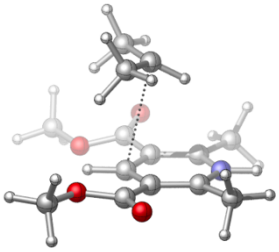
Sum of electronic and thermal Enthalpies= -1127.047472
Sum of electronic and thermal Free Energies= -1127.128433
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.295174518795
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.672981
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.6554604
A1 = A1.11-A3-TS-A3'-Isopropyl



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.330069 (Hartree/Particle)
Thermal correction to Energy= 0.351825
Thermal correction to Enthalpy= 0.352769
Thermal correction to Gibbs Free Energy= 0.278361
Sum of electronic and zero-point Energies= -900.772450
Sum of electronic and thermal Energies= -900.750694
Sum of electronic and thermal Enthalpies= -900.749750
Sum of electronic and thermal Free Energies= -900.824158
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.208160150973
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1194436
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1042925
A1 = A1.11-A3- TS-A3'-Acyl Benzene

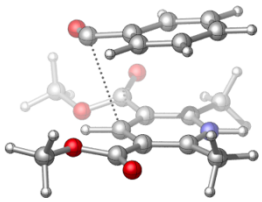


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.337895 (Hartree/Particle)
Thermal correction to Energy= 0.361904
Thermal correction to Enthalpy= 0.362848
Thermal correction to Gibbs Free Energy= 0.282044
Sum of electronic and zero-point Energies= -1127.062744
Sum of electronic and thermal Energies= -1127.038736
Sum of electronic and thermal Enthalpies= -1127.037791
Sum of electronic and thermal Free Energies= -1127.118596
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.282863067609
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.6649665
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.6470686
A1.11- A3'-Isopropyl

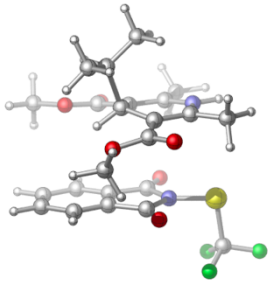


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.326550 (Hartree/Particle)
Thermal correction to Energy= 0.350472
Thermal correction to Enthalpy= 0.351416
Thermal correction to Gibbs Free Energy= 0.270103
Sum of electronic and zero-point Energies= -900.787442
Sum of electronic and thermal Energies= -900.763520

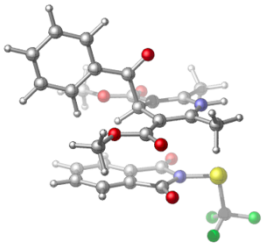
Sum of electronic and thermal Enthalpies= -900.762575
Sum of electronic and thermal Free Energies= -900.843889
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -900.229108811097
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1328418
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-902.1201325
A1 = A1.11- A3'-Acyl Benzene



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.337954 (Hartree/Particle)
Thermal correction to Energy= 0.362742
Thermal correction to Enthalpy= 0.363686
Thermal correction to Gibbs Free Energy= 0.281101
Sum of electronic and zero-point Energies= -1127.074832
Sum of electronic and thermal Energies= -1127.050044
Sum of electronic and thermal Enthalpies= -1127.049100
Sum of electronic and thermal Free Energies= -1127.131685
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1126.303824180438
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.6777059
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1128.6602024
A1 = A1.12-C3-Isopropyl

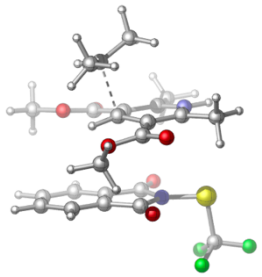


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.456357 (Hartree/Particle)
Thermal correction to Energy= 0.491964
Thermal correction to Enthalpy= 0.492908
Thermal correction to Gibbs Free Energy= 0.387011
Sum of electronic and zero-point Energies= -2148.279495
Sum of electronic and thermal Energies= -2148.243888
Sum of electronic and thermal Enthalpies= -2148.242943
Sum of electronic and thermal Free Energies= -2148.348840
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.859112987682
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8628486
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8360106
A1.12-C3-Acyl Benzene

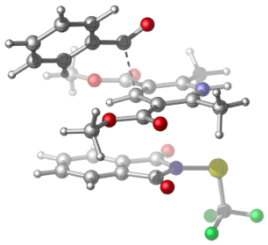


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.462598 (Hartree/Particle)
Thermal correction to Energy= 0.501028
Thermal correction to Enthalpy= 0.501973
Thermal correction to Gibbs Free Energy= 0.387355
Sum of electronic and zero-point Energies= -2374.563650

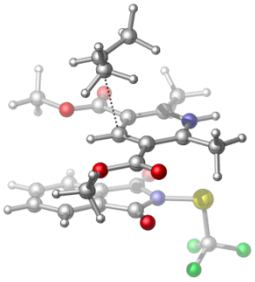
Sum of electronic and thermal Energies= -2374.525220
Sum of electronic and thermal Enthalpies= -2374.524276
Sum of electronic and thermal Free Energies= -2374.638894
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2372.915486519061
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.3983517
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.370404
A1 = A1.12-C3-TS-D3 -Isopropyl



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.453701 (Hartree/Particle)
Thermal correction to Energy= 0.489636
Thermal correction to Enthalpy= 0.490581
Thermal correction to Gibbs Free Energy= 0.383915
Sum of electronic and zero-point Energies= -2148.271514
Sum of electronic and thermal Energies= -2148.235578
Sum of electronic and thermal Enthalpies= -2148.234634
Sum of electronic and thermal Free Energies= -2148.341299
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.843914340117
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8555969
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8250287
A1 = A1.12-C3-TS-D3-Acyl Benzene

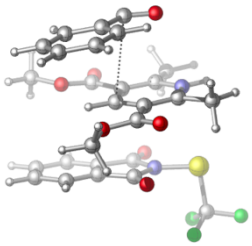


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.460164 (Hartree/Particle)
Thermal correction to Energy= 0.499010
Thermal correction to Enthalpy= 0.499954
Thermal correction to Gibbs Free Energy= 0.383329
Sum of electronic and zero-point Energies= -2374.552508
Sum of electronic and thermal Energies= -2374.513662
Sum of electronic and thermal Enthalpies= -2374.512717
Sum of electronic and thermal Free Energies= -2374.629343
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2372.958649882911
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.3899235
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.3605088
A1 = A1.12-D3-Isopropyl

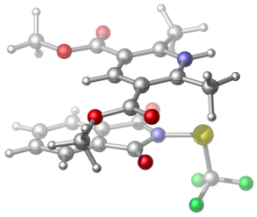


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.450640 (Hartree/Particle)
Thermal correction to Energy= 0.488984
Thermal correction to Enthalpy= 0.489928
Thermal correction to Gibbs Free Energy= 0.374368
Sum of electronic and zero-point Energies= -2148.281696

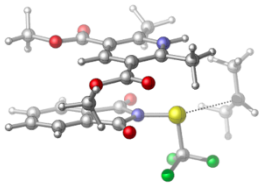
Sum of electronic and thermal Energies= -2148.243353
Sum of electronic and thermal Enthalpies= -2148.242409
Sum of electronic and thermal Free Energies= -2148.357969
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.868301663469
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.863441
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8375847
A1 = A1.12-D3-Acyl Benzene



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2030.3246213
Zero-point correction= 0.460837 (Hartree/Particle)
Thermal correction to Energy= 0.500494
Thermal correction to Enthalpy= 0.501438
Thermal correction to Gibbs Free Energy= 0.381831
Sum of electronic and zero-point Energies= -2374.565014
Sum of electronic and thermal Energies= -2374.525357
Sum of electronic and thermal Enthalpies= -2374.524413
Sum of electronic and thermal Free Energies= -2374.644020
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2372.944894836822
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.4040433
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2377.3763904
Thesis=D2, A1= A1.12-D2, A1.13-D2, A1.15-D2, A1.17-D2, A1.18-D2, A1.19-D2, A1.26-D2

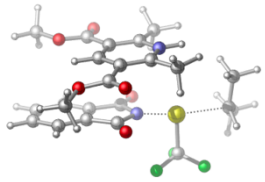


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.362077 (Hartree/Particle)
Thermal correction to Energy= 0.393323
Thermal correction to Enthalpy= 0.394268
Thermal correction to Gibbs Free Energy= 0.297724
Sum of electronic and zero-point Energies= -2029.962544
Sum of electronic and thermal Energies= -2029.931298
Sum of electronic and thermal Enthalpies= -2029.930354
Sum of electronic and thermal Free Energies= -2030.026897
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2028.615303993009
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3223082
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2980485
A1 = A1.13-E1, A1.14-step1, A1.15-E1, A1.16-E1, A1.17-E1, A1.26-E1

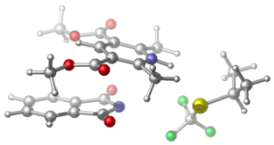


B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.7327989
Zero-point correction= 0.451049 (Hartree/Particle)
Thermal correction to Energy= 0.488920
Thermal correction to Enthalpy= 0.489864
Thermal correction to Gibbs Free Energy= 0.379058
Sum of electronic and zero-point Energies= -2148.281750

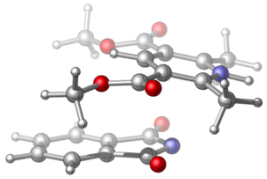
Sum of electronic and thermal Energies= -2148.243879
Sum of electronic and thermal Enthalpies= -2148.242935
Sum of electronic and thermal Free Energies= -2148.353741
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.841177296928
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8615474
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8390881
Thesis = D2-TS-E1, A1 = A1.13-E1-TS-F1, A1.14-step9, A1.15-E1-TS-F1, A1.17-E1-TS-F1



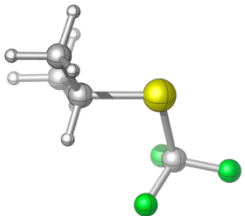
B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.724375
Thesis = E1, A1 = A1.13-F1, A1.15-F1, A1.16-F1, A1.17-F1, A1.26-F1



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.8139269
Zero-point correction= 0.457880 (Hartree/Particle)
Thermal correction to Energy= 0.494706
Thermal correction to Enthalpy= 0.495650
Thermal correction to Gibbs Free Energy= 0.384756
Sum of electronic and zero-point Energies= -2148.356047
Sum of electronic and thermal Energies= -2148.319221
Sum of electronic and thermal Enthalpies= -2148.318277
Sum of electronic and thermal Free Energies= -2148.429171
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2146.955295563632
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.9485799
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.9121836
Thesis = F1, A1 = A1.13-G1, A1.17-G1

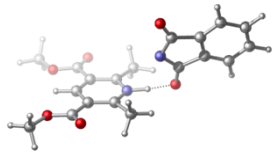


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.347484 (Hartree/Particle)
Thermal correction to Energy= 0.373140
Thermal correction to Enthalpy= 0.374084
Thermal correction to Gibbs Free Energy= 0.291066
Sum of electronic and zero-point Energies= -1294.528167
Sum of electronic and thermal Energies= -1294.502511
Sum of electronic and thermal Enthalpies= -1294.501567
Sum of electronic and thermal Free Energies= -1294.584584
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1293.635314105700
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3309552
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.2942719
Thesis = SCF3-Isopropyl, A1= SCF3-Isopropyl

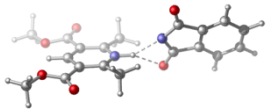


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.109359 (Hartree/Particle)
Thermal correction to Energy= 0.118458
Thermal correction to Enthalpy= 0.119402

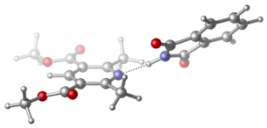
Thermal correction to Gibbs Free Energy= 0.074310
Sum of electronic and zero-point Energies= -853.815255
Sum of electronic and thermal Energies= -853.806156
Sum of electronic and thermal Enthalpies= -853.805212
Sum of electronic and thermal Free Energies= -853.850304
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -853.310631215421
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-854.6098218
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-854.6070123
A1 = H1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.345858 (Hartree/Particle)
Thermal correction to Energy= 0.371653
Thermal correction to Enthalpy= 0.372597
Thermal correction to Gibbs Free Energy= 0.285586
Sum of electronic and zero-point Energies= -1294.533907
Sum of electronic and thermal Energies= -1294.508112
Sum of electronic and thermal Enthalpies= -1294.507168
Sum of electronic and thermal Free Energies= -1294.594179
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1293.646192664067
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3373804
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3081755
Thesis = G1-TS-H1, A1 = H1-TS-I1

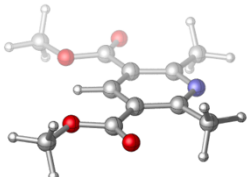


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.345819 (Hartree/Particle)
Thermal correction to Energy= 0.371374
Thermal correction to Enthalpy= 0.372318
Thermal correction to Gibbs Free Energy= 0.285899
Sum of electronic and zero-point Energies= -1294.527330
Sum of electronic and thermal Energies= -1294.501775
Sum of electronic and thermal Enthalpies= -1294.500831
Sum of electronic and thermal Free Energies= -1294.587250
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1293.638460812649
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3329352
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.300145
Thesis = H1, A1 = I1

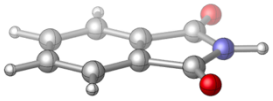


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.346440 (Hartree/Particle)
Thermal correction to Energy= 0.372487
Thermal correction to Enthalpy= 0.373431
Thermal correction to Gibbs Free Energy= 0.285812
Sum of electronic and zero-point Energies= -1294.558647
Sum of electronic and thermal Energies= -1294.532600
Sum of electronic and thermal Enthalpies= -1294.531656
Sum of electronic and thermal Free Energies= -1294.619274
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)

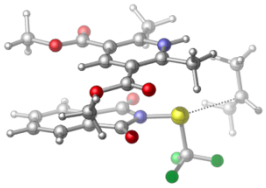
FINAL A1NGLE POINT ENERGY -1293.680593389104
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3580753
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.3414469
Thesis = I1, KA1 = A1.13-J1, A1.21-J1



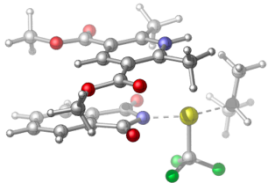
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.228707 (Hartree/Particle)
Thermal correction to Energy= 0.245042
Thermal correction to Enthalpy= 0.245986
Thermal correction to Gibbs Free Energy= 0.183605
Sum of electronic and zero-point Energies= -781.911501
Sum of electronic and thermal Energies= -781.895166
Sum of electronic and thermal Enthalpies= -781.894222
Sum of electronic and thermal Free Energies= -781.956603
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -781.419728935240
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-783.025401
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-783.0163073
Thesis = J1, A1 = K1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.116426 (Hartree/Particle)
Thermal correction to Energy= 0.124170
Thermal correction to Enthalpy= 0.125114
Thermal correction to Gibbs Free Energy= 0.083636
Sum of electronic and zero-point Energies= -512.629916
Sum of electronic and thermal Energies= -512.622171
Sum of electronic and thermal Enthalpies= -512.621227
Sum of electronic and thermal Free Energies= -512.662706
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -512.246788979234
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-513.3203263
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-513.3091998
A1 = A1.17-E3

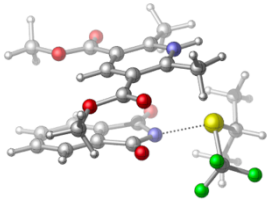


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.451042 (Hartree/Particle)
Thermal correction to Energy= 0.488918
Thermal correction to Enthalpy= 0.489862
Thermal correction to Gibbs Free Energy= 0.377981
Sum of electronic and zero-point Energies= -2148.281763
Sum of electronic and thermal Energies= -2148.243887
Sum of electronic and thermal Enthalpies= -2148.242943
Sum of electronic and thermal Free Energies= -2148.354824
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8615518
A1 = A1.17-E3-TS-F3

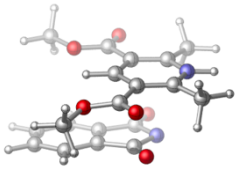


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.452764 (Hartree/Particle)

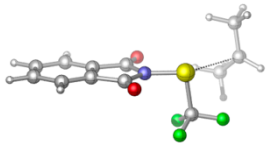
Thermal correction to Energy= 0.489062
Thermal correction to Enthalpy= 0.490006
Thermal correction to Gibbs Free Energy= 0.382853
Sum of electronic and zero-point Energies= -2148.265704
Sum of electronic and thermal Energies= -2148.229405
Sum of electronic and thermal Enthalpies= -2148.228461
Sum of electronic and thermal Free Energies= -2148.335615
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8478977
A1 = A1.17-F3



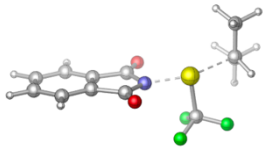
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.454642 (Hartree/Particle)
Thermal correction to Energy= 0.491116
Thermal correction to Enthalpy= 0.492060
Thermal correction to Gibbs Free Energy= 0.384732
Sum of electronic and zero-point Energies= -2148.277606
Sum of electronic and thermal Energies= -2148.241132
Sum of electronic and thermal Enthalpies= -2148.240188
Sum of electronic and thermal Free Energies= -2148.347516
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.8593782
A1 = A1.17-G3



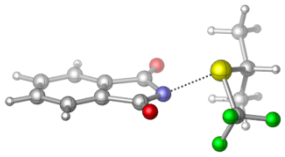
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.454642 (Hartree/Particle)
Thermal correction to Energy= 0.491116
Thermal correction to Enthalpy= 0.492060
Thermal correction to Gibbs Free Energy= 0.384732
Sum of electronic and zero-point Energies= -2148.277606
Sum of electronic and thermal Energies= -2148.241132
Sum of electronic and thermal Enthalpies= -2148.240188
Sum of electronic and thermal Free Energies= -2148.347516
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.239171
A1 = A1.18-K2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.209710 (Hartree/Particle)
Thermal correction to Energy= 0.229745
Thermal correction to Enthalpy= 0.230689
Thermal correction to Gibbs Free Energy= 0.156665
Sum of electronic and zero-point Energies= -1365.779036
Sum of electronic and thermal Energies= -1365.759001
Sum of electronic and thermal Enthalpies= -1365.758057
Sum of electronic and thermal Free Energies= -1365.832081
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1364.870597906386
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1367.241026
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1367.23079
Thesis = B1-TS-K2, A1 = A1.18-K2-TS-L2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.212194 (Hartree/Particle)
Thermal correction to Energy= 0.230314
Thermal correction to Enthalpy= 0.231258
Thermal correction to Gibbs Free Energy= 0.163949
Sum of electronic and zero-point Energies= -1365.766534
Sum of electronic and thermal Energies= -1365.748415
Sum of electronic and thermal Enthalpies= -1365.747470
Sum of electronic and thermal Free Energies= -1365.814779
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1364.857628900683
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1367.241026
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1367.23079
Thesis = K2, A1 = A1.18-L2



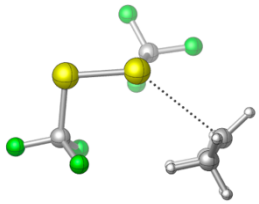
B3LYP-D3/def2-SVP-CPCM(DMSO)

DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)

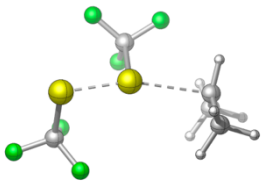
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)

B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)

Thesis = M2, A1 = A1.18-M2

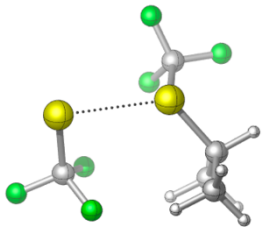


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.120005 (Hartree/Particle)
Thermal correction to Energy= 0.136928
Thermal correction to Enthalpy= 0.137873
Thermal correction to Gibbs Free Energy= 0.071370
Sum of electronic and zero-point Energies= -1589.200627
Sum of electronic and thermal Energies= -1589.183703
Sum of electronic and thermal Enthalpies= -1589.182759
Sum of electronic and thermal Free Energies= -1589.249262
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1588.232747502254
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5580358
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5563451
Thesis = M2-TS-N2, A1 = A1.18-M2-TS-N2

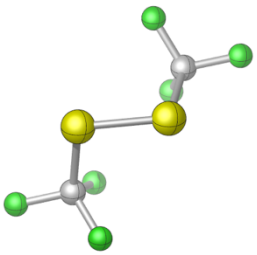


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.120895 (Hartree/Particle)
Thermal correction to Energy= 0.136626
Thermal correction to Enthalpy= 0.137571
Thermal correction to Gibbs Free Energy= 0.073732
Sum of electronic and zero-point Energies= -1589.199188
Sum of electronic and thermal Energies= -1589.183456
Sum of electronic and thermal Enthalpies= -1589.182512
Sum of electronic and thermal Free Energies= -1589.246350
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1588.227661332741
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5572006

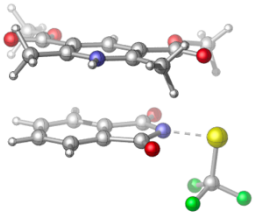
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5541053
Thesis = N2, A1 = A1.18-N2



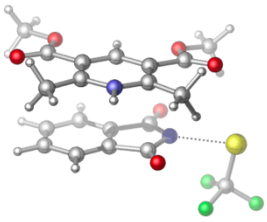
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.125129 (Hartree/Particle)
Thermal correction to Energy= 0.140421
Thermal correction to Enthalpy= 0.141365
Thermal correction to Gibbs Free Energy= 0.079825
Sum of electronic and zero-point Energies= -1589.226091
Sum of electronic and thermal Energies= -1589.210799
Sum of electronic and thermal Enthalpies= -1589.209855
Sum of electronic and thermal Free Energies= -1589.271395
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1588.254244608808
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5815742
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1590.5768217
Thesis = L1, A1= A1.18-SCF3-Dimer



B3LYP-D3/def2-SVP-CPCM(DMSO) Zero-point correction= 0.031473 (Hartree/Particle) Thermal correction to Energy= 0.041547 Thermal correction to Enthalpy= 0.042492 Thermal correction to Gibbs Free Energy= -0.007007 Sum of electronic and zero-point Energies= -1470.881757 Sum of electronic and thermal Energies= -1470.871682 Sum of electronic and thermal Enthalpies= -1470.870738 Sum of electronic and thermal Free Energies= -1470.920236
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO) FINAL SINGLE POINT ENERGY -1469.981561207114 B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO) HF=-1472.0200773 B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO) HF=-1472.0181678
Thesis = D2'-TS-O2, A1 = A1.19-D2'-TS-O2

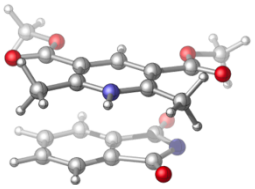


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.360432 (Hartree/Particle)
Thermal correction to Energy= 0.391701
Thermal correction to Enthalpy= 0.392645
Thermal correction to Gibbs Free Energy= 0.295870
Sum of electronic and zero-point Energies= -2029.933311
Sum of electronic and thermal Energies= -2029.902042
Sum of electronic and thermal Enthalpies= -2029.901098
Sum of electronic and thermal Free Energies= -2029.997873
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2028.578578259595
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2930629
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2643392
Thesis = O2, A1 = A1.19-O2

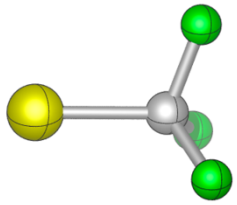


B3LYP-D3/def2-SVP-CPCM(DMSO)

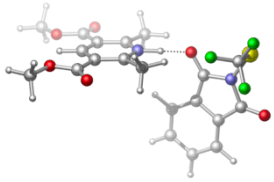
Zero-point correction= 0.363231 (Hartree/Particle)
Thermal correction to Energy= 0.395088
Thermal correction to Enthalpy= 0.396033
Thermal correction to Gibbs Free Energy= 0.296133
Sum of electronic and zero-point Energies= -2029.951584
Sum of electronic and thermal Energies= -2029.919726
Sum of electronic and thermal Enthalpies= -2029.918782
Sum of electronic and thermal Free Energies= -2030.018682
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -2028.584419969185
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3156213
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2677144
Thesis = P1, A1 = A1.19-P1



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.347759 (Hartree/Particle)
Thermal correction to Energy= 0.373295
Thermal correction to Enthalpy= 0.374239
Thermal correction to Gibbs Free Energy= 0.291657
Sum of electronic and zero-point Energies= -1294.526613
Sum of electronic and thermal Energies= -1294.501077
Sum of electronic and thermal Enthalpies= -1294.500133
Sum of electronic and thermal Free Energies= -1294.582715
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1293.624449119903
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.331366
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1296.2838974
Thesis = SCF radical, A1 = A1.19-SCF3 radical

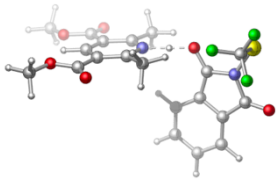


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.014131 (Hartree/Particle)
Thermal correction to Energy= 0.018767
Thermal correction to Enthalpy= 0.019711
Thermal correction to Gibbs Free Energy= -0.015028
Sum of electronic and zero-point Energies= -735.393783
Sum of electronic and thermal Energies= -735.389147
Sum of electronic and thermal Enthalpies= -735.388203
Sum of electronic and thermal Free Energies= -735.422941
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -734.938761283631
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-735.9596228
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-735.9562093
Thesis = Q2, A1 = A1.21-Q2

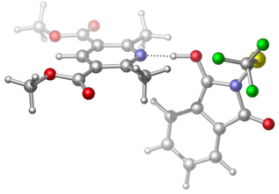


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.361642 (Hartree/Particle)
Thermal correction to Energy= 0.393021
Thermal correction to Enthalpy= 0.393965
Thermal correction to Gibbs Free Energy= 0.293093

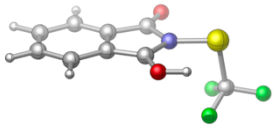
Sum of electronic and zero-point Energies= -2029.953762
Sum of electronic and thermal Energies= -2029.922383
Sum of electronic and thermal Enthalpies= -2029.921439
Sum of electronic and thermal Free Energies= -2030.022311
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3172901
Thesis = Q2-TS-R2, A1 = A1.21-Q2-TS-R2



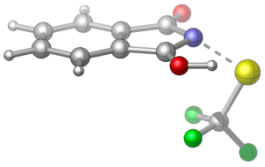
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.357877 (Hartree/Particle)
Thermal correction to Energy= 0.389000
Thermal correction to Enthalpy= 0.389944
Thermal correction to Gibbs Free Energy= 0.289568
Sum of electronic and zero-point Energies= -2029.955557
Sum of electronic and thermal Energies= -2029.924434
Sum of electronic and thermal Enthalpies= -2029.923489
Sum of electronic and thermal Free Energies= -2030.023866
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3135367
Thesis = R2, A1 = A1.21-R2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.361300 (Hartree/Particle)
Thermal correction to Energy= 0.392733
Thermal correction to Enthalpy= 0.393677
Thermal correction to Gibbs Free Energy= 0.292007
Sum of electronic and zero-point Energies= -2029.953557
Sum of electronic and thermal Energies= -2029.922124
Sum of electronic and thermal Enthalpies= -2029.921180
Sum of electronic and thermal Free Energies= -2030.022851
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3148788
Thesis = 2S, A1 = A1.21-S2

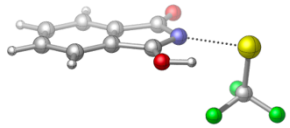


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.131327 (Hartree/Particle)
Thermal correction to Energy= 0.144908
Thermal correction to Enthalpy= 0.145852
Thermal correction to Gibbs Free Energy= 0.089013
Sum of electronic and zero-point Energies= -1248.012348
Sum of electronic and thermal Energies= -1247.998767
Sum of electronic and thermal Enthalpies= -1247.997823
Sum of electronic and thermal Free Energies= -1248.054662
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2660942
Thesis = S2-TS-T2, A1 = A1.21-S2-TS-T2

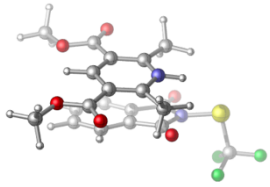


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.129552 (Hartree/Particle)
Thermal correction to Energy= 0.142973
Thermal correction to Enthalpy= 0.143917
Thermal correction to Gibbs Free Energy= 0.087050
Sum of electronic and zero-point Energies= -1247.990216
Sum of electronic and thermal Energies= -1247.976795

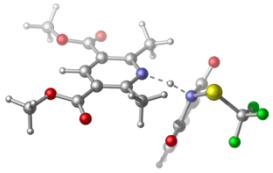
Sum of electronic and thermal Enthalpies= -1247.975851
Sum of electronic and thermal Free Energies= -1248.032718
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2411414
Thesis = T2, A1 = A1.21-T2



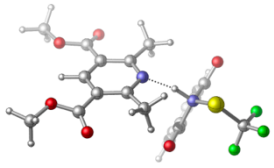
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.131597 (Hartree/Particle)
Thermal correction to Energy= 0.145527
Thermal correction to Enthalpy= 0.146472
Thermal correction to Gibbs Free Energy= 0.087573
Sum of electronic and zero-point Energies= -1248.009888
Sum of electronic and thermal Energies= -1247.995958
Sum of electronic and thermal Enthalpies= -1247.995014
Sum of electronic and thermal Free Energies= -1248.053912
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2623356
Thesis = D2''A1 = A1.21-D2''



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.362039 (Hartree/Particle)
Thermal correction to Energy= 0.393427
Thermal correction to Enthalpy= 0.394371
Thermal correction to Gibbs Free Energy= 0.295713
Sum of electronic and zero-point Energies= -2029.953820
Sum of electronic and thermal Energies= -2029.922432
Sum of electronic and thermal Enthalpies= -2029.921488
Sum of electronic and thermal Free Energies= -2030.020146
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.3168636
Thesis = D2''-TS-U2, A1 = A1.21-D2''-TS-U2

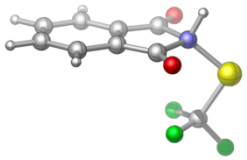


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.356964 (Hartree/Particle)
Thermal correction to Energy= 0.388129
Thermal correction to Enthalpy= 0.389074
Thermal correction to Gibbs Free Energy= 0.289163
Sum of electronic and zero-point Energies= -2029.913738
Sum of electronic and thermal Energies= -2029.882572
Sum of electronic and thermal Enthalpies= -2029.881628
Sum of electronic and thermal Free Energies= -2029.981539
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2705063
Thesis = U2, A1 = A1.21-U2

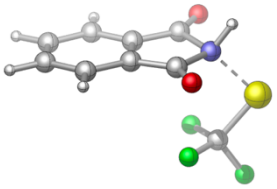


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.359809 (Hartree/Particle)
Thermal correction to Energy= 0.391470
Thermal correction to Enthalpy= 0.392414
Thermal correction to Gibbs Free Energy= 0.291046
Sum of electronic and zero-point Energies= -2029.911535
Sum of electronic and thermal Energies= -2029.879874
Sum of electronic and thermal Enthalpies= -2029.878930
Sum of electronic and thermal Free Energies= -2029.980299

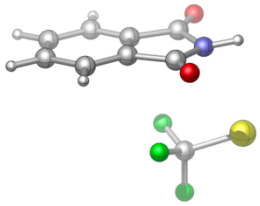
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2032.2721132
Thesis = V2, A1 = A1.21-V2



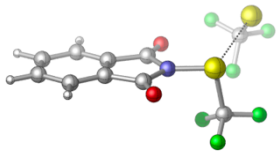
B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.130448 (Hartree/Particle)
Thermal correction to Energy= 0.144109
Thermal correction to Enthalpy= 0.145054
Thermal correction to Gibbs Free Energy= 0.087887
Sum of electronic and zero-point Energies= -1247.971323
Sum of electronic and thermal Energies= -1247.957661
Sum of electronic and thermal Enthalpies= -1247.956717
Sum of electronic and thermal Free Energies= -1248.013884
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2253091
Thesis = V2-TS-W2, A1 = A1.21-V2-TS-W2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.128920 (Hartree/Particle)
Thermal correction to Energy= 0.142299
Thermal correction to Enthalpy= 0.143244
Thermal correction to Gibbs Free Energy= 0.086476
Sum of electronic and zero-point Energies= -1247.968084
Sum of electronic and thermal Energies= -1247.954705
Sum of electronic and thermal Enthalpies= -1247.953761
Sum of electronic and thermal Free Energies= -1248.010529
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2199121
Thesis = W2, A1 = A1.21-W2

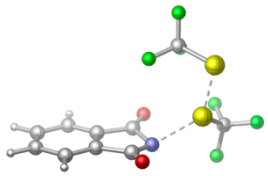


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.131613 (Hartree/Particle)
Thermal correction to Energy= 0.145846
Thermal correction to Enthalpy= 0.146790
Thermal correction to Gibbs Free Energy= 0.086767
Sum of electronic and zero-point Energies= -1248.033521
Sum of electronic and thermal Energies= -1248.019288
Sum of electronic and thermal Enthalpies= -1248.018344
Sum of electronic and thermal Free Energies= -1248.078367
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1249.2851146
A1 = A1.22-X2

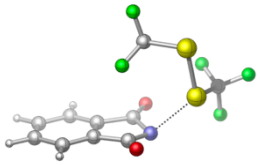


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.136464 (Hartree/Particle)
Thermal correction to Energy= 0.156123
Thermal correction to Enthalpy= 0.157067
Thermal correction to Gibbs Free Energy= 0.082069
Sum of electronic and zero-point Energies= -1982.864935
Sum of electronic and thermal Energies= -1982.845276
Sum of electronic and thermal Enthalpies= -1982.844332
Sum of electronic and thermal Free Energies= -1982.919330
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1981.559602736023

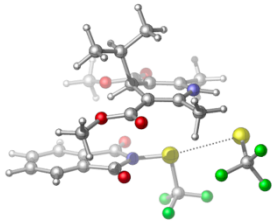
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6689544
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6563435
A1 = A1.22-X2-TS-Y2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.135230 (Hartree/Particle)
Thermal correction to Energy= 0.154091
Thermal correction to Enthalpy= 0.155035
Thermal correction to Gibbs Free Energy= 0.083734
Sum of electronic and zero-point Energies= -1982.835597
Sum of electronic and thermal Energies= -1982.816737
Sum of electronic and thermal Enthalpies= -1982.815793
Sum of electronic and thermal Free Energies= -1982.887093
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1981.528027752900
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6456268
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6343431
A1 = A1.22-Y2

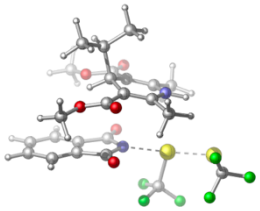


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.135123 (Hartree/Particle)
Thermal correction to Energy= 0.154843
Thermal correction to Enthalpy= 0.155787
Thermal correction to Gibbs Free Energy= 0.081904
Sum of electronic and zero-point Energies= -1982.836481
Sum of electronic and thermal Energies= -1982.816761
Sum of electronic and thermal Enthalpies= -1982.815817
Sum of electronic and thermal Free Energies= -1982.889700
DLPNO-CCSD(T)/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
FINAL A1NGLE POINT ENERGY -1981.529671685942
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6462646
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-1984.6346124
A1 = A1.23-Z2

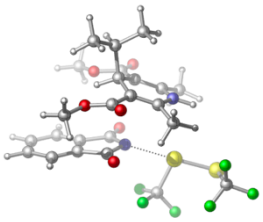


B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.474715 (Hartree/Particle)
Thermal correction to Energy= 0.516369
Thermal correction to Enthalpy= 0.517313
Thermal correction to Gibbs Free Energy= 0.396354
Sum of electronic and zero-point Energies= -2883.775257
Sum of electronic and thermal Energies= -2883.733604
Sum of electronic and thermal Enthalpies= -2883.732659
Sum of electronic and thermal Free Energies= -2883.853619

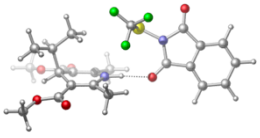
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2886.9218551
A1 = A1.23-Z2-TS-AA2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.473989 (Hartree/Particle)
Thermal correction to Energy= 0.515072
Thermal correction to Enthalpy= 0.516016
Thermal correction to Gibbs Free Energy= 0.396115
Sum of electronic and zero-point Energies= -2883.759123
Sum of electronic and thermal Energies= -2883.718040
Sum of electronic and thermal Enthalpies= -2883.717096
Sum of electronic and thermal Free Energies= -2883.836997
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2886.9074945
A1 = A1.23-AA2



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.474274 (Hartree/Particle)
Thermal correction to Energy= 0.516085
Thermal correction to Enthalpy= 0.517029
Thermal correction to Gibbs Free Energy= 0.395710
Sum of electronic and zero-point Energies= -2883.759694
Sum of electronic and thermal Energies= -2883.717883
Sum of electronic and thermal Enthalpies= -2883.716939
Sum of electronic and thermal Free Energies= -2883.838258
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2886.910876
A1 = A1.24-C1-H



B3LYP-D3/def2-SVP-CPCM(DMSO)
Zero-point correction= 0.459567 (Hartree/Particle)
Thermal correction to Energy= 0.495404
Thermal correction to Enthalpy= 0.496348
Thermal correction to Gibbs Free Energy= 0.388493
Sum of electronic and zero-point Energies= -2148.351429
Sum of electronic and thermal Energies= -2148.315593
Sum of electronic and thermal Enthalpies= -2148.314648
Sum of electronic and thermal Free Energies= -2148.422503
B3LYP-D3/def2-TZVPP-CPCM(DMSO)//B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2150.9384882
TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2148.8109961
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.2200 eV 558.49 nm f=0.0000 <S**2>=2.000
134A ->135A 0.70688
134B ->135B -0.70614

Excited state symmetry could not be determined.
Excited State 2: 1.000-?Sym 2.2205 eV 558.36 nm f=0.0002 <S**2>=0.000
134A ->135A 0.70621
134B ->135B 0.70695
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2148.72939378
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.5331 eV 489.45 nm f=0.0000 <S**2>=2.000
133A ->139A 0.10313
134A ->137A 0.69212
133B ->139B -0.10313
134B ->137B -0.69212

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.1452 eV 394.20 nm f=0.0000 <S**2>=2.000
123A ->135A 0.11012
129A ->136A -0.24835
130A ->135A 0.62828

130A ->140A 0.14525
123B ->135B -0.11012
129B ->136B 0.24835
130B ->135B -0.62828
130B ->140B -0.14525

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.4045 eV 364.17 nm f=0.0000 <S**2>=2.000
132A ->137A 0.20353
133A ->137A 0.56350
134A ->139A 0.34748
132B ->137B -0.20353
133B ->137B -0.56350
134B ->139B -0.34748

Excited state symmetry could not be determined.
Excited State 6: 1.000-?Sym 3.4237 eV 362.14 nm f=0.2301 <S**2>=0.000
134A ->136A -0.19805
134A ->137A 0.67730
134B ->136B -0.19805
134B ->137B 0.67730

Excited state symmetry could not be determined.
Excited State 7: 3.000-?Sym 3.4696 eV 357.35 nm f=0.0000 <S**2>=2.000
134A ->136A 0.70243
134B ->136B -0.70235

Excited state symmetry could not be determined.
Excited State 8: 1.000-?Sym 3.4733 eV 356.96 nm f=0.0160 <S**2>=0.000
134A ->136A 0.67604
134A ->137A 0.19735
134B ->136B 0.67612
134B ->137B 0.19735

Excited state symmetry could not be determined.
Excited State 9: 3.000-?Sym 3.5540 eV 348.86 nm f=0.0000 <S**2>=2.000
133A ->135A 0.70322
133B ->135B -0.70274

Excited state symmetry could not be determined.
Excited State 10: 1.000-?Sym 3.5544 eV 348.82 nm f=0.0002 <S**2>=0.000
133A ->135A 0.70493
133B ->135B 0.70541

Excited state symmetry could not be determined.
Excited State 11: 3.000-?Sym 3.5810 eV 346.23 nm f=0.0000 <S**2>=2.000
129A ->135A -0.69528
129B ->135B 0.69528

Excited state symmetry could not be determined.
Excited State 12: 3.000-?Sym 3.6074 eV 343.69 nm f=0.0000 <S**2>=2.000
125A ->135A -0.45632
128A ->135A 0.50351
125B ->135B 0.45632
128B ->135B -0.50351

Excited state symmetry could not be determined.
Excited State 13: 1.000-?Sym 3.9692 eV 312.37 nm f=0.0003 <S**2>=0.000
125A ->135A -0.35372
128A ->135A 0.57146
131A ->135A 0.13940
132A ->135A 0.11580
125B ->135B -0.35372
128B ->135B 0.57146
131B ->135B 0.13939
132B ->135B 0.11580

Excited state symmetry could not be determined.
Excited State 14: 3.000-?Sym 4.0810 eV 303.81 nm f=0.0000 <S**2>=2.000
122A ->135A 0.10684
123A ->135A -0.21913
129A ->136A 0.16088
130A ->135A 0.13390
132A ->135A 0.61560
122B ->135B -0.10685
123B ->135B 0.21912
129B ->136B -0.16088
130B ->135B -0.13390
132B ->135B -0.61559

Excited state symmetry could not be determined.
Excited State 15: 1.000-?Sym 4.0935 eV 302.88 nm f=0.0028 <S**2>=0.000
132A ->135A 0.69520
132B ->135B 0.69522

Excited state symmetry could not be determined.
Excited State 16: 3.000-?Sym 4.1100 eV 301.66 nm f=0.0000 <S**2>=2.000
122A ->135A 0.14061
123A ->135A -0.35352
129A ->136A 0.38602
130A ->135A 0.23454
132A ->135A -0.32403
122B ->135B -0.14062
123B ->135B 0.35351
129B ->136B -0.38602
130B ->135B -0.23454

132B ->135B 0.32402

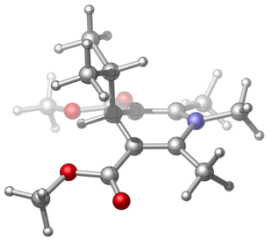
Excited state symmetry could not be determined.
Excited State 17: 3.000-?Sym 4.1351 eV 299.83 nm f=0.0000 <S**2>=2.000
134A ->138A 0.69847
134B ->138B -0.69845

Excited state symmetry could not be determined.
Excited State 18: 1.000-?Sym 4.1464 eV 299.02 nm f=0.0007 <S**2>=0.000
134A ->138A 0.70385
134B ->138B 0.70387

Excited state symmetry could not be determined.
Excited State 19: 3.000-?Sym 4.1850 eV 296.26 nm f=0.0000 <S**2>=2.000
121A ->135A -0.32342
123A ->135A -0.19358
125A ->135A -0.12196
129A ->136A -0.26959
131A ->135A -0.46049
121B ->135B 0.32342
123B ->135B 0.19357
125B ->135B 0.12195
129B ->136B 0.26958
131B ->135B 0.46049

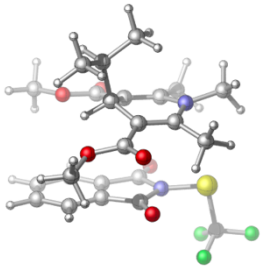
Excited state symmetry could not be determined.
Excited State 20: 1.000-?Sym 4.1897 eV 295.93 nm f=0.0356 <S**2>=0.000
123A ->135A -0.12649
130A ->135A 0.68190
123B ->135B -0.12651
130B ->135B 0.68189

A1 = A1.26-A1-Me



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-940.4774495
Zero-point correction= 0.364566 (Hartree/Particle)
Thermal correction to Energy= 0.386894
Thermal correction to Enthalpy= 0.387838
Thermal correction to Gibbs Free Energy= 0.313534
Sum of electronic and zero-point Energies= -940.112884
Sum of electronic and thermal Energies= -940.090555
Sum of electronic and thermal Enthalpies= -940.089611
Sum of electronic and thermal Free Energies= -940.163916

A1 = A1.26-C1-Me



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2188.088917
Zero-point correction= 0.487794 (Hartree/Particle)
Thermal correction to Energy= 0.524798
Thermal correction to Enthalpy= 0.525742
Thermal correction to Gibbs Free Energy= 0.417348
Sum of electronic and zero-point Energies= -2187.601123
Sum of electronic and thermal Energies= -2187.564119
Sum of electronic and thermal Enthalpies= -2187.563175
Sum of electronic and thermal Free Energies= -2187.671569
TD-B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2188.088917
B3LYP-D3/def2-SVP-CPCM(DMSO)
Excitation energies and oscillator strengths:

Excited state symmetry could not be determined.
Excited State 1: 3.000-?Sym 2.2764 eV 544.64 nm f=0.0000 <S**2>=2.000
138A ->139A -0.69807
138B ->139B 0.69810
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) = -2188.00525977
Copying the excited state denA1ty for this state as the 1-particle RhoCI denA1ty.

Excited state symmetry could not be determined.

Excited State 2: 1.000-?Sym 2.3034 eV 538.26 nm f=0.0006 <S**2>=0.000
138A ->139A 0.70651
138B ->139B 0.70648

Excited state symmetry could not be determined.
Excited State 3: 3.000-?Sym 2.6413 eV 469.40 nm f=0.0000 <S**2>=2.000
137A ->143A 0.11650
138A ->140A 0.21383
138A ->141A 0.64615
137B ->143B -0.11650
138B ->140B -0.21383
138B ->141B -0.64615

Excited state symmetry could not be determined.
Excited State 4: 3.000-?Sym 3.1819 eV 389.65 nm f=0.0000 <S**2>=2.000
128A ->139A -0.13642
133A ->139A 0.30854
133A ->140A 0.19182
134A ->139A 0.49078
134A ->140A -0.14198
134A ->144A 0.11193
135A ->139A -0.12063
137A ->139A 0.12983
128B ->139B 0.13642
133B ->139B -0.30854
133B ->140B -0.19182
134B ->139B -0.49078
134B ->140B 0.14198
134B ->144B -0.11193
135B ->139B 0.12063
137B ->139B -0.12983

Excited state symmetry could not be determined.
Excited State 5: 3.000-?Sym 3.3129 eV 374.25 nm f=0.0000 <S**2>=2.000
136A ->141A 0.16250
137A ->139A -0.16556
137A ->140A 0.12806
137A ->141A 0.41429
138A ->140A -0.16961
138A ->143A 0.42727
136B ->141B -0.16250
137B ->139B 0.16556
137B ->140B -0.12807
137B ->141B -0.41428
138B ->140B 0.16960
138B ->143B -0.42727

Excited state symmetry could not be determined.
Excited State 6: 3.000-?Sym 3.4844 eV 355.83 nm f=0.0000 <S**2>=2.000
137A ->141A 0.14403
138A ->140A 0.63495
138A ->141A -0.20814
137B ->141B -0.14403
138B ->140B -0.63456
138B ->141B 0.20838

Excited state symmetry could not be determined.
Excited State 7: 1.000-?Sym 3.4864 eV 355.62 nm f=0.0758 <S**2>=0.000
138A ->140A 0.57843
138A ->141A 0.40098
138B ->140B 0.57884
138B ->141B 0.40085

Excited state symmetry could not be determined.
Excited State 8: 1.000-?Sym 3.5363 eV 350.60 nm f=0.0630 <S**2>=0.000
138A ->140A -0.40106
138A ->141A 0.57840
138B ->140B -0.40108
138B ->141B 0.57841

Excited state symmetry could not be determined.
Excited State 9: 3.000-?Sym 3.5618 eV 348.09 nm f=0.0000 <S**2>=2.000
131A ->139A -0.35144
132A ->139A 0.55986
133A ->139A -0.10756
131B ->139B 0.35144
132B ->139B -0.55985
133B ->139B 0.10756

Excited state symmetry could not be determined.
Excited State 10: 3.000-?Sym 3.5852 eV 345.83 nm f=0.0000 <S**2>=2.000
132A ->139A 0.11813
133A ->139A 0.37683
134A ->139A -0.17047
136A ->139A 0.11584
137A ->139A -0.49915
138A ->143A -0.11656
132B ->139B -0.11813
133B ->139B -0.37683
134B ->139B 0.17048
136B ->139B -0.11584
137B ->139B 0.49917
138B ->143B 0.11656

Excited state symmetry could not be determined.
Excited State 11: 1.000-?Sym 3.6317 eV 341.39 nm f=0.0136 <S**2>=0.000
137A ->139A 0.70323
137B ->139B 0.70325

Excited state symmetry could not be determined.
Excited State 12: 3.000-?Sym 3.6546 eV 339.26 nm f=0.0000 <S**2>=2.000
133A ->139A 0.35469
134A ->139A -0.33554
136A ->139A 0.17153
137A ->139A 0.43653
133B ->139B -0.35469
134B ->139B 0.33554
136B ->139B -0.17153
137B ->139B -0.43647

Excited state symmetry could not be determined.
Excited State 13: 1.000-?Sym 3.9391 eV 314.75 nm f=0.0003 <S**2>=0.000
131A ->139A -0.29381
132A ->139A 0.62645
131B ->139B -0.29382
132B ->139B 0.62645

Excited state symmetry could not be determined.
Excited State 14: 3.000-?Sym 4.0714 eV 304.53 nm f=0.0000 <S**2>=2.000
128A ->139A 0.48175
133A ->139A 0.22729
133A ->140A -0.16724
134A ->139A 0.13669
134A ->140A 0.13883
136A ->139A -0.27651
128B ->139B -0.48174
133B ->139B -0.22729
133B ->140B 0.16723
134B ->139B -0.13669
134B ->140B -0.13883
136B ->139B 0.27650

Excited state symmetry could not be determined.
Excited State 15: 3.000-?Sym 4.1264 eV 300.47 nm f=0.0000 <S**2>=2.000
135A ->143A 0.10001
136A ->139A -0.17781
137A ->140A -0.14156
137A ->141A -0.43241
138A ->142A 0.12658
138A ->143A 0.42964
135B ->143B -0.10000
136B ->139B 0.17784
137B ->140B 0.14156
137B ->141B 0.43241
138B ->142B -0.12657
138B ->143B -0.42964

Excited state symmetry could not be determined.
Excited State 16: 1.000-?Sym 4.1378 eV 299.64 nm f=0.0095 <S**2>=0.000
136A ->139A 0.69723
136B ->139B 0.69733

Excited state symmetry could not be determined.
Excited State 17: 3.000-?Sym 4.1464 eV 299.02 nm f=0.0000 <S**2>=2.000
128A ->139A 0.10309
133A ->140A -0.21956
134A ->139A 0.19079
134A ->140A 0.16692
136A ->139A 0.52928
137A ->141A -0.12560
138A ->143A 0.18236
128B ->139B -0.10308
133B ->140B 0.21955
134B ->139B -0.19080
134B ->140B -0.16693
136B ->139B -0.52915
137B ->141B 0.12560
138B ->143B -0.18235

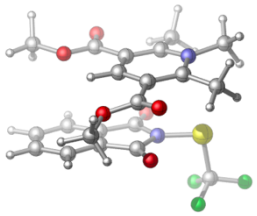
Excited state symmetry could not be determined.
Excited State 18: 3.000-?Sym 4.1708 eV 297.27 nm f=0.0000 <S**2>=2.000
127A ->139A 0.47301
128A ->139A -0.19632
132A ->140A 0.14615
133A ->139A 0.11342
133A ->140A -0.24749
134A ->139A 0.10804
134A ->140A 0.20033
136A ->139A -0.11739
127B ->139B -0.47301
128B ->139B 0.19633
132B ->140B -0.14614
133B ->139B -0.11343
133B ->140B 0.24749
134B ->139B -0.10804
134B ->140B -0.20033
136B ->139B 0.11740

Excited state symmetry could not be determined.
Excited State 19: 3.000-?Sym 4.2192 eV 293.86 nm f=0.0000 <S**2>=2.000
127A ->139A 0.38327
128A ->139A 0.27841
133A ->140A 0.19258
134A ->140A -0.15710
135A ->139A 0.36180
136A ->139A 0.12420
127B ->139B -0.38327
128B ->139B -0.27841

133B ->140B -0.19258
134B ->140B 0.15710
135B ->139B -0.36181
136B ->139B -0.12420

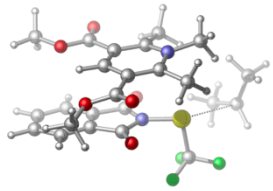
Excited state symmetry could not be determined.
Excited State 20: 1.000-?Sym 4.2612 eV 290.96 nm f=0.0074 <S**2>=0.000
133A ->139A -0.16527
134A ->139A -0.19394
135A ->139A 0.63930
133B ->139B -0.16526
134B ->139B -0.19393
135B ->139B 0.63933

A1 = A1.26-D2-Me



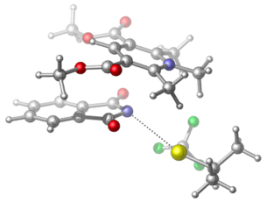
B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2069.593076
Zero-point correction= 0.389811 (Hartree/Particle)
Thermal correction to Energy= 0.422643
Thermal correction to Enthalpy= 0.423587
Thermal correction to Gibbs Free Energy= 0.323091
Sum of electronic and zero-point Energies= -2069.203265
Sum of electronic and thermal Energies= -2069.170433
Sum of electronic and thermal Enthalpies= -2069.169489

A1 = A1.26-E1-Me



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2188.0010887
Zero-point correction= 0.478319 (Hartree/Particle)
Thermal correction to Energy= 0.518091
Thermal correction to Enthalpy= 0.519035
Thermal correction to Gibbs Free Energy= 0.402554
Sum of electronic and zero-point Energies= -2187.522770
Sum of electronic and thermal Energies= -2187.482998
Sum of electronic and thermal Enthalpies= -2187.482054
Sum of electronic and thermal Free Energies= -2187.598534

A1 = A1.26-F1-Me



B3LYP-D3/def2-SVP-CPCM(DMSO)
HF=-2188.0833159 Zero-point correction= 0.486145 (Hartree/Particle)
Thermal correction to Energy= 0.524162
Thermal correction to Enthalpy= 0.525106
Thermal correction to Gibbs Free Energy= 0.413376
Sum of electronic and zero-point Energies= -2187.597171
Sum of electronic and thermal Energies= -2187.559154
Sum of electronic and thermal Enthalpies= -2187.558210
Sum of electronic and thermal Free Energies= -2187.669940

Appendix 2: Supporting Information Chapter 3

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using unrestricted using UM06-2X/DGDZVP level of the theory in implicit solvent (THF) using SMD as solvation model with the "guess=mix" keyword, as implemented in Gaussian09 Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Further, to assess the influence of dynamic correlation, open-shell domain-based local pair natural orbital Coupled-Cluster calculations using single and double excitations with perturbative triple excitations (DLPNO-CCSD(T)) with def2-TZVPP basis single point energy calculations were performed using ORCA software. This latter method provides accurate energies (within 3 kJ mol^{-1}) with the computational cost comparable to DFT calculations. Single point energy calculations in implicit solvent using (D3(BJ)-B3LYP)/def2-TZVPP and UM06-2X/ def2-TZVPP were also performed on all structures (see below). All 3-D structures were generated using CYLview. Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

Full Reference of Gaussian09 software:

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

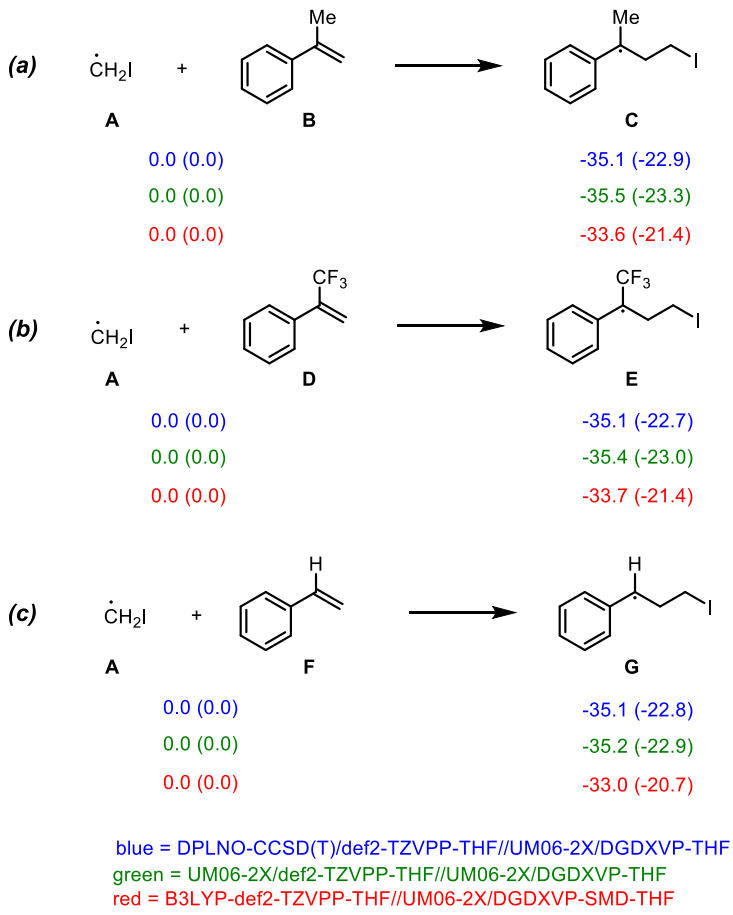


Figure A2.1: Effect of α–substituent on the relative energies for the formation of putative radical intermediates. Enthalpies and free energies (parentheses) are in kcal mol^{-1}.

As noted in **Figure A2.1**, the energies for the formation are nearly identical for all three representative substrates. This result indicates that the nature of the α–substituent has a minor effect on the stability of the radical in comparison with the effect observed for the corresponding α–substituted styrenyl substrate. Further, we performed a set of calculations using various levels of theory on two homodesmotic reactions (**Figure A2.2**) that show that, with respect to the unsubstituted (3-iodopropyl)phenyl radical, the α–CF_3 radical (Eq. d) is less stable than the corresponding α–CH_3 radical (Eq. e). This observation is rationalized on the basis of greater radical stabilizing ability of the CH_3 vs CF_3 through hyperconjugation and inductive effects. As noted in **Figure A2.3**, the corresponding barriers for the radical cyclization are higher in energy for the α–CF_3 than the α–CH_3 system by ~3 kcal mol^{-1}. We attribute this energy difference to

greater transition state stabilization in the α–CH_3 system rather than destabilization of the ground state radical intermediate (*vide supra*).

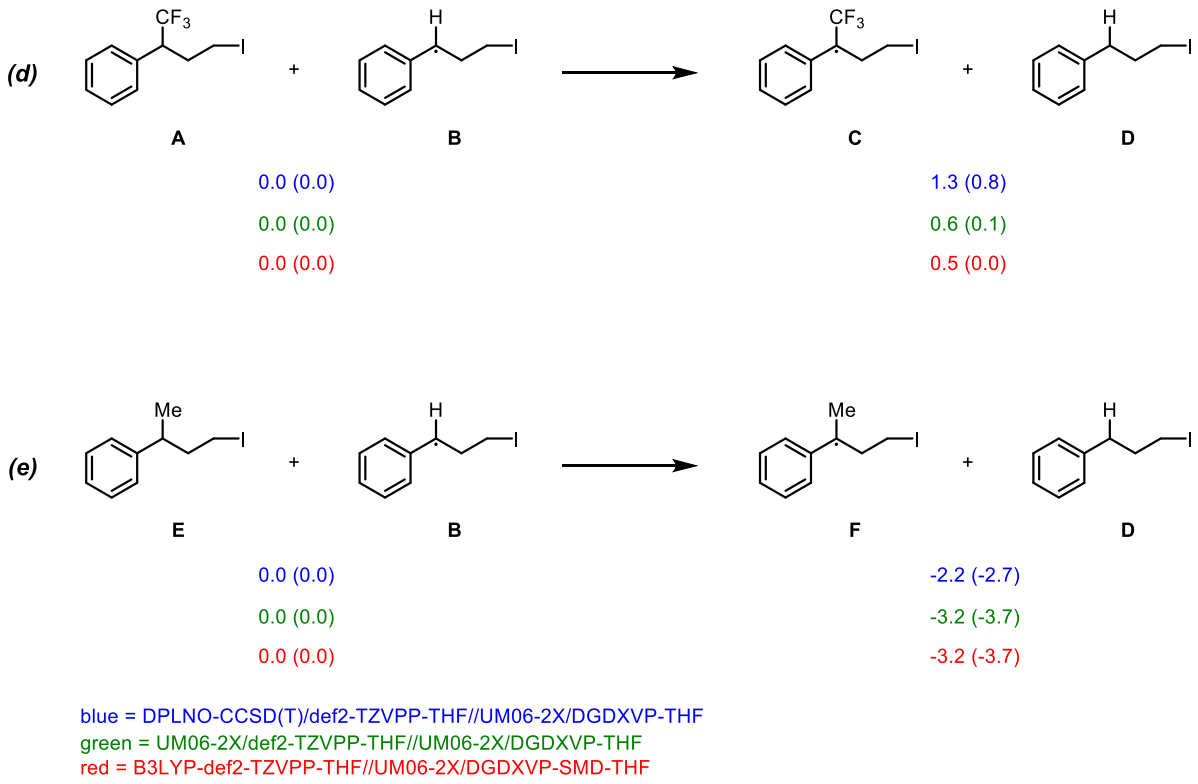


Figure A2.2: Homodesmic equations to probe the effect of α–substituent on the relative energies for the formation of putative radical intermediates. Enthalpies and free energies (parentheses) are in kcal mol^{-1}.

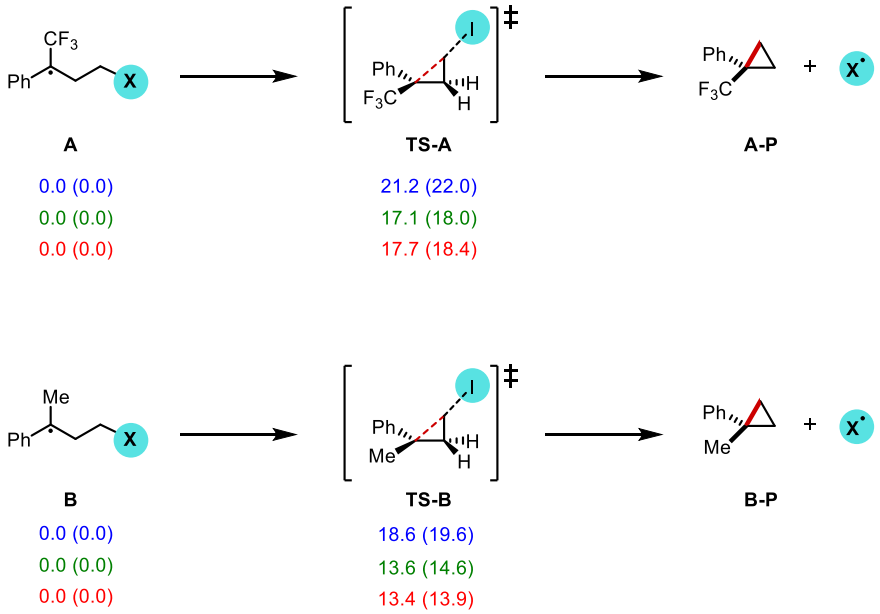
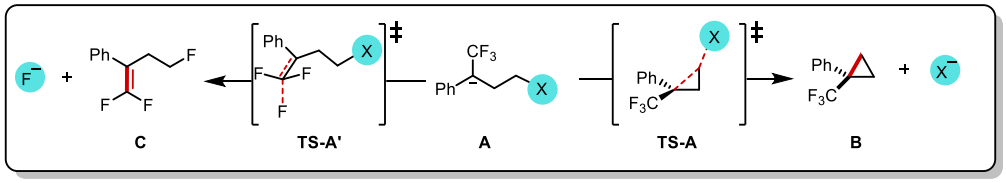


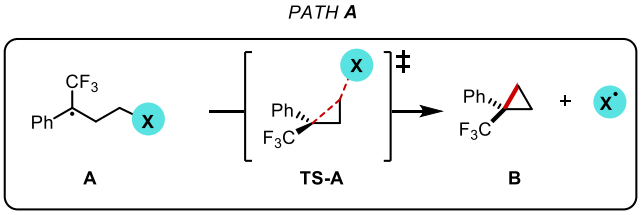
Figure A2.3: Relative barriers for radical cyclization. Enthalpies and free energies (parentheses) are in kcal mol^{-1}. BLUE are DLPNO-CCSD(T)/def2-TZVPP-THF//UM06-2X/DGDZVP-THF and GREEN are UM06-2X/def2-TZVPP-THF//UM06-2X/DGDZVP-THF.



X = I	6.0 (-3.2)	7.8 (7.5)	0.0 (0.0)	3.1 (3.7)	-36.5 (-42.8)
	9.9 (0.7)	8.7 (8.4)	0.0 (0.0)	1.9 (2.4)	-39.4 (-45.7)
	4.6 (-4.6)	3.4 (3.0)	0.0 (0.0)	0.0 (0.5)	-32.2 (-38.4)
X = Br	5.9 (-3.4)	7.4 (6.7)	0.0 (0.0)	7.5 (7.8)	-22.4 (-28.8)
	9.7 (0.4)	8.4 (7.7)	0.0 (0.0)	6.2 (6.4)	-24.6 (-31.1)
	4.2 (-5.1)	2.9 (2.2)	0.0 (0.0)	3.4 (3.7)	-19.8 (-26.3)
X = Cl	5.5 (-4.0)	7.5 (7.1)	0.0 (0.0)	8.6 (9.1)	-23.8 (-30.2)
	9.2 (-0.4)	8.4 (7.9)	0.0 (0.0)	8.6 (9.0)	-24.7 (-31.1)
	3.6 (-6.0)	2.8 (2.4)	0.0 (0.0)	5.1 (5.6)	-20.7 (-27.0)

blue = DPLNO-CCSD(T)/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
green = UM06-2X/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
red = B3LYP-def2-TZVPP-THF//UM06-2X/DGDXVP-SMD-THF

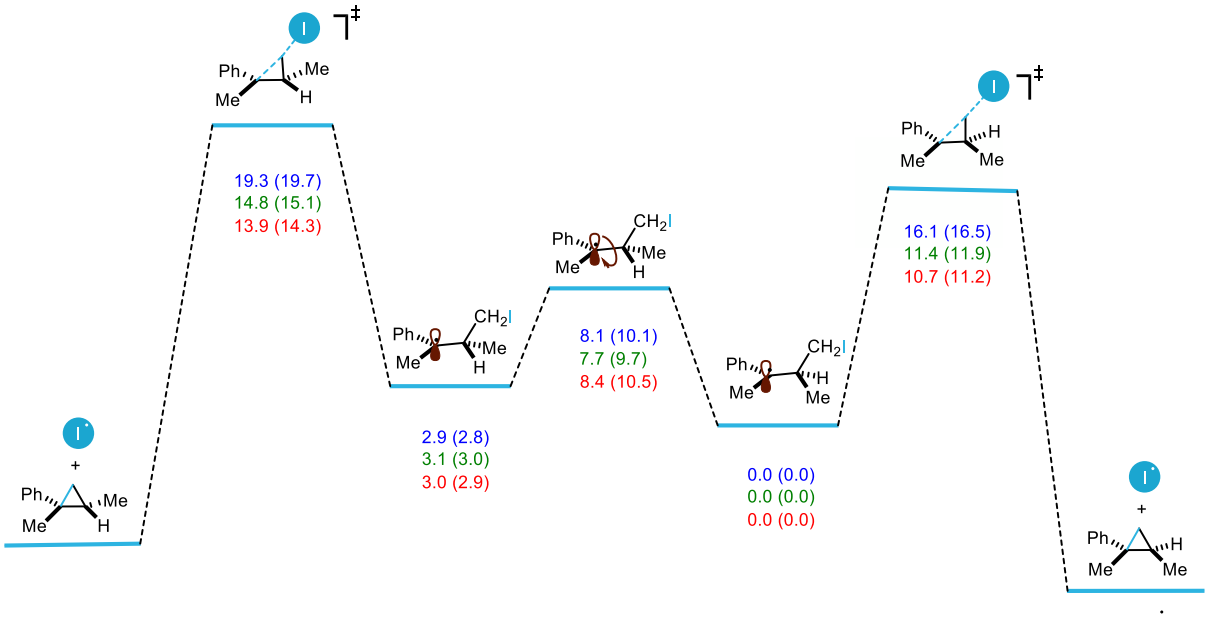
Figure A2.4: Relative barriers for anionic pathways. Enthalpies and free energies (parentheses) are in kcal mol^{-1}.



X = I	0.0 (0.0)	21.2 (22.0)	9.2 (2.9)
	0.0 (0.0)	17.1 (18.0)	-0.6 (-6.9)
	0.0 (0.0)	17.7 (18.4)	NC
X = Br	0.0 (0.0)	27.0 (27.6)	20.8 (14.3)
	0.0 (0.0)	23.8 (24.5)	15.8 (9.3)
	0.0 (0.0)	22.7 (23.6)	NC
X = Cl	0.0 (0.0)	34.0 (34.5)	31.6 (25.1)
	0.0 (0.0)	30.3 (30.9)	30.3 (23.7)
	0.0 (0.0)	29.7 (28.1)	NC

blue = DPLNO-CCSD(T)/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
green = UM06-2X/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
red = B3LYP-def2-TZVPP-THF//UM06-2X/DGDXVP-SMD-THF

Figure A2.5: Relative barriers for radical cyclization pathways. Enthalpies and free energies (parentheses) are in kcal mol^{-1}. NC= not computed.



blue = DPLNO-CCSD(T)/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
green = UM06-2X/def2-TZVPP-THF//UM06-2X/DGDXVP-THF
red = B3LYP-def2-TZVPP-THF//UM06-2X/DGDXVP-SMD-THF

[DLR1]

Figure A2.6: Relative barriers for competing radical cyclization (origin of stereoconvergence) pathways examined experimentally by Suero and co-workers. Enthalpies and free energies (parentheses) are in kcal/mol. NC= not computed.

As shown **in Figure A2.6**, we also explored the origin of stereoconvergence for the trisubstituted olefins. In agreement with experiment, the **R-*cis*** and **R-*trans*** putative radical intermediates will equilibrate at experimental conditions (barrier for rotation (via **R-*rot***) is 5 kcal/mol lower in energy than R-*cis*-TS and 10 kcal/mol lower than R-*trans*-TS, and hence will populate more the **R-*cis*** conformation (~100:1 ratio) due to fewer steric interactions between the α-phenyl and β-methyl. Finally, the radical will undergo intramolecular S_H2-type displacement of the iodo substituent to form the cyclopropane products. As observed in the experimental work, the formation of the ***cis*-dimethyl** product is favored (~3-4 kcal mol^{-1}) over the formation of the ***trans*-dimethyl** cyclopropane. Notably, the relative barriers, with respect to the putative intermediates, are nearly identical for both systems. Overall, the factors controlling the ground state geometries (e.g., **R-*cis*** vs. **R-*trans***) dictate the overall selectivity.

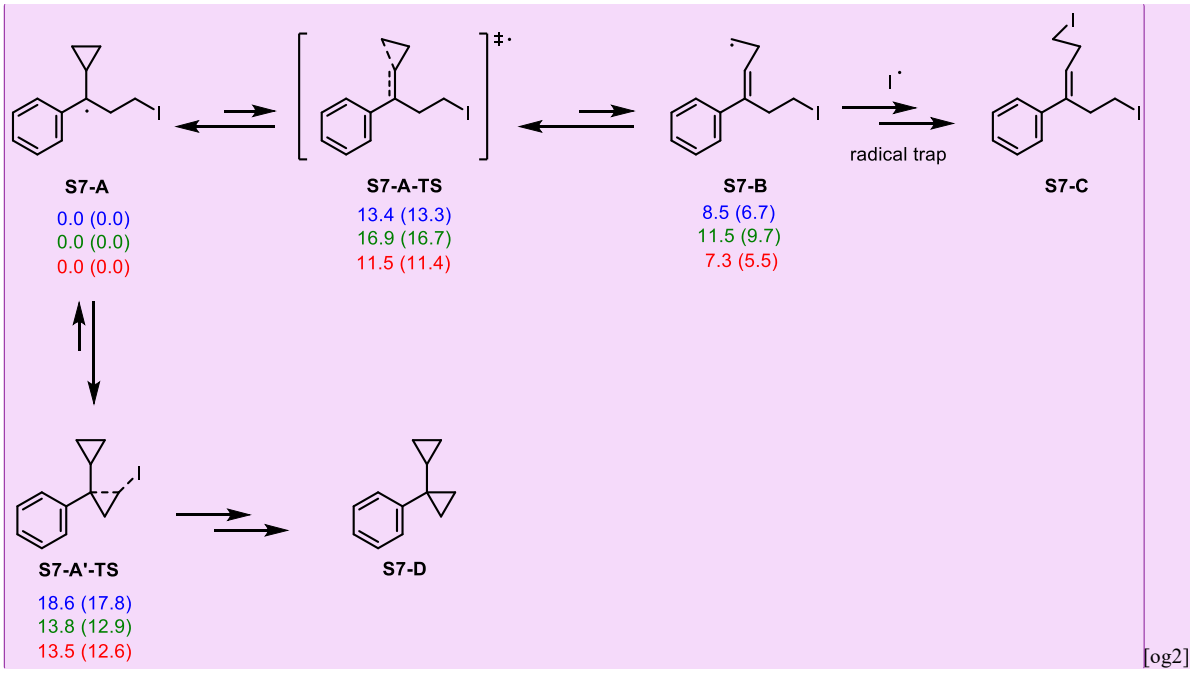


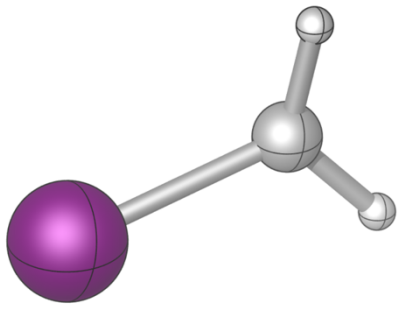
Figure A2.7: Relative barriers for competing radical cyclization and ring-opening pathways. Enthalpies and free energies (parentheses) are in kcal mol^{-1} computed using DLPNO-CCSD(T)/def2-TZVPP-THF//UM06-2X/DGDZVP-THF[og3][RHD4].

Further, Suero previously reported the radical trapping of ring-opened intermediate **S7-B** (**Figure A2.7**). Presumably, upon formation of radical trap intermediate **S7-A**, ring opening (via

S7-A-TS) will proceed with an overall barrier of ~13 kcal mol^{-1} leading to **S7-B**, which is 8-9 kcal mol^{-1} uphill in energy. On the other hand, **S7-A** can undergo competing radical cyclization (via **S7-A′-TS**), leading to cyclopropane product **S7-D**. In agreement with experiment, the barrier of cyclization is much higher than the barrier for ring-opening (18.6 vs. 13.4 kcal mol^{-1}), leading to formation of product (**S7-C**) arising from kinetically favored **S7-B**. Thus, the radical trapping (with I•) under Suero's conditions must be fast (e.g., below 18.6 kcal mol^{-1}; not computed), leading to the exclusive formation of ring-opened product **S7-C**. On the other hand, in our system, we observed formation of **S7-D** and no formation of **S7-C**. Thus, given that ring-opening (via **S7-A-TS**) is much lower in energy than radical cyclization (via **S7-A′-TS**), it is likely that 1) the barrier for radical trapping under our conditions is greater than radical cyclization o 2) single-electron-transfer to **S7-A** (e.g., reduction of **S7-A**) is fast, leading to the corresponding anionic intermediate, which will spontaneously undergo cyclization (see Thesis). Because of the strong evidence for anionic intermediates in our system, we favor the latter.

Energies and Coordinate

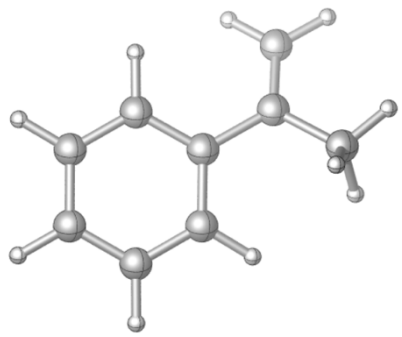
A2 = A2.1-A



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.022125 (Hartree/Particle)
Thermal correction to Energy= 0.025610
Thermal correction to Enthalpy= 0.026554
Thermal correction to Gibbs Free Energy= -0.004097
Sum of electronic and zero-point Energies= -6959.447401
Sum of electronic and thermal Energies= -6959.443917
Sum of electronic and thermal Enthalpies= -6959.442973
Sum of electronic and thermal Free Energies= -6959.473624
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-336.8594737
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-336.8602082
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -336.301643564157
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-337.0631438

I	-6.91744	0.48995	-0.52391
C	-5.08079	1.35912	-0.9092
H	-4.85125	2.28173	-0.39327
H	-4.32273	0.73269	-1.3601

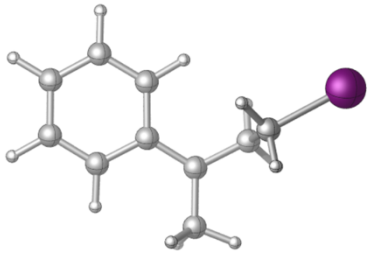
A2 = A2.1-B



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.162857 (Hartree/Particle)
Thermal correction to Energy= 0.170886
Thermal correction to Enthalpy= 0.171830
Thermal correction to Gibbs Free Energy= 0.129884
Sum of electronic and zero-point Energies= -348.662504
Sum of electronic and thermal Energies= -348.654475
Sum of electronic and thermal Enthalpies= -348.653531
Sum of electronic and thermal Free Energies= -348.695477
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF =-348.9404811
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-348.9307788
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -348.304425528041
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-349.1204175

C	-1.29582	0.15516	-0.70629
C	-2.42031	-0.51424	-0.22962
C	-2.31698	-1.35865	0.87701
C	-1.08222	-1.52312	1.50502
C	0.04613	-0.85681	1.02822
C	-0.04676	-0.01734	-0.09151
H	-1.39032	0.83392	-1.54931
H	-3.38031	-0.36594	-0.715
H	-3.19416	-1.87733	1.25213
H	-0.99338	-2.1755	2.36846
H	0.99836	-1.01222	1.52617
C	1.13813	0.68679	-0.64825
C	1.32435	0.927	-1.94814
C	2.18662	1.1518	0.32864
H	0.6107	0.56944	-2.68446
H	2.1901	1.4707	-2.31213
H	2.97766	1.63899	-0.20221
H	2.57889	0.30919	0.85878
H	1.74796	1.83746	1.02315

A2 = A2.1C

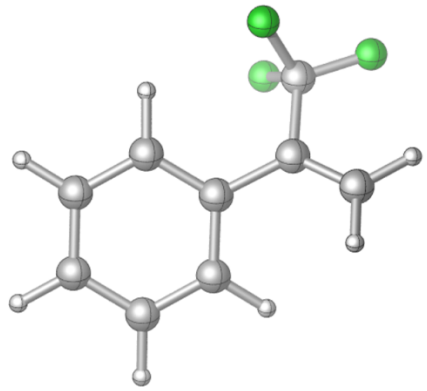


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.191903 (Hartree/Particle)
Thermal correction to Energy= 0.202565
Thermal correction to Enthalpy= 0.203509
Thermal correction to Gibbs Free Energy= 0.151612
Sum of electronic and zero-point Energies= -7308.169642
Sum of electronic and thermal Energies= -7308.158980
Sum of electronic and thermal Enthalpies= -7308.158036
Sum of electronic and thermal Free Energies= -7308.209933
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-685.8625962UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-685.850407DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.664802937223
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.2430763

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033

H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
H	0.26292	4.41073	-0.03478
H	-1.55552	4.38121	1.13135
H	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

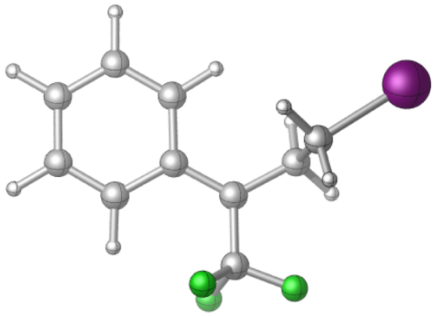
A2 = A2.1-D



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.140212 (Hartree/Particle)
Thermal correction to Energy= 0.150046
Thermal correction to Enthalpy= 0.150990
Thermal correction to Gibbs Free Energy= 0.104044
Sum of electronic and zero-point Energies= -646.397362
Sum of electronic and thermal Energies= -646.387527
Sum of electronic and thermal Enthalpies= -646.386583
Sum of electronic and thermal Free Energies= -646.433530
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF =-646.719429
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-646.7106611
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -645.734967844683
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.9809486

C	-1.13843	0.14183	-0.95079
C	-2.26292	-0.52757	-0.47412
C	-2.15958	-1.37198	0.63251
C	-0.92482	-1.53645	1.26052
C	0.20352	-0.87015	0.78372
C	0.11063	-0.03067	-0.33601
H	-1.23292	0.82059	-1.79381
H	-3.22292	-0.37928	-0.9595
H	-3.03677	-1.89067	1.00762
H	-0.83598	-2.18883	2.12396
H	1.15575	-1.02555	1.28167
C	1.29553	0.67346	-0.89275
C	1.48175	0.91367	-2.19264
C	2.34402	1.13847	0.08414
F	3.21932	1.99973	-0.4597
F	3.07721	0.11067	0.57275
F	1.80154	1.75592	1.15248
H	0.76809	0.55611	-2.92896
H	2.3475	1.45737	-2.55663

A2 = A2.1-E

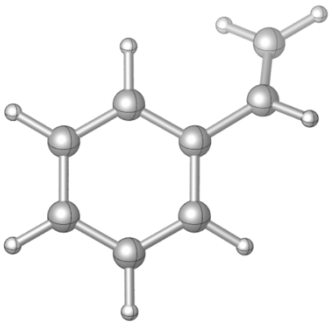


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169531 (Hartree/Particle)
Thermal correction to Energy= 0.182589
Thermal correction to Enthalpy= 0.183533
Thermal correction to Gibbs Free Energy= 0.125680
Sum of electronic and zero-point Energies= -7605.905529
Sum of electronic and thermal Energies= -7605.892471
Sum of electronic and thermal Enthalpies= -7605.891527
Sum of electronic and thermal Free Energies= -7605.949379
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6412459

UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6298922
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.095274559044
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.1038604

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033
H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
F	0.26292	4.41073	-0.03478
F	-1.55552	4.38121	1.13135
F	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

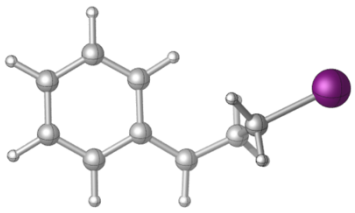
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UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.134550 (Hartree/Particle)
Thermal correction to Energy= 0.141247
Thermal correction to Enthalpy= 0.142191
Thermal correction to Gibbs Free Energy= 0.103510
Sum of electronic and zero-point Energies= -309.391782
Sum of electronic and thermal Energies= -309.385085
Sum of electronic and thermal Enthalpies= -309.384141
Sum of electronic and thermal Free Energies= -309.422822
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-309.6289559
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-309.6195033
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -309.060872536704
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-309.7863822

C	-0.99752	0.14348	-0.5217
C	-2.1237	-0.46741	0.02273
C	-2.02847	-1.1929	1.21438
C	-0.79614	-1.29765	1.85885
C	0.33158	-0.6838	1.31248
C	0.25073	0.03962	0.11417
H	-1.09442	0.7097	-1.44386
H	-3.08177	-0.37537	-0.48069
H	-2.90948	-1.66683	1.63696
H	-0.71149	-1.85524	2.78705
H	1.29062	-0.76802	1.81825
C	1.47873	0.6578	-0.42811
C	1.61198	1.25496	-1.618
H	2.34997	0.5994	0.22303
H	0.79428	1.34112	-2.32933
H	2.56697	1.67618	-1.91869

A2 = A2.1-G

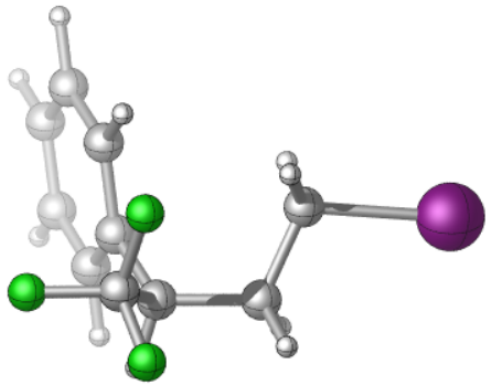


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.163818 (Hartree/Particle)
Thermal correction to Energy= 0.173551
Thermal correction to Enthalpy= 0.174495
Thermal correction to Gibbs Free Energy= 0.124756

Sum of electronic and zero-point Energies= -7268.899626
Sum of electronic and thermal Energies= -7268.889893
Sum of electronic and thermal Enthalpies= -7268.888949
Sum of electronic and thermal Free Energies= -7268.938689
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.550296
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-646.5387261
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -645.421330008022
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.9078879

C	-1.76483	1.04879	0.32358
C	-2.9649	0.36614	0.19507
C	-2.9741	-1.02574	0.02975
C	-1.76064	-1.72321	-0.00474
C	-0.553	-1.04968	0.1243
C	-0.52085	0.36129	0.29463
H	-1.76391	2.12856	0.45151
H	-3.90211	0.9146	0.22235
H	-3.91473	-1.55823	-0.07194
H	-1.76151	-2.80159	-0.1353
H	0.37578	-1.61301	0.09221
C	0.69348	1.08883	0.43262
C	2.05608	0.47016	0.3749
H	0.6273	2.1705	0.51851
C	2.4479	0.28851	-1.09155
I	4.41628	-0.62846	-1.29463
H	2.07879	-0.4972	0.8854
H	2.78405	1.12106	0.86498
H	2.52655	1.23764	-1.61875
H	1.77369	-0.38054	-1.62399

A2 = A2.2-A

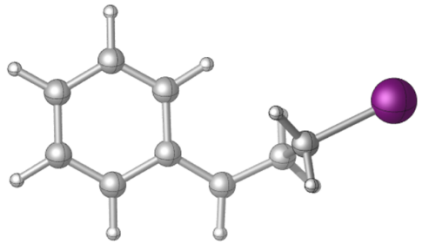


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.183375 (Hartree/Particle)
Thermal correction to Energy= 0.196422
Thermal correction to Enthalpy= 0.197366
Thermal correction to Gibbs Free Energy= 0.140566
Sum of electronic and zero-point Energies= -7606.541763
Sum of electronic and thermal Energies= -7606.528716
Sum of electronic and thermal Enthalpies= -7606.527772
Sum of electronic and thermal Free Energies= -7606.584572
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.2916764
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-984.2796588
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.746685669875
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.7529466

C	-2.93387	1.98547	-0.83558
C	-4.1182	1.30884	-1.13062
C	-4.44906	0.13523	-0.45218
C	-3.58938	-0.3586	0.52902
C	-2.4091	0.32175	0.82835
C	-2.06765	1.49762	0.15218
H	-2.69577	2.89301	-1.38327
H	-4.78249	1.70131	-1.89483
H	-5.37122	-0.38881	-0.68515
H	-3.83848	-1.26855	1.06672
H	-1.74327	-0.06337	1.59703

C	-0.74214	2.15442	0.49163
C	0.41554	1.75039	-0.45326
C	-0.84633	3.65798	0.64961
F	0.28908	4.16967	1.1699
F	-1.84344	4.00894	1.4842
F	-1.06103	4.32372	-0.50695
C	0.11202	1.93841	-1.93244
I	1.81615	1.33979	-3.14023
H	0.62305	0.69406	-0.26276
H	1.31312	2.3104	-0.17572
H	-0.06972	2.97259	-2.21472
H	-0.70023	1.30442	-2.28135
H	-0.45293	1.81903	1.49328

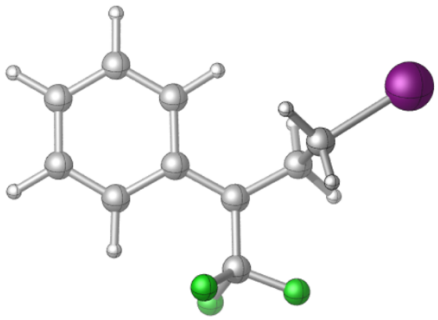
A2 = A2.2-B



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.163818 (Hartree/Particle)
Thermal correction to Energy= 0.173551
Thermal correction to Enthalpy= 0.174495
Thermal correction to Gibbs Free Energy= 0.124756
Sum of electronic and zero-point Energies= -7268.899626
Sum of electronic and thermal Energies= -7268.889893
Sum of electronic and thermal Enthalpies= -7268.888949
Sum of electronic and thermal Free Energies= -7268.938689
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.550296
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-646.5387261
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -645.421330008022
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.9078879

C	-1.76483	1.04879	0.32358
C	-2.9649	0.36614	0.19507
C	-2.9741	-1.02574	0.02975
C	-1.76064	-1.72321	-0.00474
C	-0.553	-1.04968	0.1243
C	-0.52085	0.36129	0.29463
H	-1.76391	2.12856	0.45151
H	-3.90211	0.9146	0.22235
H	-3.91473	-1.55823	-0.07194
H	-1.76151	-2.80159	-0.1353
H	0.37578	-1.61301	0.09221
C	0.69348	1.08883	0.43262
C	2.05608	0.47016	0.3749
H	0.6273	2.1705	0.51851
C	2.4479	0.28851	-1.09155
I	4.41628	-0.62846	-1.29463
H	2.07879	-0.4972	0.8854
H	2.78405	1.12106	0.86498
H	2.52655	1.23764	-1.61875
H	1.77369	-0.38054	-1.62399

A2 = A2.2-C

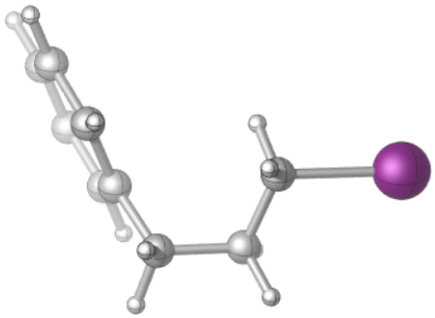


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169531 (Hartree/Particle)
Thermal correction to Energy= 0.182589
Thermal correction to Enthalpy= 0.183533
Thermal correction to Gibbs Free Energy= 0.125680
Sum of electronic and zero-point Energies= -7605.905529
Sum of electronic and thermal Energies= -7605.892471
Sum of electronic and thermal Enthalpies= -7605.891527
Sum of electronic and thermal Free Energies= -7605.949379
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6412459
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6298922

DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.095274559044
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.1038604

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033
H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
F	0.26292	4.41073	-0.03478
F	-1.55552	4.38121	1.13135
F	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

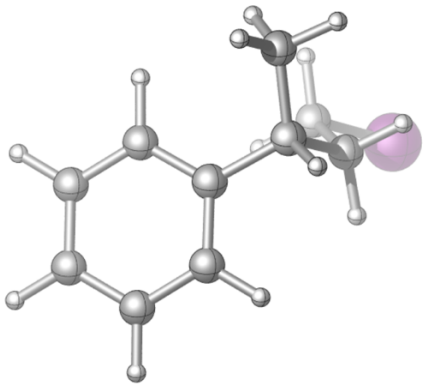
A2 = A2.2-D



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.177258 (Hartree/Particle)
Thermal correction to Energy= 0.187058
Thermal correction to Enthalpy= 0.188003
Thermal correction to Gibbs Free Energy= 0.138509
Sum of electronic and zero-point Energies= -7269.534469
Sum of electronic and thermal Energies= -7269.524668
Sum of electronic and thermal Enthalpies= -7269.523724
Sum of electronic and thermal Free Energies= -7269.573217
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-647.1993726
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-647.1880664
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -646.071301651043
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-647.5559084

C	-1.25411	0.8953	-0.16181
C	-2.42817	0.25665	-0.56867
C	-2.6833	-1.05685	-0.17358
C	-1.75862	-1.72541	0.63252
C	-0.58763	-1.08351	1.03522
C	-0.31959	0.23479	0.64353
H	-1.06166	1.91996	-0.47316
H	-3.14209	0.78587	-1.19354
H	-3.59588	-1.55524	-0.48715
H	-1.95222	-2.74647	0.94895
H	0.12756	-1.60932	1.66484
C	0.97647	0.8998	1.04512
C	2.1854	0.38486	0.24153
C	2.00706	0.66984	-1.23906
I	3.751	0.06779	-2.39379
H	2.30584	-0.69153	0.40011
H	3.09091	0.87582	0.60926
H	1.89277	1.73266	-1.45001
H	1.18456	0.11266	-1.68421
H	1.17179	0.7156	2.10642
H	0.89071	1.98334	0.91342

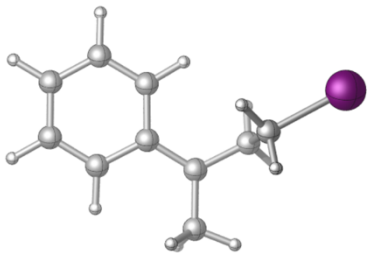
A2 = A2.2-E



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.206002 (Hartree/Particle)
Thermal correction to Energy= 0.217114
Thermal correction to Enthalpy= 0.218058
Thermal correction to Gibbs Free Energy= 0.165938
Sum of electronic and zero-point Energies= -7308.803121
Sum of electronic and thermal Energies= -7308.792009
Sum of electronic and thermal Enthalpies= -7308.791065
Sum of electronic and thermal Free Energies= -7308.843185
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.5067522
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-686.3834684
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -685.311800914941
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.8861496

C	-3.07524	2.14681	-0.64041
C	-4.23453	1.45553	-1.00471
C	-4.44475	0.15015	-0.56216
C	-3.48667	-0.46033	0.25146
C	-2.33213	0.2331	0.61101
C	-2.10643	1.54555	0.17124
H	-2.93555	3.16402	-0.99565
H	-4.97401	1.94138	-1.63492
H	-5.34662	-0.38573	-0.84291
H	-3.64136	-1.47471	0.60793
H	-1.59239	-0.24775	1.24828
C	-0.80915	2.23903	0.55415
C	0.37315	1.68452	-0.27643
C	-0.88169	3.76589	0.49666
H	0.05849	4.19663	0.8544
H	-1.68931	4.14206	1.13181
H	-1.0514	4.14307	-0.5154
C	0.20278	1.93244	-1.76581
I	1.87447	1.11632	-2.89401
H	0.4636	0.60857	-0.09768
H	1.29878	2.15368	0.07231
H	0.19459	2.98782	-2.03105
H	-0.67188	1.43499	-2.18185
H	-0.59379	1.95939	1.59164

A2 = A2.2-F



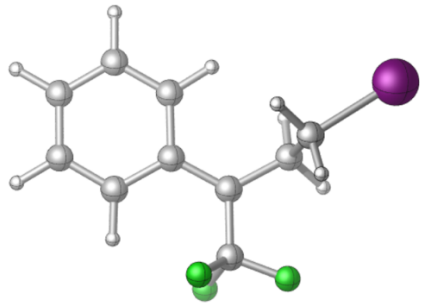
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.192199 (Hartree/Particle)
Thermal correction to Energy= 0.203458
Thermal correction to Enthalpy= 0.204402
Thermal correction to Gibbs Free Energy= 0.151277
Sum of electronic and zero-point Energies= -7308.170913
Sum of electronic and thermal Energies= -7308.159654
Sum of electronic and thermal Enthalpies= -7308.158709
Sum of electronic and thermal Free Energies= -7308.211834
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-685.8625962
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-685.850407
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.664802937223

B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.2430763

C	-3.43853	2.31618	-0.06969
C	-4.62638	1.60188	-0.16006
C	-4.61241	0.21072	-0.31098
C	-3.38294	-0.45587	-0.36914
C	-2.18961	0.24783	-0.27591
C	-2.17725	1.66198	-0.12007
H	-3.48083	3.3943	0.05079
H	-5.57376	2.13161	-0.11221
H	-5.54293	-0.34393	-0.38306
H	-3.35788	-1.53505	-0.49137
H	-1.25567	-0.30337	-0.33358
C	-0.95776	2.4083	-0.02388
C	0.37998	1.72303	-0.02944
C	-0.97624	3.90824	0.02441

H	0.03622	4.3121	-0.05162
H	-1.40639	4.2738	0.96647
H	-1.5735	4.34144	-0.786
C	0.83715	1.56237	-1.47826
I	2.75601	0.53326	-1.60479
H	0.34227	0.74583	0.45732
H	1.1114	2.32978	0.51248
H	0.99797	2.52018	-1.97168
H	0.15618	0.94918	-2.06629

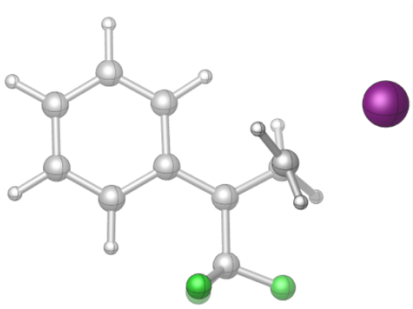
A2 = A2.3-A



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169531 (Hartree/Particle)
Thermal correction to Energy= 0.182589
Thermal correction to Enthalpy= 0.183533
Thermal correction to Gibbs Free Energy= 0.125680
Sum of electronic and zero-point Energies= -7605.905529
Sum of electronic and thermal Energies= -7605.892471
Sum of electronic and thermal Enthalpies= -7605.891527
Sum of electronic and thermal Free Energies= -7605.949379
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6412459
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6298922
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.095274559044
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.1038604

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033
H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
F	0.26292	4.41073	-0.03478
F	-1.55552	4.38121	1.13135
F	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

A2 = A2.3-TS-A

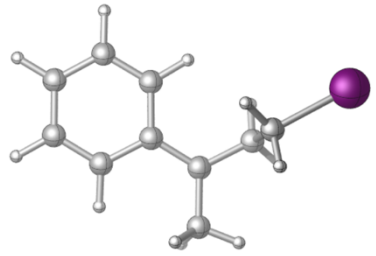


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -757.60
Zero-point correction= 0.168719 (Hartree/Particle)
Thermal correction to Energy= 0.181417
Thermal correction to Enthalpy= 0.182361
Thermal correction to Gibbs Free Energy= 0.125806
Sum of electronic and zero-point Energies= -7605.876226
Sum of electronic and thermal Energies= -7605.863528
Sum of electronic and thermal Enthalpies= -7605.862584
Sum of electronic and thermal Free Energies= -7605.919138
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6127667
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5997266

DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.058643521008
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.0745288

C	-0.45045	-2.09533	-0.84025
C	0.89096	-1.53873	-1.20596
C	0.11113	-0.30004	-1.00969
H	-1.22544	-2.16581	-1.59622
H	-0.7748	-2.08112	0.19287
H	1.1945	-1.75551	-2.22663
H	1.68416	-1.7201	-0.48766
I	-0.13138	-4.65486	-0.81304
C	-0.5236	0.30575	-2.23373
F	0.12335	1.42562	-2.62202
F	-0.50598	-0.52934	-3.28556
F	-1.81204	0.65384	-2.04183
C	0.10676	0.46585	0.23657
C	0.68464	-0.08013	1.40377
C	-0.45765	1.75711	0.31723
C	0.7024	0.63641	2.59312
H	1.1097	-1.07943	1.39665
C	-0.42474	2.47232	1.51015
H	-0.91642	2.22451	-0.54672
C	0.15234	1.91945	2.65364
H	1.14778	0.19157	3.47757
H	-0.85555	3.46818	1.54447
H	0.17032	2.4798	3.58324

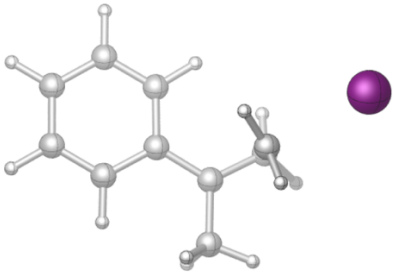
A2 = A2.3-B



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.192199 (Hartree/Particle)
Thermal correction to Energy= 0.203458
Thermal correction to Enthalpy= 0.204402
Thermal correction to Gibbs Free Energy= 0.151277
Sum of electronic and zero-point Energies= -7308.170913
Sum of electronic and thermal Energies= -7308.159654
Sum of electronic and thermal Enthalpies= -7308.158709
Sum of electronic and thermal Free Energies= -7308.211834
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-685.8625962UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-685.850407DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.664802937223
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.2430763

C	-3.43853	2.31618	-0.06969
C	-4.62638	1.60188	-0.16006
C	-4.61241	0.21072	-0.31098
C	-3.38294	-0.45587	-0.36914
C	-2.18961	0.24783	-0.27591
C	-2.17725	1.66198	-0.12007
H	-3.48083	3.3943	0.05079
H	-5.57376	2.13161	-0.11221
H	-5.54293	-0.34393	-0.38306
H	-3.35788	-1.53505	-0.49137
H	-1.25567	-0.30337	-0.33358
C	-0.95776	2.4083	-0.02388
C	0.37998	1.72303	-0.02944
C	-0.97624	3.90824	0.02441
H	0.03622	4.3121	-0.05162
H	-1.40639	4.2738	0.96647
H	-1.5735	4.34144	-0.786
C	0.83715	1.56237	-1.47826
I	2.75601	0.53326	-1.60479
H	0.34227	0.74583	0.45732
H	1.1114	2.32978	0.51248
H	0.99797	2.52018	-1.97168
H	0.15618	0.94918	-2.06629

A2 = A2.3-TS-B

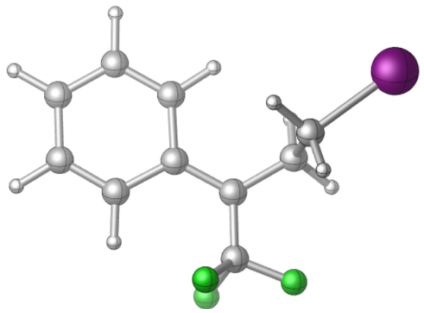


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -473.97
Zero-point correction= 0.191806 (Hartree/Particle)
Thermal correction to Energy= 0.202587

Thermal correction to Enthalpy= 0.203532
Thermal correction to Gibbs Free Energy= 0.152017
Sum of electronic and zero-point Energies= -7308.148319
Sum of electronic and thermal Energies= -7308.137538
Sum of electronic and thermal Enthalpies= -7308.136593
Sum of electronic and thermal Free Energies= -7308.188109
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-685.8401271
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-685.8238908
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.630267715450
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.2208154

C	-0.65581	-1.98249	-0.78285
C	0.6792	-1.44335	-1.17993
C	-0.12858	-0.21954	-0.99865
H	-1.44352	-2.07742	-1.5206
H	-0.94102	-2.02808	0.25965
H	0.95277	-1.66136	-2.20966
H	1.48232	-1.629	-0.47296
I	-0.32428	-4.6517	-0.78301
C	-0.78101	0.38344	-2.21076
H	-0.22897	1.27982	-2.51822
H	-0.76529	-0.32045	-3.04508
H	-1.81754	0.67494	-2.02176
C	-0.12712	0.51458	0.27175
C	0.45567	-0.02012	1.44144
C	-0.70788	1.79607	0.34823
C	0.45752	0.69941	2.62984
H	0.89882	-1.01201	1.43602
C	-0.69504	2.51723	1.53946
H	-1.16343	2.24226	-0.52965
C	-0.11496	1.97381	2.68619
H	0.90659	0.26492	3.51783
H	-1.14121	3.50666	1.57213
H	-0.10985	2.53458	3.61587

Thesis = Figure 3.6 INT-II
A2 = S2.4-A-I

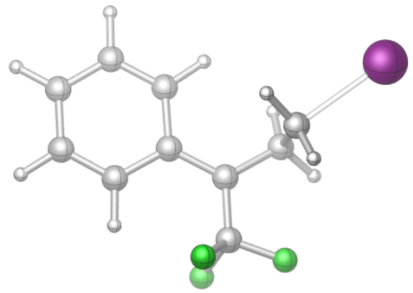


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.167550 (Hartree/Particle)
Thermal correction to Energy= 0.180734
Thermal correction to Enthalpy= 0.181678
Thermal correction to Gibbs Free Energy= 0.124507
Sum of electronic and zero-point Energies= -7606.039712
Sum of electronic and thermal Energies= -7606.026528
Sum of electronic and thermal Enthalpies= -7606.025584
Sum of electronic and thermal Free Energies= -7606.082755
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.7700173
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.7084948
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.16302341914
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.2286083

C	-3.4643	2.28901	-0.10508
C	-4.62465	1.5324	-0.21302
C	-4.58522	0.13708	-0.33562
C	-3.32762	-0.47457	-0.35275
C	-2.15604	0.269	-0.24969
C	-2.16459	1.69116	-0.10873
H	-3.56394	3.36609	-0.00626
H	-5.58416	2.04522	-0.19849
H	-5.49719	-0.44624	-0.41796
H	-3.25359	-1.55528	-0.45497
H	-1.20928	-0.26334	-0.28541
C	-0.95044	2.43476	0.02624
C	0.39481	1.76053	0.00197
C	-0.99176	3.8817	0.0241
F	0.23968	4.45855	0.06519

F	-1.68274	4.47832	1.07471
F	-1.60853	4.48217	-1.07229
C	0.79839	1.53042	-1.44919
I	2.66733	0.34857	-1.6151
H	0.3658	0.80468	0.53546
H	1.16304	2.36205	0.49402
H	1.0291	2.45658	-1.9742
H	0.071	0.94495	-2.00947

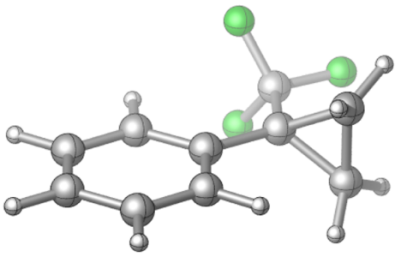
Thesis = Figure 3.6 TS-IV
A2 = S2.4-TS-A-I



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -413.43
Zero-point correction= 0.166873 (Hartree/Particle)
Thermal correction to Energy= 0.179728
Thermal correction to Enthalpy= 0.180672
Thermal correction to Gibbs Free Energy= 0.124318
Sum of electronic and zero-point Energies= -7606.036979
Sum of electronic and thermal Energies= -7606.024124
Sum of electronic and thermal Enthalpies= -7606.023180
Sum of electronic and thermal Free Energies= -7606.079534
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.7659819
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.706073
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.158630880790
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.2276677

C	-0.43992	-2.3593	-0.84208
C	0.7622	-1.55143	-1.19467
C	0.09231	-0.21629	-1.04388
H	-1.21704	-2.42073	-1.59837
H	-0.81133	-2.25796	0.17322
H	1.11104	-1.76108	-2.20675
H	1.5939	-1.69626	-0.50255
I	0.11301	-4.75245	-0.75133
C	-0.49985	0.38592	-2.23236
F	0.13145	1.52734	-2.70151
F	-0.51535	-0.45101	-3.30116
F	-1.80274	0.81042	-2.09376
C	0.10019	0.50997	0.20145
C	0.60762	-0.07654	1.39425
C	-0.38137	1.84415	0.32611
C	0.63803	0.61661	2.60072
H	0.97235	-1.1	1.38335
C	-0.34556	2.52574	1.53785
H	-0.77826	2.36363	-0.54073
C	0.16483	1.92827	2.69539
H	1.03499	0.11908	3.48241
H	-0.71973	3.54604	1.57611
H	0.18923	2.46588	3.63829

Thesis = Figure 3.6 P-IV, P-V, P-VI
A2 = S2.4-B-I, S2.4-B-Br, S2.4-B-Cl

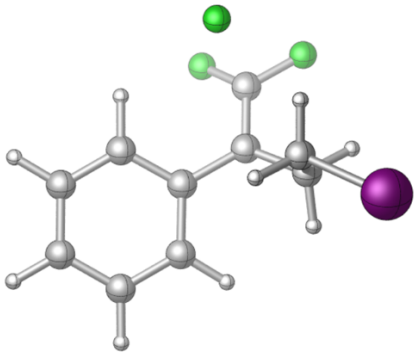


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169956 (Hartree/Particle)
Thermal correction to Energy= 0.180456
Thermal correction to Enthalpy= 0.181400
Thermal correction to Gibbs Free Energy= 0.133443
Sum of electronic and zero-point Energies= -685.664596
Sum of electronic and thermal Energies= -685.654097
Sum of electronic and thermal Enthalpies= -685.653153
Sum of electronic and thermal Free Energies= -685.701110
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.0287248
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-686.017579
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

FINAL SINGLE POINT ENERGY -684.968350369337
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.3034705

C	-4.62713	3.52715	0.09742
C	-5.80802	2.79305	0.22736
C	-5.77352	1.40565	0.34378
C	-4.5391	0.75489	0.328
C	-3.36048	1.48475	0.19793
C	-3.38161	2.88379	0.08136
H	-6.75858	3.31821	0.23694
H	-4.70648	4.60538	0.01005
H	-6.69414	0.83882	0.44441
H	-4.49014	-0.32643	0.41655
H	-2.41723	0.94509	0.18665
C	-2.08221	3.62863	-0.05461
C	-2.16951	5.12047	-0.17389
C	-0.9339	2.99693	-0.81635
C	-0.8512	3.12176	0.67109
H	-0.31159	3.65118	-1.41686
H	-1.13783	2.02579	-1.25325
H	-0.17194	3.86043	1.08207
H	-0.99801	2.23879	1.28284
F	-2.87781	5.5164	-1.25442
F	-0.95763	5.69836	-0.28948
F	-2.75723	5.69306	0.89989

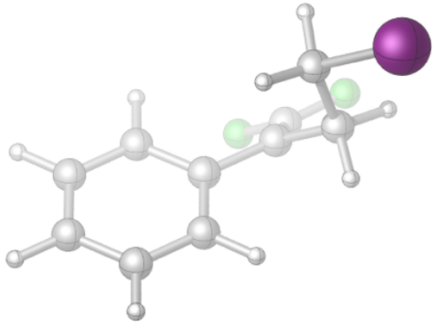
Thesis = Figure 3.6 TS-VII
A2 = S2.4-TS-A'-I



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -275.07
Zero-point correction= 0.167183 (Hartree/Particle)
Thermal correction to Energy= 0.180481
Thermal correction to Enthalpy= 0.181426
Thermal correction to Gibbs Free Energy= 0.123738
Sum of electronic and zero-point Energies= -7606.025397
Sum of electronic and thermal Energies= -7606.012099
Sum of electronic and thermal Enthalpies= -7606.011155
Sum of electronic and thermal Free Energies= -7606.068842
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.7558324
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6775319
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.133589195933
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.2230046

C	-1.82657	3.93323	0.25503
C	-2.8676	3.44046	1.03915
C	-3.13179	2.06967	1.09421
C	-2.33298	1.19763	0.35234
C	-1.29814	1.68916	-0.44311
C	-1.02868	3.06864	-0.52162
C	0.07794	3.5762	-1.35466
C	1.37791	2.8084	-1.43823
C	0.06994	4.86249	-1.77862
C	2.13882	2.98883	-0.13023
I	3.98021	1.80618	-0.1005
F	0.59201	6.10374	-0.35611
F	-1.05734	5.54507	-1.98966
F	1.01562	5.32492	-2.59877
H	-1.605	4.99625	0.25755
H	-3.46524	4.13175	1.62759
H	-3.93881	1.68783	1.7128
H	-2.51821	0.12738	0.38747
H	-0.70195	0.98793	-1.0207
H	1.98949	3.16506	-2.26995
H	1.19364	1.74545	-1.61398
H	1.578	2.63787	0.73499
H	2.46336	4.01646	0.02276

Thesis = Figure 3.6 P-VII
A2 = S2.4-C-I



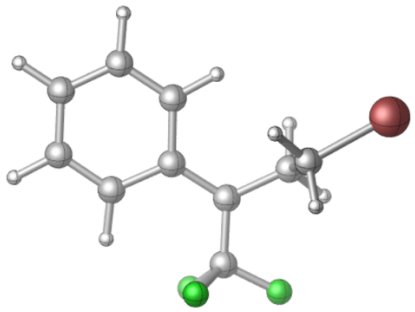
UM06-2X/DGDZVP-SMD-THF

Zero-point correction= 0.167227 (Hartree/Particle)
Thermal correction to Energy= 0.179440
Thermal correction to Enthalpy= 0.180384
Thermal correction to Gibbs Free Energy= 0.125019
Sum of electronic and zero-point Energies= -7506.076534
Sum of electronic and thermal Energies= -7506.064321
Sum of electronic and thermal Enthalpies= -7506.063377
Sum of electronic and thermal Free Energies= -7506.118741
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-883.7895195
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-883.7795136
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

FINAL SINGLE POINT ENERGY -882.356881445871
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-884.2173235

I	3.93598	1.7843	-0.02781
F	0.88614	5.26419	-2.83865
H	2.07636	3.28574	-2.16363
H	2.36533	3.92931	0.23969
C	2.08385	2.91512	-0.03906
C	1.41687	2.85615	-1.4079
C	-0.0491	4.71309	-2.07218
H	1.23764	1.81424	-1.68697
C	0.10056	3.60159	-1.36247
H	1.4762	2.46565	0.74486
F	-1.15632	5.4408	-2.15537
C	-1.00848	3.09074	-0.51235
H	-0.71471	1.03083	-1.09786
H	-1.54041	5.01588	0.30749
C	-1.28964	1.71746	-0.48268
C	-1.76443	3.95293	0.29486
C	-2.31608	1.22143	0.32017
C	-2.79157	3.45546	1.09543
H	-2.52575	0.15593	0.32599
C	-3.07245	2.08842	1.11006
H	-3.36731	4.1364	1.71531
H	-3.87019	1.70134	1.73694

Thesis = Figure 3.6 INT-II
A2 = S2.4-A-Br

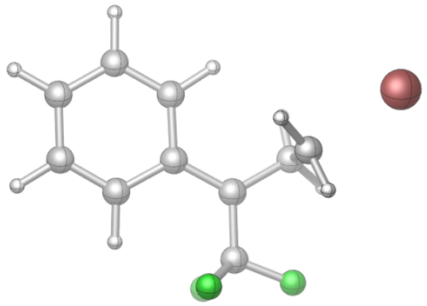


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.168119 (Hartree/Particle)
Thermal correction to Energy= 0.181144
Thermal correction to Enthalpy= 0.182089
Thermal correction to Gibbs Free Energy= 0.125956
Sum of electronic and zero-point Energies= -3259.486880
Sum of electronic and thermal Energies= -3259.473854
Sum of electronic and thermal Enthalpies= -3259.472910
Sum of electronic and thermal Free Energies= -3259.529042
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.3371115
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3260.270636
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3257.729257479883
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.6126486

C	-3.45066	2.28745	-0.11354
C	-4.61451	1.53845	-0.23328
C	-4.58413	0.14169	-0.34356
C	-3.33046	-0.4783	-0.33724
C	-2.15511	0.25759	-0.22214
C	-2.15403	1.68125	-0.09131
H	-3.54425	3.36615	-0.02897
H	-5.57001	2.05898	-0.24024
H	-5.49904	-0.43562	-0.43531
H	-3.26244	-1.5604	-0.42911
H	-1.21255	-0.28286	-0.23608
C	-0.93826	2.41847	0.05673
C	0.40982	1.74533	-0.00347
C	-0.9769	3.86451	0.03377

F	0.25291	4.442	0.1065
F	-1.70358	4.47481	1.0498
F	-1.55436	4.45664	-1.09361
C	0.80211	1.52411	-1.45806
Br	2.51994	0.51839	-1.62937
H	0.39297	0.78431	0.52099
H	1.18295	2.34397	0.48447
H	0.98099	2.46265	-1.98096
H	0.07371	0.92423	-2.00258

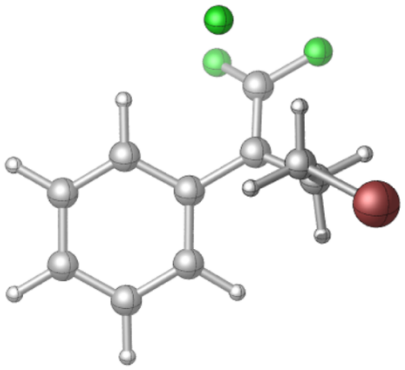
Thesis = Figure 3.6 TS-V
A2 = S2.4-TS-A-Br



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -476.43
Zero-point correction= 0.167141 (Hartree/Particle)
Thermal correction to Energy= 0.179948
Thermal correction to Enthalpy= 0.180892
Thermal correction to Gibbs Free Energy= 0.125165
Sum of electronic and zero-point Energies= -3259.477213
Sum of electronic and thermal Energies= -3259.464405
Sum of electronic and thermal Enthalpies= -3259.463461
Sum of electronic and thermal Free Energies= -3259.519189
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.3260702
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3260.2632957
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3257.719806807296
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.6059703

C	-0.4283	-2.2902	-0.84612
C	0.8007	-1.55369	-1.19989
C	0.06057	-0.25268	-1.0335
H	-1.1943	-2.37938	-1.60781
H	-0.78085	-2.22155	0.17629
H	1.14553	-1.75566	-2.21341
H	1.62506	-1.68716	-0.49933
Br	0.02249	-4.6044	-0.74079
C	-0.5076	0.35907	-2.23119
F	0.15791	1.47979	-2.69995
F	-0.53453	-0.48295	-3.29508
F	-1.79701	0.81205	-2.09847
C	0.08461	0.48768	0.20895
C	0.60903	-0.08972	1.3963
C	-0.40242	1.81804	0.32804
C	0.64594	0.60936	2.59971
H	0.9842	-1.10923	1.38577
C	-0.35897	2.50736	1.5357
H	-0.81117	2.32867	-0.53841
C	0.16517	1.91792	2.69066
H	1.05579	0.11988	3.47987
H	-0.73768	3.5259	1.57233
H	0.19583	2.4609	3.63034

Thesis = Figure 3.6 TS-VIII
A2 = S2.4-TS-A'-Br

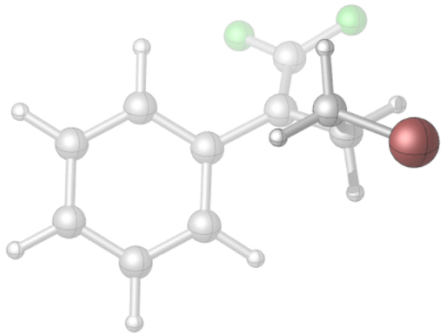


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -270.16
Zero-point correction= 0.167651 (Hartree/Particle)
Thermal correction to Energy= 0.180880
Thermal correction to Enthalpy= 0.181824
Thermal correction to Gibbs Free Energy= 0.124539
Sum of electronic and zero-point Energies= -3259.473329
Sum of electronic and thermal Energies= -3259.460100
Sum of electronic and thermal Enthalpies= -3259.459156
Sum of electronic and thermal Free Energies= -3259.516441
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF

HF=-3260.3234369
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3260.2412971
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3257.701497815834
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.6075836

C	-1.43382	0.81375	0.62528
C	-2.49121	0.29787	1.3711
C	-2.75398	-1.07475	1.38369
C	-1.93402	-1.92642	0.64143
C	-0.87948	-1.4128	-0.11334
C	-0.61338	-0.03074	-0.15033
C	0.51441	0.498	-0.93088
C	1.76485	-0.32713	-1.14783
C	0.53397	1.79214	-1.31975
C	1.74475	-0.95056	-2.53696
Br	3.31808	-2.11416	-2.82387
F	1.05757	3.00457	0.17503
F	-0.5668	2.51813	-1.51259
F	1.50735	2.25492	-2.10524
H	-1.21261	1.87583	0.66433
H	-3.10333	0.97237	1.96386
H	-3.57579	-1.47388	1.97089
H	-2.11657	-2.99758	0.64582
H	-0.26049	-2.09944	-0.68582
H	1.82832	-1.11279	-0.39008
H	2.66193	0.28989	-1.04355
H	1.79617	-0.20076	-3.32471
H	0.88081	-1.59378	-2.69657

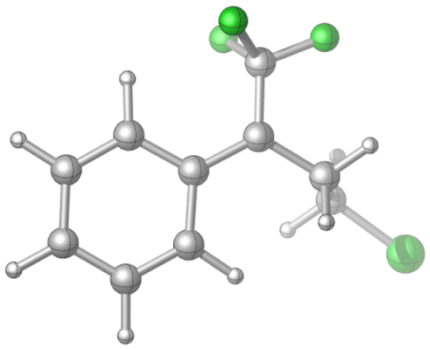
Thesis = Figure 3.6 P-VIII
A2 = S2.4-C-Br



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.167756 (Hartree/Particle)
Thermal correction to Energy= 0.179859
Thermal correction to Enthalpy= 0.180803
Thermal correction to Gibbs Free Energy= 0.126299
Sum of electronic and zero-point Energies= -3159.524207
Sum of electronic and thermal Energies= -3159.512104
Sum of electronic and thermal Enthalpies= -3159.511160
Sum of electronic and thermal Free Energies= -3159.565665
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3160.3568668
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3160.3437059
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3157.925068304705
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3160.6019278

Br	3.76881	1.88204	-0.04388
F	0.90155	5.25546	-2.83111
H	2.0816	3.26607	-2.16755
H	2.38119	3.9349	0.22163
C	2.10088	2.91623	-0.04134
C	1.4253	2.84526	-1.40399
C	-0.03576	4.70554	-2.0669
H	1.24219	1.80056	-1.66945
C	0.11079	3.5929	-1.3583
H	1.48876	2.48347	0.74867
F	-1.14149	5.43457	-2.15026
C	-1.00044	3.08359	-0.50991
H	-0.72118	1.02507	-1.10788
H	-1.51945	5.00799	0.31992
C	-1.29067	1.71208	-0.48802
C	-1.75029	3.94655	0.30212
C	-2.32004	1.21854	0.31267
C	-2.78033	3.45151	1.10044
H	-2.53703	0.15449	0.31252
C	-3.07011	2.08624	1.10772
H	-3.35149	4.13287	1.72407
H	-3.87028	1.70107	1.73269

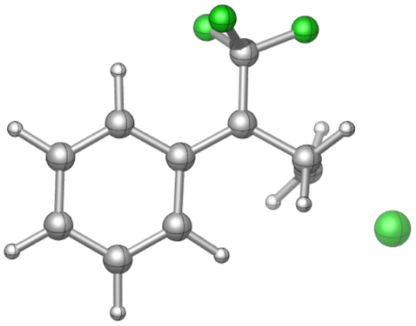
Thesis = Figure 3.6 INT-II
A2 = S2.4-A-Cl



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.168564 (Hartree/Particle)
Thermal correction to Energy= 0.181452
Thermal correction to Enthalpy= 0.182397
Thermal correction to Gibbs Free Energy= 0.127179
Sum of electronic and zero-point Energies= -1145.920480
Sum of electronic and thermal Energies= -1145.907592
Sum of electronic and thermal Enthalpies= -1145.906647
Sum of electronic and thermal Free Energies= -1145.961865
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.3404846
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1146.273204
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1144.747207096244
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.654635

C	-3.44607	2.28679	-0.11317
C	-4.60797	1.53505	-0.23375
C	-4.57449	0.13845	-0.34737
C	-3.31921	-0.47835	-0.34305
C	-2.14553	0.26003	-0.22696
C	-2.14744	1.68389	-0.09345
H	-3.54228	3.36511	-0.02634
H	-5.56483	2.05318	-0.23871
H	-5.48805	-0.44088	-0.43984
H	-3.24855	-1.56013	-0.43713
H	-1.20153	-0.27789	-0.24204
C	-0.93309	2.4222	0.05368
C	0.41415	1.74729	-0.01157
C	-0.97306	3.86724	0.03877
F	0.25608	4.44629	0.11428
F	-1.701	4.47288	1.05744
F	-1.55155	4.46606	-1.08582
C	0.81233	1.50184	-1.46243
Cl	2.37742	0.55316	-1.58812
H	0.39817	0.79131	0.52332
H	1.19045	2.34965	0.46743
H	0.99346	2.43732	-1.99255
H	0.06771	0.91332	-1.99917

