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Experimental and Computational Investigation of Selected β -Hydroxy Carbenes

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Experimental and Computational Investigation of Selected β -Hydroxy Carbenes

By Joseph D. DeAngelo

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 18, 2015

Experimental and Computational Investigation of Selected β -Hydroxy Carbenes

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“Chemistry began by saying it would change the baser metals into gold.
By not doing that it has done much greater things.”
— Ralph Waldo Emerson

“Now we know.”
— D. Thamattoor

Vitae

Joseph Daniel DeAngelo was born March 13, 1993 to Daniel J. and Ilene I. DeAngelo in Bronxville, New York. The oldest of four boys, Joe was raised in West Roxbury, Massachusetts and attended high school at Boston Latin School, graduating in 2011. Throughout high school, he became most interested in the natural sciences and mathematics and had hoped to pursue one of these fields in college.

Joe enrolled in Colby College, Waterville, ME in September of 2011. Initially unsure of what to pursue, he eventually made his way to Keyes where he found his love for chemistry. Joe began working in the Thamattoor research group in the fall of his junior year and continued his work through the following summer and his senior year. At Colby, Joe was also involved in the Chemistry Club—co-president his junior and senior year—and a four-year member of the Hounds, Colby's Club Hockey team, of which he was named captain his senior year. He will graduate from Colby on May 24, 2015 with a Bachelor of Arts with a double major in Chemistry, graduating with honors, and Mathematical Sciences.

Acknowledgments

Fist and foremost I would like to thank my parents, Dan and Ilene, for their unconditional love, encouragement, and constant support during my academic career. Through them, I have been provided countless opportunities without which none of this could have been possible. It is from them that I had developed a scientific curiosity as well as a drive to excel from a young age. Additionally, I would like to thank my three younger brothers, Stephen, Robert, and Thomas for doing their best to keep me humble and in line over the years.

When I had initially entered my freshman year at Colby, I had a notion that I had wanted to pursue something within the sciences or math, but nothing substantial past that. After less then half of a semester in Das's sophomore organic chemistry course, I had fallen in love with the subject, quickly declared my new major in chemistry, and asked Das to join his research group the following year, to which he quickly agreed. Although still not quite sure why he did, affording me the opportunity to work in his lab has been one of my best experiences at Colby. During my time in his lab, Das has been a better mentor then I could have ever asked for. His love for the subject matter as well as his passion for working with and helping students is infectious. Through Das, I have learned an enormous amount in chemistry, baseball, and otherwise and for that I am eternally grateful.

Lastly I would also like to thank the other faculty in the Chemistry Department, who have made my experience in Keyes be as great as it was, as well as my lab mates and friends who have provided the amazing encouragement and support over the years.

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Abstract

The photolytic precursor to the sterically hindered β -bis(*tert*)-butanol carbene, 3-(1a,9b-dihydro-1H-cyclopropa[*l*]phenanthren-1-yl)-2,2,4,4-tetramethylpentan-3-ol was prepared in three steps from phenanthrene. Photolysis of the precursor generates the desired β -hydroxy carbene, an intermediate, which subsequently rearranges into two different observed products from an intramolecular C-H insertion and alkyl shift. Four intramolecular mechanisms were ultimately considered to account for the possible rearrangement pathways. Computational studies using density functional theory are also presented.

In addition, the photolytic precursors to two cyclic β -hydroxy carbenes, 1-(1a,9b-dihydro-1H-cyclopropa[*l*]phenanthren-1-yl)cyclopropan-1-ol and 1-(1a,9b-dihydro-1H-cyclopropa[*l*]phenanthren-1-yl)cyclobutan-1-ol, were also prepared through different synthetic routes from phenanthrene. Photolysis of these alcohols led to the formation of β -cyclopropanol carbene and β -cyclobutanol carbene. Both carbenes were observed to undergo an alkyl shift, resulting in a ring expansion, as their major rearrangement product. Additionally, low temperature argon matrix isolation spectroscopy was performed on the β -cyclopropanol carbene in an effort to isolate and study the rearrangement intermediates.

Introduction

1.1 Overview and Structure of Carbenes

Carbenes belong to an important class of reactive organic intermediates. These species are characterized by a neutral, divalent carbon atom, which has a lone pair of electrons. The instability and reactivity of carbenes is due to this electron-deficient carbon atom, lacking the standard octet of electrons. Typically these carbon atoms have two σ -bonds formed from hybridized sp^2 -type orbitals. The remaining two unpaired electrons commonly exist in three different configurations, which characterize the spin states of the carbene (Figure 1). The spin state of a carbene both affects its preferred geometry as well as its reactivity.¹

For a singlet spin state, which has a net spin of zero, both electrons are spin-paired and occupy the same hybridized sp^2 -type orbital. For an open-shell (or excited) singlet spin state, the electrons have antiparallel spins, with one electron occupying the hybridized orbital and the other occupying the previously empty p orbital. Just like the ground singlet state, carbenes in the open-shell singlet state also have a net spin of zero. For a triplet spin state, the electrons are no longer spin paired and have parallel spins, giving the species a net spin of 1. Similar to the open-shell singlet carbenes, triplet carbenes have one electron occupying each of the sp^2 -type and p orbitals.²

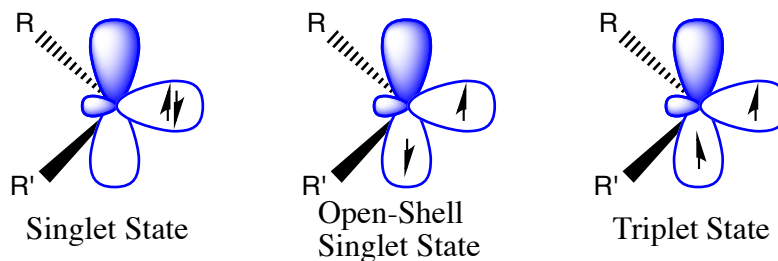
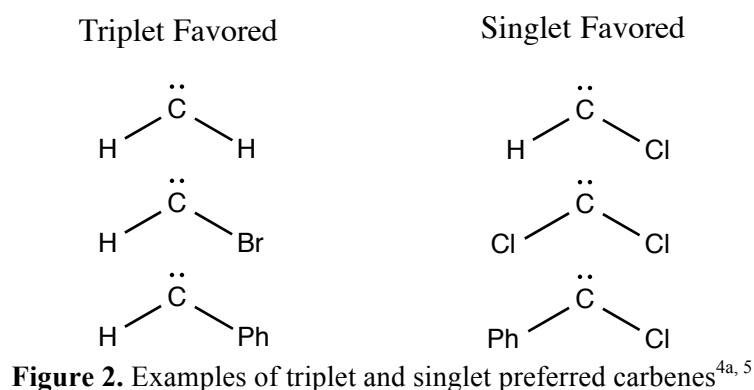


Figure 1. Electron configuration of different carbene spin states

The spin state of a carbene is initially a direct result of the method of its generation, resulting in a specific spin state due to the principle of spin conservation. Additionally, the

equilibrium distribution of the singlet and triplet spin states, referred to as singlet-triplet splitting, depends on the energy spacing between the species.¹ Typically for divalent carbenes the triplet state is lower in energy than the singlet state due to the minimization of electron-electron repulsion forces, following Hund's Rule.^{2b, 3} However in special cases the singlet state carbene can have the lower energy, for example with electron donating R groups such as dichlorocarbene (Figure 2).⁴



1.2 Methods of Generating Carbenes

Although first attempts to generate carbenes were in the 18th century, the origins of modern carbene chemistry are credited to Staudinger's work on methylene published in 1911.⁶ Since then, chemists have explored different methods of generating and studying these interesting intermediates. While there are now many ways of generating carbenes, the ones most commonly used are the decomposition of diazo-compounds, diazirines, and ketenes (Figures 3 and 4). These methods depend on the breaking of relatively weak covalent bonds, resulting in the expulsion of stable, neutral fragments such as nitrogen (N₂) or carbon monoxide gas (CO) as well as the desired carbene. For the decomposition of diazo-compounds and diazirines, the activation energies are relatively small, allowing these precursors to easily generate carbenes upon pyrolysis, the addition of heat, or photolysis, the exposure to light. These processes tend to

be both clean and efficient. Although effective in generating carbenes, diazo and diazirine compounds tend to be unstable, explosive, poisonous, mutagenic, and carcinogenic, therefore problematic and dangerous to use in the laboratory.^{1, 2b, 7}

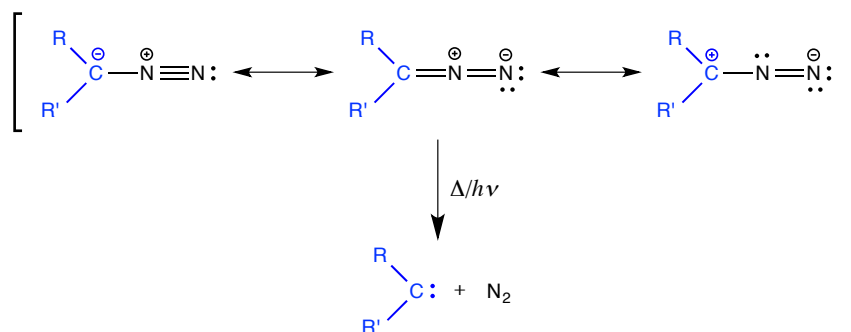


Figure 3. Carbene formation from diazo-precursors

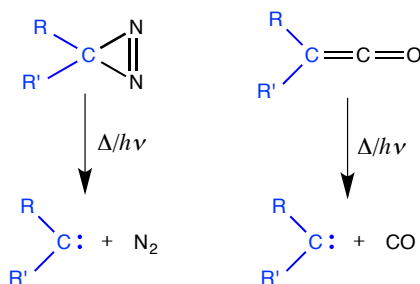


Figure 4. Carbene formation from diazirines and ketenes

Additionally, carbenes can also be generated from the basic hydrolysis of haloforms, commonly bromoform and chloroform, resulting in the corresponding carbene (Figure 5). Treatment of these halocarbons with a strong base, such as hydroxide or potassium *tert*-butoxide, is able to generate the desired carbene through a carbanion intermediate. While effective, this method is limited by the need of an acidic proton as well the presence of a base capable of this deprotonation, resulting in the carbanion intermediate.^{1, 2b}

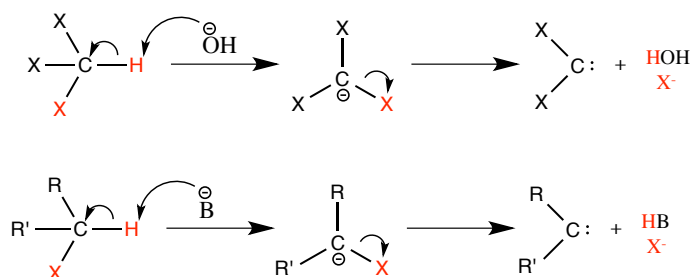


Figure 5. Carbene formation through alkyl halides

1.3 Carbenes from Phenanthrene-Based Precursors

As afore mentioned carbene precursors, the dangerous diazo compounds and synthetically limited haloforms, have noteworthy limitations, another more practical method for generating carbenes is from the photolysis of cyclopropanated aromatic precursors. In the mid-1960s, Richardson's group from the Shell Oil Company showed that their precursor (**1**), was successfully able to generate methylene (**2**), with the concomitant formation of phenanthrene (**3**) upon photolysis (Figure 6a). Their work also demonstrated that methylene carbene **2** exhibited the same reactivity as the carbene generated from diazo-precursors. Additionally, this new precursor was a convenient and shelf-stable source for generating carbenes, therefore much more favorable than the previously mentioned methods.⁸ Although a promising precursor, these phenanthrene derivatives were not used again until the early 1990s when Professor Johnson's group at the University of New Hampshire used a similar precursor (**4**) in order to generate dichlorocarbene (**5**) through photolysis, again with byproduct **3** (Figure 6b). Just as with precursor **1**, this method involved a preferable precursor and was successfully able to generate the desired carbene having the same reactivity as generated through other methods.^{4a} Given their stability, research has since tended towards using similar phenanthrene derivatives in order to generate a wide variety of carbenes.⁹

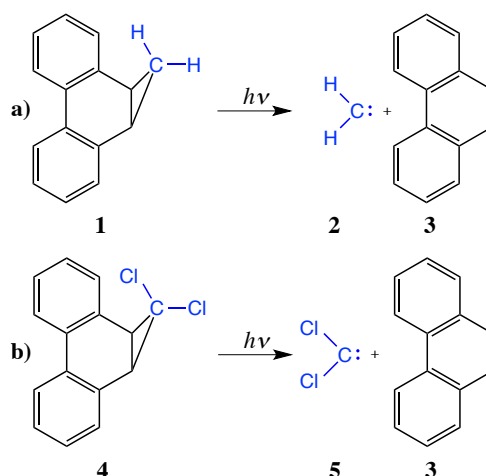


Figure 6. Generation of a) methylene and b) dichlorocarbene from phenanthrene-based precursors

1.4 Methods of Carbene Investigation

Due to their inherent instability, carbene lifetimes are often on the scale of nanoseconds at ambient temperatures.¹⁰ This short lifetime has proven problematic to physical organic chemists trying to study these intermediates. One of the most common ways of studying carbenes is to generate them in solution and study the products either resulting from a trapping agent or through intramolecular rearrangements.^{6a} Additionally two complementary techniques that have been developed to further investigate these intermediates are time-resolved absorption spectroscopy and matrix isolation spectroscopy.¹¹ The time-resolved absorption techniques have been shown to exhibit a time-resolution of about one nanosecond, allowing for the analysis of extremely short-lived intermediates.^{6a} In the case of matrix isolation spectroscopy the objective is to characterize carbenes in solid matrices, typically made from inert gases, at very low temperatures, commonly at 77 Kelvin or below. This method allows for the direct study of carbenes and other reactive species through spectroscopic methods, as in these conditions the carbenes are kinetically stabilized and bimolecular reactions are suppressed.¹¹⁻¹²

1.5 Carbene Reactivity

Due to their instability and high reactivity, carbenes will rapidly react with many different types of molecules. The reactivity of a specific carbene is directly influenced by both its electronic configuration and identity of the R groups on the carbene. One motif of carbene reactivity is that they will easily insert into different types of bonds. Most commonly, carbenes are known to insert into sigma bonds, e.g. in C-H and O-H insertions. The most common is the C-H insertion, in part due to that the C-H bond being weaker than an O-H bond and therefore easier to insert into. Another type of carbene reaction is an olefin insertion, whereby the cycloaddition to pi bonds results in cyclopropanation. (Figure 7).¹

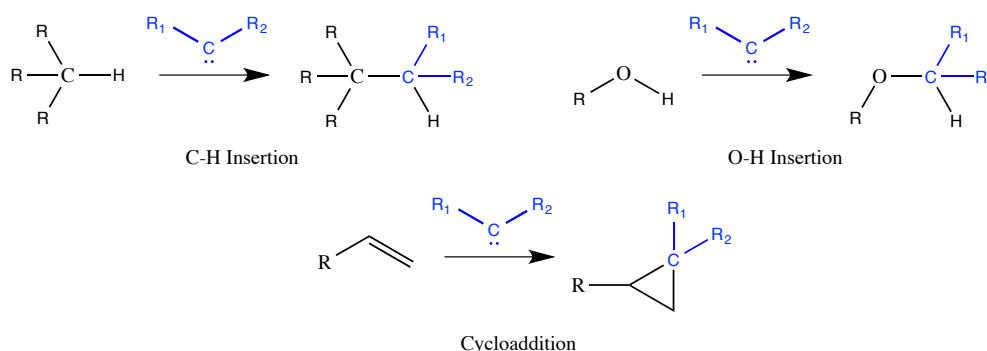


Figure 7. Examples of common carbene insertions

Carbenes are so reactive that they frequently undergo intramolecular rearrangements, including hydrogen and alkyl shifts from the β -carbon (Figure 8). This reactivity is due to the often-large decrease in energy as the carbene rearranges into a more stable conformation. These intramolecular rearrangements typically include both C-H and O-H insertions.¹

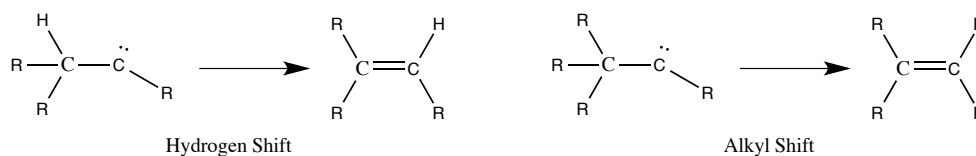


Figure 8. Examples of common carbene intramolecular rearrangements

A common carbene reaction, used to both trap and study carbenes, is the carbene cycloaddition to the pi bonds of alkenes, resulting in cyclopropanated products. The utility of this

reaction is that it allows for the characterization of the spin state of the carbene.^{1, 2b} Work done by Skell and Woodward in 1959 showed that the singlet carbene, methylene, maintained stereochemistry when reacting with cis- and trans-2-butene, arguing that these bonds must form simultaneously.¹³ They then hypothesized that triplet carbenes, which do not show stereospecificity when adding to double bonds to form the cyclopropyl products, do not occur in a single step, therefore having an intermediate.^{1, 14}

As Woodward showed, the stereospecificity of the singlet carbene addition to a double bond is a result of the reaction occurring through a concerted, single step mechanism (Figure 9).¹³

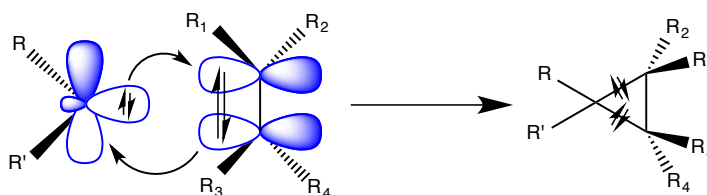


Figure 9. Single-step mechanism of a singlet carbene addition to double bonds

However for triplet carbenes, the unpaired electrons prohibit a single step mechanism, resulting in a diradical intermediate. In order for the last step of this reaction to occur, one of the radical electrons must undergo a spin flip, allowing for paired electrons to create the final covalent bond. These spin flips are typically slow when compared to the rotation around a single bond, resulting in a mixture of products, depending on what conformation is present when the final bond is formed (Figure 10).^{2b} As a result of the different mechanisms for singlet and triplet carbenes, the characterization of products can be used in order to identify the spin state of the carbene under investigation.

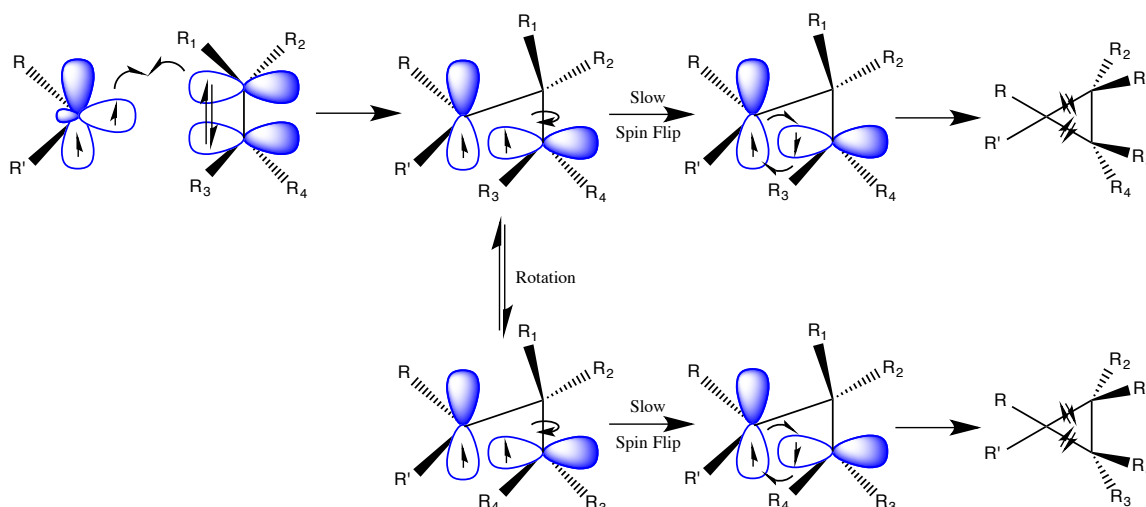


Figure 10. Two-step mechanism of a triplet carbene addition to a double bond through a diradical intermediate, allowing for bond rotation^{2b}

1.6 Intramolecular Rearrangements of β -Substituted Carbenes

Previous studies have investigated different possible intramolecular rearrangements of carbenes by selectively replacing one of the substituents in the β -position of the carbene. Past work by Kirmse on isopropylcarbene (**6**), generated from the photolysis of a diazo precursor (**7**), studied the 1,2-H shift, the 1,3-C-H insertion, as well as the possible 1,2-methyl shifts. Using deuterium labeling, he concluded that the 1,2-H shift, producing isobutylene, and the 1,3-C-H insertion, producing 1-methylcyclopropane, were the overwhelmingly major products. Additionally, he found that the 2-butene isomers, from the 1,2-methyl shifts, were both minor products (Figure 11a).¹⁵ Later work by Jones studied a similar carbene, replacing the β -H of **6** with a methyl group, giving *tert*-butylcarbene (**8**), which was generated from a phenanthrene-based precursor (**9**). Compared to **6**, the *tert*-butylcarbene has fewer possible intramolecular interactions, as it can only undergo a 1,3-C-H insertion or a 1,2-methyl shift. Interestingly, this carbene was found to heavily prefer the formation of the 1,3-C-H insertion product, a

cyclopropyl derivative, rather than the 1,2-methyl shift product, resulting in an olefin (Figure 11b).¹⁶

In earlier work done in our group, Robin Farlow studied another carbene, this time replacing one of the methyl groups in **8** with a hydroxyl group, yielding the β -hydroxy carbene, 2-hydroxy-2-methylpropylidene (**10**). This compound was generated from a phenanthrene-based precursor (**11**). Farlow's work predominantly studied the intramolecular rearrangement products of **10**. Surprisingly, their work found that unlike carbene **8**, the 1,2-methyl shift was favored, resulting in the major ketone product, followed by the 1,3-C-H insertion product and the 1,3-O-H insertion product (Figure 11c). For the hydrogen insertions, the C-H insertion was thought to be statistically favored due to the six available C-H bonds as opposed to the single O-H bond. Additionally, the insertion into the weaker C-H bond should be favored over the stronger O-H bond. However, the overall preference of the carbene to undergo a methyl shift was the result of the β -hydroxy group strongly altering the rearrangement pathways of **10**. Their work suggested that the β -hydroxy substituent polarizes the attached carbon creating a partial positive charge. This natural polarization would then act to favor the transition state for the 1,2-methyl migration as the hydroxy group results in the electrostatic stabilization of the negative charge that is generated at the carbon center during the transition state.^{9b}

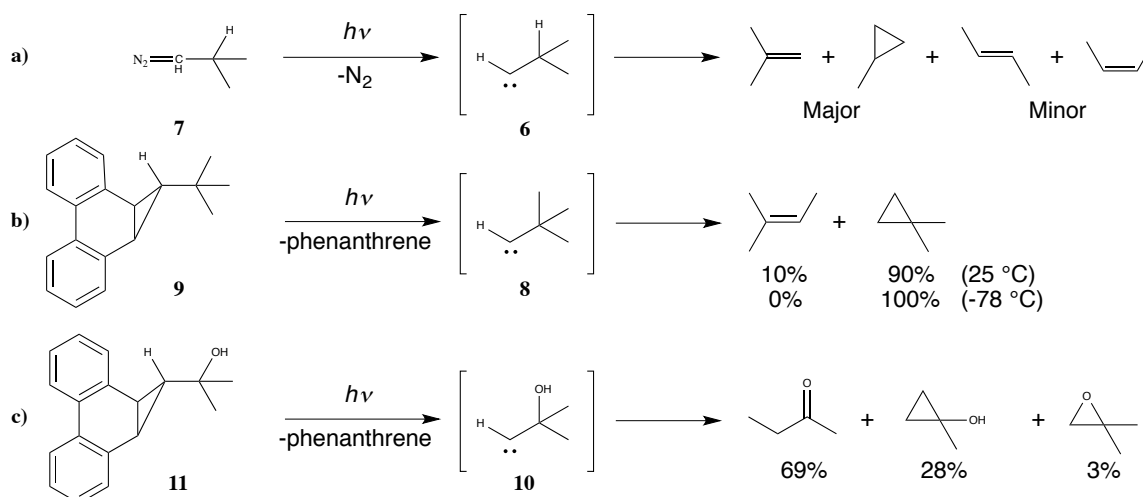


Figure 11. Generation and intramolecular rearrangement products of a) isopropylcarbene, b) *tert*-butylcarbene, and c) 2-hydroxy-2-methylpropylidene

The current study is focused on continuing the investigation of intramolecular rearrangements of β -hydroxy carbenes. This was done by replacing the remaining β -groups while maintaining the hydroxy group of the carbene. Each of these carbenes will be generated from phenanthrene-based precursors, similar to **11**. For the first carbene, the two methyl groups of **10** will be replaced with two *tert*-butyl groups, giving precursor **12** and carbene **13**. Additionally the effects of β -cyclic systems will also be explored. For a cyclopropyl system, this will result in precursor **14** and carbene **15**. Likewise for a cyclobutyl system, this will result in precursor **16** and carbene **17** (Figure 12). This investigation explores, both experimentally as well as computationally, each carbene's intramolecular rearrangement products in an attempt to further the understanding of the β -substituents' affects on carbene reactivity.

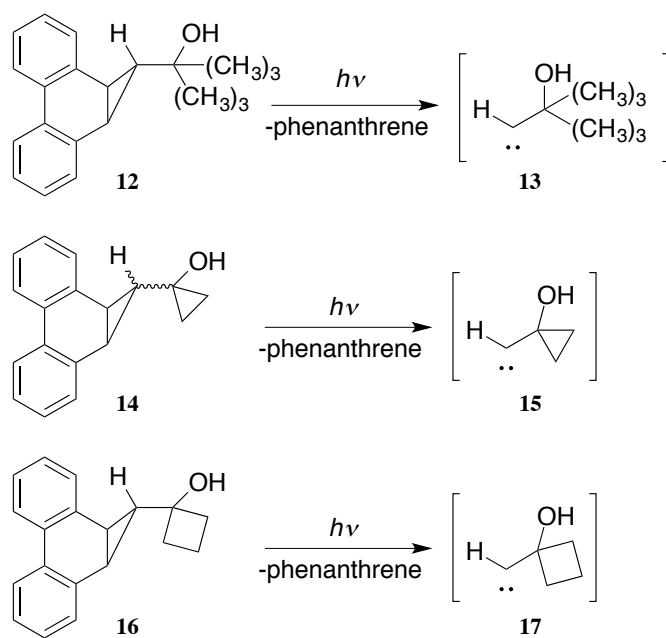


Figure 12. Generation of selected β -hydroxy carbenes via the photolysis of phenanthrene-based precursors

Results and Discussion

2.1 Synthetic Aspects of Carbene Precursors

The route to generate each of the three β -hydroxy carbenes under investigation was through their corresponding photochemically active precursor, all phenanthrene-based derivatives. The synthetic routes to each precursor are shown in Figures 13 and 14. In the first step for the synthesis of precursors **12** and **16** consisted of the cyclopropanation across the 9,10 double bond in phenanthrene (**3**), which was accomplished through the addition of bromoform and sodium hydroxide. Through basic hydrolysis, the bromoform and sodium hydroxide generate dibromocarbene, which upon cyclopropanation with **3** yields dibromo-cyclopropylphenanthrene **18**.¹⁷ This compound was converted into monobromo-cyclopropylphenanthrene **19** through the addition of butyllithium, resulting in the loss of a halide and production of a carbanion, and quenching with water. Previous work done on the reaction has shown that the *exo* product is formed exclusively.^{9c} Monobromo product **19** was subsequently used as a branching point to synthesize both **12** and **16**. For the final step of these syntheses, *tert*-butyllithium was added to **19**, again forming a carbanion intermediate. Addition of the desired ketone, hexamethylacetone for **12** and cyclobutanone for **16**, to the solution yielded the oxide intermediate and finally the alcohol upon workup with ammonium chloride. Recrystallization afforded pure products with excellent yields: 65% for **12** and 68% for **16**.

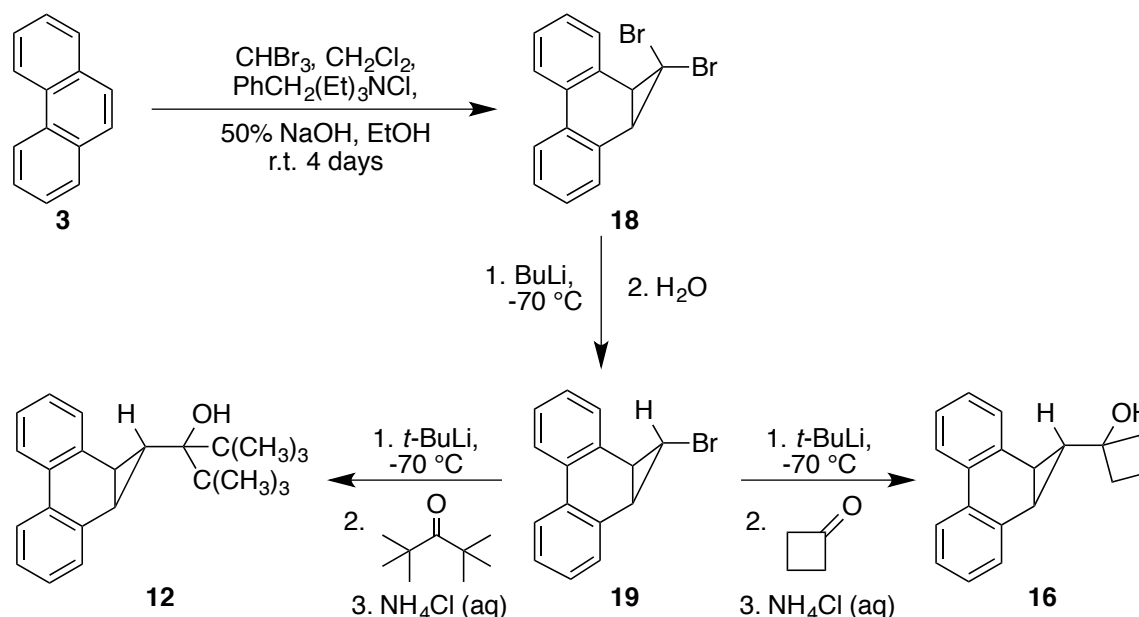


Figure 13. The synthetic routes to precursors **12** and **16**

As cyclopropanone is a gas, and therefore difficult to work with, a different synthetic route was needed for the synthesis of precursor **14** as compared to afore mentioned precursors. The synthetic route to **14** is shown in Figure 14. Instead of going through the di- and monobromo intermediates, this route relied on the use of an ethyl ester functional group. In the first step, **3** was cyclopropanated across the 9,10 double bond through the addition of ethyl diazoacetate with a catalytic amount of copper(II) sulfate to afford both the *exo*-ester, **20a**, and the *endo*-ester, **20b**. The copper is used in order to provide a surface that assists in the decomposition of the diazo compound into the carbene. The final step to make alcohol **14** was based on previous work known as the Kulnikovich reaction, separately transforming each isomer of ester **20a,b** into the corresponding cyclopropanol precursors, **14a,b**.¹⁸ Recrystallization afforded pure products with good yields, 63% for **14a** and 56% for **14b**. The identity of all precursors was primarily confirmed through GC/MS and NMR spectroscopy as well as the use of X-Ray crystallography.

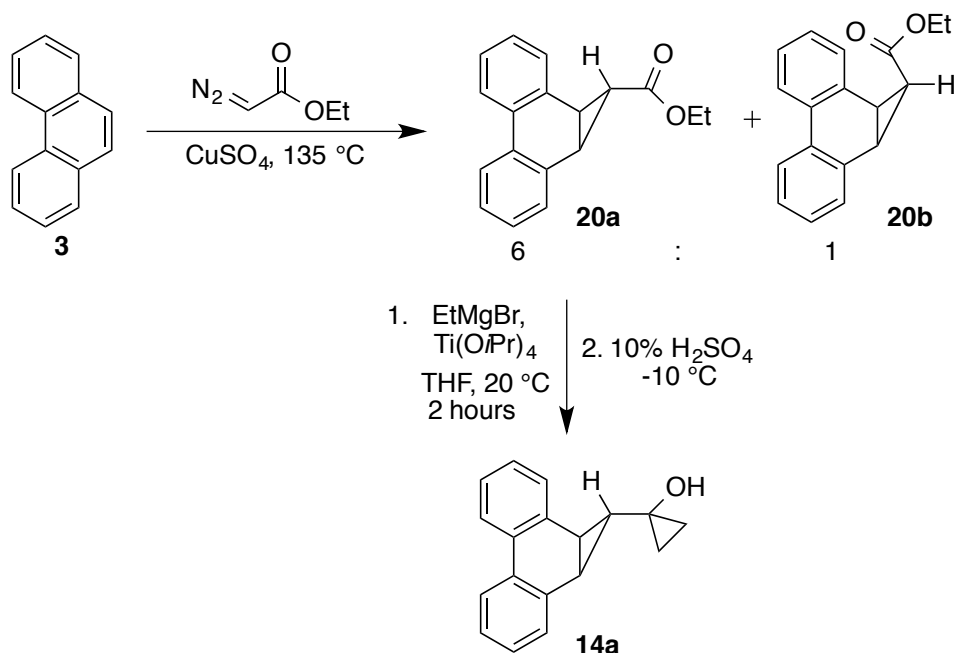


Figure 14. The synthetic route to precursor **14a**

2.2 Photochemical Generation and Implied Chemistry of Carbene **13**

Photolysis was performed on precursor **12** in benzene- d_6 to give rise to the β -hydroxy carbene, **13**. Photolysis was performed several times, initially on a small scale, such that it could be run in a glass NMR tube. This allowed for the monitoring of the progress of the photolysis through ^1H NMR scans every few hours until the starting material was consumed. The typical consumption time of the precursor was about 14-16 hours.

