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Silicon and tin substituted halocyclopropanes: approaches to new carbenes and strained cyclic allenes

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Silicon and tin substituted halocyclopropanes: approaches to new carbenes and strained cyclic allenes

By Noura Srour

A Thesis Presented to the Department of Chemistry,
Colby College, Waterville, ME
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With Honors in Chemistry

Submitted May 22, 2018

Silicon and tin substituted halocyclopropanes: approaches to new carbenes and strained cyclic allenes

By Noura Srour

Approved:

_____

(Mentor: Dasan Thamattoor, Professor of Chemistry)

_____Date

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(Reader: *Jeffrey Katz, Professor of Chemistry)*

_____Date

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I would also like to thank my little family here at Colby: all my friends who have provided a shoulder for me to cry, a hand when I am in need and a warm heart for me to laugh with. Far away from my blood ties, my heart has found and chosen a family and I consider myself blessed.

I thank the entire chemistry department for literally babying me with all the endless questions I might have had. Knowledge is power and today you have helped thrust me into my future career hopefully in pharmaceutical research. Special thanks to Professor Katz for contributing to making me love Organic Chemistry, as well as his support on this thesis.

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Abstract

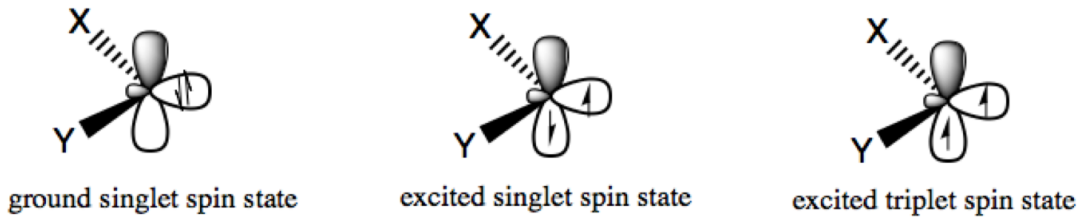
Chloro(trimethylsilyl)carbene and chloro(trimethylstannyl)carbene were generated through photolysis of cyclopropanated phenanthrene precursors which were synthesized in two steps. The photolysis reactions were done in the presence of cis and/or trans-beta-methylstyrene. Though product peaks corresponding to the carbene-alkene adducts were observed in the GCMS, the yields were too low for their isolation and complete characterization. Density functional theory (DFT) calculations were performed on the stereoisomers of the precursor to Chloro(trimethylsilyl)carbene and the carbene itself. Surprisingly, Chloro(trimethylsilyl)carbene's triplet state was found to be more stable than the singlet at this level of theory.

In a related project, (1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)trimethylstannane, was synthesized in an effort to generate bicylopropylidene dimers via a coupling reaction using copper thiophene-2-carboxylate. Instead a cyclobutane derivative was obtained. Two mechanisms leading to the observed product are proposed: (a) rearrangement of the initially formed and expected dimer(s) and/or (b) dimerization of a dibenzocycloheptatraene (allene), formed directly from a cyclopropylidenoid, or through the generation and rearrangement of a cyclopropylidene. DFT calculations were also carried out to assess the relative stabilities of the bicylopropylidene dimers and the cyclobutane derivative.

Introduction

The last few decades have witnessed an intensification of research in the carbene field. Some of the few revolutionary elucidations of carbene chemistry involve the study of carbon-hydrogen insertion reactions of methylene by Doering et al and Dvoretzky et al.,[1,2a,b] the dichlorocarbene intermediacy in the hydrolysis of chloroform by Hine[1,3] and the addition reaction between alkenes and dichlorocarbene by Doering and Hoffmann.[1,4] Carbenes are particularly interesting in that they are divalent species: their lack of octet makes them highly reactive. Therefore, they hold promising opportunities as intermediates in complex chemical synthesis.

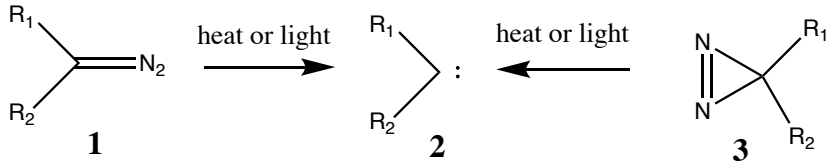
The simplest carbenes are in the form :CR_2. They exist in three different spin states (Scheme 1) : either the electrons are in the same orbital or in different orbitals. They can have the same spin, corresponding to a triplet, or opposing spins, which gives a singlet state. It is important to note that the preferred state of carbenes is highly dependent on the groups attached to them. For methylene and most carbenes, the most stable state is the triplet state, so as to follow Hund's rule and minimize electron repulsion.[1] Electron donating groups, such as halogens, would favor the singlet ground state given that they can stabilize the empty p_z orbital through resonance.[1]



Scheme 1: Carbene Spin States

How do you generate carbenes?

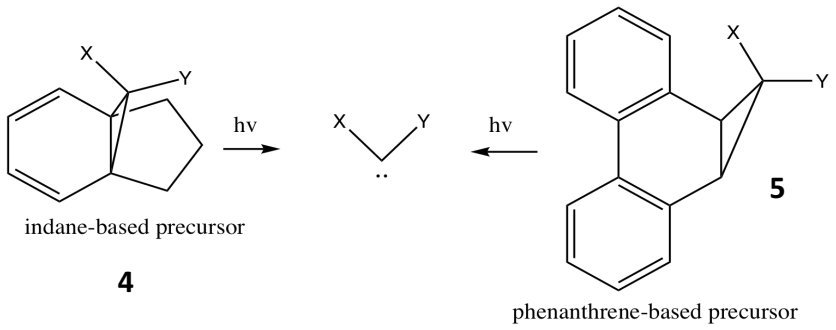
The generation of carbenes has traditionally been done using diazo and diazirine precursors.[2b,5]



1 2 3

Scheme 2: Carbene generation from diazo (1) and diazirine (3) precursors

In both techniques, the production of highly stable molecules such as nitrogen gas is essential in driving the reaction, thus compensating for the generation of the highly unstable carbene. However, they present critical safety issues since they make use of carcinogenic and explosive nitrogenous compounds. Hence, it became crucial to device better alternatives to access carbenes and investigate their chemistry. Indane-based[6] and phenanthrene-based[7] precursors are suitable candidates and have been successfully employed by our laboratory to generate carbenes through photolysis (Scheme 3).



indane-based precursor

4

5

phenanthrene-based precursor

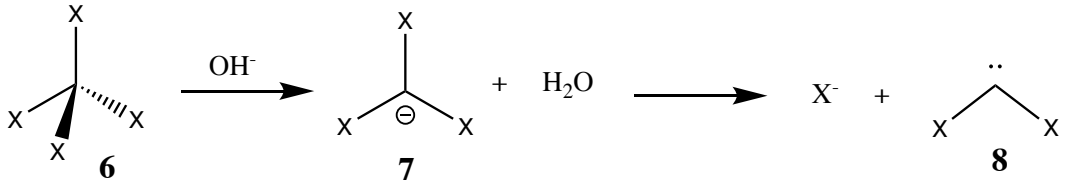
4. X, Y= Cl (3)

5. X= H, Y= CH_2OEt (4)

Scheme 3: Alternative precursors of carbenes

As seen with nitrogenous precursors, the generation of carbenes must involve a stable side product to drive the reaction. Indane and phenanthrene are regenerated from photolysis **4** and **5** respectively (Scheme 3). However, our lab chose phenanthrene-based precursors for carbene generation because they are more easily synthesized.

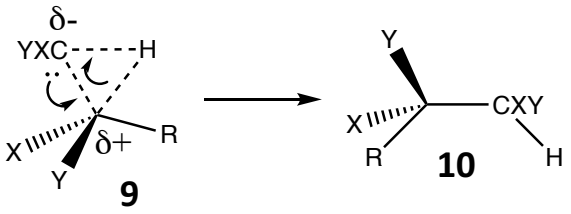
Base hydrolysis of haloforms can also afford carbenes (Scheme 4). The base removes the haloform proton forming a trihalomethyl anion.[8] A halide is lost in a subsequent step, leading to the dihalocarbene. This method of carbene generation involves the use of a phase transfer catalyst in order to mediate interactions between reactants in different phases.[5]



Scheme 4: Base Hydrolysis of haloform to generate a carbene [5]

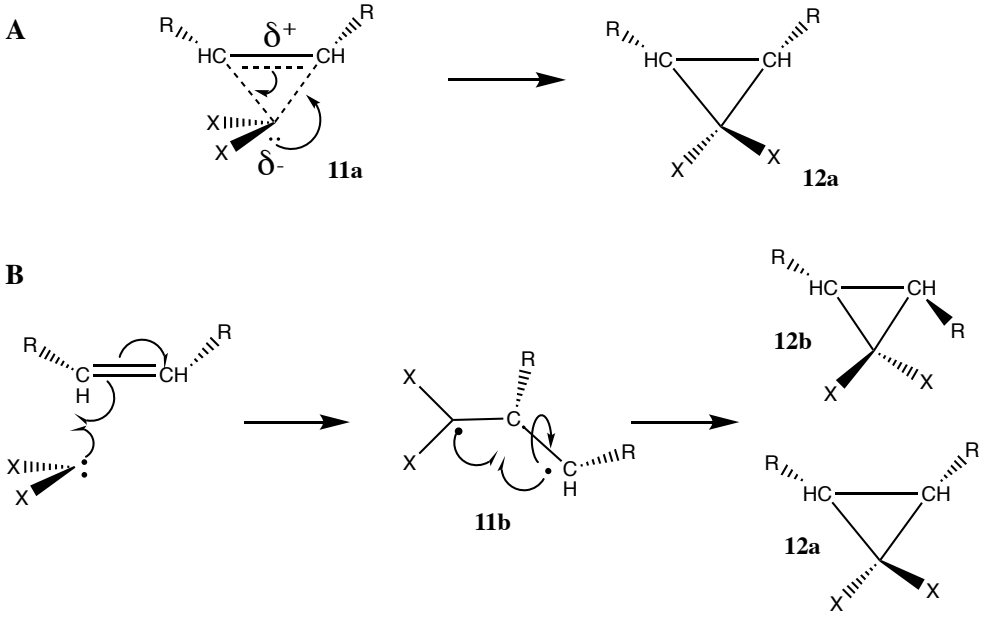
Carbene reactions: Insertion and addition

Among the different reactions that carbenes can undergo, insertion reactions are very useful and allow elongation of carbon chains. Singlet alkylcarbenes are known for inserting themselves in between X-H bonds through electrophilic attack.[1] Considering transition state **9** (Scheme 5), the substrate carbon gains a partial positive charge as its valence electrons are polarized towards the carbene, which itself becomes partially negative.[1] The insertion mechanism is concerted, meaning that the electron movements are synchronized, favoring retention of stereochemistry.[1]



Scheme 5: Transition state of singlet carbene insertion reaction to C-H[1]

Singlet alkylcarbenes can also undergo addition reactions with alkenes, which donate their pi electrons to the electrophilic carbene, forming a cyclopropane adduct (compound **12a**) (Scheme 6, A).[1] This also is a concerted mechanism with retention of stereochemistry. The rate of reaction is highly determined by the olefin substituents. For instance, the presence of electron donating groups such as alkyl or hydroxyl groups will stabilize the transition state's partial positive charge (Scheme 6, A).



Scheme 6: Transition state of A-singlet carbene addition reaction to alkenes, B- triplet carbene addition reaction to alkenes[1]

On the other hand, triplet alkylcarbenes undergo addition reactions through a stepwise mechanism.[1] The two electrons on different orbitals behave as radicals. Therefore, an initial homolytic breaking of the alkene pi bond leads to a diradical intermediate **11b**, which then combine to form the cyclopropane adduct (Scheme 6, B).[1] The intermediate is free to rotate around the bond shown in **11b**, yielding **12a** and **12b**.

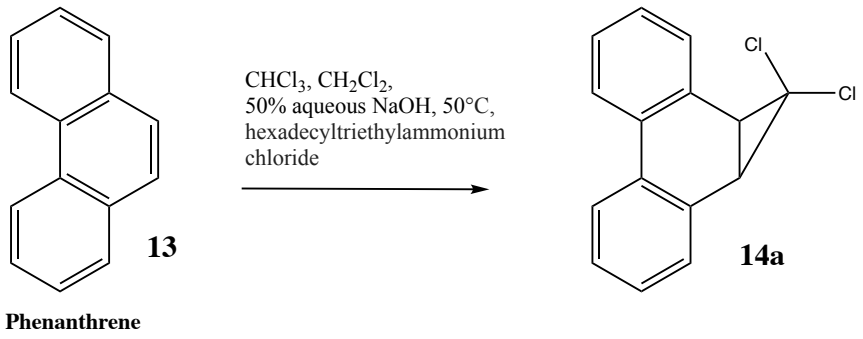
Given this background, the aim of this thesis is to generate novel chlorostannylcarbenes and chlorosilylcarbenes, as well as cyclopropylidenes through photolysis and copper-induced coupling reactions respectively. Little is known about carbenes with a chloro substituent combined with a silyl or stannyl substituent. Hence, we were interested in investigating and comparing their behavior with the known fluorotrimethylsilylcarbene, which was generated by Buron et al, and was found to exist in a singlet state.[9,10] Photochemical routes have proved to efficiently afford carbenes and have been adopted by our lab as a routine method to obtain a panoply of alkyl and alkylidene carbenes with concomitant phenanthrene release.[3,4]

Nevertheless, copper-induced coupling reactions constitute a relative new and exciting route, which was used by Murat *et. Al.* to generate bicyclopropylidene dimers.[11] Thus, we will rely on the synthesis of phenanthrene based precursors to generate the aforementioned carbenes and explore their behavior both experimentally and computationally.

Results and discussion

Synthesis of endo-1-chloro-1-trimethylsilyl-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (17a)

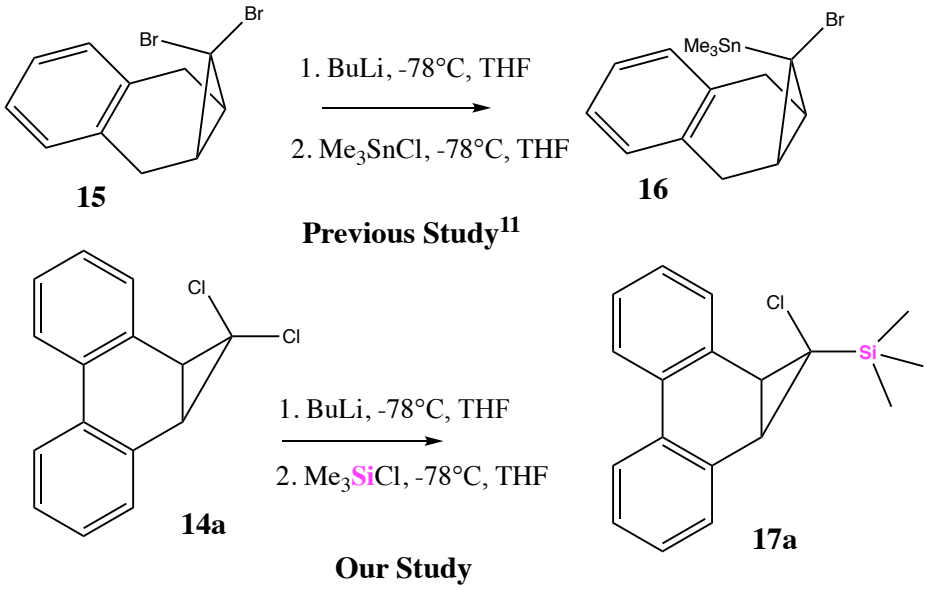
A two-step route was followed to synthesize the desired chloro(trimethylsilyl)carbene precursor.



Scheme 8: First stage of the synthesis of chlorosilylcarbene precursor[,12]

The first stage of the synthesis, demonstrated in scheme 8, involves base hydrolysis of chloroform, followed by a concerted addition of dichloromethylene to phenanthrene at the preferred 9-10 position, forming a dichlorocyclopropane adduct (Scheme 8). The procedure was developed by Daisuke Takeuchi and his colleagues at the Tokyo Institute of Technology.[2] The reaction was run at 50 °C over 3 days, successfully yielding **14a**: its ^{1}H NMR spectrum displays chemical shifts between 7.3 ppm and 8 ppm corresponding to the protons in the aromatic regions, with splitting patterns of two most downfield doublets and two triplets in a 1:1 ratio as expected. The singlet most upfield in the spectrum, at 3.42 ppm is indicative of the protons at the corners of the cyclopropane adduct (Appendix A).

Leveraging Murat and co-workers' research and using the procedure described in scheme 9, the chloro(trimethylsilyl)carbene precursor **17a** was synthesized through consecutive addition of n-butyllithium and trimethylsilyl chloride at -78 °C (scheme 9).[11]

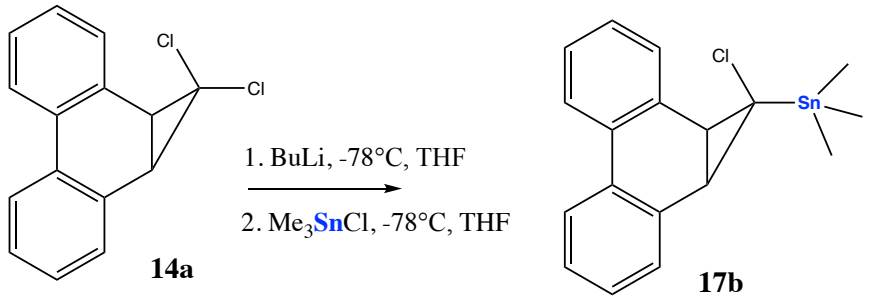


Scheme 9: Second stage of Chloro(trimethylsilyl)carbene precursor synthesis

This second step was moisture and air sensitive and was therefore run in a flask cooled under argon, which is heavier than air and would hence displace it; anhydrous tetrahydrofuran was used as a solvent to keep the reaction conditions as dry as possible. Adequate modifications were made to Murat and coworkers' method in order to obtain the desired precursor **17a**. For instance, BuLi was added to a dichlorocyclopropanated phenanthrene (**14a**) to yield **17a** while Murat and coworkers used a dibromocyclopropanated naphtalene (**15**) to synthesize their carbene precursor (**16**) (Scheme 9). Moreover, the last step involved the addition of trimethylstannyl chloride to produce **16**, which we modified by adding trimethylsilyl chloride to produce the desired precursor **17a** (Scheme 9). Overall, lithium-chlorine exchange produced a chlorolithiumcyclopropanated phenanthrene[10,11], activating the cyclopropane carbon as a strong nucleophile, which subsequently attacked the silicon from trimethylsilyl chloride to give a 22.4% yield of **17a**. Pure **17a** was thus successfully isolated and characterized. Its mass spectrum base peak is at 263.1 m/z, corresponding

to the loss of a chlorine substituent to form a trimethylcyclopropyl cation highly stabilized by the silyl group (Appendix A).

***Synthesis of endo-1-chloro-1-trimethylstannyl-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene* (17b)**



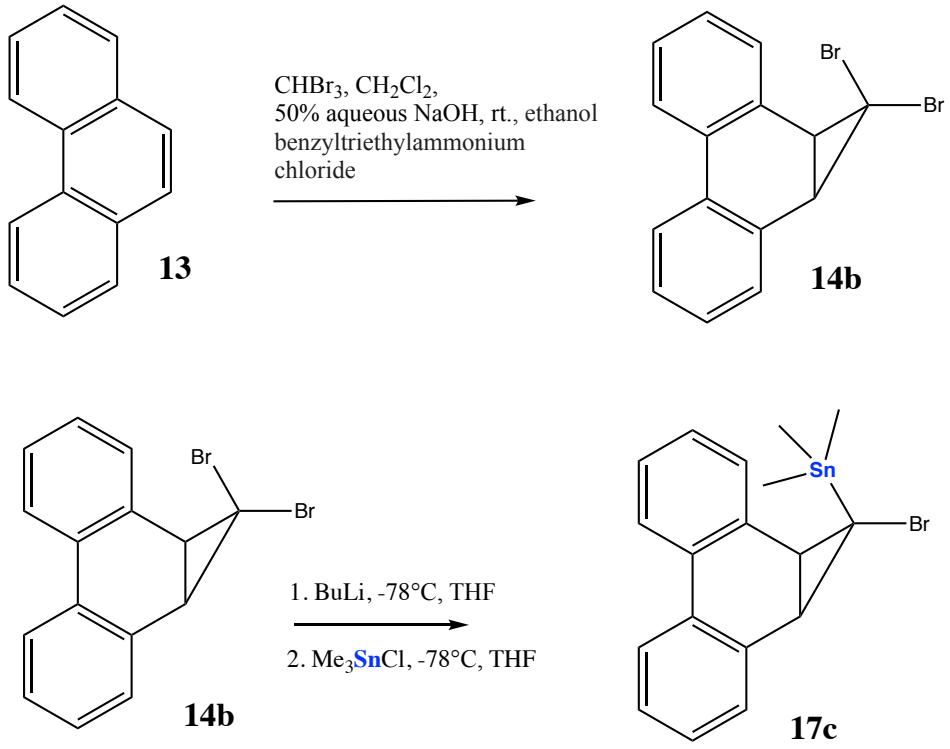
14a **17b**

Scheme 10: Second stage of chloro(trimethylstannyl)carbene precursor synthesis

Chloro(trimethylstannyl)carbene precursor **17b** was synthesized in a similar manner to **17a**. The first and second stages were similar, yielding **14a** then producing a chlorolithiumcyclopropanated phenanthrene. However, in the last step of the second stage, lithium was displaced by a trimethylstannyl group through addition of trimethylstannyl chloride, yielding 5.6% of pure **17b** that was fully characterized. The presence of tin was particularly detectable through gas chromatography-mass spectrometry (GC-MS), which showed big clusters of peaks in the fragmentations stemming from the ten different isotopes exhibited by tin (Appendix A). Moreover, the strong signal displayed upfield in the ^{1}H NMR spectrum at 0.36 ppm is indicative of the Sn-CH_3 bonding interactions (Appendix A). **17b** was obtained at a very low yield because it was particularly difficult to separate it from the monochlorocyclopropanated phenanthrene side product that resulted

from the reaction, even upon recrystallization with hexanes. Hence, better isolation methods are still being investigated.

***Synthesis of exo-1-bromo-1-trimethylstannyl-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene* (17c)**



Scheme 11: Synthesis of bromotrimethylstannylcarbene precursor synthesis

Finally, the bromotrimethylstannylcarbene precursor **17c** was also synthesized using a similar route to **17a**, except for a few modifications. Dibromocyclopropanated phenanthrene (**14b**) was produced in the first stage through base hydrolysis of bromoform, following a procedure previously developed by our lab, which is a modification of professor Takeuchi's method to synthesize compound **14a**.[5] This reaction was performed at room temperature over 4 days, currently yielding 4.8% of **14b**. The recrystallization process in chloroform is still in progress, but **14b** has still been fully characterized and was used in the second stage of **17c**'s synthesis. Addition of BuLi yielded a

bromolithiumcyclopropanated phenanthrene, which then reacted with trimethylstannyl chloride to obtain **17c** with a yield of 20.5%. **17c** was also fully characterized: its mass spectrum displayed big clusters of isotopic fragmental peaks, indicative of the presence of tin. Its highest fragmental mass on the mass spectrum appeared at 418.93 m/z, corresponding to the loss of one of the methyl groups from the trimethyltin substituent.

Structural properties of the carbene precursors

The structures of **17a-c** were determined through X-ray crystallography (Figure 1) and showed that the reactions indeed yielded the desired carbene precursors. The X-ray crystal structures might also suggest a dependency between the preferred stereochemistry and the type of halogen substituent.