Thesis = Figure 3.6 TS-VI
A2 = S2.4-TS-A-Cl

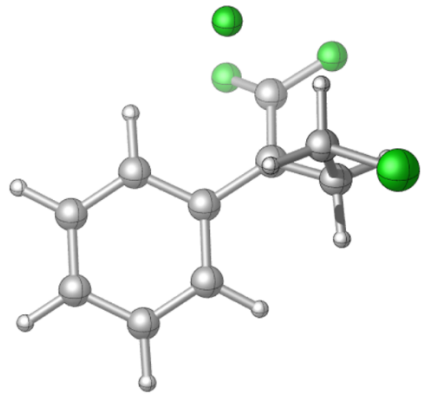


UM06-2X/DGDZVP-SMD-THF
Imaringary Frequency = -528.88
Zero-point correction= 0.167404 (Hartree/Particle)
Thermal correction to Energy= 0.180071
Thermal correction to Enthalpy= 0.181015
Thermal correction to Gibbs Free Energy= 0.126508
Sum of electronic and zero-point Energies= -1145.907843
Sum of electronic and thermal Energies= -1145.895177
Sum of electronic and thermal Enthalpies= -1145.894232
Sum of electronic and thermal Free Energies= -1145.948740
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.3257222
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1146.2580185
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1144.732010432447
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.6450701

C	-0.42241	-2.29775	-0.84017

C	0.80341	-1.56005	-1.1998
C	0.05974	-0.25905	-1.03453
H	-1.19122	-2.38412	-1.59971
H	-0.77227	-2.22092	0.183
H	1.14516	-1.76195	-2.21443
H	1.63071	-1.68724	-0.50111
Cl	-0.00088	-4.47346	-0.73606
C	-0.50627	0.35177	-2.23258
F	0.15902	1.4728	-2.70248
F	-0.53229	-0.49117	-3.29605
F	-1.79614	0.80556	-2.10224
C	0.08494	0.48138	0.20744
C	0.61161	-0.09504	1.39437
C	-0.40455	1.81091	0.32726
C	0.64712	0.60378	2.59808
H	0.98999	-1.1134	1.38311
C	-0.36234	2.49981	1.53514
H	-0.81498	2.32068	-0.53894
C	0.1633	1.91111	2.68988
H	1.05873	0.11503	3.47784
H	-0.74338	3.5175	1.57222
H	0.19297	2.4538	3.62976

Thesis = Figure 3.6 TS-IX
A2 = S2.4-TS-A'-Cl



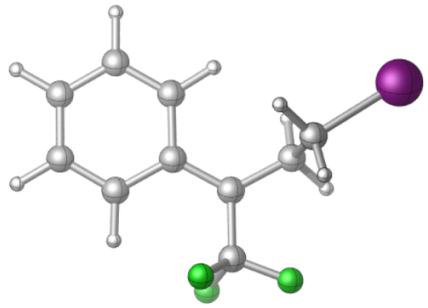
UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -261.92
Zero-point correction= 0.168230 (Hartree/Particle)
Thermal correction to Energy= 0.180245
Thermal correction to Enthalpy= 0.181189
Thermal correction to Gibbs Free Energy= 0.127227
Sum of electronic and zero-point Energies= -1045.958499
Sum of electronic and thermal Energies= -1045.946485
Sum of electronic and thermal Enthalpies= -1045.945541
Sum of electronic and thermal Free Energies= -1045.999503
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1046.3611596
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1046.3483119
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1044.944854327378
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1046.6450544

Cl	3.63489	1.94508	-0.04995
F	0.90708	5.25193	-2.83413
H	2.09306	3.2645	-2.16077
H	2.38228	3.92907	0.22359
C	2.10534	2.90806	-0.03839
C	1.43104	2.84267	-1.4025
C	-0.02998	4.70151	-2.06977
H	1.2506	1.79725	-1.66837
C	0.11712	3.58953	-1.36056
H	1.48166	2.48278	0.74768
F	-1.13642	5.42975	-2.15381
C	-0.9944	3.08102	-0.51189
H	-0.71966	1.02341	-1.11425
H	-1.50767	5.00475	0.32279
C	-1.28684	1.70997	-0.49178
C	-1.74053	3.94375	0.3037
C	-2.31484	1.21671	0.31084
C	-2.76896	3.44895	1.10429
H	-2.53371	0.15304	0.30933
C	-3.06094	2.08415	1.10993
H	-3.33695	4.13006	1.7311
H	-3.85968	1.69908	1.73679

Thesis = Figure 3.6 P-IV
A2 = S2.4-B-Iodine-Anion
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
Sum of electronic and zero-point Energies= -6920.436282
Sum of electronic and thermal Energies= -6920.434866
Sum of electronic and thermal Enthalpies= -6920.433922
Sum of electronic and thermal Free Energies= -6920.453131

UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.8061761
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.7222293
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -297.221350590763
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.9784966
I -0.74423 3.03008 0.
Thesis = Figure 3.6 P-V
A2 = S2.4-B-Bromine-Anion
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016176
Sum of electronic and zero-point Energies= -2573.860368
Sum of electronic and thermal Energies= -2573.858951
Sum of electronic and thermal Enthalpies= -2573.858007
Sum of electronic and thermal Free Energies= -2573.876543
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.3491984
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-2574.2709696
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -2572.775930449734
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.3423516
Br -0.74423 3.03008 0.
Thesis = Figure 3.6 P-VI
A2 = S2.4-B-Chlorine-Anion
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015023
Sum of electronic and zero-point Energies= -460.295573
Sum of electronic and thermal Energies= -460.294156
Sum of electronic and thermal Enthalpies= -460.293212
Sum of electronic and thermal Free Energies= -460.310595
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-460.352515
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-460.2558726
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -459.777655437201
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-460.3854977
Cl -0.74423 3.03008 0.
Thesis = Figure 3.5 P-VII, P-VIII, PIX
A2 = S2.4-C-Fluorine-Anion
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.014159
Sum of electronic and zero-point Energies= -99.942009
Sum of electronic and thermal Energies= -99.940593
Sum of electronic and thermal Enthalpies= -99.939648
Sum of electronic and thermal Free Energies= -99.956168
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=- 99.9658134
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-99.8370181
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -99.720313970503
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF

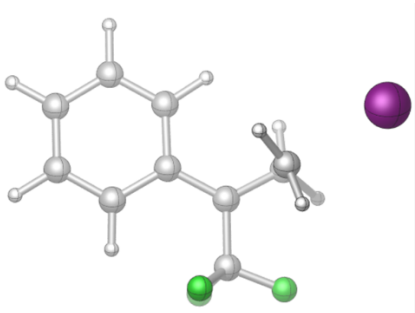
HF=-100.0050411
F -0.3074 1.56784 0.
Thesis = Figure 3.5 INT-I
A2 = S2.5-A-I



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169531 (Hartree/Particle)
Thermal correction to Energy= 0.182589
Thermal correction to Enthalpy= 0.183533
Thermal correction to Gibbs Free Energy= 0.125680
Sum of electronic and zero-point Energies= -7605.905529
Sum of electronic and thermal Energies= -7605.892471
Sum of electronic and thermal Enthalpies= -7605.891527
Sum of electronic and thermal Free Energies= -7605.949379
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6412459
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6298922
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.095274559044
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.1038604

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033
H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
F	0.26292	4.41073	-0.03478
F	-1.55552	4.38121	1.13135
F	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

Thesis = Figure 3.5 TS-I
A2 = S2.5-TS-A-I

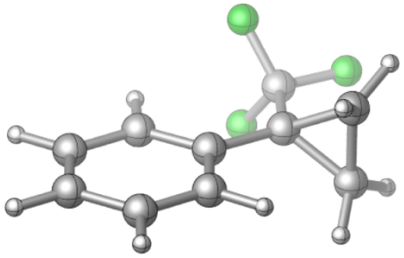


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -757.60
Zero-point correction= 0.168719 (Hartree/Particle)
Thermal correction to Energy= 0.181417
Thermal correction to Enthalpy= 0.182361
Thermal correction to Gibbs Free Energy= 0.125806
Sum of electronic and zero-point Energies= -7605.876226
Sum of electronic and thermal Energies= -7605.863528
Sum of electronic and thermal Enthalpies= -7605.862584
Sum of electronic and thermal Free Energies= -7605.919138
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6127667
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5997266
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.058643521008
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF

HF=-984.0745288

C	-0.45045	-2.09533	-0.84025
C	0.89096	-1.53873	-1.20596
C	0.11113	-0.30004	-1.00969
H	-1.22544	-2.16581	-1.59622
H	-0.7748	-2.08112	0.19287
H	1.1945	-1.75551	-2.22663
H	1.68416	-1.7201	-0.48766
I	-0.13138	-4.65486	-0.81304
C	-0.5236	0.30575	-2.23373
F	0.12335	1.42562	-2.62202
F	-0.50598	-0.52934	-3.28556
F	-1.81204	0.65384	-2.04183
C	0.10676	0.46585	0.23657
C	0.68464	-0.08013	1.40377
C	-0.45765	1.75711	0.31723
C	0.7024	0.63641	2.59312
H	1.1097	-1.07943	1.39665
C	-0.42474	2.47232	1.51015
H	-0.91642	2.22451	-0.54672
C	0.15234	1.91945	2.65364
H	1.14778	0.19157	3.47757
H	-0.85555	3.46818	1.54447
H	0.17032	2.4798	3.58324

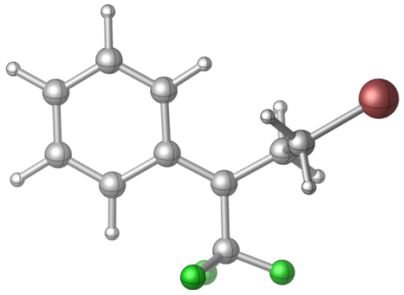
Thesis = Figure 3.5 P-I, P-II, P-III
A2 = S2.5-B-I, S2.5-B-Br, S2.5-B-Cl



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169956 (Hartree/Particle)
Thermal correction to Energy= 0.180456
Thermal correction to Enthalpy= 0.181400
Thermal correction to Gibbs Free Energy= 0.133443
Sum of electronic and zero-point Energies= -685.664596
Sum of electronic and thermal Energies= -685.654097
Sum of electronic and thermal Enthalpies= -685.653153
Sum of electronic and thermal Free Energies= -685.701110
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.0287248
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-686.017579
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.968350369337
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.3034705

C	-4.62713	3.52715	0.09742
C	-5.80802	2.79305	0.22736
C	-5.77352	1.40565	0.34378
C	-4.5391	0.75489	0.328
C	-3.36048	1.48475	0.19793
C	-3.38161	2.88379	0.08136
H	-6.75858	3.31821	0.23694
H	-4.70648	4.60538	0.01005
H	-6.69414	0.83882	0.44441
H	-4.49014	-0.32643	0.41655
H	-2.41723	0.94509	0.18665
C	-2.08221	3.62863	-0.05461
C	-2.16951	5.12047	-0.17389
C	-0.9339	2.99693	-0.81635
C	-0.8512	3.12176	0.67109
H	-0.31159	3.65118	-1.41686
H	-1.13783	2.02579	-1.25325
H	-0.17194	3.86043	1.08207
H	-0.99801	2.23879	1.28284
F	-2.87781	5.5164	-1.25442
F	-0.95763	5.69836	-0.28948
F	-2.75723	5.69306	0.89989

Thesis = Figure 3.6 INT-II
S2.5-A-Br

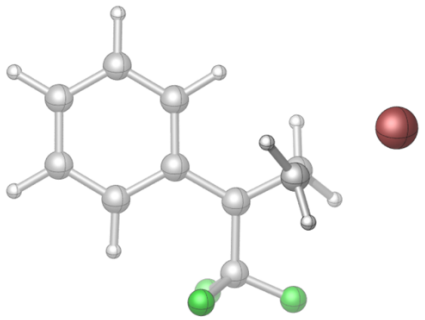


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.170095 (Hartree/Particle)
Thermal correction to Energy= 0.183043
Thermal correction to Enthalpy= 0.183987
Thermal correction to Gibbs Free Energy= 0.127162
Sum of electronic and zero-point Energies= -3259.352871

Sum of electronic and thermal Energies= -3259.339923
Sum of electronic and thermal Enthalpies= -3259.338979
Sum of electronic and thermal Free Energies= -3259.395804
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.208318
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3260.1938922
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3257.663286503138
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.4881895

C	-3.46196	2.29674	-0.08241
C	-4.63649	1.56282	-0.16297
C	-4.60124	0.17142	-0.30138
C	-3.36608	-0.48107	-0.35849
C	-2.18423	0.24053	-0.27406
C	-2.19398	1.65429	-0.13148
H	-3.53601	3.37308	0.02912
H	-5.59012	2.0797	-0.11533
H	-5.52453	-0.39615	-0.36292
H	-3.32578	-1.56029	-0.47032
H	-1.24376	-0.29793	-0.32746
C	-0.96109	2.37914	-0.04199
C	0.39076	1.72434	-0.0174
C	-0.99177	3.87638	-0.03905
F	0.24178	4.41345	-0.07123
F	-1.59935	4.38942	1.05817
F	-1.65325	4.3917	-1.1031
C	0.90648	1.55051	-1.44602
Br	2.6543	0.65027	-1.44742
H	0.33115	0.75409	0.47785
H	1.09707	2.33319	0.55111
H	1.06458	2.50562	-1.94491
H	0.24861	0.92254	-2.04485

Thesis = Figure 3.5 TS-II
A2 = S2.5-TS-A-Br

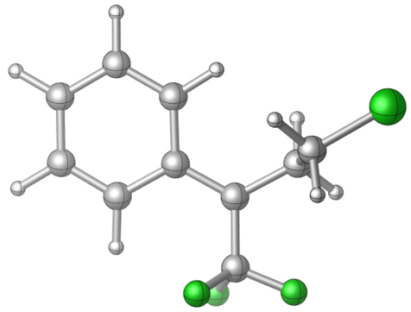


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -708.80
Zero-point correction= 0.168856 (Hartree/Particle)
Thermal correction to Energy= 0.181520
Thermal correction to Enthalpy= 0.182464
Thermal correction to Gibbs Free Energy= 0.126646
Sum of electronic and zero-point Energies= -3259.314803
Sum of electronic and thermal Energies= -3259.302138
Sum of electronic and thermal Enthalpies= -3259.301194
Sum of electronic and thermal Free Energies= -3259.357012
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.1688007
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3260.151055
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3257.615423994849
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3260.4505558

C	-0.45211	-2.06728	-0.83408
C	0.90111	-1.54971	-1.20633
C	0.10004	-0.32551	-1.00308
H	-1.23053	-2.15297	-1.58389
H	-0.75899	-2.08613	0.20351
H	1.1973	-1.76705	-2.22832
H	1.691	-1.73295	-0.48533
Br	-0.16211	-4.4828	-0.85029
C	-0.52063	0.28885	-2.23202
F	0.13841	1.404	-2.60954
F	-0.49996	-0.54356	-3.28566
F	-1.80793	0.64357	-2.04915
C	0.10212	0.45032	0.24159

C	0.68927	-0.08592	1.40768
C	-0.46847	1.73823	0.3174
C	0.70961	0.63726	2.59315
H	1.12188	-1.08204	1.40447
C	-0.43308	2.46073	1.50618
H	-0.935	2.19857	-0.54602
C	0.15264	1.91738	2.64945
H	1.16252	0.19981	3.47744
H	-0.86925	3.45436	1.53689
H	0.17215	2.48284	3.57592

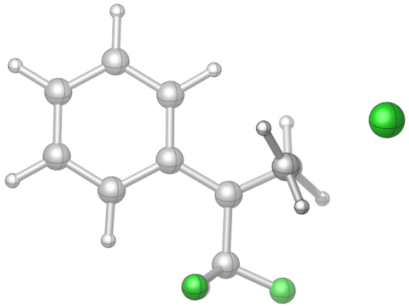
Thesis = Figure 3.5 INT-III
A2 = S2.5-A-Cl



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.170670 (Hartree/Particle)
Thermal correction to Energy= 0.183412
Thermal correction to Enthalpy= 0.184356
Thermal correction to Gibbs Free Energy= 0.128735
Sum of electronic and zero-point Energies= -1145.787098
Sum of electronic and thermal Energies= -1145.774356
Sum of electronic and thermal Enthalpies= -1145.773412
Sum of electronic and thermal Free Energies= -1145.829033
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.2125031
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1146.1984738
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1144.683020694885
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.531235

C	-1.80657	0.62287	0.29891
C	-2.9769	-0.1172	0.21241
C	-2.93337	-1.50696	0.0602
C	-1.69453	-2.15192	-0.00421
C	-0.51668	-1.42442	0.08658
C	-0.53555	-0.01219	0.24223
H	-1.88584	1.69775	0.42162
H	-3.93363	0.3933	0.26649
H	-3.8535	-2.07912	-0.00624
H	-1.64855	-3.22973	-0.12708
H	0.42797	-1.95556	0.02553
C	0.69495	0.71597	0.33558
C	2.0434	0.05712	0.36174
C	0.66167	2.21263	0.34193
F	1.89335	2.75332	0.30128
F	0.06091	2.72231	1.4449
F	-0.00955	2.72859	-0.71575
C	2.54722	-0.16764	-1.06479
Cl	4.14474	-1.01141	-1.03811
H	1.98567	-0.89871	0.88588
H	2.76275	0.67793	0.90007
H	2.70195	0.77417	-1.59147
H	1.87008	-0.80113	-1.6377

Thesis = Figure 3.5 TS-III
A2 = S2.5-TS-A-Cl



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -437.11
Zero-point correction= 0.169052 (Hartree/Particle)
Thermal correction to Energy= 0.181609
Thermal correction to Enthalpy= 0.182553
Thermal correction to Gibbs Free Energy= 0.127783
Sum of electronic and zero-point Energies= -1145.739184
Sum of electronic and thermal Energies= -1145.726627
Sum of electronic and thermal Enthalpies= -1145.725683
Sum of electronic and thermal Free Energies= -1145.780453
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.1623439
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

HF=-1146.1436884
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1144.622477432049
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1146.4837143

C	-0.45368	-2.00534	-0.82278
C	0.91718	-1.5466	-1.20816
C	0.07779	-0.34982	-0.99536
H	-1.2264	-2.15236	-1.56907
H	-0.73339	-2.09882	0.21798
H	1.19679	-1.77	-2.23288
H	1.70256	-1.72723	-0.48284
Cl	-0.13702	-4.39035	-0.89153
C	-0.53002	0.27284	-2.22988
F	0.14617	1.37789	-2.60029
F	-0.51374	-0.56052	-3.28167
F	-1.81302	0.63999	-2.05048
C	0.08783	0.43775	0.24729
C	0.67165	-0.09861	1.41418
C	-0.47121	1.73025	0.31435
C	0.70235	0.63142	2.59468
H	1.09282	-1.0997	1.41496
C	-0.42517	2.4602	1.49828
H	-0.93568	2.18912	-0.55086
C	0.15814	1.91767	2.643
H	1.15232	0.19538	3.48106
H	-0.85122	3.45825	1.52405
H	0.18495	2.48857	3.56595

Thesis = Figure 3.5 P-I
A2 = S2.5-B-Iodine-Radical
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.017503
Sum of electronic and zero-point Energies= -6920.237912
Sum of electronic and thermal Energies= -6920.236495
Sum of electronic and thermal Enthalpies= -6920.235551
Sum of electronic and thermal Free Energies= -6920.255414
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.6137243
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.6118482
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -297.110848563578
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.7800963

I	-0.74423	3.03008	0.

Thesis = Figure 3.5 P-II
A2 = S2.5-B-Bromine-Radical
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016830
Sum of electronic and zero-point Energies= -2573.667105
Sum of electronic and thermal Energies= -2573.665689
Sum of electronic and thermal Enthalpies= -2573.664745
Sum of electronic and thermal Free Energies= -2573.683935
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.1542532
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-2574.150351
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -2572.660988893114
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.1448385

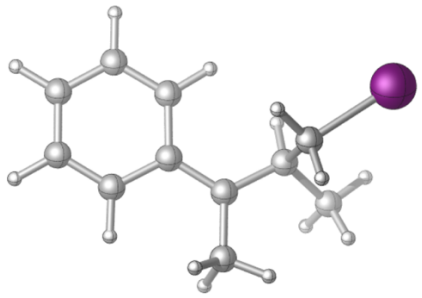
Br	-0.74423	3.03008	0.

Thesis = Figure 3.5P-III
A2 = S2.5-B-Chlorine-Radical
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015677
Sum of electronic and zero-point Energies= -460.075053

Sum of electronic and thermal Energies= -460.073637
Sum of electronic and thermal Enthalpies= -460.072692
Sum of electronic and thermal Free Energies= -460.090730
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-460.1349741
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-460.1325705
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -459.664197907915
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-460.1694148

Cl	-0.74423	3.03008	0.

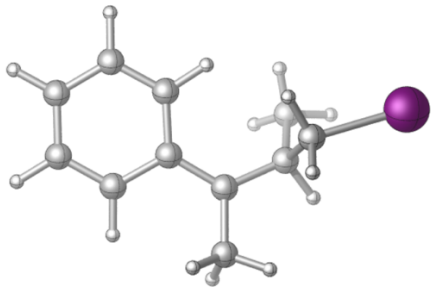
A2 = S2.6-R-cis



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.220649 (Hartree/Particle)
Thermal correction to Energy= 0.233242
Thermal correction to Enthalpy= 0.234186
Thermal correction to Gibbs Free Energy= 0.178706
Sum of electronic and zero-point Energies= -7347.437927
Sum of electronic and thermal Energies= -7347.425334
Sum of electronic and thermal Enthalpies= -7347.424390
Sum of electronic and thermal Free Energies= -7347.479870
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.1702473
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-725.1578825
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -723.904731637718
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.5731521

C	-3.79477	2.18934	-0.0044
C	-4.97745	1.46418	-0.07309
C	-4.95377	0.07535	-0.24066
C	-3.71905	-0.57631	-0.335
C	-2.53042	0.13853	-0.26128
C	-2.5267	1.55133	-0.09237
H	-3.84822	3.26437	0.13553
H	-5.92816	1.98421	0.0059
H	-5.87995	-0.48826	-0.29745
H	-3.68503	-1.65344	-0.47223
H	-1.59553	-0.40568	-0.35339
C	-1.31491	2.31837	-0.02209
C	0.03608	1.63843	0.00842
C	-1.37332	3.81856	-0.03733
H	-0.39145	4.25787	-0.22182
H	-1.73144	4.21829	0.92124
H	-2.05268	4.19038	-0.81155
C	0.46	1.49824	-1.45587
I	2.30536	0.35814	-1.72331
H	-0.07607	0.63744	0.43179
C	1.07243	2.38358	0.85703
H	0.66435	2.46513	-1.91742
H	-0.27223	0.95058	-2.04718
H	1.43986	3.28514	0.35838
H	1.93332	1.73954	1.05502
H	0.64223	2.67336	1.82033

A2 = S2.6-R-trans

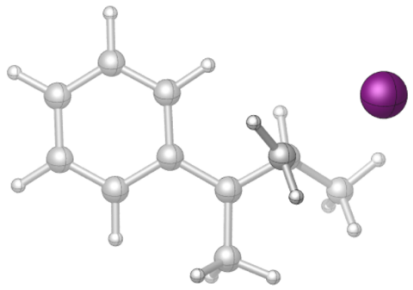


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.220653 (Hartree/Particle)
Thermal correction to Energy= 0.233358
Thermal correction to Enthalpy= 0.234303
Thermal correction to Gibbs Free Energy= 0.178682
Sum of electronic and zero-point Energies= -7347.435500

Sum of electronic and thermal Energies= -7347.422794
Sum of electronic and thermal Enthalpies= -7347.421850
Sum of electronic and thermal Free Energies= -7347.477471
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.1654375
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-725.1530356
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -723.900251556595
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.5684512

C	-3.54323	2.72306	0.12731
C	-4.76618	2.06604	0.0759
C	-4.83138	0.70444	-0.23776
C	-3.64435	0.01201	-0.50012
C	-2.41628	0.65884	-0.44259
C	-2.32026	2.04047	-0.12292
H	-3.52797	3.77686	0.38654
H	-5.6779	2.61903	0.28371
H	-5.78829	0.19367	-0.2816
H	-3.67832	-1.04256	-0.75865
H	-1.52423	0.09176	-0.67861
C	-1.07176	2.74863	-0.05802
C	0.29491	2.09075	0.00352
C	-1.06571	4.25153	-0.03265
H	-0.08972	4.63741	-0.34017
H	-1.25745	4.63658	0.97906
H	-1.82122	4.68437	-0.69444
C	0.74077	1.8595	-1.4432
I	2.82958	1.2274	-1.59845
C	0.42253	0.841	0.88905
H	0.96287	2.84885	0.42564
H	0.69802	2.77069	-2.03803
H	0.17988	1.06483	-1.93405
H	0.20224	-0.08597	0.3553
H	-0.24522	0.90758	1.75261
H	1.44671	0.75959	1.2625

A2 = S2.6-R-cis-TS

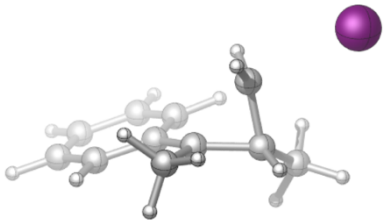


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -424.58
Zero-point correction= 0.219613 (Hartree/Particle)
Thermal correction to Energy= 0.231999
Thermal correction to Enthalpy= 0.232943
Thermal correction to Gibbs Free Energy= 0.178185
Sum of electronic and zero-point Energies= -7347.418946
Sum of electronic and thermal Energies= -7347.406560
Sum of electronic and thermal Enthalpies= -7347.405616
Sum of electronic and thermal Free Energies= -7347.460374
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.1507598
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-725.134366
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -723.873819756000
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.5547872

C	-0.6745	-1.99079	-0.78881
C	0.64882	-1.42893	-1.19658
C	-0.18215	-0.20989	-1.00636
H	-1.45756	-2.09672	-1.53218
H	-0.96922	-2.03423	0.25154
C	1.16127	-1.79046	-2.5777
H	1.40976	-1.55307	-0.42939
I	-0.33316	-4.6548	-0.75337
C	-0.8754	0.41652	-2.18306
H	-0.31036	1.29537	-2.5179
H	-0.94455	-0.27135	-3.02532
H	-1.88631	0.74539	-1.92849
C	-0.15614	0.51593	0.27107
C	0.39145	-0.04711	1.44505

C	-0.67024	1.82617	0.34839
C	0.42498	0.67114	2.6338
H	0.77941	-1.06158	1.44653
C	-0.6247	2.5461	1.53947
H	-1.09688	2.29768	-0.53038
C	-0.07893	1.97404	2.68881
H	0.84555	0.21267	3.52368
H	-1.01821	3.55771	1.56888
H	-0.04887	2.53357	3.61878
H	0.35247	-1.92281	-3.29858
H	1.70443	-2.73707	-2.51375
H	1.84409	-1.02109	-2.94841

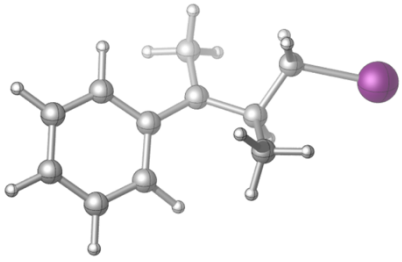
A2 = S2.6-R-trans-TS



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -433.52
Zero-point correction= 0.219807 (Hartree/Particle)
Thermal correction to Energy= 0.232136
Thermal correction to Enthalpy= 0.233080
Thermal correction to Gibbs Free Energy= 0.178150
Sum of electronic and zero-point Energies= -7347.413720
Sum of electronic and thermal Energies= -7347.401391
Sum of electronic and thermal Enthalpies= -7347.400447
Sum of electronic and thermal Free Energies= -7347.455377
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.1455999
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-725.1288756
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -723.868490248892
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.5498219

C	-0.74352	-1.85715	-0.75312
C	0.60106	-1.3457	-1.16059
C	-0.18221	-0.09066	-0.97135
H	-1.55607	-1.90274	-1.46859
H	-1.00511	-1.91098	0.29674
H	0.76897	-1.51448	-2.22339
C	1.82143	-1.71304	-0.32721
I	-0.53593	-4.52602	-0.85294
C	-0.80123	0.49537	-2.21189
H	-0.16914	1.30781	-2.59147
H	-0.87313	-0.25647	-3.00013
H	-1.79903	0.90148	-2.02686
C	-0.18589	0.7082	0.26052
C	0.17757	0.19352	1.52447
C	-0.55329	2.0695	0.19289
C	0.18553	1.0034	2.65404
H	0.43133	-0.85217	1.6447
C	-0.53483	2.87918	1.32517
H	-0.84211	2.51086	-0.75457
C	-0.16488	2.35273	2.56281
H	0.46296	0.57649	3.61316
H	-0.81363	3.92511	1.23905
H	-0.15587	2.98206	3.44746
H	2.44764	-0.83744	-0.13582
H	2.41449	-2.44214	-0.88492
H	1.56158	-2.17658	0.62491

A2 = S2.6-R-rot

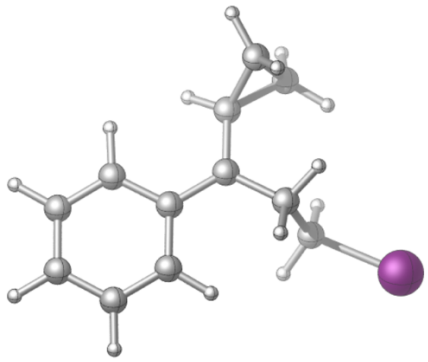


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.220796 (Hartree/Particle)
Thermal correction to Energy= 0.232338
Thermal correction to Enthalpy= 0.233282
Thermal correction to Gibbs Free Energy= 0.181114
Sum of electronic and zero-point Energies= -7347.424559
Sum of electronic and thermal Energies= -7347.413017
Sum of electronic and thermal Enthalpies= -7347.412073
Sum of electronic and thermal Free Energies= -7347.464241
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.1571397
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

HF=-725.1451259
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -723.891344269193
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-725.558854

C	-1.95514	0.7427	0.28469
C	-3.09521	0.2914	0.94105
C	-3.20452	-1.04591	1.33273
C	-2.15596	-1.9244	1.0474
C	-1.00794	-1.47471	0.40148
C	-0.86654	-0.12222	0.01163
H	-1.88808	1.78936	0.00015
H	-3.90291	0.98731	1.15014
H	-4.09642	-1.3997	1.8411
H	-2.23787	-2.97345	1.31801
H	-0.23824	-2.19387	0.14672
C	0.29369	0.39051	-0.69815
C	1.71691	-0.11303	-0.4941
C	0.0629	1.45299	-1.74053
H	0.7176	1.29298	-2.60482
H	0.26461	2.46841	-1.372
H	-0.96826	1.4344	-2.10074
C	2.65698	1.10157	-0.5771
I	4.74648	0.54095	-0.83719
H	1.9728	-0.78223	-1.32966
C	1.96192	-0.84014	0.83622
H	2.63451	1.6946	0.33833
H	2.47588	1.74009	-1.43566
H	1.46993	-0.31256	1.65954
H	3.03333	-0.87469	1.05047
H	1.60957	-1.87042	0.83025

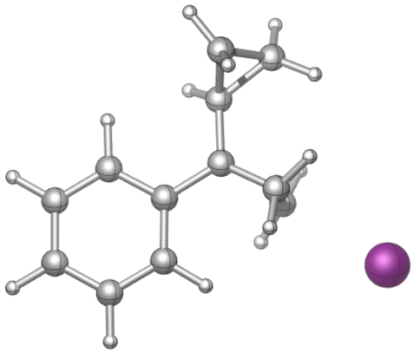
Thesis = Figure 3.8 INT-V
A2 = A2.7-A



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.227905 (Hartree/Particle)
Thermal correction to Energy= 0.240397
Thermal correction to Enthalpy= 0.241341
Thermal correction to Gibbs Free Energy= 0.185601
Sum of electronic and zero-point Energies= -7385.498196
Sum of electronic and thermal Energies= -7385.485705
Sum of electronic and thermal Enthalpies= -7385.484761
Sum of electronic and thermal Free Energies= -7385.540501
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3039.8185225
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.2362051
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -761.906683304787
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.6621129

C	-2.13898	0.07947	0.07439
C	-3.29007	-0.66995	-0.13119
C	-3.21262	-2.03529	-0.42721
C	-1.95351	-2.64043	-0.50489
C	-0.79672	-1.90125	-0.29608
C	-0.84663	-0.50919	-0.00503
H	-2.2429	1.12956	0.32609
H	-4.26015	-0.18706	-0.05235
H	-4.11541	-2.61578	-0.59059
H	-1.87481	-3.69957	-0.73366
H	0.16055	-2.40762	-0.37566
C	0.35119	0.2547	0.20894
C	1.68819	-0.42682	0.31242
C	0.30849	1.72828	0.30263
C	1.56055	2.58137	0.20574
C	0.87813	2.43964	1.52905
H	-0.57292	2.2031	-0.11195
C	2.2961	-0.55187	-1.08379
I	4.30364	-1.39762	-1.00436
H	1.60258	-1.4162	0.76815
H	2.36411	0.1505	0.95063
H	2.42082	0.4116	-1.57541
H	1.73302	-1.22454	-1.72907
H	1.35254	1.8126	2.27728
H	0.31206	3.27924	1.91722
H	1.45427	3.52293	-0.32178
H	2.51849	2.0902	0.0705

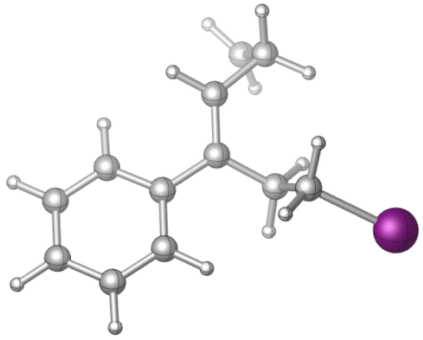
A2 = A2.7-A'-TS



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -441.83
Zero-point correction= 0.225896 (Hartree/Particle)
Thermal correction to Energy= 0.238492
Thermal correction to Enthalpy= 0.239436
Thermal correction to Gibbs Free Energy= 0.182345
Sum of electronic and zero-point Energies= -7385.476157
Sum of electronic and thermal Energies= -7385.463561
Sum of electronic and thermal Enthalpies= -7385.462617
Sum of electronic and thermal Free Energies= -7385.519708
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.2274171
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.2092512
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -761.872054598735
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.6387218

C	-0.37906	-2.10853	-0.35068
C	0.95189	-1.50266	-0.64477
C	0.07206	-0.3273	-0.47165
H	-1.10206	-2.23215	-1.14769
H	-0.73239	-2.21574	0.66586
H	1.32182	-1.69582	-1.64831
H	1.71043	-1.65297	0.11772
I	0.12054	-4.77895	-0.36101
C	-0.56153	0.32359	-1.64093
C	0.3387	1.03725	-2.64455
C	-0.41242	-0.19413	-3.04866
H	-1.5041	0.81957	-1.43555
C	0.01781	0.35957	0.83248
C	0.4607	-0.26198	2.01843
C	-0.44683	1.68582	0.91542
C	0.42958	0.41246	3.23295
H	0.81856	-1.28775	2.00662
C	-0.46733	2.36158	2.13348
H	-0.76959	2.20737	0.02056
C	-0.03469	1.72926	3.2988
H	0.76789	-0.09182	4.13311
H	-0.82041	3.3878	2.16955
H	-0.05656	2.25511	4.24847
H	1.40762	0.94233	-2.48328
H	0.00161	2.00184	-3.00786
H	-1.28078	-0.06814	-3.68542
H	0.14853	-1.10561	-3.22309

Thesis = Figure 3.8 TS-XVII
A2 = A2.7-TS-A

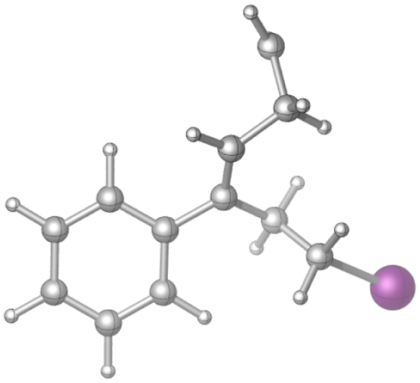


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -626.92
Zero-point correction= 0.225403 (Hartree/Particle)
Thermal correction to Energy= 0.238026
Thermal correction to Enthalpy= 0.238970
Thermal correction to Gibbs Free Energy= 0.183036
Sum of electronic and zero-point Energies= -7385.471927
Sum of electronic and thermal Energies= -7385.459304
Sum of electronic and thermal Enthalpies= -7385.458359
Sum of electronic and thermal Free Energies= -7385.514293
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.2220416
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.2076167
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

FINAL SINGLE POINT ENERGY -761.883595952901
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.6413818

C	0.03325	-0.20074	-0.41222
C	-0.93231	-0.09365	-1.39034
C	-0.91046	-0.75908	-2.73265
C	-1.75075	-1.80395	-2.09862
H	-1.80389	0.52751	-1.2054
C	-0.17017	0.4022	0.91581
C	-1.4634	0.6395	1.42655
C	0.9243	0.75407	1.73083
C	-1.64971	1.22317	2.67664
H	-2.33466	0.33687	0.85252
C	0.73565	1.34008	2.98138
H	1.93986	0.5861	1.38221
C	-0.55175	1.58313	3.46283
H	-2.65852	1.38407	3.04655
H	1.60048	1.60942	3.58102
H	-0.69835	2.03572	4.43892
H	0.06731	-1.10073	-3.06835
H	-1.41361	-0.18295	-3.50745
H	-2.8294	-1.70498	-2.0623
H	-1.28628	-2.63637	-1.58253
C	2.28602	-0.01537	-1.44614
H	2.59578	0.846	-0.85581
H	1.88695	0.31852	-2.40269
I	4.139	-1.04666	-1.95216
C	1.32532	-0.93411	-0.69872
H	1.78899	-1.28457	0.22681
H	1.13033	-1.8232	-1.3067

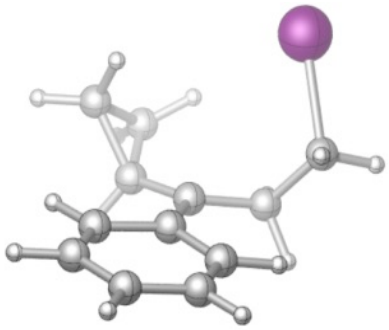
Thesis = Figure 3.8 INT-VI
A2 = A2.7-B



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.225220 (Hartree/Particle)
Thermal correction to Energy= 0.238826
Thermal correction to Enthalpy= 0.239770
Thermal correction to Gibbs Free Energy= 0.181107
Sum of electronic and zero-point Energies= -7385.481730
Sum of electronic and thermal Energies= -7385.468124
Sum of electronic and thermal Enthalpies= -7385.467180
Sum of electronic and thermal Free Energies= -7385.525843
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.2313341
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.2181237
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -761.893366327615
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.6488424

C	0.05223	-0.2546	-0.38546
C	-0.89284	-0.16598	-1.33987
C	-0.86343	-0.81514	-2.70706
C	-1.95283	-1.84146	-2.78602
H	-1.80226	0.39439	-1.12501
C	-0.15708	0.38211	0.94504
C	-1.43523	0.43881	1.52458
C	0.91766	0.93145	1.66211
C	-1.63668	1.04908	2.76139
H	-2.27633	-0.02344	1.01535
C	0.71666	1.54661	2.89792
H	1.92421	0.89044	1.25368
C	-0.56196	1.61175	3.45264
H	-2.63371	1.07301	3.19203
H	1.56265	1.9748	3.42788
H	-0.71716	2.08397	4.41817
H	0.10641	-1.2799	-2.90081
H	-1.01876	-0.04378	-3.46876
H	-2.96476	-1.55393	-3.054
H	-1.80445	-2.81928	-2.33777
C	2.29991	-0.08432	-1.46457
H	2.58433	0.83687	-0.95841
H	1.88913	0.14967	-2.4453
I	4.18018	-1.0981	-1.883
C	1.3729	-0.96474	-0.63359
H	1.85345	-1.2168	0.31496
H	1.19881	-1.90623	-1.16094

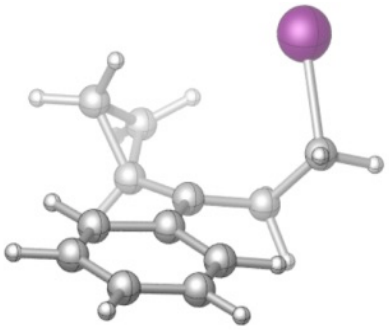
Thesis = Figure 3.8 INT-VI



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.224916 (Hartree/Particle)
Thermal correction to Energy= 0.237521
Thermal correction to Enthalpy= 0.238465
Thermal correction to Gibbs Free Energy= 0.183784
Sum of electronic and zero-point Energies= -7385.596460
Sum of electronic and thermal Energies= -7385.583855
Sum of electronic and thermal Enthalpies= -7385.582911
Sum of electronic and thermal Free Energies= -7385.637592
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.3458938
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.27604
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -761.937864542412
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.7509412

C	1.4897	-2.13424	-1.30234
C	-0.19191	-0.17379	-1.08078
H	1.57639	-3.22117	-1.32994
H	2.10857	-1.73161	-0.50296
I	2.55104	-1.47427	-3.10114
C	-0.98241	0.57607	-2.10655
C	-0.32382	1.52937	-3.09159
C	-0.93307	0.23587	-3.57478
H	-1.96478	0.94035	-1.7877
C	0.10328	0.47147	0.12561
C	0.68356	-0.18912	1.27911
C	-0.17598	1.87859	0.33872
C	0.94954	0.47939	2.46497
H	0.90909	-1.2518	1.23252
C	0.10599	2.52184	1.53409
H	-0.61764	2.45272	-0.47163
C	0.6783	1.84969	2.62975
H	1.38244	-0.08262	3.29189
H	-0.12731	3.58249	1.62115
H	0.89882	2.36427	3.55994
H	0.76089	1.58146	-3.05372
H	-0.83158	2.45724	-3.34178
H	-1.85682	0.29423	-4.14292
H	-0.25116	-0.54722	-3.89254
C	0.03851	-1.65248	-1.2371
H	-0.36675	-2.2204	-0.37734
H	-0.49132	-2.03348	-2.11658

Thesis = Figure 3.8 INT-XVI

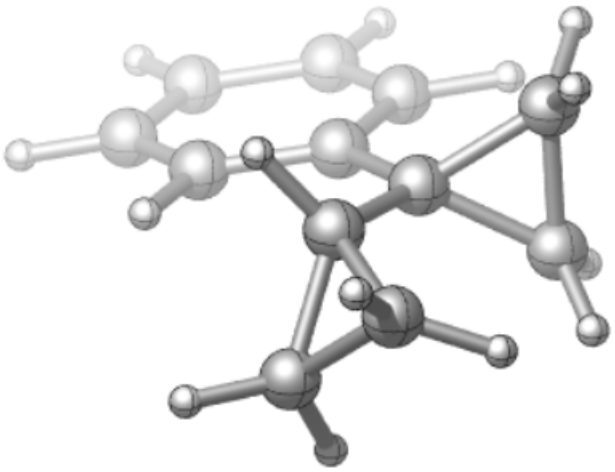


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -45.36
Zero-point correction= 0.224656 (Hartree/Particle)
Thermal correction to Energy= 0.236701
Thermal correction to Enthalpy= 0.237645
Thermal correction to Gibbs Free Energy= 0.183893
Sum of electronic and zero-point Energies= -7385.592909
Sum of electronic and thermal Energies= -7385.580863
Sum of electronic and thermal Enthalpies= -7385.579919
Sum of electronic and thermal Free Energies= -7385.633671
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.3418845
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-763.2740213
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-761.935712866524

B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-763.7474408

C	1.57865	-1.83003	-1.46015
C	-0.27916	-0.1029	-1.06473
H	1.97985	-2.56233	-0.75917
H	2.1737	-0.91875	-1.42643
I	2.11458	-2.69196	-3.41124
C	-1.04912	0.63991	-2.10864
C	-0.39999	1.74793	-2.92117
C	-0.74791	0.43255	-3.57303
H	-2.10677	0.84253	-1.91129
C	0.02737	0.51663	0.14935
C	0.73902	-0.14747	1.22435
C	-0.34534	1.88546	0.44929
C	1.01362	0.47766	2.43165
H	1.07698	-1.1729	1.08652
C	-0.04997	2.4864	1.66303
H	-0.88487	2.4565	-0.30223
C	0.63241	1.80682	2.68993
H	1.54814	-0.08294	3.19771
H	-0.36225	3.51793	1.82256
H	0.85863	2.28827	3.63631
H	0.64856	1.94655	-2.71911
H	-0.99547	2.61796	-3.18468
H	-1.57532	0.41879	-4.27635
H	0.07176	-0.2374	-3.82022
C	0.06422	-1.55352	-1.28953
H	-0.25922	-2.18343	-0.44552
H	-0.48056	-1.92542	-2.16088

Thesis = Figure 3.8 P-XVI

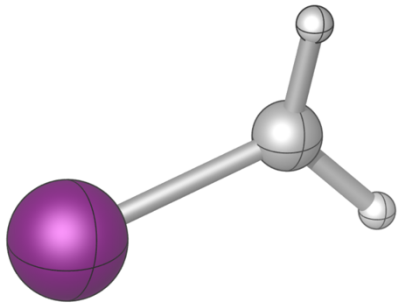


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.227037 (Hartree/Particle)
Thermal correction to Energy= 0.237254
Thermal correction to Enthalpy= 0.238198
Thermal correction to Gibbs Free Energy= 0.191091
Sum of electronic and zero-point Energies= -465.250442
Sum of electronic and thermal Energies= -465.240225
Sum of electronic and thermal Enthalpies= -465.239281
Sum of electronic and thermal Free Energies= -465.286388
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-465.6303285
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-465.6163724
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -464.773429946857
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-465.8546271

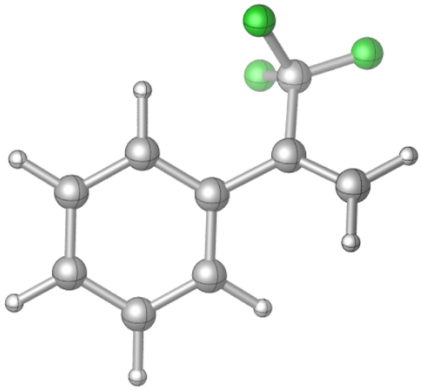
C	-1.84012	-0.09038	-0.2123
C	-0.48233	0.29254	0.341
H	-1.89595	-1.03811	-0.73846
H	-2.47508	0.68865	-0.62067
C	-0.07819	1.7423	0.35897
C	-0.00025	2.53571	-0.91984
C	-1.05507	2.85868	0.11037
H	0.68789	1.96969	1.09702
C	0.63653	-0.68473	0.10679
C	0.42962	-2.07199	0.19587
C	1.92323	-0.2379	-0.22575
C	1.46722	-2.97314	-0.032
H	-0.55284	-2.46486	0.445
C	2.9653	-1.14033	-0.45403
H	2.12007	0.82568	-0.31541
C	2.74527	-2.51272	-0.3579
H	1.27607	-4.03986	0.04487
H	3.95174	-0.76403	-0.71053
H	3.554	-3.21552	-0.53488
H	-0.32998	2.03189	-1.82391
H	0.82152	3.23218	-1.05085
H	-0.92395	3.76226	0.69599
H	-2.08715	2.62091	-0.12449
C	-1.60744	-0.11846	1.26981
H	-1.54012	-1.07845	1.77148
H	-2.05115	0.67886	1.85834

Thesis = Figure 3.8 P-XVI
UM06-2X/DGDZVP-SMD-THF

Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
Sum of electronic and zero-point Energies= -6920.436282
Sum of electronic and thermal Energies= -6920.434866
Sum of electronic and thermal Enthalpies= -6920.433922
Sum of electronic and thermal Free Energies= -6920.453131
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.8061761
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.7222293
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -297.221350590763
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.9784966
I -0.74423 3.03008 0.
A2 = S8-R-methyl-iodide



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.022125 (Hartree/Particle)
Thermal correction to Energy= 0.025610
Thermal correction to Enthalpy= 0.026554
Thermal correction to Gibbs Free Energy= -0.004097
Sum of electronic and zero-point Energies= -6959.447401
Sum of electronic and thermal Energies= -6959.443917
Sum of electronic and thermal Enthalpies= -6959.442973
Sum of electronic and thermal Free Energies= -6959.473624
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-336.8594737
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-336.8602082
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -336.301643564157
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-337.0631438
I -6.91744 0.48995 -0.52391
C -5.08079 1.35912 -0.9092
H -4.85125 2.28173 -0.39327
H -4.32273 0.73269 -1.3601
A2 = S8-R

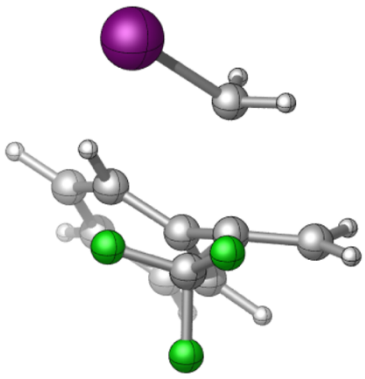


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.140212 (Hartree/Particle)
Thermal correction to Energy= 0.150046
Thermal correction to Enthalpy= 0.150990
Thermal correction to Gibbs Free Energy= 0.104044
Sum of electronic and zero-point Energies= -646.397362
Sum of electronic and thermal Energies= -646.387527
Sum of electronic and thermal Enthalpies= -646.386583
Sum of electronic and thermal Free Energies= -646.433530
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF =-646.719429

UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-646.7106611
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -645.734967844683
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-646.9809486

C	-1.13843	0.14183	-0.95079
C	-2.26292	-0.52757	-0.47412
C	-2.15958	-1.37198	0.63251
C	-0.92482	-1.53645	1.26052
C	0.20352	-0.87015	0.78372
C	0.11063	-0.03067	-0.33601
H	-1.23292	0.82059	-1.79381
H	-3.22292	-0.37928	-0.9595
H	-3.03677	-1.89067	1.00762
H	-0.83598	-2.18883	2.12396
H	1.15575	-1.02555	1.28167
C	1.29553	0.67346	-0.89275
C	1.48175	0.91367	-2.19264
C	2.34402	1.13847	0.08414
F	3.21932	1.99973	-0.4597
F	3.07721	0.11067	0.57275
F	1.80154	1.75592	1.15248
H	0.76809	0.55611	-2.92896
H	2.3475	1.45737	-2.55663

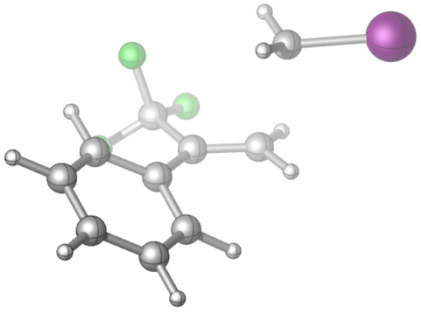
A2 = S8-R-TS-α



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -541.47
Zero-point correction= 0.164775 (Hartree/Particle)
Thermal correction to Energy= 0.178020
Thermal correction to Enthalpy= 0.178964
Thermal correction to Gibbs Free Energy= 0.121998
Sum of electronic and zero-point Energies= -7605.833353
Sum of electronic and thermal Energies= -7605.820108
Sum of electronic and thermal Enthalpies= -7605.819164
Sum of electronic and thermal Free Energies= -7605.876130UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.5659066
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5557539
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.022366996615
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.0323576

C	-0.61125	-1.53157	-1.1533
C	-1.47341	-2.58248	-0.84076
C	-1.78073	-2.863	0.4904
C	-1.2205	-2.08624	1.50588
C	-0.3629	-1.03273	1.19521
C	-0.05381	-0.739	-0.14024
H	-0.35654	-1.33375	-2.1909
H	-1.89612	-3.18623	-1.6383
H	-2.44786	-3.68392	0.73605
H	-1.45313	-2.29738	2.54536
H	0.05631	-0.43309	1.99735
C	0.86443	0.3817	-0.52517
C	0.66428	1.09393	-1.67534
C	2.2996	0.25764	-0.06387
F	2.97178	1.42093	-0.14933
F	2.97165	-0.62898	-0.83553
F	2.4257	-0.18244	1.19819
H	-0.30173	1.07728	-2.17032
H	1.42416	1.76152	-2.07049
H	-0.78846	1.85771	0.79499
C	0.27732	2.06054	0.86679
I	0.87464	2.2972	2.88764
H	0.651	2.88999	0.27282

A2 = S8-R-TS-β

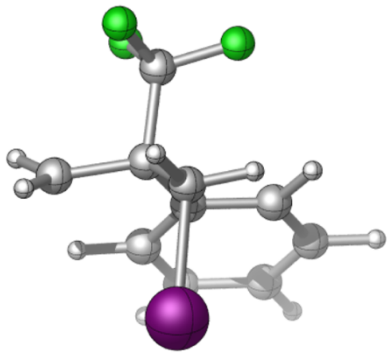


UM06-2X/DGDZVP-SMD-THF

Imaginary Frequency = -415.34
Zero-point correction= 0.164959 (Hartree/Particle)
Thermal correction to Energy= 0.178497
Thermal correction to Enthalpy= 0.179441
Thermal correction to Gibbs Free Energy= 0.120094
Sum of electronic and zero-point Energies= -7605.843753
Sum of electronic and thermal Energies= -7605.830214
Sum of electronic and thermal Enthalpies= -7605.829270
Sum of electronic and thermal Free Energies= -7605.888617
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.5780497
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5684527
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.033898790021
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.0468772

C	-1.22497	0.21864	-1.11553
C	-2.35389	-0.48425	-0.70478
C	-2.27864	-1.37093	0.37147
C	-1.06378	-1.54242	1.03477
C	0.06978	-0.84221	0.62485
C	0.00872	0.04397	-0.46446
H	-1.30978	0.92834	-1.93338
H	-3.29843	-0.32907	-1.21763
H	-3.16046	-1.91647	0.69363
H	-0.99348	-2.22673	1.87494
H	1.00324	-1.00747	1.15421
C	1.20041	0.77313	-0.94751
C	1.40614	1.11913	-2.24316
C	2.32214	1.00515	0.02146
F	3.21188	1.91251	-0.41679
F	3.03386	-0.12787	0.26004
F	1.89111	1.43446	1.22454
H	0.62209	0.98296	-2.98132
H	2.24776	1.73828	-2.53666
H	1.7872	-1.52267	-2.84947
C	2.50653	-0.76239	-3.13529
I	2.70479	-0.51963	-5.20345
H	3.4464	-0.69955	-2.59726

A2 = S8-Int-I’

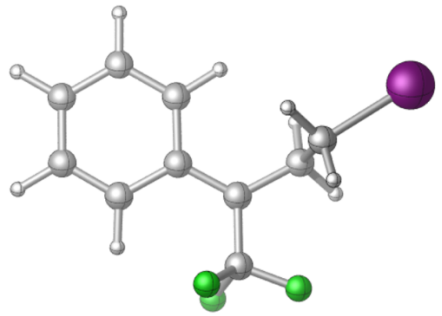


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.167644 (Hartree/Particle)
Thermal correction to Energy= 0.180769
Thermal correction to Enthalpy= 0.181713
Thermal correction to Gibbs Free Energy= 0.125232
Sum of electronic and zero-point Energies= -7605.885006
Sum of electronic and thermal Energies= -7605.871881
Sum of electronic and thermal Enthalpies= -7605.870937
Sum of electronic and thermal Free Energies= -7605.927418
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6179003
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6071701
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.072803308262
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.0724683

C	-0.98902	-0.42539	-1.01609
C	-1.90545	-1.41645	-0.6588
C	-2.04719	-1.79546	0.67405
C	-1.26873	-1.17124	1.65
C	-0.35498	-0.18164	1.29374
C	-0.19939	0.19921	-0.04655
H	-0.91088	-0.13578	-2.05879
H	-2.51053	-1.88697	-1.42809
H	-2.76013	-2.56585	0.9525
H	-1.37401	-1.45099	2.694
H	0.22998	0.2897	2.07768
C	0.79598	1.30703	-0.42914
C	0.74563	1.67839	-1.88525

C	2.22261	0.77891	-0.17261
F	3.15772	1.68483	-0.52398
F	2.47019	-0.33338	-0.88555
F	2.45814	0.47548	1.11797
H	0.72213	2.35138	1.51166
C	0.62584	2.55959	0.44834
I	-1.33711	3.43649	0.21818
H	1.32532	3.34314	0.15965
H	0.92158	0.92608	-2.6459
H	0.79432	2.7237	-2.16928

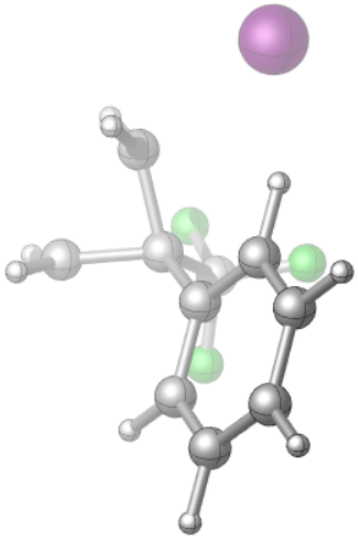
A2 = S8-Int-I



UM06-2X/DGDZVP-SMD-THF
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6412459
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.6298922
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.095274559044
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.1038604

C	-3.45872	2.31327	-0.03538
C	-4.63536	1.58424	-0.13108
C	-4.60342	0.19852	-0.31869
C	-3.3701	-0.45389	-0.4092
C	-2.18617	0.26245	-0.30944
C	-2.1934	1.6703	-0.1182
H	-3.52825	3.38525	0.11546
H	-5.58797	2.09987	-0.05674
H	-5.52839	-0.36484	-0.39295
H	-3.33338	-1.52845	-0.56033
H	-1.24575	-0.27323	-0.39209
C	-0.956	2.38644	-0.01723
C	0.38637	1.71409	-0.02488
C	-0.97411	3.88283	0.01281
F	0.26292	4.41073	-0.03478
F	-1.55552	4.38121	1.13135
F	-1.65291	4.42266	-1.02792
C	0.85191	1.52917	-1.47075
I	2.72798	0.43859	-1.5562
H	0.32453	0.74715	0.47678
H	1.11968	2.3122	0.51995
H	1.04872	2.47804	-1.96827
H	0.15243	0.93719	-2.05878

A2 = S8-TS-I’



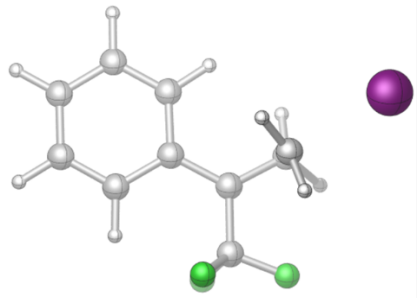
UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -647.16
Zero-point correction= 0.167286 (Hartree/Particle)
Thermal correction to Energy= 0.180040
Thermal correction to Enthalpy= 0.180984
Thermal correction to Gibbs Free Energy= 0.125212
Sum of electronic and zero-point Energies= -7605.867127
Sum of electronic and thermal Energies= -7605.854372
Sum of electronic and thermal Enthalpies= -7605.853428
Sum of electronic and thermal Free Energies= -7605.909200
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6005232
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5868082
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

FINAL SINGLE POINT ENERGY -982.050048294175
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF

HF=-984.0600088

C	-1.71212	1.30713	0.3102
C	-2.78377	0.60828	0.86926
C	-2.58344	-0.64563	1.44528
C	-1.30534	-1.20706	1.45635
C	-0.23536	-0.51427	0.8946
C	-0.43252	0.74864	0.321
H	-1.88143	2.28337	-0.13274
H	-3.77628	1.04837	0.85274
H	-3.41932	-1.185	1.88093
H	-1.14207	-2.18537	1.89822
H	0.75761	-0.9585	0.89764
C	0.77059	1.46548	-0.259
C	1.56585	0.6624	-1.20507
C	1.61899	2.12124	0.82312
F	2.60772	2.87072	0.3023
F	2.20426	1.19569	1.60604
F	0.89504	2.91247	1.62414
H	1.45688	2.8025	-1.90167
C	0.57826	2.32717	-1.48192
I	-0.43291	4.58353	-1.07818
H	-0.1725	1.97916	-2.18371
H	2.62318	0.85277	-1.35296
H	1.08592	-0.14707	-1.74155

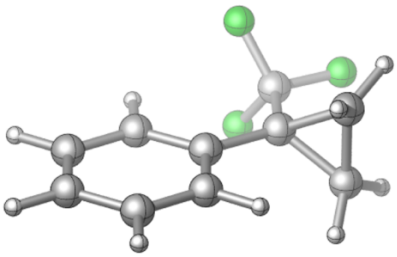
A2 = S8-TS-I



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -757.60
Zero-point correction= 0.168719 (Hartree/Particle)
Thermal correction to Energy= 0.181417
Thermal correction to Enthalpy= 0.182361
Thermal correction to Gibbs Free Energy= 0.125806
Sum of electronic and zero-point Energies= -7605.876226
Sum of electronic and thermal Energies= -7605.863528
Sum of electronic and thermal Enthalpies= -7605.862584
Sum of electronic and thermal Free Energies= -7605.919138
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-983.6127667
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-983.5997266
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -982.058643521008
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-984.0745288

C	-0.45045	-2.09533	-0.84025
C	0.89096	-1.53873	-1.20596
C	0.11113	-0.30004	-1.00969
H	-1.22544	-2.16581	-1.59622
H	-0.7748	-2.08112	0.19287
H	1.1945	-1.75551	-2.22663
H	1.68416	-1.7201	-0.48766
I	-0.13138	-4.65486	-0.81304
C	-0.5236	0.30575	-2.23373
F	0.12335	1.42562	-2.62202
F	-0.50598	-0.52934	-3.28556
F	-1.81204	0.65384	-2.04183
C	0.10676	0.46585	0.23657
C	0.68464	-0.08013	1.40377
C	-0.45765	1.75711	0.31723
C	0.7024	0.63641	2.59312
H	1.1097	-1.07943	1.39665
C	-0.42474	2.47232	1.51015
H	-0.91642	2.22451	-0.54672
C	0.15234	1.91945	2.65364
H	1.14778	0.19157	3.47757
H	-0.85555	3.46818	1.54447
H	0.17032	2.4798	3.58324

A2 = P-I



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.169956 (Hartree/Particle)
Thermal correction to Energy= 0.180456
Thermal correction to Enthalpy= 0.181400
Thermal correction to Gibbs Free Energy= 0.133443
Sum of electronic and zero-point Energies= -685.664596

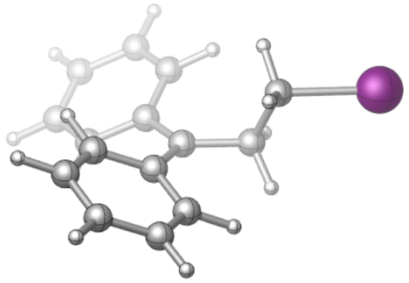
Sum of electronic and thermal Energies= -685.654097
Sum of electronic and thermal Enthalpies= -685.653153
Sum of electronic and thermal Free Energies= -685.701110
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.0287248
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-686.017579
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -684.968350369337
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-686.3034705

C	-4.62713	3.52715	0.09742
C	-5.80802	2.79305	0.22736
C	-5.77352	1.40565	0.34378
C	-4.5391	0.75489	0.328
C	-3.36048	1.48475	0.19793
C	-3.38161	2.88379	0.08136
H	-6.75858	3.31821	0.23694
H	-4.70648	4.60538	0.01005
H	-6.69414	0.83882	0.44441
H	-4.49014	-0.32643	0.41655
H	-2.41723	0.94509	0.18665
C	-2.08221	3.62863	-0.05461
C	-2.16951	5.12047	-0.17389
C	-0.9339	2.99693	-0.81635
C	-0.8512	3.12176	0.67109
H	-0.31159	3.65118	-1.41686
H	-1.13783	2.02579	-1.25325
H	-0.17194	3.86043	1.08207
H	-0.99801	2.23879	1.28284
F	-2.87781	5.5164	-1.25442
F	-0.95763	5.69836	-0.28948
F	-2.75723	5.69306	0.89989

A2 = S8-P-Iodine-Radical
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.017503
Sum of electronic and zero-point Energies= -6920.237912
Sum of electronic and thermal Energies= -6920.236495
Sum of electronic and thermal Enthalpies= -6920.235551
Sum of electronic and thermal Free Energies= -6920.255414
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.6137243
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.6118482
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -297.110848563578
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.7800963

I	-0.74423	3.03008	0.

Thesis = Figure 3.7 Int-III
A2 = S9-I-Rad-R

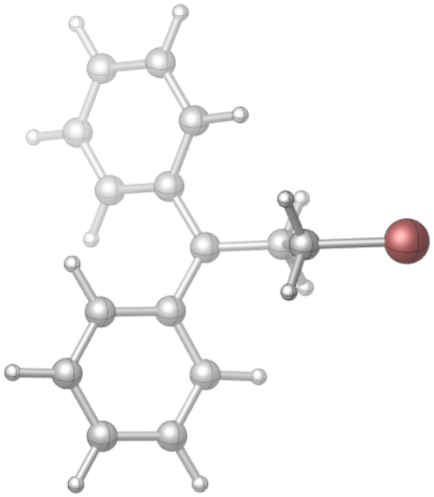


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.246407 (Hartree/Particle)
Thermal correction to Energy= 0.260530
Thermal correction to Enthalpy= 0.261474
Thermal correction to Gibbs Free Energy= 0.201343
Sum of electronic and zero-point Energies= -7499.796228
Sum of electronic and thermal Energies= -7499.782105
Sum of electronic and thermal Enthalpies= -7499.781161
Sum of electronic and thermal Free Energies= -7499.841291
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-877.6019831
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-877.5855526
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF

FINAL SINGLE POINT ENERGY -876.046515423936
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-878.0639343

C	-0.0496	-2.71015	-1.08931
C	0.98617	-1.58951	-1.03798
C	0.29287	-0.24968	-1.06316
H	-0.64372	-2.69243	-2.00179
H	-0.7048	-2.71118	-0.21932
H	1.66993	-1.68854	-1.88629
H	1.59624	-1.68794	-0.13811
I	0.89981	-4.66657	-1.08243
C	-0.33532	0.19798	-2.2941
C	0.23854	0.53005	0.16835
C	0.22168	-0.10662	1.42966
C	0.25981	1.94325	0.15128
C	0.19879	0.63187	2.60909
H	0.1995	-1.19184	1.48867
C	0.24966	2.6772	1.33284
H	0.3232	2.46603	-0.79863
C	0.2119	2.02829	2.57002
H	0.16892	0.11443	3.56364
H	0.28291	3.76201	1.28854
H	0.2011	2.60324	3.49101
C	-1.40798	1.1243	-2.28869
C	-2.02318	1.52519	-3.46857
C	-1.5978	1.01827	-4.70027
C	-0.55655	0.08697	-4.72898
C	0.05787	-0.32367	-3.55106
H	-1.78446	1.50423	-1.34419
H	-2.07809	1.33529	-5.62102
H	-2.84979	2.22875	-3.42662
H	0.8666	-1.04493	-3.61312
H	-0.2191	-0.32209	-5.67692

Thesis = Figure 3.7 Int-IV
A2 = S9-Br-Rad-R

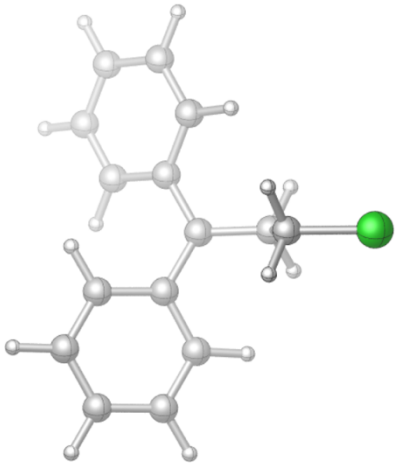


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.246991 (Hartree/Particle)
Thermal correction to Energy= 0.260943
Thermal correction to Enthalpy= 0.261887
Thermal correction to Gibbs Free Energy= 0.203251
Sum of electronic and zero-point Energies= -3153.243876
Sum of electronic and thermal Energies= -3153.229925
Sum of electronic and thermal Enthalpies= -3153.228981
Sum of electronic and thermal Free Energies= -3153.287617
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.1694237
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3154.1496151
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3151.614429292483
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.4486267

C	0.27918	-3.31828	-1.097
C	1.28695	-2.17441	-1.05036
C	0.57085	-0.84581	-1.06381
H	-0.32329	-3.30674	-2.00414
H	-0.37019	-3.32975	-0.2227
H	1.96515	-2.25665	-1.90515
H	1.90578	-2.26523	-0.15573
Br	1.19888	-5.06114	-1.09798
C	-0.07919	-0.40354	-2.28477
C	0.52689	-0.06647	0.16874
C	0.53017	-0.70362	1.42964
C	0.53711	1.34672	0.15204
C	0.51452	0.03386	2.60984
H	0.5177	-1.78892	1.48834
C	0.5346	2.07999	1.33413
H	0.5851	1.87044	-0.79827
C	0.5157	1.4303	2.5713
H	0.49986	-0.48447	3.56426
H	0.55886	3.16504	1.29007
H	0.5104	2.00477	3.49264
C	-1.15799	0.51577	-2.26259
C	-1.79244	0.91448	-3.43285
C	-1.38167	0.41225	-4.67143
C	-0.33527	-0.51255	-4.71658
C	0.29895	-0.92066	-3.54831
H	-1.5233	0.89207	-1.31231

H	-1.87711	0.72766	-5.58467
H	-2.62233	1.61326	-3.37801
H	1.11187	-1.6358	-3.62402
H	-0.00865	-0.91803	-5.66986

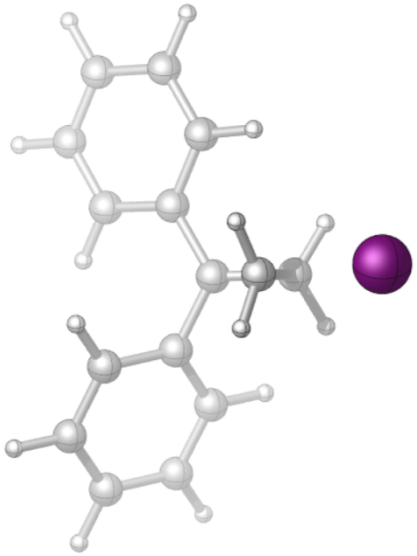
Thesis = Figure 3.7 Int V
A2 = S9-Cl-Rad-R



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.247389 (Hartree/Particle)
Thermal correction to Energy= 0.261254
Thermal correction to Enthalpy= 0.262198
Thermal correction to Gibbs Free Energy= 0.204005
Sum of electronic and zero-point Energies= -1039.678092
Sum of electronic and thermal Energies= -1039.664228
Sum of electronic and thermal Enthalpies= -1039.663284
Sum of electronic and thermal Free Energies= -1039.721476
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.1733944
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1040.1540985
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1038.633997554239
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.491401

C	0.22718	-3.33016	-1.09387
C	1.25206	-2.20158	-1.02629
C	0.56557	-0.85857	-1.05252
H	-0.37095	-3.28772	-2.00414
H	-0.43117	-3.33107	-0.22479
H	1.94336	-2.29887	-1.8693
H	1.85262	-2.30898	-0.12079
Cl	1.05663	-4.94089	-1.10849
C	-0.05681	-0.4076	-2.28494
C	0.51827	-0.07435	0.17613
C	0.49533	-0.70694	1.43931
C	0.55031	1.3386	0.15468
C	0.47681	0.03522	2.61652
H	0.46454	-1.79177	1.5011
C	0.54432	2.07621	1.33397
H	0.61835	1.85784	-0.79685
C	0.50051	1.43139	2.57314
H	0.44189	-0.47897	3.57267
H	0.5857	3.16061	1.28641
H	0.49304	2.00924	3.49235
C	-1.12421	0.52503	-2.28162
C	-1.73512	0.92908	-3.46256
C	-1.31056	0.41947	-4.6935
C	-0.27446	-0.51753	-4.72028
C	0.33566	-0.93154	-3.54121
H	-1.49991	0.90733	-1.33776
H	-1.78741	0.73911	-5.61514
H	-2.55781	1.63731	-3.42205
H	1.14083	-1.65699	-3.60205
H	0.06254	-0.92838	-5.66762

Thesis = Figure 3.7 TS-XIII
A2 = S9-I-Rad-TS



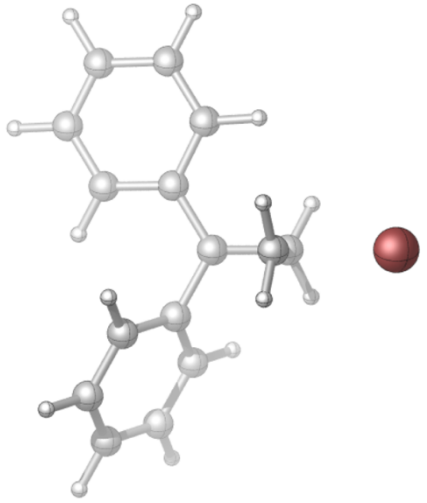
UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -543.93
Zero-point correction= 0.245109 (Hartree/Particle)
Thermal correction to Energy= 0.259060
Thermal correction to Enthalpy= 0.260004

Thermal correction to Gibbs Free Energy= 0.200395
Sum of electronic and zero-point Energies= -7499.769554
Sum of electronic and thermal Energies= -7499.755603
Sum of electronic and thermal Enthalpies= -7499.754659
Sum of electronic and thermal Free Energies= -7499.814268
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-877.5746923
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-877.5554983
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -876.008940455685
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-878.0365848

C	-0.33592	-2.042	-0.87692
C	0.98791	-1.44089	-1.22223
C	0.10389	-0.26647	-1.05942
H	-1.06599	-2.20908	-1.65911
H	-0.67902	-2.10679	0.14686
H	1.30496	-1.66242	-2.23803
H	1.77321	-1.5724	-0.48328
I	0.20211	-4.6861	-0.78207
C	-0.55801	0.30668	-2.25711
C	0.06732	0.45992	0.22494
C	0.51435	-0.14004	1.42108
C	-0.35958	1.80081	0.27829
C	0.51466	0.56598	2.61769
H	0.8537	-1.17229	1.42942
C	-0.35053	2.50676	1.4794
H	-0.67527	2.30781	-0.62755
C	0.07933	1.89389	2.65577
H	0.85516	0.07799	3.52597
H	-0.67659	3.54239	1.49161
H	0.08075	2.44398	3.59183
C	0.15561	0.47656	-3.45124
C	-0.46751	1.02112	-4.57449
C	-1.81236	1.38742	-4.52182
C	-2.5349	1.21198	-3.33798
C	-1.91205	0.68001	-2.21361
H	1.20586	0.20137	-3.49798
H	-2.29744	1.80525	-5.39895
H	0.09889	1.1592	-5.49061
H	-2.47641	0.53463	-1.29522
H	-3.58466	1.48622	-3.29473

Thesis = Figure 3.7 TS-XIV

A2 = S9-Br-Rad-TS

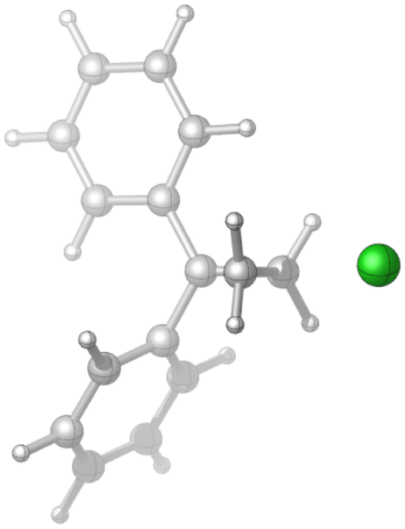


UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = =503.76
Thermal correction to Energy= 0.259194
Thermal correction to Enthalpy= 0.260138
Thermal correction to Gibbs Free Energy= 0.201265
Sum of electronic and zero-point Energies= -3153.207567
Sum of electronic and thermal Energies= -3153.193677
Sum of electronic and thermal Enthalpies= -3153.192733
Sum of electronic and thermal Free Energies= -3153.251605
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.130467
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3154.105947
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3151.565229014336
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.412315

C	-0.37588	-2.01671	-0.85457
C	0.9633	-1.46395	-1.22237
C	0.07633	-0.29429	-1.04783
H	-1.11948	-2.18757	-1.62194
H	-0.68628	-2.10872	0.1772
H	1.26025	-1.69195	-2.24221
H	1.75225	-1.60756	-0.49025
Br	0.07701	-4.5147	-0.84858
C	-0.57222	0.29405	-2.25038

C	0.06456	0.45415	0.22833
C	0.54771	-0.12018	1.42222
C	-0.38426	1.78734	0.27214
C	0.56414	0.60425	2.60823
H	0.90767	-1.14516	1.43881
C	-0.35996	2.51215	1.4623
H	-0.73315	2.27363	-0.6329
C	0.1078	1.92518	2.63715
H	0.93509	0.13642	3.51524
H	-0.7044	3.54191	1.46664
H	0.12169	2.48932	3.56471
C	0.17275	0.52475	-3.41357
C	-0.43076	1.08906	-4.53843
C	-1.78653	1.41541	-4.51641
C	-2.53964	1.17965	-3.36248
C	-1.93618	0.62689	-2.2369
H	1.23092	0.27763	-3.43446
H	-2.25652	1.84907	-5.3941
H	0.15941	1.27423	-5.431
H	-2.5236	0.43573	-1.34144
H	-3.5976	1.42359	-3.34318

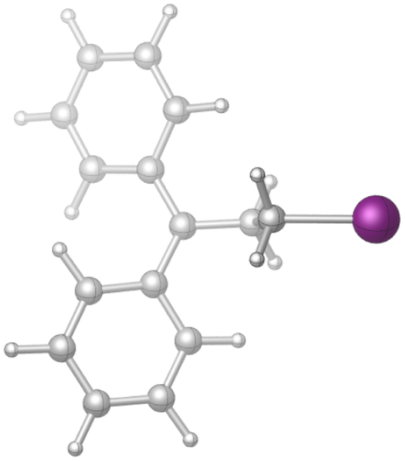
Thesis = Figure 3.7 TS-XV
A2 = S9-Cl-Rad-TS



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -202.54
Zero-point correction= 0.244991 (Hartree/Particle)
Thermal correction to Energy= 0.258718
Thermal correction to Enthalpy= 0.259663
Thermal correction to Gibbs Free Energy= 0.201313
Sum of electronic and zero-point Energies= -1039.630014
Sum of electronic and thermal Energies= -1039.616286
Sum of electronic and thermal Enthalpies= -1039.615342
Sum of electronic and thermal Free Energies= -1039.673692
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.1213564
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1040.1016843
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1038.576711201641
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.4398652

C	-0.56864	-1.91731	-0.78517
C	0.85861	-1.55633	-1.22431
C	-0.10555	-0.44687	-1.0206
H	-1.25517	-2.30449	-1.52914
H	-0.77972	-2.16608	0.24821
H	1.10563	-1.82869	-2.24494
H	1.65189	-1.69467	-0.49819
Cl	0.39128	-4.42884	-0.71363
C	-0.68042	0.21188	-2.23971
C	0.02059	0.39761	0.21848
C	0.52829	-0.13925	1.41343
C	-0.35277	1.74842	0.20455
C	0.65605	0.64897	2.55388
H	0.82909	-1.18299	1.46586
C	-0.22205	2.53853	1.34869
H	-0.74187	2.19609	-0.70503
C	0.28048	1.99439	2.52872
H	1.05017	0.21078	3.4662
H	-0.51556	3.58365	1.31169
H	0.37841	2.60786	3.4194
C	0.16411	0.70629	-3.23878
C	-0.36481	1.36698	-4.34884
C	-1.74466	1.53707	-4.46922
C	-2.59418	1.04359	-3.47564
C	-2.06361	0.38604	-2.36701
H	1.23968	0.57777	-3.14177
H	-2.15765	2.04791	-5.33412
H	0.30078	1.74841	-5.1177
H	-2.72422	0.00417	-1.59152
H	-3.66902	1.17077	-3.56648

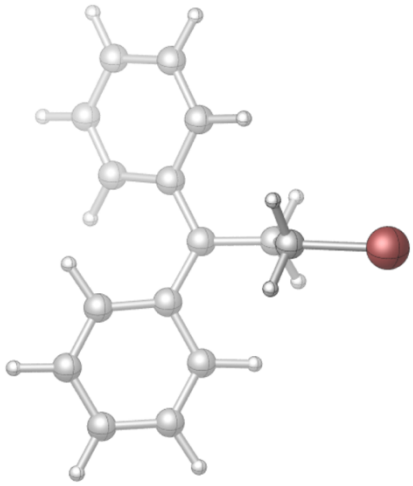
Thesis = Figure 3.7 Int-VI
A2 = S9-I-An-R



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.244250 (Hartree/Particle)
Thermal correction to Energy= 0.258543
Thermal correction to Enthalpy= 0.259487
Thermal correction to Gibbs Free Energy= 0.199607
Sum of electronic and zero-point Energies= -7499.909837
Sum of electronic and thermal Energies= -7499.895544
Sum of electronic and thermal Enthalpies= -7499.894600
Sum of electronic and thermal Free Energies= -7499.954480
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-877.712377
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-877.6477096
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -876.097918644789
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
-878.1697683

C	-0.04075	-2.6288	-1.02232
C	1.00506	-1.52748	-1.06097
C	0.2874	-0.19623	-1.07916
H	-0.7079	-2.61542	-1.88308
H	-0.6141	-2.64923	-0.09682
H	1.6501	-1.6689	-1.93504
H	1.66198	-1.61247	-0.1909
I	0.86572	-4.66115	-1.12112
C	-0.32058	0.2248	-2.31209
C	0.21447	0.53631	0.16658
C	0.32993	-0.1208	1.42871
C	0.10775	1.95785	0.24306
C	0.3174	0.56966	2.63726
H	0.40549	-1.20475	1.4625
C	0.09365	2.64069	1.45407
H	0.0957	2.53879	-0.6738
C	0.18903	1.96211	2.6759
H	0.39708	0.00766	3.56535
H	0.02713	3.7266	1.44309
H	0.1735	2.49934	3.61943
C	-1.30584	1.26144	-2.40762
C	-1.89286	1.63003	-3.61098
C	-1.56098	0.99595	-4.8166
C	-0.6352	-0.05154	-4.7553
C	-0.04414	-0.43345	-3.55533
H	-1.6486	1.75452	-1.50426
H	-2.02043	1.29061	-5.75522
H	-2.63998	2.42148	-3.60529
H	0.6527	-1.26567	-3.58506
H	-0.36764	-0.58976	-5.66241

Thesis = Figure 3.7 Int-VII
A2 = S9-Br-An-R

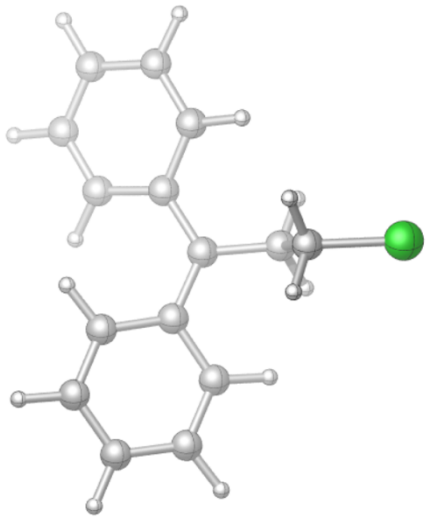


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.244955 (Hartree/Particle)
Thermal correction to Energy= 0.259057
Thermal correction to Enthalpy= 0.260001
Thermal correction to Gibbs Free Energy= 0.201291
Sum of electronic and zero-point Energies= -3153.356785
Sum of electronic and thermal Energies= -3153.342683
Sum of electronic and thermal Enthalpies= -3153.341739
Sum of electronic and thermal Free Energies= -3153.400449

UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.2795627
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-3154.2100097
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -3151.664292357887
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-3154.5536291

C	-0.05395	-2.64034	-1.03346
C	0.9774	-1.5243	-1.05586
C	0.27195	-0.18331	-1.07575
H	-0.70969	-2.62051	-1.90301
H	-0.6472	-2.64558	-0.12018
H	1.63224	-1.66152	-1.92357
H	1.6275	-1.614	-0.18112
Br	0.79179	-4.45327	-1.09556
C	-0.32993	0.24148	-2.3083
C	0.20677	0.55189	0.16696
C	0.32125	-0.10199	1.43193
C	0.10645	1.97503	0.24205
C	0.31251	0.5913	2.63888
H	0.39251	-1.18601	1.46949
C	0.0966	2.66025	1.45145
H	0.09627	2.55461	-0.67569
C	0.19012	1.98446	2.67537
H	0.39088	0.03061	3.56799
H	0.03529	3.74651	1.43784
H	0.17829	2.52385	3.61771
C	-1.30923	1.28506	-2.40722
C	-1.89259	1.65572	-3.61136
C	-1.56384	1.0186	-4.81673
C	-0.64425	-0.0343	-4.75298
C	-0.05688	-0.41909	-3.55209
H	-1.65052	1.78101	-1.50486
H	-2.02031	1.31554	-5.7561
H	-2.635	2.4517	-3.60689
H	0.63715	-1.25368	-3.58123
H	-0.37826	-0.57457	-5.65944

Thesis = Figure 3.7 Int-VIII
A2 = S9-Cl-An-R

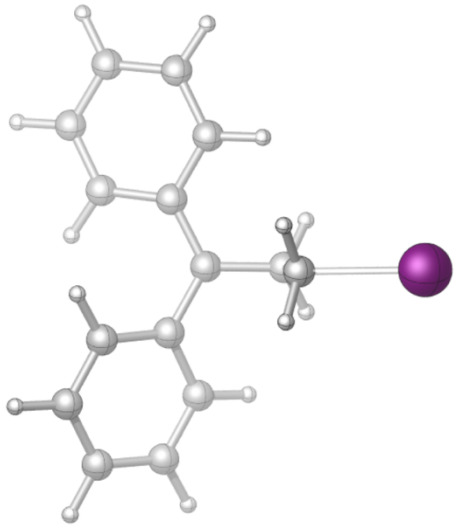


UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.245537 (Hartree/Particle)
Thermal correction to Energy= 0.259435
Thermal correction to Enthalpy= 0.260379
Thermal correction to Gibbs Free Energy= 0.203090
Sum of electronic and zero-point Energies= -1039.790213
Sum of electronic and thermal Energies= -1039.776315
Sum of electronic and thermal Enthalpies= -1039.775371
Sum of electronic and thermal Free Energies= -1039.832660
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.2830732
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1040.2126059
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1038.682317618984
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.5954903

C	-0.04176	-2.6602	-1.03707
C	0.97395	-1.52747	-1.05565
C	0.27018	-0.18512	-1.07572
H	-0.69925	-2.63542	-1.90656
H	-0.64068	-2.66093	-0.12604
H	1.63095	-1.66082	-1.92302
H	1.62415	-1.6163	-0.18044
Cl	0.77227	-4.3064	-1.09204

C	-0.33069	0.23908	-2.30762
C	0.20702	0.54976	0.16661
C	0.32116	-0.10628	1.43089
C	0.10758	1.97306	0.24451
C	0.31228	0.58472	2.63903
H	0.3918	-1.19044	1.46593
C	0.09773	2.65593	1.45526
H	0.09864	2.55463	-0.67196
C	0.19047	1.97799	2.67813
H	0.39004	0.0223	3.56717
H	0.03724	3.74228	1.44363
H	0.17871	2.51571	3.62143
C	-1.30405	1.28872	-2.41012
C	-1.88648	1.65793	-3.61502
C	-1.5635	1.01405	-4.81857
C	-0.65056	-0.04454	-4.75137
C	-0.06401	-0.42844	-3.54986
H	-1.64152	1.7907	-1.50972
H	-2.01902	1.31038	-5.75858
H	-2.62374	2.45874	-3.61275
H	0.62371	-1.26827	-3.57622
H	-0.38923	-0.59024	-5.65599

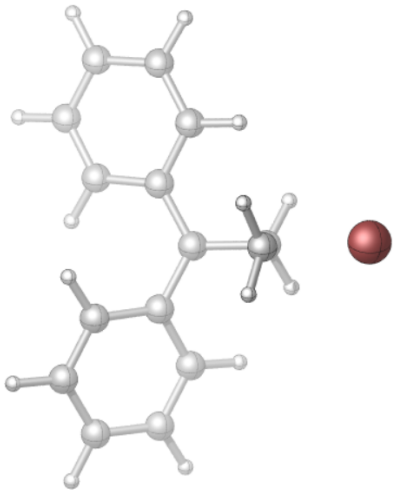
Thesis = Figure 3.7 TS-X
A2 = S9-I-An-TS



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -343.40
Zero-point correction= 0.243795 (Hartree/Particle)
Thermal correction to Energy= 0.257684
Thermal correction to Enthalpy= 0.258628
Thermal correction to Gibbs Free Energy= 0.199912
Sum of electronic and zero-point Energies= -7499.908646
Sum of electronic and thermal Energies= -7499.894756
Sum of electronic and thermal Enthalpies= -7499.893812
Sum of electronic and thermal Free Energies= -7499.952528
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-877.7096325
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-877.6455476
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -876.094035295592
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-878.1701953

C	0.28458	-2.61361	-0.06711
C	1.37503	-1.59357	-0.15172
C	0.51577	-0.35858	-0.06361
H	-0.35804	-2.67871	-0.94163
H	-0.26151	-2.66026	0.87104
H	1.93241	-1.69653	-1.0839
H	2.08752	-1.68073	0.67175
I	1.17452	-4.85559	-0.08723
C	-0.09495	0.15608	-1.28009
C	0.32732	0.23406	1.24418
C	0.61357	-0.48013	2.44537
C	-0.05909	1.59432	1.43236
C	0.50644	0.10511	3.70418
H	0.9132	-1.52367	2.39809
C	-0.16391	2.17026	2.69285
H	-0.23365	2.22315	0.56486
C	0.10848	1.43658	3.85471
H	0.73307	-0.495	4.58256
H	-0.44831	3.21751	2.76854
H	0.0212	1.88919	4.83783
C	0.46178	-0.08273	-2.56675
C	-0.1348	0.38701	-3.73454
C	-1.32581	1.11711	-3.69622
C	-1.91154	1.34843	-2.44537
C	-1.32144	0.87883	-1.2775
H	1.39397	-0.63147	-2.65948
H	-1.78761	1.48386	-4.60799
H	0.34458	0.18321	-4.68929
H	-1.83871	1.03861	-0.33603
H	-2.85409	1.88724	-2.37984

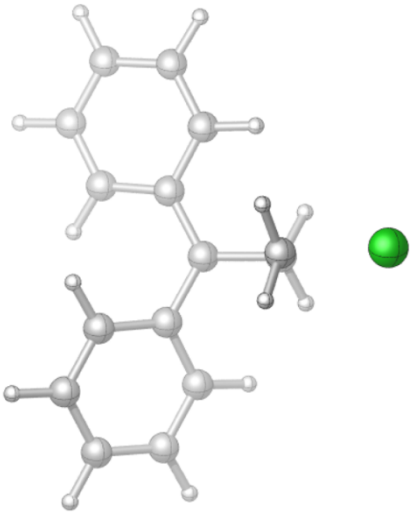
Thesis = Figure 3.7 TS-XI
A2 = S9-Br-An-TS



UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -442.19
Zero-point correction= 0.244429
(Hartree/Particle)
Thermal correction to Energy= 0.258175
Thermal correction to Enthalpy=
0.259119
Thermal correction to Gibbs Free Energy=
0.201619
Sum of electronic and zero-point Energies= -
3153.348874
Sum of electronic and thermal Energies= -
3153.335128
Sum of electronic and thermal Enthalpies= -
3153.334184
Sum of electronic and thermal Free Energies= -
3153.391684
UM06-2X/def2-TZVPP-SMD-THF//UM06-
2X/DGDZVP-SMD-THF
HF=-3154.2700125
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-
SMD-THF
HF=-3154.2021901
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-
2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -
3151.653784739843
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-
SMD-THF
HF=-3154.5488124

C	0.21888	-2.51133	-0.02706
C	1.38636	-1.6147	-0.16746
C	0.5037	-0.39345	-0.06665
H	-0.43243	-2.59794	-0.89013
H	-0.28041	-2.55113	0.93425
H	1.89569	-1.74565	-1.12137
H	2.11569	-1.7087	0.63849
Br	0.89668	-4.74876	-0.01444
C	-0.09378	0.14458	-1.28628
C	0.33615	0.21316	1.24053
C	0.66866	-0.47931	2.44084
C	-0.08487	1.56251	1.4192
C	0.5638	0.11521	3.69562
H	1.00741	-1.51075	2.39857
C	-0.18511	2.14889	2.67574
H	-0.29833	2.17462	0.54853
C	0.12766	1.43514	3.83915
H	0.82513	-0.46787	4.57569
H	-0.50048	3.1875	2.74624
H	0.04326	1.89495	4.81919
C	0.51232	-0.01999	-2.55779
C	-0.07716	0.45775	-3.7274
C	-1.30259	1.12653	-3.69534
C	-1.93221	1.29014	-2.4552
C	-1.35016	0.80751	-1.2883
H	1.47608	-0.51394	-2.63679
H	-1.75897	1.50009	-4.60716
H	0.43503	0.31118	-4.67538
H	-1.89449	0.90958	-0.35356
H	-2.90035	1.78224	-2.39869

Thesis = Figure 3.7 TS-XII
A2 = S9-Cl-An-TS



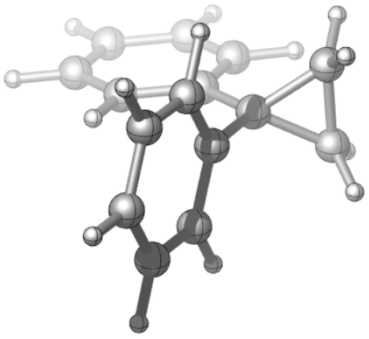
UM06-2X/DGDZVP-SMD-THF
Imaginary Frequency = -514.59
Zero-point correction= 0.244775
(Hartree/Particle)
Thermal correction to Energy= 0.258373
Thermal correction to Enthalpy=
0.259317
Thermal correction to Gibbs Free Energy=
0.203036

Sum of electronic and zero-point Energies= -1039.779174
Sum of electronic and thermal Energies= -1039.765576
Sum of electronic and thermal Enthalpies= -1039.764632
Sum of electronic and thermal Free Energies= -1039.820912
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.2689398
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-1040.1969943
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -1038.665742310585
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-1040.587581

C	0.22387	-2.50897	-0.03429
C	1.3912	-1.61327	-0.16513
C	0.50295	-0.39366	-0.06412
H	-0.42614	-2.58561	-0.89943
H	-0.27574	-2.55404	0.9269
H	1.90688	-1.73725	-1.1164
H	2.1145	-1.70632	0.64631
Cl	0.85766	-4.61746	-0.04233
C	-0.09367	0.14221	-1.28441
C	0.33553	0.21264	1.24306
C	0.66441	-0.48096	2.44374
C	-0.08236	1.56308	1.42171
C	0.55826	0.11337	3.69861
H	1.00146	-1.51297	2.4021
C	-0.1837	2.14916	2.67827
H	-0.29217	2.17627	0.55093
C	0.12494	1.43418	3.84203
H	0.81683	-0.47064	4.5789
H	-0.4963	3.18864	2.74846
H	0.04004	1.89386	4.82209
C	0.50728	-0.0321	-2.55737
C	-0.08269	0.44381	-3.72755
C	-1.30388	1.12008	-3.69564
C	-1.92899	1.29276	-2.45435
C	-1.34668	0.81227	-1.28683
H	1.46776	-0.53204	-2.63786
H	-1.76049	1.49221	-4.60792
H	0.42614	0.28941	-4.67612
H	-1.8885	0.92168	-0.35152
H	-2.89417	1.79061	-2.39736

Thesis = Figure 3.7 P-X, P-XI, P-XII, P-XIII, P-XIV, P-XV

A2 = S9-I-Rad-P, Br-Rad-P, Cl-Rad-P, I-An-P, Br-An-P, Cl-An-P



UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.245679 (Hartree/Particle)
Thermal correction to Energy= 0.257571
Thermal correction to Enthalpy= 0.258515
Thermal correction to Gibbs Free Energy= 0.206570
Sum of electronic and zero-point Energies= -579.546895
Sum of electronic and thermal Energies= -579.535003
Sum of electronic and thermal Enthalpies= -579.534059
Sum of electronic and thermal Free Energies= -579.586004
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-579.9795072
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-579.9633086
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -578.910585219423
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-580.2546971

C	-0.95974	-2.22625	-0.58632
C	0.48098	-2.20792	-1.00614
C	-0.29598	-0.90842	-0.93237
H	-1.68446	-2.61184	-1.29637
H	-1.19424	-2.40863	0.45768
H	0.71892	-2.57774	-1.99855
H	1.24547	-2.37826	-0.25486
C	-0.67709	-0.27156	-2.23911
C	0.01968	0.03644	0.19656
C	0.40202	-0.44743	1.45938
C	-0.05783	1.42534	0.02323

C 0.6968 0.42399 2.50523
H 0.47276 -1.51723 1.63941
C 0.23784 2.29982 1.07213
H -0.35235 1.83721 -0.93778
C 0.61742 1.80619 2.31836
H 0.99131 0.02149 3.47041
H 0.16982 3.3716 0.90796
H 0.84822 2.48536 3.13368
C -2.01497 0.013 -2.5323
C -2.36224 0.64963 -3.7252
C -1.37102 1.01186 -4.63905
C -0.03264 0.73159 -4.35459
C 0.30945 0.09397 -3.1615
H -2.78771 -0.26514 -1.81879
H -1.63945 1.5074 -5.56757
H -3.40533 0.86299 -3.94085
H 1.35224 -0.12201 -2.93886
H 0.74373 1.0088 -5.06205
Thesis = Figure 3.7 P-XIII
A2 = S9-I-Rad-P
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.017503
Sum of electronic and zero-point Energies= -6920.237912
Sum of electronic and thermal Energies= -6920.236495
Sum of electronic and thermal Enthalpies= -6920.235551
Sum of electronic and thermal Free Energies= -6920.255414
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.6137243
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.6118482
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -297.110848563578
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-297.7800963
I -0.74423 3.03008 0.
Thesis = Figure 3.7 P-XIV
A2 = S9-Br-Rad-P
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016830
Sum of electronic and zero-point Energies= -2573.667105
Sum of electronic and thermal Energies= -2573.665689
Sum of electronic and thermal Enthalpies= -2573.664745
Sum of electronic and thermal Free Energies= -2573.683935
UM06-2X/def2-TZVPP-SMD-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.1542532
UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-2574.150351
DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -2572.660988893114
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-2574.1448385
Br -0.74423 3.03008 0.
Thesis = Figure 3.7 P-XV
A2 = S9-Cl-Rad-P
UM06-2X/DGDZVP-SMD-THF
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015677
Sum of electronic and zero-point Energies= -460.075053
Sum of electronic and thermal Energies= -460.073637
Sum of electronic and thermal Enthalpies= -460.072692
Sum of electronic and thermal Free Energies= -460.090730
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UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-460.1325705

DLPNO-CCSD(T)-def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
FINAL SINGLE POINT ENERGY -459.664197907915
B3LYP-def2-TZVPP-THF//UM06-2X/DGDZVP-SMD-THF
HF=-460.1694148
Cl -0.74423 3.03008 0.
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A2 = S9-I-An-P
UM06-2X/DGDZVP-SMD-THF
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Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
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UM06-2X/def2-TZVPP-gas//UM06-2X/DGDZVP-SMD-THF
HF=-297.7222293
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HF=-297.9784966
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Appendix 3: Supporting Information Chapter 4

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using unrestricted M06-2X/DGDZVP level of the theory in implicit solvent (acetonitrile) using SMD as solvation model with the "guess=mix" keyword, as implemented in Gaussian09. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). 10 excited states were calculated on optimized structures using TD-DFT single points with the same method, basis set and solvation model used for optimizations. Further, to assess the influence of dynamic correlation, open-shell domain-based local pair natural orbital Coupled-Cluster calculations using single and double excitations with perturbative triple excitations (DLPNO-CCSD(T)), with def2-TZVPP basis, were performed using ORCA software. This latter method provides accurate energies (within 3 kJ mol^{-1}) with the computational cost comparable to DFT calculations. Single point energy calculations in implicit solvent using and UM06-2X/ def2-TZVPP with an ultrafine grid size were also performed on all structures for the full uphill photocatalytic isomerization pathways (Figures S3 and S3A). All minimum energy crossing points (MECP) located were obtained using the MECPro program (version 1.0.5). All 3-D structures were generated using CYLview. Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

Full Reference of Gaussian09 software:

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016

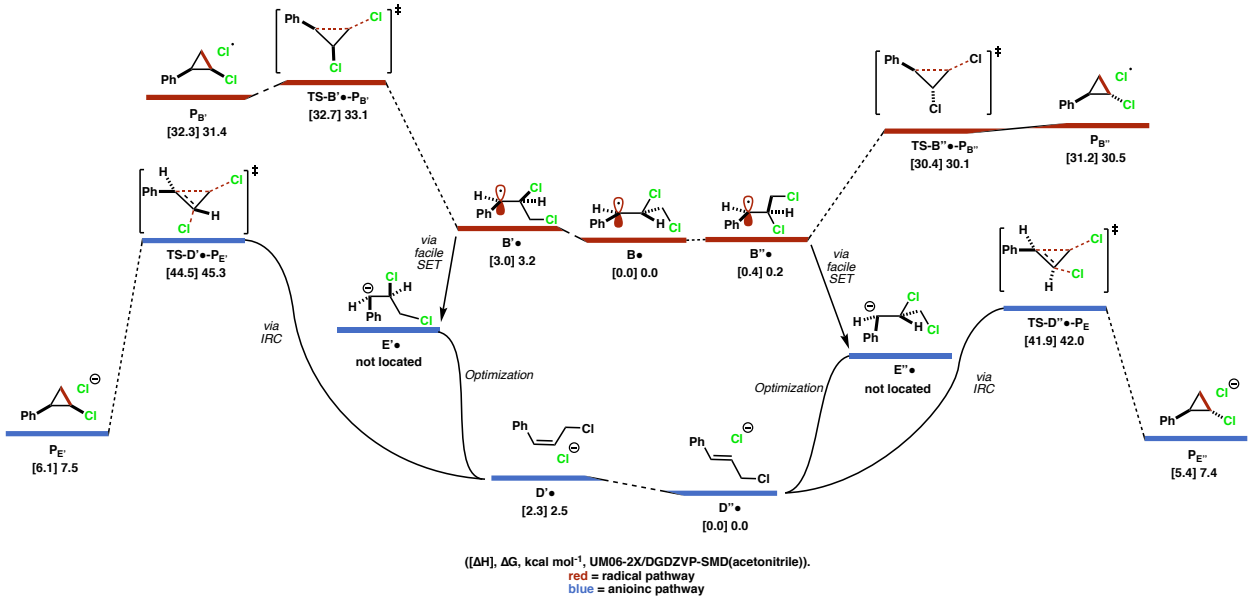


Figure A3.1: Anionic and radical potential energy surfaces calculated from intermediates which lead to product for the proposed dichloro-mechanism.

In our previous work, we found that the radical polar crossover (facile SET between radical intermediates and photocatalysts) led to anionic haloalkanes which cyclized much faster than the corresponding radical intermediates. We initially proposed a similar mechanism for this work. A chloride radical could be generated from cinnamyl chloride upon exposure to light and the proper photocatalyst. Giese addition of the chloride radical to an additional cinnamyl chloride would lead to the generation of radical intermediates **B''•** and **B'•** (**Figure A3.1**) which were calculated to differ in free energy by 3.0 kcal mol^{-1} at UM06-2X/DGDZVP-SMD(acetonitrile). Provided that radical cyclization is uphill in energy by ~30 kcal mol^{-1} from both intermediates, we decided to investigate the possibility of facile SET between the photocatalyst and radical intermediates **B•''** or **B'•** which, based on our previous calculations, should quickly cyclize to form the desired chlorocyclopropane. Optimization of the radical geometries, **B•''** and **B'•**, as anions, **E''•** and **E'•**, resulted in the barrierless elimination back to cinnamyl chloride **D''•** and **D'•** (Input and optimized geometries found in **Figure A3.1A**). The barrier of a concerted nucleophilic addition and cyclization (**TS-E''•-D''•** and **TS-E'•-D'•**) from intermediates **D''•** or **D'•** was found to be insurmountable with values of 42 kcal mol^{-1} and above. To find a rationale for the barrierless eliminations from **E''•** and **E'•**, we substituted these anionic intermediates with varying electron withdrawing groups (**Figure A3.1B**). A strong electron withdrawing group (NO_2) was required to

obtain the anionic intermediate, suggesting that the anionic charge on the traditional cinnamyl chloride intermediate was insufficiently stabilized. The results discussed above suggest regeneration of the overtly stable cinnamyl chloride which rule out radical or anionic cyclization under the presence of Cl• or Cl-, respectively, at the current reaction conditions.

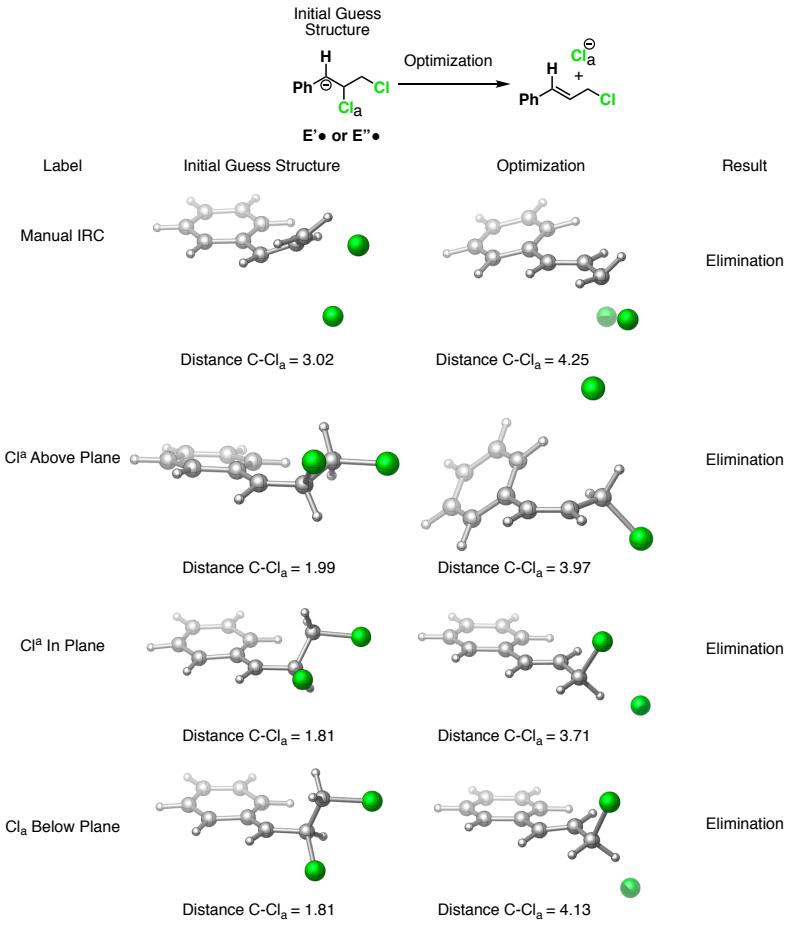
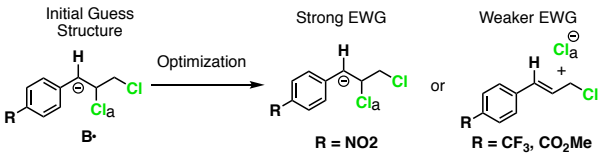
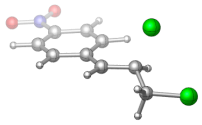
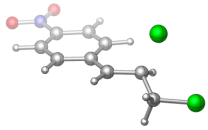
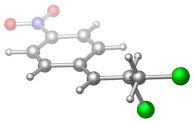
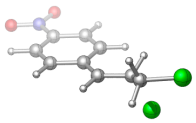


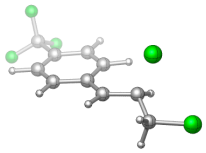
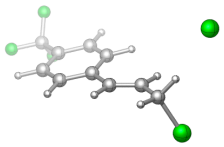
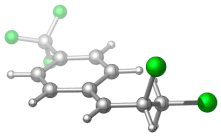
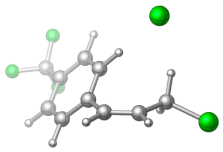
Figure A3.1A: Structure **B·** before and after optimization at UM06-2X/DGDZVP-SMD(acetonitrile). Bond lengths reported in Angstroms.



R = NO_2

Label	Initial Guess Structure	Optimization	Result
R			Anionic Int
	Distance C-Cl_a = 1.95	Distance C-Cl_a = 1.95	
S			Antionic Int
	Distance C-Cl_a = 1.76	Distance C-Cl_a = 1.95	

R = CF_3

R			Elimination
	Distance C-Cl_a = 1.95	Distance C-Cl_a = 3.73	
S			Elimination
	Distance C-Cl_a = 1.76	Distance C-Cl_a = 3.75	

R = CO_2Me

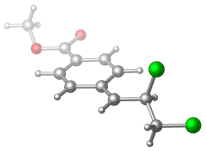
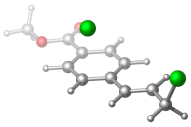
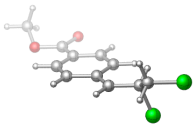
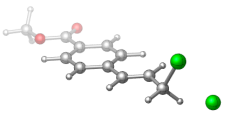
R			Elimination
	Distance C-Cl_a = 1.76	Distance C-Cl_a = 4.67	
S			Elimination
	Distance C-Cl_a = 1.76	Distance C-Cl_a = 3.66	

Figure A3.1B: Structure **B·** with varying electron withdrawing groups before and after optimization at UM06-2X/DGDZVP-SMD(acetonitrile). These results suggest that only with strongly electron-withdrawing groups, dichloro anionic intermediates can be located.

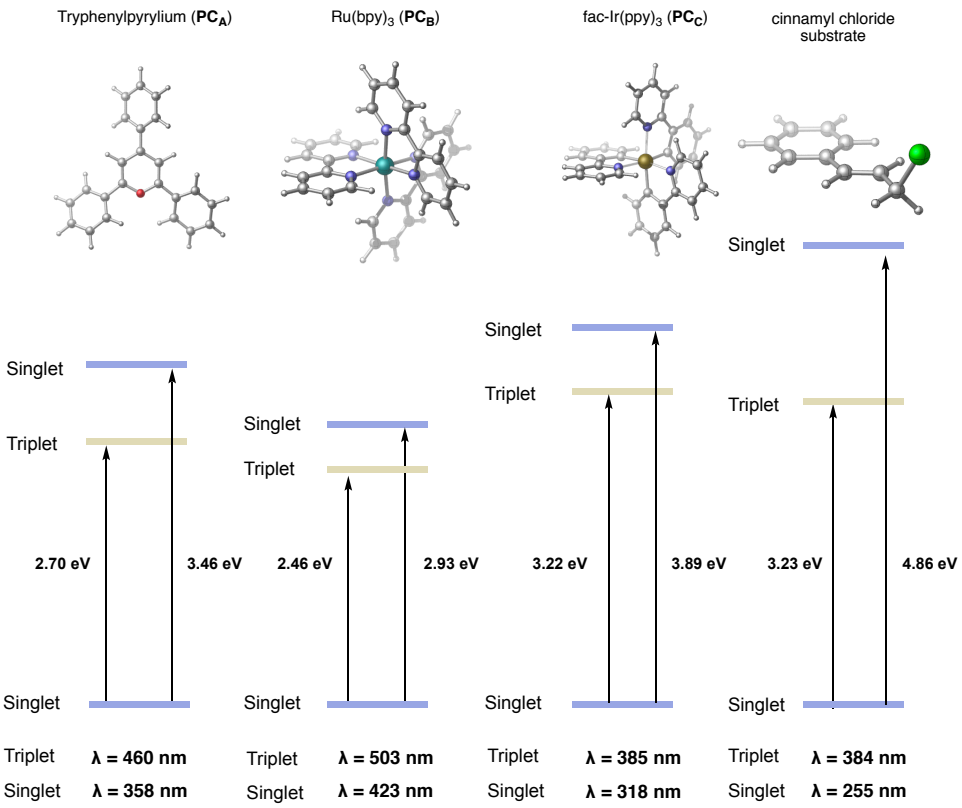


Figure A3.2: Singlet excited states closest to 400 nm and lowest energy triplet excited states of photocatalysts and substrate (cinnamyl chloride) obtained from TD-DFT calculations at UM06-2X/DGDZVP-SMD(acetonitrile).

Now knowing that the radical polar crossover does not generate the desired product, we turned to study the mechanism in which the photocatalyst interacts with the cinnamyl chloride. Prior work by Cristol on allylic chlorides stated that triplet-triplet sensitization via an organic photosensitizer allowed for isomerization to the cyclopropyl product; obtaining both *cis*- and *trans*-cyclopropyl products as well as a mixture of beta-elimination side products. Single point TD-DFT calculations on cinnamyl chloride revealed that singlet excitation was not possible using blue LEDs (**Figure A3.2**), as the lowest energy singlet excitation requires wavelengths of 255 nm. The lowest energy absorption of cinnamyl chloride calculated was a triplet excitation that occurs at 384 nm. However,

TD-DFT calculations at the same level of theory on photocatalysts $\mathbf{PC_a}$ $\mathbf{PC_b}$ and $\mathbf{PC_c}$ used in experiment revealed that $\mathbf{PC_c}$ was the only photocatalyst which had a triplet energy excitation, close to 400 nm, with enough energy to undergo triplet-triplet excitation of the cinnamyl chloride.

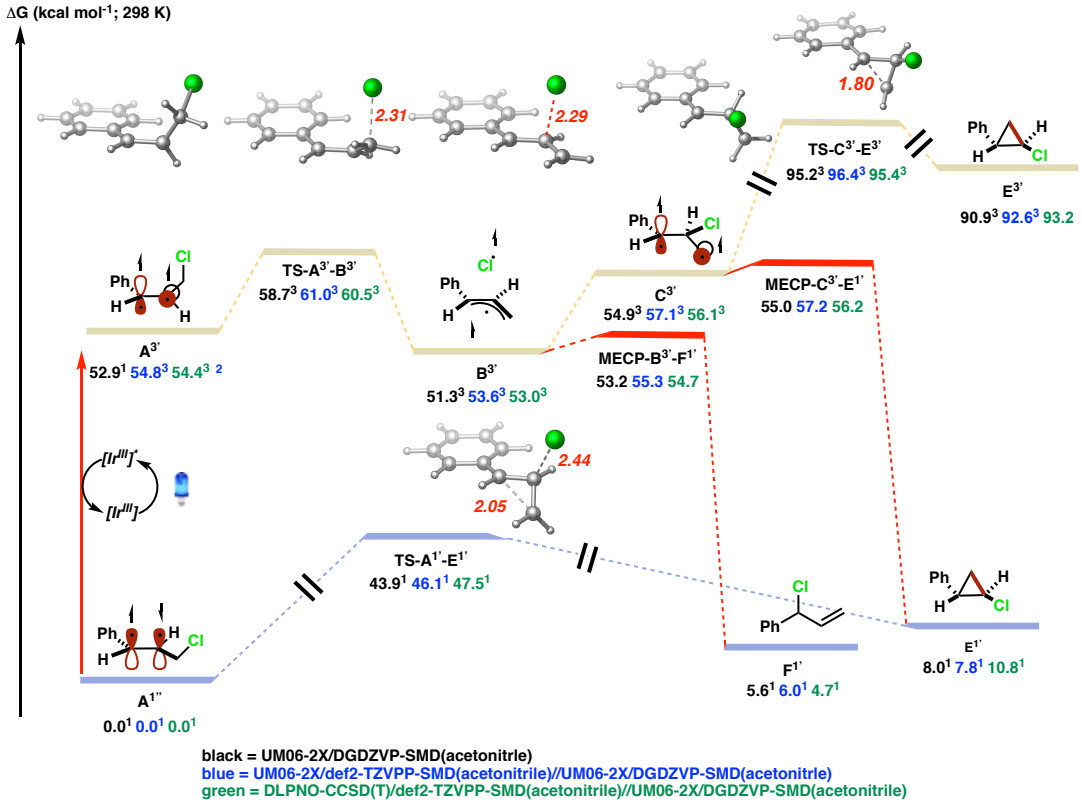


Figure A3.3: Uphill potential energy surface leading to *trans*-cyclopropyl product. Single points of MECP were calculated from triplet state geometry obtained from the MECPro program.

We then turned to explore the monochloro triplet and singlet potential energy surfaces of cinnamyl chloride (**Figures A3.3** and **A3.3A** for pathways to trans and cis-cyclopropyl products respectively). For the pathway leading to trans-cyclopropyl product, triplet-triplet energy transfer between the iridium photocatalyst and cinnamyl chloride starting material, $\mathbf{A^{1''}}$, results in the triplet diradical intermediate $\mathbf{A^{3'}}$ with a cost of ~55 kcal mol^{-1}. Radical dissociation of chlorine via **TS-**$\mathbf{A^{3'}}$**-**$\mathbf{B^{3'}}$ with a barrier of ~6 kcal mol^{-1} leads to the triplet diradical pair $\mathbf{B^{3'}}$ which is exergonic by 1.2-1.4 kcal mol^{-1} from $\mathbf{A^{3'}}$. Radical rebound of the chloride radical would lead to the 1,3 triplet diradical $\mathbf{C^{3'}}$ with a thermodynamic cost of 3.1-3.5 kcal mol^{-1}. The radical rebound transition state, **TS-**$\mathbf{B^{3'}}$**-**$\mathbf{C^{3'}}$, was not isolated but an ultrafine scan from $\mathbf{B^{3'}}$ to $\mathbf{C^{3'}}$ of the C-Cl bond (**Figure A3.3B**) suggests that this chlorine radical rebound should cost ~ 1.5 kcal mol^{-1} but rotation into the diradical

geometry of **C$^{3'}$** costs an additional 2.5 kcal mol^{-1}, giving a total barrier of ~4.0 kcal mol^{-1}. Triplet ring closure via **TS-C$^{3'}$-E$^{3'}$** is insurmountable with a barrier of > 39 kcal mol^{-1} from **A$^{3'}$**. Similar pathways were explored to the cis-cyclopropyl product following similar trends with one vary large difference in the triplet potential energy pathway (**Figure A3.3A**). Notably, intermediate **C^{3}**, from radical rebound of the chlorine radical of **B^{3}** (not shown in **Figure A3.3A**), could not be isolated. Triplet cyclization to the cis-cyclopropyl product, **TS-B$^{3'}$-C^{3}**, was found to come from **B^{3}** via IRC and subsequent optimization of the final structure of the IRC (**Figure A3.3C**). Due to the high cost of triplet cyclization and the lack of overlap between singlet and triplet pathways, we sought for potential pathways from intermediates generated from the triplet pathway that could undergo intersystem crossing to generate the low energy singlet cyclopropyl product. We performed an exhaustive conformational search on triplet intermediates **B^{3}** , **B$^{3'}$** and **C$^{3'}$** (**Figure A3.3D**). Singlet optimization of 1,3 diradical intermediate **C^{3}** always led to the trans-cyclopropyl product, **E^{3}**. Additional singlet optimization of **B^{3}** and **B$^{3'}$** resulted in the respective S-(**F^{1}**) and R-beta-elimination (**F$^{1'}$**) side products observed experimentally. The minimum energy crossing points of **MECP-B^{3}-F^{1}**, **MECP-B$^{3'}$- F$^{1'}$** and **MECP-C$^{3'}$-E$^{1'}$** were obtained using the MECPro software (**Figure A3.3E**). Optimization of all MECP geometries in the triplet and singlet states resulted in their corresponding triplet and singlet intermediates or products. Triplet and singlet frequency calculations of MECP structures revealed that all singlet MECP have a single imaginary frequency which, based on visualization of this frequency, seemed to lead to the observed products. All triplet MECP do not have an imaginary frequency, as these structures more closely resemble the optimized geometries of the triplet intermediates. The observation of these singlet state imaginary frequencies further support that the minimum energy crossing from triplet intermediates **B^{3}, B^{3}** and **C$^{3'}$** to the singlet potential energy surface results in the formation of products. Differences in the frequency between singlet and triplet MECP cause differences in the enthalpy and free energy correction terms of the singlet and triplet calculations as shown in **Figure A3.3E**. The difference in free energy between barriers of **MECP-B$^{3'}$- F$^{3'}$** and **MECP-C$^{3'}$-E$^{1'}$** is of 1.5-1.9 kcal mol^{-1} in favor of formation of cyclopropyl product which matches experimental observation. In summary, triplet-triplet energy transfer from the photocatalyst puts cinnamyl chloride in its triplet excited state. The formation of the 1,3-diradical intermediate **C$^{3'}$** is required to generate cyclopropyl product, resulting in the selective formation of the *trans*-cyclopropyl product via minimum energy crossing to its singlet state. All chlorine allyl triplet radical pairs (**B^{3}** and **B$^{3'}$**)

rearrange into their respective beta-elimination products via minimum energy crossing to their singlet states.

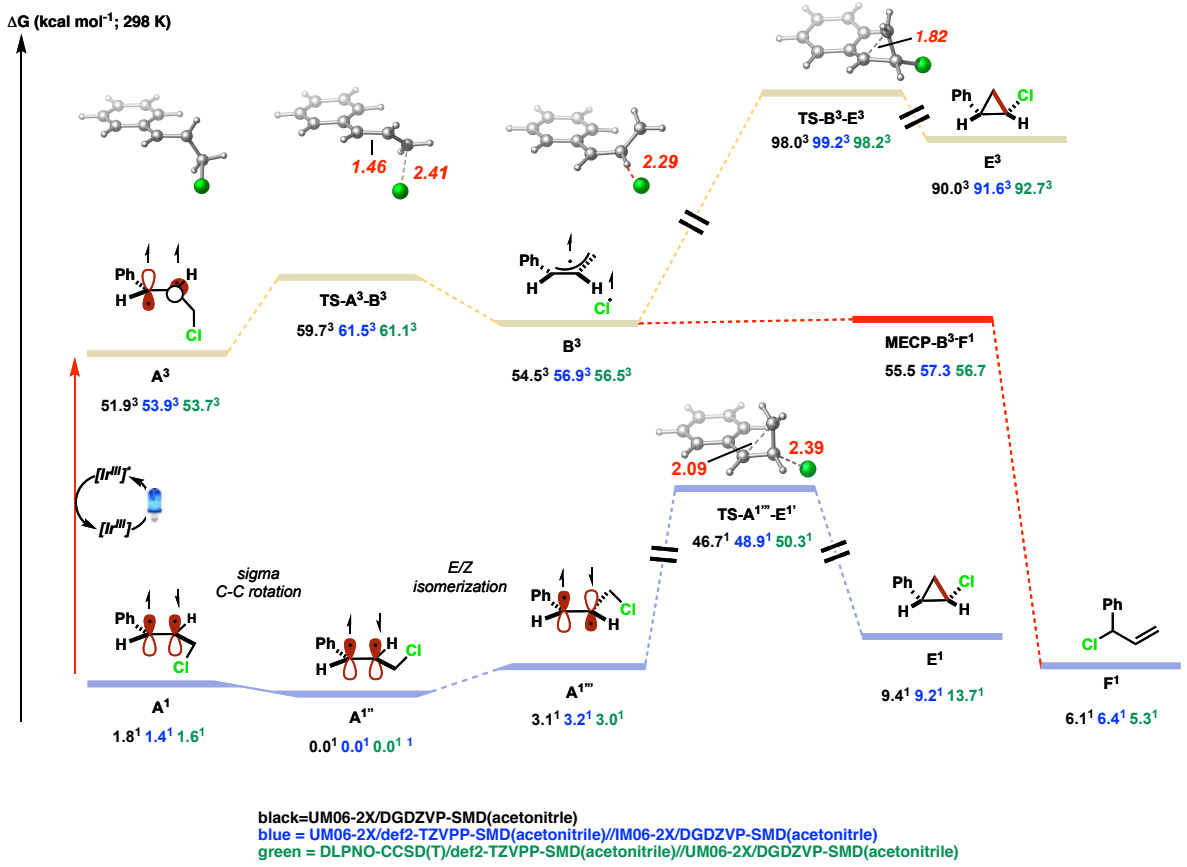


Figure A3.3A: Uphill potential energy surface leading to cis-cyclopropyl product. Single points of MECP obtained from triplet state optimizations.

