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Palladium(II) and platinum(II) synthetic peptidases: residue- and sequence-selective hydrolysis and the photochemistry of sulfoxides, S,C-sulfonium ylides, and sulfilimines: unimolecular bond cleavage

Stacey Anne Stoffregen
Iowa State University

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Palladium(II) and platinum(II) synthetic peptidases: residue- and sequence-selective hydrolysis and the photochemistry of sulfoxides, *S,C*-sulfonium ylides, and sulfilimines: unimolecular bond cleavage

by

Stacey Anne Stoffregen

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Program of Study Committee:
William Jenks, Major Professor
Robert Angelici
Mark Gordon
Emily Smith
Theresa Windus

Iowa State University

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TABLE OF CONTENTS

ABSTRACT iv

CHAPTER 1. The development of synthetic peptidases: a general review
1.1 Dissertation organization 1
1.2 Properties of the amide group 2
1.3 Hydrolysis of amide bonds 3
1.4 Proteolytic reagents 5
1.5 Metal-ion binding to amides 6
1.6 Palladium(II) and platinum(II) reagents for peptide and protein hydrolysis 7
1.7 References 11

CHAPTER 2. Thioether complexes of palladium(II) and platinum(II) as artificial peptidases: residue-selective peptide cleavage by a palladium complex
2.1 Abstract 17
2.2 Introduction 18
2.3 Experimental procedures 20
2.4 Results and discussion 26
2.5 Conclusions 36
2.6 Acknowledgments 37
2.7 Supporting information description 37
2.8 References 38

CHAPTER 3. The photochemistry and photophysics of sulfur and selenium ylides: a general review
3.1 General introduction to sulfur- and selenium-containing compounds 44
3.2 Nomenclature and properties of sulfur- and selenium-containing compounds 44
3.3 Thermal reactions of sulfoxides, selenoxides, sulfinic esters, and sulfonic esters 47
3.4 Unimolecular photochemistry of sulfoxides and selenoxides 51
3.5 Properties, preparation, and reactivity of carbenes 61
3.6 References 67

CHAPTER 4. Photochemical reactivity of *S,C*-sulfonium ylides: potential carbene precursors
4.1 Abstract 77
4.2 Introduction 78
4.3 Experimental details 79
4.4 Results and discussion 83
4.5 Conclusions 92
4.6 Acknowledgement 93
4.7 Supporting information description 93
4.8 References 93

CHAPTER 5. Correlation of thiophene-*S*-oxide and selenophene-*Se*-oxide excited states with deoxygenation products
5.1 Abstract 98
5.2 Introduction 99
5.3 Computational details 102
5.4 Results and discussion 104
5.5 Conclusions 120
5.6 Acknowledgement 121
5.7 Supporting information description 121
5.8 References 121

CHAPTER 6. Sulfur and selenium ylide bond enthalpies
6.1 Abstract 125
6.2 Introduction 126
6.3 Computational methods 127
6.4 Results and discussion 127
6.5 Summary 147
6.6 Acknowledgement 148
6.7 Supporting information description 148
6.8 References 148

CHAPTER 7. Elimination reactions of *N*-sulfilimines and *S,C*-sulfonium ylides
7.1 Abstract 154
7.2 Introduction 155
7.3 Computational details 158
7.4 Results and discussion 158
7.5 Summary and conclusions 164
7.6 Acknowledgement 165
7.7 Supporting information description 165
7.8 References 165

CHAPTER 8. General conclusions 169

APPENDIX A. Supporting information for Chapter 2 173

APPENDIX B. Supporting information for Chapter 4 178

APPENDIX C. Supporting information for Chapter 5 213

APPENDIX D. Supporting information for Chapter 6 229

APPENDIX E. Supporting information for Chapter 7 300

ABSTRACT

In this dissertation the photochemistry of sulfoxides, sulfilimines, and *S,C*-sulfonium ylides was explored both computationally and experimentally. Dibenzothiophene-*S*-oxide has been previously shown to undergo deoxygenation to form dibenzothiophene and a reactive intermediate believed to be O(^{3}P). In this study, the photochemistry of *S,C*-sulfonium ylides of thiophenes was explored and shown to result in unimolecular bond scission of the S-C ylidic bond to give the corresponding sulfide and a reactive intermediate, analogous to the chemistry of dibenzothiophene-*S*-oxide. Chemical trapping studies provide indirect evidence that the reactive intermediate produced upon photolysis is a carbene.

The mechanism of unimolecular bond cleavage for sulfoxides was further explored computationally by generating the potential energy surfaces (PES) of thiophene-*S*-oxide and selenophene-*Se*-oxide as a function of S-O and Se-O bond length using the CASSCF [18,14] method. Energy corrections were obtained with a second-order perturbation theory (MRMP2). The results for thiophene-*S*-oxide and selenophene-*Se*-oxide indicate that the second triplet excited state of each provide nearly barrierless route toward S-O and Se-O bond dissociation. The potential energy diagrams offer a new explanation for the experimentally observed unimolecular bond cleavage of DBTO and DBSeO, in which intersystem crossing from an excited singlet state to a dissociative T_2 state provides a pathway to deoxygenation products. This mechanism is consistent with the increased quantum yields of deoxygenation that were experimentally observed for heavy-atom substituted sulfoxides.

The bond dissociation enthalpies (BDEs) of several sulfoxides, sulfilimines, *S,C*-sulfonium ylides, and selenoxides were also estimated by applying MP2/6-311++G(3df,2p)//MP2/6-31G(d,p), G3, and other computational methods. Selenoxides

have the weakest ylide bond strengths, followed by *N*-H sulfilimines and CH_2-*S,C*-sulfonium ylides. Sulfilimine and *S,C*-sulfonium ylides are stabilized by electron withdrawing substituents on N or C, respectively. Incorporation of the S or Se atom into a ring system that stands to gain aromaticity upon deoxygenation results in weaker BDEs.

Finally, the elimination reactions of sulfoxides, sulfilimines, and *S*,*C*-sulfonium ylides were studied computationally. We report the reaction enthalpies and activation barriers of the forward and reverse reactions for related sulfilimines, *S,C*-sulfonium ylides, and a sulfoxide. Our results indicate that a major factor affecting the relative ease of reactivity is the strength of the S-C_α bond. Resonance stabilization of the ylide nitrogen of sulfilimines and the ylide carbon of sulfonium ylides with electron-withdrawing groups effectively delocalizes the charge rendering the ylide less nucleophilic and thereby less reactive toward eliminations. Additionally, our results show that among the compounds tested, the S-C_α bond of compounds with electron-withdrawing substituents is the strongest, further limiting the reactivity of these ylides. The estimated reaction enthalpies of *S,C*-sulfonium ylides from this study suggest that these compounds would be viable reactants for mild preparation of a variety of alkenes.

CHAPTER 1

The development of synthetic peptidases: a general review

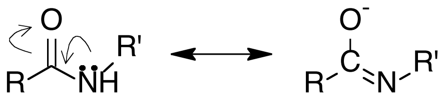
1.1 Dissertation organization.

This dissertation containing eight chapters and five appendices investigates aspects of bioinorganic chemistry and organic photochemistry. Chapter 1 is a general review of the hydrolysis of peptides and proteins. Chapter 2 is a paper that was published in 2005 in *Inorganic Chemistry*, which discusses the development of Pd(II) and Pt(II) thioether complexes that selectively hydrolyze peptide bonds. The author of this dissertation performed the bulk of the experiments, wrote the paper, and mentored undergraduate Amanda Griffin who synthesized and characterized the binuclear complex.

Chapter 3 is a general review of the chemistry of sulfoxides, selenoxides, *S,C*-sulfonium ylides, and sulfilimines. Chapter 4 is a paper being prepared for publication in the *Journal of Organic Chemistry* that discusses the photochemistry of thiophene-based *S,C*-sulfonium ylides. The author of this dissertation performed all of the experiments and wrote the paper. Chapter 5 is a paper being prepared for publication in the *Journal of the American Chemical Society*. The chapter describes a computational study designed to provide a correlation of thiophene-*S*-oxide excited states with the products of photochemical deoxygenation. The author of this dissertation performed the bulk of the calculations, wrote the paper, and mentored undergraduate Pearl Dickerson who performed the initial HF/6-31G(d) calculations on selenophene-*Se*-oxide. Chapter 6 is a paper that has been submitted for publication in the *Journal of Organic Chemistry* that computationally examines the bond strengths of various sulfoxides, selenoxides, *S,C*-sulfonium ylides, and sulfilimines. The author of this dissertation mentored undergraduate Robert Wilson who performed many of the calculations on the substituted sulfilimines and *S,C*-sulfonium ylides. The author completed the remaining calculations and wrote a portion of the paper. The remainder of the calculations were performed by Dr. Ryan McCulla, Samuel Cercone, and Jennifer Miller. Dr. McCulla also wrote a portion of the paper. Chapter 7 is a paper being prepared for publication in the *Journal of Organic Chemistry* that computationally compares elimination reactions of a sulfoxide with analogous *N*-substituted sulfilimines and *C*-substituted *S,C*-sulfonium ylides. The effect of electron withdrawing groups on the nitrogen atom of sulfilimines and the carbon atom of *S,C*-sulfonium ylides is explored. The author of this dissertation performed all of the calculations and wrote the paper describing this work.

1.2 Properties of the amide group.

Amide bonds are ubiquitous in nature, serving as the linkage between every amino acid within a peptide or protein chain. All amino acids contain secondary amide nitrogen atoms with the exception of proline, which contains a tertiary amide nitrogen atom. Amide groups are planar, have a rotational barrier of nearly 19 kcal/mol about the C-N bond, and often adopt a *trans* orientation. A comparison of typical carbon-nitrogen bond lengths places amide C-N bonds at 1.32 Å, intermediate to typical C-N single bonds (1.45 Å) and C-N double bonds (1.24 Å).[1] In other words, amide bonds exhibit approximately 40% double bond character due to resonance stabilization. The appreciable amount of negative charge that resides on the amide carbonyl oxygen atom and the low basicity of the amide nitrogen atom can also be attributed to resonance stabilization. From the protonation equilibria shown below in Figure 1, it can be seen that amides are neutral from pH 0 to 14. Since the amide nitrogen is a very weak base, protonation only occurs in strongly acidic solutions (~1 M acid). On the other hand, deprotonation of the amide nitrogen (pKa ≅ 15) to give the anionic species requires quite basic solutions (> 1 M hydroxide).[2] Protonation of a neutral amide occurs preferentially at the oxygen, rather than at the amide nitrogen. The equilibrium between protonated tautomers favors the O-protonated structure over the N-protonated structure with an equilibrium constant of approximately 10^7. Like protons, metal ions also interact preferentially with the oxygen atom of a neutral amide. However, in the presence of an anionic amide, a metal ion will coordinate to the nitrogen atom.



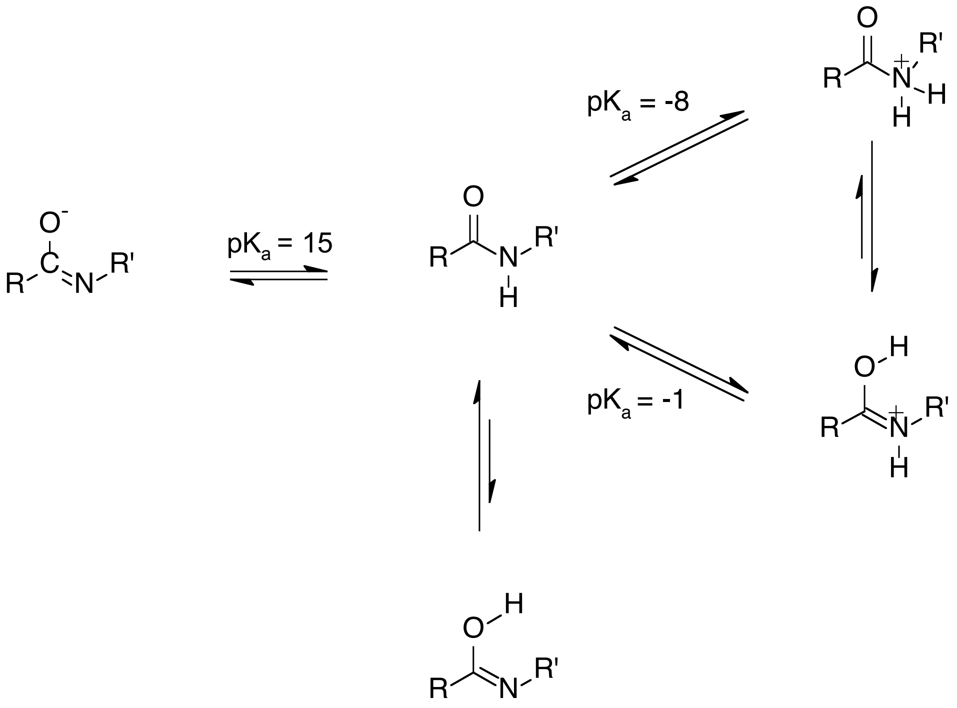
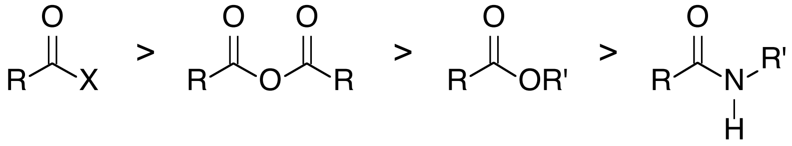


Figure 1. Protonation equilibria of a general amide.

1.3 Hydrolysis of amide bonds.

The amide bond has been extensively studied and shown to undergo nucleophilic addition-elimination reactions. The carbon-nitrogen bond of amide functional groups is extremely resistant toward hydrolysis with an estimated half-life of 250-600 years at room temperature and neutral pH.[2-4] Compared to the reactivity of other acyl derivatives amide hydrolysis is relatively slow.



The cleavage of amide bonds is an extremely important reaction in nature. The amide bonds of proteins can be cleaved nonselectively in processes such as the degradation of proteins, apoptosis, and antigen processing.[5-8] Alternatively, proteins can undergo residue- or sequence-selective hydrolysis. Several important biological functions rely on this process, including the regulation of the cell cycle, signal transduction, transcription, and the activation of proteins.[6, 9-16]

Many biochemical and bioanalytical techniques also rely on the hydrolysis of peptides and proteins, most of which require relatively selective reactions in order to produce sizeable protein fragments.[17] Among the many techniques that take advantage of peptide cleavage are protein footprinting, protein semisynthesis, and the removal of fusion tags from proteins.

Protein footprinting is a technique designed to probe protein-protein interactions. In particular, this strategy has been used to map the subunit contacts of RNA polymerase in *Escherichia coli*.[18-21] In order to determine which portions of a protein are involved in macromolecular interactions, the protein complex is subjected to a proteolytic reagent. The complexed segments of the protein will be inaccessible to the reagent and, thus, remain intact while the remainder of the sequence is susceptible to cleavage. Until the late 1990's, the most common reagents used in footprinting experiments were proteolytic enzymes, which inherently limit the detail that can be obtained due to their molecular dimensions. More recently, chemical reagents, particularly iron-EDTA complexes in the presence of H_2O_2 and ascorbate, have been used to achieve greater accuracy.[22] The same general principle has been used to study the folding patterns of proteins.

Protein semisynthesis can be used to engineer new proteins through the combination of peptide fragments. The technique makes use of the native chemical ligation reaction, which combines an N-terminal cysteine-containing peptide with a C-terminal thioester containing peptide, to produce an amide linkage.[23] Proteolytic reagents can be used to prepare the N-terminal cysteine-containing fragments that will ultimately be used in the ligation step.[24, 25] The incorporation of unnatural amino acids into proteins prepared by semisynthesis has provided insights into protein folding, translation, and enzyme mechanisms.[26]

The biosynthetic production of peptides in bacterial hosts is emerging as a viable alternative to solid-state chemical synthesis.[27] In order to prevent proteolytic degradation of the target peptides during bacterial expression, a hydrophobic carrier protein is often fused to one or more copies of the target peptide.[28] The construct is designed to contain a His-tag to aid in purification of the expressed fusion protein. The desired peptide can ultimately be isolated through controlled proteolytic digestion of the construct into its components using a chemical protease.[29]

1.4 Proteolytic reagents.

Although a multitude of proteolytic reagents have appeared in the literature, few have seen widespread utility in biochemical applications. There are two types of reagents that are used in the laboratory to promote amide hydrolysis: proteolytic enzymes and chemical reagents. Chemical reagents are often favored over proteolytic enzymes for several reasons. Although proteolytic enzymes are catalytic and can achieve sequence-selectivity, they suffer from auto-digestion, proteinaceous sample contamination, and often lack of availability. On the other hand, chemical reagents are available, but few have demonstrated sufficient selectivity and efficiency for them to be practical.

Perhaps the most common chemical reagent being used to date is cyanogen bromide (CNBr), which cleaves amide bonds C-terminal to methionine residues.[30] Despite its widespread use, CNBr is not without disadvantages. Typically, the reagent must be used in more than a hundred fold excess to methionine residues in 70% formic acid.[31] As can be seen in the mechanism below in Figure 2, the methionine residue that directs hydrolysis is covalently modified into a homoserine lactone at the completion of the reaction. Another shortcoming of CNBr is observed when a methionine residue is followed by either a serine or threonine residue; a side-reaction at methionine occurs in these sequences and hydrolysis is suppressed.[32-34]

With the exception of CNBr and a few other simple chemical reagents, the majority of synthetic proteases are metal ion complexes. Specifically, Zn(II), Fe(II), Co(II), Co(III), Cu(II), Ni(II), Pd(II), and Pt(II), have been incorporated into small synthetic proteolytic reagents to mimic the activity of metalloproteases.[35-55]

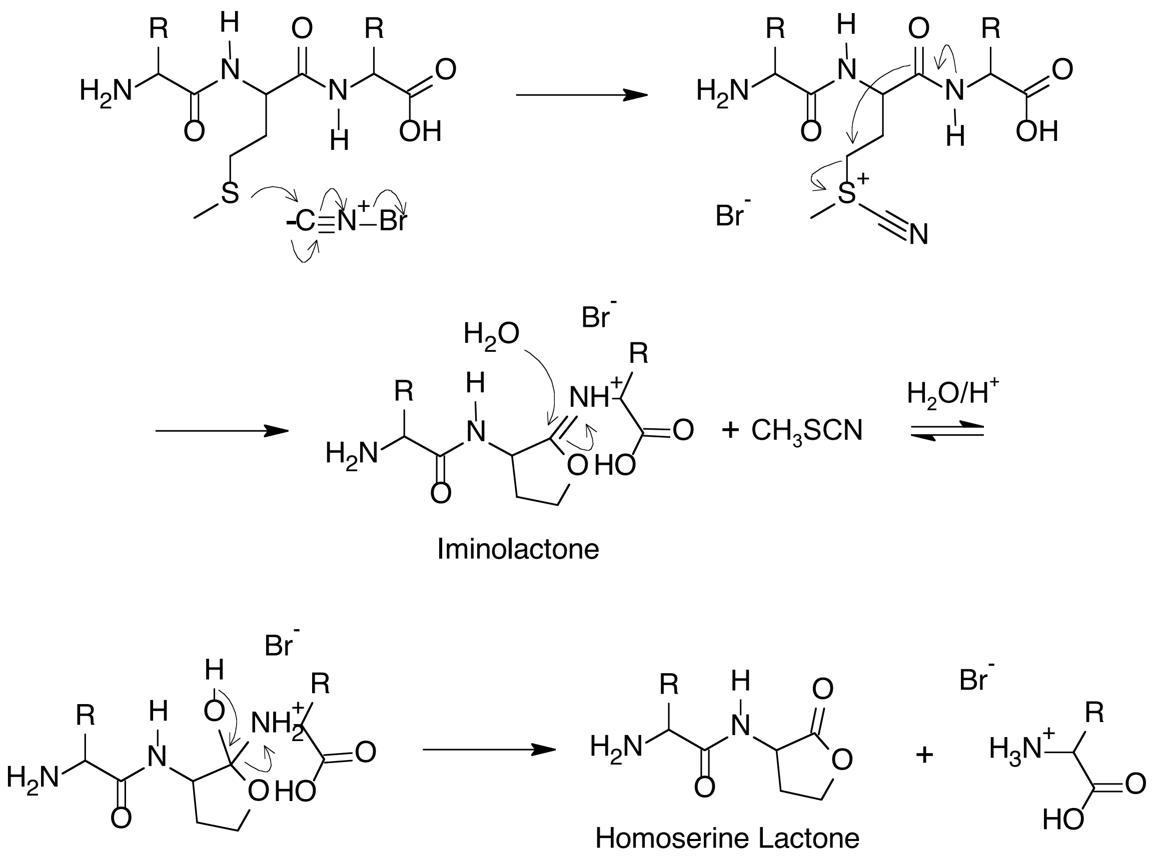


Figure 2. Mechanism of CNBr amide hydrolysis.

1.5 Metal-ion binding to amides.

As mentioned in Section 1.2, neutral amides are preferentially protonated and metallated at the oxygen, whereas metallation occurs at the nitrogen of anionic amides.[56] Upon complexation of a neutral amide oxygen by a metal ion, the C-O bond gets longer and weaker, whereas the C-N bond becomes shorter and stronger. Despite the strengthening of the C-N bond, hydrolysis is accelerated by oxygen complexation. The resulting positive charge on the metal ion-coordinated oxygen polarizes the C-O bond, thereby increasing the susceptibility of the carbonyl carbon to nucleophilic attack.[56] Three mechanisms for metal-ion promoted hydrolysis of neutral amides have been proposed: A) activation of the amide carbonyl through coordination of its oxygen atom by a metal ion, followed by nucleophilic attack of the carbonyl carbon by an external water molecule; B) delivery of a nucleophilic metal-bound aqua ligand to the amide carbonyl carbon followed by attack of the carbonyl carbon; and C) coordination of the carbonyl oxygen atom by a metal ion followed by nucleophilic attack of the carbonyl carbon by the metal-bound aqua ligand (Figure 3).[57] In addition to chelation of the amide oxygen, metal ions can bind to the side chains of a number of amino acids.

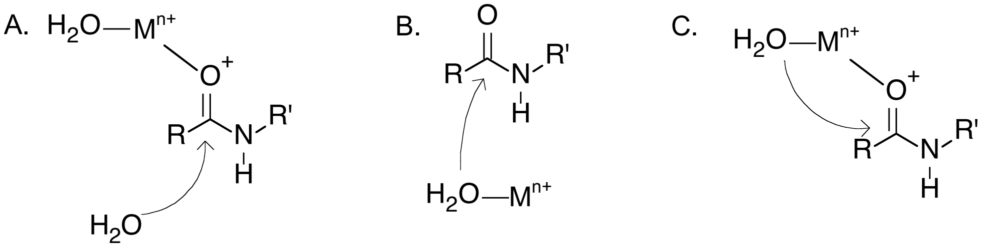
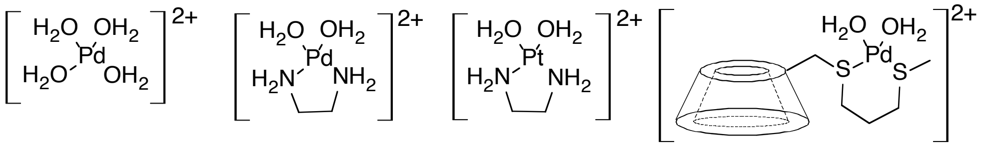


Figure 3. Proposed mechanisms of metal-ion promoted amide hydrolysis.

1.6 Palladium(II) and platinum(II) reagents for peptide and protein hydrolysis.

Palladium and platinum complexes have many synthetic, medicinal, and industrial uses.[58] The most common oxidation state of both palladium and platinum is +2. Pd(II) and Pt(II) ions have d^8 electron configurations, and in nearly all cases adopt square planar geometries. Both ions act as “soft” Lewis acids and prefer coordination with “soft” ligands like cyano and sulfur donors. Despite their similarities, Pt(II) ions have been shown to be inert to ligand substitution, while ligands bound to Pd(II) ions are considerably more labile.[59, 60] Like other metal ions, Pd(II) and Pt(II) ions are known to coordinate to the amide oxygen atom as well as to certain amino acid side chains.[60-62]

Since Pd(II) and Pt(II) ions only coordinate to a few residue side chains, they are able to provide the selectivity that is desired of new proteases. Early studies of simple Pd(II) and Pt(II) complexes revealed three requirements for the promotion of amide hydrolysis. First, the synthetic proteases need to contain at least two aqua ligands in the coordination sphere.[44] Aqua ligands are relatively “hard” and are therefore easily displaced by a “soft” anchoring side-chain, even in the case of Pt(II) ions which are reasonably inert to ligand substitution. Following coordination to a side chain, a second aqua ligand is either displaced by the amide oxygen atom or serves as the nucleophile that attacks the amide carbon. Most of the reagents are designed with a bidentate ligand occupying the other two coordination sites to limit additional ligand substitution. The second requirement for efficient hydrolysis by Pd(II) and Pt(II) complexes is the use of noncoordinating counter anions like ClO_4^- and BF_4^-. Coordinating ions, like Cl^-, limit the predominance of active complexes by displacing the aqua ligands essential for reactivity.[63] Finally, removal of the synthetic protease from the reaction mixture following hydrolysis is desirable and can be easily achieved with Pd(II) and Pt(II) ions through coordination by a strong chelating agent, such as sodium diethyldithiocarbamate.[64, 65] Although a series of reagents have been tested for hydrolytic activity, the discussion in this dissertation will be limited to the most effective of the reagents, $[Pd(OH_2)_4]^{2+}$, $[Pd(en)(OH_2)_2]^{2+}$, $[Pt(en)(OH_2)_2]^{2+}$ and a Pd(II)-cyclodextrin conjugate.



Methionine and histidine side chains serve as anchors for the Pd(II) reagents. Under acidic conditions, $[Pd(OH_2)_4]^{2+}$ and $[Pd(en)(OH_2)_2]^{2+}$ promote residue-selective cleavage at the X-Y bond in X-Y-Met-Z and X-Y-His-Z sequences provided that residues X, Y, and Z have noncoordinating side chains.[41, 44] The metal ion of both reagents first binds to the anchoring side chain, either the nitrogen atom of the histidine imidizole or the sulfur atom of the methionine thioether (Figure 4). Upon binding, the ethylenediamine ligand of $[Pd(en)(OH_2)_2]^{2+}$ is displaced by two aqua ligands to become complex A, which is identical to the complex formed upon the anchoring of $[Pd(OH_2)_4]^{2+}$ to a peptide. At low pH (< 2.0), both reagents exist predominantly in the form of complex A. As the pH increases, the first amide nitrogen upstream of the anchor is deprotonated and subsequently coordinates to the metal ion to form hydrolytically active complex B. Upon increasing the pH further, hydrolytically inactive complexes C and D are formed, in which the metal ion is coordinatively saturated with N-ligands. Near and at neutral pH, only Pro-Met and Pro-His, the most reactive amide bonds, are susceptible to cleavage (Figure 5). Since proline is the only amino acid with a tertiary amide nitrogen, the metal ion cannot coordinate to the amide nitrogen upstream of the anchor even as the pH increases. This being the case, active complex B remains available for cleavage of the X-Pro bond in X-Pro-Met-Z and X-Pro-His-Z sequences.[46]

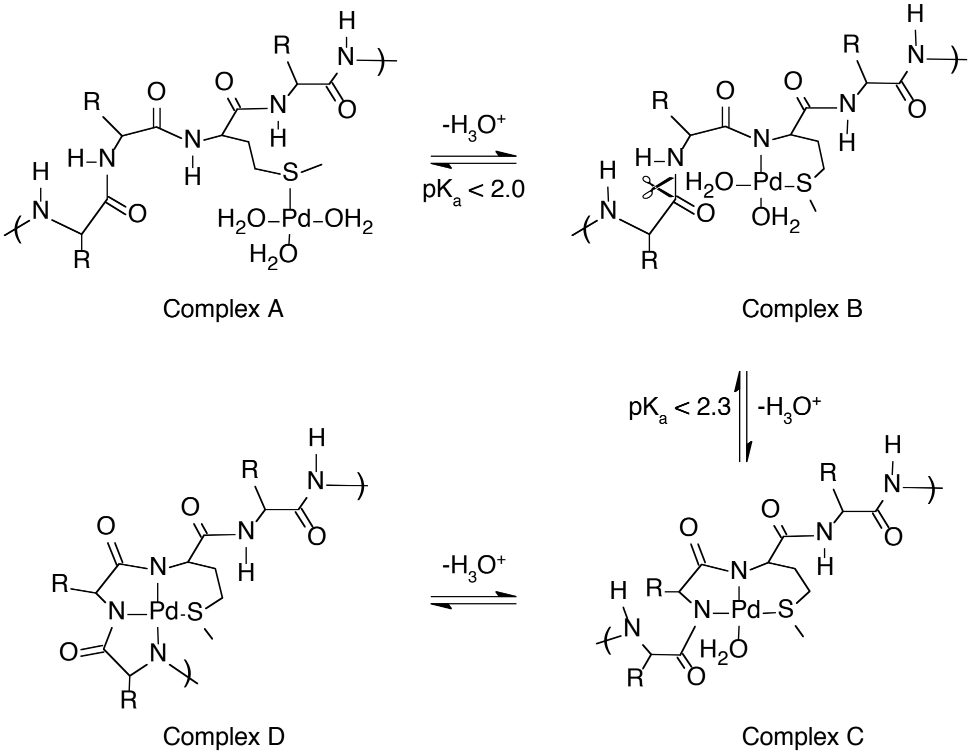


Figure 4. Pd(II) promoted hydrolysis of a Met-containing peptide in acidic conditions.

Pt(II) reagents differ in the selectivity with which they cleave peptides and proteins. Only methionine side chains act as anchors for the Pt(II) reagents and, unlike Pd(II) reagents, Pt(II) hydrolyzes the first amide bond downstream of the anchoring residue (i.e. the Met-Z bond in X-Y-Met-Z sequences) (Figure 6). Since Pt(II) is inert to ligand substitution, the ethylenediamine ligand is not displaced by aqua ligands, as is the ethylenediamine ligand of $[Pd(en)(OH_2)_2]^{2+}$. With ethylenediamine still coordinated to the metal center, only one aqua ligand remains. Under acidic conditions, active complex A promotes cleavage of the amide C-terminal to the methionine anchor; however, as the pH increases formation of inactive complex B is favored. The use of both Pd(II) and Pt(II) reagents on a single protein substrate has been tested on equine myoglobin and shown to provide a means of tuning the size and number of fragments produced from hydrolysis.[42]

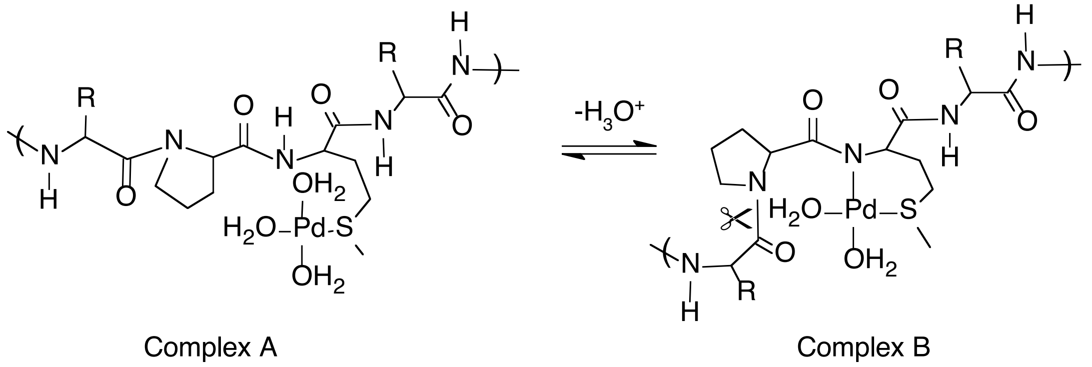


Figure 5. Pd(II) promoted hydrolysis of X-Pro-Met and X-Pro-His containing peptides in neutral conditions.

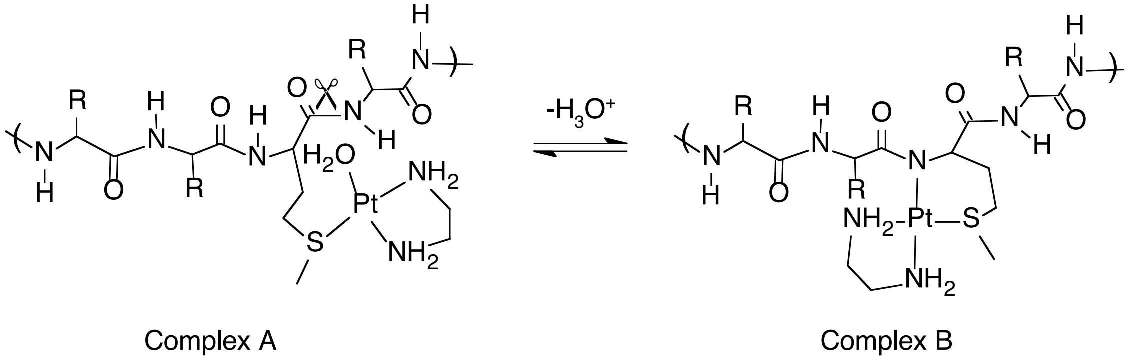


Figure 6. Pt(II) promoted hydrolysis of a Met-containing peptide in acidic conditions.

Sequence-specificity of synthetic peptidases has also been achieved through the use of host-guest complexation. By combining the ability of *β*-cyclodextrin to form inclusion complexes with aromatic side chains and the ability of palladium(II) aqua complexes to cleave polypeptide backbones, a reagent capable of promoting cleavage of the X-Pro bond in X-Pro-Y sequences in which Y is phenylalanine was created.[40] Like

$[Pd(OH_2)_4]^{2+}$, the cyclodextrin conjugate promotes sequence-selective hydrolysis, but with accelerated rates at pH 7.0.

Both Pd(II) and Pt(II) reagents have proven to be efficient and practical synthetic peptidases. The focus of Chapter 2 of this dissertation is the design and reactivity of new Pd(II) and Pt(II) synthetic proteases. The chapter discusses Pd(II) and Pt(II) dithioether complexes that demonstrate residue-selective peptide cleavage under mildly acidic conditions and sequence-selective cleavage at neutral pH.

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CHAPTER 2

Thioether complexes of palladium(II) and platinum(II) as artificial peptidases: sequence-selective peptide cleavage by a palladium(II) complex

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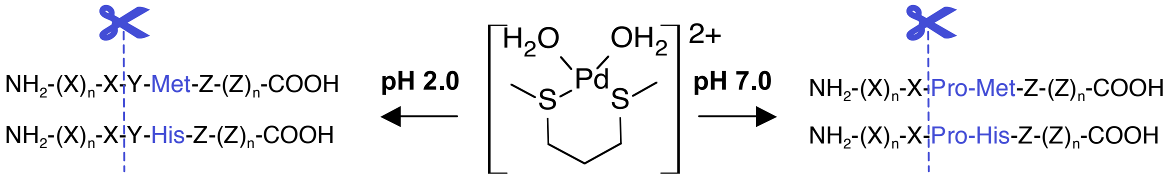
Stacey A. Stoffregen, Amanda K. K. Griffin, and Nenad M. Kostić
Department of Chemistry, Gilman Hall, Iowa State University, Ames, Iowa 50010-3111



2.1 Abstract.

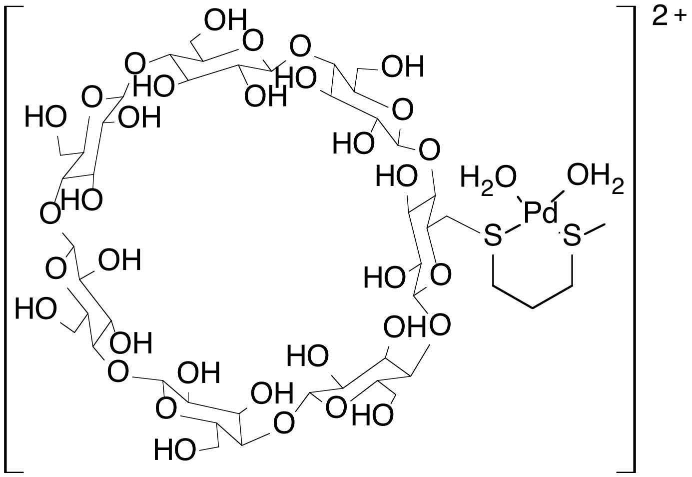
We report the synthesis and characterization of perchlorate salts containing the following three novel complex cations each with a bidentate thioether ligand: binuclear *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(\mu\text{-}OH)]_2^{2+}$, mononuclear *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, and mononuclear *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$. Despite their analogous compositions, the mononuclear Pt(II) and Pd(II) complexes differ in the selectivity with which they promote the hydrolysis of polypeptides. The complex *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ promotes slow but selective cleavage of Met-Pro peptide bonds at pH 2.0. The selectivity of the complex *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ is pH-dependent. At pH 2.0, this Pd(II) complex promotes residue-selective hydrolysis of the X-Y bond in X-Y-Met and X-Y-His sequences; the rate is enhanced when residue Y is proline. At pH 7.0, this kinetic preference becomes sequence-selective in that the Pd(II) complex exclusively cleaves the X-Pro bond in X-Pro-Met and X-Pro-His sequences. The enhanced reactivity of the X-Pro amide group is attributed to the high basicity of its carbonyl oxygen atom. Binding of the metal(II) atom enhances the electrophilicity of the carbonyl carbon atom and promotes nucleophilic attack by a solvent water molecule. The bidentate thioether ligand disfavors the formation of hydrolytically unreactive complexes allowing the Pd(II) complex to promote the cleavage reaction.

2.2 Introduction.

Selective hydrolysis of peptides and proteins. Many bioanalytical and biochemical techniques involve the selective cleavage of peptide bonds. Proteomic applications require the digestion of proteins into fragments suitable for mass spectrometric analysis.[1] In footprinting and folding studies, local protein structures can be determined by the regioselective cleavage of peptide bonds in solvent-exposed segments.[2-6] In protein semisynthesis, natural proteins are selectively hydrolyzed to give long fragments containing terminal amino and carboxylic groups, which are then reconnected to form new proteins.[7] Site-specific cleavage is also needed for the removal of fusion tags from bioengineered fusion proteins.[8] Unactivated amide groups are extremely unreactive toward hydrolysis. For instance, the *N*-acetylated dipeptide AcGly-Gly at room temperature and in the pH range between 4.0 and 8.0 has a half-life of several hundred years.[9-11] To make this reaction proceed at practical rates and regioselectively is a formidable task. Proteolytic enzymes, also called peptidases, can catalyze nonselective or selective protein cleavage. Nonselective processes are involved in protein degradation, apoptosis, and antigen processing, while selectivity is necessary in the regulation of the cell cycle, signal transduction, and transcription. Although some proteolytic enzymes are selective, react with turnover, and require only mild conditions, they also have disadvantages: they cleave themselves as well as the intended substrates, and they remain in digests as proteinaceous contaminants. For these reasons, chemical reagents for peptide and protein cleavage are much needed. The use of cyanogen bromide and other chemical reagents has been limited by poor selectivity, incomplete cleavage, toxicity, and the need for harsh reaction conditions.[12] These reagents are usually applied in a large molar excess over the substrate, and they produce chemically altered protein fragments such as covalently modified amino acid side chains. New chemical proteases that efficiently and selectively hydrolyze peptides and proteins should be capable of binding to particular amino acid residues or short sequences and promoting the hydrolysis of specific peptide bonds under mild conditions. After the reaction, these reagents should be easily removable from the cleaved fragments. Certain transition metal complexes have the desired properties, but few of them cleave peptides or proteins regioselectively.[13-30]

Complexes of palladium(II) and platinum(II) as synthetic peptidases. Our laboratory has achieved residue selective and even sequence-selective hydrolysis of many peptides and various proteins by simple Pd(II) and Pt(II) complexes containing at least two aqua ligands.[31-38] When a nucleophilic side chain displaces one of the aqua ligands, the metal(II) atom becomes anchored to the substrate. In the hydrolytically reactive complexes, the metal(II) atom acts as a Lewis acid and activates a proximate amide group toward nucleophilic attack by a solvent water molecule. Methionine and histidine side chains are anchors for the Pd(II) reagents. The residue-selective cleavage in weakly acidic solutions occurs at the X-Y bond in X-Y-Met-Z and X-Y-His-Z sequences, provided that residues X, Y, and Z have noncoordinating side chains.[36-38] Only methionine side chains act as anchors for the Pt(II) reagents, and the residue selectivity is different. These reagents cleave Met-Z bonds.[33] Both Pd(II) and Pt(II) ions can be removed from the cleaved fragments by the addition of a strong chelating agent such as sodium diethyldithiocarbamate; the pristine fragments can then be further analyzed or used.[30, 39] Because the combined abundance of histidine and methionine residues in proteins is only ca. 5.5%, the fragments are larger than those produced by trypsin and, therefore, more useful in modern biochemical practice.[40] In an effort to mimic the multiple functions of an enzyme, we combined the ability of β-cyclodextrin to recognize and bind aromatic side chains and the ability of palladium(II) aqua complexes to cleave a polypeptide backbone. A reagent containing these two moieties selectively cleaved the X-Pro bond in an X-Pro-Y sequence having phenylalanine as residue Y.[32] The organic and inorganic moieties in the new reagent were connected with a bidentate thioether ligand, as shown in Scheme 1. This new Pd(II)-cyclodextrin conjugate reacted not only sequence-selectively but also relatively fast, more rapidly than $[Pd(OH_2)_4]^{2+}$. In this study, we investigate the possible effects of the bidentate thioether ligand on the rate and selectivity of hydrolytic cleavage. We compare analogous thioether complexes of Pd(II) and Pt(II) ions because, surprisingly, these two metal ions show different selectivities in protein cleavage.

Scheme 1.



2.3 Experimental procedures.

Chemicals. Distilled water was demineralized and purified to a resistivity higher than 17 MΩcm. Palladium sponge, $Na_2[PdCl_4]$, piperidine, diethyldithiocarbamic acid sodium salt, α-cyano-4-hydroxycinnamic acid, human angiotensin II, and *N*,*N*-diisopropylethylamine were obtained from Sigma-Aldrich Chemical Co. Methyl phenyl sulfone was obtained from Lancaster Synthesis Inc. Acetonitrile of HPLC grade, dichloromethane, *N*,*N*-dimethylformamide (DMF), and diethyl ether were obtained from Fisher Scientific Co. Silver perchlorate monohydrate, 1,3-bis(methylthio)propane, trifluoroacetic acid, and $K_2[PtCl_4]$ were obtained from Alfa Aesar. The *N*-*α*-Fmoc-Ala-Wang resin, 2-(1-benzotriazol-1-yl)-1,1,3,3 tetramethyl-uronium hexafluorophosphate, and *N*-hydroxybenzotriazole were obtained from Calbiochem-Novabiochem Corp. The N-acetylated peptide Ac-Lys-Ala-Tyr-Asp-Pro-His-Ala-Ala-Arg-Ala, designated as Pro-His peptide, was custom-ordered from Sigma Genosys.

Peptide synthesis. The *N*-acetylated peptides Ac-Ala-Lys-Phe-Gly-Met-Ala-Tyr-Arg-Gly (termed Met-Ala peptide), Ac-Ala-Lys-Ala-Gly-Met-Pro-Ala-Tyr-Arg-Ala (termed Met-Pro peptide), Ac-Lys-Ala-Tyr-Asp-Pro-Met-Ala-Ala-Arg-Ala (termed Pro-Met peptide), and Ac-Lys-Gly-Gly-Ala-Ser-Pro-Phe-Ala-Ala-Arg-Ala (termed Pro-Phe peptide) were synthesized by a standard manual Fmoc solid-phase procedure[12, 41] and purified by reverse-phase high performance liquid chromatography (HPLC) on a C18 preparative column as described previously.[37] The purity, as examined by analytical HPLC, was higher than 99.5%. The respective measured and calculated molecular masses were 1043.16 and 1043.23 Da for Met-Ala peptide, 1078.95 and 1078.28 Da for Met-Pro peptide, 1136.62 and 1136.31 Da for Pro-Met peptide, and 1074.75 and 1075.21 Da for Pro-Phe peptide.

NMR spectroscopy. The ^{1}H NMR spectra were recorded in water at 25.0°C with a Bruker DRX500 spectrometer and externally referenced to the methyl signal of sodium 2,2-dimethyl-2-silapentane-5-sulfonate in aqueous solutions. Because peptide cleavage is very slow at room temperature, we safely assumed that the sample composition remained unchanged during the NMR measurements. TOCSY (total correlation spectroscopy) spectra were acquired in aqueous solution for reactions involving Met-Ala peptide. ROESY (rotating-frame Overhauser enhancement spectroscopy) resolved the assignment of the two alanine and two glycine residues in the peptide designated Met-Ala. A mixing time of 100 ms was used in TOCSY experiments. The spin-lock field strength during mixing was 6.0 kHz in TOCSY experiments and 2.5 kHz in ROESY experiments. The water signal was suppressed by incorporating WATERGATE in the pulse sequences.[42] The spectra for characterizing the bidentate thioether complexes were recorded in the temperature interval of 278-318 K.

HPLC separations. The digest components were separated by a Hewlett-Packard 1100 HPLC system containing an autosampler and a multiwavelength detector set at 215, 280, and 350 nm. Absorption at 215 nm is common to all peptides and proteins; absorption at 280 nm results from aromatic residues and bound Pd(II) or Pt(II) ions; and absorption at 350 nm is diagnostic of Pd(II) and Pt(II) ions. In the reverse-phase separations, analytical Supelco Discovery Bio Wide Pore C18 and C5 columns (sized 25 cm × 4.6 mm, beads of 5 μm) were used. The eluting solvent A was 0.10% (v/v) trifluoroacetic acid in water, and solvent B was 0.080% (v/v) trifluoroacetic acid in acetonitrile. In a typical run, the percentage of solvent B in the eluent was kept at 0% for

5 min after the injection of the sample and then raised gradually to 45% over a 35-min period. The flow rate in all analytical runs was 1.0 mL/min.

Mass spectrometry. The MALDI-TOF experiments were performed with a Bruker Proflex instrument. The samples were prepared by a standard dried-droplet procedure: 1.0 μL of the sample of interest was mixed with 9.0 μL of a saturated solution of the matrix (α-cyano-4-hydroxycinnamic acid) in a 2:1 (v/v) mixture of 0.10% (v/v) trifluoroacetic acid in water and 0.080% (v/v) trifluoroacetic acid in acetonitrile. Each spectrum consisted of 100 scans. For the sake of clarity, molecular masses are reported only for the peptide fragments free of the Pd(II) and Pt(II) complexes unless otherwise specified, although the peptide fragments bearing the metal ions were also observed in the MALDI spectra. A solution of bradykinin and α-cyano-4-hydroxycinnamic acid was used as an external standard. The measured molecular mass of a given fragment was compared with the value calculated by PAWS software, obtained from ProteoMetrics, LLC. Excellent agreement conclusively identified each peptide. The presence of Pd(II) and Pt(II) ions bound to the peptide or its fragment(s) was established not only by the matching molecular masses of the labeled peptides but also by the isotopic distributions. Diagnostic for Pd: 1.0% ^{102}Pd, 11.1% ^{104}Pd, 22.3% ^{105}Pd, 27.3% ^{106}Pd, 26.5% ^{108}Pd, and 11.8% ^{110}Pd. Diagnostic for Pt: 0.8% ^{192}Pt, 33.0% ^{194}Pt, 33.8% ^{195}Pt, 25.2% ^{196}Pt, and 7.2% ^{198}Pt. The inductively coupled plasma mass spectrometry (ICP-MS) experiments were performed with an HP 4500 instrument having a Babington nebulizer, nickel cones, and a quadrapole mass analyzer to count ^{195}Pt atoms. The samples were prepared by dissolving a known mass of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(\mu_2\text{-}OH)]_2(ClO_4)_2$ in 5 mL of fuming nitric acid. The solution was heated just below the boiling point for 4 h. The sample was then diluted with water to an appropriate concentration for analysis. A blank solution containing the same concentration of nitric acid was used in background comparisons.

Synthesis of *cis*-$[PdCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$. *cis*-$[PdCl_2(CH_3SCH_2CH_2CH_2\text{-}SCH_3)]$ was synthesized by a modification of a published procedure.[43, 44] To a round-bottomed flask 1,3-bis(methylthio)propane (1.00 mmol, 138.8 μL) and water (0.50 mL) were added while stirring. A solution of $Na_2[PdCl_4]$ (1.00 mmol, 294.1 mg) in water (4.0 mL) was added with a dropping funnel, over a period of 30 min. The reaction mixture was refluxed for 4 h, cooled to room temperature, and stored overnight at 4 °C. The orange solid product was filtered off, washed with cold water and ethanol, and dried under vacuum. Yield: 0.27 g, 87%. Mp: 238 °C. UV-vis absorption maxima in water, 390 and 295nm. That MALDI mass spectra did not show the intact dichloro compound is evidence for the lability of the chloro ligands. Molecular masses: Calcd for $[PdCl(CH_3SCH_2CH_2CH_2SCH_3)]$: 275.62, 276.63, 277.63, 279.62, and 281.63 Da. MALDI: 275.05, 276.00, 277.05, 279.05, and 281.05 Da. Calcd for $[Pd(CH_3SCH_2CH_2CH_2SCH_3)]$: 240.18, 241.18, 242.17, 244.16, and 246.17 Da. Measd: 240.30, 241.32, 242.36, 244.30, and 246.20 Da. The isotopic distribution was diagnostic of Pd.

Synthesis of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2](ClO_4)_2$. A solution of silver perchlorate monohydrate (0.20 mmol, 45.1 mg) in water (3.0 mL) was added to *cis*-$[PdCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$(0.10 mmol, 31.4 mg), and the mixture was stirred at 60 °C for 2 h in the dark. The mixture was filtered, and the yellow supernatant containing *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2](ClO_4)_2$ was collected. UV-vis absorption maxima in water: 365 nm ($\varepsilon \approx$ 1290 M^{-1} cm^{-1}) and 261 nm ($\varepsilon \approx$ 10 640 M^{-1} cm^{-1}). That MALDI mass spectra did not show the intact diaqua compound is evidence for the lability of the aqua ligands. MALDI molecular masses. Calcd: 240.18, 241.18, 242.18, 244.18, and 246.18 Da. Measd: 240.00, 241.05, 241.99, 244.00, and 246.06 Da. The isotopic distribution was diagnostic of Pd. ^{1}H NMR (D_2O): δ 2.360(s), 2.445(s), 2.515(m), 2.575(m), 2.642(m), and 2.829(m). ^{13}C NMR (D_2O): δ 19.8, 19.9, 22.1, 30.9, and 34.0.

Synthesis of *cis*-$[PtCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$. *cis*-$[PtCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$ was synthesized by a modification of a published procedure.[43, 44] To a round-bottomed flask 1,3-bis(methylthio)propane (1.00 mmol, 138.8 μL) and water (2.0 mL) were added while stirring. A solution of $K_2[PtCl_4]$ (0.5 mmol, 207.5 mg) in water (4.0 mL) was added with a dropping funnel over a period of 30 min. The solution was refluxed for 4 h. A yellow solid was collected by vacuum filtration, washed with ethanol and cold water, and recrystalized from acetonitrile. Yield: 0.13 g, 65%. Mp: 238°C. UV-vis absorption maxima in water, 311 and 368 nm. MALDI mass spectrometry detected both the dichloro and monochloro species. Molecular masses. Calcd for $[PtCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$: 406.15, 407.15, 408.15, and 409.15 Da. MALDI: 405.96, 406.96, 407.96, and 408.98 Da. Calcd for $[PtCl(CH_3SCH_2CH_2CH_2SCH_3)]$: 365.69, 366.99, 367.69, and 369.70 Da. Measd: 365.96, 366.97, 367.95, and 368.93 Da. The isotopic distribution was diagnostic of Pt.

Synthesis of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2](ClO_4)_2$. A solution of silver perchlorate monohydrate (0.16 mmol, 36.1 mg) in water (3.5 mL) was added to *cis*-$[PtCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$ (0.080 mmol, 32.2 mg), and the mixture was stirred at 60 °C for 2 h in the dark. The mixture was filtered, and the yellow supernatant, containing *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2](ClO_4)_2$, was collected. UV-vis maxima in water: 344 nm ($\varepsilon \approx 320 M^{-1} cm^{-1}$). That MALDI mass spectra did not show the intact diaqua compound is evidence for the lability of the aqua ligands. MALDI molecular masses. Calcd: 330.24, 331.24, 332.24, and 334.24 Da. Measd: 330.02, 331.00, 332.63, and 334.84 Da. The isotopic distribution was diagnostic of Pt. ^1H NMR (D_2O): δ 2.289(s), 2.44(s), 2.47(m), 2.56(m), 2.92(m), and 3.01(m).

Synthesis of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(\mu_2\text{-}OH)]_2(ClO_4)_2$. A solution of silver perchlorate monohydrate (0.60 mmol, 135.2 mg) in water (2.0 mL) was added to *cis*-$[PtCl_2(CH_3SCH_2CH_2CH_2SCH_3)]$ (0.30 mmol, 120.7 mg). The mixture was gently heated to 50 °C while stirring for 2 h in the dark and subsequently filtered. The yellow supernatant was stored at 4 °C, and yellow crystals of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)$-$(\mu_2\text{-}OH)]_2(ClO_4)_2$ were filtered off after several days. Yield: 8.1 mg, 6%. Elem anal. Calcd: C, 13.50; H, 2.95; S, 14.42; Pt, 74.7. Found: C, 13.54; H, 2.86; S, 14.38; Pt, 75.6 (by ICP-MS). UV-vis maximum: 344 nm. *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(\mu_2$-

OH)]$_2$(ClO$_4$)$_2$ was insoluble in benzene, hexane, acetone, ethanol, methanol, pyridine, acetonitrile, water, dichloromethane, and nitrobenzene; it was only slightly soluble in DMF and DMSO, perhaps owing to their coordinating ability. IR (cm^{-1}): 3450(sh), 3336(b,w), 1416(s).

Study of hydrolysis. Reactions were carried out in 2.0-mL glass vials. A 5.0 mM stock solution of each peptide in water was prepared. In a typical experiment involving 10 molar equivalent of the metal complexed to 1 molar equivalent of methionine or histidine residues, 200 μL of a 5.0 mM peptide solution was mixed with 20.0 μL of a 500 mM solution of either *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ or *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, 50.0 μL of a solution containing 25.0 mg/mL of phenyl methyl sulfone, and 730 μL of water. For reactions in which the pH was in the interval of 5.0-7.0, phosphate buffer replaced the water. The pH was measured with a Fisher Accumet instrument and an Aldrich Ag/AgCl reference electrode and was adjusted by careful addition of either 1.00 M HClO4, 1.00 M NaOH, or 0.500 M trisodium phosphate with stirring. The reaction mixture was kept in a dry bath at 60 ± 1 °C. After the reaction was complete, the pH remained within 0.10 of the initial value. Possible "background" cleavage was ruled out in control experiments in which the conditions were kept the same except that the Pd(II) or Pt(II) reagent was absent. For the kinetic measurements, 100 μL samples were periodically taken from the reaction mixture, an excess of solid sodium diethyldithiocarbamate was added to form an insoluble compound of Pd(II) or Pt(II), the precipitate was filtered off, and the clear solution was immediately subjected to reverse-phase HPLC separation. Because the cleavage is very slow at room temperature and the Pd(II) or Pt(II) reagent was removed, the species distribution in the chromatogram matched that in the digest at the time of sampling. To compensate for a possible error in the injection volume and evaporation, the areas under the chromatographic peaks were integrated and normalized to the peak of methyl phenyl sulfone, the internal standard. The error of this integration was estimated at 5%. The plots of the peak areas of the cleavage fragments versus time were fitted to a first-order rate law with SigmaPlot, version 5.0, obtained from SPSS Inc. The stated errors in the rate constants correspond to the average error in the calculated rate constants. This conservative reporting reduces the tendency for overinterpreting differences among rate constants. Representative chromatograms are shown in Figure S1 in the Supporting Information. Cleaved fragments were collected from analytical HPLC separations, dried with a stream of air, dissolved in 10.0 μL of water, and analyzed by MALDI-TOF mass spectrometry.

2.4 Results and discussion.

New bidentate thioether complexes of Pd(II) and Pt(II). The new mononuclear complexes were prepared simply by Ag^+-assisted aquation of the corresponding known chloro complexes, (Scheme 2, also see Figure S2 in the Supporting Information). Because this step reaction is practically complete, the aqua complexes prepared *in situ* can be used immediately as hydrolytic reagents. It is advantageous for practical applications to avoid isolation. In the absence of elemental analysis, the composition of these simple complexes is determined by spectroscopy and the well established methods of preparation. Binding of the bidentate ligand to the Pd(II) and Pt(II) ions causes downfield shifts of the ^{1}H NMR methyl signal by 0.245 and 0.174 ppm, respectively. The proton NMR spectra of both mononuclear diaqua complexes contained two sets of relatively broad signals: two singlets, corresponding to the methyl groups, and four multiplets, corresponding to the methylene groups. As the temperature was raised from 278 to 318 K, the methyl singlets began to coalesce for both of the mononuclear diaqua complexes indicating that two configurational isomers were interconverting by inversion at the chiral sulfur atoms as shown in Figures S3 and S4 in the Supporting Information. The hydroxo-bridged binuclear complex is formed in low yield upon concentration of a basic solution of the corresponding mononuclear complex (Scheme 2). An infrared spectrum showed three bands corresponding to the bending and stretching modes of the hydroxo ligands. This evidence for the doubly bridging hydroxo ligands agrees with the published spectra of similar complexes.[45-49]

Polypeptide substrates and hydrolytic reaction conditions. The substrates to be cleaved include five synthetic polypeptides and the bioactive polypeptide angiotensin II, designated as His-Pro, shown in Table 1. With the exception of the control peptide Pro-Phe, all of the sequences contained a methionine or histidine anchoring residue in a position appropriate for MALDI mass spectrometric analysis. All peptides except human angiotensin II were acetylated at the N terminus, to prevent binding of the Pd(II) or Pt(II) atom and to render the polypeptides more similar to proteins. Coordinating anions, such as acetate and chloride, can inhibit cleavage by Pd(II) and Pt(II) reagents and were therefore excluded from all reactions.[43] The pH was carefully chosen to avoid both background cleavage in strongly acidic solutions and the formation of hydroxo-bridged species in basic solutions. Control experiments ruled out significant background cleavage at pH values between 1.8 and 7.2.

Scheme 2.

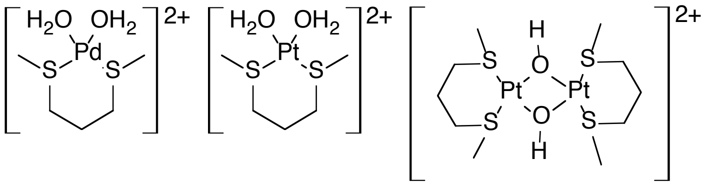


Table 1. Polypeptides used as substrates for cleavage by metal complexes.

abbreviation	**sequence**
Met-Ala	Ac-Ala-Lys-Phe-Gly-Met-Ala-Tyr-Arg-Gly
Pro-Met	Ac-Lys-Ala-Tyr-Asp-Pro-Met-Ala-Ala-Arg-Ala
Met-Pro	Ac-Ala-Lys-Ala-Gly-Met-Pro-Ala-Tyr-Arg-Ala
Pro-Phe	Ac-Lys-Gly-Gly-Ala-Ser-Pro-Phe-Ala-Ala-Arg-Ala
Pro-His	Ac-Lys-Ala-Tyr-Asp-Pro-His-Ala-Ala-Arg-Ala
His-Pro	Val-Tyr-Ile-His-Pro-Phe

Initial binding of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ to a methionine-containing polypeptide in acidic solution. Because Pt(II) reagents anchor to the thioether group of methionine, we chose the nonapeptide Met-Ala to study the initial binding of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ to substrates. ROESY ^1H NMR spectra of this nonapeptide (see Figure S5 in the Supporting Information) allowed the unambiguous assignment of the two glycine residues and the two alanine residues. A mixture of the Met-Ala peptide and a 10-fold excess of *cis*-[Pt($CH_3SCH_2CH_2CH_2S$-CH_3)(H_2O)$_2$]$^{2+}$ was incubated at 60 °C for 24 h and examined by ^{1}H NMR spectroscopy. In this and other studies, an excess of the metal complex was used to ensure its complete binding to the peptide. The aliphatic region in the one-dimensional spectrum and a part of the amide-to-aliphatic region in the TOCSY spectrum are shown in Figure 1. A comparison of the free peptide (Figure 1a) and the reaction mixture (Figure 1b) shows the disappearance of the cross peaks between the amide NH and the side chain protons within methionine which is evidence for the binding of the Pt(II) atom to the deprotonated amide nitrogen in methionine. The predominant species at pH 2.0 is, therefore, complex **2**, in which the anchoring methionine residue acts as a bidentate ligand (see Scheme 3). The p*K*a for the first NH group "upstream" (toward the amino terminus) of the methionine and Met-Ala peptide showed a persistent peak corresponding to the Pt(II) complex with the intact peptide and no appearance of the peptide fragments. A MALDI mass spectrum of the reaction mixture after 1 week of incubation at 60 °C confirmed this composition (see Table 2).

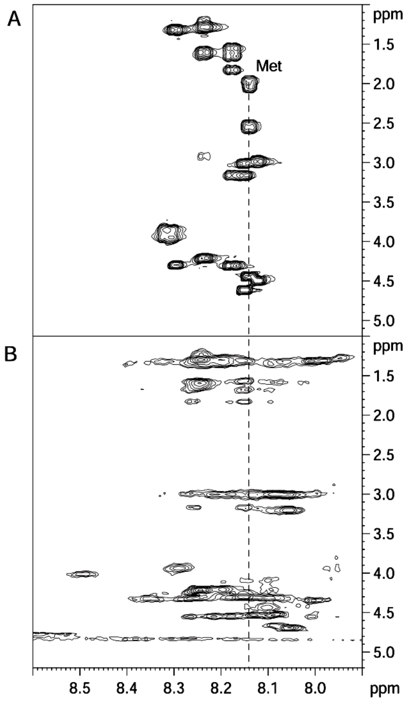


Figure 1. TOCSY 1H NMR spectra of the NH-to-aliphatic region of polypeptide designated Met-Ala at pH 2.0 and room temperature (a) free and (b) after 24 h of incubation at 60 ºC with a 10-fold excess of *cis*-[Pt($CH_3SCH_2CH_2CH_2SCH_3$)-(H_2O)$_2$]$^{2+}$. The vertical dashed line shows the presence of the Met signal in panel (a) and its absence in panel (b) residue bearing a Pt(II) atom was estimated at 1.8, consistent with the NMR results showing the presence of mostly complex 2 in the reaction mixture.[34] The two bidentate ligands are inert to substitution and render complex 2 unreactive toward hydrolysis. Indeed, an HPLC analysis of a 10:1 mixture of cis-[Pt($CH_3SCH_2CH_2CH_2SCH_3$)(H_2O)$_2$]$^{2+}$.

Scheme 3.

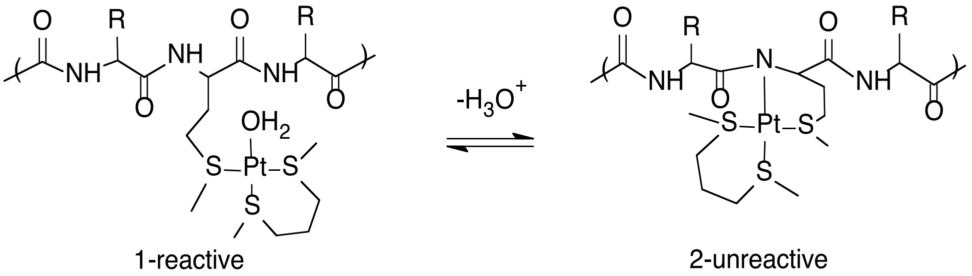


Table 2. MALDI mass spectrometric identification of fragments of the polypeptide designated Met-Ala and the polypeptide designated Met-Pro upon hydrolytic cleavage by *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 2.0.

peptide substrate	**polypeptide fragment**	**molecular mass (D)** **observed**	 **calculated**
Met-Ala	AKFGMAYRG	1042.84	1043.23
	AKFGMAYRG + Pt(II) reagent	1370.09	1371.48
Met-Pro	AKAGM	519.61	519.64
	PAYRA	578.39	577.66

Methionine-guided sequence-selective polypeptide cleavage by cis-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ in acidic solution. The decapeptide Met-Pro contains a tertiary amide group in the salient part of its sequence. When a mixture of Met-Pro peptide and a 10-fold excess of *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ was kept at pH 2.0 and 60 ºC for 7 days, HPLC and MALDI analyses showed an incomplete cleavage of the Met-Pro bond (see Table 2). The Pt(II) reagent formed mostly the unreactive complex 2 at pH 2.0, but a small amount of the hydrolytically reactive complex 1 was responsible for the cleavage (see Scheme 3). At pH values higher than 2.0, *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ formed only unreactive complexes with either Met-Ala peptide or Met-Pro peptide, and neither polypeptide was detectably cleaved. The difference in reactivity between the two peptides at pH 2.0 can be attributed to the greater reactivity of the tertiary amide group (in Met-Pro) than the secondary amide group (in Met-Ala). Because proline residues have the most basic carbonyl oxygen atom in proteins, this atom preferentially binds to the Pt(II) atom. Thus, activated by the Lewis acid, the X-Pro group is especially susceptible to nucleophilic attack by a solvent water molecule resulting in hydrolysis.[38] This study with the Pt(II) reagent at pH 2.0 shows an increased hydrolytic reactivity of X-Pro groups. Although the lower reactivity of the Pt(II) complexes, in comparison with Pd(II) complexes, makes the rate and yield of cleavage relatively low, the reaction is sequence-selective in that the cleavage site depends not only on the location of the anchoring residue (methionine) but also on the residue following it (proline).

Initial binding of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ to a methionine-containing polypeptide in acidic solution. A mixture of the polypeptide Met-Ala and a 10-fold excess of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ was prepared at pH 2.0. The modes of binding were studied by ^1H NMR spectroscopy at room temperature immediately after mixing and after 24 h of incubation at 60 °C. The aliphatic region in the one-dimensional spectrum and a part of the amide-to-aliphatic region in the TOCSY spectrum are shown in Figure 2.

Upon addition of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ to the Met-Ala peptide, the methionine amide NH signal at 8.14 ppm shifted to 8.32 ppm which is evidence for binding of the Pd(II) atom to the methionine thioether side chain (see Figure 2a,b). Furthermore, the amide NH signals of the two glycine residues at 8.30 ppm and the two alanine residues at 8.30 ppm, which overlap in the TOCSY spectrum of the free peptide, each split into multiple signals upon binding of the Pd(II) atom to the methionine side chain. TOCSY evidence shows this binding to occur immediately upon mixing of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ and the substrate before heating. Because the subsequent cleavage reaction occurs in hours, the initial binding can justifiably be neglected in fitting the cleavage kinetics to a first-order rate law.

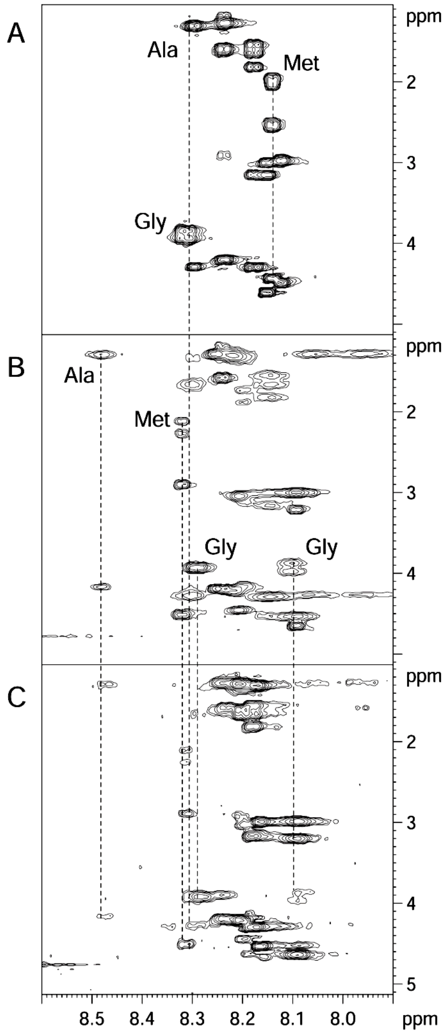
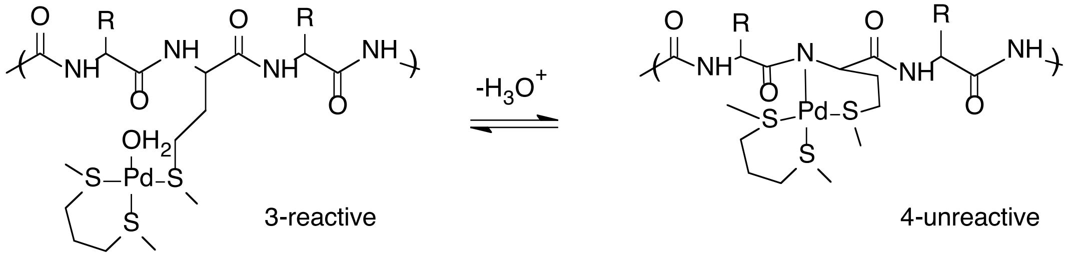


Figure 2. TOCSY ^{1}H NMR spectra of the NH-to-aliphatic region of polypeptide designated Met-Ala at pH 2.0 and room temperature (a) free, (b) immediately after the addition of a 10-fold excess of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, and (c) after 24 h of incubation at 60 ºC with a 10-fold excess of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$. Vertical dashed lines connect amide-to-sidechain cross-peaks of residues within each panel and clearly distinguish the shifts of signals.

After incubation of the reaction mixture for 24 h at 60 °C, the TOCSY spectrum showed a minor decrease in the intensity of the crosspeaks between the amide NH and the α-CH, *β*-CH, and *γ*-CH side-chain resonances in methionine (see Figure 2c). Evidently there are multiple binding modes during the reaction at pH 2.0. The decrease in intensity of the cross peaks corresponds to an increase in the ratio of complex **4** to complex **3** (see Scheme 4). Our previously reported reagents *cis*-$[Pd(en)(H_2O)_2]^{2+}$ and $[Pd(H_2O)_4]^{2+}$ at pH 2.0 predominantly bind to the thioether group and the deprotonated amide nitrogen of methionine residues, with the loss of both aqua ligands. The new reagent *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, however, binds only to the thioether group with the loss of one aqua ligand to form complex **3**. This difference in the initial anchoring can be attributed to the steric bulk of the bidentate thioether ligand, which disfavors bidentate coordination of the methionine residue. Evidently the anchoring mode of Pd(II) reagents can be controlled by the choice of ancillary ligands.

Scheme 4.



To determine whether the bidentate thioether ligand remains coordinated to the Pd(II) ion during the cleavage reaction, we compared the ^{1}H NMR spectra of free $CH_3SCH_2CH_2CH_2SCH_3$, *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, and the reaction mixture with the Met-Ala polypeptide after 24 h at 60 °C (see the Supporting Information, Figure S6). The methyl singlet occurred at 2.115 ppm in the free thioether ligand and at 2.360 ppm in the Pd(II)-bound ligand. The spectrum of the reaction mixture showed only the singlet at 2.360 ppm unaffected by binding of the Pd(II) atom to the peptide. The absence of the 2.115 ppm signal over time showed that the bidentate thioether ligand remained bound to the Pd(II) ion throughout the cleavage reaction. Furthermore, MALDI spectra at the end of the cleavage reaction showed only the mass of the $[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ species. The free thioether was not observed in the MALDI mass spectra although its detection was possible. In cleavage reactions with the *cis*-$[Pd(en)(H_2O)_2]^{2+}$ reagent, the ethylenediamine ligand detaches from the Pd(II) ion in the formation of a hydrolytically reactive complex because the hard and relatively strong Brønsted base amine has only a moderate affinity for the relatively soft Pd(II) acid and because protonation by H^+ ions in solution assists detachment of the amine.[37] In contrast, the soft and very weak Brønsted base thioether has an affinity for the Pd(II) ion and cannot be protonated under the reaction conditions, and it therefore remains bound. This chelating ligand in *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$

ensures the predominance of the hydrolytically reactive complex **3** in the reaction conditions at pH 2.0. The ancillary ligands thus control the cleavage reactivity of the Pd(II) complex.

Methionine-guided and residue-selective polypeptide cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ in acidic solution. The results in Tables 3 and 4 show that the new reagent selectively cleaved the Phe-Gly bond in the polypeptide designated as Met-Ala, the Tyr-Ile bond in angiotensin II (designated as His-Pro), the Asp-Pro bond in the polypeptide Pro-His, and the Asp-Pro bond in the polypeptide Pro-Met, while the polypeptide designated as Pro-Phe remained intact because it lacks anchoring methionine or histidine residues. Evidently, the selectivity of Pd(II) reagents for the X-Y bond in X-Y-Met and X-Y-His sequences is unaffected by the ancillary ligands. Because binding of the Pd(II) atom to the methionine side chain is very fast, a first-order fitting in Figure 3 is justified. The decrease of the rate constant with increasing pH, seen in Figure 4, is caused by the progressive conversion of the reactive complex **3** to the unreactive complex **4** in which the deprotonated amide nitrogen is coordinated to the Pd(II) ion. The published p*K*a values of the related compounds *cis*-$[Pt(CH_3CH_2SCH_2CH_2CH_2SCH_2CH_3)(H_2O)_2]^{2+}$, *cis*-$[Pd(en)(H_2O)_2]^{2+}$, and *cis*-$[Pt(en)(H_2O)_2]^{2+}$ are >3.0, 5.6, and 5.8, respectively.[50-52] The values of 5.6 and 5.8 suggest that Pd(II) and Pt(II) complexes of the same composition will have similar p*K*a values. Therefore, the p*K*a of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ can be estimated at 3.0, indicating that within the pH range in the hydrolysis experiments both *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ and *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)(OH)]^{+}$ are present. As the pH is raised, the more labile aqua complex is converted into the less labile hydoxo complex, and the rate constant for hydrolysis decreases. Because the p*K*a of the first NH group "upstream" of a histidine-anchored Pd(II) atom has been estimated at ca. 2.0, an increase in the pH is expected to favor the unreactive complex **4**.[53-59] As Table 5 shows, the cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 2.0 is significantly accelerated when the anchoring residue is preceded by a proline residue. In that case, hydrolysis is completed in less than 1 day.

Table 3. HPLC separation and MALDI mass spectrometric identification of the fragments of the polypeptide designated Met-Ala and the polypeptide designated Pro-Met upon hydrolytic cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 2.0.

peptide substrate	**elution time (min)**	**polypeptide fragment**	**molecular mass (D)**	
			observed	**calculated**
Met-Ala	21.3	AKF	407.49	407.42
	18.3	GMAYRG	654.76	655.16
Pro-Met	16.2	KAYD	538.58	539.07
	18.4	PMAARA	616.60	616.76

Table 4. HPLC separation and MALDI mass spectrometric identification of the fragments of the polypeptide designated Pro-His and angiotensin II (the polypeptide designated His-Pro) upon hydrolytic cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 2.0.

peptide substrate	**elution time (min)**	**peptide fragment**	**molecular mass (D)**	
			observed	**calculated**
Pro-His	15.2	KAYD	538.58	539.25
	13.7	PHAARA	623.71	622.70
His-Pro	∗	VY +Pd(II) reagent	387.11	387.75
	18.4	IHPF + Pd(II) reagent	620.01	620.04

[*] Fragment VY is insoluble in water and acetonitrile and could not be separated from the reaction mixture, which was analyzed without separation.

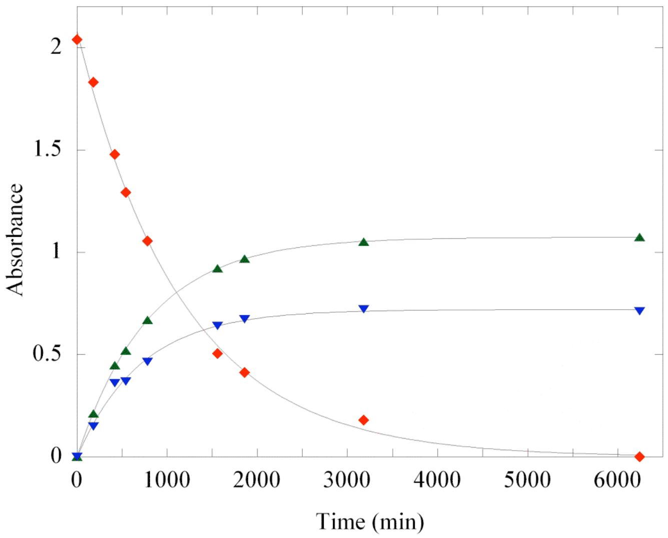


Figure 3. Representative plot of the kinetics of cleavage of the polypeptide designated Met-Ala by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$, where (♦) indicates the disappearance of the substrate, (▲) indicates the appearance of the fragment GMAYRG, and (▼) indicates the appearance of the fragment AKF.

Methionine-guided and histidine-guided sequence-selective polypeptide cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ in neutral solution. Remarkably, the selectivity of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ depends on the pH of the reaction mixture. At pH 2.0, the cleavage is residue-selective as explained in the preceding subsection. At pH 7.0, however, the cleavage becomes sequence-selective in that it occurs only at the X-Pro bonds in X-Pro-Met and X-Pro-His sequences. The substrates lacking a Pro-Met or Pro-His, namely, angiotensin II and the polypeptides designated as Pro-Phe and Met-Ala, remained intact in the presence of *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 7.0. For residue-selective cleavage in weakly acidic solutions, it is enough that the substrate contains methionine or histidine as an anchor. For sequence-selective cleavage in neutral solutions, it is necessary that the anchoring residue be preceded by proline. This useful change in selectivity can be attributed to the effect of pH on the predominant species in solution. At pH 2.0, the predominant species is the hydrolytically reactive complex **3**. At pH 7.0, the predominant species is the hydrolytically unreactive complex **4,** and complex **3** is only a minor species. Its low concentration is sufficient for cleavage only at the most reactive peptide bonds, namely, X-Pro bonds in the X-Pro-His and X-Pro-Met sequences.

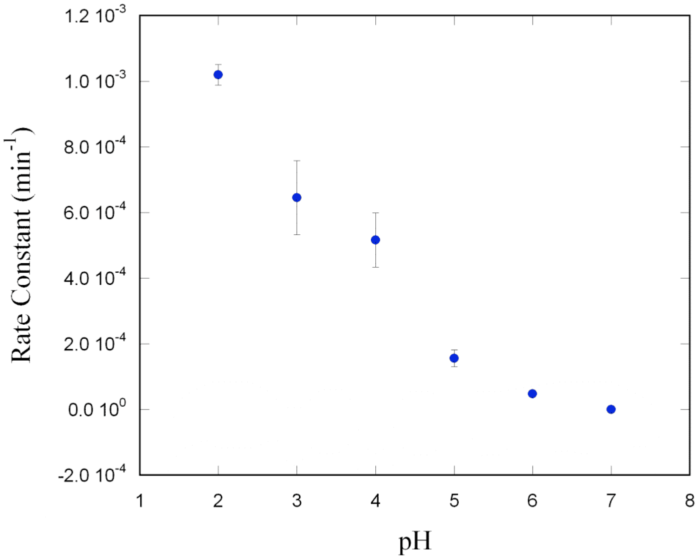


Figure 4. Dependence on pH of the rate constant for the cleavage of polypeptide designated Met-Ala by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ complex. The error bars indicate the average error in the calculated rate constants.

Table 5. HPLC separation and MALDI mass spectrometric identification of the fragments of the polypeptide designated as Pro-Met and the polypeptide designated as Pro-His upon hydrolytic cleavage by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 7.0 and the rate constants for the disappearance of the polypeptide at pH 2.0.

peptide substrate	**elution time (min)**	**peptide fragment**	**molecular mass (D)** observed	calculated	**rate constant (min^{-1})**
Pro-Met	15.6	KAYD	539.07	538.58	4.37×10^{-3}
	21.3	PMAARA	618.15	616.76	
Pro-His	13.9	KAYD	538.99	538.58	2.21×10^{-3}
	15.4	PHAARA	623.20	622.70	

2.5 Conclusions.

Complexes *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ and *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ are new reagents for the selective hydrolysis of peptides. These complexes are prepared *in situ* by two straightforward ligand substitution reactions. The simplicity of this synthetic method lends to the practicality of using *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ and *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ as reagents for the cleavage of peptides. Although these complexes are structurally similar to the established reagents *cis*-$[Pt(en)(H_2O)_2]^{2+}$ and *cis*-$[Pd(en)(H_2O)_2]^{2+}$, the thioether-containing reagents differ in reactivity from the ethylenediamine-containing reagents.

The new reagent *cis*-$[Pt(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ cleaves with the same selectivity as *cis*-$[Pt(en)(H_2O)_2]^{2+}$ in a weakly acidic solution but more slowly because of the steric bulk of the thioether ligand. The new reagent *cis*-$[Pd(CH_3SCH_2$-$CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ cleaves with the same selectivity as *cis*-$[Pd(en)(H_2O)_2]^{2+}$ in a weakly acidic solution but more slowly due to sterics. Unlike *cis*-$[Pd(en)(H_2O)_2]^{2+}$, however, the new reagent also cleaves in neutral solution. The difference in hydrolytic activity at pH 7 results from a difference in the mode of Pd(II)-substrate binding. While *cis*-$[Pd(en)(H_2O)_2]^{2+}$ loses its ethylenediamine ligand and forms unreactive multidentate complexes with the substrate, *cis*-$[Pd(CH_3SCH_2CH_2CH_2S$-$CH_3)(H_2O)_2]^{2+}$ retains its thioether ligand at pH 7.0 and forms a reactive as well as an unreactive complex with the substrate. The substrate in the reactive complex then becomes selectively cleaved. Both *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ and our previously reported Pd(II)-cyclodextrin conjugate[32] sequence-selectively cleave peptides at pH 7.0, and both require the presence of a proline residue near the site of cleavage. The two reagents, however, differ in sequence-selectivity; the Pd(II)-cyclodextrin conjugate cleaves the X-Pro bond of X-Pro-Y sequences, where Y is phenylalanine, while *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ cleaves the X-Pro bond of X-Pro-Met and X-Pro-His sequences. Although their selectivity is different, the two reagents show similar rates of hydrolysis at pH 7.0, with cleavage being nearly complete after 48 h.

2.6 Acknowledgments.

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2.7 Supporting information description.

Six figures showing the HPLC chromatograms of a hydrolytic reaction mixture, the synthetic reaction scheme for the Pd(II) and Pt(II) mononuclear complexes, the ^1H NMR spectra of the mononuclear Pd(II) and Pt(II) complexes at different temperatures, a ROESY NMR spectrum of a peptide, and the ^{1}H NMR spectra of the thioether ligand and its complexes.

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CHAPTER 3

The photochemistry and photophysics of sulfur and selenium ylides: a general review

3.1 General introduction to sulfur- and selenium-containing compounds.

Over the years, the sulfoxide functional group has offered a number of advantages to the field of synthetic chemistry and has emerged as a unique photochemical system. The chiral nature of sulfoxides has been utilized to direct the stereochemistry of a number of thermal syntheses particularly in the preparation of natural products containing quaternary carbons.[1-5]

3.2 Nomenclature and properties of sulfur- and selenium-containing compounds.

Sulfur and selenium analogs can exist in a number of different oxidation states. The nomenclature systems used for the various sulfur-containing functional groups (Figure 1) and selenium-containing functional groups (Figure 2) are provided as a reference.[6,7] Sulfur-containing compounds are typically designated with the prefix thio. For example, compounds in which an oxygen atom has been replaced by a sulfur atom use this system of nomenclature, including thioanisole, the sulfur-containing version of anisole, thiophene the sulfur-containing version of furan, and thiophenol the sulfur-containing version of phenol. On occasion the prefix mercapto is also acceptable, an example of its use appears in the name 2-mercaptoethanol ($HSCH_2CH_2OH$). Changes in the oxidation state of sulfur atoms are denoted by the change of a single letter of the compound's name. The lowest oxidation state is designated by the letter "e", the intermediate by the letter "i", and the highest by the letter "o", for example: sulfenic acid, sulfinic acid, and sulfonic acid. When a sulfur-containing heterocycle is oxidized, the suffix oxide or dioxide is used to denote the oxidation state, as seen in the following: thiophene, thiophene-*S*-oxide, and thiophene-*S,S*-dioxide.

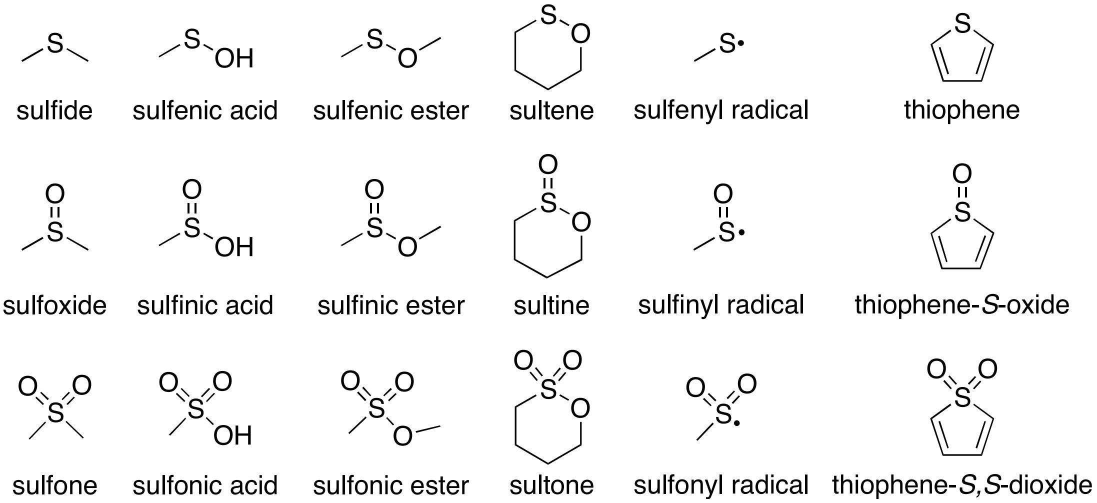


Figure 1. Nomenclature of sulfur-containing functional groups.

