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Intramolecular Chemistry of ß-acetoxyethylidene and Photochemical Generation of Vinylidenes

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The Intramolecular Chemistry of ß-acetoxyethylidene and Photochemical Generation of Vinylidenes

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With Honors in Chemistry

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The Intramolecular Chemistry of ß-acetoxyethylidene and Photochemical Generation of Vinylidenes

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Approved:

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(Mentor. Dasan Thamattoor, Associate Professor of Chemistry)

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(*Reader. Marcus Juhasz, Visiting Assistant Professor of Chemistry)*

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Quotes

“The aim of life is self-development. To realize one’s nature perfectly – that is what each of us is here for.”

- Oscar Wilde

“Be great in act, as you have been in thought.”

- William Shakespeare

Acknowledgments

I would like to thank the Colby Chemistry department for their support in my research and studies in college. The department has supported me not only on an educational level but also on a personal level.

In particular, I would like to thank my cast of lab mates who kept me company and gave me help throughout my research years. The lab family of Becca, Danny, Jon, Tatenda, and Martin were always there if I ever needed anything. I would also like to thank Mark Juhasz for his comments and criticisms on making this thesis what it is today.

Of course, this thesis would not be possible without Das's contribution. Not only did he put the time, effort, and energy into my research, he also supported me throughout my Colby years and was always willing to offer advice in any way. He has been a great mentor who always pushes his students to do the best they can, and this thesis exists because of him.

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Introduction

Results and Discussion

Abstract

The parent carbene β-acetoxyethylidene has been previously generated by the photolysis of its precursor, acetic acid 1a,9b-dihydro-*1H*-cyclopropa[*l*]phenanthren-1-yl methyl ester. Mechanistic studies on β-acetoxyethylidene have indicated the possibilities of three rearrangement pathways to the formation of vinyl acetate: a proton shift, an acyl shift, and a cyclic rearrangement (see Figure 8). A deuterium labeling study involving the replacement of the hydrogens on the methylene carbon has indicated that the simple 1,2-H shift was the primary manner of rearrangement, with an 82% yield of product. However, a primary kinetic isotope effect may have occurred due to the greater strength of a C-D bond than a C-H bond in the 1,2-H shift. Therefore, deuterium labeling studies on the carbene center were undertaken to avoid this primary kinetic isotope effect. The monodeuterated acetic acid precursor, 1a,9b-dihydro-*1D*-cyclopropa[*l*]phenanthren-1-yl methyl ester was generated from 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene, an important carbene precursor that is produced in high yields from phenanthrene. The compound was photolyzed, and the results are forthcoming.

In a second project utilizing the easily accessible 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene, efforts have been made at generating a specific precursor in the generation of successive vinylidenes. Dimerization of the starting material in an effort to form the double bonded carbene precursor was attempted in a one step reaction. However, the dimerization did not fully complete, and a dibrominated dimer was formed as a product instead.

Introduction

1.1 Overview and History of Carbenes

Carbenes are typically unstable carbon species that are highly reactive. These compounds are characterized by a lone pair of nonbonding electrons on a divalent carbon that is neutral yet defies the octet rule. While most carbenes are unstable, there have been persistent carbenes that have been isolated and characterized by x-ray crystallography.[1] Carbenes have been known since the nineteenth century and are utilized in modern times as important reactants in chemical syntheses; for instance, carbenes are often used in the syntheses of liquid crystals, molecule magnets, polymer dyes, transition metal catalysts, and more.[2,3] However, it was not until the mid-twentieth century that carbene research picked up, as the lack of information on electronic structure and insufficient synthetic techniques had hindered its progress in the past.[4]

The structure of a carbene can have either both electrons paired in a sp^2 orbital or one electron in a 2p orbital and one in a sp^2 orbital.

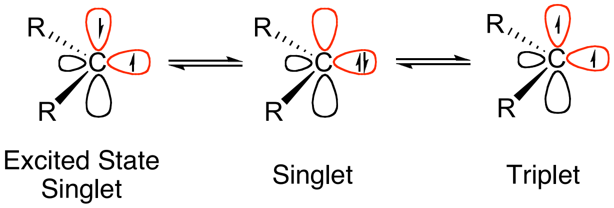


Figure 1: Singlet and triplet state equilibrium.

The former is the singlet state, and the latter is the triplet state; an excited state singlet can also be formed from the excitation of one electron into the 2p orbital, conserving spin. Normally the triplet state is favored; this is accounted for by Hund's rule, where the number of parallel spins and the number of orbitals are maximized, minimizing electron-electron repulsion.[5] However, the energy barrier between the two is often easily overcome; for example, 9-fluorenylidene rapidly converts between a singlet state and a triplet state with a 1.1 kcal/mol barrier of conversion.[6] Additionally, the singlet state may be favorable when there are electron-donating substituents that offer π donation to stabilize the empty p orbitals of the singlet.[7]

1.2 Reactivity of Carbenes

Carbenes can react in cyclopropanation or intermolecular insertion reactions in either a one step, concerted process with singlet carbenes or in a diradical, two step process with triplet carbenes. With singlet reactivity, the carbene can assume a nucleophilic stance with its paired electrons or an electrophilic nature with its empty p-orbital. In a cyclopropanation reaction involving a singlet carbene, the stereochemistry is preserved in the one step process.

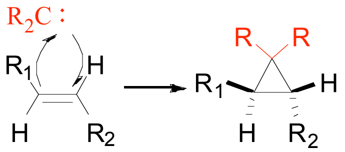


Figure 2: Singlet carbene undergoing a concerted, cyclopropanation reaction.

Stereochemistry can be preserved in the concerted reaction while a mix of isomers may occur via a diradical mechanism. Singlet carbenes often produce faster reactions than the triplet state due to this one step process, and many carbenes, such as methylene, undergo triplet to singlet conversions before reacting.[8]

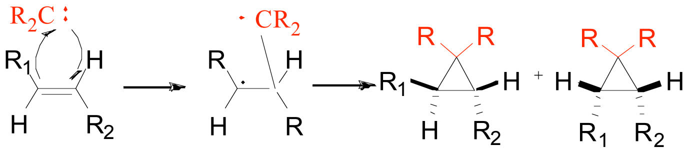


Figure 3: Triplet state carbene undergoing a two-step, radical cyclopropanation reaction.

1.3 Generation of Carbenes

Carbenes can be generated in numerous ways. They are often formed through hydrolysis, photolysis, pyrolysis, and other means; the parent carbene, methylene, is often formed through the pyrolysis and photolysis of diazo compounds and ketenes. Diazo compounds are perhaps the most common source of carbenes as well as being the most extensively studied.[4]

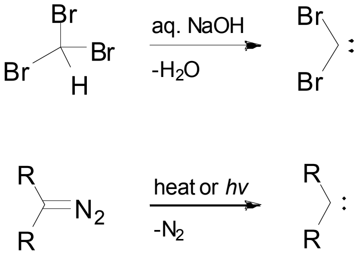


Figure 4: Generation of carbenes by hydrolysis and pyrolysis/photolysis.

Methods involving diazo compounds to generate carbenes have been discussed extensively for the value of the carbene products as well as the formation of these products. As diazo compounds are highly reactive, the mechanism through which a reaction generates a carbene product may be questionable due to other possible reaction pathways that the diazo compound may take. For instance, diazo compounds, when decomposed, can give products similar to those from carbene reactions.

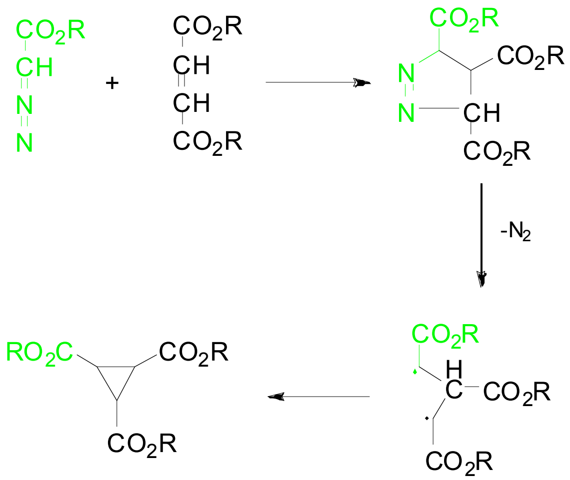


Figure 5: Diazirine reaction and rearrangement through a non-carbene mechanism.

The carbene pathway may be thus suspect in many cases concerning diazo compounds.[4]

Basic hydrolysis of haloforms to form dihalocarbenes, in contrast, have been well established since its preliminary premise in 1862 by Geuther, who stated that the hydrolysis of chloroform would produce the intermediate product of dichlorocarbene.[4] These dihalocarbenes may continue on in a wide variety of organic mechanisms. In particular, dihalocarbenes have been studied in their reactions with aromatic compounds like anthracene and phenanthrene. The reactions of anthracene and phenanthrene with dihalocarbenes produce dihalocyclopropanated products. More importantly, these products can become important reactants in the syntheses of new carbene precursors.

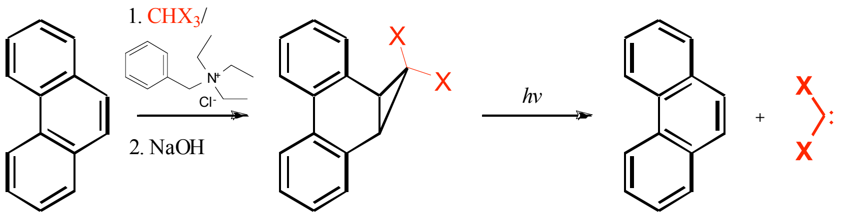


Figure 6: The reaction of phenanthrene with the hydrolysis of a haloform and the subsequent regeneration of phenanthrene with photolysis.

1.4 β-acetoxyethylidene

In previous studies by Martin Schnermann and Dasan Thamattoor, the precursor to β-acetoxyethylidene was researched and prepared by using phenanthrene as the starting material. Under photolysis, the compound gave β-acetoxyethylidene.[8]

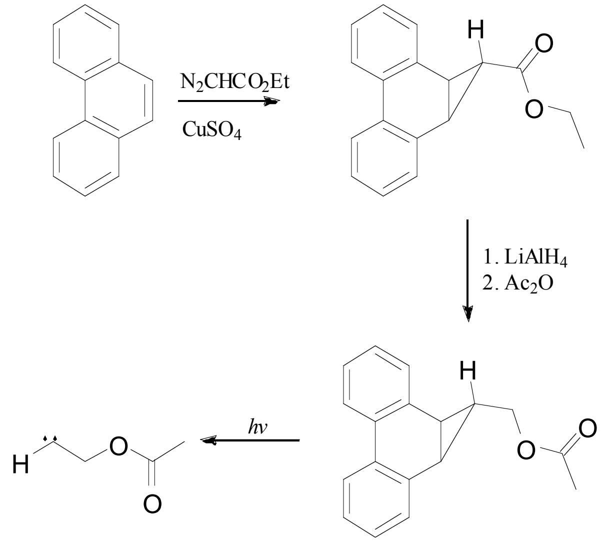


Figure 7: Synthetic scheme leading to the photochemical production of β-acetoxyethylidene.

Schnermann noted that this carbene rearranged to form vinyl acetate, but that there were also three reaction pathways that could be taken to give vinyl acetate. These pathways involved a hydrogen shift, acyl shift, or a rearrangement involving a cyclic intermediate.[8]

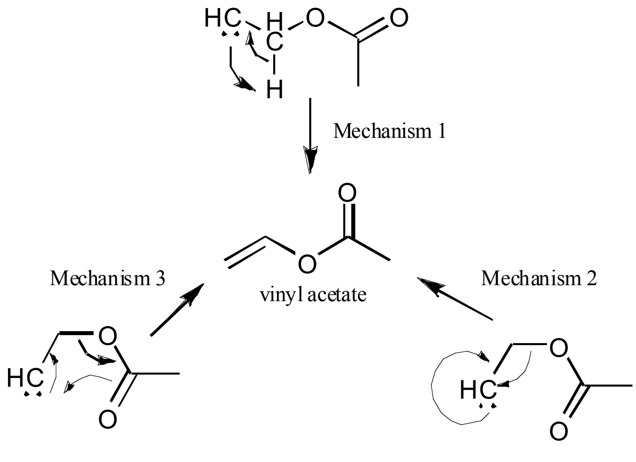


Figure 8: Three reaction pathways to the formation of vinyl acetate.

Through deuterium labeling and computational studies, Schnermann attempted to find the prevalent reaction mechanism for the conversion to vinyl acetate. He synthesized the same ester compound, only substituted with deuterium as shown below.

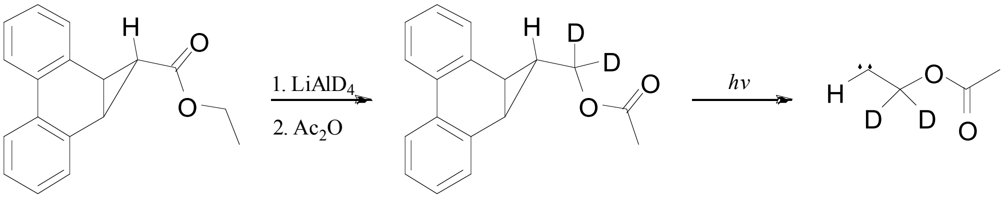
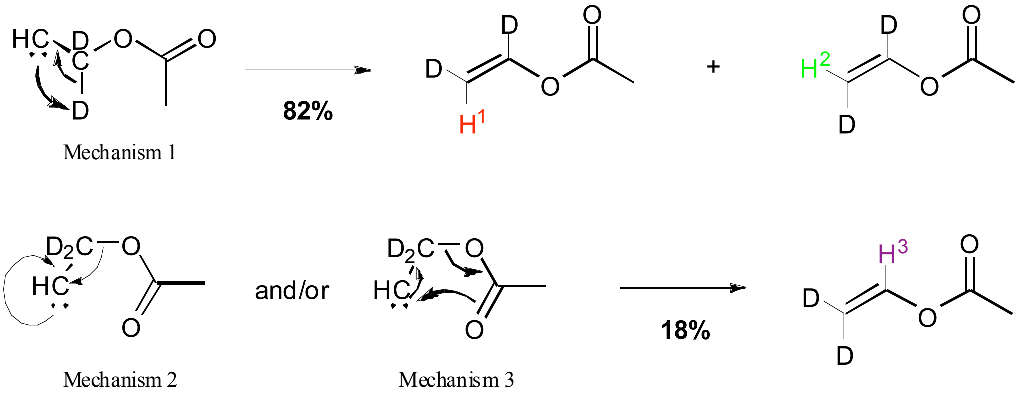


Figure 9: Schnermann's preparation of the deuterated precursor

Using this isotopic labeling experiment, Schnermann intended to integrate the proton spectrum of the vinyl acetate distillate after photolysis to determine the ratios of the three single proton peaks around the double bond. This deuterium substitution did not distinguish between the acyl shift and the cyclic intermediate mechanisms; nevertheless, it did distinguish between the proton shift mechanism and the other two mechanisms, giving an 82% yield of the proton shift mechanism occurring.[8]



Peak	Integral	% Product
H^1	1.00	18.4
H^2	2.42	44.6
H^3	2.02	37.1

Figure 10: Integration ratios and percent mechanistic yields.