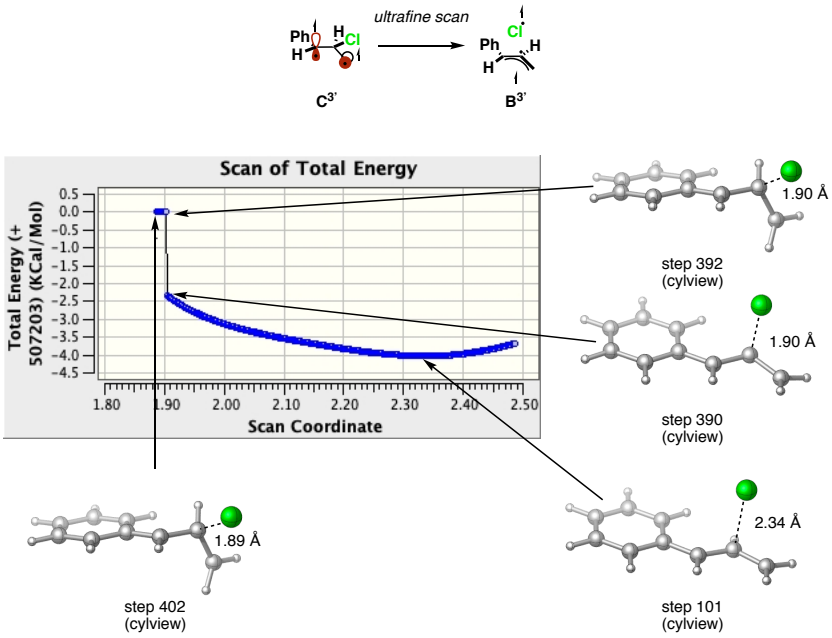


Figure A3.3B: Ultrafine scan of 1,3-biradical triplet **C**[3'] to triplet radical pair **B**[3'] at UM06-2X/DGDZVP-SMD(acetonitrile).

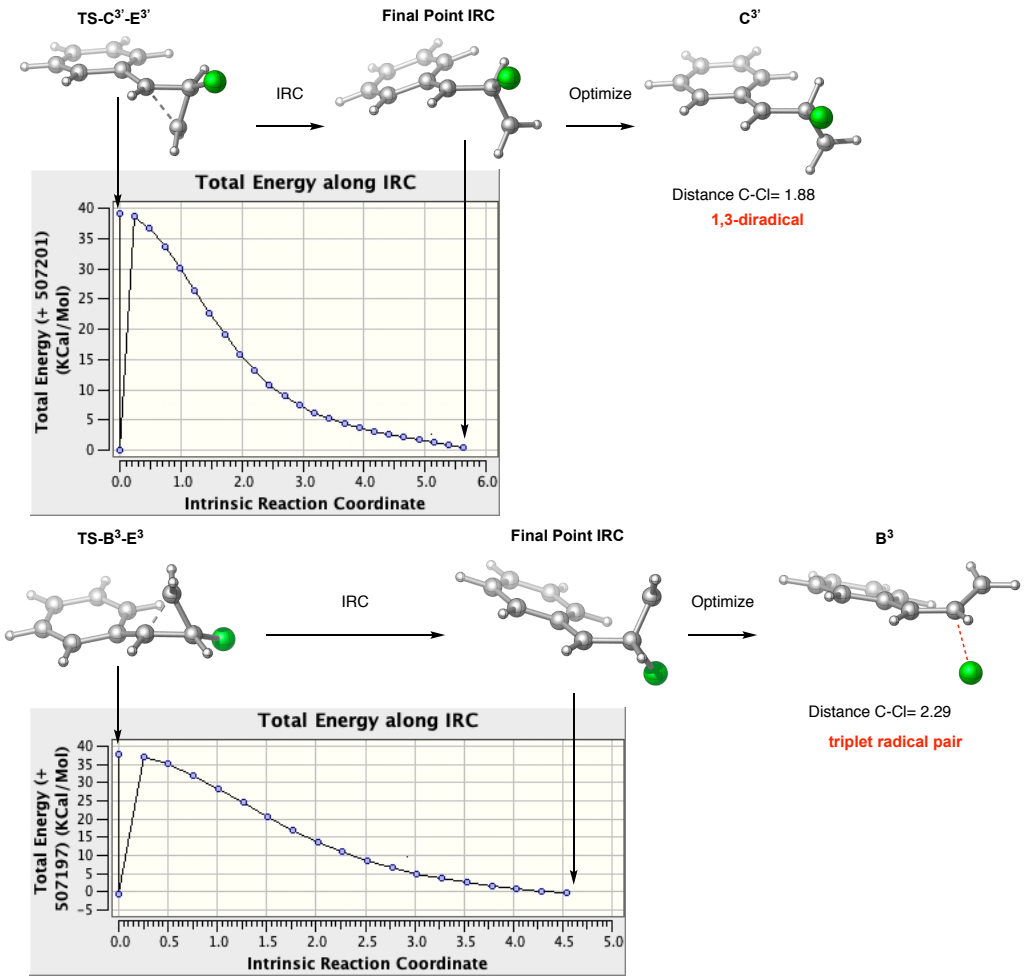


Figure A3.3C: Intrinsic Reaction Coordinate (IRC) of **TS-C³'-E³'** and **TS-B³-E³** to **C³'** and **B³** respectively. Final point on IRCs optimized to obtain intermediate geometry **C³'** and **B³**.

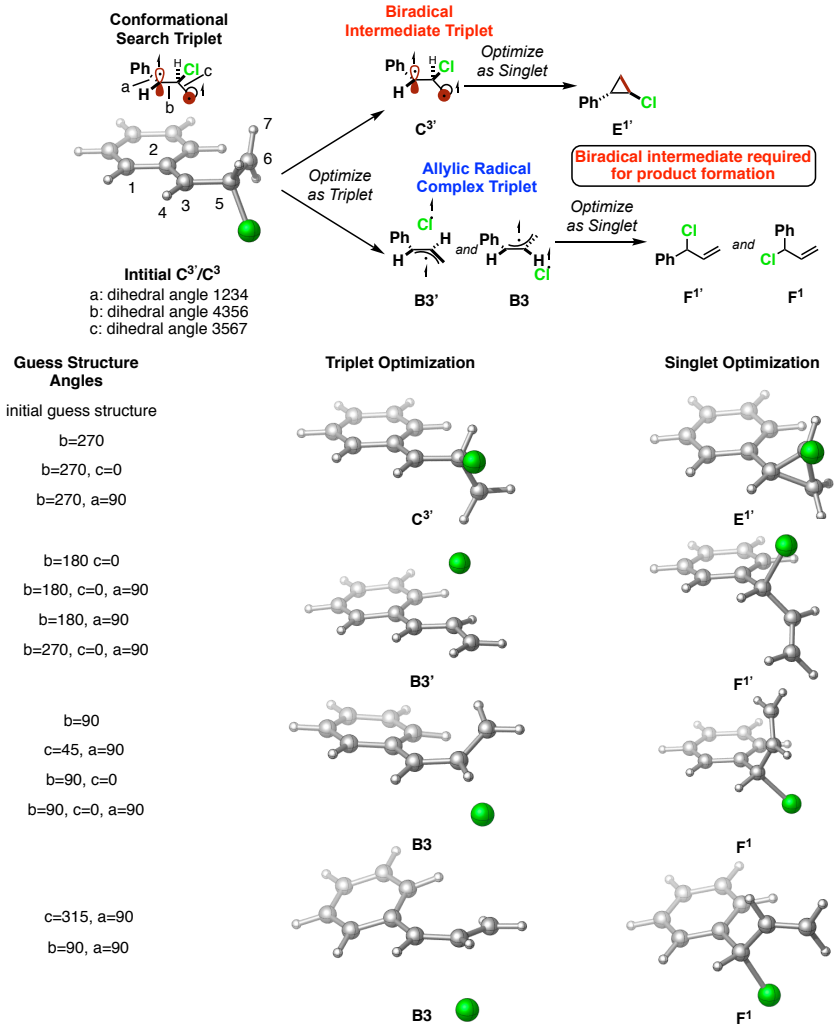


Figure A3.3D: Conformational search of triplet 1,3-diradical intermediate C3' then subsequent singlet optimization of obtained structure at UM06-2X/DGDZVP-SMD(acetonitrile). Dihedral angles relative to initial structure indicated as Intitial **C³'**.

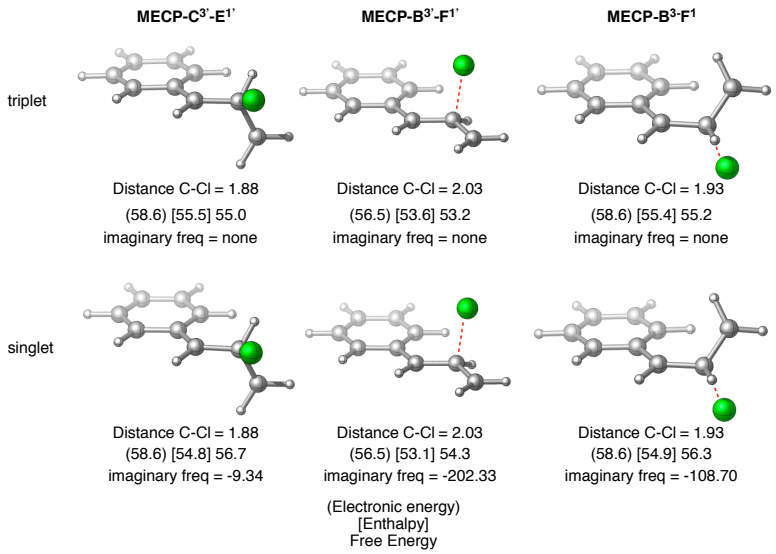


Figure A3.3E: Geometries of minimum energy crossing points obtained using the MECPro program in the singlet and triplet state with UM06-2X/DGDZVP-SMD(acetonitrile). Electronic energies, enthalpies and free energies are relative to **A1'** (Figure A3.3) above and are reported in kcal mol^{-1}.

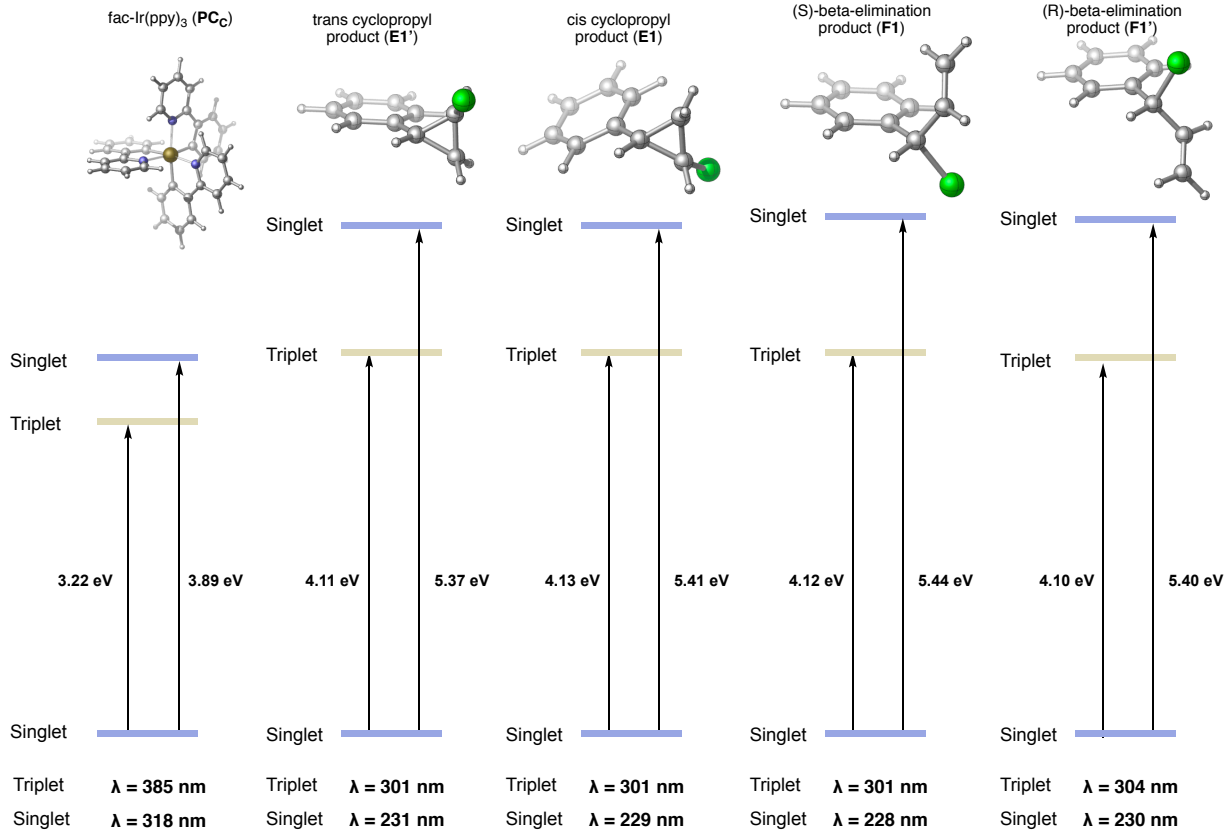


Figure A3.4A: Lowest energy singlet and triplet excited states of products obtained from TD-DFT calculations at UM06-2X/DGDZVP-SMD(acetonitrile) with prior results of $\mathbf{PC_c}$ for comparison.

In order to ensure that this photochemical isomerization is photochemically irreversible under the current conditions, additional TD-DFT calculations on products, including *cis*-cyclopropyl, were performed. As can be seen in **Figure A3.4A**, the lowest energy singlet and triplet excitations of all products occur at ~230 and ~300 nm respectively, which are inaccessible using blue LEDs. Next, we turned to investigate the reason why certain substrates did not result in cyclopropane product. TD-DFT calculations on the ground state structure of the methyl substituted cinnamyl chloride (**Figure A3.4B**) reveal that triplet excitation (3.38 eV) is slightly higher in energy than the photocatalyst triplet state (3.22 eV); which could be due to the rotation of the phenyl ring out of the plane of the alkene. Substituting the phenyl group with hexyl group results in a significant increase in energy of the triplet excitation, difference of 1.10 eV from cinnamyl chloride, making triplet-triplet energy transfer impossible. Surprisingly, cinnamyl bromide and iodide did not lead to the desired cyclopropyl product. TD-DFT calculations suggest that photoexcitation to the triplet state of these two substrates is possible, as bromide and iodide substrates lower the singlet to triplet gap from 3.23 eV of cinnamyl chloride to 3.15 eV and 3.05 eV respectively. These results suggest two possibilities. 1. Lack of overlap between acceptor and donor orbitals of the substrate and photocatalyst or 2. a lack of radical rebound along the triplet pathway to position 2 of the halogen allylic triplet radical pair, like $\mathbf{B^3}$ and $\mathbf{B^{3'}}$ (**Figures A3.3** and **A3.3A**), preventing cyclopropanation. Excitation of cinnamyl methoxide is inaccessible via triplet-triplet energy transfer. Overall, these calculations show that this photoisomerization is irreversible under the current conditions, allowing for the observed *uphill* reactivity. Some unreactive substrates can be explained due to an inability to be excited by the photocatalyst while others, such as cinnamyl bromide and iodide, are energetically capable of undergoing triplet-triplet energy transfer with the photocatalyst but do not result in product formation experimentally.

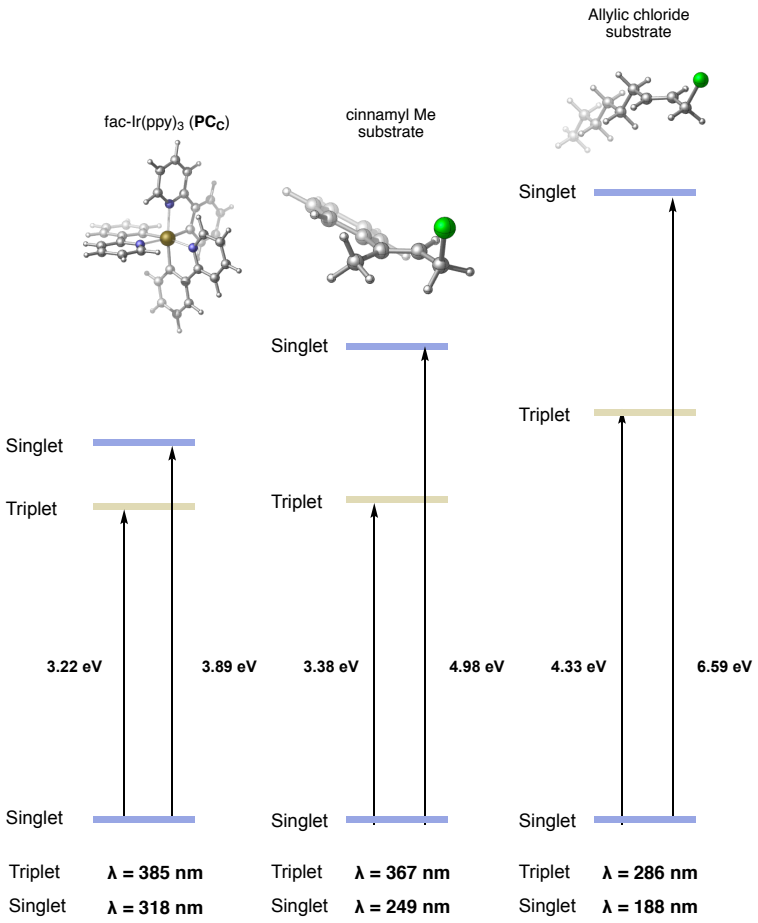


Figure A3.4B: Lowest energy singlet and triplet excited states of unproductive substrates obtained from TD-DFT calculations at UM06-2X/DGDZVP-SMD(acetonitrile) with prior results of $\mathbf{PC_c}$ for comparison.

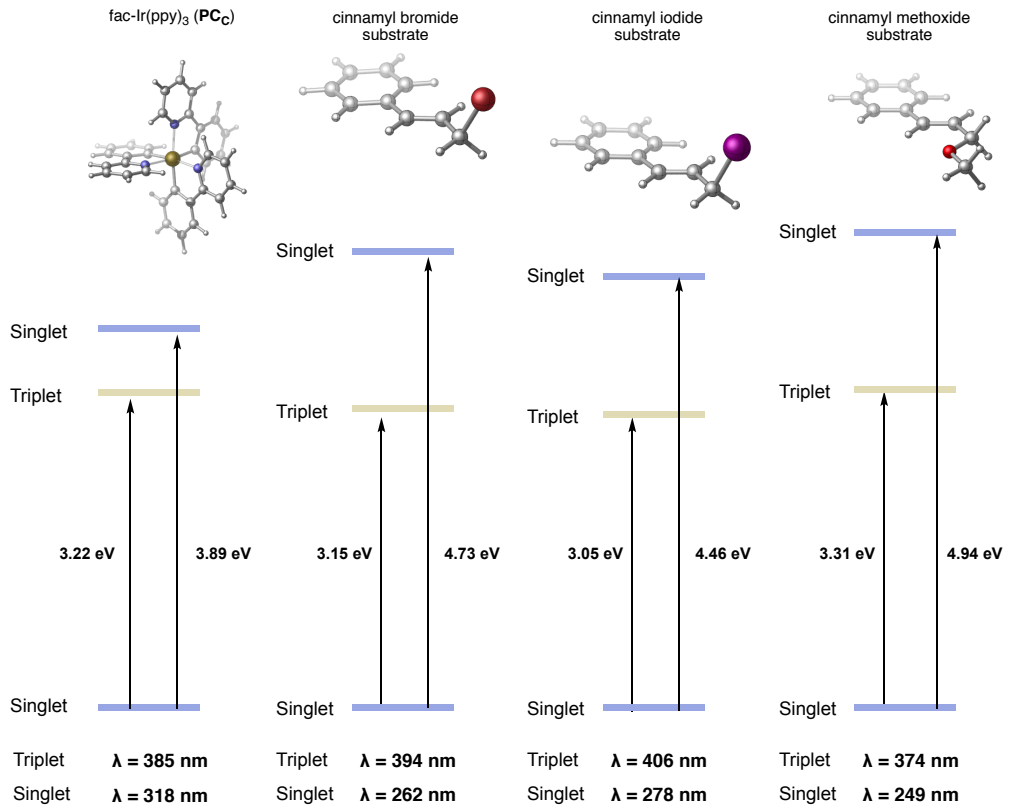
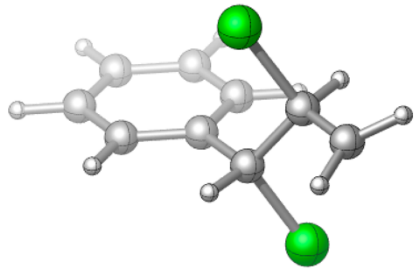


Figure A3.4C: Lowest energy singlet and triplet excited states of unproductive substrates obtained from TD-DFT calculations at UM06-2X/DGDZVP-SMD(acetonitrile)with prior results of **PC$_c$** for comparison.

Energies and Coordinates

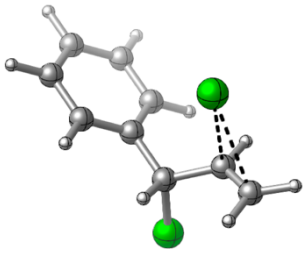
Thesis = 12



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154095 (Hartree/Particle)
Thermal correction to Energy= 0.164877
Thermal correction to Enthalpy= 0.165821
Thermal correction to Gibbs Free Energy= 0.115790
Sum of electronic and zero-point Energies= -1268.318881
Sum of electronic and thermal Energies= -1268.308099
Sum of electronic and thermal Enthalpies= -1268.307155
Sum of electronic and thermal Free Energies= -1268.357186

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H	-1.2493590000	-2.5940680000	-2.7292270000
H	-1.3654560000	-3.3413240000	-1.0145550000
Cl	1.3437980000	-1.6282720000	-1.0408270000
C	-0.2089330000	0.2079610000	0.9560080000
C	0.4934930000	0.0481620000	2.1522230000
C	-0.2389070000	1.4617190000	0.3333160000
C	1.1672240000	1.1308800000	2.7226260000
H	0.5183170000	-0.9255620000	2.6355160000
C	0.4329500000	2.5411460000	0.9026150000
H	-0.7914230000	1.5999550000	-0.5935560000
C	1.1384110000	2.3776670000	2.0988070000
H	1.7118200000	0.9979590000	3.6527030000
H	0.4054020000	3.5111760000	0.4150470000
H	1.6600350000	3.2207770000	2.5421770000
Cl	-2.7097210000	-0.6799820000	0.3191280000
H	-0.5866010000	-0.4300720000	-1.7395740000
C	-0.9066310000	-0.9790580000	0.3457630000
H	-0.7757720000	-1.8655730000	0.9686550000

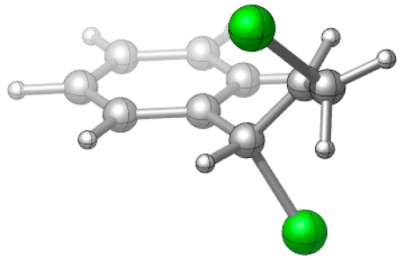
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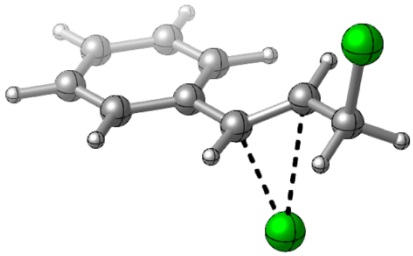
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154117 (Hartree/Particle)
Thermal correction to Energy= 0.164679
Thermal correction to Enthalpy= 0.165623
Thermal correction to Gibbs Free Energy= 0.114815
Sum of electronic and zero-point Energies= -1268.307051
Sum of electronic and thermal Energies= -1268.296489
Sum of electronic and thermal Enthalpies= -1268.295545
Sum of electronic and thermal Free Energies= -1268.346353

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C	-0.79250	-1.17630	-1.09355
H	-0.72515	-2.59576	-2.68950
H	-0.93210	-3.30979	-0.97721
Cl	1.66036	-1.66062	-1.09045
C	-0.29806	0.23983	0.95620
C	0.44927	0.03872	2.11855
C	-0.32252	1.50435	0.35657
C	1.17679	1.09208	2.67634
H	0.46792	-0.94390	2.58361
C	0.40414	2.55438	0.91373
H	-0.91174	1.67418	-0.54189
C	1.15655	2.35001	2.07426
H	1.75722	0.92748	3.57929
H	0.38268	3.53350	0.44442
H	1.72202	3.17002	2.50713

Cl -2.86008 -0.60366 0.47257
H -0.74537 -0.31529 -1.75597
C -1.05097 -0.91977 0.36279
H -0.89082 -1.82888 0.94270
Thesis = 10

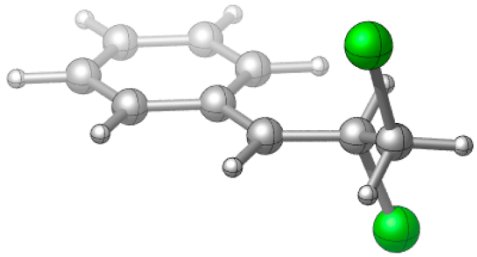


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154917 (Hartree/Particle)
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Thermal correction to Enthalpy= 0.166838
Thermal correction to Gibbs Free Energy= 0.113632
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Sum of electronic and thermal Energies= -1268.312651
Sum of electronic and thermal Enthalpies= -1268.311707
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C -0.1866060000 -0.9637700000 0.5264450000
C -0.8327580000 -0.0028500000 -0.2548440000
C -2.0960420000 -0.2823760000 -0.7919340000
C -2.7053710000 -1.5096750000 -0.5433760000
H -2.5354230000 -3.4249470000 0.4356130000
H -0.2920310000 -2.9357190000 1.3863000000
H 0.7960690000 -0.7500180000 0.9396200000
H -2.5990320000 0.4559790000 -1.4125880000
H -3.6839030000 -1.7214600000 -0.9640820000
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H -0.9907100000 4.6411600000 0.0329840000
H 0.6243860000 3.9262140000 -0.2721310000
C -0.9869050000 2.5064440000 -0.1697490000
H -2.0695180000 2.4371100000 -0.1941620000
Cl 0.0080370000 3.7887680000 2.0180610000
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Cl 0.3012140000 1.4468710000 -2.3170610000
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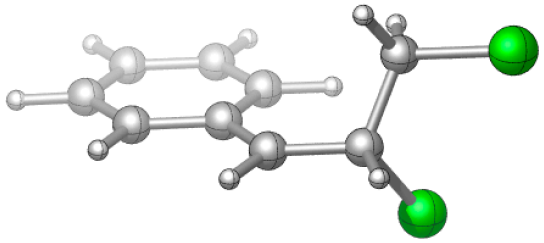


Zero-point correction= 0.155137 (Hartree/Particle)
Thermal correction to Energy= 0.165705
Thermal correction to Enthalpy= 0.166649
Thermal correction to Gibbs Free Energy= 0.115406
Sum of electronic and zero-point Energies= -1268.317576
Sum of electronic and thermal Energies= -1268.307007
Sum of electronic and thermal Enthalpies= -1268.306063
Sum of electronic and thermal Free Energies= -1268.357307
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H -1.71323 -2.45135 -2.32698
H -1.02453 -3.24587 -0.87477
Cl 0.56549 -3.00388 -2.62605
C -0.04706 0.29368 0.94938
C 0.48233 0.21980 2.24647
C -0.13386 1.54105 0.30884
C 0.93955 1.36911 2.88812
H 0.53837 -0.74425 2.74586
C 0.31763 2.68699 0.95479
H -0.56888 1.62464 -0.68300
C 0.85798 2.60381 2.24289

H 1.35348 1.30162 3.88947
H 0.24371 3.64992 0.45871
H 1.20808 3.50242 2.74227
Cl -2.85776 -0.92593 0.53301
H -0.47934 -0.31433 -1.75179
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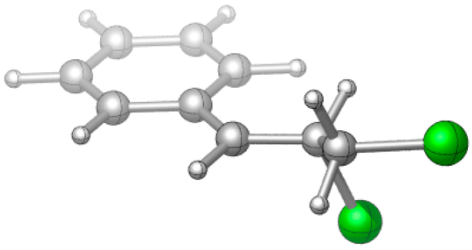
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Zero-point correction= 0.155898
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Thermal correction to Gibbs Free Energy=
0.116962
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C -0.9138220000 -0.0210420000 -
0.1089410000
C -2.3060630000 -0.2205330000
0.0795040000
C -2.8222660000 -1.5016550000
0.2292590000
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0.3166540000
H 0.0577810000 -3.3039280000 -
0.0207080000
H 0.9918740000 -1.0300000000 -
0.2963350000
H -2.9843170000 0.6275560000
0.1016330000
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0.3702140000
C -0.3290190000 1.2688910000 -
0.2640000000
H 0.7334740000 1.3322130000 -
0.4895690000
C -0.2321290000 3.7457270000
0.1255120000
H -0.8076890000 4.6678550000
0.0731940000
H 0.6550940000 3.8099900000 -
0.5036390000
C -1.0810660000 2.5371740000 -
0.2291450000
H -1.9724600000 2.4992270000
0.3965070000
Cl -1.7501040000 2.9036850000 -
1.9333340000
Cl 0.3354690000 3.5828480000
1.8321450000
A3 = A3.1-B•'



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155654
(Hartree/Particle)
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Thermal correction to Enthalpy=
0.167108
Thermal correction to Gibbs Free Energy=
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Sum of electronic and zero-point Energies= -
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Sum of electronic and thermal Energies= -
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Sum of electronic and thermal Enthalpies= -
1268.320785
Sum of electronic and thermal Free Energies= -
1268.370840
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0.5861310000
C 0.5625290000 -1.5890070000 -
1.2891540000
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1.0172540000
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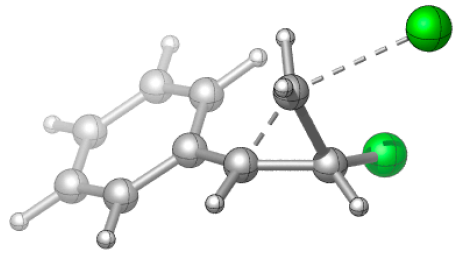
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Cl 2.3223150000 -1.9154820000 -0.8484500000

A3 = SI-B•’’



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155393 (Hartree/Particle)
Thermal correction to Energy= 0.165984
Thermal correction to Enthalpy= 0.166928
Thermal correction to Gibbs Free Energy= 0.116196
Sum of electronic and zero-point Energies= -1268.336468
Sum of electronic and thermal Energies= -1268.325876
Sum of electronic and thermal Enthalpies= -1268.324932
Sum of electronic and thermal Free Energies= -1268.375665
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C -0.6018040000 -2.4416140000 0.0067140000
C -0.0763280000 -1.1667290000 -0.1474220000
C -0.9138220000 -0.0210420000 -0.1089410000
C -2.3060630000 -0.2205330000 0.0795040000
C -2.8222660000 -1.5016550000 0.2292590000
H -2.3897910000 -3.6159880000 0.3166540000
H 0.0577810000 -3.3039280000 -0.0207080000
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H 0.7334740000 1.3322130000 -0.4895690000
C -0.2321290000 3.7457270000 0.1255120000
H -0.8076890000 4.6678550000 0.0731940000
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C -1.0810660000 2.5371740000 -0.2291450000
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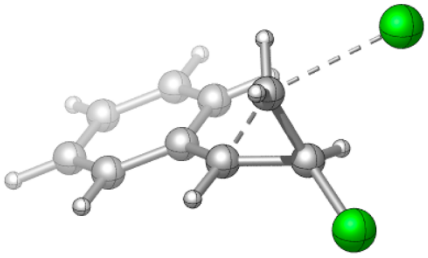
Thesis = TS-11-4a
A3 = A3.1-TS-B’•-$P_{B'}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154254 (Hartree/Particle)
Thermal correction to Energy= 0.164577
Thermal correction to Enthalpy= 0.165521
Thermal correction to Gibbs Free Energy= 0.115748
Sum of electronic and zero-point Energies= -1268.284676
Sum of electronic and thermal Energies= -1268.274353
Sum of electronic and thermal Enthalpies= -1268.273409
Sum of electronic and thermal Free Energies= -1268.323182

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C	-0.0794810000	-0.4582730000	-0.8485970000
H	-1.2368310000	-2.2959300000	-1.4130620000
H	-0.4539770000	-2.3679300000	0.2729850000
H	0.9836320000	-1.5859460000	-2.3968350000
Cl	0.1140210000	-4.5134960000	-1.3308750000
C	0.0283210000	0.3453610000	0.3911490000
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C	0.5803460000	0.6782670000	2.7314140000
H	0.7885540000	-1.1956170000	1.7185680000
C	-0.2841730000	2.5212880000	1.4343650000
H	-0.7506760000	2.0830440000	-0.6202540000
C	0.1950430000	2.0184010000	2.6451940000
H	0.9434890000	0.2770950000	3.6728920000
H	-0.5945250000	3.5591410000	1.3578760000
H	0.2582270000	2.6617100000	3.5177620000
H	-0.6144610000	0.0310260000	-1.6560910000
Cl	2.3850870000	-1.8131200000	-0.4892060000

Thesis = TA3.1$_{2\text{-}2a}$
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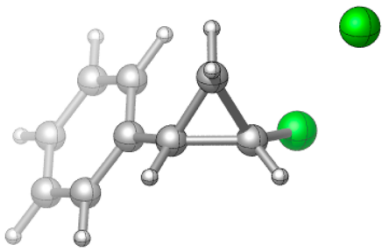
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.153276 (Hartree/Particle)
Thermal correction to Energy= 0.163859
Thermal correction to Enthalpy= 0.164803
Thermal correction to Gibbs Free Energy= 0.113937
Sum of electronic and zero-point Energies= -1268.288603
Sum of electronic and thermal Energies= -1268.278019
Sum of electronic and thermal Enthalpies= -1268.277075
Sum of electronic and thermal Free Energies= -1268.327942

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C	-0.6018040000	-2.4416140000	0.0067140000
C	-0.0763280000	-1.1667290000	-0.1474220000
C	-0.9138220000	-0.0210420000	-0.1089410000
C	-2.3060630000	-0.2205330000	0.0795040000
C	-2.8222660000	-1.5016550000	0.2292590000
H	-2.3897910000	-3.6159880000	0.3166540000

H 0.0577810000 -3.3039280000 -0.0207080000
H 0.9918740000 -1.0300000000 -0.2963350000
H -2.9843170000 0.6275560000 0.1016330000
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H 0.7334740000 1.3322130000 -0.4895690000
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Thesis = 4a

A3 = A3.1-$P_{B'}$

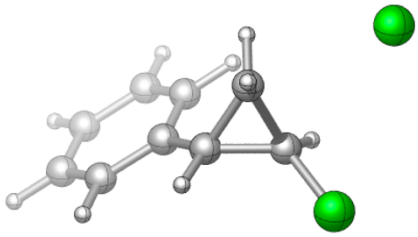


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155348 (Hartree/Particle)
Thermal correction to Energy= 0.166163
Thermal correction to Enthalpy= 0.167107
Thermal correction to Gibbs Free Energy= 0.115261
Sum of electronic and zero-point Energies= -1268.285736
Sum of electronic and thermal Energies= -1268.274920
Sum of electronic and thermal Enthalpies= -1268.273976
Sum of electronic and thermal Free Energies= -1268.325823

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H -0.3052520000 -2.5058050000 0.2617710000
Cl 0.8517480000 -4.5465860000 -1.6456040000
C -0.1069020000 0.3266550000 0.4372450000
C 0.1974480000 -0.1861550000 1.7045760000
C -0.2306940000 1.7153690000 0.2879940000
C 0.3803930000 0.6701450000 2.7916020000
H 0.2913820000 -1.2568770000 1.8606660000
C -0.0500330000 2.5718570000 1.3740290000
H -0.4726370000 2.1263530000 -0.6893050000
C 0.2587540000 2.0515660000 2.6321020000
H 0.6146900000 0.2536480000 3.7671310000
H -0.1525230000 3.6445210000 1.2364600000
H 0.3985420000 2.7155550000 3.4800870000
H -0.8818440000 -0.0506220000 -1.5558070000
Cl 2.3544870000 -1.5054370000 -0.5002080000
H 0.9220860000 -1.4390060000 -2.4057480000

Thesis = 2a

A3 = A3.1-$P_{B''}$

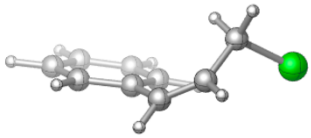


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155515 (Hartree/Particle)

Thermal correction to Energy= 0.166312
Thermal correction to Enthalpy= 0.167256
Thermal correction to Gibbs Free Energy= 0.115765
Sum of electronic and zero-point Energies= -1268.287626
Sum of electronic and thermal Energies= -1268.276829
Sum of electronic and thermal Enthalpies= -1268.275885
Sum of electronic and thermal Free Energies= -1268.327376

C	-0.5349720000	-1.9227280000	-0.8322480000
C	0.8391000000	-1.4746120000	-1.2478710000
C	-0.1748660000	-0.4365750000	-0.8934390000
H	-1.2164460000	-2.2746770000	-1.5995370000
H	-0.6466270000	-2.3630210000	0.1547360000
Cl	0.5934190000	-4.6090510000	-1.0478230000
C	-0.0270410000	0.3776330000	0.3457890000
C	0.4740370000	-0.1607630000	1.5400040000
C	-0.3931970000	1.7295620000	0.3166140000
C	0.6092780000	0.6390400000	2.6743080000
H	0.7600700000	-1.2091320000	1.5947760000
C	-0.2582590000	2.5294100000	1.4522450000
H	-0.7853380000	2.1558720000	-0.6034870000
C	0.2445120000	1.9871210000	2.6358970000
H	0.9990600000	0.2080540000	3.5919740000
H	-0.5466480000	3.5758350000	1.4111460000
H	0.3484680000	2.6067990000	3.5217060000
H	-0.6119150000	0.0857860000	-1.7389710000
H	1.6724680000	-1.6420810000	-0.5746420000
Cl	1.3269540000	-1.6408240000	-2.9444640000

A3 = A3.1-D'•



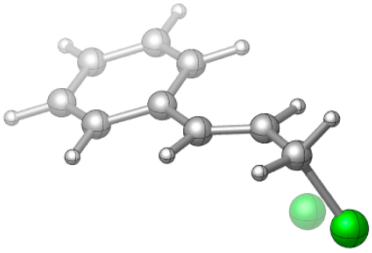


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155504 (Hartree/Particle)
Thermal correction to Energy= 0.166832
Thermal correction to Enthalpy= 0.167776
Thermal correction to Gibbs Free Energy= 0.114726
Sum of electronic and zero-point Energies= -1268.521766
Sum of electronic and thermal Energies= -1268.510439
Sum of electronic and thermal Enthalpies= -1268.509495
Sum of electronic and thermal Free Energies= -1268.562544

C	-0.7388060000	-2.4153900000	-0.5900360000
C	-0.0461660000	-1.4288120000	-1.4687810000
C	0.3059540000	-0.1805170000	-1.1240100000
H	-1.5245190000	-2.9391440000	-1.1331450000
H	-1.1482460000	-1.9772940000	0.3180100000
H	0.1380990000	-1.7535620000	-2.4904790000
Cl	0.4088810000	-3.7308060000	-0.0482820000
C	0.1736400000	0.4517760000	0.2061130000
C	0.4727390000	-0.2359320000	1.3924990000
C	-0.2310160000	1.7932730000	0.2879210000
C	0.3299420000	0.3915320000	2.6304580000
H	0.8463840000	-1.2561040000	1.3464470000
C	-0.3792700000	2.4182680000	1.5250900000
H	-0.4408720000	2.3430500000	-0.6264930000

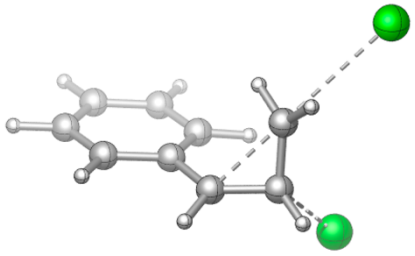
C -0.1044590000 1.7165570000 2.7017520000
H 0.5684520000 -0.1528870000 3.5395160000
H -0.7040930000 3.4536920000 1.5710380000
H -0.2155130000 2.2033890000 3.6662310000
H 0.7160310000 0.4573040000 -1.9058520000
Cl 4.3313170000 -1.2765680000 -0.9786170000

A3 = A3.1-D''•



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155298 (Hartree/Particle)
Thermal correction to Energy= 0.166750
Thermal correction to Enthalpy= 0.167694
Thermal correction to Gibbs Free Energy= 0.114327
Sum of electronic and zero-point Energies= -1268.525545
Sum of electronic and thermal Energies= -1268.514093
Sum of electronic and thermal Enthalpies= -1268.513149
Sum of electronic and thermal Free Energies= -1268.566515
C -0.8804190000 -2.9194190000 -1.4349310000
C -0.2636670000 -1.9614940000 -0.4764720000
C -0.7453570000 -0.7210800000 -0.3126690000
H -1.7845640000 -2.5221620000 -1.8933100000
H -1.0828430000 -3.8879080000 -0.9786230000
Cl 0.2709810000 -3.2812160000 -2.8092450000
C -0.2376480000 0.3004080000 0.6223380000
C 0.6672630000 0.0073650000 1.6563630000
C -0.6776080000 1.6239600000 0.4709840000
C 1.1261780000 1.0146710000 2.5013810000
H 1.0088210000 -1.0126190000 1.8093170000
C -0.2152900000 2.6341700000 1.3148260000
H -1.3833590000 1.8612450000 -0.3216180000
C 0.6897540000 2.3326440000 2.3332050000
H 1.8236770000 0.7719390000 3.2978660000
H -0.5632620000 3.6538940000 1.1779440000
H 1.0497150000 3.1146510000 2.9952910000
H -1.5874140000 -0.4096650000 -0.9315220000
H 0.5948920000 -2.3216660000 0.0871250000
Cl 3.7343100000 -0.6352630000 -1.0535320000

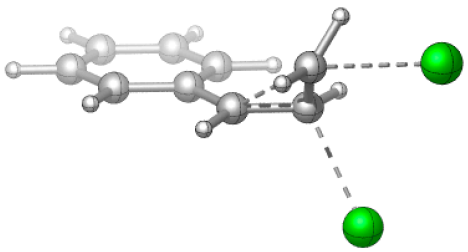
A3 = A3.1-TS-D'•-$P_{D'}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.152642 (Hartree/Particle)
Thermal correction to Energy= 0.163989
Thermal correction to Enthalpy= 0.164933
Thermal correction to Gibbs Free Energy= 0.112847
Sum of electronic and zero-point Energies= -1268.454534
Sum of electronic and thermal Energies= -1268.443188
Sum of electronic and thermal Enthalpies= -1268.442243
Sum of electronic and thermal Free Energies= -1268.494330
C -0.4568000000 -1.9861330000 -0.8867760000
C 0.6728080000 -1.3887380000 -1.4436900000

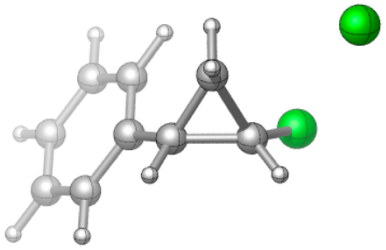
C 0.2950150000 -0.0756810000 -1.1184310000
H -1.0393680000 -2.6760050000 -1.4912590000
H -0.8237820000 -1.7716520000 0.1065540000
H 0.9243510000 -1.6222510000 -2.4697000000
Cl -0.7013590000 -4.7577110000 0.5695660000
C 0.1771150000 0.5160100000 0.2077360000
C 0.7116040000 -0.1134390000 1.3477330000
C -0.4278180000 1.7787040000 0.3300040000
C 0.6184550000 0.5093140000 2.5884320000
H 1.2147050000 -1.0719060000 1.2472250000
C -0.5197220000 2.3942710000 1.5745330000
H -0.8255600000 2.2670250000 -0.5559510000
C 0.0009060000 1.7586440000 2.7048320000
H 1.0358820000 0.0268680000 3.4669840000
H -0.9916020000 3.3677480000 1.6653470000
H -0.0671520000 2.2402180000 3.6759060000
H 0.1434210000 0.5999830000 -1.9601570000
Cl 2.8873790000 -2.0234450000 -0.7095080000

A3 = A3.1-TS-D''•-$P_{D''}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.152781 (Hartree/Particle)
Thermal correction to Energy= 0.164273
Thermal correction to Enthalpy= 0.165217
Thermal correction to Gibbs Free Energy= 0.111881
Sum of electronic and zero-point Energies= -1268.458762
Sum of electronic and thermal Energies= -1268.447270
Sum of electronic and thermal Enthalpies= -1268.446326
Sum of electronic and thermal Free Energies= -1268.499662
C -0.6087870000 -2.2870060000 -1.1224740000
C 0.5977650000 -1.7014430000 -0.7479000000
C 0.0299880000 -0.4295010000 -0.6489870000
H -1.2004920000 -1.9271470000 -1.9552980000
H -0.9948480000 -3.1333050000 -0.5623540000
Cl -0.9522180000 -4.9188830000 -2.7608440000
C 0.1218530000 0.4553450000 0.5102430000
C 0.8858260000 0.1412590000 1.6484080000
C -0.5710630000 1.6771300000 0.4622760000
C 0.9542880000 1.0366240000 2.7103190000
H 1.4266770000 -0.7980880000 1.7078640000
C -0.5029370000 2.5688440000 1.5293020000
H -1.1609000000 1.9221610000 -0.4172760000
C 0.2595080000 2.2492760000 2.6547450000
H 1.5470560000 0.7895850000 3.5855860000
H -1.0424340000 3.5098110000 1.4843300000
H 0.3127630000 2.9423350000 3.4891170000
H -0.5004330000 -0.0295880000 -1.5088350000
H 1.1868760000 -2.1353590000 0.0486770000
Cl 2.5356710000 -1.8095960000 -2.2521800000

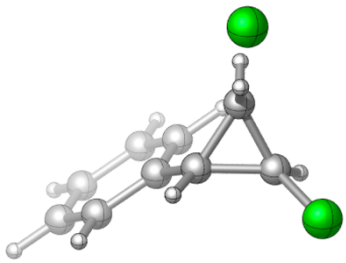
A3 = A3.1-$P_{D'}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155491 (Hartree/Particle)
Thermal correction to Energy= 0.166289
Thermal correction to Enthalpy= 0.167233
Thermal correction to Gibbs Free Energy= 0.116103
Sum of electronic and zero-point Energies= -1268.515105
Sum of electronic and thermal Energies= -1268.504307
Sum of electronic and thermal Enthalpies= -1268.503363
Sum of electronic and thermal Free Energies= -1268.554494

C	-0.2360230000	-1.8732110000	-1.2040250000
C	0.9482070000	-1.1085860000	-1.6899150000
C	-0.2053430000	-0.3659090000	-1.0529120000
H	-0.8949360000	-2.2941140000	-1.9564450000
H	-0.1112610000	-2.4728880000	-0.3049790000
H	1.1089850000	-0.9804840000	-2.7528600000
Cl	-0.0156820000	-4.1352580000	1.8760710000
C	-0.0838450000	0.3135660000	0.2705120000
C	0.1713220000	-0.3768250000	1.4632960000
C	-0.2198460000	1.7087800000	0.3168370000
C	0.2946460000	0.3173170000	2.6685750000
H	0.2623830000	-1.4618350000	1.4688410000
C	-0.1005230000	2.4013850000	1.5220140000
H	-0.4248780000	2.2547690000	-0.6012870000
C	0.1607650000	1.7067860000	2.7050060000
H	0.4910910000	-0.2335660000	3.5845220000
H	-0.2130130000	3.4818120000	1.5364390000
H	0.2532920000	2.2416400000	3.6458590000
H	-0.7843690000	0.1961590000	-1.7798880000
Cl	2.4975060000	-1.2577140000	-0.8362820000

A3 = A3.1-$P_{D''}$

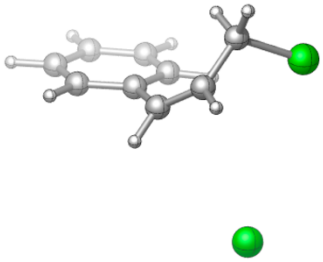


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154939 (Hartree/Particle)
Thermal correction to Energy= 0.165130
Thermal correction to Enthalpy= 0.166074
Thermal correction to Gibbs Free Energy= 0.115975
Sum of electronic and zero-point Energies= -1268.515750
Sum of electronic and thermal Energies= -1268.505559
Sum of electronic and thermal Enthalpies= -1268.504615
Sum of electronic and thermal Free Energies= -1268.554714

C	0.0061150000	-2.0852170000	-0.5877760000
C	1.2740940000	-1.4416220000	-1.0260190000
C	0.0761900000	-0.5747540000	-0.7516580000
H	-0.5743450000	-2.6311990000	-1.3284750000
H	-0.0142350000	-2.4881360000	0.4207410000
Cl	-2.0700260000	-4.2458870000	-2.9028880000
C	0.0819830000	0.3468650000	0.4192730000
C	0.6183960000	-0.0299420000	1.6594230000

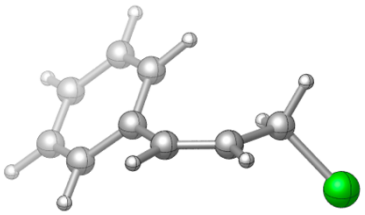
C -0.4547440000 1.6343220000 0.2845230000
C 0.6188280000 0.8599910000 2.7332970000
H 1.0401770000 -1.0233470000 1.7958190000
C -0.4564400000 2.5245990000 1.3594140000
H -0.8745770000 1.9396690000 -0.6709500000
C 0.0808370000 2.1413750000 2.5892840000
H 1.0377960000 0.5500830000 3.6864530000
H -0.8784820000 3.5177600000 1.2346760000
H 0.0801940000 2.8320840000 3.4273500000
H -0.4225660000 -0.1883740000 -1.6354130000
H 2.1162920000 -1.3917320000 -0.3451310000
Cl 1.8186710000 -1.6440820000 -2.7072230000

A3 = A3.1A-Manual IRC



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155504 (Hartree/Particle)
Thermal correction to Energy= 0.166832
Thermal correction to Enthalpy= 0.167776
Thermal correction to Gibbs Free Energy= 0.114726
Sum of electronic and zero-point Energies= -1268.521766
Sum of electronic and thermal Energies= -1268.510439
Sum of electronic and thermal Enthalpies= -1268.509495
Sum of electronic and thermal Free Energies= -1268.562544
C -0.7388060000 -2.4153900000 -0.5900360000
C -0.0461660000 -1.4288120000 -1.4687810000
C 0.3059540000 -0.1805170000 -1.1240100000
H -1.5245190000 -2.9391440000 -1.1331450000
H -1.1482460000 -1.9772940000 0.3180100000
H 0.1380990000 -1.7535620000 -2.4904790000
Cl 0.4088810000 -3.7308060000 -0.0482820000
C 0.1736400000 0.4517760000 0.2061130000
C 0.4727390000 -0.2359320000 1.3924990000
C -0.2310160000 1.7932730000 0.2879210000
C 0.3299420000 0.3915320000 2.6304580000
H 0.8463840000 -1.2561040000 1.3464470000
C -0.3792700000 2.4182680000 1.5250900000
H -0.4408720000 2.3430500000 -0.6264930000
C -0.1044590000 1.7165570000 2.7017520000
H 0.5684520000 -0.1528870000 3.5395160000
H -0.7040930000 3.4536920000 1.5710380000
H -0.2155130000 2.2033890000 3.6662310000
H 0.7160310000 0.4573040000 -1.9058520000
Cl 4.3313170000 -1.2765680000 -0.9786170000

A3 = A3.1A-Cl[a] Above Plane

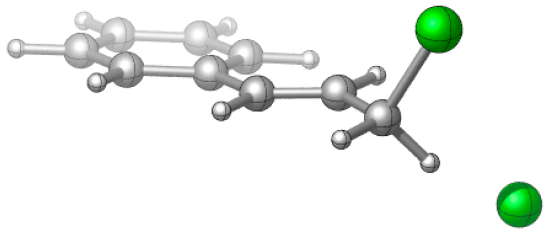


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154939 (Hartree/Particle)
Thermal correction to Energy= 0.166444
Thermal correction to Enthalpy= 0.167388
Thermal correction to Gibbs Free Energy= 0.113445

Sum of electronic and zero-point Energies= -1268.523954
Sum of electronic and thermal Energies= -1268.512449
Sum of electronic and thermal Enthalpies= -1268.511505
Sum of electronic and thermal Free Energies= -1268.565448

C	1.2044390000	-2.3576520000	0.0971330000
C	0.4081280000	-1.5989140000	-0.9127600000
C	-0.0768720000	-0.3558750000	-0.7722770000
H	0.6716930000	-3.2329590000	0.4710530000
H	1.5418370000	-1.7466910000	0.9319510000
Cl	2.7241080000	-2.9903580000	-0.6977340000
C	0.0169550000	0.5099660000	0.4229440000
C	-0.1629280000	0.0093730000	1.7224690000
C	0.2585940000	1.8828660000	0.2534230000
C	-0.0618360000	0.8598140000	2.8252330000
H	-0.4227150000	-1.0393570000	1.8670920000
C	0.3642800000	2.7287110000	1.3560170000
H	0.3730820000	2.2841710000	-0.7508340000
C	0.2098590000	2.2176730000	2.6479060000
H	-0.2076920000	0.4606480000	3.8250870000
H	0.5619380000	3.7865120000	1.2078800000
H	0.2850580000	2.8770970000	3.5077150000
H	-0.5851990000	0.0812790000	-1.6306490000
H	0.2333750000	-2.1157670000	-1.8544140000
Cl	-1.6371590000	-3.4597790000	1.9414510000

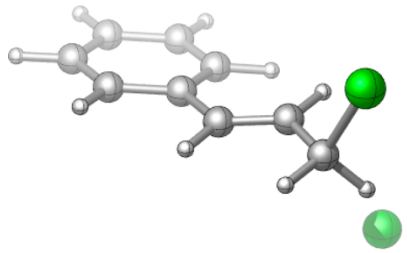
A3 = A3.1A-Cl[a] In Plane



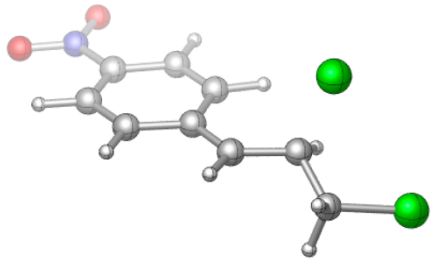
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154918 (Hartree/Particle)
Thermal correction to Energy= 0.166600
Thermal correction to Enthalpy= 0.167544
Thermal correction to Gibbs Free Energy= 0.112290
Sum of electronic and zero-point Energies= -1268.525823
Sum of electronic and thermal Energies= -1268.514142
Sum of electronic and thermal Enthalpies= -1268.513198
Sum of electronic and thermal Free Energies= -1268.568451

C	-0.4071210000	-3.1518030000	-0.2884630000
C	0.1678230000	-1.9037500000	0.2816960000
C	-0.5885320000	-0.8388710000	0.5835970000
H	0.1341720000	-3.4587630000	-1.1844080000
H	-1.4779920000	-3.0749460000	-0.4720540000
Cl	-0.1903620000	-4.5392920000	0.8872820000
C	-0.1088920000	0.4538510000	1.1088150000
C	1.2548300000	0.7647980000	1.2470740000
C	-1.0562220000	1.4177250000	1.4847080000
C	1.6511450000	1.9991790000	1.7549870000
H	2.0128650000	0.0455790000	0.9497430000
C	-0.6594970000	2.6548540000	1.9940400000
H	-2.1145090000	1.1919020000	1.3770070000
C	0.6969440000	2.9496410000	2.1325540000

H 2.7091750000 2.2243400000 1.8535150000
H -1.4092510000 3.3865400000 2.2808770000
H 1.0119040000 3.9116280000 2.5259450000
H -1.6662640000 -0.9097950000 0.4334140000
H 1.2473480000 -1.8992520000 0.4167240000
Cl 2.6113820000 -3.1228050000 -2.2283670000
A3 = A3.1A-Cl[a] Below Plane



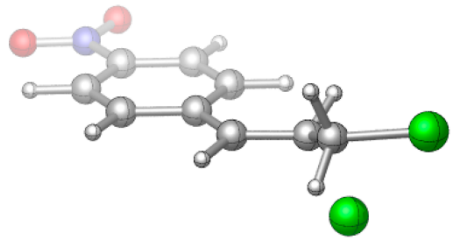
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155028 (Hartree/Particle)
Thermal correction to Energy= 0.166711
Thermal correction to Enthalpy= 0.167655
Thermal correction to Gibbs Free Energy= 0.112471
Sum of electronic and zero-point Energies= -1268.526249
Sum of electronic and thermal Energies= -1268.514567
Sum of electronic and thermal Enthalpies= -1268.513622
Sum of electronic and thermal Free Energies= -1268.568806
C -0.7971000000 -3.1401000000 -0.6156750000
C -0.1839700000 -2.0167790000 0.1440000000
C -0.7801500000 -0.8214610000 0.2528690000
H -0.1092680000 -3.5618630000 -1.3483730000
H -1.7334550000 -2.8581020000 -1.0942940000
Cl -1.1949830000 -4.5267670000 0.5093320000
C -0.2323900000 0.3644570000 0.9383430000
C 1.1060310000 0.4500410000 1.3577720000
C -1.0808400000 1.4566850000 1.1747010000
C 1.5710530000 1.5896280000 2.0092770000
H 1.7929060000 -0.3693250000 1.1642520000
C -0.6152990000 2.5978630000 1.8283020000
H -2.1158070000 1.4061200000 0.8448240000
C 0.7129040000 2.6675800000 2.2500510000
H 2.6093070000 1.6422740000 2.3240120000
H -1.2890430000 3.4311720000 2.0053800000
H 1.0808960000 3.5557320000 2.7553530000
H -1.7642640000 -0.6898310000 -0.1976730000
H 0.7861140000 -2.2128410000 0.5967520000
Cl 3.2188840000 -1.5626740000 -2.1516140000
A3 = A3.1B-NO_2-R



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.156783 (Hartree/Particle)
Thermal correction to Energy= 0.170185
Thermal correction to Enthalpy= 0.171129
Thermal correction to Gibbs Free Energy= 0.114253
Sum of electronic and zero-point Energies= -1472.951555
Sum of electronic and thermal Energies= -1472.938153
Sum of electronic and thermal Enthalpies= -1472.937209
Sum of electronic and thermal Free Energies= -1472.994085
C -0.4071210000 -3.1518030000 -0.2884630000
C 0.1678230000 -1.9037500000 0.2816960000

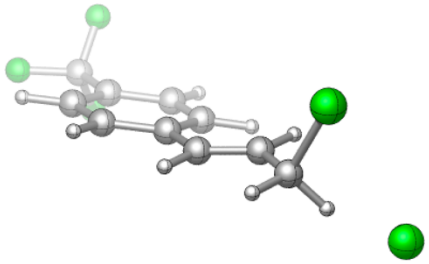
C -0.5885320000 -0.8388710000 0.5835970000
H 0.1341720000 -3.4587630000 -1.1844080000
H -1.4779920000 -3.0749460000 -0.4720540000
Cl -0.1903620000 -4.5392920000 0.8872820000
C -0.1088920000 0.4538510000 1.1088150000
C 1.2548300000 0.7647980000 1.2470740000
C -1.0562220000 1.4177250000 1.4847080000
C 1.6511450000 1.9991790000 1.7549870000
H 2.0128650000 0.0455790000 0.9497430000
C -0.6594970000 2.6548540000 1.9940400000
H -2.1145090000 1.1919020000 1.3770070000
C 0.6969440000 2.9496410000 2.1325540000
H 2.7091750000 2.2243400000 1.8535150000
H -1.4092510000 3.3865400000 2.2808770000
H 1.0119040000 3.9116280000 2.5259450000
H -1.6662640000 -0.9097950000 0.4334140000
H 1.2473480000 -1.8992520000 0.4167240000
Cl 2.6113820000 -3.1228050000 -2.2283670000

A3 = A3.1B-NO_2-S



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.156861 (Hartree/Particle)
Thermal correction to Energy= 0.170281
Thermal correction to Enthalpy= 0.171225
Thermal correction to Gibbs Free Energy= 0.114344
Sum of electronic and zero-point Energies= -1472.951501
Sum of electronic and thermal Energies= -1472.938081
Sum of electronic and thermal Enthalpies= -1472.937136
Sum of electronic and thermal Free Energies= -1472.994018
C -0.4071210000 -3.1518030000 -0.2884630000
C 0.1678230000 -1.9037500000 0.2816960000
C -0.5885320000 -0.8388710000 0.5835970000
H 0.1341720000 -3.4587630000 -1.1844080000
H -1.4779920000 -3.0749460000 -0.4720540000
Cl -0.1903620000 -4.5392920000 0.8872820000
C -0.1088920000 0.4538510000 1.1088150000
C 1.2548300000 0.7647980000 1.2470740000
C -1.0562220000 1.4177250000 1.4847080000
C 1.6511450000 1.9991790000 1.7549870000
H 2.0128650000 0.0455790000 0.9497430000
C -0.6594970000 2.6548540000 1.9940400000
H -2.1145090000 1.1919020000 1.3770070000
C 0.6969440000 2.9496410000 2.1325540000
H 2.7091750000 2.2243400000 1.8535150000
H -1.4092510000 3.3865400000 2.2808770000
H 1.0119040000 3.9116280000 2.5259450000
H -1.6662640000 -0.9097950000 0.4334140000
H 1.2473480000 -1.8992520000 0.4167240000
Cl 2.6113820000 -3.1228050000 -2.2283670000

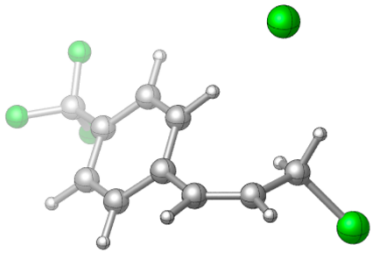
A3 = A3.1B-CF_3-R



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.159983 (Hartree/Particle)
Thermal correction to Energy= 0.175161
Thermal correction to Enthalpy= 0.176105
Thermal correction to Gibbs Free Energy= 0.112054
Sum of electronic and zero-point Energies= -1605.535465
Sum of electronic and thermal Energies= -1605.520287
Sum of electronic and thermal Enthalpies= -1605.519343
Sum of electronic and thermal Free Energies= -1605.583394

C	0.2901390000	-1.9397830000	-2.6302610000
C	0.4534390000	-1.2974810000	-1.2979230000
C	0.0095440000	-0.0597450000	-1.0394040000
H	-0.2666950000	-1.3185680000	-3.3301900000
H	-0.1532290000	-2.9317210000	-2.5317670000
H	0.9437280000	-1.9010100000	-0.5367880000
Cl	1.9302550000	-2.2248340000	-3.3882910000
C	0.1006630000	0.6339280000	0.2586410000
C	0.4582510000	-0.0256510000	1.4483880000
C	-0.1825160000	2.0052920000	0.3086120000
C	0.5484320000	0.6738400000	2.6434950000
H	0.6578080000	-1.0928650000	1.4475400000
C	-0.0943400000	2.7157480000	1.5045250000
H	-0.4695520000	2.5247260000	-0.6018100000
C	0.2733070000	2.0453710000	2.6673050000
H	0.8250890000	0.1546100000	3.5576620000
H	-0.3136870000	3.7786080000	1.5229960000
Cl	-0.4465990000	-4.8606710000	-0.6878550000
H	-0.4560270000	0.5088700000	-1.8442240000
C	0.3918940000	2.7741110000	3.9708920000
F	-0.3661670000	2.2153920000	4.9399770000
F	1.6586320000	2.7677490000	4.4445840000
F	0.0208490000	4.0630550000	3.8839940000

A3 = A3.1B-CF_3-S

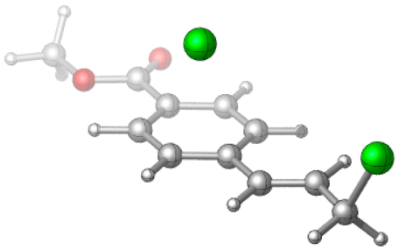


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.160108 (Hartree/Particle)
Thermal correction to Energy= 0.175071
Thermal correction to Enthalpy= 0.176015
Thermal correction to Gibbs Free Energy= 0.113583
Sum of electronic and zero-point Energies= -1605.532591
Sum of electronic and thermal Energies= -1605.517628
Sum of electronic and thermal Enthalpies= -1605.516684
Sum of electronic and thermal Free Energies= -1605.579116

C	1.4705180000	-1.6460330000	-2.1084940000
C	0.1289040000	-1.3863760000	-1.5057930000
C	-0.2617450000	-0.2685720000	-0.8761610000
H	2.0139660000	-2.4300630000	-1.5797960000
H	2.0933240000	-0.7569170000	-2.1867290000

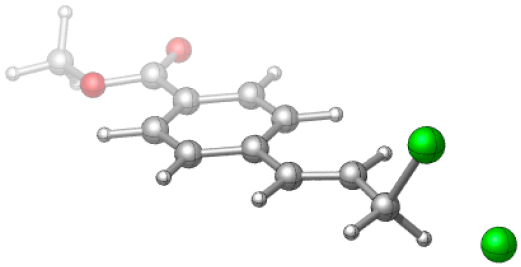
Cl 1.2445050000 -2.2452310000 -3.8177840000
C 0.5611440000 0.9259210000 -0.5916430000
C 1.8873360000 0.8241720000 -0.1465130000
C -0.0153810000 2.1987840000 -0.7341820000
C 2.6345290000 1.9722440000 0.1142510000
H 2.3276450000 -0.1562530000 0.0366250000
C 0.7253560000 3.3465140000 -0.4801030000
H -1.0502440000 2.2860770000 -1.0540640000
C 2.0518280000 3.2260590000 -0.0580460000
H 3.6585020000 1.8831240000 0.4646450000
H 0.2729470000 4.3266420000 -0.6031180000
H -1.2984130000 -0.2137190000 -0.5477730000
H -0.5966720000 -2.1894630000 -1.6179000000
Cl 3.1845770000 -2.4950930000 0.8888850000
C 2.8491700000 4.4718720000 0.1818680000
F 3.9305680000 4.2579440000 0.9529030000
F 2.1234080000 5.4355950000 0.7855100000
F 3.3044850000 5.0179330000 -0.9701020000

A3 = A3.1B-CO_2Me-R



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.199124 (Hartree/Particle)
Thermal correction to Energy= 0.215082
Thermal correction to Enthalpy= 0.216026
Thermal correction to Gibbs Free Energy= 0.151419
Sum of electronic and zero-point Energies= -1496.311938
Sum of electronic and thermal Energies= -1496.295981
Sum of electronic and thermal Enthalpies= -1496.295037
Sum of electronic and thermal Free Energies= -1496.359643
C 0.2901390000 -1.9397830000 -2.6302610000
C 0.4534390000 -1.2974810000 -1.2979230000
C 0.0095440000 -0.0597450000 -1.0394040000
H -0.2666950000 -1.3185680000 -3.3301900000
H -0.1532290000 -2.9317210000 -2.5317670000
H 0.9437280000 -1.9010100000 -0.5367880000
Cl 1.9302550000 -2.2248340000 -3.3882910000
C 0.1006630000 0.6339280000 0.2586410000
C 0.4582510000 -0.0256510000 1.4483880000
C -0.1825160000 2.0052920000 0.3086120000
C 0.5484320000 0.6738400000 2.6434950000
H 0.6578080000 -1.0928650000 1.4475400000
C -0.0943400000 2.7157480000 1.5045250000
H -0.4695520000 2.5247260000 -0.6018100000
C 0.2733070000 2.0453710000 2.6673050000
H 0.8250890000 0.1546100000 3.5576620000
H -0.3136870000 3.7786080000 1.5229960000
Cl -0.4465990000 -4.8606710000 -0.6878550000
H -0.4560270000 0.5088700000 -1.8442240000
C 0.3918940000 2.7741110000 3.9708920000
F -0.3661670000 2.2153920000 4.9399770000
F 1.6586320000 2.7677490000 4.4445840000
F 0.0208490000 4.0630550000 3.8839940000

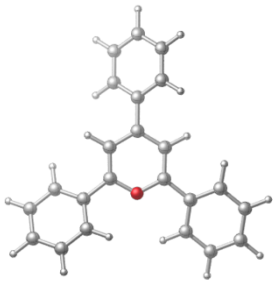
A3 = A3.1B-CO_2Me-S



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.199249 (Hartree/Particle)
Thermal correction to Energy= 0.215133
Thermal correction to Enthalpy= 0.216077
Thermal correction to Gibbs Free Energy= 0.151791
Sum of electronic and zero-point Energies= -1496.313225
Sum of electronic and thermal Energies= -1496.297341
Sum of electronic and thermal Enthalpies= -1496.296397
Sum of electronic and thermal Free Energies= -1496.360683

C	-0.5174350000	-2.1052330000	-2.3976700000
C	-0.0853070000	-1.4798160000	-1.1184980000
C	-0.6193280000	-0.3374130000	-0.6636940000
H	0.3424740000	-2.3307400000	-3.0291820000
H	-1.2608690000	-1.5112390000	-2.9270170000
Cl	-1.2990350000	-3.7257940000	-2.0673320000
C	-0.2241920000	0.3767830000	0.5639990000
C	0.7917740000	-0.0799450000	1.4225260000
C	-0.8915730000	1.5676750000	0.8876240000
C	1.1221180000	0.6347770000	2.5653860000
H	1.3298150000	-0.9963410000	1.1989340000
C	-0.5611510000	2.2896480000	2.0312570000
H	-1.6787040000	1.9300180000	0.2315130000
C	0.4501940000	1.8240360000	2.8758480000
H	1.9066990000	0.2789700000	3.2264300000
H	-1.0871660000	3.2096450000	2.2647720000
H	-1.4143270000	0.1344280000	-1.2413320000
C	0.8473000000	2.5553050000	4.1106190000
O	1.7035690000	2.1681480000	4.8842790000
O	0.1636070000	3.6921180000	4.2867530000
C	0.5025100000	4.4424090000	5.4667030000
H	-0.1255330000	5.3303620000	5.4405080000
H	0.2908170000	3.8530460000	6.3600550000
H	1.5566460000	4.7222470000	5.4464090000
H	0.7139850000	-1.9937660000	-0.5889960000
Cl	2.9690840000	-2.8452460000	-2.6143510000

UM06-2X/DGDZVP-SMD(acetonitrile)
Thesis = 5
A3 = A3.2-PC_A



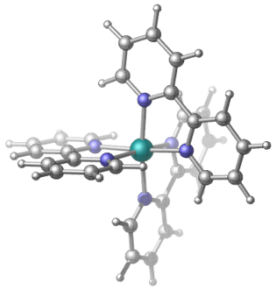
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.334914 (Hartree/Particle)
Thermal correction to Energy= 0.353140
Thermal correction to Enthalpy= 0.354084
Thermal correction to Gibbs Free Energy= 0.286893
Sum of electronic and zero-point Energies= -961.080095
Sum of electronic and thermal Energies= -961.061868
Sum of electronic and thermal Enthalpies= -961.060924
Sum of electronic and thermal Free Energies= -961.128115

C	1.4116490000	-0.9112590000	-0.2907460000

C 1.8195490000 0.3948680000 -0.4279210000
C 0.8727360000 1.3947420000 -0.7073460000
C -0.4741170000 1.0179350000 -0.8521080000
C -0.8257060000 -0.3043560000 -0.7230320000
H 2.8730110000 0.6309940000 -0.3486500000
H -1.2483790000 1.7574650000 -1.0143020000
O 0.1162600000 -1.2172390000 -0.4466990000
C -2.1724370000 -0.8725500000 -0.8256910000
C -2.4475230000 -2.1193170000 -0.2422600000
C -3.1849900000 -0.1772770000 -1.5045080000
C -3.7266570000 -2.6589060000 -0.3319590000
H -1.6715730000 -2.6569800000 0.2933660000
C -4.4598320000 -0.7276520000 -1.5935810000
H -2.9800480000 0.7748970000 -1.9840340000
C -4.7334810000 -1.9654320000 -1.0071890000
H -3.9380470000 -3.6189220000 0.1281480000
H -5.2393520000 -0.1932450000 -2.1269720000
H -5.7301720000 -2.3899930000 -1.0790910000
C 2.2534630000 -2.0743170000 0.0024490000
C 1.7286200000 -3.3700530000 -0.1317880000
C 3.5815180000 -1.8998750000 0.4223890000
C 2.5254860000 -4.4744400000 0.1512020000
H 0.7064110000 -3.5176710000 -0.4648400000
C 4.3705380000 -3.0102440000 0.7037010000
H 4.0022320000 -0.9078010000 0.5486310000
C 3.8459730000 -4.2977980000 0.5694500000
H 2.1158610000 -5.4735610000 0.0429410000
H 5.3947440000 -2.8700140000 1.0341930000
H 4.4645010000 -5.1616390000 0.7931560000
C 1.2788580000 2.8038680000 -0.8375270000
C 2.3818330000 3.2933250000 -0.1191650000
C 0.5641190000 3.6709390000 -1.6796130000
C 2.7547810000 4.6290090000 -0.2356050000
H 2.9302760000 2.6450920000 0.5578330000
C 0.9526790000 5.0012760000 -1.8060520000
H -0.2749870000 3.3021970000 -2.2623240000
C 2.0446120000 5.4838630000 -1.0813030000
H 3.5978930000 5.0032990000 0.3366190000
H 0.4040980000 5.6607090000 -2.4713040000
H 2.3413390000 6.5242160000 -1.1747060000

Thesis = 6

A3 = A3.2-PC_B



UM06-2X/DGDZVP-SMD(acetonitrile)

Zero-point correction= 0.488072 (Hartree/Particle)

Thermal correction to Energy= 0.516956

Thermal correction to Enthalpy= 0.517900

Thermal correction to Gibbs Free Energy= 0.428184

Sum of electronic and zero-point Energies= -1578.828098

Sum of electronic and thermal Energies= -1578.799214

Sum of electronic and thermal Enthalpies= -1578.798270

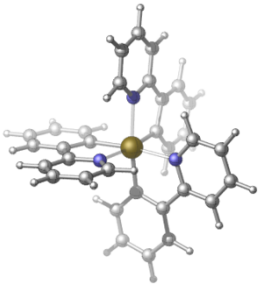
Sum of electronic and thermal Free Energies= -1578.887985

Ru	-0.0849880000	0.3464130000	-0.4234980000
C	1.3883150000	2.8878780000	-0.8771080000
C	-0.8847270000	3.2161560000	-1.2465730000
C	-0.6872000000	4.5508110000	-1.5810810000
C	0.6097660000	5.0550120000	-1.5645350000
C	1.6603530000	4.2147530000	-1.2083440000
H	-1.8768830000	2.7744820000	-1.2516970000
H	-1.5365500000	5.1687380000	-1.8498390000
H	0.8060280000	6.0900130000	-1.8254050000
H	2.6754630000	4.5928940000	-1.1932770000
C	2.4393190000	1.9149640000	-0.4822230000
C	3.7827270000	2.2590640000	-0.3395850000
C	4.6987910000	1.2798380000	0.0319640000
H	4.1169570000	3.2757420000	-0.5087230000
C	2.8973600000	-0.2906920000	0.0988090000
C	4.2527020000	-0.0198530000	0.2501630000
H	5.7477780000	1.5327460000	0.1485670000
H	2.4974180000	-1.2864920000	0.2664750000
H	4.9310030000	-0.8152350000	0.5378530000
N	0.1253100000	2.4030060000	-0.9082160000
N	2.0112250000	0.6516410000	-0.2518650000
C	-1.9120480000	0.9923260000	1.8306250000
C	0.2953330000	1.2969740000	2.4966480000
C	-0.0936530000	1.7074230000	3.7666890000
C	-1.4525350000	1.7594980000	4.0611290000
C	-2.3730080000	1.3981510000	3.0823870000
H	1.3442220000	1.2430410000	2.2198950000
H	0.6592920000	1.9793930000	4.4979670000
H	-1.7961500000	2.0786410000	5.0398040000
H	-3.4343510000	1.4370190000	3.2962310000
C	-2.8158980000	0.5862290000	0.7236080000
C	-4.2032520000	0.5347920000	0.8511740000
C	-4.9721210000	0.1503490000	-0.2429610000
H	-4.6846230000	0.7860610000	1.7887740000
C	-2.9504590000	-0.1072460000	-1.4930400000
C	-4.3379150000	-0.1747250000	-1.4380830000
H	-6.0531910000	0.1059710000	-0.1590210000
H	-2.4084600000	-0.3524600000	-2.4018930000
H	-4.8973540000	-0.4768920000	-2.3163300000
N	-0.5885150000	0.9483600000	1.5513430000
N	-2.2068760000	0.2634570000	-0.4410640000
C	0.2746030000	-1.7773740000	-2.4748510000
C	0.4207940000	0.3177350000	-3.4743930000
C	0.6429370000	-0.2419820000	-4.7272740000
C	0.6811060000	-1.6284820000	-4.8383480000
C	0.4960510000	-2.4062100000	-3.6994690000
H	0.3805980000	1.3942390000	-3.3364670000
H	0.7819540000	0.4032310000	-5.5874950000
H	0.8526430000	-2.1034780000	-5.7989730000
H	0.5262930000	-3.4868630000	-3.7709440000
C	0.0605960000	-2.5192570000	-1.2054460000
C	0.0335830000	-3.9108950000	-1.1292850000
C	-0.1674350000	-4.5198930000	0.1055240000
H	0.1654000000	-4.5166630000	-2.0177910000

C -0.3028560000 -2.3435630000 1.0856820000
C -0.3373650000 -3.7251650000 1.2350260000
H -0.1904350000 -5.6022590000 0.1807020000
H -0.4308770000 -1.6798700000 1.9358420000
H -0.4948810000 -4.1570110000 2.2169870000
N 0.2400920000 -0.4280730000 -2.3754690000
N -0.1082790000 -1.7538800000 -0.1022210000

Thesis = 7

A3 = A3.1B, A3.4A, A3.4B-, A3.4C-PC$_C$

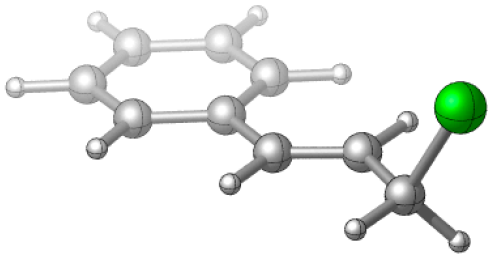


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.484697 (Hartree/Particle)
Thermal correction to Energy= 0.513476
Thermal correction to Enthalpy= 0.514420
Thermal correction to Gibbs Free Energy= 0.424242
Sum of electronic and zero-point Energies= -1539.940468
Sum of electronic and thermal Energies= -1539.911689
Sum of electronic and thermal Enthalpies= -1539.910745
Sum of electronic and thermal Free Energies= -1540.000923

Ir -0.0135970000 -0.0264010000 0.0077010000
C -2.0742640000 1.9848460000 0.8737110000
C 0.0267620000 3.0007380000 0.9752730000
C -0.5102320000 4.2000900000 1.4241550000
C -1.8924990000 4.2767860000 1.5999550000
C -2.6788890000 3.1650740000 1.3247440000
H 1.0966200000 2.8807960000 0.8231790000
H 0.1396810000 5.0428300000 1.6317920000
H -2.3525930000 5.1953110000 1.9516680000
H -3.7532090000 3.2136080000 1.4613630000
C -2.7879010000 0.7312450000 0.5513360000
C -4.1810860000 0.6189980000 0.6790430000
C -1.9865720000 -0.3637100000 0.1229130000
C -4.8199190000 -0.5815550000 0.3822550000
C -2.6699410000 -1.5595740000 -0.1718100000
C -4.0553760000 -1.6731290000 -0.0443520000
H -5.8980040000 -0.6672080000 0.4824470000
H -2.1034420000 -2.4295060000 -0.4980230000
N -0.7316260000 1.9287030000 0.7057700000
C 2.6725580000 0.1981750000 1.3414270000
C 2.8735620000 0.9991900000 -0.8435730000
C 4.2223600000 1.2843320000 -0.6776060000
C 4.8062900000 1.0037100000 0.5584970000
C 4.0296260000 0.4575210000 1.5726360000
H 2.3658150000 1.1926720000 -1.7854250000
H 5.8582650000 1.2102610000 0.7308360000
C 1.7319340000 -0.3665380000 2.3322110000
C 2.1415810000 -0.7028060000 3.6317690000
C 0.3895130000 -0.5572630000 1.8992900000
C 1.2306370000 -1.2321990000 4.5416330000
C -0.5031770000 -1.0884400000 2.8508070000
C -0.0970660000 -1.4228280000 4.1439700000
H 1.5493370000 -1.4936740000 5.5464050000

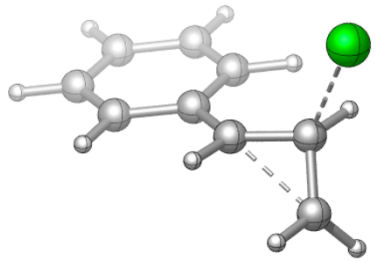
H -1.5419620000 -1.2555140000 2.5727720000
N 2.1230070000 0.4748160000 0.1352240000
C 0.4209110000 -1.8650640000 -2.2275780000
C 0.8060410000 -2.9864020000 -0.1349850000
C 1.0955600000 -4.1680510000 -0.8196680000
C 1.0460600000 -4.2080900000 -2.2174070000
C 0.7102580000 -3.0524770000 -2.9173380000
H 0.8460240000 -2.9916180000 0.9525000000
H 1.2675060000 -5.1267630000 -2.7527140000
C 0.0584070000 -0.6200270000 -2.9371090000
C -0.0120650000 -0.4743290000 -4.3282810000
C -0.3608670000 0.7550920000 -4.8727550000
H 0.2061350000 -1.3134210000 -4.9789030000
C -0.5494760000 1.6175900000 -2.6542840000
C -0.6378650000 1.8277250000 -4.0240150000
H -0.4165550000 0.8770310000 -5.9502620000
H -0.7515830000 2.4155270000 -1.9441440000
H -0.9163180000 2.8032160000 -4.4069860000
H 4.7917720000 1.7119130000 -1.4953760000
H 4.4739440000 0.2373630000 2.5366180000
C 0.4520260000 -1.7998780000 -0.8062060000
N -0.2096510000 0.4324620000 -2.1281650000
H -4.7772050000 1.4648960000 1.0106660000
H -4.5445630000 -2.6161540000 -0.2766720000
H -0.8171510000 -1.8346740000 4.8469820000
H 3.1714500000 -0.5547460000 3.9454500000
H 0.6747650000 -3.0861670000 -4.0029690000
H 1.3588860000 -5.0642030000 -0.2628780000

Thesis = 1a, 1a''
A3 = A3.2, A3.3-A1''

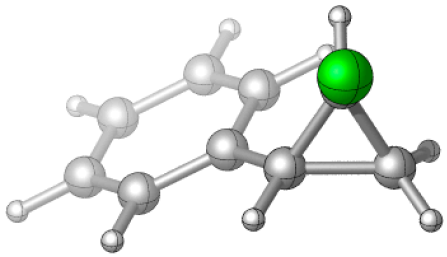


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155026 (Hartree/Particle)
Thermal correction to Energy= 0.164179
Thermal correction to Enthalpy= 0.165123
Thermal correction to Gibbs Free Energy= 0.117942
Sum of electronic and zero-point Energies= -808.217702
Sum of electronic and thermal Energies= -808.208549
Sum of electronic and thermal Enthalpies= -808.207605
Sum of electronic and thermal Free Energies= -808.254786
C -4.4313250000 6.3527170000 -0.4373980000
C -3.3136850000 6.6425640000 0.3454700000
C -2.2902190000 5.7029380000 0.4759750000
C -2.3636440000 4.4616390000 -0.1733910000
C -3.4968620000 4.1790140000 -0.9552160000
C -4.5178710000 5.1163960000 -1.0862440000
H -5.2296440000 7.0813950000 -0.5423440000
H -3.2368270000 7.5987030000 0.8548250000
H -1.4201120000 5.9330990000 1.0861470000
H -3.5874190000 3.2234780000 -1.4635310000
H -5.3868530000 4.8822990000 -1.6942440000
C -1.2476760000 3.5115710000 -0.0038870000

H -0.4530810000 3.8428000000 0.6653280000
C 0.0367150000 1.4200290000 -0.3184680000
H -0.2676310000 0.4125390000 -0.0372440000
H 0.7133020000 1.8315160000 0.4285920000
C -1.1270510000 2.3093670000 -0.5845930000
H -1.8780810000 1.9266750000 -1.2728530000
Cl 1.0291840000 1.2016000000 -1.8400010000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.5 497291
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.5327321
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=--807.431064421990
Thesis = TS-1a$^{1'}$-2a$^{1'}$
A3 = A3.3-TS-A$^{1'}$-E$^{1'}$



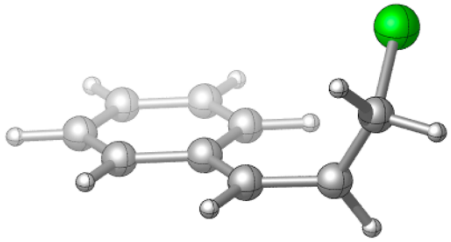
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.152402 (Hartree/Particle)
Thermal correction to Energy= 0.161606
Thermal correction to Enthalpy= 0.162550
Thermal correction to Gibbs Free Energy= 0.116195
Sum of electronic and zero-point Energies= -808.148622
Sum of electronic and thermal Energies= -808.139418
Sum of electronic and thermal Enthalpies= -808.138474
Sum of electronic and thermal Free Energies= -808.184828
C -1.7301370000 6.1578790000 -3.8316510000
C -1.5576580000 6.7224700000 -2.5658760000
C -1.2582780000 5.9053020000 -1.4802330000
C -1.1260060000 4.5154390000 -1.6524350000
C -1.3054710000 3.9551180000 -2.9313110000
C -1.6027870000 4.7761770000 -4.0120800000
H -1.9659410000 6.7928950000 -4.6803870000
H -1.6566240000 7.7944670000 -2.4271720000
H -1.1209180000 6.3347590000 -0.4913250000
H -1.2128330000 2.8845010000 -3.0843170000
H -1.7368900000 4.3428500000 -4.9981360000
C -0.7730670000 3.7185990000 -0.4889090000
H -0.5762720000 4.2700810000 0.4267760000
C -1.5003110000 2.1554080000 0.6135170000
H -2.3050630000 1.4246870000 0.5553210000
H -1.3890410000 2.7111580000 1.5380840000
C -0.6423380000 2.3227990000 -0.4618890000
H -0.7547620000 1.7154350000 -1.3495860000
Cl 1.6712940000 1.5831100000 -0.2090700000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4745618
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.433762
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.32970327507
Thesis = 2a, 2a$^{1'}$
A3 = A3.3$^{'}$,A3.4A, A3.3D, A3.4A-E^{1}



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155007 (Hartree/Particle)
Thermal correction to Energy= 0.163512
Thermal correction to Enthalpy= 0.164456
Thermal correction to Gibbs Free Energy= 0.120329
Sum of electronic and zero-point Energies= -808.207319
Sum of electronic and thermal Energies= -808.198815
Sum of electronic and thermal Enthalpies= -808.197871
Sum of electronic and thermal Free Energies= -808.241998

C	-4.3577580000	5.9927070000	-0.2748390000
C	-3.8389010000	5.2922180000	0.8167240000
C	-2.7755120000	4.4059840000	0.6456710000
C	-2.2144030000	4.2010700000	-0.6236570000
C	-2.7416260000	4.9079430000	-1.7121860000
C	-3.8032420000	5.7976650000	-1.5408130000
H	-5.1829640000	6.6853780000	-0.1386260000
H	-4.2625820000	5.4372760000	1.8064170000
H	-2.3847090000	3.8760750000	1.5116560000
H	-2.3137900000	4.7607150000	-2.7008330000
H	-4.1963500000	6.3379310000	-2.3973850000
C	-1.0856640000	3.2539400000	-0.8475310000
H	-0.7163560000	3.2174730000	-1.8678460000
C	-0.0346110000	2.9885140000	0.2186820000
H	-0.1368400000	3.4859160000	1.1783370000
H	0.9808490000	2.8411010000	-0.1324690000
C	-1.0427500000	1.9440560000	-0.1102810000
H	-1.8323000000	1.7213370000	0.5982960000
Cl	-0.5292670000	0.4830440000	-0.9823930000

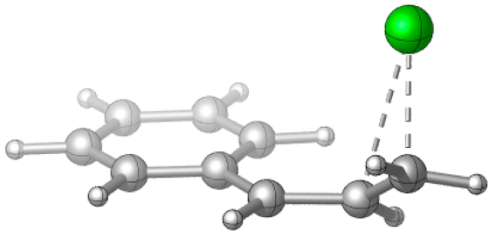
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.5397444
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.5238667
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.417315821298
Thesis = $1a^{3'}$
A3 = A3.3-$A^{3'}$



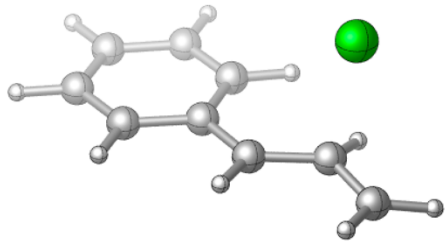
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150503 (Hartree/Particle)
Thermal correction to Energy= 0.160075
Thermal correction to Enthalpy= 0.161019
Thermal correction to Gibbs Free Energy= 0.112982
Sum of electronic and zero-point Energies= -808.133017
Sum of electronic and thermal Energies= -808.123445
Sum of electronic and thermal Enthalpies= -808.122501
Sum of electronic and thermal Free Energies= -808.170537

C	-4.1157320000	6.3148590000	-0.8295900000
C	-3.2622050000	6.6214490000	0.2398220000
C	-2.3780860000	5.6699280000	0.7274810000
C	-2.3148000000	4.3697260000	0.1545980000
C	-3.1921890000	4.0769060000	-0.9246150000
C	-4.0735170000	5.0374520000	-1.4032090000
H	-4.8072400000	7.0611170000	-1.2086070000
H	-3.2931830000	7.6092340000	0.6908980000
H	-1.7190200000	5.9114600000	1.5579090000

H -3.1725140000 3.0875250000 -1.3742240000
H -4.7360600000 4.7936240000 -2.2288670000
C -1.4071110000 3.4048320000 0.6745220000
H -0.8099770000 3.6881780000 1.5419150000
C -0.1598300000 1.6981210000 -0.7835040000
H 0.0838350000 0.6379360000 -0.7749190000
H 0.7315440000 2.3083460000 -0.6464190000
C -1.2438220000 2.0438780000 0.1508410000
H -1.9417880000 1.2596640000 0.4387750000
Cl -0.6570850000 2.0361050000 -2.5558830000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4574409
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4413297
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.340253363900
Thesis = TS-1$^{3'}$-13$^{3'}$
A3 = A3.3-TS-A$^{3'}$-B$^{3'}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149987 (Hartree/Particle)
Thermal correction to Energy= 0.159289
Thermal correction to Enthalpy= 0.160234
Thermal correction to Gibbs Free Energy= 0.112797
Sum of electronic and zero-point Energies= -808.123976
Sum of electronic and thermal Energies= -808.114673
Sum of electronic and thermal Enthalpies= -808.113729
Sum of electronic and thermal Free Energies= -808.161165
C -4.4503200000 5.9538920000 0.0501120000
C -3.2157480000 6.6220020000 0.0632980000
C -2.0448250000 5.9314120000 -0.1961880000
C -2.0653510000 4.5326520000 -0.4763800000
C -3.3306620000 3.8748370000 -0.4911230000
C -4.4951320000 4.5806880000 -0.2296420000
H -5.3671200000 6.4981300000 0.2546860000
H -3.1790130000 7.6859440000 0.2779700000
H -1.0890430000 6.4490400000 -0.1866580000
H -3.3860510000 2.8129700000 -0.7129170000
H -5.4502750000 4.0639500000 -0.2446080000
C -0.8520560000 3.8598160000 -0.7343490000
H 0.0723300000 4.4330630000 -0.7440200000
C 0.0776660000 1.9113880000 -2.0073940000
H 0.2126770000 0.8374070000 -2.0806920000
H 0.8438440000 2.5426940000 -2.4465110000
C -0.7572730000 2.4250260000 -1.0234930000
H -1.4013360000 1.7347160000 -0.4819510000
Cl -1.3994790000 2.1671610000 -3.7607820000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4473313
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4258499
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.324929822206
Thesis = 13$^{3'}$
A3 = A3.3-B$^{3'}$

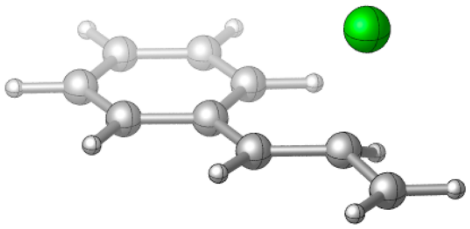


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150189 (Hartree/Particle)
Thermal correction to Energy= 0.160116
Thermal correction to Enthalpy= 0.161060
Thermal correction to Gibbs Free Energy= 0.112744
Sum of electronic and zero-point Energies= -808.135615
Sum of electronic and thermal Energies= -808.125688
Sum of electronic and thermal Enthalpies= -808.124744
Sum of electronic and thermal Free Energies= -808.173060

C	-4.4576990000	5.9613110000	-0.2512720000
C	-3.2708800000	6.5734990000	0.1667140000
C	-2.0752440000	5.8676180000	0.1377430000
C	-2.0329280000	4.5231830000	-0.3053130000
C	-3.2429850000	3.9209060000	-0.7292900000
C	-4.4339440000	4.6351070000	-0.7001390000
H	-5.3928690000	6.5125750000	-0.2305940000
H	-3.2821790000	7.6028020000	0.5124610000
H	-1.1528040000	6.3444210000	0.4596890000
H	-3.2517020000	2.8949800000	-1.0849470000
H	-5.3528340000	4.1596600000	-1.0302860000
C	-0.7714990000	3.8437420000	-0.3143090000
H	0.1096440000	4.4178780000	-0.0357750000
C	0.6914330000	1.8471760000	-0.5705450000
H	0.7913400000	0.7896610000	-0.7848850000
H	1.5799150000	2.4214370000	-0.3274220000
C	-0.5649800000	2.4847250000	-0.7069400000
H	-1.4305510000	1.8378820000	-0.8164510000
Cl	-0.4092640000	2.7735730000	-3.0287380000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.4590422
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.4396083
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= 807.338859172265

Thesis = $13^{3'}$-$3a^{1'}$
A3 = A3.3,A3.3E-MECP-$B^{3'}$-$F^{1'}$(Triplet)

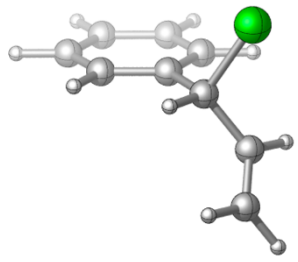


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149640 (Hartree/Particle)
Thermal correction to Energy= 0.159502
Thermal correction to Enthalpy= 0.160446
Thermal correction to Gibbs Free Energy= 0.112742
Sum of electronic and zero-point Energies= -808.133036
Sum of electronic and thermal Energies= -808.123174
Sum of electronic and thermal Enthalpies= -808.122229
Sum of electronic and thermal Free Energies= -808.169933

C	-4.4596830000	5.9647120000	-0.3035500000
C	-3.2847540000	6.5790040000	0.1469760000
C	-2.0867510000	5.8768710000	0.1573030000

C -2.0216240000 4.5292300000 -0.2789670000
C -3.2225250000 3.9224640000 -0.7263690000
C -4.4167380000 4.6349410000 -0.7376620000
H -5.3960190000 6.5142850000 -0.3148470000
H -3.3066220000 7.6106740000 0.4860520000
H -1.1762520000 6.3604420000 0.5028390000
H -3.2251180000 2.8886840000 -1.0600830000
H -5.3246780000 4.1507510000 -1.0858990000
C -0.7579270000 3.8581280000 -0.2684140000
H 0.1185590000 4.4282100000 0.0325160000
C 0.7362050000 1.8239320000 -0.6384200000
H 0.8281150000 0.8078250000 -1.0020310000
H 1.6310750000 2.3682970000 -0.3529120000
C -0.5397780000 2.5046390000 -0.7609210000
H -1.3955560000 1.8361260000 -0.6624730000
Cl -0.6499600000 2.7529230000 -2.7734370000

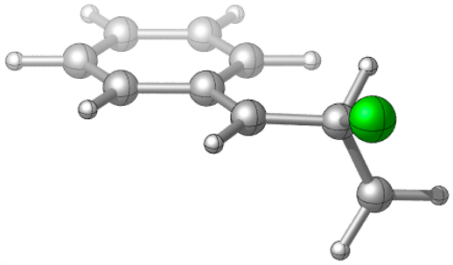
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.4563571
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.4563571
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.338477823458
Thesis = 3a, 3a[1']
A3 = A3.3,A3.4A- F[1']



UM06-2X/DGDZVP-SMD(acetonitrile)

Zero-point correction= 0.154172 (Hartree/Particle)
Thermal correction to Energy= 0.163274
Thermal correction to Enthalpy= 0.164219
Thermal correction to Gibbs Free Energy= 0.118840
Sum of electronic and zero-point Energies= -808.210482
Sum of electronic and thermal Energies= -808.201380
Sum of electronic and thermal Enthalpies= -808.200435
Sum of electronic and thermal Free Energies= -808.245814
C -4.3559360000 5.7518810000 0.0120980000
C -3.1178740000 6.3484770000 0.2488000000
C -1.9447260000 5.7161970000 -0.1712860000
C -2.0042760000 4.4840590000 -0.8271380000
C -3.2501180000 3.8874070000 -1.0627510000
C -4.4192310000 4.5195300000 -0.6461470000
H -5.2686040000 6.2432920000 0.3362510000
H -3.0611710000 7.3061300000 0.7578280000
H -0.9795510000 6.1823860000 0.0112820000
H -3.3075660000 2.9330620000 -1.5811380000
H -5.3815530000 4.0523380000 -0.8337350000
C -0.7244480000 3.7996840000 -1.2354650000
H 0.1350540000 4.4201630000 -0.9830120000
C 0.4822510000 2.0857320000 0.0942820000
H 0.5630100000 1.0918860000 0.5259420000
H 1.2857860000 2.7900230000 0.2992970000
C -0.5664010000 2.4267340000 -0.6559870000
H -1.3663380000 1.7159600000 -0.8566850000
Cl -0.6683370000 3.6571980000 -3.0727370000

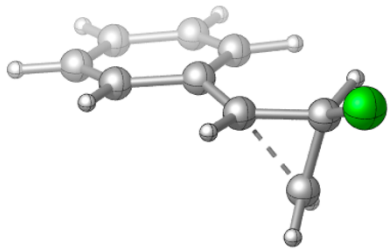
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.5411044
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.5255218
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.425925536525
Thesis = 14$^{3'}$
A3 = A3.3-C$^{3'}$



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149523 (Hartree/Particle)
Thermal correction to Energy= 0.159239
Thermal correction to Enthalpy= 0.160183
Thermal correction to Gibbs Free Energy= 0.112102
Sum of electronic and zero-point Energies= -808.129809
Sum of electronic and thermal Energies= -808.120094
Sum of electronic and thermal Enthalpies= -808.119149
Sum of electronic and thermal Free Energies= -808.167230

C	-4.4469770000	5.9986950000	-0.2854660000
C	-3.2823720000	6.5484490000	0.2695940000
C	-2.0946600000	5.8334420000	0.2555940000
C	-2.0280490000	4.5350610000	-0.3208600000
C	-3.2198550000	3.9931760000	-0.8750150000
C	-4.4043570000	4.7199580000	-0.8533490000
H	-5.3760250000	6.5602600000	-0.2731150000
H	-3.3096710000	7.5393640000	0.7137090000
H	-1.1934830000	6.2616280000	0.6874060000
H	-3.2142770000	2.9988070000	-1.3140920000
H	-5.3052430000	4.2882460000	-1.2798500000
C	-0.7952800000	3.8290380000	-0.3082240000
H	0.0556700000	4.2632120000	0.2082220000
C	-1.0371380000	1.3699510000	0.0578790000
H	-1.2085820000	0.3710850000	-0.3308830000
H	-0.9441240000	1.5182000000	1.1292440000
C	-0.6588780000	2.4533640000	-0.8685450000
H	-1.1576810000	2.3422010000	-1.8323410000
Cl	1.1522020000	2.2062060000	-1.3329860000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.4528867
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.4374442
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.337371695306
A3 = A3.3-TS-C$^{3'}$-E$^{3'}$

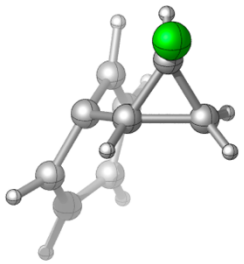


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.147283 (Hartree/Particle)
Thermal correction to Energy= 0.156725
Thermal correction to Enthalpy= 0.157669
Thermal correction to Gibbs Free Energy= 0.110640
Sum of electronic and zero-point Energies= -808.066450
Sum of electronic and thermal Energies= -808.057008
Sum of electronic and thermal Enthalpies= -808.056063

Sum of electronic and thermal Free Energies= -808.103093

C	-4.4353160000	5.8725900000	-0.0618870000
C	-3.1761300000	6.3352580000	0.5010890000
C	-2.0243700000	5.6708920000	0.2557300000
C	-2.0040030000	4.4486870000	-0.5782350000
C	-3.3008730000	4.0155110000	-1.1645930000
C	-4.4423780000	4.6983050000	-0.8973630000
H	-5.3528270000	6.4179590000	0.1259030000
H	-3.1711290000	7.2291330000	1.1182180000
H	-1.0823530000	6.0173570000	0.6746080000
H	-3.3297020000	3.1485460000	-1.8181020000
H	-5.3825170000	4.3683720000	-1.3310070000
C	-0.8678750000	3.6284100000	-0.5622990000
H	0.0414940000	4.0278130000	-0.1218840000
C	-0.9785330000	1.9420030000	0.0667830000
H	-1.9759610000	1.5982220000	0.3177590000
H	-0.1645670000	1.7757970000	0.7622830000
C	-0.7061720000	2.3515160000	-1.3147090000
H	-1.4590270000	2.1173210000	-2.0593840000
Cl	0.9212600000	2.0240230000	-1.9865250000

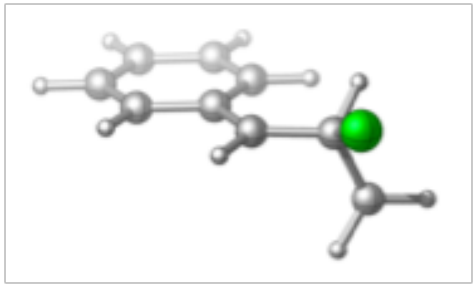
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.3887714
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.3723523
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.272340663610
A3 = A3.3 -$E^{3'}$



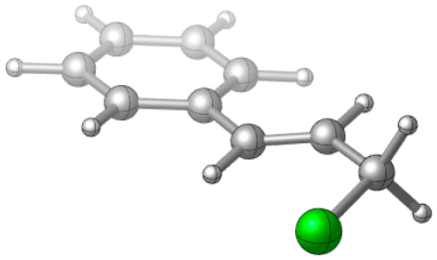
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149743 (Hartree/Particle)
Thermal correction to Energy= 0.159030
Thermal correction to Enthalpy= 0.159974
Thermal correction to Gibbs Free Energy= 0.113180
Sum of electronic and zero-point Energies= -808.073463
Sum of electronic and thermal Energies= -808.064176
Sum of electronic and thermal Enthalpies= -808.063232
Sum of electronic and thermal Free Energies= -808.110026

C	-2.5885970000	1.5996040000	1.0614740000
C	-1.3959250000	2.3700610000	1.3150160000
C	-0.2509130000	2.1053860000	0.6343590000
C	-0.1905170000	0.8703240000	-0.2006250000
C	-1.4969640000	0.4131920000	-0.7553440000
C	-2.6302160000	0.7008770000	-0.0607080000
H	-3.4990170000	1.8235610000	1.6065880000
H	-1.4481130000	3.2104620000	2.0028470000
H	0.6356490000	2.7250580000	0.7496640000
H	-1.5338010000	-0.1698880000	-1.6727770000
H	-3.5924350000	0.3199830000	-0.3943680000
C	0.7694230000	-0.1504780000	0.2720900000
H	1.6822880000	0.2441550000	0.7095710000
C	0.3156930000	-1.4825010000	0.8990600000

H -0.7497040000 -1.6838530000 0.9544360000
H 0.9180920000 -1.8437080000 1.7254690000
C 0.9246440000 -1.4596300000 -0.4556500000
H 0.3005500000 -1.6529670000 -1.3200750000
Cl 2.5621620000 -2.1087260000 -0.6863940000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.3974247
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.3821758
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.279414165802
Thesis = MECP-14^{3}-$2a^{1'}$
A3 = A3.3,A3.3E-MECP-$C^{3'}$-$E^{1'}$(Triplet)



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149548 (Hartree/Particle)
Thermal correction to Energy= 0.159249
Thermal correction to Enthalpy= 0.160193
Thermal correction to Gibbs Free Energy= 0.112177
Sum of electronic and zero-point Energies= -808.129777
Sum of electronic and thermal Energies= -808.120076
Sum of electronic and thermal Enthalpies= -808.119132
Sum of electronic and thermal Free Energies= -808.167148
C -4.4460240000 5.9971040000 -0.2781410000
C -3.2791300000 6.5477300000 0.2713940000
C -2.0911220000 5.8335600000 0.2517180000
C -2.0265250000 4.5351890000 -0.3250320000
C -3.2203940000 3.9925120000 -0.8738250000
C -4.4053610000 4.7184750000 -0.8462150000
H -5.3752850000 6.5581600000 -0.2614310000
H -3.3050110000 7.5385780000 0.7156960000
H -1.1879860000 6.2619070000 0.6791820000
H -3.2157760000 2.9986960000 -1.3142180000
H -5.3080320000 4.2862260000 -1.2684020000
C -0.7932580000 3.8303330000 -0.3181810000
H 0.0606410000 4.2664840000 0.1916370000
C -1.0443030000 1.3744020000 0.0585240000
H -1.1928070000 0.3687230000 -0.3222560000
H -0.9696870000 1.5352000000 1.1296220000
C -0.6606820000 2.4525540000 -0.8734410000
H -1.1575270000 2.3385290000 -1.8380890000
Cl 1.1494810000 2.1959760000 -1.3316240000
uM06-2X/def2-TZVPP-SMD(acetonitrile)//uM06-2X-DGDZVP- SMD(acetonitrile)
HF=-808.4528849
uM06-2X/def2-TZVPP-gas//uM06-2X-DGDZVP-SMD(acetonitrile)
HF=-808.4375682
DLPNO-CCSD(T)/def2-TZVPP-gas//uM06-2X-DGDZVP- SMD(acetonitrile)
HF=-807.337394890145
A3 = A3.3' -A^{1}

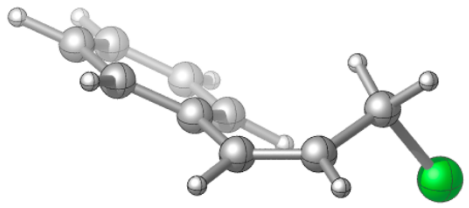


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154560 (Hartree/Particle)
Thermal correction to Energy= 0.163704

Thermal correction to Enthalpy= 0.164648
Thermal correction to Gibbs Free Energy= 0.118397
Sum of electronic and zero-point Energies= -808.215832
Sum of electronic and thermal Energies= -808.206688
Sum of electronic and thermal Enthalpies= -808.205744
Sum of electronic and thermal Free Energies= -808.251995

C	-4.3024750000	6.2895730000	-1.7037760000
C	-3.0033360000	6.6127320000	-2.0966530000
C	-1.9574150000	5.7220190000	-1.8513610000
C	-2.1888630000	4.4923060000	-1.2171150000
C	-3.4998770000	4.1825010000	-0.8169130000
C	-4.5441680000	5.0716210000	-1.0603750000
H	-5.1190380000	6.9810820000	-1.8893160000
H	-2.8026180000	7.5580490000	-2.5925890000
H	-0.9459610000	5.9783450000	-2.1576160000
H	-3.7091280000	3.2488810000	-0.3019900000
H	-5.5511560000	4.8168070000	-0.7425660000
C	-1.0420460000	3.5857030000	-0.9997110000
H	-0.0625540000	4.0269140000	-1.1776520000
C	0.0075850000	1.3498390000	-0.4026610000
H	-0.0573590000	0.5051830000	-1.0904760000
H	-0.0169210000	0.9639970000	0.6174760000
C	-1.1229150000	2.3027870000	-0.6315370000
H	-2.0925550000	1.8324100000	-0.4704510000
Cl	1.6439670000	2.0704390000	-0.6345300000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.5480168
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.5317885
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.429739352814
A3 = A3.3' -$A^{1'''}$



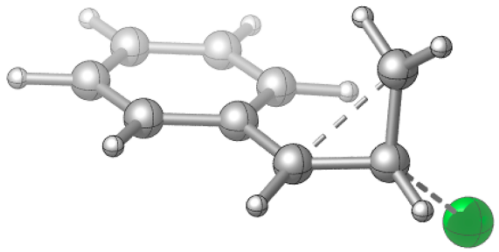
UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154994 (Hartree/Particle)
Thermal correction to Energy= 0.163924
Thermal correction to Enthalpy= 0.164868
Thermal correction to Gibbs Free Energy= 0.119484
Sum of electronic and zero-point Energies= -808.214402
Sum of electronic and thermal Energies= -808.205471
Sum of electronic and thermal Enthalpies= -808.204527
Sum of electronic and thermal Free Energies= -808.249911

C	-2.3326140000	2.2521390000	-0.0229650000
C	-1.3641910000	2.8266920000	-0.8499050000
C	-0.1259180000	2.2073010000	-1.0097380000
C	0.1593910000	0.9936440000	-0.3641470000
C	-0.8137980000	0.4352210000	0.4796710000
C	-2.0502390000	1.0597540000	0.6463980000
H	-3.2951400000	2.7373360000	0.1096060000
H	-1.5711360000	3.7604210000	-1.3647370000
H	0.6294580000	2.6612190000	-1.6467810000
H	-0.5945380000	-0.4728000000	1.0358470000
H	-2.7893860000	0.6195260000	1.3093100000

C 1.4890300000 0.3789630000 -0.5640670000
H 2.3121450000 1.0849080000 -0.6654300000
C 0.8123010000 -2.0539610000 -0.6863520000
H 1.1003150000 -2.8037370000 -1.4220360000
H -0.2146890000 -1.7399510000 -0.8624420000
C 1.7881880000 -0.9259700000 -0.6647800000
H 2.8318210000 -1.2044730000 -0.7928570000
Cl 0.8096650000 -2.9444820000 0.9103010000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.5461486
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.5312371
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.429805009608

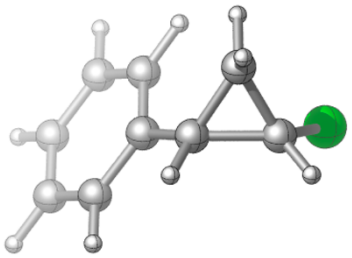
A3 = A3.3' -TS-$A^{1'''}$-E^{1}



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.151803 (Hartree/Particle)
Thermal correction to Energy= 0.160939
Thermal correction to Enthalpy= 0.161884
Thermal correction to Gibbs Free Energy= 0.116429
Sum of electronic and zero-point Energies= -808.144952
Sum of electronic and thermal Energies= -808.135815
Sum of electronic and thermal Enthalpies= -808.134871
Sum of electronic and thermal Free Energies= -808.180326
C -4.3567710000 5.8553740000 0.0704560000
C -3.2371340000 6.5114640000 -0.4489420000
C -2.0496780000 5.8118120000 -0.6308050000
C -1.9767590000 4.4453060000 -0.3027660000
C -3.1050290000 3.7935140000 0.2331070000
C -4.2879310000 4.5011350000 0.4141260000
H -5.2836420000 6.4020010000 0.2176530000
H -3.2920510000 7.5644460000 -0.7067150000
H -1.1711260000 6.3114320000 -1.0308930000
H -3.0355390000 2.7491720000 0.5256750000
H -5.1569270000 4.0036090000 0.8334900000
C -0.7100750000 3.7620500000 -0.4720820000
H 0.1647480000 4.3937650000 -0.6265010000
C -1.1743400000 2.0235520000 -1.5433610000
H -0.7112010000 1.3684430000 -2.2792880000
H -2.1752200000 2.3795780000 -1.7513430000
C -0.4576640000 2.3743480000 -0.4069950000
H 0.5679800000 2.0397870000 -0.3246960000
Cl -1.0204190000 1.3395550000 1.6768020000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4703204
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4371581
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.333207214426

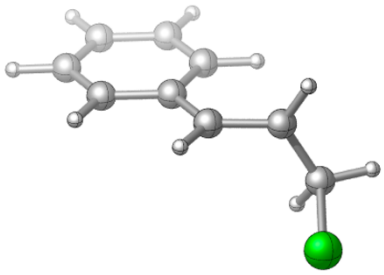
A3 = A3.3',A3.4A-E^{1}



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.155148 (Hartree/Particle)
Thermal correction to Energy= 0.163539
Thermal correction to Enthalpy= 0.164483
Thermal correction to Gibbs Free Energy= 0.120749
Sum of electronic and zero-point Energies= -808.205479
Sum of electronic and thermal Energies= -808.197087
Sum of electronic and thermal Enthalpies= -808.196143
Sum of electronic and thermal Free Energies= -808.239877

C	-2.1727790000	2.2256510000	0.2328720000
C	-0.9383050000	2.7814820000	-0.1083120000
C	0.1076740000	1.9583600000	-0.5254010000
C	-0.0564980000	0.5680730000	-0.6111250000
C	-1.3014310000	0.0214060000	-0.2732360000
C	-2.3485040000	0.8434680000	0.1473300000
H	-2.9902550000	2.8625430000	0.5579020000
H	-0.7879410000	3.8557660000	-0.0509370000
H	1.0666810000	2.3977400000	-0.7899290000
H	-1.4688830000	-1.0499430000	-0.3366320000
H	-3.3060760000	0.4003580000	0.4058500000
C	1.1132400000	-0.2531440000	-1.0418710000
H	1.8501290000	0.3074760000	-1.6093370000
C	1.0206560000	-1.7286010000	-1.3719030000
H	1.6137340000	-2.1028590000	-2.1993670000
H	0.0627320000	-2.2171010000	-1.2301160000
C	1.7512020000	-1.2925900000	-0.1472190000
H	2.8321790000	-1.3441990000	-0.1186900000
Cl	1.0628710000	-1.6413470000	1.4497540000

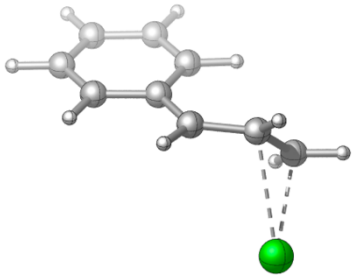
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.5378262
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.5237722
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.415027710957
A3 = A3.3'-A^3



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150351 (Hartree/Particle)
Thermal correction to Energy= 0.159974
Thermal correction to Enthalpy= 0.160918
Thermal correction to Gibbs Free Energy= 0.112598
Sum of electronic and zero-point Energies= -808.134274
Sum of electronic and thermal Energies= -808.124652
Sum of electronic and thermal Enthalpies= -808.123708
Sum of electronic and thermal Free Energies= -808.172028

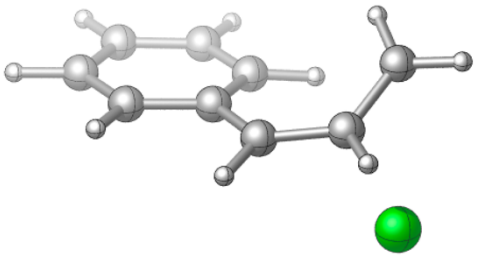
C	-4.2218580000	6.2221710000	-1.2565250000
C	-3.0371500000	6.6307560000	-1.8857340000
C	-1.9814080000	5.7441150000	-2.0387730000
C	-2.0761730000	4.4077310000	-1.5635150000

C -3.2838100000 4.0132850000 -0.9260710000
C -4.3343300000 4.9097730000 -0.7794930000
H -5.0457890000 6.9193460000 -1.1392320000
H -2.9445550000 7.6475010000 -2.2566740000
H -1.0646770000 6.0643920000 -2.5279500000
H -3.3806690000 2.9967850000 -0.5512520000
H -5.2500600000 4.5892100000 -0.2907850000
C -0.9863160000 3.5085520000 -1.7312550000
H -0.0899150000 3.8783820000 -2.2308430000
C -0.4520020000 1.7494700000 0.0486870000
H -0.7854610000 0.7738270000 0.3965270000
H -0.6032710000 2.5141600000 0.8090070000
C -1.0038980000 2.1182430000 -1.2646160000
H -1.2339850000 1.3148940000 -1.9626830000
Cl 1.4084940000 1.5885950000 -0.0686300000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4585132
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4424418
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.341089549273
A3 = A3.3'-TS-A^3-B^3



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150152 (Hartree/Particle)
Thermal correction to Energy= 0.159459
Thermal correction to Enthalpy= 0.160404
Thermal correction to Gibbs Free Energy= 0.113072
Sum of electronic and zero-point Energies= -808.122638
Sum of electronic and thermal Energies= -808.113331
Sum of electronic and thermal Enthalpies= -808.112387
Sum of electronic and thermal Free Energies= -808.159718
C -4.4686960000 5.9395660000 0.0437480000
C -3.2433510000 6.6023640000 0.2071060000
C -2.0525980000 5.9439440000 -0.0530120000
C -2.0438550000 4.5838090000 -0.4756900000
C -3.2986530000 3.9318620000 -0.6419960000
C -4.4840860000 4.6065660000 -0.3876340000
H -5.4007880000 6.4575720000 0.2475760000
H -3.2267020000 7.6373180000 0.5356820000
H -1.1033720000 6.4595250000 0.0686970000
H -3.3333120000 2.9018900000 -0.9852900000
H -5.4320930000 4.0946950000 -0.5248700000
C -0.7997260000 3.9583230000 -0.7439920000
H 0.0995830000 4.5682640000 -0.7014060000
C -1.1220410000 1.4701190000 -0.4643210000
H -0.9906620000 0.4756690000 -0.8778370000
H -1.8321770000 1.5939230000 0.3473300000
C -0.6098210000 2.5620500000 -1.1359770000
H 0.0558820000 2.3737740000 -1.9775220000
Cl 0.8176910000 1.4691060000 0.9663320000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4468255

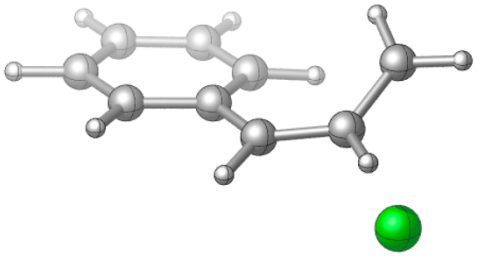
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4257724
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.324800738006
A3 = A3.3'-B^3



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150108 (Hartree/Particle)
Thermal correction to Energy= 0.160097
Thermal correction to Enthalpy= 0.161041
Thermal correction to Gibbs Free Energy= 0.112877
Sum of electronic and zero-point Energies= -808.130735
Sum of electronic and thermal Energies= -808.120746
Sum of electronic and thermal Enthalpies= -808.119802
Sum of electronic and thermal Free Energies= -808.167966

C	-2.1727790000	2.2256510000	0.2328720000
C	-0.9383050000	2.7814820000	-0.1083120000
C	0.1076740000	1.9583600000	-0.5254010000
C	-0.0564980000	0.5680730000	-0.6111250000
C	-1.3014310000	0.0214060000	-0.2732360000
C	-2.3485040000	0.8434680000	0.1473300000
H	-2.9902550000	2.8625430000	0.5579020000
H	-0.7879410000	3.8557660000	-0.0509370000
H	1.0666810000	2.3977400000	-0.7899290000
H	-1.4688830000	-1.0499430000	-0.3366320000
H	-3.3060760000	0.4003580000	0.4058500000
C	1.1132400000	-0.2531440000	-1.0418710000
H	1.8501290000	0.3074760000	-1.6093370000
C	1.0206560000	-1.7286010000	-1.3719030000
H	1.6137340000	-2.1028590000	-2.1993670000
H	0.0627320000	-2.2171010000	-1.2301160000
C	1.7512020000	-1.2925900000	-0.1472190000
H	2.8321790000	-1.3441990000	-0.1186900000
Cl	1.0628710000	-1.6413470000	1.4497540000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4540273
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4356024
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.334469071584
A3 = A3.3A, A3.3E-MECP-B^3-F^1(Triplet)

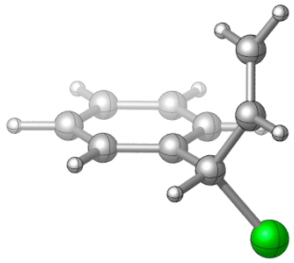


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149244 (Hartree/Particle)
Thermal correction to Energy= 0.159094
Thermal correction to Enthalpy= 0.160038
Thermal correction to Gibbs Free Energy= 0.112451
Sum of electronic and zero-point Energies= -808.130060
Sum of electronic and thermal Energies= -808.120210
Sum of electronic and thermal Enthalpies= -808.119266
Sum of electronic and thermal Free Energies= -808.166853

