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Experimental and Computational Study of Methylphenylvinylidene and Its Rearrangements

Xi Yang

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Experimental and Computational Study of Methylphenylvinylidene and Its Rearrangement

By Xi Yang

A Thesis Presented to the Department of Chemistry,
Colby College, Waterville, ME
In Partial Fulfillment of the Requirements for Graduation
With Honors in Chemistry

Submitted May, 2016

Experimental and Computational Study of Methylphenylvinylidene and Its Rearrangement

By Xi Yang

Approved:

(Mentor: Dasan M. Thamattoor, Professor of Chemistry)

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(Reader: Rebecca R. Conry, Associate Professor of Chemistry)

_____Date

“What I cannot create, I do not understand.”
— Richard P. Feynman

“Hang in there.”
— Dasan M. Thamattoor

Vitae

Xi Yang was born to Hongwei Xu and Chao Yang on May 18th, 1994, in Dalian, China. She grew up in Dalian with her grandparents and went to high school at Dalian No. 24 High School. During secondary schools, Xi developed her interests in science and decided to become a surgeon in the future. In the second year of high school, she decided to apply for liberal art colleges in the United States and applied for Colby College as early decision.

Xi enrolled in Colby College, Waterville, ME in September of 2012, with intentions to major in biology and to pursue a pre-medical track. She did not think of majoring in chemistry until the end of her sophomore year, when Professor Dasan Thamattoor and the organic chemistry course he taught persuaded her that organic chemistry was more attractive and suitable to her. After joining Professor Thamattoor's research group, she found that she enjoyed doing research in organic chemistry and would like to pursue a career in organic synthesis.

Apart from science, Xi developed interests in music and decided to minor in music at Colby. She studied piano with Professor Yuri Funahashi and guitar with Mark Leighton. In her senior year, she started to write popular songs under the instruction of Professor Kate Heidemann.

On May 22nd, 2016, Xi will graduate from Colby with double majors in Chemistry and Biology and a minor in Music. She is still uncertain about her exact future, except for continuing studies in chemistry.

Acknowledgements

First of all, I would like to thank my family, my parents, grandparents and younger sister, for supporting me in developing my interests and making my own decisions. Without them, I could not become who I am right now, and everything that I have achieved would be impossible. Additionally, I would like to thank my significant other, who would always encourage me when I got frustrated by the obstacles in research.

I would also like to thank the faculty at Colby College, especially those in the Chemistry Department. I appreciate the knowledge I learned from them and the support and advice they gave me as I struggled future plans. I am grateful to my classmates and lab mates, because with their help and encouragement, I got through the arduous class and lab work. I also very appreciate my friends' patience in waiting for me to be finished with lab work throughout my college life.

Last and foremost, I would like to thank Professor Dasan M. Thamattor. To me, he is a mentor, a friend and a father. Without him, I would not consider to pursue my career in chemistry. His passion in organic chemistry truly inspired me. He would stay up late with us waiting for results; he would encourage me when I was disappointed by failures in reactions and when I got rejections from graduate schools. In addition, he would get even more excited than me when something worked. I could not express enough appreciation to him for his guidance, support and encouragement.

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Abstract

In this study, the synthesis and properties were explored of the compound methylphenylvinylidene (MPV), a vinylidene carbene with methyl and phenyl groups as substituents. A phenanthrene-based precursor, 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene, was synthesized in three steps and was subjected to photolysis in C₆D₆ at ambient temperature. During photolysis, the MPV carbene rearranged into 1-phenylpropyne via a 1,2-phenyl shift, instead of 1,2-methyl shift, confirmed by photolysis of ¹³C-labeled precursor. This experimental result is consistent with computational results using the CCSD(T)/cc-pVTZ//B3LYP/6-31+G* method. The calculations suggest that the 1,2-phenyl shift in singlet carbene requires 3.8 kcal/mol to overcome the barrier, whereas the 1,2-methyl shift needs 11.9 kcal/mol. The generation of MPV carbene was confirmed by trapping with cyclohexene, which gave a carbene-alkene cycloadduct, with a yield of 1.5%. The identity of the trapped product was confirmed by the authentic sample of the trapped adduct, which was synthesized in three steps starting from cyclohexene. Additionally, upon photolysis, 11% of the precursor rearranged into a mixture of E- and Z- cycloheptatriene derivatives.

Introduction

1.1 Carbene

Carbene can be classified as one of the fundamental intermediates along with carbanion, carbocation and carbon-centered radicals.¹ A carbene is a neutral species with a divalent carbon, which is also known as a carbene carbon.² Typically a carbene carbon is covalently bonded to two adjacent groups, has an approximate sp^2 hybridization, and possess two non-bonding electrons (Figure 1).³ Because the carbene carbon only has six electrons instead of the more stable octet configuration, carbenes are extremely unstable, highly reactive and thus short lived. There are two common electronic states of a carbene, known as singlet and triplet.³ In the singlet state, the lone pair electrons have antiparallel spins and occupy one sp^2 -hybridized orbital, leaving an empty p orbital. In the triplet state, the two non-bonding electrons have parallel spins, and are found in two orbitals, and sp^2 hybridized orbital and a p orbital (Figure 2). Thus, the system's total spin for the singlet state is zero ($S = 0$), while that for the triplet state is 1 ($S = 1$).⁴ Generally, the triplet state has a lower energy compared to the singlet state due to minimization of electron-electron repulsion.² However, the relative stabilities of the singlet and triplet states depend greatly on the groups attached to the carbene carbon.³

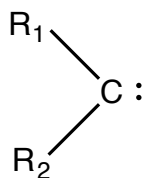


Figure 1. General form of carbene

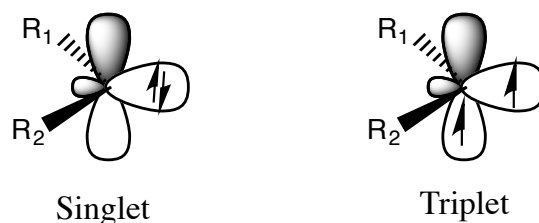


Figure 2. Common electronic states of a carbene

Usually substituents acting as electron-pair donors stabilize the singlet state more than triplet state, whereas dialkylcarbenes prefer triplet ground states.⁵ Commonly there is an equilibration between the singlet and triplet states when the energy difference between these two states is small.⁶ In this case, reactions will involve both singlet and triplet carbenes.

Singlet carbenes are electron-deficient compared to organic species with octet carbons, but they also possess two non-bonded electrons.³ Therefore, singlet carbenes can act as either an electrophile or a nucleophile. The triplet carbene is essentially as a 1,1-diradical and its reactivity is similar to that of free radicals.¹ The electrophilic or nucleophilic characteristics of a carbene carbon significantly depend on the electron-withdrawing or electron-donating nature of the adjacent groups of the carbene carbon.³ Based on the relative reactivity of a carbene towards a variety of alkenes, including both nucleophilic alkenes and electrophilic alkenes, a carbene can be classified as nucleophilic, ambiphilic or electrophilic.¹

1.2 Generation of Carbenes

The first attempts to generate carbenes were conducted in the 1830s.³ However, due to the short-lived nature of carbenes, there was little progress in this research until around 1910, when Staudinger confirmed the formation of methylene, the parent carbene

(with $R_1 = R_2 - H$).^{7,8} Starting from about 1950, interests in research on carbenes began to grow.⁷

In previous work, carbenes are usually generated through pyrolysis or through photolysis with ultraviolet light using some common precursors, including ketenes, diazo compounds and diazirine compounds.³ The photolysis or pyrolysis of ketene precursors produces a carbene and carbon monoxide (Figure 3). This reaction is favored due to a large entropic driving force from the formation of two species (one a gas) from one. However, this method has a serious drawback in that ketenes are difficult to prepare.

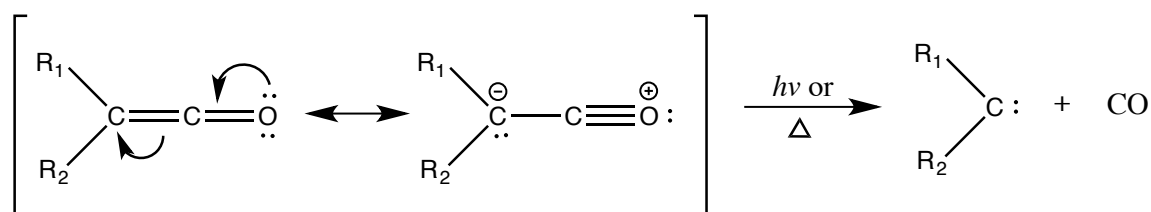


Figure 3. Generation of a carbene from a ketene precursor

Both diazo precursors and diazirine precursors yield a carbene plus dinitrogen upon decomposition (Figures 4 and 5). Similar to the photolysis of ketene, these reactions have a large increase in entropy and are favored.

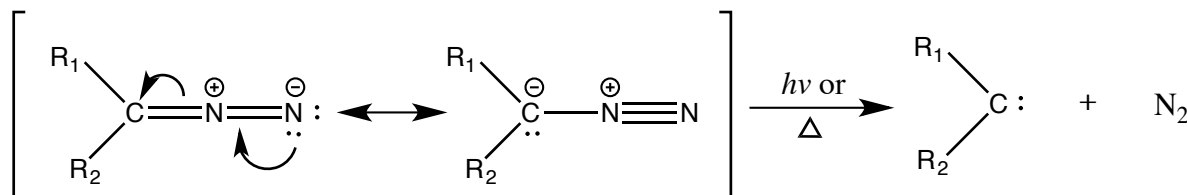


Figure 4. Generation of a carbene from a diazo precursor

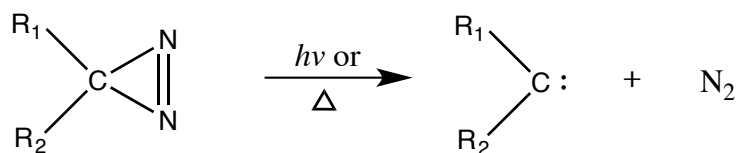


Figure 5. Generation of a carbene from a diazirine precursor

Although relatively easily accessed, diazo and diazirine compounds are considered potential human carcinogens.^{9,10} Additionally, diazo compounds are poisonous and are unstable to a potentially explosive decomposition.² Therefore, these compounds could cause health issues and working with them can be dangerous.

Another common way to generate carbene is to treat haloforms with strong bases, such as hydroxide or potassium *tert*-butoxide (Figure 6).² The halogen in the haloform precursor is usually chlorine or bromine. The strong base deprotonates this precursor yielding a carbanion and then a carbene is formed when a halide leaves. In order for this reaction to happen, the precursor has to be acidic enough for the strong base to deprotonate it. Thus, the choice of precursors is limited as the groups on the carbon have to be significantly electron-withdrawing.

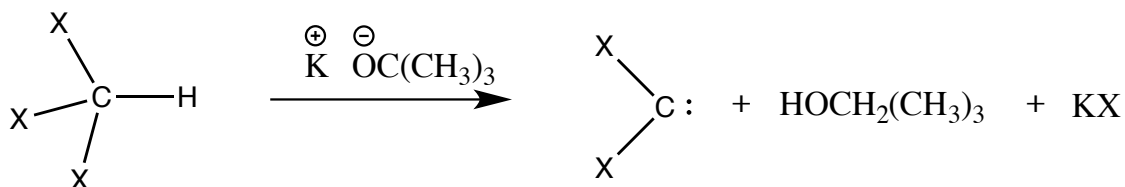


Figure 6. Generation of a carbene from an alkyl halide (X = Cl or Br) and a strong base

Another carbene source is a phenanthrene-based precursor **1** in Figure 7.¹¹ Photolysis of this precursor yields a carbene and phenanthrene. This reaction is thermodynamically favored due to the large entropy increase from the reactant to the

products. Given that this shelf-stable precursor is safe and convenient, this method of generating carbenes is widely used.

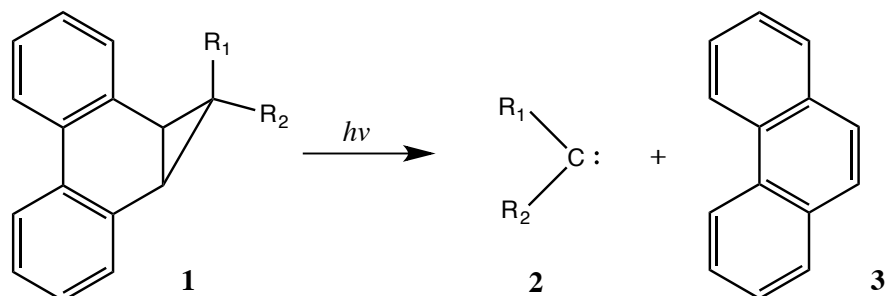


Figure 7. Generation of carbene from phenanthrene-based precursor

1.4 Vinylidene

Not all carbenes are saturated or bisubstituted. Most notably, vinylidene carbenes (4) belong to a subclass of carbenes that are unsaturated (Figure 8). These carbenes have only a singlet electronic ground state, with the two non-bonding electrons occupying an *sp*-hybridized orbital. The triplet electronic state is much higher in energy in these species due to a larger energy gap between *sp*-hybridized orbital and *p* orbital compared to that between the *sp*²-hybridized orbital and *p* orbital for saturated carbenes.

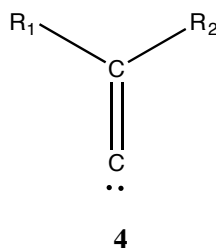


Figure 8. A general structure of a vinylidene carbene

Similar to that seen for saturated carbenes, vinylidene carbenes can be obtained through the photolysis of phenanthrene-based precursors (**5**), with the production of the phenanthrene (Figure 9).¹²

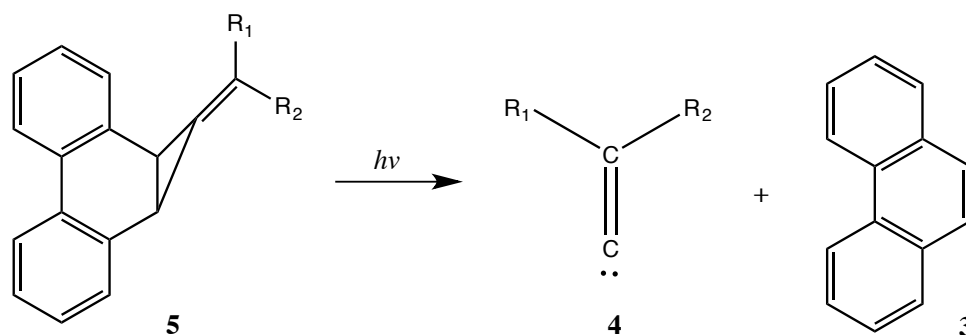


Figure 9. Generation of a vinylidene carbene from a phenanthrene-based precursor

Since carbenes, including vinylidene carbenes, are extremely reactive, their formation is usually indirectly detected through reacting with another compound referred to as a trapping reaction. For example, the addition reaction of an alkene to a carbene forms a cyclopropane derivative. The nature of the alkene utilized can be used to study how electron-rich or -poor the carbene is.¹ Such experiments have determined that the electrophilic properties of vinylidene carbenes are comparable to those of dihalocarbenes, such experiments have determined that they can be trapped by cyclohexene (Figure 10).¹³

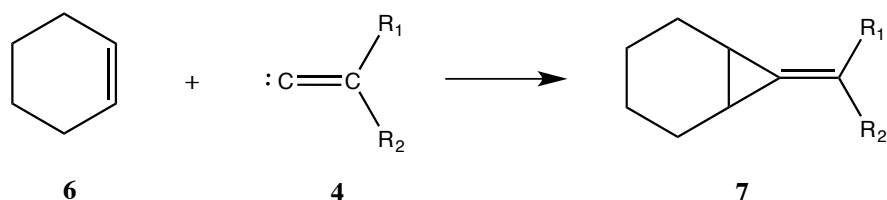


Figure 10. Trapping of Vinylidene Carbene

1.5 Rearrangement of Vinylidene Carbene

A vinylidene carbene will rearrange without a trapping reagent present. Due to the high reactivity of carbene, it tends to rearrange into alkyne, a more stable compound, through the 1,2-shift of an R group (Figure 11). Though the product is always an alkyne, it could be formed from either the shift of the R₁ group or the R₂ group. The favorability of one R group to shift over the other one depends on the transitional barrier for the rearrangement.

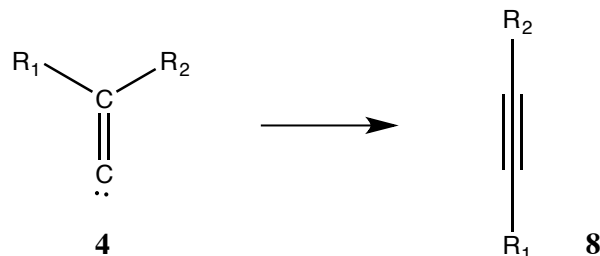


Figure 11. Rearrangement of vinylidene carbene

Apart from the vinylidene carbene rearranging into an alkyne, the precursor (**5**) rearranges into a cycloheptatriene derivative (**10**) upon photolysis. It undergoes a 1,5-sigmatropic shift, followed by electrocyclic ring opening upon photolysis (Figure 12). The 1,5-sigmatropic shift is a pericyclic reaction, with one sigma-bond changing into another sigma-bond during an intramolecular process.¹ The electrocyclic ring opening is also an intramolecular process. The resulting rearranged precursor is a mixture of *E*- and *Z*-isomers of a cycloheptatriene derivative (**10**).

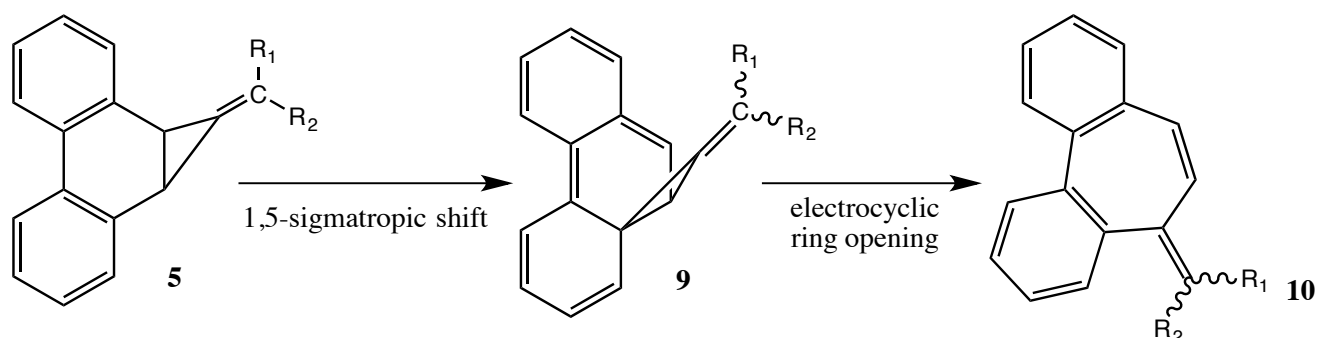


Figure 12. Addition reaction of phenanthrene with vinylidene carbene and the rearrangement

Previous studies in our lab have probed the generation and reaction of vinylidene carbenes with a variety of substituents. Moore and Jesus worked on benzyldenecarbene (12) and its arrangement to phenylacetylene (13).¹⁴ She used a ¹³C labeled precursor (11) to generate benzyldenecarbene (12) upon photolysis, which they could tell rearranged to the phenylacetylene product (13) only through hydrogen shift as the acetylenic hydrogen was bound only to the unlabeled carbon (Figure 13).¹⁴ Both computational and experimental data showed that hydrogen shift had a smaller transition-state barrier compared to phenyl shift.