However, while his study gave interesting results, the focus was upon deuterium labeling at the methylene position; at this position, there may have been a primary kinetic isotopic effect influencing the reaction pathways to vinyl acetate. There may have been less reactivity for a deuterium shift due to the increased bond strength of a C-D bond in comparison to a C-H bond, and this effect may have promoted the other mechanisms to occur. For these reasons, further research on β-acetoxyethylidene is described in this study where deuterium labeling is taken upon the carbene center instead of the methylene position.[8] With this isotopic labeling experiment, the deuterium is not involved in a 1,2-shift, and the primary kinetic isotope effect will not affect the ratio and percentage of the products formed.

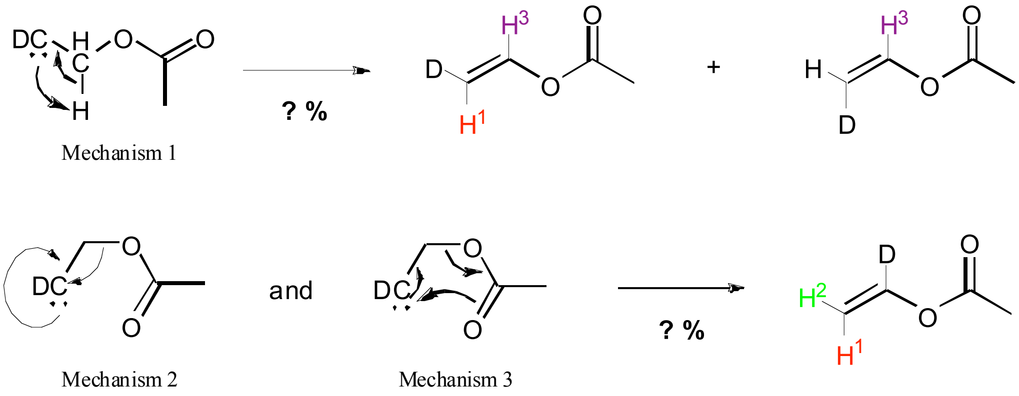


Figure 11: Rearrangement scheme of β-acetoxyethylidene with isotopic deuterium labeling at the carbene center.

1.5 Vinylidenes

Because 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene is a useful starting compound to a variety of carbene precursors, an additional study focusing on the formation of vinylidenes is described. A vinylidene is a type of carbene with a double bonded carbene center instead of two single bonds. Vinylidenes are the simplest unsaturated carbenes and are important in organic chemistry.

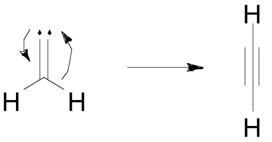


Figure 12: Rearrangement of a vinylidene to acetylene.

Studies have been conducted to determine if vinylidenes exist in bound states; its lifetime, consequently, is thought to be very short, and the reactive molecule prefers to rearrange to the more stable acetylene.[9,10] Various substituted vinylidenes are believed to have longer lifetimes, and vinylidenes such as $F_2C=C$: and $(CH_3)_2C=C$: have been generated and studied for this reason.[11,12]

The focus of this study is on the photolytic generation of successive vinylidenes from one compound. While dicarbenes have been produced from one chemical precursor, there is no indication in the literature that mentions a domino effect of successive vinylidenes from one compound.[4] By the synthesis of a specific precursor, it is possible to analyze the reactivity of successive vinylidenes by photolysis.

Recent literature by De Meijere's group has demonstrated the syntheses of an array of intricate bispirocyclopropanated dimer compounds.[13] By synthesizing and reacting dihalo compounds varying in complexity, they found that such compounds could bicyclopropanate into dimers, forming a variety of complex molecules.[13]

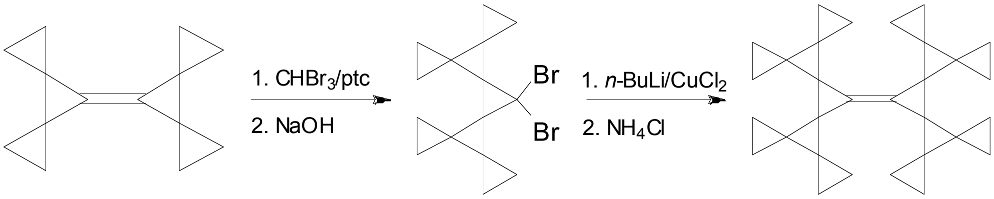


Figure 13: The dimerization of a dihalogenated compound.

Using their approach, a scheme to form the precursor to successive carbenes can be formulated under similar reaction conditions. By cyclopropanating phenanthrene to form 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene, this dihalo compound can be dimerized. Phenanthrene was chosen as the starting material for the synthesis of the photochemical precursor due to the tendency of its photochemical products to regenerate phenanthrene after photolysis.

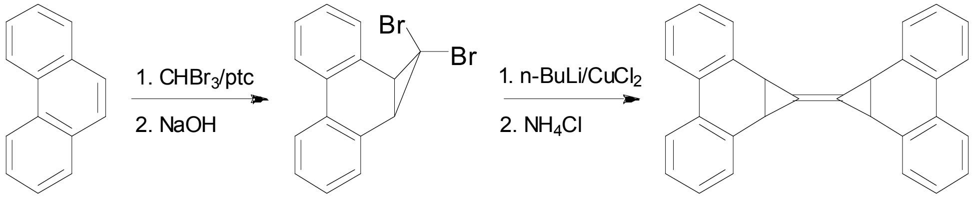


Figure 14: Synthetic scheme for the production of the photochemical precursor to successive carbenes.

Results and Discussion

2.1 Synthesis of 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene (1)

The starting route for both of the proposed projects was through the synthesis of the dibrominated compound **1** from the commercially available phenanthrene. The only published procedure in the synthesis of **1** involved the hydrolysis of bromoform with potassium *tert*-butoxide, producing low yields of 13%.[14] An improved synthesis that was recently accepted for publication proceeds through the hydrolysis of bromoform by the base sodium hydroxide with benzyltriethylammonium chloride as the phase-transfer catalyst. The mechanics of this reaction are fairly simple; the reactants and reagents are merely stirred in a lightly capped Erlenmeyer flask at room temperature for four days before workup. The yields were much higher than in the previously reported literature, giving 43% of **1** that was clean by both ^{1}H and ^{13}C NMR in each repeated trial.[15]

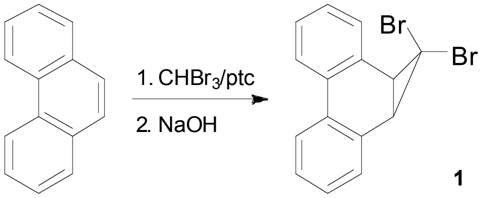


Figure 15: Preparation of 1

2.2 Synthesis of the monodeuterated ß-acetoxyethylidene Precursor

While Schnermann's synthetic scheme involved the reaction of ethyl diazoacetate to phenanthrene, our route to the monosubstituted, deuterated carbene **7** utilizes reactants that are less reactive and with less explosive potential.

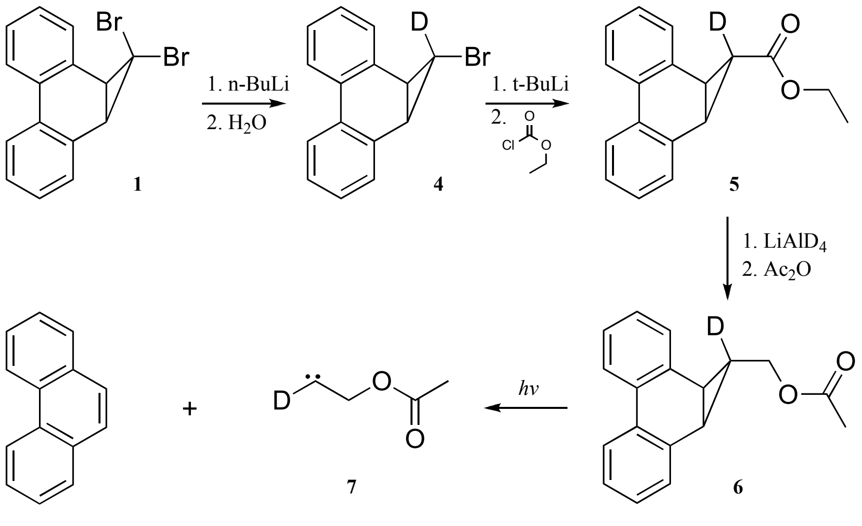


Figure 16: The synthetic route to the monodeuterated carbene 7

The synthesis of **4** is achieved by simple addition of *n*-butyllithium to **1** at -70ºC, and the reaction is quenched by the addition of D_2O, which incorporates a deuterium atom and produces **4** in good yield. Additionally, the reaction is fairly stereoselective, producing the exo isomer, whereas the reaction of ethyl diazoacetate with phenanthrene produces a mix of both endo and exo isomers. Compound **4** can then be reacted again with the more reactive t-butyllithium at low temperatures to displace the bromine. The reaction can be quenched by the addition of ethyl chloroformate, where nucleophilic attack and chlorine displacement adds the ester group to form **5** in good yield. Compound **5** can be reacted and reduced with lithium aluminum hydride in tetrahydrofuran at reflux to form the alcohol, which can be acetylated in situ with acetic anhydride to form the deuterated precursor **6**.[16]

In addition to this synthesis, the synthesis of the Schnermann's doubly deuterated carbene **11** was also prepared for data analysis and comparison. However, the reaction scheme utilized was the scheme used for the preparation of the monodeuterated carbene, where the safer method and less chance of isomerization were favored. The synthesis leading up to the intermediate ester **9** was changed, while the formation of the final ester precursor **10** proceeded in the same fashion as Schnermann's synthesis.

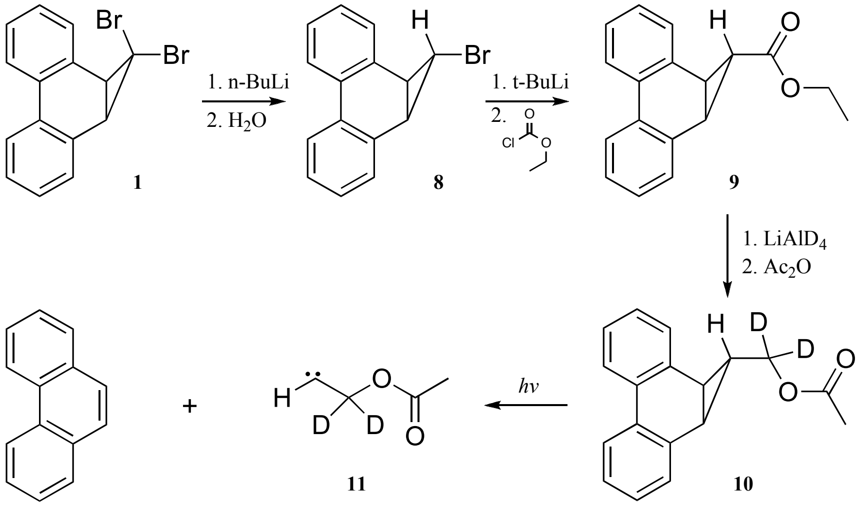


Figure 17: The synthetic route to the doubly deuterated carbene 11

Compounds **1** to **6** were identified primarily through the use of both NMR and GC/MS, and ^{1}H and ^{13}C NMR spectra were taken from a sample of Schnermann's nondeuterated precursor for comparison.

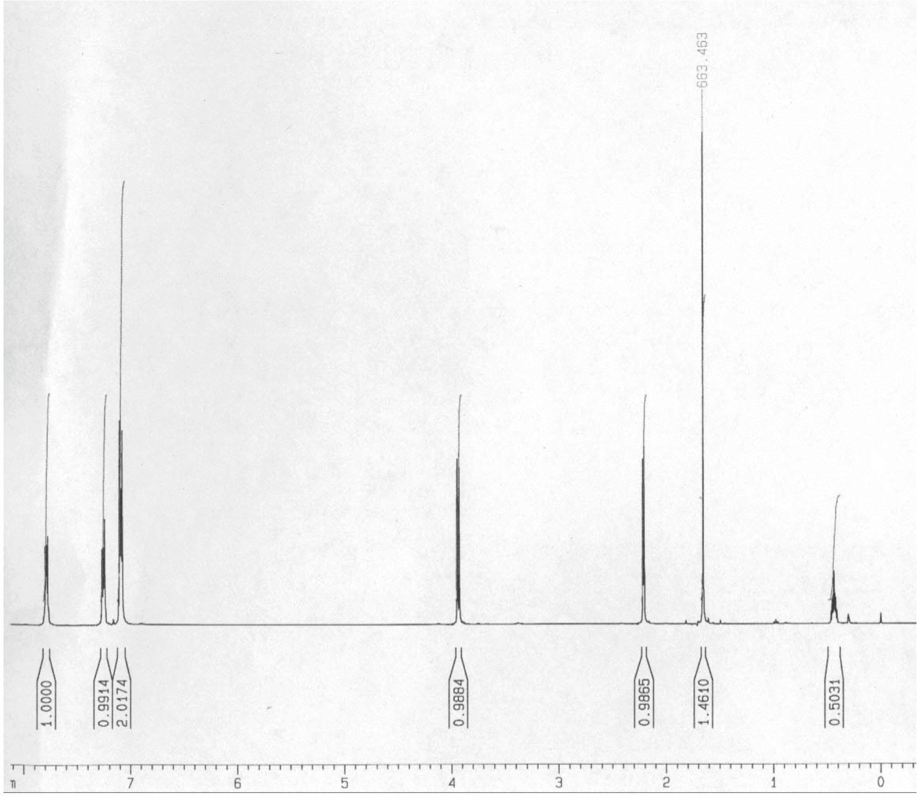


Figure 18: Proton spectrum of the nondeuterated carbene precursor.

In the proton spectrum of **6**, three peaks were shown in the aromatic region. The methylene hydrogens were found at 4.00 ppm, and the cyclopropyl hydrogens were shown at 2.27 ppm. The methyl hydrogens were found at 1.79 ppm. More importantly, the spectrum indicates that the proton signal at 1.79 ppm was missing by comparison with the proton spectrum from the nondeuterated sample, as expected by the deuterium exchange.

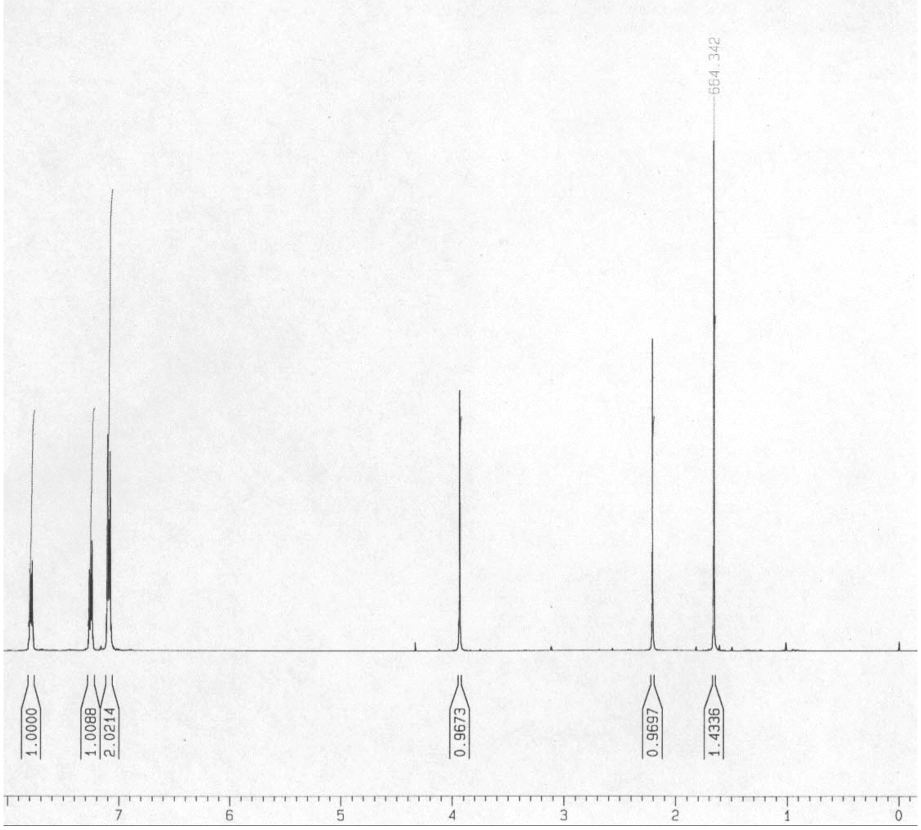


Figure 19: Proton spectrum of the monodeuterated carbene precursor.

