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New synthetic routes to strained cumulenes and reactive carbenes

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NEW SYNTHETIC ROUTES TO STRAINED CUMULENES AND REACTIVE CARBENES

BY

SUSANA HERNANDEZ
B. A. PEDAGOGIC AND TECHNOLOGICAL UNIVERSITY OF COLOMBIA, 1984

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May 6, 1998

Date

DEDICATION

To my parents, Carlos J. and Maria A., and my brothers and sisters for their love and support.

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ABSTRACT

I. DEVELOPMENTS IN THE SYNTHESIS OF STRAINED BUTATRIENES

II. PHOTOGENERATION OF REACTIVE CARBENES BY FRAGMENTATION OF CYCLOPROPANATED PHENANTHRENES

By

Susana Hernandez

University of New Hampshire, May, 1998

I. The synthesis, trapping, and strain energy estimates for cyclic butatrienes are described. Four fundamental questions have been investigated: kinetic stability limitations, molecular strain, structural limitations, and the development of a general synthetic route applicable to different ring sizes.

1,2,3-Cyclooctatriene (**29**) has been generated by magnesium induced 1,2-elimination on 2-bromo-3-chloro-1,3-cyclootadiene (**64**). Synthesis of the eight-membered ring completes the C_6-C_{10} series of cyclic butatrienes. This substance shows moderate kinetic stability, but is readily trapped in a $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition with diphenylisobenzofuran or 2,5-dimethylfuran. The total strain energy and the strain in the butatriene moiety in cumulene **29** have been assessed by *ab initio* calculations. The estimates are 17.7

kcal/mol and 12.4 kcal/mol, respectively, at the MP2/6-31G*//HF/3-21G level.

1,2,3-Cyclohepatriene (**30**) and its isomer cyclohepten-3-yne (**19**) are readily accessible by magnesium induced 1,2-elimination on appropriate precursors. The calculated total strain energy in the cyclic butatriene, and in the seven-membered enyne are 31.8 kcal/mol and 30.8 kcal/mol, respectively, at the MP2/6-31G*//HF/3-21G level.

5,5-Dimethyl-1,2,3-cyclopentatriene (**85**) remains elusive. Five likely precursors have been prepared and studied; no evidence for the existence of this compound was found.

Intramolecular vinylidene coupling has been explored as a possible ring-size-independent synthetic route to cyclic butatrienes. In the cases of tetrabromo-olefins **122** and **127** a 1,2-migration occurs faster than the ring closure which would give the cumulene.

II. A general route to cleanly photogenerate reactive carbenes by photolysis of cyclopropanated phenanthrenes has been studied. The adduct of dichlorocarbene and phenanthrene has been modified to produce shelf-stable substances that serve as photochemical precursors to vinylcarbene, and acyclic and cyclic vinylidenes.

Low temperature irradiation of 7-*endo*-ethylenedibenzo[a;b]bicyclo [4.10]heptane (**141**) at 254 nm cleanly gives phenanthrene (**135**) and vinylcarbene (**136**); the latter rapidly rearranges to cyclopropene. The strained alkene is efficiently trapped by cycloadditions with cyclopentadiene or diphenylisobenzofuran.

Fragmentation of a C_9 vinylidene precursor **158** leads to efficient formation of 1-nonyne (**160**) by 1,2-shift.

Cyclobutylidenecarbene (**163**) rearranges readily to cyclopentyne (**13**). Cycloalkyne **13** is trapped by cyclohexene to give tricyclo[6.3.0.0^{2,7}]undec-1(8)-ene (**168**) and a cylohexyl derivative **172** which has not been previously described.

Rearrangements of cyclopentylidenecarbene (**163**) and cyclohexylidenecarbene (**164**) are not observed. These carbenes are trapped in [2 + 1] cycloadditions with cyclohexene.

GENERAL INTRODUCTION

This dissertation is divided into two separate chapters:
1) Developments in Synthesis of Strained Cyclic Butatrienes,
2) Photogeneration of Reactive Carbenes by Fragmentation of Cyclopropanated Phenanthrenes. Due to the diverse nature of the topics covered, each chapter is self-contained, complete with its own introduction, statement of the goals, results and discussion, and conclusions.

CHAPTER I

DEVELOPMENTS IN THE SYNTHESIS OF STRAINED BUTATRIENES

Introduction to Strained Molecules

One longstanding challenge posed to chemists throughout the years has been the synthesis and investigation of strained hydrocarbons. The concept of strain in organic chemistry has its foundation in the 1880s with the first synthesis of small carbocyclic rings and the enunciation of the Baeyer strain energy theory (*Spannungs Theorie*). Today, the field of strained hydrocarbons presents us with examples of organic compounds with striking geometries,[1] novel reactive intermediates with unusual bonding,[2] processes involving noteworthy rearrangements,[3] and reactions of utility in synthetic organic chemistry.[4] The extraordinary ability of the chemist to create strained molecules with exceedingly high energies during the last decades has been principally due to the advances in synthetic and spectroscopic methodologies, as well as to developments in computing technology which now allow the shapes and energetics of such molecules to be predicted and probed with accuracy. In this chapter the results of studies on kinetic stability and structural limitations for strained cyclic butatrienes (cumulenes) are presented. For this reason, in the following paragraphs a brief discussion on the origin of molecular strain and several representative examples are included for completeness.

The energy of a molecule depends on its geometry.[5] Strain is introduced into a molecule whenever there is a deviation in one or more geometric parameters from the "normal" or "ideal" value(s).[5] These deviations affect their structure, stability, and reactivity.[5] The concept of strain energy (SE) is well illustrated by considering the smallest saturated and strained carbocycle, cyclopropane.[6] The "strain" connotes the fact expressed in Eq. (1) that the enthalpy of formation[7] of gaseous cyclopropane is higher than it would have been had cyclopropane been composed of three "strainless" CH_2 groups

$$\mathrm{SE}[\text{cyclo-}(\mathrm{CH_2})_3, (\mathrm{g})] = \Delta H_f[\text{cyclo-}(\mathrm{CH_2})_3, (\mathrm{g})] - 3\Delta H_f[\mathrm{CH_2}, (\mathrm{g})] \qquad \text{Eq. (1)}$$

The experimental strain energy, identified as the enthalpy change in this reaction, is obtained from ΔH^{o}_{f} data on the reacting molecules.[8] Theoretical strain energy, defined as the difference in total energy of reactants and products, is obtained from calculations of the ground state energy of the reactant molecules.[8] Accurate prediction of the strain energy in a molecule can be derived from bond-energy schemes called isodesmic[9] and homodesmic[10] reactions. A more detail description of these methods and their usefulness in calculating strain energies will be covered later in this chapter.

It has been recognized that strain introduced in a molecule in any fashion tends to be minimized by becoming distributed among several modes, such as angle strain, torsional strain, bond strain and van der Waals compressions.[11] In detail, the total strain energy of the molecule is the sum of several destabilizing terms: bond angle-deformations, bond stretching or compression (summed for all the bonds), changes of torsion angles from their optimal values, nonbonded repulsion, and electrostatic terms.[11]

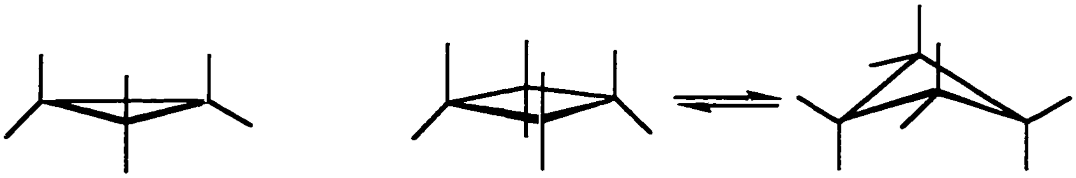


Figure 1. Conformation of cyclopropane and cyclobutane.

The classical examples of strained compounds are small rings. Three-membered rings are necessarily planar, and therefore quite highly strained (Figure 1). In cyclopropane the internuclear angle between the carbon-carbon bonds is bonds is 78.8°. This angle (Baeyer) strain is not the only source of destabilization because the planar ring necessarily has all the hydrogen atoms fully eclipsed and this causes torsional (Pitzer) strain. The total strain in cyclopropane is only slightly greater than that in cyclobutane (27.5 vs 26.3

kcal/mol),[12] which implies that the angle strain cannot exclusively account for the difference. There must be an electronic (orbital) stabilization of cyclopropane that partially offsets its greater apparent strain.[5c]

A four-membered ring can be either planar or puckered. The planar ring has minimal angle (Baeyer) strain but will have maximal torsional (Pitzer) strain because of its eight pairs of eclipsing hydrogens. The torsional strain can be reduced by puckering (at the expense of some increase in angle strain). Cyclobutane is therefore a wing-shaped molecule with an "angle of pucker" of 28° and a barrier to ring inversion of 1.45 kcal/mol.[13]

Many highly strained compounds containing small rings in fused systems have been prepared, showing that organic molecules can exhibit much more strain than simple cyclopropanes or cyclobutanes. A few of these compounds are illustrated in Figure 2. The smallest, and most strained of fused bicyclic rings is bicyclo[1.1.0]butane (**1**), with a strain of 66.5 kcal/mol.[14] Its puckering angle is 58°, much larger than that of cyclobutane and its C-C bonds are unusually short (1.498 Å). [1.1.1] Propellane (**2**), synthesized by Wilberg and Walker in 1982, is stable enough at room temperature to have its IR spectrum measured. [15a] The central σ bond in is rather long (1.60 Å), and its strain energy exceeds the sum of the strain in its three rings (103 kcal/mol).[15b] Rotane (**3**) (symmetry D_{3h}) has been recently prepared.[16] A molecular that has aroused considerable interest in connection with the

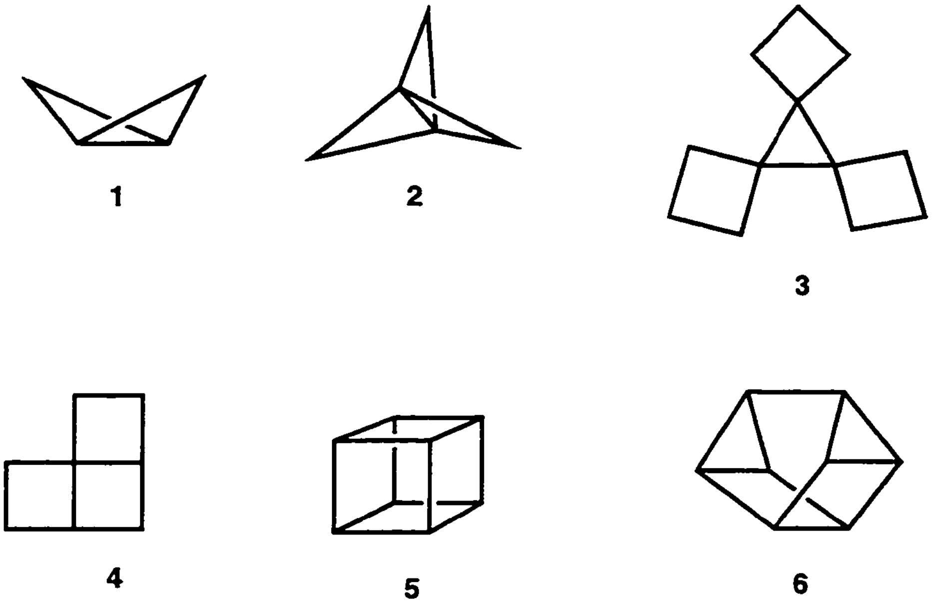


Figure 2. Strained saturated-ring hydrocarbons.

possibility of synthesizing a structure with a planar carbon is fenestrane (also called windowpane) but only its homologue **4** has been prepared by Wilberg, *et al.*[17]

Among the many families of isomeric strained hydrocarbons, the $(CH)_8$ group is one of the most interesting. An intriguing cage structure is cubane (**5**) prepared by Eaton and Cole in 1964.[18] Prior to the synthesis of **5** theoretical calculations[19] of its strain energy (160 kcal/mol) were considered as a contra-indication for the existence of cubane at room temperature. However, cubane appeared to be surprisingly thermally stable, decomposing only at 200 °C. The structure as determined by electron diffraction shows a bond length of 1.575 Å, longer than that in cyclobutane, as well as a C-C-H angle of 123-127°

suggesting a high degree of *s* character in the C-H bond concomitant with the high degree of *p* character in the C-C bonds imposed by the 90° bond angle. Molecular mechanics calculations have been used extensively to predict enthalpies of formation, strain energies, and geometries of organic compounds, including some of the homocubane series.[20] Cuneane (**6**) is another very highly strained molecule like cubane; this substance is stable, not decomposing substantially below 180 °C.[21]

Not surprisingly, there exist a large collection of small rings whose strain is due to the presence of multiple bonds. The following is a brief discussion on the origin of strain in alkenes, alkynes (small ring size alkynes are included in more detail in the second chapter of this thesis), and cycloalkenynes. Cumulenes have been omitted here, as they are the major focus of the next section.

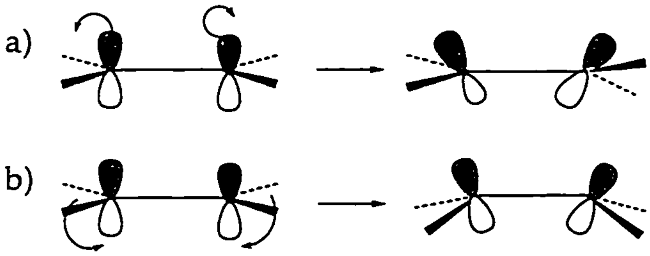
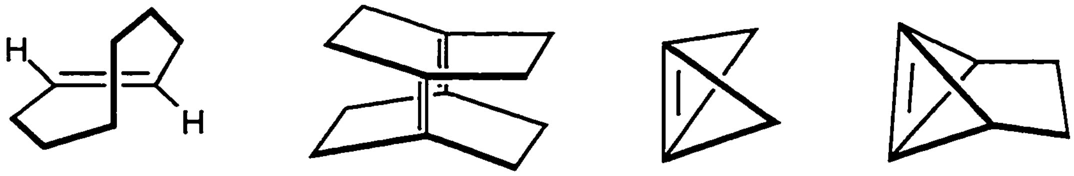


Figure 3. π-Orbital distortions caused by (a) twisting and (b) bending.

The first type of distortion in an alkene is created when the framework exerts a twisting action of the π–bond, thereby rotating the p-orbitals in opposite directions (Figure 3a).[5cd] The second type of distortion is one in which the π-bond is bent and the olefinic carbons become pyramidalized (Figure 3b).[22] Distortion of the first type is exemplified by the incorporation of a *trans*-double bond into a ring. *Trans*-cyclooctene (7) represents the smallest isolable *trans*-cycloalkene (Figure 4).[23] The strain energy (SE) in 7 is ~ 16.5 kcal/mol, some 11 kcal/mol less stable than its *cis*-isomer, and a dihedral angle across the trans-C–C=C–C unit is 136°. As the ring size is decreased in the series, the twisting angle increases, and the vinyl carbons become pyramidalized.[22] The strain energies of the lower *trans*-cycloalkenes are such that *trans*-cycloheptene and *trans*-phenylcyclohexene exist only as reactive intermediates.[24,25] Recently, our group has published a computational study on conformational analysis for *trans*-cyclohexene.[26]



7 **8** **9** **10**

Figure 4. Miscellaneous strained cycloalkenes.

Other π–bond deformations include in-plane bending, such as occurs in small rings, and pyramidalization.[5a,22] Pyramidalization of a trigonal center next to a tetrahedral center is caused by the tendency to minimize torsional strain.[22] In this deformation, attached ligands are not coplanar with the π bonds, and the result is significant rehybridization toward sp^3.[22] X-ray structural analysis of diene **8** shows a pyramidalization angle of 27.3°.[27] Other representative examples of pyramidalized olefins, are **9** and **10**, which have been of particular theoretical interest.[28] *Ab initio* studies on **9** and **10**, at the MP2/6-31G* level, and subsequent vibrational analysis indicated that both structures represent local energy minima on the C_4H_4 and the C_6H_6 energy hypersurface respectively,[28b] with a π bond distance C1-C6 in **10** of 1.390 Å. Olefinic strain (OS)[29] for **9** and **10** have been estimated to be 58.7 and 66.8 kcal/mol respectively.[30] These values indicate that **9** and **10** are highly destabilized molecules that are not expected to persist at room temperature, Their existence has been only proven by trapping experiments.[28,30]

Special efforts have been directed toward the discovery of small ring cycloalkynes (Figure 5).[31] An undistorted triple bond requires four linearly arranged carbon atoms. The incorporation of such an undistorted functionality into a ring system can only be achieved if the ring size is large enough. Otherwise, strain is introduced into the molecule with the consequences that bond angles and bond lengths differ from their "normal"

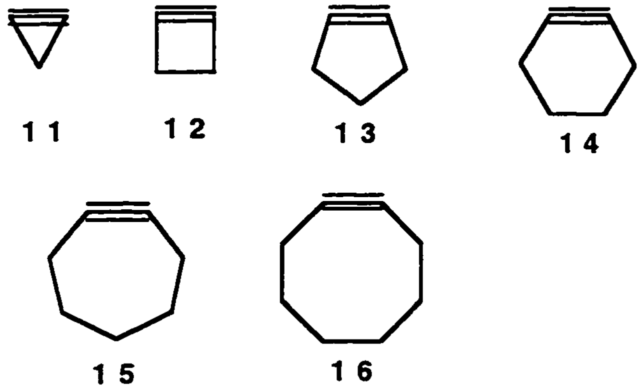


Figure 5. Cycloalkyne series

values in an unstrained compound.

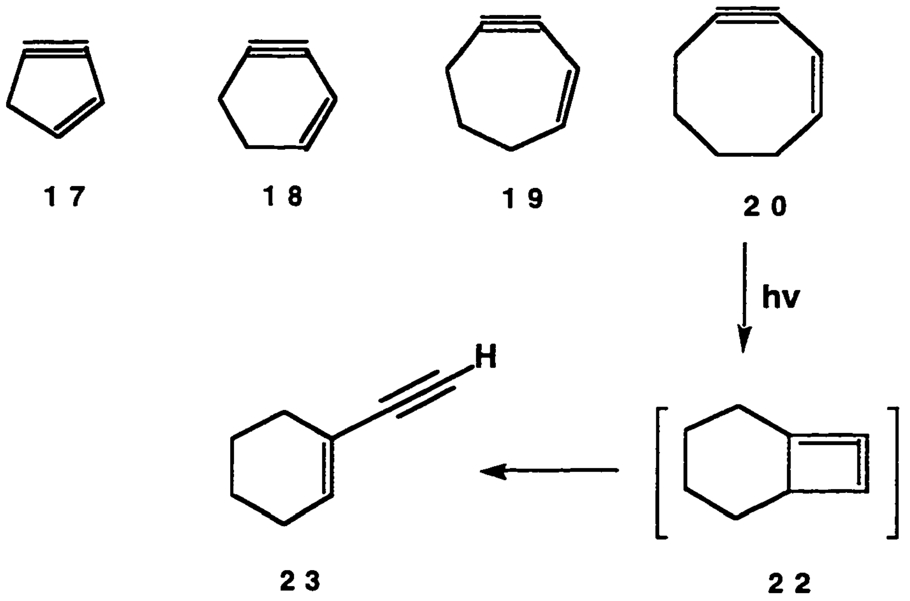
A. T. Blomquist (1953) reported the first synthesis of cyclooctyne (**16**), the smallest isolable unsubstituted cycloalkyne.[32] Part of the strain in **16** is attributable to the weak π bond in this molecule.[5e] As the groups attached to an acetylenic linkage are deformed from their preferred linear arrangement, the initial degeneracy of the two perpendicular orbitals is lost. While one π bond remains essentially normal, the other becomes higher in energy;[5e] π-bond strain in **16** is about 10 kcal/mol.[33] In the subsequent years the short-lived intermediates, cycloheptyne (**15**), cyclohexyne (**14**) and cyclopentyne (**13**) were trapped by G. Wittig and A. Krebs.[34] Cyclohexyne (**14**) has been observed in an argon matrix and its IR has been recorded.[35] The intermediacy of this transient species has been inferred through isolation of oligomers, cycloaddition, and organometallic products.[36]

The smallest cycloalkyne whose existence has been unequivocally demonstrated is cyclopentyne (**13**).[34,37] Experimental studies on cyclobutyne (**12**) and its derivatives have proved to be inconclusive.[37b,38] Recently, our group has published a complete *ab initio* study for interconversion of small ring cycloalkynes **11-14** and their corresponding cycloalkylidenecarbenes.[39] These results provide estimates of the total strain energies and π-bond strain energies for small rings cycloalkynes. According to the calculations, **12** is predicted to exist in a very shallow minimum and it will rearrange with little or no barrier to cyclopropylidenecarbene.[39] A quite unexpected result in this study was that "cyclobutyne and cyclopropyne have π-bond strain energies only slightly greater than cyclopentyne." This apparent anomaly has been explained in terms of a limit to the strain possible for in-plane bending in alkynes, which should correspond to the π-bond strength of 76 kcal/mol.[39] Thus, in cyclopentyne, the structure is already approaching the maximum strain available in the π-bond, and so with **11** and **12**, only modest additional increases in strain are possible. In cyclopropyne, the π-bond is effectively broken (Figure 6). These results are in agreement with previous calculations that predicted stability only for the triplet state of **11**.[40] The predicted MP2 vibrational frequency of cyclobutyne, 1693 cm^{-1} , is only slightly above that for a double bond.

21

Figure 6. Biradical character for the in-plane π-bond of cyclopropyne.

In the case of strained cyclic enynes, limitations of structure and isolability roughly mimic those of the parent cycloalkyne. The eight ring homologue **20** (Figure 7) is the smallest cyclic enyne that is stable at ambient temperature.[41] As in the case of cyclooctyne, part of the strain is attributed to the weak π-bond in this molecule. Distortions of the triple bond caused by



17 18 19 20 23 22

Figure 7. Strained cyclic enynes.

twisting and/or in-plane bending, lower the π-overlap, and the bond energy is decreased. Enyne **20** undergoes a photochemical rearrangement to a 6-membered ring (Figure 7).[42] A potential intermediate in the reaction pathway is 1,2-cyclobutadiene structure **22**.[43] The overall reaction bears strong resemblance to the Bergman rearrangement of enediynes.[44]

Redefinition of the structural limitations for cycloenynes was accomplished by Shakespeare and Johnson with the synthesis and trapping of cyclohexen-3-yne (**18**), the smallest cyclic enyne known to date.[45] Cycloenyne **18** is also of particular interest as this represents an isomer of benzene. Cycloenyne **17** has eluded synthesis, but presumably can be made.

The final source of strain in any molecule to be discussed here is bond stretching or compression deformation from the "equilibrium" bond length. It is clear that bond stretching or compression is expensive in terms of energy: To stretch or compress a C-C bond by 10 ppm (0.1 Å) costs 3.2 kcal/mol.[46] This is presumably the reason for the general near constancy of bond distances. The bond stretching is assumed to follow Hooke's law. Thus, each type of bond has a preferred length and force constant. Some of the structures presented above e.g., **2**, **4** and **5**, are examples of molecules for which bond length deformation engenders considerable strain energy.

STRAINED CYCLIC BUTATRIENES

Introduction to Butatrienes

Cumulenes are a broad class of organic compounds containing two or more successive double bonds.[47] The archetype cumulated hydrocarbons are allenes (**24**), butatrienes (**25**) and higher cumulenes (**26**) (Figure 8). Cis-trans isomerism exists in cumulenes with an odd number of double bonds. When the number of double bonds is even, as in allenes, etc., enantiomeric structures can exist. In a "strain free" allene the two planes of the π bonds attached to the central carbon must be orthogonal (Figure 9a). The synthesis and characterization of allenes has been an area of extensive research in organic chemistry, and several reviews and monographs are available.[48]

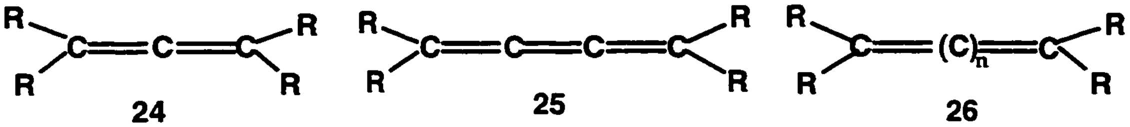


Figure 8. Cumulenes

In contrast, less is known about the structure and reactivity of butatrienes and higher cumulenes. The largest known acyclic cumulenes with an odd number of double bonds, octaheptaenes ([7] cumulenes), and decanonaenes ([9]cumulenes) polymerize with extreme ease and are only fleetingly stable in dilute solution.[49]

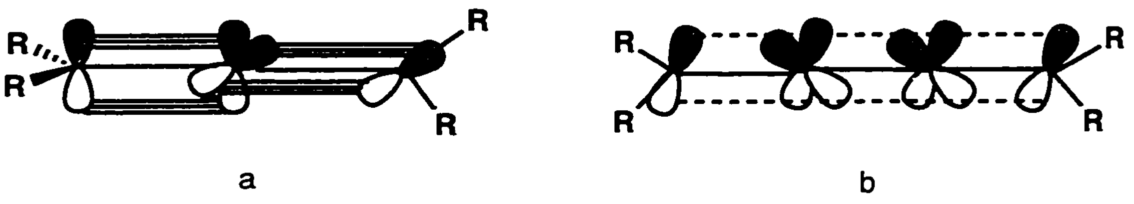
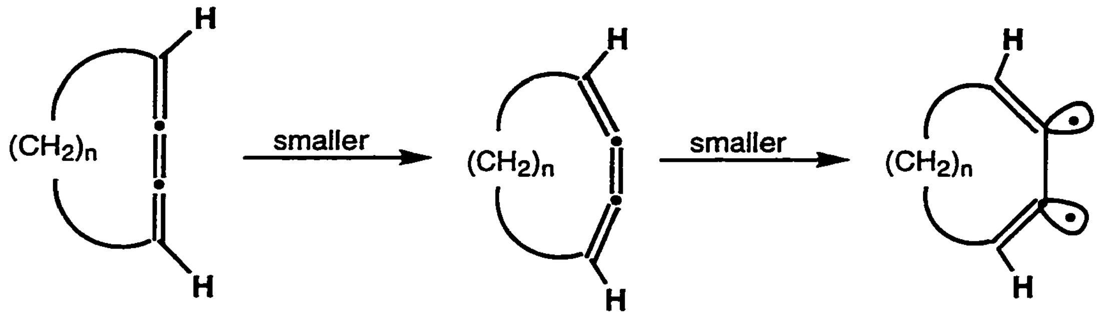


Figure 9. Orbital overlap for a) allenes; b) butatrienes.

The three cumulated double bonds in acyclic butatriene compounds constitute an interesting structural system, containing adjacent C=C bonds of different type, i.e. a central sp-sp bond and two terminal sp-sp^2 bonds (Figure 9b). The successive planes of the π bonds are orthogonal to each other with the four carbon in a preferred linear arrangement. Gundersen and coworkers have recently reported the experimental gas-phase electron diffraction bond distances for tetramethylbutratriene (**25**, R = CH_3, Figure 8) and the corresponding calculated MP2/6-31G* values, along with the vibrational frequencies.[50] The experimental value for the C_1-C_2 bond distance is 1.330 Å and for the C_2-C_3 bond this is 1.271 Å. The calculated values found were 1.331 Å and 1.274 Å respectively. The "normal" values for C=C stretching in the IR spectrum, and the high frequency counterpart are found at 1661 and 2064 cm^{-1}.

For cyclic butatrienes, molecular models suggest that the butatriene linkage can be included in only ten-membered or larger rings without severe distortions (Scheme 1). The energetic consequences of bending in 1,2,3-

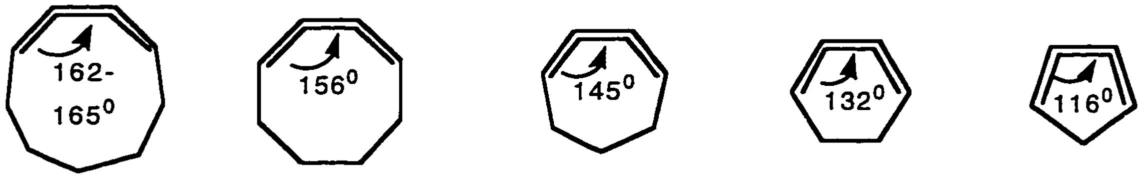
butatriene are modest for the first 10 to 20° of the bending, but rise steeply



Scheme 1

beyond this point. Therefore, the increased strain in cyclic butatrienes is due principally to in-plane bending of the central C_2-C_3 π-bond away from linearity. Bending will be accompanied by rehybridization (Scheme 1) at C_2 and C_3 from sp towards sp^2. Small ring butatrienes show a parallel behavior between strain and kinetic stability. The first estimates of the total strain energies for the series (Figure 10) were reported by Angus and Johnson, who employed semiempirical MNDO theory.[51] Strain values of 8.0, 14.0, 31.5, 60.5, and 130 kcal/mol, were predicted for **28-32**, respectively. The data indicate an approximate doubling of the strain for each subsequent removal of a methylene group. Recently our group has estimated strain energies using *ab initio* methods with electron correlation.[52] The different levels of theory are in agreement. These results will be discussed later in this section. The

MNDO values for the internal C_1-C_2-C_3 bond angles decrease from 163° to

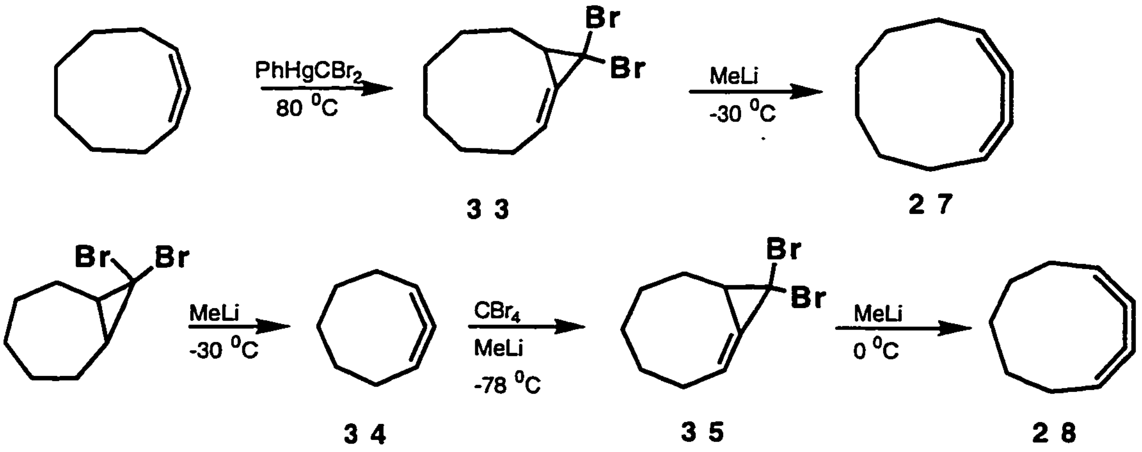


28 **29** **30** **31** **32**

Figure 10. MNDO Bending angles of cyclic butatrienes

116° in going down the series (Figure 10).

Synthesis of cyclic butatrienes have been accomplished through various routes. Moore and Ozretich reported the synthesis of 1,2,3-cyclodecatriene (**27**) in 1967 (Scheme 2).[53] The authors employed a protocol used in allene syntheses.[54] Methyllithium promoted ring expansion of dibromoadduct **33** yielded triene **27**. This butatriene was reported to be a



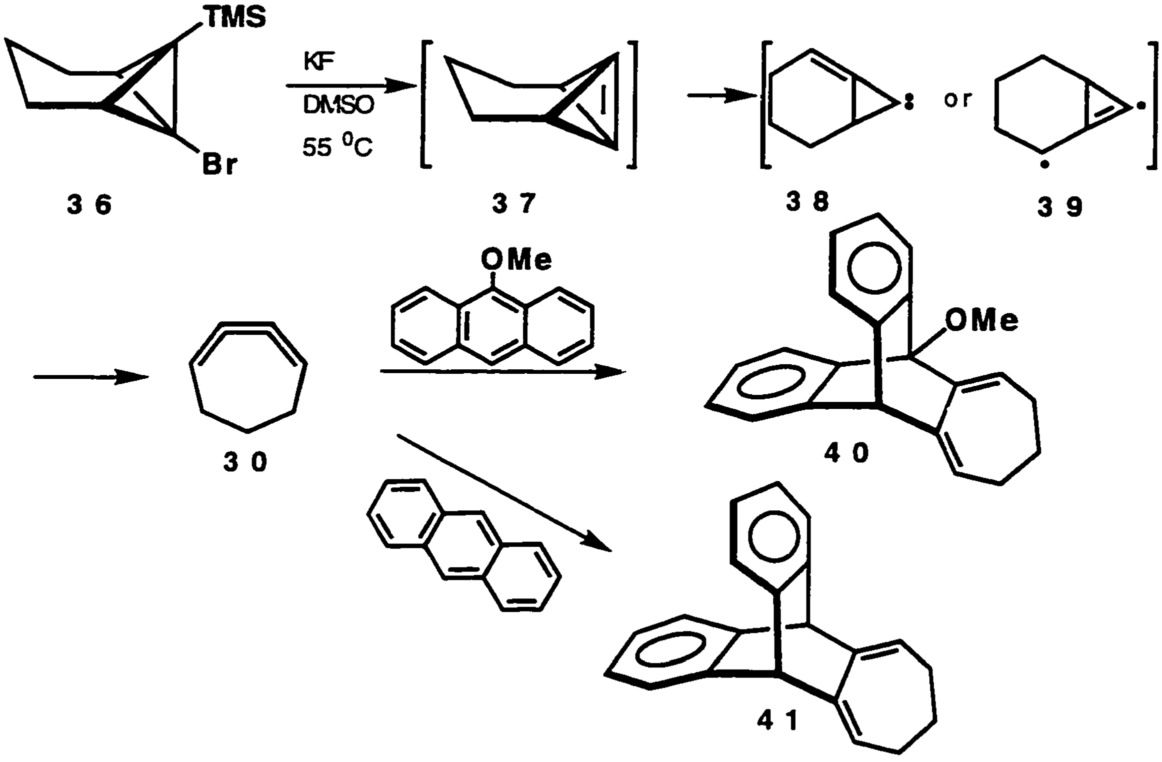
Scheme 2

stable substance, which easily polymerized when not in solution.

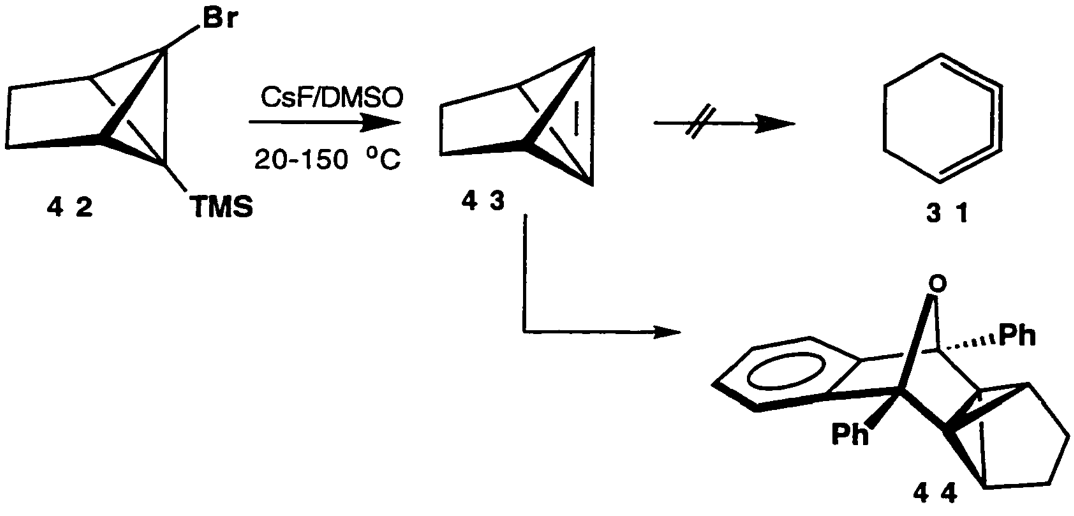
In 1984, Johnson and Angus reported the preparation of 1,2,3-cyclononatriene (**28**) through similar chemistry (Scheme 2).[51] Generation of allene **34** at -30 °C, followed by addition of dibromocarbene yielded **35**, which ring opened to **28** when treated with methyllithium at low temperature (Scheme 2). Butatriene **28** proved to be stable at ambient temperature in dilute solution, but rapidly polymerized upon concentration or exposure to air. 1,2,3-Cyclooctatriene (**29**) was prepared for the first time in our laboratory by Kirchhoff in 1993, but its existence and kinetic stability were not completely supported.[55]

Szeimies *et at.* reported the truly remarkable synthesis of the next member of the series, 1,2,3-cycloheptatriene (**30**) (Scheme 3).[56] Treatment of **36** with KF in DMSO at 55 °C yielded triene **30** which was trapped by 9-methoxyanthracene and anthracene to give adducts **40** and **41** respectively. To explain these results, the authors proposed a thermal isomerization of bicyclobutene **37** to triene **30**, possibly through a carbene pathway. Further characterization of **30** was accomplished by formation of its dimer in the presence of Nickel catalyst.[57]

In view of the preceding results, Szeimies attempted, without success to synthesize 1,2,3-cyclohexatriene (**31**) (Scheme 4). Treatment of **42** with cesium fluoride in the presence of diphenylisobenzofuran, in the temperature range of 20-150 °C, afforded only the corresponding Diels Alder



Scheme 3



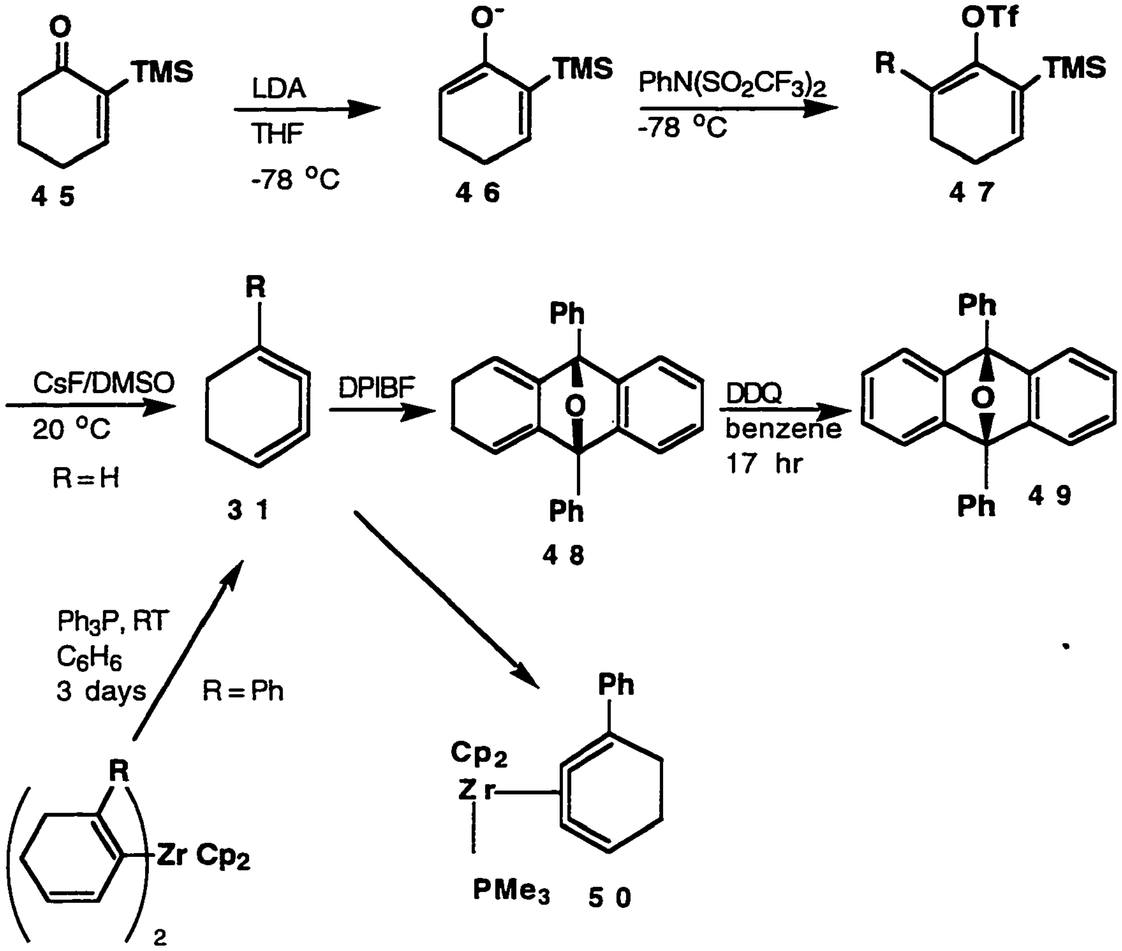
Scheme 4

adduct of **43**.[58] The authors noted that the rearrangement of **37** to **30** is considerably much more exothermic than that of **43** to triene **31**, an observation consistent with the total strain estimates for **30** and **31** which predict that **31** is near twice as strained as **30**.[51,59]

In 1990, Johnson and Shakepeare reported the synthesis and trapping of **31** (R = H), the smallest parent *cumulated hydrocarbon* ever characterized, and which also represented a new isomer of benzene (Scheme 5).[45] This synthesis employed a new route developed in our group. The key intermediate in the sequence is triflate **47** which is formed by kinetic deprotonation of enone **45** with LDA, followed by quenching with N-phenyltriflimide. β-Elimination promoted by fluoride-ion in DMSO yielded **31**, which was trapped by diphenylizobensofuran (DPIBF) and furan. Oxidation of **48** afforded the fully aromatic structure **49**.

Jones *et al.* have prepared the transition complex **50** by elimination reaction on a zirconocene δ complex (Scheme 5).[60] The X-ray crystal structure of **50** shows a nonplanar 1,2,3-cyclohexatriene with internal bond angles of 122.4° and 120.8°. Not surprisingly, the authors noted that these two bond angles are virtually identical to the corresponding zirconocene complex of benzyne.[60]

Paquette has demonstrated the synthetic utility of cumulene **31** (R = H) as a synthon of 1,3-cyclohexadiene.[61] There have been no reports on



Scheme 5

the synthesis of the next member in the series, 1,2,3-cyclopentatriene (**32**).

From the preceding discussion, it is clear that fundamental questions about kinetic stability limitations, and structural limitations for cyclic butatrienes have yet to be answered. 1,2,3-Cyclononatriene (**28**) is stable in solution, and 1,2,3-cyclohexatriene (**31**) is a reactive intermediate. Thus, one goal of this project was to prepare 1,2,3-cyclooctatriene (**29**). The objectives for synthesizing **29** were two-fold. Our primary objective was to confirm and prove its existence by trapping experiments. Second, we wished to demonstrate its isolability. A closely related goal of this study was to redefine the current known structural limitations of the homologous series by generating a 1,2,3-cyclopentatriene. The third fundamental goal was the development of a general synthetic methodology that would allow access to cyclic butatrienes independent of the ring size, based on the fact that routes to cyclic butatrienes are sparse. Such a methodology would render cumulenes readily available and increase their use as reactive intermediates in synthesis.

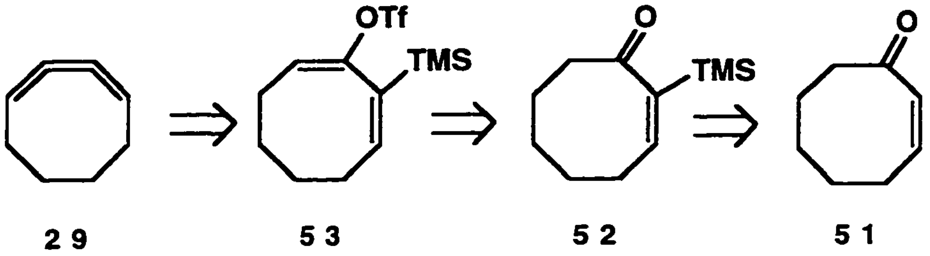
Results and Discussion

Redefining Isolability Limit for Cyclic Butatrienes

Experimental Studies

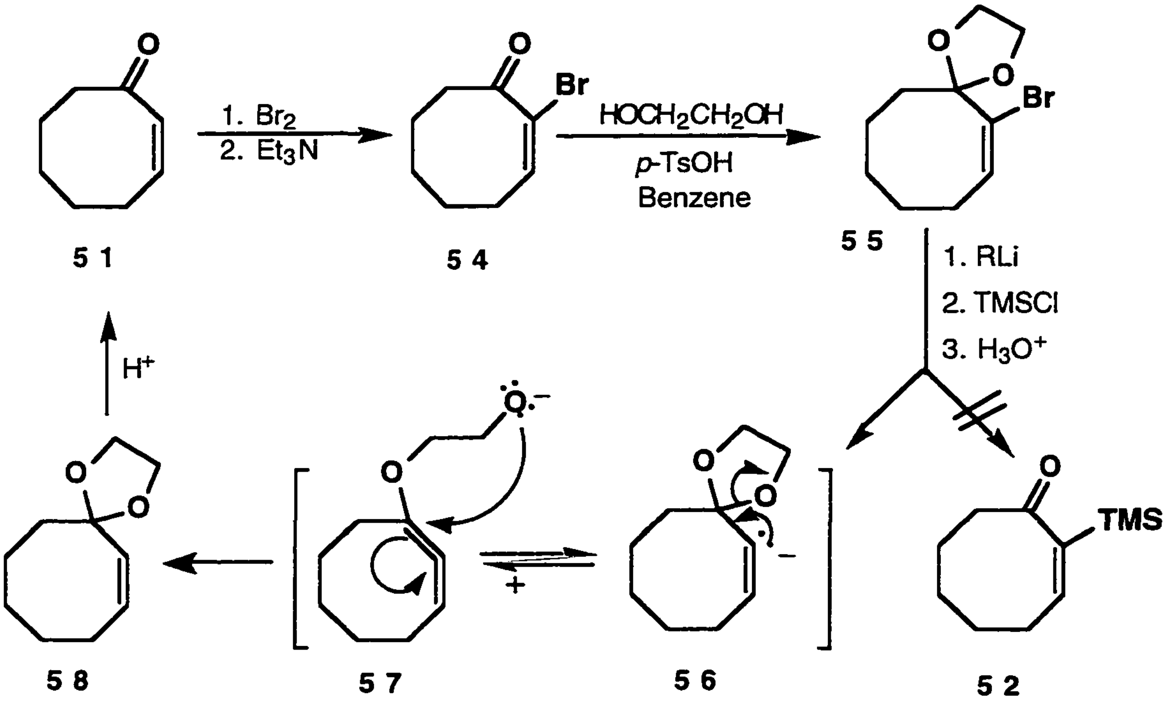
Synthesis and Trapping of 1,2,3-Cyclooctatriene (29)

The synthesis of 1,2,3-cyclooctatriene was first investigated by Swartz.[62] In accordance with methodology previously described for the synthesis of 1,2,3-cyclohexatriene, substituted triflate **53** was viewed as the logical progenitor to 1,2,3-cyclooctriene (**29**). Retrosynthetically (Scheme 6), **53** could be prepared from TMS-enone **52** which might be synthesized from the corresponding ketone **51**. Swartz's work (Scheme 7), proceeded smoothly, until treatment of the protected enone **54** with alkyllithium reagents,



Scheme 6

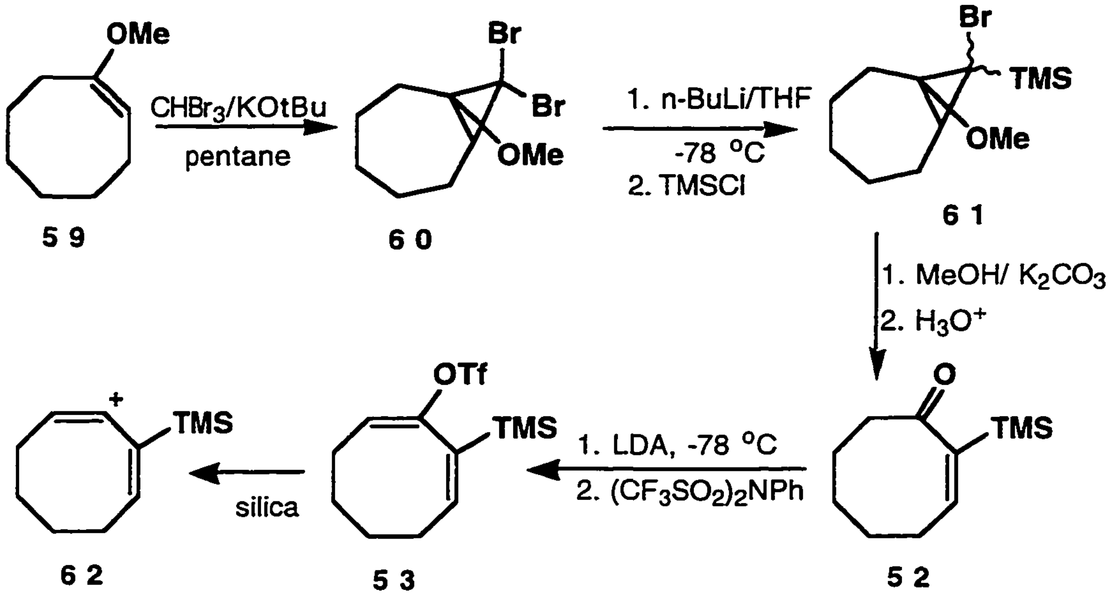
followed by quenching with TMSCl, did not give the expected product. Degradation of the starting bromoenone ketal to enone **51** and ketal **58**, in a 1:1 ratio, was observed. This result was unexpected in view of previous success of this reaction in smaller rings, but formation of **51** and **58** was



Scheme 7

explained in terms of rearrangement of the initially formed anion **56** to an allene, accompanied by ring opening of the ethylene ketal (Scheme 7).[63]

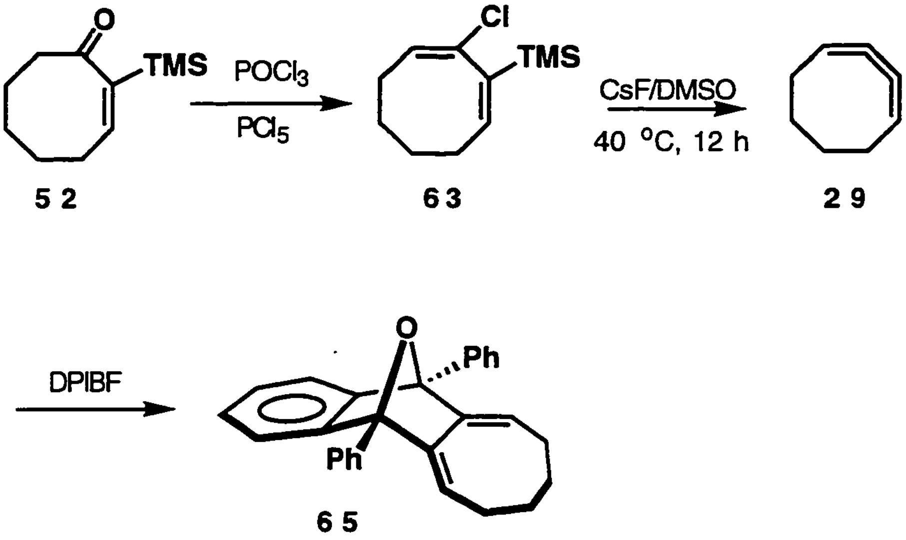
An alternate silation route to TMS-enone **52** employed by Swartz is outlined in Scheme 8. This method was reported by Morizawa and coworkers for the preparation of smaller ring analogs.[64] Although slightly longer, this route gave 40% of the desired product **52**. The final step to vinyl triflate **53** was accomplished by kinetic deprotonation of **52** with LDA, and quenching of



Scheme 8

the enol anion with N-phenyl triflimide. However, both Swartz,[62] and subsequent experiments of Kirchhoff,[55] demonstrated the extreme fragility of **53**. Swartz and Kirchhoff agreed that the observed decomposition of **53** on silica, was consistent with Hannack and Lamparter's solvolytic studies on small ring size vinyl triflates.[65] The authors believe that eight-membered ring vinyl triflates solvolyze faster, since they are flexible enough to permit stabilization of the vacant p-orbital of the vinyl cation, through interaction with the allylic double bond.[65] According to Kirchhoff, reaction of impure samples of **53** with CsF in the presence of diphenylisobenzofuran did not yield evidences for 1,2,3-cylooctatriene.[55]

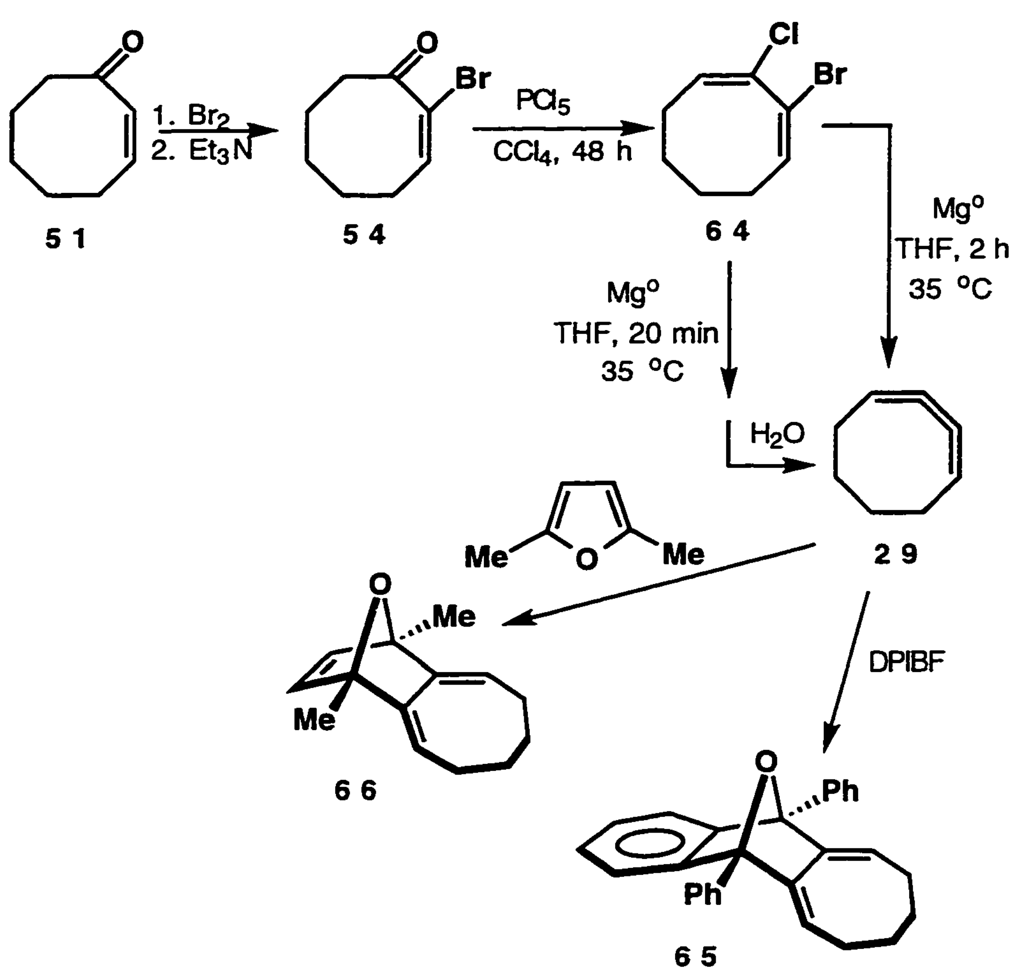
The decomposition of **53** on silica suggested that a stable precursor to triene **29**, had to be one with a less labile group than triflate. Kirchhoff was able to prepare precursor **63** from enone **52** by the Axelrad procedure in 24% yield.[55]



Scheme 9

Treatment of diene **63** with CsF/DMSO in the presence of diphenylisobenzofuran for 37 hours at room temperature, and additional stirring for 12 h at 40 °C, successfully yielded 1,2,3-cyclooctatriene adduct **65** (3.3 mg, 7.3%) which was isolated as a pale yellow solid.[55]

Having identified the appropriate leaving group to generate triene **29**, we turned our attention in the present work to improving the yield of the elimination step. It became apparent that bromochloro diene **64** (Scheme 10) might generate such compounds readily. The synthesis of **64** was then undertaken. Enone **51** was prepared according to the procedure of House[66] and brominated in a similar manner to that described by Dipascuo, to yield bromoenone **54** in 83% yield (Scheme 10).[67] Reaction of **54** with a suspension of PCl_5 in CCl_4 for 48 h, at room temperature,[68] afforded the desired 1,3-diene **64** in 5.1% yield, following purification by chromatography (silica gel, hexane). Treatment of **64** with magnesium in THF at 35 °C, in the presence of DPIBF, for 2 hours yielded 1,2,3-cyclooctatriene adduct **65** which was isolated by prepartive TLC as a pale yellow solid in 49% yield. Spectral data for **65** include a triplet at δ 5.65 (AA′ part of an AA′MM′NN′XX′YY′ system), a symmetrical multiplet at δ 2.22, (MM′NN′ part), and a multiplet at δ 1.60-1.63, (XX′YY′ part) in the ^1H NMR, 12 resonances (C_s symmetry) in the ^{13}C NMR, and a molecular ion peak (M^+) of *m/z* 376 in the mass spectrum. Spectral data were compared with Kirchhoff's results.[55]



Scheme 10

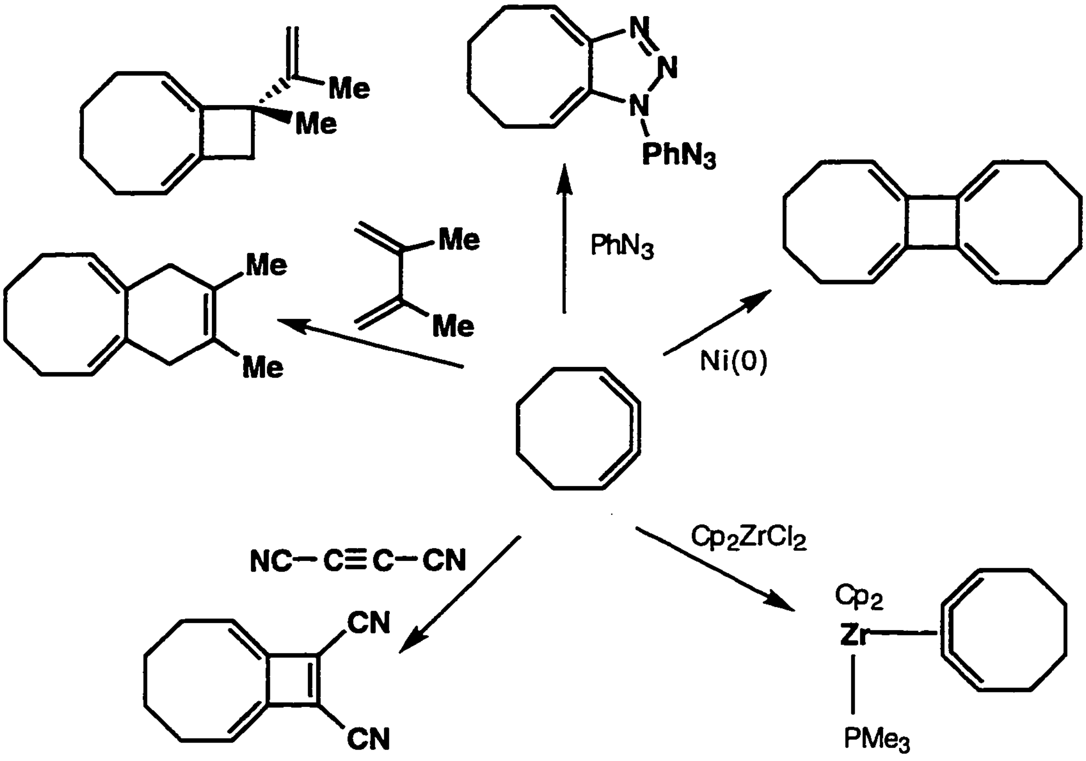
Generation of **29** in the presence of 2,5-dimethyl furan resulted in the sole isolation of adduct **66** as a yellow oil in 14% yield after flash chromatography (silica gel, 5% Et_2O, hexane) (Scheme 10). Spectral data for **66** included a singlet at δ 6.12, a triplet at δ 5.53 (AA′ part of an AA′MM′NN′XX′YY′ system), a symmetrical multiplet at δ 2.29 (MM′NN′ part), a symmetrical multiplet at δ 1.69 (XX′YY′ part), and a singlet for the methyl groups at δ 1.60 in the ^{1}H NMR, 7 resonances (C_s symmetry) in the ^{13}C NMR, and a molecular ion peak (M^+) of *m/z* 203 in the mass spectrum, consistent with a molecular formula of $C_{14}H_{18}O$.

A control experiment was performed in which diene **64** was treated with magnesium in THF at 35 °C in the absence of DPIBF. After 20 min, the mixture was quenched with water to ensure that no Grignard reagent remained. Immediate addition of 1 equivalent of DPIBF resulted in a 15% yield of adduct **65** (Scheme 10).

In conclusion, experimental results are consistent with a $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition[53,56] of butatriene **29** at its most strained π bond to diphenylisobenzofuran, and 2,5-dimethyl furan to form Diels Alder cycloadducts **65** and **66**, respectively. The exclusive reaction at the C_2-C_3 bond is in agreement with the relief of modest total strain of ca. 17.7 kcal/mol, most of which is due to in-plane bending of the butatriene unit. Strain in butatriene **29** was assessed by *ab initio* calculations, and will be further discussed later in this chapter.

The control experiment is also consistent with the intermediacy of cumulene **29**, and suggests *moderate kinetic stability* of triene **29** in solution. However, further experiments are necessary to prove unambiguously that 1,2,3-cyclooctatriene redefines the isolability borderline for cyclic butatrienes.

