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Generation and Reactions of Cyclopropyl Vinylidene Carbenes

Nguyen Nhat Thu Le

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Generation and Reactions of Cyclopropyl Vinylidene Carbenes

By Nguyen Nhat Thu Le

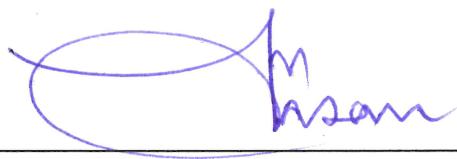
A Thesis Presented to the Department of Chemistry,
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With Honors in Chemistry

Submitted May, 2019

Generation and Reactions of Cyclopropyl Vinylidene Carbenes

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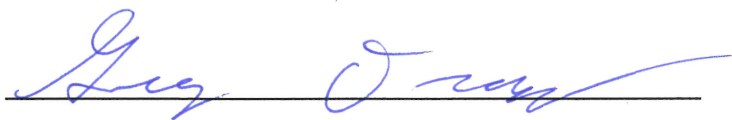
Approved:

A handwritten signature in blue ink, appearing to read 'Dasan', written over a horizontal line.

(Mentor: Dasan Thamattoor, Professor of Chemistry)

May 20, 2019

Date

A handwritten signature in blue ink, appearing to read 'Greg Drozd', written over a horizontal line.

(Reader: Greg Drozd, Assistant Professor of Chemistry)

May 20, 2019

Date

Vitae

Nguyen Nhat Thu Le, known to her friends as Thu, was born on November 9, 1996 to Ba Tung Le and Thi Le Hang Nguyen. She grew up in Nha Trang, Vietnam and went to Le Quy Don High School for the Gifted with a specialization in chemistry. In 2013, she transferred to Saint Joseph's Institution International in Singapore and earned the International Baccalaureate Diploma in 2014.

Thu entered Colby College, Waterville, ME in September 2015. Her original plan was to become a medicinal chemist. She started learning computational chemistry with Prof. Nicholas Boekelheide in her first year and then joined Prof. Dasan Thamattoor's organic chemistry research lab in her sophomore year. Beside synthesizing peculiar, highly strained and twisted organic compounds, the most memorable experiences Thu has had in the Das lab was participating in ISRIUM 2017, mentoring Katherine and Noah, two high school students working in the Das lab in summer 2017, and working with other Das lab members at Hiroshima University in summer 2018.

Thu will graduate on May 26th, 2019 with a Bachelor of Arts in Chemistry-Biochemistry and Science, Technology and Society. In fall 2019, she will start her PhD in Environmental Health Sciences at the University of Michigan, studying water quality and microbiology.

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A special thanks to all the Professors in the Colby Chemistry Department. You taught me a lot about science, but even more about the value of hard work and the joys of teaching and researching chemistry. Part of the reason I want to become a professor in the future is because of all the wonderful teachers, mentors, and professors I have had.

Finally, I am extremely grateful to my research supervisor, Professor Dasan Thamattoor. Das is the best mentor anyone could ask for, always so kind, nurturing, humorous, knowledgeable, and going the extra mile for the students. Taking organic chemistry with him and working in his lab were amazing experiences that I will not forget. My hope for the future is to become a great professor and mentor like Das.

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Abstract

This study aimed to generate cyclopropyl methyl vinylidene carbene and cyclopropyl phenyl vinylidene carbene via photochemical routes. The precursors to these two carbenes were synthesized from phenanthrene by a two-step procedure. However, these precursors could not be fully purified because the second step generated many side products with similar properties as the precursors. A crude sample of each precursor were photolyzed with UV light in the range of 315 to 400 nm. Vinylidene carbenes are known to rapidly rearrange into alkynes, so the formation of these cyclopropyl vinylidene carbenes was monitored through the formation of their rearrangement products, cyclopropyl methyl acetylene and cyclopropyl phenyl acetylene. Photolysis of the methyl-substituted precursor did not result in cyclopropyl methyl acetylene, either because the carbene was not generated or because the carbene failed to rearrange into the alkyne. In addition, two isomers of the methyl-substituted precursor were detected, which possibly formed via a 1,5-sigmatropic carbon shift and ring opening of the precursor. Photolysis of the phenyl-substituted precursor, in contrast, produced cyclopropyl phenyl acetylene, indicating that the carbene was successfully generated. Computational results show that both carbenes are singlets in their ground states, with singlet-triplet gaps of 45.4 kcal/mol for the methyl-substituted carbene and 41.9 kcal/mol for the phenyl-substituted carbene. Regarding the rearrangement of cyclopropyl methyl vinylidene carbene into the corresponding alkyne, the cyclopropyl shift is more favorable than the methyl shift by 3.9 kcal/mol. However, for the cyclopropyl phenyl vinylidene carbene, the cyclopropyl shift is less favorable than the phenyl shift by 5.4 kcal/mol.

Introduction

1.1. Overview of Carbene Chemistry

Carbenes are neutral intermediates that have a carbon with only two covalent bonds instead of four. The divalent carbon has two non-bonding electrons and lacks a full octet, so carbenes are extremely reactive and have short lifetimes, usually on the order of nanoseconds.¹ However, a small number of carbenes are stable enough to be isolated at room temperature in solid or dissolved state.²⁻⁴ The divalent carbon of a carbene generally has two substituents (Figure 1.1).

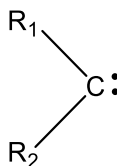


Figure 1.1. General structure of carbenes.

Efforts to generate the simplest carbene, methylene (where R₁ = R₂ = H), began in the 1830s, when the tetravalency of carbon had not been established and carbenes were speculated to be stable species.⁵ After Staudinger and his associates successfully generated methylene from diazomethane in the early 20th century,⁶ carbenes were finally recognized as transient intermediates.⁵ In the 1950s, Doering, Winstein and Woodward coined the term “carbene”.⁷ Doering was also the first to report the formation of dichlorocarbene and its addition to alkenes – one of the characteristic carbene reactions known today.⁸ From then, research on carbenes has rapidly proliferated. In 2018, for example, carbenes were mentioned in more than two thousand publications in the Chemical Abstract Service’s database.

Carbenes are capable of a wide range of chemical reactions including addition to double and triple bonds, insertions into C–H bonds, dimerization and rearrangement.⁹ Because of their instability and high reactivity, carbenes have numerous applications ranging from organic synthesis to metal complex formation and catalysis.⁴

1.2. Electronic Structure

In terms of electronic structure, a carbene can be either a singlet (spin multiplicity = 1) or a triplet (spin multiplicity = 3). In this section, only carbenes in which the divalent carbon has two substituents are considered (Figure 1.2). In the singlet state, the two non-bonding electrons have antiparallel spins and occupy the same sp^2 -like-orbital. In contrast, in the triplet state, the two non-bonding electrons have parallel spins and occupy different orbitals. In principle, the divalent carbon of a triplet carbene can be either sp - or sp^2 -hybridized, but in reality, most triplet carbenes have a mixture of these two hybridization states and thus have a bent geometry. For example, the H-C-H bond angle in methylene is between 130° and 150° , which is between the sp and sp^2 bond angles. Since this type of carbenes are hardly ever purely sp -hybridized, their frontier orbitals are denoted by σ (for the non-bonding orbital with more s character) and $p\pi$ (for the p orbital).⁹



Figure 1.2. The singlet and triplet electronic structures of a carbene in which the divalent carbon has two substituents.

Whether the ground state of a carbene is singlet or triplet depends on the energy gap between the σ and $p\pi$ orbitals. If the two frontier orbitals are close in energy, the triplet state is favored.¹⁰ This is true for most carbenes, since the reduced electron-electron repulsion in the triplet state usually compensates for the $\sigma - p\pi$ energy gap.⁹ In contrast, if the σ orbital is much lower in energy than the $p\pi$ orbital, the two non-bonding electrons will preferably occupy the σ orbital, leading to a singlet ground state.¹⁰ Therefore, the singlet state is stabilized by substituents that are σ -electron withdrawing, which lower the energy of the σ orbital, and substituents that are π -electron donating, which increase the energy of the $p\pi$ orbital. Prime examples of singlet-ground-state carbenes are dichlorocarbene and many other halogenated carbenes.⁹ The stability of the singlet state of halogenated carbenes can also be explained in terms of resonance structures (Figure 1.3).

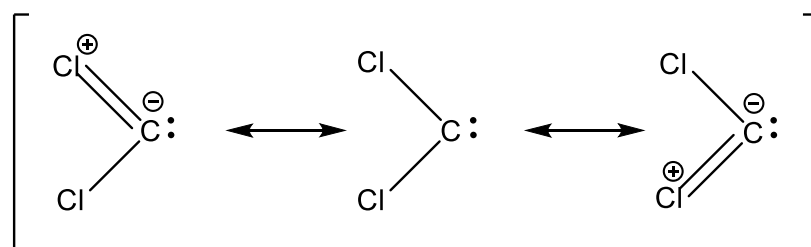


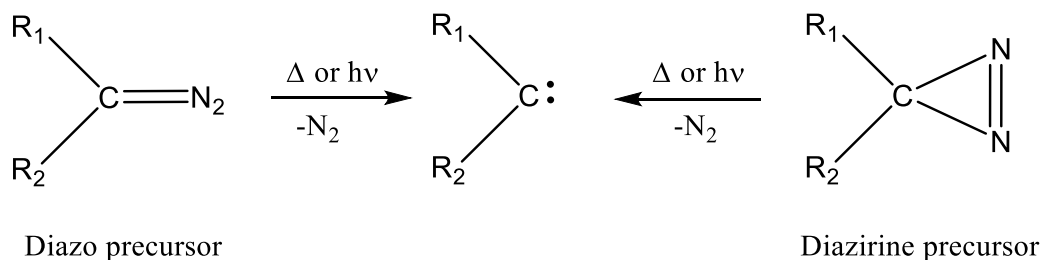
Figure 1.3. Resonance structures of dichlorocarbene.

Since singlet carbenes have one filled σ orbital and one empty $p\pi$ orbital, they can theoretically be either nucleophilic or electrophilic.⁵ In reality, however, most carbenes are electrophilic because of their incomplete octet, although strong electron-donating substituents like amino groups, methoxy groups and alkylsulfanyl groups may allow a singlet carbene to act as a nucleophile.⁹ Therefore, singlet carbene can be electrophilic, nucleophilic, or ambiphilic.

Triplet carbenes, on the other hand, are essentially diradicals, so they react in a similar manner as free radicals.⁵

1.3. Generation of Carbenes

Carbenes are commonly generated in situ by two different methods: decomposition of an unstable precursor and α -elimination. For the first method, the carbene is often released from the precursor by pyrolysis or photolysis with the accompanying loss of a small, stable molecule, which provides a thermodynamic drive for the reaction. The most widely used carbene precursors of this type are diazo and diazirine compounds.^{11,12} When heated or exposed to light, these precursors produce carbenes with the concomitant formation of nitrogen gas, an extraordinarily stable product, in an essentially irreversible reaction (Scheme 1.1).

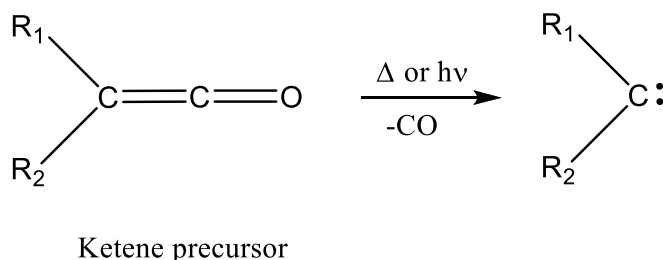


Scheme 1.1. Formation of carbene from diazo and diazirine precursors.

However, this method has many complications. First, diazo and diazirine compounds are explosive and potentially carcinogenic, so they are difficult and dangerous to handle.^{9, 13} Second, the range of substituents that can be put on a diazo or diazirine compound is limited, so this method cannot provide access to certain carbenes.¹⁴ Furthermore, in some cases products previously thought to arise from the carbenes are actually formed directly from the excited state

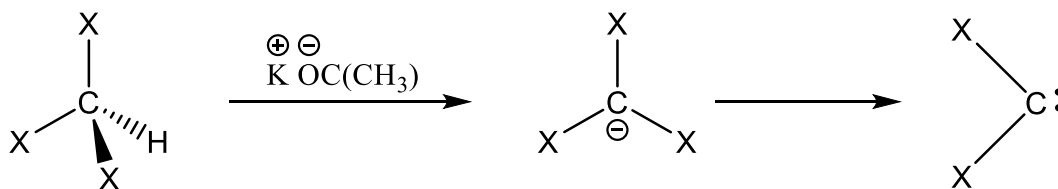
of the diazo or diazirine precursors, which means in those reactions the carbenes were actually never generated.¹⁵

A similar method uses ketene as the precursor (Scheme 1.2) and yields carbon monoxide as the stable byproduct.¹⁶ However, ketene precursors are difficult to synthesize and tend to polymerize under the reaction conditions, so this method is rather inefficient.⁹



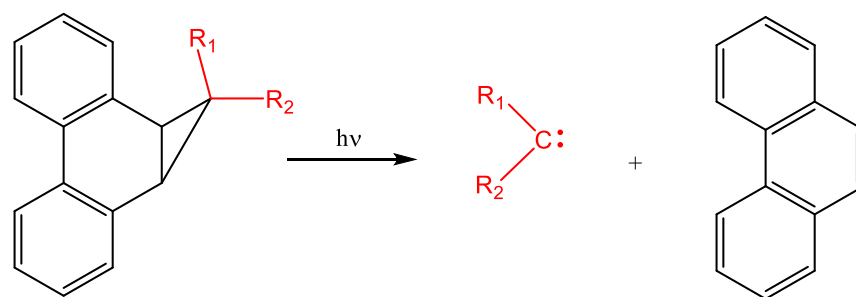
Scheme 1.2. Formation of carbene from a ketene precursor.

Another common strategy for generating carbenes is α -elimination of a haloform by a strong base to yield a dihalocarbene (Scheme 1.3).⁸ A strong base like potassium *tert*-butoxide first deprotonates the haloform to form a carbanion. Next, a halide ion is lost as a leaving group, yielding the desired dihalocarbene. One drawback of this method is that it can only be used to generate dihalocarbenes. In addition, the haloform must be acidic enough to be deprotonated by the base, so the range of carbenes accessible by this method is further limited.



Scheme 1.3. Formation of dihalocarbene via α -elimination of a haloform.

An improved method to generate carbenes that utilizes a phenanthrene-based precursor was developed by Richardson et al. in 1965 (Scheme 1.4).¹⁷ Upon photolysis, the highly strained cyclopropyl ring of the phenanthrene-based precursor is broken, releasing the carbene and phenanthrene. The instability of the cyclopropane ring in the starting material and the high stability of the byproduct phenanthrene are the thermodynamic drivers of this reaction. While this method is somewhat similar to the decomposition of diazo and ketene precursors, phenanthrene-based precursors are much more stable and safer to work with than diazo and diazirine compounds, and often easier to synthesize than ketenes. In addition, many different functional groups can be incorporated into the cyclopropyl ring of this precursor, giving rise to a wide range of carbenes. Therefore, this method was chosen to generate the carbenes of interest in this study.



Scheme 1.4. Formation of carbene from a phenanthrene-based precursor.

1.4. Vinylidene Carbene

In the carbenes mentioned so far, the divalent carbon is bonded to two substituents. However, there is a special class of carbene called vinylidene carbenes, in which the divalent carbon is joined to another atom by a double bond (Figure 1.4). The divalent carbon in a vinylidene carbene is sp -hybridized, so its σ orbital has about 50% s character. Therefore, the σ orbital would be much lower in energy than the $p\pi$ orbital, which explains why all known

vinylidene carbenes have a singlet ground state. This study will focus on the generation of certain vinylidene carbenes from phenanthrene-based precursors (Scheme 1.5).

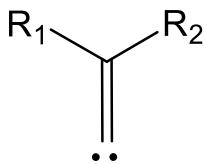
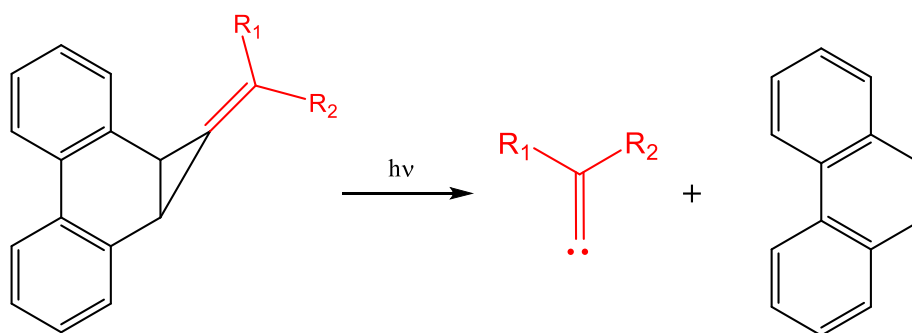
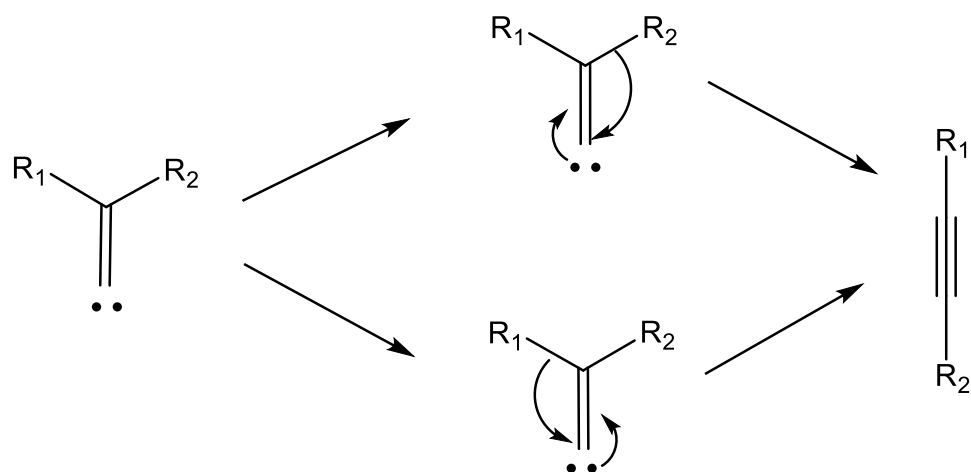


Figure 1.4. Vinylidene carbene.



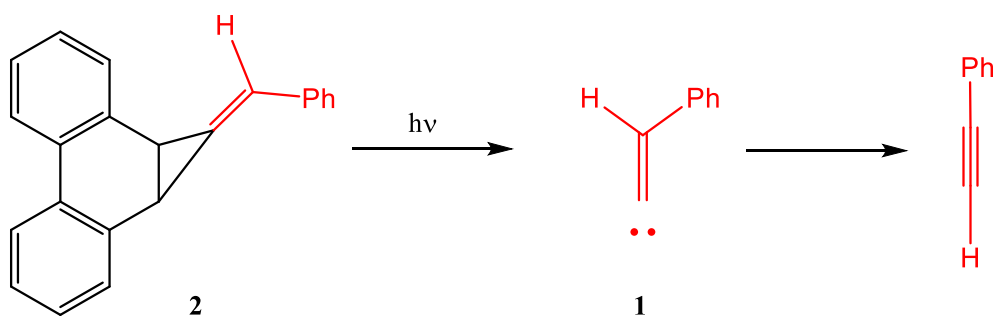
Scheme 1.5. Formation of vinylidene carbene from a phenanthrene-based precursor.

Aside from characteristic reactions of carbenes like dimerization and cyclopropanation, vinylidene carbenes can rearrange to form alkynes.¹⁸ This rearrangement can occur through two pathways, corresponding to the migration of the two substituents R_1 and R_2 (Scheme 1.6). Isotopic labels can be used to ascertain which pathway is more favorable.



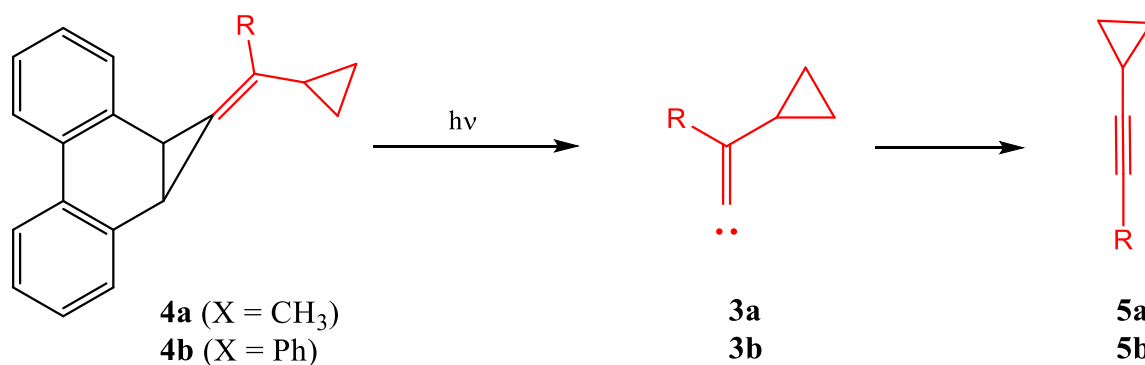
Scheme 1.6. Rearrangement of vinylidene carbenes to form alkynes.