Compounds **8** to **10** were identified through the use of GC/MS due to the lack of the NMR instrument. Compound **10** was identified through GC/MS with a base peak of 206.

2.3 Photolysis

Photolysis of **6** was found to form the carbene **7**, which generated phenanthrene from photolysis and vinyl acetate upon rearrangement of the carbene. The vinyl acetate was characterized by proton NMR. No further studies could be done because of the unfortunate quenching of the NMR magnet.

2.4 Synthesis of the Vinylidene Precursor

The synthetic route to the production of successive vinylidenes was proposed through the synthesis of the photochemically active precursor **2**. The synthesis involved the addition of a slight excess of *n*-butyllithium at -70ºC to a solution of **1** and catalytic copper (II) chloride, followed by quenching with saturated ammonium chloride. The proposed compound **2** could not be fully isolated, yet the reaction was shown to have dimerized to form product **3** with the bromines still attached.

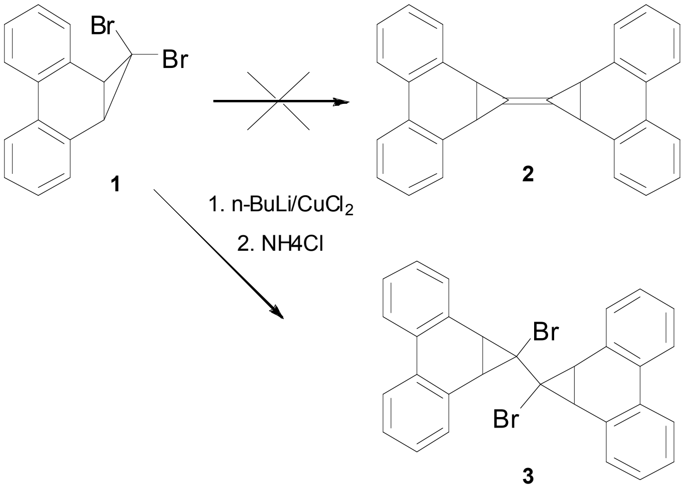


Figure 20: Formation of 3 in lieu of 2

Compound **3** was determined by x-ray crystallography and ^{1}H NMR. The cyclopropyl hydrogens were found at 3.2 ppm, but x-ray crystallography was necessary in order to distinguish between **2** and **3**. The two bromines still attached to **3** indicate that the reaction with *n*-butyllithium had only managed to displace one of the bromines from **1**, therefore leaving only one reactive site for the intermediate species to dimerize with. Subsequent reactions with *n*-butyllithium may complete the elimination process, but with the loss of the NMR, additional studies could not be fully characterized.

Conclusions

3.1 Major Highlights

The parent carbene, β-acetoxyethylidene, was successfully generated through a new synthesis that did not involve the use of nitrogenous precursors or reagents. The direct precursor to the carbene, acetic acid 1a,9b-dihydro-*1H*-cyclopropa[*l*]phenanthren-1-yl methyl ester, was developed through a series of four steps in fair yield and good purity. The carbene was formed with deuterium labeling upon the carbene center to determine the extent of the primary kinetic isotope effect if the deuterium labeling was placed on the methylene carbon and involved in the proton rearrangement instead. Analysis of the vinyl acetate rearrangement product after the photolysis of 1a,9b-dihydro-*1D*-cycloprop[*l*]phenanthren-1-yl methyl ester was halted due to the untimely demise of the Bruker Avance 400 spectrometer.

In the secondary project, the compound 1,1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene was found to dimerize under the conditions specified by De Meijere.[13] While the compound did dimerize, it did not do so fully. Instead, two bromines were left attached, producing a dibrominated dimer.

Future Work

Further research on β-acetoxyethylidene involves the use of an NMR spectrometer in order to accurately determine by proton NMR integral ratios or by deuterium NMR the extent of the primary kinetic isotope effect on the deuteration of the methylene carbon. Additionally, computational work involving the transition states of the mechanisms with the deuterium labeled compounds could be done to find energy minima. To accurately distinguish between all three mechanisms, isotopic labeling experiments involving both ^{18}O and deuterium would be necessary.

In continuing research on the vinylidene precursor, the dibrominated dimer produced by the synthesis could be used further in an attempt to complete the dimerization to a double bonded carbene precursor. The synthesis attempted could be the same, where generation of the lithium-reactant species is predicted to form the double bonded species, which may then be photolyzed and studied.

Experimental

4.1 General Comments

All chemicals and solvents were acquired from commercial sources and used in its original form if not stated otherwise. All characterizations were performed at Colby College. Thin layer chromatographic studies were performed on Merck aluminum plates coated with silica gel, 60 mesh. Column chromatography was performed on silica gel, 60 mesh. GC-MS spectra were taken on a Varian 3900 gas chromatograph connected to a Saturn 2100T ion trap mass spectrometer. ^{1}H and ^{13}C NMR spectra were taken with a Bruker Avance spectrometer referenced to trimethylsilane at 400 MHz and 100 MHz respectively. FT-IR spectra were recorded on a Perkin Elmer Spectrum One spectrophotometer using diffuse reflectance. Elemental analysis was performed on an Exeter Analytical CHN Analyzer. Photolysis was performed in a Rayonet photochemical reactor (250 watts, λ = 254-419 nm) at room temperature.

All reactions except for the synthesis of **1** were run under an argon atmosphere with oven-dried equipment and anhydrous solvents. The solvents used were dried using an alumina column.

4.2 Synthesis

Preparation of 1, 1-dibromo-1a,9b-dihydrocycloprop[*l*]phenanthrene (1), from submitted paper

Phenanthrene (35.6 g, 0.2 mol), benzyltriethylammonium chloride (0.5 g, 0.002 mol), bromoform (40 mL, 116 g, 0.46 mol), dichloromethane (40 mL), and ethanol (1 mL) were added to a 500 mL Erlenmeyer flask and stirred with a magnetic stir bar. To this solution was added 80 mL of 50% aqueous sodium hydroxide, in small portions, over 30 min. During addition, the reaction mixture became warm and frothy and turned into a slurry of solid and liquid. The flask was loosely stoppered and stirring was continued at room temperature for four days. The resultant thick, dark brown reaction mixture was poured into a 500 mL separatory funnel, and the Erlenmeyer flask was rinsed with 100 mL of dichloromethane and 100 mL of water. The rinses were added to the separatory funnel and, after shaking, the two layers were separated. The aqueous layer was extracted with dichloromethane (2 x 50 mL), and the organic layers were combined and washed sequentially with 2M HCl (2 x 100 mL), water (2 x 100 mL), and brine (1 x 100 mL). Vacuum filtration of the organic layer afforded the product as a white solid (21.2 g). Concentration of the filtrate yielded an additional crop of crystalline product (4.1 g) which was also isolated by vacuum filtration. Evaporation of solvent from the filtrate and trituration of the black residue with chloroform afforded a third crop of product as off-white crystals (4.7 g). All three crops of solids gave appropriate ^{1}H and ^{13}C NMR data consistent with the product of excellent purity. (30 g, 43% yield); mp 110-111°C; IR (diffuse reflectance): 3022, 1488, 1451, 1241 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.00 (dd, J = 7.5, 1 Hz, 2H), 7.50 (dd, J = 7.5, 1.5 Hz, 2H), 7.42 (dt, J = 7.5, 1.5 Hz, 2H), 7.35 (dt, J = 7.5, 1 Hz, 2H), 3.5 (s, 2H); ^{13}C NMR: (CDCl$_3$): δ = 131.4, 131.1, 129.7, 128.4, 128.3, 123.2, 37.6, 31.1; Anal. Calcd for $C_{15}H_8Br_2$: C, 51.47; H, 2.88. Found: C, 51.17; H, 2.84.

Project 1

Preparation of 1-bromo-1a,9b-dihydro-*1D*-cyclopropa[*l*]phenanthrene (4)

In an oven-dried 200 mL round bottom flask equipped with a low temperature thermometer, stir bar, and line open to argon, **1** (9.792 g, 0.028 mol) was added and dissolved in 100 mL dry tetrahydrofuran and stirred. The solution was brought to -70°C with a dry ice/acetone bath. Then, *n*-butyllithium (18.00 mL of 1.6 M in hexanes, 0.029 mol) was added dropwise to the solution over 45 min. During this addition, the solution turned darker as the *n*-butyllithium was added, and the solution turned dark olive green at the completion of the addition, signifying bromine anion formation. After the addition, the reaction mixture was left stirring at -70°C for 1 hr. Then, D_2O (7.0 mL, 7.0 mol) was added by syringe to the reaction flask. The reaction mixture turned brown after the addition, and the bath was taken away. The flask was left to warm to room temperature. The reaction mixture was diluted with 40 mL water, then transferred to a 250 mL separatory funnel. The layers were separated, and the aqueous layer was extracted with dichloromethane (2 x 25 mL). The organic layers were combined and washed sequentially with water (2 x 40 mL) and brine (1 x 40 mL). The organic layer was dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was evaporated under vacuum. The product was dissolved in silica gel with dichloromethane, and it was run through a short silica gel column with hexanes under vacuum to reduce the impurities and color. The product after evaporation of solvent was subsequently recrystallized in hexanes, giving white crystals. (4.502 g, 59% yield); mp 114.1-115.5°C; GC/MS: 271 (M^+), 192; ^1H NMR ($CDCl_3$): $\delta = 7.95$ (dd, $J = 7.5$ Hz, 2H), 7.52 (m, 2H), 7.35 (m, 4H), 3.00 (s, 2H); ^{13}C NMR: ($CDCl_3$): $\delta = 132.3$, 130.2, 129.7, 128.5, 127.6, 123.7, 30.125, 28.1, 27.8, 27.5; Anal. Calcd for $C_{15}H_8DBr$: C, 66.20; H, 4.44. Found: C, 66.55; H, 4.09.

Preparation of ethyl 1a,9b-dihydro-*1D*-cyclopropa[*l*]phenanthrene-1-carboxylate (5)

Compound **2** (4.030 g, 0.015 mol) was added to a 100 mL oven-dried round bottom flask equipped with a stir bar, low temperature thermometer, and line open to argon. Diethyl ether (75 mL) was added, and the solution was stirred and cooled to -70°C with a dry ice/acetone bath. To this, *tert*-butyllithium (21.2 mL of 1.5 M in pentanes, 0.032 mol) was added dropwise by syringe over 45 min. After the addition, the solution was left at -70°C for 1 hr. Then, ethyl chloroformate (5.0 mL, 5.675 g, 0.052 mol) dissolved in ether (35 mL) was added slowly over 30 min. The reaction mixture was left stirring in the bath for 1 hr. Afterwards, the bath was taken away, the solution warmed to room temperature, and water (40 mL) was added. The layers were separated, and the aqueous layer was extracted with ether (2 x 25 mL). The organic layers were combined and washed sequentially with water (2 x 40 mL) and brine (1 x 40 mL). The organic layer was dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was evaporated under vacuum. The resultant solid was recrystallized in ethanol, giving white solid. (1.245 g, 31% yield); mp 129.5-130.9°C; GC/MS: 265 (M^+), 192; ^{1}H NMR ($CDCl_3$): $\delta = 8.00$ (m, 2H), 7.55 (m, 2H), 7.35 (m, 4H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.20 (s, 2H), 1.27 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR: ($CDCl_3$): δ = N/A; Anal. Calcd for $C_{18}H_{15}DO_2$: C, 81.48; H, 6.46. Found: C, 82.16; H, 6.19.

Preparation of 1a,9b-dihydro-*1D*-cyclopropa[*l*]phenanthren-1-yl methyl ester (6)

In an oven-dried 200 mL round bottom flask equipped with a stir bar, thermometer, and line open to argon, lithium aluminum hydride (0.172 g, 0.0045 mol) was suspended in tetrahydrofuran (50 mL). The solution was stirred vigorously, and the reaction mixture was brought down to 0°C with an ice bath. Compound **3** (0.844 g, 0.0032 mol) dissolved in tetrahydrofuran (10 mL) was added dropwise to the solution over 15 min. Then, the reaction mixture was brought to a reflux while stirring for 3 hrs. After, the solution was brought back down to 0°C, and acetic anhydride (1.5 mL, 1.62 g, 0.016 mol) was quickly added. The solution turned light gray, and the reaction was brought to reflux again for 3 hrs. After the reflux, the solution was cooled to room temperature, water (25 mL) was added, and the solution was poured into a mixture of 10% hydrochloric acid solution (80 mL) and dichloromethane (50 mL). The layers were separated, and the aqueous layer was extracted with dichloromethane (1 x 40 mL). The organic layers were combined and washed sequentially with water (1 x 40 mL) and brine (1 x 40 mL). The organic layer was dried over anhydrous magnesium sulfate. The solution was filtered, and the solvent was evaporated under vacuum. The resultant solid was dissolved on silica gel with dichloromethane, and column chromatography was performed with dichloromethane. The fractions containing product were combined, and the solvent evaporated. (0.349 g, 41% yield); mp 79.5-81.0°C; GC/MS: 205; ^{1}H NMR (C_6D_6): δ = 7.90 (m, 2H), 7.30 (m, 2H), 7.21 (m, 4H), 4.00 (s, 2H), 2.27 (s, 2H), 1.79 (s, 3 H); ^{13}C NMR: (C_6D_6): δ = 170.608, 135.293, 130.252, 129.795, 128.151, 126.964, 123.968, 67.377, 25.655, 24.623, 20.869; Anal. Calcd for $C_{18}H_{15}DO_2$: C, 81.48; H, 6.46. Found: C, 81.38; H, 6.10.

Preparation of 8, 9, and 10

The identical synthetic procedure utilized for **4** was applied with the exception of quenching with water instead of D_2O for the preparation of **8,** and also with the exception of the replacement of lithium aluminum hydride with lithium aluminum deuteride in the synthesis of **10**.

1-bromo-1a,9b-dihydro-*1H*-cyclopropa[*l*]phenanthrene (8): (3.587 g, 45%, yield); GC/MS: 270, 191.

ethyl 1a,9b-dihydro-*1H*-cyclopropa[*l*]phenanthrene-1-carboxylate (9): (0.472 g, 14% yield); GC/MS: 204, 165.

10: (0.303 g); GC/MS: 206.