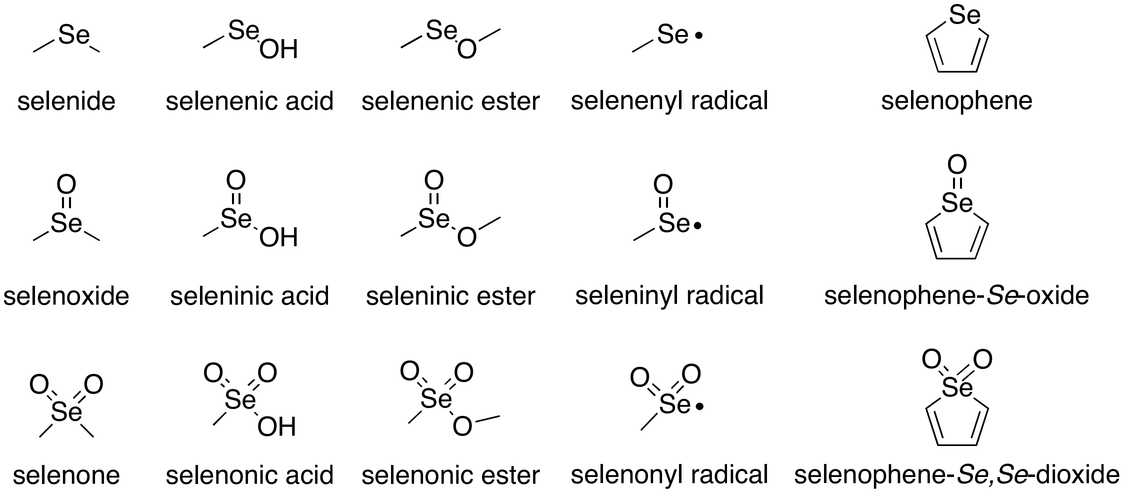


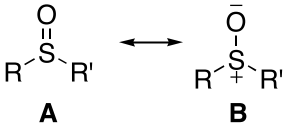
Figure 2. Nomenclature of selenium-containing functional groups.

A similar system of nomenclature is used for selenium-containing compounds, which are designated with the suffix seleno; examples include selenophenol, the selenium-containing version of phenol, and selenophene, the selenium-containing version of furan. The oxidation state of selenium is designated by the same nomenclature system as for sulfur, in which the lowest oxidation state is designated by the letter "e", the intermediate by the letter “i”, and the highest by the letter “o”, for example: selenenic acid, seleninic acid, and selenonic acid. Also, like sulfur-containing compounds, oxidized selenium-containing heterocycles include the suffix oxide or dioxide to designate the oxidation state of selenium, for example selenophene, selenophene-*Se*-oxide, selenophene-*Se,Se*-dioxide.

The general structure of sulfides and selenides, R-S-R and R-Se-R, is analogous to that of ethers. The nature of the R groups ($C(sp^3)$ vs. $C(sp^2)$) affect the R-S bond length of sulfides only slightly, varying from approximately 1.81Å to 1.78 Å respectively. On the other hand the sterics of the R group can significantly change the R-S-R angle, ranging from 99.0º for methyl groups to 113.2º for *t*-butyl groups.

The sulfoxide structure is similar to that of the carbonyl functional group in that both have polar bonds with an electronegative oxygen atom. The S-O bond strength of standard sulfoxides is typically around 87-90 kcal/mol, which is much lower than the typical C-O bond strength of carbonyls (~180 kcal/mol). The introduction of strong electron-withdrawing groups adjacent to the sulfoxide results in significant strengthening of the sulfoxide bond. An extreme example is F_2SO which has a bond dissociation energy of 114 kcal/mol.[8] Two representations of the sulfoxide functional group commonly appear in the literature, the hypervalent representation (A) and the ylide representation (B) (Scheme 1). These two representations are used interchangeably within this document to represent the sulfoxide functional group. Several studies have been dedicated to determining which better describes the sulfoxide functional group. In early studies, the hypervalent representation, in which d-orbitals are invoked, was the preferred description of the sulfoxide structure. More recently the ylide representation has emerged as the more accurate description of the bond. In the latter representation the sulfoxide is an ionic σ bond with no involvement of d-orbitals.[9,10]

Scheme 1.



3.3 Thermal reactions of sulfoxides, selenoxides, sulfinic esters, and sulfonic esters.

Pyrolytic internal elimination (Ei) reactions of sulfoxides[11-15], esters[16-18], xanthates[19-22], amine oxides[23], selenoxides[24-28], and sulfilimines[29,30] have been used extensively in the preparation of olefins. The enthalpies of reaction and activation energies of various sulfilimines and *S,C*-sulfonium ylides will be presented in Chapter 7. The following is a review of the mechanisms exhibited by sulfur-containing functional groups that undergo internal eliminations. Elimination reactions resulting in the formation of an alkene can occur by several different mechanisms (E1, E2, or $E1_{cb}$). The E1 mechanism is characterized by departure of the leaving group (i.e. S-C bond breakage) followed by transfer of a proton. The E2 mechanism involves concerted bond-breaking and bond making processes. In the $E1_{cb}$ mechanism, C-H bond cleavage occurs first and is followed by S-C bond cleavage. Figure 3 shows the three possible mechanisms, including transition states, for a general sulfoxide.

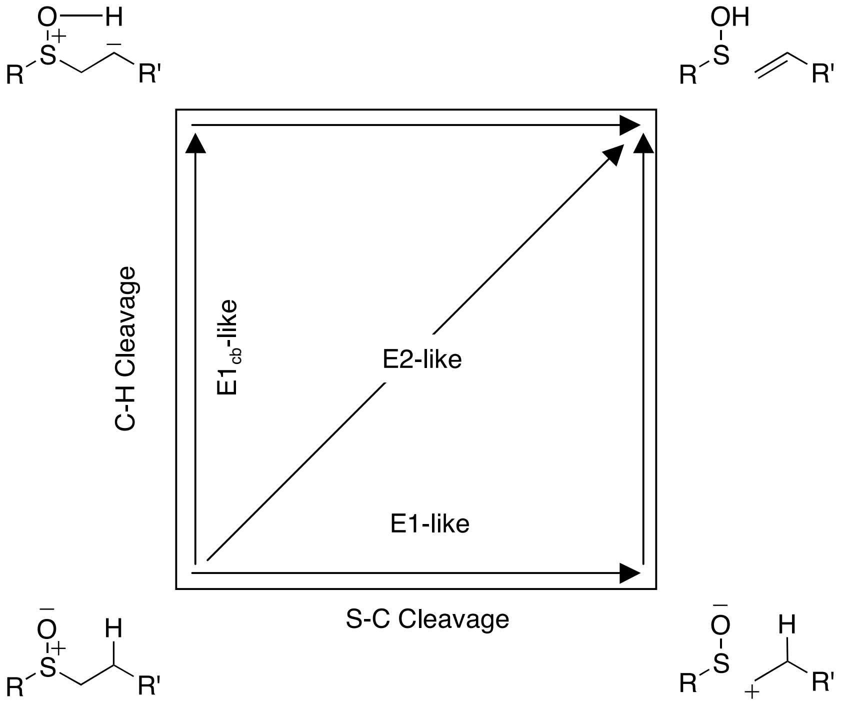


Figure 3. Three possible internal elimination mechanisms (E1, E2, and E1_{cb}) for a general sulfoxide.

Several studies have been dedicated to understanding the mechanisms by which sulfoxides, sulfinic esters, and sulfonic esters undergo eliminations. Sulfoxide eliminations are characterized by a concerted, relatively synchronous process in which a *cis*-β-hydrogen is transferred through a 5-membered cyclic transition state, similar to the Cope elimination (Figure 4).[31-33] The internal elimination of sulfoxides is not pericyclic because an orbital disconnect exists between the orbitals involved in the hydrogen transfer and those involved in the formation of the double bond. Sulfoxide eliminations are synthetically useful and have proven to be particularly valuable in the preparation of α,β-unsaturated carbonyls.[34]

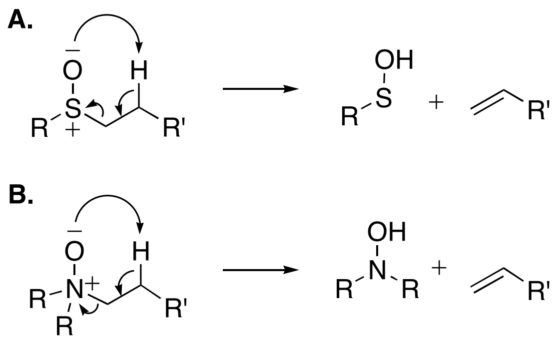
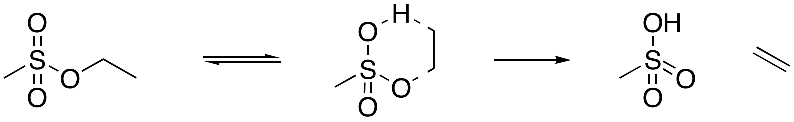


Figure 4. A) 5-centered sulfoxide elimination, B) Cope elimination.

Like sulfoxide eliminations, the internal elimination of sulfinic esters was first shown experimentally in 1970 to undergo a five-centered elimination in a *syn* fashion to produce an alkene.[35] The observed product resulted from transfer of the more acidic proton rather than elimination of the hydrogen which would lead to the more substituted olefin. Computational studies of sulfinic esters at MP2/6-311+G(3df,2p)//MP2/6-31G(d,p) were shown to estimate the activation barrier (E_a) within 3 kcal/mol of experimentally determined barriers.[32] An evaluation of the Mulliken charges of the starting material, transition state, and products showed a smooth change in the charges with no apparent maximum at the transition state suggesting that five-centered eliminations do not involve a highly charge separated transition state. These studies also indicated that in order for five-centered eliminations to occur with low activation barriers the sulfur-containing product must include a sulfur atom that is relatively nucleophilic.

Perhaps surprisingly, experimental results have shown that the internal elimination of sulfonic esters proceeds via a six-centered elimination (Scheme 2).[36-38] The activation barriers for the six-centered elimination of sulfonic esters are typically around 40 kcal/mol, more than 20 kcal/mol lower than the activation barriers estimated for five-centered eliminations of the same sulfonic esters.[32,39] The introduction of electron-withdrawing groups adjacent to the eliminated hydrogen accelerates the elimination, whereas electron-donating groups slow the reaction.[40-44] Examination of the Mulliken charges of the starting materials, transition states, and products of six-centered eliminations indicates a significant charge separation within the transition state, a result that supports Chuchani's hypothesis that the reaction proceeds through an intimate ion pair intermediate.[39] In general, the activation barriers for sulfonic esters undergoing six-centered eliminations are slightly lower, approximately 8 kcal/mol, than for sulfinic esters undergoing six-centered eliminations. This observation can be explained by the greater ability of sulfonic esters to stabilize the negative charge that develops on the oxygen atoms in the transition state. In addition, the calculations revealed that cleavage of the O-C_α bond is the most advanced process in the internal eliminations of sulfonic esters suggesting an E1-like mechanism.

Scheme 2.



Sulfilimines have also been used in the preparation of α,β-unsaturated carbonyls via internal eliminations and occur under milder synthetic conditions (i.e. lower temperatures) than sulfoxide eliminations. The difference in reactivity between sulfoxides and sulfilimines has been attributed to the enhanced basicity of the ylide nitrogen atom compared to the ylide oxygen atom. Several examples of *N*-substituted sulfilimines, including *N*-ethoxycarbonyl[45], *N*-tosyl[45-50], *N*-carbamoyl[51], *N*-acetyl[52,53], *N*-phenyl[54], and *N*-H[55] sulfilimines have been studied. In general, sulfilimines with electron-withdrawing groups on the ylide nitrogen have been shown to require elevated temperatures for elimination reactions compared to *N*-H sulfilimines.

3.4 Unimolecular photochemistry of sulfoxides and selenoxides.

The photochemistry of sulfoxides has been under investigation since at least the early 1960s. The sulfoxide chromophore has a relatively high excitation energy. Conjugation of the sulfoxide to aromatic chromophores can result in lower excitation energies (i.e. longer wavelengths). To date, studies have indicated that there are three major unimolecular reaction pathways that sulfoxides follow: homolytic α-cleavage, stereomutation, and deoxygenation. In Chapter 5 of this dissertation, the deoxygenation of thiophene-*S*-oxide, selenophene-*Se*-oxide, and to a lesser extent, dibenzothiophene-*S*-oxide is modeled computationally and will be discussed.

Homolytic α-cleavage. The most common process in sulfoxide photochemistry is homolytic cleavage of the S-C bond, known as α-cleavage. Analogous chemistry is observed for ketones under photolytic conditions; however, sulfoxides appear to be more susceptible to α-cleavage. For example, under one-photon conditions α-cleavage is not observed for benzophenone, yet diphenyl sulfoxide does undergo cleavage of the S-C bond with a low quantum yield. Homolytic α-cleavage has been shown to occur from both the singlet and triplet states.[56,57] Following S-C bond cleavage, the radical intermediates, a carbon centered radical and a sulfinyl radical, can follow a number of different pathways, including recombination to reform the sulfoxide (A), recombination to form the sulfenic ester (B), radical reactions including disproportionation, hydrogen abstraction, chain reactions, etc. (C) and extrusion of SO (D) (Figure 5). An example in which the predominant products arise from recombination to form the sulfenic ester followed by secondary photolysis can be observed in the photochemistry of dibenzyl sulfoxide (Figure 6).[58,59] The two major products of this reaction, the disulfide and benzaldehyde, arose from the decomposition of the sulfenic ester. Bibenzyl, a product of SO extrusion, is formed in only a very low yield (1%). The loss of SO from a simple sulfinyl radical ($CH_3SO\cdot$) has been estimated to be endothermic by 50 kcal/mol.[60,61] In general, SO extrusion only occurs in substantial yields if there is a significant driving force that accompanies the loss of SO, examples of which include formation of dienes (A) and acetylenes (B) (Figure 7).[62,63]

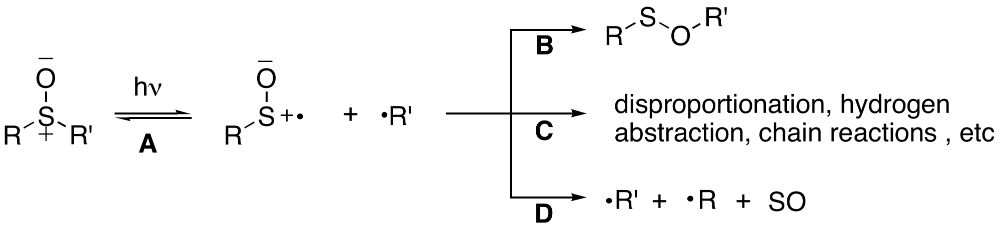


Figure 5. Four possible outcomes of α-cleavage: A) recombination to form the starting material, B) recombination to form the sulfenic ester, C) radical reactions, and D) SO extrusion.

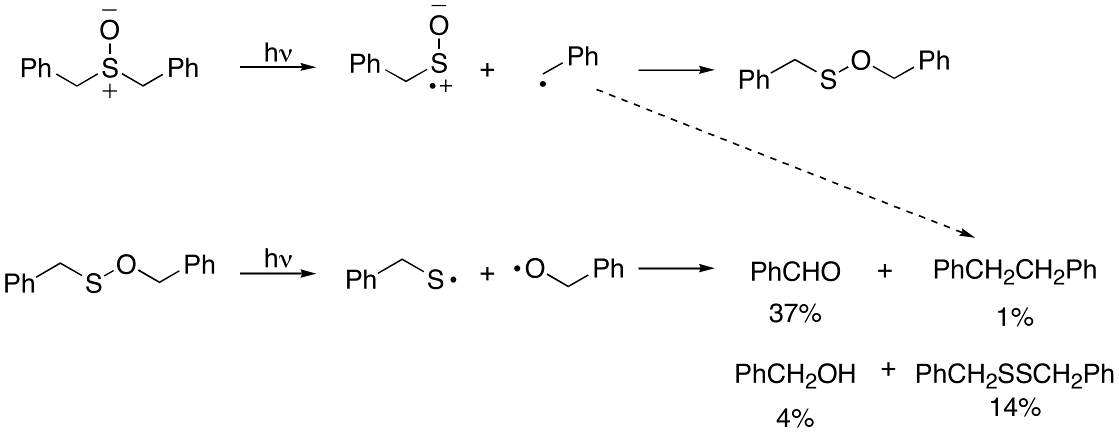


Figure 6. Photochemistry of dibenzyl sulfoxide.

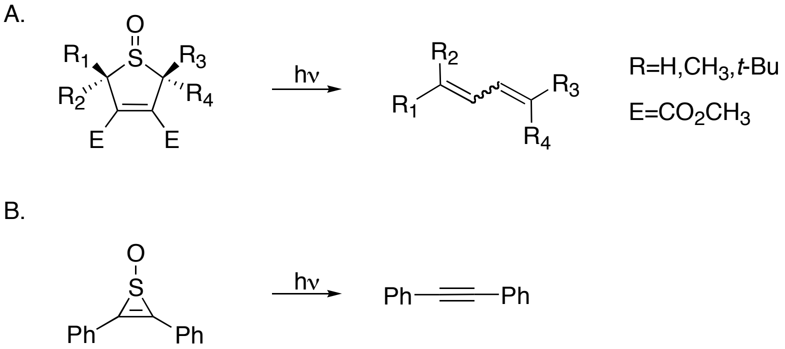


Figure 7. Examples of SO extrusion.

Stereomutation. Since the sulfur atom of sulfoxides adopts a pyramidal structure, sulfoxides containing two different carbon substituents are chiral making them useful as auxillaries in organic syntheses. Upon direct photolysis, sulfoxide racemization has been observed.[64] Two mechanisms have been proposed for the photochemical stereomutation of sulfoxides: A) α-cleavage followed by nonstereospecific recombination, and B) direct inversion about the sulfur atom (Figure 8). The formation of product 2 in the photolysis of phenyl norbornyl sulfoxide is strong evidence for proposed mechanism (A) (Figure 9).[65] The mechanism involving α-cleavage would also be expected to predominate for cases in which a stable radical can be generated upon homolytic cleavage. Evidence has also been established for the occurrence of the latter mechanism (B) in a study of diastereomeric product distributions in the photolysis of (R_s,S_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide (Figure 10).[66] The major product observed in the photolysis of (R_s,S_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide was (S_s,S_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide; small amounts of (S_s,R_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide and (R_s,R_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide were also present. These results suggest that direct inversion is the predominant mechanism. The barriers for pyramidal inversion of dimethylsulfoxide and H_2SO have been estimated to be on the order of 30-40 kcal/mol using MP2 methods.[67] The presence of the minor products is evidence that α-cleavage followed by recombination is also occurring, but to a lesser extent. In certain cases diastereomeric interactions may favor one isomer over the other making photochemical stereomutation a useful synthetic tool.

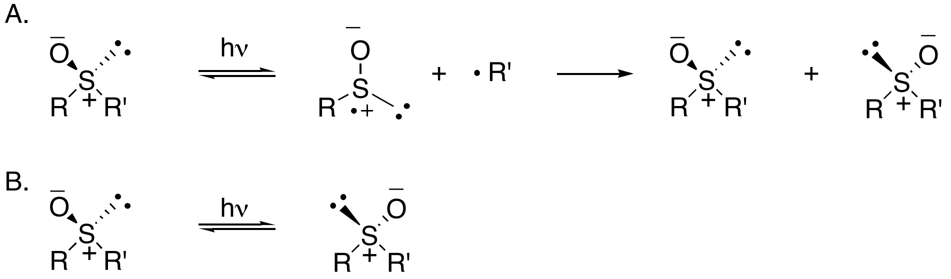
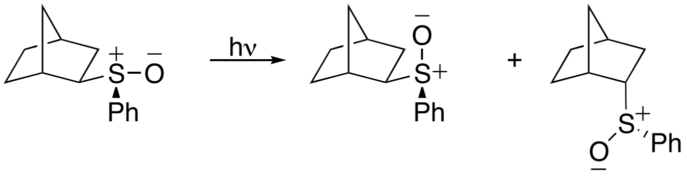


Figure 8. Proposed mechanisms for photochemical stereomutation.



1 **2**

Figure 9. Photolysis of phenyl norbornyl sulfoxide.

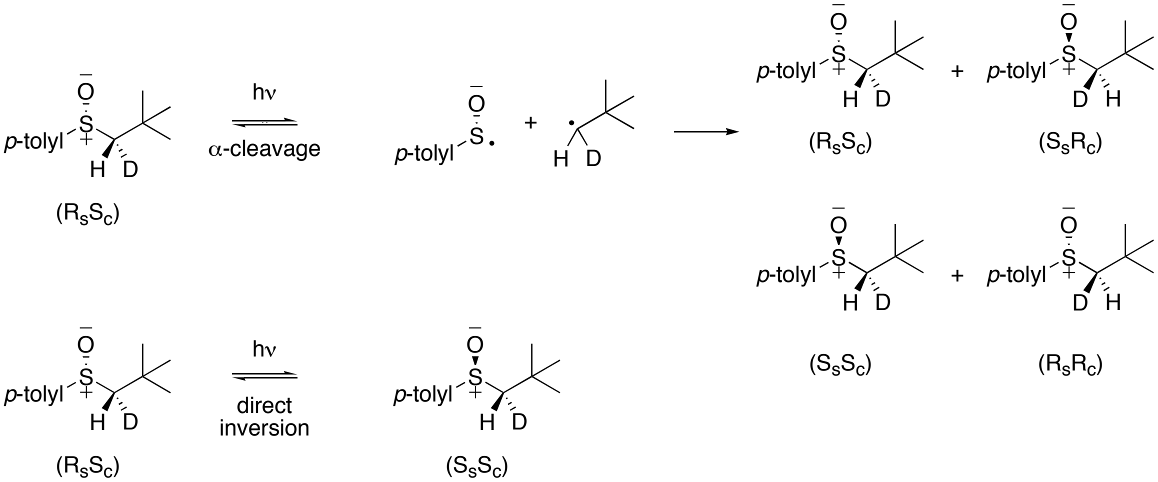


Figure 10. Possible products of the photolysis of (R_s,S_c)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide.

Hydrogen Abstraction. One of the common photochemical processes of carbonyl compounds is hydrogen abstraction. Despite its prevalence in carbonyl chemistry, there is little evidence to suggest that this process occurs for sulfoxides. Several studies have proposed the involvement of hydrogen abstraction in sulfoxide photochemistry, however, the products of these studies can also be rationalized by an α-cleavage mechanism. In a photochemical study of two alkyl aryl sulfoxides in which the abstraction of either β- or γ-hydrogen atoms might be favored, no evidence was found to suggest that hydrogen abstraction was occurring (Figure 11).[68] To date it appears unlikely that hydrogen abstraction is a significant photochemical process of sulfoxides.

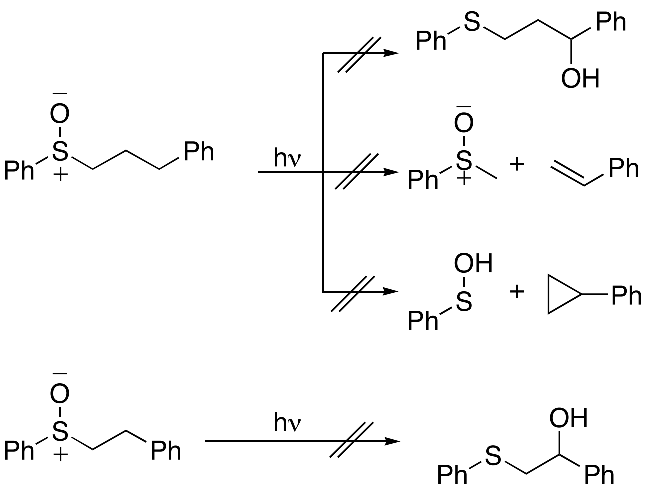


Figure 11. Evidence for the lack of sulfoxide hydrogen abstraction.

Deoxygenation. Unlike α-cleavage, deoxygenation has no analogy to carbonyl photochemistry. The deoxygenation of dialkyl, alkyl aryl, and diaryl sulfoxides was observed independently by Shelton and Davis in early 1972 and Posner in late 1972 upon direct and sensitized photolysis.[69, 70] At that time triplet sensitizers were believed to accelerate the formation of the sulfide suggesting that photodeoxygenation proceeds via the triplet state. These results led the investigators to propose a mechanism, which was motivated by the Paternó-Büchi reaction of carbonyl chemistry in which a photoexcited triplet sulfoxide forms a dimer with a ground state sulfoxide. Ultimately the triplet dimer was suggested to break down to form two sulfide molecules and molecular oxygen either in the singlet or triplet state. This mechanism will henceforth be referred to as the "dimer mechanism" (Figure 12). At the time of these studies, the triplet energies of the sulfoxides under investigation were unknown. The energies of the examined sulfoxides have since been determined to be higher in energy than most of the sensitizers that had been used in the photodeoxygenation studies, thus, eliminating the possibility that the reaction involves triplet-triplet energy transfer from the sensitizer.[40,44]

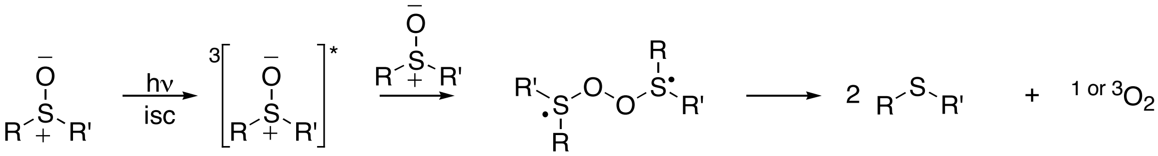


Figure 12. Proposed "dimer mechanism" of sulfoxide deoxygenation.

Nine years later, a second mechanism was proposed based on experimental chemically induced dynamic nuclear polarization (CIDNP) results (Figure 13).[56,57] This mechanism, however, has been estimated to be energetically unfavorable, particularly the reduction of the sulfinyl radical.[71] The S-O bond energy of the phenyl sulfinyl radical has been estimated at 102 kcal/mol, some 35 kcal/mol stronger than the S-C bond energy. In addition, the transfer of an oxygen atom from the phenyl sulfinyl radical to an alkyl radical has been estimated to be endothermic by 12 kcal/mol.[71]

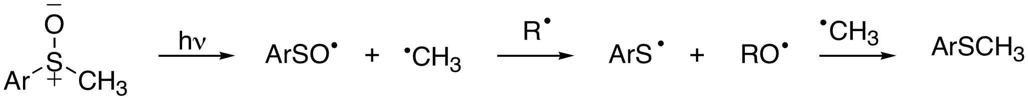


Figure 13. Proposed "sulfinyl radical mechanism" of sulfoxide deoxygenation.

A disproportionation reaction in which two sulfoxides react to produce the corresponding sulfide and sulfone might be considered to explain deoxygenation; however, studies of the photochemistry of aromatic sulfoxides have consistently failed to provide evidence for sulfone formation (Figure 14). One exception to this has been reported; however, no mechanistic studies have been performed to explain sulfone formation.[72]

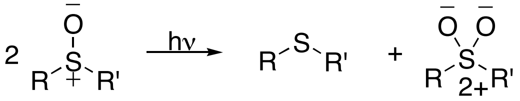


Figure 14. Proposed disproportionation reaction of sulfoxides.

More recently, several pieces of evidence have lent favor to two alternative mechanisms, a unimolecular deoxygenation mechanism and a bimolecular photoreduction mechanism, although the dimer mechanism is sometimes still considered. Unimolecular deoxygenation has been observed as the primary photoprocess of dibenzothiophene oxide from which dibenzothiophene and an electrophilic oxene species, likely O(^{3}P), are produced (Figure 15).[71] A couple of control experiments were designed to rule out the dimer mechanism. In one, matrix isolation techniques were used to effectively eliminate bimolecular collisions, a component of the dimer mechanism. Dilute dibenzothiophene-*S*-oxide was frozen in an organic glass matrix. The subsequent photolysis produced dibenzothiophene, a product of deoxygenation. A second piece of evidence against the dimer mechanism came from a study in which dibenzothiophene-*S*-oxide was selectively photolyzed in the presence of diphenyl sulfoxide. Formation of diphenyl sulfide would be expected if the dimer mechanism was occurring, yet it was not detected.

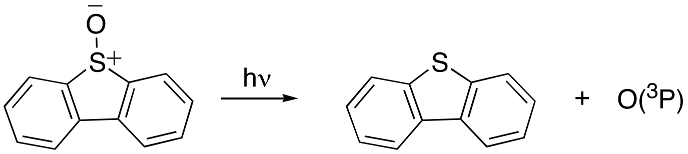


Figure 15. Observed unimolecular dissociation of dibenzothiophene-*S*-oxide upon photolysis.

The quantum yield for dibenzothiophene-*S*-oxide deoxygenation is quite low (< 0.01). The energetics of this system offer a possible explanation for the low quantum yield. The bond dissociation energy of dibenzothiophene-*S*-oxide has been estimated at MP2/6-31G(d,p) to be 78.3 kcal/mol.[73] However, the lowest triplet state of dibenzothiophene-S-oxide has been determined experimentally to be 61 kcal/mol.[74] Therefore, O(^{3}P) may be arising not from a triplet state, but rather from an excited singlet state from which S-O bond stretching is accompanied by a spin flip, which would be a forbidden process. Chapter 5 of this dissertation offers further insight into the excited states responsible for deoxygenation. The introduction of heavy atoms to the dibenzothiophene-*S*-oxide system, both substitution of selenium for sulfur and halogen substitution on the dibenzothiophene framework, has been shown to dramatically increase the quantum yield of deoxygenation.[75,76] The increase has been explained on the basis of the heavy atom effect increasing the probability of intersystem crossing.

In addition to unimolecular deoxygenation, a bimolecular reduction mechanism has been proposed in which electron transfer is followed by hydrogen abstraction and finally cleavage of the S-O bond (Figure 16). This mechanism was first proposed by Kropp who investigated the photolysis of 2-norbornyl phenyl sulfoxide (Figure 17).[65] The reaction was conducted in the presence of sodium methoxide and methanol and yielded 64% of the sulfide. Upon removal of the base, however, only trace amounts of the sulfide were generated. The bimolecular reduction mechanism was further explored with the photolysis of diphenyl sulfoxide, which undergoes deoxygenation to diphenyl sulfide.[77] The proposed intermediates of the reaction are outlined in the scheme below (Figure 18).

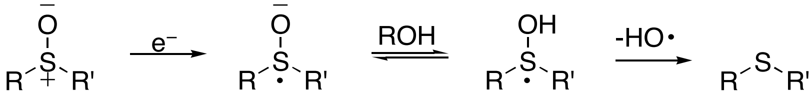


Figure 16. Proposed bimolecular reduction mechanism of sulfoxide deoxygenation.

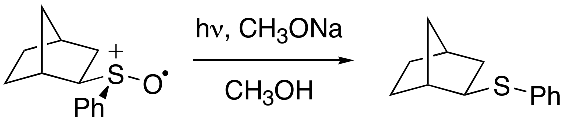


Figure 17. Photolysis of 2-norbornyl phenyl sulfoxide.

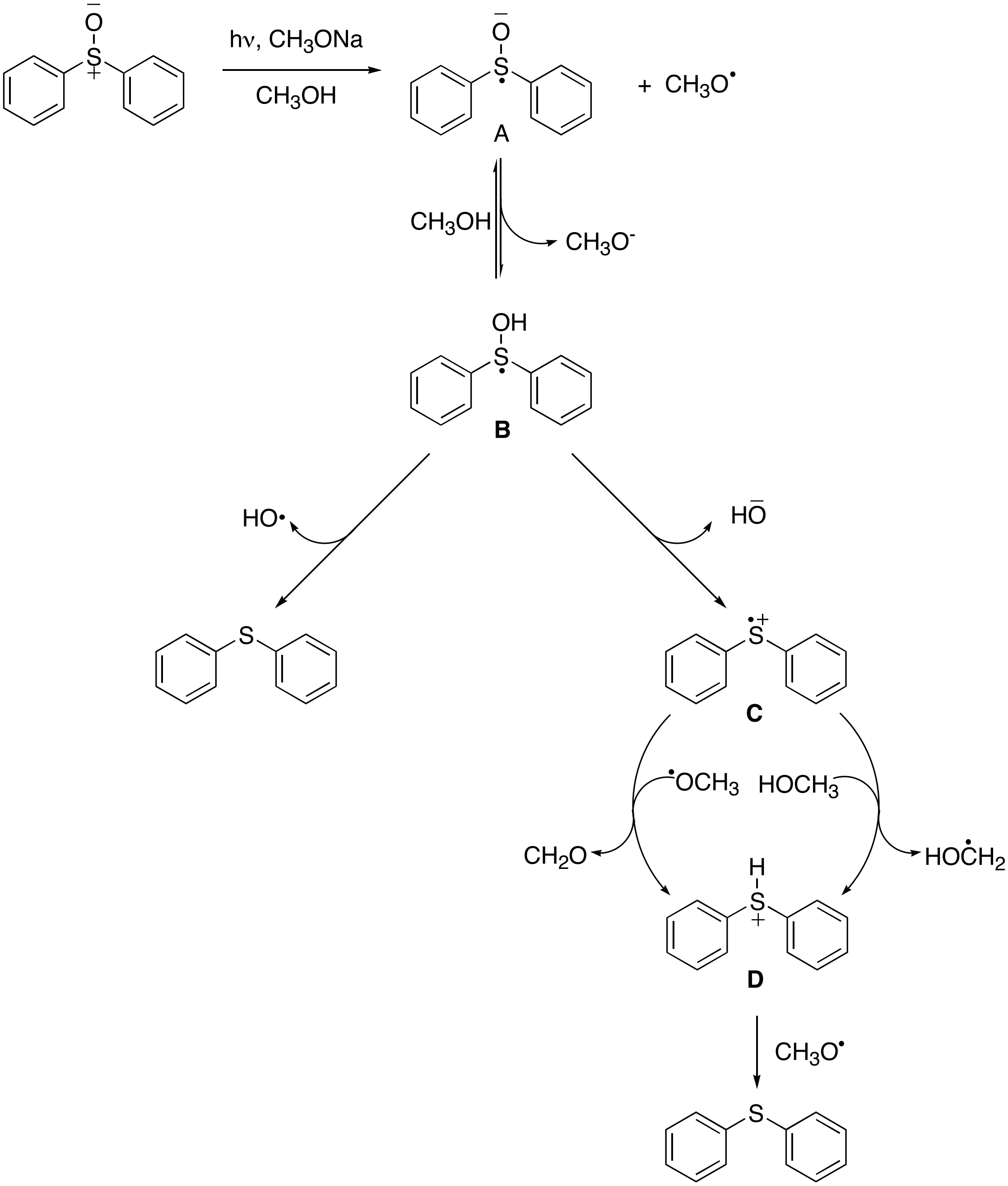


Figure 18. Proposed intermediates of the photolysis of diphenyl sulfoxide.

Upon photolysis, radical anion A is proposed to form as a result of an electron transfer from methoxide. Intermediate A then abstracts a hydrogen atom from a solvent molecule to produce hydroxysulfuranyl radical B. Intermediate B can then undergo either homolytic or heterolytic cleavage of the S-O bond. Homolytic cleavage produces diphenyl sulfide, whereas heterolytic cleavage produces radical cation C. Homolytic cleavage has been estimated to be endothermic by 11 kcal/mol, while heterolytic cleavage is slightly less endothermic at about 5 kcal/mol.[78-80] Intermediate C can then abstract a hydrogen atom from either methanol or a CH_3O radical to produce cation D which can lose a proton to methoxide to form diphenyl sulfide. Even though heterolytic cleavage is estimated to be energetically more favorable than homolytic cleavage, homolytic cleavage has not been ruled out as a possibility.

While the photochemistry of dibenzothiophene-*S*-oxide and dibenzoselenophene-*Se*-oxide has been thoroughly investigated, thiophene-*S*-oxides and selenophene-*Se*-oxides have eluded study until only recently because of the challenge of isolating and characterizing these compounds. The preparation of thiophene-*S*-oxides from thiophenes and selenophene-*Se*-oxides from selenophenes through oxidation using peracids suffers from the tendency of overoxidation to the sulfone or selenone and dimerization via a Diels Alder reaction.[81] The initial oxidation of thiophene to thiophene-*S*-oxide is relatively slow compared to the oxidation of thiophene-*S*-oxide to thiophene-*S,S*-dioxide due to the accompanied loss of aromaticity. To overcome this challenge, a Lewis acid like $BF_3{\cdot}Et_2O$ must be introduced to the reaction mixture.[81,82] It is believed that the Lewis acid interacts with the oxygen atom of the sulfoxide preventing further oxidation to the sulfone by decreasing the electron density on the sulfur atom. Our group is currently investigating the photolysis of substituted thiophene-*S*-oxides, which in certain cases results in deoxygenation like dibenzothiophene-*S*-oxide.[83]

The study of sulfoxides via computational methods can provide useful insights in the elucidation of relevant mechanisms of photodecomposition. Previous studies have indicated that in order to accurately model the S-O bond of a sulfoxide, tight d-polarization functions and core polarization are required.[32,84] Chapter 5 of this dissertation explores the potential energy surfaces of thiophene-*S*-oxide and selenophene-*Se*-oxide deoxygenation. These systems were chosen for study because they are sufficiently small to allow for rigorous computations. The results of this study are used to clarify the mechanism of sulfoxide deoxygenation. Chapter 6 of this dissertation explores the bond dissociation energies of various sulfoxides, selenoxides, sulfilimines, and *S,C*-sulfonium ylides. General trends regarding the effect of aromaticity and electron-withdrawing groups will be discussed.

3.5 Properties, Preparation, and Reactivity of Carbenes.

In Chapter 4 of this dissertation the photochemical generation of carbenes from *S,C*-sulfonium ylides will be discussed. A method for the preparation of carbenes was long sought dating back to as early as 1835 when Dumas and 1839 when Regnault unsuccessfully attempted to dehydrate methanol using phosphorus pentoxide and concentrated sulfuric acid respectively. Nearly twenty years later, in 1857 Perrot attempted to produce methylene upon the pyrolysis of methyl chloride to induce the elimination of HCl. This also failed to generate a carbene. The efforts continued in 1861 when Butlerov treated methylene iodide with copper powder in a sealed tube, but the attempt merely produced ethylene. It was not until 1912 that Staudinger recognized carbenes as the transient species formed in the decomposition of diazo compounds and ketenes.[85]

Two nomenclature systems are used to describe carbenes, the main difference of which is in the suffix used to describe the divalent carbon, either carbene or ylidene. For example, under the former nomenclature system CH_3CH: is named methylcarbene, and under the latter system it is methylidene. Structurally, carbenes are covalently bonded to two groups and possess two nonbonding electrons which are sometimes considered diradicals. The electrophilicity of the carbene carbon is strongly influenced by the electron withdrawing/donating ability of the adjacent groups. The nonbonding electrons can exist in one of two spin states: a triplet, in which the spins are parallel and unpaired, or a singlet in which the spins are anti-parallel and paired. In order to gain an understanding of the geometry and spin state that will be adopted by a given carbene, a qualitative molecular orbital diagram must be considered.[86] Figure 19 illustrates the molecular orbital diagram for linear :CH_2. If the molecule adopts a bent conformation, the molecular orbital diagram changes slightly (Figure 20). A comparison of the molecular orbital diagrams of bent and linear structures suggests that the lowest energy singlet adopts a bent structure; although, it is less clear whether the bent or linear triplet will be lower in energy. At least in the simplest example of methylene, the bent triplet is lowest in energy.

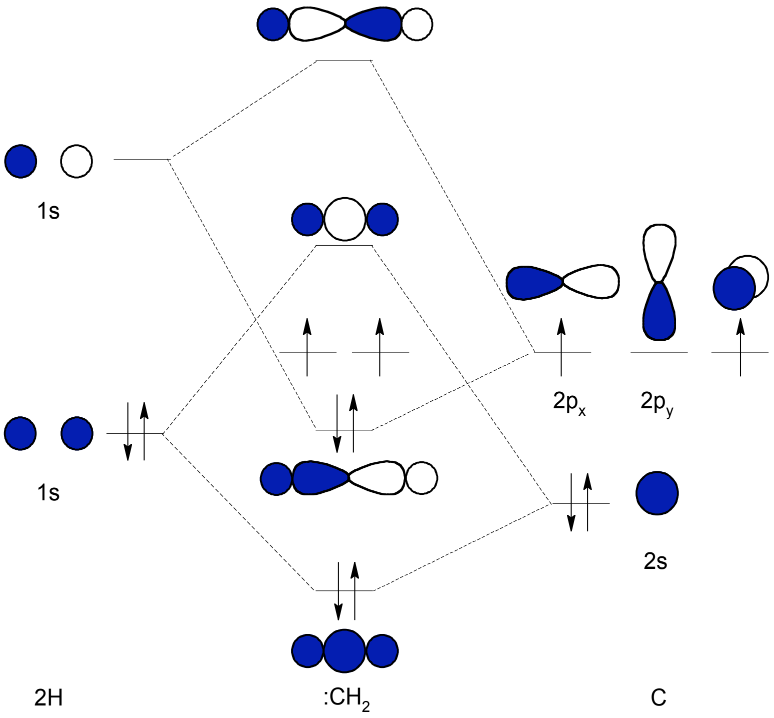


Figure 19. Qualitative molecular orbital diagram for linear :CH_2.

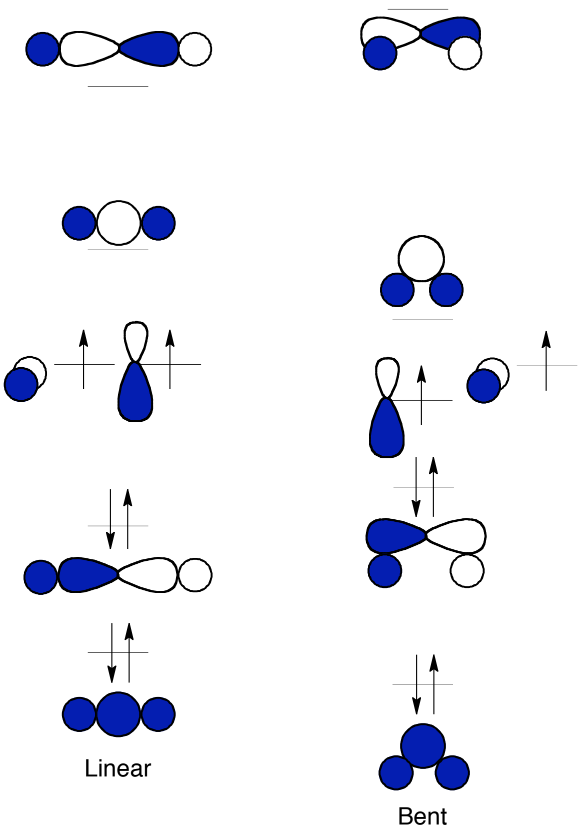


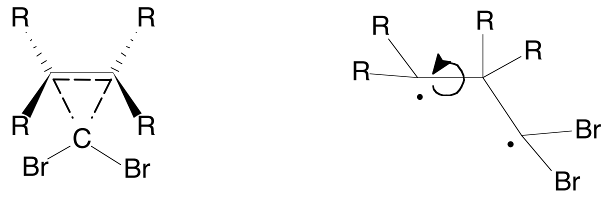
Figure 20. Qualitative molecular orbital diagrams for linear $:CH_2$ (left) and bent $:CH_2$(right).

The singlet-triplet gap for many carbenes is only a few kcal/mol. Several factors influence whether the ground state will be a singlet or a triplet including electronic and steric effects.[86] Substituents capable of donating non-bonding electrons into the empty 2p orbital of the carbene, such as $-NR_2$, -OR, -SR, -F, -Cl, -Br, and –I tend to give rise to singlet ground states; however, π-electron acceptors such as –COR, -SOR, $-SO_2R$, -NO, and $-NO_2$ and conjugating groups like alkenes, alkynes, and aryl substituents result in ground state triplet carbenes.

The magnitude of the singlet-triplet splitting is affected by the carbene carbon bond angle which is governed by the sterics of the substituents. Linear carbenes have two degenerate p orbitals. A decrease in the carbene carbon bond angle results in a loss of degeneracy and a reduction in the singlet-triplet gap. Therefore, sterically demanding substituents that force a wide bond angle stabilize a triplet ground state.

Extensive work has been done to elucidate the differences in the reactivity of singlet and triplet carbenes.[86] In the 1950s and 1960s the work of Skell and Doering demonstrated that singlet carbenes add stereospecifically to alkenes while triplets were shown to add nonstereospecifically. It was suggested and verified both experimentally and computationally that singlet carbenes tend to undergo concerted reactions while triplet carbenes react in a step-wise fashion in which a diradical intermediate is formed. The diradical intermediate can undergo rotation about the single bond and ring closure faster than spin inversion (i.e. intersystem crossing) resulting in a mixture of both stereoisomers (Scheme 3). Due to the lack of stereospecificity in their reactivity, triplet carbenes are less synthetically useful than singlet carbenes.

Scheme 3.



Singlet carbene Triplet carbene

Singlet and triplet carbenes also react differently with other compounds. Singlet carbenes tend to undergo insertion reactions with X-H bonds in which X is O, N, Si, or C. Insertion reactions with alcohols can occur very quickly. On the other hand, triplet carbenes tend to abstract hydrogens by either a double hydrogen abstraction or an abstraction-recombination mechanism, also referred to as a C-H “insertion”. The reaction of carbenes with alcohols can, therefore, provide information regarding the spin state of the carbene. Since singlet carbenes undergo O-H insertion with alcohols and triplets abstract hydrogens, trapping studies, in which the ratio of the products can be monitored, are common tests employed to indirectly determine the multiplicity of the carbene intermediate.

Common precursors of carbenes include diazo and diazirine complexes which, upon heating or photolysis, lose nitrogen gas to generate the corresponding reactive carbene species. Several studies in the middle to late 1990s provided strong evidence suggesting that some of the reactivity typically attributed to carbenes is actually arising from nitrogenated precursors in the excited state.[87-94] The possible mechanisms of product formation shown below include: 1) rearrangement in excited states (RIES), 2) carbene reactivity, and 3) formation of a carbene-olefin complex (COC) (Figure 21). The importance of all three pathways has been demonstrated for diazo and diazirine complexes with a C-H bond in the position α to the carbene carbon. Photochemical studies of alkylchlorodiazirines and alkylaryldiazos have shown that both the RIES and the COC mechanisms are occurring with varying efficiencies that are precursor dependent.[87,90]

Chapter 4 examines the preparation and photochemical reactivity of non-nitrogenous precursors to dicarbomethoxycarbene, a ground state triplet carbene. Both the photochemical and thermal reactivity of diazocarbonyl compounds leads to formation of products from two possible reactive intermediates, ketenes and carbenes (Figure 22). Carbonylcarbenes undergo the typical carbene reactivity that was described above (i.e. OH insertion, C-H insertion, and addition to π-bonds) and ketenes react with nucleophiles to form acyl derivatives, termed Wolff rearrangement. Although it is not entirely clear what factors lead to the predominance of one mechanism over the other for a given substrate, acyclic diazocarbonyls, like diethyldiazomalonate, have been shown to photochemically generate carbene trapped products. However, cyclic diazocarbonyls, like diazo Meldrum’s acid, generate products of Wolff rearrangement.[95-98] An added complexity to these reactions is the ability of excited state carbonyl carbenes to undergo isomerization which is believed to proceed through an antiaromatic oxirene (Figure 23).[99-103]

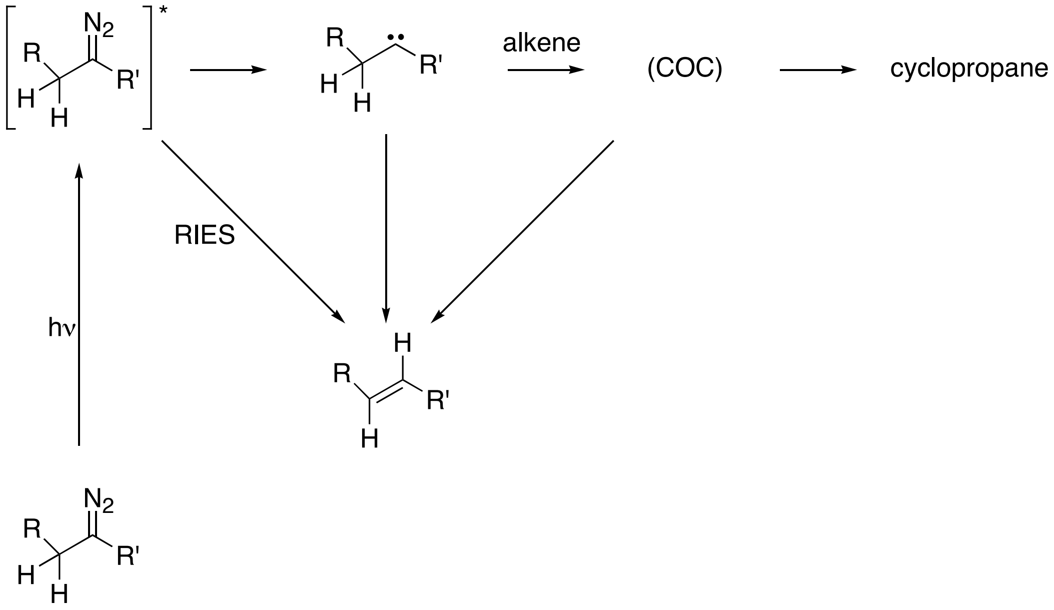


Figure 21. Possible pathways upon photoexcitation of diazo complexes.

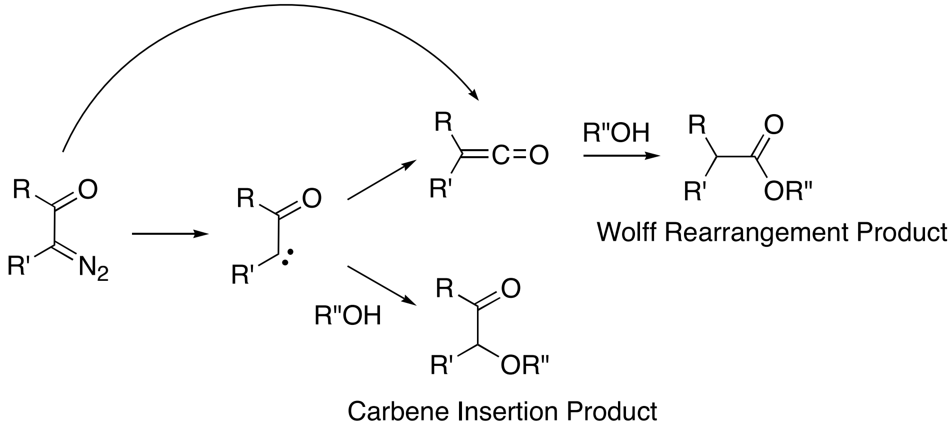


Figure 22. Photochemistry of diazocarbonyl compounds.

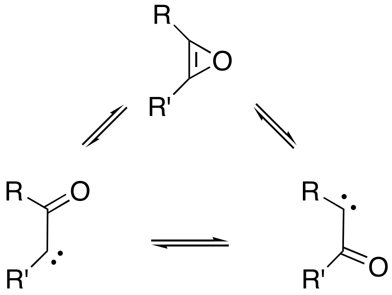


Figure 23. Isomerization of carbonyl carbenes.

Excited state carbenes undergo rapid intersystem crossing from the singlet to the triplet state and vice versa assuming the energy levels are sufficiently close. The observed reactivity of carbenes is dependent on the singlet-triplet energy splitting because reactions out of the ground state are normally expected to predominate, but reactions of carbene singlets can be three orders of magnitude faster than reactions of triplets. In general, carbenes with a singlet ground state that is well separated from the triplet state react as singlets regardless of the method of generation. On the other hand, carbenes that are ground state triplets and have a large singlet-triplet energy splitting tend to react in the multiplicity determined by the method of carbene generation (for example: direct or sensitized photolysis). Finally carbenes that are ground state triplets and have a small singlet-triplet energy splitting react as singlets regardless of the method of generation.

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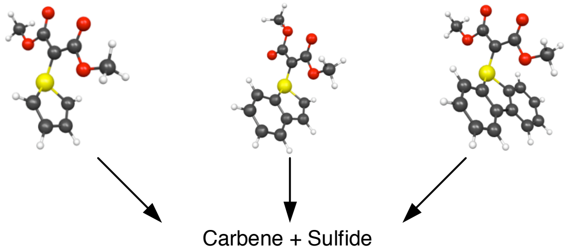
CHAPTER 4

Photochemical reactivity of *S,C*-sulfonium ylides of thiophenes: potential carbene precursors.

In the style of a paper submitted to the *Journal of Organic Chemistry*
Stacey A. Stoffregen and William S. Jenks
Department of Chemistry, Gilman Hall, Iowa State University, Ames, Iowa 50010-3111



4.1 Abstract.

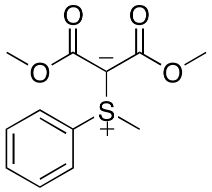
Dimethyl malonate ylides of thioanisole, thiophene, benzothiophene, and dibenzothiophene have been prepared in an effort to extend the chemistry observed for analogous sulfoxides and sulfilimines, namely, unimolecular bond cleavage. Dibenzothiophene-*S*-oxide undergoes deoxygenation to form dibenzothiophene and a reactive intermediate believed to be O(^{3}P). More recent studies of the photochemistry of *N*-substituted dibenzothiophene sulfilimines have provided direct evidence for nitrene formation upon photolysis.[1-5] In this study, the photochemistry of thioanisole- and thiophene-based *S,C*-sulfonium ylides is shown to result in scission of the S-C bond, to generate the corresponding sulfide and a reactive intermediate. Chemical trapping studies following direct photolysis of the ylides in the presence of an alkene, yield both cyclopropanation of the alkene and C-H insertion, both of which are indirectly indicative of carbene formation. Direct photolysis of the ylides in methanol produce the O-H insertion product, which is typical singlet carbene reactivity. Upon benzophenone-sensitized photolysis in methanol, the major product changes to that expected from triplet carbene reactivity (i.e. double H-abstraction), while O-H insertion persists, albeit, in minor yields. The quantum yields from the thiophene, benzothiophene, and dibenzothiophene ylide photolyses indicate quantitative return of the sulfide and a greater photochemical efficiency than that of the deoxygenation of dibenzothiophene-*S*-oxide.

4.2 Introduction.

Carbenes are interesting and important reactive intermediates that can be used synthetically for the formation of carbon-carbon bonds and provide routes to unusual products. The reactivity of a carbene depends on its spin multiplicity. Many carbenes are ground state triplets, particularly those with electron withdrawing substituents bound to the carbene carbon, yet react primarily from the singlet state.[6] These transient species are typically prepared from diazo or diazirine precursors. However, several reports have shown that some of the chemistry historically attributed to carbenes, particularly 1,2-R migrations where R = H or Ph and certain C-H insertions, is actually occurring out of excited states of the nitrogenated precursors.[7-17] Thus, there is a need for alternative practical carbene precursors.

Recent studies in our laboratory suggest that *S,C*-sulfonium ylides may be viable alternatives to nitrogenated carbene precursors. The photochemistry of dibenzothiophene-*S*-oxide, dibenzoselenophene-*Se*-oxide, and substituted thiophene-*S*-oxides results in deoxygenation to form the corresponding sulfide/selenide and an electrophilic oxene species.[2-5,18-20] A number of experiments have provided indirect evidence for the formation of O(^{3}P), although direct evidence is difficult to obtain in solution. In a separate set of studies, *N*-substituted dibenzothiophenesulfilimines have provided direct evidence, by means of time-resolved IR spectroscopy, for the formation of benzoyl nitrene and dibenzothiophene.[1] Chemical trapping studies supported this observation, showing reactivity typical of nitrenes. Based on these chemical observations for related systems, *S,C*-sulfonium ylides are expected to undergo unimolecular S-C bond cleavage upon photolysis to yield the corresponding carbene.

Herein we report the photochemistry of dimethyl malonate ylides of thioanisole **(1)**, thiophene **(2)**, benzothiophene **(3)**, and dibenzothiophene **(4)**. The main chromophore of ylides **2-4** can be photolyzed at long enough wavelengths (e.g. ~300 nm) to prevent undesirable side reactions. These particular ylides were chosen for this study because the reactivity of dicarbomethoxycarbene has been extensively studied, malonate ylides are known to be stable and easy to prepare, and we presume that we will avoid most of the potential for intramolecular excited state rearrangements of carbene precursors.[17,21,22] The results from this study provide indirect evidence for the formation of dicarbomethoxycarbene **(5)** from compounds **1-4**, with enhanced quantum yields of S-C bond scission for compounds **2-4** relative to dibenzothiophene-*S*-oxide deoxygenation.



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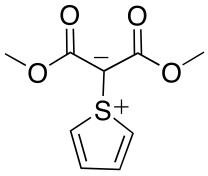

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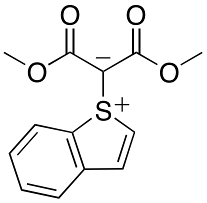

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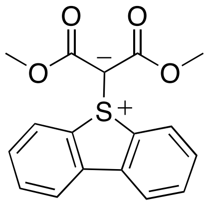

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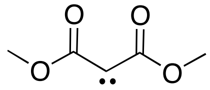

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4.3 Experimental details.

General. Cyclohexene was refluxed over sodium metal under an argon atmosphere and distilled immediately before use. Benzene and methylene chloride were refluxed over calcium hydride under an argon atmosphere and distilled immediately before use. Thiophene was distilled under vacuum using a short path distillation apparatus prior to its use. Dibenzothiophene was distilled under vacuum using a Kügelrohr apparatus at 175 °C prior to its use.

Synthesis. Dimethyl diazomalonate,[23] *p*-toluenesulfonyl azide,[24] methyl phenyl sulfonium bismethoxycarbonylmethylide **(1)**,[25] thiophenium bismethoxycarbonylmethylide **(2)**,[26] benzothiophenium bismethoxycarbonylmethylide **(3)**,[27] trimethylphosphite copper (I) chloride,[28] 7,7-dimethoxycarbonylbicyclo[4.1.0]heptane **(6)**,[29] dimethyl (3-cyclohexenyl)malonate **(7)**,[29,30] tetramethoxycarbonylethylene **(8)**,[30] dimethyl 2-thienylmalonate **(10)**,[31] and dimethyl dimethoxymalonate **(14)**[32] were prepared by methods reported in the literature.

Dibenzothiophenium bismethoxycarbonylmethylide (4). To a 100mL round bottomed flask, dibenzothiophene (0.93 g, 5.05 mmol), dimethyl diazomalonate (0.12 mL, 1.02 mmol), rhodium acetate dihydrate (2 mg), and 1,2-dichloroethane (4 mL) were added under an argon atmosphere. The mixture was stirred for 15 hrs at which time the mixture was a milky green color. The solvent was then removed under vacuum and hexane (20 mL) was added. The crude product was collected by vacuum filtration and subsequently purified by recrystallization from methanol. The pure title compound was a white solid. Yield: 79% (0.25 g) FW=314.36 g/mol. Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.29 (s, 3H), 3.88 (s, 3H), 7.54 (t, J=7.6 Hz, 2H), 7.67 (t, J=7.6 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 8.01 (d, J=8.0 Hz, 2H). ^{13}C NMR($CDCl_3$) δ: 51.1, 51.5, 57.5, 122.5, 125.0, 129.7, 131.4, 135.6, 137.4, 164.5, 167.8. EI-MS: Calc. 314 g/mol. Found 314 (M), 283 (M-OCH_3), 255 (M-CO_2CH_3), 184 (M-$C_5O_4H_6$). IR (cm^{-1}): 3054(sh), 2986(sh), 2305(sh), 1685(sh), 1649(sh).

Steady state photolysis methods. All photolyses in this study were performed with one of two different photolytic systems. A Southern New England Ultraviolet Rayonet minireactor equipped with 1-8 x 4W fluorescent bulbs was used in conjunction with a merry-go-round holder to ensure uniform irradiation. Low-pressure coated mercury lamps with broad emission around 300 nm and 350 nm, as well as low-pressure mercury lamps with emission at 254 nm were used in this study. Samples were held in either a 1 cm quartz cell or an NMR tube.

The second photolytic system, used to measure quantum yields, was a 75 W Xenon Arc lamp and monochromator from Photon Technologies, Inc. The monochromator was set to the desired wavelength for photolysis and has ± 12 nm linear dispersion. Samples were held in 1 cm quartz cells and were magnetically stirred to ensure uniform irradiation.

Spectral grade solvents were used without further purification. All solutions were flushed with Ar for at least 15 min prior to photolysis to remove oxygen. The standard sample size was 3 mL in the 1 cm quartz cells.

Quantum yield measurements. Valerophenone was used as a chemical actinometer to determine quantum yields for photolyses performed at 300 nm.[33,34] The actinometer was photolyzed in dry benzene at 300 nm and the appearance of acetophenone was monitored by a Hewlett Packard 1050 HPLC System containing a diode array detector set to monitor at 265 nm. The reverse-phase separations were performed on an analytical Supelco C18 column. The eluting solvents were methanol and acetonitrile. In a typical run, the initial ratio of solvents was 70% methanol and 30% acetonitrile. After injection of the sample, the solvent ratio was gradually changed to 50% methanol and 50% acetonitrile over a period of 10 min with a flow rate of 1.0 mL/min.

Azoxybenzene was used as a chemical actinometer to determine quantum yields for photolyses performed at 254 nm.[35,36] The actinometer was photolyzed in a solution of ethanol and potassium hydroxide and the appearance of 2-hydroxyazobenzene was monitored by a UV-2101PC Shimadzu UV/Vis Scanning Spectrophotometer at 458 nm.

The quantum yields of *S,C*-sulfonium ylide decay and sulfide growth were determined by photolysis at either 254 nm or 300 nm with a 75 W Xenon Arc lamp and monochromator. The reactions were carried out to low conversion (≤15%). Uncertainties are reported as the standard error of the quantum yield. The progress of the reactions was monitored by a Hewlett Packard 1050 HPLC System containing a diode array detector set to monitor at 265 nm, 300 nm and 320 nm. The reverse-phase separations were performed on an analytical Supelco C18 column.

For compounds **1-2**, the sulfonium ylide and sulfide were separated using an isocratic HPLC run in which the eluting solvents were water (30%), methanol (20%), and acetonitrile (50%). Each run time was 10 min with a flow rate of 1.0 mL/min. The quantum yields for compounds **3-4** were determined by HPLC; the eluting solvents were methanol and acetonitrile. In a typical run, the initial ratio of solvents was 70% methanol and 30% acetonitrile. After injection of the sample the solvent ratio was gradually changed to 50% methanol and 50% acetonitrile over a period of 10 min with a flow rate of 1.0 mL/min.

Cyclohexene trapping. In a typical trapping study, the concentration of sulfonium ylide was sufficiently high such that the absorbance of the sample at the wavelength of irradiation was above 2.0, which typically corresponded to 2-4 mM solutions. The sulfonium ylide was dissolved in 9 mL of acetonitrile, sonicated for 5 min to ensure complete dissolution, and filtered. To this solution, 1 mL of cyclohexene was added. The mixture was flushed with argon for 15 min prior to photolysis.

Methanol trapping. In a typical direct photolysis, the concentration of the sulfonium ylide was sufficiently high such that the absorbance of the sample at the wavelength of irradiation was above 2.0, which corresponded to 2-4 mM solutions. The sulfonium ylide was dissolved in methanol, sonicated for 5 min to ensure complete dissolution, filtered, and flushed with argon for 15 min prior to photolysis.

Benzophenone sensitized photolysis. In a typical sensitized photolysis, the concentration of sensitizer was sufficiently high (~100 mM) such that it absorbed at least 99.9% of the light at the wavelength of irradiation. The sensitizer and sulfonium ylide were dissolved in methanol, sonicated for 5 min to ensure complete dissolution, filtered, and flushed with argon for 15 min prior to photolysis.

All reactions were monitored by HPLC, ^{1}H NMR, and GCMS. In a typical GCMS run (EI, DB-5 column) the initial temperature (180 ºC) was held for 5 min. The temperature was then raised at a rate of 10 ºC/min until a final temperature of 280 ºC was reached, at which point the temperature was held for 5 min. The products were identified by comparison with data from authentic samples. All reported photolysis data represent experiments performed in at least triplicate or greater. The standard errors of the product yields are provided.

Computational methods. Computations were carried out using Spartan 1.0.4.e to calculate initial geometries, and GAMESS for all other calculations.[37] MacMolPlt 5.5, a graphical interface for GAMESS, was used to view all of the molecules and orbitals generated.[38] The geometries of compounds **2-3** were optimized at B3LYP/6-31G(d) and confirmed as minima by calculating the vibrational frequencies. The hessian of compound **4** showed imaginary frequencies corresponding to methyl rotations, which should have only a minor effect (~1.5 cm^{-1} or less) on the values of the carbonyl stretching frequencies. Initial coordinates for the five rotamers (two singlets and three triplets) of **5** were obtained from the literature.[21] With the exception of compounds **3-4** (whose size hindered calculations with the larger basis set), all molecules were reoptimized and confirmed as minima at B3LYP/6-311G(2df,p) to obtain more reliable IR stretching frequencies. The reported vibrational frequencies are scaled by the recommended 0.9614 for those obtained at B3LYP/6-31G(d) and 0.9679 for those obtained at B3LYP/6-311G(2df,p).[39,40]

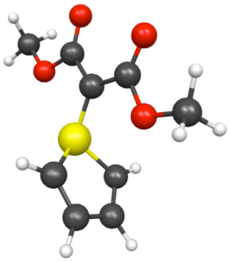
4.4 Results and discussion.

Ylide conformations. Dimethyl malonate ylides of thioanisole **(1)**, thiophene **(2)**, benzothiophene **(3)**, and dibenzothiophene **(4)** were prepared in high yields through either cupric sulfate or rhodium acetate catalyzed addition of dimethyl diazomalonate to the corresponding sulfides. All ylides prepared in this study were stable at room temperature and were purified by recrystallization prior to photolysis to ensure their purity.

At room temperature, the ^{13}C NMR of **4** shows two sets of broad signals in the carbonyl carbon region and near 51 ppm. The methyl signal in the ^{1}H NMR of **4** is also broad and split at room temperature. Upon raising the temperature, to 320K the two peaks begin to coalesce. We can conclude that two conformations of the dicarbonyl portion of the *S,C*-sulfonium ylide are in slow equilibrium with one another in solution.

A similar observation has been noted for dimethyldiazomalonate and diethyldiazomalonate, for which three relatively stable conformations are known, the *Z*,*Z*, *Z*,*E*, and *E*,*E* (notation indicates the relative arrangement of the diazo and carbonyl functionalities).[21] Of the three conformers of dimethyldiazomalonate, the *E*,*E* structure was predicted to be the least stable by less than 1 kcal/mol using the MP2(full)/aug-cc-pVTZ//B3LYP/6-311+G(3df,2p) method, while the *Z,E* conformation was predicted to be the lowest in energy.

Compounds **2-4** were optimized at B3LYP/6-31G(d) and compound **2** was subsequently reoptimized at B3LYP/6-311G(2df,p). The structures of all three compounds are shown below. Compounds **2** and **4** optimized with an *E,E* orientation, whereas compound **3** optimized with a *Z,E* geometry. The ^{1}H NMR signals for compounds **1-3** were not split at room temperature, indicating a more rapidly interconverting equilibrium for these compounds, compared to compound **4**.



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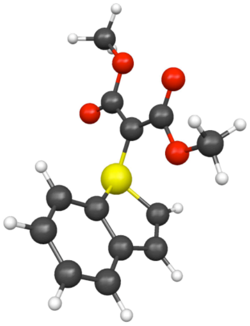

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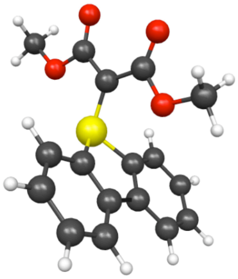

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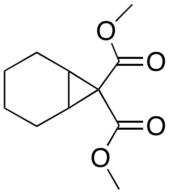
Product Studies. Chemical trapping studies were performed to determine whether **5** is generated upon photolysis of *S,C*-sulfonium ylides **1-4**. Two known carbene traps were used in this study, cyclohexene and methanol. Cyclohexene has previously been shown to react with dicarbomethoxycarbenoids to form the cyclopropanation product (**6**), the C-H insertion product (**7**), and tetramethoxycarbonylethylene (**8**), the product of carbene dimerization.[29,41] In these studies the dicarbomethoxycarbenoid was generated from either Cu(II) or $[Rh(OAc)_2]_2$ catalyzed reactions of dimethyl diazomalonate. The product ratios are highly dependent on the catalyst involved.[41-44] The photolysis of dimethyl diazomalonate in the presence of cyclohexene without a catalyst has been shown to generate only **6** and **7**.



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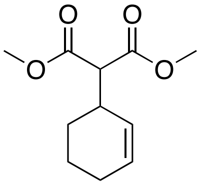

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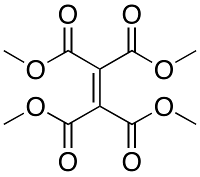

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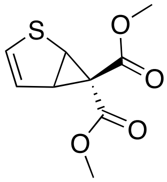

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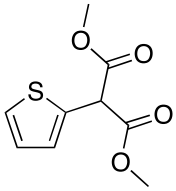


10

Compound **1** was photolyzed with 10% cyclohexene in acetonitrile at 254 nm. Analysis of the products revealed the formation of thioanisole, **6**, and **7** as photoproducts. Several other unidentified products were also observed upon photolysis of compound **1**. The quantum yields of yield decay (0.09) and sulfide growth (0.01) were measured at 254 nm using azoxybenzene as a chemical actinometer.

Compounds **2-4** were photolyzed to near completion with broad band irradiation centered at 300 nm in acetonitrile with 10% cyclohexene for product analysis. Proton NMR and GC-MS were used to monitor the reactions. Upon photolysis, thiophene, benzothiophene, and dibenzothiophene were formed from the corresponding ylides. Additional peaks, observed in the aliphatic region of the ^{1}H NMR, corresponded to trapped products, **6** and **7**, with cyclopropanation as the major product (Figure 1). Unlike the studies involving carbenoids, compounds **1-4** did not generate **8** upon direct photolysis in this or any other chemical studies. This was not unexpected since carbenoids have longer lifetimes in solution than free carbenes, thereby providing them sufficient time to encounter a second carbenoid intermediate with which to form a dimer.

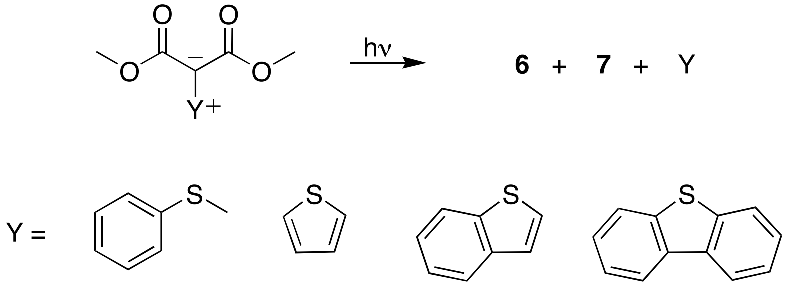


Figure 1. Photolysis of ylides **1-4** using 10% cyclohexene as a chemical trap in acetonitrile.

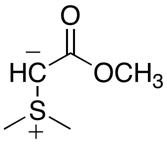
The quantum yields of ylide loss and sulfide gain were determined for compounds **2-4** in acetonitrile with 10% cyclohexene using valerophenone as a chemical actinometer (Table 1). In contrast to compound **1,** the quantum yields for compounds **2-4** reveal quantitative return of the sulfide upon ylide photodegradation and a higher quantum yield. The adducts were formed in good, but not quantitative yield. In addition to cyclopropanation and C-H insertion products, the formal insertion product **10** was observed in product mixtures from precursor **2**. We presume that **10** is formed by rearrangement of the cyclopropane **9**, but do not have any direct evidence on this point.

Table 1. Quantum yields for ylide decay and sulfide growth upon photolysis with 10% cyclohexene in acetonitrile.

Ylide	$\Phi_{\text{Ylide Decay}}$	$\Phi_{\text{Sulfide Growth}}$	**Product Yields (%)***		
			6	**7**	**6/7**
2	0.25 ± 0.02	0.25 ± 0.01	21.7	4.3	5.0 ± 0.83
3	0.20 ± 0.01	0.20 ± 0.01	40.6	8.0	5.1 ± 0.83
4	0.17 ± 0.01	0.17± 0.01	44.1	9.2	4.8 ± 0.09

* Product yields were determined by ^{1}H NMR integration following near complete conversion of the starting material and are reported as a percentage relative to the corresponding sulfide. Quantum yields were determined at low conversions (≤ 15%).

The differences in quantum yields correlate inversely with the bond dissociation energies (BDEs) of the *S,C*-sulfonium ylides. Compounds **2-4** should have lower BDEs than **1**, since the products generated from dissociation provide an increase in aromaticity. In Chapter 6, we report the BDEs of related *S,C*-sulfonium ylides estimated with an empirical method using MP2/6-311++G(3df,2p); in particular we investigated compounds **11-13**. The calculations indicate a 23 kcal/mol advantage to dissociation of **12** relative to **11**. The difference in the BDE of **13** relative to **11** is less dramatic, only 7 kcal/mol, and can be attributed to the smaller gain in aromaticity upon formation of dibenzothiophene than is expected for the formation of thiophene. *S,C*-sulfonium ylides are often prepared with electron withdrawing groups attached to the carbene carbon to stabilize the ylide formal charges.[26,45,46] Addition of a second carbomethoxy group to the ylide carbon atom raises the BDE even more (23 kcal/mol) relative to the related $C\mathrm{H}_2$-sulfonium ylide compared to substitution with a single carbomethoxy group as in compound **11** (16 kcal/mol).[47]



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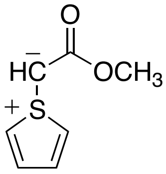

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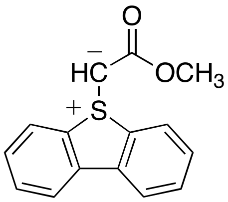


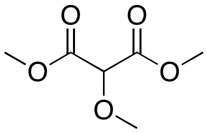
13

Carbenes are well known to accept a lone pair of electrons from the sulfur atom of sulfides to form *S,C*-sulfonium ylides.[25,48-50] In particular, competition studies with **5** generated from the corresponding diazo precursor in the presence of a 1:1 molar ratio of cyclohexene and alkyl or aryl sulfide yielded four times more of the *S,C*-sulfonium ylide product than the product of cyclopropanation.[48,50] Increasing the molar ratio of cyclohexene to sulfide lowered the yield of *S,C*-sulfonium ylide product relative to the product of cyclopropanation.[48] Thus, we might expect a significant portion of the reactive intermediates formed upon photolysis of **1-4**, to react with the sulfide, reforming the starting material**.** As the photolysis proceeds, the growing concentration of sulfide in solution might therefore result in an increase in "non-productive" reactions. Chemical trapping studies in which **4** was photolyzed in the presence of a 1:1 molar ratio of thiophene were monitored for the formation of ylide **2**. Although **2** was not observed by ^{1}H NMR in the experiment, we can not rule out the possibility that **2** is formed in undetectably low concentrations under these conditions, since it too would be subject to ylide bond scission under photolytic conditions. A gradual decline in the rates of ylide loss and sulfide gain, following an initial period of linear decay is observed in the direct photolysis of all ylides (See Supporting Information). The leveling off of the rates as the reaction proceeds could be a result of either an increasing number of "non-productive reactions" reforming the ylide or simply a filtering effect from product absorption of the light.

While the trapped products of photolysis in cyclohexene can not be used to distinguish the multiplicity of an intermediate carbene, it is interesting to note that the ratios of cyclopropanation to C-H insertion appear to be the same for each precursors, which suggests that a common photochemical intermediate is formed in each reaction.

In addition to the relatively low quantum yield of S-C bond cleavage exhibited by **1**, the ylide also suffers from complex reactivity leading to several undesired side products, likely resulting from the required use of a shorter wavelength light source (i.e. higher energy). For this reason, in all subsequent trapping studies we focused our attention on compounds **2-4**. These ylides have the advantage of providing a more convenient chromophore (i.e. lower energy), which, in the long run, will provide more versatility in the types of carbene precursors that can be prepared.

Alcohols are often used as carbene traps because of their ability to provide information regarding the multiplicity of the intermediate carbene. Singlet carbenes tend to undergo O-H insertion reactions, while triplet carbenes abstract hydrogens. The direct photolysis of diethyl diazomalonate has been reported to generate dicarboethoxycarbene, whose reactivity was characterized in methanol.[22] Upon direct photolysis, the reported predominant product was the singlet derived O-H insertion product **(14)**, with trace amounts of the triplet H-abstraction product **(15)** also present. The authors of this work attribute the presence of the triplet product to intersystem crossing from ^{1}dicarboethoxycarbene to ^{3}dicarboethoxycarbene. However, upon benzophenone sensitized photolysis, only the triplet carbene trapped product was observed.



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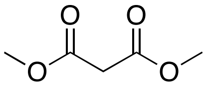

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Compounds **2-4** have been photolyzed in the presence of methanol in order to investigate the multiplicity of the intermediates being generated. HPLC, GCMS, and ^{1}H NMR results indicate the formation of the corresponding sulfide and **(14)**, the singlet carbene O-H insertion product, as the major products of direct photolysis in methanol at 300 nm (Figure 2). The quantum yields of ylide decay and sulfide growth have been determined using valerophenone as a chemical actinometer (Table 2).

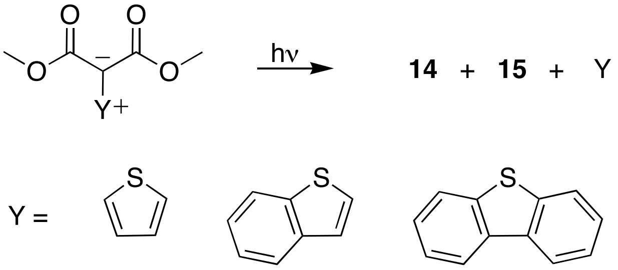


Figure 2. Photolysis of ylides using methanol as a chemical trap.

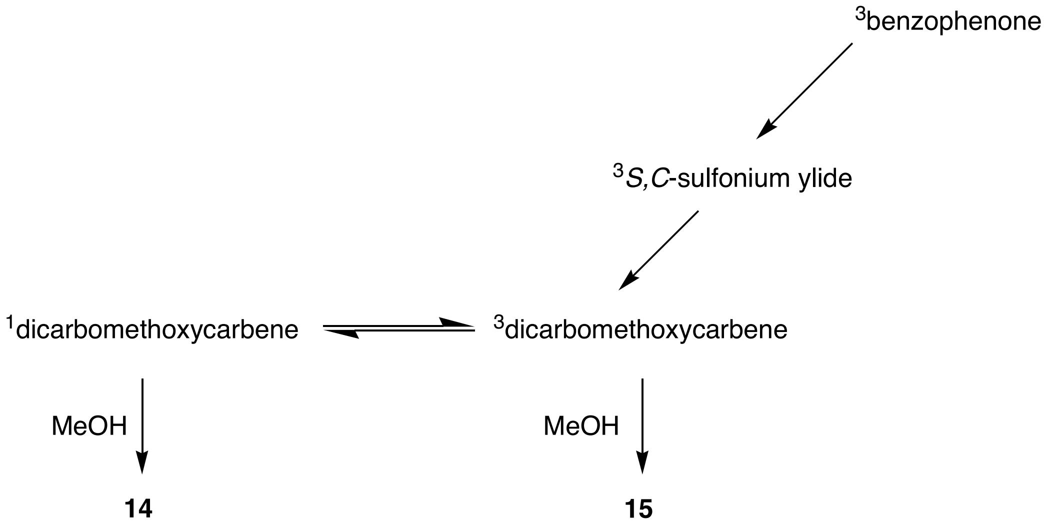
Table 2. Quantum yields for ylide loss and sulfide gain upon direct photolysis of compounds **2-4** in methanol and product yields of direct and benzophenone-sensitized photolysis.

Ylide	$\Phi_{\text{Ylide Loss}}$	$\Phi_{\text{Sulfide Gain}}$	**Product Yields (%)***			
			Direct photolysis		**Sensitized photolysis**	
			14	**15**	**14**	**15**
2	0.21 ± 0.02	0.20 ± 0.02	97.2	trace	-	-
3	0.12 ± 0.01	0.12 ± 0.01	96.6	trace	7	65
4	0.18 ± 0.01	0.19 ± 0.01	87.0	trace	9	57

* Product yields were determined by ^{1}H NMR integration following low conversion of the starting material to avoid secondary photolysis and are reported as a percentage relative to the corresponding sulfide.

Upon sensitized photolysis of compounds **2-4** with benzophenone, the ratio of trapped products changes. Dimethylmalonate **(15)**, the expected product of triplet carbene reactivity becomes the major product, while **14** is now the minor product (Table 2). Although we were unable to determine the yields of **14** and **15** relative to thiophene for compound **2** due to spectral overlap, we did observe a higher yield of **15** than **14**. The appearance of dimethyl dimethoxymalonate upon triplet sensitized photolysis is likely a result of relatively slow intersystem crossing from the triplet carbene to the singlet carbene, followed by a rapid O-H insertion reaction. The rate constant for the reaction of singlet **5** with methanol has been estimated to be 1.5 × 10^9.[21] The greater yield of **14** upon sensitized photolysis, than **15** upon direct photolysis can be rationalized by the relative rates of carbene reactivity. Singlet carbenes tend to react more rapidly than triplets. Thus, upon direct photolysis in methanol the majority of ^{1}**5** is likely trapped before it can undergo intersystem crossing (Scheme 1). However, upon triplet sensitized photolysis the double hydrogen abstraction reaction, typical of ^{3}**5**, is presumably on a more equivalent time scale with intersystem crossing to the singlet carbene which results in a higher yield of singlet trapped product.

Scheme 1.



In general, α-diazocarbonyl compounds have been shown to decompose either by ketene formation (i.e. Wolff rearrangement) or by carbene formation, where cyclic precursors yield high or quantitative Wolff rearrangement, while acyclic precursors tend to show little or no Wolff rearrangement.[21] Platz and coworkers, however, believe that on photolysis of dimethyl diazomalonate, both carbene formation and Wolff rearrangement occur in the presence of methanol.[17] While they are not certain, they imply that the rearrangement occurs out of the carbene rather than an excited state of the diazo precursor. At present our results do not allow us to rule out Wolff rearrangement, however, further studies are currently underway to investigate this issue.

The results of the trapping studies provide indirect evidence that *S,C*-sulfonium ylides **1-4** are photochemical precursors to carbenes. In order to unambiguously identify the reactive intermediate(s) responsible for the formation of the trapped products, the IR vibrational frequencies of **5** and the ylides were estimated at B3LYP/6-31G(d) and B3LYP/6-311G(2df,p). We report the carbonyl stretching frequencies of the ylides and compare them to those of the five confirmations of **5** that were reported in the literature (Table 3). The appropriate scaling factor for each basis set was included (shown in parentheses). The size of compounds **3** and **4** prevented reoptimization and calculation of the IR frequencies with the larger basis set, however since inclusion of the scaling factor results in convergence of the values from one basis set to the other, we can estimate that CO stretching frequencies obtained at B3LYP/6-311G(2df,p) for **3** and **4** would fall in line with the scaled values obtained at B3LYP/6-31G(d). Our calculations show a separation of nearly 80 cm^{-1} between the longest carbonyl stretching frequency of the carbene and that of ylide **1** with the larger basis set. This gap should be reasonably similar for **4,** which shows a difference of only 7 kcal/mol from the CO stretching frequency of **1** with the smaller basis set. Though the IR frequencies of compound **3** are predicted to be approximately 37 cm^{-1} lower than those for compounds **2** and **4**, there is still a gap of nearly 45 cm^{-1} between it and the carbene. The shift to lower frequencies of **3** relative to **2** and **4** is perhaps due to the difference in conformation (i.e. *Z,E* versus *E,E*). Therefore, our results suggest that a time-resolved IR experiment should be a viable method for distinguishing the reactive intermediate(s) generated in the reported photolyses from the ylide starting materials.

Table 3. Calculated IR frequencies of the carbonyl stretching modes of **5** and ylides **2-4** at B3LYP with the stated basis set. Scaled frequencies are provided in parentheses, using a scaling factor of 0.9614 for the calculations performed at 6-31G(d) and 0.9679 for those performed at 6-311G(2df,p).

Compound	**IR Frequencies (cm^{-1})**	
	6-31G(d)	**6-311G(2df,p)**
^{1}**5 (E)**	1693, 1699 (1628, 1633)	1675, 1680 (1621, 1626)
^{1}**5 (Z)**	1683, 1736 (1618, 1669)	1669, 1723 (1615, 1668)
^{3}**5 (E,E)**	1732, 1752 (1665, 1684)	1711, 1731 (1656, 1675)
^{3}**5 (Z,E)**	1730, 1740 (1663, 1673)	1709, 1721 (1654, 1666)
^{3}**5 (Z,Z)**	1725, 1746 (1658, 1679)	1706, 1726 (1651, 1671)
2	1770, 1830 (1702, 1759)	1748, 1811 (1692, 1753)
3	1739, 1790 (1672, 1721)	-
4	1763, 1823 (1695, 1753)	-

Although this study does not provide direct evidence for the formation of carbenes from the S,C-sulfonium ylides, the chemical trapping studies and precedent for unimolecular ylide bond cleavage set by both sulfoxides and sulfilimines strongly suggests carbene formation in this case. Further studies will be required to verify the identity of the reactive intermediate(s).

4.5 Conclusions.

Compounds **1-4** have been prepared and are sufficiently stable for the study of their reactivity. Photochemical studies of the ylides in cyclohexene and acetonitrile have shown the generation of the corresponding sulfide, along with cyclopropanation and C-H insertion. Dimerization of the carbene was not observed. Trapping studies in methanol indicate that similar chemistry is occurring, in that sulfide generation and carbene-like trapped products are observed. Dimethyl dimethoxymalonate **(14)**, the O-H insertion product, was observed upon direct photolysis. These results imply that singlet dicarbomethoxycarbene **(5)** is the predominant spin state generated upon direct irradiation of the ylides. Triplet sensitization of the *S,C*-sulfonium ylides with benzophenone showed dimethylmalonate **(15)** production, which is characteristic of triplet carbene reactivity (i.e. double hydrogen-abstraction). Further studies are underway aimed at the direct detection of the intermediate(s) of these reactions and the extension of the series of *S,C*-sulfonium ylides.