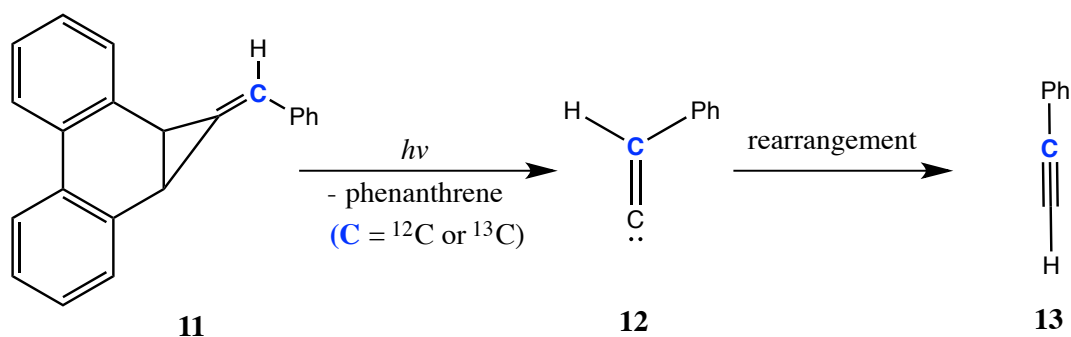


Figure 13. Generation of benzyldenecarbene and its rearrangement

Hardikar carried out a study on dimethylvinylidene carbene, which was generated upon photolysis of precursor **14** (Figure 14).¹⁵ Because the rearrangement reaction of dimethylvinylidene produces but-2-yne, the volatile compound, this product was not observed. However, the dimethylvinylidene carbene could be trapped by cyclohexene with a yield of 23% (Figure 14).¹⁵ Additionally, the cycloheptatriene derivative formed by the rearrangement reaction of the precursor was obtained after photolysis with a yield of 21% (Figure 15).¹⁵

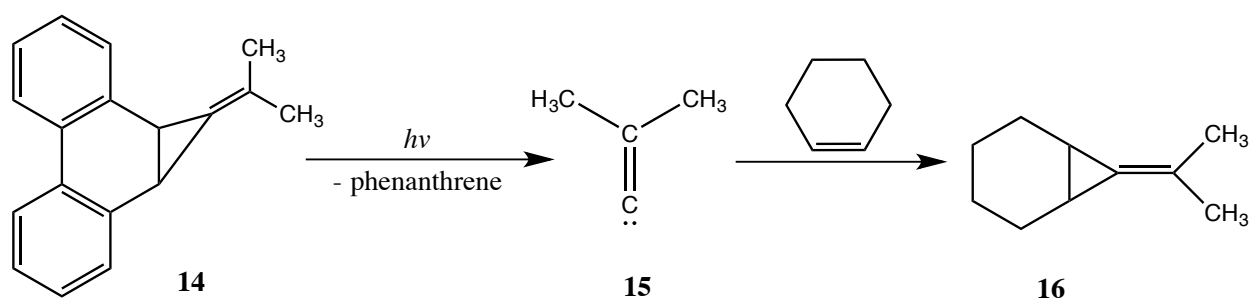


Figure 14. Generation and trapping of dimethylvinylidene carbene

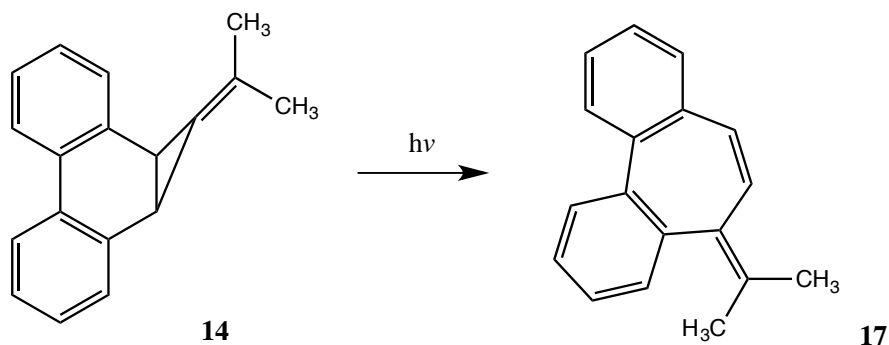


Figure 15. Generation of the cycloheptatriene derivative from the dimethyl-precursor (**14**)

This project focused on methylphenylvinylidene, a vinylidene with one methyl and one phenyl group as substituents. Analogous to Moore's work but without a hydrogen shift, the goal of this project is to probe through experiments and theoretical calculations

whether a methyl shift or a phenyl shift is favored for the rearrangement of methylphenylvinylidene (Figure 16). Predicted from Hardikar's study, the formation of a cycloheptatriene derivative from the rearrangement of the precursor (**19**) is expected, which should be a mixture of both the *E*- and *Z*- isomers of **21** (Figure 17).

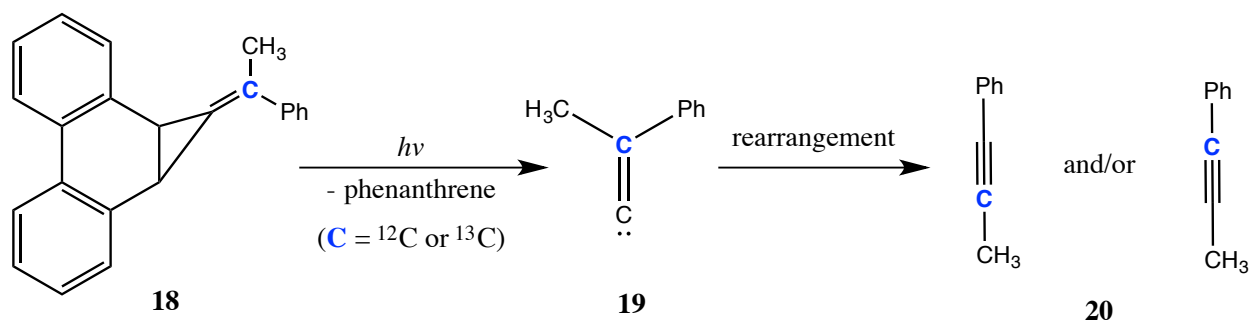


Figure 16. Possible rearrangement products for of methylphenylvinylidene carbene

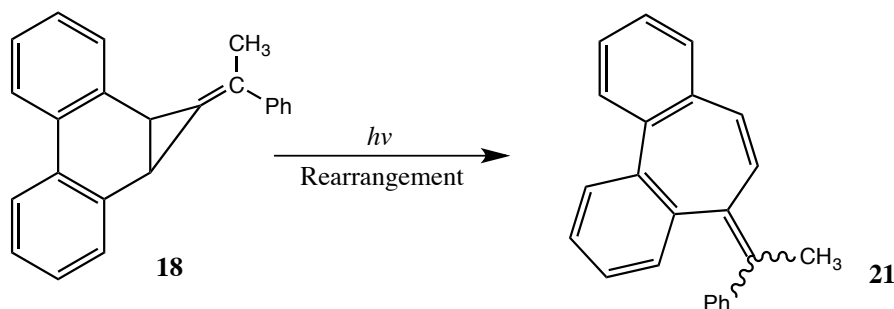


Figure 17. Predicted generation of a cycloheptatriene derivative from methylphenylvinylidene carbene

Results and Discussion

2.1 Synthesis of The Methylphenylvinylidene Carbene Precursor

The photochemically active precursor **18** for generating methylphenylvinylidene carbene was synthesized in three steps, as shown in figure 18. Following a previously published procedure, phenanthrene (**3**) was treated with bromoform, aqueous sodium hydroxide and the phase transfer catalyst triethylbenzylammonium chloride to synthesize the dibromo species **22**.¹⁶ In this step, the bromoform and sodium hydroxide formed dibromocarbene through basic hydrolysis. The dibromocyclopropyl compound was generated through cyclopropanation of the dibromocarbene onto the 9,10 double bond in phenanthrene. Then, the dibromo adduct was treated with *n*-butyllithium at -70 °C to generate the carbanion via lithium-halogen exchange, which then gave the monobromo derivative **23** upon quenching with water.¹⁷ Finally, treatment of the monobromo species **23** with *tert*-butyllithium at -70 °C gave cyclopropyllithium. Following the procedure developed by Petasis et al., the addition of titanocene chloride forms a complex with cyclopropyllithium, which is converted to the precursor **18** by the addition of acetophenone.¹⁸ The analogous method was used to synthesize the ¹³C-labeled precursor employing ¹³C-labeled acetophenone with the labeling at the carbonyl position. After purification by flash chromatography, the overall yield for pure **18** was 15% and the yield for ¹³C-labeled **18** from one reaction was 13%.

Recently, an alternative scheme for synthesizing the precursor **18** directly from the dibromo adduct **22** was developed, as shown in figure 19.¹⁹ Titanocene chloride, magnesium, and triethylphosphite are combined to give Cp₂Ti[P(OEt)₃]₂, which is reacted with **22**. The subsequent treatment of the reaction mixture with acetophenone gave the

same carbene precursor **18**. The advantage of this procedure is that it does not require low temperatures and the use of butyllithium reagents, which are extremely dangerous if not handled properly. Another advantage is that this procedure is one fewer step as the desired precursor is formed directly from the dibromo adduct **22**. However, the yield of pure **18** was not improved by this procedure as the best yield so far has been 11%.

The characterization of the precursor **18** was carried out by GC/MS, proton and carbon NMR spectroscopy and FT-IR. Unfortunately, no satisfactory crystal was grown to be able to perform X-ray crystallography on this compound.

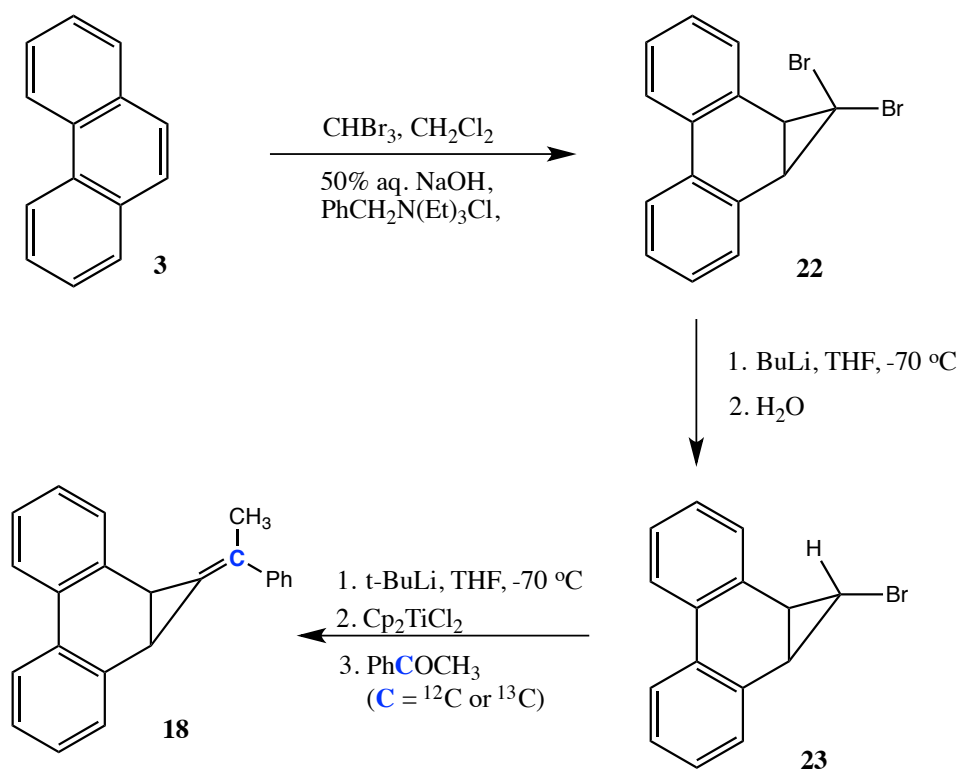


Figure 18. Synthesis of **18** or ^{13}C -labeled **18** starting from phenanthrene

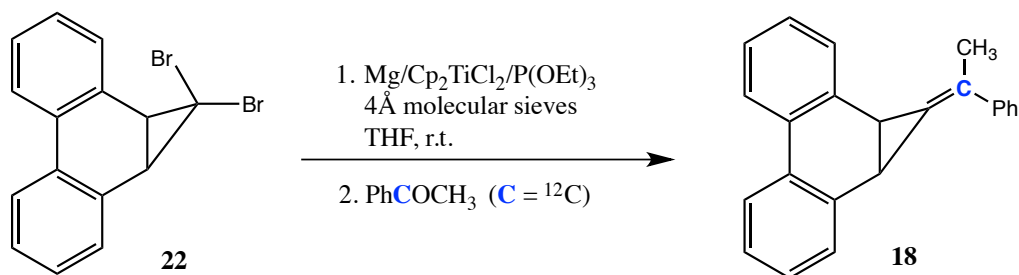


Figure 19. An alternative synthetic scheme for precursor **18**

2.2 Photochemical Generation of Methylphenylvinylidene Carbene (**19**)

Both **18** and ^{13}C -labeled **18** were photolyzed in a benzene- d_6 solution with the wavelength around 315 to 400 nm at ambient temperature for 12 hours. The photolysis was carried separately in a glass vial and pyrex NMR tube, and the photolysate was checked regularly during the photolysis by ^1H NMR spectroscopy and GC/MS. The expected reaction sequence for generating methylphenylvinylidene carbene and the rearrangement is shown in figure 20.

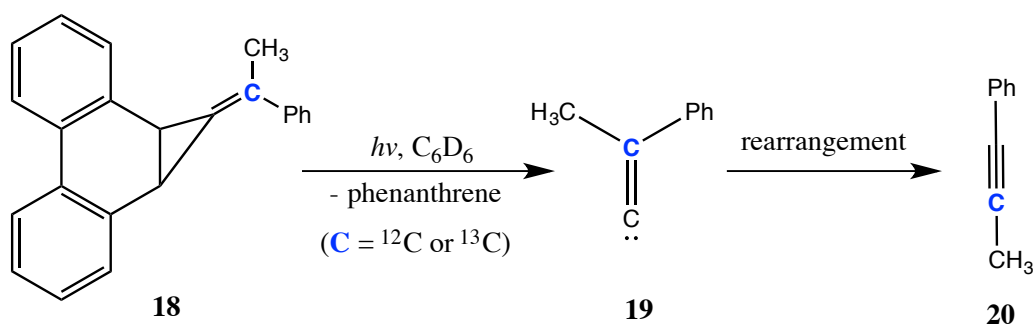


Figure 20. Generation of methylphenylvinylidene carbene and its rearrangement in benzene- d_6 from photolysis of **18** and ^{13}C -labeled **18** respectively

The methylphenylvinylidene carbene (**19**) generated from this photolysis gave only 1-phenylpropyne, which is isomeric with the carbene. The identity of the rearrangement

product was confirmed by comparison to a commercial sample using GC/MS and NMR spectroscopy. Comparing between the ^1H NMR spectral integration for the methyl group within the alkyne **20** to that for a 4-bromoanisole internal standard gives the yield to be 73%. Interestingly, the photolysis of ^{13}C -labeled **18** gave only 1-phenylpropyne resulting from a 1,2-phenyl shift, which was confirmed by ^{13}C NMR spectroscopy, giving the signal for the labeled C at 85.74 ppm. The resulted signal is confirmed by a literature report that the carbon connected to the phenyl group resonates at 85.8 ppm.²⁰ Thus, the implication is that only a 1,2-phenyl shift happened during rearrangement without any indication of a 1,2-methyl shift.

2.3 Trapping of Methylphenylvinylidene Carbene (**19**)

Vinylidene carbenes with alkyl and aryl groups are extremely difficult to trap as the intramolecular rearrangement is known to be quite fast.^{21, 22} Thus, the methylphenylvinylidene carbene generated in the photolysis reaction was expected to give low yields at best with trapping agents such as cyclohexene. The photolysis reaction of the carbene precursor **18** was carried out in the presence of 190 equivalence of cyclohexene in a glass vial for 6 hours. Though the intramolecular rearrangement was still fast to give the major product of 1-phenylpropyne, because the intramolecular process is easier to happen than the trapping reaction which is an intermolecular reaction, the carbene **19** was trapped by cyclohexene with a 1.5% yield of compound **24**, which was confirmed by integration by ^1H NMR spectroscopy using an internal standard, 1-bromo-2-methylnaphthalene.

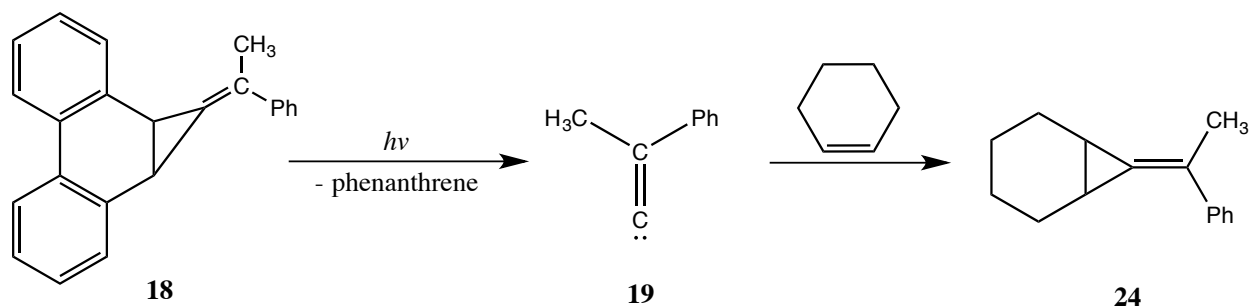


Figure 21. Trapping of methylphenylvinylidene carbene using cyclohexene

Since the yield of the trapped product **24** was extremely low, an authentic sample of **24** was synthesized in order to confirm that methylphenylvinylidene carbene was actually trapped to form this compound. A three-step scheme for synthesizing the trapped adduct **24** from cyclohexene was developed, as shown in figure 22. This synthetic scheme is similar to that for the precursor **18**. First, the dibromocarbene was generated to undergo a cyclopropanation reaction with the double bond of cyclohexene. Then the resulting dibromo adduct **25** was treated with *n*-butyllithium to form a carbanion by loss of a bromide group, and upon addition of water, the monobromo compound **26** was formed. Finally, following the procedure developed by Petasis et al., **24** was synthesized.¹⁷ Both GC/MS and ^1H NMR spectroscopic data confirmed that the trapped product from the photolysis reaction of **18** was the same as the synthesized sample of **24**. The retention time of the trapped product in the photolysate and **24** in GC/MS were the same within the error of the experiment, and addition of **24** into the photolysate increased the intensity of the peak at 2.32 ppm in the ^1H NMR spectrum, which is the proton signal for the methyl group in **24**.