To date, cumulene **29** has been trapped only with dienes in $[_{\pi}2_s + _{\pi}4_s]$

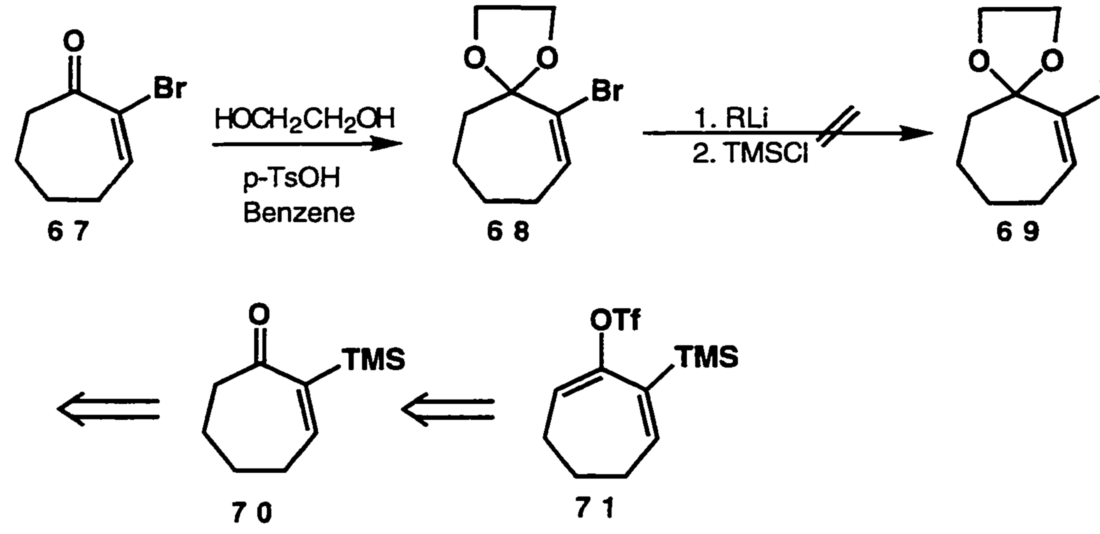


Scheme 11. Potential reactions of 1,2,3-cyclooctatriene.

cycloaddition reactions. To completely characterize the chemistry of **29**, its generation in the presence of acyclic dienes, alkynes,[69] and dipolar species[70] must be accomplished (Scheme 11). Jones and coworkers[60] have reported the synthesis of zirconocene complexes of a 1,2,3-cyclohexatriene. Through similar methods, it would be of interest to trap **29** with transition metals as this might yield a photolytic precursor, and might serve to "store" the butatriene. Additionally, it has been demonstrated that dimerization of cyclic butatrienes is facilitated by the presence of metal catalysts such nickel, copper, and zinc.[57,71] Generation of **29** in the presence of a metal catalyst might furnish a [4]radialene or a [6]radialene (Scheme 11).

New Route to 1,2,-3-Cycloheptatriene (30)

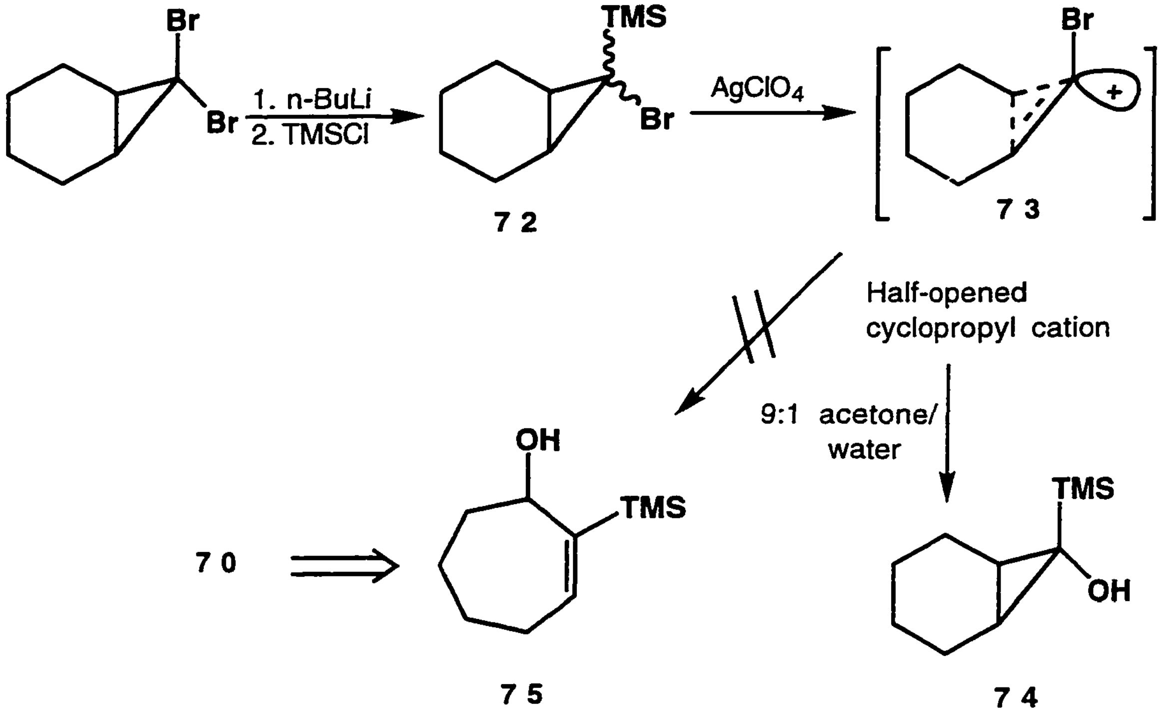
One fundamental goal of this project of perhaps equal importance was the development of what appeared to be a very general route to cyclic butatrienes from the corresponding enone.[45] Preliminary work by Swartz[62] on the synthesis of potential precursors to 1,2,3-cycloheptatriene **30** is outlined in Scheme 12. In the belief that the fluoride-induced elimination method employed by Shakespeare to generate 1,2,3-cyclohexatriene (**31**) would permit a mild, general route to cyclic butatrienes, Swartz set out to synthesize TMS-enone **70**, the expected precursor to the key vinyl triflate **71**.[45] Silation of the



Scheme 12

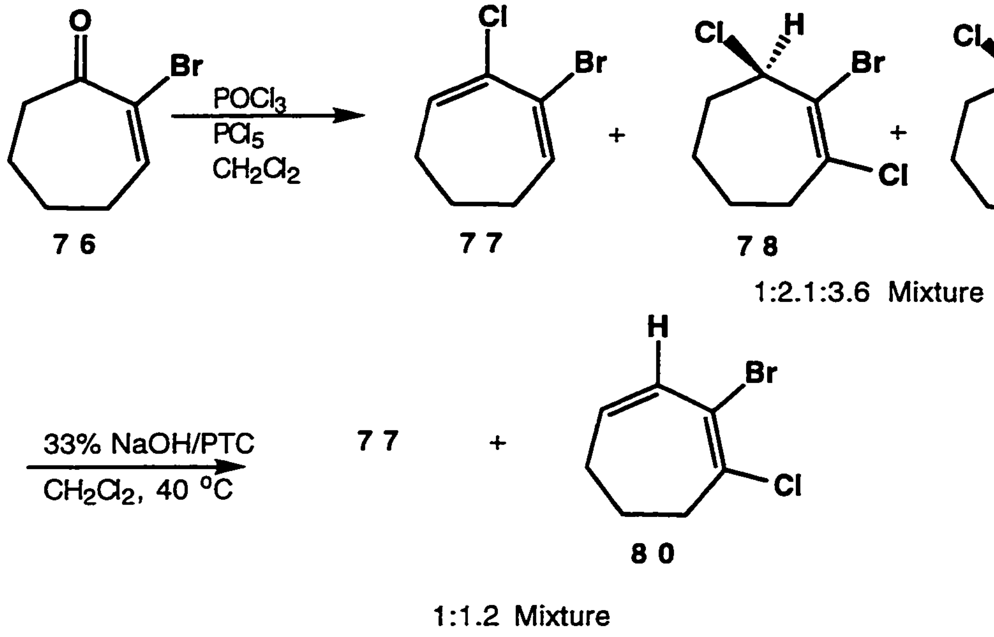
bromoketal **68** was unsuccessful. This resulted in degradation of the starting material, as had been observed for the eight-membered ring bromoketal **55**.[62]

The alternate silation route (Scheme 13) in which formation of the TMS-allyl alcohol **75** was expected, gave instead bicyclic **74** (Scheme 13). The 7-*exo* bromo norcaranyl system lead to a half-opened cyclopropyl cation which was captured by water.[62]



Scheme 13

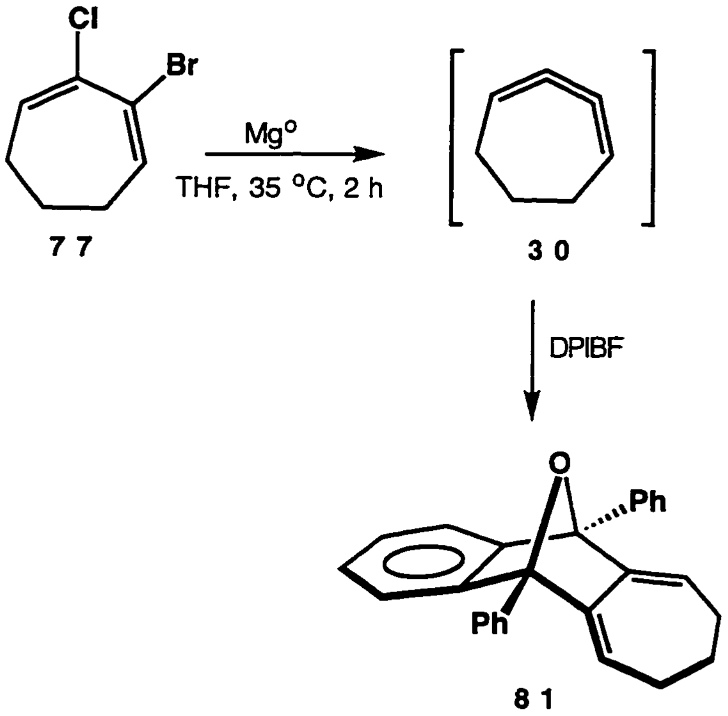
Our earlier work on the synthesis of 1,2,3-cyclooctatriene had demonstrated that magnesium-induced 1,2-elimination on an appropriate substrate, was an alternate pathway to cylic butatrienes. Thus, a similar reaction sequence for the preparation of triene **30** was investigated (Scheme 14). Bromoenone **76** was prepared according to the literature procedure in 95% yield.[72] Treatment of **76** with equimolar amounts of $POCl_3$ and PCl_5 in CH_2Cl_2 [73] resulted in the formation of vinyl chloride **77**, vinyl chloride **78** and



Scheme 14

dichloride **79** in 1:2.1:3.6 ratio, respectively. 1,2-Elimination and 1,4-elimination were induced with 30% NaOH and a phase transfer catalyst (PTC), to afford 1:1.2 mixture of the desired diene **77**, and 3-bromo-2-chloro-1,3-diene **80** in 22% overall yield (Scheme 14). Pure samples of **77** and **80** were isolated by preparative GC (Scheme 14). Spectral data for **77** included two triplets at δ 6.66 and δ 6.44 in the ^1H NMR, seven resonances in the ^{13}C NMR, and a molecular ion peak (M^+) of *m/z* 206 in the mass spectrum.

The conversion of diene **77** to 1,2,3-cycloheptatriene (**30**) followed the same protocol for β-elimination used in the synthesis of 1,2,3-cyclooctatriene. Treatment of **77** (Scheme 15) with magnesium in THF for 2 hours at 35 °C in the presence of DPIBF, yielded 1,2,3-cyloheptatriene cycloadduct **81** which was isolated by preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) as a bright yellow solid in 44% yield. Spectral data for **81** included a triplet at δ 5.86 (AA' part of an AA'MM'NN'XY system), two symmetrical multiplets at δ 2.22, (MM'NN' part), and 1.73 (XX'YY' part) in the ^1H NMR, and 12 resonances (C_s symmetry) in the ^{13}C NMR. Chemical shifts were compared with Szeimies's results.[56]



Scheme 15

Literature precedent indicates that diene **77** undergoes magnesium-promoted dehalogenation to form 1,2,3-cycloheptatriene (**30**) which is trapped in a $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition with diphenylisobenzofuran.[38,53,56] Relief of twice as much strain as that in triene **29**, ca. 32 kcal/mol, results in the exclusive cycloaddition reaction at the C_2-C_3 bond.

In summary, we have found that magnesium-promoted dehalogenation of vinyl halides provides access to cyclic butatrienes. The method demonstrates its synthetic utility by formation of two novel cyclic butatrienes: 1,2,3-cyclooctatriene and 1,2,3-cycloheptatriene. The reaction proceeds readily under mild conditions, reasonable amount of time, and requires a very simple experimental procedure. However, the poor yields in the preparation of the vinyl halide precursors are a major drawback.

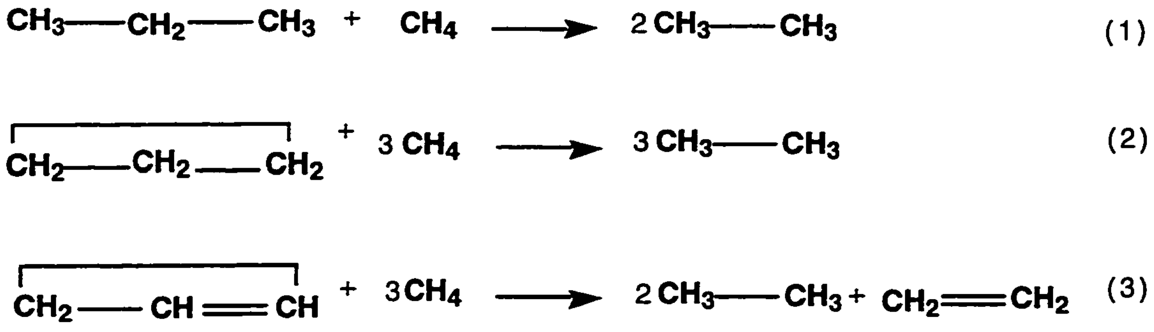
Theoretical Studies

Introduction This part of the chapter reviews briefly the isodesmic[9] and homodesmic[10] reactions, two methods that provide an alternate basis for evaluating strain energies of cyclic hydrocarbons. The results obtained from application of these reaction to estimate total strain and strain in the central π bond in small-ring size butatrienes, are also included. The concept of bond additivity[5e] is described at the beginning for completeness.

Homodesmic and Isodesmic Reaction.

Molecules may be hierarchically recognized[5e] as collections (1) of atoms, e.g., C and H; (2) of bonds, e.g., C-C, C=C and C-H; (3) of groups or "superatoms," e.g., CH_3-, -CH_2- , -CH< and >C<; or (4) of rings, e.g., a "C_3 ring." The first member of the hierarchy is the traditional basis of chemistry. It is tacitly assumed that the numbers and types of atoms are unchanged in any given reaction (excepting studies in nuclear chemistry).[5e] The second member of the hierarchy is the basis of the method of bond energies, i.e., of bond additivity schemes. The model describes cyclopropane as composed of three C-C bonds and six C-H bonds. If cyclopropane were to lack any stabilization or destabilization, then the total bond energy (the atomization energy) would equal the sum of the individual bond energies. A major ambiguity of bond additivity schemes arises from the seeming absence of unique bond energies e.g., C-H, C-C, and C=C.[5e] For example, the C-H bond strength in methane exceeds that of propene (104 vs. 85 kcal/mol) because the allyl radical that is produced by bond dissociation is stabilized by resonance.[74]

From the point of view of thermochemistry[8] the energies of isodesmic reactions measure deviation from additivity of bond energies. First introduced by Hehre and Pople in the 70's, isodesmic reactions are examples of chemical changes in which there is a retention of the number of bonds of a



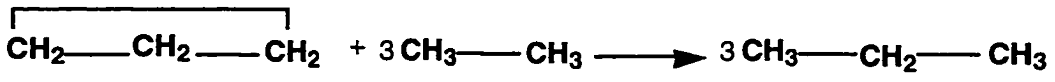
Scheme 16

given formal type (single, double, triple), but with a change in their structural relationship (Scheme 16).[9]

The hydrocarbons methane, ethane or other appropriate homologues simply serve to establish a reference level from which to measure the overall destabilization of the ring.[9] For example, reactions (2) and (3) can be used as a basis for defining and evaluating the strain energy of cyclopropane and cyclopropene rings respectively.[8] The experimental strain energy (SE), identified as the enthalpy change in the reactions, is obtained from ΔH^{o}_{f} data on the reacting molecules, and the corresponding theoretical strain energy, defined as the difference in total energy of reactants and products, is obtained from calculations of the ground state energy of the reacting molecules. This procedure is different from that of Newton and Schulman,[8] whose definition of ring strain involves a hypothetical strain free reference molecule. The isodesmic reaction formulation, which involves no hypothetical structures having averaged group energies or particular bond energy assignments, treats ring strain as a parameter for a real reaction, thus facilitating an unambiguous comparison of theory an experiment. However, these particular isodesmic reactions involve quite profound changes in the nature of the C-H and C-C bonds. For example, in reaction (2) it is necessary to convert the six secondary C-H bonds in cyclopropane and the twelve unique C-H bonds in three methane molecules into primary C-H bonds in ethane.

There is another more conceptually satisfying, bond-energy scheme that assesses the strain energy of ring systems: homodesmic reactions. Introduced by George *et al* [8] in the middle 70's, these reactions match, a) the number of each type of C-C bonds in their various states of hybridization in reactants and products as closely as possible, and b) the number of C atoms with zero, one, two, and three hydrogen atoms attached in reactants and product. Matching in this way minimizes extraneous energy contributions.[10]

For example, cyclopropane can, in principle, react with ethane to yield propane (Scheme 17). All the C atoms are sp^2 hybridized, and the C-H bonds are matched in that there are equal numbers of C atoms with two and three H atoms attached.[8]



$$\overline{CH_2—CH_2—CH_2} + 3\,CH_3—CH_3 \longrightarrow 3\,CH_3—CH_2—CH_3 \quad (4)$$

Scheme 17

It is clearly more appropriate to base measurements and calculations of the total strain energy of the cyclopropane ring on reaction (4) rather than reaction (2), since reaction (2) requires additional changes in binding energy which are unrelated to the strain in the cyclopropane. While homodesmic reactions may be regarded as a special case of isodesmic reactions, the additional matching of hybridization and bonding characteristics puts them in a class of their own.[10] All homodesmic reactions are isodesmic, but few isodesmic reactions are homodesmic.

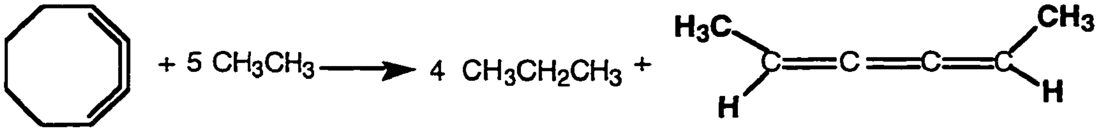
Does it mean that isodesmic reactions are not very useful? Of course not! Literature precedent supports[9,10] that these reactions serve as useful and meaningful bond-energy schemes in many cases depending on the specifics of the estimate. In the present study we have adapted isodesmic reactions to estimate strain energy in the in-plane π bond in small ring size butatrienes, and homodesmic reactions to evaluate total strain energy.

Computational Method

All the structures included in the present study were fully geometry optimized using a 3-21G basis set at the restricted Hartree-Fock (RHF) level.[75] Energies at the stationary points were calculated using MP2/6-31G* theory.[76]

Strain Estimates for 1,2,3-Cyclooctatriene

The homodesmic reaction (5), designed to estimate the total strain in butatriene **29** is shown in Scheme 18. Table 1 shows the calculated *ab initio* total energies for the reacting molecules, obtained according with the method described earlier. The reaction relates the strained cyclic butatriene with the acyclic butatriene structure. Thus, the absolute enthalpy change of 17.7 kcal/mol, corresponds to the total strain energy in **29**.



(5)

2 9

Homodesmic Estimate of Total Strain energy in **29**. $\Delta H_R = -17.7$ kcal/mol

Scheme 18

Table 1. *Ab initio* total energies for selected structures. Homodesmic reaction (5).

Total Energies (hartrees)		
1,2,3-Cyclooctatriene (**29**)	E(HF)[a]	= - 308.64152
	E(MP2)[b]	= - 309.66518
Ethane	E(HF)	= - 79.22860
	E(MP2)	= - 79.49429
Propane	E(HF)	= - 118.26339
	E(MP2)	= - 118.65963
cis-Dimethyl-1,2,3-butatriene	E(HF)	= - 231.76893
	E(MP2)	= - 232.52632

[a] HF = HF/6-31G*//HF/3-21G
[b] MP2 = MP2/6-31G*//HF/3-21G

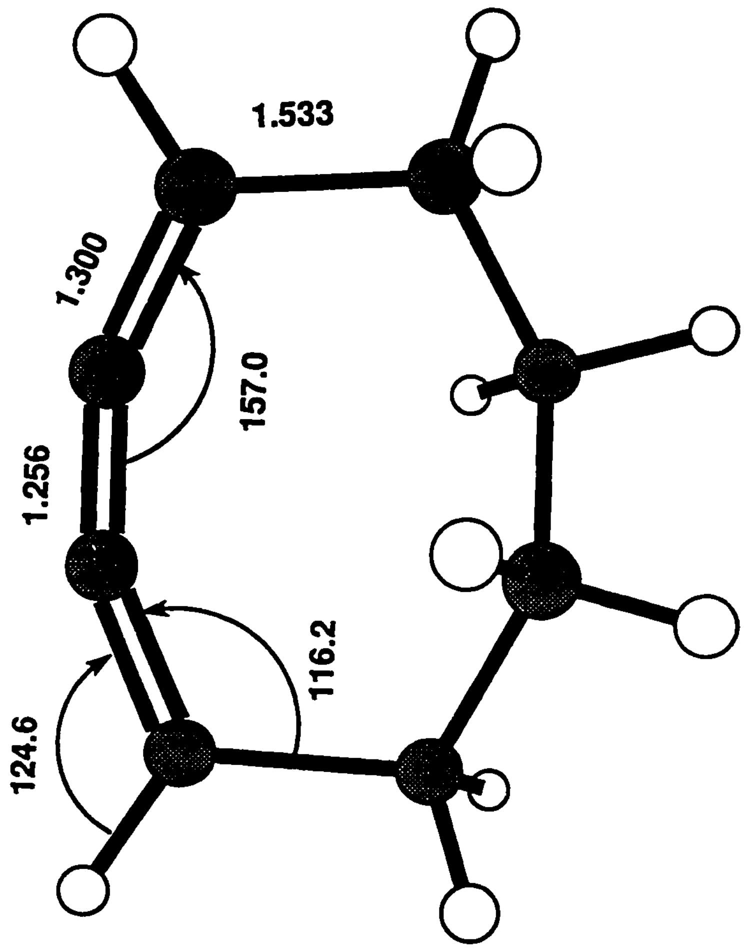
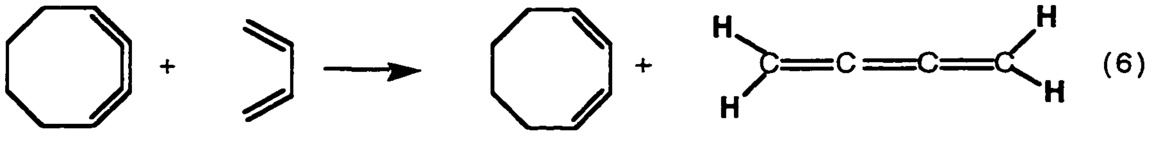


Figure 11. HF/3-21G Optimized 1,2,3-Cyclooctatriene

Figure **11** shows the optimized structure, which has C_2 symmetry. The butatriene unit is predicted to be nearly planar but is bent about 23.0° from linearity. Thus, *ab initio* predictions for total strain, and the in-plane bending angle in **29**, are in good agreement with previous semiempirical calculations carried out by Angus and Johnson[51] who estimated a total strain of 14 kcal/mol and a bending angle of 23.7°.

Strain in the butatriene central π bond was estimated from the isodesmic reaction (6) (Scheme 19). This reaction effectively trades the strained π C_2-C_3 bond for a similar unstrained π bond in the acyclic



2 9

Isodesmic Estimate of Butatriene Unit Strain Energy ΔH_R = -12.4 kcal/mol

Scheme 19

butatriene, while leaving the C_1-C_2 and C_3-C_4 π bonds minimally changed. The calculated value is 12.4 kcal/mol, and corresponds to 70% of the total strain in the molecule. Both estimates indicate only modest levels of strain, most of which is attributable to the weak π bonds in **29**. This clearly is due to poor orbital overlap caused by in-plane bending distortion of the central π

Table 2. *Ab initio* total energies for selected structures. Isodesmic reaction (6).

	Total Energies (hartrees)
1,2,3-Cyclooctatriene (**29**)	E(HF)[a] = - 308.64152
	E(MP2)[b] = - 309.66518
1,3-Butadiene- gauche conformer	E(HF) = - 154.91473
	E(MP2) = - 155.41647
1,3-Cyclooctadiene	E(HF) = - 309.89210
	E(MP2) = - 310.91726
1,2,3-Butatriene	E(HF) = - 153.69005
	E(MP2) = - 154.18409

[a] HF = HF/6-31G*//HF/3-21G

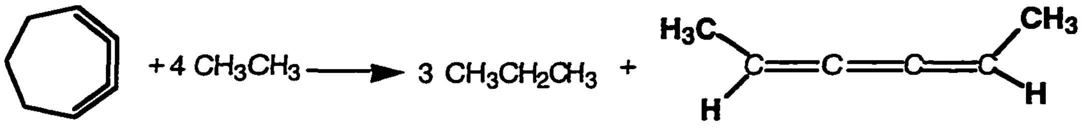
[b] MP2 = MP2/6-31G*//HF/3-21G

bond. It is worth noting (Table 2) that the reaction includes the gauche conformation of 1,3-butadiene, since the planar *s-cis* conformation is not a minimum on the energy hypersurface.[77]

Strain Estimates for 1,2,3-Cycloheptatriene (30)

The total strain energy in 1,2,3-cycloheptatriene (**30**) was estimated from the homodesmic reaction (7) (Scheme 20). *Ab initio* total energies for each structure in the reaction are given in Table 3. The absolute value of 31.8 kcal/mol, the enthalpy of reaction, corresponds to the predicted total energy in **30**. As expected, the total strain almost doubles with removal of a methylene unit from the ring.[51]

The optimized C_2 structure for butatriene **30** is shown in Figure 12. The C2-C3 double bond is strongly pyramidalized,[56] which makes it a short-lived



(7)

30

Homodesmic Estimate of Total Strain in **30**. ΔH_R = -31.8 kcal/mol

Scheme 20

Table 3. *Ab initio* total energies for selected structures. Homodesmic reaction (7).

Total Energies (hartrees)		
1,2,3-Cycloheptatriene (**30**)	E(HF)[a]	= - 269.58124
	E(MP2)[b]	= - 270.47736
Ethane	E(HF)	= - 79.22860
	E(MP2)	= - 79.49429
Propane	E(HF)	= - 118.26339
	E(MP2)	= - 118.65963
cis-dimethyl-1,2,3-Butatriene	E(HF)	= - 231.76893
	E(MP2)	= - 232.52632

[a] HF = HF/6-31G*//HF/3-21G

[b] MP2 = MP2/6-31G*//HF/3-21G

intermediate, reacting exclusively at the central π bond, consistent with the experimental observations. The internal bending angle is estimated to be 34.9° away from linearity, in good agreement with previous semiempirical calculations (145.1 vs 140.0°).[51]

The strain energy in the butatriene central π bond was estimated from

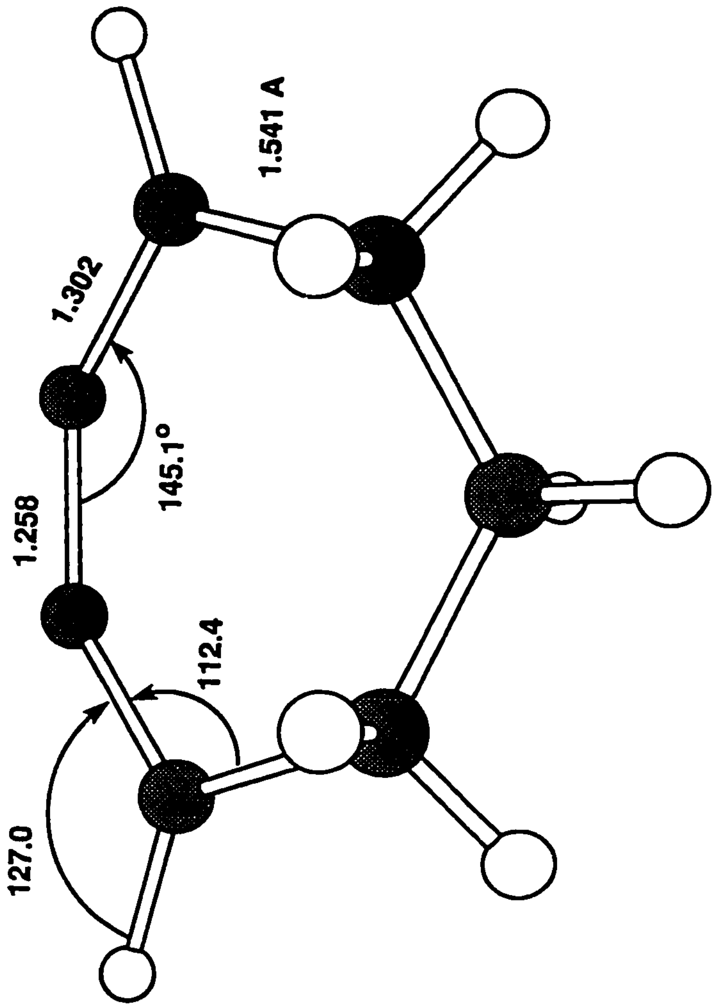
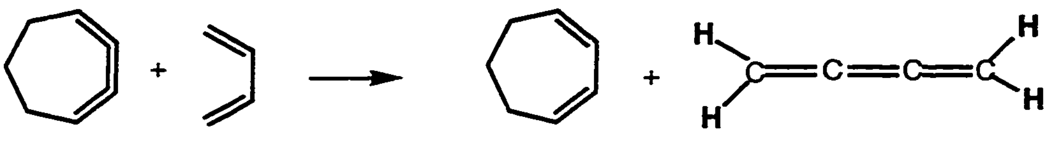


Figure 12. HF/3-21G Optimized 1,2,3-Cycloheptatriene



(8)

3 0

Isodesmic Estimate of Butatriene Unit Strain Energy. $\Delta H_R = -27.0$ kcal/mol

Scheme 21

Table 4. *Ab initio* total energies for selected structures. Isodesmic reaction (8).

Total Energies (hartrees)		
1,2,3-Cycloheptatriene (**30**)	E(HF)[a]	= - 269.58124
	E(MP2)[b]	= - 270.47736
1,3-Butadiene- gauche conformer	E(HF)	= - 154.91473
	E(MP2)	= - 155.41647
1,3-Cycloheptadiene	E(HF)	= - 270.86231
	E(MP2)	= - 271.75276
1,2,3-Butatriene	E(HF)	= - 153.69005
	E(MP2)	= - 154.18409

[a] HF = HF/6-31G*//HF/3-21G

[b] MP2 = MP2/6-31G*//HF/3-21G

the isodesmic (8) (Scheme 21) to be 27.0 kcal/mol. Not surprisingly, this value corresponds to a contribution of 84.9% to the total strain in the molecule. Table 4 includes *ab initio* total energies for the reacting molecules.

Conclusion

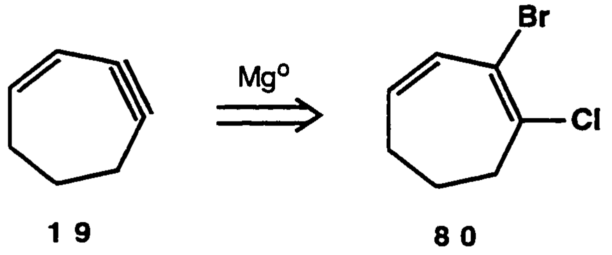
Structures and strain energies for 1,2,3-cyclooctatriene (**29**) and

1,2,3-cycloheptatriene (**30**) have been predicted using MP2/6-31G*//HF/3-21G theory. These results have been used to interpret the observed chemistry of these strained hydrocarbons. In-plane bending of the central π bond is shown to be important in explaining the high reactivity at the C2-C3 bond. We have noted a surprisingly good agreement between semiempirical and *ab initio* estimates.

Cycloenynes

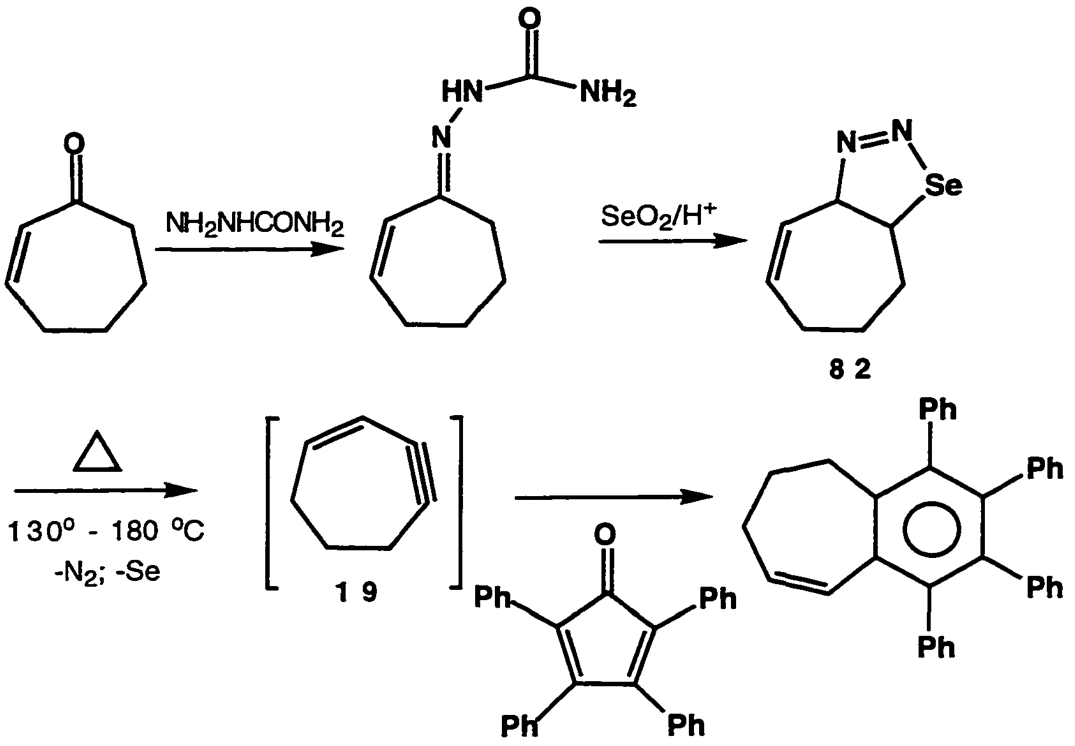
New Route to Cyclohepten-3-yne

In the course of our work on the synthesis of 1,2,3-cycloheptatriene we accidentally prepared 2-bromo-1-chloro-cyclohepta-1,3-diene (**80**), which appeared to be a logical precursor to cyclohepten-3-yne (**19**) (Scheme 22). Although, **19** had been already prepared by Meier from 1,2,3-selenadiazole



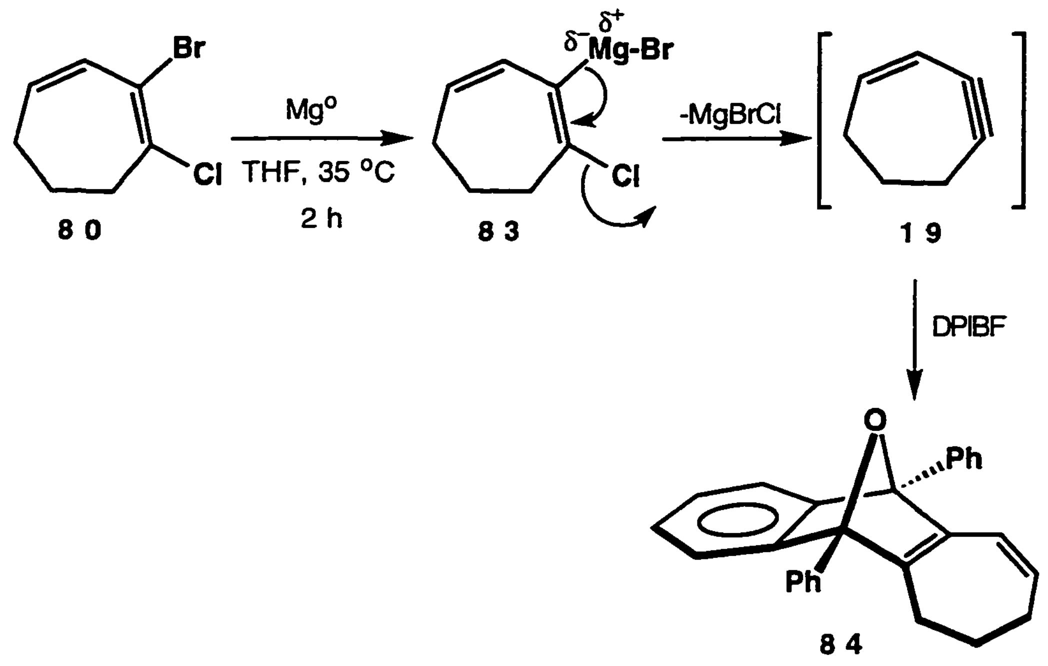
Scheme 22

82 (Scheme 23),[78] it was of interest to generate this novel reactive intermediate from a simple molecular precursor, and under mild conditions.



Scheme 23

The formation of enyne **19** from **80** was carried out in a straightforward manner following the Grignard protocol employed in the synthesis of strained butatrienes, as described above. Diene **80** (Scheme 24) was treated with magnesium in THF at 35 °C, in the presence of DPIBF. After 2 h, the reaction had gone to completion, according to TLC analysis. The cycloadduct **84** was isolated by preparative TLC (silica gel, 3:2 hexane/ CH_2Cl_2) as a bright yellow oil in 24% yield. Spectral data for **84** include a broad doublet at δ 5.95, a



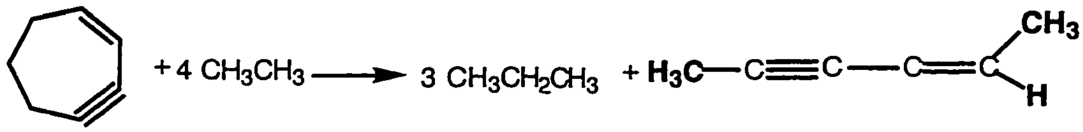
Scheme 24

doublet of triplets at δ 5.75, two multiplets at δ 2.3 and at δ 1.67 in the ^{1}H NMR, 22 resonances in the ^{13}C NMR (C_1 symmetry), a strong UV absorption at 239 nm, which is characteristic of dienes, and a molecular ion peak (M^+) of *m/z* 363, consistent with a molecular formula of $C_{27}H_{23}O$.

Ample literature precedent supports the conclusion that enyne **19** has been formed at the surface of magnesium metal.[34,78] Initial reduction of the carbon-bromine bond (order of reactivity of the halides RI > RBr > RCl) results in formation of the Grignard reagent **83**, which undergoes 1,2-elimination of MgBrCl to give **19**. The cyclic enyne **19** reacts in a $[_{\pi}2_s + {}_{\pi}4_s]$ cycloaddition at its most strained triple bond with diphenylisobenzofuran to relieve substantial strain energy and generate **84**. These results are consistent with the *ab initio* strain energy estimates, which are discussed below. Perhaps of greater significance is the remarkably mild conditions under which this reactive intermediate has been formed and trapped.

Strain Estimate for Cyclohepten-3-yne (19)

Strain energy in enyne **19** was assessed by *ab initio* calculations, using the method describe for cyclic butatrienes. The homodesmic reaction (9) to estimate the total strain energy in **19** is shown in Scheme 25. Total energies



(9)

19

Homodesmic Estimate of Total Strain in **30**. ΔH_R = -30.8 kcal/mol

Scheme 25

for the reacting molecules are included in Table 5. Reaction (9) relates the cyclic enyne to a completely unstrained acyclic enyne structure, matching the number of each type of C-C bonds (sp^2-sp^2, sp^2-sp^3, etc.). Therefore, homodesmic reaction (9) should evaluate total molecular strain in **19**. The absolute enthalpy change of 30.8 kcal/mol corresponds to the calculated total strain energy. Our results are in good agreement with Meier's MNDO calculations[78] for the total energy in cycloocten-3-yne (20.8 kcal/mol), the next

Table 5. *Ab initio* total energies for selected structures. Homodesmic reaction (9).

Total Energies (hartrees)		
1-Cyclohepten-3-yne (C_1 Symmetry)	E(HF)[a]	= - 269.60694
	E(MP2)[b]	= - 270.50163
Ethane	E(HF)	= - 79.22860
	E(MP2)	= - 79.49429
Propane	E(HF)	= - 118.26339
	E(MP2)	= - 118.65963
2-Hexen-4-yne	E(HF)	= - 231.79336
	E(MP2)	= - 232.54904

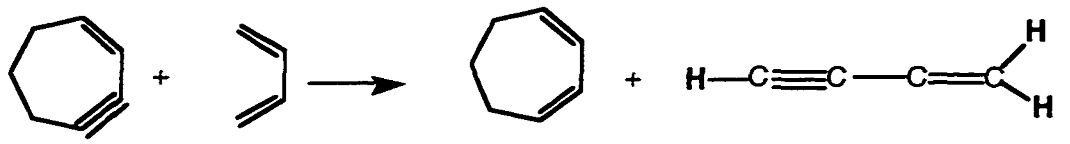
[a] HF = HF/6-31G*//HF/3-21G

[b] MP2 = MP2/6-31G*//HF/3-21G

higher homologue in the series.

The isodesmic reaction (10) (Scheme 26) estimates the triple bond strain in **19**. Table 6 includes the estimated total energies for the reacting molecules. In-plane π triple bond strain in enyne **19** was estimated from reaction (10) to be 23.2 kcal/mol. This strain contributes 75.3% of the total strain energy in the molecule! Nicolaides and Borden reported the strength of the π bond in acetylene to be 76 kcal/mol.[79] Compared with our results, this indicates that the π bond in cyclohepten-3-yne should have a strength of only 52.8 kcal/mol.

The fully optimized C_1 structure of **19** is shown in Figure 13. The angle bending of the triple bond is 37.7°, introducing a significant deformation from linearity.



19

(10)

Isodesmic Estimate of Butatriene Unit Strain Energy. ΔH_R = -23.2 kcal/mol

Scheme 26

Table 6. *Ab initio* total energies for selected structures. Isodesmic reaction (10).

Total Energies (hartrees)		
Cyclohepten-3-yne (C_1 Symmetry)	E(HF)[a]	= - 269.60694
	E(MP2)[b]	= - 270.50163
1,3-Butadiene- gauche conformer	E(HF)	= - 154.91473
	E(MP2)	= - 155.41647
1,3-Cycloheptadiene	E(HF)	= - 270.86231
	E(MP2)	= - 271.75276
2-Buten-4-yne	E(HF)	= - 153.70778
	E(MP2)	= - 154.20234

[a] HF = HF/6-31G*//HF/3-21G

[b] MP2 = MP2/6-31G*//HF/3-21G

In conclusion, the exclusive and exceptional reactivity of cyclohepten-3-yne (**19**) at the triple bond is principally due to a high-energy weak π bond. Since, the force constant[78] for the angle bending at the triple bond is relatively low, a significant part of the deformation in the molecule is localized in these angles, in good agreement with our calculations. The bent triple bond is

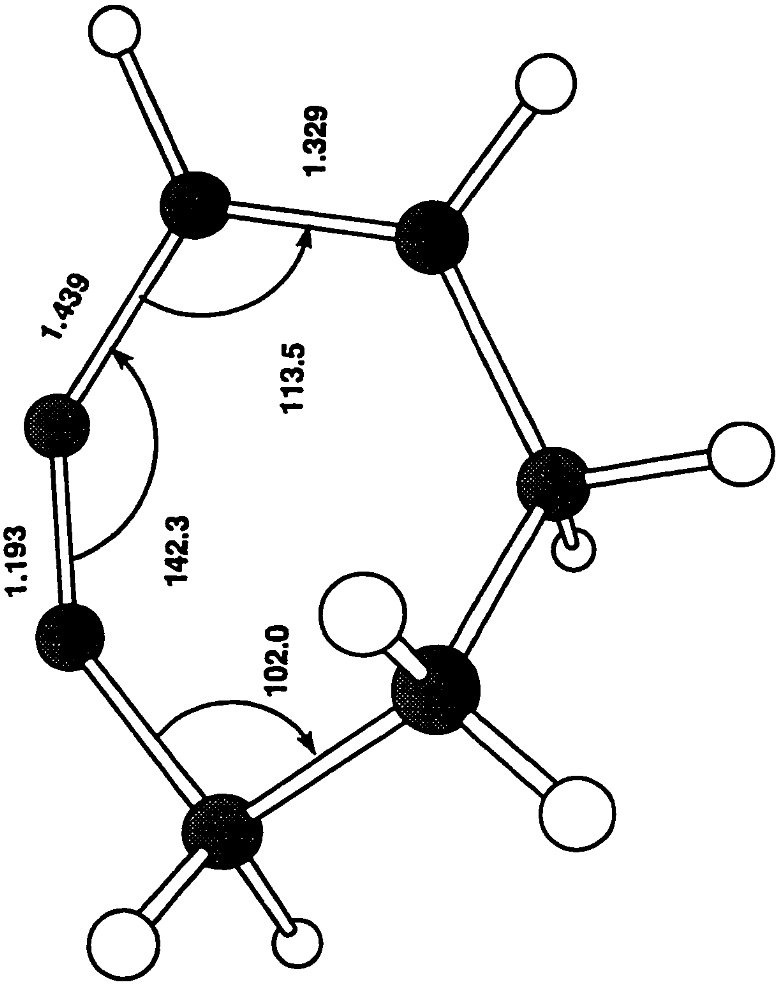


Figure 13. HF/3-21G Optimized Cyclohepten-yne

capable of initiating some unusual chemistry.

Redefining Structural Limitations for Cyclic Butatrienes

Introduction to 1,2,3-Cyclopentatriene

With the successful synthesis of 1,2,3-cyclohexatriene by Shakespeare,[45] the next goal in our group was to generate 1,2,3-cyclopentatriene (**32**). The synthesis of butatriene **32** would not only redefine the current known limitations of cyclic butatrienes, but would also contribute to basic knowledge of structural limitations and chemical reactivity.

Computational studies at various levels of theory have been carried out in our group in order to accurately predict the total strain energy and geometric structure in this highly strained hydrocarbon.[51,59] The total strain energy estimate for 1,2,3-cyclopentatriene (**32**) at the MP4//MP2 level is 79.0 kcal/mol; this is 29.6 kcal/mol higher than the total strain energy in 1,2,3-cyclohexatriene (**31**).[59] The butatriene moiety is predicted to deviate from linearity 15.9° greater than that in **31** (internal angles, 113.9° vs 129.8°). The central π bond is 0.016 Å longer (1.314Å vs 1.298Å) than that in **31**, and 0.057Å longer than the triple bond in cyclopentyne (1.314Å vs 1.257Å). These results indicate that a tremendous deformation is introduced in the molecule by bending the butatriene unit 66.1° away from linearity. Therefore, we should expect butatriene **31** to be a short-lived intermediate, with a very weak in-plane π bond and biradical-like structure.

Can we make and trap 1,2,3-cyclopentatriene (**32**) in solution? The unsubstituted cyclic butatriene **32** should resist synthesis because of the low barrier for [1,5] hydrogen shifts. Activation barriers for 1,5 hydrogen shifts, estimated at the MP2/6-31G* level, are in a range of 0.9 - 10.0 kcal/mol.[80] These thermal rearrangements, being suprafacial, are quite common in cyclopentadienes, and are called *circumambulatory rearrangements*.[81] At the same time, the acidity of the methylene hydrogens (pKa ≈ 15-18) on an unsubstituted diene precursor might also prevent its preparation. Thus, it was proposed that the 5,5-dimethyl derivative **85** (Figure 14) may be more amenable to synthesis. We would expect that the total strain energy and geometric structure in **85** should closely resemble those in the unsubstituted cyclic butatriene (**32**).

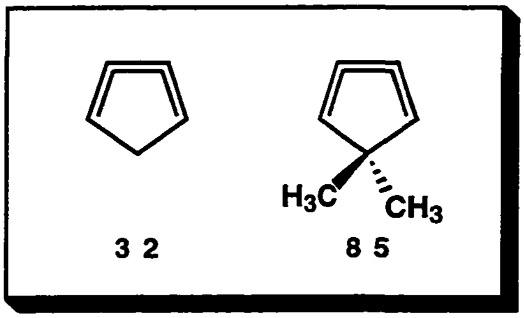


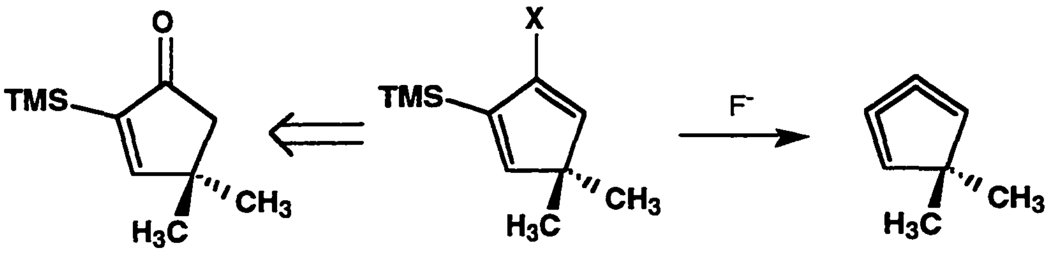
Figure 14. Cyclic 1,2,3-cyclopentatrienes

In order to explore several routes to the potential existence of this "truly extraordinary hydrocarbon," six different potential precursors were prepared, and investigated during the course of this study. Their syntheses, and exploratory chemistry are described below.

Synthesis of Potential Precursors for 5,5-Dimethyl-1,2,3-cyclopentatriene and their Exploratory Reactions

Route 1: Synthesis of 5,5,-Dimethyl-3-trifluoromethanesulfonyl-4-trimethyl silyl-1,3-cyclopentadiene (88) and Reaction with Cesium Fluoride

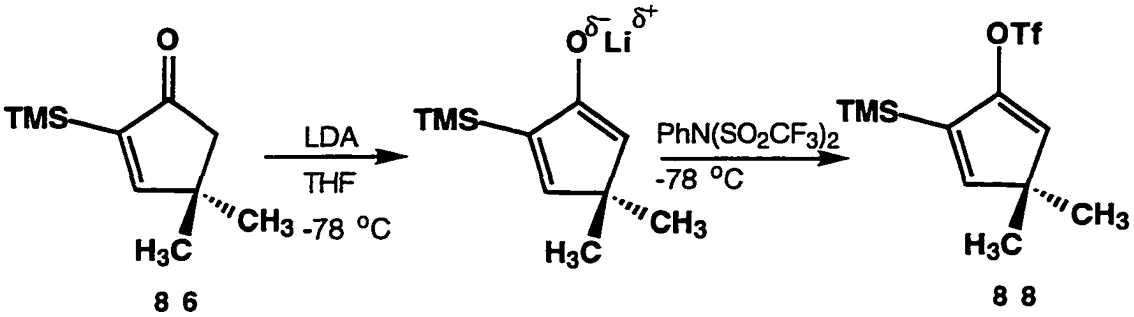
Since a vinylsilane was the key intermediate in the preparation of 1,2,3-cyclohexatriene (**31**),[45] vinylsilane **87** were X is a good leaving group, was viewed as the most logical progenitor of **85** (Scheme 27). As described previously for the synthesis of 1,2,3-cylohexatriene, **85** may be accessible by introduction of the strained π bond through fluoride-ion induced 1,2-elimination[82] of vicinal trimethylsilyl and X groups. We chose this route not only because of the previous results in the synthesis of 1,2,3-cyclohexatriene,



Scheme 27

but because of the very mild conditions under which **85** might be generated.

Earlier work on this approach was carried out carried by Andro who accomplished the first synthesis of vinyltriflate **88** (Scheme 28), and attempted unsuccessfully to generate **85** from this precursor.[83] We were hoping that some variations in the conditions employed by Andro might afford **85**.

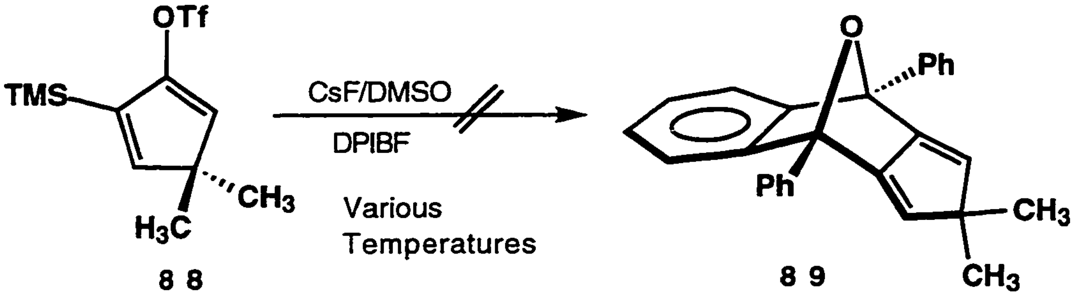


Scheme 28

Following the Andro procedure, the synthesis of diene **88** was straightforward.[83] Deprotonation of TMS-enone **86** (Scheme 28) under kinetic conditions with lithium diisoprolpylamide (LDA), followed by addition of N-phenyltriflimide gave vinyltriflate **88** in 72.5% yield after purification by chromatography (silica gel, hexane). Spectral data for **88** were compared with Andro's results.[83] Diene **88** displays two doublets at δ 6.46 and at δ 6.02 in the ^{1}H NMR and eight resonances in the ^{13}C NMR.

The first attempt at the conversion of diene **88** into 5,5-dimethyl-1,2,3-cyclopentatriene (**85**) followed the desilation protocol employed by

Shakespeare in the preparation of 1,2,3-cyclohexatriene.[45] Reaction of **88** (Scheme 29) with CsF in DMSO at 25 °C, in the presence of DPIBF, gave unreacted starting material. The reaction was conducted at 30 °C and 50 °C. ^{1}H NMR analysis of the crude material indicated that vinyltriflate **88** had been completely consumed; however, there were no vinyl resonances which could result from adduct formation in a $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition.[53,56] Attempts to trap any volatile products failed. Perhaps more disturbing

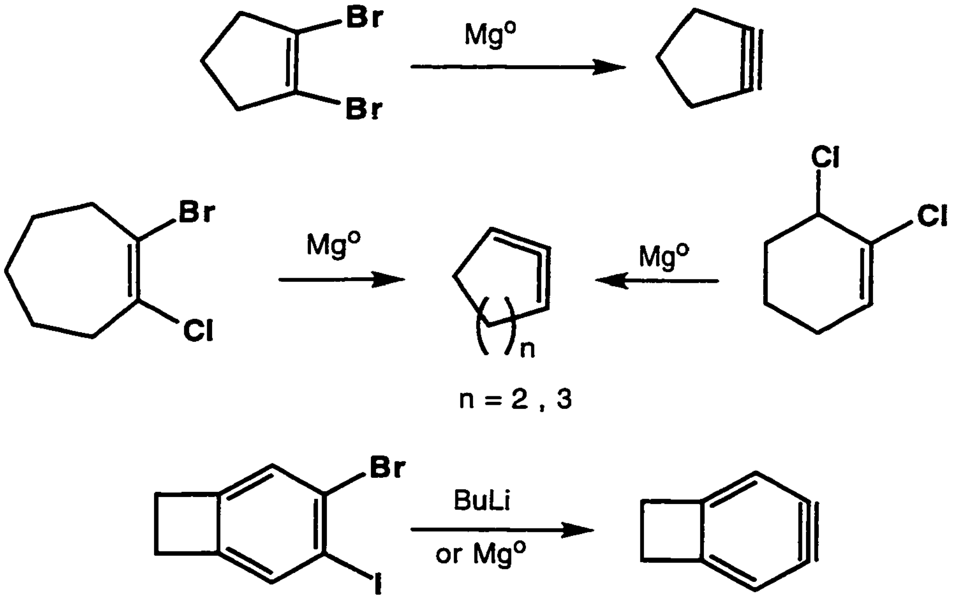


Scheme 29

than our apparent inability to generate 5,5-dimethyl-1,2,3-cyclopentatriene, is the absence of any isolable products suggesting alternative reactions. By ^{1}H NMR analysis, the starting diene **88** was completely consumed; however, it is unclear what is being generated. Attack by fluoride ion on silicon presumably would be accompanied by loss of the triflate group, in accordance with the E2 mechanism.[84] This suggests that butatriene **85** may be initially formed, but does not survive the reaction conditions and undergoes further chemistry.

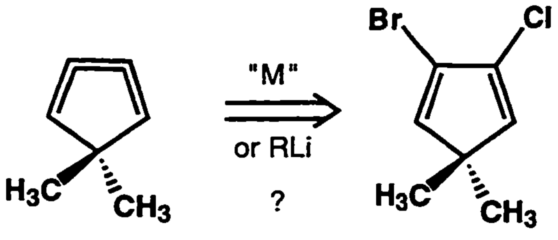
Route 2: Synthesis of 2-Bromo-3-chloro-5,5-dimethyl-1,3-cyclopentadiene (90) and Reaction with Metals

Vicinal dihalides have been recognized historically as useful intermediates in the syntheses of strained cyclic allenes and alkynes through reaction with metals or organolithium reagents.[85] A classic example is the pioneering work of Wittig on the preparation of strained cycloalkynes (Scheme 30).[34] Favorski reported the first attempts to synthesize strained cyclic allenes by reaction of a vinylhalide with magnesium metal (Scheme 30).[85a] The synthesis of cyclobutabenzyne was reported by Vollhardt in 1976



Scheme 30

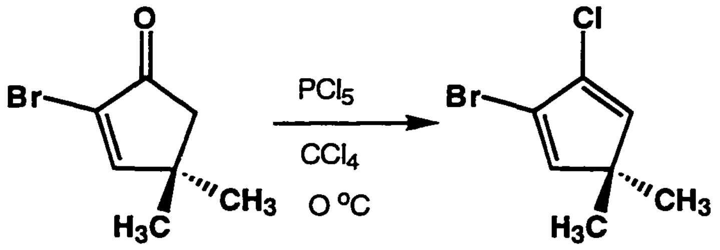
(Scheme 30).[85c] Thus, another logical precursor to butatriene **85** was thought to be diene **90** which may undergo 1,2-elimination of MBrCl or LiCl when treated with a metal or an alkyllithium reagent, leaving behind triene **85** (Scheme 31).



85 **90**

Scheme 31

The synthesis of 2-bromo-3-chlorodiene **90** was accomplished in a single step reaction by treatment of bromoenone **91** with a suspension of PCl_5/CCl_4 at 0 °C (Scheme 32).[68] Diene **90** was the major product of this reaction, and it was isolated in 67% yield after chromatography (silica gel,

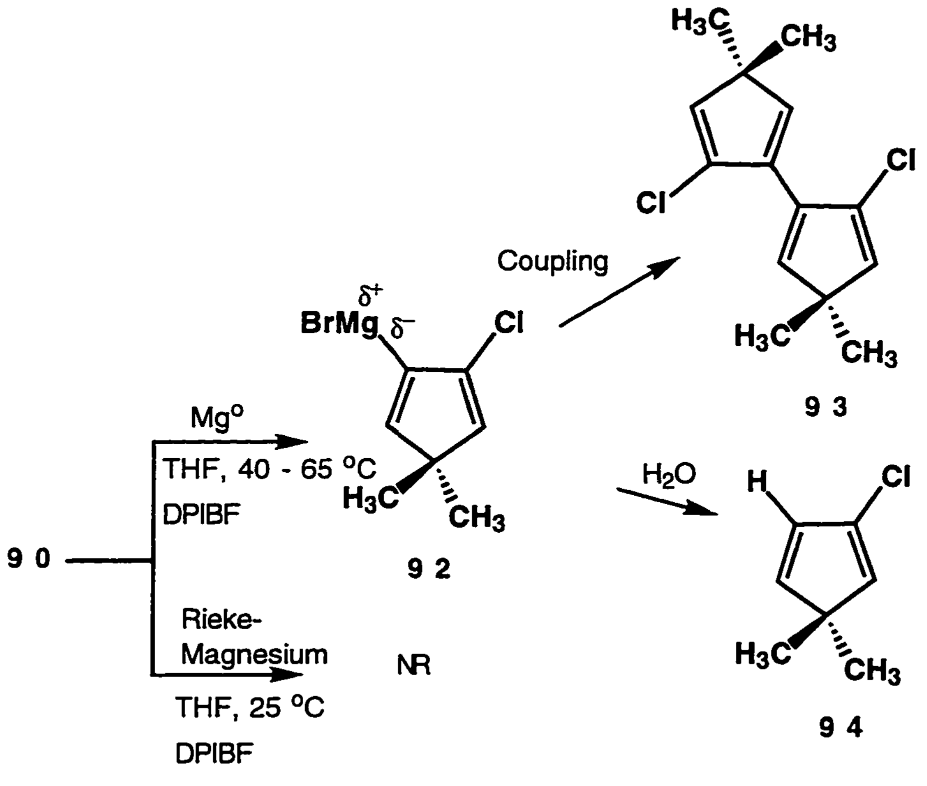


91 **90**

Major product

Scheme 32

hexane). Spectral data for **90** include two doublets at δ 6.40 and at δ 6.18 in the ^{1}H NMR, seven resonances in the ^{13}C NMR, and a molecular ion (M^+) of *m/z* 206 in the mass spectrum. Treatment of **90** (Scheme 33) with mechanically activated magnesium in THF at 40 °C in the presence of DPIBF yielded substances characterized as dimer **93** and **94** in a ratio of 1:1.4. Spectral data for **93** include two doublets at δ 6.57 and at δ 6.20, a singlet at δ 1.21 in the ^{1}H NMR, 3 resonances in the DEPT 135, and a molecular ion peak (M^+) of *m/z* 254 in the mass spectrum. Diene **94** displays three doublets of doublets at

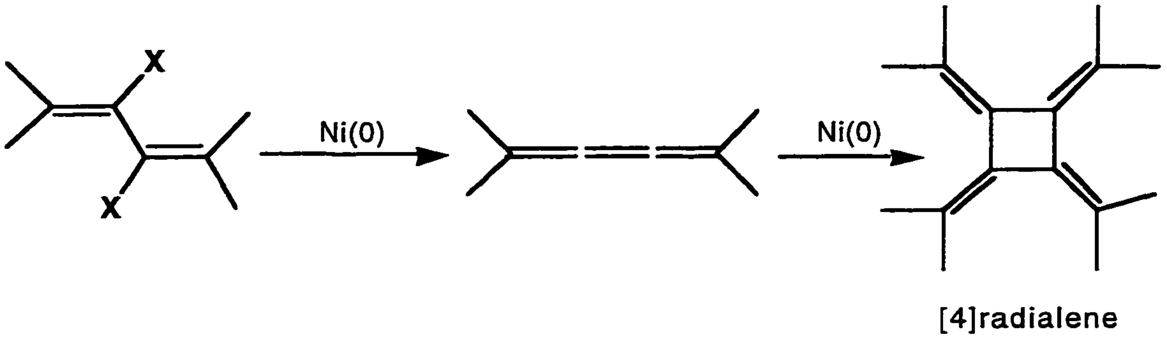


Scheme 33

δ 6.24, δ 6.07 and δ 6.02, and a singlet at δ 1.21 in the ^{1}H NMR. When the reaction was carried out in a more dilute solution at 65 °C, vinylchlorodiene **94** was the only identified product. These two products probably are the result of a well documented Wurtz-type coupling[86] between Grignards to give **93**, or aqueous quenching of the Grignard to give chlorocyclopentadiene **94**. Remarkable stability of some vinyl Grignards have been observed and reported in the literature.[87] In most of the cases, this stability has been explained in terms of resistance of the molecule to form strained double or triple bonds that would result from an intramolecular elimination of MgX_2.

