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Photogenerated reactive intermediates from thiophene ylides: thiophenes, oxenes and carbenes, oh my

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**Photogenerated reactive intermediates from thiophene ylides: thiophenes,
oxenes and carbenes, oh my**

by

Melanie Jean Heying

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Organic Chemistry

Program of Study Committee:
William S. Jenks, Major Professor
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Yan Zhao

Iowa State University

Ames, Iowa

2008

My thanks go to those who were integral to my happiness throughout this journey. I'm pretty sure you know who you are, and I probably owe you a beer.

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Chapter 1: General Introduction

1.1 Dissertation Organization

This dissertation, containing five chapters, describes the investigation of the reactive intermediates gained upon photolysis of aromatic chalcogen ylides, namely those of sulfur and selenium. Chapter 1 is a general review of relevant reactive intermediates and sulfur and selenium ylide photochemistry. Chapter 2 is based on a paper published in 2008 in the *Journal of Physical Organic Chemistry*. This focuses on the photochemistry of small aromatic sulfoxides. The majority of the work was carried out by the author, but Mrinmoy Nag, a former group member, also contributed to the project and reported an early portion of the work for his dissertation. Chapter 3 is the extension of work done on sulfonium-S,C-ylides for a communication published in 2007 in JACS, on which the current author was named as the second author. The project was begun by Stacey Stoffregen, prior to her graduation, and was completed by the author. The work for chapter 4 consists of an exploration of perturbing the pattern of reactivity of photogenerated carbenes by means of heavy atom substitution and is an expansion of the ideas elaborated in Chapter 3. Chapter 5 contains the general conclusions of the previous chapters.

1.2 Nomenclature of reactive intermediates and sulfur and selenium ylides.

1.2.1 Reactive intermediates

The most common chemical bonding environment of a neutral oxygen is two lone pairs and two bonds. Likewise, as all beginning organic chemistry students are taught, neutral carbon most often has four bonds and no lone pairs. Both of these species have a full octet. If methane (CH_4) or water (H_2O) undergo heterolytic cleavage, and one bond is removed leaving behind the electron pair, the result is

anionic 8-electron versions of these molecules: methanide and hydroxide. If water is protonated, the result is one of the more common forms of cationic oxygen, hydronium, an oxonium ion. Due to the lack of unshared pairs on methane, CH_5^+ is not a true covalent structure, however, it does exist.

Two of the seven-electron derivatives of methane and water are their radical versions. If the molecules undergo homolytic cleavage, the methane becomes a methyl radical, while water becomes a hydroxyl radical; both are neutral radicals.

Water can lose a proton to generate a six-electron, cationic HO^+ , but this is not often observed, given the high electronegativity of oxygen. Methane, with the removal of a hydride yields the simplest common carbocation or carbenium ion: methylum. If two bonds undergo homolytic cleavage, the species left have two new unbonded electrons, but are neutral. These species are known as oxene and methylene. Methylene is the simplest carbene. Because of the presence of the two electrons, oxenes and carbenes can exist in either singlet (closed or open shell) or triplet (open shell) states. This will be explored further in the section regarding reactive intermediates.

Table 1. Common forms of methane and water

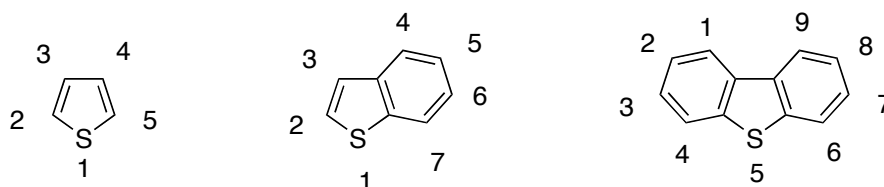
		8-electron		7-electron	6-electron	
		$-\text{H}^+$	$+\text{H}^+ \text{ } ^a$	$-\text{H}^\bullet$	$-\text{H}^-$	-2H^\bullet
methane						
water						

^a The structure of CH_5^+ is ambiguous, as it is not a true covalent compound.

1.2.2 Sulfur and selenium ylides

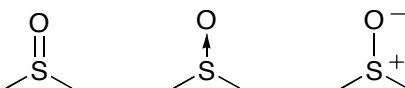
The average student who has taken organic chemistry has been exposed to a small fraction of the nomenclature associated with sulfur containing compounds. In

order to provide a certain level of comfort to the reader, a brief review of the most common structures, and those found within the text, is provided here. In many compounds, thia- or thio- is used to designate that the oxygen has been replaced by a sulfur, such as in thiol, as opposed to alcohol, or thiophenol, instead of phenol. In compounds where the thiol group is a substituent, the prefix mercapto- is also acceptable. Sulfur substituting for the oxygen of furan gives thiophene, and like furan, numbering begins on the heteroatom and continues around the ring. Likewise, the analogs of benzofuran and dibenzofuran are benzothiophene and dibenzothiophene (DBT). The numbering of DBT strays from the previous statement of numbering by following the pattern shown below, where substituents on the sulfur are numbered 5 instead of 1.

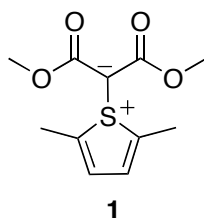


Besides its common divalent form, sulfur can exist in a number of other oxidation states. In general, the 2^+ oxidation state is designated by “o”, while the 1^+ is designated by “i” and the neutral form is represented by “e”. The simplest demonstration is alkyl sulfur containing acids: sulfonic acid (RSO_3H), sulfinic acid (RSO_2H), and sulfenic acid (RSOH).

When a thioether or sulfide is oxidized, the resulting structure is either a sulfoxide or a sulfone, depending on the number of oxygens bonded to the sulfur. The sulfoxide can be named as such, as seen in dimethylsulfoxide, or it can be named as an “S-oxide”, seen commonly with heterocycles, as in thiophene-S-oxide. The sulfone follows an analogous system, except that the heterocycle would be known as thiophene-S,S-dioxide. These oxides are represented in texts in various forms, either with a double bond, an arrow, or an ylide bond connecting the sulfur and oxygen. The most common notation in literature is the double bond, which is somewhat misleading, as there is no pi character to the functionality. All three representations are illustrated below. To maintain consistency throughout this dissertation, S-O bonds will be represented in their ylide form.



Sulfur is not limited to forming ylides with oxygen. In fact, the term ylide was previously reserved for negatively charged carbon atoms bound to positively charged heteroatoms, usually S, P or N. The form these usually take is $R_mX^+-C^-R_2$, and the naming can follow a number of strategies. The structure of **1** can be named first by the R_mX group's name, followed by the elements involved in the ylide bond, followed by the suffix ylide. This would give us the name 2,5-dimethylthiophene-S,C-ylide. However, this name does not identify the groups bonded to the anionic carbon. To ameliorate that, the name of the bonded group can be listed before the rest of the molecule, to give dimethylmalonate 2,5-dimethylthiophene-S,C-ylide. Some chemists prefer to indicate the positive charge on the sulfur atom by naming it a sulfonium ylide, however, this could lead to misidentification of the sulfur-containing group. To that end, the previous nomenclature will be used.



When considering the nomenclature of selenium containing compounds, one would notice the distinct similarity of sulfur and selenium naming. Most often, the prefix “thio” or “sulf” is substituted by “seleno” or “selen”, to indicate the presence of selenium. To this end, thiophene turns to selenophene, sulfonic acid turns to selenonic acid, and sulfoxide turns to selenoxide. The numbering of heterocyclic systems remains the same.

1.3 Preparation and properties of reactive intermediates

1.3.1 Oxenes

Atomic oxygen (oxene) was initially identified as a six electron species with similar reactivity as that seen for carbenes.¹ It can exist in either a singlet or triplet state, although the ground state is the triplet state, O(³P). In singlet states, the electrons have anti-parallel spins, and can be either paired or unpaired. The lowest energy state of the singlet oxene has unpaired electrons, and the atomic term symbol ¹D. Most work with oxenes has been done in the gas phase. Unlike their carbon-based cousins, atomic oxygen is, well, atomic, so the idea of stabilizing it through substitution is irrelevant. There is also the problem of detection in solution, as there is no way to view oxene through any conventional technique relying on absorbance, given the absence of a spectroscopic handle. However, some chemists and physicists have been able to detect it using mass spectroscopy.²

As stated above, the gas phase has provided a larger arena in which oxene could be studied. As early as the 1930s, chemists and other atmospheric scientists were investigating atomic oxygen, generated at high temperatures, to determine the oxidation potential of the species. In the 1960s, several researchers worked to determine the rates with which this reactive intermediate would combine with common components of air and other simple compounds. The oxenes were reacting with methane and ammonia at rates of $10^{12} - 10^{13} \text{ cm}^2\text{mol}^{-1}\text{s}^{-1}$.

Triplet oxene in the solution phase is much less well studied than in the gas phase. Many biological processes are attributed to its transfer, and elsewhere, it is involved in metal catalyzed reactions.³⁻⁵ However, as mentioned above, direct detection of this species has not yet been attained in solution, mainly because of its lack of chromophore. Instead, indirect evidence, such as the use of pyridinium oxide and chemical trapping, has been used to confirm its generation;⁶⁻⁸ generation of triplet oxene from aromatic sulfoxide precursors, and subsequent molecular fingerprinting will be discussed in detail below.

1.3.2 Carbenes

The carbene is the six electron carbon species parallel to the oxene. However, the carbene's chemistry was noted earlier and is better characterized than that of its oxygen cousin. From as far back as the 1800s, carbenes have intrigued chemists. By the early 1900s, it had been proven that certain carbenes were remarkably unselective when inserting into a carbon hydrogen bond. Concurrently in the literature, the tendency of carbenes to add across alkenes to yield cyclopropanes was discovered, as was the high probability of the carbene structure of $:CCl_2$ generated from chloroform. This led to a high level of interest in the community, which can be seen by the sudden explosion of work with this intermediate.⁹

Unlike the aforementioned oxenes, carbenes do have substituents, which generally can make their detection easier, while also adding in variables that can complicate the chemistry. The identity of the substituents and the ground spin state of the carbene are not independent of each other. The substituents can effect both the electronic and geometric parameters of the molecule.

If a simple MO diagram were drawn for triplet methylene, the two non-bonded electrons would be placed into 2p orbitals. If the theory held, the ideal geometry for a triplet carbene would then be close to linear, as each non-bonded electron would occupy a 2p orbital, leaving behind sp-hybridized orbitals for the substituents. However, experimental data indicated that the actual lowest conformation of methylene has an H-C-H angle of 137° . It could be argued that repulsion between the non-bonding and bonding electrons would cause the bond angle to collapse slightly. The approximate change in orbital energies caused by the structural change from linear to bent can be seen in Figure 1. A more accurate perspective from which to consider the bent conformation would be taking into account that Walsh rules indicate that non-bonded electrons preferentially occupy orbitals with s-character. The addition of substituents with electron withdrawing properties can lower the energy of the triplet state, with respect to the energy of the singlet state, as the removal of electron density from the non-bonding orbitals will increase the bond

angle between the substituents. The addition of substituents that are bulky will increase the bond angle, which also lowers the triplet with respect to the singlet.

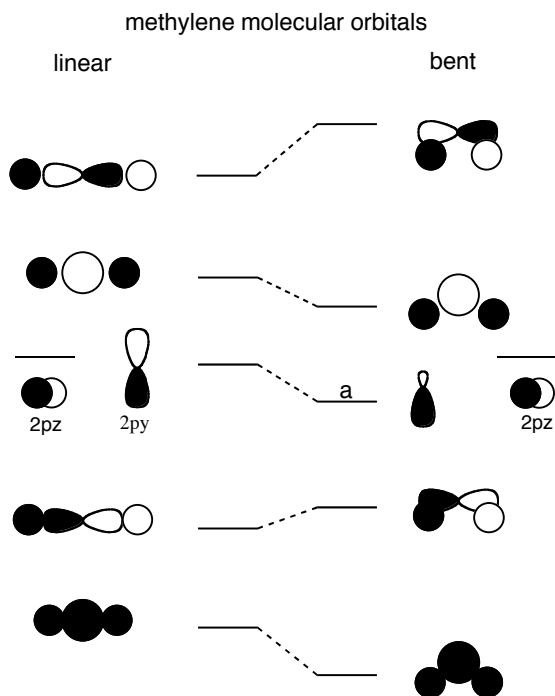


Figure 1. Molecular orbital diagrams of methylene

The singlet carbene can either exist in a closed or open-shell form. Once again, a simple MO diagram indicates the placement of the non-bonded electrons of a closed-shell singlet into a degenerate p orbital if a linear conformation is assumed, or a sp^2 -hybridized orbital if the molecule is bent. The experimentally determined geometry of singlet methylene is 102° , conforming to Walsh rules, placing the electron pair into an orbital with s character. Unlike in the case of the triplet carbene, the size of substituents does not overly influence the ground state of the carbene for the singlet case, as methylene itself has a triplet ground state. However, electronic effects are extremely important. Groups that push electron density towards the empty low-lying orbital either with the donation of nonbonding electrons or

hyperconjugative effects can lower the energy of the singlet. Often these are halogens or alkyl substituents.

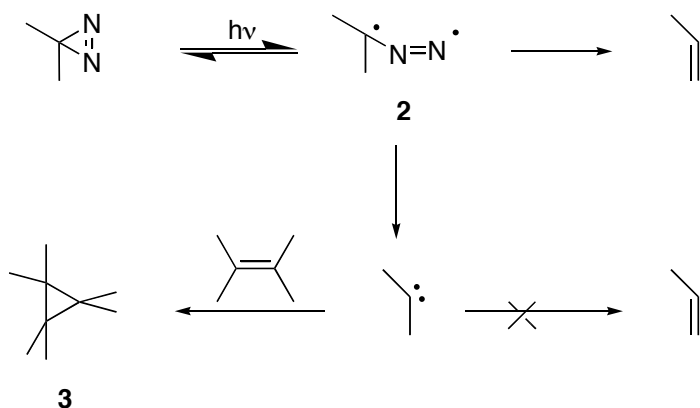
The Skell hypothesis states that the cycloaddition of carbenes to alkenes is stereospecific in the case of singlet carbenes, and non-stereospecific in the case of triplet carbenes. The addition of the singlet is a simultaneous transition of the electrons in the sp^2 HOMO of the carbene to the π^* LUMO of the alkene and the electrons in the π HOMO of the alkene to the vacant p LUMO of the carbene. Depending on the nature of the singlet carbene, the former or latter process could be dominant.

The diradical nature of the triplet carbene causes an asymmetric bridging, in which an open diradical structure is formed. The parallel spins prevent formation of the bond until one electron has changed spin, causing the closing to be slow, permitting rotation and loss of stereospecificity.

After the addition of carbenes to alkenes was demonstrated to give cyclopropanes with spin-determined results, Skell and Doering demonstrated that halocarbenes reacted preferentially with more highly substituted alkenes. This was a preference generally associated with electrophilicity, as the carbenes reacted with the nucleophilic alkenes. Hammett plots were made to measure the philicities of a variety of carbenes. Besides the traditional nucleophilic and electrophilic designations, the term ambiphilic can be applied here to some that show no strong preference to either mode of addition.

Carbenes can be formed from a number of precursors. The most common precursors for photochemical generation are diazo and diazereine compounds. Under thermal and photochemical conditions, both lose nitrogen gas to generate the carbene. However, in the 1990s, research suggested that many of the reactions thought to be executed by carbenes were actually a result of the excited state of the nitrogenous starting material. It was determined that dimethyldiazirine and dimethyldiazomethane were not efficient precursors for dimethylcarbene. In the case of dimethyldiazirine, the excitation of the diazirine would promote an electron into an $S_1 n\pi^*$ state, which is nearly energetically equivalent to S_2 , which would give

2, a biradical. From the biradical, more than one outcome is possible, although formation of propene via a “rearrangement in excited state” (RIES) was the major decay route. The formation of a cyclopropane ring (**3**) is from actual carbene reactivity. Although propene could be a product of the carbene, formation of the alkene from dimethylcarbene was ruled out by isotope effect studies on diazirene fluorescence and the yield of carbene. More recently, ultrafast techniques in IR and UV-vis have allowed direct observation of singlet and triplet carbenes, leading to a better understanding of carbene and carbene precursor behaviors.^{10,11}



Scheme 1. Example of a product from an excited diazirene

1.4 Photochemistry of sulfoxides and selenoxides

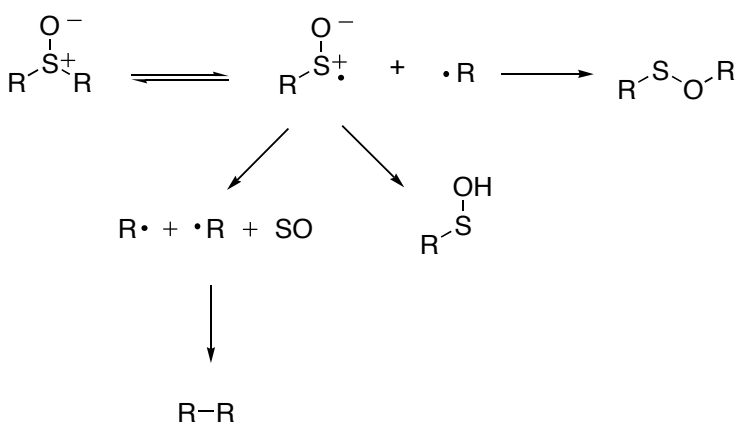
1.4.1 Sulfoxide photochemistry

As the sulfur-containing analog of a carbonyl, the expected photochemical behavior of a sulfoxide is that mimicking the behavior of the carbonyl. For some processes, this holds true, while for others, the path to the ground state is unique to the sulfoxide. Below are brief descriptions of the most common photochemical observations.

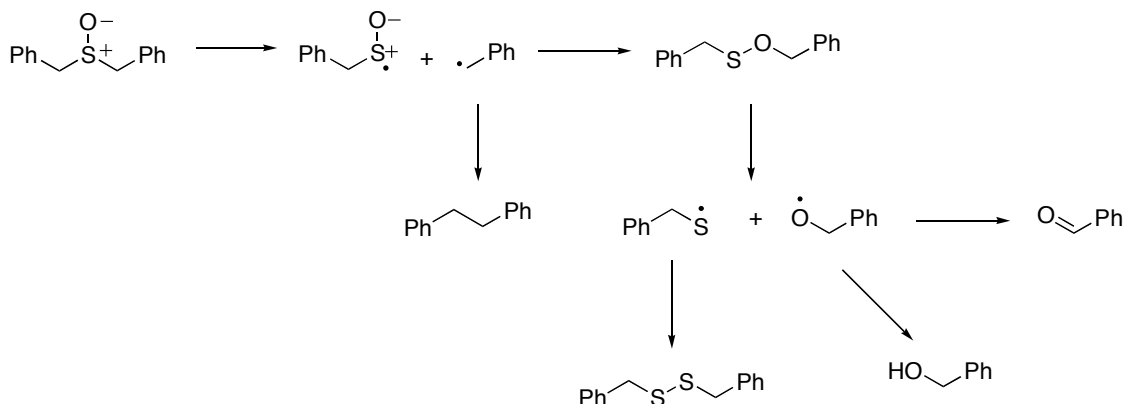
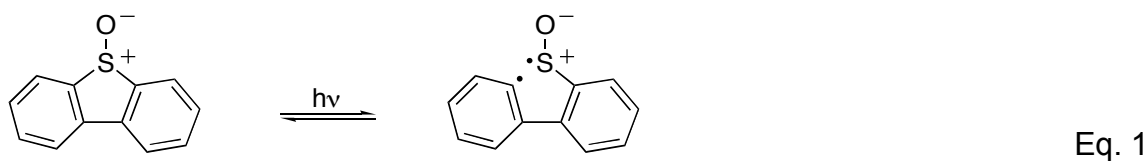
1.4.1.1 α -Cleavage

The similarity of the double bonded sulfoxide notation to the form of the ketone leads one to expect chemistry of a familiar nature to dominate: α -cleavage. A sulfoxide lacks a true π bond, but the carbon-sulfur bond is often lower in energy than that of the sulfur-oxygen bond. For example, in dimethyl sulfoxide, the energy difference between the two types of cleavage is 32.5 kcal/mol. This results in the appearance of α -cleavage as a major process.

Like ketones, this homolytic α -cleavage can take place from either the singlet or triplet state, and depending on the nature of the groups flanking the sulfoxide, the excitation will be either $n\pi^*$ or $\pi\pi^*$ in nature.^{12,13} Compared to ketones, sulfoxides seem to be more susceptible to this process, as seen in the example of benzophenone and its sulfoxide analog. In one photon conditions, benzophenone will not cleave, while diphenyl sulfoxide will undergo α -cleavage with a low quantum yield. Following the cleavage, the resulting sulfinyl radical has one of four options, as shown in Scheme 2. The first (Scheme 3) is to recombine to form the sulfoxide, as is proposed to be the case with dibenzothiophene-S-oxide (DBTO) (Equation 1).



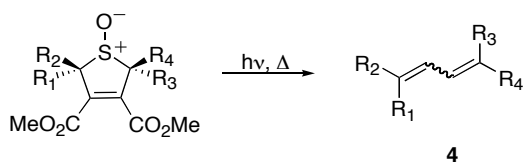
Scheme 2. Outcomes of α -cleavage



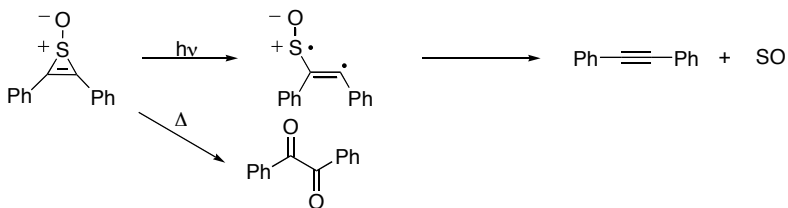
Scheme 3. Formation of sulfenic ester

The second possible pathway for the radical is to recombine as the sulfenic ester, which is also photoactive. The ubiquitous example for sulfenic ester formation following α -cleavage is dibenzyl sulfoxide (Scheme 3).¹⁴ The disulfide and benzaldehyde, both major products, arise from secondary photolysis of the sulfenic ester, while bibenzyl, which is only formed in very low yield, is unlikely to be formed by SO extrusion.

The extrusion of SO from a sulfinyl radical is an uncommon process. The reaction is endothermic by approximately 50 kcal/mol for a methylsulfinyl radical, so it is unlikely to be observed at room temperature in solution.¹⁵ That stated, there are exceptions when the product formed after the breaking of the second S-C bond will be more stable. The first extrusion of SO was reported by Kellogg and Prins, after they observed the production of diene **4** after both thermal and photolytic decompositions of 2,5-dihydrothiophene-S-oxide (Scheme 4).¹⁶ A later case involved the formation of diphenylacetylene. In this example, pyrolysis provided a different product (Scheme 5).¹⁷



Scheme 4. SO extrusion from dihydrothiophene



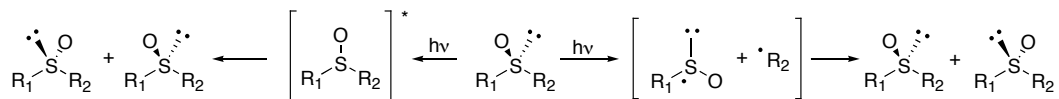
Scheme 5 Photochemical SO extrusion to yield acetylene

The last pathway for the radicals formed from α -cleavage is to undergo common radical reactions, such as hydrogen abstraction, disproportionation, and chain reactions. Hydrogen abstraction can account for trace amounts of benzyl alcohol in the previously mentioned photolysis of dibenzylsulfoxide,

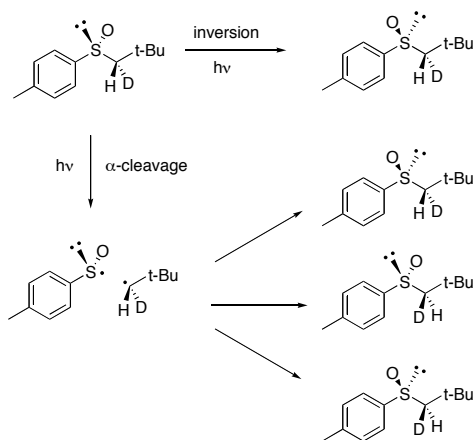
1.4.1.2 Inversion

The sulfur atom of a sulfoxide can be envisioned as having four entities around it: the two carbon substituents, the oxygen, and the lone pair. Because of this, the sulfur center adopts a tetrahedral geometry. When the two carbon groups are identical, there is little of note about this characteristic. However, when the two groups differ, the sulfoxide becomes chiral, making them synthetically useful. Racemization of these centers can be accomplished photochemically, although the pathway can differ for different sulfoxides. There have been two pathways suggested for this stereomutation: α -cleavage followed by recombination, and direct inversion (Scheme 6). The first mechanism would give a non-stereospecific recombination of the sulfoxide center, as was observed by Kropp in the photolysis of 2-phenyl norbornyl sulfoxide. However, the photolysis of (R_S, S_C)-1-deuterio-2,2-dimethylpropyl *p*-tolyl sulfoxide studied by Vos and Jenks (Scheme 7) gave a

majority of the S_S, S_C product, along with a small amount of a mixture of the other stereoisomers.¹⁸ This indicated the presence of both pathways, with direct inversion predominating.



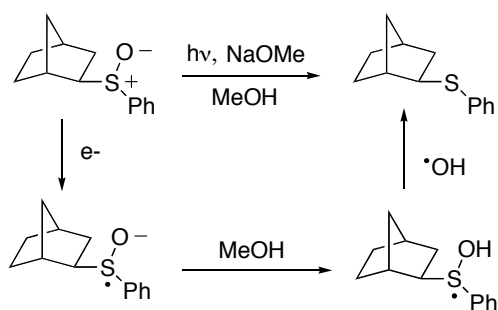
Scheme 6. Stereomutation pathways



Scheme 7. Competing stereomutation pathways and products

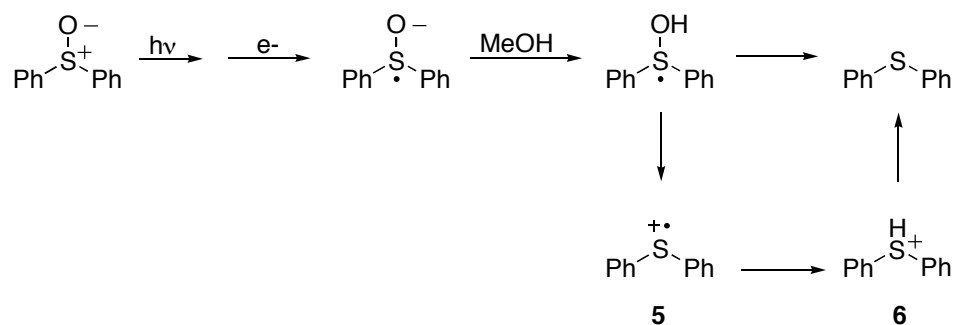
1.4.1.3 Deoxygenation

Photochemical deoxygenation can be accomplished one of two ways: bimolecularly in reducing conditions (Scheme 8), or unimolecularly, from the excited state of the sulfoxide.



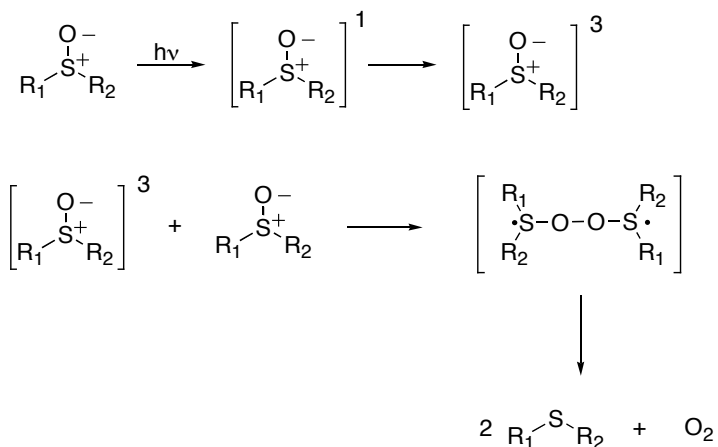
Scheme 8. Bimolecular deoxygenation of norbornyl phenyl sulfoxide

The photolysis of norbornyl phenyl sulfoxide in methanol yielded trace amounts of sulfide.¹⁹ Upon the addition of base, the yield of sulfide increased to 64%, which led Kropp to propose a bimolecular mechanism of deoxygenation (Scheme 8), which involves the formation of a hydroxysulfuranyl radical. The radical then yields a sulfide by losing a hydroxy radical by homolytic cleavage. In order to further elucidate the mechanism proposed by Kropp, Cabbage and Jenks studied the behavior of diphenylsulfoxide.²⁰ The excited sulfoxide would produce a radical anion after electron transfer from the methoxide anion, followed by proton transfer from the solvent to produce the aforementioned hydroxysulfuranyl radical. (Scheme 9) However, although Krupp predicted homolytic cleavage to give the sulfide, heterolytic cleavage to **5** could not be ruled out. Calculations predicted homolytic cleavage to be endothermic by 11 kcal/mol, while heterolytic cleavage (in aqueous solution) was predicted to be endothermic by 5 kcal/mol.²¹⁻²³ After heterolytic cleavage, hydrogen abstraction from methanol or another radical would give **6**, which then could easily transfer a proton to methoxide to form methanol and diphenyl sulfide. The strength of the S-H bond was calculated to be approximately 17 kcal/mol less than the O-H bond of methanol. Although heterolytic cleavage is preferential, the homolytic pathway could not be ruled out. Diphenyl sulfoxide was also photolyzed with sensitizers like carbazole, which are known to react by electron transfer, resulting in the production of the sulfide.



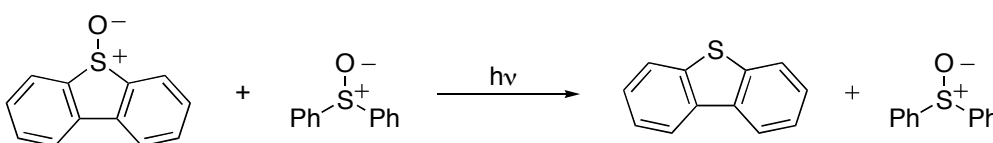
Scheme 9. Mechanism of bimolecular deoxygenation

Shelton and Davis published the first reports of sulfoxide deoxygenation in early 1973, followed by Posner in late 1973.^{24,25} Alkyl, alkyl aryl and aryl sulfoxides had deoxygenated upon both sensitized and direct photolysis. At the time of publication, the triplet sensitizers seemed to accelerate the reaction, leading to the proposition of the mechanism shown in Scheme 10, in which the excited sulfoxide dimerizes with a ground state sulfoxide, which then cleaves to give two molecules of sulfide and one molecule of oxygen. At the time these studies were conducted, the triplet energies of the molecules under consideration were unknown. In retrospect, the triplet energies of the sulfoxides are above those of the sensitizers used in the photolyses, negating the idea of triplet-triplet energy transfer to excite the sulfoxide.²⁶

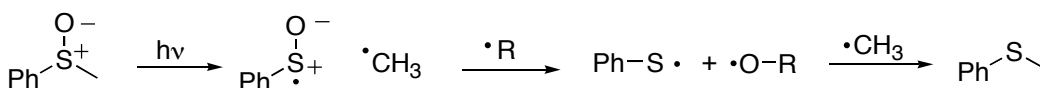


Scheme 10. Proposed dimer mechanism of deoxygenation

Experimental evidence against the “dimer mechanism” (whether sensitized or not) came from a study in which DBTO was excited in the presence of diphenylsulfoxide (scheme 11). During the photolysis, if the dimer mechanism were a possibility, the excited DBTO would react with ground state diphenyl sulfoxide to yield a mixture of DBT and diphenyl sulfide. The only sulfide produced was DBT; there was no consumption of the diphenyl sulfoxide.