C	-4.3273080000	6.0831490000	-0.2346110000

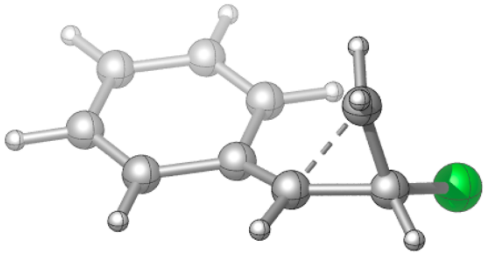
C -3.1745300000 6.7993570000 -0.5788880000
C -1.9858580000 6.1291360000 -0.8340380000
C -1.9088410000 4.7138730000 -0.7575160000
C -3.0890740000 4.0065470000 -0.4094680000
C -4.2723590000 4.6866020000 -0.1493090000
H -5.2571990000 6.6066750000 -0.0341650000
H -3.2067120000 7.8831050000 -0.6433850000
H -1.0909360000 6.6894960000 -1.0931750000
H -3.0742220000 2.9226590000 -0.3358000000
H -5.1631330000 4.1262270000 0.1193220000
C -0.6447540000 4.0879340000 -0.9885780000
H 0.2107240000 4.7390960000 -1.1431220000
C -1.2880380000 1.7213130000 -1.6424410000
H -2.0098700000 2.1006260000 -2.3570950000
H -1.2115130000 0.6536350000 -1.4719570000
C -0.3633580000 2.6405350000 -0.9525280000
H 0.6763110000 2.4481120000 -1.2248870000
Cl -0.3144550000 2.1010810000 0.8991510000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.4528743
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.4372638
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.336494312086
A3 = A3.3',AA3.4A-F[1]

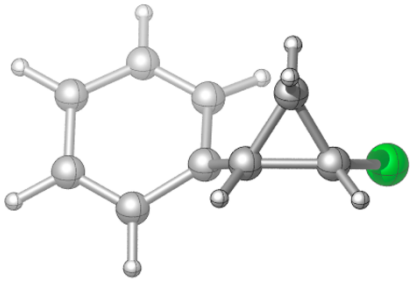


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.153997 (Hartree/Particle)
Thermal correction to Energy= 0.163064
Thermal correction to Enthalpy= 0.164008
Thermal correction to Gibbs Free Energy= 0.118769
Sum of electronic and zero-point Energies= -808.209818
Sum of electronic and thermal Energies= -808.200752
Sum of electronic and thermal Enthalpies= -808.199807
Sum of electronic and thermal Free Energies= -808.245046
C -4.2995000000 5.9130770000 -0.4839960000
C -3.1000600000 6.5365280000 -0.8252610000
C -1.8963470000 5.8313780000 -0.7403120000
C -1.8868940000 4.4997570000 -0.3188010000
C -3.0942340000 3.8775620000 0.0242870000
C -4.2936110000 4.5813470000 -0.0567820000
H -5.2355170000 6.4604560000 -0.5456500000
H -3.0962580000 7.5716650000 -1.1535670000
H -0.9614000000 6.3200910000 -1.0033750000
H -3.0944890000 2.8418060000 0.3562000000
H -5.2251820000 4.0919850000 0.2120450000
C -0.5827100000 3.7493570000 -0.2884200000
H 0.2489690000 4.4448580000 -0.4111640000
C -1.3309960000 2.3179290000 -2.2265650000

H -2.2707750000 2.8511670000 -2.3460680000
H -1.1246090000 1.5095320000 -2.9228680000
C -0.4429470000 2.6277970000 -1.2803770000
H 0.4909990000 2.0733150000 -1.2097510000
Cl -0.2995670000 3.0395530000 1.3879340000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.5404298
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.5262632
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.426243485475
A3 = A3.3'-TS-B^3-E^3



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.147500 (Hartree/Particle)
Thermal correction to Energy= 0.156840
Thermal correction to Enthalpy= 0.157784
Thermal correction to Gibbs Free Energy= 0.110927
Sum of electronic and zero-point Energies= -808.062018
Sum of electronic and thermal Energies= -808.052679
Sum of electronic and thermal Enthalpies= -808.051735
Sum of electronic and thermal Free Energies= -808.098592
C 2.0788300000 5.7074710000 1.7269060000
C 0.7432930000 6.2434440000 1.5217490000
C -0.1343910000 5.6152120000 0.7073630000
C 0.2148180000 4.3552840000 0.0110850000
C 1.6107450000 3.8651100000 0.1953240000
C 2.4652300000 4.5121010000 1.0312680000
H 2.7822690000 6.2201800000 2.3727010000
H 0.4593110000 7.1630680000 2.0254010000
H -1.1319030000 6.0201140000 0.5532380000
H 1.9445030000 2.9799420000 -0.3341930000
H 3.4733310000 4.1293360000 1.1656130000
C -0.8346580000 3.5726390000 -0.4896350000
H -1.8214690000 4.0273160000 -0.4742300000
C -0.9208490000 1.8661470000 0.1240810000
H -1.8794600000 1.5513670000 0.5214290000
H -0.0177890000 1.6471010000 0.6831060000
C -0.8183750000 2.2982260000 -1.2713270000
H -1.7112670000 2.1645280000 -1.8733710000
Cl 0.6031580000 1.8224680000 -2.2555650000
UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.3845717
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.3683562
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.268325113920
A3 = A3.3'-E^3

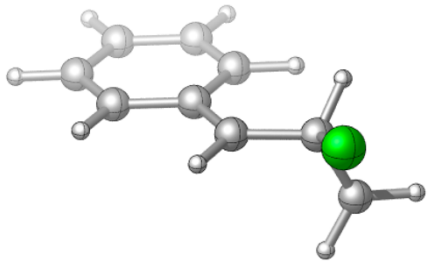


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149222 (Hartree/Particle)
Thermal correction to Energy= 0.158692

Thermal correction to Enthalpy= 0.159636
Thermal correction to Gibbs Free Energy= 0.109799
Sum of electronic and zero-point Energies= -808.071988
Sum of electronic and thermal Energies= -808.062519
Sum of electronic and thermal Enthalpies= -808.061575
Sum of electronic and thermal Free Energies= -808.111412

C	1.3136940000	1.8359940000	2.1279040000
C	0.2185630000	2.5894590000	1.5538710000
C	-0.4562570000	2.1024220000	0.4850840000
C	-0.1827570000	0.7078860000	0.0387190000
C	1.1863850000	0.1945820000	0.3407710000
C	1.8379280000	0.6964210000	1.4236900000
H	1.8440910000	2.2292920000	2.9882750000
H	-0.0087170000	3.5750960000	1.9523340000
H	-1.2338720000	2.6819010000	-0.0079360000
H	1.6355930000	-0.5850430000	-0.2699360000
H	2.8034380000	0.2938450000	1.7208000000
C	-1.3405670000	-0.2087600000	0.0297990000
H	-2.2862290000	0.2553270000	0.2968250000
C	-1.2059340000	-1.6944140000	0.3646130000
H	-1.9976990000	-2.1645260000	0.9381730000
H	-0.2012250000	-2.0510800000	0.5671810000
C	-1.5153410000	-1.2887640000	-1.0298570000
H	-2.5119490000	-1.4391370000	-1.4258110000
Cl	-0.2919080000	-1.4915500000	-2.3000240000

UM06-2X/def2-TZVPP-SMD(acetonitrile)//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -808.3956138
UM06-2X/def2-TZVPP-gas//UM06-2X-DGDZVP-SMD(acetonitrile)
HF= -808.3803169
DLPNO-CCSD(T)/def2-TZVPP-gas//UM06-2X-DGDZVP- SMD(acetonitrile)
HF= -807.276922084260
A3 = A3.3C-initial guess structure-triplet ($C^{3'}$)

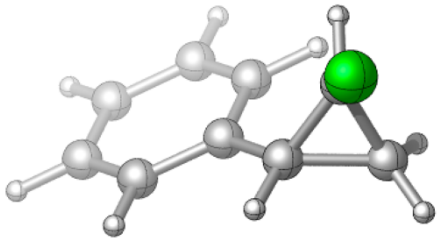


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149594 (Hartree/Particle)
Thermal correction to Energy= 0.159335
Thermal correction to Enthalpy= 0.160279
Thermal correction to Gibbs Free Energy= 0.112465
Sum of electronic and zero-point Energies= -808.129864
Sum of electronic and thermal Energies= -808.120123
Sum of electronic and thermal Enthalpies= -808.119179
Sum of electronic and thermal Free Energies= -808.166993

C	-4.3318850000	6.3781710000	-0.5723920000
C	-3.3591540000	6.5561840000	0.4221500000
C	-2.3035440000	5.6647670000	0.5369500000
C	-2.1808170000	4.5577360000	-0.3461850000
C	-3.1796160000	4.3903340000	-1.3439360000
C	-4.2331120000	5.2908090000	-1.4484220000
H	-5.1568670000	7.0782730000	-0.6613890000
H	-3.4317470000	7.3959500000	1.1071480000
H	-1.5514170000	5.8055670000	1.3090620000
H	-3.1292380000	3.5494970000	-2.0311410000
H	-4.9868750000	5.1463990000	-2.2169470000

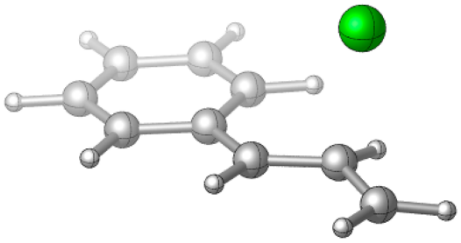
C -1.0874580000 3.6630390000 -0.1957190000
H -0.4005000000 3.8012530000 0.6336780000
C -1.7326540000 1.3016870000 -0.6894870000
H -1.8876770000 0.4989790000 -1.4033610000
H -1.9995420000 1.1495920000 0.3517310000
C -0.9150370000 2.4679100000 -1.0735330000
H -1.0401820000 2.7057860000 -2.1316380000
Cl 0.8934460000 1.9554310000 -0.9918380000

A3 = A3.3C-initial guess structure-singlet ($E^{1'}$)



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154651 (Hartree/Particle)
Thermal correction to Energy= 0.163195
Thermal correction to Enthalpy= 0.164139
Thermal correction to Gibbs Free Energy= 0.119908
Sum of electronic and zero-point Energies= -808.207664
Sum of electronic and thermal Energies= -808.199120
Sum of electronic and thermal Enthalpies= -808.198176
Sum of electronic and thermal Free Energies= -808.242407
C -4.2110390000 6.3969790000 -0.5937350000
C -3.2748050000 6.4318540000 0.4407790000
C -2.3515130000 5.3949120000 0.5876190000
C -2.3507970000 4.3055620000 -0.2935710000
C -3.2972270000 4.2777710000 -1.3281170000
C -4.2174570000 5.3149170000 -1.4771360000
H -4.9303650000 7.2022390000 -0.7098540000
H -3.2603560000 7.2673890000 1.1349470000
H -1.6231710000 5.4290840000 1.3945370000
H -3.3254960000 3.4439000000 -2.0260260000
H -4.9430660000 5.2765250000 -2.2846930000
C -1.3453290000 3.2195810000 -0.1191330000
H -0.6870720000 3.3368810000 0.7361080000
C -1.6460840000 1.7769900000 -0.4962970000
H -2.6166520000 1.5484450000 -0.9263710000
H -1.2212450000 1.0133230000 0.1460300000
C -0.7124580000 2.5849360000 -1.3266940000
H -1.0253210000 2.9192570000 -2.3092830000
Cl 1.0255760000 2.2168200000 -1.2943790000

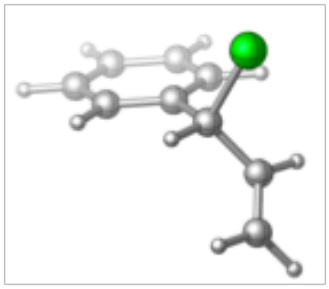
A3 = A3.3C-b180-triplet ($B^{3'}$)



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150189 (Hartree/Particle)
Thermal correction to Energy= 0.160116
Thermal correction to Enthalpy= 0.161060
Thermal correction to Gibbs Free Energy= 0.112744
Sum of electronic and zero-point Energies= -808.135615
Sum of electronic and thermal Energies= -808.125688
Sum of electronic and thermal Enthalpies= -808.124744
Sum of electronic and thermal Free Energies= -808.173060
C -4.4576990000 5.9613110000 -0.2512720000

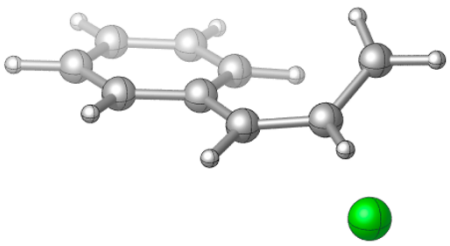
C -3.2708800000 6.5734990000 0.1667140000
C -2.0752440000 5.8676180000 0.1377430000
C -2.0329280000 4.5231830000 -0.3053130000
C -3.2429850000 3.9209060000 -0.7292900000
C -4.4339440000 4.6351070000 -0.7001390000
H -5.3928690000 6.5125750000 -0.2305940000
H -3.2821790000 7.6028020000 0.5124610000
H -1.1528040000 6.3444210000 0.4596890000
H -3.2517020000 2.8949800000 -1.0849470000
H -5.3528340000 4.1596600000 -1.0302860000
C -0.7714990000 3.8437420000 -0.3143090000
H 0.1096440000 4.4178780000 -0.0357750000
C 0.6914330000 1.8471760000 -0.5705450000
H 0.7913400000 0.7896610000 -0.7848850000
H 1.5799150000 2.4214370000 -0.3274220000
C -0.5649800000 2.4847250000 -0.7069400000
H -1.4305510000 1.8378820000 -0.8164510000
Cl -0.4092640000 2.7735730000 -3.0287380000

A3 = A3.3C-b180-singlet ($F^{1'}$)



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154191 (Hartree/Particle)
Thermal correction to Energy= 0.163295
Thermal correction to Enthalpy= 0.164239
Thermal correction to Gibbs Free Energy= 0.118853
Sum of electronic and zero-point Energies= -808.210434
Sum of electronic and thermal Energies= -808.201330
Sum of electronic and thermal Enthalpies= -808.200386
Sum of electronic and thermal Free Energies= -808.245772
C -4.3341420000 5.7856700000 0.0188470000
C -3.0892170000 6.3606380000 0.2721810000
C -1.9224060000 5.7151280000 -0.1452200000
C -1.9948120000 4.4911450000 -0.8151890000
C -3.2477210000 3.9165680000 -1.0679860000
C -4.4105120000 4.5618510000 -0.6537260000
H -5.2419830000 6.2872750000 0.3409210000
H -3.0223810000 7.3117140000 0.7921750000
H -0.9518890000 6.1647530000 0.0501720000
H -3.3166260000 2.9691440000 -1.5974710000
H -5.3781500000 4.1113230000 -0.8543840000
C -0.7214650000 3.7947180000 -1.2234780000
H 0.1449120000 4.3922970000 -0.9410920000
C 0.4355710000 2.0191410000 0.0702090000
H 0.4916280000 1.0106580000 0.4707380000
H 1.2486160000 2.7013020000 0.3094230000
C -0.5957330000 2.4024270000 -0.6836790000
H -1.4037720000 1.7119050000 -0.9192350000
Cl -0.6399490000 3.7044810000 -3.0635050000

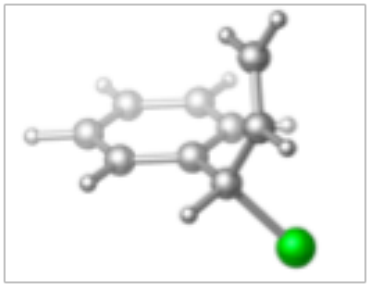
A3 = A3.3C-b90-triplet (B^3)



UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150473 (Hartree/Particle)
Thermal correction to Energy= 0.160318
Thermal correction to Enthalpy= 0.161263
Thermal correction to Gibbs Free Energy= 0.113480
Sum of electronic and zero-point Energies= -808.130294
Sum of electronic and thermal Energies= -808.120448
Sum of electronic and thermal Enthalpies= -808.119504
Sum of electronic and thermal Free Energies= -808.167287

C	-4.4052200000	6.0392230000	-0.3876490000
C	-3.3407920000	6.4608680000	0.4169710000
C	-2.1659350000	5.7217000000	0.4600010000
C	-2.0116870000	4.5480220000	-0.3172700000
C	-3.1054840000	4.1264630000	-1.1108530000
C	-4.2830550000	4.8659010000	-1.1394860000
H	-5.3264830000	6.6129840000	-0.4188690000
H	-3.4326890000	7.3641190000	1.0127160000
H	-1.3416440000	6.0458510000	1.0901940000
H	-3.0521170000	3.1974900000	-1.6690290000
H	-5.1161690000	4.5227940000	-1.7457440000
C	-0.7699950000	3.8311330000	-0.2161210000
H	-0.1310430000	4.0877170000	0.6244570000
C	-0.5964010000	2.5918660000	-2.4416940000
H	-0.0695090000	1.8226110000	-2.9944860000
H	-1.3643010000	3.1595600000	-2.9526500000
C	-0.2764850000	2.7862280000	-1.0689660000
H	0.6839890000	2.3813740000	-0.7621850000
Cl	-1.3901110000	0.9732550000	-0.2118280000

A3 = A3.3C-b90-singlet (F1)

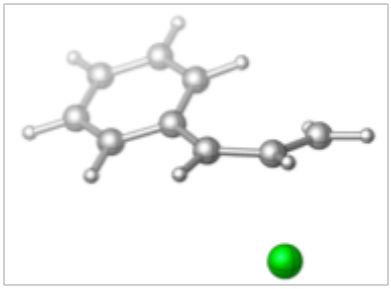


UM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154349 (Hartree/Particle)
Thermal correction to Energy= 0.163368
Thermal correction to Enthalpy= 0.164313
Thermal correction to Gibbs Free Energy= 0.119222
Sum of electronic and zero-point Energies= -808.209567
Sum of electronic and thermal Energies= -808.200547
Sum of electronic and thermal Enthalpies= -808.199603
Sum of electronic and thermal Free Energies= -808.244694

C	-4.2592640000	5.9673740000	-0.6016920000
C	-3.1255940000	6.3481190000	0.1153230000
C	-2.0915040000	5.4321330000	0.3267190000
C	-2.1834210000	4.1341250000	-0.1814820000
C	-3.3245520000	3.7556330000	-0.9007920000
C	-4.3572700000	4.6673740000	-1.1080320000
H	-5.0649350000	6.6772250000	-0.7640680000
H	-3.0439610000	7.3548770000	0.5141200000
H	-1.2084960000	5.7288400000	0.8873160000

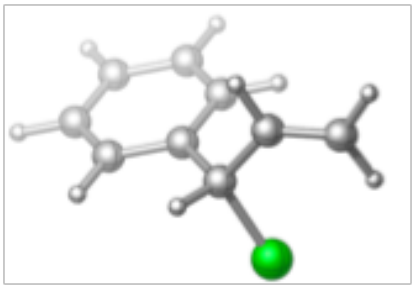
H -3.4049540000 2.7462660000 -1.2976450000
H -5.2391490000 4.3663400000 -1.6658160000
C -1.0261800000 3.1902400000 0.0073250000
H -0.3389210000 3.5863130000 0.7568970000
C -0.4544670000 3.3852050000 -2.4403550000
H 0.1768070000 3.1012300000 -3.2780000000
H -1.2295020000 4.1241880000 -2.6278690000
C -0.2559150000 2.8438350000 -1.2374110000
H 0.5428170000 2.1191140000 -1.0917600000
Cl -1.6066720000 1.6107280000 0.7547300000

A3 = A3.3C -F[1]-c315-a90-triplet



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.150532 (Hartree/Particle)
Thermal correction to Energy= 0.160385
Thermal correction to Enthalpy= 0.161329
Thermal correction to Gibbs Free Energy= 0.113000
Sum of electronic and zero-point Energies= -808.129173
Sum of electronic and thermal Energies= -808.119320
Sum of electronic and thermal Enthalpies= -808.118375
Sum of electronic and thermal Free Energies= -808.166705
C -4.4529140000 6.1738510000 -0.0572840000
C -3.9549070000 5.7368840000 -1.2888790000
C -2.8694340000 4.8693800000 -1.3453440000
C -2.2477770000 4.4160920000 -0.1576100000
C -2.7461440000 4.8968820000 1.0782580000
C -3.8383630000 5.7527120000 1.1273210000
H -5.3050540000 6.8458760000 -0.0216120000
H -4.4114300000 6.0830500000 -2.2113940000
H -2.4781940000 4.5815910000 -2.3148510000
H -2.2647860000 4.5759150000 1.9986350000
H -4.2109250000 6.0990330000 2.0866480000
C -1.1000620000 3.5474320000 -0.1236100000
H -0.5601350000 3.5091880000 0.8183530000
C -1.1943790000 2.3402840000 -2.3768500000
H -0.6294540000 1.7432210000 -3.0838910000
H -2.2326260000 2.5504740000 -2.6013440000
C -0.6065460000 2.6634910000 -1.1344160000
H 0.4303560000 2.3633810000 -1.0060030000
Cl -1.3411040000 0.6086290000 -0.1314000000

A3 = A3.3C -F[1]-c315-a90-singlet

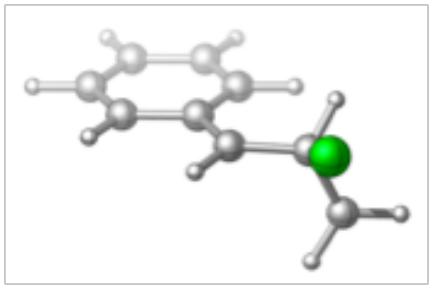


uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.153858 (Hartree/Particle)
Thermal correction to Energy= 0.163009
Thermal correction to Enthalpy= 0.163953
Thermal correction to Gibbs Free Energy= 0.118089
Sum of electronic and zero-point Energies= -808.209596
Sum of electronic and thermal Energies= -808.200445
Sum of electronic and thermal Enthalpies= -808.199501

Sum of electronic and thermal Free Energies= -808.245366

C	-4.1878490000	6.3759720000	0.0447110000
C	-4.0063830000	5.7270970000	-1.1801020000
C	-3.1678530000	4.6169590000	-1.2665250000
C	-2.5071360000	4.1444350000	-0.1268100000
C	-2.6915720000	4.7945310000	1.0964550000
C	-3.5292760000	5.9083930000	1.1825390000
H	-4.8391020000	7.2426790000	0.1092020000
H	-4.5166410000	6.0887750000	-2.0680120000
H	-3.0284900000	4.1144740000	-2.2211330000
H	-2.1792350000	4.4271160000	1.9825430000
H	-3.6660080000	6.4085920000	2.1367250000
C	-1.6069700000	2.9320810000	-0.2015330000
H	-1.0133180000	2.8707180000	0.7127530000
C	-0.6047470000	2.0766900000	-2.3849150000
H	0.1159690000	2.2232330000	-3.1843980000
H	-1.2390240000	1.1961550000	-2.4369350000
C	-0.6838120000	2.9575850000	-1.3890610000
H	-0.0258310000	3.8265810000	-1.3820480000
Cl	-2.6366020000	1.4252990000	-0.1687290000

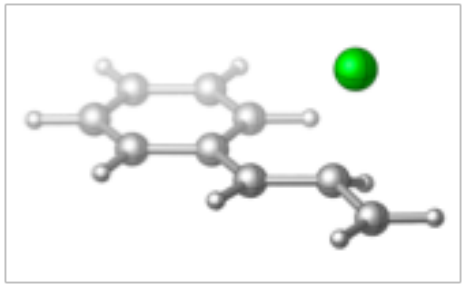
A3 = A3.3E-MECP-C$^{3'}$-E$^{1'}$(Singlet)



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149249 (Hartree/Particle)
Thermal correction to Energy= 0.158173
Thermal correction to Enthalpy= 0.159117
Thermal correction to Gibbs Free Energy= 0.114947
Sum of electronic and zero-point Energies= -808.130104
Sum of electronic and thermal Energies= -808.121180
Sum of electronic and thermal Enthalpies= -808.120236
Sum of electronic and thermal Free Energies= -808.164406

C	-4.4460240000	5.9971040000	-0.2781410000
C	-3.2791300000	6.5477300000	0.2713940000
C	-2.0911220000	5.8335600000	0.2517180000
C	-2.0265250000	4.5351890000	-0.3250320000
C	-3.2203940000	3.9925120000	-0.8738250000
C	-4.4053610000	4.7184750000	-0.8462150000
H	-5.3752850000	6.5581600000	-0.2614310000
H	-3.3050110000	7.5385780000	0.7156960000
H	-1.1879860000	6.2619070000	0.6791820000
H	-3.2157760000	2.9986960000	-1.3142180000
H	-5.3080320000	4.2862260000	-1.2684020000
C	-0.7932580000	3.8303330000	-0.3181810000
H	0.0606410000	4.2664840000	0.1916370000
C	-1.0443030000	1.3744020000	0.0585240000
H	-1.1928070000	0.3687230000	-0.3222560000
H	-0.9696870000	1.5352000000	1.1296220000
C	-0.6606820000	2.4525540000	-0.8734410000
H	-1.1575270000	2.3385290000	-1.8380890000
Cl	1.1494810000	2.1959760000	-1.3316240000

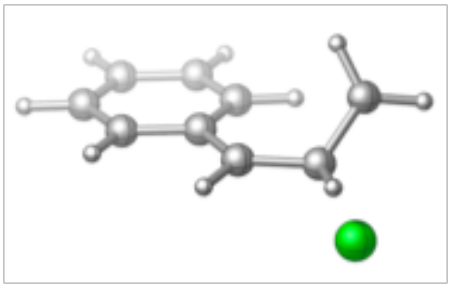
A3 = A3.3E-MECP-B$^{3'}$-F$^{1'}$(Singlet)



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149544 (Hartree/Particle)
Thermal correction to Energy= 0.158728
Thermal correction to Enthalpy= 0.159672
Thermal correction to Gibbs Free Energy= 0.114387
Sum of electronic and zero-point Energies= -808.133141
Sum of electronic and thermal Energies= -808.123957
Sum of electronic and thermal Enthalpies= -808.123012
Sum of electronic and thermal Free Energies= -808.168297

C	-4.4596830000	5.9647120000	-0.3035500000
C	-3.2847540000	6.5790040000	0.1469760000
C	-2.0867510000	5.8768710000	0.1573030000
C	-2.0216240000	4.5292300000	-0.2789670000
C	-3.2225250000	3.9224640000	-0.7263690000
C	-4.4167380000	4.6349410000	-0.7376620000
H	-5.3960190000	6.5142850000	-0.3148470000
H	-3.3066220000	7.6106740000	0.4860520000
H	-1.1762520000	6.3604420000	0.5028390000
H	-3.2251180000	2.8886840000	-1.0600830000
H	-5.3246780000	4.1507510000	-1.0858990000
C	-0.7579270000	3.8581280000	-0.2684140000
H	0.1185590000	4.4282100000	0.0325160000
C	0.7362050000	1.8239320000	-0.6384200000
H	0.8281150000	0.8078250000	-1.0020310000
H	1.6310750000	2.3682970000	-0.3529120000
C	-0.5397780000	2.5046390000	-0.7609210000
H	-1.3955560000	1.8361260000	-0.6624730000
Cl	-0.6499600000	2.7529230000	-2.7734370000

A3 = A3.3E-MECP-B^3-F^1(Singlet)

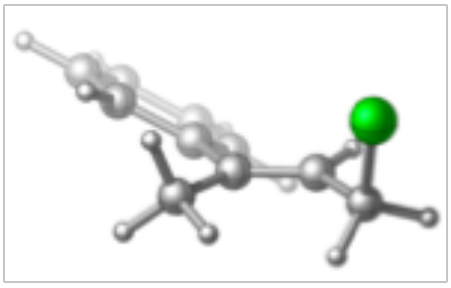


uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.149045 (Hartree/Particle)
Thermal correction to Energy= 0.158204
Thermal correction to Enthalpy= 0.159148
Thermal correction to Gibbs Free Energy= 0.114205
Sum of electronic and zero-point Energies= -808.130249
Sum of electronic and thermal Energies= -808.121091
Sum of electronic and thermal Enthalpies= -808.120147
Sum of electronic and thermal Free Energies= -808.165090

C	-4.3273080000	6.0831490000	-0.2346110000
C	-3.1745300000	6.7993570000	-0.5788880000
C	-1.9858580000	6.1291360000	-0.8340380000
C	-1.9088410000	4.7138730000	-0.7575160000
C	-3.0890740000	4.0065470000	-0.4094680000
C	-4.2723590000	4.6866020000	-0.1493090000
H	-5.2571990000	6.6066750000	-0.0341650000
H	-3.2067120000	7.8831050000	-0.6433850000
H	-1.0909360000	6.6894960000	-1.0931750000

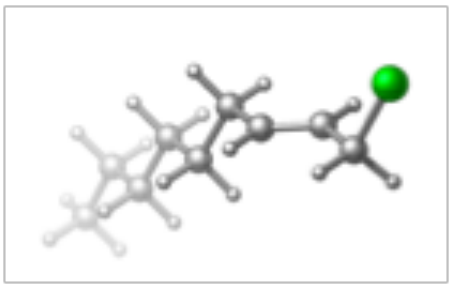
H -3.0742220000 2.9226590000 -0.3358000000
H -5.1631330000 4.1262270000 0.1193220000
C -0.6447540000 4.0879340000 -0.9885780000
H 0.2107240000 4.7390960000 -1.1431220000
C -1.2880380000 1.7213130000 -1.6424410000
H -2.0098700000 2.1006260000 -2.3570950000
H -1.2115130000 0.6536350000 -1.4719570000
C -0.3633580000 2.6405350000 -0.9525280000
H 0.6763110000 2.4481120000 -1.2248870000
Cl -0.3144550000 2.1010810000 0.8991510000

A3 = A3.4B-cinnamyl Me



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.183126 (Hartree/Particle)
Thermal correction to Energy= 0.193669
Thermal correction to Enthalpy= 0.194613
Thermal correction to Gibbs Free Energy= 0.145196
Sum of electronic and zero-point Energies= -847.486262
Sum of electronic and thermal Energies= -847.475719
Sum of electronic and thermal Enthalpies= -847.474775
Sum of electronic and thermal Free Energies= -847.524192
C -4.4147280000 6.3240490000 -0.5329770000
C -3.1772820000 6.7594940000 -0.0569990000
C -2.1462530000 5.8449730000 0.1622900000
C -2.3264440000 4.4790050000 -0.1064140000
C -3.5811810000 4.0519080000 -0.5725790000
C -4.6131230000 4.9641830000 -0.7852370000
H -5.2191520000 7.0349930000 -0.6966650000
H -3.0121000000 7.8135590000 0.1465650000
H -1.1901120000 6.2052270000 0.5308000000
H -3.7608750000 2.9949410000 -0.7485730000
H -5.5774090000 4.6109050000 -1.1389330000
C -1.2114140000 3.5155340000 0.1097190000
C -0.0311540000 1.3925820000 -0.5443900000
H -0.3108210000 0.4628390000 -1.0356260000
H 0.2601500000 1.1872890000 0.4835970000
C -1.0998830000 2.4253820000 -0.6726960000
H -1.8034210000 2.2778110000 -1.4886150000
Cl 1.5104920000 1.9267360000 -1.3859190000
C -0.2066320000 3.8624100000 1.1781950000
H 0.4702080000 4.6470140000 0.8223760000
H -0.7051620000 4.2424020000 2.0743150000
H 0.4085950000 3.0068590000 1.4611600000

A3 = A3.4B-Allylic chloride

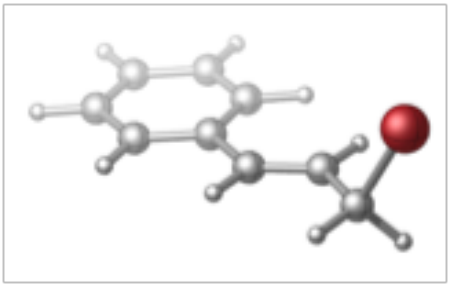


uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.243974 (Hartree/Particle)
Thermal correction to Energy= 0.257080
Thermal correction to Enthalpy= 0.258024
Thermal correction to Gibbs Free Energy= 0.201325

Sum of electronic and zero-point Energies= -812.928571
Sum of electronic and thermal Energies= -812.915465
Sum of electronic and thermal Enthalpies= -812.914521
Sum of electronic and thermal Free Energies= -812.971220

C	-1.0733560000	3.1319910000	0.0431630000
H	-0.1330810000	3.1802110000	0.5963110000
C	-0.9513590000	0.6540020000	0.1778290000
H	-1.6408700000	-0.0104170000	0.6973690000
H	-0.0586630000	0.8166590000	0.7797290000
C	-1.5935260000	1.9321800000	-0.2390650000
H	-2.5312280000	1.8551540000	-0.7891360000
Cl	-0.4070460000	-0.2957780000	-1.2902630000
C	-4.2833400000	9.5332080000	2.6267280000
H	-4.9875940000	8.9573090000	3.2362260000
H	-3.4252750000	9.7852340000	3.2586110000
H	-4.7746210000	10.4684900000	2.3418200000
C	-3.8439880000	8.7341930000	1.4009080000
H	-3.1573250000	9.3375140000	0.7951960000
H	-4.7151400000	8.5235500000	0.7690010000
C	-3.1650170000	7.4158450000	1.7718270000
H	-3.8492650000	6.8192350000	2.3893250000
H	-2.2847810000	7.6246010000	2.3940530000
C	-2.7435870000	6.5969300000	0.5518710000
H	-3.6234180000	6.4066050000	-0.0763980000
H	-2.0448540000	7.1840940000	-0.0579820000
C	-2.0959460000	5.2628480000	0.9207440000
H	-1.2019940000	5.4434130000	1.5307090000
H	-2.7880870000	4.6774130000	1.5384500000
C	-1.7118800000	4.4411540000	-0.3173980000
H	-1.0097000000	5.0270570000	-0.9237620000
H	-2.6012920000	4.2589680000	-0.9299620000

A3 = A3.4C-cinnamyl bromide

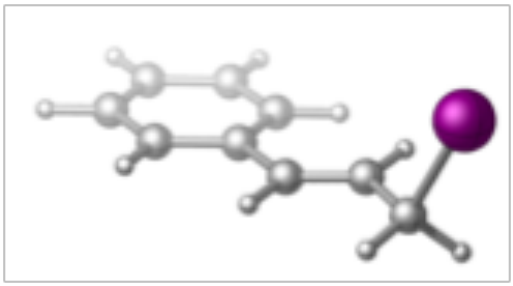


uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154692 (Hartree/Particle)
Thermal correction to Energy= 0.163870
Thermal correction to Enthalpy= 0.164814
Thermal correction to Gibbs Free Energy= 0.117870
Sum of electronic and zero-point Energies= -2921.783913
Sum of electronic and thermal Energies= -2921.774734
Sum of electronic and thermal Enthalpies= -2921.773790
Sum of electronic and thermal Free Energies= -2921.820735

C	-4.4334590000	6.3533330000	-0.4366720000
C	-3.3195570000	6.6403910000	0.3525330000
C	-2.2944630000	5.7023350000	0.4806630000
C	-2.3625150000	4.4645380000	-0.1763950000
C	-3.4905820000	4.1863150000	-0.9677130000
C	-4.5134610000	5.1219910000	-1.0957320000
H	-5.2327650000	7.0810940000	-0.5404450000
H	-3.2465930000	7.5935170000	0.8680780000
H	-1.4270130000	5.9307220000	1.0952860000
H	-3.5742130000	3.2376450000	-1.4899070000

H -5.3779370000 4.8912260000 -1.7114010000
C -1.2453160000 3.5168270000 -0.0073240000
H -0.4316780000 3.8659070000 0.6292070000
C 0.0267740000 1.4179320000 -0.2991660000
H -0.2536770000 0.4003360000 -0.0342710000
H 0.7168720000 1.8298200000 0.4338960000
C -1.1434970000 2.2952510000 -0.5523730000
H -1.9183860000 1.8936770000 -1.2021030000
Br 1.0962470000 1.1978930000 -1.9660200000

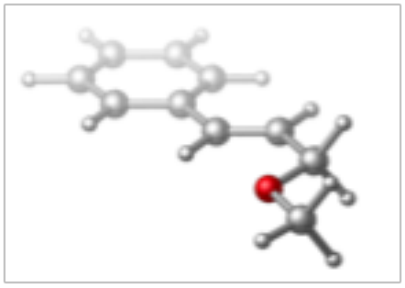
A3 = A3.4C-cinnamyl iodide



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.154159 (Hartree/Particle)
Thermal correction to Energy= 0.163434
Thermal correction to Enthalpy= 0.164378
Thermal correction to Gibbs Free Energy= 0.116677
Sum of electronic and zero-point Energies= -7268.337022
Sum of electronic and thermal Energies= -7268.327747
Sum of electronic and thermal Enthalpies= -7268.326803
Sum of electronic and thermal Free Energies= -7268.374504

C -4.4246520000 6.3635680000 -0.4465330000
C -3.2900020000 6.6616370000 0.3086050000
C -2.2762800000 5.7133170000 0.4497750000
C -2.3739500000 4.4549100000 -0.1639180000
C -3.5251900000 4.1638600000 -0.9165230000
C -4.5372420000 5.1097120000 -1.0567540000
H -5.2162310000 7.0985000000 -0.5584610000
H -3.1924170000 7.6310880000 0.7884160000
H -1.3935300000 5.9499080000 1.0389150000
H -3.6386650000 3.1933560000 -1.3908470000
H -5.4205070000 4.8680170000 -1.6407210000
C -1.2668250000 3.4981730000 0.0137950000
H -0.4806010000 3.8178730000 0.6984020000
C 0.0093930000 1.4068970000 -0.3091820000
H -0.2799160000 0.3682100000 -0.1661860000
H 0.6430240000 1.7537490000 0.5037860000
C -1.1384130000 2.3034830000 -0.5846710000
H -1.8761120000 1.9412350000 -1.2980010000
I 1.3559580000 1.3005760000 -2.0477600000

A3 = A3.4C-cinnamyl methoxide



uM06-2X/DGDZVP-SMD(acetonitrile)
Zero-point correction= 0.197537 (Hartree/Particle)
Thermal correction to Energy= 0.207992
Thermal correction to Enthalpy= 0.208936
Thermal correction to Gibbs Free Energy= 0.160716
Sum of electronic and zero-point Energies= -463.119568
Sum of electronic and thermal Energies= -463.109114
Sum of electronic and thermal Enthalpies= -463.108169
Sum of electronic and thermal Free Energies= -463.156389

C	-4.4963660000	6.3228500000	-0.4172130000	H	-0.4349410000	3.9370910000	0.6903820000
C	-3.3876150000	6.6468150000	0.3651990000	C	0.1758650000	1.5431300000	-0.4176460000
C	-2.3300280000	5.7443530000	0.4863840000	H	0.6830620000	1.3793850000	-1.3814560000
C	-2.3550970000	4.5046470000	-0.1705630000	H	-0.1605790000	0.5548190000	-0.0667440000
C	-3.4808860000	4.1881460000	-0.9510330000	C	-1.0156380000	2.4255960000	-0.6255890000
C	-4.5368940000	5.0881200000	-1.0732460000	H	-1.7421700000	2.0399220000	-1.3388950000
H	-5.3218050000	7.0217900000	-0.5144660000	O	1.0697410000	2.1133470000	0.5135770000
H	-3.3444600000	7.6010060000	0.8824580000	C	2.1854410000	1.2714560000	0.7497510000
H	-1.4681870000	6.0026000000	1.0970890000	H	2.7547030000	1.1025350000	-0.1731710000
H	-3.5397060000	3.2326360000	-1.4646510000	H	2.8237390000	1.7721700000	1.4790130000
H	-5.3986110000	4.8251950000	-1.6800830000	H	1.8679600000	0.3016170000	1.1532910000
C	-1.2009000000	3.5970790000	-0.0044590000				

Appendix 4: Supporting Information Chapter 5

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using unrestricted B3LYP/6-31G(d)-LANL2DZ (for Br, S, and Ni) with the "guess=mix" keyword as implemented in Gaussian09. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). To refine the energies calculated, we carried out single point energy calculations using UM06/6-311+G(d,p)-SDD (for Br, S, and Ni) in THF using SMD as the solvation model. Similar methods have been used before to rationalize selectivity and reactivity on related systems. All structural figures were generated using CYLview. Exhaustive conformational searches were performed for all structures to elucidate the lowest energy profiles for each potential reaction pathway.

Full Reference of Gaussian09:

Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

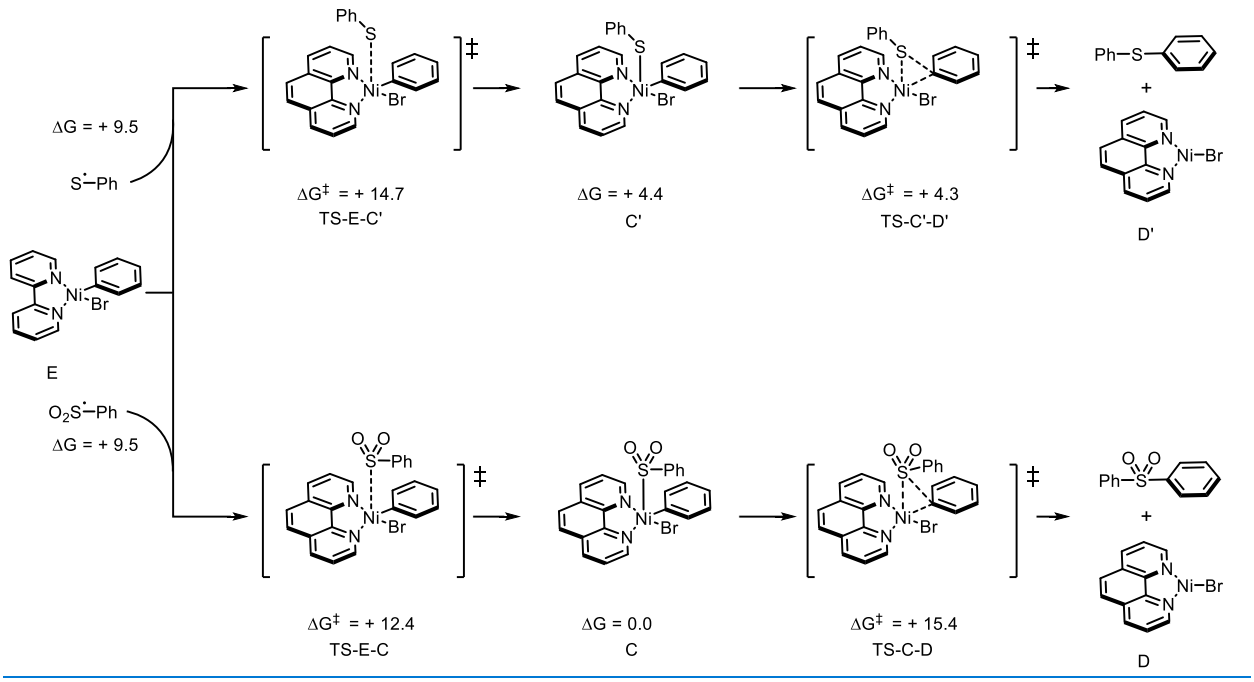


Figure A4.1: Competing mechanistic pathway (kcal/mol; 298.15 K).

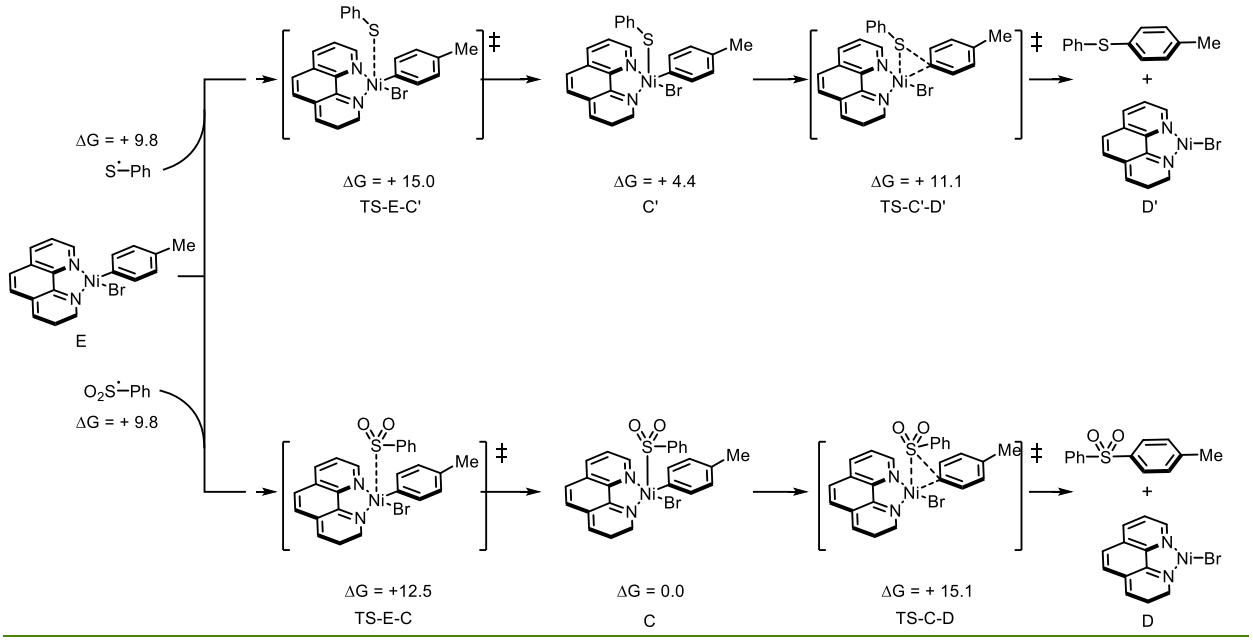


Figure A4.2: Competing mechanistic pathway (kcal/mol; 298.15 K).

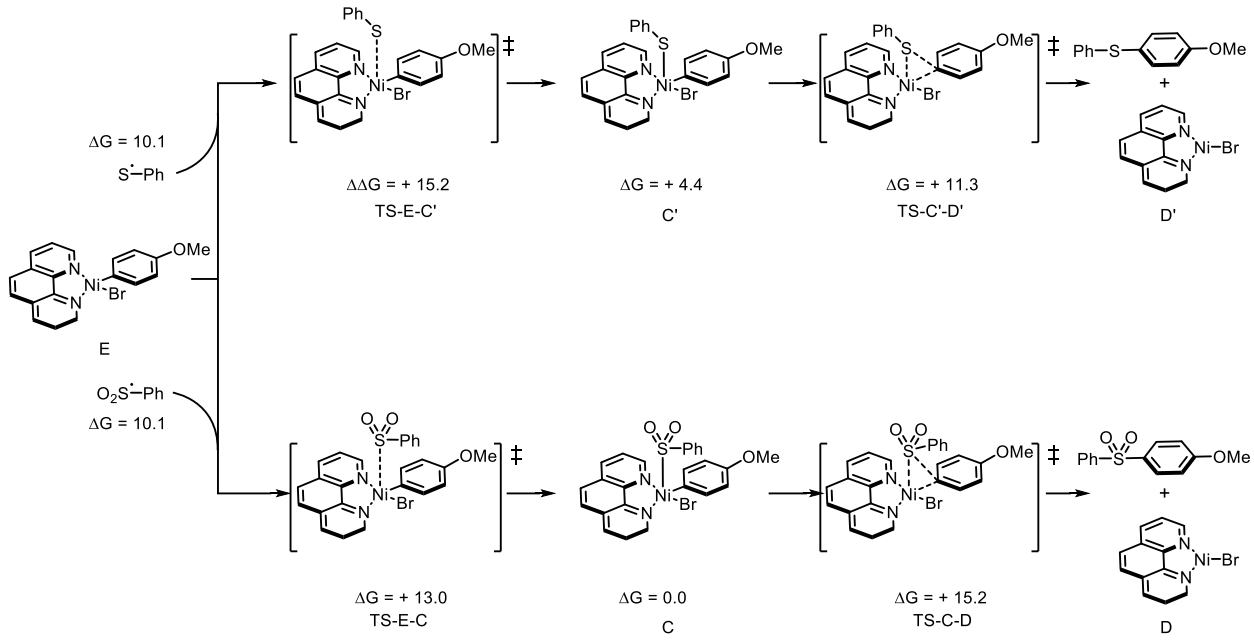


Figure A4.3: Competing mechanistic pathway (kcal/mol; 298.15 K).

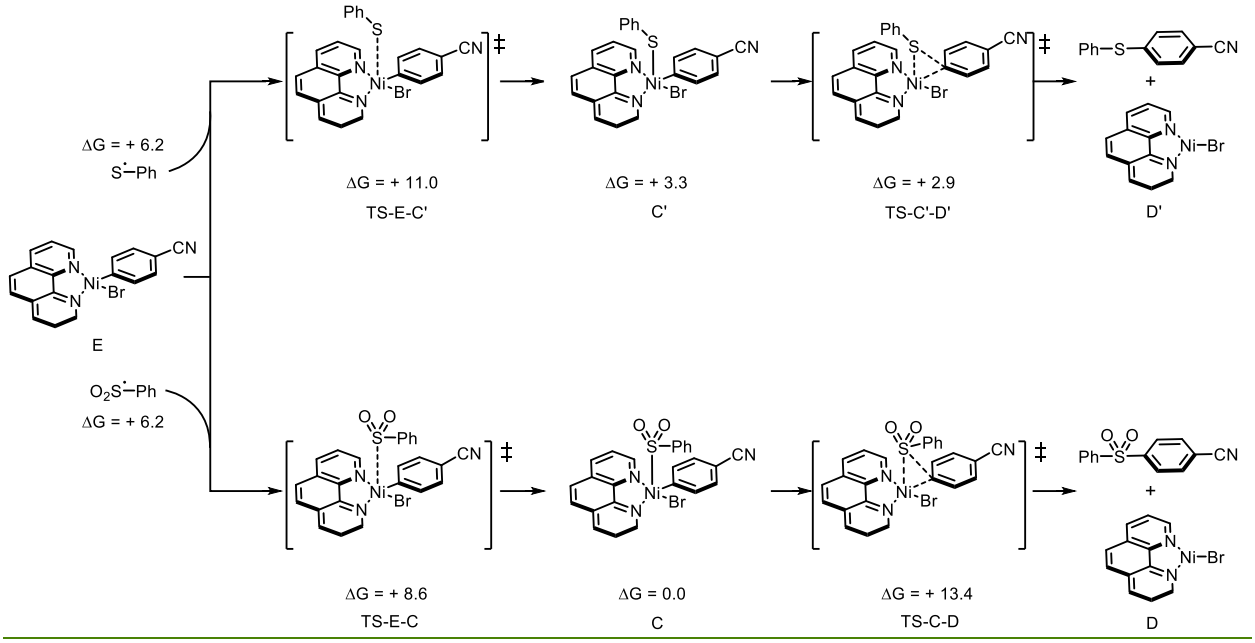


Figure A4.4: Competing mechanistic pathway (kcal/mol; 298.15 K).

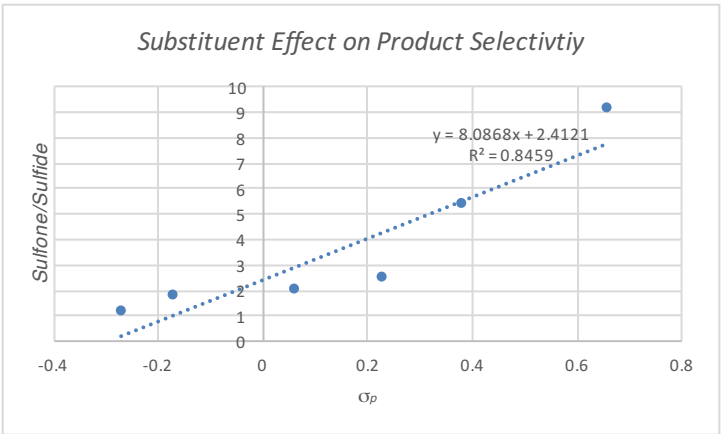
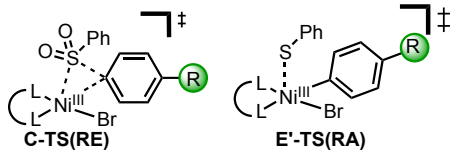


Figure A4.5: Correlation between experimental product selectivity (sulfone/sulfide) as a function of Hammett σ_p.



R =	σ (para)	ΔG ‡	ΔG ‡
CN	0.66	13.4	11.0
Ac	0.38	13.5	12.7
Cl	0.23	14.8	12.4
F	0.06	15.3	13.1
Me	-0.17	15.1	15.0
OMe	-0.27	15.2	15.2

Figure A4.6: Correlation between overall free energy barriers (UM06/6-311+G(d,p)-(Br,Ni, Cl, and S-SDD)-TMH(SMD)//UB3LYP/6-31G(d)-(Br, Ni, Cl, and S-LANL2DZ) for reductive elimination leading to sulfone and radical addition leading to sulfide, with respect to Ni(III)-aryl-bromo-SO_2Ph, and Hammett σ_p.

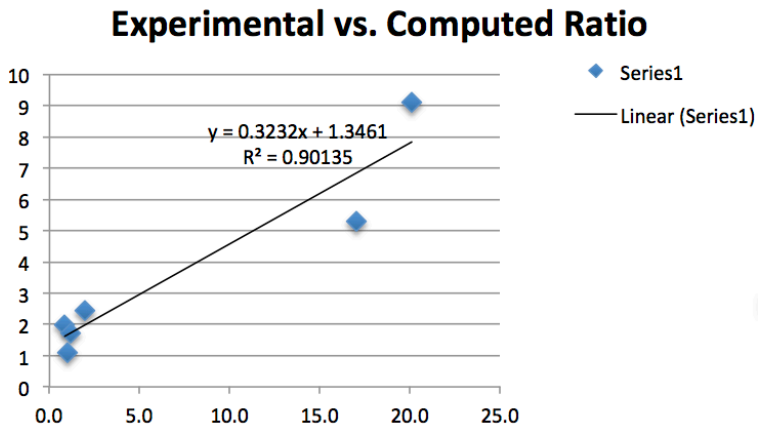
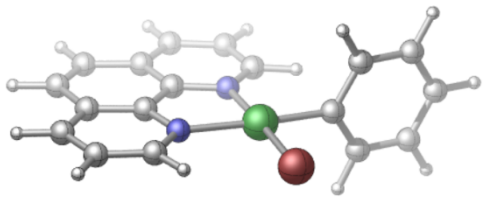


Figure A4.7: Experimental vs. calculated product selectivity.[Error! Bookmark not defined.] Calculated p roduct selectivity was determine from free energy difference between "complex disproportionation" threshold (15.2 kcal/mol; UM06/6-311+G(d,p)-(Br,Ni, Cl, and S-SDD-TMH(SMD)//UB3LYP/6-31G(d)-(Br, Ni, Cl, and S-LANL2DZ)) and overall barrier for sulfone reductive elimination.

Energies and Coordinates

Thesis = D, A4 = A4.1-E

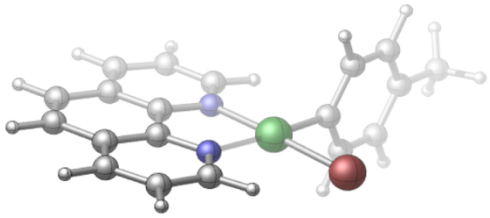


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.265679 (Hartree/Particle)
Thermal correction to Energy= 0.283659
Thermal correction to Enthalpy= 0.284603
Thermal correction to Gibbs Free Energy= 0.217389
Sum of electronic and zero-point Energies= -985.543483
Sum of electronic and thermal Energies= -985.525503
Sum of electronic and thermal Enthalpies= -985.524559
Sum of electronic and thermal Free Energies= -985.591774
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-987.2725757

C	-0.4332	1.90515	0.86978
C	1.42778	2.28609	2.18064
C	0.9153	3.53141	2.59586
C	-0.31036	3.95866	2.12322
C	-1.03054	3.13578	1.2278
C	-1.09906	1.01641	-0.03387
C	-1.05463	-0.99723	-1.16927
C	-2.309	-0.73054	-1.74834
C	-2.96526	0.4482	-1.45338
C	-2.35982	1.36848	-0.56907
H	2.38634	1.90822	2.52492
H	1.49381	4.13896	3.28396
H	-0.7262	4.91511	2.42947
H	-0.51697	-1.91266	-1.38257
H	-2.74249	-1.46176	-2.4225
H	-3.93454	0.67522	-1.88931
N	0.77194	1.4924	1.34006
N	-0.4563	-0.14991	-0.33137
Ni	1.28826	-0.33935	0.57899
C	1.19353	-3.20707	0.37805
C	2.42895	-3.32197	-2.11817
C	1.34795	-4.43671	-0.27306
H	0.72662	-3.18461	1.36065
C	1.96306	-4.49779	-1.52557
H	2.9213	-3.35933	-3.08799
H	0.99306	-5.34821	0.20397
H	2.08712	-5.45304	-2.02996
Br	3.3548	-0.47471	1.73041
C	2.27333	-2.09355	-1.46542
H	2.65785	-1.19201	-1.93809

C	1.64562	-2.01817	-0.21316
C	-2.94612	2.62376	-0.18962
H	-3.91488	2.88688	-0.60533
C	-2.3104	3.47076	0.67057
H	-2.76683	4.41714	0.9477

Thesis = D, A4 = A4.2-E

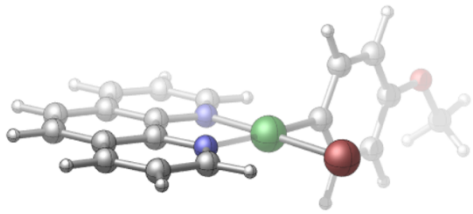


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.293184 (Hartree/Particle)
Thermal correction to Energy= 0.313069
Thermal correction to Enthalpy= 0.314013
Thermal correction to Gibbs Free Energy= 0.241789
Sum of electronic and zero-point Energies= -1024.832773
Sum of electronic and thermal Energies= -1024.812888
Sum of electronic and thermal Enthalpies= -1024.811943
Sum of electronic and thermal Free Energies= -1024.884167

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1026.5665331

C	-0.61609	2.40781	1.06305
C	1.24142	2.79108	2.37806
C	0.72636	4.03561	2.79232
C	-0.49887	4.46142	2.31691
C	-1.21577	3.63765	1.41982
C	-1.27905	1.51793	0.15772
C	-1.22926	-0.49601	-0.9771
C	-2.4826	-0.23106	-1.55911
C	-3.14118	0.94696	-1.26591
C	-2.53904	1.86815	-0.38041
H	2.19973	2.41443	2.72437
H	1.30252	4.64378	3.48185
H	-0.91664	5.41729	2.62232
H	-0.68929	-1.41052	-1.18857
H	-2.91365	-0.96292	-2.23414
H	-4.10975	1.17258	-1.70415
N	0.5885	1.99652	1.53584
N	-0.63405	0.3525	-0.13803
Ni	1.10887	0.1646	0.77537
C	1.02206	-2.70594	0.57313
C	2.2497	-2.82666	-1.91585
C	1.1805	-3.93444	-0.07785
H	0.55063	-2.68885	1.55376
C	1.79792	-4.01767	-1.33236
H	2.73778	-2.86055	-2.88919
H	0.82357	-4.84457	0.40262
Br	3.17421	0.03368	1.9302
C	2.09298	-1.59688	-1.26806
H	2.47138	-0.69791	-1.75068
C	1.46885	-1.51476	-0.01508
C	-3.12824	3.12278	-0.00238
H	-4.09641	3.38498	-0.42011
C	-2.49506	3.97076	0.85931
H	-2.95287	4.91652	1.13611
C	2.00539	-5.35069	-2.01598
H	1.95996	-5.2561	-3.10723
H	2.98682	-5.77955	-1.77082
H	1.24866	-6.08193	-1.7097

Thesis = D, A4 = A4.3-E



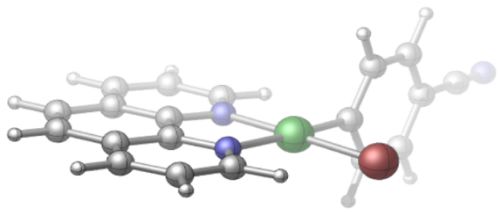
UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.298433 (Hartree/Particle)
Thermal correction to Energy= 0.319041
Thermal correction to Enthalpy= 0.319985
Thermal correction to Gibbs Free Energy= 0.246420
Sum of electronic and zero-point Energies= -1100.030457
Sum of electronic and thermal Energies= -1100.009849
Sum of electronic and thermal Enthalpies= -1100.008905
Sum of electronic and thermal Free Energies= -1100.082470

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=- 1101.7649963

C	-0.60225	2.6667	0.99179
C	1.2541	3.04418	2.30994
C	0.7551	4.30249	2.70162
C	-0.46152	4.73825	2.21331
C	-1.1859	3.91054	1.32596
C	-1.27373	1.77216	0.09747

C	-1.24742	-0.26041	-1.00425
C	-2.49477	0.01225	-1.59558
C	-3.13795	1.20401	-1.32443
C	-2.52653	2.13112	-0.45152
H	2.20518	2.65945	2.6671
H	1.33674	4.9133	3.38419
H	-0.86684	5.70483	2.50129
H	-0.71786	-1.18457	-1.19946
H	-2.93319	-0.72431	-2.26069
H	-4.10141	1.43599	-1.77055
N	0.59393	2.24558	1.47717
N	-0.64358	0.59362	-0.17716
Ni	1.0937	0.3956	0.74581
C	1.02692	-2.48272	0.59141
C	2.19626	-2.62853	-1.92704
C	1.18067	-3.73148	-0.03079
H	0.58693	-2.45687	1.58613
C	1.76802	-3.8052	-1.29757
H	2.66231	-2.70417	-2.90581
H	0.85088	-4.62685	0.48601
Br	3.15013	0.2566	1.91585
C	2.03535	-1.39657	-1.29392
H	2.39409	-0.50294	-1.80066
C	1.43819	-1.29768	-0.02549
C	-3.09937	3.4	-0.09655
H	-4.0619	3.66914	-0.52278
C	-2.45775	4.25272	0.75415
H	-2.90311	5.20933	1.01342
O	1.96858	-4.96695	-2.00208
C	1.61876	-6.18743	-1.37952
H	0.54168	-6.24453	-1.16584
H	1.88414	-6.97587	-2.08753
H	2.17345	-6.3408	-0.44342

Thesis = D , A4 = A4.4-E

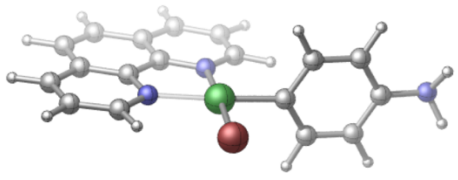


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.264442 (Hartree/Particle)
Thermal correction to Energy= 0.284218
Thermal correction to Enthalpy= 0.285162
Thermal correction to Gibbs Free Energy= 0.213531
Sum of electronic and zero-point Energies= -1077.790561
Sum of electronic and thermal Energies= -1077.770786
Sum of electronic and thermal Enthalpies= -1077.769841
Sum of electronic and thermal Free Energies= -1077.841472

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1079.4909238

C	-0.50445	2.10063	0.94495
C	1.36033	2.47396	2.25369
C	0.85133	3.71948	2.67233
C	-0.37407	4.15078	2.20274
C	-1.09777	3.3316	1.30669
C	-1.17426	1.21576	0.04036
C	-1.13643	-0.79538	-1.09958
C	-2.3908	-0.52551	-1.67671
C	-3.04347	0.6543	-1.37778
C	-2.43482	1.57145	-0.49234
H	2.31854	2.09451	2.5963
H	1.43263	4.32385	3.36072
H	-0.78677	5.10753	2.51191
H	-0.60391	-1.71238	-1.31786
H	-2.82661	-1.25434	-2.35177
H	-4.01276	0.88417	-1.81194
N	0.70077	1.68363	1.4123
N	-0.53478	0.04852	-0.26075
Ni	1.20867	-0.1393	0.6504
C	1.13974	-3.01088	0.46466
C	2.39298	-3.12062	-2.02833
C	1.30776	-4.24166	-0.16825
H	0.66824	-2.98825	1.44416
C	1.9322	-4.305	-1.42657
H	2.88705	-3.1691	-2.99461
H	0.96288	-5.15714	0.30408
Br	3.27618	-0.2889	1.79405
C	2.21732	-1.89777	-1.38255
H	2.59482	-0.99697	-1.86038
C	1.57951	-1.81753	-0.13285
C	-3.0181	2.82727	-0.10935
H	-3.98678	3.094	-0.52263
C	-2.37813	3.67074	0.75184
H	-2.83109	4.61755	1.03258
C	2.09211	-5.56376	-2.09186
N	2.21194	-6.58525	-2.63762

(Byp)Ni(II)-Br-Aniline



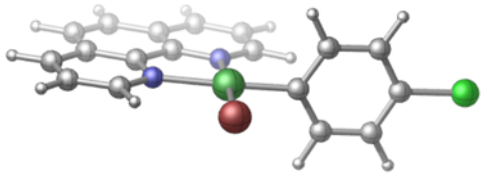
UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.282352 (Hartree/Particle)
Thermal correction to Energy= 0.301836
Thermal correction to Enthalpy= 0.302780
Thermal correction to Gibbs Free Energy= 0.232308
Sum of electronic and zero-point Energies= -1040.877404
Sum of electronic and thermal Energies= -1040.857920
Sum of electronic and thermal Enthalpies= -1040.856976
Sum of electronic and thermal Free Energies= -1040.927448

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1042.6175588

C	-0.43359	1.90682	0.87098
C	1.43292	2.27383	2.17774
C	0.92915	3.52132	2.5969
C	-0.29528	3.95701	2.12833
C	-1.02253	3.14032	1.23319
C	-1.10728	1.02391	-0.03336
C	-1.07647	-0.98753	-1.17327
C	-2.33089	-0.71239	-1.7485
C	-2.98	0.46942	-1.44942
C	-2.36727	1.38438	-0.56462
H	2.39009	1.88916	2.51854
H	1.51313	4.12398	3.28473
H	-0.70453	4.91533	2.43762
H	-0.54287	-1.90483	-1.38912
H	-2.77001	-1.43978	-2.4232
H	-3.94908	0.70281	-1.88252
N	0.77016	1.48564	1.33722
N	-0.47175	-0.145	-0.335
Ni	1.2752	-0.34958	0.56951
C	1.16883	-3.22268	0.3479
C	2.38829	-3.33515	-2.14727
C	1.31462	-4.45113	-0.30359
H	0.70766	-3.2118	1.3335
C	1.92732	-4.52469	-1.56356
H	2.87417	-3.37009	-3.12162
H	0.95656	-5.36356	0.17168
N	2.02432	-5.75294	-2.25068
Br	3.34361	-0.49715	1.71896
C	2.237	-2.11205	-1.48741
H	2.6264	-1.2154	-1.96558
C	1.61558	-2.02836	-0.23375
C	-2.94553	2.64235	-0.18093
H	-3.9138	2.91244	-0.59339
C	-2.30209	3.48387	0.67952
H	-2.75171	4.43237	0.96045
H	2.80196	-5.78466	-2.90125
H	2.06622	-6.55424	-1.63011

(Byp)Ni(II)-Br-Chlorobenzene

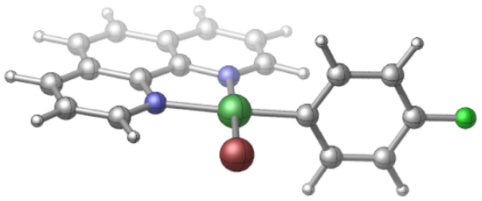


UB3LYP/6-31g(d)-(Br, Ni, Cl-LANL2DZ)-gas
Zero-point correction= 0.255986 (Hartree/Particle)
Thermal correction to Energy= 0.275243
Thermal correction to Enthalpy= 0.276187
Thermal correction to Gibbs Free Energy= 0.205470
Sum of electronic and zero-point Energies= -999.898666
Sum of electronic and thermal Energies= -999.879409
Sum of electronic and thermal Enthalpies= -999.878465
Sum of electronic and thermal Free Energies= -999.949182
UM06/6-311+g(d,p)-(Br, Ni, Cl -SDD)-SMD(THF)
HF=-1446.8285917

C	-0.43665	1.90643	0.86835
C	1.42806	2.28237	2.1759
C	0.91827	3.52777	2.59397
C	-0.30776	3.95769	2.1247
C	-1.03106	3.13723	1.22959
C	-1.106	1.02037	-0.03555
C	-1.06642	-0.99113	-1.17464
C	-2.32134	-0.72233	-1.75131
C	-2.97531	0.45685	-1.45272
C	-2.36713	1.37485	-0.56788
H	2.38674	1.90333	2.51803
H	1.49937	4.13319	3.28168
H	-0.72129	4.91429	2.43337
H	-0.53174	-1.90726	-1.39156
H	-2.75671	-1.45183	-2.426
H	-3.94503	0.68573	-1.88654
N	0.76901	1.4908	1.3354
N	-0.46549	-0.14631	-0.33622
Ni	1.27967	-0.33605	0.57341
C	1.19536	-3.20736	0.37567
C	2.45112	-3.32376	-2.11672
C	1.3559	-4.44415	-0.26106
H	0.72223	-3.18931	1.35488
C	1.97869	-4.47778	-1.50304
H	2.94665	-3.37929	-3.08065
H	1.00859	-5.3617	0.20293

Cl	2.18182	-6.0686	-2.34395
Br	3.34684	-0.47746	1.72029
C	2.27975	-2.09794	-1.46228
H	2.66557	-1.20029	-1.94013
C	1.64235	-2.01636	-0.2153
C	-2.95133	2.63033	-0.1852
H	-3.92049	2.89593	-0.59823
C	-2.31188	3.47489	0.67522
H	-2.76571	4.42145	0.95556

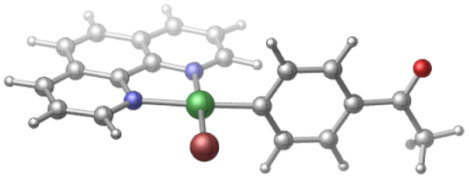
(Byp)Ni(II)-Br-Fluorobenzene



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.257561 (Hartree/Particle)
Thermal correction to Energy= 0.276373
Thermal correction to Enthalpy= 0.277318
Thermal correction to Gibbs Free Energy= 0.207968
Sum of electronic and zero-point Energies= -1084.785016
Sum of electronic and thermal Energies= -1084.766203
Sum of electronic and thermal Enthalpies= -1084.765259
Sum of electronic and thermal Free Energies= -1084.834609
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1086.5146061

C	-0.43621	1.90657	0.86885
C	1.42726	2.28226	2.17784
C	0.91742	3.5278	2.59548
C	-0.30813	3.95799	2.12511
C	-1.03076	3.13762	1.22946
C	-1.10505	1.0204	-0.03549
C	-1.065	-0.99144	-1.17386
C	-2.3195	-0.72236	-1.75136
C	-2.97355	0.45706	-1.45377
C	-2.36578	1.37512	-0.56879
H	2.3856	1.90266	2.52056
H	1.49801	4.13317	3.2837
H	-0.72179	4.91471	2.43333
H	-0.52899	-1.90723	-1.38918
H	-2.75478	-1.45188	-2.42614
H	-3.94293	0.68609	-1.88836
N	0.76888	1.49073	1.33684
N	-0.46449	-0.14637	-0.33537
Ni	1.28083	-0.33891	0.57386
C	1.19566	-3.21111	0.37514
C	2.44479	-3.32598	-2.12071
C	1.35779	-4.44712	-0.26233
H	0.72535	-3.19131	1.35566
C	1.97999	-4.48118	-1.50421
H	2.93763	-3.39455	-3.08617
H	1.01965	-5.37315	0.19356
F	2.1378	-5.67347	-2.13131
Br	3.34756	-0.47717	1.72365
C	2.27313	-2.09967	-1.46755
H	2.65452	-1.20018	-1.9455
C	1.63946	-2.01979	-0.21821
C	-2.94995	2.63084	-0.18681
H	-3.91875	2.8966	-0.60067
C	-2.31104	3.47545	0.67397
H	-2.76492	4.42218	0.95378

(Byp)Ni(II)-Br-Acetophenone

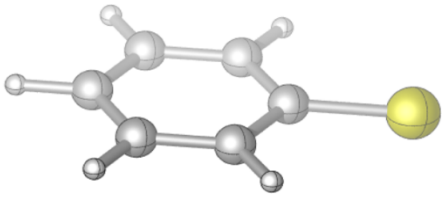


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.303391 (Hartree/Particle)
Thermal correction to Energy= 0.324917
Thermal correction to Enthalpy= 0.325861
Thermal correction to Gibbs Free Energy= 0.250082
Sum of electronic and zero-point Energies= -1138.153382
Sum of electronic and thermal Energies= -1138.131857
Sum of electronic and thermal Enthalpies= -1138.130912
Sum of electronic and thermal Free Energies= -1138.206691
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1139.8803023

C	-0.43736	1.90202	0.86997
C	1.41688	2.25473	2.19884
C	0.91168	3.50045	2.62154
C	-0.30677	3.94238	2.1437
C	-1.02681	3.13406	1.23501
C	-1.10317	1.02809	-0.04829
C	-1.06472	-0.97308	-1.20574
C	-2.3114	-0.6903	-1.79344
C	-2.96086	0.49023	-1.49055

C	-2.35613	1.39589	-0.59077
H	2.36939	1.86631	2.54758
H	1.49017	4.09662	3.31944
H	-0.71671	4.89942	2.45575
H	-0.53234	-1.88895	-1.42939
H	-2.74366	-1.40988	-2.48065
H	-3.9241	0.72987	-1.9329
N	0.76051	1.47434	1.34595
N	-0.46724	-0.14017	-0.35293
Ni	1.26351	-0.35124	0.57678
C	1.23195	-3.22425	0.40477
C	2.3608	-3.32486	-2.14058
C	1.39553	-4.45291	-0.23775
H	0.80874	-3.2065	1.40635
C	1.95728	-4.52123	-1.5233
H	2.80362	-3.38372	-3.13051
H	1.08378	-5.36051	0.27238
C	2.14652	-5.80376	-2.26153
Br	3.3145	-0.52519	1.74886
C	2.20112	-2.10109	-1.49507
H	2.53846	-1.19465	-1.99344
C	1.62332	-2.02697	-0.2146
C	-2.93579	2.65205	-0.20344
H	-3.8987	2.92775	-0.62437
C	-2.2996	3.48505	0.67055
H	-2.74985	4.4324	0.954
O	2.58652	-5.81942	-3.40415
C	1.78355	-7.11107	-1.5682
H	0.72353	-7.13141	-1.2873
H	2.36608	-7.24413	-0.64875
H	1.99113	-7.93692	-2.25115

Thesis =Thiophenol radical, A4 = Thiophenol radical

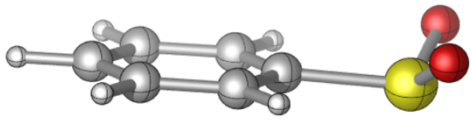


UB3LYP-(S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.090799 (Hartree/Particle)
Thermal correction to Energy= 0.096381
Thermal correction to Enthalpy= 0.097325
Thermal correction to Gibbs Free Energy= 0.060292
Sum of electronic and zero-point Energies= -241.631247
Sum of electronic and thermal Energies= -241.625665
Sum of electronic and thermal Enthalpies= -241.624721
Sum of electronic and thermal Free Energies= -241.66175

UM06/6-311+g(d,p)-(S-SDD)-SMD(THF)
HF=-629.6371416

C	0.37694	-0.33749	-1.27684
C	1.37058	-0.27635	-0.30737
C	1.04345	0.06272	1.01212
C	-0.28462	0.34158	1.36075
C	-1.28395	0.28286	0.39706
C	-0.96987	-0.05834	-0.94077
H	0.61524	-0.59853	-2.30281
H	2.40189	-0.49155	-0.57286
H	1.82269	0.10964	1.76795
H	-0.53334	0.60385	2.38533
H	-2.31685	0.49634	0.65223
S	-2.24215	-0.13474	-2.17479

Thesis = phenyl-λ^5-sulfanedione radical, A4 = phenyl-λ^5-sulfanedione radical



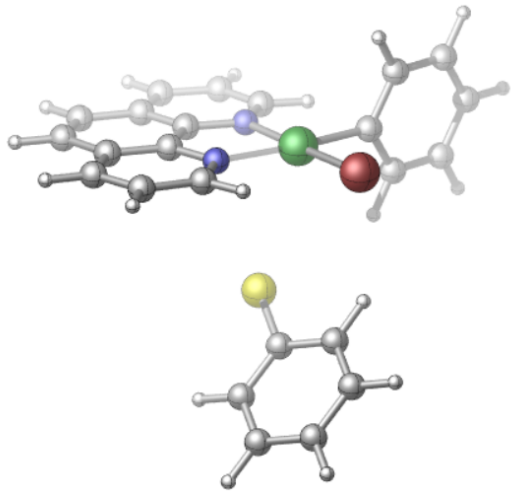
UB3LYP-(S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.097095 (Hartree/Particle)
Thermal correction to Energy= 0.105000
Thermal correction to Enthalpy= 0.105944
Thermal correction to Gibbs Free Energy= 0.063082
Sum of electronic and zero-point Energies= -391.918574
Sum of electronic and thermal Energies= -391.910670
Sum of electronic and thermal Enthalpies= -391.909726
Sum of electronic and thermal Free Energies= -391.952587

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-779.9046333

C	-1.11814	0.00012	-0.51761
C	-0.41916	0.33519	-1.67943
C	0.95981	0.55687	-1.63009
C	1.65454	0.44197	-0.42287
C	0.97367	0.10763	0.7499
C	-0.395	-0.10875	0.66259

H	-2.18578	-0.19144	-0.52573
H	-0.95313	0.41785	-2.62159
H	1.49611	0.8194	-2.5375
H	2.72751	0.6074	-0.39149
H	1.48733	-0.00254	1.69897
S	-1.33082	-0.50722	2.23872
O	-0.27604	-1.18484	3.19781
O	-2.62091	-1.29165	1.77833

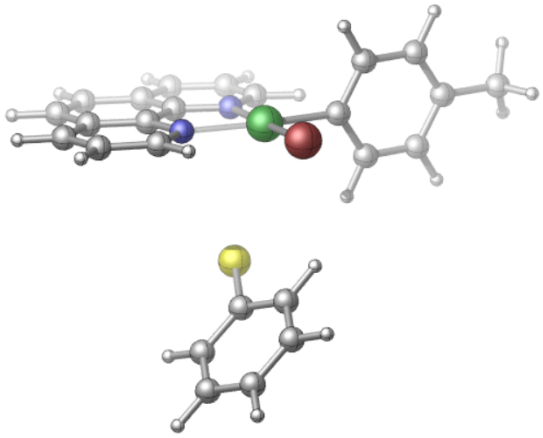
Thesis = D-TS-E, A4 = A4.1-TS-E-C'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -37.72 cm^{-1}
Zero-point correction= 0.356856 (Hartree/Particle)
Thermal correction to Energy= 0.381983
Thermal correction to Enthalpy= 0.382928
Thermal correction to Gibbs Free Energy= 0.294710
Sum of electronic and zero-point Energies= -1227.178275
Sum of electronic and thermal Energies= -1227.153148
Sum of electronic and thermal Enthalpies= -1227.152204
Sum of electronic and thermal Free Energies= -1227.240422
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1616.9185565

C	-1.05231	2.13083	-0.24943
C	1.00271	2.71756	0.62181
C	0.44387	3.84408	1.25769
C	-0.90593	4.10499	1.12324
C	-1.70429	3.23391	0.34828
C	-1.79333	1.20213	-1.04926
C	-1.75835	-0.71683	-2.33862
C	-3.14022	-0.61208	-2.58293
C	-3.85569	0.4361	-2.03893
C	-3.18189	1.38754	-1.24162
H	2.05838	2.47316	0.69605
H	1.0848	4.49251	1.84596
H	-1.36011	4.96757	1.60409
H	-1.17167	-1.52958	-2.74851
H	-3.62346	-1.36311	-3.19892
H	-4.92348	0.53729	-2.21417
N	0.27529	1.8825	-0.1125
N	-1.09397	0.16478	-1.59195
Ni	0.83132	0.19056	-1.13264
C	1.00914	-2.63735	-1.63069
C	1.77438	-2.37138	-4.29962
C	1.1821	-3.77448	-2.42984
H	0.71101	-2.75569	-0.5913
C	1.56125	-3.64536	-3.76768
H	2.0813	-2.25925	-5.33771
H	1.02216	-4.76267	-2.00249
C	1.60616	-1.2355	-3.49941
H	1.80003	-0.25424	-3.92721
C	1.21218	-1.35394	-2.15854
C	2.08483	-1.44018	2.7469
C	3.07724	-1.37431	3.71847
C	2.75044	-1.03936	5.03828
C	1.42256	-0.75582	5.38705
C	0.42534	-0.80449	4.42116
C	0.73991	-1.15734	3.08641
H	2.33182	-1.67888	1.71813
H	4.1086	-1.58126	3.44782
H	3.52938	-0.99466	5.79485
H	1.17379	-0.49384	6.41196
H	-0.60651	-0.58251	4.6749
S	-0.53649	-1.25091	1.85701
C	-3.82145	2.5161	-0.62442
H	-4.88873	2.65151	-0.77669
C	-3.11456	3.40089	0.1368
H	-3.61203	4.2497	0.59806
Br	3.14702	0.36966	-0.60232
H	1.69746	-4.52839	-4.38754

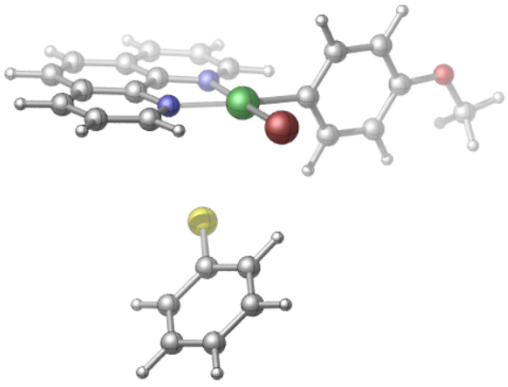
Thesis = D-TS-E, A4 = A4.2-TS-E-C'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -37.97 cm^{-1}
Zero-point correction= 0.384385 (Hartree/Particle)
Thermal correction to Energy= 0.411411
Thermal correction to Enthalpy= 0.412356
Thermal correction to Gibbs Free Energy= 0.319240
Sum of electronic and zero-point Energies= -1266.467511
Sum of electronic and thermal Energies= -1266.440485
Sum of electronic and thermal Enthalpies= -1266.439541
Sum of electronic and thermal Free Energies= -1266.532656
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1656.212499

C	-1.15934	2.46207	0.0458
C	0.89382	3.04235	0.92558
C	0.33566	4.17002	1.56002
C	-1.01286	4.43489	1.42039
C	-1.81057	3.56662	0.64163
C	-1.89977	1.53603	-0.75764
C	-1.86477	-0.38209	-2.04823
C	-3.24529	-0.27311	-2.29826
C	-3.96011	0.77669	-1.7565
C	-3.28698	1.72561	-0.95565
H	1.94849	2.79485	1.0038
H	0.97608	4.81622	2.15129
H	-1.46649	5.29844	1.90002
H	-1.27818	-1.19604	-2.45589
H	-3.72817	-1.02226	-2.91685
H	-5.02687	0.88105	-1.93617
N	0.167	2.20985	0.18776
N	-1.20113	0.49705	-1.29802
Ni	0.72227	0.51639	-0.83113
C	0.8892	-2.31399	-1.33429
C	1.67129	-2.05809	-3.989
C	1.0619	-3.4497	-2.13414
H	0.57795	-2.43684	-0.29919
C	1.45626	-3.34316	-3.47383
H	1.98213	-1.94404	-5.02684
H	0.88831	-4.43629	-1.70573
C	1.50482	-0.92015	-3.19295
H	1.70328	0.05761	-3.62675
C	1.10228	-1.03008	-1.85473
C	1.95403	-1.13691	3.04028
C	2.94768	-1.08364	4.01138
C	2.6244	-0.75381	5.33333
C	1.29889	-0.46262	5.68481
C	0.30058	-0.49861	4.7195
C	0.61148	-0.8463	3.38255
H	2.19848	-1.37142	2.00995
H	3.97732	-1.29635	3.73864
H	3.40427	-0.71893	6.08946
H	1.05286	-0.20451	6.71137
H	-0.72941	-0.27043	4.97533
S	-0.66653	-0.92363	2.15365
C	-3.9258	2.85558	-0.34025
H	-4.99205	2.99421	-0.49682
C	-3.21949	3.73776	0.42452
H	-3.71641	4.58767	0.88437
Br	3.03662	0.69028	-0.29192
C	1.67799	-4.57371	-4.32476
H	2.71664	-4.92649	-4.2597
H	1.03608	-5.4036	-4.00739
H	1.47214	-4.37445	-5.38281

Thesis = D-TS-E , A4 = A4.3-TS-E-C'

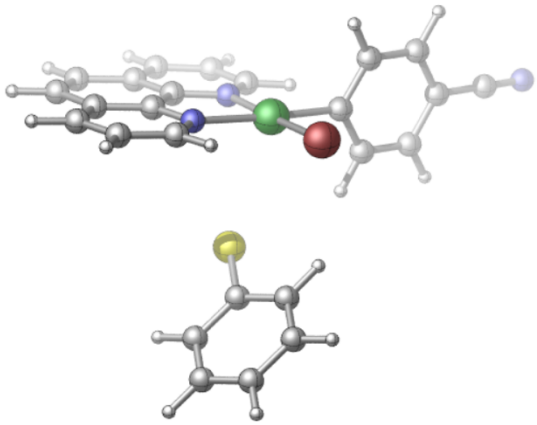


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -37.49 cm^{-1}
Zero-point correction= 0.389646 (Hartree/Particle)
Thermal correction to Energy= 0.417398
Thermal correction to Enthalpy= 0.418342

Thermal correction to Gibbs Free Energy= 0.323738
Sum of electronic and zero-point Energies= -1341.665220
Sum of electronic and thermal Energies= -1341.637468
Sum of electronic and thermal Enthalpies= -1341.636524
Sum of electronic and thermal Free Energies= -1341.731128
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1731.4110566

C	-1.14936	2.62952	0.05015
C	0.9139	3.20555	0.90867
C	0.36721	4.34199	1.53741
C	-0.98079	4.61354	1.40593
C	-1.78953	3.74319	0.64103
C	-1.90132	1.70123	-0.73976
C	-1.88661	-0.22729	-2.01499
C	-3.26811	-0.11182	-2.25671
C	-3.97294	0.9465	-1.71835
C	-3.28867	1.89769	-0.92973
H	1.96781	2.9529	0.98054
H	1.016	4.98969	2.1178
H	-1.42557	5.48404	1.88127
H	-1.30668	-1.04723	-2.4202
H	-3.75964	-0.86248	-2.86659
H	-5.04021	1.05601	-1.89181
N	0.17657	2.3706	0.18409
N	-1.21276	0.65365	-1.27623
Ni	0.71462	0.66482	-0.82443
C	0.87201	-2.17055	-1.30375
C	1.63287	-1.94066	-3.96963
C	1.03636	-3.32805	-2.08184
H	0.57535	-2.28414	-0.2634
C	1.41658	-3.21279	-3.42215
H	1.93987	-1.86922	-5.00963
H	0.8703	-4.29995	-1.62834
C	1.47125	-0.80165	-3.18221
H	1.67144	0.17025	-3.62774
C	1.07641	-0.89477	-1.83693
C	1.94785	-0.89029	3.08338
C	2.93597	-0.79216	4.05664
C	2.59844	-0.44988	5.37187
C	1.26379	-0.19124	5.71418
C	0.27051	-0.27189	4.74639
C	0.59625	-0.6326	3.4164
H	2.20294	-1.13471	2.05788
H	3.97228	-0.9796	3.79069
H	3.37416	-0.38002	6.12985
H	1.00665	0.07655	6.73553
H	-0.76655	-0.06926	4.99501
S	-0.67449	-0.76678	2.18483
C	-3.9162	3.03667	-0.3193
H	-4.98267	3.18063	-0.46946
C	-3.19898	3.92098	0.43277
H	-3.68735	4.77787	0.88881
Br	3.03374	0.83236	-0.30402
O	1.60194	-4.2713	-4.27817
C	1.4483	-5.57667	-3.75785
H	1.66054	-6.25948	-4.58382
H	2.15151	-5.77372	-2.93664
H	0.42506	-5.75606	-3.39745

Thesis = D-TS-E , A4 = A4.4-TS-E-C'

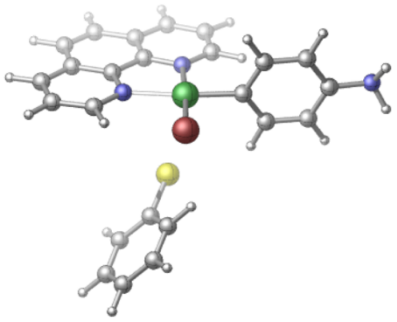


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -33.24 cm^{-1}
Zero-point correction= 0.355624 (Hartree/Particle)
Thermal correction to Energy= 0.382553
Thermal correction to Enthalpy= 0.383498
Thermal correction to Gibbs Free Energy= 0.290868
Sum of electronic and zero-point Energies= -1319.425817
Sum of electronic and thermal Energies= -1319.398888
Sum of electronic and thermal Enthalpies= -1319.397944
Sum of electronic and thermal Free Energies= -1319.490574
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF =-1709.1373936

C	-1.08381	2.24208	-0.12963
C	0.98293	2.81602	0.72383
C	0.43619	3.94565	1.36453
C	-0.91306	4.21469	1.24211
C	-1.72364	3.34854	0.47415
C	-1.83742	1.31847	-0.9226
C	-1.82554	-0.60099	-2.21149
C	-3.209	-0.49006	-2.44249
C	-3.91305	0.56243	-1.89189
C	-3.22666	1.51078	-1.10159

H	2.03772	2.56656	0.78958
H	1.08632	4.59004	1.94695
H	-1.35746	5.07994	1.72708
H	-1.2501	-1.41784	-2.62861
H	-3.70194	-1.23895	-3.05321
H	-4.98186	0.6689	-2.0569
N	0.24379	1.9855	-0.0043
N	-1.14883	0.27752	-1.47248
Ni	0.77898	0.30021	-1.02684
C	0.98565	-2.52674	-1.53883
C	1.73037	-2.22893	-4.21546
C	1.16744	-3.65745	-2.33484
H	0.6987	-2.65374	-0.49806
C	1.5364	-3.51654	-3.68418
H	2.02654	-2.11831	-5.2548
H	1.02585	-4.65188	-1.92066
C	1.54942	-1.10799	-3.40718
H	1.72596	-0.1236	-3.83339
C	1.16432	-1.23509	-2.06176
C	2.08485	-1.31573	2.88881
C	3.03797	-1.22577	3.89676
C	2.65819	-0.86368	5.19527
C	1.31678	-0.57782	5.48542
C	0.35844	-0.65081	4.48251
C	0.72664	-1.03049	3.1689
H	2.37193	-1.5772	1.87612
H	4.07968	-1.4362	3.67248
H	3.40645	-0.8006	5.98081
H	1.02707	-0.29582	6.49404
H	-0.68338	-0.42865	4.6911
S	-0.50064	-1.15599	1.89391
C	-3.85419	2.64283	-0.47846
H	-4.92199	2.78423	-0.6205
C	-3.13488	3.52358	0.27579
H	-3.62305	4.37521	0.74155
Br	3.10001	0.46075	-0.5241
C	1.70789	-4.67343	-4.51148
N	1.83801	-5.61363	-5.18596

TS-Radical Sulfide (Byp)Ni(II)-Br-Aniline

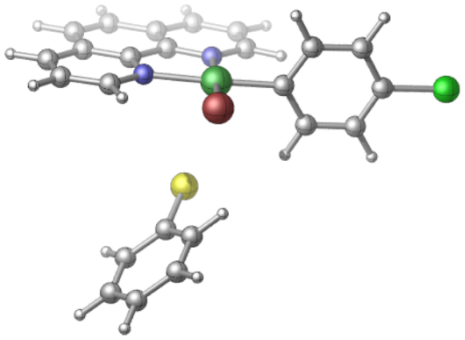


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -38.25 cm^{-1}
Zero-point correction= 0.373539 (Hartree/Particle)
Thermal correction to Energy= 0.400179
Thermal correction to Enthalpy= 0.401123
Thermal correction to Gibbs Free Energy= 0.309574
Sum of electronic and zero-point Energies= -1282.512082
Sum of electronic and thermal Energies= -1282.485441
Sum of electronic and thermal Enthalpies= -1282.484497
Sum of electronic and thermal Free Energies= -1282.576047
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1672.2635138

C	-1.06063	2.34021	-0.10177
C	1.02963	2.90969	0.69349
C	0.51284	4.06875	1.30589
C	-0.83435	4.35491	1.19944
C	-1.6722	3.47679	0.47595
C	-1.84322	1.40311	-0.85065
C	-1.88411	-0.55631	-2.07757
C	-3.26987	-0.42893	-2.2875
C	-3.94772	0.65182	-1.75926
C	-3.23215	1.61334	-1.01201
H	2.0817	2.64491	0.74687
H	1.18353	4.72205	1.85427
H	-1.25645	5.24289	1.66305
H	-1.32458	-1.39355	-2.47635
H	-3.78563	-1.18857	-2.86542
H	-5.01756	0.77103	-1.90904
N	0.26461	2.06666	0.00797
N	-1.18131	0.33394	-1.37786
Ni	0.75735	0.32941	-0.97333
C	0.84966	-2.51968	-1.41332
C	1.57212	-2.34186	-4.09319
C	0.97769	-3.68108	-2.18241
H	0.57074	-2.61461	-0.36611
C	1.33957	-3.60828	-3.53564
H	1.86149	-2.26274	-5.14042
H	0.79705	-4.65475	-1.72816
C	1.44656	-1.18699	-3.3162
H	1.66257	-0.22613	-3.77843
C	1.07157	-1.25184	-1.96739
C	2.01052	-1.06542	2.97549
C	3.00399	-0.9204	3.9375
C	2.66918	-0.55618	5.2475
C	1.33143	-0.32255	5.59565
C	0.33243	-0.44981	4.63876
C	0.65587	-0.83296	3.31451
H	2.2632	-1.32735	1.95364
H	4.0423	-1.08867	3.66648
H	3.4492	-0.44989	5.99682
H	1.0762	-0.03775	6.61288

H	-0.70724	-0.26692	4.8918
S	-0.62131	-1.02623	2.09745
C	-3.83015	2.77541	-0.41562
H	-4.89804	2.92981	-0.54382
C	-3.08377	3.6685	0.29663
H	-3.54991	4.543	0.74241
Br	3.09002	0.4708	-0.50078
N	1.40979	-4.77203	-4.33054
H	2.04834	-4.68101	-5.11343
H	1.63897	-5.60452	-3.79823

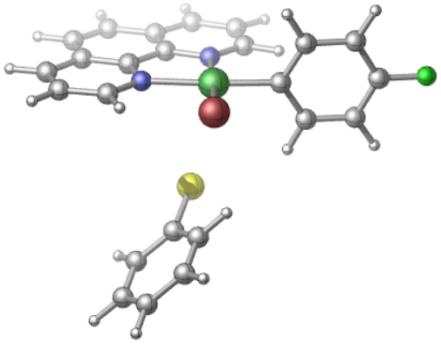
Radical Sulfide (Byp)Ni(II)-Br-Chlorobenzene



UB3LYP/6-31g(d)-(Br, Ni,Cl-LANL2DZ)-gas
Imaginary frequency = -35.23 cm^{-1}
Zero-point correction= 0.347174 (Hartree/Particle)
Thermal correction to Energy= 0.373585
Thermal correction to Enthalpy= 0.374529
Thermal correction to Gibbs Free Energy= 0.282812
Sum of electronic and zero-point Energies= -1241.533770
Sum of electronic and thermal Energies= -1241.507360
Sum of electronic and thermal Enthalpies= -1241.506416
Sum of electronic and thermal Free Energies= -1241.598133
UM06/6-311+g(d,p)-(Br, Ni ,Cl-SDD)-SMD(THF)
HF=-2076.4751655

C	-1.11774	2.12229	-0.18262
C	0.89232	2.70942	0.78817
C	0.28431	3.78634	1.46357
C	-1.06644	4.02233	1.29713
C	-1.81658	3.17572	0.45005
C	-1.80863	1.2202	-1.05404
C	-1.68338	-0.62722	-2.43839
C	-3.05788	-0.54074	-2.72682
C	-3.81667	0.46072	-2.15428
C	-3.19395	1.38368	-1.28515
H	1.95067	2.48666	0.88616
H	0.88912	4.41684	2.10689
H	-1.55782	4.84675	1.80733
H	-1.0653	-1.40482	-2.86929
H	-3.50095	-1.26866	-3.39818
H	-4.87996	0.54671	-2.36169
N	0.21087	1.89851	-0.01436
N	-1.06637	0.22799	-1.62366
Ni	0.84009	0.27614	-1.09129
C	1.09691	-2.52616	-1.68322
C	1.98904	-2.15651	-4.30598
C	1.32827	-3.6403	-2.50029
H	0.7517	-2.68871	-0.66491
C	1.7661	-3.4328	-3.80252
H	2.34359	-2.02235	-5.32292
H	1.17114	-4.64799	-2.1288
C	1.75656	-1.05654	-3.47178
H	1.95505	-0.06154	-3.8629
C	1.29778	-1.2212	-2.15654
C	2.06179	-1.5201	2.74654
C	3.02142	-1.47846	3.75154
C	2.65176	-1.16861	5.06626
C	1.314	-0.88653	5.37637
C	0.34931	-0.91171	4.37721
C	0.70718	-1.23858	3.04667
H	2.34172	-1.73919	1.72196
H	4.06051	-1.68463	3.51174
H	3.40517	-1.14256	5.84902
H	1.03221	-0.6444	6.39756
H	-0.6897	-0.69128	4.60115
S	-0.52796	-1.30109	1.7743
C	-3.88177	2.46244	-0.63194
H	-4.94632	2.58123	-0.81384
C	-3.22288	3.32078	0.19942
H	-3.7564	4.13173	0.68761
Br	3.13325	0.49141	-0.48753
Cl	2.0548	-4.86521	-4.87372

Radical Sulfide (Byp)Ni(II)-Br-Fluorobenzene

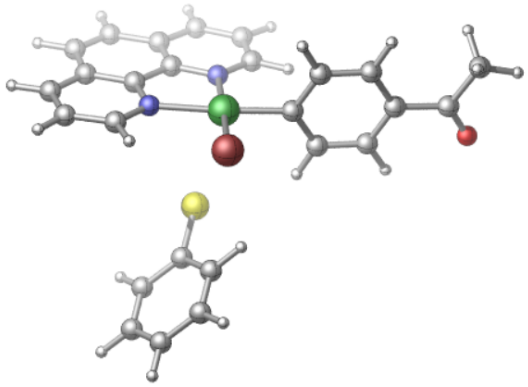


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -37.00 cm^{-1}

Zero-point correction= 0.348740 (Hartree/Particle)
Thermal correction to Energy= 0.374711
Thermal correction to Enthalpy= 0.375655
Thermal correction to Gibbs Free Energy= 0.285071
Sum of electronic and zero-point Energies= -1326.419990
Sum of electronic and thermal Energies= -1326.394019
Sum of electronic and thermal Enthalpies= -1326.393075
Sum of electronic and thermal Free Energies= -1326.483659
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1716.161073

C	-1.11122	2.11174	-0.18556
C	0.89911	2.69744	0.78505
C	0.2915	3.77334	1.46246
C	-1.05937	4.00959	1.29706
C	-1.80985	3.16428	0.44906
C	-1.80258	1.21082	-1.05803
C	-1.67794	-0.63471	-2.44485
C	-3.05264	-0.54768	-2.73231
C	-3.81126	0.45304	-2.1582
C	-3.18806	1.37477	-1.28817
H	1.95754	2.47421	0.88194
H	0.89657	4.40287	2.10654
H	-1.55057	4.83321	1.80878
H	-1.05872	-1.41128	-2.87612
H	-3.49632	-1.2747	-3.4043
H	-4.87469	0.53937	-2.36493
N	0.21737	1.88772	-0.01837
N	-1.06061	0.21946	-1.62931
Ni	0.84695	0.26464	-1.10002
C	1.09609	-2.53818	-1.69638
C	1.98934	-2.16632	-4.31831
C	1.32731	-3.65068	-2.51549
H	0.75019	-2.69961	-0.67816
C	1.76847	-3.44316	-3.81625
H	2.34585	-2.04493	-5.3371
H	1.1742	-4.66445	-2.15646
C	1.75806	-1.06628	-3.48426
H	1.95666	-0.07013	-3.87236
C	1.29908	-1.233	-2.16904
C	2.05005	-1.51153	2.74046
C	3.01474	-1.46212	3.74037
C	2.64919	-1.15936	5.05785
C	1.31029	-0.89198	5.37597
C	0.34046	-0.9248	4.38198
C	0.69431	-1.24488	3.04876
H	2.32681	-1.72479	1.71376
H	4.05461	-1.65648	3.49412
H	3.40661	-1.1272	5.83653
H	1.03162	-0.65508	6.39926
H	-0.69951	-0.71539	4.61204
S	-0.54698	-1.31704	1.78267
C	-3.87551	2.45263	-0.63308
H	-4.94017	2.57171	-0.81429
C	-3.21626	3.30973	0.19927
H	-3.74957	4.11997	0.68894
Br	3.14018	0.48026	-0.49311
F	1.98866	-4.51507	-4.6184

Radical Sulfide (Byp)Ni(II)-Br-Aniline

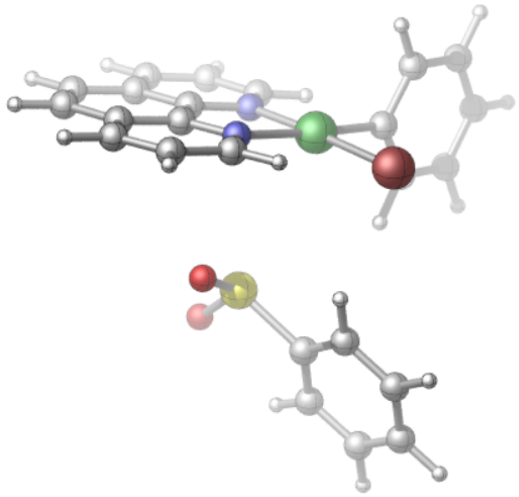


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -35.02 cm^{-1}
Zero-point correction= 0.394595 (Hartree/Particle)
Thermal correction to Energy= 0.423263
Thermal correction to Enthalpy= 0.424207
Thermal correction to Gibbs Free Energy= 0.327833
Sum of electronic and zero-point Energies= -1379.788330
Sum of electronic and thermal Energies= -1379.759662
Sum of electronic and thermal Enthalpies= -1379.758718
Sum of electronic and thermal Free Energies= -1379.855092
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1769.5267553

C	-1.12409	2.14927	-0.20919
C	0.89094	2.73745	0.75076
C	0.29313	3.83484	1.4019
C	-1.05508	4.08052	1.22883
C	-1.81297	3.223	0.39981
C	-1.82331	1.23461	-1.06072
C	-1.71648	-0.64611	-2.40129
C	-3.0907	-0.5547	-2.68939
C	-3.8395	0.46732	-2.1406
C	-3.20738	1.40501	-1.29432
H	1.94693	2.50643	0.85477

H	0.90352	4.47305	2.03221
H	-1.53873	4.9206	1.72052
H	-1.10703	-1.4409	-2.81282
H	-3.54153	-1.29545	-3.34125
H	-4.90233	0.55773	-2.34853
N	0.20206	1.91629	-0.03474
N	-1.09051	0.22326	-1.60864
Ni	0.81685	0.26875	-1.08106
C	1.03746	-2.54272	-1.65458
C	1.979	-2.19197	-4.25532
C	1.26359	-3.6498	-2.46995
H	0.67236	-2.69226	-0.64113
C	1.73428	-3.49285	-3.78467
H	2.35402	-2.03573	-5.26341
H	1.08284	-4.65792	-2.10829
C	1.75149	-1.0836	-3.43787
H	1.97054	-0.09114	-3.82425
C	1.26872	-1.23895	-2.12874
C	2.04762	-1.60263	2.71118
C	3.02366	-1.62207	3.70087
C	2.69345	-1.29772	5.02255
C	1.37952	-0.93967	5.35502
C	0.39955	-0.90336	4.37115
C	0.71678	-1.24394	3.03389
H	2.29761	-1.83373	1.68158
H	4.045	-1.88768	3.44389
H	3.45927	-1.31968	5.79329
H	1.1283	-0.68662	6.38153
H	-0.62115	-0.6236	4.61247
S	-0.53959	-1.22838	1.78098
C	-3.88486	2.50484	-0.6659
H	-4.94838	2.62912	-0.85013
C	-3.21778	3.37582	0.14553
H	-3.74366	4.20249	0.6153
Br	3.11368	0.47549	-0.48731
C	1.95278	-4.71261	-4.61486
O	1.6881	-5.82901	-4.18653
C	2.51736	-4.55284	-6.02113
H	1.85932	-3.93607	-6.64526
H	2.61685	-5.54242	-6.47103
H	3.49798	-4.06256	-5.99946

Thesis = A-TS-D, A4 = A4.1-TS-E-C

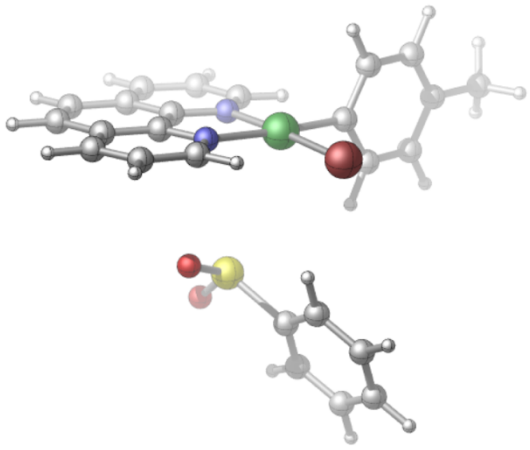


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -27.27 cm^{-1}
Zero-point correction= 0.363064 (Hartree/Particle)
Thermal correction to Energy= 0.390587
Thermal correction to Enthalpy= 0.391531
Thermal correction to Gibbs Free Energy= 0.297814
Sum of electronic and zero-point Energies= -1377.470391
Sum of electronic and thermal Energies= -1377.442869
Sum of electronic and thermal Enthalpies= -1377.441924
Sum of electronic and thermal Free Energies= -1377.535641
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1767.1899119

C	-1.47433	2.3488	-0.41401
C	0.44542	3.46607	0.20281
C	-0.30987	4.52092	0.75184
C	-1.6888	4.46829	0.70816
C	-2.31792	3.35427	0.10912
C	-2.038	1.18846	-1.03426
C	-1.65522	-0.83285	-2.09381
C	-3.03731	-1.05388	-2.23384
C	-3.9333	-0.11996	-1.75213
C	-3.44193	1.04767	-1.128
H	1.53089	3.46404	0.22096
H	0.20562	5.36066	1.20595
H	-2.29351	5.26767	1.12844
H	-0.92892	-1.54915	-2.45683
H	-3.37803	-1.96309	-2.71769
H	-5.00533	-0.2721	-1.84461
N	-0.11961	2.40762	-0.36632
N	-1.15949	0.25807	-1.50862

Ni	0.72963	0.73526	-1.1859
C	1.56781	-2.03277	-1.336
C	1.97935	-1.98657	-4.09146
C	1.942	-3.20167	-2.0094
H	1.43481	-2.0699	-0.25678
C	2.14553	-3.18339	-3.39078
H	2.14763	-1.95695	-5.16618
H	2.08026	-4.12524	-1.45071
C	1.60393	-0.81992	-3.41548
H	1.4944	0.10407	-3.97999
C	1.38388	-0.82788	-2.02964
C	1.06847	-2.36361	3.76568
C	2.26244	-2.79893	4.34411
C	3.45434	-2.11203	4.0962
C	3.46621	-0.98589	3.26949
C	2.2827	-0.527	2.68572
C	1.1182	-1.23115	2.9625
H	0.126	-2.87334	3.93237
H	2.25831	-3.67408	4.98765
H	4.38062	-2.46216	4.54308
H	4.39526	-0.46284	3.06417
H	2.28634	0.33154	2.02084
C	-4.2783	2.08359	-0.58931
H	-5.35604	1.96693	-0.66117
C	-3.73982	3.18808	0.00384
H	-4.38423	3.96254	0.41066
Br	2.97103	1.36397	-0.68181
H	2.43968	-4.08976	-3.91435
S	-0.47693	-0.64936	2.15988
O	-0.56777	0.91111	2.39861
O	-1.61612	-1.57416	2.73693

Thesis = A-TS-D, A4 = A4.2-TS-E-C

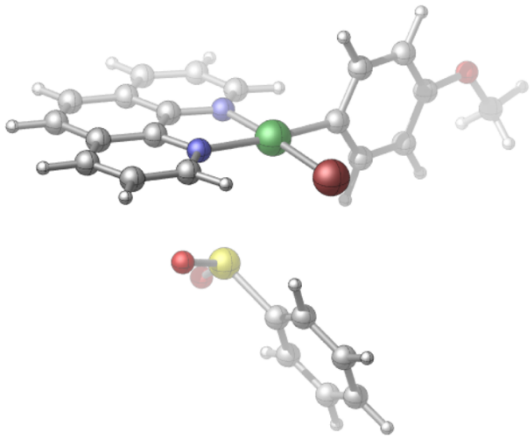


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -27.49 cm^{-1}
Zero-point correction= 0.390574 (Hartree/Particle)
Thermal correction to Energy= 0.420015
Thermal correction to Enthalpy= 0.420959
Thermal correction to Gibbs Free Energy= 0.322044
Sum of electronic and zero-point Energies= -1416.759706
Sum of electronic and thermal Energies= -1416.730265
Sum of electronic and thermal Enthalpies= -1416.729320
Sum of electronic and thermal Free Energies= -1416.828236
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1806.4839776

C	-1.63867	2.63205	-0.15661
C	0.28286	3.7545	0.44485
C	-0.47085	4.80955	0.99567
C	-1.84995	4.75431	0.96092
C	-2.48079	3.63747	0.369
C	-2.20415	1.46912	-0.77034
C	-1.82415	-0.554	-1.82742
C	-3.20669	-0.77777	-1.95843
C	-4.10144	0.15566	-1.4734
C	-3.60836	1.32565	-0.8551
H	1.36844	3.75445	0.45603
H	0.04598	5.65155	1.44406
H	-2.45344	5.55379	1.38275
H	-1.0983	-1.2695	-2.19292
H	-3.54883	-1.6887	-2.43802
H	-5.17375	0.00136	-1.55892
N	-0.28381	2.69335	-0.1176
N	-1.32693	0.53921	-1.24781
Ni	0.56336	1.01944	-0.93773
C	1.40392	-1.75085	-1.09161
C	1.80058	-1.71531	-3.83935
C	1.7754	-2.91867	-1.76652
H	1.27259	-1.79336	-0.01229
C	1.98164	-2.92236	-3.15188
H	1.9582	-1.68568	-4.91675
H	1.91234	-3.84106	-1.20345
C	1.42793	-0.54653	-3.16715
H	1.31074	0.3717	-3.7396
C	1.21485	-0.54528	-1.7811
C	0.93663	-2.07203	4.01868
C	2.13462	-2.49844	4.59543
C	3.32239	-1.80734	4.33949
C	3.32606	-0.68593	3.50631
C	2.13839	-0.23592	2.92408
C	0.97821	-0.94396	3.20891
H	-0.00284	-2.58529	4.19138
H	2.13686	-3.36993	5.24394
H	4.25185	-2.15052	4.78518
H	4.25191	-0.15969	3.29473
H	2.13587	0.61879	2.25424
C	-4.44321	2.36147	-0.31385
H	-5.52118	2.24274	-0.37871

C	-3.90303	3.46847	0.27304
H	-4.54628	4.24287	0.68181
Br	2.80661	1.65383	-0.44781
S	-0.62272	-0.37387	2.40921
O	-0.72244	1.18662	2.64438
O	-1.75455	-1.30383	2.99246
C	2.42092	-4.17621	-3.87437
H	2.08096	-4.17991	-4.9163
H	3.51574	-4.26762	-3.89201
H	2.0305	-5.0784	-3.38952

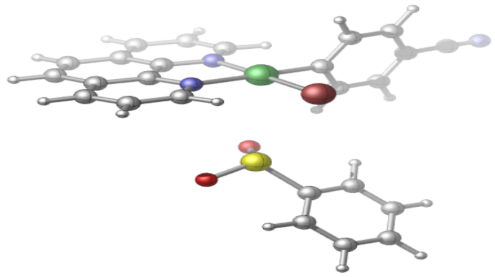
Thesis = A-TS-D, A4 = A4.3-TS-E-C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -28.47 cm^{-1}
Zero-point correction= 0.395930 (Hartree/Particle)
Thermal correction to Energy= 0.426048
Thermal correction to Enthalpy= 0.426993
Thermal correction to Gibbs Free Energy= 0.327190
Sum of electronic and zero-point Energies= -1491.957274
Sum of electronic and thermal Energies= -1491.927156
Sum of electronic and thermal Enthalpies= -1491.926212
Sum of electronic and thermal Free Energies= -1492.026014
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1881.6826728

C	-1.66742	2.79629	-0.19398
C	0.26156	3.90184	0.41493
C	-0.48444	4.97486	0.94103
C	-1.86369	4.93736	0.89008
C	-2.50219	3.82031	0.30689
C	-2.24113	1.63248	-0.79814
C	-1.87561	-0.41032	-1.82159
C	-3.25938	-0.61949	-1.96298
C	-4.14728	0.33229	-1.50164
C	-3.646	1.50528	-0.89576
H	1.34684	3.88741	0.43924
H	0.03823	5.81665	1.38305
H	-2.4615	5.75095	1.29263
H	-1.1543	-1.13895	-2.16971
H	-3.60792	-1.53344	-2.4321
H	-5.2205	0.18999	-1.59612
N	-0.31246	2.84	-0.13879
N	-1.37092	0.68578	-1.25422
Ni	0.52302	1.14593	-0.93093
C	1.38444	-1.62419	-1.07656
C	1.72139	-1.60207	-3.83524
C	1.75755	-2.80428	-1.73882
H	1.2853	-1.65966	0.00623
C	1.92546	-2.79413	-3.12664
H	1.86853	-1.6071	-4.91187
H	1.92038	-3.70855	-1.16162
C	1.34973	-0.44039	-3.16018
H	1.21363	0.47205	-3.73748
C	1.1632	-0.42917	-1.7667
C	0.83938	-1.90418	4.06598
C	2.01733	-2.28225	4.71345
C	3.19811	-1.56578	4.49824
C	3.21477	-0.46728	3.63519
C	2.04673	-0.06564	2.98212
C	0.89231	-0.79724	3.22817
H	-0.09392	-2.43839	4.20541
H	2.0094	-3.13585	5.38533
H	4.11231	-1.87108	4.99963
H	4.13621	0.07838	3.45594
H	2.05562	0.77005	2.28859
C	-4.47331	2.55964	-0.37926
H	-5.55196	2.45378	-0.45452
C	-3.92539	3.6684	0.19692
H	-4.56301	4.45722	0.58654
Br	2.76678	1.75721	-0.41361
S	-0.68233	-0.28643	2.34025
O	-0.85144	1.26933	2.56778
O	-1.80925	-1.25582	2.86575
O	2.28429	-3.88336	-3.88109
C	2.55195	-5.09731	-3.20688
H	1.66749	-5.47177	-2.67189
H	2.83344	-5.81694	-3.97897
H	3.37999	-4.99248	-2.49205

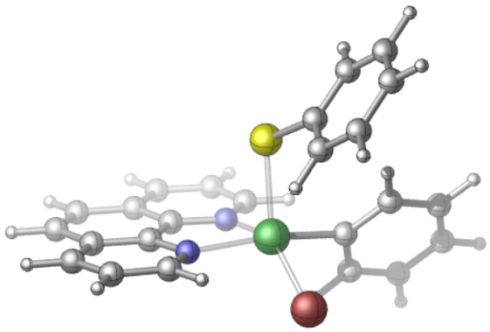
Thesis = A-TS-D, A4 = A4.4-TS-E-C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -11.24 cm^{-1}
Zero-point correction= 0.362175 (Hartree/Particle)
Thermal correction to Energy= 0.391328
Thermal correction to Enthalpy= 0.392272
Thermal correction to Gibbs Free Energy= 0.295746
Sum of electronic and zero-point Energies= -1469.719185
Sum of electronic and thermal Energies= -1469.690032
Sum of electronic and thermal Enthalpies= -1469.689088
Sum of electronic and thermal Free Energies= -1469.785614
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1859.4109009

C	-1.92674	2.34475	-0.33148
C	-0.09504	3.35927	0.63878
C	-0.91953	4.30792	1.27493
C	-2.28631	4.25636	1.09053
C	-2.83421	3.2513	0.26155
C	-2.40627	1.30366	-1.18866
C	-1.88797	-0.49869	-2.54098
C	-3.24521	-0.69048	-2.85773
C	-4.19974	0.14409	-2.3115
C	-3.79137	1.18347	-1.44689
H	0.98342	3.36382	0.76082
H	-0.46558	5.06259	1.90803
H	-2.94378	4.97427	1.57366
H	-1.1213	-1.14497	-2.94843
H	-3.51983	-1.49819	-3.52777
H	-5.25448	0.01314	-2.53794
N	-0.58244	2.40111	-0.14336
N	-1.47038	0.46908	-1.72561
Ni	0.36107	0.86793	-1.11011
C	1.02781	-1.89095	-1.45704
C	2.17086	-1.58536	-3.98824
C	1.49673	-3.01145	-2.14193
H	0.58232	-2.01653	-0.4731
C	2.06933	-2.86691	-3.41829
H	2.62054	-1.4714	-4.97056
H	1.42123	-4.00138	-1.70012
C	1.70217	-0.47318	-3.29003
H	1.80968	0.51014	-3.741
C	1.11719	-0.6055	-2.02014
C	2.29033	-0.56358	4.65899
C	3.19466	-1.39346	5.32565
C	3.71466	-2.52202	4.68671
C	3.33645	-2.83346	3.37775
C	2.43081	-2.01843	2.69577
C	1.92743	-0.90994	3.3644
H	1.86618	0.31883	5.12562
H	3.49013	-1.15657	6.34376
H	4.4221	-3.15966	5.20925
H	3.74652	-3.70912	2.88324
H	2.12839	-2.23746	1.67743
C	-4.69448	2.1129	-0.82784
H	-5.75757	2.01068	-1.027
C	-4.23632	3.10328	-0.0088
H	-4.93017	3.79988	0.45348
Br	2.54676	1.41662	-0.30542
S	0.75148	0.21838	2.43852
O	0.11041	1.16558	3.52764
O	-0.20468	-0.73085	1.60886
C	2.53983	-4.01634	-4.13222
N	2.9149	-4.95314	-4.71318

Thesis = E, A4 = A4.1-C'

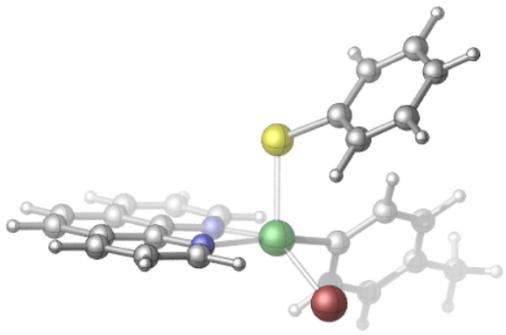


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.357041 (Hartree/Particle)
Thermal correction to Energy= 0.382809
Thermal correction to Enthalpy= 0.383753
Thermal correction to Gibbs Free Energy= 0.296382
Sum of electronic and zero-point Energies= -1227.189545
Sum of electronic and thermal Energies= -1227.163777
Sum of electronic and thermal Enthalpies= -1227.162833

Sum of electronic and thermal Free Energies= -1227.250204
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1616.936638

C	-1.78678	1.21254	1.8777
C	-0.06494	0.64205	3.3064
C	-0.51551	1.55798	4.27678
C	-1.63986	2.31642	4.01931
C	-2.31658	2.15817	2.78931
C	-2.42674	1.01283	0.60404
C	-2.42254	-0.07072	-1.43805
C	-3.5534	0.64882	-1.8672
C	-4.1318	1.56747	-1.01407
C	-3.56869	1.77967	0.2637
H	0.80105	0.01032	3.47641
H	0.02676	1.65354	5.21158
H	-2.01053	3.03277	4.74792
H	-1.94267	-0.80241	-2.07839
H	-3.95286	0.47124	-2.86007
H	-5.00827	2.13529	-1.31542
N	-0.67786	0.47919	2.14084
N	-1.88566	0.09213	-0.23434
Ni	-0.05015	-0.75929	0.5112
C	1.34106	-2.2198	-1.72598
C	-0.86056	-3.92184	-2.0328
C	1.34702	-3.22062	-2.70467
H	2.20772	-1.57992	-1.6098
C	0.24879	-4.06772	-2.8651
H	-1.71318	-4.59036	-2.12787
H	2.22085	-3.33265	-3.34221
H	0.26273	-4.84444	-3.62528
Br	1.00678	-2.38604	2.03559
C	-0.87516	-2.92451	-1.04788
H	-1.73355	-2.84646	-0.38513
C	0.21998	-2.06774	-0.91849
C	3.56751	0.25566	0.39327
C	4.94418	0.0625	0.28417
C	5.60426	0.32912	-0.91862
C	4.87233	0.7781	-2.02039
C	3.49128	0.95192	-1.92416
C	2.82452	0.70298	-0.71177
H	3.06004	0.04378	1.32826
H	5.50361	-0.29478	1.14505
H	6.67836	0.18354	-0.99736
H	5.37504	0.98357	-2.96237
H	2.91831	1.28654	-2.78376
C	-3.4877	2.90385	2.4243
H	-3.88553	3.62392	3.13418
C	-4.08593	2.72518	1.21223
H	-4.96614	3.30167	0.94116
S	1.04041	1.02652	-0.61223

Thesis = E, A4 = A4.2-C’

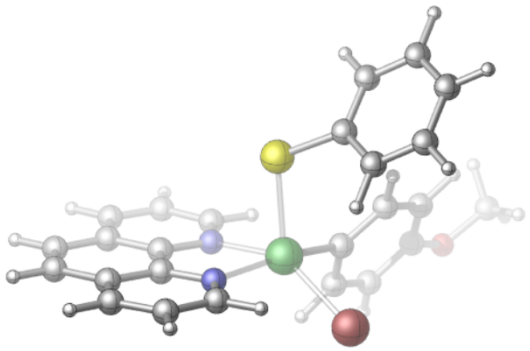


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.384560 (Hartree/Particle)
Thermal correction to Energy= 0.412248
Thermal correction to Enthalpy= 0.413192
Thermal correction to Gibbs Free Energy= 0.320809
Sum of electronic and zero-point Energies= -1266.479091
Sum of electronic and thermal Energies= -1266.451403
Sum of electronic and thermal Enthalpies= -1266.450459
Sum of electronic and thermal Free Energies= -1266.542842
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1656.2310687