Project 2

Preparation of dibrominated vinylidene precursor (3)

In an oven-dried 100 mL round bottom equipped with a low temperature thermometer, stir bar, and line under argon, **1** (3.571 g, 0.010 mol) was added and dissolved in ~50 mL dry tetrahydrofuran and kept stirring. Anhydrous copper (II) chloride (0.1388 g, 0.001 mol) was added, and the solution was cooled to -100°C with a methanol/liquid nitrogen bath. Then, *n*-

butyllithium (5.00 mL of a 2.5 M in hexanes, 0.0125 mol) was added slowly over 25 min. The solution was kept at -100°C while this addition occurred. After the completion, the reaction mixture was left to sit at the low temperature for 1 hr. After 1 hr, the low temperature bath was removed, and the reaction mixture was warmed to room temperature overnight.

A 50 mL dichloromethane/50 mL saturated aqueous ammonium chloride solution was made, and the reaction mixture was slowly added. The solution was filtered by vacuum. The layers were separated, and the aqueous layer was extracted with dichloromethane (2 x 30 mL). The organic layers were combined and washed with water (2 x 40 mL). The organic layer was dried over anhydrous magnesium sulfate, filtered into a round bottom flask, and the solvent was evaporated under vacuum. A long chromatography column of silica gel was set up, and the reaction product was dissolved onto silica gel by dichloromethane. Fractions were collected using 5% ethyl acetate/95% hexanes as the solvent, separated, and left to evaporate by air, eventually forming crystals. (0.102 g); ^{1}H NMR ($CDCl_3$): $\delta = 7.3$ (m, 16H), 3.2 (s, 4H).

4.3 Photolysis

Photolysis experiments were carried out in C_6D_6. Compound **4** (0.111 g in 0.75 mL C_6D_6) and compound **8** (0.086 g in 0.75 mL C_6D_6) were photolyzed for 18 hrs. ^{1}H NMR was taken to confirm the disappearance of the starting material. Distillation under vacuum was performed where the distillate was condensed in a 5 mL pear shaped flask and dissolved in deuterated benzene before the proton spectrum was taken.

References

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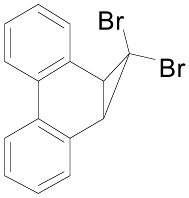
Vitae

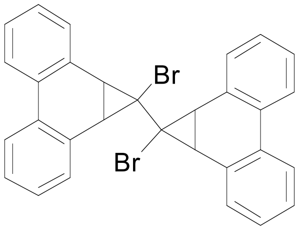
Jennifer Marie Nguyen was born to Hung and Lanh Nguyen on May 6, 1985, in York, Pennsylvania, with an identical twin clone following closely behind. She and her clone are two of four siblings, the other two of who are also deeply involved with the sciences. She prefers to go by Jenn, as Jennifer simply has too many syllables.

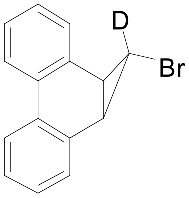
Jenn made her way through the teenage years and high school interested in the sciences, English, and music. She eventually made her way to Maine, where she attended Colby College and braved the cold weather. Originally intending to be a biology major, she decided to switch to chemistry after seeing how tightly knit the department was. While Jenn is often found in Keyes at late hours of the day, she also spends much time at Bixler, working towards her second major in music and studying voice. She is often told that she has a big voice (and appetite) for such a small and quiet person.

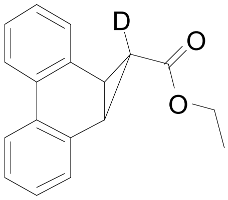
Jenn will graduate on May 27, 2007, with a bachelor's of arts in both chemistry, as accredited by the American Chemical Society, and music. She will attend Pennsylvania State University in the fall of 2007 in hopes of obtaining a doctorate in chemistry.

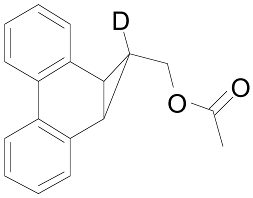
Appendix: Spectral Data

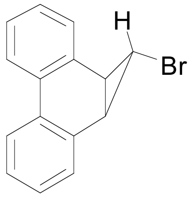








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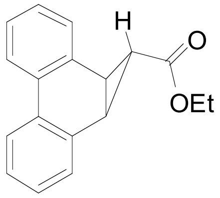
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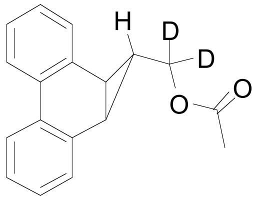
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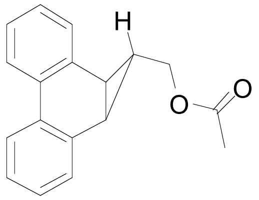
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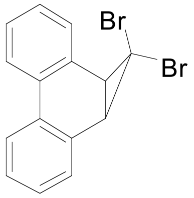

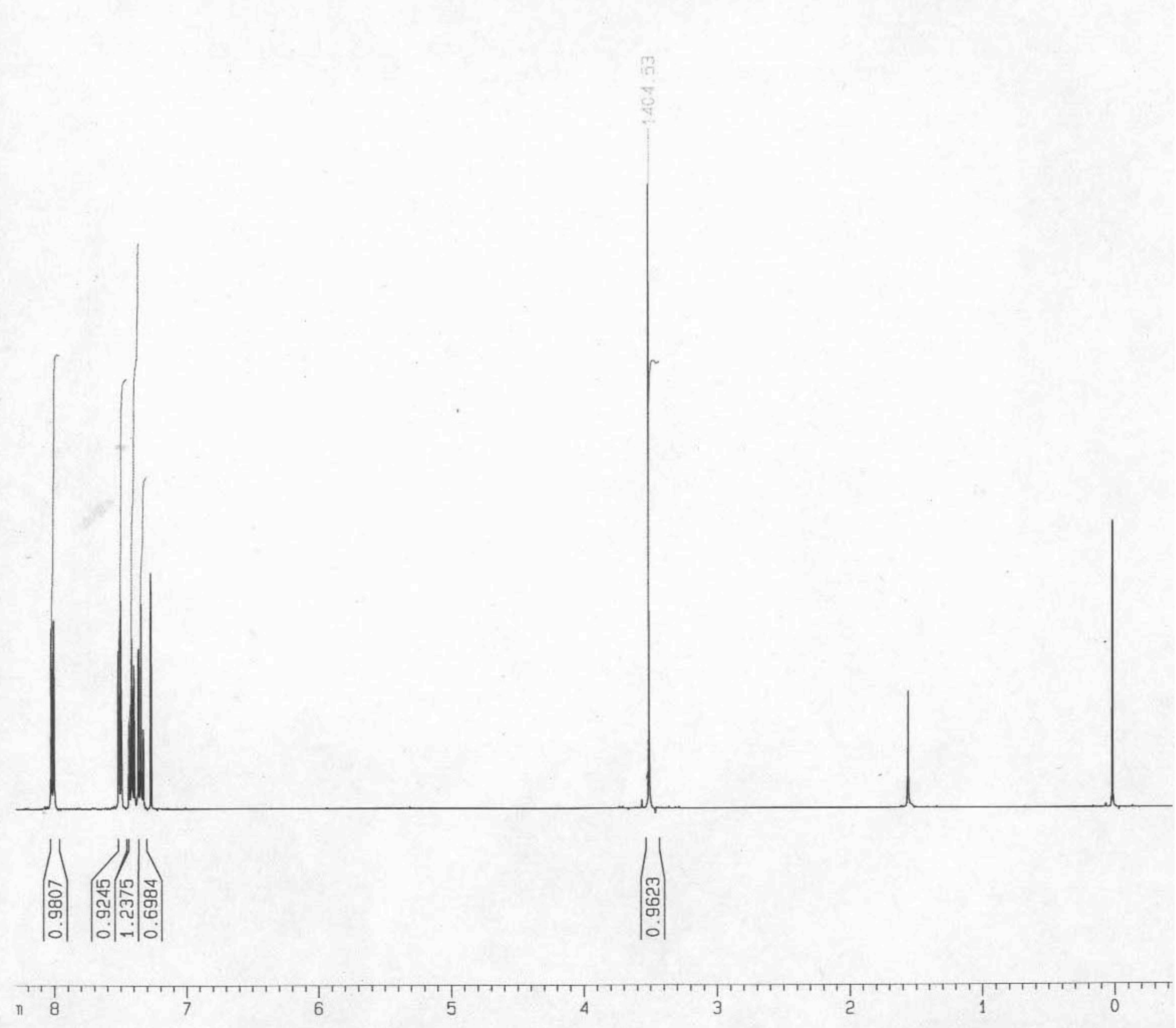

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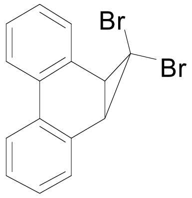
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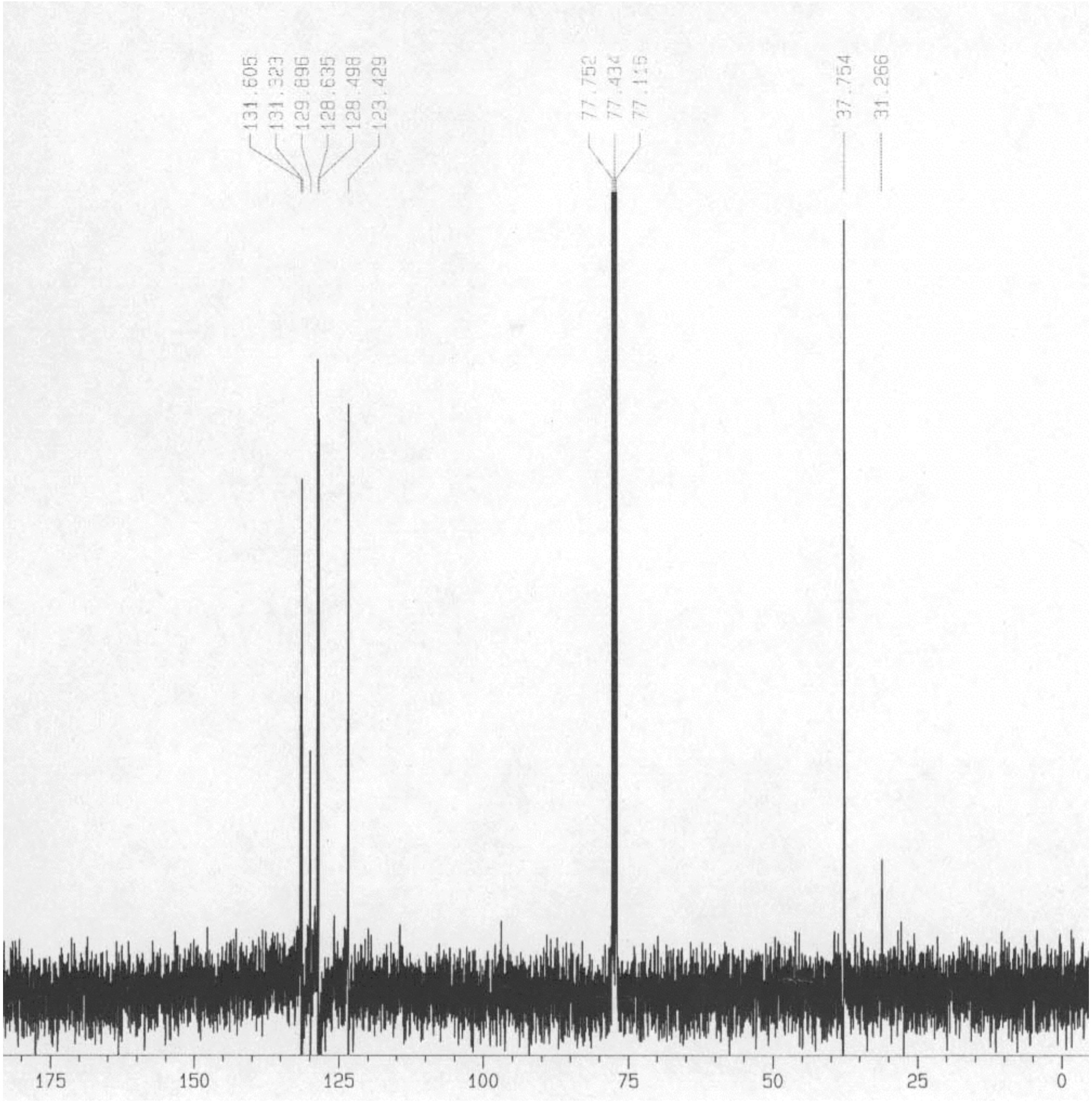
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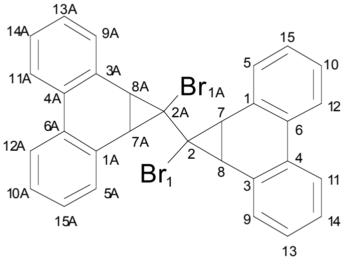
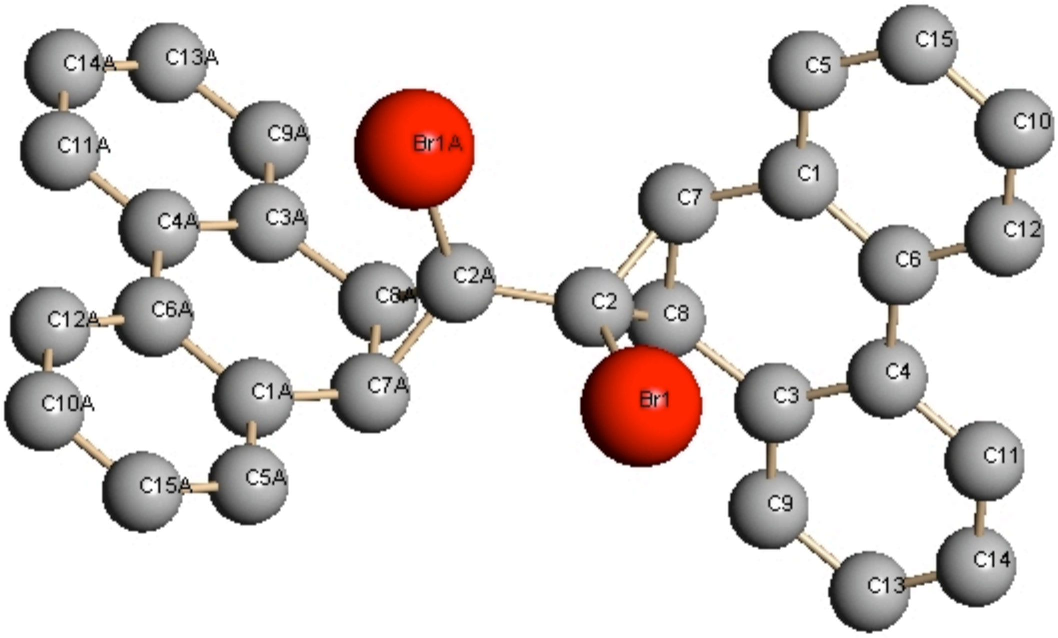
3. X-Ray Crystal Structure





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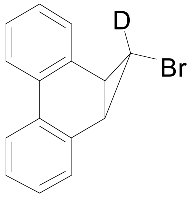