Scheme 11. Photolysis of DBTO in the presence of another sulfoxide

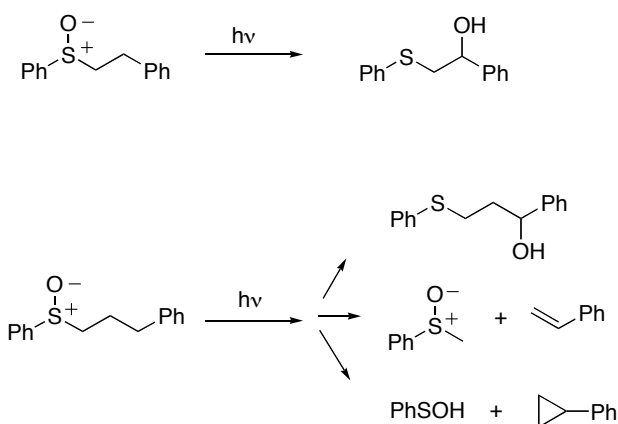


Scheme 12. Mechanism of sulfoxide deoxygenation based on CDNP results

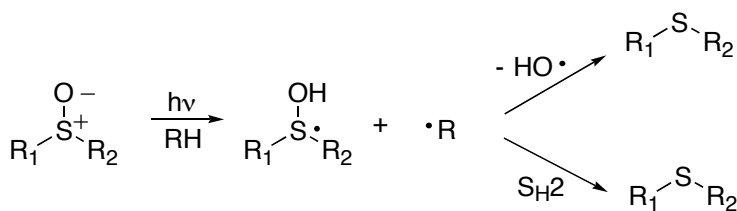
A second mechanism was proposed in 1981 using data obtained from a chemically induced dynamic nuclear polarization (CIDNP) experiment (Scheme 12).¹³ The first step, α -cleavage, was completely logical, however, the next step later proved to be problematic. In the case of thioanisole sulfoxide, the S-O bond strength is calculated to be 102 kcal/mol, which is 35 kcal/mol stronger than the S-phenyl bond. Besides the unlikely breaking of the S-O bond prior to the breaking of the S-phenyl bond, the overall energy for transferring the oxygen from the phenyl sulfinyl radical to an alkyl radical is endothermic by 12 kcal/mol, making this mechanism highly improbable.



Mechanisms involving disproportionation and hydrogen abstraction have also proven to be unfounded. Disproportionation should produce the sulfone, besides the sulfide (Eq. 2). The only experiment in which this has occurred has been the photolysis of DMSO. Numerous studies of aromatic sulfoxides have failed to produce any evidence of sulfone formation. Hydrogen abstraction is a major photochemical pathway for excited carbonyls, but there is little evidence that this process occurs with sulfoxides. Independent hydrogen abstraction mechanisms have been proposed, but have always been able to be explained by α -cleavage. Attempts to find conclusive evidence include the study of two alkyl aryl sulfoxides (Scheme 13), either of which provided easily accessible hydrogens. In both cases, neither provided any hard evidence of hydrogen abstraction, as every product could be explained by alternative, more substantiated mechanisms. Hydrogen abstraction by the oxygen, as seen in Scheme 14 can also be ruled out, as solvent choice would play a major role in governing the quantum yield of the reaction. Photolyses of DBTO carried out in the Jenks lab displayed no solvent dependence of quantum yields that correlated with hydrogen abstraction.^{27,28}

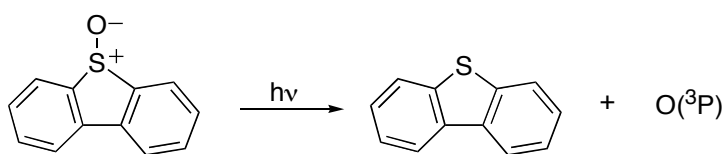


Scheme 13. Reactions expected from hydrogen abstraction



Scheme 14. Hydrogen abstraction assisted deoxygenation

Jenks proposed a unimolecular S-O bond cleavage mechanism for DBTO in 1997.²⁹ Other than the corresponding sulfide, the photolytic products include an electrophilic oxene species, likely $O(^3P)$. To rule out the dimer mechanism, a variety of controls were performed, including the one mentioned earlier. A second control was the photolysis of an extremely low concentration of DBTO in an organic glass matrix. Upon photolysis of this matrix, the DBTO deoxygenated to dibenzothiophene (DBT), despite its inability to react with another molecule of DBTO.



Eq. 3

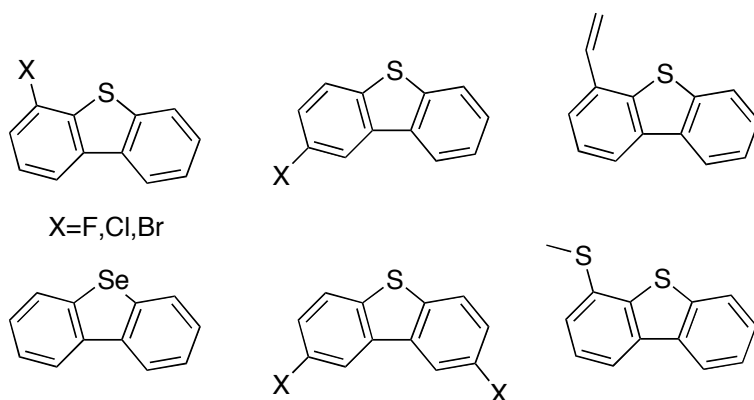
As of yet, there is no direct evidence of $O(^3P)$ in solution, but indirect evidence suggests its presence, and oxene has been detected in the gas phase, with a well defined oxidation pattern.^{7,30} Important indirect evidence has come from chemical trapping studies and the detection of triplet reactive intermediates photogenerated from parallel systems. Photolysis of DBTO in the presence of trapping agents gave oxidized products with relative rates of oxidation that when correlated to their ionization potential gave a slope similar to gas phase data. The oxidation of 2-methylbutane by photolysis of DBTO gave primarily oxidation at the tertiary position.⁸ If the oxidant produced were $O(^1D)$, an even distribution of

insertion into the primary, secondary, and tertiary positions would be expected. Besides the Jenks research group, Greer et al. has published aromatic sulfoxide deoxygenation data that support the existence of $O(^3P)$ in solution, based on chemical trapping of the oxidant.³¹

Although oxenes could not be observed directly, the nitrenes generated from the photolysis of analogous dibenzothiophene sulfilimine systems were detected through the use of TR-IR. The sulfilimines produced both singlet and triplet nitrenes, as the ground states of the nitrenes were influenced by the identity of the R group attached to the nitrogen atom.^{32,33}

The quantum yield of deoxygenation is extremely low, as it involves the spin forbidden process of cleaving the $O(^3P)$ from the excited singlet of DBTO. The energy of the S-O bond is estimated to be 78.3 kcal/mol, while the lowest triplet energy is 61 kcal/mol.³⁴ Therefore, scission of the S-O bond cannot take place from the lowest triplet state, making the triplet oxygen release from the excited singlet the likely possibility. Sensitized photolyses of DBTO in the presence of various photosensitizers by Rockafellow et al. demonstrated some deoxygenation when the energy should have been too low, but the mechanism is not the same observed in direct photolysis, based on chemical trapping results.³⁵ Also, calculations done by Stoffregen show the presence of a second triplet potential energy surface that correlates with $O(^3P)$ after an avoided crossing.

In order to enhance the ISC, Nag and McCulla used the heavy atom effect to increase the quantum yield of deoxygenation.^{36,37} Nag synthesized halogenated derivatives of DBTO, while McCulla substituted selenium for sulfur. The more notable effect was seen for dibenzoselenophene-Se-oxide (DBSeO), while the effect of the halogenation was more subtle. This could be a result of the proximity of the heavy atom, but it could also be related to the change in bond strength between Se-O and S-O. Oxene trapping groups, such as alkenes and sulfides, attached to DBTO also increased the yield, indicating that recombination is a competitive process.³⁸



1.4.2 Selenoxide photochemistry

In many ways, the photochemistry of selenoxides is nearly identical to that of sulfoxides. The photolysis of dibenzoselenophene-Se-oxide (DBSeO) yielded a significantly higher amount of $O(^3P)$ than DBTO.³⁷ This could be a result of the increased ISC, or the lower bond dissociation energy. The identity of the oxidizing species was confirmed through the pattern of substitution in toluene, which was the same as observed for DBTO, suggesting the $O(^3P)$ as a common intermediate. Besides the expected oxene and selenide (dibenzoselenide), a selenenic ester may be observed, as proposed from NMR data. This was proposed to occur after α -cleavage of the Se-C bond.³⁹ The photolytic behavior of diphenylselenoxide, although quantitatively different from that of diphenylsulfoxide, involves both deoxygenation and α -cleavage, as evidenced by the production of the selenide and phenyl radicals, the latter of which undergo a plethora of secondary reactions, as indicated by complex reaction mixtures.

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Chapter 2: Photochemistry of thiophene-S-oxide derivatives

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Adapted from:

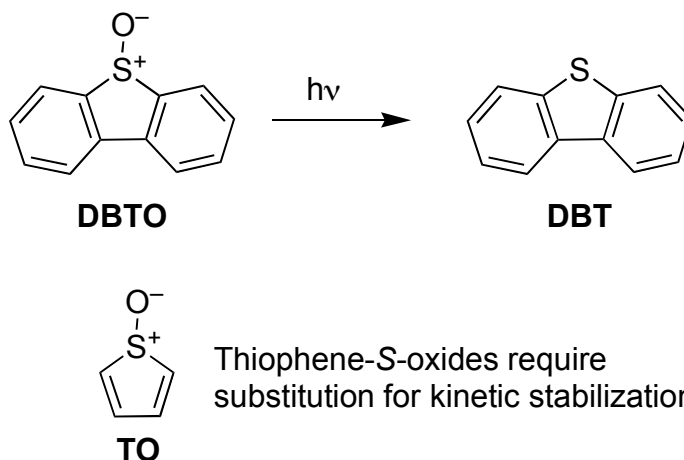
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Abstract: Photolysis of substituted thiophene-S-oxides in solution results in formation of either the corresponding thiophene or furan, in addition to uncharacterized materials. No good rationalization is available for the choice of which pathway may predominate, but it is demonstrated that the photolysis of 2,5-bistrimethylsilylthiophene-S-oxide produces O(³P) in the same manner as the well established photolysis dibenzothiophene-S-oxide.

2.1 Introduction

The photochemical deoxygenation of dibenzothiophene-S-oxides (DBTOs) to dibenzothiophenes (DBTs) and the corresponding reactions of thiophene-S-oxide (TO) derivatives has a history going back into the 1970s, when first reported by Gurria and Posner.^[1] Deoxygenation of other sulfoxides is known,^[2-4] but it appears that the cases with the greatest chemical yield are generally limited to those in which the sulfur atom resides within a formal thiophene ring.

In 1997, we reported a mechanistic study on DBTO photolysis, in which we suggested that the primary mechanism for photochemical deoxygenation of DBTO was direct dissociation of the molecule to dibenzothiophene and atomic oxygen, $O(^3P)$.^[5,6] This proposal was based mainly on experiments that were thought to exclude other mechanisms – including transient dimer formation and hydrogen



abstraction – and on the observation of oxidized solvent in a pattern that seemed appropriate for triplet atomic oxygen. For example, benzene is oxidized to phenol and alkanes are hydroxylated with some selectivity. Although the chemical yield of DBT is high, the photochemical efficiency is poor and subject to solvent and wavelength effects. More recent work on DBTO derivatives from our laboratories has shown that solvent effects in the quantum yield were due to solvent functionality, rather than polarity, viscosity, or other “physical” parameters.^[7] The solvents and substituents that led to higher quantum yields contained functionalities that shared in common a high reactivity with $O(^3P)$. Other workers showed that the reactivity of the oxidizing species followed an electrophilic trend in the oxidation of sulfides and alkenes that was consistent with known reactivity from gas phase chemistry.^[8,9]

We believed that DBTO or a related derivative would make an excellent source for flash photolysis experiments and/or other work in which photochemical release of $O(^3P)$ was desired, but this was hampered by the low quantum yield (generally < 0.01). Thus, we began to look for ways of increasing the quantum yield of

deoxygenation. One successful approach was to substitute Se for S, making the corresponding selenoxide.^[10] A much more modest degree of success was found with heavy atom substitution on the arene.^[11]

A much earlier hypothesis, though, was that derivatives of TO might be particularly good at deoxygenation because of their lower S-O bond dissociation enthalpies^[12,13] and higher excited state energies. (A potential flaw in this reasoning is the low triplet energy of cyclopentadiene, which might reasonably be used as a first estimate for the triplet energy of TO.) This made them an attractive target, even though the anticipated absorption spectrum took them out of the range that might be useful with a 355 nm laser line.^[14] An important issue, however, was that TO derivatives must be substituted with relatively bulky groups to kinetically stabilize them against dimerization. Furthermore, it was only in the mid 1990s that the synthesis of TO derivatives became practical.^[15,16]

Table 1. Relevant energies for thiophene sulfoxides.

	S-O Bond Dissociation Energy, kcal/mol	E_S	E_T
		kcal/mol	kcal/mol
DBTO	73 ^a	ca. 85 ^b	ca. 60 ^b
TO	61 ^a	78.6 ^c	ca. 59 ^d

^aRef [13]; ^bRef [96]; ^cApparent 0,0 band from absorption spectrum of **1c** (this work); ^dTriplet energy of cyclopentadiene.

In work unpublished from our laboratories, save for a Ph.D. dissertation,^[17] we made the observation that photolysis of 2,5-diphenylthiophene-S-oxide did yield the corresponding sulfide in low quantum yield, along with other products. Since we understood that the phenyl groups also would affect the chromophore and we were also interested in doing computational chemistry on the system, we did not pursue this TO derivative further. However, we also observed at this time that photolysis of 2,5-di-*t*-butylthiophene-S-oxide resulted in the surprising formation of the

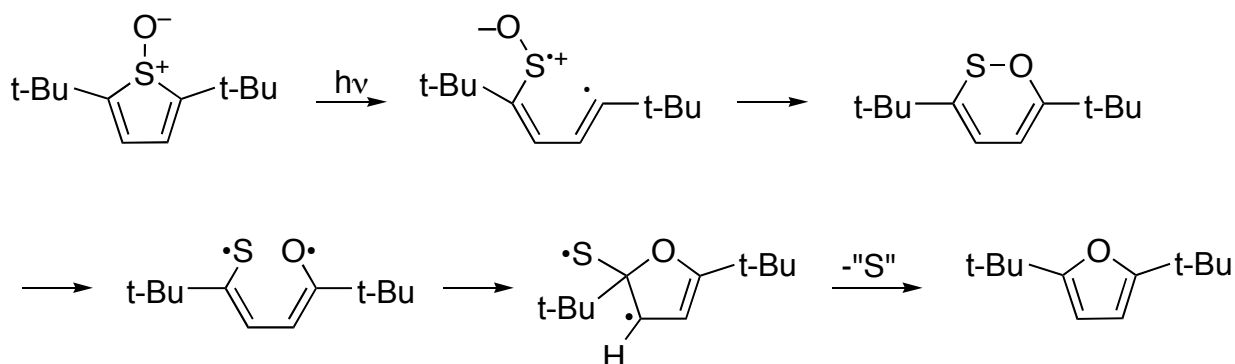
corresponding *furan*.^[17] We were thus relieved and pleased to see the work of Thiemann, et al., in which they more thoroughly documented this transformation.^[18,19] They have recently elaborated these studies with several more sulfoxides.

Thiemann has recently reviewed his group's work in this area,^[20] but a short synopsis is useful here.

2.1.2 Furan formation

Certain **TO** derivatives produce the corresponding furan on photolysis, in minor to major yield, depending on structure. There is not yet a good rationalization for the choice of *which* sulfoxides produce the furan. Among them are 2,4- or 2,5-di-*t*-butylthiophene-*S*-oxide and tetraphenylthiophene-*S*-oxide. No firm mechanism can yet be established. However, Thiemann has proposed a mechanism passing through the cyclic oxathiin isomer (Scheme 1, illustrated for 2,5-di-*t*-butylthiophene-*S*-oxide).^[20] The first step, α -cleavage, is a mechanism that is well established in sulfoxide photochemistry.^[3,4] There is ample precedent for analogous dithiins photochemically desulfurizing to produce thiophene.^[21-23] There is nothing published that distinguishes whether a second photon is required for desulfurization of TOs, but the general pathway of going through the oxathiin seems quite reasonable.

Scheme 1.



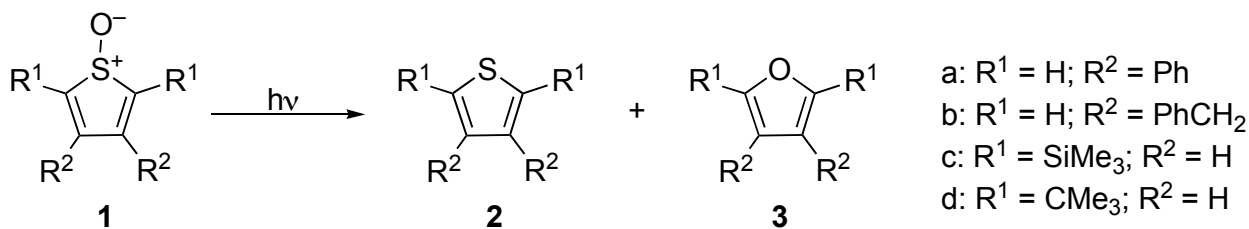
2.1.2. Deoxygenation

Nearly every sulfoxide examined by Thiemann, save 2,5-di-*t*-butylthiophene-*S*-oxide, undergoes deoxygenation to form the thiophene in some measurable yield.^[20] Those that produce other products (e.g., the furan) can be induced to yield mainly the thiophene by addition of several equivalents of an amine, triphenylphosphine, or an electron rich thiol. This may be mechanistically related to the observation of electron-transfer sensitized photoreductions of a number of sulfoxides.^[24,25]

2.1.3 “Benzyl” functionalization.

Thiemann examined a series of TO derivatives that contained methyl groups in the 2 and 5 positions. In the absence of hydroxylic solvent, the thienyl alcohol and/or thienyl ether is observed as part of the product mixture; ethanol was used to form the ethyl thienyl ether in at least one case.^[19,20,26] This reactivity was attributed to secondary reactions between water or an alcohol and the corresponding 2-methylene-3*H*-thiophene-*S*-oxides or 2-methylene-5*H*-thiophene-*S*-oxides, though neither of these intermediates has been observed directly.

In that the “benzyl” functionalization was avoidable by not using certain substituents, we undertook a study of some of these reactions that was meant to be more mechanistic in nature and that we report here. We now report the photochemistry of thiophene-*S*-oxides **1a-1c**, which show both deoxygenation and furan formation without the complication of benzyl functionalization. We also report a brief computational investigation on the mechanism of furan formation.



2.2 Results

We wished to study the photochemistry of a series of thiophene oxides that did not include the potentially complicating substituents of Br (photochemical cleavage) or 2,5-dimethyl (isomerization). Ideal substrates seemed to be 3,4-di-*t*-butylthiophene-*S*-oxide or 3,4-di-neopentylthiophene-*S*-oxide, which are prepared by oxidation of the appropriate thiophene. The former of these has been prepared (via a McMurry coupling for the key cyclization step)^[27-30] and its chemistry has been reported.^[31-33] We do not dispute these reports, but in our hands, the McMurry coupling was extremely problematic for this substrate and did not result in synthetically useful product mixtures.^[34] We had similar difficulties preparing the di-neopentylthiophene and were also unsuccessful in coupling neopentyl groups to dibromothiophene via the Kumada method. A second synthetic procedure toward di-*t*-butylthiophene, in which 2,5-dibromothiophene was subjected to Friedel-Crafts alkylation with *t*BuCl and AlCl₃, followed by debromination, resulted in the isolation of 2,5-di-*t*-butylthiophene.^[35] Ultimately, we prepared and studied the photochemistry of three sulfoxides 3,4-diphenylthiophene-*S*-oxide **1a**, 3,4-dibenzylthiophene-*S*-oxide, **1b**, and 2,5-bis(trimethylsilyl)thiophene-*S*-oxide, **1c**. These sulfoxides were prepared by oxidation of the corresponding thiophenes, whose individual preparations are described in the Experimental section, by oxidation by *m*CPBA in the presence of BF₃.^[15,29]

2.2.1 Direct photolysis

Table 2 summarizes the results obtained on photolysis of sulfoxides **1a**, **1b**, and **1c**. Photolyses were carried out in Ar-flushed solutions with initial concentrations of 1-5 mM. Modest yields of **2** or **3** were obtained. No other identifiable products were ever obtained, nor were any other soluble products ever formed as major products. The quantum yield for loss is defined as the observed quantum yield for all processes leading to loss of the respective starting material.

Table 2. Results of direct photolysis of thiophene sulfoxides.^a

Sulfoxide	Solvent	λ_{ex} , nm	Φ_{loss}	Yield 2 , %	Yield 3 , %
1a	CH ₃ CN	300	0.006	0	22
	CH ₃ OH	300	0.0072	0	23
1b	CH ₃ CN	325	0.064	0	17
	iPrOH	325	0.042	0	17
	CDCl ₃	325	0.021	0	12
1c	CH ₃ CN	260	0.080	26	0
	CH ₃ CN	325	0.11	12	0
	C ₆ H ₆	325	0.13	17	0

^a Quantum yield is for loss of starting sulfoxide by all processes. Yields are relative to consumed starting material.

Photolysis of 3,4-diphenylthiophene-S-oxide in either acetonitrile or methanol resulted in modest amounts of furan (**3a**) formation, near 22%. Yields were determined by ¹H NMR and GC. No thiophene was observed, regardless of the degree of conversion. Several minor, unidentifiable products were formed. At least some appeared to be isomeric with **3a**, in that they had aromatic protons in the NMR, differing chromatographic retention times and apparent masses identical to **3a**

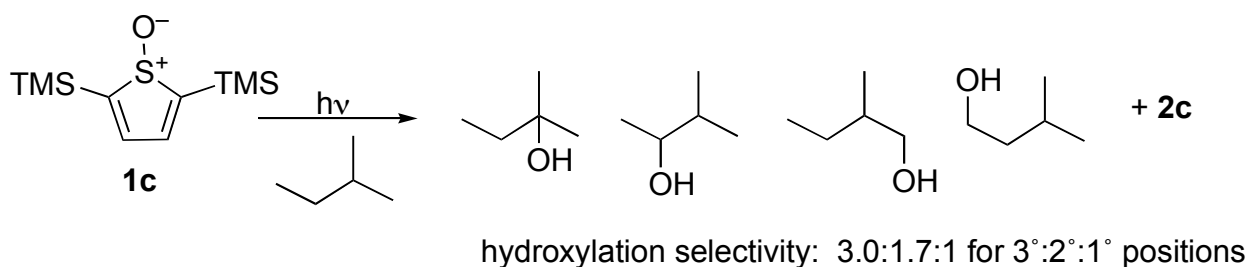
(GCMS). In methanol, an unidentified precipitate was formed if solutions of ca. 20 mM initial concentration were photolyzed.

Photolysis of dibenzyl derivative **1b** also led to furan (**3b**) in low yield without observation of the thiophene. A small quantity of bibenzyl was detected in all three solvents, but no other identifiable compounds were noted.

In contrast to **1a** and **1b**, photolysis of 2,5-bis(trimethylsilyl)thiophene-*S*-oxide (**1c**) led to deoxygenation (**2c**) to the exclusion of furan formation. Consistent with our observation on DBTO,^[5] excitation at a shorter wavelength increased the quantum yield of sulfide formation.^[36] No product corresponding to the mass or ¹H NMR of **3c**^[37] was obtained.

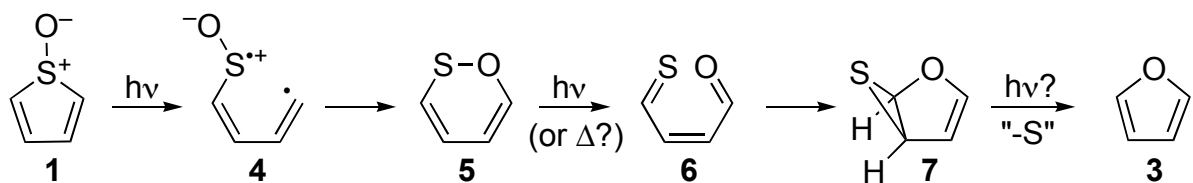
In order to probe for O(³P) formation, a suitable probe that did not absorb the incident light was sought; alkane hydroxylation seemed ideal. Photolyses of **1c** or DBTO in 2-methylbutane led to very similar quantities of alkane hydroxylation products. Adjusting for the number of hydrogens, a hydroxylation selectivity of 3.0:1.7:1 was observed for tertiary:secondary:primary positions (Scheme 2). This agrees well with our previously reported result for DBTO.^[6]

Scheme 2.



We wished to probe the mechanism for furan formation. As suggested by Thiemann, a mechanism for formation of the furan can be elaborated from the now well-documented mechanism for thiophene formation from dithiins.^[21-23] Substituting oxygen for sulfur results in the pathway illustrated in Scheme 3. Although this varies from the Thiemann pathway shown in Scheme 1, it shares in common the key oxathiin intermediate. Certainly troubling in both pathways is the unspecified mechanism for loss of sulfur in the final step, but this process is well documented for thiiranes.^[21-23] Our primary interest was thus in the initial photochemical step(s) postulated to provide the isomers of **5**.

Scheme 3. A potential pathway for furan formation from thiophene oxides.

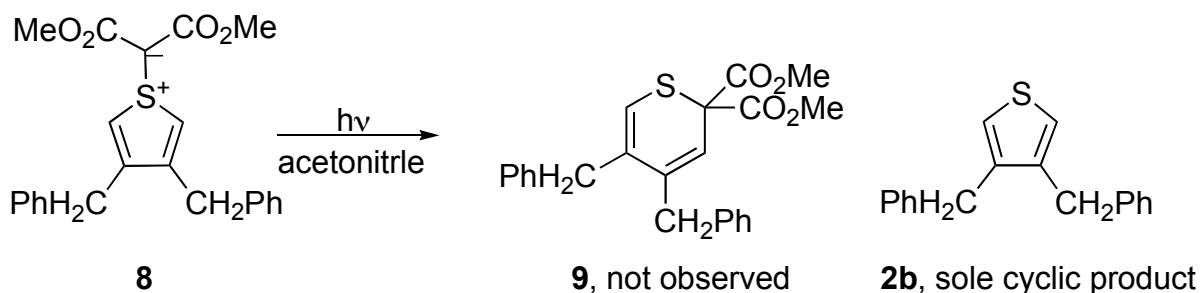


We sought direct evidence for the oxathiin intermediate. Photolyses of **1a** were carried out at $-20\text{ }^{\circ}\text{C}$ in CD_3CN to low and then higher conversion, with analysis by NMR at the same temperature, to try to observe any evidence for the oxathiin **5a**. The only identifiable protons, aside from starting material, were attributable to **3a**, the furan. No protons from any asymmetric compounds, which would display ^1H - ^1H coupling, were observed. The low-temperature reaction was repeated with O_2 saturation instead of Ar saturation in an unsuccessful attempt to trap intermediates in the formation of the furan by oxidation.^[10] (See below for a precedent for O_2 as a trap for an intermediate analogous to this with selenoxide photochemistry.) If the unstable oxathiin **5a** had been formed, there would have been potential to trap it as the more stable sultine. No difference was observed between this and the Ar-saturated case.

Photolysis of **1a** was carried out in a perdeuterated ethanol/methanol glass at 77 K in an NMR tube. The frozen glass was warmed to $-50\text{ }^{\circ}\text{C}$ in the NMR probe, and

analysis was carried out. Again, the only identifiable product was the furan **3a** at both ~5% conversion and complete conversion.

We have recently shown^[38] that malonate *S,C*-sulfonium ylides of thiophene generate carbenes, but we thought there might be a chance of observing an isomeric product analogous to the proposed oxathiin with the correct substitution pattern. We chose **8**, based on the sulfoxide results. However, irradiation of **8** in acetonitrile resulted only in thiophene **2b** and carbene-derived products.^[38] The thiophene was formed nearly quantitatively relative to consumption of **8**. NMR indicated the presence of carbene-solvent adduct; aside from protons attributable directly to **2b**, no alkenyl nor aromatic hydrogens were observed. By HPLC analysis, the only benzyl-containing product was **2b**.



2.2.2 Computations regarding furan formation

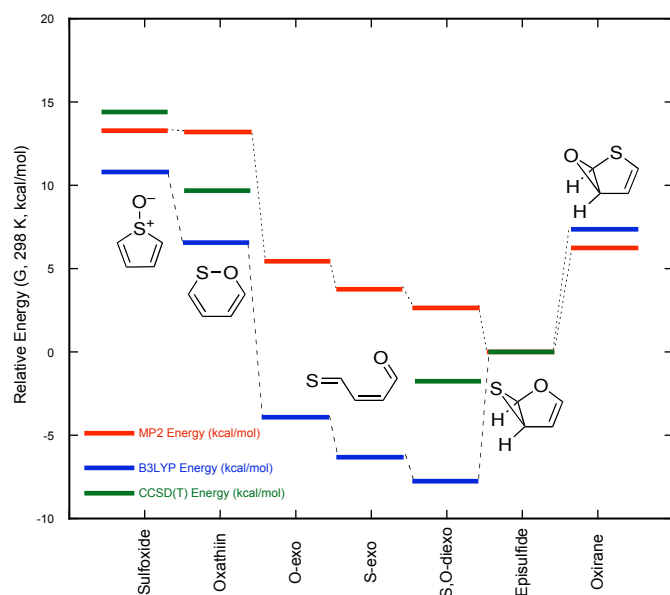
The inability to isolate intermediates as illustrated in Scheme 3 does not necessarily eliminate this general pathway for the formation of furan. In particular, if the intermediates are destroyed more rapidly than they are formed under the reaction conditions, they will never accumulate. We thus undertook a brief computational study to investigate the relative energies of the various isomers.

Computations were carried out at the B3LYP and MP2 levels of theory with the GAMESS^[39] suite of programs. Geometries were optimized with the 6-31G(d) basis set, and the respective vibrational matrices showed that each structure was a minimum. It is well known that fairly large basis sets that contain tight d polarization functions are required to get good relative energies for the oxides of sulfur^[13,40-52] We thus used the aug-cc-pV(T+d)Z basis set to obtain single point energies at the so-obtained geometries (i.e., MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d) or B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)). We did not attempt to find transition structures connecting the compounds.