4.6 Acknowledgement. We thank the National Science Foundation (Grant CHE-0211371) for support of this research.

4.7 Supporting information description. Spectra of all compounds prepared for this study and those used to identify trapped products are provided in the supporting information. Coordinates of carbenes and ylides are also provided.

4.8 References

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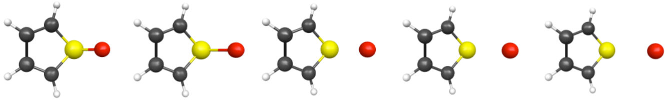
CHAPTER 5

Correlation of thiophene-*S*-oxide and selenophene-*Se*-oxide excited states with deoxygenation products.

In the style of a paper submitted to the *Journal of the American Chemical Society.*

Stacey A. Stoffregen, Pearl Dickerson, and William S. Jenks
Department of Chemistry, Iowa State University, Ames, Iowa, 50011-3111.

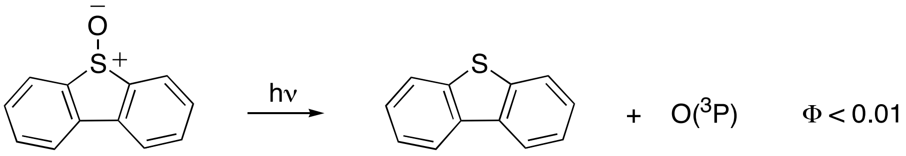


5.1 Abstract.

Dibenzothiophene-*S*-oxide (DBTO) and dibenzoselenophene-*Se*-oxide (DBSeO) undergo deoxygenation upon photolysis to form O(^{3}P) and dibenzothiophene or dibenzoselenophene respectively. In this study the potential energy surfaces (PES) of thiophene-*S*-oxide and selenophene-*Se*-oxide were generated as a function of S-O and Se-O bond length using the CASSCF [18,14] method and include energy corrections with second-order perturbation theory (MRMP2). The results for thiophene-*S*-oxide using MRMP2/G3Large*//CASSCF/6-31G(d) and selenophene-*Se*-oxide using MRMP2/6-31G(d)//CASSCF/6-31G(d) indicate that the second triplet excited states of each provide nearly barrierless routes toward S-O and Se-O bond dissociation. Vertical excitation energies were also determined for DBTO at a lower level of theory and indicate a similar system of excited states. The potential energy diagrams generated in this study offer a new explanation for the experimentally observed unimolecular bond cleavage of DBTO and DBSeO. Upon photoexcitation of the sulfoxide/selenoxide to the singlet excited state, intersystem crossing to the T_1 or T_2 state is possible. Elongation of the S-O bond in the T_2 state results in formation of the corresponding sulfide/selenide and O(^{3}P). However, a small barrier must be overcome in order for elongation of the T_1 state to yield products of deoxygenation.

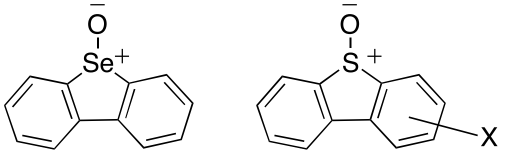
5.2 Introduction.

Since the early 1960s the photochemistry of sulfoxides has been under investigation. Numerous studies have revealed that sulfoxides follow three major unimolecular reaction pathways: homolytic α-cleavage, stereomutation, and deoxygenation.[1-16] Deoxygenation was first observed in 1972 for dialkyl, alkyl aryl, and diaryl sulfoxides. More recent studies have shown that dibenzothiophene-*S*-oxide (DBTO) also undergoes photochemical deoxygenation, albeit, with low quantum efficiency.[17] The products of DBTO deoxygenation include dibenzothiophene and an electrophilic species, believed to be $O(^3P)$. Chemical trapping studies with DBTO in various solvents have indirectly indicated the formation of $O(^3P)$, as the reactive intermediate of photochemical deoxygenation.[18-20 10, 16]

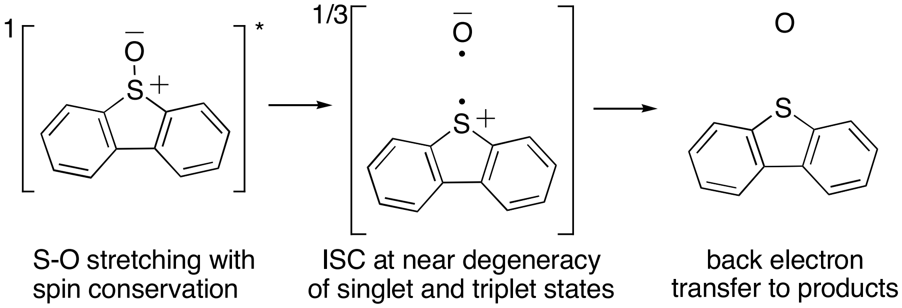


Several mechanisms have been proposed for photochemical deoxygenation of sulfoxides, but nearly all can be discarded on the basis of more recent experiments. In one of the proposed mechanisms, a photoexcited triplet sulfoxide was suggested to form a dimer with a ground state sulfoxide and subsequently break down into two sulfides and molecular oxygen.[9, 14, 21] This mechanism has since been ruled out for DBTO, following a study showing that deoxygenation persisted upon photolysis of DBTO that had been isolated in an organic glass matrix to prevent bimolecular reactions.[17] In a second experiment, DBTO was photolyzed in the presence of an excess of diphenylsulfoxide. Diphenyl sulfide was not formed upon photolysis, providing further evidence that the dimer mechanism is not occurring upon DBTO deoxygenation.[17] In a second proposed mechanism, deoxygenation was suggested to occur by the reduction of a photogenerated sulfinyl radical.[22, 23] This mechanism has also been rejected because the reduction has been estimated to be energetically unfavorable.[17] Another proposed mechanism involves hydrogen abstraction (typical of carbonyl photochemistry), followed by homolytic cleavage.[24] This too is unlikely, since deoxygenation is not dependent on the hydrogen donating ability of the solvent and there is no other evidence suggesting that hydrogen abstraction is a common photochemical process for sulfoxides.[3, 7, 8]

Fluorescence and phosphorescence studies have placed the first singlet excited state (S_1) at 82 kcal/mol and the triplet state (T_1) at 61 kcal/mol above the ground state ($^1A'$) of DBTO.[25, 26] In Chapter 6, the bond dissociation energy of DBTO was estimated to be nearly 73 kcal/mol, 11 kcal/mol higher in energy than the T_1 state.[26, 27] Thus the energetics of the system suggest that there is insufficient energy in the spectroscopic triplet state to promote efficent S-O bond scission.[27] The introduction of a heavy atom into the system, (i.e. the exchange of selenium for sulfur or the addition of bromine substituents on the dibenzothiophene ring), results in higher quantum yields of deoxygenation than seen for unmodified DBTO.[18, 19] These results led us to propose a new mechanism for unimolecular photodeoxygenation in which an S-O bond stretch from the first excited singlet state is coupled to intersystem crossing to yield DBT and $O(^3P)$ (Scheme 1).[18] This could occur either by direct spin-surface crossing along the S-O elongation pathway or by a mechanism whose logical extreme limit would be formation of an ion-pair ($DBT^{\cdot+}$ and O^-) followed by back-electron transfer. The proposed route is consistent with the enhanced quantum efficiency of DBSeO, in that heavy atom substitution increases the probability of intersystem crossing and selenium has a lower ionization potential than sulfur.



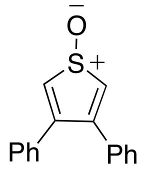
X = 4-iodo
4-bromo
4-chloro
2-bromo
2,8-dibromo
2,8-dichloro



Scheme 1. A limiting mechanism of S-O bond stretching, followed by back electron transfer.

While substituted thiophene-*S*-oxides are sufficiently stable to be studied experimentally, thiophene-*S*-oxide itself is extremely susceptible to overoxidation to thiophene-*S,S*-dioxide and dimerization via Diels Alder reactions, making it an unsuitable substrate for experimental studies.[21, 28, 29] However, thiophene-*S*-oxide and its selenium-containing analog, selenophene-*Se*-oxide are sufficiently small and can be studied computationally. The oxidation of thiophene results in a loss of aromatic stabilization. Due to the significant gain in resonance stabilization upon deoxygenation, thiophene sulfoxides should have even weaker S-O bonds than dibenzothiophene-*S*-oxide. The BDEs of various sulfoxides are reported in Chapter 6.[27] The best estimate places the BDE of thiophene-*S*-oxide 7 kcal/mol lower than benzothiophene-*S*-oxide and almost 12 kcal/mol lower than DBTO.

The photochemistry of the substituted thiophene-*S*-oxides, shown below, is currently under investigation. Compound **4** has been shown to undergo deoxygenation yielding the corresponding sulfide, while compounds **1-3** follow an alternate pathway, forming the corresponding furan upon photolysis.[30]



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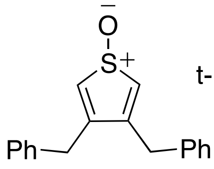

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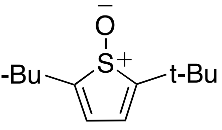

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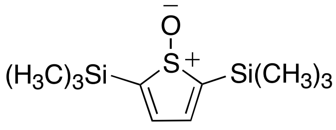


4

In this study we have determined the state energies of thiophene-*S*-oxide and selenophene-*Se*-oxide as a function of S-O and Se-O bond length. Stretching the sulfoxide or selenoxide bond mimics the photochemical deoxygenation that is observed in experimental studies of similar systems, namely DBTO and DBSeO. The presumed products of the deoxygenation of thiophene-*S*-oxide are thiophene and O(^{3}P) and of selenophene-*Se*-oxide are selenophene and O(^{3}P). These calculations allow correlation of the electronic excited states with the products of deoxygenation. We have also calculated the vertical excitation energies from the optimized ground state of DBTO to identify the excited state(s) from which S-O bond cleavage can occur.

5.3 Computational Details.

Computations were carried out using Spartan 1.0.4.e to calculate initial geometries, and GAMESS for all other calculations.[31] MacMolPlt 5.5, a graphical interface for GAMESS, was used to view all of the molecules and orbitals generated.[32] RHF and ROHF methods were used to generate orbitals for the singlet states and triplet states respectively of thiophene-*S*-oxide and selenophene-*Se*-oxide with Cs symmetry. The coordinates and orbitals obtained from the HF methods were used as initial coordinates and orbitals for the active space of the complete active space self-consistent field (CASSCF) calculations. The active space, which had 18 electrons in 14 orbitals, included the orbitals of the three lone pairs of electrons on oxygen, one lone pair of electrons on sulfur, the S-O σ and σ* orbitals, the C-S σ and σ* orbitals, and the C-C π and π* orbitals (Figure 1). Geometries of the sulfoxides and selenoxides were confirmed as minima by calculating the vibrational frequencies.

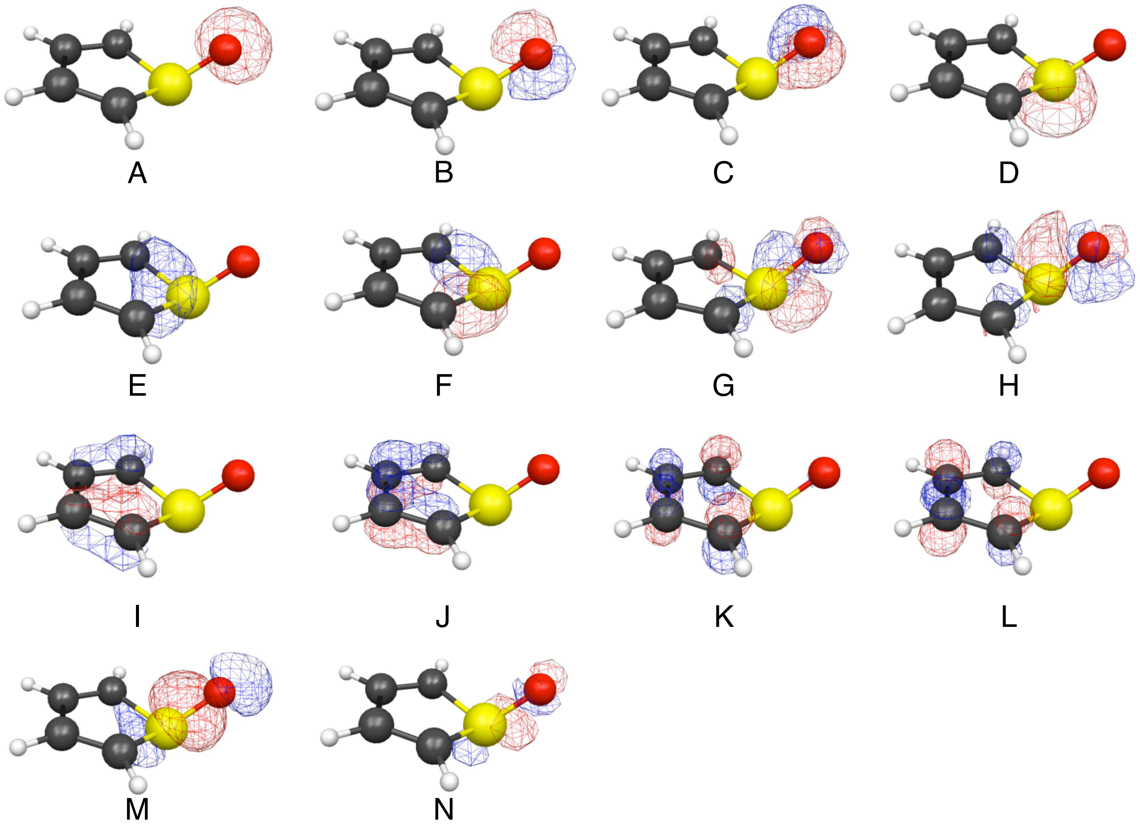


Figure 1. Initial orbitals included in the active space in all CASSCF calculations of thiophene-*S*-oxide (shown) and selenophene-*Se*-oxide, where A-C are the lone pairs on O, D is the lone pair on S, E-H are the C-S σ and σ* orbitals, I-L are the C-C π and π* orbitals, and M-N are the S-O σ and σ* orbitals.

Energy corrections were obtained from single point energy calculations performed at MRMP2/6-31G(d)//CASSCF/6-31G(d), a multi-reference second-order perturbation theory used to recover the electron correlation outside of the active space. The G3Large basis set was chosen for sulfur, selenium, and oxygen.[33, 34] Previous studies in our group have examined various sulfur and selenium ylide bond strengths computationally.[26, 27] In those and other studies it was found that the use of tight d-polarizations on the heavy atoms was crucial for accurate prediction of the BDE of sulfur and selenium ylides.[35, 36] In Chapter 6 we demostrate that without tight d-polarization functions BDEs were underestimated by as much as 20 kcal/mol; hence our choice of the G3Large basis set for this study. We chose to use the 6-31G(d) basis set on all carbon and hydrogen atoms and the G3Large basis set on sulfur, selenium, and oxygen. This combination of basis sets on different atoms within the molecule will be henceforth designated as G3Large*. Coefficients and exponents for the G3Large basis set for selenium, sulfur, and oxygen were obtained from http://chemistry.anl.gov/compmat/g3theory.htm. The absolute energies obtained from CASSCF/G3Large*//CASSCF/6-31G(d) and sample CASSCF/G3Large* calculations were found to be sufficiently close to one another (Figure S1), that all subsequent calculations were single point energy runs with the G3Large* basis set using the optimized coordinates from the CASSCF/6-31G(d) calculations. The single point energy calculations were thus performed at CASSCF/G3Large*//CASSCF/6-31G(d) and MRMP2/G3Large*//CASSCF/6-31G(d). All energies reported in this study are the total electronic energy and do not include entropy, the zero-point energy, or temperature corrections.

The potential energy surfaces of sulfoxide and selenoxide deoxygenation were generated by performing optimizations in which the S-O or Se-O bond length was constrained but all other coordinates were optimized. The constrained optimizations were performed independently for each state located in the potential energy surface. The minimum energy crossing point between the two lowest triplet states of thiophene-*S*-oxide is currently being located. The coordinates from CASSCF/6-31G(d) constrained optimizations are provided in the supporting information.

Additionally, DBTO was optimized at CASSCF/6-31G(d) and single point energies were obtained for the first four electronic states at CASSCF/6-31G(d) and MRMP2/6-31G(d)//CASSCF/6-31G(d) using the same active space that was used for thiophene-*S*-oxide and selenophene-*Se*-oxide.

5.4 Results and Discussion.

Thiophene-*S*-oxide. In this study the ground electronic state of thiophene-*S*-oxide was optimized at CASSCF/6-31G(d) with Cs symmetry. A series of constrained optimizations, in which the S-O bond length was varied, were then performed on each of the first four electronic states (S_0, T_1, T_2, and S_1) to generate the potential energy surface of thiophene-*S*-oxide deoxygenation. The symmetries of the states were S_0 = A', T_1 = A", T_2 = A', and S_1 = A".

The optimized ground state of thiophene-*S*-oxide (Figure 2) has an S-O bond length of 1.51 Å, with a geometry in which the sulfur and oxygen atoms lie below and above the plane of the ring respectively. The "dip" of the sulfur below the plane of the ring is well established.[26, 37] The bond lengths and angles of the ^{1}A' state are provide in Table 1. These values compare can be compared to the bond lengths and angles obtained from the X-ray crystallography of 2,5-diphenylthiophene-*S*-oxide which are provided in parentheses in Table 1.[37] As expected, the bond lengths are slightly overestimated. The natural orbital occupation numbers for the active space are 1.998, 1.998, 1.997, 1.995, 1.974, 1.968, 1.967, 1.933, 1.892, 0.114, 0.066, 0.036, 0.033, and 0.028. For the optimized ground state structure, the three highest occupied molecular orbitals, (HOMOs), according to the preliminary Hartree-Fock calculations, are the a" lone pair of electrons on oxygen (HOMO-2), and the π orbitals of the ring system with a' (HOMO-1) and a" (HOMO) symmetry. The two lowest unoccupied molecular orbitals (LUMOs) are the π* orbitals in the ring system with a' (LUMO) and a" (LUMO+1) symmetry.

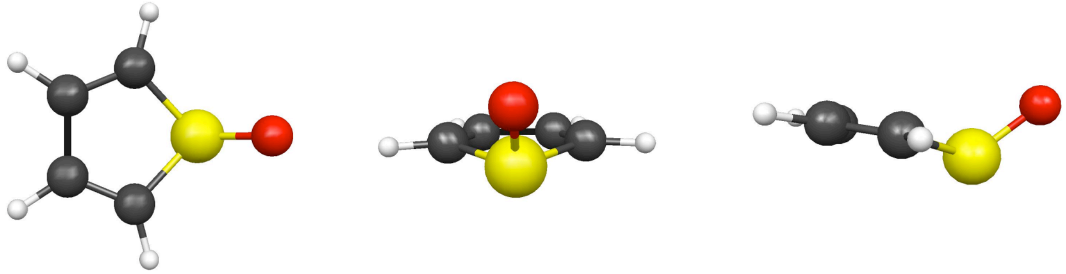
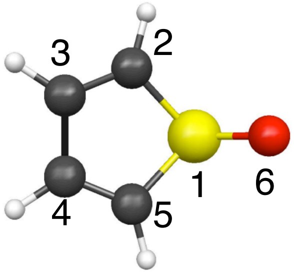


Figure 2. Optimized structure of the ^{1}A' state of thiophene-*S*-oxide.

Table 1. Bond lengths and angles of the ^{1}A' state of thiophene-*S*-oxide.



Atoms	Bond Length (Å)	Atoms	Angle (º)
S1-O6	1.510 (1.484)	O6-S1-C2	113.9 (112.6)
S1-C2	1.787 (1.781)	S1-C2-C3	112.1 (108.9)
C2-C3	1.345 (1.345)	C2-C3-C4	112.8 (114.5)
C3-C4	1.471 (1.433)	C2-S1-C5	89.3 (91.3)

Using the ground state geometry as a starting point, the two triplet states (^{3}A" and ^{3}A') were optimized. The ^{3}A" optimized structure has a similar geometry to the ^{1}A' state. The NOONs for the active space are 1.999, 1.998, 1.997, 1.997, 1.974, 1.969, 1.965, 1.910, 1.024, 0.980, 0.090, 0.035, 0.033, and 0.028, of which, the singly occupied molecular orbitals (SOMOs) are the π orbitals of the ring system with a" symmetry and the π* orbitals with a' symmetry, making this a simple ππ* state. The bond lengths and angles for the ^{3}A" state are provided in Table 2, which uses the same numbering system as Table 1. The most notable differences from the ^{1}A' geometry are the position of the sulfur atom, which is tipped slightly above the plane of the ring in this structure, and the alternation of the C-C bond lengths in the ring.

Table 2. Bond lengths and angles of the $^3A''$ state of thiophene-*S*-oxide.

Atoms	Bond Length (Å)	Atoms	Angle (º)
S1-O6	1.513	O6-S1-C2	110.9
S1-C2	1.782	S1-C2-C3	113.7
C2-C3	1.452	C2-C3-C4	112.2
C3-C4	1.363	C2-S1-C5	87.3

The $^3A'$ state of thiophene-*S*-oxide yielded the dissociated products, thiophene and O(^3P) (Figure 3). The NOONs for the active space were 1.999, 1.998, 1.996, 1.984, 1.973, 1.968, 1.948, 1.909, 1.000, 1.000, 0.100, 0.060, 0.037, and 0.0290, of which the SOMOs were the a' and a" lone pairs on oxygen. The bond lengths and angles of the $^3A'$ state at an S-O separation of 4.0 Å, thiophene and O(^3P), are provided in Table 3 which uses the same numbering system as Table 1. These values compare well with the experimentally determined bond lengths and angles of thiophene (shown in parentheses).[38] As expected the sulfur atom of thiophene-*S*-oxide moved back into the plane of the ring as the molecule regained aromaticity upon deoxygenation. At an S-O distance of 2.1 Å, the position of the oxygen atom shifts dramatically. For distances less than this (and all distances in the other states), the position of the oxygen atom is approximately as if the original S-O bond had been stretched. At distances of 2.1 Å and longer in the $^3A'$ state, the oxygen atom projects straight out from the thiophene sulfur, such that all four carbon atoms, the sulfur atom, and the oxygen atom all lay in the same plane with C_{2v} symmetry. We assume, since there is no particular discontinuity in the energies that there is a very loose potential for the position of the sulfur atom at distances in this range. We did not intentionally measure the energy difference between the optimized geometries in other states and in analogous C_{2v} structures.

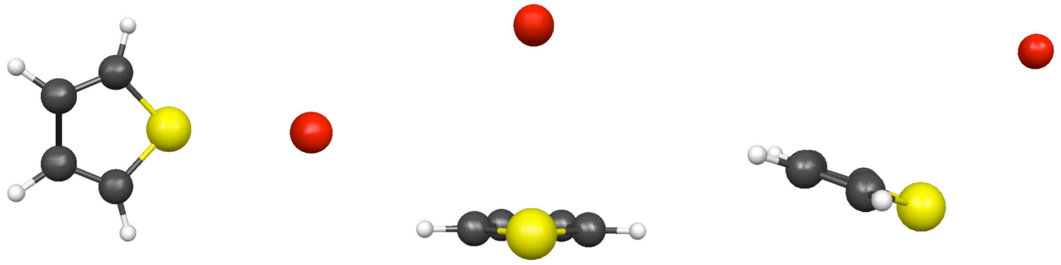


Figure 3. Structure of the $^3A'$ state of thiophene-*S*-oxide with 4.00Å S-O bond length.

Table 3. Bond lengths and angles of the $^3A'$ state of thiophene-*S*-oxide. The values in parentheses are the experimentally determined bond lengths and angles for thiophene.

Atoms	Bond Length (Å)	Atoms	Angle (°)
S1-O6	4.0	O6-S1-C2	102.6
S1-C2	1.763 (1.7140)	S1-C2-C3	111.7 (111.47)
C2-C3	1.362 (1.3696)	C2-C3-C4	113.1 (112.45)
C3-C4	1.433 (1.4322)	C2-S1-C5	90.4 (92.17)

A fully optimized structure of the $^1A''$ state also could not be obtained because the surface is dissociative with respect to S-O cleavage. A constrained optimization at the S-O bond length of the optimized ground state (i.e. 1.510 Å) was used to locate the $^1A''$ state. This state is similar in structure to the $^3A''$ state, in that it also adopts a geometry in which the sulfur and oxygen atoms are on the same side of the carbon plane. The bond lengths and angles are supplied in Table 4. The NOONs for the active space are 1.998, 1.995, 1.988, 1.981, 1.974, 1.967, 1.942, 1.967, 1.942, 1.921, 1.041, 1.038, 0.053, 0.042, 0.033, and 0.026, of which the SOMOs include the a'' lone pair on oxygen and the a' π* orbitals of the ring system. This, then, may be referred to as an $n_o\pi^*$ state.

Table 4. Bond lengths and angles of the $^{1}A''$ state of thiophene-*S*-oxide.

Atoms	Bond Length (Å)	Atoms	Angle (º)
S1-O6	1.510	O6-S1-C2	106.4
S1-C2	1.758	S1-C2-C3	111.3
C2-C3	1.395	C2-C3-C4	113.3
C3-C4	1.396	C2-S1-C5	90.6

The data obtained from the constrained optimizations allows us to test the mechanistic hypothesis put forward in Scheme 1, i.e., that charge separation along the stretching S-O coordinate would lead to intersystem crossing due to a decreased singlet-triplet gap. Mulliken charges obtained at a modest basis set, such as 6-31G(d), can be used as a qualitative guide to determine if charge separation has a maximum along any of the electronic surfaces through the bond stretching process. A plot of the Mulliken charges of the various states as a function of S-O bond length reveals a relatively smooth decrease in the magnitude of both the positive charge on the sulfur and the negative charge on the oxygen as the S-O bond elongates (Figure 4). The data in Figure 4 clearly indicate that none of the three excited states shows a distinct maximum of charge separation at any distance beyond the equilibrium S-O bond distance of 1.51 Å, thus substantially questioning the hypothesis in Scheme 1. It might be reasonably argued that these gas phase calculations substantially inhibit charger separation because of its energetic cost. However, it is also the case that, experimentally, there is little if any effect of solvent polarity on the efficiency of the photochemical reaction, as might be expected if charge separation were important. We thus tentatively conclude that charge separation is not the mechanism that drives intersystem crossing and look for another explanation.

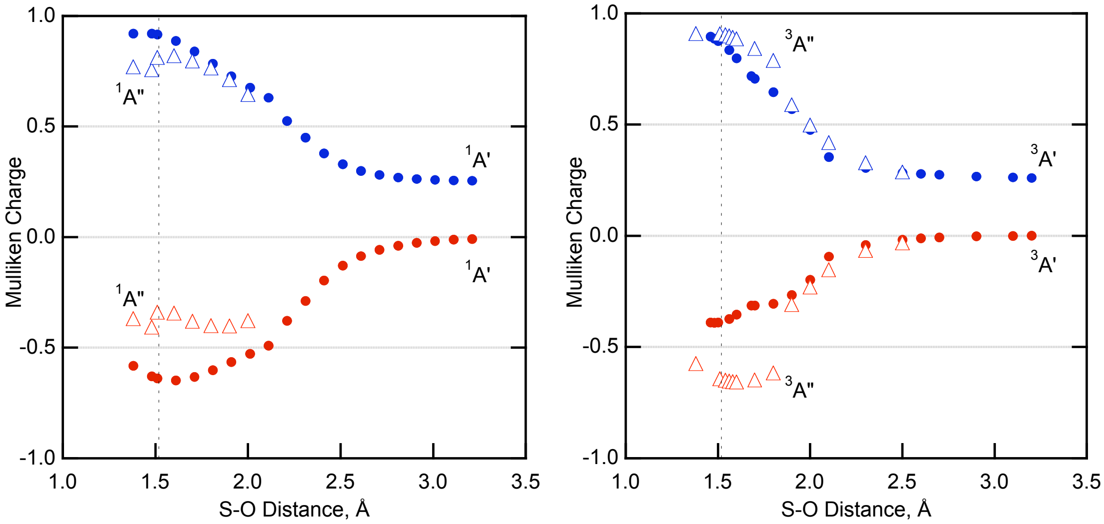


Figure 4. Mulliken charges on sulfur (blue) and oxygen (red) of thiophene-*S*-oxide as a function of S-O distance. Filled circles are for A' states and open triangles are for A" states. (a) Singlet states. (b) Triplet states. The dotted line at 1.51 Å reflects the equilibrium S-O bond distance in the ground state.

A preliminary potential energy surface map of thiophene-*S*-oxide deoxygenation, including the ^{1}A', ^{3}A", and ^{3}A' states, was created from optimized HF/6-31G(d) structures and energies (Figure S2) and was then reoptimized with CASSCF/6-31G(d) at which point the ^{1}A" state was also located (Figure 5a). Further energy refinements were obtained at the CASSCF/6-31G(d) geometry: MRMP2/6-31G(d) (Figure 5b), and CASSCF/G3Large* (Figure 5c). A limited number of energy runs using MRMP2/G3Large*//CASSCF/6-31G(d) were also performed for regions of particular interest in the potential energy surface. These points are also shown in Figure 5c. The ground state ^{1}A' state of the sulfoxide smoothly correlates to separated thiophene plus O(^{1}D) – some 84 kcal/mol uphill – at distances that approach 3 Å. The natural orbital occupation numbers in the optimized active space are all very near 2 or 0 until the oxygen atom begins to achieve substantial separation from the thiophene at ca. 2.5 Å. At the infinite separation limit, each oxygen lone pair (p orbital) would have a 1.33 occupation, and the data begin to trend in this direction as the separation gets longer. The remaining orbitals at longer distances correspond to expectations for thiophene, and have occupancies near 2 or 0.

The dihedral angle, defined by three carbon atoms of the thiophene ring and the sulfur atom (S1,C2,C3,C4), can be used as a measure the degree with which the sulfur atom lies below the plane of the ring at a given point on the potential energy surface (Figure S3). At the optimized ground state for thiophene-*S*-oxide, the sulfur atom sits below the plane of the ring at a dihedral angle of 11°. Upon deoxygenation this angle gradually decreases to zero. It is also evident from the changes in the C2-C3 bond length in the ring (Figure S4) that aromaticity is regained as the sulfoxide loses its oxygen. The C2-C3 bond length grows smaller as the double bond character increase, associated with aromaticity, is realized.

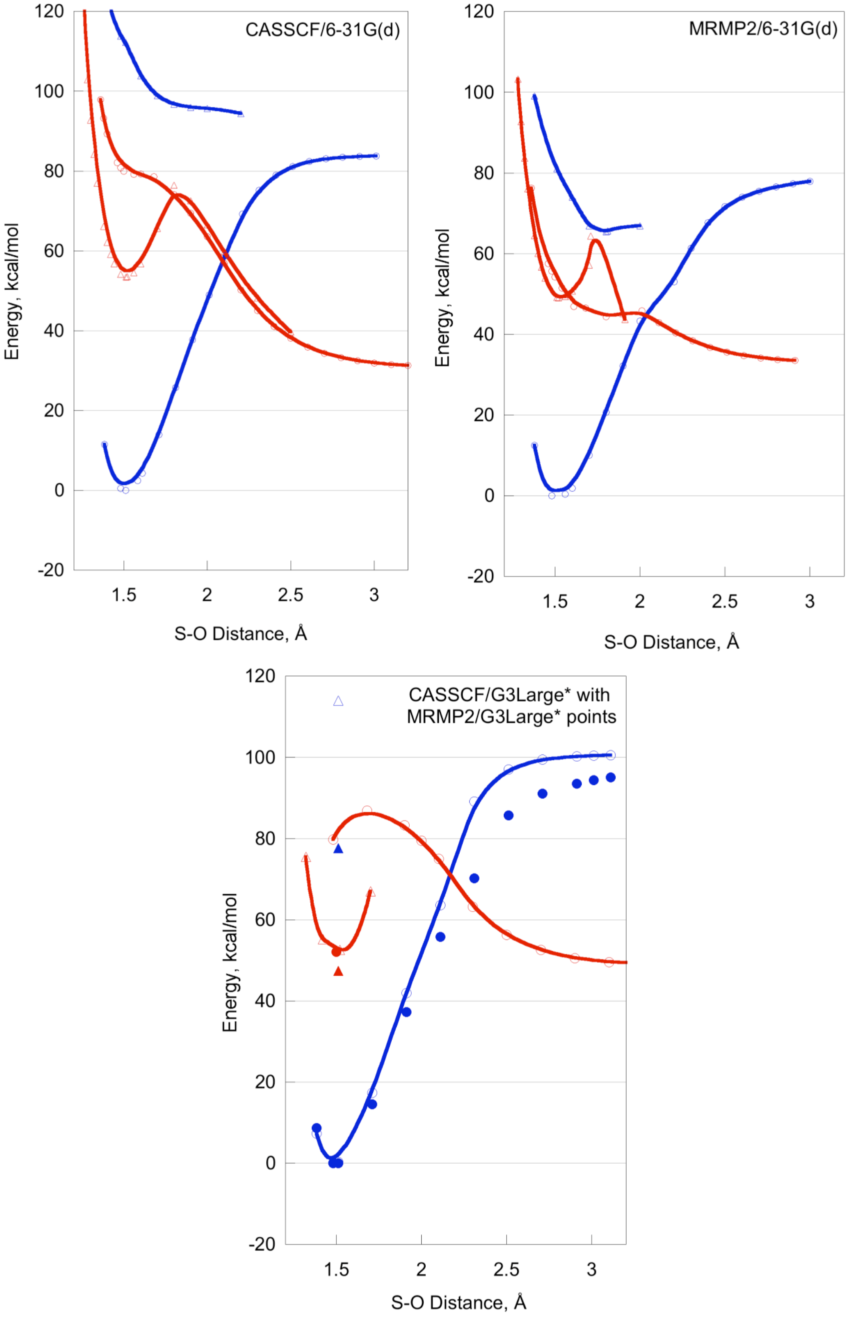


Figure 5. Energies of the electronic states of thiophene-*S*-oxide as a function of S-O separation. (a) CASSCF/6-31G(d). (b) MRMP2/6-31G(d). (c) CASSCF/G3Large* with selected points (solid) for MRMP2/G3Large*. Circles are A' states. Triangles are A" states. Singlets are blue and triplets are red, e.g., the ^{1}A' state is a blue circle.

The $^1A''$ state necessarily has net singlet occupancy in an a' and in an a" orbital. We believe it is because of this restriction that the energy does not appear to be reaching the same asymptotic limit at large S-O separation as the $^1A'$ state, i.e., there is a different restriction on orbital occupancies that is an artifact of the symmetry restrictions that would not be meaningful at infinite separation of the O atom from thiophene. At the near-molecular S-O distances whose energies are plotted, the state can be described as deriving from the excitation of an a" lone pair electron from oxygen into the π system of the thiophene ring, not so different than a traditional $n_O\pi^*$ state. At all S-O distances from 1.5 Å to 2.2 Å, the active space contains these two orbitals with occupancies near 1 and all the others near 2 or 0. The a" orbital transforms smoothly from being mixed with an a" element of the thiophene π system to residing nearly entirely on the oxygen atom. Similarly, as the S-O distance increases to 2.2 Å the singly occupied a' orbital smoothly shifts from a π orbital lightly mixed with an oxygen-centered p-component to a mainly oxygen-centered p orbital with slight mixing from the π system.

The two triplet states lie below the $^1A''$ state and are nearly degenerate at distances of 1.8 Å and beyond. Both triplet states correlate with the deoxygenation products, thiophene + O(^{3}P), when the S-O bond is stretched to a sufficient length. The appearance of the energy profiles of both states are strongly suggestive of an avoided crossing between what could be described as the "original" state that correlates with thiophene and O(^{3}P) and a state that is lower energy at S-O separations near 1.5 Å. As with the energy profile, the avoided crossing is more dramatically observed in the singly occupied orbitals of the $^3A''$ state. At 1.5 Å, the state may be reasonably described as a $\pi\pi^*$ state – analogous to that of cyclopentadiene – with some admixture of an oxygen p-type component to the a' orbital. As the distance grows to 1.8 Å, the admixture of the oxygen a' component slowly and smoothly increases. So, too, does a p-type oxygen-centered lone pair slowly grow into the a" singly occupied orbital. However, at 1.9 Å, the contribution of the O-centered components is dramatically larger, particularly for the a" orbital. The discontinuity in the smooth orbital progression is *not* – as is sometimes observed with avoided crossings – accompanied by contributions to the orbitals by entirely different parts of the molecule. The singly occupied orbitals for the ^{3}A" state at 1.8 and 1.9 Å S-O separation are illustrated in Figure 6.

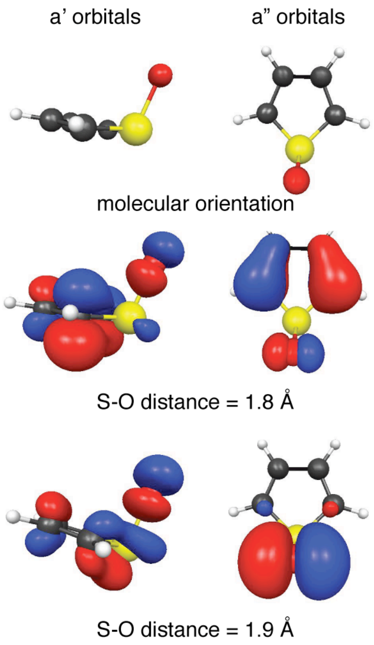


Figure 6. Singly occupied orbitals for the ^{3}A" state of thiophene-*S*-oxide at S-O distances of 1.8 and 1.9 Å, illustrating the avoided crossing also observed from the energy plot in Figure 5. Orbitals are illustrated at the 0.05 contour.

Although the potential energy surface generated at CASSCF/6-31G(d) is useful for visualizing the general shapes of the surfaces as a function of S-O bond length, it is well understood that CASSCF excited state energies can be grossly overestimated, and thus the energetics of the system were refined with a more rigorous level of theory. A comparison of the various state energies at the S-O bond length of the optimized ground state structure (1.51 Å) reveals that at all levels of theory except MRMP2/G3Large*//CASSCF/6-31G(d), at least one triplet state is predicted to be higher in energy than the estimated bond dissociation energy of the sulfoxide (Figure 7). At the most rigorous level of theory the $^3A''$ and $^3A'$ states of thiophene-*S*-oxide lie only 6.9 kcal/mol and 2.2 kcal/mol respectively below the S-O bond dissociation energy.

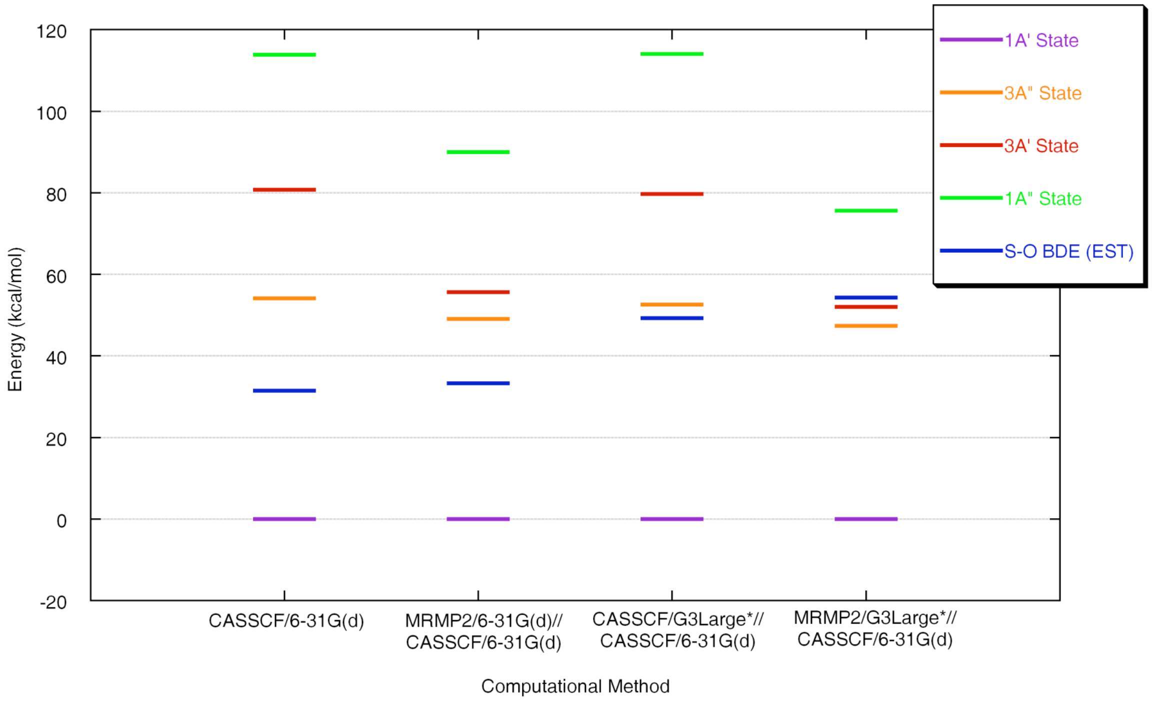


Figure 7. Comparison of thiophene-*S*-oxide state energies at an S-O bond length of 1.51 Å as a function of method.

Several trends can be observed when comparing the methods used in this study. As mentioned previously, the inclusion of tight d-polarization functions is necessary to accurately estimate sulfoxide bond dissociation energies. Generally, smaller basis sets underestimate the stability of the S-O bonds relative to other isomers of the molecule or to bond dissociation. The methods in this study that include tight d-polarization functions and diffuse sp shells on the heavy atoms (i.e. those using the G3Large* basis set), show that this is indeed the case. The asymptotic limit of both the singlet and triplet dissociation limits go up, by approximately 15 kcal/mol. (Note that a similar energy difference is seen for the singlet dissociation surface at MRMP2/G3Large* vs. MRMP2/6-31G(d).)

However, it should be noted that at the CASSCF level of theory changing from the 6-31G(d) basis set to the G3Large* basis set had little effect on the relative energies of the excited states, the greatest change was only 1.5 kcal/mol in magnitude. On the other hand, the excited state energies were significantly reduced upon addition of the MRMP2 energy correction, which was expected since CASSCF is known to provide unreliable excited state energies.[39] The largest differences are seen for the excited state energies, the $^1A''$ state and the $^3A'$ state, for which there were decreases of 38 kcal/mol and nearly 28 kcal/mol respectively.

Another quantitative comparison can be made: the asymptotic energy limit at long S-O distances between the singlet and triplet manifolds should correspond to the energy difference between O(^{1}D) and O(^{3}P), which is experimentally known to be 45.4 kcal/mol.[40] These data, shown in Table 5, indicate that all of the calculations are off by several kcal/mol; thus these calculations cannot be trusted to provide "chemical accuracy" in the range of 1-2 kcal/mol error. Similarly, even the (ground state) BDE of thiophene-S-oxide is not known with certainty; we estimate it to be near 61 kcal/mol in Chapter 6.[27] As defined, this corresponds to the energy of the asymptotic limit of the lowest energy triplet surface in Figure 5.

Table 5. Calculated O(^{3}P)-O(^{1}D) energy gaps at various levels of theory.

Method	Energy difference (kcal/mol)
CASSCF/6-31G(d)	51.8
MRMP2/6-31G(d)//CASSCF/6-31G(d)	44.4
CASSCF/G3Large*//CASSCF/6-31G(d)	50.9
MRMP2/G3Large*//CASSCF/6-31G(d)	40.8
Experimental	45.4

At MRMP2/6-31G(d)//CASSCF/6-31G(d), the ^{3}A" energy of thiophene-*S*-oxide is estimated to be 47.4 kcal/mol relative to the 1A' state (Table 6). The ^{3}A' state of thiophene-*S*-oxide is quite close to the ^{3}A" at 52.1 kcal/mol (Table 7). For reference, the energy of the cyclopentadiene ^{3}A" state is known to be 58.9 kcal/mol above the ground state.[41]

Table 6. Calculated ^{3}A" energies for thiophene-*S*-oxide at an S-O bond length of 1.51 Å at various levels of theory.

Method	Energy (kcal/mol)
CASSCF/6-31G(d)	54.1
MRMP2/6-31G(d)//CASSCF/6-31G(d)	49.1
CASSCF/G3Large*//CASSCF/6-31G(d)	52.6
MRMP2/G3Large*//CASSCF/6-31G(d)	47.4

Table 7. Calculated ^{3}A' energies for thiophene-*S*-oxide at an S-O bond length of 1.51 Å at various levels of theory.

Method	Energy (kcal/mol)
CASSCF/6-31G(d)	80.8
MRMP2/6-31G(d)//CASSCF/6-31G(d)	55.7
CASSCF/G3Large*//CASSCF/6-31G(d)	79.7
MRMP2/ G3Large*//CASSCF/6-31G(d)	52.1

Selenophene-*Se*-oxide. The first four electronic states of selenophene-*Se*-oxide were optimized at CASSCF/6-31G(d) with Cs symmetry. The optimized ground state of selenophene oxide has an Se-O bond length of 1.65 Å. Like thiophene-*S*-oxide, both the selenium and oxygen atoms deviate from the plane of the ring. Also like thiophene-*S*-oxide, the two triplet states of selenophene-*Se*-oxide also correlate with the dissociated products, selenophene and O(^{3}P) at long Se-O separations. The gain in aromaticity upon deoxygenation is evidenced by the movement of the selenium atom of back into the plane of the ring and the shortening of the C2-C3 bond length (Figures S5 and S6). To compare to the order of states found for thiophene-*S*-oxide, we calculated energies of the four analogous states at geometries optimized with the constraint of a 1.65 Å Se-O bond distance. The relative state energies are provided in Figure 8 and Tables 8 and 9.

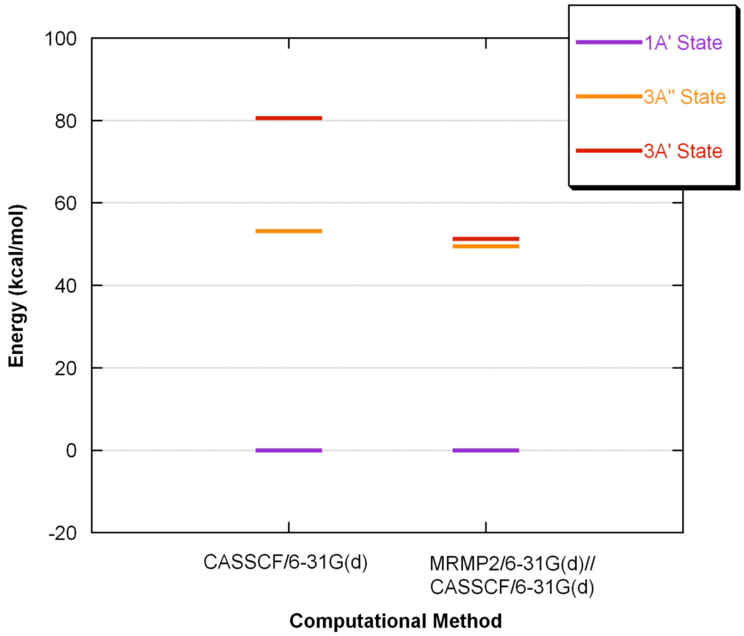


Figure 8. Comparison of selenophene-*Se*-oxide state energies as a function of method at the S-O bond length of the optimized structure (1.65 Å).

Table 8. Calculated ^{3}A" energies for selenophene-*Se*-oxide at an Se-O bond length of 1.65 Å at various levels of theory.

Method	Energy (kcal/mol)
CASSCF/6-31G(d)	53.2
MRMP2/6-31G(d)//CASSCF/6-31G(d)	49.4

Table 9. Calculated ^{3}A' energies for selenophene-*Se*-oxide at an Se-O bond length of 1.65 Å at various levels of theory.

Method	Energy (kcal/mol)
CASSCF/6-31G(d)	80.6
MRMP2/6-31G(d)//CASSCF/6-31G(d)	51.3

Dibenzothiophene-*S*-oxide.

While thiophene-*S*-oxide is sufficiently small to do energy calculations at the MRMP2/G3Large* level, we were only able to get energies for DBTO at CASSCF/6-31G(d) and MRMP2/6-31Gd). The relative state energies of DBTO are provided in Figure 9 and Table 10.

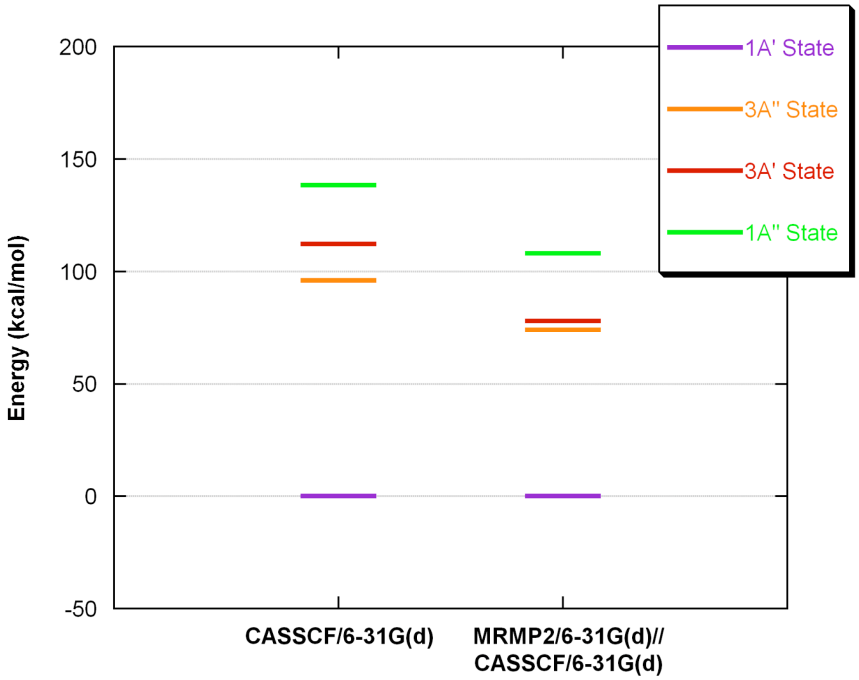


Figure 9. Comparison of DBTO state energies.

Table 10. DBTO state energies.

Method	^{3}A"	^{3}A'	^{1}A"
CASSCF/6-31G(d)	96.0	112.3	138.3
MRMP2/6-31G(d)	74.0	77.9	108.1

The bond dissociation energies of thiophene-*S*-oxide, DBTO, and selenophene-*Se*-oxide have all been estimated in Chapter 6 using an empirically derived combination of methods shown to best estimate sulfoxide bond strengths. These methods gave BDEs for thiophene-*S*-oxide, DBTO, and selenophene-*Se*-oxide of 60.9, 72.7, and 57.5 respectively. The MRMP2/G3Large* methods from this study gives a BDE that is 6.6

kcal/mol lower than the previous best estimate for thiophene-*S*-oxide. Assuming this drop in energy is consistent among sulfoxides, the BDEs for DBTO and selenophene-*Se*-oxide would be 66.1 kcal/mol and 50.9 kcal/mol respectively. Relative to the two triplet states and the singlet excited state, the BDE of DBTO may be below that of the ^{3}A' state and ^{1}A'' state.

We are currently investigating the state crossings observed in the potential energy surfaces more closely in order to determine the minimum energy crossing point of the two triplet states. In addition, we are refining the potential energy surface of selenophene-*Se*-oxide with the more rigorous methods used for thiophene-*S*-oxide.

The results of this study provide a new explanation for the observed photochemical behavior of dibenzothiophene-*S*-oxide, dibenzoselenophene-*Se*-oxide, and trimethylsilyl-substituted thiophene-*S*-oxide **(4)**. From the potential energy diagrams generated in this study, deoxygenation is shown to be energetically feasible from a low-lying triplet state. Upon photoexcitation to the singlet excited state, intersystem crossing to the ^{3}A' (i.e. T_2) state provides a nearly barrierless route to O(^{3}P) and the corresponding sulfide. These results are consistent with the observed increase in quantum yield for heavy atom-substituted dibenzothiophene-*S*-oxides, for which intersystem crossing events are expected to be more probable.

5.5 Conclusions.

Using CASSCF and MRMP2 energy calculations with a G3Large basis set on both S/Se and O and a 6-31G(d) basis set on C and H, the potential energy surfaces of thiophene-*S*-oxide and selenophene-*Se*-oxide deoxygenation have been modeled as a function of the S-O and Se-O bond length. We have been able to locate two low lying triplet excited states that would be accessible via intersystem crossing from the first singlet excited state. Following a spin flip, a minimal energy barrier exists to reach the corresponding sulfide and O(^{3}P). Our results further suggest that, like thiophene-*S*-oxide and selenophene-*Se*-oxide, dibenzothiophene-*S*-oxide has four analogous states whose calculated energies fall in the same order as those of the former, suggesting that DBTO may follow a similar mechanism of deoxygenation. This study offers a new and important understanding of the energetics of sulfoxide unimolecular bond cleavage, particularly for thiophene-*S*-oxide, selenophene-*Se*-oxide, dibenzothiophene-*S*-oxide, and related systems.

5.6 Acknowledgement.

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5.7 Supporting information description.

Coordinates for the constrained optimization of thiophene-S-oxide and selenophene-Se-oxide are provided at various S-O and Se-O bond lengths. The potential energy surfaces generated at HF/6-31G(d) are also provided.

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CHAPTER 6

Sulfur and selenium ylide bond enthalpies

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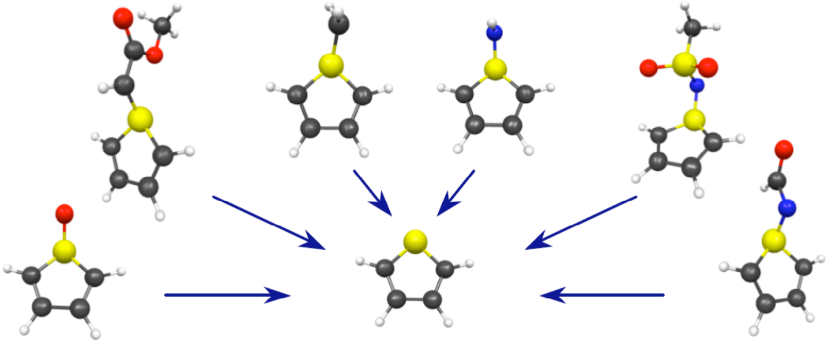
Stacey A. Stoffregen, Ryan D. McCulla, Robert Wilson,
Samuel Cercone, Jennifer Miller, and William S. Jenks
Department of Chemistry, Iowa State University, Ames, IA 50011-3111

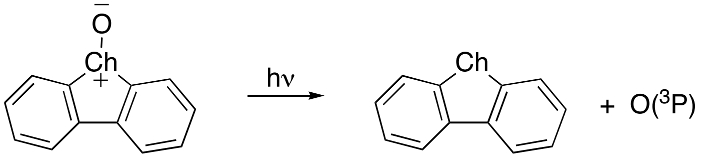


6.1 Abstract.

The bond dissociation enthalpies (BDEs) of sulfur and selenium ylides have been estimated by applying MP2/6-311++G(3df,2p)//MP2/6-31G(d,p), G3, and other computational methods. Computed sulfoxide bond enthalpies were compared to experimental results to ensure the reliability of the computational methods before extending to related compounds. The examined ylides include: sulfoxides, sulfilimines, *S,C*-sulfonium ylides, and selenoxides. Selenoxides have BDEs about 10 kcal/mol smaller than the corresponding sulfoxides. *N*-H sulfilimines and CH_2-*S,C*-sulfonium ylides have low BDEs, unless the sulfilimine or *S,C*-sulfonium ylide is stabilized by an electronegative substituent on N or C, respectively. Incorporation of the S or Se into a thiophene or selenophene-type ring lowers the BDE for the ylide.

6.2 Introduction.

Sulfur and selenium ylides of various sorts are useful compounds in organic chemistry.[1-9] Our own interests have focused on the chemistry and photochemistry of a common ylide, the sulfoxide. In particular, we have been interested in the formation of atomic oxygen, $O(^3P)$, by means of photolysis of dibenzothiphene-*S*-oxide and dibenzoselenophene-*Se*-oxide.[10-14] In separate publications, we will additionally present evidence for the formation of nitrenes and carbenes upon photolysis of related sufilimines and *S,C*-sulfonium ylides.



Ch = S, Se

From a mechanistic perspective for such reactions,[15-22] the bond dissociation enthalpy (BDE) of the sulfur ylide bond is critical to help determine whether unimolecular dissociation is plausible. One needs to know whether the lowest triplet and singlet excited states are sufficiently energetic to activate the cleavage. Unlike other sulfur and selenium ylides, detailed thermochemical data allowing calculation of sulfoxide bond strengths are available for representative compounds.[23-30] Standard sulfoxide S-O BDEs are on the order of 87-90 kcal/mol. Electronegative substituents raise the bond strength; for example the BDE for F_2SO is 114 kcal/mol.[28] On the other hand, conjugation of the sulfoxide to phenyl or vinyl substituents does not have a large effect.[29] However, the S-O bond strengths of thiophene derivatives are weakened because of the extra stabilization of the thiophene ring, compared to the non-aromatic sulfoxides. Previous calculations predict a BDE of about 65 kcal/mol for thiophene-*S*-oxide. [29]

Comparable experimental data are not available for sulfilimines (nitrogen ylides) or *S,C*-sulfonium ylides (carbon ylides), although discussion of the type of bonding in sufilimines, parallel to the descriptions of sulfoxides, has appeared.[24, 31, 32] An older study estimated the BDE of the S-CH_2 bond in H_2SCH_2 to be 27.5 kcal/mol using MP3/6-31G(d,p),[33] but a more recent G2 calculation for dimethylsulfonium methylide put the BDE at 51 kcal/mol for dissociation to singlet methylene,[34] which is about 9 kcal/mol above the triplet methylene ground state. To the best of our knowledge, there are no reports on the BDEs of sulfilimines or selenoxides. In this paper, we report estimates of the BDEs for a variety of model sulfilimines, *S,C*-sulfonium ylides, sulfoxides, and their selenium analogs. Because of the size of the molecules, we use a set of empirically determined methods based on *ab initio* calculations to arrive at reasonable estimates of the ylide-like BDE for a number of compounds. We explore the effect of electron withdrawing substituents, which are typical in the most commonly observed compounds.

6.3 Computational methods.

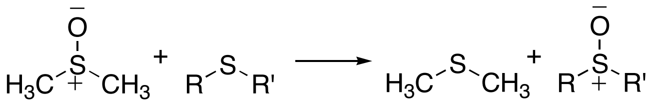
Initial geometries were acquired from the lowest energy conformation obtained from a semiempirical (PM3) conformational search performed using MacSpartan.[35] Geometries were then optimized at the MP2/6-31G(d,p) level. All further calculations were carried out at this geometry. All sulfur ylide geometry optimizations were performed using the GAMESS suite of programs[36] and the results were visualized using MacMolPlt.[37] Geometries of Se-containing compounds were obtained using Gaussian03[38] and visualized using GaussviewM. All geometries were confirmed as minima by calculating the vibrational frequencies, and the reported ΔH values include unscaled zero point energies (ZPEs) and a temperature correction at 298.15K. The G3 calculations[39-41] for Se-containing compounds were done manually (using Gaussian03), whereas the rest were done using the automated G3 input. Coefficients and exponents for the G3Large basis set for selenium were obtained from http://chemistry.anl.gov/compmat/g3theory.htm.

6.4 Results and discussion.

A decided benefit of computational chemistry is the ability to calculate thermochemical data for experimentally inaccessible or untested molecules. That said, a distinct disadvantage is that we are not yet at the point that the ordinary chemist is able to do arbitrarily good calculations on groups of even moderate-sized molecules from the perspective of the organic chemist. This is a particular problem for certain quantities, such as the one addressed here, BDEs. The challenge derives, at least in part, from the fact that most BDEs involve non-isogyric reactions (e.g., producing radicals from closed shell molecules) that highlight some of the shortcomings of the less expensive computational methods.

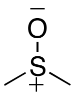
For dissociations of Ch-E ylide-type bonds, of which the sulfoxide S-O bond is the archetypal example, there are at least two difficulties. First, the ground state products generally include a triplet species (e.g., O(^{3}P)), meaning the reactions are not isogyric. Second, it is well established that oxides of sulfur require extensive basis sets in order to obtain accurate energies.[42-49] The stability of sulfur oxides is typically underestimated without these large basis sets. At minimum, "tight valence" d-polarization functions (e.g., "3d" in the Pople basis set notation) are required for qualitative results, and the most accurate results require even tighter core polarization functions. There is every reason to believe that these difficulties would extend to other sulfur/selenium ylides, e.g., sulfilimines and *S,C*-sulfonium ylides.

One reasonable way around these difficulties is the use of isodesmic reactions which allow for the maximal cancellation of errors. This can be done for a series of very closely related molecules, and absolute values can be obtained from experimental data for benchmark reactions. Our earlier work, in which we examined the sulfoxide bond strength as a function of substitution, used this approach with the well-established experimental data for dimethyl sulfoxide as the reference.[29, 50, 51]



However, for the broader group of compounds that we now report, it was clear that the standard isodesmic approach would not work in most cases, because there are so few known experimental data. We are unaware of even a single case in which the heats of formation of a corresponding sulfilimine, sulfide, and nitrene are all known.

Thus the approach we take here is empirical, based on obtaining a balance between accuracy and practical achievability, recognizing that we must calculate the energies of non-isodesmic, non-isogyric reactions for some fairly large molecules. It is clearly beyond our ability to do the kinds of calculations that have been carried out most rigorously for molecules of the size of SO_2 and SO_3 on larger systems. Our approach is to use as many isodesmic reactions as possible. For reference reactions with sulfoxides, we use experimental data. For the other compounds, we establish a reference value using calculations done for a small "parent" compound. We believe that – even if allowances of a few kcal/mol must be made – the data outlined below are useful first estimates of BDEs for these compounds.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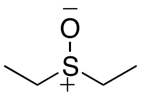
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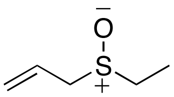
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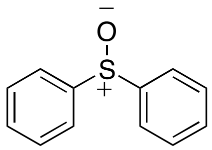
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Establishing a base method for sulfoxides. Experimental data are available for compounds **1-4** and the corresponding sulfides, so bond enthalpies at 298.15K can be calculated.[51] We approached these compounds in order to develop primary "standard methods" that could be used with other molecules. Calculations were done using MP2 and B3LYP with various basis sets including tight valence polarization. Additionally, the G3 method, whose "G3Large" basis set includes core polarization, was used. Pople-style basis sets, rather than Dunning-style cc basis sets were used, because the predominant factor in qualitative accuracy is the presence of adequate polarization functions, rather than large underlying valence functions. Results are shown in Table 1, with the first entry being the experimental value, and the remaining entries reflecting the error of the given method, where positive numbers imply an overestimation of the BDE. The data confirm that the difference in error between double and triple zeta basis sets is small, compared to the changes observed with polarization function increase.

For all four molecules, MP2 calculations with three d-polarization functions are within about 4 kcal/mol, overestimating the bond strength for DMSO and underestimating that of Ph_2SO. B3LYP calculations show the same general trend, but consistently underestimate the dissociation enthalpy. G3 results are only available for sulfoxides **1-3**. While expected to have the greatest accuracy, G3 underestimates the S-O bond strength by a range of 4.2 to 7.9 kcal/mol. A disturbing result is that all of the methods predict that dimethyl sulfoxide has the strongest bond and diphenyl sulfoxide has the weakest, which is the opposite of the reported experimental values.

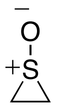
However, we can minimize the scatter in the data empirically by averaging some of the best calculations. The average error of the calculations is reduced to 2.1 kcal/mol if one averages the BDEs obtained from G3, MP2/6-311++G(3df,2p), and MP2/6-311(3df,2p). Not coincidentally, these two MP2 calculations are also the methods that give the values closest to experiment for **2** and **3**, and **1** and **4**, respectively. Also, in a sense, this can be viewed as an arbitrary tweak to the Gn methods, whose philosophy is to sum several calculations to approximate the value that would be obtained at a particular higher level calculation with a large basis set. Thus we define an empirical "Method A" for estimation of the BDE as the average of the values from MP2/6-311++G(3df,2p), MP2/6-311(3df,2p), and G3, plus 2.1 kcal/mol. We take this to be the best estimate available for all molecules in our data set to which it can be applied.

Table 1. Difference between computational and experimental S-O BDEs for sulfoxides (1-4) in kcal/mol.[a]

Method[b]	**1**	**2**	**3**	**4**
Expt.[c]	86.5 ± 0.5	88.8 ± 0.6	88.7 ± 1.2	89.3 ± 1.4
MP2/6-311++G(3df,2p)	3.1	-0.1	-1.3	-4.2
MP2/6-311G(3df,2p)	1.6	-1.0	-2.2	-4.0
MP2/6-311++G(d)	-18.6	-21.4	-22.5	-26.2
MP2/6-31+G(2d,p)	-8.1	-10.8	-11.8	-14.6
MP2/6-31G(2d)	-13.1	-14.9	-16.0	-17.2
MP2/6-31G(d,p)	-19.2	-21.2	-22.0	-23.3
MP2/6-311G(d)	-22.2	-23.8	-24.8	-26.6
MP2/6-31+G(d)	-13.9	-16.8	-17.7	-21.1
MP2/6-31G(d)	-18.8	-20.8	-21.7	-23.2
B3LYP/6-311++G(3df,2p)	-4.6	-8.0	-8.8	-11.6
B3LYP/6-311G(3df,2p)	-4.6	-7.5	-8.2	-10.1
B3LYP/6-311++G(d)	-19.3	-22.0	-22.7	-25.2
B3LYP/6-31+G(2d,p)	-11.4	-14.7	-15.4	-18.1
B3LYP/6-31G(2d)	-14.4	-16.8	-17.4	-18.6
B3LYP/6-31G(d,p)	-18.6	-20.7	-21.4	-22.5
B3LYP/6-311G(d)	-20.9	-23.4	-23.1	-24.3
B3LYP/6-31+G(d)	-17.2	-20.2	-20.8	-23.5
B3LYP/6-31G(d)	-18.6	-20.8	-21.4	-22.7
G3	-4.2	-7.0	-7.9	N/A

[a] A positive number means an overestimation and a negative number an underestimation of the BDE. [b] All ΔH values were determined from the listed method energy runs performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and the 298.15K temperature correction. [c] Experimental BDEs were determined from the ΔH of reaction (1) using ΔH_f° values from the NIST webbook.

Expanding to other sulfoxides. Sulfoxides **5**-**9** are compounds that were investigated previously, using the isodesmic approach with DMSO as a standard,[29] though experimental results are not available. Method A can be applied to molecules **5**-**7**, but not **8** and **9**, which are too large for practical G3 computations at this time. However, we can use compounds **1**-**4** as references for isodesmic reactions involving **5**-**7**. Because the computations for **1**-**4** showed inconsistent errors, we believed that the best approach to obtain BDEs for **5**-**7** would be to average the four possible isodesmic reactions for a given test molecule, using each of **1**-**4** as the reference. We define this as "Method B", where we must also stipulate a level of theory at which the isodesmic reaction was calculated. Here, the choice of computational method is less important because the errors tend to cancel out. Data in the Supporting Information show this to be the case for a larger set of calculations, and data obtained with the better basis sets are provided in Table 2.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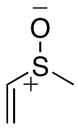
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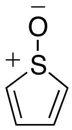
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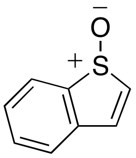
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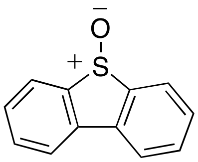
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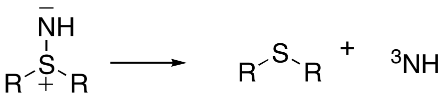
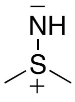
Table 2. Computed S-O BDEs for sulfoxides 5-9 in kcal/mol.

Method[a]	**5**	**6**	**7**	**8**	**9**
MP2/6-311++G(3df,2p)	89.3	86.0	60.4	67.3	72.1
MP2/6-311G(3df,2p)	86.5	85.5	59.6	66.4	71.3
B3LYP/6-311++G(3df,2p)	80.7	77.8	56.4		
B3LYP/6-311G(3df,2p)	80.9	78.7	57.0		
G3	79.1	79.0	56.6		
Method A[b]	87.1	85.6	60.9		
B:[c] MP2/6-311++G(3df,2p)	89.9	86.7	61.1	67.9	72.7
B: MP2/6-311G(3df,2p)	87.9	86.9	61.0	67.8	72.7
B: MP2/6-31G(d,p)	87.2	87.3	63.7	70.4	75.2
B: B3LYP/6-311++G(3df,2p)	88.9	86.1	64.7		
B: G3	85.4	85.3	62.9		

[a] All ΔH were determined from the listed method energy runs performed at the MP2/6-31G(d,p) geometry, and include the unscaled ZPE and the 298.15K temperature correction. [b] Average of MP2/6-311++G(3df,2p), MP2/6-311G(3df,2p), and G3, plus 2.1 kcal/mol. [c] Method B is the average of the BDE determined from equation 1 by four isodesmic reactions using **1** (BDE_{std} = 86.5 kcal/mol), **2** (BDE_{std} = 88.8 kcal/mol), **3** (BDE_{std} = 88.7 kcal/mol), and **4** (BDE_{std} = 89.3 kcal/mol) as the standard sulfoxide.



Sulfilimines. Following the analogy to sulfoxides, sulfilimines can formally dissociate to sulfides and nitrenes. Although most experimentally relevant sulfilimines are *N*-substituted with electron withdrawing groups, we chose to begin this exploration of the thermochemistry with the parent *N*-H sulfilimines **10-18**. Based on the notion that nitrogen is less electronegative than O, our initial assumption was that the bond enthalpy would be lower for sulfilimines than for sulfoxides, but we did not know by how much. Because the ground states of simple nitrenes are triplets, the dissociation reactions are again neither isogyric nor isodesmic. Worse, there are not sufficient experimental data to establish appropriate reference benchmarks. Thus, we rely on some of the patterns established for the sulfoxides.



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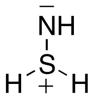

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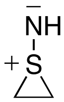

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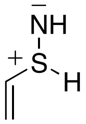

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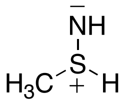

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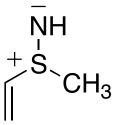

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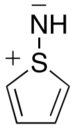

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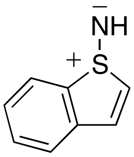

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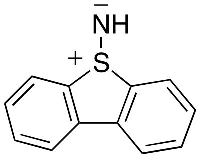


18

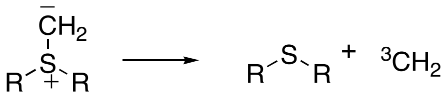
Of the sulfilimines **10-18**, G3 calculations were carried out for **10-15**. The enthalpies of the dissociation reactions, calculated at several levels including G3 and using Method A (defined above in the sulfoxide case), are shown in Table 3. The results are approximately 40 kcal/mol lower than for the corresponding sulfoxide.

Table 3. Calculated S-N BDEs to form ^{3}NH and the corresponding sulfide in kcal/mol.

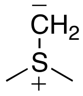
Method[a]	**10**	**11**	**12**	**13**	**14**	**15**
MP2/6-311++G(3df,2p)	47.5	25.5	43.1	34.2	38.3	42.4
MP2/6-311G(3df,2p)	46.2	23.3	41.2	33.2	37.0	41.5
B3LYP/6-311++G(3df,2p)	39.6	20.3	37.1	27.3	32.0	34.5
B3LYP /6-311G(3df,2p)	39.4	19.2	36.4	27.3	31.7	34.7
G3	39.2	17.8	35.0	23.8	30.3	34.5
Method A	46.4	24.3	41.9	32.5	37.3	41.6

[a] All ΔH were determined from the listed method energy runs performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and the temperature correction to 298.15K.

How to treat compounds **16-18** is another question that must be addressed empirically, because they are too large for G3 calculations, and therefore cannot be treated by Method A. Using the results for compounds **10-15** as benchmarks, we looked for a single calculation that best tracked Method A and thus would be used in isodesmic reactions for **16-18**. The MP2/6-311++G(3df,2p) calculations give higher BDEs than Method A by an average of 0.6 kcal/mol, but the standard deviation of that difference is only 0.8 kcal/mol. Thus, very similar BDEs for **11-15** would be obtained by either (a) using compound **10** and its Method A BDE for a reference in an isodesmic reaction between **11-15** and dimethyl sulfide (the base sulfide of **10**) or (b) calculating the BDE for **11-15** directly by Method A. We thus define this as Method C for determining a BDE: an isodesmic reaction, calculated at the MP2/6-311++G(3df,2p) level, between the large test compound (e.g., **16**) and a parent molecule (e.g., **10**), where the parent compound's BDE, calculated with Method A, is used as the reference value. In subsequent paragraphs, we will present other data using Method C, based on different parent compounds, e.g., dimethyl selenoxide for various Se-O BDEs. Complete data are shown in the Supporting Information. Using Method C, the BDEs are 21.4, 28.7, and 33.4 kcal/mol for **16**, **17**, and **18**, respectively.



***S,C*-sulfonium ylides.** A similar approach was taken for sulfonium methylides **19-26** in the formation of methylene. Again, there are no good experimental data to use for comparison to calculations. Table 4 shows data obtained for **19-23** and the BDEs obtained with Method A. We again use Method C for the larger compounds, i.e., using an isodesmic reaction of **24-26** with compound **19** as the reference dissociation reaction. The resulting BDEs for **24-26** using Method C are 24.2, 31.4, and 36.8 kcal/mol, respectively.



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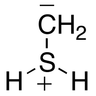

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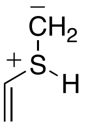

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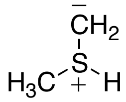

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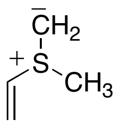

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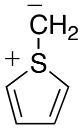

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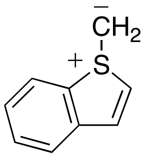

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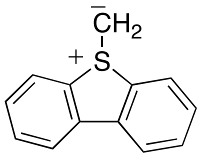

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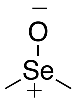
Table 4. Calculated S-C BDEs to form $^3CH_2$ and the corresponding sulfide, in kcal/mol.

Method[a]	19	20	21	22	23
MP2/6-311++G(3df,2p)	45.8	26.5	33.7	38.4	43.6
MP2/6-311G(3df,2p)	44.9	25.6	32.9	37.5	43.1
B3LYP/6-311++G(3df,2p)	40.4	24.7	29.4	34.7	37.2
B3LYP/6-311G(3df,2p)	40.1	24.5	29.4	34.5	37.4
G3	40.6	22.3	29.2	33.6	38.1
Method A	45.9	26.9	34.0	38.6	43.7

[a] All ΔH were determined from the listed method energy runs performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and temperature correction to 298.15K.

Selenoxides. In Table 5 are the data, similarly obtained, for the dissociation of selenoxides **27-29** to form the corresponding selenides and O(^{3}P). The use of dimethyl selenoxide (**27**) as the standard for an isodesmic reaction using MP2/6-311++G(3df,2p) energies, allows us to estimate bond enthalpies of **30**, **31**, and **32** using Method C as 57.5, 59.8, and 64.2 kcal/mol, respectively.



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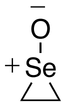

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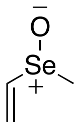

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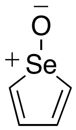

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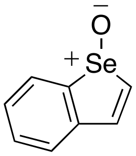

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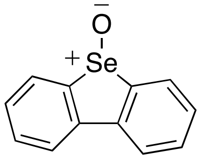

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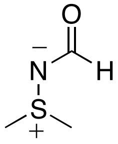
Table 5. Calculated Se-O BDEs for 27-29 in kcal/mol.

Method[a]	**27**	**28**	**29**
MP2/6-311++G(3df,2p)	79.1	75.7	74.6
MP2/6-311G(3df,2p)	78.5	75.2	74.4
B3LYP/6-311++G(3df,2p)	69.6	68.5	65.5
B3LYP /6-311G(3df,2p)	70.3	69.3	61.0
G3	70.2	68.9	66.3
Method A	78.0	75.4	73.9

[a] All ΔH were determined from the listed method energy runs performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and the temperature correction to 298.15K.

Substituted sulfilimines and *S,C*-sulfonium ylides. The sulfilimines and *S,C*-sulfonium ylides that are most straightforward to prepare and handle in the laboratory are not those that have been shown in the previous cases with no *N*- or *C*- substitution, but those bearing electron withdrawing groups.[52] In principle, this could be due to hydrolytic (kinetic) stability, but it also stands to reason that electron withdrawing groups would increase the bond dissociation enthalpy toward nitrene/carbene formation by stabilizing the formal negative charge on the N or C. Thus, we calculated BDEs for compounds **33-42**.



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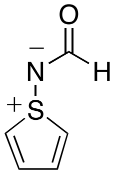

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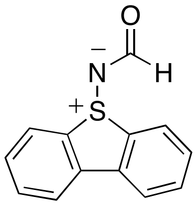

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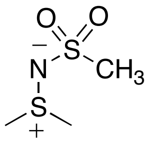

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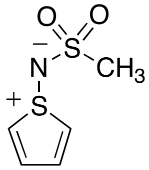

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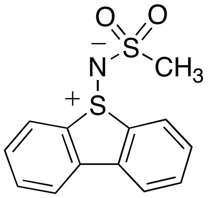

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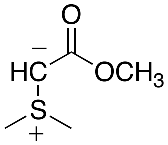

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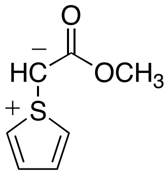

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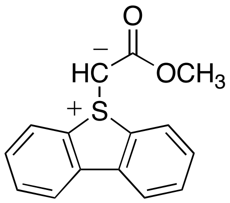

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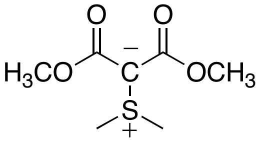

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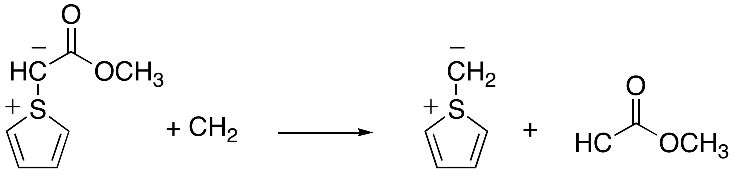
Estimates of the BDEs for these compounds were obtained from isodesmic reactions as well, using compound **40** as an illustration. The base calculations were done at the MP2/6-311++G(3df,2p) level, and the reference BDE used was the best available (Method A or C) for the corresponding NH-sulfilimine or CH_2-sulfonium ylide. For **40**, the reference was the BDE reported for **24** using Method A. The values are reported in Tables 6 and 7.



40 **24**

Table 6. Estimated S-N BDEs for substituted sulfilimines.

Method[a]	**33**	**34**	**35**	**36**	**37**	**38**
MP2/6-311++G(3df,2p)//MP2/6-31G(d,p)	81.2 (80.5)	52.9 (52.2)	71.7 (71.0)	70.2	47.7	62.1

[a] All ΔH were determined from isodesmic reactions with NH, and include the unscaled ZPE and the 298.15K temperature correction. The reference reaction is the corresponding dissociation of the analogous NH-sulfilimine, whose energy was taken from Method A or C, as appropriate.

Table 7. Estimated S-C BDEs for substituted sulfonium ylides.

Method[a]	**39**	**40**	**41**	**42**
MP2/6-311++G(3df,2p)// MP2/6-31G(d,p)	61.5	39.0	54.5	68.8

[a] All ΔH were determined from isodesmic reactions with CH_2, and include the unscaled ZPE and the 298.15K temperature correction. The reference reaction is the corresponding dissociation of the analogous CH_2-sulfonium ylide, whose energy was taken from Method A or C, as appropriate.

An additional complication for the nitrenes is that the groups that stabilize the ylide also exert substantial stabilization to the hypovalent intermediates, especially the singlet states. In fact, while the ground state of the parent nitrene NH is the open shell triplet, by 36 kcal/mol, the ground state of several α-carbonyl nitrenes, as established by rigorous computational work, is the closed-shell singlet, due to what might be called a partial bond between the oxygen atom and the nitrogen, using the oxygen lone pair and the formally empty orbital on the nitrogen.[53-57] (No currently available experimental or computational evidence suggests that the sulfonyl nitrenes have singlet ground states.) Such stabilization is considerably less important for the triplet states of carbonyl nitrenes, in which the *N*-centered orbital is half-filled and the extra bonding interaction is attenuated. For the substituted carbenes implied in compounds **39-42**, we are unaware of any evidence that the ground state is other than a triplet.

Thus, in Table 6, a second, slightly lower BDE is given in parentheses for compounds **33-35**. This is the BDE to give the singlet formylnitrene, where the singlet is taken to be 0.7 kcal/mol lower in energy on the basis of reported calculations at the CCSD(T)/cc-pVTZ level extrapolated to an infinite basis set.[57]

Chemical interpretations. We now turn to a discussion of several trends revealed in the data. Among these are (a) trends within a structure type, based on the underlying sulfide/selenide; (b) trends between sulfoxide, sulfilimine, *S,C*-sulfonium ylide, and selenoxide for the same underlying sulfide/selenide; and (c) trends for *N*- or *C*-substitution on sulfilimines and *S,C*-sulfonium ylides. It is beyond the scope of this paper to quantitatively parse various contributions to the estimated BDEs; nonetheless the trends are important, and we can make attractive speculative arguments.

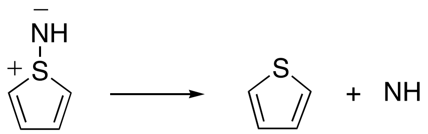
Table 8 illustrates the relevant data. The computations consistently give a slightly lower BDE for the conjugated methyl vinyl derivative than for the dimethyl derivative for each structure type. Were it not for the experimental value available for diphenyl sulfoxide that *exceeds* the BDE of dimethyl sulfide by 2.8 kcal/mol, it would be tempting to conclude that there was a genuine, if not large, effect on the ylide BDEs by conjugation. With the present data, however, this will have to await either better calculations or additional experimental work.

Table 8. Comparison of BDEs Based on the Underlying Sulfide/Selenide.

		BDE (Difference from dimethyl parent), kcal/mol			
Entry	Sulfide (or Selenide)	Sulfoxide	*N*-H Sulfilimine	*C*-H_2 Sulfonium	Selenoxide
1	Dimethyl sulfide	86.5^{a}	44.8^{b}	44.3^{b}	76.4^{b}
	(selenide)				
2	Methyl vinyl sulfide	85.6^{b}	41.6^{b}	43.7^{b}	73.9^{b}
	(selenide)	(-0.9)	(-3.2)	(-0.6)	(-2.5)
3	Thiophene	60.9^{b}	21.4^{d}	24.2^{d}	57.5^{d}
	(selenophene)	(-25.6)	(-23.4)	(-20.1)	(-18.9)
4	Benzothiophene	67.9^{c}	28.7^{d}	31.4^{d}	59.8^{d}
	(benzoselenophene)	(-18.6)	(-16.1)	(-12.9)	(-16.6)
5	Dibenzothiophene	72.7^{c}	33.4^{d}	36.8^{d}	64.2^{d}
	(dibenzoselenophene)	(-13.8)	(-11.4)	(-7.5)	(-12.2)

[a] Experimental value. [b] Method A. [c] Method B: MP2/6-311++G(3df,2p). [d] Method C.

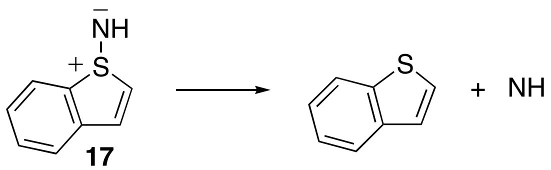
It is unambiguous, however, that there is a major effect on the BDEs that is based on the aromaticity of the underlying sulfide (entries 3, 4, 5). Cleavage of the sulfoxide, sulfilimine, *S,C*-sulfonium ylide, or selenoxide always results in a "more" aromatic product, as illustrated for compounds **16** and **17**.



16

non-aromatic
starting material

aromatic
product



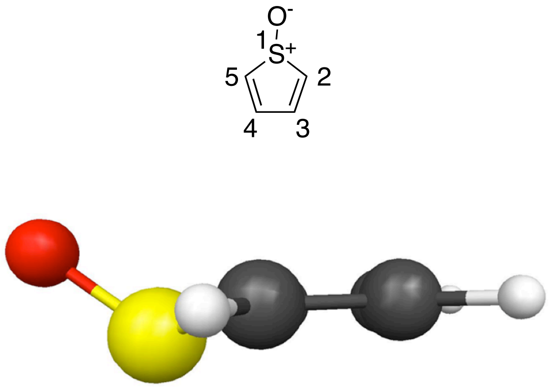
17

partially aromatic
starting material

enhanced aromaticity
in product

Even if we postulate that thiophene-*S*-oxide is essentially non-aromatic (similar to cyclopentadiene), it may be an oversimplification to say the same for the corresponding sulfilimine (**16**) or *S,C*-sulfonium ylide (**24**). The bond destabilizations for the latter two compounds (23.4 kcal/mol and 20.1 kcal/mol), compared to the respective appropriate dimethyl sulfide compounds, are somewhat smaller than the bond destabilization of 25.6 kcal/mol for the sulfoxide. Although **16** and **24** and their analogs certainly have a largely reduced aromatic stabilization compared to thiophene, there is some structural evidence that they may retain more than does thiophene-*S*-oxide itself. It is well known that the sulfur atom in thiophene-S-oxide derivatives "dips" below the plane of the carbon atoms in the rest of the ring.[29, 53] This is simply a variation of the standard "envelope" conformation of 5-membered rings. Such a dip minimizes interactions of the sulfur atom orbitals with the rest of the pi system and obviously goes to zero in the limit of thiophene (or selenophene). The dihedral angle 1(S),2,3,4 as illustrated in Figure 1 is indicative of how far below the plane the sulfur atom resides. These angles are 9.9˚, 7.3˚, and 5.3˚, for the oxide, sulfilimine and methylide of thiophene, respectively. This trend is consistent with the descending destabilization of the thiophene-based sulfoxide, sulfilimine and *S,C*-sulfonium ylides, when compared to the corresponding dimethyl sulfide-based sulfide, sulfilimine and *S,C*-sulfonium ylide.