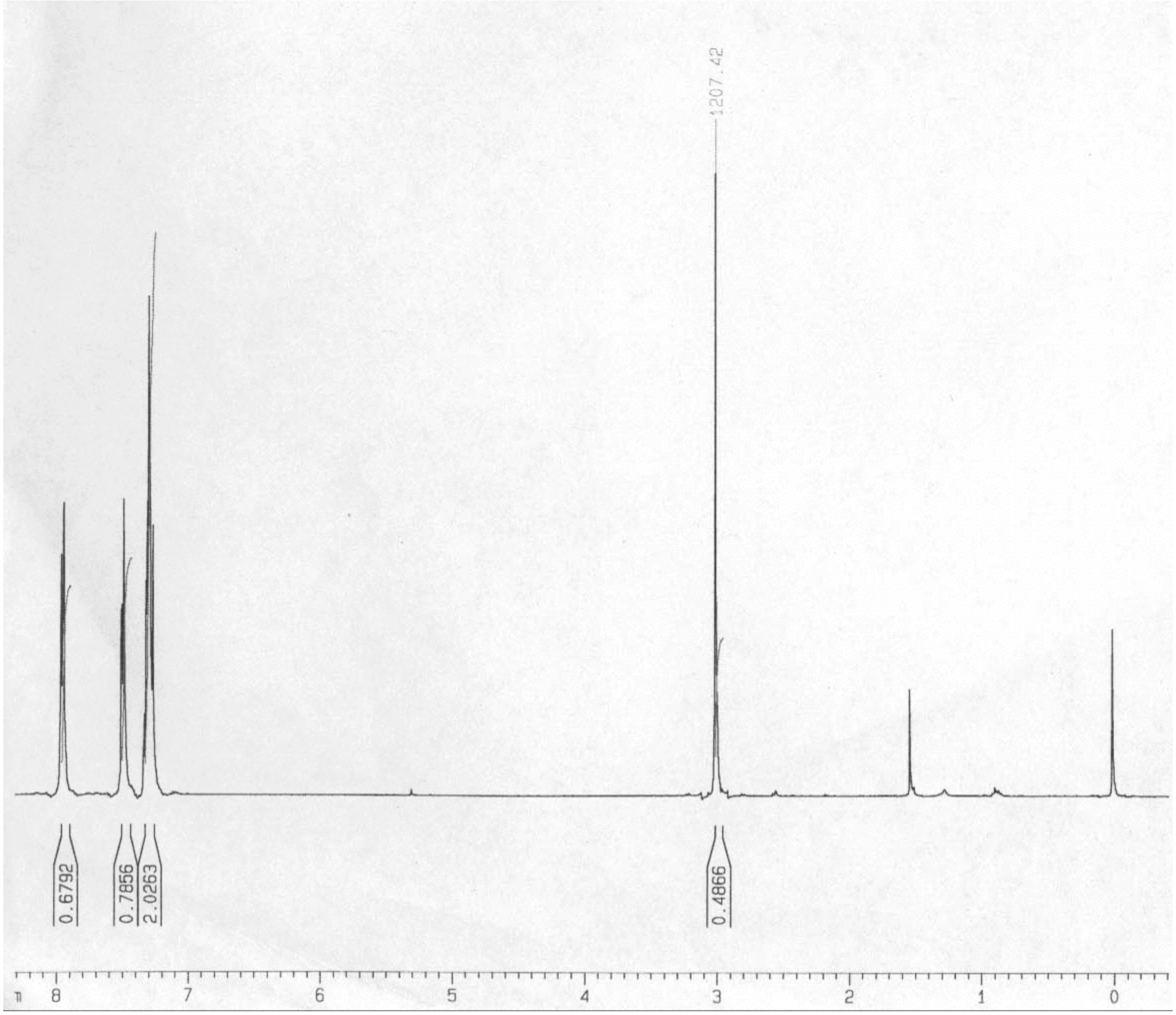

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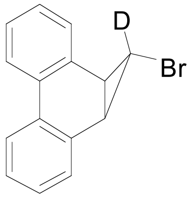
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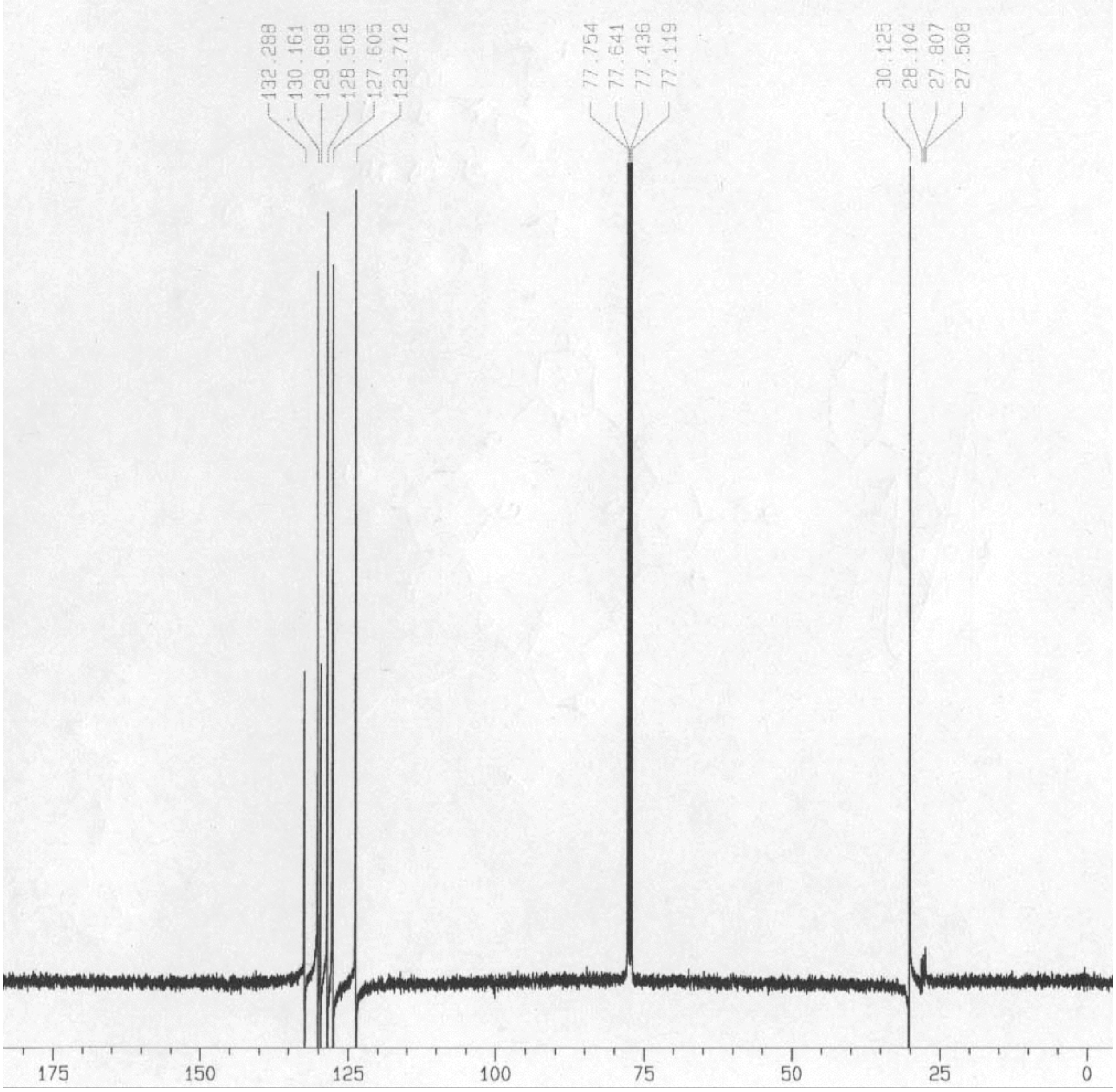
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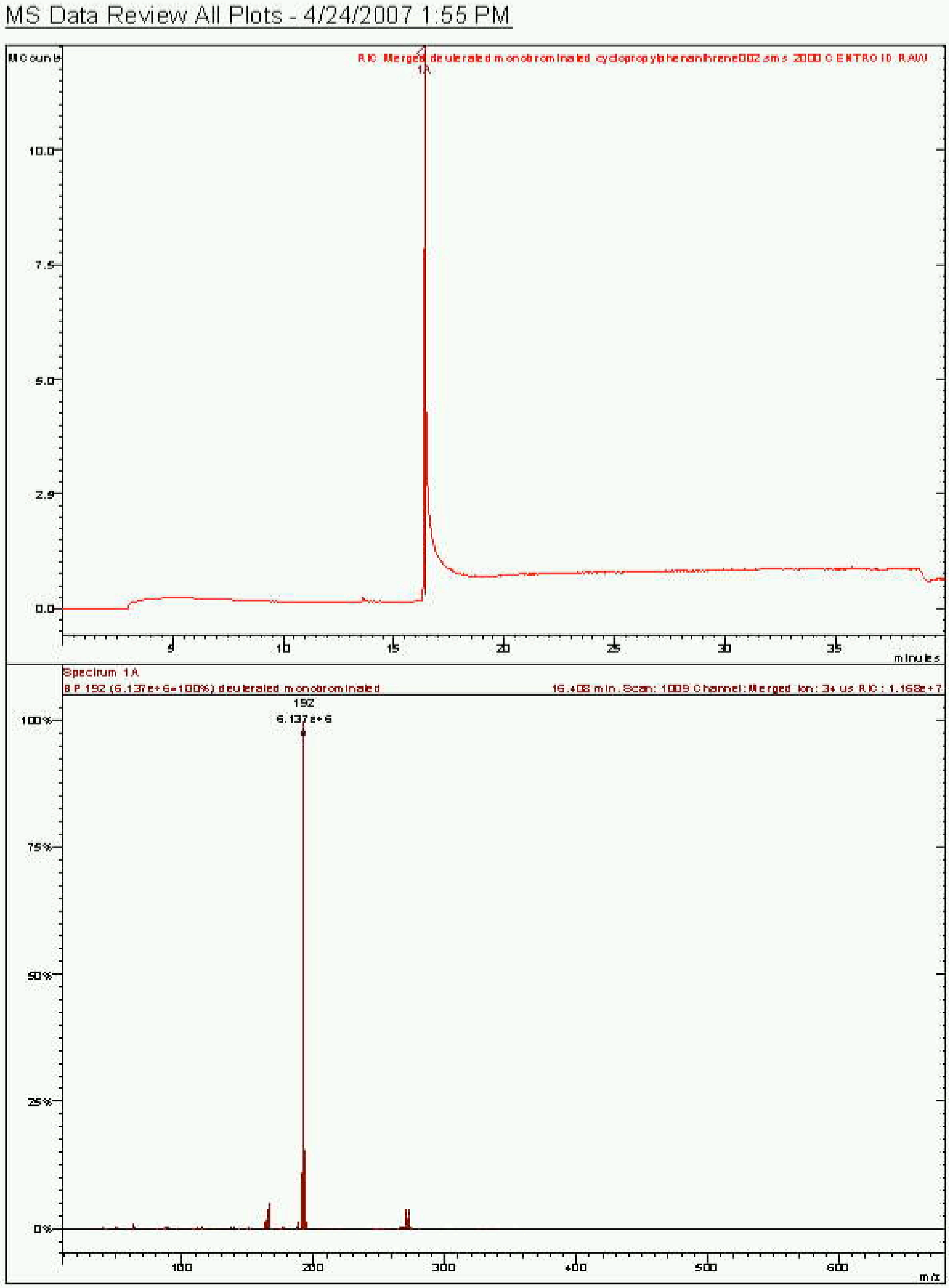

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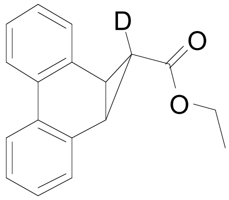