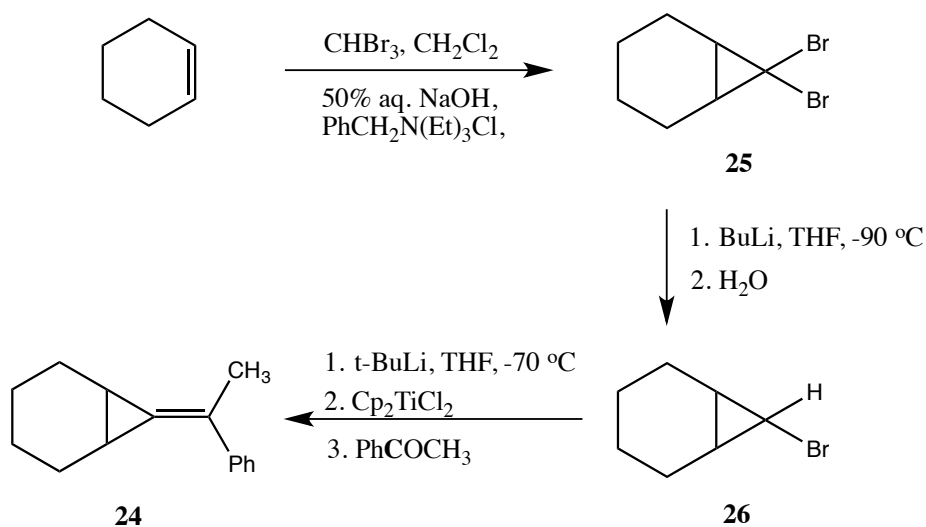


Figure 22. Synthetic scheme for making the trapped product **24**

2.4 Rearrangement of the Precursor **18**

Apart from 73% of the precursor **18** generating methylphenylvinylidene carbene, which then rearranged into 1-phenylpropyne, 13% of the precursor **18** was unreacted. Additionally, 11% of the precursor rearranged into the cycloheptatriene derivative **21** upon photolysis, as shown in figure 23. As proposed, the precursor **18** underwent 1,5-sigmatropic shift and then electrocyclic ring opening upon photolysis to give the *E*- and *Z*-isomers of cycloheptatriene derivative **21**.

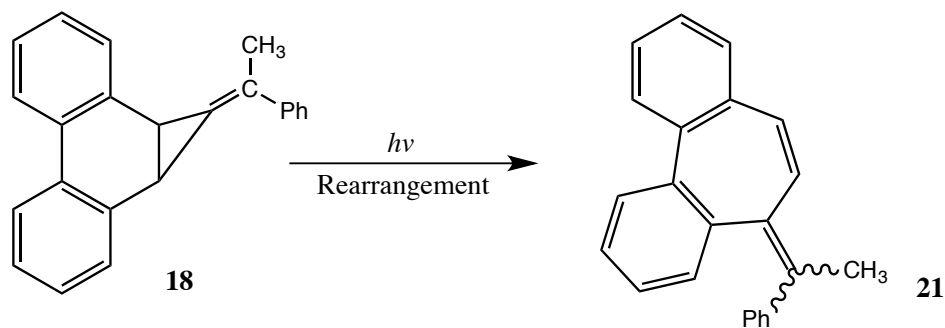


Figure 23. Rearrangement of the carbene precursor **18** upon photolysis

In the ^1H NMR spectrum for the photolysate there were two methyl peaks for the methyl group in the rearranged precursor **21**, one at 1.93 ppm and the other at 1.95 ppm. These two peaks correspond to the two isomers of the rearranged precursor **21**, one for the *E*-isomer and the other for the *Z*-isomer, shown in figure 24. Since the methyl group for the *E*-isomer is closer to the aromatic rings, the methyl protons in this compound should resonate more upfield compared to that of the *Z*-isomer, because of shielding from the π -electrons within the aromatic rings. Therefore, the methyl group of the *E*-isomer most likely corresponds to the proton signal at 1.93 ppm and that of the *Z*-isomer has the proton signal at 1.95 ppm. Thus, according to ^1H NMR integrations in comparison to the internal standard 4-bromoanisole, the yield of the *E*-isomer of **20** was 4% and that of the *Z*-isomer was 7%. The calculation using the B3LYP/6-31+G** method indicated a slight preference towards the *E*-isomer by 0.53 kcal/mol. This is consistent with the experimental results since the *Z*-isomer has a larger steric hindrance from the interaction of the bulky phenyl group with the other rings in the cycloheptatriene derivative **21**.

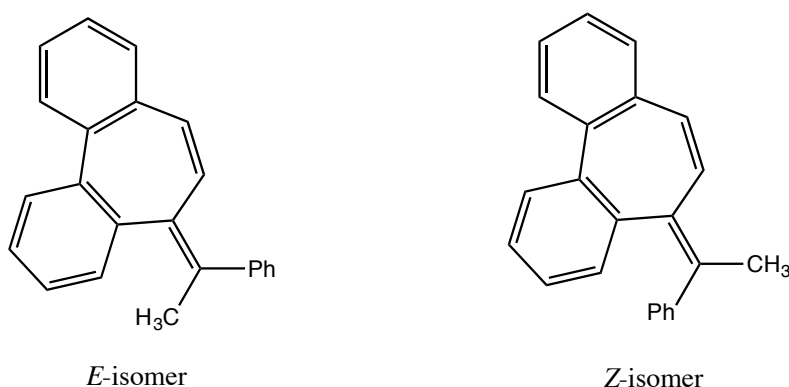


Figure 24. *E*-isomer and *Z*-isomer for **21**

2.5 Computational Study

Additional theoretical calculations were performed using density functional theory to probe the methylphenylvinylidene carbene and its rearrangement into alkyne **20**. The B3LYP method with a 6-311+G** basis set was incorporated for optimization and frequency calculation.²³ The calculation gave two minimal energy geometries for the singlet methylphenylvinylidene carbene **19**, one planar and one twisted as shown in figure 25. The dihedral angle C2 – C3 – C12 – C17 (two adjacent carbons on the phenyl ring and the two unsaturated carbons on the vinylidene carbene **19**) is 180° for the planar singlet carbene **19** and is 107° for the twisted singlet, with the phenyl group twisted away from the plane where the vinylidene carbons and the methyl carbon reside (Figure 25). Noticeably, the energies for the two structures are not significantly different, with the planar singlet carbene only favored by 0.13 kcal/mol. The triplet **19** has only one optimized structure, which is planar and is calculated to be 37 kcal/mol, higher in energy compared to the planar singlet structure. Singlet alkylidenecarbenes are known to be favored because the *sp* hybridization of the carbene carbon makes the singlet more stable. The calculation supports that the singlet is much more favored for this system.

Additionally, the reaction energy for the rearrangement from carbene **19** to alkyne **20** was calculated for two pathways, the 1,2-methyl shift and the 1,2-phenyl shift. The calculated relative energies of the product alkyne **20** and the transitional states leading to that product from compared planar singlet **19** after zero-point vibrational energy corrections are shown in table 1. The rearrangement from carbene **19** to alkyne **20** is calculated to be -52.7 kcal/mol, showing that there is a great thermodynamic drive for the rearrangement. Furthermore, the computation indicates the transitional barrier for 1,2-

methyl shift is 10.3 kcal/mol, whereas the transitional barrier for 1,2-phenyl shift is only 2.6 kcal/mol. Thus, the phenyl shift is much more favorable compared to the methyl shift. This is consistent with the experimental results in that only the phenyl shift product was observed upon photolysis.

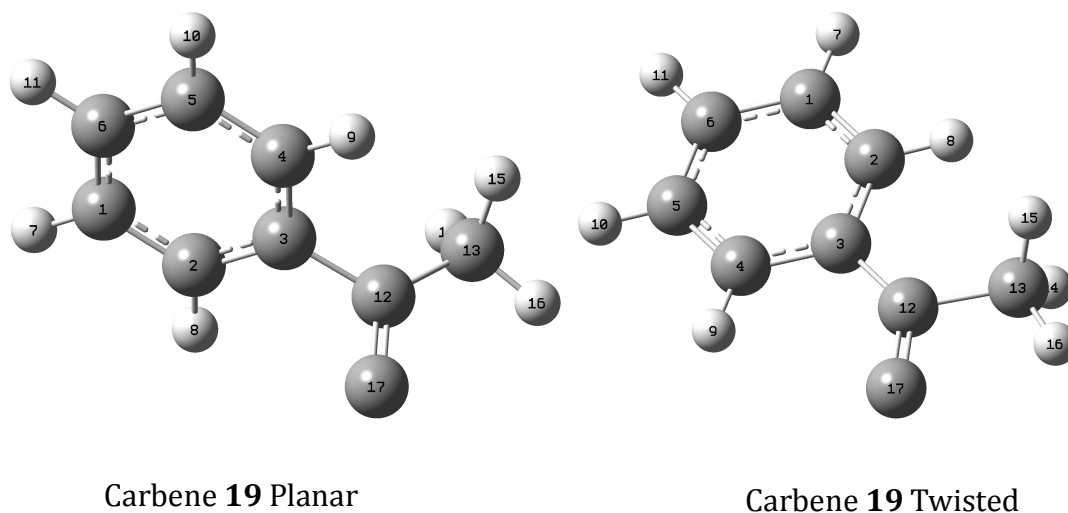


Figure 25. Planar and twisted structures of singlet carbene (**19**) with optimization by B3LYP/6-311+G** method

Table 1. Relative energies for carbene **19** and alkyne **18** plus transitional states between these species using the B3LYP/6-311+G** method and after a zero-point vibrational energy corrections

Molecule	Relative Energy (kcal/mol)
Singlet 19 (Planar)	0
Singlet 19 (Twisted)	0.13
Triplet 19	37.04
Alkyne 20	- 52.73
Transitional State (Methyl Shift)	10.31
Transitional State (Phenyl Shift)	2.56

In the calculations of the transitional states, only a rearrangement from the planar singlet carbene **19** to the alkyne **20** is allowed. The energy diagram shown in figure 26 illustrates the reaction energy relative to the energy of planar singlet carbene **19** as calculated using a CCSD(T)/cc-pVTZ//B3LYP/6-311+G** basis set. The B3LYP method is used for optimization and frequency calculations and the coupled-cluster method is used for single-point energy calculations. These calculations indicate that the energy of the rearrangement from carbene **19** to alkyne **20** is -50.8 kcal/mol, and the transitional barrier for methyl shift is 11.9 kcal/mol and that for phenyl shift is 3.8 kcal/mol relative to the singlet carbene **19**.

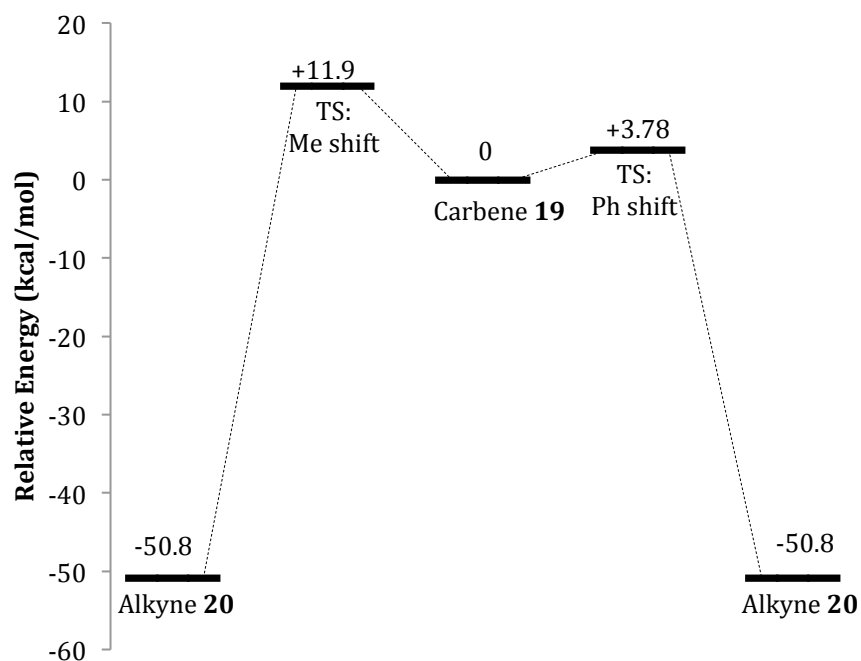


Figure 26. Energy diagram for the rearrangement reactions from carbene **19** to alkyne **20** via the two proposed pathways: the 1,2-methyl shift and the 1,2-phenyl shift, relative to the energy for the singlet carbene **19**. Data from CCSD(T)/cc-pVTZ//B3LYP/6-311+G** method calculations.

Conclusion

The methylphenylvinylidene carbene **19** was generated by the photolysis of the photochemically active precursor **18**, which was synthesized in two different ways in moderate yields. The rearrangement of **19** to 1-phenylpropyne (**20**) was fast compared to the rearrangement of dimethylvinylidene carbene (from Hardikar's project), but was not as fast as that of benzylidene carbene (from Moore and Jesus' work).^{14,15} Carbene **19** was trapped by cyclohexene to give a 1.5 % yield. The trapped product was confirmed by comparing spectra of an authentic sample of the compound, which was synthesized from cyclohexene in three steps. This demonstrated that alkylidene carbenes with methyl and phenyl groups as substituents can be trapped, although with a low yield. Photolysis of the ¹³C-labeled precursor **18** indicated that alkyne **20** resulted from a 1,2-phenyl shift. Upon photolysis, a mixture of the *E*- and *Z*- isomers of cycloheptatriene derivative **21** was generated from the precursor **18** in a combined yield of 11%. Computational study was carried on using B3LYP/6-311+G** for geometrical optimization and frequency. These calculations indicate that the *E*-isomer of cycloheptatriene derivative **21** is 0.53 kcal/mol more favorable and the planar singlet carbene **19** is favored compared to the twisted singlet carbene **19** by 0.13 kcal/mol. Calculations at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level suggest that the ΔG for the rearrangement reaction from carbene **19** to alkyne **20** is 50.8 kcal/mol, and the transitional barriers for the 1,2-methyl and the 1,2-phenyl shifts are 11.9 kcal/mol and 3.8 kcal/mol, respectively. These computational results are consistent with the experimental data in that only the product generated by the 1,2-phenyl shift was observed.

Further studies should focus on obtaining crystal structure for the precursor **18**, in order to further confirm its identity. Additionally, in order to confirm that the precursor **18** was rearranged into **21** upon photolysis and to characterize the identity of the cycloheptatriene derivative **21**, a scheme for synthesizing **21** should be conceived and executed.

Experimental

General notes:

Solvents and all other reagents used were obtained from commercial sources. Tetrahydrofuran (THF) was dried by passage through two columns (2 ft × 4 in) of activated alumina. All reactions with requirement of anhydrous condition were carried out under argon throughout, and all glassware was dried in oven before use. Flash chromatography was performed on pre-packed silica gel columns (70 – 230 mesh), using a Teledyne ISCO Combiflash Rf 200 instrument. GC/MS data were obtained using a capillary gas chromatograph, which was interfaced with a quadrupole, triple-axis mass selective detector operating in the electron impact (EI) mode. ¹H NMR and ¹³C NMR was conducted at 500 MHz and 125 MHz respectively, with the solvents indicated. The shifts were reported in δ ppm and were referred to either tetramethylsilane (TMS) or the residual proton signal from the solvent. Infrared spectra were obtained from a Perkin Elmer Spectrum One FT-IR Spectrometer.

1,1-dibromo-1a,9b-dihydro-1H-cyclopropa[*l*]phenanthrene (22): ¹⁶

Following the previously published procedure, Phenanthrene (35.6 g, 0.2 mol), benzyltriethylammonium chloride (0.5 g, 0.002 mol), CHBr₃ (40 mL, 116 g, 0.46 mol), CH₂Cl₂ (40 mL) and EtOH (1 mL) were combined with stirring. Aqueous NaOH (50%, 80 mL) was added into the mixture in small portions over 30 minutes. The reaction mixture was loosely stoppered and stirred for 4 days in room temperature. The resulting dark brown mixture was combined with CH₂Cl₂ (100 mL) and H₂O (100 mL). The aqueous layer was separated from the organic layer and the aqueous layer was extracted with additional

CH₂Cl₂ (2 × 50 mL). The organic layers were then combined, and washed with 2 M of HCl (2 × 100 mL), H₂O (2 × 100 mL) and brine (100 mL). The resulted organic layer was filtered to isolate, and the crude product was a brown solid. This product was recrystallized using chloroform and filtered with carbon black. The final product after recrystallization was a white solid. Yield: 28%; ¹H NMR (500 MHz, CDCl₃) δ 8.01 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.51 (dd, *J* = 7.4, 1.5 Hz, 2H), 7.42 (td, *J* = 7.6, 1.7 Hz, 2H), 7.35 (dd, *J* = 7.5, 6.2 Hz, 2H), 3.51 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 135.4, 131.7, 131.2, 130.9, 129.5, 129.2, 128.3, 128.3, 128.1, 127.7, 126.9, 123.0, 77.3, 77.0, 76.8, 56.3, 37.4, 30.9.

1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (23): ¹⁷

1,1-dibromo-1a,9b-dihydrocyclopropa[*l*]phenanthrene (**22**) (10.5 g, 30 mmol) was dissolved in anhydrous THF (140 mL) were added into a 250 mL 3-necked round bottom flask. The mixture was stirred by a stir bar and was kept under -70 °C. *N*-butyllithium (14 mL, 2.5 M in hexanes, 35 mmol) was added dropwise over 15 minutes. The temperature was kept between -70 °C to -60 °C during the addition. The resulted dark green mixture was stirred for 90 minutes while keeping the temperature under -60 °C. H₂O (8 mL) was added into the flask dropwise over 8 minutes while keeping the temperature below -60 °C. The resulted light-brown mixture was slowly warmed up to room temperature. An additional 50 mL aliquot of water was added into the reaction mixture. The aqueous layer was separated from the organic layer. The aqueous layer was extracted with ethyl ether (2 × 50 mL). The organic layer was extracted with H₂O (100 mL) and brine (100 mL) sequentially. Evaporation of the solvent gave brown-colored solid. The crude product was recrystallized in hexanes and filtered with carbon black. Yellow crystals were resulted.

Yield: 55%; ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, J = 7.3 Hz, 2H), 7.50 (d, J = 7.0 Hz, 2H), 7.32 (q, J = 7.1 Hz, 4H), 3.03 (s, 2H), 2.43 (d, J = 3.2 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 131.9, 129.7, 129.3, 128.1, 127.2, 123.3, 77.3, 77.0, 76.8, 29.9, 27.7; LRMS (EI): m/z 270 (M^+), 191, 165.