Figure 1. Out-of-plane sulfur geometry



The bond destabilization effect of thiophene is attenuated with benzannulation in a qualitatively consistent manner across all of the compounds. We assert that the origins of this effect come from the quantitatively smaller energy of aromaticity of the “second” ring of benzothiophene and “third” central ring of dibenzothiophene. It is of course, widely recognized that anthracene is more reactive than naphthalene, which is in turn more reactive than benzene, for this same reason. Note that we speak not of a “per carbon” level of aromatic stabilization, but rather the total aromatic stabilization energy that is lost on dearomatization of one ring of the fused compounds.

Next, we consider the series of compounds in the other dimension, i.e., comparing sulfoxide to sulfilimine to sulfonium and selenoxide. As alluded to earlier, because of the ylide nature of the bonds, it is not surprising that the sulfoxide is the strongest bond among the sulfoxide, sulfilimine, and sulfonium ylide. Upon dissociation, the compound goes from a highly polar bond to a situation of no charge separation between the S and O (or NH or CH_2). Thus, the greater ability of O to stabilize negative charge (as reflected in its electronegativity) ought to lead to a stronger bond through greater relaxation of the S-O charge distribution. This is qualitatively reflected in the stronger sulfoxide bond, but the fact that the sulfonium ylide S-C bonds are consistently a few kcal/mol stronger than the sulfilimine S-N bonds is confounding.

However, at least a qualitative solution is reached when one considers the product side of the dissociation reaction. Underlying the above argument is the assumption that the “stability” of the hypovalent product (O, NH, or CH_2) is the same. One way to check this is to consider the heats of other simple reactions using these compounds. In Table 9 are given the enthalpies of hydrogenation of O, NH, and CH_2, along with the enthalpies of insertion into the C-C bond of ethane.

Table 9. Heats of insertion of methylene, imidogen, and oxene.

	Reaction	ΔH° (kcal/mol)[a]
1	$CH_2 + H_2 \rightarrow CH_4$	-110.3
2	$NH + H_2 \rightarrow NH_3$	-101.0
3	$O + H_2 \rightarrow OH_2$	-117.4
4	$CH_2 + CH_3\text{-}CH_3 \rightarrow CH_3\text{-}CH_2\text{-}CH_3$	-97.4
5	$NH + CH_3\text{-}CH_3 \rightarrow CH_3\text{-}NH\text{-}CH_3$	-74.4
6	$O + CH_3\text{-}CH_3 \rightarrow CH_3\text{-}O\text{-}CH_3$	-83.6

[a] Data taken from heats of formation from NIST webbook.

Strikingly, although it is most exothermic to hydrogenate O (entry 3 among 1-3), and most exothermic to insert CH_2 into ethane (entry 4 among 4-6), it is least exothermic both to hydrogenate or insert NH by 10-15 kcal/mol, compared to the other reactions. We can infer, then, that the nitrene is the most "stable" of the three hypovalent intermediates by 10-15 kcal/mol. This -10 to -15 kcal/mol contribution to the BDE of the sulfilimines in Table 8 can thus at least potentially explain why the sulfilimine S-NH and S-CH_2 BDEs are more comparable than originally expected.

Now, we turn to the substituted sulfilimines and *S,C*-sulfonium ylides. Many sulfilimines and *S,C*-sulfonium ylides are stable enough to be stored and handled, even the parent compounds in some instances. The parent *N*-H sulfilimines of many simple alkyl and aryl sulfides have been characterized for many years,[52] but in work to be published elsewhere, we will present the first characterization of **18**; we are unaware of the isolation and characterization of **16**. However, the clear majority of work involving sulfilimines and *S,C*-sulfonium ylides uses compounds with electron withdrawing substituents on the *N* or *C*, respectively.[52, 54] The data clearly demonstrate that electron withdrawing groups add to the stability of the sulfilimine or *S,C*-sulfonium ylide, presumably because delocalizing the charge in the starting material is a larger stabilizing effect than is any stabilization on the triplet nitrene or carbene.[55]

If the BDEs determined for *N*-formyl sulfilimines **33-35** are compared to the corresponding *N*-H derivatives **10**, **16**, and **18**, the S-N BDE is seen to increase by a remarkable 31-38 kcal/mol. These were chosen as representatives of the large group of *N*-acyl sulfilimines. Other acyl substituents, such as *N*-benzoyl and *N*-acetyl, would be expected to have BDEs within a few kcal/mol of the formyl derivatives.

The *N*-mesyl substituents of **36-38** were chosen to represent the family of *N*-mesyl, *N*-benzenesulfonyl, and *N*-tosyl sulfilimines in a similar fashion. The mesyl group has a slightly smaller effect on BDEs than does the formyl group, but it is still large. The S-N bonds are stronger for **36-38** by 24-29 kcal/mol than their *N*-H counterparts.

Because carbenes derived from precursors such as ethyl diazoacetate or dimethyl diazomalonate are comparatively common, we chose compounds **39-41** as models for the singly-substituted case. Compared to their CH_2 analogs **19**, **24**, and **26**, respectively, the BDE enhancements are 15-18 kcal/mol. Adding a second carbomethoxy group, as with **42**, increases the BDE enhancement as expected, but to only about 23 kcal/mol (again, compared to the BDE of **19**).

Finally, we turn to the selenoxides. Like sulfoxides, sulfilimines, and *S,C*-sulfonium ylides, the BDEs of selenoxides are also only marginally affected by conjugation to a vinyl group. The selenophene derivatives have selenium-oxygen bond strengths that are lower than the corresponding sulfoxide bonds in the thiophene derivatives. Selenophene-*Se*-oxide has the weakest ylide bond, but it is only approximately 7 kcal/mol weaker than dibenzoselenophene-*Se*-oxide. The others are all about 10 kcal/mol weaker than the corresponding sulfoxide.

We have previously shown that photolysis of **32** produces an oxidizing agent we suggest is O(^{3}P).[12] The estimated BDE of 64.2 kcal/mol is thus particularly important, because it lies well below the singlet excited state energy of **32**, but is also very close to the triplet energy we anticipate for **32**. Unfortunately, we have been unable to obtain phosphorescence data for dibenzoselenophene-*Se*-oxide, but the triplet energy of dibenzothiophene-*S*-oxide – which should be very similar – is about 60 kcal/mol.[56] It is thus at least possible that photochemical cleavage of O(^{3}P) may be induced from **32** from its triplet state. (Similar energetic arguments show that this is *not* the case for dibenzothiophene-*S*-oxide.) The observed quantum yield for photochemical deoxygenation of **32** is in the range of 0.1-0.3, depending on conditions, while that of dibenzothiophene-*S*-oxide ranges from 0.003 to 0.01. The possible compatibility of the lowest triplet energy of dibenzoselenophene-*Se*-oxide with the Se-O BDE may account for this much greater photochemical efficiency.

6.5. Summary.

The determination of BDEs for sulfoxides, sulfilimines, and *S,C*-sulfonium ylides remains challenging. Recognizing the shortcomings of several individual computational approaches, we have taken an empirically devised method involving three sets of *ab initio* calculations as our "best estimate" for a variety of relatively small molecules in these classes. We have then taken the isodesmic approach to relate these BDEs to those of other, larger compounds. While we therefore do not claim a reliable "chemical accuracy" of 1-2 kcal/mol, we do believe the method does justify viewing these as reasonable first estimates for the unknown BDEs of compounds **5-42**.

In qualitative terms, the sulfoxides' S-O bond is the strongest of the ylide-type bonds, followed by Se-O in selenoxides, S-N in *N*-H sulfilimines, and S-C in *C*-H_2 *S,C*-sulfonium ylides. Inclusion of the sulfur atom in a thiophene ring lowers the BDE due to increased aromaticity in the thiophene products after S-O, S-N or S-C cleavage. The data suggest that the NH-sulfilimine and the CH_2-sulfonium ylide of thiophene may, in fact, be very difficult to isolate at room temperature, due to BDEs of 21 and 24 kcal/mol.[57] The BDEs of the sulfilimines are increased by 31-38 kcal/mol by substitution of *N*-CHO for *N*-H or by 24-29 kcal/mol by use of a mesyl group. The substitution of a carbomethoxy group on the *S,C*-sulfonium ylide raises the BDE by 15-18 kcal/mol, with a smaller increment for a second carbomethoxy substitution.

6.6. Acknowledgment.

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6.7 Supporting information description.

Geometries, absolute energies, and energy differences at several basis sets are available in the supporting information, which can be obtained, free of charge, at http://pubs.acs.org.

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55. Carbonyl groups strongly stabilize the singlet state of the nitrene, but as noted previously, this only gets the nitrene singlet state to be near or just barely below the energy of the triplet nitrene.

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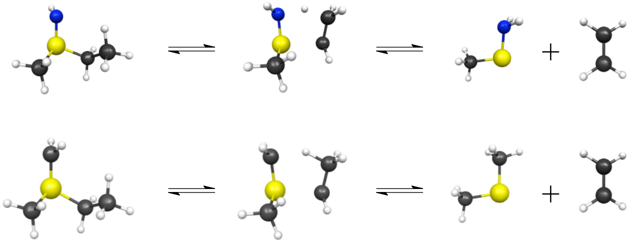
57. Thiophene sulfoxide itself cannot be isolated because of self-condensation reactions. However, alkyl substitution of the ring gives sufficient kinetic stabiization against the self condensations that they may be handled and isolated. This type of self-condensation of the parent compounds would undoubtedly also plague the sulfilimine and *S,C*-sulfonium ylides.

CHAPTER 7

Elimination reactions of *N*-sulfilimines and *S,C*-sulfonium ylides

In the style of a paper submitted to the *Journal of Organic Chemistry*
Stacey A. Stoffregen and William S. Jenks
Department of Chemistry, *Iowa State University, Ames, Iowa, 50011-3111.*

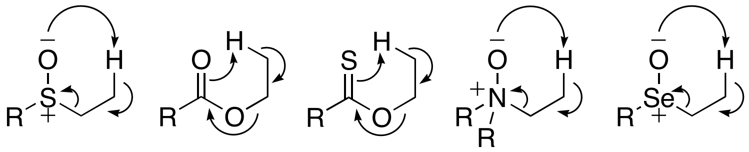


7.1 Abstract

Sulfoxides, sulfilimines, and *S*,*C*-sulfonium ylides have all been shown to undergo *cis*-eliminations to form a carbon-carbon double bond. The eliminations of sulfilimines, and *S*,*C*-sulfonium ylides proceed under relatively mild conditions compared to sulfoxides. In this study we present the reaction enthalpies and activation barriers of the forward and reverse reactions for related sulfilimines, *S,C*-sulfonium ylides, and a sulfoxide that were calculated at MP2//6-311++G(3df,2p). Our results indicate that a predominant factor affecting the relative ease of reactivity is the strength of the S-C_α bond, i.e. the ease of breaking the S-C_α bond, which is the most advanced process of the reaction. Resonance stabilization of the ylide nitrogen of sulfilimines and the ylide carbon of sulfonium ylides with electron-withdrawing groups, effectively delocalizes the charge rendering the ylide less nucleophilic and thereby less reactive toward eliminations. Additionally, our results show that among the compounds tested, the S-C_α bond of compounds with electron-withdrawing substituents is the strongest, further limiting the reactivity of these ylides. While few reports of eliminations of *S,C*-sulfonium ylides exist, our calculations suggest that they would be viable reactants for mild preparation of a variety of alkenes.

7.2 Introduction.

Pyrolytic internal elimination (Ei) reactions of sulfoxides[1-5], esters[6-8], xanthates[6-12], amine oxides[13], and selenoxides[14-18] have proven to be useful in the preparation of alkenes. The eliminations of sulfoxides, amine oxides, and selenoxides are all concerted, synchronous processes that proceed through planar 5-centered transition states. On the other hand, xanthates and esters undergo elimination via 6-membered ring transition states.

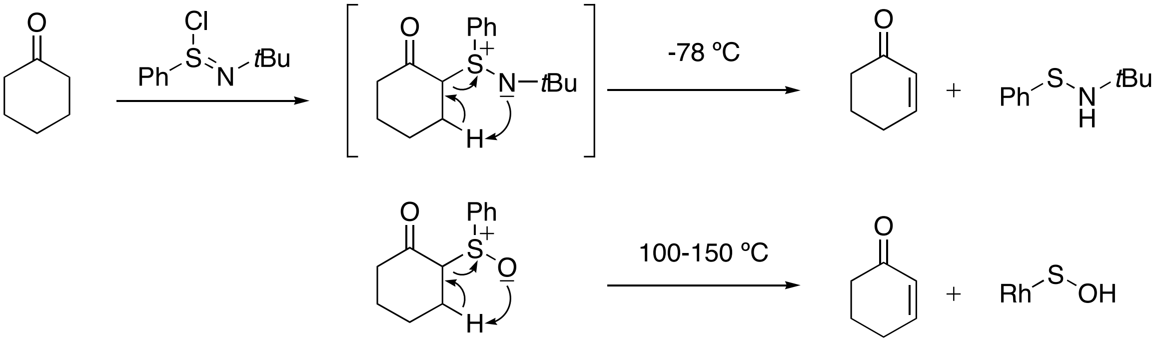


Several computational and experimental studies have been dedicated to elucidating the structural parameters that influence the activation barrier of elimination reactions. In particular, early studies suggest that the stability of the leaving group heavily influences the ease with which eliminations with six-membered cyclic transition states occur.[19] This however seems not to be the case for elimination reactions with 5-centered transition states.[20] The basicity of the nucleophile in 5-centered eliminations (i.e. the O of sulfoxides, the N of sulfilimines, etc) has been offered as a means of explaining the relative reactivity of various functional groups, yet within a given functional group, e.g. sulfilimines, this comparison fails to provide a measure for the ease of reactivity. Qualitatively, the distance between the nucleophile and the β-hydrogen has been shown to follow the observed ease of reactivity of the Ei reactions. [20]

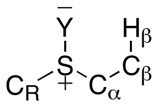
Our group recently considered the elimination reactions of sulfinate esters, sulfonate esters, and substituted sulfoxides.[21-24] Six-centered eliminations were predicted to be lower in energy than five-centered eliminations for sulfonate esters, while elimination of the sulfinate esters proceeds via a five-centered transition state. Placing silyl groups in either the C_α or C_β position lowers the activation enthalpy of the sulfoxide eliminations.[24]

Sulfilimines and *S,C*-sulfonium ylides have also been shown to undergo internal eliminations, but under milder conditions than sulfoxides. For example, as illustrated in Scheme 1, *N*-*t*Bu sulfilimines were shown to react with carbonyl compounds to produce α,β-unsaturated carbonyls, under much milder conditions (-78 ºC) than the related sulfoxide (100-150 ºC).[20, 25, 26] In general, sulfilimines with electron-withdrawing groups on the nitrogen atom and *S,C*-sulfonium ylides with electron-withdrawing substituents on the ylide carbon atom require higher temperatures for elimination than those with electron donating groups or hydrogen.[27, 28] Electron-withdrawing substituents effectively delocalize the negative charge on the ylide nitrogen or carbon, [20] making them easier to prepare and handle in the laboratory, but consequently also increase the activation barrier toward elimination reactions.[19] Alternatively, sulfilimines that have electron-withdrawing substituents on either the C_α or C_β position relative to the sulfur atom (Scheme 2) have been shown to proceed under milder conditions.[20] In certain cases sulfilimines have been shown to undergo β-eliminations with greater stereospecificity than sulfoxides. However, if carried out under sufficiently high temperatures (~80-100 ºC), the sulfur atom of sulfilimines is susceptible to pyramidal inversion thereby reducing the stereospecificity of the products.[29, 30]

Scheme 1



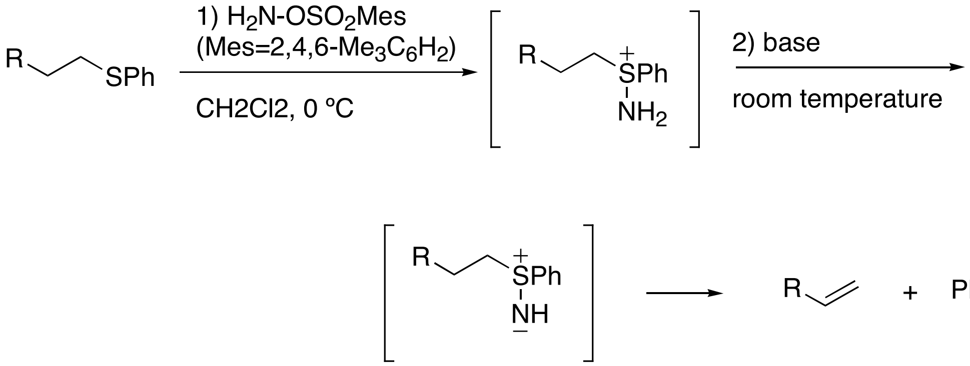
Scheme 2.



Y = O, NH, NCOH, NCH_3,
CH_2, CHCOH, $CHCH_3$

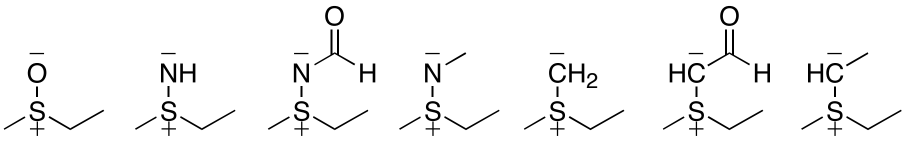
In a recent study *N*-H sulfilimines were prepared *in situ* and used at ambient temperatures to generate a variety of alkenes via *cis*-elimination reactions (Scheme 3).[27] These one-pot eliminations of *N*-H sulfilimines show greater stereoselectivity than *N*-Ts sulfilimine.

Scheme 3.



In this study we present the calculated activation barriers of 5-centered eliminations involving *N*-H sulfilimines and *S,C*-sulfonium ylides (Scheme 4). We compare the affects of electron-withdrawing versus electron-donating substituents on the N and C of the respective ylides.

Scheme 4.



1 **2** **3** **4** **5** **6** **7**

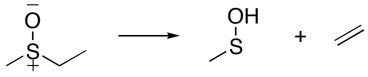
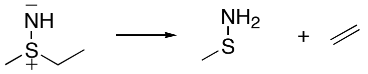
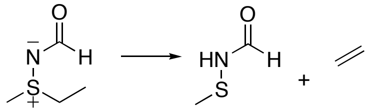
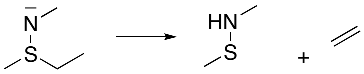
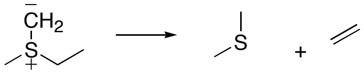
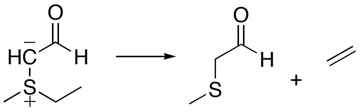
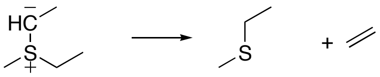
7.3 Computational details.

Spartan 1.0.4.e was used to perform low energy conformational searches using the PM3 semiempirical method for the starting materials and products. Initial transition state geometries were also located at this level of theory. All subsequent calculations were performed using GAMESS.[31] MacMolPlt 5.5, a graphical interface for GAMESS, was used to view all of the molecules and orbitals generated.[32] Hessians were performed at MP2/6-31G(d,p) to confirm the nature of the stationary points that were located and to provide zero point energy and 298.15K temperature corrections. Geometries were optimized at HF/6-31G(d,p) and then refined at MP2/6-31G(d,p). Finally, single point energies were obtained at the MP2/6-311++G(3df,2p)//MP2/6-31G(d,p) level. This level of theory has been shown to be able to reproduce the experimental activation energies for sulfoxide eliminations.[21] In addition, we have used this method in several studies to predict the activation enthalpies for various substituted sulfoxides, sulfinate esters, and sulfonate esters.[23, 24] The products were optimized as isolated molecules. The intrinsic reaction coordinates (IRC) were determined using the Gonzales-Schlegel second-order method.[33] IRC paths showed a connection between the transition state geometries and the starting material/products. Coordinates and absolute energies of the reactants, transition states, and products are provided in the supporting information.

7.4 Results and discussion.

The reactants, transition states, and products of the five-centered elimination reactions of ethyl methyl sulfoxide (**1**) and related sulfilimines (**2-4**), and *S,C*-sulfonium ylides (**5-7**) have been optimized at MP2/6-31G(d,p) and the energies have been refined at MP2/6-311++G(3df,2p). Our past success in using this method to model the elimination reactions of sulfoxides, sulfinate esters, and sulfonate esters prompted us to choose it for this study and thereby provides consistency between studies. The calculated reaction enthalpies (ΔH_{rxn}), activation enthalpies of the forward reaction ($\Delta H^{\ddagger}_{elim}$), and activation enthalpies of the reverse reaction ($\Delta H^{\ddagger}_{addn}$) are provided in Table 1. The Mulliken charges for the starting materials (**1-7**), transition states (**1TS-7TS**), and products are provided in Table 2. A smooth change in the charges progressing from the reactants to the products is observed, with no apparent maximum at the transition state. These results suggest that five-centered eliminations of sulfilimines and *S,C*-sulfonium ylides do not involve a highly charge separated transition state. The bond order indices of the bonds most affected by the elimination are provided in Table 3. The structure in Scheme 2 serves as a guide for the atom labels in Tables 2 and 3.

Table 1. Calculated ΔH_{rxn}, $\Delta H^{\ddagger}_{elim}$, and $\Delta H^{\ddagger}_{addn}$ values for **1-7**.[a]

MP2/6-311++G(3df,2p)	ΔH_{rxn}	$\Delta H^{\ddagger}_{elim}$	$\Delta H^{\ddagger}_{addn}$
 **1**	20.1	28.2	8.1
 **2**	-3.6	22.7	26.3
 **3**	-1.3	28.7	30.0
 **4**	-7.8	18.6	26.4
 **5**	-32.9	14.5	47.4
 **6**	-6.4	27.4	33.7
 **7**	-28.7	12.6	41.3

[a] All ΔH were determined from MP2/6-311++(3df,2p) energy runs performed at the MP2/6-31G(d,p) geometry, and include the unscaled ZPE and the 298.15K temperature correction.

Table 2. MP2/6-31G(d,p) calculated Mulliken charges of the reactants, transition states and products of the 5-centered elimination reactions of compounds **1-7**.

Compounds	**S**	**Y**	**H**	C_α	C_β
1	0.82	-0.67	0.16	-0.41	-0.36
1TS	0.55	-0.62	0.30	-0.29	-0.41
products	0.33	-0.62	0.35	-0.22	-0.22
2	0.64	-0.78	0.17	-0.38	-0.35
2TS	0.51	-0.70	0.19	-0.32	-0.37
products	0.20	-0.73	0.28	-0.22	-0.22
3	0.71	-0.62	0.18	-0.41	-0.35
3TS	0.52	-0.65	0.24	-0.29	-0.39
products	0.28	-0.64	0.31	-0.22	-0.22
4	0.68	-0.61	0.13	-0.42	-0.34
4TS	0.47	-0.61	0.19	-0.31	-0.37
products	0.21	-0.64	0.28	-0.22	-0.22
5	0.47	-0.56	0.13	-0.38	-0.34
5TS	0.37	-0.51	0.11	-0.33	-0.34
products	0.10	-0.46	0.15	-0.22	-0.22
6	0.52	-0.50	0.18	-0.37	-0.33
6TS	0.31	-0.45	0.12	-0.28	-0.33
products	0.13	-0.43	0.16	-0.22	-0.22
7	0.44	-0.41	0.13	-0.38	-0.34
7TS	0.36	-0.36	0.09	-0.33	-0.33
products	0.11	-0.34	0.13	-0.22	-0.22

Table 3. MP2/6-31G(d,p) calculated bond order indices for the reactants, transition states and products of the 5-centered elimination reactions of compounds **1**-**7**.

Compound(s)	S-Y	S-C$_{\alpha}$	C$_{\alpha}$-C$_{\beta}$	C$_{\beta}$-H	Y-H
1	1.41	0.78	0.93	0.92	-
1TS	1.08	0.42	1.30	0.43	0.41
products	0.82	-	1.85	-	0.83
2	1.35	0.76	0.93	0.91	-
2TS	1.12	0.42	1.21	0.56	0.34
products	0.89	-	1.85	-	0.87
3	1.05	0.81	0.92	0.91	-
3TS	1.01	0.47	1.24	0.51	0.34
products	0.87	-	1.85	-	0.83
4	1.35	0.74	0.92	0.93	-
4TS	1.10	0.40	1.21	0.56	0.34
products	0.88	-	1.85	-	0.86
5	1.35	0.69	0.93	0.92	-
5TS	1.18	0.37	1.14	0.67	0.26
products	0.91	-	1.85	-	0.92
6	1.08	0.81	0.93	0.92	-
6TS	1.07	0.34	1.25	0.55	0.34
products	0.90	-	1.85	-	0.91
7	1.37	0.68	0.93	0.93	-
7TS	1.19	0.34	1.11	0.72	0.22
products	0.91	-	1.85	-	0.92

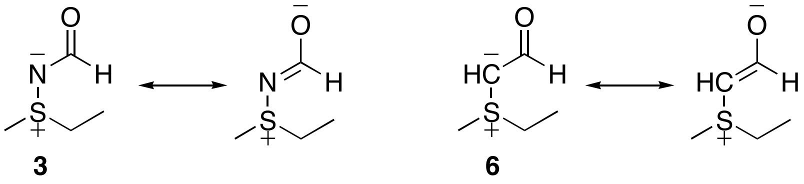
The five-centered elimination of ethyl methyl sulfoxide was estimated at the MP2/6-311++G(3df,2p) level of theory to have a positive $\Delta H_{rxn,}$ while the β-elimination of all sulfilimines and *S,C*-sulfonium ylides was calculated to be exothermic. Ylides **5** and **7** had the most exothermic elimination reactions with energies 53 kcal/mol and 49 kcal/mol lower than the analogous sulfoxide respectively. The calculated values for $\Delta H^{\ddagger}_{elim}$ roughly follow the order observed for the reaction enthalpies. Again, the lowest activation barriers were for compounds **5** and **7**, followed by **2** and **4**. The activation barriers for **1**,**3**, and **6** were all within one kcal/mol of each other. The calculated activation barriers are consistent with the experimental observation that sulfilimine eliminations proceed under milder conditions than sulfoxides and that sulfilmines that have electron-withdrawing substituents require higher temperatures.

The delocalization of charge afforded by the electron-withdrawing groups can be recognized in both the bond order indices and the Mulliken charges of compounds **3** and **6** (Table 4, Scheme 5). Prior to elimination, there is a charge maximum on the oxygen atom of the carbonyl. Additionally, the carbonyl bond has a relatively weak bond order while the nitrogen-carbonyl carbon bond of **3** and the carbon-carbonyl carbon bond of **6** are relatively strong. As the elimination proceeds, there is a gradual increase in the bond order indices of the carbonyls of **3** and **6**. The increase in bond order is less dramatic for **3** than for **6** upon elimination, presumably because the amide product of the β-elimination of **3** can also be stabilized by resonance.

Table 4. MP2/6-31G(d,p) calculated Mulliken charges of the formyl substituent in compounds **3** and **6.**

	Mulliken Charges		**Bond Order Indices**	
Compound(s)	$C_{c=o}$	**O**	**Y-**$C_{c=o}$	$C_{c=o}$**-O**
3	0.31	-0.49	1.22	1.63
3TS	0.37	-0.44	1.07	1.74
Products	0.41	-0.43	0.99	1.80
6	0.27	-0.52	1.20	1.59
6TS	0.29	-0.43	0.98	1.73
Products	0.28	-0.37	0.88	1.81

Scheme 5.



A comparison of the charges on the ylidic oxygen, carbon, and nitrogen of the compounds shows the following order **2** > **1** > **3** > **4** > **5** > **6** > **7**, where **2** has the greatest negative charge. For both the sulfilimine and the *S,C*-sulfonium ylide, the hydrogen substituted ylide has a more negative charge than the formyl substituted ylide. The smaller charge on the formyl substituent is likely a consequence of the resonance stabilization of compounds **3** and **6,** which effectively reduces the nucleophilicity of the nitrogen atom and carbon atom respectively in the elimination reaction.

Intrinsic reaction coordinate (IRC) calculations were performed on compounds **1, 2,** and **5,** and are currently being obtained for the remaining ylides. IRCs can be used to monitor the bond breaking and bond forming as a function of the reaction coordinate. The IRC for compound **5** is provided in Figure 1. From the plot, it can be seen that the S-C_α bond breaking is more advanced than the C_β-H bond breaking. Shortly after the S-C_α bond breaking begins, the C_α–C_β bond begins to strengthen and the S-C ylide bond weakens.

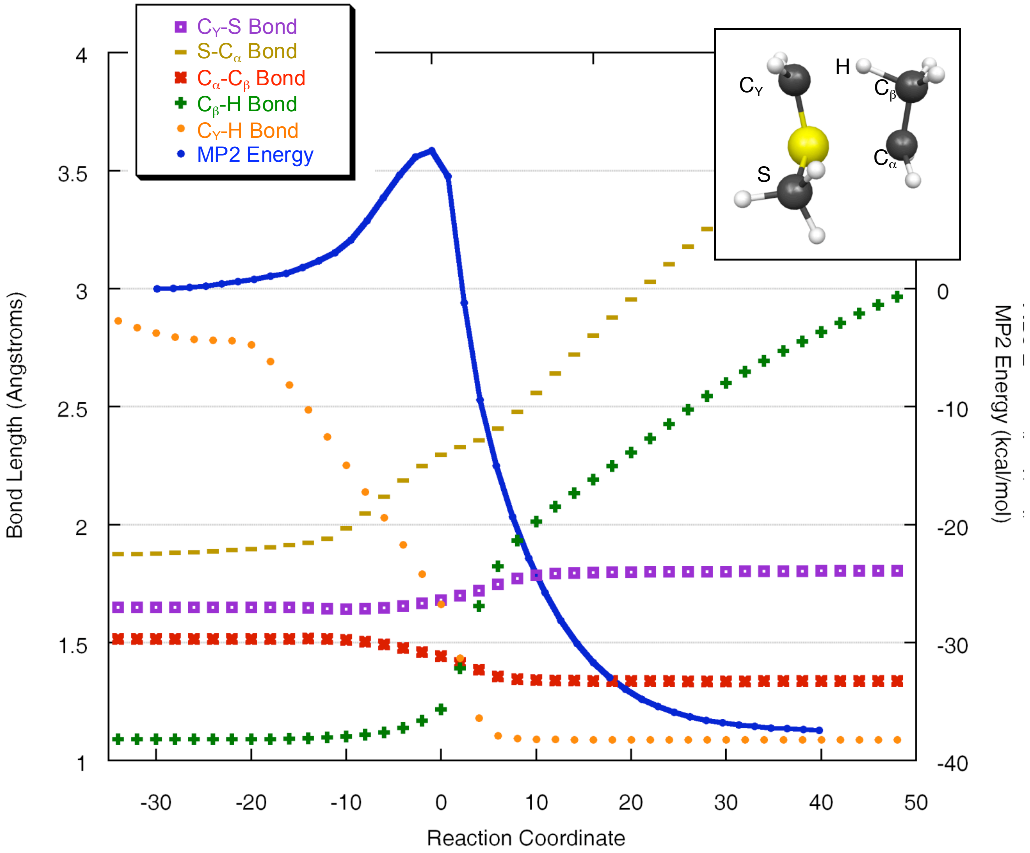


Figure 1. IRC calculation for the elimination of **5** at MP2/6-31G(d). The insert on the top right shows the transition state structure of **5**.

The leaving group ability of a particular functional group is indicated by both the activation barrier of the elimination reaction and the advancement of the S-C_α bond breaking. Compound **7** has both the smallest activation barrier and the most advance S-C_α bond breaking at the transition state, indicating that it is a relatively good leaving group. Following **7** are the other two *S,C*-sulfonium ylides, then the sulfilimines without an electron-withdrawing group (**2** and **4)**. From the Mulliken charges of the reactants it should be noted that *S,C*-sulfonium ylides **5** and **7** have the weakest S-C_α bonds at the onset of the reaction. They are followed by the analogous sulfilimines, **2** and **4**.

The reverse addition reaction can also be used to understand the factors influencing the ease of the Ei reaction. The lowest barrier to the addition reaction is that of sulfoxide **1** at only 8 kcal/mol. The barriers to the back reaction forming sulfilimines **2-4** range from 26-30 kcal/mol and forming *S,C*-sulfonium ylides **5-7** range from 34-47 kcal/mol. Compounds **5** and **7** have the highest barriers to the addition reaction, which is indicative of the stability of the elimination products and contributes to the exothermicity of the forward elimination reaction. We can also consider the strength of the Y-H bond that is formed upon elimination as a measure of product stability. The *S*,*C*-sulfonium ylides form the strongest bond with the transferred β-hydrogen, followed by sulfilimines **2** and **4**, and lastly **3** and **1**.

7.5 Summary and conclusions

MP2 calculations were performed in this study to gain a better understanding of the factors that influence the *cis*-elimination of sulfoxides, sulfilimines, and *S*,*C*-sulfonium ylides. The reaction enthalpies of compounds **1**-**7** show all but the sulfoxide to undergo exothermic β-elimination reactions. These results can be attributed to the relatively low activation barriers that the *S,C*-sulfonium ylides have. The magnitude of the activation barrier appears to be, in part, affected by the S-C_α bond strength, particularly since the breaking of this bond is the most advanced process in these eliminations. In addition to the relatively weak S-C_α bond, *S,C*-sulfonium ylides have the advantage of producing especially stable products, leading to a higher activation barrier for the reverse reaction, unlike sulfoxides and ylides with electron-withdrawing substituents. Reactants in which electron-withdrawing substituents are bound to the ylide have more positive reaction enthalpies than those with electron-donating substituents or hydrogen attached. Apparently the resonance stabilize that makes these compounds easy to prepare and handle in the lab inherently reduces the ease with which such compounds undergo elimination reactions. Therefore, while electron-withdrawing substituents on the C_α and C_β carbons enhance the reactivity of ylides, they reduce the reactivity if attached to the ylide itself. Though there are currently few reports of elimination reactions of *S,C*-sulfonium ylides our results suggest that such reactions should also be feasible under as mild of conditions as the related sulfilimines, if not milder. Further studies are underway to gain an understanding of which processes are most advanced for sulfilimines **3-4** and sulfonium ylides **6-7**, and to compare those compounds with the mesyl derivatives, for which there are experimental data.

7.6 Acknowledgement.

We thank the National Science Foundation for support of this research.

7.7 Supporting information description

Coordinates and absolute energies of compounds **1-7**, their transition states, and products of elimination are provided.

7.8 References

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CHAPTER 8

General conclusions

Since the early 1970's when the deoxygenation of sulfoxides was first observed by Shelton, Davis, and Posner[1, 2], studies have been aimed at elucidating the mechanism by which this photoprocess occurs.[3-10] At present, the most compelling evidence is in favor of a unimolecular S-O bond scission that results in the formation of O(^{3}P) and a sulfide. The studies described in this dissertation offer additional support for the proposed unimolecular bond cleavage and new insights into the process.

We now have substantial evidence that analogues of sulfoxides, namely *N*-substituted sulfilimines and *S,C*-sulfonium ylides of dibenzothiophene, all undergo unimolecular cleavage of the ylide bond upon photolysis. Direct evidence for the formation of nitrenes from sulfilimines has been established by means of time resolved IR spectroscopy.[11] We provide indirect evidence for the formation of carbenes from *S,C*-sulfonium ylides in Chapter 4 by means of chemical trapping studies. Dicarbomethoxycarbene-like reactivity is observed upon the photolysis of dimethyl malonate ylides of thiophene derivatives. The quantum yields of ylide bond cleavage are higher for sulfilimines and *S,C*-sulfonium ylides than for dibenzothiophene-*S*-oxide. The observed ylide bond cleavage of sulfilimines and S,C-sulfonium yildes supports the proposed unimolecular S-O bond cleavage of dibenzothiophene-*S*-oxide and its selenium-containing analogue.

Although the size of dibenzothiophene-*S*-oxide does not permit rigorous electronic structure calculations at the CASSCF level with a relatively large active space and basis set at this time, the deoxygenation of smaller systems has been modeled in order to gain a clearer understanding of which excited states are involved in the deoxygenation process. In Chapter 5, the potential energy surfaces of thiophene-*S*-oxide and selenophene-*Se*-oxide deoxygenation provide new insights into the observed photochemistry of dibenzothiophene-*S*-oxide. Of the first four electronic states of the modeled sulfoxides, the two lowest triplet states dissociate to the corresponding sulfide and O(^{3}P) upon S-O elongation. While the T_1 state must cross a sizeable energy barrier in order to dissociate to the products, the T_2 state provides a nearly barrierless pathway to product formation. Therefore, upon photoexcitation to the excited sulfoxide singlet state, intersystem crossing to the lower lying triplet state provides an energetically feasible means of arriving at the product sulfide and $O(^3P)$, which is yet another convincing piece of evidence in favor of the proposed unimolecular bond cleavage of sulfoxides. These results are consistent with the enhanced quantum efficiency of dibenzoselenophene-*Se*-oxide and heavy-atom substituted dibenzothiophene-*S*-oxide relative to dibenzothiophene-S-oxide for which intersystem crossing events are more probable.

Although there is limited experimental data regarding the bond strengths of various sulfoxides, in Chapter 6 we explored several computational methods and basis sets in an effort to determine which provide the most accurate estimates for the bond dissociation energies (BDEs) of a range of sulfoxides. Using four sulfoxides for which the BDEs are known, we find that by averaging the data from multiple computational methods provides the most accurate values for sulfoxide bond strengths. We then applied this empirical method to a wide range of sulfoxides in order to gain insight into the factors that stabilize sulfur ylides. The BDEs of sulfur ylides are largely affected by the structure type (i.e. sulfoxide, *S,C*-sulfonium ylide, sulfilmine, or selenoxide) and aromaticity. Among the four structure types, sulfoxides have the strongest BDEs, selenoxides are about 10 kcal/mol weaker than the corresponding sulfoxides, and sulfilimines and *S,C*-sulfonium ylides are weaker yet. Sulfur and selenium ylides for which the S or Se is incorporated into a thiophene or selenophene-type ring have relatively weak bond strengths due to the gain in aromaticity that comes with scission of the ylide bond.

Finally in Chapter 7 we have provided insights into the energetics of the thermal elimination reactions of sulfoxides, *S,C*-sulfonium ylides, and sulfilimines. The elimination reactions of each have been modeled and shown to proceed through 5-centered transition states. Among the three structure types, sulfilimines and *S,C*-sulfonium ylides have been shown experimentally to occur under milder conditions than sulfoxides. However electron-withdrawing groups on the N of sulfilimines or the C of *S,C*-sulfonium ylides reduces the ease with which the eliminations occur. Intrinsic reaction coordinates for the elimination reactions of all three provide information regarding which processes are the most advanced and suggest that the ease of S-Cα bond breaking (see Scheme 7.1) and product stability have a large effect on the activation energies of these ylides.

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APPENDIX A

Supporting information for Chapter 2

Figure S1. Typical HPLC chromatograms of cleavage reaction mixtures. Separation of the cleaved fragments was achieved by use of a C18 analytical column. Cleavage of Pro-Met peptide promoted by *cis*-$[Pd(CH_3SCH_2CH_2CH_2SCH_3)(H_2O)_2]^{2+}$ at pH 2.0 at 60°C for (a) 0 , (b) 5, (c) 15, and (d) 24hrs.

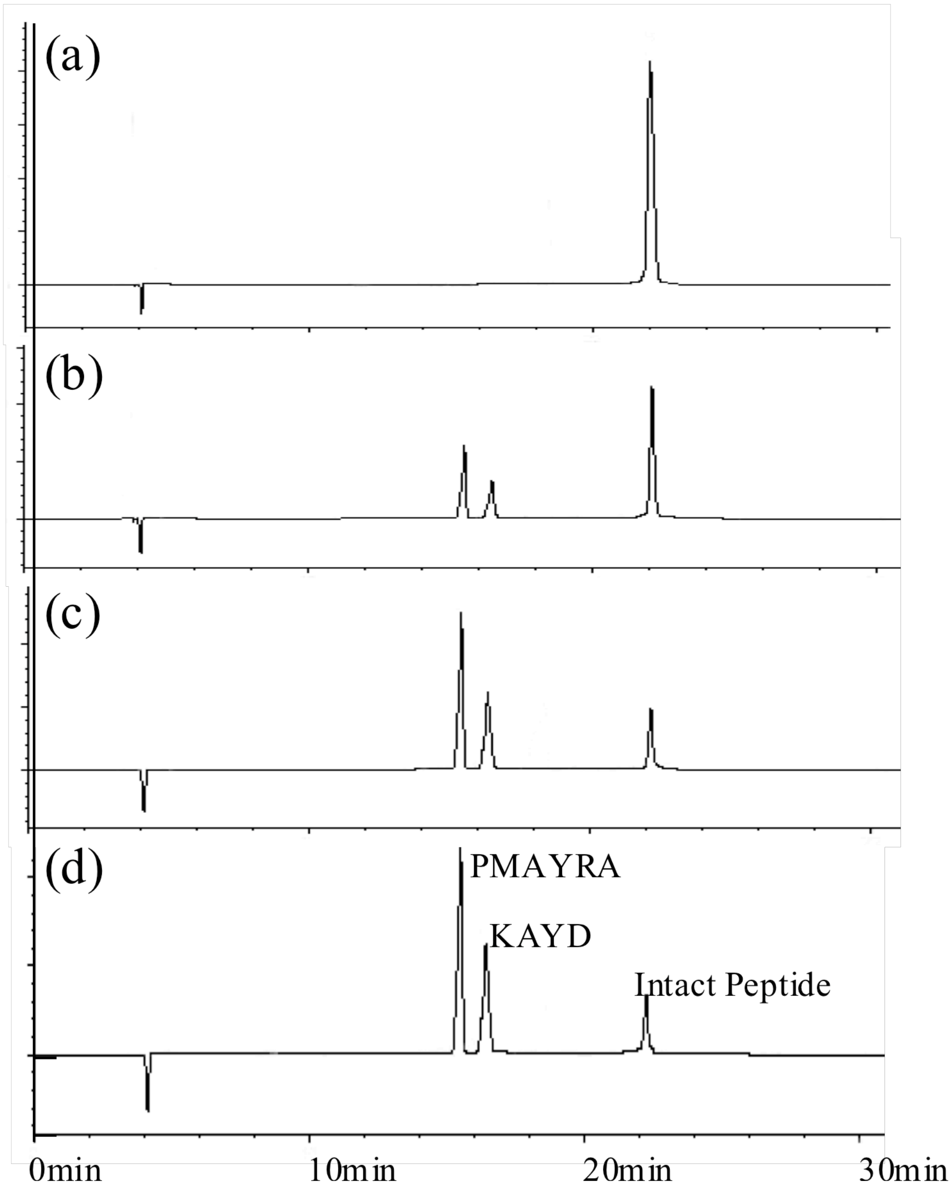


Figure S2. ^{1}H NMR spectra of *cis*-[Pd($CH_3SCH_2CH_2CH_2SCH_3$)(H_2O)$_2$](ClO_4)$_2$. The spectra were obtained at three different temperatures and indicate the presence of two configurational isomers interconverting at room temperature.

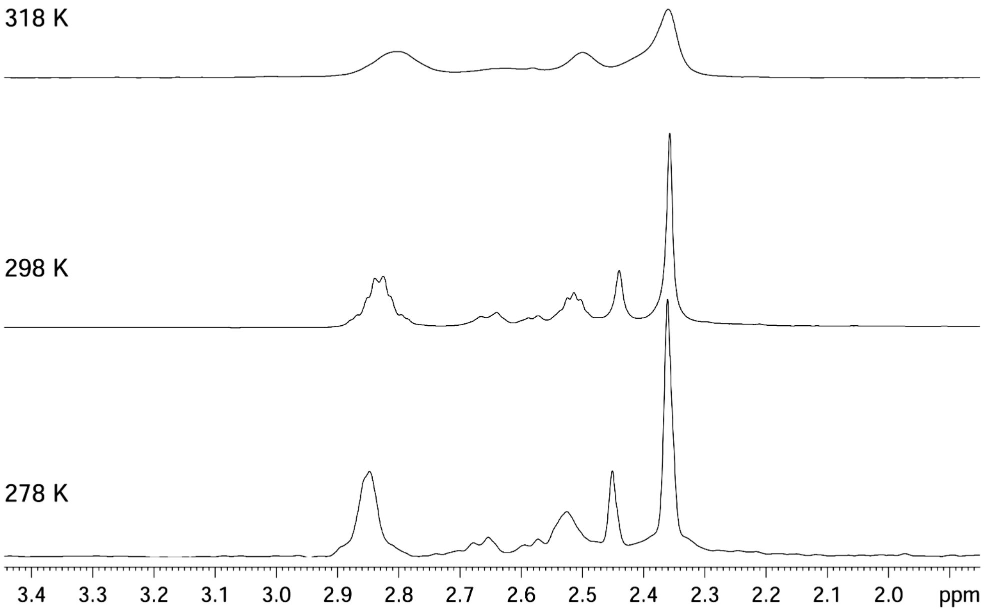


Figure S3. ^{1}H NMR spectrum of *cis*-[Pt($CH_3SCH_2CH_2CH_2SCH_3$)(H_2O)$_2$](ClO_4)$_2$. The spectra were obtained at three different temperatures and indicate the presence of two configurational isomers interconverting at room temperature.

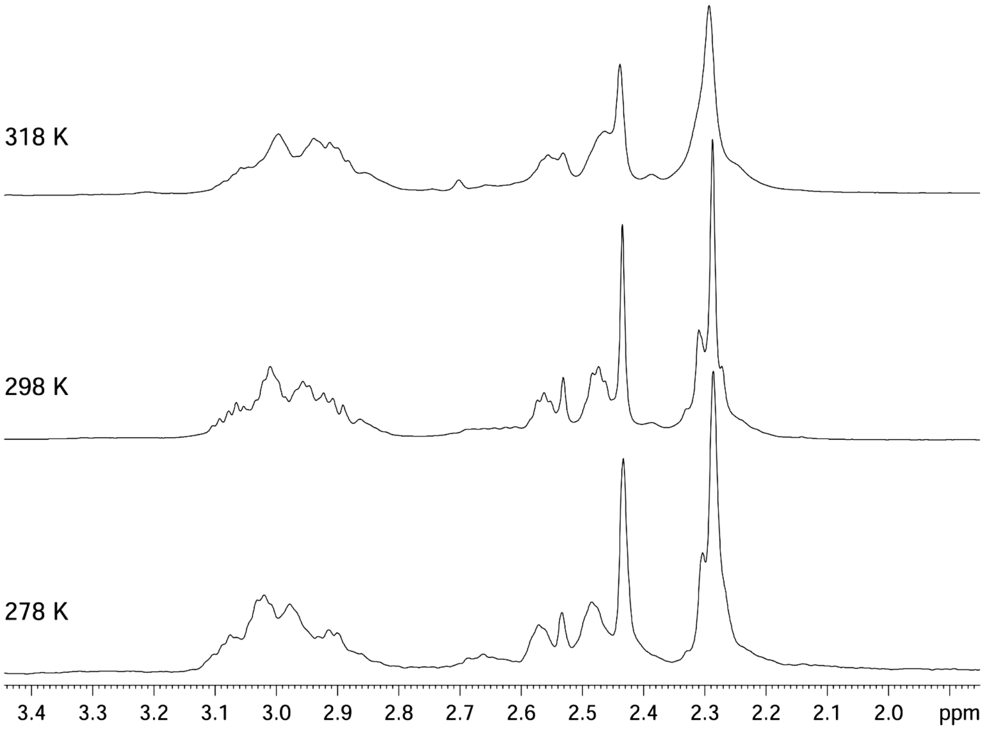


Figure S4. ROESY ^{1}H NMR spectrum of Met-Ala peptide used for the assignment of each residue in the peptide.

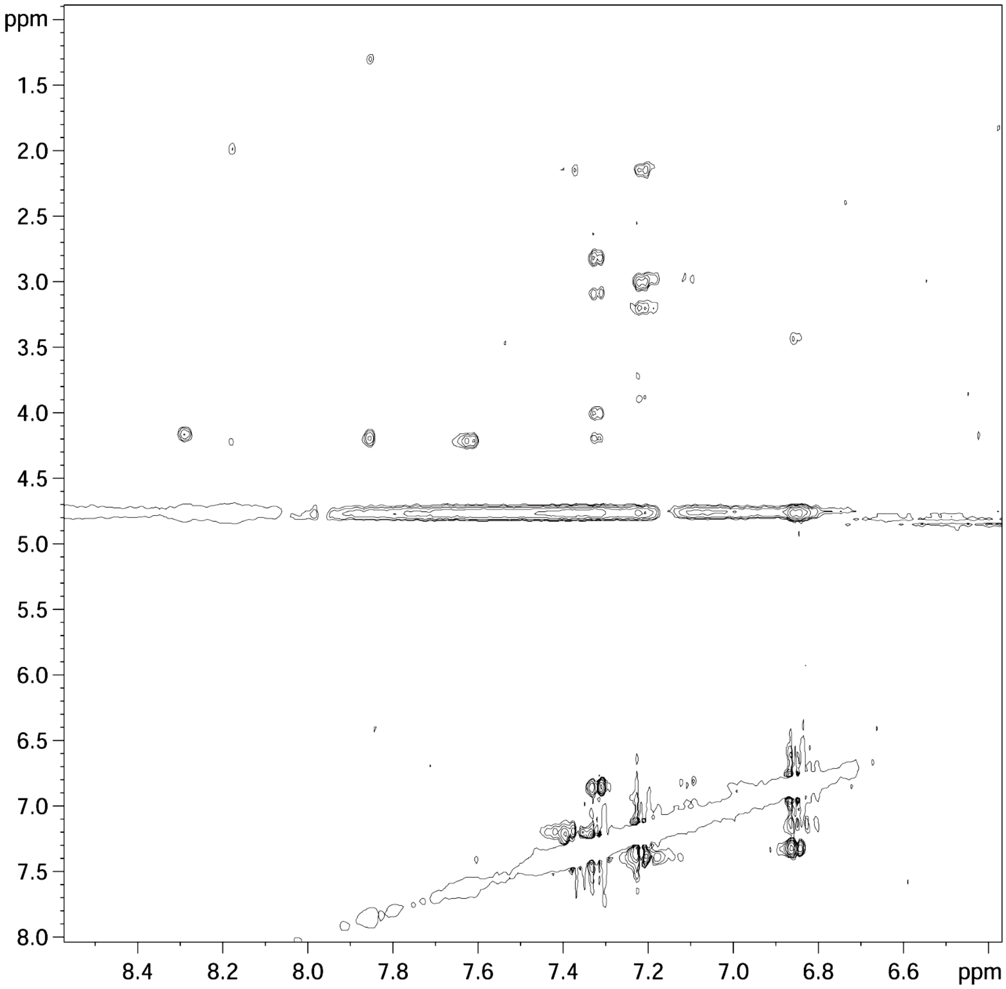
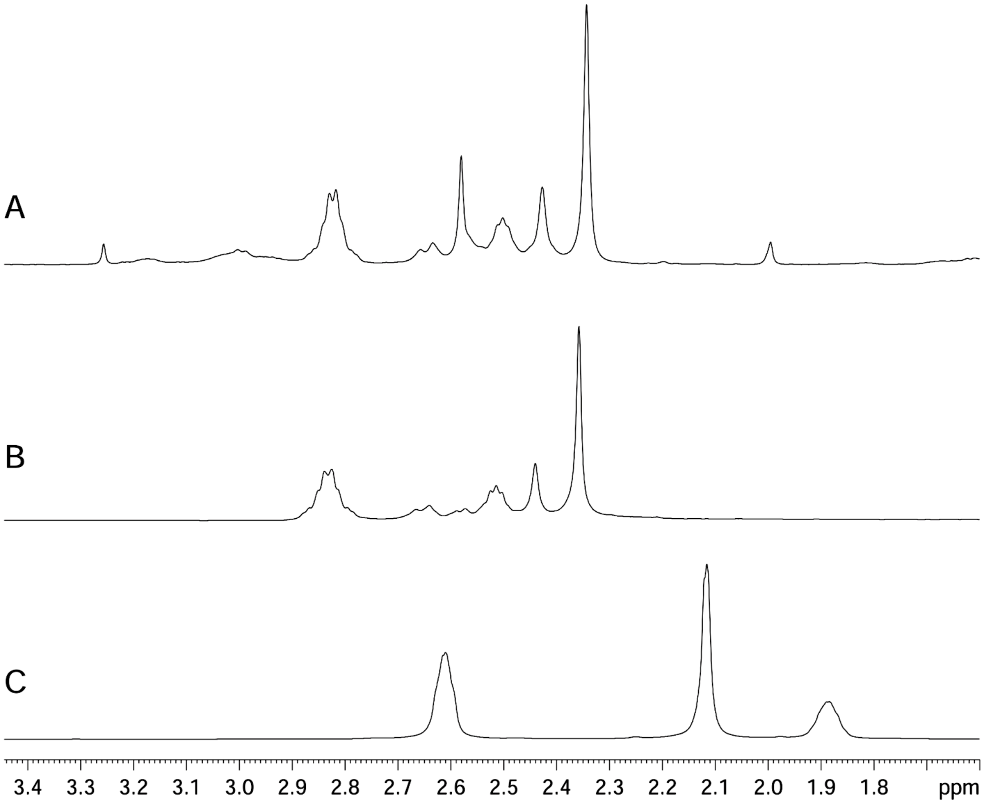


Figure S5. ^{1}H NMR spectra of (a) the cleavage reaction mixture of Met-Ala peptide with *cis*-[Pd($CH_3SCH_2CH_2CH_2SCH_3$)(H_2O)$_2$](ClO_4)$_2$ after 24 hours of incubation at 60ºC, (b) *cis*-[Pd($CH_3SCH_2CH_2CH_2SCH_3$)(H_2O)$_2$](ClO_4)$_2$, and (c) $CH_3SCH_2CH_2CH_2SCH_3$. The spectra are aligned to indicate the absence of the free dithioether ligand in the cleavage reaction mixture.



APPENDIX B

Supporting information for Chapter 4

Preparation and characterization of *S,C*-sulfonium ylides.

Preparation of *p*-toluenesulfonyl azide.[1]

In a 250 mL round bottomed flask sodium azide (7.2 g, 0.11 mol) was dissolved in a solution of acetone (50 mL) and water (30 mL). In a 100 mL round bottomed flask *p*-toluenesulfonyl chloride (19 g, 0.11 mol) was dissolved in acetone (50 mL). The tosyl chloride solution was then added slowly to the sodium azide solution and allowed to stir for 2 hours at room temperature. The acetone was removed under vacuum from the solution and 20 mL of dichloromethane was added. The aqueous layer was removed and the organic layer was washed two times with 20 mL of water, dried with magnesium sulfate, and filtered through a glass frit. The methylene chloride was removed under vacuum leaving *p*-toluenesulfonyl azide, a yellow oil. Yield: 86% (17 g). FW=197.2 g/mol. d= 1.26g/ml. ^{1}H NMR ($CDCl_3$) δ: 2.48 (s, 3H), 7.41 (d, J=8.2, 2H), and 7.84 (d, J=8.2, 2H). IR(cm^{-1}): 2126.38 (sh), 1172.74 (sh).

Figure S1. ^{1}H-NMR *p*-toluenesulfonyl azide.
Solvent: deuterated chloroform.

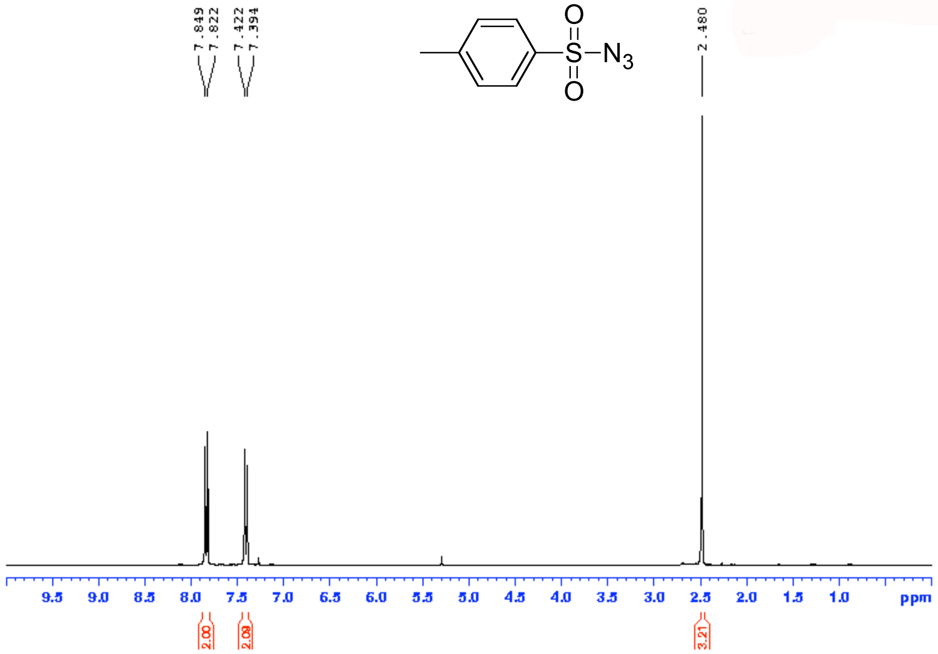
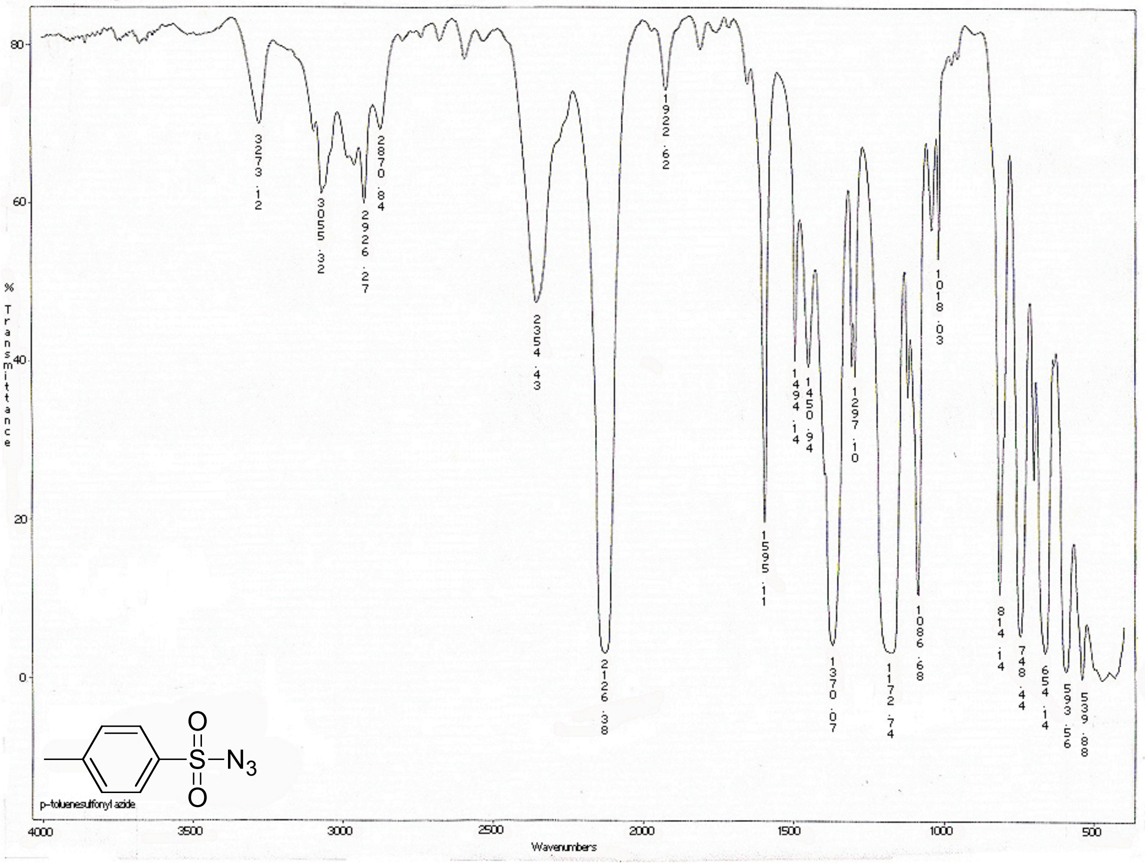


Figure S2. IR *p*-toluenesulfonyl azide.



Preparation of dimethyl diazomalonate.[2]

To a flame-dried 50mL round bottomed flask triethylamine (1.96 mL), dimethyl malonate (1.61 mL), and *p*-toluenesulfonyl azide (2.1 mL, 0.01 mol) were added under an argon atmosphere. Dry benzene (12 mL) was stirred into the mixture. After standing 15 hours, a white precipitate was removed from the mixture by filtration and washed with cold benzene. The filtrate was dried under vacuum, yielding a yellow-orange oil. Hexane (25 mL) was added to precipitate any remaining tosyl amine. The solution was then filtered and dried under vacuum. The resulting oil was distilled with a short path distillation apparatus in vacuo to obtain dimethyl diazomalonate as a clear yellow oil. Yield: 65% (5.1 g). FW=158.1 g/mol d=1.34g/ml. Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.82 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 41.0, 52.5, 161.4. IR (cm^{-1}) 2139.44 (sh), 1756.71 (sh), 1693.98 (sh). GCMS: Calc. 158 g/mol. Found 159 (M+1), 127 (M-OCH_3).

Figure S3. ^{1}H-NMR dimethyldiazomalonate.
Solvent: deuterated chloroform.

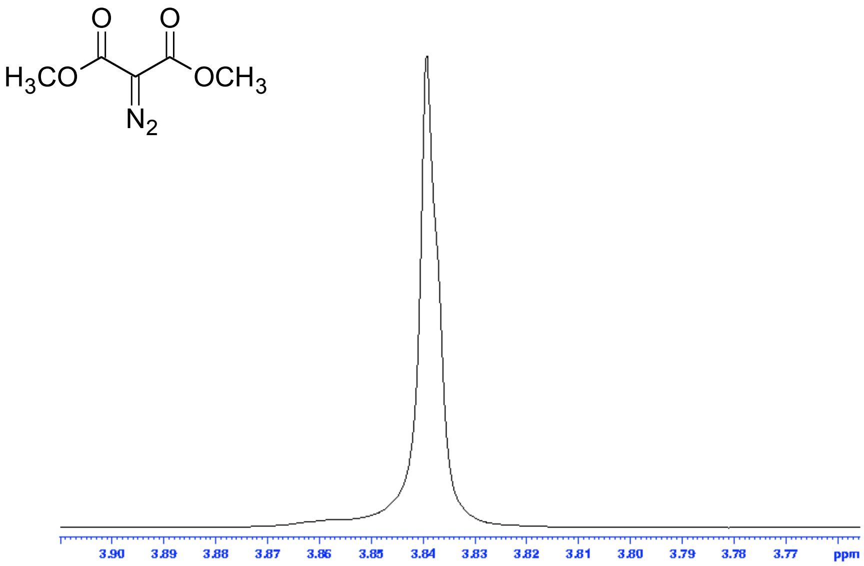


Figure S4. ^{13}C-NMR dimethyldiazomalonate.
Solvent: deuterated chloroform.

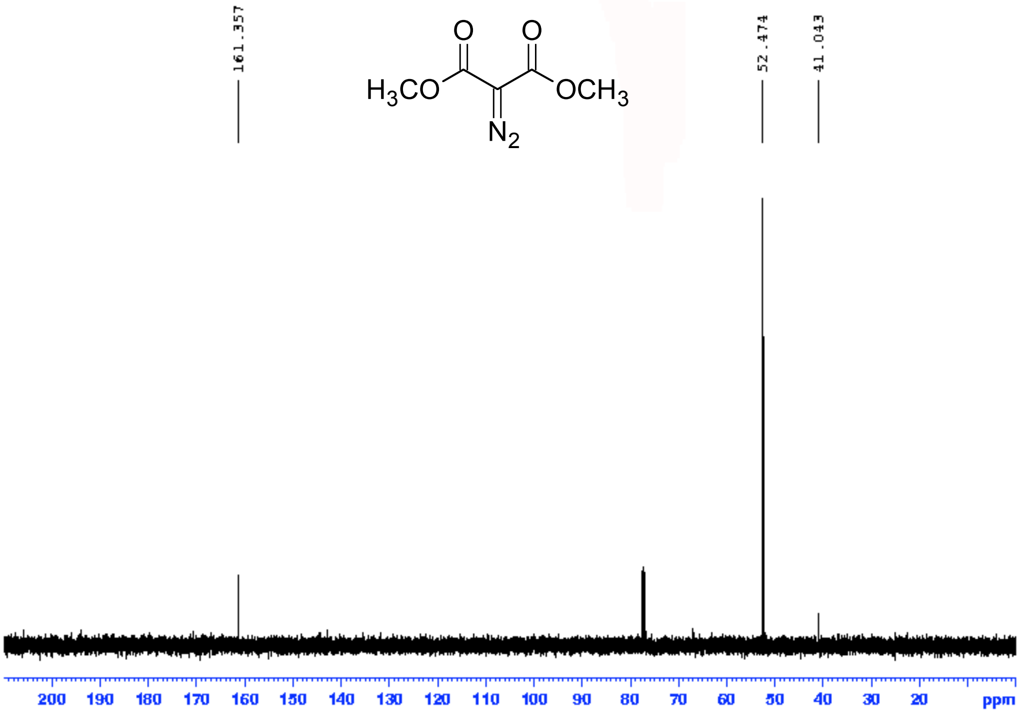


Figure S5. IR dimethyldiazomalonate.

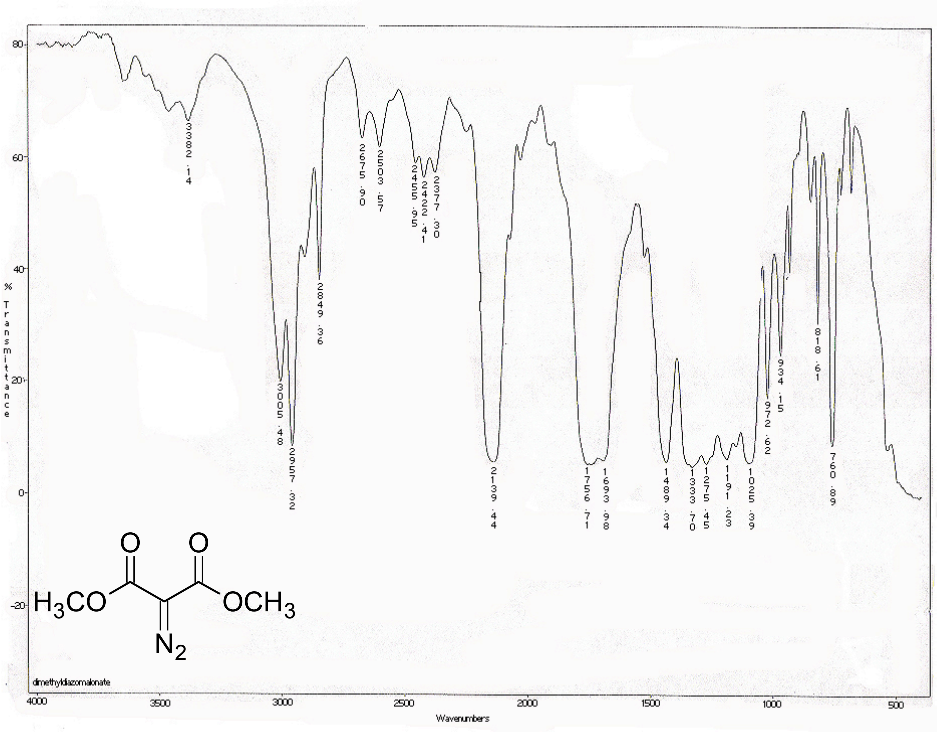
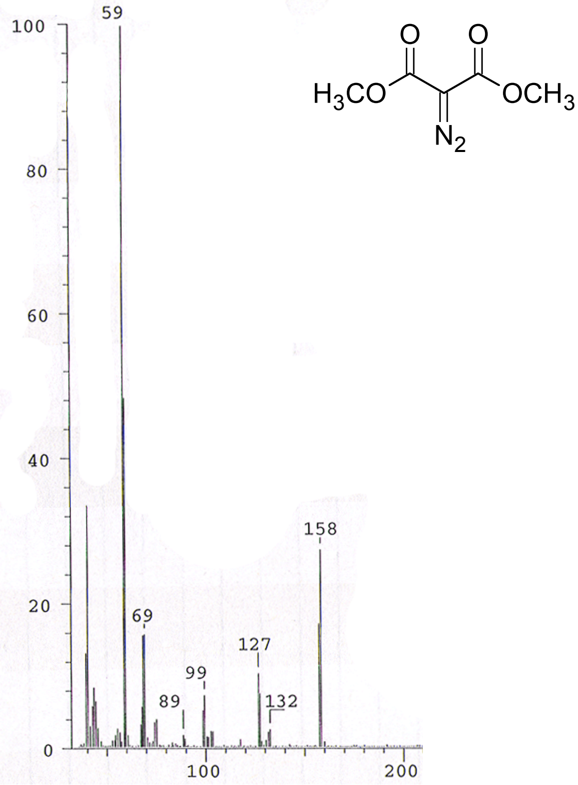


Figure S6. EI-MS dimethyldiazomalonate.
Retention time: 3.4 min.



Preparation of methyl phenyl sulfonium bismethoxycarbonylmethylide (1).

To a 100mL round bottomed flask, dimethyl diazomalonate (0.64 mL, 0.005 mol), freshly distilled thioanisole (2.71mL, 0.023mol), and anhydrous cupric sulfate (16 mg), were added while stirring. The solution was flushed with argon for five minutes and then refluxed between 95°C and 115°C for 48 hours. The progress of the reaction was monitored by TLC 75% hexane: 25% ethyl acetate. Following the reflux, chloroform was added to the mixture and the solution was filtered. The solvent was removed under vacuum and the crude product was recrystalized from ethanol. FW=254.30 g/mol. Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.28 (s, 3H), 3.71 (s, 6H), 7.49-7.51 (m, 3H), 7.62-7.63 (m, 3H). ^{13}C NMR ($CDCl_3$) δ: 27.4, 51.2, 59.6, 127.0, 129.8, 131.0, 132.6, 167.0. IR (cm^{-1}) : 3054(sh), 2987(sh), 2305(sh), 1717(sh), 1682(sh), 1641(sh). EI-MS: Calc. 254 g/mol. Found 254 (M), 222 (M-OCH_3), 194 (M-CO_2CH_3).

Figure S7. ^{1}H NMR methyl phenyl sulfonium biscarbomethoxymethylide.
Solvent: deuterated chloroform.

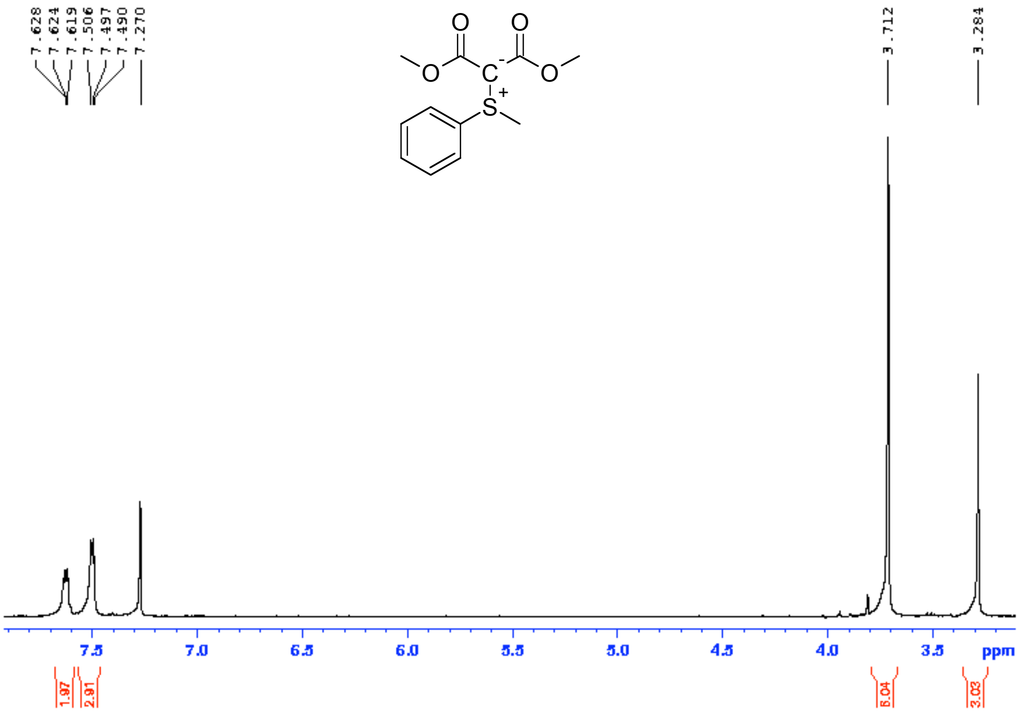


Figure S8. ^{13}C NMR methyl phenyl sulfonium biscarbomethoxymethylide. Solvent: deuterated chloroform.

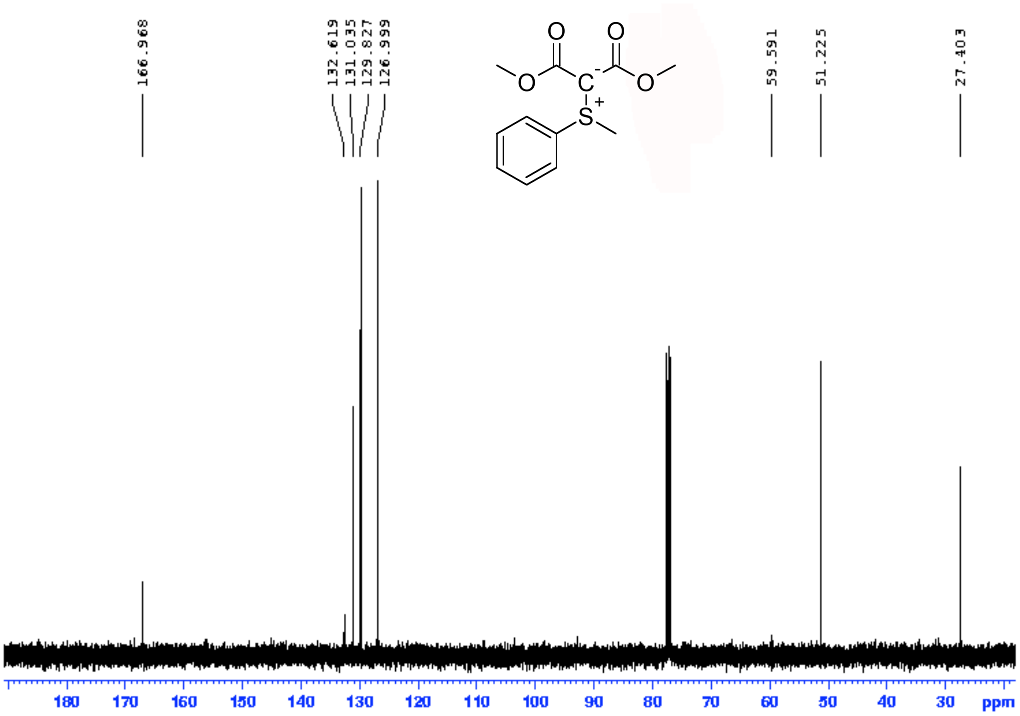


Figure S9. IR methyl phenyl sulfonium biscarbomethoxymethylide.

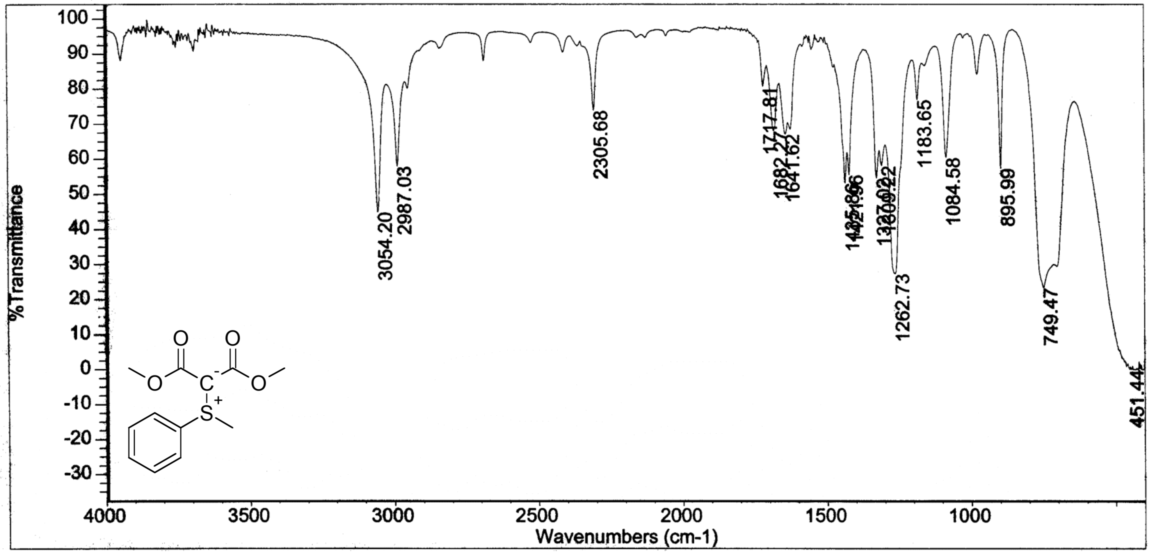
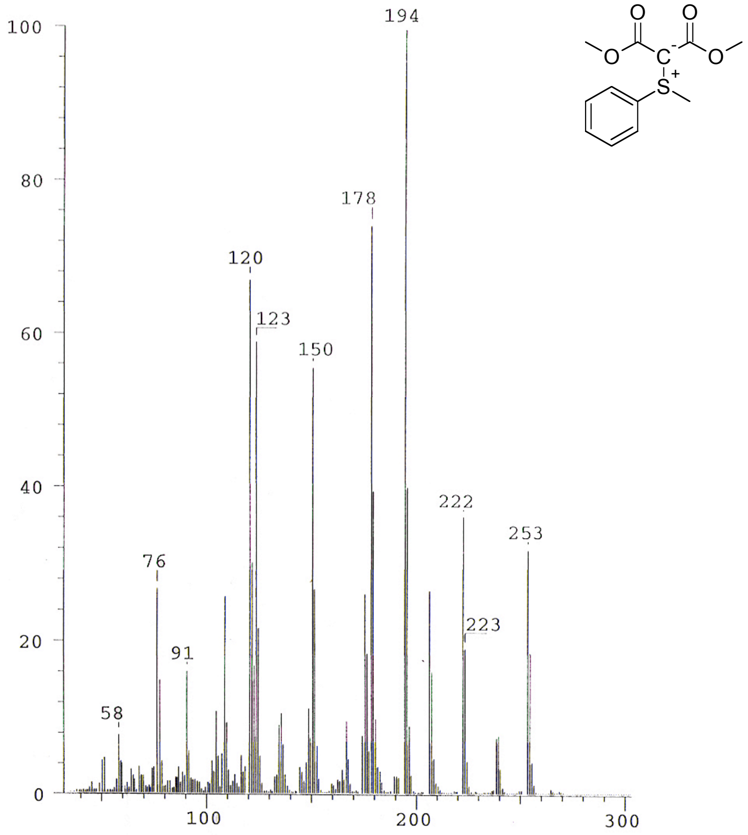


Figure S10. EI-MS-methyl phenyl sulfonium biscarbomethoxymethylide.
Retention Time: 16.5 min.



Preparation of thiophenium bismethoxycarbonylmethylide (2).[3]

To a 50 mL round bottomed flask, dimethyl diazomalonate (0.59 mL), freshly distilled thiophene (2.00mL), and rhodium acetate (2 mg) were added under an argon atmosphere. The mixture was stirred for 2 days and the precipitate was collected by filtration. The crude product was recrystalized from methanol to yield the pure title compound, a white solid. Yield: 87% (1.07g). FW=214.24 g/mol Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.70 (s, 6H), 6.98 (d, J=6.3, 2H) 7.21 (d, J=6.3, 2H). ^{13}C NMR ($CDCl_3$) δ: 50.2, 51.7, 131.2, 133.9, 165.9. IR (cm^{-1}): 3019.04 (sh), 2400.06 (sh), 1680.87 (sh), 1653.68 (sh). UV/vis maxima: 325nm (ε=151.9M^{-1}cm^{-1} ± 3.5) and 215nm. EI-MS: Calc. 214 g/mol. Found. 214 (M), 183 (M-OCH_3), 152 (M-OCH_3 x 2), 84 (M-$C_5O_4H_6$).

Figure S11. ^{1}H NMR thiophenium biscarbomethoxymethylide.
Solvent: deuterated chloroform.

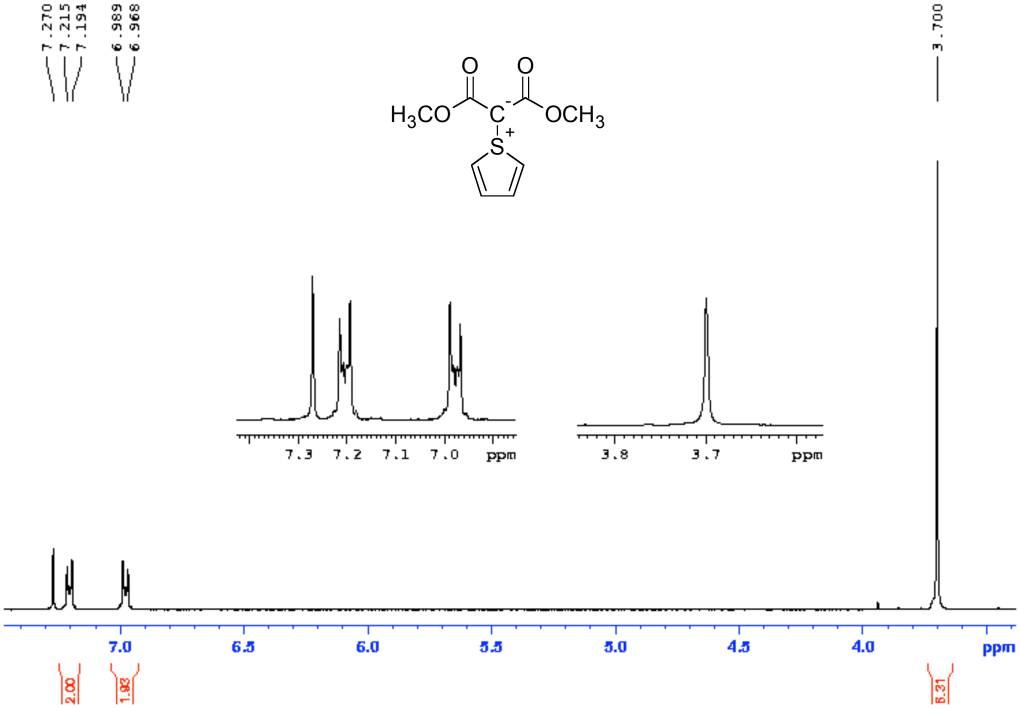


Figure S12. ^{13}C NMR-thiophenium biscarbomethoxymethylide.
Solvent: deuterated chloroform.

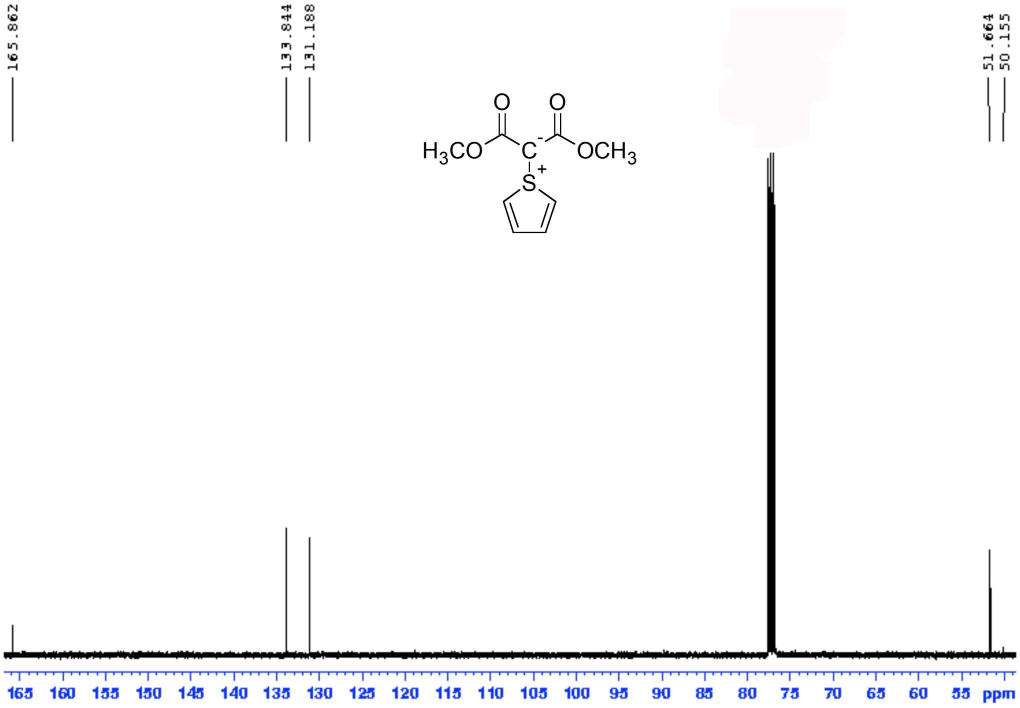


Figure S13. IR thiophenium biscarbomethoxymethylide.