H	5.34099	1.33485	-2.72765
C	4.84296	1.12555	-1.78401
H	2.88413	1.62929	-2.53801
H	6.6553	0.53445	-0.77003
C	3.4618	1.29469	-1.68156
C	5.58106	0.67632	-0.68644
H	2.21115	-3.01022	-3.06386
C	2.80088	1.0409	-0.46702
C	4.9268	0.40463	0.51836
C	1.33149	-2.89737	-2.43252
H	2.19377	-1.25712	-1.346
S	1.01623	1.35929	-0.35959
C	3.54994	0.59318	0.63372
H	5.49091	0.04704	1.37607
C	1.32439	-1.89372	-1.46039
C	0.26119	-4.82774	-3.67905
C	0.23947	-3.75862	-2.61023
H	-3.98848	0.78413	-2.5805
H	-1.97028	-0.48137	-1.80423
C	-3.58449	0.96615	-1.59025
H	3.04715	0.37723	1.57032
C	-2.44943	0.25125	-1.16439

C	0.20269	-1.73406	-0.65418
C	-0.86498	-3.59451	-1.76952
C	-4.16124	1.88604	-0.73735
H	-5.04082	2.45039	-1.0362
N	-1.90717	0.4196	0.03608
C	-0.88631	-2.59482	-0.78671
Ni	-0.06545	-0.42528	0.77462
H	-1.71805	-4.26442	-1.86096
C	-3.59238	2.1041	0.53688
C	-2.44665	1.34151	0.87407
H	-1.74802	-2.52279	-0.12752
C	-4.10745	3.0514	1.48481
H	-4.99056	3.6246	1.21622
C	-1.80095	1.54712	2.14392
N	-0.68895	0.81745	2.40401
Br	1.00041	-2.04519	2.30042
C	-3.50363	3.2358	2.69326
C	-2.32873	2.49446	3.05495
C	-0.0707	0.98584	3.56593
H	0.79766	0.3568	3.73377
H	-3.89985	3.95722	3.40267
C	-1.6463	2.65866	4.281
C	-0.51874	1.90397	4.53542
H	-2.01519	3.37656	5.00901
H	0.02795	2.00414	5.46717
H	1.20043	-5.39312	-3.66136
H	0.16645	-4.39437	-4.68383
H	-0.56043	-5.53993	-3.54937

Thesis = E, A4 = A4.3-C'

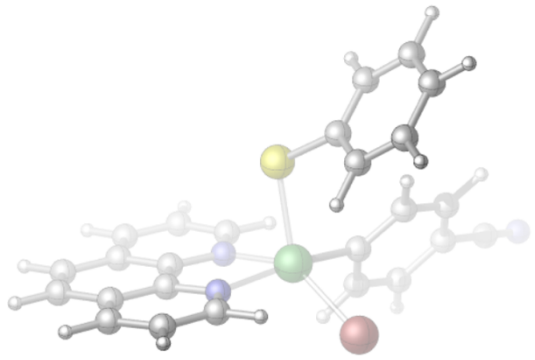


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.389837 (Hartree/Particle)
Thermal correction to Energy= 0.418257
Thermal correction to Enthalpy= 0.419201
Thermal correction to Gibbs Free Energy= 0.325372
Sum of electronic and zero-point Energies= -1341.676947
Sum of electronic and thermal Energies= -1341.648527
Sum of electronic and thermal Enthalpies= -1341.647583
Sum of electronic and thermal Free Energies= -1341.741413
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1731.4299491

H	5.3252	1.50665	-2.4422
C	4.80906	1.25059	-1.52
H	2.87099	1.83183	-2.2719
H	6.59556	0.57118	-0.51539
C	3.42922	1.4369	-1.42823
C	5.52248	0.72594	-0.43981
H	2.09215	-2.77716	-3.04642
C	2.74501	1.12428	-0.24047
C	4.84458	0.39574	0.73708
C	1.23022	-2.71606	-2.39116
H	2.06423	-1.0729	-1.29468
S	0.96411	1.46764	-0.14291
C	3.46931	0.60049	0.84318
H	5.38901	-0.02093	1.58076
C	1.21173	-1.73506	-1.38944
C	0.15128	-3.59488	-2.533
H	-4.00838	0.88912	-2.53095
H	-2.00335	-0.37699	-1.72106
C	-3.62739	1.06332	-1.53024
H	2.94814	0.33672	1.75718
C	-2.49972	0.34796	-1.08564
C	0.11715	-1.62453	-0.545
C	-0.94068	-3.49506	-1.66086
C	-4.22642	1.97363	-0.6823
H	-5.10043	2.53839	-0.99632
N	-1.98582	0.50755	0.12837
C	-0.95088	-2.52152	-0.66201
Ni	-0.16711	-0.34175	0.90188
H	-1.76015	-4.20049	-1.76329
C	-3.6887	2.18044	0.60734
C	-2.54929	1.41744	0.96362
H	-1.79323	-2.48714	0.02441
C	-4.22855	3.11593	1.55329
H	-5.10609	3.69057	1.26994
C	-1.93656	1.60781	2.25185
N	-0.83128	0.87489	2.53113
Br	0.86839	-1.98394	2.42298
C	-3.65478	3.28741	2.77829
C	-2.48816	2.54331	3.16076
C	-0.24227	1.02915	3.71001
H	0.62274	0.39914	3.89127
H	-4.06972	4.00008	3.48586
C	-1.83692	2.69248	4.40561
C	-0.71546	1.93518	4.67898
H	-2.22454	3.40102	5.13305
H	-0.19251	2.02427	5.62536
O	0.06541	-4.58014	-3.47894
C	1.16498	-4.76183	-4.35345

H	0.8937	-5.59108	-5.01012
H	2.08094	-5.01903	-3.80439
H	1.35278	-3.86653	-4.962

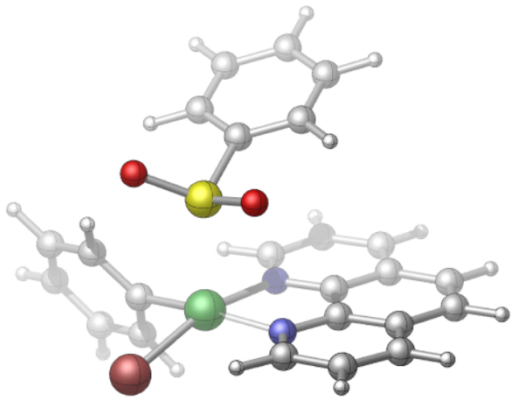
Thesis = E, A4 = A4.4-C'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.355925 (Hartree/Particle)
Thermal correction to Energy= 0.383413
Thermal correction to Enthalpy= 0.384358
Thermal correction to Gibbs Free Energy= 0.293257
Sum of electronic and zero-point Energies= -1319.433770
Sum of electronic and thermal Energies= -1319.406281
Sum of electronic and thermal Enthalpies= -1319.405337
Sum of electronic and thermal Free Energies= -1319.496438
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1709.1520757

H	6.64312	0.33293	-0.80341
C	5.5668	0.47397	-0.75469
H	5.44334	0.06107	1.36012
C	4.89246	0.3225	0.46037
H	5.36396	0.9197	-2.85643
C	4.84837	0.80337	-1.9065
C	3.51279	0.51027	0.52951
C	3.46446	0.9706	-1.84807
H	2.99337	0.39401	1.47482
C	2.78261	0.8349	-0.626
H	2.90107	1.21148	-2.74445
H	0.08217	1.7994	5.26521
C	-0.47552	1.6996	4.34006
H	0.83533	0.15872	3.52119
S	0.99409	1.1413	-0.57956
C	-0.03604	0.78576	3.36318
H	-1.97235	3.16411	4.83609
C	-1.60957	2.44984	4.10159
H	2.25342	-1.49829	-1.41734
N	-0.66787	0.61803	2.20802
Br	0.91831	-2.28586	2.12267
C	-2.30704	2.28525	2.88415
Ni	-0.07174	-0.62565	0.59247
C	-1.78717	1.34275	1.96374
H	-3.8804	3.73934	3.25652
C	1.38055	-2.12051	-1.57503
C	-3.48992	3.02216	2.53981
H	2.32353	-3.25469	-3.14399
C	0.22237	-1.93749	-0.82287
C	-2.44849	1.13715	0.70256
C	1.42602	-3.11745	-2.54841
C	-4.10798	2.83896	1.33846
N	-1.9159	0.21913	-0.14462
C	-3.60054	1.89689	0.38126
H	-4.99672	3.40912	1.08271
C	-2.4699	0.0569	-1.34086
C	-0.87899	-2.77986	-1.0114
H	-1.99544	-0.66749	-1.9933
C	0.31365	-3.94846	-2.76697
C	-4.18291	1.68239	-0.8875
C	-3.61152	0.76967	-1.7517
H	-1.76876	-2.68661	-0.39472
C	-0.8398	-3.77897	-1.9854
H	-5.06796	2.24435	-1.17404
H	-4.02454	0.59149	-2.73882
H	-1.69269	-4.43524	-2.13082
C	0.35507	-4.96475	-3.77657
N	0.38291	-5.78576	-4.60104

Thesis = A, A4 = A4.1-C

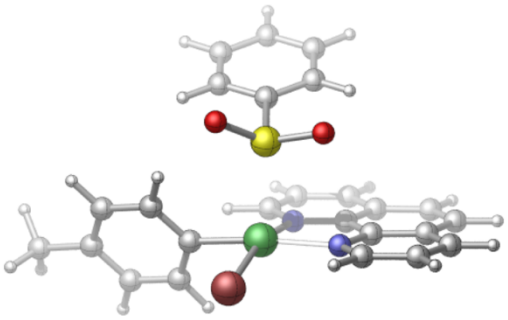


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.364218 (Hartree/Particle)
Thermal correction to Energy= 0.391961
Thermal correction to Enthalpy= 0.392905
Thermal correction to Gibbs Free Energy= 0.301387

Sum of electronic and zero-point Energies= -1377.470110
Sum of electronic and thermal Energies= -1377.442367
Sum of electronic and thermal Enthalpies= -1377.441423
Sum of electronic and thermal Free Energies= -1377.532941
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1767.2133162

C	0.53639	2.51904	-0.18184
C	2.81488	2.63674	-0.52946
C	2.86167	3.93543	0.01531
C	1.69813	4.52899	0.46059
C	0.47972	3.81736	0.37345
C	-0.65358	1.72277	-0.26805
C	-1.60568	-0.30808	-0.8426
C	-2.87237	0.12604	-0.41117
C	-3.01604	1.39996	0.10134
C	-1.88651	2.24331	0.19146
H	3.70442	2.13636	-0.89783
H	3.81495	4.44891	0.07932
H	1.7074	5.53044	0.88281
H	-1.45789	-1.29929	-1.25395
H	-3.71659	-0.55098	-0.48405
H	-3.98352	1.75875	0.44258
N	1.68208	1.95606	-0.63529
N	-0.52697	0.46787	-0.78263
Ni	1.38828	0.02915	-1.3301
C	1.40947	-2.88836	-1.62613
C	-0.27873	-2.80527	-3.86012
C	0.96866	-4.07376	-2.22867
H	2.09901	-2.92846	-0.78629
C	0.12321	-4.0365	-3.33939
H	-0.91729	-2.7629	-4.73966
H	1.30602	-5.02886	-1.83255
C	0.15214	-1.6149	-3.26061
H	-0.15178	-0.66284	-3.69069
C	0.97265	-1.66281	-2.12857
C	-0.24958	-0.33173	2.86112
C	-1.41046	-0.70208	3.54575
C	-1.94592	-1.98156	3.37551
C	-1.32063	-2.9	2.52712
C	-0.15738	-2.54198	1.84077
C	0.34782	-1.25934	2.01803
H	0.21067	0.643	2.9881
H	-1.88754	0.00304	4.2217
H	-2.84642	-2.26774	3.91259
H	-1.73004	-3.89969	2.40841
H	0.35512	-3.24496	1.19266
S	1.91943	-0.75964	1.09681
O	2.80861	-2.0646	1.15006
O	2.40508	0.52844	1.87701
C	-1.92072	3.57396	0.72983
H	-2.87244	3.96789	1.07529
C	-0.78605	4.32678	0.8194
H	-0.82326	5.32851	1.23859
Br	3.45736	-0.09196	-2.50791
H	-0.20582	-4.96051	-3.808

Thesis = A, A4 = A4.2-C

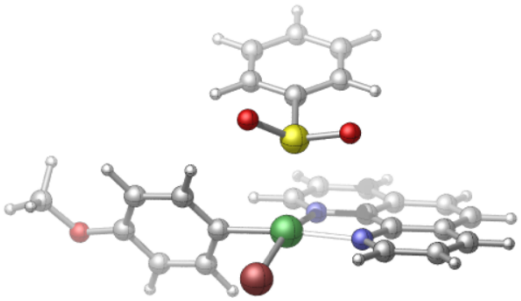


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.391743 (Hartree/Particle)
Thermal correction to Energy= 0.421389
Thermal correction to Enthalpy= 0.422333
Thermal correction to Gibbs Free Energy= 0.326189
Sum of electronic and zero-point Energies= -1416.759663
Sum of electronic and thermal Energies= -1416.730016
Sum of electronic and thermal Enthalpies= -1416.729072
Sum of electronic and thermal Free Energies= -1416.825216
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1806.5080694

C	0.5796	2.87183	0.21022
C	2.86317	2.99464	-0.09991
C	2.90779	4.26654	0.50472
C	1.74063	4.84446	0.96079
C	0.52065	4.14379	0.82341
C	-0.61318	2.08754	0.06933
C	-1.56827	0.09252	-0.61572
C	-2.83915	0.51424	-0.18436
C	-2.98322	1.76334	0.38588
C	-1.85037	2.59404	0.53327
H	3.75576	2.50793	-0.47929
H	3.86215	4.77213	0.60527
H	1.74815	5.82529	1.42894
H	-1.41921	-0.87889	-1.07161
H	-3.68618	-0.15281	-0.30248
H	-3.95378	2.11215	0.72875
N	1.72942	2.32429	-0.25171

N	-0.48608	0.85735	-0.50142
Ni	1.43858	0.42886	-1.03331
C	1.4695	-2.4748	-1.46193
C	-0.19369	-2.3069	-3.69702
C	1.03982	-3.63118	-2.12113
H	2.14888	-2.5547	-0.61676
C	0.2039	-3.57011	-3.24479
H	-0.82835	-2.22547	-4.57777
H	1.37884	-4.60053	-1.75933
C	0.22436	-1.14004	-3.04461
H	-0.0873	-0.17484	-3.43855
C	1.03354	-1.22721	-1.90889
C	-0.34638	-0.18981	3.06692
C	-1.51866	-0.62358	3.69212
C	-2.01079	-1.90779	3.44418
C	-1.33031	-2.76774	2.57728
C	-0.15524	-2.3459	1.94969
C	0.30597	-1.05954	2.20302
H	0.08111	0.78977	3.25567
H	-2.03858	0.03552	4.38277
H	-2.92031	-2.2435	3.93543
H	-1.70599	-3.77168	2.39826
H	0.39942	-3.00329	1.28881
S	1.89439	-0.47333	1.3645
O	2.81739	-1.75523	1.38297
O	2.31603	0.78394	2.22806
C	-1.88606	3.89849	1.13234
H	-2.84092	4.28168	1.48124
C	-0.749	4.63951	1.27365
H	-0.78722	5.62097	1.73823
Br	3.52758	0.34933	-2.18081
C	-0.21726	-4.82917	-3.96865
H	0.5905	-5.2108	-4.60727
H	-0.47613	-5.63	-3.26621
H	-1.08549	-4.6513	-4.6122

Thesis = A, A4 = A4.3-C



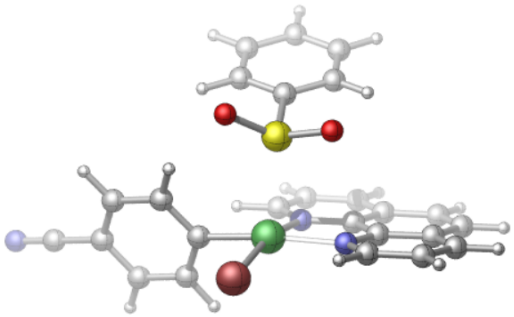
UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.396987 (Hartree/Particle)
Thermal correction to Energy= 0.427359
Thermal correction to Enthalpy= 0.428303
Thermal correction to Gibbs Free Energy= 0.331050
Sum of electronic and zero-point Energies= -1491.957903
Sum of electronic and thermal Energies= -1491.927531
Sum of electronic and thermal Enthalpies= -1491.926587
Sum of electronic and thermal Free Energies= -1492.023840

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1881.7072537

C	0.55075	3.03865	0.25445
C	2.83126	3.15029	-0.08156
C	2.89053	4.41757	0.53142
C	1.73215	4.99928	1.00481
C	0.50649	4.30677	0.8769
C	-0.64816	2.26188	0.12353
C	-1.62166	0.27521	-0.559
C	-2.88508	0.70111	-0.11001
C	-3.01559	1.94804	0.4682
C	-1.87665	2.77209	0.60604
H	3.71645	2.66124	-0.47487
H	3.84903	4.9167	0.62457
H	1.75095	5.97682	1.47951
H	-1.48262	-0.69522	-1.02012
H	-3.73694	0.03902	-0.22114
H	-3.98005	2.30006	0.82477
N	1.69178	2.48788	-0.22511
N	-0.53469	1.03442	-0.45534
Ni	1.38351	0.59928	-1.01888
C	1.41646	-2.29843	-1.48118
C	-0.30701	-2.11556	-3.67222
C	0.98692	-3.46352	-2.13328
H	2.11982	-2.38226	-0.65617
C	0.11983	-3.37527	-3.22809
H	-0.95875	-2.06116	-4.5395
H	1.35373	-4.42341	-1.786
C	0.12096	-0.96127	-3.01725
H	-0.20331	0.00524	-3.39708
C	0.95723	-1.0521	-1.89624
C	-0.32035	-0.03695	3.10611
C	-1.48758	-0.46209	3.74661
C	-2.00637	-1.73316	3.48576
C	-1.35768	-2.58869	2.59052
C	-0.18795	-2.17536	1.94755
C	0.30019	-0.90169	2.21433
H	0.12741	0.93204	3.30261
H	-1.98293	0.19326	4.45855
H	-2.91198	-2.06227	3.98859
H	-1.75435	-3.58262	2.40104
H	0.34219	-2.82962	1.26374
S	1.88033	-0.32626	1.35345
O	2.78756	-1.61985	1.34185

O	2.33462	0.91495	2.22371
C	-1.89777	4.07307	1.21328
H	-2.84614	4.45943	1.5761
C	-0.75486	4.80677	1.34546
H	-0.78184	5.78545	1.81665
Br	3.44739	0.53125	-2.21234
O	-0.35853	-4.44577	-3.93331
C	0.09536	-5.73871	-3.57202
H	-0.38657	-6.43117	-4.26523
H	1.18545	-5.82732	-3.6702
H	-0.19293	-5.99805	-2.54398

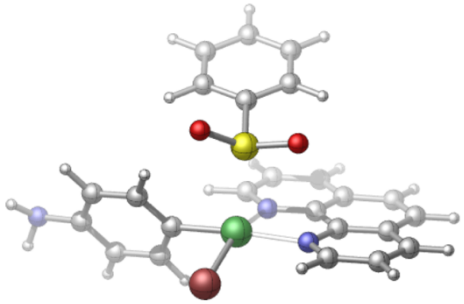
Thesis = A, A4 = A4.4-C



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Zero-point correction= 0.362896 (Hartree/Particle)
Thermal correction to Energy= 0.392468
Thermal correction to Enthalpy= 0.393412
Thermal correction to Gibbs Free Energy= 0.297797
Sum of electronic and zero-point Energies= -1469.714607
Sum of electronic and thermal Energies= -1469.685035
Sum of electronic and thermal Enthalpies= -1469.684090
Sum of electronic and thermal Free Energies= -1469.779705
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1859.4266451

C	0.53876	2.62112	-0.02656
C	2.82251	2.75519	-0.33663
C	2.85454	4.0405	0.23999
C	1.68206	4.61898	0.68183
C	0.46799	3.90489	0.55938
C	-0.64459	1.82212	-0.15082
C	-1.57504	-0.19876	-0.79189
C	-2.85043	0.21696	-0.36857
C	-3.0101	1.4766	0.17394
C	-1.88718	2.32383	0.30243
H	3.71994	2.26753	-0.70251
H	3.80451	4.55601	0.33042
H	1.68122	5.61013	1.12759
H	-1.41866	-1.17866	-1.22573
H	-3.68916	-0.46273	-0.47275
H	-3.98507	1.82076	0.50853
N	1.69385	2.07241	-0.47636
N	-0.50083	0.58094	-0.69572
Ni	1.40501	0.18859	-1.2421
C	1.39699	-2.71792	-1.6171
C	-0.19108	-2.5451	-3.92096
C	0.97205	-3.88136	-2.25987
H	2.04847	-2.79555	-0.75013
C	0.16898	-3.80398	-3.41088
H	-0.792	-2.48153	-4.82338
H	1.27034	-4.85412	-1.87997
Br	3.51374	0.06622	-2.32863
C	0.23173	-1.38653	-3.26979
H	-0.04384	-0.42126	-3.68802
C	1.00558	-1.46568	-2.10256
C	-0.21353	-0.2164	2.9888
C	-1.38125	-0.56943	3.6708
C	-1.93668	-1.84013	3.49863
C	-1.3257	-2.76838	2.65063
C	-0.15611	-2.429	1.96578
C	0.36883	-1.15522	2.14757
H	0.26059	0.75098	3.11934
H	-1.84758	0.14258	4.34671
H	-2.84218	-2.1121	4.03431
H	-1.75055	-3.76126	2.53098
H	0.34816	-3.14039	1.32048
S	1.9455	-0.68352	1.2244
O	2.78881	-2.0191	1.22302
O	2.48473	0.5699	2.0214
C	-1.93645	3.64062	0.87297
H	-2.89531	4.02149	1.21302
C	-0.80724	4.39683	0.99824
H	-0.85644	5.38788	1.44073
C	-0.28036	-4.99847	-4.0631
N	-0.65756	-5.96649	-4.58789

Intermediate-Radical Sulfone (Byp)Ni(II)-Br-Aniline

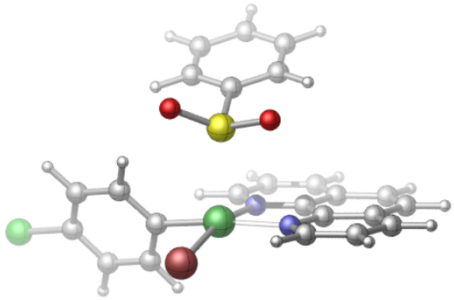


UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

Zero-point correction= 0.380904 (Hartree/Particle)
Thermal correction to Energy= 0.410133
Thermal correction to Enthalpy= 0.411077
Thermal correction to Gibbs Free Energy= 0.316749
Sum of electronic and zero-point Energies= -1432.805356
Sum of electronic and thermal Energies= -1432.776127
Sum of electronic and thermal Enthalpies= -1432.775182
Sum of electronic and thermal Free Energies= -1432.869511
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1822.5608658

C	-0.11044	2.73466	1.11939
C	2.16433	2.82641	0.74325
C	2.23277	4.12616	1.28299
C	1.08137	4.73409	1.74019
C	-0.14571	4.03594	1.6697
C	-1.31131	1.95254	1.05047
C	-2.29437	-0.06911	0.49646
C	-3.5513	0.38249	0.93875
C	-3.67343	1.66041	1.44693
C	-2.53263	2.49015	1.52155
H	3.04376	2.31589	0.36445
H	3.19248	4.6291	1.33361
H	1.10668	5.73667	2.15908
H	-2.16034	-1.06507	0.09119
H	-4.40449	-0.28448	0.87861
H	-4.6326	2.03274	1.79718
N	1.02338	2.15727	0.65466
N	-1.2067	0.69453	0.54045
Ni	0.70896	0.22044	-0.01884
C	0.77575	-2.70271	-0.30592
C	-1.00023	-2.68329	-2.46243
C	0.34981	-3.90295	-0.87848
H	1.50051	-2.72357	0.50441
C	-0.54579	-3.91322	-1.96079
H	-1.67874	-2.66468	-3.31347
H	0.73113	-4.84584	-0.4901
C	-0.57793	-1.48175	-1.8857
H	-0.92644	-0.54623	-2.31842
C	0.27948	-1.48882	-0.78197
C	-0.98316	-0.22797	4.12863
C	-2.14197	-0.6426	4.79084
C	-2.63707	-1.93439	4.59337
C	-1.97275	-2.8205	3.74031
C	-0.81092	-2.41777	3.07651
C	-0.34644	-1.12355	3.27962
H	-0.55379	0.75806	4.27528
H	-2.64945	0.03779	5.47009
H	-3.53661	-2.2551	5.11233
H	-2.35132	-3.82939	3.59908
H	-0.27137	-3.09527	2.42341
S	1.2209	-0.5581	2.38872
O	2.16275	-1.8254	2.45004
O	1.64151	0.74244	3.18755
C	-2.54468	3.82327	2.05475
H	-3.48751	4.23014	2.40959
C	-1.40002	4.56242	2.12814
H	-1.42003	5.56612	2.54385
Br	2.74408	0.0988	-1.26407
N	-1.01171	-5.12361	-2.4969
H	-1.28888	-5.06519	-3.47012
H	-0.38202	-5.90497	-2.35393

Intermediate-Radical Sulfone (Byp)Ni(II)-Br-Chlorobenzene

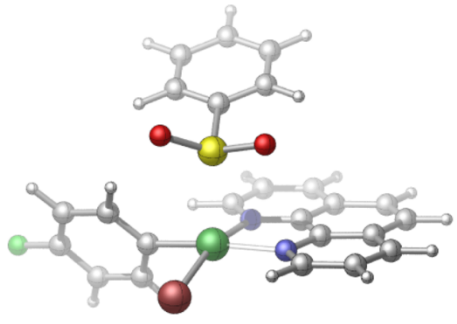


UB3LYP/6-31g(d)-(Br, Ni,Cl-LANL2DZ)-gas
Zero-point correction= 0.373539 (Hartree/Particle)
Thermal correction to Energy= 0.400179
Thermal correction to Enthalpy= 0.401123
Thermal correction to Gibbs Free Energy= 0.309574
Sum of electronic and zero-point Energies= -1282.512082
Sum of electronic and thermal Energies= -1282.485441
Sum of electronic and thermal Enthalpies= -1282.484497
Sum of electronic and thermal Free Energies= -1282.576047
UM06/6-311+g(d,p)-(Br, Ni,Cl -SDD)-SMD(THF)
HF=-1672.2635138

C	-1.06063	2.34021	-0.10177
C	1.02963	2.90969	0.69349
C	0.51284	4.06875	1.30589
C	-0.83435	4.35491	1.19944
C	-1.6722	3.47679	0.47595
C	-1.84322	1.40311	-0.85065
C	-1.88411	-0.55631	-2.07757
C	-3.26987	-0.42893	-2.2875
C	-3.94772	0.65182	-1.75926
C	-3.23215	1.61334	-1.01201

H	2.0817	2.64491	0.74687
H	1.18353	4.72205	1.85427
H	-1.25645	5.24289	1.66305
H	-1.32458	-1.39355	-2.47635
H	-3.78563	-1.18857	-2.86542
H	-5.01756	0.77103	-1.90904
N	0.26461	2.06666	0.00797
N	-1.18131	0.33394	-1.37786
Ni	0.75735	0.32941	-0.97333
C	0.84966	-2.51968	-1.41332
C	1.57212	-2.34186	-4.09319
C	0.97769	-3.68108	-2.18241
H	0.57074	-2.61461	-0.36611
C	1.33957	-3.60828	-3.53564
H	1.86149	-2.26274	-5.14042
H	0.79705	-4.65475	-1.72816
C	1.44656	-1.18699	-3.3162
H	1.66257	-0.22613	-3.77843
C	1.07157	-1.25184	-1.96739
C	2.01052	-1.06542	2.97549
C	3.00399	-0.9204	3.9375
C	2.66918	-0.55618	5.2475
C	1.33143	-0.32255	5.59565
C	0.33243	-0.44981	4.63876
C	0.65587	-0.83296	3.31451
H	2.2632	-1.32735	1.95364
H	4.0423	-1.08867	3.66648
H	3.4492	-0.44989	5.99682
H	1.0762	-0.03775	6.61288
H	-0.70724	-0.26692	4.8918
S	-0.62131	-1.02623	2.09745
C	-3.83015	2.77541	-0.41562
H	-4.89804	2.92981	-0.54382
C	-3.08377	3.6685	0.29663
H	-3.54991	4.543	0.74241
Br	3.09002	0.4708	-0.50078
N	1.40979	-4.77203	-4.33054
H	2.04834	-4.68101	-5.11343
H	1.63897	-5.60452	-3.79823

Intermediate-Radical Sulfone (Byp)Ni(II)-Br-FluoroBenzene



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas

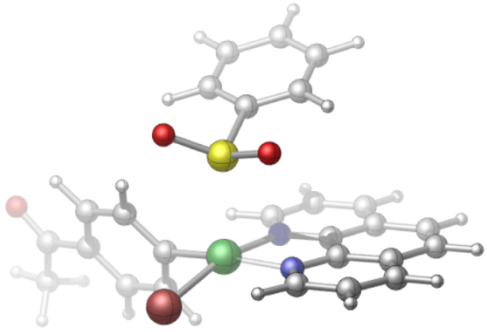
Zero-point correction= 0.356106 (Hartree/Particle)
Thermal correction to Energy= 0.384690
Thermal correction to Enthalpy= 0.385634
Thermal correction to Gibbs Free Energy= 0.292001
Sum of electronic and zero-point Energies= -1476.710885
Sum of electronic and thermal Energies= -1476.682301
Sum of electronic and thermal Enthalpies= -1476.681357
Sum of electronic and thermal Free Energies= -1476.774991

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1866.4536196

C	-0.11441	2.70688	1.10865
C	2.16251	2.80899	0.74691
C	2.22039	4.10974	1.28557
C	1.06325	4.71284	1.73454
C	-0.15988	4.0083	1.65733
C	-1.30934	1.91789	1.03311
C	-2.27625	-0.11051	0.47568
C	-3.53822	0.33365	0.91036
C	-3.67198	1.61149	1.4158
C	-2.5368	2.44825	1.49603
H	3.04696	2.30243	0.37482
H	3.17729	4.61739	1.34143
H	1.08111	5.71617	2.15189
H	-2.13638	-1.10567	0.07146
H	-4.38664	-0.33888	0.84546
H	-4.63574	1.97814	1.75914
N	1.02521	2.13384	0.65142
N	-1.19249	0.65935	0.52464
Ni	0.71337	0.21177	-0.03515
C	0.76692	-2.70552	-0.32213
C	-0.96763	-2.66293	-2.5268
C	0.34972	-3.90624	-0.90746
H	1.47271	-2.73154	0.50437
C	-0.51323	-3.86416	-1.99636
H	-1.62111	-2.66858	-3.39385
H	0.70257	-4.86503	-0.53968
C	-0.54966	-1.46678	-1.93072
H	-0.88652	-0.52557	-2.3594
C	0.29253	-1.48655	-0.81288
C	-0.97634	-0.21035	4.13271
C	-2.13687	-0.61446	4.79832
C	-2.62634	-1.91228	4.62805
C	-1.955	-2.81565	3.79901
C	-0.7916	-2.42418	3.13137
C	-0.33311	-1.1242	3.30841
H	-0.55213	0.78032	4.26097
H	-2.64962	0.07924	5.45971

H	-3.52695	-2.22424	5.15025
H	-2.32861	-3.82917	3.68038
H	-0.24376	-3.11471	2.49915
S	1.23462	-0.57767	2.40911
O	2.1592	-1.85746	2.46118
O	1.67656	0.72058	3.19741
C	-2.55997	3.78197	2.02737
H	-3.5074	4.1838	2.37541
C	-1.42011	4.528	2.10714
H	-1.4488	5.53212	2.52117
Br	2.77955	0.07656	-1.21242
F	-0.91612	-5.02454	-2.5634

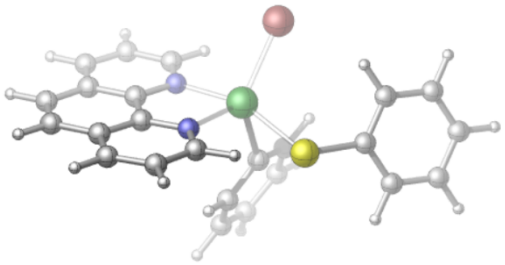
Intermediate-Radical Sulfone (Byp)Ni(II)-Br-Acetophenone



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Zero-point correction= 0.401750 (Hartree/Particle)
Thermal correction to Energy= 0.433130
Thermal correction to Enthalpy= 0.434074
Thermal correction to Gibbs Free Energy= 0.333389
Sum of electronic and zero-point Energies= -1530.077853
Sum of electronic and thermal Energies= -1530.046473
Sum of electronic and thermal Enthalpies= -1530.045529
Sum of electronic and thermal Free Energies= -1530.146214
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1919.8172184

C	-0.10716	2.66626	1.10786
C	2.17057	2.76321	0.74903
C	2.22944	4.06547	1.2841
C	1.07268	4.67167	1.73014
C	-0.15157	3.96884	1.65339
C	-1.30263	1.87867	1.03156
C	-2.27013	-0.14982	0.47417
C	-3.5321	0.29597	0.907
C	-3.66592	1.57461	1.41061
C	-2.53033	2.41077	1.49129
H	3.05472	2.25363	0.3803
H	3.18699	4.5719	1.33977
H	1.09179	5.67608	2.14478
H	-2.13186	-1.14542	0.07071
H	-4.38084	-0.37615	0.84205
H	-4.63001	1.94213	1.75201
N	1.03216	2.08971	0.6538
N	-1.18538	0.61916	0.52467
Ni	0.70983	0.17586	-0.0357
C	0.67695	-2.74315	-0.30357
C	-0.9644	-2.64868	-2.56831
C	0.22093	-3.92139	-0.89377
H	1.35503	-2.79125	0.54483
C	-0.60738	-3.89351	-2.02785
H	-1.58447	-2.59087	-3.45869
H	0.51142	-4.88868	-0.49497
C	-0.52353	-1.46407	-1.97272
H	-0.8047	-0.51253	-2.41855
C	0.279	-1.50731	-0.82517
C	-0.97053	-0.19348	4.15833
C	-2.13386	-0.57493	4.83231
C	-2.63464	-1.87152	4.68719
C	-1.9722	-2.7966	3.87521
C	-0.80601	-2.42855	3.19914
C	-0.33642	-1.12948	3.35189
H	-0.53801	0.79571	4.2684
H	-2.63964	0.13567	5.48093
H	-3.53728	-2.16559	5.21616
H	-2.35417	-3.80902	3.77637
H	-0.26452	-3.13655	2.58102
S	1.23457	-0.61534	2.44016
O	2.13702	-1.91009	2.49348
O	1.70253	0.68339	3.21155
C	-2.55265	3.74561	2.02005
H	-3.50014	4.14925	2.36578
C	-1.41209	4.49072	2.10008
H	-1.44061	5.49576	2.51186
Br	2.78966	0.00305	-1.17568
C	-1.06192	-5.19291	-2.61215
O	-0.78248	-6.25611	-2.07629
C	-1.88408	-5.1744	-3.89367
H	-2.82085	-4.62073	-3.75586
H	-2.11313	-6.20361	-4.17563
H	-1.33426	-4.6877	-4.70809

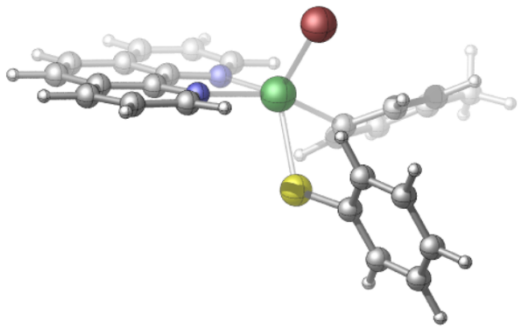
Thesis = E-TS-F, A4 = A4.1-TS-C'-D'



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -111.61 cm^{-1}
Zero-point correction= 0.356495 (Hartree/Particle)
Thermal correction to Energy= 0.381654
Thermal correction to Enthalpy= 0.382599
Thermal correction to Gibbs Free Energy= 0.297510
Sum of electronic and zero-point Energies= -1227.193206
Sum of electronic and thermal Energies= -1227.168046
Sum of electronic and thermal Enthalpies= -1227.167102
Sum of electronic and thermal Free Energies= -1227.252191
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1616.9378483

C	-1.41706	2.1822	1.22094
C	-0.16181	1.2981	2.9494
C	-0.98385	1.91109	3.91396
C	-2.05822	2.67257	3.4971
C	-2.30397	2.83196	2.11511
C	-1.59863	2.33592	-0.20076
C	-0.82033	1.87433	-2.3279
C	-1.8618	2.62162	-2.9114
C	-2.78664	3.24342	-2.09542
C	-2.67081	3.11999	-0.69268
H	0.68872	0.68865	3.23877
H	-0.76344	1.77597	4.96762
H	-2.71326	3.15543	4.21774
H	-0.05015	1.39891	-2.92654
H	-1.91818	2.70545	-3.99159
H	-3.59685	3.8327	-2.51711
N	-0.37498	1.42059	1.64297
N	-0.70185	1.72989	-1.01414
Ni	0.77818	0.60508	-0.01607
C	0.49078	-1.81609	-1.53565
C	-2.05909	-2.42308	-0.54968
C	-0.35948	-2.66674	-2.25122
H	1.48653	-1.59383	-1.90674
C	-1.63294	-2.96966	-1.76462
H	-3.04202	-2.67018	-0.15468
H	-0.01529	-3.09887	-3.18791
H	-2.28324	-3.64215	-2.31772
Br	2.58855	1.5226	-1.51479
C	-1.22121	-1.57071	0.17265
H	-1.54501	-1.17136	1.12924
C	0.0348	-1.23768	-0.34732
C	2.98121	-3.45718	0.71267
C	4.00967	-4.24592	0.19795
C	5.09612	-3.64804	-0.44675
C	5.14999	-2.25838	-0.57426
C	4.12863	-1.45842	-0.05734
C	3.04313	-2.06157	0.58996
H	2.13204	-3.91336	1.21208
H	3.96043	-5.32725	0.2977
H	5.8961	-4.26402	-0.84939
H	5.98949	-1.78854	-1.07982
H	4.15542	-0.38091	-0.17233
C	-3.38664	3.61271	1.58532
H	-4.06296	4.10012	2.28226
C	-3.5636	3.74817	0.23996
H	-4.38431	4.34448	-0.1496
S	1.72785	-1.06797	1.37005

Thesis = E-TS-F, A4 = A4.2-TS-C'-D'

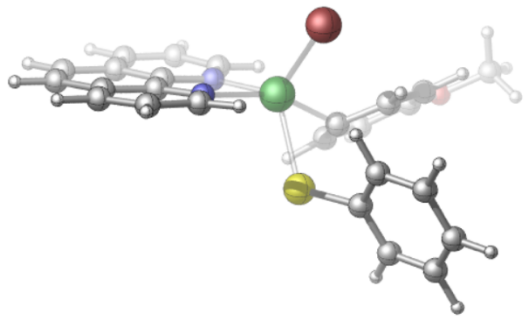


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -189.48 cm^{-1}
Zero-point correction= 0.383786 (Hartree/Particle)
Thermal correction to Energy= 0.411000
Thermal correction to Enthalpy= 0.411944
Thermal correction to Gibbs Free Energy= 0.320467
Sum of electronic and zero-point Energies= -1266.471751
Sum of electronic and thermal Energies= -1266.444538
Sum of electronic and thermal Enthalpies= -1266.443593
Sum of electronic and thermal Free Energies= -1266.535070

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1656.2199237

C	-0.99538	2.77434	1.45767
C	1.21303	2.63211	2.10277
C	1.02876	3.61055	3.09961
C	-0.21848	4.18293	3.25728
C	-1.27963	3.77914	2.41657
C	-2.02777	2.33363	0.55179
C	-2.63	1.01834	-1.24993
C	-3.91523	1.58889	-1.29391
C	-4.25967	2.54131	-0.35585
C	-3.30525	2.94778	0.60205
H	2.18382	2.1804	1.92537
H	1.86672	3.90745	3.72177
H	-0.39189	4.94711	4.01064
H	-2.33469	0.25304	-1.95975
H	-4.61634	1.26778	-2.05711
H	-5.24927	2.99106	-0.35196
N	0.22936	2.22252	1.31522
N	-1.71733	1.35806	-0.34417
Ni	0.31975	0.64792	-0.22457
C	1.22146	-1.59997	-1.89469
C	-1.32721	-2.59108	-2.45289
C	0.99044	-2.3664	-3.03732
H	2.21703	-1.22351	-1.69252
C	-0.28287	-2.8659	-3.34669
H	-2.31727	-3.00305	-2.64104
H	1.82397	-2.57498	-3.70517
Br	2.31129	1.72986	-1.32006
C	-1.1119	-1.83019	-1.30258
H	-1.92109	-1.69238	-0.59123
C	0.15245	-1.27854	-1.04819
C	2.25275	-3.29908	1.67949
C	3.51228	-3.88357	1.8149
C	4.66442	-3.14362	1.53857
C	4.55011	-1.81302	1.13073
C	3.29488	-1.21284	1.01057
C	2.14268	-1.95881	1.28515
H	1.35459	-3.8753	1.87973
H	3.59096	-4.92207	2.12618
H	5.64449	-3.60296	1.63604
H	5.44041	-1.23209	0.90454
H	3.21253	-0.18328	0.67626
C	-2.59781	4.3442	2.47133
H	-2.80517	5.10842	3.21567
C	-3.56641	3.95053	1.59657
H	-4.55632	4.39736	1.6314
S	0.46168	-1.23596	1.22443
C	-0.51736	-3.67406	-4.601
H	0.32456	-4.34337	-4.81118
H	-1.42305	-4.28505	-4.52202
H	-0.63704	-3.02365	-5.47844

Thesis = E-TS-F, A4 = A4.3-TS-C'-D'

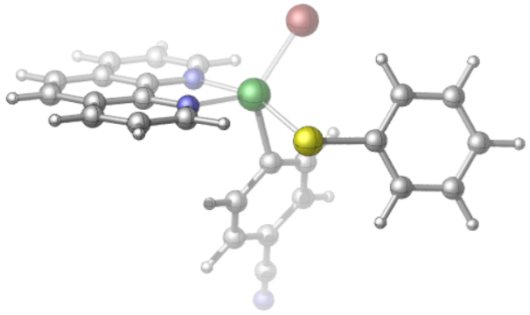


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -196.68 cm^{-1}
Zero-point correction= 0.389137 (Hartree/Particle)
Thermal correction to Energy= 0.417072
Thermal correction to Enthalpy= 0.418017
Thermal correction to Gibbs Free Energy= 0.325643
Sum of electronic and zero-point Energies= -1341.670456
Sum of electronic and thermal Energies= -1341.642521
Sum of electronic and thermal Enthalpies= -1341.641576
Sum of electronic and thermal Free Energies= -1341.733950
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1731.4191365

C	-1.0918	2.88342	1.59067
C	1.08721	2.70574	2.3225
C	0.87654	3.68177	3.3165
C	-0.36768	4.27164	3.42734
C	-1.4001	3.88727	2.54287
C	-2.09311	2.46084	0.64257
C	-2.64036	1.15827	-1.18524
C	-3.91671	1.74336	-1.27586
C	-4.28576	2.69746	-0.3488
C	-3.36414	3.08999	0.64642
H	2.05751	2.24141	2.17858
H	1.69305	3.96357	3.97324
H	-0.56009	5.03461	4.17733
H	-2.32782	0.39167	-1.88624
H	-4.5921	1.43183	-2.06577
H	-5.26965	3.15847	-0.38134
N	0.1298	2.31471	1.4939
N	-1.75879	1.48552	-0.24471
Ni	0.26944	0.75001	-0.03904
C	1.17688	-1.46876	-1.72129
C	-1.36511	-2.45485	-2.32951
C	0.98135	-2.21992	-2.88476

H	2.16894	-1.094	-1.49858
C	-0.29243	-2.707	-3.2013
H	-2.33757	-2.87777	-2.56527
H	1.83005	-2.40714	-3.53312
Br	2.38355	1.77789	-0.9728
C	-1.16336	-1.71151	-1.1732
H	-1.9868	-1.57788	-0.47767
C	0.09737	-1.15453	-0.8893
C	2.03343	-3.32064	1.79479
C	3.26087	-3.96833	1.93824
C	4.45278	-3.26871	1.73479
C	4.41088	-1.9156	1.39198
C	3.18797	-1.2536	1.26394
C	1.99603	-1.95908	1.46554
H	1.10424	-3.86348	1.93855
H	3.28379	-5.02333	2.19919
H	5.40801	-3.77648	1.83906
H	5.33311	-1.36563	1.22363
H	3.15959	-0.20627	0.97998
C	-2.71189	4.4697	2.54814
H	-2.93838	5.23347	3.28736
C	-3.65077	4.09225	1.6345
H	-4.63544	4.55186	1.63296
S	0.35466	-1.15143	1.39538
O	-0.59159	-3.44726	-4.30809
C	0.45696	-3.75308	-5.21342
H	0.00075	-4.34018	-6.01284
H	0.90098	-2.8436	-5.63925
H	1.2457	-4.34666	-4.73256

Thesis = E-TS-F, A4 = A4.4-TS-C'-D'

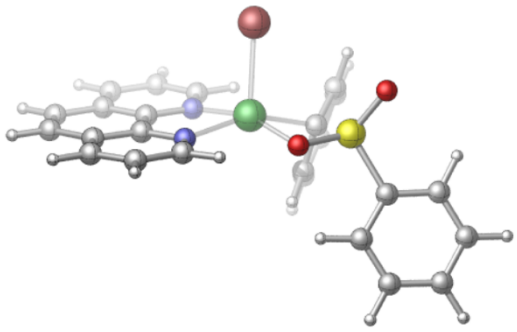


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -83.81 cm^{-1}
Zero-point correction= 0.355230 (Hartree/Particle)
Thermal correction to Energy= 0.382163
Thermal correction to Enthalpy= 0.383107
Thermal correction to Gibbs Free Energy= 0.293748
Sum of electronic and zero-point Energies= -1319.437987
Sum of electronic and thermal Energies= -1319.411054
Sum of electronic and thermal Enthalpies= -1319.410110
Sum of electronic and thermal Free Energies= -1319.499469

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1709.1532681

C	-1.44089	2.22654	1.28529
C	-0.25189	1.31448	3.04677
C	-1.1327	1.88126	3.98732
C	-2.20161	2.63351	3.54076
C	-2.38372	2.83049	2.15362
C	-1.5564	2.41992	-0.13801
C	-0.66544	2.04	-2.23823
C	-1.69346	2.78341	-2.84944
C	-2.67028	3.36028	-2.06164
C	-2.61985	3.19664	-0.65893
H	0.59606	0.71364	3.36051
H	-0.96087	1.71828	5.04598
H	-2.90107	3.08047	4.24244
H	0.14346	1.59989	-2.81212
H	-1.69955	2.89842	-3.92809
H	-3.47231	3.94439	-2.50526
N	-0.40413	1.47324	1.73551
N	-0.60836	1.85714	-0.92482
Ni	0.83893	0.73491	0.10914
C	0.64163	-1.65742	-1.4873
C	-1.91787	-2.35378	-0.57925
C	-0.14124	-2.53917	-2.23036
H	1.63939	-1.39861	-1.82779
C	-1.42832	-2.89037	-1.78566
H	-2.90443	-2.64017	-0.2267
H	0.24164	-2.96283	-3.15405
Br	2.69554	1.67608	-1.29654
C	-1.13614	-1.47147	0.15886
H	-1.51288	-1.08198	1.09957
C	0.12749	-1.09022	-0.31398
C	3.05235	-3.30825	0.77924
C	4.10352	-4.07462	0.27737
C	5.22161	-3.44957	-0.28211
C	5.28537	-2.05551	-0.33754
C	4.24092	-1.27777	0.16613
C	3.12315	-1.90817	0.72776
H	2.17998	-3.78529	1.21495
H	4.04784	-5.15914	0.32095
H	6.03928	-4.04832	-0.67473
H	6.15029	-1.56545	-0.77631
H	4.27584	-0.19635	0.10639
C	-3.45609	3.60497	1.59464
H	-4.17609	4.05677	2.27136
C	-3.57036	3.77778	0.24674
H	-4.38415	4.36842	-0.16502
S	1.77536	-0.9488	1.49182
C	-2.23435	-3.79714	-2.54602
N	-2.89516	-4.53052	-3.16321

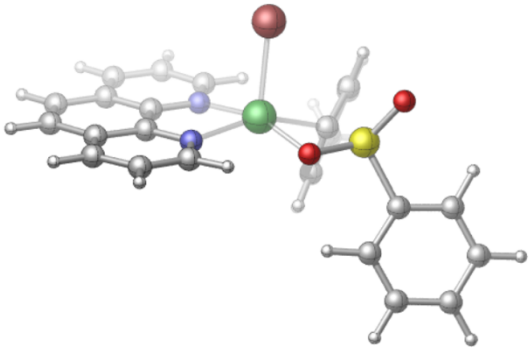
Thesis = A-TS-B, A4 = A4.1-TS-C-D



UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -196.30 cm^{-1}
Zero-point correction= 0.362262 (Hartree/Particle)
Thermal correction to Energy= 0.389632
Thermal correction to Enthalpy= 0.390576
Thermal correction to Gibbs Free Energy= 0.300525
Sum of electronic and zero-point Energies= -1377.459815
Sum of electronic and thermal Energies= -1377.432445
Sum of electronic and thermal Enthalpies= -1377.431501
Sum of electronic and thermal Free Energies= -1377.521552
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1767.1879182

C	-1.23922	2.61631	1.21607
C	-0.06404	1.63454	2.9508
C	-0.69077	2.46834	3.8965
C	-1.62271	3.39481	3.46647
C	-1.92226	3.49701	2.08928
C	-1.47252	2.68527	-0.20491
C	-0.93606	1.9113	-2.31458
C	-1.83513	2.81228	-2.91593
C	-2.56541	3.67158	-2.11767
C	-2.39367	3.632	-0.71624
H	0.68075	0.89712	3.23508
H	-0.43438	2.37555	4.94671
H	-2.12248	4.05165	4.1739
H	-0.33425	1.23426	-2.91098
H	-1.93644	2.8253	-3.9961
H	-3.26246	4.38265	-2.5537
N	-0.34012	1.70358	1.65375
N	-0.76491	1.84326	-0.99969
Ni	0.71587	0.73382	0.08228
C	1.88646	-0.69809	-2.49396
C	-0.69614	-1.81552	-2.45585
C	1.2306	-0.99605	-3.68039
H	2.88132	-0.26478	-2.49148
C	-0.06507	-1.54905	-3.67132
H	-1.68614	-2.26517	-2.4398
H	1.72688	-0.79707	-4.62729
C	-0.04817	-1.53774	-1.24676
H	-0.52166	-1.79716	-0.30288
C	1.21328	-0.8995	-1.26835
C	0.97059	-3.49667	1.7266
C	0.7299	-4.8155	2.11901
C	1.58275	-5.83937	1.69826
C	2.6867	-5.55375	0.88963
C	2.94014	-4.24059	0.48959
C	2.07159	-3.24298	0.91716
H	0.34415	-2.67687	2.06181
H	-0.1181	-5.04047	2.76002
H	1.39016	-6.86318	2.0068
H	3.35488	-6.35076	0.57591
H	3.80234	-3.98547	-0.11848
C	-2.85972	4.43615	1.53992
H	-3.38269	5.10503	2.21822
C	-3.08631	4.49869	0.19642
H	-3.79256	5.21801	-0.2095
S	2.41327	-1.49407	0.33532
O	1.61989	-0.58017	1.41335
O	3.95557	-1.37046	0.18033
Br	2.55468	2.33598	-0.49574
H	-0.5584	-1.79404	-4.60761

Thesis = A-TS-B, A4 = A4.2-TS-C-D

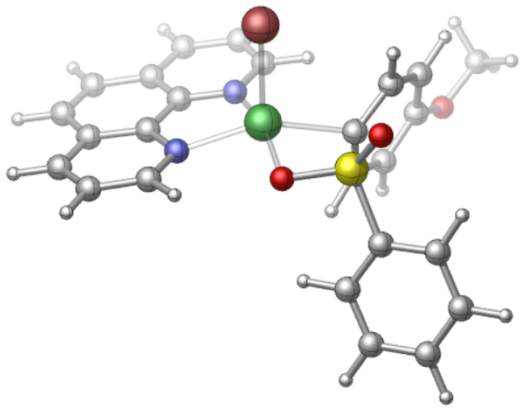


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -195.67 cm^{-1}
Zero-point correction= 0.389773 (Hartree/Particle)
Thermal correction to Energy= 0.419035
Thermal correction to Enthalpy= 0.419979
Thermal correction to Gibbs Free Energy= 0.325259
Sum of electronic and zero-point Energies= -1416.749596

Sum of electronic and thermal Energies= -1416.720334
Sum of electronic and thermal Enthalpies= -1416.719390
Sum of electronic and thermal Free Energies= -1416.814110
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1806.4830318

C	-1.18475	2.73587	1.52368
C	-0.02029	1.75116	3.26388
C	-0.6544	2.58198	4.20724
C	-1.58449	3.50855	3.77323
C	-1.8747	3.61375	2.3943
C	-1.40857	2.80803	0.10139
C	-0.85567	2.04003	-2.00603
C	-1.75094	2.94173	-2.61182
C	-2.48825	3.79816	-1.81673
C	-2.32689	3.75524	-0.41422
H	0.72318	1.01365	3.55136
H	-0.40513	2.48682	5.25896
H	-2.08983	4.16304	4.47888
H	-0.24726	1.36536	-2.59867
H	-1.84401	2.95815	-3.69271
H	-3.18269	4.5097	-2.25619
N	-0.2875	1.82301	1.96503
N	-0.69465	1.96857	-0.69019
Ni	0.77896	0.85509	0.39977
C	1.948	-0.58487	-2.17165
C	-0.62442	-1.70082	-2.14585
C	1.29809	-0.89055	-3.35644
H	2.94169	-0.14865	-2.17215
C	-0.0016	-1.45084	-3.37221
H	-1.61571	-2.14957	-2.12892
H	1.80178	-0.6927	-4.301
C	0.01511	-1.41741	-0.93306
H	-0.4693	-1.67331	0.00632
C	1.27352	-0.77768	-0.94473
C	1.00801	-3.37073	2.04944
C	0.75832	-4.68792	2.44178
C	1.60977	-5.71623	2.02906
C	2.7212	-5.43654	1.22866
C	2.98347	-4.12502	0.82885
C	2.11623	-3.12279	1.24813
H	0.38271	-2.54765	2.37876
H	-0.09561	-4.90821	3.07654
H	1.41026	-6.73875	2.33754
H	3.38837	-6.23691	0.92135
H	3.85158	-3.87441	0.2273
C	-2.80939	4.55321	1.84065
H	-3.33776	5.21987	2.51697
C	-3.02677	4.61896	0.49577
H	-3.73091	5.33864	0.08681
S	2.46988	-1.37598	0.66568
O	1.67606	-0.45749	1.7395
O	4.01445	-1.2614	0.5218
Br	2.62341	2.455	-0.17327
C	-0.66628	-1.80723	-4.6804
H	-0.66556	-0.96038	-5.37841
H	-1.70552	-2.11705	-4.52993
H	-0.14519	-2.63248	-5.18407

Thesis = A-TS-B, A4 = A4.3-TS-C-D

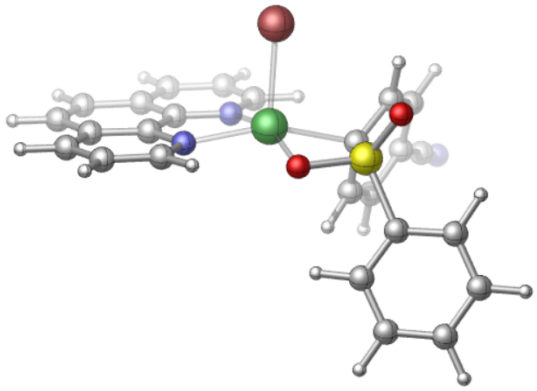


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -226.45 cm^{-1}
Zero-point correction= 0.394855 (Hartree/Particle)
Thermal correction to Energy= 0.424989
Thermal correction to Enthalpy= 0.425934
Thermal correction to Gibbs Free Energy= 0.328917
Sum of electronic and zero-point Energies= -1491.947544
Sum of electronic and thermal Energies= -1491.917409
Sum of electronic and thermal Enthalpies= -1491.916465
Sum of electronic and thermal Free Energies= -1492.013482
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1881.6809623

C	-1.1961	2.73176	1.72954
C	0.05829	1.78731	3.42882
C	-0.5568	2.61047	4.39096
C	-1.52556	3.51154	3.98826
C	-1.87239	3.59913	2.6214
C	-1.47807	2.78773	0.31708
C	-0.99388	2.01668	-1.80581
C	-1.93857	2.88734	-2.3804
C	-2.66377	3.73198	-1.56169
C	-2.44197	3.70609	-0.16725
H	0.82826	1.06816	3.69208
H	-0.26417	2.52884	5.43263
H	-2.01856	4.15885	4.7091

H	-0.39398	1.35342	-2.41945
H	-2.07921	2.88941	-3.45624
H	-3.3952	4.42064	-1.97689
N	-0.26106	1.84259	2.14063
N	-0.7742	1.96124	-0.49745
Ni	0.77334	0.89778	0.53218
C	1.9061	-0.55777	-2.04293
C	-0.65038	-1.71217	-2.05052
C	1.28443	-0.85406	-3.24968
H	2.89588	-0.11324	-2.02886
C	-0.00403	-1.42848	-3.26264
H	-1.63102	-2.17794	-2.08041
H	1.80494	-0.63603	-4.17588
C	-0.0257	-1.43011	-0.83878
H	-0.51863	-1.70049	0.09188
C	1.22403	-0.76519	-0.82622
C	0.94404	-3.28273	2.22017
C	0.65958	-4.58376	2.64145
C	1.46764	-5.64697	2.22959
C	2.56965	-5.41857	1.40045
C	2.86599	-4.12379	0.97083
C	2.04215	-3.0861	1.39097
H	0.35273	-2.43387	2.54728
H	-0.18724	-4.76434	3.29789
H	1.24128	-6.65669	2.56079
H	3.20303	-6.24611	1.09354
H	3.72765	-3.91218	0.34549
C	-2.85219	4.51046	2.09957
H	-3.36955	5.16912	2.79208
C	-3.12609	4.55927	0.76437
H	-3.8649	5.25709	0.37935
S	2.4363	-1.36282	0.76697
O	1.72677	-0.39805	1.85416
O	3.97652	-1.30843	0.5539
Br	2.57411	2.50773	-0.15641
O	-0.68965	-1.76233	-4.39484
C	-0.0575	-1.56547	-5.65005
H	-0.76729	-1.91807	-6.40063
H	0.87205	-2.144	-5.72949
H	0.16289	-0.50485	-5.83086

Thesis = A-TS-B, A4 = A4.4-TS-C-D

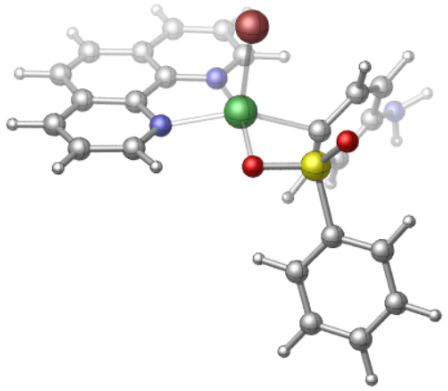


UB3LYP-(Br, Ni, S-LANL2DZ)/6-31g(d)-gas
Imaginary frequency = -122.19 cm^{-1}
Zero-point correction= 0.361111 (Hartree/Particle)
Thermal correction to Energy= 0.390184
Thermal correction to Enthalpy= 0.391128
Thermal correction to Gibbs Free Energy= 0.297094
Sum of electronic and zero-point Energies= -1469.705045
Sum of electronic and thermal Energies= -1469.675973
Sum of electronic and thermal Enthalpies= -1469.675028
Sum of electronic and thermal Free Energies= -1469.769062
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1859.4045318

C	-1.19302	2.69803	1.37443
C	0.04787	1.79097	3.10494
C	-0.5545	2.65552	4.03913
C	-1.50644	3.55898	3.6051
C	-1.85316	3.60691	2.23567
C	-1.47586	2.7092	-0.03906
C	-1.01074	1.85474	-2.13533
C	-1.9344	2.72784	-2.74012
C	-2.64078	3.61381	-1.95021
C	-2.41971	3.63014	-0.55482
H	0.8074	1.07025	3.39281
H	-0.26308	2.60436	5.08293
H	-1.98704	4.23936	4.3034
H	-0.42801	1.15869	-2.72813
H	-2.07388	2.69568	-3.81543
H	-3.35753	4.30325	-2.38874
N	-0.27146	1.81059	1.81674
N	-0.79316	1.83831	-0.82546
Ni	0.71643	0.77719	0.24322
C	1.96552	-0.61669	-2.31781

C	-0.57614	-1.82926	-2.4117
C	1.38603	-0.90685	-3.53658
H	2.94489	-0.15335	-2.26154
C	0.09944	-1.50597	-3.60609
H	-1.54889	-2.30978	-2.46036
H	1.91198	-0.67222	-4.45726
C	0.00396	-1.55421	-1.18089
H	-0.50977	-1.84731	-0.26877
C	1.24214	-0.85504	-1.1183
C	0.94518	-3.46855	1.83957
C	0.69975	-4.79072	2.21707
C	1.54211	-5.81442	1.77518
C	2.64072	-5.52663	0.96017
C	2.90028	-4.2105	0.5742
C	2.04125	-3.21413	1.02346
H	0.32584	-2.64975	2.18987
H	-0.14418	-5.01832	2.8622
H	1.34489	-6.84072	2.07177
H	3.29968	-6.32411	0.62935
H	3.7581	-3.95469	-0.03955
C	-2.81513	4.51874	1.68305
H	-3.31988	5.2101	2.35235
C	-3.08676	4.52811	0.34649
H	-3.81112	5.22692	-0.06294
S	2.38919	-1.46341	0.46247
O	1.60276	-0.54903	1.54765
O	3.92631	-1.33186	0.29007
Br	2.52251	2.39731	-0.35537
C	-0.49727	-1.79499	-4.86911
N	-0.99226	-2.02248	-5.89972

TS-Reductive Elimination (Byp)Ni(II)-Br-Aniline



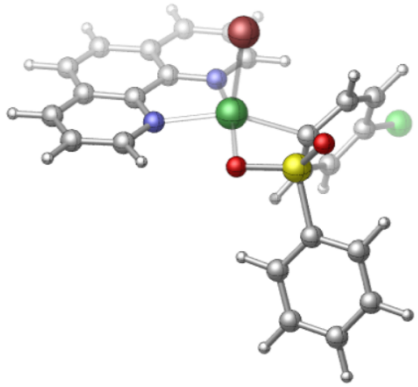
UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -232.86 cm^{-1}
Zero-point correction= 0.378752 (Hartree/Particle)
Thermal correction to Energy= 0.407721
Thermal correction to Enthalpy= 0.408665
Thermal correction to Gibbs Free Energy= 0.314841
Sum of electronic and zero-point Energies= -1432.796179
Sum of electronic and thermal Energies= -1432.767211
Sum of electronic and thermal Enthalpies= -1432.766266
Sum of electronic and thermal Free Energies= -1432.860090

UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1822.5360531

C	-1.20591	2.69429	1.42309
C	0.07651	1.79621	3.12673
C	-0.54096	2.6275	4.08012
C	-1.5259	3.50818	3.6712
C	-1.88619	3.56741	2.3064
C	-1.50083	2.72244	0.01262
C	-1.02433	1.92134	-2.10094
C	-1.9876	2.7675	-2.68158
C	-2.71766	3.61594	-1.87104
C	-2.48265	3.61794	-0.47847
H	0.85887	1.09239	3.39477
H	-0.23757	2.56798	5.12024
H	-2.02128	4.161	4.38545
H	-0.42089	1.2568	-2.70958
H	-2.13752	2.74752	-3.75597
H	-3.46287	4.28663	-2.29125
N	-0.25539	1.82459	1.84073
N	-0.79157	1.89261	-0.79376
Ni	0.7775	0.86494	0.24623
C	1.91102	-0.5828	-2.31938
C	-0.61559	-1.80309	-2.27761
C	1.27541	-0.90633	-3.50411
H	2.88998	-0.11453	-2.32582
C	-0.00421	-1.51591	-3.50801
H	-1.58837	-2.29076	-2.25999
H	1.76038	-0.68292	-4.45257
C	0.02238	-1.49002	-1.07626
H	-0.44835	-1.76767	-0.13626
C	1.25001	-0.79002	-1.0862
C	1.06527	-3.29622	1.98472
C	0.81982	-4.59955	2.42329
C	1.65674	-5.6442	2.02164
C	2.7489	-5.39421	1.18564
C	3.00596	-4.09672	0.73905
C	2.15408	-3.07769	1.14883
H	0.45158	-2.46039	2.30423
H	-0.01872	-4.79617	3.08582
H	1.46123	-6.65576	2.36673
H	3.4055	-6.20673	0.88731
H	3.85966	-3.86769	0.10884
C	-2.88362	4.45559	1.77806
H	-3.40394	5.11885	2.46398
C	-3.17053	4.47714	0.44485
H	-3.92285	5.1576	0.05484

S	2.49772	-1.35009	0.5029
O	1.76442	-0.39645	1.58497
O	4.03698	-1.25781	0.28976
Br	2.54891	2.5082	-0.45321
N	-0.65088	-1.78352	-4.71708
H	-0.0348	-1.91572	-5.51027
H	-1.35785	-2.50765	-4.67369

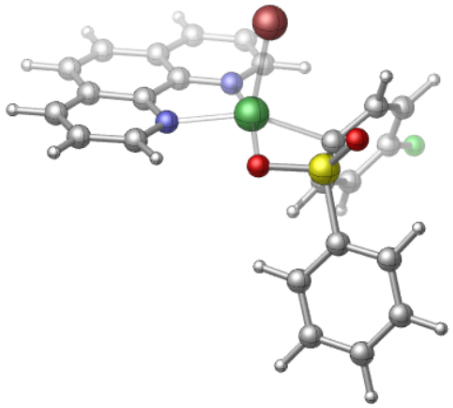
TS-Reductive Elimination (Byp)Ni(II)-Br-Chlorobenzene



UB3LYP/6-31g(d)-(Br, Ni, Cl-LANL2DZ)-gas
Imaginary frequency = -174.66 cm^{-1}
Zero-point correction= 0.352460 (Hartree/Particle)
Thermal correction to Energy= 0.381145
Thermal correction to Enthalpy= 0.382089
Thermal correction to Gibbs Free Energy= 0.288349
Sum of electronic and zero-point Energies= -1391.812464
Sum of electronic and thermal Energies= -1391.783779
Sum of electronic and thermal Enthalpies= -1391.782835
Sum of electronic and thermal Free Energies= -1391.876575
UM06/6-311+g(d,p)-(Br, Ni, Cl -SDD)-SMD(THF)
HF=-2226.7415173

C	-1.22223	2.63253	1.2194
C	-0.01614	1.68941	2.95477
C	-0.64521	2.52625	3.89617
C	-1.59418	3.434	3.46369
C	-1.90905	3.51441	2.08838
C	-1.47112	2.67995	-0.19984
C	-0.94549	1.88868	-2.30562
C	-1.86385	2.76823	-2.90907
C	-2.59835	3.62615	-2.11339
C	-2.4108	3.60693	-0.7134
H	0.74107	0.96575	3.24151
H	-0.37727	2.45039	4.94482
H	-2.09616	4.09271	4.16776
H	-0.33848	1.21612	-2.90151
H	-1.9769	2.76439	-3.98802
H	-3.31098	4.32079	-2.55057
N	-0.30563	1.73847	1.65973
N	-0.7602	1.8377	-0.99181
Ni	0.73725	0.75452	0.08871
C	1.89667	-0.71147	-2.47201
C	-0.68351	-1.84655	-2.4295
C	1.25445	-1.01648	-3.66235
H	2.88956	-0.27379	-2.47413
C	-0.03469	-1.57094	-3.62749
H	-1.6688	-2.30094	-2.4303
H	1.73782	-0.82586	-4.61497
C	-0.03432	-1.55417	-1.22622
H	-0.51436	-1.81138	-0.28545
C	1.22342	-0.90363	-1.24165
C	0.98593	-3.46384	1.76863
C	0.73998	-4.77889	2.17013
C	1.57641	-5.81203	1.7391
C	2.66925	-5.54009	0.91094
C	2.92831	-4.23107	0.50115
C	2.07584	-3.22449	0.93991
H	0.37232	-2.63724	2.11082
H	-0.09924	-4.99362	2.82588
H	1.37942	-6.83279	2.05462
H	3.3243	-6.3445	0.58887
H	3.78211	-3.98682	-0.12295
C	-2.86541	4.4331	1.53713
H	-3.39106	5.10291	2.21235
C	-3.10642	4.47529	0.19537
H	-3.82707	5.17905	-0.21237
S	2.42203	-1.48259	0.34533
O	1.6528	-0.55192	1.42334
O	3.95957	-1.36773	0.15361
Br	2.57362	2.33097	-0.54838
Cl	-0.85519	-1.96587	-5.18109

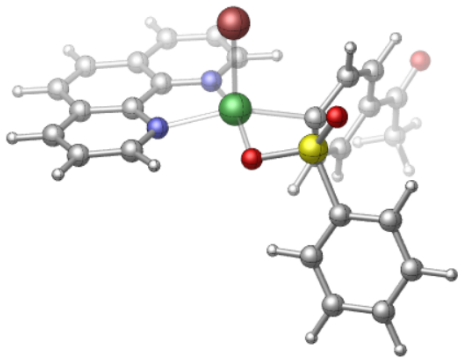
TS-Reductive Elimination (Byp)Ni(II)-Br-Fluorobenzene



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -200.31 cm^{-1}
Zero-point correction= 0.353989 (Hartree/Particle)
Thermal correction to Energy= 0.382266
Thermal correction to Enthalpy= 0.383210
Thermal correction to Gibbs Free Energy= 0.290700
Sum of electronic and zero-point Energies= -1476.699666
Sum of electronic and thermal Energies= -1476.671389
Sum of electronic and thermal Enthalpies= -1476.670445
Sum of electronic and thermal Free Energies= -1476.762955
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1866.4279038

C	-1.22519	2.62183	1.20954
C	-0.02115	1.66399	2.938
C	-0.65025	2.49369	3.88552
C	-1.59874	3.40542	3.45995
C	-1.91224	3.49704	2.08516
C	-1.47237	2.68146	-0.20941
C	-0.94337	1.90843	-2.32072
C	-1.8604	2.79331	-2.91815
C	-2.59611	3.64483	-2.11638
C	-2.41101	3.61334	-0.71647
H	0.73542	0.93748	3.21915
H	-0.38302	2.40922	4.93373
H	-2.10101	4.05857	4.16899
H	-0.33497	1.24031	-2.9204
H	-1.97124	2.80017	-3.9974
H	-3.30737	4.34385	-2.54885
N	-0.30965	1.72315	1.64291
N	-0.76013	1.84599	-1.00718
Ni	0.74017	0.75525	0.06665
C	1.88392	-0.71983	-2.49775
C	-0.70141	-1.84515	-2.43796
C	1.2344	-1.02838	-3.68329
H	2.87838	-0.28593	-2.50369
C	-0.05416	-1.57987	-3.63743
H	-1.68779	-2.29847	-2.44669
H	1.7032	-0.85083	-4.64647
C	-0.04494	-1.54956	-1.23829
H	-0.51899	-1.79974	-0.29268
C	1.21461	-0.9064	-1.26532
C	0.98324	-3.4547	1.76136
C	0.73409	-4.76678	2.17063
C	1.5714	-5.80367	1.75043
C	2.66814	-5.53808	0.92534
C	2.92998	-4.23199	0.50794
C	2.07689	-3.22131	0.93588
H	0.36922	-2.62515	2.0957
H	-0.10814	-4.97627	2.82429
H	1.37223	-6.8221	2.07218
H	3.32422	-6.34517	0.61201
H	3.78695	-3.99223	-0.1136
C	-2.86767	4.42068	1.54042
H	-3.39368	5.08517	2.22065
C	-3.10737	4.47426	0.19883
H	-3.82721	5.18187	-0.20369
S	2.42713	-1.48295	0.33018
O	1.66359	-0.54645	1.40632
O	3.96644	-1.37691	0.14008
Br	2.57741	2.33216	-0.57984
F	-0.67144	-1.88357	-4.80014

TS-Reductive Elimination (Byp)Ni(II)-Br-Acetophenone



UB3LYP/6-31g(d)-(Br, Ni-LANL2DZ)-gas
Imaginary frequency = -134.03 cm^{-1}
Zero-point correction= 0.400016 (Hartree/Particle)
Thermal correction to Energy= 0.430867
Thermal correction to Enthalpy= 0.431811
Thermal correction to Gibbs Free Energy= 0.333627
Sum of electronic and zero-point Energies= -1530.069383
Sum of electronic and thermal Energies= -1530.038532
Sum of electronic and thermal Enthalpies= -1530.037588
Sum of electronic and thermal Free Energies= -1530.135772
UM06/6-311+g(d,p)-(Br, Ni -SDD)-SMD(THF)
HF=-1919.795899

C	-1.22538	2.66058	1.24621
C	-0.01628	1.72234	2.98252
C	-0.61957	2.58543	3.91759
C	-1.55515	3.50461	3.48086
C	-1.88436	3.56987	2.10784
C	-1.48927	2.68968	-0.17071

C	-1.002	1.85165	-2.26904
C	-1.90238	2.7465	-2.87786
C	-2.60963	3.63299	-2.08914
C	-2.4118	3.62984	-0.69015
H	0.73198	0.9904	3.27172
H	-0.34114	2.52127	4.96423
H	-2.03548	4.18457	4.17978
H	-0.41742	1.15453	-2.85935
H	-2.02174	2.73211	-3.95605
H	-3.30808	4.33884	-2.53124
N	-0.32025	1.75769	1.69104
N	-0.80744	1.81772	-0.95601
Ni	0.67638	0.72711	0.12178
C	1.86965	-0.65154	-2.46882
C	-0.65912	-1.88307	-2.48914
C	1.25397	-0.96083	-3.66516
H	2.84586	-0.17832	-2.44413
C	-0.02503	-1.57501	-3.70664
H	-1.62904	-2.37243	-2.48398
H	1.73922	-0.73694	-4.61019
C	-0.05305	-1.58896	-1.27181
H	-0.54116	-1.8742	-0.34291
C	1.18055	-0.88478	-1.24967
C	0.95573	-3.52602	1.71548
C	0.73436	-4.85087	2.0987
C	1.59649	-5.86065	1.66297
C	2.69087	-5.55548	0.84856
C	2.92604	-4.23621	0.45759
C	2.048	-3.25354	0.90026
H	0.32118	-2.71709	2.06143
H	-0.10594	-5.09141	2.74403
H	1.4185	-6.88915	1.96435
H	3.36584	-6.34173	0.52287
H	3.78055	-3.96665	-0.15499
C	-2.82662	4.49998	1.55158
H	-3.331	5.19149	2.22106
C	-3.07931	4.52722	0.21147
H	-3.7878	5.24082	-0.20034
S	2.36772	-1.49687	0.3334
O	1.55987	-0.59879	1.42186
O	3.90621	-1.34399	0.18247
Br	2.48993	2.35583	-0.43752
C	-0.62124	-1.88341	-5.03212
O	-0.04775	-1.57105	-6.07012
C	-1.96484	-2.60025	-5.08861
H	-2.74823	-2.02531	-4.57965
H	-1.91201	-3.58165	-4.6017
H	-2.24172	-2.7342	-6.13583

Appendix 5: Supporting Information Chapter 6

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3)/def2-SVP level of the theory in implicit solvent (PhCl) using CPCM as the solvation model with the “guess=mix” keyword, as implemented in Gaussian 16, Revision C.01. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Single point energy calculations in implicit solvent using and B3LYP-D3/def2-TZVPP-CPCM(DMSO) were also performed. All energy decomposition analysis (EDA) was done using the second-generation absolutely-localized molecular orbital EDA available in Q-Chem version 5.3. These calculations were performed at the same level of theory used for single point energy calculations but in the gas phase. All 3-D structures were generated using CYLview20. NBO analysis was performed using NBO version 3.1 as available in the Gaussian software package. Orbitals visualizied using GaussView 6. Non-covalent interaction (NCI) analysis was performed using the Multiwfn software with the isosurfaces visualized using VMD and colored scatter plots made with Multiwfn scripts and gnuplot 5.4.

Full reference for Gaussian 16 Software:

Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Full reference for Q-Chem 5.0 Software:

Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kús, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock III, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio Jr., H. Dop, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, P. A. Pieniazek, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, N. Sergueev, S. M. Sharada, S. Sharmaa, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, V. Vanovschi, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhou, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard III, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer III, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xua, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon

Reference GaussView 6:

GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

Reference CYLview20:

CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org)

Reference NBO 3.1:

NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

Multiwfn 3.8:

Tian Lu, Feiwu Chen, *J. Comput. Chem.*, 33, 580-592 (2012).

VMD:

Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38.

GNUplot

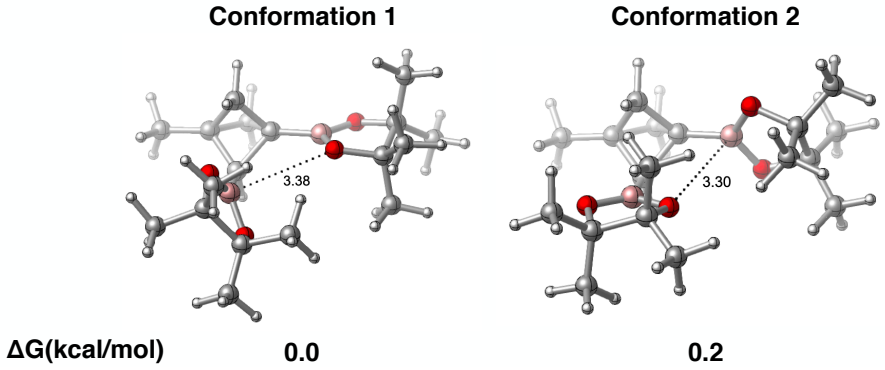


Figure A5.1: Lowest energy conformations obtained from conformational search of the BCP bis-**14**. NBO energies reported in kcal/mol.

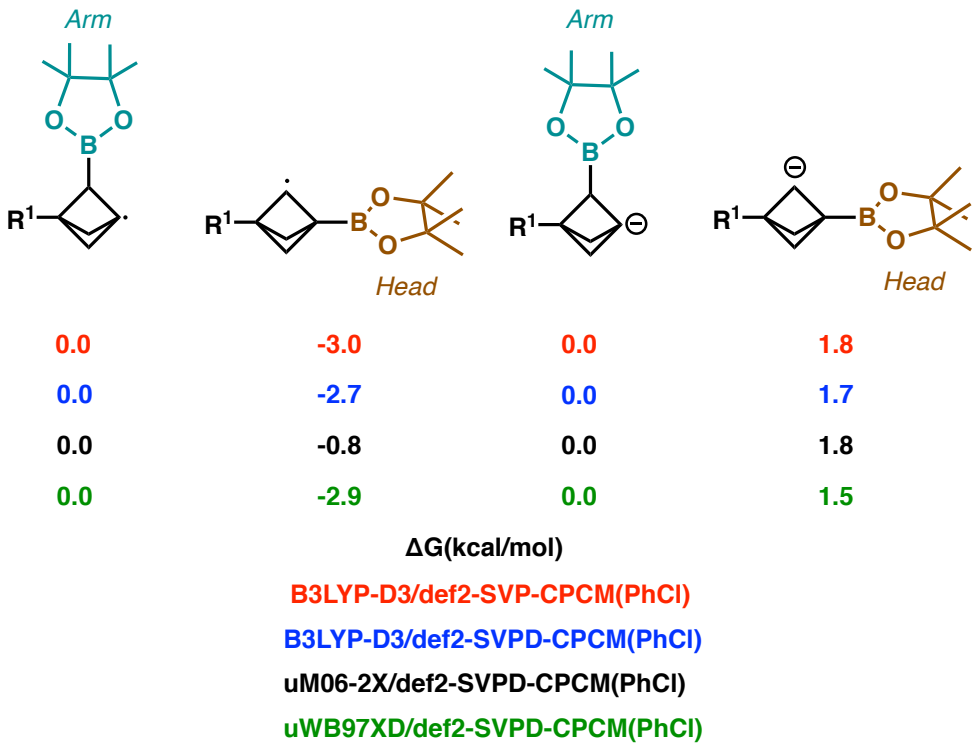
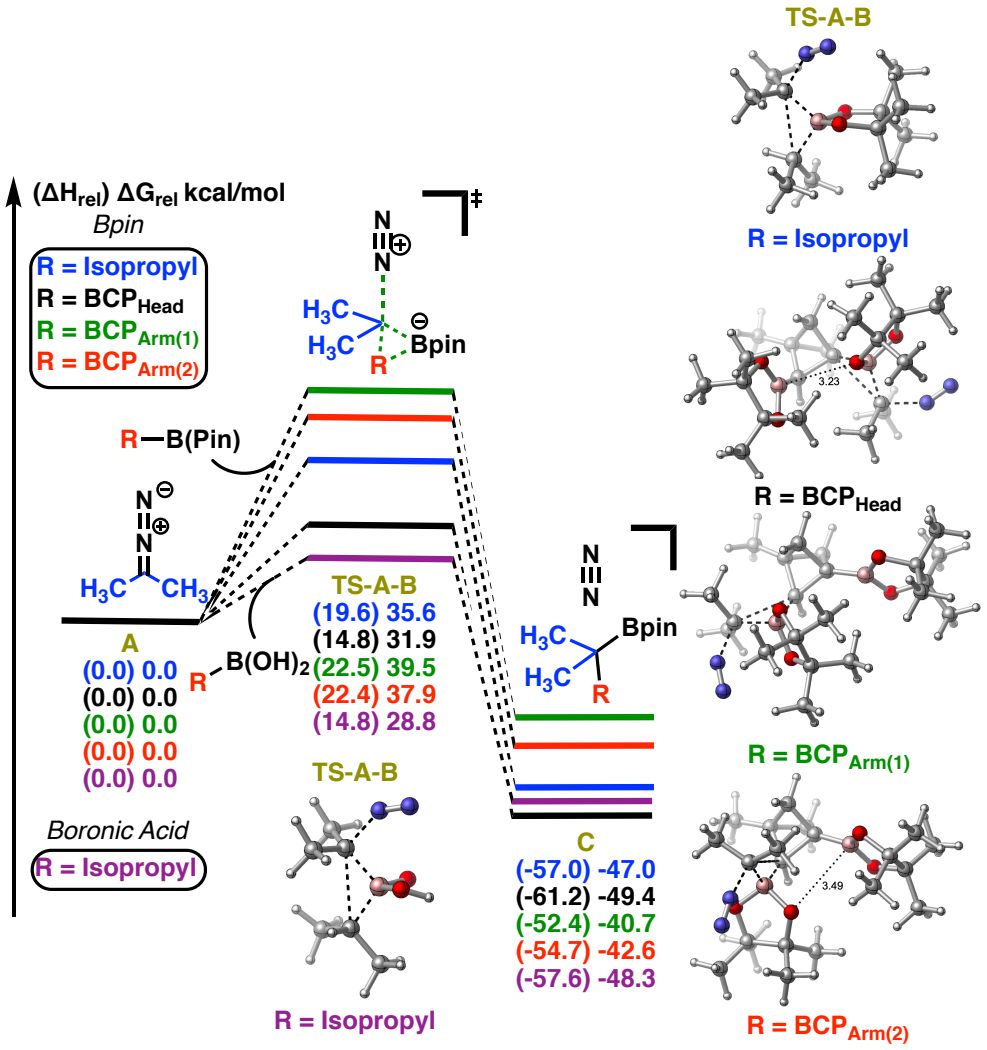


Figure A5.2: Relative free energies of both the radical and anionic intermediates that could be formed from 1 and $2e^{--}$ pathways. All free energies were obtained from optimizations done at the indicated level of theory at the bottom of the figure.

Initially, the stability of both the radical and anionic intermediate at both the head and arm position of **14** were modeled (**Figure A5.2**). All calculations suggested that the radical was thermodynamically preferred at the arm while the anion was preferred at the head of **14**. As both 1 and $2e^{-}$ pathways were shown to react exclusively at the head Bpin of the bis-boronate BCPs, the relative stability of the putative radical and anionic intermediates does not correlate with observed reactivity. As such, we then explored the full reaction profile of a model reaction (see below) to gain insights into the factors controlling reactivity and selectivity.



B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)

Figure A5.3: Reaction coordinate diagrams of concerted boron insertion pathways with bis-boronate BCP **14** at both the head and arm boronate. R = Isopropyl included for comparison. All pathways made relative to lowest energy conformation.

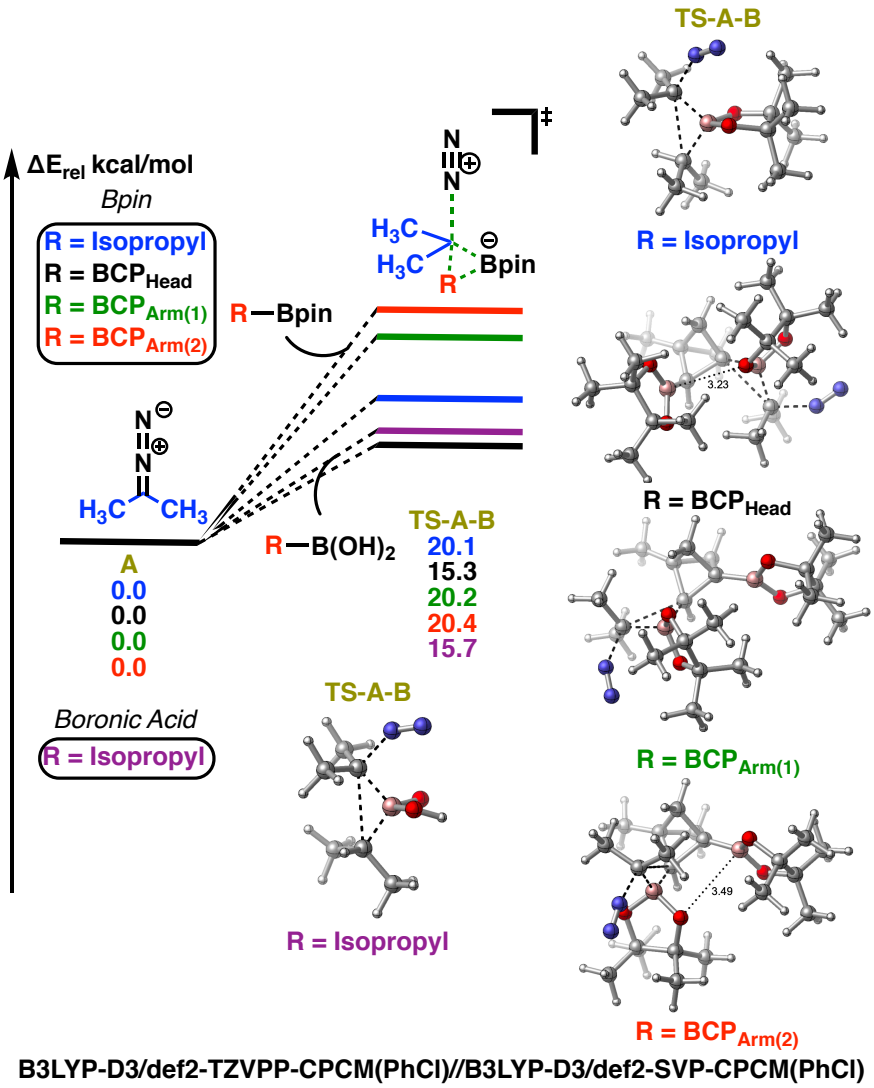


Figure A5.4: Reaction coordinate diagrams of concerted boron insertion pathways with bis-boronate BCP **14** at both the head and arm boronate in terms of total energy (E). R = Isopropyl included for comparison.

Modeling the reaction coordinate diagram of the boron insertion reaction which shows a preference in reactivity for the head Bpin in **14** (**Figure 6.5A** in the Thesis). Preliminary calculations of the boron insertion pathway revealed that this transformation proceeds via a concerted transition state. All attempts at locating putative intermediates previously proposed for these transformations failed (i.e., optimizations lead to either lead to reactants or products). Pathways were modeled for reactions at the head and arm of **14** from both conformations 1 and 2 (**Figure A5.3**). An additional

pathway where the alkyl boronic ester with the alkyl group as an isopropyl is also shown as a reference for the barriers of these transformations, which was not reported in the previous publication. The alkyl model system has a barrier of 35.6 kcal/mol. The computed barrier via the head of **14** is 31.9 kcal/mol which is much closer to the barrier of 28.8 kcal/mol of the alkyl boronic acid. However, reactions at the arm from conformations **1** and **2** ($BCP_{Arm(1)}$ and $BCP_{Arm(2)}$) are substantially higher in free energy, 39.5 and 37.9 kcal/mol respectfully. These results reveal that the experimentally observed regioselectivity of these reactions are *kinetically* controlled. The relative barriers of the total energy of these calculations (**Figure A5.4**) retained similar trends, making energy decomposition analysis a viable next step in further interpretation of these results.

Equation Energy Decomposition Analysis

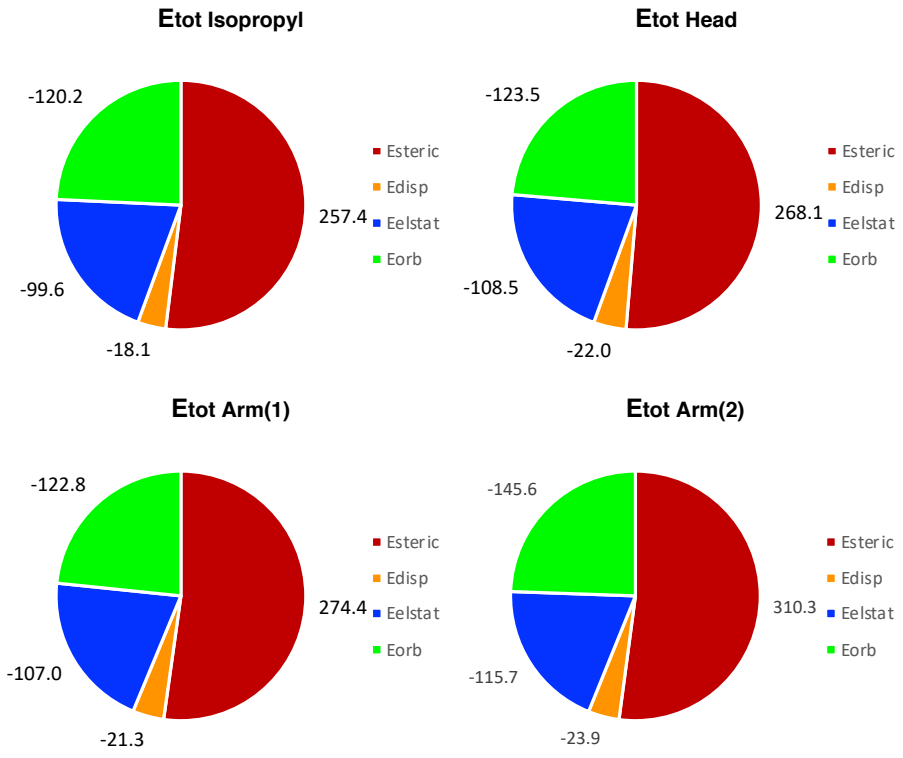
$$\Delta E_{act} = \Delta E_{dist} + \Delta E_{int}$$

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{pol} + \Delta E_{ct} + \Delta E_{disp}$$

$$\Delta E_{Sterics} = \Delta E_{Pauli} + \Delta E_{dist}$$

$$\Delta E_{Orb} = \Delta E_{pol} + \Delta E_{ct}$$

Total Energy Decomposition Analysis



B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl)

Figure A5.5: Energy decomposition analysis of indicated transition states using the second-generation ALMO-EDA.

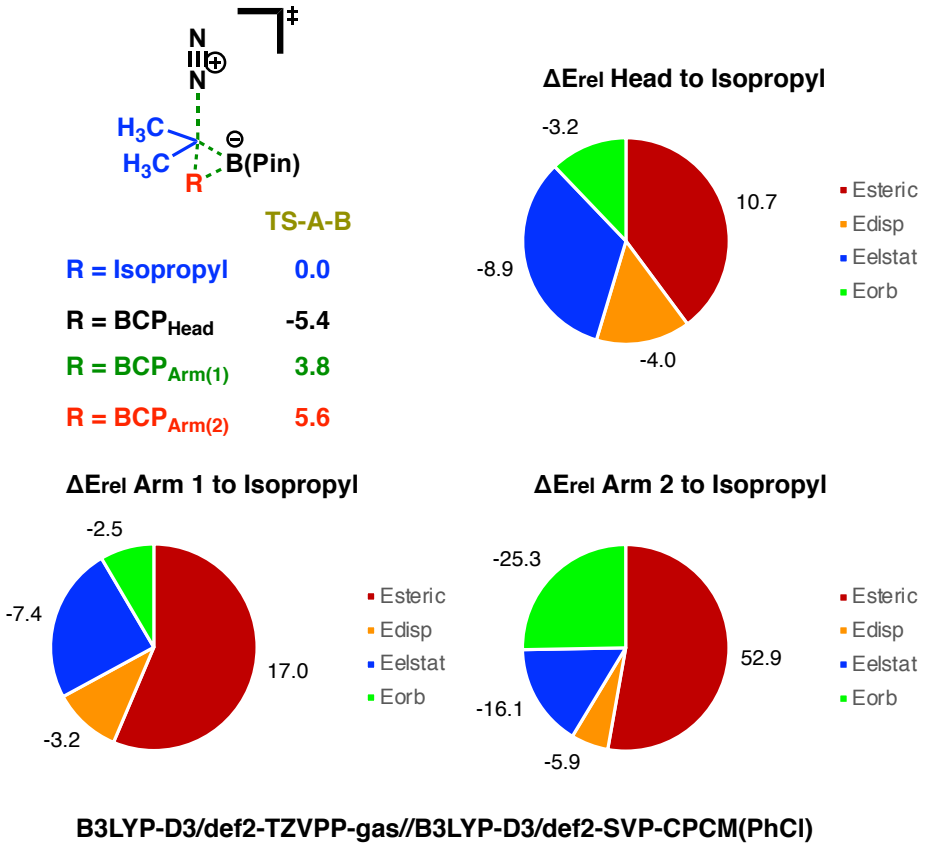


Figure A5.6: Energy decomposition analysis of indicated transition states made relative to R=Isopropyl transition state.

Energy decomposition analysis (EDA) using the second generation ALMO-EDA decomposes the activation energy into one unfavorable E_{steric} and three favorable E_{disp}, E_{elstat}, and E_{orb}, electronic interactions where disp = dispersion, elstat = electrostatic and orb = orbital (**Figure A5.5**). The EDA of the transition states was made relative to R = Isopropyl (**Figure A5.6**) to highlight the change in the decomposed energies between the transition states modeled at the head and arm Bpin of the BCP. Reactions through the head Bpin of BCP (ΔE_{rel} Head; **Figure A5.6**) has an increase in favorable electronic interactions which overcome the increase in disfavorable steric interactions; resulting in a lower barrier (~5.4 kcal/mol) with respect to the R = Isopropyl transition state. Transition states at the arm Bpin of BCP (ΔE_{rel} **Arm 1** and ΔE_{rel} **Arm 2**) have larger increase in

steric interactions which outweigh the change in favorable electronic interactions, resulting in higher barriers (~3.8 kcal/mol) through R = $BCP_{Arm(1)}$ and $BCP_{Arm(2)}$.

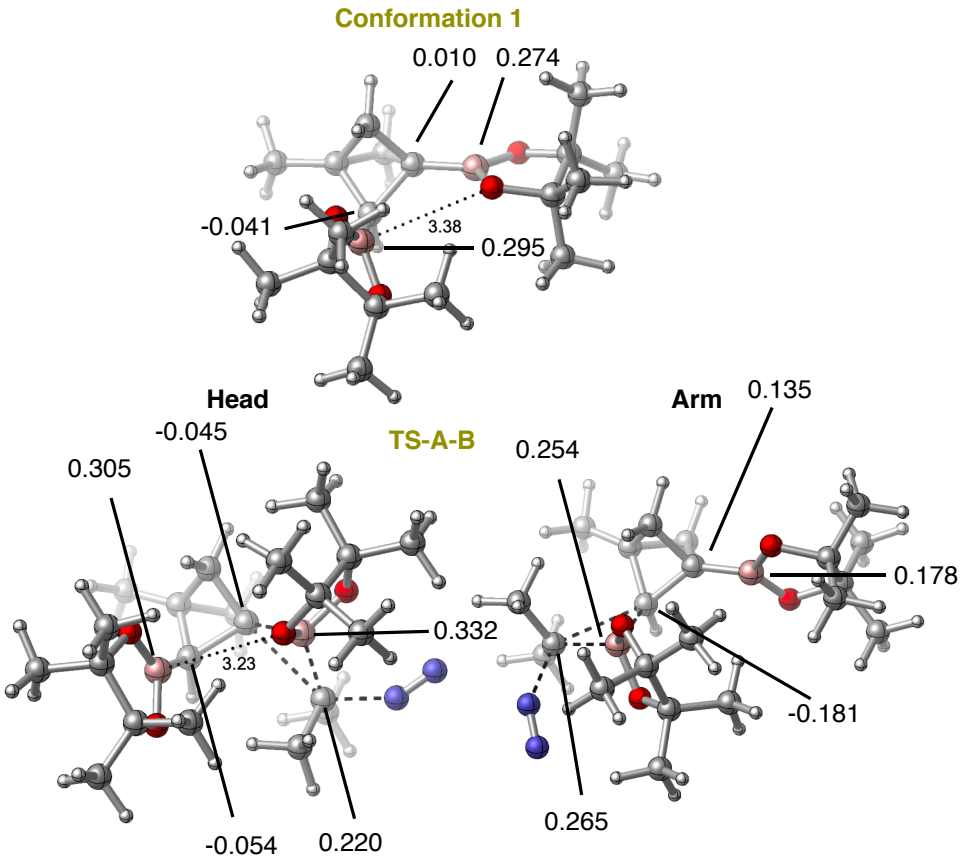
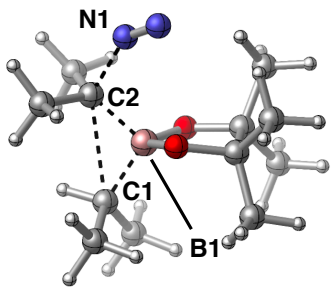


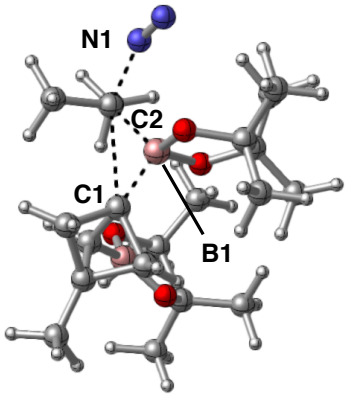
Figure A5.7: Mulliken charges labeled at head and arm boron and carbon for conformation 1 and additionally at the carbene carbon through TS-A-B for both arm and head transition states.

Moreover, analysis of the Mulliken charges (**Figure A5.7**) of the lowest energy intermediate of **14** show that there is more negative charge at the arm carbon than at the bridgehead carbon (-0.041 vs. 0.10). Performing the same analysis of the lowest energy transition states shows a larger quantity of negative charge building up through **TS-A-B Arm** then through **TS-A-B Head** on the reacting BCP carbon (-0.181 vs. -0.045). Overall, these results suggest that the hybridization of the bridgehead carbon $sp^{2.0}$ reduces the negative charge through **TS-A-B** which corresponds to the lower barrier.

TS-A-B

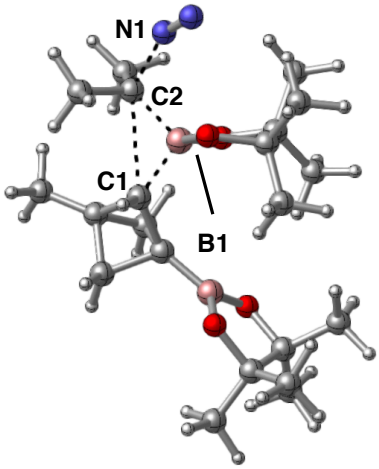


R = Isopropyl

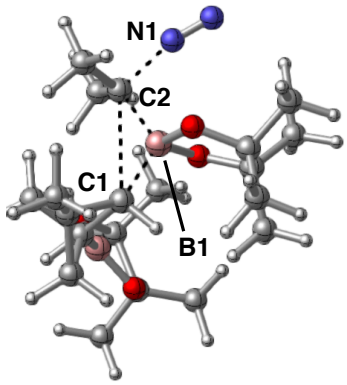


R = BCP_{Head}

Bond	Distance	Distance	Distance(rel)
B1-C2	1.68743	1.70969	0.02226
C1-N5	1.75364	1.77047	0.01683
C2-C1	2.57488	2.62439	0.04951
B1-C1	1.72005	1.65654	-0.06351
Angle	**Degrees**	**Degrees**	**Degrees(rel)**
C1-B1-C2	98.51224	102.44058	3.92814



R = $BCP_{Arm(1)}$



R = $BCP_{Arm(2)}$

Bond	Distance	Distance(rel)	Distance	Distance(rel)
B1-C2	1.69545	0.00802	1.66660	-0.02083
C1-N5	1.76429	0.01065	1.76531	0.01167
C2-C1	2.60583	0.03095	2.77832	0.20344
B1-C1	1.69214	-0.02791	1.66136	-0.05869
Angle	**Degrees**	**Degrees(rel)**	**Degrees**	**Degrees(rel)**
C1-B1-C2	100.56923	2.05679	113.1988	14.68636

Figure A5.8: Bond lengths (Å) and angles (°) of the boron insertion transition states for TS-A-B. All bond distances and angles were made relative to the isopropyl system under Distance(rel) and Angle(rel).

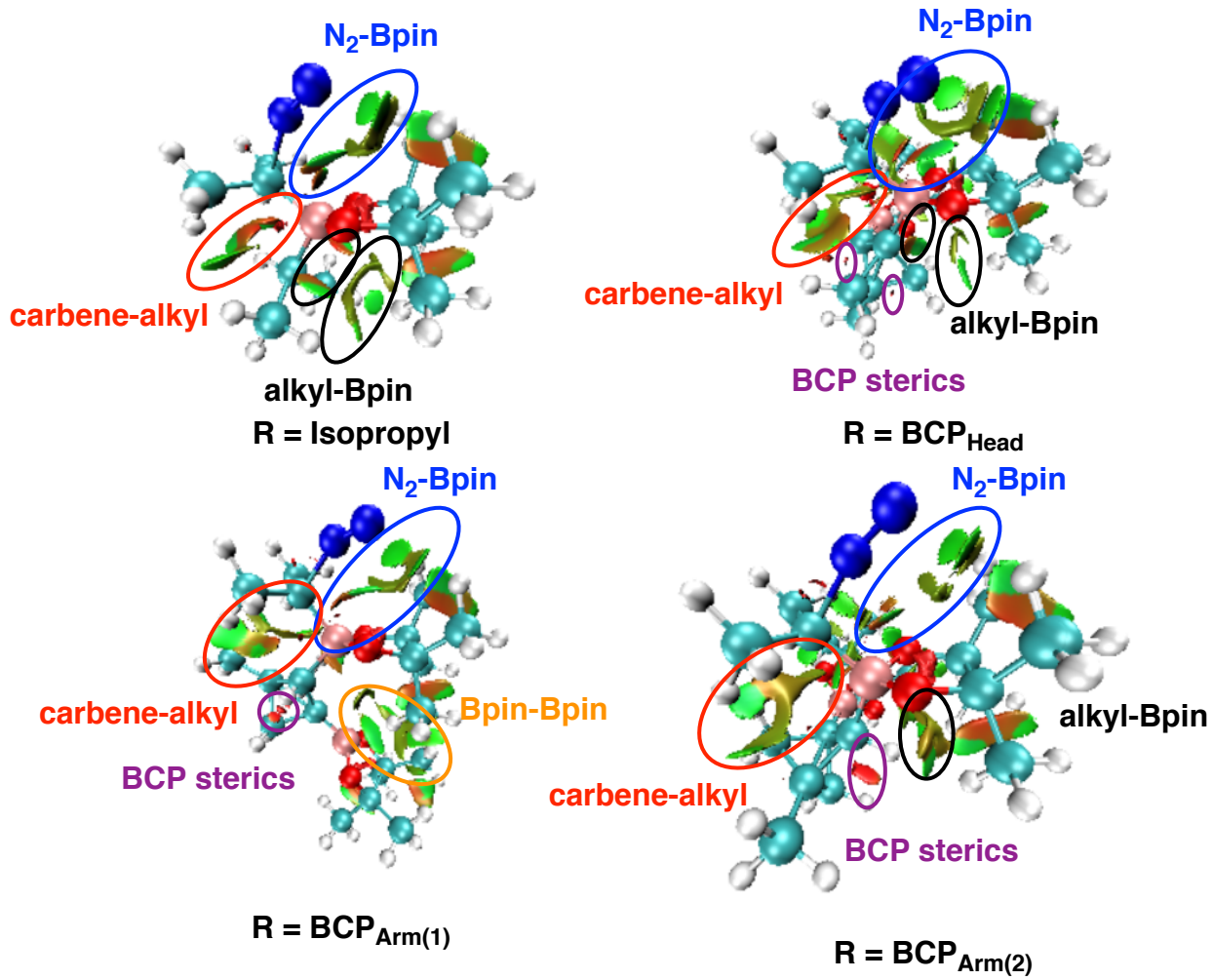
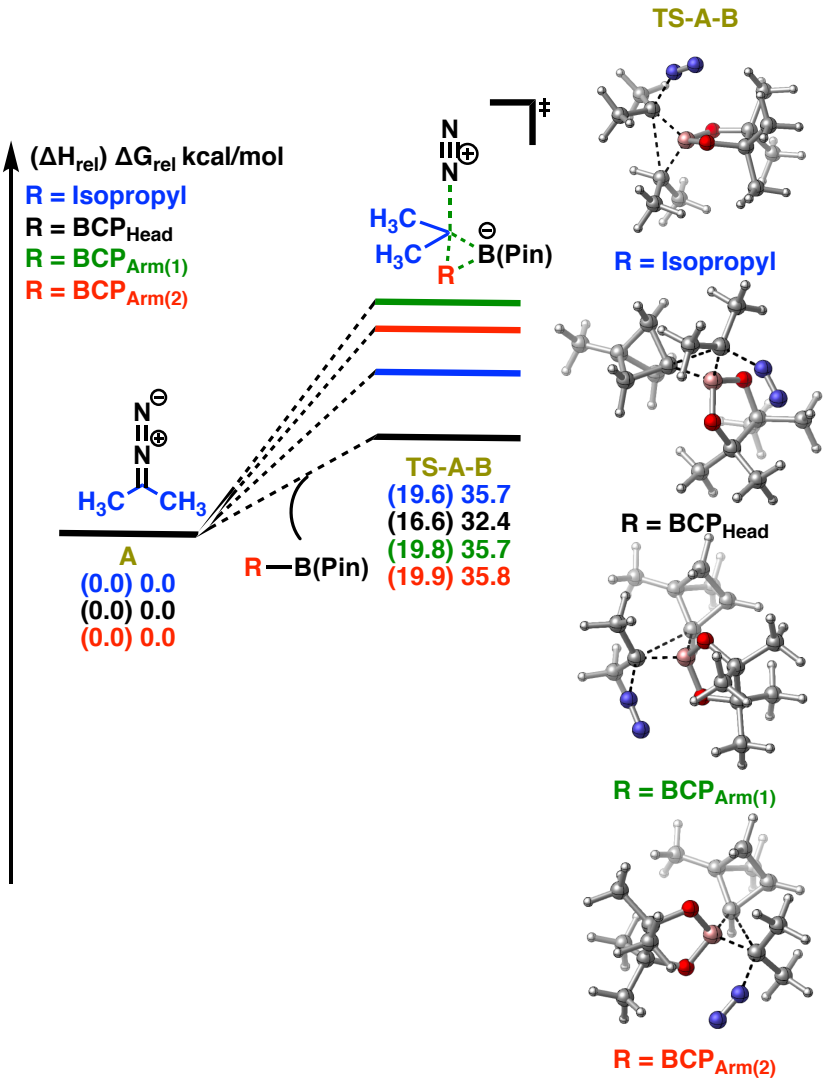


Figure A5.9: Non-covalent interaction analysis of TS-A-B as available in Multiwfn. Blue indicates attractive non-covalent interactions, green indicates dispersion interactions while red indicates repulsive interactions.

To better understand the results of the EDA, the bond distances and bond angles of the decomposed transition states as well as weak non-covalent interaction analysis (NCI) of BCP **14** were compared to the isopropyl system (Figure **A5.8** and **A5.9**). As observed from the EDA, all transition states with the BCP have increases steric and favorable electronic interactions through **TS-A-B** when compared to the isopropyl system. NCI analysis reveals that the increase in C1-C2 distance of the

BCP transition states results in lower steric interaction between the alkyl and carbene (red to brown color from alkyl to BCP system) while all BCP systems show a steric interaction within the BCP scaffold (red color between arms of BCP; circled in purple). The BCP transition state with the least BCP steric interactions is the head transition state (R = BCP_{Head}) while the transition state with the largest BCP steric interaction is the second arm transition state (R= $BCP_{Arm(2)}$), in agreement with the EDA. As the NCI analysis was for weak electronic interactions (RDG ≤ 0.5 used for constructing isosurfaces), the stronger electrostatic interactions were not visualized using this method, as can be seen in Figure A5.11.



B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)

Figure A5.10: Reaction coordinate diagram of boron insertions for mono-boronate BCP. All barriers are relative to the lowest energy conformations.

To evaluate the influence of the additional boron on the barriers of boron insertion of the bis-boronate BCP, the mono-boronate BCP of **14** was modeled (**Figure A5.10**) for both the Bpin substituted at the head and arm position of the BCP. The trends in reactivity is still observed without the additional Bpin: TS-A-B has a lower barrier (32.4 kcal/mol) than the transition states at the arm BCP (~ 35.7 kcal/mol), reinforcing that the *BCP scaffold* is responsible for the observed reactivity.

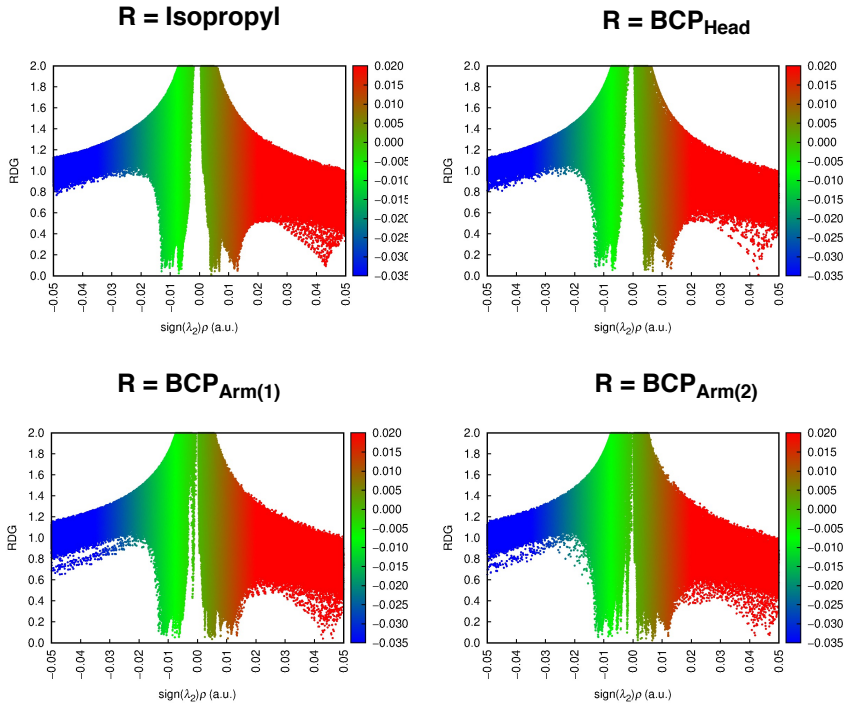
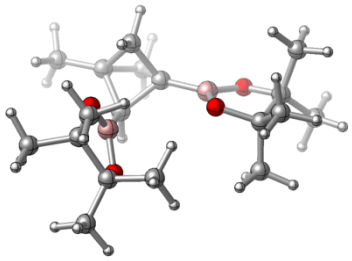


Figure A5.11: Scatter graphs of TS-A-B for the indicated transition states. The RDG isosurface cutoff is set to 0.5.