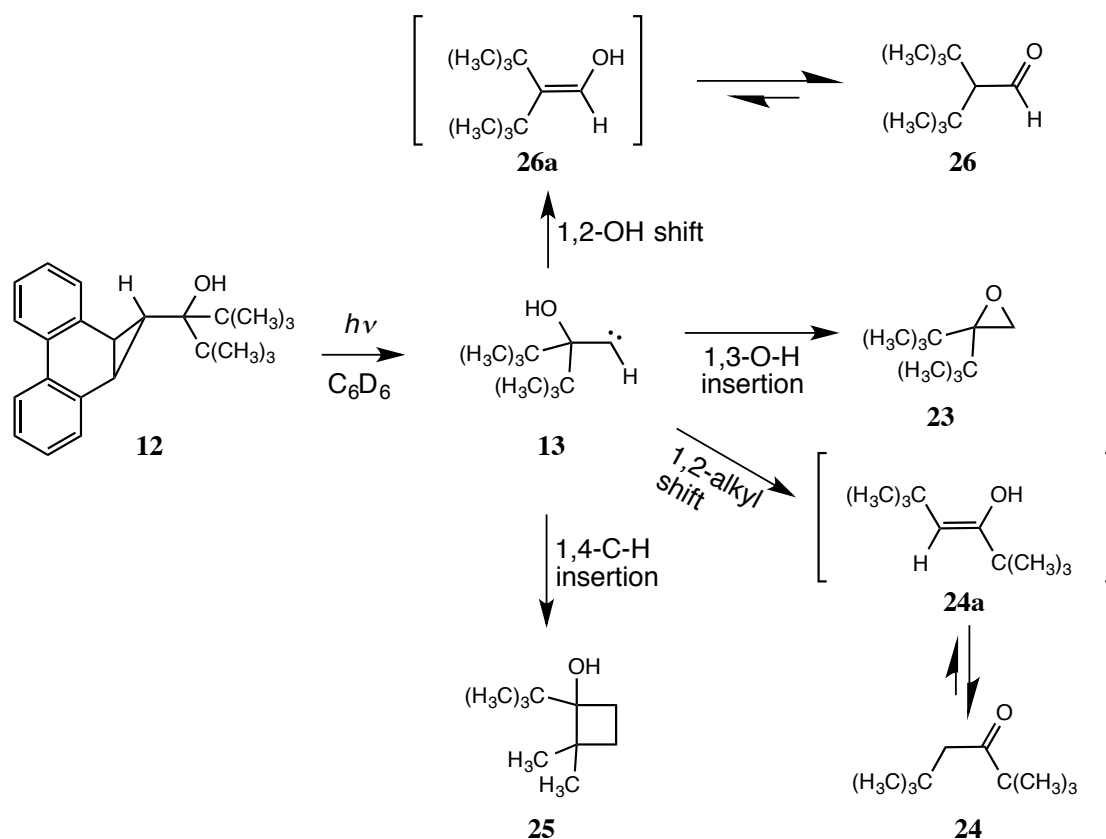


Figure 15. Photolysis of alcohol **12**

Four different possible intramolecular rearrangements were initially proposed which could occur to form products from this carbene (Figure 15). The post photolysis NMR showed no proton signals that would correspond to an aldehyde proton environment, thereby indicating that the carbene **13** was not undergoing an OH shift, resulting in the enol and finally aldehyde **26**. Further analysis of the photolysis products was conducted through GC/MS analysis. In order to compare both retention time and fragmentation patterns, authentic samples of both the epoxide **23** and ketone **24** were synthesized (Figure 16).¹⁹ GM/MS spectrum showed no evidence of the epoxide in solution but there was a peak, which corresponded to the ketone product. Currently there is still one partially unidentified peak, which is believed to correspond to the rearrangement that gives the cyclobutanol product **25**. This peak consistently has a higher abundance, giving indication that it is the major rearrangement product being formed.

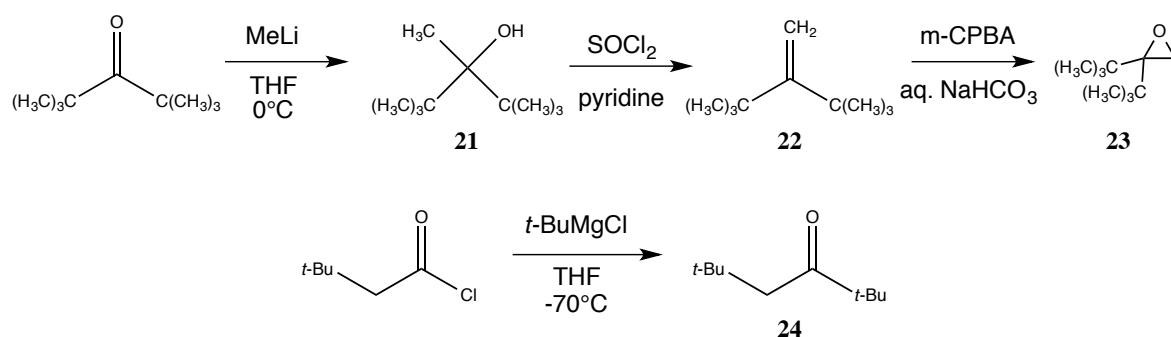


Figure 16. Synthesis of the authentic standards for epoxide **23** and ketone **24**

In comparison to the past work on 2-hydroxy-2-methylpropylidene **10**, it was not surprising that the OH shift resulting in the enol intermediate and aldehyde **26** was not observed, as it was found to have a much higher transition state barrier.^{9b} Similarly the evidence of the absence of epoxide **23** in solution is also consistent with those findings as the O-H bond is a much stronger and therefore more difficult bond to insert into as compared to the C-H bond, leading to a higher transition state barrier. The study on **10** showed that the alkyl shift leading to the ketone was the major rearrangement product over the C-H insertion leading to the cyclopropyl product. However, the experiments performed on carbene **13** show that now the C-H insertion product is the major product found in solution.

One possible cause for this result is that even though the hydroxy group is still able to help stabilize the partial positive charge on the β -carbon during the transition state, the nature of the alkyl group directly affects these trends. It is possible that by replacing the methyl groups in **10** with *tert*-butyl groups, the alkyl shift becomes less stable due to the migration of a 3° carbanion, which is much less stable than the 1° methyl carbanion. Additionally, while there are only 6 different possible C-H bonds to insert into in **10**, carbene **13** had 18 different insertion opportunities. Therefore, the statistical possibility of one of these insertions taking place is much more likely with this carbene. Lastly, while the C-H insertion in **10** leads to a strained

cyclopropyl product, the C-H insertions in **13** leads to a slightly less strained cyclobutyl produce, again possibly explaining why the C-H insertion might be a favored rearrangement over the alkyl shift.

The chemical analysis of carbene **13** was complicated due to the presence of a second unexpected product upon photolysis. Instead of generating only the desired carbene, photolysis of **12** also afforded the radical products **31a** and **31b**. Radical **31b** then was able to rearrange into hexamethylacetone **32** and 2,2,4,4-tetramethylpentan-3-ol **33** (Figure 17). The rearrangement of radical **31a** is still under investigation; however, the initial spectrum shows the formation of an alkene, indicating a possible ring expansion or opening from **31a**. While the radical products do not directly affect the carbene, their generation consumes a considerable amount of the starting material, lowering the yield of the carbene and its rearrangement products. Additionally, their presence in solution complicates the use of different spectroscopy and separation techniques, which would be used to identify and characterize the carbene rearrangement products.

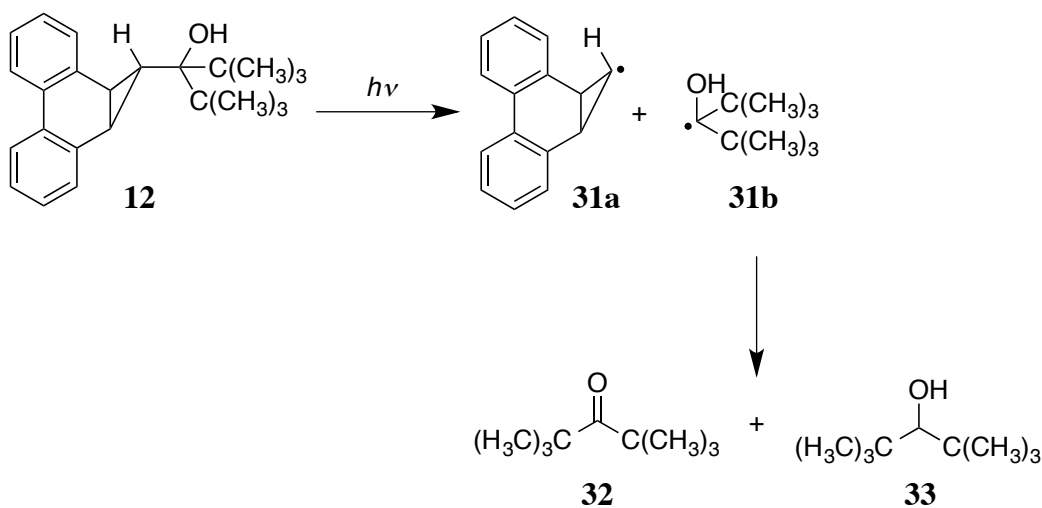


Figure 17. Radical formation and products upon photolysis of precursor **12**

2.3 Photochemical Generation and Implied Chemistry of Carbenes **15** and **17**

Photolysis was performed on precursors **14a** and **16** in order to yield the two cyclic β -hydroxy carbenes, **15** and **17**. As before, photolysis was performed on a small scale, such that it could be conducted in an NMR tube. This allowed for the monitoring of the progress of the photolysis through ^1H NMR scans every few hours until the starting material was consumed. The typical consumption time of the precursor was about 1-3 hours.

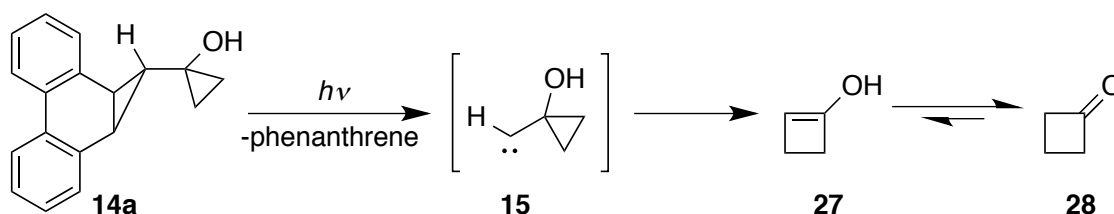


Figure 18. Photolysis of alcohol **14a**

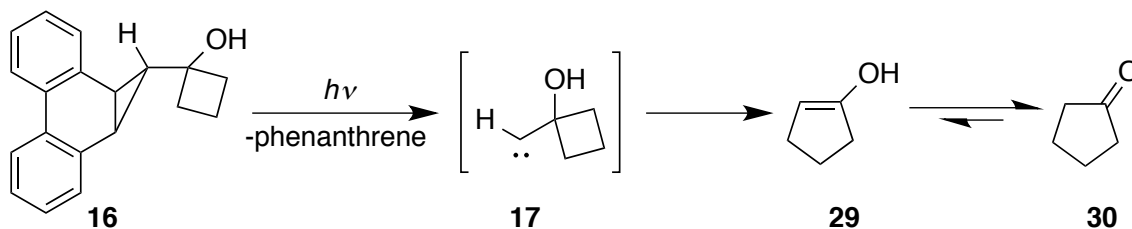


Figure 19. Photolysis of alcohol **16**

Unlike the study of **13**, it was felt that only the alkyl shift, resulting in a ring expansion, would be the observed intramolecular rearrangement product. The stabilization of the ring expansion, along with the combination that other bond insertions would afford highly strained bicyclic systems, suggests that the ring expansion to the enol intermediate would be the overwhelmingly favored rearrangement. Using commercially available standards of both **28** and **30**, NMR spectroscopy of the precursors, both pre- and post-photolysis, showed that the ketones resulting from the ring expansion were, in fact, the major products generated in solution (Figures 20 and 21). For the photolysis experiments of both precursors, albeit more significant in the photolysis of **14a**, there are two additional singlet peaks in the post photolysis ^1H NMR, the first

centered at 0.3 ppm and the second between 3 and 3.5 ppm. At this time it is uncertain whether these peaks are a direct result of the photolysis and subsequent rearrangements of the carbenes or rather if some secondary photolysis product or reaction is taking place. Future work will aim to fully identify the source of these peaks.

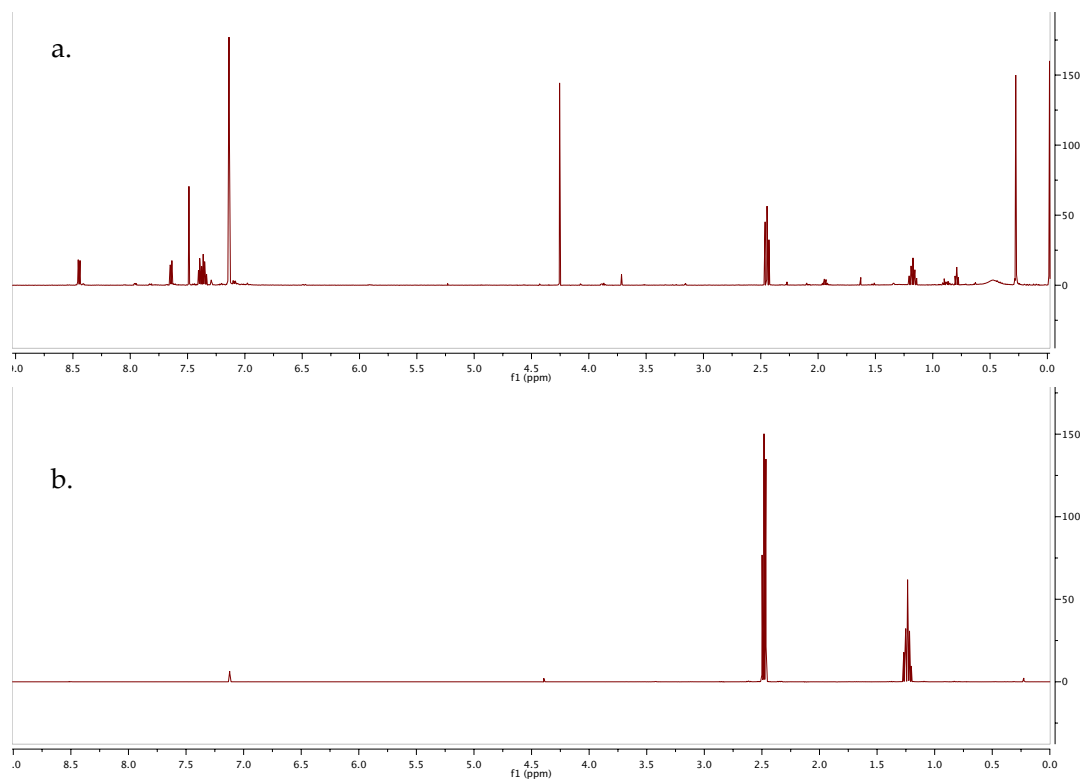


Figure 20. ^1H NMR of **14a** following 1 hour of photolysis (a) compared to an authentic standard of cyclobutanone **28** (b)

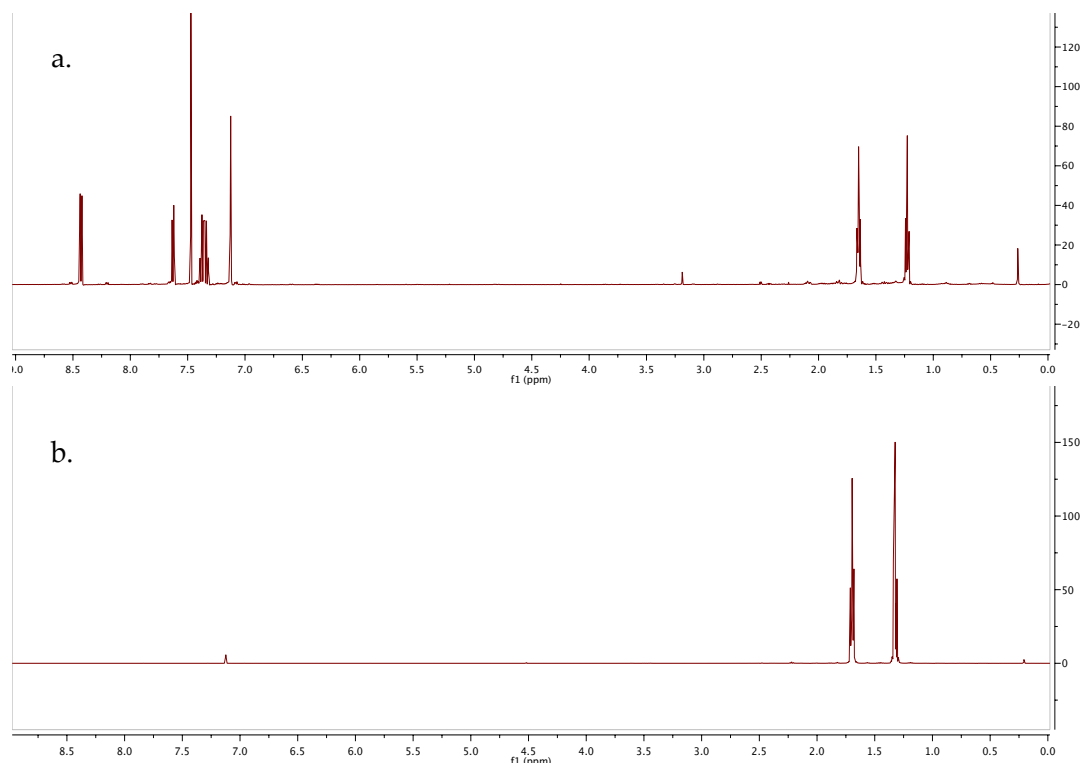


Figure 21. ^1H NMR of **16** following 2 hours of photolysis (a) compared to an authentic standard of cyclopentanone **30** (b)

In addition to solution-based experiments, the cyclic carbenes are also under investigation using matrix isolation spectroscopy. This work was performed in Professor Dr. Wolfram Sander's laboratory at the Ruhr-Universität, Bochum under the supervision of Joel Mieres Perez and Enrique Mendez Vega. Endo alcohol **14b** was deposited on the matrix window in an Argon matrix and cooled to 8K in an effort to isolate and study the rearrangement intermediates. Figure 22 depicts the difference spectrum of the matrix post photolysis (bottom) as well as the computed vibrational spectrum of various molecules thought to be in the matrix (top). The spectrum indicates that there is a large amount of cyclobutenol **27** in the matrix as well as evidence of cyclobutanone **28**. Work is still being done in order to identify the peak around 2100 cm^{-1} . Absorbance in this area of the spectrum possibly indicates the presence of a ketene. However the intensity of this peak is surprising as it has a much higher intensity than the other observed rearrangement products. Interestingly, this peak could correspond to the same unknown

peak that was observed in the post-photolysis ^1H NMR. Repeated experiments are still needed in order to both confirm the legitimacy and identity of this peak. At this time, matrix experiments are still to be performed on the cyclobutanol precursor **16**.

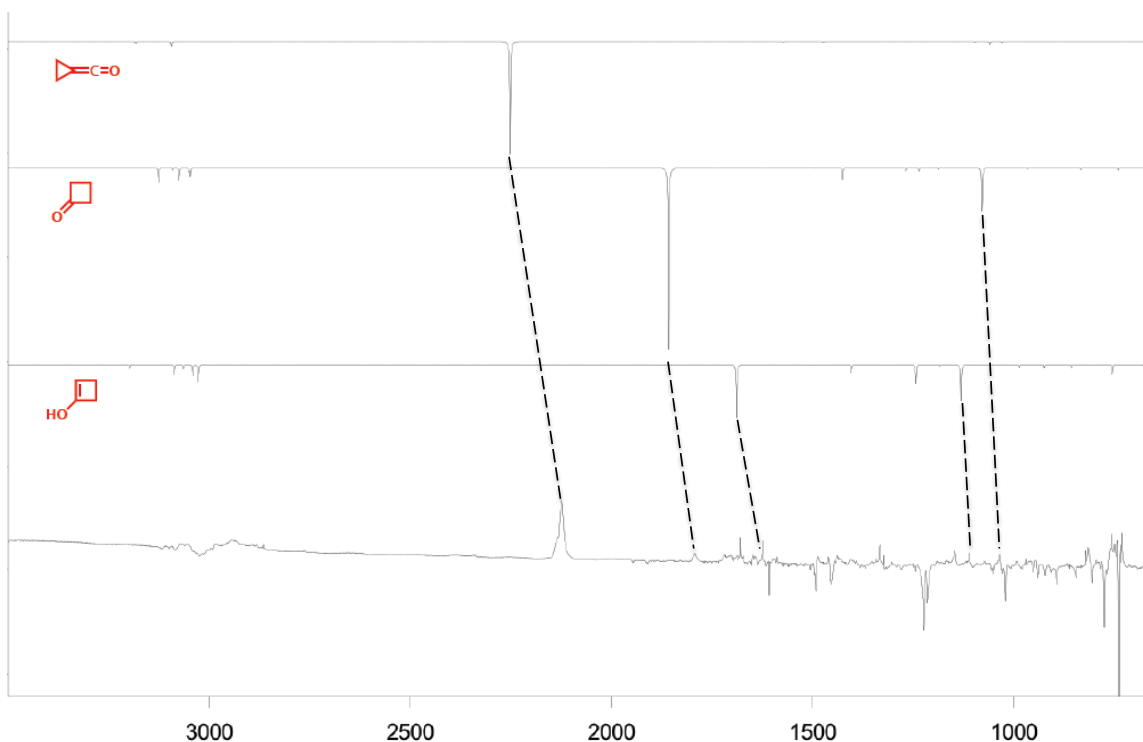


Figure 22. IR difference spectrum of Ar matrix at 8K, post photolysis of precursor **14b**, as compared to computed vibrational spectrum

2.4 Computational Studies

Geometry optimizations of bis(*tert*)-butanol carbene **13** were performed on both its singlet and triplet forms were performed at a density functional theory level of calculation. Both carbene states were found to have two different minimum energy conformations, specifically one local and one global minima (Table 1). These conformations differ by the $\text{C}\alpha\text{-C}\beta\text{-O-H}$ dihedral angle. For comparison, the energy of all calculations is reported as relative to the lowest conformation of the singlet state carbene.

Carbene Spin State	C α -C β -O-H Dihedral Angle	Relative Energy (kcal/mol)
Singlet	180	0
	30	0.262
Triplet	45	-2.201
	180	0.274

Table 1. Relative energies of the conformations of carbene **13** due to the varying of the C α -C β -O-H dihedral angle

ΔE_{rxn} and transition state energies between the singlet carbene and its intramolecular rearrangement products were also calculated at a DFT level of theory (Figure 23). As a result of the conservation of spin, the carbene is initially generated as a singlet and it is assumed that it will undergo rearrangements quicker than a change of spin state. Therefore, the energies from the transition state calculations were all made relative to the singlet state of carbene **13** with a dihedral angle of 180°. The natures of the calculated transition states were confirmed by the presence of a single imaginary frequency as well as through subsequent intrinsic reaction coordinate (IRC) calculations.²⁰ It should also be noted that the transition state for the O-H insertion, resulting in epoxide **23** was able to be calculated from the singlet carbene with a dihedral angle of 30°, while all of the others used the 180° dihedral conformation. One possible explanation for this conformation could be from the necessary orbital alignment needed for the insertion.

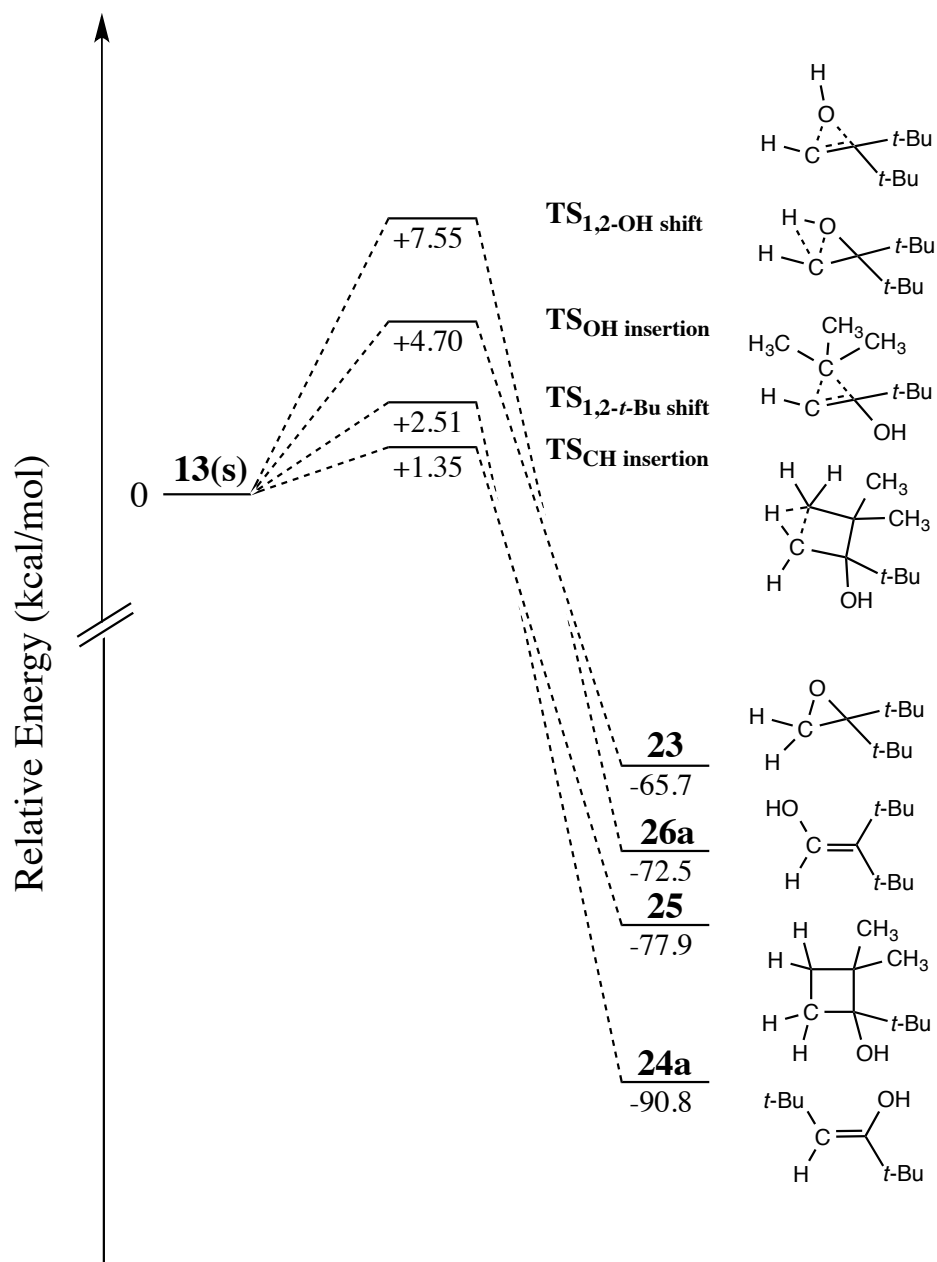


Figure 23. Summary of computational results for intramolecular rearrangements of **13**

As depicted in Figure 23, the calculations are in agreement with the experimental results from the photolysis, NMR, and GC/MS experiments. The kinetically favored C-H insertion, which results in cyclobutanol **25**, was the apparent major product formed from the carbene, followed by the alkyl shift resulting in ketone **24**. **25** is the kinetically favored product as it has the lowest activation energy towards the formation of the product. Contrary to previous work^{9b},

the alkyl shift requires a higher activation energy than that of the C-H insertion. This is likely a result from having the alkyl group be a 3° carbon, whereas the previous study had a methyl group migration. Since the transition state goes through a partial carbanion, we would therefore expect the 3° carbanion to be less stable than the 1° methyl carbanion. Similarly, the other two rearrangement products giving epoxide **23** and aldehyde **26** had significantly higher transition state barriers. As these two products were not found in solution, this provides further evidence that these two rearrangements were not formed.

Minimized structures for the carbene conformations and rearrangement products, as well as the calculated transition states are presented in Appendix B. DFT calculations perform exceptionally well, with a much lower computational cost than traditional ab initio methods, for finding local minima, providing accurate molecular structures and vibrational calculations. However, when comparing the relative energies of larger-scale systems, the DFT calculated values tend to be poor, with large error bars.²¹ For that reason, coupled cluster calculations will be used in order to obtain more accurate energies for these structures and transition states. At this time, work is still being done to obtain these single point energy values.

It was originally intended to perform similar ΔE_{rxn} and transition state for the two cyclic carbenes, **15** and **17**. While the triplet state of the carbenes could be calculated, the singlet state geometries were unable to be obtained, even at lower levels of computation. For both species, the result of geometry optimization calculations resulted in the ring expansion to the enol. While not explicitly giving any results on the intramolecular rearrangements of the carbenes, this does help indicate that the ring expansion would be the major rearrangement product.

Conclusions

3.1 Final Remarks

The three β -hydroxy carbenes, bis(*tert*)-butanol **13**, cyclopropanol **15**, and cyclobutanol **17**, have been generated for the first time through the photolysis of their respective phenanthrene-derived precursors. For bis(*tert*)-butanol carbene **13**, NMR and GC/MS studies suggest that the major intramolecular rearrangement is cyclobutanol **25**, resulting from a C-H insertion, followed by the alkyl shift resulting in ketone **24**. The O-H insertion and OH shift products were not observed. Geometry optimizations were performed on the singlet and triplet state of **13** as well as the transition states to the products from the singlet species. The computed results supported the solution-based experiments as it was found that the C-H insertion and alkyl shift transition states had a significantly lower energy barrier compared to the other two rearrangements (see Figure 23). The nature of stationary points was verified by frequency calculation on the optimized structure. The photolysis of precursor **12** additionally generated the radicals: **31a** and **31b**, along with carbene **13**. While rearrangement products of **31b** have been identified through GC/MS, work is still being done in order to identify the rearranged phenanthrene-based system resulting from **31a**.

For carbenes **15** and **17**, NMR studies of the photolysis indicate that the ring expansion resulting in the cyclic ketones **28** and **30** are the major products of the photolysis. Additionally, matrix isolation spectroscopy of **15** further shows that the ring expansion is taking place, as evidence from the IR spectrum of the intermediate enol **27** as well as ketone **28**.

3.2 Future Work

Future work on bis(*tert*)-butanol carbene **13** will focus on the quantitative analysis of the photolysis products as well as the synthesis of an authentic standard of cyclobutanol **25**.

Quantitative analysis would also provide a more in-depth insight as to the nature of the rearrangement pathways as well the ability to have a more comprehensive comparison to the computed energies. In addition, the coupled cluster single point energy calculations could also provide more accurate transition state energy barriers for each rearrangement.

For the two cyclic β -hydroxy carbenes, cyclopropanol **15** and cyclobutanol **17**, further work will be done in order to identify the two unidentified peaks on the NMR spectra. Computational studies will help investigate the nature of their rearrangements. Furthermore, work using matrix isolation spectroscopy will help isolate and study the rearrangement intermediates. Lastly, in collaboration with Professor Hadad's laboratory at the Ohio State University, experiments will be performed using laser flash photolysis with pico-second time resolved IR. These experiments will be used to measure the kinetics of the ring expansion rearrangement pathways.

Experimental

4.1 General Comments

All reactions requiring anhydrous conditions were carried out under an inert argon atmosphere in oven-dried glassware. Tetrahydrofuran was dried through two columns (2 ft × 4 in.) of activated alumina. All other solvents and reagents were used as obtained from commercial sources.

NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C in the indicated solvents using an Agilent 500 MHz NMR. The shifts are reported in δ ppm and referenced to either tetramethylsilane (TMS) or the residual proton signal from the solvent. Column chromatography was performed using a Teledyne ISCO Combiflash Rf 200 instrument with preppacked HP Silica columns. Gas chromatography-mass spectrometry (GC/MS) analysis was performed on an Agilent Technologies dual inert MSD and GC System instrument. GC/MS data were obtained with a capillary gas chromatograph interfaced with a quadrupole, triple-axis mass selective detector operating in the electron impact (EI) mode. Infrared spectra were obtained using a Perkin Elmer Spectrum One FT-IR Spectrometer.

4.2 Synthesis

Preparation of 1,1-Dibromo-1a,9b-dihydro-1H-cyclopropa[*l*]phenanthrene (18). As described in a previously published procedure¹⁷, phenanthrene **3** (35.6 g, 0.2 mol), benzyltriethylammoniumchloride (0.5 g, 0.002 mol), CH_2Cl_2 (40 mL), CHBr_3 (40 mL, 116 g, 0.46 mol), and EtOH (1 mL) were added to a 500 mL Erlenmeyer flask. The resulting mixture was stirred with a magnetic stir bar. Once the mixture was dissolved, 50% aq. NaOH (80 mL) was slowly added in small portions over about 20 minutes. The reaction mixture was loosely stoppered and was left to stir for 4 days at r.t. The resulting thick, dark brown mixture was

poured into a 500 mL separatory funnel. The reaction flask was washed with CH_2Cl_2 (100 mL) and H_2O (100 mL), which was added to the separatory funnel. Following shaking, the aqueous layer was separated from a suspension of the product in CH_2Cl_2 . The aqueous layer was extracted with CH_2Cl_2 (2×50 mL) and the extracts were combined with the organic, product suspension. Following the extraction, the combined suspension was washed sequentially with 2M HCl (2×100 mL), H_2O , (2×100 mL), and brine (1×100 mL). The resulting suspension was filtered twice using vacuum filtration and afforded the product as a light brown solid. The final product, a white solid, was recrystallized from CHCl_3 and filtered with carbon black. Solvent was stripped from the filtrate and this was repeated for a second crop of product. Yield: 23%; mp 110-111 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, $J = 7.9, 1.2$ Hz, 2H), 7.50 (dd, $J = 7.5, 1.4$ Hz, 2H), 7.45 - 7.38 (m, 2H), 7.37 - 7.30 (m, 2H), 3.51 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 211.7, 211.4, 176.7, 176.5, 142.2, 141.90, 141.7, 129.5, 123.0, 107.3, 107.1, 77.2, 77.0, 76.7, 37.4, 30.8.

Preparation of 1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (19). Under an argon atmosphere, dibromo phenanthrene **18** (10.44 g, 30 mmol) was suspended in 150 mL dry THF and cooled to -70 °C using a dry ice/acetone bath. Once cooled, *tert*-butyllithium (40 mL, 68 mmol) was added drop wise over 45 minutes, keeping the temperature below -65 °C. The resulting dark green reaction mixture was left to stir at -70 °C for 1 hr. H_2O (25 mL) was then slowly added to the mixture over 5 min, quenching the reaction. The resulting solution was then left to stir for 4 hrs., slowly warming to room temperature. Once at room temperature, the mixture was poured into a 500 mL separatory funnel and the round bottom flask was rinsed with Et_2O (10 mL) and H_2O (10 mL). The rinses were added to the separatory funnel and the aqueous layer was separated from the organic suspension of the product. The aqueous layer was then

extracted with Et₂O (2 × 50 mL) and the extracts were combined with the organic suspension. The suspension was washed sequentially with H₂O (2 × 50 mL) and brine (1 × 50 mL). After stripping the solvent from the organic layer, the resulting yellow solid was recrystallized in Hexanes with a carbon black filter, yielding the white product. Solvent was stripped from the filtrate and this was repeated for a second crop of product. Yield: 48%; mp 109-114 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.96 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.50 (dd, *J* = 6.9, 2.0 Hz, 2H), 7.38 - 7.25 (m, 5H), 3.02 (d, *J* = 3.1 Hz, 2H), 2.43 (t, *J* = 3.1 Hz, 1H).

Preparation of 3-(1a,9b-dihydro-1H-cyclopropa[*l*]phenanthren-1-yl)-2,2,4,4-tetramethylpentan-3-ol (12). Under an argon atmosphere, monobromo phenanthrene **19** (2.71 g, 10 mmol) was suspended in 100 mL dry THF and cooled to -70 °C using a dry ice/acetone bath. Once cooled, *tert*-butyllithium (13 mL, 22 mmol) was added drop wise over 10 minutes, keeping the temperature below -65 °C. The resulting dark green reaction mixture was left to stir at -70 °C for 1 hr. Hexamethylacetone (1.57 g, 11 mmol) was then added to the reaction mixture, which was then left to stir for an additional hour at -70 °C. The solution was then left to stir for 3 hours, slowly warming to room temperature, upon which the reaction was quenched with the addition of saturated NH₄Cl (25 mL). The resulting mixture was poured into a separatory funnel and the reaction flask was rinsed with Et₂O (10 mL) and H₂O (10 mL). The rinses were added to the separatory funnel and the aqueous layer was separated from the organic suspension of the product. The aqueous layer was then extracted with Et₂O (2 × 25 mL) and the extracts were combined with the organic suspension. The suspension was washed sequentially with H₂O (2 × 25 mL) and brine (1 × 25 mL). The solvent was stripped, resulting in 3.5 g of the crude, yellow product. The resulting solid was dissolved purified using a 40g silica gel column using a gradient of hexanes and ethyl acetate. Combination of the pure fractions yielded the pure, white product.