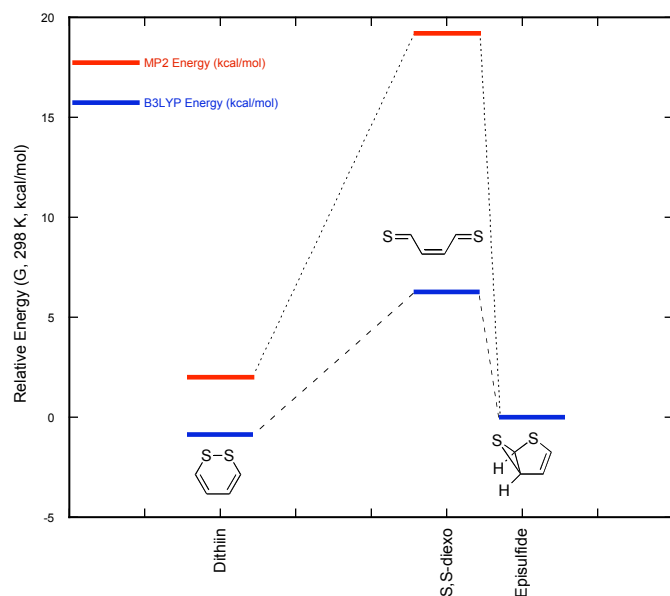
The free energies (G) in Figure 1 include zero point energies and a temperature correction to 298 K. The energy of the episulfide (**7**) is arbitrarily set to zero. In Figure 1a, the energies of the sulfoxide, oxathiin, and episulfide are all given. Additionally, the isomeric epoxide is shown.

Figure 1. Calculated Free Energies for Isomeric Structures

a.



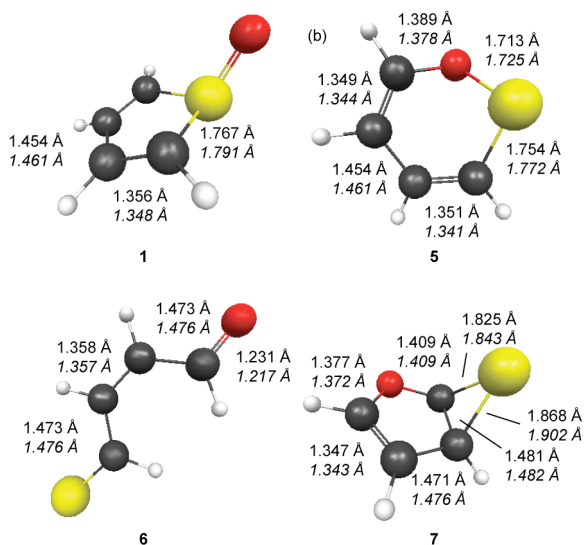
b.



Energies are MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d), CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d), or B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d) with ZPE and 298 K temperature corrections taken from MP2/6-31G(d) or B3LYP/6-31G(d) vibrational calculations, as appropriate.

Three conformations for compound **6** were obtained. The lowest energy conformation had both the C=S and C=O rotated away (“exo”) from the internal pi bond. The “O-exo” conformation has the sulfur atom canted out of plane by $\sim 15^\circ$ and the highest energy. The S-exo conformation was approximately planar, and the di-exo conformation was rigorously planar. For oxathiin, the O and S are displaced above and below the plane of the carbons, as expected. Figure 2 illustrates the CC, CS, CO and SO bond lengths calculated at the MP2/6-31G(d) and B3LYP/6-31G(d) levels. Bond lengths shown in normal text are from MP2/6-31G(d) and those in italics are from B3LYP/6-31G(d) calculations. CH bond lengths are not illustrated.

Figure 2. Optimized Geometries for C₄H₄OS Isomers



By way of comparison, three corresponding structures corresponding to the C₄H₄S₂ energy surface were optimized and their energies calculated in the same way. They are plotted on the same energy scale in Figure 1b. The thiosulfoxide is not a relevant structure. The larger C=S substituent in the acyclic isomer makes only the single diexo conformation a relevant minimum, and of course, there is not a second bicyclic analog, since both heteroatoms are sulfur.

As can be seen in Figure 1a, the relative energies of the C₄H₄OS species differ dramatically, depending on the computational method. As a check against great sensitivity to the geometries, additional single point energies were calculated at the B3LYP/aug-cc-pV(T+d)Z//MP2/6-31G(d) level. Only small differences between these energies and those obtained at B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d) were observed, so the qualitative picture in Figure 1 would not change. Similarly, the use of Jensen's a-PC2 basis set (i.e., B3LYP/a-PC2//B3LYP/6-31G(d)), specifically optimized for use in density functional applications,^[53] gave very similar results to the B3LYP results with the aug-cc-pV(T+d)Z calculations. Qualitatively, the HF//aug-cc-pV(T+d)Z//MP2/6-31G(d) energies, i.e., not including any correlation energy, followed the same pattern as the B3LYP calculations, rather

than the MP2 calculations. (All of the absolute and relative energies are given in the supporting information.)

This kind of huge discrepancy between B3LYP and MP2 calculations is not expected. Moreover, the kind of bonding involved in the various molecules in the series is so different that these isomerizations are far from isodesmic reactions. Any method-dependent errors that are sensitive to functional groups will be highlighted, rather than cancelled out. We thus face the reality that at least one of these two methods is highly flawed for this set of compounds. As a check for the MP2 data, we examined the natural orbital occupation numbers, and all were in the natural range of 0 to 2.

We are unaware of a similar straightforward diagnostic for troublesome B3LYP calculations. Furthermore, while many density functionals are available, there is no straightforward, rational sequence that one can follow to ensure an improvement of the quality of the calculations. However, it is now fairly well accepted that the sequence of HF \rightarrow MP2 \rightarrow CCSD(T) is a rigorously improving sequence of methodology for single-reference problems. While CCSD(T) computations are expensive, we felt the need to try to resolve the strong disagreement between the B3LYP and MP2 methodologies.

Thus CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d) calculations^[54] were run on the episulfide and diexo conformation of **6** as well as on **1** and **5**. The temperature correction obtained from the MP2 calculations was added to obtain the G(298 K) values. The CCSD(T) energy differences, which are clearly the most reliable of the three types obtained, remarkably reflect almost the average of the widely differing MP2 and B3LYP values. As can be seen in Figure 1 and Table 3, the relative energy of the diexo ring-opened compound is slightly below that of the episulfide. The relative energies of the conformers of **6** was not explored by the high level calculations, as the pattern was in agreement in both lower level methods.

Table 3. Relative energies of C₄H₄OS isomers at various computational levels.^a

Methods	1	5	6 O exo	6 S exo	6 di exo	7	Oxirane ^b
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	10.8	6.6	-3.9	-6.3	-7.7	0.0	7.4
MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	13.3	13.2	5.5	3.8	2.7	0.0	6.3
HF/aug-cc-pV(T+d)Z//MP2/6-31G(d)	16.4	7.8	-5.5	-8.1	-9.4	0.0	6.8
B3LYP/aug-cc-pV(T+d)Z//MP2/6-31G(d)	10.7	6.6	-3.7	-6.0	-7.5	0.0	5.9
CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d)		9.7			-1.7	0.0	

All energies in kcal/mol. Unscaled ZPE and temperature correction to 298 K, calculated at MP2/6-31G(d) [or B3LYP/6-31G(d) for the density functional calculations] are included. ^b Oxirane refers to the structure obtained by exchanging the O and S in structure 7.

2.1.3 Sensitized photolysis

Benzophenone-sensitized photolysis of **1a** or **1b** in acetonitrile resulted in a complex product mixture that contained neither the corresponding thiophenes nor furans. No isolable products were identified. Both low and high conversion experiments were run. The benzophenone concentration was approximately 30 mM, near the minimum required to ensure absorption of at least 99.9% of the light by benzophenone in the presence of 0.5 mM of the respective sulfoxide. Benzophenone-sensitized photolysis of **1c** was not practical because the absorption spectrum of **1c** extended too far to the red to exclusively irradiate benzophenone.

2.3 Discussion

2.3.1 Deoxygenation

Of the three sulfoxides examined, only **1c** showed significant yields of deoxygenation, i.e., the thiophene **2c**. The observed hydroxylation selectivity of 2-methylbutane is quite similar to that we reported previously for DBTO,^[6] and we thus tentatively conclude that the mechanism of deoxygenation is the same as that for DBTO, i.e., direct dissociation to form O(³P). Although the quantum yield is higher

than for DBTO, the chemical yield is poor enough that **1c** is probably not an especially useful compound for the intentional generation of oxygen atoms.

A full study on the sensitized deoxygenation of DBTO is being reported elsewhere,^[55] but it can briefly be stated that benzophenone-sensitization of DBTO does not produce $O(^3P)$, and the subsequent deoxygenation certainly does not go by the same mechanism as is observed for direct photolysis of DBTO. Thus, particularly considering the low triplet energy of thiophene-S-oxide we expect, it does not come as a surprise that no evidence of unimolecular deoxygenation was found on sensitization of either **1b** or **1c**. (We routinely examine sulfoxides for phosphorescence to determine the triplet energies, but it is only the exceptional case in which any is observed, e.g., DBTO itself or methanesulfinylpyrene.^[56,57])

Thiemann has reported^[20] that addition of easily oxidizable substrates (e.g., amines and sulfides) to solutions containing thiophene-S-oxides increases the yield of thiophene after photolysis. This effect occurs regardless of whether direct photolysis in neat solvent produces mainly furan, thiophene, or other products. The clear implication is that there is a second reduction mechanism in those instances. We believe that it is quite likely that this is related to the electron-transfer mediated sulfoxide reduction previously demonstrated by Kropp and ourselves.^[24,25] Thus, while of interest, we did not believe it was critical to our current investigation to reproduce such results for these particular substrates.

2.3.2 Furan formation.

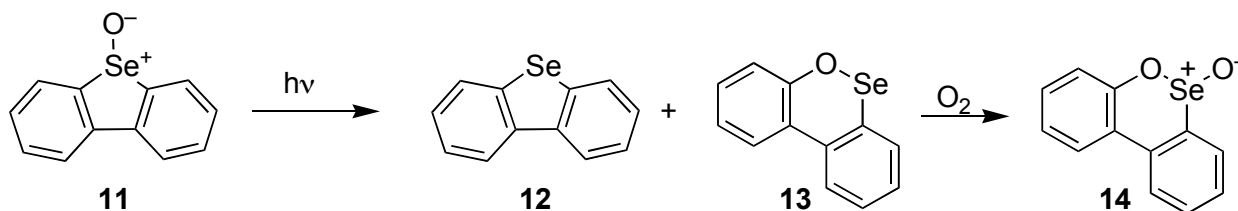
We have assumed from the beginning that photochemical furan formation from thiophene-based sulfoxides is “unimolecular”, in that it involves only a single thiophene-S-oxide molecule. That assumption is due to two lines of thought. First, although we do not report a systematic study here, we have never seen evidence for a concentration-dependence on a product distribution. We are confident that under

our conditions, deoxygenation is unimolecular (based on the analogous studies of DBTO). If furan formation involved two TO derivatives, then we would likely have seen more thiophene formation at low initial concentrations and more furan formation at higher concentrations, or perhaps a conversion-dependent product distribution. Nothing of the sort has been observed in the concentration range of ca. 10^{-4} to 10^{-2} M. The second line of reasoning is that the reaction would have to be rather complex. The initial step might be oxygen atom transfer, but this should lead to observation of a thiophene derivative in the mixture. The initial step might also be electron transfer (single-electron disproportionation), but again, the best analogous evidence is that this should ultimately lead to observation of thiophene derivative as part of the product mixture. This said, the large amount of uncharacterized product material implied by the low yields does leave the door at least a little open to such a possibility. Nonetheless, we will proceed further with the assumption that the initial steps of photochemical furan formation do not require a second TO nucleus.

Given a fundamentally unimolecular initial step, the formation of the furan due to irradiation of thiophene oxides seemingly “must” proceed through the oxathiin in the sense that it is hard to come up with a sensible alternative. The known chemistry of the dithiins^[21-23] that leads to thiophenes seems quite analogous. In the current sulfoxide-based case, the initial bond C-O bond formation by way of the oxathiin **5** seems inescapably logical and inescapably photochemical in origin, due to α -cleavage and isomerism.

However, direct evidence for **5** is lacking, to the best of our knowledge. The closest analog of which we are aware is our own assignment of the analogous structure during the photolysis of dibenzoselenophene-Se-oxide, **11**.^[10] In addition to deoxygenating (**12**) on direct irradiation, **11** yields an isomeric compound whose ^1H NMR is indicative of an asymmetric compound with two aromatic ABCD spin systems and whose mass is the same as **11**. We assigned the structure **13** to that compound, in part due to chemical deduction, but also in part because the presence

of O₂ in the sample converted that compound (assigned to **13**) to another compound. The new product also had with two aromatic ABCD ¹H spin systems, but had a mass 16 g/mol higher than that of **11** and **13** and was assigned to the sultine analog **14**.



Given the room-temperature existence of certain dithiins, we believed that observation of the oxathiin might be possible, though we failed in that attempt. However, it is possible that the strategy was doomed to fail to begin with because of greater absorption by **5** (which would prevent the accumulation of **5**, regardless of temperature). Dithiins are characterized by a low energy absorption in the visible, assigned to an n→σ* band.^[58,59] The lamp systems used by the Thiemann group and ourselves in the great majority of experiments provide relatively broad irradiation, which implies that a compound with an absorption to the red of the starting material is likely to absorb light efficiently under the experimental conditions. It is possible that narrow irradiation at a well-chosen wavelength (where absorption by the starting sulfoxide is much greater than that of **5**) could allow for accumulation of **5**, but unfortunately, we do not know the absorption spectrum of **5**, a requirement to design that experiment properly.

The carbon analog **8** would have yielded **9**, which should not have had extra low-energy bands of the dithiin sort. However, it simply does not undergo any process besides loss of the carbene to a substantial degree.

We thus sought further information on the relative stabilities of the structures in Scheme 3 by computational methods. In principle, the postulated ring opening of **5**

to **6** could be thermal, but it is photochemical in the dithiin cases.^[21-23] However, formation of **6** involves the formation of a C=O pi bond in lieu of a C=S pi bond for the dithiin analog. Given basic knowledge of the relative strengths of C=S vs C=O pi bonds and S-S vs. S-O sigma bonds,^[51] it seemed reasonable to expect that the conversion of **5** to **6** would be more exergonic than the corresponding opening of a dithiin to a dithial. This expectation is clearly borne out in the computational results, though the latter are hardly quantitatively definitive.

Although the conflict between the MP2 and B3LYP calculations cannot be explained fully at this time, there is still worthwhile information that can be extracted. The CCSD(T) calculations clearly show that the ring opening of the oxathiin to **6** is exothermic by about 10 kcal/mol. Assuming this general pathway is followed, we cannot at this time distinguish secondary photolysis of the oxathiin or a low-barrier thermal process. The relative stability of these isomers is apparently reversed in the case of the dithiin, and thus it is probably not surprising that a limited number of simple dithiins have been observed at room temperature, while no simple stable oxathiins are known.

The transformation of **6** to **7** is endergonic, according to the CCSD(T) calculations, by a couple of kcal/mol, starting from the lowest energy conformation of **6**. The process will be energy-neutral or slightly exergonic from the initial conformation of **6** formed from **5**. However, the final equilibrium favoring formation of thiophene is almost certainly driven by an unspecified, but exergonic desulfurization mechanism.

The lack of observation of any derivative of **6** or **7** at low temperature suggests (but does not prove) that the conversion of derivatives of **6** to furans is photochemical. The bulky substituents will surely change the relative energies of **6** and **7** a little bit,^[60] so it is hard to say which of these two will be lower energy. Regardless, it should also be noted that desulfurization must also take place at low temperature.^[61] (It should also be pointed out that the “-S” notation is commonly used in this

literature, but should not be taken to imply that atomic sulfur is necessarily produced.)

Clearly, a more extensive computational investigation is required to give convincing quantitative data on these reactions, and we did not pursue the transition state between **5** and **6** at this time. However, what can be concluded is that (1) the thermal barrier to ring opening will certainly be lower for the oxathiin than for the dithiin; and (2) if the product of photochemical ring opening of **5** is mainly determined by product stability, the quantum yield of oxathiin ring opening should also be higher than that of dithiin.

2.4 Conclusions

Although we have demonstrated a single thiophene-based sulfoxide (**1c**) that does undergo deoxygenation with a higher quantum yield than does DBTO, this compound would appear to have limited utility as an O(³P) precursor due to its low chemical yield and uncharacterizable byproducts.

More notable, though, in the sum of both this work and that of others in this field is the unpredictability of the major isolable product: the corresponding thiophene or the furan (except, perhaps, in the instances with a methyl group in the 2-position^[20] due to the intervention of a third major process). With the transformation of the sulfoxide to a *S,C*-sulfonium ylide, however, we have seen no process other than the analog of deoxygenation, i.e., carbene formation.^[38]

Thus, at this stage we are left to tentatively conclude that the competition between furan formation – which we presume to begin with the α -cleavage event – and deoxygenation compete with one another based on closely spaced energy surfaces in the relevant excited states. Until a more detailed understanding of the subtleties of the effect of molecular structure on those dynamics can be obtained, it is likely

that the finding of furan or thiophene formation from the photolysis of thiophene sulfoxides will remain empirical.

2.5 Experimental

2.5.1 Materials

Unless otherwise noted, all solvents for photochemical experiments were the highest purity commercially available, and all reagents were used as received.

2.5.2 Thiophenes.

3,4-Diphenylthiophene (**2a**),^[62] 3,4-Dibenzylthiophene (**2b**),^[63,64] and 2,5-bis(trimethylsilyl)thiophene (**2c**)^[65] were prepared as previously described

2.5.3 Thiophene S-oxides: General Procedure.^[15,29]

To a solution of substituted thiophene (1 eq.) in dry dichloromethane was added boron trifluoride-diethyl etherate (4 eq.). The solution was stirred at $-20\text{ }^{\circ}\text{C}$ for 10 minutes. Then *m*CPBA (1 eq.) in dry dichloromethane was added to the stirred solution drop-wise. The solution was stirred $-20\text{ }^{\circ}\text{C}$ under argon for another 2 hours. Saturated sodium bicarbonate solution was then added to the reaction mixture and stirred for half an hour at room temperature. The aqueous layer was extracted twice with methylene chloride and the organic layer was washed with water and brine. The solution was dried over magnesium sulfate and concentrated in vacuo. The sulfoxide was isolated by chromatography using 30% ethyl acetate in hexane. 3,4-Diphenylthiophene-S-oxide (**1a**): Typical yield 25%. ^1H NMR (CDCl_3 , 400 MHz): δ 7.39 (dt, 2H, $J = 7.6\text{ Hz}, 1.6\text{ Hz}$), 7.29 (t, 4H, $J = 7.6\text{ Hz}$), 7.06 (dd, 4H, $J = 7.2\text{ Hz}, 1.6\text{ Hz}$), 6.63 (d, 2H, $J = 0.8\text{ Hz}$). ^{13}C : δ 145.2, 131.4, 130.2, 128.7, 128.6, 127.6; MS (TOF, EI) m/z 236.07; 3,4-Dibenzylthiophene-S-oxide (**1b**):

Typical yield 18%. ^1H NMR (CDCl_3 , 300 MHz): δ 7.34 (m, 4H), 7.15 (m, 6H), 6.06 (s, 2H), 3.63 (s, 4H). ^{13}C : d 146.4, 135.4, 129.3, 129.1, 128.1, 127.8, 34.9; MS (TOF, EI) m/z 264.10.; 2,5-Bis(trimethylsilyl)thiophene-S-oxide^[15] (**1c**): Typical yield 45%. ^1H NMR (CDCl_3 , 300 MHz): δ 6.83 (s, 2H), 0.36 (s, 18H).

2.5.4 Furans.

3,4-Diphenylfuran (**3a**) was prepared as described by Fallis.^[66] 3,4-Dibenzylfuran (**3b**) was prepared from 3,4-bis(tributylstannyl)furan^[67] by the method of Yang.^[68]

2.5.5 Dibenzylthiophenium bismethoxycarbonylmethylide (**8**).

In a small vial, 3,4-dibenzylthiophene (204 mg, 0.77 mmol), dimethyldiazomalonate (132 mg, 0.77 mmol) and a rhodium catalyst $[\text{Rh}(\text{OAc})_2]_2$ (2 mg, 0.0045 mmol) were mixed together. The mixture was allowed to stir for 2 d in the dark, open to the air, after which the color had changed from an emerald green to a brownish-teal. IR indicated the diazo compound had been completely consumed. The mixture was washed with hexane to leave behind a dark green precipitate. Another washing with 75% ethyl acetate and 25% hexane removed the residual catalyst, leaving behind a white residue, which proved to be 3,4-dibenzylthiophenium bismethoxycarbonylmethylide (136 mg, 57.4% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.32 (t, $J = 7.2$ Hz, 4H), 7.26 (t, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 7.2$ Hz, 4H), 6.36 (s, 2H), 3.73 (s, 4H), 3.65 (s, 6H); ^{13}C NMR: δ 165.8, 149.6, 136.5, 129.1, 128.9, 127.4, 126.4, 51.3, 35.6; MS (EI) m/z 394.

2.5.6 Photolyses.

Photolyses were carried out using spectro grade solvents with initial concentration in the range of 1-5 mM and all solutions were purged with Ar to remove O_2 , unless otherwise noted. Dodecane was used as an internal standard for

GC and dioxane was used as an internal standard for reactions monitored by NMR. Valerophenone was used as the actinometer.^[69] The light source was a 75 W Xe lamp coupled to a monochromator with a cell-holder mounted at the exit. The slit widths allow a linear dispersion of ± 12 nm from the stated wavelength, which was adjusted for each compound to minimize absorption by the products. Samples, held either in 1 cm quartz cells or NMR tubes, depending on the method of analysis, were deoxygenated by flushing with Ar. Stirring was provided either by a small magnetic bar or by constant slow Ar bubbling. Analysis was conducted preliminarily by NMR, and further by HPLC, LCMS, and GC, including GCMS. GC work was limited by the fact that the sulfoxides did not survive the chromatography. Quantification was generally carried out using HPLC. Mass spectra were obtained to help confirm product identification, using LCMS. Analyses and quantifications of alcohols was carried out by GC. Control experiments showed that all compounds **2a-c** and **3a-c** were photostable under the conditions used.

Some preliminary and low-temperature experiments were carried out using the broad emission centered at 300 nm from low pressure fluorescent tubes in a Rayonet mini-reactor from Southern New England Ultraviolet company.

The photolysis at 77 K was carried out with an initial sulfoxide concentration of 10.1 mM in a 1:9 mixture of perdeuterated ethanol:methanol solvent mixture. The solution was flushed with Ar in an NMR tube and then plunged into liquid nitrogen in a transparent quartz dewar. The light source was the broadly emitting 300 nm tubes described previously. In separate experiments, after 2-3 minutes (6 bulbs) or 40 min (8 bulbs), the NMR tube was allowed to warm in the dark to -68 °C in an acetone/dry ice bath before being lowered into a pre-cooled NMR probe held at -50 °C. Spectra were obtained at -50 °C and periodically as the sample was allowed to warm slowly to room temperature. No significant change was observed in the spectrum over this period of time, save for a small change in the chemical shift of the thiophene protons

(< 0.1 ppm). The short photolysis resulted in an approximate 5% conversion of **1a**, while the longer photolysis converted all of the material. After withdrawal of the sample from the NMR instrument at room temperature, a small quantity of solid material was observed in the high conversion sample, as in the room temperature photolyses in methanol.

2.5.7 Computational Methods.

All computations were done using the GAMESS suite of programs^[70] and all structures and orbitals were visualized using the MacMolPlt^[71] application.

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Chapter 3: Investigation of the reactivity of photogenerated carbenes from thiophene platforms

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Abstract: Photolysis of various aromatic sulfur-S,C ylides leads to the clean production of dicarbomethoxycarbene. In the presence of cyclohexene, the carbene demonstrated both allylic insertion into a C-H bond, and addition across the pi bond. When produced in the presence of methanol, both the triplet product, hydrogen abstraction, and the singlet product, O-H insertion, were observed. In some specific cases with thiophenes, an additional product was formed, most likely from addition across the pi bond followed by rearrangement.

3.1 Introduction

Carbenes are interesting reactive intermediates that can have tremendous synthetic utility, if their reactivity can be predicted and controlled. The reactivity of a carbene depends on its philicity and spin multiplicity. Electron withdrawing substituents on a carbene usually adjust the orbitals such that the ground state is the triplet.¹ However, these carbenes still often react from the singlet state instead, as the singlet and triplet states are frequently close to each other, and singlet reactions are generally much faster. One of the more ubiquitous ways of creating carbenes is

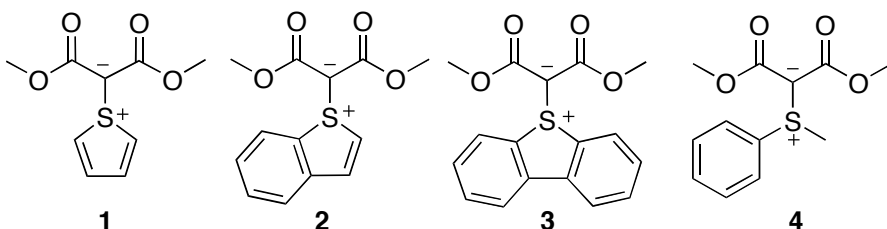
through the photolysis of diazo compounds or diazirines, but later research revealed that some of the observed chemistry could be attributed to an excited state of the precursors.^{2,3}

Our previous communication suggested that *S,C*-sulfonium ylides may be viable alternatives to nitrogenated carbene precursors.⁴ The idea was based on an analogy to studies demonstrating that the photochemistry of dibenzothiophene-*S*-oxide, dibenzoselenophene-*Se*-oxide, and select substituted thiophene-*S*-oxides resulted in deoxygenation to form the corresponding sulfide/selenide and an electrophilic oxene species.⁵⁻⁸ A number of these experiments provided indirect evidence for the formation of $O(^3P)$, as direct evidence is difficult to obtain in solution. In a separate set of studies, *N*-substituted dibenzothiophenesulfilimines have provided direct evidence for the formation of nitrenes and dibenzothiophene, by means of time-resolved IR spectroscopy.^{9,10} Chemical trapping studies supported this observation, showing reactivity typical of nitrenes, which included both singlet and triplet products. Based on these chemical observations for related systems, *S,C*-sulfonium ylides were expected to undergo unimolecular *S-C* bond cleavage upon photolysis to yield the corresponding carbene.

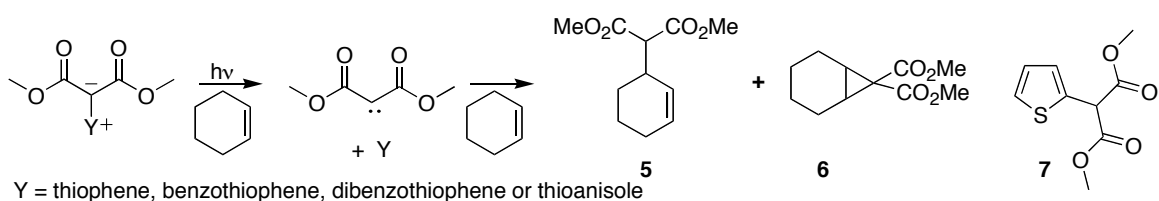
We report here the further exploration of the photochemistry of dimethyl malonate ylides of thiophene and its derivatives, and the reactivity of the photogenerated carbene. The main chromophore of these ylides can be photolyzed at long enough wavelengths to prevent undesirable side reactions and the post-cleavage thiophenes are generally resistant to secondary photolyses. Furthermore, given the stability imparted to the ylide bond by stabilization of the negative charge by the electron-withdrawing carbonyls and their resistance to thermal reactions at room temperature, these compounds were ideal for study.

3.2 Results

3.2.1 Direct Photolyses



The photolyses of dimethylmalonate thiophene-S,C-ylide (**1**), dimethylmalonate benzothiophene-S,C-ylide (**2**), and dimethylmalonate-dibenzothiophene-S,C-ylide (**3**) in acetonitrile with 10% cyclohexene as a carbene trap led to the expected chemistry shown in Scheme 1. The product mixture for **1** was slightly different than for **2** or **3**, as it included **7**, an apparent C-H insertion product (table 1). Photolysis of dimethylmalonate thioanisole-S,C-ylide (**4**) led to a more complex mixture, which contained products **5** and **6**, other unidentified products and only 11% of the predicted thioanisole. A photolysis of **1** in neat acetonitrile gave a portion of **7**, but also appeared to form adducts with the solvent.

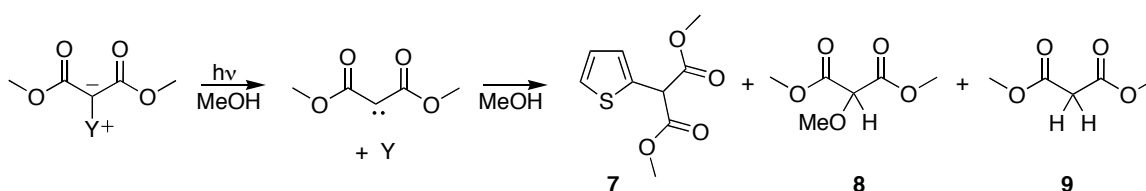


Scheme 1. Cyclohexene trapping of a carbene.

Table 1. Photolysis of 1-3 in acetonitrile with cyclohexene

Ylide	$\Phi_{\text{ylide decay}}$	$\Phi_{\text{sulfide growth}}$	Yields (%) ^a			
			5	6	7	5/6
1	0.25 ± 0.02	0.25 ± 0.01	18.4	3.5	15	5.0 ± 0.8
2	0.20 ± 0.01	0.20 ± 0.02	40.6	8.0	-	5.2 ± 0.8
3	0.18 ± 0.01	0.17 ± 0.01	44.1	9.2	-	4.8 ± 0.1

^a Relative to sulfide formation, or sulfide + **10** for **2** as precursor



Y = thiophene, benzothiophene, dibenzothiophene or thioanisole

Scheme 2. Methanol trapping of a carbene.

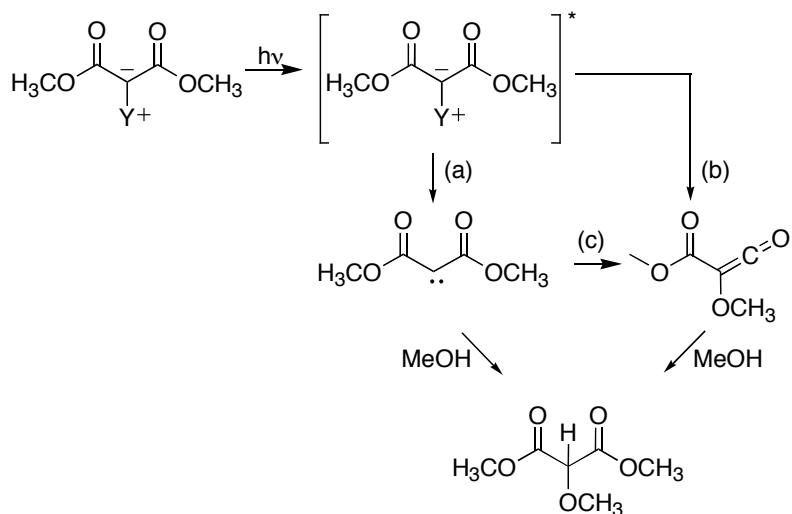
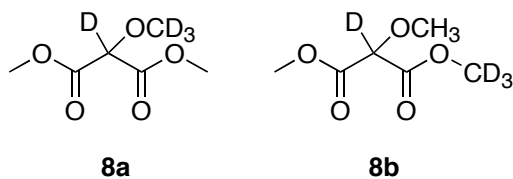
Photolyses of **1-3** in methanol (CH₃OH) resulted in the production of 2-methoxydimethylmalonate (**8**), dimethylmalonate (**9**) and the appropriate thiophene precursors (Scheme 2, Table 2). The triplet carbene is responsible for dimethylmalonate (**9**), as a hydrogen abstraction product,¹¹⁻¹⁴ while the singlet carbene is associated with the 2-methoxydimethylmalonate (**8**), as an O-H insertion product.¹⁵⁻¹⁸ As seen in Table 2, the relative amount of hydrogen abstraction product **7** is negligible for precursors **1** and **2**, while for **3** there is a significant increase. Once again, in the photolysis of **1**, **7** accounts for a significant portion of the products.