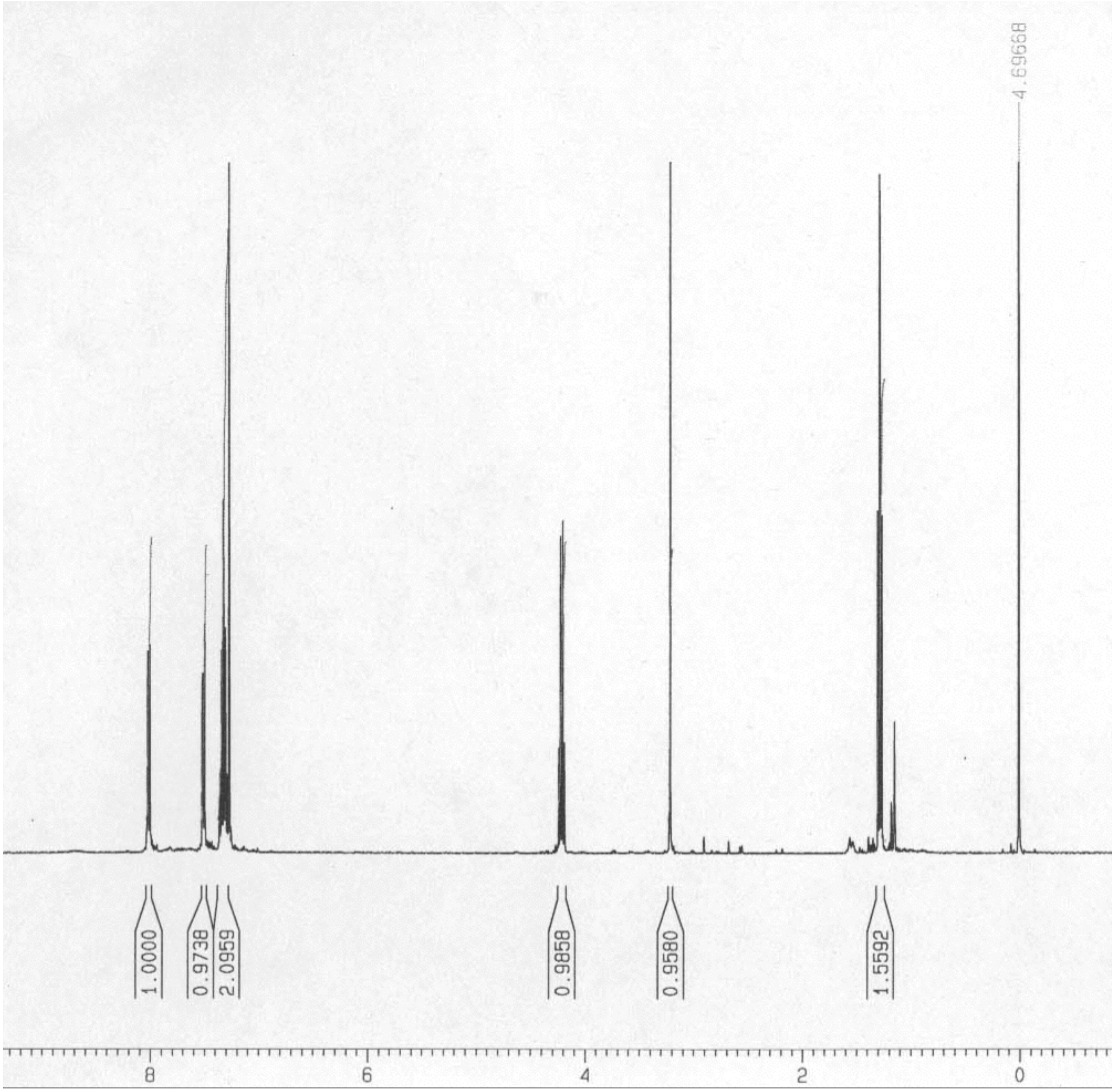

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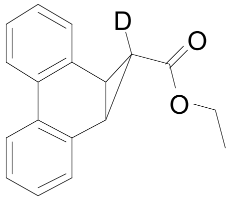
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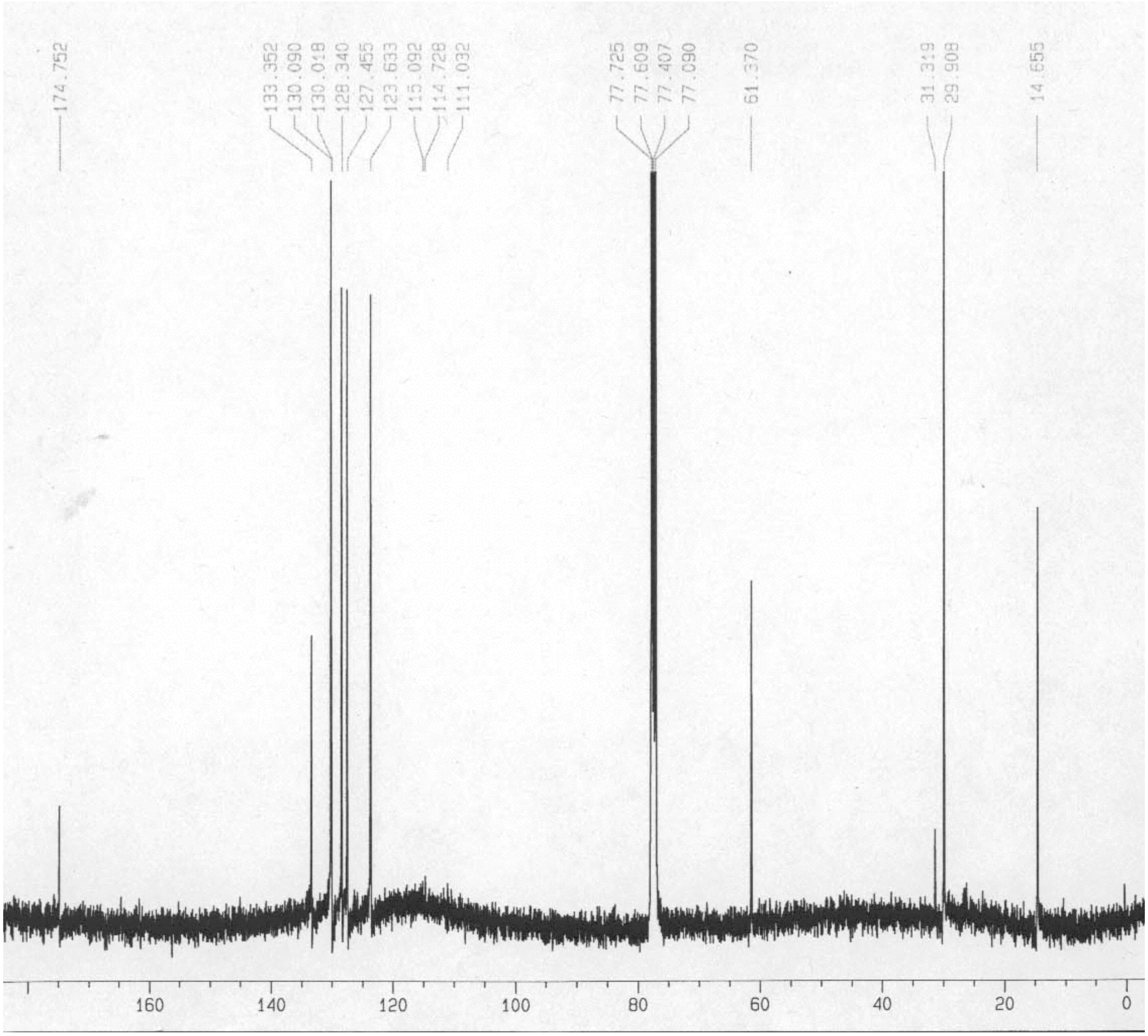
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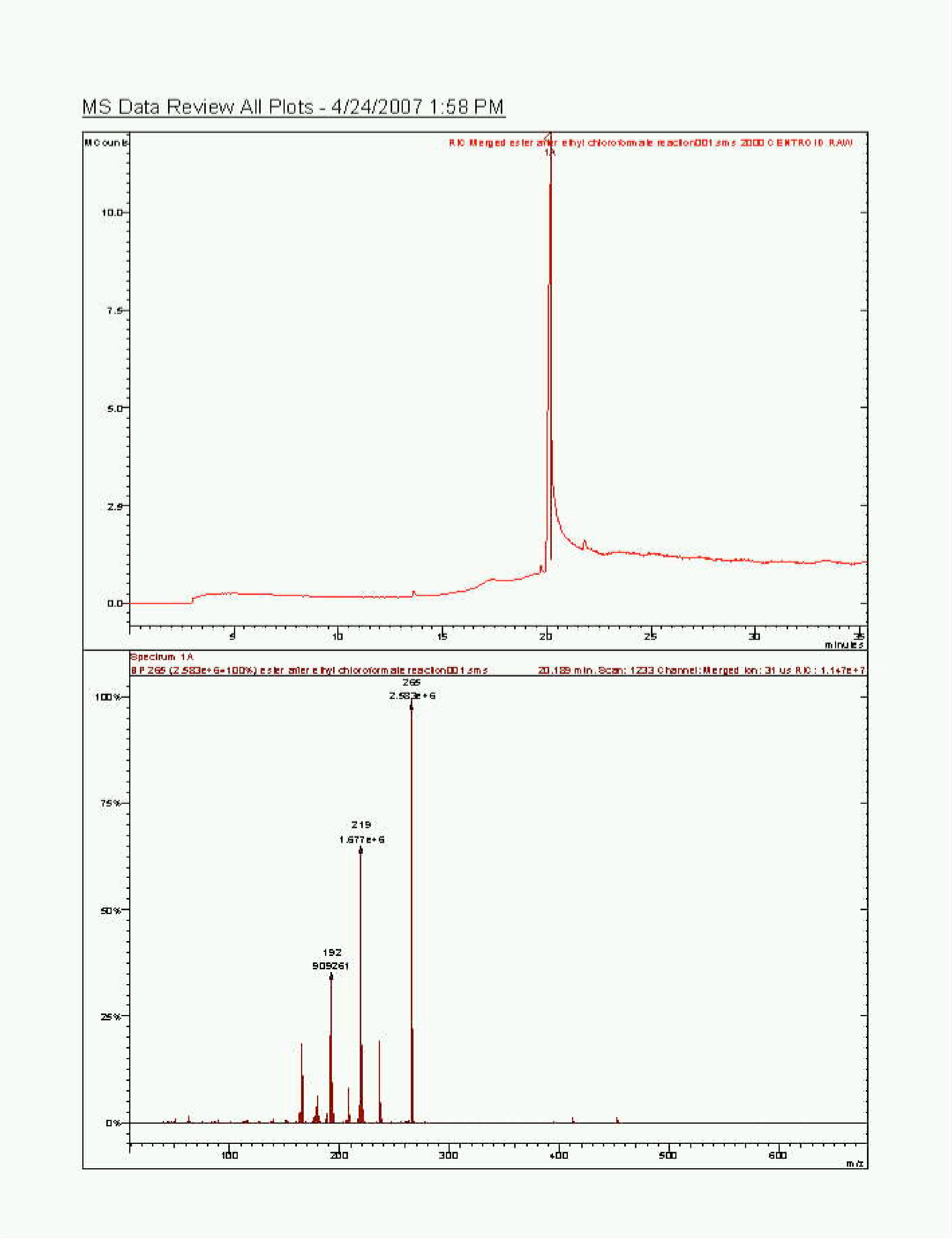
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minutes
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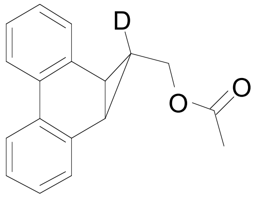
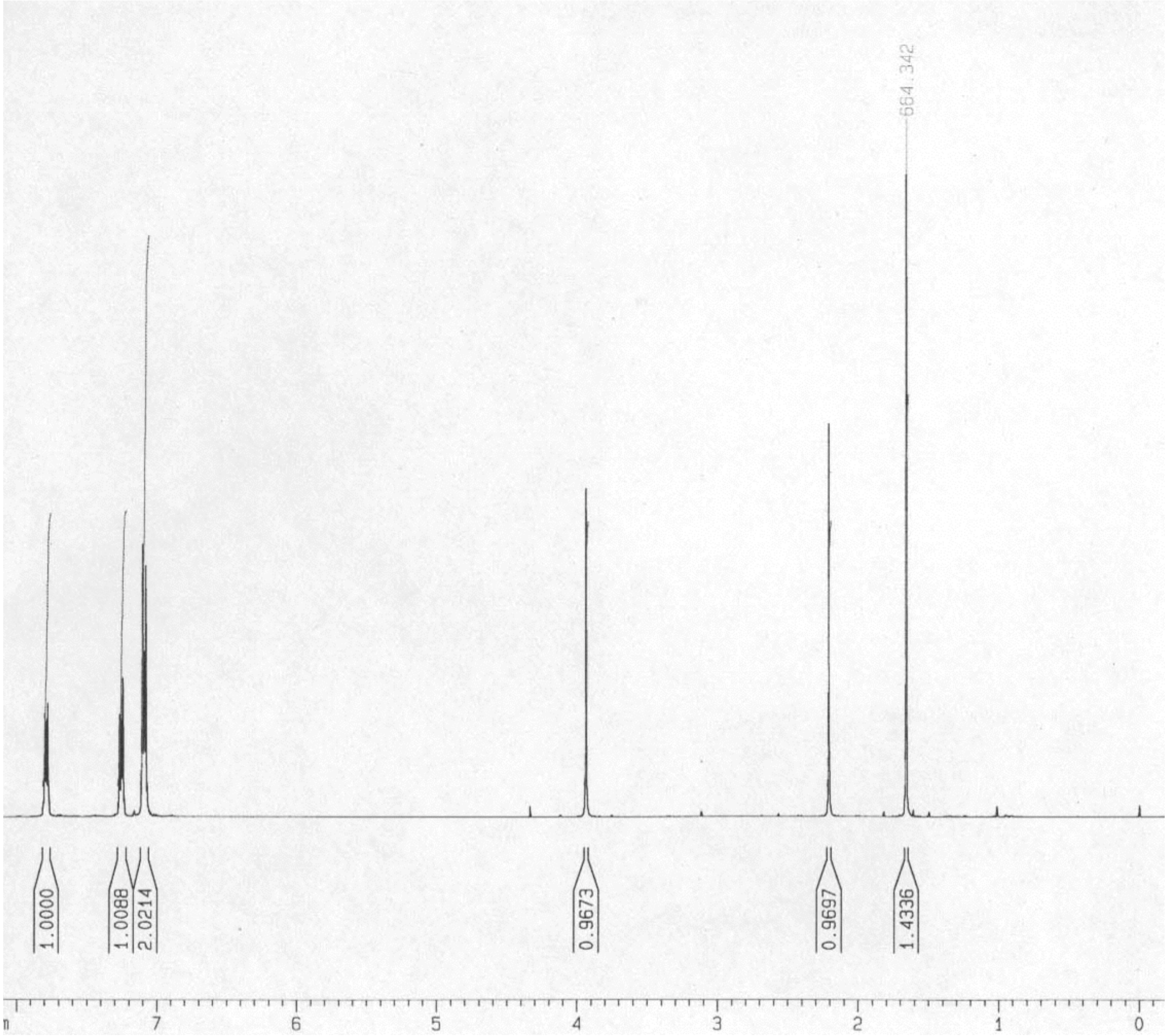
6. ^{1}H NMR