Yield: 65%; mp 144-148 °C; ^1H NMR (500 MHz, C_6D_6) δ 7.84 (dd, $J = 7.2, 2.0$ Hz, 2H), 7.39 - 7.34 (m, 2H), 7.15 - 7.05 (m, 4H), 2.62 (d, $J = 5.0$ Hz, 2H), 1.33 - 1.20 (m, 1H), 0.97 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 128.9, 127.9, 127.8, 127.6, 127.4, 123.4, 77.9, 33.2, 29.4, 23.3.

Preparation of ethyl 1a,9b-dihydro-1H-cyclopropa[*l*]phenanthrene-1-carboxylate (20a-b). Under an argon atmosphere, phenanthrene **3** (17.82 g, 100 mmol) and copper sulfate (487 mg, 3 mmol) were heated to 135 °C, melting **3** into a brown liquid, whereupon ethyldiazoacetate (15 g, 114 mmol) was slowly added drop wise to the mixture. Once added, the solution was left to stir for an additional hour at 135 °C and then left to cool to room temperature overnight, producing a grey solid. The solid was then dissolved in CH_2Cl_2 (75 mL) and filtered to remove residual CuSO_4 . Stripping the solvent yielded 26.2 g of crude solid. The solid was recrystallized in absolute EtOH repeatedly as to remove as much phenanthrene as possible. The remaining product mixture was chromatographed on a silica column using a gradient of hexanes and ethyl acetate. The product esters were efficiently separated from each other and the phenanthrene. The *exo* to *endo* ratio was approximately 6:1, with an overall yield of 22%. For *exo*-ester **20a**: mp 135-142 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.01 (dd, $J = 7.6, 1.5$ Hz, 2H), 7.51 (dd, $J = 7.3, 1.7$ Hz, 2H), 7.38 - 7.26 (m, 4H), 4.27 - 4.16 (m, 2H), 3.22 (d, $J = 3.9$ Hz, 2H), 1.35 - 1.18 (m, 4H), 1.07 (s, 1H). For *endo*-ester **20b**: mp 131-140 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (dd, $J = 8.0, 1.3$ Hz, 2H), 7.57 - 7.24 (m, 6H), 4.31 - 4.14 (m, 1H), 3.71 (q, $J = 7.1$ Hz, 2H), 3.13 (d, $J = 8.9$ Hz, 2H), 2.31 (t, $J = 9.0$ Hz, 1H), 1.38 - 1.19 (m, 2H), 0.85 (s, 3H).

Preparation of *exo*-1-(1a,9b-dihydro-1H-cyclopropa[*l*]phenanthren-1-yl)cyclopropan-1-ol (14a). Under an argon atmosphere, ethylmagnesium bromide (3.0 mL, 3.0 M in Et_2O , 9 mmol) was added drop wise by syringe to a magnetically stirred solution of *exo*-ester **20a** (1.06 g, 4.0 mmol) and titanium tetrakisopropoxide (237 μL , 0.8 mmol, 20 mol %) in

anhydrous THF (20 mL). The temperature was maintained between 22 and 30 °C with a water bath. Stirring was continued at room temperature for an additional 30 min after the completion of the addition. The dark green reaction mixture was then cooled to -5 °C using an acetone/dry ice bath and was then quenched by the dropwise addition of 10% aqueous sulfuric acid (40 mL), forming a white precipitate. During the addition, the temperature was maintained between -10 and 0 °C. The reaction mixture was stirred at 0 °C for an additional hour, maintaining temperature with an ice bath. After warming to room temperature, the organic and aqueous layers were separated, and the latter was extracted with diethyl ether (2 × 20 mL). The organic layers were combined, washed with saturated sodium bicarbonate (2 × 20 mL), and freed of solvent. The final product, a white solid, was recrystallized from a solution of hexanes and ethyl acetate. Yield: 63%; mp 155.0 – 173.6 °C; ¹H NMR (500 MHz, CDCl₃) δ = 8.01 – 7.95 (m, 2H), 7.40 (dd, *J* = 5.0, 2.2 Hz, 2H), 7.31 – 7.22 (m, 4H), 2.50 (d, *J* = 4.4 Hz, 2H), 1.99 (s, 1H), 1.56 (s, 1H), 0.92 – 0.86 (m, 2H), 0.77 – 0.72 (m, 1H), 0.67 – 0.60 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 134.9, 129.4, 128.8, 127.7, 126.1, 123.1, 56.0, 30.9, 24.5, 12.7; FTIR (KBr pellet) ν 3315, 3018, 3002, 1488, 1451, 1213, 1009, 929, 765, 734 cm⁻¹.

Preparation of *endo*-1-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)cyclopropan-1-ol (14b). Under an argon atmosphere, ethylmagnesium bromide (2.2 mL, 3.0 M in Et₂O, 6.6 mmol) was added drop wise by syringe to a magnetically stirred solution of *endo*-ester **20b** (793 mg, 3.0 mmol) and titanium tetraisopropoxide (178 μL, 0.6 mmol, 20 mol %) in anhydrous THF (15 mL). The temperature was maintained between 22 and 30 °C with a water bath. Stirring was continued at room temperature for an additional 30 min after the completion of the addition. The dark green reaction mixture was then cooled to -5 °C using an acetone/dry ice bath and was then quenched by the dropwise addition of 10% aqueous sulfuric acid (25 mL),

forming a white precipitate. During the addition, the temperature was maintained between -10 and 0 °C. The reaction mixture was stirred at 0 °C for an additional hour, maintaining temperature with an ice bath. After warming to room temperature, the organic and aqueous layers were separated, and the latter was extracted with diethyl ether (2 × 20 mL). The organic layers were combined, washed with saturated sodium bicarbonate (2 × 20 mL), and freed of solvent. The final product, a white solid, was recrystallized from ethanol. Yield: 56%; mp 127-129 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.32 (dt, *J* = 22.6, 7.1 Hz, 5H), 2.81 (d, *J* = 9.2 Hz, 2H), 2.20 (t, *J* = 9.1 Hz, 1H), 1.45 (s, 1H), 0.21 (q, *J* = 5.0 Hz, 2H), 0.09 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 132.3, 131.5, 130.1, 128.0, 126.7, 122.9, 77.3, 77.1, 77.0, 76.7, 53.2, 20.45, 15.7.

Preparation of 1-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)cyclobutan-1-ol (16). Under an argon atmosphere, monobromo phenanthrene **19** (2.71 g, 10 mmol) was suspended in 100 mL dry THF and cooled to -70 °C using a dry ice/acetone bath. Once cooled, *tert*-butyllithium (13 mL, 22 mmol) was added drop wise over 10 minutes, keeping the temperature below -65 °C. The resulting dark green reaction mixture was left to stir at -70 °C for 1 hr. Cyclobutanone (0.9 mL, 13.7 mmol) was then added to the reaction mixture, which was then left to stir for an additional 45 minutes at -70 °C. The solution was then left to stir, slowly warming to room temperature, upon which the reaction was quenched with the addition of saturated, aqueous NH₄Cl (25 mL). The resulting mixture was poured into a separatory funnel and the reaction flask was rinsed with Et₂O (10 mL) and H₂O (10 mL). The rinses were added to the separatory funnel and the aqueous layer was separated from the organic suspension of the product. The aqueous layer was then extracted with Et₂O (2 × 25 mL) and the extracts were combined with the organic suspension. The suspension was washed sequentially with H₂O (2 ×

25 mL) and brine (1 × 25 mL). The solvent was stripped, resulting in the crude, yellow product. The resulting solid was recrystallized in a solution of Hexanes and ethyl acetate, affording the white, solid product. Solvent was stripped from the filtrate and this was repeated for a second crop of product. Yield: 68%; mp 126-130 °C; ¹H NMR (500 MHz, C₆D₆) δ 7.87 - 7.79 (m, 2H), 7.27 - 7.20 (m, 2H), 7.15 - 7.04 (m, 7H), 2.49 (d, *J* = 4.5 Hz, 2H), 1.88 - 1.74 (m, 4H), 1.46 (dtd, *J* = 11.5, 9.4, 4.6 Hz, 1H), 1.19 (dp, *J* = 11.3, 8.8 Hz, 1H), 1.02 (s, 1H), 0.46 (q, *J* = 5.9, 5.3 Hz, 1H); ¹³C NMR (125 MHz, C₆D₆) δ 128.8, 127.9, 127.8, 127.6, 127.4, 125.9, 123.2, 73.0, 35.9, 22.8, 12.0.

Preparation of 2,2,3,4,4-pentamethylpentan-3-ol (21). Under an argon atmosphere, hexamethylacetone (6.29 g, 44.2 mmol) was mixed in dry THF (100 mL) and cooled to 0 °C with an ice bath. Methyllithium (30 mL, 48 mmol) was added drop wise to the solution. The reaction mixture was left on the ice bath overnight, warming up to r.t. After quenching the reaction with H₂O (10 mL) the mixture was poured into a 250 mL separatory funnel and the aqueous layer was separated from the organic suspension of the product. The aqueous layer was then extracted with Et₂O (2 × 20 mL) and the extracts were combined with the organic suspension. The suspension was washed sequentially with H₂O (2 × 20 mL) and brine (1 × 20 mL). Stripping the majority of the solvent afforded 5.86 g of crude solid. Yield: 83.6 %

Preparation of 2,2,4,4-tetramethyl-3-methylenepentane (22). Under an argon atmosphere, alcohol **21** was suspended in dry pyridine (25 mL) and cooled to 0 °C with an ice bath. Once cooled, thionyl chloride (6.00 g, 50.8 mmol) was added drop wise and upon addition, the solution would smoke, indicating the creation of HCl gas and a brown solid formed, likely pyridine chloride salt. The reaction mixture was left overnight to warm up to room temperature. The reaction mixture was then quenched by pouring it over ice chips, upon which, the mixture

was poured into a separatory funnel. The aqueous layer was then extracted and the organic layer was washed with aqueous NaHCO_3 (1×40 mL) and diethyl ether (1×40 mL). The organic suspension was then washed sequentially with H_2O (2×40 mL) and brine (1×40 mL). Stripping the majority solvent yielded a yellow liquid. Yield: 117%.

Preparation of 2,2-di-*tert*-butyloxirane (23). Alkene **22** (1.5 g, 10.7 mmol) was suspended in a 5% aqueous sodium bicarbonate solution (60 mL) and cooled to 0°C with an ice bath. Once cooled, m-CPBA (4.00 g, 23.2 mmol) was added to the solution. Upon addition, the ice bath was removed and the solution was left to stir vigorously overnight. The organic and aqueous layers were separated, and the latter was extracted with diethyl ether (2×20 mL). The organic suspension was then washed sequentially with 10% NaOH (2×25 mL) and brine (1×25 mL). The organic layer was then dried over anhydrous sodium sulfate and partially stripped of solvent to yield the product solution.

Preparation of 2,2,5,5-tetramethylhexan-3-one (24). Under an argon atmosphere, *tert*-butyl acetyl chloride (1.08 g, 8.02 mmol) was suspended in dry THF (30 mL) and cooled to -70°C using a dry ice/acetone bath. Once cooled, *tert*-butyl Magnesium chloride (5 mL, 10 mmol) was slowly added to the reaction mixture. The resulting solution was left to stir overnight, warming to r.t. The mixture was then quenched with H_2O (10 mL) and after an initial separation, the aqueous layer was extracted with diethyl ether (2×20 mL) and the extracts were combined with the organic suspension. The suspension was washed sequentially with H_2O (2×20 mL) and brine (2×20 mL). After separation, the organic suspension was dried over anhydrous sodium sulfate and filtered. Upon GC-MS analysis only two compounds were present in solution, one of which indicated a mass of 156, expected to be the desired compound **24**. No further workup was performed as the solution of **24** was only used on GC-MS experiments.

4.3 Photolysis

Photolysis was performed at room temperature in a Rayonet photochemical reactor equipped with 16 12-inch 8W lamps with output centered at ~ 350 nm (range ~ 315 to 400 nm). The typical photolysis experiment followed the following procedure. The carbene precursor was weighed out and dissolved in benzene- d_6 . The amount of precursor used typically ranged from 10-15 mg and the solvent ranged from about 0.6 to 0.8 mL. The resulting solution was then placed into an NMR tube (glass) for the photolysis and an initial ^1H and ^{13}C spectra was taken. The photolysis was monitored, typically in hour intervals, by ^1H NMR, until it was deemed that no precursor remained. For precursor **12**, all starting material was consumed in about 14-16 hours, while for precursors **14** and **16**, all starting material was consumed in about 1-3 hours. Lastly, a final ^1H and ^{13}C NMR and GC/MS spectra were taken of the post-photolysis solution.

4.4 Computations

Geometry Optimizations

All geometry calculations were performed using Becke's three-parameter hybrid functional and the correlation functional of Lee, Yang, and Parr (B3LYP) as implemented in Gaussian 09.²² The 6-31+G(d,p) basis set was used for geometry optimization and vibrational frequency calculations. Scans of the dihedral angle $\text{C}\alpha\text{-C}\beta\text{-O-H}$ of the three carbenes were performed on carbenes **13**, **15**, and **17**. The scans were followed by geometry optimizations and frequency calculations of the lowest energy conformations as well as their corresponding intramolecular rearrangements.

Transition State Optimizations

For all calculated transition states, either QST2 or QST3 optimizations were used on the optimized singlet forms of carbenes **13**, **15**, and **17** and their corresponding rearrangement

intermediates with the B3LYP/6-31+G(d,p) method. Transition states were tested by a frequency calculation, which showed the corresponding imaginary normal mode.

Single Point Energy

For carbenes **15**, **17**, the intramolecular rearrangements, and the corresponding transition states, a single point energy calculation was made from the previously found optimizations using the CCSD(T)/cc-pVTZ method.²³ T1 diagnostic values were used in order to assess the accuracy of each calculation.

4.5 Matrix Isolation Spectroscopy

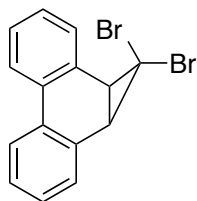
Matrix-isolation experiments were performed by standard techniques with an APD HC-4 closed-cycle helium compressor for cooling to 8 K. Precursors **14** and **16** were separately deposited in an argon matrix through an 8 cm quartz tube heated electrically with a tantalum wire. Infrared spectra in the range between 400 and 4000 cm^{-1} were recorded on FTIR spectrometers with 0.2 and 0.5 cm^{-1} resolutions. Broadband irradiation with 320 nm light was carried out with mercury high-pressure arc lamps in housings equipped with quartz optics and dichroic mirrors in combination with cutoff filters (50% transmission at the specified wavelength). Additionally, photolysis was ultimately performed on the matrix through the use of a 308 nm XeCl excimer laser.

References

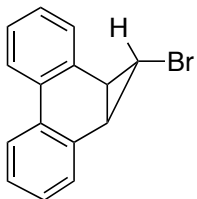
1. Wentrup, C., *Reactive Molecules*. John Wiley & Sons, Inc.: New York, 1984.
2. (a) Kirmse, W., *Carbene Chemistry*. Academic Press: New York 1964; Vol. 1; (b) Jones, M.; Fleming, S. A., *Organic Chemistry*. 4th ed.; W.W. Norton: New York, 2010.
3. Arkins, P.; Paula, J. d., *Physical Chemistry*. 7th ed.; W. H. Freeman and Company: New York, 2002.
4. (a) Chateaneuf, J. E.; Johnson, R. P.; Kirchhoff, M. M., Absolute kinetics of dichlorocarbene in solution. *J. Am. Chem. Soc.* **1990**, *112* (8), 3217–3218; (b) Tomioka, H., Approach to A Persistent Triplet Carbene. In *Carbene Chemistry* Bertrand, G., Ed. Marcel Dekker Inc.: New York, 2002.
5. Closs, G. L., Carbene. In *Encyclopedia Britannica*, Web.
6. (a) Platz, M. S., Observing Invisible Carbenes By Trapping Them with Pyridine. In *Carbene Chemistry* Bertrand, G., Ed. Marcel Dekker Inc.: New York, 2002; (b) Staudinger, H.; Kupfer, O., Preparation of Methylene Derivatives. *Ber.* **1911**, *44* (3), 2194–2197.
7. Jones, M., Carbenes. *Scientific American* 1976.
8. Richardson, D. B.; Durrett, L. R.; Martin, J. M., Jr.; Putnam, W. E.; Slaymaker, S. C.; Dvoretzky, I., Generation of methylene by photolysis of hydrocarbons. *J. Am. Chem. Soc.* **1965**, *87* (12), 2763-5.
9. (a) Moore, K. A.; Vidaurri-Martinez, J. S.; Thamattoor, D. M., The benzyldenecarbene-phenylacetylene rearrangement: an experimental and computational study. *J. Am. Chem. Soc.* **2012**, *134* (49), 20037-40; (b) Farlow, R. A.; Thamattoor, D. M.; Sunoj, R. B.; Hadad, C. M., Rearrangement Pathways of 2-Hydroxy-2-methylpropylidene: An Experimental and Computational Study. *J. Org. Chem.* **2002**, *67* (10), 3257-3265; (c) Graves, K. S.; Thamattoor, D. M.; Rablen, P. R., Experimental and theoretical study of the 2-alkoxyethylidene rearrangement. *J. Org. Chem.* **2011**, *76* (6), 1584-91; (d) Thamattoor, D. M.; Snoonian, J. R.; Sulzbach, H. M.; Hadad, C. M., Experimental and Theoretical Investigations of Ring-Expansion in 1-Methylcyclopropylcarbene. *J. Org. Chem.* **1999**, *64* (16), 5886–5895.
10. Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mullins, M.; Celebi, S.; Toscano, J. P., Lifetimes of alkyl- and dialkylcarbenes in solution. *Progress in Reaction Kinetics* **1994**, *19* (2), 93-137.
11. Sander, W., Matrix Isolation of Highly Electrophilic Carbenes. In *Carbene Chemistry* Bertrand, G., Ed. Marcel Dekker Inc.: New York, 2002.
12. (a) Sander, W.; Bucher, G.; Wierlacher, S., Carbenes in matrixes: spectroscopy, structure, and reactivity. *Chemical Reviews* **1993**, *93* (4), 1583-1621; (b) Dunkin, I. R., *Matrix-Isolation Techniques*. Oxford University Press: New York, 1998.
13. Woodworth, R. C.; Skell, P. S., Methylene, CH₂. Stereospecific reaction with cis- and trans-2-butene. *J. Am. Chem. Soc.* **1959**, *81*, 3383-6.
14. Skell, P. S.; Woodworth, R. C., Structure of Carbene, CH₂. *Journal of the American Chemical Society* **1956**, *78*, 4496-4497.
15. Kirmse, W.; Von Scholz, H. D.; Arold, H., Isotope effects on hydrogen displacement in alkylcarbenes. *Justus Liebigs Annalen der Chemie* **1968**, *711*, 22-30.
16. Ruck, R. T.; Jones, M., Solvent perturbs the reactivity of tert-butylcarbene. *Tetrahedron Letters* **1998**, *39* (16), 2277–2280.
17. Nguyen, J. M.; Thamattoor, D. M., A Simple Synthesis of 1,1-Dibromo-1a,9b-dihydrocyclopropa[1]phenanthrene. *Synthesis* **2007**, (14), 2093-2094.

18. (a) Meijere, A. d.; Seebach, M. v.; Kozhushkov, S. I.; Boese, R.; Bläser, D.; Cicchi, S.; Dimoulas, T.; Brandi, A., Cyclobutylidenecyclopropane: New Synthesis and Use in 1,3-Dipolar Cycloadditions 2 A Direct Route to Spirocyclopropane-Annulated Azepinone Derivatives. *Eur. J. Org. Chem.* **2001**, 2001 (20), 3789-3795; (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevski, D. A., Titanium(IV) Isopropoxide-Catalyzed Formation of 1-Substituted Cyclopropanols in the Reaction of Ethylmagnesium Bromide with Methyl Alkanecarboxylates. *Synthesis* **1991**, 1991 (3), 234.
19. De Kimpe, N.; Buyck, L. D.; Verhé, R.; Schamp, N., A unique and highly remarkable boron Trifluoride catalyzed rearrangement Of 2,2-di-t-butyloxirane into 2,2,3,3,4,4-hexamethyltetrahydrofuran. *Tetrahedron* **1984**, 40 (17), 3291-3294.
20. (a) Fukui, K., The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **1981**, 14 (12), 363-368; (b) Gonzalez, C.; Schlegel, H. B., Reaction path following in mass-weighted internal coordinates. *J. Phys. Chem.* **1990**, 94 (14), 5523-5527.
21. Peter R. Schreiner, Relative energy computations with approximate density functional theory - a caveat! *Angewandte Chemie, International Edition* **2007**, 46 (23), 4217-4219.
22. (a) Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics* **1993**, 98 (7), 5648-5652; (b) Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, 37 (2), 785-789; (c) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.
23. Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M., A fifth-order perturbation comparison of electron correlation theories. *Chemical Physics Letters* **1989**, 157 (6), 479-483.

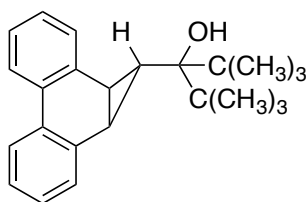
Appendix A: Spectral Data (NMR, GC/MS, IR, X-Ray Crystal Structure)



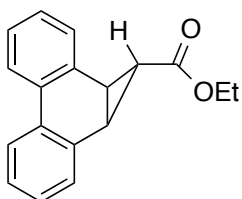
18 (^1H NMR, ^{13}C NMR)..... **41**



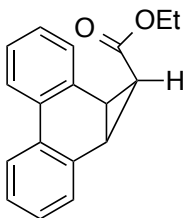
19 (^1H NMR, GC/MS)..... **42**



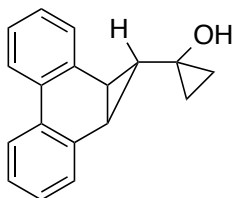
12 (^1H NMR, ^{13}C NMR, GC/MS, X-Ray Structure)..... **44**



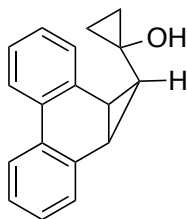
20a (^1H NMR, GC/MS)..... **47**



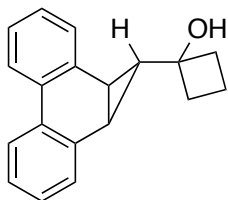
20b (^1H NMR, GC/MS)..... **49**



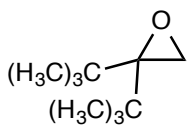
14a (^1H NMR, ^{13}C NMR, GC/MS, IR, X-Ray Structure)..... **51**



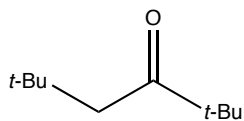
14b (^1H NMR, ^{13}C NMR, GC/MS)..... **55**



16 (^1H NMR, ^{13}C NMR, GC/MS,)..... **57**



23 (GC/MS)..... **59**



24 (GC/MS)..... **60**

Photolysis Products

Photolysis of **12** (^1H NMR, ^{13}C NMR, GC/MS)..... **61**

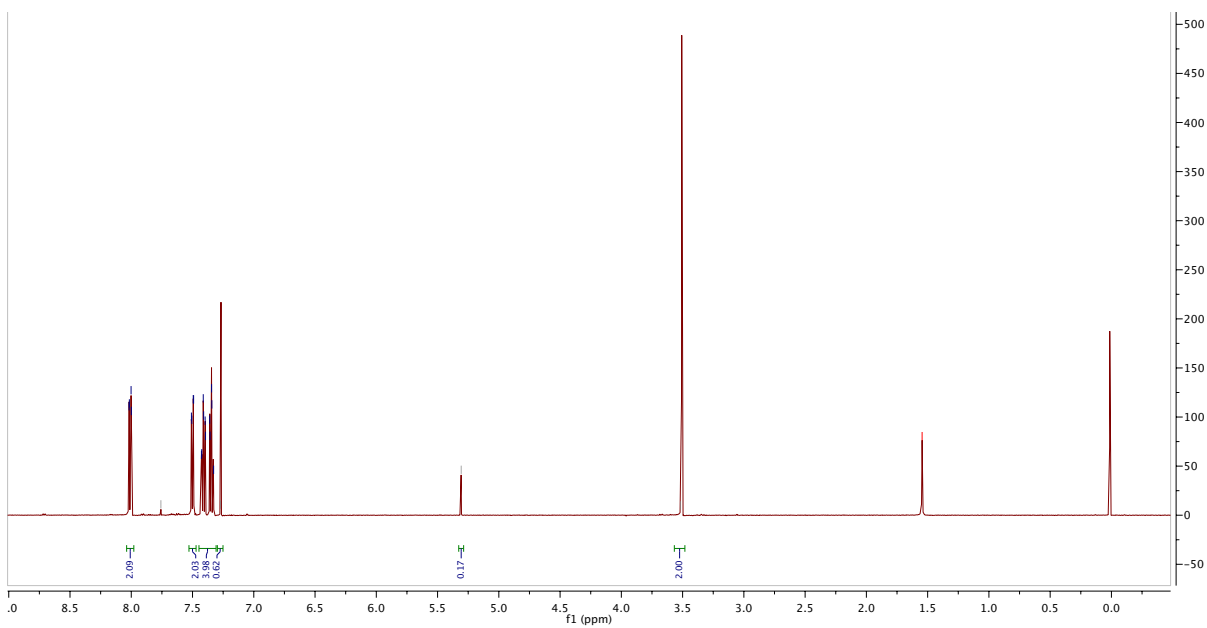
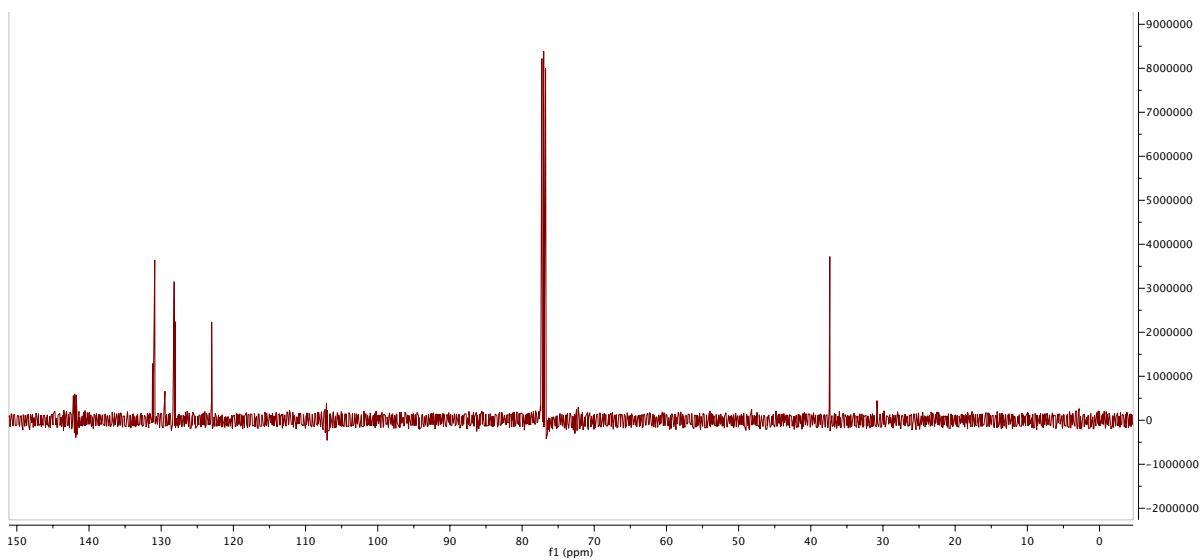
Photolysis of **14a** (^1H NMR)..... **68**

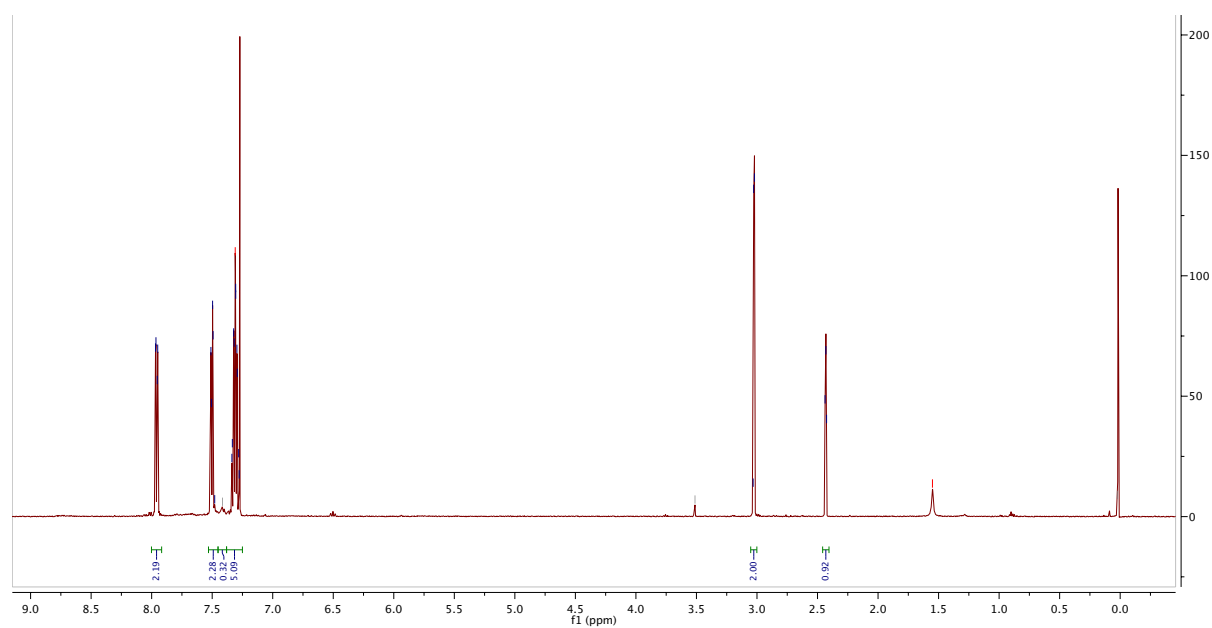
Photolysis of **16** (^1H NMR, ^{13}C NMR)..... **69**

Commercial Standards

Cyclobutanone **28** (^1H NMR)..... **70**

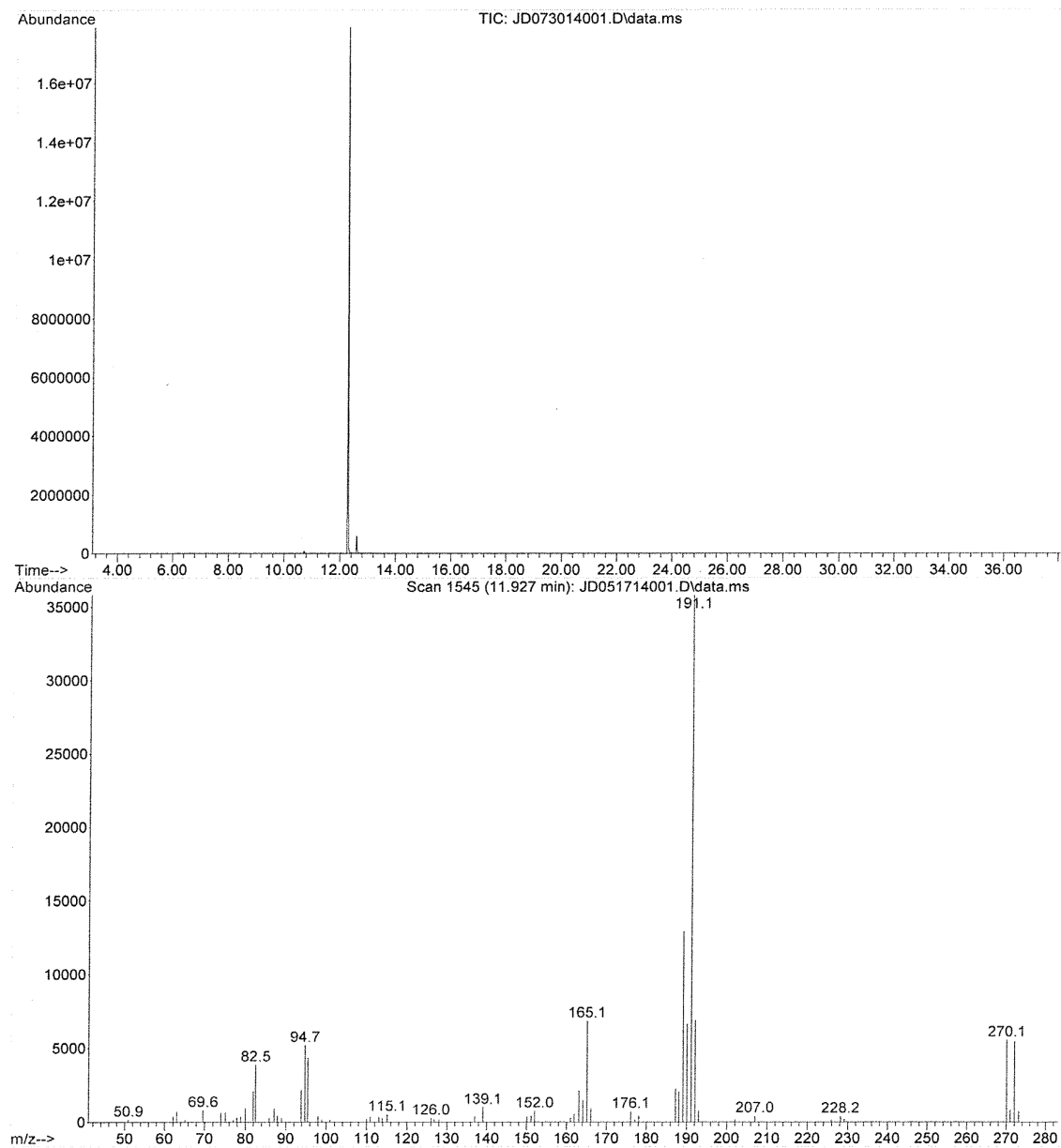
Cyclopentanone **30** (^1H NMR, ^{13}C NMR)..... **71**