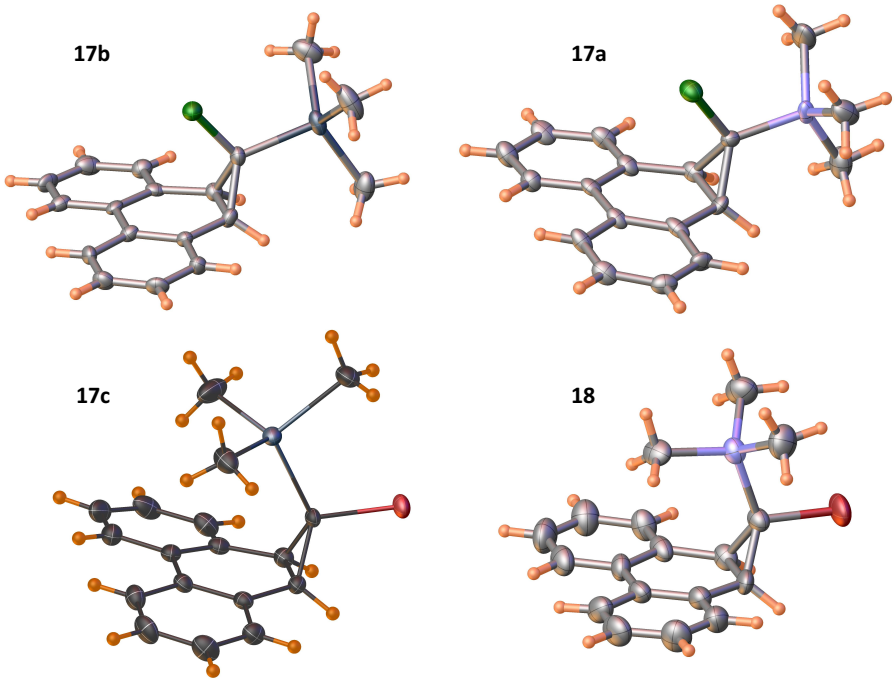


Figure 1: X-Ray crystal structures of the carbene precursors

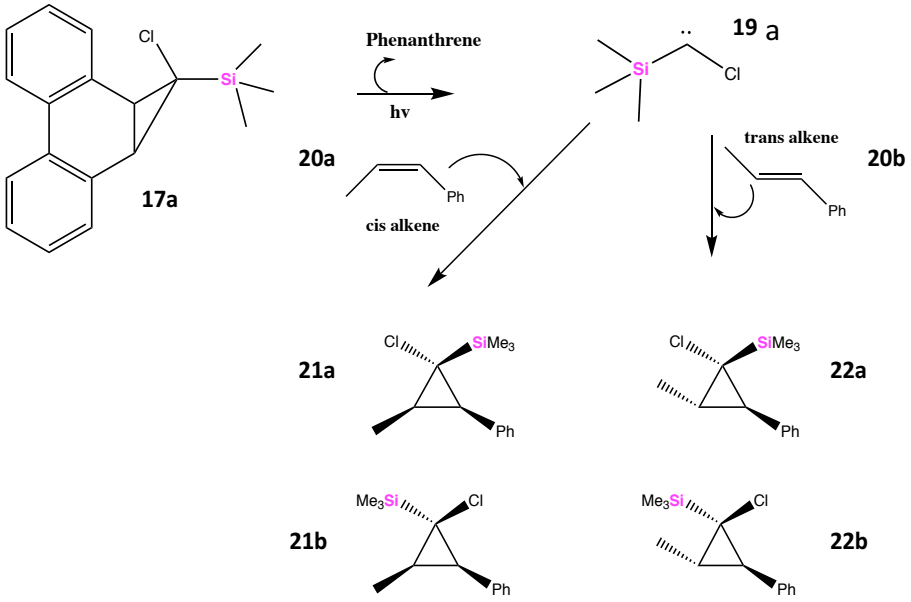
For instance, crystal structures of **17a** and **17b** both showed a chlorine substituent endo to the relatively flat phenanthrene base. However, this stereochemistry was reversed in the presence of

a bromine substituent, which adopted an exo position as observed in **17c** (Figure 1). In a related study, Ernesto Esquivel-Amores, a member of our lab, synthesized and fully characterized the crystal structure of **18,** whose bromine substituent was also in an exo position. There could potentially be a different isomer to each of these precursors, in which the positions of the substituents would be flipped. Hence, for comparison purposes, the relative stability of the possible isomeric structures was computed for **17a** and **18** using the model chemistry B3LYP/6-31+G(d). Energy calculations for the tin substituted compounds **17b** and **17c** are still in progress: we are still investigating a good method to model tin's electronic system. Surprisingly, the results suggested that endo Cl and endo Br were more stable than exo Cl and exo Br by 1.52 kcal/mol and 2.35 kcal/mol respectively. This is understandable given the size of the trimethylsilyl group and trimethylstannyl groups relative to the two halogens, and would experience less hindrance with the phenanthrene base. However, the aforementioned calculations only allowed us to determine the relative stability of the products. The kinetic barrier to the formation of the supposedly most stable endo Br isomer of **18** might be very high, thus preventing its formation or leading to yields that are too small for isolation and characterization.

***Generation of Chloro(trimethylsilyl)carbene* (19a)**

Chloro(trimethylsilyl)carbene (**19a**) was generated through photolysis of **17a** in a Rayonet reactor (~ 315 to 400 nm) in benzene containing an alkene trapping agent (Scheme 13)**.** This procedure generated the carbene by cleaving the strained cyclopropane bonds,[6,7] and concurrently releasing the stable phenanthrene byproduct. As carbenes have a short lifespan because of their high reactivity, they generally cannot be isolated. Hence, a trapping agent is necessary in the photolysis reaction to yield a product that can be isolated and characterized. beta-Methylstyrene was used as a

trapping agent, taking advantage of the addition reaction of carbenes to alkenes to form cyclopropane adducts. Two different reactions were thus set up, one with each beta-methyl-styrene isomer **20a** or **20b**, to gain information regarding chloro(trimethylsilyl)carbene's spin state. As discussed earlier, carbenes can react as singlets or triplets, which add to alkenes differently. Singlets tend to retain stereochemistry through concerted addition reactions. In contrast, triplets generally behave as 1,1-diradicals and would yield the most stable products, with less regard to stereochemistry retention.[1] Scheme 13 shows products that should be obtained if the chloro(trimethylsilyl)carbene was reacting as a singlet. This is a fair assumption because the presence of the electron pairs on the chlorine substituent should stabilize the carbene singlet state through resonance.



Scheme 13: Generation of Chloro(trimethylsilyl)carbene through photolysis

Upon photolysis, the products were not obtained in a good enough yield to allow isolation and characterization. Yet, GC-MS revealed two product peaks with a mass to charge ratio of 238 at 7.37mins and 8.05mins for the trans- alkene reaction, and 7.35 mins and 8.04 mins for the cis-alkene (Appendix 2 D-G). This means that two isomeric products were formed in both reactions. In addition, the fragmentation pattern of the products appears to be the same in both reactions, leading to the conclusion that both reactions yielded the same products (Appendix 2 D-G). These observations suggest that the carbene is likely reacting as a triplet. To gain more insight into the relative stability of the different states of chloro(trimethylsilyl)carbene, calculations were performed using B3LYP/6-31+G(d) model chemistry.

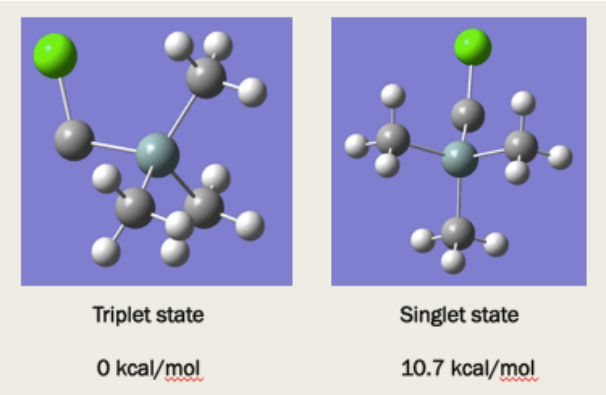


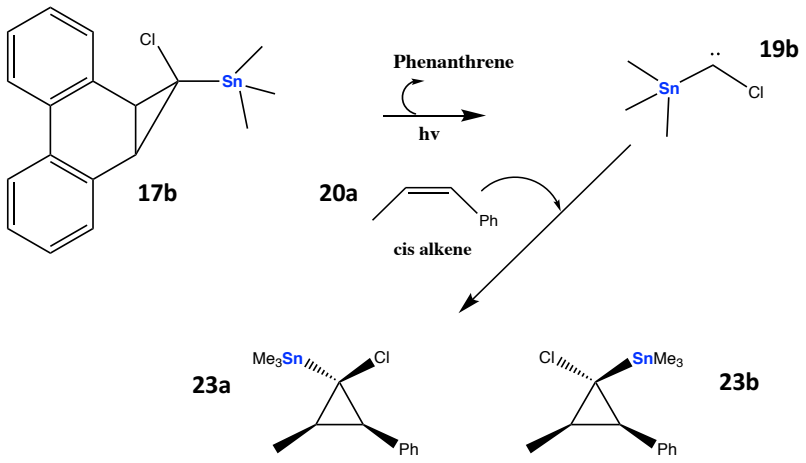
Figure 2: Triplet and singlet state structures of chloro(trimethylsilyl)carbene

At this level of theory, the triplet state carbene was more stable than the singlet state by 10.7 kcal/mol. The difference in energy between the states is quite significant and thus corroborates the experimental findings. Quite interestingly, the singlet state prefers a staggered conformation (figure 2). In contrast, the triplet state favors the arrangement where the chlorine forms a 0 ° dihedral angle with one of the methyl groups on the trimethylsilyl substituent (Figure 2). This could mean that the triplet state might be stabilized through interactions (still undetermined) between directly adjacent chlorine and methyl substituents. These interactions might be lost at 180 ° dihedral angle as

observed with the staggered structure, in which case the singlet becomes more stable (Figure 2). However, experimental investigations still need to be done by finding a better trapping agent to accurately determine the spin state of **19a**.

Generation of chloro(trimethylstannyl)carbene (19b)

Chloro(trimethylstannyl)carbene (**19b**) was also generated through photolysis of compound **17b** in the presence of *cis*-beta-Methylstyrene (Scheme 12). At the time of writing, photolysis with the trans-alkene has not yet been performed due to time constraints. However, the cis-alkene was a better trapping agent in order to determine experimentally **19b**'s spin state. Not much information can be gained from trans-alkenes trapping alone, since they are generally more stable because of minimized steric effects. Therefore, both triplet and singlet additions would lead to the same product. The products depicted in scheme 12 are those that we would obtain upon addition of a singlet carbene, which is a fair hypothesis given the presence of the chlorine, which can stabilize the carbene through hyperconjugation.

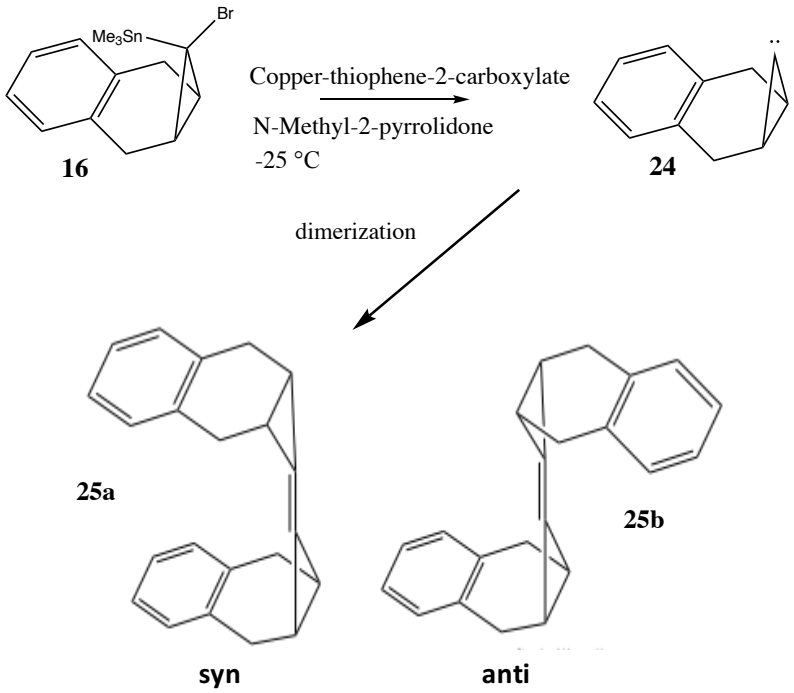


Scheme 12: Generation of chloro(trimethylstannyl)carbene through photolysis

The product yield in the photolysis to generate **19b** was even lower than the yield for **19a** since GC-MS only revealed traces of trapping product at around 13.01 mins (Appendix 2B). The fragments of 165 and 296 m/z correspond to a loss of the trimethylsilyl group and the methyl group respectively. In addition, the big clusters for most of the peaks suggest the presence of the multi-isotopic tin. Another isomer was also expected but was not found, probably because its yield was too low. Nonetheless, these results are still inconclusive and the carbene **19b** needs to be further investigated. Calculations are still in progress as we are trying to find the best model chemistry for compounds containing tin.

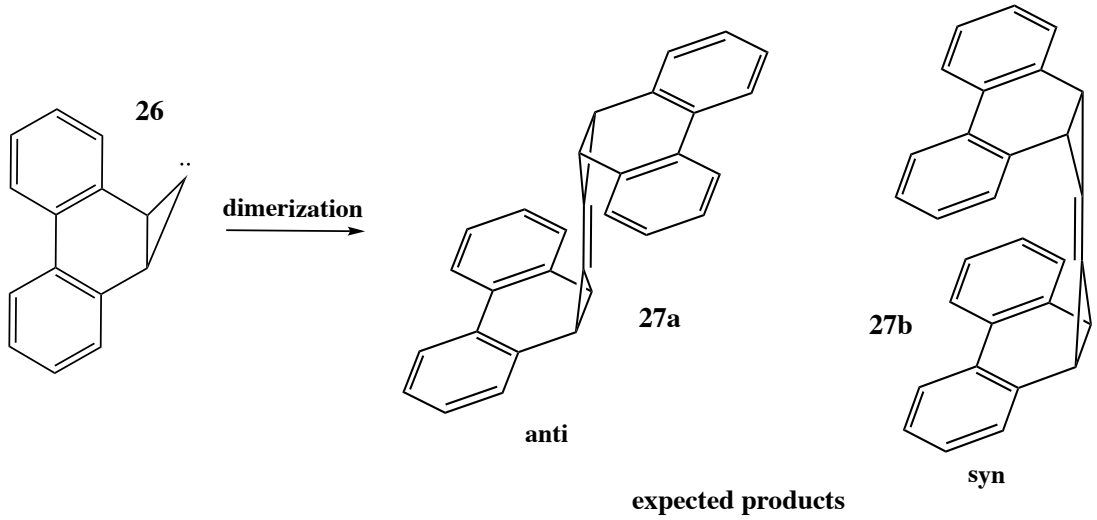
Generation of cylopropylidene (26)

Carbene generation through copper-induced coupling reactions was studied by Murat et al, who produced a cyclopropylidene (**24**) from geminally substituted bromotrimethylstannyl cyclopropane derivative **16** in the presence of copper thiophene-2-carboxylate (CuTC).[11] The subsequent dimerization of the carbenes yielded a tetrasubstituted olefin with two bicyclic substituting groups, forming syn (**25a**) and anti (**25b**) isomers (Scheme 13).



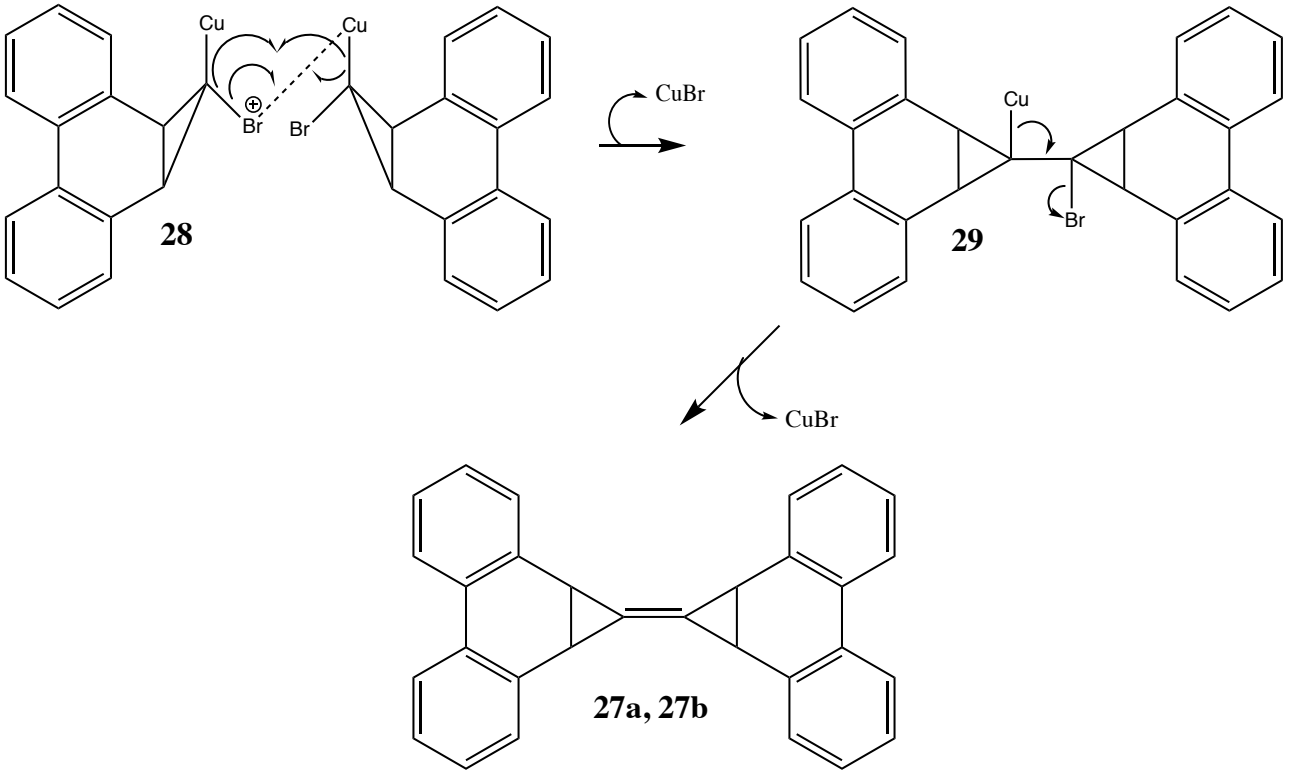
Scheme 13: Generation of cyclopropylidene through Stille-like coupling reaction [11]

On the premise of Murat and coworkers' study, **17c** was subjected to a Stille-like coupling reaction with copper thiophene-2-carboxylate (CuTC), in order to generate a cyclopropylidene that should dimerize in a manner similar to the anti and syn structures (Scheme 14) obtained by Murat and co-workers.



Scheme 14: Expected products from dimerization of the generated cyclopropylidenes

The moisture and air sensitive reaction was run under argon; CuTC, **17c,** and N-methyl-2-pyrrolidone (NMP) solvent were added and left to stir for an hour at -15 °C, before removing the cold bath and letting the reaction mixture warm up to room temperature (20 °C) overnight. One important experimental observation was that the bath temperature indicated by Murat and coworkers[11] was too cold for the solvent, which started forming a thick paste at -15 °C even though its normal freezing point is -25 °C. Therefore, this experiment should be repeated at 0 °C as an improvement to the procedure. Based on the mechanism proposed by Murat and coworkers, ligand exchange was expected between copper thiophene-2-carboxylate and **2c** leading to a geminally substituted bromocuprate cyclopropanated phenanthrene (compound **28**), which would dimerize to form the intermediate (compound **29**) shown in Scheme 12 with release of CuBr (Scheme 15).[11] The final expected bicyclopropylidenes **27a** and **27b** would then be obtained from a subsequent release of a second CuBr (Scheme 15).[11]



Scheme 15: Mechanism of carbene generation through Stille like coupling[11]

Quite unexpectedly, flash chromatography with silica gel column and hexanes as the eluting solvent gave a 9.1% yield of crystals, whose X-ray structure revealed a cyclobutane derivative (**30**) (Figure 3). The twisted bow tie looking structure presents no symmetry, which makes it chiral, although a racemic mixture of enantiomers is formed.

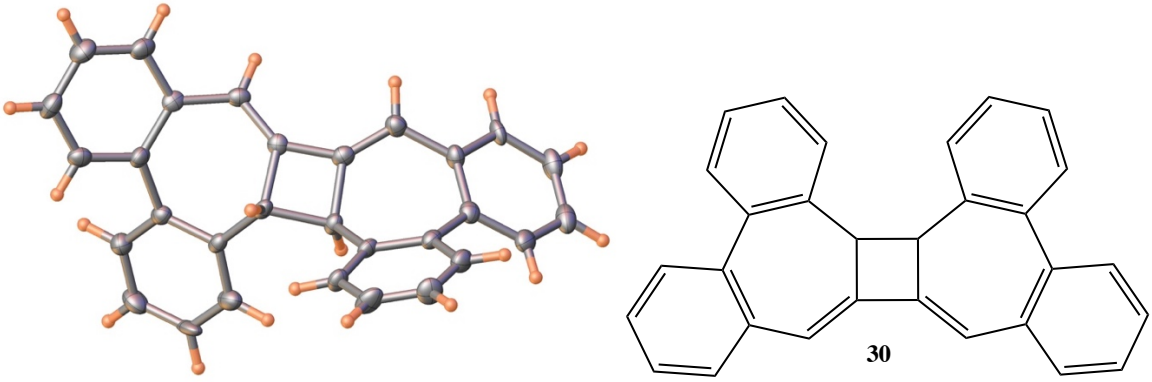
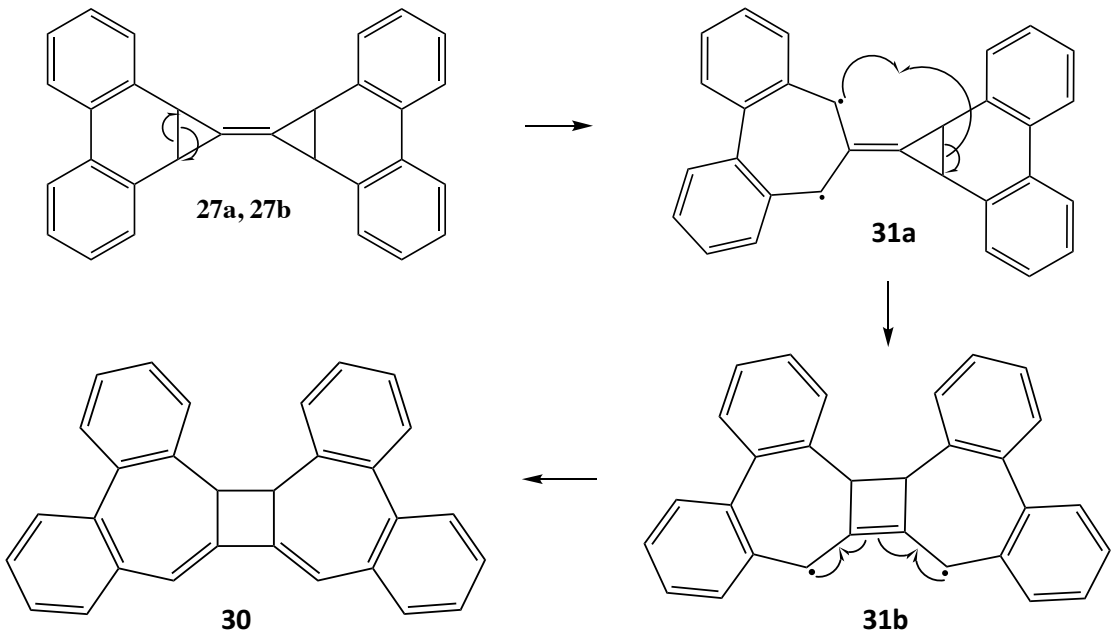


Figure 3: Xray crystallography of the actual dimer product

We considered two possible mechanisms to explain the formation of the observed product.