In order to rule out the possibility of **8** coming from a Wolff-type rearrangement (Scheme 3), the photolyses in CH₃OH were repeated in deuterated methanol (CD₃OD), such that there would be a distinguishable difference between **8a** and **8b**. The results of the photolyses in CD₃OD gave **8a** as the sole OH insertion product, for all precursors, indicating that the Wolff-type rearrangement is not obviously involved in the reaction mechanism.

Table 2. Photolysis of 1-3 in methanol

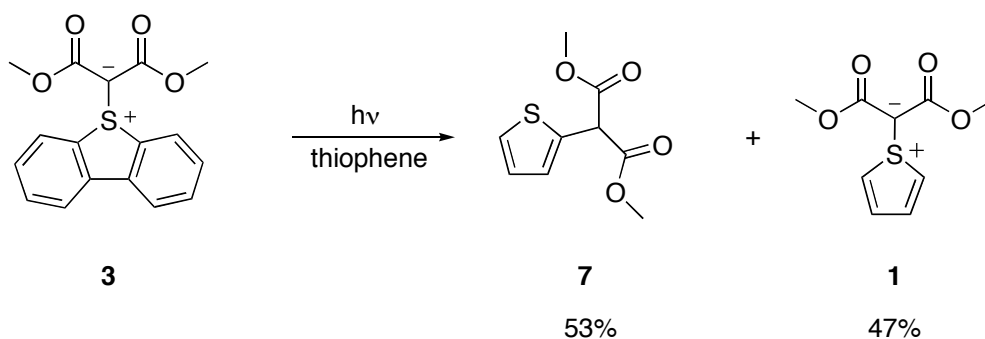
Ylide	$\Phi_{\text{-ylide}}$	$\Phi_{\text{+sulfide}}$	Product Yields (%) ^a		
			8	9	7
1	0.21 ± 0.03	0.20 ± 0.03	52	5	22
2	0.12 ± 0.01	0.12 ± 0.01	70	5	
3	0.17 ± 0.01	0.16 ± 0.02	54	39	

^aRelative to sulfide formation or sulfide + **7**. $\Phi_{\text{-ylide}}$ also includes **7** for **1** precursor.
^bOverlapping absorption spectra made experiment impractical.

**Scheme 3. Potential pathways to 8**

A photolysis of **3** centered at 350nm in neat thiophene was conducted in order to determine whether product **7** was a direct rearrangement of **1**, or whether it involved the actual carbene postulated in the formation of products **4-6**. Initial results with a broad spectrum light source showed the only product to be **7**, but there

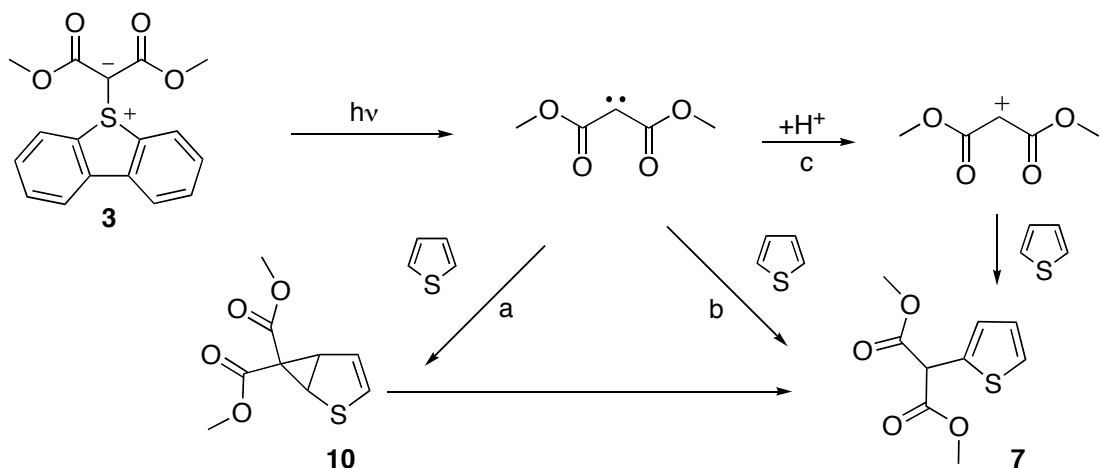
still was the possibility that the carbene formed from the photolysis of **3** was reacting with thiophene to produce the ylide **1** which was then undergoing a secondary photolysis to produce **7**. A second photolysis in a lamp coupled with a monochromator at 365 nm, a wavelength at which **1** does not absorb, gave nearly equivalent yields of **7** and **1** (Scheme 4). A control photolysis showed that **1** is not degraded appreciably at the wavelength used in the second photolysis. This implied that **7** can form independently of **1**.



Scheme 4. Photolysis of 3 in the presence of thiophene

While the identity of **7** was not difficult to elucidate, the determination of the route by which it was formed was more complicated. The ubiquitous carbene mechanism involves the addition of the carbene across the pi bond. If this cyclopropanation is applied to the thiophene system, product **10** is formed (Scheme 5, a). However, this could rearrange to **7** and regain aromaticity. The two difficulties lie in explaining why it only rearranges to the 2 position of the thiophene, and why the cyclopropyl intermediate (**10**) has not been detected. Possible alternatives to a very facile rearrangement of **7** include direct insertion into the C-H bond (b) and proton transfer to the carbene, followed by electrophilic aromatic substitution (c).

A low temperature experiment was conducted in an effort to detect the cyclopropyl adduct. After a photolysis of **1** at 350 nm in degassed methanol at -30 °C, there was no sign of any photolytic product other than **7,8** and **9**, the reaction mixture being monitored by ¹H NMR.



Scheme 5. Pathways to 7

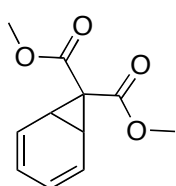
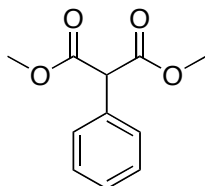
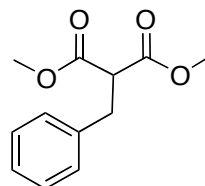
As positive controls, photolyses of **2** and **3** were carried out in benzene and toluene. The absorption spectrum of **1** does not allow for its direct photolysis as a dilute solution in benzene or toluene. The main photoproduct of the photolyses of **2** or **3** in distilled benzene was **11** (Table 3). Analysis by ^1H NMR indicated that there were other small peaks, but none that could be associated with an aromatic C-H insertion (**12**). However, when benzyl C-H bonds were present, as are in toluene, the major photoproduct was **13**. In toluene there was no sign of a bridged compound, or of an aromatic C-H insertion. The ^1H NMR spectrum showed some small, unidentified peaks that were not associated with the known or expected products.

Table 3. Photolysis of ylides 2 and 3 in aromatic solvents.

Ylide	Solvent	Product Yields ^a	
		11	13
2	Benzene	73	-
3	Benzene	79	-
2	Toluene	-	85

3	Toluene	-	76
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^a yields are with respect to the quantity of ylide consumed.

**11****12****13**

3.2.2 Sensitized Photolyses

The formation of dimethylmalonate (**9**) could have been the result of initial formation of triplet carbene, or a fast interconversion between singlet and triplet states. To examine that idea, benzophenone-sensitized photolyses were performed, which demonstrated that **9** was the major product, but **8** was also present. (Table 4) Ylide **1** was not used, as there were difficulties with absorption spectra overlapping in a manner that was prohibitive to analysis.

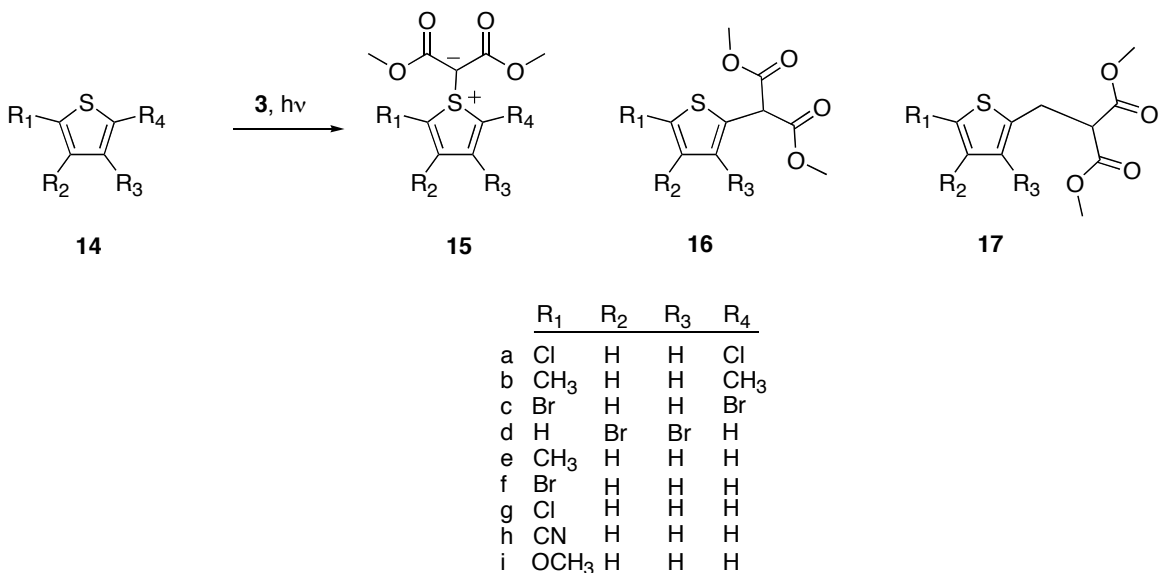
Table 4. Sensitized photolyses of 2 and 3 in methanol

Ylide	Product Yields (%)	
	8	9
2-Sens	7	65
3-Sens	9	57

3.2.3 Thiophene-carbene trapping

If intermediate **10** were being formed, the behavior of the addition could be altered by substituents, either by physically blocking the ideal position or by electronic effects. Photolyses of **3** in neat disubstituted thiophenes **14a-d** resulted in no formation of derivatives of **10** or **7** (Table 5). However, to some interest, the photolysis of **3** in 2,5-dimethylthiophene led to a benzyl insertion product (**16**). Ylides **15a**, **15b** and **15d** were synthesized and photolyzed in CD₃OD to facilitate

analysis by $^1\text{H-NMR}$, and to determine if proximity would increase the likelihood of a reaction. This yielded no aryl insertions, but the photolysis of **15b** did result the formation **16b**.



Scheme 6. Photolysis of 3 in neat thiophenes 14 a-j

Table 5. Photolysis of 3 in neat thiophenes 14a-j

14	Product Yields (%) ^a			
	% 3 _{deg}	15	16 ^c	17
a	95	81	-	-
b	95	13	-	76
c ^b	12	65	-	-
d	68	82	-	-
e	93		78	
f	89	63		
g	93	39	47	
h	95	68		
i	93		84	

^a Percentages are with respect to the yield of DBT ^b Debromination of **14c** began before an appreciable quantity of 3 degraded.

Photolyses of **3** in neat monosubstituted thiophenes led to a mixture of ylides, and insertion products (Table 5). Using 2-methylthiophene (**14e**), the product formed was **16e**, while benzyl insertion product **17e** was not detected. The photolysis in 2-bromothiophene (**14f**) yielded ylide **15f**. In the presence of the 2-chlorothiophene **14g**, both the ylide and insertion product were observed, but as demonstrated in the case of unsubstituted thiophene, some **16g** may be attributed to the secondary photolysis of **15g**. The results indicate that the electronic characteristics of the substituted thiophenes play a role in determining whether addition would take place.

Table 7. Substituent effects on the rate of insertion

Substituent	σ^+	mol _R /mol _H ^a	log (mol _R /mol _H)
Cl	0.11	0.6	-0.222
H	0	1	0.000
Me	-0.31	11	1.041
OMe	-0.78	30	1.477

^a Mol_R/Mol_H refers to the average product ratio of the competition between thiophene and its substituted derivatives

To examine the reactivity of the carbene intermediate, a Hammett plot was constructed, using σ^+ for the substituent values (Table 7). The Hammett-Brown values were chosen, as they are the most commonly used for electrophilic aromatic substitution, which seems comparable to the reaction at hand. Under normal circumstances, Equation 1 would be used, but given the current resources, an approximation using the product ratios of competition experiments is allowable (Equation 2). The thiophenes were used as neat solvents for the photolysis, and demonstrated addition of the carbene to the 5-position. Competition photolyses between thiophene, methylthiophene, methoxythiophene, and chlorothiophene, were used to determine the product ratios. Each photolysis was conducted at multiple solvent ratios to better determine the appropriate reactivity. (Table S1)

$$\ln(k_{RT}/k_{HT}) = \sigma\rho \quad (1)$$

$$\ln (\text{mol}_{\text{RT}}/\text{mol}_{\text{HT}}) = \sigma\rho \quad (2)$$

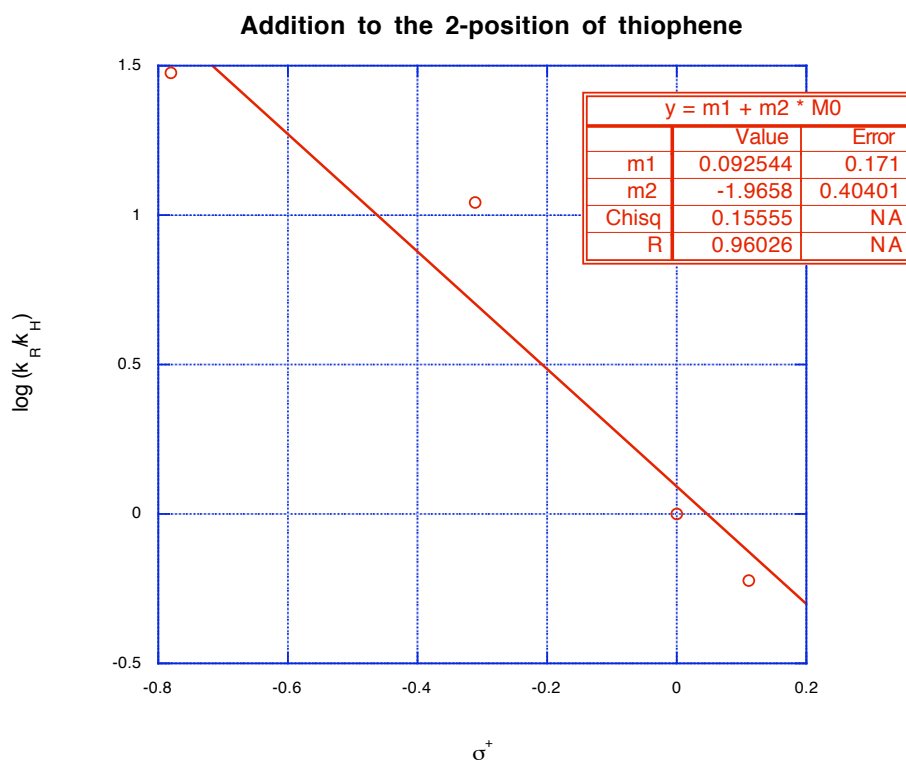
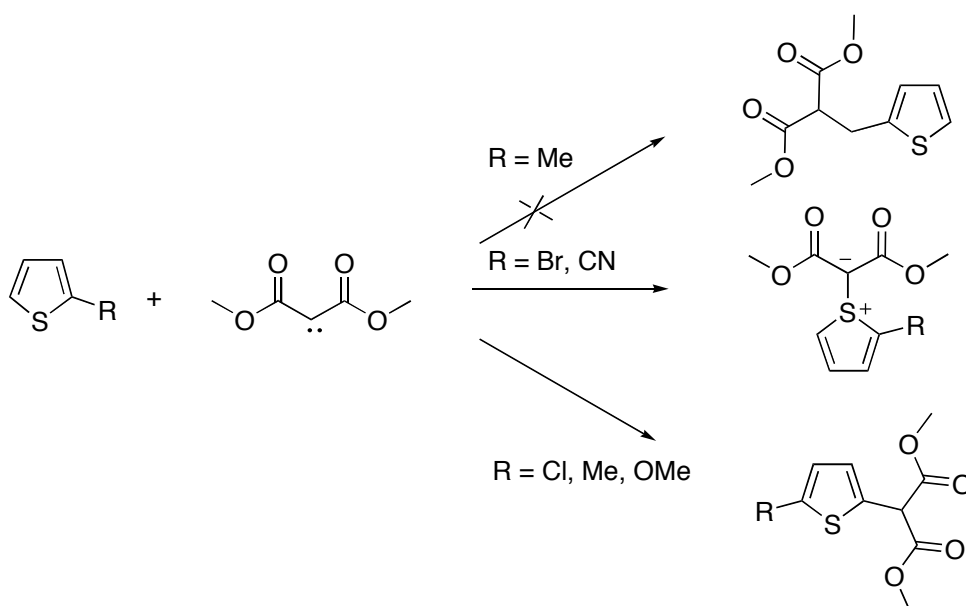


Figure 1. Hammett plot for formation of **7 and its derivatives**

The difficulty in constructing this plot lay in the difficulty of finding thiophenes with a range of substituents that a) would allow the addition to take place, and b) wouldn't absorb in the range in which **3** needed to be irradiated. As the carbene generated is electrophilic in nature, electron-withdrawing substituents should slow down the addition to the thiophene ring. This was further demonstrated by the photolyses of **3** in the presence of 2-thiophene carbonitrile (**14h**) resulted in the formation of its corresponding ylide, as opposed to the apparent insertion product

(Scheme 6, Table 5). As 2-bromothiophene is inactive with respect to product formation with the carbene, so is 2-trifluoromethylthiophene. Groups considered activating towards electrophilic aromatic substitution increased the yield of their corresponding derivatives of **7**.



Scheme 7. Outcomes of carbene trapping by substituted thiophenes

3.3 Discussion

The early work with the ylides revealed some interesting facets of the carbene chemistry resulting from these platforms. The complex chemistry of the thioanisole ylide **4** was not entirely unexpected, as the analogous sulfoxide also has demonstrated reactivity unlike that of thiophene-S-oxides or dibenzothiophene-S-oxides. Breaking the S-C bond of **4** does not afford the energy gain associated with the rearomatization that thiophene derivatives undergo, so other processes, like α -cleavage can compete, and possibly even dominate.

In order to rule out the involvement of excited states of ylides **1-3** in the reaction with cyclohexene, a spectroscopic study would be in order, however, some assumptions can be made on the basis of product yield. As seen, the ratio of **5** to **6** (Table 1) is fairly invariant, which would be unlikely if there were two intermediates:

the carbene and the excited state of **1-3**. Given the differences in the platforms, if the excited state were involved, one would expect to see a noticeable change in the percentages. The reasonable assumption is that there exists a common intermediate, the carbene.

Once the presence of the carbene was established, the next topic of interest was the pattern of reactivity. The reaction of the carbene with methanol indicated that both the singlet and triplet states of the carbene were being formed. This has been documented in other cases with dibenzothiophene-sulfilimines. The only oddity was the precipitous increase in the triplet product from **3** (Table 2). This could be a result of sterics preventing free rotation of the dimethylmalonate substituent. This hindrance can be observed by NMR; the two ester methyls are broadened in the ^1H spectrum and have different chemical shifts in both the ^1H and ^{13}C spectra (see supporting information). The nearly equivalent yield of both singlet and triplet carbenes did not seem to have an impact in the later photolyses in which the carbene was trapped by thiophenes.

It appears that the Wolff-type rearrangement is not a mechanistic route to the 2-methoxymalonate from the carbene from ylides **1-3**. This could be explained by the geometry of the carbene, after it cleaves from the thiophene derivatives.¹⁹⁻²¹ It has been shown elsewhere that for the rearrangement to take place, the geometry needs to align as seen in Figure 2. With the speed at which O-H insertion takes place, the direct insertion is the major product. It has been reported elsewhere that the Wolff rearrangement is more likely to occur with carbenes to which are conjugated ketones, as opposed to esters.

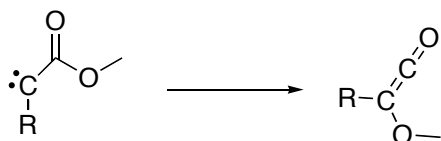


Figure 2. Transition from syn carbene to ketene

Despite efforts to discern the route by which the 2-(2'-thienyl)-dimethylmalonate (**7**) is formed, some ambiguities remain. Of the three possible mechanisms, the addition across the pi bond still seems to be the most reasonable. While the mechanism involving protonation of the carbene followed by electrophilic aromatic substitution is attractive, as it explains the exclusive substitution at position 2, there remains the question of the initial proton source. When the substitution takes place in neat thiophenes, there should be a decided lack of protons available for simple protonation. To explore the next alternative, it can be found that there is no literature example of an aryl C-H carbene insertion, either with benzene and its derivatives or with any heteroaromatic system. Also, the negative value of ρ given by the Hammett plot indicates a buildup of positive charge in the transition state, which would not be present in the insertion mechanism. This charge buildup could be related to both the EAS mechanism and the formation of **10**. Unlike the insertion pathway, here are reports of carbene addition across pi bonds in benzene, related systems and also on thiophene. In none of the cases with thiophene is a rearrangement indicated, but none of the previous work has been with the dimethylmalonate carbene.

Given the high ρ value of the addition, it is unsurprising that the addition reaction in methanol was only seen for thiophene, out of the first three platforms. The benzene ring portions of **2** and **3** are relatively unreactive compared to thiophene. As no addition was seen to the thiophene ring of **2**, it is apparent that formation of the ylide was energetically favorable to the addition. Even in the benzothiophene, the thiophene ring never appeared to be reactive toward the carbene. Granted, only thiophene could be used as a solvent, which made examining reactivity simpler. Adjusting the electronics of the aromatic systems such that the dominant mechanism is addition to the pi bonds is a fine process, as exhibited by the difference in benzene and thiophene. Addition of a methyl group to benzene gives the insertion into the benzyl position of the toluene, which addition of a methyl group to thiophene simply makes the pi addition easier.

3.4 Conclusions

Thiophene-S,C-ylides have proven to be stable platforms for the production of the dimethylmalonate carbene. Of ylides **1-3**, **1** is easier to work with, as it is more soluble, but **2** and **3** are less likely to react with the generated carbene. This makes them more useful for generating other electron deficient carbenes. **2** and **3** also extend further into the red, which makes them easier to use in the presence of other aromatics.

Although some questions regarding the addition of the dimethylmalonate group onto the thiophene have been answered, others still remain, such as why the addition only opens to the 2 position. Despite the likelihood that the pi addition is the mechanism by which the thienyl-malonate is formed, it is not completely confirmed, as the cyclopropyl adduct has not been observed.

3.5 Experimental

3.5.1 Materials

Unless otherwise noted, all solvents were the highest purity commercially available, and reagents were used as received.

3.5.2 Synthesis

3.5.2.1 General procedure for the synthesis of thiophene ylides

In a small round bottom flask, 1 equivalent of the thiophene derivative was mixed with 3 eq of the dimethyldiazomalonate, and 0.02 eq of the rhodium acetate dimer. In occasions when the thiophene derivative was a solid, a minimal amount of 1,2-dichloroethane was added. The mixture was allowed to stir until the color changed from dark green or a precipitate formed. Analysis by IR showed no diazo stretch. The crude product was washed with hexane, decanted, washed again with 50/50 ethyl acetate/hexane solution, and decanted again. The remaining light green solid was then recrystallized from ethanol to yield a white solid.

Dimethylmalonate-benzothiophene-S,C-ylide (**2**) ^1H NMR δ 7.78 (d, $J = 7.6$ Hz, 1H) 7.70 (d, $J = 7.6$ Hz, 1H) 7.58-7.63 (m, 1H) 7.51-7.56 (mm, 1H) 7.50 (d, $J = 5.7$ Hz, 1H) 6.79 (d, $J = 5.7$ Hz, 1H) 3.65 (s, 6H) (yield: 74.6)

Dimethylmalonate-dibenzothiophene-S,C-ylide (**3**) ^1H NMR δ 8.01 (d, $J = 7.8$ Hz, 2H) 7.80 (d, $J = 7.8$ Hz, 2H) 7.67 (t, $J = 7.5$ Hz, 2H) 7.54 (d, $J = 7.5$ Hz, 2H) 3.88 (s, 3H) 3.29 (s, 3H) (yield: 79.1%)

Dimethylmalonate-2,5-dichlorothiophene-S,C-ylide (**15a**) ^1H NMR δ 7.02 (s, 2H) 3.78 (s, 3H) 3.62 (s, 3H) (yield: 72.3%)

Dimethylmalonate-2,5-dimethylthiophene-S,C-ylide (**15b**) ^1H NMR δ 6.95 (s, 2H) 3.76 (s, 6H) (yield: 84.5%)

Dimethylmalonate-2,5-bromothiophene-S,C-ylide (**15c**) ^1H NMR δ 7.13 (s, 2H) 3.77 (s 3H) 3.65 (s, 3H) (yield: 5.3%)

Dimethylmalonate-2-methylthiophene-S,C-ylide (**15e**) ^1H NMR δ 7.12 (d, $J = 3.6$ Hz, 1H) 6.84 (d, $J = 5.4$ Hz, 1H); 6.79 (dd, $J = 3.6$ Hz, 5.4 Hz, 1H) 3.75 (s, 6H) (yield: 87.3%)

Dimethylmalonate-2-bromothiophene-S,C-ylide (**15f**) ^1H NMR δ 7.33 (d, $J = 6.0$ Hz, 1H) 7.23 (d, $J = 3.2$ Hz, 1H); 7.17 (dd, $J = 3.2$ Hz, 6.0, 1H) 3.76 (s, 6H) (yield: 89.2%)

Dimethylmalonate-2-thiophenecarbonitrile-S,C-ylide (**15g**) ^1H NMR δ 7.21 (d, $J = 4.0$ Hz, 1H) 7.02 (d, $J = 6.0$ Hz, 1H) 6.95 (dd $J = 6.0, 4.0$ Hz, 1H) 3.72 (s, 6H). ^{13}C NMR δ 171.4, 136.9, 133.3, 127.2, 116.1, 114.7,

Dimethylmalonate-2-chlorothiophene-S,C-ylide (**15h**) ^1H NMR δ 7.18 (d, $J = 3.2$ Hz, 1H) 7.05 (d, $J = 4.8$ Hz, 1H) 6.91 (dd $J = 3.2$ Hz, 4.8, 1H) 3.73 (s, 6H) (yield: 77.2%)

Dimethylmalonate-2-methoxythiophene-S,C-ylide (**15i**) ^1H NMR δ 6.78 (dd, $J = 3.0, 4.2$ Hz, 1H), 6.63 (d, $J = 4.2$ Hz, 1H), 6.29 (d, $J = 3.0$ Hz, 1H), 3.84 (s, 3H). ^{13}C NMR δ 171.4, 164.7, 123.6, 117.1, 60.6, 59.1 HRMS calc. 244.041 observed 244.044.(yield: 78.2%)

3.6.3 Photolytic procedures

3.6.3.1 General Details

Prior to photolyses, all solutions were degassed with argon for a minimum of 15 minutes. The photolyses took place in either a Rayonet photochemical reactor, or a 75W xenon-arc lamp coupled to a monochromator that allowed a maximum of ± 12 nm linear dispersity of the set wavelengths

3.6.3.2 Photolyses with cyclohexene

Degassed solutions of 2-8 mM **1-4** in acetonitrile with 10% cyclohexene were photolyzed at 356 nm. The progress of the reaction was monitored by HPLC.

3.6.3.3 Photolyses at low temperature

A 3 mM solution of **1** in CD₃OD was kept at -30 °C in a methanol bath chilled with careful addition of dry ice. The mixture was photolyzed in the rayonet at 300 nm, and then transferred to an NMR cooled to -30 °C.

3.6.3.4 Thiophene trapping photolyses

A weighed mixture of thiophenes, or of a neat thiophene was mixed with 4-6 mg of **3**, degassed, and photolyzed at 365 nm in the rayonet until completion. Afterwards, the low-boiling thiophenes were gently evaporated, and the remaining substances analyzed by ¹H NMR. In the cases where the thiophenes were too high boiling, the mixture was analyzed by GCMS.

3.6.3.5 Photolyses of ylides in benzene and toluene

Toluene and benzene, freshly distilled from calcium hydride, were used to prepare 4-8 mM solutions of **2** and **3**. The resulting solutions were degassed and irradiated for 60 minutes at 365 nm in the rayonet. After the photolysis the solvent was gently evaporated, and the remaining solids dissolved in CDCl₃ and analyzed by ¹H NMR.

3.6.3.6 Competition photolyses

A weighed mixture of thiophenes, or of a neat thiophene was mixed with 4-6 mg of **3**, degassed, and photolyzed at 365 nm in the rayonet until completion. Afterwards, the low-boiling thiophenes were gently evaporated, and the remaining substances analyzed by ^1H NMR. In the cases where the thiophenes were too high boiling, the mixture was analyzed by GCMS.

3.6 Acknowledgement

Thanks to NSF for funding, to the chemistry department staff for their support, and to my labmates, and Erin Rockafellow, for spectral acquisition.

3.7 References

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Chapter 4: Electronic effects on the spin state of photogenerated carbenes: the heavy atom effect

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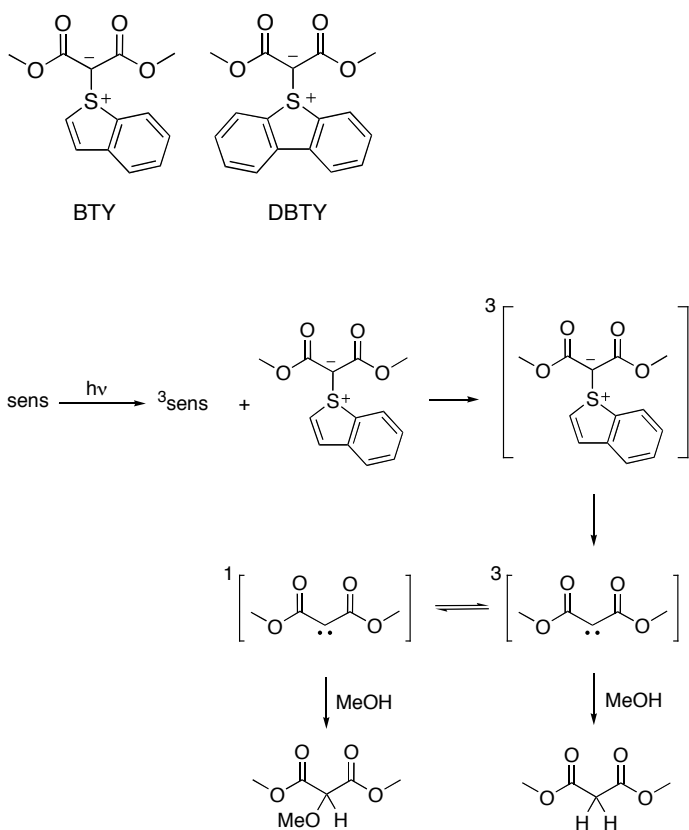
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Abstract: The photolyses of halogenated thiophene ylides in the presence of carbene traps produce an increased yield of triplet product that correlates well to the increase in molecular mass of the atoms substituted on the thiophene moiety. Exploration of the ratio of cis to trans products as they relate to singlet and triplet carbene addition to a cis alkene revealed a majority of cis product when the triplet state was exclusively populated. Contribution from a fast crossing to the singlet state could not be ruled out.