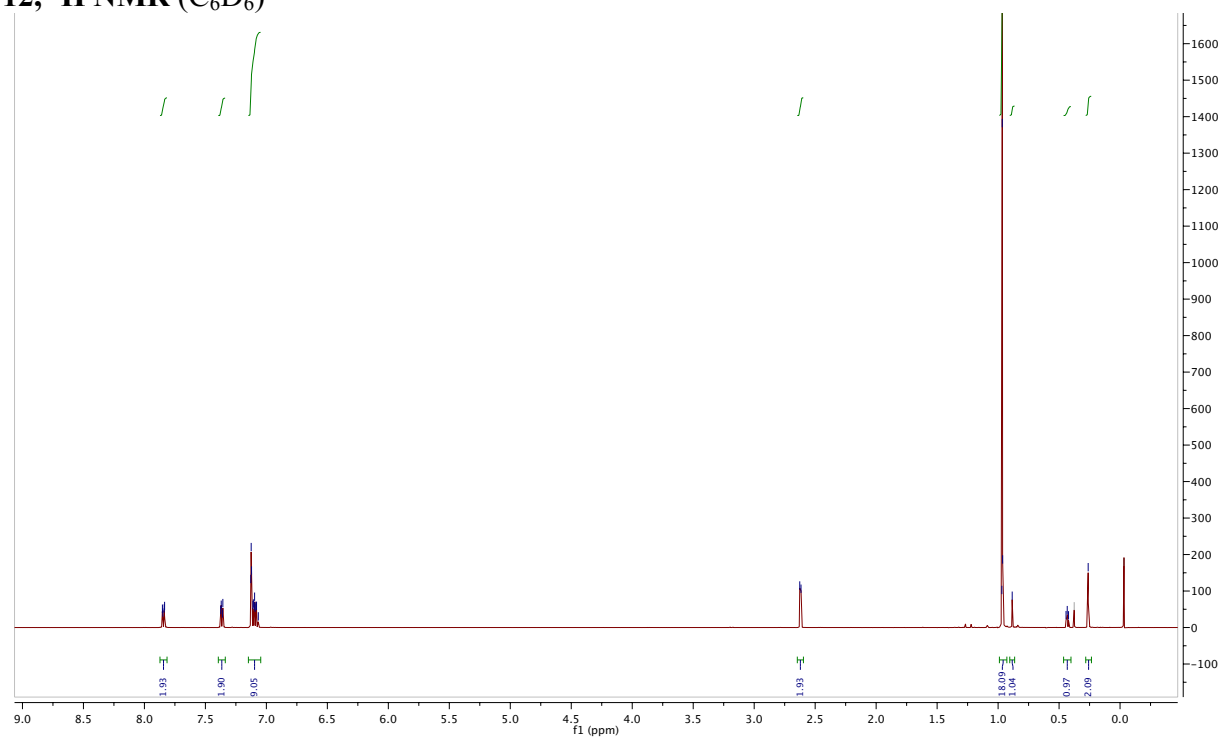
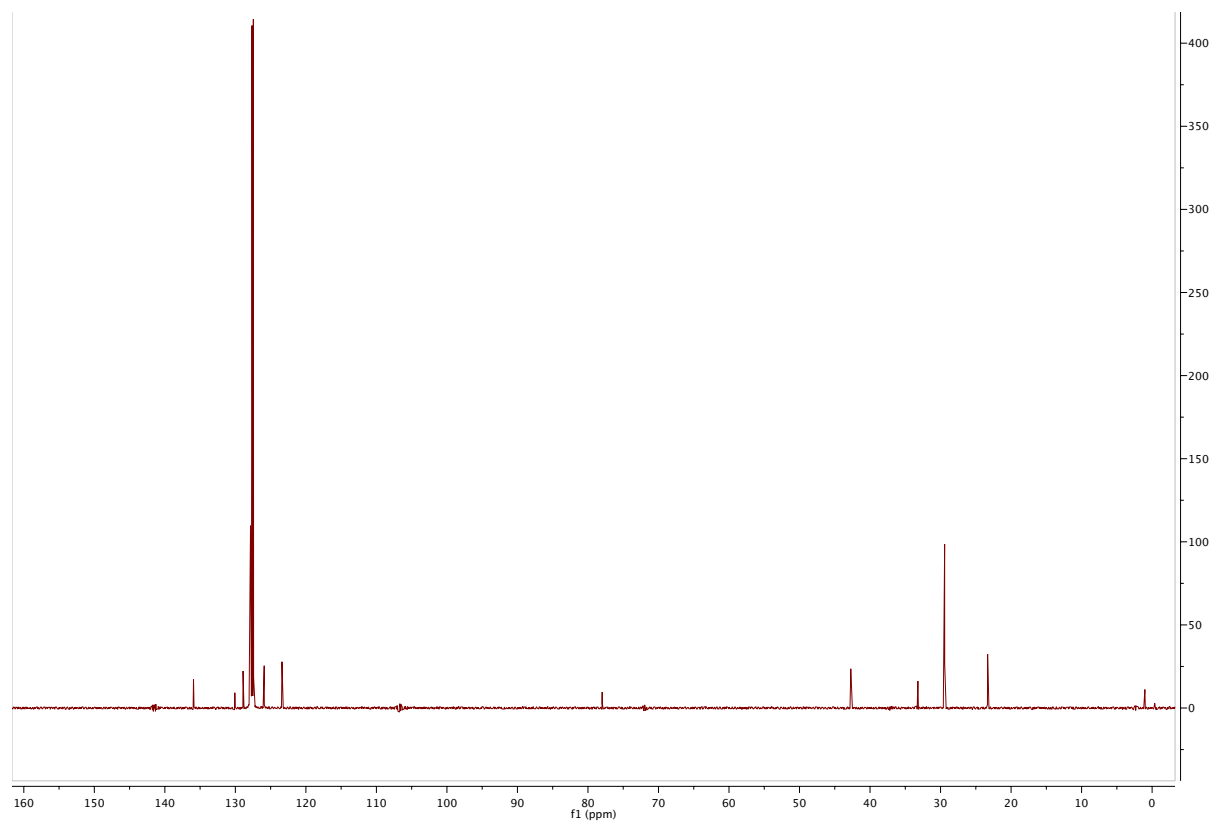
18, ^1H NMR (CDCl_3)**18, ^{13}C NMR (CDCl_3)**

19, ^1H NMR (CDCl_3)

19, GC/MS

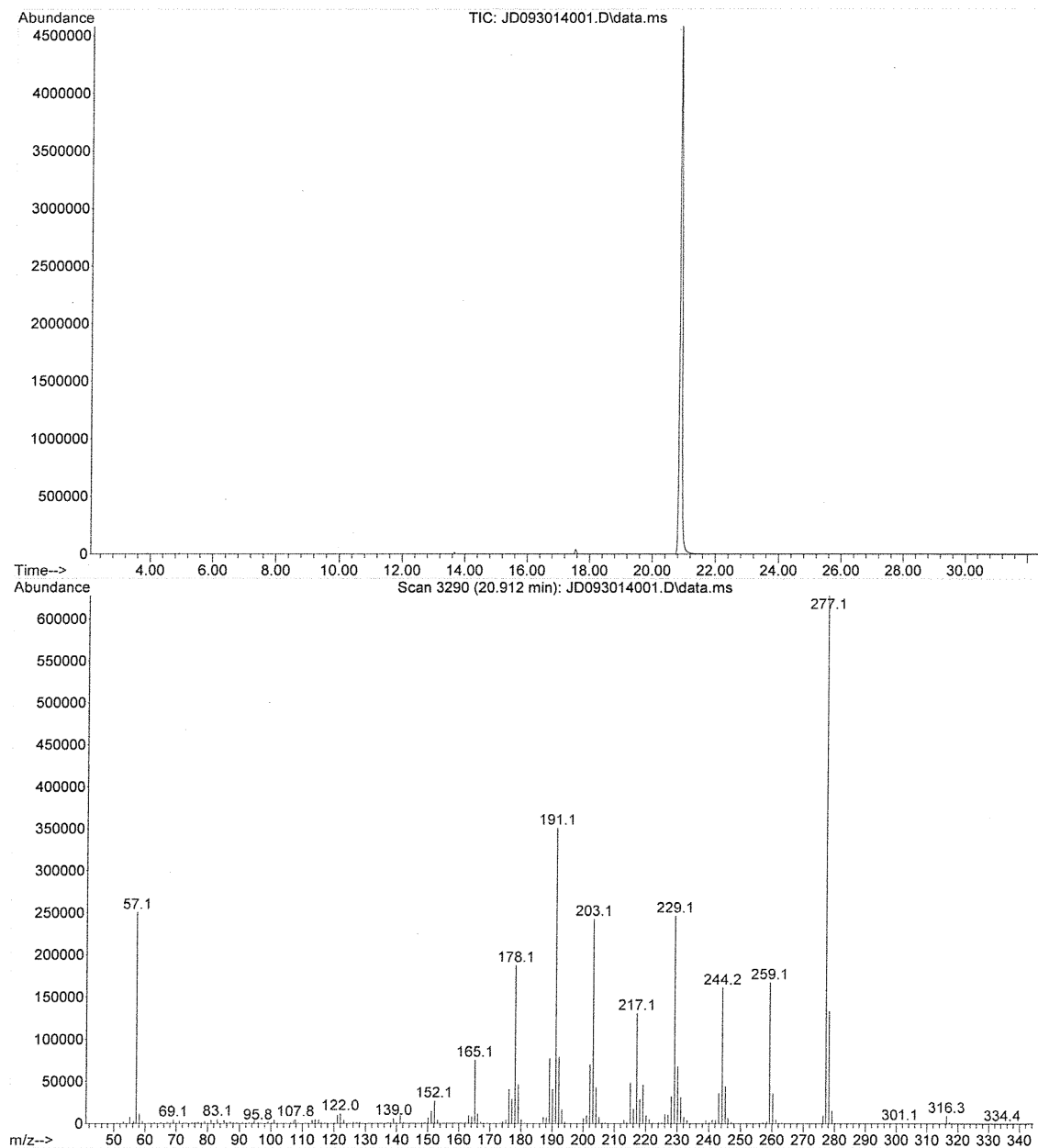
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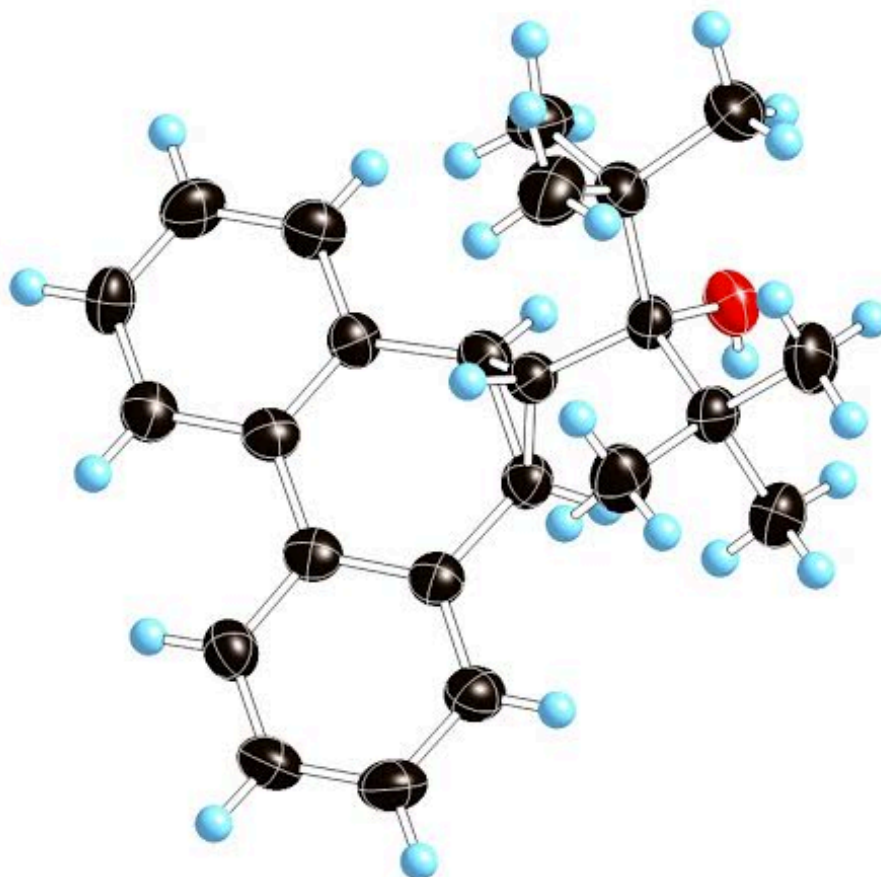
12, ^1H NMR (C_6D_6)**12, ^{13}C NMR (C_6D_6)**

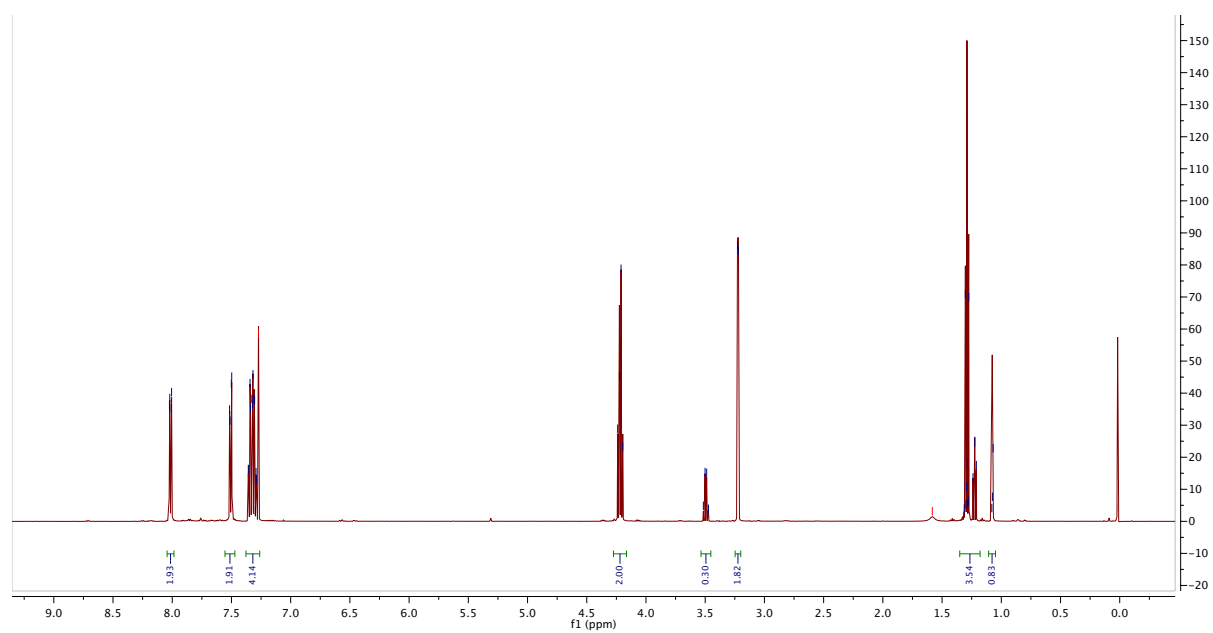
12, GC/MS

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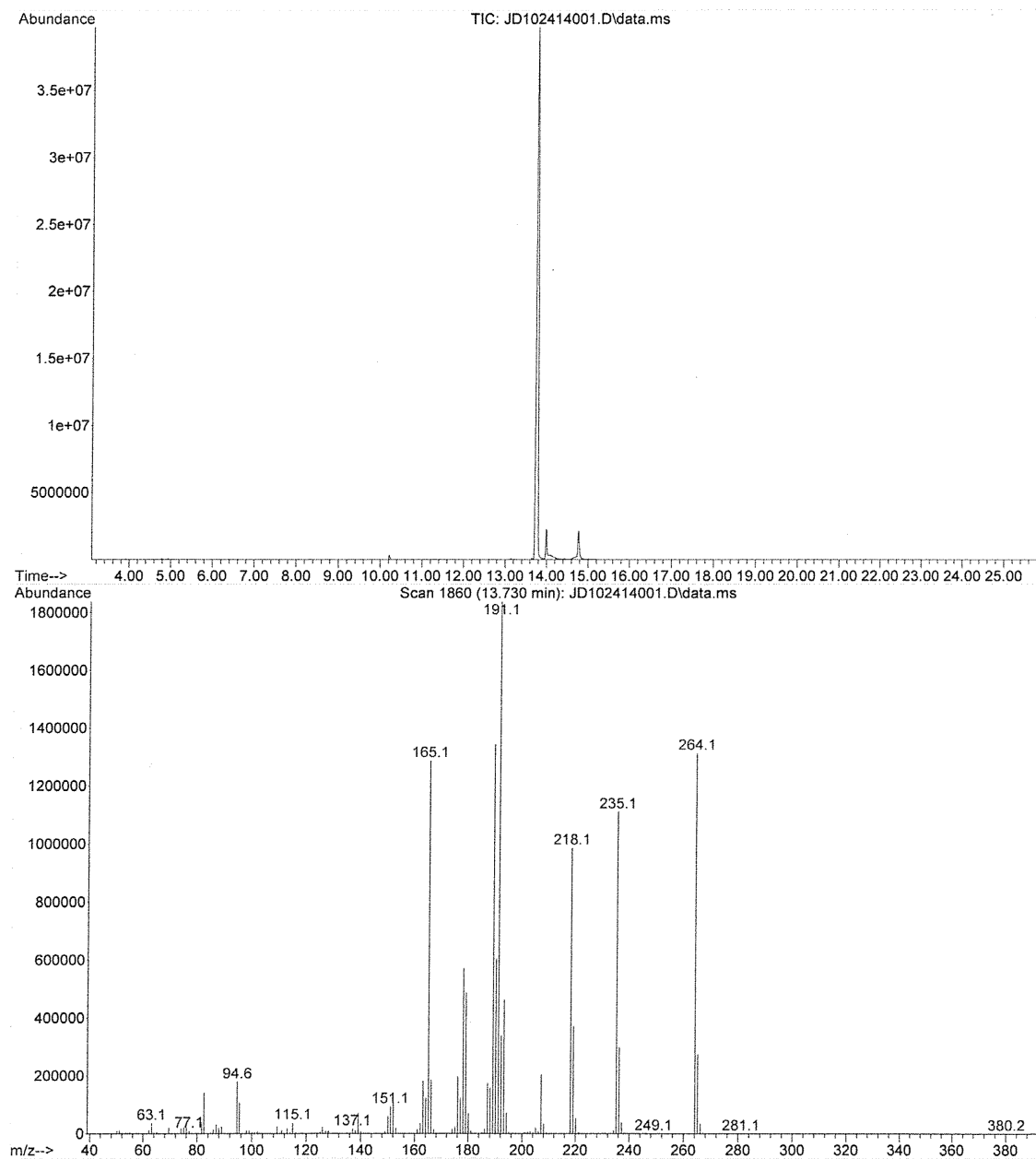
12, X-Ray Structure

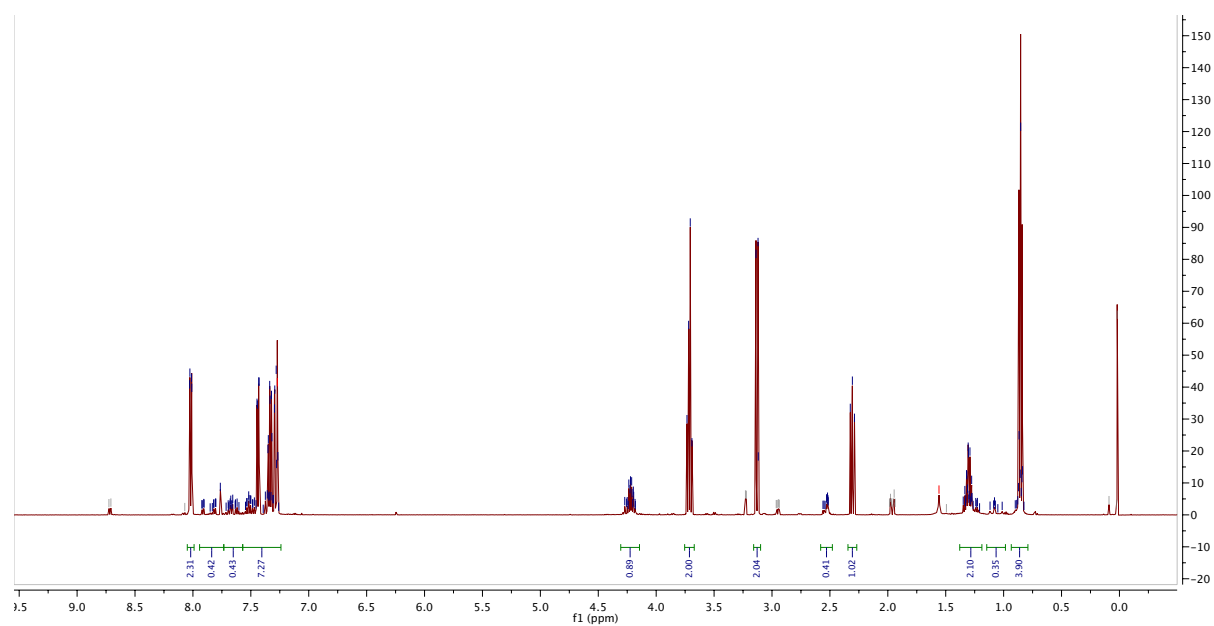


20a, ^1H NMR (CDCl_3)

20a, GC/MS

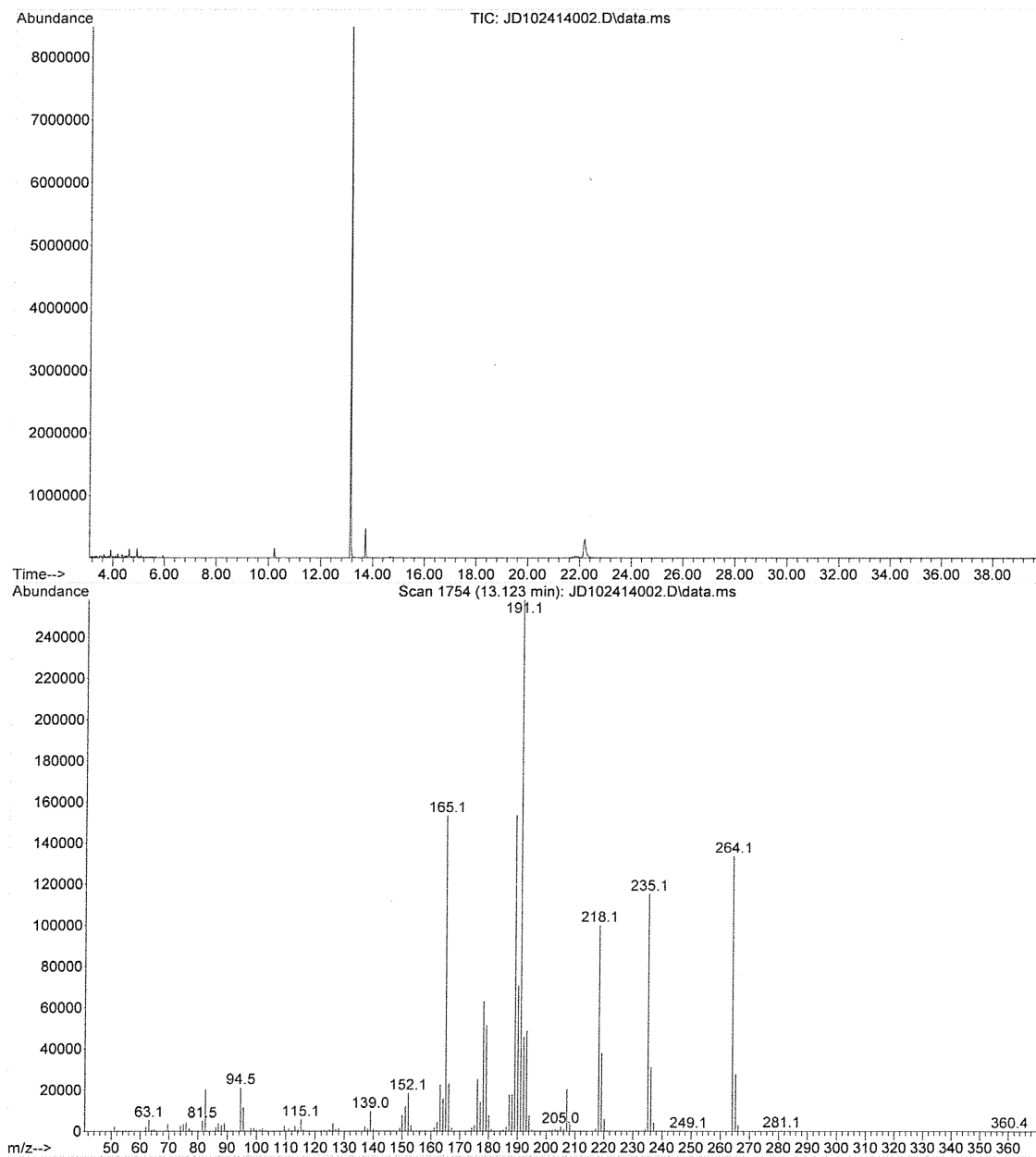
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Vial Number: 1

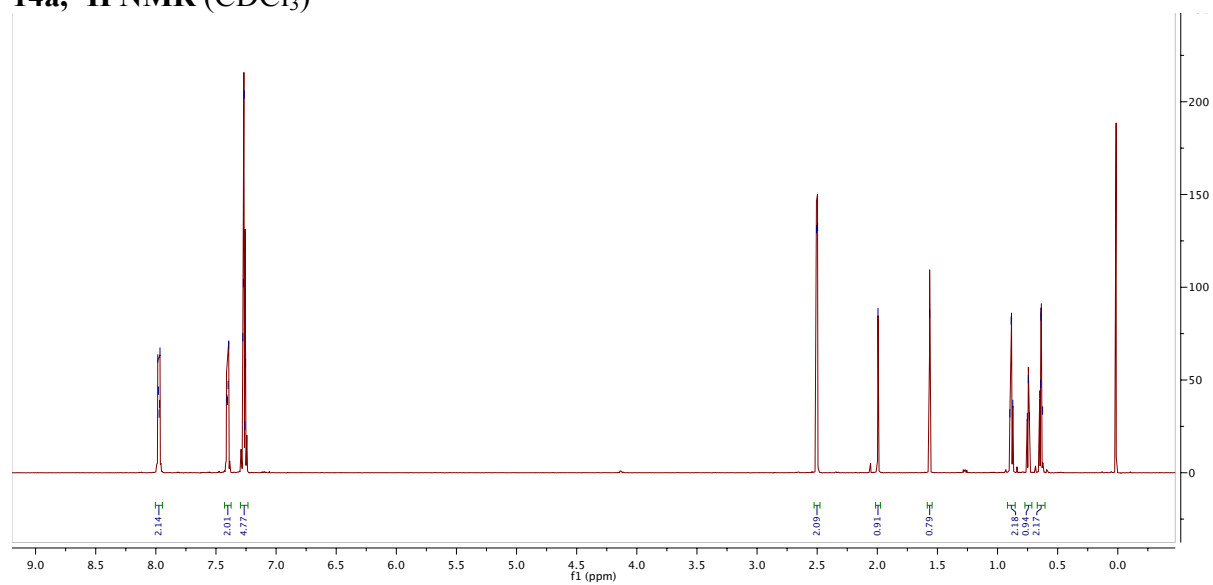
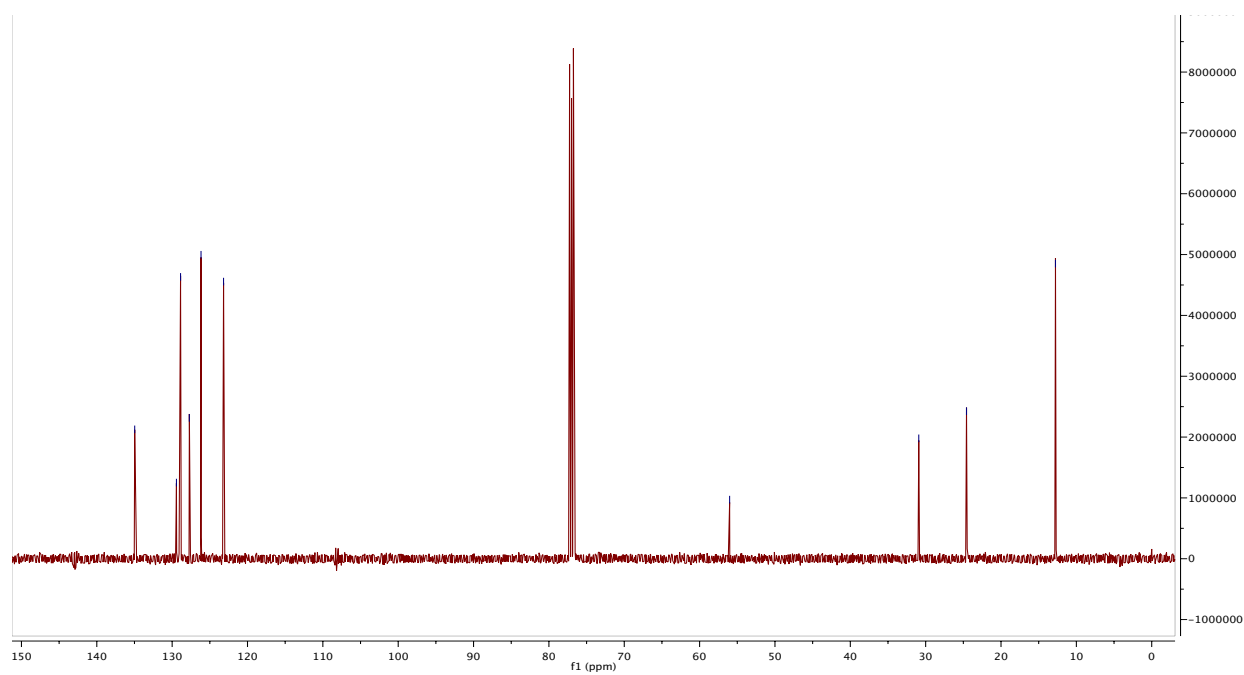


20b, ^1H NMR (CDCl_3)

20b, GC/MS

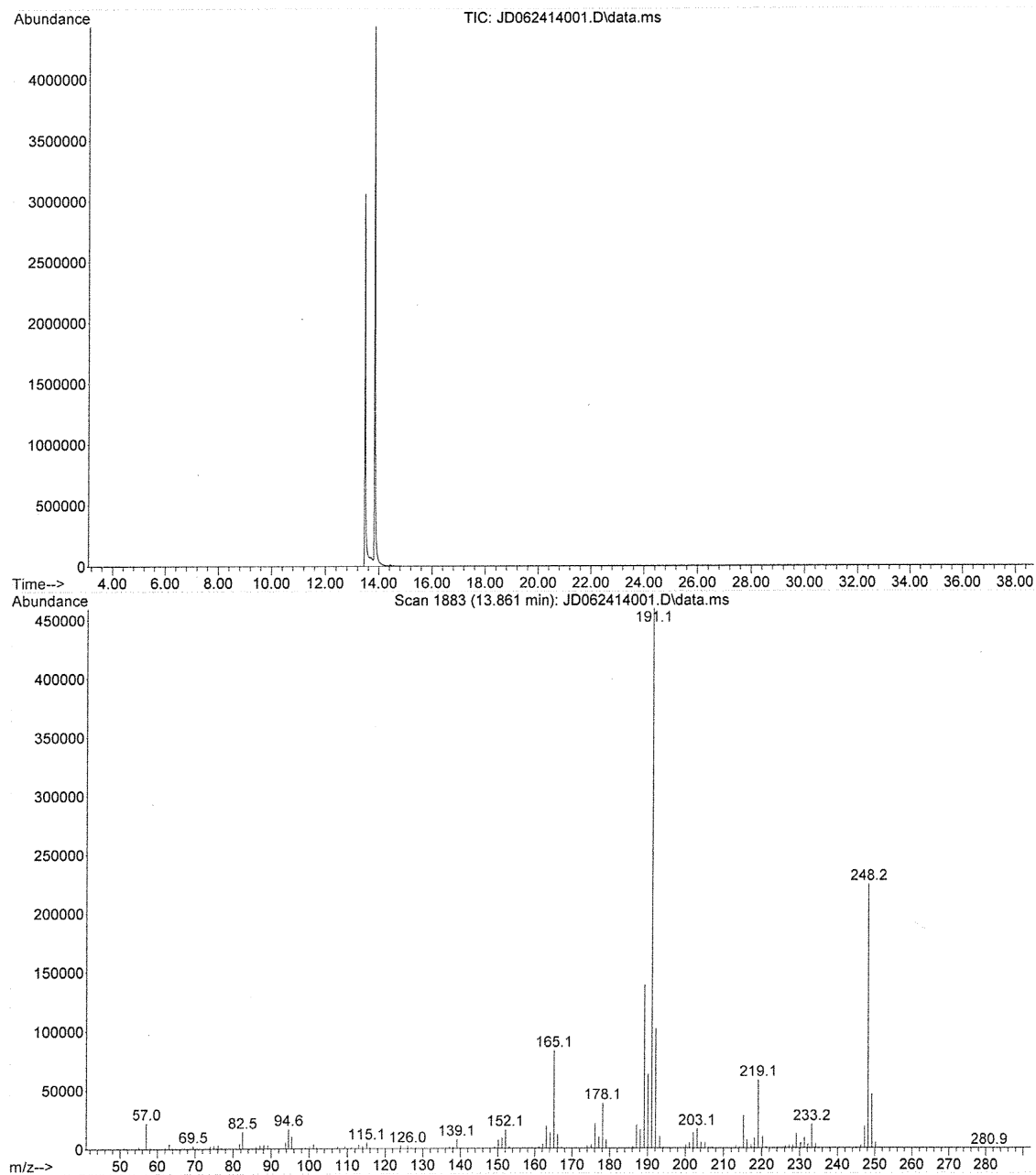
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Vial Number: 1



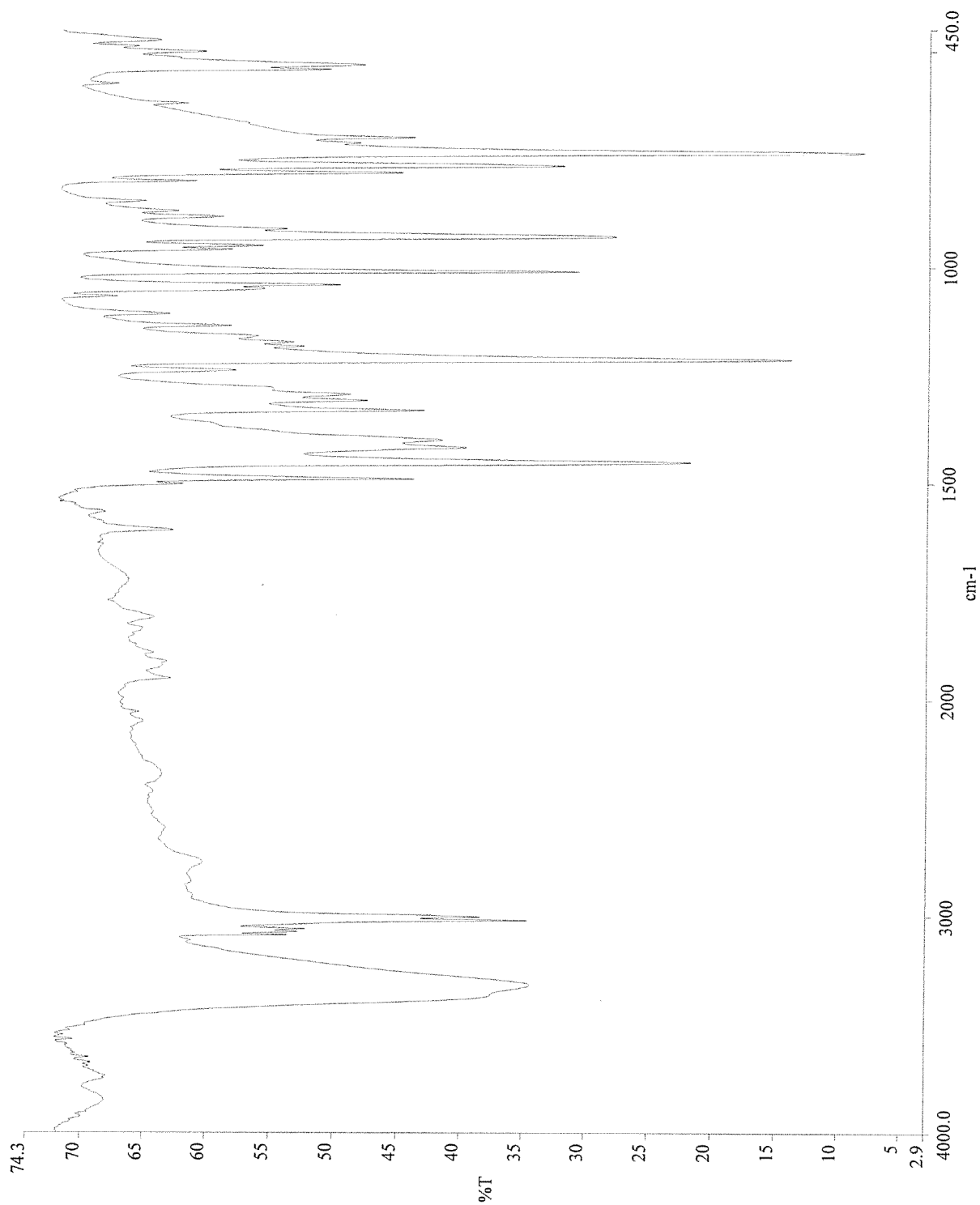
14a, ^1H NMR (CDCl_3)**14a, ^{13}C NMR (CDCl_3)**