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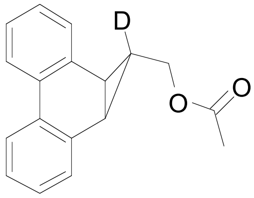
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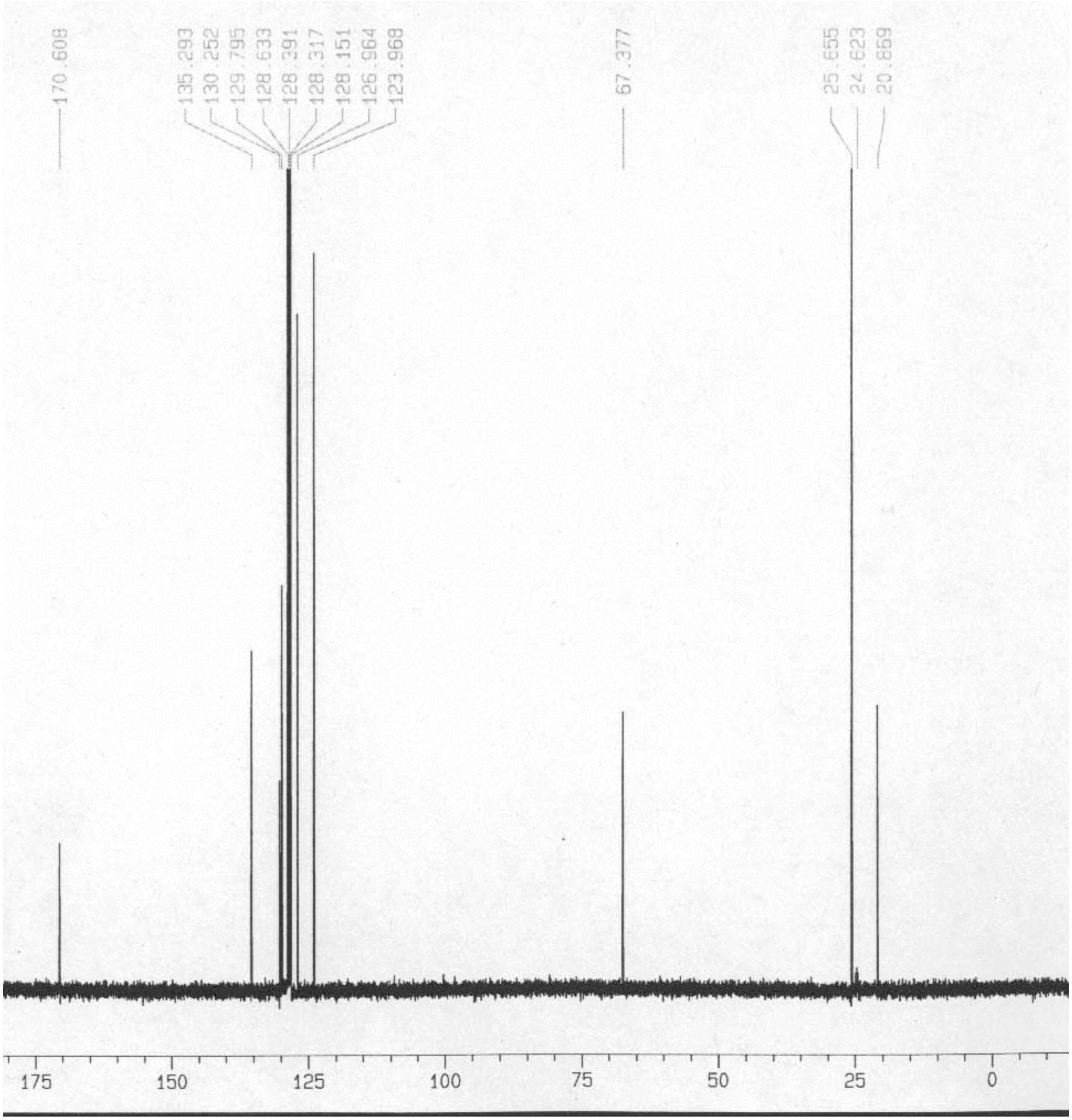
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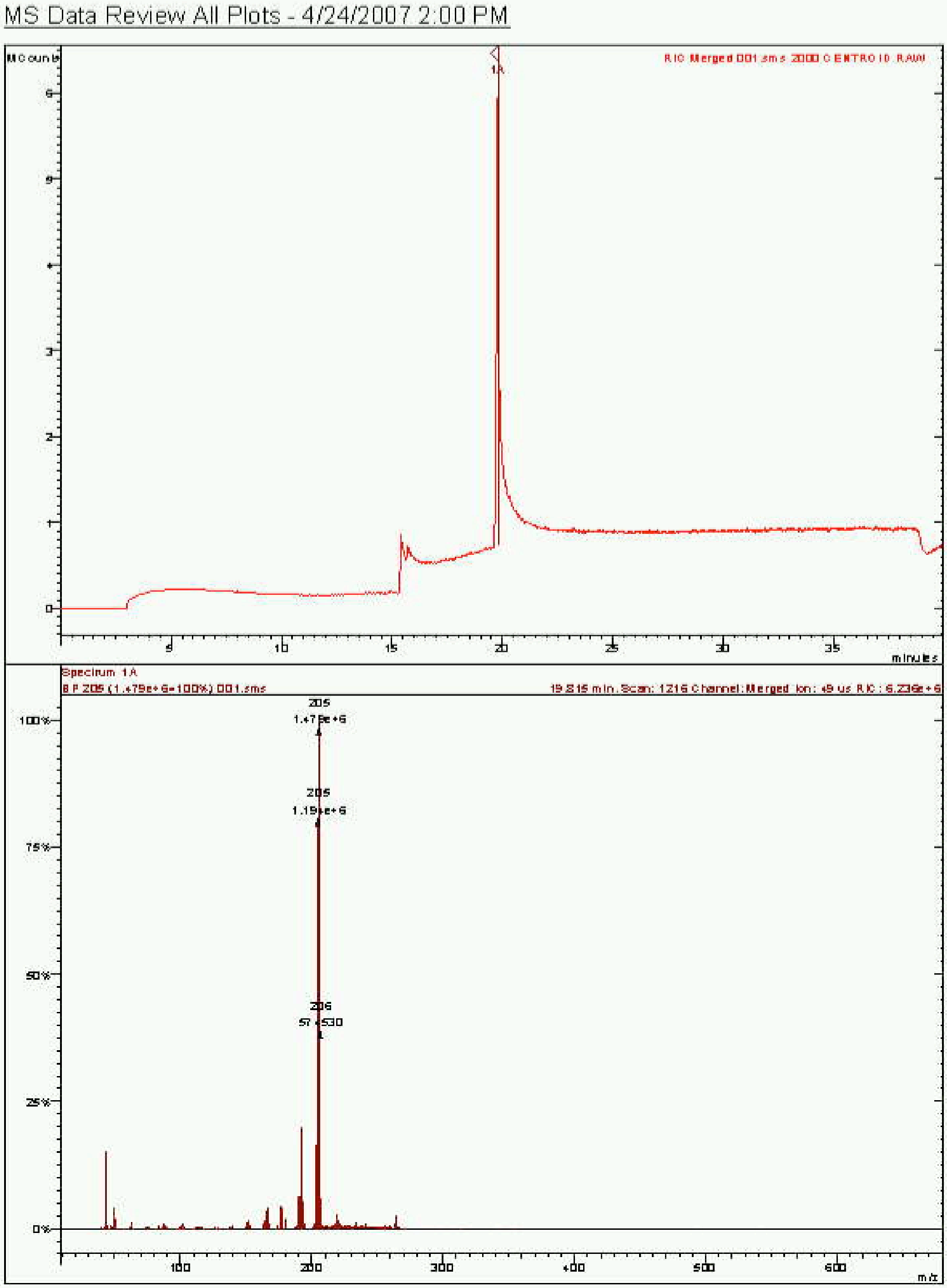
6. GC/MS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minutes
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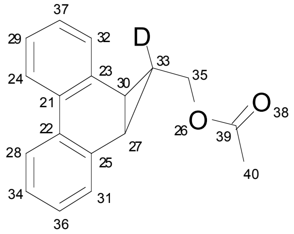
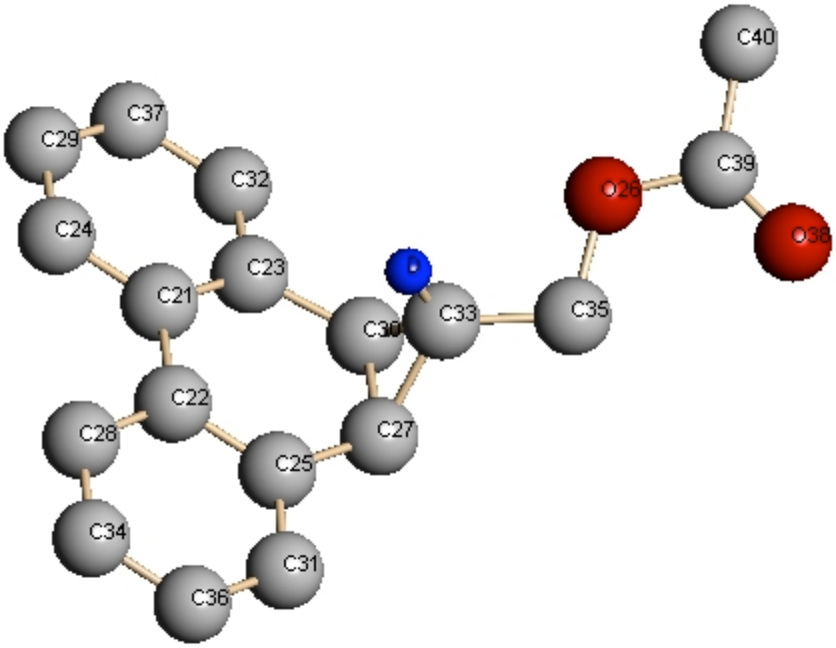
6. X-Ray Crystal Structure





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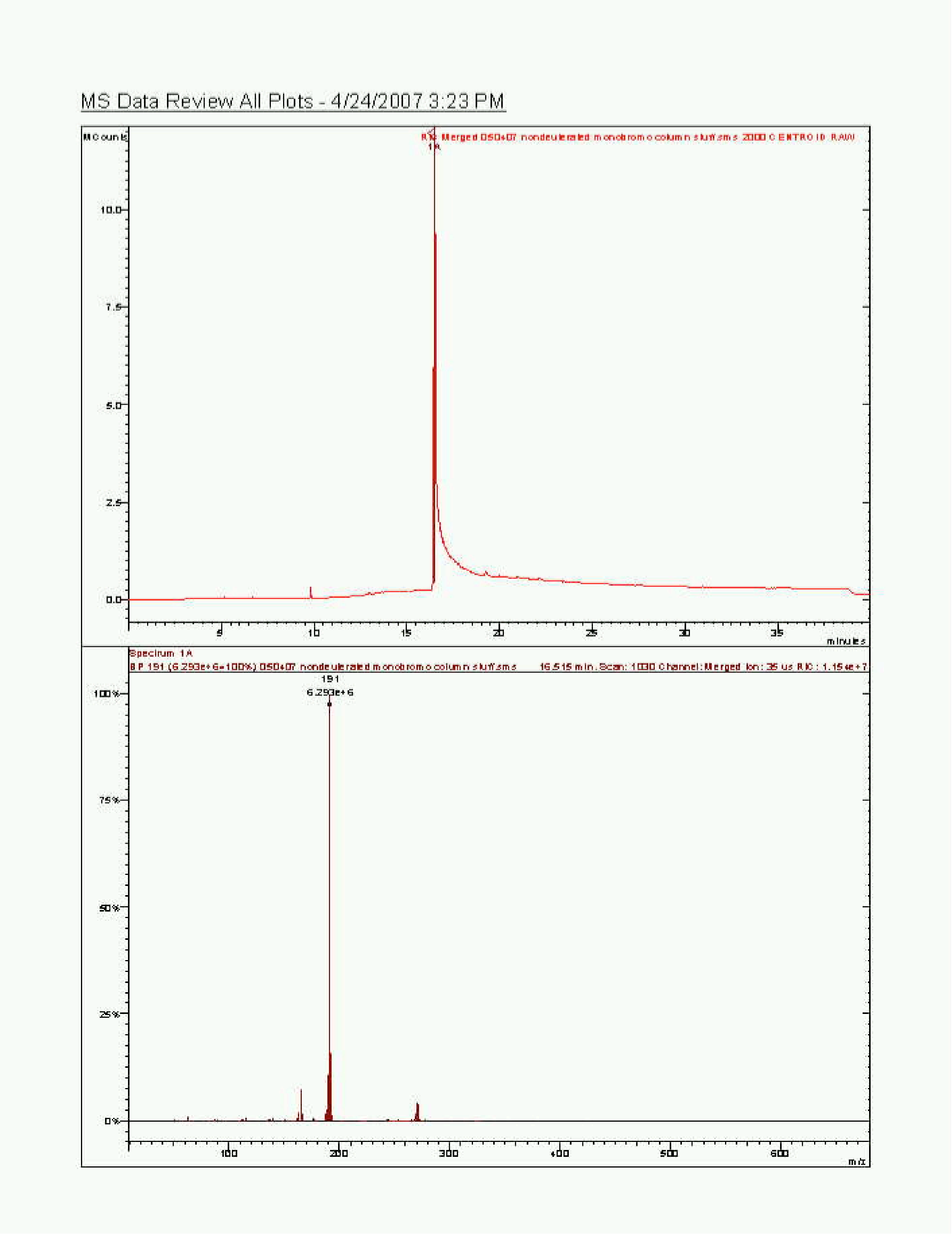
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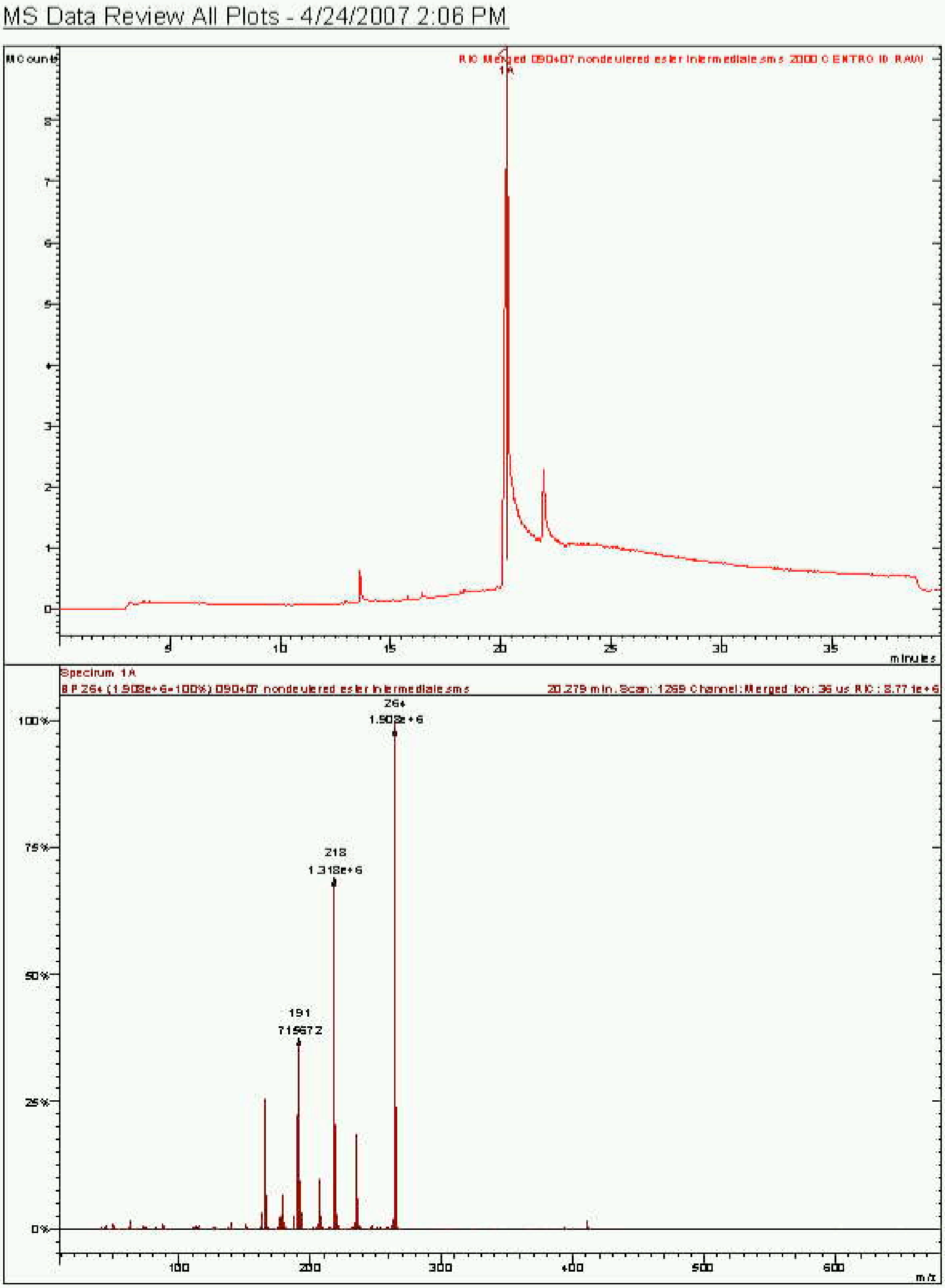
m/z