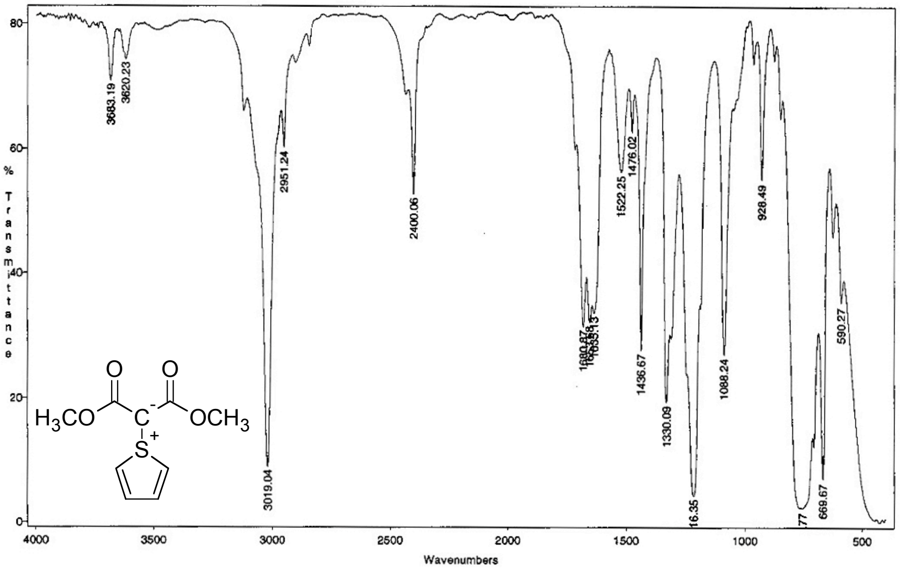


Figure S14. EI-MS thiophenium biscarbomethoxymethylide.
Retention time: 9.0 min.

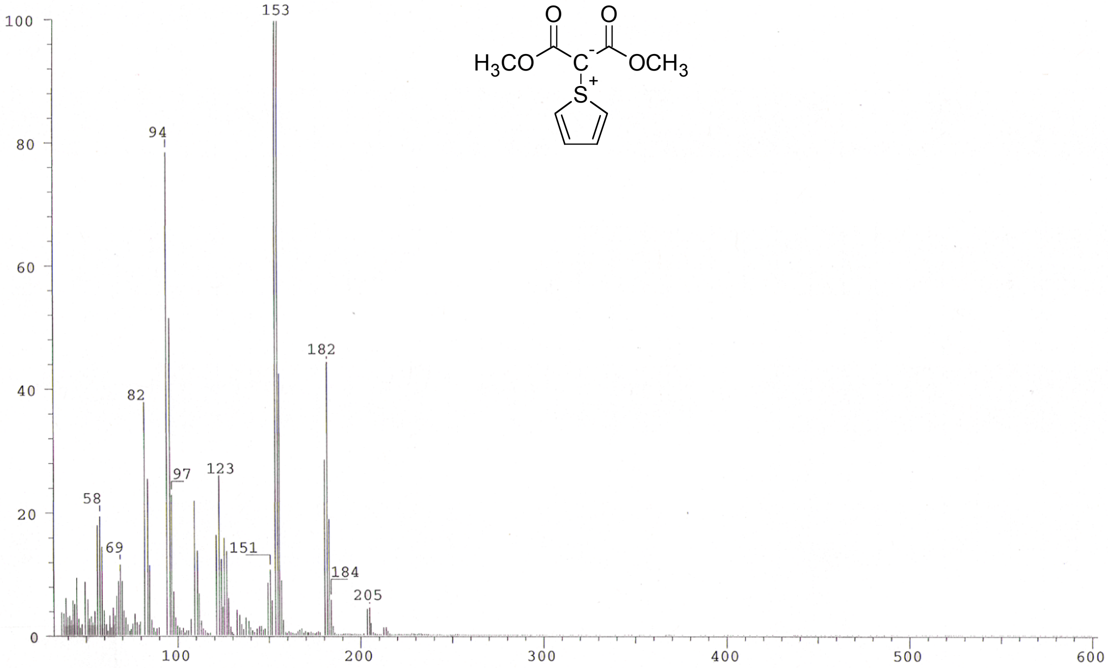
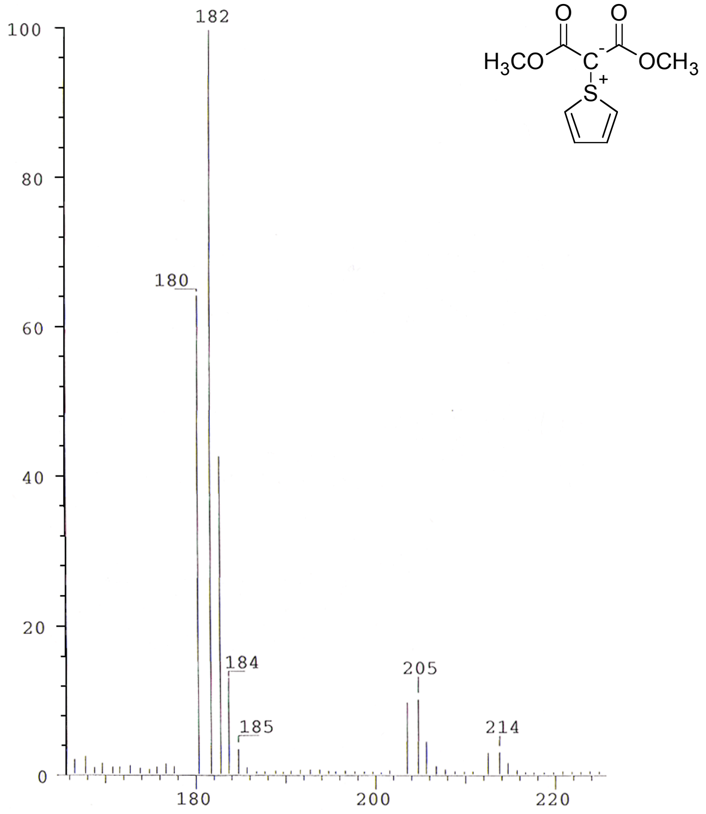


Figure S15. EI-MS thiophenium biscarbomethoxymethylide.



Preparation of benzothiophenium bismethoxycarbonylmethylide (3).[4]

To a 50mL round bottomed flask, benzothiophene (3.729 g, 0.025 mol), dimethyl diazomalonate (0.59 mL, 0.005 mol), rhodium acetate dihydrate (2 mg), and 1,2-dichloroethane (4 mL) were added under an argon atmosphere. The reactants were stirred for 36 hours at which time the mixture was a milky green color. The solvent was then removed under vacuum and hexane (20 mL) was added. The crude product was collected by vacuum filtration and subsequently purified by recrystallization from methanol. The pure title compound was a white solid. FW=264.30 g/mol Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.65 (s, 6H) 6.79 (d, J=5.7, 1H) 7.50 (d, 1H) 7.51-7.56 (m, 1H) 7.58-7.63 (m, 1H) 7.70 (d, J=7.6, 1H) 7.7 (d, J=7.6, 1H). ^{13}C NMR ($CDCl_3$) δ: 51.6, 53.2, 124.1, 126.1, 127.3, 129.2, 131.1, 135.1, 136.9, 138.7, 166.1. UV/vis maxima: 325nm (ε=151.9$M^{-1}cm^{-1}$ ± 3.5) and 215nm. EI-MS: Calc. 264 g/mol. Found 233 (M –OCH_3), 205 (M-CO_2CH_3), 134 (M- $C_5O_4H_6$). ESI-MS-positive ion mode: Found 265 (M+1).

Figure S16. ^{1}H NMR benzothiophenium biscarbomethoxymethylide. Solvent: deuterated chloroform.

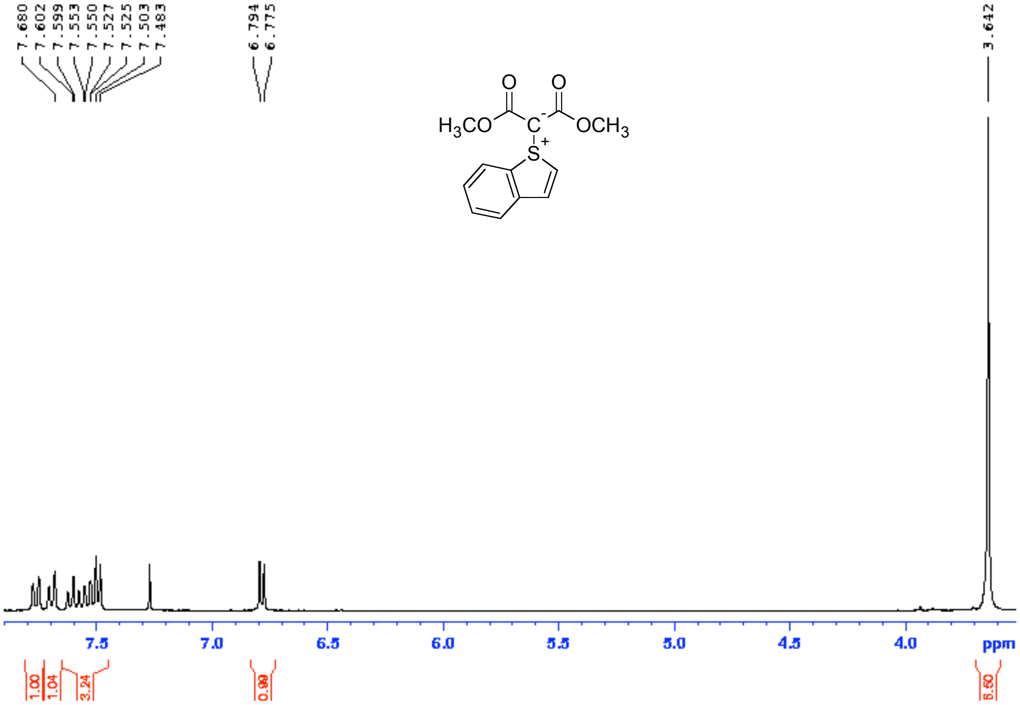


Figure S17. ^{13}C NMR benzothiophenium biscarbomethoxymethylide. Solvent: deuterated chloroform.

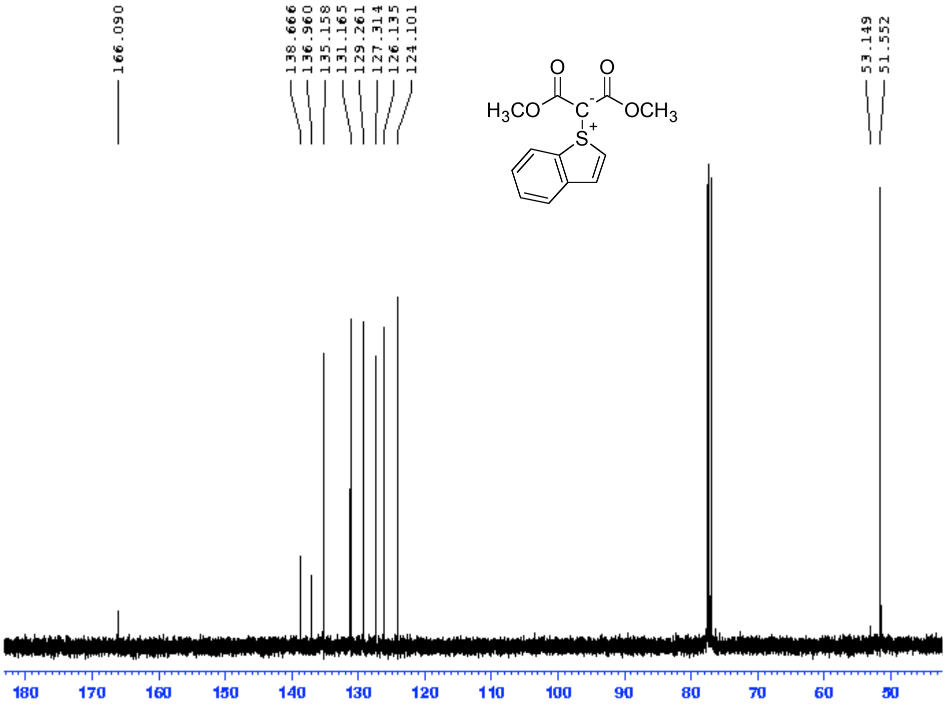


Figure 18. IR benzothiophenium biscarbomethoxymethylide.

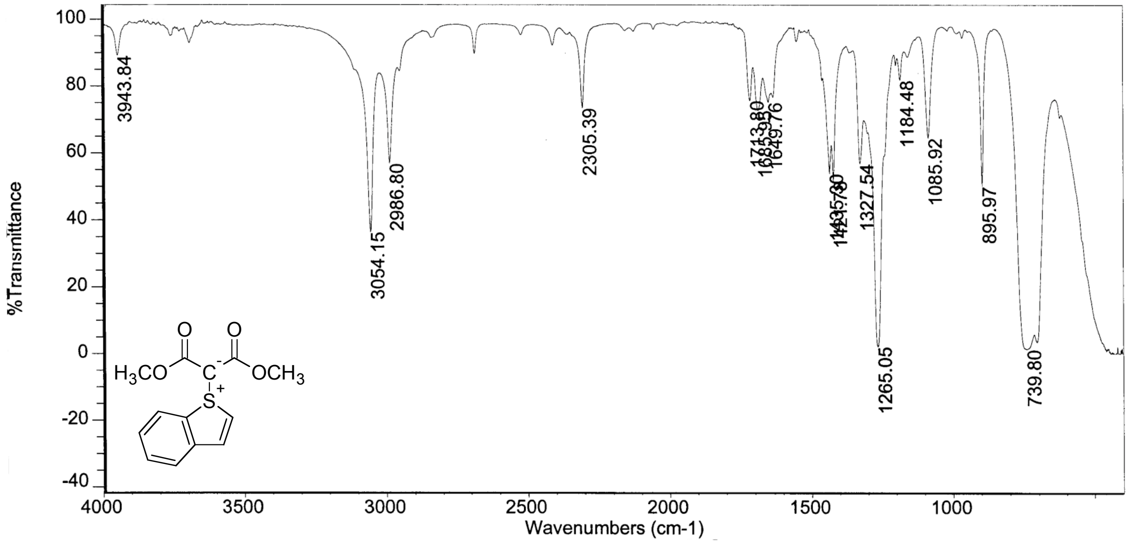


Figure 19. EI-MS benzothiophenium biscarbomethoxymethylide.
Retention time: 14.4 min

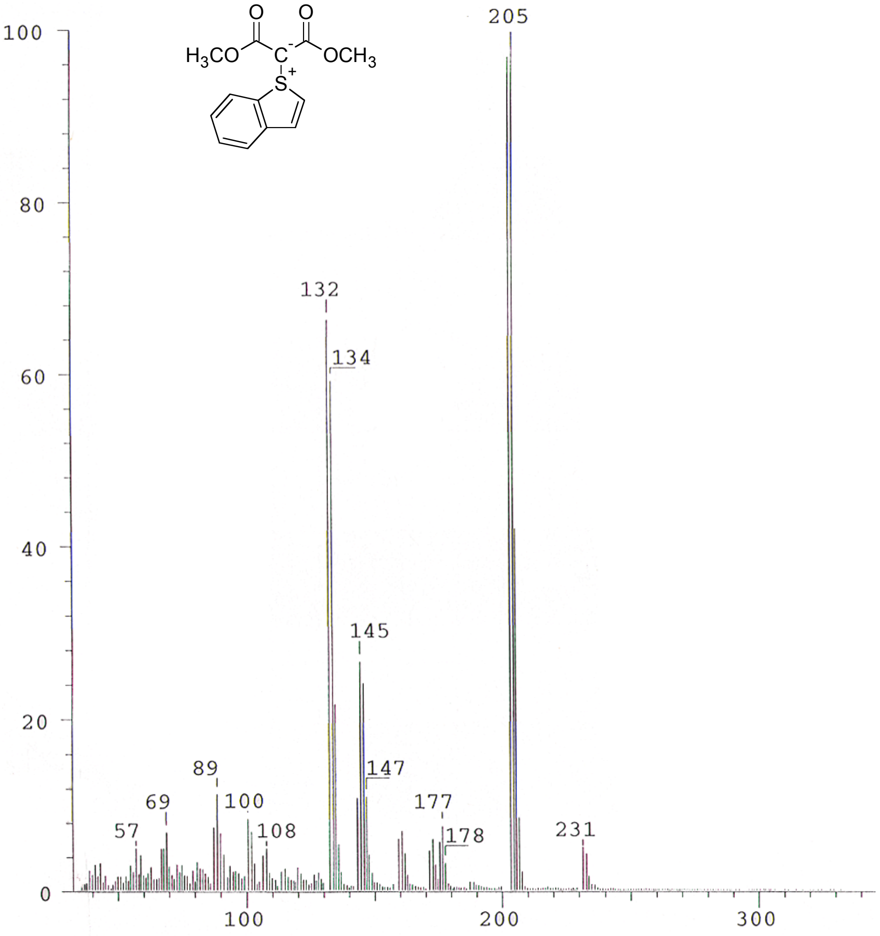
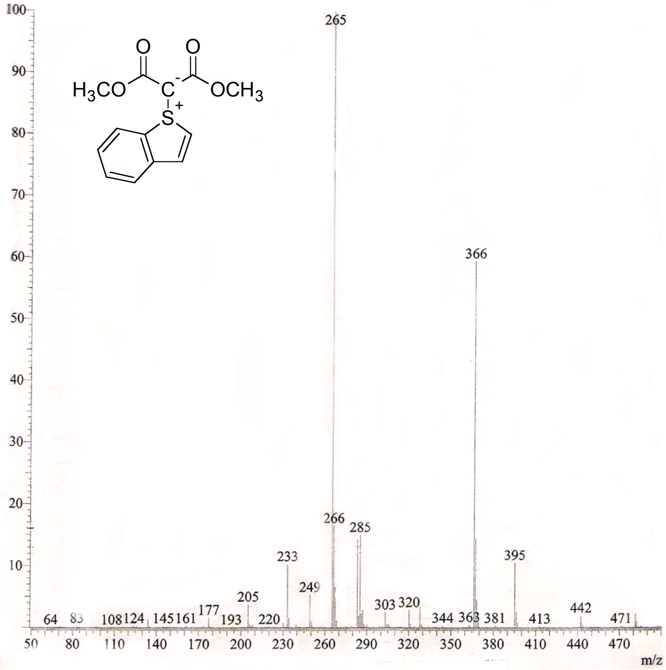


Figure 20. ESI-MS benzothiophenium biscarbomethoxymethylide.



Preparation of dibenzothiophenium bismethoxycarbonylmethylide (4).

To a 100mL round bottomed flask, dibenzothiophene (0.93 g, 5.05 mmol), dimethyl diazomalonate (0.12 mL, 1.02 mmol), rhodium acetate dihydrate (2 mg), and 1,2-dichloroethane (4 mL) were added under an argon atmosphere. The mixture was stirred for 15 hours at which time the mixture was a milky green color. The solvent was then removed under vacuum and hexane (20 mL) was added. The crude product was collected by vacuum filtration and subsequently purified by recrystallization from methanol. The pure title compound was a white solid. Yield: 79% (0.2543g) FW=314.36 g/mol Characterization: ^{1}H NMR ($CDCl_3$) δ: 3.29 (s, 3H), 3.88 (s, 3H), 7.54 (t, J=7.5, 2H), 7.67 (t, J=7.5, 2H), 7.80 (d, J=7.8, 2H), 8.01 (d, J=7.8, 2H). ^{13}C NMR($CDCl_3$) δ: 51.1, 51.5, 57.5, 122.5, 125.0, 129.7, 131.4, 135.6, 137.4, 164.5, 167.8 EI-MS: Calc. 314 g/mol. Found 314 (M), 283 (M-OCH_3), 255 (M-CO_2CH_3), 184 (M-$C_5O_4H_6$). IR (cm^{-1}): 3054(sh), 2986(sh), 2305(sh), 1685(sh), 1649(sh).

Figure S21. ^{1}H NMR dibenzothiophenium biscarbomethoxymethylide.
Solvent: deuterated chloroform.

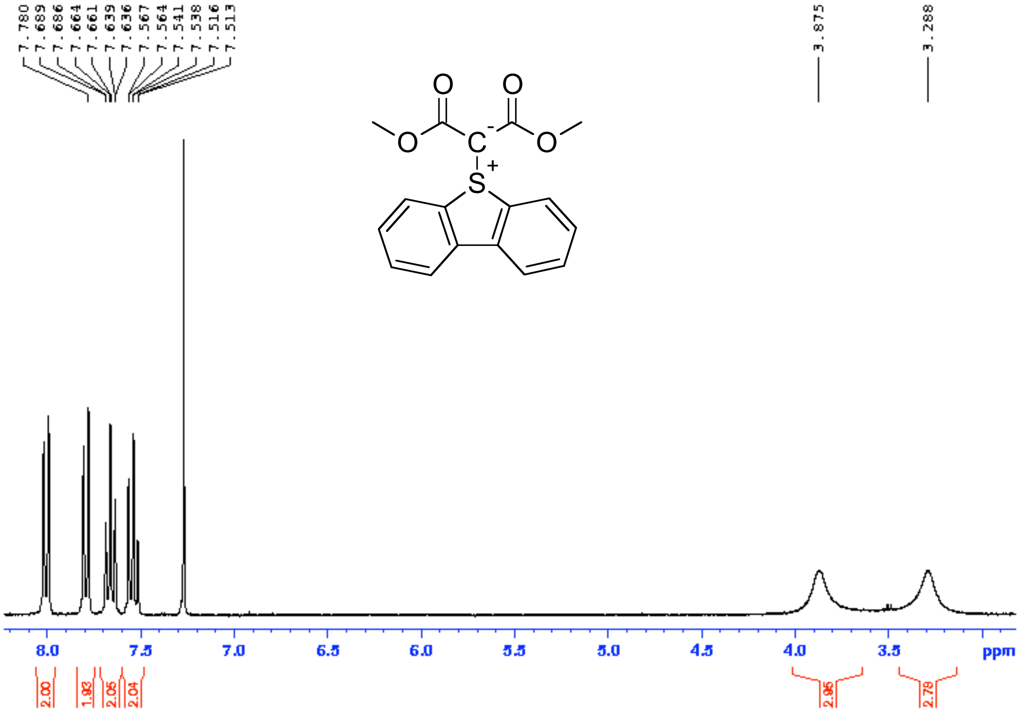


Figure S22. ^{13}C NMR dibenzothiophenium biscarbomethoxymethylide.
Solvent: deuterated chloroform.

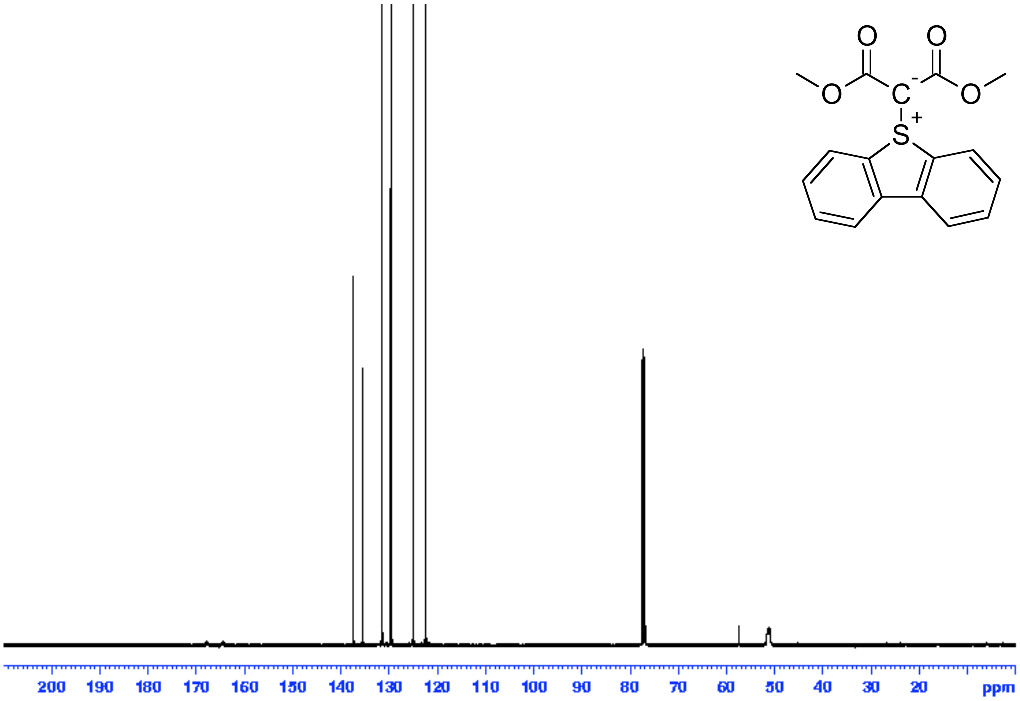


Figure S23. ^{13}C NMR-dibenzothiophenium biscarbomethoxymethylide (expanded). Solvent: deuterated chloroform.

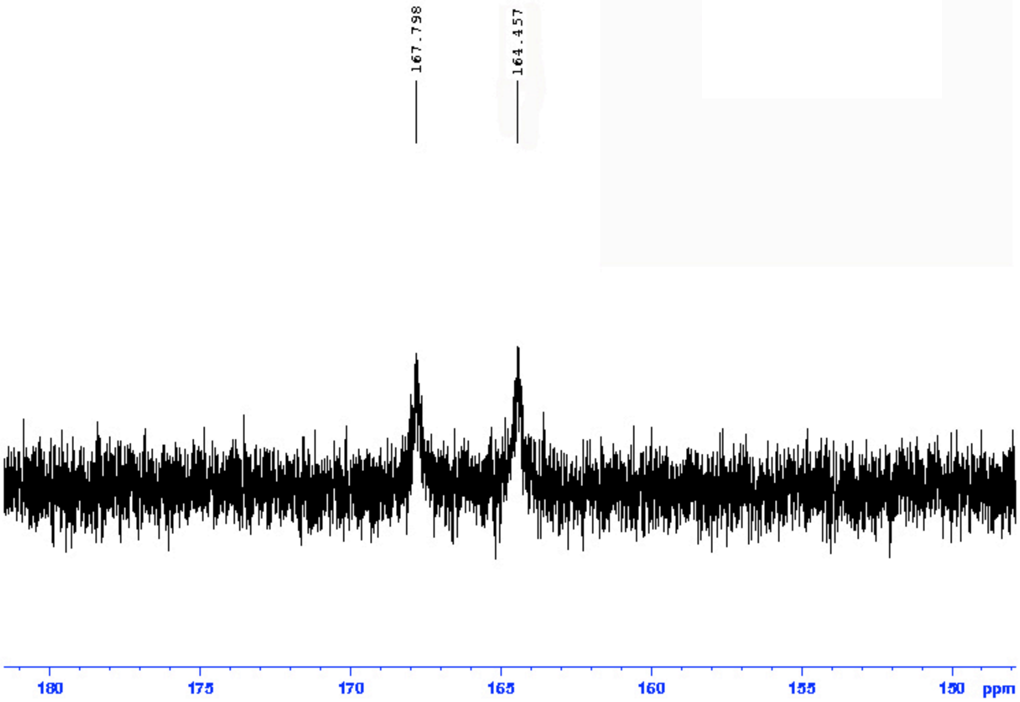


Figure S24. ^{13}C NMR-dibenzothiophenium biscarbomethoxymethylide (expanded). Solvent: deuterated chloroform.

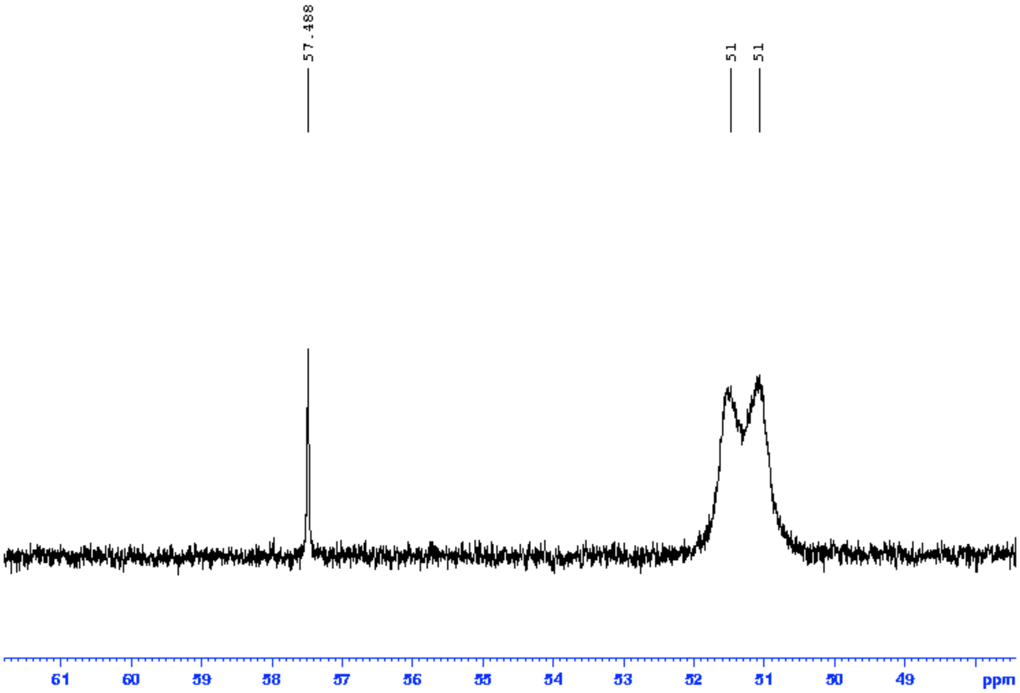


Figure S25. IR dibenzothiophenium biscarbomethoxymethylide.

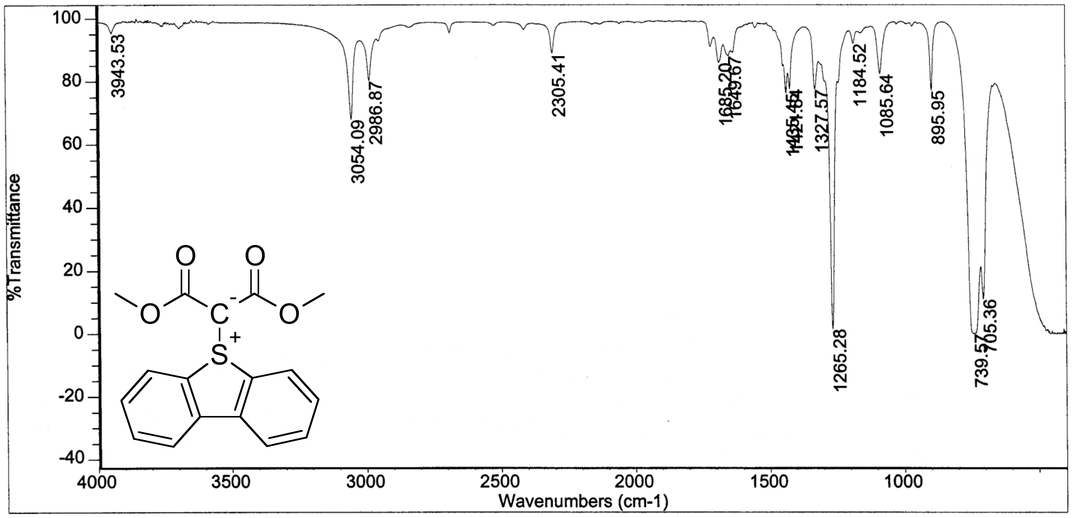
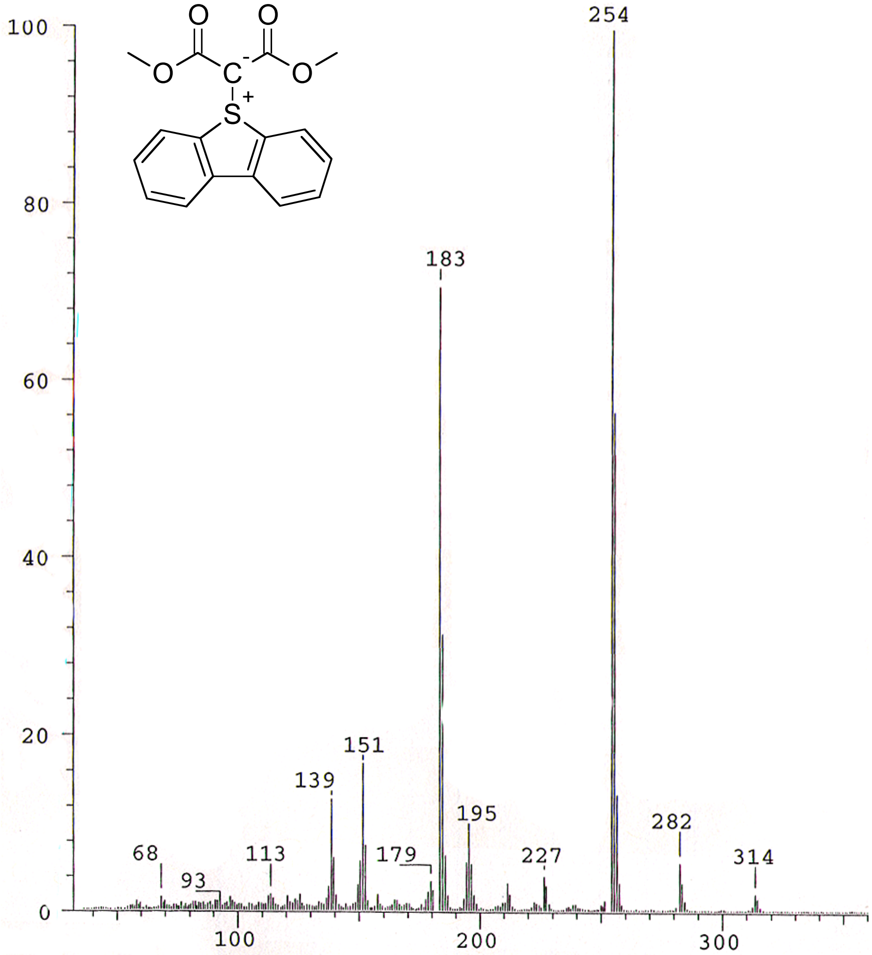


Figure S26. EI-MS dibenzothiophenium biscarbomethoxymethylide.
Retention time: 13.3 min.



Characterization of authentic samples matching trapped products.

Figure S27. ^{1}H NMR thioanisole.
Solvent: deuterated chloroform.

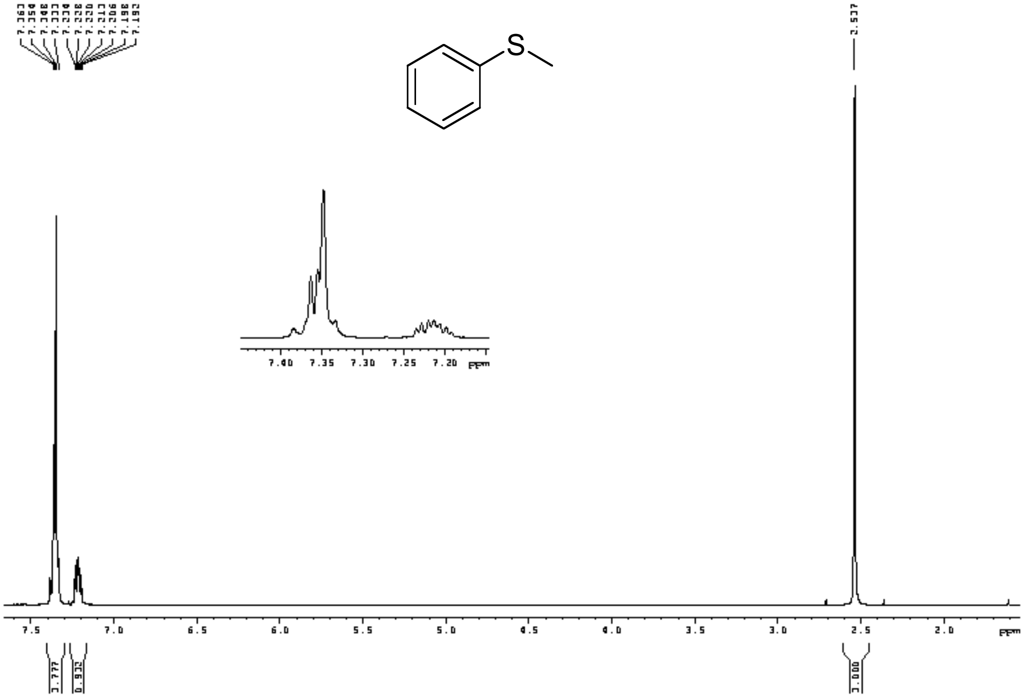


Figure S28. EI-MS thioanisole.
Retention time: 3.6 min

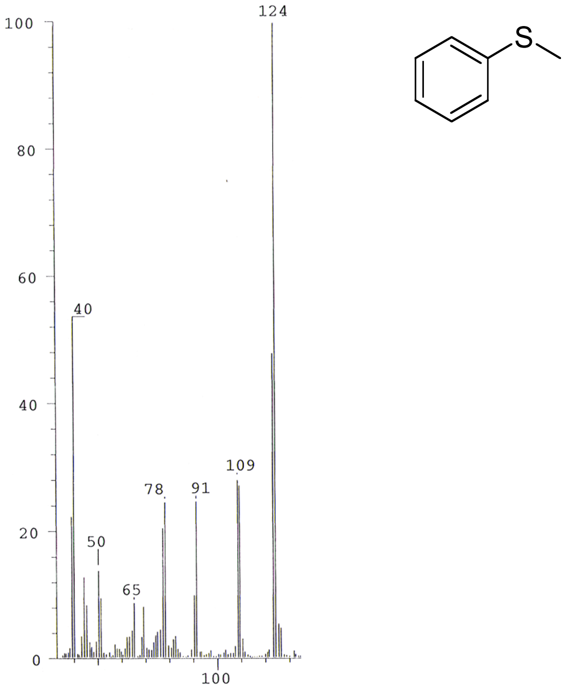


Figure S29. ^{1}H NMR thiophene.
Solvent: deuterated chloroform.

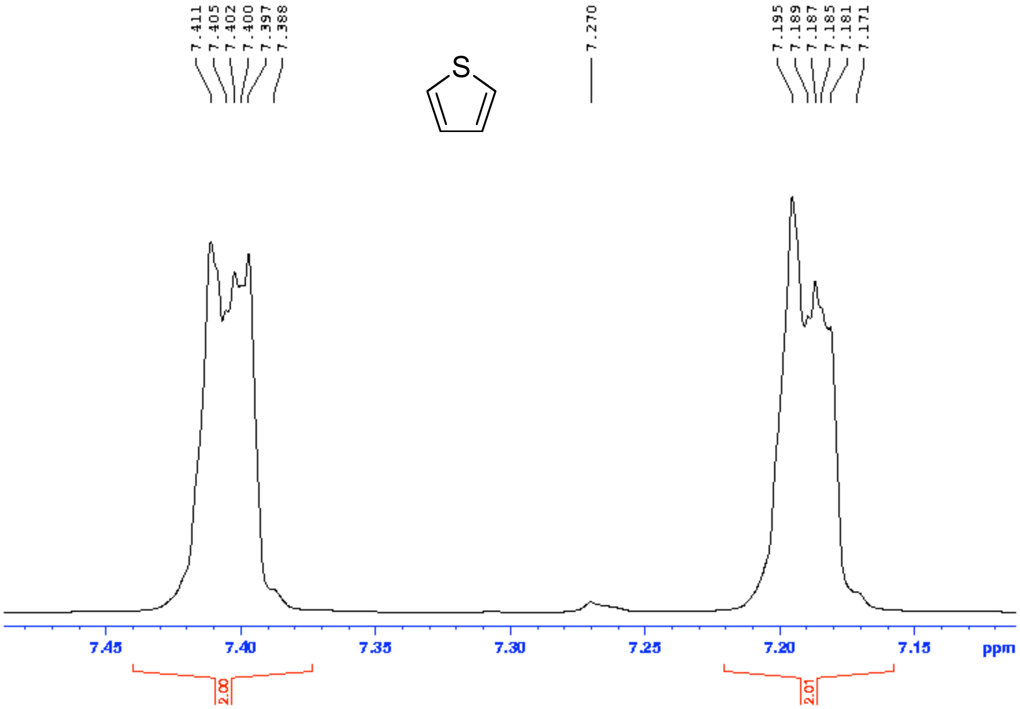


Figure S30. ^{1}H NMR benzothiophene.
Solvent: deuterated methanol.

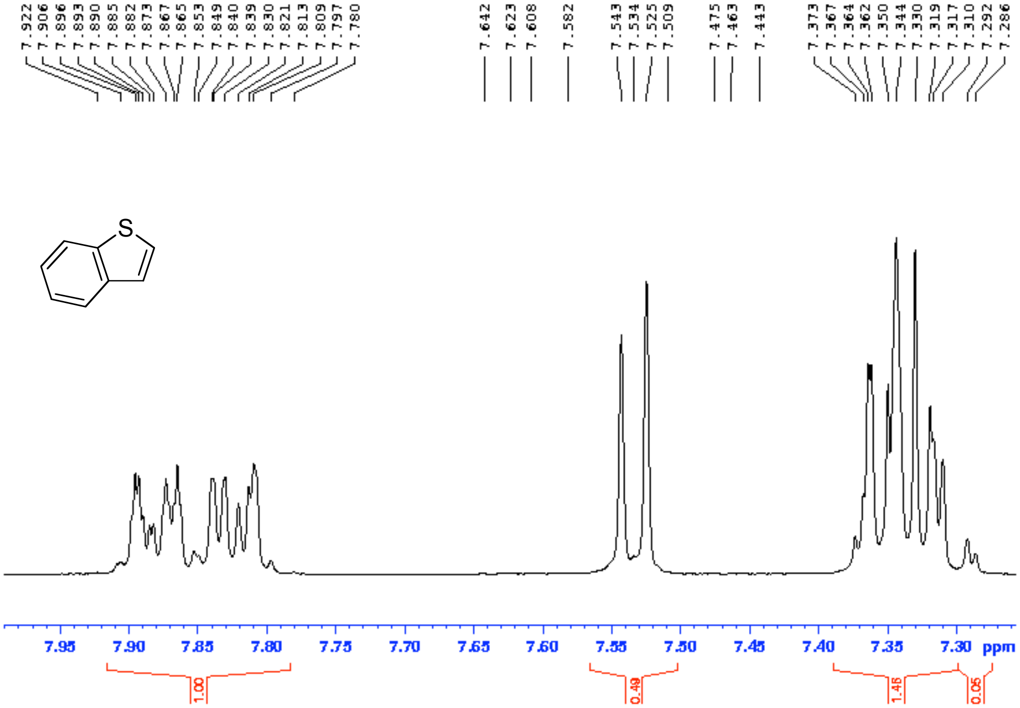
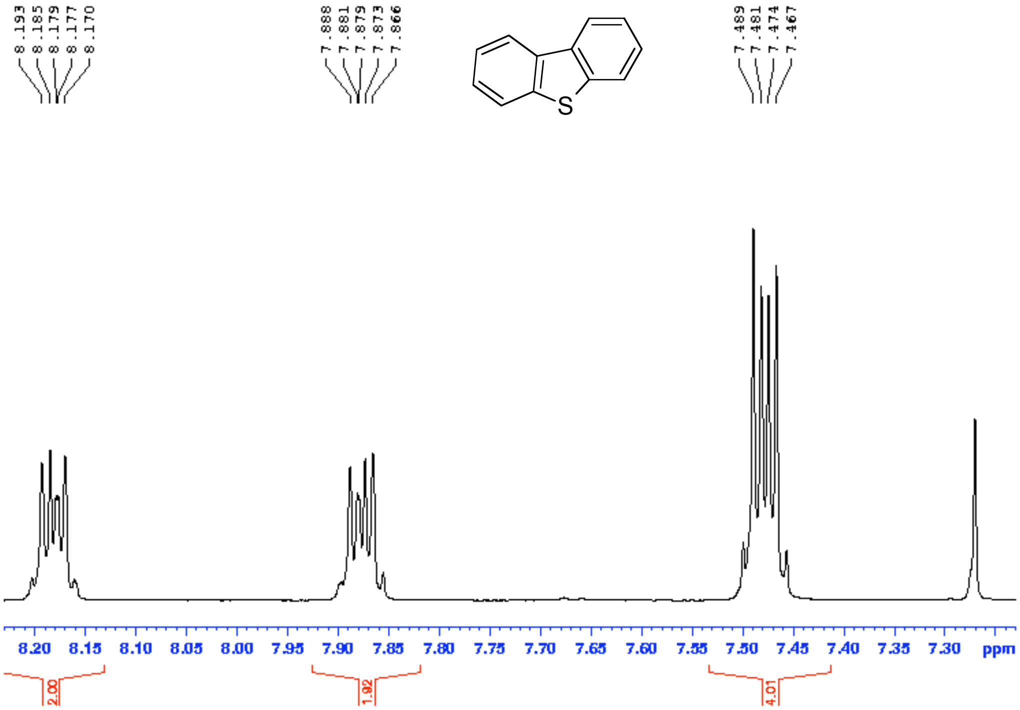


Figure S31. ^{1}H NMR dibenzothiophene.
Solvent: deuterated chloroform.



Preparation of trimethylphosphite copper (I) chloride.[5]

To a solution of $CuCl_2.2H_20$ (1.7 g) in methanol (50 mL), $P(OMe)_3$ (6.2 mL) was added. The solution was cooled to 0° C. Approximately half of the solvent was removed under vacuum and the solution was allowed to set for 3 days at room temperature. White crystals formed and were washed with ethanol and ether.

Preparation of tetramethoxycarbonylethylene.[6]

Trimethylphosphite copper (I) chloride (0.05 g) was dissolved in benzene (5 mL) in a 100mL 3-necked round bottomed flash. The solution was heated to reflux, then a solution of dimethyldiazomalonate (1.2 mL) in benzene (5 ml) was added dropwise. The mixture was refluxed for 4 hours, filtered, and the solvent was removed under vacuum. The solid was recrystalized twice from hot methanol. ^{1}H NMR ($CDCl_3$) δ: 3.87 (s, 12H) ^{13}C NMR ($CDCl_3$) δ: 53.7, 135.6, 162.8. EI-MS: Calc. 260 g/mol. Found 260. Retention time: 2.36 min.

Figure S32. ^{1}H NMR tetramethoxycarbonylethylene.
Solvent: deuterated chloroform.

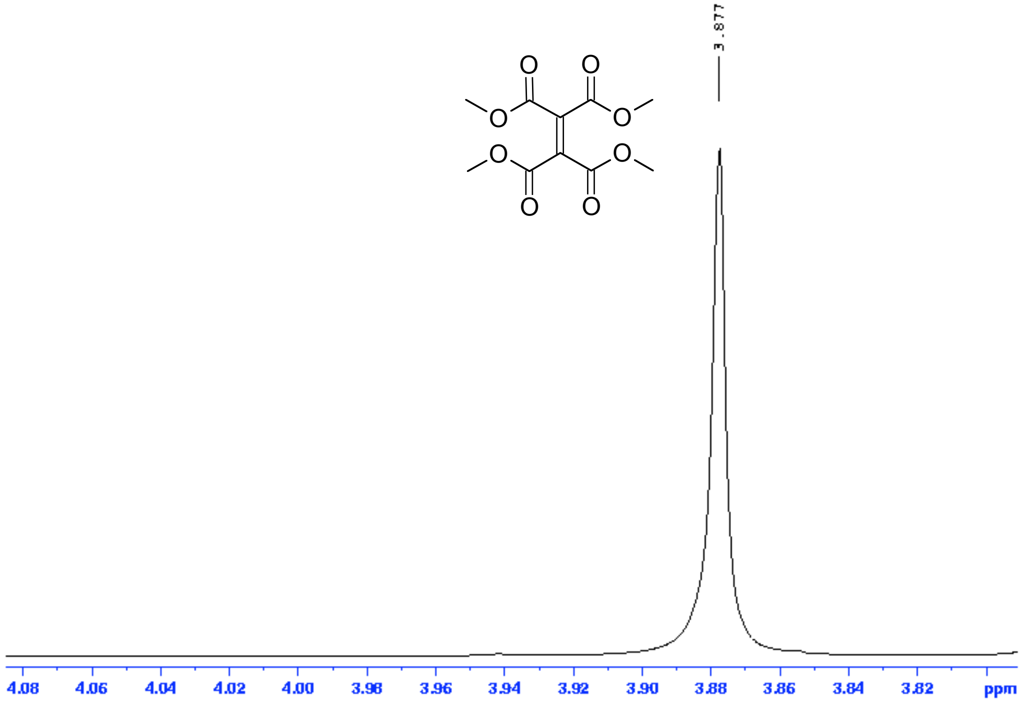
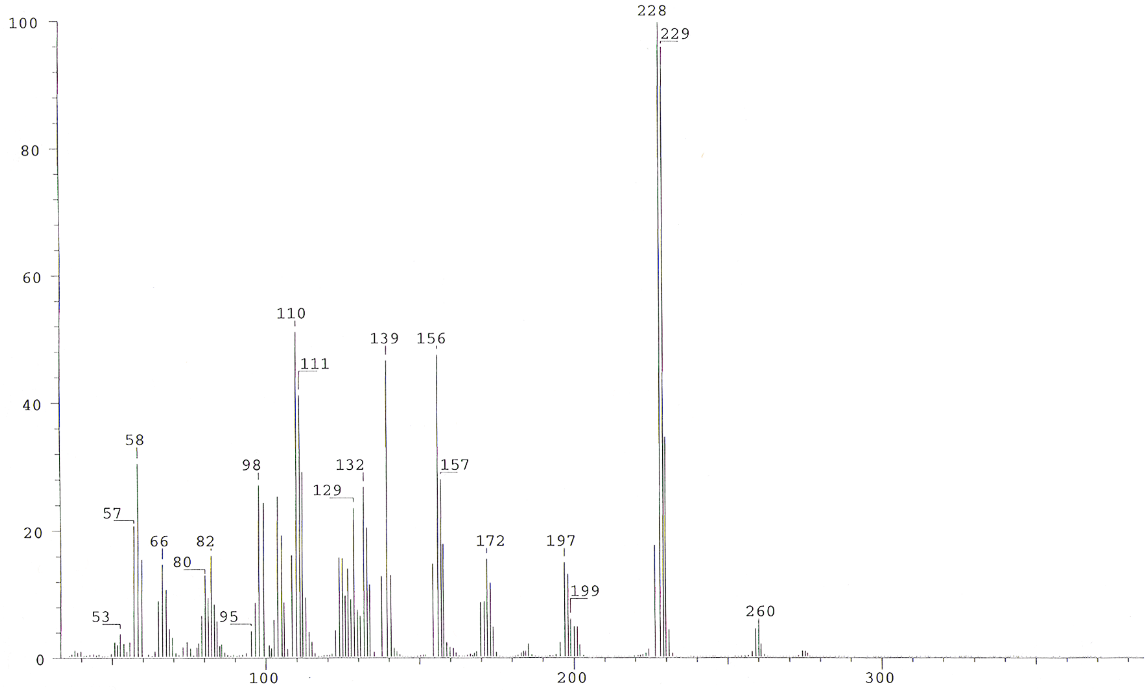


Figure S33. EI-MS tetramethoxycarbonylethylene.
Retention time: 10.0 min.



Preparation of 7,7-dimethoxycarbonylbicyclo[4.1.0]heptane.[7]

A solution of $[Rh(OAc)_2]_2$ (2 mg), methylene chloride (5 mL, freshly distilled over CaH_2), and cyclohexene (1mL, freshly distilled over sodium metal) was prepared under an argon atmosphere in a 100 mL 3-necked round bottomed flask. To the mixture, a solution of dimethyl diazomalonate (0.1mL) in methylene chloride (10 mL, freshly distilled over CaH_2) was added slowly. The dark green solution was stirred under argon for ~24 hours. The mixture was then filtered through a silica plug to remove the catalyst. The solvent and excess cyclohexene were removed under vacuum. The crude mixture was purified on a silica gel column with a mobile phase of (15:10, chloroform: diethylether) and monitored by $KMnO_4$ staining. ^1H NMR ($CDCl_3$) δ: 0.95-1.10 (m, 2H), 1.20-1.35 (m, 2H), 1.80-2.00 (m, 6H), 3.70 (s, 3H), 3.80 (s, 3H). GCMS: Calc. 212 g/mol. Found. 212, 181 (loss of OCH_3).

Figure S34. ^1H NMR 7,7-dimethoxycarbonylbicyclo[4.1.0]heptane and dimethyl (3-cyclohexenyl)malonate.
Solvent: deuterated chloroform.

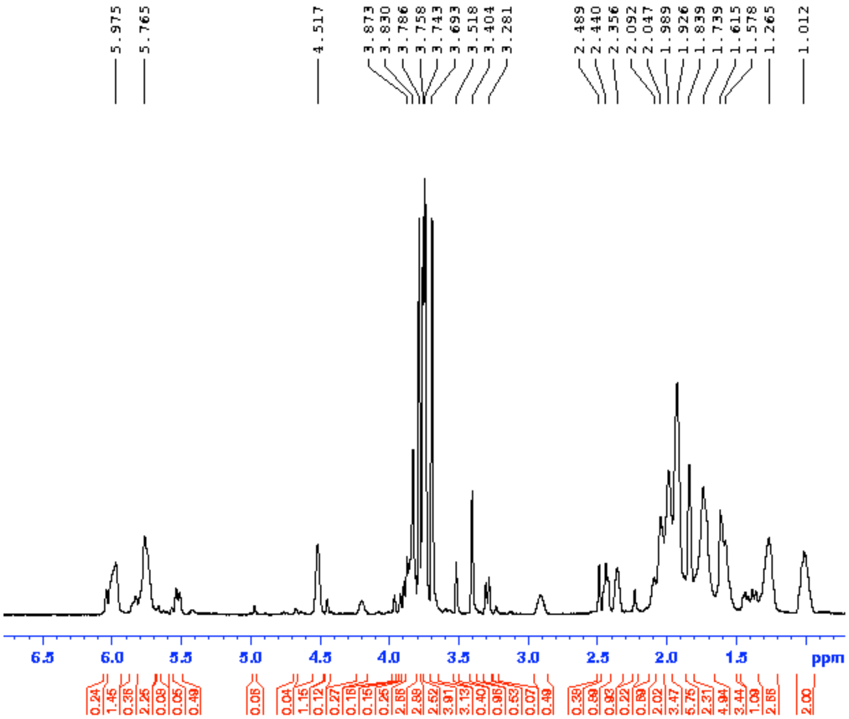
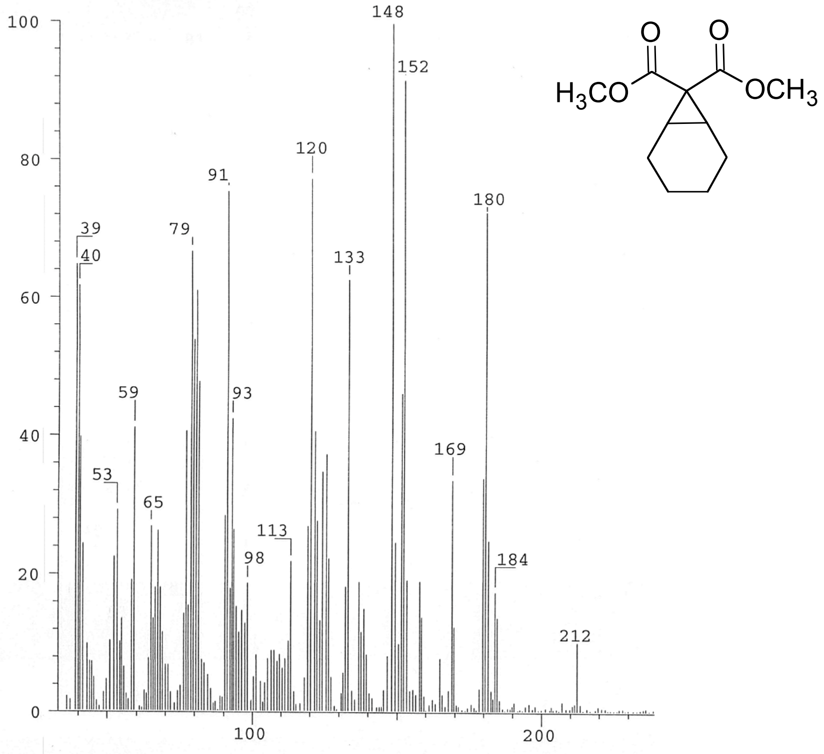


Figure S35. EI-MS 7,7-dimethoxycarbonylbicyclo[4.1.0]heptane.
Retention time: 8.7 min.



Preparation of dimethyl (3-cyclohexenyl)malonate.[6-7]

Dimethylmalonate (1.2 g, 9.1 mmol), 3-bromocyclohexene ( ), and sodium methoxide (0.49g,) were dissolved in methanol (12 mL) in a 100 mL 3-necked round bottomed flask. The solution was refluxed at 60°C for 12 hours after which the solvent was removed leaving an oil and NaBr. The oil was taken up in diethylether and filtered to removed the NaBr. The diethylether was removed under vacuum and the resulting oil was distilled to give dimethyl (3-cyclohexenyl)malonate. ^{1}H NMR ($CDCl_3$) δ: 1.25-1.42 (2H, m), 1.48-1.62 (2H, m), 1.66-1.81 (2H, m), 2.85-2.95 (2H, m) 3.28 (1H, d), 3.78 (6H, s), 5.49-5.53 (1H, m) 5.74-5.79 (1H, m). GCMS: Calc. 213 g/mol. Found. 213 g/mol, 181 (loss of OCH_3), 152 (loss of 2 x OCH_3).

Figure S36. ^{1}H NMR dimethyl (3-cyclohexenyl)malonate.
Solvent: deuterated chloroform.

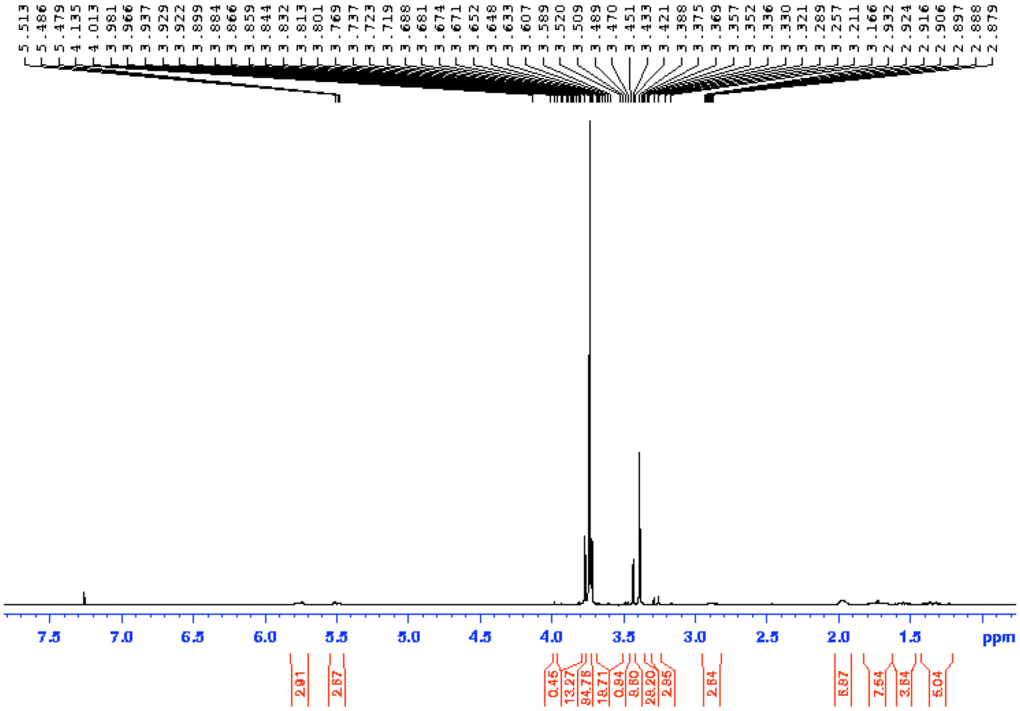


Figure S36. EI-MS dimethyl (3-cyclohexenyl)malonate.
Retention time: 8.3 min.

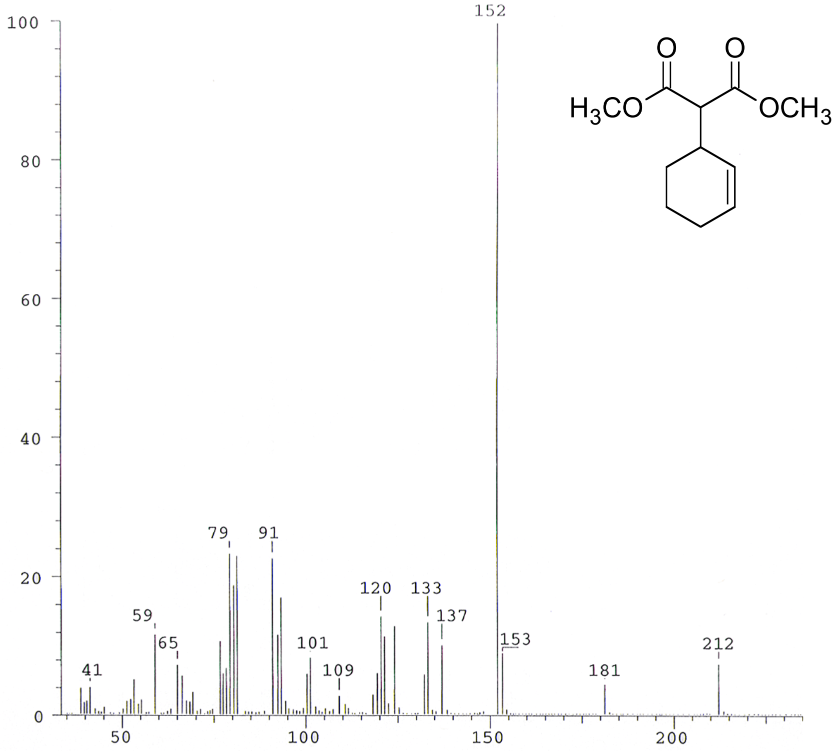


Figure S37. ^{1}H-NMR dimethylmalonate.
Solvent: deuterated chloroform.

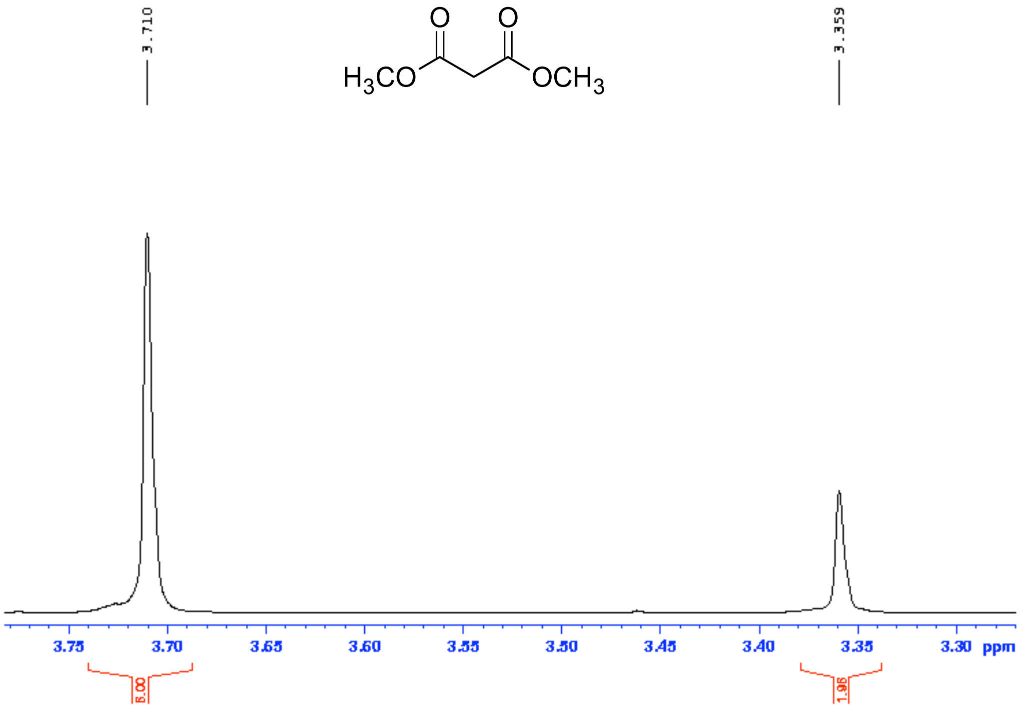


Figure S38. ^{1}H-NMR dimethylmalonate.
Solvent: deuterated methanol.

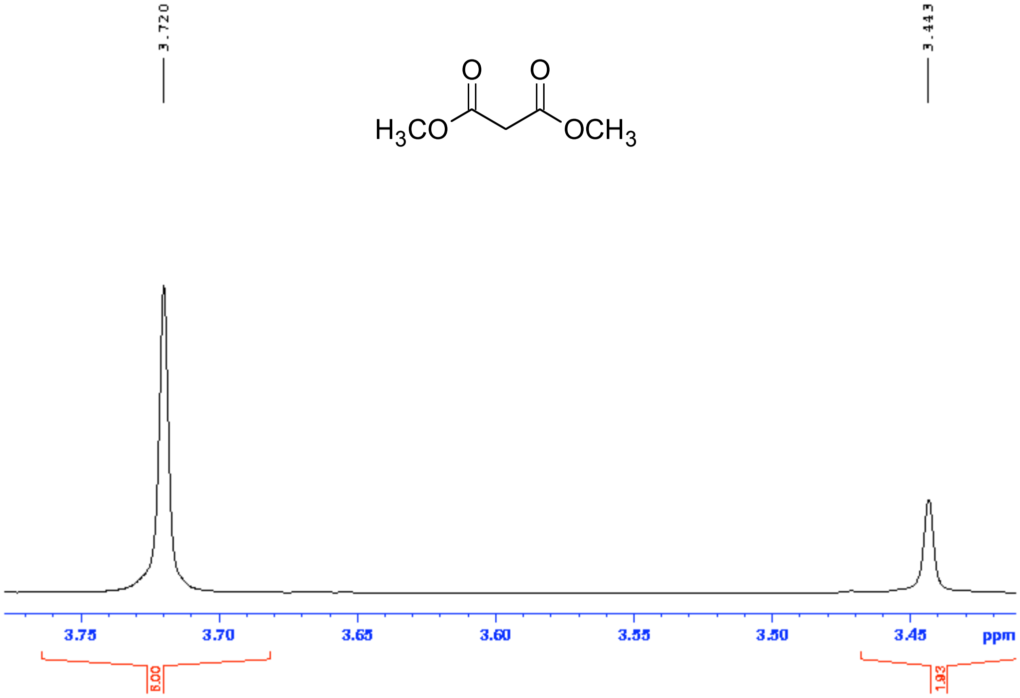
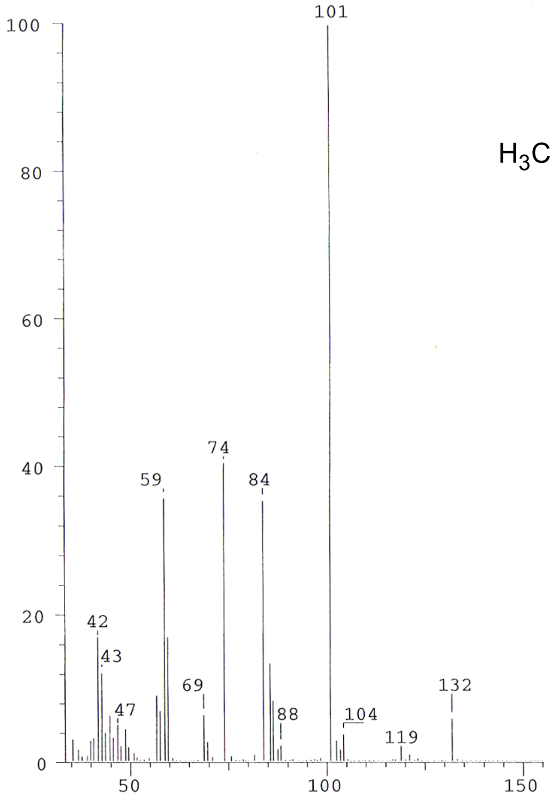
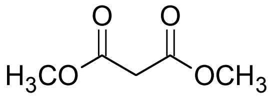


Figure S39. EI-MS dimethylmalonate.
Retention time: 2.05 min.





Preparation of dimethyl dimethoxymalonate.[8]

Dimethyldiazomalonate (0.006mol) was dissolved in methanol (2mL) in a quartz cell. The solution was photolyzed for 2 hours in a rayonet with 6-350 nm centered bulbs. A mixture of dimethylmalonate and dimethyl dimethoxymalonate were obtained upon photolysis. ^{1}H NMR ($CDCl_3$) δ: 3.54 (s, 3H) 3.83 (s, 6H) 4.45 (s, 1H). GCMS: Calc. 162 g/mol. Found. 162 g/mol, 132 g/mol, 103 g/mol, 75 g/mol, and 47 g/mol. Retention time: 3.05 min.

Figure S40. ^{1}H NMR A. dimethylmethoxymalonate, B. dimethylmalonate, C. dimethyldiazomalonate.
Solvent: deuterated chloroform.

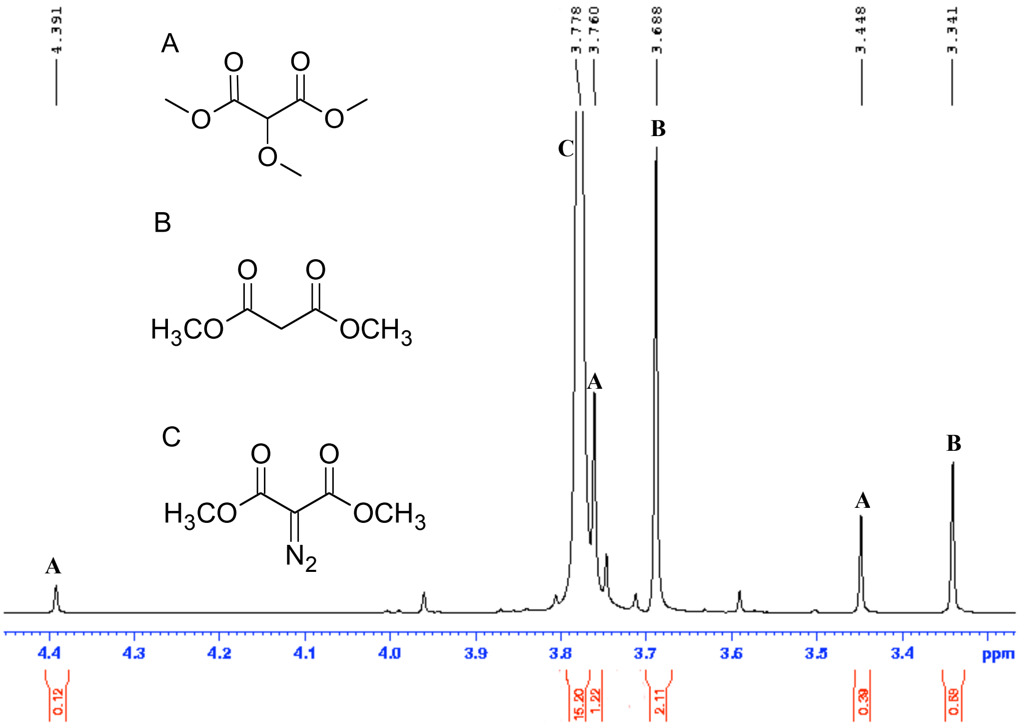


Figure S41. GC/MS of dimethylmethoxymalonate.
Retention Time: 3.4 min.

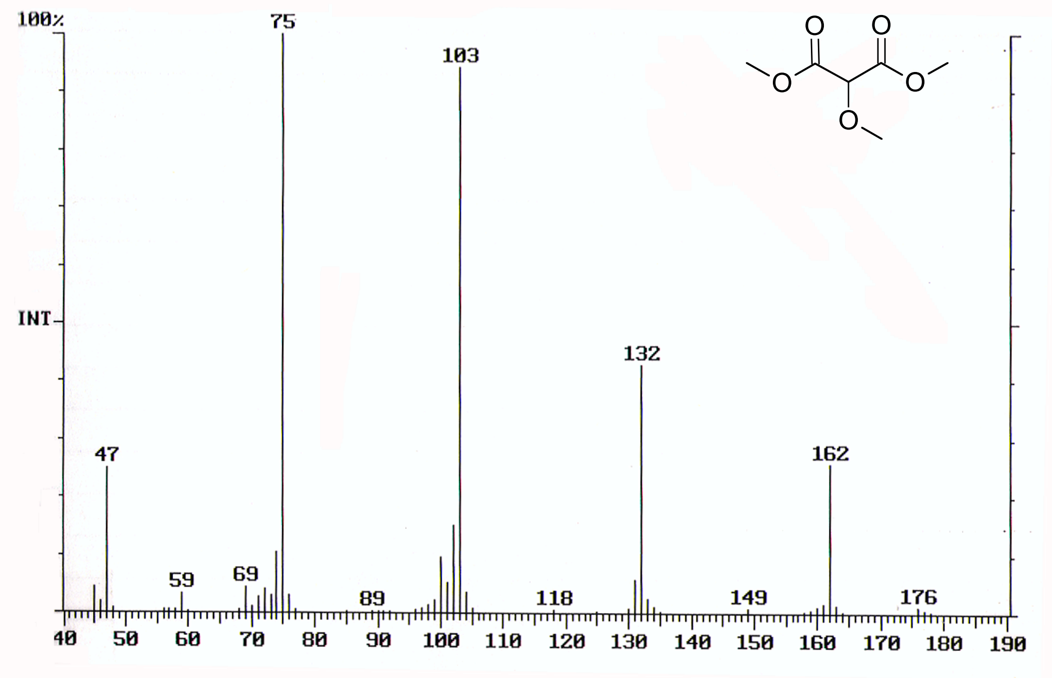
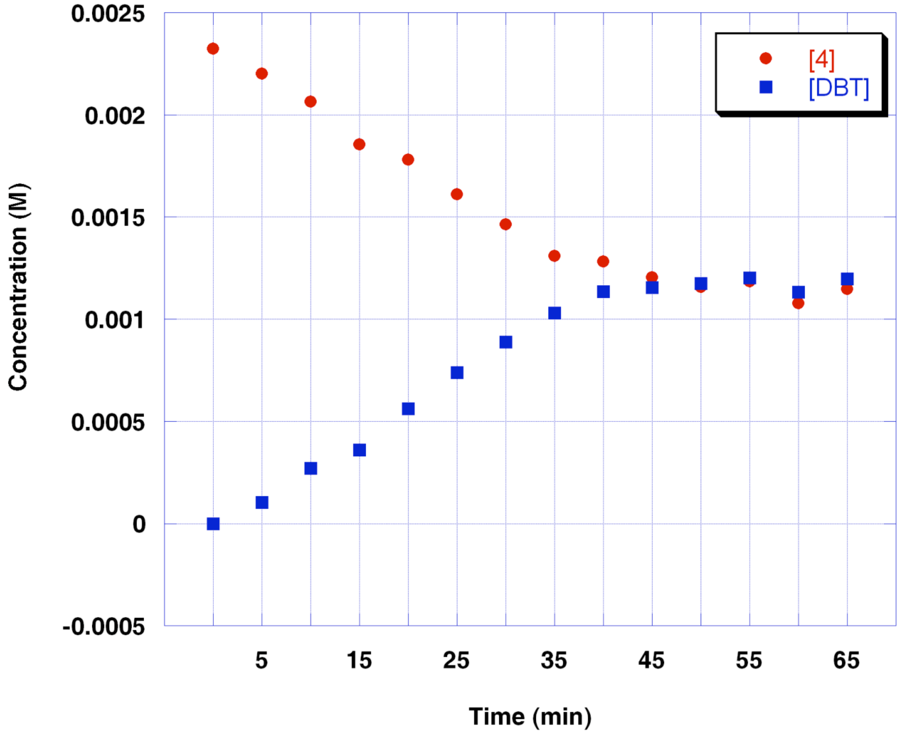


Figure S42. Representative plot monitoring *S*,*C*-sulfonium ylide decay and sulfide growth upon direct photolysis in acetonitrile with 10% cyclohexene as a function of time.