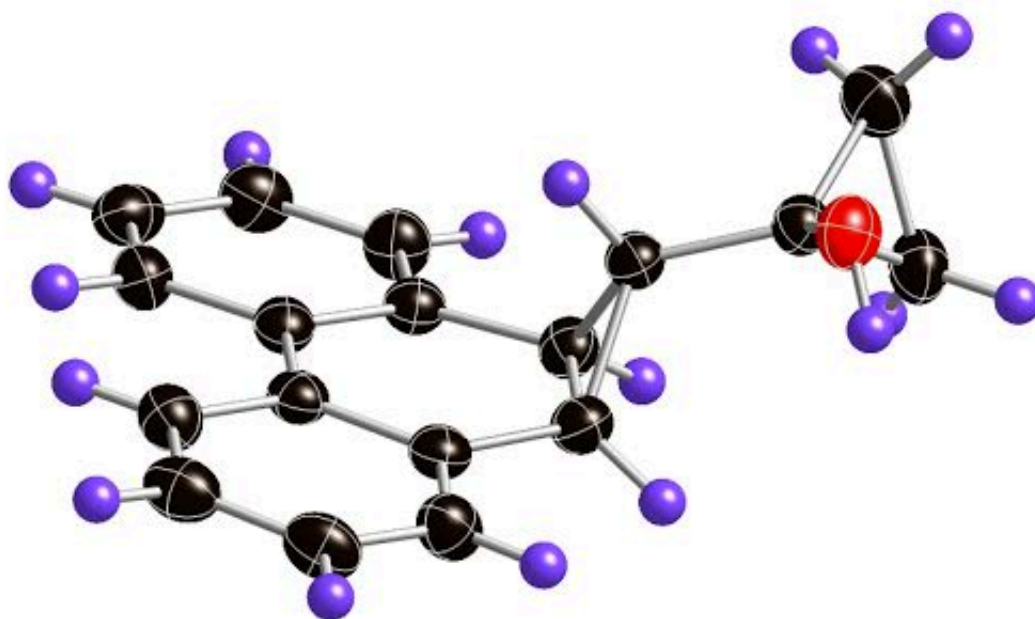
14a, GC/MS

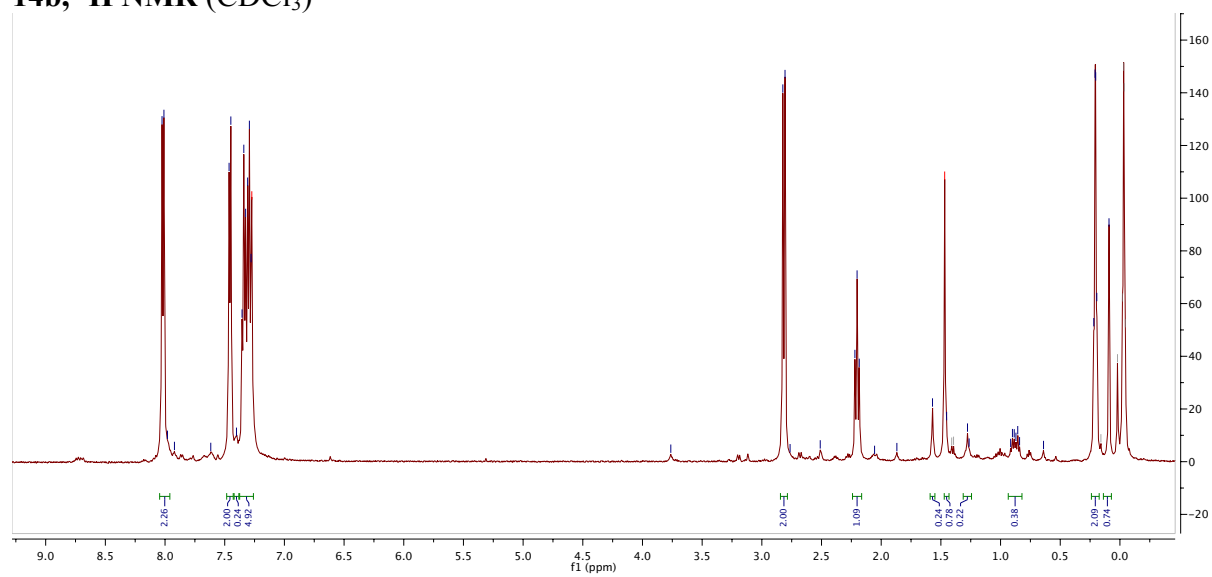
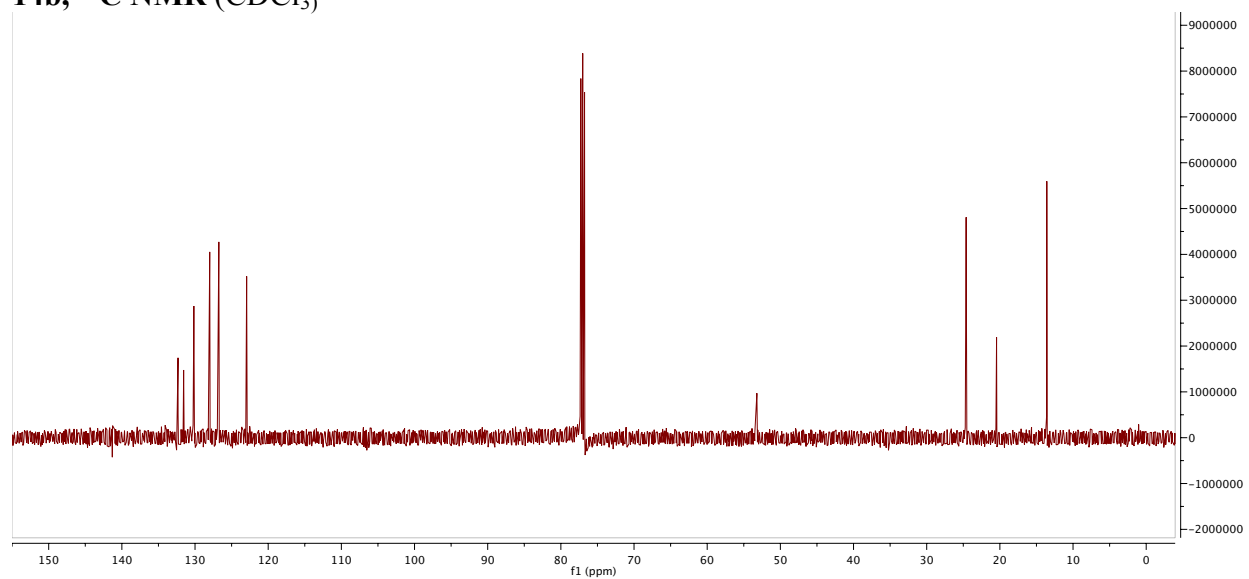
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14a, IR

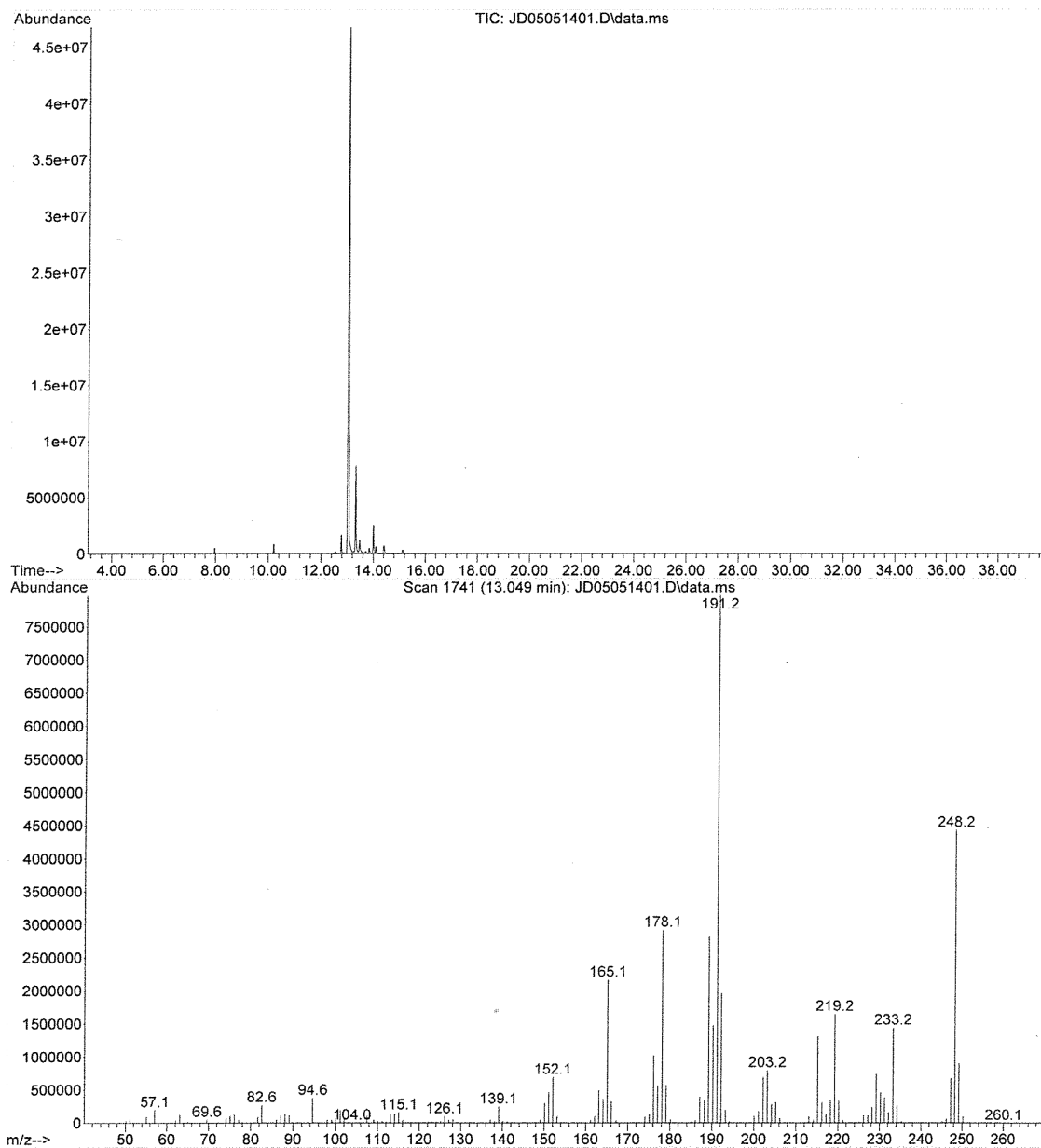


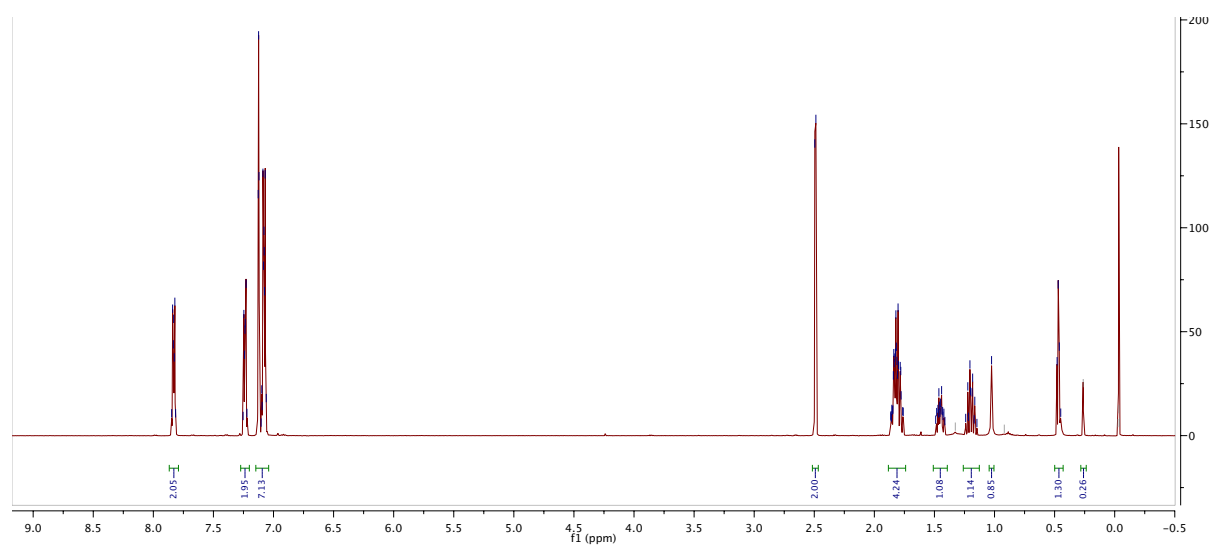
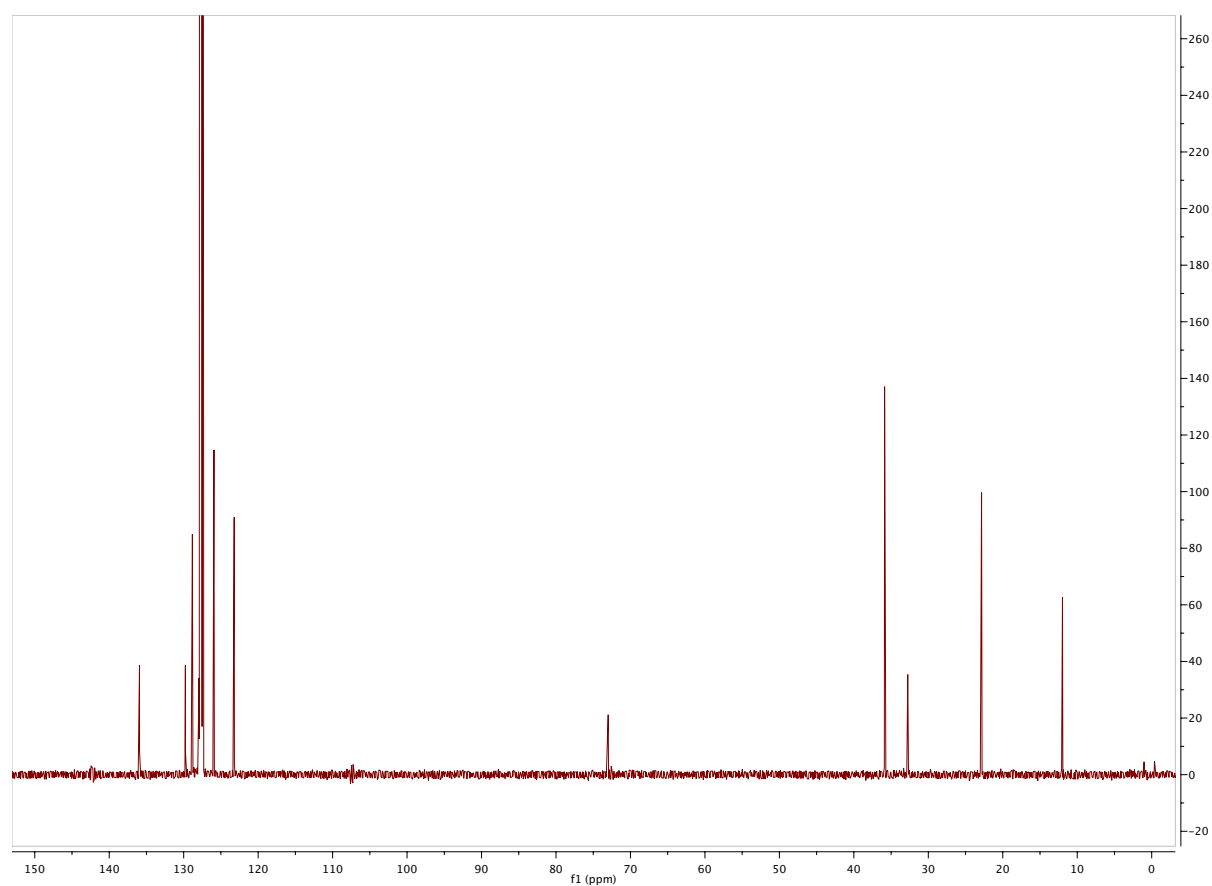
14a, X-Ray Crystal Structure

14b, ^1H NMR (CDCl_3)**14b, ^{13}C NMR (CDCl_3)**

14b, GC/MS

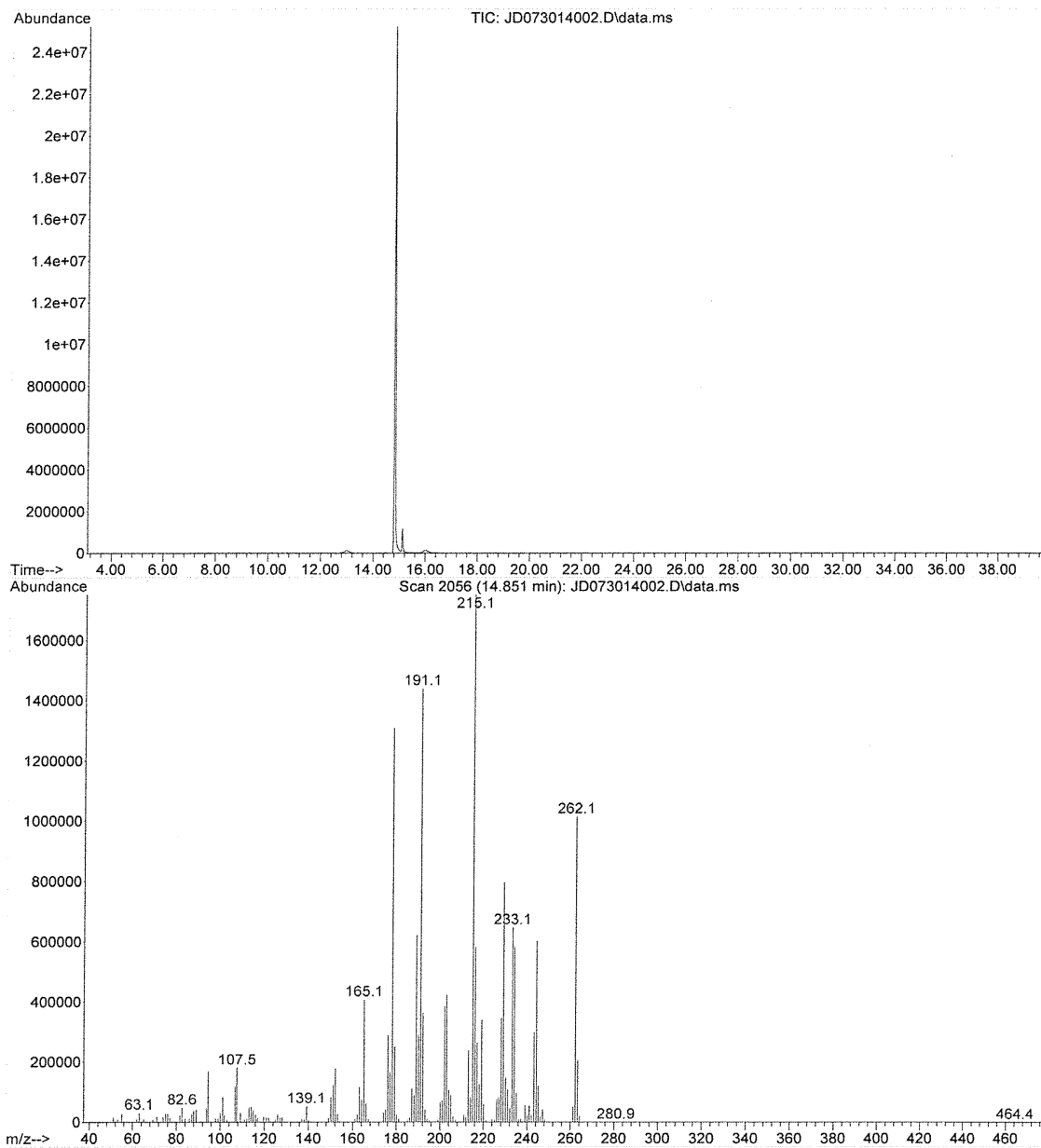
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Vial Number: 1



16, ^1H NMR (C_6D_6)**16, ^{13}C NMR (C_6D_6)**

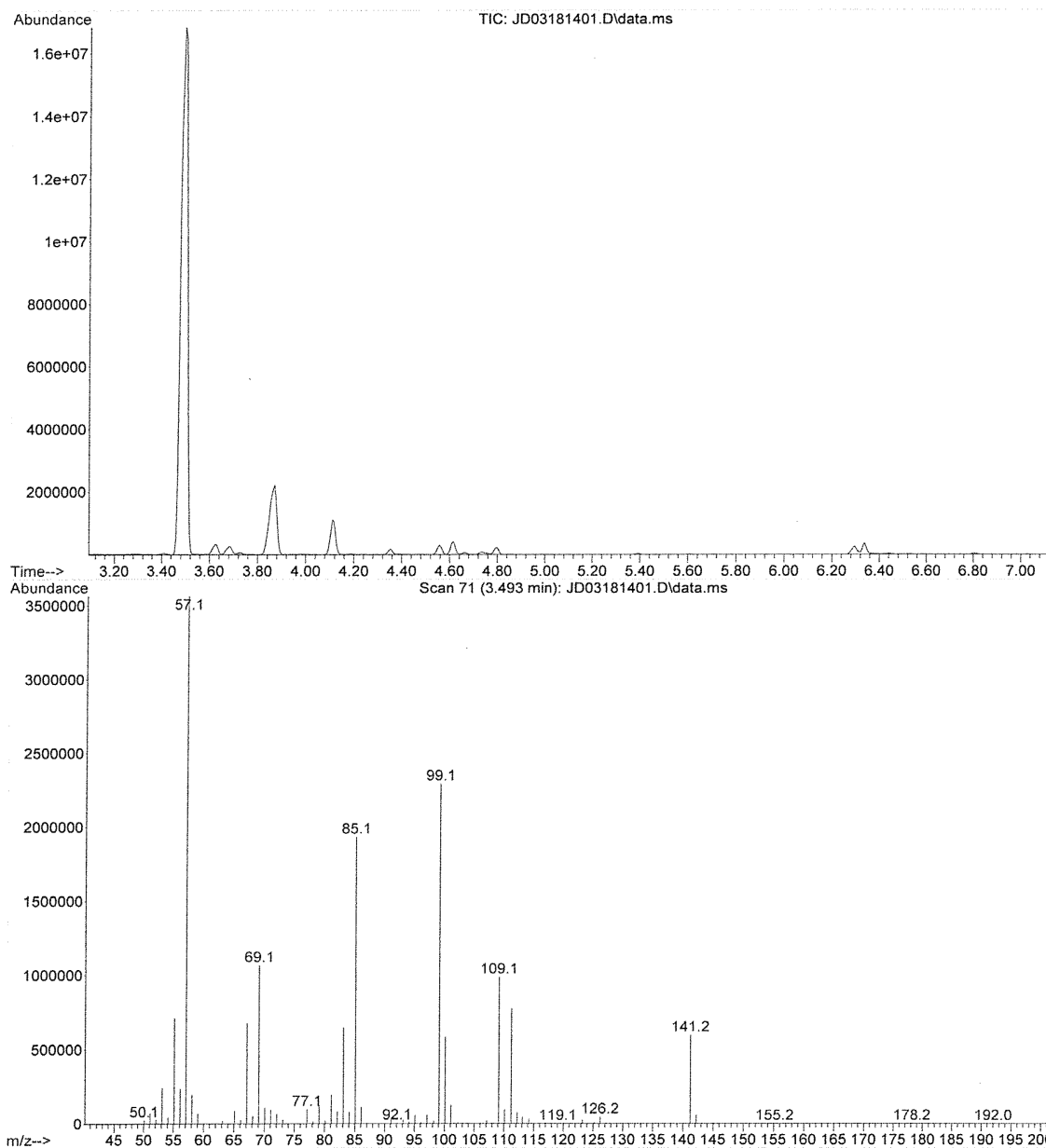
16, GC/MS

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Vial Number: 1



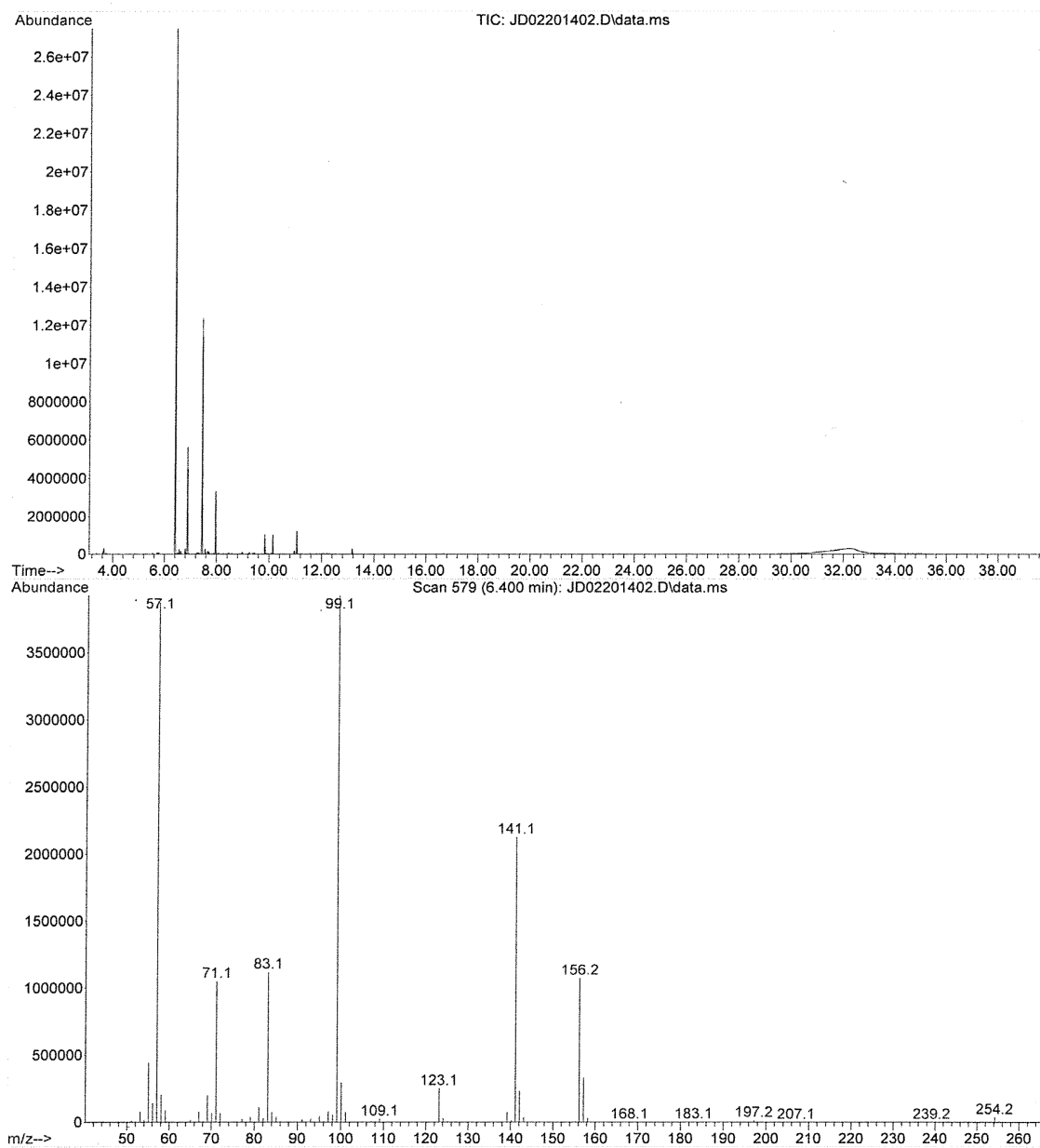
23, GC/MS

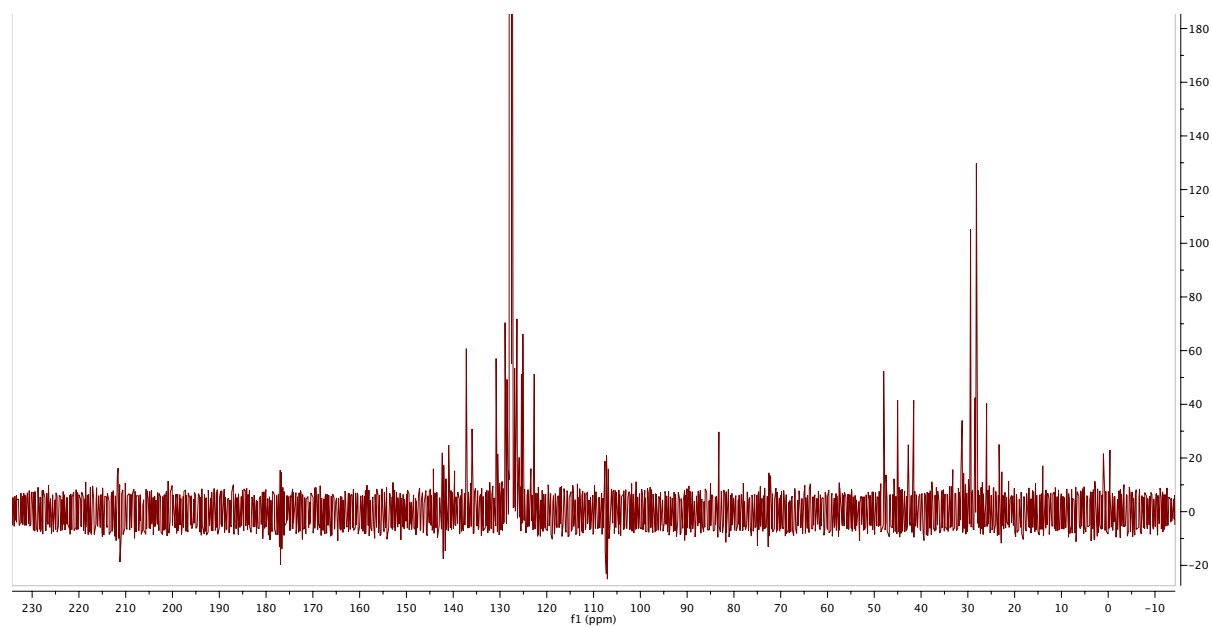
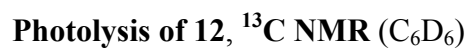
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Sample Name: epoxide std
Misc Info :
Vial Number: 1



24, GC/MS

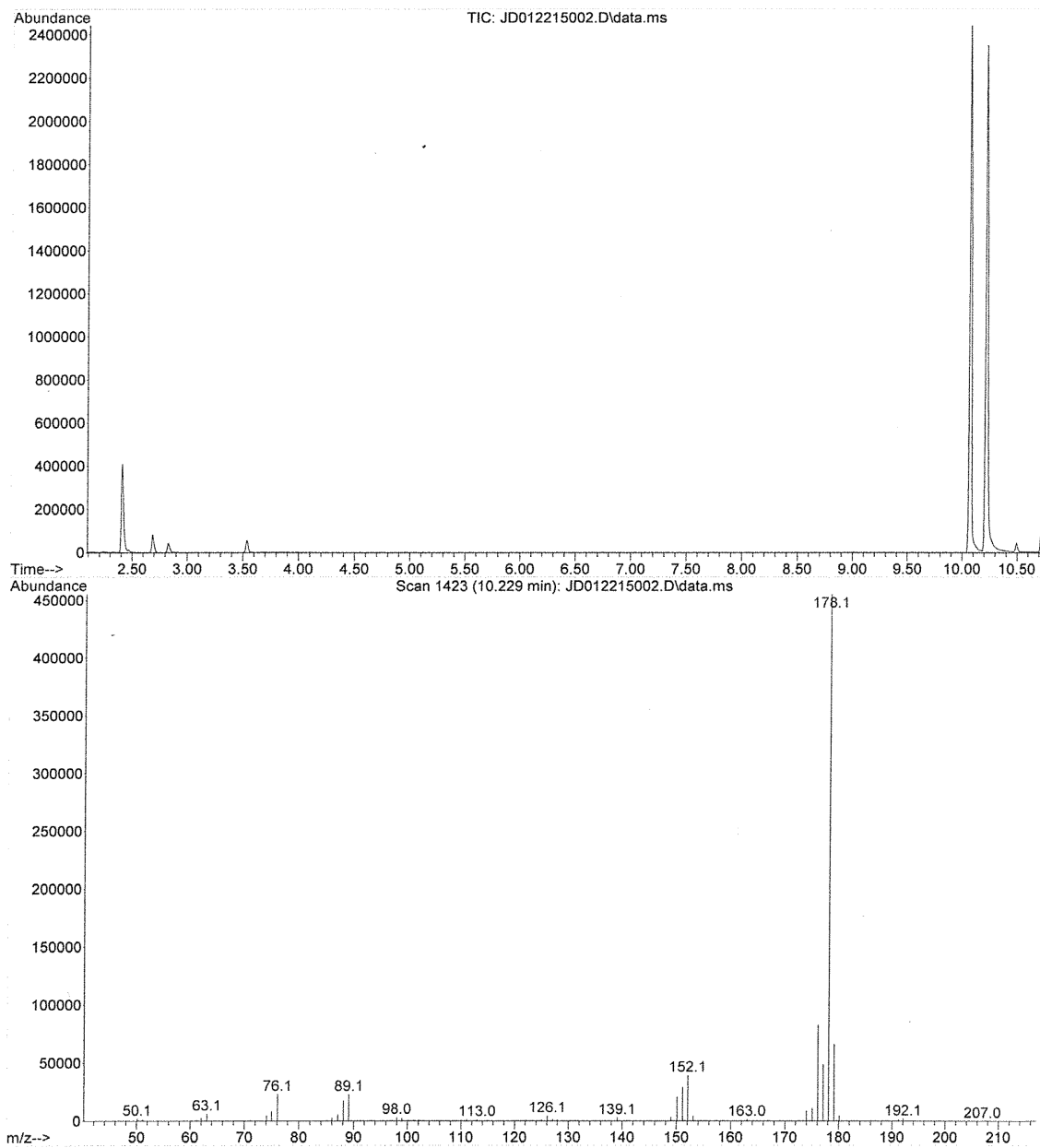
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Sample Name: ketone post workup
Misc Info :
Vial Number: 2