4.1 Introduction

The introduction of heavy atoms into molecular systems has long been a useful tool for the promotion of spin forbidden transitions. With the perturbation in importance of quantum values, transitions like those found in the production of oxene ($O(^3P)$) from the photolysis of dibenzothiophene-S-oxide (DBTO) are eased, so as to potentially increase the quantum yield of $O(^3P)$. In the case of DBTO, both the substitution of the heavier halogens for hydrogens and the substitution of selenium for sulfur demonstrated an increase in the quantum yield of deoxygenation.^{1,2}

The ground state of dicarbomethoxycarbene is the triplet state, only a few kcal/mol below the singlet.^{3,4} In our previous work, sensitized photolyses of dimethylmalonate benzothiophene-S,C-ylide (BTY) and dimethylmalonate dibenzothiophene-S,C-ylide (DBTY) in methanol led to a majority of the hydrogen abstraction product associated with triplet reactivity (Scheme 1).⁵ A small amount of the singlet product, insertion into the O-H bond, was also formed. Despite the care taken to assure at least 99.9% of light was absorbed by the sensitizer (benzophenone), singlet reactivity was unavoidable. The small singlet-triplet gap allows a fraction of the excited triplet carbene to convert to the singlet carbene. Given the rapid rate of O-H insertion ($10^9 \text{ M}^{-1} \text{ sec}^{-1}$) as compared to hydrogen abstraction ($10^6 \text{ M}^{-1} \text{ sec}^{-1}$), the singlet carbene is consumed as it is formed, and does not cross back to the triplet.^{6,7}



Scheme 1. Sensitized photolysis of dimethylmalonate thiophene-S,C-ylide in methanol

Table 1. Sensitized photolyses of BTY and DBTY in methanol

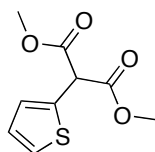
Ylide	Product Yields (%)	
	OH_{ins}	H_{abs}
BTY	7	65
DBTY	9	57

Direct photolyses with methanol gave a mixture of products associated with singlet and triplet reactivity: while ylides based on thiophene and benzothiophene gave a clear majority of singlet product with a small percentage of triplet product, dibenzothiophene gave a nearly even yield of both.⁵ This seemed to indicate that the platform was correlated with the spin state with which the carbene departed, either by differences in the two different thiophene based chromophores, or simply by preventing the malonate group from assuming a geometry beneficial to the singlet state.

Table 2. Photolysis of TY, BTY and DBTY in methanol

Ylide	Φ_{-ylide}	$\Phi_{+sulfide}$	Product Yields (%) ^a		
			OH_{ins}	H_{abs}	T_{add}
TY	0.21 ± 0.03	0.20 ± 0.03	52	5	22
BTY	0.12 ± 0.01	0.12 ± 0.01	70	5	
DBTY	0.17 ± 0.01	0.16 ± 0.02	54	39	

^aRelative to sulfide formation or sulfide + **7**. Φ_{-ylide} also includes **7** for **1** precursor.
^bOverlapping absorption spectra made experiment impractical.

**T_{add}**

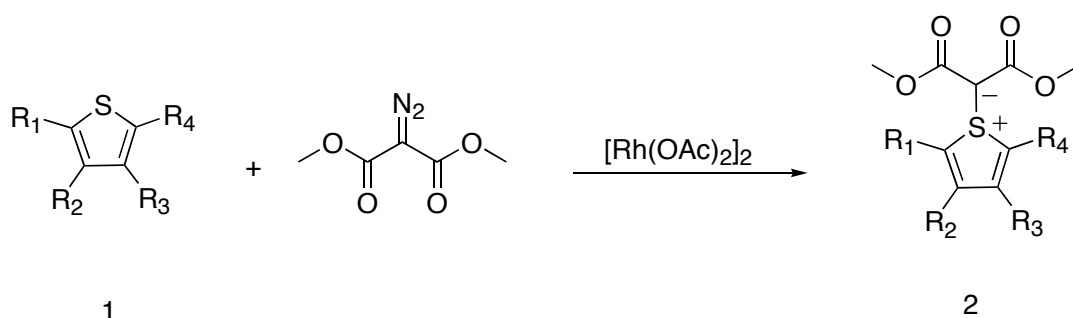
This chapter reports the use of the heavy atom effect to test the hypothesis that electronic effects drive the difference between the singlet to triplet product ratios observed for the thiophene series in the original work. If this holds, the substitution

of halogens and sulfur's heavier analog, selenium, should increase the rate of ISC to the triplet ground state of the carbene from the excited state.

4.2 Results

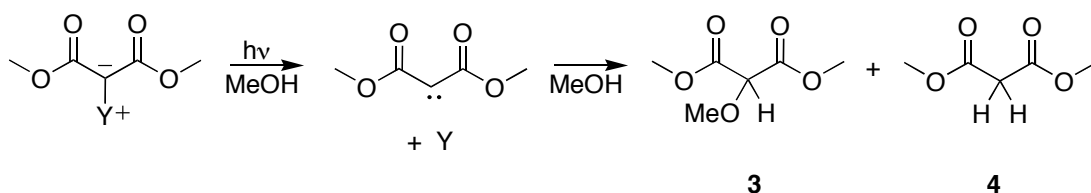
4.2.1 Thiophenes

Halogenated thiophenes **1a-e** were coupled with diazomalonate to yield **2a-e**. The thiophene ylides were then photolyzed in methanol (CH₃OH) and deuterated methanol (CD₃OD) at 300 nm. Periodic analysis of the reaction in CH₃OH by GC and the reaction in CD₃OD by ¹H NMR assured that all products were primary photoproducts, and not the result of a secondary photolysis. The ratios seen in the table below for the reaction in CD₃OD were those observed at completion, as the signals of the ester methyls of the thiophene ylides sometimes obscured the signals of the two carbene-methanol products.



- a: R₁ = Cl, R₂ = H, R₃ = H, R₄ = Cl
 b: R₁ = Br, R₂ = H, R₃ = H, R₄ = H
 c: R₁ = Br, R₂ = H, R₃ = Br, R₄ = H
 d: R₁ = H, R₂ = Br, R₃ = Br, R₄ = H
 e: R₁ = I, R₂ = H, R₃ = H, R₄ = H

Scheme 2. Synthesis of ylides 2a-e



Y = thiophene derivatives

Scheme 3. Photolysis of ylides in methanol

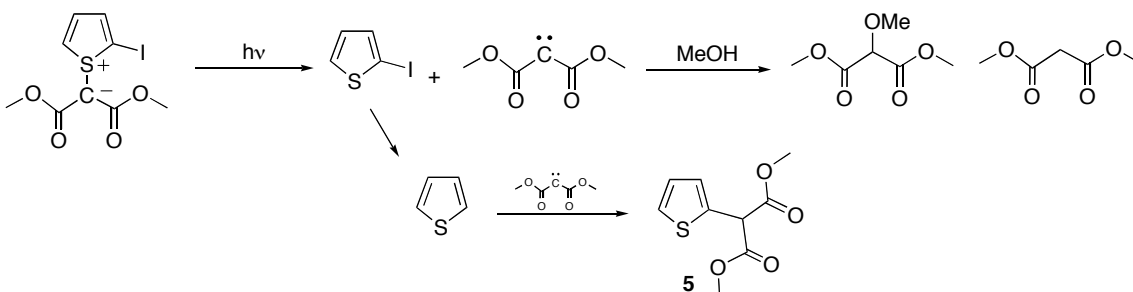
Table 1. Photolysis of halogenated thiophene ylides 2a-e in methanol

Ylide	Yields				3/4	3a/4a
	3 ^a	4 ^a	3a ^b	4a ^b		
2a	7.2	0.47	94.2 ± 1.3	4.8 ± 0.6	15.3	19.2
2b	16.8	0.96	94.7 ± 4.3	5.9 ± 1.1	17.5	16.2
2c	6.3	0.84	86.5 ± 2.5	9.4 ± 1.4	7.5	9.2
2d	5.7	1.42	86.2 ± 2.1	12.0 ± 2.1	4.0	6.6
2e	7.9	3.59	49.3 ± 1.4	27.6 ± 1.3	2.2	1.8

^a The photolysis was carried out to low to moderate conversion in CH₃OH and monitored by HPLC. ^b The photolysis was carried out to complete conversion in CD₃OD and analyzed by ¹H NMR.

As seen in table 1, the dibrominated thiophene ylides, dimethylmalonate-2,4-S,C-ylide (**2c**) dimethylmalonate-3,4-dibromothiophene-S,C-ylide (**2d**), and dimethylmalonate-2-iodothiophene-S,C-ylide (**2e**) were the only halogenated thiophenes with which a difference in the ratio of **3/4** was observed, indicating an increase in the percentage of the carbene reacting from the triplet state. It should be noted that **2c** was the least stable at room temperature, even in the absence of light. A control decomposition in methanol in the dark over a period of two days yielded 2,4-dibromothiophene and dimethylmethoxymalonate (**3**). The photolysis of ylide **2e** yielded the expected malonate derivatives, while also yielding thiophene, and thiophene addition product **5** (Scheme 3). No **1e** was detected in the reaction mixture. A photolysis of **1e** in methanol resulted in the deiodination of the thiophene.

A closely monitored photolysis of **2e** in methanol showed that the growth of the triplet product preceded the dissociation of iodine from the thiophene.

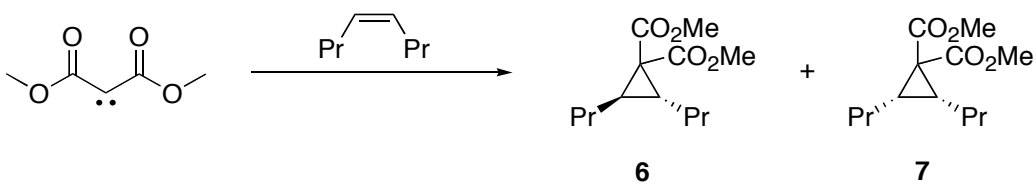


Scheme 3. Photolysis of 2e

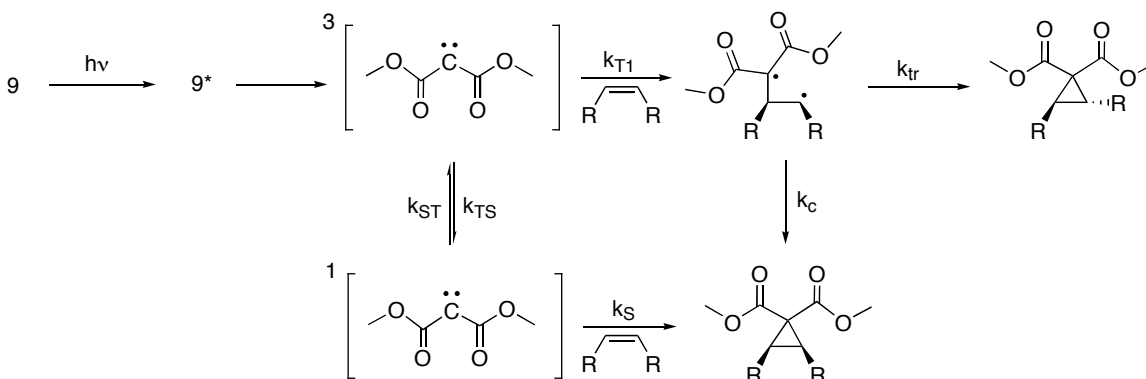
Photolyses of ylides **2a-e** (scheme 4) in acetonitrile in the presence of 10% *cis*-4-octene gave a mixture of *cis*- and *trans*-2,3-dipropyl-1,1-dicarbomethoxycyclopropane. The expected outcome of the triplet carbene addition to an alkene is a mixture of **6** (*trans*) and **7** (*cis*), while the singlet is expected to form **7** exclusively. In order to find an analytical method that could differentiate between **6** and **7**, they were independently synthesized. Analysis by GC at low temperature demonstrated different retention times for the two compounds. ¹H-NMR was not useful as the signals for the two hydrogens on the cyclopropane ring overlapped significantly, making quantitative analysis impossible.

The ratio of *cis* and *trans* products from the direct photolyses does not give a completely accurate depiction of the singlet to triplet ratio. Because the triplet carbene will give both products, the “absolute” limit of the triplet *cis* to *trans* ratio was sought (scheme 5). The ester linked benzophenone and thiophene **8** was coupled with dimethyl diazomalonate to give ylide **9** (scheme 6). In a solution of acetonitrile and 10% *cis* octene, the benzophenone moiety was then excited, causing triplet sensitization of the thiophene ylide moiety. Although there is likely some S-T equilibration, the rate of crossing (k_{TS}) cannot be superfast, as the difference in product distributions in this and past photolyses would not have existed. However,

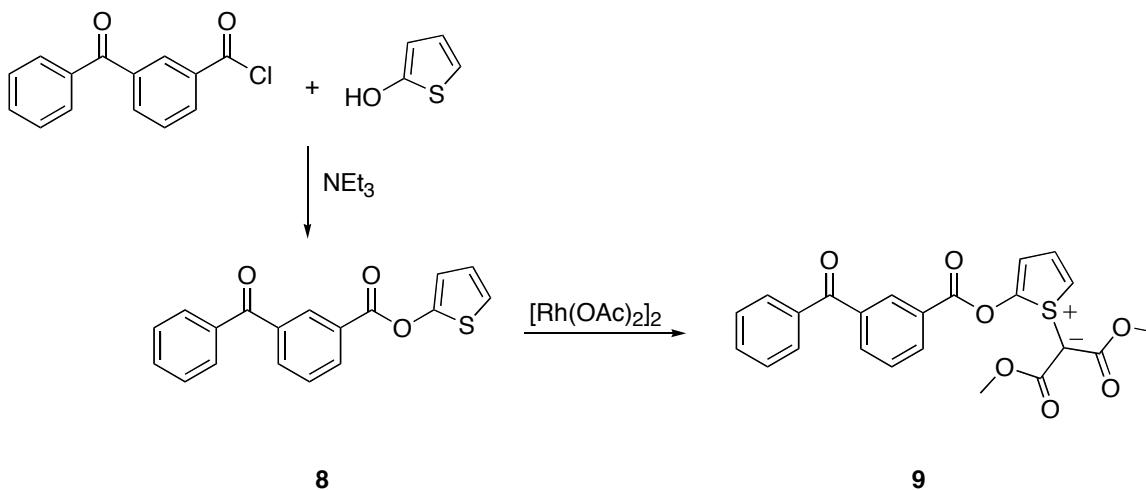
there may still be contribution from both states to **7**. The observed distribution at room temperature was $58.3\% \pm 0.3$ **6**, $41.7\% \pm 0.5$ **7**.



Scheme 4. Reaction of dicarbomethoxy-methylide with cis-4-octene



Scheme 5. Routes to cis and trans products



Scheme 6. Synthesis of 9

Table 2. Photolysis of halogenated thiophene ylides 2a-e with *cis*-4-octene

Ylide	Yields	
	6	7
2a	3.7	95.2
2b	4.2	93.5
2c	8.3	89.5
2d	8.6	86.8
2e	20.4	70.2

4.2.3 Dibenzothiophenes

Halogenated dibenzothiophenes **10a-b** were coupled with dimethyldiazomalonate to give the corresponding ylides. All derivatives showed the asymmetry of the ester methyls evident in the $^1\text{H-NMR}$ of DBTY. The photolyses of these ylides resulted in a small increase (ca. 10%) in the yield of **4** relative to DBTY. This increase is comparable to that seen for the yield of $\text{O}(^3\text{P})$ from the photodeoxygenation of halogenated DBTOs.²

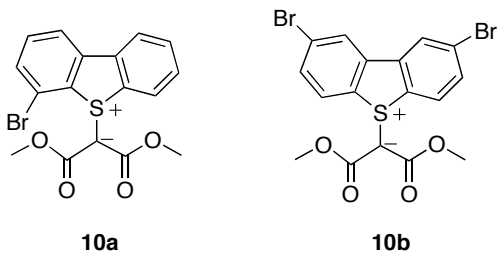


Table 3. Photolysis of halogenated dibenzothiophene ylides 10a-c in methanol

Ylide	Yields					
	3	4	3a	4a	3/4	3a/4a
10a	39.2	36.1	50.3	44.6	1.1	1.1
10b	46.9	39.3	51.5	48.0	1.2	1.1

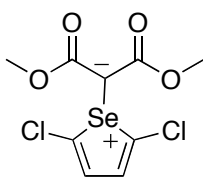
The photolyses of these derivatives in the presence of *cis*-4-octene (scheme 4) resulted in a larger yield of **6** that seen for any of the substituted thiophenes, near the limit of the singlet-triplet equilibration.

Table 4. Photolysis of halogenated dibenzothiophene ylides 10a-c with *cis*-4-octene

Ylide	Yields	
	6	7
10a	35.4	62.1
10b	36.8	61.5

4.2.4 Selenophenes

2,5-Dichloroselenophene was synthesized by the method published by Gronowitz.^{8,9} The unsubstituted selenophene ylide has been made, but is known to be thermally unstable to the point where it is rendered useless to this study.¹⁰ However, substitution of chlorine for hydrogen at the 2 and 5 positions allows the coupled selenophene ylide to be stable at room temperature. The photolysis of **11** in methanol resulted in a dramatic increase in the yield of triplet product (28% **3**, 65% **4**).



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An attempt to synthesize the ylide of dibenzoselenophene was unsuccessful. Coupling methods attempted included the standard rhodium catalyzed synthesis, copper sulfate and heat, and photochemical procedures.

4.2.5 Thermal Decomposition

As a control, ylides **2a-e**, **9**, and **10a-b**, were dissolved in an argon flushed solution of methanol, and then were allowed to decompose thermally in the absence of light. Analysis by ^1H NMR revealed high yields of **3**, with no detectable levels of **4** (Table S1).

The control was repeated in the *cis*-4-octene solution, and similar results were observed (Table S2).

4.3 Discussion

. The photolyses of **2a-e** provide a high yield of the carbene products. Increasing the number of halogens, or using the heavier bromine and iodine causes the yield of triplet carbene products to increase modestly, indicating that perturbation of the thiophene platforms will alter the initial populations of the triplet and singlet carbenes. Trapping of the carbenes with methanol demonstrated a noticeable change in the ratio of **3** to **4**. Debromination of **2b-d** did not occur, as it has been known to in other photochemical reactions. Ylide **2e** did demonstrate deiodination, which was unsurprising, as the photochemical schism of aryl iodine bonds has been noted elsewhere. It appears from the high yield of the triplet product and from a carefully monitored reaction that the cleavage of the S-C bond occurred prior to that

of the I-C bond. As the control photolysis demonstrated, the thiophene seen in the methanol photolysis of **2e** must be a result of a secondary reaction of **1a**.

As documented in previous work by Nag, et al, the heavy atom effect for the series of DBT derivatives was confirmed by phosphorescence.² The change in the triplet carbene product yield was not as dramatic as the effect seen in the smaller thiophenes. This may be due to the proximity of the halogens in the thiophene system, or because there was already a high yield of triplet carbene from the dibenzothiophene system. One of the possible explanations for the increased triplet yield in the base system was the steric imposition the large system placed on the ylide. However, the simple explanation of hindered rotation is ineffective, as for the chlorinated molecule **1a** both the ¹H and ¹³C NMR spectra displayed non-equivalent ester methyls, which did not impact the spin state of the photogenerated carbene.

The dichloroselenophene-S,C-ylide displayed a large increase in the yield of hydrogen abstraction product, which can be attributed to the proximity of the selenium. The chlorine substituents should not have any impact, as was seen for 2,5-dichlorothiophene.

4.4 Conclusions

Photophysical properties of the thiophene chromophore can alter the spin state of the carbene, as demonstrated by the product ratios. The halogenation of thiophene derivatives proved to promote ISC such that a higher yield of triplet carbene product was observed. The equilibration between the singlet and triplet states is rapid enough to rule out complete exclusion of singlet products. This is exhibited in the results of the octene studies, where some preference is shown to the *cis* state. This could be the result of either a contribution from the singlet state, or from a rotation that is slightly slower or comparable with the rate of ring closure. An LFP study would be helpful to determine the actual yield of triplet carbene and the rate constants accompanying each step in the addition to the *cis*-4-octene.

4.5 Experimental

4.5.1 Materials

Unless otherwise noted, all solvents were the highest purity commercially available, and reagents used as received.

4.5.2 Syntheses

4.5.2.1 General procedure for the synthesis of ylides

In a small, foil-covered round bottom flask at ambient conditions, 1 equivalent of the thiophene derivative was mixed with 3 equivalents of the dimethyldiazomalonate, and 0.02 eq of the rhodium acetate dimer. When the thiophene derivative was a solid, a minimal amount of 1,2-dichloroethane was added. The mixture was allowed to stir until the color changed from dark green or a precipitate formed. Analysis of the resulting mixture by IR showed no diazo stretch. The crude product was washed with hexane, decanted, washed again with 50/50 ethyl acetate/hexane solution, and decanted again. The remaining light green solid was then recrystallized from ethanol to yield a white solid.

Dimethylmalonate-2,5-dichlorothiophene-S,C-ylide(**2a**) ^1H NMR δ 7.02 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H); Yield: 72.3%

Dimethylmalonate-2-bromothiophene-S,C-ylide(**2b**) ^1H NMR δ 7.33 (d, J = 6.0 Hz, 1H), 7.23 (d, J = 3.2 Hz, 1H), 7.17 (dd J = 3.2, 6.0 Hz, 1H), 3.76 (s, 6H); Yield: 89.2%

Dimethylmalonate-2,4-dibromothiophene-S,C-ylide (**2c**) ^1H NMR δ 7.11 (d, J = 1.5 Hz, 1H), 6.90 (d, J = 1.5 Hz, 1H), 3.71 (broad s, 6H) ^{13}C δ 165.5, 128.2, 127.3, 124.6, 123.5, 56.0 HRMS calc 369.8510 observed 369.849; Yield: 15.2%

Dimethylmalonate-3,4-dibromothiophene-S,C-ylide (**2d**) ^1H NMR δ 6.99, (s, 2H) 3.70 (s, 6H) ^{13}C 165.4, 129.0, 127.3, 51.9; Yield: 22.6%

Dimethylmalonate-2-iodothiophene-S,C-ylide (**2e**) ^1H NMR δ 7.39 (dd, $J = 4.0$, 0.8 Hz, 1H), 7.08 (dd, $J = 6.0$, 0.8 Hz, 1H), 7.01 (dd $J = 6.0$, 4.0 Hz, 1H), 3.71 (broad s, 6H). ^{13}C δ 136.4, 131.1, 129.0, 59.1; Yield: 49.1%

cis-2,3-Dipropyl-1,1-dicarbomethoxycyclopropane (**6**) ^1H NMR δ 3.68 (s, 6H) 1.83 (m, 1H) 1.71 (m, 1H) 1.35 (m, 4H) 1.22 (m, 4H) 0.86 (t, $J = 7.2$ HZ, 6H); HRMS: calc 242.1518 observed 242.155

trans-2,3-Dipropyl-1,1-dicarbomethoxycyclopropane (**7**) ^1H NMR δ 3.70 (s, 6H) 1.87 (m, 1H) 1.60 (m, 1H) 1.39 (m, 4H) 1.22 (m, 4H) 0.86 (t, $J = 7.2$ HZ, 6H); HRMS: calc 242.1518 observed 242.150

Dimethylmalonate ylides of the benzophenone ester (**9**). ^1H NMR δ 8.47 (s, 1H) 8.27 (d, $J = 2.7$ Hz, 1H) 8.00 (d, $J = 6.0$) 7.79 (d, $J = 5.4$ Hz, 2H) 7.59 (m, 2H), 7.52 (t, $J = 5.7$ Hz, 1H), 7.36 (m, 1H) 7.16 (m, 1H) 7.00 (m, 1H) 4.61 (s, 2H) 3.84 (s, 6H). ^{13}C NMR δ 199.3, 171.3, 171.1, 138.5, 136.9, 133.5, 133.2, 131.7, 130.4, 128.3, 127.9, 127.1, 125.1, 124.0, 122.8, 121.5, 60.6, 58.9; HRMS calc 452.093 observed 452.089; Yield: 72%

Dimethylmalonate-4-bromodibenzothiophene-S,C-ylide (**10a**) δ 7.96, (dd, $J = 7.2$, 4.0 Hz, 2H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.68 (t, $J = 7.2$ Hz, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, H), 3.88 (s, 3H), 3.32 (s, 3H). ^{13}C δ 171.4, 140.1, 136.5, 133.3, 133.0, 131.7, 130.4, 125.1, 122.8, 121.6, 120.2, 51.7, 51.3; HRMS calc 391.9718 observed 391.9728; Yield: 30.4%

Dimethylmalonate-2,8-dibromodibenzothiophene-S,C-ylide (**10b**) ^1H NMR δ 7.88 (d, $J = 7.2$ Hz, 2H), 7.75 (d, $J = 7.2$ Hz, 2H), 7.2 (s, 2H), 3.83 (s, 3H), 3.47 (s, 3H). ^{13}C δ 171.4, 140.1, 136.5, 133.3, 133.0, 131.7, 130.4, 125.1, 122.8, 121.6, 120.2, 51.7, 51.3; 165.9, 164.4, 139.0, 135.2, 131.9, 126.2, 124.1, 53.0, 50.6; Yield: 17.7%

4.5.2.3 Synthesis of 2,3-dipropyl-1,1-dicarbomethoxycyclopropane (6,7)

A mixture of 1.1 equivalent of dimethyldiazomalonate and 1 equivalent of *cis* or *trans*-4-octene were mixed with enough acetonitrile to prevent separation. The

mixture was degassed and photolyzed at 254 nm until the diazo compound had been consumed. These reactions yielded *cis* isomer in 96% purity (yield: 78%) and *trans* isomer in 97% purity (yield: 73%). The products were isolated by recrystallization from ethanol.

4.5.2.4 Synthesis of 3-benzoyl benzoic acid thiophen-2-yl-methyl ester (8)

A mixture of 1.5 equivalents of thiophene methanol and 1.5 equivalents of triethylamine in dry ether were stirred at room temperature for an hour. A solution of 3-benzoylbenzoyl chloride in ether was added dropwise at 0 °C. The mixture was allowed to warm to room temperature and react for 2 hours, at which point the acid chloride had been consumed. The ester was recrystallized from hexane. Yield: 53%

4.5.3 Photolytic Procedures

4.5.3.1 Photolyses in methanol

A known amount of ylide was added to a vial and dissolved in methanol containing 1.14 mM dodecane as an internal standard. The concentrations of the ylide ranged from 1-8 mMol, dependent on solubility. The sample was then sealed with a septum and degassed with argon. The photolysis took place in a rayonet (Southern New England Ultraviolet) equipped with six 300nm centered bulbs. The reaction was monitored by use of a GC equipped with a 15m DB-1 column, 1mL/min flow. Response factors were obtained for both **3** and **4**.

4.5.3.2 Photolyses in deuterated methanol

Ylide, in an amount to give an approximate 4 mM concentration, was added to an NMR tube, dissolved in methanol-d₄ and degassed with argon. 1,4-Dioxane was present in the methanol as an internal standard. The photolysis took place in a rayonet (Southern New England Ultraviolet) equipped with six 300 nm centered bulbs. The reaction was monitored by ¹H-NMR.

4.5.3.3 Photolyses of thiophene ylides in *cis*-4-octene

A 2-6 mM solution of thiophene ylide, *cis*-4-octene (10%) and 5.13 mM dodecane (as an internal standard) in acetonitrile was degassed with argon. The mixture was photolyzed in a rayonet with 300 nm centered bulbs. The reaction was monitored by use of a GC equipped with a 15m DB-1 column, 1ml/min flow. Response factors were obtained for both products **6** and **7**.

4.5.4 Thermolytic Procedures

4.5.4.1 Thermolyses in deuterated methanol

Ylide, in an amount to give an approximate 4 mM concentration, was added to an NMR tube, dissolved in methanol-d₄ and degassed with argon. 1,4-Dioxane was present in the methanol as an internal standard. The solution was then placed in an oven at 80 °C for 12-36 hours. Periodic analysis was performed by use of ¹H-NMR.

4.5.4.2 Thermolysis of thiophene ylides in *cis*-4-octene

A 2-6 mM solution of thiophene ylide, *cis*-4-octene (10%) and 5.13mM dodecane (as an internal standard) in acetonitrile was degassed with argon. The solution was then placed in an oven at 80 °C for 12-36 hours. Periodic analysis was performed by use of ¹H NMR.

4.7 Acknowledgement

Thank you to NSF for funding, and to the Iowa State University Department of Chemistry for being populated with the friendliest chemists and staff I have chanced to encounter. An extra thank you to Erin Rockafellow for spectral assistance.

4.8 References

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Chapter 5: General conclusions

The photolytic degradation of thiophene ylides has illustrated the complexity of reactive intermediate chemistry. In the case of the sulfoxides, the simple route of deoxygenation was clouded by the rearrangement to the furan. The photochemistry of the ylides was somewhat less problematic, while the chemistry of resulting carbenes provided unique opportunities for study.

The degradation of thiophene-S-oxides 3,4-dibenzylthiophene-S-oxide and 3,4-diphenylthiophene-S-oxide led to the furan. Despite efforts to locate the possible 6-member-ring intermediate responsible for furan formation, there is still no physical confirmation of the proposed pathway. Attempts to determine the form in which the sulfur was excluded were also unsuccessful.

The successful deoxygenation of 2,5-bis(trimethylsilyl)thiophene-S-oxide led to the production of an oxidizing species that followed the same pattern of solvent trapping seen in past work by the group, leading to the conclusion of the same $O(^3P)$ species. Calculations carried out by William Jenks supported the plausibility of the mechanism proposed by Nakayama, but were not as conclusive as hoped, as there was a disagreement between different methods about the energies of some intermediate structures.

The photolysis of the thiophene-S,C-ylides led to the clean production of dicarbomethoxycarbene. Once the carbene was generated, it behaved as electrophilic carbenes are known to behave. In the presence of an alkene, the carbene would add across the pi bond, or insert into an allylic C-H bond. In the presence of an alcohol, the carbene would insert into the O-H bond, or abstract hydrogens. In the presence of benzene, the carbene would form a norcaradiene derivative, while in the presence of toluene, the carbene more readily inserted into benzyl C-H bonds. The only unexpected twist in the carbene's behavior was its reaction with thiophene.

The mechanism for the apparent insertion into the 2-position of thiophene has not yet been ascertained. Intuitively, the most likely option is that of an electrophilic addition or electrophilic aromatic substitution. Arguments for a C-H insertion, or a rearrangement from the ylide were taken into consideration, and rebutted. The negative ρ value given by the Hammett plot was the most convincing argument against direct insertion, while the ability of the product to form when the carbene is generated from another platform in the presence of thiophene was evidence against the rearrangement. As of now, the options of an addition across the pi bond of the thiophene followed by a fast rearrangement to the product, or a more traditional electrophilic aromatic substitution are still possibilities that cannot be eliminated.