1-(1-phenylethylidene)-1a,9b-dihydro-1H-cyclopropa[*l*]phenanthrene (18): ¹⁸

1-bromo-1a,9b-dihydro-1H-cyclopropa[*l*]phenanthrene (2.70 g, 10 mmol) was dissolved in anhydrous THF (80 mL) in a round-bottom flask at $-70\text{ }^\circ\text{C}$. *Tert*-butyllithium (13 mL, 1.7 M in pentanes, 22 mmol) was added to the solution dropwise, while keeping the temperature below $-60\text{ }^\circ\text{C}$. After stirring at $-70\text{ }^\circ\text{C}$ for 30 minutes, bis(cyclopentadienyl)titanium (IV) dichloride (1.1g, 4.4 mmol) was added to the reaction mixture. With another 15 minutes of stirring at this temperature, the temperature of the reaction mixture was brought up to $0\text{ }^\circ\text{C}$ to $5\text{ }^\circ\text{C}$. After 90 minutes of stirring at between $0\text{ }^\circ\text{C}$ to $5\text{ }^\circ\text{C}$, acetophenone (2.5 mL, 20 mmol) was added. Reaction was refluxed at $75\text{ }^\circ\text{C}$ for 12 hours. The resulted mixture was directly purified by silica gel column chromatography with hexanes. Yield: 15%; mp: $135\text{--}136\text{ }^\circ\text{C}$; ^1H NMR (500 MHz, C_6D_6) δ 7.69 (dd, J = 19.2, 7.9 Hz, 2H), 7.42 - 7.35 (m, 2H), 7.30 (dd, J = 7.5, 1.5 Hz, 1H), 7.23 (dd, J = 7.4, 1.6 Hz, 1H), 7.12 (s, 1H), 7.10 (d, J = 1.5 Hz, 1H), 7.03 (td, J = 7.9, 1.6 Hz, 1H), 7.01 - 6.92 (m, 2H), 3.07 (dd, J = 7.8, 2.1 Hz, 1H), 2.79 (d, J = 7.9 Hz, 1H), 1.90 (t, J = 2.0 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 139.3, 133.1, 132.6, 129.7, 129.5, 129.1, 128.8, 127.9, 127.8, 127.7, 127.5, 126.8, 126.3, 126.0, 126.0, 124.2, 124.0, 123.5, 25.0, 20.6, 18.3; FTIR (ATR): ν 3063, 2977, 1598, 1484, 1439 cm^{-1} ; LRMS (EI): m/z 294 (M^+), 279, 178.

¹³C labeled 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (18):

¹³C-labeled precursor was prepared using Ph¹³COCH₃ (1g, 3.4 mmol), instead of PhCOCH₃, in the same procedure described above and using the same purification method. Yield: 13%; mp: 127-129 °C; ¹H NMR (500 MHz, C₆D₆) δ 7.73 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.71 - 7.67 (m, 1H), 7.39 (ddd, *J* = 8.2, 4.1, 1.5 Hz, 2H), 7.31 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.24 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.14 (s, 2H), 7.10 (d, *J* = 2.0 Hz, 2H), 7.09 (d, *J* = 1.4 Hz, 1H), 7.08 - 7.02 (m, 1H), 6.98 (qd, *J* = 7.6, 1.5 Hz, 2H), 3.09 (dt, *J* = 8.2, 2.4 Hz, 1H), 2.81 (ddd, *J* = 7.8, 2.9, 1.5 Hz, 1H), 1.90 (dt, *J* = 6.4, 1.5 Hz, 3H); ¹³C NMR (126 MHz, C₆D₆) δ 124.0; FTIR (ATR): ν 3063, 2977, 1598, 1484, 1439 cm⁻¹; LRMS (EI): *m/z* 295 (M⁺), 280, 178;

1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (alternative method by Takeda et al.) (18):¹⁹

Oven-dried 4 Å molecular sieves (900 mg), magnesium turnings (450 mg, 18 mmol) and bis(cyclopentadienyl)titanium (IV) dichloride (4.5 g, 18 mmol) were added in an oven-dried round-bottom flask successively at room temperature. The mixture were then dissolved and stirred in anhydrous THF (24 mL), and triethyl phosphite (6.2 mL, 36 mmol) was added. Within 30 minutes of stirring, the reaction mixture turned dark green. After 3 hours, 1,1-dibromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (2.1 g, 6 mmol) dissolved in anhydrous THF (15 mL) was added to the stirring mixture. After 30 minutes of stirring, acetophenone (350 μL, 3 mmol) was added. After 1 hour of stirring, the reaction mixture was poured out, diluted by ethyl acetate (180 mL) and filtered through celite. The

resulted mixture was purified by silica gel column chromatography with hexanes. Yield: 11%.

7,7-dibromobicyclo[4.1.0]heptane (25): ²⁴

Cyclohexene (10.1 mL, 8.2g, 0.1 mol), benzyltriethylammonium chloride (0.25 g, 0.001 mol), CHBr₃ (20 mL, 58 g, 0.23 mol), CH₂Cl₂ (20 mL) and EtOH (1 mL) were added into a round bottom flask in an ice-water bath. 50% aqueous NaOH (40 mL) was added into the flask in small portions. The reaction mixture was stirred for 21 hours at room temperature. The reaction mixture was transferred into a separatory funnel, and the flask was washed with CH₂Cl₂ (50 mL) and H₂O (50 mL), which was combined into the separatory funnel. The organic layer was separated from the aqueous layer, which was washed with CH₂Cl₂ (2 × 50 mL). The organic layers were combined and washed with 2 M of HCl (2 × 50 mL) and brine (50 mL). Upon evaporation and distillation at 70 °C in vacuum, yellow oily distillate was resulted at 28 °C. Yield: 58%; ¹H NMR (500 MHz, CDCl₃) δ 2.08 – 1.94 (m, 2H), 1.88 – 1.78 (m, 2H), 1.63 – 1.52 (m, 2H), 1.44 – 1.31 (m, 2H), 1.27 – 1.11 (m, 2H); LRMS (EI): *m/z* 254 (M⁺), 173, 93.

7-bromobicyclo[4.1.0]heptane (26): ²⁵

7,7-dibromobicyclo[4.1.0]heptane (7.62 g, 30 mmol) was dissolved in anhydrous THF (140 mL) in a round-bottom flask at – 90 °C in a methanol-liquid nitrogen bath. N-butyllithium (14 mL, 2.5 M in hexanes, 35 mmol) was added dropwise, while the temperature was kept below – 80 °C. After the reaction mixture was stirred below – 90 °C for 1 hour, methanol (10 mL) was added dropwise and the temperature was kept below –

80 °C. The reaction was warmed up slowly overnight, while stirring. The resulted mixture was transferred in to a separatory funnel, along with H₂O (50 mL). The organic layer was separated from the aqueous layer, which was washed with CH₂Cl₂ (2 × 50 mL). The organic layer was combined and washed with H₂O (100 mL) and brine (100 mL). After evaporation of solvent, the product was distilled at 90 °C upon vacuum. The yellow distillate was resulted at 42 °C. Yield: 65%; ¹H NMR (500 MHz, CDCl₃) δ 3.79 – 3.74 (m, 2H), 1.89 – 1.86 (m, 3H), 1.86 – 1.81 (m, 2H), 1.65 – 1.53 (m, 2H), 1.30 – 1.15 (m, 2H), 0.99 – 0.83 (m, 1H); LRMS (EI): *m/z* 174 (M⁺), 95, 79.

7-(1-phenylethylidene)bicyclo[4.1.0]heptane (24): ¹⁸

7-bromobicyclo[4.1.0]heptane (1.07 g, 6.1 mmol) was dissolved in anhydrous THF (80 mL) in a round-bottom flask at – 70 °C. *tert*-Butyllithium (8 mL, 1.7 M in pentanes, 14 mmol) was added into the flask dropwise, while keeping the temperature below – 60 °C. The reaction was stirred at – 70 °C for 30 minutes, and bis(cyclopentadienyl)titanium (IV) dichloride (0.72 g, 2.8 mmol) was added to the reaction mixture. After continued stirring for 5 minutes at this temperature, the temperature was raised to 0 °C. Acetophenone (1.5 mL, 12 mmol) was added after 90 minutes of stirring at between 0 °C to 5 °C. Reaction was refluxed at 70 °C for 22 hours. The resulted mixture was purified through silicon gel column chromatography with hexanes. Yield: 8.2%; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.52 - 7.36 (m, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 2.29 (s, 3H), 2.01 (ddt, *J* = 8.8, 6.8, 2.0 Hz, 1H), 1.96 - 1.81 (m, 4H), 1.70 (ddt, *J* = 8.9, 7.1, 1.6 Hz, 1H), 1.39 - 1.26 (m, 3H), 1.26 - 1.16 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 131.5, 128.2, 126.2, 125.4, 22.4, 21.9, 21.5, 21.4, 18.8, 15.6, 11.0; LRMS (EI): *m/z* 198 (M⁺), 183.

Photolysis:

The photolysis reactions were carried out in glass vials or in NMR tubes (glass) using a Rayonet photochemical reactor equipped with 16 12-inch 8W lamps with output centered at ~ 350 nm (range ~ 315 to 400 nm). The precursor (**18**) (100.1 mg, 0.34 mmol) was dissolved in benzene- D_6 (2 mL) in a glass vial. Photolysis was carried out for 12 hours. 4-bromoanisole (52.5 mg, 0.28 mmol) was dissolved in the solution as standard to determine the yield. The rearranged carbene (73% yield), 1-phenylpropyne (**20**), was confirmed using 1H NMR. For the trapping experiment, the precursor (76.0 mg, 0.26 mmol) was dissolved in cyclohexene (5 mL) and photolysis was carried out for 6 hours. The trapped product was shown on GC/MS and NMR spectra and was confirmed by the synthesized adduct. The 1.5% yield of the trapped product was determined by adding 1-bromo-2-methylnaphthalene (0.065 mmol) and compared the integrations in 1H NMR spectrum.

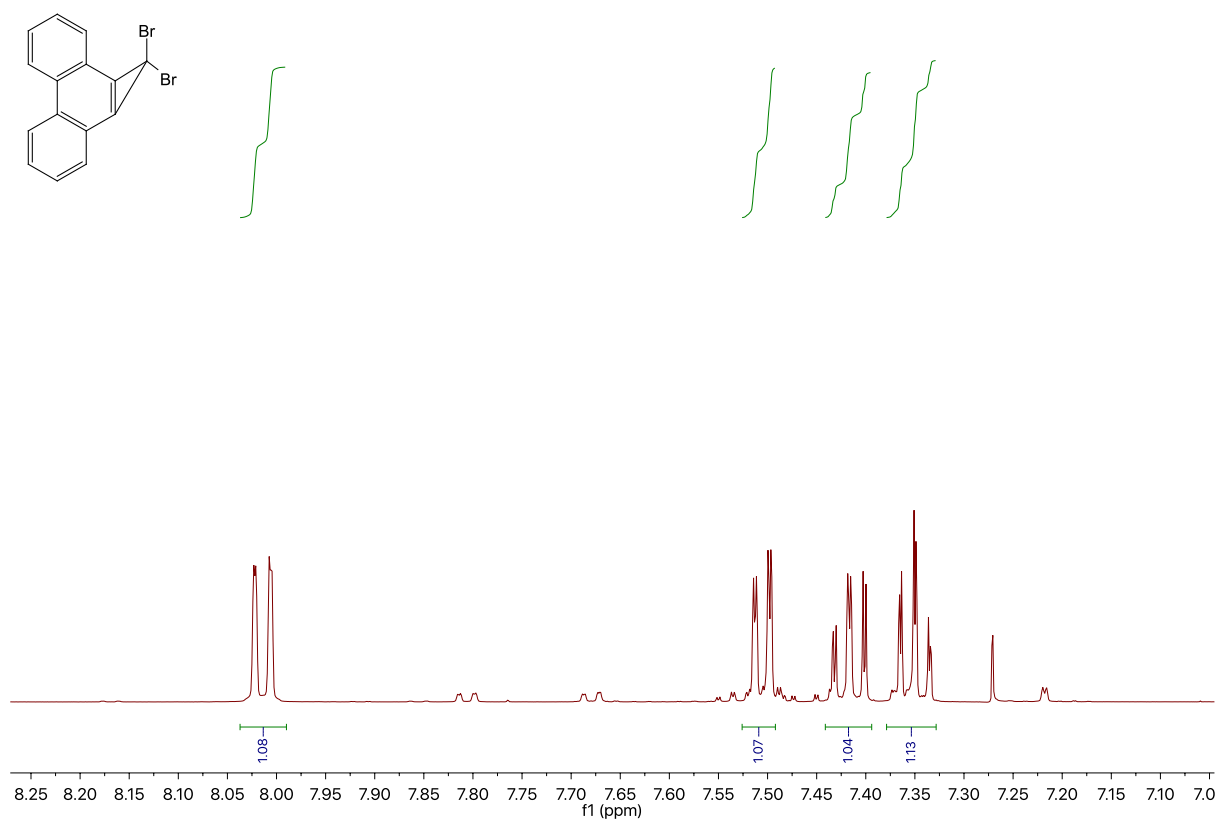
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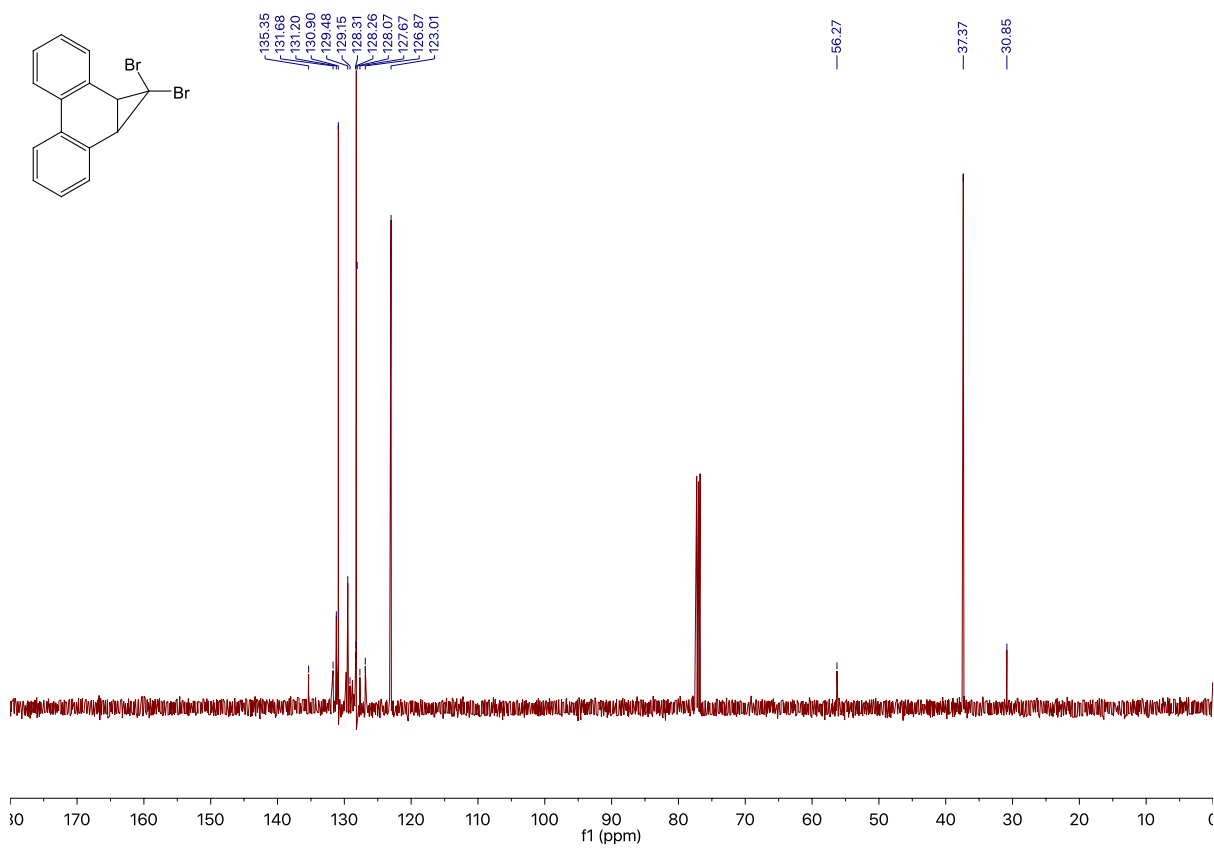
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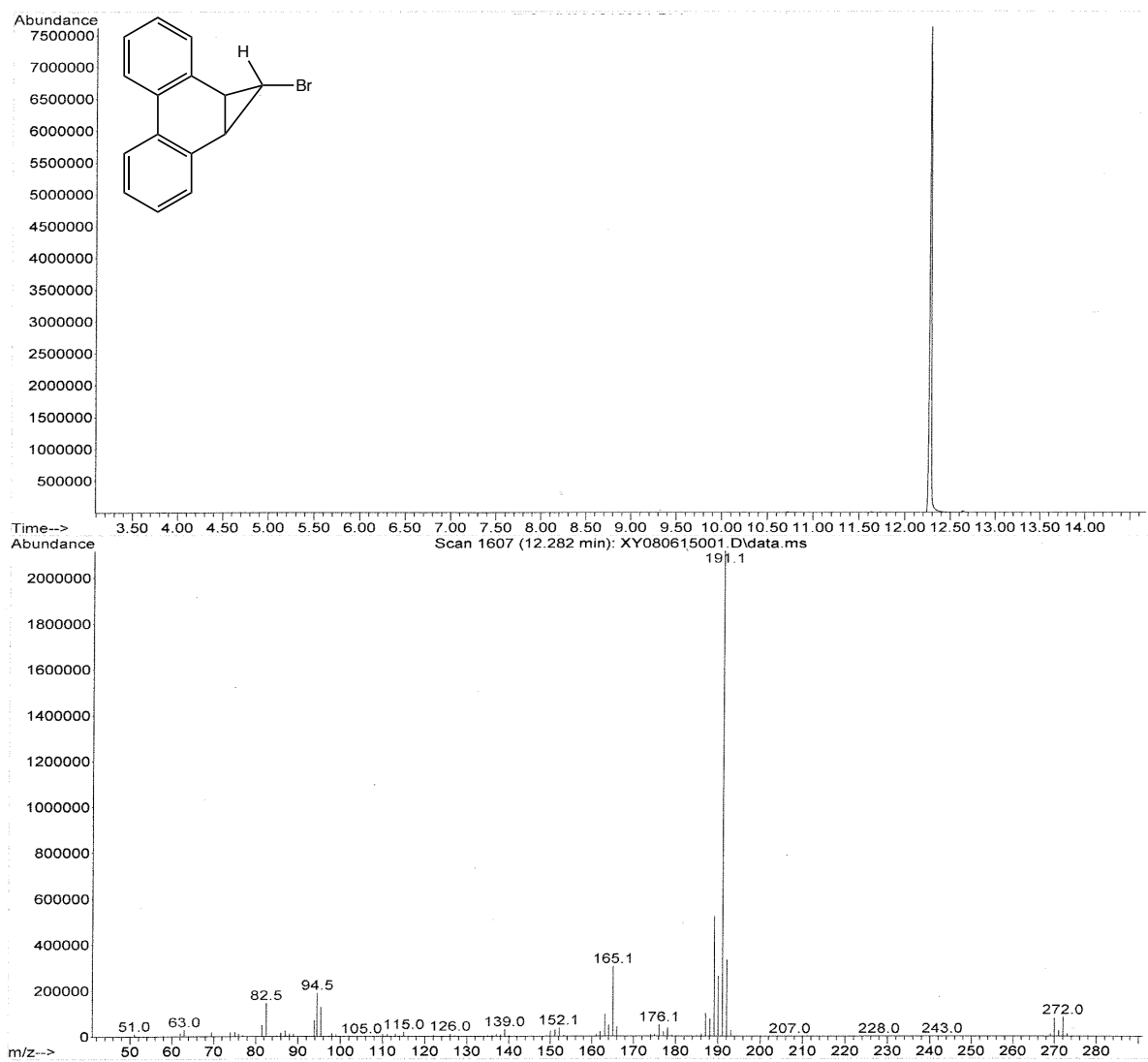
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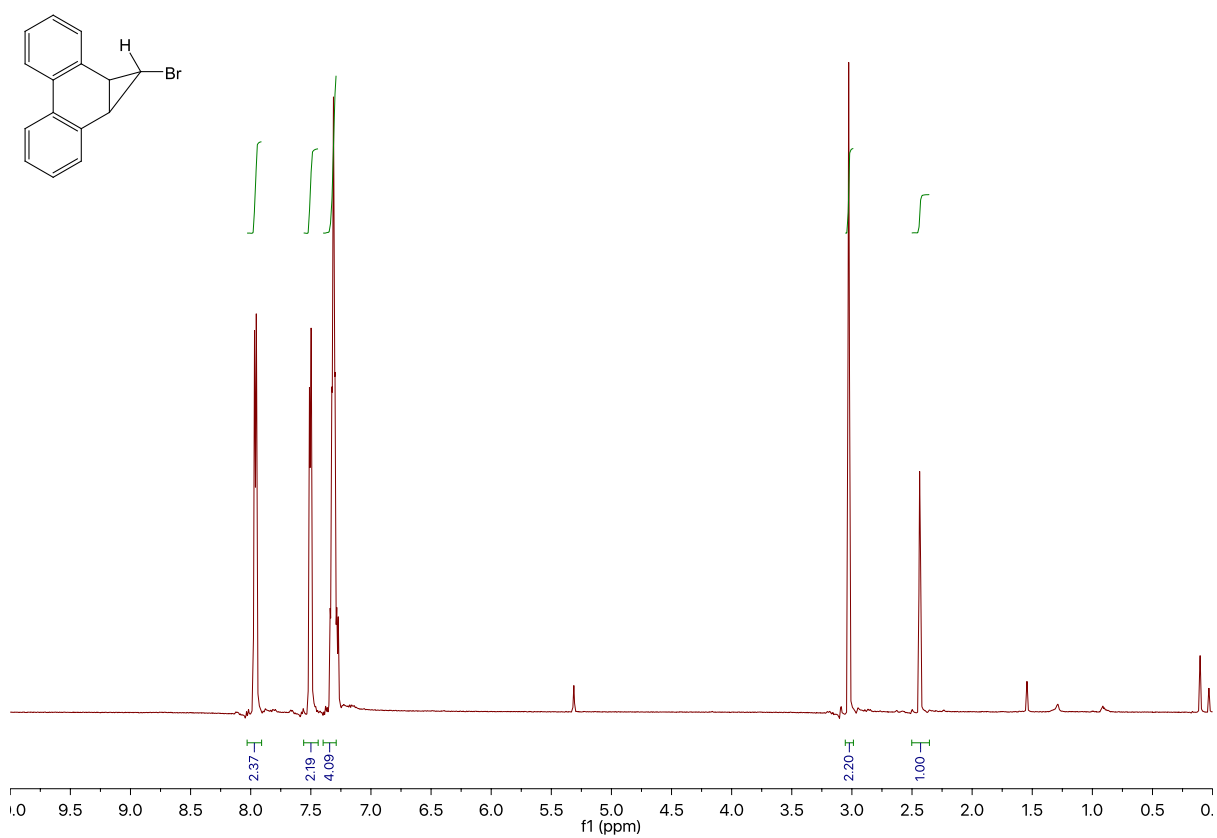
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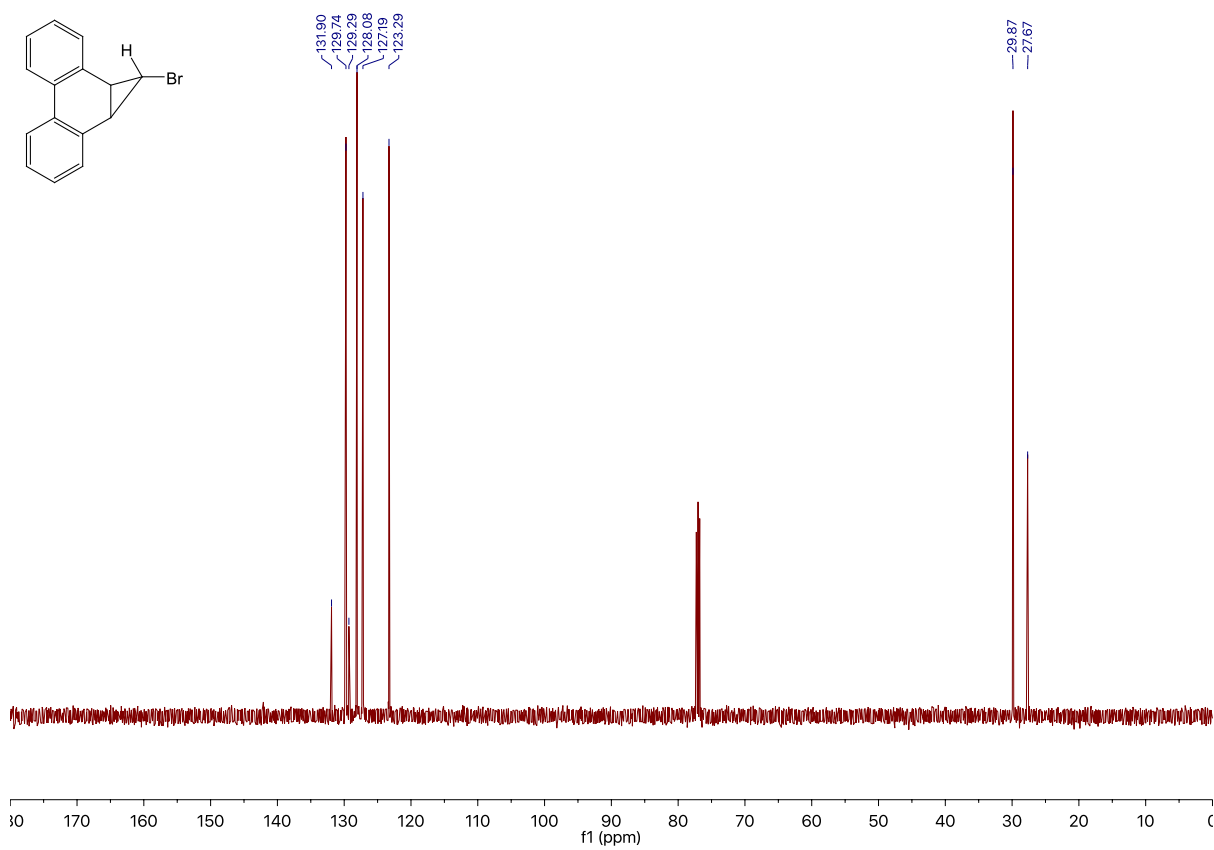
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(b) Summary output of CCSD(T)/cc-pVTZ//B3LYP/6-311+G** calculations	68