Energies and Coordinates

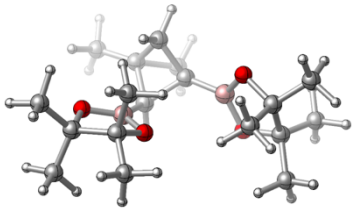
Thesis = 10 Conformation 1, A5 = A5.1-Conformation 1, A5.2-Conformation 1, A5.3-Alkyl Boronate R = BCP, A5.4-Alkyl Boronate R = BCP, A5.8-Conformation 1



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.486137 (Hartree/Particle)
Thermal correction to Energy= 0.511476
Thermal correction to Enthalpy= 0.512420
Thermal correction to Gibbs Free Energy= 0.431314
Sum of electronic and zero-point Energies= -1054.769665
Sum of electronic and thermal Energies= -1054.744325
Sum of electronic and thermal Enthalpies= -1054.743381
Sum of electronic and thermal Free Energies= -1054.824488
B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1056.4296851
Coordinates

C	1.10632	3.16225	-0.05968
C	0.87511	1.79274	-0.77985
C	-0.4483	2.07875	0.07806
C	-0.35418	3.53688	-0.4628
H	-0.85151	4.3158	0.14042
H	-0.55049	3.68162	-1.53793
B	-1.57572	1.0052	0.10751
O	-1.58619	-0.00681	1.0354
O	-2.54925	0.86373	-0.84559
C	-2.76792	-0.81923	0.7929
C	-3.09208	-0.48148	-0.71368
C	-2.42818	-2.27953	1.06252
H	-3.27736	-2.92809	0.79851
H	-1.55051	-2.60088	0.48886
H	-2.20696	-2.4196	2.13117
C	-2.31878	-1.3599	-1.70334
H	-1.2442	-1.37287	-1.46759
H	-2.69822	-2.39216	-1.7089
H	-2.43818	-0.94157	-2.71389
C	-3.84656	-0.33493	1.76574
H	-4.10926	0.71634	1.57645
H	-4.75896	-0.94438	1.69224
H	-3.45896	-0.41073	2.79247
C	-4.57445	-0.45511	-1.06151
H	-5.11569	0.29915	-0.47569
H	-4.70115	-0.21351	-2.1275
H	-5.03035	-1.43991	-0.87666
C	0.49869	2.53662	1.22905
H	1.08974	1.76186	1.73579
H	0.06212	3.24226	1.95585
C	2.33563	4.02844	-0.16005
H	3.22388	3.48652	0.20413
H	2.52258	4.32882	-1.20444
H	2.22235	4.94443	0.44341
B	1.6154	0.44901	-0.46049
O	1.29554	-0.699	-1.14692
O	2.54001	0.22666	0.52731
C	2.19051	-1.75359	-0.70137
C	2.6531	-1.21367	0.70601
C	1.42442	-3.06973	-0.66169
C	3.32954	-1.8312	-1.72195
C	1.68911	-1.58866	1.83711
C	4.08758	-1.55475	1.08694
H	2.05174	-3.86868	-0.23783
H	0.51112	-2.98559	-0.06046
H	1.13503	-3.36354	-1.68174
H	3.89867	-0.89041	-1.75399
H	4.02226	-2.65393	-1.49261
H	2.90087	-2.00529	-2.72002
H	0.65208	-1.3269	1.57949
H	1.74119	-2.66174	2.07224
H	1.96612	-1.0235	2.73955
H	4.8077	-1.14223	0.36841
H	4.31748	-1.13539	2.07793
H	4.22358	-2.64604	1.13659
H	0.68658	1.8791	-1.86541

Thesis = 10 Conformation, 2 A5 = A5.1-Conformation 2, A5.2-Conformation 2

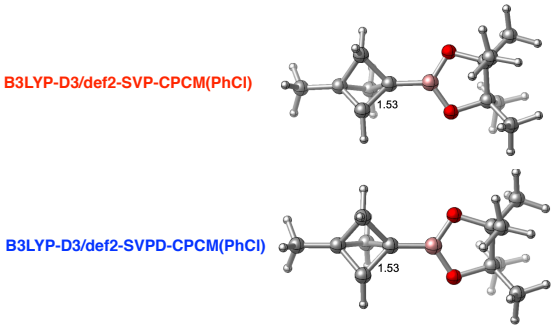


B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.485805 (Hartree/Particle)
Thermal correction to Energy= 0.511160
Thermal correction to Enthalpy= 0.512104
Thermal correction to Gibbs Free Energy= 0.431792
Sum of electronic and zero-point Energies= -1054.769886
Sum of electronic and thermal Energies= -1054.744531

Sum of electronic and thermal Enthalpies= -1054.743586
Sum of electronic and thermal Free Energies= -1054.823898
Coordinates

C	-0.98323	3.03724	0.10615
C	-0.79039	1.71887	-0.71645
C	0.53838	1.89117	0.12538
C	-0.38033	2.27994	1.32497
H	-0.64873	1.88005	-1.80269
H	0.07748	2.89646	2.11662
H	-0.99306	1.47738	1.77014
B	1.70051	0.85194	0.08289
O	2.33992	0.4977	-1.07624
O	2.13932	0.14456	1.17153
C	3.4219	-0.40875	-0.73393
C	2.97371	-0.94265	0.68495
C	3.52498	-1.47736	-1.81611
H	4.2704	-2.23872	-1.53973
H	2.56016	-1.9727	-1.98518
H	3.84106	-1.01572	-2.76374
C	2.07503	-2.181	0.60564
H	1.2277	-2.00943	-0.07319
H	2.63496	-3.06738	0.2742
H	1.66713	-2.3849	1.607
C	4.70383	0.42786	-0.68728
H	4.64366	1.20355	0.09036
H	5.58809	-0.19661	-0.49359
H	4.83691	0.92857	-1.65778
C	4.11161	-1.17262	1.67215
H	4.66752	-0.2479	1.8739
H	3.70513	-1.53961	2.62662
H	4.81203	-1.92835	1.28469
B	-1.65392	0.43811	-0.44081
O	-1.10117	-0.81881	-0.39798
O	-3.00304	0.42752	-0.20758
C	-2.10507	-1.73184	0.12319
C	-3.4466	-0.95852	-0.1897
C	-1.9586	-3.07775	-0.57622
C	-4.00593	-1.26234	-1.58223
C	-1.82984	-1.87839	1.62275
C	-4.53604	-1.11069	0.86482
H	-2.76988	-3.75916	-0.27782
H	-1.97217	-2.96968	-1.66843
H	-1.00104	-3.5396	-0.29225
H	-3.22886	-1.15981	-2.35402
H	-4.42326	-2.2783	-1.63636
H	-4.80774	-0.54391	-1.80819
H	-1.93403	-0.91474	2.1426
H	-2.51055	-2.60499	2.08935
H	-0.79666	-2.22689	1.76119
H	-4.20902	-0.73146	1.84151
H	-5.42802	-0.5425	0.56089
H	-4.82317	-2.16768	0.97392
C	0.48161	3.40153	-0.28072
H	0.67067	3.63395	-1.34181
H	1.01113	4.10857	0.38098
C	-2.19168	3.93659	0.09955
H	-2.37698	4.33971	-0.90995
H	-3.08857	3.3784	0.41351
H	-2.05556	4.78757	0.78755

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1056.4297817
Thesis = 10-C2-radical, A5 = A5.2-Bpin Head Radical, Thesis = $14^{C2\bullet}$



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.302322 (Hartree/Particle)
Thermal correction to Energy= 0.317629
Thermal correction to Enthalpy= 0.318573
Thermal correction to Gibbs Free Energy= 0.259871
Sum of electronic and zero-point Energies= -643.856364
Sum of electronic and thermal Energies= -643.841057
Sum of electronic and thermal Enthalpies= -643.840113
Sum of electronic and thermal Free Energies= -643.898815
Coordinate

C	2.80353	0.30522	-0.16781
C	1.66271	-0.71938	-0.5175
C	2.60457	-1.31795	0.57608
C	2.60368	0.0112	1.35361
H	1.78951	-1.20083	-1.50215
H	3.47172	0.21082	1.99943
H	1.66068	0.34743	1.80036
B	0.15308	-0.38072	-0.25973
O	-0.86068	-1.11283	-0.82108
O	-0.3107	0.6689	0.49276
C	-2.11413	-0.66728	-0.23411
C	-1.74399	0.78146	0.27245
C	-3.20317	-0.7168	-1.29889

C	-1.94082	1.86201	-0.79471
C	-2.43795	-1.63831	0.9051
C	-2.41211	1.19712	1.57734
H	-4.14173	-0.29288	-0.91022
H	-2.91343	-0.1633	-2.20138
H	-3.39244	-1.76174	-1.58713
H	-1.46408	1.57446	-1.7434
H	-3.00701	2.05595	-0.98135
H	-1.47285	2.79481	-0.44681
H	-1.66201	-1.60958	1.68433
H	-3.40912	-1.40919	1.36713
H	-2.47675	-2.66056	0.50074
H	-2.14106	0.52679	2.40308
H	-2.09494	2.21543	1.84802
H	-3.50727	1.19692	1.46686
C	3.84169	-0.8548	-0.22386
H	4.00907	-1.31629	-1.2081
H	4.77775	-0.70577	0.33528
C	2.9442	1.68418	-0.79081
H	3.07756	1.60248	-1.88111
H	2.03885	2.27784	-0.59049
H	3.81395	2.21228	-0.36918

B3LYP-D3/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.302575 (Hartree/Particle)
Thermal correction to Energy= 0.317887
Thermal correction to Enthalpy= 0.318831
Thermal correction to Gibbs Free Energy= 0.260077
Sum of electronic and zero-point Energies= -643.898188
Sum of electronic and thermal Energies= -643.882876
Sum of electronic and thermal Enthalpies= -643.881931
Sum of electronic and thermal Free Energies= -643.940685

Coordinate

C	-2.7601	-0.2488	0.31534
C	-1.67306	-0.37295	-0.83467
C	-2.66926	0.77428	-1.15389
C	-2.6015	1.30206	0.29624
H	-1.81955	-1.27978	-1.43842
H	-3.46378	1.8749	0.65729
H	-1.64964	1.70921	0.64701
B	-0.16127	-0.16174	-0.48968
O	0.68139	-1.22895	-0.2938
O	0.4785	1.04144	-0.32972
C	2.04032	-0.71798	-0.17841
C	1.78971	0.77868	0.24814
C	2.80042	-1.55495	0.8422
C	1.6452	0.95506	1.76198
C	2.6829	-0.84845	-1.5613
C	2.78974	1.78079	-0.31212
H	3.79495	-1.12473	1.02187
H	2.26452	-1.6148	1.79503
H	2.93409	-2.57445	0.45901
H	0.93003	0.23633	2.18073
H	2.60976	0.83014	2.26982
H	1.27489	1.9667	1.96727
H	2.15194	-0.24338	-2.30664
H	3.73535	-0.53849	-1.53912
H	2.6385	-1.89817	-1.87602
H	2.78144	1.78987	-1.40677
H	2.54098	2.78937	0.04123
H	3.80407	1.53835	0.03238
C	-3.86656	-0.12697	-0.77376
H	-4.04514	-1.01592	-1.39055
H	-4.79651	0.3705	-0.4714
C	-2.79977	-1.12975	1.55167
H	-2.9027	-2.18529	1.26495
H	-1.87342	-1.01399	2.13116
H	-3.65079	-0.85369	2.18931

M06-2X/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.305205 (Hartree/Particle)
Thermal correction to Energy= 0.320438
Thermal correction to Enthalpy= 0.321382
Thermal correction to Gibbs Free Energy= 0.262884
Sum of electronic and zero-point Energies= -643.564527
Sum of electronic and thermal Energies= -643.549295
Sum of electronic and thermal Enthalpies= -643.548351
Sum of electronic and thermal Free Energies= -643.606848

Coordinates

C	3.50096400	-0.00422500	-0.04673200
C	2.54691300	-0.71674100	-0.99047000
C	1.58863700	0.03444700	-0.07496000
C	2.57496900	1.23640800	-0.19067500
H	2.52458100	-1.78683200	-1.21831200
H	2.57682600	1.93989400	0.65302500
H	2.59668200	1.75163100	-1.15835700
B	0.02760400	0.02967700	-0.04825100

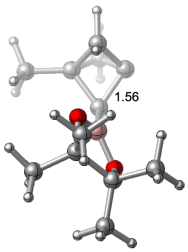
O	-0.73367600	1.07425400	0.40595000
O	-0.73385100	-1.03730800	-0.44804600
C	-2.11427000	0.77508000	0.09755500
C	-2.09197400	-0.78662700	-0.02042700
C	-3.00562500	1.31179600	1.20318300
H	-4.04478300	1.00044400	1.03406000
H	-2.68355900	0.95401200	2.18579500
H	-2.97204200	2.40743100	1.20221200
C	-2.27114000	-1.48068800	1.32606400
H	-1.59386800	-1.06134100	2.08048700
H	-3.30336100	-1.38309900	1.68325600
H	-2.04302200	-2.54566600	1.20664100
C	-2.43528700	1.46042600	-1.22684500
H	-1.81288300	1.06427300	-2.03865000
H	-3.49104500	1.32567400	-1.49157900
H	-2.23553000	2.53304200	-1.12638800
C	-3.05649000	-1.35640900	-1.04487500
H	-2.83522700	-0.98735500	-2.05091100
H	-2.98228700	-2.45004700	-1.04990600
H	-4.08744800	-1.08352300	-0.78425800
C	2.53114900	-0.47855200	1.07419200
H	2.50251100	-1.55355700	1.29031100
H	2.52500000	0.12869400	1.99270400
C	5.00309000	-0.03573300	-0.02960000
H	5.36746800	-1.06433100	0.09119700
H	5.40692500	0.36452000	-0.96865600
H	5.39390900	0.56859200	0.79927000

WB97XD/ def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.305423 (Hartree/Particle)
Thermal correction to Energy= 0.320572
Thermal correction to Enthalpy= 0.321517
Thermal correction to Gibbs Free Energy= 0.263147
Sum of electronic and zero-point Energies= -643.678897
Sum of electronic and thermal Energies= -643.663747
Sum of electronic and thermal Enthalpies= -643.662803
Sum of electronic and thermal Free Energies= -643.721173
Coordinates

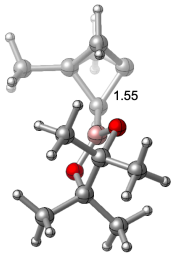
C	2.73403	-0.29951	-0.30765
C	1.68233	-0.284	0.86978
C	2.66918	0.89667	1.0363
C	2.56334	1.23907	-0.46253
H	1.84188	-1.11257	1.57518
H	3.41023	1.77112	-0.91157
H	1.59866	1.59768	-0.83532
B	0.1655	-0.10544	0.51876
O	-0.64205	-1.18007	0.25095
O	-0.50778	1.08263	0.4215
C	-2.00053	-0.70383	0.14386
C	-1.7868	0.81607	-0.19236
C	-2.72497	-1.49447	-0.93364
C	-1.62287	1.07838	-1.68859
C	-2.66503	-0.92804	1.50062
C	-2.83131	1.7498	0.39588
H	-3.72639	-1.07629	-1.1033
H	-2.17508	-1.4853	-1.88064
H	-2.84202	-2.5372	-0.61327
H	-0.88228	0.40312	-2.1362
H	-2.57513	0.95589	-2.21979
H	-1.27817	2.10954	-1.83284
H	-2.16822	-0.35288	2.29234
H	-3.72485	-0.64465	1.47275
H	-2.60071	-1.99251	1.75704
H	-2.84904	1.69842	1.48954
H	-2.61168	2.78403	0.10316
H	-3.82862	1.49229	0.01437
C	3.85832	-0.03721	0.73263
H	4.05831	-0.84466	1.44723
H	4.77667	0.42587	0.35057
C	2.75824	-1.31361	-1.42979
H	2.87321	-2.32819	-1.02599
H	1.82207	-1.27109	-2.00263
H	3.59546	-1.10996	-2.11045

Thesis = 10-C3-radical, A5 = A5.2-Bpin Arm Radical, Thesis = $14^{C3\bullet}$

B3LYP-D3/def2-SVP-CPCM(PhCl)



B3LYP-D3/def2-SVPD-CPCM(PhCl)



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.300862 (Hartree/Particle)
Thermal correction to Energy= 0.316495
Thermal correction to Enthalpy= 0.317439
Thermal correction to Gibbs Free Energy= 0.256682
Sum of electronic and zero-point Energies= -643.859447
Sum of electronic and thermal Energies= -643.843814
Sum of electronic and thermal Enthalpies= -643.842869
Sum of electronic and thermal Free Energies= -643.903626
Coordinates

C	3.51795	-0.00544	-0.04135
C	2.56308	-0.59717	-1.07712
C	1.58842	0.03622	-0.07814
C	2.58242	1.24779	-0.03737
H	2.54333	-1.63063	-1.45312
H	2.57799	1.85166	0.88605
H	2.61011	1.88626	-0.93422
B	0.02731	0.02921	-0.06346
O	-0.73339	1.08903	0.35126
O	-0.72297	-1.0533	-0.43944
C	-2.12458	0.78197	0.05555
C	-2.10087	-0.79447	-0.0511
C	-3.00016	1.33693	1.17262
H	-4.0489	1.03645	1.0259
H	-2.66818	0.9885	2.1591
H	-2.95473	2.43636	1.1676
C	-2.31709	-1.49274	1.29473
H	-1.65503	-1.07754	2.06894
H	-3.35832	-1.39963	1.63578
H	-2.08144	-2.56136	1.18244
C	-2.45473	1.47093	-1.27171
H	-1.83225	1.07811	-2.08914
H	-3.5128	1.34101	-1.54162
H	-2.24954	2.54725	-1.17432
C	-3.02979	-1.38081	-1.10724
H	-2.77743	-1.02199	-2.11336
H	-2.94573	-2.47797	-1.10669
H	-4.07607	-1.11692	-0.88973
C	2.53301	-0.6204	1.00867
H	2.50433	-1.71846	1.09422
H	2.51876	-0.13939	2.00526
C	5.02194	-0.03637	-0.01391
H	5.39436	-1.07394	-0.01297
H	5.43945	0.47522	-0.8965
H	5.40888	0.46666	0.88726

B3LYP-D3/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.301072 (Hartree/Particle)
Thermal correction to Energy= 0.316673
Thermal correction to Enthalpy= 0.317617
Thermal correction to Gibbs Free Energy= 0.257601
Sum of electronic and zero-point Energies= -643.901582
Sum of electronic and thermal Energies= -643.885981
Sum of electronic and thermal Enthalpies= -643.885037
Sum of electronic and thermal Free Energies= -643.945053
Coordinates

C	3.52094	-0.00968	-0.04065
C	2.56543	-0.71139	-1.00391
C	1.59009	0.02488	-0.08029
C	2.58362	1.23756	-0.16731
H	2.54711	-1.77404	-1.27259
H	2.57811	1.93267	0.68568
H	2.60868	1.77628	-1.12383
B	0.03121	0.02179	-0.06485
O	-0.72916	1.07472	0.37521
O	-0.72903	-1.0476	-0.46467
C	-2.12333	0.78065	0.06632
C	-2.10649	-0.79139	-0.06172
C	-3.00498	1.3213	1.18422
H	-4.04949	1.02283	1.02156
H	-2.68282	0.95745	2.16521
H	-2.96087	2.41765	1.19309
C	-2.31481	-1.50495	1.2761
H	-1.6503	-1.10268	2.05094
H	-3.35343	-1.41027	1.61729
H	-2.0885	-2.57051	1.14903
C	-2.44159	1.48714	-1.25349

H	-1.82008	1.10303	-2.07189
H	-3.49805	1.36285	-1.5234
H	-2.23731	2.5588	-1.14109
C	-3.0467	-1.35688	-1.11766
H	-2.8017	-0.98516	-2.11781
H	-2.9732	-2.45163	-1.13065
H	-4.08544	-1.0868	-0.8842
C	2.53742	-0.51123	1.07229
H	2.50938	-1.59063	1.27392
H	2.52267	0.0745	2.00749
C	5.02414	-0.0373	-0.01347
H	5.39459	-1.06786	0.08928
H	5.43713	0.38358	-0.94184
H	5.41062	0.55173	0.83096

M06-2X/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.303901 (Hartree/Particle)
Thermal correction to Energy= 0.319427
Thermal correction to Enthalpy= 0.320372
Thermal correction to Gibbs Free Energy= 0.260702
Sum of electronic and zero-point Energies= -643.565006
Sum of electronic and thermal Energies= -643.549480
Sum of electronic and thermal Enthalpies= -643.548536
Sum of electronic and thermal Free Energies= -643.608205
Coordinates

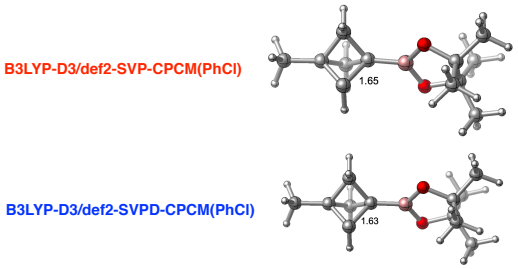
C	3.50096	-0.00423	-0.04673
C	2.54691	-0.71674	-0.99047
C	1.58864	0.03445	-0.07496
C	2.57497	1.23641	-0.19068
H	2.52458	-1.78683	-1.21831
H	2.57683	1.93989	0.65303
H	2.59668	1.75163	-1.15836
B	0.0276	0.02968	-0.04825
O	-0.73368	1.07425	0.40595
O	-0.73385	-1.03731	-0.44805
C	-2.11427	0.77508	0.09756
C	-2.09197	-0.78663	-0.02043
C	-3.00563	1.3118	1.20318
H	-4.04478	1.00044	1.03406
H	-2.68356	0.95401	2.1858
H	-2.97204	2.40743	1.20221
C	-2.27114	-1.48069	1.32606
H	-1.59387	-1.06134	2.08049
H	-3.30336	-1.3831	1.68326
H	-2.04302	-2.54567	1.20664
C	-2.43529	1.46043	-1.22685
H	-1.81288	1.06427	-2.03865
H	-3.49105	1.32567	-1.49158
H	-2.23553	2.53304	-1.12639
C	-3.05649	-1.35641	-1.04487
H	-2.83523	-0.98736	-2.05091
H	-2.98229	-2.45005	-1.04991
H	-4.08745	-1.08352	-0.78426
C	2.53115	-0.47855	1.07419
H	2.50251	-1.55356	1.29031
H	2.525	0.12869	1.9927
C	5.00309	-0.03573	-0.0296
H	5.36747	-1.06433	0.0912
H	5.40693	0.36452	-0.96866
H	5.39391	0.56859	0.79927

WB97XD/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.304156 (Hartree/Particle)
Thermal correction to Energy= 0.319572
Thermal correction to Enthalpy= 0.320516
Thermal correction to Gibbs Free Energy= 0.261072
Sum of electronic and zero-point Energies= -643.682668
Sum of electronic and thermal Energies= -643.667252
Sum of electronic and thermal Enthalpies= -643.666308
Sum of electronic and thermal Free Energies= -643.725752
Coordinates

C	3.51331	-0.00432	-0.04756
C	2.5547	-0.73193	-0.98304
C	1.58705	0.02831	-0.07672
C	2.57658	1.23196	-0.20624
H	2.53563	-1.80404	-1.21152
H	2.57617	1.9506	0.6269
H	2.59616	1.74268	-1.17792
B	0.02685	0.02357	-0.04953
O	-0.73091	1.07537	0.38798
O	-0.73439	-1.04748	-0.4319
C	-2.114	0.77681	0.09642
C	-2.09499	-0.7914	-0.01947
C	-2.99031	1.31829	1.21418
H	-4.03405	1.01277	1.05967
H	-2.66115	0.96169	2.19581
H	-2.95387	2.41478	1.21574
C	-2.29389	-1.49226	1.32298
H	-1.62367	-1.08704	2.09196
H	-3.32963	-1.39219	1.67141
H	-2.07294	-2.55979	1.2031
C	-2.45274	1.46944	-1.22207
H	-1.84097	1.08458	-2.04797
H	-3.51177	1.33612	-1.4772
H	-2.25594	2.54362	-1.12083
C	-3.0492	-1.36125	-1.05615

H	-2.81961	-0.99508	-2.0623
H	-2.97834	-2.45603	-1.06319
H	-4.08415	-1.08855	-0.80916
C	2.53712	-0.47048	1.07783
H	2.51165	-1.54376	1.31041
H	2.5287	0.14243	1.99461
C	5.01379	-0.03002	-0.02592
H	5.38461	-1.05624	0.10544
H	5.42221	0.36382	-0.967
H	5.40183	0.58327	0.79924

Thesis = 10-C2-anion, A5 = A5.2-Bpin Head Anion, Thesis = 14^{C2-}



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.298804 (Hartree/Particle)
Thermal correction to Energy= 0.314316
Thermal correction to Enthalpy= 0.315260
Thermal correction to Gibbs Free Energy= 0.256909
Sum of electronic and zero-point Energies= -643.931514
Sum of electronic and thermal Energies= -643.916002
Sum of electronic and thermal Enthalpies= -643.915058
Sum of electronic and thermal Free Energies= -643.973409
Coordinates

C	2.8514	0.31166	-0.17122
C	1.66231	-0.59745	-0.55094
C	2.48194	-1.43596	0.67451
C	2.59212	0.03545	1.31818
H	1.77649	-1.10837	-1.52977
H	3.45547	0.20006	1.99662
H	1.68367	0.47305	1.76642
B	0.17397	-0.26365	-0.31861
O	-0.84455	-0.98508	-0.93148
O	-0.35705	0.71023	0.51574
C	-2.08978	-0.65978	-0.28103
C	-1.78435	0.76739	0.31341
C	-3.21851	-0.70191	-1.30631
C	-2.05394	1.90049	-0.68419
C	-2.32181	-1.71955	0.80343
C	-2.46517	1.0689	1.6449
H	-4.16468	-0.3599	-0.85835
H	-2.99483	-0.07433	-2.17904
H	-3.36045	-1.73467	-1.66013
H	-1.58109	1.68959	-1.65479
H	-3.13103	2.05932	-0.8433
H	-1.61839	2.8306	-0.28908
H	-1.51684	-1.69576	1.55295
H	-3.28684	-1.58113	1.31349
H	-2.31497	-2.71417	0.33284
H	-2.15064	0.36461	2.42606
H	-2.1979	2.08377	1.97736
H	-3.56063	1.01842	1.54296
C	3.76084	-0.9264	-0.16595
H	3.94946	-1.41089	-1.14616
H	4.71552	-0.83998	0.39522
C	3.14737	1.66684	-0.8102
H	3.30329	1.56723	-1.90005
H	2.30676	2.36638	-0.65287
H	4.05602	2.12519	-0.37902

B3LYP-D3/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.299747 (Hartree/Particle)
Thermal correction to Energy= 0.315147
Thermal correction to Enthalpy= 0.316091
Thermal correction to Gibbs Free Energy= 0.258113
Sum of electronic and zero-point Energies= -643.987038
Sum of electronic and thermal Energies= -643.971638
Sum of electronic and thermal Enthalpies= -643.970694
Sum of electronic and thermal Free Energies= -644.028672
Coordinates

C	2.84094	0.31799	-0.18117
C	1.66784	-0.64346	-0.5019
C	2.54681	-1.41286	0.68834
C	2.63127	0.055	1.32318
H	1.76679	-1.16355	-1.47303
H	3.50457	0.24727	1.97298
H	1.72388	0.46579	1.78867
B	0.17606	-0.30847	-0.26412
O	-0.8406	-1.00111	-0.9107
O	-0.35678	0.65711	0.57603
C	-2.10177	-0.65191	-0.2942
C	-1.7785	0.75788	0.32656
C	-3.19683	-0.64853	-1.35473
C	-1.98105	1.90764	-0.6662
C	-2.397	-1.71629	0.7681
C	-2.49677	1.06091	1.63657
H	-4.1414	-0.28282	-0.92861

H	-2.92771	-0.01862	-2.20919
H	-3.36068	-1.67013	-1.72137
H	-1.4813	1.69807	-1.62014
H	-3.04692	2.08973	-0.85625
H	-1.54381	2.8208	-0.24361
H	-1.62386	-1.723	1.54638
H	-3.37514	-1.55091	1.2386
H	-2.40601	-2.70253	0.28786
H	-2.22907	0.34068	2.41654
H	-2.22024	2.06361	1.98741
H	-3.58561	1.03781	1.49105
C	3.7885	-0.89578	-0.18545
H	3.95737	-1.38979	-1.15947
H	4.74906	-0.77798	0.35
C	3.06968	1.66522	-0.8552
H	3.19363	1.54108	-1.94349
H	2.21211	2.33596	-0.68604
H	3.97435	2.15791	-0.46372

M06-2X/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.302623 (Hartree/Particle)
Thermal correction to Energy= 0.317935
Thermal correction to Enthalpy= 0.318879
Thermal correction to Gibbs Free Energy= 0.261020
Sum of electronic and zero-point Energies= -643.653307
Sum of electronic and thermal Energies= -643.637995
Sum of electronic and thermal Enthalpies= -643.637051
Sum of electronic and thermal Free Energies= -643.694910
Coordinates

C	2.84724	0.24579	-0.18591
C	1.65533	-0.65252	-0.56262
C	2.42615	-1.45536	0.64107
C	2.55467	-0.01353	1.29632
H	1.76752	-1.17224	-1.53077
H	3.40614	0.12265	1.98408
H	1.64482	0.43526	1.71635
B	0.16815	-0.28511	-0.33228
O	-0.85872	-1.00593	-0.92624
O	-0.35285	0.72546	0.4593
C	-2.09264	-0.63167	-0.29594
C	-1.76698	0.80761	0.21889
C	-3.22409	-0.70034	-1.30775
C	-1.98605	1.875	-0.85101
C	-2.33881	-1.61667	0.84483
C	-2.47813	1.19554	1.50445
H	-4.15225	-0.31159	-0.86777
H	-2.9887	-0.1231	-2.20741
H	-3.39359	-1.74392	-1.59859
H	-1.50105	1.59044	-1.79297
H	-3.05517	2.0373	-1.03627
H	-1.54556	2.81652	-0.50329
H	-1.5385	-1.55613	1.59308
H	-3.30195	-1.4246	1.334
H	-2.3515	-2.63279	0.4345
H	-2.20158	0.52886	2.327
H	-2.20486	2.22099	1.78056
H	-3.5666	1.15622	1.3641
C	3.72792	-1.00745	-0.15535
H	3.91118	-1.50316	-1.12343
H	4.65994	-0.94037	0.43213
C	3.17975	1.58086	-0.83573
H	3.35425	1.45324	-1.91464
H	2.35147	2.29305	-0.70564
H	4.08574	2.01969	-0.39209

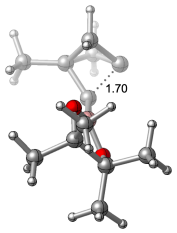
WB97XD/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.302956 (Hartree/Particle)
Thermal correction to Energy= 0.318170
Thermal correction to Enthalpy= 0.319114
Thermal correction to Gibbs Free Energy= 0.261368
Sum of electronic and zero-point Energies= -643.766698
Sum of electronic and thermal Energies= -643.751484
Sum of electronic and thermal Enthalpies= -643.750540
Sum of electronic and thermal Free Energies= -643.808286
Coordinates

C	2.84742	0.25224	-0.18276
C	1.66136	-0.67414	-0.53247
C	2.46884	-1.47202	0.65583
C	2.58663	-0.02273	1.30756
H	1.76423	-1.18626	-1.50834
H	3.44659	0.1327	1.98412
H	1.67968	0.41447	1.75116
B	0.17029	-0.30895	-0.30865
O	-0.8536	-1.03727	-0.89265
O	-0.34885	0.7189	0.45693
C	-2.09496	-0.64095	-0.29325
C	-1.76128	0.80459	0.21805
C	-3.20406	-0.70561	-1.3326
C	-1.97803	1.87788	-0.84938
C	-2.38558	-1.62	0.84491
C	-2.46785	1.20095	1.5058
H	-4.13969	-0.30374	-0.9195
H	-2.94547	-0.13921	-2.23381
H	-3.3808	-1.74935	-1.62213
H	-1.49191	1.60434	-1.79464
H	-3.04678	2.04421	-1.03769

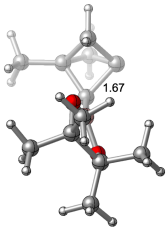
H	-1.5394	2.82042	-0.49877
H	-1.60542	-1.57828	1.61585
H	-3.35722	-1.4124	1.31214
H	-2.40851	-2.6388	0.43889
H	-2.1958	0.5378	2.3338
H	-2.18975	2.22622	1.78146
H	-3.5578	1.16827	1.37048
C	3.74745	-0.99336	-0.16934
H	3.92627	-1.48364	-1.14342
H	4.69537	-0.91256	0.39448
C	3.14306	1.59157	-0.83399
H	3.2972	1.47328	-1.91817
H	2.30737	2.29275	-0.68523
H	4.05171	2.04664	-0.40972

Thesis = 10-C3-anion, A5 = A5.3-Bpin Arm Anion, Thesis = 14^{C3-}

B3LYP-D3/def2-SVP-CPCM(PhCl)



B3LYP-D3/def2-SVPD-CPCM(PhCl)



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.298391 (Hartree/Particle)
Thermal correction to Energy= 0.313959
Thermal correction to Enthalpy= 0.314904
Thermal correction to Gibbs Free Energy= 0.256304
Sum of electronic and zero-point Energies= -643.928449
Sum of electronic and thermal Energies= -643.912881
Sum of electronic and thermal Enthalpies= -643.911937
Sum of electronic and thermal Free Energies= -643.970537
Coordinates

C	-3.45211	0.02421	0.08453
C	-2.37255	0.27202	1.22365
C	-1.58909	-0.06209	-0.19132
C	-2.59294	0.93325	-0.83177
H	-2.31294	-0.68188	1.82497
H	-2.75136	0.85553	-1.92851
H	-2.50154	1.98375	-0.5081
B	-0.05168	-0.06027	-0.19482
O	0.73131	1.03535	-0.51968
O	0.72775	-1.11679	0.24734
C	2.06217	0.80261	-0.00955
C	2.11727	-0.77291	0.05914
C	3.07811	1.4413	-0.95082
H	4.10556	1.19553	-0.63985
H	2.93404	1.10753	-1.98681
H	2.96617	2.53618	-0.92977
C	2.56763	-1.41365	-1.25909
H	1.99966	-1.0067	-2.10876
H	3.64071	-1.25696	-1.44487
H	2.37662	-2.49625	-1.20994
C	2.13211	1.46436	1.37225
H	1.39679	1.01838	2.05841
H	3.13425	1.3799	1.81832
H	1.88572	2.53138	1.265
C	2.93079	-1.33584	1.22054
H	2.51606	-1.02574	2.18854
H	2.91828	-2.43603	1.18412
H	3.97869	-1.00232	1.16087
C	-2.63378	-1.18057	-0.46421
H	-2.5825	-2.0703	0.18888
H	-2.79741	-1.49687	-1.52564
C	-4.95734	0.08116	0.23144
H	-5.31792	-0.70815	0.91564
H	-5.26549	1.05289	0.65664
H	-5.47897	-0.05002	-0.73508

B3LYP-D3/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.298391 (Hartree/Particle)
Thermal correction to Energy= 0.313959
Thermal correction to Enthalpy= 0.314904
Thermal correction to Gibbs Free Energy= 0.256304
Sum of electronic and zero-point Energies= -643.928449
Sum of electronic and thermal Energies= -643.912881
Sum of electronic and thermal Enthalpies= -643.911937
Sum of electronic and thermal Free Energies= -643.970537
Coordinates

C	-3.48379	0.05344	0.05297
C	-2.4953	0.19565	1.28168
C	-1.59815	0.02431	-0.07075
C	-2.57548	1.05169	-0.71456
H	-2.46455	-0.7817	1.82391
H	-2.64101	1.05024	-1.81919
H	-2.53623	2.07558	-0.31535

B	-0.05608	0.01396	-0.07437
O	0.74103	1.11783	-0.32154
O	0.71424	-1.09651	0.22897
C	2.09825	0.79889	0.07424
C	2.10432	-0.77419	-0.01932
C	3.07182	1.50011	-0.86569
H	4.10374	1.19203	-0.64773
H	2.85081	1.27639	-1.91459
H	3.00297	2.5866	-0.72582
C	2.4417	-1.28719	-1.4231
H	1.83369	-0.78401	-2.18527
H	3.5031	-1.13563	-1.65954
H	2.22711	-2.36209	-1.46833
C	2.28164	1.31158	1.50617
H	1.59206	0.81112	2.19725
H	3.31085	1.15798	1.85608
H	2.06474	2.38664	1.52796
C	2.97388	-1.47308	1.01947
H	2.63889	-1.25134	2.03802
H	2.92529	-2.55976	0.87226
H	4.02207	-1.16038	0.91503
C	-2.59425	-1.08565	-0.53016
H	-2.57219	-2.02827	0.03858
H	-2.66264	-1.29532	-1.62166
C	-4.99408	0.07009	0.0858
H	-5.38239	-0.76937	0.68517
H	-5.35893	1.00465	0.54108
H	-5.42594	-0.00923	-0.92621

M06-2X/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.302072 (Hartree/Particle)
Thermal correction to Energy= 0.317481
Thermal correction to Enthalpy= 0.318425
Thermal correction to Gibbs Free Energy= 0.260349
Sum of electronic and zero-point Energies= -643.650278
Sum of electronic and thermal Energies= -643.634869
Sum of electronic and thermal Enthalpies= -643.633925
Sum of electronic and thermal Free Energies= -643.692001
Coordinates

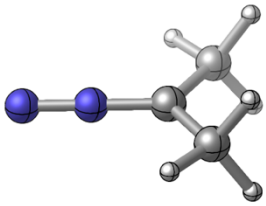
C	-3.44544	0.06784	0.06155
C	-2.39524	0.23379	1.21929
C	-1.59346	0.00108	-0.1619
C	-2.57602	1.01868	-0.78893
H	-2.35054	-0.72638	1.78624
H	-2.70322	0.97017	-1.88444
H	-2.49861	2.05109	-0.42436
B	-0.05085	-0.01264	-0.16736
O	0.74727	1.09093	-0.40628
O	0.71797	-1.11352	0.16756
C	2.07206	0.78476	0.06135
C	2.09949	-0.77575	-0.04262
C	3.09561	1.4951	-0.80755
H	4.11153	1.18606	-0.52752
H	2.93741	1.27655	-1.86826
H	3.01352	2.5784	-0.65929
C	2.4811	-1.2614	-1.43883
H	1.89076	-0.74767	-2.20761
H	3.54699	-1.09396	-1.63827
H	2.27858	-2.33648	-1.50491
C	2.16628	1.27431	1.50448
H	1.44543	0.74896	2.14364
H	3.17597	1.12755	1.90777
H	1.93175	2.34455	1.52823
C	2.95558	-1.46331	1.0075
H	2.59115	-1.25125	2.01737
H	2.93061	-2.54806	0.84892
H	3.99839	-1.12828	0.92684
C	-2.61726	-1.10246	-0.52746
H	-2.57831	-2.01863	0.0785
H	-2.75046	-1.33831	-1.60309
C	-4.9497	0.1134	0.18202
H	-5.30977	-0.68896	0.84301
H	-5.26773	1.07415	0.61257
H	-5.43965	-0.00519	-0.79674

WB97XD/def2-SVPD-CPCM(PhCl)
Zero-point correction= 0.302336 (Hartree/Particle)
Thermal correction to Energy= 0.317653
Thermal correction to Enthalpy= 0.318597
Thermal correction to Gibbs Free Energy= 0.260788
Sum of electronic and zero-point Energies= -643.764267
Sum of electronic and thermal Energies= -643.748950
Sum of electronic and thermal Enthalpies= -643.748006
Sum of electronic and thermal Free Energies= -643.805815
Coordinates

C	-3.47601	0.05518	0.05498
C	-2.47341	0.19198	1.26546
C	-1.59645	0.0208	-0.08322
C	-2.57318	1.04585	-0.71858
H	-2.44308	-0.78684	1.80455
H	-2.64801	1.04129	-1.82208
H	-2.52797	2.07017	-0.32116
B	-0.05224	0.01038	-0.08883
O	0.74373	1.11129	-0.33329
O	0.71631	-1.09642	0.21564
C	2.08584	0.7952	0.07066

C	2.09513	-0.77284	-0.02296
C	3.07022	1.49158	-0.85651
H	4.09859	1.18139	-0.62497
H	2.86297	1.26573	-1.90807
H	3.00342	2.57827	-0.71885
C	2.44735	-1.28271	-1.42063
H	1.84645	-0.78336	-2.19149
H	3.51041	-1.12601	-1.6461
H	2.2401	-2.35893	-1.46858
C	2.26127	1.30558	1.501
H	1.56836	0.8068	2.19081
H	3.28826	1.15031	1.85666
H	2.04723	2.3812	1.5227
C	2.96352	-1.46415	1.01738
H	2.62582	-1.24179	2.0352
H	2.92244	-2.55114	0.87164
H	4.01028	-1.14594	0.91491
C	-2.59617	-1.08152	-0.53407
H	-2.57201	-2.0236	0.03575
H	-2.67482	-1.28719	-1.62321
C	-4.98271	0.0763	0.10291
H	-5.36601	-0.75738	0.71195
H	-5.34006	1.01433	0.55516
H	-5.42437	-0.00872	-0.90332

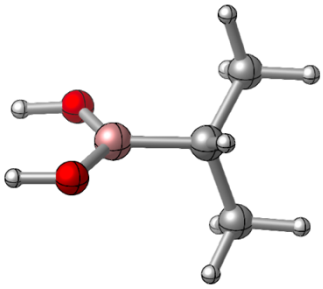
Thesis = diazoalkyl A5 = A5.3-A, A4.5-A, A5.10-A



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.088598 (Hartree/Particle)
Thermal correction to Energy= 0.094821
Thermal correction to Enthalpy= 0.095765
Thermal correction to Gibbs Free Energy= 0.059275
Sum of electronic and zero-point Energies= -227.125932
Sum of electronic and thermal Energies= -227.119709
Sum of electronic and thermal Enthalpies= -227.118765
Sum of electronic and thermal Free Energies= -227.155255
Coordinates

C	-3.02018	-0.39249	-0.13894
C	-1.81145	0.45466	0.16272
H	-2.80624	-1.46121	0.04302
H	-3.31266	-0.29577	-1.20014
H	-3.88312	-0.10711	0.48005
C	-0.51046	0.24266	-0.56679
N	-1.89166	1.37783	1.06261
H	-0.13641	-0.78556	-0.41222
H	0.26644	0.94294	-0.22726
H	-0.64355	0.3798	-1.65515
N	-1.96301	2.20004	1.86395

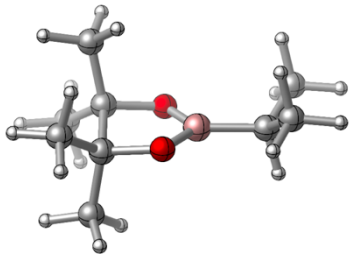
B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-227.4750045
A5 = A5.3-Alkyl Boronic Acid R =Isopropyl, A5 = A5.4-Alkyl Boronic Acid R =Isopropyl



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.127308 (Hartree/Particle)
Thermal correction to Energy= 0.134941
Thermal correction to Enthalpy= 0.135885
Thermal correction to Gibbs Free Energy= 0.095542
Sum of electronic and zero-point Energies= -294.828884
Sum of electronic and thermal Energies= -294.821251
Sum of electronic and thermal Enthalpies= -294.820307
Sum of electronic and thermal Free Energies= -294.860651
Coordinates

B	3.72944	1.89023	-0.00466
C	5.31512	1.86214	0.00019
O	3.08859	2.68646	-0.91507
O	3.07077	1.07866	0.88065
C	5.79308	0.69643	-0.89169
H	5.63403	1.63936	1.0354
C	5.94929	3.18958	-0.43699
H	5.37512	-0.26919	-0.56288
H	6.89347	0.60664	-0.87895
H	5.48958	0.85123	-1.94178
H	5.64086	3.45463	-1.46195
H	7.05172	3.13363	-0.42425
H	5.64893	4.02244	0.22018
H	2.12328	2.6374	-0.90197
H	2.10628	1.08998	0.81475

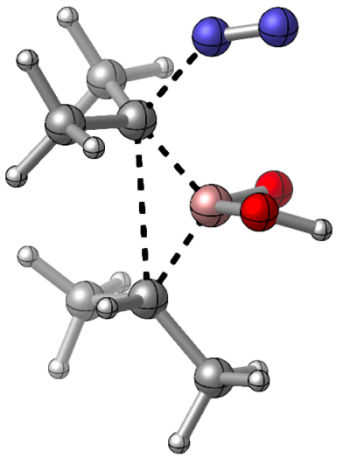
B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-295.3041431
A5 = A5.3-Alkyl Boronate R = Isopropyl, A5.4-Alkyl Boronate R = Isopropyl, A5.4-Alkyl Boronate R = Isopropyl



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.274188 (Hartree/Particle)
Thermal correction to Energy= 0.288102
Thermal correction to Enthalpy= 0.289046
Thermal correction to Gibbs Free Energy= 0.234363
Sum of electronic and zero-point Energies= -529.199505
Sum of electronic and thermal Energies= -529.185592
Sum of electronic and thermal Enthalpies= -529.184647
Sum of electronic and thermal Free Energies= -529.239330
Coordinates

B	3.76506	2.06148	-0.12715
C	5.34159	2.03946	-0.11487
O	3.01399	3.16849	-0.42747
O	2.99221	0.9623	0.14981
C	1.62285	2.86061	-0.14115
C	1.6168	1.28205	-0.19239
C	5.95202	3.44423	-0.00291
H	5.62773	1.62171	-1.10258
C	5.88589	1.08594	0.9628
H	5.58264	4.11194	-0.79699
H	7.05301	3.41259	-0.06962
H	5.69374	3.911	0.96327
H	5.63142	1.44671	1.97455
H	6.98511	1.0048	0.9106
H	5.46442	0.074	0.85877
C	1.32714	3.41825	1.25432
H	1.55405	4.49461	1.26241
H	0.27096	3.28242	1.52873
H	1.95405	2.93229	2.01654
C	0.74142	3.54205	-1.18104
H	-0.3113	3.25005	-1.04645
H	0.81126	4.63434	-1.06721
H	1.04988	3.28776	-2.2033
C	0.68923	0.60947	0.81265
H	-0.35468	0.91177	0.6381
H	0.7526	-0.48349	0.70142
H	0.96109	0.86089	1.84592
C	1.3691	0.72707	-1.59834
H	1.58477	-0.35165	-1.5981
H	0.32554	0.87359	-1.91269
H	2.02902	1.20629	-2.33658

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-530.070631
A5 = A5.3-TS-A-B Alkyl Boronic Acid R = Isopropyl, A5.4-TS-A-B Alkyl Boronic Acid R = Isopropyl

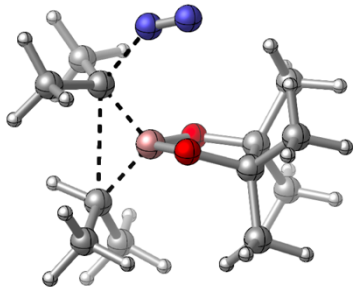


B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.214887 (Hartree/Particle)
Thermal correction to Energy= 0.229307
Thermal correction to Enthalpy= 0.230251
Thermal correction to Gibbs Free Energy= 0.175594
Sum of electronic and zero-point Energies= -521.930921
Sum of electronic and thermal Energies= -521.916502
Sum of electronic and thermal Enthalpies= -521.915557
Sum of electronic and thermal Free Energies= -521.970214
Coordinates

C	-0.50829	0.45172	-0.38822
C	0.55881	-0.20812	0.44255
H	-1.32905	0.86819	0.21468
H	-0.93657	-0.3246	-1.03802
H	-0.07581	1.2242	-1.03843

C	0.05918	-1.11091	1.53912
H	-0.74653	-0.66274	2.14002
H	0.87786	-1.45349	2.18662
H	-0.36324	-1.99484	1.03337
B	1.98881	-0.65535	-0.34429
C	1.67143	-2.19128	-0.97755
O	3.03818	-0.75135	0.65498
O	2.34368	0.32961	-1.35314
C	2.9721	-2.63683	-1.6669
H	3.20466	-1.98945	-2.52978
H	2.89719	-3.67345	-2.0427
H	3.82728	-2.58542	-0.97658
C	0.49183	-2.35348	-1.94197
H	1.50849	-2.85887	-0.11266
H	0.50659	-3.34174	-2.43578
H	0.51465	-1.59868	-2.7497
H	-0.48675	-2.26989	-1.4427
N	1.22713	1.15499	1.35894
N	2.1734	1.59751	1.72841
H	3.86403	-0.45763	0.25401
H	1.92321	0.14608	-2.20025

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-522.7540859
A5 = A5.3-TS-A-B Alkyl Boronate R = Isopropyl, A5.4-TS-A-B Alkyl Boronate R = Isopropyl, A5.5-TS-A-B Alkyl Boronate R = Isopropyl, A5.6-TS-A-B Alkyl Boronate R = Isopropyl, A5.10-TS-A-B Alkyl Boronate R = Isopropyl



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.363146 (Hartree/Particle)
Thermal correction to Energy= 0.383262
Thermal correction to Enthalpy= 0.384206
Thermal correction to Gibbs Free Energy= 0.318394
Sum of electronic and zero-point Energies= -756.296132
Sum of electronic and thermal Energies= -756.276016
Sum of electronic and thermal Enthalpies= -756.275072
Sum of electronic and thermal Free Energies= -756.340884
Coordinates

C	-0.20802	0.14023	-1.11988
C	0.51704	-0.30022	0.12713
H	0.37113	0.90316	-1.65618
H	-1.23041	0.49365	-0.9197
H	-0.28103	-0.73937	-1.77734
C	-0.31393	-1.11356	1.09722
H	-1.28458	-0.64292	1.31312
H	0.2249	-1.30875	2.03442
H	-0.5242	-2.07953	0.6145
B	2.12741	-0.70721	-0.11349
C	1.90172	-2.31594	-0.67883
O	2.92029	-0.58355	1.09205
O	2.75729	0.15494	-1.09863
C	3.97541	0.70715	-0.6089
C	4.20555	-0.04443	0.78219
C	2.19943	-3.34038	0.42218
H	3.23932	-3.2564	0.76988
H	2.04648	-4.37341	0.05906
H	1.558	-3.20467	1.30635
C	2.75587	-2.57259	-1.92667
H	0.85835	-2.48162	-0.9986
H	2.5828	-3.59234	-2.31734
H	3.83189	-2.48621	-1.71023
H	2.5313	-1.85347	-2.72764
N	0.69206	1.16931	1.06793
N	1.32524	1.65198	1.84082
C	4.64516	0.87143	1.92841
H	4.74335	0.27817	2.85097
H	5.62161	1.33245	1.71344
H	3.91683	1.66806	2.12012
C	5.21304	-1.203	0.68888
H	6.23792	-0.8435	0.51412
H	5.19891	-1.75894	1.63865
H	4.95075	-1.90424	-0.11211
C	5.08167	0.45676	-1.64285
H	4.83514	0.99074	-2.57382
H	6.05595	0.82548	-1.28586
H	5.17748	-0.60808	-1.88697
C	3.80124	2.22881	-0.47123
H	4.73797	2.72489	-0.17506
H	3.49057	2.63438	-1.44648
H	3.02853	2.49424	0.25937

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1283.8803397
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl) (Q-Chem)
==========
Results of EDA2
==========
Basic EDA Quantities

Fragment Energies (Ha):
1 -530.0059102052
2 -227.4200466208

E_prp (kJ/mol) = 0.0000
E_frz (kJ/mol) = 287.5572
E_pol (kJ/mol) = -277.1456
E_vct (kJ/mol) = -225.9103
E_int (kJ/mol) = -215.4988

Decomposition of frozen interaction energy

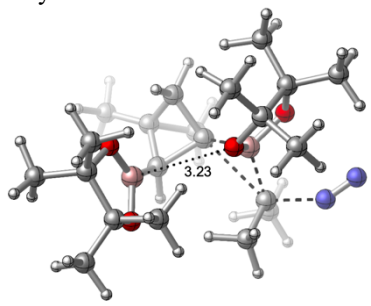
Orthogonal Frozen Decomposition:

E_elec (ELEC) (kJ/mol) = -416.9188
E_pauli (PAULI) (kJ/mol) = 780.0871
E_disp (DISP) (kJ/mol) = -75.6111

Classical Frozen Decomposition:

E_cls_elec (CLS ELEC) (kJ/mol) = -531.8755
E_mod_pauli (MOD PAULI) (kJ/mol) = 895.0438
(FRZ - CLS ELEC - DISP)
E_disp (DISP) (kJ/mol) = -75.6111

A5 = A5.3-TS-A-B Alkyl Boronate R = BCP_{Head}, A5.4-TS-A-B Alkyl Boronate R = BCP_{Head}, A5.5-TS-A-B Alkyl Boronate R = BCP_{Head}, A5.6-TS-A-B Alkyl Boronate R = BCP_{Head}



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.575036
(Hartree/Particle)
Thermal correction to Energy= 0.606487
Thermal correction to Enthalpy=
0.607431
Thermal correction to Gibbs Free Energy=
0.517097
Sum of electronic and zero-point Energies= -
1281.875990
Sum of electronic and thermal Energies= -
1281.844538
Sum of electronic and thermal Enthalpies= -
1281.843594
Sum of electronic and thermal Free Energies= -
1281.933928
Coordinates

C	0.48879	-0.7052	1.95378
C	1.90964	-0.87655	1.49912
H	0.06688	0.23664	1.58184
H	0.36323	-0.79675	3.04331
H	-0.09299	-1.50271	1.46565
C	2.68761	-1.92061	2.26362
H	2.66907	-1.7482	3.35003
H	3.72297	-2.01729	1.90987
H	2.1737	-2.87614	2.08368
B	2.11424	-0.7519	-0.19371
O	3.32386	-0.04775	-0.57761
O	1.00592	-0.01809	-0.79275
C	1.46332	1.16666	-1.42972
C	3.02998	0.92752	-1.58335
N	2.74777	0.57375	2.07247
N	3.5825	1.27783	1.88554
C	3.88346	2.174	-1.33151
H	4.94891	1.91433	-1.43196
H	3.65357	2.96134	-2.06636
H	3.73353	2.58409	-0.32577
C	3.4167	0.35568	-2.95646
H	3.33209	1.11167	-3.75153
H	4.46237	0.0145	-2.91192
H	2.79251	-0.50167	-3.22712
C	0.72188	1.32252	-2.7624
H	-0.34482	1.51568	-2.56981
H	1.11881	2.16719	-3.34664
H	0.79189	0.40897	-3.3661
C	1.1087	2.37107	-0.54001
H	1.37049	3.3289	-1.01471
H	0.02324	2.36304	-0.35753
H	1.60887	2.32439	0.43491
C	2.02009	-2.33209	-0.68185
C	0.7658	-3.30256	-0.54072
C	2.01567	-2.702	-2.21043
C	2.90516	-3.61241	-0.49959
C	1.77625	-4.04108	-1.47725
H	0.68507	-3.75751	0.46562
B	-0.64427	-2.79085	-0.99214
H	2.98445	-2.60562	-2.72568
H	1.19611	-2.29646	-2.81655
H	2.90314	-4.10431	0.4861
H	3.92847	-3.56607	-0.91103
C	1.57824	-5.39859	-2.10738
O	-1.62361	-2.5105	-0.06519
O	-1.06493	-2.55207	-2.27581
H	1.43794	-6.17594	-1.33762
H	0.68811	-5.39795	-2.75815
H	2.45008	-5.67993	-2.72153

C -2.68196 -1.77518 -0.73489
C -2.4708 -2.19508 -2.2449
C -4.0221 -2.18815 -0.13709
C -2.41703 -0.28824 -0.47887
C -3.25432 -3.44972 -2.64083
C -2.70726 -1.07962 -3.25706
H -4.85145 -1.71142 -0.6819
H -4.16318 -3.27647 -0.1634
H -4.07244 -1.86461 0.91355
H -1.42205 -0.00087 -0.84531
H -3.18529 0.34473 -0.94628
H -2.43591 -0.10748 0.60643
H -3.08575 -4.26501 -1.92196
H -4.3343 -3.25118 -2.70199
H -2.90626 -3.78919 -3.62778
H -2.02144 -0.23923 -3.09145
H -2.53726 -1.46146 -4.27511
H -3.74285 -0.71153 -3.19663
B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1283.8803397
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl) (Q-Chem)
==========
Results of EDA2
==========
Basic EDA Quantities

Fragment Energies (Ha):
1-1056.3701426585
2 -227.4193315592

E_prp (kJ/mol) = -0.0204
E_frz (kJ/mol) = 298.1109
E_pol (kJ/mol) = -287.1362
E_vct (kJ/mol) = -229.5163
E_int (kJ/mol) = -218.5620

Initial Wavefunction Relaxation

Energy lowering from initial wavefunction relaxation (kJ/mol) = -0.8092

Decomposition of frozen interaction energy

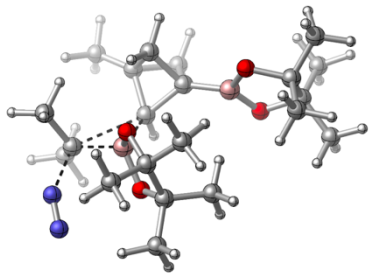
Orthogonal Frozen Decomposition:

E_elec (ELEC) (kJ/mol) = -454.1314
E_pauli (PAULI) (kJ/mol) = 844.4123
E_disp (DISP) (kJ/mol) = -92.1700

Classical Frozen Decomposition:

E_cls_elec (CLS ELEC) (kJ/mol) = -553.7282
E_mod_pauli (MOD PAULI) (kJ/mol) = 944.0092
(FRZ - CLS ELEC - DISP)
E_disp (DISP) (kJ/mol) = -92.1700

A5 = A5.3-TS-A-B Alkyl Boronate R = $BCP_{Arm(1)}$, A5.4-TS-A-B Alkyl Boronate R = $BCP_{Arm(1)}$, A5.5-TS-A-B Alkyl Boronate R = $BCP_{Arm(1)}$, A5.6-TS-A-B Alkyl Boronate R = $BCP_{Arm(1)}$



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.575172 (Hartree/Particle)
Thermal correction to Energy= 0.606653
Thermal correction to Enthalpy= 0.607597
Thermal correction to Gibbs Free Energy= 0.517075
Sum of electronic and zero-point Energies= -1281.862894
Sum of electronic and thermal Energies= -1281.831413
Sum of electronic and thermal Enthalpies= -1281.830469
Sum of electronic and thermal Free Energies= -1281.920991
Coordinates
C 1.95625 0.84117 -2.4652
C 1.12867 0.21009 -1.37784
H 2.62819 1.59861 -2.04107
H 1.35947 1.25985 -3.28933
H 2.60517 0.05384 -2.87018
C -0.1436 -0.4834 -1.8093
H -0.75339 0.12886 -2.49032
H -0.74303 -0.80219 -0.94514
H 0.1517 -1.38432 -2.36026
B 2.03882 -0.49715 -0.13446
O 1.34628 -0.40158 1.14203
O 3.31617 0.16479 0.04734
C 3.45723 0.67743 1.36782
C 2.24898 0.01009 2.1681
N 0.39791 1.59329 -0.56206
N -0.0428 1.98062 0.37716
C 1.52924 0.9639 3.12671
H 0.68497 0.43779 3.59891

H	2.2094	1.302	3.92411
H	1.12842	1.84754	2.6169
C	2.65813	-1.23733	2.96162
H	3.31366	-0.99823	3.81181
H	1.75017	-1.72357	3.34936
H	3.16336	-1.96425	2.32056
C	4.84295	0.28197	1.8894
H	5.61654	0.79147	1.2937
H	4.97841	0.57183	2.94311
H	5.01018	-0.79595	1.79187
C	3.38823	2.21256	1.30724
H	3.57498	2.67286	2.28941
H	4.16072	2.56807	0.60811
H	2.41933	2.57097	0.93983
C	2.14738	-2.08954	-0.69646
C	2.62126	-2.65438	-2.10725
C	3.4654	-2.93547	-0.42253
H	1.22967	-2.59512	-0.33973
C	4.07088	-2.26845	-1.69744
C	2.85741	-4.00361	-1.39487
C	2.01286	-2.58166	-3.4915
B	4.23612	-3.44827	0.83292
H	4.87963	-2.82857	-2.19901
H	4.31386	-1.20173	-1.61308
H	1.96759	-4.54787	-1.03784
H	3.57952	-4.69089	-1.87243
H	1.00863	-3.03773	-3.50679
H	1.93104	-1.56223	-3.89499
H	2.64224	-3.15924	-4.18925
O	3.68658	-4.31536	1.74453
O	5.5756	-3.24599	1.04436
C	4.75996	-4.94085	2.49317
C	5.97932	-3.95393	2.24818
C	4.32574	-5.07301	3.94922
C	4.96725	-6.32787	1.87678
C	6.15801	-2.91532	3.358
C	7.31283	-4.64243	1.97013
H	5.14265	-5.48055	4.56375
H	4.01666	-4.10719	4.36894
H	3.46968	-5.76107	4.01621
H	5.25137	-6.25251	0.81698
H	5.74157	-6.89843	2.40965
H	4.02136	-6.88661	1.93397
H	5.21701	-2.3996	3.58411
H	6.53235	-3.38211	4.28052
H	6.88749	-2.16117	3.02879
H	7.26398	-5.27798	1.07675
H	8.08993	-3.88169	1.80233
H	7.61772	-5.26063	2.82807

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1283.868212
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl) (Q-Chem)

==========
Results of EDA2
==========
Basic EDA Quantities

Fragment Energies (Ha):
1-1056.3628221600
2 -227.4193908644

E_prp (kJ/mol) = -0.0011
E_frz (kJ/mol) = 314.9806
E_pol (kJ/mol) = -285.4009
E_vct (kJ/mol) = -228.3139
E_int (kJ/mol) = -198.7353

Initial Wavefunction Relaxation

Energy lowering from initial wavefunction relaxation (kJ/mol) = -0.7976

Decomposition of frozen interaction energy

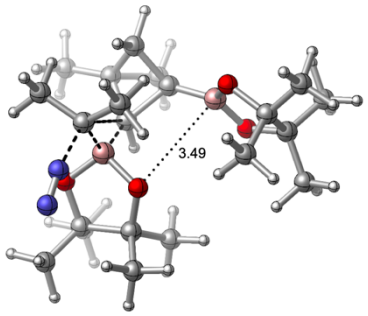
Orthogonal Frozen Decomposition:

E_elec (ELEC) (kJ/mol) = -447.7464
E_pauli (PAULI) (kJ/mol) = 851.8187
E_disp (DISP) (kJ/mol) = -89.0917

Classical Frozen Decomposition:

E_cls_elec (CLS ELEC) (kJ/mol) = -557.8102
E_mod_pauli (MOD PAULI) (kJ/mol) = 961.8825 (FRZ - CLS ELEC - DISP)
E_disp (DISP) (kJ/mol) = -89.0917

A5 = A5.3-TS-A-B Alkyl Boronate R = $BCP_{Arm(2)}$, A5.4-TS-A-B Alkyl Boronate R = $BCP_{Arm(2)}$, A5.5-TS-A-B Alkyl Boronate R = $BCP_{Arm(2)}$, A5.6-TS-A-B Alkyl Boronate R = $BCP_{Arm(2)}$,



B3LYP-D3/def2-SVP-CPCM(PhCl)

Zero-point correction= 0.574393 (Hartree/Particle)
Thermal correction to Energy= 0.606441
Thermal correction to Enthalpy= 0.607385
Thermal correction to Gibbs Free Energy= 0.514542
Sum of electronic and zero-point Energies= -1281.863415
Sum of electronic and thermal Energies= -1281.831367
Sum of electronic and thermal Enthalpies= -1281.830423
Sum of electronic and thermal Free Energies= -1281.923267
Coordinates

C	1.20098	0.73959	-0.51599
C	2.00941	-0.16733	0.37463
H	1.83718	1.16785	-1.30071
H	0.66254	1.52938	0.029
H	0.47415	0.10977	-1.04765
C	1.46233	-0.48173	1.74401
H	1.05267	0.3981	2.26245
H	2.22138	-0.97976	2.36288
H	0.64104	-1.19549	1.59532
B	2.89854	-1.3625	-0.37274
O	3.96794	-1.79723	0.53319
O	3.59806	-0.78908	-1.5323
C	4.93393	-1.27447	-1.60482
C	5.18162	-1.99502	-0.18316
N	3.33853	0.91236	0.80361
N	4.30356	1.43032	0.91434
C	6.32142	-1.37764	0.64092
H	6.35683	-1.87204	1.62417
H	7.29811	-1.51564	0.15267
H	6.17385	-0.30506	0.8159
C	5.45954	-3.50579	-0.29102
H	6.40873	-3.7132	-0.80821
H	5.5238	-3.92426	0.72544
H	4.65586	-4.03613	-0.81604
C	5.05942	-2.22299	-2.80935
H	4.82352	-1.66429	-3.72782
H	6.07779	-2.62881	-2.90744
H	4.35205	-3.05877	-2.74729
C	5.85409	-0.07211	-1.86394
H	6.90956	-0.37298	-1.94629
H	5.55886	0.40266	-2.81255
H	5.77221	0.68653	-1.07556
C	1.97721	-2.65699	-0.8581
C	0.89437	-3.55408	-0.16433
C	0.74764	-2.70315	-1.86217
H	2.78829	-3.29429	-1.2538
C	-0.19487	-2.54394	-0.63048
C	0.70167	-4.23539	-1.55404
C	1.00076	-4.2521	1.1686
B	0.77175	-1.94419	-3.21845
H	-1.21726	-2.9447	-0.74639
H	-0.24148	-1.56435	-0.14197
H	1.54311	-4.84086	-1.92918
H	-0.26363	-4.74395	-1.72952
H	1.86733	-4.93405	1.17838
H	1.13725	-3.53051	1.99013
H	0.09611	-4.84602	1.38277
O	0.17765	-0.72211	-3.42327
O	1.47616	-2.37884	-4.31163
C	0.72082	-0.1652	-4.65235
C	1.23141	-1.45874	-5.40615
C	-0.38058	0.60273	-5.37362
C	1.85501	0.781	-4.24535
C	0.16325	-2.10176	-6.29587
C	2.52792	-1.27376	-6.18648
H	-0.02325	0.96439	-6.35007
H	-1.27258	-0.01689	-5.53283
H	-0.67671	1.47584	-4.77275
H	2.61834	0.25225	-3.65585
H	2.32389	1.24832	-5.1234
H	1.43851	1.58148	-3.61601
H	-0.7778	-2.24502	-5.74459
H	-0.04082	-1.49346	-7.18906
H	0.52029	-3.09008	-6.6216
H	3.35102	-0.96372	-5.53018
H	2.81173	-2.22458	-6.66226
H	2.40136	-0.51816	-6.97692

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-1283.868267
B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl) (Q-Chem)
==========
Results of EDA2
==========
Basic EDA Quantities

Fragment Energies (Ha):
1-1056.3480248492
2 -227.4172590553

E_prp (kJ/mol) = 0.0046
E_frz (kJ/mol) = 373.5238
E_pol (kJ/mol) = -358.1304
E_vct (kJ/mol) = -250.8733
E_int (kJ/mol) = -235.4752

Initial Wavefunction Relaxation

Energy lowering from initial wavefunction relaxation (kJ/mol) = -0.9061

Decomposition of frozen interaction energy

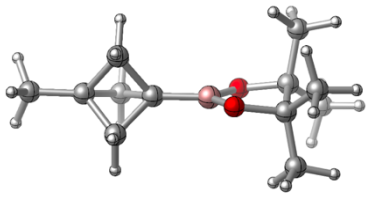
Orthogonal Frozen Decomposition:

E_elec (ELEC) (kJ/mol) = -484.2929
E_pauli (PAULI) (kJ/mol) = 957.9307
E_disp (DISP) (kJ/mol) = -100.1140

Classical Frozen Decomposition:

E_cls_elec (CLS ELEC) (kJ/mol) = -652.9758
E_mod_pauli (MOD PAULI) (kJ/mol) = 1126.6137 (FRZ - CLS ELEC - DISP)
E_disp (DISP) (kJ/mol) = -100.1140

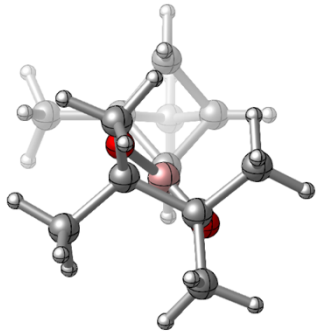
A5 = A5.10 Alkyl Boronate R = BCP_{Head}



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.314472 (Hartree/Particle)
Thermal correction to Energy= 0.330030
Thermal correction to Enthalpy= 0.330975
Thermal correction to Gibbs Free Energy= 0.271125
Sum of electronic and zero-point Energies= -644.523342
Sum of electronic and thermal Energies= -644.507783
Sum of electronic and thermal Enthalpies= -644.506839
Sum of electronic and thermal Free Energies= -644.566688
Coordinates

C	3.47877	0.00087	0.00643
C	2.5074	-0.02319	1.22205
C	1.57214	-0.01132	-0.03999
C	2.55106	-1.06414	-0.64884
H	2.57575	-1.13439	-1.74946
H	2.54565	-2.06737	-0.19053
B	0.01124	-0.00643	-0.03497
O	-0.7361	1.0687	0.37043
O	-0.75747	-1.07519	-0.41475
C	-2.12775	0.78969	0.05494
C	-2.13483	-0.78704	-0.04664
C	-3.00907	1.36599	1.15671
H	-4.06142	1.08638	0.99513
H	-2.69912	1.01429	2.14919
H	-2.9412	2.46427	1.14906
C	-2.3838	-1.47616	1.29827
H	-1.72437	-1.07135	2.08017
H	-3.42763	-1.36102	1.62442
H	-2.168	-2.54968	1.19291
C	-2.42464	1.48051	-1.27943
H	-1.79853	1.07187	-2.08631
H	-3.48108	1.37195	-1.5648
H	-2.19821	2.55265	-1.18256
C	-3.06097	-1.35818	-1.11364
H	-2.78765	-1.00802	-2.11737
H	-2.99927	-2.45684	-1.10857
H	-4.10464	-1.07245	-0.91159
C	2.54082	1.0794	-0.60959
H	2.52152	2.06439	-0.11405
H	2.56235	1.18949	-1.70707
C	4.98505	0.00803	0.03923
H	5.36349	0.89272	0.5777
H	5.37211	-0.8912	0.54664
H	5.40043	0.02757	-0.98205
H	2.49414	-0.94218	1.83195
H	2.48293	0.8763	1.85958

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-645.5544776
A5 = A5.10 Alkyl Boronate R = $BCP_{Arm(1)}$



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.314771 (Hartree/Particle)
Thermal correction to Energy= 0.330079
Thermal correction to Enthalpy= 0.331023
Thermal correction to Gibbs Free Energy= 0.272849
Sum of electronic and zero-point Energies= -644.520837
Sum of electronic and thermal Energies= -644.505528
Sum of electronic and thermal Enthalpies= -644.504584

Sum of electronic and thermal Free Energies= -644.562758

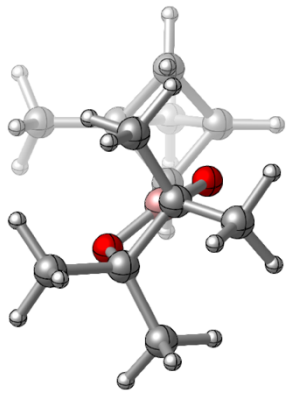
Coordinates

C	2.71824	0.42752	0.23925
C	1.67479	0.04551	-0.88488
C	2.62091	-1.18698	-0.72216
C	2.51276	-1.0055	0.81739
H	3.34107	-1.40876	1.42384
H	1.5393	-1.22806	1.27976
C	3.8138	-0.19173	-0.6789
H	4.04187	0.35469	-1.60922
H	4.73698	-0.53667	-0.18239
C	2.77247	1.72449	1.00139
H	2.93678	2.57461	0.31906
H	1.82611	1.89937	1.53893
H	3.59103	1.71452	1.74001
B	0.15201	-0.00572	-0.51078
O	-0.61991	1.12657	-0.43534
O	-0.5533	-1.14254	-0.20906
C	-2.00336	0.71831	-0.25619
C	-1.84357	-0.7406	0.32685
C	-2.69376	1.70899	0.6737
C	-2.65648	0.74528	-1.64125
C	-1.71287	-0.76726	1.85287
C	-2.90188	-1.73633	-0.13175
H	-3.7145	1.37058	0.90907
H	-2.13951	1.83716	1.61242
H	-2.76294	2.6917	0.18339
H	-2.17237	0.03011	-2.32255
H	-3.72911	0.5089	-1.58731
H	-2.54311	1.75282	-2.06806
H	-0.95042	-0.05356	2.19838
H	-2.66685	-0.52912	2.34515
H	-1.4017	-1.77498	2.16557
H	-2.89553	-1.86115	-1.22224
H	-2.70822	-2.71911	0.3238
H	-3.90423	-1.40522	0.1803
H	1.82985	0.62199	-1.81652
H	2.56498	-2.13363	-1.28013

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)

HF=-645.551276

A5 = A5.10 Alkyl Boronate R = $BCP_{Arm(2)}$



B3LYP-D3/def2-SVP-CPCM(PhCl)

Zero-point correction= 0.314730 (Hartree/Particle)

Thermal correction to Energy= 0.330059

Thermal correction to Enthalpy= 0.331004

Thermal correction to Gibbs Free Energy= 0.272752

Sum of electronic and zero-point Energies= -644.521137

Sum of electronic and thermal Energies= -644.505808

Sum of electronic and thermal Enthalpies= -644.504863

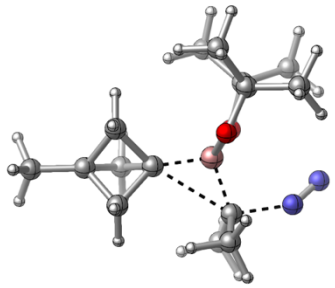
Sum of electronic and thermal Free Energies= -644.563115

Coordinates

C	2.71824	0.42752	0.23925
C	1.67479	0.04551	-0.88488
C	2.62091	-1.18698	-0.72216
C	2.51276	-1.0055	0.81739
H	3.34107	-1.40876	1.42384
H	1.5393	-1.22806	1.27976
C	3.8138	-0.19173	-0.6789
H	4.04187	0.35469	-1.60922
H	4.73698	-0.53667	-0.18239
C	2.77247	1.72449	1.00139
H	2.93678	2.57461	0.31906
H	1.82611	1.89937	1.53893
H	3.59103	1.71452	1.74001
B	0.15201	-0.00572	-0.51078
O	-0.61991	1.12657	-0.43534
O	-0.5533	-1.14254	-0.20906
C	-2.00336	0.71831	-0.25619
C	-1.84357	-0.7406	0.32685
C	-2.69376	1.70899	0.6737
C	-2.65648	0.74528	-1.64125
C	-1.71287	-0.76726	1.85287
C	-2.90188	-1.73633	-0.13175
H	-3.7145	1.37058	0.90907
H	-2.13951	1.83716	1.61242

H	-2.76294	2.6917	0.18339
H	-2.17237	0.03011	-2.32255
H	-3.72911	0.5089	-1.58731
H	-2.54311	1.75282	-2.06806
H	-0.95042	-0.05356	2.19838
H	-2.66685	-0.52912	2.34515
H	-1.4017	-1.77498	2.16557
H	-2.89553	-1.86115	-1.22224
H	-2.70822	-2.71911	0.3238
H	-3.90423	-1.40522	0.1803
H	1.82985	0.62199	-1.81652
H	2.56498	-2.13363	-1.28013

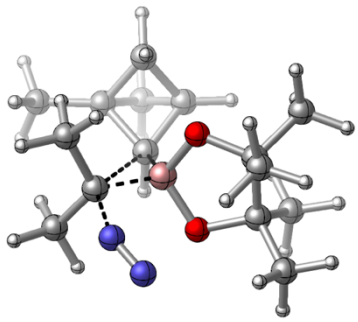
B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-645.551276
A5 = A5.10-TS-A-B Alkyl Boronate R = BCP_{Head}



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.402873 (Hartree/Particle)
Thermal correction to Energy= 0.424862
Thermal correction to Enthalpy= 0.425807
Thermal correction to Gibbs Free Energy= 0.354891
Sum of electronic and zero-point Energies= -871.625623
Sum of electronic and thermal Energies= -871.603633
Sum of electronic and thermal Enthalpies= -871.602689
Sum of electronic and thermal Free Energies= -871.673604
Coordinates

C	0.73733	-1.05797	2.30125
C	2.09525	-0.94067	1.66189
H	0.0761	-0.24977	1.96136
H	0.78178	-1.09004	3.40003
H	0.30352	-2.0076	1.95727
C	3.16572	-1.8409	2.23268
H	3.23168	-1.78096	3.32926
H	4.14711	-1.64396	1.77956
H	2.87625	-2.87156	1.98158
B	2.09554	-0.69607	0.005
O	3.33469	-0.09985	-0.45606
O	1.03065	0.19411	-0.41822
C	1.51689	1.2032	-1.29929
C	3.07548	0.86571	-1.47423
N	2.68115	0.62061	2.20978
N	3.33602	1.47947	1.96085
C	4.00533	2.06671	-1.26342
H	5.05117	1.72979	-1.33593
H	3.84006	2.83487	-2.03454
H	3.87214	2.52826	-0.2786
C	3.42887	0.24275	-2.83528
H	3.29465	0.95464	-3.66323
H	4.48489	-0.06759	-2.81428
H	2.82601	-0.64775	-3.0405
C	0.71872	1.13265	-2.60853
H	-0.34221	1.33641	-2.39535
H	1.0702	1.8777	-3.3391
H	0.78094	0.13643	-3.06399
C	1.24691	2.56887	-0.64839
H	1.54838	3.40422	-1.29836
H	0.16703	2.65685	-0.45283
H	1.76644	2.67348	0.31239
C	1.85296	-2.26126	-0.53585
C	1.00954	-3.47976	-0.01087
C	1.19092	-2.57148	-1.93003
C	2.93668	-3.31713	-0.93276
C	1.58858	-3.95764	-1.3665
H	1.37617	-4.00314	0.88953
H	1.73469	-2.23209	-2.82462
H	0.11424	-2.35428	-2.01872
H	3.47864	-3.81883	-0.1131
H	3.63089	-3.02068	-1.73613
C	1.38271	-5.30207	-2.021
H	1.76124	-6.11517	-1.37927
H	0.31234	-5.48779	-2.21067
H	1.91351	-5.35521	-2.98609
H	-0.08496	-3.34702	0.03608

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-873.0021374
A5 = A5.10-TS-A-B Alkyl Boronate R = $BCP_{Arm(1)}$

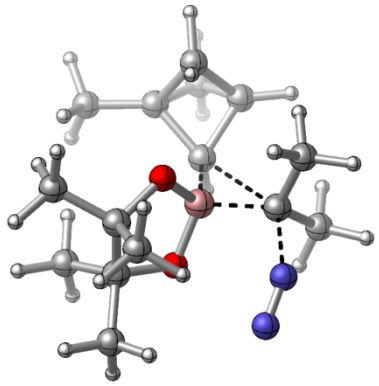


B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.403576 (Hartree/Particle)

Thermal correction to Energy= 0.425152
Thermal correction to Enthalpy= 0.426097
Thermal correction to Gibbs Free Energy= 0.356707
Sum of electronic and zero-point Energies= -871.617701
Sum of electronic and thermal Energies= -871.596125
Sum of electronic and thermal Enthalpies= -871.595180
Sum of electronic and thermal Free Energies= -871.664570
Coordinates

C	1.48625	0.53636	-2.41631
C	1.09815	0.06884	-1.03763
H	2.36391	1.19429	-2.36483
H	0.66196	1.02376	-2.95788
H	1.7911	-0.35128	-2.98479
C	-0.28534	-0.52615	-0.89622
H	-1.06505	0.09816	-1.35732
H	-0.53213	-0.72641	0.1558
H	-0.27893	-1.48626	-1.42776
B	2.33369	-0.63636	-0.15417
O	2.12176	-0.48643	1.27636
O	3.63086	-0.04682	-0.43154
C	4.29475	0.33913	0.76885
C	3.36464	-0.24058	1.93138
N	0.8641	1.56009	-0.15147
N	0.92235	2.03573	0.84835
C	3.12991	0.7334	3.09037
H	2.44783	0.27173	3.82129
H	4.07425	0.96791	3.60576
H	2.67292	1.67169	2.75456
C	3.8695	-1.56775	2.5235
H	4.80418	-1.4405	3.08981
H	3.10103	-1.95824	3.20824
H	4.03271	-2.32037	1.74407
C	5.71185	-0.24769	0.75631
H	6.27699	0.18378	-0.08457
H	6.25208	-0.01372	1.687
H	5.6976	-1.33654	0.62337
C	4.41587	1.87177	0.77837
H	4.99	2.23643	1.64361
H	4.93769	2.18593	-0.13876
H	3.43461	2.36183	0.7856
C	2.18964	-2.25758	-0.62051
C	2.10073	-2.96794	-2.03799
C	3.51865	-3.06682	-0.80686
H	1.49037	-2.711	0.10767
C	3.58276	-2.54305	-2.2661
C	2.66235	-4.2397	-1.33788
C	0.9868	-3.02036	-3.05814
H	4.15608	-3.15468	-2.98451
H	3.79491	-1.47326	-2.38847
H	1.99446	-4.74376	-0.61948
H	3.16782	-4.97052	-1.99472
H	0.06672	-3.43604	-2.61413
H	0.74173	-2.03974	-3.49249
H	1.27946	-3.68309	-3.88954
H	4.35764	-3.12801	-0.10053

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-872.9940458
A5 = A5.10-TS-A-B Alkyl Boronate R = $BCP_{Arm(2)}$



B3LYP-D3/def2-SVP-CPCM(PhCl)
Zero-point correction= 0.403464 (Hartree/Particle)
Thermal correction to Energy= 0.425081
Thermal correction to Enthalpy= 0.426025
Thermal correction to Gibbs Free Energy= 0.356540
Sum of electronic and zero-point Energies= -871.617385
Sum of electronic and thermal Energies= -871.595768
Sum of electronic and thermal Enthalpies= -871.594824
Sum of electronic and thermal Free Energies= -871.664309
Coordinates

C	1.24968	0.92229	-0.98236
C	2.07269	0.16911	0.04427
H	1.78517	1.02047	-1.93684
H	0.93141	1.91266	-0.6239
H	0.33819	0.33649	-1.16269
C	1.46829	0.08213	1.42009
H	1.02576	1.03116	1.75769
H	2.20594	-0.28671	2.14509
H	0.66263	-0.66317	1.37051
B	2.90657	-1.2198	-0.47601
O	3.54874	-1.94969	0.6027
O	3.96405	-0.8567	-1.40696
C	5.15722	-1.58076	-1.10883

C	4.95897	-2.02482	0.40925
N	3.37338	1.33848	0.22378
N	4.32538	1.70772	-0.20685
C	5.64529	-1.09651	1.42666
H	5.31966	-1.38794	2.4371
H	6.74208	-1.17569	1.38294
H	5.3735	-0.0451	1.28317
C	5.42567	-3.45505	0.70425
H	6.50705	-3.56444	0.52726
H	5.2258	-3.69524	1.76009
H	4.89806	-4.19263	0.08861
C	5.24686	-2.76224	-2.08678
H	5.23493	-2.36592	-3.1137
H	6.16766	-3.34964	-1.95346
H	4.38586	-3.42798	-1.97634
C	6.37215	-0.67776	-1.34097
H	7.30595	-1.2106	-1.10215
H	6.41015	-0.3812	-2.40078
H	6.33244	0.23806	-0.73977
C	1.61913	-2.03264	-1.20318
C	1.38376	-3.59784	-1.06155
C	0.17171	-2.23178	-0.62797
H	1.60349	-1.68927	-2.2555
C	0.74664	-3.30913	0.32935
C	-0.0286	-3.35766	-1.66842
C	2.27734	-4.75992	-1.40273
H	0.0336	-4.0647	0.70265
H	1.43707	-2.97918	1.11643
H	-0.07102	-3.05904	-2.72917
H	-0.79266	-4.12109	-1.43629
H	2.59503	-4.72956	-2.45718
H	3.17311	-4.77717	-0.76727
H	1.73397	-5.70626	-1.242
H	-0.56435	-1.45145	-0.37531

B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)
HF=-872.9937875

Appendix 6: Supporting Information Chapter 7

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3BJ)/def2-SVP level of the theory in implicit solvent (THF) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, Revision C.01. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Single point energy calculations in implicit solvent using and B3LYP-D3BJ/def2-TZVPP-CPCM(DMSO) were also performed. All 3-D structures were generated using CYLview20.

Full reference for Gaussian 16 Software:

Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Reference GaussView 6:

GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

Reference CYLview20:

CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org)

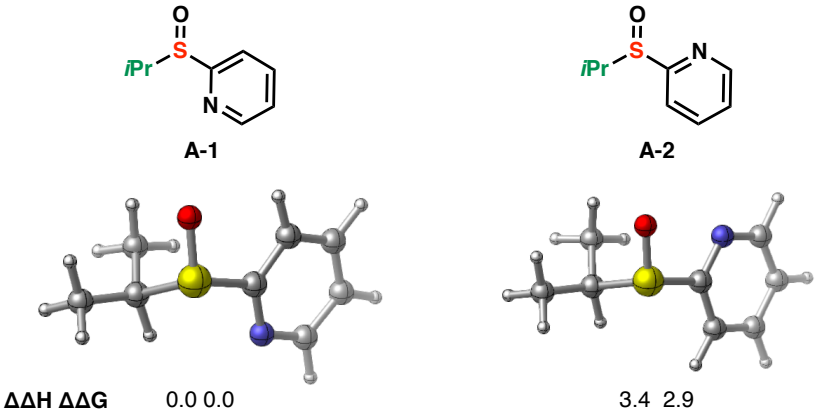


Figure A6.1: Lowest energy conformations obtained from conformational search sulfoxide.

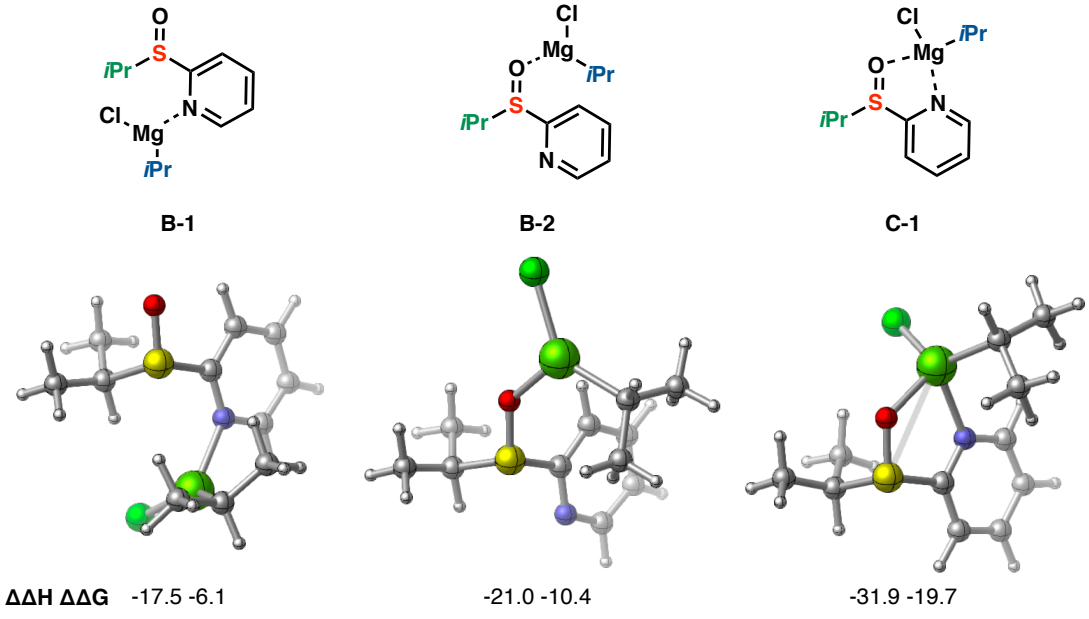


Figure A6.2: Relative enthalpies and free energies of complexation between the chloroalkyl Grignard and sulfoxide reagent.

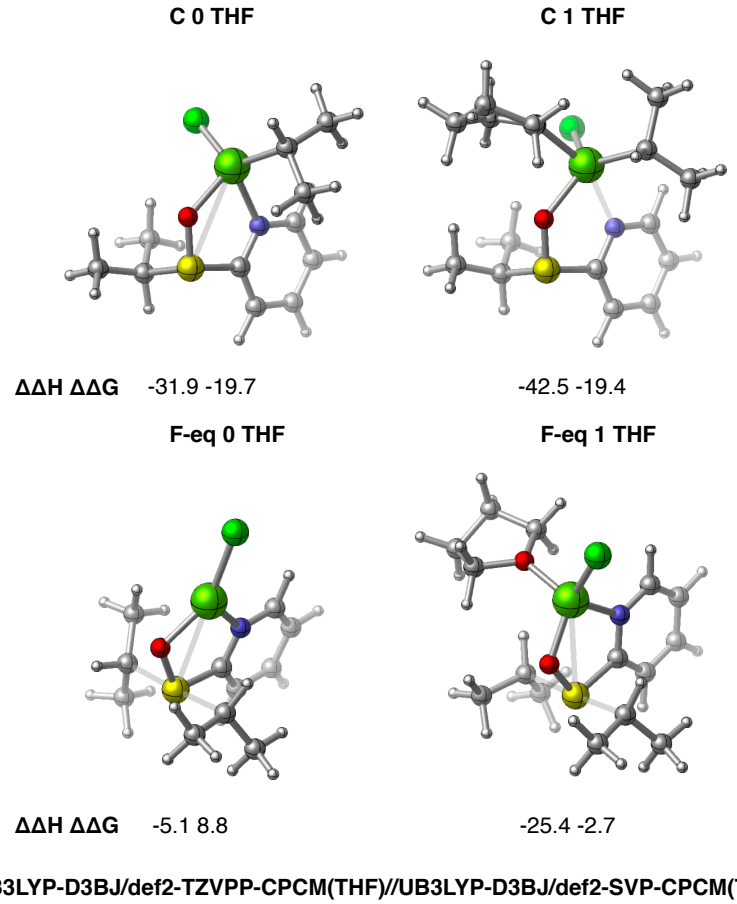


Figure A6.3: Relative enthalpies and free energies of sulfoxide reagent and sulfurane intermediate with and without explicit THF solvent.

We began our investigation by determining the lowest energy conformation of the sulfoxide intermediate (**Figure A6.1**). Once located, various complexes of the chloroalkyl Grignard reagent were calculated to determine the lowest energy complex (**Figure A6.2**). The complex in which both the nitrogen and oxygen atoms of the sulfoxide are bound to the Grignard has a complexation energy of -19.7 kcal/mol. However, it was found that the sulfoxide intermediate was uphill in energy by 28.5 kcal/mol. Adding an explicit THF molecule to the sulfurane intermediate lowered by free energy of the complex by 11.5 kcal/mol, suggesting that THF coordination to the Grignard is required for these intermediates to be accessible.

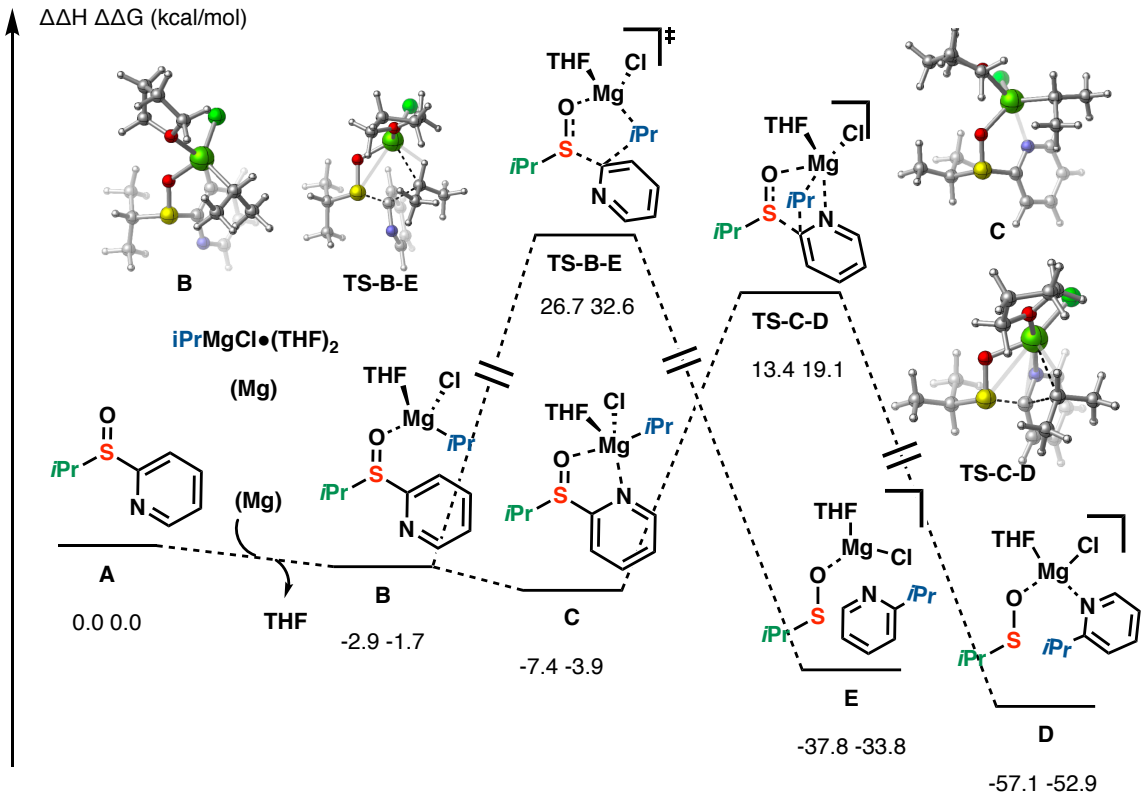


Figure A6.4: Reaction coordinate diagrams of direct C-C bond formation from intermediate **B** and from intermediate **C**.

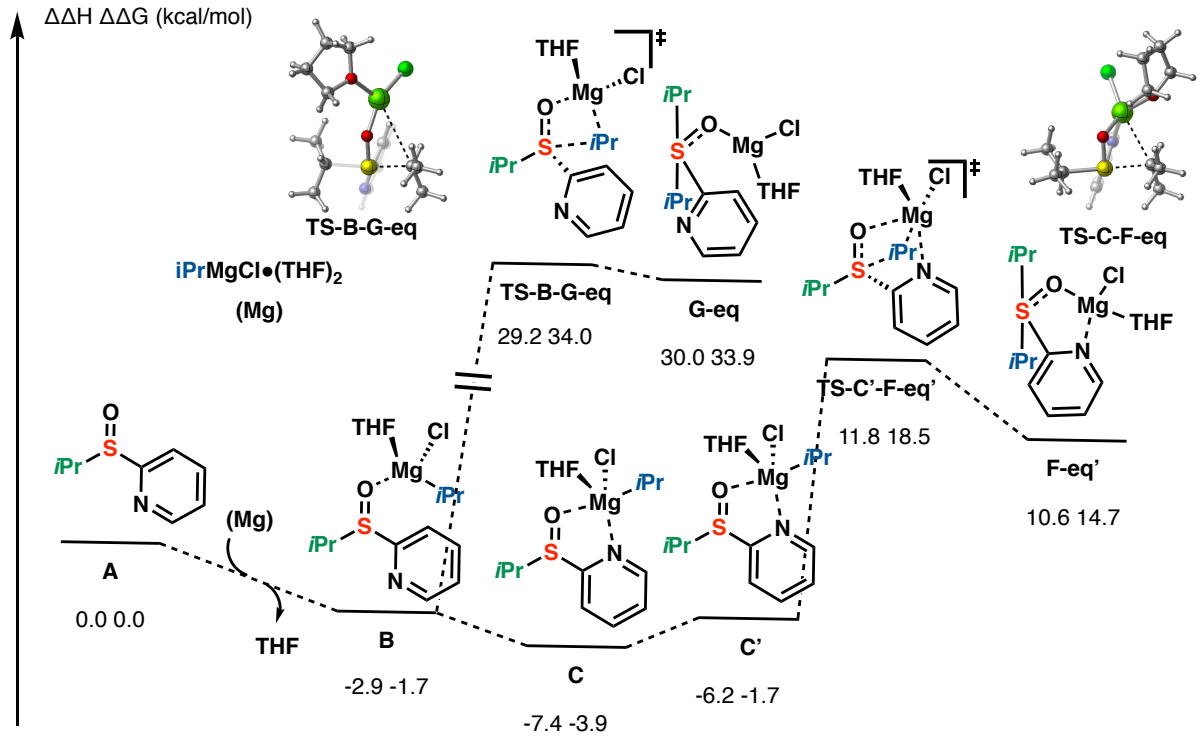


Figure A6.5: Reaction coordinate diagram to S-C bond formation from intermediate **B** and **C**.

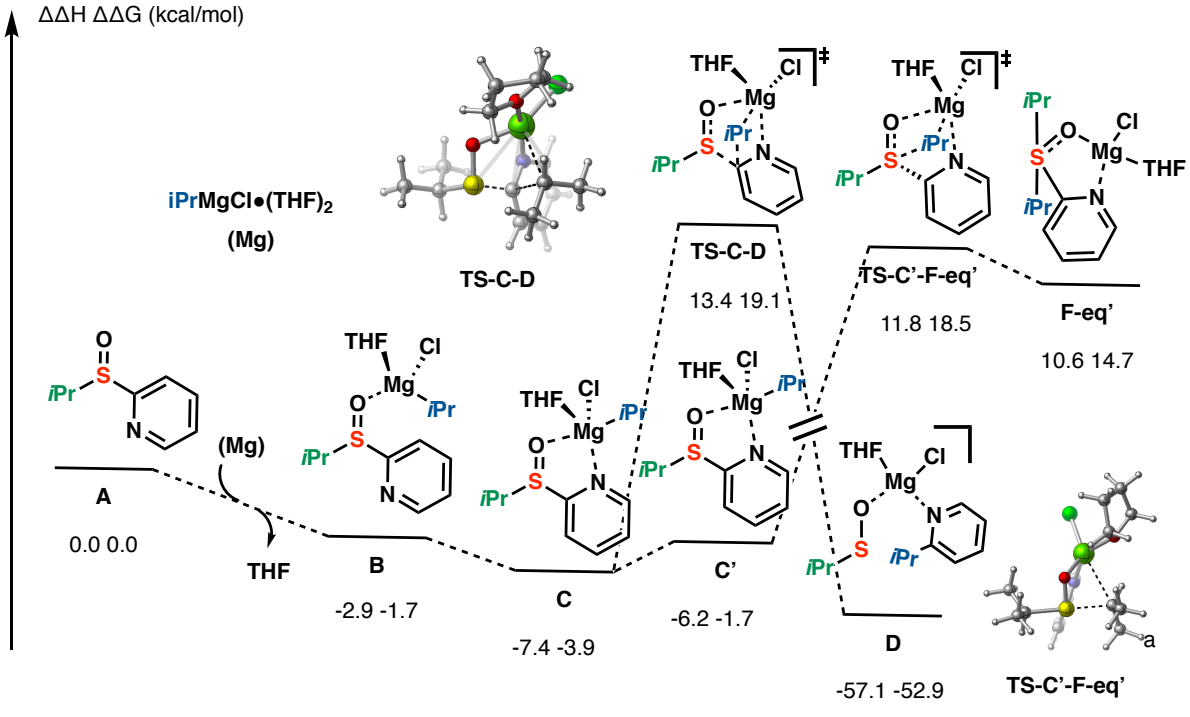


Figure A6.6: Reaction coordinate diagram of lowest energy pathways to direct C-C from Grignard reagent and

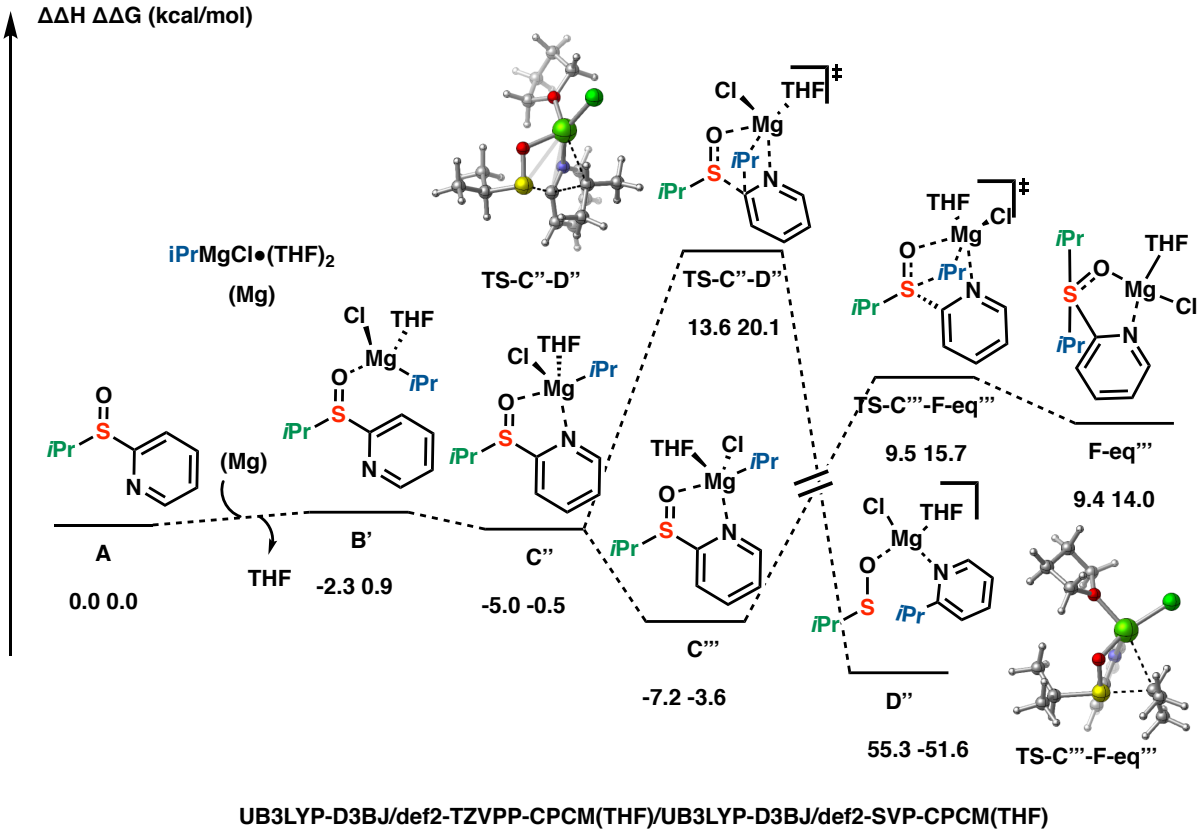


Figure A6.7: Mulliken charges labeled at head and arm boron and carbon for conformation 1 and additionally at the carbene carbon through TS-A-B for both arm and head transition states.

Next, we modeled the direct C-C bond formation from the Grignard reagent from complexes **B** and **C** (**Figure A6.4**). The barrier of C-C bond formation was substantially lower via complex **C**, with a barrier of 23.0 kcal/mol vs a barrier of 34.3 kcal/mol from intermediate **B**. C-S bond formation was then modeled from intermediates **B** and **C** with barriers of 35.7 kcal/mol and 22.4 kcal/mol (**Figure A6.5**). Work by Ainara and Michele highlighted that the coordination of the bound THF molecule must be trans of the alkyl group to afford for alkyl migration in the Schlenk equilibrium. Inspired by this work, we considered transition states in with the THF molecule coordinated trans to the isopropyl functionality (**Figure A6.7**). **TS-C''-D''** did not result in the THF molecule completely trans to the alkyl group, resulting in a barrier of 17.9 kcal/mol from **C''**.

However, **TS-C'''-F-eq'''** resulted in the trans coordination through the transition state, affording a barrier of isopropyl migration to the sulfur of the sulfoxide with the lowest energy barrier (19.3 kcal/mol) to product. Additionally, intermediate **C'''** is only 0.3 kcal/mol higher in free energy than the lowest energy conformation C. Overall, the calculations reveal that alkyl migration to the sulfur atom is kinetically faster than direct C-C bond formation form the chloroalkyl Grignard reagent due to the trans coordination of THF through the transition state.

Mg/Sulf Angle	S TS-F-eq-D $\Delta\Delta G^{\ddagger}$	Mg TS-F-eq-D $\Delta\Delta G^{\ddagger}$
0/0	15.0	16.0
0/120	XX	16.4
0/240	XX	16.8
120/0	15.1	17.9
120/120	XX	17.7
120/240	XX	15.2
240/0	16.0	18.1
240/120	16.7	18.5
240/240	15.9	14.9

UB3LYP-D3BJ/def2-TZVPP-CPCM(THF)/UB3LYP-D3BJ/def2-SVP-CPCM(THF)

Table A6.1: Relative free energies of all conformations of C-C bond formation from sulfurane intermediate F-eq of alkyls from Grignard and Sulfoxide.

To ensure that the lowest energy conformation was obtained, a series of transition states about various conformations of C-C bond formation from sulfurane intermediate (**TS-F-eq-D**) were calculated of isopropyl groups from sulfoxide and Grignard feedstocks (**Figure A6.8**). All transition states were obtained for transition states for the isopropyl from the Grignard reagent

while only 5 out of 9 transition states for the sulfoxide isopropyl could be obtained. This is attributed to an incredibly flat potential energy surface leading to C-C bond formation from the sulfoxide alkyl.

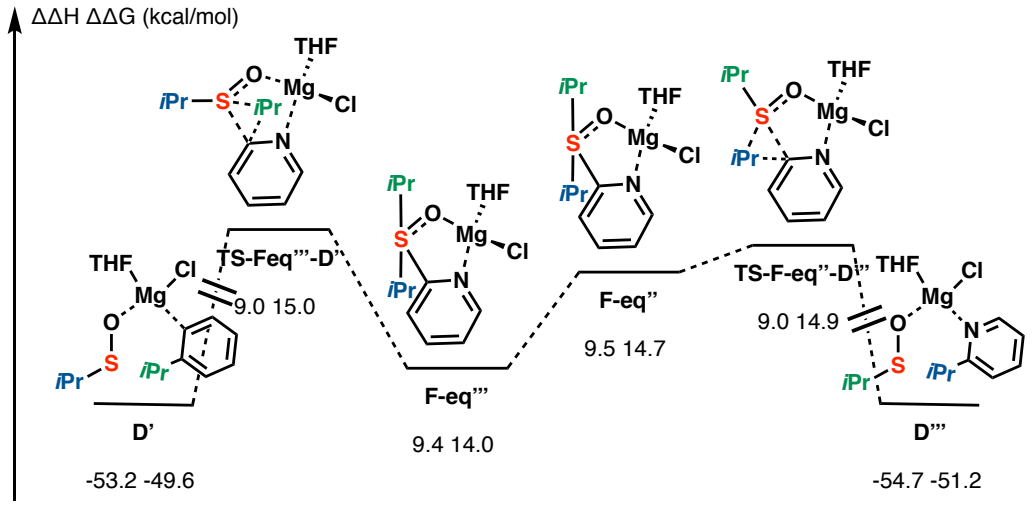


Figure A6.8: Kinetic pathways to C-C bond formation from the Grignard alkyl and sulfoxide alkyl from sulfurane intermediates.

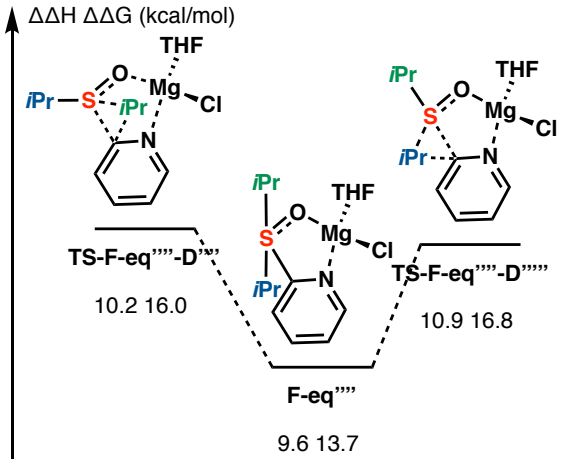


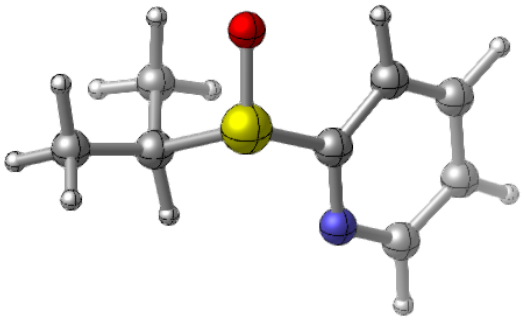
Figure A6.9: Thermodyanic pathways to C-C bond formation from the Grignard alkyl and sulfoxide alkyl from sulfurane intermediates.

Next, we turned to modeling the lowest energy pathways to product from the sulfurane intermediate. It was found that both transition states to product, isopropyl from sulfoxide and Grignard, are almost identical in free energy and enthalpy. However, the free energy of the intermediates attached to the corresponding transition states differ in free energy by 0.7 kcal/mol,

preferring the intermediate leading to the sulfoxide alkyl C-C formation. Finally, we investigated the transition states from the lowest energy sulfurane intermediate (**Figure A6.9**; **F-eq’’’’**), which is 0.3 kcal/mol lower than F-eq’’’. The barriers to C-C bond formation from this intermediate are slightly higher compared to the previous pathways, 16.0 and 16.8 kcal/mol, making this pathway the thermodynamic pathway with regards to the sulfurane intermediate. This reaction still prefers C-C bond formation via the sulfoxide alkyl group (**TS-F-eq’’’’-D’’’’**), with a barrier 0.8 kcal/mol lower than the Grignard alkyl pathway (**TS-F-eq’’’’-D’’’’’**). These calculations strongly agree with the experimental results, preferring product formation form the sulfoxide feedstock over the Grignard reagent by a ratio over 80:20 when following the kinetic pathways (**Figure A6.8**). In addition, these calculations also highlight the instability of the sulfurane intermediates (having barriers leading to product and complexes of starting materials with barriers less than 2.0 kcal/mol), making these intermediates impossible to isolate experimentally.

Energies and Coordinates

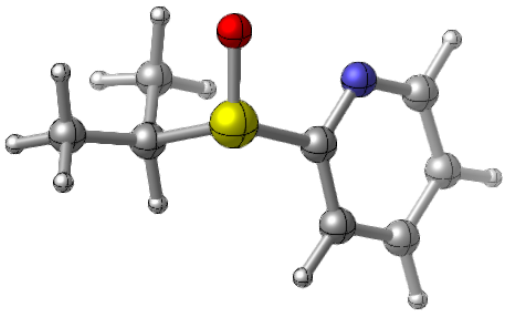
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Thesis = A



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Zero-point correction= 0.177142 (Hartree/Particle)
Thermal correction to Energy= 0.188352
Thermal correction to Enthalpy= 0.189296
Thermal correction to Gibbs Free Energy= 0.139652
Sum of electronic and zero-point Energies= -839.039978
Sum of electronic and thermal Energies= -839.028768
Sum of electronic and thermal Enthalpies= -839.027824
Sum of electronic and thermal Free Energies= -839.077468
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -839.8759647
Coordinates

S	-5.44871	3.89406	-1.07263
O	-6.77565	4.59811	-1.32292
C	-4.39382	5.0549	-0.04383
H	-3.59052	4.39799	0.32527
C	-3.85105	6.10908	-1.00047
H	-4.67601	6.67841	-1.45826
H	-3.21102	6.81847	-0.45223
H	-3.2507	5.65879	-1.80663
C	-5.22395	5.63259	1.0888
H	-4.65585	6.42348	1.60427
H	-6.1502	6.07498	0.69006
H	-5.49499	4.86854	1.83256
C	-5.75998	2.6655	0.24508
C	-7.07574	2.43201	0.6373
C	-4.90039	1.10419	1.66106
C	-7.28045	1.4597	1.61906
H	-7.88501	3.00634	0.18406
C	-6.17473	0.78384	2.14146
H	-4.01445	0.59146	2.05063
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H	-6.29256	0.01703	2.90973
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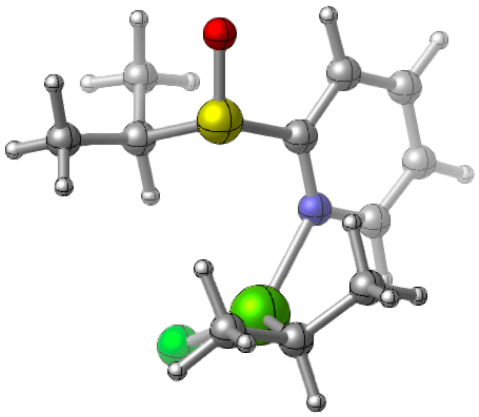
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Thermal correction to Enthalpy= 0.189170
Thermal correction to Gibbs Free Energy= 0.138733
Sum of electronic and zero-point Energies= -839.033104
Sum of electronic and thermal Energies= -839.021778
Sum of electronic and thermal Enthalpies= -839.020834
Sum of electronic and thermal Free Energies= -839.071271
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -839.8704931
Coordinates

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C	-4.11263	6.30106	-0.83859
H	-4.93371	6.70158	-1.45604
H	-3.83139	7.08085	-0.11234
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C	-5.70768	5.2517	0.85815
H	-5.40336	5.923	1.67727
H	-6.57113	5.70939	0.34639
H	-6.02518	4.29401	1.2952
C	-5.74163	2.56917	-0.05039
C	-5.19975	1.28849	0.05954
C	-5.7743	0.42117	0.99379
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C	-6.85493	0.87297	1.7519
H	-5.38517	-0.59167	1.12262
H	-8.16562	2.5622	2.1289
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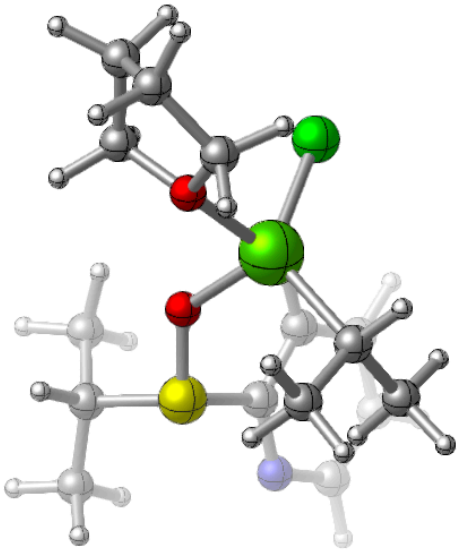


B3LYP-D3BJ/def2-SVP-CPCM(THF)
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Thermal correction to Enthalpy= 0.292348
Thermal correction to Gibbs Free Energy= 0.219963
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Sum of electronic and thermal Energies= -1617.619008
Sum of electronic and thermal Enthalpies= -1617.618064
Sum of electronic and thermal Free Energies= -1617.690449
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1618.9286802
Coordinates

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H	-10.02757	5.62592	-2.17886
H	-9.86295	4.18857	-3.21909
C	-8.83958	4.55724	0.11405
H	-8.9819	5.6492	0.1407
H	-9.69159	4.08479	0.62638
H	-7.91971	4.32233	0.67005
C	-7.14185	1.95882	-0.56237
C	-7.13638	1.42377	0.71936
C	-4.84457	2.0286	-0.67238
C	-5.89696	1.20037	1.32256

H	-8.08715	1.20339	1.20678
C	-4.73226	1.51094	0.61668
H	-3.95649	2.27709	-1.2613
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N	-6.03625	2.24387	-1.25947
Mg	-5.92711	2.82889	-3.36769
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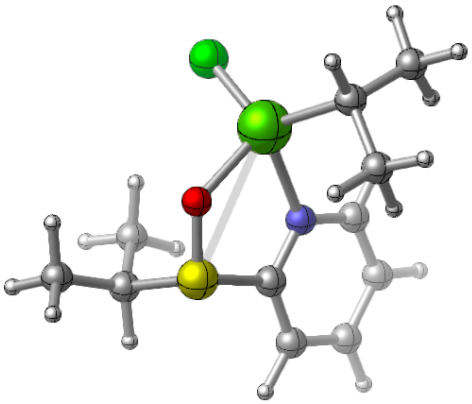


B3LYP-D3BJ/def2-SVP-CPCM(THF)
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Sum of electronic and thermal Energies= -1617.630933
Sum of electronic and thermal Enthalpies= -1617.629989
Sum of electronic and thermal Free Energies= -1617.703727

B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1618.9341741
Coordinates

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C	-5.08844	1.97933	-1.68828
H	-4.19239	2.5313	-1.36487
H	-4.81299	0.91893	-1.79709
H	-5.39897	2.35409	-2.67573
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H	-5.48284	0.55895	0.64636
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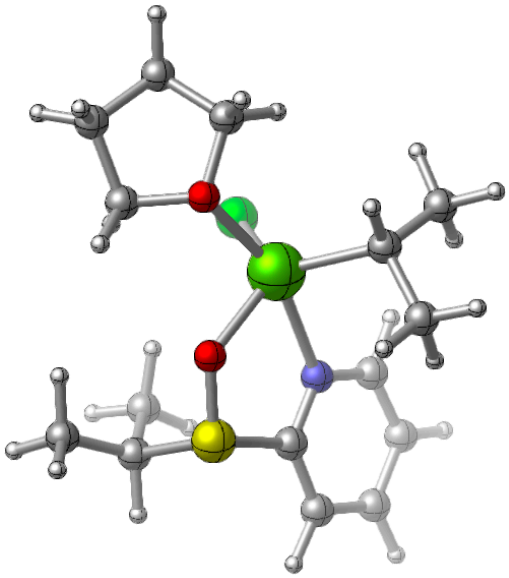
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D3BJ/def2-SVP-CPCM(THF)
HF= -1618.9514576
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H	-5.50009	3.25436	-4.5282
H	-6.3231	2.24191	-3.32057
C	-6.52552	5.7419	-3.63229
H	-5.66224	5.907	-4.29559
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C	-6.48457	7.62375	0.4995
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H	-9.30808	8.64101	-1.11742
H	-5.71032	7.96526	1.18989
H	-7.54028	9.52131	0.43327
N	-8.47075	6.74726	-1.23714
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H	-12.59497	5.15124	-1.23331
C	-11.29484	5.41469	0.45299
H	-12.07451	5.42438	1.24905
H	-10.88379	4.38907	0.42841
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C	-12.46857	7.25065	-0.81065
H	-12.91125	7.57889	-1.76826
H	-13.28092	7.30037	-0.04916
H	-11.74095	8.03378	-0.51996

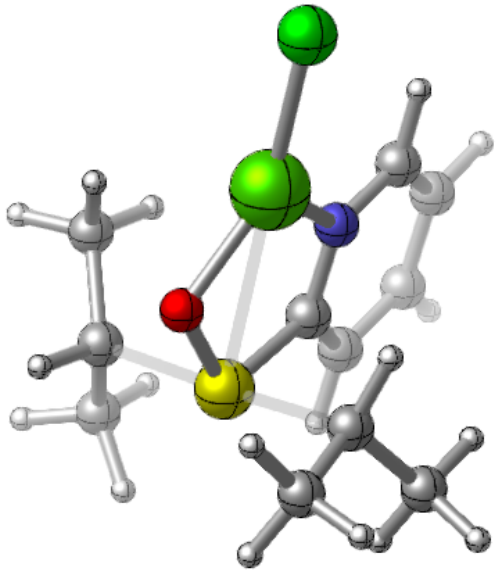
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(Hartree/Particle)
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Thermal correction to Enthalpy=
0.416768
Thermal correction to Gibbs Free Energy=
0.330874
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Sum of electronic and thermal Energies= -
1849.853994
Sum of electronic and thermal Enthalpies= -
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Sum of electronic and thermal Free Energies= -
1849.938945
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-
D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5388473
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C	-5.21342	7.95299	-3.18044
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H	-4.47419	8.47883	-5.1295
H	-4.25028	6.75413	-4.74376
C	-6.1986	9.09597	-2.99943
H	-5.8587	9.94876	-3.60847
H	-7.21407	8.82758	-3.32901
H	-6.25578	9.43263	-1.95501
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C	-5.53421	7.3773	0.22697
C	-8.27076	7.67899	0.34697
C	-6.10974	7.91335	1.38143
H	-4.45595	7.23309	0.13498
C	-7.49752	8.07123	1.44011
H	-9.35808	7.77984	0.34679
H	-5.48054	8.20211	2.2262
H	-7.98021	8.48849	2.32527
N	-7.72007	7.16287	-0.76008
Mg	-9.00832	6.27941	-2.47018
Cl	-9.98255	8.4086	-2.88214
C	-9.93512	4.72152	-1.26345
H	-10.32896	3.97294	-1.98496
C	-8.90858	3.99963	-0.38444
H	-9.33314	3.15769	0.21233
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H	-8.44644	4.68246	0.35465
C	-11.11763	5.19733	-0.41471
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H	-10.81264	5.96802	0.31955
O	-9.57233	5.61537	-4.42004
C	-10.98885	5.40659	-4.6229
C	-8.9808	6.22547	-5.59071
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H	-11.52362	7.2847	-5.53989
H	-12.23139	5.86529	-6.36976
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H	-10.00538	5.18319	-7.20015

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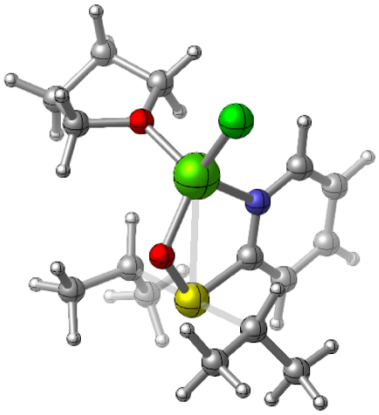


B3LYP-D3BJ/def2-SVP-CPCM(THF)
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Thermal correction to Enthalpy= 0.291642
Thermal correction to Gibbs Free Energy= 0.223210
Sum of electronic and zero-point Energies= -1617.628440
Sum of electronic and thermal Energies= -1617.608825
Sum of electronic and thermal Enthalpies= -1617.607881
Sum of electronic and thermal Free Energies= -1617.676313
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1618.9081272
Coordinates

S	-7.3184	4.4607	-0.20597
O	-6.52647	5.87029	-0.12528
C	-6.63727	4.29473	-2.17268
H	-7.08089	5.23774	-2.53174
C	-5.13693	4.30649	-2.39282
H	-4.65968	3.3883	-2.00862
H	-4.87887	4.36854	-3.46871
H	-4.65681	5.16842	-1.90147
C	-7.34412	3.1127	-2.8077
H	-7.4133	3.21278	-3.90699
H	-6.81975	2.16277	-2.60988
H	-8.37801	3.0112	-2.42772
C	-6.15597	3.16969	0.28901

C	-6.36825	1.80742	0.07939
C	-4.10398	2.78371	1.30717
C	-5.38691	0.9176	0.51592
H	-7.28185	1.45538	-0.39657
C	-4.2342	1.41033	1.1394
H	-3.22692	3.22372	1.78873
H	-5.52414	-0.15734	0.3774
H	-3.4501	0.74006	1.49434
N	-5.05319	3.64282	0.88875
Mg	-4.98474	5.76976	1.01487
Cl	-3.23067	6.80939	1.98618
C	-7.91751	4.72942	1.79699
H	-7.08201	5.01154	2.46647
C	-8.93933	5.84919	1.71794
H	-8.46827	6.81717	1.48894
H	-9.67624	5.64639	0.91621
H	-9.51675	5.96447	2.65555
C	-8.52433	3.40604	2.21834
H	-7.76211	2.66149	2.49853
H	-9.21603	3.50684	3.0761
H	-9.11638	2.97156	1.38645

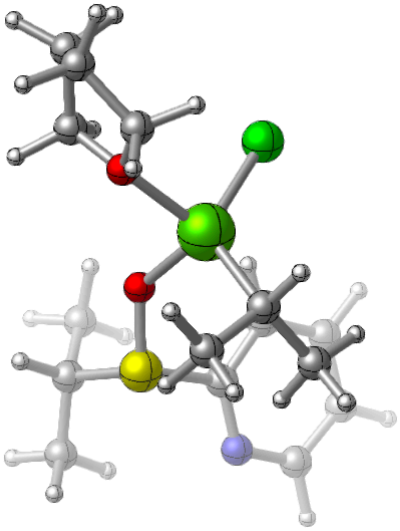
A6 = A6.3-F-eq 1 THF



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388951 (Hartree/Particle)
Thermal correction to Energy= 0.415206
Thermal correction to Enthalpy= 0.416150
Thermal correction to Gibbs Free Energy= 0.329794
Sum of electronic and zero-point Energies= -1849.853132
Sum of electronic and thermal Energies= -1849.826877
Sum of electronic and thermal Enthalpies= -1849.825932
Sum of electronic and thermal Free Energies= -1849.912289
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5110796
Coordinates

S	-7.9665	5.22754	-1.47435
O	-8.55326	5.67566	-2.90576
C	-6.04496	5.80245	-2.139
H	-6.07506	6.83639	-2.51796
C	-5.1045	5.65087	-0.96004
H	-5.37242	4.75309	-0.36458
H	-4.05076	5.51243	-1.27048
H	-5.13073	6.51558	-0.27863
C	-5.74273	4.80843	-3.24472
H	-4.68749	4.85138	-3.57942
H	-5.91751	3.77247	-2.89165
H	-6.38806	4.96115	-4.12156
C	-8.02977	6.693	-0.40942
C	-7.56935	6.70734	0.90857
C	-8.69128	8.91372	-0.28779
C	-7.68636	7.89302	1.6335
H	-7.13572	5.81324	1.35347
C	-8.25796	9.01788	1.02931
H	-9.14921	9.75941	-0.80745
H	-7.33666	7.93772	2.66755
H	-8.3697	9.95911	1.56934
N	-8.57316	7.77206	-0.98912
Mg	-9.14931	7.50796	-3.04107
C	-9.89759	4.71257	-0.88396
H	-10.57286	5.57344	-1.02567
C	-10.273	3.55945	-1.79684
H	-11.17981	3.02728	-1.44978
H	-10.44708	3.89762	-2.82823
H	-9.45943	2.80721	-1.82935
C	-9.80719	4.29431	0.57118
H	-9.78509	5.15257	1.26077
H	-10.65315	3.65105	0.87869
H	-8.88398	3.70441	0.74756
O	-7.65762	8.51795	-3.96804
C	-7.02138	9.71985	-3.45626
C	-6.95063	8.01183	-5.13369
C	-5.98459	10.09014	-4.51014
H	-7.79801	10.48354	-3.30598
H	-6.55916	9.47576	-2.48667
C	-5.60867	8.72525	-5.09939
H	-6.88566	6.9199	-5.04016
H	-7.5371	8.2695	-6.03069
H	-5.13056	10.62662	-4.07327
H	-6.43696	10.73005	-5.28417
H	-4.91307	8.19255	-4.43144
H	-5.15167	8.79306	-6.09662
Cl	-11.13683	8.42703	-3.67855

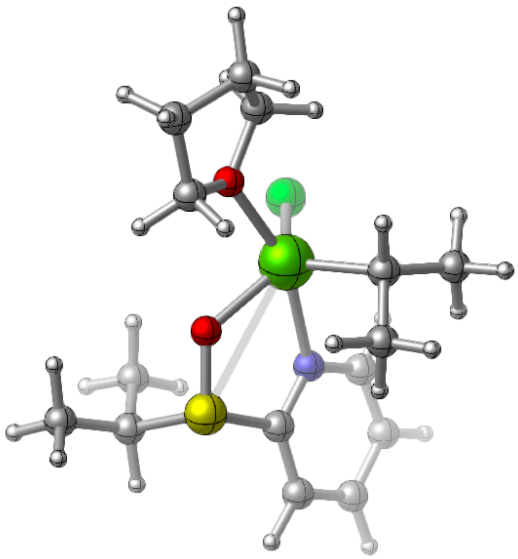
A6 = A6.4-B, A6.5-B, A6.6-B



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389010 (Hartree/Particle)
Thermal correction to Energy= 0.415916
Thermal correction to Enthalpy= 0.416861
Thermal correction to Gibbs Free Energy= 0.326172
Sum of electronic and zero-point Energies= -1849.872130
Sum of electronic and thermal Energies= -1849.845224
Sum of electronic and thermal Enthalpies= -1849.844279
Sum of electronic and thermal Free Energies= -1849.934968
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5317901
Coordinates

S	-6.41422	2.86405	-0.41796
O	-7.72131	2.77903	0.42022
C	-6.5039	1.32555	-1.46506
H	-6.46964	0.56734	-0.66438
C	-7.82309	1.24033	-2.21043
H	-7.86232	1.95779	-3.04422
H	-7.92933	0.22676	-2.62908
H	-8.67492	1.42297	-1.53952
C	-5.26197	1.2202	-2.33811
H	-5.24992	0.22558	-2.81119
H	-5.26067	1.97897	-3.13349
H	-4.33605	1.32896	-1.75258
C	-6.73532	4.14394	-1.66621
C	-7.99272	4.73145	-1.78075
C	-5.7941	5.4441	-3.27912
C	-8.11548	5.75357	-2.72644
H	-8.83384	4.42574	-1.15574
C	-7.00311	6.11609	-3.48827
H	-4.90199	5.70424	-3.85774
H	-9.07413	6.26032	-2.85898
H	-7.06382	6.91354	-4.23143
N	-5.65977	4.47393	-2.36889
Mg	-8.4269	4.10469	1.76127
Cl	-10.51381	4.75385	0.9268
C	-6.8876	5.43672	2.45749
H	-7.33728	6.13948	3.19108
C	-5.77382	4.66921	3.1808
H	-4.94621	5.31983	3.54721
H	-6.14636	4.11202	4.05978
H	-5.29522	3.92075	2.51958
C	-6.29421	6.28389	1.32423
H	-7.06038	6.87915	0.79547
H	-5.51181	7.00001	1.6661
H	-5.8027	5.6585	0.55474
O	-8.99045	2.71661	3.16952
C	-9.82489	1.59305	2.78176
C	-9.30437	3.14528	4.52179
C	-10.92541	1.54752	3.83176
H	-10.19331	1.77447	1.76287
H	-9.20201	0.68369	2.78825
C	-10.19692	2.04633	5.08465
H	-8.35994	3.28135	5.06722
H	-9.82973	4.11311	4.46662
H	-11.35123	0.54029	3.94462
H	-11.7355	2.24176	3.55676
H	-9.58483	1.24033	5.5206
H	-10.87453	2.42495	5.86303

A6 = A6.4-C, A6.5-C, A6.6-C

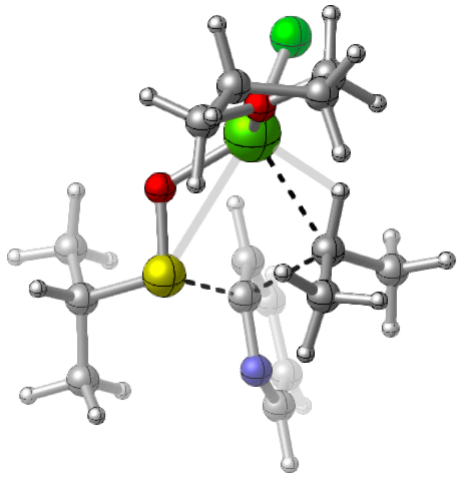


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389188 (Hartree/Particle)

Thermal correction to Energy= 0.415641
Thermal correction to Enthalpy= 0.416585
Thermal correction to Gibbs Free Energy= 0.329524
Sum of electronic and zero-point Energies= -1849.878948
Sum of electronic and thermal Energies= -1849.852495
Sum of electronic and thermal Enthalpies= -1849.851551
Sum of electronic and thermal Free Energies= -1849.938612
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5386551
Coordinates

S	-6.98361	4.53847	-1.68826
O	-7.70764	5.24309	-2.85705
C	-5.16778	4.8303	-2.00893
H	-4.70025	4.48844	-1.06995
C	-4.78306	3.91459	-3.1655
H	-5.3081	4.207	-4.08799
H	-3.70098	4.00138	-3.34927
H	-5.0093	2.85907	-2.94876
C	-4.88583	6.2992	-2.27277
H	-3.82001	6.41433	-2.52528
H	-5.4779	6.6685	-3.12344
H	-5.0977	6.93219	-1.39982
C	-7.20629	5.69139	-0.29492
C	-6.75066	5.3887	0.98503
C	-8.0319	7.7369	0.31663
C	-6.95923	6.35585	1.97146
H	-6.25099	4.44289	1.20399
C	-7.60367	7.54899	1.63111
H	-8.53063	8.65231	-0.00901
H	-6.62108	6.17847	2.99473
H	-7.77712	8.32754	2.37571
N	-7.83852	6.8062	-0.62876
Mg	-8.9293	6.8979	-2.66059
Cl	-8.27876	9.15196	-2.92974
C	-10.86987	6.3532	-1.82215
H	-11.5745	6.29246	-2.68049
C	-10.8076	4.96133	-1.18654
H	-11.77264	4.61685	-0.7436
H	-10.49964	4.18197	-1.90731
H	-10.07489	4.92105	-0.35533
C	-11.4452	7.36452	-0.82974
H	-11.56355	8.36878	-1.27622
H	-12.44152	7.08011	-0.41409
H	-10.78703	7.49402	0.05149
O	-9.33059	6.59633	-4.72185
C	-9.4021	5.29405	-5.34163
C	-10.22975	7.5224	-5.37737
C	-10.07427	5.53981	-6.68552
H	-8.38312	4.89126	-5.40821
H	-10.00378	4.62534	-4.70271
C	-11.04821	6.67192	-6.34351
H	-10.83773	8.02474	-4.61155
H	-9.623	8.28142	-5.89625
H	-10.56795	4.63822	-7.07639
H	-9.33369	5.87931	-7.42823
H	-11.93794	6.26654	-5.83519
H	-11.38303	7.24552	-7.21976