In 2012, Kathryn Moore and Jesus Vidaurri-Martinez in the Thamattoor lab were able to generate the alkyne phenylacetylene from the rearrangement of the vinylidene carbene **1**, which was obtained from the photolysis of precursor **2** (Scheme 1.7). They also determined, using ^{13}C labelling, that the rearrangement occurred exclusively through a 1,2-hydrogen shift.¹⁸



Scheme 1.7. Photochemical generation of phenylacetylene.

This study seeks to further explore such rearrangements by generating the cyclopropyl vinylidene carbenes **3a** and **3b**, which have never been made before, from the precursors **4a** and **4b**. Then, the reactions of carbenes **3a** and **3b**, and their rearrangement into alkynes **5a** and **5b** in particular, will be investigated (Scheme 1.8).

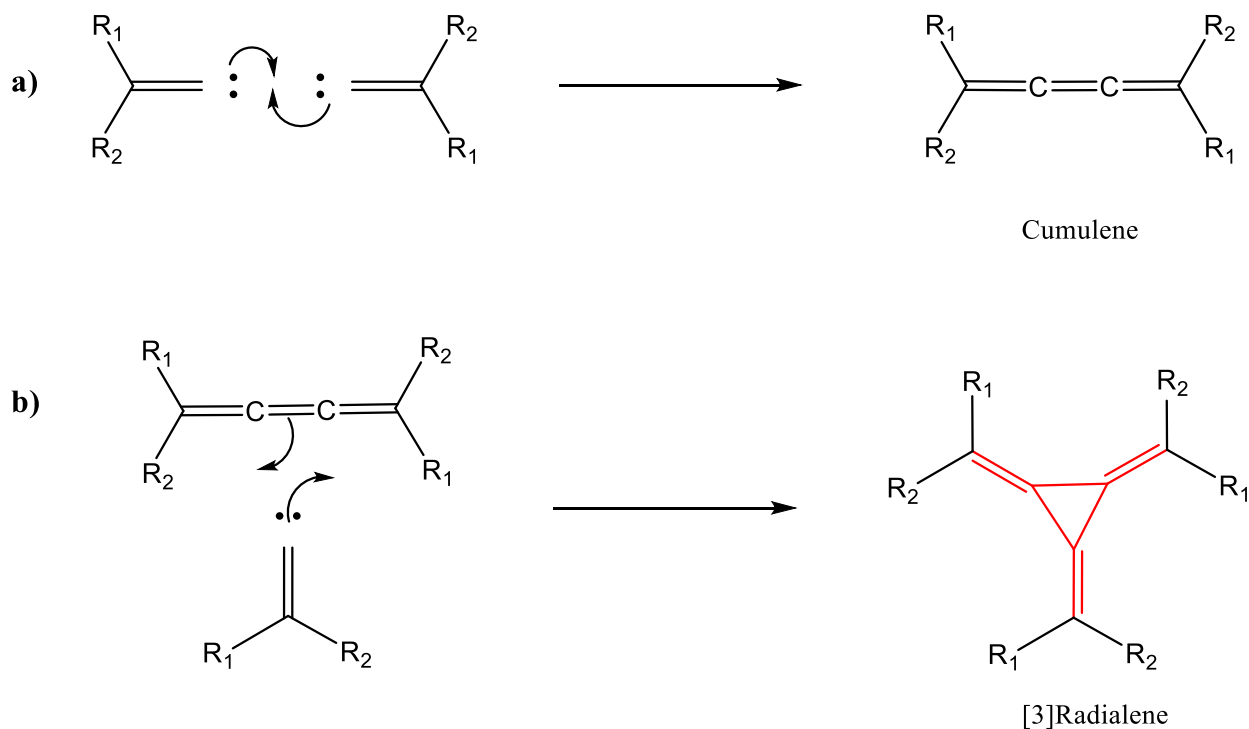


Scheme 1.8. The synthetic targets of this study.

The rearrangements of **3a** into **5a** and **3b** into **5b** are of particular interest because they may occur through a 1,2-cyclopropyl shift, which has not been extensively researched. Most known examples of 1,2-cyclopropyl shift involve opening of the cyclopropyl ring, which has been reported in a few cations and carbenes.^{19,20} This migration often occurs when one carbon in the cyclopropyl ring is adjacent to the positively charged atom of a cation or the divalent carbon of a carbene, causing one bond on that α carbon to shift to the electron-deficient atom. Much rarer are 1,2-cyclopropyl shifts that involve the migration of an entire cyclopropyl group without ring opening, which have only been reported in cations and metal carbene complexes, not free carbenes.^{21,22} In these cases, the cyclopropyl group is not at the α position relative to the electron-deficient atom, but rather at the β position, like in carbenes **3a** and **3b**. If the vinylidene carbenes **3a** and **3b** can be shown to undergo 1,2-cyclopropyl shifts without ring opening to form **5a** and **5b**, these will be the first examples of this type of migration in free carbenes. Therefore, from this point onward, only cyclopropyl shifts without ring opening are considered.

Vinylidene carbenes can also participate in characteristic carbene reactions such as dimerization and cyclopropanation by addition to double bonds. Since singlet carbenes are ambiphilic, they readily dimerize to form an alkene.⁹ In the case of vinylidene carbenes, dimerization yields a cumulene (Scheme 1.9a). When the carbene is generated in the presence of

an alkene, it rapidly adds to the double bond to form a cyclopropane ring.²³ Therefore, after a vinylidene carbene is generated and dimerizes to form a cumulene, there is a chance that the carbene will further react with the cumulene to form a [3]radialene (Scheme 1.9b). Therefore, during the photolysis of precursors **4a** and **4b**, cumulenes and [3]radialenes may arise as side products.



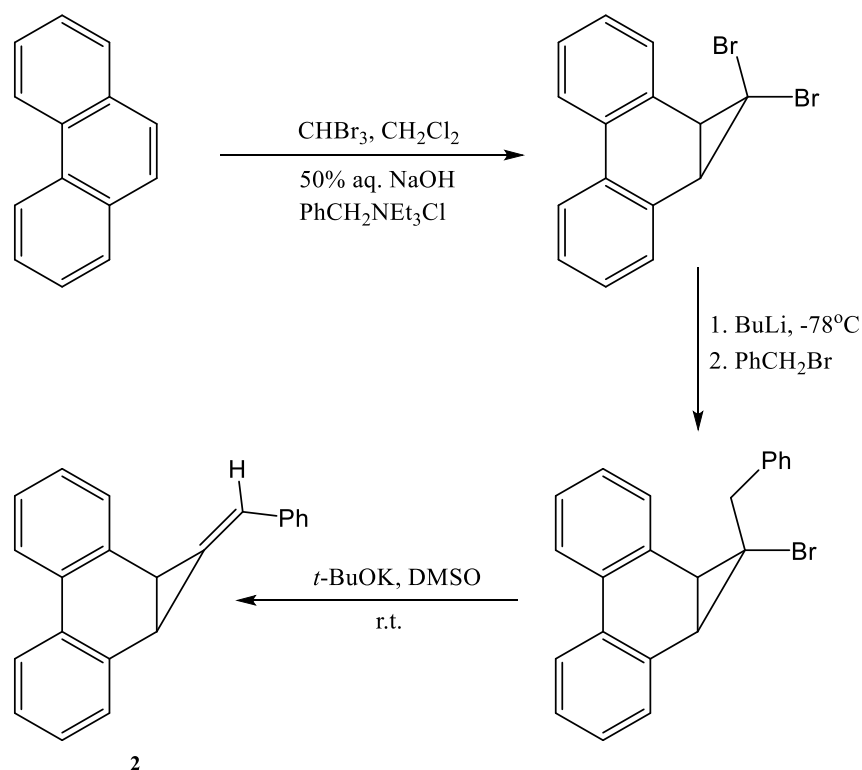
Scheme 1.9. Dimerization of vinylidene carbene to yield a cumulene, and subsequent cycloaddition to produce a [3]radialene.

Radialenes are cyclic compounds with cross-conjugated exocyclic alkene groups. Because of their cross-conjugated electronic structure and their ability to donate as well as receive electrons, radialenes have attracted considerable attention from theoretical and experimental chemists in the past few decades.²⁴ In addition, radialenes' potential as a dopant in organic semiconductors has recently been discovered,²⁵ and [3]radialenes have been noted to

possess unique electrochemical and optical properties.²⁶ While [3]radialenes have been successfully synthesized since 1965,²⁷ the range of procedures for radialene synthesis is still limited.²⁴ Therefore, if [3]radialenes can be produced from vinylidene carbenes like **3a** and **3b**, this study will augment the range of synthetic routes to access this peculiar class of compounds.

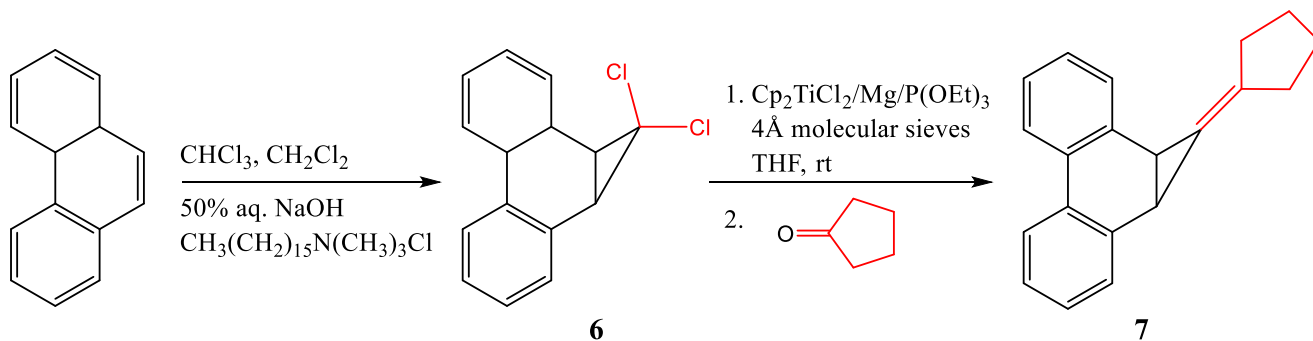
1.5. Synthesis of Precursors to Vinylidene Carbenes

When Moore and Vidaurri-Martinez synthesized precursor **2** in 2012, they used a three-step procedure starting with phenanthrene (Scheme 1.10).¹⁸ In particular, the second step requires butyllithium, a pyrophoric organometallic reagent that is extremely air- and moisture-sensitive. Therefore, this step must be carried out in an inert atmosphere at very low temperatures (about -70°C).



Scheme 1.10. Procedure for the synthesis of precursor **2** from phenanthrene employed by Moore and Vidaurri-Martinez.

However, Maurer and Fan later found that similar vinylidene precursors could be synthesized from phenanthrene in a more efficient two-step procedure (Scheme 1.11).²⁸ In the first step, the dichloro compound **6** is generated from phenanthrene in a similar manner as the first step in Scheme 1.10. Then, a procedure adapted from Takeda et al. was used to synthesize the precursor **7** from **6** and a ketone.²⁹ This circumvents the need to use hazardous reagents like butyllithium. Furthermore, Maurer and Fan's procedure only has two steps, so it requires less time and material to purify intermediate products than the three-step synthetic route used by Kathryn and Vidaurri-Martinez. Therefore, in this thesis, Maurer and Fan's procedure will be employed to synthesize the precursors **4a** and **4b**. Mechanistic details of this procedure will be given in the Results and Discussion.

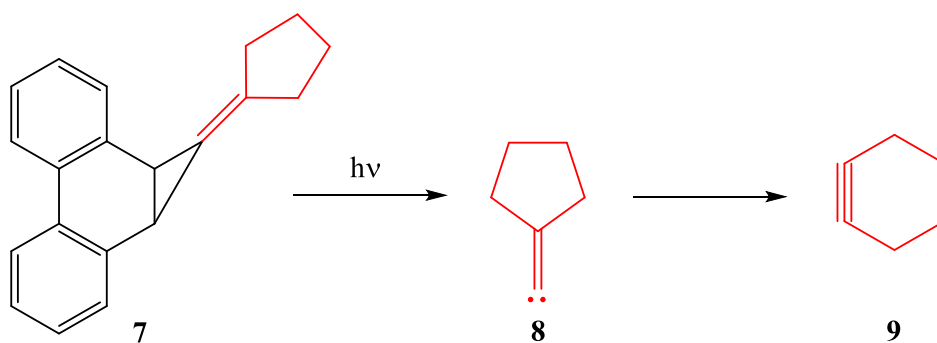


Scheme 1.11. Maurer and Fan's procedure for the synthesis of the vinylidene precursor **7** by a modified Takeda reaction.

1.6. Computational Studies

In addition to experimental work, computational studies were carried out to predict the structure and stability of the precursors, the cyclopropyl vinylidene carbenes and the alkynes produced from carbene rearrangement. These calculations were performed at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level of theory. Previous experimental and computational studies

have always shown the singlet to be the more stable configuration for vinylidene carbenes. For example, Moore and Vidaurri-Martinez found the singlet-triplet gap of carbene **1** to be 38.9 kcal/mol, favoring the singlet state.¹⁸ Maurer and Fan also found the singlet to be the more stable configuration for the cyclopentylidene carbene **8** generated from precursor **7** (Scheme 1.12), which have a singlet-triplet gap of 40.3 kcal/mol.²⁸ Therefore, the singlets carbenes **3a** and **3b** are predicted to be about 40 kcal/mol below the triplets.



Scheme 1.12. The generation of the cyclopentylidene carbene **8** from precursor **7**, and subsequent rearrangement of **8** into cyclohexyne (**9**).

As for the rearrangement of vinylidene carbenes into alkynes, previous studies have found that this process is thermodynamically favorable in general, with a small energy barrier. The rearrangement of carbene **1** has a computed energy change of -43.71 kcal/mol, with virtually no energy barrier for the hydrogen shift and a barrier of 10.24 kcal/mol for the phenyl shift.¹⁸ As for carbene **8**, the barrier of rearrangement into cyclohexyne (**9**) is 9.1 kcal/mol while the computed energy change is -15.1 kcal/mol.²⁸ This energy change is much smaller than the energy change of the rearrangement of **1**, since cyclohexyne is only a transient intermediate at room temperature. Since the alkynes **5a** and **5b**, obtained from the rearrangement of **3a** and **3b**, are

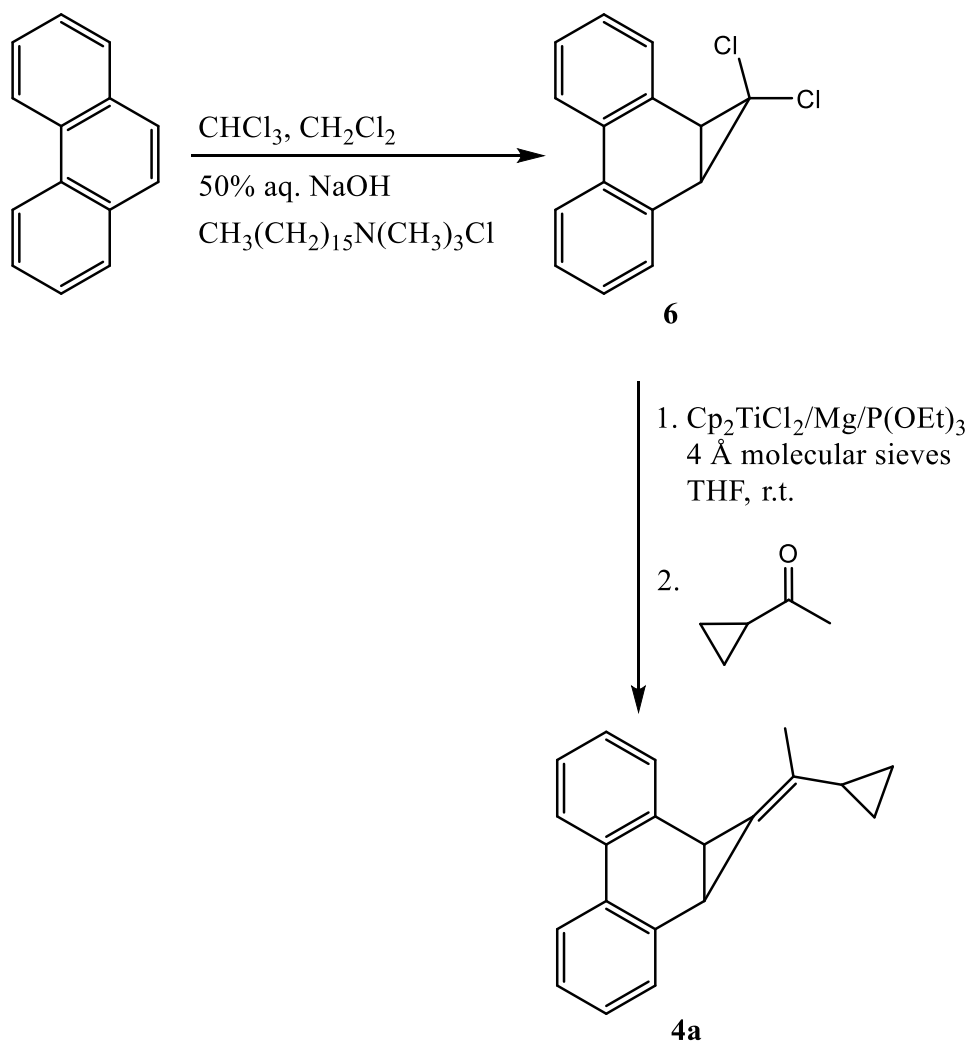
stable compounds, they should be about 40 kcal/mol more stable than the carbenes **3a** and **3b**.

All the energies reported in this study are from CCSD(T) calculations.

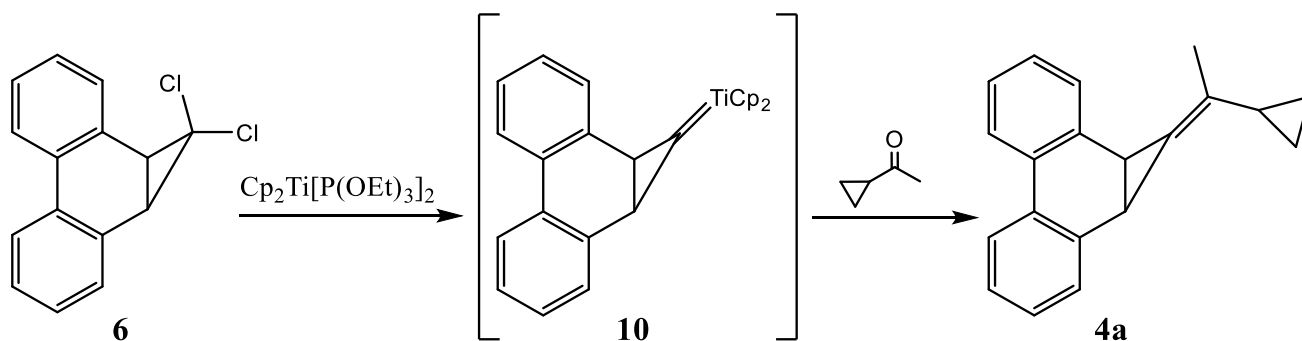
Results and Discussion

2.1. Synthesis of Cyclopropyl Methyl Vinylidene Precursor

The precursor to the cyclopropyl methyl vinylidene carbene (**4a**) was synthesized by a 2-step procedure (Scheme 2.1). The first step was adapted from a phase transfer catalyst method previously reported by Takeuchi et al.³⁰ In this step, the strong base NaOH deprotonates chloroform to form a relatively stable trichloro anion. Chloride is a good leaving group, so the trichloro anion quickly loses a chloride to produce dichlorocarbene, which then adds to the 9,10-double bond of phenanthrene to give rise to **6**. The dichloro compound **6** was the main adduct as the 9,10-bond of phenanthrene has the greatest double bond character in the molecule. Other typical alkene reactions like bromination also occur at the 9,10-bond of phenanthrene.³¹ In the second step, the carbon-chlorine bonds of **6** are reduced by the $\text{Cp}_2\text{Ti}[\text{P}(\text{OEt})_3]_2$ complex, which is generated *in situ* from titanocene dichloride and triethyl phosphite, resulting in the alkylidenetitanocene species **10**.^{29,32} The intermediate **10** then reacts with the carbonyl group of cyclopropyl methyl ketone to form the precursor **4a** (Scheme 2.2).