The distribution of the carbene-based products mentioned previously is dependent on the spin of the carbene. As with the majority of carbenes, the singlet and triplet states are very close together, resulting in the observation of chemistry stemming from both states. Heavy atom substitution was expected to increase the yield of triplet products, as the increase in ISC would increase the population of triplet carbene. In the thiophene and dibenzothiophene series, as the halogens increased in number and molecular weight, the yield of triplet carbene products also increased. Substituting Se for the S in thiophene also increased the triplet yield, more dramatically than observed in the case of the halogens.

Appendix A

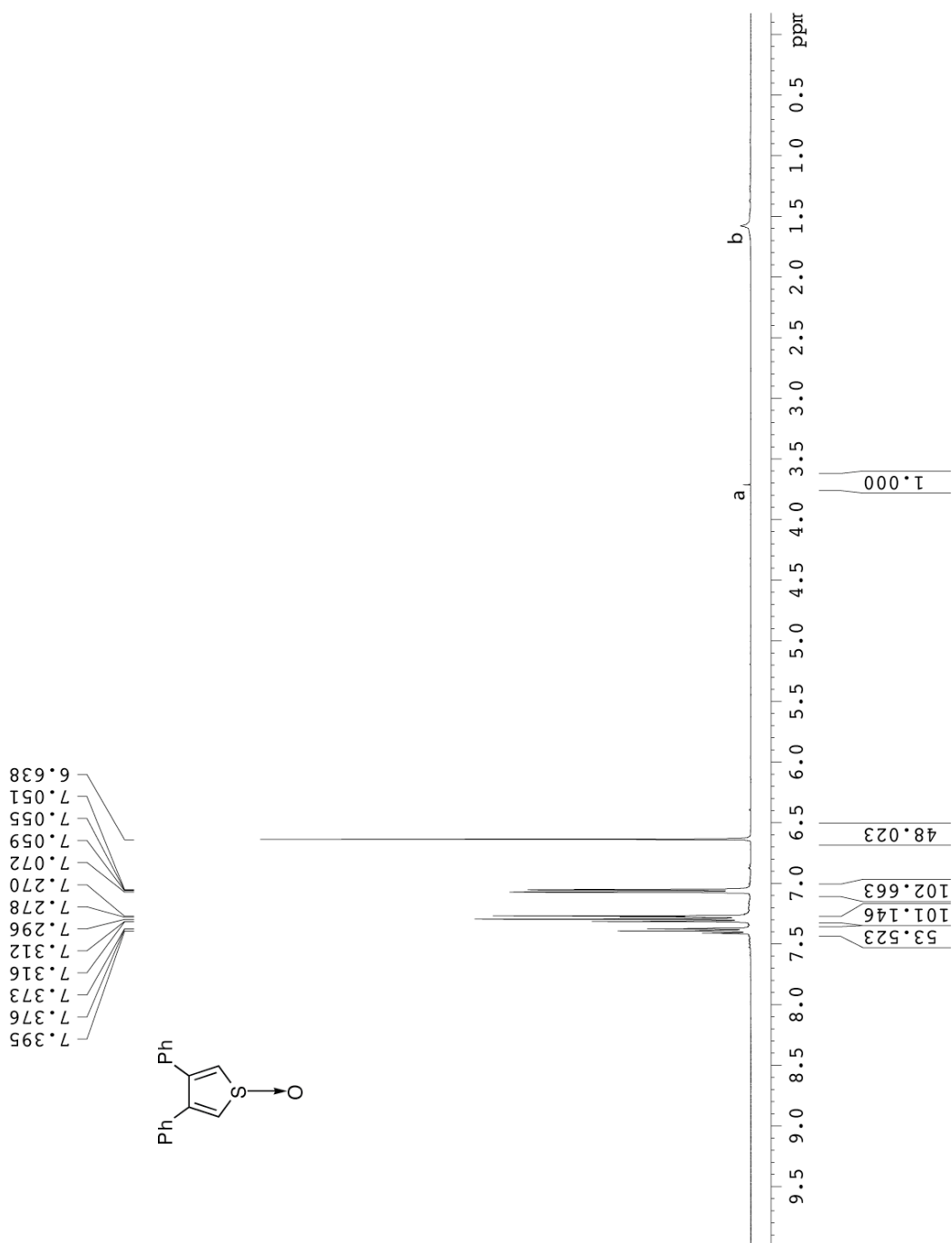
Photochemistry of Thiophene-S-Oxide Derivatives

Melanie J. Heying, Mrinmoy Nag and William S. Jenks

Supporting Information

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Spectral data for 1a**Figure S1.** ^1H NMR 3,4-diphenylthiophene-S-oxide (**1a**)

CDCl₃, 400 MHz; ^a 1,4-dioxane as an internal standard; ^b water

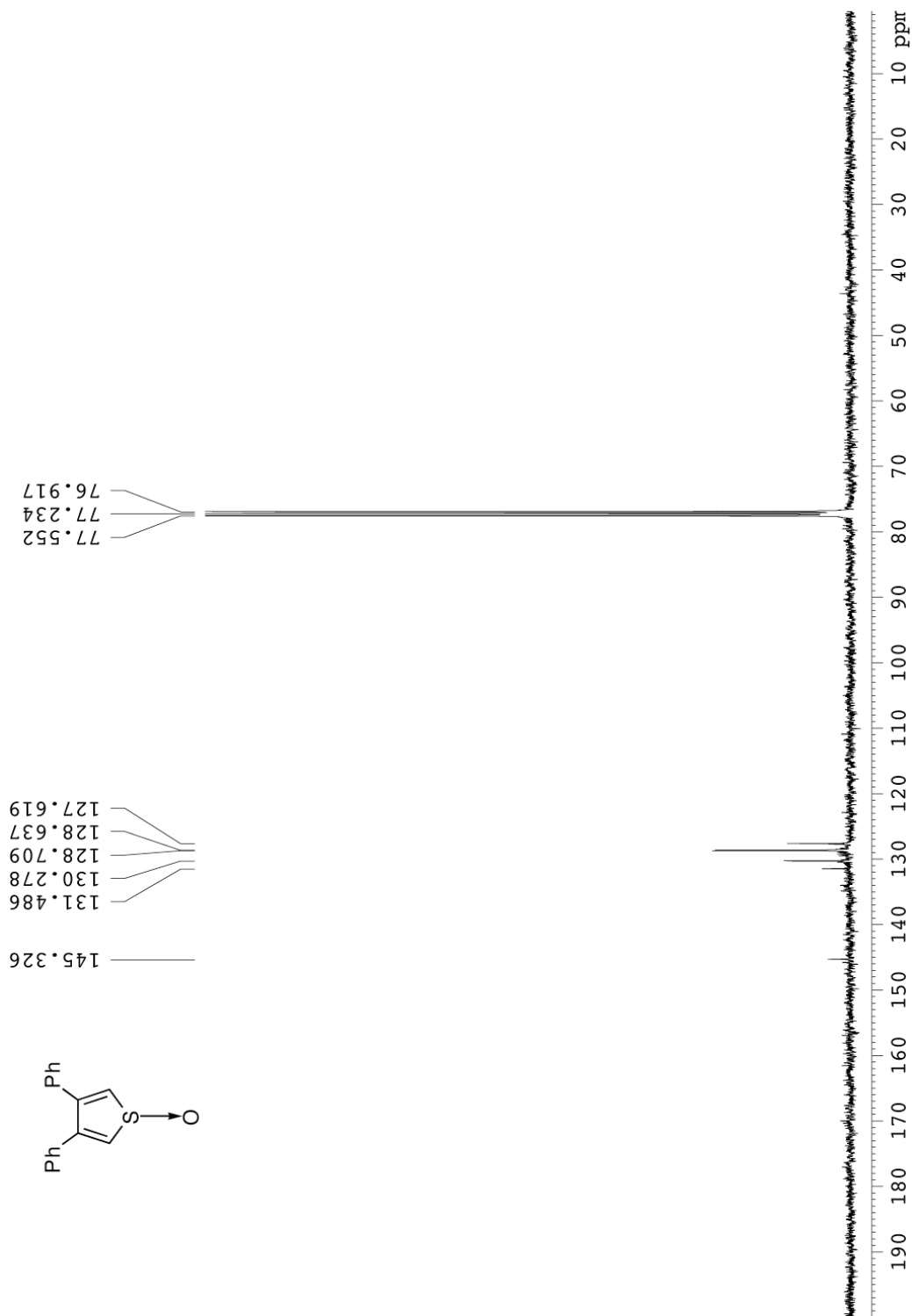
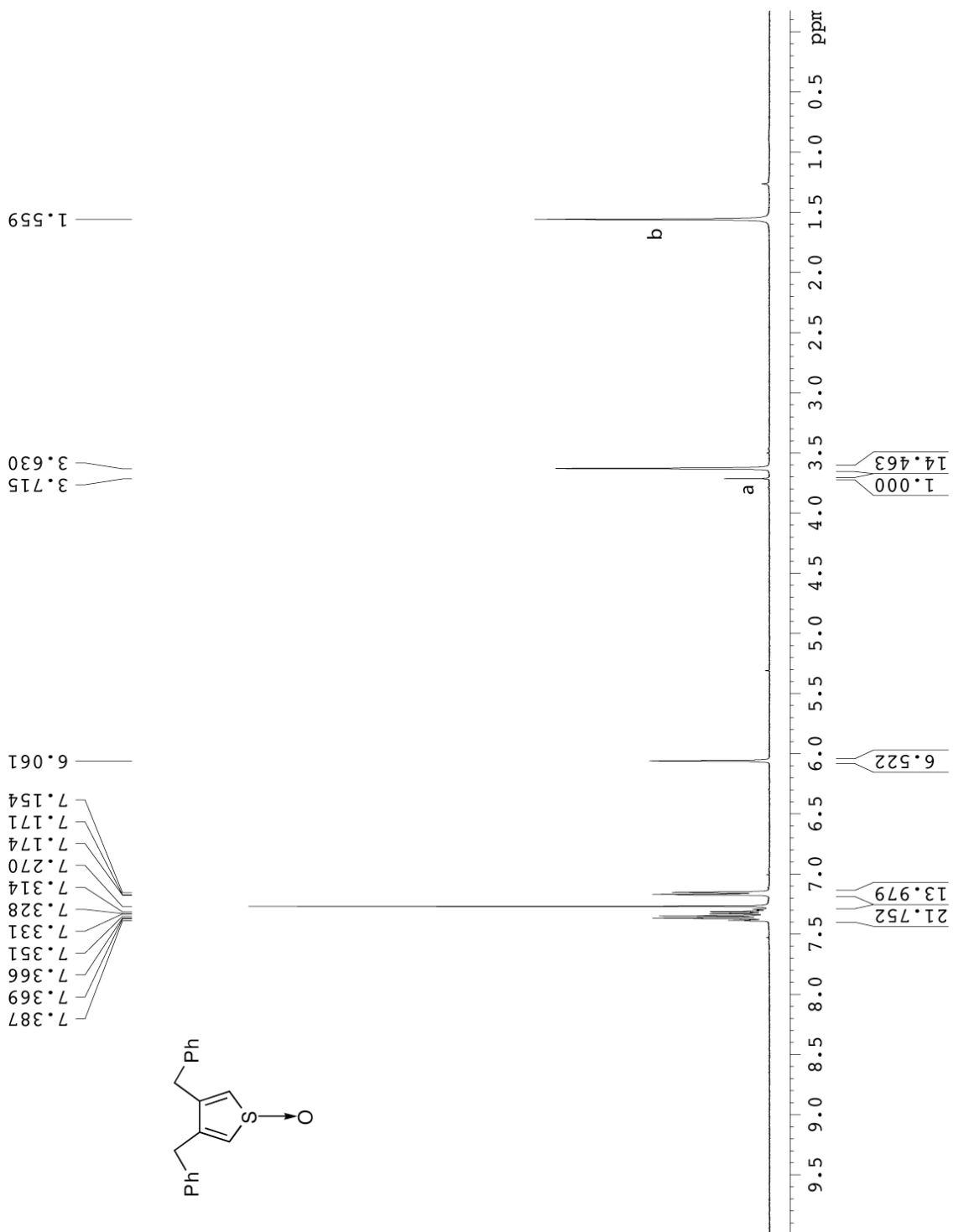


Figure S2. ¹³C NMR 3,4-diphenylthiophene-S-oxide (**1a**)

CDCl₃, 400 MHz**Spectral data for 1b****Figure S3.** ¹H NMR 3,4-dibenzylthiophene-S-oxide (1b)

CDCl₃, 400 MHz; ^a 1,4-dioxane as an internal standard; ^b water

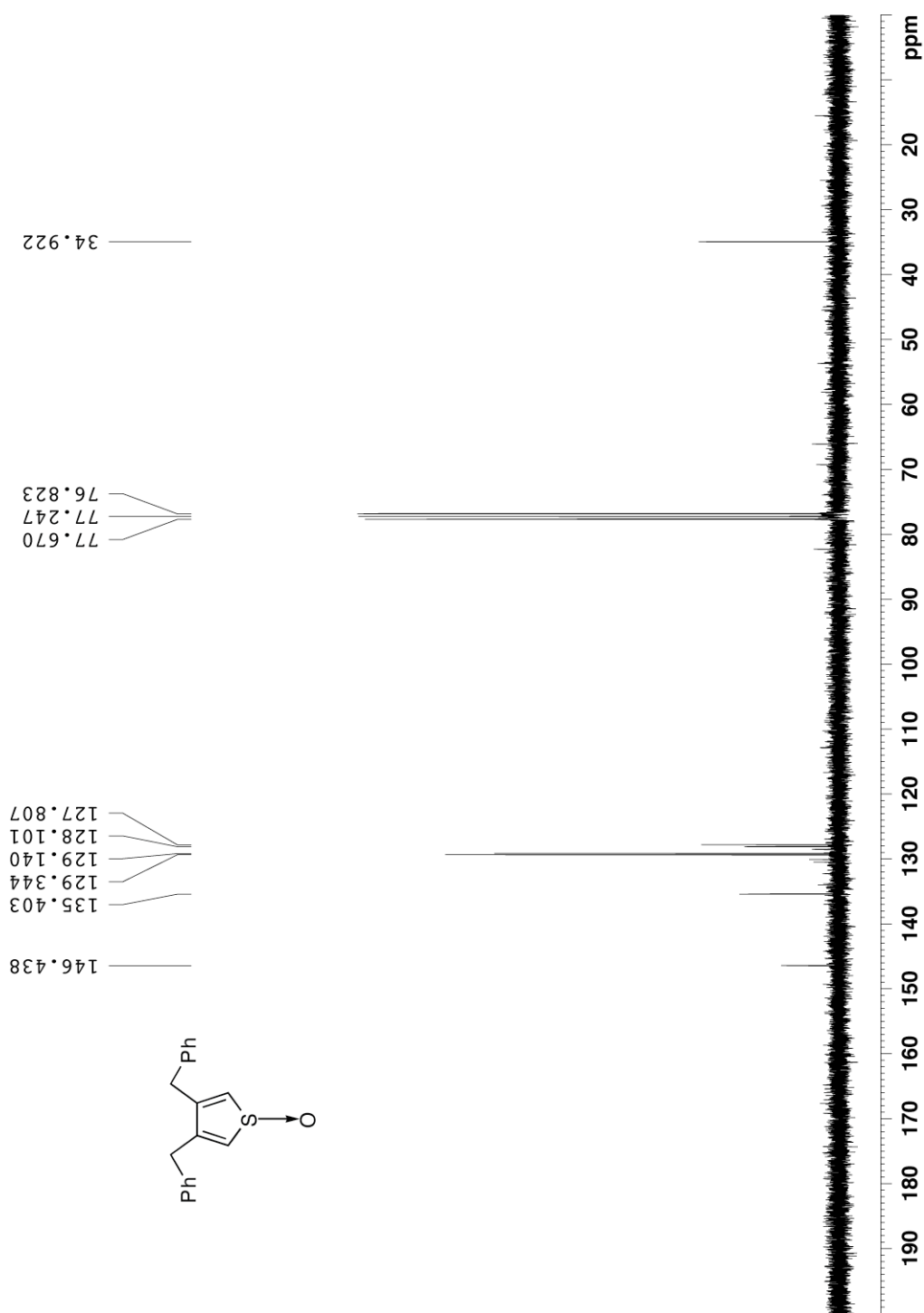
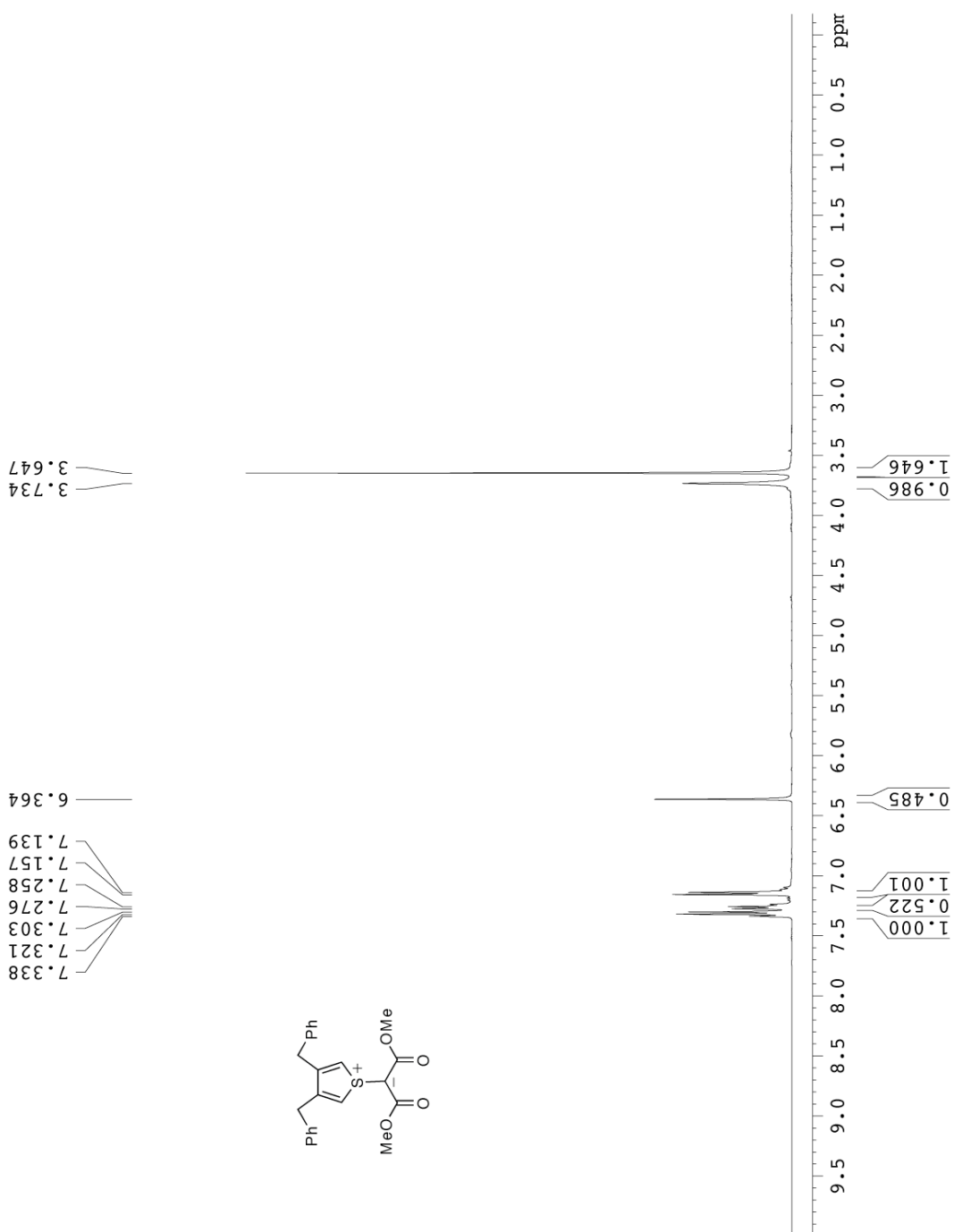


Figure S4. ¹³C NMR 3,4-dibenzylthiophene-S-oxide (1b)

CDCl₃, 400 MHz**Spectral data for 8****Figure S5.** ¹H NMR 3,4-dibenzylthiophenium methylene (8)

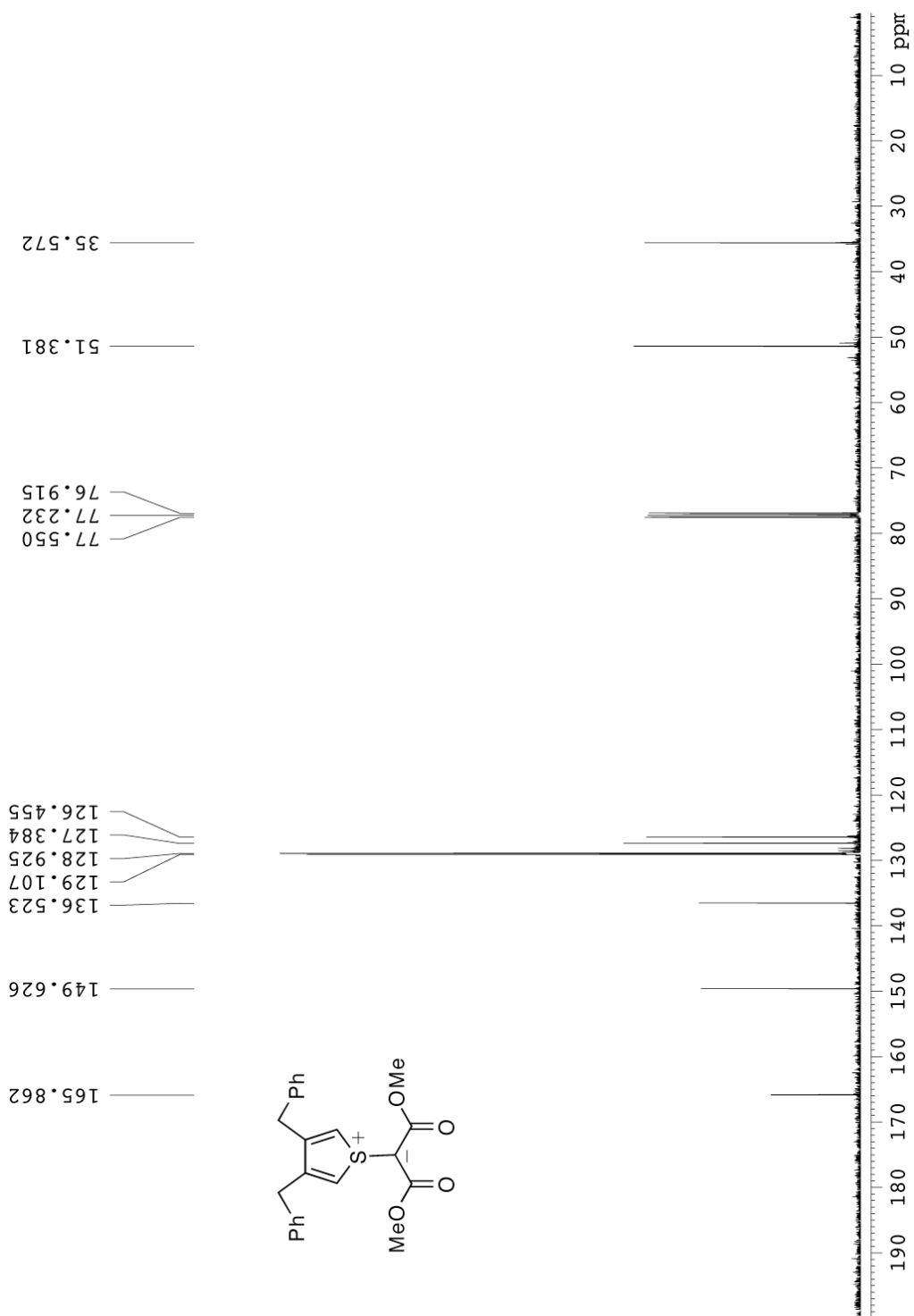
CDCl₃, 400 MHz

Figure S6. ¹³C NMR 3,4-dibenzylthiophenium methylide (8)

CDCl₃, 400 MHz

Note: No signal from the anionic carbon

Computational data

Table S1. Absolute energies of C₄H₄OS isomers (Energies in Hartrees, except as noted)

	1	5	6 O exo	6 S exo	6 di exo	7	oxirane
HF/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-626.2018	-626.2163	-626.2337	-626.2385	-626.2401	-626.2314	626.2193
B3LYP/6-31G(d)	-627.9459	-627.9689	-627.9901	-627.9970	-627.9966	-627.9914	627.9775
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	-628.1032	-628.1101	-628.1236	-628.1286	-628.1301	-628.1233	628.1101
B3LYP/aPC2//B3LYP/6-31G(d)	-628.1099	-628.1188			-628.1392	-628.1324	
MP2/6-31G(d)	-626.8762	-626.8946	-626.9147	-626.9202	-626.9198	-626.9233	626.9112
MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-627.2811	-627.2819	-627.2904	-627.2937	-627.2951	-627.3057	627.2944
B3LYP/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-628.1031	-628.1100	-628.1232	-628.1280	-628.1297	-628.1232	628.1124
CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-627.3591	-627.3674			-627.3820	-627.3856	
ZPE (B3LYP)	0.069993	0.070421	0.069541	0.07021	0.069703	0.072505	0.071049
G 298 K (B3LYP); kcal/mol	25.794	26.019	23.969	24.709	24.28	27.676	26.783
ZPE (MP2)	0.070552	0.071264	0.07005	0.070285	0.070008	0.073481	0.07223
298 K (MP2); kcal/mol	26.142	26.59	24.272	24.61	24.379	28.324	27.55

Table S2. Relative Energies of C₄H₄OS (kcal/mol)

	1	5	6 O exo	6 S exo	6 di exo	7	oxirane
H_{rel} (0 K)							
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	11.1	7.0	-2.0	-4.7	-6.0	0.0	7.4
B3LYP/aPC2//B3LYP/6-31G(d)	12.5	7.2			-6.1	0.0	
MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	13.6	13.5	7.4	5.5	4.5	0.0	6.3
CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d)		10.0			0.0	0.0	
G_{rel} (298 K) kcal/mol							
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	10.8	6.6	-3.9	-6.3	-7.7	0.0	7.4
B3LYP/aPC2//B3LYP/6-31G(d)	12.2	6.8			-7.7	0.0	
MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	13.3	13.2	5.5	3.8	2.7	0.0	6.3
CCSD(T)/aug-cc-pV(T+d)Z//MP2/6-31G(d)	14.4	9.7			-1.7	0.0	

Table S3. Absolute energies of C₄H₄S₂ isomers

	dithiin	di exo	episulfide
B3LYP/6-31G(d)	-950.9393	-950.9305	-950.9395
B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	-951.0796	-951.0677	-951.0796
MP2/6-31G(d)	-949.5231	-949.5109	-949.5351
MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-949.9136	-949.8832	-949.9181
ZPE, B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	0.068193	0.068715	0.069128
G 298 K, B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d), (kcal/mol)	24.057	23.753	24.948
ZPE MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	0.069382	0.068135	0.0704
G 298 K, MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d) (kcal/mol)	24.889	23.061	25.806
G(298) B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d)	-951.0412	-951.0299	-951.0398
G(298) MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d)	-949.8739	-949.8464	-949.8770
G _{rel.} , B3LYP/aug-cc-pV(T+d)Z//B3LYP/6-31G(d) (kcal/mol)	-0.9	6.3	0.0
G _{rel.} , MP2/aug-cc-pV(T+d)Z//MP2/6-31G(d) (kcal/mol)	2.0	19.2	0.0

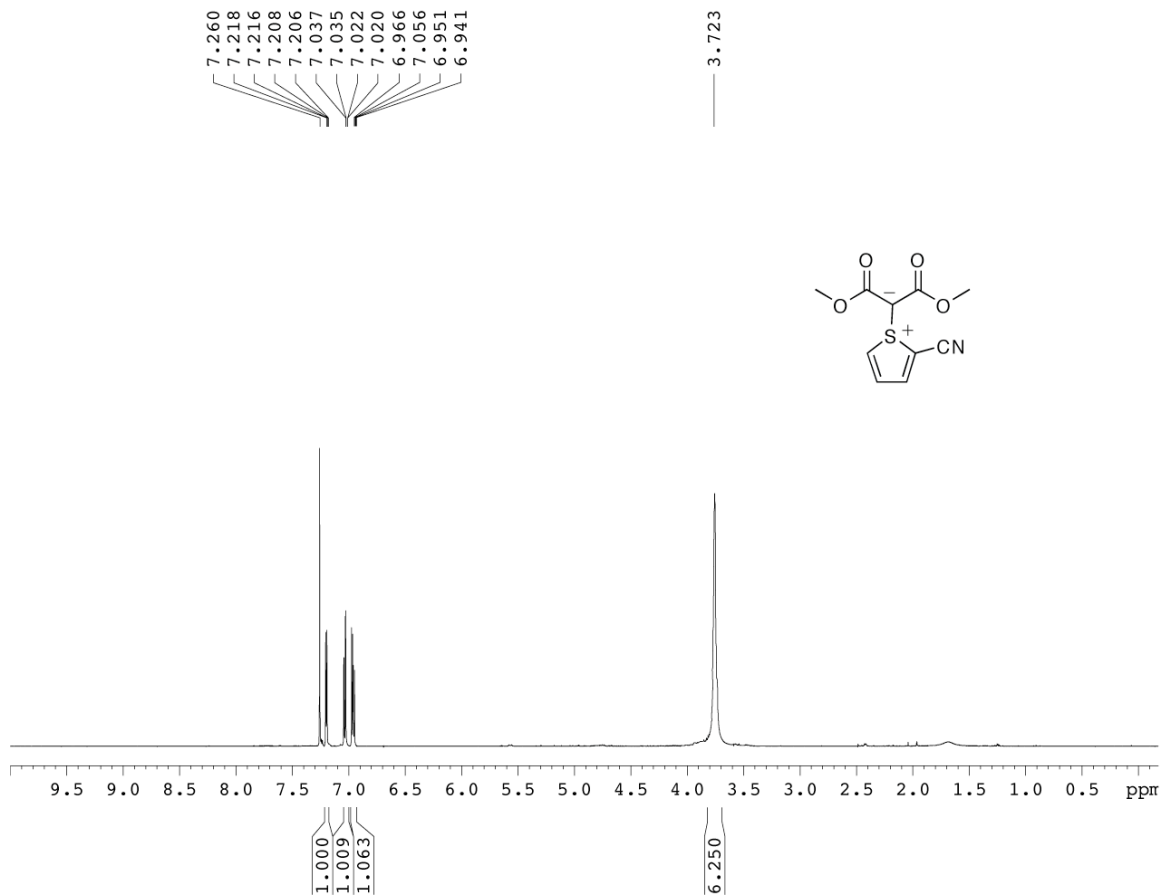
Appendix B

Investigation of the reactivity of photogenerated carbenes from thiophene platforms

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Spectral data for 15g**Figure S1.** ¹H NMR Dimethylmalonate-2-thiophenecarbonitrile-S,C-ylide(**15g**)CDCl₃, 400 MHz