Computational Results: Coordinates and absolute energies.

thiophenium bismethoxycarbonylmethylide (2)

B3LYP/6-31G(d)

S	16.0	-0.9624663872	-0.5126737174	0.0148052708
C	6.0	-0.5419444394	-2.9507259024	0.7309878201
C	6.0	-0.5344472780	-2.9424280142	-0.7266779274
C	6.0	-0.6651451306	-1.7267396878	1.2802947205
C	6.0	-0.6516834884	-1.7117020494	-1.2619286346
H	1.0	-0.4574906147	-3.8628332786	1.3131637813
H	1.0	-0.4444625103	-3.8476669074	-1.3185763369
H	1.0	-0.7123466250	-1.4295789443	2.3193849047
H	1.0	-0.6898068002	-1.4028197285	-2.2981157179
C	6.0	0.0557650239	0.8696560292	0.0250183027
C	6.0	1.5086946850	0.7390162019	0.0222558487
C	6.0	-0.6139301451	2.1675086931	0.0121909853
O	8.0	2.3139867122	1.6461193478	0.0153394355
O	8.0	1.8762841683	-0.5919195895	0.0315293800
O	8.0	-0.0684080464	3.2509105796	-0.0189601541
O	8.0	-1.9863333382	2.0440846241	0.0391703153
C	6.0	3.2786132715	-0.8712057979	-0.0076590633

H	1.0	3.8482585169	0.0495333511	0.1306360918
H	1.0	3.5239506255	-1.3193994320	-0.9766819670
H	1.0	3.5005163054	-1.5854972391	0.7907781964
C	6.0	-2.6954591787	3.2860880166	-0.0178105676
H	1.0	-2.3843977704	3.9537027945	0.7902759440
H	1.0	-2.5202416745	3.7897158721	-0.9738184310
H	1.0	-3.7512890714	3.0270180184	0.0843977126

B3LYP/6-311G(2df,p)

S	16.0	-0.9430002782	-0.5103227885	0.0144104765
C	6.0	-0.5560719860	-2.9353938396	0.7275396461
C	6.0	-0.5495521499	-2.9273258561	-0.7246080369
C	6.0	-0.6610242873	-1.7150934321	1.2733212522
C	6.0	-0.6495946536	-1.7003687992	-1.2561033272
H	1.0	-0.4868085130	-3.8457614935	1.3087290890
H	1.0	-0.4753895249	-3.8308627250	-1.3156482739
H	1.0	-0.7008017893	-1.4182361205	2.3093811748
H	1.0	-0.6814948462	-1.3919180666	-2.2892049031
C	6.0	0.0627719133	0.8657269837	0.0232615118
C	6.0	1.5144906531	0.7393211830	0.0213641448
C	6.0	-0.6099257426	2.1599879884	0.0098742821
O	8.0	2.3120041374	1.6399106666	0.0148281055
O	8.0	1.8850494038	-0.5871645729	0.0309285854
O	8.0	-0.0730140553	3.2370729686	-0.0237191165
O	8.0	-1.9770361665	2.0329380426	0.0394058182
C	6.0	3.2850326801	-0.8689952700	-0.0058206119
H	1.0	3.8544891709	0.0481898413	0.1325531706
H	1.0	3.5304933828	-1.3158281775	-0.9714778668
H	1.0	3.5049399233	-1.5805066080	0.7909322966
C	6.0	-2.6964373845	3.2662690244	-0.0162908479
H	1.0	-2.3884275261	3.9348503498	0.7878801162
H	1.0	-2.5269561820	3.7691626437	-0.9700027211
H	1.0	-3.7475193695	3.0025112976	0.0884659467

benzothiophenium bismethoxycarbonylmethylide (3)

B3LYP/6-31G(d)

C	6.0	-0.4957595101	-0.8708613248	-0.8486689714
C	6.0	-0.1825550792	-1.4022827835	0.3438836237
S	16.0	0.5993849898	-0.2077650904	1.4326582654
C	6.0	-0.2596603662	0.5675167521	-0.9428151738
H	1.0	-0.8957211275	-1.4483863084	-1.6768961208
C	6.0	0.2649245935	1.1029284325	0.2448028516
C	6.0	-0.4971989527	1.4273510221	-2.0208976425
H	1.0	-0.8933364680	1.0378964826	-2.9553102368

C	6.0	-0.2287733590	2.7898569787	-1.8765630016
H	1.0	-0.4203234452	3.4632710637	-2.7073630828
C	6.0	0.2834942594	3.2993847952	-0.6771098298
H	1.0	0.4774543741	4.3637360309	-0.5796686820
C	6.0	0.5507596086	2.4499966628	0.4018740115
H	1.0	0.9526714464	2.8344189173	1.3349454232
H	1.0	-0.2581702259	-2.4277183013	0.6815814258
C	6.0	-0.2159747471	0.0169854076	2.9297741912
C	6.0	-1.6374572654	0.3193512818	3.0095465219
C	6.0	0.7180899514	-0.0926991290	4.0514916934
O	8.0	-2.2797178942	0.5567528664	4.0147019240
O	8.0	-2.2221210456	0.3171595745	1.7631031067
O	8.0	1.9200315268	-0.3116540417	3.9379573320
O	8.0	0.1237892521	0.0725647207	5.2533033580
C	6.0	1.0078677944	0.0060223852	6.3781536934
C	6.0	-3.6135360627	0.6488104757	1.7562831415
H	1.0	1.7713009186	0.7881670254	6.3211003357
H	1.0	1.5065190251	-0.9661154700	6.4327584652
H	1.0	0.3704165313	0.1593981000	7.2504497421
H	1.0	-3.9252278360	0.5858953005	0.7116557303
H	1.0	-3.7750385160	1.6607455828	2.1401743292
H	1.0	-4.1866099704	-0.0523928395	2.3696448258

dibenzothiophenium bismethoxycarbonylmethylide (4)

B3LYP/6-31G(d)

S	16.0	-0.6496112881	2.2329460134	0.0000000000
C	6.0	-0.1283901972	-0.2811723623	-0.7337748633
C	6.0	-0.3197789995	0.9966980127	-1.2799126952
C	6.0	0.0510524404	-1.3593082941	-1.6068466430
H	1.0	0.1966813094	-2.3632079128	-1.2178107990
C	6.0	0.0517409391	-1.1356982472	-2.9843270125
H	1.0	0.1990683224	-1.9726990424	-3.6609070447
C	6.0	-0.1325513743	0.1517968308	-3.5028923679
H	1.0	-0.1236493571	0.3106285103	-4.5771380454
C	6.0	-0.3318995947	1.2380863750	-2.6459281234
H	1.0	-0.4723265087	2.2435682528	-3.0316723005
C	6.0	0.4791971643	3.5286578445	0.0000000000
C	6.0	1.9194962578	3.2971902632	0.0000000000
C	6.0	-0.0861912393	4.8768150188	0.0000000000
O	8.0	2.7952117895	4.1383108258	0.0000000000
O	8.0	2.2049631561	1.9502875230	0.0000000000
O	8.0	0.5381768485	5.9175825260	0.0000000000
O	8.0	-1.4660251513	4.8594205590	0.0000000000
C	6.0	3.6000753310	1.6350705290	0.0000000000
C	6.0	-2.0790580428	6.1521144331	0.0000000000

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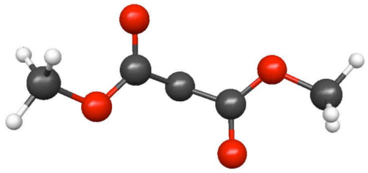
H          1.0   4.0923824717   2.0416000808  -0.8887561314
H          1.0   3.6534650026   0.5445818407   0.0000000000
H          1.0  -1.7913850686   6.7225693690  -0.8885189520
H          1.0  -3.1543392344   5.9632504283  -0.0000000200
```

[1]dicarbomethoxycarbene E rotamer



B3LYP/6-31G(d)

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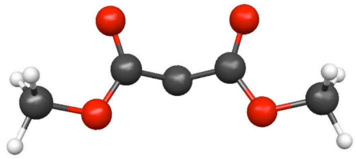
C    6.0  -0.8574475281   0.8714506930   0.3821743936
O    8.0  -0.8292799914   0.9044179996   1.6120979594
C    6.0   0.4606028834   0.8622898143  -0.1565074609
C    6.0   1.1367939312  -0.3440512180  -0.5030579313
O    8.0   1.0071048294  -0.6097939132  -1.6966346717
O    8.0  -1.9281303440   0.9399081475  -0.4004528260
O    8.0   1.8775155130  -0.9929279412   0.3892706870
C    6.0  -3.1926202697   1.0552265535   0.2921774501
H    1.0  -3.4134434633   0.1308806514   0.8325687379
H    1.0  -3.9313050886   1.2254081366  -0.4904966586
H    1.0  -3.1683604678   1.8923986816   0.9932879456
C    6.0   2.6088709971  -2.1305205085  -0.1226831004
H    1.0   3.3331801917  -1.8069241420  -0.8746779727
H    1.0   1.9252857454  -2.8602840045  -0.5630248617
H    1.0   3.1167254332  -2.5526345422   0.7439076648
```

B3LYP/6-311G(2df,p)

```
C    6.0  -0.8437826980   0.8841301217   0.3805467654
O    8.0  -0.8143425966   0.9191979153   1.6017251336
C    6.0   0.4705733410   0.8812880308  -0.1603172143
C    6.0   1.1390631993  -0.3264389773  -0.5060291159
O    8.0   1.0044666794  -0.5932361907  -1.6898690469
O    8.0  -1.9120664156   0.9320980200  -0.3954663397
O    8.0   1.8674806045  -0.9805718054   0.3826445380
C    6.0  -3.1782645701   1.0352453274   0.2921171284
H    1.0  -3.3898165581   0.1114706123   0.8305293560
H    1.0  -3.9158293047   1.1985378317  -0.4886966138
H    1.0  -3.1629548413   1.8696866881   0.9916624207
C    6.0   2.5858865770  -2.1281174921  -0.1199165175
H    1.0   3.3187400466  -1.8169203433  -0.8641302626
H    1.0   1.8968514574  -2.8449772656  -0.5647112766
H    1.0   3.0794874507  -2.5565480649   0.7478604001
```

^{1}dicarbomethoxycarbene Z rotamer



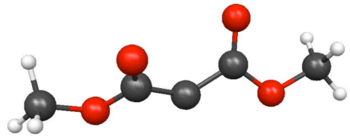
B3LYP/6-31G(d)

C	6.0	-0.8436239196	-0.8202198433	0.5681782024
O	8.0	-0.8007788844	-0.8145680916	1.7909801557
C	6.0	0.4133386738	-0.8016022404	-0.1178701391
C	6.0	1.2179579116	0.3719105511	-0.2639741253
O	8.0	1.8643984663	0.7005965674	0.7223765926
O	8.0	-1.9341168536	-0.9451594038	-0.1953512332
O	8.0	1.2668099942	0.9275219364	-1.4781627697
C	6.0	-3.1780343058	-1.0922563967	0.5259676459
H	1.0	-3.1185067524	-1.9306106019	1.2238830487
H	1.0	-3.9307690297	-1.2784586431	-0.2397284740
H	1.0	-3.4091626748	-0.1761154210	1.0759070923
C	6.0	2.2179622290	2.0071765108	-1.6251649274
H	1.0	3.2102768554	1.6846945842	-1.3017872299
H	1.0	1.9053150500	2.8729413799	-1.0358523077
H	1.0	2.2147451555	2.2456892770	-2.6882930032

B3LYP/6-311G(2df,p)

C	6.0	-0.8059214034	-0.8559074165	0.5737821562
O	8.0	-0.7773821200	-0.8606483514	1.7884865851
C	6.0	0.4629045702	-0.8661765644	-0.0834148031
C	6.0	1.2551138822	0.3172340474	-0.2306405444
O	8.0	1.8899283671	0.6804606642	0.7375508578
O	8.0	-1.8848538896	-0.9268577243	-0.2005104286
O	8.0	1.2775021061	0.8540701038	-1.4490063180
C	6.0	-3.1456876331	-1.0322990435	0.4957542354
H	1.0	-3.1207259056	-1.8613445886	1.2015510929
H	1.0	-3.8876216607	-1.2057790563	-0.2789375870
H	1.0	-3.3598492983	-0.1067048684	1.0299771921
C	6.0	2.1444009664	1.9957757046	-1.6154859938
H	1.0	3.1573064537	1.7592021743	-1.2914693078
H	1.0	1.7692269694	2.8408336923	-1.0382829345
H	1.0	2.1214705111	2.2196813918	-2.6782456741

^{3}dicarbomethoxycarbene EE rotamer



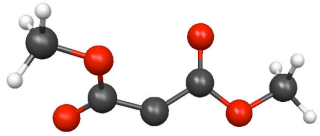
B3LYP/6-31G(d)

C	6.0	-0.4842618621	-0.0550549365	-0.2079954781
C	6.0	-0.4520275510	-0.1907459005	1.2392190217
C	6.0	0.5826999479	0.1249785999	-1.1778732423
O	8.0	0.5018902057	-0.6353170973	1.8521344749
O	8.0	1.6693742432	0.6004194562	-0.8999412442
O	8.0	-1.6155411956	0.1932962015	1.7987210985
O	8.0	0.1978913435	-0.2461060730	-2.4138523609
C	6.0	1.1788419779	-0.0437464114	-3.4473855784
H	1.0	1.4468247660	1.0141883449	-3.5192888716
H	1.0	2.0801037136	-0.6281298669	-3.2425891955
H	1.0	0.7022957349	-0.3833017294	-4.3673690026
C	6.0	-1.6701404779	0.0793503493	3.2326649763
H	1.0	-0.8841237098	0.6849763582	3.6921999106
H	1.0	-2.6555599401	0.4495988849	3.5158021425
H	1.0	-1.5445127124	-0.9621940591	3.5413819418

B3LYP/6-311G(2df,p)

C	6.0	-0.4722839057	-0.0553737188	-0.2030518046
C	6.0	-0.4526637851	-0.2079642125	1.2377121434
C	6.0	0.5808440893	0.1417261394	-1.1769960790
O	8.0	0.4767580942	-0.6922879985	1.8406422878
O	8.0	1.6439876026	0.6518274067	-0.9079624622
O	8.0	-1.5966077469	0.2112393865	1.7987327921
O	8.0	0.2103713364	-0.2600355408	-2.4016357047
C	6.0	1.1792058911	-0.0491539122	-3.4417720856
H	1.0	1.4343094027	1.0082133915	-3.5174985044
H	1.0	2.0860256819	-0.6203424711	-3.2407979169
H	1.0	0.7040330423	-0.3964362731	-4.3557774481
C	6.0	-1.6650426710	0.0860141175	3.2288251638
H	1.0	-0.8813217943	0.6816435311	3.6981277466
H	1.0	-2.6471090688	0.4585175161	3.5082312842
H	1.0	-1.5467516847	-0.9553752410	3.5290491801

^{3}dicarbomethoxycarbene ZE rotamer



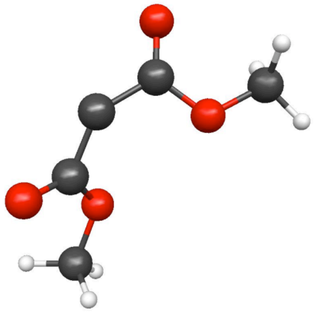
B3LYP/6-31G(d)

C	6.0	-0.7777464687	0.2178449167	-0.1681605117
C	6.0	-0.7673301742	0.1839978936	1.2859126032
C	6.0	0.2421933683	0.1807218568	-1.1951653680
O	8.0	-1.5228403526	0.8581048288	1.9626792580
O	8.0	1.4250903101	0.3587780571	-0.9545496847
O	8.0	0.1282358633	-0.6970820846	1.7766196820
O	8.0	-0.2715835169	-0.0367652496	-2.4189032219
C	6.0	0.6876084147	-0.0587992004	-3.4923825075
H	1.0	1.2024176347	0.9031653998	-3.5662661544
H	1.0	1.4257820990	-0.8488788822	-3.3297577571
H	1.0	0.1070230857	-0.2553528489	-4.3938812118
C	6.0	0.1856725039	-0.7697267314	3.2150536466
H	1.0	-0.8097012896	-0.9526172500	3.6273264861
H	1.0	0.8591021620	-1.5975844827	3.4368352322
H	1.0	0.5785720764	0.1657064581	3.6230131788

B3LYP/6-311G(2df,p)

C	6.0	-0.7583453963	0.1918849429	-0.1652969532
C	6.0	-0.7515809331	0.1793081750	1.2850748175
C	6.0	0.2462937505	0.1907971715	-1.1997412506
O	8.0	-1.4799012886	0.8800689194	1.9479656903
O	8.0	1.4140716230	0.4186358025	-0.9699442010
O	8.0	0.1160488712	-0.7155485634	1.7857931237
O	8.0	-0.2630713417	-0.0598332486	-2.4128477913
C	6.0	0.6839446491	-0.0620147125	-3.4942978354
H	1.0	1.1834193513	0.9041351100	-3.5679460371
H	1.0	1.4328939368	-0.8395013802	-3.3410038817
H	1.0	0.1014357743	-0.2634665320	-4.3895697687
C	6.0	0.1748219783	-0.7769811634	3.2224834673
H	1.0	-0.8195952444	-0.9468524719	3.6343087939
H	1.0	0.8391724076	-1.6056921888	3.4525944450
H	1.0	0.5728875782	0.1565728208	3.6208010512

^{3}dicarbomethoxycarbene ZZ rotamer



B3LYP/6-31G(d)

C	6.0	-1.0207772392	-0.0504533630	-0.3489647462
C	6.0	-0.9877221347	-0.0371494501	1.1008050889
C	6.0	-0.1245185622	-0.0155813570	-1.4872755864
O	8.0	-1.8828069247	0.4302301928	1.7812011653
O	8.0	-0.4145172332	-0.4654067473	-2.5808916050
O	8.0	0.1263594787	-0.6254785504	1.5890061125
O	8.0	1.0426486013	0.5981389509	-1.1904400912
C	6.0	1.9817079787	0.6809443676	-2.2799956822
H	1.0	2.2654384222	-0.3200422398	-2.6165029879
H	1.0	1.5458588598	1.2304645331	-3.1188871398
H	1.0	2.8445022302	1.2108272381	-1.8761420156
C	6.0	0.2209929258	-0.6485827410	3.0273012221
H	1.0	-0.6841853532	-1.0800476797	3.4613583102
H	1.0	1.0927193129	-1.2637482567	3.2506589361
H	1.0	0.3563860684	0.3659195590	3.4126091681

B3LYP/6-311G(2df,p)

C	6.0	-0.9984234747	-0.0428508979	-0.3399059321
C	6.0	-0.9763690418	-0.0272059347	1.1052614403
C	6.0	-0.1160784107	-0.0161075046	-1.4834150580
O	8.0	-1.8568982117	0.4587073939	1.7754733781
O	8.0	-0.4026184114	-0.4893831702	-2.5578170143
O	8.0	0.1190615566	-0.6342373575	1.5994970300
O	8.0	1.0404018959	0.6164810468	-1.2069066743
C	6.0	1.9782525189	0.6896087680	-2.2951476033
H	1.0	2.2775851990	-0.3118974233	-2.6055472332
H	1.0	1.5351970256	1.2087062754	-3.1452421714
H	1.0	2.8302173897	1.2415286160	-1.9064445193
C	6.0	0.2093277737	-0.6622366220	3.0357854065
H	1.0	-0.6996099733	-1.0846843841	3.4628380114
H	1.0	1.0716098422	-1.2837019779	3.2625330349
H	1.0	0.3504307527	0.3473076287	3.4228780537

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APPENDIX C
Supporting information for Chapter 5

Thiophene-*S*-oxide-Coordinates: S_0 A′ State

1.38Å S-O Bond Length

S	16.0	1.6100335373	-.5021242834	.0000000000
H	1.0	-1.7424797485	.1423629575	-1.3163189517
C	6.0	-.8450953250	.0384292144	-.7355988566
H	1.0	.6498815566	-.1694727270	-2.2937245745
C	6.0	.3859728527	-.1147481045	-1.2555271751
O	8.0	2.7246512577	.3172155488	.0000000000

1.48Å S-O Bond Length

S	16.0	1.6727391380	-0.4086038296	0.0000000000
H	1.0	-1.7311402701	-0.3046121733	-1.3174730480
C	6.0	-0.8292828761	-0.2751506261	-0.7356040397
H	1.0	0.6869788356	-0.2455974950	-2.2915215191
C	6.0	0.4102634491	-0.2389025392	-1.2560002571
O	8.0	2.6774813331	0.6780852342	0.0000000000

1.51Å S-O Bond Length:Optimized Ground State

S	16.0	1.5867450935	-.5305123333	.0000000000
H	1.0	-1.7385686200	.1924410918	-1.3177754645
C	6.0	-.8472477369	.0538425381	-.7355520953
H	1.0	.6501665394	-.1953546969	-2.2910690103
C	6.0	.3773759978	-.1400381860	-1.2561617749
O	8.0	2.7868025461	.3857308394	.0000000000

1.58Å S-O Bond Length

S	16.0	1.5731680184	-0.5471732880	0.0000000000
H	1.0	-1.7361794202	0.2190985962	-1.3187065043
C	6.0	-0.8488027387	0.0624270806	-0.7353405342
H	1.0	0.6497044334	-0.2085852363	-2.2893644108
C	6.0	0.3722532812	-0.1530533349	-1.2561807426
O	8.0	2.8237185457	0.4239902420	0.0000000000

1.61Å S-O Bond Length

S	16.0	1.5684507073	-.5536988404	.0000000000
H	1.0	-1.7349877848	.2289320905	-1.3190279851
C	6.0	-.8490479016	.0660836885	-.7352720289
H	1.0	.6490624898	-.2143375696	-2.2888475037
C	6.0	.3704877073	-.1581051654	-1.2561367795
O	8.0	2.8360957267	.4386133046	.0000000000

1.71Å S-O Bond Length

S	16.0	1.5505550562	-0.5785319443	0.0000000000
H	1.0	-1.7292560127	0.2686204345	-1.3199364793
C	6.0	-0.8496329616	0.0799208951	-0.7347407529
H	1.0	0.6462285106	-0.2360701004	-2.2869379201
C	6.0	0.3637469446	-0.1770245423	-1.2559172530
O	8.0	2.8824942260	0.4936148763	0.0000000000

1.81Å S-O Bond Length

S	16.0	1.5329814494	-0.6056694524	0.0000000000
H	1.0	-1.7213729384	0.3091587132	-1.3207991545
C	6.0	-0.8487172817	0.0952428439	-0.7341306392
H	1.0	0.6423576734	-0.2591002735	-2.2851846298
C	6.0	0.3575719868	-0.1958936578	-1.2553896558
O	8.0	2.9250077501	0.5509758802	0.0000000000

1.91Å S-O Bond Length

S	16.0	1.5156053589	-0.6361449207	0.0000000000
H	1.0	-1.7098934981	0.3531332042	-1.3216605194
C	6.0	-0.8453974482	0.1125672049	-0.7334819673
H	1.0	0.6383061170	-0.2828499702	-2.2836243153
C	6.0	0.3524746886	-0.2147481509	-1.2546816649
O	8.0	2.9614716452	0.6116402334	0.0000000000

2.01Å S-O Bond Length

S	16.0	1.4987569804	-0.6726131854	0.0000000000
H	1.0	-1.6923136717	0.4042484405	-1.3223115621
C	6.0	-0.8376853549	0.1339753666	-0.7328322794
H	1.0	0.6349109046	-0.3083783865	-2.2824093303
C	6.0	0.3491614529	-0.2342462783	-1.2540422894
O	8.0	2.9867617992	0.6784459243	0.0000000000

2.11Å S-O Bond Length

S	16.0	1.4828387955	-.7222748441	.0000000000
H	1.0	-1.6588109070	.4777038029	-1.3232799099
C	6.0	-.8197909963	.1651772405	-.7323567939
H	1.0	.6351047070	-.3347705527	-2.2816572131
C	6.0	.3499152432	-.2561522165	-1.2536004821
O	8.0	2.9863542806	.7578200110	.0000000000

2.21Å S-O Bond Length

S	16.0	1.4830224414	-0.7537988454	0.0000000000
H	1.0	-1.6678225449	0.5021539123	-1.3150730466
C	6.0	-0.8309535332	0.1775430059	-0.7272713869
H	1.0	0.5994550867	-0.3527556957	-2.2943512788
C	6.0	0.3277915961	-0.2637305109	-1.2632454349

O	8.0	3.0415604894	0.8128348353	0.0000000000

2.31Å S-O Bond Length

S	16.0	1.4672563703	-0.7909090412	0.0000000000
H	1.0	-1.6480815270	0.5464252346	-1.3144931477
C	6.0	-0.8223743103	0.1972414147	-0.7249435846
H	1.0	0.5914128542	-0.3772854262	-2.2927777639
C	6.0	0.3246182652	-0.2795354303	-1.2611679771
O	8.0	3.0634894571	0.8786841519	0.0000000000

2.41Å S-O Bond Length

S	16.0	1.4506107819	-0.8195331326	0.0000000000
H	1.0	-1.6367350078	0.5768648581	-1.3136196813
C	6.0	-0.8196927314	0.2101375937	-0.7225152450
H	1.0	0.5815763357	-0.3981553250	-2.2905043284
C	6.0	0.3187470078	-0.2934265946	-1.2584459067
O	8.0	3.1013579144	0.9361875632	0.0000000000

2.51Å S-O Bond Length

S	16.0	1.4340595230	-0.8410633973	0.0000000000
H	1.0	-1.6341165106	0.5936572799	-1.3131488297
C	6.0	-0.8226659751	0.2165045656	-0.7207615650
H	1.0	0.5685525627	-0.4166887997	-2.2887868773
C	6.0	0.3100174335	-0.3051434997	-1.2562291677
O	8.0	3.1533131323	0.9874710578	0.0000000000

2.61Å S-O Bond Length

S	16.0	1.4177708197	-0.8560969459	0.0000000000
H	1.0	-1.6389028176	0.5999923431	-1.3132069757
C	6.0	-0.8311299942	0.2166947882	-0.7196470386
H	1.0	0.5545585060	-0.4292923491	-2.2875781667
C	6.0	0.2985398800	-0.3153362863	-1.2545496949
O	8.0	3.2181610086	1.0333200359	0.0000000000

2.71Å S-O Bond Length

S	16.0	1.4017907632	-0.8711348237	0.0000000000
H	1.0	-1.6443037085	0.6058066217	-1.3129844855
C	6.0	-0.8396635352	0.2167062046	-0.7188543089
H	1.0	0.5404738359	-0.4423340230	-2.2867109624
C	6.0	0.2865620505	-0.3251584822	-1.2534402018
O	8.0	3.2833357702	1.0790107392	0.0000000000

2.81Å S-O Bond Length

S	16.0	1.3857739230	-0.8859613246	0.0000000000
H	1.0	-1.6506387121	0.6099604954	-1.3126662217
C	6.0	-0.8486669415	0.2157760775	-0.7182567475
H	1.0	0.5273472075	-0.4531199551	-2.2860838869

C	6.0	0.2746307090	-0.3339541490	-1.2526685791
O	8.0	3.3492163110	1.1240763811	0.0000000000

2.91Å S-O Bond Length

S	16.0	1.3699577590	-0.9001647499	0.0000000000
H	1.0	-1.6571420417	0.6137755599	-1.3127332517
C	6.0	-0.8578564304	0.2146630728	-0.7179367016
H	1.0	0.5130112845	-0.4649539529	-2.2856765375
C	6.0	0.2621193466	-0.3431001799	-1.2520824021
O	8.0	3.4160188484	1.1688714520	0.0000000000

3.01Å S-O Bond Length

S	16.0	1.3542193622	-0.9145222076	0.0000000000
H	1.0	-1.6643198360	0.6167528767	-1.3125420153
C	6.0	-0.8673378992	0.2130479886	-0.7176742035
H	1.0	0.4997302634	-0.4748794388	-2.2853389193
C	6.0	0.2496925057	-0.3514073436	-1.2517109852
O	8.0	3.4829292824	1.2133341385	0.0000000000

3.11Å S-O Bond Length

S	16.0	1.3388683371	-0.9287118737	0.0000000000
H	1.0	-1.6717288195	0.6194778649	-1.3124047053
C	6.0	-0.8770923357	0.2112569210	-0.7174791149
H	1.0	0.4853602113	-0.4845148743	-2.2856488037
C	6.0	0.2367478542	-0.3596699267	-1.2516300692
O	8.0	3.5504183194	1.2576538412	0.0000000000

3.21Å S-O Bond Length

S	16.0	1.3231592038	-0.9424149549	0.0000000000
H	1.0	-1.6792074618	0.6215747343	-1.3124413467
C	6.0	-0.8868195188	0.2091593846	-0.7173503961
H	1.0	0.4716428065	-0.4944894645	-2.2854528574
C	6.0	0.2240281525	-0.3680086753	-1.2513951856
O	8.0	3.6181712831	1.3016969425	0.0000000000

Thiophene-*S*-oxide-Coordinates: T_1 A″ State

1.38Å S-O Bond Length

S	16.0	1.7478470331	-0.4633150175	0.0000000000
H	1.0	-1.7387392753	0.0666345902	-1.2971793947
C	6.0	-0.8740735465	-0.0915577456	-0.6817814002
H	1.0	0.6916251199	-0.3483649662	-2.2726089754
C	6.0	0.4431659222	-0.3619487896	-1.2293745879
O	8.0	2.5455589597	0.6627647678	0.0000000000

1.48Å S-O Bond Length

S	16.0	1.7312903933	-0.4903135819	0.0000000000
H	1.0	-1.7260131788	0.1051219487	-1.2982231751

C	6.0	-0.8673283820	-0.0773953997	-0.6816353886
H	1.0	0.6999792954	-0.3651426844	-2.2695638143
C	6.0	0.4411625120	-0.3866880402	-1.2296686730
O	8.0	2.5688824726	0.7298665315	0.0000000000

1.52Å S-O Bond Length

S	16.0	1.7248035427	-0.5013891036	0.0000000000
H	1.0	-1.7213721674	0.1183294608	-1.2985171112
C	6.0	-0.8648218954	-0.0722307846	-0.6815452675
H	1.0	0.7026084500	-0.3720805067	-2.2685592940
C	6.0	0.4402738157	-0.3951914672	-1.2298320969
O	8.0	2.5785053442	0.7562250005	0.0000000000

1.60Å S-O Bond Length

S	16.0	1.7116322853	-0.5238832505	0.0000000000
H	1.0	-1.7120387263	0.1439757296	-1.2990518142
C	6.0	-0.8598399250	-0.0622575729	-0.6813985037
H	1.0	0.7075849679	-0.3868376533	-2.2663538831
C	6.0	0.4388012428	-0.4108333420	-1.2297121097
O	8.0	2.5977641554	0.8083218048	0.0000000000

1.70Å S-O Bond Length

S	16.0	1.6952116952	-0.5536530144	0.0000000000
H	1.0	-1.6998858208	0.1718712742	-1.3002922880
C	6.0	-0.8528779384	-0.0499520854	-0.6812419240
H	1.0	0.7124930039	-0.4060719598	-2.2638490540
C	6.0	0.4378551501	-0.4274339147	-1.2291327522
O	8.0	2.6194104114	0.8731815006	0.0000000000

1.80Å S-O Bond Length

S	16.0	1.6781925801	-0.5910684389	0.0000000000
H	1.0	-1.6781705303	0.2087492612	-1.3017985711
C	6.0	-0.8372564348	-0.0318758682	-0.6817605260
H	1.0	0.7209728736	-0.4304106200	-2.2612594540
C	6.0	0.4417634442	-0.4430394430	-1.2280212148
O	8.0	2.6203205959	0.9426834324	0.0000000000

1.90Å S-O Bond Length

S	16.0	1.6491480895	-0.7015412000	0.0000000000
H	1.0	-1.5804922918	0.2511361620	-1.3121753444
C	6.0	-0.7247660047	0.0049805565	-0.7137092101
H	1.0	0.7477101980	-0.4814698124	-2.2789079445
C	6.0	0.4751609934	-0.3863937867	-1.2484466601
O	8.0	2.4437971116	1.0243014729	0.0000000000

2.00Å S-O Bond Length

S	16.0	1.6392211541	-0.7220346276	0.0000000000

H	1.0	-1.5890830317	0.2514155875	-1.3132118796
C	6.0	-0.7354484983	-0.0045058271	-0.7156085950
H	1.0	0.7334940447	-0.4760945933	-2.2803797910
C	6.0	0.4620239852	-0.3886518089	-1.2486462522
O	8.0	2.5022546725	1.0821752123	0.0000000000

2.10Å S-O Bond Length

S	16.0	1.6270532638	-0.7302100086	0.0000000000
H	1.0	-1.6101246176	0.2329744435	-1.3128315515
C	6.0	-0.7555644235	-0.0224495211	-0.7160884520
H	1.0	0.7131759217	-0.4755078784	-2.2825754082
C	6.0	0.4432594087	-0.3941441392	-1.2496219430
O	8.0	2.5901283384	1.1359321084	0.0000000000

2.30Å S-O Bond Length

S	16.0	1.6048048479	-0.7734623012	0.0000000000
H	1.0	-1.6210787726	0.2411766726	-1.3125034726
C	6.0	-0.7697270319	-0.0269297564	-0.7164786672
H	1.0	0.6905947673	-0.4929814621	-2.2837252037
C	6.0	0.4238116429	-0.4105044864	-1.2498992238
O	8.0	2.6892581452	1.2548278767	0.0000000000

2.50Å S-O Bond Length

S	16.0	1.5850607934	-0.8331531908	0.0000000000
H	1.0	-1.6121515820	0.2806988533	-1.3135279355
C	6.0	-0.7700099054	-0.0130477815	-0.7163811958
H	1.0	0.6747618566	-0.5215679183	-2.2843887532
C	6.0	0.4119170652	-0.4291833058	-1.2502065130
O	8.0	2.7478665796	1.3799628711	0.0000000000

Thiophene-*S*-oxide-Coordinates: T_2 A′ State

1.36Å S-O Bond Length

S	16.0	1.6423688302	-0.3141236056	0.0000000000
H	1.0	-1.6754300357	-0.0309144303	-1.3038026024
C	6.0	-0.7993819353	-0.2177351393	-0.7131725655
H	1.0	0.7555808953	-0.3959576619	-2.2933540795
C	6.0	0.4541295077	-0.4069415320	-1.2674683963
O	8.0	2.6118369217	0.6396749162	0.0000000000

1.48Å S-O Bond Length

S	16.0	1.6293971968	-0.3432109857	0.0000000000
H	1.0	-1.6853652611	-0.0320847282	-1.3063722688
C	6.0	-0.8102461574	-0.2141565696	-0.7131808085

H	1.0	0.7461594211	-0.4092075744	-2.2895676029
C	6.0	0.4413786191	-0.4131516477	-1.2649728424
O	8.0	2.6756390288	0.7035831817	0.0000000000

1.60Å S-O Bond Length

S	16.0	1.6144642928	-0.4220765755	0.0000000000
H	1.0	-1.6889937102	0.0559617962	-1.3097877205
C	6.0	-0.8192437276	-0.1379890322	-0.7126469917
H	1.0	0.7240568532	-0.4245752740	-2.2830961310
C	6.0	0.4219130090	-0.3904135499	-1.2582187267
O	8.0	2.7514391992	0.7036623221	0.0000000000

1.70Å S-O Bond Length

S	16.0	1.6279480683	-0.5217828385	0.0000000000
H	1.0	-1.6751730782	0.0791687527	-1.3102169725
C	6.0	-0.8012878952	-0.0940440240	-0.7127863068
H	1.0	0.7208687059	-0.4503108834	-2.2815419195
C	6.0	0.4306969040	-0.3729822036	-1.2551096727
O	8.0	2.6830243698	0.8111890285	0.0000000000

1.80Å S-O Bond Length

S	16.0	1.6238009200	-0.5659396882	0.0000000000
H	1.0	-1.6737167765	0.0980991327	-1.3123221822
C	6.0	-0.8013179688	-0.0832165649	-0.7149946955
H	1.0	0.7123155225	-0.4434778396	-2.2799916045
C	6.0	0.4257001064	-0.3710682025	-1.2518149801
O	8.0	2.6997511069	0.8770887928	0.0000000000

1.90Å S-O Bond Length

S	16.0	1.6141523859	-0.5876851929	0.0000000000
H	1.0	-1.6849739052	0.0970977384	-1.3136066277
C	6.0	-0.8133840324	-0.0892301498	-0.7164068816
H	1.0	0.6962466072	-0.4333852118	-2.2803108882
C	6.0	0.4123936703	-0.3704422629	-1.2504393360
O	8.0	2.7605519079	0.9274940493	0.0000000000

2.00Å S-O Bond Length

S	16.0	1.5976566825	-0.5670479680	0.0000000000
H	1.0	-1.7267383953	0.0374652495	-1.3132100833
C	6.0	-0.8501247948	-0.1286876846	-0.7169977999
H	1.0	0.6630306138	-0.4155409121	-2.2832601292
C	6.0	0.3813453100	-0.3678275416	-1.2515148090
O	8.0	2.9046899579	0.9467903812	0.0000000000

2.10Å S-O Bond Length

S	16.0	1.4813182271	-0.0170721919	0.0000000000
H	1.0	-1.8407628066	-0.7334065578	-1.3140654548
C	6.0	-0.9679497950	-0.5447492050	-0.7181902595

H	1.0	0.5255911476	-0.2218213893	-2.2870814622
C	6.0	0.2541687215	-0.2810402444	-1.2525832591
O	8.0	3.5365461259	0.4142493635	0.0000000000

2.20Å S-O Bond Length

S	16.0	1.4639048672	-0.0206739226	0.0000000000
H	1.0	-1.8550743774	-0.7362676842	-1.3137942756
C	6.0	-0.9823949560	-0.5477663519	-0.7177694002
H	1.0	0.5120589972	-0.2250210890	-2.2860426355
C	6.0	0.2405402983	-0.2840504703	-1.2515964078
O	8.0	3.6169861146	0.4312565387	0.0000000000

2.30Å S-O Bond Length

S	16.0	1.4470374117	-0.0241878295	0.0000000000
H	1.0	-1.8696404512	-0.7392460172	-1.3138903944
C	6.0	-0.9972133865	-0.5508940749	-0.7174535150
H	1.0	0.4979345134	-0.2282017134	-2.2854552923
C	6.0	0.2262694310	-0.2871344669	-1.2510532153
O	8.0	3.6979656723	0.4483771383	0.0000000000

2.40Å S-O Bond Length

S	16.0	1.4304825153	-.0276430913	.0000000000
H	1.0	-1.8845725721	-.7423688583	-1.3137334670
C	6.0	-1.0122165265	-.5540843451	-.7172251877
H	1.0	.4835283580	-.2313476010	-2.2851084545
C	6.0	.2116028410	-.2902634704	-1.2507980200
O	8.0	3.7792730084	.4655557284	.0000000000

2.50Å S-O Bond Length

S	16.0	1.4140904775	-0.0310724289	0.0000000000
H	1.0	-1.8995413695	-0.7455236644	-1.3137483220
C	6.0	-1.0273199957	-0.5572991465	-0.7170810757
H	1.0	0.4688659815	-0.2345130522	-2.2848999468
C	6.0	0.1967609831	-0.2934175060	-1.2506804291
O	8.0	3.8607052457	0.4827633611	0.0000000000

2.60Å S-O Bond Length

S	16.0	1.3980409395	-0.0344256616	0.0000000000
H	1.0	-1.9149039445	-0.7487965005	-1.3136792878
C	6.0	-1.0426886539	-0.5605825074	-0.7169569932
H	1.0	0.4536212875	-0.2377716525	-2.2848407469
C	6.0	0.1815369114	-0.2966379987	-1.2505894374
O	8.0	3.9425472824	0.5000480703	0.0000000000

2.70Å S-O Bond Length

S	16.0	1.3819877137	-0.0377836654	0.0000000000
H	1.0	-1.9301925684	-0.7520457116	-1.3136474918
C	6.0	-1.0579978380	-0.5638468745	-0.7168813347

H	1.0	0.4383955500	-0.2410253078	-2.2848157416
C	6.0	0.1662724088	-0.2998729186	-1.2505993063
O	8.0	4.0243564086	0.5173318639	0.0000000000

2.80Å S-O Bond Length

S	16.0	1.3660685424	-0.0411147295	0.0000000000
H	1.0	-1.9455975756	-0.7553240742	-1.3135470002
C	6.0	-1.0734276693	-0.5671376402	-0.7168031828
H	1.0	0.4230993939	-0.2442877979	-2.2847730017
C	6.0	0.1509017378	-0.3031282436	-1.2505891352
O	8.0	4.1062614468	0.5346368229	0.0000000000

2.90Å S-O Bond Length

S	16.0	1.3502254287	-0.0444294890	0.0000000000
H	1.0	-1.9610778946	-0.7586269855	-1.3135253649
C	6.0	-1.0889352058	-0.5704466974	-0.7167608446
H	1.0	0.4077224391	-0.2475598893	-2.2847622105
C	6.0	0.1354747462	-0.3063930361	-1.2506261485
O	8.0	4.1882352296	0.5519551460	0.0000000000

3.00Å S-O Bond Length

S	16.0	1.3344710810	-0.0477269369	0.0000000000
H	1.0	-1.9766192378	-0.7619592474	-1.3135234868
C	6.0	-1.1044728003	-0.5737626962	-0.7167473709
H	1.0	0.3921606372	-0.2508515697	-2.2848097977
C	6.0	0.1198983042	-0.3096869386	-1.2506550071
O	8.0	4.2703319115	0.5692991271	0.0000000000

3.10Å S-O Bond Length

S	16.0	1.3187067512	-0.0510292131	0.0000000000
H	1.0	-1.9921824759	-0.7652896734	-1.3134868872
C	6.0	-1.1200408487	-0.5770820677	-0.7167265014
H	1.0	0.3766588406	-0.2541336041	-2.2848092213
C	6.0	0.1043491506	-0.3129770582	-1.2506866120
O	8.0	4.3524484937	0.5866506969	0.0000000000

3.20Å S-O Bond Length

S	16.0	1.2874032150	-0.0580835272	0.0000000000
H	1.0	-2.0240751755	-0.7689375241	-1.3135180730
C	6.0	-1.1517197137	-0.5816175836	-0.7167017489
H	1.0	0.3453537847	-0.2601904841	-2.2848398654
C	6.0	0.0730218765	-0.3187419450	-1.2506651063
O	8.0	4.5175241800	0.6174299906	0.0000000000

3.40Å S-O Bond Length

S	16.0	1.2874031319	-0.0580835390	0.0000000000
H	1.0	-2.0240746938	-0.7689374593	-1.3135178526
C	6.0	-1.1517193808	-0.5816175390	-0.7167016286

H	1.0	0.3453538623	-0.2601904741	-2.2848394820
C	6.0	0.0730220006	-0.3187419287	-1.2506648964
O	8.0	4.5175235900	0.6174299133	0.0000000000

Thiophene-*S*-oxide-Coordinates: ^{1}A″ State

1.48Å S-O Bond Length

S	16.0	1.6561888376	-0.3002565885	0.0000000000
H	1.0	-1.7590303280	-0.1013836034	-1.3169268787
C	6.0	-0.9108655883	-0.2263771388	-0.6736077920
H	1.0	0.7232520004	-0.5039927567	-2.2337957855
C	6.0	0.4511168243	-0.4244059937	-1.2008154844
O	8.0	2.7706205906	0.6736232134	0.0000000000

1.51Å S-O Bond Length

S	16.0	1.6054651894	-0.6124315050	0.0000000000
H	1.0	-1.6445937184	0.3871195458	-1.3037482705
C	6.0	-0.7841015998	0.1775523657	-0.6981030920
H	1.0	0.7349191595	-0.3045946775	-2.2695889510
C	6.0	0.4170577321	-0.2694237338	-1.2496166892
O	8.0	2.5725693145	0.5472277603	0.0000000000

1.60Å S-O Bond Length

S	16.0	1.5858540739	-0.6474666122	0.0000000000
H	1.0	-1.6030206711	0.4589079431	-1.3063113270
C	6.0	-0.7541326299	0.1989836208	-0.7040974679
H	1.0	0.7067000512	-0.4129234483	-2.2732643706
C	6.0	0.4219843594	-0.2919734896	-1.2503522934
O	8.0	2.5577268901	0.6235421328	0.0000000000

1.70Å S-O Bond Length

S	16.0	1.5734114251	-0.6886564780	0.0000000000
H	1.0	-1.5781666098	0.5068304209	-1.3060210227
C	6.0	-0.7353074816	0.2157121005	-0.7096682696
H	1.0	0.6798861067	-0.4637733865	-2.2815196909
C	6.0	0.4204779340	-0.3032105292	-1.2570293873
O	8.0	2.5568590095	0.6980052867	0.0000000000

1.80Å S-O Bond Length

S	16.0	1.5576391061	-0.7148427145	0.0000000000
H	1.0	-1.5714777179	0.5259638216	-1.3092734209
C	6.0	-0.7348444100	0.2174596390	-0.7130159463
H	1.0	0.6719238511	-0.4645812587	-2.2812834431
C	6.0	0.4142118481	-0.3093166516	-1.2552365090
O	8.0	2.5972539028	0.7545793061	0.0000000000

1.90Å S-O Bond Length

S	16.0	1.5432143074	-0.7414753624	0.0000000000
H	1.0	-1.5679226707	0.5416135019	-1.3120360857
C	6.0	-0.7373033622	0.2171400967	-0.7158857324
H	1.0	0.6656193213	-0.4565795533	-2.2813941068
C	6.0	0.4070756969	-0.3120446658	-1.2536758732
O	8.0	2.6408312128	0.8094073311	0.0000000000

2.00Å S-O Bond Length

S	16.0	1.5298925140	-0.7699016339	0.0000000000
H	1.0	-1.5644013706	0.5575598998	-1.3138380115
C	6.0	-0.7398104129	0.2174995015	-0.7179454187
H	1.0	0.6596483290	-0.4474724528	-2.2821214130
C	6.0	0.4000611655	-0.3136114624	-1.2529456678
O	8.0	2.6820556400	0.8648827957	0.0000000000

2.20Å S-O Bond Length

S	16.0	1.5055560665	-0.8159704407	0.0000000000
H	1.0	-1.5720742055	0.5757917642	-1.3135646600
C	6.0	-0.7566227239	0.2118831494	-0.7187627629
H	1.0	0.6373579253	-0.4369686087	-2.2853080989
C	6.0	0.3783786943	-0.3181146390	-1.2535715954
O	8.0	2.7922379905	0.9685321864	0.0000000000

Selenophene-*Se*-oxide-Optimized Geometry

C	6.0	-.8434234720	.0604081850	-.7375828784
SE	34.0	1.7071384915	-.6184554663	.0000000000
C	6.0	.3470106986	-.1879992344	-1.3095936583
H	1.0	.5603507407	-.2417836683	-2.3588677665
O	8.0	2.9041269549	.5285611667	.0000000000
H	1.0	-1.7410706905	.2528218675	-1.2968645279

Dibenzothiophene-*S*-oxide-Optimized Geometry

S	16.0	1.6213256014	-.4184904228	.0000000000
C	6.0	-2.0024416587	.1148183371	1.6029682735
C	6.0	-.9467240768	-.0257524420	.7367079883
C	6.0	.5970059706	-.1462881257	2.6108556731
C	6.0	.3543561662	-.1727227364	1.2565125096
O	8.0	2.6480785308	.6869948846	.0000000000
C	6.0	-1.7634090579	.1355060410	2.9824039317
C	6.0	-.4872979773	.0155819059	3.4818117291
H	1.0	1.5966982025	-.2425519677	2.9939922912
H	1.0	-.3182926580	.0449790147	4.5427968650
H	1.0	-2.5919001382	.2536715453	3.6572896537
H	1.0	-3.0073767437	.2200270728	1.2357728641

Figure S1. Comparison of CASSCF/G3Large* vs CASSCF/G3Large*//CASSCF/6-31G(d).

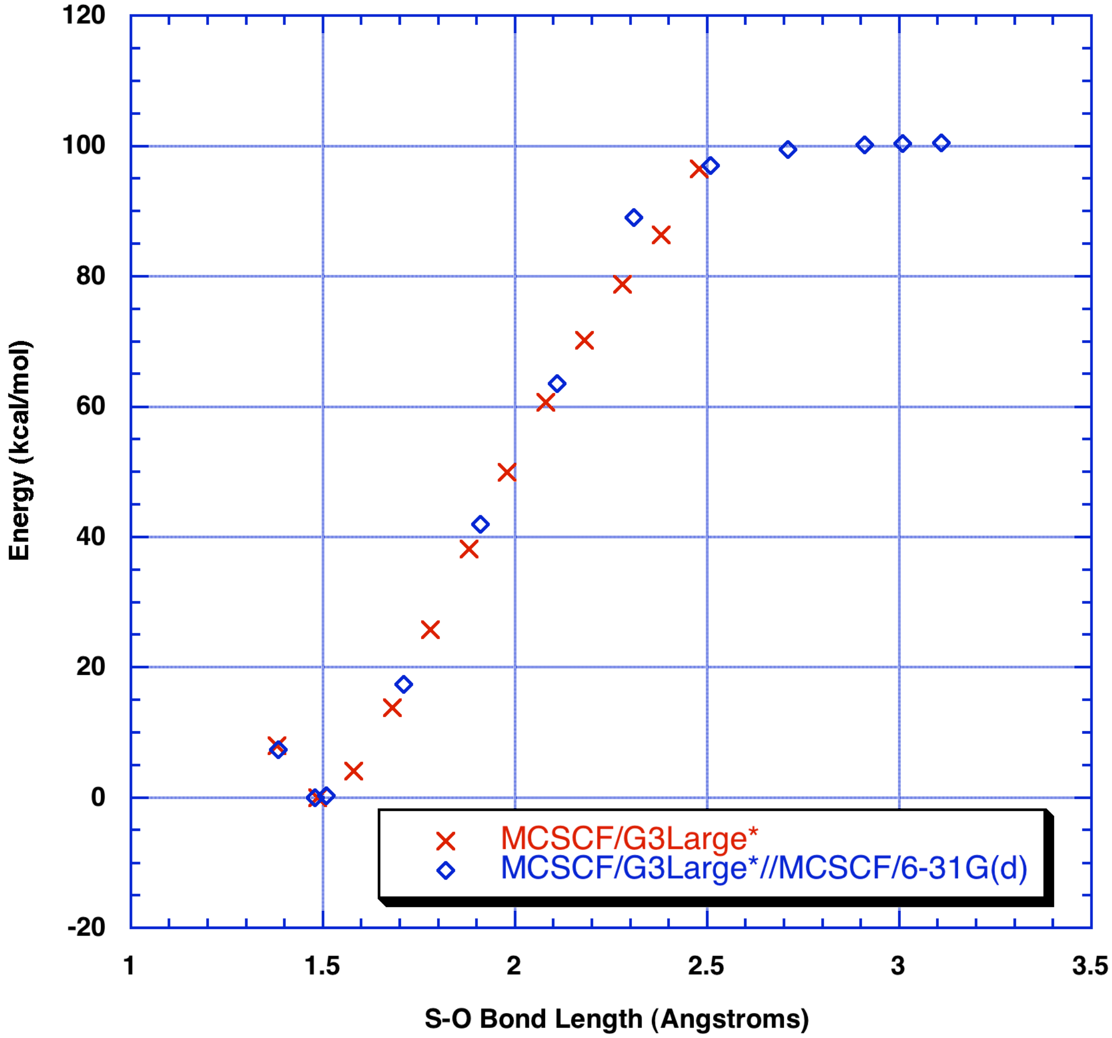


Figure S2. Thiophene-*S*-oxide potential energy surface generated at HF/6-31G(d).

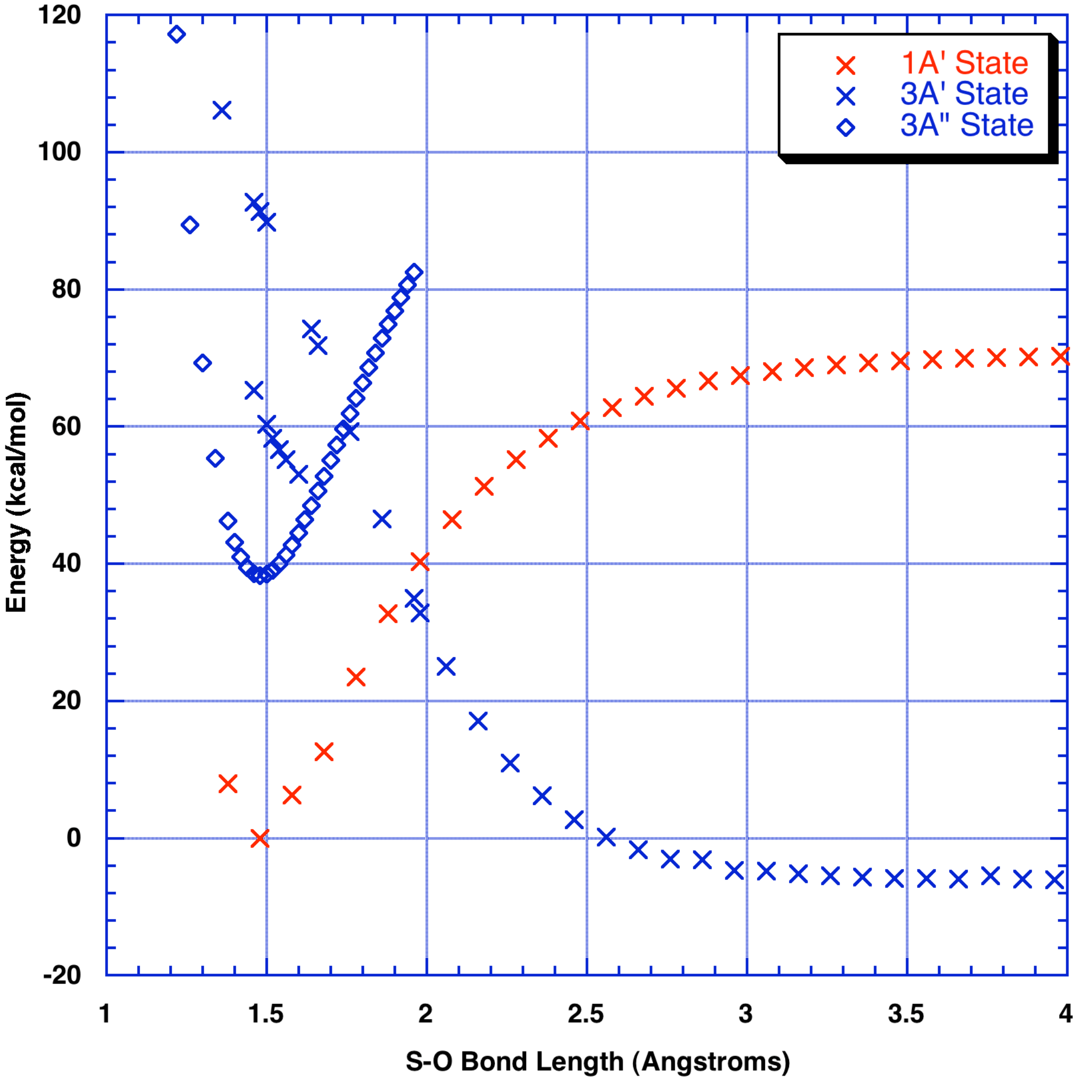
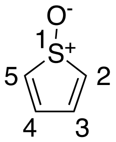


Figure S3. Thiophene-*S*-oxide dihedral angle 1(S),2,3,4 (angle of S out of plane of thiophene ring) versus S-O bond length.



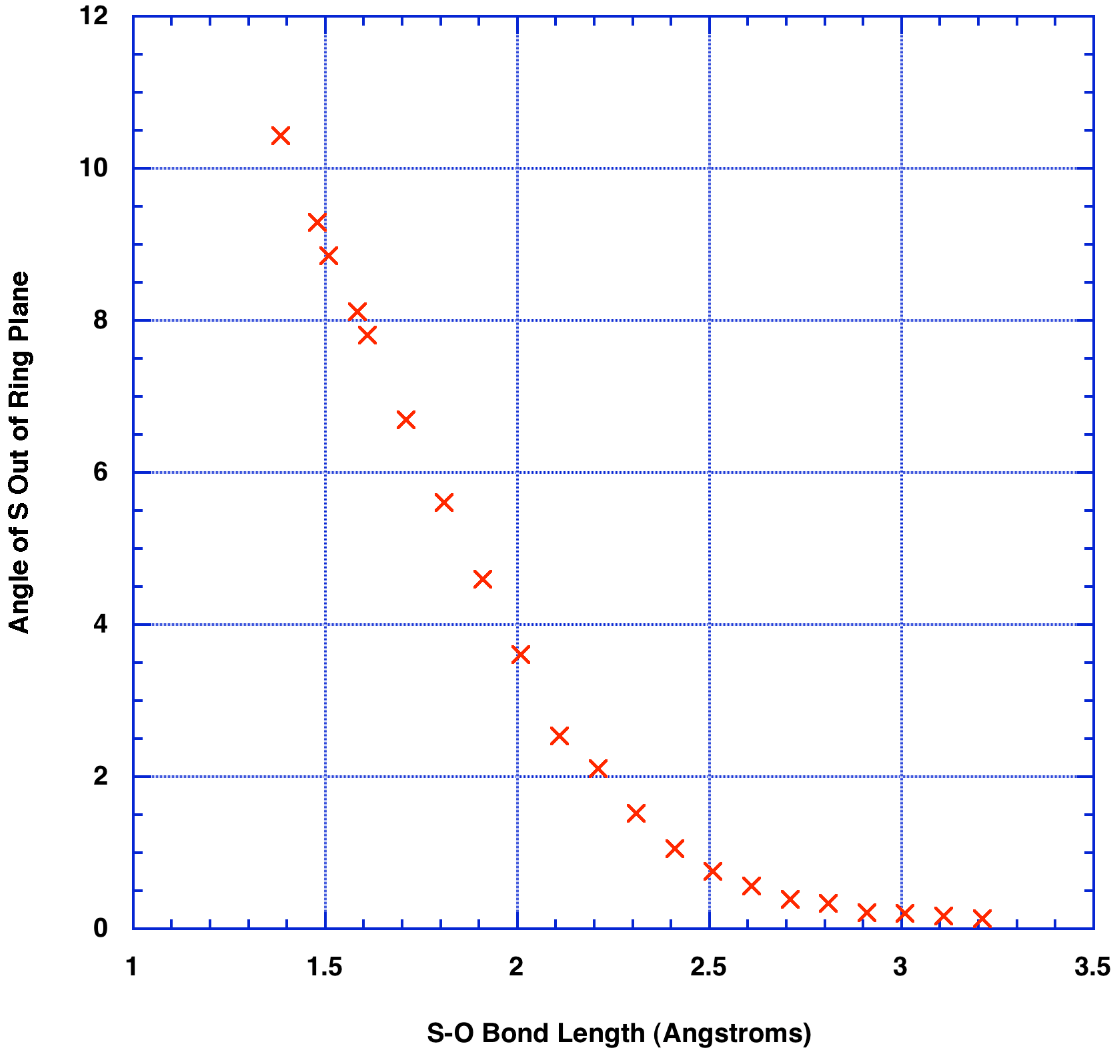
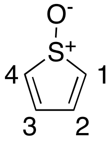


Figure S4. Thiophene-*S*-oxide C2-C3 bond length versus S-O bond length.



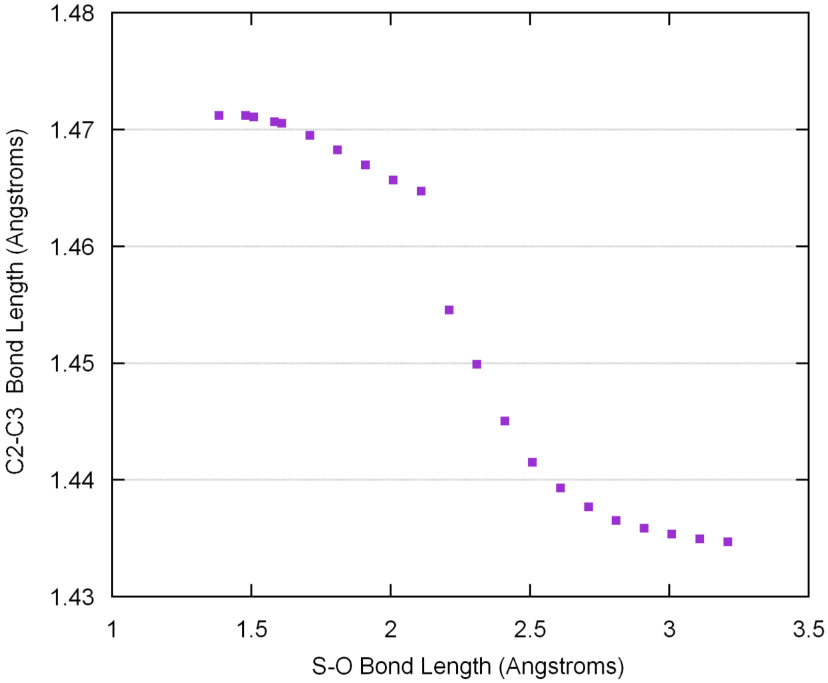
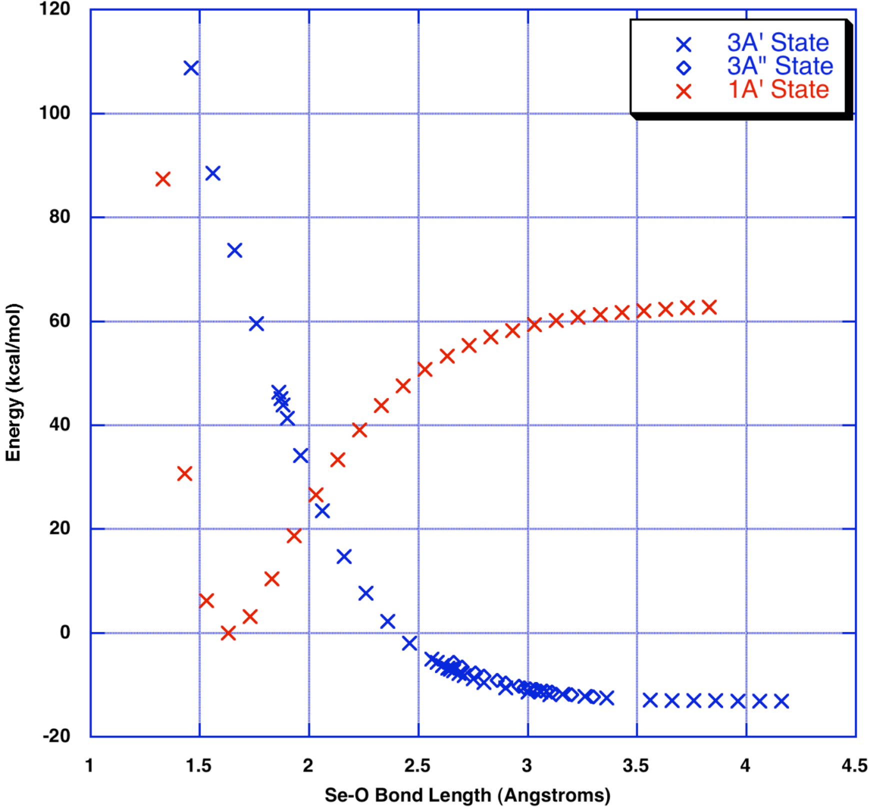


Figure S5. Selenophene-*Se*-oxide potential energy surface generated at HF/6-31G(d).



APPENDIX D

Supporting information for Chapter 6

Coordinates and Absolute Energies

O(^{3}P)

MP2/6-31G(d,p)

```
O          8.0    .00000000000    .0000000000    .0000000000
```

```
Energy                                -46986.768 KCAL/MOL
ZPE Correction                             0.000 KCAL/MOL
298.15K Temperature Correction             1.481 KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-46986.76779	-47081.58153
6-31G(2d)	-46999.70479	-47083.33631
6-31G(d,p)	-46986.76779	-47081.58153
6-31+G(d)	-46989.90189	-47085.87546
6-31+G(2d,p)	-47002.75640	-47087.68341
6-311G(d)	-47013.53427	-47097.52784
6-311G(3df,2p)	-47034.84814	-47098.62731
6-311++G(d)	-47015.47389	-47100.23089
6-311++G(3df,2p)	-47036.97187	-47101.60628
G3 (298.15K)	-47081.80861	
G3 (0K)	-47082.69716	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM           MULL.POP.     CHARGE          LOW.POP.      CHARGE
1 O            8.000000      .000000         8.000000      .000000
```

^{3}NH

MP2/6-31G(d,p)

```
H            1.0     .0000000000    .0000000000    -.5177663015
N            7.0     .0000000000    .0000000000     .5177663015
```

```
Energy                                -34554.518  KCAL/MOL
ZPE Correction                             4.91   KCAL/MOL
298.15K Temperature Correction             6.982  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-34548.73119	-34630.91062
6-31G(2d)	-34556.24559	-34631.27856

6-31G(d,p)	-34554.51817	-34632.72434
6-31+G(d)	-34551.19051	-34633.90160
6-31G+(2d,p)	-34564.31893	-34636.21335
6-311G(d)	-34563.12358	-34640.51514
6-311(3df,2p)	-34585.90638	-34644.32007
6-311++G(d)	-34564.31893	-34642.86776
6-311++G(3df,2p)	-34587.70596	-34646.60617
G3 (298.15K)	-34632.44821	
G3 (0K)	-34633.92976	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.     CHARGE          LOW.POP.     CHARGE
1 H           .752252      .247748          .841911      .158089
2 N          7.247748     -.247748         7.158089     -.158089
```

$^{3}CH_2$

MP2/6-31G(d,p)

```
H           1.0     .0000000000   -.9785778959    .7429948987
H           1.0     .0000000000    .9785778959    .7429948987
C           6.0     .0000000000    .0000000000    .3000882006
```

```
Energy                                 -24483.642 KCAL/MOL
ZPE Correction                             11.36  KCAL/MOL
298.15K Temperature Correction             13.739 KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-24473.6073	-24547.83779
6-31G(2d)	-24478.25298	-24547.54653
6-31G(d,p)	-24483.64159	-24550.00374
6-31+G(d)	-24475.88709	-24528.29615
6-311G(d)	-24483.9349	-24554.81581
6-311G(3df,2p)	-24504.80837	-24558.55652
6-311++G(d)	-24484.62501	-24555.73821
6-311++G(3df,2p)	-24505.58167	-24559.58917
G3 (298.15K)	-24545.23312	
G3 (0K)	-24547.02654	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.     CHARGE          LOW.POP.     CHARGE
1 H            .863418      .136582          .880810      .119190
2 H            .863418      .136582          .880810      .119190
3 C           6.273164     -.273164         6.238380     -.238380
```

^{1}**formyl nitrene**

```
MP2/6-31G(d,p)

O           8.0   0.0703654337   0.0000000000  -1.6669564839
C           6.0   0.0861994625   0.0000000000  -0.4828143987
N           7.0   0.2845912933   0.0000000000   0.7274471013
H           1.0  -0.4411561896   0.0000000000   1.4223237812

MP2/6-31G(d,p) Energy                -105566.4547 KCAL/MOL
ZPE Correction                            13.4865 KCAL/MOL
298.15K Temperature Correction            16.126  KCAL/MOL

MP2/6-311G(3df,2p) Energy            -105685.4209 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 O          8.345064   -0.345064         8.124792   -0.124792
2 C          5.413879    0.586121         5.821196    0.178804
3 N          7.562215   -0.562215         7.289390   -0.289390
4 H          0.678842    0.321158         0.764621    0.235379
```

^{3}**formyl nitrene**

```
MP2/6-31G(d,p)

O           8.0   -.1190489357    .0000000000  -1.2882293950
C           6.0    .0125097388    .0000000000    .0406944977
N           7.0   1.0804003451    .0000000000    .7265151066
H           1.0   -.9738611482    .0000000000    .5210197905

MP2/6-31G(d,p) Energy                -105454.581  KCAL/MOL
ZPE Correction                            12.119  KCAL/MOL
298.15K Temperature Correction            14.672  KCAL/MOL

MP2/6-311G(3df,2p) Energy            -105567.113  KCAL/MOL

ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 O          8.210090    -.210090         8.038091    -.038091
2 C          5.684055     .315945         5.984167     .015833
3 N          7.284783    -.284783         7.122309    -.122309
4 H           .821073     .178927          .855433     .144567
```

^{3}**methylsulfonyl nitrene**

```
MP2/6-31G(d,p)
O           8.0   0.8772741700   1.0237010808  -1.4029063756
S          16.0  -0.0915960667   0.7881695797  -0.3353279792
```

```
O           8.0  -1.5022662333   1.1465927975  -0.4593311495
N           7.0   0.5098252861   1.6148141747   1.0691430719
C           6.0   0.0379838284  -0.8973142132   0.2146715634
H           1.0   1.0779627302  -1.1241674706   0.4304326206
H           1.0  -0.3191546113  -1.5146636779  -0.6063754819
H           1.0  -0.5900291035  -1.0371322179   1.0896937313

MP2/6-31G(d,p) Energy                 -402798.017  KCAL/MOL
ZPE Correction                             31.802  KCAL/MOL
298.15K Temperature Correction             35.838  KCAL/MOL
MP2/6-311G(3df,2p) Energy             -403041.265  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM           MULL.POP.     CHARGE          LOW.POP.     CHARGE
1 O            8.390744     -.390744         8.364159    -.364159
2 S           14.798581     1.201419        14.707160    1.292840
3 O            8.453931     -.453931         8.517116    -.517116
4 N            7.388824     -.388824         7.426737    -.426737
5 C            6.537977     -.537977         6.439010    -.439010
6 H             .802752      .197248          .847755     .152245
7 H             .810567      .189433          .847340     .152660
8 H             .816624      .183376          .850724     .149276
```

SH_2

```
MP2/6-31G(d,p)

H           1.0    .0000000000    .9638021397    .3055777504
S          16.0    .0000000000    .0000000001   -.6111555020
H           1.0    .0000000000   -.9638021398    .3055777505

MP2/6-31G(d,p) Energy                 -250257.32467 KCAL/MOL
ZPE Correction                             9.95     KCAL/MOL
298.15K Temperature Correction            12.331    KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-250243.65435	-250575.22533
6-31G(2d)	-250256.40862	-250577.23986
6-31G(d,p)	-250257.32467	-250579.15187
6-31+G(d)	-250244.76749	-250576.39538
6-31G+(2d,p)	-250270.24063	-250582.29571
6-311G(d)	-250263.47234	-250593.26484
6-311(3df,2p)	-250311.81844	-250603.20855
6-311++G(d)	-250264.31644	-250593.7648
6-311++G(3df,2p)	-250312.13480	-250603.58962
G3 (298.15K)	-250524.2818	

```
 G3 (0K)                               -250526.0689
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE            LOW.POP.     CHARGE
1 H              0.930177    0.069823          0.931204    0.068796
2 S             16.139647   -0.139647         16.137593   -0.137593
3 H              0.930177    0.069823          0.931204    0.068796
```

^{3}carbomethoxycarbene

```
MP2/6-31G(d,p)
O            8.0  -1.1380377594  -0.1701499695  -1.0215712642
C            6.0  -0.8666653671  -0.0190309967   0.1615518003
O            8.0   0.3875348640   0.0937383148   0.6534391713
C            6.0  -1.8687571330   0.0613052059   1.2141283236
H            1.0  -2.9385016061   0.0029079750   1.1101718382
C            6.0   1.4134404843   0.0199492250  -0.3545468162
H            1.0   2.3470060928   0.1254966772   0.1858049925
H            1.0   1.2928891472   0.8218389853  -1.0786291782
H            1.0   1.3710512770  -0.9360554171  -0.8703388674

MP2/6-31G(d,p) Energy                  -167092.4429 KCAL/MOL
ZPE Correction                              41.5974 KCAL/MOL
298.15K Temperature Correction              45.64   KCAL/MOL

MP2/6-311G(3df,2p) Energy              -167276.1669 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE            LOW.POP.     CHARGE
1 O              8.443306   -0.443306          8.247754   -0.247754
2 C              5.434905    0.565095          5.818626    0.181374
3 O              8.485192   -0.485192          8.200444   -0.200444
4 C              6.121907   -0.121907          6.076128   -0.076128
5 H              0.836035    0.163965          0.866543    0.133457
6 C              6.084238   -0.084238          6.127551   -0.127551
7 H              0.865658    0.134342          0.885058    0.114942
8 H              0.864366    0.135634          0.888363    0.111637
9 H              0.864394    0.135606          0.889534    0.110466
```

^{3}dicarbomethoxycarbene

```
MP2/6-31G(d,p)

C            6.0    -.5023634738   -.0006562954   -.2142555325
C            6.0    -.4483548889   -.1244418933   1.2411814800
C            6.0     .5849545679    .1250182628  -1.1829933020
O            8.0     .5390364723   -.4859056981   1.8620682268
```

```
O            8.0   1.7156863398    .4895288911   -.9005633909
O            8.0  -1.6417758000    .1869784562   1.7907129184
O            8.0    .1561471936   -.1886796545  -2.4243542421
C            6.0   1.1718366688   -.0512994823  -3.4386433969
H            1.0   1.5268862006    .9752727229  -3.4809294212
H            1.0   2.0085990294   -.7118051467  -3.2266067954
H            1.0    .6827022351   -.3306807010  -4.3643507386
C            6.0  -1.6701750166    .0511530815   3.2259887379
H            1.0   -.9381863810    .7125678101   3.6821592264
H            1.0  -2.6769793832    .3301517709   3.5137781149
H            1.0  -1.4542592801   -.9749900035   3.5126367079

MP2/6-31G(d,p) Energy              -309698.7107 KCAL/MOL
ZPE Correction                          70.0037 KCAL/MOL
298.15K Temperature Correction          76.772  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -310043.3131 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE          LOW.POP.     CHARGE
 1 C          6.016356    -.016356         5.971392      .028608
 2 C          5.419698     .580302         5.814244      .185756
 3 C          5.419689     .580311         5.816373      .183627
 4 O          8.417258    -.417258         8.222206    -.222206
 5 O          8.417279    -.417279         8.221498    -.221498
 6 O          8.485741    -.485741         8.195268    -.195268
 7 O          8.485761    -.485761         8.193867    -.193867
 8 C          6.086316    -.086316         6.125748    -.125748
 9 H           .861570     .138430          .889027      .110973
10 H           .859434     .140566          .885814      .114186
11 H           .861780     .138220          .882944      .117056
12 C          6.086327    -.086327         6.123906    -.123906
13 H           .859400     .140600          .884731      .115269
14 H           .861788     .138212          .884110      .115890
15 H           .861604     .138396          .888872      .111128
```

dimethylsulfide

```
MP2/6-31G(d,p)

C            6.0   -.9356015305   -.6682076868   -.7394741407
S           16.0   -.8185911339    .8455464993    .2362777688
C            6.0    .9057452030    .6986579416    .7484506166
H            1.0   1.5732196651    .6864359744   -.1114430910
H            1.0   1.0663234024   -.1983516082   1.3438444577
H            1.0   1.1429734108   1.5668362514   1.3586847004
H            1.0   -.2350057657   -.6559080958  -1.5725990999
H            1.0  -1.9459031085   -.7260693222  -1.1373993668
```

```
H           1.0   -.7531606187  -1.5489396887   -.1263417921

MP2/6-31G(d,p) Energy           -299428.53866 KCAL/MOL
ZPE Correction                       49.41    KCAL/MOL
298.15K Temperature Correction       52.995   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-299398.21971	-299878.54633
6-31G(2d)	-299420.36864	-299878.29406
6-31G(d,p)	-299428.53866	-299883.91823
6-31+G(d)	-299401.19796	-299881.02809
6-31G+(2d,p)	-299453.31291	-299887.44316
6-311G(d)	-299440.87434	-299907.76820
6-311(3df,2p)	-299531.18690	-299921.17182
6-311++G(d)	-299443.10333	-299908.54632
6-311++G(3df,2p)	-299531.91535	-299921.67480
G3 (298.15K)	-299802.6465	
G3 (0K)	-299805.7476	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 C           6.464376   -0.464376        6.406122   -0.406122
2 S          15.896877    0.103123       15.878172    0.121828
3 C           6.464376   -0.464376        6.408067   -0.408067
4 H           0.866308    0.133692        0.889748    0.110252
5 H           0.866120    0.133880        0.890064    0.109936
6 H           0.854757    0.145243        0.873396    0.126604
7 H           0.866309    0.133691        0.889639    0.110361
8 H           0.854757    0.145243        0.875091    0.124909
9 H           0.866120    0.133880        0.889700    0.110300
```

CH_3SH

```
MP2/6-31G(d,p)

C          6.0   0.0944885526   0.4764196287  -0.0669216366
H          1.0   1.1176693744   0.4889201579   0.2971684725
S         16.0  -0.8321068124  -0.9378791716   0.5906587973
H          1.0  -0.4080602493   1.3713421983   0.2893290366
H          1.0  -0.0679700276  -1.8833906230   0.0493601256
H          1.0   0.0891614033   0.4885774335  -1.1529173754

MP2/6-31G(d,p) Energy           -274841.7152 KCAL/MOL
ZPE Correction                       30.12   KCAL/MOL
298.15K Temperature Correction       32.926  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-274819.6223	-275226.1094
6-31G(2d)	-274836.7898	-275226.9354
6-31G(d,p)	-274841.7152	-275230.7364
6-31+G(d)	-274821.5476	-275227.9033
6-311G(d)	-274850.7988	-275249.7059
6-311G(3df,2p)	-274919.9373	-275261.2911
6-311++G(d)	-274852.2258	-275250.3488
6-311++G(3df,2p)	-274920.4715	-275261.7396
G3 (298.15K)	-275161.8681	
G3 (0K)	-275164.1522	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 C            6.467140   -.467140         6.398952    -.398952
2 H             .856620    .143380          .886547     .113453
3 S           16.021335   -.021335        16.009563    -.009563
4 H             .851733    .148267          .873969     .126031
5 H             .946557    .053443          .942988     .057012
6 H             .856615    .143385          .887981     .112019
```

ethenethiol

MP2/6-31G(d,p)

H	1.0	-1.7151159828	0.2000932598	-1.0404537998
S	16.0	-1.8408670513	0.1113105377	0.2829151987
C	6.0	-0.1197259641	-0.0230879710	0.6295453206
C	6.0	0.8925529634	-0.0229748723	-0.2457525270
H	1.0	0.0724046078	-0.1127358588	1.6908421195
H	1.0	1.9099463949	-0.1127046837	0.1039414324
H	1.0	0.7352248682	0.0651871553	-1.3117131105

MP2/6-31G(d,p) Energy	-298663.89536	KCAL/MOL
ZPE Correction	33.08	KCAL/MOL
298.15K Temperature Correction	36.225	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-298641.76791	-299106.86099
6-31G(2d)	-298664.32031	-299108.28517
6-31G(d,p)	-298663.89536	-299111.87120
6-31+G(d)	-298646.48031	-299110.64823
6-311G(d)	-298684.33162	-299136.58707
6-311G(3df,2p)	-298764.73834	-299151.36067
6-311++G(d)	-298682.92185	-299137.90015
6-311++G(3df,2p)	-298765.99031	-299152.33862
G3 (298.15K)	-299044.792	
G3 (0K)	-299047.4169	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 H             .944531     .055469          .941100     .058900
2 S           15.958152     .041848        15.935407     .064593
3 C            6.230910    -.230910         6.218118    -.218118
4 C            6.247625    -.247625         6.256502    -.256502
5 H             .852896     .147104          .875161     .124839
6 H             .876206     .123794          .881486     .118514
7 H             .889679     .110321          .892225     .107775
```

thiirane

MP2/6-31g(d,p)

```
H         1.0  -1.2466717881    .9115354684    .3591001536
C         6.0   -.7402086504  -.0000000004    .0732107641
C         6.0    .7402086461  -.0000000002    .0732107603
H         1.0  -1.2466717885  -.9115354687    .3591001533
H         1.0   1.2466717904    .9115354723    .3591001538
H         1.0   1.2466717889  -.9115354713    .3591001538
S        16.0    .0000000016  -.0000000001  -1.5828221399
```

```
MP2/6-31G(d,p) Energy              -298670.3413 KCAL/MOL
ZPE Correction                          35.87   KCAL/MOL
298.15K Temperature Correction          38.528  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-298650.3138	-299110.8023
6-31G(2d)	-298671.5823	-299110.9153
6-31G(d,p)	-298670.3413	-299114.4541
6-31+G(d)	-298653.6779	-299113.274
6-31+G(2d,p)	-298694.1158	-299118.0182
6-311G(d)	-298691.5966	-299139.3633
6-311G(3df,2p)	-298770.8459	-299151.578
6-311++G(d)	-298693.5236	-299140.1352
6-311++G(3df,2p)	-298771.6278	-299152.1221
G3 (298.15K)	-299044.9426	
G3 (0K)	-299047.078	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 H            0.843151    0.156849         0.876679    0.123321
2 C            6.316714   -0.316714         6.265985   -0.265985
3 C            6.316714   -0.316714         6.265985   -0.265985
4 H            0.843151    0.156849         0.876679    0.123321
5 H            0.843151    0.156849         0.876679    0.123321
6 H            0.843151    0.156849         0.876679    0.123321
```

```
7 S          15.993969    0.006031        15.961314    0.038686
```

methyl vinyl sulfide

MP2/6-31G(d,p)

```
C         6.0   -.2510613838  -1.3513930757   -.7406270654
S        16.0  -1.5221887952   -.2826840183   -.0431148871
C         6.0   -.5426244717   1.0150413208    .6100440214
H         1.0    .4240121313  -1.7130982228    .0319879677
H         1.0    .3166146053   -.8316541694  -1.5094483548
H         1.0   -.7616947340  -2.1991607342  -1.1899517996
C         6.0    .7917601161   1.1473203768    .5882011422
H         1.0  -1.1538880824   1.7774471600   1.0775379746
H         1.0   1.4509763914    .4208412359    .1389781919
H         1.0   1.2480922641   2.0173407620   1.0363933380
```

```
MP2/6-31G(d,p) Energy                  -323251.8287  KCAL/MOL
ZPE Correction                               52.51   KCAL/MOL
298.15K Temperature Correction               56.414  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-323221.3369	-323760.1308
6-31G(2d)	-323249.212	-323760.5558
6-31G(d,p)	-323251.8287	-323765.9305
6-31+G(d)	-323227.0857	-323764.6355
6-31+G(2d,p)	-323284.207	-323772.1336
6-311G(d)	-323272.9771	-323795.4542
6-311G(3df,2p)	-323377.7002	-323812.2837
6-311++G(d)	-323276.1397	-323796.9318
6-311++G(3df,2p)	-323379.2241	-323813.3946
G3 (298.15K)	-323687.0319	
G3 (0K)	-323690.4643	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE          LOW.POP.     CHARGE
 1 C          6.486402   -0.486402         6.409247   -0.409247
 2 S         15.833377    0.166623        15.808330    0.191670
 3 C          6.234715   -0.234715         6.230959   -0.230959
 4 H          0.853186    0.146814         0.882307    0.117693
 5 H          0.853217    0.146783         0.881909    0.118091
 6 H          0.850490    0.149510         0.870713    0.129287
 7 C          6.260801   -0.260801         6.275151   -0.275151
 8 H          0.858210    0.141790         0.871713    0.128287
 9 H          0.889119    0.110881         0.888480    0.111520
10 H          0.880483    0.119517         0.881191    0.118809
```

diethyl sulfide

MP2/6-31G(d,p)

H	1.0	.1130717859	1.6307272874	-.7284786713
C	6.0	-.7262725049	1.2592508337	-1.3139941397
H	1.0	-1.6265392489	1.7713375261	-.9795508998
C	6.0	-.8826455155	-.2475554707	-1.1754641698
H	1.0	-.5436377419	1.5235772674	-2.3558316435
S	16.0	-1.3425461523	-.8123241680	.4873246569
H	1.0	.0182673511	-.7636389512	-1.5075262102
H	1.0	-1.6969060042	-.5985941264	-1.8100732139
C	6.0	.0744553691	-.2384984669	1.4658250777
C	6.0	1.4100087419	-.8485972336	1.0685343354
H	1.0	-.1754538049	-.5219771271	2.4887022379
H	1.0	.1226920881	.8503087415	1.4449065387
H	1.0	2.1917157893	-.5175636562	1.7526447965
H	1.0	1.7040080053	-.5510106619	.0632865621
H	1.0	1.3597816828	-1.9354412081	1.0996949550

MP2/6-31G(d,p) Energy	-348604.5935	KCAL/MOL
ZPE Correction	86.74	KCAL/MOL
298.15K Temperature Correction	91.72	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-348553.4483	-349181.6700
6-31G(2d)	-348586.6531	-349180.8646
6-31G(d,p)	-348604.5935	-349190.5021
6-31+G(d)	-348558.7049	-349185.4464
6-31+G(2d,p)	-348641.0076	-349195.2273
6-311G(d)	-348617.0452	-349222.8724
6-311G(3df,2p)	-348755.9586	-349241.5496
6-311++G(d)	-348620.0984	-349222.8724
6-311++G(3df,2p)	-348757.0943	-349242.1869
G3 (298.15K)	-349088.1980	
G3 (0K)	-349092.9138	

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS

ATOM		MULL.POP.	CHARGE	LOW.POP.	CHARGE
1	H	.886542	.113458	.895836	.104164
2	C	6.331503	-.331503	6.310208	-.310208
3	H	.869929	.130071	.887542	.112458
4	C	6.353471	-.353471	6.293367	-.293367
5	H	.883844	.116156	.894292	.105708
6	S	15.903643	.096357	15.890693	.109307
7	H	.865352	.134648	.894295	.105705
8	H	.857480	.142520	.879184	.120816
9	C	6.353679	-.353679	6.287542	-.287542

10	C	6.331028	-.331028	6.307646	-.307646
11	H	.857508	.142492	.881477	.118523
12	H	.865308	.134692	.897667	.102333
13	H	.884018	.115982	.891482	.108518
14	H	.886631	.113369	.897876	.102124
15	H	.870065	.129935	.890893	.109107

allyl ethyl sulfide

MP2/6-31G(d,p)

H	1.0	-0.4009802946	1.4272704198	-1.7098930780
C	6.0	-1.2310604290	0.7333889416	-1.6775947200
C	6.0	-1.7197177852	0.2871633598	-0.5133568646
H	1.0	-1.6567530958	0.4300321168	-2.6233056408
C	6.0	-1.1569062438	0.6609509795	0.8175579115
H	1.0	-2.5471097527	-0.4140825197	-0.5062956176
S	16.0	-0.4124886089	-0.7621337711	1.6828161057
H	1.0	-1.9436344650	1.0061427109	1.4902670755
H	1.0	-0.4315242691	1.4690715871	0.7186752356
C	6.0	0.8827891563	-1.2148849957	0.4962527809
C	6.0	2.0153943118	-0.2057237887	0.3863388573
H	1.0	0.4248318923	-1.3895294007	-0.4774059968
H	1.0	1.2621010488	-2.1723610355	0.8542315636
H	1.0	2.7788290153	-0.5713743412	-0.3010449488
H	1.0	2.4763644251	-0.0340947958	1.3570473521
H	1.0	1.6598646696	0.7501633138	0.0057098796

MP2/6-31G(d,p) Energy	-372427.0882	KCAL/MOL
ZPE Correction	89.40	KCAL/MOL
298.15K Temperature Correction	94.96	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-372376.1199	-373062.4294
6-31G(2d)	-372415.2141	-373062.1400
6-31G(d,p)	-372427.0882	-373071.6508
6-31+G(d)	-372384.0753	-373067.8323
6-31+G(2d,p)	-372471.1529	-373078.6424
6-311G(d)	-372448.5966	-373108.7626
6-311G(3df,2p)	-372601.6182	-373131.2436
6-311++G(d)	-372452.8722	-373110.2244
6-311++G(3df,2p)	-372603.3496	-373132.3588
G3 (298.15K)	-372971.3560	
G3 (0K)	-372976.5217	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 H          0.891897     0.108103        0.892059     0.107941
 2 C          6.252230    -0.252230        6.239117    -0.239117
 3 C          6.051998    -0.051998        6.107903    -0.107903
 4 H          0.882261     0.117739        0.885845     0.114155
 5 C          6.393801    -0.393801        6.289389    -0.289389
 6 H          0.875588     0.124412        0.886342     0.113658
 7 S         15.898221     0.101779       15.884813     0.115187
 8 H          0.847398     0.152602        0.872727     0.127273
 9 H          0.860521     0.139479        0.889510     0.110490
10 C          6.355931    -0.355931        6.290170    -0.290170
11 C          6.325972    -0.325972        6.310042    -0.310042
12 H          0.857566     0.142434        0.889960     0.110040
13 H          0.858913     0.141087        0.881731     0.118269
14 H          0.885037     0.114963        0.892044     0.107956
15 H          0.872298     0.127702        0.889875     0.110125
16 H          0.890368     0.109632        0.898474     0.101526
```

diphenyl sulfide

MP2/6-31G(d,p)

```
S        16.0   -.4336611576   1.6990780817    .8321789996
C         6.0  -1.4946632059    .3591288022    .3320202178
C         6.0   1.1354317353   1.0756646598    .2658844182
C         6.0  -3.2618210696  -1.6708083064   -.4382310950
C         6.0  -1.4547919196   -.1498449461   -.9733616641
C         6.0  -2.4276787136   -.1448747357   1.2453512768
C         6.0  -3.3133527597  -1.1516629623    .8555665001
C         6.0  -2.3242042833  -1.1726883631  -1.3473576457
H         1.0   -.7382856411    .2473476880  -1.6813828650
H         1.0  -2.4481344808    .2418326527   2.2565698941
H         1.0  -4.0327268933  -1.5364151749   1.5674183184
H         1.0  -2.2824947690  -1.5674302161  -2.3548372478
H         1.0  -3.9418350035  -2.4587712163   -.7353327143
C         6.0   3.6599345403    .1823900844   -.5502517456
C         6.0   1.5630680697   -.2184667367    .5931938458
C         6.0   1.9790521700   1.9218639030   -.4626960262
C         6.0   3.2410665610   1.4763205981   -.8611752890
C         6.0   2.8131195736   -.6653000292    .1693518253
H         1.0    .9124112130   -.8693058149   1.1636513860
H         1.0   1.6410523630   2.9165844501   -.7247931893
H         1.0   3.8881232892   2.1371696214  -1.4241316540
H         1.0   3.1344352872  -1.6690069322    .4183358102
H         1.0   4.6340671509   -.1655196188   -.8690132746
```

```
MP2/6-31G(d,p) Energy               -539329.9728 KCAL/MOL
ZPE Correction                           115.06   KCAL/MOL
298.15K Temperature Correction           122.58   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-539280.1292	-540361.6415
6-31G(2d)	-539357.1008	-540365.0398
6-31G(d,p)	-539329.9728	-540371.6461
6-31+G(d)	-539300.4046	-540373.0855
6-31+G(2d,p)	-539420.8938	-540388.2683
6-311G(d)	-539408.4941	-540442.2620
6-311G(3df,2p)	-539660.9393	-540481.9237
6-311++G(d)	-539418.2606	-540445.6606
6-311++G(3df,2p)	-539664.7363	-540484.1543

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 S          15.828917     .171083        15.800284     .199716
 2 C           6.173905   -.173905          6.131341   -.131341
 3 C           6.173943   -.173943          6.131711   -.131711
 4 C           6.123389   -.123389          6.113363   -.113363
 5 C           6.095005   -.095005          6.112287   -.112287
 6 C           6.115726   -.115726          6.119181   -.119181
 7 C           6.112760   -.112760          6.108049   -.108049
 8 C           6.113293   -.113293          6.104728   -.104728
 9 H            .863607     .136393          .877052     .122948
10 H            .864294     .135706          .880641     .119359
11 H            .874054     .125946          .882936     .117064
12 H            .873863     .126137          .885536     .114464
13 H            .875663     .124337          .884608     .115392
14 C           6.123388   -.123388          6.112192   -.112192
15 C           6.094991   -.094991          6.112578   -.112578
16 C           6.115700   -.115700          6.119447   -.119447
17 C           6.112767   -.112767          6.108431   -.108431
18 C           6.113289   -.113289          6.104647   -.104647
19 H            .863600     .136400          .876672     .123328
20 H            .864284     .135716          .880365     .119635
21 H            .874049     .125951          .882507     .117493
22 H            .873856     .126144          .885441     .114559
23 H            .875658     .124342          .886005     .113995
```

thiophene

MP2/6-31G(d,p)

```
C         6.0   1.3432233692    .0287798859   -.4695180412
C         6.0    .7410252109    .3799513794    .7168596147
C         6.0   -.6629219158    .1728553760    .6928940554
C         6.0  -1.0981048558   -.3315425902   -.5111261761
H         1.0   2.3883440501    .0812702270   -.7263801131
```

```
H          1.0    1.2873219433    .7682183186   1.5638912997
H          1.0   -1.3259336831    .3833748260   1.5191698146
H          1.0   -2.1049312732   -.5806278543   -.8033792182
S         16.0     .2008792735   -.5527461483  -1.6114038658
```

```
MP2/6-31G(d,p) Energy              -346358.5203 KCAL/MOL
ZPE Correction                           42.478   KCAL/MOL
298.15K Temperature Correction           45.629   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-346338.4039	-346911.1695
6-31G(2d)	-346371.3186	-346913.2678
6-31G(d,p)	-346358.5203	-346915.3726
6-31+G(d)	-346346.0829	-346916.7319
6-31+G(2d,p)	-346397.7064	-346924.1867
6-311G(d)	-346396.6926	-346950.8663
6-311G(3df,2p)	-346505.6794	-346970.1119
6-311++G(d)	-346400.5672	-346952.8251
6-311++G(3df,2p)	-346507.8208	-346971.3842
G3 (298.15K)	-346850.0983	
G3 (0K)	-346852.6999	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 C             6.332026    -.332026         6.286543    -.286543
2 C             6.095078    -.095078         6.143178    -.143178
3 C             6.095073    -.095073         6.143205    -.143205
4 C             6.332036    -.332036         6.287697    -.287697
5 H              .846795     .153205          .869547     .130453
6 H              .871802     .128198          .878906     .121094
7 H              .871803     .128197          .878924     .121076
8 H              .846791     .153209          .868725     .131275
9 S            15.708598     .291402        15.643277     .356723
```

benzothiophene

MP2/6-31G(d,p)

```
C          6.0     .6280061147    .0000000000  -2.6246953663
S         16.0   -1.0741410182    .0000000000  -2.2976133704
C          6.0    -.7784339223    .0000000000   -.5814489227
C          6.0     .0841033506    .0000000000   2.0584296627
C          6.0     .6104913868    .0000000000   -.2976848494
C          6.0   -1.7353507812    .0000000000    .4427631875
C          6.0   -1.2925997708    .0000000000   1.7585276086
C          6.0    1.0317849430    .0000000000   1.0467768542
H          1.0   -2.7938514242    .0000000000    .2141338155
H          1.0   -2.0159036457    .0000000000   2.5640766303
```

```
H          1.0   2.0898624700    .0000000000   1.2806649867
H          1.0    .4029408928    .0000000000   3.0930460717
C          6.0   1.3966909524    .0000000000  -1.4962685701
H          1.0    .9686609462    .0000000000  -3.6483848935
H          1.0   2.4777394520    .0000000000  -1.5123227908

MP2/6-31G(d,p) Energy               -442479.8978 KCAL/MOL
ZPE Correction                           71.7    KCAL/MOL
298.15K Temperature Correction           76.6    KCAL/MOL

MP2/6-311G(3df,2p) Energy           -442720.7059 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE            LOW.POP.     CHARGE
 1 C            6.328220   -0.328220           6.256950   -0.256950
 2 S           15.727380    0.272620          15.685029    0.314971
 3 C            6.206994   -0.206994           6.150020   -0.150020
 4 C            6.132718   -0.132718           6.115236   -0.115236
 5 C            5.960425    0.039575           6.024954   -0.024954
 6 C            6.113145   -0.113145           6.112655   -0.112655
 7 C            6.117976   -0.117976           6.115664   -0.115664
 8 C            6.113014   -0.113014           6.107925   -0.107925
 9 H            0.869054    0.130946           0.883697    0.116303
10 H            0.877595    0.122405           0.884206    0.115794
11 H            0.876423    0.123577           0.887534    0.112466
12 H            0.878278    0.121722           0.887740    0.112260
13 C            6.086715   -0.086715           6.138721   -0.138721
14 H            0.845209    0.154791           0.868747    0.131253
15 H            0.866855    0.133145           0.880921    0.119079
```

dibenzothiophene