Scheme 2.1. Synthesis of cyclopropyl methyl vinylidene precursor (**4a**) from phenanthrene via the dichloro compound **6**.



Scheme 2.2. Details of the Takeda reaction to convert dichloro compound **6** into cyclopropyl methyl vinylidene precursor (**4a**) via the alkylidenetitanocene intermediate **10**.

For both steps, isolation and purification of product presented a challenge. Since the product mixture after the first step contained both organic and aqueous phases, the dichloro compound **6** was not fully dissolved, but instead precipitated as a brown solid with many intractable impurities. Therefore, normal extraction procedures often led to significant loss of product. However, if the brown precipitation was completely dissolved in dichloromethane, followed by a normal extraction procedure, then the yield was substantially increased. After extraction, the solid needed to be recrystallized with pure hexanes. Overall, the yield of the first step was 18%, which is a low estimate since part of the product was lost during recrystallization.

An issue with the second step was that aside from the desired precursor **4a**, it generated many side products such as the dihydrogen compound **11** and the monochloro compound **12** (Figure 2.1). Some unreacted dichloro **6** remained in the product mixture as well. These compounds have similar polarity as the precursor **4a**, which made it difficult to purify **4a** by flash chromatography. In fact, most column fractions containing **4a** also contained **6**. Another attempt at purification by preparatory TLC did not yield the pure precursor either. Recrystallization of the precursor was attempted, but this turned out to be a poor strategy since the precursor **4a** apparently rearranged into unknown isomers upon heating (see Appendix A - Figure A.10). Therefore, the precursor **4a** has not been successfully purified. The peak ratio in the ^1H NMR spectrum of the crude product was used to estimate the yield of the second step, which was 6%. Since some of the precursor was lost during workup and flash chromatography, the true yield was likely higher than 6%.

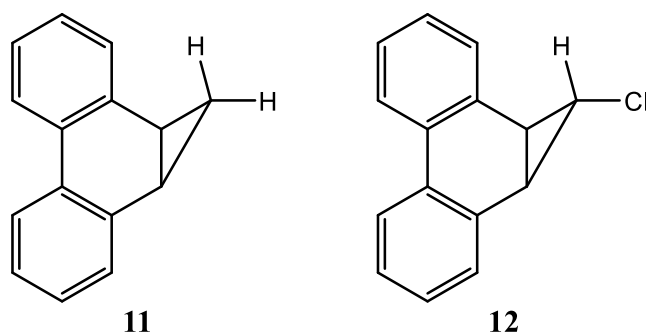
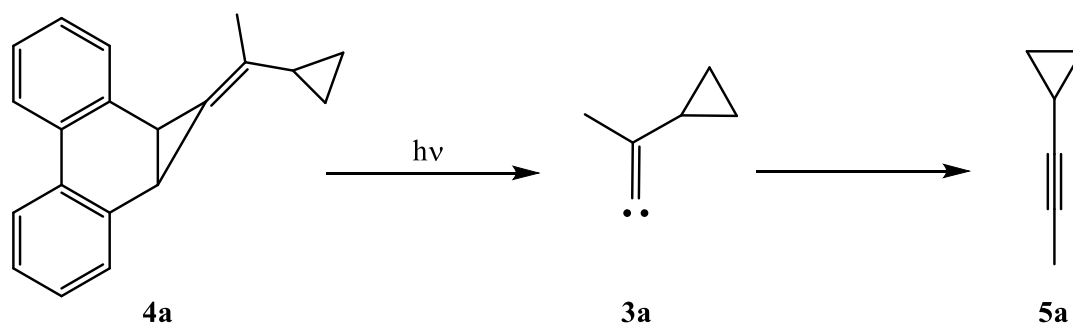


Figure 2.1. Major side products in the second step of the synthesis of **4a**.

In addition, the composition of the product mixture from the second step depended on the time between the additions of **6** and the ketone. In the original procedure, the ketone was added 20 minutes after the dihalogen starting material.²⁹ However, for the dichloro compound **6** and the cyclopropyl methyl ketone in this reaction, following the original procedure caused a significant amount of **6** to remain unreacted. After a few experiments, it was found that as the time between addition of **6** and addition of ketone increased, less of **6** remained unreacted, which was helpful for the purification of **4a**. However, this longer waiting time tended to produce more dihydrogen **11** and reduce the yield of **4a** as well. In the end, increasing the waiting time before adding ketone to 45 minutes gave the highest yield of **4a** while reducing the amount of unreacted **6**.

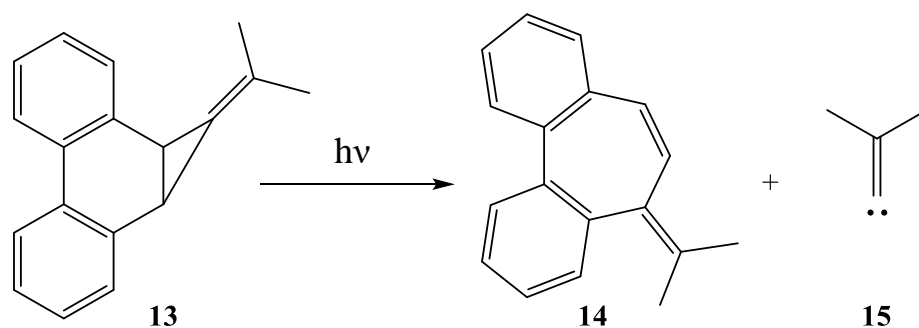
2.2. Generation and Rearrangement of Cyclopropyl Methyl Vinylidene Carbene

The precursor **4a** was not fully purified, so a crude sample of **4a** with **6** as impurity was photolyzed to study the generation of carbene **3a** and its rearrangement into the alkyne **5a** (Scheme 2.3).



Scheme 2.3. Photolysis of the precursor **4a** to generate cyclopropyl methyl vinylidene carbene (**3a**), followed by rearrangement of **3a** into cyclopropyl methyl acetylene (**5a**).

The photolysis was monitored with ^1H NMR and GC/MS. Although the ^1H NMR signal of precursor **4a** decreased over time, no trace of alkyne **5a** was found in the ^1H NMR spectrum. **5a** was not observed in the GC spectrum either, but this could be because this alkyne is highly volatile, so it exited the column before the solvent delay. Therefore, it was inconclusive whether the carbene **3a** was not generated or it was formed but did not rearrange into the alkyne **5a**. However, two new compounds with the same molecular weight as the precursor **4a** appeared at 12.8 and 13.0 minutes on the GC spectrum after photolysis. Therefore, it is possible that the precursor **4a** isomerized upon exposure to UV radiation. The isomerization of a similar phenanthrene-based precursor has been reported before by Hardikar et al. from our lab. In 2015, Hardikar et al. noted that upon photolysis, the dimethyl vinylidene precursor **13** isomerized into **14** by a 1,5-sigmatropic carbon shift and subsequent ring opening, in addition to releasing the dimethyl vinylidene carbene **15** (Scheme 2.4).³³ Therefore, precursor **4a** has probably isomerized in a similar manner. Furthermore, since **4a** is asymmetrical, it most likely resulted in two isomers, **16** and **17**, rather than one as in the case of **13** (Figure 2.2).



Scheme 2.4. Upon photolysis, the dimethyl vinylidene carbene precursor (**13**) produces **14** by isomerization and the carbene **15**.

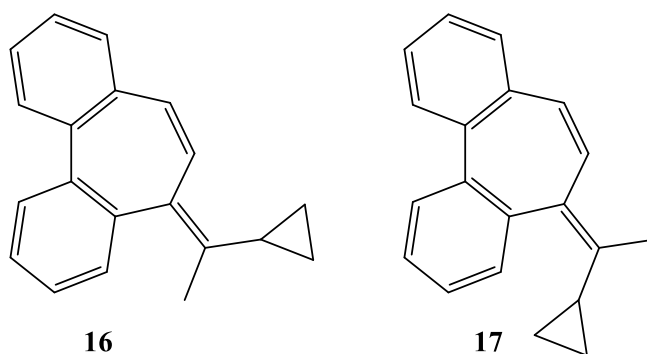


Figure 2.2. Possible structures of the two new compounds formed during the photolysis of precursor **4a**.

2.3. Computational Results for Cyclopropyl Methyl Vinylidene Carbene

Computational models were used to calculate the optimized geometries and energies of the cyclopropyl methyl vinylidene carbene precursor (**4a**), the resulting carbene (**3a**), the rearrangement product cyclopropyl methyl acetylene (**5a**), and the two transition states. The optimized geometry of **4a** is shown in Figure 2.3, while computational results for the other species are shown in Figure 2.4. All species were computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level of theory.

The singlet **3a** is more stable than the triplet by 45.4 kcal/mol. This singlet-triplet gap is similar to other vinylidene carbenes generated by members of our lab.^{18,28} In addition, cyclopropyl methyl acetylene (**5a**) is more stable than singlet **3a** by 49.9 kcal/mol, so the rearrangement from singlet **3a** into the alkyne is thermodynamically favorable. This rearrangement could occur via two pathways: cyclopropyl shift or methyl shift. The energy barrier of the cyclopropyl shift is 8.9 kcal/mol while the barrier of the methyl shift is 12.7 kcal/mol. Therefore, the rearrangement likely occurred through a 1,2-cyclopropyl shift. All the CCSD(T) calculations have a T1 diagnostic value below 0.02, indicating that the computed energies are highly reliable since the system is well represented without a multi-reference wavefunction.

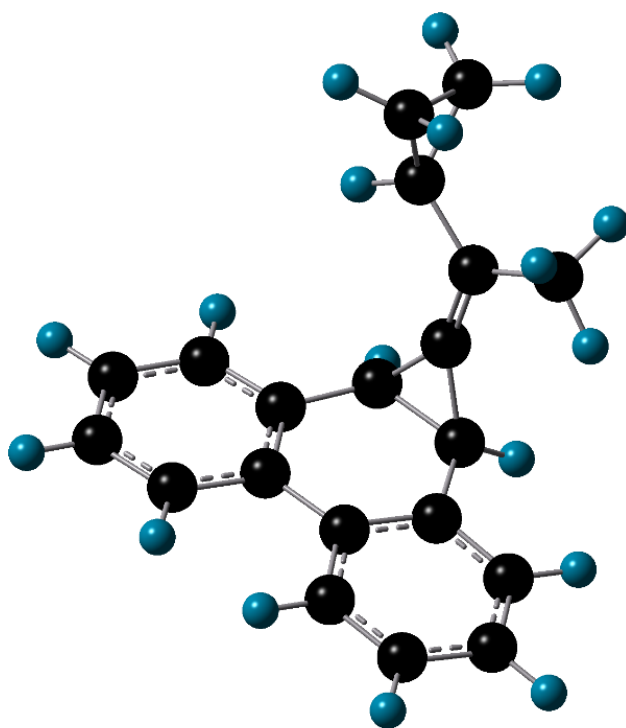


Figure 2.3. Optimized structure of the cyclopropyl methyl vinylidene carbene precursor (**4a**).

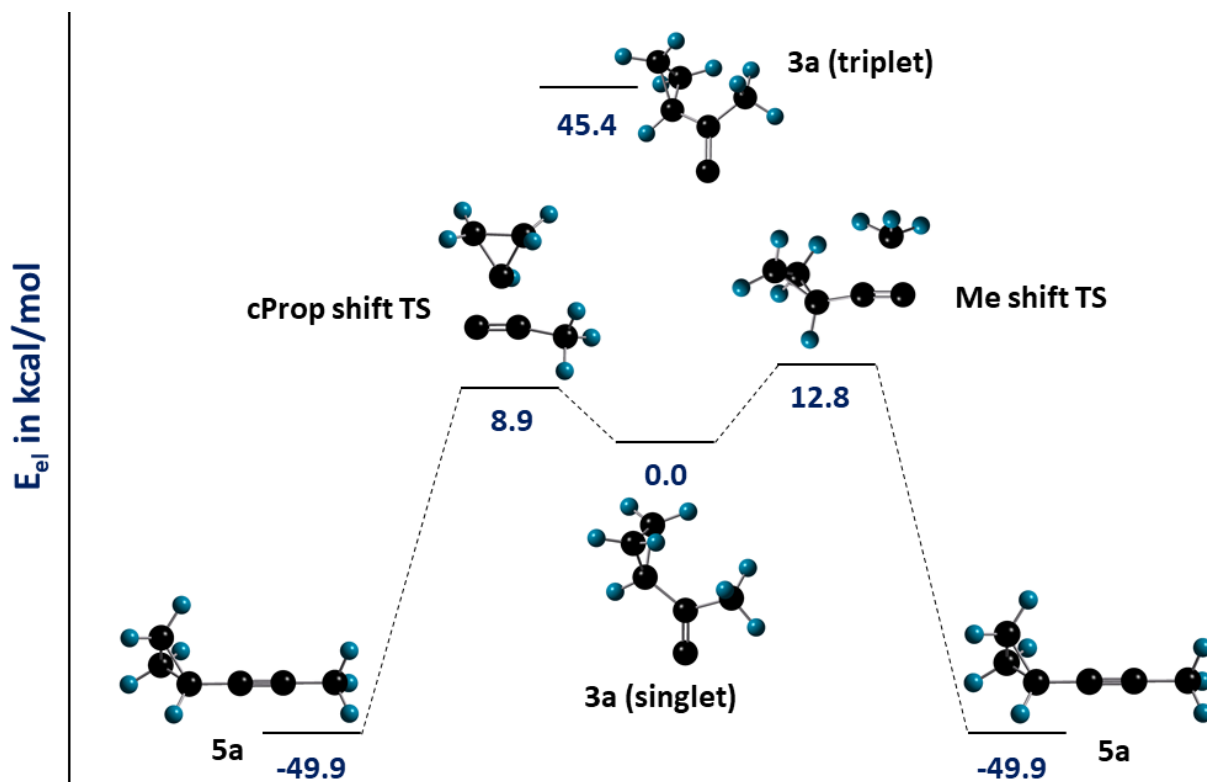
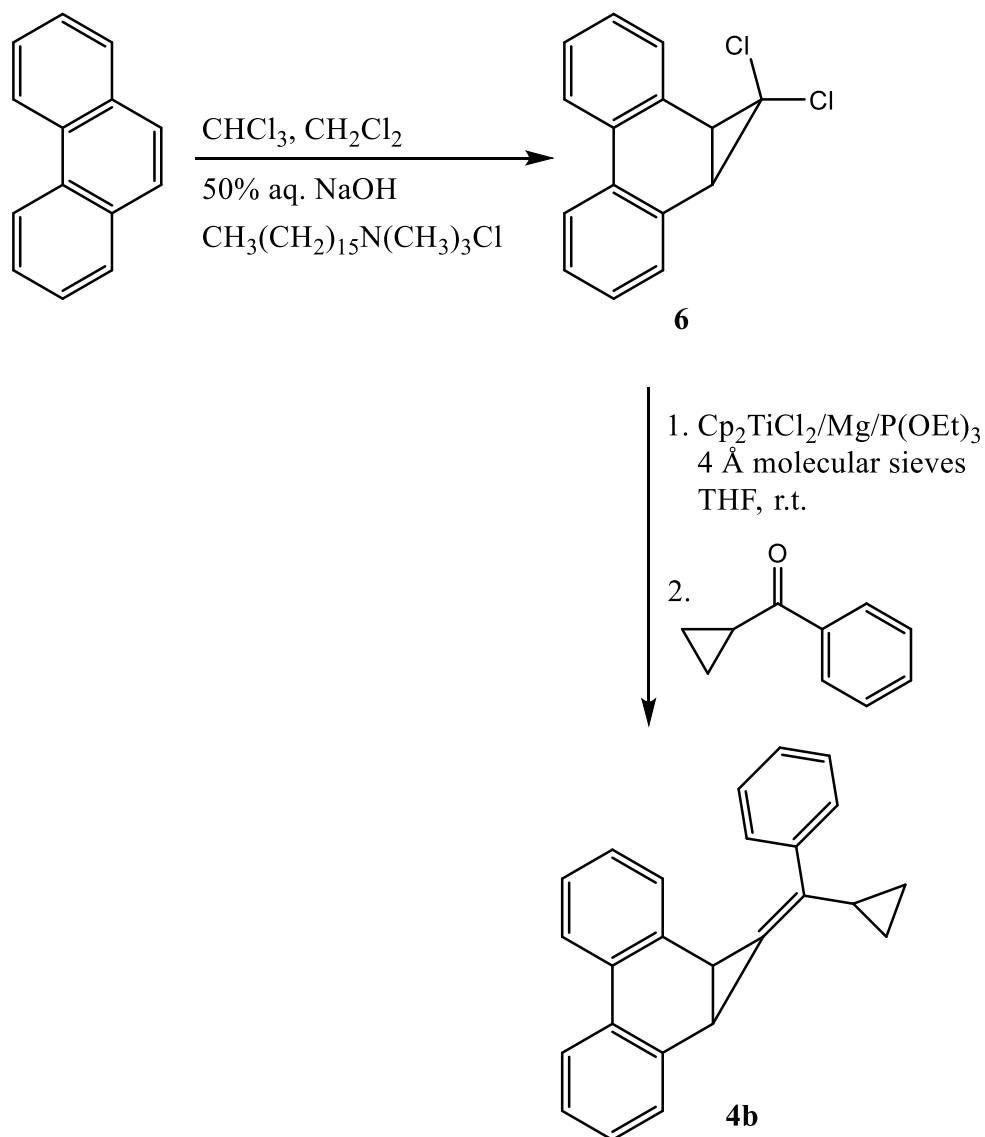


Figure 2.4. Structures and energies of singlet and triplet **3a**, along with the potential energy surfaces for the rearrangement of singlet **3a** into cyclopropyl methyl acetylene (**5a**) via two pathways – cyclopropyl shift and methyl shift.

2.4. Synthesis of Cyclopropyl Phenyl Vinylidene Precursor



Scheme 2.5. Synthesis of cyclopropyl phenyl vinylidene precursor (**4b**) from phenanthrene via the dichloro compound **6**.

The synthesis of the cyclopropyl phenyl vinylidene precursor (**4b**) from phenanthrene is shown in Scheme 2.5. The reaction mechanism is the same as the synthesis of cyclopropyl methyl vinylidene precursor (**4a**). Interestingly, GC spectra of **4b** always show two peaks with the same molecular weight as **4b** at 22.3 minutes and 25.6 minutes (see Appendix A – Figure

A.11), while ^1H NMR spectra only show one compound. Therefore, it seems that the high temperature of the GC injection port can cause **4b** to rearrange into an unidentified isomer.

Precursor **4b** was also very difficult to isolate and purify because flash chromatography and subsequent recrystallization were unable to separate **4b** from the monochloro side product **12**, possibly due to their similar polarity. Furthermore, the yield of this precursor was only 4%, as estimated from the ^1H NMR of the crude product. Therefore, further experiments are needed to determine the optimal reaction conditions to increase the yield of **4b**. Other methods of isolating and purifying **4b**, such as flash chromatography with alumina solid phase and HPLC, should also be explored.

It was also noted that over time, the precursor **4b** seemed to be converted into two new compounds with the same molecular weights. They could be isomers of **4b** formed via 1,5-sigmatropic carbon shift and ring opening as in the case of precursor **4a**, which would give **18** and **19** (Figure 2.5). It is interesting that while precursor **4a** and the dimethyl vinylidene carbene precursor isomerized in this manner upon UV irradiation, the precursor **4b** isomerized in ambient light. However, further experiment is needed to confirm that **18** and **19** are indeed the two new compounds that were observed.