First postulate

The initial predictions could potentially be accurate. The expected **27a** and **27b** might have formed through dimerization of the generated cyclopropylidene, before rearranging into **30**. Scheme 16 exposes the mechanism of rearrangement to yield compound **30**.

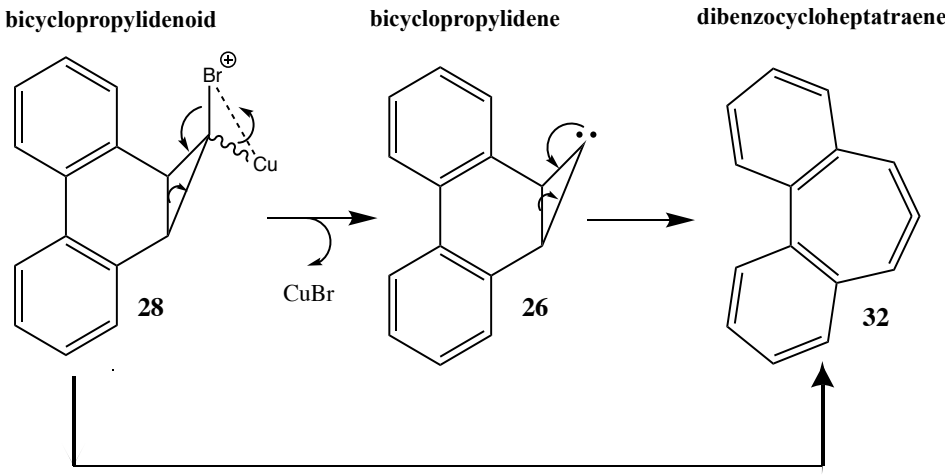


Scheme 16: Rearrangement of expected products into observed product

A homolytic breaking of the bond shown in the first step of scheme 16 leads to a ring expansion, relieving the highly strained cyclopropane adduct. A first diradical intermediate (**31a**) is thus formed, which is stabilized through resonance. A subsequent ring opening relieves another strained cyclopropane adduct, forming another resonance-stabilized diradical intermediate (**31b**). Finally, a regeneration of two conjugated π bonds from the second intermediate yields **30**.

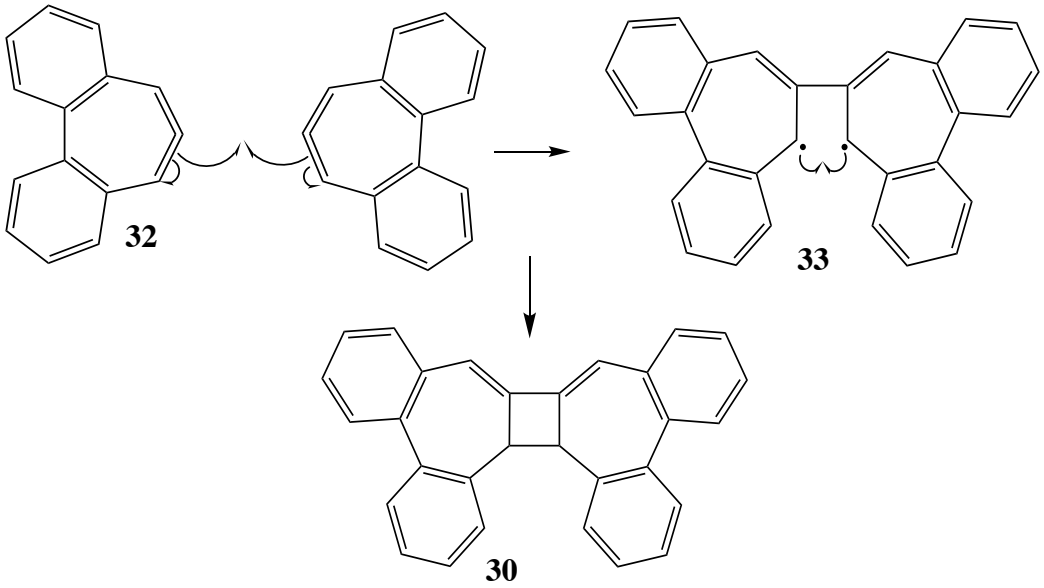
Second postulate

Another explanation to producing **30** could be through the formation of a strained cyclic allene, which then dimerized. Earlier this year, our laboratory published a paper reporting a similar cyclopropane ring opening to a dibenzocycloheptatetraene (compound **32**).[15] **32** was observed in small amounts: it was thus postulated that it was generated, either directly from rearrangement of **28**, or through the formation of **26** (scheme 17).[15]



Scheme 17: Rearrangement of bicyclopropylidenoid/bicyclopropylidene to form dibenzocycloheptatraene [13]

Therefore, the presence of the dibenzoheptatraene group in compound **30** might suggest that it also stems from a reaction initiated by cyclopropylidene/ cyclopropylidenoid's rearrangement into compound **32**. In light of this information, a possible mechanism could be postulated involving the dimerization of the allene.



Scheme 18: Dimerization of dibenzocycloheptatraene into observed product

The strain in the allene, which is part of a seven membered ring, is relieved through homolytic breaking of one of the pi bonds, forming a sigma bond. In the process, two radicals are formed, which are resonance stabilized. Intramolecular recombination of the radicals to form a sigma bond completes the formation of **30** (Scheme 18).

Calculations and rationale

Energy calculations were again performed using the B3LYP/6-31+G(d) in order to determine the stability of the compounds relative to each other.

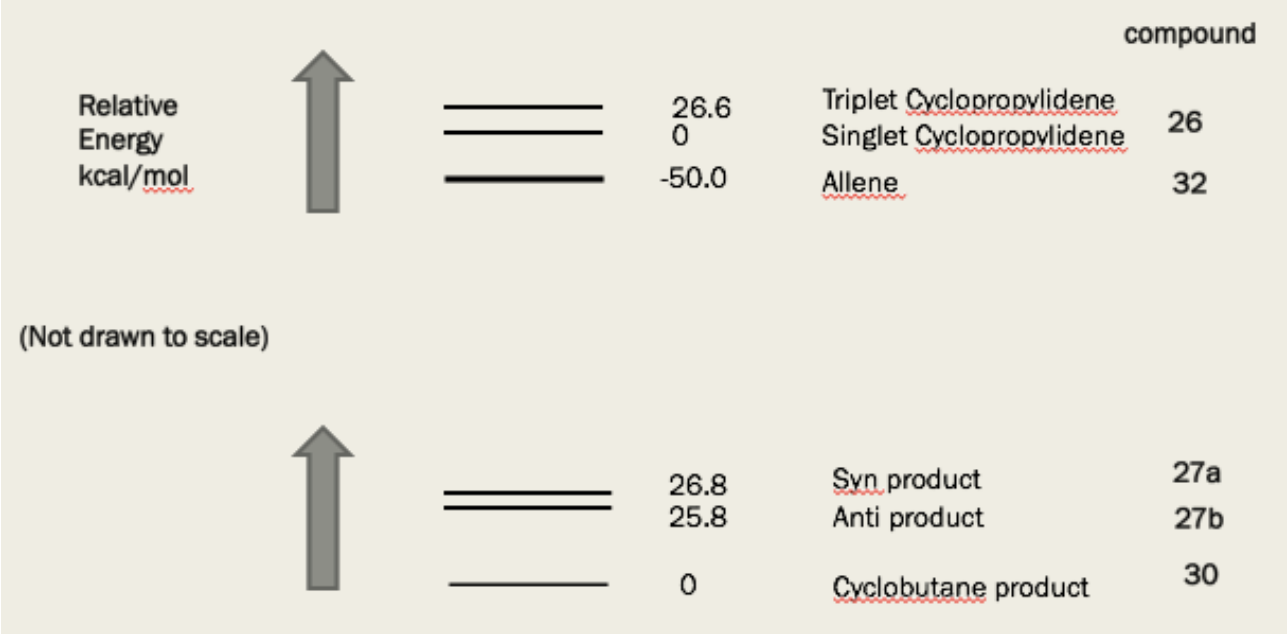


Figure 4: Energy calculations for the bicyclopropylidene, the allene, the expected and observed products (model B3LYP/6-31+G(d))

According to the calculations (Figure 4), compound **26** prefers to adopt the singlet state, which is more stable than the triplet by 27 kcal/mol (Figure 4). Furthermore, the first hypothesis states that **27a** and **27b** are first produced from dimerization of the generated cyclopropylidene before rearranging into compound **30.** The dimerization of carbenes is very exothermic and would yield **27a** and **27b** .[1] In addition, we know that compound **30** is more stable than **27a** and **27b** by about 26 kcal/mol (Figure 4). Ring opening of the highly strained cyclopropane from **27a** and **27b,** relieves torsional and angle strains and provides a drive for rearrangement into compound **30**. Hence, the first postulate is plausible.

Considering the second postulate, compound **32** is more stable than **26** by about 50 kcal/mol (Figure 4). This is understandable as all the carbons in the allene have a full octet. **32** also provides an additional stabilization through ring opening, relieving cyclopropane torsional strains. Finally, dimerization and stabilization of **32** yields compound **30**. Thermodynamically, the second postulate mechanism also is plausible. The cyclopropylidene could thus either undergo a dimerization, or an

intramolecular rearrangement before dimerization. The mechanism of formation of **30** will thus depend on the kinetic barriers of the reactions involved. Further transition state computations and kinetic experiments have to be done, in order to understand the mechanism(s) actually involved. However, there is a chance that compound **32** forms directly from **28**, without ever making the highly unstable cyclopropylidene.[15] Therefore, we might have to investigate the presence of **26** by adding an alkene trapping agent into the copper-induced coupling reactions. The presence of singlet cyclopropylidenes will lead to cyclopropanation of alkenes with retention of stereochemistry.

Conclusion

All of the carbene precursors **17a**, **17b**, and **17c** were successfully synthesized and characterized, though the yields were relatively low. Their X-ray crystal structures suggest an interesting relationship between the type of halogen substituent and the preferred precursor structure. Endo Cl is favored in **17a** and **17b**, while exo Br is favored in **17c**. The endo preference of the Cl substituent is easily explained, since it is smaller than both trimethylsilyl and trimethylstannyl groups and thus interfers less with the phenanthrene adduct. However, formation of the exo Br structures are not well understood yet and need to be studied further.

Chloro(trimethylsilyl)carbene was successfully generated through photolysis of carbene precursor **17a** in the presence of cis-beta-Methylstyrene or trans-beta-Methylstryrene, but the yield was too low for characterization. Two isomeric products were obtained upon photolysis, suggesting a triplet state, which was corroborated by computational analysis. However, a better trapping agent has to be found in order to isolate the trapping products and make definitive conclusions regarding the electronic states of the carbene.

Chloro(trimethylstannyl)carbene also was generated through photolysis of precursor **17b**, with traces of one product peak that seemed to suggest that indeed photolysis was happening, but at a very slow rate. Calculations for the tin substituted compounds are still in progress as we are investigating the best model chemistry for the tin electronic system.

Finally, copper coupling reaction of precursor **17c** led to the formation of **30,** which contains two seven membered rings. Two possible mechanisms that are thermodynamically favorable could potentially lead to the observed dimer. Either a formation of the expected olefins from dimerization of the cyclopropylidene, which then rearranges to compound **30**, or the formation of an allene, which dimerizes to give compound **30**. However, the possibility that the cyclopropylidene never

forms still remains, and instead the allene **32** is formed from **28**. Therefore, further experimentations have to be done to understand the mechanism better.

Future work

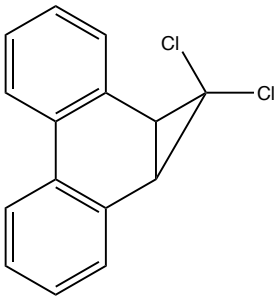
Research is still in progress to determine which calculation method and basis set is best for tin substituted compounds. Tin is relatively hard to model because it contains a complicated electronic system. Hence the balance between a relatively simple model with less complicated calculations and one that still gives enough information regarding the precursor and carbene structures is needed. With regards to photolysis reactions, less volatile trapping agents, with heavier substituents should be used in order to obtain products suitable for characterization by X-ray crystallography. Finally, the copper coupling reactions should be done in the presence of a trapping agent in order to determine whether the cyclopropylidene actually is formed. This would help direct further experiments and calculations to discover the right mechanism leading to compound **30**.

Materials and Methods

General information

The air and moisture sensitive reactions were run under argon. All glassware was dried in the oven at least a day before the experiment. Anhydrous tetrahydrofuran (THF) was dried through two activated alumina columns (2ft x 4in). Flash chromatography (FC) purification was done using Teledyne ISCO Combiflash Rf200 instrument, with commercial HP Silica columns. The Nuclear Magnetic Resonance Spectra (NMR) were obtained using an Agilent instrument at 500 MHz for the ^{1}H spectra and 125 MHz for the ^{13}C NMR spectra. The NMR shifts are reported in ppm. Tetramethylsilane (TMS) or proton signal from deuterated chloroform were used as references. Infra Red Spectra were obtained using a Perkin Spectrum One FT-IR Spectrometer. Mass spectrometry, coupled with gas chromatography were performed using an Agilent Technologies duel inert MSD and GC System instrument. Melting points were recorded using a digital hot plate and are uncorrected. X-ray data were acquired at 173K on a Briker D8 Quest Eco diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and PHOTON 50^{TM} CMOS (complementary metal-oxide semiconductor) detector. The Bruker Apex 3 suite of programs was used to collect diffraction data. The Olex2 suite of programs was used for data processing.

Preparation of 1,1-Dichloro-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (14a)[12]

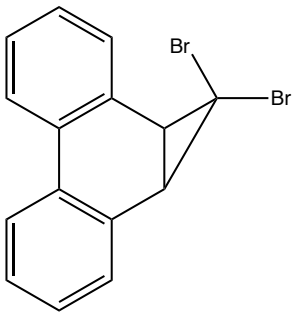


The method to obtain compound **14a** is a modification of the one developed by Takeuchi et al from the Tokyo Institute of Technology. In a 500mL pear shaped flask, a solution of phenanthrene (0.20 mol, 36.13 g), phase transfer catalyst hexadecyltriethylammonium chloride (1.5 mmol, 0.54 g) and chloroform (60.0 mL, 0.75 mol, solvent and reagent) was prepared. 50 % NaOH (40.0 mL) was slowly added to the solution over a period of 30 mins, which was left to stir

for 2 days at 50 °C. The aqueous layer was extracted with dichloromethane (3 x 75 mL). The combined organic layer was quenched with 2M hydrochloric acid (2 x 100 mL), washed with water (1 x 100 mL), brine (1 x 100 mL) and left to concentrate. The residues were recrystallized with hexanes to obtain **14a** (white crystals).

Yield: 22.5%; mp: 138.0-141.3°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J=5Hz, J=1Hz, 2H), 7.49 (dd, J=5Hz, J=1.5Hz, 2H), 7.41 (td, J=5Hz, J=1.5Hz, 2H), 7.35 (td, J=5Hz, J=1.25Hz, 2H) , 3.42 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.26, 130.94, 128.18,128.05, 127.93, 123.01, 77.27, 77.01, 76.76, 58.84, 36.52.

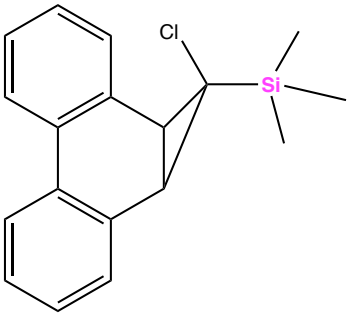
Preparation of 1,1-Dibromo-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (14b) [5]



Compound **14b** was obtained using a procedure developed by our lab. [2] In a 500 mL Erlenmeyer flask stabilized with rings, a solution of phenanthrene (0.201 mol, 35.756 g) and phase transfer catalyst benzyltriethylammonium chloride (2.4 mmol, 0.550g) was prepared using the solvents dichloromethane (40.0 mL) and bromoform (40.0 mL, 0.46 mol, also a reagent). 50 % NaOH (80.0 mL) was slowly added to the solution over a period of 30 mins and the emulsion was stabilized with ethanol (1.0 mL). Evaporation was prevented by placing a beaker on top of the flask. The solution was left to stir for 4 days. The aqueous layer was extracted with dichloromethane (3x75mL). The combined organic layer was quenched with 2M hydrochloric acid (2x100mL), washed with water (1x100mL), brine (1x100mL) and left to concentrate. The solid residues fallen out of solution were gravity filtered and recrystallized with chloroform to obtain compound **14b** (beige crystals).

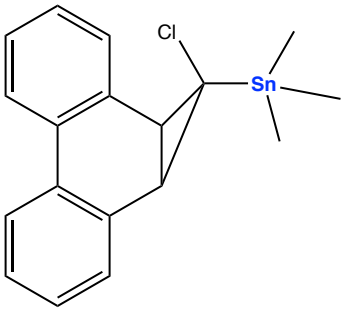
Yield: 4.8%; mp: 119.7-121.9°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, J=10Hz, 2H), 7.50 (dd, J=7.5Hz, 2H), 7.42 (td, J=7.5Hz, 2H), 7.35 (td, J=7.5Hz, 2H), 3.5 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 131.20, 130.89, 129.48, 128.21, 128.07, 123.91, 37.37, 30.84.

Preparation of endo-1-chloro-1-trimethylsilicon-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (17a) [11]



The method followed by Murat Guney et al was used to synthesize compounds **17a,** to which some modifications were added. In a 100mL three necked round bottom flask cooled under Argon, BuLi in hexanes (4.6 mL, 10.725 mmol) was added over 5mins to a solution of 10.725 mmol **14a** in dry THF (85mL) between -60 and -70 °C (turned green) and was left to stir, still maintaining that temperature range. An hour later, chlorotrimethylsilane (1.5 mL, 10.725 mmol) was added to the mixture between -55 and -60 °C (turned brown), which was left to stir and warm up to room temperature over night. The reaction was quenched with 50 mL water. The aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layer was washed with water (1x50 mL) and brine (1x100 mL), dried with sodium sulfate and concentrated. The residues were purified FC (hexanes, silica gel). Yields: 22.4%; mp: 154.3-166.2°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (7.5 Hz, 2H), 7.35 (m, 6H), 2.84 (s, 2H), 0.26 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.22, 130.53, 130.21, 127.56, 127.00, 122.48, 77.28, 77.03, 76.77, 29.12, 28.17.

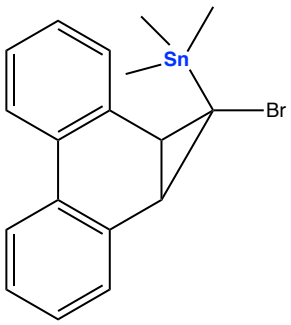
endo-1-chloro-1-trimethyltin-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (17b) [11]



The method followed by Murat Guney et al was used to synthesize compounds **17b**, to which some modifications were added. In a 100mL three necked round bottom flask cooled under Argon, BuLi in hexanes (4.6 mL, 10.725 mmol) was added over 5mins to a solution of 10.725 mmol **14a** in dry THF (85mL) between -60 and -70 °C (turned green) and was left to stir, still maintaining that temperature range. An hour later, chlorotrimethylstannane (11.4 mL, 10.725 mmol) was added to the mixture between -55 and -60 °C (turned brown), which was left to stir and warm up to room temperature over night. The reaction was quenched with 50 mL water. The aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layer was washed with water (1x50 mL) and brine (1x100 mL), dried with sodium sulfate and concentrated. The residues were purified through flash chromatography (FC) (hexanes, silica gel).

Yields: 5.6%; 140.0-143.1°C; ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.055 (dd, J=7.5Hz, 2H), 7.33 (sep d, 10Hz, 1.25hz, 6H), 2.84 (s, signs of weak triplet but not significantly detected, 2H), 0.36 (t, 27Hz, 9H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 132.08, 130.67, 130.25, 127.49, 126.62, 122.41, 77.27, 77.01, 76.76, 29.17, 26.69.

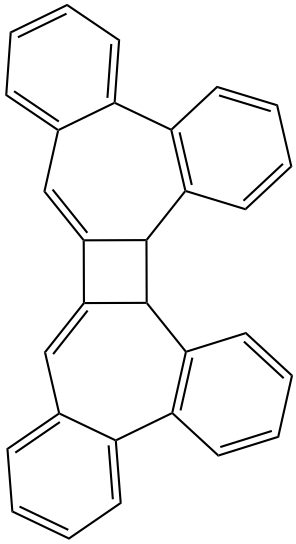
exo-1-bromo-1-trimethyltin-1a,9b-dihydro-1H-cyclopropa[l]phenanthrene (17c) [11]



The method followed by Murat Guney et al was used to synthesize compounds **17c**, to which some modifications were added. In a 100mL three necked round bottom flask cooled under Argon, BuLi in hexanes (4.6 mL, 10.725 mmol) was added over 5mins to a solution of 10.725 mmol **14b** in dry THF (85mL) between -60 and -70 °C (turned green) and was left to stir, still maintaining that temperature range. An hour later, chlorotrimethylstannane (11.4 mL, 10.725 mmol) was added to the mixture between -55 and -60 °C (turned brown), which was left to stir and warm up to room temperature over night. The reaction was quenched with 50 mL water. The aqueous layer was extracted with dichloromethane (3x50 mL). The combined organic layer was washed with water (1x50 mL) and brine (1x100 mL), dried with sodium sulfate and concentrated. The residues were purified through flash chromatography (FC) (hexanes, silica gel).

Yields: 20.5%, mp: 123.1-124.5°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, 7.5Hz, 0.65Hz, 2H), 7.51 (dd, 7.5Hz, 1.75Hz, 2H), 7.28 (m, 8.75Hz, 1.75Hz, 4), 3.27 (t, 55 Hz, 2H), -0.33 (t, 27.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 133.03, 130.72, 130.09, 128.18, 127.18, 123.14, 77.27, 77.02, 76.76, 34.75, 31.58.

Generation of cyclopropylidene leading to the cyclobutane-linked bicycloheptane dimer (30)[11]

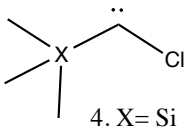


In a 100mL three necked round bottom flask purged with argon, CuTC (1.5747 g, 5.2 mol), compound **2c** (0.94 g, 2.2 mmol) and NMP (25.0 mL) were added at temperatures between -20 and 0 °C. The mixture was left to stir for an hour at -15 °C and then warmed up to room temperature overnight. The reaction was quenched with ammonium hydroxide (35 mL) and stirred until most of the brown solid precipitate was dissolved. The aqueous layer was extracted with dichloromethane (2 x 40 mL). The combined organic layer was washed with ammonium hydroxide (2 x 40 mL), water (1 x 40 mL) and brine (1 x 40 mL), dried with sodium sulfate and concentrated. The residues were purified through FC (hexanes, silica gel) to isolate compound **3**.

Yield: 9.1%; mp: 231-249 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.50 (dd, J=6.25Hz, 2.5Hz, 2H), 7.34 (m, 12H), 4.53 (s, 2H), 6.80 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.13, 143.74, 139.86, 139.21, 135.76, 131.97, 131.79, 129.46, 127.76, 127.19, 126.68, 126.57, 124.51, 119.62, 109.98, 77.26, 77.01, 76.75, 47.16.

Generation of Chloro(trimethylsilyl)carbene (19a) and chloro(trimethylstannyl)carbene (19b)

To a 5 mL photolysis tube, were added 150 mg of compound **17a** (**19a**) or **17b** (**19b**), 1 mL of cis-(or trans)-beta-methylstyrene and 3 mL of benzene. All solid was dissolved and the tube sealed. Argon was bubbled through the reaction and a prephotolysis mass spectrum was taken. The reaction was placed in a photolyzer and was irradiated with a 315-400 nm light. Mass spectra were taken over time and the rate of disappearance of the starting material was monitored until no peak was found. Photolysis was stopped and the reaction mixture was purified through FC (silica gel, hexanes).



4. X= Si
5. X= Sn

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(Corrigendum: *Tetrahedron Lett*. **2004**, *45*, 3007.)