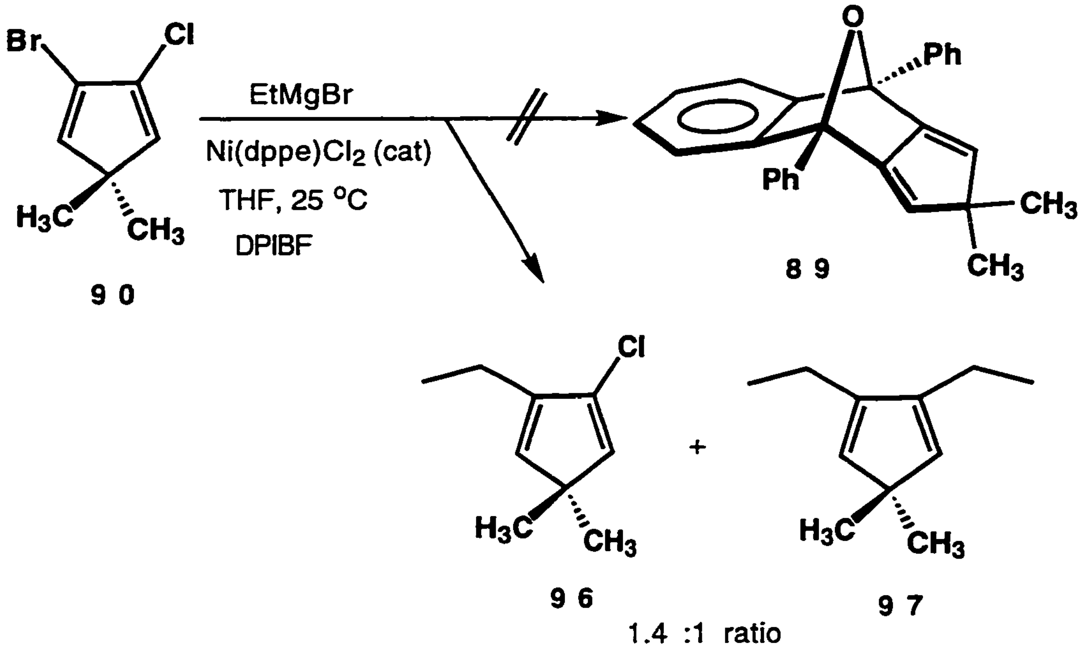
A more active magnesium was next prepared. Diene **90** was treated with Rieke magnesium[88] in THF at 35 °C in the presence of DPIBF. ^{1}H NMR analysis of the crude material indicated that diene **90** had been completely consumed; however, there were no vinyl resonances which could result from adduct formation. Reaction was then conducted at 0 °C and 25 °C, whereupon starting material was recovered unchanged. In the first case, the starting diene **90** is completely consumed (Scheme 33); however, again it is unclear what is being generated. In the second case, the lack of reactivity of diene **90** in the presence of Rieke magnesium at low temperatures was unexpected. Rieke has demonstrated the ability of this active metal to form Grignard reagents from bromobenzene at -78 °C, and from chlorobenzene at 0 °C.[88]

The possibility that **90** would eliminate MgBrCl in the presence of a transition metal was then explored. Ni(0)-species prepared *in situ* have proved quite efficient in the preparation of acyclic butatrienes (Scheme 34).[89]



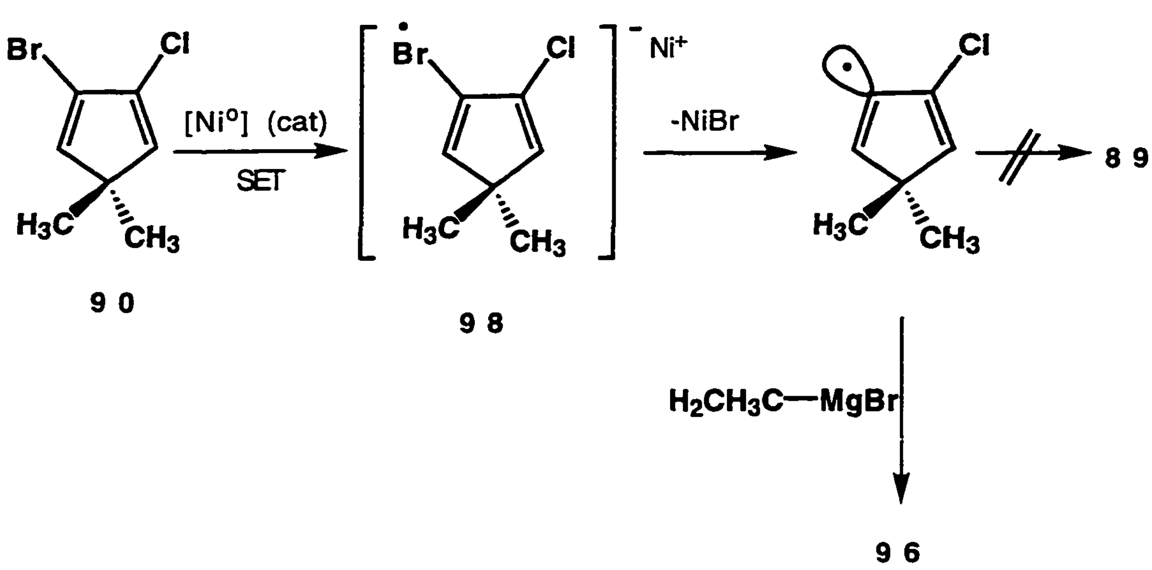
Scheme 34

The attempted 1,2-elimination reaction on **90** in the presence of Ni(0) followed a similar protocol for formation of acyclic butatrienes. Treatment of diene **90** with Ni(0) (Scheme 35), generated *in situ* by reaction of Ni(dppe)Cl_2 with ethyl magnesium bromide,[90] in the presence of DPIBF at 25 °C gave no cycloadduct **89** (Scheme 35). The only observed products of this reaction were 56% of monoalkylated cyclopentadiene **96** (GC, 110 °C, rt 5.1 min), and 40% of dialkylated cyclopentadiene **97** (GC, 110 °C, rt 5.2 min). Compounds **96** and **97** were characterized from the crude material by normal spectroscopic methods (^{1}H, ^{13}C NMR, GC-MS); they resisted isolation due to polymerization. Several mechanisms have been proposed for similar coupling reactions



Scheme 35

and this topic has excited some debate.[86] A likely scenario involves a single electron transfer (SET) process in which the radical anion **98** gives a vinyl radical, which is the direct precursor of **96** (Scheme 36). Many examples of coupling reactions between alkyl Grignard reagents and vinylic halides in the presence of transition metals have been reported.[86] The formation of **97** may be explained through a similar pathway. An alternate mechanism involves initial formation of a nickel carbenoid. Clearly these results suggest that the intermediate formed in the reaction of nickel zero with **90** undergoes a fast coupling side reaction.

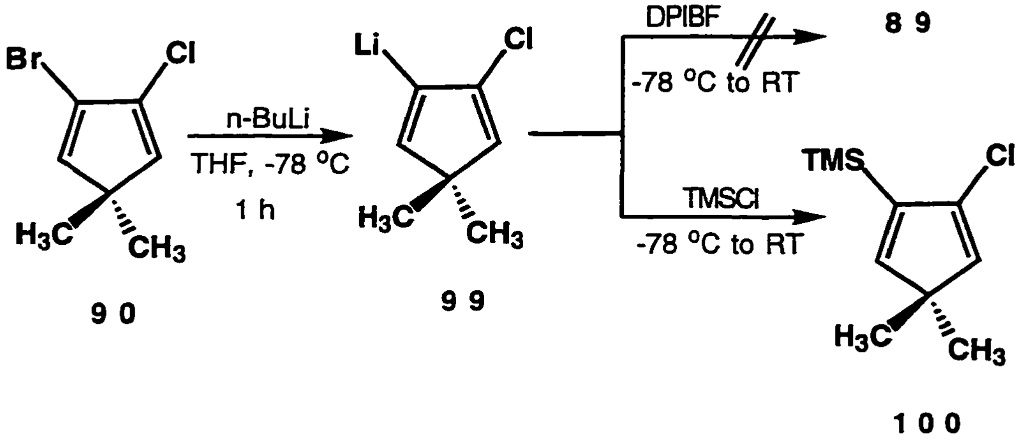


Scheme 36

Reaction of Diene (90) with *n*-Butyllithium

There are many examples of transient species which violate Bredt's rule or are otherwise strained. Some of these have been generated by halogen-metal exchange reactions, 1,2-elimination of LiX, and are then trapped by an excess of organolithium reagents.[91]

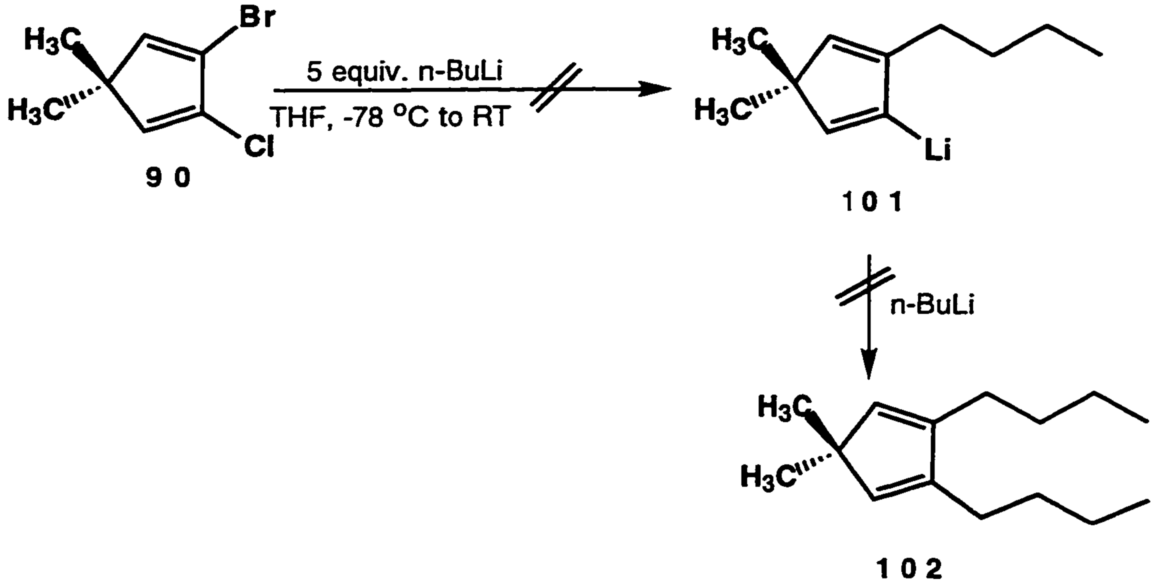
We began to explore the utility of this method in the preparation of triene **85**. Treatment of diene **90** with 2.0 equivalents of *n*-butyllithium in tetrahydrofuran at -78 °C, addition of DPIBF, and warming quickly to room temperature, led only to intractable material (Scheme 37). This result questioned the extent of halogen-metal exchange and the stablility of the lithium species **99** at -78 °C. Thus, we sought evidence for formation of **99** at -78 °C. Reaction of **90** (Scheme 37) with 2.0 equivalents of *n*-butyllithium in tetrahydrofuran at -78 °C, followed by addition of chlorotrimethylsilane gave a 79% yield of **100**, which thus proved the intermediacy of **99** and its stability at -78 °C. This reaction was then run with a large excess of *n*-butyllithium



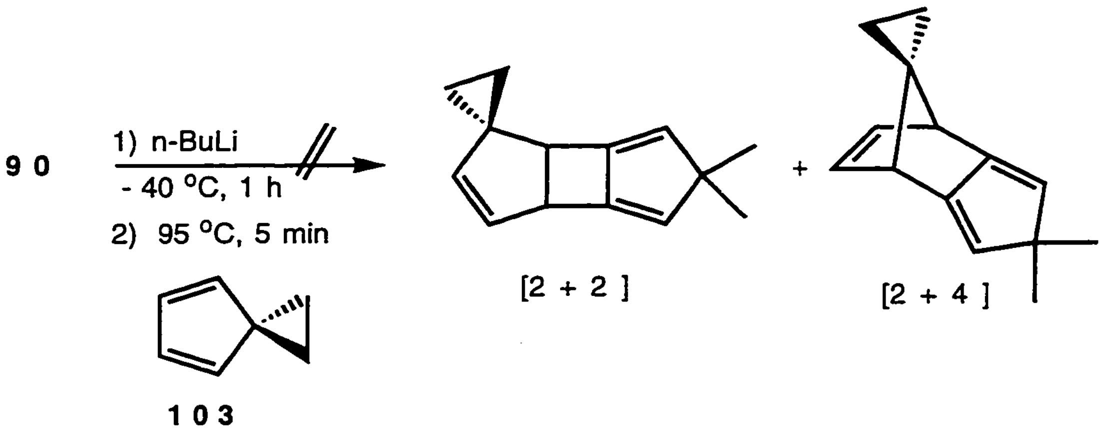
Scheme 37

in hopes of obtaining alkylated products **101** and **102** which could also prove the intermediacy of triene **85** (Scheme 38).[91] Treatment of **90** with 5 equivalents of *n*-butyllithium in tetrahydrofuran at -78 °C, followed by warming to room temperature, gave an intractable gum. We felt that decomposition of **99** might be promoted by excess of organolithium reagent.

Lastly, we attempted the intramolecular elimination of lithium chloride from **99** at higher temperatures. It is known that 1-lithio-2-bromocyclopentene,[34c] 2-lithio-3-chlorobicyclo[2.2.1]hept-2-ene,[91a] and 1-



Scheme 38



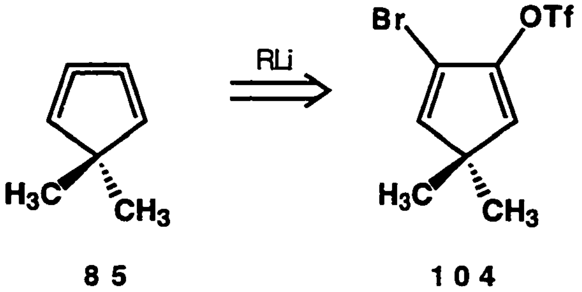
Scheme 39

lithio-2-bromoacenaphthene[92] all lose LiX at 25 °C, 45 °C, and 100 °C, respectively. Thus, it was of interest to explore the possibility to generating and trapping triene **85** by heating the reaction mixture after lithiation had taken place. Reaction was conducted in the presence of spiro diene **103** (which may give [2 + 2] and [2 + 4] cycloadducts)[93] with addition of *n*-butyllithium at -40 °C (Scheme 39). After one hour, the reaction was heated at 95 °C for 5 min, then quenched. ^1H NMR analysis of the crude material indicated that diene **90** had been completely consumed. Attempts to isolate any cycloadduct or other product by preparative GC failed.

In conclusion, efforts to generate and trap **85** from diene **90** by metal-induced 1,2-elimination of MgBrCl or loss of lithium chloride from **99** were unsuccessful.

Route 3: Synthesis of 2-Bromo-5,5-dimethyl-3-trifluoromethanesulphonyl-1,3-cyclopentadiene (104) and Reaction with *n*-Butyllithium.

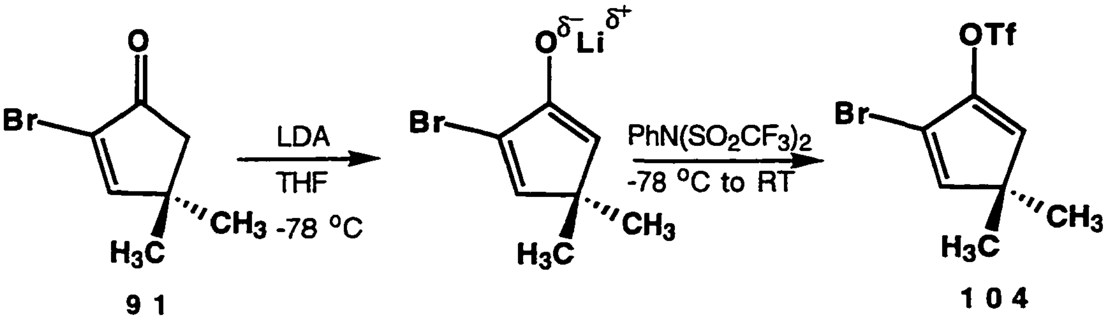
One other potential route to butatriene **85** involves diene **104** (Scheme 40). The elimination of OR and halogen from a β-halo ether to yield olefins is called the *Boord* reaction.[94] In principle, by taking advantage of the



Scheme 40

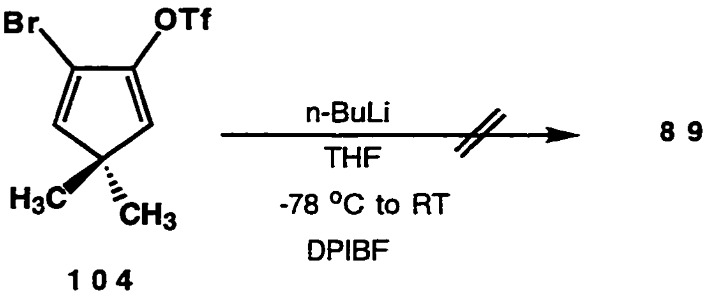
exceptional leaving group ability of triflates, **104** may undergo intramolecular elimination of LiOTf when treated with an alkyllithium reagent (Scheme 40). In view of our previous problems eliminating chlorine, we thought that diene **104** might be a promising precursor to **85**.

Synthesis of diene **104** was accomplished by deprotonation of bromoenone **91** under kinetic conditions with lithium diisopropylamide (LDA), followed by addition of N-phenyltriflimide (Scheme 41).[95] Spectral data for **104** included doublets at δ 6.45 and at δ 6.09, a singlet at δ 1.26 in the ^{1}H NMR, seven resonances in the ^{13}C NMR, and a parent molecular ion (M^+) at *m/z* = 320 in the mass spectrum.



Scheme 41

The attempted conversion of diene **104** into 5,5-dimethyl-1,2,3-cyclopentatriene (**85**) was carried out in THF with *n*-butyllithium at -78 °C in the presence of DPIBF (Scheme 42). However, no adduct which could be attributed to a $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition between butatriene **85** and



Scheme 42

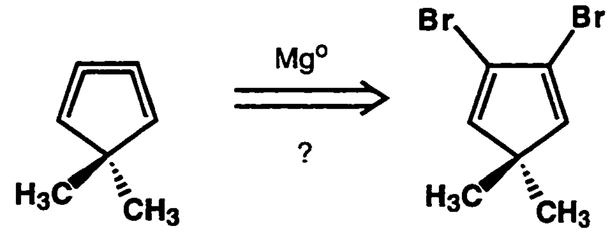
diphenylisobenzofuran was observed. ^{1}H NMR analysis of the crude material indicated that diene **104** had completely reacted. Preparative TLC of the crude product showed only aromatic resonances. No vinyl resonances were present. Attempts to isolate any low molecular component which could suggest alternative reactions failed.

Route 4: Synthesis of 2,3-Dibromo-5,5-dimethyl-1,3-cyclopentadiene (105) and Reaction with Magnesium Turnings

Among the vicinal dihalides, vinyl dibromides have been demonstrated to form strained bonds quite readily.[34] In terms of the activation barrier for the elimination reactions, 1,2-alkenyl-dibromides have an advantage over 1,2-alkenyldichlorides due to the weaker carbon-bromine bond, compared to the strength of the carbon-chlorine bond (66 kcal/mol vs 79 kcal/mol).[96]

Concerning their limitations, vinyl dibromides are synthetically less accessible, and their preparation often requires many steps, carefully controlled conditions, and the use of expensive reagents.[97]

During the course of this study we prepared 2,3-dibromodiene **105** (Scheme 43). We envisioned formation of butatriene **85** through intramolecular β-elimination of $MgBr_2$, using similar reaction conditions



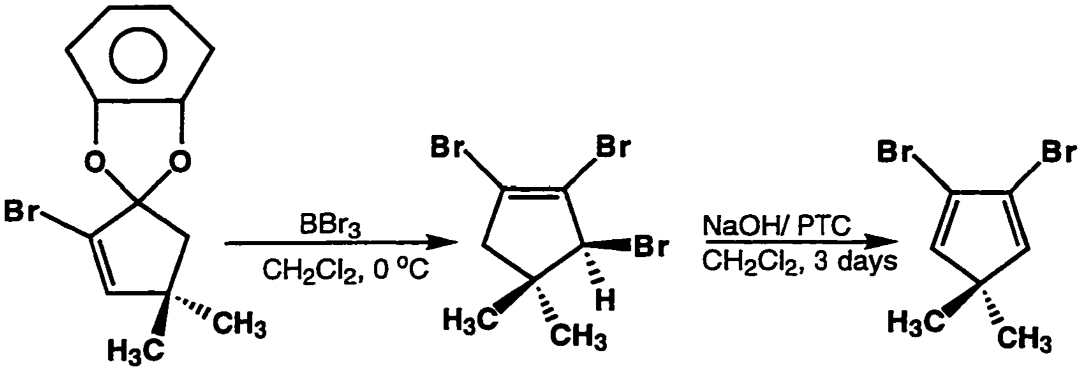
85 **105**

Scheme 43

to those employed for the preparation of cyclobutatrienes **29** and **30**. With bromine as the leaving group, we would have a leaving group with intermediate ability between chlorine and triflate, which might be important in the formation of triene **85**.

The synthesis of diene **105** is outlined in Scheme 44. 1,3-Benzodioxol **106** was prepared according to the literature procedure.[98] Cleavage of the ring in **106** with a solution of boron tribromide in CH_2Cl_2 gave tribromide **107** in 79% yield. Treatment of **107** with 33% NaOH solution under PTC conditions afforded **105** in 38% yield. Spectral data for **105** include two singlets at δ 6.37

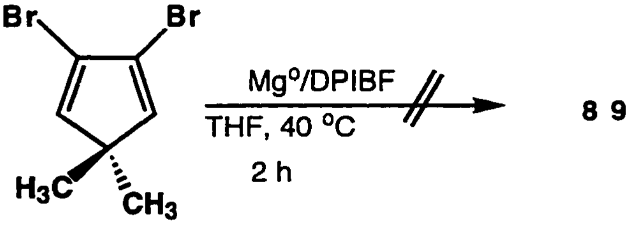
and at δ 1.20 in the ^{1}H NMR, four resonances in the ^{13}C NMR, and a parent molecular ion at *m/z* = 249.8 in the HRMS.



106 **107** **105**

Scheme 44

The attempted reduction of **105** to triene **85** followed a similar procedure as used for formation of trienes **29** and **30**. Treatment of diene **105** with magnesium in THF at 40 °C in the presence of DPIBF resulted in the total consumption of the starting diene, according to TLC and ^{1}H NMR analysis of the crude material (Scheme 45). However, preparative TLC



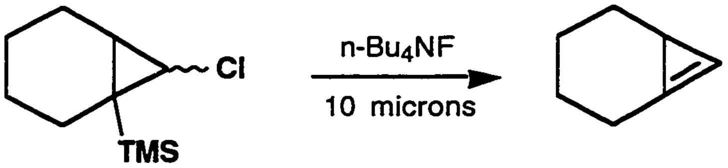
105

Scheme 45

(silica gel, 3:2 hexane/CH_2Cl_2) of the crude product failed to give evidence for adduct formation. Attempts to trap any volatile components were once again unsuccessful.

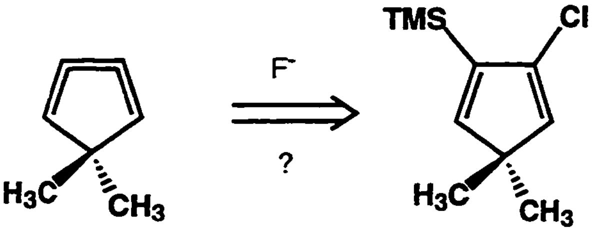
Route 5: Synthesis of 2-Chloro-5,5,-dimethyl-3-trimethylsilyl-1,3-cyclopentadiene (108) and Reaction with Potassium Fluoride

Since standard reduction methods failed in the preparation of **85**, we turned again to fluoride-induced elimination of β-substituted silanes. Fluoride-induced elimination on β-halosilanes is an approach that has enjoyed much success in the synthesis of strained molecules. Billups has employed fluoride columns to effect elimination, leading to strained cyclopropenes (Scheme 46).[99]



Scheme 46

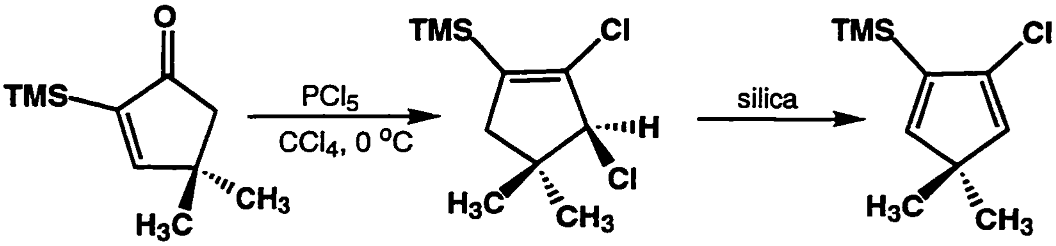
This route explored the potential formation of triene **85** from β-chlorosilane **108** (Scheme 47). The advantage of this synthetic method appeared to be the mild conditions for cumulene formation.



8 5 **1 0 8**

Scheme 47

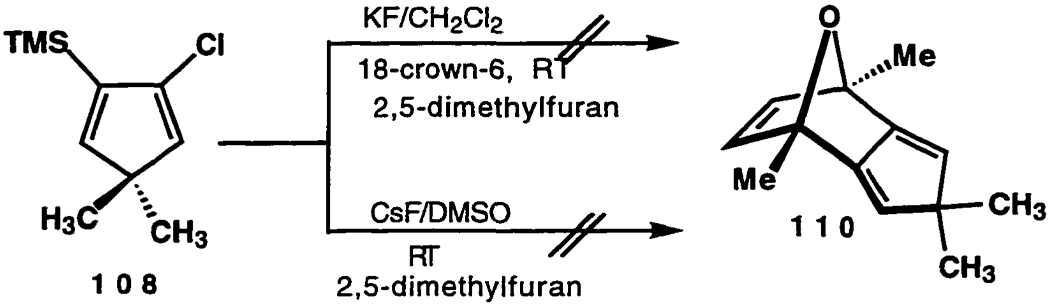
Earlier work on this approach was due to Winstanley.[100] The preparation of diene **108** was accomplished in two steps according to his method (Scheme 48). Treatment of TMS-enone **86** with a suspension of PCl_5 in CH_2Cl_2 at 0 °C gave a substance characterized as dichloride **109** in 84.6% yield. Reaction of **109** on silica afforded diene **108** in 28.6% yield. Spectral data for **108** include two doublets at δ 6.40 and at δ 6.08, two singlets at δ 1.15 and at δ 0.21 in the ^{1}H NMR, seven resonances in the ^{13}C NMR, and a parent molecular (M^+) at *m/z* 200 in the mass spectrum.



8 6 **1 0 9** **1 0 8**

Scheme 48

The conditions employed in our first attempt at inducing fluoride-ion assisted 1,2-elimination on **108** were different from those used with substrate **88**. A more reactive fluoride ion would be generated by addition of 18-crown-6 ether to the reaction mixture. Reaction of **108** (Scheme 49) with KF, 18-crown-6 in CH_2Cl_2 in the presence of 2,5-dimethylfuran gave

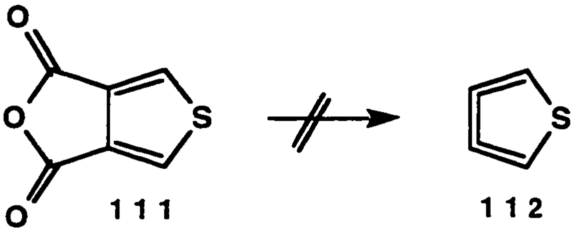


Scheme 49

a complex reaction mixture according to ^{1}H-NMR analysis of the crude material. The only identifiable compound was unreacted starting material. The reaction was then conducted following the desilyation procedure which had been employed by Shakespeare in the synthesis of 1,2,3-cyclohexatriene.[45] ^{1}H NMR analysis of the crude indicated that diene **108** had reacted to a greater extent than that in the previous run; however, the crude product was only intractable material with aromatic resonances! Attempts by chromatography to isolate anything that could suggest alternate reaction pathways were unsuccessful.

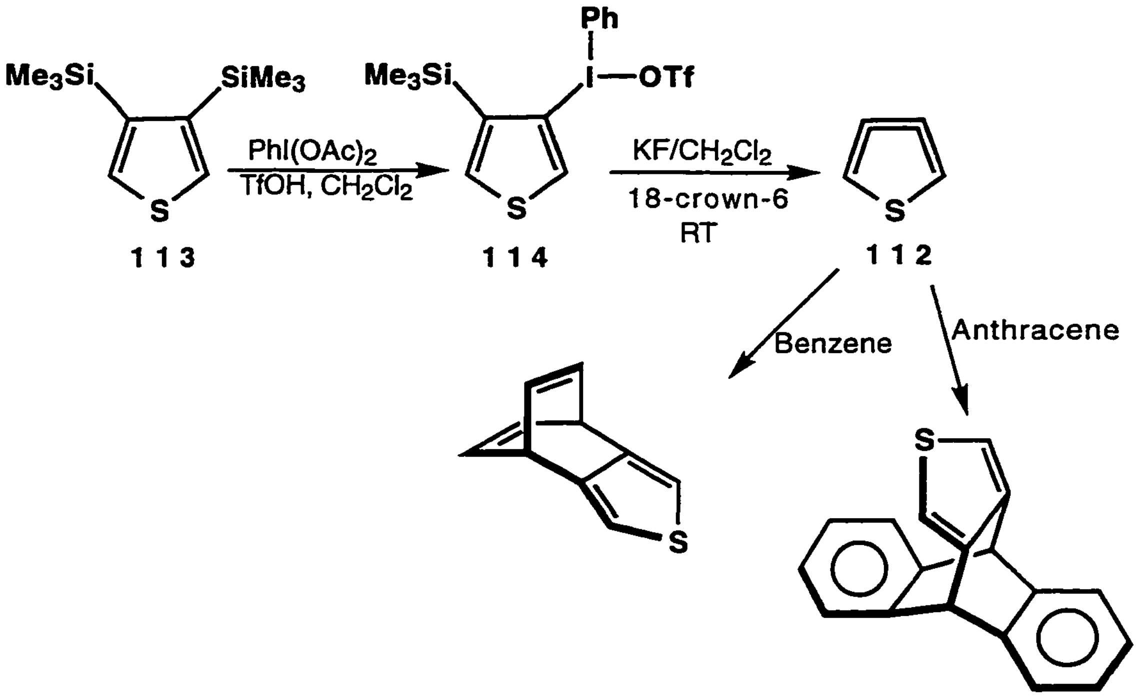
Route 6: Synthesis of 2,3-Bis(trimethylsilyl)-5,5-dimethyl-1,3-cyclopentadiene (116) and Attempted Synthesis of a Vinylidonium Salt Precursor

Recently, Wong and coworkers[101] have reported the generation, trapping reactions, and *ab initio* study of 3,4-didehydrothiophene (**112**). The optimized CASSCF structure for **112** shows a bending angle for the butatriene moiety of 116.4°. The occupancies of the S and A orbitals of the in-plane sp^2-type orbitals for the C3 and C4 bond indicate that the in-plane π bond of **112** has a fairly large degree of biradical character, as expected for a highly bent bond. Strain estimates were not reported. In retrospect, it is of interest to note that although **112** had been previously mentioned in the literature, its existence was never proved.[102] An earlier attempt to generate this strained heterocarbon by pyrolysis of anhydride **111** was unsuccessful (Scheme 50).[103]



Scheme 50

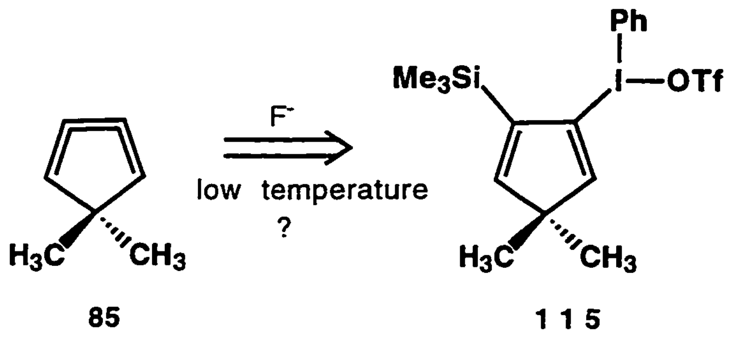
The precursor for the successful synthesis of **112** was the iodonium salt



Scheme 51

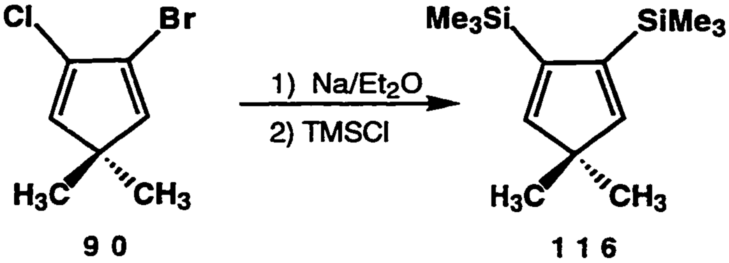
114 (Scheme 50), prepared from 3,4-bis(trimethylsilyl)-thiophene (**113**) and phenyliodonium tosylate PhI(OTf)$_2$, which was generated *in situ* from (diacetoxyiodo)benzene (DIB) and trifluromethanesulfonic acid in CH_2Cl_2. 1,2-Fluoride-promoted elimination on **114** gave **112** which was trapped in $[_{\pi}2_{s} + {}_{\pi}4_{s}]$ cycloadditions. Interestingly, the remarkable reactivity of **112** was established by its reaction with benzene. Many other examples of the synthetic utility of polyvalent organic iodine compounds have been recently reviewed.[104] The best results for benzyne generation have been claimed from fluoride-induced elimination on an iodonium salt.

The method was appealing and appeared to present a practical advantage over those described above, due to the high nucleofugacity of the phenyliodonium triflate group at low temperature. Kinetic studies[104] have demonstrated that I(III) salts are some 10^6 times more reactive than triflates! Thus, we decided to explore this approach to generate cumulene **85**. We envisioned formation of triene **85** by 1,2-elimination on vinylidonium salt **115** in the presence of fluoride ions at temperatures lower than room temperature (Scheme 52).



Scheme 52

Synthesis of 2,3-bis(trimethylsilyl) diene **116** was accomplished in a single step process by Wurtz-type coupling of 2-bromo-3-chloro-5,5-dimethyl-1,3-cyclopentadiene (**90**) with chlorotrimethylsilane (Scheme 53). Reaction of **90** in Et_2O with TMSCl in the presence of sodium wire[105] gave **116** in 39% yield after chromatography (silica gel, hexane). Spectral data for **116** include three singlets at δ 6.48, at δ 1.15 and δ 0.17 in the ^1H NMR, five resonances



Scheme 53

in the ^{13}C NMR and a parent molecular ion at m/z = 238 in the mass spectrum.

The synthesis of precursor **115** was attempted by three different methods (Scheme 54). These methods are summarized below.

Method A: Reaction of (**116**) with (Diacetoxyiodo)benzene (DIB)[101]

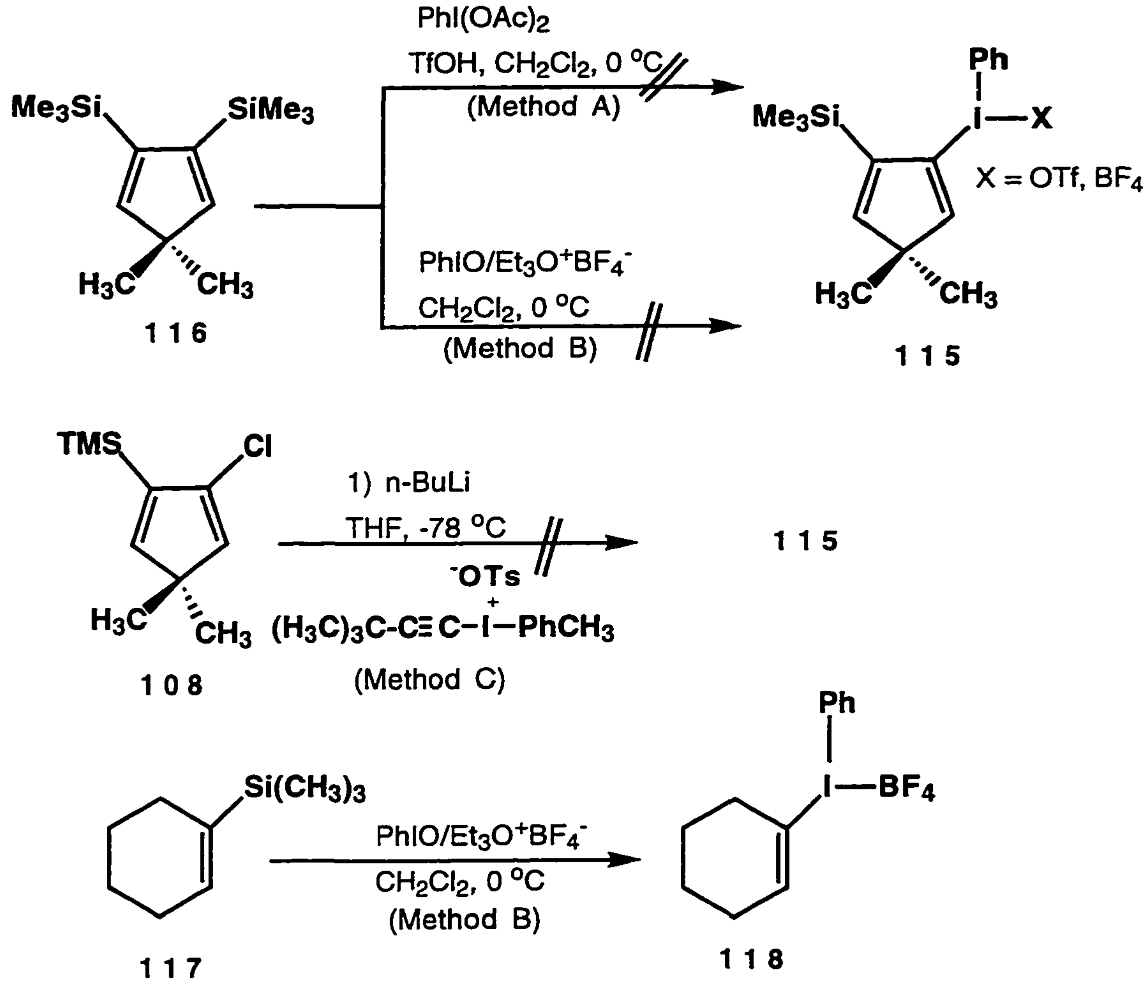
This method followed the Wong protocol for the preparation of **114**. This involved treatment of **116** with (diacetoxyiodo)benzene in the presence of trifluoromethanesulfonic acid in dry CH_2Cl_2 at 0 °C.

Method B: Reaction of (**116**) with Lewis Acid-Activated Iodosylbenzene[106]

Iodosylbenzene was prepared in 97% yield following the literature procedure, and securely characterized by its IR spectrum (its low solubility precludes characterization by NMR spectroscopy).[107] The IR absorptions of iodosylbenzene include 1568, 1377, 1303, 410 cm^{-1}. Absorption bands were compared to the literature values. Diene **116** was treated with iodosylbenzene and triethyloxonium tetrafluoroborate in CH_2Cl_2 at 0 °C.

Method C: Reaction of (108) with (*tert*-Butylethynyl)phenyliodonium Tosylate[108]

This method followed the Koser procedure for the preparation of iodonium salts. Diene **108** was reacted sequentially with *n*-butyllithium in THF at -78 °C and (*tert*-butylethynyl)phenyliodonium tosylate.

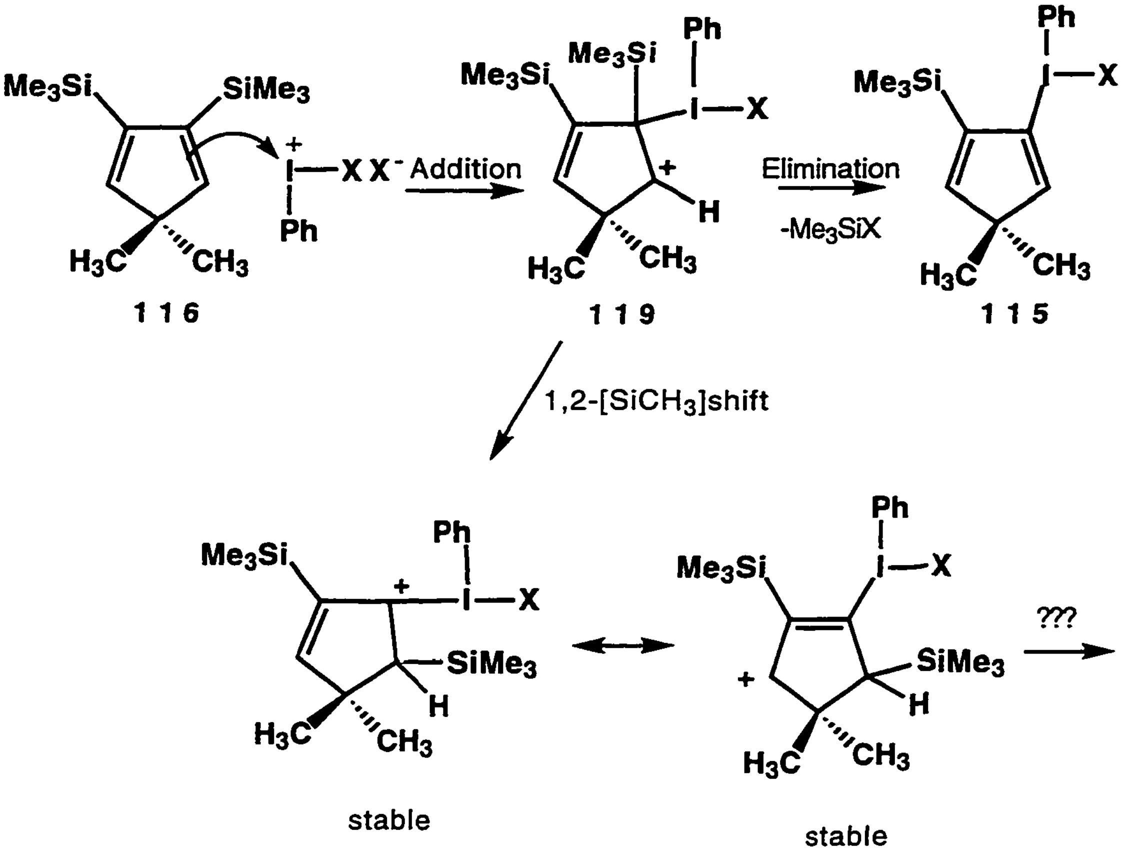


Scheme 54

Methods A and B yielded no vinylidonium salt. However, ^{1}H NMR analysis of the crude material indicated that the starting bis(trimethyl)silane **116** had been consumed. The only byproduct from both trials was iodobenzene which was identified by GC (125°C, rt 5.2 min) and ^{1}H-NMR. The retention time and the chemical shifts for iodobenzene were compared to an authentic sample. The validity of method B was confirmed by preparation of phenyl(1-cyclohexenyl)iodonium tetrafluoroborate (**118**), isolated as white crystals in 75% yield (Scheme 54). The ^{1}H NMR spectrum for **118** included a multiplet at δ 7.05 (vinyl proton), two multiplets at δ 2.50 and δ 1.75, two multiplets at δ 7.40 - 7.80 (aromatic protons) and δ 7.90 - 8.12 (aromatic protons). Chemical shifts were compared to the literature values.[106]

Vinylsilanes are known to react readily with electrophiles.[104] Electrophilic addition of I(III) to diene **116** would result in formation of intermediate **119** which eliminates Me_3SiX, so that the net effect would be the replacement of the silyl group by I(III) to form the salt **115** (Scheme 55). The formation of iodobenzene suggests that decomposition has occurred, either of the salt **115**, or an intermediate during the addition. Successive 1,2-shifts are likely to happen, giving stabilized carbocations which are allylic, and β to the silyl substituent. If the salt was formed during the course of the reaction, it is not clear why it was so labile and resisted isolation.

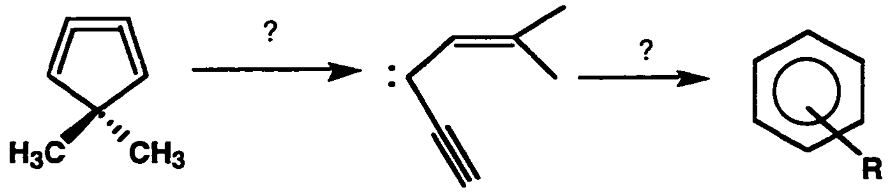
In method C, ^{1}H NMR analysis of the crude product showed mostly unreacted starting material which indicates that halogen-metal exchange did not occur. Thus, efforts to prepare vinylidonium salt precursor **115** by standard methods for preparation of iodonium salts were unsuccessful.



Scheme 55

Conclusion and Future Work

5,5-Dimethyl-1,2,3-cyclopentatriene (**85**) remains elusive. Although many likely precursors were prepared and studied, none appeared to provide **85**. The total strain energy of cumulene **85** has been predicted to be 75 kcal/mol. Because this is so highly strained, it would not be surprising if **85** rearranges at temperatures above 0 °C via ring opening before reacting with the trapping reagent (Scheme 56). However, many pathways to generate



85

Scheme 56

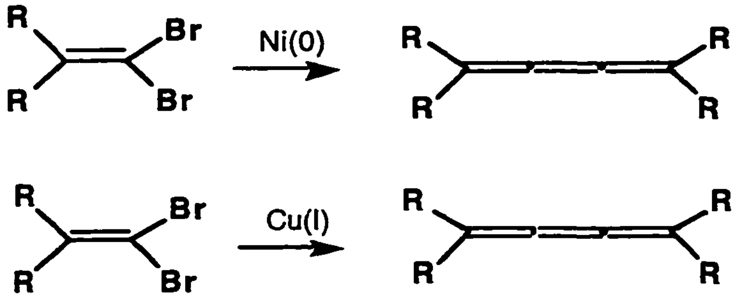
85 have yet to be explored. There are alternate routes which, in principle, may yield 5,5-dimethyl-1,2,3-cyclopentatriene. The first entails low temperature photogeneration of **85** in the presence of a suitable trap. As will be discussed in chapter II of this thesis, we have cleanly generated cyclopropene and cyclopentyne by photochemical reactions. Similarly, a retro [2 + 2] to this substance is now being planned. Fluoride induced elimination on either **86** or **108** in the gas phase may give **85**. The alternate gas phase route will overcome barriers encountered in solution. Billups[99] has developed fluoride coated columns which may be suitable for vapor phase preparation of **85**. We can envision the formation of **85** through the loss of LiX from a lithium carbenoid. Spontaneous loss of LiX is not likely. However, the use of a transition metal-complex such as nickelocene could prove useful in the preparation of **85**. Gassman and co-workers[91a] have employed this methodology to synthesize the trimer of norbornyne.

Formation of trimers is catalyzed by the transition metal-complex, and has been used as evidence for formation of strained cycloalkynes.

Attempted Synthesis of Cyclic Butatrienes by Intramolecular Vinylidene Coupling

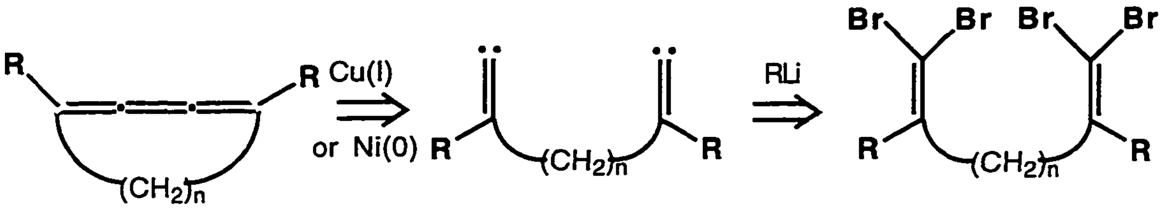
Another important goal of this project was the development of a general synthetic methodology that would allow access to cyclic butatrienes, independent of ring size. The addition of dibromocarbene to cyclic allenes followed by ring opening is suitable for larger systems, however, its adaption in construction of smaller homologues is foiled by the instability of small ring allenes.[48b] The new route developed in this study for the synthesis of 1,2,3-cyclooctatriene (**29**) and 1,2,3-cycloheptatriene (**30**) yields cyclic cumulenes under very mild reaction conditions. However, low yields in the preparation of the dihalo-precursors preclude using this route for synthetic purposes. Thus, we began to research other general methods to obtain cyclic cumulenes in one step and from convenient starting materials, avoiding the multistep procedures that usually characterize cyclic butatriene syntheses.

The synthesis of acyclic butatrienes by intermolecular vinylidene coupling in the presence of a transition metal, is a well documented reaction. Iyoda and co-workers have reported the preparation of several acyclic butatrienes by reaction of 1,1-dibromo-alkenes with Ni(0) or Cu(I) (Scheme 57).[89,109]



Scheme 57

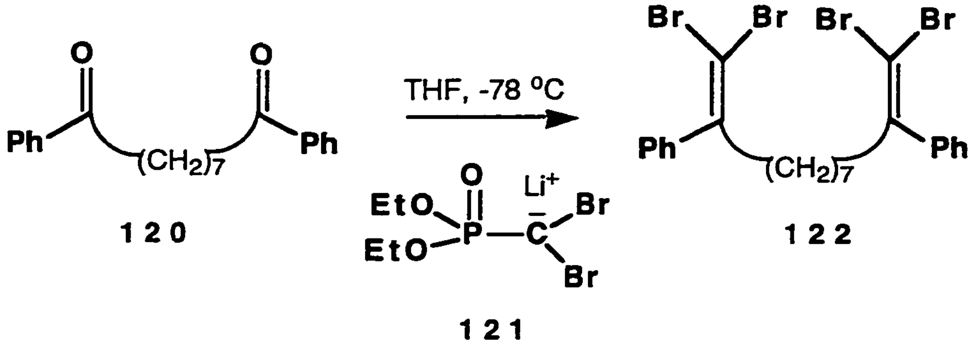
It was proposed that the intramolecular version of this reaction may give cyclic compounds (Scheme 58). Since large ring butatrienes are isolable, and can be characterized by common spectroscopic methods, we began our study with the synthesis of precursors that would give kinetically stable butatrienes. Synthesis of these potential precursor and their reaction with Cu(I) are described below.



Scheme 58

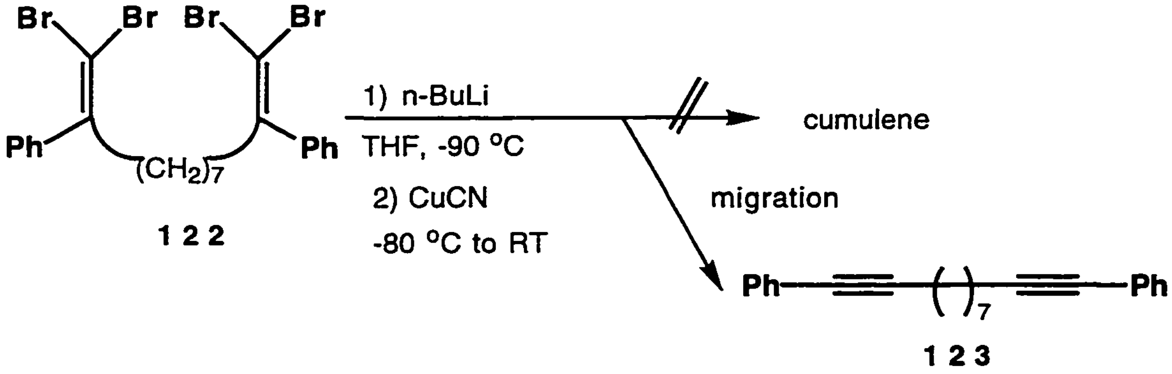
Synthesis of Tetrabromo-olefin 122 and Reaction with CuCN

Reaction of 1,9-bis(phenyl)nonane-1,9-dione[110] (**120**) (Scheme 59) with the anion of diethyl dibromomethanephosphonate **121** (generated by kinetic deprotonation with LDA)[111] afforded tetrabromo-olefin **122** in 56% yield.



Scheme 59

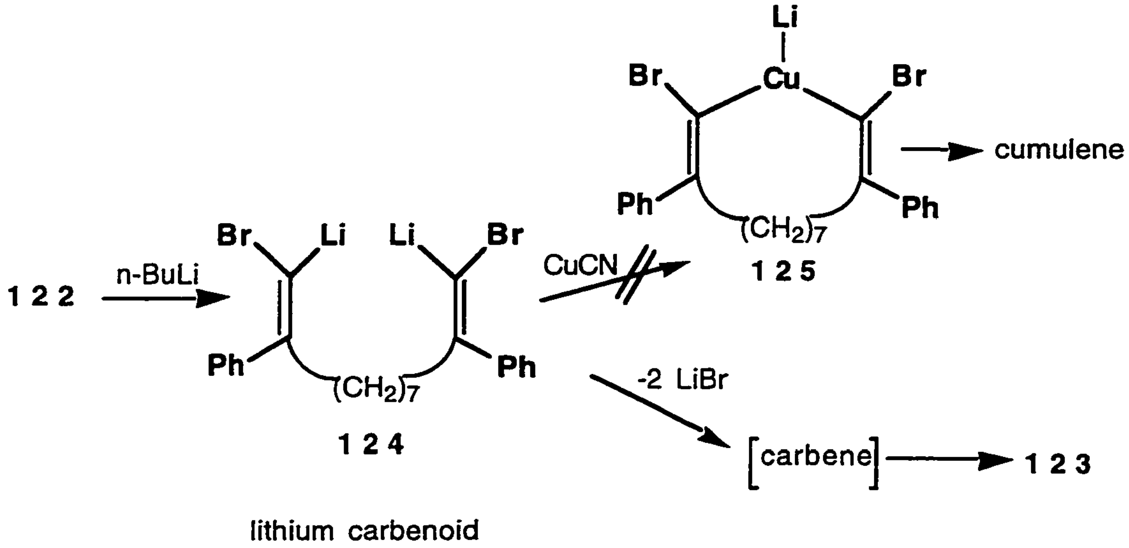
Spectral data for **122** include a doublet of doublets at δ 2.56, two multiplets at δ 1.33-1.23 and δ 7.40-7.15 in the ^{1}H NMR, ten resonances in the ^{13}C NMR and an absorption at 1609 cm^{-1} in its IR spectrum. Treatment of **122** with *n*-butyllithium and CuCN at -90 °C did not give the expected product, but instead **123** was formed (Scheme 60). Diyne **123** was isolated by preparative



Scheme 60

TLC (silica gel, 4% CH_2Cl_2, hexane) in 42% yield, and securely characterized by ^1H and ^{13}C NMR, IR and UV spectra. The elapsed time between the addition of *n*-butyllithium and CuCN was varied from 10 to 30 min; however, this did not alter the observed results.

The results obtained in this experiment are consistent with the simplified mechanistic rationale presented in Scheme 61. Reaction of tetrabromo olefin **122** with *n*-butyllithium results in formation of the lithium carbenoid **124** which losses LiBr in an α-elimination process to generate

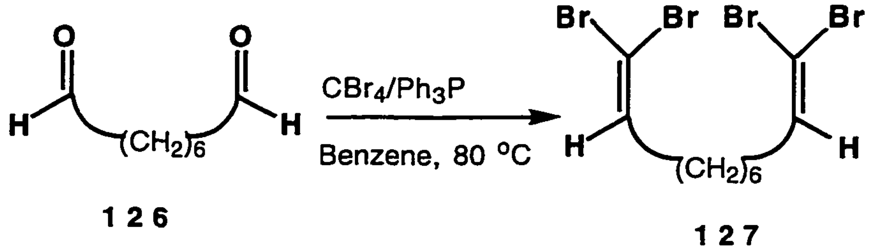


Scheme 61

a carbene intermediate which is the precursor of dialkyne **123**. Thus, vinylidene-acetylene rearrangement occurs faster than the formation of alkyl cuprate **125**. Therefore, intramolecular coupling is not observed. This rearrangement has been known for over a hundred years and has since been the subject of many investigations.[109] The poor solubility of tetrabromo-olefin **122** precluded the use of a constant *ultra* low temperature. Any increase in temperature will facilitate the rearrangement.

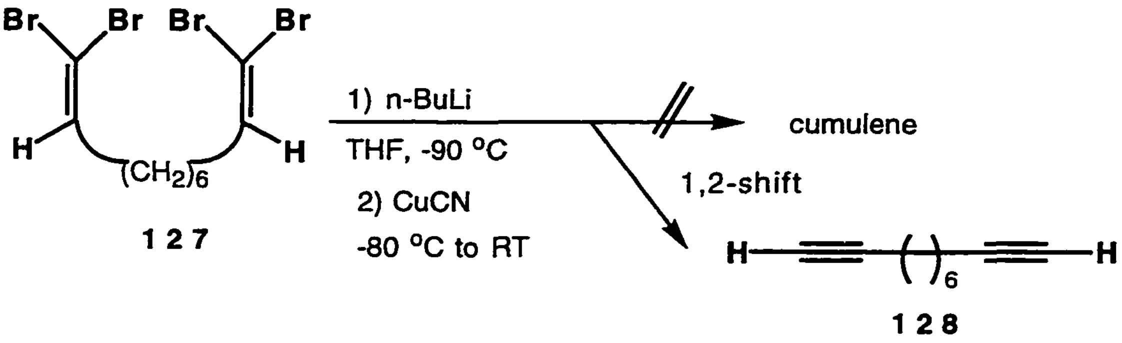
Synthesis of Tetrabromo-olefin 127 and Reaction with CuCN

With the idea of diminishing problems encountered with solubility of olefin **122**, we prepared a lower molecular weight olefin. Tetrabromide **127** (Scheme 62) was prepared in 43% yield by reaction of subaraldehyde (**126**)[112] with CBr_4 and PPh_3 in refluxing benzene.[113] Treatment of **127** with



Scheme 62

n-butyllithium and CuCN at -90 °C gave no intramolecular coupling product (Scheme 63). ^{13}C NMR analysis of the crude material showed two carbons at δ 84.7 and δ 68.3, indicating that diyne **128** had been formed as the major reaction product. Again, vinylidene-acetylene rearrangement occurs faster than formation of the copper carbenoid. This result was not totally surprising since hydrogen migration is known to occur faster than phenyl migration.[80] Although, we did solve some solubility problems, the expected

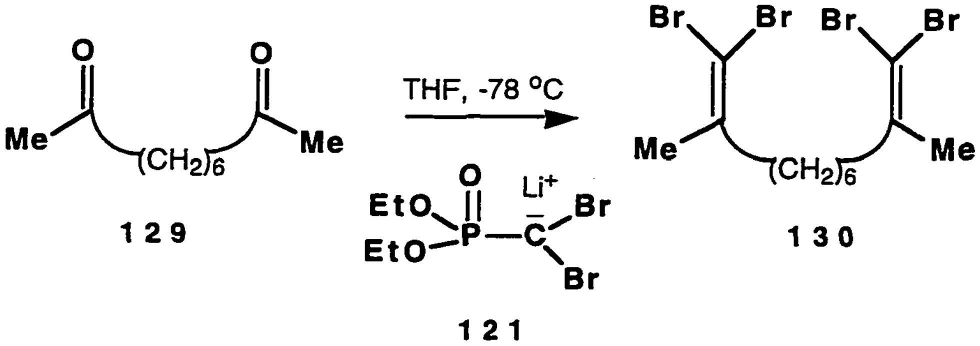


Scheme 63

intramolecular vinylidene coupling did not occur.