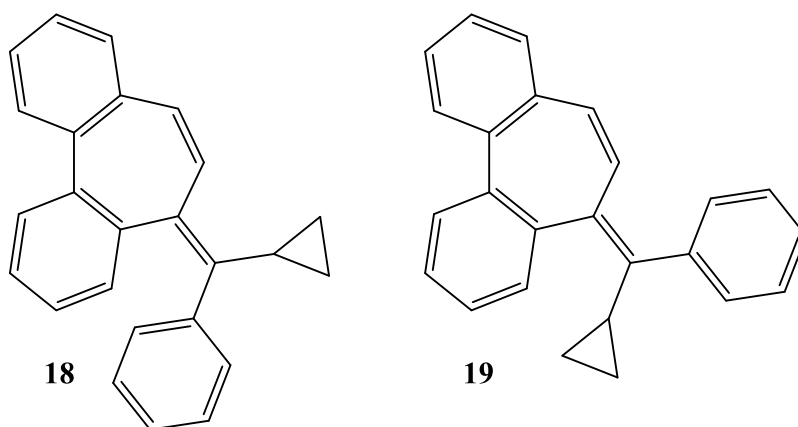
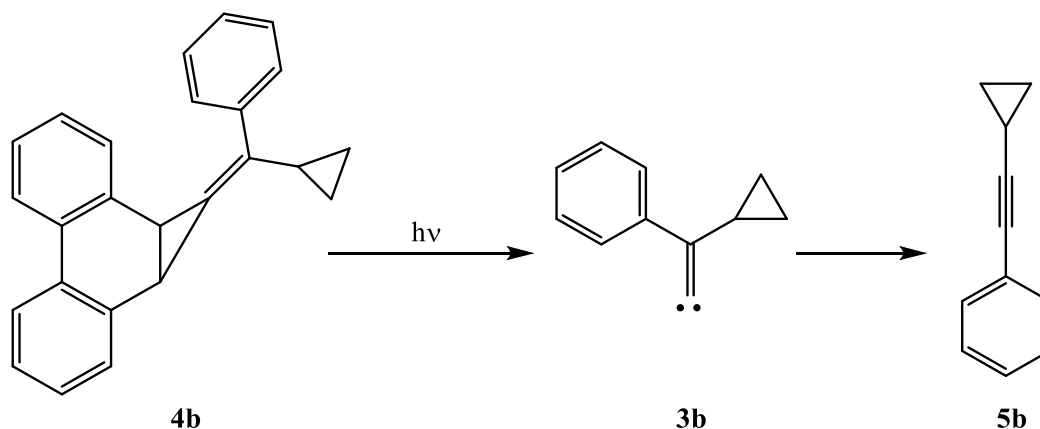


Figure 2.5. Possible structures of the two new compounds formed by precursor **4b** at room temperature and under ambient light.

2.5. Generation and Rearrangement of Cyclopropyl Phenyl Vinylidene Carbene



Scheme 2.6. Photolysis of the precursor **4b** to generate cyclopropyl phenyl vinylidene carbene (**3b**), followed by rearrangement of **3b** into cyclopropyl phenyl acetylene (**5b**).

A crude sample containing precursor **4b**, the monochloro compound **12**, and the two new compounds (which were possibly **18** and **19**) was photolyzed to study the generation and rearrangement of the cyclopropyl phenyl vinylidene carbene (**3b**) (Scheme 2.6). Formation of phenanthrene (a side product of carbene generation) and the rearrangement product **5b** was

confirmed by ^1H NMR and GC/MS. Therefore, the precursor **4b** released the cyclopropyl phenyl vinylidene carbene (**3b**) as expected, which rearranged to form the alkyne **5b**. Furthermore, the two unidentified compounds with the same molecular weight as precursor **4b** did not seem to be photolabile, which is consistent with previous observations on the isomer formed via 1,5-sigmatropic carbon shift and ring opening of the dimethyl vinylidene carbene precursor (**13**).³³ This is further evidence that these two compounds are likely **18** and **19**.

2.6. Computational Results for Cyclopropyl Phenyl Vinylidene Carbene

Computational models were used to calculate the optimized geometries and energies of the cyclopropyl phenyl vinylidene carbene precursor (**4b**), the resulting carbene (**3b**), the rearrangement product (**5a**), and the two transition states. The optimized geometry of **4b** is shown in Figure 2.6, while computational results for the other species are shown in Figure 2.7. All species were computed at the CCSD(T)/cc-pVTZ// B3LYP/6-311+G** level of theory.

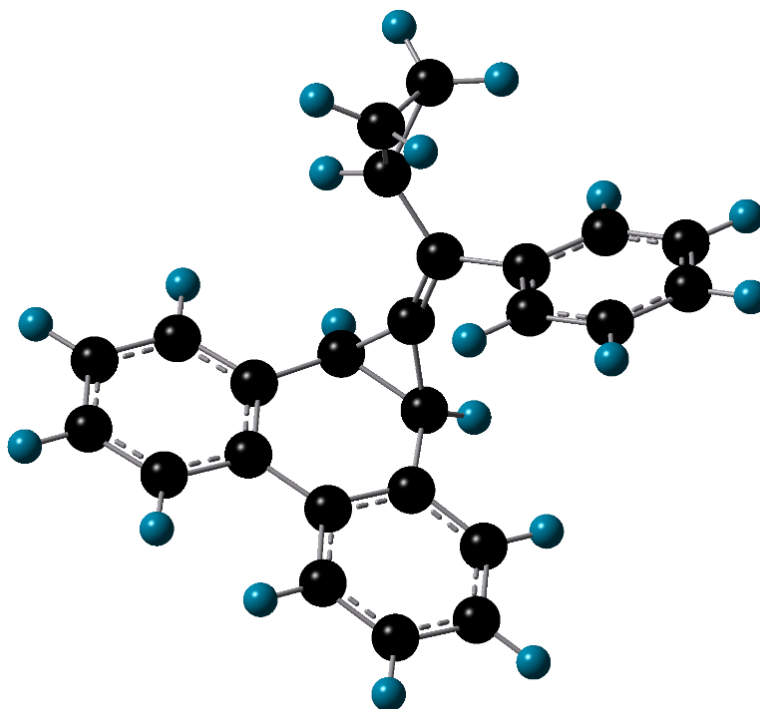


Figure 2.6. Optimized structure of the cyclopropyl phenyl vinylidene carbene precursor (**4b**).

Consistent with computational results for carbene **3a** and other vinylidene carbenes, the singlet-triplet gap for carbene **3b** is 41.9 kcal/mol, favoring the singlet. Similar to the case of **3a**, singlet **3b** is 50.9 kcal/mol higher in energy than cyclopropyl phenyl acetylene (**5b**), so the rearrangement of singlet **3b** into the alkyne **5b** is thermodynamically favorable. Between the two possible pathways for this rearrangement, the cyclopropyl shift has a higher energy barrier than the phenyl shift by 5.4 kcal/mol, so the rearrangement likely occurred through a 1,2-phenyl shift. In fact, the barrier for the phenyl shift is exceptionally low, only 3.6 kcal/mol. This is because the aromatic phenyl ring is weakly nucleophilic, so it migrates toward the electron-deficient divalent carbon more readily than the cyclopropyl group. All the CCSD(T) calculations have a T1 diagnostic value below 0.02 except for the triplet **3b**, which has a T1 diagnostic value of 0.034. However, this value is not too much above 0.02, so the computed singlet-triplet gap for **3b** should still be reliable.

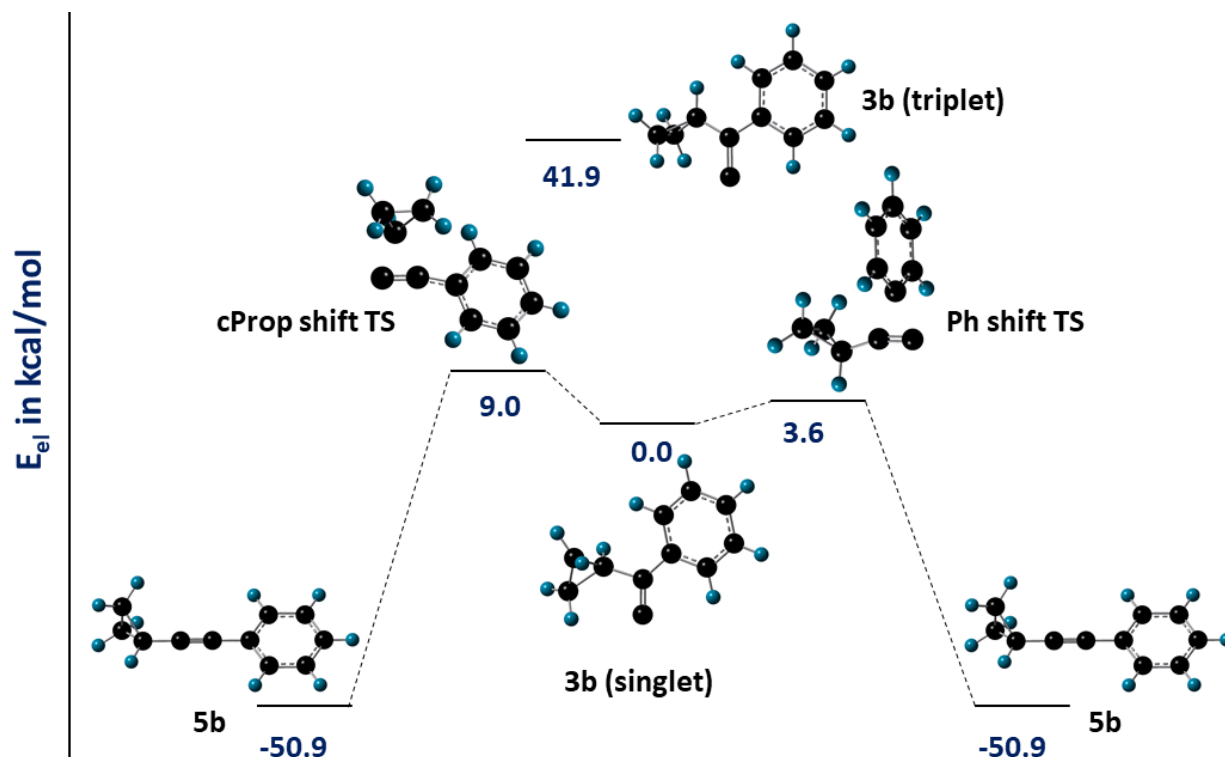


Figure 2.7. Structures and energies of singlet and triplet **3b**, along with the potential energy surfaces for the rearrangement of singlet **3b** into cyclopropyl phenyl acetylene (**5b**) via two pathways – cyclopropyl shift and phenyl shift.

2.7. Conclusion and Future Directions

This study aimed to synthesize phenanthrene-based precursors (**4a** and **4b**) for the cyclopropyl methyl vinylidene carbene (**3a**) and the cyclopropyl phenyl vinylidene carbene (**3b**) to examine their generation and rearrangement. The synthetic route employed, especially the Takeda reaction in the second step, gave very low yields for the precursor (4 – 6%). However, by varying reaction conditions, such as the amount of time between addition of the dichloro compound **6** and the addition of ketone, higher yields may be achieved. Furthermore, the isolation and purification of these precursors (**4a** and **4b**) were unsuccessful. The product

contained a significant amount of an impurity, which was unreacted **6** in the case of **4a** and the side product **13** in the case of **4b**.

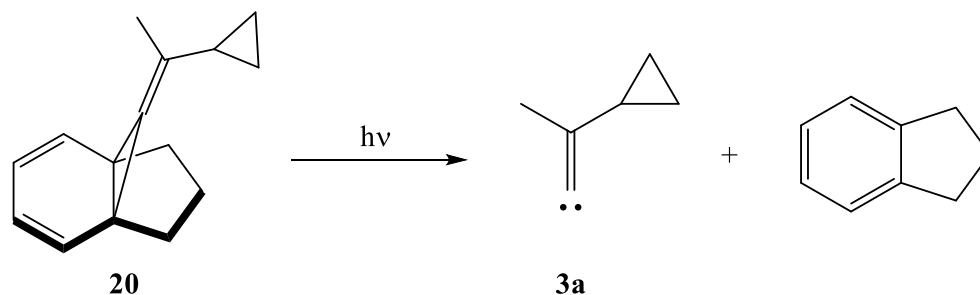
The precursors were photolyzed along with the aforementioned impurities. There was no evidence that **4a** generated the cyclopropyl methyl vinylidene carbene (**3a**) upon photolysis, as the rearrangement product – cyclopropyl methyl acetylene (**5a**) – was not observed. Meanwhile, the cyclopropyl phenyl vinylidene carbene (**3b**) was successfully generated from **4b** upon photolysis and then rearranged as expected into cyclopropyl phenyl acetylene (**5b**).

An interesting observation was that both precursors **4a** and **4b** were highly prone to isomerization. Some of the isomers of **4a** and **4b** were possibly formed via 1,5-sigmatropic carbon shifts and then ring opening to form compounds with 7-membered rings (**16-19**). While **4a** formed isomer upon irradiation with UV light, **4b** seemed able to isomerize under ambient light, without the need for photolysis. Further experiments are needed to confirm the structures and formation mechanism of these putative isomers of **4a** and **4b**.

Computational results agreed with the prediction that both vinylidene carbenes **3a** and **3b** exist as singlets in their ground states. Both singlet carbenes were also about 50 kcal/mol higher in energy than the rearrangement products (**5a** and **5b**). The cyclopropyl shift was more favorable for **3a**, while the phenyl shift was more favorable for the rearrangement of **3b**.

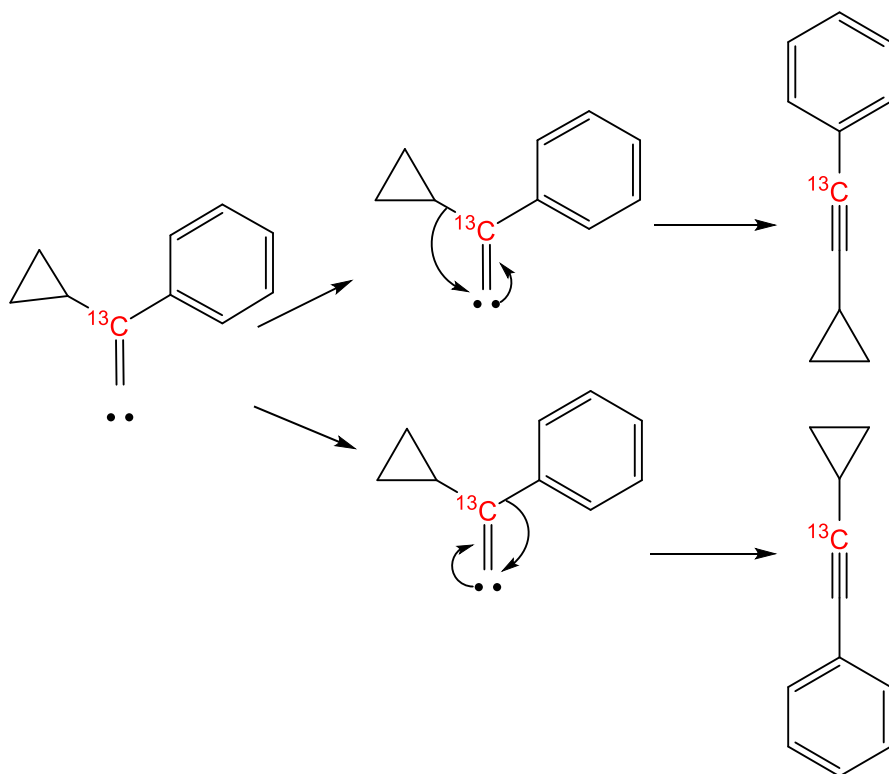
In the future, a priority would be increasing the yield of the Takeda reactions and finding better methods to purify **4a** and **4b**. After the precursors are successfully purified, their spectroscopic data including IR, ¹H NMR, ¹³C NMR, and GC/MS spectra can be collected. In addition, the melting points and crystal structures of **4a** and **4b** should also be determined. Using pure precursors in photolysis experiments would also give clearer results. If the photolysis of a pure sample of precursor **4a** still fails to generate the carbene **3a**, another type of precursor

should be considered. One example is the indene-based precursor **20** shown in Scheme 2.7 below, as precursors of this type have been used to successfully generate vinylidene carbenes before.³⁴



Scheme 2.7. A potential route to access cyclopropyl methyl vinylidene carbene (**3a**) from an indene-based precursor (**20**).

Although computational results could help to predict the mechanism of the rearrangements of vinylidene carbenes **3a** and **3b** into alkynes, the mechanism should still be confirmed via experiments. For example, cyclopropyl phenyl ketone with ^{13}C label on the carbonyl carbon can be used in the synthesis of **4b**. Upon photolysis, **4b** will release a labeled cyclopropyl phenyl vinylidene carbene. In that case, the migration of the cyclopropyl group will yield an alkyne in which the labeled carbon is closer to the phenyl group, while the migration of the phenyl group will yield an alkyne in which the labeled carbon is closer to the cyclopropyl group (Scheme 2.8). Therefore, if only one of these two rearrangement products arises, then the shift resulting in that product must be much more favorable than the other shift. However, if both products arise, then the two shifts do not differ significantly in their energy barriers, and the ratio of products will provide information about whether the cyclopropyl shift or the phenyl shift is more favorable.



Scheme 2.8. Isotope labeling technique to determine whether the rearrangement of cyclopropyl phenyl vinylidene carbene occurs via phenyl shift or cyclopropyl shift.

Another useful technique in the study of carbenes is laser flash photolysis. With this technique, UV laser provides the energy for carbene generation, while another lamp is used to monitor the UV-visible absorption spectra of the precursor and carbene during photolysis. This is an ultra-fast technique that can collect data on the time scale of nanoseconds or picoseconds. With laser flash photolysis, the kinetics of the formation and rearrangement of cyclopropyl phenyl vinylidene carbene can be quantitatively studied.

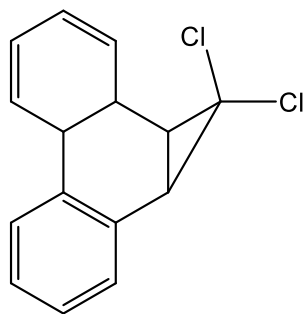
Experimental Procedures

3.1. General Remarks

Anhydrous tetrahydrofuran was obtained by passing the solvent through two columns of activated alumina (2 ft \times 4 in). The Takeda reactions were carried out under an inert argon atmosphere. The glassware, magnesium and molecular sieve used for the Takeda reactions were stored in the oven at 120°C, and the magnesium was stirred under argon in the reaction vessel (no solvent) for 10-14 hours before the start of the reaction. All other reagents and solvents were used as obtained from commercial sources. The columns used for flash chromatography was pre-packed with silica gel, 70-230 mesh. As for GC/MS spectra, the GC column used was an Agilent HP-5ms capillary column with dimensions 30 m \times 0.250 mm \times 0.25 μ m. The initial temperature of the GC was 100°C, followed by a ramp of 15°C/min to reach 250°C. The solvent delay was 3 minutes for most runs and 2 minutes when volatile compounds were expected. NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C with CDCl_3 as the solvent. FT-IR spectra were obtained on pure solids using an attenuated total reflectance (ATR) accessory.

3.2. Synthesis of Cyclopropyl Vinylidene Carbene Precursors

Step 1: Synthesis of 1,1-dichloro-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (6)

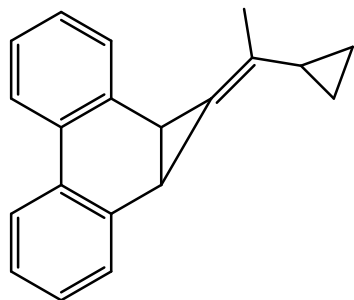


To a stirring suspension of phenanthrene (35.6 g, 200 mmol) and cetyltrimethylammonium chloride (0.444 g, 1.39 mmol) in chloroform (50 mL), 50 mL of aqueous NaOH 50% solution was added dropwise over 20 minutes. After stirring at 50°C for 24 hours, 100 mL of dichloromethane was added to the resulting mixture to dissolve most of the solid. Then, the layers were separated, and the reaction mixture was extracted with

dichloromethane (100 mL) and washed with water (400 mL) and brine (200 mL). The solvent was then evaporated, and the solid was recrystallized from pure hexanes to obtain a white solid. Yield: 18%; melting point: 131.3 – 131.6°C; ^1H NMR (CDCl_3) δ 7.96 (dd, J = 8.0, 1.3 Hz, 2H), 7.43 (dd, J = 7.4, 1.6 Hz, 2H), 7.35 (td, J = 7.7, 1.6 Hz, 2H), 7.29 (td, J = 7.4, 1.3 Hz, 2H), 3.34 (s, 2H); ^{13}C NMR (CDCl_3) δ 131.3, 131.0, 128.2, 128.1, 128.0, 123.1, 58.9, 36.6.

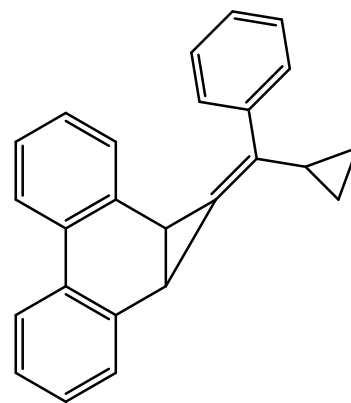
Step 2: Takeda reactions

The precursors **4a** and **4b** were synthesized via Takeda reactions adapted from a known procedure.²⁹ Triethyl phosphite (6.2 mL, 6.0 g, 36 mmol) was added to a stirring suspension of crushed magnesium turnings (0.45 g, 18.5 mmol), powdered 4 Å molecular sieves (1.05 g), and bis(cyclopentadienyl)titanium(IV) dichloride (4.5 g, 18 mmol) in 35 mL anhydrous tetrahydrofuran at room temperature. Within 1 hour, the suspension turned black. After stirring for 3 hours since the addition of triethyl phosphite, a solution of **7** (1.57 g, 6.0 mmol) in 15 mL anhydrous tetrahydrofuran was added to the reaction mixture. After stirring for an additional 30 minutes, either cyclopropyl methyl ketone (0.60 mL, 0.51 g, 6.1 mmol) was added to the reaction mixture to synthesize **4a**, or cyclopropyl phenyl ketone (0.83 mL, 0.88 g, 6.0 mmol) was added to synthesize **4b**. After 10 hours, the reaction mixture was diluted with pure hexanes (1 : 7 volume ratio) and vacuum filtered through a column of silica gel. After that, the product was purified by flash chromatography on silica gel (hexanes) to afford an off-white solid. Additional purification by flash chromatography on silica gel (hexanes), preparatory thin layer chromatography, and recrystallization were used as needed to further purify **4a** and **4b**.