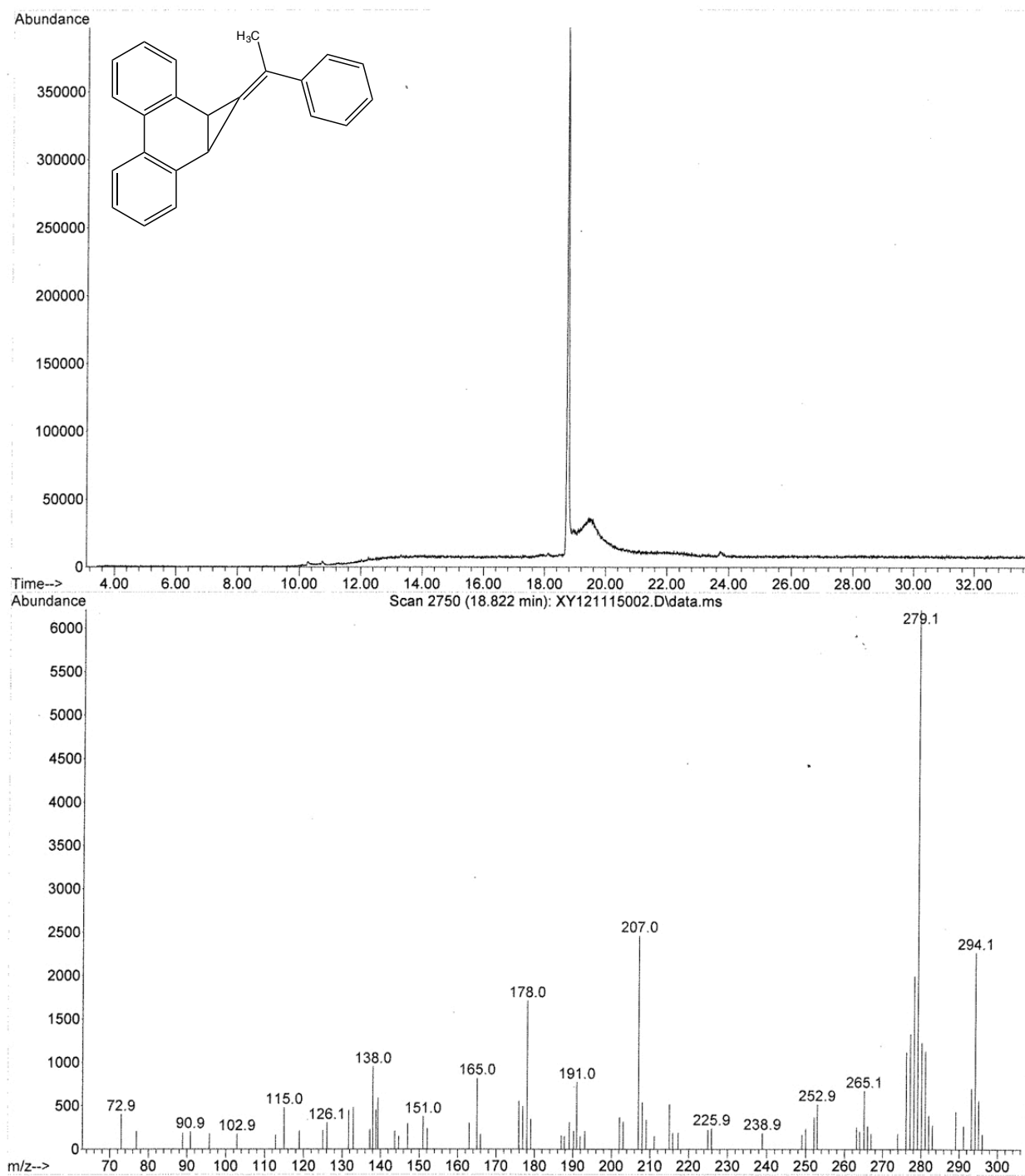


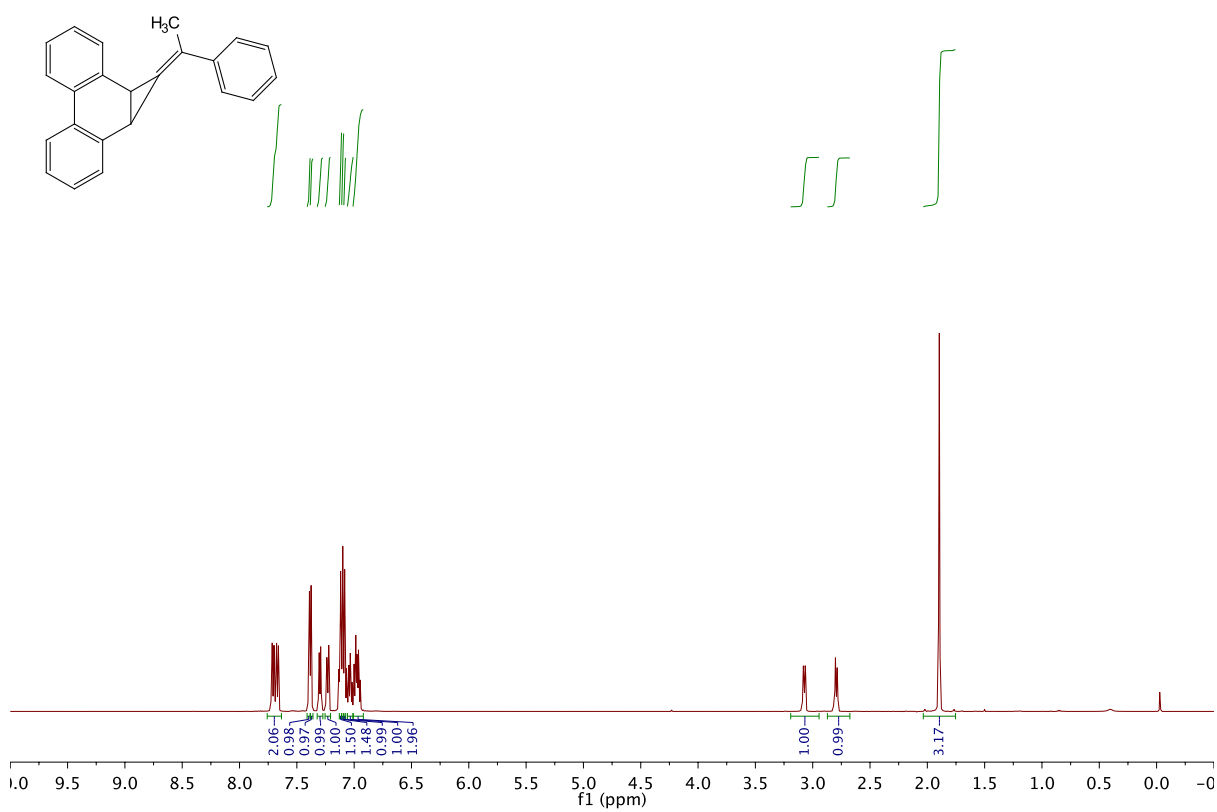


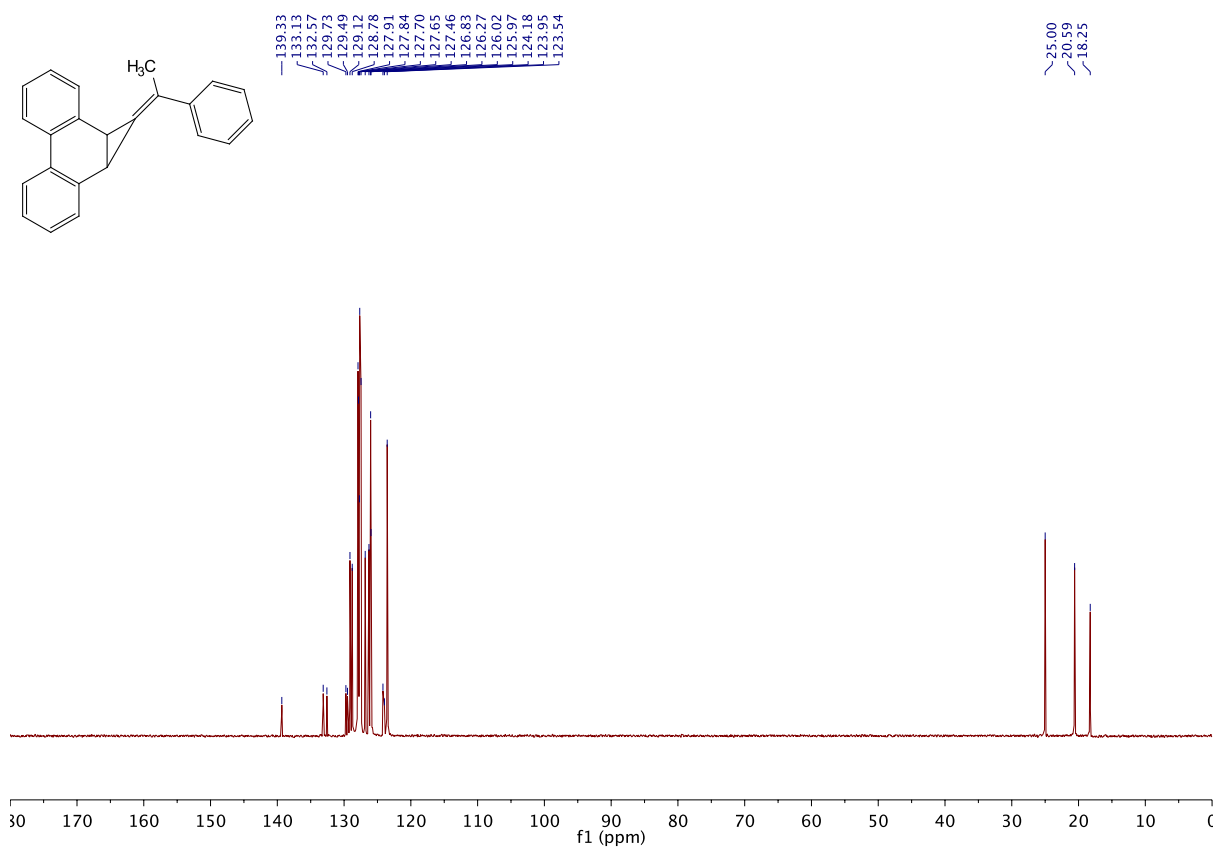


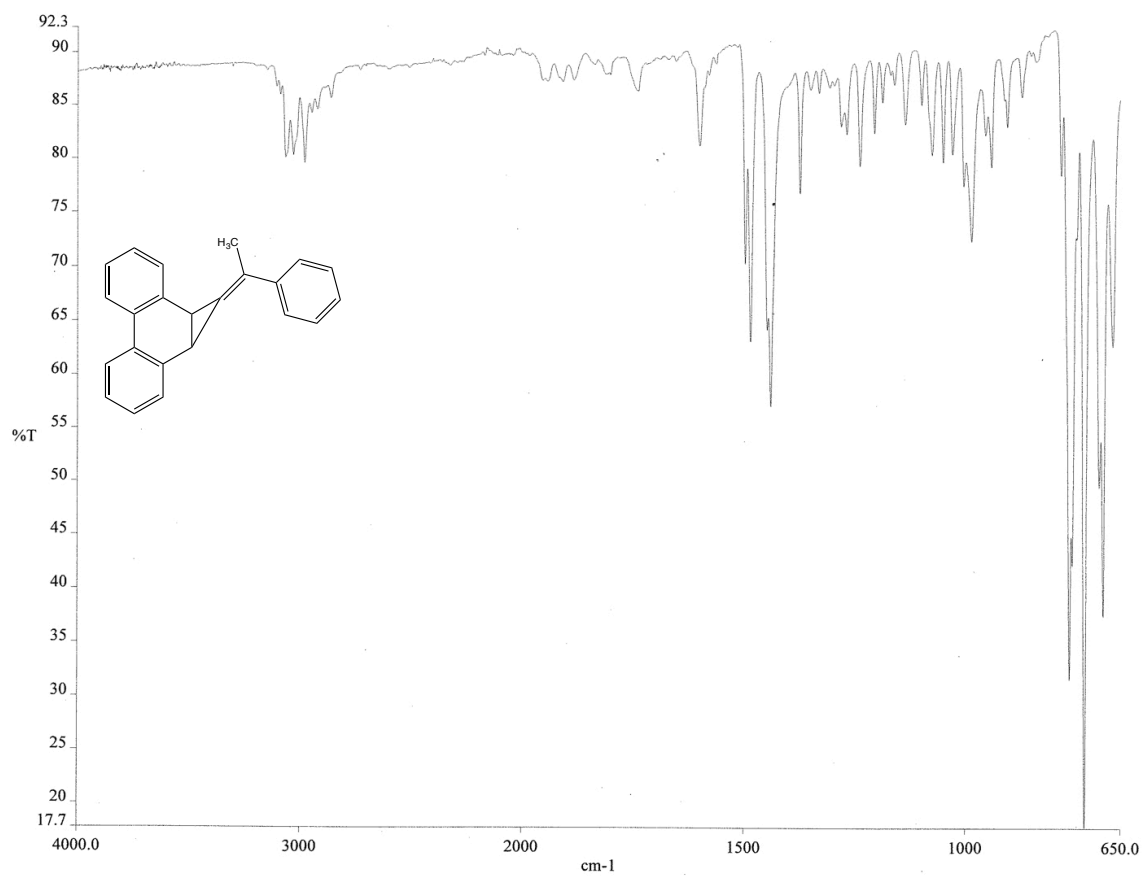


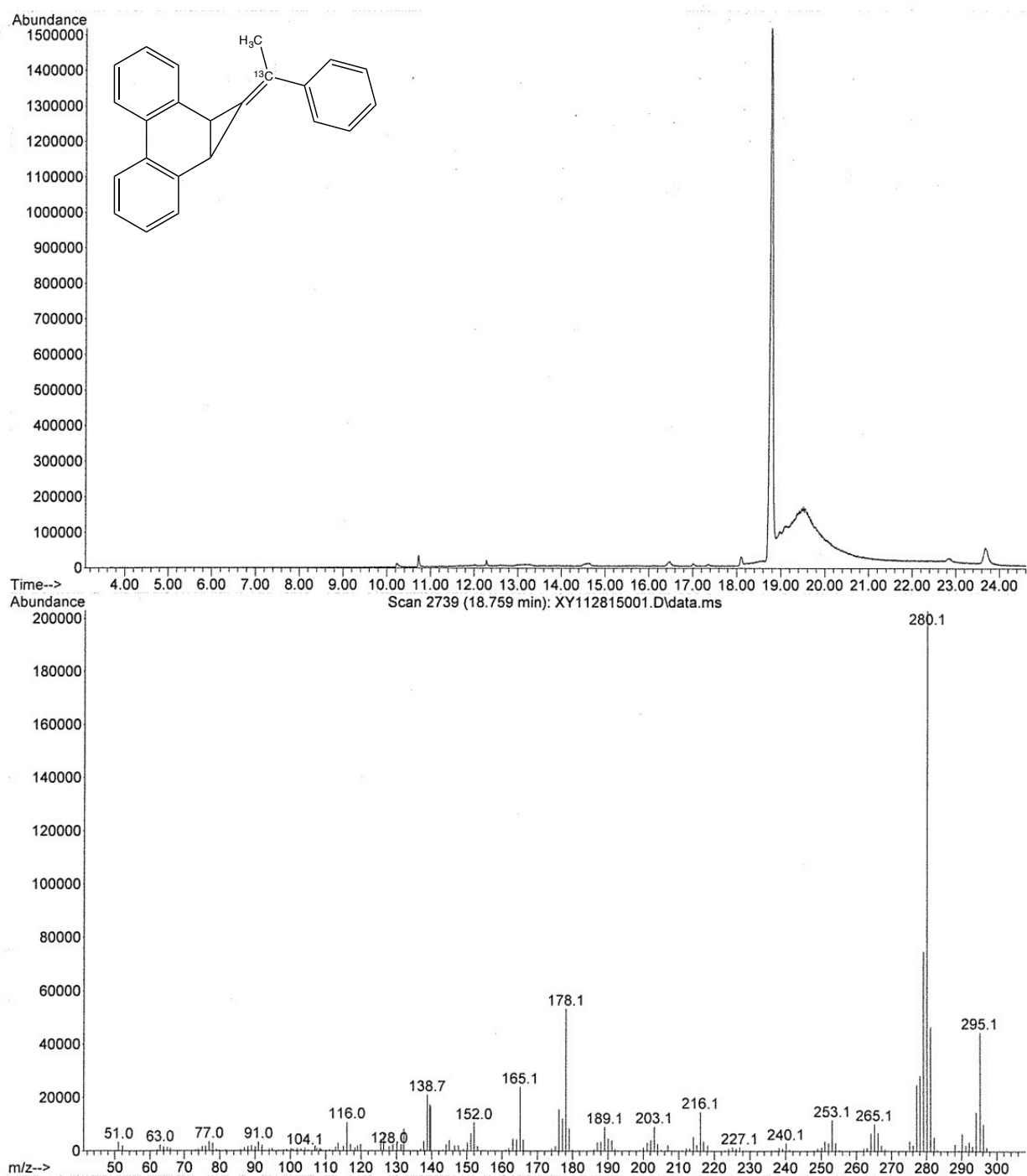


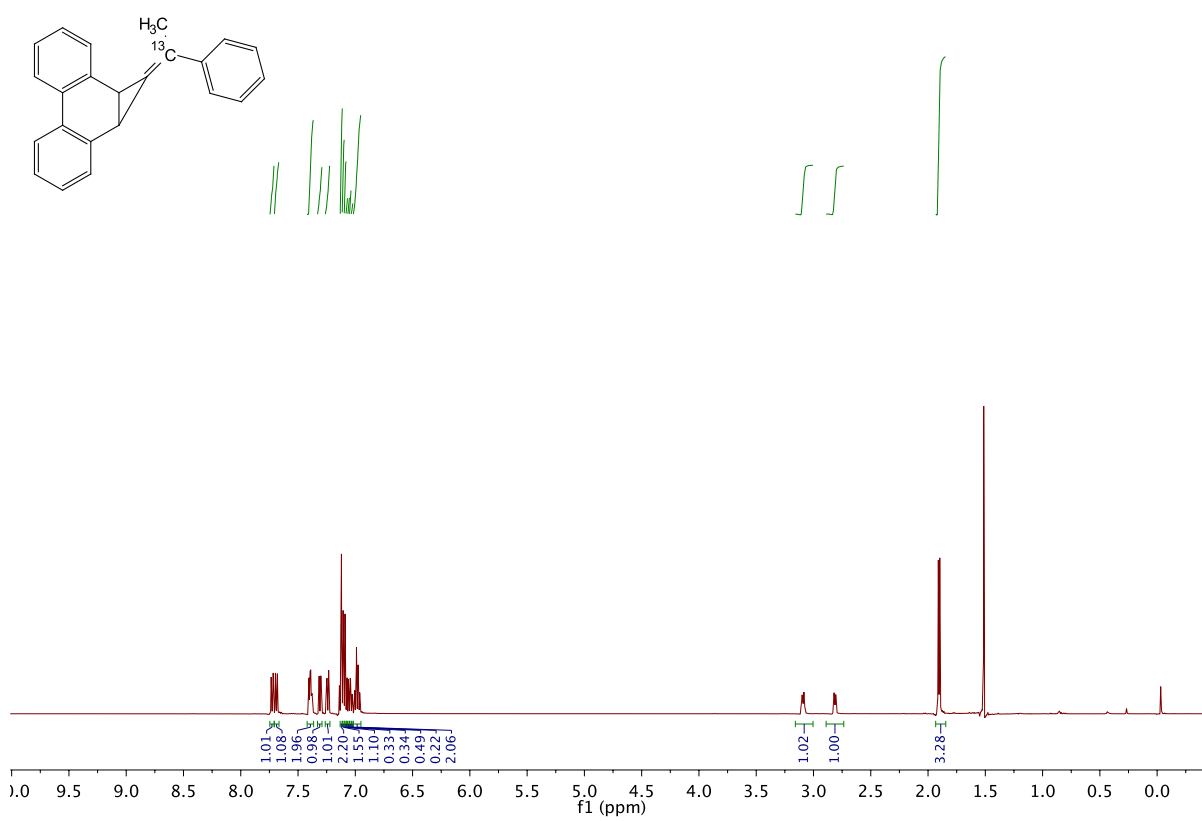