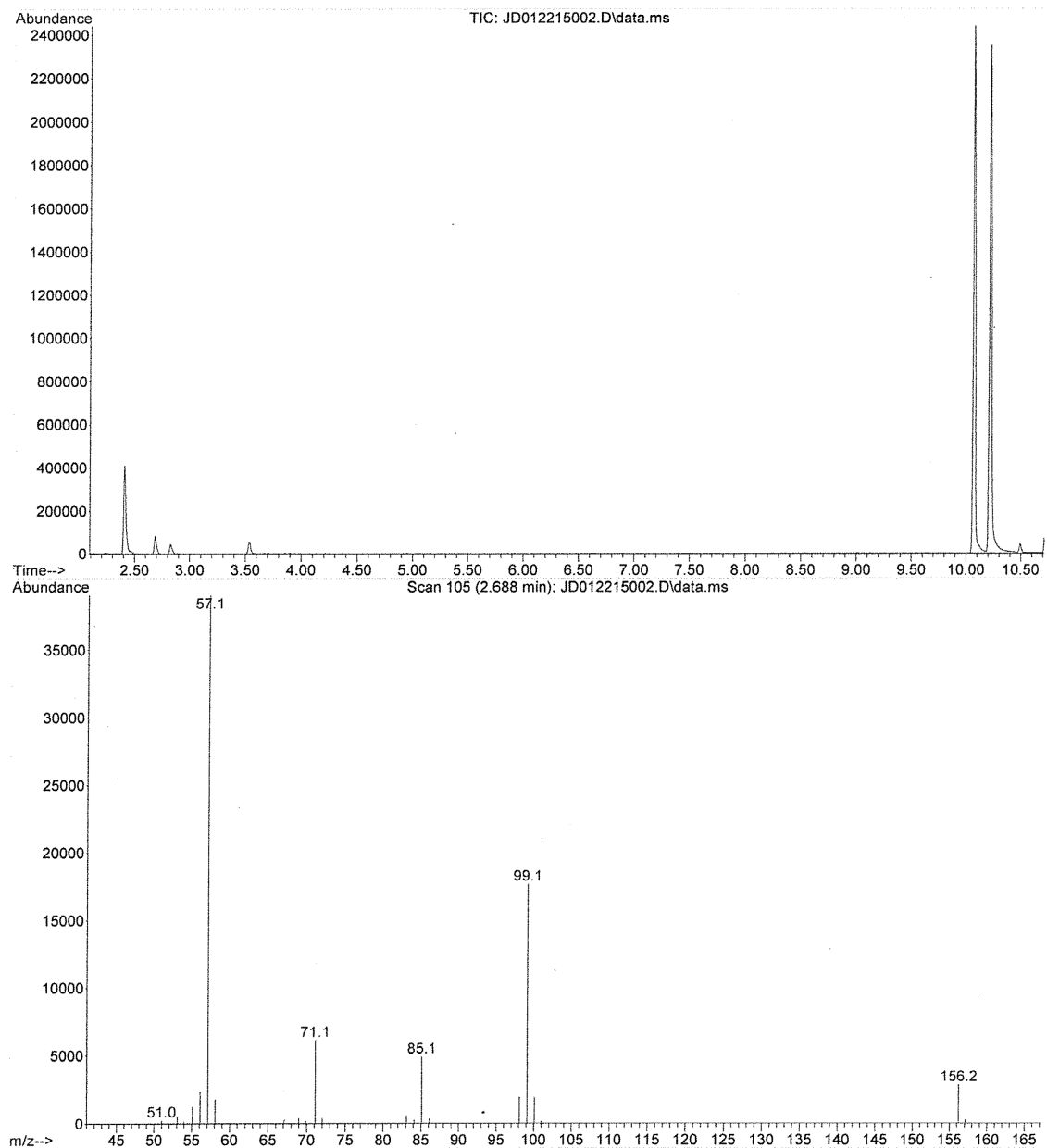
Photolysis of 12, GC/MS (Identification of 3)

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Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1



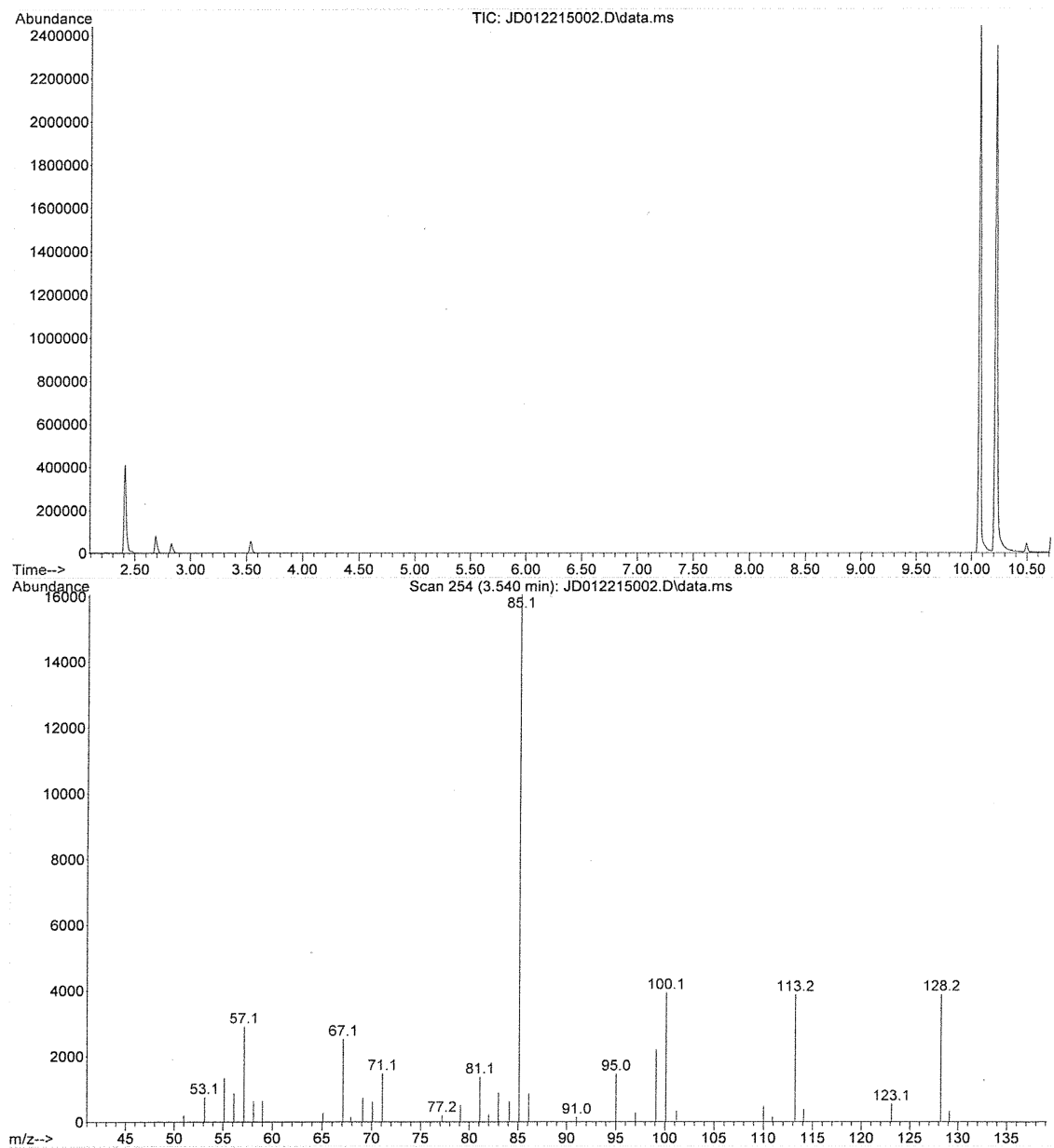
Photolysis of 12, GC/MS (Identification of 24)

File :D:\1\data\JoeD\JD012215002.D
Operator : Joe
Acquired : 22 Jan 2015 15:29 using AcqMethod DASLAB2MIN.M
Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1



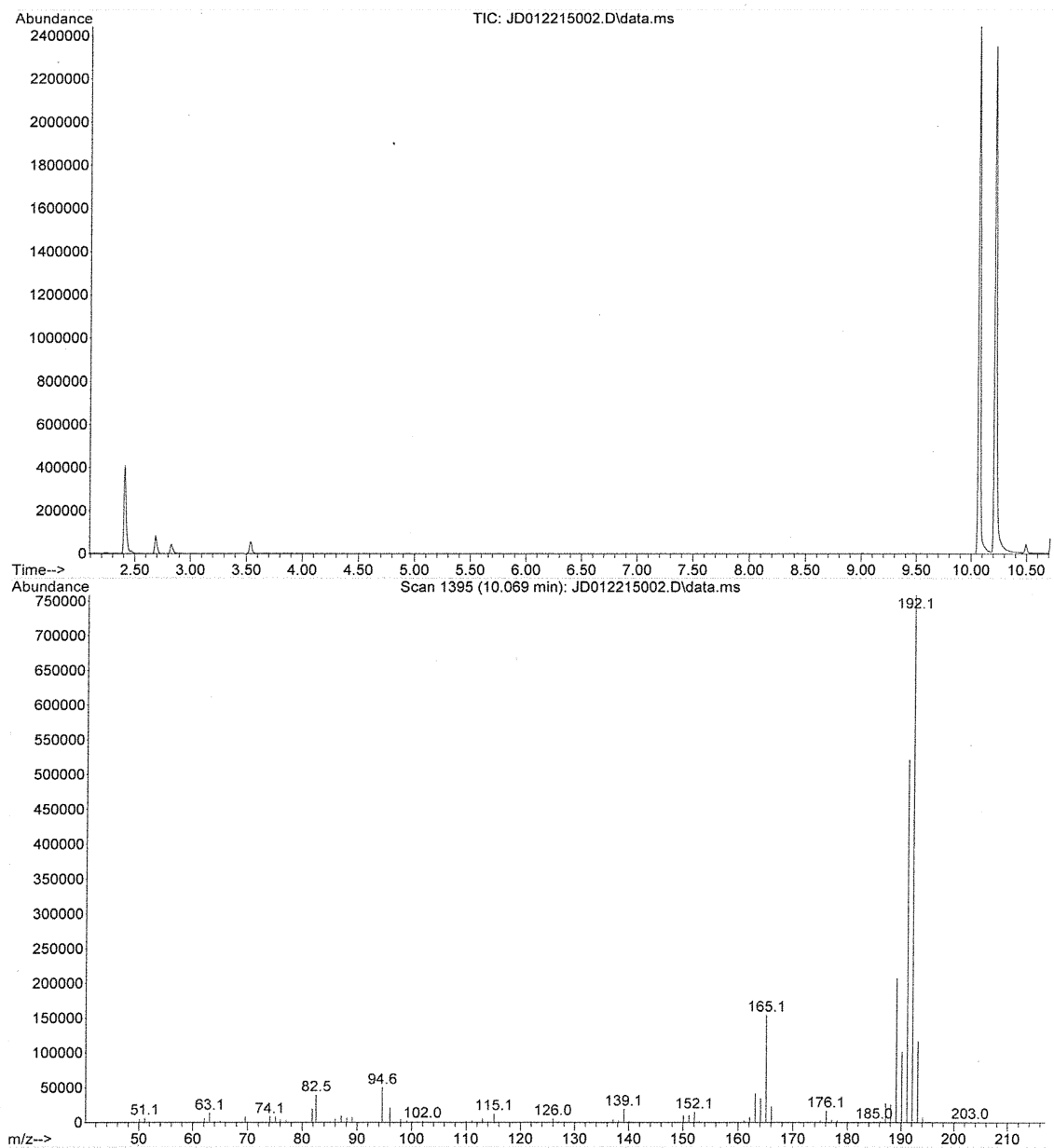
Photolysis of 12, GC/MS (Identification of 25)

File :D:\1\data\JoeD\JD012215002.D
Operator : Joe
Acquired : 22 Jan 2015 15:29 using AcqMethod DASLAB2MIN.M
Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1



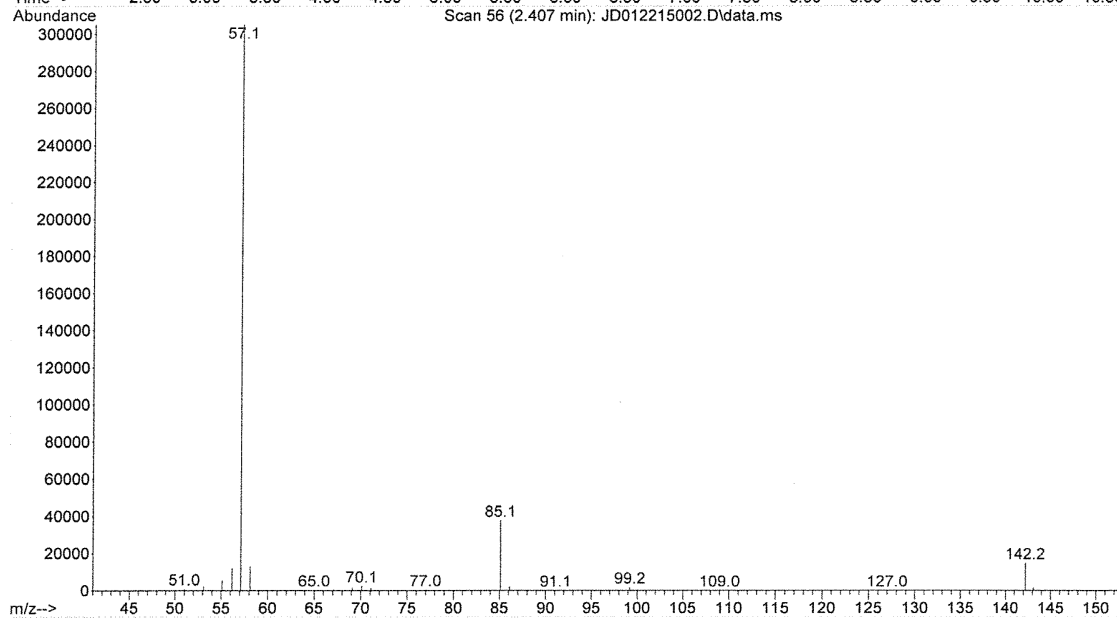
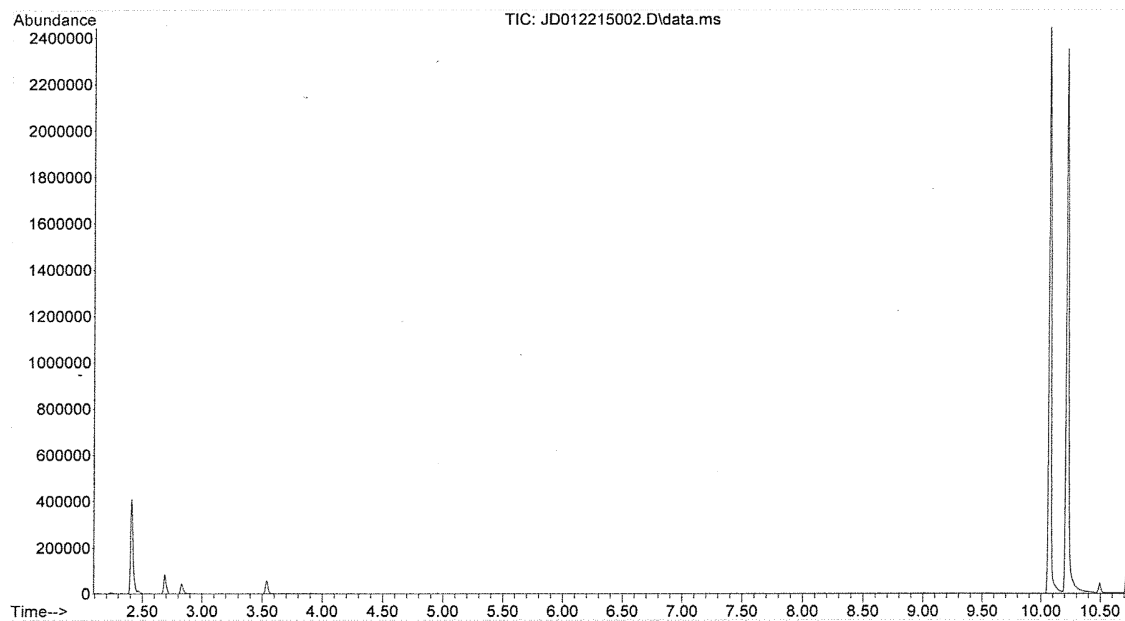
Photolysis of 12, GC/MS (Identification of rearrangement from 31a)

File :D:\1\data\JoeD\JD012215002.D
Operator : Joe
Acquired : 22 Jan 2015 15:29 using AcqMethod DASLAB2MIN.M
Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1



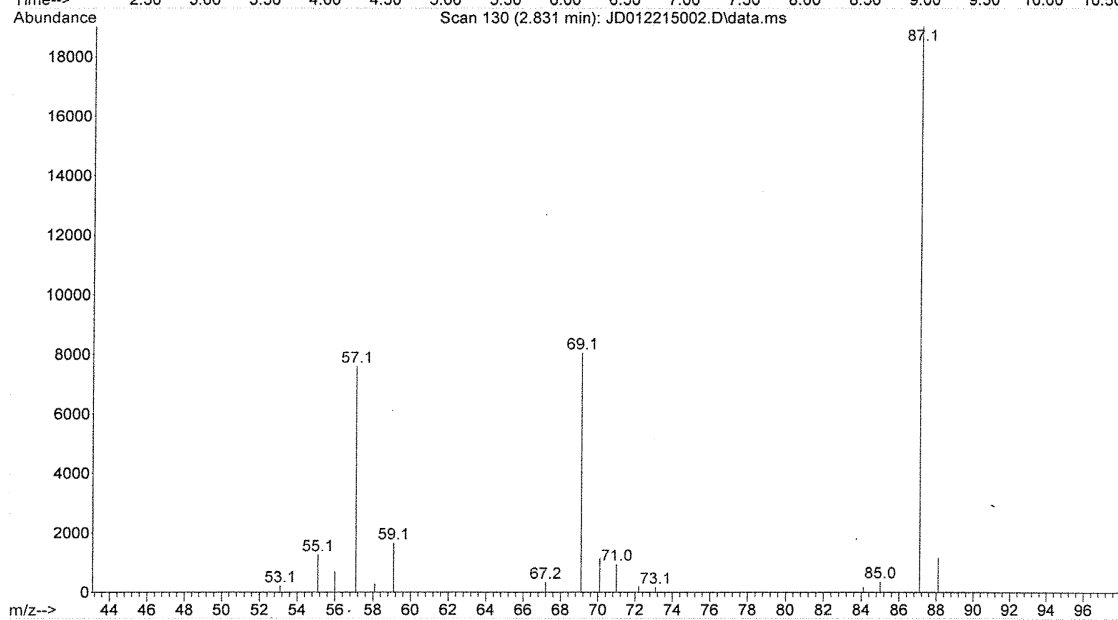
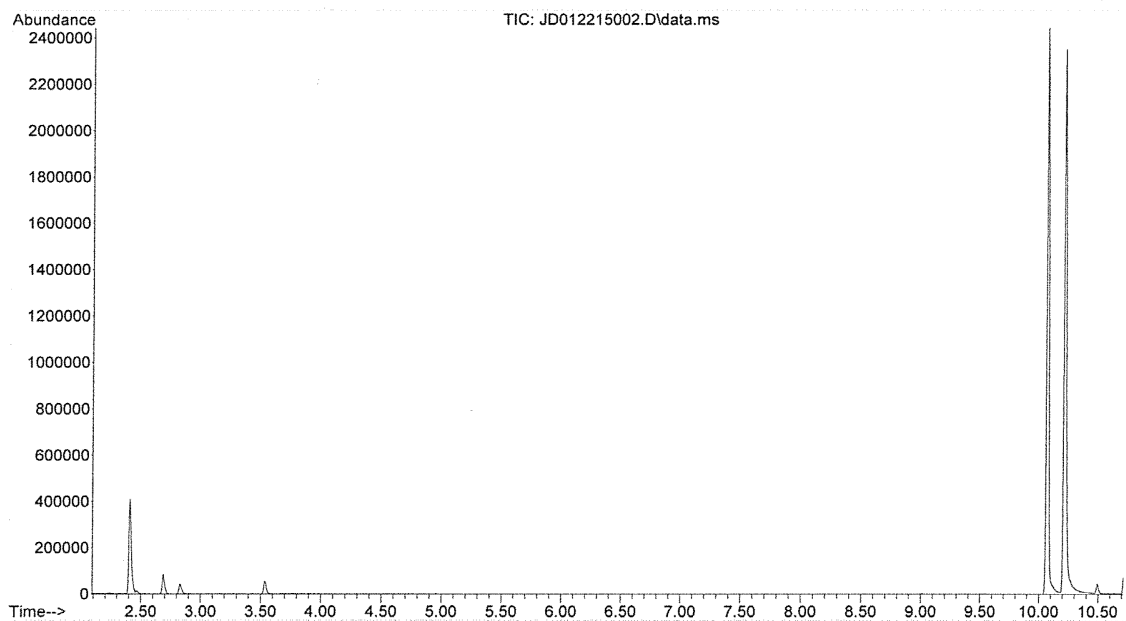
Photolysis of 12, GC/MS (Identification of 32)

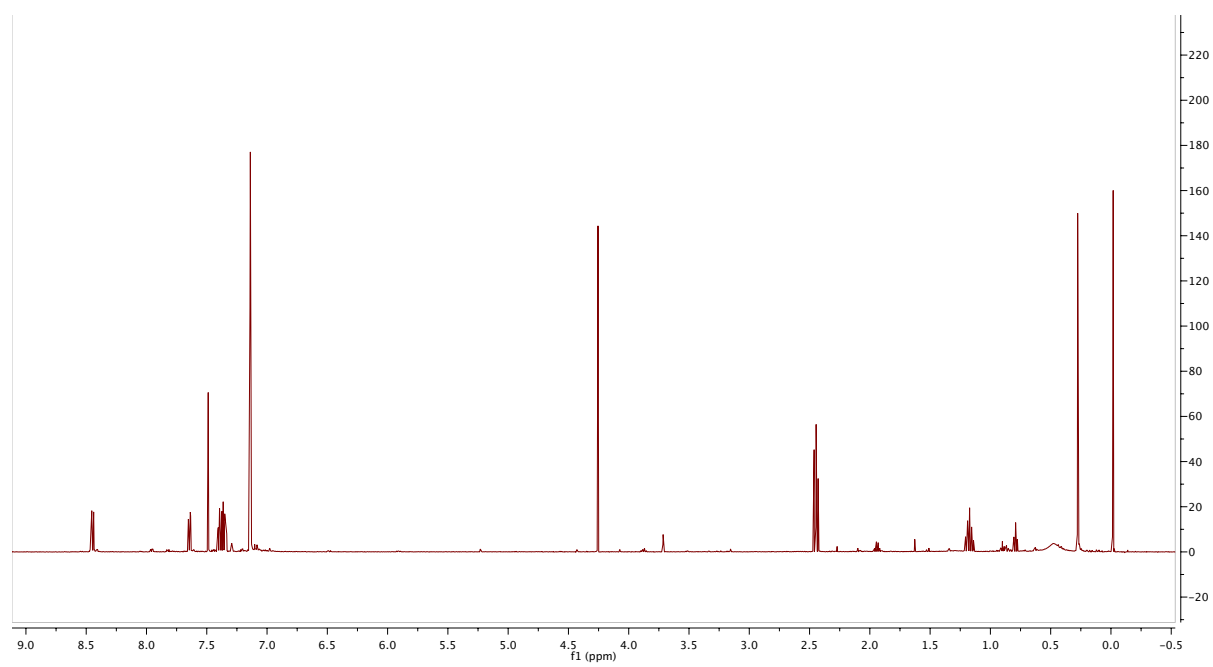
File :D:\1\data\JoeD\JD012215002.D
Operator : Joe
Acquired : 22 Jan 2015 15:29 using AcqMethod DASLAB2MIN.M
Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1

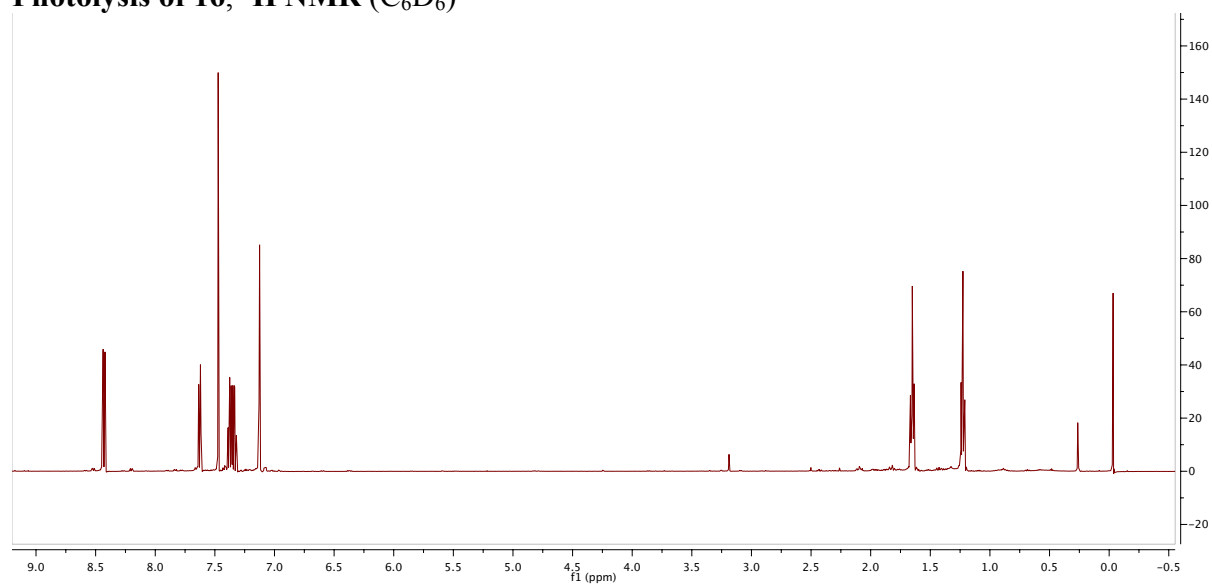
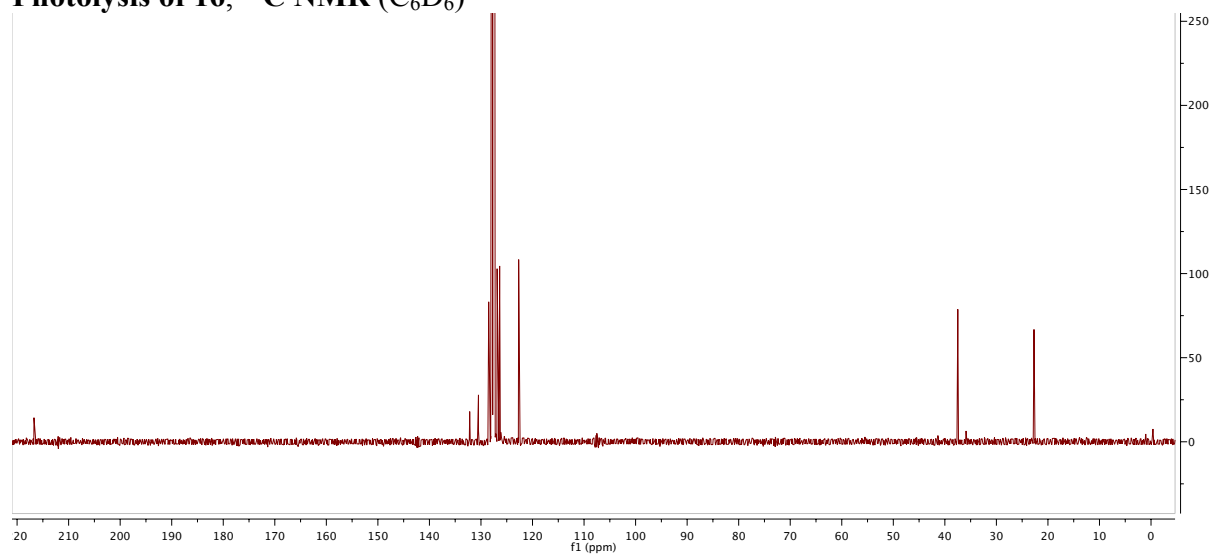


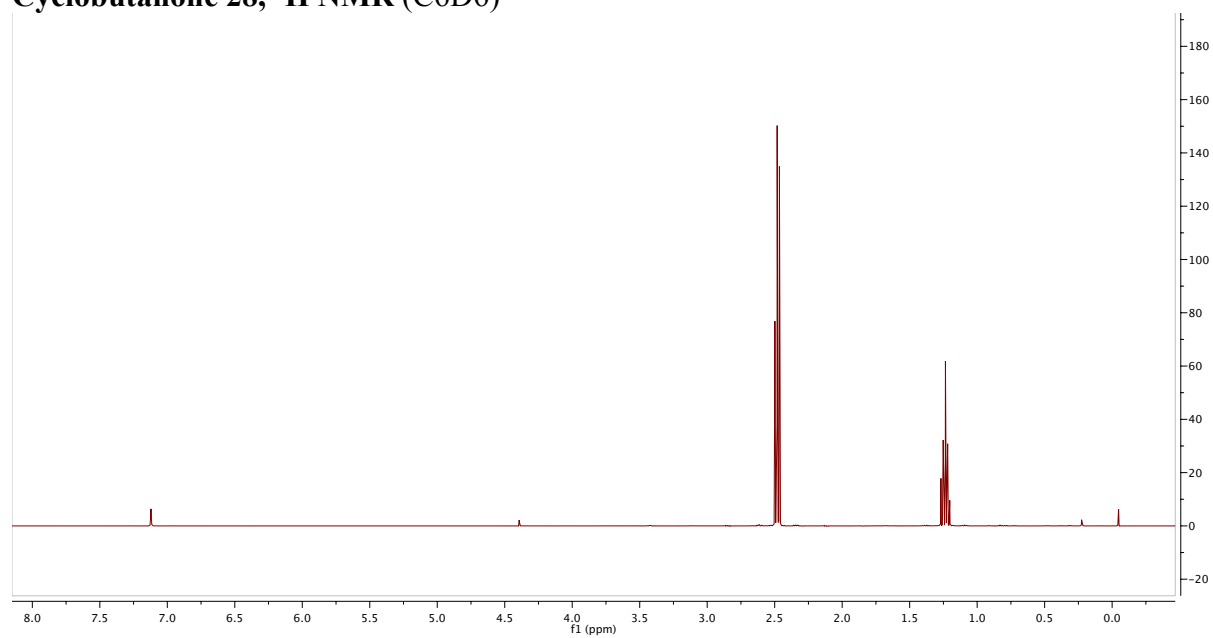
Photolysis of 12, GC/MS (Identification of 33)

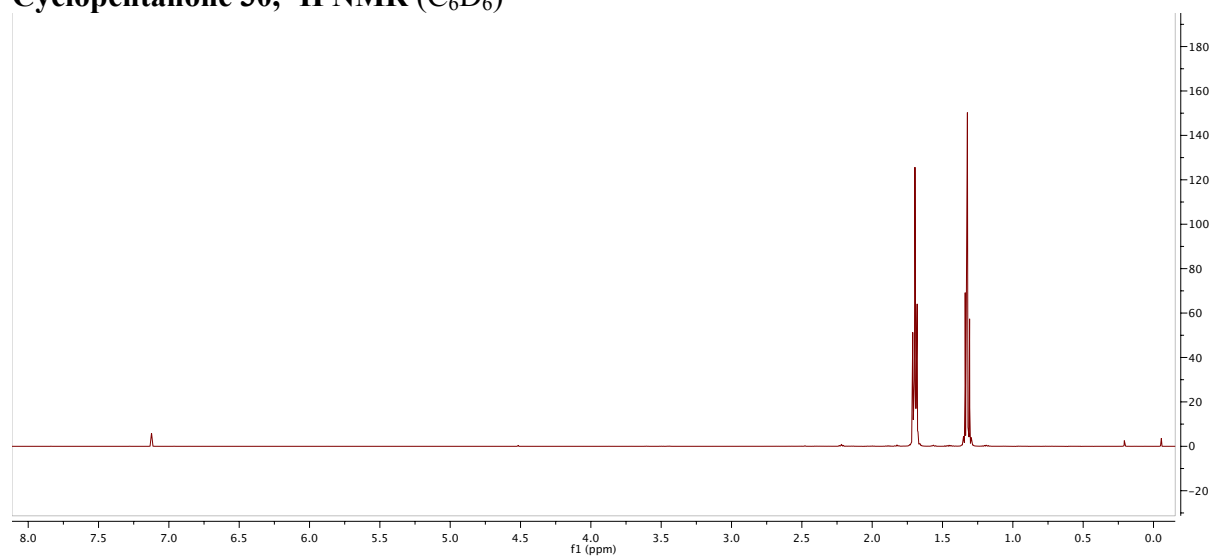
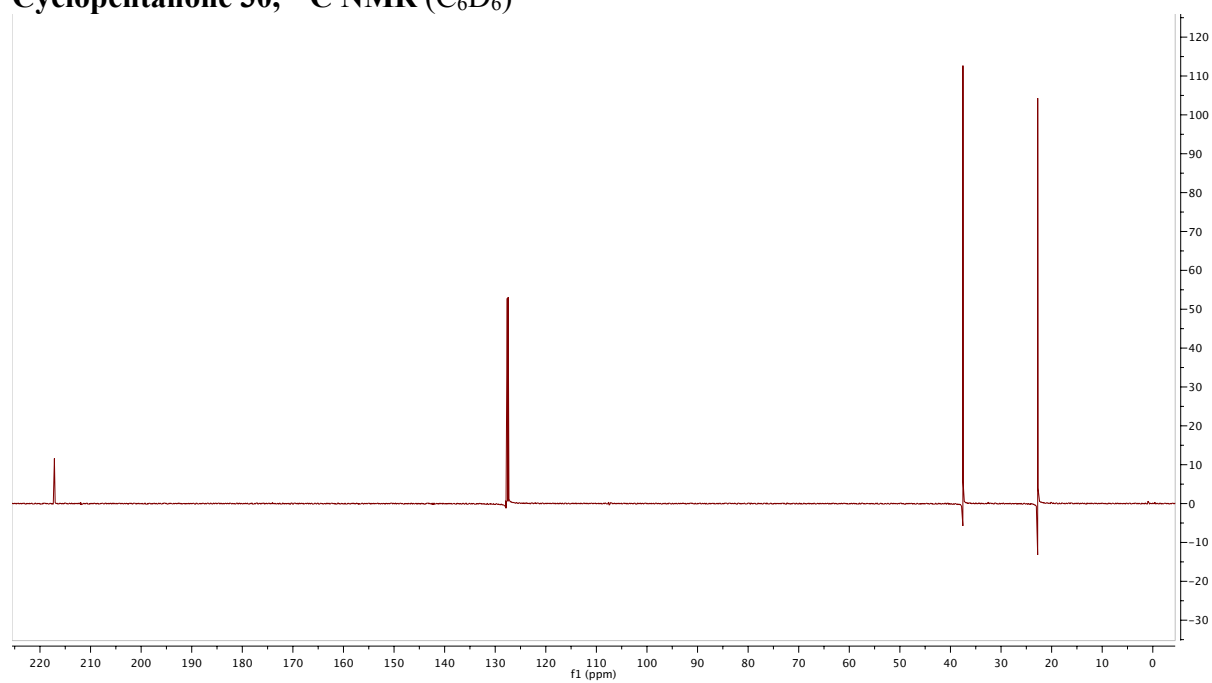
File :D:\1\data\JoeD\JD012215002.D
Operator : Joe
Acquired : 22 Jan 2015 15:29 using AcqMethod DASLAB2MIN.M
Instrument : GCMS1
Sample Name: bistertbutanol photolysis
Misc Info : pst 2hr in dasbox
Vial Number: 1