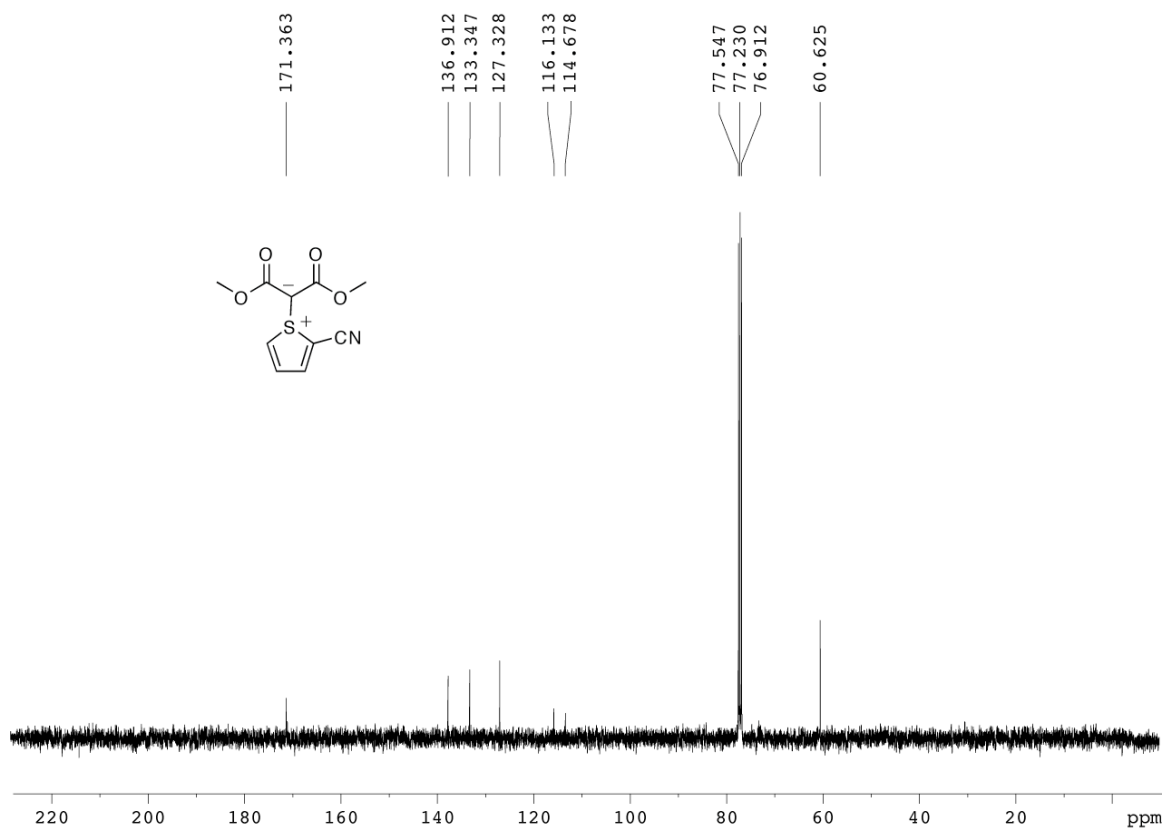
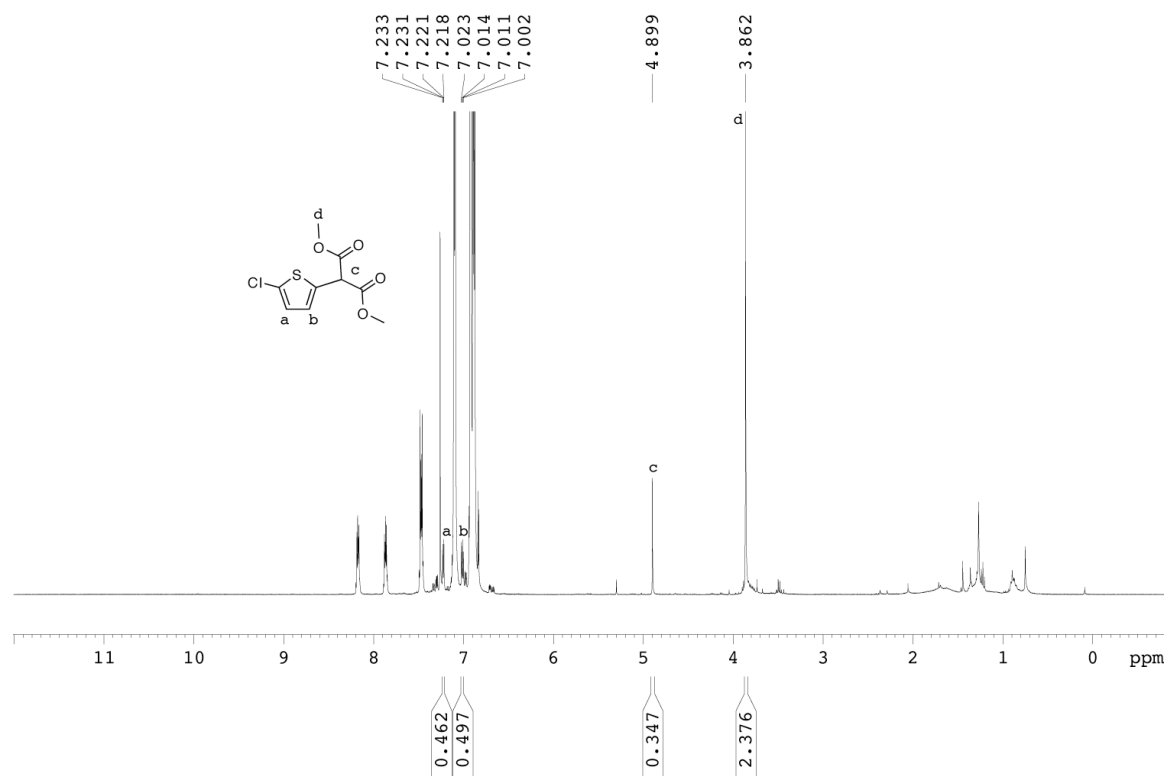


Figure S2. ^{13}C NMR Dimethylmalonate-2-thiophenecarbonitrile-S,C-ylide(15g)

CDCl_3 , 400 MHz

Spectral data for 16a**Figure S3.** ¹H NMR 2-(5-chlorothiophen-2-yl)-dimethylmalonate (**16a**)

CDCl₃, 400 MHz; in the presence of degraded dibenzothiophene ylide

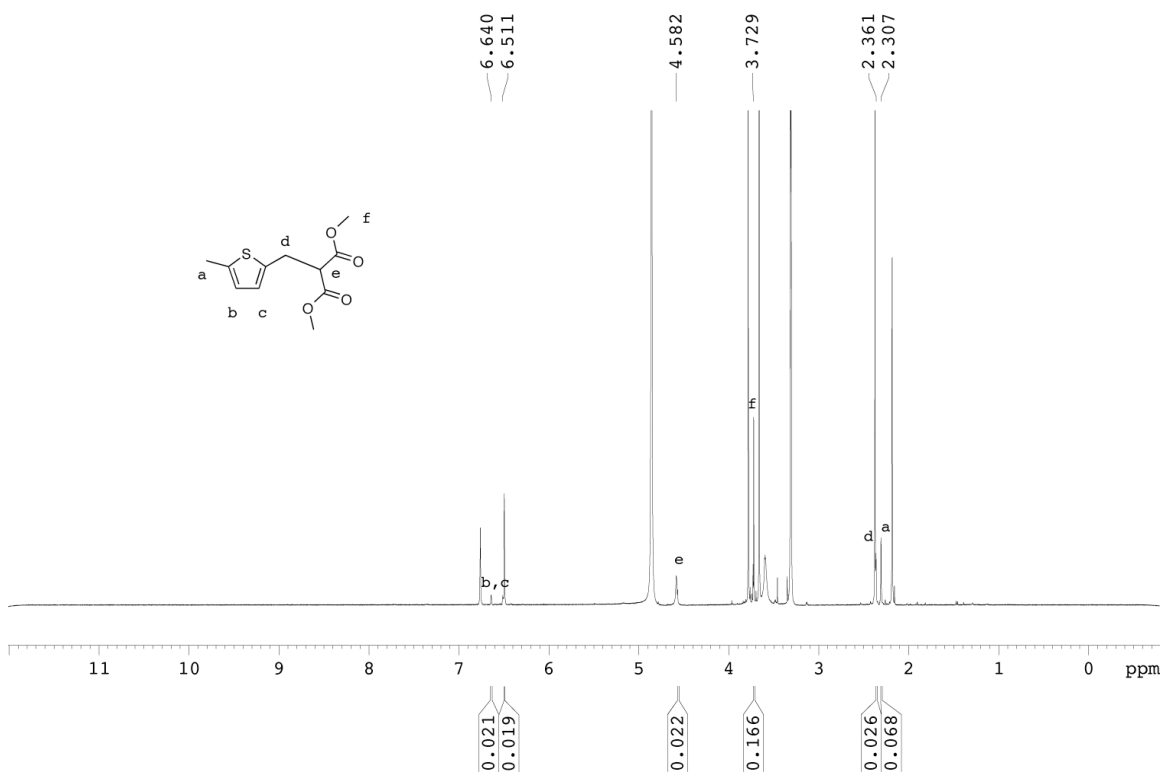
Spectral data for 17b

Figure S4. ¹H NMR 2-(5-methylthiophen-2-ylmethyl)-dimethylmalonate (**17b**)

CD₃OD, 400 MHz, from a degradation of **15b**

Table S1. Competition photolyses of **3** in thiophenes

thiophene deriv.	mol		ratio td/t	td product	t product	ratio td _p /t _p	(td _p /t _p)/(td _p /t _p)
(td)	mol td	thiophene					
	3.00E-				1.10E-		
15g	03	3.00E-03	1	6.70E-04	03	6.09E-01	6.09E-01
	6.00E-				9.00E-		
15g	03	3.00E-03	2	1.10E-03	04	1.22E+00	6.11E-01
	3.00E-				1.70E-		
15g	03	6.00E-03	0.5	5.10E-04	03	3.00E-01	6.00E-01
	3.00E-				3.60E-		
15g	02	3.00E-03	10	2.10E-03	04	5.83E+00	5.83E-01
	3.00E-				1.90E-		
15e	03	3.00E-03	1	2.10E-03	04	1.11E+01	1.11E+01
	6.00E-				1.00E-		
15e	03	3.00E-03	2	2.21E-03	04	2.21E+01	1.11E+01
	3.00E-				3.10E-		
15e	03	6.00E-03	0.5	1.70E-03	04	5.48E+00	1.10E+01
	3.00E-				2.00E-		
15e	02	3.00E-03	10	2.24E-03	05	1.12E+02	1.12E+01
	3.00E-				2.10E-		
15e	03	3.00E-03	1	2.30E-03	04	1.10E+01	1.10E+01
	1.50E-				5.00E-		
15e	02	3.00E-03	5	2.70E-03	05	5.40E+01	1.08E+01
	3.00E-				8.00E-		
15i	03	3.00E-03	1	2.42E-03	05	3.03E+01	3.03E+01
	6.00E-				5.00E-		
15i	03	3.00E-03	2	2.99E-03	05	5.98E+01	2.99E+01
	3.00E-				1.40E-		
15i	03	6.00E-03	0.5	2.11E-03	04	1.51E+01	3.01E+01
	3.00E-				1.00E-		
15i	02	3.00E-03	10	2.98E-03	05	2.98E+02	2.98E+01

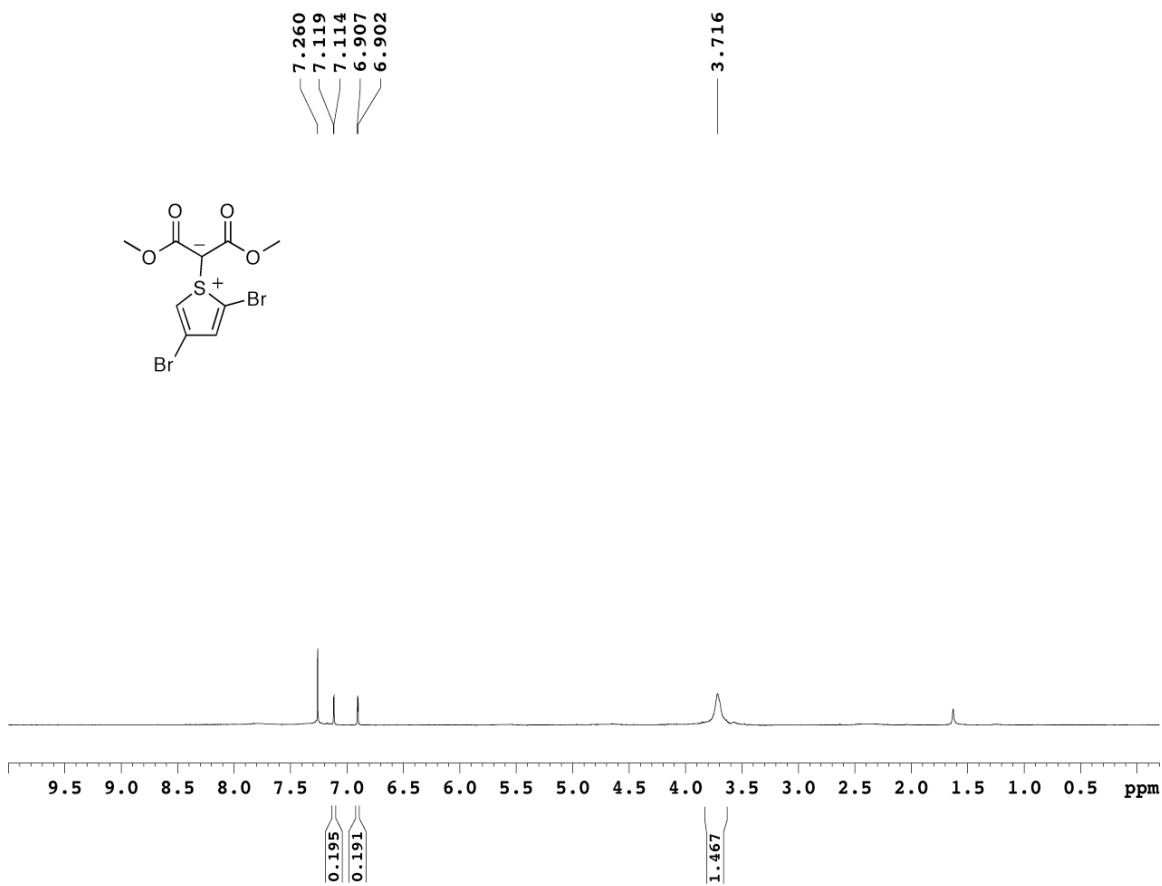
Appendix C

Electronic effects on the spin state of photogenerated carbenes: the heavy atom effect

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Spectral data for 2c**Figure S1.** ¹H NMR Dimethylmalonate-2,4-dibromothiophene-S,C-ylide (**2c**)CDCl₃, 400 MHz

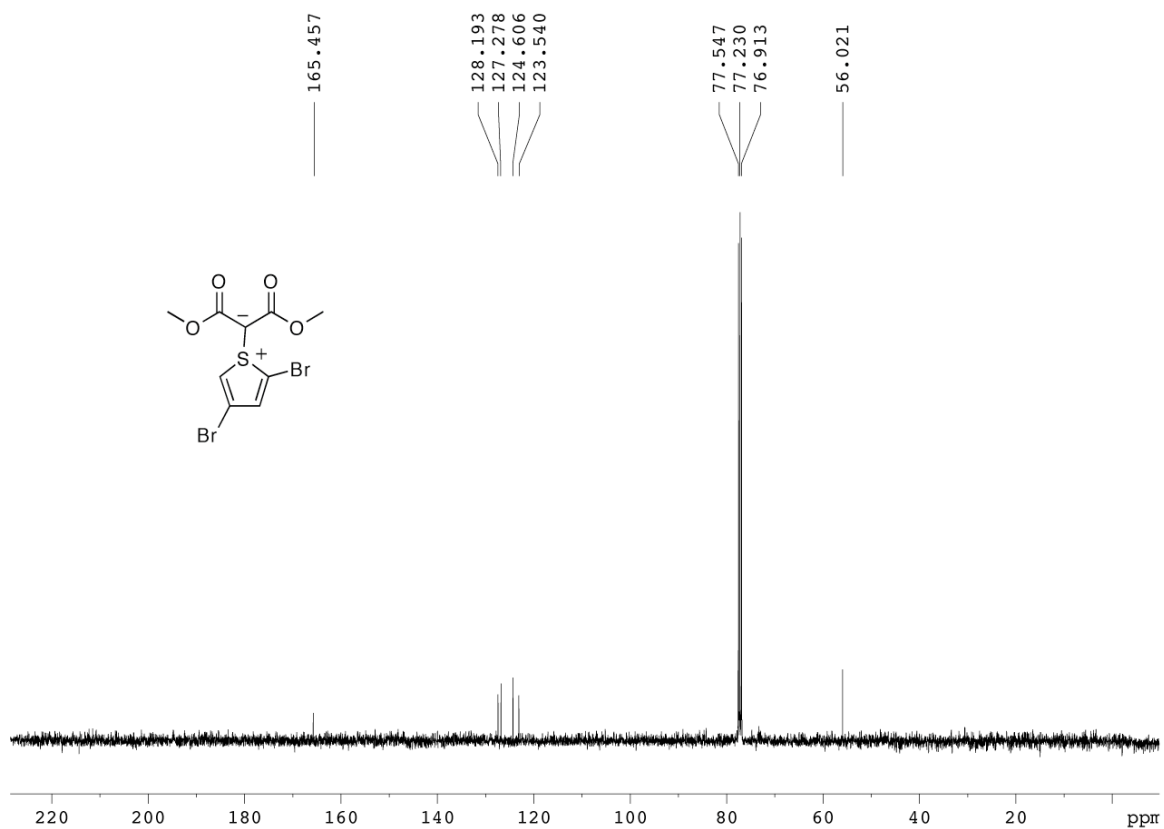
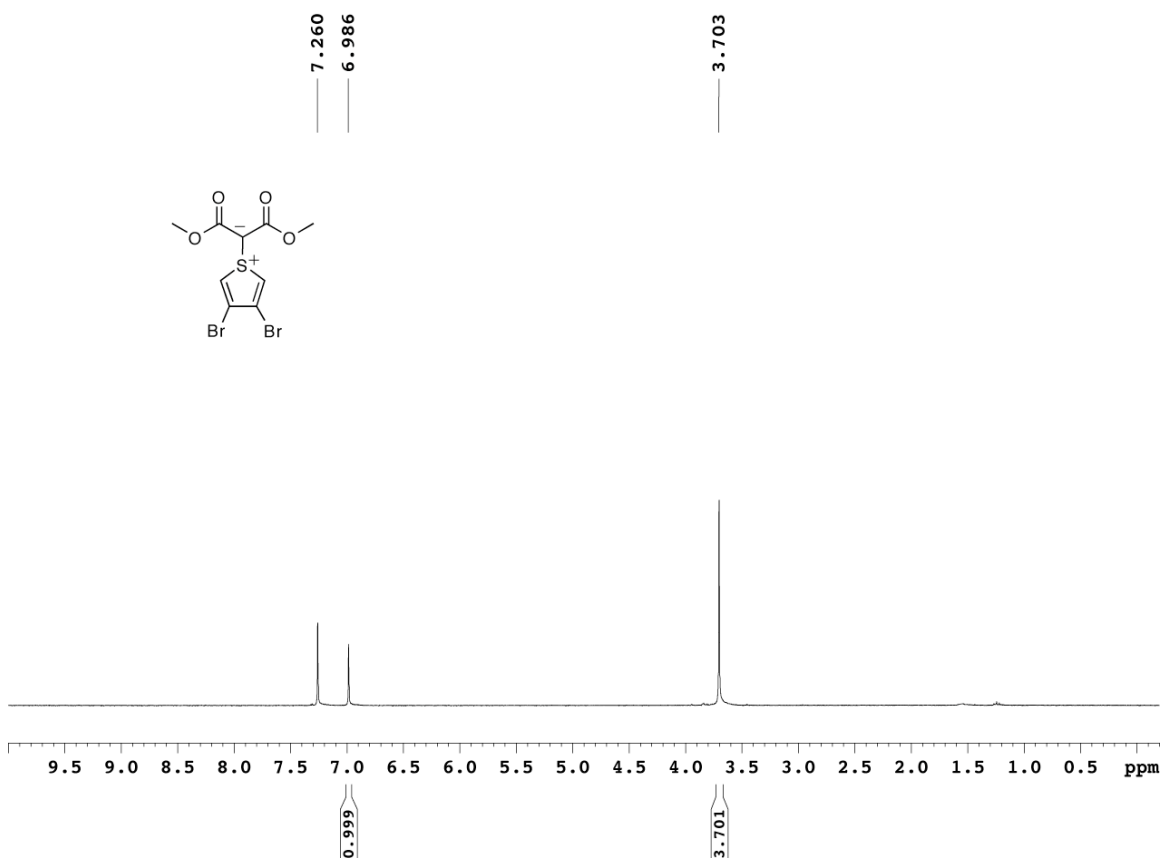


Figure S2. ^{13}C NMR Dimethylmalonate-2,4-dibromothiophene-S,C-ylide (**2c**)

CDCl_3 , 400 MHz

Spectral data for 2d**Figure S3.** ¹H NMR Dimethylmalonate-3,4-dibromothiophene-S,C-ylide (**2d**)CDCl₃, 400 MHz

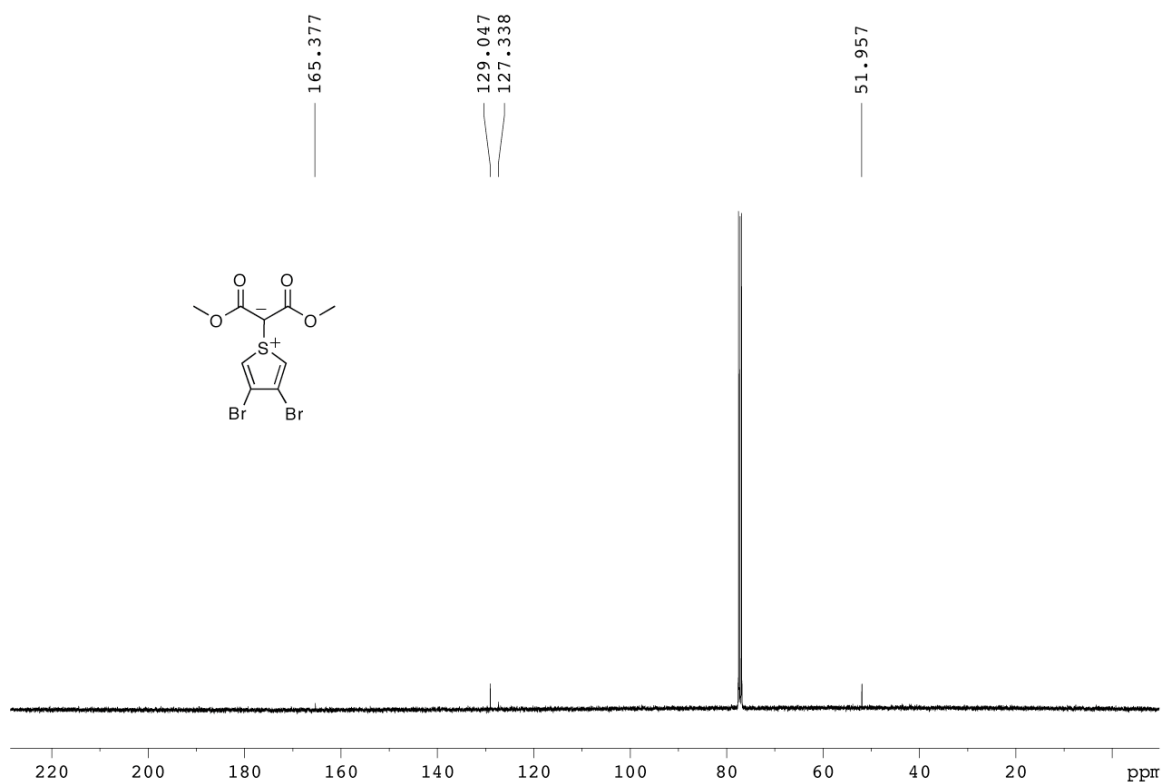
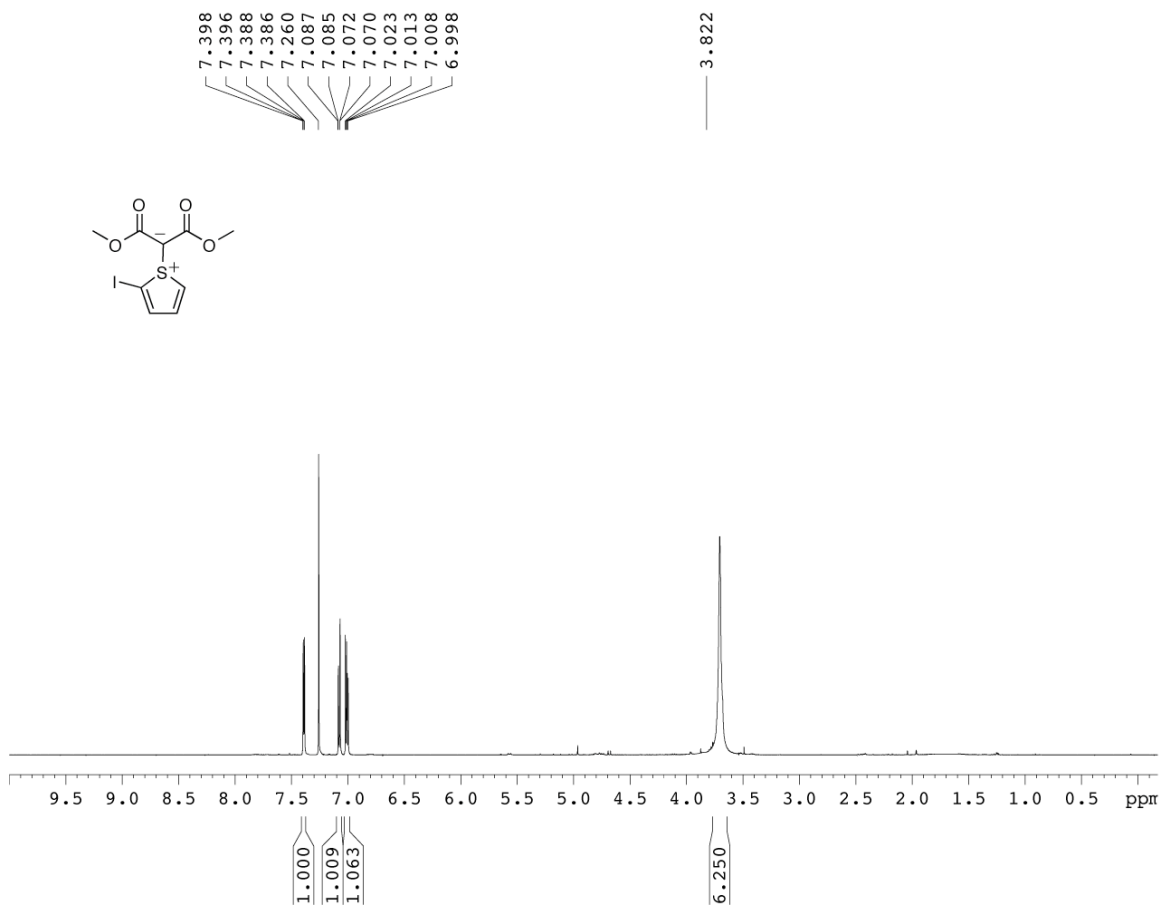


Figure S4. ^{13}C NMR Dimethylmalonate-3,4-dibromothiophene-S,C-ylide (**2d**)

CDCl₃, 400 MHz

Spectral data for 2e**Figure S5.** ¹H NMR Dimethylmalonate-2-iodothiophene-S,C-ylide (**2e**)CDCl₃, 400 MHz