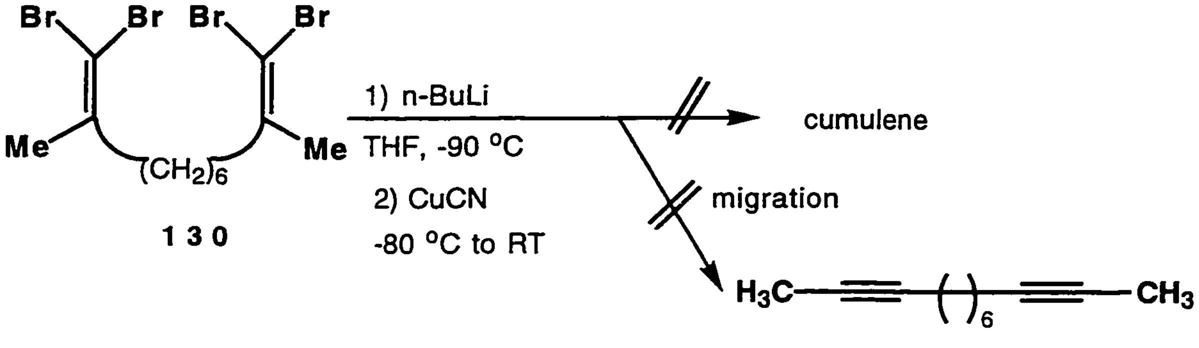
Synthesis of Tetrabromo-olefin 130 and Reaction with CuCN

In view of the previous results, we investigated the potential coupling of dimethyl-tetrabromo-olefin **130**. Methyl groups are known to migrate slower than phenyl and hydrogen.[114] Synthesis of **130** was accomplished by reaction of diketone **129**[115] with the deprotonated form of diethyl dibromomethanephosphonate (**121**) in THF (Scheme 64). Chromatography



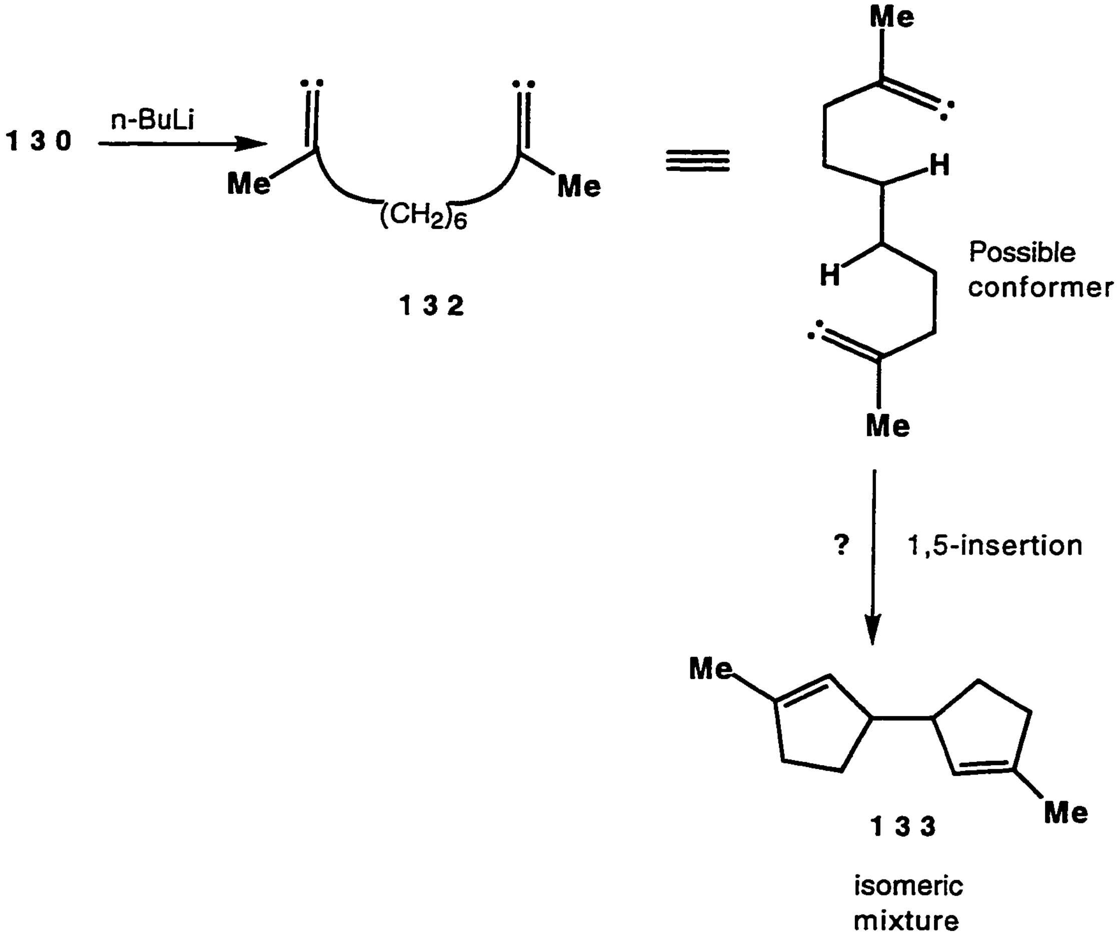
Scheme 64

(silica gel, hexane) gave **130** in 23% yield. Spectral data for **130** include a doublet of doublets at δ 2.27, a singlet at δ 1.87 and a multiplet at δ 1.46-1.21 in the ^{1}H NMR, and six resonances in the ^{13}C NMR. Treatment of **130** with *n*-butyllithium and CuCN at -90 °C yielded no evidence for an intramolecular coupling product (Scheme 65). Capillary GC (100 °C) analysis of the crude material indicated several components. The main component had retention time of 7.3 min. According to GCMS, this had a molecular ion peak of *m/z* = 162. IR analysis of the crude product in THF gave no absorption band in the region of 1850-1990 cm^{-1} which is characteristic of butatrienes.[50] ^{1}H-NMR



Scheme 65

analysis of the crude material was consistent with the complexity detected by capillary GC, but showed a well defined doublet at δ 5.88 with a *J* = 9.6 Hz and several other resonances between 2.10 ppm and 2.80 ppm characteristic of allylic protons. ^{13}C NMR did not indicate the presence of acetylenic carbons of diyne **131**. It seems reasonable to propose that reaction of *n*-butyllithium with tetrabromo-olefin **130** gives the corresponding carbenoid, which would eliminate LiBr to give carbene **132** (Scheme 66). This carbene could undergo 1,5-insertion faster than formation of the copper carbenoid, or migration of the methyl group, to form dicyclopentene derivatives **133** which could be the major reaction products. 1,5-Insertion of this type has been previously reported and has application in the synthesis of cyclopentene derivatives.[116] However, isolation of pure samples of **133** will be necessary



Scheme 66

in order to obtain evidence for 1,5-insertion.

Conclusion

One important goal of this study was the development of a new and general route to cyclic butatrienes. This part of the project was exploratory in nature and is by no means complete. It is clear that many other reactions warrant investigation to explore fully the potential intramolecular vinylidene coupling toward cyclic butatrienes. In the cases of tetrabromo-olefins **122** and **127** a competing 1,2-migration reaction occurs faster than the ring closure to give the cumulene. It has been recognized that large rings, despite their low strain, present synthetic difficulties. A complicating factor is the difficulty of getting the ends of a long chain to approach each other. The conformational entropy[117] of a chain compound is greater than that of a ring. The possibility of rotation about a large number of bonds leads to a high conformational entropy in the open-chain precursor, which is largely lost in the cyclic product. Thus, their derivatives are relatively difficult to obtain. Finn and coworkers have reported the synthesis of macrocyclic allenes from condensation of nonenolizable aldehyde with Ti(IV) reagents.[118] They found that yields were lower for 11-membered and 19-membered rings. Therefore, 1,1-dibromides tethered by fewer carbons may be better substrates to explore a possible intramolecular cyclization. They should be more soluble at low temperatures, and may couple faster with Cu(I) or other transition metal, thus avoiding competing reaction. The cyclic butatrienes generated in this fashion can be trapped in a $[{}_{\pi}2_s + {}_{\pi}4_s]$ cycloaddition with diphenylisobenzofuran or other suitable dienes.

CHAPTER II

PHOTOGENERATION OF REACTIVE CARBENES BY FRAGMENTATION OF CYCLOPROPANATED PHENANTHRENES

Introduction

Definitions and Nomenclature

Carbenes can be classed with carbanions, carbocations, and carbon-centered radicals as among the fundamental intermediates in the reactions of carbon compounds. Carbenes are neutral, divalent derivatives of carbon in which a carbon atom has two covalent bonds to other groups and two non-bonding orbitals containing two electrons between them. Depending on whether the non-bonding electrons are of the same or opposite spin, carbenes are *singlet* and *triplet* species. This follows from the fact that the spin multiplicity is given by $2S + 1$, where S is the total spin. For two spin-paired electrons, $S = 0$ and the carbene is a singlet. If the spins of the electrons are parallel, then the carbene is a *triplet.*

The possible arrangements of two electrons between two orbitals of different energy are shown in Figure 15. A carbene in the lowest singlet state resembles a carbocation as a bent sp^2 hybrid (Figure 16). A triplet carbene resembles a free radical. An alternative structure for the triplet carbene, and

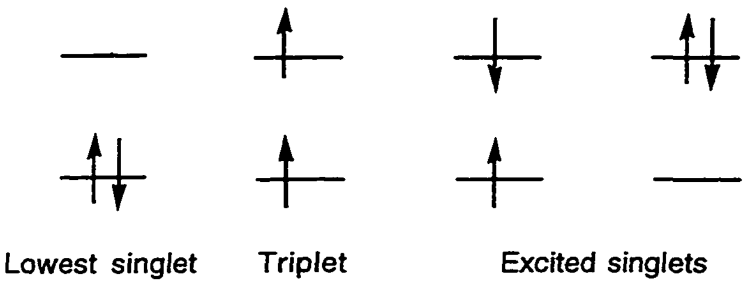
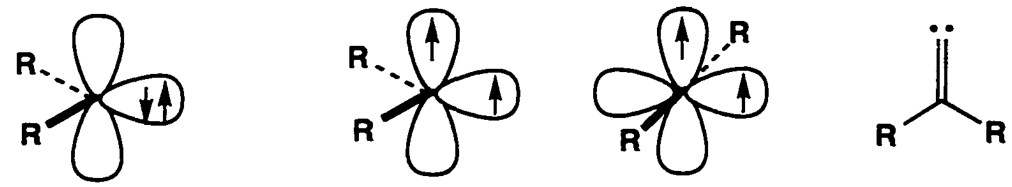


Figure 15. Spin multiplicity

for the excited singlet, might be a linear sp hybrid.[119]



Lowest singlet (sp^2) Triplet (sp^2) Triplet (sp) Vinylidene (sp)

Figure 16. Possible carbene hybrids.

The parent species, $:CH_2$, is usually called *methylene,* though derivatives are more often named by the carbene nomenclature. Thus, $:CCl_2$, is generally known as dichlorocarbene, though it can also be called dichloromethylene. Cyclic carbenes are most conveniently named by using the suffix -ylidenes, e.g., cyclopropylidenes, cyclobutylidenes, and so on. Vinylidene, also shown in Figure 16, possesses a divalent sp carbon atom.

Structure and Reactivity

Depending upon the mode of generation, a carbene may initially be formed in either the singlet or triplet state, no matter which is lower in energy. These two electronic configurations possess different geometries and chemical reactivities. Both theoretical and experimental studies have provided more detailed information about carbene structures.[120] Molecular orbital calculations lead to the predictions of H-C-H angles for methylene of ~135° for the triplet and ~105° for the singlet (Figure 17). The triplet is calculated to be about 8 kcal/mol lower in energy than the singlet.[120a] Experimental determinations of the geometry of CH_2 tend to confirm the theoretical results. The H-C-H angle of the triplet state, as estimated from the EPR spectrum, is 125-140 °C.[121] The H-C-H angle of the singlet state is found

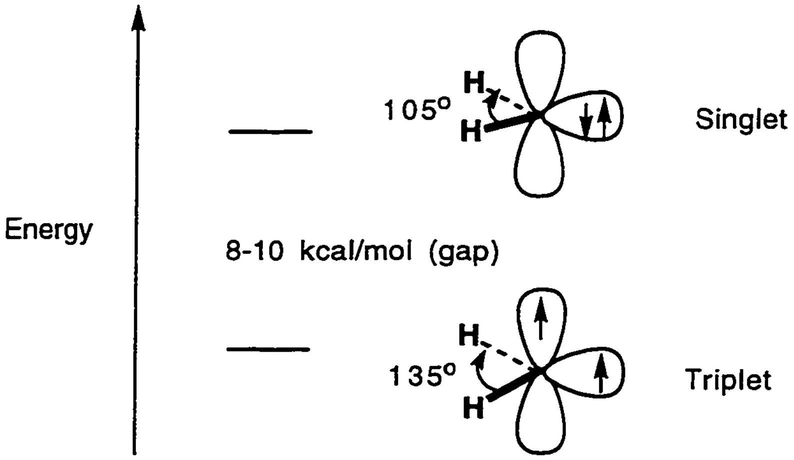


Figure 17. Singlet-triplet splitting in methylene.

to be 102° by electron spectroscopy. All the evidence is consistent with the triplet being the ground state.

The fact that substituents on methylene perturb the relative energies of the singlet and triplet states has attracted some interest. The effect of alkyl substitution is rather mild. Therefore, dialkylcarbenes are ground state triplets. Substituents that act as electron-pair donors stabilize the singlet state more than the triplet state by delocalization of an electron pair into the empty p-orbital (Figure 18).[122] However, there is not a simple and obvious way of predicting the ground state of carbenes. Direct detection of the ground state and the excited states by spectroscopic means have been carried out in many cases.[123] Electron paramagnetic resonance (EPR) is a particularly satisfactory spectroscopy tool for detecting triplet ground states since triplet species are diradicals. EPR measurements cannot be made on singlet species, but electronic spectra have been used instead.

Figure 18. Stabilization of singlet carbenes by electron-pair donors.

Numerous studies of carbene relative reactivity have been reported.[124] Various singlet carbenes have been characterized as nucleophilic, ambiphilic, or electrophilic.[124b,c] The "phylicity" or selectivity of carbenes is based on the relative reactivity toward a series of different alkenes containing both nucleophilic alkenes, such as tetramethylethylene, and electrophilic ones, such as acrylonitrile. The principal structure feature which determines the reactivity of the carbene is the ability of the substituent to act as an electron donor (Table 7).

Table 7. Classification of Carbenes on the Basis of Reactivity toward Alkenes.[124b]

Nucleophilic	Ambiphilic	Electrophilic
$CH_3O\underset{\cdot\cdot}{C}OCH_3$	$CH_3O\underset{\cdot\cdot}{C}Cl$	$Cl\underset{\cdot\cdot}{C}Cl$
$CH_3O\underset{\cdot\cdot}{C}N(CH_3)_2$	$CH_3O\underset{\cdot\cdot}{C}F$	$Ph\underset{\cdot\cdot}{C}Cl$
		$CH_3\underset{\cdot\cdot}{C}Cl$

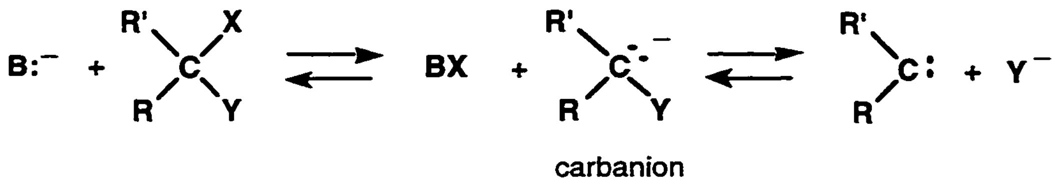
Although this chapter deals with highly reactive carbenes, practically all having short lifetimes, it is important to recognize that stable carbenes have been prepared,[125] and that divalent carbon ligands can be stabilized by coordination to transition metals (metal-carbenes).[126]

The Generation and Reactions of Carbenes

The mechanisms by which carbenes are generated from many precursors have not been fully investigated. However, two main pathways have been recognized:

1. Direct formation in an α elimination process via a carbanion.[127]

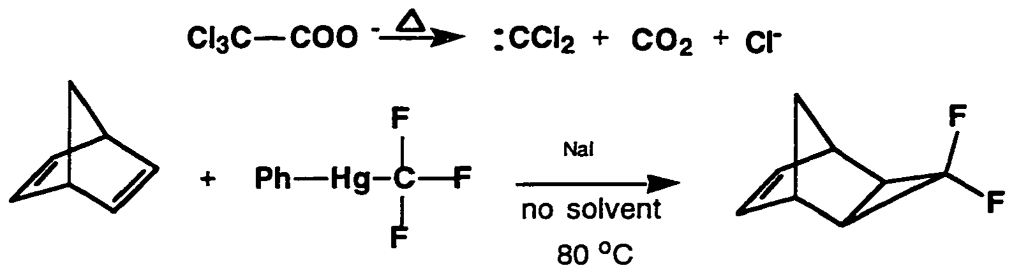
This denotes the removal of two substituents from the same carbon (Scheme 67).



Scheme 67

Examples

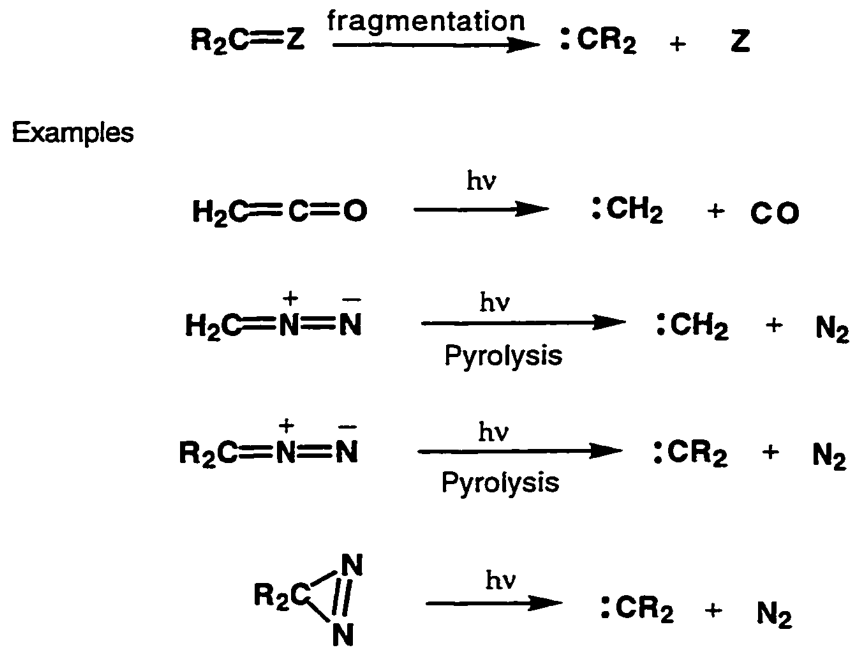
The reaction of chloroform with a base to yield dichlorocarbene is one of the most thoroughly investigated cases of α-elimination.[128a] Many other examples are known, two of which are shown in Scheme 68.[128b,c]



Scheme 68

2. Structures that fragment to give small stable molecules provide many important ways of forming $:CH_2$. Pyrolysis or photolysis of a ketene or diazomethane are sources of methylene (Scheme 69).[129] Alkylcarbenes can be generated by photolysis of diazirines .[130] In general, these methods

involve unstable substances which are difficult to work with.

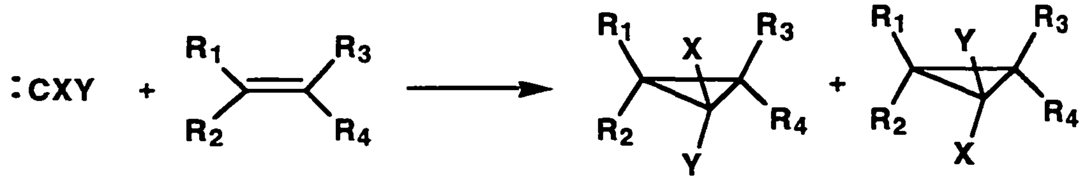


Scheme 69

The photolysis or thermolysis of diazoalkanes provides the most common general route to carbenes (Scheme 69). Carbenes formed by photolysis of diazoalkanes are highly energetic species, and their reactions may be indiscriminate. For example, the photolysis of diazomethane produces methylene, which can insert into primary, secondary, and tertiary C-H bonds of an alkane with almost equal ease, as well as adding to double bonds. For this reason, photolysis of the diazoalkane is not a good way of generating the carbene for kinetic measurements or synthetic purposes involving other molecules.

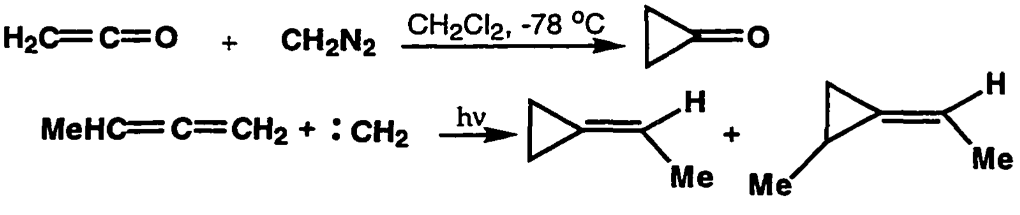
The reactions of carbenes are more varied than those of carbanions, carbocations, and radicals:

1. Addition Of Carbenes to Double and Triple Bonds. One of the most characteristic reactions of carbenes is their addition to olefins to give cyclopropane derivatives (1 + 2 cycloadditions) (Scheme 70).[131] The reaction, first reported by Doering and Hoffmann in 1954, has become an important method of synthesis of cyclopropanes and has been extended to other unsaturated systems, including ketenes, allenes, acetylenes, and aromatic compounds.



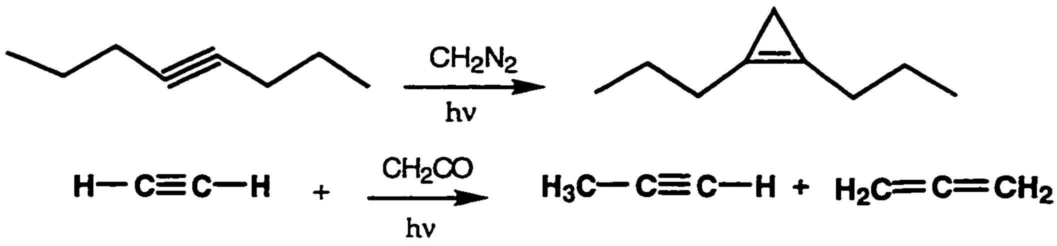
Scheme 70

Methylene from diazomethane adds to ketene to give cyclopropanones (Scheme 71).[132] It adds to allenes to yield methylenecyclopropane, and to methylallene to give the two possible alkylidenecyclopropanes (Scheme 71).[133]



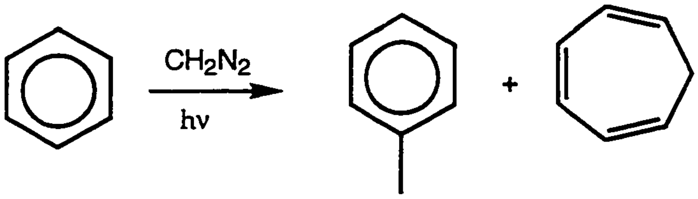
Scheme 71

Decomposition of diazomethane in acetylenes gives cyclopropenes,[134] but only allene and methyl acetylene were isolated on irradiation of diazomethane in acetylene-argon matrix (Scheme 72).[134b] Doering reported the addition of 2 moles of methylene to an alkyne to give a bicyclobutane.[135]



Scheme 72

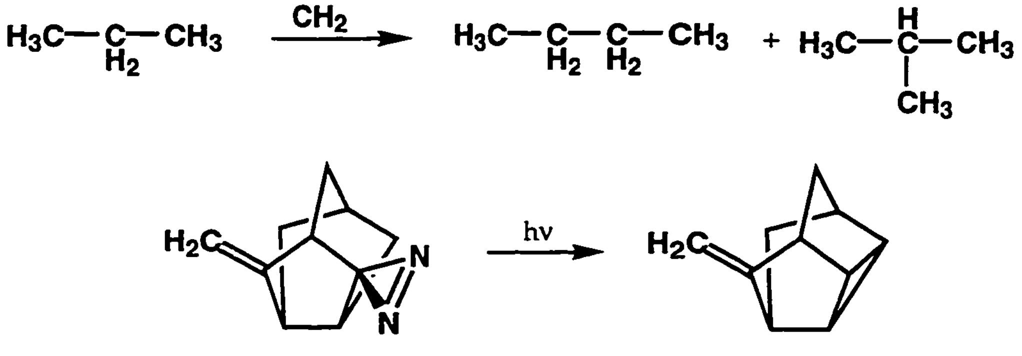
In general, the cycloadditions of the singlet carbenes are stereospecific and *syn*.[136] Skell rationalized this observation by pointing out that a singlet carbene could add to an olefin in a concerted manner.[136,137] Carbenes in the triplet state react nonstereospecifically.[138] Free rotation about the C-C bond of the diradical can occur faster than spin inversion.[137]



Scheme 73

The high reactivity of carbenes is also manifested in their addition reaction to aromatic systems, to give the products of ring-expansion.[139] Methylene reacts with benzene to give tropilidene and toluene in the ratio of ~3.5 (Scheme 73).[140]

2. Insertion Reactions of Carbenes. An unusual reaction of carbenes is that of insertion into C-H bonds. With methylene in the liquid phase, the insertion process is virtually indiscriminate,[141] and all types of C-H bond in a substrate are attacked in a nearly statistical ratio. Singlet methylene generated by photolysis of diazomethane is probably the most reactive organic species known. Triplet methylene is somewhat less reactive, and other carbenes are still less reactive. Some examples are given in Scheme 74. In the gas phase, there is some discrimination in favor of tertiary C-H bonds over secondary, and of secondary over primary. The selectivity of the carbene has been related to the amount of excess of energy with which it is generated, but

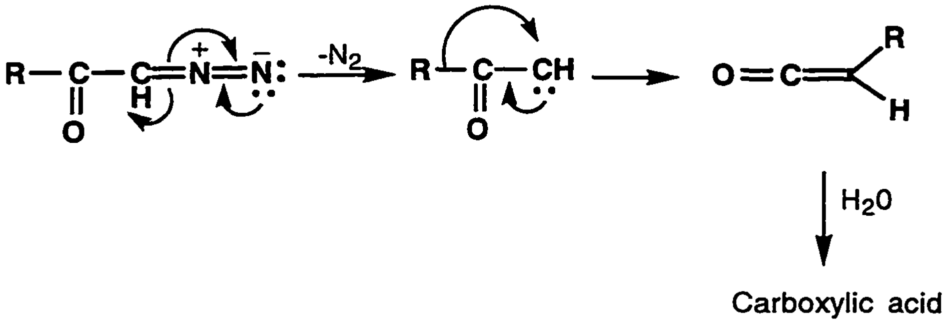


Scheme 74

also has been connected with the spin state of the carbene.[141] The following series of carbenes of decreasing reactivity has been proposed on the basis of discrimination between insertion and addition reactions: $CH_2 > HCCOOR > PhCH > BrCH \approx ClCH$. Insertion of carbenes into other bonds has been reported, including O-H, N-H, C-O, C-Cl, C-Si, though not insertion into C-C bonds.[142]

3. Skeletal Rearrangements. Many of the rearrangements that have been ascribed to carbenes are 1,2-shifts of hydrogen, alkyl or aryl groups. Indeed these rearrangements are generally so rapid that additions to multiple bonds and insertion reactions are seldom encountered with alkyl or dialkylcarbenes.[143] Most rearrangements of carbenes directly give stable molecules.

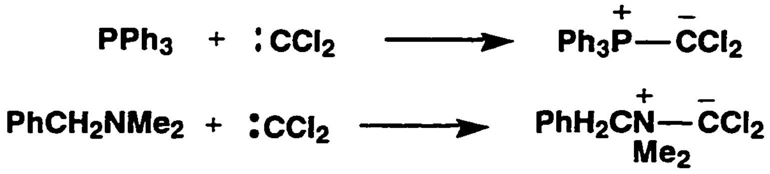
One important rearrangement of carbenes, from the synthetic point of view, is the Wolff rearrangement of diazoketones.[144] This reaction is the key step in the Arndt-Eistert synthesis of aliphatic carboxylic acids (Scheme 75).



Scheme 75

The initial product of the reaction is thus the ketene, which then reacts with water to give the carboxylic acid. Some other novel examples of skeletal rearrangement of carbenes will be discussed in the next section of this chapter.

4. Reaction with Nucleophiles. Carbenes can react with a variety of nucleophiles besides the nucleophilic olefins. Examples are known of reactions of carbenes with carbon, oxygen, nitrogen, sulfur, and phosphorous nucleophiles.[145] This usually involves a relatively stable carbene, such as dichlorocarbene. Scheme 76 shows some of these examples.



$$PPh_3 + :CCl_2 \longrightarrow Ph_3\overset{+}{P}-\overset{-}{C}Cl_2$$

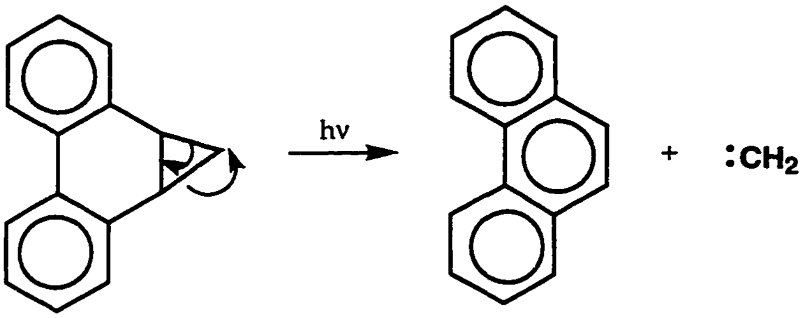
$$PhCH_2NMe_2 + :CCl_2 \longrightarrow PhH_2C\underset{Me_2}{\overset{+}{N}}-\overset{-}{C}Cl_2$$

Scheme 76

Results and Discussion

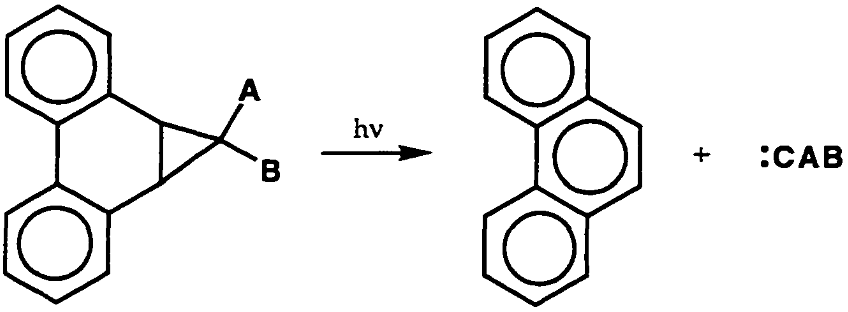
Cyclopropanated phenanthrenes give carbenes on photolysis. This photochemical cycloelimination [3→ 2 + 1] is usually described as a Griffin fragmentation.[146] The parent compound, benzo[a;c]bicyclo[4.1.0]heptane (**134**), was shown to yield methylene efficiently many years ago (Scheme 77).[147]

For the past several years our group has been interested in the development of a general route to carbenes from the phenanthrene platform. (Scheme 78). The goals of the project were set in the earlier stages of our



1 3 4 **1 3 5**

Scheme 77



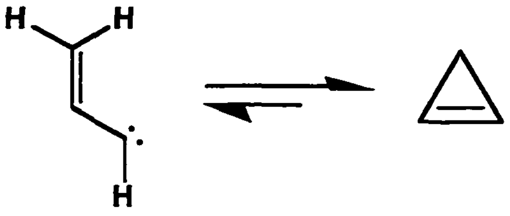
Scheme 78

investigation: 1) synthesis of cyclopropanated phenanthrenes as carbene precursors and identification of the primary photoproducts, and 2) studies on carbene kinetics in collaboration with the Platz group at Ohio State. Preliminary work by Kirchhoff and Abbot resulted in measurement of the first absolute kinetics for dichlorocarbene[148] and chlorocarbene,[149] respectively. The major advantage of this method is a clean photoextrusion which is indicated by formation of the corresponding carbene and phenanthrene as the principal products following irradiation. Another important characteristic of this approach is the possibility of generating only singlet carbenes.

In the present work, vinylcarbene, acyclic and cyclic vinylidenes were photogenerated. Alternative synthetic routes toward potential photochemical precursors of cyclopropylidenecarbenes were explored.

Photochemical Generation of Vinylcarbene (136) and Trapping of Cyclopropene (137)

The vinylcarbene (**136**) - cyclopropene (**137**) rearrangement (Scheme 79) is of considerable interest in preparative organic chemistry and therefore this reaction has been studied in some detail.[150]



136 **137**

Scheme 79

Photolysis of vinyldiazomethane in a variety of organic glasses at 6 °K produced vinylcarbene in its triplet ground state.[151] *Cis/trans* stereoisomers have been identified by EPR spectra (Figure 19); ratios varied from 0.65 to 0.05. In the dark, the vinylmethylenes are stable between 6° and 15 °K. For

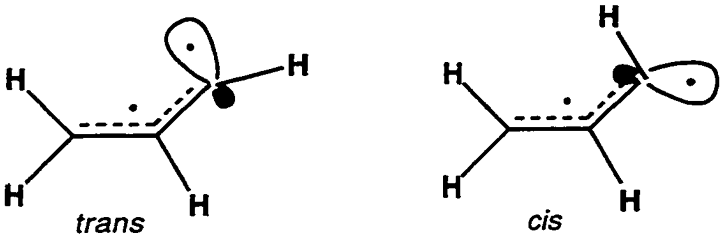


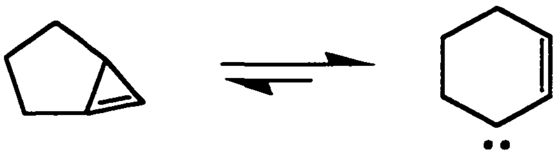
Figure 19. Stereoisomers of vinylcarbene

the *cis/trans* vinylmethylenes of the singlet state, the structures represent local minima on the C_3H_4 surface.[152]

Chapman reported that when nitrogen/argon matrices containing the stereoisomeric triplet vinylmethylenes were warmed (T° > 10 °K), the ESR signals shifted, broadened, and disappeared. On cooling back to 10 °K, the ESR signals reappeared. This reversible loss was attributed to the thermal population of the singlet state lying just above the triplet state.[153]

The activation energy for the cyclopropene-vinylcarbene rearrangement is on the order of 30-40 kcal/mol,[154] depending on the degree of substitution, and the equilibrium greatly favors the cyclopropene. When cyclopropenes are incorporated into small fused systems, the equilibrium is shifted in favor of the vinylcarbene (Scheme 80).[155] Thus, **138** and its derivatives open thermally to give cyclohexylidenes **139** which have been trapped in solution in several cases.[155]

Cyclopropene (**137**) is a potentially explosive gas (bp -36 °C), was first

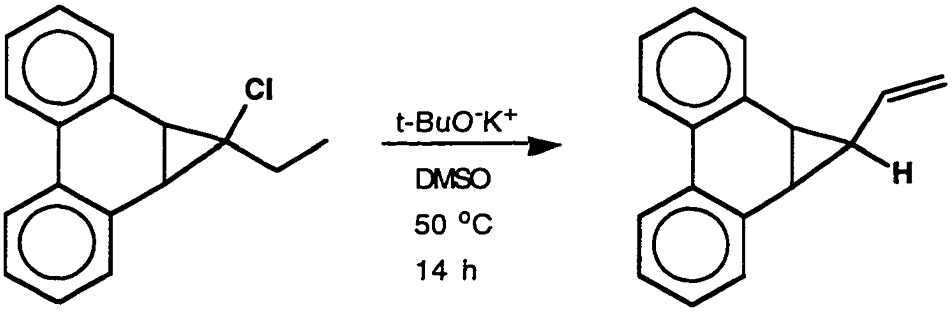


1 3 8　　　　**1 3 9**

Scheme 80

reported in 1922.[156] The length of the double bond is 1.296 Å, and its strain energy has been estimated to be 54.5 kcal/mol.[157] While the increased angle strain of the σ molecular framework contributes to its destabilization, it is release of ring strain which drives reactions of cyclopropene. A manifestation of this reactivity is seen in the tendency of the molecule to polymerize with explosive violence at room temperature.[157]

Our interest in vinylcarbene studies led Abbot[158] to prepare precursor **141** from adduct **140** by elimination of HCl with potassium *tert*-butoxide in DMSO at 50 °C (Scheme 81). The major product of this reaction is the *endo*

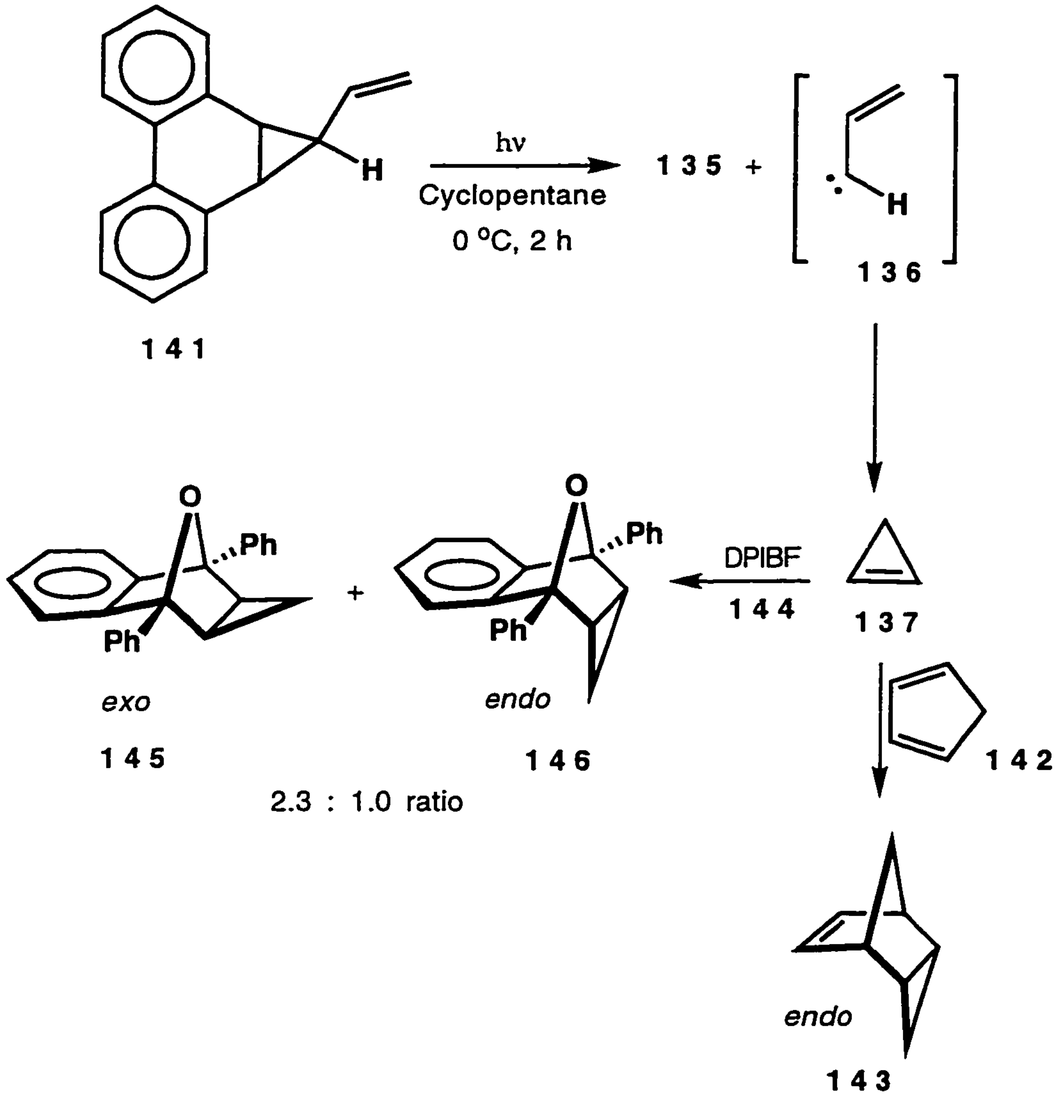


1 4 0　　　　**1 4 1**

Scheme 81

vinyl isomer **141** as indicated by the 8.8 Hz coupling constant for the bridgehead protons. Presumably, this reaction proceeds by E_2 elimination, followed by isomerization of the double bond.

Low temperature irradiation of **141** (Scheme 82) in N_2-saturated cyclopentane (C_5H_{10}) for 2 hours, followed by addition of freshly distilled 1,3-



Scheme 82

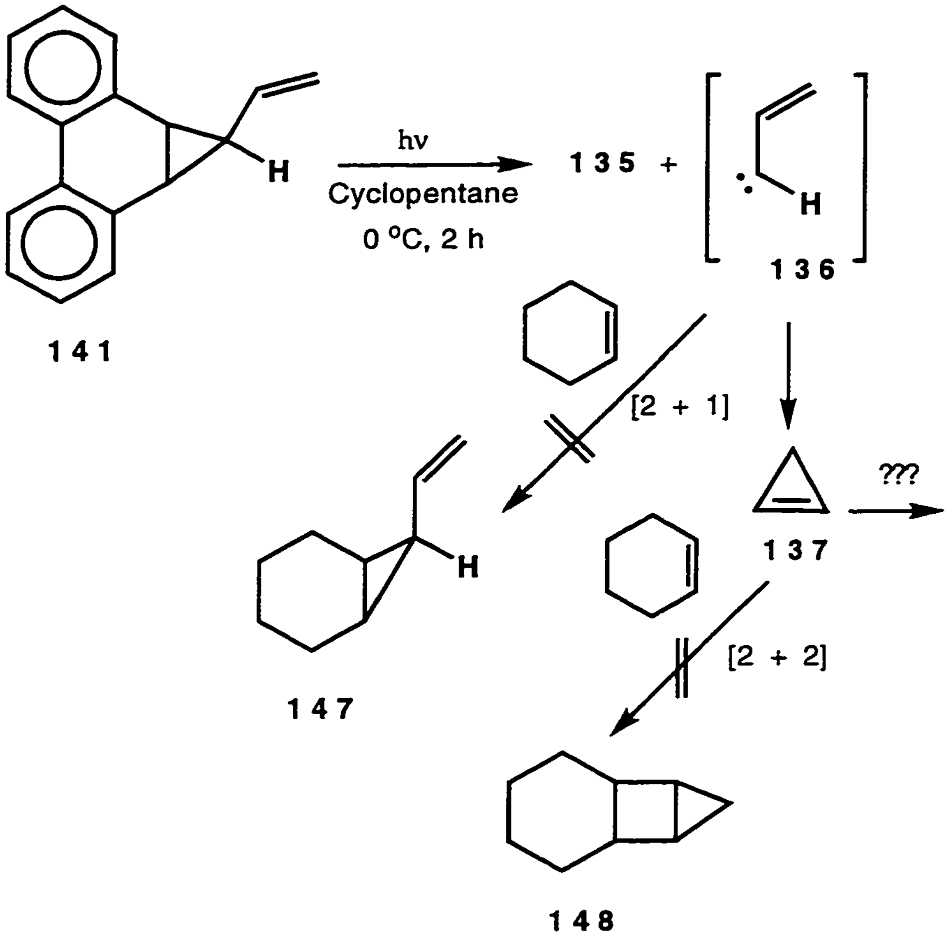
cyclopentadiene (**142**) gives phenanthrene (**135**) plus the expected *endo* cyclopropene adduct **143**.[159] Adduct **143** is formed in 62% yield with respect to phenanthrene, as indicated by ^{1}H-NMR integration. Capillary GC (T° program, $T_i = 70$ °C, $T_f = 200$ °C) analysis of the crude mixture indicated the presence of three components, *endo* -adduct **143** (rt 3.0 min), 1,3-cyclopentadiene dimer (rt 7.6 min), and phenanthrene (rt 16.9 min). GC retention time for **143** was compared with an authentic sample independently synthesized by the Closs procedure.[159]

When a saturated solution of diphenylisobenzofuran (**144**) in toluene was added after irradiation, *exo-* and *endo*-cyloadducts (**145** and **146**)[160] were formed in 2.3:1.0 ratio, in 96% yield, with respect to phenanthrene. Spectral data for all three cycloadducts were compared to the literature values.[159,160]

Irradiation of **141** in the presence of cyclohexene did not yield [2 + 1] cycloadduct **147** (Scheme 83). Neither was there evidence for cycloadduct **148**, which could have been formed by [2 + 2] cycloaddition reaction.

These results indicate a clean photoextrusion of vinylcarbene (**136**) from **141**, and a rapid rearrangement of **136** to cyclopropene (**137**) which is trapped in $[_{\pi}2_s + _{\pi}4_s]$ cycloaddition reactions to yield adducts **143, 145** and **146.**

It is known that **137** and many substituted cyclopropenes[161] add to dienes with predominant *endo* selectivity in agreement with Alder's "*endo*



Scheme 83

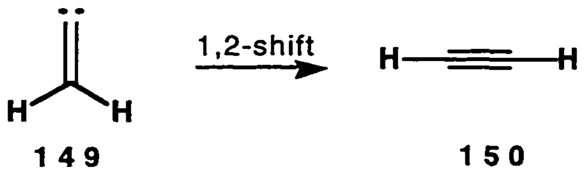
rule".[162] As Wiberg had reported some 37 years ago, the reaction of **137** with cyclopentadiene affords exclusively *endo* -adduct **143.**[161c] Our results are in agreement with these previous observations.

The reaction of **137** with diphenylisobenzofuran (DPIBF) had already been studied.[160, 163] The discrepancies concerning the exclusive formation of *endo* -adduct **143** and the preponderant formation of *exo* -adduct **145** have been explained in terms of possible differences in the potential energy surfaces for the Diels-Alder reactions.[160,163]

Synthesis of Precursors to Simple Vinylidenes and Photogeneration of 1-Nonyne

Vinylidene and related unsaturated carbenes are highly reactive ground-state singlet carbenes.[164] Lineberg and co-workers observed :C=CH_2 (**149**) spectroscopically, the simplest unsaturated carbene.[165] Vibrational structure in the spectrum yielded frequencies for the scissors bend and C-C stretch of 1120 and 1650 cm^{-1}, respectively. Singlet vinylidene was calculated to be a shallow minimum on the C_2H_2 surface.[166]

Vinylidenes undergo rapid thermal 1,2-shifts to yield the corresponding acetylenes. This reaction determines the lifetime of these carbenes in many cases. The activation energy for the rearrangement of vinylidene to acetylene (Scheme 84) is very small. One of the most recent values obtained by means of high level *ab initio* theory is 2.16

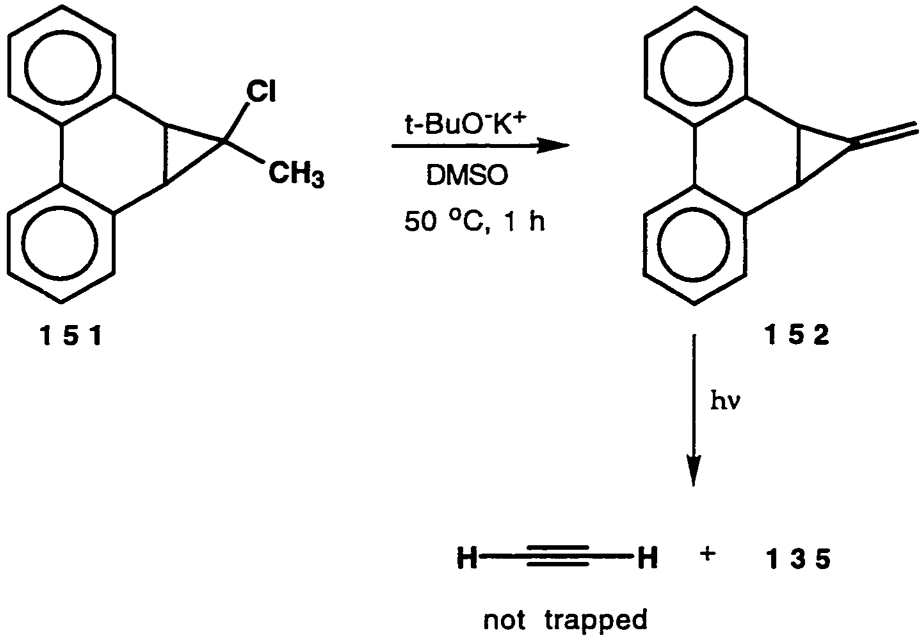


Scheme 84

kcal/mol while the experimental value is 2 kcal/mol.[167] The energy change of the reaction has been estimated to be -43.9 kcal/mol.[167] Several gas-phase studies on vinylidenes have been published, but because of the low barrier toward rearrangement, matrix isolation has not been possible. Due to the lack of appropriate photochemical precursors, only a few direct experimental observations of vinylidenes have yet been reported.

We were interested in photochemical vinylidene precursors that may allow kinetic studies, detection of the rearranged product in solution phase by common spectroscopic techniques, and a possible direct observation of vinylidenes.

Abbot[158] was able to prepare vinylidene precursor **152** by treatment of adduct **151** with potassium *tert-* butoxide in DMSO at 50 °C (Scheme 85).



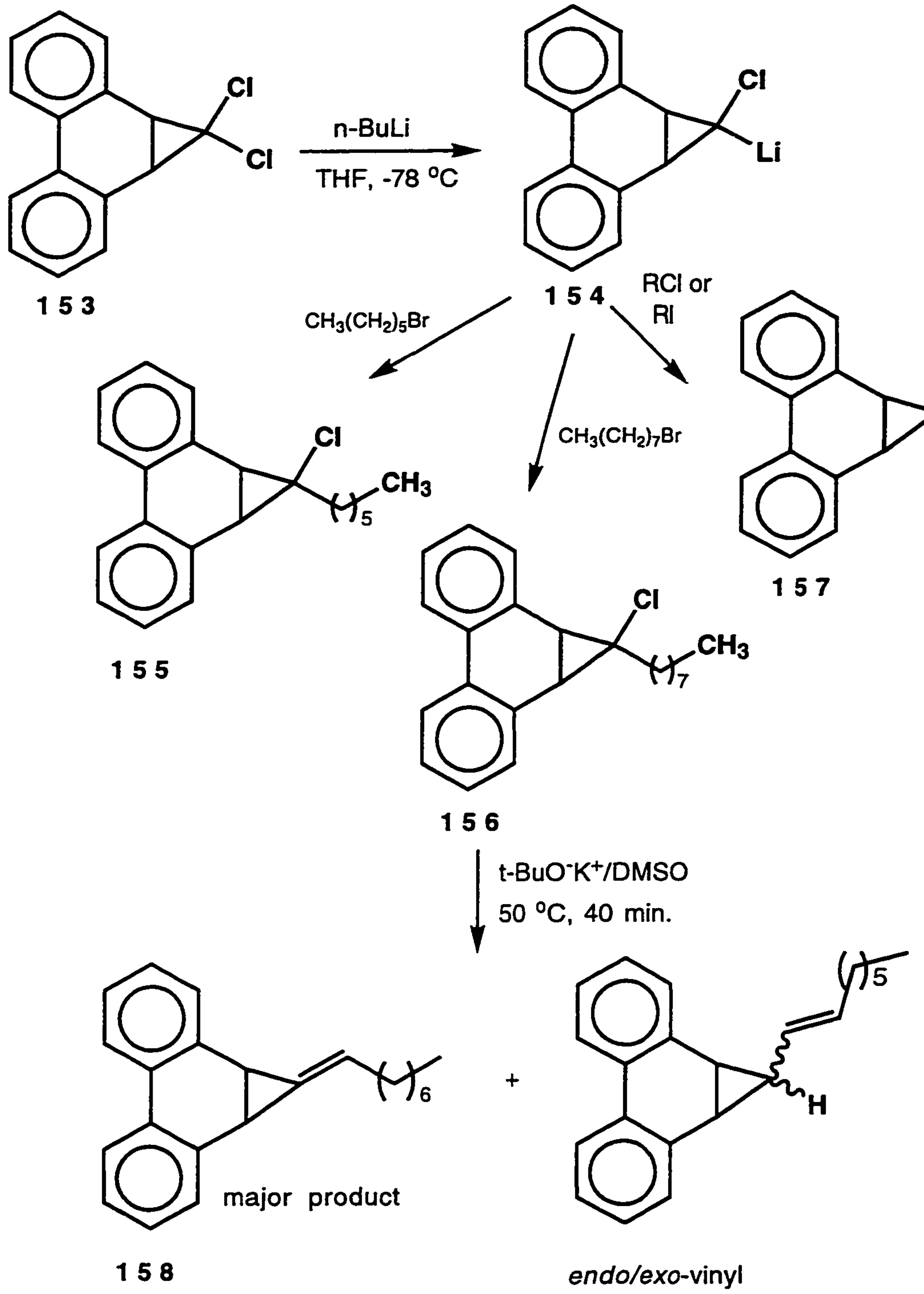
Scheme 85

Preliminary photolysis of **152** at 254 nm for 1 hour afforded phenanthrene (**135**). However, no evidence for vinylidene formation was obtained. Thus, it was thought that vinyldene precursors with longer alkyl chains might facilitate identification of the photoproducts, establishing in this way vinylidene formation from cyclopropanated phenanthrene precursors.

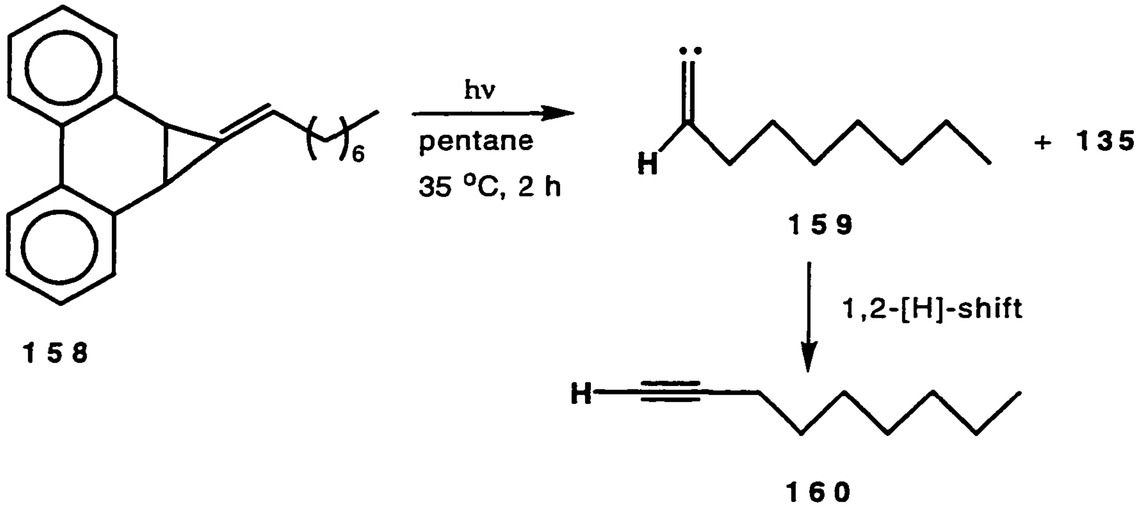
Alkylcyclopropane adducts **155** and **156** (Scheme 86) were prepared by reaction of dichlorocarbene adduct **153** with *n*-butyllithium in THF at -78 °C, followed by electrophilic quenching of the carbenoid **154** with bromohexane and bromooctane, respectively. We found that bromoalkanes effectively gave the desired alkylated products, while chloroalkanes or iodoalkanes yielded monochloro adduct **157** as the major reaction product.

Elimination of HCl from **156** (Scheme 86) to give the potential vinylidene precursor **158** followed a similar protocol to that employed by Abbot for the preparation of **152**. Treatment of adduct **156** with *tert*-butoxide in DMSO at 50 °C for 40 min afforded **158** as the major reaction product, plus the two vinyl stereoisomers in a 3.5:1.1:2 ratio. Preparative TLC gave adduct **158** in 55% yield (> 95% pure). The IR spectrum of **158** shows strong absorptions at 3069, 2930, 2855 cm^{-1} and a weak band at 1601 cm^{-1}.

Photolysis of **158** (Scheme 87) in pentane for 2 hours gave a colorless solution. Capillary GC (T° program, $T_i = 80$ °C, $T_f = 200$ °C) analysis of the photolyzed solution indicated the presence of 1-nonyne (**160**, rt, 3.1 min), and phenanthrene (**135**, rt, 16.5 min). Retention times were compared with


Cl
Cl
n-BuLi
THF, -78 °C
Cl
Li
1 5 3
1 5 4
RCl or RI
CH3(CH2)5Br
CH3(CH2)7Br
Cl
CH3
5
Cl
H
1 5 7
1 5 5
Cl
CH3
7
1 5 6
t-BuO-K+/DMSO
50 °C, 40 min.
6
+
5
H
major product
1 5 8
endo/exo-vinyl

Scheme 86



158

159

160

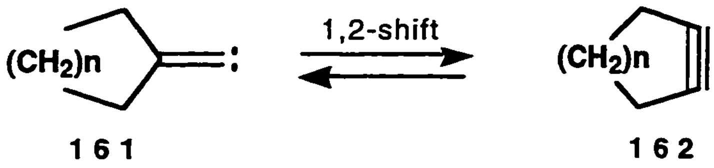
Scheme 87

authentic samples of 1-nonyne and phenanthrene. ^{1}H-NMR and ^{13}C-NMR spectra of the crude mixture were consistent with the GC analysis. Comparison of the calibrated response (three runs average of 1 μL) for 1-nonyne and phenanthrene in the irradiated solution, versus the averaged responses for 1-nonyne and phenanthrene in a freshly prepared standard solution, indicated that 1-nonyne (**160**) and phenanthrene (**135**) had been formed in 94% and 98% yield, respectively.

Ample literature supports the conclusion that 1-nonyne (**160**) is formed from vinylidene **159** by 1,2-[H]-shift.[164-167] Carbene **159** is generated from **158** by a cycloelimination [3 → 2 + 1] reaction[146] which also gives phenanthrene (**135**) in a nearly quantitative yield.

Cyclic Vinylidenes

An important carbene rearrangement that has been the subject of diverse experimental and theoretical investigations is the cycloalkylidenecarbene (**161**)-cycloalkyne (**162**) rearrangement (Scheme 88).[37d,e,39,168] The first systematic theoretical study for interconversions of



Scheme 88

C_4 to C_6 cycloalkynes with their isomeric cycloalkylidenemethylenes was published by our group in 1995.[39] This study addressed many questions left unanswered by previous work and provided accurate predictions for structures and barrier to rearrangements. Some of these results are summarized in Table 8. *Ab initio* calculations indicate that the barrier for 1,2-shift should increase with ring size. Thus, cyclobutylidenecarbene (**163**) should rearrange readily. Previous experimental studies have shown that cyclopentylidenecarbene (**164**) and cyclohexylidenecarbene (**180**) do not rearrange as readily as cyclobutylidenecarbene, in agreement with calculations.[37e,168d,169]

In order to verify that theory and experiments were looking at the same species, we carried out a systematic experimental study to investigate

Table 8. *Ab Initio* Estimates for Interconversion of Cycloalkylidenes and Cycloalkynes. Values are in kcal/mol.[39]

163 **13**

($E_{Rel} = 0.0$)		
MCSCF/6-31G*	15.2	-7.81
MP4/6-31G*	4.07	-7.98

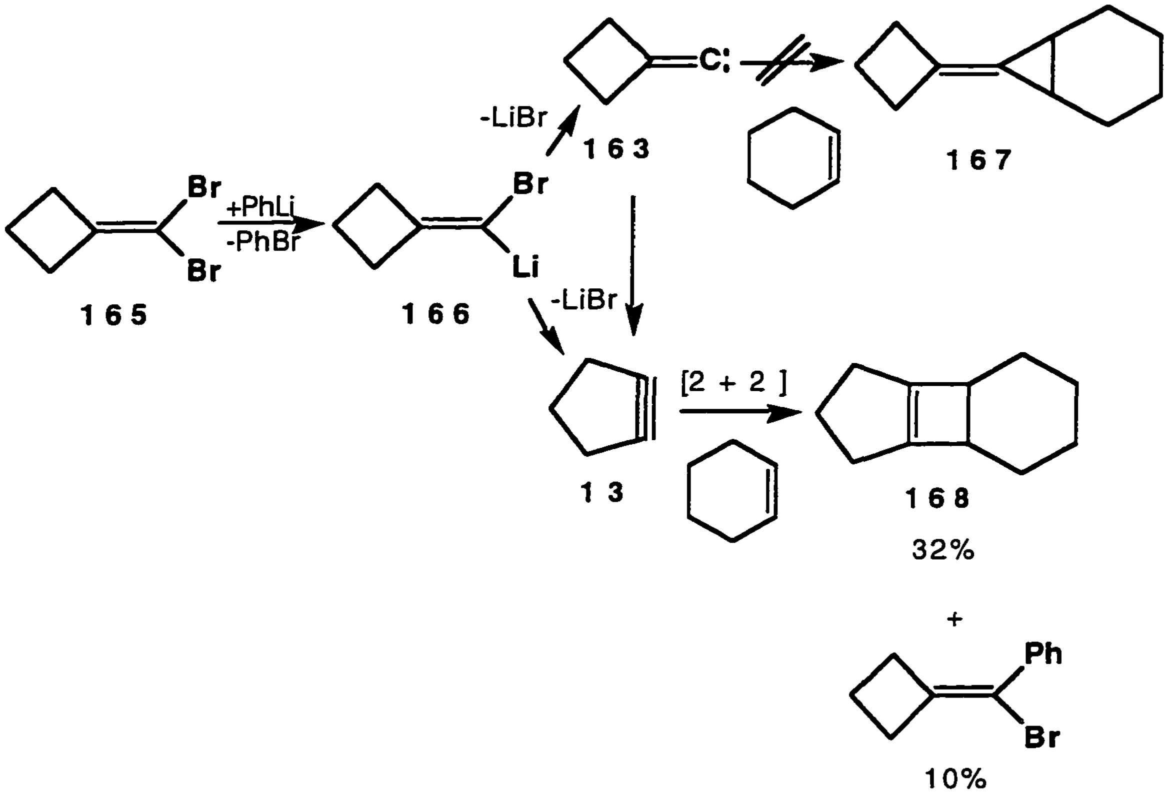
164 **14**

($E_{Rel} = 0.0$)		
MCSCF/6-31G*	23.5	-14.7
MP4/6-31G*	11.03	-17.7

the reactivity of C_5 to C_7 cycloalkylidenemethylenes. No photochemical precursors to these important vinylidenes are known! The synthesis of cyloalkylidenecarbene precursors and their exploratory photochemistry are described below.