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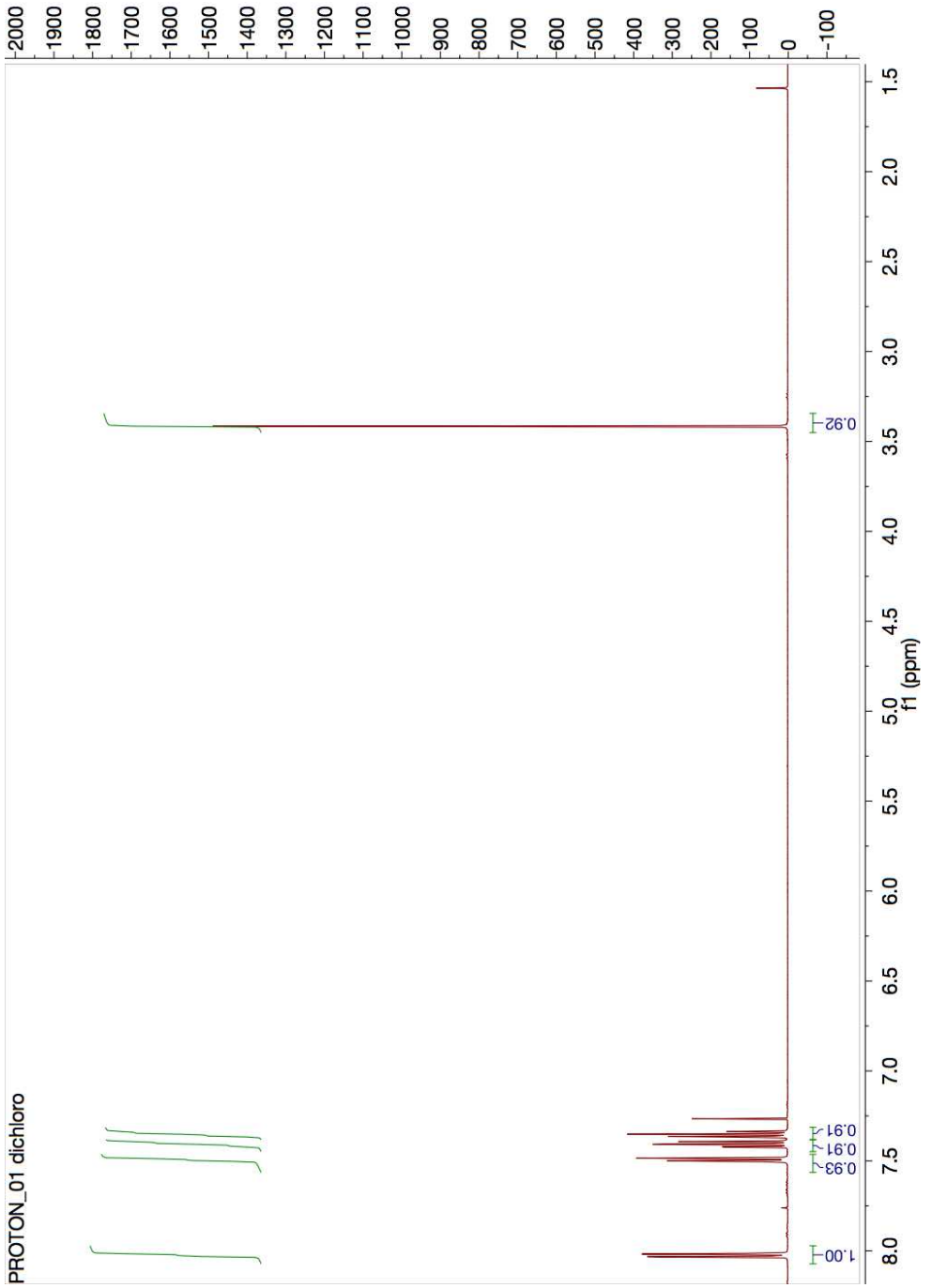
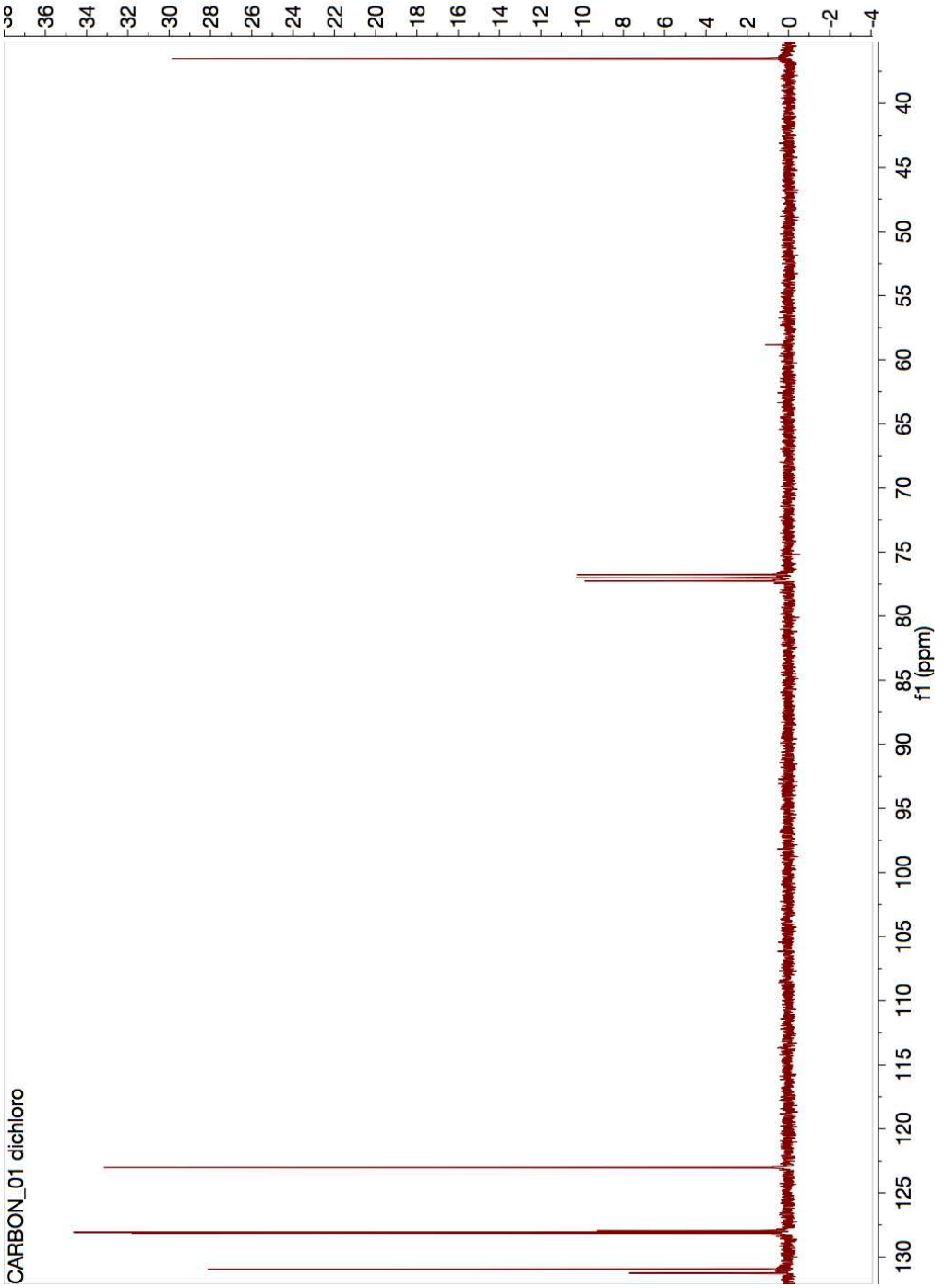
Appendix 1: Characterization Data

Compound 14a ^{1}H NMR

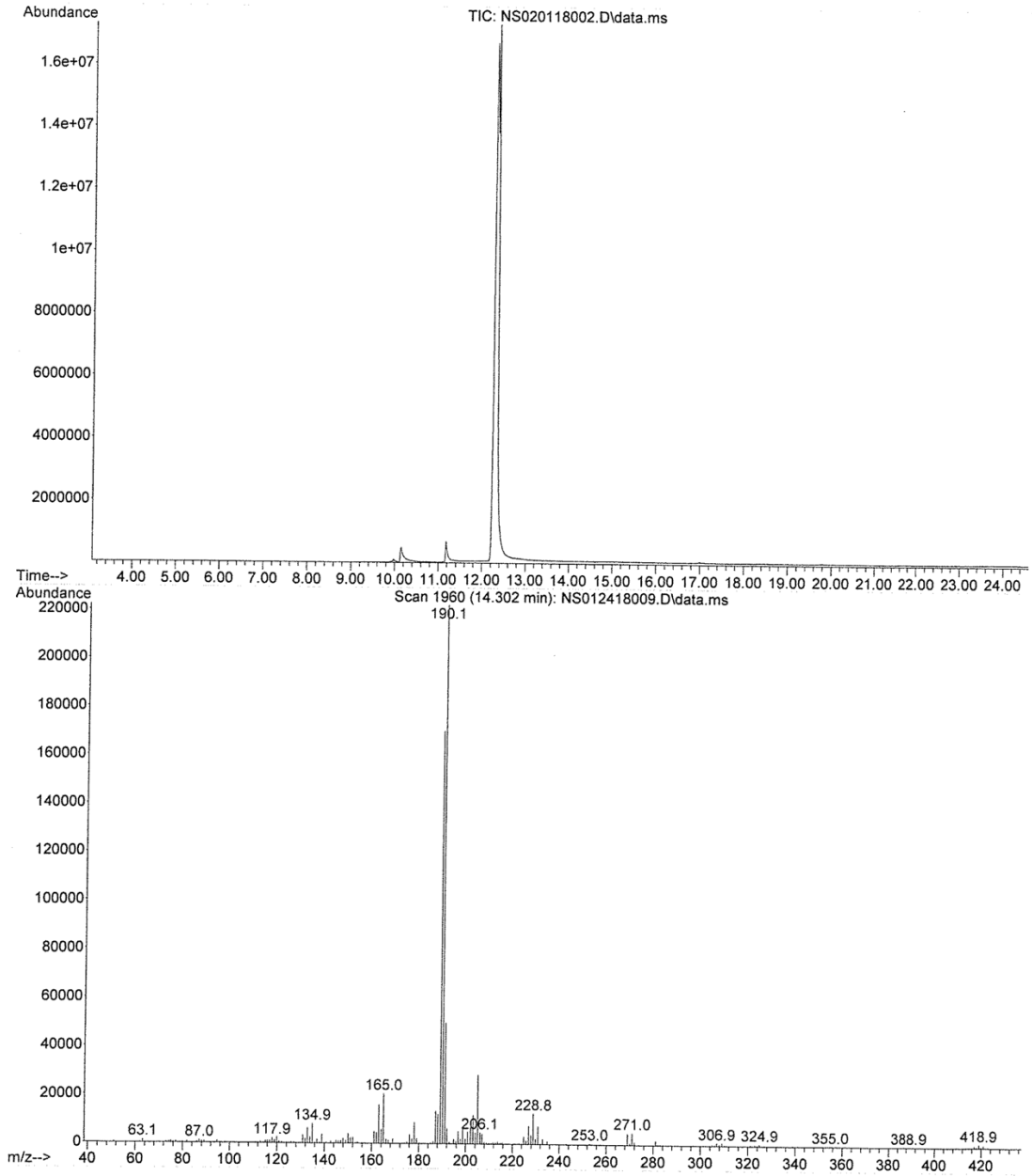


Compound 14a ^{13}C NMR

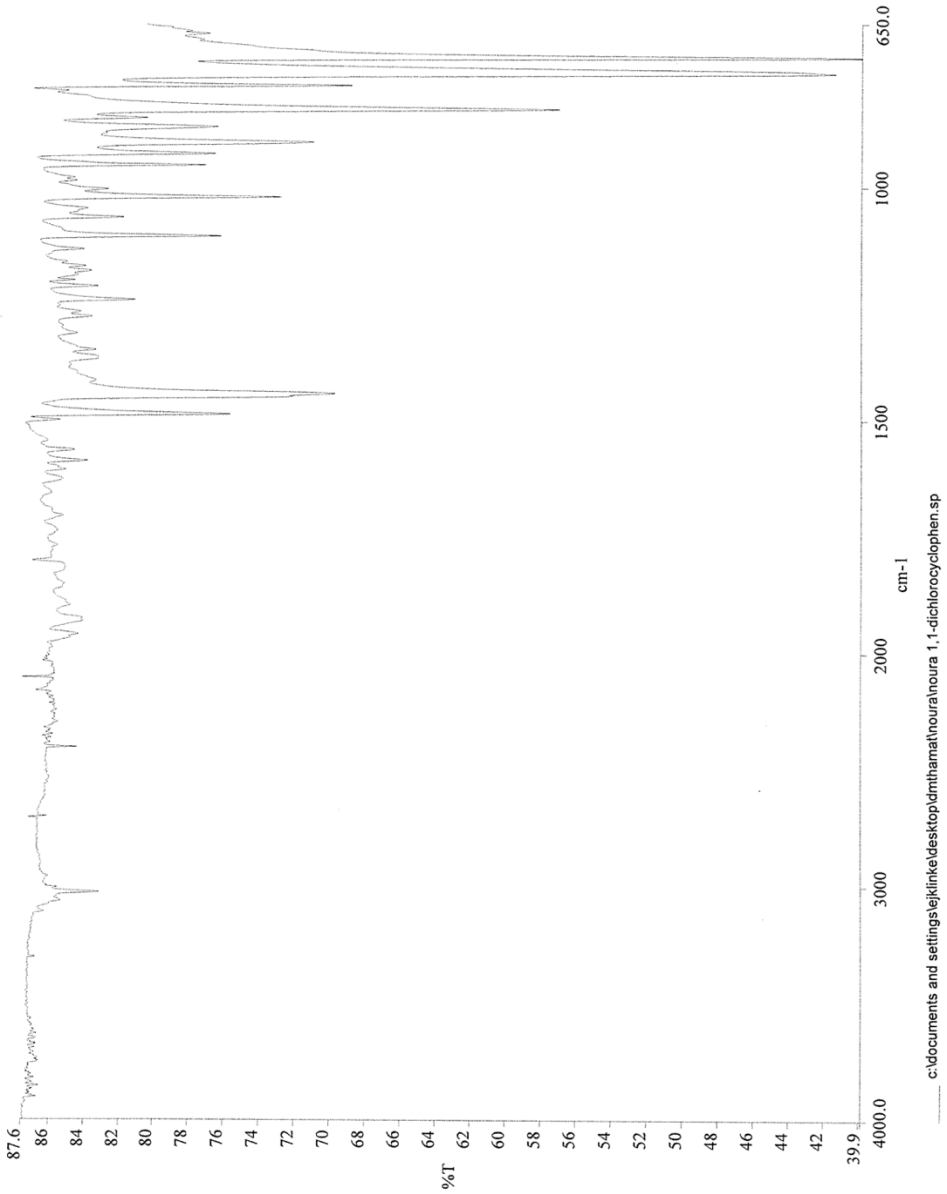


Compound 14a Mass Spectrum

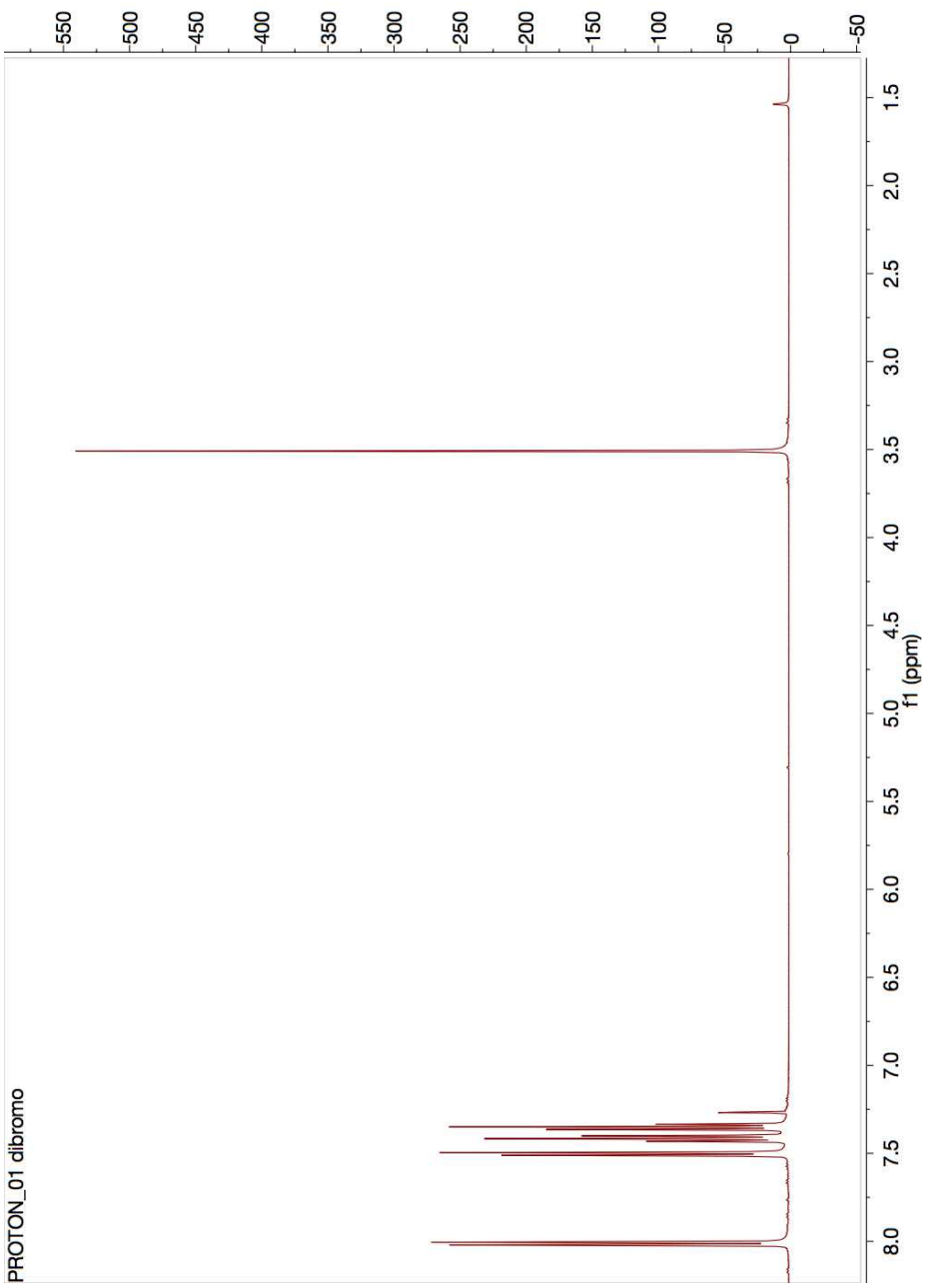
```
File       :D:\1\data\Noura\NS020118002.D
Operator   : Noura Srour
Acquired   :  1 Feb 2018  11:49     using AcqMethod DASLAB3MIN60.M
Instrument :    GCMS1
Sample Name: 1,1-diClcyclophen
Misc Info  : purified through recrystallization
Vial Number: 1
```