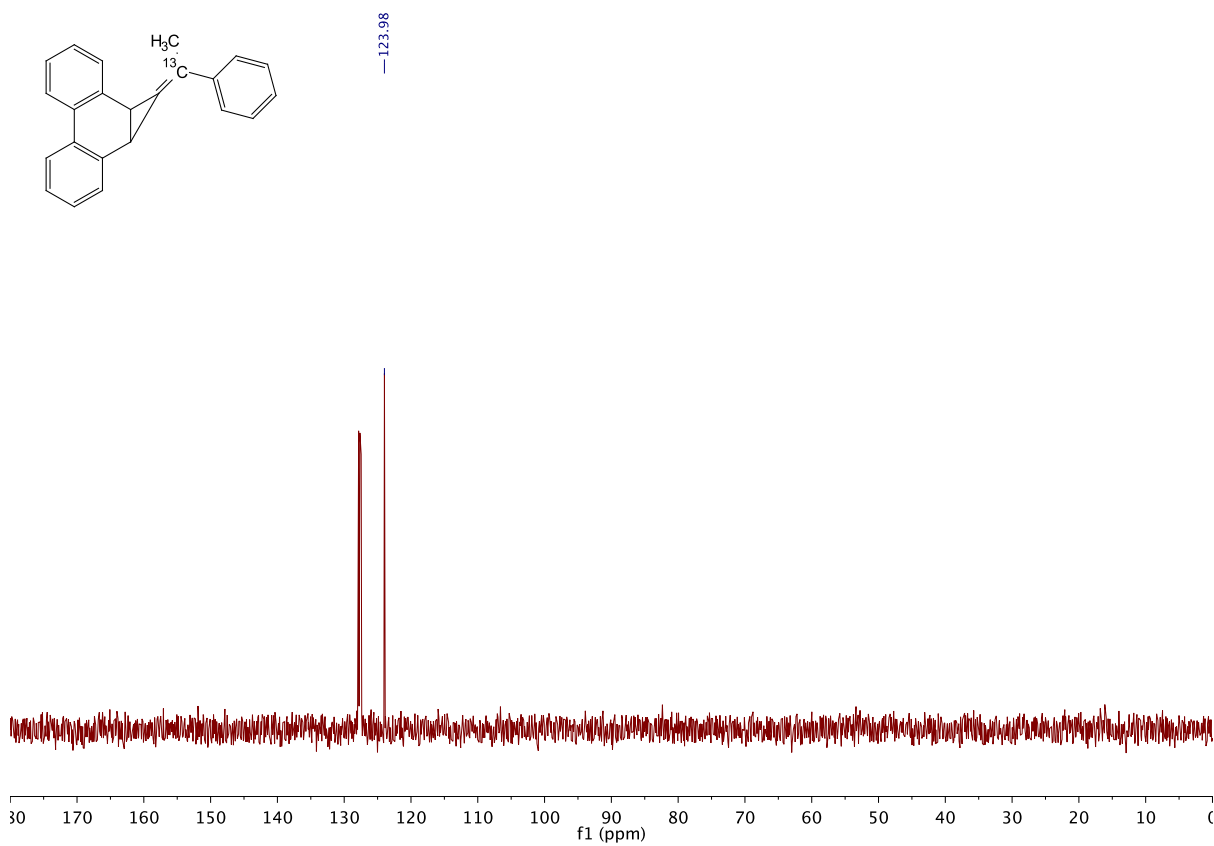


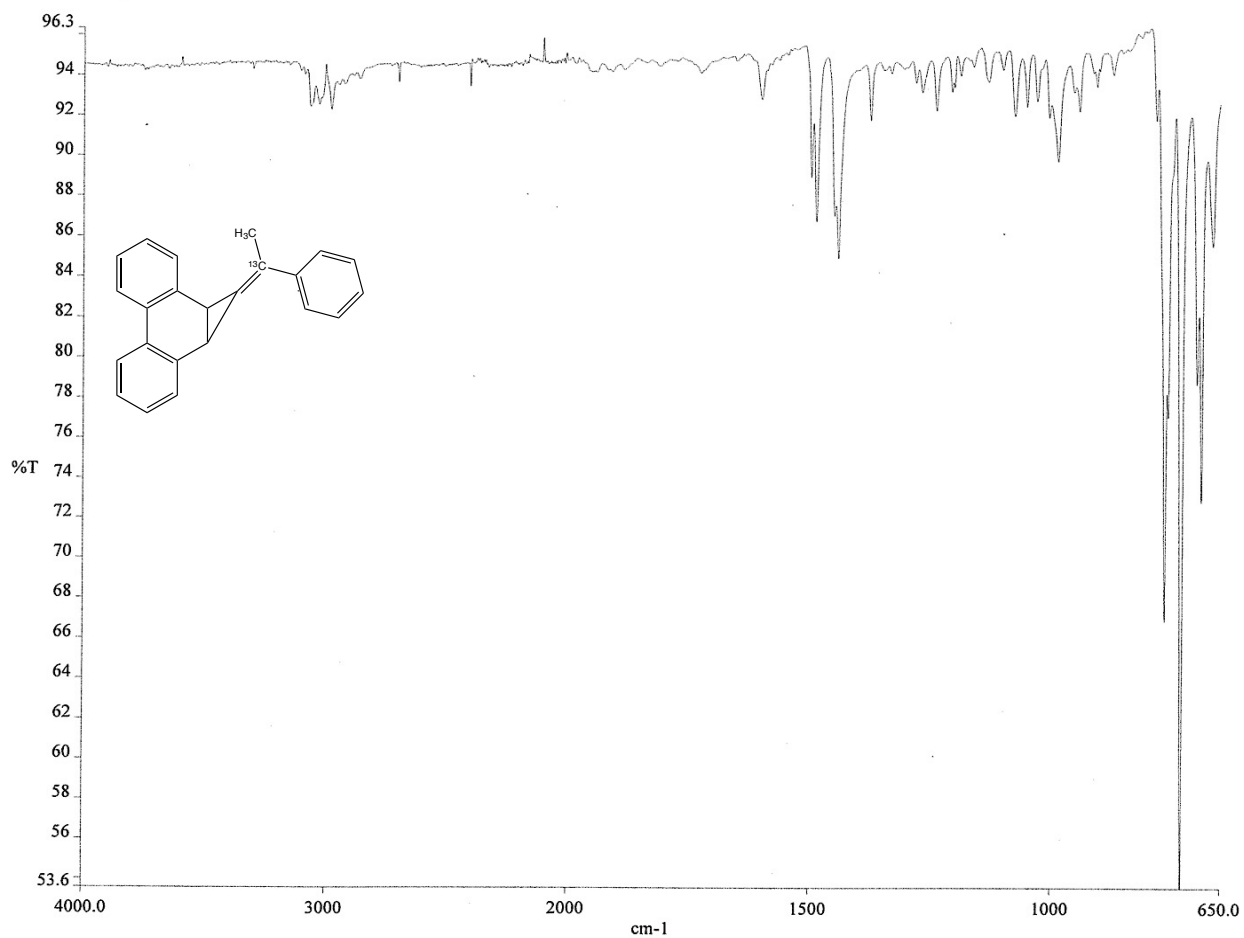


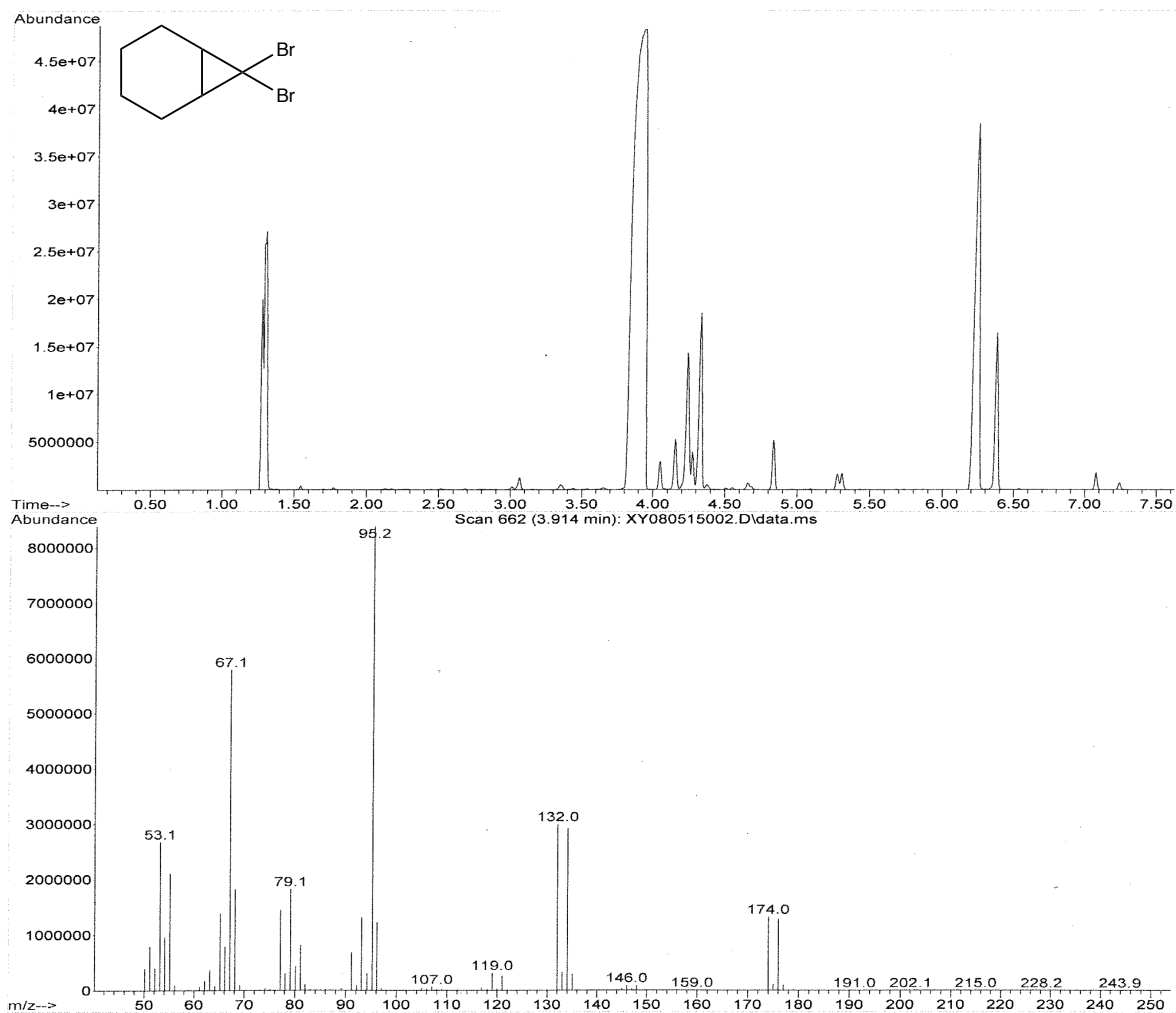


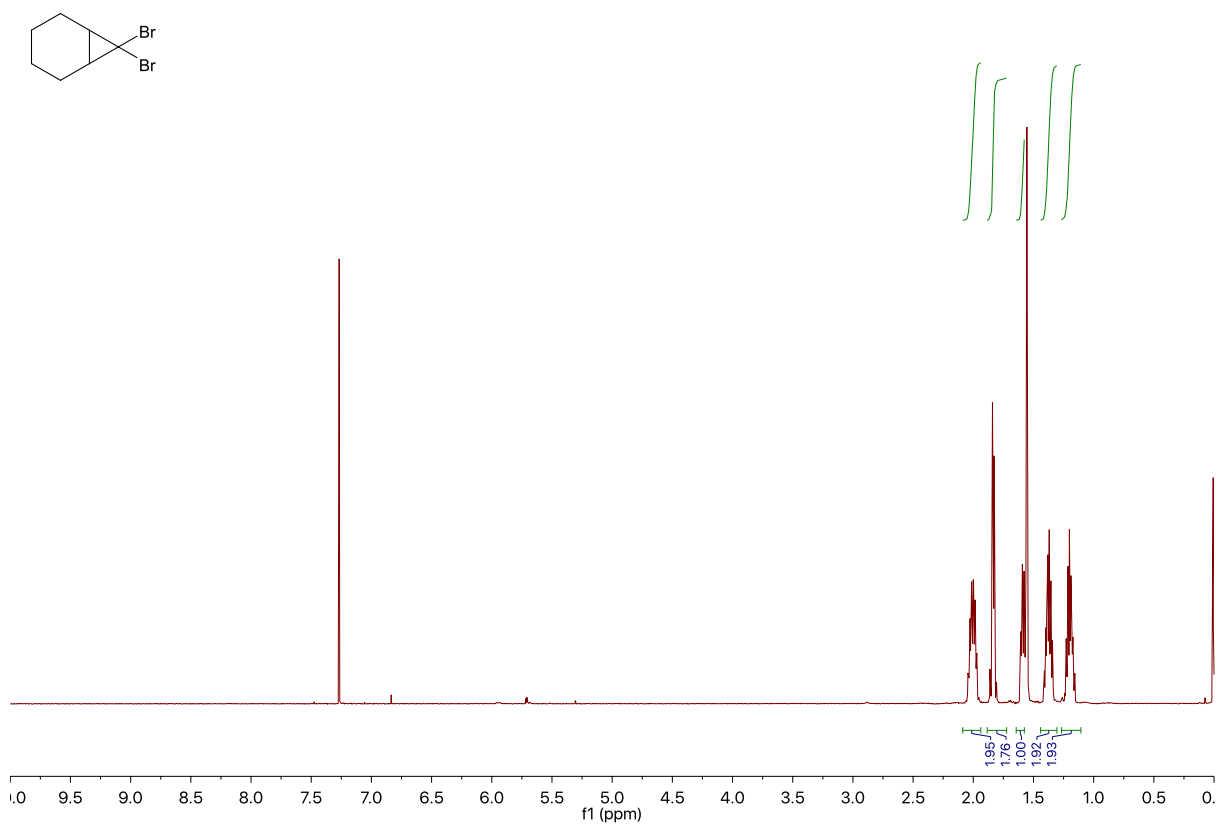


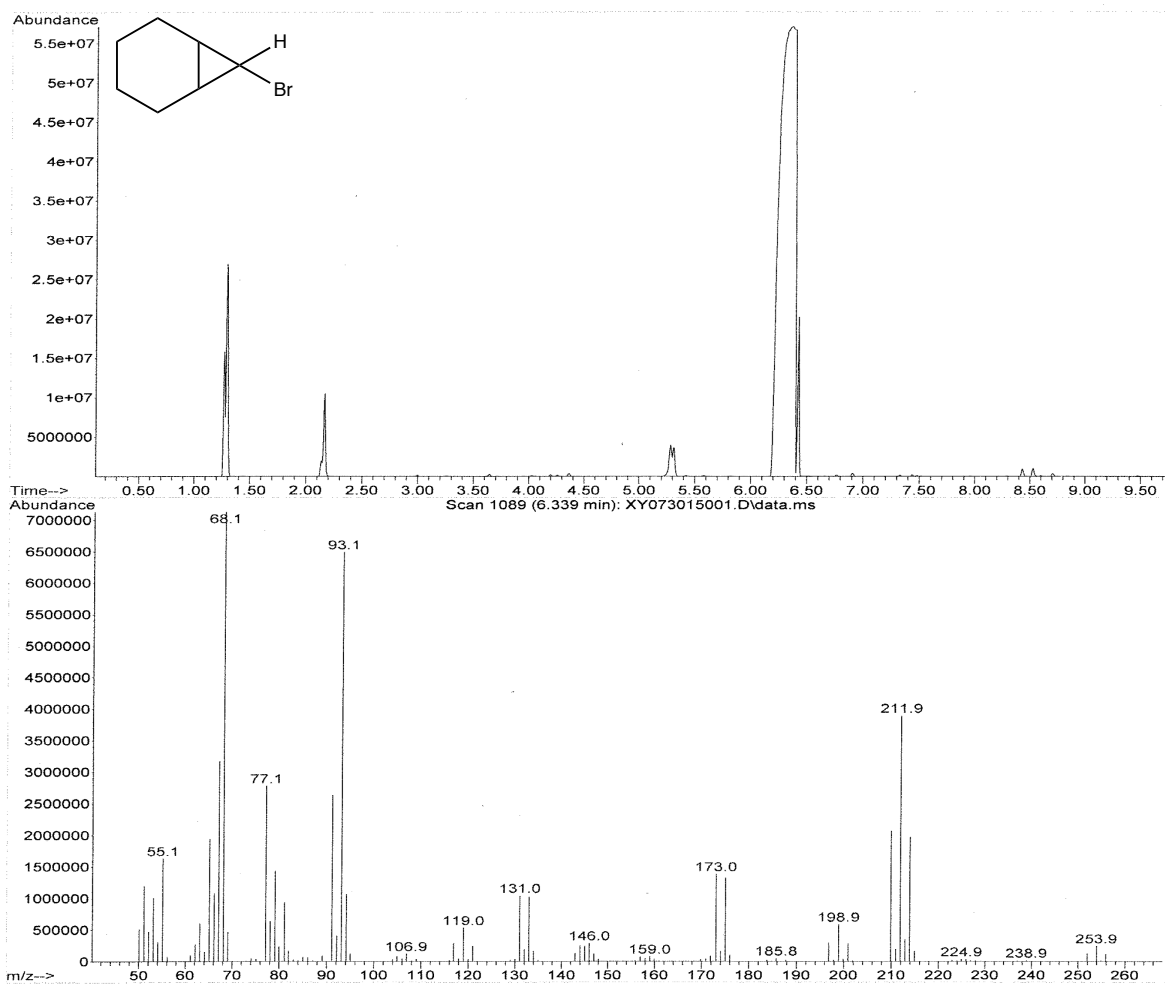


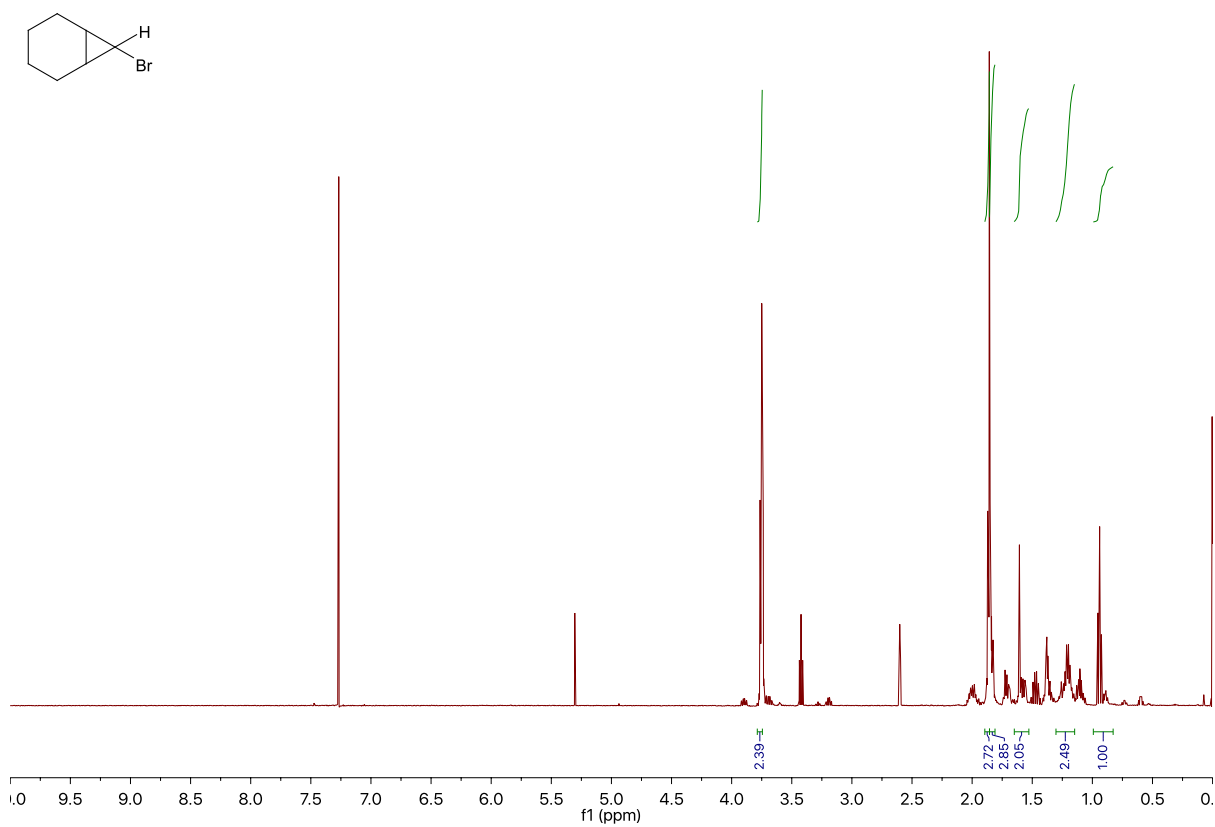