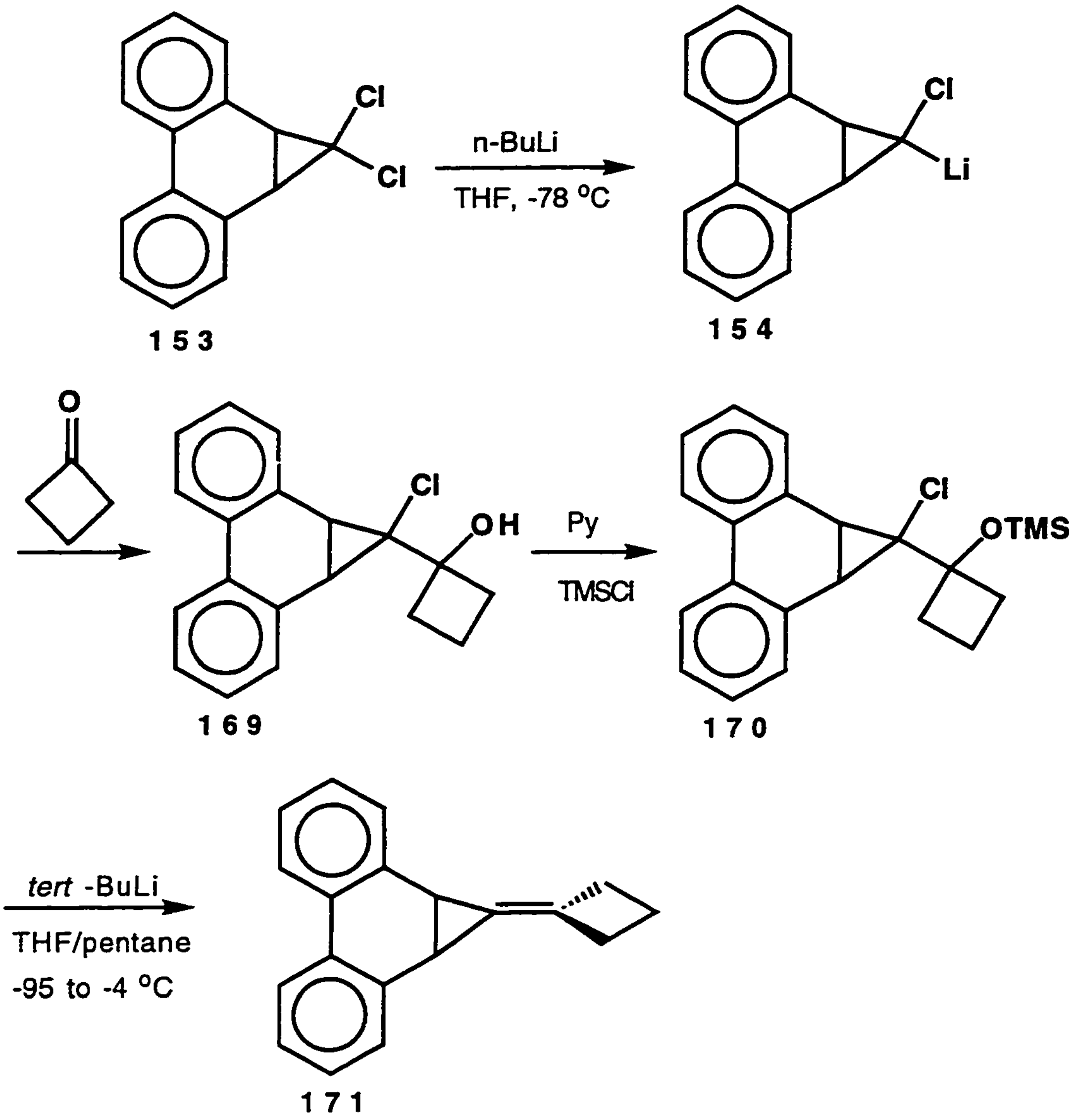
Synthesis of a Cyclobutylidenecarbene Precursor (171) and Trapping of Cyclopentyne (13).

Cyclopentyne (**13**) is relatively well known and often is prepared by the intermediacy of carbene **163** (Table 8).[34,37d,e,169] Fitjer[37e] found that **13** could be generated from dibromomethylenecyclobutane **165** (Scheme 89). Instead of the expected **167**, thought to be formed by [2 + 1]-cycloaddition of cyclobutylidenecarbene (**163**) with cyclohexene, the isomeric tricyclo $[6.3.0.0^{2,7}]$undec-1(8)-ene (**168**) was isolated. Thus, this work established the thermal interconversion of **163** to **13**, but it did not rule out direct formation of cyclopentyne from carbenoid **166**.



Scheme 89

Our interest in systematically studying the rearrangement prompted us to prepare precursor **171** (Scheme 90) which was expected to be a potential photolytic source of carbene **163**, and, therefore, of cyclopentyne. The

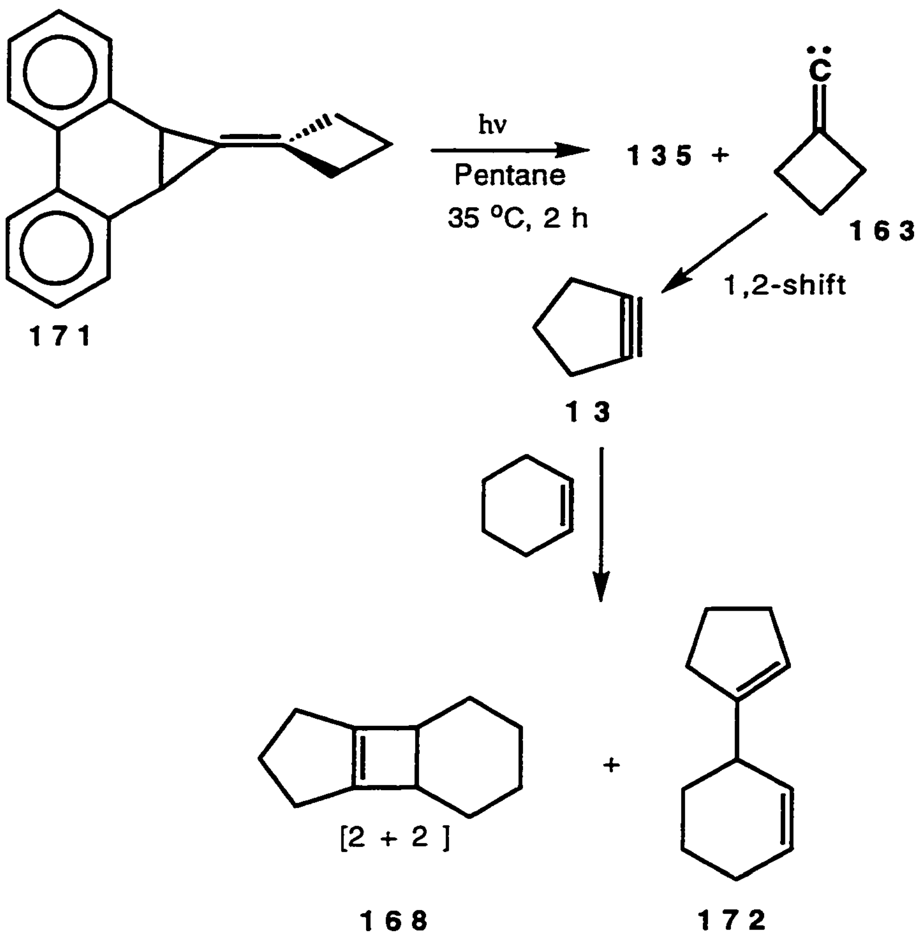


Scheme 90

synthetic strategy to structure **171**, was based on an approach reported by Seebach for the preparation of methylenecyclopropanes.[170] Reaction of dichlorocarbene adduct **153** with *n*-butyllithium gave carbenoid **154** (Scheme 90). Electrophilic quenching of **154** with cyclobutanone afforded small white crystals of chlorohydrin **169** in 56% yield after radial chromatography. Treatment of **169** with TMSCl in dry pyridine smoothly gave TMS-ether **170** in 46% yield (Scheme 90).

1,2-Elimination of TMSOLi was accomplished by reaction of **170** with *tert*-butyllithium at -95 °C in THF/pentane, followed by warming to -4 °C (Scheme 90). Purification of adduct **171** proved to be difficult, due in part to the rapidity with which it decomposed at warm temperatures. However, careful preparative TLC of the crude product furnished **171** in 37% yield (~ 95% pure). Spectral data for **171** include a narrow quintet at δ 3.10 (bridgehead protons), two symmetrical multiplets at δ 2.79 and δ 2.53 for the diastereotopic protons of the cyclobutylidene ring, a symmetrical multiplet at δ 1.90, three multiplets at δ 7.20-7.27, δ 7.31-7.38 and δ 7.90-8.00 (aromatic protons) in the ^{1}H-NMR, 11 resonances in the ^{13}C-NMR, a weak absorption band at 1605 cm^{-1} in the IR for the stretching frequency of the C=C bond, and a molecular ion peak (M$^+$) of *m/z* 244 in the HRMS, consistent with a molecular formula of $C_{19}H_{16}$.

Irradiation of a pentane solution of **171** and cyclohexene was performed at 254 nm for 2 hours (Scheme 91). Capillary GC (T° program, T_i = 80 °C, T_f = 200 °C) analysis of the irradiated solution indicated the presence of three major components, which were identified as **172** (rt 11.92 min), **168** (rt 11.95 min), and phenanthrene (**135**, rt 16.5 min). Chromatography (Florisil,

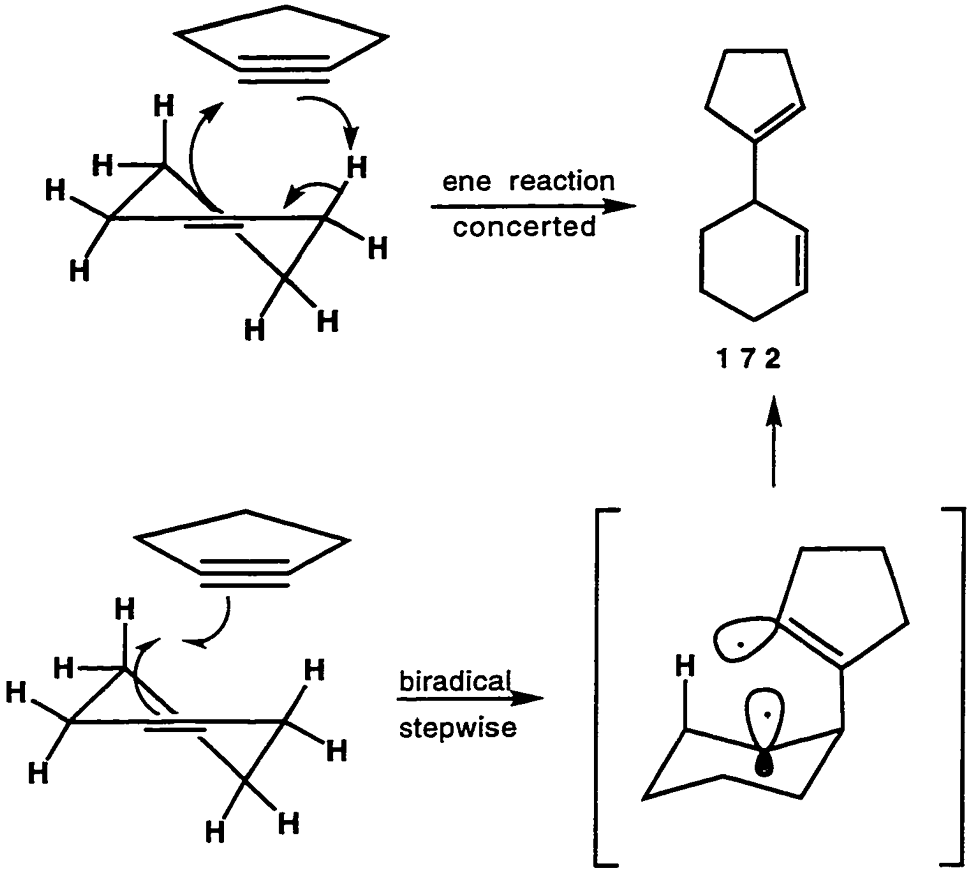


Scheme 91

pentane) afforded a 1.2:1.0 mixture of isomers **168** and **172** as colorless liquids in 66% isolated yield. The presence of the [2 + 2] cycloadduct **168** was confirmed by comparison of its ^{1}H-NMR, ^{13}C-NMR, and MS spectral data to the literature values.[37e] ^{1}H-NMR, ^{13}C-NMR spectral data for the other isomeric component **172** was obtained by subtraction of chemical shifts from the known spectral data of tricyclic **168** and the structure was assigned by spectral analysis. The ^{1}H-NMR of **172** shows an AB system at δ 5.69 (two vinyl protons in the cyclohexenyl-ring), a symmetrical multiplet at δ 5.36 (vinyl proton in the cyclopentenyl-ring), four well resolved multiplets at δ 2.88-2.85, 2.32-2.23, 1.99-1.96, and 1.56-1.49. The ^{13}C-NMR exhibits eleven lines (C_1 symmetry) at δ 148.3, 130.1, 127.3, 123.5, 37.5, 33.7, 32.5, 28.1, 25.4, 23.6, 21.2. The DEPT 135 displays ten lines, consistent with three CH (sp^2 carbons), a CH (sp^3 carbon) and six methylenes (CH_2, sp^3 carbons). GCMS (EI) analysis of **172** gives *m/z* = 148 for the molecular ion peak (M^+), consistent with a molecular formula of $C_{11}H_{16}$. These data securely characterize the structure of isomer **172**.

These results suggest a clean photogeneration of carbene **163** from precursor **171**. Cyclobutylidenecarbene (**163**) rearranges readily to cyclopentyne (**13**) which undergoes a [2 + 2] cycloaddition with cyclohexene to give the known tricyclic **168**. These observations are in agreement with a low calculated activation barrier of 4.07 kcal/mol for the carbene-cycloalkyne rearrangement.[39]

A major second product from photolysis of **171** is isomer **172**. This isomeric component isolated might result from a concerted, "ene reaction" between cyclopentyne and cyclohexene (Scheme 92). Levin[31b] has pointed out the absence of an ene component in previous reported reactions of cyclopentyne. This absence was explained in terms of an increased biradical character of **13**, and inversion of the HOMO-LUMO ordering such that the antisymmetric A combination (Figure 20a) is located at a lower energy than the symmetric S wave function (Figure 20b), precluding a concerted, suprafacial ene reaction from taking place. However, this description of cyclopentyne is inconsistent with MCSCF calculations carried out in our own group.



Scheme 92

An alternative and more likely mechanism for the formation of isomer **172** is a stepwise biradical process (Scheme 92). Stepwise addition gives a diradical which can undergo intramolecular disproportionation. The

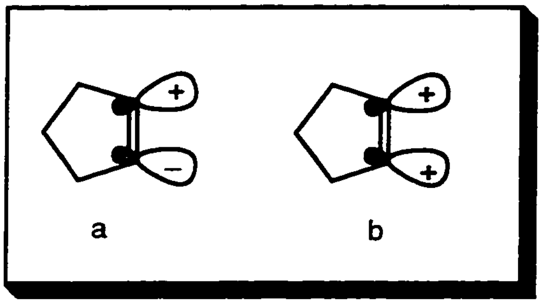


Figure 20. Proposed antisymmetric/symmetric cyclopentyne wave functions

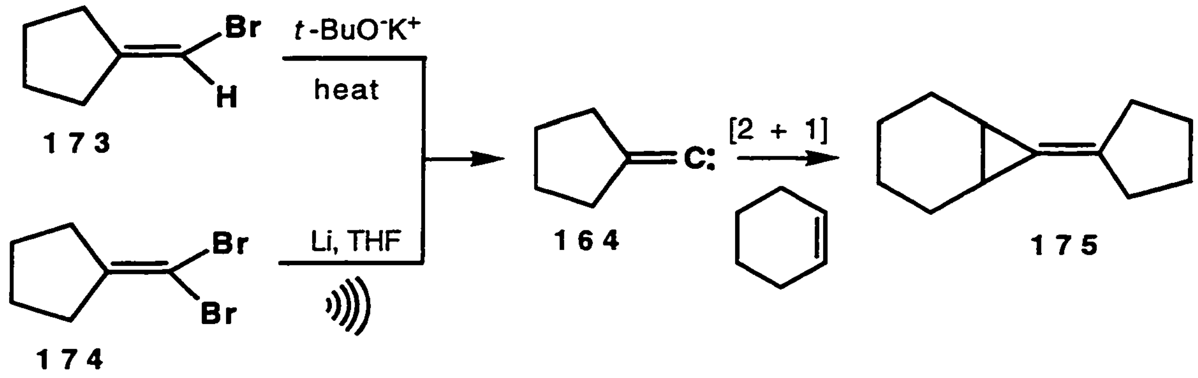
biradical process would be a higher energy pathway since formation of a vinyl radical is involved, but may account for formation of both isomers. Gilbert[37d,168c] has proposed antarafacial participation of cyclopentyne in a concerted cycloaddition for formation of the [2 + 2] cycloadducts of cyclopentyne with olefins.

It would clearly be of interest to better understand the structure-reactivity relationship of this novel strained hydrocarbon. Only further mechanistic studies will elucidate the origin of **172**. Also, it will be necessary to carried out in our laboratory Fitjer's cyclopentyne synthesis,[37e] before reaching any final conclusion about the reactivity of cyclopentyne. An independent synthesis of compound **172** is also highly desirable.

Comparison of the calibrated response (2,7-dimethylnaphthalene added as internal standard) for phenanthrene in the irradiated solution versus the calibrated response for phenanthrene in a freshly prepared standard solution, indicated nearly quantitative formation of phenanthrene (95.5%), which supports a clean photodecomposition of precursor **171** to generate cyclobutylidenecarbene (**163**).

Synthesis of a Cyclopentylidenecarbene Precursor (178) and Photogeneration of a C_6 Vinylidene.

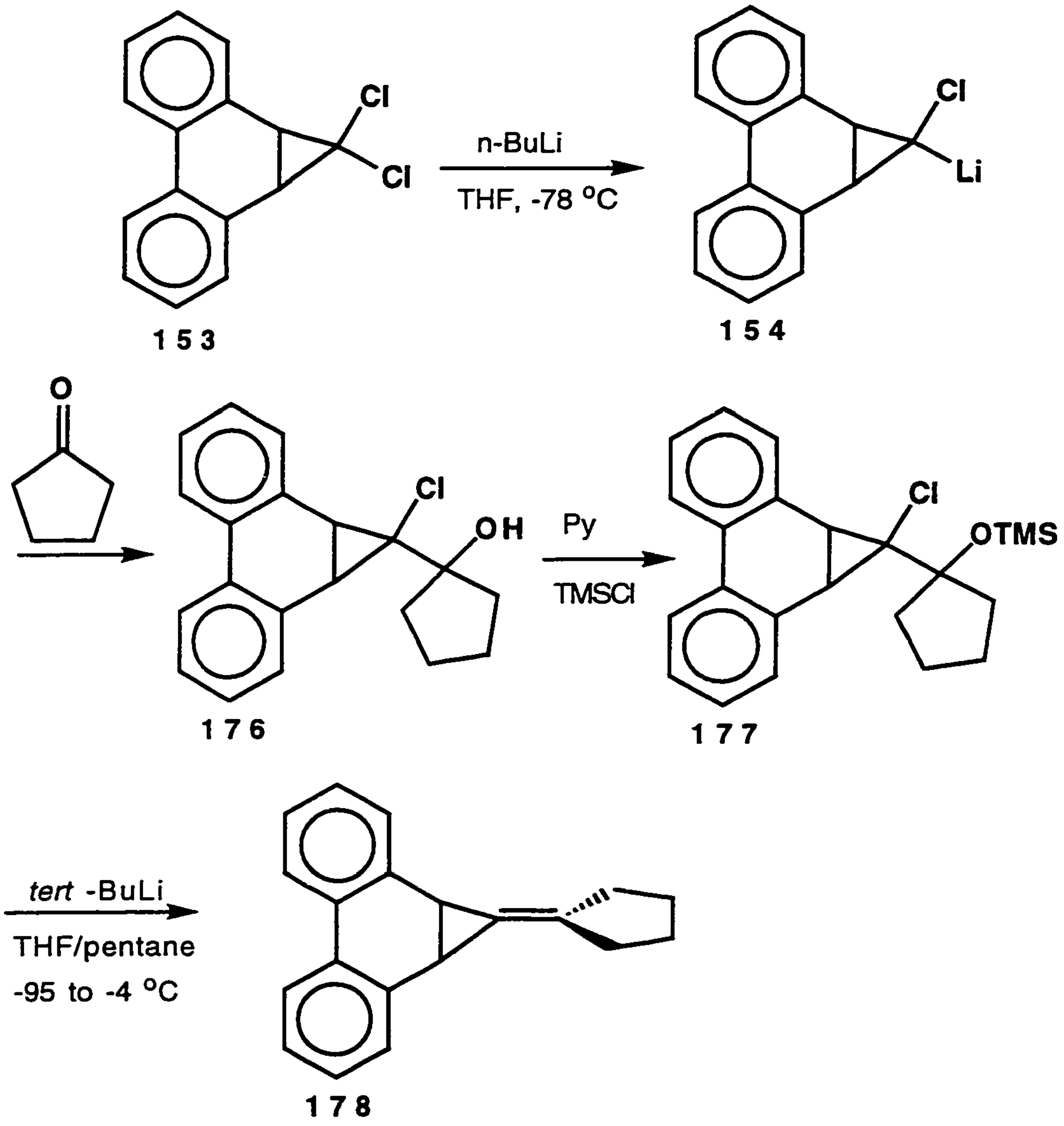
The next target in the series C_5-C_7 was cyclopentlylidenecarbene (**164**). Carbene **164** has been previously reported in several experimental studies.



Scheme 93

In 1965 Wolinsky and co-workers reported formation of **164**, when bromomethylenecyclopentane (**173**) was heated with strong base (Scheme 93).[171] The [2 + 1] cycloaddition product **175** was isolated. Brinker prepared **164** by ultrasonication of **174** with lithium (Scheme 93).[169] To date, no literature reports concerning photochemical generation or kinetic studies of **164** have appeared.

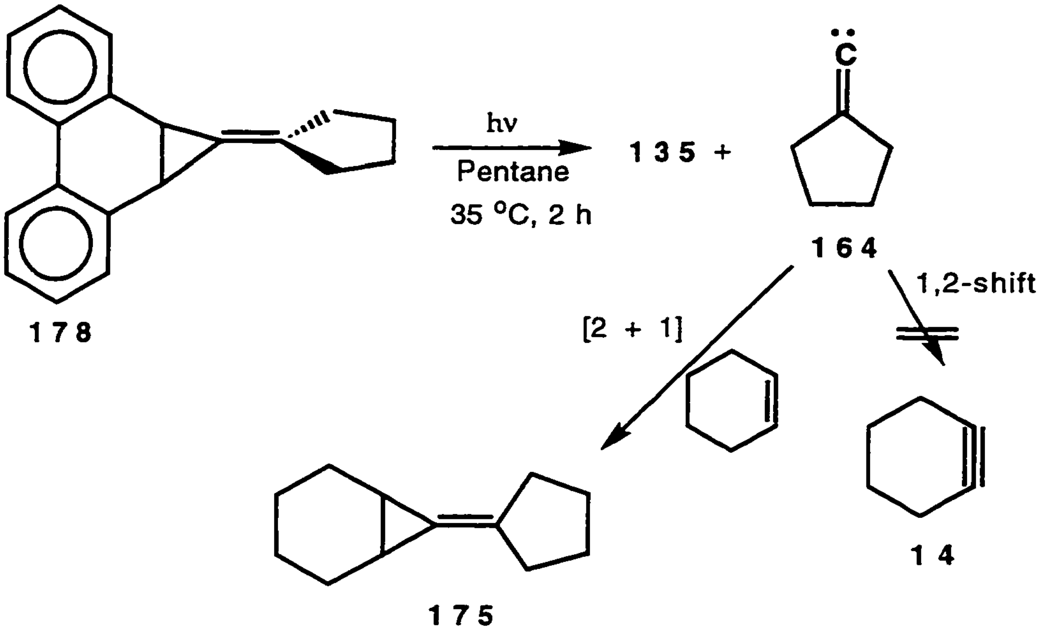
We envisioned photogeneration of cyclopentylidenecarbene (**164**) from precursor **178** (Scheme 94). Preparation of **178** was accomplished following a similar protocol for formation of **171**. Lithium-halogen exchange between dicholoro adduct **153** and *n*-butyllithium yields carbenoid **154** which was quenched with cyclopentanone to give chlorohydrin **176** in 53% yield after radial chromatography. Deprotonation of **176** with pyridine followed by addition of TMSCl furnished TMS-ether **177** as a white solid in 62% yield (Scheme 94).



Scheme 94

Reaction of *tert*-butyllithium[170] with substrate **177** in a liquid nitrogen cooled mixture of THF/pentane, and slow warming to -4 °C gave alkene **178** in 30% yield after preparative TLC purification (silica gel, hexane) (Scheme 94). Spectral data for **178** include a narrow quintet at δ 3.07 (bridgehead protons), two pairs of diasterotopic protons which appear as symmetrical multiplets at δ 2.45, 2.10, 1.62 and 1.53, three multiplets at δ 7.20-7.27, δ 7.31-7.38 and δ 7.90-8.00 (aromatic protons) in the ^{1}H-NMR spectrum, a weak absorption band at 1601 cm^{-1} in the IR for the stretching frequency of the C=C bond, and a molecular ion peak (M^+) of m/z = 258 in the mass spectrum, consistent with a molecular formula of $C_{20}H_{18}$.

Continuing our photochemistry studies on interconversion of cycloalkylidenecarbenes to cyloalkynes, a pentane/cyclohexene solution of **178** was irradiated at 254 nm for 2 hours (Scheme 95). The reaction was monitored by TLC. Capillary GC (T° program, T_i = 120 °C, T_f = 200 °C) analysis of the irradiated solution indicated the presence of two major components; these were identified as 7-cyclopentylidenebicyclo[4.1.0]heptane (**175**, rt 5.8 min), and phenanthrene (**135**, rt 14.3 min). Comparison of the calibrated response (2,7-dimethylnaphthalene added as internal standard) for phenanthrene in the irradiated solution versus the calibrated response for phenanthrene in a freshly prepared solution, indicated that phenanthrene (**135**) had been formed in 94% yield. Adduct **175** was obtained in 62% isolated



Scheme 95

yield as a colorless liquid after chromatography (Florisil, pentane). Spectral data for **175** include four multiplets at δ 2.35-2.28 (allylic protons), 1.73-1.60, 1.55-1.50 (bridgehead protons) and at δ 1.22-1.15 in the ^{1}H-NMR, seven lines in the ^{13}C-NMR, a molecular ion peak (M^+) of *m/z* = 162 and a base peak at *m/z* = 91. Spectral data were compared with Brinker's reported values.[169]

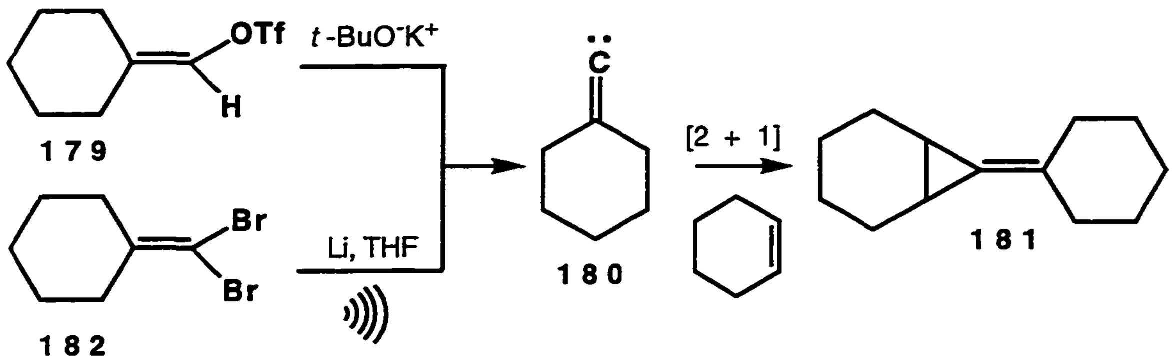
The results of photolysis of **178** (Scheme 95) are in good agreement with expectations based on the calculated activation barrier for 1,2-shift (Table 8). Substrate **178** undergoes photocycloelimination [3→2 + 1] to give phenanthrene (**135**) and carbene **164**. Due to a relative high activation barrier

164 does not readily rearrange to the strained cylohexyne (**14**), but is trapped instead with cyclohexene in a [2 + 1] cycloaddition to give the known adduct **175**. The relative rate of this rearrangement also agrees with previous experimental observation.[169,172]

Although the predicted total strain energy for cyclohexyne is less than that for cyclopentyne (41 vs 74 kcal/mol), and the calculated exothermicity of the carbene-cyclohexyne transformation is roughly twice as much as that for carbene-cylopentyne rearrangement, the optimized geometry of **14**[39] shows a shorter triple bond (1.231 vs 1.252 Å) which may contribute to its higher rearrangement barrier. However, there may be other less obvious factors that increase the activation energy for 1,2-shift.

Synthesis of a Cyclohexylidenecarbene Precursor (178) and Photogeneration of a C_7 Vinylidene.

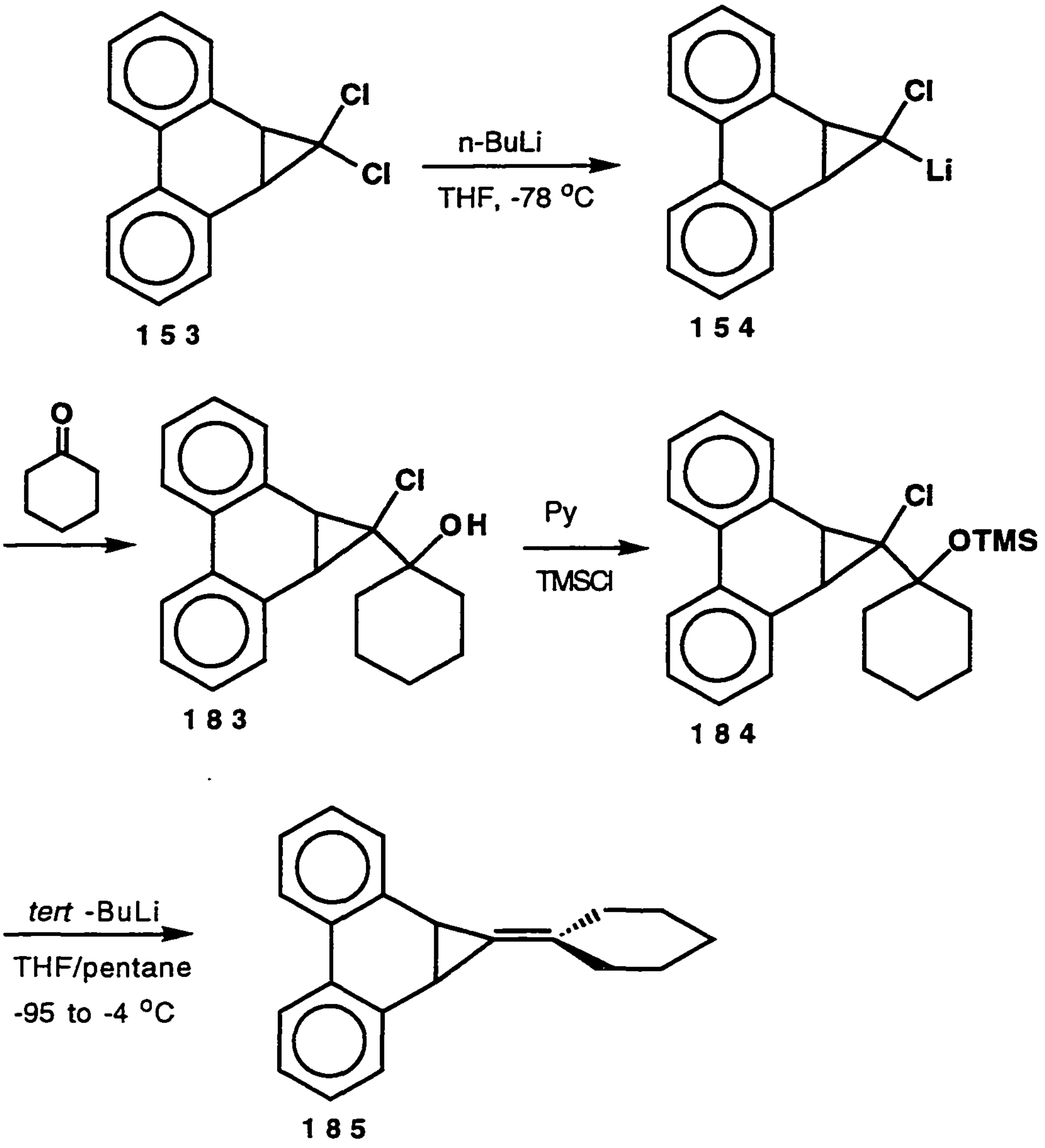
Stang and co-worker reported a series of unsaturated carbenes from primary vinyl triflates some years ago.[172] Among the vinylidenes, cyclohexylidienecarbene (**180**) was prepared from triflate **179** (Scheme 96). Products resulting from nucleophilic attack of *tert*-butoxide on **180**, and the [2 + 1] cycloaduct with cyclohexene **181** were isolated. Recently, Brinker reported generation of **180** by ultrasonicated reaction of **182** with lithium wire (Scheme 96).[169]



Scheme 96

To complete our systematic study on the cycloalkylidencarbene-cyclohexyne rearrangement, precursor **185** was prepared (Scheme 97). Substrate **185** was viewed as a potential photolytic source of **180**. The first step in the synthesis as in all the other precursor preparations, involved lithium-halogen exchange between dichloroadduct **153** and *n*-butyllithium to form carbenoid **154**. Kinetic quenching of **154** with cyclohexanone gave chlorohydrin **183** in 33% yield after radial chromatography. Dissolution of **183** in pyridine and subsequent addition of TMSCl furnished TMS-ether **184** as a white solid in 41% yield (Scheme 97).

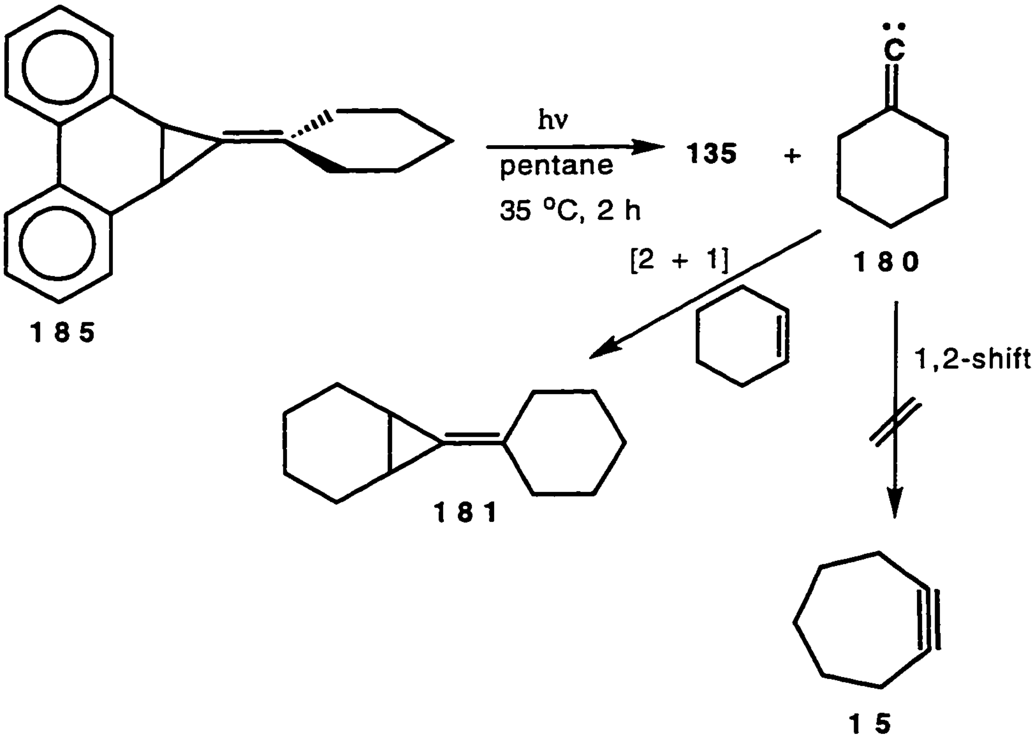
tert-Butyllithium induced 1,2-elimination of TMSOLi on **184** in a mixture THF/pentane at -95 °C, and slow warming to -4 °C gave **185** as an off white solid in 55% yield (~ 92% pure) after preparative TLC. The ^{1}H-NMR spectrum of **185** shows a broad singlet at δ 3.14 (bridgehead protons), two symmetrical multiplets at δ 2.21 and δ 1.99, a mutiplet at δ 1.66-1.24, three



Scheme 97

multiplets for the aromatic protons at δ 8.01-7.97, 7.46-7.39 and 7.29-7.23. The IR spectrum displays absorption bands at 2933, 2849 and at 1601 cm^{-1}. The HRMS gives a parent molecular ion (M^{+}) of *m/z* = 272, consistent with a molecular formula $C_{21}H_{20}$.

Photolysis of a N_2 saturated pentane/cyclohexene solution of **185** was carried out at 254 nm for two hours (Scheme 98). Capillary GC (T° program, T_i = 30 °C, T_f = 200 °C) analysis of the irradiated solution indicated the presence of phenanthrene (**135**, rt 18.6 min) as the only major component in the photolyzed mixture. However, the crude product was carefully concentrated under reduced pressure, and chromatographed on florisil (1 x 20 cm, pentane). GC (isothermal, 120 °C) analysis of the isolated colorless liquid indicated the presence of 7-cyclohexylidenebicyclo[4.1.0]heptane (**181**, rt 8.7 min). The ^{1}H-NMR spectrum for the bicyclic compound **181** shows three



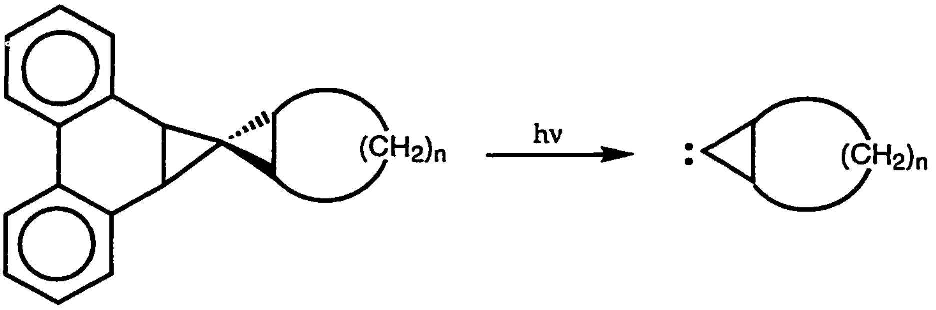
Scheme 98

unsymmetrical multiplets at δ 2.22, 1.75-1.19 and 0.91-0.85. The GCMS gives a molecular ion peak (M^+) of *m/z* = 179 with a relative intensity of 32%. Spectral data were compared to those reported by Stang.[172] The isolated yield for **181**, and that calculated for phenanthrene from the calibrated GC response analysis were 58% and 99%, respectively.

The results obtained in this experiment are consistent with the simplified mechanistic rationale presented in Scheme 98. Substrate **185** undergoes a clean photoextrusion to give phenanthrene (**135**) and cyclohexylidenecarbene (**180**). Carbene **180** does not readily undergo 1,2-shift to yield the strained cycloheptyne (**15**). Thus, the lifetime of **180** is determined by its [2 + 1] cycloaddition with cyclohexene, which gives adduct **181**. These results are in agreement with previous observations.[169,173] The activation barrier for the interconversion of **181** to **15** has not yet been calculated. It will be of interest to estimate this value, and compare it to the barriers for rearrangement of the C_4 to C_6 series.

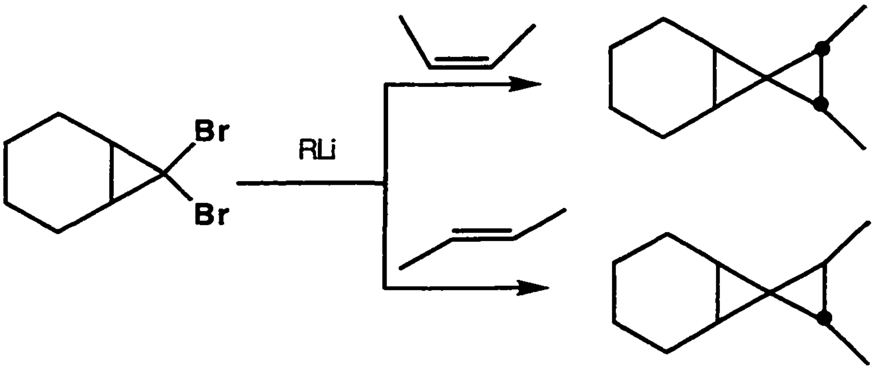
Attempted Synthesis of Cyclopropylidene Precursors

In the course of our synthetic work on potential carbene precursors from phenanthrene, we investigated the preparation of cyclopropylidene precursors. The ultimate goal of synthesizing these precursors was to photochemical generate cyclopropylidenes, another type of carbene whose absolute kinetics have never been measured (Scheme 99).



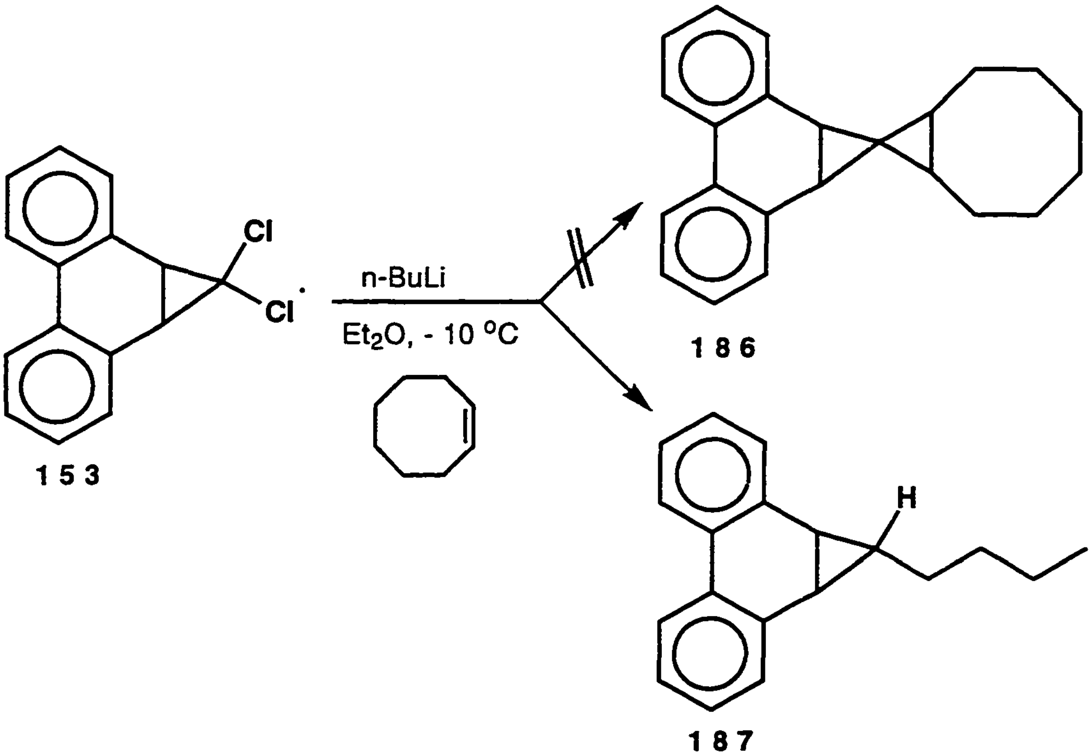
Scheme 99

The reaction of gem-dihalocyclopropanes with alkyllithium provides access to allenes (Doering-Moore-Skatebol method).[54] When this reaction is carried out in the presence of an alkene spirocycles can be formed (Scheme 100).[173]



Scheme 100

In principle, reaction of dichloro adduct **153** with an alkyllithium reagent in the presence of alkenes could give spiro adducts. Treatment of **153** with 2.5 equivalents of *n*-butyllithium in dry ether at -10 °C did not yield the expected spiro product **186** (Scheme 101). Monoalkylated cyclopropane **187** was the major reaction product, as indicated by the chemical shifts observed in the ^{1}H-NMR, ^{13}C-NMR, and DEPT 135 spectra for the crude reaction mixture. The ^{1}H-NMR spectrum of **187** shows a doublet at δ 2.36 with a *trans* couple constant of 4.2 Hz (bridgehead protons), a multiplet at δ 1.65-1.41, a triplet at δ 1.01, a high field multiplet for the methyne proton in the cyclopropyl ring at δ 0.31, two set of multiplets for the aromatic protons at δ 8.04 and 7.50-7.21. Isolation of **187** was not carried out. Based on spectroscopic



Scheme 101

analysis no evidence of spiropentane product **186** was present.

Kirchhoff attempted synthesis of **186** from **153** with n-butyllitium using different sets of reaction conditions. These trials were also unsuccessful.[55]

Based on the above result we attempted preparation of **186** by reaction of the dibromocarbene-phenanthrene adduct with lithium wire in refluxing ether for 24 hours. ^{1}H-NMR of the crude mixture indicated unreacted starting material.

The attempts to prepare cyclopropylidene precursors via lithium carbenoid were abandoned. This synthesis remains an important goal, but clearly requires a different synthetic approach.

Conclusions

The main objective of the present study has been to contribute to the development of a general route to cleanly photogenerate carbenes. The present results support a previous conclusion that phenanthrene provides a simple platform for "storing" carbenes. The adduct of dichlorocarbene to phenanthrene has been modified to produce shelf-stable substances that serve as photochemical precursors to vinylcarbene, and acyclic and cyclic vinylidenes.

Evidence for the formation of vinylcarbene is provided by the efficient trapping of cyclopropene with cyclopentadiene and diphenylisobenzofuran after low temperature photolysis of a suitable cyclopropanated phenanthrene precursor.

Photolysis of methylenecyclopropanes provides evidence for clean formation of vinylidenes. Fragmentation of a C_9 vinylidene leads to efficient formation of 1-nonyne by 1,2-shift.

Previous calculations and experiments indicate that cyclobuylidenecarbene will rearrange readily to cyclopentyne. The present results support this and provide the first photochemical route to generate this novel strained hydrocarbon. Interestingly, besides the known [2 + 2] cycloaddition reaction of cyclopentyne with olefins, this strained cycloalkyne undergoes a major second reaction with cyclohexene which has not been previously described. Only further mechanistic studies will elucidate the origin of this unprecedented result.

Rearrangement of cyclopentylidenecarbene and cyclohexylidenecarbene is not observed, in agreement with previous calculations and experiments. These carbenes are trapped in [2 + 1] cycloadditions with cyclohexene.

Based on capillary GC calibrated response analysis, photochemical formation of phenanthrene is highly efficient.

EXPERIMENTAL SECTION

General Experimental

Instrumentation:

^{1}**H NMR Spectra** were recorded on a Bruker AM-360 FT-NMR spectrometer operating at 360.134 MHz. All spectra were measured in $CDCl_3$ as solvent and Me_4Si as internal reference unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to Me_4Si and coupling constants (J values) are in hertz (Hz).

^{13}**C NMR Spectra** were recorded on a Bruker AM-360 FT-NMR spectrometer operating at 90.556 MHz. All spectra were measured in $CDCl_3$ as solvent and Me_4Si as internal reference unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to Me_4Si and coupling constants (J values) are in hertz (Hz).

^{31}**P NMR Spectra** were recorded on a Jeol FX-90Q FT-NMR spectrometer operating at 90.556 MHz. All spectra were measured in $CDCl_3$ as solvent and Me_4Si as internal reference unless otherwise noted. Chemical shifts (δ) are reported in parts per million (ppm) relative to Me_4Si and coupling constants (J values) are in hertz (Hz).

Melting Points (mp) were recorded on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Infrared Spectra (IR) were recorded on a Nicolet MX-1 FT-IR spectrometer and a Perkin-Elmer 283 B grating spectrometer. Absorptions are reported in wavenumbers (cm^{-1}), with polystyrene (1601 cm^{-1}) as the calibration peak.

Ultraviolet Spectra (UV) were recorded on a UV/Visible, Hewlett-Packard 8543, Diode Array spectrophotometer.

High Resolution Mass Spectra (HRMS) were obtained through the University of California-Riverside Mass Spectrometry Facility.

Gas Chromatography Mass Spectra (GCMS) were obtained through the University of New Hampshire Instrumentation Center on a Hewlett-Packard 5988A GC/MS quadropolar spectrometer equipped with a 25 meter crosslinked methyl silicone capillary column. Electron impact (EI) mass spectra were obtained with an ionization voltage of 70 eV. Chemical ionization (CI) mass spectra were obtained with methane as ionization gas.

Analytical Gas Chromatography (GC) was performed with a Hewlett-Packard 5793A or 6890 instrument equipped with a flame ionization detector (FID), connected to a Hewlett-Packard 3395 integrator. A 25 meter crosslinked methyl silicone capillary column was used.

Preparative Gas Chromatography was performed with a Varian 920 instrument equipped with a thermal conductivity detector (TCD), connected to a Fisher Recordall 5000 chart recorder. The following columns were used:

(A) 15% SE-30 20M on Supelcoport 80/100 mesh (10′ x 1/4′ stainless steel) at specified temperatures. (B) 15% Carbowax 20M on Chromosorb W-HP 80/100 mesh (10′ x 1/4′ stainless steel) at specified temperatures.

Molecular Modeling was performed using Spartan Version 4.01 on a Silicon Graphics Indigo or O_2 work station.

Photochemical Experiments:

In all photochemical experiments, quartz tubes and spectroquality solvents were used. All solutions were degassed with nitrogen prior to irradiation. The light source was a Rayonet RPR-100 reactor fitted with 254 nm lamps. Low temperature experiments (Rayonet only) were performed by circulating coolant through coils immersed in a quartz Dewar vessel. The desired temperature was controlled with a Lauda RC3 recirculating bath.

Solvents:

n-Pentane, *n*-hexane and cylopentane used in photochemical experiments were spectroquality grade, purchased from Fischer Scientific. The following chromatographic solvents (Reagent/ACS grade) were obtained from Fischer Scientific or VWR Scientific and used without further purification: ethyl acetate, *n*-pentane, *n*-hexane, methanol and diethyl ether. The following solvents used for experimentation were freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere and used immediately: benzene, diethyl ether (Et_2O) and tetrahydrofuran (THF). Anhydrous dimethyl sulfoxide (DMSO) was purchased from Aldrich and used without further purification. Anhydrous methylene chloride (CH_2Cl_2) was distilled over phosphorous pentoxide prior to use. Anhydrous ethanol (EtOH) was purchased from Pharmaco and used without further purification. Carbon tetrachloride (CCl_4) was purchased from J.T. Baker Chemical Co. was used without further purification. Chloroform ($CHCl_3$) was used as obtained from Fisher Scientific. Diethylamine, diisopropylamine and pyridine were distilled from potassium hydroxide and stored over 4Å molecular sieves prior to use. The following deuterated solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and stored over 4Å molecular sieves: chloroform-d ($CDCl_3$), benzene-d_6 and tetrahydrofuran-d_8.

Reagents:

All reagents purchased were of sufficient quality and used as obtained from the following companies: Aldrich, Lancaster, Fischer (Acros), Farchan and Alfa.

Column Chromatography and Adsorbents:

Silica Gel: 60-200 mesh Fischer Scientific or Davision Chemical silica gel were used as obtained from the company. 200-442 mesh Fischer Scientific "flash" silica gel was used as obtained from the company. Where necessary, the silica gel was doped with Sylvania 2282 green phosphor to allow observation with ultraviolet light in quartz chromatography columns.

Preparative Thin Layer Chromatography (TLC): Silica gel (1 mm) preparative

TLC plates were purchased from Analtech. Where necessary, these plates were oven dried for 24 hr prior to use.

Alumina: 80-200 mesh Fischer Scientific alumina adsorption was used as obtained from the company.

Florisil: 100-200 mesh Fischer Scientific was used as obtained from the company.

Thin Layer Chromatography (TLC) was performed using Whatman polyester plates coated with 250 µm layer silica gel doped with phosphor. Visualization was accomplished through the use of ultraviolet light or an iodine vapor stain.

Radial Chromatography was performed on a Chromatotron apparatus purchased from Harrison Research, under a nitrogen atmosphere. The rotors (1 mm, 2 mm and 4 mm thickness), precoated with gypsum bound silica made by Analtech, were purchased from Alltech. Where necessary these rotors were oven dried for 24 hours prior to use. The typical chromatography procedure was to dissolve the prepurified sample in a minimum amount of a polar solvent and then to introduce the solution into a rotor (thickness given in following procedures) that had been completed wetted with a non polar solvent. Once all the mixture had been introduced and the inlet rinsed with a minimum amount of solvent, the nitrogen flow was increased between 1000 and 1500 mL/min and the rotor was completely dried for 1 to 2 hours. The nitrogen flow was then reduced back to 15 mL/min and the dried mixture eluted with a solvent combination which provided the best separation of the mixture's components. Visualization was accomplished through the use of ultraviolet light.

Experimental

Synthesis of 2- Bromo-3-chlorocycloocta-1,3-diene (29)

Enone **51** was prepared according to the procedure of House[66] and brominated in a similar manner to that described by Dipasquo.[67] Neat bromoenone **54** (1.00 g, 4.95 mmol) was added dropwise to a stirred solution of PCl_5 (1.20 g, 5.87 mmol) in CCl_4[68] (7 mL) at room temperature under an atmosphere of nitrogen. After 48 h, the mixture was poured over cracked ice and extracted with ether (3 x 20 mL). The united organic extracts were washed with 5 % $NaHCO_3$ (4 x 10 mL), brine (10 mL), and then dried ($MgSO_4$). Solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel/hexane) to afford diene **64** (0.110 g, 0.5 mmol, 5.1%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 6.28 (dd, 1H, J = 8.5 Hz, A-part of an AB system), 6.03 (dd, 1H, J = 8.5 Hz, B part of an AB system), 2.38 - 2.27 (m, 2H), 2.00 (symmetrical mult., 2 H), 1.75 (symmetrical mult., 2H), 1.15 (symmetrical mult., 2H); ^{13}C NMR ($CDCl_3$) δ 173.6, 132.9, 128.9, 117.3, 29.4, 28.1, 22.7, 22.5; DEPT 135 δ ($CDCl_3$) 137.6 (CH), 132.9 (CH), 29.4 (CH_2), 28.1

(CH_2), 22.7 (CH_2) , 22.5 (CH_2); MS: *m/z* 220 (M^+); HRMS calc for $C_8H_{10}BrCl$ 219.9654, found 219.9663.

1,2,3-Cyclooctatriene Adduct with Diphenylisobenzofuran (65)

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (200 mg, 8.22 mmol) under nitrogen. The flask was dried with a heat gun and allowed to cool for 10 min; then it was charged with diphenylisobenzofuran (200 mg, 0.74 mmol) and dry THF (1 mL). The surface of the magnesium turning was activated by the addition of 2 drops of ethylene bromide. The reaction was initiated by adding dropwise a solution of diene **64** (76.5 mg, 0.344 mmol) in THF (0.5 mL) via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (4 mL), and warmed with an oil bath to 40 °C. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase containing all the unreacted diene was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). After two hours the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a bright yellow oil. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2, $R_f = 0.341$) yielded 9,10-epoxy-9,10-dihydro-9,10-diphenyl-anthracene (**65**, 64.4 mg, 0.171 mmol, 49 %) as a pale yellow solid, mp 83 - 85 °C. ^{1}H NMR ($CDCl_3$) δ 5.65 (t, 2H, J = 6.5 Hz, AA′ part of an AA′MM′NN′XX′YY′ system), 2.22 (symmetrical mult., 4H, MM′NN′ part of AA′MM′NN′XX′YY″), 1.60 - 1.63 (m, 4H XX′YY′ part of AA′MM′NN′XX′YY′), 7.88 - 7.15 (m, 14H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 147.3, 141.8, 135.8, 128.3, 128.0, 127.6, 126.4, 123.8, 119.4, 90.4, 27.2, 24.7. HRMS *m/z* (M^+) calc for $C_{28}H_{24}O$ 376.1827, found 376.1840.

Control Experiment : 1,2,3-Cyclooctatriene Adduct with Diphenylisobenzofuran (**65**)

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (200 mg, 8.22 mmol) under nitrogen. The flask was dried with a heat gun and allowed to cool for 10 min. Dry THF (1 mL) was added via syringe. The surface of the magnesium was activated by the addition of 2 drops of ethylene bromide at 35 °C. The reaction was initiated by adding dropwise a solution of diene **64** (91 mg, 0.409 mmol) in THF (0.5 mL). The resulting brown reaction mixture was diluted with more THF (4 mL), and stirred rapidly at room temperature. After 20 min the reaction was quenched with brine (1 mL); the organic layer was dried ($MgSO_4$), filtered and, added fast to a degassed solution of diphenylisobenzofuran (200 mg, 8.22 mmol) in THF (1 mL) under an atmosphere of nitrogen. After 1,5 h of stirring at room temperature the solvent was removed under reduced pressure to give a mixture of unreacted diene plus Diels Alder adduct **65** (9.8 mg, 0.02 mmol 15%) in a ratio of 1:1.3, respectively. The ratio was determined from the crude oil using ^{1}H NMR integration for the vinylic protons.

1,2,3-Cyclooctatriene Adduct with 2,5-Dimethylfuran (66)

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (250 mg, 10.28 mmol) under nitrogen. The flask was dried with a heat gun and allowed to cool for 10 min; then it was charged with 2,5 dimethylfuran 0.147 g, 1.53 mmol) and dry THF (1 mL). The surface of the magnesium was activated by the addition of 2 drops of ethylene bromide. The reaction was initiated by adding dropwise a solution of diene **64** (149 mg, 0.677 mmol) in THF (0.5 mL) via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (4 mL), and warmed with an oil bath to 40 ^{0}C. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase containing all the unreacted diene was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). After two hours the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml) and dried ($MgSO_4$). Solvent was removed under reduced pressure, and the organic residue was purified by flash chromatography (silica gel, 5 % diethyl ether/hexane, R_f = 0.117) to yield adduct **66** (19.2 mg, 0.094 mmol, 14%) as a yellow viscous liquid: ^{1}H NMR ($CDCl_3$) δ 6.12 (s, 2H), 5.53 (t, 2H, J = 6.3 Hz, AA′ part of an AA′MM′NN′XX′YY′ system), 2.29 (symmetrical mult., 4H, MM′NN′ part of AA′MM′NN′XX′YY′), 1.69 (symmetrical mult., 4H, XX′YY′ part of AA′MM′NN′XX′YY′), 1.60 (s, 6 H, methy protons); ^{13}C NMR ($CDCl_3$) δ 142.8, 139.0, 120.1, 87.8, 26.8, 25.5, 16.0; DEPT 135 δ ($CDCl_3$) 139.0 (CH),120.1 (CH), 26.8 (CH_2), 25.5 (CH_2), 16.0 (CH_3); HRMS (CI, *m/z* M^+) calc for $C_{14}H_{18}O$ 203.1435, found 203.1431

Synthesis of 2-Bromo-3-chlorocyclohepta-1,3-diene (77); 1-Chloro-2-bromocyclohepta-1,3-diene (80)

2-Bromocyclohepten-1-one (**76**) was prepared according to the procedure of Garbisch.[72] To an equimolar mixture of PCl_5 (545 mg, 2.65 mmol) and $POCl_3$ (408 mg, 2.65 mmol) in 10 mL of CH_2Cl_2 at 0 °C was added dropwise bromoenone **76** (0.5 g, 2.65 mmol). The mixture was stirred for 48 h at room temperature. After this time the brown mixture was recooled to 0 °C and added slow to a 10 mL of saturated solution of $NaHCO_3$ and extracted with ether (2 x 15 mL). The extracts were washed with water (10 mL), brine

(10 mL), dried ($MgSO_4$) and concentrated to give a yellow oil (654 mg). ^1H NMR of the crude indicated 64% conversion to three major products (1:2.1:3.6) characterized as **77**, **78**, **79**. Dehydrochlorination with 33% NaOH, under phase transfer catalyst (PTC, *n*-hexadecyltrimethylammonium bromide) in CH_2Cl_2 at 40 °C for 3 days afforded 1:1.2 mixture of isomers **77** and **80** (120 mg, 0.682 mmol, 22%) as clear oils after preparative GC purification (column B, 115 ^{0}C). (**77**): ^1H NMR ($CDCl_3$) δ 6.66 (t, 1H, J = 7.3 Hz), 6.44 (t, 1H, J = 7.3 Hz) 2.29 2.09 (unsymmetrical mult., 6H); ^{13}C NMR ($CDCl_3$) δ 138.5, 133.6, 130.3, 118.8, 36.0, 27.5, 26.2; DEPT 135 δ ($CDCl_3$) 138.5 (CH), 133.6 (CH), 36.0 (CH_2), 27.5 (CH_2), 26.2 (CH_2); UV (Hexane) λ_{max} 212 nm (ε 3633), 243 nm (ε 5924); HRMS (EI, *m/z* M^+) calc for C_7H_8BrCl 205.9497, found 205.9497. (**80**): ^1H NMR ($CDCl_3$) δ 6.11 (bd, 1H, J = 11.6 Hz), 5.93 (dt, 1H, J = 11.7, 5.6 Hz), 2.69 (dd, 2H, J = 5.8 Hz), 2.27 (m, apparent q, 2H), 2.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 136.5, 134.6, 129.8, 116.8, 38.4, 29.1, 28.8; MS: *m/z* 206 (M^+).