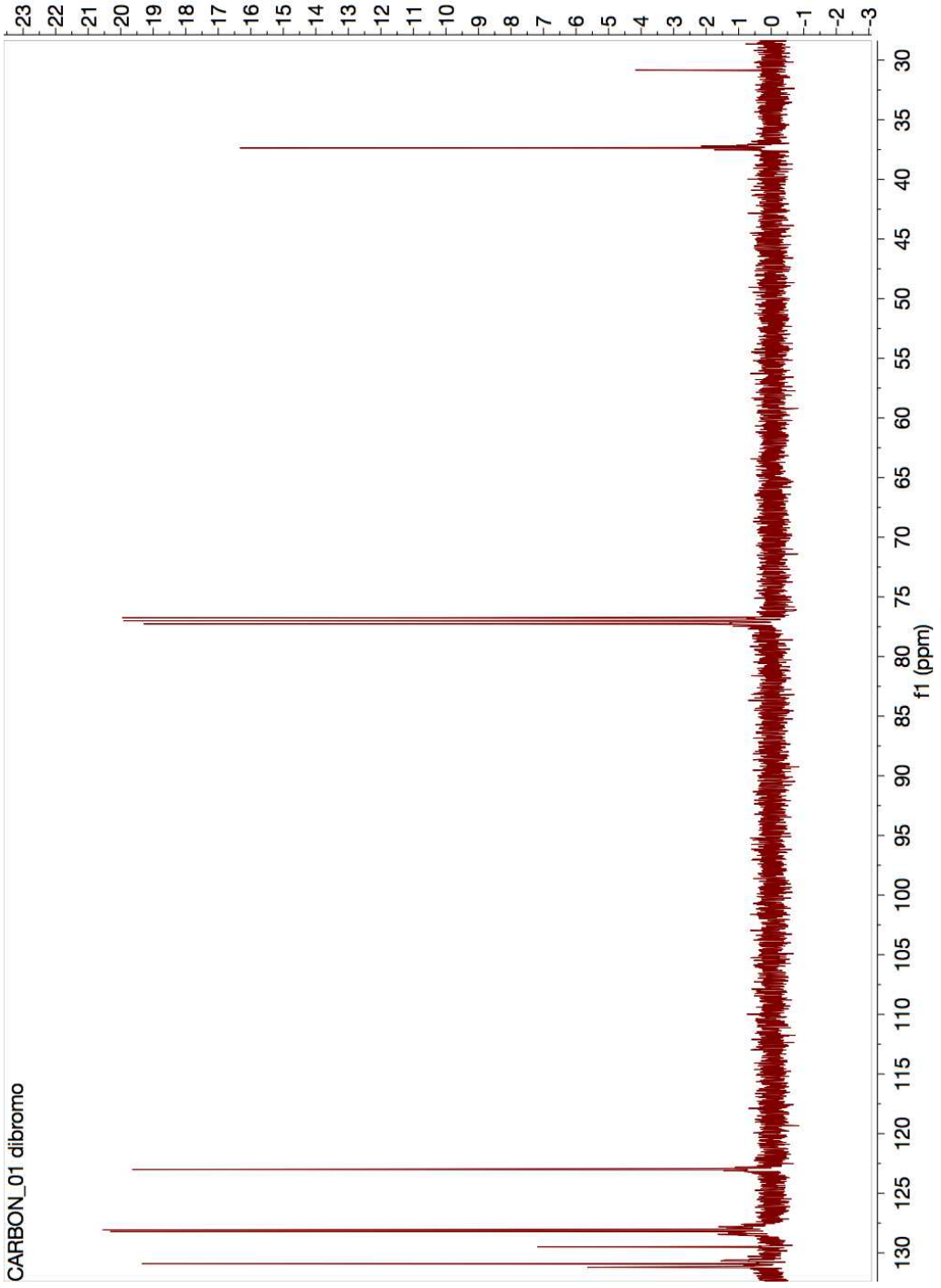
Compound 14a IR spectrum



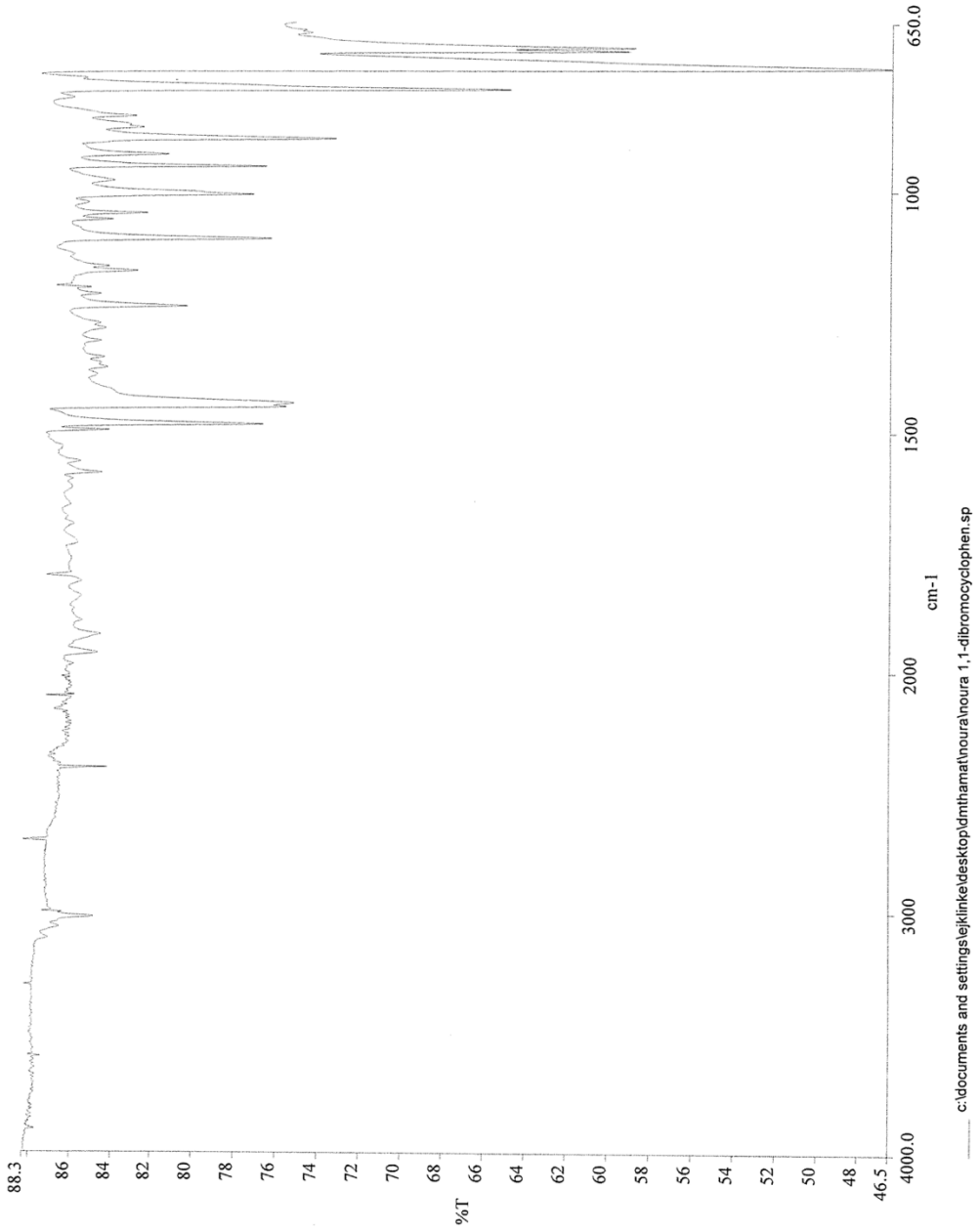
Compound 14b ^{1}H NMR



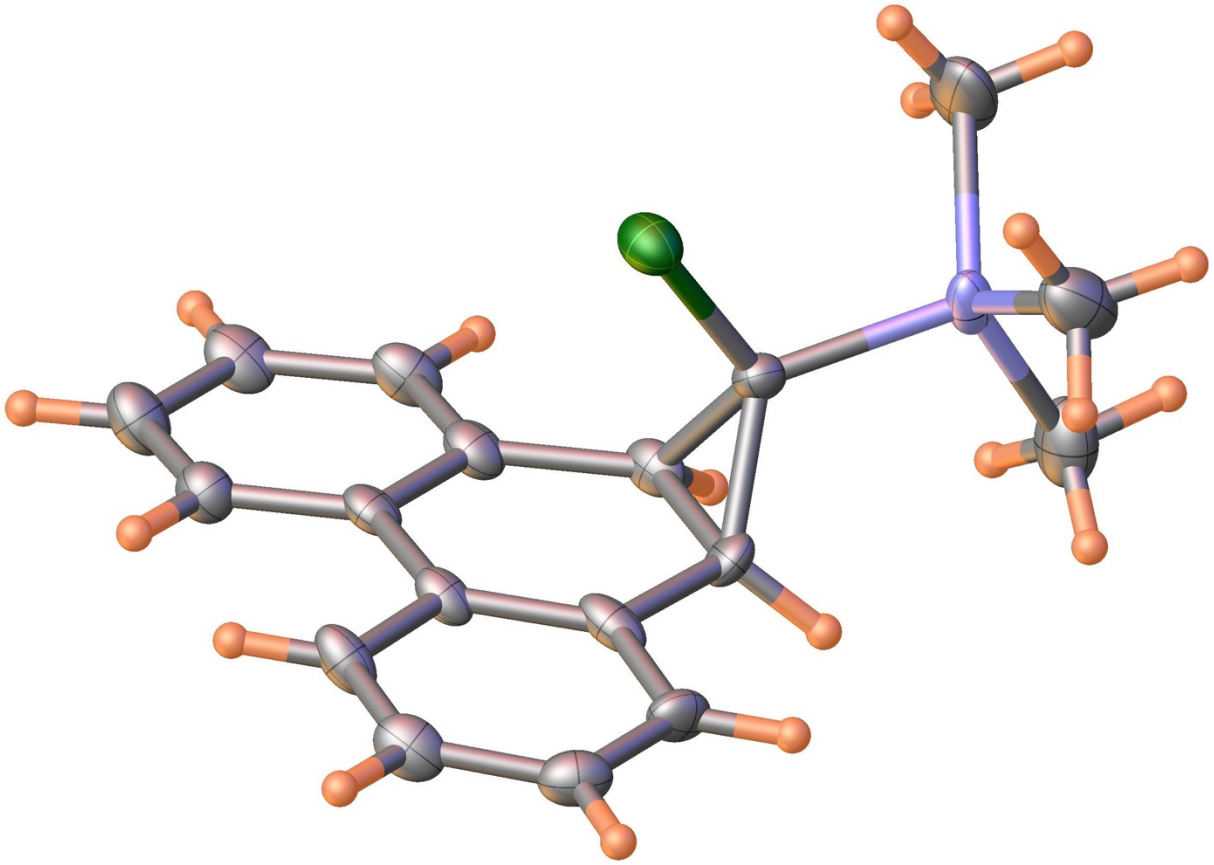
Compound 14b ^{13}C NMR



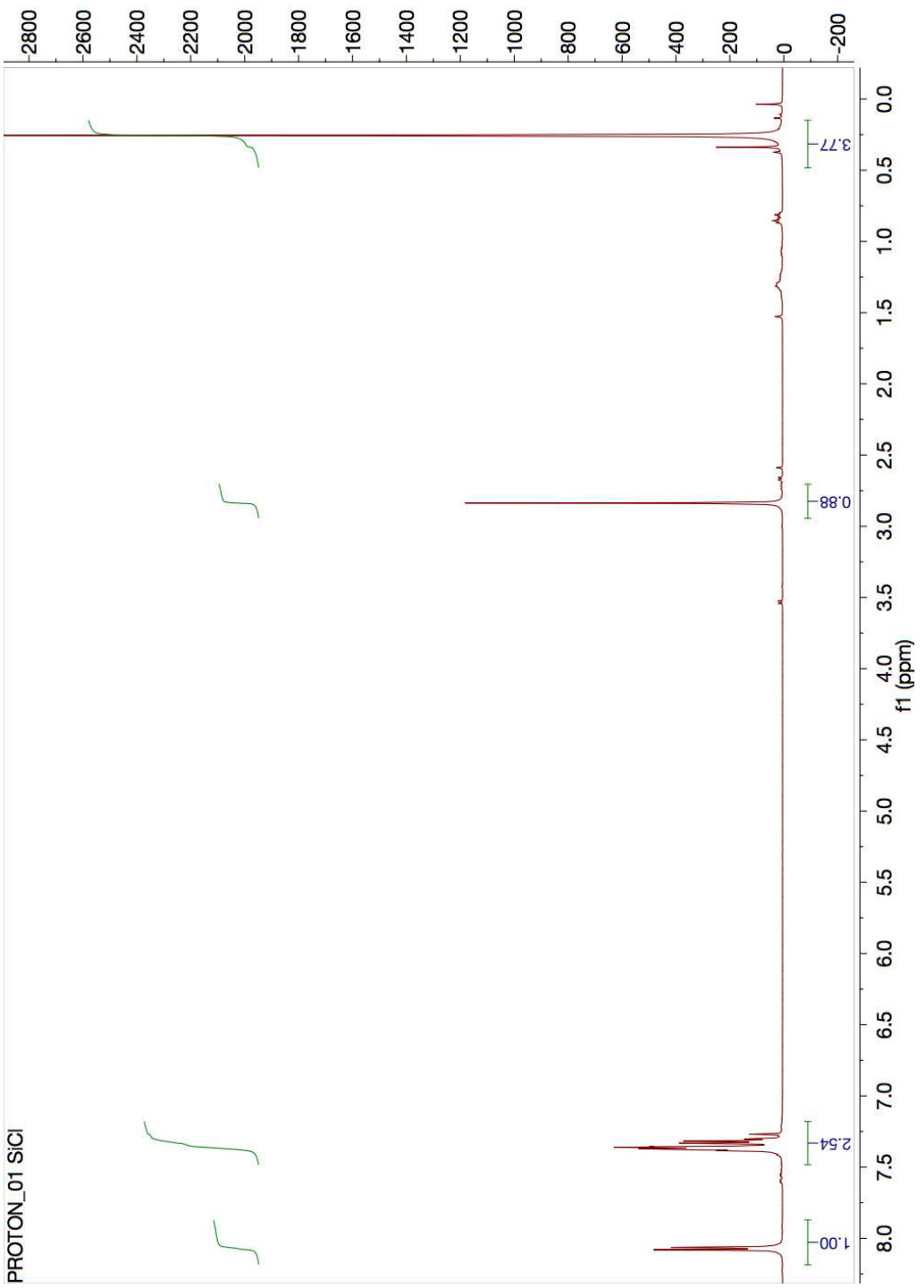
Compound 14b IR Spectrum



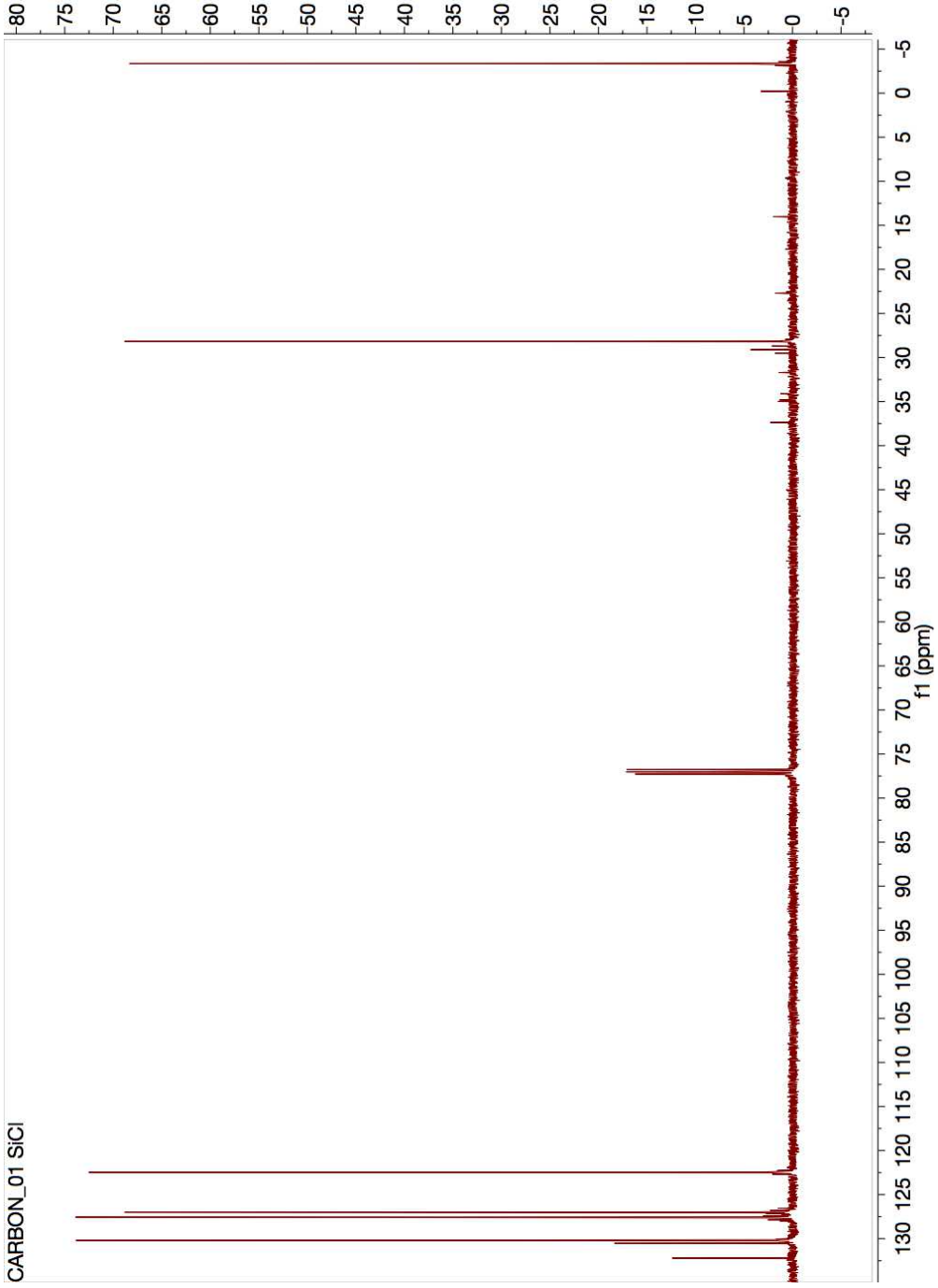
Compound 17a X-Ray Structure



Compound 17a H1 NMR

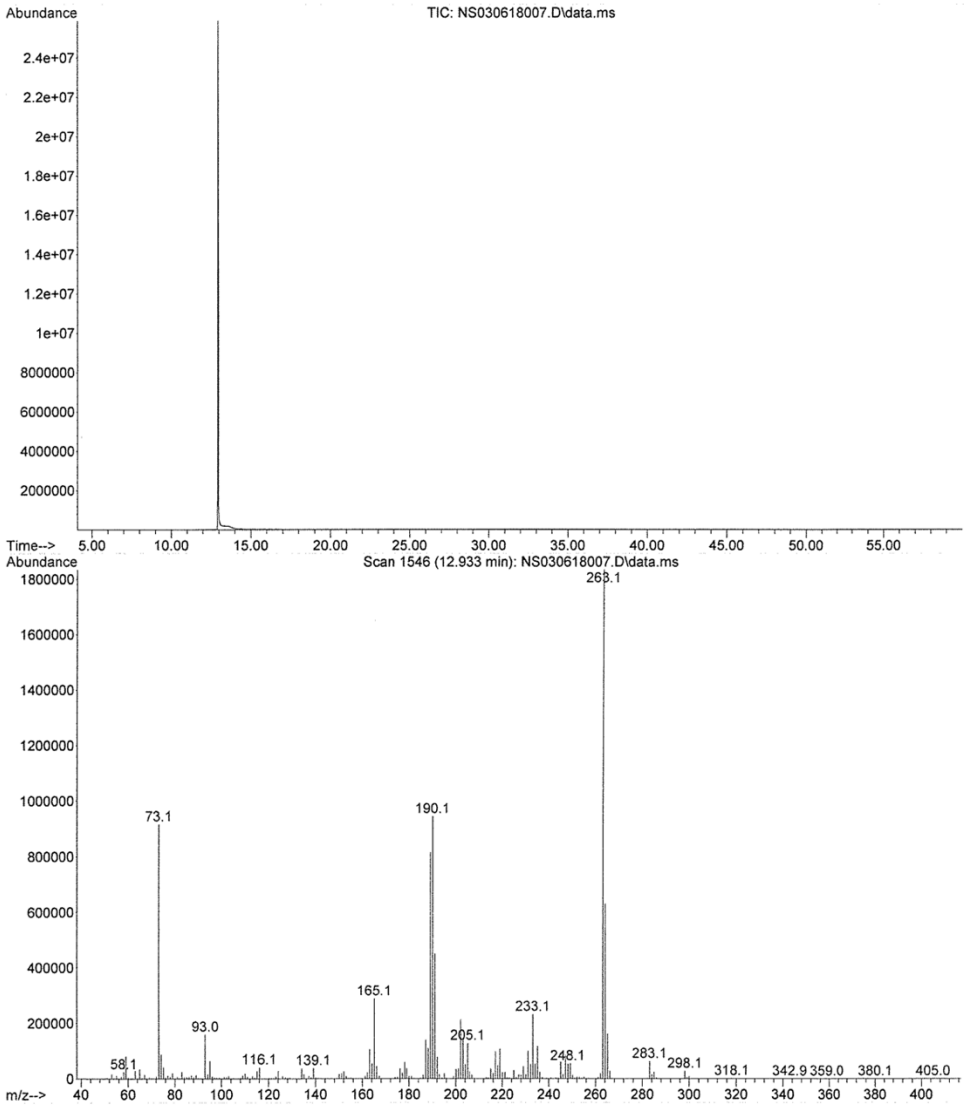


Compound 17a ^{13}C NMR

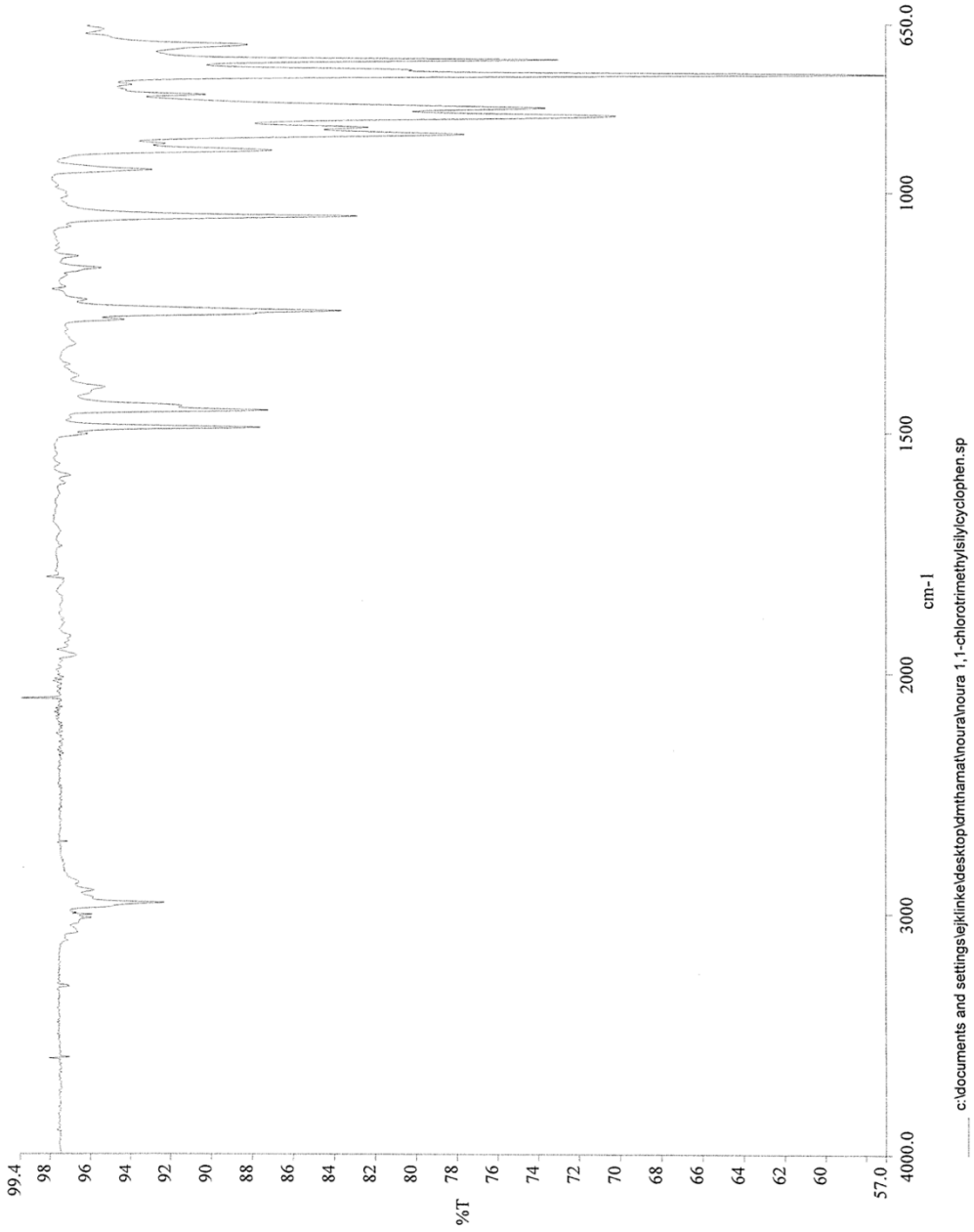


Compound 17a Mass Spectrum

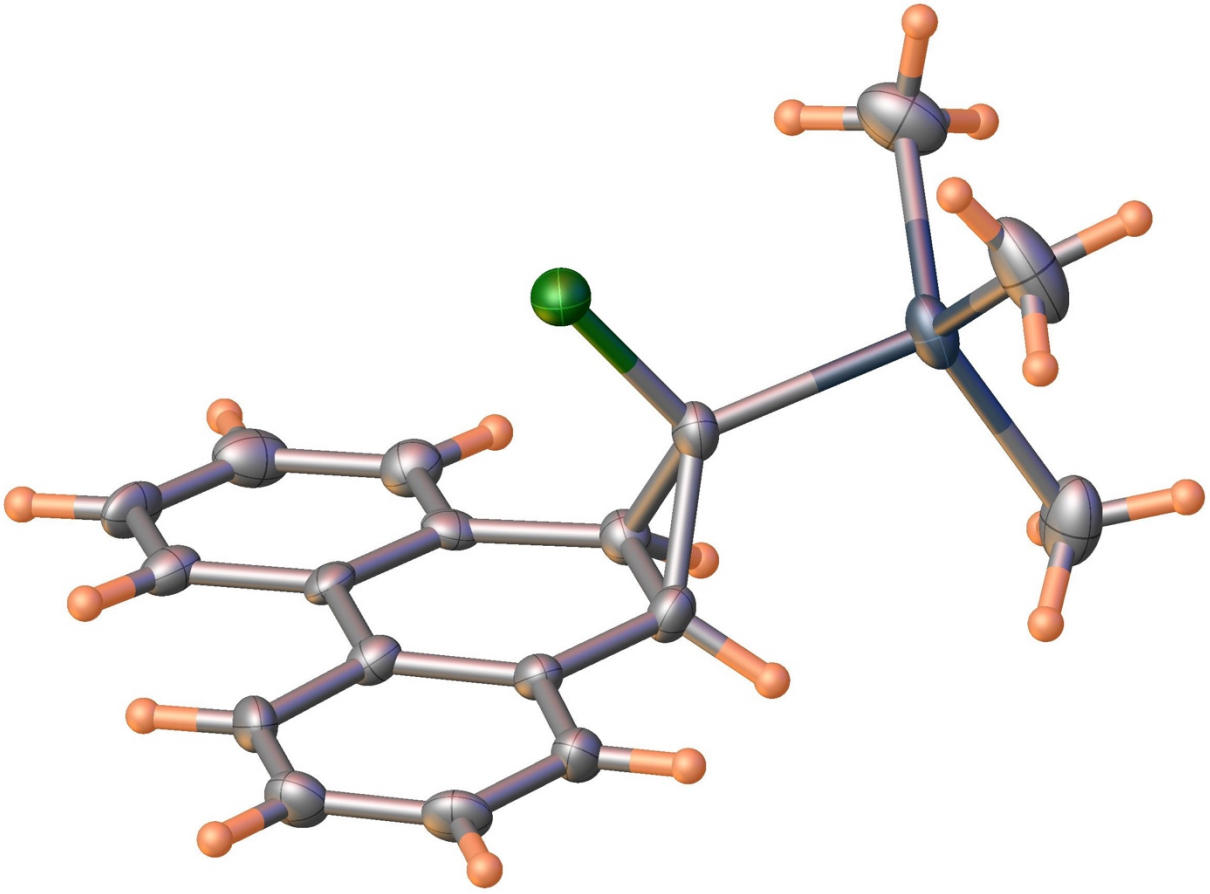
```
File       :D:\1\data\Noura\NS030618007.D
Operator   : Noura Srour
Acquired   :  6 Mar 2018  18:56     using AcqMethod DASLAB4MIN60.M
Instrument :    GCMS1
Sample Name: trimethylsilicon chloride precursor
Misc Info  : FC  purified
Vial Number: 1
```