4a: Yield: 6%; ^1H NMR (CDCl_3) δ 7.94 (dd, $J = 7.4, 1.9$ Hz, 2H), 7.40 – 7.36 (m, 2H), 7.27 – 7.21 (m, 4H), 3.17 (dd, $J = 7.5, 1.9$ Hz, 1H), 3.01 (dd, $J = 7.5, 1.6$ Hz, 1H), 1.58 (s, 3H), 1.37 (qd, $J = 7.2, 5.1$ Hz, 1H), 0.53-0.46 (m, 3H), 0.37 – 0.33 (m, 1H).

4b: Yield: 4%; ^1H NMR (CDCl_3) δ 7.94 (td, $J = 7.8, 1.5$ Hz, 2H), 7.54 (dd, $J = 8.4, 1.3$ Hz, 2H), 7.50 (dd, $J = 7.4, 1.6$ Hz, 1H), 7.42 (dd, $J = 7.2, 1.9$ Hz, 1H), 7.27 – 7.22 (m, 6H), 7.19 – 7.15 (m, 1H), 3.26 (s, 2H), 1.60 (dddd, $J = 8.3, 6.8, 6.1, 4.6$ Hz, 1H), 0.83 – 0.78 (m, 1H), 0.73 – 0.68 (m, 1H), 0.61 – 0.58 (m, 2H).



3.3. Photolysis Experiments

The photolysis experiments were carried out in a Rayonet photochemical reactor, which had 16 12-inch 8 W lamps with output centered at about 350 nm (range: 315 to 400 nm). Crude samples of the precursors **4a** and **4b** were dissolved in benzene- d_6 and photolyzed in NMR tubes. The progress of the reaction was monitored with ^1H NMR and GC/MS.

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Appendix A: Characterization Data

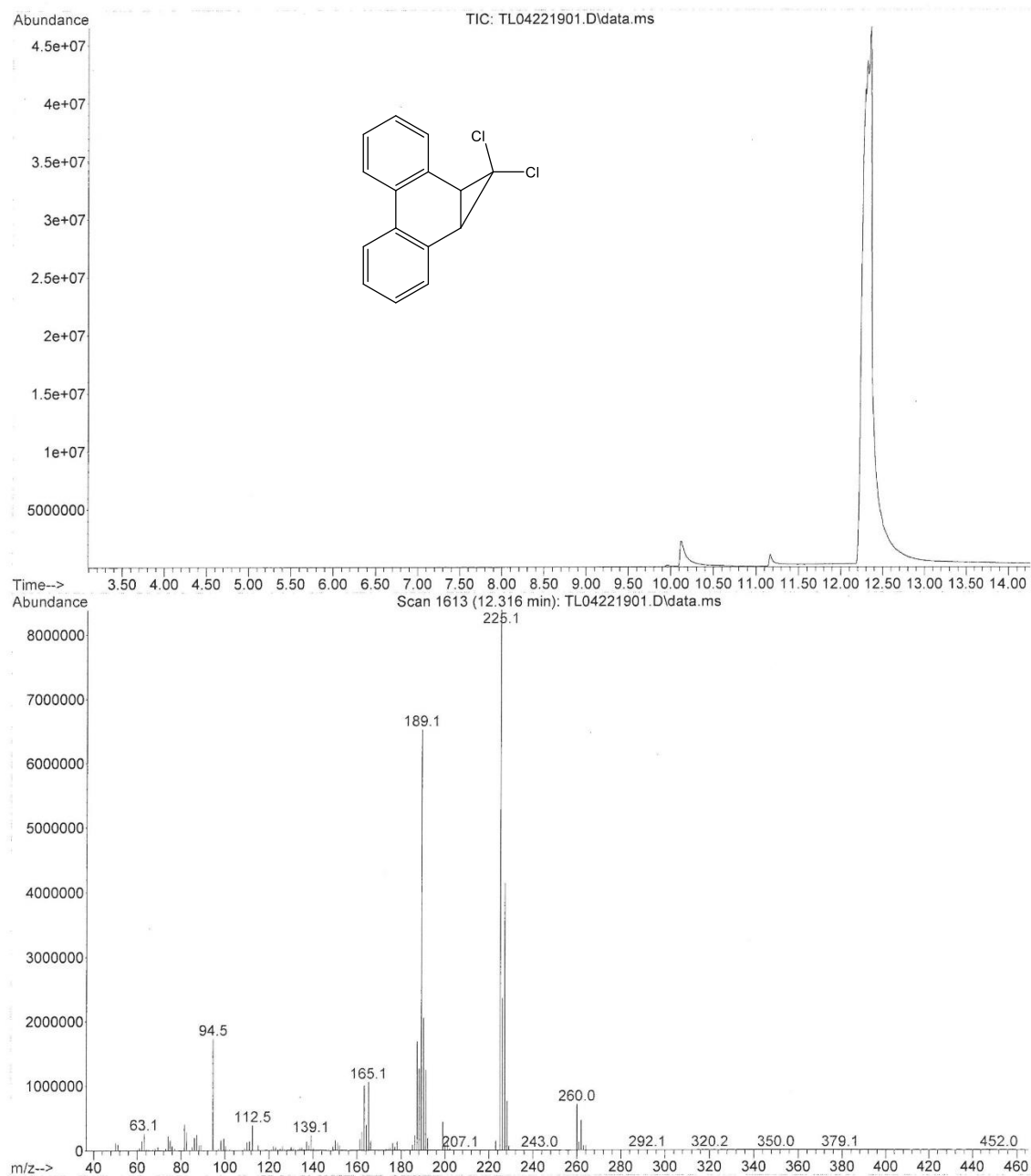


Figure A.1. GC/MS spectrum of the dichloro compound **6**.

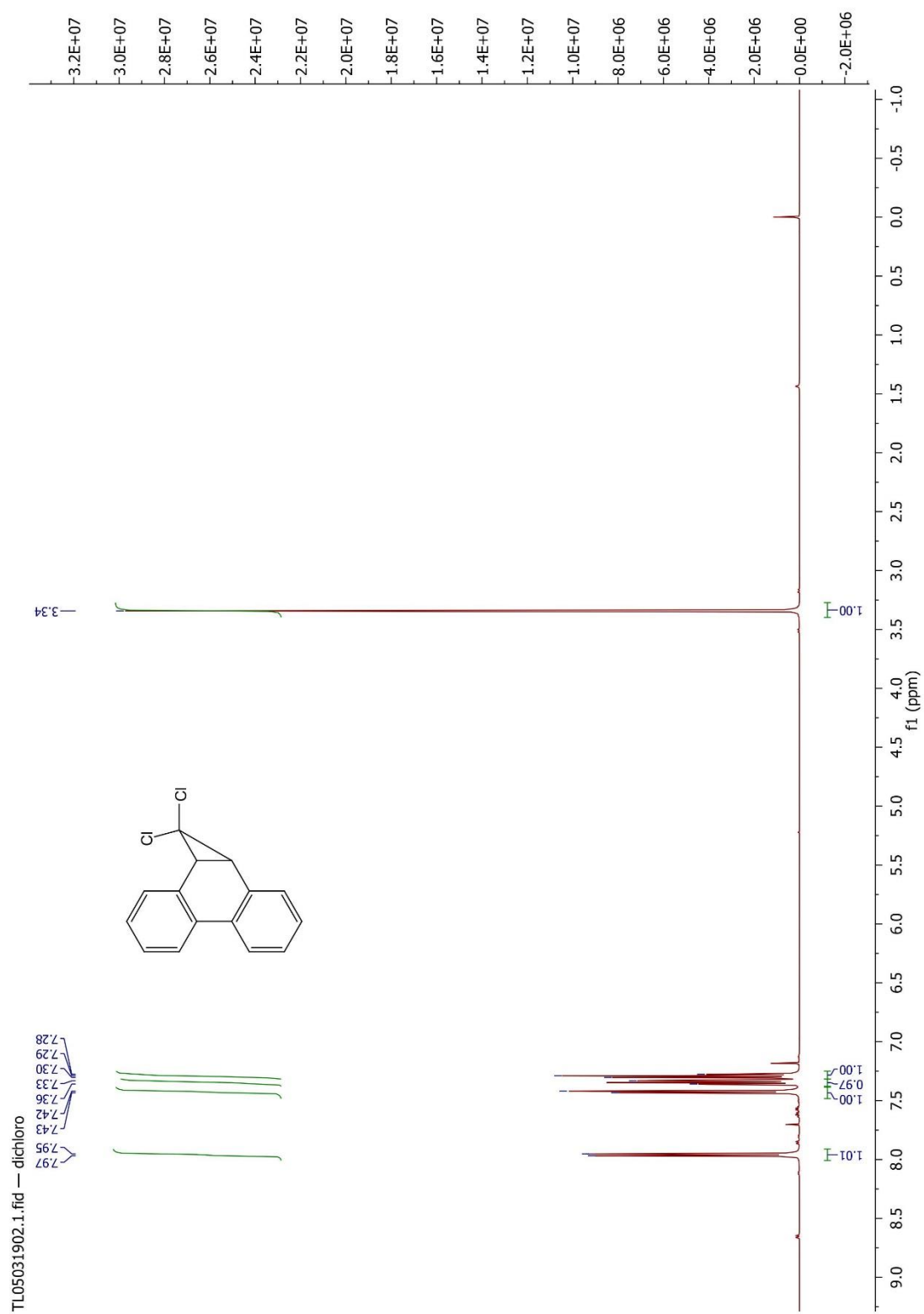


Figure A.2. ¹H NMR spectrum of the dichloro compound **6**.

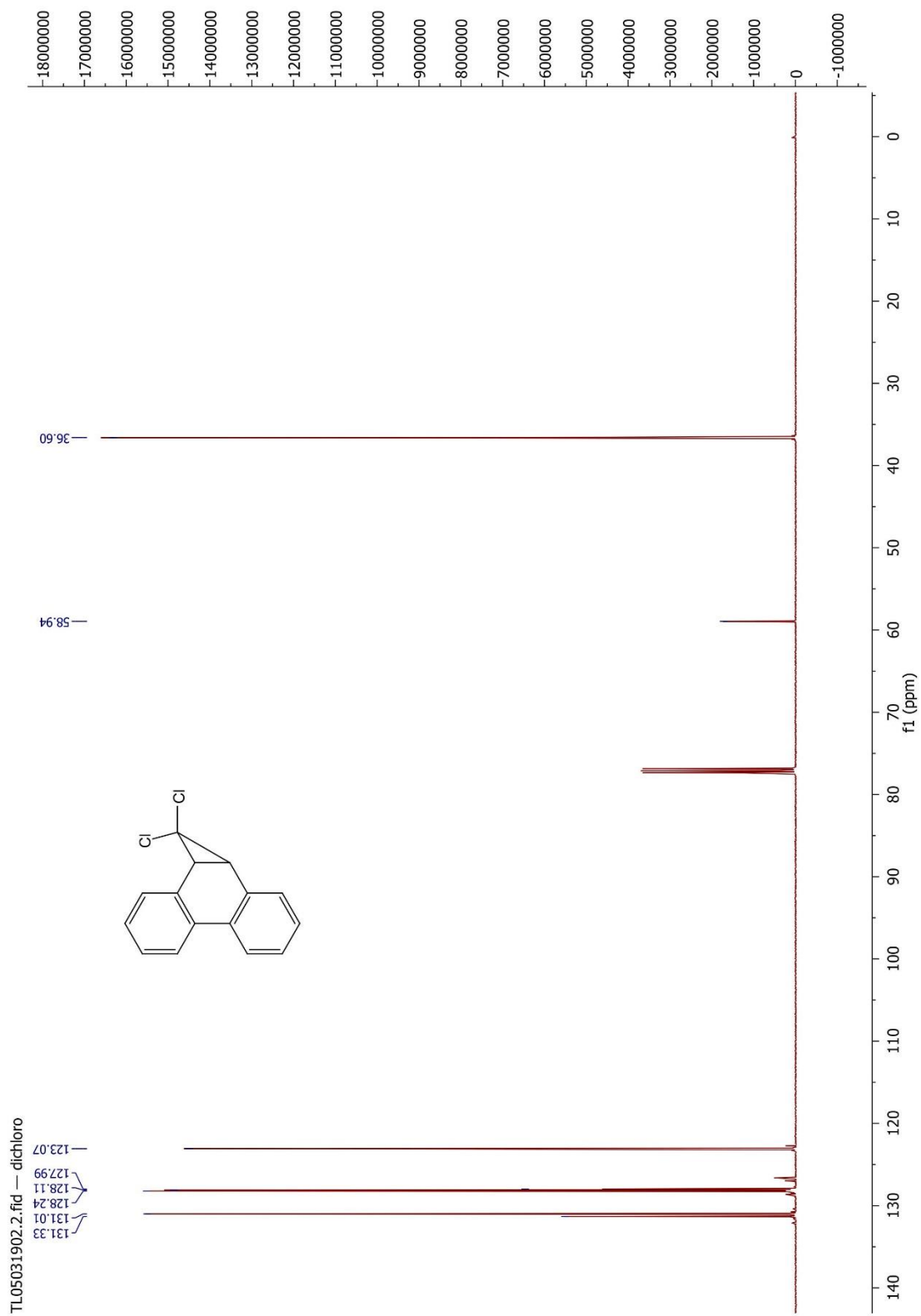


Figure A.3. ^{13}C NMR spectrum of the dichloro compound 6.

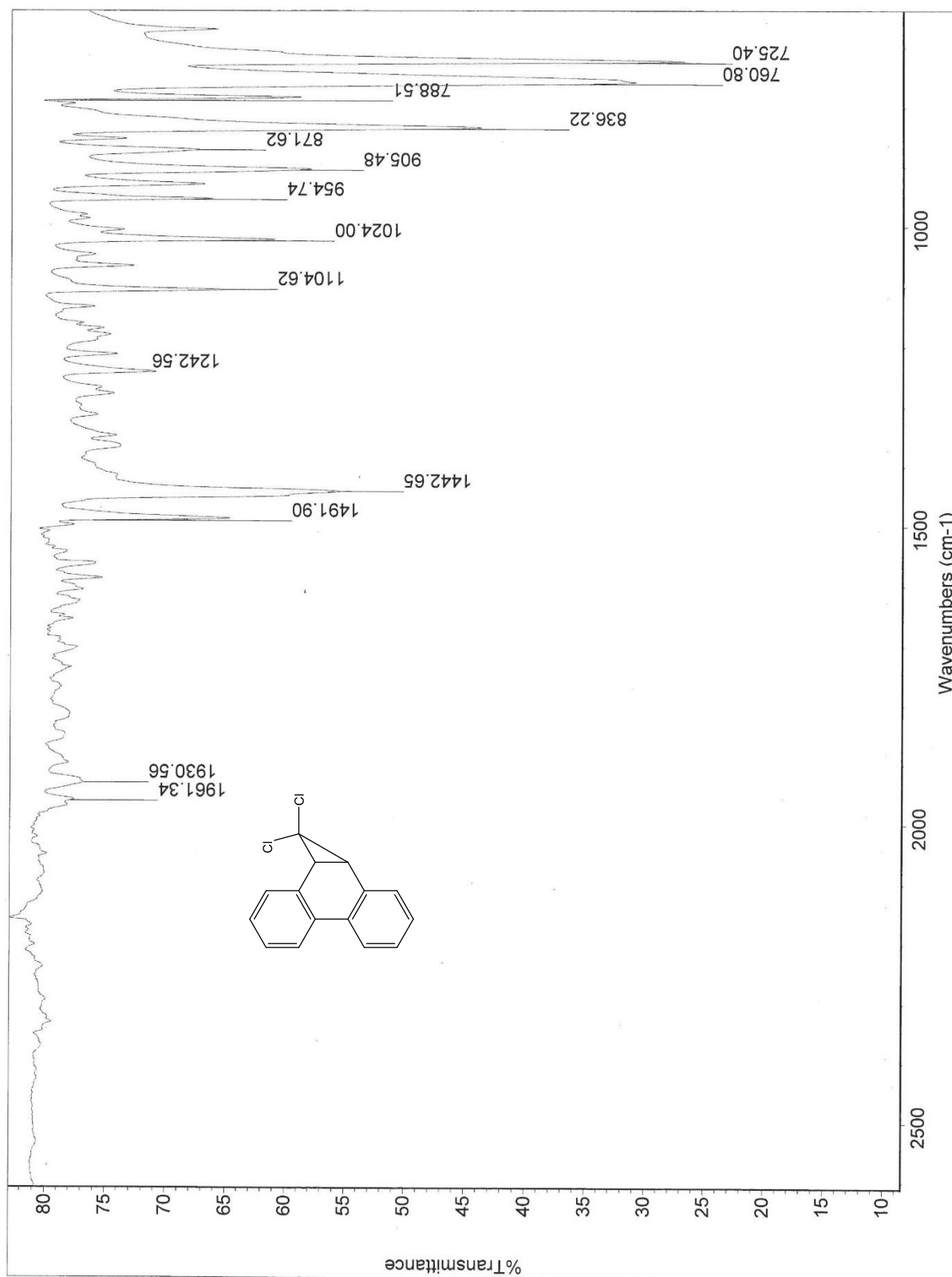


Figure A.4. FT-IR spectrum of the dichloro compound **6**.

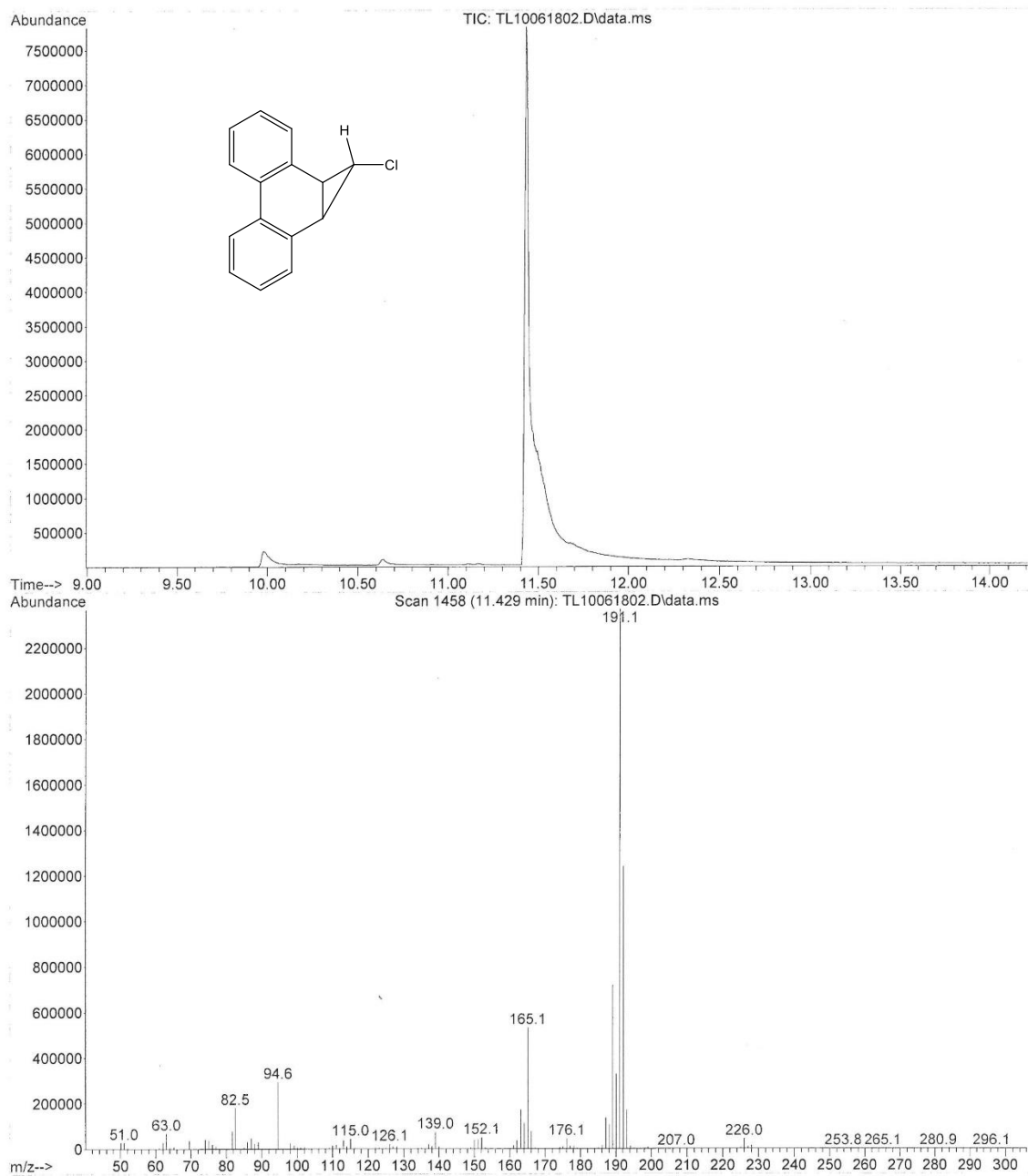


Figure A.5. GC/MS spectrum of the monochloro compound **12**.