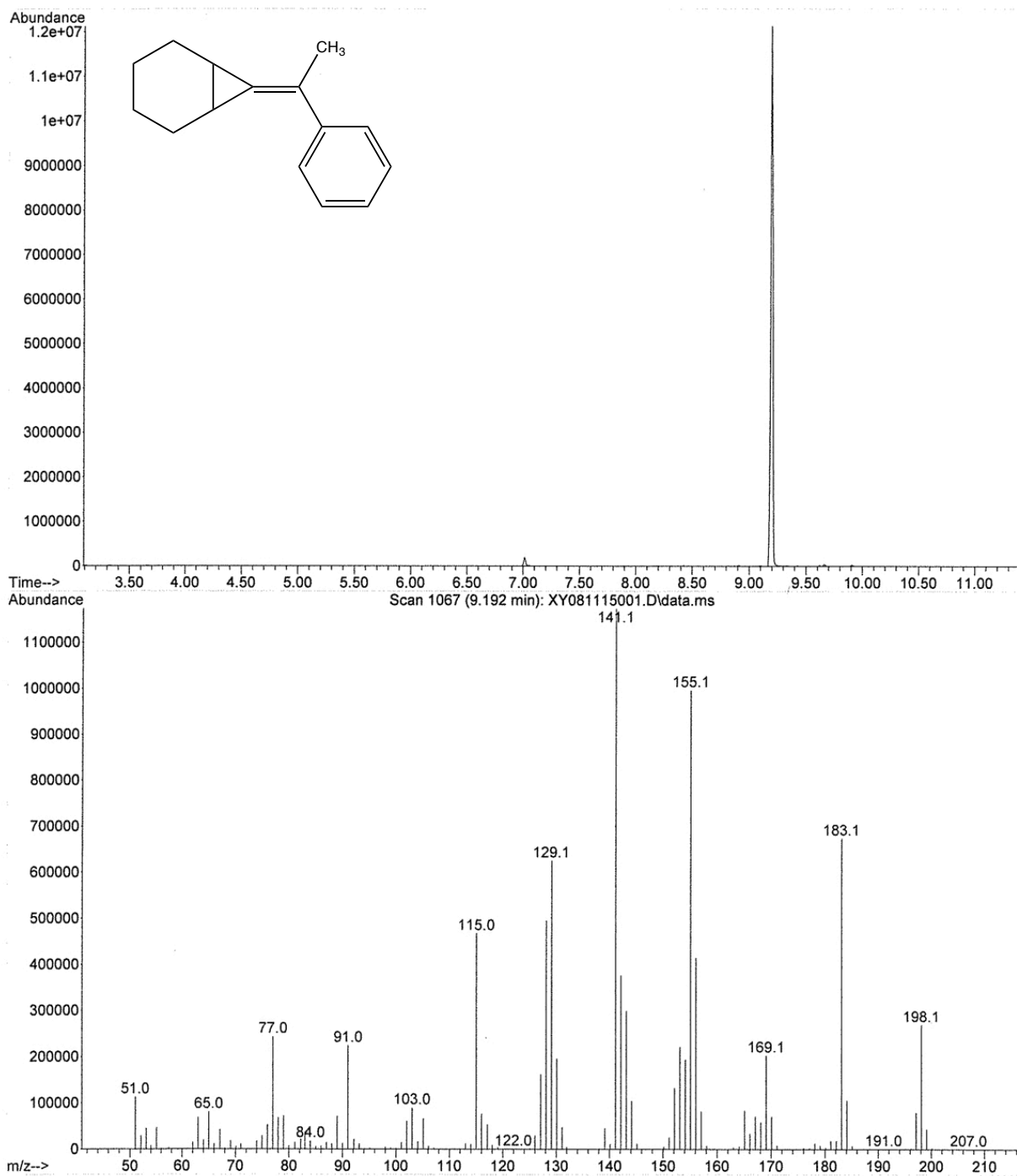


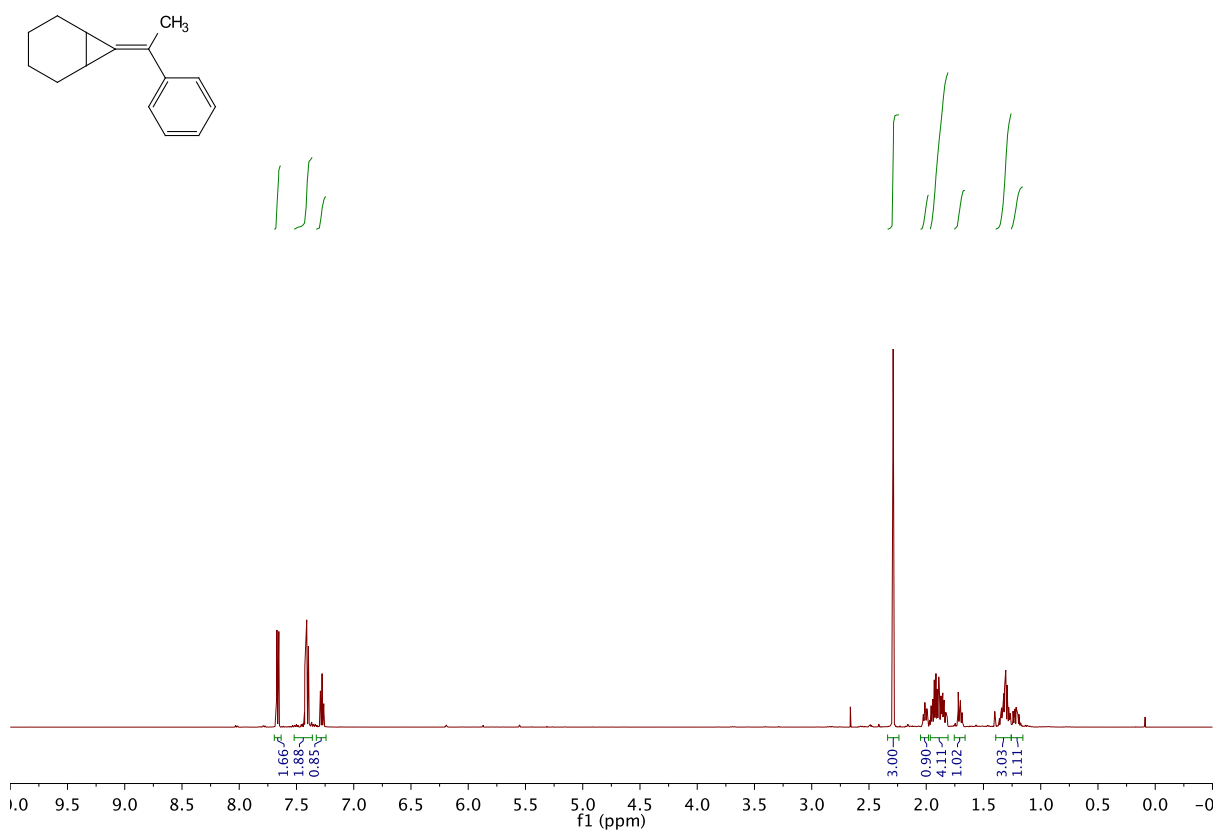


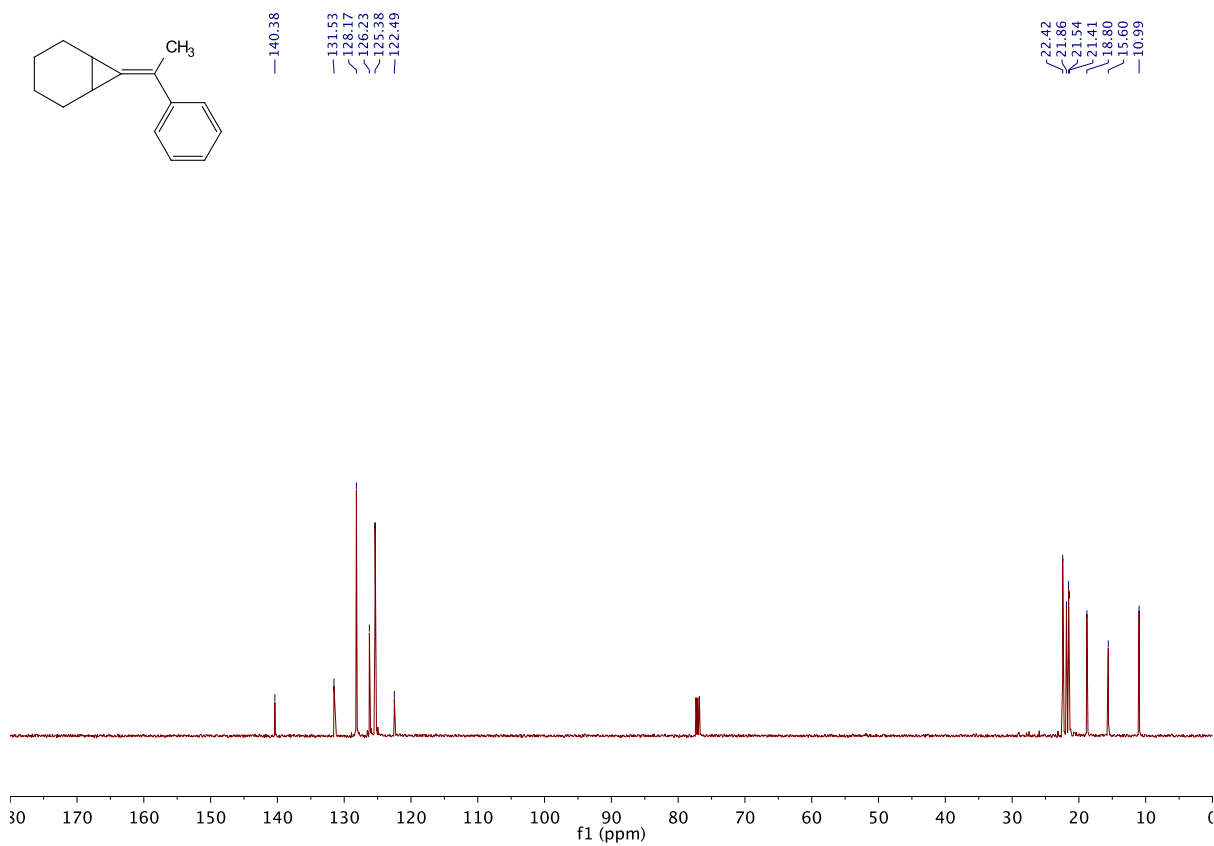












Cartesian coordinates and energies for B3LYP/6-311+G optimized structures**

Methylphenylvinylidene carbene (planar singlet) (**19**)