```
MP2/6-31G(d,p)
S         16.0   -.0000009366    .0000000000  -2.3545281574
C          6.0  -1.2502063949    .0000000000  -1.1247123788
C          6.0   1.2502114373    .0000000000  -1.1247157374
C          6.0  -2.9774051471    .0000000000   1.0513689287
C          6.0   -.7239106730    .0000000000    .1863464813
C          6.0  -2.6303661156    .0000000000  -1.3548029346
C          6.0  -3.4863910706    .0000000000   -.2584728017
C          6.0  -1.6068021457    .0000000000   1.2784106178
H          1.0  -3.0241639978    .0000000000  -2.3635719638
H          1.0  -4.5571897849    .0000000000   -.4182918302
H          1.0  -1.2197779780    .0000000000   2.2905501159
H          1.0  -3.6613107649    .0000000000   1.8904398247
C          6.0   2.9774143077    .0000000000   1.0513720716
C          6.0   2.6303661672    .0000000000  -1.3547838337
C          6.0    .7239099816    .0000000000    .1863457347
C          6.0   1.6067944778    .0000000000   1.2784163428
C          6.0   3.4863801341    .0000000000   -.2584848010
H          1.0   3.0241665426    .0000000000  -2.3635792296
H          1.0   1.2197796652    .0000000000   2.2905467620
H          1.0   4.5571936557    .0000000000   -.4182915855
```

```
H         1.0   3.6613086399    .0000000000   1.8904381632

MP2/6-31G(d,p) Energy               -538604.489 KCAL/MOL
ZPE Correction                          100.47  KCAL/MOL
298.15K Temperature Correction          107.5   KCAL/MOL
MP2/6-311G(3df,2p) Energy           -538937.244 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE          LOW.POP.     CHARGE
 1 S         15.735740    0.264260        15.717735    0.282265
 2 C          6.196928   -0.196928         6.135312   -0.135312
 3 C          6.196922   -0.196922         6.135312   -0.135312
 4 C          6.139454   -0.139454         6.116282   -0.116282
 5 C          5.968774    0.031226         6.023915   -0.023915
 6 C          6.127589   -0.127589         6.114502   -0.114502
 7 C          6.110192   -0.110192         6.106283   -0.106283
 8 C          6.096049   -0.096049         6.105958   -0.105958
 9 H          0.866984    0.133016         0.881638    0.118362
10 H          0.875360    0.124640         0.886710    0.113290
11 H          0.874722    0.125278         0.886299    0.113701
12 H          0.876077    0.123923         0.884232    0.115768
13 C          6.139456   -0.139456         6.116283   -0.116283
14 C          6.127590   -0.127590         6.114500   -0.114500
15 C          5.968778    0.031222         6.023914   -0.023914
16 C          6.096052   -0.096052         6.105960   -0.105960
17 C          6.110190   -0.110190         6.106283   -0.106283
18 H          0.866985    0.133015         0.881639    0.118361
19 H          0.874722    0.125278         0.886299    0.113701
20 H          0.875360    0.124640         0.886711    0.113289
21 H          0.876076    0.123924         0.884232    0.115768
```

dimethyl selenide

```
MP2/6-31g(d,p)

C         6.0   1.4500939122    .0000170736   -.0058103875
SE       34.0   -.0000000345  -.0000822221  -1.3051163153
C         6.0  -1.4500948675    .0000211826   -.0058117184
H         1.0   1.3991811338  -.8929683023    .6110263873
H         1.0   1.3993561441    .8931970519    .6106664843
H         1.0   2.3828581732  -.0002031898   -.5633242542
H         1.0  -1.3991811236  -.8929709347    .6110279754
H         1.0  -2.3828573048  -.0002032332   -.5633236884
H         1.0  -1.3993560330    .8931954337    .6106655708

MP2/6-31G(d,p) Energy               -1554502.477643 KCAL/MOL
ZPE Correction                            48.4      KCAL/MOL
298.15K Temperature Correction            52.173    KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1554471.647425	-1555616.774921
6-31G(2d)	-1554571.415981	-1555693.317194
6-31G(d,p)	-1554502.477643	-1555622.798761
6-31+G(d)	-1554485.229319	-1555629.816120
6-31+G(2d,p)	-1554610.962258	-1555708.541470
6-311G(d)	-1555874.429914	-1556973.245152
6-311G(3df,2p)	-1555959.852014	-1556985.741316
6-311++G(d)	-1555875.525965	-1556973.705192
6-311++G(3df,2p)	-1555960.544073	-1556986.234998
G3 (298.15K)	-1556658.3690	
G3 (0K)	-1556661.1748	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 C          6.419739    -.419739         6.386648    -.386648
2 SE        33.994745     .005255        33.922328     .077672
3 C          6.419739    -.419739         6.386648    -.386648
4 H           .862700     .137300          .887202     .112798
5 H           .862682     .137318          .887202     .112798
6 H           .857506     .142494          .877784     .122216
7 H           .862697     .137303          .887201     .112799
8 H           .857505     .142495          .877784     .122216
9 H           .862686     .137314          .887203     .112797
```

selenirane

MP2/6-31G(d,p)

```
SE       34.0    .0000000006    .0000000000  -1.7190312090
C         6.0  -.7372628793    .0000000004    .1098592251
H         1.0 -1.2493481973   -.9141969100    .3748281495
C         6.0    .7372628781    .0000000001    .1098592216
H         1.0 -1.2493481973    .9141969095    .3748281510
H         1.0  1.2493481979    .9141969103    .3748281501
H         1.0  1.2493481973   -.9141969103    .3748281518
```

```
MP2/6-31G(d,p) Energy                 -1553743.742 KCAL/MOL
ZPE Correction                              35.04  KCAL/MOL
298.15K Temperature Correction              37.809 KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1553723.394	-1554848.268
6-31G(2d)	-1553822.846	-1554925.987
6-31G(d,p)	-1553743.742	-1554852.453
6-31+G(d)	-1553738.427	-1554862.515
6-31+G(2d,p)	-1553853.067	-1554940.373
6-311G(d)	-1555126.673	-1556206.323
6-311G(3df,2p)	-1555200.819	-1556217.718
6-311++G(d)	-1555127.672	-1556206.769
6-311++G(3df,2p)	-1555201.548	-1556218.267
G3 (298.15K)	-1555900.7050	
G3 (0K)	-1555904.0878	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE          LOW.POP.     CHARGE
1 SE         34.107651   -0.107651       34.031735   -0.031735
2 C           6.267231   -0.267231        6.235767   -0.235767
3 H           0.839472    0.160528        0.874183    0.125817
4 C           6.267231   -0.267231        6.235767   -0.235767
5 H           0.839472    0.160528        0.874183    0.125817
6 H           0.839472    0.160528        0.874183    0.125817
7 H           0.839472    0.160528        0.874183    0.125817
```

methyl vinyl selenide

MP2/6-31G(d,p)

C	6.0	-.2295547819	-1.4202224780	-.7814652934
SE	34.0	-1.6292037166	-.2971061037	-.0393914980
C	6.0	-.5427262477	1.0890172620	.6554347567
H	1.0	.4378321270	-1.7485993598	.0099108957
H	1.0	.3164832783	-.8739686212	-1.5451024252
H	1.0	-.7228877321	-2.2797990580	-1.2263457023
C	6.0	.7923259449	1.1862525844	.6058016085
H	1.0	-1.1296416068	1.8623302283	1.1361798783
H	1.0	1.4198665700	.4428007198	.1378335286
H	1.0	1.2875042058	2.0392954613	1.0471447804

```
MP2/6-31G(d,p) Energy              1578323.9338 KCAL/MOL
ZPE Correction                          51.5437 KCAL/MOL
298.15K Temperature Correction          55.687  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1578293.073	-1579496.991
6-31G(2d)	-1578399.927	-1579574.889
6-31G(d,p)	-1578323.936	-1579503.306
6-31+G(d)	-1578312.804	-1579515.260
6-31+G(2d,p)	-1578443.142	-1579594.083
6-311G(d)	-1579704.734	-1580859.329
6-311G(3df,2p)	-1579804.663	-1580874.795
6-311++G(d)	-1579706.791	-1580860.414
6-311++G(3df,2p)	-1579806.047	-1580875.823
G3 (298.15K)	-1580541.0580	
G3 (0K)	-1580544.1427	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE          LOW.POP.      CHARGE
 1 C            6.438004    -.438004          6.387679    -.387679
 2 SE          33.950870     .049130         33.866014     .133986
 3 C            6.162443    -.162443          6.198583    -.198583
 4 H             .851445     .148555           .880799     .119201
 5 H             .851468     .148532           .880383     .119617
 6 H             .853718     .146282           .873592     .126408
 7 C            6.256105    -.256105          6.266126    -.266126
 8 H             .864299     .135701           .876092     .123908
 9 H             .890834     .109166           .888886     .111114
10 H             .880813     .119187           .881846     .118154
```

selenophene

MP2/6-31G(d,p)

```
C          6.0   -1.2845599352    .0000376878   -.5553659411
C          6.0    -.7110015139  -.0000116293    .6927145916
C          6.0     .7110013313  -.0000116425    .6927155114
C          6.0    1.2845605400    .0000376492   -.5553666274
H          1.0   -2.3363305215  -.0000043432   -.7905266463
H          1.0   -1.3015342076  -.0000043280   1.5985647623
H          1.0    1.3015341209  -.0000044091   1.5985645467
H          1.0    2.3363302167  -.0000042732   -.7905265581
SE        34.0    -.0000000307  -.0000347121  -1.8907737452
```

```
MP2/6-31G(d,p) Energy                -1601427.2925 KCAL/MOL
ZPE Correction                             41.69   KCAL/MOL
298.15K Temperature Correction             44.988  KCAL/MOL
MP2/6-311G(3df,2p) Energy              -1602925.436 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE           LOW.POP.     CHARGE
1 C          6.244234   -0.244234         6.247936   -0.247936
2 C          6.099703   -0.099703         6.140235   -0.140235
3 C          6.099703   -0.099703         6.140235   -0.140235
4 C          6.244234   -0.244234         6.247936   -0.247936
5 H          0.854096    0.145904         0.873625    0.126375
6 H          0.873359    0.126641         0.880685    0.119315
7 H          0.873359    0.126641         0.880685    0.119315
8 H          0.854097    0.145903         0.873625    0.126375
9 SE        33.857215    0.142785        33.715038    0.284962
```

benzoselenophene

```
MP2/6-31G(d,p)

C          6.0   1.2688758489    .0000000000  -2.4414686384
SE        34.0   -.5947764889    .0000000000  -2.6098406215
C          6.0   -.6688026055    .0000000000   -.7344192198
C          6.0   -.3748418874    .0000000000   2.0293403249
C          6.0  -1.8142806607    .0000000000    .0710811926
C          6.0    .6307236167    .0000000000   -.1707557474
C          6.0    .7598226410    .0000000000   1.2323194264
C          6.0  -1.6582089660    .0000000000   1.4512797023
H          1.0  -2.8034008770    .0000000000   -.3696336441
H          1.0   1.7470892581    .0000000000   1.6794364140
H          1.0  -2.5341157732    .0000000000   2.0876403587
H          1.0   -.2750105377    .0000000000   3.1073631639
H          1.0   1.8967148611    .0000000000  -3.3188257231
C          6.0   1.6866406935    .0000000000  -1.1442681108
H          1.0   2.7335709291    .0000000000   -.8692488248

MP2/6-31G(d,p) Energy             -1697551.06299 KCAL/MOL
ZPE Correction                          71.26    KCAL/MOL
298.15K Temperature Correction          76.261   KCAL/MOL

MP2/6-311G(3df,2p) Energy         -1699141.573   KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE           LOW.POP.     CHARGE
 1 C         6.245838    -.245838         6.227994    -.227994
 2 SE       33.878453     .121547        33.750769     .249231
 3 C         6.108596    -.108596         6.112733    -.112733
 4 C         6.130038    -.130038         6.113237    -.113237
 5 C         6.116710    -.116710         6.116599    -.116599
 6 C         5.973847     .026153         6.024557    -.024557
 7 C         6.116324    -.116324         6.108943    -.108943
 8 C         6.120827    -.120827         6.114691    -.114691
 9 H          .870762     .129238          .884002     .115998
10 H          .876580     .123420          .886303     .113697
```

```
11 H          .876948     .123052          .884445     .115555
12 H          .877722     .122278          .888619     .111381
13 H          .851344     .148656          .870639     .129361
14 C         6.086731    -.086731         6.135151    -.135151
15 H          .869279     .130721          .881317     .118683
```

dibenzoselenophene

MP2/6-31G(d,p)

```
H          1.0  -3.1172621713   -.0001441883  -2.3316431483
C          6.0  -2.6871622640   -.0000848793  -1.3377930002
C          6.0  -1.5763147720    .0000818764   1.2507529306
C          6.0  -3.5089325298   -.0001010718   -.2153408270
C          6.0  -1.3005900034    .0000536347  -1.1579113148
C          6.0   -.7260534951    .0001039482    .1320974441
C          6.0  -2.9544873569    .0000905484   1.0745039515
H          1.0  -4.5845034781   -.0001815380   -.3395084726
SE        34.0    .0000037935   -.0000470427  -2.5276972629
H          1.0  -3.6066549646    .0000209037   1.9384689218
H          1.0  -1.1578729463    .0001896909   2.2502203299
C          6.0   1.3006158167   -.0000121722  -1.1579631094
C          6.0   2.9545113122   -.0000063661   1.044657138
C          6.0    .7260239797    .0000942785    .1321457426
C          6.0   2.6871403144   -.0000351229  -1.3378263549
C          6.0   3.5089353158   -.0001187288   -.2152771724
C          6.0   1.5763152766    .0001773701   1.2507737007
H          1.0   3.1172569851   -.0001369842  -2.3316362832
H          1.0   4.5845044253   -.0001559627   -.3395109379
H          1.0   1.1578739308    .0001901593   2.2502093556
H          1.0   3.6066528315    .0000256670   1.9384697382
```

```
MP2/6-31G(d,p) Energy              -1793677.5472 KCAL/MOL
ZPE Correction                           100.49   KCAL/MOL
298.15K Temperature Correction           107.422  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -1795362.888  KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 H         0.868926    0.131074         0.883394    0.116606
  2 C         6.126196   -0.126196         6.116695   -0.116695
  3 C         6.100671   -0.100671         6.106021   -0.106021
  4 C         6.113275   -0.113275         6.105939   -0.105939
  5 C         6.105219   -0.105219         6.099037   -0.099037
  6 C         5.978209    0.021791         6.022551   -0.022551
  7 C         6.137262   -0.137262         6.115426   -0.115426
  8 H         0.874900    0.125100         0.886860    0.113140
  9 SE       33.889185    0.110815        33.786700    0.213300
 10 H         0.875758    0.124242         0.884289    0.115711
 11 H         0.874949    0.125051         0.886432    0.113568
```

```
12 C          6.105058   -0.105058           6.099040   -0.099040
13 C          6.137275   -0.137275           6.115424   -0.115424
14 C          5.978443    0.021557           6.022544   -0.022544
15 C          6.126285   -0.126285           6.116708   -0.116708
16 C          6.113240   -0.113240           6.105938   -0.105938
17 C          6.100605   -0.100605           6.106025   -0.106025
18 H          0.868927    0.131073           0.883393    0.116607
19 H          0.874903    0.125097           0.886860    0.113140
20 H          0.874948    0.125052           0.886432    0.113568
21 H          0.875763    0.124237           0.884291    0.115709
```

dimethyl sulfoxide (1)

MP2/6-31G(d,p)

```
O         8.0   1.7410121543    .8287919793   -.8324894360
S        16.0    .9997064042    .1370858800    .2877715296
C         6.0    .1370755965  -1.2809664783   -.4284036690
C         6.0   -.4930784575   1.0994748473    .6243859034
H         1.0   -.1776259904   2.0512229129   1.0440720942
H         1.0  -1.1246024839    .5732199747   1.3382344963
H         1.0  -1.0255642490   1.2751345332   -.3088830422
H         1.0    .8933763543  -1.9944427151   -.7453244209
H         1.0   -.4357119307   -.9533832497  -1.2944453572
H         1.0   -.5124963010  -1.7387593852    .3157584538
```

```
MP2/6-31G(d,p) Energy                 -346485.927 KCAL/MOL
ZPE Correction                             51.55  KCAL/MOL
298.15K Temperature Correction             55.64  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-346455.9582	-347031.2884
6-31G(2d)	-346496.7756	-347037.0735
6-31G(d,p)	-346485.9270	-347036.7247
6-31+G(d)	-346466.9680	-347039.5520
6-31+G(2d,p)	-346537.8025	-347053.5119
6-311G(d)	-346522.0576	-347074.2171
6-311G(3df,2p)	-346657.4402	-347104.9657
6-311++G(d)	-346529.8094	-347079.2778
6-311++G(3df,2p)	-346661.8254	-347108.5033
G3 (298.15K)	-346969.1683	
G3 (0K)	-346972.7112	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM     MULL.POP.     CHARGE     LOW.POP.     CHARGE
 1 O      8.659566    -.659566     8.695232    -.695232
 2 S     15.182643     .817357    15.141645     .858355
 3 C      6.530981    -.530981     6.463207    -.463207
```

```
 4 C      6.530978    -.530978     6.462249    -.462249
 5 H       .838406     .161594      .867794     .132206
 6 H       .864918     .135082      .875256     .124744
 7 H       .844593     .155407      .876511     .123489
 8 H       .838404     .161596      .866770     .133230
 9 H       .844599     .155401      .875739     .124261
10 H       .864913     .135087      .875598     .124402
```

diethyl sulfoxide (2)

MP2/6-31G(d,p)

```
S        16.0  -0.4178558478   0.6965458748  -1.2794538799
O         8.0   0.0464371392  -0.0518684232  -2.5137271763
C         6.0  -1.3042828096  -0.5167111686  -0.2461026055
C         6.0   1.0543256554   0.9212487355  -0.2362185686
C         6.0  -0.5496722215  -1.8251942353  -0.0887356176
H         1.0  -2.2349927621  -0.6786073918  -0.7909838584
H         1.0  -1.5560810784  -0.0427262561   0.7030204620
H         1.0   0.2830174613  -1.7337964737   0.6061134372
H         1.0  -0.1632393176  -2.1327332356  -1.0593081550
H         1.0  -1.2139261239  -2.6024334536   0.2848663318
H         1.0   1.6720493464   1.6086515900  -0.8149012374
H         1.0   1.5799101733  -0.0327257118  -0.1996996668
C         6.0   0.7519300032   1.4857068952   1.1434027892
H         1.0   0.1048358806   2.3604346549   1.0788812894
H         1.0   1.6767859280   1.7936087336   1.6280581047
H         1.0   0.2705436835   0.7507132357   1.7851350614
```

```
MP2/6-31G(d,p) Energy               -395662.7348 KCAL/MOL
ZPE Correction                           89.06   KCAL/MOL
298.15K Temperature Correction           94.63   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-395611.9249	-396334.9591
6-31G(2d)	-395663.9647	-396339.9792
6-31G(d,p)	-395662.7348	-396343.9067
6-31+G(d)	-395624.3657	-396343.6370
6-31+G(2d,p)	-395725.5519	-396360.7340
6-311G(d)	-395699.3273	-396389.5268
6-311G(3df,2p)	-395882.3701	-396425.2243
6-311++G(d)	-395706.7625	-396393.6095
6-311++G(3df,2p)	-395886.5474	-396428.3348
G3 (298.15K)	-396254.3465	
G3 (0K)	-396259.5768	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE     LOW.POP.     CHARGE
 1 S      15.174507    0.825493   15.164532    0.835468
 2 O       8.676491   -0.676491    8.696827   -0.696827
 3 C       6.420020   -0.420020    6.342271   -0.342271
```

4	C	6.415316	-0.415316	6.341528	-0.341528
5	C	6.352919	-0.352919	6.312322	-0.312322
6	H	0.843190	0.156810	0.875351	0.124649
7	H	0.864718	0.135282	0.884203	0.115797
8	H	0.885761	0.114239	0.896145	0.103855
9	H	0.838231	0.161769	0.875838	0.124162
10	H	0.872206	0.127794	0.885039	0.114961
11	H	0.842984	0.157016	0.872601	0.127399
12	H	0.842653	0.157347	0.881815	0.118185
13	C	6.362758	-0.362758	6.310577	-0.310577
14	H	0.868246	0.131754	0.887963	0.112037
15	H	0.864217	0.135783	0.881984	0.118016
16	H	0.875782	0.124218	0.891003	0.108997

allyl ethyl sulfoxide (3)

MP2/6-31G(d,p)

C	6.0	0.3808459216	0.7239467196	-1.0006904390
C	6.0	0.8611342750	-0.6665228313	-1.2473848012
C	6.0	2.1407425601	-0.9691068617	-1.5061089150
H	1.0	0.1313818574	-1.4644566891	-1.1678393949
H	1.0	2.8948877454	-0.1976124640	-1.5918818052
H	1.0	2.4606295102	-1.9909504441	-1.6497052707
H	1.0	-0.6625362456	0.8799286828	-1.2734948027
H	1.0	0.9833294904	1.4594012175	-1.5344232683
S	16.0	0.5438113797	1.2170277288	0.7621124340
C	6.0	-0.4450320115	-0.1330695789	1.4876224886
O	8.0	-0.2657329379	2.4848635913	0.9364372296
H	1.0	0.0485224012	-1.0762516270	1.2522574759
C	6.0	-1.9034092844	-0.0869475258	1.0670000014
H	1.0	-0.3545538612	0.0330615746	2.5618276565
H	1.0	-2.5027830541	-0.7285600434	1.7102740912
H	1.0	-2.0420012795	-0.4197191371	0.0397849851
H	1.0	-2.2692363668	0.9349678477	1.1542124849

MP2/6-31G(d,p) Energy	-419484.5513	KCAL/MOL
ZPE Correction	91.86	KCAL/MOL
298.15K Temperature Correction	97.96	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-419433.8215	-420215.2447
6-31G(2d)	-419491.6022	-420220.7753
6-31G(d,p)	-419484.5513	-420224.5583
6-31+G(d)	-419448.9117	-420225.5565
6-31+G(2d,p)	-419554.7592	-420243.5759
6-311G(d)	-419529.9949	-420275.8789
6-311G(3df,2p)	-419726.9787	-420314.3251
6-311++G(d)	-419538.5587	-420280.4411
6-311++G(3df,2p)	-419731.6825	-420317.8096

G3 (298.15K)	-420136.4879
G3 (0K)	-420142.2039

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C          6.457344   -0.457344        6.334116   -0.334116
 2 C          6.079147   -0.079147        6.111999   -0.111999
 3 C          6.242155   -0.242155        6.224014   -0.224014
 4 H          0.871136    0.128864        0.886305    0.113695
 5 H          0.883021    0.116979        0.888438    0.111562
 6 H          0.875928    0.124072        0.882692    0.117308
 7 H          0.842910    0.157090        0.879902    0.120098
 8 H          0.834160    0.165840        0.869270    0.130730
 9 S         15.165990    0.834010       15.161369    0.838631
10 C          6.421624   -0.421624        6.335598   -0.335598
11 O          8.667462   -0.667462        8.691944   -0.691944
12 H          0.834203    0.165797        0.872651    0.127349
13 C          6.348191   -0.348191        6.305771   -0.305771
14 H          0.859335    0.140665        0.887638    0.112362
15 H          0.872505    0.127495        0.885010    0.114990
16 H          0.871068    0.128932        0.890705    0.109295
17 H          0.873821    0.126179        0.892578    0.107422
```

diphenyl sulfoxide (4)

MP2/6-31G(d,p)

```
O          8.0   -.4889894138   1.4224244421   2.5874639095
S         16.0   -.4428551985   1.6897494513   1.0967079359
C          6.0  -1.4796817188    .4284164649    .3177132029
C          6.0   1.1160999638   1.0055456369    .4923111809
C          6.0  -3.1078491690  -1.5161160453   -.8026999595
C          6.0  -1.7767373201    .4908256893  -1.0447915803
C          6.0  -2.0029947738   -.5715648496   1.1337552888
C          6.0  -2.8172120606  -1.5511179743    .5627952237
C          6.0  -2.5890771565   -.4954353960  -1.6043906301
H          1.0  -1.3833175189   1.2907322383  -1.6610200297
H          1.0  -1.7692593794   -.5583855774   2.1910838985
H          1.0  -3.2299368236  -2.3365060188   1.1834390064
H          1.0  -2.8255297311   -.4620233434  -2.6604135555
H          1.0  -3.7412165927  -2.2766516917  -1.2408721652
C          6.0   3.5241995855   -.0574677522   -.3758596592
C          6.0   1.8318432503    .1640002334   1.3412729116
C          6.0   1.5956598653   1.3497533044   -.7722052581
C          6.0   2.8038143148    .8036313776  -1.2076598967
C          6.0   3.0406089372   -.3722751882    .8967128841
H          1.0   1.4370437062   -.0418517657   2.3285795857
H          1.0   1.0448845832   2.0376863018  -1.4031885891
H          1.0   3.1881788674   1.0596806585  -2.1868567510
H          1.0   3.6079752199  -1.0300383444   1.5430840828
```

```
H          1.0   4.4643588804   -.4729485625   -.7149271173
```

```
MP2/6-31G(d,p) Energy             -586386.3836 KCAL/MOL
ZPE Correction                        117.32   KCAL/MOL
298.15K Temperature Correction        125.47   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-586336.6831	-587513.5234
6-31G(2d)	-586432.5834	-587522.7935
6-31G(d,p)	-586386.3836	-587523.6627
6-31+G(d)	-586362.1428	-587528.4624
6-31+G(2d,p)	-586501.9876	-587550.8152
6-311G(d)	-586488.3678	-587608.4153
6-311G(3df,2p)	-586784.7574	-587663.4424
6-311++G(d)	-586500.5452	-587613.6807
6-311++G(3df,2p)	-586790.4382	-587667.1162

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.      CHARGE
 1 O      8.665025    -.665025     8.673160    -.673160
 2 S     15.120558     .879442    15.126386     .873614
 3 C      6.245733    -.245733     6.172288    -.172288
 4 C      6.242560    -.242560     6.172846    -.172846
 5 C      6.118926    -.118926     6.109471    -.109471
 6 C      6.104133    -.104133     6.116514    -.116514
 7 C      6.102952    -.102952     6.104204    -.104204
 8 C      6.110348    -.110348     6.098925    -.098925
 9 C      6.112404    -.112404     6.099139    -.099139
10 H       .872967     .127033      .882965     .117035
11 H       .830876     .169124      .869073     .130927
12 H       .869116     .130884      .880952     .119048
13 H       .870933     .129067      .885329     .114671
14 H       .872077     .127923      .882449     .117551
15 C      6.118686    -.118686     6.107421    -.107421
16 C      6.097896    -.097896     6.102492    -.102492
17 C      6.108538    -.108538     6.118917    -.118917
18 C      6.112551    -.112551     6.100479    -.100479
19 C      6.109943    -.109943     6.098544    -.098544
20 H       .832819     .167181      .868560     .131440
21 H       .870383     .129617      .882253     .117747
22 H       .870504     .129496      .883639     .116361
23 H       .868504     .131496      .880281     .119719
24 H       .871568     .128432      .883711     .116289
```

thiirane oxide (5)

MP2/6-31G(d,p)

```
C          6.0   -.5829264165    .0408975030  -1.2116099442
C          6.0    .8918715981    .0408741821  -1.0061651218
```

```
H          1.0  -1.0816868200   1.0007704394  -1.2378994219
H          1.0  -1.0353018690   -.7414920381  -1.8063924729
H          1.0   1.3788846504   1.0007191781   -.8951194184
H          1.0   1.4895511907   -.7415460820  -1.4546454602
S         16.0   -.0668101573   -.4233045020    .4795112166
O          8.0   -.2013441764    .7215373195   1.4455006227

MP2/6-31G(d,p) Energy                -345725.4984 KCAL/MOL
ZPE Correction                            37.60   KCAL/MOL
298.15K Temperature Correction            40.853  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-345705.7661	-346262.2150
6-31G(2d)	-345744.3994	-346268.1301
6-31G(d,p)	-345725.4984	-346265.8984
6-31+G(d)	-345716.7609	-346270.4567
6-31+G(2d,p)	-345774.4986	-346282.0894
6-311G(d)	-345770.2050	-346304.6990
6-311G(3df,2p)	-345894.7514	-346333.6410
6-311++G(d)	-345777.6915	-346309.6715
6-311++G(3df,2p)	-345900.4427	-346336.9871
G3 (298.15K)	-346207.9256	
G3 (0K)	-346210.6129	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.      CHARGE
 1 C       6.402081    -.402081    6.339688     -.339688
 2 C       6.402174    -.402174    6.338832     -.338832
 3 H        .815515     .184485     .860438      .139562
 4 H        .840082     .159918     .868938      .131062
 5 H        .815387     .184613     .860450      .139550
 6 H        .840169     .159831     .868983      .131017
 7 S      15.258785     .741215   15.197410      .802590
 8 O        8.625806   -.625806    8.665261     -.665261
```

methyl vinyl sulfoxide (6)

MP2/6-31G(d,p)

```
C          6.0   0.8425123786  -0.4684376445   0.4572211372
C          6.0   1.3869592096  -1.2703555370  -0.4593228711
H          1.0   1.7777758662  -2.2424564226  -0.1970371129
H          1.0   1.4364058052  -0.9428085435  -1.4894459914
H          1.0   0.7700926580  -0.6991989126   1.5133199051
S         16.0   0.2722033539   1.1518277236  -0.0416956383
C          6.0  -1.4607220560   0.8503701879   0.3842838585
O          8.0   0.3678152037   1.2193493576  -1.5491314001
H          1.0  -1.8302973026   0.0266732818  -0.2228846243
H          1.0  -2.0176328903   1.7568329580   0.1599202415
H          1.0  -1.5451102691   0.6182057203   1.4447750358
```

MP2/6-31G(d,p) Energy	-370307.8587	KCAL/MOL
ZPE Correction	54.67	KCAL/MOL
298.15K Temperature Correction	59.141	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-370277.8258	-370910.7708
6-31G(2d)	-370324.1876	-370917.0688
6-31G(d,p)	-370307.8587	-370916.5633
6-31+G(d)	-370290.3638	-370919.8062
6-31+G(2d,p)	-370365.7810	-370934.5607
6-311G(d)	-370352.7180	-370959.9608
6-311G(3df,2p)	-370501.4559	-370992.9827
6-311++G(d)	-370360.3396	-370964.4806
6-311++G(3df,2p)	-370505.6401	-370996.2293
G3 (298.15K)	-370850.1639	
G3 (0K)	-370854.1291	

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS

ATOM		MULL.POP.	CHARGE	LOW.POP.	CHARGE
1	C	6.322260	-0.322260	6.288031	-0.288031
2	C	6.228335	-0.228335	6.203666	-0.203666
3	H	0.868638	0.131362	0.878284	0.121716
4	H	0.832762	0.167238	0.866614	0.133386
5	H	0.855669	0.144331	0.876079	0.123921
6	S	15.165770	0.834230	15.131791	0.868209
7	C	6.531090	-0.531090	6.453874	-0.453874
8	O	8.656263	-0.656263	8.684531	-0.684531
9	H	0.834710	0.165290	0.870131	0.129869
10	H	0.840767	0.159233	0.869424	0.130576
11	H	0.863736	0.136264	0.877576	0.122424

thiophene-*S*-oxide (7)

MP2/6-31G(d,p)

C	6.0	-0.0375150337	1.2567679972	-0.2455906399
C	6.0	0.1087333374	0.7265915985	0.9940768542
C	6.0	0.1087336956	-0.7265851878	0.9940645294
C	6.0	-0.0375250373	-1.2567537315	-0.2455622101
H	1.0	-0.1006437957	2.2954186542	-0.5280786800
H	1.0	0.1997311760	1.3166069014	1.8953366139
H	1.0	0.1997147104	-1.3166151632	1.8953227094
H	1.0	-0.1006480551	-2.2954065450	-0.5280733280
S	16.0	-0.4605853975	-0.0000546075	-1.4129079122
O	8.0	0.3078191598	0.0000300825	-2.7137399298

MP2/6-31G(d,p) Energy	-393390.8183	KCAL/MOL
ZPE Correction	44.47	KCAL/MOL
298.15K Temperature Correction	48.351	KCAL/MOL

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-393371.0323	-394042.0675
6-31G(2d)	-393421.7221	-394049.1976
6-31G(d,p)	-393390.8183	-394046.2208
6-31+G(d)	-393384.3530	-394051.0861
6-31+G(2d,p)	-393453.9898	-394065.2401
6-311G(d)	-393450.0461	-394093.4536
6-311G(3df,2p)	-393603.4040	-394128.9835
6-311++G(d)	-393459.3304	-394099.2260
6-311++G(3df,2p)	-393608.4547	-394132.6490
G3 (298.15K)	-393990.5772	
G3 (0K)	-393993.9011	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C      6.357429   -0.357429      6.285911   -0.285911
 2 C      6.082414   -0.082414      6.103256   -0.103256
 3 C      6.082406   -0.082406      6.103250   -0.103250
 4 C      6.357437   -0.357437      6.285933   -0.285933
 5 H      0.827821    0.172179      0.859207    0.140793
 6 H      0.851815    0.148185      0.873176    0.126824
 7 H      0.851814    0.148186      0.873175    0.126825
 8 H      0.827814    0.172186      0.859207    0.140793
 9 S     15.159079    0.840921     15.106143    0.893857
10 O      8.601970   -0.601970      8.650743   -0.650743
```

benzothiophene-*S*-oxide (8)

MP2/6-31G(d,p)

C	6.0	-0.0121352322	-0.2524124049	-0.7179325641
C	6.0	-0.4713041518	0.2335345925	0.5166151294
C	6.0	-1.8885107473	-0.0575218614	0.7124679209
C	6.0	-2.4427100060	-0.7340048824	-0.3166447385
C	6.0	1.3177932992	-0.1498637359	-1.1055111987
H	1.0	-2.4309352269	0.2391227183	1.6016207993
H	1.0	-3.4672086177	-1.0609679868	-0.4124252167
S	16.0	-1.3543365550	-0.8809499419	-1.7279219710
O	8.0	-1.1284815007	-2.3019989712	-2.1937962269
C	6.0	2.2136857659	0.4512046539	-0.2167549879
H	1.0	1.6521919568	-0.5459715851	-2.0563728576
H	1.0	3.2612874103	0.5249297885	-0.4789201506
C	6.0	1.7667216757	0.9664398209	1.0069821583
C	6.0	0.4258382918	0.8660594742	1.3825516333
H	1.0	2.4745806990	1.4405865169	1.6748869701
H	1.0	0.0870267788	1.2645081624	2.3314503157

MP2/6-31G(d,p) Energy -489519.5851 KCAL/MOL
ZPE Correction 74.04 KCAL/MOL

```
298.15K Temperature Correction          79.65   KCAL/MOL

MP2/6-311G(3df,2p) Energy            -489828.91   KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C      6.265309   -0.265309     6.177940   -0.177940
 2 C      5.958366    0.041634     6.016199   -0.016199
 3 C      6.052741   -0.052741     6.091463   -0.091463
 4 C      6.378284   -0.378284     6.278652   -0.278652
 5 C      6.109718   -0.109718     6.093187   -0.093187
 6 H      0.852180    0.147820     0.873736    0.126264
 7 H      0.833773    0.166227     0.862466    0.137534
 8 S     15.143139    0.856861    15.127653    0.872347
 9 O      8.612216   -0.612216     8.656509   -0.656509
10 C      6.111235   -0.111235     6.098033   -0.098033
11 H      0.846261    0.153739     0.872026    0.127974
12 H      0.865485    0.134515     0.882107    0.117893
13 C      6.125903   -0.125903     6.104310   -0.104310
14 C      6.111430   -0.111430     6.104354   -0.104354
15 H      0.867422    0.132578     0.879663    0.120337
16 H      0.866537    0.133463     0.881702    0.118298
```

dibenzothiophene-*S*-oxide (9)

```
MP2/6-31G(d,p)

C          6.0   -.9443662031   1.2552396225    .2249483537
C          6.0    .3498345325    .7327061757    .0735135941
C          6.0    .3497983435   -.7327014579    .0734760219
C          6.0   -.9443808146  -1.2552445574    .2249474254
C          6.0  -1.1982273792   2.6219112468    .1926438245
S         16.0  -2.1943213982    .0001312673    .5535228580
O          8.0  -3.2991097165   -.0000629056   -.4792971119
C          6.0   -.1195988094   3.4884726638   -.0013672529
H          1.0  -2.2080239632   2.9998798764    .2968487342
H          1.0   -.2887362103   4.5565976324   -.0476654203
C          6.0   1.1809384704   2.9841854042   -.1273157889
C          6.0   1.4255482435   1.6103793138   -.0912871369
H          1.0   2.0080986085   3.6692358417   -.2639771030
H          1.0   2.4356059602   1.2333073369   -.1986898782
C          6.0   1.4255518244  -1.6103915094   -.0912545541
C          6.0   1.1809326029  -2.9841840998   -.1273717850
H          1.0   2.4356354110  -1.2333298819   -.1987248278
H          1.0   2.0080910487  -3.6692365005   -.2640195513
C          6.0   -.1195808181  -3.4884895792   -.0013275390
C          6.0  -1.1982105648  -2.6219147547    .1926552121
H          1.0   -.2887321013  -4.5565940725   -.0476794105
H          1.0  -2.2080166429  -2.9998970648    .2968918367

MP2/6-31G(d,p) Energy                -585649.5602 KCAL/MOL
ZPE Correction                           103.2    KCAL/MOL
298.15K Temperature Correction           110.77   KCAL/MOL
```

```
MP2/6-311G(3df,2p) Energy          -586050.8578 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C      6.270628    -.270628     6.177588    -.177588
 2 C      5.950831     .049169     6.009762    -.009762
 3 C      5.950834     .049166     6.009773    -.009773
 4 C      6.270601    -.270601     6.177541    -.177541
 5 C      6.123762    -.123762     6.094666    -.094666
 6 S     15.125761     .874239    15.133286     .866714
 7 O      8.613307    -.613307     8.657246    -.657246
 8 C      6.105718    -.105718     6.096662    -.096662
 9 H       .847659     .152341      .873346     .126654
10 H       .866104     .133896      .882784     .117216
11 C      6.132696    -.132696     6.102838    -.102838
12 C      6.096638    -.096638     6.102512    -.102512
13 H       .868018     .131982      .880739     .119261
14 H       .868400     .131600      .883847     .116153
15 C      6.096636    -.096636     6.102517    -.102517
16 C      6.132697    -.132697     6.102843    -.102843
17 H       .868404     .131596      .883850     .116150
18 H       .868023     .131977      .880742     .119258
19 C      6.105711    -.105711     6.096663    -.096663
20 C      6.123803    -.123803     6.094665    -.094665
21 H       .866103     .133897      .882783     .117217
22 H       .847664     .152336      .873347     .126653
```

dimethyl sulfilimine (10)

```
MP2/6-31G(d,p)

N         7.0   1.7288880220   -.2919610533  -1.0713234126
S        16.0    .1824994865    .0147905844   -.9508987770
C         6.0   -.1592200189   1.3961021568    .1897478006
C         6.0   -.6858755952  -1.2373966359    .0497964562
H         1.0    .2505097655   1.1821254882   1.1768491044
H         1.0  -1.2324358937   1.5678083643    .2608170735
H         1.0    .3292530584   2.2743071188   -.2244291854
H         1.0   -.2381511957  -1.3023321991   1.0414270714
H         1.0   -.5687007526  -2.1875302714   -.4647974413
H         1.0  -1.7427886690   -.9880639430    .1333409668
H         1.0   2.1360216338   -.4278489759   -.1405314036

MP2/6-31G(d,p) Energy              -334017.6321 KCAL/MOL
ZPE Correction                          58.77   KCAL/MOL
298.15K Temperature Correction          62.968  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-333980.9405	-334544.744
6-31G(2d)	-334016.9821	-334549.2482
6-31G(d,p)	-334017.6321	-334552.5362
6-31+G(d)	-333990.5815	-334551.4129
6-31+G(2d,p)	-334062.4480	-334566.1203
6-311G(d)	-334040.1773	-334584.0759
6-311G(3df,2p)	-334170.7417	-334612.2972
6-311++G(d)	-334046.1571	-334587.4031
6-311++G(3df,2p)	-334174.5177	-334615.2992
G3 (298.15K)	-334478.8798	
G3 (0K)	-334482.6254	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.      CHARGE
  1 N     7.724342    -.724342     7.714447    -.714447
  2 S    15.325461     .674539    15.248562     .751438
  3 C     6.516525    -.516525     6.461094    -.461094
  4 C     6.516276    -.516276     6.459555    -.459555
  5 H      .863111     .136889      .886462     .113538
  6 H      .863329     .136671      .879350     .120650
  7 H      .838831     .161169      .867449     .132551
  8 H      .863035     .136965      .886618     .113382
  9 H      .838747     .161253      .868370     .131630
 10 H      .863335     .136665      .878824     .121176
 11 H      .787008     .212992      .849269     .150731
```

dihydro sulifilimine (11)

MP2/6-31G(d,p)

```
N          7.0    -.1115277382    .3766483045  -1.0302336294
S         16.0     .0083515461  -.3596589277    .3836544690
H          1.0    1.1449015298    .0487091765   1.0041225038
H          1.0    -.7139608123    .3272655967   1.3052959500
H          1.0    -.3277644724  -.3929640429  -1.6628392404
```

```
MP2/6-31G(d,p) Energy              -284827.48320 KCAL/MOL
ZPE Correction                          20.9     KCAL/MOL
298.15K Temperature Correction          23.669   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-284807.79252	-285224.42816
6-31G(2d)	-284834.46561	-285232.99433
6-31G(d,p)	-284827.48320	-285229.99065
6-31+G(d)	-284815.32555	-285230.13926
6-31+G(2d,p)	-284860.29857	-285244.73324

6-311G(d)	-284842.84300	-285251.69729
6-311G(3df,2p)	-284931.46434	-285277.13809
6-311++G(d)	-284849.04763	
6-311++G(3df,2p)	-284935.69805	-285280.84256
G3 (298.15K)	-285180.6400	
G3 (0K)	-285182.8043	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 N      7.742163    -.742163     7.749721    -.749721
 2 S     15.536739     .463261    15.432495     .567505
 3 H       .982333     .017667      .996742     .003258
 4 H       .981917     .018083      .994609     .005391
 5 H       .756847     .243153      .826433     .173567
```

thiirane sulfilimine (12)

MP2/6-31g(d,p)

```
H          1.0   -.9577341266    .8835459998    .9382196965
C          6.0   -.0358836914    .3169308926    .9790935873
C          6.0    .9422853270    .4908846569   -.1226142303
H          1.0    .3292977804    .0894474166   1.9716239753
H          1.0    .6703327541   1.1605671840   -.9268182328
H          1.0   1.9972440684    .3695868896    .0845183357
S         16.0   -.1112752470  -1.0791554758   -.1473166807
N          7.0  -1.4759792116   -.8667206626   -.9458742531
H          1.0  -1.3582877065  -1.3650869010  -1.8308320398
```

```
MP2/6-31G(d,p) Energy                 -333254.75852 KCAL/MOL
ZPE Correction                             44.49    KCAL/MOL
298.15K Temperature Correction             48.083   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-333228.33601	-333773.26278
6-31G(2d)	-333262.30041	-333777.88495
6-31G(d,p)	-333254.75852	-333779.38134
6-31+G(d)	-333239.00251	-333780.82714
6-31+G(2d,p)	-333297.95176	-333793.27233
6-311G(d)	-333285.41530	-333812.05892
6-311G(3df,2p)	-333404.27181	-333838.56503
6-311++G(d)	-333292.37409	-333816.32102
6-311++G(3df,2p)	-333408.74521	-333842.12489
G3 (298.15K)	-333716.4640	
G3 (0K)	-333719.4986	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 H        .804006     .195994       .854839     .145161
 2 C       6.350615    -.350615      6.289137    -.289137
 3 C       6.393243    -.393243      6.352980    -.352980
 4 H        .835360     .164640       .869866     .130134
 5 H        .829875     .170125       .866218     .133782
 6 H        .851949     .148051       .877086     .122914
 7 S      15.417520     .582480     15.326039     .673961
 8 N       7.753288    -.753288      7.735199    -.735199
 9 H        .764144     .235856       .828636     .171364
```

vinyl sulfilimine (13)

MP2/6-31g(d,p)

```
N           7.0  -2.0016227080  -1.1098660687   -.1395847156
S          16.0  -1.0117366705   -.0255439483   -.7302358598
C           6.0    .4386587767    .2889013829    .2859858052
H           1.0  -1.4349532102   1.2665855309   -.5478451636
C           6.0   1.6560778955    .0187232280   -.1950859628
H           1.0    .2771250799    .6362242096   1.3001793938
H           1.0   2.5439639961    .1668990541    .4035854198
H           1.0   1.7897919467   -.3513036451  -1.2029979932
H           1.0  -2.2573049481   -.8906196904    .8259990752
```

```
MP2/6-31G(d,p) Energy                  -333242.43930 KCAL/MOL
ZPE Correction                              43.05     KCAL/MOL
298.15K Temperature Correction              46.862    KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-333214.20020	-333763.10257
6-31G(2d)	-333250.29756	-333769.88648
6-31G(d,p)	-333242.43930	-333770.06968
6-31+G(d)	-333224.73692	-333770.55144
6-31+G(2d,p)	-333287.19958	-333785.87861
6-311G(d)	-333270.45144	-333802.76410
6-311G(3df,2p)	-333392.60948	-333831.77631
6-311++G(d)	-333276.60454	-333806.54767
6-311++G(3df,2p)	-333396.70755	-333835.07934
G3 (298.15K)	-333708.8987	
G3 (0K)	-333712.1969	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
1 N            7.706030   -0.706030         7.709744   -0.709744
2 S           15.408942    0.591058        15.316155    0.683845
3 C            6.300454   -0.300454         6.286759   -0.286759
```

```
4 H         1.020588   -0.020588         1.018971   -0.018971
5 C         6.217868   -0.217868         6.192982   -0.192982
6 H         0.852608    0.147392         0.880595    0.119405
7 H         0.863656    0.136344         0.876554    0.123446
8 H         0.858111    0.141889         0.877136    0.122864
9 H         0.771745    0.228255         0.841103    0.158897
```

methane sulfilimine (14)

MP2/6-31G(d,p)

```
N          7.0  -1.1566389047   1.1477263743  -1.0186427781
S         16.0  -1.0305456804    .0269196674    .0881094715
C          6.0    .6778203464   -.2012954533    .6812149550
H          1.0  -1.0453325436  -1.2585200291   -.3962189080
H          1.0   -.4755631275   1.0006692624  -1.7672991811
H          1.0   1.3530149984   -.3793452474   -.1534270700
H          1.0    .7075846692  -1.0457693546   1.3694690098
H          1.0    .9696599252    .7096155743   1.1967952949
```

```
MP2/6-31G(d,p) Energy               -309423.78061 KCAL/MOL
ZPE Correction                           40.2     KCAL/MOL
298.15K Temperature Correction           43.474   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-309395.58652	-309886.22734
6-31G(2d)	-309426.14124	-309892.40305
6-31G(d,p)	-309423.78061	-309892.84833
6-31+G(d)	-309403.49812	-309891.99673
6-31+G(2d,p)	-309461.41160	-309906.43094
6-311G(d)	-309443.01444	-309919.86640
6-311G(3df,2p)	-309551.61688	-309946.05674
6-311++G(d)	-309448.40519	-309923.28808
6-311++G(3df,2p)	-309555.22512	-309949.03704
G3 (298.15K)	-309829.8835	
G3 (0K)	-309832.6703	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.    CHARGE      LOW.POP.     CHARGE
 1 N      7.714175    -.714175     7.717452    -.717452
 2 S     15.401457     .598543    15.320003     .679997
 3 C      6.528725    -.528725     6.470410    -.470410
 4 H      1.028728    -.028728     1.026291    -.026291
 5 H       .774020     .225980      .840624     .159376
 6 H       .853637     .146363      .881132     .118868
 7 H       .860545     .139455      .874118     .125882
 8 H       .838712     .161288      .869969     .130031
```

methyl vinyl sulfilimine (15)

MP2/6-31G(d,p)

```
N         7.0   1.6434275994  -1.3045775145    .7836345351
S        16.0    .9889139202   -.0610973695    .0549538339
C         6.0   -.6184703437    .3823201608    .7251285416
C         6.0    .3349559930   -.5082895397  -1.5866235735
H         1.0   1.1754625144   -.8683070726  -2.1755169666
H         1.0   -.1075920416    .3681270549  -2.0574356333
H         1.0   -.4095699328  -1.2988864737  -1.4941871807
C         6.0   -.8204527706   1.5900668468   1.2613554704
H         1.0  -1.3765228891   -.3954504077    .7370831786
H         1.0  -1.7676479965   1.8571745796   1.7092947436
H         1.0   -.0398378077   2.3391405689   1.2603189266
H         1.0    .9973328561  -2.1001291272    .7821822464
```

```
MP2/6-31G(d,p) Energy                  -357837.01900  KCAL/MOL
ZPE Correction                              61.63     KCAL/MOL
298.15K Temperature Correction              66.451    KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-357800.29100	-358422.24108
6-31G(2d)	-357841.81056	-358427.40126
6-31G(d,p)	-357837.01900	-358430.34716
6-31+G(d)	-357812.34939	-358430.37547
6-31+G(2d,p)	-357888.70249	-358445.96939
6-311G(d)	-357868.24996	-358467.41126
6-311G(3df,2p)	-358012.37191	-358498.52743
6-311++G(d)	-357874.98067	-358471.09433
6-311++G(3df,2p)	-358016.55370	-358501.77208
G3 (298.15K)	-358358.3474	
G3 (0K)	-358362.6302	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE     LOW.POP.     CHARGE
 1 N       7.715492    -.715492    7.708575    -.708575
 2 S      15.322588     .677412   15.238607     .761393
 3 C       6.283850    -.283850    6.279500    -.279500
 4 C       6.519755    -.519755    6.463473    -.463473
 5 H        .840701     .159299     .868837     .131163
 6 H        .855968     .144032     .872745     .127255
 7 H        .862955     .137045     .884940     .115060
 8 C       6.227022    -.227022    6.201687    -.201687
 9 H        .859554     .140446     .881835     .118165
10 H        .867185     .132815     .878687     .121313
11 H        .860323     .139677     .875757     .124243
12 H        .784607     .215393     .845358     .154642
```

thiophene sulfilimine (16)

```
MP2/6-31g(d,p)

C          6.0   -.3014173190    .2993285001  -1.1987223869
C          6.0    .6317437681   1.1139106873   -.6507272750
C          6.0    .8000284786    .9054901737    .7787017063
C          6.0   -.0088898165   -.0624110961   1.2722702946
H          1.0   -.6409665191    .2519636395  -2.2214684218
H          1.0   1.1929053981   1.8520320488  -1.2069344859
H          1.0   1.4962327033   1.4763614199   1.3775045068
H          1.0   -.1074549585   -.4066854117   2.2898078660
S         16.0  -1.1688399667   -.6217200895    .0479437609
N          7.0  -1.4004265480  -2.1815676570   -.1563741018
H          1.0   -.4946191702  -2.6264262480   -.3320486661

MP2/6-31G(d,p) Energy              -380926.5498 KCAL/MOL
ZPE Correction                          51.72   KCAL/MOL
298.15K Temperature Correction          55.784  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -381125.4577 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.      CHARGE      LOW.POP.      CHARGE
 1 C      6.352291     -.352291      6.288549     -.288549
 2 C      6.079937     -.079937      6.110066     -.110066
 3 C      6.080215     -.080215      6.110133     -.110133
 4 C      6.352093     -.352093      6.289138     -.289138
 5 H       .832286      .167714       .860936      .139064
 6 H       .854991      .145009       .873429      .126571
 7 H       .854992      .145008       .873270      .126730
 8 H       .832457      .167543       .860917      .139083
 9 S     15.302127      .697873     15.215878      .784122
10 N      7.691847     -.691847      7.682505     -.682505
11 H       .766764      .233236       .835178      .164822
```

benzothiophene sulfilimine (17)

```
MP2/6-31G(d,p)

H          1.0   -.4099330481   1.1032105089  -2.3432218414
C          6.0   -.2771675748   1.1021145774  -1.2680334524
C          6.0    .0814592152   1.0604943318   1.5405817419
C          6.0   -.2814944323   -.0905383635   -.5555174048
C          6.0   -.0756269378   2.2878107399   -.5564861333
C          6.0    .0901100649   2.2647832154    .8353330342
C          6.0   -.0904092777   -.1345358891    .8333984349
S         16.0   -.5904707439  -1.7234100015  -1.2530845244
H          1.0   -.0517000459   3.2333943315  -1.0829781559
H          1.0    .2338119129   3.1954348306   1.3693636284
C          6.0   -.0724674619  -1.5065022331   1.3319569083
H          1.0    .2130289193   1.0494427172   2.6162000132
H          1.0    .0605359668  -1.7451528079   2.3800502507
```

```
C          6.0   -.2305166476  -2.4312369908    .3612109671
N          7.0    .3388023469  -2.1486733658  -2.4690074283
H          1.0   -.2583507562  -3.5056693569    .4685532252
H          1.0   1.3203877594  -2.0109660331  -2.2083195784

MP2/6-31G(d,p) Energy              -477055.4315 KCAL/MOL
ZPE Correction                          81.25   KCAL/MOL
298.15K Temperature Correction          87.024  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -477346.297 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.      CHARGE      LOW.POP.      CHARGE
 1 H       .847186      .152814       .874512      .125488
 2 C      6.114182     -.114182      6.094837     -.094837
 3 C      6.113010     -.113010      6.103268     -.103268
 4 C      6.265546     -.265546      6.183553     -.183553
 5 C      6.112049     -.112049      6.101893     -.101893
 6 C      6.126700     -.126700      6.105257     -.105257
 7 C      5.955316      .044684      6.019654     -.019654
 8 S     15.275337      .724663     15.227001      .772999
 9 H       .867240      .132760       .881098      .118902
10 H       .869166      .130834       .882041      .117959
11 C      6.052914     -.052914      6.096141     -.096141
12 H       .868633      .131367       .885108      .114892
13 H       .855227      .144773       .877493      .122507
14 C      6.373604     -.373604      6.282550     -.282550
15 N      7.696034     -.696034      7.682385     -.682385
16 H       .838039      .161961       .865224      .134776
17 H       .769817      .230183       .837983      .162017
```

dibenzothiophene sulfilimine (18)

```
MP2/6-31G(d,p)

H          1.0   0.5050339476  -3.5909463896  -0.4610351059
C          6.0   0.4988955948  -2.7814020230   0.2590616450
C          6.0   0.4862963372  -0.6396139296   2.1034182784
C          6.0   0.0853855527  -1.5079731143  -0.1155717633
C          6.0   0.9186153467  -2.9767357658   1.5769468331
C          6.0   0.9015292479  -1.9145360029   2.4906144583
C          6.0   0.0837810926  -0.4283128704   0.7802030333
S         16.0  -0.5410681213  -1.0925221631  -1.7649737619
H          1.0   1.2543637732  -3.9550889429   1.8966729202
H          1.0   1.2223509755  -2.0837687789   3.5106323235
C          6.0  -0.3287373153   0.8203926575   0.1333709275
H          1.0   0.4865925698   0.1744942656   2.8186976128
C          6.0  -1.0434077545   2.9728709805  -1.5038693373
C          6.0  -0.6222708861   0.6358895176  -1.2259725397
C          6.0  -0.4209991322   2.1036215033   0.6830092688
C          6.0  -0.7775791087   3.1710454668  -0.1423866078
C          6.0  -0.9756817672   1.6923221983  -2.0578447255
H          1.0  -0.2094377817   2.2719433691   1.7324164637
```

```
H          1.0  -0.8426781731   4.1682982978   0.2740223944
H          1.0  -1.1783004469   1.5201797513  -3.1082650016
H          1.0  -1.3073715905   3.8169584911  -2.1282504477
N          7.0   0.4422837669  -1.3924438033  -2.9734215884
H          1.0   1.3624034486  -0.9846729789  -2.7774746978
```

```
MP2/6-31G(d,p) Energy                  -573185.4619 KCAL/MOL
ZPE Correction                              110.5    KCAL/MOL
298.15K Temperature Correction              118.192  KCAL/MOL
MP2/6-311G(3df,2p) Energy              -573568.2915 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
  1 H      0.848056    0.151944     0.871321    0.128679
  2 C      6.128803   -0.128803     6.101119   -0.101119
  3 C      6.098288   -0.098288     6.106066   -0.106066
  4 C      6.269130   -0.269130     6.181942   -0.181942
  5 C      6.106459   -0.106459     6.100230   -0.100230
  6 C      6.133446   -0.133446     6.102341   -0.102341
  7 C      5.950428    0.049572     6.013581   -0.013581
  8 S     15.250377    0.749623    15.230917    0.769083
  9 H      0.867569    0.132431     0.881711    0.118289
 10 H      0.869563    0.130437     0.884030    0.115970
 11 C      5.950418    0.049582     6.014524   -0.014524
 12 H      0.869839    0.130161     0.882604    0.117396
 13 C      6.106498   -0.106498     6.102122   -0.102122
 14 C      6.269165   -0.269165     6.182995   -0.182995
 15 C      6.098288   -0.098288     6.102267   -0.102267
 16 C      6.133431   -0.133431     6.103271   -0.103271
 17 C      6.128765   -0.128765     6.097541   -0.097541
 18 H      0.869858    0.130142     0.885604    0.114396
 19 H      0.869506    0.130494     0.883369    0.116631
 20 H      0.848009    0.151991     0.874261    0.125739
 21 H      0.867579    0.132421     0.880049    0.119951
 22 N      7.696631   -0.696631     7.680936   -0.680936
 23 H      0.769894    0.230106     0.837200    0.162800
```

dimethyl *S*,*C*-methylide (19)

MP2/6-31G(d,p)

```
C          6.0   -.6562984871   1.4606426170   -.9104075704
S         16.0   -.3630566530    .5565951478    .4365279593
C          6.0   1.3818188757   -.0184173865    .6815744356
C          6.0  -1.0236716860  -1.0940858401    .0962387515
H          1.0   -.2386515811   1.1536252787  -1.8581191191
H          1.0   -.7783479246   2.5097704247   -.7027659080
H          1.0   -.7696135879  -1.7751113705    .9064714858
H          1.0   -.6146983431  -1.4631510425   -.8430562088
H          1.0  -2.1006324311   -.9908968369    .0077185505
H          1.0   1.7359426927   -.5310900584   -.2123403215
H          1.0   1.4474403164   -.6807337820   1.5445509116
H          1.0   1.9797693901    .8728530596    .8536072435
```

```
MP2/6-31G(d,p) Energy               -323949.7292 KCAL/MOL
ZPE Correction                           65.49   KCAL/MOL
298.15K Temperature Correction           70.059  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-323908.8677	-324467.5814
6-31G(2d)	-323940.6027	-324469.3150
6-31G(d,p)	-323949.7292	-324475.2630
6-31+G(d)	-323917.7242	-324473.7618
6-31+G(2d,p)	-323989.5210	-324485.8678
6-311G(d)	-323966.9474	-324504.5792
6-311G(3df,2p)	-324088.8786	-324527.8981
6-311++G(d)	-323971.2012	-324506.4519
6-311++G(3df,2p)	-324091.3596	-324529.6722
G3 (298.15K)	-324393.2159	
G3 (0K)	-324397.3274	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C       6.560064    -.560064     6.689490    -.689490
 2 S      15.530696     .469304    15.348773     .651227
 3 C       6.494033    -.494033     6.471655    -.471655
 4 C       6.468453    -.468453     6.431169    -.431169
 5 H        .907274     .092726      .900714     .099286
 6 H        .883086     .116914      .881759     .118241
 7 H        .868985     .131015      .880726     .119274
 8 H        .854865     .145135      .881378     .118622
 9 H        .839128     .160872      .869808     .130192
10 H        .866631     .133369      .886593     .113407
11 H        .871800     .128200      .882571     .117429
12 H        .854985     .145015      .875363     .124637
```

dihydro *S,C*-methylide (20)

MP2/6-31G(d,p)

```
C         6.0    .1100668266   -.1405637976   -.8844062460
S        16.0  -.2248857277   -.3875611773    .7184608294
H         1.0    .9351774418   -.2970535027   1.3918219726
H         1.0  -.7517499455    .6432287385   1.4911015708
H         1.0  -.6328596013   -.6005249670  -1.5126678278
H         1.0    .5642510062    .7824747072  -1.2043102990
```

```
MP2/6-31G(d,p) Energy               -274764.1455338 KCAL/MOL
ZPE Correction                           27.69      KCAL/MOL
298.15K Temperature Correction           30.48      KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-274740.5236467	-275152.5614458
6-31G(d,P)	-274764.1455338	-275157.8725817
6-31+G(d)	-274746.0567227	-275156.7363445
6-311G(d)	-274775.0109740	-275178.3211522
6-311G(3df,2p)	-274853.0370655	-275197.0891772
6-311++G(3df,2p)	-274854.9772404	-275198.6525371
G3 (298.15K)	-275098.1306	
G3 (0K)	-275100.4442	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C       6.556184    -.556184     6.682328    -.682328
 2 S      15.703424     .296576    15.531441     .468559
 3 H        .943462     .056538      .973835     .026165
 4 H       1.034717    -.034717     1.041625    -.041625
 5 H        .874543     .125457      .877755     .122245
 6 H        .887670     .112330      .893015     .106985
```

vinyl *S,C*-methylide (21)

MP2/6-31G(d,p)

```
C          6.0  -0.6283065886   0.3554247880  -1.8664033292
S         16.0  -0.8808264380  -0.3106882107  -0.3809816338
C          6.0   0.4563692353   0.1791590138   0.7015139702
H          1.0  -1.8304790953   0.2906083185   0.4244162407
H          1.0  -0.6219150725   1.4245133535  -1.9970991395
H          1.0  -0.9441350981  -0.2847549514  -2.6706356199
H          1.0   0.7671697104   1.2141385268   0.6301434155
S          6.0   1.0576028529  -0.7084733800   1.4971880538
H          1.0   1.8818482544  -0.4174296201   2.1329290669
H          1.0   0.7426728196  -1.7424976793   1.5289287103
```

```
MP2/6-31G(d,p) Energy                  -323175.1892 KCAL/MOL
ZPE Correction                              49.48   KCAL/MOL
298.15K Temperature Correction              53.70   KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-323142.9117	-323686.5893
6-31G(2d)	-323174.4426	-323690.6436
6-31G(d,p)	-323175.1892	-323693.4038
6-31+G(d)	-323152.5211	-323693.4012
6-311G(d)	-323197.8313	-323723.9264
6-311G(3df,2p)	-323311.2642	-323748.0860
6-311++G(d)	-323202.0424	-323726.0075
6-311++G(3df,2p)	-323314.0228	-323750.1381
G3 (298.15K)	-323624.2928	

G3 (0K)	-323627.9982

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C      6.564649   -0.564649    6.684863   -0.684863
 2 S     15.612758    0.387242   15.430026    0.569974
 3 C      6.240086   -0.240086    6.252740   -0.252740
 4 H      1.011406   -0.011406    1.022324   -0.022324
 5 H      0.892234    0.107766    0.896006    0.103994
 6 H      0.873258    0.126742    0.874671    0.125329
 7 H      0.847204    0.152796    0.876752    0.123248
 8 S      6.227644   -0.227644    6.205425   -0.205425
 9 H      0.866569    0.133431    0.877209    0.122791
10 H      0.864194    0.135806    0.879983    0.120017
```

methane *S*,*C*-methylide (22)

MP2/6-31G(d,p)

```
C          6.0  -1.2387177501  -0.1460988956   0.1774452124
S         16.0   0.2928310045  -0.3259645005  -0.7659029262
C          6.0   1.5436599571  -0.1042993134   0.2877286165
H          1.0  -0.0686830052   0.7241220359  -1.6019184319
H          1.0   2.4352085140  -0.6306331287  -0.0071715037
H          1.0   1.6375656027   0.8294808339   0.8199725462
H          1.0  -1.2053249127   0.7683761810   0.7644612426
H          1.0  -1.3173840732  -1.0021220549   0.8405540204
H          1.0  -2.0791550190  -0.1128611577  -0.5151686693
```

```
MP2/6-31G(d,p) Energy              -299357.8883 KCAL/MOL
ZPE Correction                           46.86   KCAL/MOL
298.15K Temperature Correction           50.372  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-299325.6531	-299811.2052
6-31G(2d)	-299351.5459	-299814.5538
6-31G(d,p)	-299357.8883	-299817.6413
6-31+G(d)	-299332.7065	-299816.3411
6-311G(d)	-299371.7425	-299842.4823
6-311G(3df,2p)	-299471.3475	-299863.4011
6-311++G(d)	-299375.3117	-299844.2565
6-311++G(3df,2p)	-299473.5586	-299865.0698
G3 (298.15K)	-299746.1097	
G3 (0K)	-299749.1952	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 C      6.474730   -0.474730    6.438236   -0.438236
 2 S     15.597257    0.402743   15.434998    0.565002
 3 C      6.558977   -0.558977    6.684839   -0.684839
```

```
  4 H     1.039100   -0.039100     1.040688    -0.040688
  5 H     0.877285    0.122715     0.877900     0.122100
  6 H     0.896175    0.103825     0.896530     0.103470
  7 H     0.847481    0.152519     0.877810     0.122190
  8 H     0.840527    0.159473     0.869120     0.130880
  9 H     0.868467    0.131533     0.879878     0.120122
```

methyl vinyl *S,C*-methylide (23)

MP2/6-31G(d,p)

```
C          6.0  -0.6283065886   0.3554247880  -1.8664033292
S         16.0  -0.8808264380  -0.3106882107  -0.3809816338
C          6.0   0.4563692353   0.1791590138   0.7015139702
H          1.0  -1.8304790953   0.2906083185   0.4244162407
H          1.0  -0.6219150725   1.4245133535  -1.9970991395
H          1.0  -0.9441350981  -0.2847549514  -2.6706356199
H          1.0   0.7671697104   1.2141385268   0.6301434155
S          6.0   1.0576028529  -0.7084733800   1.4971880538
H          1.0   1.8818482544  -0.4174296201   2.1329290669
H          1.0   0.7426728196  -1.7424976793   1.5289287103
```

```
MP2/6-31G(d,p) Energy              -347771.7553 KCAL/MOL
ZPE Correction                           68.44   KCAL/MOL
298.15K Temperature Correction           73.453  KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-347730.8485	-348347.0647
6-31G(2d)	-347768.3948	-348349.4485
6-31G(d,p)	-347771.7553	-348355.1279
6-31+G(d)	-347741.6146	-348354.3408
6-311G(d)	-347797.5031	-348389.8556
6-311G(3df,2p)	-347933.4787	-348416.1332
6-311++G(d)	-347802.2068	-348391.8336
6-311++G(3df,2p)	-347936.2515	-348418.0730
G3 (298.15K)	-348275.0386	
G3 (0K)	-348279.5912	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE       LOW.POP.      CHARGE
  1 C     6.274128   -0.274128     6.287019    -0.287019
  2 C     6.233598   -0.233598     6.221648    -0.221648
  3 H     0.873389    0.126611     0.880595     0.119405
  4 H     0.869749    0.130251     0.879572     0.120428
  5 H     0.868479    0.131521     0.879304     0.120696
  6 S    15.509626    0.490374    15.335834     0.664166
  7 C     6.471667   -0.471667     6.428427    -0.428427
  8 C     6.568975   -0.568975     6.686522    -0.686522
  9 H     0.876025    0.123975     0.878339     0.121661
 10 H     0.898198    0.101802     0.895411     0.104589
```

```
11 H     0.868037    0.131963     0.880245    0.119755
12 H     0.846863    0.153137     0.877351    0.122649
13 H     0.841267    0.158733     0.869734    0.130266
```

thiophene *S,C*-methylide (24)

```
MP2/6-31G(d,p)

C          6.0   -.6069701274    .9028444423    .7724252010
C          6.0  -1.1572638994   1.1814645112   -.4340661626
C          6.0   -.5196268920    .4707682617  -1.5283341084
C          6.0    .5081788313   -.3145860042  -1.1271187171
H          1.0   -.8592755659   1.3033693234   1.7421547059
H          1.0  -1.9845434712   1.8620398596   -.5829289402
H          1.0   -.8378057921    .5655003994  -2.5565908462
H          1.0   1.1539379786   -.9529545774  -1.7080332100
S         16.0    .8562757656   -.1185383395    .5850526911
C          6.0   1.1405832193  -1.5517453221   1.3608838363
H          1.0   1.8456722798  -1.4468403847   2.1677133106
H          1.0    .3287347203  -2.2553953995   1.4521724758

MP2/6-31G(d,p) Energy              -370861.2280 KCAL/MOL
ZPE Correction                           58.58   KCAL/MOL
298.15K Temperature Correction           62.906  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -371045.8281 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.      CHARGE      LOW.POP.     CHARGE
 1 C      6.328511     -.328511     6.292410     -.292410
 2 C      6.084331     -.084331     6.115134     -.115134
 3 C      6.085460     -.085460     6.115403     -.115403
 4 C      6.311802     -.311802     6.273449     -.273449
 5 H       .846252      .153748      .865838      .134162
 6 H       .859931      .140069      .877109      .122891
 7 H       .857920      .142080      .876547      .123453
 8 H       .831500      .168500      .856719      .143281
 9 S      15.489141     .510859    15.301787      .698213
10 C       6.538890    -.538890     6.661141     -.661141
11 H        .879453     .120547      .876778      .123222
12 H        .886807     .113193      .887686      .112314
```

benzothiophene *S,C*-methylide (25)

```
MP2/6-31G(d,p)

H          1.0   1.7569594114   -.0880228066  -1.7512753690
C          6.0   1.4689124326    .1217771364   -.7284616618
C          6.0    .6233641178    .6843184953   1.9141416734
C          6.0    .2416102071   -.3165038672   -.2496599341
C          6.0   2.2785591927    .8588758554    .1378669216
C          6.0   1.8630561382   1.1243214310   1.4513011099
C          6.0   -.2072015521   -.0371029884   1.0477317032
```

```
S          16.0   -.9091800406  -1.3244258669  -1.1678596351
H           1.0   3.2368420141   1.2275837007   -.2054640737
H           1.0   2.5084163897   1.6918984450   2.1096630193
H           1.0    .3006771837    .9045843957   2.9250121027
C           6.0  -2.0979544303  -1.1429840772    .2036813743
C           6.0  -1.1248079809   -.6806168968  -2.6765660988
H           1.0  -3.0717327135  -1.6030289595    .1156747359
C           6.0  -1.5598043319   -.5317215146   1.2796931885
H           1.0  -2.0673898365   -.4030228137   2.2281439119
H           1.0  -1.3814790964  -1.4287008497  -3.4084523025
H           1.0  -1.5396228351    .3117411312  -2.7676491357

MP2/6-31G(d,p) Energy              -466989.9632 KCAL/MOL
ZPE Correction                           87.99   KCAL/MOL
298.15K Temperature Correction           94.016  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -467266.2121 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.      CHARGE
  1 H       .848747     .151253      .872670      .127330
  2 C      6.103948    -.103948     6.094875     -.094875
  3 C      6.114958    -.114958     6.106817     -.106817
  4 C      6.227225    -.227225     6.159744     -.159744
  5 C      6.113999    -.113999     6.103329     -.103329
  6 C      6.127378    -.127378     6.110338     -.110338
  7 C      5.956037     .043963     6.020122     -.020122
  8 S     15.472159     .527841    15.328978      .671022
  9 H       .870651     .129349      .883077      .116923
 10 H       .872849     .127151      .882083      .117917
 11 H       .872253     .127747      .885224      .114776
 12 C      6.348089    -.348089     6.284370     -.284370
 13 C      6.535781    -.535781     6.648509     -.648509
 14 H       .852070     .147930      .868845      .131155
 15 C      6.056973    -.056973     6.106447     -.106447
 16 H       .860489     .139511      .878006      .121994
 17 H       .879373     .120627      .876526      .123474
 18 H       .887021     .112979      .890041      .109959
```

dibenzothiophene *S*,*C*-methylide (26)

MP2/6-31G(d,p)

```
H           1.0  -2.4446278123  -1.8562766526  -1.8378993925
C           6.0  -2.1717556951  -1.5511436585   -.8337683207
C           6.0  -1.4330426480   -.7449121422   1.7713881305
C           6.0   -.9670219665   -.9012345336   -.5947924753
C           6.0  -3.0212374450  -1.7873873060    .2497292105
C           6.0  -2.6478658534  -1.3914480627   1.5417410644
C           6.0   -.5873399128   -.4816758047    .6869315233
S          16.0    .3219490305   -.5609018491  -1.8682822613
H           1.0  -3.9734223942  -2.2788853142    .0934102734
H           1.0  -3.3129498850  -1.5885974751   2.3732247088
```

```
H          1.0   -1.1573001337   -.4429038905   2.7751043271
C          6.0    1.2438754222    .3232726024   -.6068921049
C          6.0     .0622565085    .4547008238  -3.1438101772
C          6.0    2.5567031558   1.5169524804   1.5043999676
C          6.0    2.4176211525   1.0186410931   -.8679786981
C          6.0     .6981590787    .2215414560    .6795162284
C          6.0    1.3709336289    .8244465184   1.7491151061
C          6.0    3.0709242390   1.6275863686    .2049560089
H          1.0    2.7815248140   1.0984947263  -1.8850763377
H          1.0     .9739452990    .7609407683   2.7552948187
H          1.0    3.9833653469   2.1847370211    .0343140838
H          1.0    3.0781858718   1.9899590141   2.3269555808
H          1.0    -.0411161136   -.0710806929  -4.0787089721
H          1.0    -.4717976985   1.3800501807  -2.9893083205

MP2/6-31G(d,p) Energy               -563119.5975 KCAL/MOL
ZPE Correction                          117.32   KCAL/MOL
298.15K Temperature Correction          125.239  KCAL/MOL
MP2/6-311G(3df,2p) Energy           -563489.0401 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE          LOW.POP.     CHARGE
  1 H          .905468      .094532          .934994      .065006
  2 C         6.065510     -.065510         6.056461     -.056461
  3 C         6.031825     -.031825         6.052638     -.052638
  4 C         6.234702     -.234702         6.203005     -.203005
  5 C         6.070909     -.070909         6.051876     -.051876
  6 C         6.095908     -.095908         6.058732     -.058732
  7 C         5.971702      .028298         6.023972     -.023972
  8 S        15.522559      .477441        15.195129      .804871
  9 H          .901351      .098649          .934525      .065475
 10 H          .902390      .097610          .932731      .067269
 11 H          .911140      .088860          .937324      .062676
 12 C         6.226751     -.226751         6.184757     -.184757
 13 C         6.591037     -.591037         6.580098     -.580098
 14 C         6.094762     -.094762         6.059275     -.059275
 15 C         6.036314     -.036314         6.049370     -.049370
 16 C         5.992240      .007760         6.024301     -.024301
 17 C         6.033714     -.033714         6.051622     -.051622
 18 C         6.070838     -.070838         6.050522     -.050522
 19 H          .894389      .105611          .930812      .069188
 20 H          .910476      .089524          .936918      .063082
 21 H          .899289      .100711          .933104      .066896
 22 H          .902356      .097644          .932109      .067891
 23 H          .859080      .140920          .937195      .062805
 24 H          .875289      .124711          .948530      .051470
```

dimethyl selenoxide (27)

MP2/6-31g(d,p)

```
O          8.0     .8208529984   -.9001033183   1.8200983778
SE        34.0     .9635044466    .2122385688    .5999354568
```

```
C          6.0    .6144882918   -.8458651523   -.9968954576
C          6.0   -.7874339346   1.0633275595    .5786769120
H          1.0   -.8517280888   1.6810318258   1.4703345958
H          1.0  -1.5207509857    .2621709362    .6308749700
H          1.0   -.9141853857   1.6725012016   -.3136604272
H          1.0   -.2395055334  -1.4764012848   -.7609458405
H          1.0   1.4915625420  -1.4627947097  -1.1727418037
H          1.0    .4231958095   -.2061058388  -1.8556769424
```

```
MP2/6-31G(d,p) Energy                 -1554502.477643 KCAL/MOL
ZPE Correction                              48.4      KCAL/MOL
298.15K Temperature Correction              52.173    KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1554471.647425	-1555616.774921
6-31G(2d)	-1554571.415981	-1555693.317194
6-31G(d,p)	-1554502.477643	-1555622.798761
6-31+G(d)	-1554485.229319	-1555629.816120
6-31+G(2d,p)	-1554610.962258	-1555708.541470
6-311G(d)	-1555874.429914	-1556973.245152
6-311G(3df,2p)	-1555959.852014	-1556985.741316
6-311++G(d)	-1555875.525965	-1556973.705192
6-311++G(3df,2p)	-1555960.544073	-1556986.234998
G3 (298.15K)	-1603812.0811	
G3 (0K)	-1603815.3824	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE       LOW.POP.      CHARGE
 1 O      8.691582    -.691582      8.658991    -.658991
 2 SE    33.225381     .774619     33.229096     .770904
 3 C      6.485990    -.485990      6.430092    -.430092
 4 C      6.485821    -.485821      6.429217    -.429217
 5 H       .843368     .156632       .871096     .128904
 6 H       .843092     .156908       .873442     .126558
 7 H       .869330     .130670       .882091     .117909
 8 H       .842187     .157813       .872741     .127259
 9 H       .844044     .155956       .871464     .128536
10 H       .869206     .130794       .881771     .118229
```

selenirane oxide (28)

MP2/6-31g(d,p)

```
C          6.0   -.5722063260    .0364229451  -1.2608373103
C          6.0    .8950487900    .0363569995  -1.0564500619
H          1.0  -1.0909645650    .9857808610  -1.2285650228
H          1.0  -1.0191014569   -.7338039491  -1.8754086608
H          1.0   1.3852370708    .9857175566   -.8836108083
H          1.0   1.4928243227   -.7338385138  -1.5254685201
SE        34.0   -.0824531030   -.5073128356    .5918096339
```

```
O          8.0   -.2161467325    .8291329363   1.5517107502
```

```
MP2/6-31G(d,p) Energy                  -1553743.742 KCAL/MOL
ZPE Correction                               35.04  KCAL/MOL
298.15K Temperature Correction               37.809 KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1553723.394	-1554848.268
6-31G(2d)	-1553822.846	-1554925.987
6-31G(d,p)	-1553743.742	-1554852.453
6-31+G(d)	-1553738.427	-1554862.515
6-31+G(2d,p)	-1553853.067	-1554940.373
6-311G(d)	-1555126.673	-1556206.323
6-311G(3df,2p)	-1555200.819	-1556217.718
6-311++G(d)	-1555127.672	-1556206.769
6-311++G(3df,2p)	-1555201.548	-1556218.267
G3 (298.15K)	-1603052.7149	
G3 (0K)	-1603055.1942	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM             MULL.POP.    CHARGE             LOW.POP.     CHARGE
1 C             6.341793    -.341793           6.293027    -.293027
2 C             6.341795    -.341795           6.291138    -.291138
3 H              .818943     .181057            .862484     .137516
4 H              .843319     .156681            .872060     .127940
5 H              .818943     .181057            .862514     .137486
6 H              .843310     .156690            .871994     .128006
7 SE           33.340530     .659470          33.317216     .682784
8 O             8.651369    -.651369           8.629568    -.629568
```

methyl vinyl selenoxide (29)

MP2/6-31G(d,p)

```
O          8.0   -.7959386755   1.8732242106  -1.4601676824
SE        34.0   -.6524741597    .2702255083  -1.0675310352
C          6.0  -1.6142038901    .1556069020    .6224744558
C          6.0   1.0722514415    .1371171570   -.2188006147
H          1.0  -1.3939803687   -.7879915956   1.1155043644
H          1.0  -2.6748392218    .2391058649    .3995504062
H          1.0  -1.2913968836   1.0085544884   1.2141288317
C          6.0   1.7798576093   -.9946527271   -.2708557329
H          1.0   1.4134804744   1.0507432235    .2554242417
H          1.0   1.4049959700  -1.8708735585   -.7846144052
H          1.0   2.7522477051  -1.0810592584    .1948865325
```

```
MP2/6-31G(d,p) Energy                  -1578323.936 KCAL/MOL
ZPE Correction                               51.54  KCAL/MOL
298.15K Temperature Correction               55.687 KCAL/MOL
```

Basis Set	MP2(kcal/mol)	B3LYP(kcal/mol)
6-31G(d)	-1578293.073	-1579496.991
6-31G(2d)	-1578399.927	-1579574.889
6-31G(d,p)	-1578323.936	-1579503.306
6-31+G(d)	-1578312.804	-1579515.26
6-31+G(2d,p)	-1578443.142	-1579594.083
6-311G(d)	-1579704.734	-1580859.329
6-311G(3df,2p)	-1579804.663	-1580874.795
6-311++G(d)	-1579706.791	-1580860.414
6-311++G(3df,2p)	-1579806.047	-1580875.823
G3 (298.15K)	-1627690.7725	
G3 (0K)	-1627694.4666	

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.      CHARGE
  1 O      8.693016   -.693016     8.652477    -.652477
  2 SE    33.214578    .785422    33.222984     .777016
  3 C      6.483545   -.483545     6.423368    -.423368
  4 C      6.244044   -.244044     6.230824    -.230824
  5 H       .865051    .134949      .880006     .119994
  6 H       .846862    .153138      .875369     .124631
  7 H       .841466    .158534      .871645     .128355
  8 C      6.234002   -.234002     6.210654    -.210654
  9 H       .841982    .158018      .871035     .128965
 10 H       .871753    .128247      .883915     .116085
 11 H       .863699    .136301      .877723     .122277
```

selenophene-*Se*-oxide (30)

MP2/6-31G(d,p)

```
C          6.0   1.2816361341   -.3548905868   -.1317331837
C          6.0    .7019857259    .1219183535    .9905357023
C          6.0   -.7432991567    .3351393742    .9074391717
C          6.0  -1.3064707862    .0266361110   -.2802020659
H          1.0   2.3245242242   -.5898350287   -.2784649430
H          1.0   1.2555634058    .3494343250   1.8928589365
H          1.0  -1.3052257248    .7283700519   1.7451055142
H          1.0  -2.3495913162    .0999037527   -.5465290752
SE        34.0   -.0358897283   -.8125356673  -1.4643953442
O          8.0    .1767442031    .0958442355  -2.8345410517
```

```
MP2/6-31G(d,p) Energy                  -1648457.0292 KCAL/MOL
ZPE Correction                               43.22   KCAL/MOL
298.15K Temperature Correction               47.427  KCAL/MOL
```

```
MP2/6-311G(3df,2p) Energy          -1650023.469  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM     MULL.POP.     CHARGE     LOW.POP.     CHARGE
 1 C     6.293989    -.293989     6.236481    -.236481
 2 C     6.080826    -.080826     6.101541    -.101541
 3 C     6.080882    -.080882     6.101951    -.101951
 4 C     6.293994    -.293994     6.235965    -.235965
 5 H      .840959     .159041      .866348     .133652
 6 H      .855242     .144758      .875217     .124783
 7 H      .855277     .144723      .874565     .125435
 8 H      .840924     .159076      .866364     .133636
 9 SE   33.214375     .785625    33.228131     .771869
10 O     8.643532    -.643532     8.613437    -.613437
```

benzoselenophene-*Se*-oxide (31)

```
MP2/6-31G(d,p)

H          1.0   -.3396760481  -1.4780281445  -2.3509599192
C          6.0   -.3207433789  -1.2808220417  -1.2859637291
C          6.0   -.2524964904   -.7607661128   1.4876404357
C          6.0   -.2451952265    .0176902623   -.8006507524
C          6.0   -.3483079929  -2.3332418226   -.3647265436
C          6.0   -.3240637172  -2.0711831989   1.0094611562
C          6.0   -.2014598479    .2967143887    .5743912281
SE        34.0   -.2189574623   1.6289974824  -1.8786036660
H          1.0   -.3905567268  -3.3561341958   -.7167294256
H          1.0   -.3531600969  -2.8952104971   1.7108127570
H          1.0   -.2312715177   -.5658412637   2.5535713678
O          8.0   1.2125100288   1.6712576831  -2.7124312600
C          6.0    .0054396238   2.5456710743   -.1828483904
C          6.0   -.0672356177   1.7209017478    .8812278559
H          1.0    .1170549402   3.6195222164   -.1552107478
H          1.0   -.0106695805   2.0710585120   1.9060028214

MP2/6-31G(d,p) Energy              -1744588.4509 KCAL/MOL
ZPE Correction                           73.01   KCAL/MOL
298.15K Temperature Correction           78.908  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -1746242.322  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM     MULL.POP.     CHARGE     LOW.POP.     CHARGE
 1 H      .852959     .147041      .878240     .121760
 2 C     6.118780    -.118780     6.095854    -.095854
 3 C     6.115113    -.115113     6.101791    -.101791
 4 C     6.194052    -.194052     6.133743    -.133743
 5 C     6.112724    -.112724     6.098747    -.098747
 6 C     6.123479    -.123479     6.103045    -.103045
 7 C     5.967497     .032503     6.017910    -.017910
 8 SE   33.190254     .809746    33.230071     .769929
```

```
 9 H      .865788     .134212      .881853     .118147
10 H      .867509     .132491      .880508     .119492
11 H      .867437     .132563      .884415     .115585
12 O     8.649557    -.649557     8.617166    -.617166
13 C     6.322363    -.322363     6.239106    -.239106
14 C     6.050411    -.050411     6.089845    -.089845
15 H      .844720     .155280      .869740     .130260
16 H      .857359     .142641      .877966     .122034
```

dibenzoselenophene-*Se*-oxide (32)