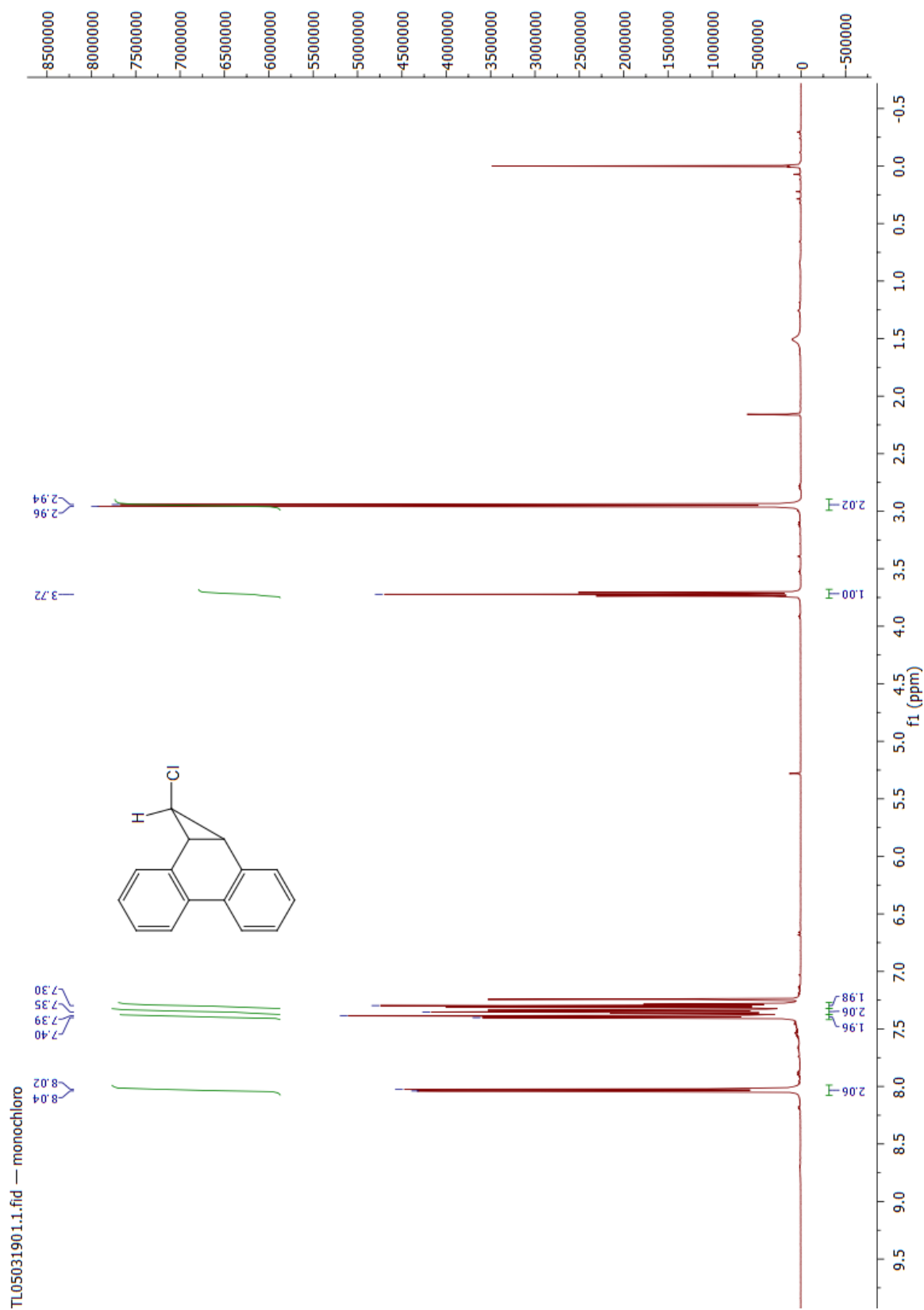


Figure A.6. ¹H NMR spectrum of the monochloro compound **12**.

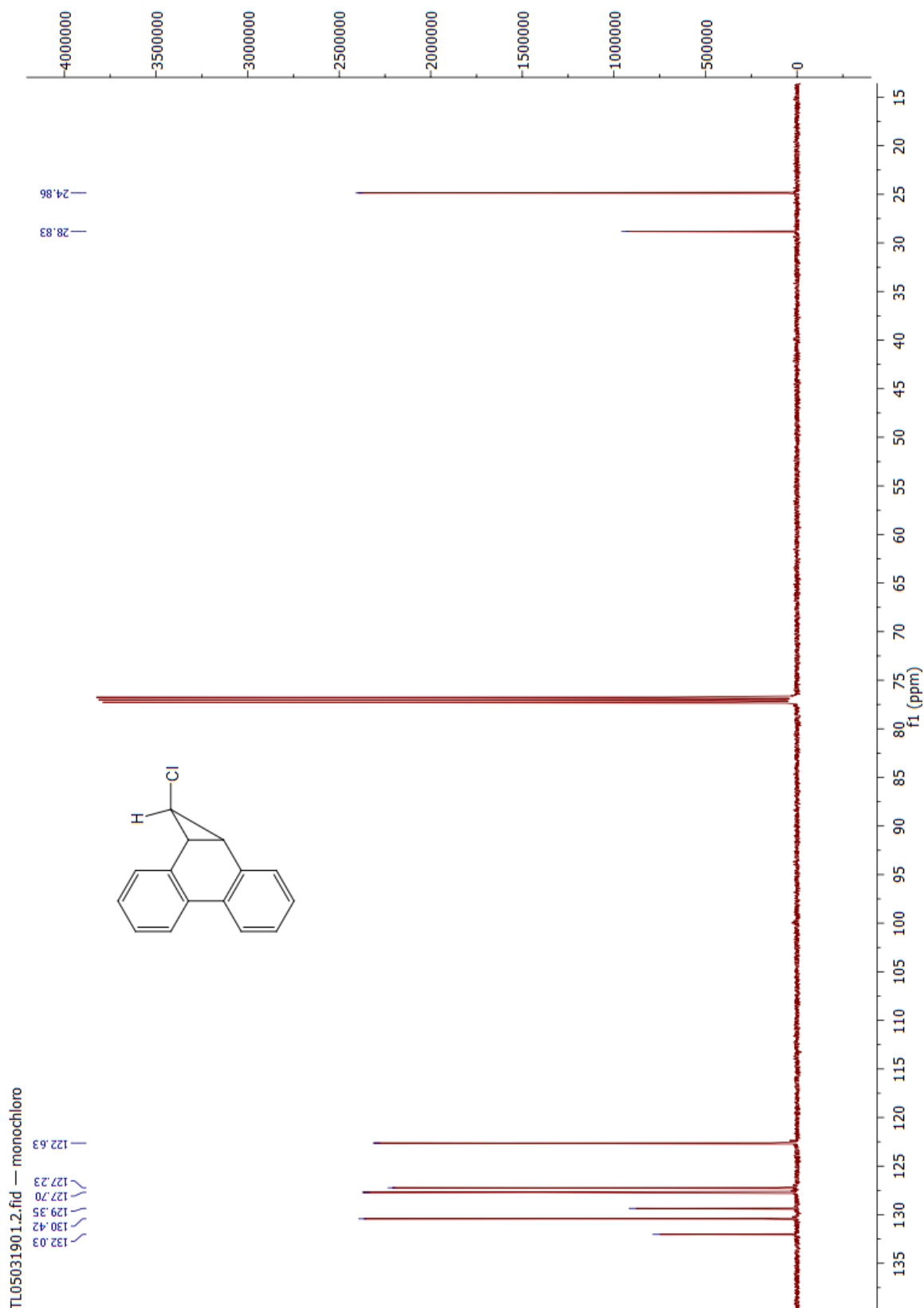


Figure A.7. ^{13}C NMR spectrum of the monochloro compound **12**.

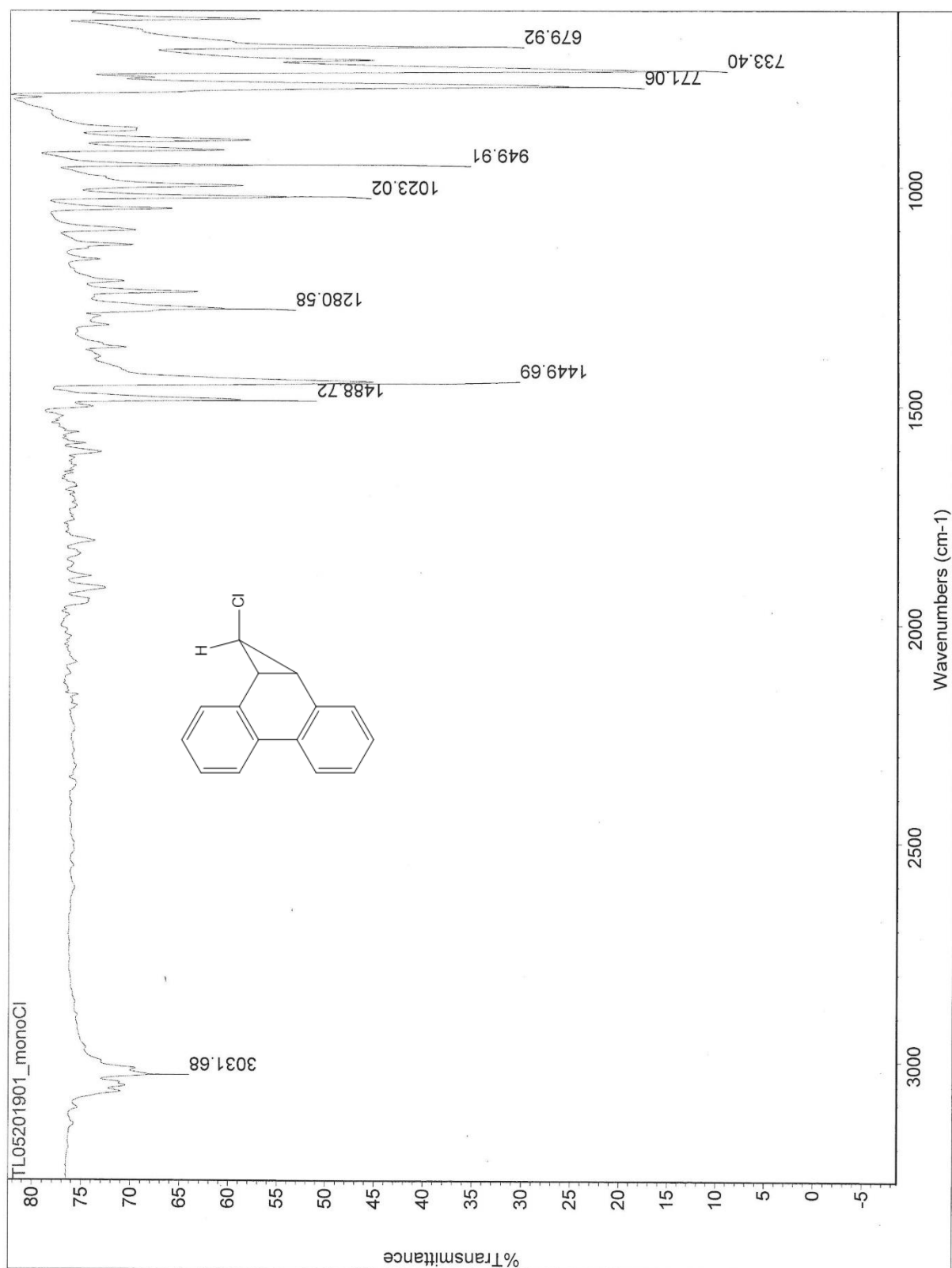


Figure A.8. FT-IR spectrum of the monochloro compound **12**.