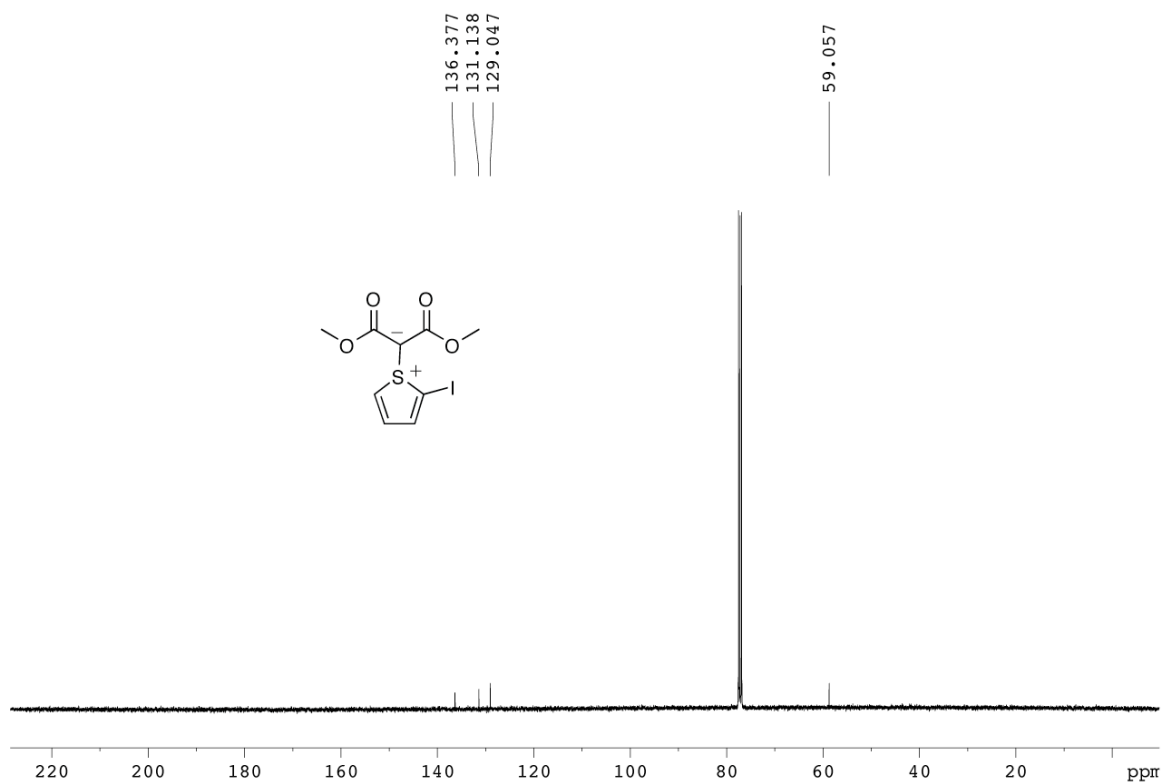
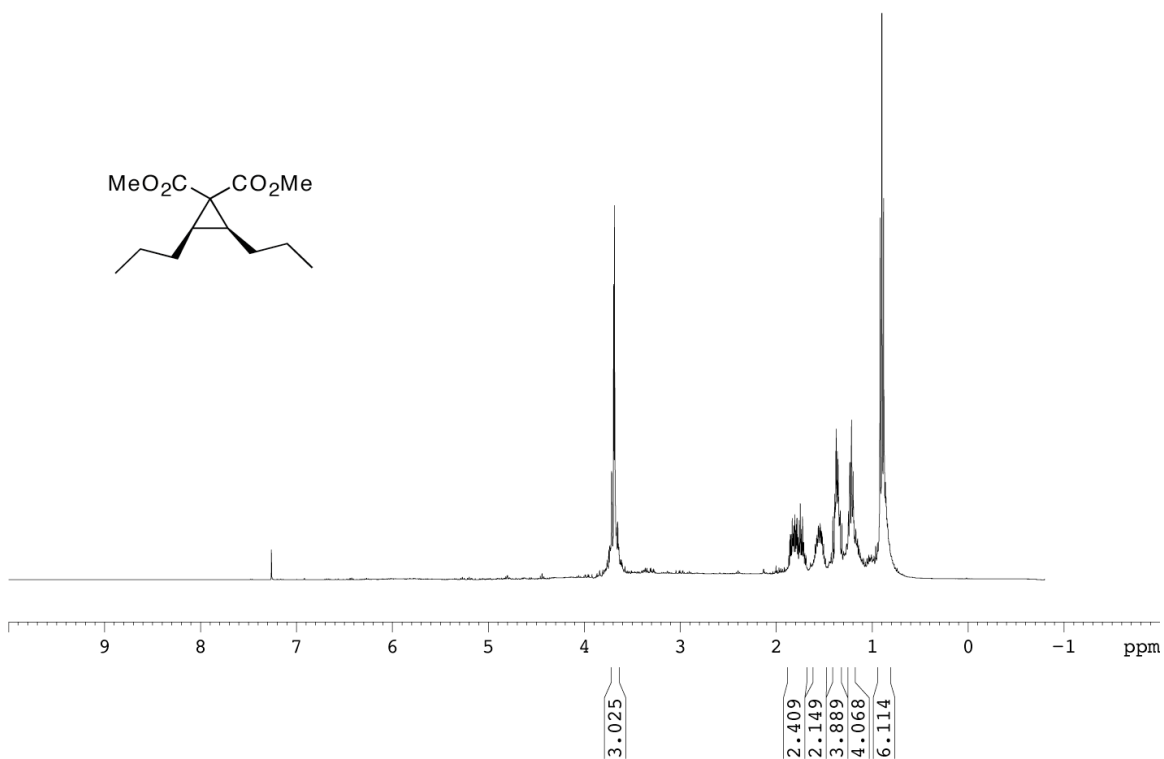
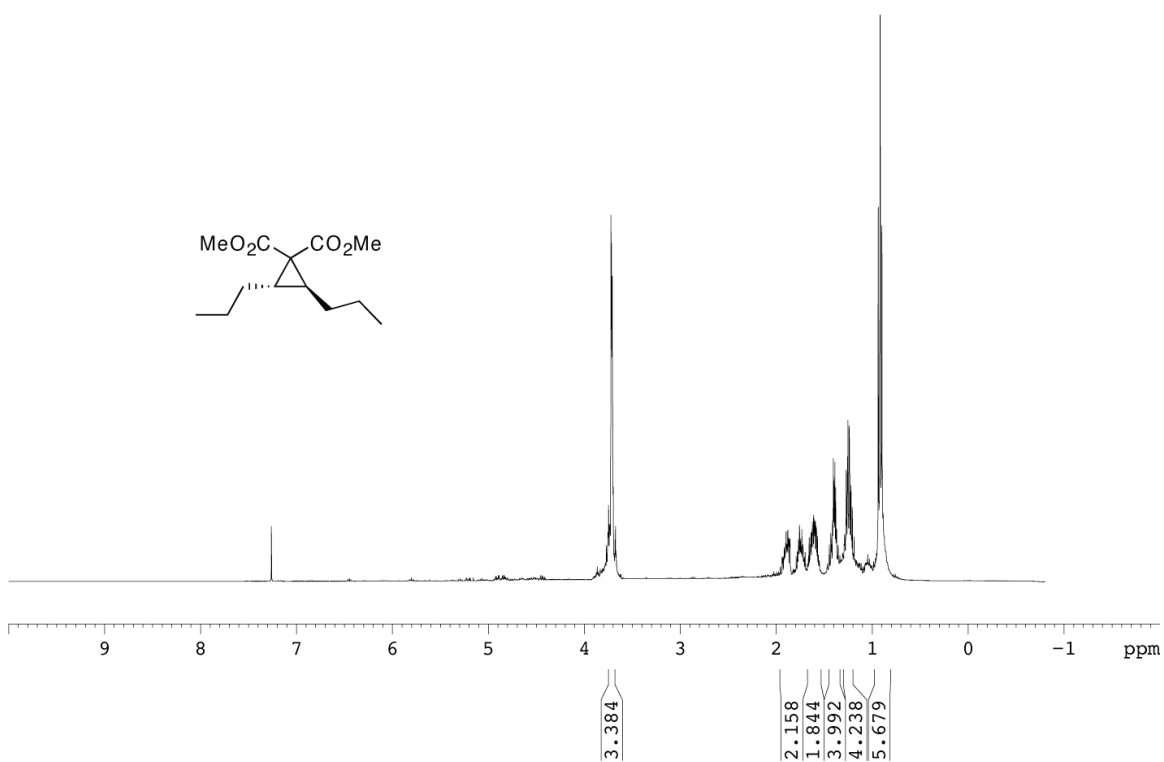


Figure S6. ^{13}C NMR Dimethylmalonate-2-iodothiophene-S,C-ylide (**2e**)

CDCl_3 , 400 MHz

Spectral data for 6**Figure S7.** ¹H NMR *cis*-2,3-dipropyl-1,1-dicarbomethoxycyclopropane (**6**)CDCl₃, 400 MHz

Spectral data for 7**Figure S8.** ¹H NMR *trans*-2,3-dipropyl-1,1-dicarbomethoxycyclopropane (7)CDCl₃, 400 MHz

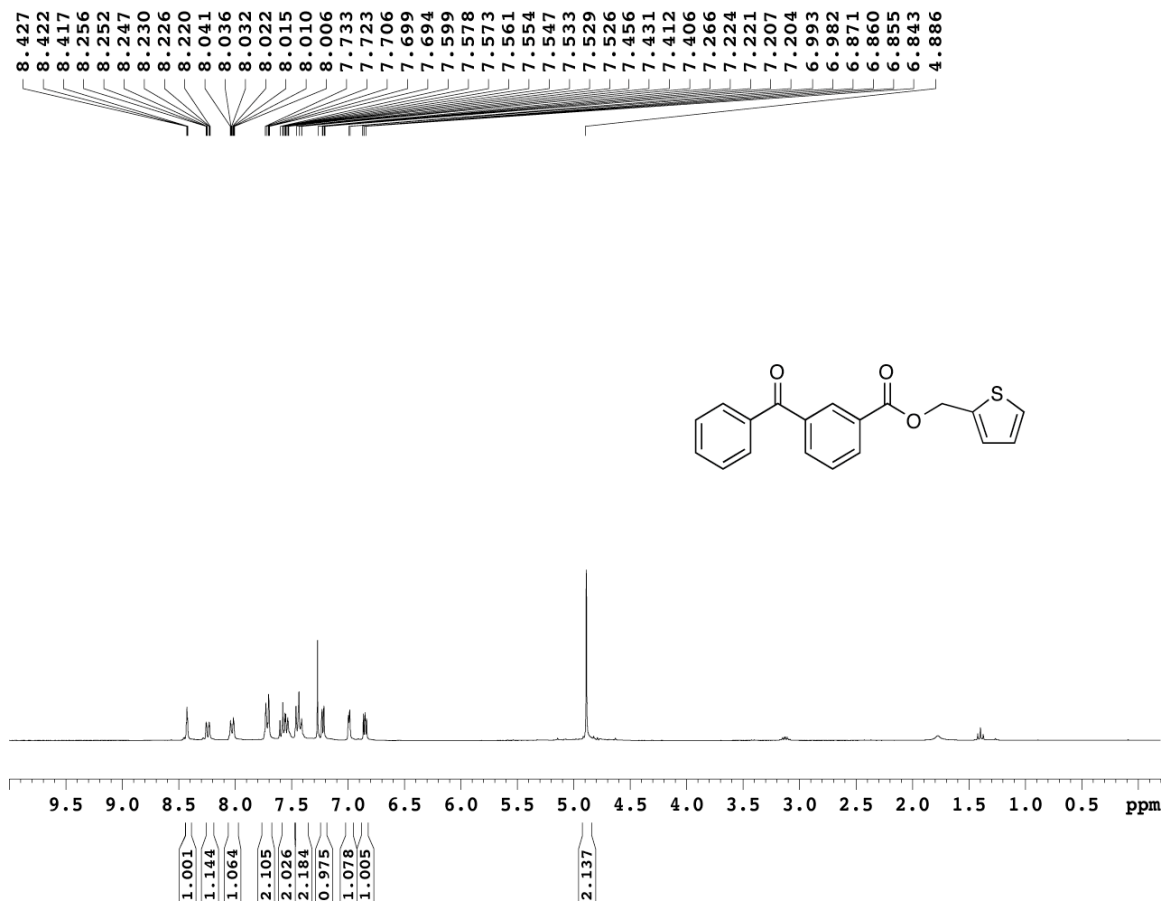
Spectral data for **8**

Figure S9. ¹H NMR 3-Benzoyl benzoic acid thiophen-2-yl-methyl ester (**8**)

CDCl₃, 400 MHz

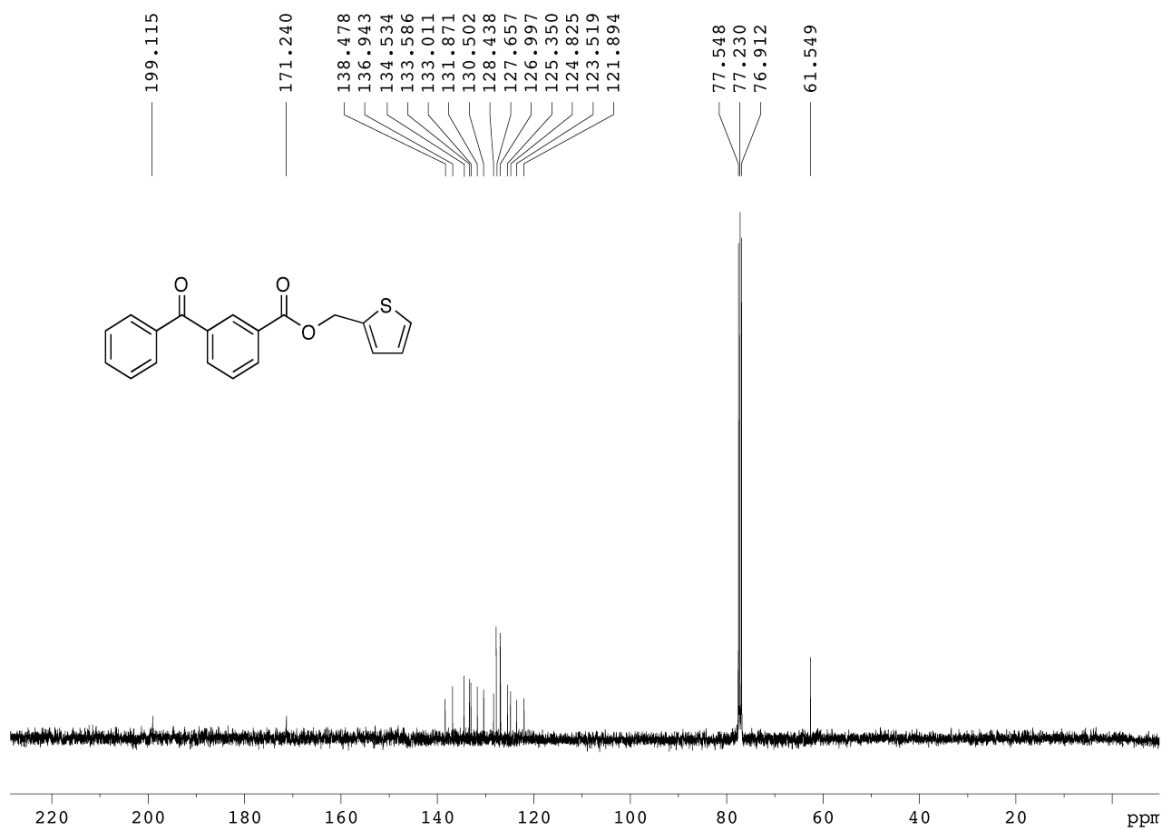


Figure S10. ^{13}C NMR 3-Benzoyl benzoic acid thiophen-2-yl-methyl ester (**8**)

CDCl_3 , 400 MHz

Spectral data for 9

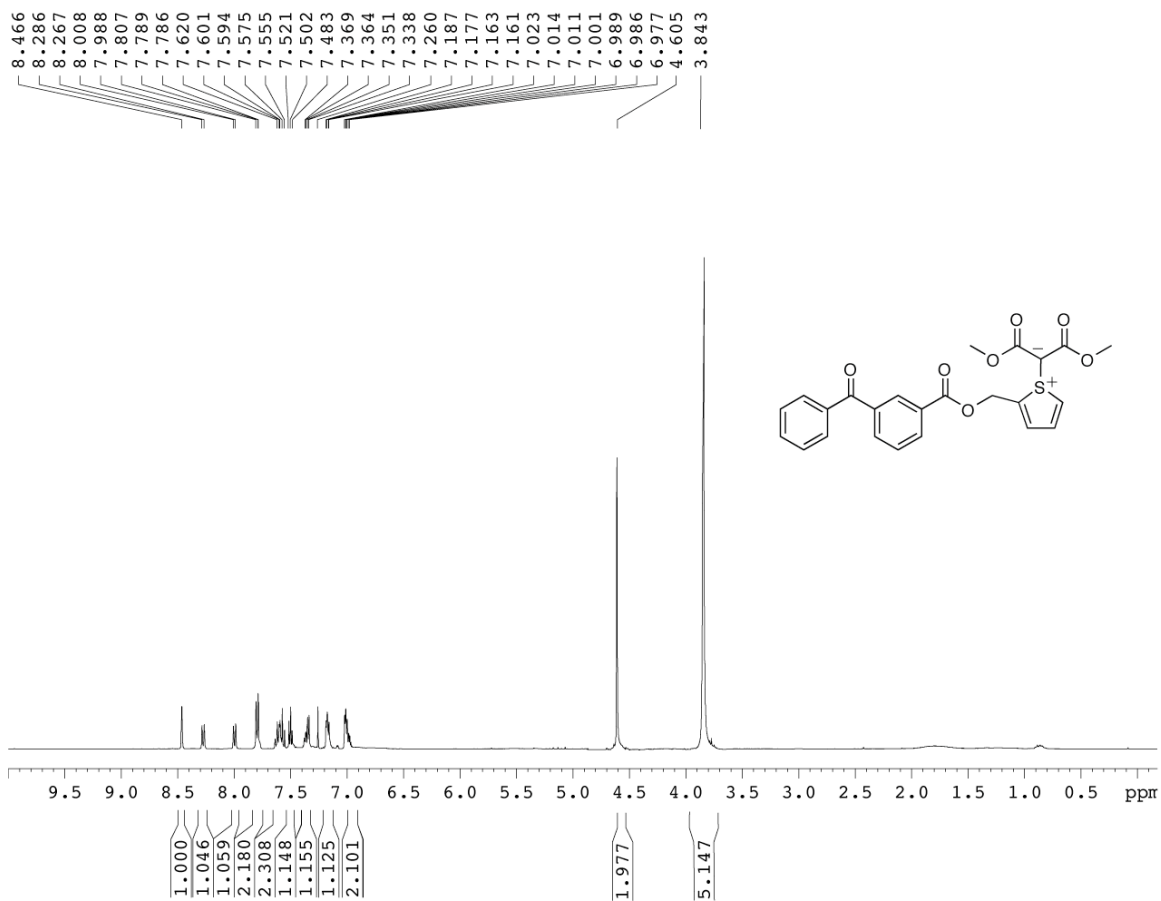


Figure S11. ^1H NMR Dimethylmalonate-(3-benzoyl benzoic acid thiophen-2-yl-methyl ester)-S,C-ylide (**9**)

CDCl_3 , 400 MHz

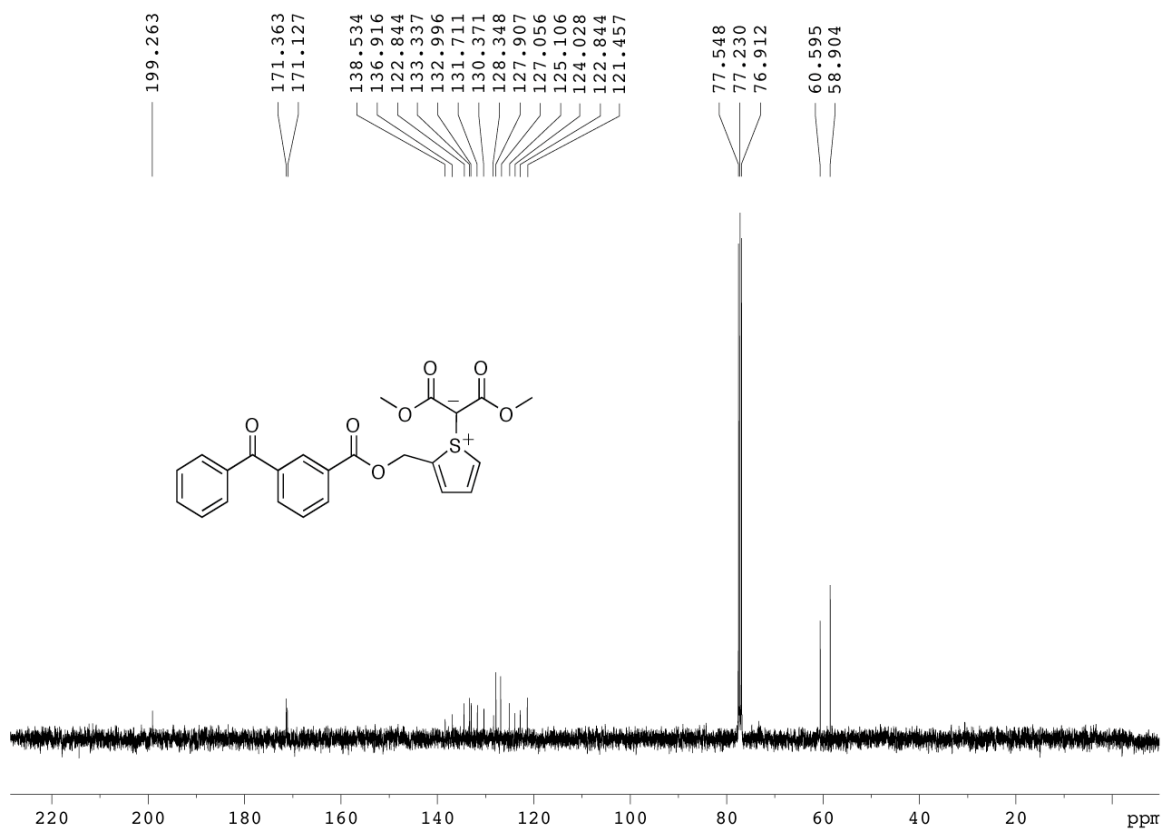
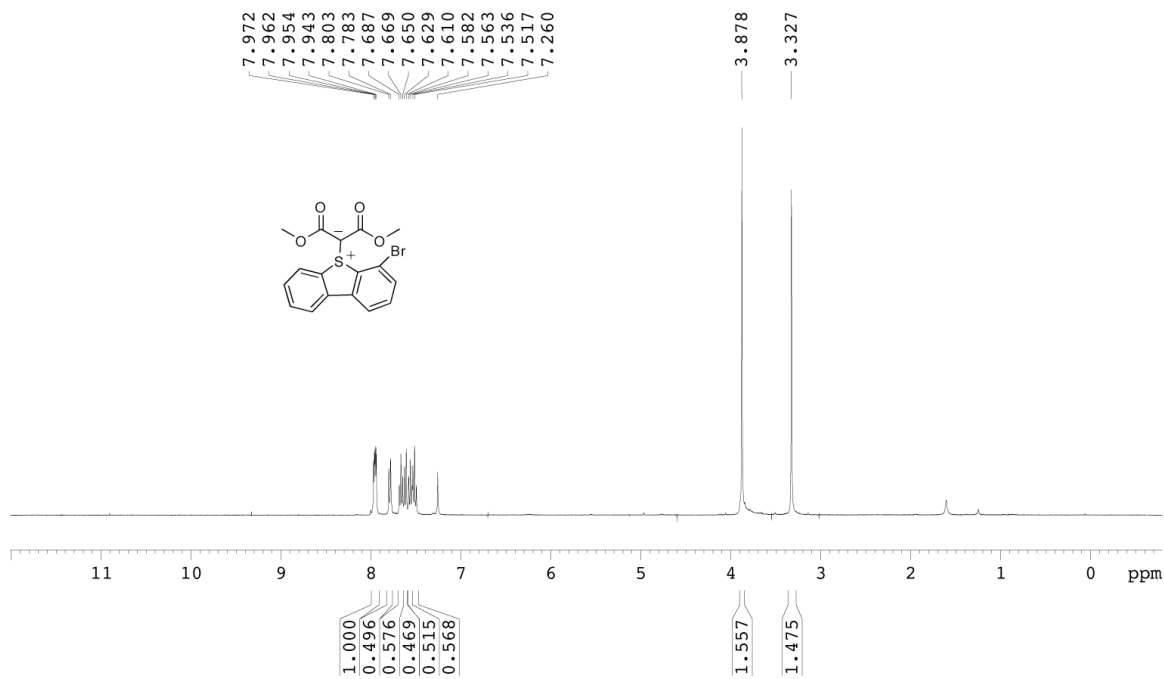


Figure S12. ¹³C NMR Dimethylmalonate-(3-benzoyl benzoic acid thiophen-2-yl-methyl ester)-S,C-ylide (**9**)

CDCl₃, 400 MHz

Spectral data for 10a**Figure S13.** ¹H NMR Dimethylmalonate-4-bromodibenzothiophene-S,C-ylide (**10a**)CDCl₃, 400 MHz

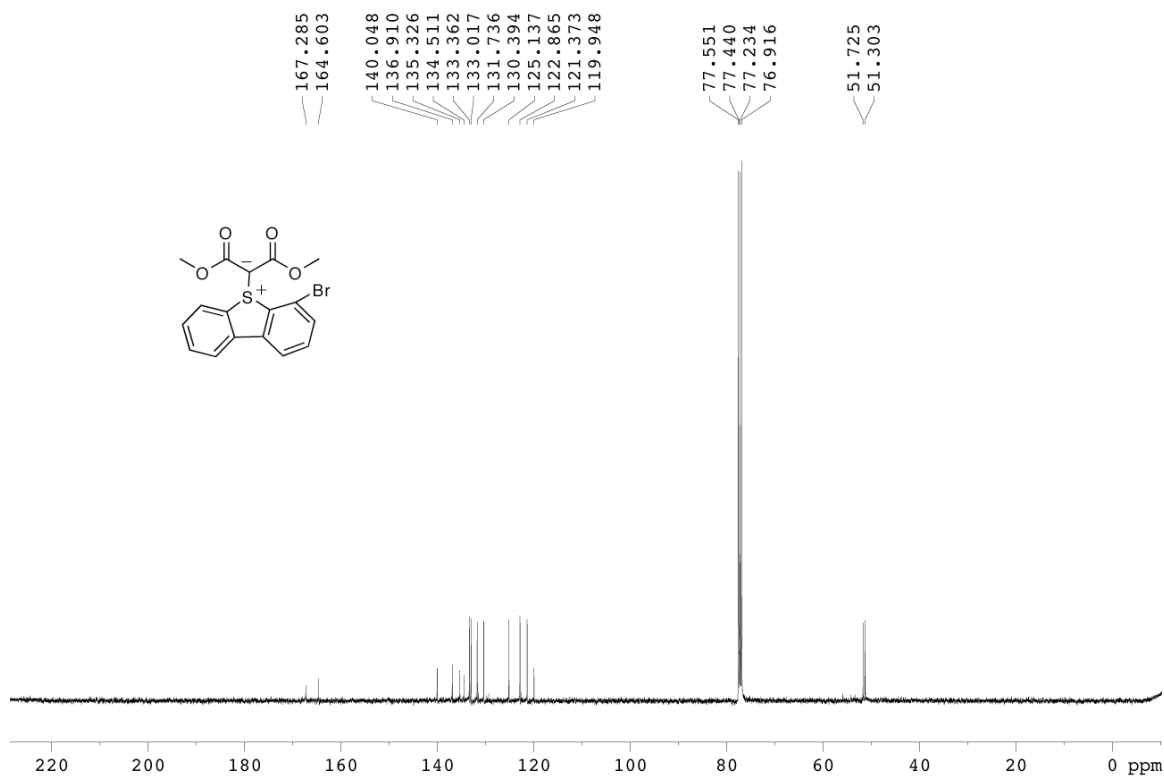
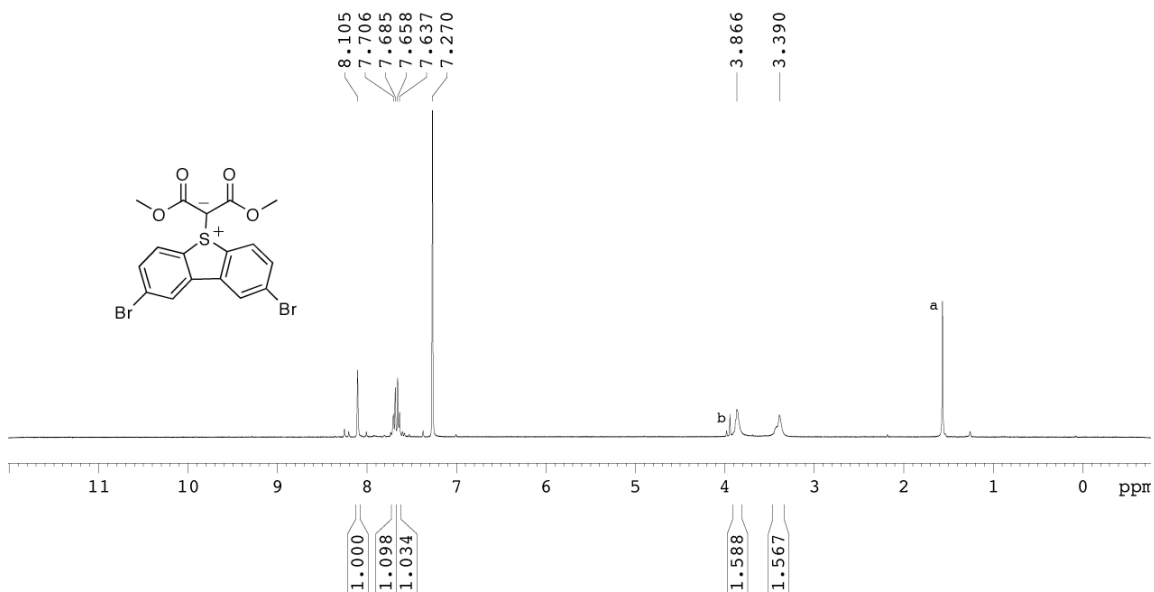


Figure S14. ^{13}C NMR Dimethylmalonate-4-bromodibenzothiophene-S,C-ylide (**10a**)

CDCl_3 , 400 MHz

Spectral data for 10b**Figure S15.** ¹H NMR Dimethylmalonate-2,8-dibromodibenzothiophene-S,C-ylide (**10b**)CDCl₃, 400 MHz

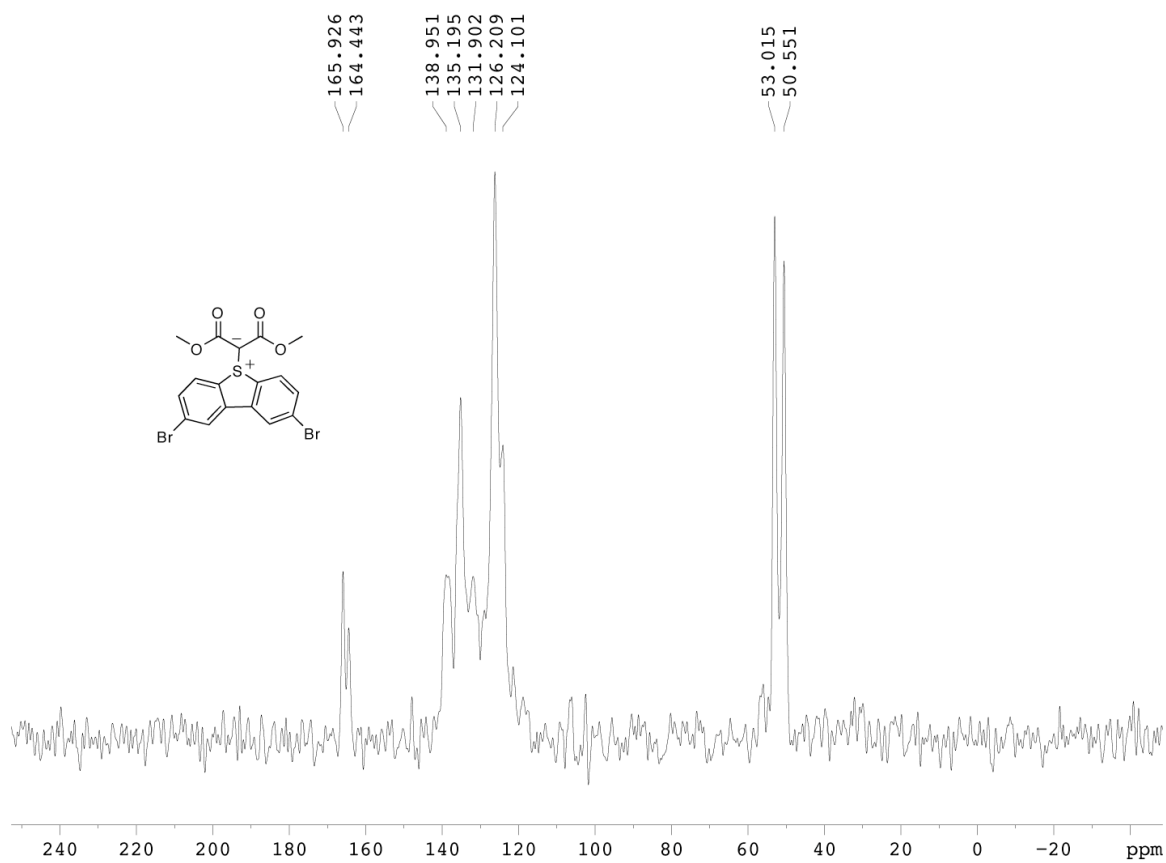


Figure S16. ^{13}C NMR Dimethylmalonate-2,8-dibromodibenzothiophene-S,C-ylide (**10b**)

Solid state, 400 MHz

Table S1. Thermal Decomposition of ylides in the presence of methanol

Ylide	Yields (%)	
	3^a	4^a
2a	87	0
2b	93	0
2c	92	0
2d	94	0
2e	91	0
9	88	0
10a	85	0
10b	89	0

^a yields are calculated with respect to the % decomposition of the ylide

Table S2. Thermal Decomposition of ylides in the presence of cis-octene

Ylide	Yields	
	6^a	7^a
2a	0	85
2b	0	87
2c	0	83
2d	0	91
2e	1	89
9	2	90
10a	0	85
10b	0	89

^a yields are calculated with respect to the % decomposition of the ylide