1,2,3-Cycloheptatriene Adduct with Diphenylisobenzofuran (**81**)

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (61 mg, 2.5 mmol) under nitrogen. The flask was dried with a heat gun and allowed to cool for 10 min; then it was charged with diphenylisobenzofuran (35 mg, 0.13 mmol) and dry THF (1 mL). The surface of the magnesium was activated by the addition of 2 drops of ethylene bromide. The reaction was initiated by adding dropwise a solution of diene **77** (10 mg, 0.05 mmol) in THF (0.5 mL) via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (4 mL), and warmed with an oil bath to 40 °C. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase containing all the unreacted diene was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). After two hours, the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a bright yellow solid. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2, $R_f = 0.321$) yielded 1,9-epoxy-9,10-dihydro-9,10-diphenyl-anthracene (**81**, 7 mg, 0.019 mmol, 44 %) as a bright yellow solid. ^1H NMR ($CDCl_3$) δ 5.86 (t, 2H, J = 4.4 Hz, AA′ part of an AA′MM′NN′XY system), 2.22 (symmetrical mult., 4H, MM′NN′ part of AA′MM′NN′XY), 1.73 (symmetrical mult., 2H, XY part of AA′MM′NN′XY), 7.15 - 7.87 (m, 14H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 147.0, 140.0, 136.0, 128.2, 127.7, 126.9, 126.5, 124.3, 119.5, 89.5, 30.7, 24.3. Chemical shifts were compared with the literature values.[56]

1-Cyclohepten-3-yne Adduct with Diphenylisobenzofuran (**84**)

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (61 mg, 2.5 mmol) under nitrogen. The flask was dried with a heat gun and allowed to cool for 10 min; then it was charged with diphenylisobenzofuran (35 mg, 0.13 mmol) and dry THF (1 mL). The surface of the magnesium was activated by the addition of 2 drops of ethylene bromide. The reaction was initiated by adding dropwise a solution of diene **80** (7 mg, 0.03 mmol) in THF (0.5 mL) via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (4 mL) and warmed with an oil bath to 40 °C. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase containing all the unreacted diene was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). After two hours the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a bright yellow solid. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2, $R_f = 0.321$) yielded 1,9-epoxy-9,10-dihydro-9,10-diphenyl-anthracene (**84**, 3 mg, 0.008 mmol, 24 %) as a bright yellow oil. ^1H NMR ($CDCl_3$) δ 5.95 (brd, 1H, J = 11.2 Hz), 5.75 (dt, 1H, J = 11.2, 5.6 Hz), 2.30 (m, 4H), 1.67 (symmetrical mult., 2H), 7.00 - 7.85 (m, 14H, aromatic protons);

^{13}C NMR ($CDCl_3$) δ 154.3, 151.4, 151.1, 145.9, 135.6, 135.4, 134.2, 128.6, 128.5, 128.2, 128.1, 127.1, 125.1, 124.9, 120.7, 120.0, 119.7, 93.1, 92.2, 30.6, 30.5, 23.9; UV (hexane) λ_{max} 240 nm (ε6327), 207 nm (ε3091), 296 nm (ε2292); HRMS (FAB, *m/z* MH$^+$) calc for $C_{27}H_{23}O$ 363.1748, found 363.1759.

Attempted Synthesis of 5,5-Dimethyl-1,2,3-cyclopentatriene

Route 1: Synthesis of 5,5-Dimethyl-2-trifluoromethanesulfonyl-3-trimethylsilyl-1,3-cyclopentadiene (88) and Reaction with Cesium Fluoride

Lithium diisopropylamide (LDA) was prepared by the addition of *n*-butyllithium (1.2 ml of a 2.46M/hexane solution, 2.95 mmol) to diisopropylamine (0.24 mL, 1.72 mmol) in dry THF (10 mL) and HMPA (1 mL) at -78 °C. 2-Trimethylsilyl-5,5-dimethyl-2-cyclopenten-1-one[83] (**86**, 0.3 g, 1.65 mmol) in THF (2 mL) was then added slowly, and the resulting yellow solution was stirred for 2 h at -78 °C. N-Phenyl trifluoromethanesulfonimide (0.64 g, 1.85 mmol) in THF (4 ml) was added dropwise and the mixture was warmed to 0 °C and maintained for an additional 3 h. After further warming to room temperature, the resulting orange solution was stirred overnight. The mixture was poured into water (50 mL) and extracted with ether (3 x 30 mL). The aqueous and organic layer were separated, and the organic layer was washed with water (10 mL), dried ($MgSO_4$), filtered, and concentrated to yield an orange oil. Purification by chromatography (silica gel, hexane, R_f = 0.88) yielded **88** (188 mg, 0.6 mmol, 72.5%) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 6.46 (d,1H, J = 2.5 Hz), 6.02 (d, 1H, J = 2.5 Hz), 1.21 (s, 6H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 158.4, 150.1, 136.9, 126.5, 118.6 (q), 51.9, 21.9, -1.47; MS (EI) *m/z* 314 (M^+). Chemical shifts were compared to Andro's results.[83]

Diene **88** (60 mg, 0.19 mmol) was added to dry DMSO (2 mL) containing CsF (76.5 mg, 0.50 mmol) and DPIBF (51 mg, 0.19 mmol) maintained at room temperature. The mixture was stirred overnight and quenched by the dropwise addition of water (10 mL). The resulting solution was extracted with ether (3 x 10 mL) and the combined ether extracts were washed with water (4 x 5 mL), dried ($MgSO_4$), filtered and concentrated to give a yellow solid. TLC (silica gel, 3:2 hexane/CH_2Cl_2) and ^{1}H NMR analysis of the crude product indicated that no reaction had taken place.

Similar reactions were conducted at 30 °C, and 50 °C. ^{1}H NMR analysis of the crude material indicated that **88** had been completely consumed. However, there were no vinyl resonances which would indicate formation of a cycloaddition product.

Route 2: Synthesis of 2-Bromo-3-chloro-5,5-dimethyl-1,3-cylopentadiene (**90**) and Reaction with Metals

Bromoenone **91** was prepared according to the procedure employed by Andro.[83] To a suspension of PCl_5 (690 mg, 3.3 mmol) in CCl_4 (10 mL) at 0 °C under nitrogen was added bromoenone **91** (0.5 g, 2.6 mmol) in CCl_4 (5 mL). After stirring at 0 °C for 48 h the solvent was removed under reduced pressure and the residue was poured on ice and extracted with ether (3 x 15 mL). The extracts were washed with 5 % Na_2CO_3 (3 x 10 mL) water (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated to give a yellow oil (480 mg). Capillary GC (110 ^{0}C) analysis indicated the presence of **90** (84.9 %, rt 7.4 min), and the geminal dicloride (15.0 %, rt 15.4 min). Purification by chromatography (silica gel, hexane, $R_f = 0.83$) gave **90** (360 mg, 1.74 mmol, 67%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 6.40 (d, 1H, J = 2.8 Hz), 6.18 (d, 1H, J = 2.8 Hz), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 145.6, 140.3, 130.1, 117.8, 52.2, 21.9; MS (EI) *m/z* (rel inten) 206 (3.1, M^+), 208 (4.6, $M^+ + 2$), 210 (1.5, $M^+ + 4$), 193 (0.20), 127 (36), 112 (16), 92 (15), 91 (100), 77 (11), 51 (18), 39 (13), 36 (0.38), 15 (4.7).

Reaction of 90 with Magnesium

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (140 mg, 5.76 mmol) which were mechanical activated for 24 h, under nitrogen. The flask was heated with a heat gun and allowed to cool for 10 min; dry THF (1 mL) was added via syringe to cover the magnesium surface followed by addition of diphenylisobenzofuran (200 mg, 0.74 mmol), reaction was warmed to 40 °C. Diene **90** (139 mg, 0.67 mmol) in THF (0.5 mL) was slowly added via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (2 mL), and refluxed. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). TLC analysis indicated the presence of three components with R_f values of 0.89, 0.70 and DPIBF (R_f = 0.68). After two hours the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a mixture of dimer **93** and diene **94** in a ratio of 1:1.4, respectively. The ratio was determined from the crude solid using ^1H NMR ($CDCl_3$) integration for the vinylic protons. (**93**): ^1H NMR ($CDCl_3$) δ 6.57 (d, 2H, J = 2.5 Hz), 6.20 (d, 2H, J = 2.5 Hz), 1.21 (s, 12H); DEPT 135 ($CDCl_3$) δ 145.0 (CH), 141.0 (CH), 22.3 (CH_3); MS (EI) *m/z* 254 (M^+), 256 (M^++ 2), 256 (M^++ 4). (**94**): ^1H NMR ($CDCl_3$) δ 6.24 (dd, 1H, J = 5.3, 2.5 Hz), 6.07 (dd, 1H, J = 2.5, 1.5 Hz), 6.02 (dd, 1H, J = 5.3, 1.5 Hz), 1.18 (s, 6H). Based on TLC, ^1H NMR and GCMS analysis, no evidence for a trapped adduct was observed.

In other experiments, the reaction mixture was diluted with dry THF, and the temperature raised to 65 °C, however, diene **94** was the major product.

Reaction of **90** with Rieke Magnesium[88]

Lithium rod (224 mg, 33 mmol), anhydrous $MgCl_2$ (1.57 g, 16.5 mmol), and naphthalene were placed in a three-necked round-bottomed flask equipped with a magnetic stirring bar, condenser and vacuum pump adaptor. The system was purged by pumping it for 5 min to ensure O_2 free atmosphere. THF (10 mL) was added and the green solution was stirred at room temperature. After 24 h the magnesium appeared as a dark gray powder which slowly settled when stirring was stopped. Solvent was removed and freshly distilled THF (10 mL) was added via syringe. A degassed solution of DPIBF (270 mg, 1.0 mmol) in THF (3 mL) was added and mixture was warmed to 35 °C. Diene **90** (180 mg, 0.9 mmol) in THF (0.5 mL) was slowly added which reacted instantly (gas evolution and a development of a red brown color). After stirring at 35 °C for 2 h, the reaction was quenched with brine (5 mL), extracted with ether (2 x 15 ml), dried ($MgS0_4$), filtered and concentrated to give a dark solid residue. TLC analysis (silica gel, 3:2 hexane/CH_2Cl_2) showed only DPIBF (R_f = 0.68). ^1H NMR of the crude material showed no vinyl peaks.

In other experiments, the reaction temperature was varied to 0 °C and 25 °C, however, diene **90** was found to be unreactive under these reaction temperatures.

Reaction of **90** with Ni(0)

A solution of EtMgBr (1.2 mL, 1.2 mmol, 1 M/THF) was added to a solution of diene **90** (128 mg, 0.62 mmol), nickel 1,4-bis(diphenylphosphino) ethane dichloride (nidppeCl$_2$, 10 mg, 2x10^{-5} mol), furan (1 mL) and THF (0.5 mL) at room temperature. The orange reaction mixture was stirred for 1 h, quenched with brine (10 mL), organic layer dried (MgSO$_4$), filtered and concentrated to give a yellow oil (71 mg) by capillary GC (110 °C) to contain a mixture of **96** (56%, rt 5.1 min) and **97** (56%, rt 5.2 min). Pure samples of **96** and **97** were not isolated due to the instability of these compounds, but their structures were assigned by spectral analysis obtained from the crude mixture. (**96**): ^{1}H NMR (CDCl$_3$) δ 6.09 (d, 1H, J = 2.6 Hz), 5.86 (dt, 1H, J = 2.6, 1.7 Hz), 2.24 (qd, 2H, J = 7.4, 1.7 Hz), 1.11 (t, 3H, J = 7.4 Hz), 1.15 (s, 6H); MS (EI) *m/z* 156 (M$^+$), 158 (M$^+$ + 2). (**97**): ^{1}H NMR (CDCl$_3$) δ 5.78 (t, 2H, J = 1.2 Hz), 2.18 (qd, 4H, J = 7.0, 1.2 Hz), 1.11 (t, 6H, J = 7.0 Hz), 1.15 (s, 6H); MS (EI) *m/z* 150 (M$^+$).

In other experiments, different trapping reagents were used; however, this did not alter the above results.

Reaction of **90** with *n*-Butyllithium

To a solution of diene **90** (100 mg, 0.48 mmol), DPIBF (270 mg, 1.0 mmol) and THF (5 mL) was added dropwise *n*-butyllithium (0.6 mL, 0.96 mmol of a 1.6 M hexane solution) at -78 °C. The reaction mixture turned bright yellow. After stirring for 45 min at -78 °C, the reaction was allowed to warm to room temperature and was then quenched with water (5 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a yellow solid residue. TLC (3:2 hexane/CH_2Cl_2, R_f = 0.89), and ^1H NMR indicated only intractable material.

In other experiments, the number of equivalents of *n*-butyllithium was varied to 5 equivalents; however, this did not significantly alter the above results.

Halogen-lithium exchange was examined at -78 °C by quenching the reaction mixture with TMSCl (0.5 mL). After similar work up diene **100** was isolated by chromatography (silica gel, hexane) as a yellow oil (93 mg, 0.46 mmol, 79%). Spectral data of **100** were compared with those of an authentic sample.

Reaction of 90 with n-Butyllithium in the Presence of Spirodiene (**103**)[93]

Diene **90** (122 mg, 0.59 mmol) and spirodiene **103** (1.0 g, 10.9 mmol) were added to a dry 15-mL flask equipped with stirbar and reflux condenser under nitrogen. The flask was then immediately cooled in a -40 °C bath, and its contents were stirred for 10 min, after which a solution of *n*-butyllithium 0.95 mL, 2.36 mmol of a 2.5 M/hexane solution) was added. The resulting yellow solution was held at -40 °C for 1 h, and then heated under reflux (95-

100 °C) for 5 min. The pale yellow reaction mixture turned cloudy (salt precipitation). Reaction was quenched with a mixture of 1:1 pentane/brine; the organic layer was dried ($MgSO_4$), excess of spirodiene and solvent were evaporated to give a yellow oil (192 mg). Reduced pressure distillation (40 °C, 0.02 mm) followed by preparative GC (column B, 140 °C) of the crude yielded the dimer of **103**, as the only identified product of the reaction. Based on ^1H NMR and GCMS analysis, no evidence for a trapped adduct was observed.

Route 3: Synthesis of 2-Bromo-5,5-dimethyl-3-trifluoromethanesulphonyl-1,3-cyclopentadiene (**104**) and Reaction with n-Butyllithium

Lithium diisopropylamide (LDA) was prepared by the addition of *n*-butyllithium (2.6 ml of a 2.46M/hexane solution, 6.34 mmol) to diisopropylamine (0.81 mL, 5.82 mmol) in dry THF (10 mL) and HMPA (1 mL) at -78 °C. 2-Bromo-5,5-dimethyl-2-cyclopenten-1-one[83] (**91**, 1.00 g, 5.3 mmol) in THF (2 mL) was then added slowly, and the resulting yellow solution was stirred for 2 h at -78 °C. N-Phenyl trifluoromethanesulfonimide[95] (2.0 g, 5.6 mmol) in THF (4 ml) was added dropwise and the mixture was warmed to 0 °C and maintained for an additional 3 h. After further warming to room temperature, the resulting orange solution was stirred overnight. The mixture was poured into water (50 mL) and extracted with ether (3 x 30 ml). The aqueous and organic layer were separated, and the organic layer was washed with water (10 mL), dried ($MgSO_4$), filtered, and concentrated to yield an orange oil. Purification by chromatography (silica gel, hexane, R_f = 0.82) yielded vinyl triflate **104** (906 mg, 2.83 mmol, 53%) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 6.45 (d, 1H, J = 2.8 Hz), 6.09 (d, 1H, J = 2.8 Hz), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 146.3, 143.7, 129.5, 119.0 (q), 111.4, 50.4, 21.8; MS (EI, *m/z*) 320 (M^+), 322 (M^+ + 2).

To a solution of diene **104** (40 mg, 0.125 mmol) in THF (5 mL) at -78 °C under nitrogen was added dropwise *n*-butyllithium (0.25 mmol + 10% excess of a 1.6 M hexane solution). After stirring for 30 min, DPIBF (50 mg, 0.18 mmol) was added in one portion. The reaction was allowed to warm to room temperature, quenched with water (5 mL), extracted with ether (2 x 10 ml), dried ($MgS0_4$), filtered and concentrated to give a yellow solid residue. TLC (3:2 hexane/CH_2Cl_2) analysis showed besides DPIBF (R_f = 0.68), two other spots with R_f of 0.31 and 0.12. ^{1}H NMR of the crude product showed aromatic resonances, no vinyl peaks between 5.10 ppm and 7.00 ppm, a quartet at 5.00 ppm, two symmetrical multiplets between 3.50 - 4.00 ppm and several up field singlets. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) followed by ^{1}H NMR analysis of the isolated bands showed only aromatic resonances.

Route 4: Synthesis of 2,3-Dibromo-5,5-dimethyl-1,3-cyclopentadiene (**105**), and Reaction with Magnesium Turnings

A mixture of bromoenone[83] **91** (2.0 g, 10.5 mmol), trimethyl orthoformate[98] (1.34 g, 12.6 mmol), freshly distilled over $CaSO_4$, methanol (10 mL), and *p*-toluensulfonic acid (20 mg) was gently heated while methyl formate was distilled off through a short Vigreux column. The cooled reaction mixture was made basic by addition of few drops of a solution of 10% NaOH, and partitioned between ether (20 mL) and water (20 mL). The organic phase was washed with brine (5 mL) and dried ($MgSO_4$). Evaporation of the solvent afforded a yellow oil (2.7 g, 85%) by capillary GC (125 °C, rt 10.2 min), which was used in the following step without further purification.

To a solution of catechol (1.32 g, 12 mmol) in benzene[98] (20 mL) was added dropwise the crude mixture of ketone dimethyl acetal (2.47 g, 10.5 mmol). Reaction was brought to reflux and part of the solvent (2.5 mL) was distilled through a short Vigreux column. Heating was discontinued, the temperature was lowered to 60 °C and *p*-toluenesulfonic acid (20 mg) was added. The distillation of the solvent was slowly continued until pure benzene was collected. Triethylamine (0.2 mL) was added to the cooled reaction mixture, which was then partitioned between ether (20 mL) and water (20 mL). The organic phase was washed with water (2 x 10 mL), 10% NaOH (10 mL), dried ($MgSO_4$) and concentrated to give a solid residue (2.09 g).

Chromatography on silica gel (hexane) afforded 612 mg of a white solid which was recrystallized from methanol to give 1,3-benzodioxol **106** (745 mg, 2.7 mmol) as white pellets, mp 51-54 °C. ^{1}H NMR ($CDCl_3$) δ 6.80 (symmetrical mult., 4H, aromatic protons), 6.11 (s, 1H), 2.34 (s, 2H), 1.23 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 148.2, 147.4, 124.2, 121.2, 118.3, 107.7, 50.0, 42.6, 28.5.

To a magnetically stirred solution of **106** (745 mg, 2.7 mmol) in CH_2Cl_2 (5 mL) cooled in an ice-salt bath, was added dropwise a 1M solution of BBr_3 (3.19 mL, 3.19 mmol) under nitrogen. The pale yellow mixture was stirred for 8 h at 0 °C, and reaction was followed by TLC. The reaction was then quenched with cold water/hexane (3 ml:5 mL), the organic phase was washed with 10% NaOH (5 mL), brine (5 mL), dried ($MgSO_4$) and concentrated to give tribromide **107** (709 mg, 2.09 mmol) as a yellow oil which was used without further purification in the following step: ^{1}H NMR ($CDCl_3$) δ 4.58 (br, 1H), 2.69 (br, 1H, J = 16.3 Hz), 2.28 (br, 1H, J = 16.3 Hz), 1.36 (s, 3H), 1.25 (s, 3H).

The crude mixture of **107** (709 mg, 2.09 mmol) in CH_2Cl_2 (7 mL), 33% NaOH (20 mL), and *n*-hexadecyltrimethylammonium bromide (10 mg) were stirred for 3 days at 40 °C. The mixture was partitioned between ether (20 mL) and ice-water (20 mL). The organic phase washed with water (2 x 10 ml), dried ($MgSO_4$) and concentrated. Purification by chromatography (silica gel, hexane, R_f = 0.67) yielded **105** (202 mg, 0.80 mmol, 38%) as a colorless oil:

Capillary GC (125 °C, rt 7.6 min); ^{1}H NMR ($CDCl_3$) δ 6.37 (s, 2H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 145.1, 119.4, 53.9, 21.8; HRMS (EI, *m/z* M^+) calc for $C_7H_8Br_2$ 249.8992, found 249.8980.

To a three-necked, 15-ml, round bottomed flask, equipped with a magnetic stirring bar and condenser, was added magnesium turnings (200 mg, 8.8 mmol) which were mechanical activated by stirring for 24 h, under nitrogen. The flask was heated with a heat gun and allowed to cool for 10 min. Dry THF (1 mL) was added to cover the magnesium surface, diphenylisobenzofuran (80 mg, 0.74 mmol) was added in one portion, and reaction warmed to 40°C. Diene **105** (30 mg, 0.11 mmol) in THF (0.3 mL) was slowly added via syringe. The resulting brown reaction mixture was stirred rapidly, diluted with more THF (2 mL), and refluxed. Aliquots of the reaction mixture (*ca.* 0.05 mL) were withdrawn at appropriate times by syringe and added it to a vial containing (*ca.* 0.2 mL) of brine. The ethereal phase was filtered through a plug of glass wool, dried ($MgSO_4$) and analyzed by TLC (3:2 hexane/CH_2Cl_2). TLC analysis indicated the presence of several components. After two hours the reaction was quenched with brine (1 mL), extracted with ether (2 x 10 ml), dried ($MgSO_4$), filtered and concentrated to give a solid residue (78 mg). TLC and ^{1}H NMR spectroscopy of the crude product indicated that starting material had reacted. Resonances in the ^{1}H NMR showed a broad singlet at 5.25 ppm and two singlets at 1.45 and 1.46 ppm, respectively. Preparative TLC (3:2 hexane/CH_2Cl_2) of the crude material followed by ^1H NMR analysis of isolated band (R_f = 0.30) showed only aromatic resonances.

Route 5: Synthesis of 2-Chloro-5,5-dimethyl-3-trimethylsilyl-1,3-cyclo pentadiene (**108**) and Reaction with Potassium Fluoride

5,5-Dimethyl-2-trimethylsilyl-2-cyclopenten-1-one (**86**) was prepared according to the procedure described by Andro.[83] To a suspension of PCl_5 (690 mg, 3.3 mmol) in CCl_4 (10 mL) at 0 °C under nitrogen was added enone **86** (0.5 g, 2.7 mmol) in CCl_4 (5 mL). After stirring at 0 °C for 48 h, the solvent was removed under reduced pressure and the residue was poured on ice and extracted with ether (3 x 15 mL). The extracts were washed with 5 % Na_2CO_3 (3 x 10 mL) water (10 mL), brine (10 mL), dried ($MgSO_4$) and concentrated to give a yellow oil (850 mg) shown by capillary GC (110 °C) to contain **109** (84.6 %, rt 15.4 min) which was used in the following step without further purification.

Purification by chromatography (silica gel, hexane, R_f = 0.77) yielded chloro vinylsilane **108** (158 mg, 0.79 mmol, 28.6%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.40 (d, 1H, J = 2.4 Hz), 6.08 (d, 1H, J = 2.4 Hz), 1.15 (s, 6H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 158.2, 141.6, 140.3, 133.3, 53.4, 22.2, -0.97; MS (EI) *m/z* 200

(M^+), 202 ($M^+ + 2$). Chemical shifts were compared to the literature values.[100]

To a solution of diene **108** (108 mg, 0.5 mmol), 18-crown-6 (79 mg, 0.3 mmol), 2,5-dimethylfuran (1 mL) in dry CH_2CL_2 (5 mL) at room temperature under a nitrogen atmosphere, was added KF (87 mg, 1.5 mmol). After 8 h of stirring at room temperature, the orange reaction mixture was slowly quenched with brine. The organic phase was washed with water (3 mL), dried ($MgSO_4$) and concentrated. ^1H NMR analysis of the crude material indicated a very complex mixture, including aromatic resonances, sets of vinyl resonances and some unreacted starting material. Chromatography (silica gel, 5% ether, hexane) of the crude product gave no evidence for a trapped adduct of the butatriene.

In other experiment, CsF in DMSO was used with the same trapping reagent, with stirring the reaction mixture for 18 h at room temperature; however, even though diene **108** had reacted to a greater extent, this did not alter the above results.

Route 6: Synthesis of 2,3-Bis(trimethylsilyl)-5,5-dimethyl-1,3-cyclopentadiene (116) and Attempted Synthesis of a Vinylidonium Salt Precursor

To sodium wire (207 mg, 9 mmol) in dry ether[105] (6 mL) stirred under a nitrogen atmosphere was added TMSCl (434 mg, 3.98 mmol) in one portion. After stirring for 15 min, diene **90** (248 mg, 1.2 mmol) in ether (0.5 mL) was added over a period of 20 min. During the addition, the reaction became slightly warm and refluxed gently. After refluxing the reaction mixture for an additional 3 h, excess sodium and solid products were filtered off through a plug of glass wool and the residue was washed with ether (2 x 30 ml). The filtrate was carefully washed with saturated $NaHCO_3$ (50 mL), water (2 x 10 mL), brine (15 mL), dried ($MgSO_4$) and concentrated to give a yellow oil (216 mg), shown by capillary GC (110 °C) to contain **116** (62%, rt 15.3 min). Purification by chromatography (silica gel, hexane, $R_f = 0.81$) yielded **116** (111 mg, 0.46 mmol, 39%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.48 (s, 2H), 1.15 (s, 6H), 0.17 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 160.1, 144.9, 55.7, 23.1, 1.43; MS (EI) *m/z* 238 (M^+).

Attempted Synthesis of Vinylidonium Salt precursor

Method A: Reaction of (116) with (Diacetoxyiodo)benzene (DIB)[101]

To a stirred suspension of (diacetoxyiodo)benzene (DIB) (128.5 mg, 0.39 mmol) in dry CH_2Cl_2 (1.5 mL) was slowly added trifluoromethanesulfonic acid (0.07 mL, 0.78 mmol) at 0 °C via syringe. The mixture was stirred for 1 h at room temperature during which time the mixture became a clear yellowish solution. The solution was then recooled to 0 °C and diene **116** (95 mg, 0.39 mmol) in CH_2Cl_2 (0.8 mL) was added dropwise. After addition, the dark purple reaction mixture was stirred for 10 min. After evaporation of the solvent Et_2O was added to induce recrystallization. After 5 days a pale blue solid was formed which was identified by ^{1}H-NMR spectroscopy as unreacted (DIB). Decomposition of the (diacetoxyiodo)benzene into iodobenzene was observed as indicated by comparison to an authentic sample of idobenzene. TLC (silica gel, hexane, R_f = 0.64), capillary GC (125 °C, rt 5.2 min) and AA'BB'C system in the ^{1}H NMR spectrum. This procedure failed to give vinylidonium salt.

In other experiments, the reaction temperature was varied between -25 °C and 0 °C; however, this did not alter the above results.

Method B: Reaction of (116) with Lewis Acid-Activated Iodosylbenzene[106]

Iodosylbenzene was prepared following the literature procedure.[107] A solution of triethyloxonium tetrafluoroborate (0.95 mmol, 2.5 equiv) was added dropwise to a suspension of diene (92 mg, 0.38 mmol) and iodosylbenzene (209 mg, 0.95 mmol) in CH_2Cl_2 (5 mL) under nitrogen. The pale yellow color of the suspension turned dark brown. The reaction mixture was stirred for 1 h at 0 °C, quenched by slow addition of water (5 mL), extracted with CH_2Cl_2 (2 x 10 mL), dried ($MgSO_4$) and concentrated to give a yellow solid which was washed several times with cold hexane. The yellow solid was identified as unreacted iodosylbenzene as confirmed by its poor solubility in $CDCl_3$. ^{1}H NMR ($CDCL_3$) spectrum of the hexane wash showed three sets of resonances at δ 7.71 (dd, 2H, J = 8.0, 1.1 Hz), 7.33 (tt, 1H, J = 7.4, 1.0 Hz), and 7.11 (brt, 2H, J = 7.7 Hz) wich matched the chemical shifts for iodobenzene, consistent with TLC (silica gel, hexane, R_f = 0.64) and capillary GC (125 °C, rt 5.2 min). This method failed to give vinylidonium salt **115**, but proved to be successful for preparation of vinylidonium salt **118**.

Method C: Reaction of (**108**) with (tert-Butylethynyl)phenyliodonium Tosylate[108]

(*tert*-Butylethynyl)phenyliodonium tosylate was prepared by the Koser procedure.[108] To a solution of diene **108** (63 mg, 0.31 mmol) in THF (2 mL) under nitrogen at -78 °C was added dropwise *n*-butyllithium (0.5 mL, 1.25 mmol of a 2.5 M/hexane solution). After 2 h of stirring at -78 °C, the tosylate (128 mg, 0.28 mmol) was introduced in one portion under a positive nitrogen pressure. The resulting mixture was stirred for 1 h at 0 °C, during which time it became slightly darker, and was then quenched with water (2 mL), extracted with CH_2Cl_2 (2 x 5 mL) and concentrated to give a colorless liquid. ^1H NMR of the crude material showed resonances which were correlated only to the starting material (diene **108**), and to the hydrolyzed tosylate: ^1H NMR ($CDCl_3$) δ 7.69 (d, 2H, J = 8.1 Hz, A′ part of an AA′BB′ system), 7.22 (d, 2H, J = 8.1 Hz, part BB′ of an AA′BB′ system), 2.36 (s, 3H).

Attempted Synthesis of Cyclic Butatrienes by Intramolecular Vinylidene Coupling

Synthesis of Bis(1,1-dibromo-2-phenyl)-1,10-undecadiene (**122**), and Reaction with CuCN.

Anhydrous LiBr[111] (3.5 g, 0.04 mol) was dissolved under nitrogen in THF (100 ml), butyllithium (0.02 mol + 10% excess of a 2.46 M/hexane solution) was added at - 10 °C, the mixture was cooled to -78 °C and diethyl chloromethanephosphonate (3.7 g, 0.02 mol) in THF (20 mL) was added dropwise with stirring. After 8 min of stirring at -78 °C, CBr_4 (6.6 g, 0.02 mol) in THF (30 mL) was added dropwise (solution turned dark). The stirring was continued for 40 min, and water (40 mL) was then added. The resultant mixture was extracted with CH_2Cl_2 (2 x 50 mL). The extracts were dried ($MgSO_4$) and the solvent and tribromomethane formed were removed under vaccum to leave a crude mixture of 68% of dibromomethanephosphonate and 18.5% of bromochloromethanephosphonate according to ^{31}P NMR integration.

Anhydrous LiBr (3.5 g, 0.04) was dissolved under nitrogen in THF (100 mL), diisopropylamine (2.02 g, 0.02 mol) was added dropwise followed by addition of butyllithium (0.02 mol + 10% excess of a 2.56 M/hexane solution) at 0 °C. After 1 h the prepared crude mixture of phosphonates (0.02 mol) dissolved in THF (30 mL) was added at -78 °C. After 30 min dione **120**[110]

(3.08 g, 0.01 mmol) in THF (10 mL) was slowly added. The mixture was stirred for 2 h at -78 °C and allowed to warm to room temperature, quenched with water (40 mL) and extracted with ether (3 x 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated to give a dark oil. Purification by chromatography (alumina, Et_2O) followed by recrystallization from EtOH gave **122** (3.5 g, 5.7 mmol, 56%) as white pellets, mp 95-96 °C. ^1H NMR ($CDCl_3$) δ 2.56 (dd, 4H, J = 6.9 Hz), 1.33 - 1.23 (m. 10 H), 7.40 - 7.15 (m, 10H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 147.7, 141.0, 128.3, 127.8, 127.6, 87.9, 39.2, 28.9, 28.8, 26.6; IR (KBr, cm^{-1}) 2931, 2853, 1609, 1489, 1447, 1039, 920, 695, 582.

A solution of **122** (50 mg, 0.08 mmol) in THF (5 mL) was treated with *n*-butyllithium (2 equiv. + 15% excess of a 2.46 M/hexane solution) at -90 °C. After the yellow solution was allowed to stir at -90 °C for 45 min, CuCN (7.3 mg, 0.08 mmol) was added in one portion (a green olive color was developed) and the reaction mixture was stirred at -80 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 17 h, followed by quenching with water (1.5 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. ^1H NMR and ^{13}C NMR analysis of the crude material indicated formation of diyne **123** as the major product of the reaction. Diyne **123** was isolated by preparative TLC (silica gel, 4% CH_2Cl_2/ hexane, $R_f = 0.10$)

as a clear liquid (10 mg, 0.03 mmol, 42%). ^1H NMR ($CDCl_3$) δ 2.40 (t, 4H, J = Hz), 1.66 - 1.33 (m, 10H), 7.22 - 7.41 (m, 10H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 131.5, 128.1, 127.4, 124.0, 90.3, 80.6, 28.7, 28.6, 19.3; IR (neat, cm^{-1}) 3061, 2933, 2857, 2230w, 1689br, 1597, 1492; UV (hexane) λ_{max} 214 nm (ε18,607), 237 nm (ε18,007).

In other experiments, the elapsed time between addition of *n*-butyllithium and the CuCN was varied from 10 min to 30 min; however, this did not change the above results. Furthermore, shorter times e.g., 10 min, yielded crude mixtures with the starting material almost unchanged.

Synthesis of Bis(1,1-dibromo)-1,9-decadiene (127) and Reaction with CuCN.

A mixture of PPh_3 (9.2 g, 35.2 mmol), CBr_4 (5.8 g, 17.6 mmol), and dialdehyde **126**[112] (0.5 g, 3.52 mmol) in benzene (80 mL) was refluxed under nitrogen for 14 h. After allowing the mixture to cool to room temperature, solid material was removed via vacuum filtration. The crude product was washed with 2N HCl (200 mL), 5% $NaHCO_3$ (50 mL), water (20 mL), brine (20 mL), dried ($MgSO_4$) and concentrated. Purification by chromatography (silica gel, hexane, $R_f = 0.60$) yielded **127** (612 mg, 1.35 mmol, 43%) as a clear oil: ^1H NMR ($CDCl_3$) δ 6.39 (t, 2H, 7.2 Hz), 2.09 (td, apparent q, 4H, J = 14.3, 7.0 Hz), 1.45 - 1.33 (unsymmetrical mult., 8H); ^{13}C NMR ($CDCl_3$) δ 138.8, 88.4, 33.0, 28.8, 27.8; IR (neat, cm^{-1})) 2931, 2853, 1630, 1454, 1264, 1145, 779.6.

A solution of **127** (100 mg, 0.22 mmol) in THF (5 mL) was treated with *n*-butyllithium (0.2 mL, 2 equiv. + 15% excess of a 2.46 M/hexane solution) at -90 °C. After the yellow solution was allowed to stir at -90 °C for 45 min, CuCN (20 mg, 0.22 mmol) was added in one portion (a green olive color was developed), and the reaction mixture was stirred at -80 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 17 h, followed by quenching with water (1.5 mL). The organic layer was dried ($MgSO_4$), and concentrated *in vacuo*. ^{13}C NMR analysis of the crude material showed two acetylenic carbons at 84.7 ppm and 68.3 ppm which were assigned to diyne **128**. Based on ^{13}C NMR analysis there was no evidence for the intramolecular vinylidene coupling product.

Synthesis of Bis(1,1-dibromo-2-dimethy)-1,9-decadiene (130) and Reaction with CuCN.

Anhydrous LiBr[111] (3.5 g, 0.04 mol) was dissolved under nitrogen in THF (100 ml), butyllithium (0.02 mol + 10% excess of a 2.46 M/hexane solution) was added at - 10 °C, the mixture was cooled to -78 °C, and diethyl chloromethanephosphonate (3.7 g, 0.02 mol) in THF (20 mL) was added dropwise with stirring. After 8 min of stirring at -78 °C, CBr_4 (6.6 g, 0.02 mol) in THF (30 mL) was added dropwise (solution turned dark). The stirring was continued for 40 min and water (40 mL) was then added. The resultant mixture was extracted with CH_2Cl_2 (2 x 50 mL). The extracts were dried ($MgSO_4$) and the solvent and the tribromomethane formed were removed under vacuum to leave a crude mixture of 68% of dibromomethanephosponate and 18% of bromochloromethanephosphonate according to ^{31}P NMR integration.

Anhydrous LiBr (3.5 g, 0.04) was dissolved under nitrogen in THF (100 mL), diisopropylamine (2.02 g, 0.02 mol) was added dropwise followed by addition of *n*-butyllithium (0.02 mol + 10% of a 2.56 M/hexane solution) at 0 °C. After 1 h the prepared crude mixture of phosphonates (0.02 mol) dissolved in THF (30 mL) was added at -78 °C. After 30 min diketone **129** (1.7 g, 0.01 mmol) in THF (10 mL) was slowly added. The mixture was stirred for 2 h at -78 °C and allowed to warm to room temperature, followed by quenching with water (40 mL), and extraction with ether (3 x 50 mL). The combined extracts were dried(($MgSO_4$) and concentrated to give a dark oil. Purification by chromatography (silica gel, hexane, R_f = 0.62) yielded **130** (1.02 g, 2.12 mmol, 21%) as a clear oil: ^1H NMR ($CDCl_3$) δ 2.27 (dd, 4H, J = 7.4 Hz), 1.87 (s, 6H), 1.46 - 1.21 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 142.1, 84.7, 38.0, 28.9, 26.7, 22.7.

A solution of **130** (106 mg, 0.22 mmol) in THF (5 mL) was treated with *n*-butyllithium (0.2 mL, 2 equiv. + 15% excess of a 2.46 M/hexane solution) at -90 °C. After the yellow solution was allowed to stir at -90 °C for 45 min, CuCN (20 mg, 0.22 mmol) was added in one portion (a green olive color was developed), and the reaction mixture was stirred at -80 °C for 1 h. The mixture was allowed to warm to room temperature and stirred for 17 h, followed by quenching with brine (1.5 mL). The organic layer was quickly dried ($MgSO_4$), and 80% of the solvent was removed in *vacuo*. Capillary GC (100 °C) analysis of the crude material indicated a complex mixture with three major components: (9.6%, rt 6.8 min), (34.0%, rt 7.3 min), (14.1%, rt 7.5 min). GCMS analysis gave a molecular ion peak (M^+) at *m/z* 162 for the compounds with retention times of 7.3 min and 7.5 min. IR analysis of the THF crude solution did not give an absorption band in the region of 1850-1990 cm^{-1} which is characteristic of butatrienes. ^1H NMR spectrum of the crude showed vinyl resonances at 5.88 (d, J = 9.6 Hz) and several resonances between 2.10 ppm and 2.80 ppm. ^{13}C NMR spectrum of the crude material showed 14 peaks between 100 ppm and 156 ppm. Based on ^1H NMR, ^{13}C NMR, IR, capillary GC and GCMS analysis there was no evidence for a butatriene.

Synthesis of 7-*exo* -Hexyl,7-*endo* -chlorodibenzo[a;c]bicyclo[4.1.0]heptane (155)

To a solution of adduct **153** (250 mg, 0.97 mmol) in dry THF (8 mL) at -78 °C was added dropwise *n*-butyllithium (1.25 mmol, 1.3 equiv. of a 2.46 M/hexane solution) resulting in the formation of a dark forest green color.

After 1 h, bromohexane (2.80 g, 17 mmol) was added dropwise and the yellow reaction mixture was stirred at -78 °C for 2 h, then gradually warmed to room temperature. Stirring was continued overnight. After 20 h, brine (4 mL) was injected into the flask. The organic layer was separated out and washed with brine (2 x 4 mL), dried ($MgSO_4$), filtered and concentrated. The crude mixture was pumped up overnight. ^1H NMR analysis indicated the presence of monochloroadduct as a minor byproduct. Chromatography (silica gel, hexane) afforded 630 mg of a yellow solid residue which was dissolved in CH_2Cl_2 (1 mL) and purified further by radial chromatography (silica gel rotor, 2 mm, 2% ether, hexane) to yield **155** as white needles (98 mg, 0.31 mmol, 32.4%), mp (hexane/ethanol) 82 °C. ^1H NMR ($CDCl_3$) δ 2.69 (s, 2H), 1.92 (m, 2H), 1.71 (symmetrical mult., 2H), 1.50-1.23 (m, 6H), 0.93 (t, 3H, J = 6.9 Hz), 8.01 (d, 2H, J = 8.2 Hz, aromatic protons), 7.36-7.22 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 131.9, 130.9, 130.3, 127.8, 127.2, 126.7, 122.8, 43.5, 41.6, 32.1, 31.9, 29.0, 26.8 22.8, 14.3; IR (KBr, cm^{-1}) 3066, 2931, 2851, 1921w, 1835w, 1486, 1446, 954, 761, 729, 573.

Synthesis of 7-Cyclooctylidenedibenzo[a;c]bicyclo[4.1.0]heptane (**158**)

To a solution of adduct **153** (0.4 g, 1.53 mmol) in dry THF (16 mL) at -78 °C was added dropwise *n*-butyllithium (1.98 mmol, 1.3 equiv. of a 2.46 M/hexane solution) resulting in the formation of a dark forest green color.

After 1 h of stirring at -78 °C, bromooctane (3.2 g, 17 mmol) was added dropwise and the deep red reaction mixture was stirred at -78 °C for 2 h, then gradually warmed to room temperature. Stirring was continued overnight. After 20 h, brine (4 mL) was injected into the flask. The organic layer was separated out and washed with brine (2 x 4 mL), dried ($MgSO_4$), filtered and concentrated. The crude mixture was pumped up overnight. ^{1}H NMR analysis indicated the presence of monochloroadduct as a minor byproduct. Chromatography (silica gel, hexane, R_f = 0.18) afforded 330 mg of a yellow solid residue which was dissolved in CH_2Cl_2 (1 mL) and purified further by radial chromatography (silica gel rotor, 2 mm, 2% ether, hexane) to yield **156** as white crystals (143 mg, 0.42 mmol, 31%), mp 79 °C. ^{1}H NMR ($CDCl_3$) δ 2.73 (s, 2H), 1.97 (m, 2H0, 1.72 (symmetrical mult., 2H), 0.92 (t, 3H, J = 7.0 Hz), 8.01 (d, 2H, J = 7.7 Hz, aromatic protons), 7.38-7.25 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 131.7, 130.7, 130.1, 127.6, 127.0, 122.6, 43.3, 41.4, 31.9, 31.7, 29.6, 29.3, 29.1, 26.6, 22.6, 14.1; IR (KBr, cm^{-1}) 3068, 2921, 2851, 1921w, 1486, 1448, 964, 763, 731, 578; HRMS (DEI, *m/z*) calc for $C_{23}H_{27}Cl$ 338.1801, found 338.1800.

Potassium *tert*-butoxide (62 mg, 0.54 mmol) was placed in a dry 25 mL three-necked, round-bottomed flask outfitted with magnetic stir bar, nitrogen inlet, and condenser. Dry DMSO (2 mL) was injected into the flask, and the flask warmed with a 50-55 °C oil bath. A solution of **156** (93 mg, 0.27 mmol) in DMSO (3 mL) was added dropwise via syringe resulting in the formation of a dark green color. After 45 min, the solution was cooled to room temperature, quenched with water (5 mL), and extracted with ether (3 x 15 mL). The combined extracts were washed with water (3 x 5 mL), dried ($MgSO_4$), filtered, and concentrated to yield 72 mg of a pale yellow oil. ^1H NMR analysis of the crude mixture indicated the presence of **158** as the major reaction product plus the two vinyl stereoisomers (3.5 vs 1:1.2 ratio). Preparative TLC (silica gel, hexane, R_f = 0.21) yielded **158** (45.6 mg, 0.15 mmol, 55%) as a colorless oil (> 95% pure): ^1H NMR ($CDCl_3$) δ 5.73 (tt, 1H, J = 6.7, 2.0 Hz), 3.15-3.10 (br m, 2H), 2.10-2.0 (symmetrical mult., 2H), 1.44-1.00 (m, 12H), 0.86 (t, 3H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 133.9, 133.8, 129.3, 129.0, 128.9, 127.9, 126.2, 126.1, 125.0, 123.4, 123.4, 118.9, 31.9, 31.1, 29.3, 29.1, 29.0, 22.8, 22.2, 22.0, 14.3; IR (neat, cm^{-1}) 3069, 3026, 2930, 2855, 1948w, 1601w, 1478, 1441, 1436, 1051, 768, 731; HRMS (EI, *m/z*, M^+) calc for $C_{23}H_{26}$ 302.2034, found 302.2040.

Synthesis of 7-Cyclobutylidenedibenzo[a;c]bicyclo[4.1.0]heptane (171)

To a solution of adduct **153** (0.5 g, 1.9 mmol) in dry THF (16 mL) at -78 °C was added dropwise *n*-butyllithium (2.5 mmol, 1.3 equiv. of a 2.46 M/hexane solution) resulting in the formation of a dark forest green color. After 1 h of stirring at -78 °C, cyclobutanone (469 mg, 6.7 mmol) was added dropwise and the orange reaction mixture was stirred at -78 °C for 2 h, then gradually warmed to room temperature. Stirring was continued overnight. After 20 h, brine (4 mL) was injected into the flask. The organic layer was separated out and washed with brine (2 x 4 mL), dried ($MgSO_4$), filtered and concentrated. Radial chromatography (silica gel rotor, 2 mm, 2% ether, hexane, the initial polarity of the eluent mixture was gradually changed during the elution time to 5% ether, hexane) yielded **169** (578.2 mg, 1.95 mmol, 56%) as small white pellets, mp 122-124 °C. ^1H NMR ($CDCl_3$) δ 3.01 (s, 2H), 2.57 (s, 1H), 2.26 (t, 4H, J = 7.5 Hz), 2.02 (symmetrical mult., 1H), 1.74 (symmetrical mult., 1H), 8.03 (d, 2H, J = 7.6 Hz, aromatic protons), 7.40-7.20 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 131.8, 130.2, 129.9, 127.7, 127.3, 122.7, 78.8, 49.3, 32.7, 27.7, 12.7; IR (KBr, cm^{-1}) 3310, 3062, 2960, 2987, 2936, 1939w, 1609w, 1447, 1257, 751, 723.

To a solution of adduct **169** (193 mg, 0.65 mmol) in dry pyridine (10 mL) under nitrogen at room temperature was added dropwise TMSCl (3.5 mL). After stirring for 3 h at room temperature, the reaction mixture was slowly quenched with cold water (5 mL). The organic layer was separated out and the aqueous layer was extracted with ether (2 x 15 mL). The extracts and the initial organic layer were combined, washed with 5% NaOH (5 mL), water (5 mL), brine (5 mL), dried ($MgSO_4$), filtered, and concentrated. The excess of pyridine was removed by use of the vacuum pump to give 233 mg of a pale yellow solid. Radial chromatography (silica gel rotor, 2 mm, hexane) yielded

170 (110 mg, 0.29 mmol, 46%) as a white solid, mp 106-108 °C. ^{1}H NMR ($CDCl_3$) δ 2.92 (s, 2H), 2.36-2.26 (m, 4H), 1.82 (symmetrical mult., 1H), 1.65 (symmetrical mult., 1H), 0.13 (s, 9H), 7.95 (d, 2H, J = 7.6 Hz), 7.29-7.17 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 132.3, 130.9, 130.3, 127.7, 127.3, 122.8, 80.0, 48.1, 35.3, 28.1, 13.2, 2.32; IR (KBr, cm^{-1}) 3071w, 3001, 2959, 1925w, 1714, 1489, 1454, 1363, 1257, 1159, 1004, 842, 758, 582; HRMS (DCI, *m/z* MNH_4^+) calc for $C_{22}H_{29}ClNOSi$ 386.1706, found 386.1704.

A solution of silyl ether adduct **170** (185 mg, 0.50 mmol) in THF/pentane (6 mL, 1:1, v:v) under nitrogen was cooled (hexane/liquid N_2) to -90 °C. *tert*-Butyllithium (1.1 mmol, 2.2 equiv. of a 1.57 M pentane solution) was added dropwise resulting in the formation of a brigth yellow color. After stirring for 1 h at -90 °C, the reaction mixture was allowed to slowly warm to -4 °C and quenched with water (2 mL). The organic layer was washed with brine (3 mL), dried ($MgSO_4$), filtered and concentrated to give 163 mg of a clear oil. Radial chromatography (silica gel rotor, 1 mm, hexane) afforded 37 mg of a white solid which was further purified by preparative TLC (silica gel, hexane, R_f = 0.22) to yield **171** (27 mg, 0.11 mmol, 37%, ~ 95% pure) as an off white solid, mp 110-112 °C. ^{1}H NMR ($CDCl_3$) δ 3.10 (p, 2H, J = 2.3 Hz), 2.79 (symmetrical mult., 2H), 2.53 (symmetrical mult., 2H), 1.90 (symmetrical mult., 2H, diasterotopic protons, XY system), 7.20-7.27 (m, 4H, aromatic protons), 7.31-7.38 (m, 2H, aromatic protons), 7.90-8.00 (m, 2H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 133.7, 129.9, 129.2, 128.8, 127.6, 125.8,123.2, 114.1, 30.6, 21.9, 17.5; (IR KBr, cm^{-1}) 3064, 2984, 2947, 1947w, 1915w, 1787, 1605w, 1482, 1440, 1247, 841, 766, 729; HRMS (EI, *m/z*, M^+) calc for $C_{19}H_{16}$ 244.1252, found 244.1252.

Synthesis of 7-Cyclopentylidenedibenzo[a;c]bicyclo[4.1.0]heptane (**178**)

To a solution of adduct **153** (0.5 g, 1.9 mmol) in dry THF (16 mL) at -78 °C was added dropwise *n*-butyllithium (2.5 mmol, 1.3 equiv. of a 2.46 M/hexane solution) resulting in the formation of a dark forest green color. After 1 h of stirring at -78 °C, freshly distilled cyclopentanone (1.43 g, 17 mmol) was added dropwise and the orange reaction mixture was stirred at -78 °C for 2 h, then gradually warmed to room temperature. Stirring was continued overnight. After 20 h, brine (4 mL) was injected into the flask. The organic layer was separated out and washed with brine (2 x 4 mL), dried ($MgSO_4$), filtered and concentrated. Radial chromatography (silica gel rotor, 2 mm, 2% ether, hexane, the initial polarity of the eluent mixture was gradually changed during the elution time to 5% ether, hexane) yielded **176** (319 mg, 1.02 mmol, 53%) as white solid: ^{1}H NMR ($CDCl_3$) δ 2.99 (s, 2H), 2.12 (s, 1H), 1.99-1.55 (m, 8H), 8.01 (d, 2H, J = 7.3 Hz, aromatic protons), 7.41-7.24 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 132.1, 130.5, 130.4, 127.8, 127.4, 122.8, 85.6, 49.9, 37.8, 28.6, 42.4; IR (KBr, cm^{-1}) 3557, 2960, 1632, 1492, 1443, 754.

To a solution of adduct **176** (50 mg, 0.16 mmol) in dry pyridine (2.5 mL) under nitrogen at room temperature was added dropwise TMSCl (1 mL). After stirring for 3 h at room temperature, the reaction mixture was slowly quenched with cold water (5 mL). The organic layer was separated out and the aqueous layer was extracted with ether (2 x 10 mL). The extracts and the initial organic layer were combined, washed with 5% NaOH (5 mL), water (5 mL), brine (5 mL), dried ($MgSO_4$), filtered and concentrated. The excess of pyridine was removed by vacuum pump to give 67 mg of a pale yellow oil. TLC (silica gel, 10% ether, hexane) analysis of the crude mixture indicated the presence of **177** ($R_f = 0.69$). Radial chromatography (silica gel rotor, 1 mm, hexane) yielded pure **177** (38 mg, 0.09 mmol, 62%) as a white solid, mp 94-96 °C. ^{1}H NMR ($CDCl_3$) δ 3.01 (s, 2H), 2.13-1.51 (m, 8H), 0.20 (s, 9H), 8.00 (d, 2H, J = 7.6 Hz, aromatic protons), 7.34-7.22 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 131.1, 130.1, 129.1, 126.4, 125.9, 121.5, 86.5, 47.2, 37.2, 27.0, 23.9, 1.00; IR (KBr, cm^{-1}) 3075w, 3019w, 2962, 1952w, 1486, 1448, 1252, 1208, 1076, 866, 734, 584, 539; HRMS (DCI, *m/z* MNH_4^+) calc for $C_{23}H_{31}ClNOSi$ 400.1863, found 400.1867.

A solution of silyl ether adduct **177** (100 mg, 0.26 mmol) in THF/pentane (4 mL, 1:1, v:v) under nitrogen was cooled (hexane/liquid N_2)

to -90 °C. *tert*-Butyllithium (0.57 mmol, 2.2 equiv. of a 1.57 M pentane solution) was added dropwise resulting in the formation of a bright yellow color. After stirring for 1 h at -90 °C, the reaction mixture was allowed to slowly warm to -4 °C, and quenched with water (2 mL). The organic layer was washed with brine (3 mL), dried ($MgSO_4$), filtered, and concentrated to give 80 mg of a yellow oil. Radial chromatography (silica gel rotor, 1 mm, hexane) afforded 18 mg of a white solid which was further purified by preparative TLC (silica gel, hexane, R_f = 0.20) to yield **178** (10 mg, 0.03 mmol, 30%, > 92% pure) as an off white solid, mp 80 °C. ^{1}H NMR ($CDCl_3$) δ 3.07 (p, 2H, J = 2.1 Hz), 2.45 (symmetrical mult., 2H) 2.10 (symmetrical multi., 2H), 1.62 (m, 2H), 1.63 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 133.9, 133.0, 129.2, 128.8, 127.5, 125.7, 123.2, 114.7, 30.8, 26.3, 22.2; IR (KBr, cm^{-1}) 3064, 2956, 2868, 1934w, 1777, 1601, 1487, 1441; HRMS (EI, *m/z*, M$^+$) calc for $C_{20}H_{18}$ 258.1408, found 258.1407.

Synthesis of 7-Cyclohexylidenedibenzo[a;c]bicyclo[4.1.0]heptane (**178**)

To a solution of adduct **153** (0.5 g, 1.9 mmol) in dry THF (16 mL) at -78 °C was added dropwise *n*-butyllithium (2.5 mmol, 1.3 equiv. of a 2.46 M/hexane solution) resulting in the formation of a dark forest green color. After 1 h of stirring at -78 °C, freshly distilled cyclohexanone (1.13 g, 11.5 mmol) was added dropwise and the orange reaction mixture was stirred at

-78 °C for 2 h, then gradually warmed to room temperature. Stirring was continued overnight. After 20 h, brine (4 mL) was injected into the flask. The organic layer was separated out and washed with brine (2 x 4 mL), dried ($MgSO_4$), filtered and concentrated. Radial chromatography (silica gel rotor, 2 mm, 2% ether, hexane, the initial polarity of the eluent mixture was gradually changed during the elution time to 5% ether, hexane-) yielded **183** (206 mg, 0.63 mmol, 33%) as a yellow solid which was suitable for use without further purification: IR (KBr, cm^{-1}) 3561, 3076, 2933, 2858, 2832w, 1628w, 1491, 1448, 975.

To a solution of adduct **183** (179 mg, 0.55 mmol) in dry pyridine (10 mL) under nitrogen at room temperature was added dropwise TMSCl (3 mL). After stirring for 3 h at room temperature, reaction mixture was slowly quenched with cold water (5 mL). The organic layer was separated out and the aqueous layer was extracted with ether (2 x 10 mL). The extracts and the initial organic layer were combined, washed with 5% NaOH (5 mL), water (5 mL), brine (5 mL), dried ($MgSO_4$), filtered and concentrated. The excess of pyridine was removed by vacuum pump to give 150 mg of a yellow solid. Radial chromatography (silica gel rotor, 1 mm, hexane) yielded **184** (90 mg, 0.22 mmol, 41%) as a white solid, mp 132-134 °C. ^1H NMR ($CDCl_3$) δ 2.97 (s, 2H), 1.86-1.57 (m, 10H), 0.24 (s, 9H), 7.99 (d, 2H, J = 7.3 Hz, aromatic protons), 7.33-7.19 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 132.4, 131.1, 130.3, 127.7, 127.2, 122.8, 78.9, 49.9, 34.3, 27.5, 25.6, 22.0, 2.93; IR (KBr, cm^{-1}) 3076w, 2939, 2859, 1600w, 1482, 1253, 1160, 1079, 837, 732, 589; HRMS (FAB$^+$, *m/z* MNa$^+$) calc for $C_{24}H_{29}ClNaOSi$ 419.1573, found 419.1573.

A solution of silyl ether adduct **184** (90 mg, 0.22 mmol) in THF/pentane (4 mL, 1:1, v:v) under nitrogen was cooled (hexane/liquid N_2) to -90 °C. *tert*-Butyllithium (0.50 mmol, 2.2 equiv. of a 1.57 M pentane solution) was added dropwise resulting in the formation of a bright yellow color. After stirring for 1 h at -90 °C, the reaction mixture was allowed to slowly warm to -4 °C, and quenched with water (2 mL). The organic layer was washed with brine (3 mL), dried ($MgSO_4$), filtered and concentrated to give 94 mg of a white solid. Radial chromatography (silica gel rotor, 1 mm, hexane) afforded 47 mg of a white solid which was further purified by preparative TLC (silica gel, hexane, R_f = 0.20) to afford **185** (23 mg, 0.09 mmol, 55%, > 92% pure) as an off white solid, mp 117-119 °C. ^{1}H NMR ($CDCl_3$) δ 3.14 (br s, 2H), 2.21 (symmetrical mult., 2H), 1.99 (symmetrical mult., 2H), 1.66-1.24 (m, 6H), 8.01-7.97 (m, 2H, aromatic protons), 7.46-7.39 (m, 2H, aromatic protons), 7.29-7.23 (m, 4H, aromatic protons); 134.5, 130.2, 129.3, 128.9, 127.8, 125.8, 123.4, 116.3, 32.7, 27.8, 26.5, 22.1; IR (KBr, cm^{-1}) 3073, 3023, 2933, 2849, 1944w,1601w, 1489, 1450, 1247, 1051, 837, 730; HRMS (EI, m/z, M$^+$) calc for $C_{21}H_{20}$ 272.1565, found 272.1552.

Reaction of **153** with n-Butyllithium and Cyclootene

A cooled (-10 °C bath) mixture of adduct (200 mg, 0.78 mmol), freshly distilled cyclooctene (2 mL), and dry ether (3 mL) was treated with *n*-butyllithium (1.95 mmol, 2.5 equiv. of a 2.46 M solution in hexane) over a period of 10 min, resulting in the formation of a yellow color. After 1 h of stirring at -10 °C, the mixture was allow to warm gradually to room temperature. Stirring was continud overnight. After then, the reaction was quenched by addition of water (2 mL). The layers were separated and the aqueous phase was extracted with ether (2 x 5 mL). The organic layers were combined and washed with brine (5 mL), dried ($MgSO_4$) and concentrated to give a yellow oil. ^{1}H NMR spectrum of the crude mixture showed the following chemical shifts (δ): 2.36 (d, 2H, J = 4.2 Hz), 1.65-1.41 (m, 6H), 1.01 (t, 3H, J = 7.1 Hz), 0.31 (m, 1H), 8.04 (m, 2H, aromatic protons), 7.50-7.21 (m, 6H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 136.3, 129.3, 128.9, 127.6, 125.8, 123.1, 33.1, 31.4, 27.0, 26.2, 22.6, 14.2; DEPT 135 ($CDCl_3$) δ 128.9 (CH), 127.6 (CH), 125.8 (CH), 123.1 (CH), 33.1 (CH_2), 31.4 (CH_2), 27.0 (CH_3), 26.4 (CH), 22.5 (CH_2), 14.2 (CH), consistent with the monoalkylated product **187**, but not further characterization of this structure was undertaken. Based on TLC (silica gel, hexane), ^{1}H NMR and ^{13}C NMR analysis, no evidence for spiropentane **186** was present.

In other experiment, cyclohexene was used as the reactive olefin;

however, this did not alter the above results.

Reaction of **153** with Lithium Wire and Cyclooctene

To a solution of adduct **153** (200 mg, 0.78 mmol), freshly distilled cyclooctene (2 mL), and dry ether (5 mL) under nitrogen, was added, cut in hexane, Li wire (54 mg, 10 equiv.). The reaction mixture was refluxed for 24 hours. After then, the mixture was cooled to room temperature and quenched with water (2 mL). The resulting solution was extracted with ether (2 x 10 mL) and the combined ether extracts were washed with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a brown solid. ^1H NMR analysis of the crude mixture indicated unreacted starting material.

Exploratory Photochemistry

Photolysis of 7-*endo* -vinyldibenzo[a;c]bicyclo[4.1.0]heptane (**141**). 1,3-Cyclopentadiene Adduct (**143**).

A solution of **141** (50 mg, 0.23 mmol) in cyclopentane (100 mL) was placed in a quartz Dewar vessel and saturated with nitrogen. The solution was irradiated in the Rayonet with 254 nm lamps at 0 °C for 1 h. An aliquot of the photolyzed mixture (*ca.* 1.0 mL) was removed by syringe, concentrated under reduced pressure, and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24) and the presence of some unreacted starting material (R_f = 0.14). Irradiation was continued an additional hour. A second aliquot was withdrawn (*ca.* 1.0 mL), concentrated under reduced pressure, and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. Freshly distilled 1,3-cyclopentadiene (**142**, 10 mL) was added via syringe. The Dewar vessel was gently shacked for 10 min, clamped in a dark place and allowed to warm to room temperature. After 1 h, the solvent and excess of 1,3-cyclopentadiene were removed *in vacuo*. Capillary GC (T° program, T_i = 70 °C, T_f = 200 °C) analysis of the crude mixture indicated the presence of three components, *endo* -adduct (**143**, rt 3.0 min), 1,2-cyclopentadiene dimer (rt 7.6 min, and phenanthrene (**135**, rt 16.9 min). GC retention times were compared with authentic samples of *endo* -adduct **143**, independently synthesized by the procedure of Closs,[159] 1,2-cyclopentadiene dimer and phenanthrene purchased from Aldrich. ^{1}H NMR ($CDCl_3$) analysis of the crude indicated a mixture of phenanthrene (**135**), 8.56 (d, 2H, J = 8.1 Hz), 7.78-7.45 (m, 6H), *endo*-cycloadduct (**143**), 5.72 (t, 2H, J = 2.0 Hz), 0.60 (symmetrical mult., 1H), 0.38 (symmetrical mult., 1H) and 1,3-cyclopentadiene dimer which resonances buried some of the *endo*-cycloadduct peaks. The yield of *endo*-cycloadduct (**143**) respect to phenanthrene (**135**) was 62%; it was calculated from the crude oil using ^{1}H NMR integration.

Photolysis of 7-*endo* -vinyldibenzo [a;c]bicyclo[4.1.0]heptane (**141**). Diphenylisobenzofuran Adducts **145** and **146**.