A6 = A6.4-TS-B-E

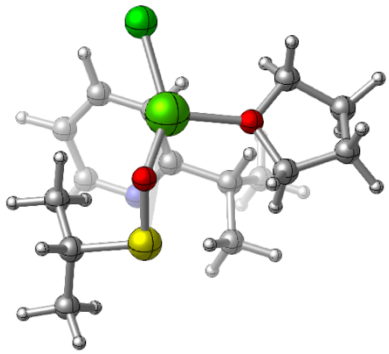


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389327 (Hartree/Particle)
Thermal correction to Energy= 0.414751
Thermal correction to Enthalpy= 0.415695
Thermal correction to Gibbs Free Energy= 0.332375
Sum of electronic and zero-point Energies= -1849.827807
Sum of electronic and thermal Energies= -1849.802383
Sum of electronic and thermal Enthalpies= -1849.801439
Sum of electronic and thermal Free Energies= -1849.884759
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.4834385
Coordinates

S	-7.16495	3.66918	-0.26204
O	-8.57803	3.32329	0.3578
C	-6.64476	2.03508	-0.98074
H	-6.3784	1.5036	-0.05111
C	-7.77312	1.29403	-1.67838
H	-8.00386	1.73929	-2.65531

H	-7.45763	0.25051	-1.84139
H	-8.68595	1.28352	-1.06649
C	-5.39367	2.21844	-1.83273
H	-4.94662	1.22818	-2.01574
H	-5.63281	2.67202	-2.80454
H	-4.63844	2.8455	-1.33506
C	-7.53468	4.76994	-1.74099
C	-8.52796	4.32844	-2.69504
C	-6.15416	5.44591	-3.49265
C	-8.29105	4.52265	-4.03562
H	-9.46717	3.88455	-2.35611
C	-7.07626	5.10865	-4.47455
H	-5.18372	5.8751	-3.77478
H	-9.04802	4.21395	-4.76312
H	-6.86358	5.27086	-5.53208
N	-6.33779	5.24478	-2.17919
Mg	-9.93135	4.69804	0.35527
Cl	-12.12549	4.677	-0.24595
C	-8.34367	6.40695	-0.5934
H	-9.27177	6.50394	0.02306
C	-7.18939	6.83954	0.28798
H	-7.22662	7.91929	0.53326
H	-7.15969	6.2902	1.2431
H	-6.23681	6.65669	-0.23864
C	-8.60069	7.31946	-1.77477
H	-9.42136	6.94139	-2.40652
H	-8.87261	8.34351	-1.45503
H	-7.70304	7.40724	-2.40584
O	-9.7917	5.32278	2.26814
C	-8.93582	4.72988	3.28863
C	-10.40703	6.54816	2.75683
C	-9.23578	5.52625	4.55153
H	-9.17949	3.6616	3.36206
H	-7.89	4.83987	2.96333
C	-9.60188	6.90698	3.99544
H	-10.35814	7.29872	1.95463
H	-11.46266	6.33522	2.98782
H	-8.37581	5.54616	5.23569
H	-10.09398	5.08881	5.08596
H	-8.69428	7.46342	3.71212
H	-10.18113	7.52114	4.69911

A6 = A6.4-E

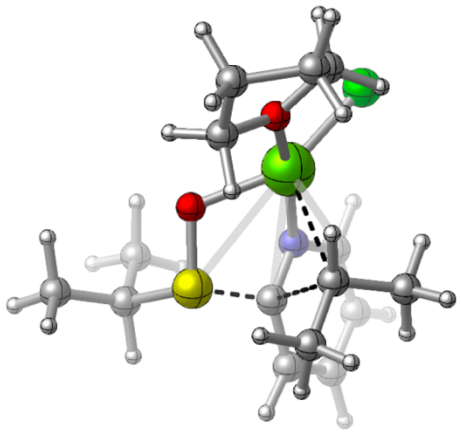


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.392638 (Hartree/Particle)
Thermal correction to Energy= 0.419009
Thermal correction to Enthalpy= 0.419953
Thermal correction to Gibbs Free Energy= 0.333576
Sum of electronic and zero-point Energies= -1849.935698
Sum of electronic and thermal Energies= -1849.909327
Sum of electronic and thermal Enthalpies= -1849.908383
Sum of electronic and thermal Free Energies= -1849.994760
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.590412
Coordinates

S	-6.90704	2.34605	0.99267
O	-8.50824	1.92164	1.14037
C	-6.44802	1.60663	-0.62938
H	-6.57526	0.5157	-0.5173
C	-7.34076	2.10903	-1.755
H	-7.22865	3.19528	-1.88181
H	-7.07709	1.62342	-2.70973
H	-8.40223	1.88282	-1.56386
C	-4.97411	1.92705	-0.86592
H	-4.61877	1.4241	-1.77991
H	-4.81963	3.01089	-0.9975
H	-4.34484	1.58715	-0.0273
C	-7.95082	6.00159	-1.8341
C	-9.2125	5.44503	-2.09191
C	-7.14448	5.20534	-3.84354
C	-9.42197	4.73597	-3.27577
H	-10.02612	5.56812	-1.37589
C	-8.36588	4.61334	-4.17898
H	-6.29075	5.12621	-4.52711
H	-10.39471	4.28141	-3.47659
H	-8.47733	4.06822	-5.11845

N	-6.93824	5.87533	-2.70696
Mg	-9.83285	3.11548	0.52687
Cl	-11.77236	3.13718	-0.65402
C	-7.68201	6.8024	-0.57282
H	-8.54552	6.65252	0.09368
C	-6.42048	6.31559	0.14795
H	-6.25746	6.89059	1.07384
H	-6.49401	5.24824	0.41037
H	-5.53625	6.44419	-0.49514
C	-7.59287	8.29822	-0.90857
H	-8.52013	8.66135	-1.38029
H	-7.41532	8.89383	0.00174
H	-6.76209	8.48405	-1.60839
O	-9.80548	4.72508	1.72312
C	-8.84808	4.8937	2.81634
C	-10.78091	5.81118	1.72138
C	-9.4508	5.98609	3.68625
H	-8.73381	3.92446	3.3185
H	-7.88491	5.18942	2.37684
C	-10.1941	6.8511	2.66281
H	-10.90694	6.16026	0.68828
H	-11.7396	5.40974	2.08423
H	-8.67847	6.53629	4.24194
H	-10.1589	5.55381	4.41098
H	-9.48799	7.50127	2.12223
H	-10.97405	7.48334	3.10981

A6 = A6.4-TS-C-D, A6.6-TS-C-D; Thesis = TS-C-D



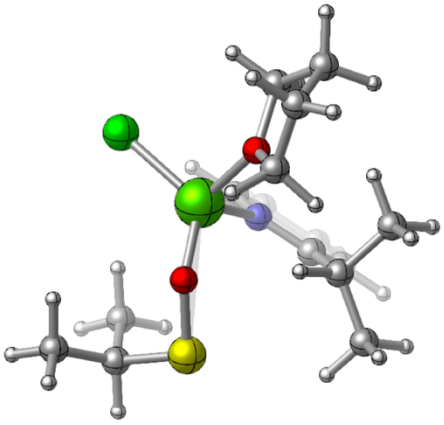
B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388356 (Hartree/Particle)
Thermal correction to Energy= 0.413990
Thermal correction to Enthalpy= 0.414935
Thermal correction to Gibbs Free Energy= 0.331290
Sum of electronic and zero-point Energies= -1849.848221
Sum of electronic and thermal Energies= -1849.822587
Sum of electronic and thermal Enthalpies= -1849.821643
Sum of electronic and thermal Free Energies= -1849.905288

B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5038307
Coordinates

S	-7.24684	4.9184	-2.04533
O	-7.30488	5.80899	-3.33349
C	-5.41854	4.73647	-1.74568
H	-5.40047	4.25141	-0.75408
C	-4.89059	3.77635	-2.80791
H	-4.95067	4.22955	-3.80943
H	-3.83373	3.54403	-2.60099
H	-5.45021	2.82762	-2.81942
C	-4.68306	6.06606	-1.71214
H	-3.60166	5.87372	-1.6196
H	-4.84977	6.63006	-2.64197
H	-4.9918	6.69104	-0.86394
C	-7.74963	6.08345	-0.74225
C	-7.73014	5.63903	0.60434
C	-7.50554	8.30161	-0.08928
C	-7.63795	6.60464	1.59927
H	-7.77702	4.57601	0.84602
C	-7.51921	7.9652	1.26642
H	-7.44419	9.34228	-0.42181
H	-7.6364	6.29543	2.64829
H	-7.4442	8.73826	2.03149
N	-7.57624	7.39046	-1.05956
Mg	-8.54615	7.36632	-3.01667
Cl	-8.95065	9.6473	-3.15985
C	-10.01714	5.80173	-1.6201
H	-10.39474	6.02147	-2.64126
C	-10.27983	4.34459	-1.31388
H	-11.35689	4.12469	-1.14438
H	-9.9397	3.67305	-2.11941
H	-9.7638	4.02576	-0.38658
C	-10.66192	6.74283	-0.62349
H	-10.49432	7.80496	-0.87424
H	-11.76278	6.60653	-0.5481
H	-10.26276	6.57993	0.39362
O	-9.544	6.89107	-4.78062
C	-9.47294	5.58415	-5.41204
C	-10.63847	7.66799	-5.34058
C	-10.35557	5.70155	-6.64577
H	-8.4197	5.36231	-5.62036
H	-9.85778	4.83311	-4.70257
C	-11.43903	6.67407	-6.1708
H	-11.20269	8.12013	-4.51468
H	-10.20766	8.47505	-5.953
H	-10.74993	4.72621	-6.96526
H	-9.78764	6.13702	-7.4839
H	-12.17235	6.14952	-5.53694

H -11.98071 7.16538 -6.99166 s

A6 = A6.4-D, A6.6-D; Thesis =D



s

B3LYP-D3BJ/def2-SVP-CPCM(THF)

Zero-point correction= 0.393219 (Hartree/Particle)

Thermal correction to Energy= 0.419336

Thermal correction to Enthalpy= 0.420280

Thermal correction to Gibbs Free Energy= 0.334183

Sum of electronic and zero-point Energies= -1849.968850

Sum of electronic and thermal Energies= -1849.942733

Sum of electronic and thermal Enthalpies= -1849.941789

Sum of electronic and thermal Free Energies= -1850.027886

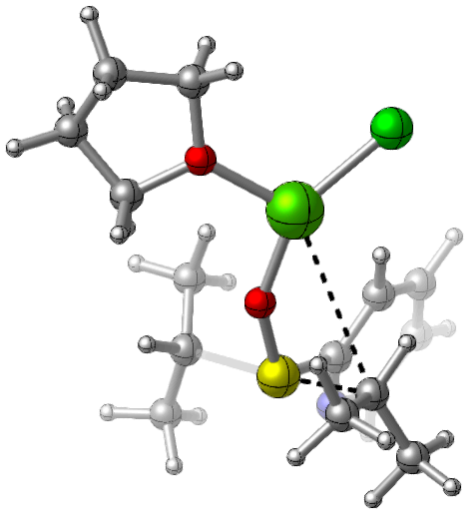
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)

HF= -1851.6215114

Coordinates

S	-6.58149	3.74976	-2.46282
O	-7.1463	4.8101	-3.59958
C	-4.87517	4.34593	-2.11642
H	-4.51399	3.56782	-1.41836
C	-4.01737	4.34268	-3.37932
H	-4.43118	5.04283	-4.12244
H	-2.98422	4.65995	-3.15541
H	-3.98398	3.341	-3.83481
C	-4.8478	5.70194	-1.41203
H	-3.81891	5.95992	-1.1071
H	-5.18675	6.5072	-2.08363
H	-5.48501	5.70337	-0.51532
C	-9.02136	6.30263	-0.58253
C	-9.19613	6.56815	0.78227
C	-7.58454	8.13525	-0.76685
C	-8.54138	7.6488	1.36877
H	-9.84576	5.92699	1.37824
C	-7.71985	8.45612	0.57845
H	-6.94918	8.7229	-1.43516
H	-8.67203	7.86033	2.43286
H	-7.18935	9.31494	0.99244
N	-8.21274	7.08516	-1.33083
Mg	-7.65567	6.61825	-3.35427
Cl	-6.41286	8.42194	-4.08815
C	-9.76767	5.18326	-1.28014
H	-9.21883	4.96529	-2.20857
C	-9.80739	3.88769	-0.46443
H	-10.25411	3.0825	-1.06875
H	-8.79261	3.57276	-0.18079
H	-10.41755	3.99081	0.4474
C	-11.18275	5.65581	-1.65236
H	-11.15584	6.57399	-2.2568
H	-11.70732	4.87851	-2.23014
H	-11.77663	5.86381	-0.74718
O	-9.39467	6.75602	-4.37672
C	-9.98095	5.68761	-5.16935
C	-10.11329	8.00303	-4.57081
C	-10.9507	6.39424	-6.10699
H	-9.16831	5.15154	-5.67666
H	-10.49339	4.9949	-4.48386
C	-11.40273	7.59662	-5.26971
H	-10.25912	8.46938	-3.58572
H	-9.49084	8.66673	-5.19098
H	-11.77904	5.73924	-6.41207
H	-10.42572	6.73479	-7.01371
H	-12.15971	7.28838	-4.53107
H	-11.81973	8.41592	-5.8721

A6 = A6.5-TS-B-G-eq



B3LYP-D3BJ/def2-SVP-CPCM(THF)

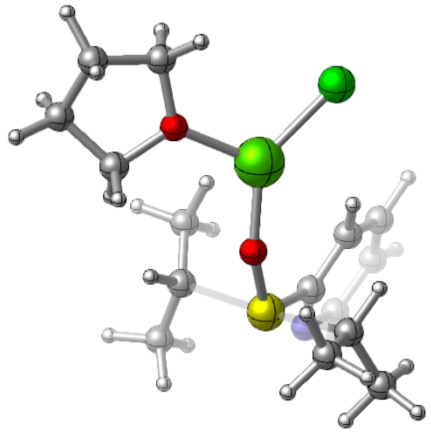
Zero-point correction= 0.388196 (Hartree/Particle)

Thermal correction to Energy= 0.414035

Thermal correction to Enthalpy= 0.414979
Thermal correction to Gibbs Free Energy= 0.329919
Sum of electronic and zero-point Energies= -1849.820311
Sum of electronic and thermal Energies= -1849.794473
Sum of electronic and thermal Enthalpies= -1849.793528
Sum of electronic and thermal Free Energies= -1849.878588
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.4786579
Coordinates

S	-6.17968	3.6695	0.30392
O	-7.39885	3.52276	1.35781
C	-6.81559	1.82707	-0.44905
H	-6.80865	1.28601	0.51166
C	-8.2061	1.79686	-1.05227
H	-8.24616	2.346	-2.00919
H	-8.54971	0.76478	-1.26828
H	-8.95402	2.24974	-0.37944
C	-5.73547	1.27107	-1.35741
H	-5.80657	0.17073	-1.4627
H	-5.78761	1.70384	-2.36832
H	-4.72833	1.49714	-0.96146
C	-6.68683	4.47859	-1.23937
C	-7.82342	5.29141	-1.27885
C	-6.23693	4.82542	-3.45589
C	-8.15798	5.89016	-2.49389
H	-8.42476	5.47872	-0.38962
C	-7.34911	5.65769	-3.60862
H	-5.57668	4.62064	-4.30594
H	-9.03647	6.53642	-2.56352
H	-7.57027	6.11217	-4.57641
N	-5.91318	4.24419	-2.29516
Mg	-8.95704	4.2847	2.01983
Cl	-10.39313	6.03398	1.89317
C	-5.71609	5.5093	1.16209
H	-6.6043	6.16284	1.21595
C	-5.20122	5.17506	2.55182
H	-4.67195	6.02529	3.02411
H	-6.0113	4.86912	3.23264
H	-4.47764	4.33707	2.50936
C	-4.63965	6.10579	0.27346
H	-5.05349	6.57245	-0.63423
H	-4.03438	6.87306	0.79236
H	-3.93711	5.31629	-0.06214
O	-9.77918	2.75008	2.99042
C	-9.17886	1.41597	3.02143
C	-11.08012	2.74711	3.65555
C	-10.3252	0.50072	3.41767
H	-8.74858	1.21736	2.03223
H	-8.37156	1.42522	3.77037
C	-11.15142	1.39452	4.34924
H	-11.11881	3.60703	4.33782
H	-11.85584	2.86352	2.883
H	-9.96611	-0.41827	3.90193
H	-10.9139	0.21859	2.53002
H	-10.68267	1.4491	5.34469
H	-12.1891	1.05448	4.47381

A6 = A6.5-G-eq

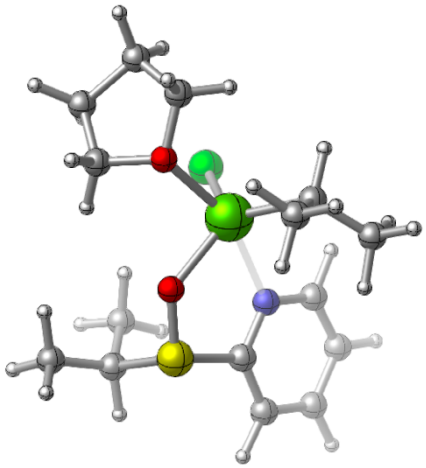


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389003 (Hartree/Particle)
Thermal correction to Energy= 0.415333
Thermal correction to Enthalpy= 0.416277
Thermal correction to Gibbs Free Energy= 0.329796
Sum of electronic and zero-point Energies= -1849.819806
Sum of electronic and thermal Energies= -1849.793476
Sum of electronic and thermal Enthalpies= -1849.792532
Sum of electronic and thermal Free Energies= -1849.879013
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.4787863
Coordinates

S	-6.14356	3.79827	0.36125
O	-7.31129	3.80535	1.48178
C	-6.99063	1.96261	-0.32075
H	-7.08421	1.48313	0.66698
C	-8.33967	2.02829	-1.00916
H	-8.25452	2.45348	-2.02385
H	-8.80895	1.02971	-1.12579
H	-9.07616	2.65296	-0.46962
C	-5.92355	1.25898	-1.13551

H	-6.12333	0.17494	-1.2518
H	-5.83587	1.68909	-2.14591
H	-4.93189	1.35746	-0.65692
C	-6.68081	4.57318	-1.18569
C	-7.76319	5.45876	-1.19231
C	-6.37536	4.76379	-3.44459
C	-8.15167	6.00468	-2.41656
H	-8.28302	5.73198	-0.27324
C	-7.44507	5.65509	-3.56957
H	-5.79327	4.46951	-4.32501
H	-8.99332	6.70015	-2.46479
H	-7.71139	6.06408	-4.54621
N	-6.00193	4.22967	-2.27673
Mg	-9.08525	4.14441	1.89882
Cl	-10.55414	5.86191	1.76961
C	-5.48302	5.58643	1.10482
H	-6.31754	6.30408	1.16285
C	-4.93628	5.27775	2.48828
H	-4.3522	6.12022	2.90548
H	-5.74069	5.03859	3.19989
H	-4.25479	4.40522	2.45395
C	-4.40335	6.05722	0.14532
H	-4.81942	6.50084	-0.77279
H	-3.73432	6.81024	0.60158
H	-3.76551	5.20639	-0.16685
O	-9.85711	2.58331	2.86008
C	-9.14989	1.3186	3.06523
C	-11.20348	2.52124	3.42756
C	-10.22804	0.35347	3.53294
H	-8.67129	1.03928	2.11788
H	-8.37441	1.48641	3.82842
C	-11.18954	1.27254	4.29448
H	-11.38557	3.45453	3.97657
H	-11.91932	2.44501	2.59428
H	-9.81189	-0.45172	4.15447
H	-10.73491	-0.10285	2.66786
H	-10.79029	1.50549	5.2945
H	-12.19605	0.84749	4.41337

A6 = A6.5-C', A6.6-C'

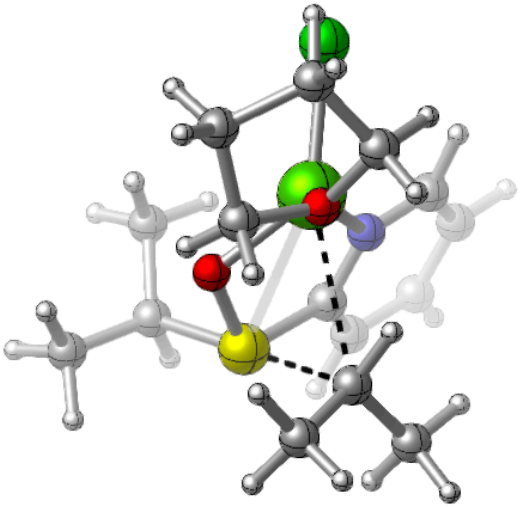


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389853 (Hartree/Particle)
Thermal correction to Energy= 0.416091
Thermal correction to Enthalpy= 0.417035
Thermal correction to Gibbs Free Energy= 0.331464
Sum of electronic and zero-point Energies= -1849.878702
Sum of electronic and thermal Energies= -1849.852464
Sum of electronic and thermal Enthalpies= -1849.851520
Sum of electronic and thermal Free Energies= -1849.937090
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5371276
Coordinates

S	-7.11999	4.39896	-1.30129
O	-8.1507	4.78275	-2.38564
C	-5.45169	4.61322	-2.11271
H	-4.75931	4.37037	-1.28822
C	-5.37474	3.55109	-3.20383
H	-6.0947	3.76381	-4.00855
H	-4.36387	3.55957	-3.63971
H	-5.56935	2.53991	-2.81364
C	-5.23801	6.0287	-2.62176
H	-4.30213	6.05459	-3.20217
H	-6.0553	6.3583	-3.28046
H	-5.1462	6.7561	-1.80347
C	-7.09178	5.85721	-0.21107
C	-6.34009	5.87579	0.96056
C	-7.85919	7.99375	0.06527
C	-6.36445	7.05829	1.70364
H	-5.75642	5.00958	1.2789
C	-7.12996	8.13474	1.24608
H	-8.47241	8.80538	-0.33148
H	-5.79169	7.13659	2.63029
H	-7.16838	9.07415	1.7998
N	-7.84017	6.85897	-0.64693
Mg	-9.19666	6.55339	-2.51236
Cl	-8.12318	8.39308	-3.57364
C	-11.13575	6.60783	-1.51476
H	-11.80598	7.29639	-2.07356
C	-11.74684	5.20413	-1.61331
H	-12.76176	5.11934	-1.15743
H	-11.83827	4.85678	-2.65753
H	-11.12255	4.45098	-1.09318
C	-11.13527	7.06975	-0.05532
H	-10.79715	8.11536	0.05658
H	-12.13542	7.00881	0.43521
H	-10.45828	6.45683	0.57096

O	-9.86404	5.75442	-4.39233
C	-8.96068	5.24094	-5.38136
C	-10.8992	6.43828	-5.11339
C	-8.87054	6.33557	-6.45072
H	-8.01321	5.01076	-4.87986
H	-9.38325	4.30535	-5.79057
C	-10.19016	7.13073	-6.28551
H	-11.6329	5.69182	-5.46671
H	-11.39908	7.12283	-4.41669
H	-8.75358	5.90356	-7.45528
H	-8.01181	6.98806	-6.24487
H	-10.81437	7.11402	-7.19071
H	-9.97142	8.17596	-6.03078

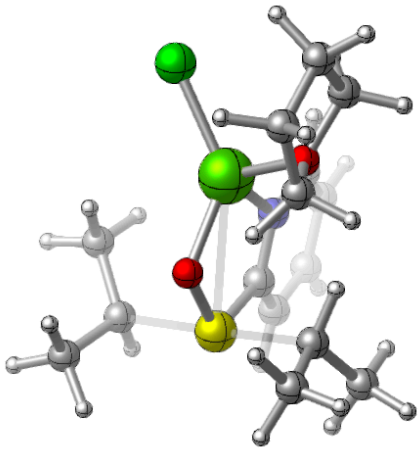
A6 = A6.5-TS-C'-Feq', A6.6-TS-C'-Feq'



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389512 (Hartree/Particle)
Thermal correction to Energy= 0.414710
Thermal correction to Enthalpy= 0.415654
Thermal correction to Gibbs Free Energy= 0.333654
Sum of electronic and zero-point Energies= -1849.849217
Sum of electronic and thermal Energies= -1849.824020
Sum of electronic and thermal Enthalpies= -1849.823076
Sum of electronic and thermal Free Energies= -1849.905075
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5071663
Coordinates

S	-7.76465	4.90547	-1.4324
O	-7.76358	5.32605	-2.98202
C	-5.79771	4.56929	-1.48747
H	-5.56646	4.39918	-0.42011
C	-5.63851	3.26574	-2.25357
H	-5.85898	3.41167	-3.32276
H	-4.6095	2.87211	-2.17088
H	-6.3214	2.48681	-1.87118
C	-4.95206	5.69909	-2.04659
H	-3.8785	5.43154	-2.0431
H	-5.23815	5.91809	-3.08672
H	-5.05637	6.6299	-1.46688
C	-7.52585	6.43013	-0.48332
C	-7.03191	6.46752	0.81784
C	-7.79388	8.7271	-0.56197
C	-6.94904	7.71314	1.44487
H	-6.72844	5.55227	1.32662
C	-7.33291	8.86188	0.74536
H	-8.0848	9.5908	-1.16496
H	-6.58434	7.78635	2.47207
H	-7.27187	9.85052	1.20284
N	-7.89792	7.52507	-1.15308
Mg	-8.56265	7.09431	-3.17214
Cl	-7.79835	8.97451	-4.27581
C	-9.97152	5.29963	-1.33988
H	-10.396	6.19754	-1.82974
C	-10.49759	4.04604	-2.009
H	-11.57721	3.86767	-1.82481
H	-10.34746	4.06508	-3.09876
H	-9.96631	3.15085	-1.62742
C	-10.24753	5.33343	0.14745
H	-10.07826	6.33061	0.58616
H	-11.28149	5.03158	0.41226
H	-9.5765	4.62799	0.68354
O	-10.16476	6.69103	-4.39365
C	-10.05724	5.63485	-5.37469
C	-10.9687	7.72427	-5.00368
C	-9.85552	6.37255	-6.69852
H	-9.22797	4.98391	-5.07202
H	-10.99675	5.05755	-5.36219
C	-10.55062	7.74147	-6.47989
H	-12.0283	7.44769	-4.87556
H	-10.76805	8.66276	-4.47187
H	-10.2813	5.80622	-7.53875
H	-8.78226	6.51319	-6.89103
H	-11.42517	7.87811	-7.13158
H	-9.84753	8.56424	-6.66451

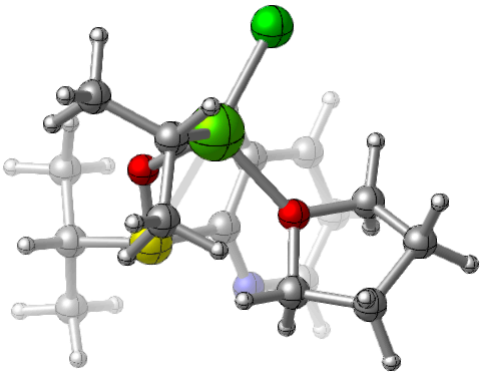
A6 = A6.5-F-eq', A6.6-F-eq



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389380 (Hartree/Particle)
Thermal correction to Energy= 0.415654
Thermal correction to Enthalpy= 0.416598
Thermal correction to Gibbs Free Energy= 0.330478
Sum of electronic and zero-point Energies= -1849.851800
Sum of electronic and thermal Energies= -1849.825525
Sum of electronic and thermal Enthalpies= -1849.824581
Sum of electronic and thermal Free Energies= -1849.910702
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.510052
Coordinates

S	-7.79289	4.75705	-1.40733
O	-7.7463	5.01468	-2.99924
C	-5.68252	4.73286	-1.38251
H	-5.4974	4.68833	-0.29247
C	-5.33771	3.40039	-2.02009
H	-5.50254	3.43278	-3.1095
H	-4.28138	3.11299	-1.85225
H	-5.96417	2.58503	-1.61387
C	-4.9445	5.90181	-2.00304
H	-3.84401	5.77934	-1.94014
H	-5.18571	6.00171	-3.0746
H	-5.18323	6.86246	-1.5182
C	-7.69854	6.37172	-0.60992
C	-7.40348	6.5404	0.74357
C	-7.84464	8.66074	-0.9548
C	-7.35047	7.83956	1.24484
H	-7.22934	5.67477	1.38308
C	-7.5801	8.92122	0.3839
H	-8.00588	9.46754	-1.6743
H	-7.13456	8.01072	2.30206
H	-7.5455	9.9504	0.74395
N	-7.90517	7.40504	-1.43897
Mg	-7.97961	6.86855	-3.51627
Cl	-6.81523	8.31084	-4.85782
C	-9.87014	4.82698	-1.45679
H	-10.23154	5.68425	-2.0458
C	-10.25233	3.50939	-2.10628
H	-11.34005	3.3091	-2.05783
H	-9.94679	3.46901	-3.16217
H	-9.75176	2.66553	-1.59195
C	-10.32131	4.91182	-0.01119
H	-10.25052	5.93394	0.39411
H	-11.36584	4.57454	0.1296
H	-9.6929	4.26034	0.63068
O	-9.86971	7.01939	-4.24701
C	-10.50062	5.92735	-4.95475
C	-10.42271	8.23589	-4.79872
C	-10.55682	6.4059	-6.40506
H	-9.89579	5.02814	-4.78791
H	-11.50423	5.77255	-4.52523
C	-10.59816	7.95253	-6.29632
H	-11.38518	8.42692	-4.29664
H	-9.7234	9.05131	-4.57534
H	-11.43024	5.99109	-6.92742
H	-9.65384	6.08238	-6.94265
H	-11.5447	8.37374	-6.66305
H	-9.77846	8.40375	-6.87186

A6 = A6.7-B’

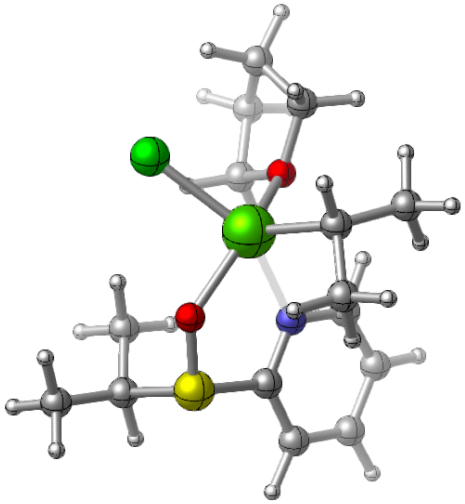


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389768 (Hartree/Particle)
Thermal correction to Energy= 0.416405
Thermal correction to Enthalpy= 0.417350
Thermal correction to Gibbs Free Energy= 0.329196

Sum of electronic and zero-point Energies= -1849.871916
Sum of electronic and thermal Energies= -1849.845279
Sum of electronic and thermal Enthalpies= -1849.844335
Sum of electronic and thermal Free Energies= -1849.932488
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5310558
Coordinates

S	-6.44532	4.13506	-0.61191
O	-7.04437	3.50629	0.6787
C	-5.52908	2.71344	-1.38711
H	-4.75018	2.56295	-0.62067
C	-6.4032	1.47762	-1.49417
H	-7.15973	1.58549	-2.28632
H	-5.7668	0.61478	-1.74774
H	-6.90789	1.26079	-0.54186
C	-4.89581	3.16945	-2.69408
H	-4.2098	2.3823	-3.04447
H	-5.65255	3.33435	-3.47491
H	-4.31399	4.09588	-2.57078
C	-7.8409	4.31367	-1.75886
C	-9.06401	3.69914	-1.50297
C	-8.56346	5.33442	-3.66115
C	-10.08781	3.94492	-2.42086
H	-9.22266	3.09185	-0.61168
C	-9.83524	4.77031	-3.51924
H	-8.33371	5.99204	-4.50549
H	-11.07391	3.49968	-2.27031
H	-10.61377	4.98584	-4.25352
N	-7.57788	5.11548	-2.78253
Mg	-8.20282	4.4721	2.02736
C	-7.18333	4.88189	3.87942
H	-7.92633	5.24648	4.61992
C	-6.61366	3.56331	4.42172
H	-6.08321	3.67459	5.39571
H	-7.39703	2.7987	4.57496
H	-5.8758	3.11824	3.72652
C	-6.07484	5.93658	3.78902
H	-6.46468	6.93526	3.52187
H	-5.50785	6.06586	4.74004
H	-5.31765	5.67717	3.02333
Cl	-10.3301	3.51663	1.8699
O	-8.41868	6.12623	0.75054
C	-9.66068	6.63667	0.22083
C	-7.45629	7.18511	0.56961
C	-9.71105	8.08461	0.71271
H	-9.61285	6.58062	-0.87961
H	-10.46554	5.98684	0.58331
C	-8.22067	8.46784	0.91427
H	-6.59632	6.97685	1.2168
H	-7.12878	7.17394	-0.48404
H	-10.25817	8.14497	1.66449
H	-10.222	8.73229	-0.01364
H	-8.03178	8.76105	1.95672
H	-7.90429	9.29789	0.26699

A6 = A6.7-C''

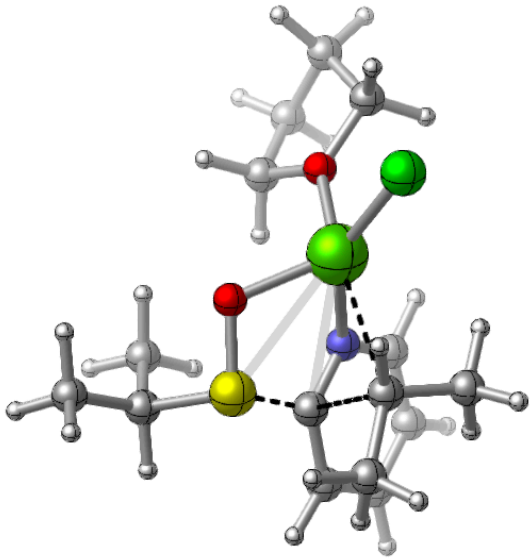


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389789 (Hartree/Particle)
Thermal correction to Energy= 0.415906
Thermal correction to Enthalpy= 0.416850
Thermal correction to Gibbs Free Energy= 0.331300
Sum of electronic and zero-point Energies= -1849.875468
Sum of electronic and thermal Energies= -1849.849351
Sum of electronic and thermal Enthalpies= -1849.848407
Sum of electronic and thermal Free Energies= -1849.933957
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5351448
Coordinates

S	-6.83209	4.64781	-1.67873
O	-7.87492	5.0679	-2.72907
C	-5.1917	5.23726	-2.3544
H	-4.51896	5.13547	-1.48589
C	-4.80616	4.25585	-3.45557
H	-5.52737	4.29822	-4.28632
H	-3.81604	4.52962	-3.8521
H	-4.75161	3.22048	-3.08517
C	-5.28321	6.67629	-2.83261
H	-4.31176	6.96636	-3.26326

H	-6.04749	6.78235	-3.61798
H	-5.50953	7.37517	-2.01545
C	-7.05521	5.87175	-0.35108
C	-6.44509	5.70581	0.88857
C	-8.13668	7.78899	0.27924
C	-6.7108	6.67101	1.86262
H	-5.79333	4.8535	1.08951
C	-7.57224	7.72642	1.55332
H	-8.81348	8.59283	-0.0146
H	-6.25837	6.59215	2.85351
H	-7.81231	8.49386	2.29079
N	-7.87562	6.86906	-0.66261
Mg	-9.0554	6.7851	-2.67002
C	-10.9801	6.14744	-1.86973
H	-11.68827	6.0025	-2.71382
C	-10.79446	4.78314	-1.19472
H	-11.72834	4.37507	-0.74098
H	-10.41805	4.01651	-1.89406
H	-10.06076	4.83101	-0.36463
C	-11.63424	7.12249	-0.88717
H	-11.88381	8.09229	-1.35111
H	-12.5799	6.73793	-0.43675
H	-10.97171	7.34893	-0.02908
O	-8.991	8.93688	-2.36913
C	-7.74716	9.63406	-2.62409
C	-10.10227	9.67597	-2.9347
C	-8.15379	11.01537	-3.12342
H	-7.16138	9.65157	-1.69331
H	-7.19513	9.07646	-3.39596
C	-9.46749	10.71192	-3.85093
H	-10.75794	8.96747	-3.45821
H	-10.66193	10.14331	-2.10732
H	-7.38585	11.46076	-3.7724
H	-8.32896	11.69846	-2.27603
H	-9.26226	10.25598	-4.8311
H	-10.10785	11.59466	-3.99136
Cl	-8.6829	7.22065	-4.99076

A6 = A6.7-TS-C''-D''

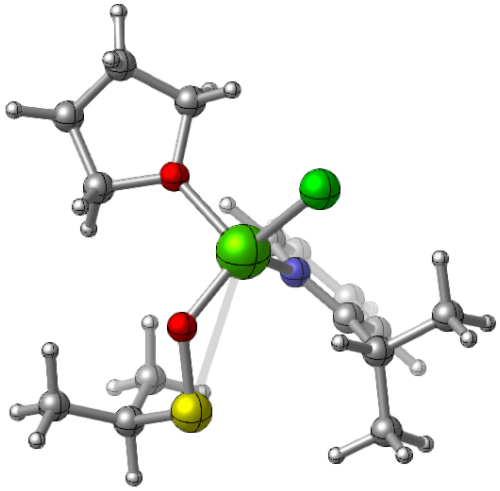


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388528 (Hartree/Particle)
Thermal correction to Energy= 0.414021
Thermal correction to Enthalpy= 0.414965
Thermal correction to Gibbs Free Energy= 0.332640
Sum of electronic and zero-point Energies= -1849.847380
Sum of electronic and thermal Energies= -1849.821887
Sum of electronic and thermal Enthalpies= -1849.820943
Sum of electronic and thermal Free Energies= -1849.903268
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5035443
Coordinates

S	-7.57698	5.19436	-2.08911
O	-8.03164	6.09315	-3.29871
C	-5.7073	5.36005	-2.2573
H	-5.35541	4.86814	-1.33318
C	-5.29819	4.53445	-3.47176
H	-5.67376	4.9913	-4.40034
H	-4.19911	4.48142	-3.53696
H	-5.68165	3.50295	-3.41347
C	-5.23014	6.80021	-2.31372
H	-4.13126	6.81964	-2.40704
H	-5.65408	7.31513	-3.18695
H	-5.49959	7.36215	-1.40782
C	-7.90148	6.21052	-0.64375
C	-7.47793	5.78826	0.63106

C	-8.40144	8.33755	0.13023
C	-7.57258	6.7037	1.67773
H	-7.07082	4.78884	0.78681
C	-8.02763	8.00691	1.43662
H	-8.78188	9.33361	-0.11671
H	-7.26347	6.40653	2.68328
H	-8.0992	8.74526	2.23565
N	-8.32722	7.46907	-0.88025
Mg	-9.48833	7.30992	-2.72815
C	-10.21508	5.1065	-1.23419
H	-10.74757	5.02565	-2.19927
C	-9.93397	3.73462	-0.66987
H	-10.83687	3.2365	-0.24907
H	-9.51595	3.04599	-1.42332
H	-9.20723	3.77271	0.16903
C	-10.97738	5.98532	-0.26318
H	-11.19078	6.99795	-0.65435
H	-11.96937	5.56766	0.02426
H	-10.41876	6.11833	0.6815
O	-8.87994	9.19596	-3.30305
C	-7.49349	9.62282	-3.30555
C	-9.75656	10.30187	-3.66049
C	-7.556	11.14286	-3.32631
H	-7.00495	9.20161	-2.41897
H	-7.00821	9.21811	-4.20868
C	-8.82103	11.39759	-4.15204
H	-10.47426	9.93954	-4.40617
H	-10.30927	10.60496	-2.75588
H	-6.64983	11.58824	-3.76113
H	-7.67782	11.53451	-2.3031
H	-8.61004	11.26735	-5.22572
H	-9.24773	12.39985	-4.00378
Cl	-11.53177	7.37448	-3.7949

A6 = A6.7-D''

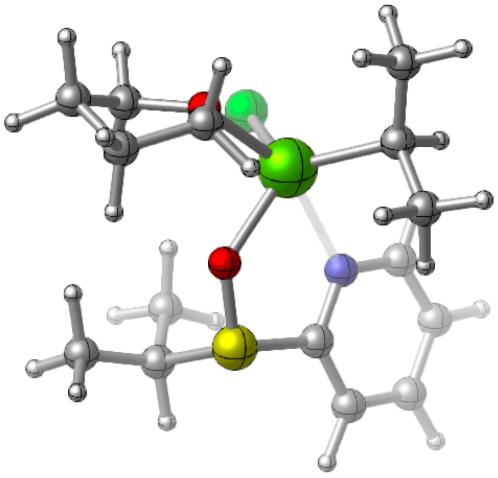


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.392820
(Hartree/Particle)
Thermal correction to Energy= 0.419096
Thermal correction to Enthalpy=
0.420040
Thermal correction to Gibbs Free Energy=
0.333300
Sum of electronic and zero-point Energies= -
1849.966061
Sum of electronic and thermal Energies= -
1849.939785
Sum of electronic and thermal Enthalpies= -
1849.938841
Sum of electronic and thermal Free Energies= -
1850.025581
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.6185104
Coordinates

S	-7.41922	4.76254	-3.2286
O	-8.10384	6.17616	-3.74669
C	-5.69012	5.26998	-2.86213
H	-5.2321	4.30959	-2.56108
C	-4.9968	5.79936	-4.11566
H	-5.52586	6.6886	-4.49268
H	-3.95269	6.08649	-3.90133
H	-4.99274	5.04349	-4.91596
C	-5.60635	6.25788	-1.70083
H	-4.55613	6.51268	-1.47627
H	-6.12743	7.19365	-1.95415
H	-6.06636	5.84896	-0.78911
C	-9.21456	6.20457	0.12006
C	-8.85341	6.16486	1.47468
C	-8.12362	8.25297	-0.12075
C	-8.10845	7.20388	2.02554
H	-9.16001	5.31873	2.09039
C	-7.73395	8.27672	1.21194
H	-7.84889	9.06072	-0.80257
H	-7.82225	7.17858	3.07967
H	-7.15023	9.11366	1.5981
N	-8.84126	7.2456	-0.6536
Mg	-9.24027	7.32684	-2.76288
C	-10.06204	5.11358	-0.5034
H	-10.00539	5.24043	-1.59598
C	-9.53776	3.70883	-0.18854
H	-10.13221	2.95988	-0.73506
H	-8.4898	3.60443	-0.50523
H	-9.61397	3.47272	0.8849
C	-11.53242	5.28088	-0.09087
H	-11.91448	6.27104	-0.37906
H	-12.15331	4.5205	-0.59066
H	-11.65286	5.15866	0.9981
O	-8.47119	9.17043	-3.1845
C	-7.28341	9.35695	-4.00899
C	-9.21852	10.41453	-3.0726
C	-7.18785	10.86283	-4.21708

H	-6.42564	8.92126	-3.47993
H	-7.43472	8.81077	-4.95177
C	-8.65753	11.29585	-4.17709
H	-10.2845	10.1726	-3.17292
H	-9.03431	10.83922	-2.07144
H	-6.68292	11.11394	-5.16063
H	-6.62851	11.33105	-3.39102
H	-9.15361	11.06763	-5.13412
H	-8.79297	12.3653	-3.96176
Cl	-11.50849	7.61428	-3.08455

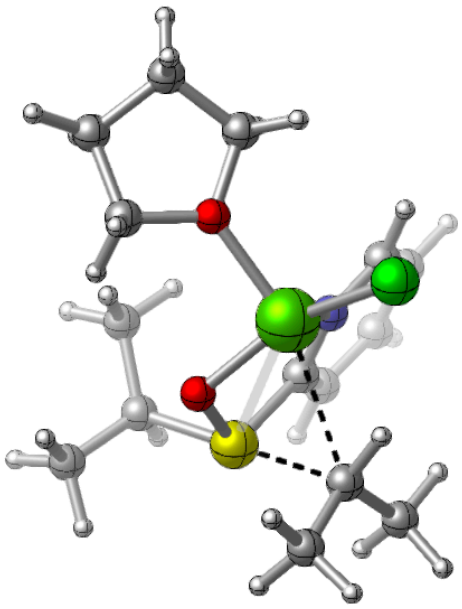
A6 = A6.7-C’’’



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389229 (Hartree/Particle)
Thermal correction to Energy= 0.415641
Thermal correction to Enthalpy= 0.416585
Thermal correction to Gibbs Free Energy= 0.329592
Sum of electronic and zero-point Energies= -1849.879439
Sum of electronic and thermal Energies= -1849.853027
Sum of electronic and thermal Enthalpies= -1849.852083
Sum of electronic and thermal Free Energies= -1849.939076
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5383123
Coordinates

S	-6.17139	5.5957	-1.2581
O	-6.98102	6.29828	-2.37081
C	-4.58946	6.57691	-1.10448
H	-4.04835	6.01883	-0.321
C	-3.88085	6.434	-2.44709
H	-4.43998	6.95524	-3.23854
H	-2.88227	6.89163	-2.37442
H	-3.75223	5.38014	-2.74009
C	-4.83051	8.01962	-0.69311
H	-3.87307	8.56205	-0.74719
H	-5.54694	8.52799	-1.35604
H	-5.20314	8.10107	0.33747
C	-7.00381	6.13483	0.26901
C	-6.65439	5.61559	1.51247
C	-8.62901	7.49802	1.12427
C	-7.35263	6.10738	2.61781
H	-5.87157	4.86171	1.61698
C	-8.352	7.06491	2.42139
H	-9.40581	8.23846	0.91992
H	-7.12119	5.74216	3.6208
H	-8.91809	7.469	3.26218
N	-7.95751	7.0302	0.06396
Mg	-8.55319	7.62647	-2.11416
C	-10.5564	6.8211	-1.86157
H	-10.91712	7.26046	-0.9052
C	-11.56931	7.20766	-2.94174
H	-12.60141	6.82714	-2.75295
H	-11.65403	8.30333	-3.06085
H	-11.28503	6.81115	-3.93435
C	-10.52786	5.30126	-1.66961
H	-9.86731	4.99575	-0.83701
H	-11.52613	4.84833	-1.45999
H	-10.14954	4.77919	-2.57069
O	-8.3527	7.76624	-4.23723
C	-7.21014	8.45969	-4.795
C	-8.64674	6.5828	-5.01298
C	-6.93576	7.77697	-6.13058
H	-7.45597	9.52722	-4.87287
H	-6.36262	8.34625	-4.10114
C	-7.4048	6.34361	-5.8599
H	-8.87988	5.76193	-4.32187
H	-9.53278	6.7835	-5.63888
H	-5.87701	7.84644	-6.4201
H	-7.54173	8.23327	-6.9302
H	-6.65	5.79592	-5.27407
H	-7.62458	5.77201	-6.77328
Cl	-7.96566	9.8809	-1.73032

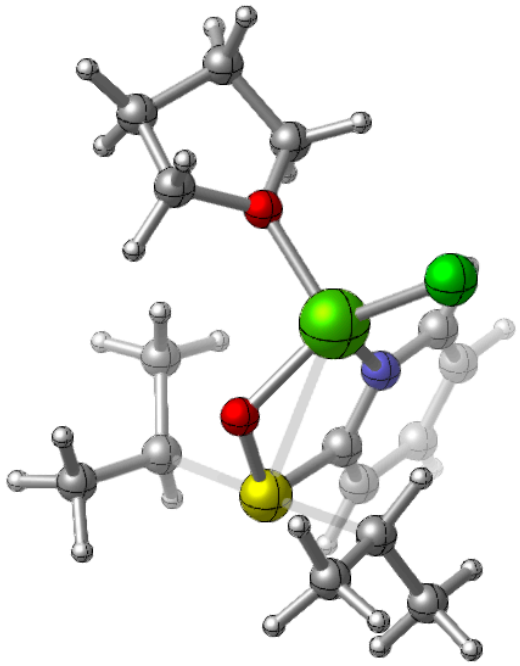
A6 = A6.7-TS-C’’’-F-eq’’’; Thesis = TS-C’-E



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389214 (Hartree/Particle)
Thermal correction to Energy= 0.414513
Thermal correction to Enthalpy= 0.415457
Thermal correction to Gibbs Free Energy= 0.332665
Sum of electronic and zero-point Energies= -1849.853257
Sum of electronic and thermal Energies= -1849.827959
Sum of electronic and thermal Enthalpies= -1849.827015
Sum of electronic and thermal Free Energies= -1849.909807
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.510617
Coordinates

S	-7.75401	5.16676	-1.49261
O	-7.89431	5.77889	-2.96786
C	-5.76852	5.13126	-1.6441
H	-5.47535	4.83095	-0.6216
C	-5.45592	4.00013	-2.61056
H	-5.72667	4.27862	-3.64104
H	-4.38071	3.74667	-2.59879
H	-6.0139	3.08316	-2.3522
C	-5.10603	6.44327	-2.02431
H	-4.00843	6.32689	-2.09841
H	-5.4707	6.79183	-3.00159
H	-5.29899	7.24123	-1.2902
C	-7.69192	6.57714	-0.35164
C	-7.16217	6.51108	0.93447
C	-8.31418	8.79117	-0.09441
C	-7.24005	7.65747	1.72944
H	-6.7102	5.59141	1.30678
C	-7.82313	8.81689	1.20891
H	-8.78543	9.66663	-0.54844
H	-6.85163	7.64355	2.75041
H	-7.90171	9.72813	1.80376
N	-8.2473	7.68505	-0.85366
Mg	-9.05035	7.35813	-2.83748
C	-9.99596	5.19473	-1.28832
H	-10.59622	6.08553	-1.5561
C	-10.36537	4.03205	-2.18935
H	-11.36342	3.60324	-1.96361
H	-10.36557	4.32058	-3.25334
H	-9.63935	3.20035	-2.08107
C	-10.16581	4.89259	0.18425
H	-10.12207	5.80283	0.80497
H	-11.12069	4.38156	0.42225
H	-9.35784	4.21778	0.54178
O	-7.85396	8.53059	-4.00911
C	-7.70232	9.9642	-3.84615
C	-7.0461	8.04522	-5.11138
C	-6.87879	10.41146	-5.04927
H	-8.70475	10.41154	-3.79518
H	-7.17611	10.14348	-2.89423
C	-6.04633	9.16244	-5.3637
H	-6.60561	7.08811	-4.80417
H	-7.70524	7.87857	-5.98005
H	-6.26948	11.29814	-4.82384
H	-7.53969	10.65305	-5.89685
H	-5.19693	9.07739	-4.66649
H	-5.65539	9.14575	-6.39094
Cl	-11.04828	8.47485	-3.10615

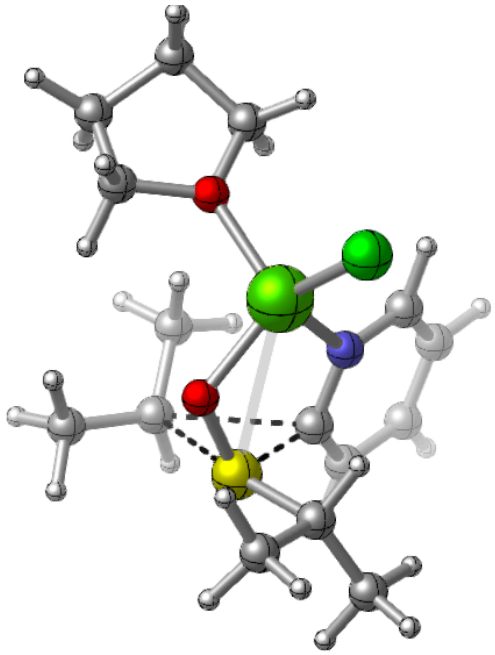
A6 = A6.7-F-eq’’’, A6.8-F-eq’’’; Thesis = E



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389239 (Hartree/Particle)
Thermal correction to Energy= 0.415447
Thermal correction to Enthalpy= 0.416391
Thermal correction to Gibbs Free Energy= 0.331118
Sum of electronic and zero-point Energies= -1849.853721
Sum of electronic and thermal Energies= -1849.827513
Sum of electronic and thermal Enthalpies= -1849.826569
Sum of electronic and thermal Free Energies= -1849.911842
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5117147
Coordinates

S	-7.87223	5.13679	-1.43375
O	-8.12026	5.68742	-2.92699
C	-5.82082	5.35591	-1.71753
H	-5.44743	5.08823	-0.71108
C	-5.46122	4.26154	-2.70518
H	-5.79999	4.52161	-3.72085
H	-4.3697	4.08294	-2.7516
H	-5.93636	3.30123	-2.43364
C	-5.31715	6.72529	-2.13016
H	-4.22549	6.72453	-2.32348
H	-5.81083	7.05518	-3.05625
H	-5.50425	7.49197	-1.36104
C	-7.8173	6.57781	-0.34556
C	-7.26261	6.55633	0.93381
C	-8.38331	8.81827	-0.16393
C	-7.29442	7.73402	1.67969
H	-6.82788	5.64011	1.33395
C	-7.86567	8.88619	1.12444
H	-8.83915	9.68766	-0.64483
H	-6.88229	7.75363	2.69128
H	-7.91031	9.82243	1.68269
N	-8.35547	7.6808	-0.8834
Mg	-9.01893	7.41135	-2.9195
C	-9.95589	4.96874	-1.15132
H	-10.52243	5.8771	-1.42232
C	-10.33964	3.81287	-2.05621
H	-11.34588	3.4098	-1.82978
H	-10.32516	4.10626	-3.11699
H	-9.62839	2.97055	-1.93941
C	-10.11771	4.65165	0.32186
H	-10.0503	5.55156	0.95457
H	-11.08305	4.16176	0.55179
H	-9.32212	3.95469	0.65853
O	-7.76243	8.54433	-4.03246
C	-7.2949	9.87021	-3.67084
C	-7.16097	8.09973	-5.27899
C	-6.55059	10.36749	-4.90371
H	-8.16821	10.48103	-3.40043
H	-6.63212	9.77248	-2.79604
C	-6.00937	9.06665	-5.5091
H	-6.85655	7.05182	-5.15164
H	-7.92483	8.16424	-6.07099
H	-5.76241	11.08831	-4.64452
H	-7.25024	10.85381	-5.60174
H	-5.11431	8.72959	-4.96242
H	-5.75311	9.15617	-6.57408
Cl	-11.11924	8.23026	-3.32206

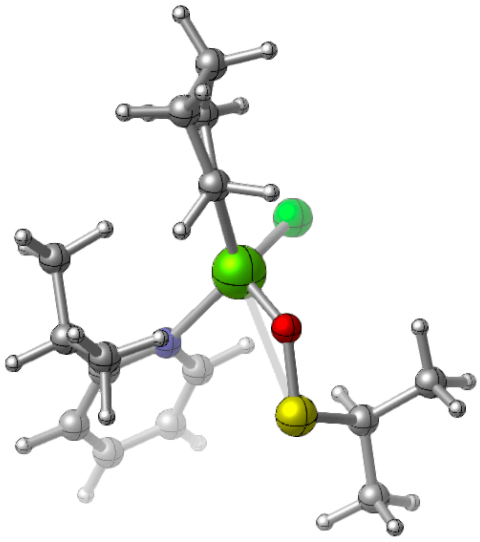
A6 = A6.8-TS-Feq’’’-D’; Thesis = TS-E-F



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388701 (Hartree/Particle)
Thermal correction to Energy= 0.414152
Thermal correction to Enthalpy= 0.415096
Thermal correction to Gibbs Free Energy= 0.332010
Sum of electronic and zero-point Energies= -1849.853248
Sum of electronic and thermal Energies= -1849.827797
Sum of electronic and thermal Enthalpies= -1849.826852
Sum of electronic and thermal Free Energies= -1849.909938
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5105226
Coordinates

S	-8.11855	5.15286	-1.32869
O	-8.34376	5.73831	-2.79566
C	-5.78347	5.72223	-1.5642
H	-5.42296	5.32123	-0.60046
C	-5.43791	4.8104	-2.7171
H	-5.87436	5.17988	-3.6602
H	-4.34072	4.72524	-2.88204
H	-5.8166	3.78372	-2.56397
C	-5.38115	7.15918	-1.77435
H	-4.33176	7.26918	-2.12927
H	-6.01355	7.64107	-2.53891
H	-5.46957	7.7601	-0.85483
C	-7.91303	6.57938	-0.2951
C	-7.3532	6.51634	0.99491
C	-8.28964	8.86757	-0.09836
C	-7.25514	7.6896	1.72169
H	-7.00746	5.56332	1.39681
C	-7.73127	8.89955	1.16647
H	-8.68426	9.77101	-0.57199
H	-6.82481	7.67628	2.72583
H	-7.67465	9.83804	1.71926
N	-8.39339	7.72728	-0.81892
Mg	-9.02751	7.56888	-2.84702
C	-10.02938	4.83994	-1.00928
H	-10.5587	5.79405	-1.1668
C	-10.49293	3.79654	-2.0124
H	-11.52863	3.47604	-1.8022
H	-10.45636	4.18288	-3.04086
H	-9.85706	2.8932	-1.96612
C	-10.16006	4.38323	0.43502
H	-9.90173	5.1813	1.14881
H	-11.19334	4.06555	0.65697
H	-9.50115	3.51965	0.63953
O	-7.73672	8.59112	-4.01157
C	-7.35398	9.97678	-3.79358
C	-7.01445	8.02045	-5.13922
C	-6.53195	10.34728	-5.02115
H	-8.27137	10.57015	-3.67138
H	-6.76103	10.02396	-2.86614
C	-5.88946	9.00872	-5.40495
H	-6.67783	7.01575	-4.84993
H	-7.71341	7.94274	-5.98757
H	-5.79803	11.13494	-4.8
H	-7.19055	10.70319	-5.82912
H	-5.03037	8.79087	-4.75075
H	-5.54921	8.97355	-6.44936
Cl	-11.12256	8.34731	-3.33036SI

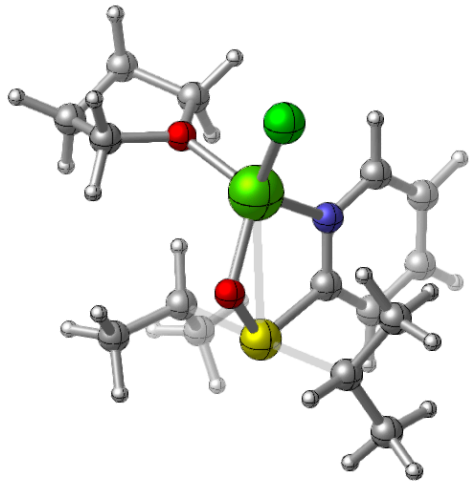
Figure = A6.8-D’



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.393533 (Hartree/Particle)
Thermal correction to Energy= 0.419649
Thermal correction to Enthalpy= 0.420593
Thermal correction to Gibbs Free Energy= 0.333558
Sum of electronic and zero-point Energies= -1849.961826
Sum of electronic and thermal Energies= -1849.935710
Sum of electronic and thermal Enthalpies= -1849.934766
Sum of electronic and thermal Free Energies= -1850.021801
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.6156228
Coordinates

S	-8.90604	4.62195	-1.89953
O	-8.61942	5.88187	-2.93729
C	-5.03346	6.92776	-0.99991
H	-4.10681	6.70884	-0.44711
C	-5.25899	5.77685	-1.99251
H	-6.21628	5.87203	-2.52785
H	-4.44576	5.74867	-2.73483
H	-5.2798	4.80793	-1.47034
C	-4.84086	8.28014	-1.69715
H	-3.98745	8.2324	-2.39154
H	-5.72149	8.57081	-2.28613
H	-4.64503	9.08106	-0.96734
C	-6.13458	6.97834	0.04148
C	-5.86865	6.59803	1.36341
C	-8.34488	7.43803	0.6092
C	-6.88148	6.6355	2.31952
H	-4.8615	6.27302	1.62978
C	-8.15027	7.07062	1.9361
H	-9.31711	7.80114	0.26516
H	-6.6811	6.33503	3.35076
H	-8.97799	7.12895	2.64455
N	-7.37138	7.38563	-0.32046
Mg	-8.25204	7.64226	-2.30935
C	-10.58918	5.00271	-1.25814
H	-10.51967	5.97792	-0.74457
C	-11.60208	5.11467	-2.38984
H	-12.5883	5.42856	-2.00482
H	-11.27212	5.85904	-3.13023
H	-11.7198	4.14655	-2.90509
C	-10.94365	3.9268	-0.2358
H	-10.21273	3.89758	0.58861
H	-11.93861	4.12081	0.19746
H	-10.97067	2.92857	-0.70496
O	-7.35455	8.39976	-3.98103
C	-7.28127	9.80992	-4.33391
C	-6.81089	7.5728	-5.04891
C	-6.9588	9.81746	-5.82053
H	-8.23968	10.27221	-4.06674
H	-6.47836	10.27202	-3.73556
C	-6.10466	8.55446	-5.97279
H	-6.14809	6.82246	-4.60013
H	-7.64975	7.05888	-5.54188
H	-6.43843	10.73714	-6.12354
H	-7.88386	9.73053	-6.41265
H	-5.07737	8.74123	-5.61983
H	-6.05291	8.18187	-7.00564
Cl	-9.85114	9.27904	-1.93659

A6 = A6.8-F-eq’’; Thesis = E’

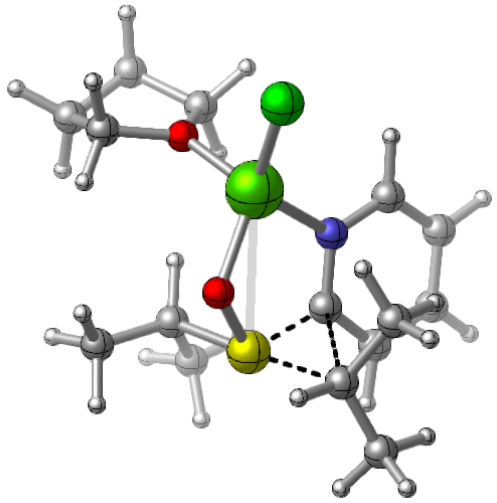


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389295 (Hartree/Particle)
Thermal correction to Energy= 0.415383
Thermal correction to Enthalpy= 0.416327
Thermal correction to Gibbs Free Energy= 0.331926
Sum of electronic and zero-point Energies= -1849.853919
Sum of electronic and thermal Energies= -1849.827831
Sum of electronic and thermal Enthalpies= -1849.826887
Sum of electronic and thermal Free Energies= -1849.911288
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5114827
Coordinates

S	-7.91474	5.37517	-1.33099
O	-8.69849	5.78117	-2.67372
C	-6.11957	5.82202	-2.21444
C	-7.89372	6.84516	-0.29372

C	-7.49856	6.83191	1.04727
C	-8.37719	9.11469	-0.21134
C	-7.55977	8.02546	1.76191
H	-7.14107	5.91259	1.50856
C	-8.00632	9.1917	1.12461
H	-8.73715	9.99225	-0.75506
H	-7.25204	8.05134	2.80984
H	-8.06382	10.14298	1.6553
N	-8.31584	7.96273	-0.90706
Mg	-9.01797	7.67577	-2.92177
C	-9.84388	4.9444	-0.43798
O	-7.48925	8.51079	-3.96232
C	-6.58206	9.53825	-3.48009
C	-7.05434	7.99679	-5.25073
C	-5.63044	9.79629	-4.64312
H	-7.17737	10.41554	-3.18896
H	-6.0595	9.14463	-2.59393
C	-5.60534	8.44196	-5.36225
H	-7.19433	6.90704	-5.24476
H	-7.69031	8.44185	-6.03315
H	-4.64016	10.12335	-4.29617
H	-6.03919	10.57396	-5.30739
H	-4.94858	7.73314	-4.83324
H	-5.27379	8.51127	-6.40779
Cl	-10.91067	8.60604	-3.79392
C	-10.88649	6.04017	-0.38359
H	-10.61382	6.83071	0.33783
H	-11.03543	6.52154	-1.36436
H	-11.88172	5.66199	-0.06938
H	-10.11674	4.19149	-1.19595
C	-9.56849	4.27989	0.8934
H	-8.64848	3.66494	0.85295
H	-9.4375	5.01929	1.70264
H	-10.3878	3.60693	1.21421
C	-5.07576	5.70819	-1.11902
H	-5.08036	6.57659	-0.44081
H	-5.25752	4.8062	-0.50051
H	-4.05063	5.61333	-1.52273
H	-6.15522	6.8371	-2.63528
C	-5.9389	4.7841	-3.30765
H	-6.08754	3.76317	-2.90502
H	-6.66599	4.92184	-4.12114
H	-4.92278	4.80625	-3.74563

A6 = A6.8-TS-F-eq''-D'''; Thesis = TS-C'-E

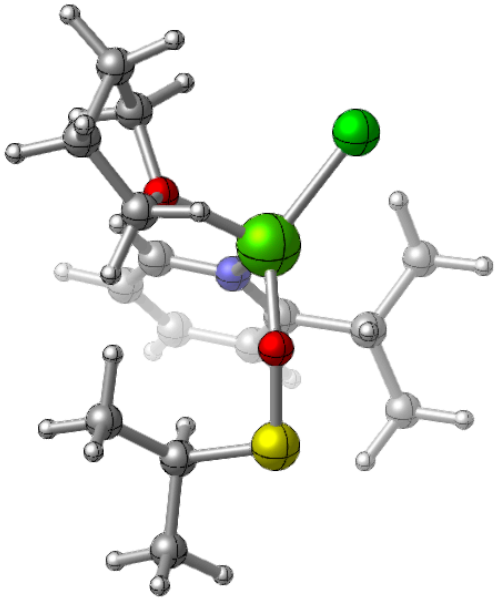


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388645 (Hartree/Particle)
Thermal correction to Energy= 0.414149
Thermal correction to Enthalpy= 0.415093
Thermal correction to Gibbs Free Energy= 0.331932
Sum of electronic and zero-point Energies= -1849.854459
Sum of electronic and thermal Energies= -1849.828955
Sum of electronic and thermal Enthalpies= -1849.828011
Sum of electronic and thermal Free Energies= -1849.911172
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5111055
Coordinates

S	-7.85552	5.39939	-1.34971
O	-8.67854	5.79569	-2.66513
C	-6.10771	5.80254	-2.22592
C	-7.90239	6.83874	-0.2967
C	-7.52313	6.80812	1.05417
C	-8.4191	9.10285	-0.17515
C	-7.62298	7.9811	1.78999
H	-7.14881	5.88769	1.49984
C	-8.07941	9.1578	1.16747
H	-8.78051	9.98658	-0.70824
H	-7.33222	7.99103	2.84307
H	-8.16241	10.09622	1.71709
N	-8.32324	7.96812	-0.89905
Mg	-9.02669	7.69368	-2.90313
C	-9.88729	5.03012	-0.35136
O	-7.48038	8.49718	-3.94394
C	-6.56798	9.52274	-3.46735

C	-7.06832	7.99868	-5.24535
C	-5.63673	9.79408	-4.64383
H	-7.16024	10.39579	-3.15791
H	-6.03057	9.12245	-2.59306
C	-5.62206	8.44731	-5.37734
H	-7.20747	6.90878	-5.24916
H	-7.71834	8.4515	-6.01165
H	-4.64113	10.11947	-4.31081
H	-6.05817	10.57766	-5.29301
H	-4.95475	7.73422	-4.8674
H	-5.30863	8.52789	-6.42765
Cl	-10.9037	8.62509	-3.80479
C	-10.89966	6.14736	-0.2957
H	-10.61614	6.92301	0.43806
H	-11.02507	6.64532	-1.27235
H	-11.9123	5.79616	-0.00082
H	-10.14895	4.29741	-1.13152
C	-9.61297	4.3507	0.96701
H	-8.71971	3.69873	0.91
H	-9.43944	5.08029	1.77777
H	-10.45159	3.70775	1.3061
C	-5.04572	5.69266	-1.14538
H	-5.0936	6.52512	-0.42547
H	-5.16066	4.7512	-0.57508
H	-4.02761	5.68669	-1.5738
H	-6.15741	6.82108	-2.63591
C	-5.93068	4.78031	-3.33596
H	-6.03488	3.75151	-2.94286
H	-6.68332	4.90955	-4.12683
H	-4.92852	4.84654	-3.79772

A6 = A6.8-D'''

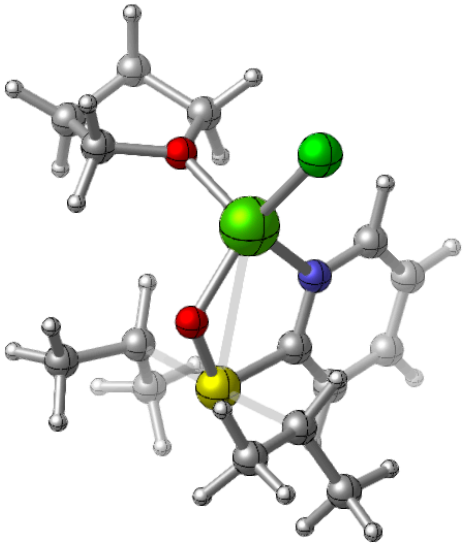


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.393395 (Hartree/Particle)
Thermal correction to Energy= 0.419612
Thermal correction to Enthalpy= 0.420556
Thermal correction to Gibbs Free Energy= 0.333513
Sum of electronic and zero-point Energies= -1849.963810
Sum of electronic and thermal Energies= -1849.937592
Sum of electronic and thermal Enthalpies= -1849.936648
Sum of electronic and thermal Free Energies= -1850.023691
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.6180611
Coordinates

S	-7.37954	4.2531	-2.23437
O	-7.93666	5.46509	-3.19948
C	-5.97396	4.98923	-1.28799
C	-8.7065	6.96212	0.15934
C	-8.23637	7.11219	1.47043
C	-7.13294	8.51378	-0.59345
C	-7.18716	7.98983	1.73614
H	-8.69048	6.53904	2.2782
C	-6.62102	8.71152	0.68343
H	-6.70873	9.04111	-1.45013
H	-6.81313	8.10756	2.75595
H	-5.79669	9.40838	0.84152
N	-8.14328	7.66358	-0.85066
Mg	-8.59044	7.21151	-2.90646
C	-9.86893	6.0528	-0.18561
O	-7.23415	8.38789	-3.90012
C	-7.40473	9.82845	-4.01616
C	-6.66107	7.84547	-5.12911
C	-7.24914	10.1196	-5.50032
H	-8.39298	10.08773	-3.61274
H	-6.61877	10.3175	-3.41729
C	-6.2211	9.06581	-5.92487
H	-5.84826	7.16182	-4.85374
H	-7.44576	7.27572	-5.6512
H	-6.92344	11.15257	-5.68813
H	-8.20736	9.95385	-6.01789
H	-5.20654	9.37543	-5.62621
H	-6.21813	8.8687	-7.00624
Cl	-10.55587	8.12222	-3.71449
C	-11.18572	6.84595	-0.13977
H	-11.38569	7.20992	0.88153
H	-11.15946	7.70859	-0.8217
H	-12.02558	6.20216	-0.44551
H	-9.70367	5.71076	-1.22058
C	-9.93911	4.79437	0.68138
H	-8.98811	4.24221	0.65567
H	-10.19155	5.02466	1.72886

H	-10.72462	4.1265	0.29525
C	-5.27461	3.82696	-0.58741
H	-5.97499	3.25022	0.03955
H	-4.82523	3.13606	-1.31959
H	-4.47169	4.20194	0.06858
H	-6.39178	5.66175	-0.52148
C	-5.03955	5.78884	-2.1842
H	-4.60144	5.14952	-2.96875
H	-5.57289	6.6142	-2.67629
H	-4.21785	6.22575	-1.59034

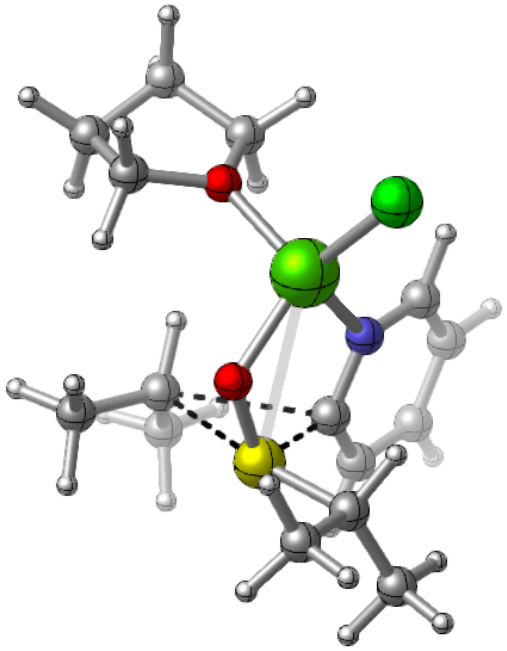
A6 = A6.9-F-eq’’’’



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389002 (Hartree/Particle)
Thermal correction to Energy= 0.415234
Thermal correction to Enthalpy= 0.416179
Thermal correction to Gibbs Free Energy= 0.329957
Sum of electronic and zero-point Energies= -1849.853109
Sum of electronic and thermal Energies= -1849.826876
Sum of electronic and thermal Enthalpies= -1849.825932
Sum of electronic and thermal Free Energies= -1849.912154
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5111517
Coordinates

S	-7.91825	5.32056	-1.38412
O	-8.5502	5.77094	-2.79568
C	-6.01016	5.8332	-2.13236
H	-6.02876	6.86201	-2.52568
C	-5.02738	5.67392	-0.98944
H	-5.29434	4.79238	-0.36979
H	-3.99093	5.50309	-1.33941
H	-5.00377	6.54882	-0.3211
C	-5.77712	4.81605	-3.23362
H	-4.73509	4.8268	-3.60972
H	-5.96401	3.79017	-2.85808
H	-6.45197	4.97284	-4.08716
C	-7.89318	6.79737	-0.33316
C	-7.38414	6.80742	0.96688
C	-8.4711	9.04112	-0.21103
C	-7.43293	8.00306	1.68309
H	-6.96557	5.90255	1.4044
C	-7.9857	9.14207	1.08798
H	-8.91878	9.89749	-0.72217
H	-7.04467	8.04489	2.70343
H	-8.04379	10.09167	1.62175
N	-8.42024	7.88929	-0.9038
Mg	-9.10828	7.6166	-2.92006
C	-9.83805	4.8703	-0.70941
H	-10.49227	5.75038	-0.83096
C	-10.2863	3.72197	-1.59521
H	-11.19358	3.22086	-1.20577
H	-10.493	4.0572	-2.6215
H	-9.49816	2.94469	-1.65469
C	-9.70062	4.46078	0.74459
H	-9.62642	5.32324	1.42518
H	-10.55143	3.84447	1.0914
H	-8.78819	3.8459	0.88883
O	-7.64602	8.55435	-3.95931
C	-6.92431	9.7309	-3.50518
C	-7.01734	7.98291	-5.13985
C	-5.91758	10.02079	-4.61188
H	-7.65213	10.5383	-3.3398
H	-6.43256	9.48358	-2.55101
C	-5.6397	8.62426	-5.18117
H	-7.00582	6.89171	-5.01985
H	-7.62798	8.24974	-6.01777
H	-5.01826	10.52138	-4.22629
H	-6.36999	10.66545	-5.38197
H	-4.9442	8.07109	-4.52998
H	-5.22403	8.64403	-6.19839
Cl	-11.10426	8.60484	-3.4242

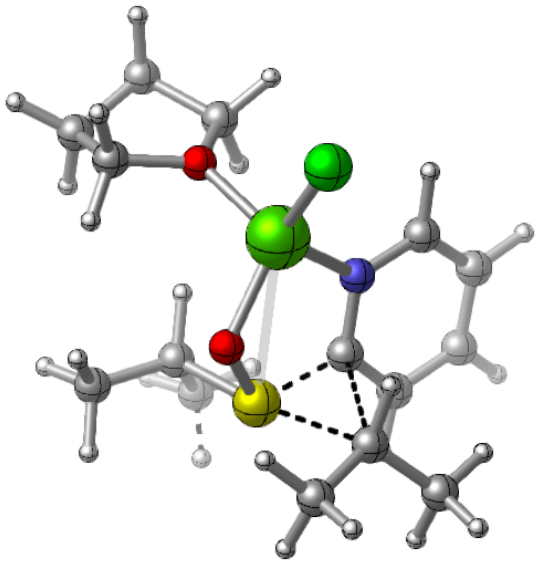
A6 = A6.9-TS-F-eq’’’’-D’’’’



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388487 (Hartree/Particle)
Thermal correction to Energy= 0.414015
Thermal correction to Enthalpy= 0.414959
Thermal correction to Gibbs Free Energy= 0.331503
Sum of electronic and zero-point Energies= -1849.851889
Sum of electronic and thermal Energies= -1849.826362
Sum of electronic and thermal Enthalpies= -1849.825418
Sum of electronic and thermal Free Energies= -1849.908873
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5089855
Coordinates

S	-8.27646	5.16727	-1.39211
O	-8.68389	5.71878	-2.8299
C	-6.01311	5.98507	-1.95262
C	-8.06356	6.61221	-0.38537
C	-7.50769	6.55062	0.90714
C	-8.52038	8.88258	-0.15403
C	-7.44481	7.71831	1.64871
H	-7.14077	5.60388	1.30257
C	-7.95453	8.91893	1.11044
H	-8.94916	9.77864	-0.61186
H	-7.01574	7.7032	2.65345
H	-7.92711	9.85195	1.6744
N	-8.59309	7.75156	-0.88559
Mg	-9.20038	7.59983	-2.91591
C	-10.11062	4.71452	-0.90465
H	-10.70649	5.63154	-1.04338
C	-10.57421	3.62004	-1.85299
H	-11.57423	3.2493	-1.56733
H	-10.62413	3.9805	-2.88993
H	-9.88609	2.75538	-1.825
C	-10.10501	4.27636	0.55165
H	-9.87504	5.10619	1.23741
H	-11.08975	3.87195	0.84198
H	-9.36115	3.47708	0.72284
O	-7.70655	8.52285	-3.91171
C	-7.02017	9.71113	-3.43056
C	-7.01129	7.94748	-5.05354
C	-5.98542	10.02135	-4.50415
H	-7.7685	10.50356	-3.28582
H	-6.55357	9.46874	-2.46268
C	-5.65166	8.6286	-5.05226
H	-6.97062	6.85979	-4.91107
H	-7.59395	8.1792	-5.95978
H	-5.11299	10.5471	-4.09123
H	-6.4282	10.64951	-5.29331
H	-4.96438	8.10043	-4.37263
H	-5.20223	8.65227	-6.05495
Cl	-11.20989	8.50274	-3.51077
C	-5.01592	5.9562	-0.82471
H	-5.13031	6.80155	-0.12765
H	-5.10824	5.02599	-0.22831
H	-3.96091	5.97799	-1.17948
H	-6.145	6.99	-2.38154
C	-5.74193	4.93489	-3.00532
H	-5.77003	3.91768	-2.56784
H	-6.48643	4.95666	-3.81529
H	-4.73556	5.03753	-3.47049

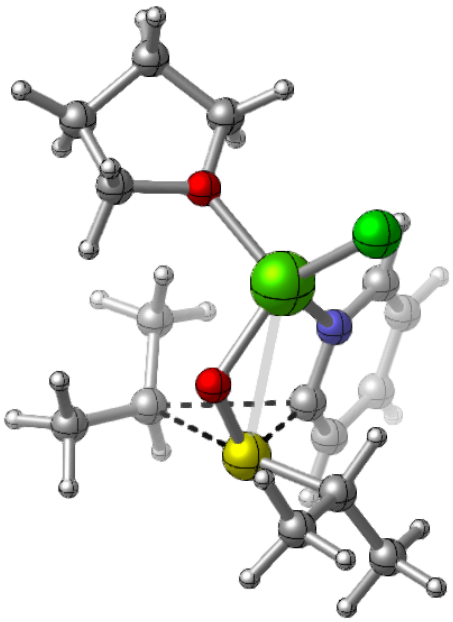
A6 = A6.9-TS-F-eq’’’’-D’’’’



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388518 (Hartree/Particle)
Thermal correction to Energy= 0.414021
Thermal correction to Enthalpy= 0.414965
Thermal correction to Gibbs Free Energy= 0.331602
Sum of electronic and zero-point Energies= -1849.850947
Sum of electronic and thermal Energies= -1849.825444
Sum of electronic and thermal Enthalpies= -1849.824499
Sum of electronic and thermal Free Energies= -1849.907863
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5078561
Coordinates

S	-7.73157	5.32462	-1.47758
O	-8.54628	5.7398	-2.78151
C	-5.99517	5.76252	-2.26056
C	-7.91128	6.68743	-0.36069
C	-7.4849	6.61465	0.98127
C	-8.49729	8.92743	-0.12092
C	-7.61257	7.74404	1.77072
H	-7.07195	5.68669	1.37617
C	-8.13873	8.93147	1.2172
H	-8.90007	9.82233	-0.60421
H	-7.29583	7.71655	2.81608
H	-8.25172	9.83695	1.81433
N	-8.36261	7.84012	-0.90846
Mg	-9.08284	7.6156	-2.89277
C	-9.96152	5.04592	-0.46155
H	-10.54362	5.92108	-0.79588
C	-10.30255	3.79404	-1.23655
H	-11.30136	3.38347	-0.96774
H	-10.29693	3.96853	-2.3229
H	-9.57582	2.98424	-1.02805
C	-10.00652	4.8471	1.0301
H	-9.88795	5.78594	1.59327
H	-10.96101	4.3887	1.37218
H	-9.20718	4.15802	1.36971
O	-7.59612	8.49886	-3.95429
C	-6.72204	9.54701	-3.45306
C	-7.12043	7.99266	-5.23168
C	-5.76314	9.83689	-4.60169
H	-7.34436	10.40566	-3.16335
H	-6.20226	9.16097	-2.56198
C	-5.68475	8.48481	-5.32098
H	-7.22444	6.89903	-5.22206
H	-7.75583	8.41272	-6.02815
H	-4.78896	10.19538	-4.24062
H	-6.18735	10.60172	-5.27116
H	-5.0119	7.79742	-4.78374
H	-5.34014	8.56528	-6.36146
Cl	-11.08594	8.49191	-3.53584
C	-4.94774	5.64968	-1.16408
H	-5.05704	6.43418	-0.39962
H	-5.00735	4.67004	-0.65608
H	-3.93027	5.73595	-1.58293
H	-6.0752	6.79549	-2.62971
C	-5.76041	4.79355	-3.40831
H	-5.80813	3.74716	-3.05607
H	-6.5129	4.91567	-4.19991
H	-4.76063	4.94006	-3.85373

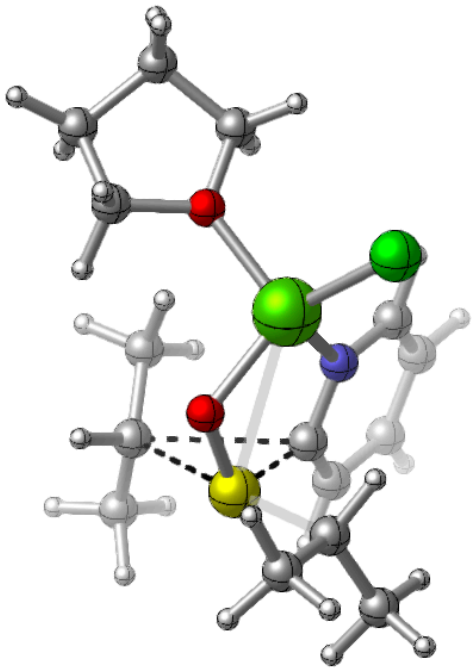
SI Table = A6.1-S TS-F-eq-D 0/0



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388701 (Hartree/Particle)
Thermal correction to Energy= 0.414152
Thermal correction to Enthalpy= 0.415096
Thermal correction to Gibbs Free Energy= 0.332010
Sum of electronic and zero-point Energies= -1849.853248
Sum of electronic and thermal Energies= -1849.827797
Sum of electronic and thermal Enthalpies= -1849.826852
Sum of electronic and thermal Free Energies= -1849.909938
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5105226
Coordinates

S	-8.11855	5.15286	-1.32869
O	-8.34376	5.73831	-2.79566
C	-5.78347	5.72223	-1.5642
H	-5.42296	5.32123	-0.60046
C	-5.43791	4.8104	-2.7171
H	-5.87436	5.17988	-3.6602
H	-4.34072	4.72524	-2.88204
H	-5.8166	3.78372	-2.56397
C	-5.38115	7.15918	-1.77435
H	-4.33176	7.26918	-2.12927
H	-6.01355	7.64107	-2.53891
H	-5.46957	7.7601	-0.85483
C	-7.91303	6.57938	-0.2951
C	-7.3532	6.51634	0.99491
C	-8.28964	8.86757	-0.09836
C	-7.25514	7.6896	1.72169
H	-7.00746	5.56332	1.39681
C	-7.73127	8.89955	1.16647
H	-8.68426	9.77101	-0.57199
H	-6.82481	7.67628	2.72583
H	-7.67465	9.83804	1.71926
N	-8.39339	7.72728	-0.81892
Mg	-9.02751	7.56888	-2.84702
C	-10.02938	4.83994	-1.00928
H	-10.5587	5.79405	-1.1668
C	-10.49293	3.79654	-2.0124
H	-11.52863	3.47604	-1.8022
H	-10.45636	4.18288	-3.04086
H	-9.85706	2.8932	-1.96612
C	-10.16006	4.38323	0.43502
H	-9.90173	5.1813	1.14881
H	-11.19334	4.06555	0.65697
H	-9.50115	3.51965	0.63953
O	-7.73672	8.59112	-4.01157
C	-7.35398	9.97678	-3.79358
C	-7.01445	8.02045	-5.13922
C	-6.53195	10.34728	-5.02115
H	-8.27137	10.57015	-3.67138
H	-6.76103	10.02396	-2.86614
C	-5.88946	9.00872	-5.40495
H	-6.67783	7.01575	-4.84993
H	-7.71341	7.94274	-5.98757
H	-5.79803	11.13494	-4.8
H	-7.19055	10.70319	-5.82912
H	-5.03037	8.79087	-4.75075
H	-5.54921	8.97355	-6.44936
Cl	-11.12256	8.34731	-3.33036

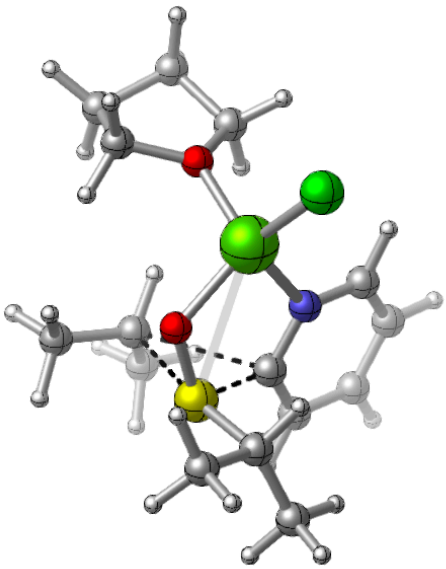
SI Table = A6.1-S TS-F-eq-D 120/0



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389095 (Hartree/Particle)
Thermal correction to Energy= 0.414482
Thermal correction to Enthalpy= 0.415427
Thermal correction to Gibbs Free Energy= 0.332178
Sum of electronic and zero-point Energies= -1849.853746
Sum of electronic and thermal Energies= -1849.828358
Sum of electronic and thermal Enthalpies= -1849.827414
Sum of electronic and thermal Free Energies= -1849.910663
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5110652
Coordinates

S	-8.05434	5.21994	-1.27537
O	-8.29306	5.80154	-2.75145
C	-5.84451	5.6767	-1.5749
C	-5.3916	7.10969	-1.72666
H	-4.3626	7.19911	-2.13818
H	-6.05057	7.68057	-2.39796
H	-5.38261	7.63506	-0.75492
C	-7.96268	6.64859	-0.20596
C	-7.46585	6.60057	1.10348
C	-8.36966	8.93093	-0.05215
C	-7.41719	7.78475	1.82831
H	-7.1424	5.65455	1.53553
C	-7.87618	8.97832	1.24275
H	-8.75312	9.8251	-0.55134
H	-7.03968	7.78253	2.85352
H	-7.86037	9.92177	1.78996
N	-8.41641	7.78571	-0.76338
Mg	-9.02113	7.60391	-2.81134
C	-10.01485	4.89431	-1.00573
H	-10.57077	5.82932	-1.18833
C	-10.41755	3.82316	-2.00494
H	-11.43858	3.44679	-1.81085
H	-10.38328	4.2004	-3.03719
H	-9.73704	2.95258	-1.94356
C	-10.16841	4.44683	0.43785
H	-10.00744	5.27127	1.15057
H	-11.17537	4.03703	0.63256
H	-9.44117	3.64849	0.68089
O	-7.70133	8.59247	-3.97378
C	-7.43604	10.01913	-3.88864
C	-6.89318	7.97162	-5.01319
C	-6.59398	10.32919	-5.11941
H	-8.40063	10.54507	-3.85893
H	-6.88751	10.20757	-2.95145
C	-5.83591	9.0146	-5.34047
H	-6.49827	7.02858	-4.61325
H	-7.54875	7.75734	-5.87282
H	-5.9325	11.1918	-4.95695
H	-7.24388	10.5478	-5.98152
H	-4.99142	8.93287	-4.63769
H	-5.44928	8.9021	-6.3631
Cl	-11.05645	8.55425	-3.25107
C	-5.11883	4.89375	-0.50728
H	-5.05523	5.45607	0.44132
H	-5.62751	3.93492	-0.28959
H	-4.07433	4.64289	-0.78566
H	-5.82524	5.14746	-2.54096

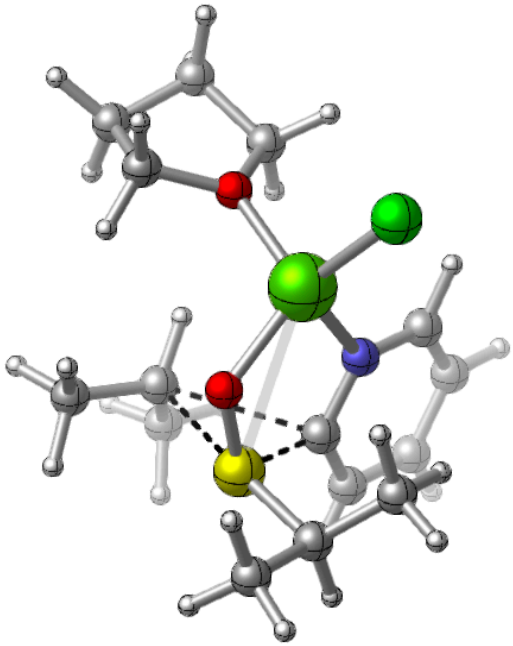
SI Table = A6.1-S TS-F-eq-D 240/0



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388487 (Hartree/Particle)
Thermal correction to Energy= 0.414015
Thermal correction to Enthalpy= 0.414959
Thermal correction to Gibbs Free Energy= 0.331503
Sum of electronic and zero-point Energies= -1849.851889
Sum of electronic and thermal Energies= -1849.826362
Sum of electronic and thermal Enthalpies= -1849.825418
Sum of electronic and thermal Free Energies= -1849.908873
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5089855
Coordinates

S	-8.27646	5.16727	-1.39211
O	-8.68389	5.71878	-2.8299
C	-6.01311	5.98507	-1.95262
C	-8.06356	6.61221	-0.38537
C	-7.50769	6.55062	0.90714
C	-8.52038	8.88258	-0.15403
C	-7.44481	7.71831	1.64871
H	-7.14077	5.60388	1.30257
C	-7.95453	8.91893	1.11044
H	-8.94916	9.77864	-0.61186
H	-7.01574	7.7032	2.65345
H	-7.92711	9.85195	1.6744
N	-8.59309	7.75156	-0.88559
Mg	-9.20038	7.59983	-2.91591
C	-10.11062	4.71452	-0.90465
H	-10.70649	5.63154	-1.04338
C	-10.57421	3.62004	-1.85299
H	-11.57423	3.2493	-1.56733
H	-10.62413	3.9805	-2.88993
H	-9.88609	2.75538	-1.825
C	-10.10501	4.27636	0.55165
H	-9.87504	5.10619	1.23741
H	-11.08975	3.87195	0.84198
H	-9.36115	3.47708	0.72284
O	-7.70655	8.52285	-3.91171
C	-7.02017	9.71113	-3.43056
C	-7.01129	7.94748	-5.05354
C	-5.98542	10.02135	-4.50415
H	-7.7685	10.50356	-3.28582
H	-6.55357	9.46874	-2.46268
C	-5.65166	8.6286	-5.05226
H	-6.97062	6.85979	-4.91107
H	-7.59395	8.1792	-5.95978
H	-5.11299	10.5471	-4.09123
H	-6.4282	10.64951	-5.29331
H	-4.96438	8.10043	-4.37263
H	-5.20223	8.65227	-6.05495
Cl	-11.20989	8.50274	-3.51077
C	-5.01592	5.9562	-0.82471
H	-5.13031	6.80155	-0.12765
H	-5.10824	5.02599	-0.22831
H	-3.96091	5.97799	-1.17948
H	-6.145	6.99	-2.38154
C	-5.74193	4.93489	-3.00532
H	-5.77003	3.91768	-2.56784
H	-6.48643	4.95666	-3.81529
H	-4.73556	5.03753	-3.47049

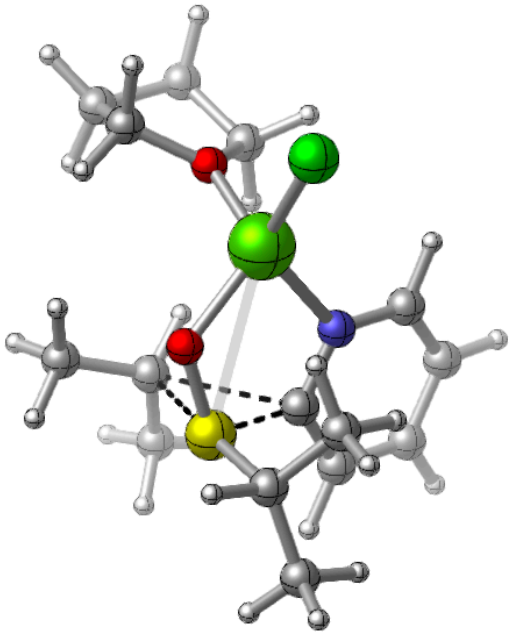
SI Table = A6.1-S TS-F-eq-D 240/120



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388553 (Hartree/Particle)
Thermal correction to Energy= 0.413997
Thermal correction to Enthalpy= 0.414941
Thermal correction to Gibbs Free Energy= 0.331985
Sum of electronic and zero-point Energies= -1849.851659
Sum of electronic and thermal Energies= -1849.826214
Sum of electronic and thermal Enthalpies= -1849.825270
Sum of electronic and thermal Free Energies= -1849.908226
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5083848
Coordinates

S	-8.30819	5.23222	-1.44502
O	-8.7712	5.79431	-2.85897
C	-6.05565	6.056	-2.00153
C	-8.10444	6.66824	-0.41992
C	-7.63689	6.56477	0.90295
C	-8.43032	8.95911	-0.20335
C	-7.53991	7.72713	1.65377
H	-7.35962	5.59495	1.31694
C	-7.93469	8.95703	1.09448
H	-8.77681	9.88153	-0.67806
H	-7.17387	7.68205	2.68239
H	-7.87888	9.88588	1.6631
N	-8.53173	7.83962	-0.94141
Mg	-9.09955	7.71513	-2.98527
C	-10.0883	4.67552	-0.88049
C	-10.45361	3.46991	-1.73325
H	-11.34189	2.95316	-1.33012
H	-10.68036	3.77751	-2.76615
H	-9.63126	2.73451	-1.7706
O	-7.55502	8.5735	-3.96198
C	-6.85506	9.75821	-3.49285
C	-6.88637	7.99835	-5.119
C	-5.82865	10.05682	-4.57828
H	-7.5955	10.55735	-3.34441
H	-6.38101	9.51522	-2.52875
C	-5.51816	8.66118	-5.13265
H	-6.85808	6.90907	-4.98661
H	-7.4792	8.24513	-6.01474
H	-4.94515	10.57143	-4.17503
H	-6.27281	10.69121	-5.36161
H	-4.83017	8.1226	-4.46189
H	-5.08015	8.68115	-6.14047
Cl	-10.99667	8.80752	-3.63744
C	-5.09764	6.00169	-0.84083
H	-5.19557	6.8665	-0.16504
H	-5.2602	5.09187	-0.22625
H	-4.02955	5.96026	-1.15309
H	-6.14628	7.06384	-2.43339
C	-5.7822	4.99831	-3.04545
H	-5.85367	3.98273	-2.6078
H	-6.50432	5.0372	-3.87595
H	-4.76175	5.06725	-3.48594
H	-9.87554	4.34994	0.15492
C	-11.15119	5.76035	-0.87948
H	-10.88457	6.60731	-0.22985
H	-11.33225	6.15026	-1.89341
H	-12.11257	5.35595	-0.51395

SI Table = A6.1-S TS-F-eq-D 240/240

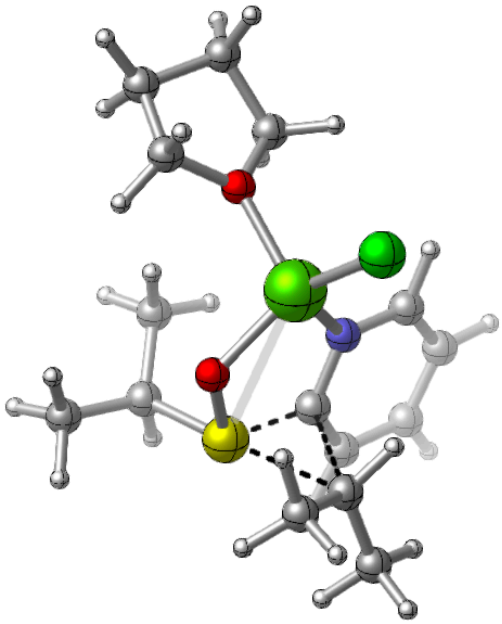


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388476 (Hartree/Particle)
Thermal correction to Energy= 0.413979
Thermal correction to Enthalpy= 0.414923
Thermal correction to Gibbs Free Energy= 0.331072
Sum of electronic and zero-point Energies= -1849.852017
Sum of electronic and thermal Energies= -1849.826514
Sum of electronic and thermal Enthalpies= -1849.825570
Sum of electronic and thermal Free Energies= -1849.909421
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)

HF= -1851.5087047
Coordinates

S	-8.29102	5.24518	-1.3061
O	-8.74177	5.72504	-2.7485
C	-6.00519	6.08891	-1.829
C	-8.09165	6.74644	-0.37897
C	-7.59964	6.74159	0.94326
C	-8.5238	9.03253	-0.27394
C	-7.54115	7.94504	1.62547
H	-7.27667	5.80985	1.40599
C	-8.00418	9.12604	1.00831
H	-8.92135	9.91118	-0.79029
H	-7.15561	7.97247	2.64757
H	-7.98182	10.08588	1.52533
N	-8.58718	7.87004	-0.95176
Mg	-9.11192	7.62575	-2.99398
C	-10.05982	4.66992	-0.74444
O	-7.56834	8.53569	-3.93615
C	-6.7376	9.60835	-3.41181
C	-7.10435	8.11987	-5.24779
C	-5.74664	9.9237	-4.52925
H	-7.38806	10.45458	-3.14741
H	-6.24047	9.23554	-2.50392
C	-5.66407	8.59836	-5.29659
H	-7.22515	7.03034	-5.32001
H	-7.73253	8.6063	-6.01227
H	-4.77752	10.25652	-4.13191
H	-6.14338	10.71714	-5.18189
H	-5.01099	7.88326	-4.77176
H	-5.30035	8.71517	-6.32714
Cl	-11.00419	8.40417	-4.00404
C	-5.11607	5.72552	-0.67076
H	-5.15122	6.46445	0.14571
H	-5.40617	4.74454	-0.23823
H	-4.0453	5.62049	-0.95495
H	-5.98084	7.16212	-2.07134
C	-5.78247	5.21907	-3.04402
H	-5.98823	4.15414	-2.81769
H	-6.43491	5.49741	-3.88398
H	-4.73082	5.25068	-3.41013
C	-11.15793	5.71043	-0.87915
H	-10.97883	6.575	-0.22005
H	-11.2607	6.0771	-1.91078
H	-12.13296	5.278	-0.59081
C	-9.91674	4.11802	0.66696
H	-9.04182	3.45157	0.75811
H	-9.80757	4.92768	1.40736
H	-10.80785	3.53309	0.95065
H	-10.22793	3.84272	-1.45579

A6 = A6.1-Mg TS-F-eq-D 0/0

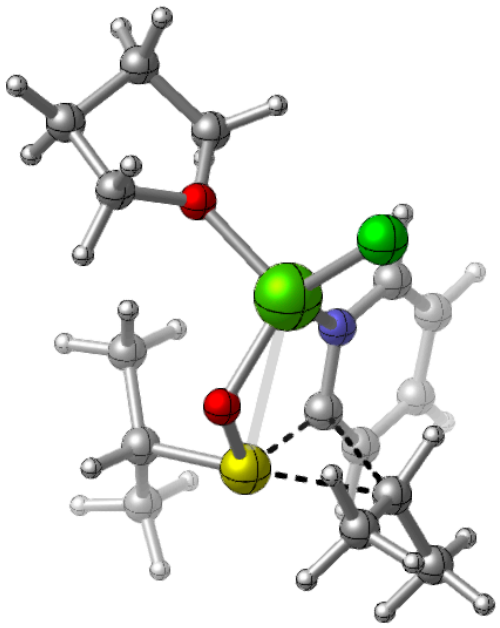


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.387996 (Hartree/Particle)
Thermal correction to Energy= 0.413781
Thermal correction to Enthalpy= 0.414725
Thermal correction to Gibbs Free Energy= 0.329461
Sum of electronic and zero-point Energies= -1849.850943
Sum of electronic and thermal Energies= -1849.825158
Sum of electronic and thermal Enthalpies= -1849.824214
Sum of electronic and thermal Free Energies= -1849.909479
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5070209
Coordinates

S	-7.57296	5.22099	-1.37271
O	-8.10301	5.69968	-2.78781
C	-5.69137	5.31864	-1.81398
H	-5.23878	5.06151	-0.83842
C	-5.4143	4.20827	-2.81648
H	-5.84682	4.45235	-3.79936
H	-4.32875	4.0595	-2.94914
H	-5.84238	3.24607	-2.48674
C	-5.21348	6.68511	-2.27278
H	-4.13193	6.6584	-2.49656
H	-5.73633	6.99601	-3.18793
H	-5.37277	7.4581	-1.50635

C	-7.74977	6.63741	-0.32
C	-7.36859	6.58317	1.03742
C	-8.21035	8.91197	-0.16913
C	-7.47173	7.7416	1.79109
H	-7.0056	5.65145	1.47239
C	-7.91004	8.93669	1.18718
H	-8.54087	9.81422	-0.69197
H	-7.19415	7.72881	2.84807
H	-7.99691	9.86426	1.75375
N	-8.10836	7.80027	-0.91697
Mg	-8.83861	7.50317	-2.88998
C	-9.93575	5.26236	-0.55905
H	-10.42448	6.24962	-0.62039
C	-10.48276	4.28936	-1.57841
H	-11.4935	3.90883	-1.30666
H	-10.56197	4.73485	-2.58171
H	-9.83798	3.3926	-1.67055
C	-9.90921	4.70792	0.83977
H	-9.65756	5.46815	1.59675
H	-10.87677	4.25733	1.15355
H	-9.15784	3.8951	0.93054
O	-7.54192	8.5267	-4.06132
C	-6.97555	9.81682	-3.70742
C	-7.18769	8.15638	-5.42102
C	-6.4309	10.37276	-5.01732
H	-7.76949	10.43224	-3.26008
H	-6.18286	9.64729	-2.96173
C	-6.05173	9.10042	-5.78457
H	-6.91154	7.0926	-5.42172
H	-8.07329	8.30236	-6.06076
H	-5.58273	11.05226	-4.85365
H	-7.21861	10.92353	-5.55518
H	-5.0919	8.70073	-5.42014
H	-5.97471	9.2538	-6.87008
Cl	-10.91195	8.27035	-3.46071

A6 = A6.1-Mg TS-F-eq-D 0/120

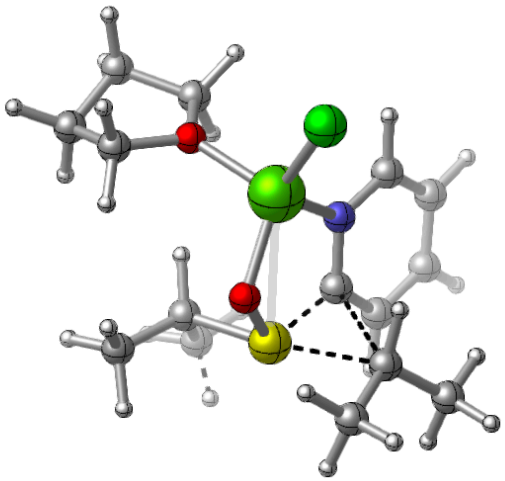


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388210 (Hartree/Particle)
Thermal correction to Energy= 0.413897
Thermal correction to Enthalpy= 0.414842
Thermal correction to Gibbs Free Energy= 0.330064
Sum of electronic and zero-point Energies= -1849.850949
Sum of electronic and thermal Energies= -1849.825261
Sum of electronic and thermal Enthalpies= -1849.824317
Sum of electronic and thermal Free Energies= -1849.909095
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF=-1851.5068867
Coordinates

S	-7.56319	5.25188	-1.32819
O	-8.08416	5.72142	-2.75048
C	-5.68043	5.3585	-1.77776
C	-5.21958	6.72902	-2.24082
H	-4.16628	6.69126	-2.57183
H	-5.8227	7.09536	-3.08085
H	-5.27926	7.46711	-1.42476
C	-7.77845	6.67053	-0.28238
C	-7.45122	6.62851	1.09068
C	-8.24018	8.94933	-0.16523
C	-7.5782	7.79318	1.82949
H	-7.11179	5.69978	1.54822
C	-7.98708	8.98621	1.19916

H	-8.55095	9.84707	-0.70763
H	-7.34245	7.78731	2.89661
H	-8.08981	9.91918	1.7541
N	-8.11577	7.8297	-0.89969
Mg	-8.8378	7.51642	-2.87146
C	-9.94247	5.27017	-0.53662
H	-10.43306	6.25754	-0.57073
C	-10.48659	4.32452	-1.58287
H	-11.5023	3.94632	-1.32672
H	-10.55591	4.79245	-2.57652
H	-9.84803	3.42549	-1.68973
C	-9.91366	4.67733	0.84593
H	-9.67833	5.41983	1.62516
H	-10.8763	4.20471	1.14123
H	-9.15094	3.87305	0.91808
O	-7.55449	8.53636	-4.05931
C	-7.02522	9.85164	-3.7408
C	-7.1511	8.11989	-5.39187
C	-6.43593	10.36042	-5.05093
H	-7.84768	10.47131	-3.35531
H	-6.26203	9.72915	-2.95608
C	-6.01409	9.06366	-5.75207
H	-6.86318	7.06043	-5.34266
H	-8.01619	8.23104	-6.06582
H	-5.60187	11.05606	-4.88271
H	-7.20785	10.8801	-5.64011
H	-5.06376	8.69107	-5.33746
H	-5.89928	9.17475	-6.8394
Cl	-10.91856	8.27335	-3.42878
H	-5.63447	4.63511	-2.60988
C	-4.90312	4.8261	-0.58218
H	-4.8892	5.5538	0.24581
H	-5.33298	3.884	-0.20165
H	-3.85428	4.62393	-0.85748

A6 = A6.1-Mg TS-F-eq-D 0/240



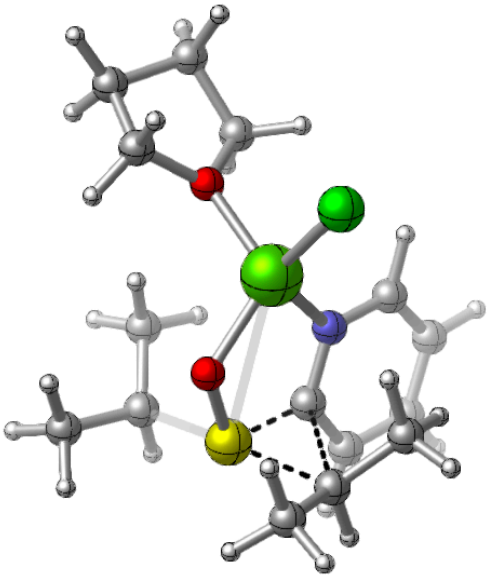
B3LYP-D3BJ/def2-SVP-CPCM(THF)

Zero-point correction= 0.388518 (Hartree/Particle)
Thermal correction to Energy= 0.414021
Thermal correction to Enthalpy= 0.414965
Thermal correction to Gibbs Free Energy= 0.331602
Sum of electronic and zero-point Energies= -1849.850947
Sum of electronic and thermal Energies= -1849.825444
Sum of electronic and thermal Enthalpies= -1849.824499
Sum of electronic and thermal Free Energies= -1849.907863
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5078561
Coordinates

S	-7.73157	5.32462	-1.47758
O	-8.54628	5.7398	-2.78151
C	-5.99517	5.76252	-2.26056
C	-7.91128	6.68743	-0.36069
C	-7.4849	6.61465	0.98127
C	-8.49729	8.92743	-0.12092
C	-7.61257	7.74404	1.77072
H	-7.07195	5.68669	1.37617
C	-8.13873	8.93147	1.2172
H	-8.90007	9.82233	-0.60421
H	-7.29583	7.71655	2.81608
H	-8.25172	9.83695	1.81433
N	-8.36261	7.84012	-0.90846
Mg	-9.08284	7.6156	-2.89277
C	-9.96152	5.04592	-0.46155
H	-10.54362	5.92108	-0.79588
C	-10.30255	3.79404	-1.23655
H	-11.30136	3.38347	-0.96774
H	-10.29693	3.96853	-2.3229
H	-9.57582	2.98424	-1.02805
C	-10.00652	4.8471	1.0301
H	-9.88795	5.78594	1.59327
H	-10.96101	4.3887	1.37218
H	-9.20718	4.15802	1.36971
O	-7.59612	8.49886	-3.95429
C	-6.72204	9.54701	-3.45306
C	-7.12043	7.99266	-5.23168
C	-5.76314	9.83689	-4.60169
H	-7.34436	10.40566	-3.16335
H	-6.20226	9.16097	-2.56198
C	-5.68475	8.48481	-5.32098
H	-7.22444	6.89903	-5.22206
H	-7.75583	8.41272	-6.02815
H	-4.78896	10.19538	-4.24062
H	-6.18735	10.60172	-5.27116

H	-5.0119	7.79742	-4.78374
H	-5.34014	8.56528	-6.36146
Cl	-11.08594	8.49191	-3.53584
C	-4.94774	5.64968	-1.16408
H	-5.05704	6.43418	-0.39962
H	-5.00735	4.67004	-0.65608
H	-3.93027	5.73595	-1.58293
H	-6.0752	6.79549	-2.62971
C	-5.76041	4.79355	-3.40831
H	-5.80813	3.74716	-3.05607
H	-6.5129	4.91567	-4.19991
H	-4.76063	4.94006	-3.85373

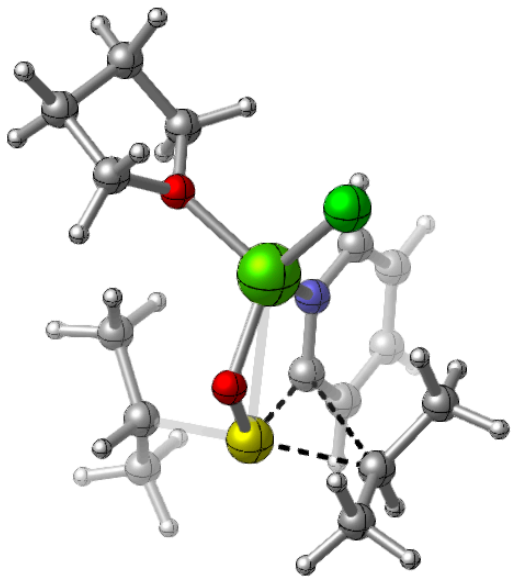
A6 = A6.1-Mg TS-F-eq-D 120/0



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388669 (Hartree/Particle)
Thermal correction to Energy= 0.414215
Thermal correction to Enthalpy= 0.415159
Thermal correction to Gibbs Free Energy= 0.331425
Sum of electronic and zero-point Energies= -1849.849582
Sum of electronic and thermal Energies= -1849.824036
Sum of electronic and thermal Enthalpies= -1849.823091
Sum of electronic and thermal Free Energies= -1849.906826
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.505873
Coordinates

S	-7.76079	5.2588	-1.32069
O	-8.28649	5.72578	-2.75475
C	-5.82557	5.34681	-1.85191
H	-5.3768	5.04723	-0.88458
C	-5.62671	4.23592	-2.86898
H	-6.03116	4.52848	-3.85143
H	-4.55817	3.98678	-3.00536
H	-6.14147	3.30796	-2.56047
C	-5.24835	6.67705	-2.29846
H	-4.16334	6.5937	-2.50425
H	-5.72785	7.02585	-3.2239
H	-5.3709	7.46297	-1.53667
C	-7.74797	6.7376	-0.31193
C	-7.45755	6.69893	1.05634
C	-8.11563	9.02749	-0.25401
C	-7.51352	7.89094	1.77116
H	-7.1948	5.75615	1.53853
C	-7.84362	9.08261	1.10691
H	-8.38967	9.92434	-0.81595
H	-7.29194	7.89844	2.84105
H	-7.89163	10.03435	1.63743
N	-8.06326	7.87759	-0.95232
Mg	-8.73314	7.60046	-2.97649
C	-9.8933	5.12165	-0.55765
C	-10.42763	3.98745	-1.40516
H	-11.3426	3.52145	-0.98123
H	-10.68705	4.34025	-2.41786
H	-9.6833	3.17713	-1.52187
O	-7.33958	8.56288	-4.08662
C	-6.74922	9.83312	-3.70061
C	-7.09213	8.27949	-5.49038
C	-6.27468	10.45645	-5.00788
H	-7.51402	10.42829	-3.18058
H	-5.91931	9.62304	-3.00791
C	-5.96545	9.22719	-5.87075
H	-6.84038	7.21318	-5.57938
H	-8.01735	8.48407	-6.05303
H	-5.40637	11.11317	-4.85749
H	-7.08369	11.04885	-5.46339
H	-4.99138	8.7937	-5.59316
H	-5.95568	9.44414	-6.94808
Cl	-10.66619	8.5121	-3.80592
C	-10.82943	6.30737	-0.48425
H	-10.45837	7.10114	0.18534
H	-10.99645	6.76491	-1.47629
H	-11.84115	6.03066	-0.11341
H	-9.63211	4.76308	0.45713

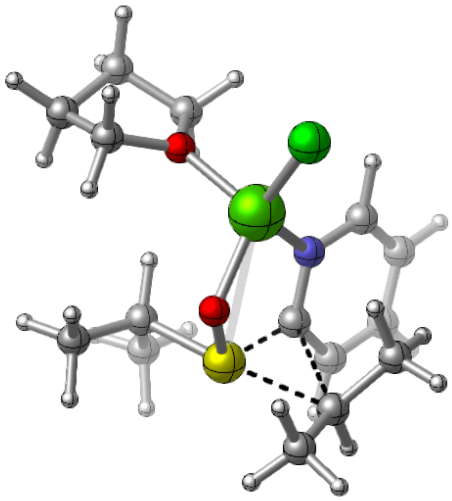
A6 = A6.1-Mg TS-F-eq-D 120/120



B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388603 (Hartree/Particle)
Thermal correction to Energy= 0.414136
Thermal correction to Enthalpy= 0.415080
Thermal correction to Gibbs Free Energy= 0.331256
Sum of electronic and zero-point Energies= -1849.849998
Sum of electronic and thermal Energies= -1849.824466
Sum of electronic and thermal Enthalpies= -1849.823522
Sum of electronic and thermal Free Energies= -1849.907346
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5059796
Coordinates

S	-7.75471	5.26476	-1.26916
O	-8.26059	5.71219	-2.71697
C	-5.81512	5.33891	-1.7934
C	-5.26477	6.64178	-2.34102
H	-4.19421	6.54615	-2.60799
H	-5.79913	6.96612	-3.24274
H	-5.33288	7.452	-1.59539
C	-7.77655	6.75531	-0.27849
C	-7.56203	6.73686	1.10533
C	-8.12276	9.05113	-0.2736
C	-7.64084	7.94044	1.79685
H	-7.33964	5.79964	1.6163
C	-7.91887	9.12622	1.09729
H	-8.35808	9.94045	-0.86451
H	-7.47654	7.96209	2.87678
H	-7.9816	10.08705	1.60956
N	-8.04915	7.8886	-0.95065
Mg	-8.70483	7.58337	-2.97408
C	-9.90888	5.13324	-0.53979
C	-10.43181	3.99428	-1.38768
H	-11.36385	3.54528	-0.98258
H	-10.65978	4.33692	-2.41128
H	-9.69471	3.17401	-1.47308
O	-7.32747	8.56481	-4.0869
C	-6.73913	9.82942	-3.67893
C	-7.10053	8.31786	-5.50103
C	-6.29585	10.49013	-4.97852
H	-7.49776	10.40428	-3.12789
H	-5.89395	9.60805	-3.00859
C	-5.9895	9.28579	-5.87671
H	-6.83976	7.25656	-5.61977
H	-8.03676	8.52641	-6.04341
H	-5.43219	11.15289	-4.82784
H	-7.11984	11.08411	-5.40421
H	-5.00678	8.85546	-5.62594
H	-6.00005	9.52914	-6.94837
Cl	-10.64437	8.48609	-3.80214
C	-10.83831	6.32458	-0.49562
H	-10.47872	7.11933	0.17902
H	-10.97796	6.77782	-1.49376
H	-11.86053	6.05571	-0.14852
H	-9.66313	4.78338	0.48148
C	-5.06009	4.84176	-0.57044
H	-4.99396	5.62318	0.20684
H	-5.55269	3.96215	-0.11882
H	-4.025	4.5466	-0.81859
H	-5.81322	4.56198	-2.57827

A6 = A6.1-Mg TS-F-eq-D 120/240

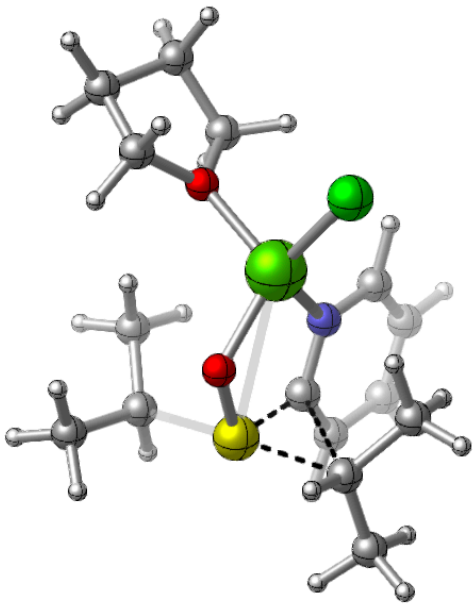


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388467 (Hartree/Particle)
Thermal correction to Energy= 0.413983

Thermal correction to Enthalpy= 0.414927
Thermal correction to Gibbs Free Energy= 0.331767
Sum of electronic and zero-point Energies= -1849.853696
Sum of electronic and thermal Energies= -1849.828180
Sum of electronic and thermal Enthalpies= -1849.827236
Sum of electronic and thermal Free Energies= -1849.910396
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5104571
Coordinates

S	-7.80028	5.39016	-1.47278
O	-8.63829	5.80472	-2.76553
C	-6.06711	5.81258	-2.30321
C	-7.91748	6.77799	-0.37285
C	-7.59915	6.68907	0.99548
C	-8.42711	9.04049	-0.17891
C	-7.72541	7.8279	1.77144
H	-7.26579	5.7414	1.41993
C	-8.14878	9.03752	1.17575
H	-8.76322	9.94722	-0.68975
H	-7.48682	7.79257	2.83706
H	-8.25402	9.95193	1.76078
N	-8.30084	7.93663	-0.95063
Mg	-8.99433	7.71523	-2.95672
C	-9.88734	5.04694	-0.353
C	-10.39341	3.87804	-1.16497
H	-11.26826	3.37859	-0.69379
H	-10.7128	4.20289	-2.16915
H	-9.61936	3.101	-1.3012
O	-7.43307	8.52348	-3.9717
C	-6.52913	9.54652	-3.47349
C	-7.01814	8.05726	-5.2839
C	-5.59793	9.84775	-4.64278
H	-7.12816	10.40911	-3.14827
H	-5.99127	9.13311	-2.60563
C	-5.57441	8.51706	-5.40475
H	-7.15129	6.96695	-5.31258
H	-7.67027	8.52364	-6.04022
H	-4.6047	10.17197	-4.30166
H	-6.02315	10.64232	-5.2759
H	-4.9032	7.79725	-4.90942
H	-5.26024	8.62172	-6.4527
Cl	-10.85989	8.66398	-3.86553
C	-10.86838	6.18502	-0.23898
H	-10.53688	6.96095	0.46966
H	-11.03664	6.68015	-1.2142
H	-11.87471	5.85211	0.09884
H	-9.50335	4.72782	0.63208
C	-5.01305	5.70046	-1.21401
H	-5.10836	6.49654	-0.45873
H	-5.08498	4.7294	-0.69029
H	-3.99497	5.76639	-1.63579
H	-6.13025	6.83859	-2.69108
C	-5.86385	4.81938	-3.43556
H	-5.94116	3.7799	-3.06698
H	-6.61704	4.94962	-4.22566
H	-4.86301	4.92695	-3.8905

A6 = A6.1-Mg TS-F-eq-D 240/0

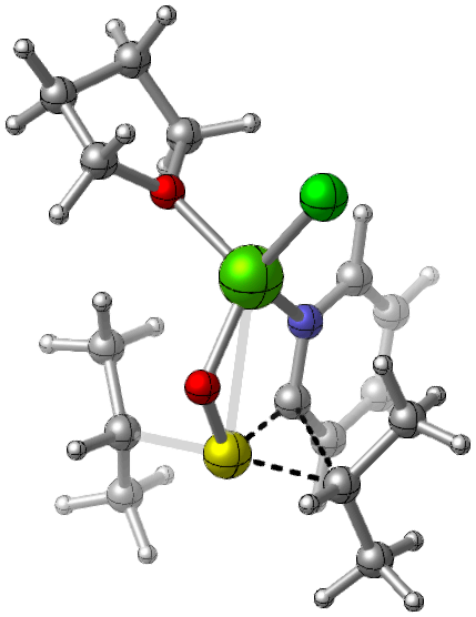


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.388979 (Hartree/Particle)
Thermal correction to Energy= 0.414299
Thermal correction to Enthalpy= 0.415243
Thermal correction to Gibbs Free Energy= 0.332526
Sum of electronic and zero-point Energies= -1849.850258
Sum of electronic and thermal Energies= -1849.824939
Sum of electronic and thermal Enthalpies= -1849.823995
Sum of electronic and thermal Free Energies= -1849.906711
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.506607
Coordinates

S	-7.81113	5.25968	-1.23361
O	-8.31943	5.71468	-2.68174
C	-5.85556	5.3369	-1.77659

H	-5.41111	5.05053	-0.80296
C	-5.66334	4.20731	-2.77334
H	-6.07282	4.48173	-3.75916
H	-4.59617	3.95131	-2.91305
H	-6.17853	3.28639	-2.4446
C	-5.26675	6.6535	-2.24631
H	-4.18033	6.56318	-2.44493
H	-5.73947	6.9875	-3.18078
H	-5.38898	7.45674	-1.50208
C	-7.73319	6.76316	-0.2548
C	-7.33465	6.76531	1.08444
C	-8.10507	9.05228	-0.23568
C	-7.34345	7.97912	1.76899
H	-7.01968	5.8413	1.5693
C	-7.73326	9.14664	1.10092
H	-8.42116	9.9322	-0.80198
H	-7.03832	8.01799	2.81737
H	-7.74764	10.11315	1.60623
N	-8.09984	7.88309	-0.90021
Mg	-8.75954	7.58535	-2.92822
C	-9.91359	5.1177	-0.54101
O	-7.34413	8.52118	-4.03957
C	-6.7722	9.80746	-3.6817
C	-7.11701	8.22393	-5.44393
C	-6.3449	10.42679	-5.00682
H	-7.53605	10.39195	-3.14833
H	-5.9205	9.62284	-3.0082
C	-6.02368	9.19495	-5.86144
H	-6.83912	7.16334	-5.52291
H	-8.0584	8.39634	-5.99025
H	-5.49139	11.10845	-4.88543
H	-7.18045	10.99123	-5.44983
H	-5.03276	8.79006	-5.60079
H	-6.04371	9.39825	-6.9413
Cl	-10.65001	8.54042	-3.80856
C	-10.86838	6.29064	-0.58283
H	-10.55264	7.10229	0.09748
H	-10.96582	6.72679	-1.59117
H	-11.89988	6.01518	-0.27277
H	-10.19149	4.36354	-1.29786
C	-9.79104	4.48121	0.82585
H	-8.94609	3.76573	0.86313
H	-9.61357	5.23758	1.61216
H	-10.69633	3.9197	1.13298

A6 = A6.1-Mg TS-F-eq-D 240/120

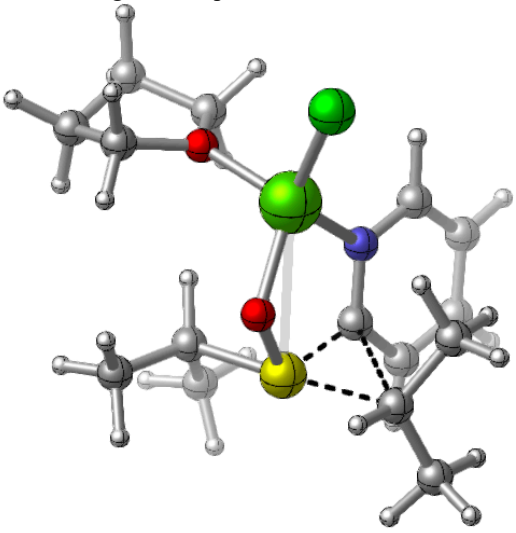


B3LYP-D3BJ/def2-SVP-CPCM(THF)
Zero-point correction= 0.389127 (Hartree/Particle)
Thermal correction to Energy= 0.414357
Thermal correction to Enthalpy= 0.415301
Thermal correction to Gibbs Free Energy= 0.333187
Sum of electronic and zero-point Energies= -1849.850638
Sum of electronic and thermal Energies= -1849.825408
Sum of electronic and thermal Enthalpies= -1849.824464
Sum of electronic and thermal Free Energies= -1849.906578
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5067148
Coordinates

S	-7.81743	5.26904	-1.16254
O	-8.29633	5.70195	-2.62879
C	-5.84345	5.3365	-1.70627
C	-5.27433	6.6346	-2.2448
H	-4.20242	6.53392	-2.50883
H	-5.8012	6.97161	-3.14663
H	-5.33608	7.44357	-1.49602
C	-7.76023	6.79218	-0.20912
C	-7.4322	6.82365	1.14903
C	-8.10383	9.08652	-0.2618
C	-7.4555	8.05465	1.80206
H	-7.16229	5.90807	1.67351
C	-7.79282	9.21059	1.08728

H	-8.38113	9.95455	-0.86577
H	-7.20399	8.11466	2.86359
H	-7.81629	10.1899	1.56701
N	-8.08466	7.90029	-0.8959
Mg	-8.72264	7.56724	-2.92478
C	-9.92007	5.1134	-0.52048
O	-7.32183	8.51383	-4.04548
C	-6.75004	9.79826	-3.6788
C	-7.13803	8.2493	-5.46303
C	-6.37224	10.44921	-5.00371
H	-7.5008	10.36393	-3.10788
H	-5.87524	9.6073	-3.03752
C	-6.06667	9.23871	-5.8937
H	-6.85438	7.19302	-5.57364
H	-8.09819	8.42568	-5.97419
H	-5.52214	11.13736	-4.89567
H	-7.22752	11.0135	-5.40757
H	-5.06459	8.83791	-5.67219
H	-6.12225	9.46417	-6.96791
Cl	-10.61748	8.51069	-3.81245
C	-10.87029	6.28914	-0.58869
H	-10.56565	7.1034	0.09349
H	-10.94673	6.71934	-1.60108
H	-11.90751	6.01661	-0.29699
H	-10.18588	4.3549	-1.27696
C	-9.82545	4.48669	0.85331
H	-8.96855	3.78752	0.91966
H	-9.68636	5.25029	1.63985
H	-10.72882	3.90978	1.13478
C	-5.09094	4.81331	-0.49453
H	-4.96032	5.59913	0.27019
H	-5.62689	3.97178	-0.01796
H	-4.07996	4.44999	-0.75473
H	-5.8626	4.5683	-2.49926

A6 = A6.1-Mg TS-F-eq-D 240/240



B3LYP-D3BJ/def2-SVP-CPCM(THF)

Zero-point correction= 0.388645 (Hartree/Particle)
Thermal correction to Energy= 0.414149
Thermal correction to Enthalpy= 0.415093
Thermal correction to Gibbs Free Energy= 0.331932
Sum of electronic and zero-point Energies= -1849.854459
Sum of electronic and thermal Energies= -1849.828955
Sum of electronic and thermal Enthalpies= -1849.828011
Sum of electronic and thermal Free Energies= -1849.911172
B3LYP-D3BJ/def2-TZVPP-CPCM(THF)//B3LYP-D3BJ/def2-SVP-CPCM(THF)
HF= -1851.5111055
Coordinates

S	-7.85552	5.39939	-1.34971
O	-8.67854	5.79569	-2.66513
C	-6.10771	5.80254	-2.22592
C	-7.90239	6.83874	-0.2967
C	-7.52313	6.80812	1.05417
C	-8.4191	9.10285	-0.17515
C	-7.62298	7.9811	1.78999
H	-7.14881	5.88769	1.49984
C	-8.07941	9.1578	1.16747
H	-8.78051	9.98658	-0.70824
H	-7.33222	7.99103	2.84307
H	-8.16241	10.09622	1.71709
N	-8.32324	7.96812	-0.89905
Mg	-9.02669	7.69368	-2.90313
C	-9.88729	5.03012	-0.35136
O	-7.48038	8.49718	-3.94394
C	-6.56798	9.52274	-3.46735
C	-7.06832	7.99868	-5.24535
C	-5.63673	9.79408	-4.64383
H	-7.16024	10.39579	-3.15791
H	-6.03057	9.12245	-2.59306
C	-5.62206	8.44731	-5.37734
H	-7.20747	6.90878	-5.24916
H	-7.71834	8.4515	-6.01165
H	-4.64113	10.11947	-4.31081
H	-6.05817	10.57766	-5.29301
H	-4.95475	7.73422	-4.8674
H	-5.30863	8.52789	-6.42765
Cl	-10.9037	8.62509	-3.80479
C	-10.89966	6.14736	-0.2957
H	-10.61614	6.92301	0.43806
H	-11.02507	6.64532	-1.27235
H	-11.9123	5.79616	-0.00082
H	-10.14895	4.29741	-1.13152
C	-9.61297	4.3507	0.96701

H	-8.71971	3.69873	0.91
H	-9.43944	5.08029	1.77777
H	-10.45159	3.70775	1.3061
C	-5.04572	5.69266	-1.14538
H	-5.0936	6.52512	-0.42547
H	-5.16066	4.7512	-0.57508
H	-4.02761	5.68669	-1.5738
H	-6.15741	6.82108	-2.63591
C	-5.93068	4.78031	-3.33596
H	-6.03488	3.75151	-2.94286
H	-6.68332	4.90955	-4.12683
H	-4.92852	4.84654	-3.79772

Bibliography

(1) Sperger, T.; Sanhueza, I. A.; Schoenebeck, F. Computation and Experiment: A Powerful Combination to Understand and Predict Reactivities. *Acc. Chem. Res.* **2016**, *49*, 1311–1319.