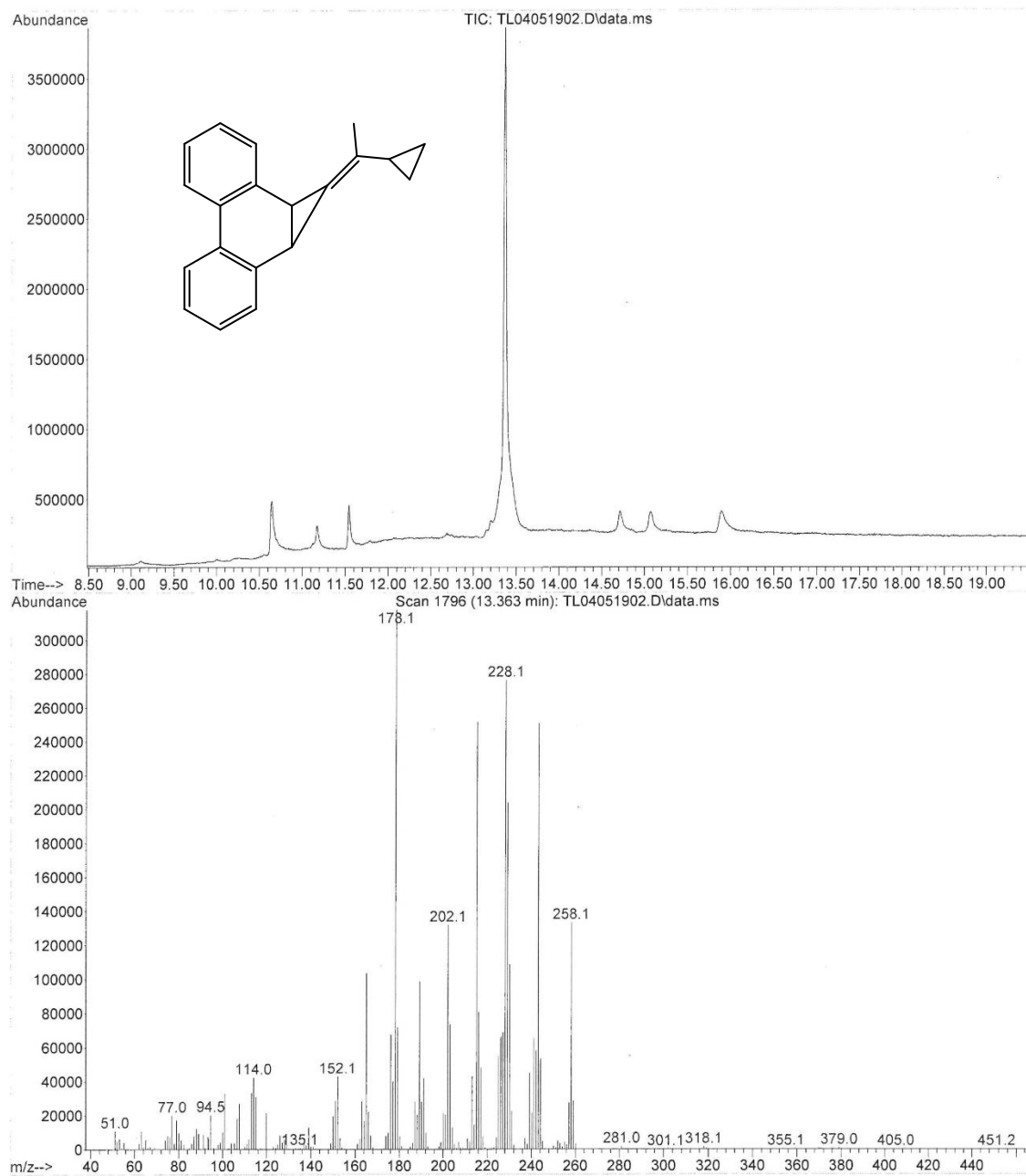


Figure A.9. GC/MS spectrum of the cyclopropyl methyl vinylidene precursor **4a**

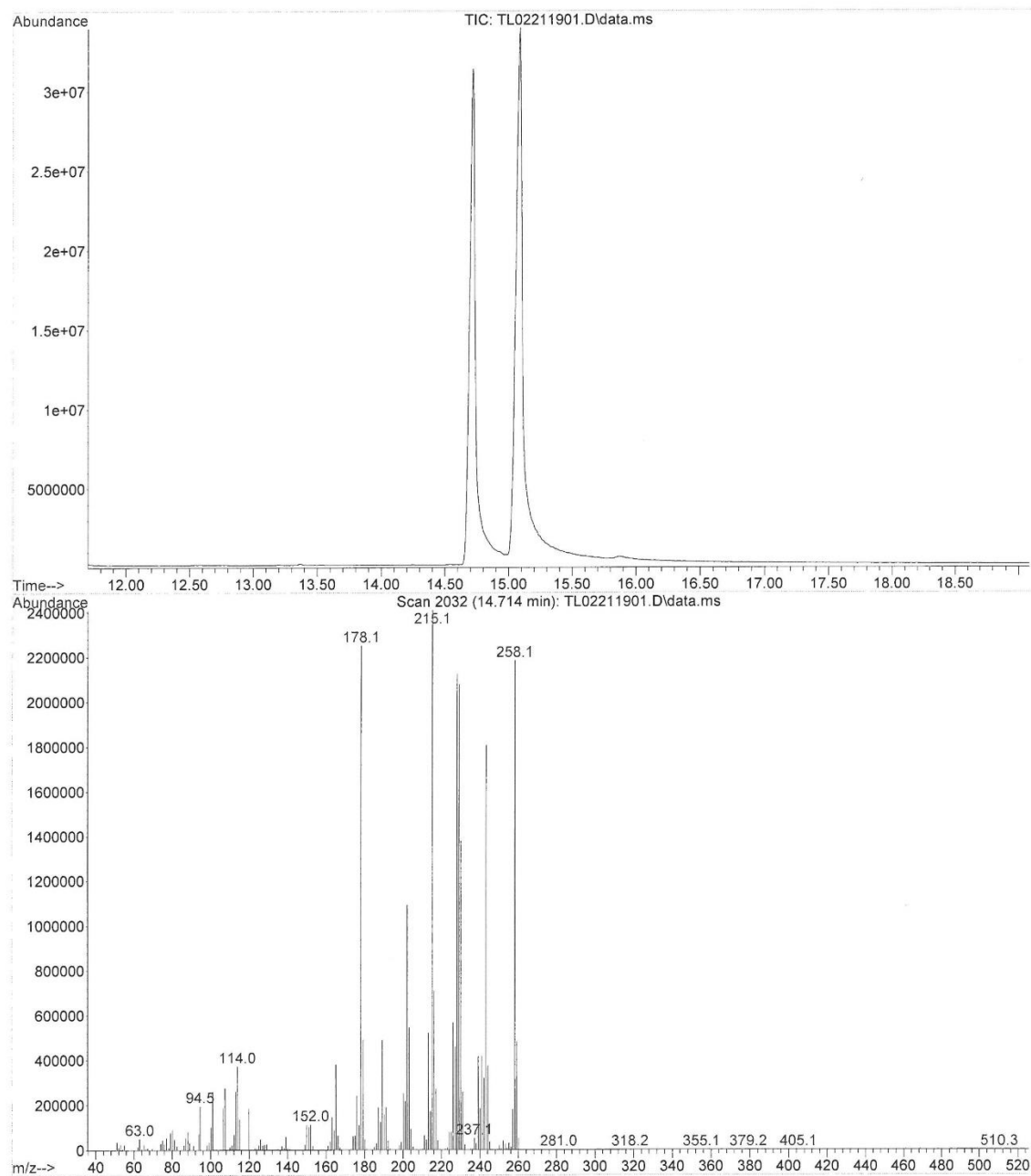


Figure A.10. GC/MS spectrum of the isomers obtained from heating **4a**

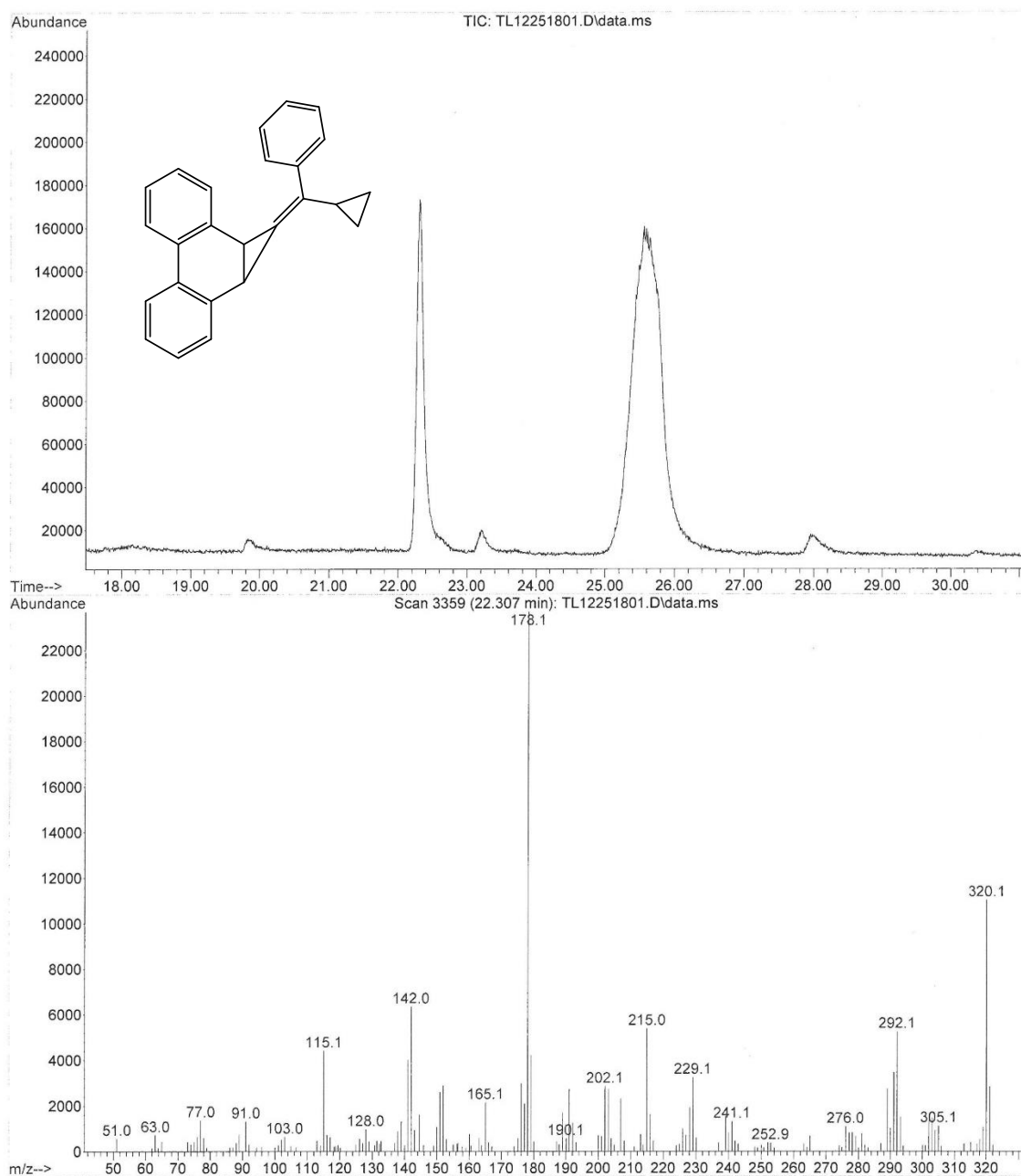


Figure A.11. GC/MS spectrum of the cyclopropyl phenyl vinylidene precursor **4b**. The two peaks are always observed together in GC spectra of **4b**, so one is **4b** and the other is likely due to isomerization of **4b** in the high temperature of the GC injection port.

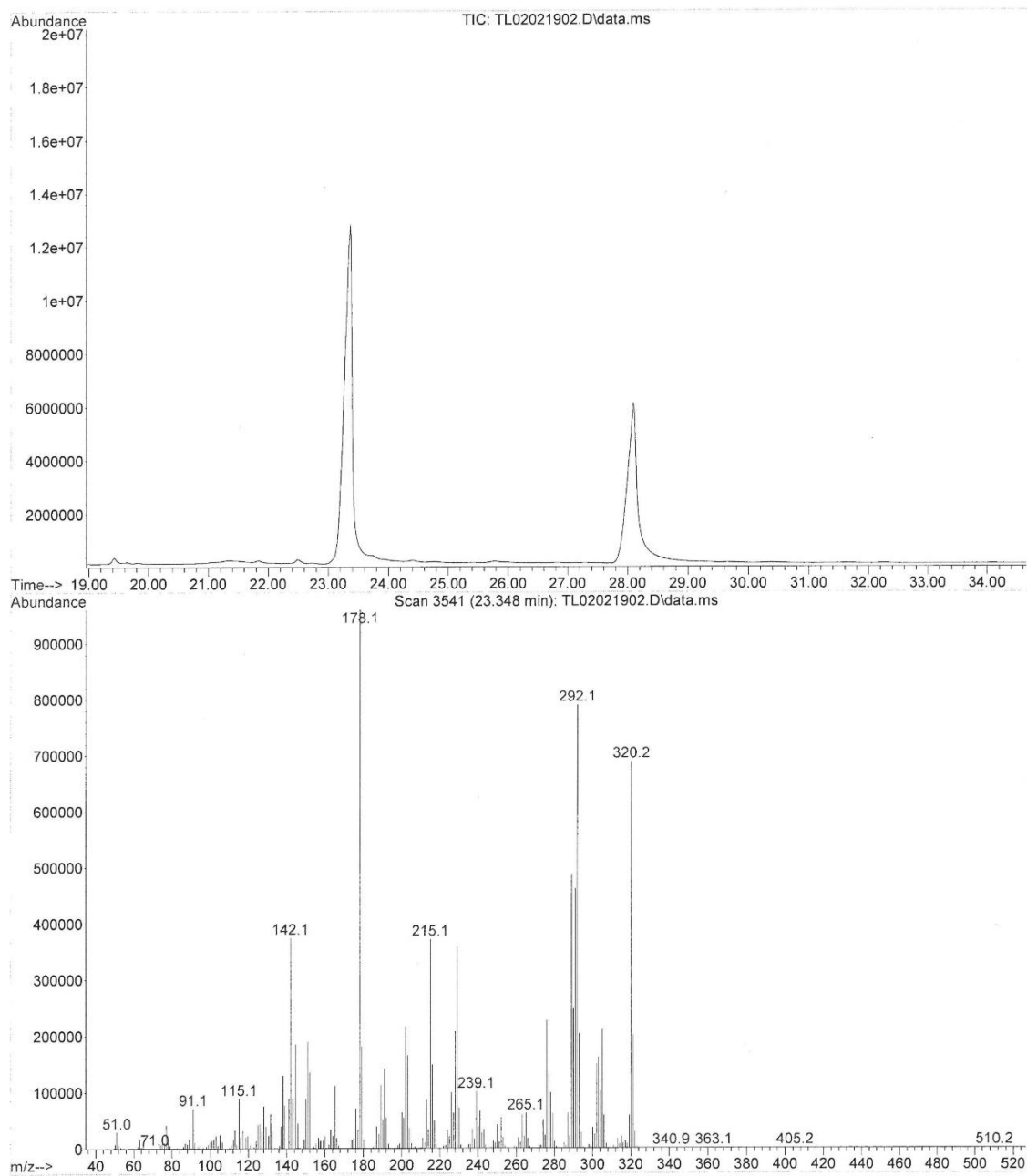


Figure A.12. GC/MS spectrum of the two isomers of **4a**, which could be **18** and **19**.

Appendix B: Computational Data

B.1. Cartesian coordinates and energies for (R/U)B3LYP/6-311+G optimized structures
(298.150K)**

Cyclopropyl methyl vinylidene carbene singlet (3a)

Charge = 0 Multiplicity = 1

C,0,-1.7002565237,2.4654827538,0.0293768928

C,0,-0.1969759971,2.2982983537,-0.0341218654

C,0,-0.7997684425,3.6805741297,-0.0375976013

H,0,-2.2317928917,2.2314317191,-0.8856834597

H,0,0.2209604096,1.9080507543,-0.9540005372

H,0,0.323730016,1.9803880177,0.8607023999

H,0,-0.6800750703,4.2822287114,0.85492252

H,0,-0.7997201862,4.2484933467,-0.9598808879

C,0,-2.4690983426,2.1333326843,1.2630635702

C,0,-1.9351619337,2.3703683665,2.6709283199

H,0,-1.0176200085,1.7974250228,2.8272087222

H,0,-1.7318600121,3.4334959375,2.8225848779

H,0,-2.6590034736,2.0564933529,3.4261497552

C,0,-3.6647061637,1.6114494298,1.2572066034

Zero-point correction= 0.117239 (Hartree/Particle)

Thermal correction to Energy= 0.124120

Thermal correction to Enthalpy= 0.125065

Thermal correction to Gibbs Free Energy= 0.086718

Sum of electronic and zero-point Energies= -233.228069

Sum of electronic and thermal Energies= -233.221188

Sum of electronic and thermal Enthalpies= -233.220244

Sum of electronic and thermal Free Energies= -233.258590

Cyclopropyl methyl vinylidene carbene triplet (3a)

Charge = 0 Multiplicity = 3

C,0,0.4651413,-0.6672155,-0.07756048

C,0,1.56845542,0.03348052,0.75573942

C,0,1.55853215,0.22004876,-0.71019289

H,0,0.59803766,-1.73533443,-0.19726869

H,0,2.29604676,-0.63432846,1.19954188

H,0,1.2538484,0.85196246,1.39044177

H,0,1.24060435,1.1747338,-1.10969324

H,0,2.28726627,-0.30730954,-1.31333671

C,0,-0.92648692,-0.24543682,-0.00963769

C,0,-1.29341815,1.21291824,0.04519493

H,0,-0.52294419,1.85192045,0.48592479

H,0,-1.47254133,1.57184263,-0.97748263

H,0,-2.22977965,1.3415414,0.59017602

C,0,-1.9473135,-1.23963325,-0.01492717

Zero-point correction= 0.115682 (Hartree/Particle)

Thermal correction to Energy= 0.122658

Thermal correction to Enthalpy= 0.123602

Thermal correction to Gibbs Free Energy= 0.083849

Sum of electronic and zero-point Energies= -233.166504

Sum of electronic and thermal Energies= -233.159529

Sum of electronic and thermal Enthalpies= -233.158585

Sum of electronic and thermal Free Energies= -233.198337

Cyclopropyl methyl acetylene (5a)

Charge = 0 Multiplicity = 1

C,0,1.0212939738,0.0000006349,0.5954224255

C,0,1.9869872138,0.7509137912,-0.3085937721

C,0,1.9869872665,-0.7509145053,-0.3085920497

H,0,1.2735081699,0.0000017616,1.6512069706

H,0,2.8109219377,1.2690257714,0.1672493883

H,0,1.5617935745,1.2599484555,-1.1641502502

H,0,1.5617937919,-1.2599512,-1.1641473706

H,0,2.8109220121,-1.2690252949,0.1672523717

C,0,-0.3894389883,0.0000004237,0.3144322699

C,0,-3.0053856503,0.0000000557,-0.1908175575

H,0,-3.3005785849,-0.8841679535,-0.7639517547

H,0,-3.5816441632,0.0000080131,0.739275513

H,0,-3.3005751138,0.8841607276,-0.7639648612

C,0,-1.5733323096,-0.0000006311,0.0842566971

Zero-point correction= 0.118584 (Hartree/Particle)

Thermal correction to Energy= 0.125585

Thermal correction to Enthalpy= 0.126529

Thermal correction to Gibbs Free Energy= 0.086572

Sum of electronic and zero-point Energies= -233.310242

Sum of electronic and thermal Energies= -233.303241

Sum of electronic and thermal Enthalpies= -233.302297

Sum of electronic and thermal Free Energies= -233.342254

TS singlet **3a** to **5a** – cyclopropyl shift

Charge = 0 Multiplicity = 1

C,0,-0.492843136,1.5718963687,0.3486315633

C,0,-1.4301974541,0.7904151387,-0.6033907305

C,0,-1.4776507518,2.27438672,-0.5695639591

H,0,-0.7683143228,1.5307850942,1.3946346099

H,0,-0.9930996861,0.3156199656,-1.4726688635

H,0,-2.2221525962,0.2225937309,-0.1286893247

H,0,-2.3112848343,2.7664313296,-0.0813293853

H,0,-1.0428481544,2.8208262864,-1.3960980782

C,0,1.1316212718,0.8755621548,0.013759625

C,0,1.432590606,-0.5510924706,-0.1048486301

H,0,2.5103053713,-0.6519276872,-0.2607631244

H,0,1.1702537053,-1.097835538,0.8054471186

H,0,0.9224655045,-1.014804671,-0.953468429

C,0,1.105487957,2.127664648,0.1665791179

Zero-point correction= 0.115876 (Hartree/Particle)

Thermal correction to Energy= 0.122397

Thermal correction to Enthalpy= 0.123341

Thermal correction to Gibbs Free Energy= 0.085964

Sum of electronic and zero-point Energies= -233.216408

Sum of electronic and thermal Energies= -233.209886

Sum of electronic and thermal Enthalpies= -233.208942

Sum of electronic and thermal Free Energies= -233.246319

***** 1 imaginary frequencies (negative Signs) *****

Frequencies -- -353.7050

TS singlet **3a** to **5a** – methyl shift

Charge = 0 Multiplicity = 1

C,0,-0.7183228985,-0.6780724448,0.0021623018

C,0,-1.6060695176,0.2871819293,-0.7554849931

C,0,-1.6075263491,0.291685963,0.7522446347

H,0,-1.0394329005,-1.71468646,0.0049985665

H,0,-2.4619548436,-0.126816014,-1.2741596873

H,0,-1.1333364968,1.1156470427,-1.2689900157

H,0,-1.1357510707,1.1231570515,1.2617495879

H,0,-2.4644546086,-0.1191731137,1.2716939758

C,0,0.7335176782,-0.6103905034,0.003178285

C,0,1.7213281328,0.9101687088,-0.0002115316

H,0,2.2653730767,1.1729005932,-0.9019328738

H,0,0.7816706259,1.4757037845,-0.0025130441

H,0,2.2636150159,1.1771532664,0.9013191741

C,0,1.9658981561,-0.8786238038,0.0042646201

Zero-point correction= 0.115815 (Hartree/Particle)

Thermal correction to Energy= 0.122423

Thermal correction to Enthalpy= 0.123367

Thermal correction to Gibbs Free Energy= 0.085460

Sum of electronic and zero-point Energies= -233.209462

Sum of electronic and thermal Energies= -233.202853

Sum of electronic and thermal Enthalpies= -233.201909

Sum of electronic and thermal Free Energies= -233.239816

***** 1 imaginary frequencies (negative Signs) *****

Frequencies -- -378.6697

Cyclopropyl phenyl vinylidene carbene singlet (3b)

Charge = 0 Multiplicity = 1

C,0,0.9156086858,2.3043426487,-0.0008540067

C,0,1.1077427843,1.0161408189,-0.0003637873

C,0,-0.2982340797,0.4461105567,-0.0001823596

C,0,-0.9490946914,0.1719576644,1.2101314957

C,0,-0.9490359086,0.1710419578,-1.2103200437

C,0,-2.2144329987,-0.4091411046,1.2084228827

H,0,-0.4590570597,0.4230429253,2.1431296598

C,0,-2.2143743262,-0.4100553468,-1.2082331711

H,0,-0.458953099,0.4214214163,-2.1434841269

C,0,-2.8458948253,-0.703424047,0.0001906864

H,0,-2.7123262533,-0.619884086,2.147986036
H,0,-2.7122219846,-0.6215091811,-2.147660773
H,0,-3.8343756595,-1.1488378576,0.000335156
C,0,2.3459205869,0.1939425507,-0.0000193434
C,0,2.4164995797,-1.118506517,-0.7522644433
C,0,2.416458331,-1.1179385038,0.753219808
H,0,3.2509429419,0.7899739884,-0.0002192755
H,0,1.5191162107,-1.4651683441,-1.2499902954
H,0,3.3381533107,-1.3415290471,-1.2760051795
H,0,3.3380835725,-1.3405656663,1.2771788583
H,0,1.5190478826,-1.4642248257,1.2511582226

Zero-point correction= 0.170188 (Hartree/Particle)

Thermal correction to Energy= 0.180086

Thermal correction to Enthalpy= 0.181030

Thermal correction to Gibbs Free Energy= 0.133937

Sum of electronic and zero-point Energies= -424.957500

Sum of electronic and thermal Energies= -424.947602

Sum of electronic and thermal Enthalpies= -424.946657

Sum of electronic and thermal Free Energies= -424.993751

Cyclopropyl phenyl vinylidene carbene triplet (3b)

Charge = 0 Multiplicity = 3

C,0,1.3350130591,1.8648087603,0.1005419587
C,0,0.9244211122,0.5046583086,0.017955865

C,0,-0.5016325702,0.1691906024,0.0057872366
 C,0,-1.4513754858,1.2202594288,-0.0167876167
 C,0,-0.9908821762,-1.157346582,0.0224553705
 C,0,-2.8120125601,0.9558535161,-0.0288228404
 H,0,-1.0830094187,2.2386639231,-0.024718745
 C,0,-2.3541147537,-1.416352111,0.0154062965
 H,0,-0.3044629346,-1.9930172643,0.0498718511
 C,0,-3.2714003279,-0.3629761018,-0.0124620483
 H,0,-3.5197085972,1.7767267314,-0.04952781
 H,0,-2.707171282,-2.4412532173,0.0326551461
 H,0,-4.3356182648,-0.5700892917,-0.0195149175
 C,0,1.9456405591,-0.5509490427,-0.0495910726
 C,0,3.2849983684,-0.2535061641,-0.750450337
 C,0,3.2660360873,-0.3701421357,0.7246310546
 H,0,1.6154112565,-1.5773368918,-0.138981503
 H,0,3.3835894906,0.7370087703,-1.1755248337
 H,0,3.6918042856,-1.0666273857,-1.3401281684
 H,0,3.6598592771,-1.2658643686,1.1905183595
 H,0,3.3511794152,0.5410051657,1.3026689739
 Zero-point correction= 0.169720 (Hartree/Particle)
 Thermal correction to Energy= 0.179337
 Thermal correction to Enthalpy= 0.180281
 Thermal correction to Gibbs Free Energy= 0.131984

Sum of electronic and zero-point Energies= -424.903768

Sum of electronic and thermal Energies= -424.894150

Sum of electronic and thermal Enthalpies= -424.893206

Sum of electronic and thermal Free Energies= -424.941503

Cyclopropyl phenyl acetylene (5b)

Charge = 0 Multiplicity = 1

C,0,-0.8395074935,3.0247168071,-0.870993507

C,0,-0.2296546669,2.1767450611,-1.4805797061

C,0,-1.558792453,4.0260302213,-0.1539028557

C,0,-1.8994256473,3.8371230512,1.1977221317

C,0,-1.9421732374,5.2234929779,-0.7846814128

C,0,-2.6008757614,4.8164786967,1.8926932668

H,0,-1.6084341054,2.9179935321,1.6920922272

C,0,-2.643456361,6.1979302986,-0.0827775095

H,0,-1.6840978335,5.3776384856,-1.8255454815

C,0,-2.9760291188,6.0001004205,1.2573122555

H,0,-2.8556338608,4.6550971763,2.934254433

H,0,-2.9315128064,7.1153913729,-0.5838490383

H,0,-3.5227220375,6.7616115304,1.8016548158

C,0,0.49373363,1.1732354029,-2.2070402658

C,0,1.5518596273,0.3294199421,-1.5079387562

C,0,0.2571561732,-0.3042749972,-1.9219388863

H,0,0.7017862108,1.4242908157,-3.2420881074

H,0,1.7125104827,0.5210150905,-0.4547660286
 H,0,2.4473506284,0.0972180774,-2.0715327557
 H,0,0.2560341353,-0.975251137,-2.7723872336
 H,0,-0.4633955746,-0.5442274463,-1.1506300854
 Zero-point correction= 0.172015 (Hartree/Particle)
 Thermal correction to Energy= 0.181695
 Thermal correction to Enthalpy= 0.182639
 Thermal correction to Gibbs Free Energy= 0.134667
 Sum of electronic and zero-point Energies= -425.042818
 Sum of electronic and thermal Energies= -425.033138
 Sum of electronic and thermal Enthalpies= -425.032193
 Sum of electronic and thermal Free Energies= -425.080166