A solution of **141** (50 mg, 0.23 mmol) in cyclopentane (100 mL) was placed in a quartz Dewar vessel and saturated with nitrogen. The solution was irradiated in the Rayonet with 254 nm lamps for 1 h, at 0 °C. An aliquot of the photolyzed mixture (*ca.* 1.0 mL) was removed by syringe, concentrated under reduced pressure, and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24) and the presence of some unreacted starting material (R_f = 0.14). Irradiation was continued an additional hour. A second aliquot was withdrawn, concentrated under reduced pressure, and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. A nitrogen saturated solution of DPIBF (**144**, 0.5 g, 1.8 mmol) in toluene (10 mL) was added via syringe. The Dewar vessel was gently shacked for 10 min, clamped in a dark place and allowed to stand overnight at 14 °C. Solvents were removed *in vacuo* to obtain a bright yellow solid. TLC (silica gel, 3:2 hexane/CH_2Cl_2) analysis of the crude mixture indicated the presence of two compounds, one of which was DPIBF (**144**, R_f = 0.62). ^{1}H NMR ($CDCl_3$) analysis of the crude indicated a mixture of phenanthrene (**135**), 8.56 (d, 2H, J = 8.1 Hz), 7.78-7.45 (m, 6H), *endo*- and *exo*-cycloadducts (**146** and **145**) in a ratio of 1:2.3. The yields of *endo*- and *exo*-cycloadducts respect to phenanthrene (**135**) were 24% and 75%, respectively.

They were calculated from the crude solid using ^{1}H NMR integration. Preparative TLC (silica gel, 3:2 hexane/CH_2Cl_2) yielded *exo*-1a,2,7,7a-tetrahydro-2,7-diphenyl-2,7-epoxy-1H-cyclopropa[b]naphthaline (**145**, 22 mg, 0.07 mmol, 31% isolated) as a yellow solid: ^{1}H NMR (C_6D_6) δ 1.82 (dt, 1H, J_{gem} = 5.1 Hz, J_{trans} = 3.6 Hz, A part of an ABX_2 system) 1.58 (dd, 2H, J_{cis} = 6.7 Hz, J_{trans}= 3.6 Hz, X_2 part of an ABX_2 system), 0.80 (td, 1H, J_{cis}= 6.7, J_{gem} = 5.2 Hz, B part of an ABX_2 system), 7.75-7.15 (m, 10H, aromatic protons), 6.98-6.73 (m, 4H, aromatic protons); ^{13}C NMR (C_6D_6) δ 151.5, 137.5, 128.5, 128.4, 128.0, 127.7, 126.3, 119.5, 88.9, 26.0, 15.7. Chemical shifts were compared to the literature values where erroneously reported proton B as a doublet of triplet.[160]

Photolysis of 7-*endo*-vinyldibenzo[a;c]bicyclo[4.1.0]heptane (**141**) in Cyclohexene

A solution of **141** (15 mg, 0.07 mmol) in cyclopentane (10 mL) and freshly distilled cyclohexene (5 mL) was placed in a quartz test tube and saturated with nitrogen. The solution was irradiated in the Rayonet with 254 nm lamps for 2 h at 0 °C. The reaction was followed by TLC. The resulting photolized mixture was cooled in an ice-water bath for 30 min and transferred to a 50 mL round-bottomed flask. The solvent was carefully evaporated in *vacuo* at 0 °C. Capillary GC (T° program, T_i = 70 °C, T_f = 200

°C) analysis of the crude mixture indicated the presence of phenanthrene (**135**, rt 17.0 min) and two low boiling point components with retention times of 3.4 min and rt 4.4 min. GCMS analysis did not indicate a molecular ion peak (M^+) at *m/z* 122. ^{1}H NMR analysis of the crude material indicated formation of phenanthrene (**135**), but there were no vinyl resonances present. Based on GC, GCMS, and ^{1}H NMR, no evidence for a trapped vinylcarbene was obtained.

Photolysis of 7-Cyclootylidenedibenzo [a;c]bicyclo[4.1.0]heptane (158)

Adduct **158** (8 mg, 26.4 X 10^{-3} mol) was dissolved in pentane in a 10 mL volumetric flask. The solution was placed in a quartz test tube and saturated with nitrogen. It was irradiated in the Rayonet with 254 nm lamps for 1 h at 32 °C. An aliquot (*ca.* 0.2 mL) of the photolyzed mixture was removed by syringe and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24). Irradiation was continued an additional hour. A second aliquot was withdrawn and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. The irradiated solution was cooled (refrigerator) for 20 min. 2,7-Dimethylnaphthalene (4.7 mg) was added as an internal standard (IS). Capillary GC (T° program, T_i = 80 °C, T_f = 200 °C) analysis of the photolyzed solution indicated the presence of two components, 1-nonyne (**160**, rt 3.1 min) and phenanthrene (**135**, rt 16.5 min).

GC retention times were compared with authentic samples. The solution was concentrated under reduced pressure at 0 °C. ^{1}H NMR of the crude material indicated a mixture of phenanthrene (**135**), 8.56 (d, 2H, J = 8.1 Hz), 7.78-7.45 (m, 6H), and 1-nonyne (**160**), 2.18 (td, 2H, J = 7.0, 2.6 Hz), 1.92 (t, 1H, J = 2.6 Hz, acetylenic proton), 1.57-1.23 (m, 10H), 0.88 (t, 3H, J = 6.2 Hz). Comparison of the calibrated response (three runs average of 1 μL sample) for 1-nonyne and phenanthrene in the irradiated solution versus the averaged responses for 1-nonyne and phenanthrene in a freshly prepared standard solution gave 1-nonyne (3.1 mg, 94%) and phenanthrene (4.6 mg, 98%) yield.

Photolysis of 7-Cyclobutylidenedibenzo[a;c]bicyclo[4.1.0]heptane (171)

Adduct **171** (50 mg, 0.20 mmol), pentane (30 mL) and distilled cyclohexene (20 mL) were combined in a 50 mL volumetric flask. The solution was placed in a quartz tube and saturated with nitrogen. It was irradiated in the Rayonet with 254 nm lamps for 1 h at 32 °C. An aliquot (*ca.* 0.2 mL) of the photolyzed mixture was removed via syringe and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24). Irradiation was continued for an additional hour. A second aliquot was withdrawn and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. The irradiated solution was cooled (refrigerator) for 20 min. An aliquot of 5 ml was removed and 2,7-dimethylnaphthalene (3.0 mg) was added as internal standard. The solvent of the remaining 45 mL solution was evaporated under reduced pressure at 0 °C. Capillary GC (T_i = 80 °C, T_f = 200 °C) analysis of the spiked solution indicated the presence of two major components with retention times of 11.92 min and 11.95 min, plus phenanthrene (**135**, rt 16.5 min). GC retention time for phenanthrene was compared with an authentic sample. ^{1}H NMR of the crude material indicated a mixture of phenanthrene (**135**), 8.56 (d, 2H, J = 8.1 Hz), 7.78-7.45 (m, 6H), and constitutional isomers **172** and **168** in a 1:1.2 ratio. Chromatography (Florisil, pentane) afforded a 1:1.2 mixture of compounds **172** and **168** (20 mg, 66%) as colorless liquids (**172**): Capillary GC (70 °C, rt 23.9 min); ^{1}H NMR ($CDCl_3$) δ 5.69 (AB system, 2H, J_{cis} = 11.0 Hz), 5.36 (symmetrical mult., 1H) 2.88-285 (m, 1H) 2.32-2.23 (m, 4H), 1.99-196 (m, 2H), 156-1.49 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 148.3, 130.1, 127.3, 123.5, 37.5, 33.7, 32.5, 28.1, 25.4, 23.6, 21.2; DEPT 135 ($CDCl_3$) δ 129.8 (CH), 127.1 (CH), 123.2 (CH), 37.3 (CH), 33.5 (CH_2), 32.3 (CH_2), 27.9 (CH_2), 25.2 (CH_2), 23.4 (CH_2), 21.0 (CH_2); MS (EI) *m/z* 148 (M^+). (**168**): Capillary GC (70 °C, rt 24.5 min); ^{1}H- NMR ($CDCl_3$) δ 2.87 (symmetrical mult., 2H), 2.26-2.23 (m, 4H), 2.10 -2.04 (m, 2H), 1.70-1.26 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 153.4, 39.4, 30.6, 26.5, 23.6, 18.5; MS (EI) *m/z* 148 (M^+). Chemical shifts for **168** were compared to the literature values.[37e] Comparison of the calibrated response (three runs average of 1 µL sample) for phenanthrene in the irradiated solution versus the calibrated response for phenanthrene in a freshly prepared standard solution gave (34.9 mg, 95.5%) yield.

Photolysis of 7-Cyclopentylidenedibenzo[a;c]bicyclo[4.1.0]heptane(**178**)

Adduct **178** (8 mg, 0.03 mmol), distilled cyclohexene (8 mL) and pentane (2 mL) were combined in a 10 mL volumetric flask. The solution was placed in a quartz test tube and saturated with nitrogen. It was irradiated in the Rayonet with 254 nm lamps for 1 h at 32 °C. An aliquot (*ca.* 0.2 mL) of the reaction mixture was removed by syringe and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24). Irradiation was continued for an additional hour. A second aliquot was withdrawn and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. The irradiated solution was cooled (refrigerator) for 20 min. 2,7-Dimethylnaphthalene (5.5 mg) was added as an internal standard (IS). Capillary GC (T_i = 120 °C, T_f = 200 °C) analysis of the photolyzed solution indicated the presence of two components, 7-cyclopentylidenebicyclo[4.1.0]heptane (**175**, rt 5.8 min) and phenathrene (**135**, rt 14.3 min). GC retention time for phenanthrene was compared with an authentic sample. The solution was concentrated under reduced pressure, and chromatographed on florisil (1 x 20 cm, pentane) to yield **175** (3.4 mg, 0.02 mmol, 62%) as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.35-2.28 (m, 4H), 1.73-

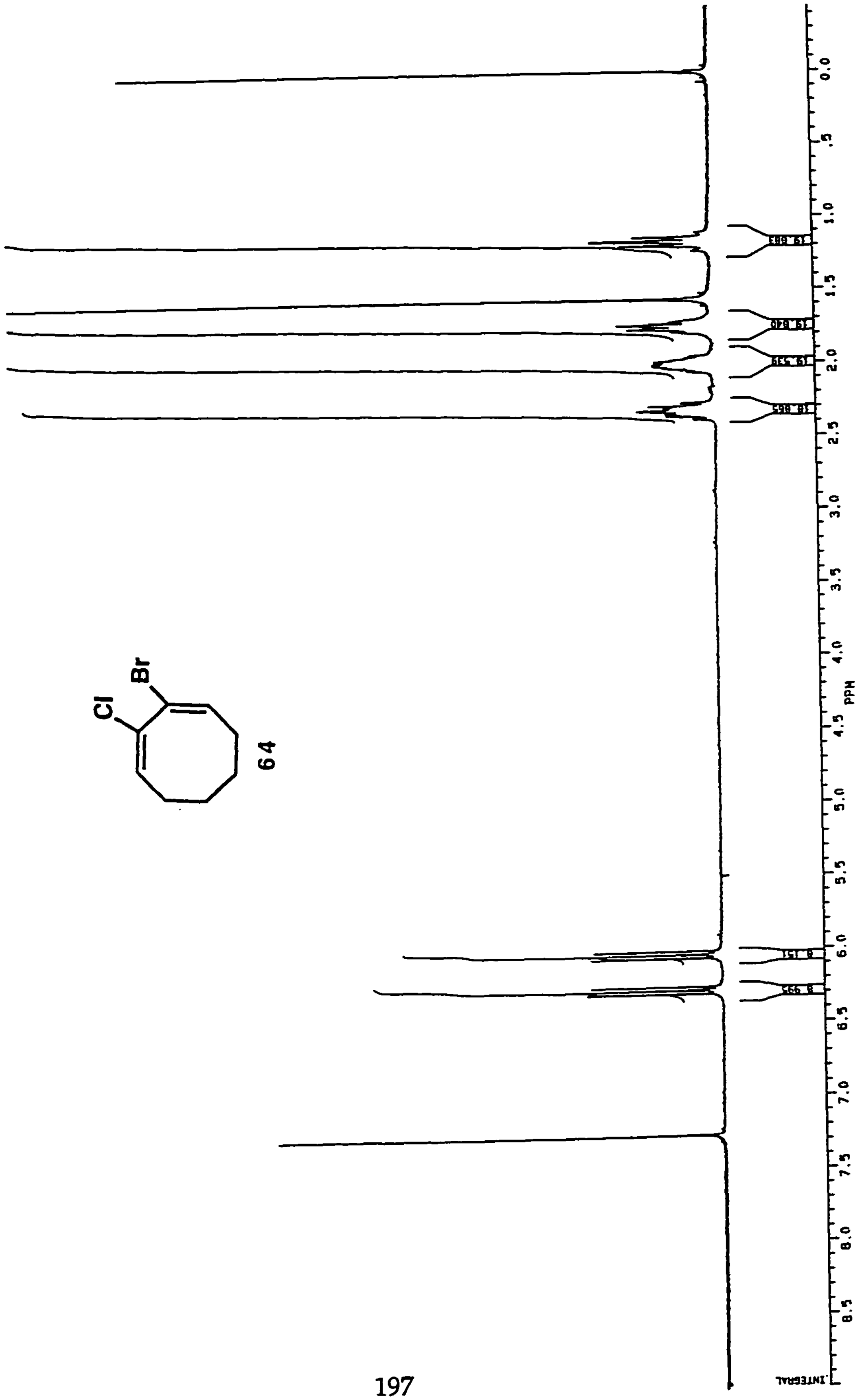
1.60 (m, 8H), 1.55-1.50 (m, 2H), 1.22-1.15 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 131.0, 120.5, 31.2, 26.6, 22.1, 21.4, 12.8; MS (EI) *m/z* (%) 162 (M^+, 39), 133(27), 119(32), 105(36), 93(66), 91(100), 79(88), 67(32), 105(36), 93(66); IR ($CDCl_3$, cm^{-1}). Chemical shifts, and mass spectrum data were compared with the literature values.[169] Comparison of the calibrated response (three runs average of 1 μL sample) for phenanthrene in the irradiated solution versus the calibrated response for phenanthrene in a freshly prepared standard solution gave (5.1 mg, 94%) yield.

Photolysis of 7-Cyclohexylidenedibenzo[a;c]bicyclo[4.1.0]heptane (185)

Adduct **185** (10 mg, 0.03 mmol), distilled cyclohexene (8 mL) and pentane (2 mL) were combined in a 10 mL volumetric flask. The solution was placed in a quartz test tube and saturated with nitrogen. It was irradiated in the Rayonet with 254 nm lamps for 1 h at 32 °C. An aliquot (*ca.* 0.2 mL) of the reaction mixture was removed by syringe and analyzed by TLC (silica gel, hexane) which indicated formation of phenanthrene (**135**, R_f = 0.24). Irradiation was continued an additional hour. A second aliquot was withdrawn and analyzed by TLC (silica gel, hexane). The reaction was judged to be completed. The irradiated solution was cooled (refrigerator) for 20 min. 2,7-Dimethylnaphthalene (6.4 mg) was added as an internal standard (IS). Capillary GC (T_i = 30 °C, T_f = 200 °C) analysis of the photolyzed solution indicated the presence of phenanthrene (**135**, rt 18.6 min). GC retention time for phenanthrene was compared with an authentic sample. The solution was concentrated under reduced pressure, and chromatographed on florisil (1 x 20 cm, pentane) to yield 7-cyclohexylidenebicyclo[4.1.0]heptane (**181**, 3.7 mg, 0.02 mmol, 58%) as a colorless liquid: Capillary GC (120 °C, rt 8.7 min); ^1H NMR ($CDCl_3$) δ 2.22 (m, 4H), 1.75-1.19 (m, 14H), 0.91-0.85 (m, 2H); MS (EI) *m/z* (%) 176(M^+, 32), 133(49), 119(43), 91(87), 79(100), 67(61), 41(54); IR ($CDCl_3$, cm^{-1}). Chemical shifts and mass spectrum data were compared with the literature values.[172] Comparison of the calibrated response (three runs average of 1 μL sample) for phenanthrene in the irradiated solution versus the calibrated response for phenanthrene in a freshly prepared standard solution gave (6.4 mg, 99%) yield.

APPENDIX A

SPECTRA FOR COMPOUNDS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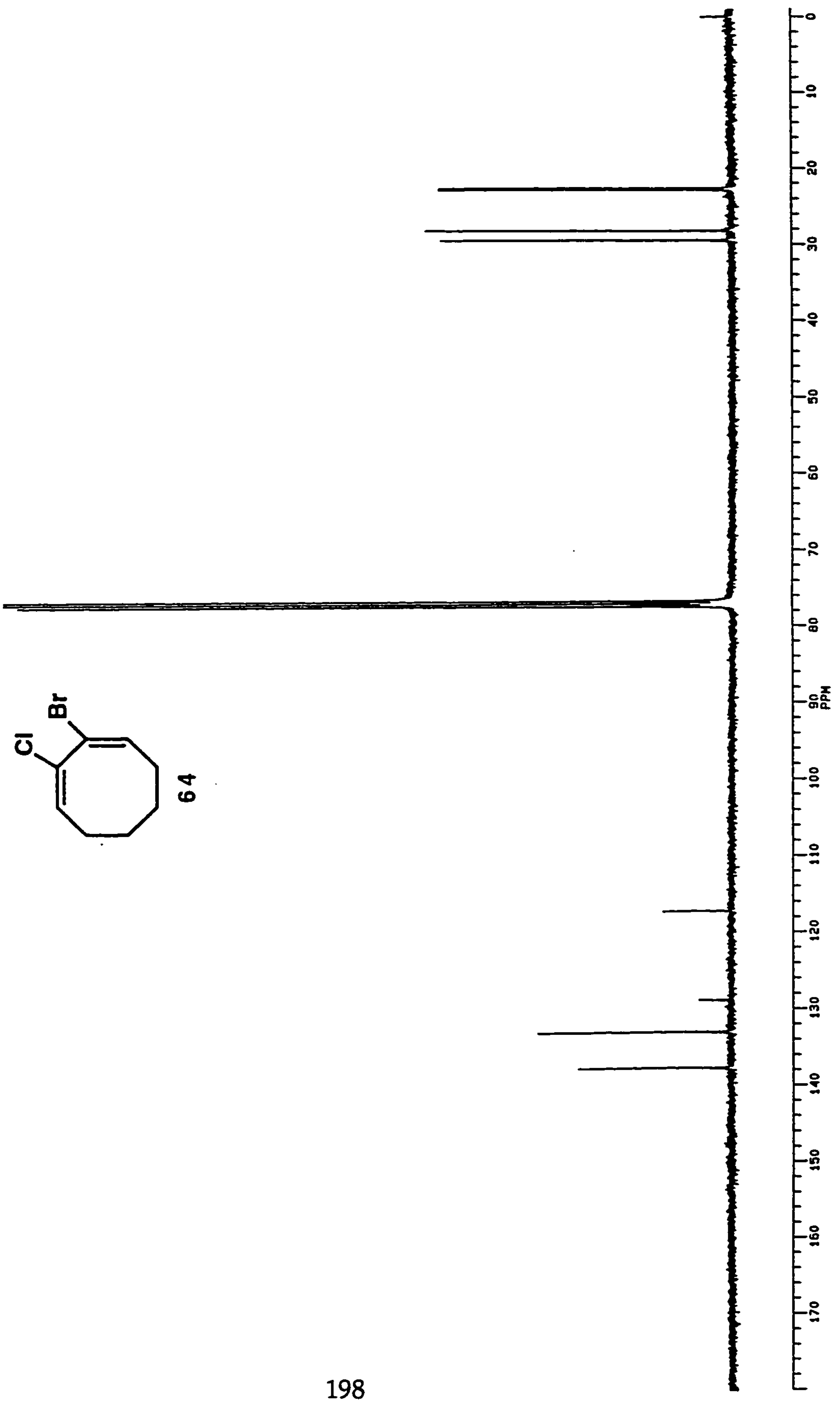
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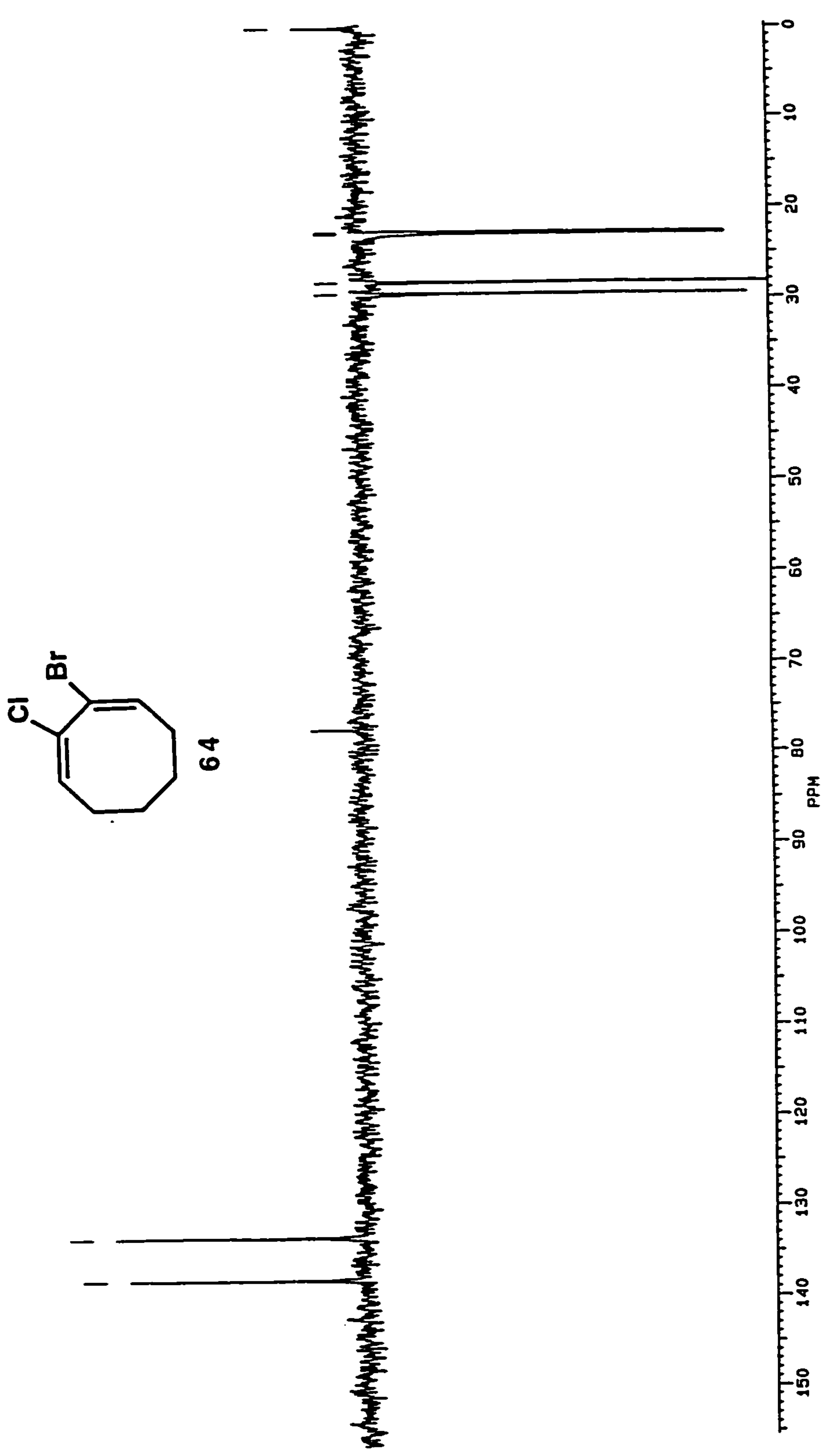

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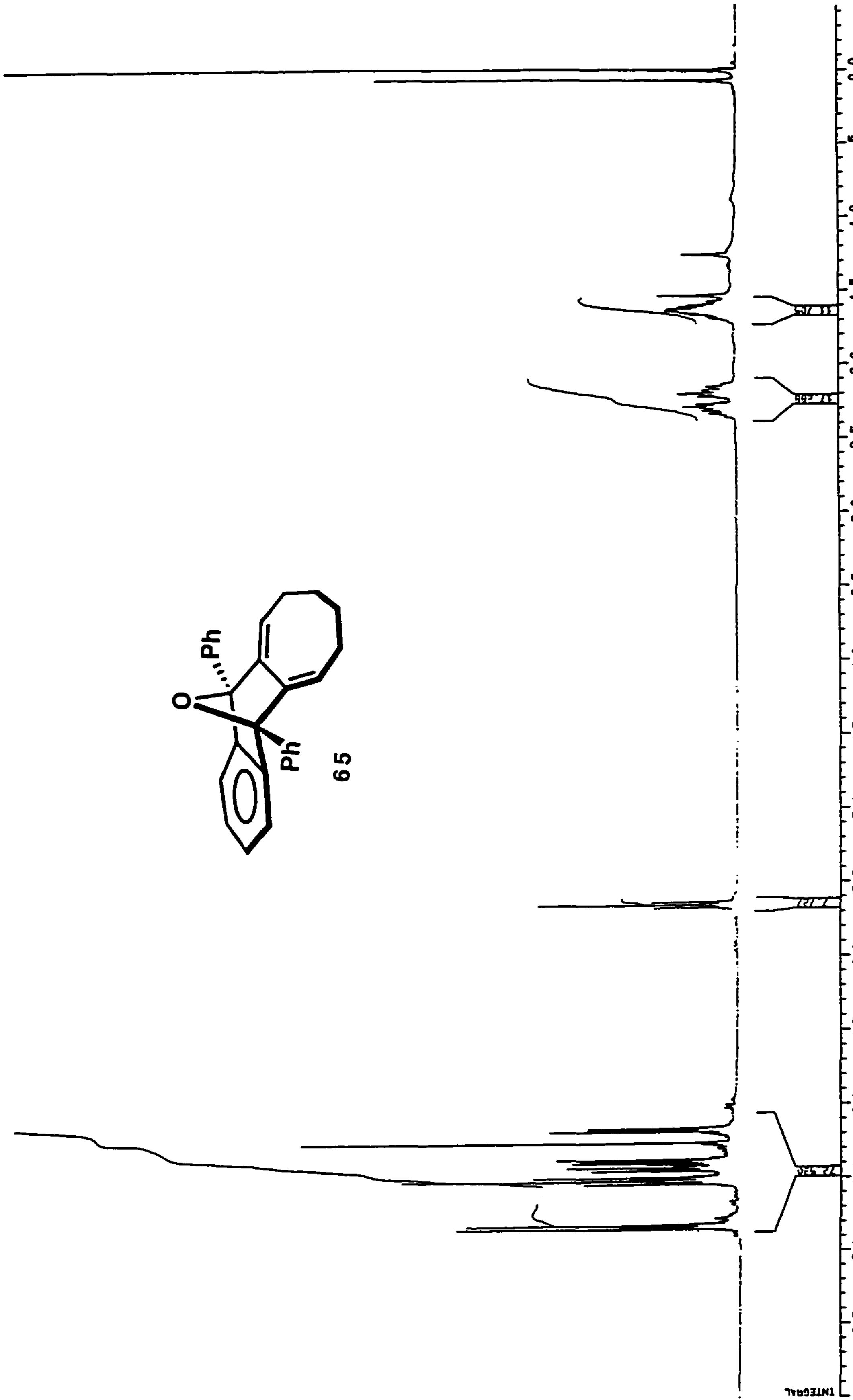
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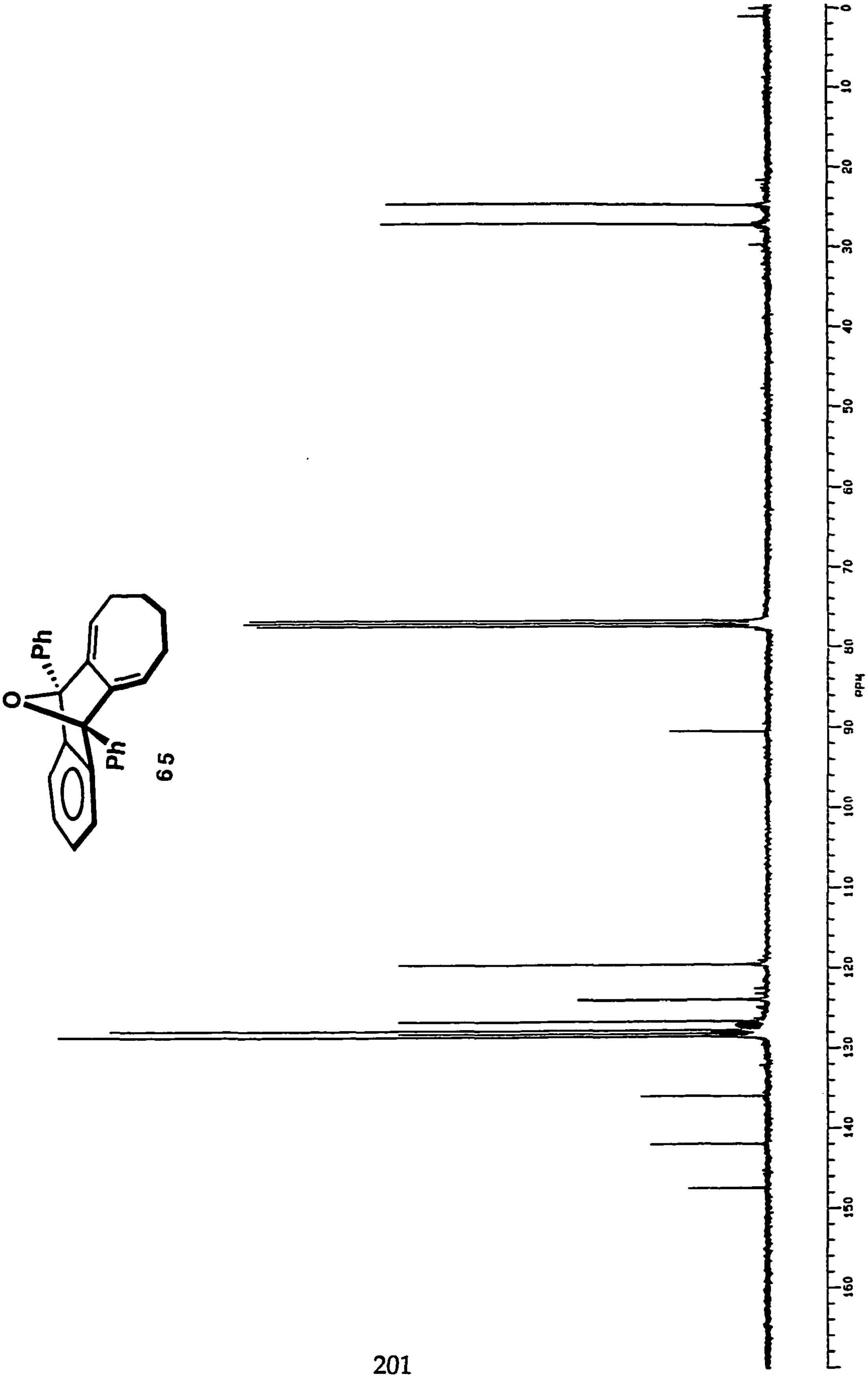

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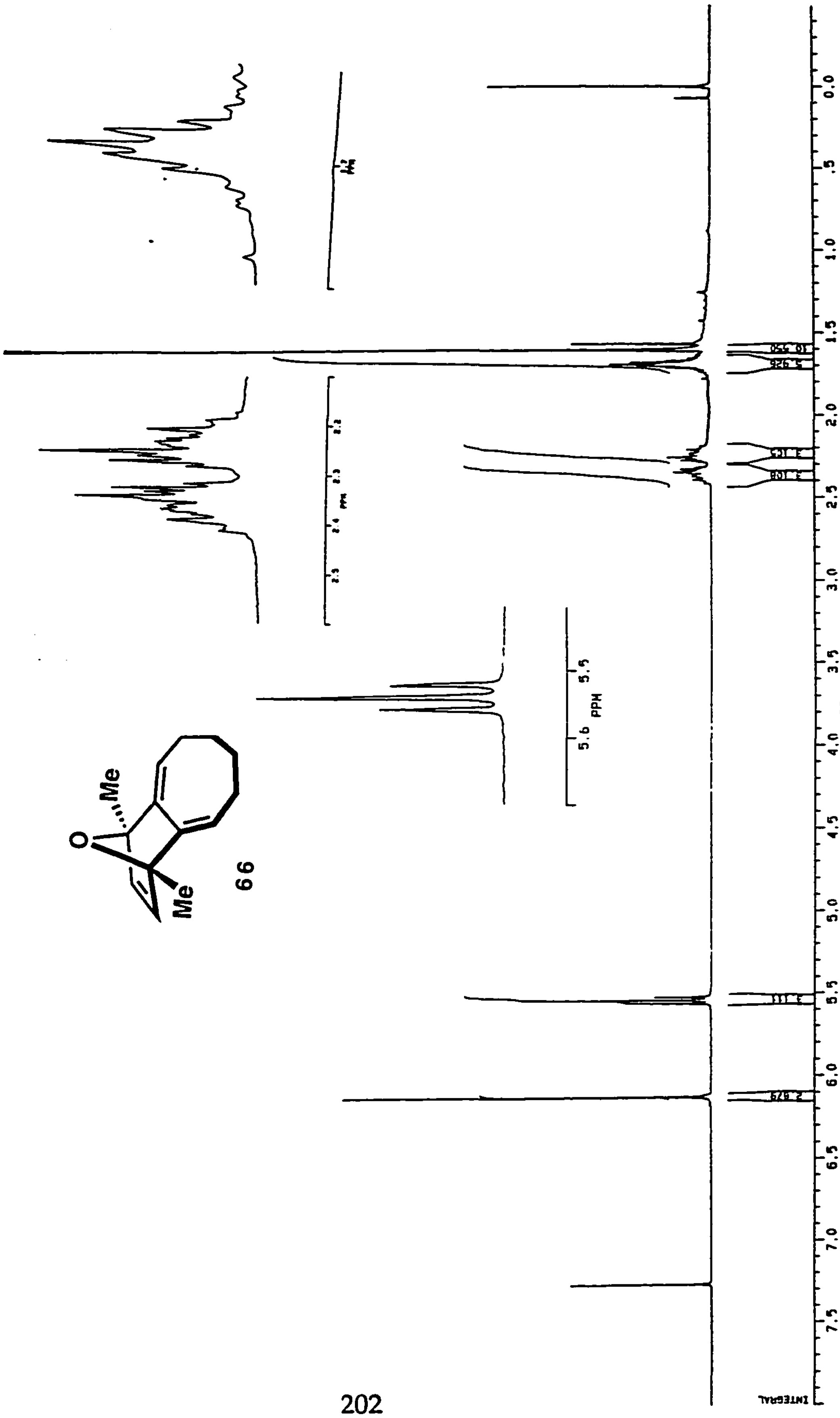
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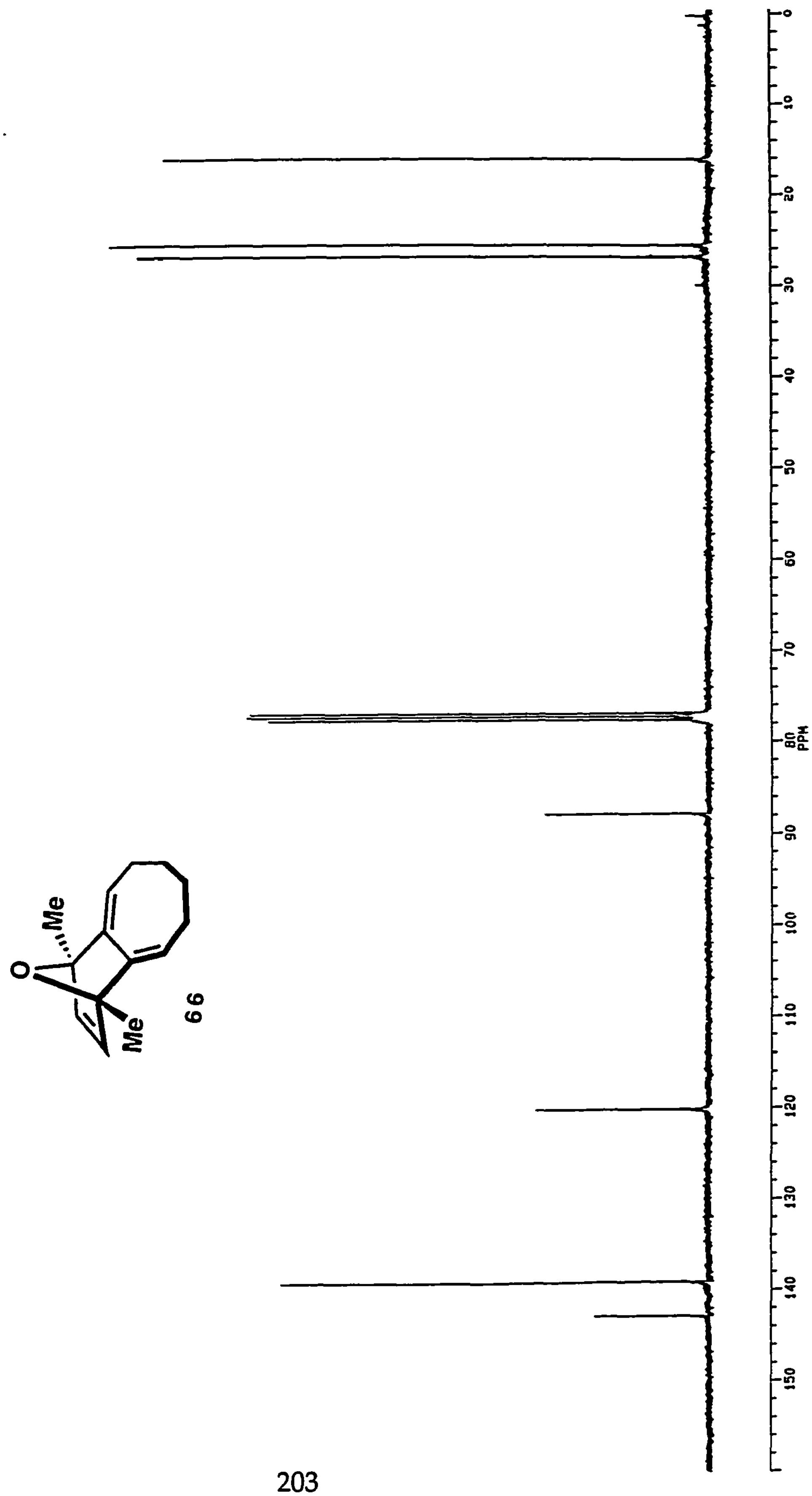

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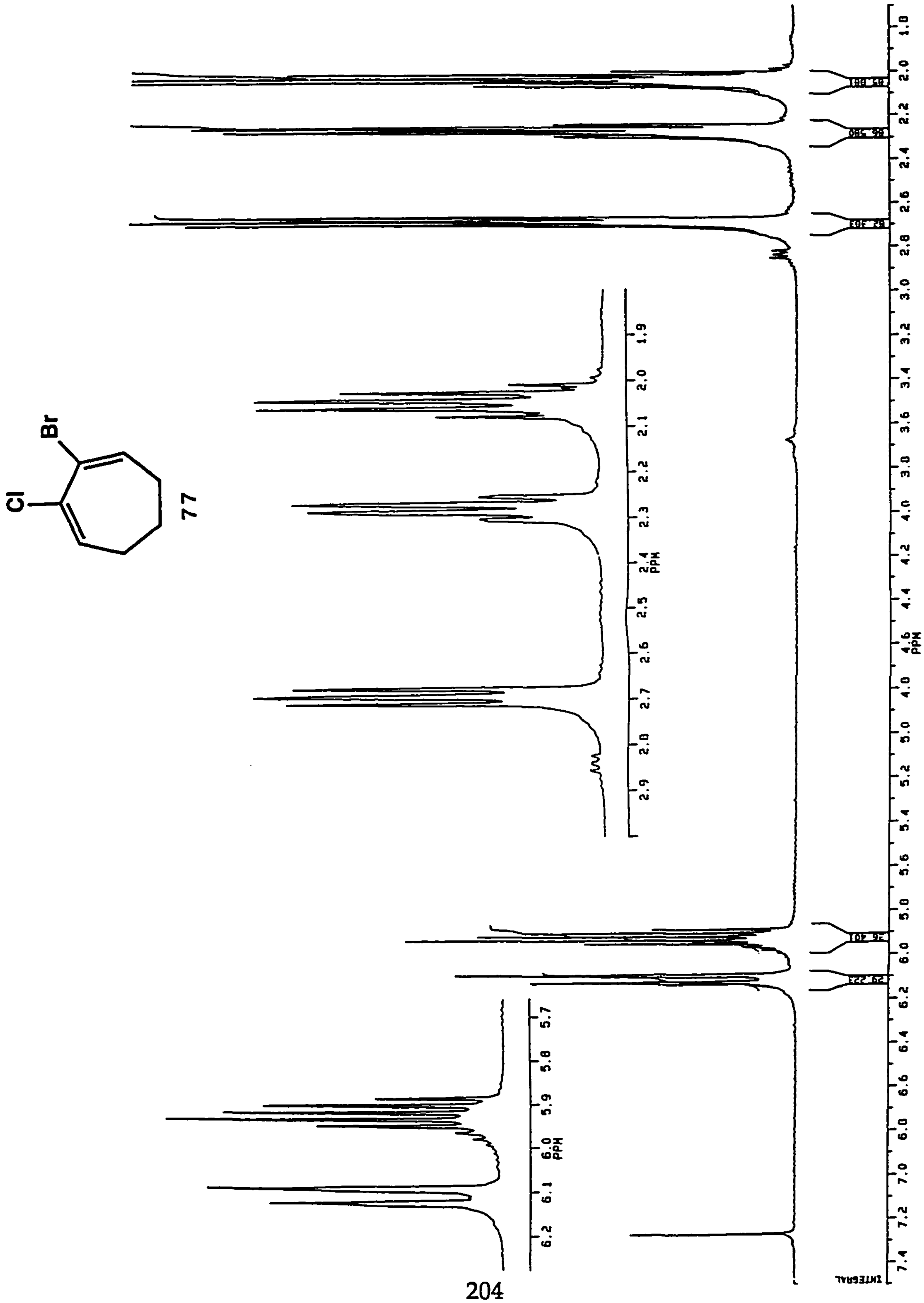
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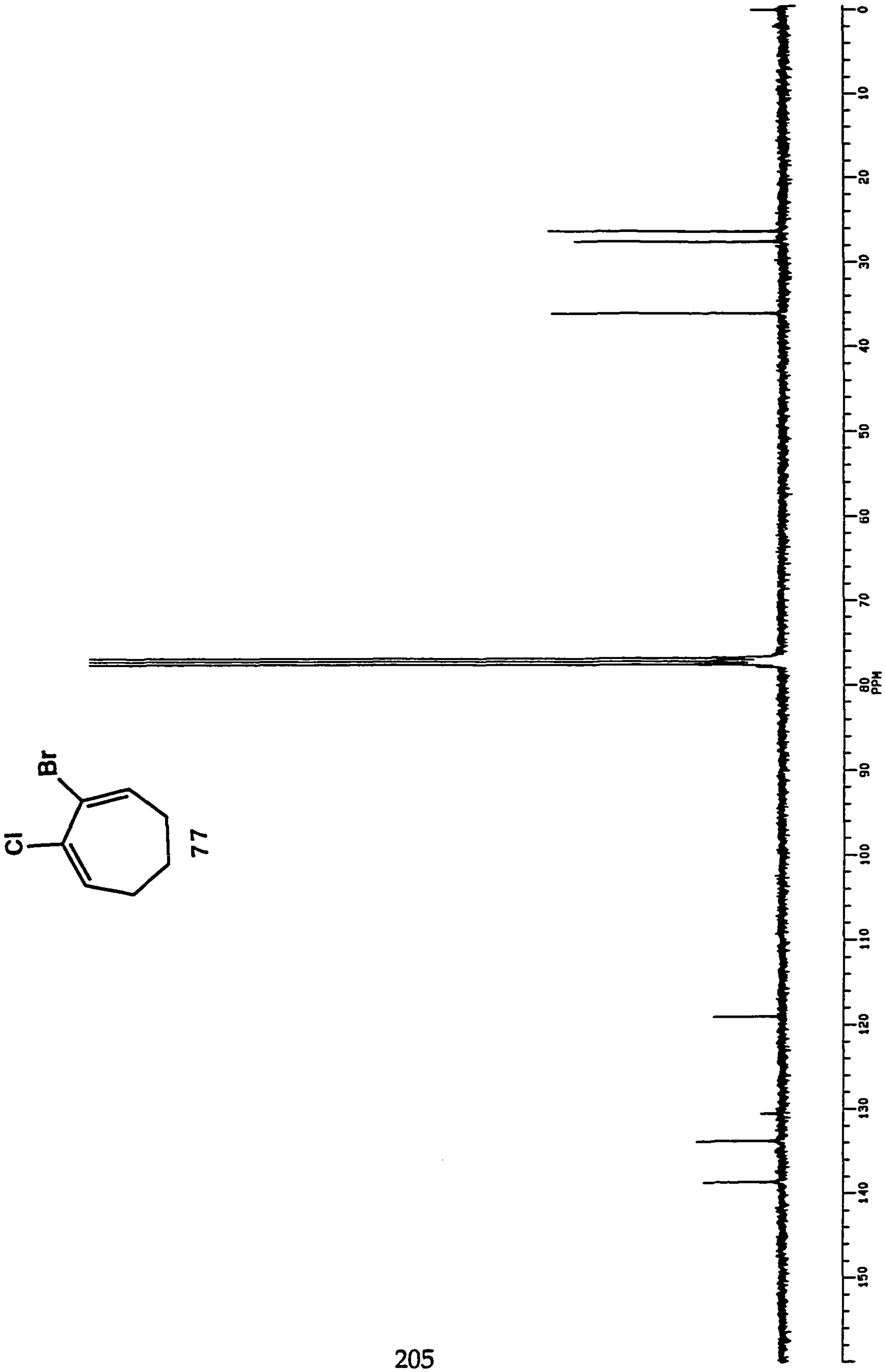

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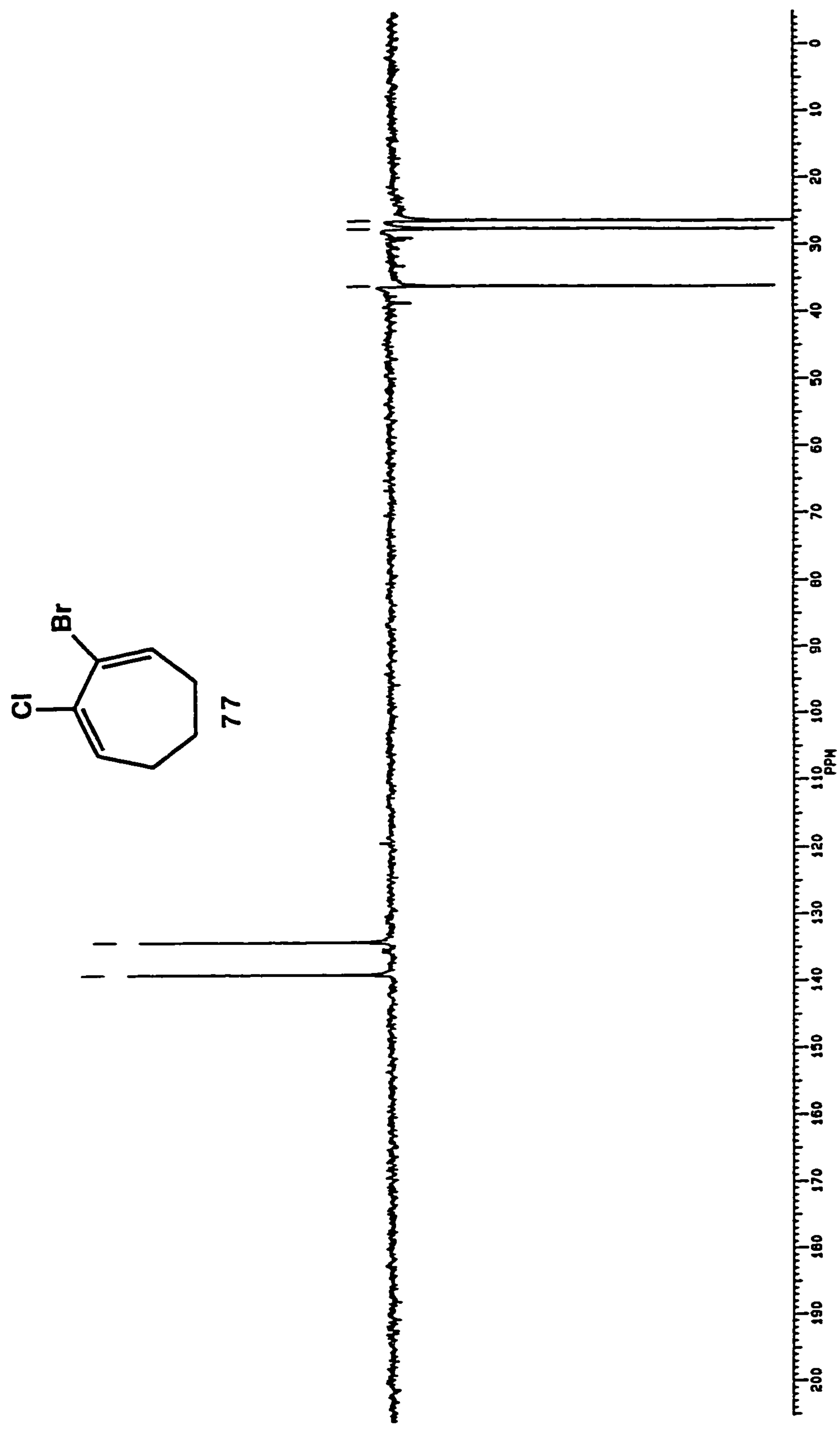
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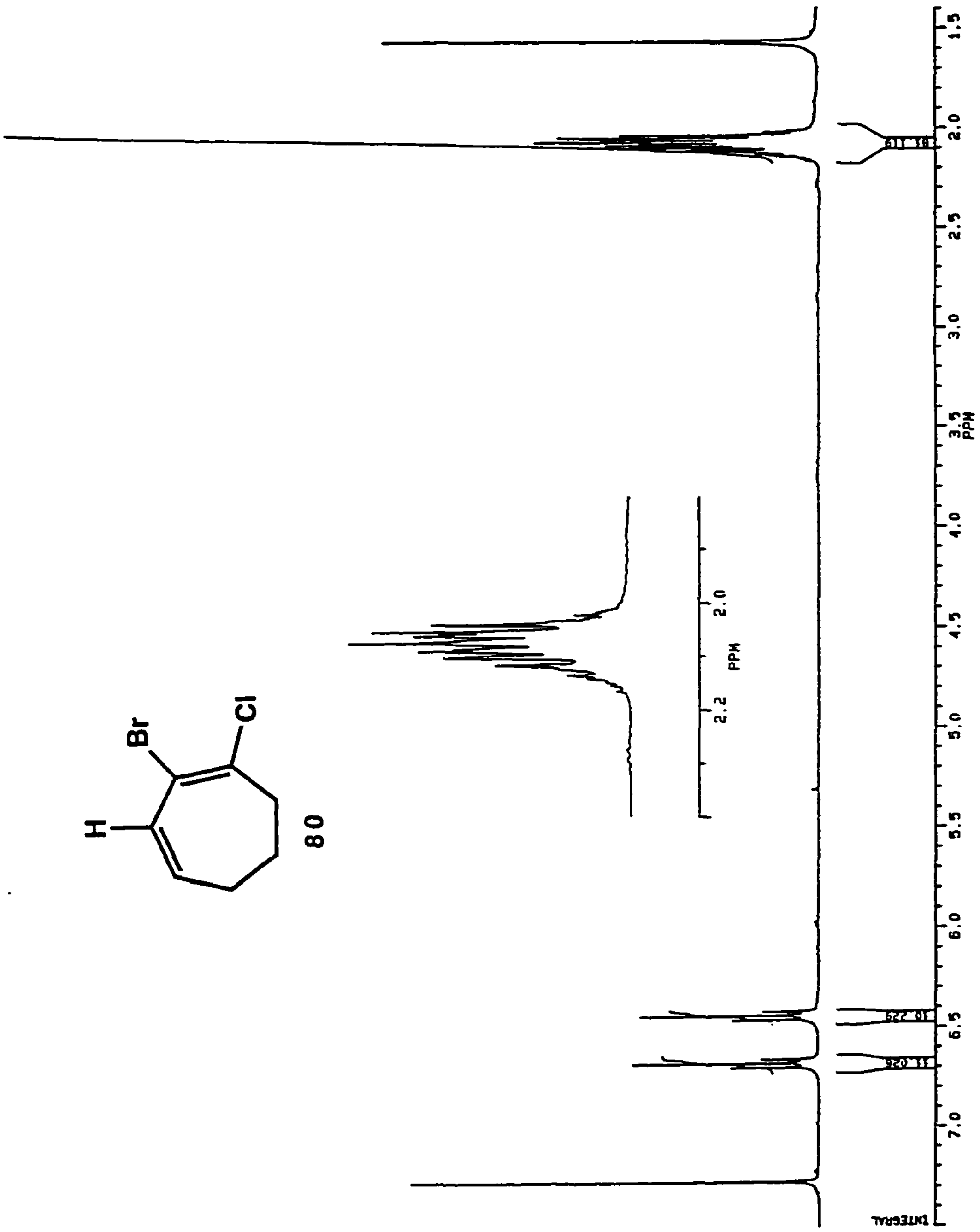