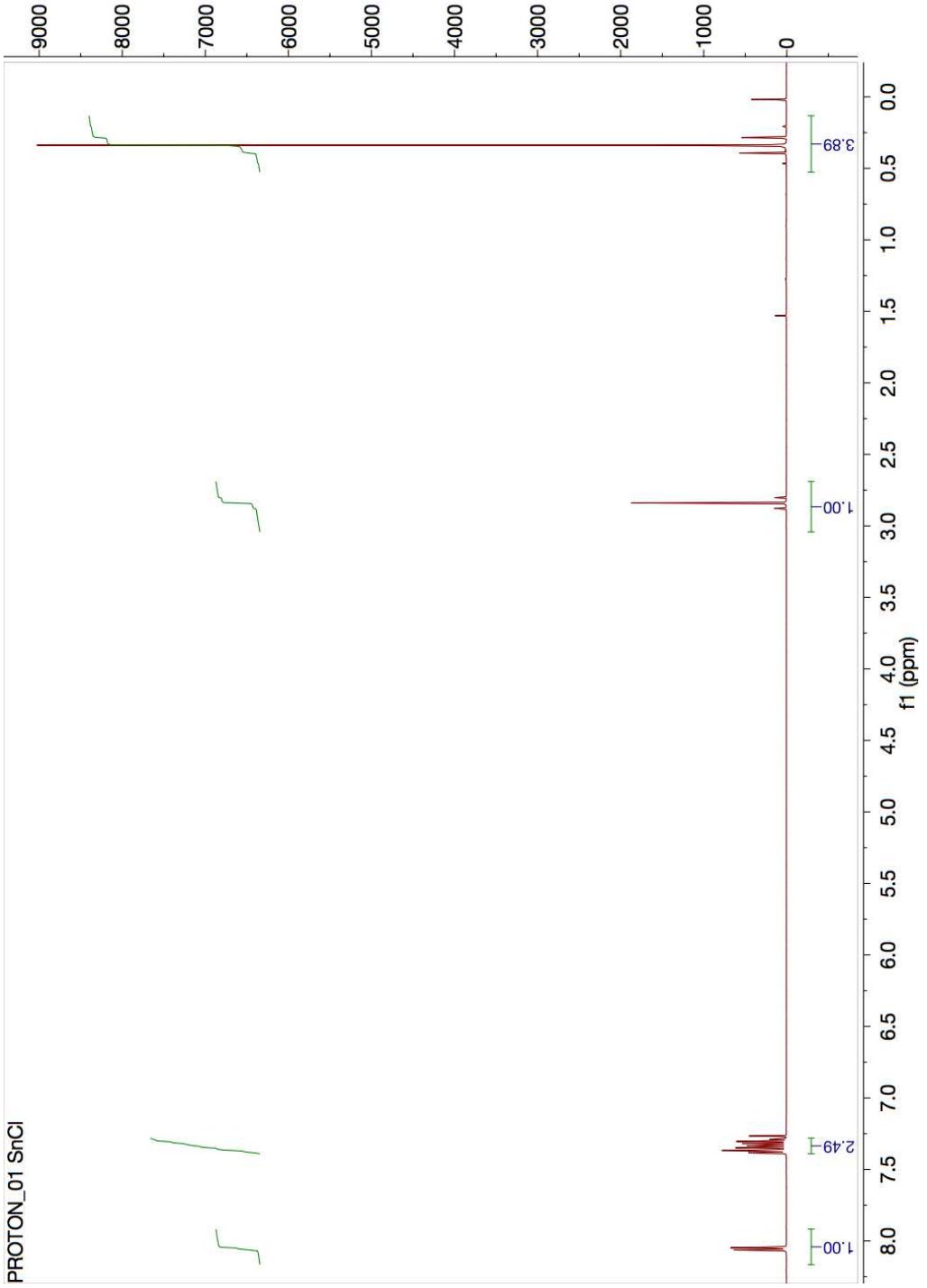
Compound 17a IR Spectrum



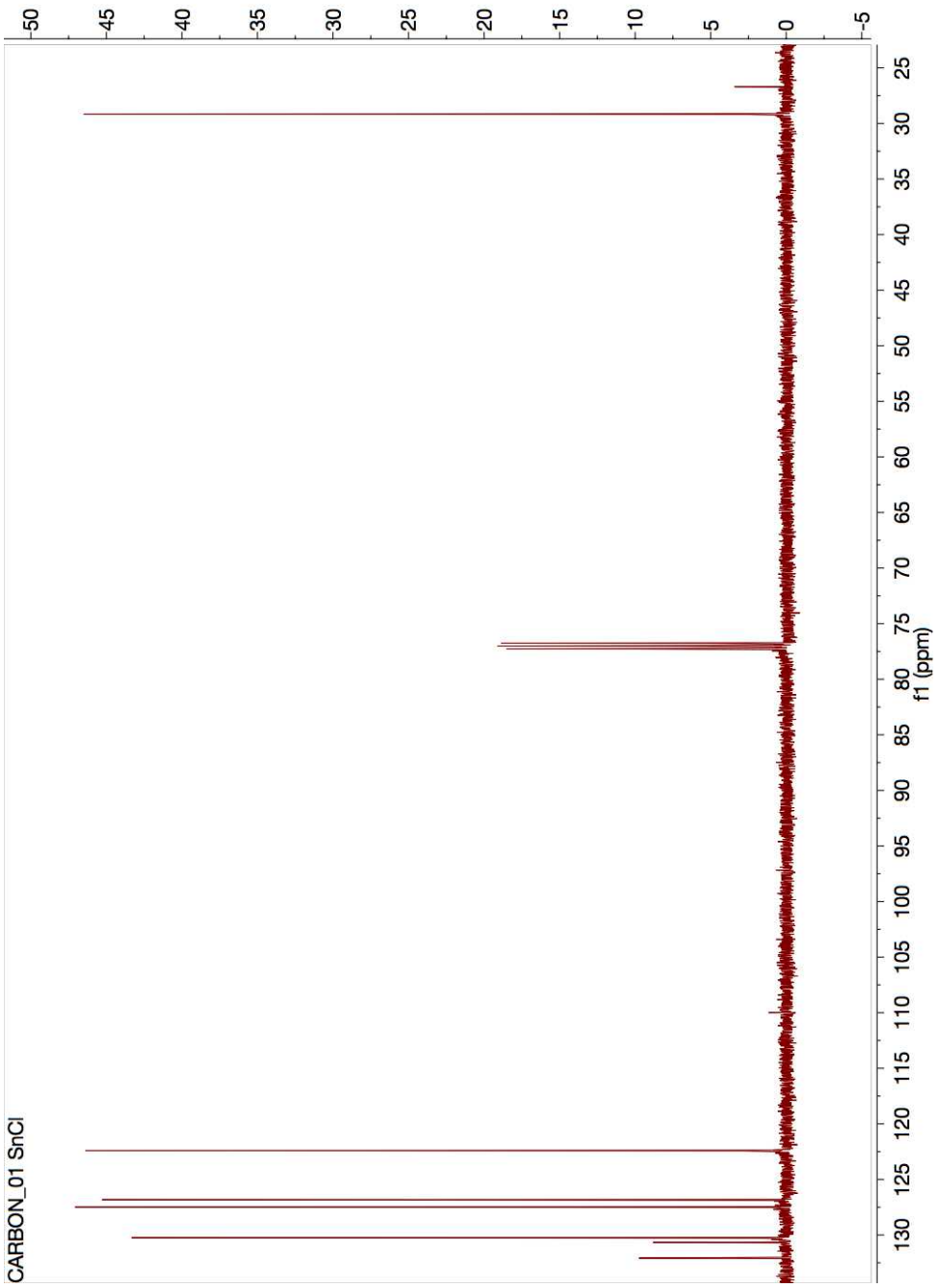
Compound 17b X-Ray Structure



Compound 17b ^{1}H NMR

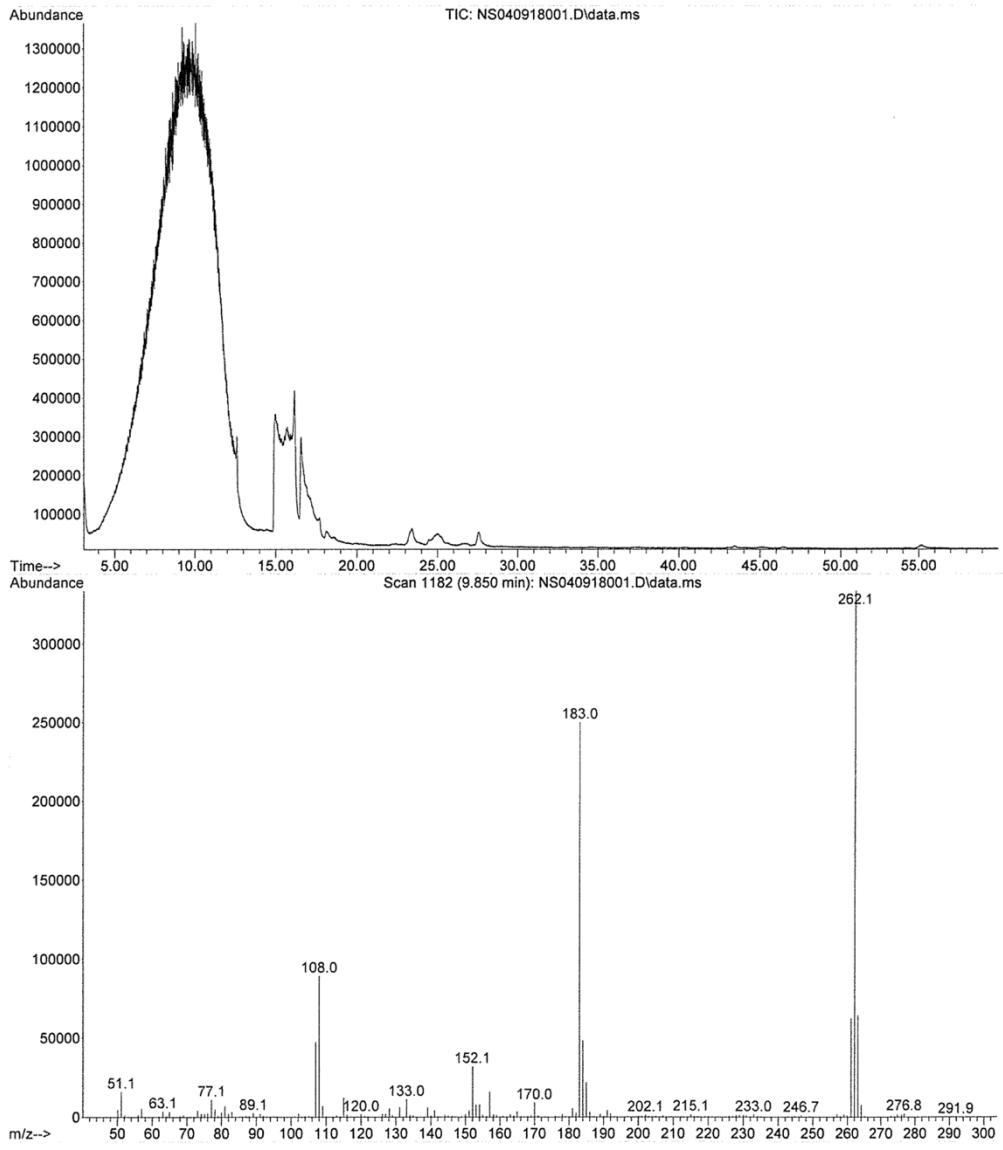


Compound 17b ^{13}C NMR

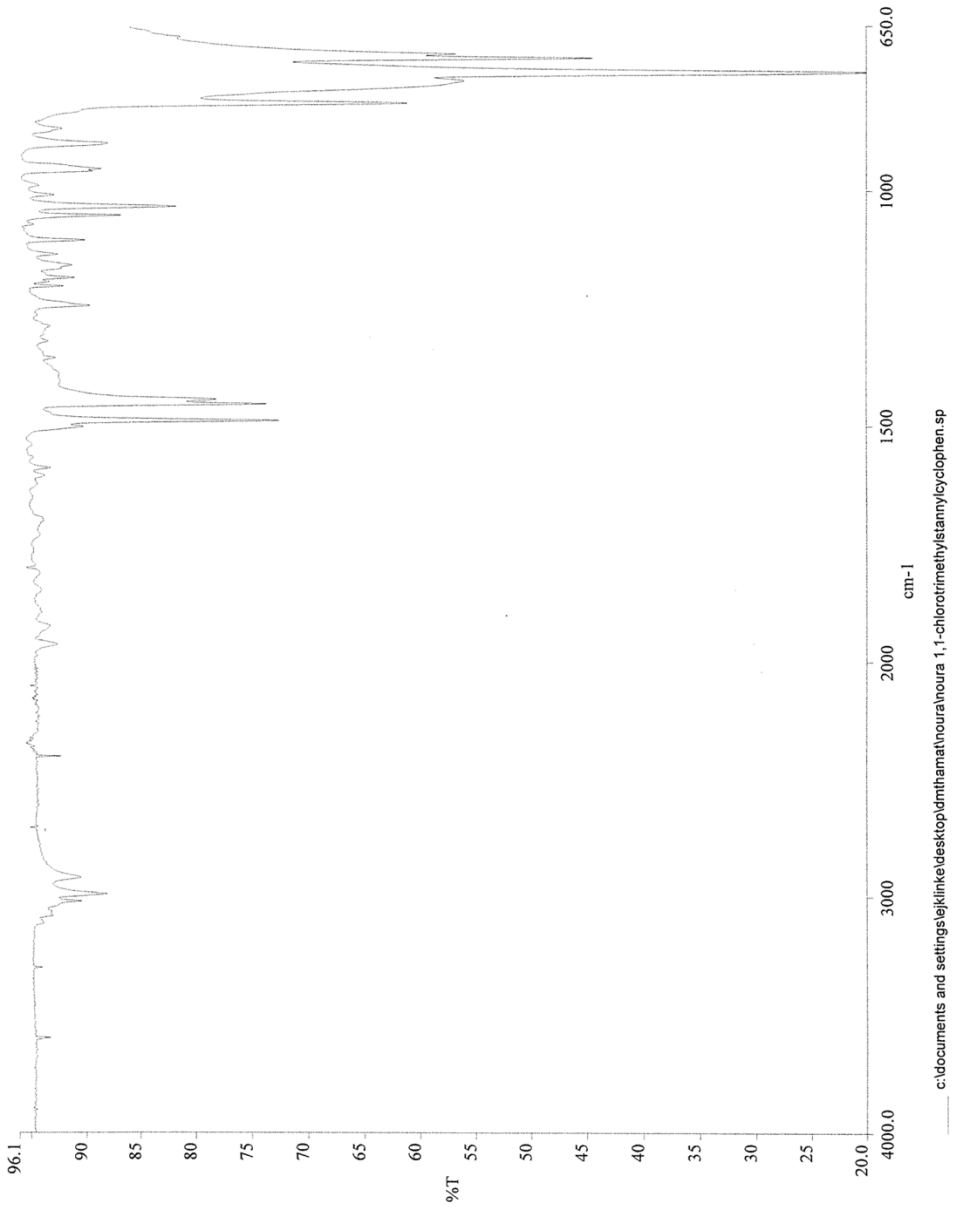


Compound 17b Mass Spectrum

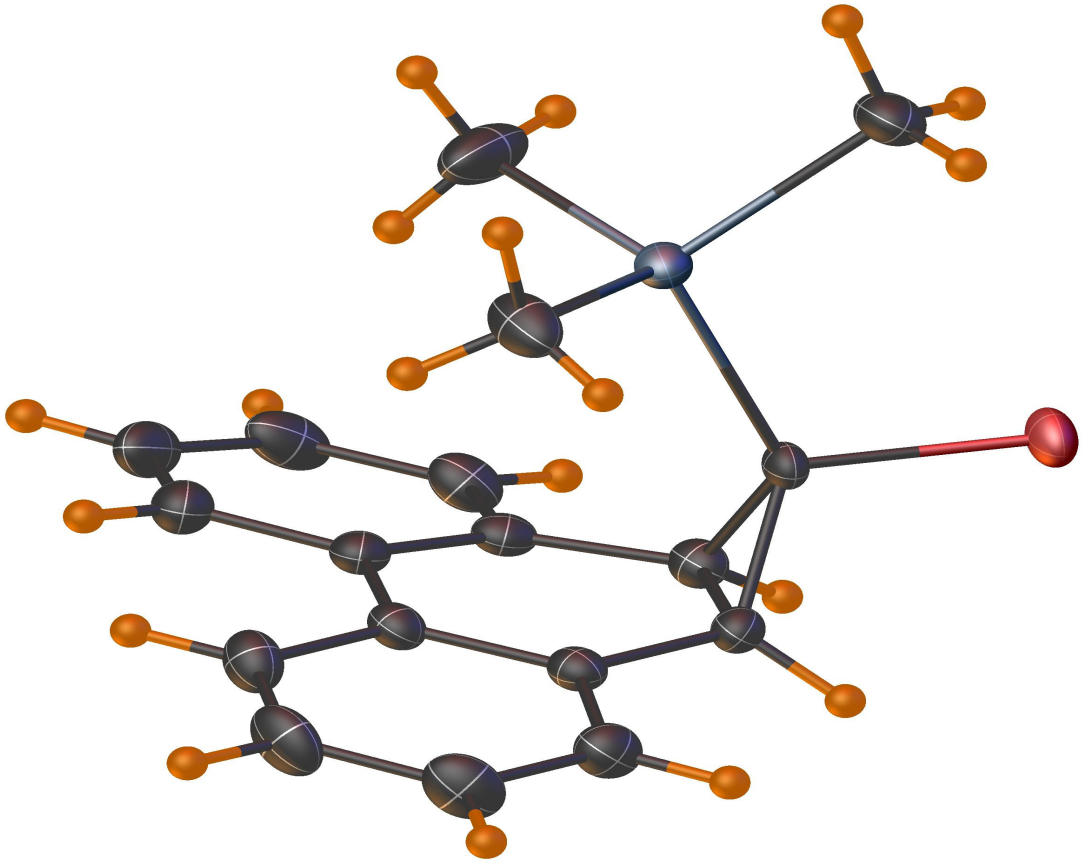
```
File       :D:\1\data\Noura\NS040918001.D
Operator   : NS
Acquired   :  9 Apr 2018  13:03     using AcqMethod DASLAB3MIN60T.M
Instrument :    GCMS1
Sample Name: trimethyltin chloride
Misc Info  : purified through FC and recryst. in hexanes
Vial Number: 1
```