9. GC/MS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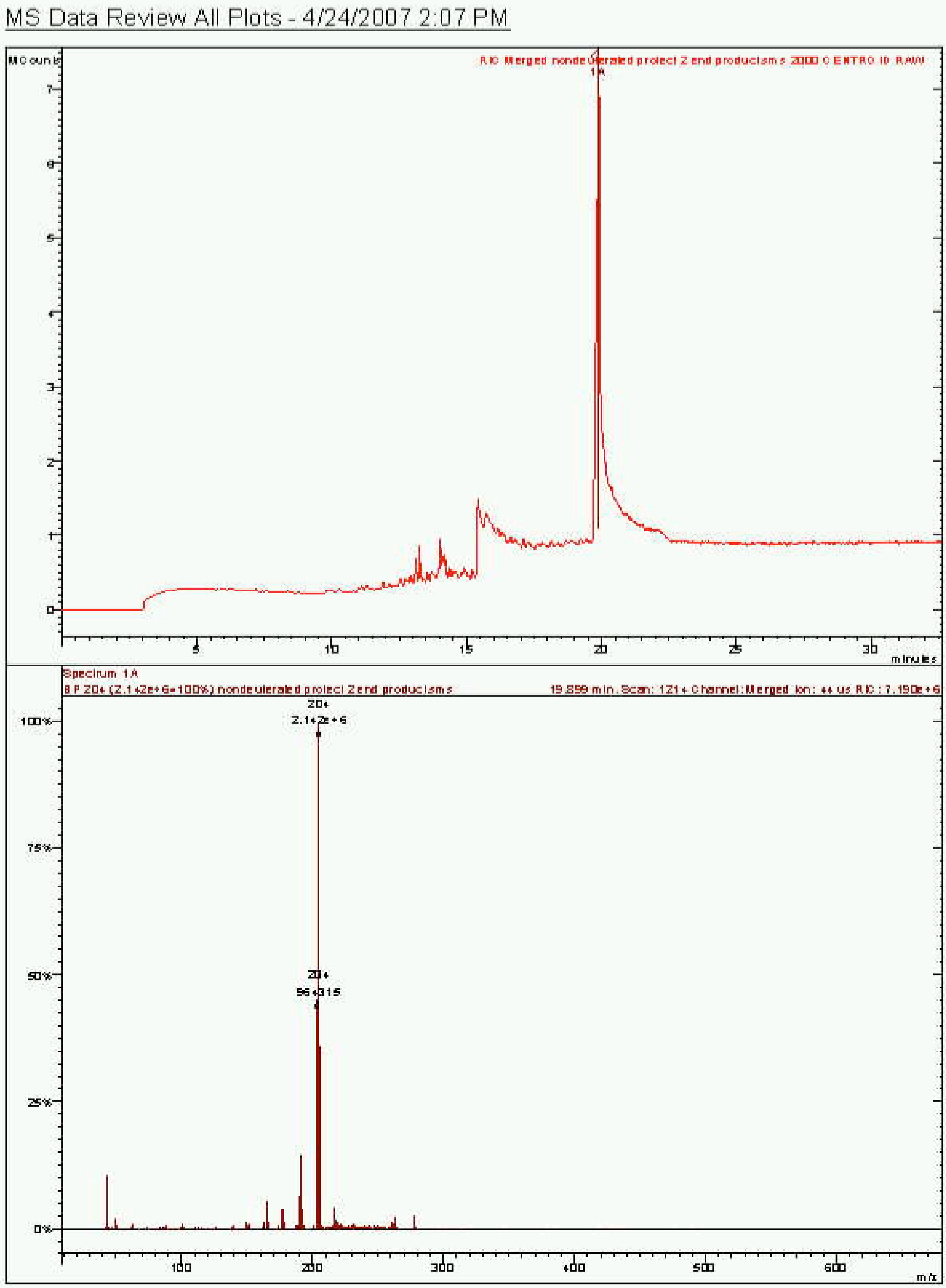
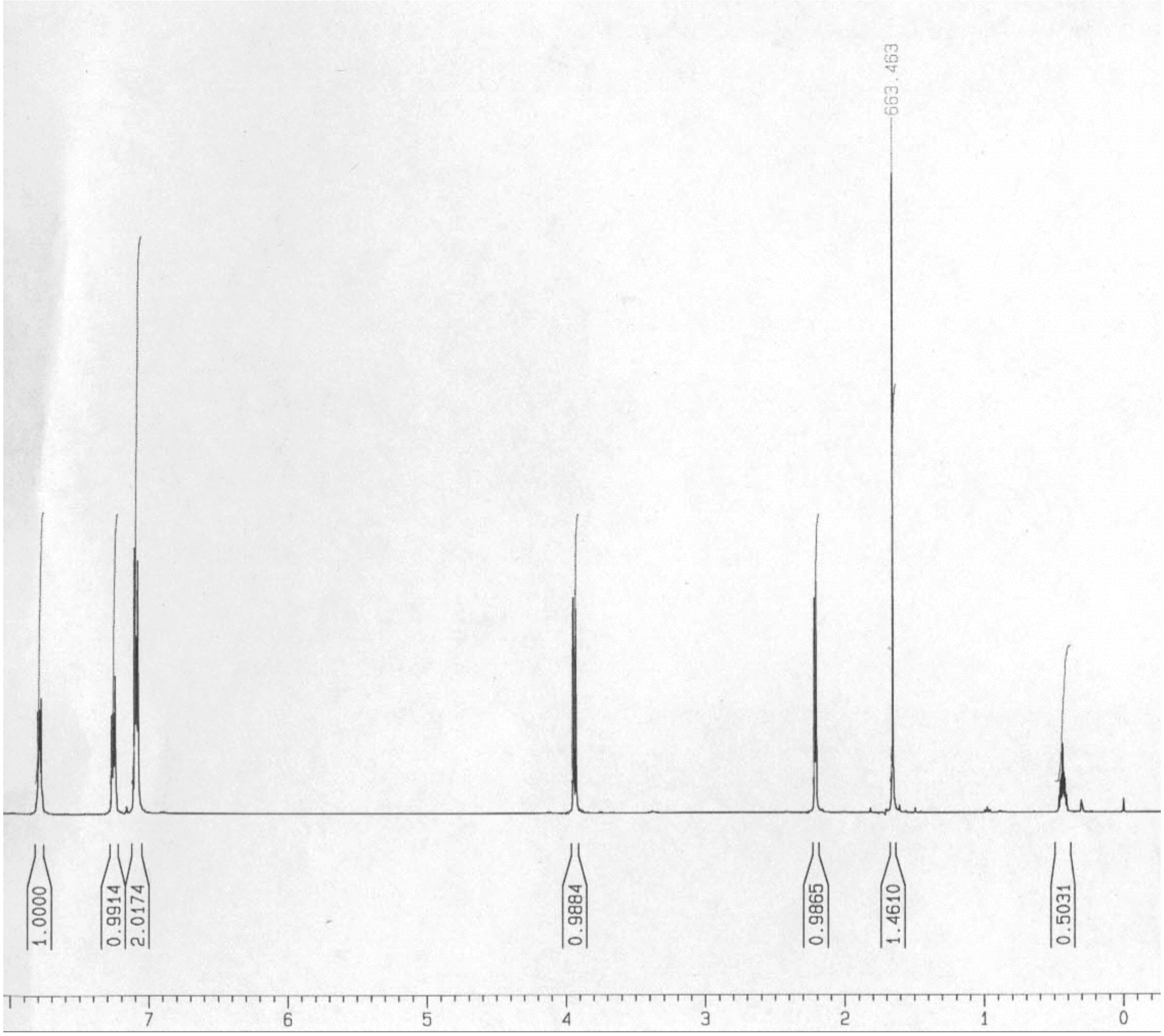
MCounts
RIC Merged 090407 nondeuterated ester intermediate.sms 2000 CENTROID RAW
1A
8
7
6
5
4
3
2
1
0
5
10
15
20
25
30
35
minutes
Spectrum 1A
BP 264 (1.903e+6=100%) 090407 nondeuterated ester intermediate.sms
20.279 min. Scan: 1269 Channel: Merged Ion: 36 us RIC: 8.771e+6
264
1.903e+6
218
1.318e+6
191
715672
100%
75%
50%
25%
0%
100
200
300
400
500
600
m/z

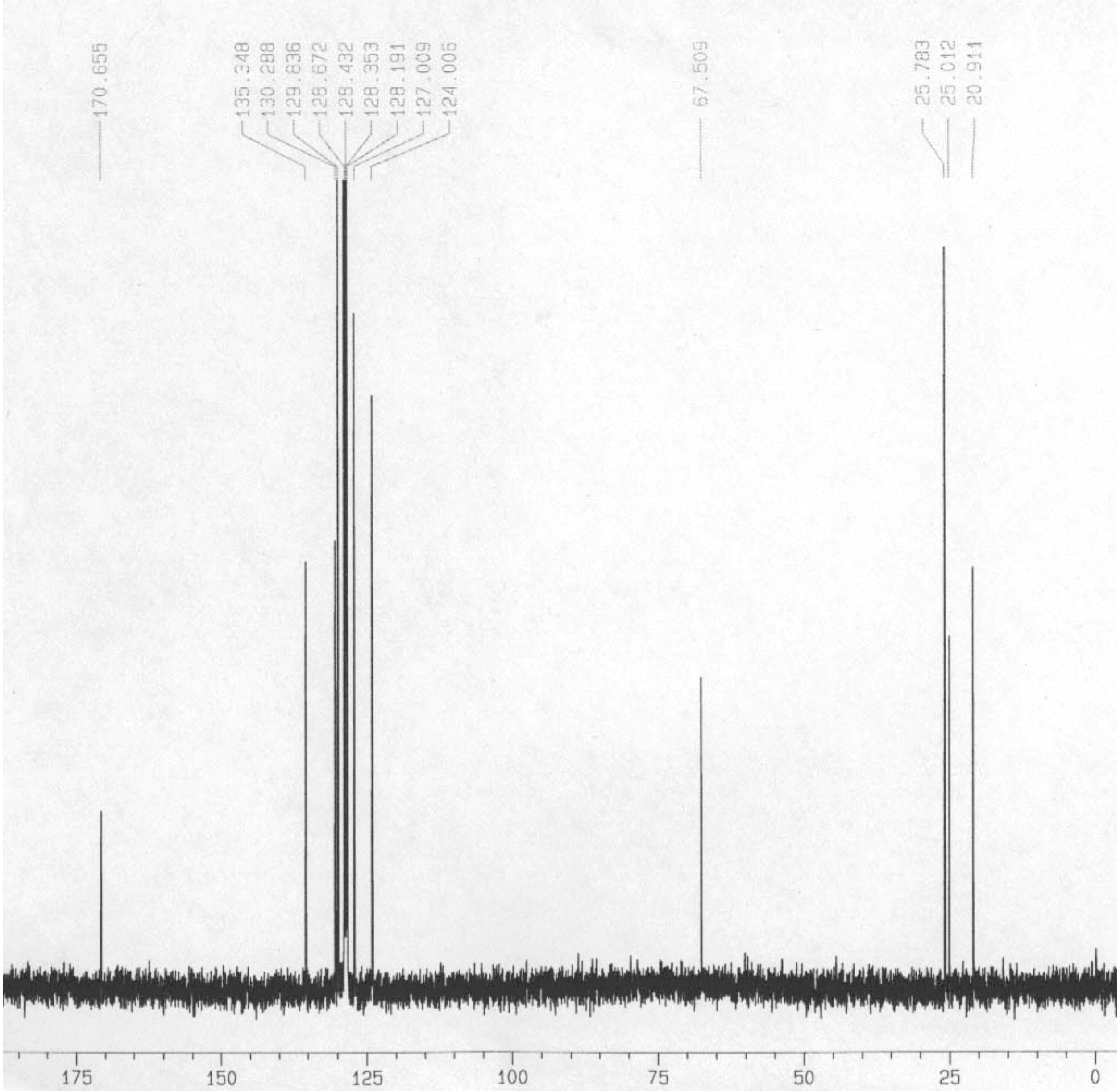
10. GC/MS


MS Data Review All Plots - 4/24/2007 2:07 PM
MCounts
RIC Merged nondeuterated project 2 end products.sms 2000 CENTROID RAW
1A
7
6
5
4
3
2
1
0
5
10
15
20
25
30
minutes
Spectrum 1A
BP 204 (2.142e+6=100%) nondeuterated project 2 end products.sms
19.899 min. Scan: 1214 Channel: Merged Ion: 44 us RIC: 7.190e+6
204
2.142e+6
204
964315
100%
75%
50%
25%
0%
100
200
300
400
500
600
m/z

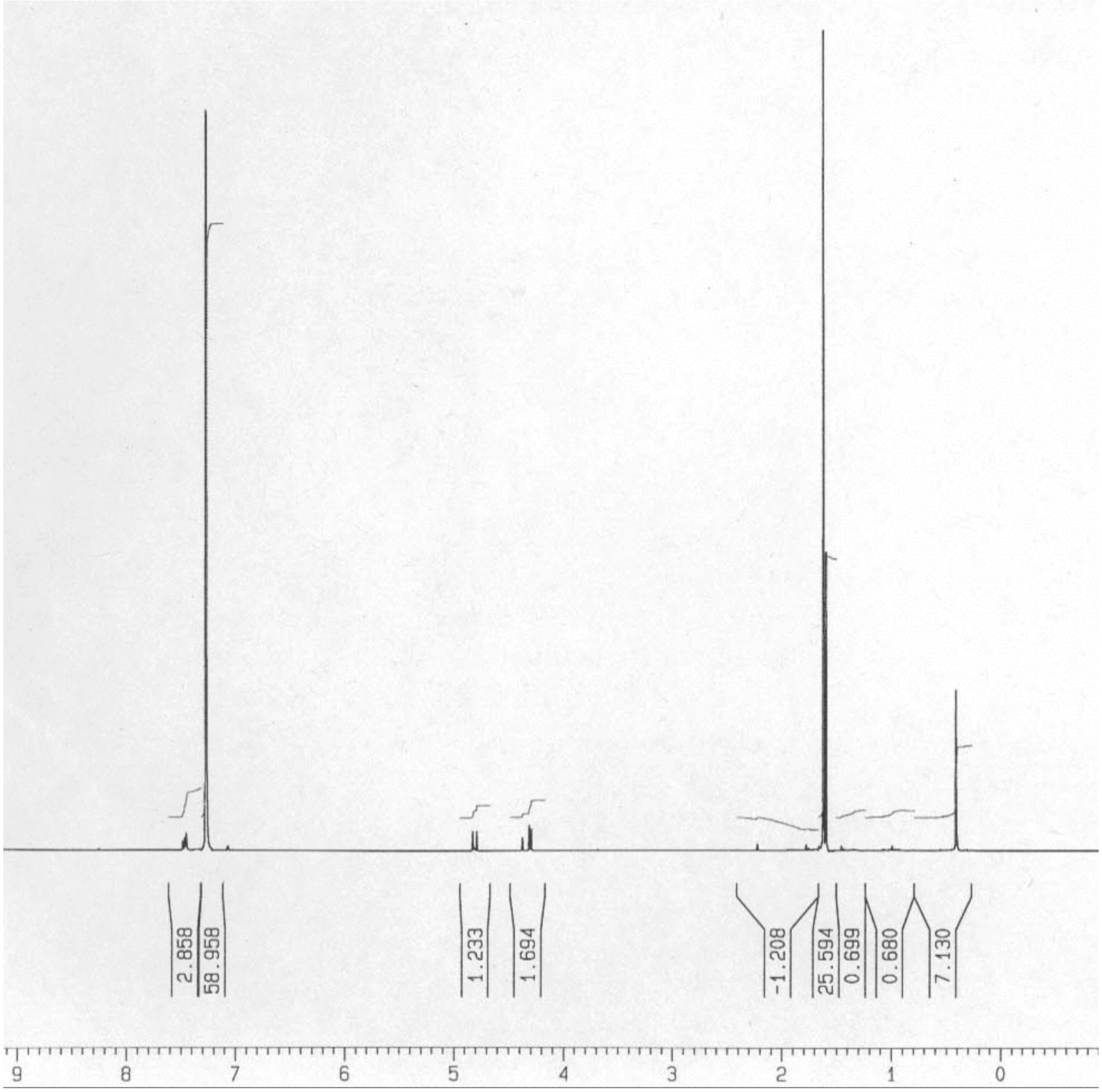
Nondeuterated carbene precursor from Schnermann:



Nondeuterated carbene precursor from Schnermann, ^{13}C NMR



Vinyl acetate after photolysis of the monodeuterated compound 6, ^{1}H NMR



Vinyl Acetate Standard, ^{1}H NMR