(2) Atkins, P. W.; De Paula, J. *Physical Chemistry*, 9th ed.; W.H. Freeman: New York, 2010.

(3) Echenique, P.; Alonso, J. L. A Mathematical and Computational Review of Hartree-Fock SCF Methods in Quantum Chemistry. **2007**.

(4) Griffiths, D. J. *Introduction to Quantum Mechanics*, Second edition.; Cambridge University Press: Cambridge, 2017.

(5) Hartree, D. R. The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I. Theory and Methods. *Math. Proc. Camb. Philos. Soc.* **1928**, *24*, 89–110.

(6) Fock, V. Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems. *Z. Für Phys.* **1930**, *61*, 126–148.

(7) Slater, J. C. Note on Hartree's Method. *Phys. Rev.* **1930**, *35*, 210–211.

(8) Jensen, F. *Introduction to Computational Chemistry*, Third edition.; Wiley: Chichester, UK ; Hoboken, NJ, 2017.

(9) Roothaan, C. C. J. New Developments in Molecular Orbital Theory. *Rev. Mod. Phys.* **1951**, *23*, 69–89.

(10) Löwdin, P.-O. Quantum Theory of Many-Particle Systems. III. Extension of the Hartree-Fock Scheme to Include Degenerate Systems and Correlation Effects. *Phys. Rev.* **1955**, *97*, 1509–1520.

(11) Ruiz, I.; Matito, E.; Holguín-Gallego, F. J.; Francisco, E.; Martín Pendás, Á.; Rocha-Rinza, T. Fermi and Coulomb Correlation Effects upon the Interacting Quantum Atoms Energy Partition. *Theor. Chem. Acc.* **2016**, *135*, 209.

(12) Hättig, C.; Klopper, W.; Köhn, A.; Tew, D. P. Explicitly Correlated Electrons in Molecules. *Chem. Rev.* **2012**, *112*, 4–74.

(13) Ramos-Cordoba, E.; Salvador, P.; Matito, E. Separation of Dynamic and Nondynamic Correlation. *Phys. Chem. Chem. Phys.* **2016**, *18*, 24015–24023.

(14) Maurice, D.; Head-Gordon, M. Analytical Second Derivatives for Excited Electronic States Using the Single Excitation Configuration Interaction Method: Theory and Application to Benzo[a]Pyrene and Chalcone. *Mol. Phys.* **1999**, *96*, 1533–1541.

(15) Purvis, G. D.; Bartlett, R. J. A Full Coupled-cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.

(16) Møller, Chr.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, *46*, 618–622.

(17) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. Quadratic Configuration Interaction. A General Technique for Determining Electron Correlation Energies. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

(18) Neese, F. Prediction of Molecular Properties and Molecular Spectroscopy with Density Functional Theory: From Fundamental Theory to Exchange-Coupling. *Coord. Chem. Rev.* **2009**, *253*, 526–563.

(19) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.

(20) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(21) Perdew, J. P.; Zunger, A. Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.
(22) Kümmel, S.; Perdew, J. P. Two Avenues to Self-Interaction Correction within Kohn—Sham Theory: Unitary Invariance Is the Shortcut. *Mol. Phys.* **2003**, *101*, 1363–1368.
(23) Bretonnet, J.-L.; Université de Lorraine, LCP-A2MC, EA 3469, 1 Bd. François Arago, Metz, F-57078, France. Basics of the Density Functional Theory. *AIMS Mater. Sci.* **2017**, *4*, 1372–1405.
(24) Grimme, S.; Hansen, A.; Brandenburg, J. G.; Bannwarth, C. Dispersion-Corrected Mean-Field Electronic Structure Methods. *Chem. Rev.* **2016**, *116*, 5105–5154.
(25) Kim, K.; Jordan, K. D. Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer. *J. Phys. Chem.* **1994**, *98*, 10089–10094.
(26) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
(27) Lee, C.; Sosa, C. Local Density Component of the Lee–Yang–Parr Correlation Energy Functional. *J. Chem. Phys.* **1994**, *100*, 9018–9024.
(28) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
(29) Chai, J.-D.; Head-Gordon, M. Systematic Optimization of Long-Range Corrected Hybrid Density Functionals. *J. Chem. Phys.* **2008**, *128*, 084106.
(30) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
(31) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.
(32) Hirata, S.; Head-Gordon, M. Time-Dependent Density Functional Theory within the Tamm–Dancoff Approximation. *Chem. Phys. Lett.* **1999**, *314*, 291–299.
(33) Casida, M. E.; Huix-Rotllant, M. Progress in Time-Dependent Density-Functional Theory. *Annu. Rev. Phys. Chem.* **2012**, *63*, 287–323.
(34) S Saebo, and; Pulay, P. Local Treatment of Electron Correlation. *Annual Review of Physical Chemistry*, 1993, *44*, 213–236.
(35) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural Triple Excitations in Local Coupled Cluster Calculations with Pair Natural Orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.
(36) Riplinger, C.; Neese, F. An Efficient and near Linear Scaling Pair Natural Orbital Based Local Coupled Cluster Method. *J. Chem. Phys.* **2013**, *138*, 034106.
(37) Neese, F. The ORCA Program System: The ORCA Program System. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 73–78.
(38) Friedrich, J.; Hänchen, J. Incremental CCSD(T)(F12*)|MP2: A Black Box Method To Obtain Highly Accurate Reaction Energies. *J. Chem. Theory Comput.* **2013**, *9*, 5381–5394.

(39) Řezáč, J.; Riley, K. E.; Hobza, P. S66: A Well-Balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures. *J. Chem. Theory Comput.* **2011**, *7*, 2427–2438.
(40) Slater, J. C. Atomic Shielding Constants. *Phys. Rev.* **1930**, *36*, 57–64.
(41) Electronic Wave Functions - I. A General Method of Calculation for the Stationary States of Any Molecular System. *Proc. R. Soc. Lond. Ser. Math. Phys. Sci.* **1950**, *200*, 542–554.
(42) Jensen, F. Atomic Orbital Basis Sets. *WIREs Comput. Mol. Sci.* **2013**, *3*, 273–295.
(43) Hill, J. G. Gaussian Basis Sets for Molecular Applications. *Int. J. Quantum Chem.* **2013**, *113*, 21–34.
(44) Schwerdtfeger, P. The Pseudopotential Approximation in Electronic Structure Theory. *ChemPhysChem* **2011**, *12*, 3143–3155.
(45) Hay, P. J.; Wadt, W. R. *Ab Initio* Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299–310.
(46) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999–3094.
(47) Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
(48) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
(49) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54*, 724–728.
(50) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
(51) Schlegel, H. B. Optimization of Equilibrium Geometries and Transition Structures. *J. Comput. Chem.* **1982**, *3*, 214–218.
(52) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. Fluorine in Medicinal Chemistry. *Chem Soc Rev* **2008**, *37*, 320–330.
(53) Wang, J.; Sánchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. Fluorine in Pharmaceutical Industry: Fluorine-Containing Drugs Introduced to the Market in the Last Decade (2001–2011). *Chem. Rev.* **2014**, *114*, 2432–2506.
(54) Hansch, Corwin.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91*, 165–195.
(55) Toulgoat, F.; Alazet, S.; Billard, T. Direct Trifluoromethylthiolation Reactions: The "Renaissance" of an Old Concept: Direct Trifluoromethylthiolation Reactions. *Eur. J. Org. Chem.* **2014**, *2014*, 2415–2428.
(56) Barata-Vallejo, S.; Bonesi, S.; Postigo, A. Late Stage Trifluoromethylthiolation Strategies for Organic Compounds. *Org. Biomol. Chem.* **2016**, *14*, 7150–7182.

(57) Xu, X.-H.; Matsuzaki, K.; Shibata, N. Synthetic Methods for Compounds Having CF3–S Units on Carbon by Trifluoromethylation, Trifluoromethylthiolation, Triflylation, and Related Reactions. *Chem. Rev.* **2015**, *115*, 731–764.
(58) Landelle, G.; Panossian, A.; Pazenok, S.; Vors, J.-P.; Leroux, F. R. Recent Advances in Transition Metal-Catalyzed Csp ^{2} -Monofluoro-, Difluoro-, Perfluoromethylation and Trifluoromethylthiolation. *Beilstein J. Org. Chem.* **2013**, *9*, 2476–2536.
(59) Zheng, H.; Huang, Y.; Weng, Z. Recent Advances in Trifluoromethylthiolation Using Nucleophilic Trifluoromethylthiolating Reagents. *Tetrahedron Lett.* **2016**, *57*, 1397–1409.
(60) Zhang, C. Advances in Trifluoromethylation or Trifluoromethylthiolation with Copper CF_3 or SCF_3 Complexes. *J. Chem. Sci.* **2017**, *129*, 1795–1805.
(61) Guo, Y.; Huang, M.-W.; Fu, X.-L.; Liu, C.; Chen, Q.-Y.; Zhao, Z.-G.; Zeng, B.-Z.; Chen, J. Recent Catalytic Syntheses of Trifluoromethylthio-Containing Organic Compounds by Transition Metals, Chiral Organocatalysts, and Photocatalysts. *Chin. Chem. Lett.* **2017**, *28*, 719–728.
(62) Hamzehloo, M.; Hosseinian, A.; Ebrahimiasl, S.; Monfared, A.; Vessally, E. Direct C-H Trifluoromethylthiolation of (Hetero)Arenes: A Review. *J. Fluor. Chem.* **2019**, *224*, 52–60.
(63) Lin, J.-H.; Ji, Y.-L.; Xiao, J.-C. Recent Advances in C-H Trifluoromethylthiolation and Trifluoromethoxylation Reactions. *Curr. Org. Chem.* **2015**, *19*, 1541–1553.
(64) Hardy, M. A.; Chachignon, H.; Cahard, D. Advances in Asymmetric Di-and Trifluoromethylthiolation, and Di- and Trifluoromethoxylation Reactions. *Asian J. Org. Chem.* **2019**, *8*, 591–609.
(65) Guo-Liang, X.; Shang-Hua, J.; Xiangdong, S.; Behmagham, F. Recent Trends in Direct Trifluoromethylthiolation of N H Bonds. *J. Fluor. Chem.* **2020**, *235*, 109524.
(66) Zhang, K.; Xu, X.; Qing, F. Recent Advances of Direct Trifluoromethylthiolation. *Chin. J. Org. Chem.* **2015**, *35*, 556.
(67) Ge, H.; Liu, H.; Shen, Q. Introduction of Trifluoromethylthio Group into Organic Molecules. In *Organofluorine Chemistry*; Szabó, K., Selander, N., Eds.; Wiley, 2021; pp 99–172.
(68) Toulgoat, F.; Liger, F.; Billard, T. Chemistry of OCF_3 , SCF_3 , and $SECF_3$ Functional Groups. In *Organofluorine Chemistry*; Szabó, K., Selander, N., Eds.; Wiley, 2021; pp 49–97.
(69) Liu, Y.; Xu, X.; Qing, F. Deoxygenative 1,1-Bis-trifluoromethylthiolation of Aromatic Aldehydes to Access Bis(Trifluoromethylthio)Methylarenes. *Adv. Synth. Catal.* **2020**, *362*, 5031–5035.
(70) Alazet, S.; Zimmer, L.; Billard, T. Electrophilic Trifluoromethylthiolation of Carbonyl Compounds. *Chem. - Eur. J.* **2014**, *20*, 8589–8593.
(71) Alazet, S.; Ismalaj, E.; Glenadel, Q.; Le Bars, D.; Billard, T. Acid-Catalyzed Synthesis of α-Trifluoromethylthiolated Carbonyl Compounds: Acid Catalyzed α-Trifluoromethylthiolation. *Eur. J. Org. Chem.* **2015**, *2015*, 4607–4610.
(72) Xu, C.; Ma, B.; Shen, Q. *N* -Trifluoromethylthiosaccharin: An Easily Accessible, Shelf-Stable, Broadly Applicable Trifluoromethylthiolating Reagent. *Angew. Chem.* **2014**, *126*, 9470–9474.

(73) Hu, L.; Wu, M.; Wan, H.; Wang, J.; Wang, G.; Guo, H.; Sun, S. Efficient Catalytic α-Trifluoromethylthiolation of Aldehydes. *New J. Chem.* **2016**, *40*, 6550–6553.
(74) Mukherjee, S.; Patra, T.; Glorius, F. Cooperative Catalysis: A Strategy To Synthesize Trifluoromethyl-Thioesters from Aldehydes. *ACS Catal.* **2018**, *8*, 5842–5846.
(75) Wang, M.-Y.; Zhu, X.-Q.; Zhang, X.-L.; Guo, R.-L.; Jia, Q.; Wang, Y.-Q. Synthesis of Trifluoromethylthioesters from Aldehydes *via* a Visible Light-Promoted Radical Process. *Org. Biomol. Chem.* **2020**, *18*, 5918–5926.
(76) Xu, B.; Li, D.; Lu, L.; Wang, D.; Hu, Y.; Shen, Q. Radical Fluoroalkylthiolation of Aldehydes with $PhSO_2SR_f$ ($R_f = CF_3$, C_2F_5, CF_2H or CH_2F): A General Protocol for the Preparation of Fluoroalkylthioesters. *Org. Chem. Front.* **2018**, *5*, 2163–2166.
(77) Zhang, F.; Wang, X.; Zhou, Y.; Shi, H.; Feng, Z.; Ma, J.; Marek, I. Remote Fluorination and Fluoroalkyl(Thiol)Ation Reactions. *Chem. – Eur. J.* **2020**, *26*, 15378–15396.
(78) Mukherjee, S.; Maji, B.; Tlahuext-Aca, A.; Glorius, F. Visible-Light-Promoted Activation of Unactivated C(Sp^3)–H Bonds and Their Selective Trifluoromethylthiolation. *J. Am. Chem. Soc.* **2016**, *138*, 16200–16203.
(79) Modak, A.; Pinter, E. N.; Cook, S. P. Copper-Catalyzed, N-Directed Csp^3–H Trifluoromethylthiolation ($-SCF_3$) and Trifluoromethylselenation ($-SeCF_3$). *J. Am. Chem. Soc.* **2019**, *141*, 18405–18410.
(80) Davies, J.; Sheikh, N. S.; Leonori, D. Photoredox Imino Functionalizations of Olefins. *Angew. Chem.* **2017**, *129*, 13546–13550.
(81) Xu, W.; Wang, W.; Liu, T.; Xie, J.; Zhu, C. Late-Stage Trifluoromethylthiolation of Benzylic C-H Bonds. *Nat. Commun.* **2019**, *10*, 4867.
(82) Barday, M.; Blieck, R.; Ruyet, L.; Besset, T. Remote Trifluoromethylthiolation of Alcohols under Visible Light. *Tetrahedron* **2020**, *76*, 131153.
(83) Zhao, Y.; Lin, J.-H.; Hang, X.-C.; Xiao, J.-C. Ag-Mediated Trifluoromethylthiolation of Inert Csp^3–H Bond. *J. Org. Chem.* **2018**, *83*, 14120–14125.
(84) Candish, L.; Pitzer, L.; Gómez-Suárez, A.; Glorius, F. Visible Light-Promoted Decarboxylative Di- and Trifluoromethylthiolation of Alkyl Carboxylic Acids. *Chem. - Eur. J.* **2016**, *22*, 4753–4756.
(85) Ghiazza, C.; Billard, T.; Tlili, A. Merging Visible-Light Catalysis for the Direct Late-Stage Group-16–Trifluoromethyl Bond Formation. *Chem. – Eur. J.* **2019**, *25*, 6482–6495.
(86) Xu, W.; Ma, J.; Yuan, X.-A.; Dai, J.; Xie, J.; Zhu, C. Synergistic Catalysis for the Umpolung Trifluoromethylthiolation of Tertiary Ethers. *Angew. Chem. Int. Ed.* **2018**, *57*, 10357–10361.
(87) Dagousset, G.; Simon, C.; Anselmi, E.; Tuccio, B.; Billard, T.; Magnier, E. Generation of the SCF_3 Radical by Photoredox Catalysis: Intra- and Intermolecular Carbotrifluoromethylthiolation of Alkenes. *Chem. - Eur. J.* **2017**, *23*, 4282–4286.
(88) Ji, T.; Chen, X.-Y.; Huang, L.; Rueping, M. Remote Trifluoromethylthiolation Enabled by Organophotocatalytic C–C Bond Cleavage. *Org. Lett.* **2020**, *22*, 2579–2583.
(89) Zhao, X.; Tian, M.; Ji, L.; Liu, J.; Lu, K. Metal-Free Sp^3 C-SCF_3 Coupling Reactions between Cycloketone Oxime Esters and *S*-Trifluoromethyl 4-Methylbenzenesulfonothioate. *Org. Lett.* **2020**, *22*, 863–866.

(90) Pan, S.; Huang, Y.; Xu, X.-H.; Qing, F.-L. Copper-Assisted Oxidative Trifluoromethylthiolation of 2,3-Allenoic Acids with AgSCF $_3$. *Org. Lett.* **2017**, *19*, 4624–4627.
(91) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. *Chem. Rev.* **2016**, *116*, 10035–10074.
(92) Matsui, J. K.; Lang, S. B.; Heitz, D. R.; Molander, G. A. Photoredox-Mediated Routes to Radicals: The Value of Catalytic Radical Generation in Synthetic Methods Development. *ACS Catal.* **2017**, *7*, 2563–2575.
(93) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322–5363.
(94) Romero, N. A.; Nicewicz, D. A. Organic Photoredox Catalysis. *Chem. Rev.* **2016**, *116*, 10075–10166.
(95) Narayanam, J. M. R.; Stephenson, C. R. J. Visible Light Photoredox Catalysis: Applications in Organic Synthesis. *Chem. Soc. Rev.* **2010**, *40*, 102–113.
(96) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.* **2016**, *81*, 6898–6926.
(97) Milligan, J. A.; Phelan, J. P.; Badir, S. O.; Molander, G. A. Alkyl Carbon–Carbon Bond Formation by Nickel/Photoredox Cross-Coupling. *Angew. Chem. Int. Ed.* **2019**, *58*, 6152–6163.
(98) Lipp, A.; Badir, S. O.; Molander, G. A. Stereoinduction in Metallaphotoredox Catalysis. *Angew. Chem. Int. Ed.* **2021**, *60*, 1714–1726.
(99) Badir, S. O.; Molander, G. A. Developments in Photoredox/Nickel Dual-Catalyzed 1,2-Difunctionalizations. *Chem* **2020**, *6*, 1327–1339.
(100) Crisenza, G. E. M.; Mazzarella, D.; Melchiorre, P. Synthetic Methods Driven by the Photoactivity of Electron Donor–Acceptor Complexes. *J. Am. Chem. Soc.* **2020**, *142*, 5461–5476.
(101) Cong, F.; Lv, X.-Y.; Day, C. S.; Martin, R. Dual Catalytic Strategy for Forging Sp ^{2} – Sp ^{3} and Sp ^{3} – Sp ^{3} Architectures via β - Scission of Aliphatic Alcohol Derivatives. *J. Am. Chem. Soc.* **2020**, *142*, 20594–20599.
(102) Lima, C. G. S.; de M. Lima, T.; Duarte, M.; Jurberg, I. D.; Paixão, M. W. Organic Synthesis Enabled by Light-Irradiation of EDA Complexes: Theoretical Background and Synthetic Applications. *ACS Catal.* **2016**, *6*, 1389–1407.
(103) Yuan, Y.; Majumder, S.; Yang, M.; Guo, S. Recent Advances in Catalyst-Free Photochemical Reactions via Electron-Donor-Acceptor (EDA) Complex Process. *Tetrahedron Lett.* **2020**, *61*, 151506.
(104) Shin, S.; Lee, S.; Choi, W.; Kim, N.; Hong, S. Visible-Light-Induced 1,3-Aminopyridylation of [1.1.1]Propellane with *N* -Aminopyridinium Salts. *Angew. Chem. Int. Ed.* **2021**, *60*, 7873–7879.
(105) Zhang, J.; Li, Y.; Xu, R.; Chen, Y. Donor–Acceptor Complex Enables Alkoxyl Radical Generation for Metal-Free C(Sp3)–C(Sp3) Cleavage and Allylation/Alkenylation. *Angew. Chem. Int. Ed.* **2017**, *56*, 12619–12623.
(106) Wu, J.; Grant, P. S.; Li, X.; Noble, A.; Aggarwal, V. K. Catalyst-Free Deaminative Functionalizations of Primary Amines by Photoinduced Single-Electron Transfer. *Angew. Chem.* **2019**, *131*, 5753–5757.

(107) Fawcett, A.; Pradeilles, J.; Wang, Y.; Mutsuga, T.; Myers, E. L.; Aggarwal, V. K. Photoinduced Decarboxylative Borylation of Carboxylic Acids. *Science* **2017**, *357*, 283–286.
(108) Fu, M.-C.; Shang, R.; Zhao, B.; Wang, B.; Fu, Y. Photocatalytic Decarboxylative Alkylations Mediated by Triphenylphosphine and Sodium Iodide. *Science* **2019**, *363*, 1429–1434.
(109) Pitre, S. P.; Allred, T. K.; Overman, L. E. Lewis Acid Activation of Fragment-Coupling Reactions of Tertiary Carbon Radicals Promoted by Visible-Light Irradiation of EDA Complexes. *Org. Lett.* **2021**, *23*, 1103–1106.
(110) Fu, M.-C.; Wang, J.-X.; Shang, R. Triphenylphosphine-Catalyzed Alkylative Iododecarboxylation with Lithium Iodide under Visible Light. *Org. Lett.* **2020**, *22*, 8572–8577.
(111) Shu, C.; Madhavachary, R.; Noble, A.; Aggarwal, V. K. Photoinduced Fragmentation Borylation of Cyclic Alcohols and Hemiacetals. *Org. Lett.* **2020**, *22*, 7213–7218.
(112) Chen, K.-Q.; Wang, Z.-X.; Chen, X.-Y. Photochemical Decarboxylative C(Sp^3)–X Coupling Facilitated by Weak Interaction of N-Heterocyclic Carbene. *Org. Lett.* **2020**, *22*, 8059–8064.
(113) Kim, I.; Park, S.; Hong, S. Functionalization of Pyridinium Derivatives with 1,4-Dihydropyridines Enabled by Photoinduced Charge Transfer. *Org. Lett.* **2020**, *22*, 8730–8734.
(114) Correia, J. T. M.; Piva da Silva, G.; Kisukuri, C. M.; André, E.; Pires, B.; Carneiro, P. S.; Paixão, M. W. Metal-Free Photoinduced Hydroalkylation Cascade Enabled by an Electron-Donor–Acceptor Complex. *J. Org. Chem.* **2020**, *85*, 9820–9834.
(115) Wang, G.-Z.; Fu, M.-C.; Zhao, B.; Shang, R. Photocatalytic Decarboxylative Alkylations of C(Sp3)-H and C(Sp2)-H Bonds Enabled by Ammonium Iodide in Amide Solvent. *Sci. China Chem.* **2021**, *64*, 439–444.
(116) Bosque, I.; Bach, T. 3-Acetoxyquinuclidine as Catalyst in Electron Donor–Acceptor Complex-Mediated Reactions Triggered by Visible Light. *ACS Catal.* **2019**, *9*, 9103–9109.
(117) Emmanuel, M. A.; Greenberg, N. R.; Oblinsky, D. G.; Hyster, T. K. Accessing Non-Natural Reactivity by Irradiating Nicotinamide-Dependent Enzymes with Light. *Nature* **2016**, *540*, 414–417.
(118) Luo, Y.; Gutiérrez-Bonet, Á.; Matsui, J. K.; Rotella, M. E.; Dykstra, R.; Gutierrez, O.; Molander, G. A. Oxa- and Azabenzonorbornadienes as Electrophilic Partners under Photoredox/Nickel Dual Catalysis. *ACS Catal.* **2019**, *9*, 8835–8842.
(119) Dumoulin, A.; Matsui, J. K.; Gutiérrez-Bonet, Á.; Molander, G. A. Synthesis of Non-Classical Arylated C-Saccharides through Nickel/Photoredox Dual Catalysis. *Angew. Chem.* **2018**, *130*, 6724–6728.
(120) Badir, S. O.; Dumoulin, A.; Matsui, J. K.; Molander, G. A. Synthesis of Reversed *C* -Acyl Glycosides through Ni/Photoredox Dual Catalysis. *Angew. Chem.* **2018**, *130*, 6720–6723.
(121) Wang, P.-Z.; Chen, J.-R.; Xiao, W.-J. Hantzsch Esters: An Emerging Versatile Class of Reagents in Photoredox Catalyzed Organic Synthesis. *Org. Biomol. Chem.* **2019**, *17*, 6936–6951.

(122) Huang, W.; Cheng, X. Hantzsch Esters as Multifunctional Reagents in Visible-Light Photoredox Catalysis. *Synlett* **2016**, *28*, 148–158.
(123) Gutiérrez-Bonet, Á.; Remeur, C.; Matsui, J. K.; Molander, G. A. Late-Stage C–H Alkylation of Heterocycles and 1,4-Quinones via Oxidative Homolysis of 1,4-Dihydropyridines. *J. Am. Chem. Soc.* **2017**, *139*, 12251–12258.
(124) Paul, S.; Guin, J. Dioxygen-Mediated Decarbonylative C□H Alkylation of Heteroaromatic Bases with Aldehydes. *Chem. - Eur. J.* **2015**, *21*, 17618–17622.
(125) Tang, R.-J.; Kang, L.; Yang, L. Metal-Free Oxidative Decarbonylative Coupling of Aliphatic Aldehydes with Azaarenes: Successful Minisci-Type Alkylation of Various Heterocycles. *Adv. Synth. Catal.* **2015**, *357*, 2055–2060.
(126) Mai, D. N.; Baxter, R. D. Unprotected Amino Acids as Stable Radical Precursors for Heterocycle C–H Functionalization. *Org. Lett.* **2016**, *18*, 3738–3741.
(127) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. Chemistry of Acyl Radicals. *Chem. Rev.* **1999**, *99*, 1991–2070.
(128) Siddaraju, Y.; Prabhu, K. R. Transition Metal-Free Minisci Reaction Promoted by NCS, and TBHP: Acylation of Heteroarenes. *Tetrahedron* **2016**, *72*, 959–967.
(129) Siddaraju, Y.; Lamani, M.; Prabhu, K. R. A Transition Metal-Free Minisci Reaction: Acylation of Isoquinolines, Quinolines, and Quinoxaline. *J. Org. Chem.* **2014**, *79*, 3856–3865.
(130) Munavalli, S.; Rohrbaugh, D. K.; Rossman, D. I.; Berg, F. J.; Wagner, G. W.; Durst, H. D. Trifluoromethylsulfenylation of Masked Carbonyl Compounds. *Synth. Commun.* **2000**, *30*, 2847–2854.
(131) Li, M.; Zhou, B.; Xue, X.-S.; Cheng, J.-P. Establishing the Trifluoromethylthio Radical Donating Abilities of Electrophilic SCF_3 -Transfer Reagents. *J. Org. Chem.* **2017**, *82*, 8697–8702.
(132) Mulliken, R. S. Structures of Complexes Formed by Halogen Molecules with Aromatic and with Oxygenated Solvents1. *J. Am. Chem. Soc.* **1950**, *72*, 600–608.
(133) Mulliken, R. S. Molecular Compounds and Their Spectra. II. *J. Am. Chem. Soc.* **1952**, *74*, 811–824.
(134) Mulliken, R. S. Molecular Compounds and Their Spectra. III. The Interaction of Electron Donors and Acceptors. *J. Phys. Chem.* **1952**, *56*, 801–822.
(135) Taube, H.; Myers, H.; Rich, R. L. OBSERVATIONS ON THE MECHANISM OF ELECTRON TRANSFER IN SOLUTION1. *J. Am. Chem. Soc.* **1953**, *75*, 4118–4119.
(136) Taube, H. Electron Transfer Between Metal Complexes: Retrospective. *Science* **1984**, *226*, 1028–1036.
(137) Marcus, R. A. Electron Transfer Reactions in Chemistry Theory and Experiment. *J. Electroanal. Chem.* **1997**, *438*, 251–259.
(138) Marcus, R. A. Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture). *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111–1121.
(139) Hush, N. S. Adiabatic Theory of Outer Sphere Electron-Transfer Reactions in Solution. *Trans. Faraday Soc.* **1961**, *57*, 557.
(140) Hush, N. S. Intervalence-Transfer Absorption. Part 2. Theoretical Considerations and Spectroscopic Data. *Prog Inorg Chem* **1967**, *8*, 12.

(141) Rosokha, S. V.; Kochi, J. K. Fresh Look at Electron-Transfer Mechanisms via the Donor/Acceptor Bindings in the Critical Encounter Complex. *Acc. Chem. Res.* **2008**, *41*, 641–653.
(142) Rosokha, S. V.; Kochi, J. K. Continuum of Outer- and Inner-Sphere Mechanisms for Organic Electron Transfer. Steric Modulation of the Precursor Complex in Paramagnetic (Ion-Radical) Self-Exchanges. *J. Am. Chem. Soc.* **2007**, *129*, 3683–3697.
(143) Davies, J.; Booth, S. G.; Essafi, S.; Dryfe, R. A. W.; Leonori, D. Visible-Light-Mediated Generation of Nitrogen-Centered Radicals: Metal-Free Hydroimination and Iminohydroxylation Cyclization Reactions. *Angew. Chem. Int. Ed.* **2015**, *54*, 14017–14021.
(144) Fernández-Alvarez, V. M.; Nappi, M.; Melchiorre, P.; Maseras, F. Computational Study with DFT and Kinetic Models on the Mechanism of Photoinitiated Aromatic Perfluoroalkylations. *Org. Lett.* **2015**, *17*, 2676–2679.
(145) Liu, B.; Lim, C.-H.; Miyake, G. M. Light-Driven Intermolecular Charge Transfer Induced Reactivity of Ethynylbenziodoxol(on)e and Phenols. *J. Am. Chem. Soc.* **2018**, *140*, 12829–12835.
(146) Sandfort, F.; Strieth-Kalthoff, F.; Klauck, F. J. R.; James, M. J.; Glorius, F. Deaminative Borylation of Aliphatic Amines Enabled by Visible Light Excitation of an Electron Donor-Acceptor Complex. *Chem. - Eur. J.* **2018**, *24*, 17210–17214.
(147) Morack, T.; Mück-Lichtenfeld, C.; Gilmour, R. Bioinspired Radical Stetter Reaction: Radical Umpolung Enabled by Ion-Pair Photocatalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 1208–1212.
(148) Ho, H. E.; Pagano, A.; Rossi-Ashton, J. A.; Donald, J. R.; Epton, R. G.; Churchill, J. C.; James, M. J.; O'Brien, P.; Taylor, R. J. K.; Unsworth, W. P. Visible-Light-Induced Intramolecular Charge Transfer in the Radical Spirocyclisation of Indole-Tethered Ynones. *Chem. Sci.* **2020**, *11*, 1353–1360.
(149) Gu, G.; Huang, M.; Kim, J. K.; Zhang, J.; Li, Y.; Wu, Y. Visible-Light-Induced Photocatalyst-Free C-3 Functionalization of Indoles with Diethyl Bromomalonate. *Green Chem.* **2020**, *22*, 2543–2548.
(150) Rigotti, T.; Mas-Ballesté, R.; Alemán, J. Enantioselective Aminocatalytic [2 + 2] Cycloaddition through Visible Light Excitation. *ACS Catal.* **2020**, *10*, 5335–5346.
(151) Sheng, H.; Liu, Q.; Su, X.-D.; Lu, Y.; Wang, Z.-X.; Chen, X.-Y. Visible-Light-Triggered Iodinations Facilitated by Weak Electrostatic Interaction of N-Heterocyclic Carbenes. *Org. Lett.* **2020**, *22*, 7187–7192.
(152) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785–789.
(153) Becke, A. D. Density-functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
(154) Weigend, F. Accurate Coulomb-Fitting Basis Sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.
(155) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, Structures, and Electronic Properties of Molecules in Solution with the C-PCM Solvation Model. *J. Comput. Chem.* **2003**, *24*, 669–681.

(156) Hamel, S.; Duffy, P.; Casida, M. E.; Salahub, D. R. Kohn–Sham Orbitals and Orbital Energies: Fictitious Constructs but Good Approximations All the Same. *J. Electron Spectrosc. Relat. Phenom.* **2002**, *123*, 345–363.
(157) Shankar, R.; Senthilkumar, K.; Kolandaivel, P. Calculation of ionization potential and chemical hardness: A comparative study of different methods. *Int. J. Quantum Chem.* **2009**, *109*, 764–771.
(158) and, G. Z.; Musgrave*, C. B. Comparison of DFT Methods for Molecular Orbital Eigenvalue Calculations https://pubs.acs.org/doi/pdf/10.1021/jp061633o (accessed May 31, 2020).
(159) Hua, X.; Chen, X.; Goddard, W. A. Generalized Generalized Gradient Approximation:An Improved Density-Functional Theory for Accurate Orbital Eigenvalues. *Phys. Rev. B* **1997**, *55*, 16103–16109.
(160) Manby, F. R.; Knowles, P. J. An Exchange Functional for Accurate Virtual Orbital Energies. *J. Chem. Phys.* **2000**, *112*, 7002–7007.
(161) Legault, C. Y. CYLview, 1.0 b. *Univ. Sherbrooke* **2009**, *436*, 437.
(162) *Dennington, R., Keith, T. and Millam, J. (2009) Gauss View, Version 5. Semichem Inc., Shawnee Mission.*
(163) Kavarnos, G. J.; Turro, N. J. Photosensitization by Reversible Electron Transfer: Theories, Experimental Evidence, and Examples. *Chem. Rev.* **1986**, *86*, 401–449.
(164) Lipp, A.; Badir, S. O.; Dykstra, R.; Gutierrez, O.; Molander, G. A. Catalyst-Free Decarbonylative Trifluoromethylthiolation Enabled by Electron Donor-Acceptor Complex Photoactivation. *Adv. Synth. Catal.* **2021**, *363*, 3507–3520.
(165) Goti, G.; Bieszczad, B.; Vega-Peñaloza, A.; Melchiorre, P. Stereocontrolled Synthesis of 1,4-Dicarbonyl Compounds by Photochemical Organocatalytic Acyl Radical Addition to Enals. *Angew. Chem.* **2019**, *131*, 1226–1230.
(166) Benesi, H. A.; Hildebrand, J. H. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.
(167) Buzzetti, L.; Prieto, A.; Roy, S. R.; Melchiorre, P. Radical-Based C−C Bond-Forming Processes Enabled by the Photoexcitation of 4-Alkyl-1,4-Dihydropyridines. *Angew. Chem.* **2017**, *129*, 15235–15239.
(168) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. Selective One-Electron and Two-Electron Reduction of C60 with NADH and NAD Dimer Analogues via Photoinduced Electron Transfer. *J. Am. Chem. Soc.* **1998**, *120*, 8060–8068.
(169) Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. Photocatalytic Hydrogen Production from Hantzsch 1,4-Dihydropyridines by Platinum(II) Terpyridyl Complexes in Homogeneous Solution. *J. Am. Chem. Soc.* **2004**, *126*, 3440–3441.
(170) Wang, D.; Liu, Q.; Chen, B.; Zhang, L.; Tung, C.; Wu, L. Photooxidation of Hantzsch 1,4-Dihydropyridines by Molecular Oxygen. *Chin. Sci. Bull.* **2010**, *55*, 2855–2858.
(171) Wei, X.; Wang, L.; Jia, W.; Du, S.; Wu, L.; Liu, Q. Metal-Free-Mediated Oxidation Aromatization of 1,4-Dihydropyridines to Pyridines Using Visible Light and Air. *Chin. J. Chem.* **2014**, *32*, 1245–1250.

(172) Gutiérrez-Bonet, Á.; Tellis, J. C.; Matsui, J. K.; Vara, B. A.; Molander, G. A. 1,4-Dihydropyridines as Alkyl Radical Precursors: Introducing the Aldehyde Feedstock to Nickel/Photoredox Dual Catalysis. *ACS Catal.* **2016**, *6*, 8004–8008.
(173) Nakajima, K.; Nojima, S.; Sakata, K.; Nishibayashi, Y. Visible-Light-Mediated Aromatic Substitution Reactions of Cyanoarenes with 4-Alkyl-1,4-dihydropyridines through Double Carbon–Carbon Bond Cleavage. *ChemCatChem* **2016**, *8*, 1028–1032.
(174) Zhang, J.; Li, Y.; Xu, R.; Chen, Y. Donor–Acceptor Complex Enables Alkoxyl Radical Generation for Metal-Free C(Sp^3)–C(Sp^3) Cleavage and Allylation/Alkenylation. *Angew. Chem.* **2017**, *129*, 12793–12797.
(175) Li, Y.; Zhang, J.; Li, D.; Chen, Y. Metal-Free C(Sp3)–H Allylation via Aryl Carboxyl Radicals Enabled by Donor–Acceptor Complex. *Org. Lett.* **2018**, *20*, 3296–3299.
(176) Li, Y.; Koike, T.; Akita, M. Photocatalytic Trifluoromethylthiolation of Aromatic Alkenes Associated with Hydroxylation and Alkoxylation. *Asian J. Org. Chem.* **2017**, *6*, 445–448.
(177) Talele, T. T. The "Cyclopropyl Fragment" Is a Versatile Player That Frequently Appears in Preclinical/Clinical Drug Molecules. *J. Med. Chem.* **2016**, *59*, 8712–8756.
(178) Smith, D.; Delost, M.; Qureshi, H.; Njarðarson, J. Top 200 Pharmaceutical Products by Retail Sales in 2016.
(179) Chen, D. Y.-K.; Pouwer, R. H.; Richard, J.-A. Recent Advances in the Total Synthesis of Cyclopropane-Containing Natural Products. *Chem. Soc. Rev.* **2012**, *41*, 4631.
(180) Barnes-Seeman, D.; Jain, M.; Bell, L.; Ferreira, S.; Cohen, S.; Chen, X.-H.; Amin, J.; Snodgrass, B.; Hatsis, P. Metabolically Stable *Tert* -Butyl Replacement. *ACS Med. Chem. Lett.* **2013**, *4*, 514–516.
(181) Lazerwith, S. E.; Lew, W.; Zhang, J.; Morganelli, P.; Liu, Q.; Canales, E.; Clarke, M. O.; Doerffler, E.; Byun, D.; Mertzman, M.; Ye, H.; Chong, L.; Xu, L.; Appleby, T.; Chen, X.; Fenaux, M.; Hashash, A.; Leavitt, S. A.; Mabery, E.; Matles, M.; Mwangi, J. W.; Tian, Y.; Lee, Y.-J.; Zhang, J.; Zhu, C.; Murray, B. P.; Watkins, W. J. Discovery of GS-9669, a Thumb Site II Non-Nucleoside Inhibitor of NS5B for the Treatment of Genotype 1 Chronic Hepatitis C Infection. *J. Med. Chem.* **2014**, *57*, 1893–1901.
(182) Westphal, M. V.; Wolfstädter, B. T.; Plancher, J.-M.; Gatfield, J.; Carreira, E. M. Evaluation of *Tert* -Butyl Isosteres: Case Studies of Physicochemical and Pharmacokinetic Properties, Efficacies, and Activities. *ChemMedChem* **2015**, *10*, 461–469.
(183) Bezençon, O.; Heidmann, B.; Siegrist, R.; Stamm, S.; Richard, S.; Pozzi, D.; Corminboeuf, O.; Roch, C.; Kessler, M.; Ertel, E. A.; Reymond, I.; Pfeifer, T.; de Kanter, R.; Toeroek-Schafroth, M.; Moccia, L. G.; Mawet, J.; Moon, R.; Rey, M.; Capeleto, B.; Fournier, E. Discovery of a Potent, Selective T-Type Calcium Channel Blocker as a Drug Candidate for the Treatment of Generalized Epilepsies. *J. Med. Chem.* **2017**, *60*, 9769–9789.
(184) Bos, M.; Poisson, T.; Pannecoucke, X.; Charette, A. B.; Jubault, P. Recent Progress Toward the Synthesis of Trifluoromethyl- and Difluoromethyl-Substituted Cyclopropanes. *Chem. - Eur. J.* **2017**, *23*, 4950–4961.
(185) Grygorenko, O. O.; Artamonov, O. S.; Komarov, I. V.; Mykhailiuk, P. K. Trifluoromethyl-Substituted Cyclopropanes. *Tetrahedron* **2011**, *67*, 803–823.

(186) Mercadante, M. A.; Kelly, C. B.; Hamlin, T. A.; Delle Chiaie, K. R.; Drago, M. D.; Duffy, K. K.; Dumas, M. T.; Fager, D. C.; Glod, B. L. C.; Hansen, K. E.; Hill, C. R.; Leising, R. M.; Lynes, C. L.; MacInnis, A. E.; McGohey, M. R.; Murray, S. A.; Piquette, M. C.; Roy, S. L.; Smith, R. M.; Sullivan, K. R.; Truong, B. H.; Vailonis, K. M.; Gorbatyuk, V.; Leadbeater, N. E.; Tilley, L. J. 1,3-γ-Silyl-Elimination in Electron-Deficient Cationic Systems. *Chem. Sci.* **2014**, *5*, 3983.

(187) Kelly, C. B.; Mercadante, M. A.; Carnaghan, E. R.; Doherty, M. J.; Fager, D. C.; Hauck, J. J.; MacInnis, A. E.; Tilley, L. J.; Leadbeater, N. E. Synthesis of Perfluoroalkyl-Substituted Vinylcyclopropanes by Way of Enhanced Neighboring Group Participation: Perfluoroalkyl-Substituted Vinylcyclopropanes. *Eur. J. Org. Chem.* **2015**, *2015*, 4071–4076.

(188) Gianatassio, R.; Kawamura, S.; Eprile, C. L.; Foo, K.; Ge, J.; Burns, A. C.; Collins, M. R.; Baran, P. S. Simple Sulfinate Synthesis Enables C□H Trifluoromethylcyclopropanation. *Angew. Chem. Int. Ed.* **2014**, *53*, 9851–9855.

(189) Simmons, H. E.; Smith, R. D. A NEW SYNTHESIS OF CYCLOPROPANES FROM OLEFINS. *J. Am. Chem. Soc.* **1958**, *80*, 5323–5324.

(190) Simmons, H. E.; Smith, R. D. A New Synthesis of Cyclopropanes1. *J. Am. Chem. Soc.* **1959**, *81*, 4256–4264.

(191) Furukawa, J.; Kawabata, N.; Nishimura, J. A Novel Route to Cyclopropanes from Olefins. *Tetrahedron Lett.* **1966**, *7*, 3353–3354.

(192) Denmark, S. E.; Edwards, J. P. A Comparison of (Chloromethyl)- and (Iodomethyl)Zinc Cyclopropanation Reagents. *J. Org. Chem.* **1991**, *56*, 6974–6981.

(193) Charette, A. B.; Francoeur, S.; Martel, J.; Wilb, N. New Family of Cyclopropanating Reagents: Synthesis, Reactivity, and Stability Studies of Iodomethylzinc Phenoxides. *Angew. Chem. Int. Ed.* **2000**, *39*, 4539–4542.

(194) Charette, A. B.; Beauchemin, A.; Francoeur, S. Acyloxymethylzinc Reagents: Preparation, Reactivity, and Solid-State Structure of This Novel Class of Cyclopropanating Reagents. *J. Am. Chem. Soc.* **2001**, *123*, 8139–8140.

(195) Charette, A. B.; Beauchemin, A. Simmons-Smith Cyclopropanation Reaction. In *Organic Reactions*; John Wiley & Sons, Inc., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2001; pp 1–415.

(196) Morandi, B.; Carreira, E. M. Iron-Catalyzed Cyclopropanation in 6 M KOH with in Situ Generation of Diazomethane. *Science* **2012**, *335*, 1471–1474.

(197) Ebner, C.; Carreira, E. M. Cyclopropanation Strategies in Recent Total Syntheses. *Chem. Rev.* **2017**, *117*, 11651–11679.

(198) Johnson, A. W.; LaCount, R. B. The Chemistry of Ylids. VI. Dimethylsulfonium Fluorenylide—A Synthesis of Epoxides1. *J. Am. Chem. Soc.* **1961**, *83*, 417–423.

(199) Corey, E. J.; Chaykovsky, M. Dimethyloxosulfonium Methylide ((CH3)2SOCH2) and Dimethylsulfonium Methylide ((CH3)2SCH2). Formation and Application to Organic Synthesis. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364.

(200) Huang, L.; Chen, Y.; Gao, G.-Y.; Zhang, X. P. Diastereoselective and Enantioselective Cyclopropanation of Alkenes Catalyzed by Cobalt Porphyrins. *J. Org. Chem.* **2003**, *68*, 8179–8184.

(201) Dzik, W. I.; Xu, X.; Zhang, X. P.; Reek, J. N. H.; de Bruin, B. 'Carbene Radicals' in Co ^{II} (Por)-Catalyzed Olefin Cyclopropanation. *J. Am. Chem. Soc.* **2010**, *132*, 10891–10902.

(202) Wang, Y.; Wen, X.; Cui, X.; Wojtas, L.; Zhang, X. P. Asymmetric Radical Cyclopropanation of Alkenes with In Situ-Generated Donor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 1049–1052.
(203) Xu, X.; Wang, Y.; Cui, X.; Wojtas, L.; Zhang, X. P. Metalloradical Activation of α-Formyldiazoacetates for the Catalytic Asymmetric Radical Cyclopropanation of Alkenes. *Chem. Sci.* **2017**, *8*, 4347–4351.
(204) Sarabia, F. J.; Ferreira, E. M. Radical Cation Cyclopropanations via Chromium Photooxidative Catalysis. *Org. Lett.* **2017**, *19*, 2865–2868.
(205) Čeković, Ž.; Saičić, R. Radical Cyclization Reactions. Cyclopropane Ring Formation by 3-Exo-Cyclization of 5-Phenylthio-3-Pentenyl Radicals. *Tetrahedron Lett.* **1990**, *31*, 6085–6088.
(206) Ye, L.; Gu, Q.-S.; Tian, Y.; Meng, X.; Chen, G.-C.; Liu, X.-Y. Radical Asymmetric Intramolecular α-Cyclopropanation of Aldehydes towards Bicyclo[3.1.0]Hexanes Containing Vicinal All-Carbon Quaternary Stereocenters. *Nat. Commun.* **2018**, *9*, 227.
(207) del Hoyo, A. M.; Herraiz, A. G.; Suero, M. G. A Stereoconvergent Cyclopropanation Reaction of Styrenes. *Angew. Chem. Int. Ed.* **2017**, *56*, 1610–1613.
(208) del Hoyo, A. M.; García Suero, M. Photoredox-Catalyzed Cyclopropanation of Michael Acceptors: Photoredox-Catalyzed Cyclopropanation of Michael Acceptors. *Eur. J. Org. Chem.* **2017**, *2017*, 2122–2125.
(209) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Single-Electron Transmetalation via Photoredox/Nickel Dual Catalysis: Unlocking a New Paradigm for Sp^3 –Sp^2 Cross-Coupling. *Acc. Chem. Res.* **2016**, *49*, 1429–1439.
(210) Twilton, J.; Le, C. (Chip); Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. The Merger of Transition Metal and Photocatalysis. *Nat. Rev. Chem.* **2017**, *1*, 0052.
(211) Koike, T.; Akita, M. Visible-Light Radical Reaction Designed by Ru- and Ir-Based Photoredox Catalysis. *Inorg Chem Front* **2014**, *1*, 562–576.
(212) Corcé, V.; Chamoreau, L.; Derat, E.; Goddard, J.; Ollivier, C.; Fensterbank, L. Silicates as Latent Alkyl Radical Precursors: Visible-Light Photocatalytic Oxidation of Hypervalent Bis-Catecholato Silicon Compounds. *Angew. Chem. Int. Ed.* **2015**, *54*, 11414–11418.
(213) Blomstrom, D. C.; Herbig, K.; Simmons, H. E. Photolysis of Methylene Iodide in the Presence of Olefins. *J. Org. Chem.* **1965**, *30*, 959–964.
(214) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. Photochemistry of Alkyl Halides—VII. *Tetrahedron* **1981**, *37*, 3229–3236.
(215) Kropp, P. J. Photobehavior of Alkyl Halides in Solution: Radical, Carbocation, and Carbene Intermediates. *Acc. Chem. Res.* **1984**, *17*, 131–137.
(216) Phillips, D. L.; Fang, W.-H.; Zheng, X. Isodiiodomethane Is the Methylene Transfer Agent in Cyclopropanation Reactions with Olefins Using Ultraviolet Photolysis of Diiodomethane in Solutions: A Density Functional Theory Investigation of the Reactions of Isodiiodomethane, Iodomethyl Radical, and Iodomethyl Cation with Ethylene. *J. Am. Chem. Soc.* **2001**, *123*, 4197–4203.
(217) Tsunoi, S.; Tanaka, M.; Tsunoi, S.; Ryu, I.; Yamasaki, S.; Sonoda, N.; Komatsu, M. Tandem Annulations: A One Operation Construction of Bicyclo[3.3.0]Octan-1-Ol and Bicyclo[3.2.1]Octan-1-Ol Skeletons by a Three-Component Coupling Reaction of Alk-4-

Enyl Iodides with CO and Alkenes in the Presence of Zinc. *Chem. Commun.* **1997**, No. 19, 1889–1890.
(218) Yatham, V. R.; Shen, Y.; Martin, R. Catalytic Intermolecular Dicarbofunctionalization of Styrenes with CO2 and Radical Precursors. *Angew. Chem. Int. Ed.* **2017**, *56*, 10915–10919.
(219) Pitzer, L.; Schwarz, J. L.; Glorius, F. Reductive Radical-Polar Crossover: Traditional Electrophiles in Modern Radical Reactions. *Chem. Sci.* **2019**, *10*, 8285–8291.
(220) Liakos, D. G.; Sparta, M.; Kesharwani, M. K.; Martin, J. M. L.; Neese, F. Exploring the Accuracy Limits of Local Pair Natural Orbital Coupled-Cluster Theory. *J. Chem. Theory Comput.* **2015**, *11*, 1525–1539.
(221) Paulechka, E.; Kazakov, A. Efficient DLPNO–CCSD(T)-Based Estimation of Formation Enthalpies for C-, H-, O-, and N-Containing Closed-Shell Compounds Validated Against Critically Evaluated Experimental Data. *J. Phys. Chem. A* **2017**, *121*, 4379–4387.
(222) Li, X.; Liao, T.; Chung, L. W. Computational Prediction of Excited-State Carbon Tunneling in the Two Steps of Triplet Zimmerman Di-π-Methane Rearrangement. *J. Am. Chem. Soc.* **2017**, *139*, 16438–16441.
(223) Phelan, J. P.; Lang, S. B.; Compton, J. S.; Kelly, C. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. Redox-Neutral Photocatalytic Cyclopropanation via Radical/Polar Crossover. *J. Am. Chem. Soc.* **2018**, *140*, 8037–8047.
(224) Renaud, P.; Gerster, M. Use of Lewis Acids in Free Radical Reactions. *Angew. Chem. Int. Ed.* **1998**, *37*, 2562–2579.
(225) Sibi, M. P.; Porter, N. A. Enantioselective Free Radical Reactions. *Acc. Chem. Res.* **1999**, *32*, 163–171.
(226) Zhang, W. Intramolecular Free Radical Conjugate Additions. *Tetrahedron* **2001**, *57*, 7237–7262.
(227) Sibi, M. P.; Manyem, S.; Zimmerman, J. Enantioselective Radical Processes. *Chem. Rev.* **2003**, *103*, 3263–3296.
(228) Srikanth, G. S. C.; Castle, S. L. Advances in Radical Conjugate Additions. *Tetrahedron* **2005**, *61*, 10377–10441.
(229) Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003**, *36*, 255–263.
(230) Xiao, T.; Li, L.; Zhou, L. Synthesis of Functionalized *Gem* -Difluoroalkenes via a Photocatalytic Decarboxylative/Defluorinative Reaction. *J. Org. Chem.* **2016**, *81*, 7908–7916.
(231) Lang, S. B.; Wiles, R. J.; Kelly, C. B.; Molander, G. A. Photoredox Generation of Carbon-Centered Radicals Enables the Construction of 1,1-Difluoroalkene Carbonyl Mimics. *Angew. Chem. Int. Ed.* **2017**, *56*, 15073–15077.
(232) Chu, L.; Ohta, C.; Zuo, Z.; MacMillan, D. W. C. Carboxylic Acids as A Traceless Activation Group for Conjugate Additions: A Three-Step Synthesis of (±)-Pregabalin. *J. Am. Chem. Soc.* **2014**, *136*, 10886–10889.
(233) Millet, A.; Lefebvre, Q.; Rueping, M. Visible-Light Photoredox-Catalyzed Giese Reaction: Decarboxylative Addition of Amino Acid Derived α-Amino Radicals to Electron-Deficient Olefins. *Chem. - Eur. J.* **2016**, *22*, 13464–13468.
(234) Ramirez, N. P.; Gonzalez-Gomez, J. C. Decarboxylative Giese-Type Reaction of Carboxylic Acids Promoted by Visible Light: A Sustainable and Photoredox-Neutral

Protocol: Decarboxylative Giese-Type Reaction of Carboxylic Acids Promoted by Visible Light: A Sustainable and Photoredox-Neutral Protocol. *Eur. J. Org. Chem.* **2017**, *2017*, 2154–2163.
(235) Noble, A.; Mega, R. S.; Pflästerer, D.; Myers, E. L.; Aggarwal, V. K. Visible-Light-Mediated Decarboxylative Radical Additions to Vinyl Boronic Esters: Rapid Access to γ-Amino Boronic Esters. *Angew. Chem. Int. Ed.* **2018**, *57*, 2155–2159.
(236) Lovinger, G. J.; Morken, J. P. Ni-Catalyzed Enantioselective Conjunctive Coupling with C(Sp^3) Electrophiles: A Radical-Ionic Mechanistic Dichotomy. *J. Am. Chem. Soc.* **2017**, *139*, 17293–17296.
(237) Silvi, M.; Sandford, C.; Aggarwal, V. K. Merging Photoredox with 1,2-Metallate Rearrangements: The Photochemical Alkylation of Vinyl Boronate Complexes. *J. Am. Chem. Soc.* **2017**, *139*, 5736–5739.
(238) Kischkewitz, M.; Okamoto, K.; Mück-Lichtenfeld, C.; Studer, A. Radical-Polar Crossover Reactions of Vinylboron Ate Complexes. *Science* **2017**, *355*, 936–938.
(239) Fernandez Reina, D.; Ruffoni, A.; Al-Faiyz, Y. S. S.; Douglas, J. J.; Sheikh, N. S.; Leonori, D. Visible-Light-Mediated Reactions of Electrophilic Radicals with Vinyl and Allyl Trifluoroborates. *ACS Catal.* **2017**, *7*, 4126–4130.
(240) Quiclet-Sire, B.; Zard, S. Z. Radical Instability in Aid of Efficiency: A Powerful Route to Highly Functional MIDA Boronates. *J. Am. Chem. Soc.* **2015**, *137*, 6762–6765.
(241) Halgren, T. A.; Roberts, J. D.; Horner, J. H.; Martinez, F. N.; Tronche, C.; Newcomb, M. Kinetics and Equilibrium Constants for Reactions of α-Phenyl-Substituted Cyclopropylcarbinyl Radicals. *J. Am. Chem. Soc.* **2000**, *122*, 2988–2994.
(242) McGrath, N. A.; Brichacek, M.; Njardarson, J. T. A Graphical Journey of Innovative Organic Architectures That Have Improved Our Lives. *J. Chem. Educ.* **2010**, *87*, 1348–1349.
(243) Wessjohann, L. A.; Brandt, W.; Thiemann, T. Biosynthesis and Metabolism of Cyclopropane Rings in Natural Compounds. *Chem. Rev.* **2003**, *103*, 1625–1648.
(244) Dill, J. D.; Greenberg, A.; Liebman, J. F. Substituent Effects on Strain Energies. *J. Am. Chem. Soc.* **1979**, *101*, 6814–6826.
(245) de Meijere, A. Bonding Properties of Cyclopropane and Their Chemical Consequences. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809–826.
(246) Wong, H. N. C.; Hon, M. Y.; Tse, C. W.; Yip, Y. C.; Tanko, J.; Hudlicky, T. Use of Cyclopropanes and Their Derivatives in Organic Synthesis. *Chem. Rev.* **1989**, *89*, 165–198.
(247) *Carbocyclic Three-Membered Ring Compounds: Cyclopropanes, Transformations*; Thieme, 1997.
(248) Carson, C. A.; Kerr, M. A. Heterocycles from Cyclopropanes: Applications in Natural Product Synthesis. *Chem. Soc. Rev.* **2009**, *38*, 3051.
(249) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. Cyclopropanes from Unsaturated Compounds, Methylene Iodide, and Zinc-Copper Couple. In *Organic Reactions*; John Wiley & Sons, Inc., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2011; pp 1–131.
(250) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley: New York, 1998.

(251) L. Davies, H. M. Dirhodium Tetra(N-Arylsulfonylprolinates) as Chiral Catalysts For Asymmetric Transformations of Vinyl- and Aryldiazoacetates. *Eur. J. Org. Chem.* **1999**, *1999*, 2459–2469.
(252) Rappoport, Z. *THE CHEMISTRY OF THE CYCLOPROPYL GROUP/Ed. ZVI RAPPOPORT.*; 1987.
(253) Herraiz, A. G.; Suero, M. G. New Alkene Cyclopropanation Reactions Enabled by Photoredox Catalysis via Radical Carbenoids. *Synthesis* **2019**, *51*, 2821–2828.
(254) Herraiz, A. G.; Suero, M. G. A Transition-Metal-Free & Diazo-Free Styrene Cyclopropanation. *Chem. Sci.* **2019**, *10*, 9374–9379.
(255) Milligan, J. A.; Phelan, J. P.; Polites, V. C.; Kelly, C. B.; Molander, G. A. Radical/Polar Annulation Reactions (RPARs) Enable the Modular Construction of Cyclopropanes. *Org. Lett.* **2018**, *20*, 6840–6844.
(256) Milligan, J. A.; Burns, K. L.; Le, A. V.; Polites, V. C.; Wang, Z.-J.; Molander, G. A.; Kelly, C. B. Radical-Polar Crossover Annulation: A Platform for Accessing Polycyclic Cyclopropanes. *Adv. Synth. Catal.* **2020**, *362*, 242–247.
(257) Shu, C.; Mega, R. S.; Andreassen, B. J.; Noble, A.; Aggarwal, V. K. Synthesis of Functionalized Cyclopropanes from Carboxylic Acids by a Radical Addition–Polar Cyclization Cascade. *Angew. Chem. Int. Ed.* **2018**, *57*, 15430–15434.
(258) Guo, T.; Zhang, L.; Liu, X.; Fang, Y.; Jin, X.; Yang, Y.; Li, Y.; Chen, B.; Ouyang, M. Visible-Light-Promoted Redox-Neutral Cyclopropanation Reactions of α-Substituted Vinylphosphonates and Other Michael Acceptors with Chloromethyl Silicate as Methylene Transfer Reagent. *Adv. Synth. Catal.* **2018**, *360*, 4459–4463.
(259) Li, P.; Zhao, J.; Shi, L.; Wang, J.; Shi, X.; Li, F. Iodine-Catalyzed Diazo Activation to Access Radical Reactivity. *Nat. Commun.* **2018**, *9*, 1972.
(260) Sayes, M.; Benoit, G.; Charette, A. B. Borocyclopropanation of Styrenes Mediated by UV-Light Under Continuous Flow Conditions. *Angew. Chem. Int. Ed.* **2018**, *57*, 13514–13518.
(261) Luo, W.; Yang, Y.; Fang, Y.; Zhang, X.; Jin, X.; Zhao, G.; Zhang, L.; Li, Y.; Zhou, W.; Xia, T.; Chen, B. Photoredox-Catalyzed Cyclopropanation of 1,1-Disubstituted Alkenes via Radical-Polar Crossover Process. *Adv. Synth. Catal.* **2019**, *361*, 4215–4221.
(262) Ohtani, T.; Tsuchiya, Y.; Uraguchi, D.; Ooi, T. Photocatalytic Borylcyclopropanation of α-Boryl Styrenes. *Org. Chem. Front.* **2019**, *6*, 1734–1737.
(263) Strieth-Kalthoff, F.; James, M. J.; Teders, M.; Pitzer, L.; Glorius, F. Energy Transfer Catalysis Mediated by Visible Light: Principles, Applications, Directions. *Chem. Soc. Rev.* **2018**, *47*, 7190–7202.
(264) Wigner, E. Nachr. Akad. Wiss. Goettingen, Math.-Physik. Kl. **1927**, 375–381.
(265) Mayo, P. D. *Rearrangements in Ground and Excited States*; Academic Press, 1980.
(266) Singh, K.; Staig, S. J.; Weaver, J. D. Facile Synthesis of *Z* -Alkenes via Uphill Catalysis. *J. Am. Chem. Soc.* **2014**, *136*, 5275–5278.
(267) Zheng, C.; Cheng, W.-M.; Li, H.-L.; Na, R.-S.; Shang, R. *Cis* -Selective Decarboxylative Alkenylation of Aliphatic Carboxylic Acids with Vinyl Arenes Enabled by Photoredox/Palladium/Uphill Triple Catalysis. *Org. Lett.* **2018**, *20*, 2559–2563.
(268) Metternich, J. B.; Gilmour, R. A Bio-Inspired, Catalytic $E \rightarrow Z$ Isomerization of Activated Olefins. *J. Am. Chem. Soc.* **2015**, *137*, 11254–11257.

(269) Metternich, J. B.; Artiukhin, D. G.; Holland, M. C.; von Bremen-Kühne, M.; Neugebauer, J.; Gilmour, R. Photocatalytic $E \rightarrow Z$ Isomerization of Polarized Alkenes Inspired by the Visual Cycle: Mechanistic Dichotomy and Origin of Selectivity. *J. Org. Chem.* **2017**, *82*, 9955–9977.
(270) Pearson, C. M.; Snaddon, T. N. Alkene Photo-Isomerization Inspired by Vision. *ACS Cent. Sci.* **2017**, *3*, 922–924.
(271) Litman, Z. C.; Wang, Y.; Zhao, H.; Hartwig, J. F. Cooperative Asymmetric Reactions Combining Photocatalysis and Enzymatic Catalysis. *Nature* **2018**, *560*, 355–359.
(272) Molloy, J. J.; Metternich, J. B.; Daniliuc, C. G.; Watson, A. J. B.; Gilmour, R. Contra-Thermodynamic, Photocatalytic $E \rightarrow Z$ Isomerization of Styrenyl Boron Species: Vectors to Facilitate Exploration of Two-Dimensional Chemical Space. *Angew. Chem. Int. Ed.* **2018**, *57*, 3168–3172.
(273) Faßbender, S. I.; Molloy, J. J.; Mück-Lichtenfeld, C.; Gilmour, R. Geometric $E \rightarrow Z$ Isomerisation of Alkenyl Silanes by Selective Energy Transfer Catalysis: Stereodivergent Synthesis of Triarylethylenes via a Formal *Anti* -Metallometallation. *Angew. Chem. Int. Ed.* **2019**, *58*, 18619–18626.
(274) Livingstone, K.; Tenberge, M.; Pape, F.; Daniliuc, C. G.; Jamieson, C.; Gilmour, R. Photocatalytic $E \rightarrow Z$ Isomerization of β-Ionyl Derivatives. *Org. Lett.* **2019**, *21*, 9677–9680.
(275) Meng, Q.; Schirmer, T. E.; Katou, K.; König, B. Controllable Isomerization of Alkenes by Dual Visible-Light-Cobalt Catalysis. *Angew. Chem. Int. Ed.* **2019**, *58*, 5723–5728.
(276) Naskar, S.; Roy Chowdhury, S.; Mondal, S.; Maiti, D. K.; Mishra, S.; Das, I. Visible-Light-Activated Divergent Reactivity of Dienones: Dimerization in Neat Conditions and Regioselective *E* to *Z* Isomerization in the Solvent. *Org. Lett.* **2019**, *21*, 1578–1582.
(277) Ota, E.; Wang, H.; Frye, N. L.; Knowles, R. R. A Redox Strategy for Light-Driven, Out-of-Equilibrium Isomerizations and Application to Catalytic C–C Bond Cleavage Reactions. *J. Am. Chem. Soc.* **2019**, *141*, 1457–1462.
(278) Snyder, J. D.; Hamill, L.-A.; Faleumu, K. E.; Ess, D. H. *MECPro Version 1.0.5: Minimum Energy Crossing Program*; 2019.
(279) Yoon, T. P.; Ischay, M. A.; Du, J. Visible Light Photocatalysis as a Greener Approach to Photochemical Synthesis. *Nat. Chem.* **2010**, *2*, 527–532.
(280) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. *Chem. Soc. Rev.* **2016**, *45*, 5803–5820.
(281) Douglas, J. J.; Sevrin, M. J.; Stephenson, C. R. J. Visible Light Photocatalysis: Applications and New Disconnections in the Synthesis of Pharmaceutical Agents. *Org. Process Res. Dev.* **2016**, *20*, 1134–1147.
(282) Cristol, S. J.; Lee, G. A. Photochemical Transformations. V. Allylic Rearrangements and Rearrangement of Allylic Halides to Cyclopropyl Halides. *J. Am. Chem. Soc.* **1969**, *91*, 7554–7555.
(283) Cristol, S. J.; Lee, G. A.; Noreen, A. L. Photochemical Transformations. VIII. Photosensitized Rearrangements of Some Acyclic Allylic Halides. *J. Am. Chem. Soc.* **1973**, *95*, 7067–7074.
(284) Cristol, S. J.; Micheli, R. P. Photochemical Transformations. XI. Photochemical and Thermal Rearrangements of Some .Beta.-Substituted Allylic Systems. *J. Org. Chem.* **1975**, *40*, 667–672.

(285) Cristol, S. J.; Daughenbaugh, R. J.; Opitz, R. J. Photochemical Transformations. 19. Photosensitized Reactions of .Beta.-Methylallyl Chloride. *J. Am. Chem. Soc.* **1977**, *99*, 6347–6353.
(286) Andrews, L. J.; Linden, S. L. Allylidene Halides. II. The Structure and Reactivity of Cinnamal Chloride. *J. Am. Chem. Soc.* **1947**, *69*, 2091–2094.
(287) Kazmaier, U. Palladium Catalyzed Allylic Alkylations of Nonstabilized Enolates. *Curr. Org. Chem.* **2003**, *7*, 317–328.
(288) Miyabe, H.; Takemoto, Y. Regio- and Stereocontrolled Palladium- or Iridium-Catalyzed Allylation. *Synlett* **2005**, No. 11, 1641–1655.
(289) Nishibayashi, Y.; Uemura, S. C–C Bond Formation (Part 2) by Substitution Reactions: Allylic Alkylation. **2007**.
(290) Falciola, C. A.; Alexakis, A. Copper-Catalyzed Asymmetric Allylic Alkylation. *Eur. J. Org. Chem.* **2008**, *2008*, 3765–3780.
(291) Hong, A. Y.; Stoltz, B. M. The Construction of All-Carbon Quaternary Stereocenters by Use of Pd-Catalyzed Asymmetric Allylic Alkylation Reactions in Total Synthesis: Construction of All-Carbon Quaternary Stereocenters. *Eur. J. Org. Chem.* **2013**, *2013*, 2745–2759.
(292) Trost, B. M. Metal Catalyzed Allylic Alkylation: Its Development in the Trost Laboratories. *Tetrahedron* **2015**, *71*, 5708–5733.
(293) Hethcox, J. C.; Shockley, S. E.; Stoltz, B. M. Iridium-Catalyzed Diastereo-, Enantio-, and Regioselective Allylic Alkylation with Prochiral Enolates. *ACS Catal.* **2016**, *6*, 6207–6213.
(294) Hornillos, V.; Gualtierotti, J.-B.; Feringa, B. L. Asymmetric Allylic Substitutions Using Organometallic Reagents. In *Progress in Enantioselective Cu(I)-catalyzed Formation of Stereogenic Centers*; Harutyunyan, S. R., Ed.; Topics in Organometallic Chemistry; Springer International Publishing: Cham, 2016; Vol. 58, pp 1–39.
(295) Trost, B.; Schultz, J. Palladium-Catalyzed Asymmetric Allylic Alkylation Strategies for the Synthesis of Acyclic Tetrasubstituted Stereocenters. *Synthesis* **2019**, *51*, 1–30.
(296) Cheng, Q.; Tu, H.-F.; Zheng, C.; Qu, J.-P.; Helmchen, G.; You, S.-L. Iridium-Catalyzed Asymmetric Allylic Substitution Reactions. *Chem. Rev.* **2019**, *119*, 1855–1969.
(297) Xu, B.; Tambar, U. K. Remote Allylation of Unactivated C(Sp^3)–H Bonds Triggered by Photogenerated Amidyl Radicals. *ACS Catal.* **2019**, *9*, 4627–4631.
(298) Bevernaegie, R.; Marcélis, L.; Laramée-Milette, B.; De Winter, J.; Robeyns, K.; Gerbaux, P.; Hanan, G. S.; Elias, B. Trifluoromethyl-Substituted Iridium(III) Complexes: From Photophysics to Photooxidation of a Biological Target. *Inorg. Chem.* **2018**, *57*, 1356–1367.
(299) Zysman-Colman, E. *Iridium (III) in Optoelectronic and Photonics Applications*; John Wiley & Sons, 2017.
(300) Bevernaegie, R.; Marcélis, L.; Moreno-Betancourt, A.; Laramée-Milette, B.; Hanan, G. S.; Loiseau, F.; Sliwa, M.; Elias, B. Ultrafast Charge Transfer Excited State Dynamics in Trifluoromethyl-Substituted Iridium(III) Complexes. *Phys. Chem. Chem. Phys.* **2018**, *20*, 27256–27260.
(301) Xu, B.; Troian-Gautier, L.; Dykstra, R.; Martin, R. T.; Gutierrez, O.; Tambar, U. K. Photocatalyzed Diastereoselective Isomerization of Cinnamyl Chlorides to Cyclopropanes. *J. Am. Chem. Soc.* **2020**, *142*, 6206–6215.

(302) Instrumentation for Fluorescence Spectroscopy. In *Principles of Fluorescence Spectroscopy*; Lakowicz, J. R., Ed.; Springer US: Boston, MA, 2006; pp 27–61.
(303) Troian-Gautier, L.; Turlington, M. D.; Wehlin, S. A. M.; Maurer, A. B.; Brady, M. D.; Swords, W. B.; Meyer, G. J. Halide Photoredox Chemistry. *Chem. Rev.* **2019**, *119*, 4628–4683.
(304) DiMarco, B. N.; Troian-Gautier, L.; Sampaio, R. N.; Meyer, G. J. Dye-Sensitized Electron Transfer from TiO_2 to Oxidized Triphenylamines That Follows First-Order Kinetics. *Chem. Sci.* **2018**, *9*, 940–949.
(305) Kerzig, C.; Wenger, O. S. Reactivity Control of a Photocatalytic System by Changing the Light Intensity. *Chem. Sci.* **2019**, *10*, 11023–11029.
(306) Feng, M.; Tang, B.; H. Liang, S.; Jiang, X. Sulfur Containing Scaffolds in Drugs: Synthesis and Application in Medicinal Chemistry. *Curr. Top. Med. Chem.* **2016**, *16*, 1200–1216.
(307) Dörwald, F. Z. *Lead Optimization for Medicinal Chemists: Pharmacokinetic Properties of Functional Groups and Organic Compounds*; Wiley-VCH: Weinheim, 2012.
(308) El-Hibri, M. J.; Weinberg, S. A. Polysulfones. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2001; p pst291.
(309) Su, W. An Efficient Method for the Oxidation of Sulfides to Sulfones. *Tetrahedron Lett.* **1994**, *35*, 4955–4958.
(310) Rayner, C. M. Synthesis of Thiols, Sulfides, Sulfoxides and Sulfones. *Contemp. Org. Synth.* **1995**, *2*, 409.
(311) Hartwig, J. F. Evolution of a Fourth Generation Catalyst for the Amination and Thioetherification of Aryl Halides. *Acc. Chem. Res.* **2008**, *41*, 1534–1544.
(312) Beletskaya, I. P.; Ananikov, V. P. Transition-Metal-Catalyzed C−S, C−Se, and C−Te Bond Formation via Cross-Coupling and Atom-Economic Addition Reactions. *Chem. Rev.* **2011**, *111*, 1596–1636.
(313) Liang, S.; Zhang, R.-Y.; Xi, L.-Y.; Chen, S.-Y.; Yu, X.-Q. Sulfonylation of Five-Membered Heterocycles via an S_NAr Reaction. *J. Org. Chem.* **2013**, *78*, 11874–11880.
(314) Maloney, K. M.; Kuethe, J. T.; Linn, K. A Practical, One-Pot Synthesis of Sulfonylated Pyridines. *Org. Lett.* **2011**, *13*, 102–105.
(315) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. Unsymmetrical Diaryl Sulfones and Aryl Vinyl Sulfones through Palladium-Catalyzed Coupling of Aryl and Vinyl Halides or Triflates with Sulfinic Acid Salts. *J. Org. Chem.* **2004**, *69*, 5608–5614.
(316) Reeves, D. C.; Rodriguez, S.; Lee, H.; Haddad, N.; Krishnamurthy, D.; Senanayake, C. H. Palladium-Catalyzed Coupling of Vinyl Tosylates with Arylsulfinate Salts. *Tetrahedron Lett.* **2009**, *50*, 2870–2873.
(317) Beaulieu, C.; Guay, D.; Wang, Z.; Evans, D. A. A Mild and Efficient New Synthesis of Aryl Sulfones from Boronic Acids and Sulfinic Acid Salts. *Tetrahedron Lett.* **2004**, *45*, 3233–3236.
(318) Baskin, J. M.; Wang, Z. An Efficient Copper Catalyst for the Formation of Sulfones from Sulfinic Acid Salts and Aryl Iodides. *Org. Lett.* **2002**, *4*, 4423–4425.
(319) Kar, A.; Sayyed, I. A.; Lo, W. F.; Kaiser, H. M.; Beller, M.; Tse, M. K. A General Copper-Catalyzed Sulfonylation of Arylboronic Acids. *Org. Lett.* **2007**, *9*, 3405–3408.

(320) Chen, Y.; Willis, M. C. Copper(I)-Catalyzed Sulfonylative Suzuki–Miyaura Cross-Coupling. *Chem. Sci.* **2017**, *8*, 3249–3253.
(321) Deeming, A. S.; Russell, C. J.; Hennessy, A. J.; Willis, M. C. DABSO-Based, Three-Component, One-Pot Sulfone Synthesis. *Org. Lett.* **2014**, *16*, 150–153.
(322) Emmett, E. J.; Hayter, B. R.; Willis, M. C. Palladium-Catalyzed Three-Component Diaryl Sulfone Synthesis Exploiting the Sulfur Dioxide Surrogate DABSO. *Angew. Chem. Int. Ed.* **2013**, *52*, 12679–12683.
(323) Tellis, J. C.; Primer, D. N.; Molander, G. A. Single-Electron Transmetalation in Organoboron Cross-Coupling by Photoredox/Nickel Dual Catalysis. *Science* **2014**, *345*, 433–436.
(324) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. C. Merging Photoredox with Nickel Catalysis: Coupling of α-Carboxyl Sp ^{3} -Carbons with Aryl Halides. *Science* **2014**, *345*, 437–440.
(325) Gui, Y.-Y.; Sun, L.; Lu, Z.-P.; Yu, D.-G. Photoredox Sheds New Light on Nickel Catalysis: From Carbon–Carbon to Carbon–Heteroatom Bond Formation. *Org. Chem. Front.* **2016**, *3*, 522–526.
(326) Kelly, C. B.; Patel, N. R.; Primer, D. N.; Jouffroy, M.; Tellis, J. C.; Molander, G. A. Preparation of Visible-Light-Activated Metal Complexes and Their Use in Photoredox/Nickel Dual Catalysis. *Nat. Protoc.* **2017**, *12*, 472–492.
(327) Yue, H.; Zhu, C.; Rueping, M. Cross-Coupling of Sodium Sulfinates with Aryl, Heteroaryl, and Vinyl Halides by Nickel/Photoredox Dual Catalysis. *Angew. Chem. Int. Ed.* **2018**, *57*, 1371–1375.
(328) Liu, N.-W.; Hofman, K.; Herbert, A.; Manolikakes, G. Visible-Light Photoredox/Nickel Dual Catalysis for the Cross-Coupling of Sulfinic Acid Salts with Aryl Iodides. *Org. Lett.* **2018**, *20*, 760–763.
(329) Meyer, A. U.; Jäger, S.; Prasad Hari, D.; König, B. Visible Light-Mediated Metal-Free Synthesis of Vinyl Sulfones from Aryl Sulfinates. *Adv. Synth. Catal.* **2015**, *357*, 2050–2054.
(330) Chatgilialoglu, C.; Lunazzi, L.; Ingold, K. U. Kinetic Studies on the Formation and Decay of Some Sulfonium Radicals. *J. Org. Chem.* **1983**, *48*, 3588–3589.
(331) Gualandi, A.; Mazzarella, D.; Ortega-Martínez, A.; Mengozzi, L.; Calcinelli, F.; Matteucci, E.; Monti, F.; Armaroli, N.; Sambri, L.; Cozzi, P. G. Photocatalytic Radical Alkylation of Electrophilic Olefins by Benzylic and Alkylic Zinc-Sulfinates. *ACS Catal.* **2017**, *7*, 5357–5362.
(332) Hering, T.; Meyer, A. U.; König, B. Photocatalytic Anion Oxidation and Applications in Organic Synthesis. *J. Org. Chem.* **2016**, *81*, 6927–6936.
(333) Gutierrez, O.; Tellis, J. C.; Primer, D. N.; Molander, G. A.; Kozlowski, M. C. Nickel-Catalyzed Cross-Coupling of Photoredox-Generated Radicals: Uncovering a General Manifold for Stereoconvergence in Nickel-Catalyzed Cross-Couplings. *J. Am. Chem. Soc.* **2015**, *137*, 4896–4899.
(334) Heitz, D. R.; Tellis, J. C.; Molander, G. A. Photochemical Nickel-Catalyzed C–H Arylation: Synthetic Scope and Mechanistic Investigations. *J. Am. Chem. Soc.* **2016**, *138*, 12715–12718.

(335) Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W. C. Photosensitized, Energy Transfer-Mediated Organometallic Catalysis through Electronically Excited Nickel(II). *Science* **2017**, *355*, 380–385.
(336) Sperger, T.; Sanhueza, I. A.; Kalvet, I.; Schoenebeck, F. Computational Studies of Synthetically Relevant Homogeneous Organometallic Catalysis Involving Ni, Pd, Ir, and Rh: An Overview of Commonly Employed DFT Methods and Mechanistic Insights. *Chem. Rev.* **2015**, *115*, 9532–9586.
(337) Kice, J. L.; Guaraldi, G.; Venier, C. G. The Mechanism of the Disproportionation of Sulfinic Acids. Rate and Equilibrium Constants for the Sulfinic Acid-Sulfinyl Sulfone (Sulfinic Anhydride) Equilibrium [1]. *J. Org. Chem.* **1966**, *31*, 3561–3567.
(338) Koch, P.; Ciuffarin, E.; Fava, A. Thermal Disproportionation of Aryl Arenethiolsulfinates. Kinetics and Mechanism. *J. Am. Chem. Soc.* **1970**, *92*, 5971–5977.
(339) Hoyle, J. The Oxidation and Reduction of Sulphinic Acids and Their Derivatives. In *Sulphinic Acids, Esters and Derivatives (1990)*; Patai, S., Ed.; John Wiley & Sons, Inc.: Chichester, UK, 1990; pp 453–474.
(340) Jouffroy, M.; Kelly, C. B.; Molander, G. A. Thioetherification via Photoredox/Nickel Dual Catalysis. *Org. Lett.* **2016**, *18*, 876–879.
(341) Oderinde, M. S.; Frenette, M.; Robbins, D. W.; Aquila, B.; Johannes, J. W. Photoredox Mediated Nickel Catalyzed Cross-Coupling of Thiols With Aryl and Heteroaryl Iodides via Thiyl Radicals. *J. Am. Chem. Soc.* **2016**, *138*, 1760–1763.
(342) Santandrea, J.; Minozzi, C.; Cruché, C.; Collins, S. K. Photochemical Dual-Catalytic Synthesis of Alkynyl Sulfides. *Angew. Chem. Int. Ed.* **2017**, *56*, 12255–12259.
(343) Cabrera-Afonso, M. J.; Lu, Z.-P.; Kelly, C. B.; Lang, S. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A. Engaging Sulfinate Salts via Ni/Photoredox Dual Catalysis Enables Facile Csp2–SO2R Coupling. *Chem. Sci.* **2018**, *9*, 3186–3191.
(344) Lin, K.; Wiles, R. J.; Kelly, C. B.; Davies, G. H. M.; Molander, G. A. Haloselective Cross-Coupling via Ni/Photoredox Dual Catalysis. *ACS Catal.* **2017**, *7*, 5129–5133.
(345) Aziz, J.; Messaoudi, S.; Alami, M.; Hamze, A. Sulfinate Derivatives: Dual and Versatile Partners in Organic Synthesis. *Org Biomol Chem* **2014**, *12*, 9743–9759.
(346) Pinnick, H. W.; Reynolds, M. A. An Improved Preparation of Sulfinate Salts and Their Michael Addition to Enones. *J. Org. Chem.* **1979**, *44*, 160–161.
(347) Lovering, F.; Bikker, J.; Humblet, C. Escape from Flatland: Increasing Saturation as an Approach to Improving Clinical Success. *J. Med. Chem.* **2009**, *52*, 6752–6756.
(348) Talele, T. T. Opportunities for Tapping into Three-Dimensional Chemical Space through a Quaternary Carbon. *J. Med. Chem.* **2020**, *63*, 13291–13315.
(349) Costantino, G.; Maltoni, K.; Marinozzi, M.; Camaioni, E.; Prezeau, L.; Pin, J.-P.; Pellicciari, R. Synthesis and Biological Evaluation of 2-(3′-(1 H -Tetrazol-5-Yl)Bicyclo[1.1.1]Pent-1-Yl)Glycine (S -TBPG), a Novel MGlu1 Receptor Antagonist. *Bioorg. Med. Chem.* **2001**, *9*, 221–227.
(350) Mikhailiuk, P. K.; Afonin, S.; Chernega, A. N.; Rusanov, E. B.; Platonov, M. O.; Dubinina, G. G.; Berditsch, M.; Ulrich, A. S.; Komarov, I. V. Conformationally Rigid Trifluoromethyl-Substituted α-Amino Acid Designed for Peptide Structure Analysis by Solid-State19F NMR Spectroscopy. *Angew. Chem. Int. Ed.* **2006**, *45*, 5659–5661.
(351) Stepan, A. F.; Subramanyam, C.; Efremov, I. V.; Dutra, J. K.; O'Sullivan, T. J.; DiRico, K. J.; McDonald, W. S.; Won, A.; Dorff, P. H.; Nolan, C. E.; Becker, S. L.; Pustilnik, L.

R.; Riddell, D. R.; Kauffman, G. W.; Kormos, B. L.; Zhang, L.; Lu, Y.; Capetta, S. H.; Green, M. E.; Karki, K.; Sibley, E.; Atchison, K. P.; Hallgren, A. J.; Oborski, C. E.; Robshaw, A. E.; Sneed, B.; O'Donnell, C. J. Application of the Bicyclo[1.1.1]Pentane Motif as a Nonclassical Phenyl Ring Bioisostere in the Design of a Potent and Orally Active γ-Secretase Inhibitor. *J. Med. Chem.* **2012**, *55*, 3414–3424.

(352) Measom, N. D.; Down, K. D.; Hirst, D. J.; Jamieson, C.; Manas, E. S.; Patel, V. K.; Somers, D. O. Investigation of a Bicyclo[1.1.1]Pentane as a Phenyl Replacement within an LpPLA $_2$ Inhibitor. *ACS Med. Chem. Lett.* **2017**, *8*, 43–48.

(353) Auberson, Y. P.; Brocklehurst, C.; Furegati, M.; Fessard, T. C.; Koch, G.; Decker, A.; La Vecchia, L.; Briard, E. Improving Nonspecific Binding and Solubility: Bicycloalkyl Groups and Cubanes as *Para* -Phenyl Bioisosteres. *ChemMedChem* **2017**, *12*, 590–598.

(354) Mykhailiuk, P. K. Saturated Bioisosteres of Benzene: Where to Go Next? *Org. Biomol. Chem.* **2019**, *17*, 2839–2849.

(355) Subbaiah, M. A. M.; Meanwell, N. A. Bioisosteres of the Phenyl Ring: Recent Strategic Applications in Lead Optimization and Drug Design. *J. Med. Chem.* **2021**, *64*, 14046–14128.

(356) Levin, M. D.; Kaszynski, P.; Michl, J. Bicyclo[1.1.1]Pentanes, [n]Staffanes, [1.1.1]Propellanes, and Tricyclo[2.1.0.02,5]Pentanes. *Chem. Rev.* **2000**, *100*, 169–234.

(357) Feng, Y.; Liu, L.; Wang, J.-T.; Zhao, S.-W.; Guo, Q.-X. Homolytic C−H and N−H Bond Dissociation Energies of Strained Organic Compounds. *J. Org. Chem.* **2004**, *69*, 3129–3138.

(358) Gianatassio, R.; Lopchuk, J. M.; Wang, J.; Pan, C.-M.; Malins, L. R.; Prieto, L.; Brandt, T. A.; Collins, M. R.; Gallego, G. M.; Sach, N. W.; Spangler, J. E.; Zhu, H.; Zhu, J.; Baran, P. S. Strain-Release Amination. *Science* **2016**, *351*, 241–246.

(359) Caputo, D. F. J.; Arroniz, C.; Dürr, A. B.; Mousseau, J. J.; Stepan, A. F.; Mansfield, S. J.; Anderson, E. A. Synthesis and Applications of Highly Functionalized 1-Halo-3-Substituted Bicyclo[1.1.1]Pentanes. *Chem. Sci.* **2018**, *9*, 5295–5300.

(360) Nugent, J.; Arroniz, C.; Shire, B. R.; Sterling, A. J.; Pickford, H. D.; Wong, M. L. J.; Mansfield, S. J.; Caputo, D. F. J.; Owen, B.; Mousseau, J. J.; Duarte, F.; Anderson, E. A. A General Route to Bicyclo[1.1.1]Pentanes through Photoredox Catalysis. *ACS Catal.* **2019**, *9*, 9568–9574.

(361) Zhang, X.; Smith, R. T.; Le, C.; McCarver, S. J.; Shireman, B. T.; Carruthers, N. I.; MacMillan, D. W. C. Copper-Mediated Synthesis of Drug-like Bicyclopentanes. *Nature* **2020**, *580*, 220–226.

(362) Trongsiriwat, N.; Pu, Y.; Nieves-Quinones, Y.; Shelp, R. A.; Kozlowski, M. C.; Walsh, P. J. Reactions of 2-Aryl-1,3-Dithianes and [1.1.1]Propellane. *Angew. Chem. Int. Ed.* **2019**, *58*, 13416–13420.

(363) Yu, S.; Jing, C.; Noble, A.; Aggarwal, V. K. 1,3-Difunctionalizations of [1.1.1]Propellane via 1,2-Metallate Rearrangements of Boronate Complexes. *Angew. Chem. Int. Ed.* **2020**, *59*, 3917–3921.

(364) Kim, J. H.; Ruffoni, A.; Al-Faiyz, Y. S. S.; Sheikh, N. S.; Leonori, D. Divergent Strain-Release Amino-Functionalization of [1.1.1]Propellane with Electrophilic Nitrogen-Radicals. *Angew. Chem. Int. Ed.* **2020**, *59*, 8225–8231.

(365) Garlets, Z. J.; Sanders, J. N.; Malik, H.; Gampe, C.; Houk, K. N.; Davies, H. M. L. Enantioselective C–H Functionalization of Bicyclo[1.1.1]Pentanes. *Nat. Catal.* **2020**, *3*, 351–357.
(366) Harmata, A. S.; Spiller, T. E.; Sowden, M. J.; Stephenson, C. R. J. Photochemical Formal (4 + 2)-Cycloaddition of Imine-Substituted Bicyclo[1.1.1]Pentanes and Alkenes. *J. Am. Chem. Soc.* **2021**, *143*, 21223–21228.
(367) Yu, S.; Jing, C.; Noble, A.; Aggarwal, V. K. Iridium-Catalyzed Enantioselective Synthesis of α-Chiral Bicyclo[1.1.1]Pentanes by 1,3-Difunctionalization of [1.1.1]Propellane. *Org. Lett.* **2020**, *22*, 5650–5655.
(368) Polites, V. C.; Badir, S. O.; Keess, S.; Jolit, A.; Molander, G. A. Nickel-Catalyzed Decarboxylative Cross-Coupling of Bicyclo[1.1.1]Pentyl Radicals Enabled by Electron Donor–Acceptor Complex Photoactivation. *Org. Lett.* **2021**, *23*, 4828–4833.
(369) Nugent, J.; Sterling, A. J.; Frank, N.; Mousseau, J. J.; Anderson, E. A. Synthesis of α-Quaternary Bicyclo[1.1.1]Pentanes through Synergistic Organophotoredox and Hydrogen Atom Transfer Catalysis. *Org. Lett.* **2021**, *23*, 8628–8633.
(370) Wong, M. L. J.; Sterling, A. J.; Mousseau, J. J.; Duarte, F.; Anderson, E. A. Direct Catalytic Asymmetric Synthesis of α-Chiral Bicyclo[1.1.1]Pentanes. *Nat. Commun.* **2021**, *12*, 1644.
(371) Pickford, H. D.; Nugent, J.; Owen, B.; Mousseau, James. J.; Smith, R. C.; Anderson, E. A. Twofold Radical-Based Synthesis of *N* , *C* -Difunctionalized Bicyclo[1.1.1]Pentanes. *J. Am. Chem. Soc.* **2021**, *143*, 9729–9736.
(372) Denisenko, A.; Garbuz, P.; Shishkina, S. V.; Voloshchuk, N. M.; Mykhailiuk, P. K. Saturated Bioisosteres of *Ortho* -Substituted Benzenes. *Angew. Chem. Int. Ed.* **2020**, *59*, 20515–20521.
(373) Anderson, J. M.; Measom, N. D.; Murphy, J. A.; Poole, D. L. Bridge Functionalisation of Bicyclo[1.1.1]Pentane Derivatives. *Angew. Chem. Int. Ed.* **2021**, *60*, 24754–24769.
(374) Zhao, J.-X.; Chang, Y.-X.; He, C.; Burke, B. J.; Collins, M. R.; Del Bel, M.; Elleraas, J.; Gallego, G. M.; Montgomery, T. P.; Mousseau, J. J.; Nair, S. K.; Perry, M. A.; Spangler, J. E.; Vantourout, J. C.; Baran, P. S. 1,2-Difunctionalized Bicyclo[1.1.1]Pentanes: Long–Sought-after Mimetics for *Ortho* / *Meta* -Substituted Arenes. *Proc. Natl. Acad. Sci.* **2021**, *118*, e2108881118.
(375) Ma, X.; Han, Y.; Bennett, D. J. Selective Synthesis of 1-Dialkylamino-2-Alkylbicyclo-[1.1.1]Pentanes. *Org. Lett.* **2020**, *22*, 9133–9138.
(376) Ma, X.; Sloman, D. L.; Han, Y.; Bennett, D. J. A Selective Synthesis of 2,2-Difluorobicyclo[1.1.1]Pentane Analogues: "BCP-F $_2$." *Org. Lett.* **2019**, *21*, 7199–7203.
(377) Yang, Y.; Tsien, J.; Hughes, J. M. E.; Peters, B. K.; Merchant, R. R.; Qin, T. An Intramolecular Coupling Approach to Alkyl Bioisosteres for the Synthesis of Multisubstituted Bicycloalkyl Boronates. *Nat. Chem.* **2021**, *13*, 950–955.
(378) Applequist, D. E.; Renken, T. L.; Wheeler, J. W. Polar Substituent Effects in 1,3-Disubstituted Bicyclo[1.1.1]Pentanes. *J. Org. Chem.* **1982**, *47*, 4985–4995.
(379) Bychek, R. M.; Hutskalova, V.; Bas, Y. P.; Zaporozhets, O. A.; Zozulya, S.; Levterov, V. V.; Mykhailiuk, P. K. Difluoro-Substituted Bicyclo[1.1.1]Pentanes for Medicinal Chemistry: Design, Synthesis, and Characterization. *J. Org. Chem.* **2019**, *84*, 15106–15117.

(380) McNamee, R. E.; Thompson, A. L.; Anderson, E. A. Synthesis and Applications of Polysubstituted Bicyclo[1.1.0]Butanes. *J. Am. Chem. Soc.* **2021**, *143*, 21246–21251.
(381) Buskes, M. J.; Blanco, M.-J. Impact of Cross-Coupling Reactions in Drug Discovery and Development. *Molecules* **2020**, *25*, 3493.
(382) Nóvoa, L.; Trulli, L.; Parra, A.; Tortosa, M. Stereoselective Diboration of Spirocyclobutenes: A Platform for the Synthesis of Spirocycles with Orthogonal Exit Vectors. *Angew. Chem. Int. Ed.* **2021**, *60*, 11763–11768.
(383) Kaiser, D.; Noble, A.; Fasano, V.; Aggarwal, V. K. 1,2-Boron Shifts of β-Boryl Radicals Generated from Bis-Boronic Esters Using Photoredox Catalysis. *J. Am. Chem. Soc.* **2019**, *141*, 14104–14109.
(384) Fawcett, A.; Nitsch, D.; Ali, M.; Bateman, J. M.; Myers, E. L.; Aggarwal, V. K. Regio- and Stereoselective Homologation of 1,2-Bis(Boronic Esters): Stereocontrolled Synthesis of 1,3-Diols and Sch 725674. *Angew. Chem. Int. Ed.* **2016**, *55*, 14663–14667.
(385) Crudden, C. M.; Ziebenhaus, C.; Rygus, J. P. G.; Ghozati, K.; Unsworth, P. J.; Nambo, M.; Voth, S.; Hutchinson, M.; Laberge, V. S.; Maekawa, Y.; Imao, D. Iterative Protecting Group-Free Cross-Coupling Leading to Chiral Multiply Arylated Structures. *Nat. Commun.* **2016**, *7*, 11065.
(386) Mlynarski, S. N.; Schuster, C. H.; Morken, J. P. Asymmetric Synthesis from Terminal Alkenes by Cascades of Diboration and Cross-Coupling. *Nature* **2014**, *505*, 386–390.
(387) Blaisdell, T. P.; Morken, J. P. Hydroxyl-Directed Cross-Coupling: A Scalable Synthesis of Debromohamigeran E and Other Targets of Interest. *J. Am. Chem. Soc.* **2015**, *137*, 8712–8715.
(388) Jarret, R. M.; Cusumano, L. 13C-13C Coupling in [1.1.1]Propellane. *Tetrahedron Lett.* **1990**, *31*, 171–174.
(389) Yang, Y.; Tsien, J.; Ben David, A.; Hughes, J. M. E.; Merchant, R. R.; Qin, T. Practical and Modular Construction of C(Sp3)-Rich Alkyl Boron Compounds. *J. Am. Chem. Soc.* **2021**, *143*, 471–480.
(390) Li, H.; Wang, L.; Zhang, Y.; Wang, J. Transition-Metal-Free Synthesis of Pinacol Alkylboronates from Tosylhydrazones. *Angew. Chem. Int. Ed.* **2012**, *51*, 2943–2946.
(391) Yang, C.-T.; Zhang, Z.-Q.; Liu, Y.-C.; Liu, L. Copper-Catalyzed Cross-Coupling Reaction of Organoboron Compounds with Primary Alkyl Halides and Pseudohalides. *Angew. Chem. Int. Ed.* **2011**, *50*, 3904–3907.
(392) Liu, X.; Sun, C.; Mlynarski, S.; Morken, J. P. Synthesis and Stereochemical Assignment of Arenolide. *Org. Lett.* **2018**, *20*, 1898–1901.
(393) Pozzi, D.; Scanlan, E. M.; Renaud, P. A Mild Radical Procedure for the Reduction of *B* -Alkylcatecholboranes to Alkanes. *J. Am. Chem. Soc.* **2005**, *127*, 14204–14205.
(394) André-Joyaux, E.; Kuzovlev, A.; Tappin, N. D. C.; Renaud, P. A General Approach to Deboronative Radical Chain Reactions with Pinacol Alkylboronic Esters. *Angew. Chem. Int. Ed.* **2020**, *59*, 13859–13864.
(395) Lima, F.; Sharma, U. K.; Grunenberg, L.; Saha, D.; Johannsen, S.; Sedelmeier, J.; Van der Eycken, E. V.; Ley, S. V. A Lewis Base Catalysis Approach for the Photoredox Activation of Boronic Acids and Esters. *Angew. Chem. Int. Ed.* **2017**, *56*, 15136–15140.
(396) Lima, F.; Grunenberg, L.; Rahman, H. B. A.; Labes, R.; Sedelmeier, J.; Ley, S. V. Organic Photocatalysis for the Radical Couplings of Boronic Acid Derivatives in Batch and Flow. *Chem. Commun.* **2018**, *54*, 5606–5609.

(397) Lima, F.; Kabeshov, M. A.; Tran, D. N.; Battilocchio, C.; Sedelmeier, J.; Sedelmeier, G.; Schenkel, B.; Ley, S. V. Visible Light Activation of Boronic Esters Enables Efficient Photoredox C(Sp^2)-C(Sp^3) Cross-Couplings in Flow. *Angew. Chem. Int. Ed.* **2016**, *55*, 14085–14089.
(398) Primer, D. N.; Molander, G. A. Enabling the Cross-Coupling of Tertiary Organoboron Nucleophiles through Radical-Mediated Alkyl Transfer. *J. Am. Chem. Soc.* **2017**, *139*, 9847–9850.
(399) Yuan, M.; Song, Z.; Badir, S. O.; Molander, G. A.; Gutierrez, O. On the Nature of C(Sp^3)–C(Sp^2) Bond Formation in Nickel-Catalyzed Tertiary Radical Cross-Couplings: A Case Study of Ni/Photoredox Catalytic Cross-Coupling of Alkyl Radicals and Aryl Halides. *J. Am. Chem. Soc.* **2020**, *142*, 7225–7234.
(400) Bauer, M. R.; Di Fruscia, P.; Lucas, S. C. C.; Michaelides, I. N.; Nelson, J. E.; Storer, R. I.; Whitehurst, B. C. Put a Ring on It: Application of Small Aliphatic Rings in Medicinal Chemistry. *RSC Med. Chem.* **2021**, *12*, 448–471.
(401) Li, J. J. *Medicinal Chemistry for Practitioners*, First edition.; Wiley: Hoboken, NJ, 2020.
(402) Meanwell, N. A. Fluorine and Fluorinated Motifs in the Design and Application of Bioisosteres for Drug Design. *J. Med. Chem.* **2018**, *61*, 5822–5880.
(403) Gillis, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. Applications of Fluorine in Medicinal Chemistry. *J. Med. Chem.* **2015**, *58*, 8315–8359.
(404) Kautzky, J. A.; Wang, T.; Evans, R. W.; MacMillan, D. W. C. Decarboxylative Trifluoromethylation of Aliphatic Carboxylic Acids. *J. Am. Chem. Soc.* **2018**, *140*, 6522–6526.
(405) Cyr, P.; Flynn-Robitaille, J.; Boissarie, P.; Marinier, A. Mild and Diazo-Free Synthesis of Trifluoromethyl-Cyclopropanes Using Sulfonium Ylides. *Org. Lett.* **2019**, *21*, 2265–2268.
(406) Zhao, Q.; Yu, G.; Meng, Y.; Sui, F.; Yang, M.; Liu, L.; Li, H.; Li, F.; Ma, H. An Efficient Substrate-Induced Method for the Synthesis of CF3-Substituted Cyclopropanes by Metal-Free Reaction of Trifluoromethyl Styrylisoxazoles with Nitromethane. *Synthesis* **2021**, *53*, 1597–1604.
(407) Bugera, M.; Trofymchuk, S.; Tarasenko, K.; Zaporozhets, O.; Pustovit, Y.; Mykhailiuk, P. K. Deoxofluorination of Aliphatic Carboxylic Acids: A Route to Trifluoromethyl-Substituted Derivatives. *J. Org. Chem.* **2019**, *84*, 16105–16115.
(408) Liu, S.; Huang, Y.; Qing, F.-L.; Xu, X.-H. Transition-Metal-Free Decarboxylation of 3,3,3-Trifluoro-2,2-Dimethylpropanoic Acid for the Preparation of C(CF_3)Me_2-Containing Heteroarenes. *Org. Lett.* **2018**, *20*, 5497–5501.
(409) Smith, J. M.; Dixon, J. A.; deGruyter, J. N.; Baran, P. S. Alkyl Sulfinates: Radical Precursors Enabling Drug Discovery: Miniperspective. *J. Med. Chem.* **2019**, *62*, 2256–2264.
(410) Kuttruff, C. A.; Haile, M.; Kraml, J.; Tautermann, C. S. Late-Stage Functionalization of Drug-Like Molecules Using Diversinates. *ChemMedChem* **2018**, *13*, 983–987.
(411) Michaudel, Q.; Ishihara, Y.; Baran, P. S. Academia–Industry Symbiosis in Organic Chemistry. *Acc. Chem. Res.* **2015**, *48*, 712–721.
(412) Fujiwara, Y.; Dixon, J. A.; O'Hara, F.; Funder, E. D.; Dixon, D. D.; Rodriguez, R. A.; Baxter, R. D.; Herlé, B.; Sach, N.; Collins, M. R.; Ishihara, Y.; Baran, P. S. Practical and Innate Carbon–Hydrogen Functionalization of Heterocycles. *Nature* **2012**, *492*, 95–99.

(413) Yan, M.; Lo, J. C.; Edwards, J. T.; Baran, P. S. Radicals: Reactive Intermediates with Translational Potential. *J. Am. Chem. Soc.* **2016**, *138*, 12692–12714.
(414) Smith, J. M.; Harwood, S. J.; Baran, P. S. Radical Retrosynthesis. *Acc. Chem. Res.* **2018**, *51*, 1807–1817.
(415) Proctor, R. S. J.; Phipps, R. J. Recent Advances in Minisci-Type Reactions. *Angew. Chem. Int. Ed.* **2019**, *58*, 13666–13699.
(416) Oae, S.; Furukawa, N. Heteroaromatic Sulfoxides and Sulfones: Ligand Exchange and Coupling in Sulfuranes and Ipso-Substitutions. In *Advances in Heterocyclic Chemistry*; Elsevier, 1990; Vol. 48, pp 1–63.
(417) Oae, S.; Uchida, Y. Ligand-Coupling Reactions of Hypervalent Species. *Acc. Chem. Res.* **1991**, *24*, 202–208.
(418) Oae, S. Ligand Coupling Reactions of Hypervalent Species. *Pure Appl. Chem.* **1996**, *68*, 805–812.
(419) Zhou, M.; Tsien, J.; Qin, T. Unsymmetrical Heterocycle Cross-Couplings Enabled by Sulfur(IV) Reagents. *Synlett* **2020**, *31*, 1962–1966.
(420) Oae, S.; Kawai, T.; Furukawa, N. Ligand Coupling through σ-Sulfurane — Complete Retention of Configuration of 1-Phenylethyl Group in the Reaction of 1-Phenylethyl 2-Pyridyl Sulfoxide with Grignard Reagent1. *Tetrahedron Lett.* **1984**, *25*, 69–72.
(421) Oae, S.; Kawai, T.; Furukawa, N.; Iwasaki, F. Ligand Coupling within σ-Sulphurane Intermediates Formed in the Reaction of Benzyl 2-Pyridyl and Related Sulphoxides with Grignard Reagents. *J Chem Soc Perkin Trans 2* **1987**, No. 3, 405–411.
(422) Wakabayashi, S.; Ishida, M.; Takeda, T.; Oae, S. Sensitive Nature of Ligand Coupling and Pseudorotation to Electronic Effect of Substituent---Ligand Coupling in the Reactions of Benzylic Aryl Sulfoxides with Benzylic Grignard Reagents. *Tetrahedron Lett.* **1988**, *29*, 4441–4444.
(423) Oae, S.; Kawai, T.; Furukawa, N. LIGAND EXCHANGE AND LIGAND COUPLING VIA THE σ-SULFURANE INTERMEDIATE IN THE REACTION OF ALKYL 2-PYRIDYL SULFOXIDE WITH GRIGNARD REAGENTS: CONVENIENT PREPARATION OF 2,2′-BIPYRIDINES. *Phosphorous Sulfur Relat. Elem.* **1987**, *34*, 123–132.
(424) Furukawa, N.; Shibutani, T.; Fujihara, H. Preparation of Pyridyl Grignard Reagents and Cross Coupling Reactions with Sulfoxides Bearing Azaheterocycles. *Tetrahedron Lett.* **1987**, *28*, 5845–5848.
(425) Oae, S.; Takeda, T.; Wakabayashi, S. Ligand Coupling through σ-Sulfurane — Complete Retention of Geometric Configuration of Allylic and Vinylic Groups in the Reactions of Allylic and Vinylic Sulfoxides with Grignard Reagents. *Tetrahedron Lett.* **1988**, *29*, 4445–4448.
(426) Kawai, T.; Furukawa, N.; Oae, S. A Convenient Preparation of Bipyridines through Ligand Coupling Reaction with A-Sulfurane Formed by Treatment of Methyl 2-Pyridyl Sulfoxide with Grignard Reagents. *Tetrahedron Lett.* **1984**, *25*, 2549–2552.
(427) LaRochelle, R. W.; Trost, B. M. Reactions of Organolithiums with Arylsulfonium Salts. *J. Am. Chem. Soc.* **1971**, *93*, 6077–6086.
(428) Trost, B. M.; Arndt, H. C. ..Sigma.-Sulfurane Chemistry. Effect of Substituents on the Coupling Reactions. *J. Am. Chem. Soc.* **1973**, *95*, 5288–5298.

(429) Dean, W. M.; Šiaučiulis, M.; Storr, T. E.; Lewis, W.; Stockman, R. A. Versatile C(Sp ^{2})−C(Sp ^{3}) Ligand Couplings of Sulfoxides for the Enantioselective Synthesis of Diarylalkanes. *Angew. Chem. Int. Ed.* **2016**, *55*, 10013–10016.
(430) Šiaučiulis, M.; Ahlsten, N.; Pulis, A. P.; Procter, D. J. Transition-Metal-Free Cross-Coupling of Benzothiophenes and Styrenes in a Stereoselective Synthesis of Substituted (*E,Z*)-1,3-Dienes. *Angew. Chem. Int. Ed.* **2019**, *58*, 8779–8783.
(431) Duong, V. K.; Horan, A. M.; McGarrigle, E. M. Synthesis of Pyridylsulfonium Salts and Their Application in the Formation of Functionalized Bipyridines. *Org. Lett.* **2020**, *22*, 8451–8457.
(432) Morofuji, T.; Yoshida, T.; Tsutsumi, R.; Yamanaka, M.; Kano, N. Arylation of Aryllithiums with *S* -Arylphenothiazinium Ions for Biaryl Synthesis. *Chem. Commun.* **2020**, *56*, 13995–13998.
(433) Chen, D.-L.; Sun, Y.; Chen, M.; Li, X.; Zhang, L.; Huang, X.; Bai, Y.; Luo, F.; Peng, B. Desulfurization of Diaryl(Heteroaryl) Sulfoxides with Benzyne. *Org. Lett.* **2019**, *21*, 3986–3989.
(434) Ritts, C. B.; Hoye, T. R. Sulfurane [S(IV)]-Mediated Fusion of Benzynes Leads to Helical Dibenzofurans. *J. Am. Chem. Soc.* **2021**, *143*, 13501–13506.
(435) Zhou, M.; Tsien, J.; Qin, T. Sulfur(IV)-Mediated Unsymmetrical Heterocycle Cross-Couplings. *Angew. Chem. Int. Ed.* **2020**, *59*, 7372–7376.
(436) Kawai, T.; Kodera, Y.; Oae, S.; Ishida, M.; Takeda, T.; Wakabayashi, S.; Furukawa, N. OCCURRENCE OF LIGAND COUPLING IN THE REACTIONS OF VARIOUS SULFOXIDES WITH GRIGNARD REAGENTS. *Phosphorous Sulfur Relat. Elem.* **1987**, *34*, 139–148.
(437) Shi, W.-Q.; Liu, S.; Wang, C.-Z.; Huang, Y.; Qing, F.-L.; Xu, X.-H. Synthesis of CMe $_{2}$ CF $_{3}$ -Containing Heteroarenes via Tandem 1,1-Dimethyltrifluoroethylation and Cyclization of Isonitriles. *J. Org. Chem.* **2018**, *83*, 15236–15244.
(438) Johnston, L. J.; Scaiano, J. C.; Ingold, K. U. Kinetics of Cyclopropyl Radical Reactions. 1. Absolute Rate Constants for Some Addition and Abstraction Reactions. *J. Am. Chem. Soc.* **1984**, *106*, 4877–4881.
(439) Sun, A. C.; McClain, E. J.; Beatty, J. W.; Stephenson, C. R. J. Visible Light-Mediated Decarboxylative Alkylation of Pharmaceutically Relevant Heterocycles. *Org. Lett.* **2018**, *20*, 3487–3490.
(440) Kirihara, M.; Kambayashi, T.; Momose, T. Allylic Fluorides via the Cleavage of Tertiary Cyclopropyl Silyl Ethers with Diethlaminosulfur Trifluoride. *Chem. Commun.* **1996**, No. 10, 1103.
(441) Meyer, O. G. J.; Fröhlich, R.; Haufe, G. Asymmetric Cyclopropanation of Vinyl Fluorides: Access to Enantiopure Monofluorinated Cyclopropane Carboxylates. *Synthesis* **2000**, *2000*, 1479–1490.
(442) Arlt, A.; Schwarz, H.-G.; Yolanda Can-Cho Grande; Füsslein, M.; Jeschke, P.; Ebbinghaus-Kintscher, U.; Linka, M.; Lösel, P.; DAMIJONAITIS, A. J.; Turberg, A.; Heisler, I.; MANDZHULO, O. Novel Heteroaryl-Triazole Compounds as Pesticides. WO 2021013720 A1, January 28, 2021.
(443) Fang, Z.; Cordes, D. B.; Slawin, A. M. Z.; O'Hagan, D. Fluorine Containing Cyclopropanes: Synthesis of Aryl Substituted All- *Cis* 1,2,3-Trifluorocyclopropanes, a Facially Polar Motif. *Chem. Commun.* **2019**, *55*, 10539–10542.

(444) Conte, A.; Kuehne, H.; Luebbers, T.; Mattei, P.; Maugeais, C. M.; Mueller, W.; Pflieger, P. Anthranilamide/2-Amino-Heteroarene Carboxamide Derivatives. WO 2007090752 A1, August 16, 2007.
(445) Lapointe, B. T.; Fuller, P. H.; Gunaydin, H.; Liu, K.; Scott, M. E.; Trotter, B. W.; Zhang, H. Substituted Indazole Compounds as Rorgammat Inhibitors and Uses Thereof. WO 2017075182 A1, May 4, 2017.
(446) Liang, S.; Hofman, K.; Friedrich, M.; Manolikakes, G. Recent Advances in the Synthesis and Direct Application of Sulfinate Salts. *Eur. J. Org. Chem.* **2020**, *2020*, 4664–4676.
(447) Reddy, R. J.; Kumari, A. H. Synthesis and Applications of Sodium Sulfinates (RSO_2Na): A Powerful Building Block for the Synthesis of Organosulfur Compounds. *RSC Adv.* **2021**, *11*, 9130–9221.
(448) Sarver, P. J.; Bissonnette, N. B.; MacMillan, D. W. C. Decatungstate-Catalyzed C(Sp^3)–H Sulfinylation: Rapid Access to Diverse Organosulfur Functionality. *J. Am. Chem. Soc.* **2021**, *143*, 9737–9743.
(449) Johnson, M. G.; Gribble, M. W.; Houze, J. B.; Paras, N. A. Convenient Route to Secondary Sulfinates: Application to the Stereospecific Synthesis of α-*C*-Chiral Sulfonamides. *Org. Lett.* **2014**, *16*, 6248–6251.
(450) O'Neill, M.; Cornella, J. Retaining Alkyl Nucleophile Regiofidelity in Transition-Metal-Mediated Cross-Couplings to Aryl Electrophiles. *Synthesis* **2018**, *50*, 3974–3996.
(451) Li, L.; Wang, C.-Y.; Huang, R.; Biscoe, M. R. Stereoretentive Pd-Catalysed Stille Cross-Coupling Reactions of Secondary Alkyl Azastannatranes and Aryl Halides. *Nat. Chem.* **2013**, *5*, 607–612.
(452) Zhou, M.; Tsien, J.; Dykstra, R.; Hughes, J. M. E.; Byron, P. K.; Merchant, R. R.; Gutierrez, O.; Qin, T. Alkyl Sulfinates as Cross-Coupling Partners: Programmable and Stereospecific Installation of C(Sp3) Bioisosteres. *Nat. Chem.* **2022**.
(453) Peltzer, R. M.; Eisenstein, O.; Nova, A.; Cascella, M. How Solvent Dynamics Controls the Schlenk Equilibrium of Grignard Reagents: A Computational Study of CH_3MgCl in Tetrahydrofuran. *J. Phys. Chem. B* **2017**, *121*, 4226–4237.
(454) Peltzer, R. M.; Gauss, J.; Eisenstein, O.; Cascella, M. The Grignard Reaction – Unraveling a Chemical Puzzle. *J. Am. Chem. Soc.* **2020**, *142*, 2984–2994.
(455) Park, J. W.; Al-Saadon, R.; MacLeod, M. K.; Shiozaki, T.; Vlaisavljevich, B. Multireference Electron Correlation Methods: Journeys along Potential Energy Surfaces. *Chem. Rev.* **2020**, *120*, 5878–5909.
(456) Gräfenstein, J.; Cremer, D. Can Density Functional Theory Describe Multi-Reference Systems? Investigation of Carbenes and Organic Biradicals. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2091–2103.
(457) Grampp, G. The Marcus Inverted Region from Theory to Experiment. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 691–693.
(458) López-Estrada, O.; Laguna, H. G.; Barrueta-Flores, C.; Amador-Bedolla, C. Reassessment of the Four-Point Approach to the Electron-Transfer Marcus–Hush Theory. *ACS Omega* **2018**, *3*, 2130–2140.