MP2/6-31G(d,p)

```
O          8.0  -1.8775564466    .0005392725  -2.4117512446
SE        34.0   -.3297641113   -.0000284436  -1.8218138627
C          6.0   -.2376360463  -1.3049193542   -.3853360889
C          6.0   -.2373929240   1.3048029007   -.3853564212
C          6.0   -.0672601548  -2.9627735106   1.8204094796
C          6.0   -.3088152624  -2.6804844360   -.5742265582
C          6.0   -.0952376515   -.7346207063    .8901069486
C          6.0    .0019513778  -1.5802962308   2.0006359495
C          6.0   -.2283008434  -3.5138331743    .5442903673
H          1.0   -.4348645105  -3.0982873885  -1.5658978583
H          1.0    .1198515975  -1.1706541714   2.9968118905
H          1.0   -.2908237988  -4.5878580350    .4237209654
H          1.0    .0007245299  -3.6166707407   2.6806602412
C          6.0   -.0672112318   2.9627851727   1.8204146874
C          6.0   -.0951600624    .7345976517    .8900777776
C          6.0   -.3087446504   2.6803413719   -.5742445654
C          6.0   -.2283112062   3.5137661833    .5442289238
C          6.0    .0019939172   1.5803013825   2.0006601487
H          1.0   -.4348952426   3.0981113644  -1.5659755792
H          1.0   -.2910759198   4.5877657162    .4237030788
H          1.0    .1197389630   1.1707208745   2.9967863560
H          1.0    .0006745962   3.6166944602   2.6806517290
```

```
MP2/6-31G(d,p) Energy                  -1840719.9327 KCAL/MOL
ZPE Correction                               102.45   KCAL/MOL
298.15K Temperature Correction               110.225  KCAL/MOL

MP2/6-311G(3df,2p) Energy              -1842468.382   KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.     CHARGE      LOW.POP.     CHARGE
 1 O      8.651418    -.651418     8.615908    -.615908
 2 SE    33.168517     .831483    33.236655     .763345
 3 C      6.206091    -.206091     6.133786    -.133786
 4 C      6.206076    -.206076     6.133776    -.133776
 5 C      6.131054    -.131054     6.102445    -.102445
 6 C      6.126939    -.126939     6.100012    -.100012
 7 C      5.958020     .041980     6.010975    -.010975
 8 C      6.100881    -.100881     6.102766    -.102766
 9 C      6.107714    -.107714     6.097265    -.097265
```

```
10 H      .854837     .145163      .877557     .122443
11 H      .869538     .130462      .884371     .115629
12 H      .866630     .133370      .883378     .116622
13 H      .868370     .131630      .881173     .118827
14 C     6.131057    -.131057     6.102447    -.102447
15 C     5.957986     .042014     6.010976    -.010976
16 C     6.126925    -.126925     6.099997    -.099997
17 C     6.107714    -.107714     6.097266    -.097266
18 C     6.100859    -.100859     6.102772    -.102772
19 H      .854832     .145168      .877554     .122446
20 H      .866631     .133369      .883378     .116622
21 H      .869543     .130457      .884372     .115628
22 H      .868367     .131633      .881172     .118828
```

***N*-formyl-*S*,*S*-dimethylsulfilimine (33)**

MP2/6-31G(d,p)

```
N           7.0    .1359908717    .5476199662  -1.1985811673
S          16.0    .0879343664   -.5256491625    .0286680160
C           6.0   1.1124330185    .2396978552   1.2931183453
C           6.0  -1.5187306304   -.2288640660    .7797752409
H           1.0  -1.5730397327   -.7174708177   1.7507189217
H           1.0  -2.2650682487   -.6448187691    .1089864813
H           1.0  -1.6610561413    .8461558236    .8660520630
H           1.0   2.1447358810    .1403147800    .9699370556
H           1.0    .9674726470   -.2645551371   2.2466079441
H           1.0    .8472194743   1.2929072372   1.3551902474
C           6.0    .4789406869   -.0653960435  -2.3952392135
H           1.0    .6658588326  -1.1620466630  -2.3517384983
O           8.0    .5772689749    .5421049966  -3.4534854362
```

```
MP2/6-31G(d,p) Energy              -404954.7689  KCAL/MOL
ZPE Correction                          65.06413 KCAL/MOL
298.15K Temperature Correction          70.519   KCAL/MOL

MP2/6-311G(3df,2p) Energy          -405189.5009  KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE          LOW.POP.     CHARGE
  1 N          7.621051    -.621051         7.547406    -.547406
  2 S         15.318740     .681260        15.234004     .765996
  3 C          6.493699    -.493699         6.422436    -.422436
  4 C          6.493659    -.493659         6.424433    -.424433
  5 H           .853203     .146797          .872688     .127312
  6 H           .824099     .175901          .857158     .142842
  7 H           .821314     .178686          .866310     .133690
  8 H           .824109     .175891          .859874     .140126
  9 H           .853225     .146775          .872286     .127714
```

```
10 H          .821332     .178668          .865704     .134296
11 C         5.666209     .333791         5.941585     .058415
12 H          .968621     .031379          .957225     .042775
13 O         8.440738    -.440738         8.278891    -.278891
```

N-formyl thiophenesulfilimine (34)

```
MP2/6-31G(d,p)

N           7.0   -.4904082770    .5399339217    .3391093478
S          16.0   1.0004411367    .4879215498   -.3303838065
C           6.0   1.8163845411  -1.0387826270   -.0382669246
C           6.0   3.0110767319   -.8326101107    .5664776950
C           6.0   3.2287632822    .5553905005    .9426041818
C           6.0   2.1932512271   1.3646183332    .6133216874
H           1.0   2.0749985170   2.4251807749    .7646673282
H           1.0   4.1242324216    .9008783189   1.4385005747
H           1.0   3.7296999398  -1.6168175048    .7557210094
H           1.0   1.3888902494  -1.9508633927   -.4217163321
C           6.0  -1.4205472349    .9483469501   -.6200869769
H           1.0  -1.0232945391   1.1632099631  -1.6370420365
O           8.0  -2.6087203002   1.0661181430   -.3651637400

MP2/6-31G(d,p) Energy                 -451859.6206 KCAL/MOL
ZPE Correction                             57.8868 KCAL/MOL
298.15K Temperature Correction             63.138  KCAL/MOL

MP2/6-311G(3df,2p) Energy             -452136.7981 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 N         7.569965    -.569965         7.508114    -.508114
 2 S        15.272297     .727703        15.198368     .801632
 3 C         6.326557    -.326557         6.261934    -.261934
 4 C         6.078314    -.078314         6.096347    -.096347
 5 C         6.078440    -.078440         6.095032    -.095032
 6 C         6.326497    -.326497         6.258011    -.258011
 7 H          .811865     .188135          .851782     .148218
 8 H          .838219     .161781          .865918     .134082
 9 H          .838195     .161805          .865026     .134974
10 H          .811857     .188143          .849073     .150927
11 C         5.662368     .337632         5.943749     .056251
12 H          .959874     .040126          .949272     .050728
13 O         8.425552    -.425552         8.257374    -.257374
```

N-formyl dibenzothiophenesulfilimine (35)

```
H           1.0  -0.5614045386  -1.3372427924  -3.2697609724
```

```
C            6.0  -0.3789573238  -1.6311110177  -2.2435537460
C            6.0   0.1204423090  -2.3584150723   0.4437382630
C            6.0  -0.0325840949  -2.9432369815  -1.9137546134
C            6.0  -0.4419012821  -0.7017277752  -1.2129892499
C            6.0  -0.2030070038  -1.0350632570   0.1287651112
C            6.0   0.2018163111  -3.3027081605  -0.5803055895
H            1.0   0.0434555385  -3.6900662106  -2.6933621837
C            6.0  -0.2964384829   0.1248206607   1.0128024642
H            1.0   0.4603308466  -4.3264708714  -0.3418711399
H            1.0   0.3118139595  -2.6481966409   1.4698786919
C            6.0  -0.4788681695   2.5993170278   2.3111733997
C            6.0  -0.0855356376   0.1989726709   2.3930388046
C            6.0  -0.6029767616   1.3025927153   0.3146671152
C            6.0  -0.7146165038   2.5400978861   0.9359237856
C            6.0  -0.1798027788   1.4359243708   3.0318158160
H            1.0   0.1541139782  -0.6917471401   2.9611896494
S           16.0  -0.9604662494   1.0042391497  -1.4187693133
H            1.0  -0.9455393688   3.4306402482   0.3646946123
H            1.0  -0.0087452102   1.4993232375   4.0988062370
H            1.0  -0.5394187942   3.5498687161   2.8252875994
N            7.0  -0.0005279553   1.8564109139  -2.4351892533
C            6.0   1.3403792304   1.7309835486  -2.1299928896
O            8.0   1.8508880137   1.0755432092  -1.2164741640
H            1.0   1.9475495783   2.3172516646  -2.8357575044

MP2/6-31G(d,p) Energy              -644127.3891 KCAL/MOL
ZPE Correction                         116.8032 KCAL/MOL
298.15K Temperature Correction         125.624  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -644586.6728 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE            LOW.POP.     CHARGE
  1 H           0.848361    0.151639           0.873090    0.126910
  2 C           6.121406   -0.121406           6.098843   -0.098843
  3 C           6.095232   -0.095232           6.096013   -0.096013
  4 C           6.104933   -0.104933           6.097240   -0.097240
  5 C           6.246630   -0.246630           6.149262   -0.149262
  6 C           5.930288    0.069712           6.002522   -0.002522
  7 C           6.130984   -0.130984           6.099458   -0.099458
  8 H           0.864776    0.135224           0.878345    0.121655
  9 C           5.930530    0.069470           6.002323   -0.002323
 10 H           0.866643    0.133357           0.882437    0.117563
 11 H           0.866034    0.133966           0.882846    0.117154
 12 C           6.104959   -0.104959           6.095951   -0.095951
 13 C           6.095260   -0.095260           6.098405   -0.098405
 14 C           6.246512   -0.246512           6.148888   -0.148888
```

```
15 C         6.121402   -0.121402          6.101118   -0.101118
16 C         6.130975   -0.130975          6.098359   -0.098359
17 H         0.866044    0.133956          0.880733    0.119267
18 S        15.184231    0.815769         15.202327    0.797673
19 H         0.848358    0.151642          0.871024    0.128976
20 H         0.866638    0.133362          0.883430    0.116570
21 H         0.864779    0.135221          0.879524    0.120476
22 N         7.625798   -0.625798          7.525963   -0.525963
23 C         5.686715    0.313285          5.942360    0.057640
24 O         8.446164   -0.446164          8.297636   -0.297636
25 H         0.906349    0.093651          0.911902    0.088098
```

_N_-mesyl-_S_,_S_-dimethylsulfilimine (36)

```
MP2/6-31g(d,p)

N          7.0   -.1977336457    .6738670365    .3862493406
S         16.0    .7693178061  -.6071838667    .0233288990
C          6.0    .3447444119  -1.9081947615  1.1954494272
C          6.0   2.2673822714  -.0001094084    .7923182946
H          1.0   2.0184755007    .3617826365  1.7866060898
H          1.0   2.6350448408    .8197959367    .1831663265
H          1.0   2.9997518472  -.8033307797    .8307974837
H          1.0   1.1091742625  -2.6835933064  1.1805514443
H          1.0   -.6105265219  -2.3024486803    .8609077512
H          1.0    .2450850893  -1.4595066453  2.1818509256
S         16.0  -1.6329268962    .5973729658   -.4268312336
C          6.0  -1.3904507211   1.5622810179  -1.9099828523
O          8.0  -1.8766870752   -.7971525415   -.8703048559
O          8.0  -2.6313582714   1.3022037072    .3764375903
H          1.0  -2.3305966439   1.5770802327  -2.4557375306
H          1.0   -.6151981446   1.0981794301  -2.5140806273
H          1.0  -1.1045566219   2.5692813064  -1.6212000331

MP2/6-31G(d,p) Energy              -702280.8179 KCAL/MOL
ZPE Correction                          84.1987 KCAL/MOL
298.15K Temperature Correction          91.182  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -702654.814  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 N         7.802614   -0.802614          7.795078   -0.795078
  2 S        15.263627    0.736373         15.206299    0.793701
  3 C         6.514292   -0.514292          6.431407   -0.431407
  4 C         6.496793   -0.496793          6.411063   -0.411063
  5 H         0.816007    0.183993          0.861262    0.138738
  6 H         0.820657    0.179343          0.855393    0.144607
  7 H         0.847155    0.152845          0.869277    0.130723
  8 H         0.854925    0.145075          0.871591    0.128409
```

```
  9 H          0.789871    0.210129          0.845114    0.154886
 10 H          0.828099    0.171901          0.867112    0.132888
 11 S         14.762480    1.237520         14.679469    1.320531
 12 C          6.524394   -0.524394          6.460316   -0.460316
 13 O          8.615744   -0.615744          8.651433   -0.651433
 14 O          8.535824   -0.535824          8.598175   -0.598175
 15 H          0.832929    0.167071          0.861151    0.138849
 16 H          0.856706    0.143294          0.871606    0.128394
 17 H          0.837885    0.162115          0.864253    0.135747
```

***N*-mesyl thiophenesulfilimine (37)**

```
H           1.0  -1.4794772163   0.2572346599  -1.9701050695
H           1.0  -2.0065402528  -0.0666001899   0.5997520017
C           6.0  -0.8027232900   0.3233046772  -1.1346409992
C           6.0  -1.0352588883   0.1686380805   0.1889214433
C           6.0   0.1576269845   0.3214187169   1.0093421895
H           1.0   0.1513590339   0.2099203468   2.0841174827
C           6.0   1.2739590138   0.5890103201   0.2937528366
H           1.0   2.2885524618   0.7404673401   0.6223811721
S          16.0   0.8527232529   0.8946752061  -1.3995129039
N           7.0   1.7157232309   0.0955026234  -2.5062282986
S          16.0   1.7456482309  -1.5642951625  -2.2482302798
C           6.0   2.7594081841  -1.9938570159  -3.6418718174
O           8.0   0.4071038043  -2.1512700101  -2.4384209318
O           8.0   2.4780915250  -1.8923254408  -1.0119883237
H           1.0   3.7205256066  -1.5004100411  -3.5406994223
H           1.0   2.2541302176  -1.6836524614  -4.5506850277
H           1.0   2.8781952861  -3.0740446473  -3.6181337082

MP2/6-31G(d,p) Energy             -749189.1357 KCAL/MOL
ZPE Correction                         76.7419 KCAL/MOL
298.15K Temperature Correction         83.667  KCAL/MOL

MP2/6-311G(3df,2p) Energy         -749604.864  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE           LOW.POP.     CHARGE
  1 H          0.808844    0.191156          0.846503    0.153497
  2 H          0.840553    0.159447          0.867203    0.132797
  3 C          6.315926   -0.315926          6.257001   -0.257001
  4 C          6.071551   -0.071551          6.094661   -0.094661
  5 C          6.071746   -0.071746          6.092462   -0.092462
  6 H          0.840599    0.159401          0.869440    0.130560
  7 C          6.315745   -0.315745          6.254553   -0.254553
  8 H          0.809080    0.190920          0.848523    0.151477
  9 S         15.258047    0.741953         15.176330    0.823670
```

```
10 N         7.743655   -0.743655         7.750831   -0.750831
11 S        14.777256    1.222744        14.684563    1.315437
12 C         6.535985   -0.535985         6.442270   -0.442270
13 O         8.561882   -0.561882         8.619799   -0.619799
14 O         8.561740   -0.561740         8.619801   -0.619801
15 H         0.828614    0.171386         0.857999    0.142001
16 H         0.828628    0.171372         0.857239    0.142761
17 H         0.830152    0.169848         0.860821    0.139179
```

_N_-mesyl dibenzothiophenesulfilimine (38)

```
H            1.0   -1.3904225899   0.5532307829  -3.2459595148
C            6.0   -1.6780422267   0.3931713927  -2.2140679878
C            6.0   -2.3861803629  -0.0425123898   0.4894852303
C            6.0   -2.9790029366   0.0196496690  -1.8709148032
C            6.0   -0.7473448972   0.5024428941  -1.1891806126
C            6.0   -1.0723624856   0.3052169159   0.1607698701
C            6.0   -3.3299437265  -0.1792890679  -0.5292775602
H            1.0   -3.7257400517  -0.0997787808  -2.6452834341
C            6.0    0.0887736178   0.4476108033   1.0396258549
H            1.0   -4.3462259357  -0.4565040866  -0.2800723491
H            1.0   -2.6715292693  -0.2010342995   1.5224588773
C            6.0    2.5714522585   0.6856361747   2.3140115006
C            6.0    0.1780918359   0.2483216762   2.4207942574
C            6.0    1.2512333276   0.7968384129   0.3369316341
C            6.0    2.4985593904   0.9113093656   0.9382001412
C            6.0    1.4195788695   0.3690581963   3.0462315152
H            1.0   -0.6998437543  -0.0188880612   2.9963328010
S           16.0    0.9374520600   1.0978902745  -1.4014573582
H            1.0    3.3806513095   1.1321752401   0.3513860627
H            1.0    1.4964510298   0.2017585780   4.1129756127
H            1.0    3.5276364023   0.7493741438   2.8166890589
N            7.0    1.8762832193   0.2204175900  -2.3782868421
S           16.0    2.0668894544  -1.3901765047  -1.9416903410
C            6.0    2.2399181649  -2.0910372000  -3.5673895587
O            8.0    0.8312831772  -1.9119000588  -1.3256030884
O            8.0    3.3424441392  -1.5827894139  -1.2366889277
H            1.0    3.0597576393  -1.5909192382  -4.0738191735
H            1.0    1.3090037606  -1.9566713976  -4.1090123256
H            1.0    2.4617046507  -3.1471063676  -3.4351996751

MP2/6-31G(d,p) Energy               -941447.7661 KCAL/MOL
ZPE Correction                          135.4656 KCAL/MOL
298.15K Temperature Correction          146.061  KCAL/MOL

MP2/6-311G(3df,2p) Energy           -942047.6661 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM             MULL.POP.     CHARGE           LOW.POP.     CHARGE
 1 H             0.853209     0.146791          0.875089     0.124911
 2 C             6.119459    -0.119459          6.096354    -0.096354
 3 C             6.094857    -0.094857          6.095448    -0.095448
 4 C             6.105323    -0.105323          6.097138    -0.097138
 5 C             6.228518    -0.228518          6.154291    -0.154291
 6 C             5.938537     0.061463          6.002668    -0.002668
 7 C             6.129547    -0.129547          6.097449    -0.097449
 8 H             0.865038     0.134962          0.878413     0.121587
 9 C             5.916444     0.083556          6.005050    -0.005050
10 H             0.865771     0.134229          0.881875     0.118125
11 H             0.865206     0.134794          0.882532     0.117468
12 C             6.103832    -0.103832          6.089469    -0.089469
13 C             6.093900    -0.093900          6.096593    -0.096593
14 C             6.290879    -0.290879          6.165927    -0.165927
15 C             6.093965    -0.093965          6.088587    -0.088587
16 C             6.130204    -0.130204          6.096513    -0.096513
17 H             0.864886     0.135114          0.880038     0.119962
18 S            15.192520     0.807480         15.188968     0.811032
19 H             0.833231     0.166769          0.863515     0.136485
20 H             0.865322     0.134678          0.882793     0.117207
21 H             0.860517     0.139483          0.877343     0.122657
22 N             7.762419    -0.762419          7.755241    -0.755241
23 S            14.767049     1.232951         14.679605     1.320395
24 C             6.529079    -0.529079          6.447809    -0.447809
25 O             8.578251    -0.578251          8.625657    -0.625657
26 O             8.548220    -0.548220          8.612188    -0.612188
27 H             0.828385     0.171615          0.856482     0.143518
28 H             0.842133     0.157867          0.864621     0.135379
29 H             0.833300     0.166700          0.862346     0.137654
```

_C_-carbomethoxycarbonyl-_S,S_-dimethylsulfonium ylide (39)

```
C           6.0     .8796490779   -.6302756135   -.6161649025
S          16.0   -.3369675181    .2938293294    .3644563476
C           6.0  -1.4267988067   -.7968981825    .9972199764
C           6.0  -2.8341539552   -.6084620560    .8250237896
O           8.0  -3.7136577077  -1.3514590442   1.2508442318
O           8.0  -3.1378051728    .5374285883    .1027664771
C           6.0  -4.5441019837    .7339489995   -.0742367875
H           1.0  -5.0484563505    .8357206015    .8845209736
H           1.0  -4.9903816338   -.0990394924   -.6134705270
H           1.0  -4.6345532683   1.6505729944   -.6495568922
H           1.0  -1.0715273467  -1.6558126883   1.5439973933
C           6.0    .7872905327    .8040895662   1.6956160358
H           1.0    .1949812985   1.3847714852   2.3967110926
```

```
H          1.0   1.5914984708   1.4142745994   1.2876603424
H          1.0   1.1926898959   -.0741223208   2.1946306753
H          1.0    .3502505214  -1.0201845024  -1.4805984973
H          1.0   1.2809991121  -1.4533071838   -.0278193154
H          1.0   1.6806148343    .0348949199   -.9347204132

MP2/6-31G(d,p) Energy              -466573.3529 KCAL/MOL
ZPE Correction                          94.0294 KCAL/MOL
298.15K Temperature Correction         100.647  KCAL/MOL

MP2/6-311G(3df,2p) Energy          -466868.941  KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C         6.483744    -.483744         6.431270    -.431270
 2 S        15.445206     .554794        15.286359     .713641
 3 C         6.530958    -.530958         6.549389    -.549389
 4 C         5.364054     .635946         5.799662     .200338
 5 O         8.516547    -.516547         8.318860    -.318860
 6 O         8.538632    -.538632         8.259489    -.259489
 7 C         6.061593    -.061593         6.131422    -.131422
 8 H          .880049     .119951          .897713     .102287
 9 H          .879815     .120185          .896060     .103940
10 H          .891654     .108346          .898048     .101952
11 H          .865584     .134416          .880125     .119875
12 C         6.483760    -.483760         6.431908    -.431908
13 H          .827212     .172788          .859433     .140567
14 H          .856377     .143623          .874230     .125770
15 H          .845635     .154365          .875896     .124104
16 H          .827195     .172805          .860272     .139728
17 H          .845605     .154395          .875400     .124600
18 H          .856380     .143620          .874464     .125536
```

***C*-carbomethoxycarbonyl thiophenesulfonium ylide (40)**

```
C          6.0   -.3826843357    .7460177610   -.8291535984
S         16.0   -.2695554129   -.0228255176    .6425759102
C          6.0  -1.7679149566   -.6951639822   1.2892422593
C          6.0  -1.9798660315   -.2704988224   2.5584319521
C          6.0  -1.0115242218    .7180451246   3.0000005132
C          6.0   -.0881235944   1.0194962932   2.0552749020
H          1.0    .7456294214   1.7015578373   2.0993791176
H          1.0  -1.0324052266   1.1656545900   3.9833507043
H          1.0  -2.7868159689   -.6255677624   3.1833441618
H          1.0  -2.3120487254  -1.4197079719    .7050663233
C          6.0    .4926633858    .3670874425  -1.9013709844
O          8.0   1.3672217941   -.6465642860  -1.5517636164
```

```
C            6.0   2.2436262178  -1.0288409956  -2.6185653903
H            1.0   2.8634140124  -1.8202907515  -2.2086739133
H            1.0   2.8578553088   -.1892214126  -2.9366235153
H            1.0   1.6785374982  -1.3912143539  -3.4745842906
O            8.0    .4924603827    .8674770782  -3.0205778368
H            1.0  -1.1104795471   1.5245597290   -.9753626985

MP2/6-31G(d,p) Energy              -513483.2346 KCAL/MOL
ZPE Correction                          86.6304 KCAL/MOL
298.15K Temperature Correction          93.72   KCAL/MOL
MP2/6-311G(3df,2p) Energy          -513827.9102 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C           6.509939    -.509939         6.522317    -.522317
 2 S          15.372382     .627618        15.237128     .762872
 3 C           6.331538    -.331538         6.269417    -.269417
 4 C           6.080960    -.080960         6.107306    -.107306
 5 C           6.080953    -.080953         6.105464    -.105464
 6 C           6.331542    -.331542         6.267321    -.267321
 7 H            .820574     .179426          .853354     .146646
 8 H            .846041     .153959          .870744     .129256
 9 H            .846038     .153962          .868786     .131214
10 H            .820591     .179409          .852158     .147842
11 C           5.366853     .633147         5.801231     .198769
12 O           8.534188    -.534188         8.252391    -.252391
13 C           6.064793    -.064793         6.132990    -.132990
14 H            .887261     .112739          .894603     .105397
15 H            .876894     .123106          .894913     .105087
16 H            .876863     .123137          .895022     .104978
17 O           8.506800    -.506800         8.306352    -.306352
18 H            .845790     .154210          .868502     .131498
```

***C*-carbomethoxycarbonyl dibenzothiophenesulfonium ylide (41)**

```
H            1.0  -1.5645906065   0.7092911630  -3.1016764194
C            6.0  -1.8519680274   0.7003456231  -2.0572477823
C            6.0  -2.5502481706   0.6398771875   0.6823280230
C            6.0  -3.1759469846   0.4923237011  -1.6652640130
C            6.0  -0.9004211796   0.8631488079  -1.0595051300
C            6.0  -1.2159534534   0.8292439394   0.3050737832
C            6.0  -3.5200395419   0.4738053568  -0.3067605399
H            1.0  -3.9424112412   0.3486199540  -2.4160733786
C            6.0  -0.0311071723   0.9614874493   1.1543041714
H            1.0  -4.5526385791   0.3191342604  -0.0207778991
H            1.0  -2.8285024831   0.6128529683   1.7291399011
C            6.0   2.4774339638   1.1223852339   2.3866836441
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C           6.0   0.0565493730   0.9300815375   2.5507005815
C           6.0   1.1477115617   1.0913661722   0.4084870441
C           6.0   2.4041086176   1.1748030977   0.9932248024
C           6.0   1.3109618684   1.0122524651   3.1557518325
H           1.0  -0.8363165436   0.8339399920   3.1569733221
S          16.0   0.8405837097   1.2028990280  -1.3607211676
H           1.0   3.2946514279   1.2499682826   0.3811063354
H           1.0   1.3855612397   0.9805475727   4.2353107779
H           1.0   3.4416350133   1.1716012637   2.8763128295
C           6.0   1.6074240945   0.0214725453  -2.2459725084
H           1.0   2.1714796805   0.3782563419  -3.0888572719
C           6.0   1.5367249504  -1.3760741057  -1.9286750136
O           8.0   2.0744540742  -2.2964830307  -2.5339694149
O           8.0   0.7545263983  -1.5848710105  -0.8056151255
C           6.0   0.6434788497  -2.9635898515  -0.4334183666
H           1.0   0.1903497551  -3.5450020467  -1.2337219590
H           1.0   0.0111488012  -2.9703866533   0.4492126689
H           1.0   1.6213616943  -3.3832970048  -0.2063540271

MP2/6-31G(d,p) Energy                 -705744.0161 KCAL/MOL
ZPE Correction                            145.1005 KCAL/MOL
298.15K Temperature Correction            155.937  KCAL/MOL

MP2/6-311G(3df,2p) Energy             -706273.6884 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 H         0.851158    0.148842         0.874444    0.125556
  2 C         6.121811   -0.121811         6.097440   -0.097440
  3 C         6.099999   -0.099999         6.100257   -0.100257
  4 C         6.107585   -0.107585         6.099418   -0.099418
  5 C         6.225399   -0.225399         6.150736   -0.150736
  6 C         5.941808    0.058192         6.009511   -0.009511
  7 C         6.132247   -0.132247         6.102333   -0.102333
  8 H         0.865645    0.134355         0.878868    0.121132
  9 C         5.941906    0.058094         6.009189   -0.009189
 10 H         0.868227    0.131773         0.883392    0.116608
 11 H         0.868512    0.131488         0.884671    0.115329
 12 C         6.107587   -0.107587         6.097847   -0.097847
 13 C         6.099999   -0.099999         6.103121   -0.103121
 14 C         6.225365   -0.225365         6.150136   -0.150136
 15 C         6.121797   -0.121797         6.100125   -0.100125
 16 C         6.132252   -0.132252         6.101008   -0.101008
 17 H         0.868508    0.131492         0.882207    0.117793
 18 S        15.364044    0.635956        15.282411    0.717589
 19 H         0.851127    0.148873         0.872070    0.127930
 20 H         0.868235    0.131765         0.884538    0.115462
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21 H         0.865642    0.134358          0.880310    0.119690
22 C         6.524120   -0.524120          6.527860   -0.527860
23 H         0.844455    0.155545          0.860245    0.139755
24 C         5.359418    0.640582          5.801730    0.198270
25 O         8.499241   -0.499241          8.301099   -0.301099
26 O         8.540004   -0.540004          8.249149   -0.249149
27 C         6.063807   -0.063807          6.130796   -0.130796
28 H         0.876269    0.123731          0.893751    0.106249
29 H         0.887489    0.112511          0.895528    0.104472
30 H         0.876348    0.123652          0.895812    0.104188
```

***C*-dicarbomethoxycarbonyl-*S,S*-dimethylsulfonium ylide (42)**

```
S          16.0  -0.7666248948  -1.6048660991  -0.9662789832
C           6.0  -0.0603509566  -0.6290787874   0.2624784976
C           6.0  -0.8373300053   0.1406994390   1.1975853341
C           6.0   1.2326829787  -1.2175640657   0.6353210791
C           6.0  -1.9809349644  -2.7272538714  -0.2354876758
C           6.0  -1.8329512112  -0.5334087296  -1.9448448740
O           8.0   1.5021787794  -2.3975369319   0.4063868470
O           8.0   2.1678545570  -0.4515742759   1.2477881658
O           8.0  -2.1886644548   0.1781700226   0.8610369534
O           8.0  -0.4294421100   0.7169065474   2.2010063960
C           6.0   2.1655738100   0.9756985485   1.0922595186
C           6.0  -2.9786208727   0.9414267550   1.7883874069
H           1.0   1.8281831410   1.4432401733   2.0100259374
H           1.0   1.5167229674   1.2729006126   0.2712873925
H           1.0   3.1947263338   1.2513942920   0.8731499397
H           1.0  -3.9946720620   0.8852128734   1.4098447211
H           1.0  -2.6394792553   1.9737732412   1.8238464498
H           1.0  -2.9174779783   0.5171029575   2.7874704533
H           1.0  -1.4044134603  -3.4025973113   0.3909829773
H           1.0  -2.4741470419  -3.2830687740  -1.0307658302
H           1.0  -2.6925116537  -2.1569148451   0.3532841964
H           1.0  -1.1913906229   0.2374466880  -2.3625437534
H           1.0  -2.6044887595  -0.0912054300  -1.3264610569
H           1.0  -2.2550206732  -1.1364099194  -2.7462314522

MP2/6-31G(d,p) Energy             -609188.1826 KCAL/MOL
ZPE Correction                        121.9832 KCAL/MOL
298.15K Temperature Correction        131.749  KCAL/MOL

MP2/6-311G(3df,2p) Energy         -609648.4771 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 S        15.386457    0.613543         15.268977    0.731023
  2 C         6.542455   -0.542455          6.444724   -0.444724
  3 C         5.347274    0.652726          5.804434    0.195566
  4 C         5.371609    0.628391          5.803549    0.196451
```

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   5  C          6.504166   -0.504166        6.423388   -0.423388
   6  C          6.497520   -0.497520        6.416429   -0.416429
   7  O          8.472162   -0.472162        8.297814   -0.297814
   8  O          8.484830   -0.484830        8.197585   -0.197585
   9  O          8.560322   -0.560322        8.260959   -0.260959
  10  O          8.489294   -0.489294        8.292240   -0.292240
  11  C          6.067001   -0.067001        6.127354   -0.127354
  12  C          6.069792   -0.069792        6.127843   -0.127843
  13  H          0.851758    0.148242        0.884792    0.115208
  14  H          0.890962    0.109038        0.897825    0.102175
  15  H          0.883906    0.116094        0.898885    0.101115
  16  H          0.886545    0.113455        0.897107    0.102893
  17  H          0.868343    0.131657        0.893378    0.106622
  18  H          0.865757    0.134243        0.891566    0.108434
  19  H          0.805452    0.194548        0.848571    0.151429
  20  H          0.850712    0.149288        0.869833    0.130167
  21  H          0.819684    0.180316        0.864637    0.135363
  22  H          0.826337    0.173663        0.857133    0.142867
  23  H          0.809350    0.190650        0.861177    0.138823
  24  H          0.848313    0.151687        0.869801    0.130199
```

Computed BDEs as a function of basis set

Table S1. Computational and experimental BDEs for sulfoxides (**1-4**) in kcal/mol.

Method[a]	**1**	**2**	**3**	**4**
MP2/6-311++G(3df,2p)	89.6	88.7	87.4	85.1
MP2/6-311G(3df,2p)	88.1	87.8	86.5	85.3
MP2/6-311++G(d)	67.9	67.4	66.2	63.1
MP2/6-31+G(2d,p)	78.4	78.0	76.9	74.7
MP2/6-31G(2d)	73.4	73.9	72.7	72.1
MP2/6-31G(d,p)	67.3	67.6	66.7	66.0
MP2/6-311G(d)	64.3	65.0	63.9	62.7
MP2/6-31+G(d)	72.6	72.0	71.0	68.2
MP2/6-31G(d)	67.7	68.0	67.0	66.1
B3LYP/6-311++G(3df,2p)	81.9	80.8	79.9	77.7
B3LYP/6-311G(3df,2p)	81.9	81.3	80.5	79.2
B3LYP/6-311++G(d)	67.2	66.8	66.0	64.1
B3LYP/6-31+G(2d,p)	75.1	74.1	73.3	71.2
B3LYP/6-31G(2d)	72.1	72.0	71.3	70.7
B3LYP/6-31G(d,p)	67.9	68.1	67.3	66.8
B3LYP/6-311G(d)	65.6	65.3	65.6	65.0
B3LYP/6-31+G(d)	69.3	68.6	67.9	65.8
B3LYP/6-31G(d)	67.9	68.0	67.3	66.6
G3 (0 K)	84.3	84.0	83.0	N/A
G3 (298 K)	82.3	81.8	80.8	N/A
Expt[b]	86.5 ± 0.5	88.8 ± 0.6	88.7 ± 1.2	89.3 ± 1.4

[a] All BDE were determined from the listed method energies performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and temperature correction to 298.15 K. [b] Experimental BDE determined from ΔH_f° values from the NIST webbook.

Table S2. Computational and experimental BDEs for sulfoxides (**5-9**) in kcal/mol.

Method[a]	**5**	**6**	**7**	**8**	**9**
MP2/6-311++G(3df,2p)	89.3	86.0	60.4	67.3	72.1
MP2/6-311G(3df,2p)	86.5	85.5	59.6	66.4	71.3
MP2/6-311++G(d)	66.1	65.3	40.1		
MP2/6-31+G(2d,p)	75.1	75.4	50.3		
MP2/6-31G(2d)	70.5	71.9	47.5		
MP2/6-31G(d,p)	65.8	65.9	42.3		
MP2/6-311G(d)	62.5	62.8	36.6		
MP2/6-31+G(d)	70.6	70.0	45.1		
MP2/6-31G(d)	66.1	66.3	42.6		
B3LYP/6-311++G(3df,2p)	80.7	77.8	56.4		
B3LYP/6-311G(3df,2p)	80.9	78.7	57.0		
B3LYP/6-311++G(d)	66.7	63.9	42.9		
B3LYP/6-31+G(2d,p)	73.8	71.3	50.1		
B3LYP/6-31G(2d)	71.3	69.8	49.4		
B3LYP/6-31G(d,p)	67.3	65.6	46.0		
B3LYP/6-311G(d)	65.2	63.6	41.8		
B3LYP/6-31+G(d)	68.7	65.9	45.2		
B3LYP/6-31G(d)	67.3	65.7	46.1		
G3 (0 K)	80.8	81.0	58.5	N/A	N/A
G3 (298 K)	79.1	79.0	56.5	N/A	N/A

[a] All BDE were determined from the listed method energies performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and a temperature correction to 298.15 K.

Table S3. BDEs for **1-4** from isodesmic reactions at different basis sets, in kcal/mol.

Method[a]	**1**	**2**	**3**	**4**
MP2/6-311++G(3df,2p)	N/A	85.6	84.2	86.1
	(89.8)	(N/A)	(87.6)	(85.2)
	{91.0}	{90.0}	{N/A}	{86.4}
	[93.9]	[93.0]	[91.6]	[N/A]
MP2/6-311G(3df,2p)	N/A	86.2	84.9	84.9
	(89.2)	(N/A)	(87.6)	(86.4)
	{90.3}	{90.0}	{N/A}	{87.5}
	[92.1]	[91.8]	[90.5]	[N/A]
MP2/6-311++G(d)	N/A	86.0	84.8	84.7
	(89.4)	(N/A)	(87.7)	(84.6)
	{90.4}	{89.9}	{N/A}	{85.6}
	[94.1]	[93.6]	[92.4]	[N/A]
MP2/6-31+G(2d,p)	N/A	86.1	84.9	83.1
	(89.3)	(N/A)	(87.7)	(85.5)
	{90.3}	{89.9}	{N/A}	{86.5}
	[93.1]	[92.7]	[91.5]	[N/A]
MP2/6-31G(2d)	N/A	86.9	85.8	83.6
	(88.5)	(N/A)	(87.8)	(87.2)
	{89.4}	{89.8}	{N/A}	{88.1}
	[90.6]	[91.0]	[89.9]	[N/A]
MP2/6-31G(d,p)	N/A	86.8	85.9	85.0
	(88.6)	(N/A)	(88.0)	(87.2)
	{89.3}	{89.6}	{N/A}	{87.9}
	[90.7]	[91.0]	[90.1]	[N/A]
MP2/6-311G(d)	N/A	87.1	86.0	84.6
	(88.3)	(N/A)	(87.8)	(86.6)
	{89.2}	{89.8}	{86.6}	{87.5}
	[91.0]	[91.6]	[90.5]	[N/A]
MP2/6-31+G(d)	N/A	85.9	84.9	84.5
	(89.5)	(N/A)	(87.9)	(85.1)
	{90.3}	{89.7}	{N/A}	{85.9}
	[93.7]	[93.1]	[92.1]	[N/A]
MP2/6-31G(d)	N/A	86.8	85.8	84.9
	(88.6)	(N/A)	(87.9)	(87.1)
	{89.4}	{89.7}	{N/A}	{87.8}
	[90.9]	[91.1]	[90.2]	[N/A]
B3LYP/6-311++G(3df,2p)	N/A	84.2	84.4	82.3
	(90.0)	(N/A)	(88.0)	(85.8)
	{90.8}	{89.6}	{N/A}	{86.5}
	[93.5]	[92.4]	[91.5]	[N/A]
B3LYP/6-311G(3df,2p)	N/A	84.9	85.1	83.8
	(89.5)	(N/A)	(88.1)	(86.8)
	{90.1}	{89.5}	{N/A}	{87.4}

	[92.0]	[91.4]	[90.6]	[N/A]
B3LYP/6-311++G(d)	N/A	84.8	85.3	83.4
	(89.4)	(N/A)	(88.2)	(86.3)
	{89.9}	{89.4}	{N/A}	{86.8}
	[92.4]	[91.9]	[91.2]	[N/A]
B3LYP/6-31+G(2d,p)	N/A	84.9	84.7	82.6
	(89.9)	(N/A)	(88.1)	(86.0)
	{90.5}	{89.5}	{N/A}	{86.6}
	[93.2]	[92.2]	[91.4]	[N/A]
B3LYP/6-31G(2d)	N/A	85.8	85.7	85.1
	(89.0)	(N/A)	(88.2)	(87.6)
	{89.5}	{89.4}	{N/A}	{88.1}
	[90.7]	[90.6]	[89.9]	[N/A]
B3LYP/6-31G(d,p)	N/A	85.9	85.9	85.3
	(88.8)	(N/A)	(88.2)	(87.6)
	{89.3}	{89.4}	{N/A}	{88.1}
	[90.5]	[90.6]	[89.9]	[N/A]
B3LYP/6-311G(d)	N/A	86.0	86.5	85.8
	(88.2)	(N/A)	(88.2)	(87.2)
	{88.7}	{89.4}	{N/A}	{88.0}
	[90.0]	[90.6]	[90.0]	[N/A]
B3LYP/6-31+G(d)	N/A	84.9	85.0	83.0
	(89.7)	(N/A)	(88.2)	(86.2)
	{90.2}	{89.4}	{N/A}	{86.6}
	[92.8]	[92.0]	[91.4]	[N/A]
B3LYP/6-31G(d)	N/A	85.8	85.9	85.3
	(88.8)	(N/A)	(88.2)	(87.6)
	{89.3}	{89.4}	{N/A}	{88.1}
	[90.5]	[90.6]	[89.9]	[N/A]
G3 (0 K)	N/A	86.2	85.2	N/A
	(89.2)	(N/A)	(87.9)	(N/A)
	{90.0}	{89.7}	{N/A}	{N/A}
	[N/A]	[N/A]	[N/A]	[N/A]
G3 (298 K)	N/A	86.1	85.1	N/A
	(89.2)	(N/A)	(87.9)	(N/A)
	{90.1}	{89.7}	{N/A}	{N/A}
	[N/A]	[N/A]	[N/A]	[N/A]
Expt[b]	86.5 ± 0.5	88.8 ± 0.6	88.7 ± 1.2	89.3 ± 1.4

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[a] All BDE were determined from the listed method energies performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and temperature correction to 298.15 K. BDE were determined by four isodesmic reactions using 1: BDE_{std} = 86.5 kcal/mol, 2: (BDE_{std} = 88.8 kcal/mol), 3: {BDE_{std} = 88.7 kcal/mol}, and 4: [BDE_{std} = 89.3 kcal/mol][b] Experimental BDE determined from ΔH_f° values from the NIST webbook.

Table S4. BDEs for sulfilimines **10**-**15** as a function of basis set.

Method[a]	10	11	12	13	14	15
MP2/6-311++G(3df,2p)	47.5	25.5	43.1	34.2	38.3	42.4
MP2/6-311G(3df,2p)	46.2	23.3	41.2	33.2	37.0	41.5
MP2/6-311++G(d)	31.3	9.3	27.6	20.0	22.4	26.6
MP2/6-31+G(2d,p)	37.4	15.3	33.2	24.6	28.2	32.9
MP2/6-31G(2d)	32.9	11.4	28.2	21.0	24.4	29.1
MP2/6-31G(d,p)	27.1	5.2	23.6	15.3	18.8	23.4
MP2/6-311G(d)	28.7	5.9	24.4	14.3	20.4	24.9
MP2/6-31+G(d)	30.8	9.0	27.9	18.4	22.0	26.8
MP2/6-31G(d)	26.5	5.0	23.0	15.0	18.5	23.0
B3LYP/6-311++G(3df,2p)	39.6	20.3	37.1	27.3	32.0	34.5
B3LYP/6-311G(3df,2p)	39.4	19.2	36.4	27.3	31.7	34.7
B3LYP/6-311++G(d)	28.6	9.3	27.0	17.0	21.3	24.0
B3LYP/6-31+G(2d,p)	35.0	15.8	32.8	23.2	27.5	30.4
B3LYP/6-31G(2d)	32.2	14.1	29.4	21.5	25.5	28.3
B3LYP/6-31G(d,p)	28.4	7.7	25.9	16.7	20.7	24.4
B3LYP/6-311G(d)	28.4	7.5	25.9	16.8	20.9	24.2
B3LYP/6-31+G(d)	29.0	9.4	27.4	17.2	21.5	24.6
B3LYP/6-31G(d)	27.8	7.9	25.3	16.5	20.5	23.9
G3 (0 K)	42.9	22.8	38.5	30.9	34.6	38.2
G3 (298 K)	39.2	17.8	35.0	23.8	30.3	34.5

[a] All BDE were determined from the listed method energies performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and temperature correction to 298.15 K. Calculations are for the direct dissociation reactions, not an isodesmic reaction.

Table S5. Calculated BDEs for sulfonium carbenes **19-23** in kcal/mol.

Method[a]	**19**	**20**	**21**	**22**	**23**
MP2/6-311++G(3df,2p)	45.8	26.5	33.7	38.4	43.6
MP2/6-311G(3df,2p)	44.9	25.6	32.9	37.5	43.1
MP2/6-311++G(d)	35.4	18.1	25.7	29.4	33.6
MP2/6-31+G(2d,p)	37.7	18.5	25.7	30.2	35.6
MP2/6-31G(2d)	33.9	16.5	23.1	27.4	33.1
MP2/6-31G(d,p)	29.5	12.4	18.9	23.4	28.4
MP2/6-311G(d)	34.1	16.8	20.8	27.9	32.7
MP2/6-31+G(d)	32.6	14.6	21.4	26.2	30.8
MP2/6-31G(d)	29.0	12.5	18.8	23.3	28.0
B3LYP/6-311++G(3df,2p)	40.4	24.7	29.4	34.7	37.2
B3LYP/6-311G(3df,2p)	40.1	24.5	29.4	34.5	37.4
B3LYP/6-311++G(d)	34.1	19.6	23.6	29.1	31.3
B3LYP/6-31+G(2d,p)	37.1	21.8	26.5	31.7	34.2
B3LYP/6-31G(2d)	35.4	22.2	26.0	31.0	33.5
B3LYP/6-31G(d,p)	33.3	17.9	22.8	27.8	31.3
B3LYP/6-311G(d)	34.0	19.5	23.7	28.9	31.7
B3LYP/6-31+G(d)	56.4	41.3	45.7	51.1	53.5
B3LYP/6-31G(d)	33.2	18.7	23.1	28.2	31.2
G3 (0 K)	44.6	27.3	33.6	38.0	42.1
G3 (298 K)	40.6	22.3	29.1	33.6	38.1

[a] All BDE were determined from the listed method energies performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and temperature correction to 298.15 K. Calculations are for the direct dissociation reactions, not an isodesmic reaction.

Table S6. Computed BDEs for selenoxides **27-32,** in kcal/mol

Method[a]	**27**	**28**	**29**	**30**	**31**	**32**
MP2/6-311++G(3df,2p)	79.1	75.7	74.6	57.5	59.8	64.2
MP2/6-311G(3df,2p)	78.5	75.1	74.4			
MP2/6-311++G(d)	62.3	59.6	58.8			
MP2/6-31+G(2d,p)	80.0	71.1	75.0			
MP2/6-31G(2d)	74.4	71.7	71.4			
MP2/6-31G(d,p)	64.7	61.2	62.5			
MP2/6-311G(d)	57.2	54.4	54.2			
MP2/6-31+G(d)	74.5	71.1	69.5			
MP2/6-31G(d)	64.8	61.4	62.9			
B3LYP/6-311++G(3df,2p)	69.6	68.5	65.5			
B3LYP/6-311G(3df,2p)	70.3	69.3	61.0			
B3LYP/6-311++G(d)	61.6	61.0	57.9			
B3LYP/6-31+G(2d,p)	73.4	72.3	68.4			
B3LYP/6-31G(2d)	70.4	69.9	67.4			
B3LYP/6-31G(d,p)	65.4	64.0	62.9			
B3LYP/6-311G(d)	59.1	58.6	55.9			
B3LYP/6-31+G(d)	71.2	70.0	65.9			
B3LYP/6-31G(d)	65.2	64.0	62.9			
G3 (0 K)	71.5	67.6	68.4			
G3	70.2	68.9	66.3			

[a] All ΔH were determined from the listed method energies runs performed at the MP2/6-31G(d,p) geometry and include the unscaled ZPE and a 298.15 K temperature correction. Calculations for **27-29** are for the direct dissociation reactions, not an isodesmic reaction. The entries for **30-32** corresponds to Method C.

APPENDIX E

Supporting information for Chapter 7

ethyl methyl sulfilimine

MP2/6-31G(d,p)

```
N           7.0   0.5806365703   0.1097102198  -1.9206855725
S          16.0   0.5732218339   0.9833020576  -0.5776492578
C           6.0   1.6993347667   0.0928990095   0.5107504783
C           6.0  -0.9748540273   0.6086824397   0.3324397792
H           1.0   0.6062433166   0.7958300268  -2.6750141548
H           1.0  -0.8651608723   0.9865794662   1.3506523284
C           6.0  -1.3483788137  -0.8615982310   0.2747240581
H           1.0  -1.7271019764   1.2160821116  -0.1720058501
H           1.0   2.7089094144   0.3331847421   0.1897944792
H           1.0   1.5280436369  -0.9731262197   0.3790231771
H           1.0   1.5534602790   0.3909256581   1.5473848966
H           1.0  -0.7254860336  -1.4639277066   0.9331434026
H           1.0  -1.2231226281  -1.2187491294  -0.7471344928
H           1.0  -2.3857457364  -0.9997943950   0.5745766386
```

```
MP2/6-31G(d,p)Energy                 -358606.5915 KCAL/MOL
ZPE Correction                       77.553755 KCAL/MOL
298.15K Temperature Correction       82.609 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -358788.1819 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM             MULL.POP.     CHARGE          LOW.POP.      CHARGE
  1 N            7.780673    -0.780673         7.755606    -0.755606
  2 S           15.363460     0.636540        15.279369     0.720631
  3 C            6.489713    -0.489713         6.435260    -0.435260
  4 C            6.384417    -0.384417         6.337111    -0.337111
  5 H            0.761843     0.238157         0.827488     0.172512
  6 H            0.871352     0.128648         0.889458     0.110542
  7 C            6.351377    -0.351377         6.312321    -0.312321
  8 H            0.855405     0.144595         0.879719     0.120281
  9 H            0.843778     0.156222         0.869797     0.130203
 10 H            0.832199     0.167801         0.872596     0.127404
 11 H            0.869637     0.130363         0.882388     0.117612
 12 H            0.887525     0.112475         0.894841     0.105159
 13 H            0.831304     0.168696         0.873654     0.126346
 14 H            0.877317     0.122683         0.890393     0.109607
```

ethyl methyl sulfilimine-transition state

```
MP2/6-31G(d,p)

C           6.0  -1.0708869125  -1.1287969323   1.0296578410
S          16.0  -1.0604690754  -0.2490836068  -0.5542258622
N           7.0  -1.1767174684   1.3377142048  -0.2146154891
C           6.0   1.2401381541  -0.1867736699  -0.5679660790
H           1.0  -2.0704022888  -1.1050163809   1.4575936343
H           1.0  -0.3634013294  -0.6597409841   1.7107290433
H           1.0  -0.7777230530  -2.1630792753   0.8573420948
C           6.0   1.4208152310   1.1410712719  -0.0905193494
H           1.0   1.4146612679  -0.4003101622  -1.6154652512
H           1.0   1.4323124355  -1.0288083784   0.0877708356
H           1.0   1.8814671992   1.8416558346  -0.7786043926
H           1.0   1.7898229003   1.2429303363   0.9250222033
H           1.0   0.2128782151   1.5743431143  -0.0571914364
H           1.0  -1.5027784657   1.4856533481   0.7406315677

MP2/6-31G(d,p)Energy                 -358582.0056 KCAL/MOL
ZPE Correction                       75.812644 KCAL/MOL
298.15K Temperature Correction       80.007 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -358761.1615 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 C          6.511612   -0.511612         6.433503   -0.433503
  2 S         15.490347    0.509653        15.460885    0.539115
  3 N          7.695693   -0.695693         7.599939   -0.599939
  4 C          6.319076   -0.319076         6.291818   -0.291818
  5 H          0.847165    0.152835         0.878525    0.121475
  6 H          0.848504    0.151496         0.877037    0.122963
  7 H          0.848846    0.151154         0.871573    0.128427
  8 C          6.374260   -0.374260         6.350996   -0.350996
  9 H          0.871046    0.128954         0.891849    0.108151
 10 H          0.886956    0.113044         0.896367    0.103633
 11 H          0.868113    0.131887         0.880876    0.119124
 12 H          0.888450    0.111550         0.895869    0.104131
 13 H          0.809766    0.190234         0.847399    0.152601
 14 H          0.740166    0.259834         0.823364    0.176636
```

CH_3SNH_2

```
MP2/6-31G(d,p)

N           7.0  -0.6554417196  -0.0160501563  -1.3132987534
S          16.0  -0.9382007627  -0.3745856220   0.3537610882
C           6.0   0.6793445550   0.0729007543   1.0037663695
H           1.0  -0.7825479467  -0.8488507650  -1.8747680600
```

```
H             1.0  -1.3059217035   0.6910738655  -1.6323640570
H             1.0   0.8928728165   1.1229476312   0.8234268074
H             1.0   1.4586746984  -0.5415721859   0.5612938293
H             1.0   0.6512200627  -0.1058635213   2.0781827261

MP2/6-31G(d,p)Energy                -309472.096 KCAL/MOL
ZPE Correction                      42.010693 KCAL/MOL
298.15K Temperature Correction      45.533 KCAL/MOL

MP2/6-311G(3df,2p)Energy            -309592.4374 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE          LOW.POP.     CHARGE
1 N             7.729970   -0.729970         7.525682   -0.525682
2 S            15.797659    0.202341        15.783667    0.216333
3 C             6.443744   -0.443744         6.409473   -0.409473
4 H             0.719416    0.280584         0.813833    0.186167
5 H             0.719416    0.280584         0.813299    0.186701
6 H             0.859588    0.140412         0.887415    0.112585
7 H             0.859585    0.140415         0.884008    0.115992
8 H             0.870622    0.129378         0.882624    0.117376
```

ethyl methyl *S,C*-sulfonium ylide

```
MP2/6-31G(d,p)

C             6.0    .5036799809    .4573943550  -1.9429701273
S            16.0    .5022129804   1.0555822944   -.4045862199
C             6.0   1.7378387148    .0864726266    .4959918952
C             6.0   -.9547215547    .5842126437    .6770433265
H             1.0    .2038470845   1.1741661960  -2.6880792523
H             1.0    .3193099574   -.5937499025  -2.1102384509
H             1.0   2.7049280472    .3591263278    .0851700422
H             1.0   1.5669870137   -.9758526818    .3361257727
H             1.0   1.6963969441    .3182190415   1.5587400870
H             1.0   -.7047362147    .8421074112   1.7082366521
C             6.0  -1.3726492878   -.8644591326    .5207757058
H             1.0  -1.7465578903   1.2546126584    .3414322862
H             1.0   -.6496201422  -1.5478839241    .9634222485
H             1.0  -1.4714562070  -1.1062202908   -.5385546653
H             1.0  -2.3354592765  -1.0437275725    .9974908394

MP2/6-31G(d,p)Energy                -348538.2308 KCAL/MOL
ZPE Correction                      84.147679 KCAL/MOL
298.15K Temperature Correction      89.469 KCAL/MOL

MP2/6-311G(3df,2p)Energy            -348704.1732 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE          LOW.POP.     CHARGE
 1 C            6.562883    -.562883         6.689070    -.689070
```

```
  2 S          15.532709     .467291         15.364250      .635750
  3 C           6.470978    -.470978          6.424370     -.424370
  4 C           6.376976    -.376976          6.347111     -.347111
  5 H            .882927     .117073           .879104      .120896
  6 H            .903903     .096097           .902181      .097819
  7 H            .838356     .161644           .866980      .133020
  8 H            .850942     .149058           .881915      .118085
  9 H            .869217     .130783           .883964      .116036
 10 H            .876284     .123716           .892147      .107853
 11 C           6.341796    -.341796          6.311420     -.311420
 12 H            .861552     .138448           .883423      .116577
 13 H            .886963     .113037           .895536      .104464
 14 H            .871340     .128660           .890648      .109352
 15 H            .873176     .126824           .887881      .112119
```

ethyl methyl *S,C*-sulfonium ylide-transition state

```
MP2/6-31G(d,p)

C            6.0   -1.0972726197  -1.1897509143   1.0001113657
S           16.0   -1.0447834523  -0.3183510418  -0.5769030624
C            6.0   -1.3358313804   1.2791472248  -0.1470073361
C            6.0    1.2486546370  -0.2280327384  -0.5217003804
H            1.0   -2.1289232884  -1.3215754657   1.3145558621
H            1.0   -0.5501126855  -0.6176946187   1.7459795153
H            1.0   -0.6209666161  -2.1584900467   0.8713551845
C            6.0    1.4171318656   1.1629017420  -0.1797598176
H            1.0    1.4712870224  -0.5473796550  -1.5331034163
H            1.0    1.4729271259  -0.9803512774   0.2272774698
H            1.0    1.9036649335   1.7700871340  -0.9383351630
H            1.0    1.8426569433   1.3501396593   0.8026182688
H            1.0    0.2915067644   1.6226887868  -0.1212619732
H            1.0   -1.5631813278   1.4958620122   0.8865646700
H            1.0   -1.8370410918   1.8677989793  -0.9002318273

MP2/6-31G(d,p)Energy                 -348526.5387 KCAL/MOL
ZPE Correction                       84.490697 KCAL/MOL
298.15K Temperature Correction       89.206 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -348689.7268 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE          LOW.POP.      CHARGE
  1 C           6.473649    -0.473649         6.402744    -0.402744
  2 S          15.634334     0.365666        15.527901     0.472099
  3 C           6.512345    -0.512345         6.548115    -0.548115
  4 C           6.331430    -0.331430         6.336877    -0.336877
  5 H           0.846651     0.153349         0.877903     0.122097
  6 H           0.845806     0.154194         0.875044     0.124956
  7 H           0.849685     0.150315         0.873064     0.126936
  8 C           6.336009    -0.336009         6.336457    -0.336457
```

```
 9 H         0.886081    0.113919           0.897947    0.102053
10 H         0.898289    0.101711           0.901218    0.098782
11 H         0.882457    0.117543           0.888992    0.111008
12 H         0.890818    0.109182           0.896088    0.103912
13 H         0.887355    0.112645           0.882523    0.117477
14 H         0.866199    0.133801           0.883097    0.116903
15 H         0.858894    0.141106           0.872031    0.127969
```

dimethylsulfide

MP2/6-31G(d,p)

```
C            6.0   -.9356015305   -.6682076868   -.7394741407
S           16.0   -.8185911339    .8455464993    .2362777688
C            6.0    .9057452030    .6986579416    .7484506166
H            1.0   1.5732196651    .6864359744   -.1114430910
H            1.0   1.0663234024   -.1983516082   1.3438444577
H            1.0   1.1429734108   1.5668362514   1.3586847004
H            1.0   -.2350057657   -.6559080958  -1.5725990999
H            1.0  -1.9459031085   -.7260693222  -1.1373993668
H            1.0   -.7531606187  -1.5489396887   -.1263417921
```

```
MP2/6-31G(d,p)Energy                 -299428.3008 KCAL/MOL
ZPE Correction                       45.909448 KCAL/MOL
298.15K Temperature Correction       49.306 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -299531.9154 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE            LOW.POP.     CHARGE
1 C          6.464376   -0.464376           6.406122   -0.406122
2 S         15.896877    0.103123          15.878172    0.121828
3 C          6.464376   -0.464376           6.408067   -0.408067
4 H          0.866308    0.133692           0.889748    0.110252
5 H          0.866120    0.133880           0.890064    0.109936
6 H          0.854757    0.145243           0.873396    0.126604
7 H          0.866309    0.133691           0.889639    0.110361
8 H          0.854757    0.145243           0.875091    0.124909
9 H          0.866120    0.133880           0.889700    0.110300
```

ethyl methyl sulfide-NCOH

MP2/6-31G(d,p)

```
N            7.0   0.4261892774   1.7270001219  -1.2865494672
S           16.0   0.3982027816   1.2905754916   0.3012037856
C            6.0   1.6759201220   0.0418819032   0.5778996262
C            6.0  -1.1455698240   0.3697268699   0.7130695566
H            1.0  -1.4872596898   0.8389364660   1.6365138854
C            6.0  -1.0909517076  -1.1412863973   0.8561614477
H            1.0  -1.8252712330   0.6658430220  -0.0847479236
H            1.0   2.6139100554   0.5257572217   0.3185580862
```

```
H            1.0   1.5030737787  -0.8184035235  -0.0577688526
H            1.0   1.6820644575  -0.2257566689   1.6321567799
H            1.0  -0.4287062566  -1.4507446567   1.6625916759
H            1.0  -0.7771336386  -1.5999132920  -0.0749602845
H            1.0  -2.0928811541  -1.4912744136   1.1043118344
C            6.0   0.2366151396   0.6993432800  -2.1661982606
O            8.0   0.0179830631  -0.5015293765  -1.9322647281
H            1.0   0.2936682485   1.0698440422  -3.1999775012
```

```
MP2/6-31G(d,p)Energy                 -429549.2617 KCAL/MOL
ZPE Correction                       84.292651 KCAL/MOL
298.15K Temperature Correction       90.330 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -429805.032 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE            LOW.POP.     CHARGE
 1 N          7.617008   -0.617008           7.525790   -0.525790
 2 S         15.294548    0.705452          15.249164    0.750836
 3 C          6.522281   -0.522281           6.425380   -0.425380
 4 C          6.405238   -0.405238           6.308026   -0.308026
 5 H          0.849826    0.150174           0.878982    0.121018
 6 C          6.345982   -0.345982           6.307751   -0.307751
 7 H          0.817974    0.182026           0.859800    0.140200
 8 H          0.828194    0.171806           0.860451    0.139549
 9 H          0.797938    0.202062           0.855511    0.144489
10 H          0.852757    0.147243           0.873571    0.126429
11 H          0.889309    0.110691           0.896491    0.103509
12 H          0.819496    0.180504           0.867946    0.132054
13 H          0.870239    0.129761           0.883818    0.116182
14 C          5.690811    0.309189           5.946721    0.053279
15 O          8.490663   -0.490663           8.344289   -0.344289
16 H          0.907735    0.092265           0.916309    0.083691
```

ethyl methyl sulfide-NCOH transition state

MP2/6-31G(d,p)

```
C            6.0   -.9006233267  -1.2382628247   1.1240893912
S           16.0   -.9987317329   -.2999370590   -.4231634924
N            7.0   -.9612827759   1.2801491737    .0182393748
C            6.0   1.2615203460   -.1834186525   -.7111981566
H            1.0  -1.8470198971  -1.1497185811   1.6465339257
H            1.0   -.0983119785   -.8368996453   1.7393597495
H            1.0   -.6920271916  -2.2760385436    .8692291813
C            6.0   1.5875631749   1.0828370654   -.1717831358
H            1.0   1.2689046109   -.3201389453  -1.7854570574
H            1.0   1.4836310375  -1.0861314915   -.1538108512
```

```
H            1.0   1.9605710707   1.8251563155   -.8672863613
H            1.0   2.0741859944   1.0924697285    .7964573222
H            1.0    .3671810206   1.5276749453    .0507046821
C            6.0  -1.8195212589   1.7734841083    .9746283266
O            8.0  -2.7537136371   1.1899830451   1.5223855121
H            1.0  -1.5681647064   2.8205501816   1.2012308895

MP2/6-31G(d,p)Energy                 -429520.373 KCAL/MOL
ZPE Correction                       83.960316 KCAL/MOL
298.15K Temperature Correction       89.765 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -429775.4156 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C          6.507007   -.507007         6.422414   -.422414
 2 S         15.480317    .519683        15.450966    .549034
 3 N          7.645742   -.645742         7.458870   -.458870
 4 C          6.285589   -.285589         6.222348   -.222348
 5 H           .801355    .198645          .856432    .143568
 6 H           .848147    .151853          .875322    .124678
 7 H           .855316    .144684          .874709    .125291
 8 C          6.394877   -.394877         6.364375   -.364375
 9 H           .850760    .149240          .883232    .116768
10 H           .863521    .136479          .886157    .113843
11 H           .858421    .141579          .876134    .123866
12 H           .871970    .128030          .886473    .113527
13 H           .755979    .244021          .818874    .181126
14 C          5.630855    .369145         5.917337    .082663
15 O          8.443255   -.443255         8.289414   -.289414
16 H           .906889    .093111          .916943    .083057
```

CH_3SNHCOH

```
MP2/6-31G(d,p)

S           16.0   -.9667623632    .0473335018   -.9045101971
C            6.0   -.0567460261   1.5912843115   -.6838615591
H            1.0   1.0145478669   1.4126465744   -.6461271109
H            1.0   -.3806087400   2.1123113736    .2132674822
H            1.0   -.2821775176   2.2106912455  -1.5514320793
N            7.0   -.5249301083   -.7895863767    .5083579356
C            6.0    .4975940628  -1.7147808157    .5632298206
H            1.0  -1.1054366556   -.7175245825   1.3340870331
H            1.0   1.0439062582  -1.7775194962   -.3894506646
O            8.0    .7606122627  -2.3748555457   1.5564392397

MP2/6-31G(d,p)Energy                 -380406.7699 KCAL/MOL
ZPE Correction                       48.141755 KCAL/MOL
```

```
298.15K Temperature Correction     52.682 KCAL/MOL

MP2/6-311G(3df,2p)Energy           -380605.726 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE            LOW.POP.     CHARGE
 1 S         15.721677     .278323          15.722322     .277678
 2 C          6.472088    -.472088           6.416010    -.416010
 3 H           .850883     .149117            .883926     .116074
 4 H           .852635     .147365            .881509     .118491
 5 H           .854728     .145272            .871428     .128572
 6 N          7.639440    -.639440           7.361896    -.361896
 7 C          5.589868     .410132           5.895480     .104520
 8 H           .691118     .308882            .795022     .204978
 9 H           .900687     .099313            .912446     .087554
10 O          8.426876    -.426876           8.259961    -.259961
```

ethyl methyl sulfide-NCH_3

```
MP2/6-31G(d,p)

N            7.0   0.3168495989   1.5790736164  -1.2431435562
S           16.0   0.3372903063   1.3575134733   0.3204425336
C            6.0   1.6448071170   0.1882821153   0.8548088778
C            6.0  -1.0925672381   0.3805568881   0.9820090756
H            1.0  -1.1251806498   0.6135691673   2.0492979927
C            6.0  -1.1306938539  -1.1244177181   0.7563496453
H            1.0  -1.9510087128   0.8677979022   0.5169018081
H            1.0   2.5935537555   0.6725940139   0.6384262475
H            1.0   1.5944675499  -0.7624243189   0.3312416602
H            1.0   1.5504552226   0.0242890928   1.9275029117
H            1.0  -0.3356857407  -1.6358321874   1.2948140236
H            1.0  -1.0474818340  -1.3779876328  -0.2974133195
H            1.0  -2.0788404835  -1.5198070724   1.1213898165
C            6.0   0.2028466786   0.4114300532  -2.1148977212
H            1.0   0.8882124336  -0.4100495731  -1.8689565033
H            1.0   0.4439394348   0.7397580357  -3.1247764059
H            1.0  -0.8109632844  -0.0043457255  -2.1439971265

MP2/6-31G(d,p)Energy               -383184.3921 KCAL/MOL
ZPE Correction                     95.610258 KCAL/MOL
298.15K Temperature Correction     101.558 KCAL/MOL

MP2/6-311G(3df,2p)Energy           -383388.2588 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.     CHARGE            LOW.POP.     CHARGE
 1 N          7.611298   -0.611298           7.587961   -0.587961
 2 S         15.324063    0.675937          15.273404    0.726596
```

```
  3 C           6.528988   -0.528988          6.460390   -0.460390
  4 C           6.415314   -0.415314          6.345694   -0.345694
  5 H           0.861240    0.138760          0.884244    0.115756
  6 C           6.340429   -0.340429          6.309820   -0.309820
  7 H           0.845129    0.154871          0.874832    0.125168
  8 H           0.841874    0.158126          0.869745    0.130255
  9 H           0.851307    0.148693          0.881533    0.118467
 10 H           0.863313    0.136687          0.878486    0.121514
 11 H           0.880835    0.119165          0.892531    0.107469
 12 H           0.867745    0.132255          0.889053    0.110947
 13 H           0.870861    0.129139          0.885490    0.114510
 14 C           6.184407   -0.184407          6.231300   -0.231300
 15 H           0.926832    0.073168          0.923271    0.076729
 16 H           0.875846    0.124154          0.893167    0.106833
 17 H           0.910519    0.089481          0.919079    0.080921
```

ethyl methyl sulfide-NCH$_3$ transition state

MP2/6-31G(d,p)

```
C            6.0   -.6461686236  -1.5910057143   1.2746278312
S           16.0  -1.1619680161   -.3505512977    .0812273872
N            7.0  -1.0294918524    .9866237200   1.0130304010
C            6.0    .9700330419   -.0787799244   -.8106995024
H            1.0  -1.4523221773  -1.7836981036   1.9763746345
H            1.0    .2227209583  -1.2118574993   1.8069581320
H            1.0   -.3874704045  -2.5019274221    .7377776339
C            6.0   1.3352975306   1.0863366734   -.0810770201
H            1.0    .7027836105    .0038548553  -1.8570808893
H            1.0   1.3953449516  -1.0389271901   -.5399237950
H            1.0   1.4350416344   2.0010724050   -.6575047020
H            1.0   2.1199773150    .9679724680    .6590994753
H            1.0    .2972671826   1.2998801260    .6461602141
C            6.0  -1.8108377090   2.1198670153    .4819306689
H            1.0  -2.8781873228   1.9731807388    .6470131873
H            1.0  -1.4955501411   3.0016941919   1.0363178987
H            1.0  -1.6523095079   2.3180236974   -.5840721451
```

```
MP2/6-31G(d,p)Energy                -383168.1203 KCAL/MOL
ZPE Correction                      96.020060 KCAL/MOL
298.15K Temperature Correction      101.664 KCAL/MOL

MP2/6-311G(3df,2p)Energy            -383370.1587 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 C           6.469012    -.469012          6.410831    -.410831
  2 S          15.530598     .469402         15.490472     .509528
  3 N           7.611959    -.611959          7.495495    -.495495
```

```
  4 C          6.308799    -.308799          6.294079    -.294079
  5 H           .842773     .157227           .872258     .127742
  6 H           .836516     .163484           .869655     .130345
  7 H           .863459     .136541           .877651     .122349
  8 C          6.372694    -.372694          6.349985    -.349985
  9 H           .878899     .121101           .895464     .104536
 10 H           .886452     .113548           .897056     .102944
 11 H           .881613     .118387           .890294     .109706
 12 H           .879449     .120551           .888468     .111532
 13 H           .806900     .193100           .848182     .151818
 14 C          6.183410    -.183410          6.220011    -.220011
 15 H           .874168     .125832           .897318     .102682
 16 H           .871093     .128907           .888383     .111617
 17 H           .902205     .097795           .914397     .085603
```

CH_3SNHCH_3

```
MP2/6-31G(d,p)

S          16.0    -.6244445523   1.0621298049   -.3651646532
C           6.0    -.0295479323   1.5060912370   1.2759852460
H           1.0    1.0021444872   1.8443805615   1.2354980946
H           1.0    -.1141416629    .6644116775   1.9584517027
H           1.0    -.6592169439   2.3192274718   1.6358854812
N           7.0     .4786349314   -.2245855910   -.7027292722
H           1.0    1.0109180001    .0153746286  -1.5316240420
C           6.0    -.1539780833  -1.5349181698   -.8596276839
H           1.0     .6266286016  -2.2645390909  -1.0738310704
H           1.0    -.9062388968  -1.5820396313  -1.6524121222
H           1.0    -.6307578690  -1.8055329383    .0795683293

MP2/6-31G(d,p)Energy                 -334053.1869 KCAL/MOL
ZPE Correction                       60.368978 KCAL/MOL
298.15K Temperature Correction       64.712 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -334197.179 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.     CHARGE            LOW.POP.     CHARGE
  1 S         15.791482     .208518         15.782143     .217857
  2 C          6.443618    -.443618          6.410032    -.410032
  3 H           .858959     .141041           .886897     .113103
  4 H           .861403     .138597           .885833     .114167
  5 H           .870747     .129253           .879474     .120526
  6 N          7.639975    -.639975          7.423058    -.423058
  7 H           .720623     .279377           .817909     .182091
  8 C          6.164482    -.164482          6.219923    -.219923
  9 H           .883111     .116889           .894255     .105745
 10 H           .894655     .105345           .910501     .089499
```

```
11 H           .870945     .129055           .889975     .110025
```

ethyl methyl sulfide-CHCOH

```
MP2/6-31G(d,p)

C            6.0   0.2035436748   1.4525238920  -1.4186123756
S           16.0   0.3128037960   1.3487059644   0.2709712506
C            6.0   1.6872045394   0.2421754256   0.6691575199
C            6.0  -1.0931019603   0.4198885627   0.9816591465
H            1.0  -0.9756906060   0.5180819802   2.0639069799
C            6.0  -1.2612929848  -1.0295529739   0.5601329798
H            1.0  -1.9524449237   1.0216039470   0.6858743587
H            1.0   2.5970966416   0.8051599149   0.4826259736
H            1.0   1.6306070188  -0.6244032940   0.0179591180
H            1.0   1.6247469280  -0.0276618393   1.7212259579
H            1.0  -0.4235102812  -1.6417100753   0.8852025237
H            1.0  -1.3355542401  -1.1193633594  -0.5179341488
H            1.0  -2.1660348224  -1.4205486651   1.0262273107
C            6.0   0.3857115264   0.3400439776  -2.2666818615
O            8.0   0.5434470066  -0.8564106471  -1.9326194387
H            1.0   0.3925805636   0.6102708666  -3.3400205615
H            1.0   0.1297415932   2.4611963232  -1.7890749431

MP2/6-31G(d,p)Energy                -419484.5074 KCAL/MOL
ZPE Correction                      91.373848 KCAL/MOL
298.15K Temperature Correction      97.621 KCAL/MOL

MP2/6-311G(3df,2p)Energy            -419726.9823 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C           6.496505   -0.496505         6.533502   -0.533502
 2 S          15.480117    0.519883        15.327125    0.672875
 3 C           6.501836   -0.501836         6.415953   -0.415953
 4 C           6.371983   -0.371983         6.301349   -0.301349
 5 H           0.859139    0.140861         0.885389    0.114611
 6 C           6.334860   -0.334860         6.304464   -0.304464
 7 H           0.839059    0.160941         0.870648    0.129352
 8 H           0.837203    0.162797         0.864097    0.135903
 9 H           0.781806    0.218194         0.850457    0.149543
10 H           0.858635    0.141365         0.877200    0.122800
11 H           0.875277    0.124723         0.888267    0.111733
12 H           0.823999    0.176001         0.868472    0.131528
13 H           0.880946    0.119054         0.889481    0.110519
14 C           5.731206    0.268794         5.950302    0.049698
15 O           8.523857   -0.523857         8.366331   -0.366331
16 H           0.939563    0.060437         0.931683    0.068317
17 H           0.864008    0.135992         0.875280    0.124720
```

ethyl methyl sulfide-CHCOH transition state

```
MP2/6-31G(d,p)
```

```
C           6.0  -1.1106358477  -1.3091184875    .9461673801
S          16.0  -1.0023084489   -.3811534055   -.6040960370
C           6.0  -1.1752268809   1.2824201447   -.2185644336
C           6.0   1.4023336081   -.2085432525   -.5088346116
H           1.0  -2.1161974559  -1.2498217351   1.3490821059
H           1.0   -.4069105764   -.9351735363   1.6779885935
H           1.0   -.8816300089  -2.3380753432    .6758899093
C           6.0   1.5063563849   1.1647908234   -.1879758890
H           1.0   1.6057425601   -.5464670020  -1.5165935155
H           1.0   1.5318628812   -.9597523101    .2604119566
H           1.0   1.9509984197   1.8090919012   -.9395056659
H           1.0   1.8090966596   1.4076354016    .8256482174
H           1.0    .2822293478   1.5743950585   -.1933866960
C           6.0  -1.5102535536   1.7962519680   1.1040349305
O           8.0  -1.2922099287   1.2403689545   2.1825452383
H           1.0  -1.9376239596   2.8158654705   1.0781338842
H           1.0  -1.5914624210   1.8390441895  -1.0507860070

MP2/6-31G(d,p)Energy                  -419458.8476 KCAL/MOL
ZPE Correction                        91.61746 KCAL/MOL
298.15K Temperature Correction        97.529 KCAL/MOL

MP2/6-311G(3df,2p)Energy              -419699.7674 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 C          6.464913    -.464913         6.394238    -.394238
  2 S         15.691665     .308335        15.599635     .400365
  3 C          6.452969    -.452969         6.416098    -.416098
  4 C          6.278676    -.278676         6.269075    -.269075
  5 H           .834276     .165724          .870531     .129469
  6 H           .819332     .180668          .864668     .135332
  7 H           .858879     .141121          .877260     .122740
  8 C          6.327988    -.327988         6.321840    -.321840
  9 H           .872929     .127071          .890322     .109678
 10 H           .877781     .122219          .890487     .109513
 11 H           .869742     .130258          .882461     .117539
 12 H           .862604     .137396          .882604     .117396
 13 H           .882086     .117914          .859536     .140464
 14 C          5.714702     .285298         5.926200     .073800
 15 O          8.427773    -.427773         8.263944    -.263944
 16 H           .918114     .081886          .922764     .077236
 17 H           .845571     .154429          .868335     .131665
```

CH_3SCH_2COH

```
MP2/6-31G(d,p)

C           6.0  -0.7121225763  -0.6752475403  -0.7124666056
S          16.0  -0.6043454586  -0.7326687421   1.1016576033
C           6.0   0.0629090294   0.9232799231   1.3858925411
C           6.0   0.6900379352  -0.6570599626  -1.2534391070
H           1.0  -1.2556187753   0.2089439951  -1.0427545090
```

```
H            1.0  -1.2394431034  -1.5778997801  -1.0207678141
H            1.0   1.0070005888   1.0705677702   0.8672323678
H            1.0   0.2279710824   1.0163909245   2.4565910915
H            1.0  -0.6461896723   1.6854577108   1.0703457483
H            1.0   1.2176805597  -1.6262694648  -1.2250598537
O            8.0   1.2521203006   0.3645052363  -1.6272314024

MP2/6-31G(d,p)Energy                  -370349.4773 KCAL/MOL
ZPE Correction                        55.429229 KCAL/MOL
298.15K Temperature Correction        60.070 KCAL/MOL

MP2/6-311G(3df,2p)Energy              -370533.0865 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM            MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C            6.431298   -0.431298         6.328766   -0.328766
 2 S           15.873421    0.126579        15.847339    0.152661
 3 C            6.479976   -0.479976         6.404480   -0.404480
 4 C            5.719046    0.280954         5.909941    0.090059
 5 H            0.835063    0.164937         0.875792    0.124208
 6 H            0.840947    0.159053         0.868345    0.131655
 7 H            0.839456    0.160544         0.878517    0.121483
 8 H            0.850933    0.149067         0.874448    0.125552
 9 H            0.855584    0.144416         0.883166    0.116834
10 H            0.903576    0.096424         0.915998    0.084002
11 O            8.370699   -0.370699         8.213208   -0.213208
```

ethyl methyl sulfide-CHCH$_3$

MP2/6-31G(d,p)

```
C            6.0    .3663668416   1.4513220047  -1.3232564170
S           16.0    .3124265275   1.3768936458    .3242282071
C            6.0   1.6642508538    .2913093370    .8685444806
C            6.0  -1.0639901119    .3936950543   1.1457065938
H            1.0   -.8937936450    .4614894871   2.2236479344
C            6.0  -1.2240162925  -1.0468458170    .6897384885
H            1.0  -1.9547048278    .9775688682    .9108530031
H            1.0   2.5885200343    .8227704911    .6627336571
H            1.0   1.6574409277   -.6476075943    .3210249996
H            1.0   1.5692526017    .0956159149   1.9354050620
H            1.0   -.3564513950  -1.6536869778    .9441558346
H            1.0  -1.3709616897  -1.0973757804   -.3873196562
H            1.0  -2.0922457441  -1.5005344444   1.1684362559
C            6.0    .3066328008    .2759853876  -2.2564500802
H            1.0    .7943642108   -.6030799318  -1.8297226571
H            1.0    .8436657301    .5081341330  -3.1781013479
H            1.0   -.7044424237   -.0305579428  -2.5470039282
H            1.0    .0576858812   2.4249041948  -1.6726206001
```

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MP2/6-31G(d,p)Energy                 -373123.8267 KCAL/MOL
ZPE Correction                       102.534339 KCAL/MOL
298.15K Temperature Correction       108.798 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -373313.2663 KCAL/MOL
```

```
TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM          MULL.POP.    CHARGE          LOW.POP.     CHARGE
  1 C          6.408140    -.408140         6.540916    -.540916
  2 S         15.556569     .443431        15.381996     .618004
  3 C          6.477047    -.477047         6.432996    -.432996
  4 C          6.376730    -.376730         6.348331    -.348331
  5 H           .876947     .123053          .893759     .106241
  6 C          6.341098    -.341098         6.310100    -.310100
  7 H           .863252     .136748          .884567     .115433
  8 H           .842460     .157540          .868944     .131056
  9 H           .852346     .147654          .881825     .118175
 10 H           .868548     .131452          .883296     .116704
 11 H           .886793     .113207          .896083     .103917
 12 H           .865714     .134286          .887954     .112046
 13 H           .875477     .124523          .887792     .112208
 14 C          6.320886    -.320886         6.301372    -.301372
 15 H           .912387     .087613          .905888     .094112
 16 H           .887175     .112825          .894111     .105889
 17 H           .904568     .095432          .914526     .085474
 18 H           .883862     .116138          .885542     .114458
```

ethyl methyl sulfide-CHCH$_3$ transition state

MP2/6-31G(d,p)

```
C            6.0    -.6531911716  -1.6317012424   1.2004824607
S           16.0   -1.1320950590   -.3309032060    .0479698539
C            6.0   -1.1575511542   1.0422867672   1.0121094989
C            6.0    1.0687069724   -.1825072699   -.7493307499
H            1.0   -1.5009798984  -1.9100101124   1.8205699690
H            1.0     .1657253951  -1.2778084430   1.8224787899
H            1.0    -.3158890219  -2.4875548148    .6212255056
C            6.0    1.4395424902   1.0437670772   -.0715431821
H            1.0     .8805849676   -.1533765360  -1.8161430273
H            1.0    1.4983280650  -1.1178574044   -.4062492905
H            1.0    1.6642454123   1.8786446649   -.7318284836
H            1.0    2.2219013719    .9329159242    .6761031605
H            1.0     .4838269764   1.4067490501    .5375835002
C            6.0   -2.0304923687   2.1996317140    .6107655610
H            1.0   -3.0391189154   2.1364647090   1.0264832387
H            1.0   -1.5904786089   3.1392074814    .9455338920
H            1.0   -2.1248327657   2.2585252918   -.4738784082
H            1.0    -.9140723872    .9052852494   2.0578269415
```

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MP2/6-31G(d,p)Energy                 -373114.7288 KCAL/MOL
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ZPE Correction                       103.39994 KCAL/MOL
298.15K Temperature Correction       109.142 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -373301.897 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C          6.474597   -.474597          6.402614   -.402614
 2 S         15.643273    .356727         15.542694    .457306
 3 C          6.362540   -.362540          6.403262   -.403262
 4 C          6.329056   -.329056          6.348385   -.348385
 5 H           .848855    .151145           .877079    .122921
 6 H           .845627    .154373           .875420    .124580
 7 H           .849573    .150427           .871434    .128566
 8 C          6.328799   -.328799          6.328938   -.328938
 9 H           .893352    .106648           .902185    .097815
10 H           .905047    .094953           .904956    .095044
11 H           .884942    .115058           .891652    .108348
12 H           .891773    .108227           .895726    .104274
13 H           .908788    .091212           .893257    .106743
14 C          6.320272   -.320272          6.289713   -.289713
15 H           .883370    .116630           .899283    .100717
16 H           .879215    .120785           .890873    .109127
17 H           .882334    .117666           .892936    .107064
18 H           .868587    .131413           .889592    .110408
```

$CH_3SCH_2CH_3$

```
MP2/6-31G(d,p)

C            6.0   0.2553445467   0.0000001793  -0.5784163856
S           16.0  -0.9844731053   0.0000004573   0.7442076252
C            6.0   0.1314298092  -0.0000000640   2.1637070925
H            1.0   0.7602032532   0.8885304721   2.1723425478
H            1.0   0.7602029901  -0.8885307765   2.1723421999
H            1.0  -0.4801523081  -0.0000001396   3.0629477707
H            1.0   0.8889051296   0.8822290494  -0.4748611651
C            6.0  -0.4283661105  -0.0000000758  -1.9379758767
H            1.0   0.8889050763  -0.8822287049  -0.4748608737
H            1.0  -1.0544117383   0.8822579867  -2.0586336453
H            1.0  -1.0544115269  -0.8822583211  -2.0586334160
H            1.0   0.3168239241  -0.0000000628  -2.7321664039

MP2/6-31G(d,p)Energy                 -324016.4137 KCAL/MOL
ZPE Correction                       67.932258 KCAL/MOL
298.15K Temperature Correction       72.33 KCAL/MOL

MP2/6-311G(3df,2p)Energy             -324144.1753 KCAL/MOL

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM         MULL.POP.    CHARGE          LOW.POP.     CHARGE
 1 C          6.335277  -0.335277          6.286213  -0.286213
 2 S         15.894391   0.105609         15.885799   0.114201
 3 C          6.469802  -0.469802          6.407213  -0.407213
```

4	H	0.865812	0.134188	0.889752	0.110248
5	H	0.865812	0.134188	0.889752	0.110248
6	H	0.856415	0.143585	0.874755	0.125245
7	H	0.870652	0.129348	0.896306	0.103694
8	C	6.348508	-0.348508	6.306598	-0.306598
9	H	0.870652	0.129348	0.896306	0.103694
10	H	0.870817	0.129183	0.888522	0.111478
11	H	0.870817	0.129183	0.888522	0.111478
12	H	0.881047	0.118953	0.890263	0.109737

Calculated enthalpies of reaction, addition, and elimination at MP2/6-31G(d,p).

MP2/6-31G(d,p)	ΔH_{rxn}	$\Delta H^{\ddagger}_{elim}$	$\Delta H^{\ddagger}_{addn}$
1	10.38	24.86	14.48
2	-14.81	20.24	35.05
3	-45.16	11.77	56.93
4	-8.01	27.99	36.00
5	-17.58	16.79	34.36
6	-15.15	25.81	40.96
7	-40.34	10.31	50.65

Absolute energies, zero point energies, and 298.15K temperature corrections for all compounds in this study.

	MP2/6-31G(d)	ZPE	298.15K	MP2/-6311++G(3df,2p)
1	-371074.79	70.180782	75.033	-371274.5992
1TS	-371041.87	66.276653	70.875	-371238.3263
9	-321913.33	33.727833	37.098	-322053.3456
8	-49144.873	32.84584	35.343	-49194.95317
2	-358606.59	77.553755	82.609	-358788.1819
2TS	-358582.01	75.812644	80.007	-358761.1615
10	-309472.1	42.010693	45.533	-309592.4374
3	-348538.23	84.147679	89.469	-348704.1732
3TS	-348526.54	84.490697	89.206	-348689.7268
11	-299428.3	45.909448	49.306	-299531.9154
4	-429549.26	84.292651	90.330	-429805.0320
4TS	-429520.37	83.960316	89.765	-429775.4156
12	-380406.79	48.141755	52.682	-380605.7260

5	-383184.39	95.610258	101.558	-383388.2588
5TS	-383168.12	96.02006	101.664	-383370.1587
13	-334053.2	60.368978	64.712	-334197.1790
6	-419484.51	91.373848	97.621	-419726.9823
6TS	-419458.8476	91.61746	97.529	-419699.7674
14	-370349.4773	55.429229	60.07	-370533.0865
7	-373123.83	102.53434	108.798	-373313.2663
7TS	-373114.7288	103.39994	109.142	-373301.897
15	-324016.4137	67.932258	72.33	-324144.1753