Charge = 0 Multiplicity = 1

C,0,1.724615217,-1.2924382105,-0.0000099084

C,0,0.3381684926,-1.1439988861,0.0000172404

C,0,-0.2425353147,0.1303571901,0.0000506019

C,0,0.601437909,1.2553894561,0.000055822

C,0,1.9811032747,1.1031155476,0.0000287006

C,0,2.5505226695,-0.172479139,0.0000009936

H,0,2.1560229309,-2.2870802675,-0.0000337784

H,0,-0.2892693574,-2.0271221893,0.0000131222

H,0,0.1680892389,2.24924883,0.0000804704

H,0,2.6169292057,1.9812925122,0.0000333696

H,0,3.6282221127,-0.2884408416,-0.0000178056

C,0,-1.7022413795,0.2994507196,0.0000690071

C,0,-2.6852318021,-0.8865680827,0.0000777011

H,0,-2.5288316339,-1.4874452846,-0.8985935429

H,0,-2.5284166987,-1.4878023367,0.8984383107

H,0,-3.7254363858,-0.5482919071,0.0003791679

C,0,-2.4815644788,1.3455468895,0.0000555278

Zero-point correction= 0.135970 (Hartree/Particle)

Thermal correction to Energy= 0.144115

Thermal correction to Enthalpy= 0.145059

Thermal correction to Gibbs Free Energy= 0.102819

Sum of electronic and zero-point Energies= -347.591047

Sum of electronic and thermal Energies= -347.582901

Sum of electronic and thermal Enthalpies= -347.581957

Sum of electronic and thermal Free Energies= -347.624197

Methylphenylvinylidene carbene (twisted singlet) (**19**)

Charge = 0 Multiplicity = 1

C,0,-1.8591135081,-1.1632956346,-0.2083821317

C,0,-0.4716928038,-1.2365707575,-0.0871975114

C,0,0.2800637332,-0.072170786,0.1055645101

C,0,-0.3756163525,1.1636536126,0.2008841115

C,0,-1.7579948734,1.2331943001,0.0681994223

C,0,-2.5024000459,0.0693240131,-0.1357689728

H,0,-2.4343073796,-2.0702545961,-0.3557079009

H,0,0.0364006703,-2.1912960587,-0.1440557702

H,0,0.201158843,2.0633604259,0.3825153046

H,0,-2.2577974989,2.1928701268,0.1360425519

H,0,-3.5809679116,0.1258299395,-0.2297914758

C,0,1.7870302334,-0.1330170065,0.1929561173

C,0,2.677174415,0.3669419048,-0.9172476093

H,0,2.4866363629,-0.1994154559,-1.8331389343

H,0,2.4684032517,1.4207424503,-1.1221211475

H,0,3.730670133,0.2654617981,-0.652728712

C,0,2.1172007314,-0.6402062762,1.3454301482

Zero-point correction= 0.135512 (Hartree/Particle)

Thermal correction to Energy= 0.144062

Thermal correction to Enthalpy= 0.145006

Thermal correction to Gibbs Free Energy= 0.100862

Sum of electronic and zero-point Energies= -347.590834

Sum of electronic and thermal Energies= -347.582284

Sum of electronic and thermal Enthalpies= -347.581339

Sum of electronic and thermal Free Energies= -347.625484

Methylphenylvinylidene carbene (triplet) (**19**)

Charge = 0 Multiplicity = 3

C,0,-2.3902638693,1.6607620315,0.1862630131

C,0,-1.0065197984,1.6432415617,0.126376877

C,0,-0.2680931475,2.8480836182,0.0123004539
 C,0,-0.9917717382,4.0687341352,-0.0384861182
 C,0,-2.3754340495,4.0781860265,0.0219306529
 C,0,-3.080993833,2.8769466075,0.1344309129
 H,0,-2.9399413962,0.7305188022,0.2734958428
 H,0,-0.4858168192,0.6949707577,0.1675577095
 H,0,-0.4285383575,4.9896841679,-0.1257540726
 H,0,-2.9114065013,5.0194296949,-0.0181846198
 H,0,-4.1641731722,2.8854697556,0.1816800587
 C,0,1.181240594,2.8685398701,-0.0528591271
 C,0,1.9592776673,1.5754286817,0.0003522415
 H,0,1.7631129339,1.029032296,0.9305621557
 H,0,1.6865136649,0.9104031557,-0.8276149813
 H,0,3.026682545,1.7840678007,-0.0602102329
 C,0,1.8901076371,4.0984128369,-0.1672104359

Zero-point correction= 0.134843 (Hartree/Particle)

Thermal correction to Energy= 0.142991

Thermal correction to Enthalpy= 0.143935

Thermal correction to Gibbs Free Energy= 0.100958

Sum of electronic and zero-point Energies= -347.532018

Sum of electronic and thermal Energies= -347.523870

Sum of electronic and thermal Enthalpies= -347.522926

Sum of electronic and thermal Free Energies= -347.565904

S**2 before annihilation 2.0161, after 2.0001

1-Phenylpropyne (**20**)

Charge = 0 Multiplicity = 1

C,0,-2.1417980854,-1.2055771604,0.0000002011

C,0,-0.7508945788,-1.2094713393,0.0000170035

C,0,-0.0337378851,-0.0000546825,0.0000276071

C,0,-0.7507586379,1.2094687029,0.0000172441

C,0,-2.1416119998,1.2057926588,0.0000005714

C,0,-2.8428538532,0.0001421693,-0.0000063607

H,0,-2.6802105834,-2.1467352409,-0.000007187

H,0,-0.205975371,-2.1458536918,0.0000211447

H,0,-0.2057612146,2.1458044137,0.0000215091

H,0,-2.6798794636,2.1470351644,-0.0000065552

H,0,-3.9268799427,0.0002298391,-0.0000186747

C,0,1.3945863435,0.000000259,0.0000350471

C,0,4.0582335885,0.0001826563,0.0000625823

H,0,4.4524919857,-0.510738197,0.8838238451

H,0,4.4525178146,-0.5106891808,-0.8837149116

H,0,4.4514095795,1.0208449257,0.0000966108

C,0,2.6017703036,0.0004227034,0.0000363229

Zero-point correction= 0.137320 (Hartree/Particle)

Thermal correction to Energy= 0.145669

Thermal correction to Enthalpy= 0.146613

Thermal correction to Gibbs Free Energy= 0.102851

Sum of electronic and zero-point Energies= -347.675071

Sum of electronic and thermal Energies= -347.666722

Sum of electronic and thermal Enthalpies= -347.665778

Sum of electronic and thermal Free Energies= -347.709540

TS for 1,2-phenyl shift from planar singlet **19** to **20**

Charge = 0 Multiplicity = 1

C,0,1.4751131179,-1.2277381824,-0.608285078

C,0,0.1868294278,-0.8673746301,-0.9860241688

C,0,-0.3629770524,0.3540994917,-0.5608350645

C,0,0.4075357177,1.2048496897,0.2501035932

C,0,1.6954874781,0.8412966802,0.6259117624

C,0,2.2310615555,-0.3749431347,0.1981499662

H,0,1.8940900975,-2.1687633357,-0.9463543906

H,0,-0.4037827169,-1.5140186164,-1.6240317392

H,0,-0.0132322122,2.1529116281,0.5634051715

H,0,2.2855539604,1.5065970549,1.2460413703

H,0,3.2372138789,-0.6554394683,0.4887468541

C,0,-2.0174144614,0.4719943284,-0.4632476294

C,0,-2.8351341923,-0.0912051331,0.6265496445

H,0,-2.7252367941,-1.1770762043,0.6909223893

H,0,-2.5638746241,0.3378738316,1.594866213

H,0,-3.8849818046,0.1385579421,0.4288708343

C,0,-1.6569103757,1.0672360584,-1.5252207283

Zero-point correction= 0.134746 (Hartree/Particle)

Thermal correction to Energy= 0.142596

Thermal correction to Enthalpy= 0.143541

Thermal correction to Gibbs Free Energy= 0.102287

Sum of electronic and zero-point Energies= -347.586975

Sum of electronic and thermal Energies= -347.579125

Sum of electronic and thermal Enthalpies= -347.578181

Sum of electronic and thermal Free Energies= -347.619434

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

Frequencies -- -267.7591

TS for 1,2-methyl shift from planar singlet **19** to **20**

Charge = 0 Multiplicity = 1

C,0,-1.7723697467,-1.2656299385,0.3085567852

C,0,-0.391024873,-1.1027863456,0.3521915795

C,0,0.1811722543,0.1578200929,0.1244273266

C,0,-0.6617710258,1.251811413,-0.1391071396

C,0,-2.0413510784,1.0825989624,-0.1651103702

C,0,-2.6024674073,-0.1756192401,0.0530150625

H,0,-2.200493147,-2.2459282318,0.4840520656

H,0,0.2415925554,-1.9534869055,0.5759744741

H,0,-0.223777559,2.225189222,-0.322802057

H,0,-2.6799173,1.9350687165,-0.3668272641

H,0,-3.6781017095,-0.3051965305,0.0236459012

C,0,1.6021917284,0.3940406514,0.1887771029

C,0,2.8794036916,-0.803060683,-0.2674162736

H,0,2.0855367414,-1.4547072237,-0.6465357386

H,0,3.5456554546,-0.5905999765,-1.0976527759

H,0,3.3893508169,-1.2976770516,0.5527302539

C,0,2.7465606042,0.9089510687,0.3420870677

Zero-point correction= 0.134563 (Hartree/Particle)

Thermal correction to Energy= 0.142600

Thermal correction to Enthalpy= 0.143544

Thermal correction to Gibbs Free Energy= 0.101134

Sum of electronic and zero-point Energies= -347.574615

Sum of electronic and thermal Energies= -347.566578

Sum of electronic and thermal Enthalpies= -347.565634

Sum of electronic and thermal Free Energies= -347.608043

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

Frequencies -- -372.4318

Summary output of (R/U)CCSD(T)/cc-pVTZ//B3LYP/6-311++G** calculations

Methylphenylvinylidene carbene (planar singlet) (**19**)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C9H8\DMTHAMAT\04-Dec-2015\0\#\#
 ccscd=(t,t1diag)/cc-pvtz geom=connectivity\PhMevinylidene singlet CCS
 DT\0,1\C,0,-1.724183,-1.291897,0.000048\C,0,-0.33778,-1.143045,0.0000
 21\C,0,0.242544,0.131484,-0.000012\C,0,-0.601765,1.256265,-0.000018\C,
 0,-1.981385,1.10358,0.00001\C,0,-2.550424,-0.172185,0.000037\H,0,-2.15
 5294,-2.286668,0.000072\H,0,0.289921,-2.025981,0.000025\H,0,-0.168712,
 2.250253,-0.000042\H,0,-2.617472,1.981567,0.000005\H,0,-3.628089,-0.28
 8468,0.000056\C,0,1.702199,0.301013,-0.000031\C,0,2.685543,-0.884713,-
 0.000039\H,0,2.529322,-1.485637,0.898632\H,0,2.528907,-1.485994,-0.898
 4\H,0,3.725647,-0.546127,-0.000341\C,0,2.481211,1.347341,-0.000017\Ve
 rsion=EM64L-G09RevA.02\State=1-A\HF=-345.462052\MP2=-346.8566474\MP3=-
 346.8990553\MP4D=-346.9342261\MP4DQ=-346.8881841\MP4SDQ=-346.9005731\C
 CSD=-346.9008103\CCSD(T)=-346.9784378\RMSD=4.127e-09\PG=C01 [X(C9H8)]\
 \@

T1 Diagnostic = 0.01251984

Methylphenylvinylidene carbene (twisted singlet) (**19**)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C9H8\DMTHAMAT\06-Dec-2015\0\#\n#
 ccscd=(t,t1diag)/cc-pvtz geom=connectivity\\PhMevinylidene singlet twi
 sted CCSD(T)\\0,1\C,0,-1.859111,-1.130738,-0.289937\C,0,-0.471856,-1.2
 13054,-0.172723\C,0,0.279618,-0.066545,0.108216\C,0,-0.37621,1.158648,
 0.295448\C,0,-1.758407,1.238105,0.166492\C,0,-2.502515,0.092968,-0.125
 571\H,0,-2.434089,-2.023974,-0.505938\H,0,0.036329,-2.160829,-0.300633
 \H,0,0.200302,2.042068,0.545113\H,0,-2.258317,2.189989,0.30574\H,0,-3.
 580954,0.15649,-0.216542\C,0,1.786465,-0.133933,0.192832\C,0,2.678118,
 0.448145,-0.875347\H,0,2.488841,-0.047605,-1.831552\H,0,2.469611,1.514
 401,-1.000555\H,0,3.731253,0.326938,-0.617786\C,0,2.115068,-0.726511,1
 .304283\\Version=EM64L-G09RevA.02\State=1-A\HF=-345.462499\MP2=-346.85
 5251\MP3=-346.8975087\MP4D=-346.9329075\MP4DQ=-346.8872011\MP4SDQ=-346
 .8994899\CCSD=-346.8998405\CCSD(T)=-346.977076\RMSD=3.039e-09\PG=C01 [
 X(C9H8)]\\@
 T1 Diagnostic = 0.01243131

1-Phenylpropyne (20)

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C9H8\DMTHAMAT\03-Dec-2015\0\#\n#
 ccscd=(t,t1diag)/cc-pvtz geom=connectivity\\Methyl shifted alkyne CCSD
 T\\0,1\C,0,-2.142061,-1.205634,-0.000022\C,0,-0.751158,-1.209547,-0.00
 0005\C,0,-0.033985,-0.00014,0.000006\C,0,-0.75099,1.209393,-0.000005\C

,0,-2.141843,1.205735,-0.000021\C,0,-2.843101,0.000094,-0.000028\H,0,-
 2.680487,-2.146785,-0.000029\H,0,-0.206251,-2.145937,-0.000001\H,0,-0.
 20598,2.145721,0.\H,0,-2.680098,2.146985,-0.000028\H,0,-3.927127,0.000
 197,-0.000041\C,0,1.394339,-0.000104,0.000013\C,0,4.057986,0.000042,0.
 000041\H,0,4.452238,-0.510884,0.883802\H,0,4.452264,-0.510835,-0.88373
 7\H,0,4.451176,1.020699,0.000075\C,0,2.601523,0.000302,0.000014\\Versi
 on=EM64L-G09RevA.02\State=1-A\HF=-345.5353891\MP2=-346.9500369\MP3=-34
 6.9802712\MP4D=-347.0159614\MP4DQ=-346.9694091\MP4SDQ=-346.98189\CCSD=
 -346.9810539\CCSD(T)=-347.059458\RMSD=6.680e-09\PG=C01 [X(C9H8)]\ \@
 T1 Diagnostic = 0.01082363

TS for 1,2-phenyl shift from planar singlet **19** to **20**

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C9H8\DMTHAMAT\05-Dec-2015\0\#\#
 ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\TS for Ph shift CCSDT\\0,1
 \C,0,1.737741,1.209683,-0.150468\C,0,0.397859,1.211431,0.219584\C,0,-0
 .288744,-0.000114,0.408806\C,0,0.397975,-1.21155,0.21926\C,0,1.737863,
 -1.209555,-0.150765\C,0,2.40957,0.000122,-0.336646\H,0,2.261689,2.1488
 35,-0.287703\H,0,-0.129967,2.143708,0.381711\H,0,-0.129763,-2.143924,0
 .381111\H,0,2.261905,-2.14862,-0.288243\H,0,3.455701,0.000198,-0.62138
 6\C,0,-1.938389,-0.00008,0.210668\C,0,-2.626072,0.000235,-1.093406\H,0
 ,-2.371427,0.886152,-1.681321\H,0,-2.371322,-0.885351,-1.681765\H,0,-3

.704706,0.000137,-0.918486\C,0,-1.706489,-0.000362,1.458981\\Version=E
 M64L-G09RevA.02\State=1-A\HF=-345.4420339\MP2=-346.8599539\MP3=-346.89
 0779\MP4D=-346.9271584\MP4DQ=-346.8790272\MP4SDQ=-346.8913879\CCSD=-34
 6.8912689\CCSD(T)=-346.9724144\RMSD=5.691e-09\PG=C01 [X(C9H8)]\\@
 T1 Diagnostic = 0.01275721

TS for 1,2-methyl shift from planar singlet **19** to **20**

1\1\GINC-NSCC-N2\SP\RCCSD(T)-FC\CC-pVTZ\C9H8\DMTHAMAT\01-Dec-2015\0\\#
 ccsd=(t,t1diag)/cc-pvtz geom=connectivity\\TS for methyl shift CCSD(T
)\\0,1\C,0,-1.750244,1.302308,-0.099384\C,0,-0.373149,1.11714,-0.17592
 7\C,0,0.174881,-0.170757,-0.078982\C,0,-0.687975,-1.268298,0.08747\C,0
 ,-2.063357,-1.07511,0.147063\C,0,-2.600258,0.209252,0.059339\H,0,-2.15
 9561,2.303336,-0.173368\H,0,0.27476,1.972892,-0.323841\H,0,-0.268559,-
 2.263436,0.170163\H,0,-2.717483,-1.930353,0.272919\H,0,-3.672573,0.356
 648,0.114625\C,0,1.589884,-0.427706,-0.183771\C,0,2.896623,0.693681,0.
 37063\H,0,2.120615,1.320885,0.821213\H,0,3.566979,0.388151,1.167874\H,
 0,3.40816,1.255667,-0.40386\C,0,2.721538,-0.947808,-0.400725\\Version=
 EM64L-G09RevA.02\State=1-A\HF=-345.4308108\MP2=-346.8460179\MP3=-346.8
 79063\MP4D=-346.9149116\MP4DQ=-346.8670073\MP4SDQ=-346.8793704\CCSD=-3
 46.8788654\CCSD(T)=-346.9595405\RMSD=6.881e-09\PG=C01 [X(C9H8)]\\@
 T1 Diagnostic = 0.01152408