TS singlet **3b** to **5b** – cyclopropyl shift

Charge = 0 Multiplicity = 1
 C,0,-0.3129520187,1.4671632655,1.0826773558
 C,0,-1.2063829599,0.648613855,0.7169188428
 C,0,-2.3995662273,-0.0393773858,0.3090426488
 C,0,-3.631040697,0.3914046704,0.8343213669
 C,0,-2.3820431498,-1.0939547152,-0.6165106929
 C,0,-4.8140938874,-0.2159550502,0.4290551701
 H,0,-3.6468982733,1.2008429059,1.553950491
 C,0,-3.5705691447,-1.7057611947,-1.0025047201
 H,0,-1.4392493906,-1.4275832275,-1.0311462292

C,0,-4.7893760945,-1.2686832986,-0.485849531

H,0,-5.7577674802,0.1279015695,0.837008029

H,0,-3.5444090156,-2.5217898492,-1.7157307267

H,0,-5.7131894112,-1.745243615,-0.7927316873

C,0,0.4827193551,0.003710905,0.7669537753

C,0,1.293453991,-0.4981685381,1.9520765655

C,0,0.3064098272,-1.4231231334,1.3427052342

H,0,1.0046144453,0.0572411348,-0.1792400333

H,0,1.0551898137,-0.0491268086,2.9074850508

H,0,2.3507889955,-0.6516306003,1.7670451866

H,0,0.6601059497,-2.2309891746,0.7123839463

H,0,-0.6028784572,-1.641763975,1.8869276576

Zero-point correction= 0.169172 (Hartree/Particle)

Thermal correction to Energy= 0.178510

Thermal correction to Enthalpy= 0.179454

Thermal correction to Gibbs Free Energy= 0.133668

Sum of electronic and zero-point Energies= -424.945761

Sum of electronic and thermal Energies= -424.936423

Sum of electronic and thermal Enthalpies= -424.935479

Sum of electronic and thermal Free Energies= -424.981265

***** 1 imaginary frequencies (negative Signs) *****

Frequencies -- -360.3446

TS singlet **3b** to **5b** – phenyl shift

Charge = 0 Multiplicity = 1

C,0,1.7280482357,0.5021453281,-1.5859337564

C,0,0.7241933011,0.2970523912,-0.8360897634

C,0,1.7641964154,-1.0188012764,-0.7670693103

C,0,1.4021361009,-2.1765879403,-1.4805888073

C,0,2.5774595718,-1.1501625492,0.3740014214

C,0,1.8490831783,-3.4266475925,-1.0688121724

H,0,0.7868635453,-2.0725155294,-2.3662488439

C,0,3.0220414486,-2.4022740977,0.782077779

H,0,2.8660186682,-0.2567148385,0.9146192723

C,0,2.6594303515,-3.5423797777,0.0622810425

H,0,1.5724756958,-4.3111791685,-1.6314423066

H,0,3.6563411869,-2.4912876426,1.6568355542

H,0,3.0111814459,-4.5176942403,0.3791528401

C,0,-0.5374744105,0.4587079197,-0.1258333145

C,0,-0.7647452816,-0.050197237,1.2834447437

C,0,-1.4947079978,-0.6876117438,0.1317494613

H,0,-0.9921513306,1.4144271115,-0.3665562894

H,0,0.034043963,-0.6158716689,1.7457450359

H,0,-1.3161698772,0.5928188337,1.9585917268

H,0,-2.5519380811,-0.4863070083,0.0088587065

H,0,-1.1823597798,-1.6780796932,-0.1735158893

Zero-point correction= 0.169261 (Hartree/Particle)

Thermal correction to Energy= 0.178551

Thermal correction to Enthalpy= 0.179495

Thermal correction to Gibbs Free Energy= 0.133799

Sum of electronic and zero-point Energies= -424.952564

Sum of electronic and thermal Energies= -424.943274

Sum of electronic and thermal Enthalpies= -424.942330

Sum of electronic and thermal Free Energies= -424.988026

***** 1 imaginary frequencies (negative Signs) *****

Frequencies -- -273.4359

B.2. Summary output for (R/U) CCSD(T)/cc-pVTZ//B#LYP/6-311+G**

Cyclopropyl methyl vinylidene carbene singlet (3a)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C6H8\NNLE\11-Apr-2019\0\# ccs
d=(t,t1diag)/cc-pvtz geom=connectivity\Cyclopropyl Me Vinylidene sing
let CCSDT\0,1\C,0,-0.54612,-0.658364,0.000324\C,0,-1.557472,0.178202,
-0.754102\C,0,-1.557384,0.179064,0.753895\H,0,-0.735403,-1.725518,0.00
0987\H,0,-2.346856,-0.348304,-1.276409\H,0,-1.212563,1.073637,-1.25624
5\H,0,-1.21241,1.075077,1.254955\H,0,-2.346674,-0.346868,1.27692\C,0,0
.904596,-0.313622,0.000069\C,0,1.424065,1.119385,-0.000182\H,0,1.07661
4,1.645823,-0.892769\H,0,1.076895,1.645991,0.892417\H,0,2.515954,1.143
923,-0.000366\C,0,1.863054,-1.198626,0.00008\Version=ES64L-G16RevA.03
\State=1-A\HF=-231.7854602\MP2=-232.7403671\MP3=-232.7894339\MP4D=-232
.812651\MP4DQ=-232.7863426\MP4SDQ=-232.7941231\CCSD=-232.7939526\CCSD(
T)=-232.8404735\RMSD=4.758e-09\PG=C01 [X(C6H8)]\@

T1 Diagnostic = 0.01240832

Cyclopropyl methyl vinylidene carbene triplet (3a)

1\1\GINC-NSCC-N2\SP\UCCSD(T)-FC\CC-pVTZ\C6H8(3)\NNLE\20-Apr-2019\0\#\nccsd=(t,t1diag)/cc-pvtz geom=connectivity\\cProp Me Vinylidene triplet
CCSDT\0,3\C,0,0.46514133,-0.66721555,-0.07756049\C,0,1.56845553,0.03348052,0.75573948\C,0,1.55853226,0.22004878,-0.71019294\H,0,0.5980377,-1.73533456,-0.1972687\H,0,2.29604693,-0.6343285,1.19954197\H,0,1.25384849,0.85196252,1.39044187\H,0,1.24060444,1.17473388,-1.10969332\H,0,2.28726643,-0.30730956,-1.3133368\C,0,-0.92648699,-0.24543684,-0.00963769\C,0,-1.29341824,1.21291833,0.04519493\H,0,-0.52294423,1.85192058,0.48592482\H,0,-1.47254144,1.57184274,-0.9774827\H,0,-2.22977981,1.3415415,0.59017606\C,0,-1.94731364,-1.23963334,-0.01492717\\Version=ES64L-G16RevA.03\State=3-A\HF=-231.7430625\MP2=-232.6653575\MP3=-232.7194327\MP4D=-232.7409095\MP4DQ=-232.7163167\PUHF=-231.7463194\PMP2-0=-232.6674555\PMP3-0=-232.7206434\MP4SDQ=-232.7237989\CCSD=-232.7241313\CCSD(T)=-232.768071\S2=2.019134\S2-1=2.005438\S2A=2.000167\RMSD=5.208e-09\PG=C01 [X(C6H8)]\\@

T1 Diagnostic = 0.01495797

Cyclopropyl methyl acetylene (5a)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C6H8\NNLE\20-Apr-2019\0\#\nccsd=(t,t1diag)/cc-pvtz geom=connectivity\\cProp Me Acetylene CCSDT\0,1\C,0,-1.02132108,-0.00000068,0.59575387\C,0,-1.98701437,-0.75091391,-0.30826239\C,0,-1.98701446,0.75091449,-0.30826066\H,0,-1.27353529,-0.000

00182,1.6515385\H,0,-2.81094914,-1.26902595,0.16758081\H,0,-1.56182069
 ,-1.25994861,-1.16381893\H,0,-1.56182096,1.25995123,-1.16381605\H,0,-2
 .81094927,1.26902529,0.16758379\C,0,0.38941199,-0.00000044,0.3147637\C
 ,0,3.00535884,-0.00000001,-0.19048616\H,0,3.30055177,0.88416806,-0.763
 6204\H,0,3.58161739,-0.00000796,0.73960697\H,0,3.30054834,-0.88416074,
 -0.76363351\C,0,1.57330539,0.00000064,0.08458811\\Version=ES64L-G16Rev
 A.03\State=1-A\HF=-231.8554068\MP2=-232.8330691\MP3=-232.8692323\MP4D=
 -232.8927494\MP4DQ=-232.8657477\MP4SDQ=-232.8736602\CCSD=-232.8722863\
 CCSD(T)=-232.9200151\RMSD=5.203e-09\PG=C01 [X(C6H8)]\\@
 T1 Diagnostic = 0.00996026

TS singlet **3a** to **5a** – cyclopropyl shift

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C6H8\NNLE\16-Apr-2019\0\\# ccs
 d=(t,t1diag)/cc-pvtz geom=connectivity\\cProp Me vinylidene - TS cProp
 shift CCSDT\\0,1\C,0,0.607426,-0.291683,0.50676\C,0,1.044474,1.080317
 ,-0.060952\C,0,1.9073,-0.112304,-0.257812\H,0,0.700398,-0.391151,1.580
 613\H,0,0.512057,1.469673,-0.919476\H,0,1.329631,1.827387,0.670844\H,0
 ,2.816235,-0.210186,0.325012\H,0,1.941598,-0.564517,-1.240226\C,0,-1.0
 82808,-0.477033,-0.080318\C,0,-2.113424,0.560078,-0.033146\H,0,-3.0404
 59,0.125627,-0.4176\H,0,-2.298775,0.901244,0.989418\H,0,-1.861944,1.42
 5066,-0.652796\C,0,-0.379425,-1.523232,-0.130497\\Version=ES64L-G16Rev
 A.03\State=1-A\HF=-231.7543206\MP2=-232.7364341\MP3=-232.7730844\MP4D=
 -232.797124\MP4DQ=-232.7685767\MP4SDQ=-232.7767445\CCSD=-232.7757671\C
 CSD(T)=-232.8262767\RMSD=3.655e-09\PG=C01 [X(C6H8)]\\@

T1 Diagnostic = 0.01248113

TS singlet **3a** to **5a** – methyl shift

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C6H8\NNLE\21-Apr-2019\0\#\# ccs
d=(t,t1diag)/cc-pvtz geom=connectivity\cProp Me vinylidene TS Me shif
t CCSDT\0,1\C,0,0.718649,-0.678747,-0.00045\C,0,1.606844,0.288518,0.7
54101\C,0,1.607038,0.289351,-0.753635\H,0,1.039955,-1.715304,-0.00103\
H,0,2.463242,-0.124053,1.273066\H,0,1.134382,1.118142,1.265983\H,0,1.1
34678,1.119489,-1.264769\H,0,2.46361,-0.12261,-1.2728\C,0,-0.733205,-0
.611343,-0.000415\C,0,-1.721304,0.909033,0.000099\H,0,-2.264644,1.1738
57,0.901633\H,0,-0.781753,1.47475,0.000237\H,0,-2.264396,1.173718,-0.9
01625\C,0,-1.965535,-0.879811,0.000184\Version=ES64L-G16RevA.03\State
=1-A\HF=-231.7501514\MP2=-232.7289865\MP3=-232.7679949\MP4D=-232.79166
66\MP4DQ=-232.7632884\MP4SDQ=-232.771175\CCSD=-232.7700705\CCSD(T)=-23
2.820091\RMSD=9.402e-09\PG=C01 [X(C6H8)]\@

T1 Diagnostic = 0.01120396

Cyclopropyl phenyl vinylidene carbene singlet (**3b**)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C11H10\NNLE\16-Apr-2019\0\#\# c
csd=(t,t1diag)/cc-pvtz geom=connectivity\cProp Ph vinylidene CCSDT si
nglet\0,1\C,0,1.517957,1.896748,-0.211597\C,0,0.908887,0.742259,-0.21
9688\C,0,-0.491853,0.313374,-0.106852\C,0,-1.501784,1.255624,0.155033\
C,0,-0.850418,-1.031159,-0.263275\C,0,-2.828726,0.858687,0.25455\H,0,-
1.239226,2.300059,0.281113\C,0,-2.18406,-1.42508,-0.163972\H,0,-0.0853
8,-1.771716,-0.461401\C,0,-3.177057,-0.4845,0.095178\H,0,-3.595513,1.5

97851,0.457621\H,0,-2.444532,-2.470172,-0.288986\H,0,-4.213598,-0.7918
 24,0.173425\C,0,2.064093,-0.213024,-0.476814\C,0,3.45473,-0.048413,0.1
 42766\C,0,2.545315,-1.126039,0.637481\H,0,2.06525,-0.621817,-1.48217\H
 ,0,3.638194,0.801586,0.783151\H,0,4.287519,-0.323181,-0.492248\H,0,2.7
 56952,-2.153031,0.361796\H,0,2.087828,-0.998612,1.610836\\Version=ES64
 L-G16RevA.03\State=1-A\HF=-422.3502144\MP2=-424.071664\MP3=-424.120864
 3\MP4D=-424.1635406\MP4DQ=-424.1077759\MP4SDQ=-424.1226315\CCSD=-424.1
 221912\CCSD(T)=-424.217175\RMSD=4.383e-09\PG=C01 [X(C11H10)]\\@
 T1 Diagnostic = 0.01207767

Cyclopropyl phenyl vinylidene carbene triplet (3b)

1\1\GINC-NSCC-N2\SP\UCCSD(T)-FC\CC-pVTZ\C11H10(3)\NNLE\26-Apr-2019\0\\
 # ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\cProp Ph vinylidene CCSDT
 triplet\\0,3\C,0,1.335021,1.864791,0.100647\C,0,0.924417,0.504629,0.0
 18001\C,0,-0.501634,0.169192,0.005812\C,0,-1.451374,1.220264,-0.016833
 \C,0,-0.990885,-1.157345,0.022539\C,0,-2.812008,0.955855,-0.0289\H,0,-
 1.083005,2.238665,-0.024793\C,0,-2.354121,-1.41635,0.015467\H,0,-0.304
 462,-1.993007,0.050031\C,0,-3.271402,-0.362976,-0.012488\H,0,-3.519702
 ,1.776726,-0.049667\H,0,-2.707176,-2.441249,0.032766\H,0,-4.335617,-0.
 570083,-0.019564\C,0,1.945647,-0.550969,-0.04958\C,0,3.284979,-0.25343
 9,-0.750473\C,0,3.266046,-0.370195,0.724611\H,0,1.615397,-1.57734,-0.1
 39069\H,0,3.383522,0.737111,-1.175464\H,0,3.691795,-1.066515,-1.340199
 \H,0,3.659917,-1.265945,1.1904\H,0,3.351208,0.540893,1.302736\\Version
 =ES64L-G16RevA.03\State=3-A\HF=-422.3271235\MP2=-423.9658227\MP3=-424.

0379074\MP4D=-424.0745834\MP4DQ=-424.0269466\PUHF=-422.3538908\PMP2-0=-
-423.9898276\PMP3-0=-424.0569452\MP4SDQ=-424.0469755\CCSD=-424.059214\
CCSD(T)=-424.1503386\S2=2.556696\S2-1=2.418204\S2A=2.181673\RMSD=7.717
e-09\PG=C01 [X(C11H10)]\ \@

T1 Diagnostic = 0.03358319

Cyclopropyl phenyl acetylene (5b)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C11H10\NNLE\23-Apr-2019\0\# c
csd=(t,t1diag)/cc-pvtz geom=connectivity\cProp Ph Acetylene CCSDT\0,
1\C,0,0.46098401,-0.27746765,0.00021687\C,0,1.66193865,-0.41987562,0.0
0033267\C,0,-0.95561294,-0.11172152,0.00010155\C,0,-1.52895709,1.17275
649,0.00003512\C,0,-1.80829514,-1.23052124,0.00003895\C,0,-2.91086789,
1.32920907,-0.0000887\H,0,-0.88024317,2.0405395,0.00008944\C,0,-3.1891
668,-1.06563059,-0.00007044\H,0,-1.37552966,-2.22373621,0.00009037\C,0
,-3.74697758,0.21281741,-0.00013779\H,0,-3.33671859,2.32642855,-0.0001
4203\H,0,-3.83242108,-1.93856135,-0.00010055\H,0,-4.82374014,0.3379721
,-0.0002318\C,0,3.08606467,-0.59288595,0.00042464\C,0,3.98041654,0.385
42172,-0.75020661\C,0,3.98051423,0.38644253,0.74953394\H,0,3.41728357,
-1.62629411,0.00114047\H,0,3.48920601,1.20358397,-1.26110101\H,0,4.836
08036,-0.02905162,-1.26935158\H,0,4.83624908,-0.02749052,1.26900491\H,
0,3.48958962,1.20534183,1.25952059\Version=ES64L-G16RevA.03\State=1-A
\HF=-422.4260217\MP2=-424.1645379\MP3=-424.2026669\MP4D=-424.2457472\M
P4DQ=-424.1895059\MP4SDQ=-424.2042811\CCSD=-424.2029736\CCSD(T)=-424.2
98275\RMSD=7.138e-09\PG=C01 [X(C11H10)]\ \@

T1 Diagnostic = 0.01044159

TS singlet **3b** to **5b** – cyclopropyl shift

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C11H10\NNLE\19-Apr-2019\0\# c
csd=(t,t1diag)/cc-pvtz geom=connectivity\cProp Ph vinylidene CCSDT -
TS cProp shift\0,1\C,0,-1.860678,-1.525895,-0.70039\C,0,-0.81097,-0.8
66934,-0.443671\C,0,0.52021,-0.376814,-0.217562\C,0,1.477936,-1.263559
,0.306332\C,0,0.903676,0.935463,-0.533744\C,0,2.789508,-0.84313,0.4954
32\H,0,1.183103,-2.275144,0.557484\C,0,2.215121,1.350615,-0.324813\H,0
,0.174667,1.62283,-0.943822\C,0,3.16274,0.464862,0.185991\H,0,3.520196
, -1.536977,0.895251\H,0,2.499025,2.367825,-0.569681\H,0,4.184281,0.791
256,0.342952\C,0,-2.350933,0.081252,-0.474125\C,0,-3.418459,0.230074,0
.599155\C,0,-2.194448,1.060367,0.715529\H,0,-2.565484,0.545543,-1.4275
\H,0,-3.532679,-0.613408,1.267516\H,0,-4.345795,0.69184,0.2789\H,0,-2.
246504,2.114107,0.466579\H,0,-1.473028,0.814319,1.483513\\Version=ES64
L-G16RevA.03\State=1-A\HF=-422.3216171\MP2=-424.0662495\MP3=-424.10424
77\MP4D=-424.1479963\MP4DQ=-424.0901767\MP4SDQ=-424.1053457\CCSD=-424.
1044091\CCSD(T)=-424.2028141\RMSD=4.886e-09\PG=C01 [X(C11H10)]\\@

T1 Diagnostic = 0.01206733

TS singlet **3b** to **5b** – phenyl shift

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C11H10\NNLE\28-Apr-2019\0\# c
csd=(t,t1diag)/cc-pvtz geom=connectivity\cProp Ph vinylidene - TS Ph
shift CCSDT\0,1\C,0,0.61677379,2.20651619,-0.00076816\C,0,1.26619199,
1.11550292,-0.00039249\C,0,-0.38188429,0.79662029,-0.00025911\C,0,-0.9

6864561,0.38738625,1.21172547\C,0,-0.96847831,0.38638868,-1.21199874\C
 ,0,-2.11349135,-0.40083616,1.20954017\H,0,-0.5234819,0.71483826,2.1435
 9977\C,0,-2.11331245,-0.40184396,-1.20933675\H,0,-0.52314666,0.7130470
 1,-2.14407012\C,0,-2.68810483,-0.79682316,0.00022538\H,0,-2.56319945,-
 0.70229527,2.14887274\H,0,-2.56288098,-0.70408941,-2.14848356\H,0,-3.5
 8389257,-1.40751074,0.00041443\C,0,2.35003756,0.14201378,-0.00003844\C
 ,0,2.28228866,-1.17193783,-0.75213068\C,0,2.28224524,-1.17136665,0.753
 04201\H,0,3.31332989,0.64215961,-0.00023536\H,0,1.35396819,-1.41378362
 ,-1.25363369\H,0,3.17690362,-1.49012269,-1.27346056\H,0,3.17680621,-1.
 48917265,1.27469456\H,0,1.35387118,-1.41279251,1.25464986\\Version=ES6
 4L-G16RevA.03\State=1-A\HF=-422.3291021\MP2=-424.0752017\MP3=-424.1125
 161\MP4D=-424.1565798\MP4DQ=-424.0984866\MP4SDQ=-424.1133172\CCSD=-424
 .1126498\CCSD(T)=-424.2113666\RMSD=9.010e-09\PG=C01 [X(C11H10)]\@
 T1 Diagnostic = 0.01250319