Photolysis of 14a, ^1H NMR (C_6D_6)

Photolysis of 16, ^1H NMR (C_6D_6)**Photolysis of 16, ^{13}C NMR (C_6D_6)**

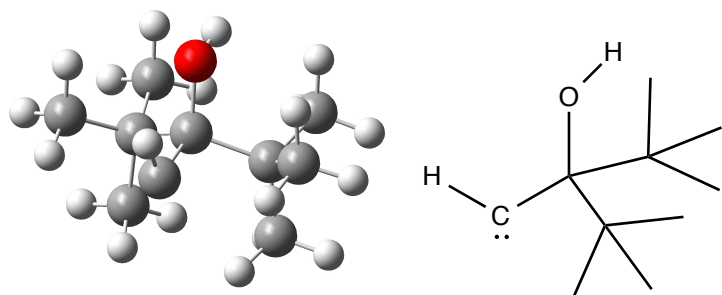
Cyclobutanone 28, ^1H NMR (C_6D_6)

Cyclopentanone 30, ^1H NMR (C_6D_6)**Cyclopentanone 30, ^{13}C NMR (C_6D_6)**

Appendix B: Optimized Structures and Energies from Computational Studies

Part One: Geometry Optimized Structures

β -bis(*tert*)-butanol carbene: **13** (Singlet with $\text{C}\alpha\text{-C}\beta\text{-O-H}$ of 180°)



SCF Done: E(RB3LYP) = -468.219574520 A.U. after 6 cycles
 Conv g = 0.5787D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.000005	-0.542498	-0.135770
2	6	0	-1.415900	0.214874	0.015124
3	6	0	1.415896	0.214884	0.015125
4	6	0	1.731514	0.587497	1.477412
5	1	0	2.737222	1.022305	1.516361
6	1	0	1.042113	1.334574	1.879323
7	1	0	1.740518	-0.280760	2.144166
8	6	0	1.565488	1.481139	-0.851495
9	1	0	2.623715	1.767755	-0.870934
10	1	0	1.240364	1.308245	-1.878977
11	1	0	1.012906	2.331306	-0.446448
12	6	0	2.476134	-0.812565	-0.463246
13	1	0	2.421575	-1.740475	0.110308
14	1	0	2.333957	-1.048504	-1.528787
15	1	0	3.484169	-0.395073	-0.360605
16	6	0	-1.565518	1.481097	-0.851543
17	1	0	-1.012947	2.331288	-0.446534
18	1	0	-1.240398	1.308168	-1.879021
19	1	0	-2.623750	1.767694	-0.870985
20	6	0	-1.731507	0.587544	1.477398
21	1	0	-1.740461	-0.280676	2.144201
22	1	0	-1.042127	1.334671	1.879256
23	1	0	-2.737231	1.022312	1.516348
24	6	0	-2.476132	-0.812600	-0.463207
25	1	0	-3.484170	-0.395116	-0.360572
26	1	0	-2.333956	-1.048569	-1.528741
27	1	0	-2.421559	-1.740494	0.110370
28	6	0	0.000027	-1.045567	-1.520501
29	1	0	0.000083	-2.151224	-1.461471
30	8	0	0.000003	-1.655911	0.803284
31	1	0	-0.000034	-1.322962	1.710692

Input File:

%nprocshared=4

%mem=300MW

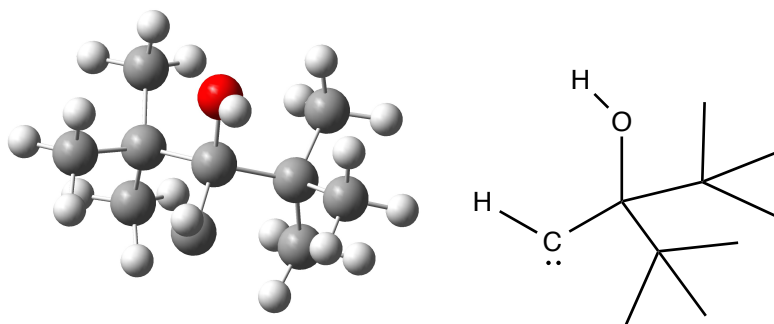
%chk=singcarbd180.chk

opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1

C	-0.00000600	-0.54206600	-0.13584800
C	-1.41675900	0.21431300	0.01522800
C	1.41674700	0.21437000	0.01520000
C	1.73807100	0.58004300	1.47829000
H	2.73930200	1.02820700	1.51382000
H	1.04197300	1.31598500	1.89195100
H	1.76358800	-0.29331900	2.13977300
C	1.56549000	1.48541000	-0.84478900
H	2.62553400	1.76963500	-0.86905000
H	1.23440100	1.32076000	-1.87275900
H	1.01783200	2.33622100	-0.43143100
C	2.47750800	-0.80946600	-0.46982600
H	2.42260100	-1.74313600	0.09632300
H	2.33895600	-1.03757000	-1.53858200
H	3.48666300	-0.39315000	-0.36058500
C	-1.56580900	1.48502300	-0.84523800
H	-1.01823100	2.33606900	-0.43227300
H	-1.23482300	1.32002300	-1.87318100
H	-2.62589900	1.76906400	-0.86946500
C	-1.73783800	0.58058100	1.47819700
H	-1.76279900	-0.29241400	2.14019900
H	-1.04192600	1.31702500	1.89126400
H	-2.73924900	1.02834200	1.51378300
C	-2.47752500	-0.80978900	-0.46925600
H	-3.48669900	-0.39351300	-0.36000800
H	-2.33910000	-1.03821500	-1.53796400
H	-2.42243600	-1.74327900	0.09716100
C	0.00006200	-1.04363000	-1.52124900
H	0.00027600	-2.14986900	-1.46500200
O	0.00004900	-1.65776800	0.80119700
H	-0.00000300	-1.32345700	1.71220400

β -bis(*tert*)-butanol carbene: **13** (Singlet with $C\alpha-C\beta-O-H$ of 30°)



SCF Done: E(RB3LYP) = -468.218592749 A.U. after 7 cycles
 Conv = 0.3871D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.002117	-0.547112	-0.150307
2	6	0	-1.410579	0.222822	0.015271
3	6	0	1.413171	0.217336	0.020617
4	6	0	1.619642	0.694149	1.469125
5	1	0	2.665005	1.001669	1.595753
6	1	0	0.996255	1.560657	1.704946
7	1	0	1.402835	-0.098527	2.188117
8	6	0	1.635880	1.405773	-0.938193
9	1	0	2.686512	1.712869	-0.871247
10	1	0	1.420417	1.140360	-1.975119
11	1	0	1.034448	2.275455	-0.671762
12	6	0	2.501296	-0.840819	-0.308848
13	1	0	2.466781	-1.695564	0.373019
14	1	0	2.405492	-1.204654	-1.342294
15	1	0	3.497570	-0.394623	-0.219288
16	6	0	-1.518806	1.533223	-0.785185
17	1	0	-0.947272	2.344052	-0.327754
18	1	0	-1.191212	1.410817	-1.819623
19	1	0	-2.568629	1.849315	-0.793469
20	6	0	-1.736113	0.508235	1.493764
21	1	0	-1.675930	-0.394954	2.102628
22	1	0	-1.076999	1.264181	1.926462
23	1	0	-2.760851	0.896128	1.549954
24	6	0	-2.477253	-0.763456	-0.531799
25	1	0	-3.479009	-0.328660	-0.441162
26	1	0	-2.313877	-0.966314	-1.602094
27	1	0	-2.461592	-1.707834	0.017376
28	6	0	-0.019764	-1.024460	-1.538559
29	1	0	-0.055702	-2.134935	-1.538482
30	8	0	-0.054728	-1.573478	0.889511
31	1	0	0.361453	-2.375759	0.552634

Input File:

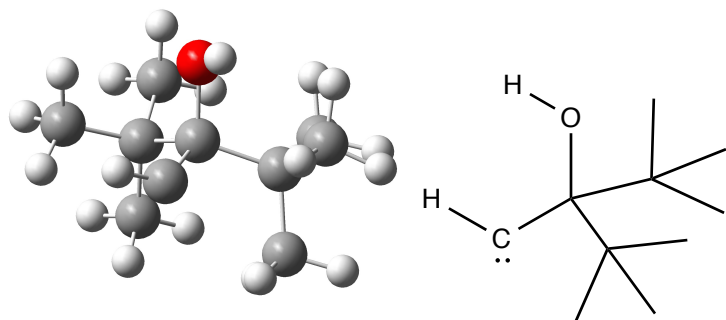
%chk=singcarbd30.chk

opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1

C	-0.00188400	-0.54759400	-0.15154200
C	-1.41050200	0.22282700	0.01474500
C	1.41342300	0.21596000	0.02021900
C	1.61529900	0.70547300	1.46525800
H	2.66278900	1.00858800	1.59556100
H	0.99570600	1.57908400	1.68993900
H	1.39035700	-0.07887700	2.19244700
C	1.64486600	1.39630300	-0.94707200
H	2.69549000	1.70593200	-0.87211500
H	1.44099100	1.12221900	-1.98516100
H	1.03963600	2.26903200	-0.69567500
C	2.50235400	-0.84571600	-0.29494100
H	2.46850200	-1.69308600	0.39780700
H	2.40886000	-1.22353000	-1.32475300
H	3.49949000	-0.39782300	-0.20945200
C	-1.51353300	1.54068900	-0.77411200
H	-0.94491600	2.34825400	-0.30453500
H	-1.17871000	1.42918200	-1.80852800
H	-2.56425400	1.85787800	-0.78717200
C	-1.74094400	0.49681200	1.49457900
H	-1.69384700	-0.41327700	2.09595100
H	-1.07612300	1.24192400	1.93962400
H	-2.76302800	0.89517400	1.54965600
C	-2.47971300	-0.75519900	-0.54216800
H	-3.48166700	-0.31956800	-0.44349700
H	-2.32060700	-0.94724000	-1.61604400
H	-2.46615700	-1.70708900	-0.00380700
C	-0.02256000	-1.02421600	-1.54017500
H	-0.06836900	-2.13482800	-1.54125500
O	-0.05605600	-1.57432200	0.88878500
H	0.36347000	-2.37941200	0.55198100

β -bis(*tert*)-butanol carbene: **13** (Triplet with $C\alpha-C\beta-O-H$ of 45°)



SCF Done: E(UB3LYP) = -468.223768161 A.U. after 7 cycles
 Conv = 0.3202D-08 -V/T = 2.0098
 S**2= 2.0067

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.003356	0.577712	-0.098652
2	6	0	1.387190	-0.225817	-0.007755
3	6	0	-1.395179	-0.211469	-0.005335
4	6	0	-1.461146	-1.222570	1.154671
5	1	0	-2.493006	-1.577133	1.262926
6	1	0	-0.836506	-2.101837	0.978519
7	1	0	-1.164008	-0.765345	2.102586
8	6	0	-1.742144	-0.933934	-1.328061
9	1	0	-2.740257	-1.379351	-1.243562
10	1	0	-1.759993	-0.236365	-2.172151
11	1	0	-1.046746	-1.737873	-1.570458
12	6	0	-2.519852	0.829855	0.237880
13	1	0	-2.457059	1.278356	1.234783
14	1	0	-2.505519	1.627051	-0.514380
15	1	0	-3.494489	0.334979	0.172464
16	6	0	1.454782	-1.416269	-0.981959
17	1	0	0.798187	-2.238646	-0.686264
18	1	0	1.203172	-1.119984	-2.005603
19	1	0	2.477753	-1.809708	-0.993715
20	6	0	1.687813	-0.724599	1.425641
21	1	0	1.651073	0.094768	2.146323
22	1	0	1.008005	-1.507832	1.759702
23	1	0	2.699700	-1.146311	1.441704
24	6	0	2.535702	0.747366	-0.382577
25	1	0	3.498188	0.260958	-0.190467
26	1	0	2.515900	1.018207	-1.442804
27	1	0	2.492921	1.661615	0.215271
28	6	0	-0.039681	1.397893	-1.338143
29	1	0	0.539948	2.247985	-1.681369
30	8	0	0.094641	1.499463	1.027682
31	1	0	-0.569161	2.191750	0.910781

Input File:

%nprocshared=4

%mem=300MW

%chk=tripcarbd30.chk

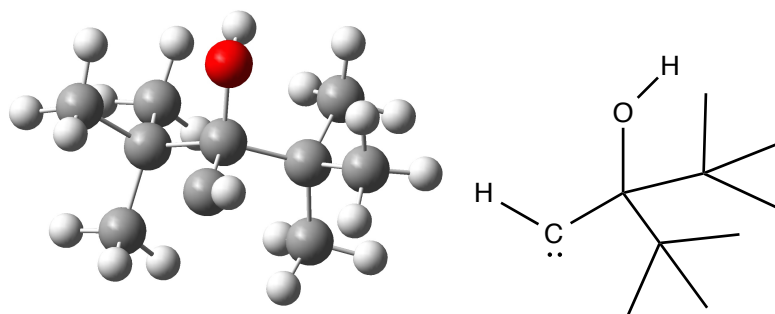
opt=tight freq ub3lyp/6-31+g(d,p) geom=connectivity

0 3

C	-0.00188400	-0.54759400	-0.15154200
C	-1.41050200	0.22282700	0.01474500
C	1.41342300	0.21596000	0.02021900
C	1.61529900	0.70547300	1.46525800
H	2.66278900	1.00858800	1.59556100
H	0.99570600	1.57908400	1.68993900
H	1.39035700	-0.07887700	2.19244700
C	1.64486600	1.39630300	-0.94707200
H	2.69549000	1.70593200	-0.87211500
H	1.44099100	1.12221900	-1.98516100
H	1.03963600	2.26903200	-0.69567500

C	2.50235400	-0.84571600	-0.29494100
H	2.46850200	-1.69308600	0.39780700
H	2.40886000	-1.22353000	-1.32475300
H	3.49949000	-0.39782300	-0.20945200
C	-1.51353300	1.54068900	-0.77411200
H	-0.94491600	2.34825400	-0.30453500
H	-1.17871000	1.42918200	-1.80852800
H	-2.56425400	1.85787800	-0.78717200
C	-1.74094400	0.49681200	1.49457900
H	-1.69384700	-0.41327700	2.09595100
H	-1.07612300	1.24192400	1.93962400
H	-2.76302800	0.89517400	1.54965600
C	-2.47971300	-0.75519900	-0.54216800
H	-3.48166700	-0.31956800	-0.44349700
H	-2.32060700	-0.94724000	-1.61604400
H	-2.46615700	-1.70708900	-0.00380700
C	-0.02256000	-1.02421600	-1.54017500
H	-0.06836900	-2.13482800	-1.54125500
O	-0.05605600	-1.57432200	0.88878500
H	0.36347000	-2.37941200	0.55198100

β -bis(*tert*)-butanol carbene: **13** (Triplet with $C\alpha-C\beta-O-H$ of 180°)



SCF Done: E(UB3LYP) = -468.218996219 A.U. after 8 cycles
 Conv g = 0.4593D-08 -V/T = 2.0098
 S**2= 2.0060

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.005211	0.589168	-0.085431
2	6	0	1.401119	-0.201382	-0.005320
3	6	0	-1.388427	-0.222622	-0.018205
4	6	0	-1.713359	-0.748280	1.401415
5	1	0	-2.680474	-1.262850	1.371418
6	1	0	-0.983570	-1.462384	1.783269
7	1	0	-1.820935	0.066382	2.126159
8	6	0	-1.448085	-1.402674	-1.006467
9	1	0	-2.476206	-1.779942	-1.056906
10	1	0	-1.159025	-1.096705	-2.016806
11	1	0	-0.812763	-2.238727	-0.701982
12	6	0	-2.530594	0.757755	-0.388862

13	1	0	-2.474019	1.675172	0.203667
14	1	0	-2.506923	1.026870	-1.449113
15	1	0	-3.498658	0.283104	-0.193053
16	6	0	1.730468	-0.947669	-1.319667
17	1	0	1.069582	-1.793637	-1.511547
18	1	0	1.681551	-0.274635	-2.182060
19	1	0	2.752933	-1.338712	-1.263277
20	6	0	1.487703	-1.207896	1.160220
21	1	0	1.239383	-0.756675	2.128052
22	1	0	0.846185	-2.080159	1.011454
23	1	0	2.517850	-1.573401	1.239159
24	6	0	2.519884	0.851097	0.205286
25	1	0	3.495074	0.351763	0.186773
26	1	0	2.508263	1.605422	-0.587540
27	1	0	2.418282	1.373321	1.158938
28	6	0	0.044287	1.408059	-1.325881
29	1	0	-0.452678	2.319795	-1.634945
30	8	0	-0.032573	1.574427	0.982135
31	1	0	-0.052499	1.107248	1.828729

Input File:

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%mem=300MW

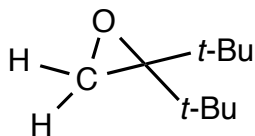
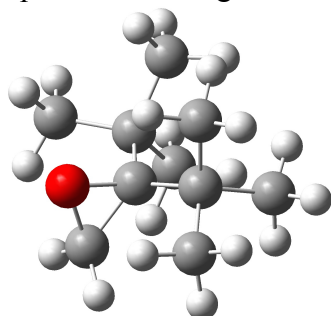
%chk=tripcarbd180.chk

opt=tight freq ub3lyp/6-31+g(d,p) geom=connectivity

0 3

C	-0.00000600	-0.54206600	-0.13584800
C	-1.41675900	0.21431300	0.01522800
C	1.41674700	0.21437000	0.01520000
C	1.73807100	0.58004300	1.47829000
H	2.73930200	1.02820700	1.51382000
H	1.04197300	1.31598500	1.89195100
H	1.76358800	-0.29331900	2.13977300
C	1.56549000	1.48541000	-0.84478900
H	2.62553400	1.76963500	-0.86905000
H	1.23440100	1.32076000	-1.87275900
H	1.01783200	2.33622100	-0.43143100
C	2.47750800	-0.80946600	-0.46982600
H	2.42260100	-1.74313600	0.09632300
H	2.33895600	-1.03757000	-1.53858200
H	3.48666300	-0.39315000	-0.36058500
C	-1.56580900	1.48502300	-0.84523800
H	-1.01823100	2.33606900	-0.43227300
H	-1.23482300	1.32002300	-1.87318100
H	-2.62589900	1.76906400	-0.86946500
C	-1.73783800	0.58058100	1.47819700
H	-1.76279900	-0.29241400	2.14019900
H	-1.04192600	1.31702500	1.89126400
H	-2.73924900	1.02834200	1.51378300
C	-2.47752500	-0.80978900	-0.46925600
H	-3.48669900	-0.39351300	-0.36000800
H	-2.33910000	-1.03821500	-1.53796400

H	-2.42243600	-1.74327900	0.09716100
C	0.00006200	-1.04363000	-1.52124900
H	0.00027600	-2.14986900	-1.46500200
O	0.00004900	-1.65776800	0.80119700
H	-0.00000300	-1.32345700	1.71220400

Epoxide Rearrangement Product: **23**

SCF Done: E(RB3LYP) = -468.330151159 A.U. after 8 cycles
 Conv g = 0.3199D-08 -V/T = 2.0099

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.005205	0.487836	0.044570
2	6	0	-1.380236	-0.262092	0.018623
3	6	0	1.379857	-0.272625	0.014488
4	6	0	1.667233	-0.788311	-1.417648
5	1	0	2.685014	-1.191762	-1.463592
6	1	0	0.989671	-1.581447	-1.732934
7	1	0	1.596947	0.031495	-2.139163
8	6	0	1.445934	-1.439101	1.023832
9	1	0	2.450254	-1.877070	1.000220
10	1	0	1.263328	-1.092956	2.047040
11	1	0	0.740250	-2.242772	0.804526
12	6	0	2.548299	0.680521	0.371259
13	1	0	2.553166	1.571400	-0.263378
14	1	0	2.524477	0.990228	1.421233
15	1	0	3.495500	0.154657	0.213397
16	6	0	-1.424351	-1.490436	-0.919823
17	1	0	-1.208848	-1.211301	-1.955538
18	1	0	-0.737523	-2.286430	-0.626194
19	1	0	-2.434275	-1.914946	-0.898550
20	6	0	-2.496175	0.686943	-0.487598
21	1	0	-2.645729	1.556057	0.158363
22	1	0	-2.284249	1.049466	-1.495637
23	1	0	-3.443316	0.137458	-0.507253
24	6	0	-1.755310	-0.709631	1.452289
25	1	0	-1.072681	-1.461475	1.853437
26	1	0	-1.764165	0.139822	2.143905
27	1	0	-2.760825	-1.145978	1.451918
28	6	0	-0.026458	1.853067	0.620663
29	1	0	0.857369	2.288552	1.075813

30	8	0	0.046941	1.667661	-0.799363
31	1	0	-0.963884	2.268685	0.983365

Input File:

%nprocshared=6

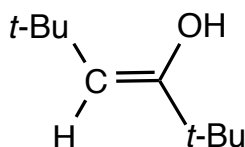
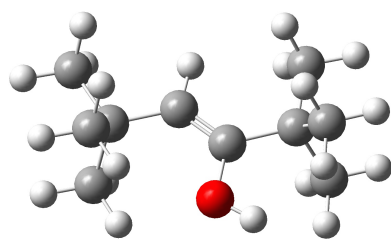
%mem=300MW

%chk=epoxideder.chk

opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1

C	0.38178352	3.13937194	-0.01692818
C	-1.14798684	3.14751228	0.16009267
C	0.67263829	4.44694270	-0.77670592
C	0.65706864	5.62868954	0.21062989
H	0.85915605	6.53719649	-0.31726763
H	-0.30463620	5.69256137	0.67532784
H	1.40586820	5.47739460	0.95983551
C	-0.40507323	4.66469430	-1.85500185
H	-0.20298582	5.57320125	-2.38289937
H	-0.39425536	3.84361046	-2.54100790
H	-1.36677807	4.72856613	-1.39030390
C	2.05677423	4.35501502	-1.44552353
H	2.80557379	4.20372008	-0.69631791
H	2.06759210	3.53393118	-2.13152958
H	2.25886164	5.26352198	-1.97342105
C	-1.56426023	4.38848012	0.97145898
H	-1.09417544	4.36058843	1.93226194
H	-1.26068153	5.27294678	0.45140252
H	-2.62715262	4.39413607	1.09445398
C	-1.58491318	1.87454158	0.90858514
H	-1.29568427	1.01231067	0.34484362
H	-1.11482839	1.84664988	1.86938811
H	-2.64780558	1.88019753	1.03158015
C	-1.82455747	3.18765547	-1.22274524
H	-1.52097878	4.07212212	-1.74280170
H	-1.53532856	2.32542456	-1.78648676
H	-2.88744986	3.19331141	-1.09975024
C	1.08959495	1.97486865	-0.25660801
H	1.80658122	2.74542343	-0.44915937
O	1.38661110	2.54362301	1.10954668
H	0.26667010	1.64634635	0.34319845

Ketone-enol Rearrangement Product: **24a**

SCF Done: E(RB3LYP) = -468.367870372 A.U. after 16 cycles
 Convg = 0.1587D-08 -V/T = 2.0100

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.499428	-0.253428	0.000001
2	6	0	1.963243	0.199363	-0.000004
3	6	0	-2.050362	0.131820	0.000002
4	6	0	-2.391182	-0.693341	1.263537
5	1	0	-3.455119	-0.961642	1.268035
6	1	0	-1.803598	-1.613717	1.303245
7	1	0	-2.184356	-0.115921	2.171797
8	6	0	-2.391175	-0.693360	-1.263529
9	1	0	-3.455113	-0.961653	-1.268035
10	1	0	-2.184328	-0.115955	-2.171793
11	1	0	-1.803596	-1.613740	-1.303212
12	6	0	-2.910947	1.412990	-0.000010
13	1	0	-2.708176	2.025156	0.887005
14	1	0	-2.708174	2.025140	-0.887036
15	1	0	-3.978176	1.164219	-0.000009
16	6	0	2.093426	1.733078	-0.000005
17	1	0	1.632415	2.177093	-0.887621
18	1	0	1.632377	2.177098	0.887587
19	1	0	3.153169	2.009612	0.000016
20	6	0	2.673828	-0.345592	-1.266080
21	1	0	2.668453	-1.440745	-1.319543
22	1	0	2.193352	0.031845	-2.174289
23	1	0	3.722951	-0.030222	-1.274058
24	6	0	2.673827	-0.345580	1.266088
25	1	0	3.722951	-0.030216	1.274054
26	1	0	2.193350	0.031885	2.174285
27	1	0	2.668437	-1.440730	1.319569
28	6	0	-0.579346	0.546584	-0.000001
29	1	0	-0.389601	1.613519	-0.000016
30	8	0	0.305617	-1.625273	-0.000001
31	1	0	1.153402	-2.084045	0.000033

Input File:

%nprocshared=4

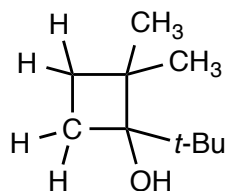
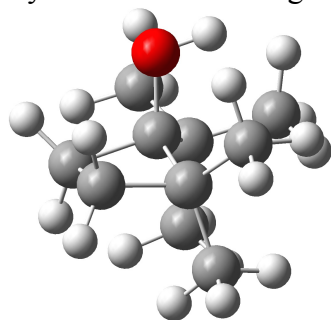
%mem=300MW

%chk=ketoneenolder.chk

opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1			
C	-0.48021988	0.15018174	0.42890857
C	-1.96898134	0.16940612	0.03543718
C	1.96274665	0.07864269	-0.13851696
C	2.12281202	-0.60617338	1.23152173
H	3.15721125	-0.61952866	1.50490763
H	1.56622563	-0.06506129	1.96793826
H	1.75621341	-1.60974397	1.17362930
C	2.49037455	1.52303401	-0.05519515
H	3.52477379	1.50967873	0.21819075
H	2.37916030	1.99884777	-1.00710515
H	1.93378817	2.06414610	0.68122137
C	2.76381490	-0.70015416	-1.19840617
H	2.39721629	-1.70372475	-1.25629859
H	2.65260065	-0.22434039	-2.15031617
H	3.79821414	-0.71350943	-0.92502026
C	-2.12904559	0.85422444	-1.33460052
H	-1.76244551	1.85779441	-1.27670659
H	-1.57245995	0.31311260	-2.07101779
H	-3.16344479	0.86758164	-1.60798649
C	-2.77004853	0.94820260	1.09532746
H	-2.65883506	0.47238728	2.04723678
H	-2.40344845	1.95177257	1.15322139
H	-3.80444773	0.96155980	0.82194150
C	-2.49661137	-1.27498429	-0.04788679
H	-3.53101057	-1.26162709	-0.32127275
H	-1.94002573	-1.81609613	-0.78430406
H	-2.38539790	-1.75079962	0.90402253
C	0.47398513	0.09786430	-0.53198826
H	0.19297975	0.06991227	-1.56405156
O	-0.10467069	0.18753562	1.80820821
H	-0.00107252	1.10028843	2.08704460

Cyclobutanol Rearrangement Product: 25



SCF Done: E(RB3LYP) = -468.349406609 A.U. after 6 cycles
 Conv = 0.4041D-08 -V/T = 2.0099

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	O	-0.004024	-0.494525	0.023339
2	6	O	-1.408062	0.202523	0.004420

3	6	0	1.408541	0.269357	0.040530
4	6	0	2.088891	0.435903	1.403152
5	1	0	3.119268	0.783554	1.260610
6	1	0	1.579499	1.182639	2.026067
7	1	0	2.139050	-0.506377	1.955656
8	6	0	1.485552	1.600773	-0.720921
9	1	0	2.539462	1.887653	-0.823164
10	1	0	1.068813	1.535389	-1.729221
11	1	0	0.975724	2.412934	-0.191401
12	6	0	1.945666	-0.894319	-0.854946
13	1	0	2.436530	-1.673891	-0.266784
14	1	0	0.166891	-0.824311	-2.160133
15	1	0	2.604670	-0.599612	-1.678453
16	6	0	-1.626834	1.162386	-1.186560
17	1	0	-1.035982	2.076489	-1.112138
18	1	0	-1.404359	0.686631	-2.146806
19	1	0	-2.681048	1.460924	-1.212886
20	6	0	-1.625453	1.002991	1.308901
21	1	0	-1.606247	0.362610	2.198560
22	1	0	-0.871832	1.788236	1.434334
23	1	0	-2.607846	1.488474	1.294642
24	6	0	-2.487017	-0.901984	-0.097925
25	1	0	-3.486104	-0.451276	-0.084440
26	1	0	-2.388213	-1.461477	-1.035195
27	1	0	-2.415245	-1.615793	0.725237
28	6	0	0.489530	-1.275771	-1.218874
29	1	0	0.230955	-2.337589	-1.221364
30	8	0	0.007613	-1.477083	1.078714
31	1	0	-0.025622	-1.022551	1.930467

Input File:

%nprocshared=6

%mem=300MW

%chk=cyclobutanolder.chk

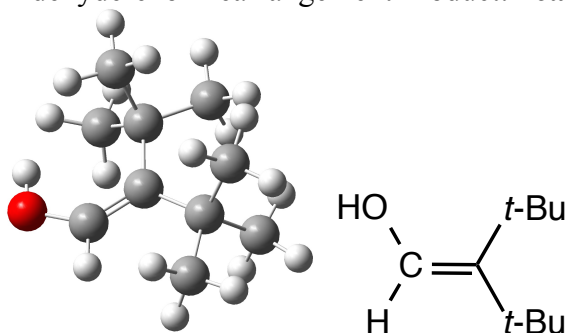
opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1

C	-2.53123932	1.91041169	0.12000286
C	-3.91185254	2.59204997	0.09039892
C	-1.29926780	2.69798096	0.37332297
C	-0.92007157	3.16525108	1.79088032
H	0.06381810	3.58555776	1.77661823
H	-1.61908589	3.90479651	2.12156378
H	-0.94147943	2.33006070	2.45938517
C	-1.23156946	3.97856846	-0.47938601
H	-0.24068895	4.38055678	-0.44116016
H	-1.48319980	3.74584703	-1.49300473
H	-1.92378246	4.69906041	-0.09645976
C	-0.62397831	1.55717773	-0.26441761
H	-0.54901506	0.74069699	0.42307037
H	-1.53721567	2.10912858	-1.91819875
H	0.34990003	1.68316288	-0.68937493
C	-3.89162225	3.74862753	-0.92622248

H	-3.14758272	4.46226526	-0.63982003
H	-3.66234844	3.36498009	-1.89840978
H	-4.85087949	4.22223335	-0.94679145
C	-4.24183542	3.14421544	1.48962177
H	-4.25589153	2.34061934	2.19597560
H	-3.49779589	3.85785317	1.77602422
H	-5.20109266	3.61782126	1.46905280
C	-4.98271318	1.56494519	-0.32180647
H	-5.94197042	2.03855101	-0.34237545
H	-4.75343936	1.18129775	-1.29399378
H	-4.99676929	0.76134909	0.38454735
C	-1.88782825	1.36704056	-1.23170316
H	-1.66118905	0.33921383	-1.42433464
O	-2.63428048	0.85983940	1.08466881
H	-2.85337497	1.23273197	1.94172700

Aldehyde-enol Rearrangement Product: **26a**



SCF Done: E(RB3LYP) = -468.340746745 A.U. after 5 cycles
 Convgt = 0.6885D-08 -V/T = 2.0100

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.014090	0.400520	-0.070020
2	6	0	1.184134	-0.605122	0.004760
3	6	0	-1.509130	-0.051680	-0.021707
4	6	0	-1.801514	-0.892218	1.250403
5	1	0	-2.855642	-1.194129	1.262149
6	1	0	-1.205539	-1.803126	1.320219
7	1	0	-1.613050	-0.299784	2.152407
8	6	0	-1.928026	-0.841109	-1.291924
9	1	0	-3.009311	-1.022398	-1.273911
10	1	0	-1.701198	-0.261762	-2.193656
11	1	0	-1.442490	-1.811472	-1.382822
12	6	0	-2.492195	1.145475	0.052835
13	1	0	-2.327506	1.764509	0.940287
14	1	0	-2.440459	1.784001	-0.835269
15	1	0	-3.513740	0.756070	0.111828
16	6	0	0.873230	-2.046123	-0.472591
17	1	0	0.036840	-2.512674	0.046386
18	1	0	0.674337	-2.079844	-1.547724
19	1	0	1.754667	-2.669145	-0.284004

20	6	0	1.682714	-0.687588	1.472878
21	1	0	1.934976	0.302995	1.866170
22	1	0	0.919589	-1.116381	2.128202
23	1	0	2.577755	-1.318912	1.540980
24	6	0	2.382873	-0.167652	-0.898329
25	1	0	3.007420	-1.037772	-1.125948
26	1	0	2.046367	0.259411	-1.847603
27	1	0	3.072042	0.538955	-0.416644
28	6	0	0.206163	1.732481	-0.060071
29	1	0	-0.603827	2.445657	-0.071568
30	8	0	1.380454	2.438444	-0.016794
31	1	0	2.140196	1.846346	-0.052523

Input File:

%nprocshared=4

%mem=300MW

%chk=aldehydeenolder.chk

opt=tight freq b3lyp/6-31+g(d,p) geom=connectivity

0 1

C	0.02775538	-0.50515828	0.02685211
C	-1.23339055	0.35170625	0.24340264
C	1.38188783	0.17398066	-0.25008763
C	2.10498387	0.43996451	1.08332330
H	3.04584213	0.91183377	0.89090413
H	1.50314790	1.08017973	1.69391149
H	2.26837247	-0.48731301	1.59161512
C	1.14673040	1.50856699	-0.98164781
H	2.08758866	1.98043625	-1.17406698
H	0.64431951	1.32376003	-1.90810865
H	0.54489443	2.14878221	-0.37105962
C	2.24808165	-0.74745059	-1.12887811
H	2.41147025	-1.67472811	-0.62058629
H	1.74567076	-0.93225755	-2.05533895
H	3.18893991	-0.27558133	-1.32129728
C	-1.10745338	1.66175380	-0.55629433
H	-0.24699295	2.20259623	-0.22163433
H	-1.00416127	1.43578528	-1.59704837
H	-1.98370412	2.25710773	-0.40583390
C	-1.38205396	0.67693196	1.74131032
H	-1.46955576	-0.23329588	2.29694393
H	-0.52159353	1.21777440	2.07597032
H	-2.25830470	1.27228589	1.89177075
C	-2.47181023	-0.42670249	-0.23825755
H	-3.34806097	0.16865144	-0.08779712
H	-2.36851812	-0.65267100	-1.27901159
H	-2.55931202	-1.33693033	0.31737606
C	-0.05407276	-1.85684133	0.07999462
H	0.82217797	-2.45219526	-0.07046589
O	-1.31148144	-2.48747034	0.33715305
H	-1.85144637	-1.91307164	0.88497054

Part Two: Minimized Transition State Structured
(one imaginary frequency found for each TS structure)

13 (S, C α -C β -O-H = 30°) to **13** (S, C α -C β -O-H = 180°): Transition State