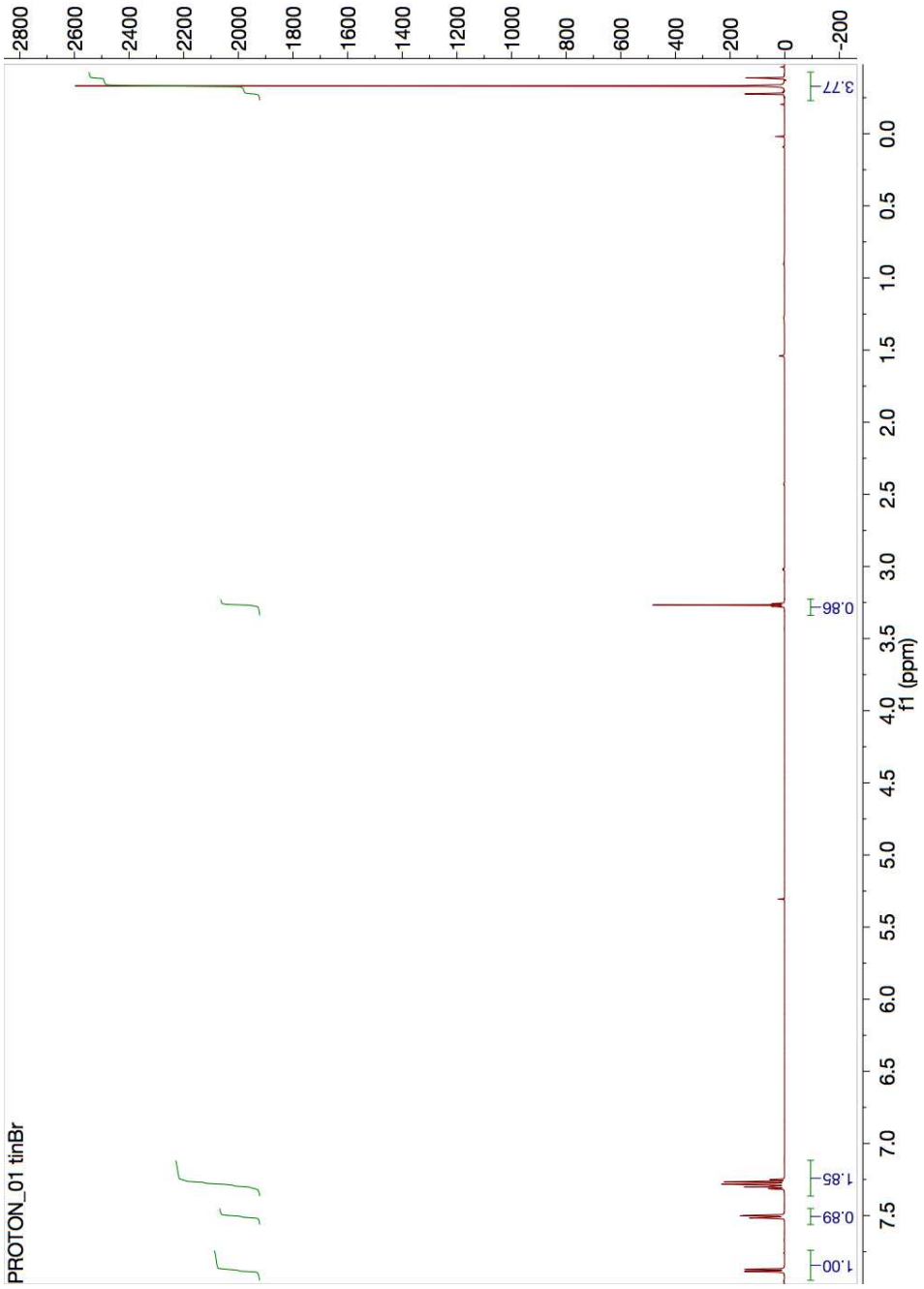
Compound 17b IR Spectrum



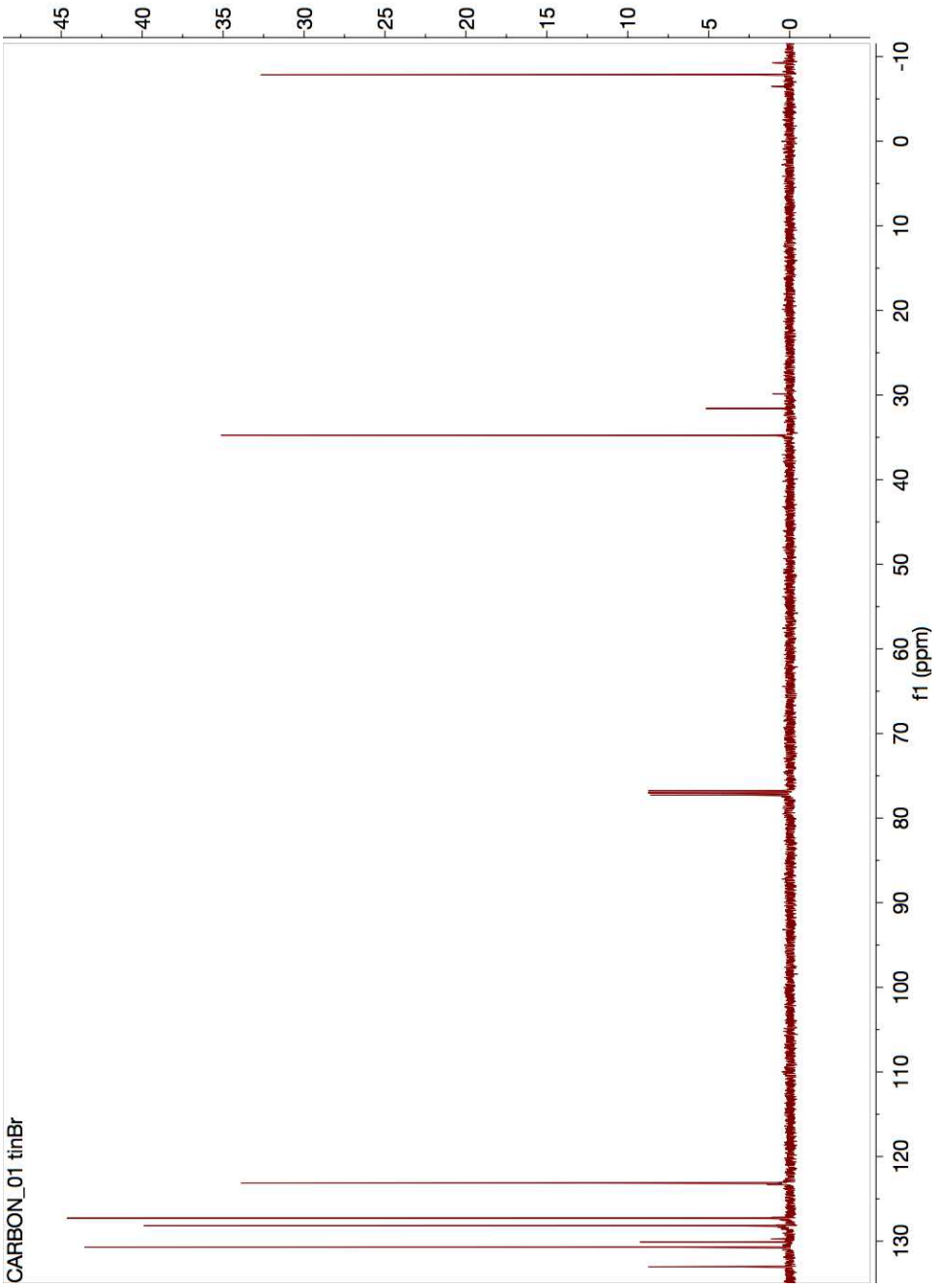
Compound 17c X-Ray Structure



Compound 17c ^{1}H NMR

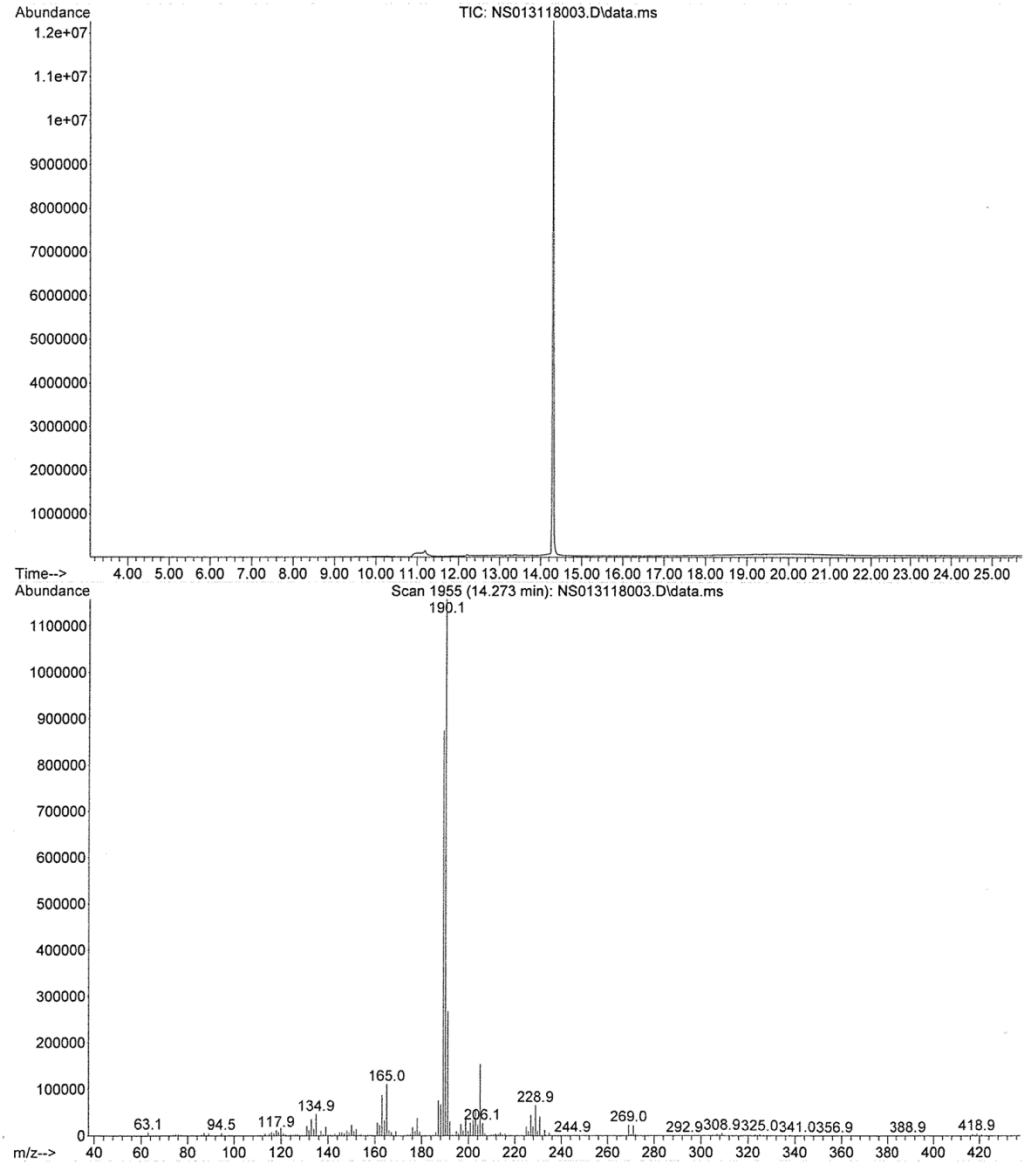


Compound 17c ^{13}C NMR

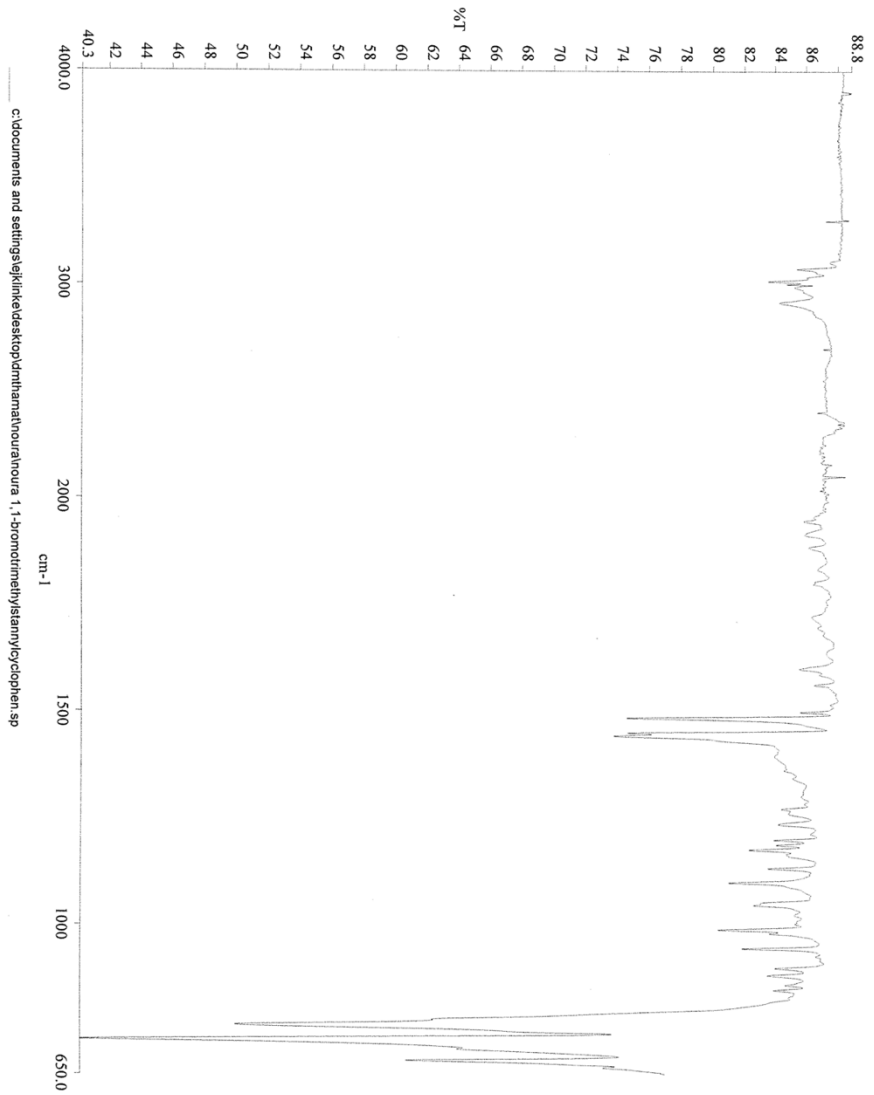


Compound 17c Mass Spectrum

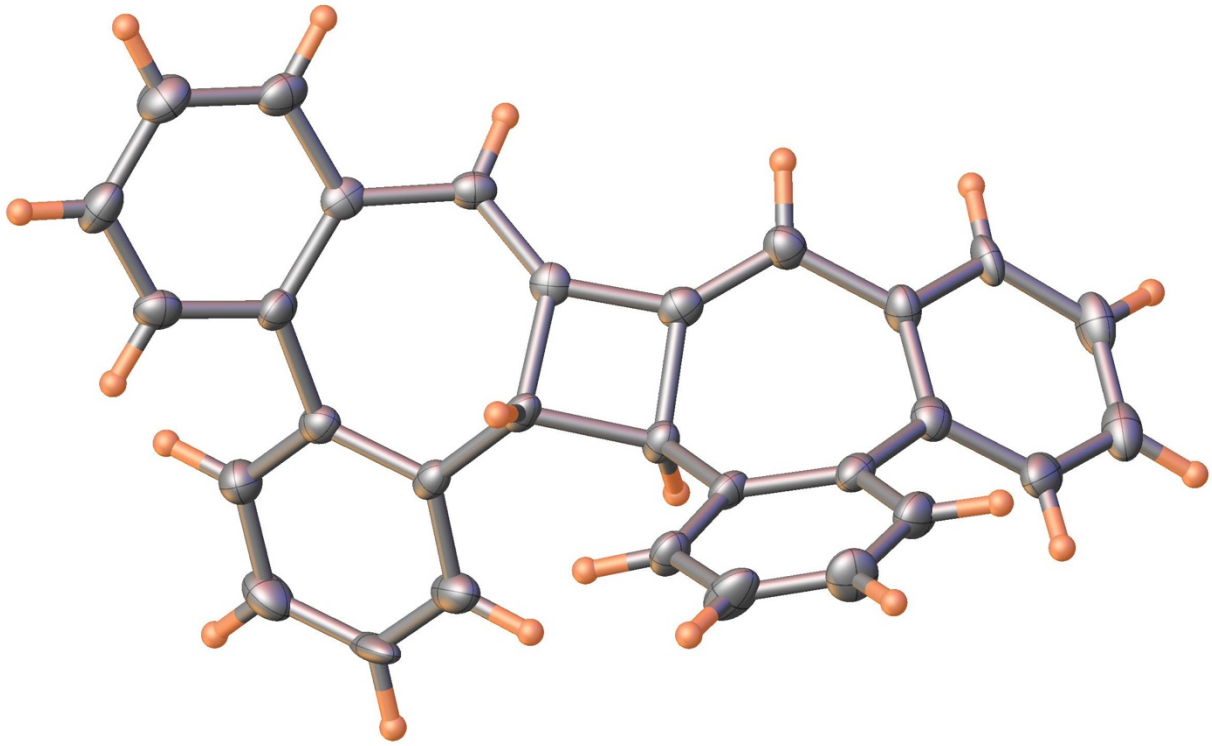
```
File       :D:\1\data\Noura\NS013118003.D
Operator   : Noura Srour
Acquired   : 31 Jan 2018  14:02     using AcqMethod DASLAB3MIN60.M
Instrument :    GCMS1
Sample Name: trimethyltin bromide
Misc Info  : FC column purified
Vial Number: 1
```



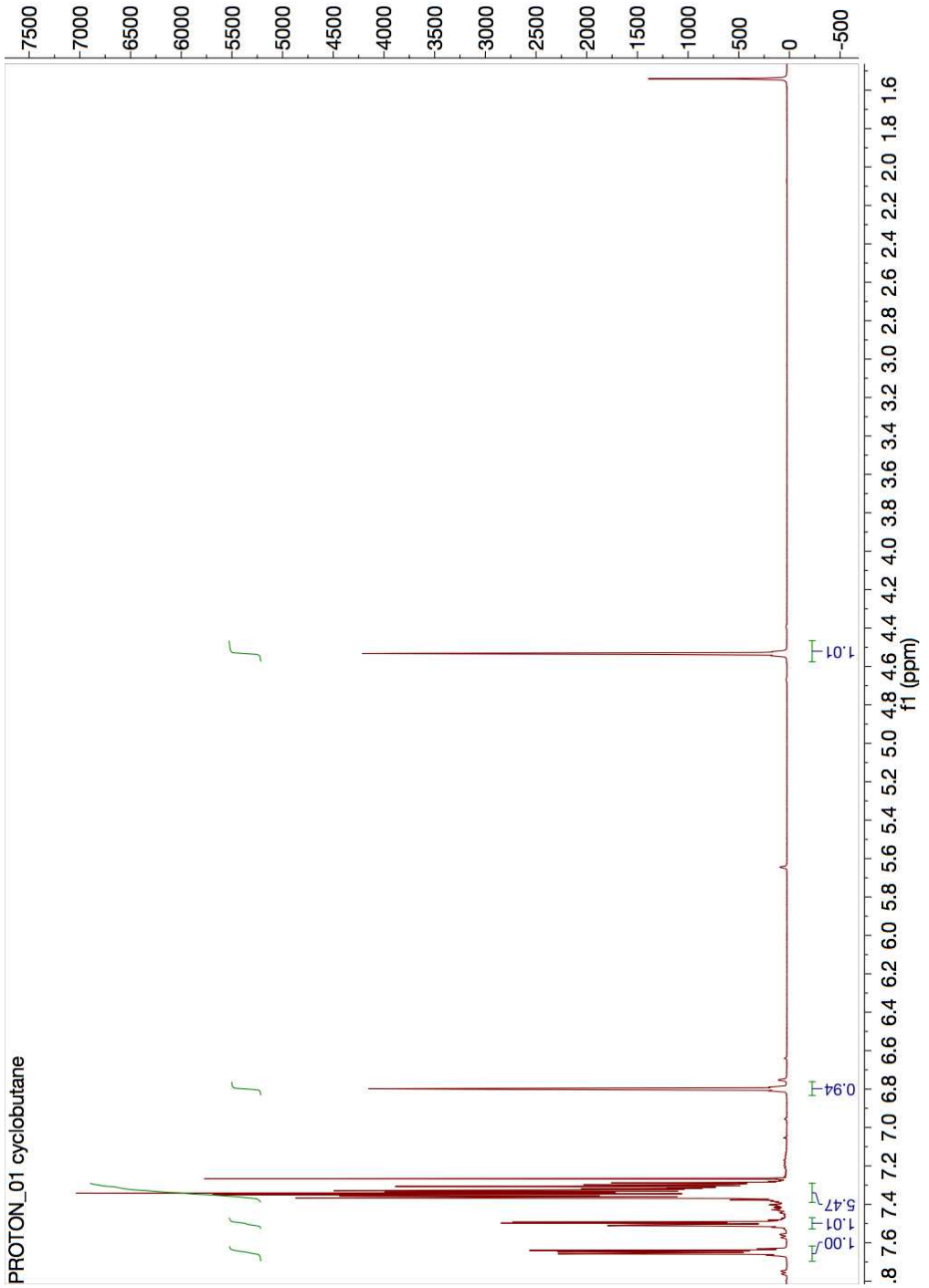
Compound 17c IR Spectrum



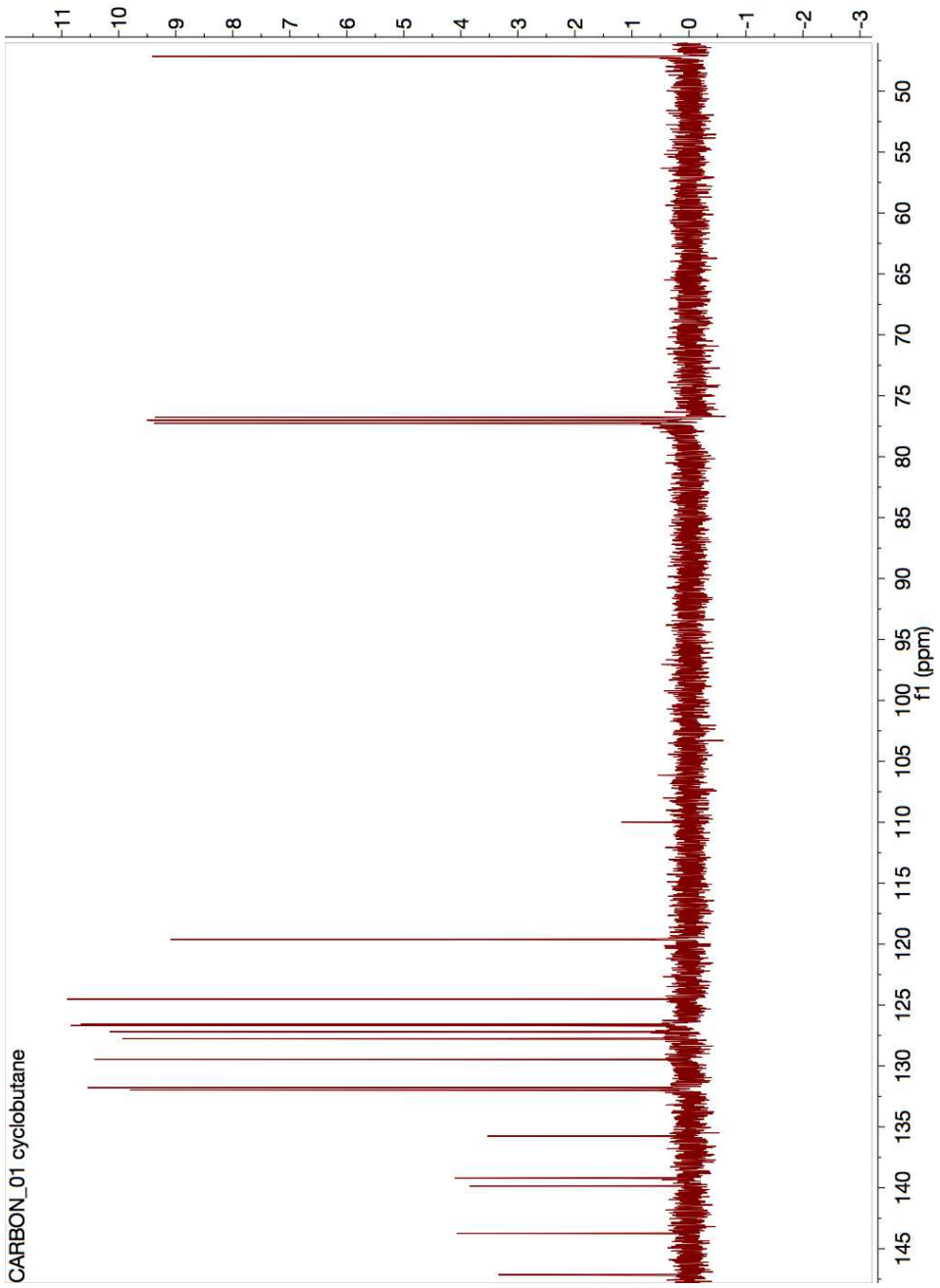
Compound 30 X-Ray Structure



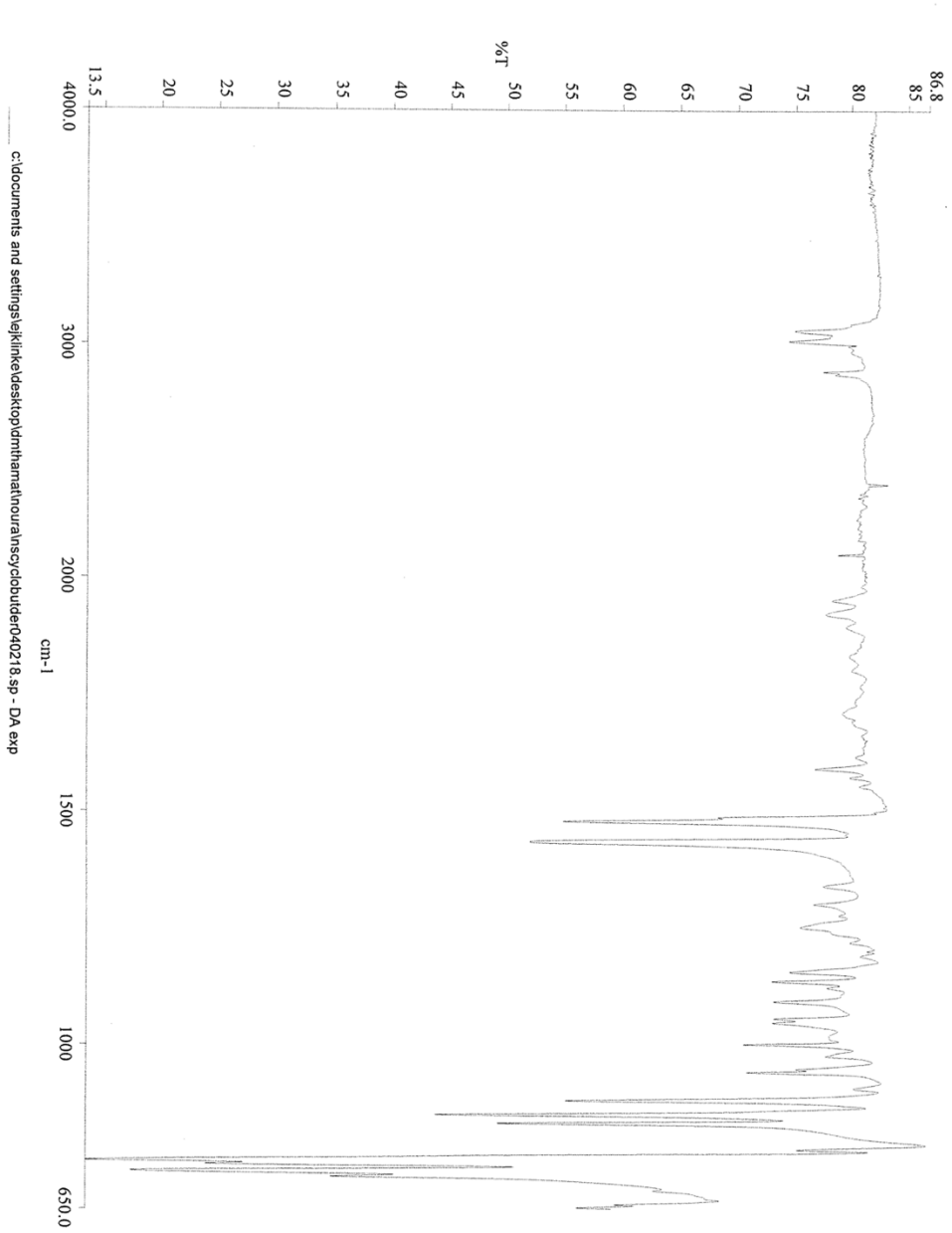
Compound 30 ^{1}H NMR



Compound 30 ^{13}C NMR



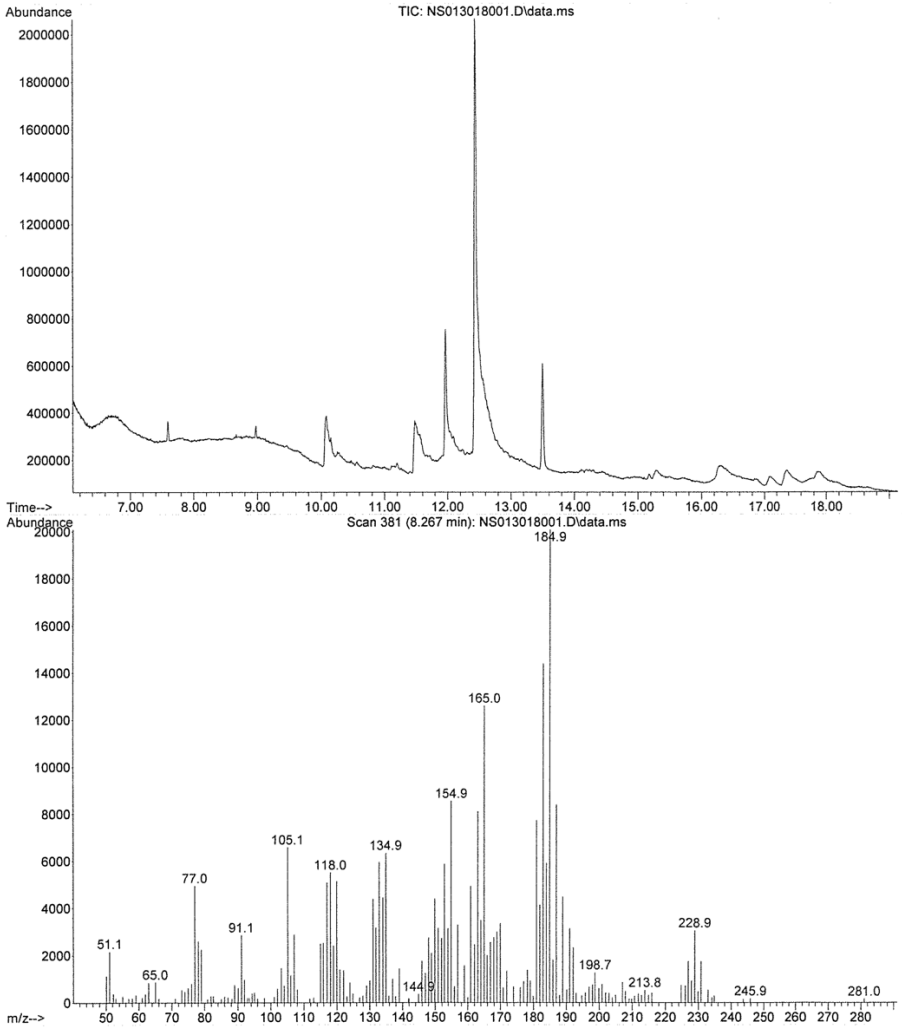
Compound 30 IR Spectrum



Appendix 2: Photolysis Mass Spectra

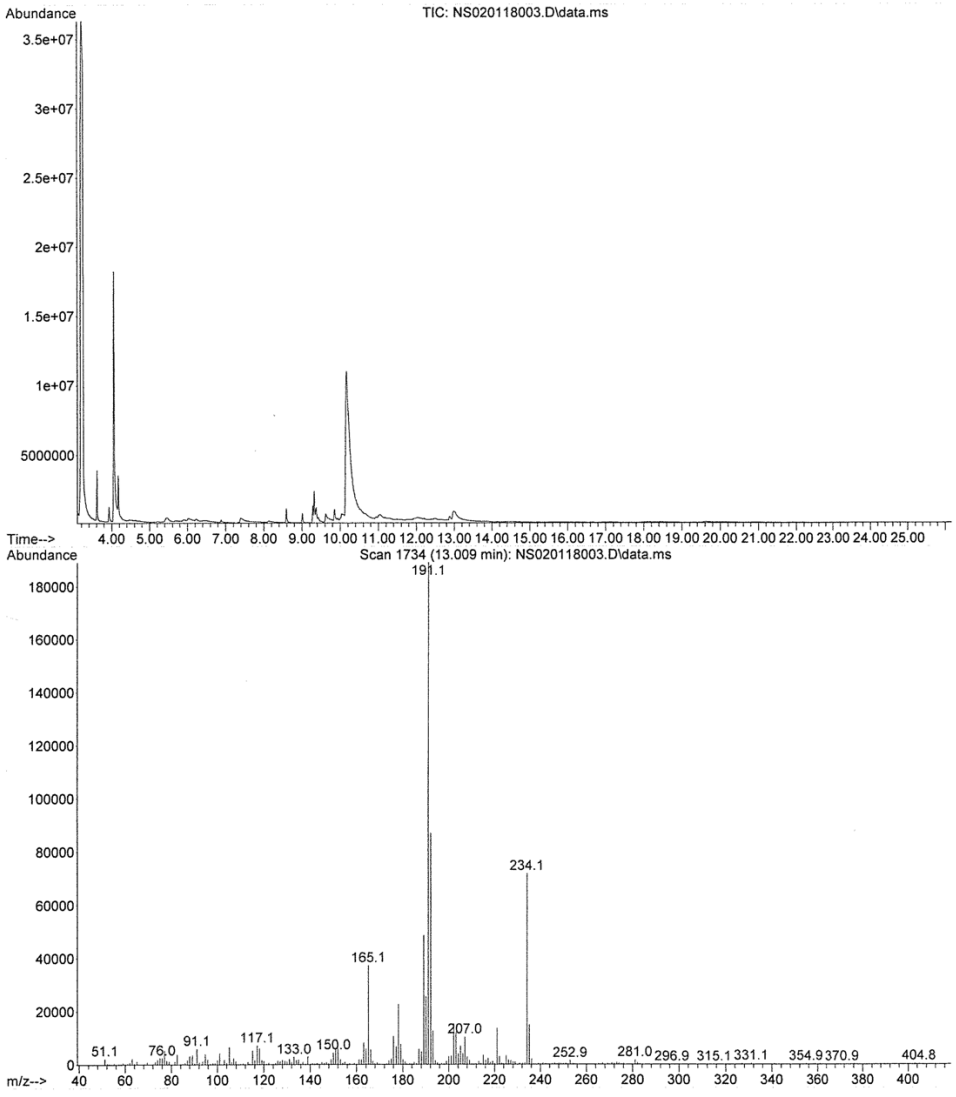
Chloro(trimethylstannyl)carbene (A)

```
File       :D:\1\data\Noura\NS013018001.D
Operator   : NS
Acquired   : 30 Jan 2018  11:15     using AcqMethod DASLAB6MIN60t.M
Instrument :    GCMS1
Sample Name: chloroTMSn cyclophen cis alkene
Misc Info  : prephotolysis
Vial Number: 1
```



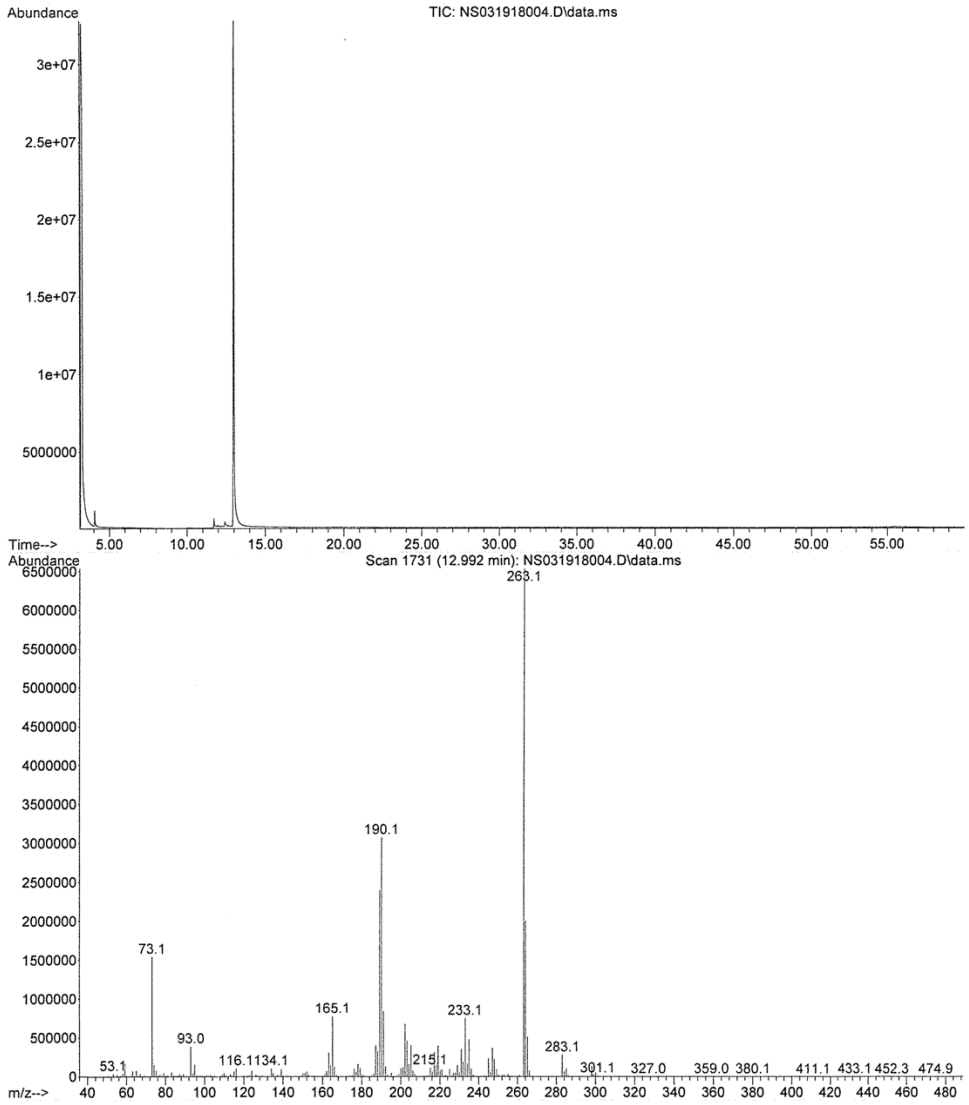
Chloro(trimethylstannyl)carbene (B)

```
File       :D:\1\data\Noura\NS020118003.D
Operator   : NS
Acquired   :  1 Feb 2018  12:21     using AcqMethod DASLAB3MIN60.M
Instrument :    GCMS1
Sample Name: chloroTMSn cyclophen photolysis cic alkene
Misc Info  : 16h
Vial Number: 1
```



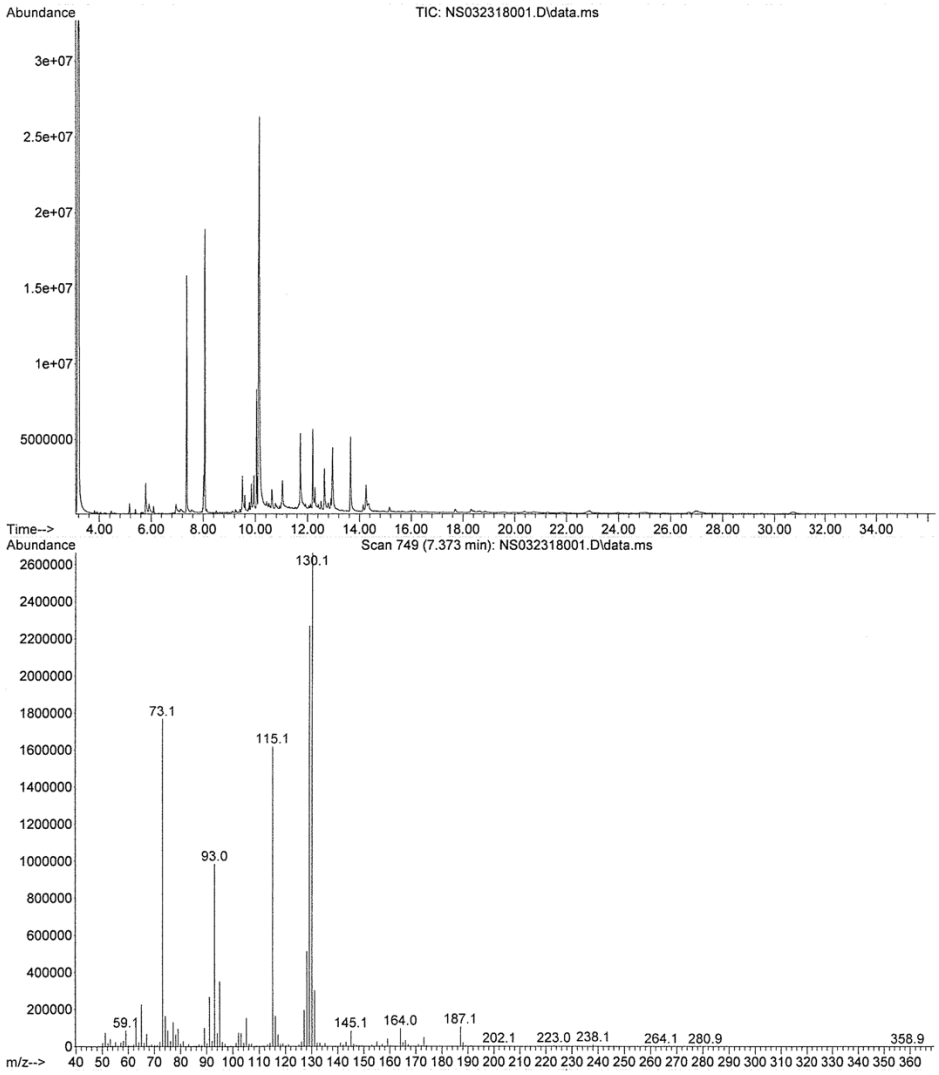
Chloro(trimethylsilyl)carbene (C)

```
File       :D:\1\data\Noura\NS031918004.D
Operator   : NS
Acquired   : 19 Mar 2018  17:19     using AcqMethod DASLAB3MIN60.M
Instrument :    GCMS1
Sample Name: chloroTMSi cyclophen phot. trans alkene
Misc Info  : prephotolysis
Vial Number: 1
```



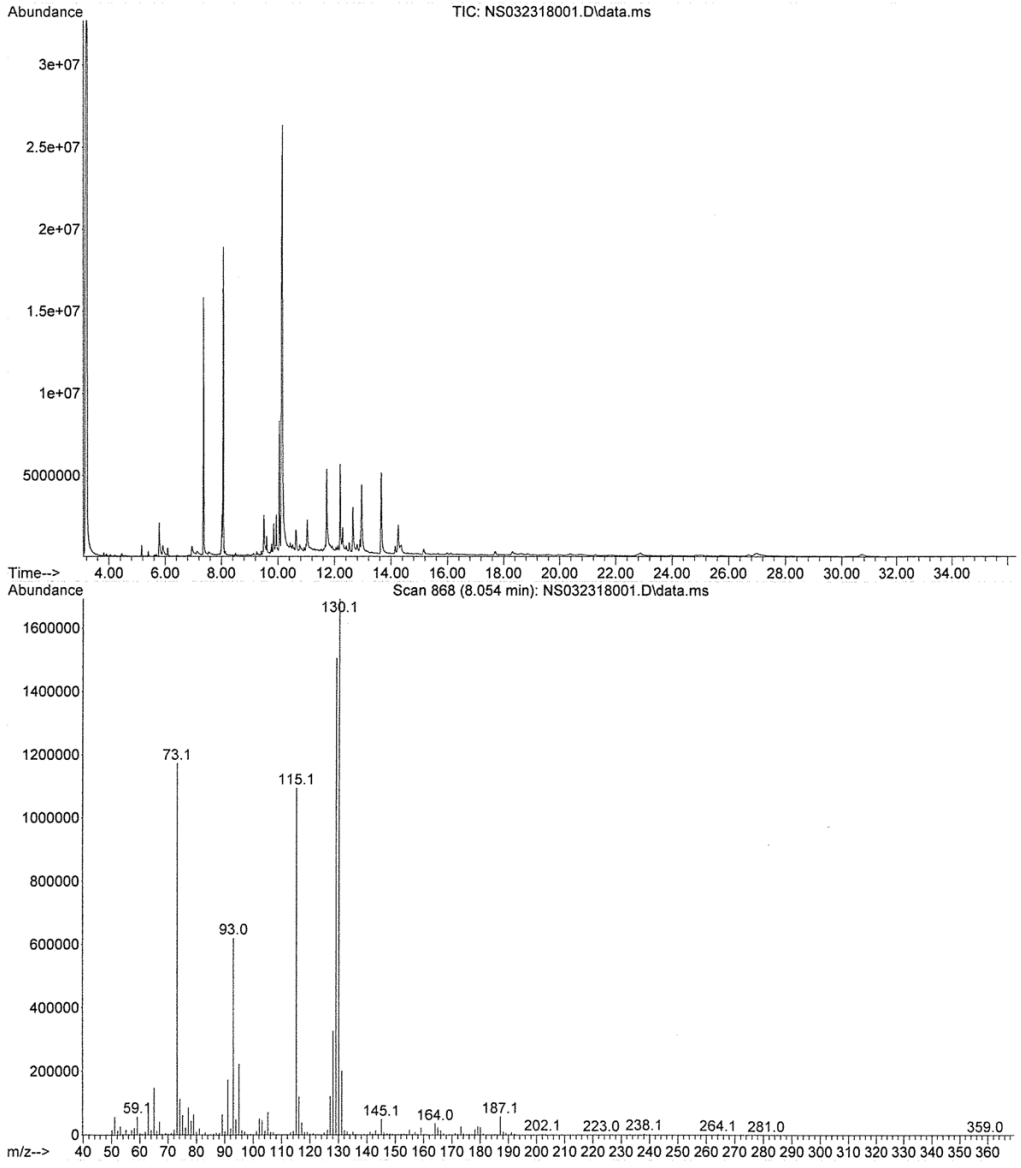
Chloro(trimethylsilyl)carbene (D)

```
File       :D:\1\data\Noura\NS032318001.D
Operator   : NS
Acquired   : 23 Mar 2018  15:31     using AcqMethod DASLAB3MIN60T.M
Instrument :    GCMS1
Sample Name: chloroTMSi cyclophen photolysis with trans al
Misc Info  : 67h12mins
Vial Number: 1
```



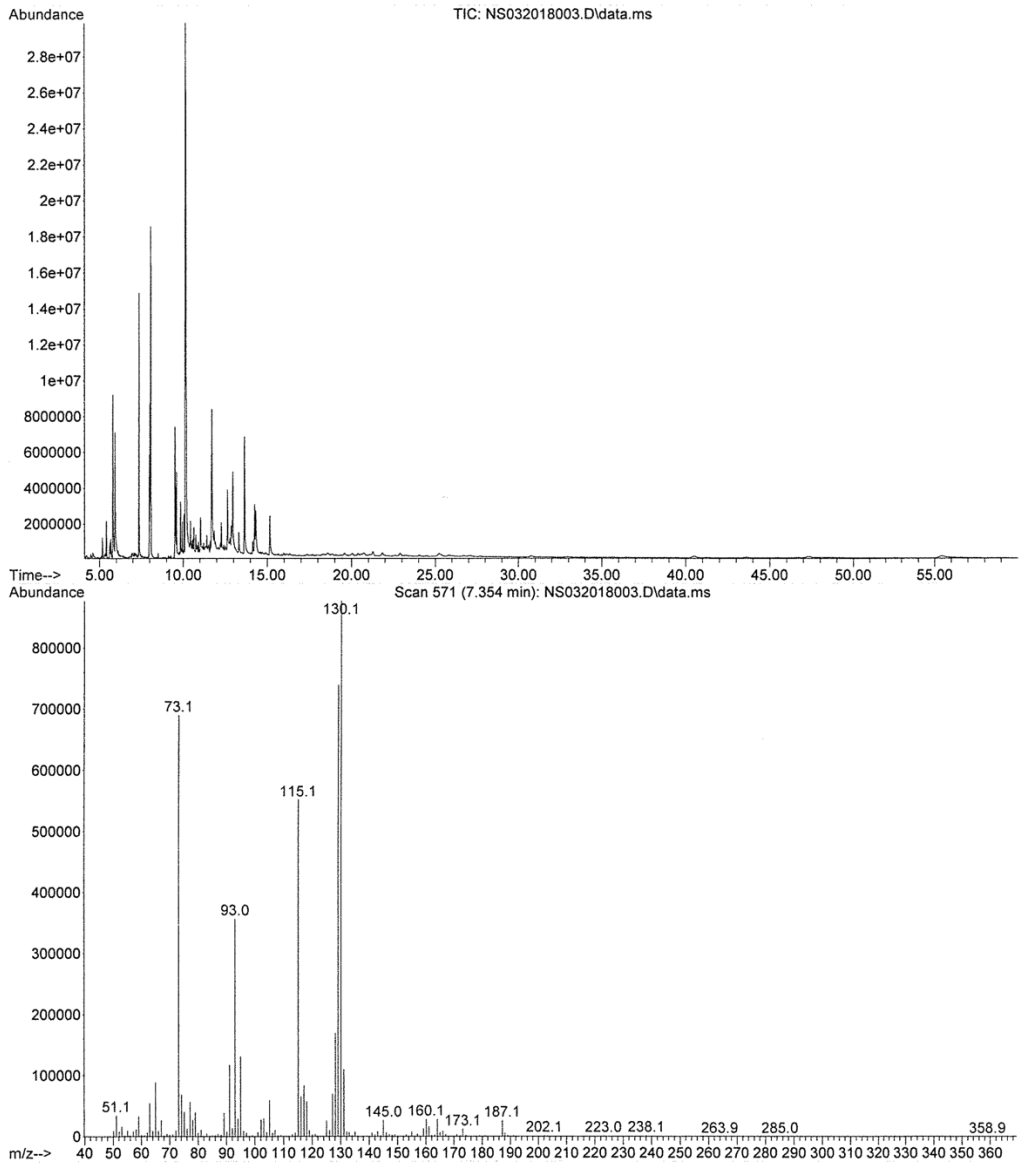
Chloro(trimethylsilyl)carbene (E)

```
File       :D:\1\data\Noura\NS032318001.D
Operator   : NS
Acquired   : 23 Mar 2018  15:31     using AcqMethod DASLAB3MIN60T.M
Instrument :    GCMS1
Sample Name: chloroTMSi cyclophen photolysis with trans al
Misc Info  : 67h12mins
Vial Number: 1
```



Chloro(trimethylsilyl)carbene (F)

```
File       :D:\1\data\Noura\NS032018003.D
Operator   : NS
Acquired   : 20 Mar 2018  14:16     using AcqMethod DASLAB4MIN60.M
Instrument :    GCMS1
Sample Name: chloroTMSi cyclophen photolysis cis alkene
Misc Info  : 35h19mins
Vial Number: 1
```



Chloro(trimethylsilyl)carbene (G)

```
File       :D:\1\data\Noura\NS031918002.D
Operator   : NS
Acquired   : 19 Mar 2018  13:05     using AcqMethod DASLAB4MIN60.M
Instrument :    GCMS1
Sample Name: chloroTMSi cyclophen phot with cis alkene
Misc Info  : 35h19mins
Vial Number: 1
```