SCF Done: E(RB3LYP) = -468.215845827 A.U. after 9 cycles
 Conv = 0.3432D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.003751	-0.546627	-0.153823
2	6	0	-1.413074	0.216239	0.028920
3	6	0	1.409791	0.209211	0.011532
4	6	0	1.751715	0.546373	1.478618
5	1	0	2.753028	0.991429	1.507756
6	1	0	1.056307	1.267771	1.911155
7	1	0	1.775922	-0.326518	2.140037
8	6	0	1.520892	1.505863	-0.814918
9	1	0	2.572708	1.813254	-0.848648
10	1	0	1.172361	1.361028	-1.838940
11	1	0	0.961533	2.328501	-0.365066
12	6	0	2.485350	-0.773632	-0.532074
13	1	0	2.503490	-1.728773	0.003557
14	1	0	2.314194	-0.983284	-1.597518
15	1	0	3.483073	-0.329885	-0.444820
16	6	0	-1.622539	1.443140	-0.882600
17	1	0	-1.047553	2.311199	-0.555610
18	1	0	-1.370211	1.228622	-1.922745
19	1	0	-2.680520	1.728055	-0.837794
20	6	0	-1.640225	0.637671	1.491630
21	1	0	-1.459200	-0.189374	2.180682
22	1	0	-1.010208	1.484518	1.778344
23	1	0	-2.682981	0.958564	1.605402
24	6	0	-2.490498	-0.835602	-0.353450
25	1	0	-3.491306	-0.410609	-0.217557
26	1	0	-2.405373	-1.120577	-1.412737
27	1	0	-2.408497	-1.736392	0.257870
28	6	0	-0.034433	-1.017479	-1.552649
29	1	0	-0.106359	-2.121300	-1.513671
30	8	0	-0.066832	-1.636806	0.821896
31	1	0	0.779858	-1.742723	1.268014

Input File:

%nprocshared=4

%mem=12GB

%chk=ts_singletdihedrals.chk

opt=(tight,qst2) freq b3lyp/6-31+g(d,p) geom=connectivity

singlet carbene dihedral 30 to 180 ts

0 1

C	-3.43579235	4.08469939	0.00000000
C	-4.85168735	4.84207139	0.15089400
C	-2.01989135	4.84208139	0.15089500
C	-1.70427335	5.21469439	1.61318200
H	-0.69856535	5.64950239	1.65213100
H	-2.39367435	5.96177139	2.01509300
H	-1.69526935	4.34643739	2.27993600
C	-1.87029935	6.10833639	-0.71572500
H	-0.81207235	6.39495239	-0.73516400
H	-2.19542335	5.93544239	-1.74320700
H	-2.42288135	6.95850339	-0.31067800
C	-0.95965335	3.81463239	-0.32747600
H	-1.01421235	2.88672239	0.24607800
H	-1.10183035	3.57869339	-1.39301700
H	0.04838165	4.23212439	-0.22483500
C	-5.00130535	6.10829439	-0.71577300
H	-4.44873435	6.95848539	-0.31076400
H	-4.67618535	5.93536539	-1.74325100
H	-6.05953735	6.39489139	-0.73521500
C	-5.16729435	5.21474139	1.61316800
H	-5.17624835	4.34652139	2.27997100
H	-4.47791435	5.96186839	2.01502600
H	-6.17301835	5.64950939	1.65211800
C	-5.91191935	3.81459739	-0.32743700
H	-6.91995735	4.23208139	-0.22480200
H	-5.76974335	3.57862839	-1.39297100
H	-5.85734635	2.88670339	0.24614000
C	-3.43576035	3.58163039	-1.38473100
H	-3.43570435	2.47597339	-1.32570100
O	-3.43578435	2.97128639	0.93905400
H	-3.43582135	3.30423539	1.84646200
0 1			
C	-0.00211700	-0.54711200	-0.15030700
C	-1.41057900	0.22282200	0.01527100
C	1.41317100	0.21733600	0.02061700
C	1.61964200	0.69414900	1.46912500
H	2.66500500	1.00166900	1.59575300
H	0.99625500	1.56065700	1.70494600
H	1.40283500	-0.09852700	2.18811700
C	1.63588000	1.40577300	-0.93819300
H	2.68651200	1.71286900	-0.87124700
H	1.42041700	1.14036000	-1.97511900
H	1.03444800	2.27545500	-0.67176200
C	2.50129600	-0.84081900	-0.30884800
H	2.46678100	-1.69556400	0.37301900
H	2.40549200	-1.20465400	-1.34229400
H	3.49757000	-0.39462300	-0.21928800
C	-1.51880600	1.53322300	-0.78518500
H	-0.94727200	2.34405200	-0.32775400
H	-1.19121200	1.41081700	-1.81962300
H	-2.56862900	1.84931500	-0.79346900
C	-1.73611300	0.50823500	1.49376400
H	-1.67593000	-0.39495400	2.10262800
H	-1.07699900	1.26418100	1.92646200

H	-2.76085100	0.89612800	1.54995400
C	-2.47725300	-0.76345600	-0.53179900
H	-3.47900900	-0.32866000	-0.44116200
H	-2.31387700	-0.96631400	-1.60209400
H	-2.46159200	-1.70783400	0.01737600
C	-0.01976400	-1.02446000	-1.53855900
H	-0.05570200	-2.13493500	-1.53848200
O	-0.05472800	-1.57347800	0.88951100
H	0.36145300	-2.37575900	0.55263400

13 (T, C α -C β -O-H = 180°) to 13 (T, C α -C β -O-H = 45°): Transition State

SCF Done: E(UB3LYP) = -468.218575008 A.U. after 9 cycles
 Conv = 0.5369D-08 -V/T = 2.0098
 S**2= 2.0064

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.011878	0.584563	-0.084117
2	6	0	1.402835	-0.207198	0.001149
3	6	0	-1.383885	-0.219894	-0.021822
4	6	0	-1.718816	-0.776993	1.385338
5	1	0	-2.680774	-1.298691	1.332058
6	1	0	-0.982014	-1.485208	1.760805
7	1	0	-1.851603	0.006604	2.143566
8	6	0	-1.435240	-1.387441	-1.025415
9	1	0	-2.463449	-1.761293	-1.092691
10	1	0	-1.132156	-1.067582	-2.026818
11	1	0	-0.804383	-2.226755	-0.722527
12	6	0	-2.530107	0.758068	-0.393274
13	1	0	-2.508753	1.668926	0.213384
14	1	0	-2.482298	1.052788	-1.445254
15	1	0	-3.495995	0.267491	-0.229300
16	6	0	1.735464	-0.961155	-1.307524
17	1	0	1.097595	-1.829213	-1.479843
18	1	0	1.658108	-0.302192	-2.178984
19	1	0	2.769107	-1.322609	-1.258883
20	6	0	1.484253	-1.195417	1.180434
21	1	0	1.214096	-0.719905	2.128830
22	1	0	0.854002	-2.077226	1.034616
23	1	0	2.515840	-1.552605	1.278439
24	6	0	2.517953	0.850514	0.206726
25	1	0	3.492998	0.350701	0.218023
26	1	0	2.523935	1.584797	-0.605430
27	1	0	2.390967	1.389756	1.147070
28	6	0	0.045726	1.412358	-1.324066
29	1	0	-0.340624	2.400194	-1.549829
30	8	0	0.008901	1.561249	0.995055
31	1	0	-0.626179	1.287605	1.667766

Input File:

%nprocshared=4

%mem=16GB

%chk=ts_tripletdihedrals.chk

opt=(tight,qst2) freq ub3lyp/6-31+g(d,p) geom=connectivity

triplet dihedral 48 180 ts

0 3

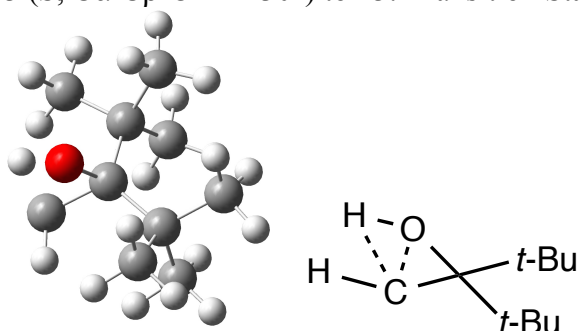
C	-0.12978142	0.56010928	0.00000000
C	1.26076458	-0.24341972	0.09089700
C	-1.52160442	-0.22907172	0.09331700
C	-1.58757142	-1.24017272	1.25332300
H	-2.61943142	-1.59473572	1.36157800
H	-0.96293142	-2.11943972	1.07717100
H	-1.29043342	-0.78294772	2.20123800
C	-1.86856942	-0.95153672	-1.22940900
H	-2.86668242	-1.39695372	-1.14491000
H	-1.88641842	-0.25396772	-2.07349900
H	-1.17317142	-1.75547572	-1.47180600
C	-2.64627742	0.81225228	0.33653200
H	-2.58348442	1.26075328	1.33343500
H	-2.63194442	1.60944828	-0.41572800
H	-3.62091442	0.31737628	0.27111600
C	1.32835658	-1.43387172	-0.88330700
H	0.67176158	-2.25624872	-0.58761200
H	1.07674658	-1.13758672	-1.90695100
H	2.35132758	-1.82731072	-0.89506300
C	1.56138758	-0.74220172	1.52429300
H	1.52464758	0.07716528	2.24497500
H	0.88157958	-1.52543472	1.85835400
H	2.57327458	-1.16391372	1.54035600
C	2.40927658	0.72976328	-0.28392500
H	3.37176258	0.24335528	-0.09181500
H	2.38947458	1.00060428	-1.34415200
H	2.36649558	1.64401228	0.31392300
C	-0.16610642	1.38029028	-1.23949100
H	0.41352258	2.23038228	-1.58271700
O	-0.03178442	1.48186028	1.12633400
H	-0.69558642	2.17414728	1.00943300

0 3

C	0.00521100	0.58916800	-0.08543100
C	1.40111900	-0.20138200	-0.00532000
C	-1.38842700	-0.22262200	-0.01820500
C	-1.71335900	-0.74828000	1.40141500
H	-2.68047400	-1.26285000	1.37141800
H	-0.98357000	-1.46238400	1.78326900
H	-1.82093500	0.06638200	2.12615900
C	-1.44808500	-1.40267400	-1.00646700
H	-2.47620600	-1.77994200	-1.05690600
H	-1.15902500	-1.09670500	-2.01680600
H	-0.81276300	-2.23872700	-0.70198200
C	-2.53059400	0.75775500	-0.38886200
H	-2.47401900	1.67517200	0.20366700

H	-2.50692300	1.02687000	-1.44911300
H	-3.49865800	0.28310400	-0.19305300
C	1.73046800	-0.94766900	-1.31966700
H	1.06958200	-1.79363700	-1.51154700
H	1.68155100	-0.27463500	-2.18206000
H	2.75293300	-1.33871200	-1.26327700
C	1.48770300	-1.20789600	1.16022000
H	1.23938300	-0.75667500	2.12805200
H	0.84618500	-2.08015900	1.01145400
H	2.51785000	-1.57340100	1.23915900
C	2.51988400	0.85109700	0.20528600
H	3.49507400	0.35176300	0.18677300
H	2.50826300	1.60542200	-0.58754000
H	2.41828200	1.37332100	1.15893800
C	0.04428700	1.40805900	-1.32588100
H	-0.45267800	2.31979500	-1.63494500
O	-0.03257300	1.57442700	0.98213500
H	-0.05249900	1.10724800	1.8287290

13 (S, C α -C β -O-H = 30°) to 23: Transition State



SCF Done: E(RB3LYP) = -468.211486147 A.U. after 7 cycles
 Convrg = 0.3769D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.012057	0.513767	0.102524
2	6	0	-1.387163	-0.253499	0.014298
3	6	0	1.370631	-0.249711	0.004995
4	6	0	1.386779	-1.464529	-0.951307
5	1	0	2.400581	-1.879580	-0.970646
6	1	0	0.719056	-2.269340	-0.638815
7	1	0	1.131510	-1.177565	-1.975224
8	6	0	1.774386	-0.736327	1.419939
9	1	0	2.756707	-1.219390	1.373962
10	1	0	1.852182	0.096878	2.126525
11	1	0	1.071823	-1.462307	1.833652
12	6	0	2.490042	0.693149	-0.508921
13	1	0	2.313727	0.998717	-1.542443
14	1	0	2.606034	1.597253	0.093521
15	1	0	3.442750	0.154515	-0.469817
16	6	0	-1.462929	-1.401225	1.044440
17	1	0	-0.752365	-2.206612	0.846784

18	1	0	-1.293626	-1.033157	2.062473
19	1	0	-2.465692	-1.841763	1.018672
20	6	0	-1.650351	-0.792762	-1.412894
21	1	0	-1.475459	-0.013248	-2.161639
22	1	0	-1.040760	-1.658202	-1.670518
23	1	0	-2.698699	-1.099785	-1.494576
24	6	0	-2.562585	0.703130	0.342541
25	1	0	-2.490660	1.114869	1.350366
26	1	0	-2.625716	1.541226	-0.359573
27	1	0	-3.499761	0.142495	0.258542
28	6	0	-0.000615	1.750319	0.947665
29	1	0	1.027030	2.047626	1.184548
30	8	0	-0.006426	1.657815	-0.833834
31	1	0	-0.604077	2.330966	-0.214797

Input File:

%nprocshared=4

%mem=8GB

%chk=ts_singd30epoxide.chk

opt=(tight,qst2) freq b3lyp/6-31+g(d,p) geom=connectivity

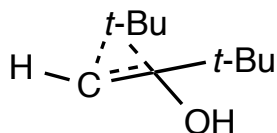
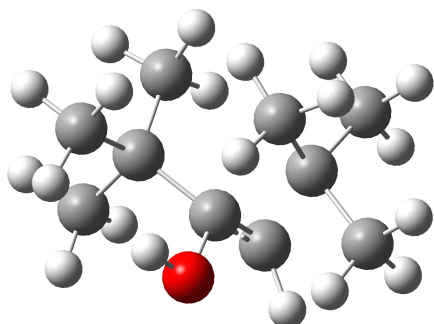
singlet dihedral 30 to epoxide transition state

0 1

C	0.00520500	0.48783600	0.04457000
C	-1.38023600	-0.26209200	0.01862300
C	1.37985700	-0.27262500	0.01448800
C	1.66723300	-0.78831100	-1.41764800
H	2.68501400	-1.19176200	-1.46359200
H	0.98967100	-1.58144700	-1.73293400
H	1.59694700	0.03149500	-2.13916300
C	1.44593400	-1.43910100	1.02383200
H	2.45025400	-1.87707000	1.00022000
H	1.26332800	-1.09295600	2.04704000
H	0.74025000	-2.24277200	0.80452600
C	2.54829900	0.68052100	0.37125900
H	2.55316600	1.57140000	-0.26337800
H	2.52447700	0.99022800	1.42123300
H	3.49550000	0.15465700	0.21339700
C	-1.42435100	-1.49043600	-0.91982300
H	-1.20884800	-1.21130100	-1.95553800
H	-0.73752300	-2.28643000	-0.62619400
H	-2.43427500	-1.91494600	-0.89855000
C	-2.49617500	0.68694300	-0.48759800
H	-2.64572900	1.55605700	0.15836300
H	-2.28424900	1.04946600	-1.49563700
H	-3.44331600	0.13745800	-0.50725300
C	-1.75531000	-0.70963100	1.45228900
H	-1.07268100	-1.46147500	1.85343700
H	-1.76416500	0.13982200	2.14390500
H	-2.76082500	-1.14597800	1.45191800
C	-0.02645800	1.85306700	0.62066300
H	0.85736900	2.28855200	1.07581300

O	0.04694100	1.66766100	-0.79936300
H	-0.96388400	2.26868500	0.98336500
0 1			
C	-0.00211700	-0.54711200	-0.15030700
C	-1.41057900	0.22282200	0.01527100
C	1.41317100	0.21733600	0.02061700
C	1.61964200	0.69414900	1.46912500
H	2.66500500	1.00166900	1.59575300
H	0.99625500	1.56065700	1.70494600
H	1.40283500	-0.09852700	2.18811700
C	1.63588000	1.40577300	-0.93819300
H	2.68651200	1.71286900	-0.87124700
H	1.42041700	1.14036000	-1.97511900
H	1.03444800	2.27545500	-0.67176200
C	2.50129600	-0.84081900	-0.30884800
H	2.46678100	-1.69556400	0.37301900
H	2.40549200	-1.20465400	-1.34229400
H	3.49757000	-0.39462300	-0.21928800
C	-1.51880600	1.53322300	-0.78518500
H	-0.94727200	2.34405200	-0.32775400
H	-1.19121200	1.41081700	-1.81962300
H	-2.56862900	1.84931500	-0.79346900
C	-1.73611300	0.50823500	1.49376400
H	-1.67593000	-0.39495400	2.10262800
H	-1.07699900	1.26418100	1.92646200
H	-2.76085100	0.89612800	1.54995400
C	-2.47725300	-0.76345600	-0.53179900
H	-3.47900900	-0.32866000	-0.44116200
H	-2.31387700	-0.96631400	-1.60209400
H	-2.46159200	-1.70783400	0.01737600
C	-0.01976400	-1.02446000	-1.53855900
H	-0.05570200	-2.13493500	-1.53848200
O	-0.05472800	-1.57347800	0.88951100
H	0.36145300	-2.37575900	0.55263400

13 (S, C α -C β -O-H = 180°) to 24a: Transition State



SCF Done: E(RB3LYP) = -468.216309657 A.U. after 10 cycles
 Conv = 0.2940D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	-0.116795	-0.579675	-0.303385
2	6	0	-1.461451	0.195784	-0.000908
3	6	0	1.480707	0.191997	0.060162
4	6	0	1.351591	0.560807	1.549308
5	1	0	2.341794	0.885496	1.892875
6	1	0	0.661345	1.389058	1.718456
7	1	0	1.058193	-0.289368	2.170759
8	6	0	1.878805	1.454319	-0.727172
9	1	0	2.781352	1.874297	-0.260568
10	1	0	2.099524	1.234840	-1.771943
11	1	0	1.109107	2.224658	-0.704575
12	6	0	2.588504	-0.871550	-0.076341
13	1	0	2.280945	-1.826377	0.354306
14	1	0	2.882104	-1.031949	-1.116829
15	1	0	3.476982	-0.520967	0.463748
16	6	0	-1.427994	1.671333	-0.434959
17	1	0	-0.823531	2.289138	0.235735
18	1	0	-1.041468	1.768779	-1.451693
19	1	0	-2.446877	2.074521	-0.413754
20	6	0	-1.935087	0.119224	1.470766
21	1	0	-2.143335	-0.907779	1.796376
22	1	0	-1.239858	0.574666	2.178741
23	1	0	-2.884328	0.658049	1.560467
24	6	0	-2.528626	-0.529311	-0.864648
25	1	0	-3.519305	-0.096149	-0.684673
26	1	0	-2.294776	-0.418670	-1.928571
27	1	0	-2.575166	-1.596804	-0.628026
28	6	0	0.290905	-0.605894	-1.661269
29	1	0	0.807302	-1.567722	-1.825945
30	8	0	-0.097143	-1.828808	0.384664
31	1	0	-0.476214	-1.729466	1.268484

Input File:

%nprocshared=8

%mem=8GB

%chk=ts_singd180ketoneenol_V3.chk

opt=qst3 freq b3lyp/6-31+g(d,p) geom=connectivity

Singletd180 to ketone enol transition state using qst3 method

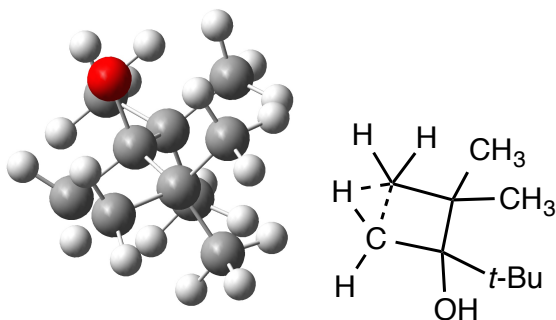
0 1

C	0.15598734	0.79621569	0.04979132
C	-1.25990766	1.55358769	0.20068532
C	1.57188834	1.55359769	0.20068632
C	1.88750634	1.92621069	1.66297332
H	2.89321434	2.36101869	1.70192232
H	1.19810534	2.67328769	2.06488432
H	1.89651034	1.05795369	2.32972732
C	1.72148034	2.81985269	-0.66593368
H	2.77970734	3.10646869	-0.68537268
H	1.39635634	2.64695869	-1.69341568
H	1.16889834	3.67001969	-0.26088668

C	2.63212634	0.52614869	-0.27768468
H	2.57756734	-0.40176131	0.29586932
H	2.48994934	0.29020969	-1.34322568
H	3.64016134	0.94364069	-0.17504368
C	-1.40952566	2.81981069	-0.66598168
H	-0.85695466	3.67000169	-0.26097268
H	-1.08440566	2.64688169	-1.69345968
H	-2.46775766	3.10640769	-0.68542368
C	-1.57551466	1.92625769	1.66295932
H	-1.58446866	1.05803769	2.32976232
H	-0.88613466	2.67338469	2.06481732
H	-2.58123866	2.36102569	1.70190932
C	-2.32013966	0.52611369	-0.27764568
H	-3.32817766	0.94359769	-0.17501068
H	-2.17796366	0.29014469	-1.34317968
H	-2.26556666	-0.40178031	0.29593132
C	0.15601934	0.29314669	-1.33493968
H	0.15607534	-0.81251031	-1.27590968
O	0.15599534	-0.31719731	0.98884532
H	0.15595834	0.01575169	1.89625332
0 1			
C	0.49942800	-0.25342800	0.00000100
C	1.96324300	0.19936300	-0.00000400
C	-2.05036200	0.13182000	0.00000200
C	-2.39118200	-0.69334100	1.26353700
H	-3.45511900	-0.96164200	1.26803500
H	-1.80359800	-1.61371700	1.30324500
H	-2.18435600	-0.11592100	2.17179700
C	-2.39117500	-0.69336000	-1.26352900
H	-3.45511300	-0.96165300	-1.26803500
H	-2.18432800	-0.11595500	-2.17179300
H	-1.80359600	-1.61374000	-1.30321200
C	-2.91094700	1.41299000	-0.00001000
H	-2.70817600	2.02515600	0.88700500
H	-2.70817400	2.02514000	-0.88703600
H	-3.97817600	1.16421900	-0.00000900
C	2.09342600	1.73307800	-0.00000500
H	1.63241500	2.17709300	-0.88762100
H	1.63237700	2.17709800	0.88758700
H	3.15316900	2.00961200	0.00001600
C	2.67382800	-0.34559200	-1.26608000
H	2.66845300	-1.44074500	-1.31954300
H	2.19335200	0.03184500	-2.17428900
H	3.72295100	-0.03022200	-1.27405800
C	2.67382700	-0.34558000	1.26608800
H	3.72295100	-0.03021600	1.27405400
H	2.19335000	0.03188500	2.17428500
H	2.66843700	-1.44073000	1.31956900
C	-0.57934600	0.54658400	-0.00000100
H	-0.38960100	1.61351900	-0.00001600
O	0.30561700	-1.62527300	-0.00000100
H	1.15340200	-2.08404500	0.00003300

0 1			
C	-0.00925511	0.66940073	0.17448923
C	-1.32192041	1.47463105	0.18516283
C	1.45880882	1.26168642	0.04115026
C	1.65805190	1.62425892	1.52453941
H	2.52422843	2.24405167	1.62698533
H	0.79804438	2.15139846	1.88148614
H	1.79031802	0.72924390	2.09581324
C	1.66168857	2.71471530	-0.42698100
H	2.66612852	3.01941554	-0.21923562
H	1.47991582	2.77902505	-1.47946517
H	0.97998326	3.35527731	0.09249775
C	2.89032991	0.81551121	-0.30995523
H	3.09234096	-0.12927716	0.14989961
H	2.98471271	0.72282359	-1.37174658
H	3.58856434	1.54298236	0.04803138
C	-1.27025681	2.55512909	-0.91094613
H	-0.44691606	3.21272922	-0.72501047
H	-1.14565474	2.08878639	-1.86588006
H	-2.18230348	3.11460730	-0.90353006
C	-1.50125423	2.14581586	1.55955373
H	-1.53715037	1.39508021	2.32113593
H	-0.67791348	2.80341600	1.74548939
H	-2.41330090	2.70529407	1.56696980
C	-2.50691551	0.52817852	-0.08244550
H	-3.41896219	1.08765672	-0.07502943
H	-2.38231345	0.06183582	-1.03737943
H	-2.54281165	-0.22255714	0.67913670
C	0.61971280	0.22728199	-1.01539868
H	0.58148403	-0.31519653	-1.93689508
O	-0.22511328	-0.26004086	1.23959186
H	-0.35651927	0.21932237	2.06089775

13 (S, C α -C β -O-H = 180°) to 25: Transition State



SCF Done: E(RB3LYP) = -468.217044422 A.U. after 7 cycles
 Conv g = 0.1967D-08 -V/T = 2.0098

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.001943	-0.523721	-0.065041
2	6	0	-1.408085	0.205719	-0.001092

3	6	0	1.393659	0.242958	0.032547
4	6	0	1.893065	0.518064	1.459247
5	1	0	2.908052	0.930827	1.410958
6	1	0	1.270640	1.253863	1.979424
7	1	0	1.943468	-0.391625	2.063815
8	6	0	1.482240	1.546984	-0.780175
9	1	0	2.532907	1.857718	-0.834533
10	1	0	1.112981	1.420189	-1.799901
11	1	0	0.929390	2.362082	-0.305608
12	6	0	2.279905	-0.818109	-0.663043
13	1	0	2.439437	-1.709168	-0.056794
14	1	0	1.704662	-1.091535	-1.627682
15	1	0	3.230930	-0.434818	-1.050685
16	6	0	-1.622295	1.270371	-1.100541
17	1	0	-1.064383	2.189548	-0.915150
18	1	0	-1.343578	0.886934	-2.084628
19	1	0	-2.684431	1.540300	-1.125902
20	6	0	-1.643044	0.872610	1.370650
21	1	0	-1.606781	0.160417	2.203410
22	1	0	-0.922569	1.672709	1.568086
23	1	0	-2.642392	1.322129	1.389863
24	6	0	-2.482045	-0.891168	-0.217844
25	1	0	-3.483777	-0.451048	-0.158755
26	1	0	-2.382307	-1.341069	-1.214443
27	1	0	-2.405229	-1.687987	0.524711
28	6	0	0.152759	-1.185120	-1.412068
29	1	0	0.146449	-2.276416	-1.241093
30	8	0	0.015574	-1.560935	0.963052
31	1	0	-0.096673	-1.157092	1.834646

Input File:

%nprocshared=4

%mem=8GB

%chk=ts_singd180cyclobutanol.chk

opt=(tight,qst2) freq b3lyp/6-31+g(d,p) geom=connectivity

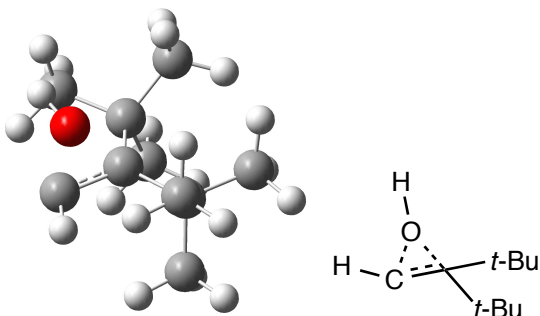
Singletd180 to cyclobutanol transition state

0 1

C	-0.00000500	-0.54249800	-0.13577000
C	-1.41590000	0.21487400	0.01512400
C	1.41589600	0.21488400	0.01512500
C	1.73151400	0.58749700	1.47741200
H	2.73722200	1.02230500	1.51636100
H	1.04211300	1.33457400	1.87932300
H	1.74051800	-0.28076000	2.14416600
C	1.56548800	1.48113900	-0.85149500
H	2.62371500	1.76775500	-0.87093400
H	1.24036400	1.30824500	-1.87897700
H	1.01290600	2.33130600	-0.44644800
C	2.47613400	-0.81256500	-0.46324600
H	2.42157500	-1.74047500	0.11030800
H	2.33395700	-1.04850400	-1.52878700

H	3.48416900	-0.39507300	-0.36060500
C	-1.56551800	1.48109700	-0.85154300
H	-1.01294700	2.33128800	-0.44653400
H	-1.24039800	1.30816800	-1.87902100
H	-2.62375000	1.76769400	-0.87098500
C	-1.73150700	0.58754400	1.47739800
H	-1.74046100	-0.28067600	2.14420100
H	-1.04212700	1.33467100	1.87925600
H	-2.73723100	1.02231200	1.51634800
C	-2.47613200	-0.81260000	-0.46320700
H	-3.48417000	-0.39511600	-0.36057200
H	-2.33395600	-1.04856900	-1.52874100
H	-2.42155900	-1.74049400	0.11037000
C	0.00002700	-1.04556700	-1.52050100
H	0.00008300	-2.15122400	-1.46147100
O	0.00000300	-1.65591100	0.80328400
H	-0.00003400	-1.32296200	1.71069200
0 1			
C	-0.00402400	-0.49452500	0.02333900
C	-1.40806200	0.20252300	0.00442000
C	1.40854100	0.26935700	0.04053000
C	2.08889100	0.43590300	1.40315200
H	3.11926800	0.78355400	1.26061000
H	1.57949900	1.18263900	2.02606700
H	2.13905000	-0.50637700	1.95565600
C	1.48555200	1.60077300	-0.72092100
H	2.53946200	1.88765300	-0.82316400
H	1.06881300	1.53538900	-1.72922100
H	0.97572400	2.41293400	-0.19140100
C	1.94566600	-0.89431900	-0.85494600
H	2.43653000	-1.67389100	-0.26678400
H	0.16689100	-0.82431100	-2.16013300
H	2.60467000	-0.59961200	-1.67845300
C	-1.62683400	1.16238600	-1.18656000
H	-1.03598200	2.07648900	-1.11213800
H	-1.40435900	0.68663100	-2.14680600
H	-2.68104800	1.46092400	-1.21288600
C	-1.62545300	1.00299100	1.30890100
H	-1.60624700	0.36261000	2.19856000
H	-0.87183200	1.78823600	1.43433400
H	-2.60784600	1.48847400	1.29464200
C	-2.48701700	-0.90198400	-0.09792500
H	-3.48610400	-0.45127600	-0.08444000
H	-2.38821300	-1.46147700	-1.03519500
H	-2.41524500	-1.61579300	0.72523700
C	0.48953000	-1.27577100	-1.21887400
H	0.23095500	-2.33758900	-1.22136400
O	0.00761300	-1.47708300	1.07871400
H	-0.02562200	-1.02255100	1.93046700

13 (S, C α -C β -O-H = 180°) to **26a**: Transition State



SCF Done: E(RB3LYP) = -468.209857155 A.U. after 7 cycles
 Convrg = 0.6021D-08 -V/T = 2.009

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.006033	0.415621	0.220522
2	6	0	-1.349601	-0.339423	0.003488
3	6	0	1.386556	-0.239219	-0.023560
4	6	0	1.460560	-1.562618	-0.819258
5	1	0	2.503740	-1.898109	-0.828451
6	1	0	0.871831	-2.370022	-0.378891
7	1	0	1.155361	-1.432742	-1.860119
8	6	0	1.983340	-0.500930	1.389702
9	1	0	3.017826	-0.844223	1.278910
10	1	0	1.994228	0.401386	2.006200
11	1	0	1.430994	-1.276277	1.928189
12	6	0	2.307535	0.760443	-0.772836
13	1	0	1.941815	0.953702	-1.784561
14	1	0	2.390572	1.718155	-0.257079
15	1	0	3.308875	0.323162	-0.846323
16	6	0	-1.397897	-1.411137	1.129029
17	1	0	-0.582896	-2.135534	1.070629
18	1	0	-1.371241	-0.935245	2.114442
19	1	0	-2.337953	-1.967029	1.044788
20	6	0	-1.521913	-1.001921	-1.384635
21	1	0	-1.279931	-0.298227	-2.188587
22	1	0	-0.919198	-1.898170	-1.519996
23	1	0	-2.569683	-1.296057	-1.508311
24	6	0	-2.581969	0.572893	0.223069
25	1	0	-3.467764	-0.054287	0.365762
26	1	0	-2.445316	1.216334	1.094743
27	1	0	-2.794257	1.194837	-0.656498
28	6	0	-0.069212	1.668151	0.938997
29	1	0	0.924894	2.071093	1.147237
30	8	0	-0.233763	2.014440	-0.615197
31	1	0	-1.169997	2.240569	-0.727608

Input File:


```
%nprocshared=4
%mem=8GB
%chk=ts_singd180aldehydeenol.chk
# opt=(tight,qst2) freq b3lyp/6-31+g(d,p) geom=connectivity
```

Singletd180 to aldehyde enol transition state

0 1

C	-0.76763490	0.87828491	0.00000000
C	-2.18352990	1.63565691	0.15089400
C	0.64826610	1.63566691	0.15089500
C	0.96388410	2.00827991	1.61318200
H	1.96959210	2.44308791	1.65213100
H	0.27448310	2.75535691	2.01509300
H	0.97288810	1.14002291	2.27993600
C	0.79785810	2.90192191	-0.71572500
H	1.85608510	3.18853791	-0.73516400
H	0.47273410	2.72902791	-1.74320700
H	0.24527610	3.75208891	-0.31067800
C	1.70850410	0.60821791	-0.32747600
H	1.65394510	-0.31969209	0.24607800
H	1.56632710	0.37227891	-1.39301700
H	2.71653910	1.02570991	-0.22483500
C	-2.33314790	2.90187991	-0.71577300
H	-1.78057690	3.75207091	-0.31076400
H	-2.00802790	2.72895091	-1.74325100
H	-3.39137990	3.18847691	-0.73521500
C	-2.49913690	2.00832691	1.61316800
H	-2.50809090	1.14010691	2.27997100
H	-1.80975690	2.75545391	2.01502600
H	-3.50486090	2.44309491	1.65211800
C	-3.24376190	0.60818291	-0.32743700
H	-4.25179990	1.02566691	-0.22480200
H	-3.10158590	0.37221391	-1.39297100
H	-3.18918890	-0.31971109	0.24614000
C	-0.76760290	0.37521591	-1.38473100
H	-0.76754690	-0.73044109	-1.32570100
O	-0.76762690	-0.23512809	0.93905400
H	-0.76766390	0.09782091	1.84646200

0 1

C	-0.01409000	0.40052000	-0.07002000
C	1.18413400	-0.60512200	0.00476000
C	-1.50913000	-0.05168000	-0.02170700
C	-1.80151400	-0.89221800	1.25040300
H	-2.85564200	-1.19412900	1.26214900
H	-1.20553900	-1.80312600	1.32021900
H	-1.61305000	-0.29978400	2.15240700
C	-1.92802600	-0.84110900	-1.29192400
H	-3.00931100	-1.02239800	-1.27391100
H	-1.70119800	-0.26176200	-2.19365600
H	-1.44249000	-1.81147200	-1.38282200
C	-2.49219500	1.14547500	0.05283500
H	-2.32750600	1.76450900	0.94028700
H	-2.44045900	1.78400100	-0.83526900

H	-3.51374000	0.75607000	0.11182800
C	0.87323000	-2.04612300	-0.47259100
H	0.03684000	-2.51267400	0.04638600
H	0.67433700	-2.07984400	-1.54772400
H	1.75466700	-2.66914500	-0.28400400
C	1.68271400	-0.68758800	1.47287800
H	1.93497600	0.30299500	1.86617000
H	0.91958900	-1.11638100	2.12820200
H	2.57775500	-1.31891200	1.54098000
C	2.38287300	-0.16765200	-0.89832900
H	3.00742000	-1.03777200	-1.12594800
H	2.04636700	0.25941100	-1.84760300
H	3.07204200	0.53895500	-0.41664400
C	0.20616300	1.73248100	-0.06007100
H	-0.60382700	2.44565700	-0.07156800
O	1.38045400	2.43844400	-0.01679400
H	2.14019600	1.84634600	-0.05252300