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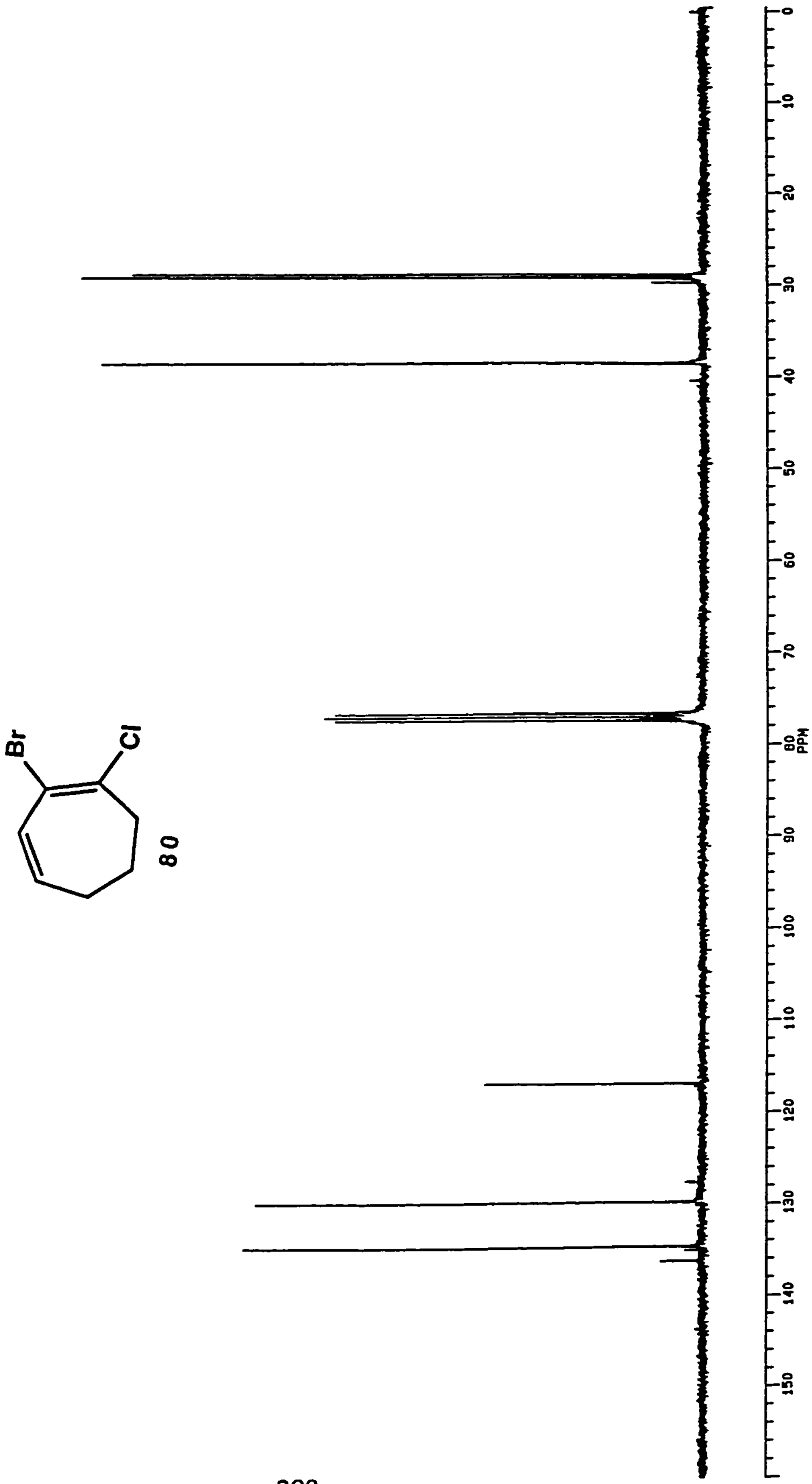Br
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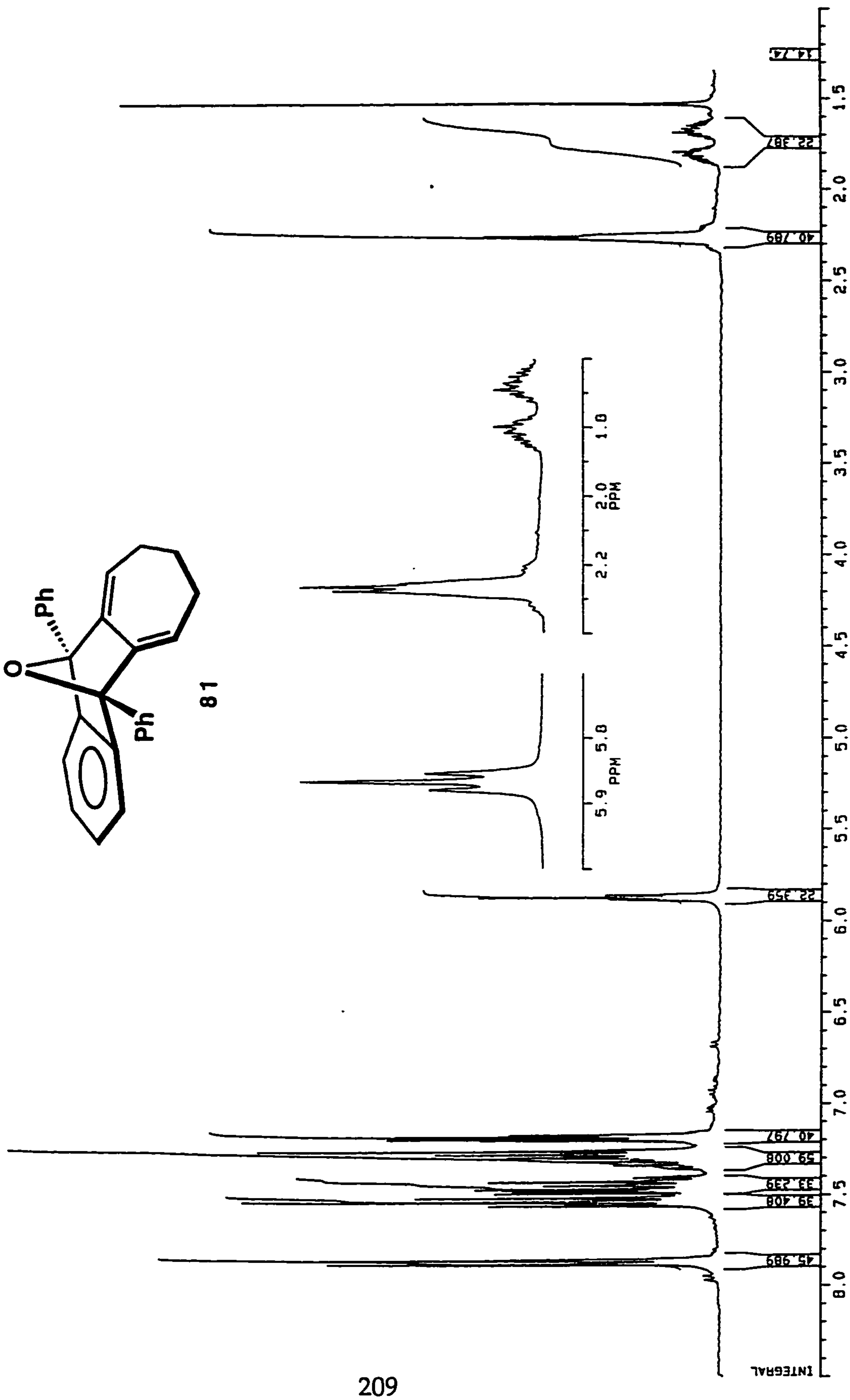
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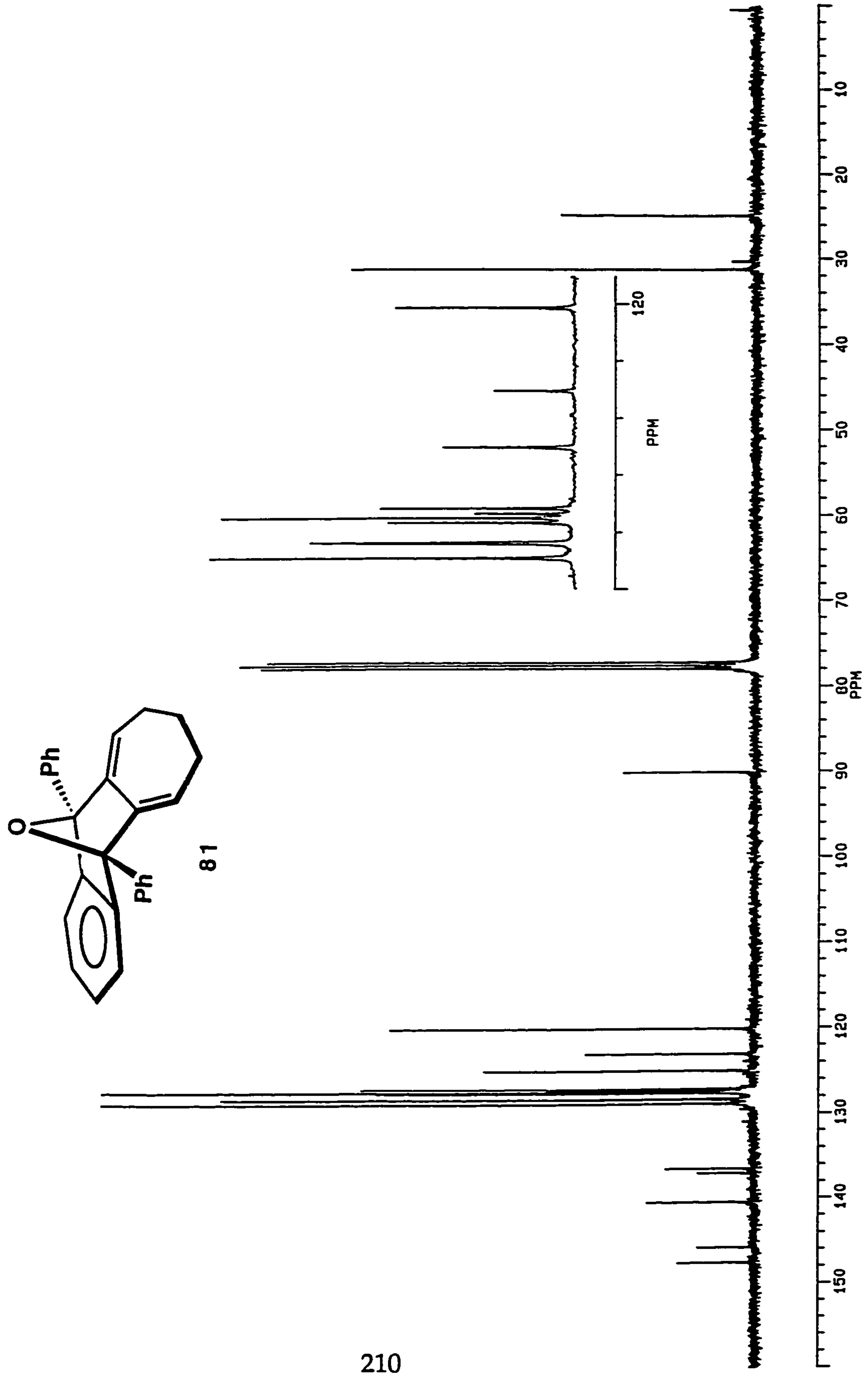
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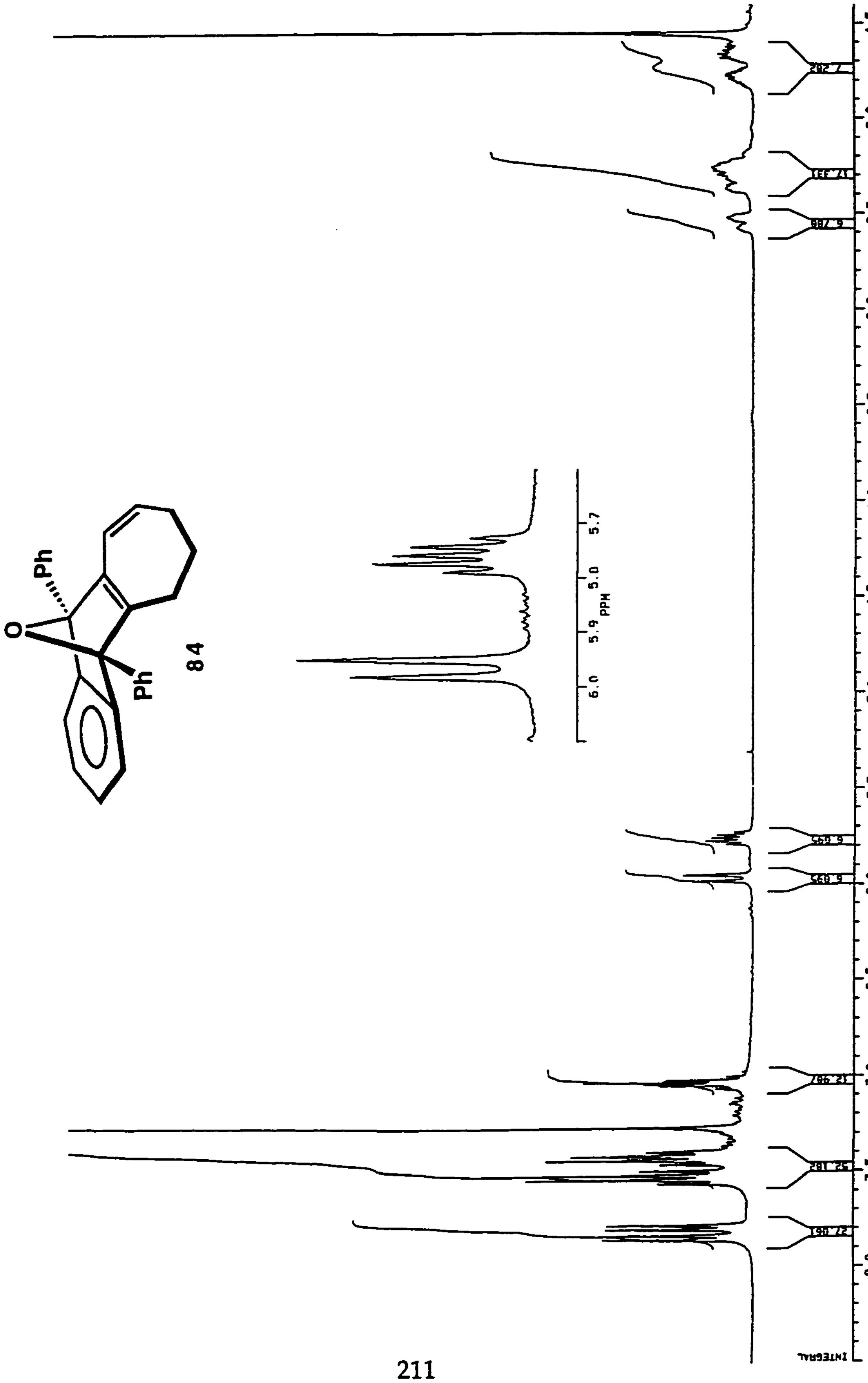
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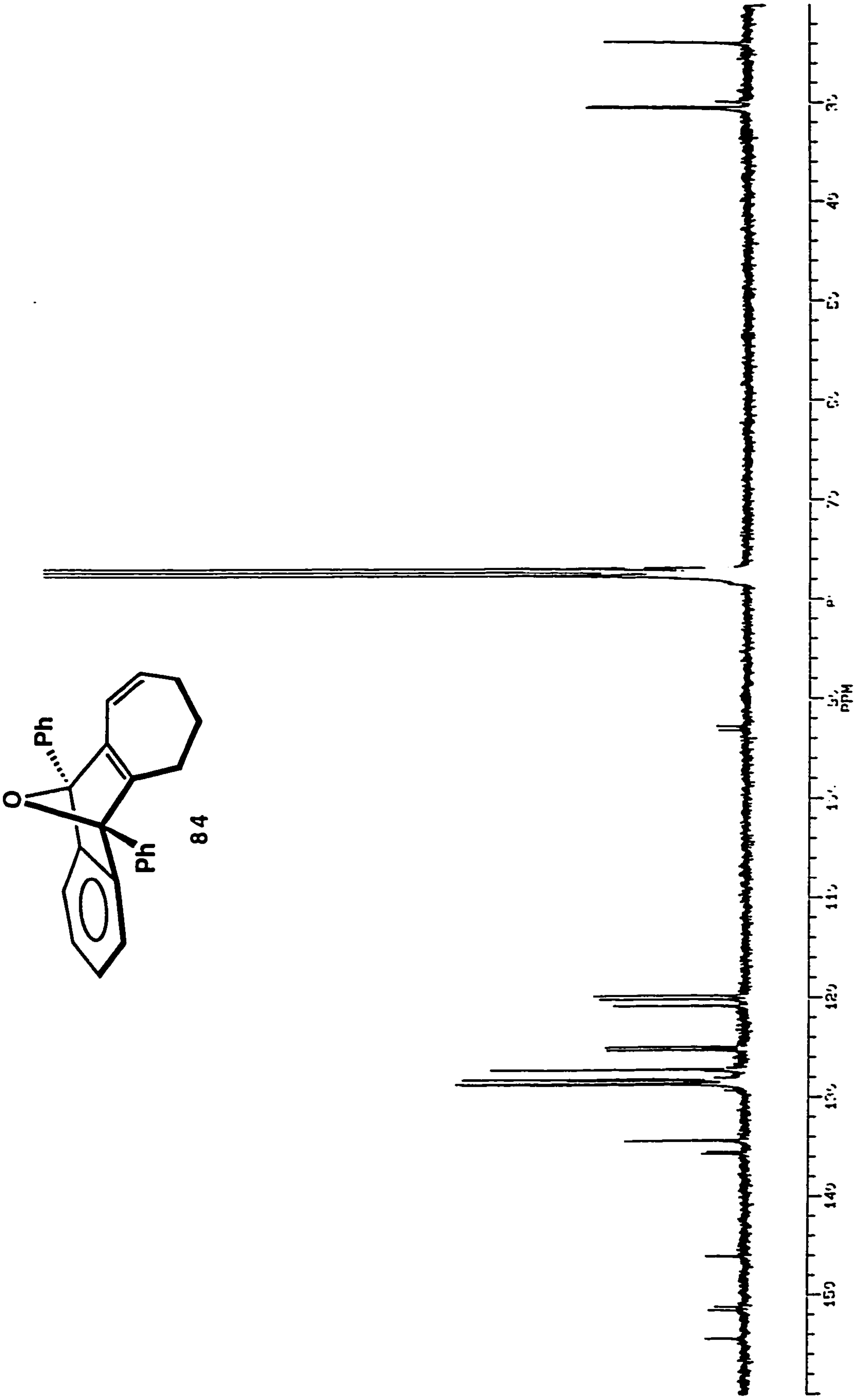

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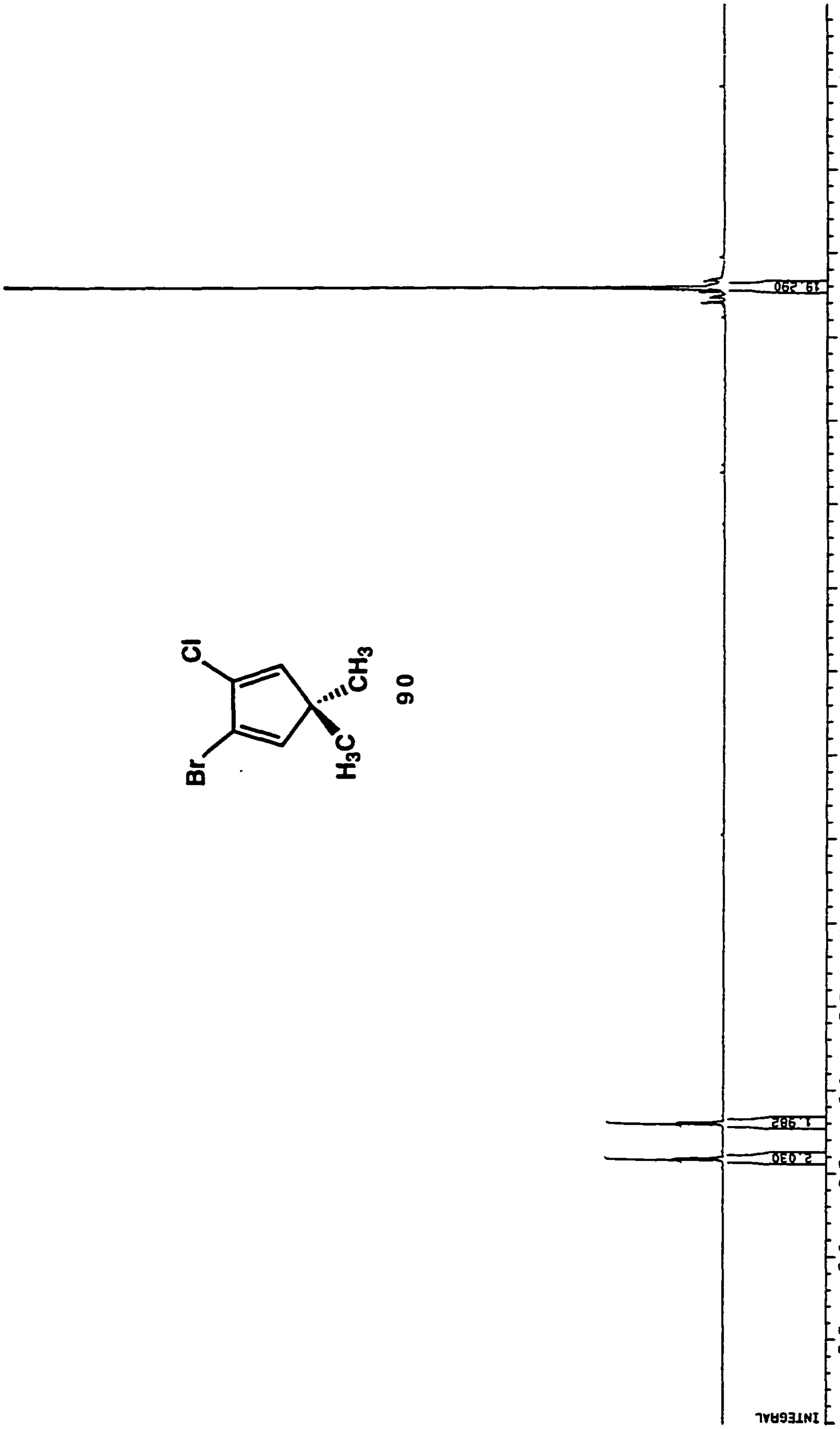
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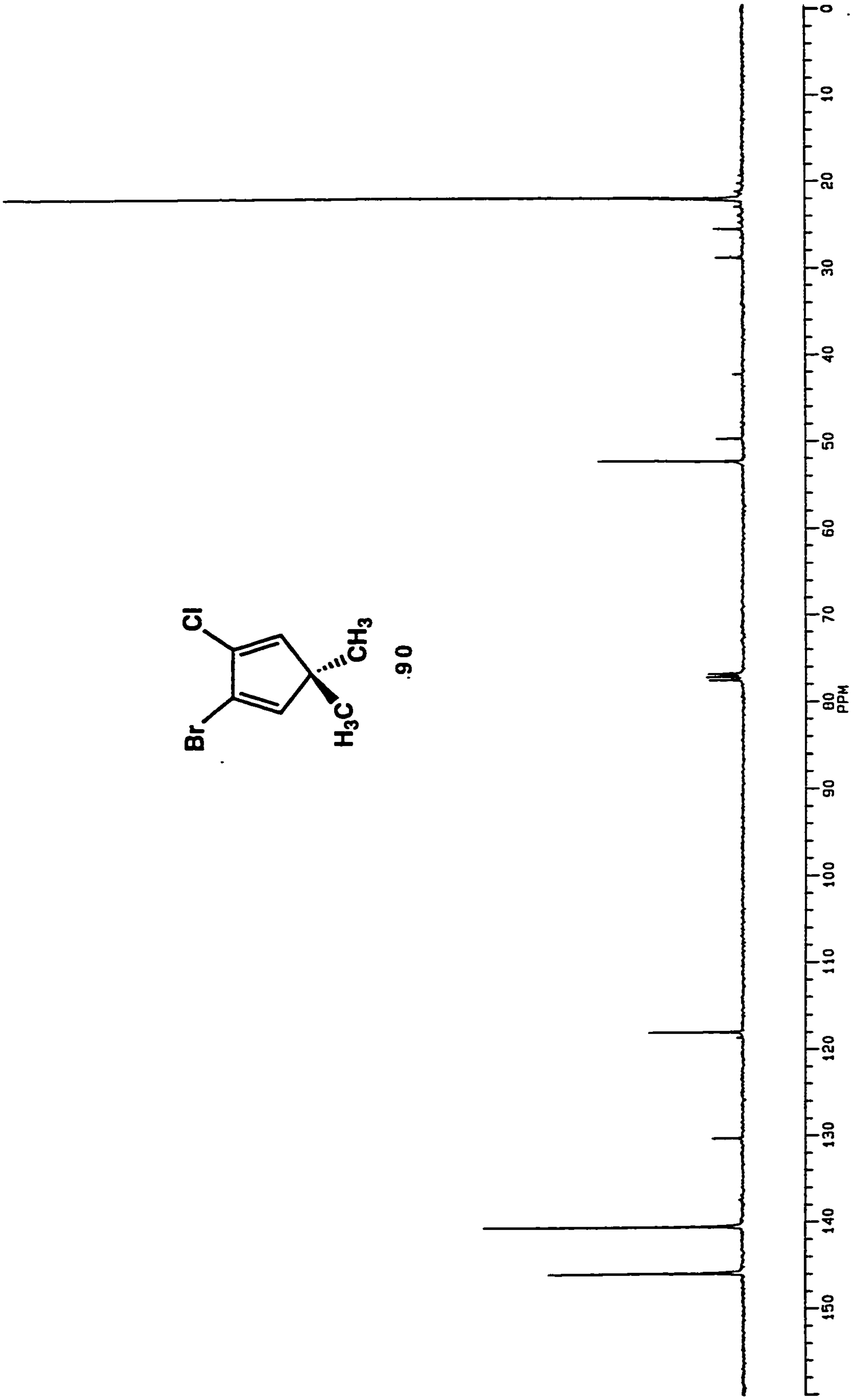

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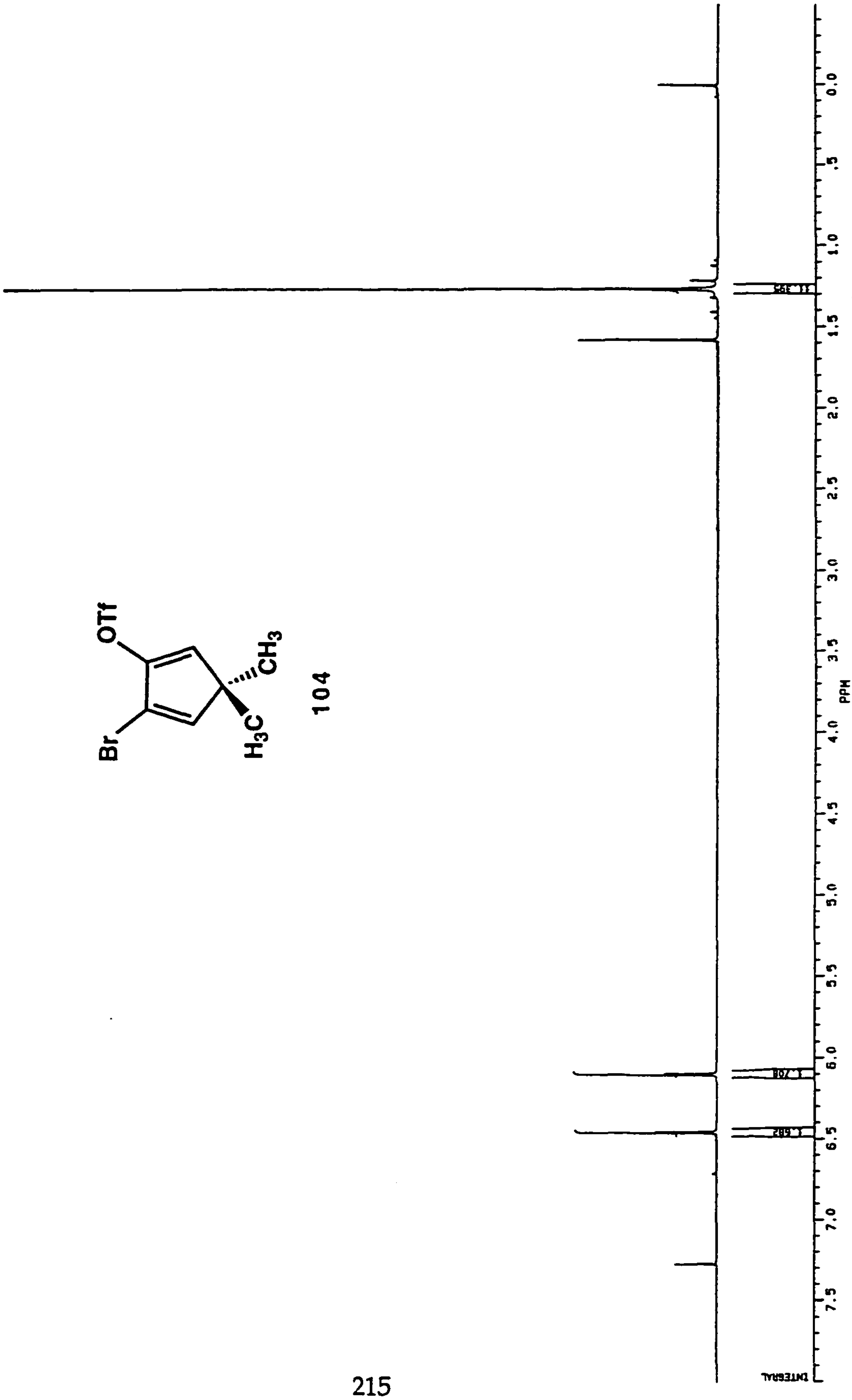

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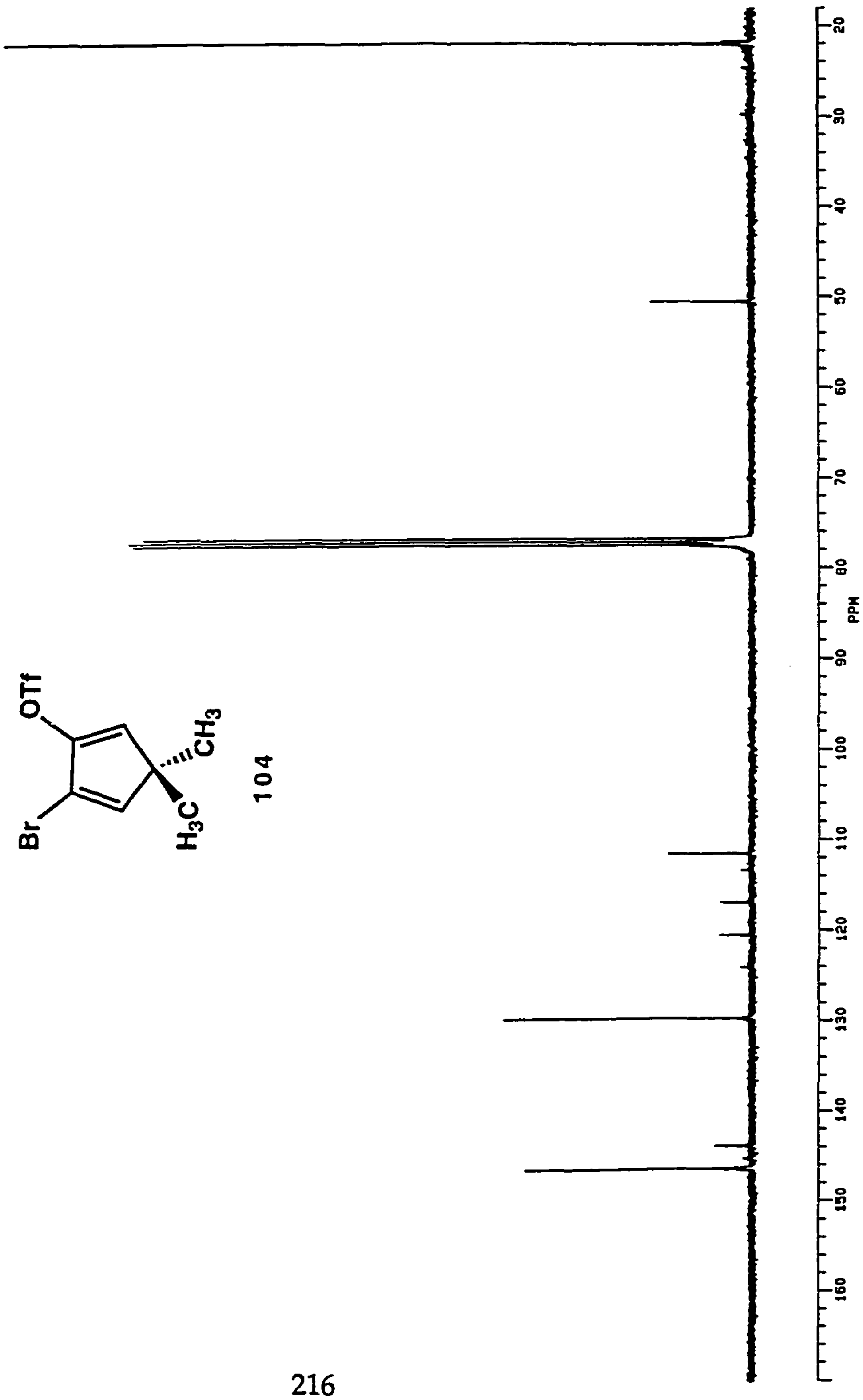

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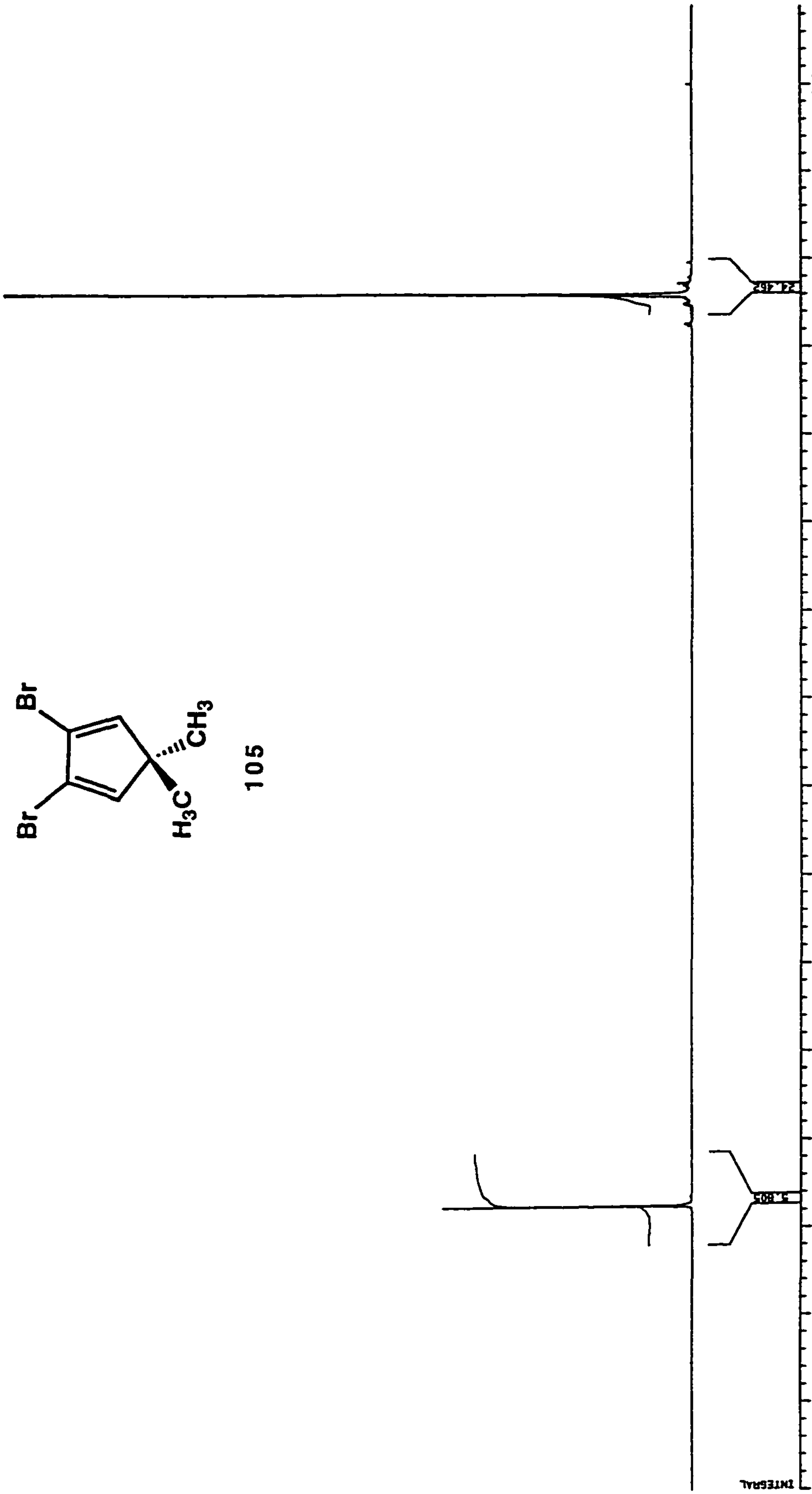
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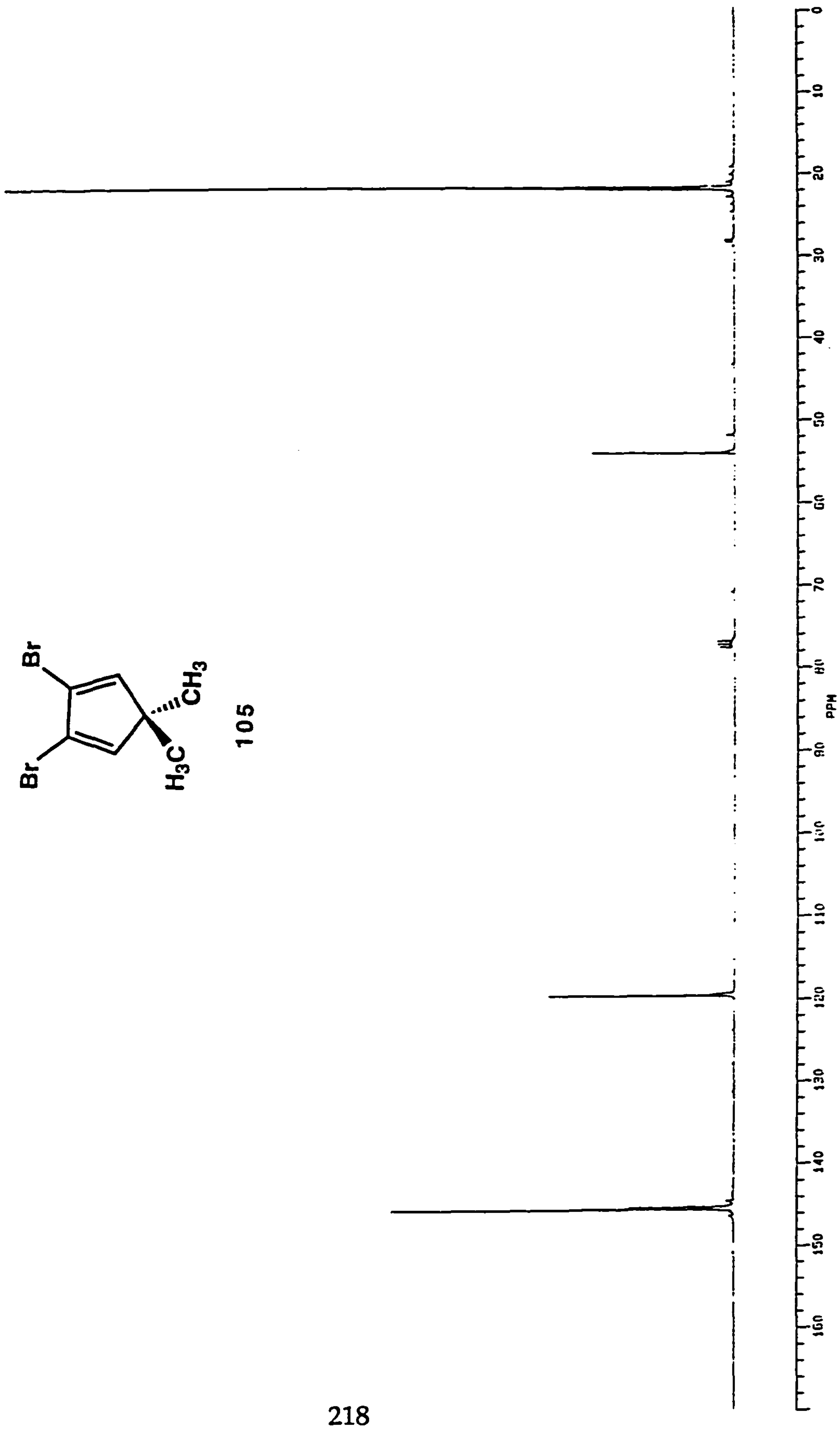
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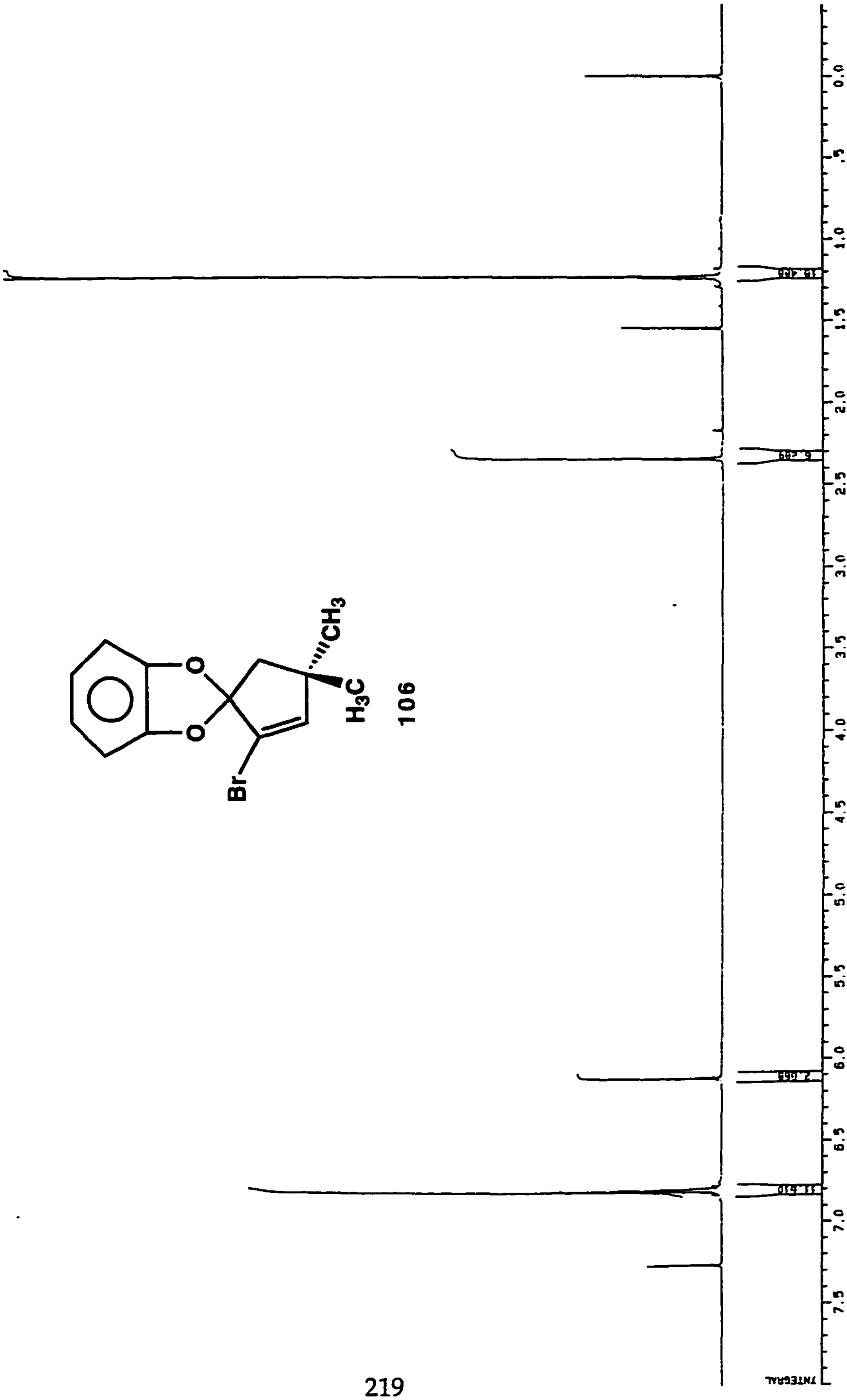
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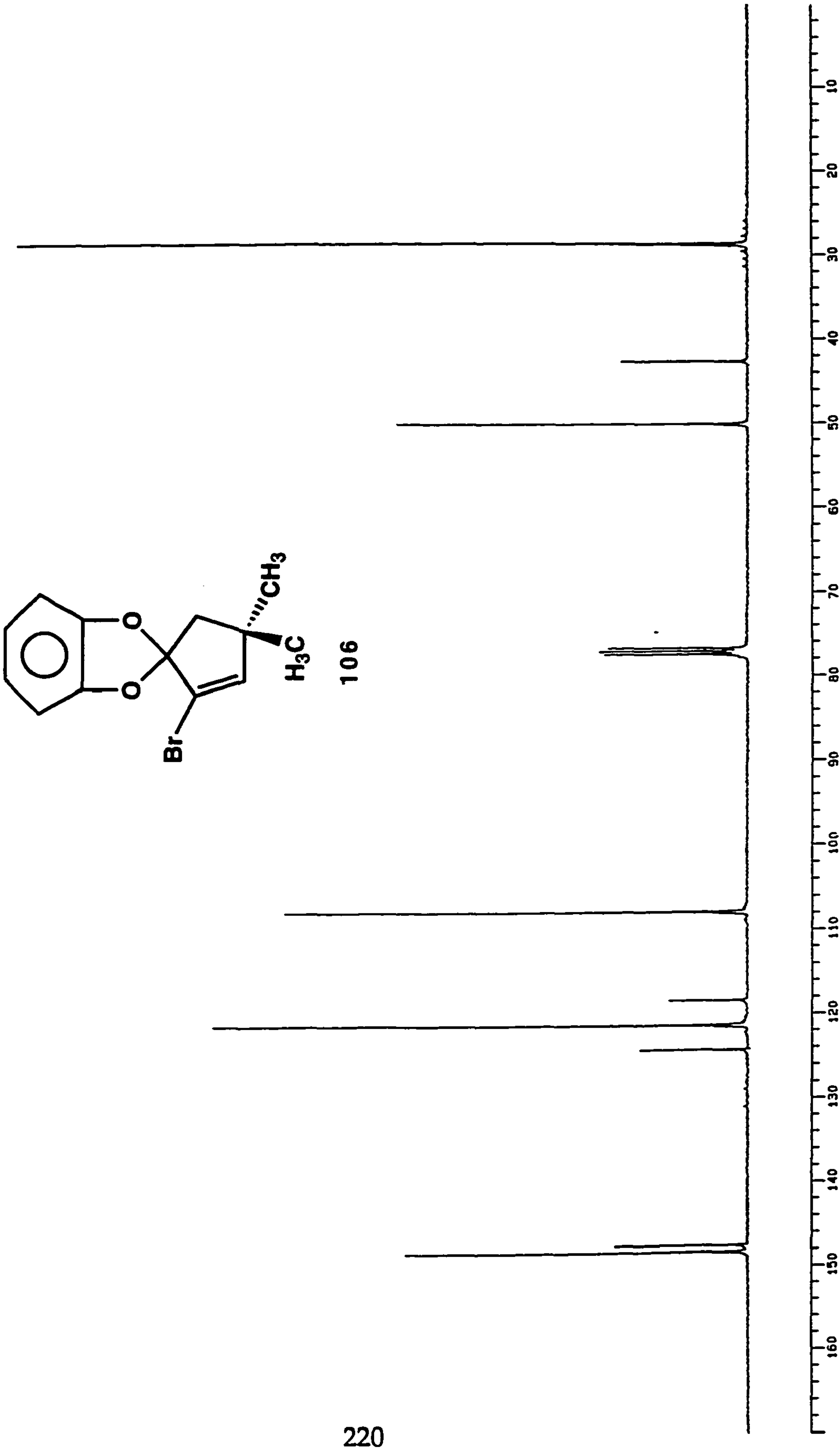

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PPM

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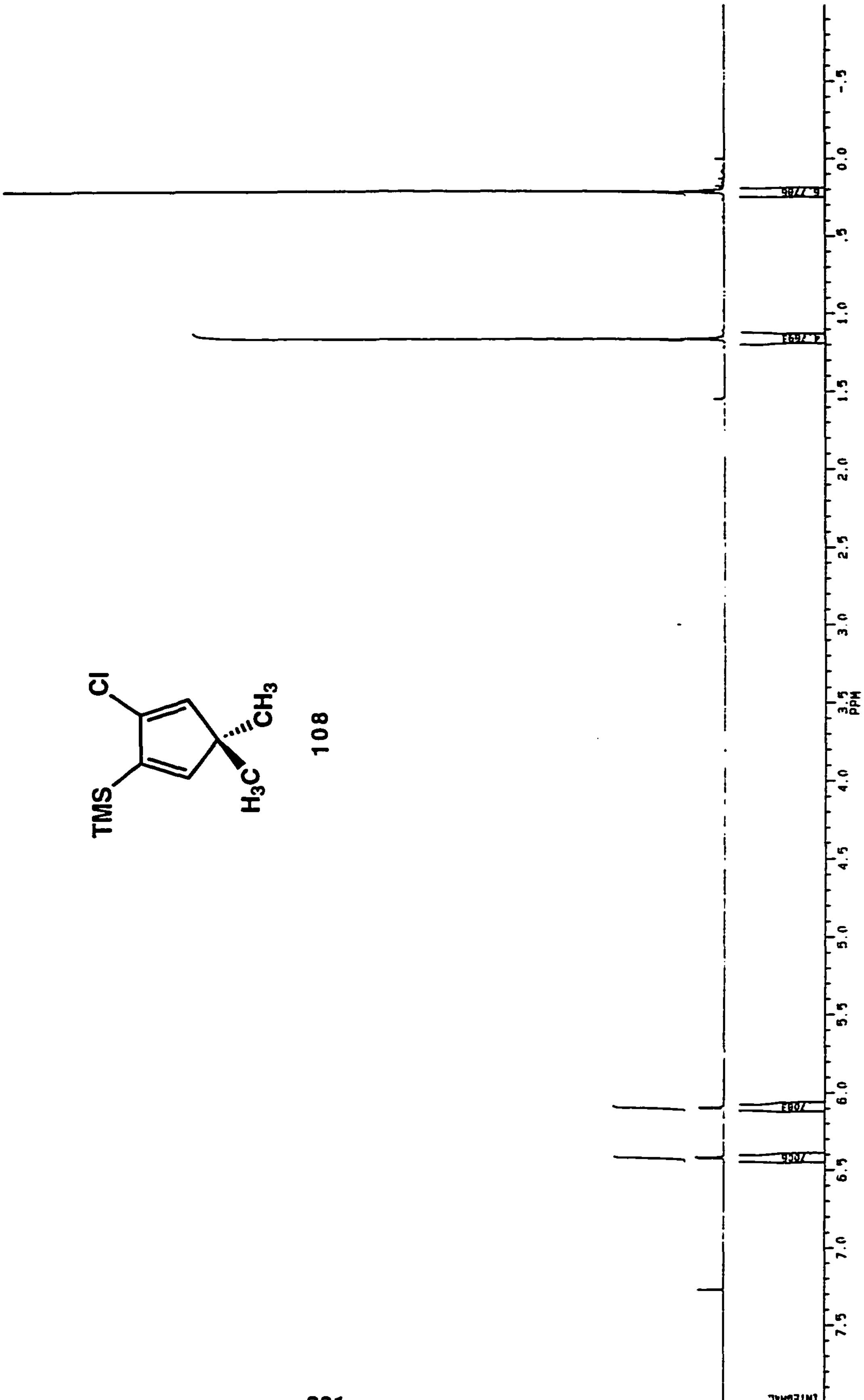
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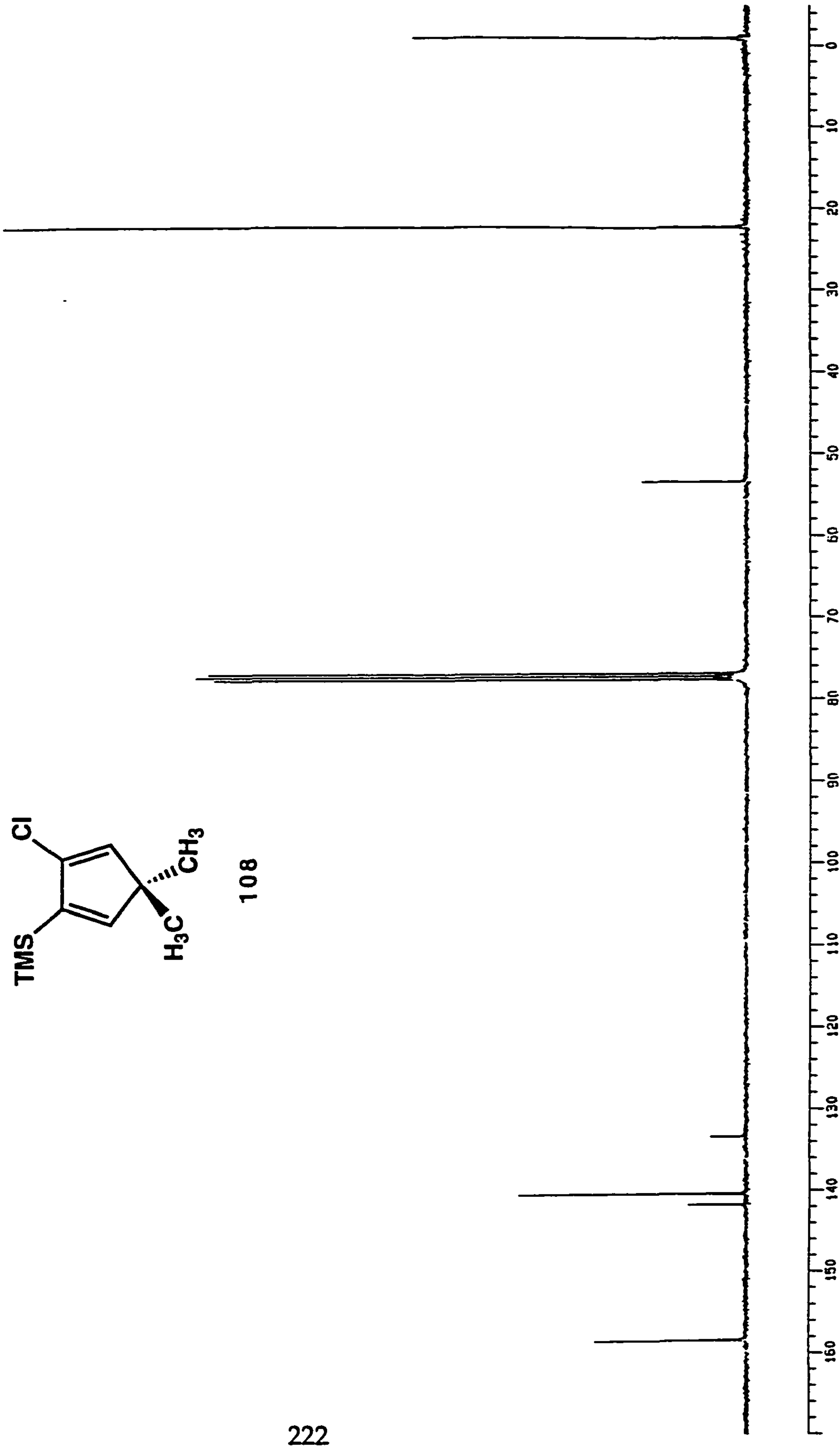
108



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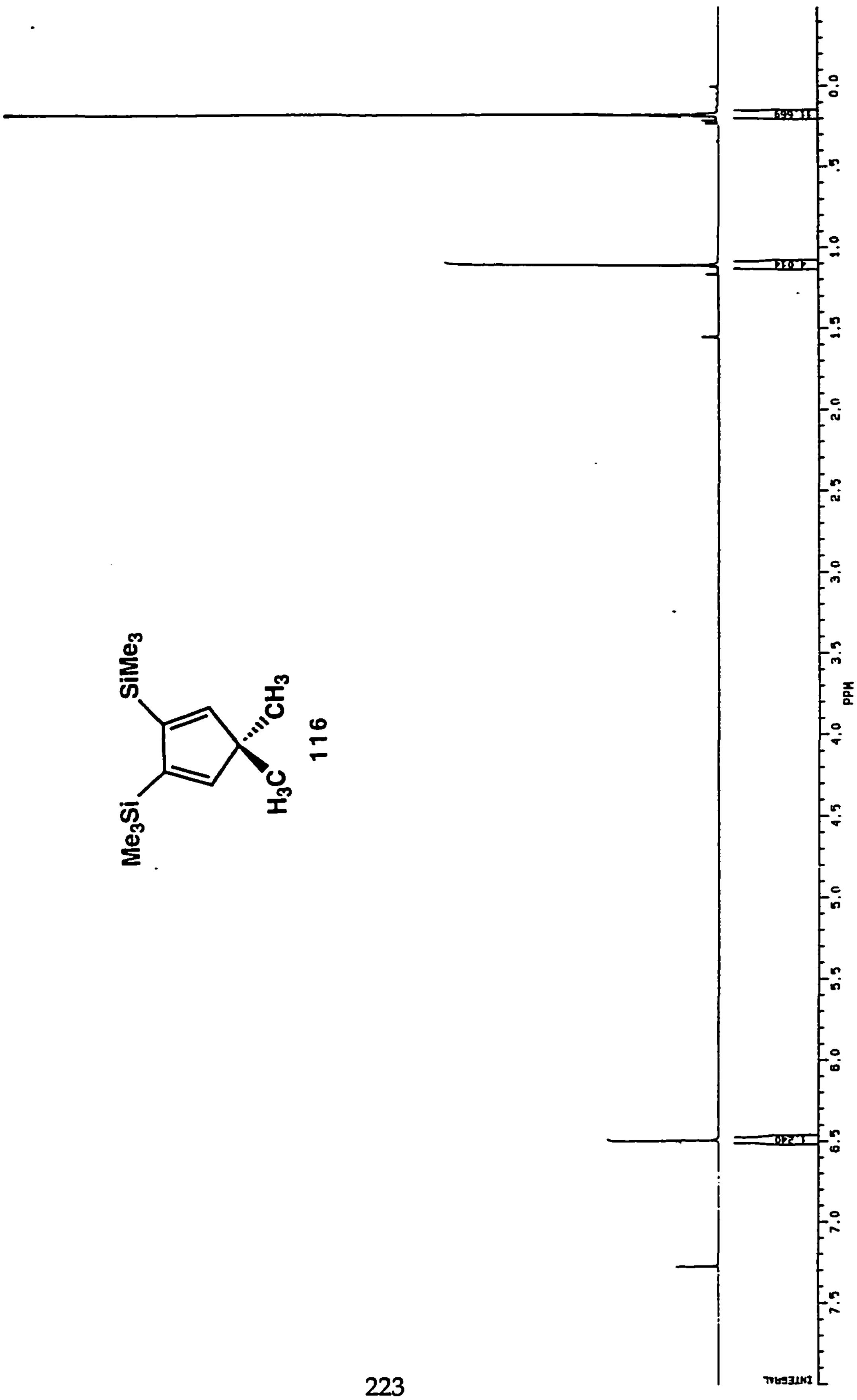
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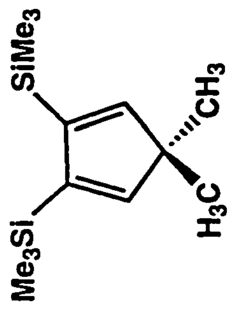

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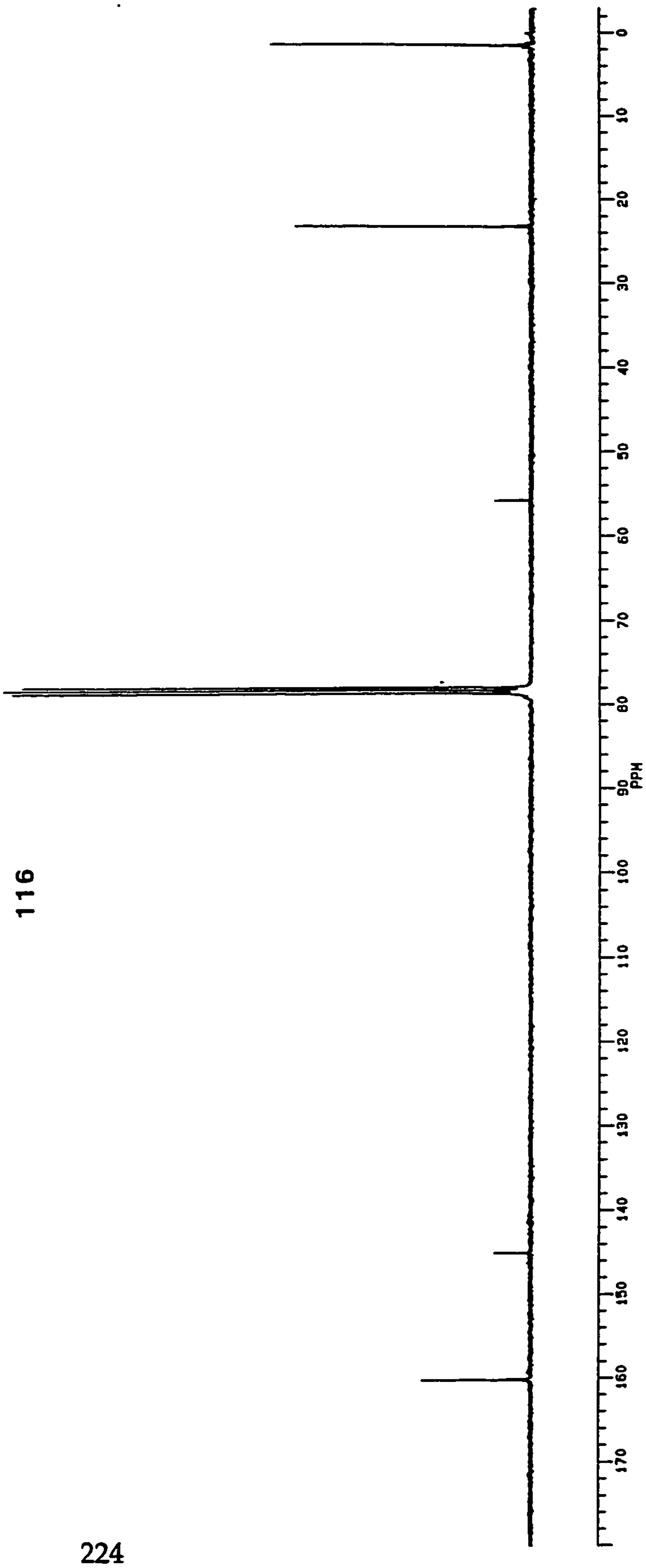

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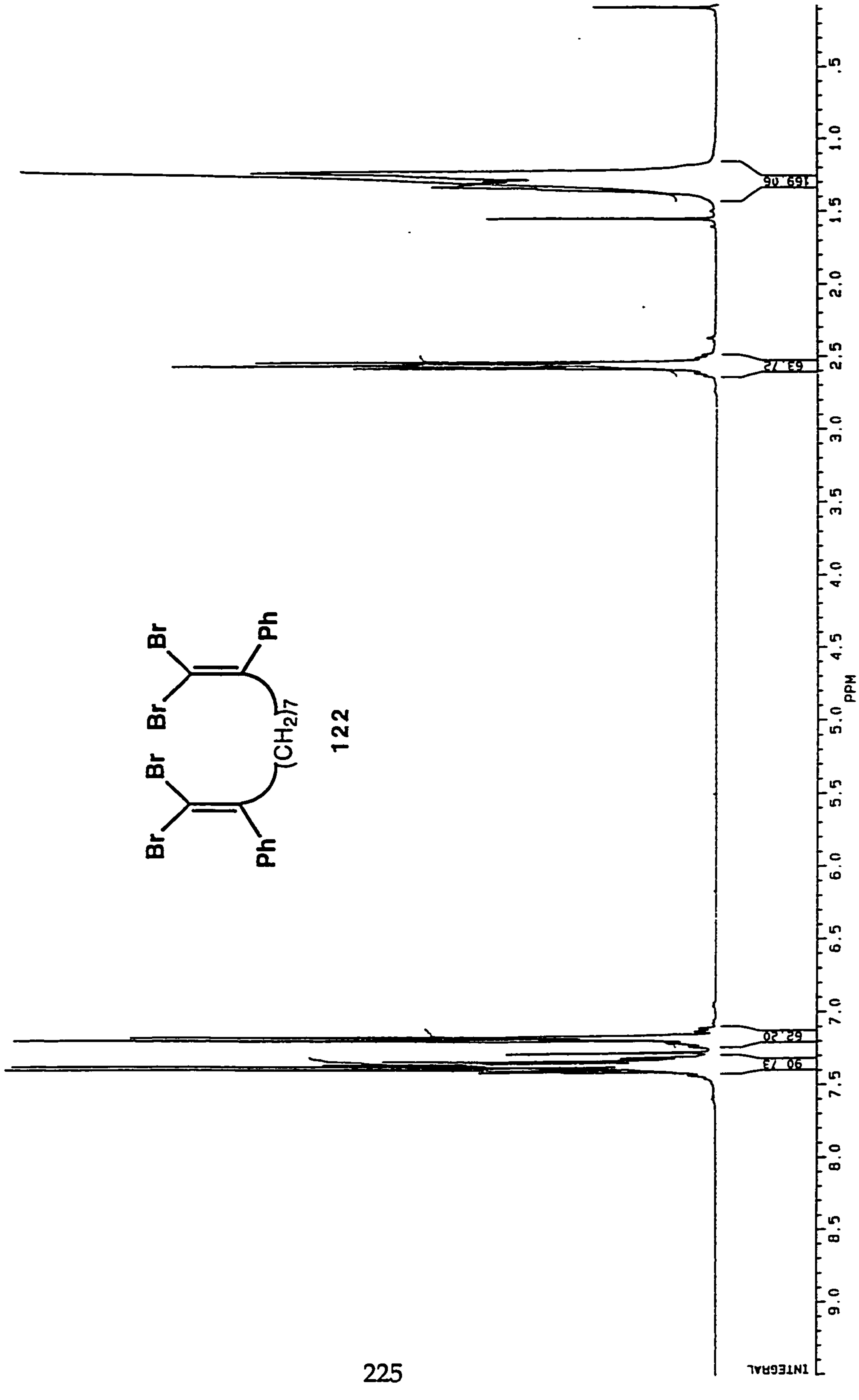
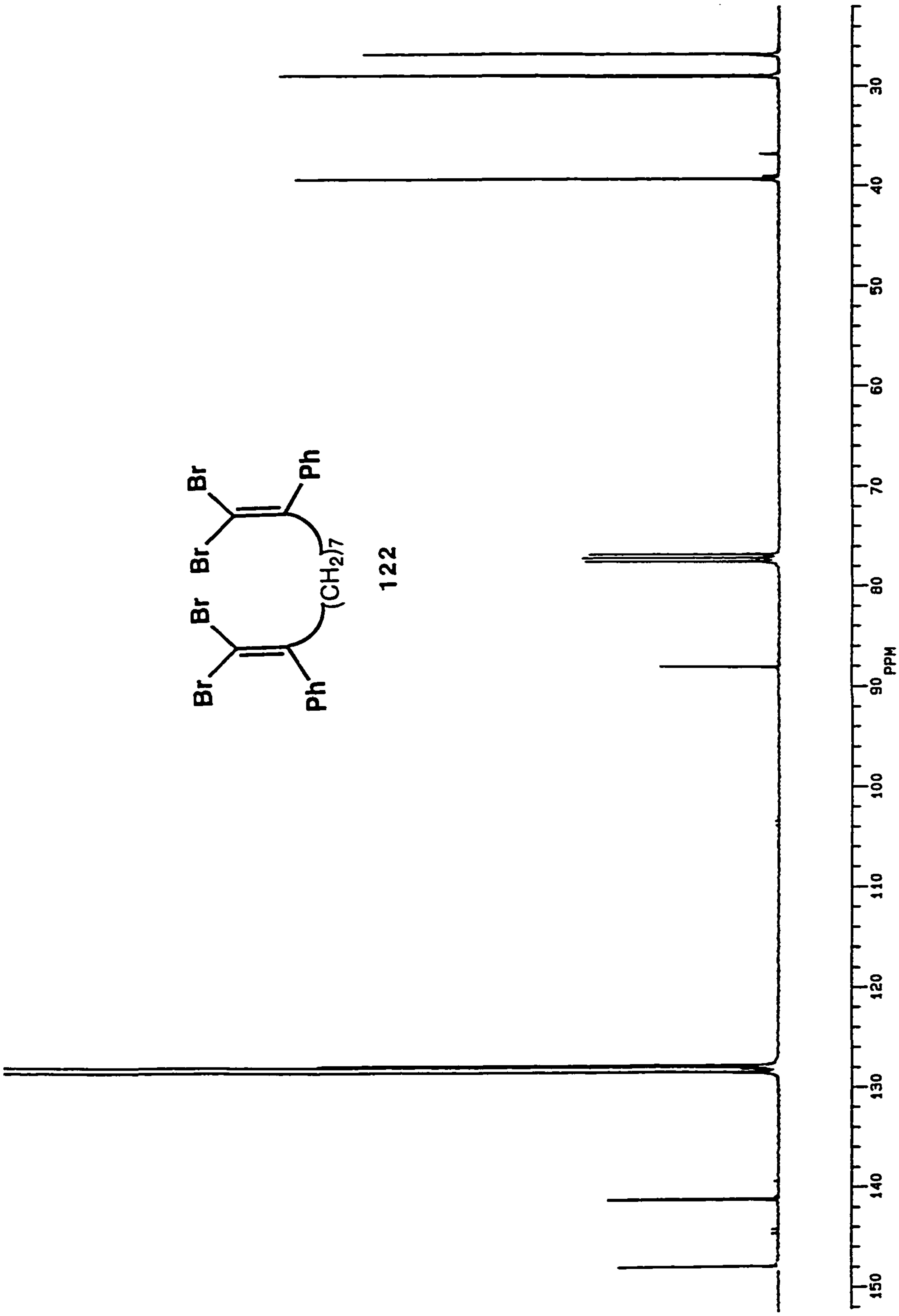
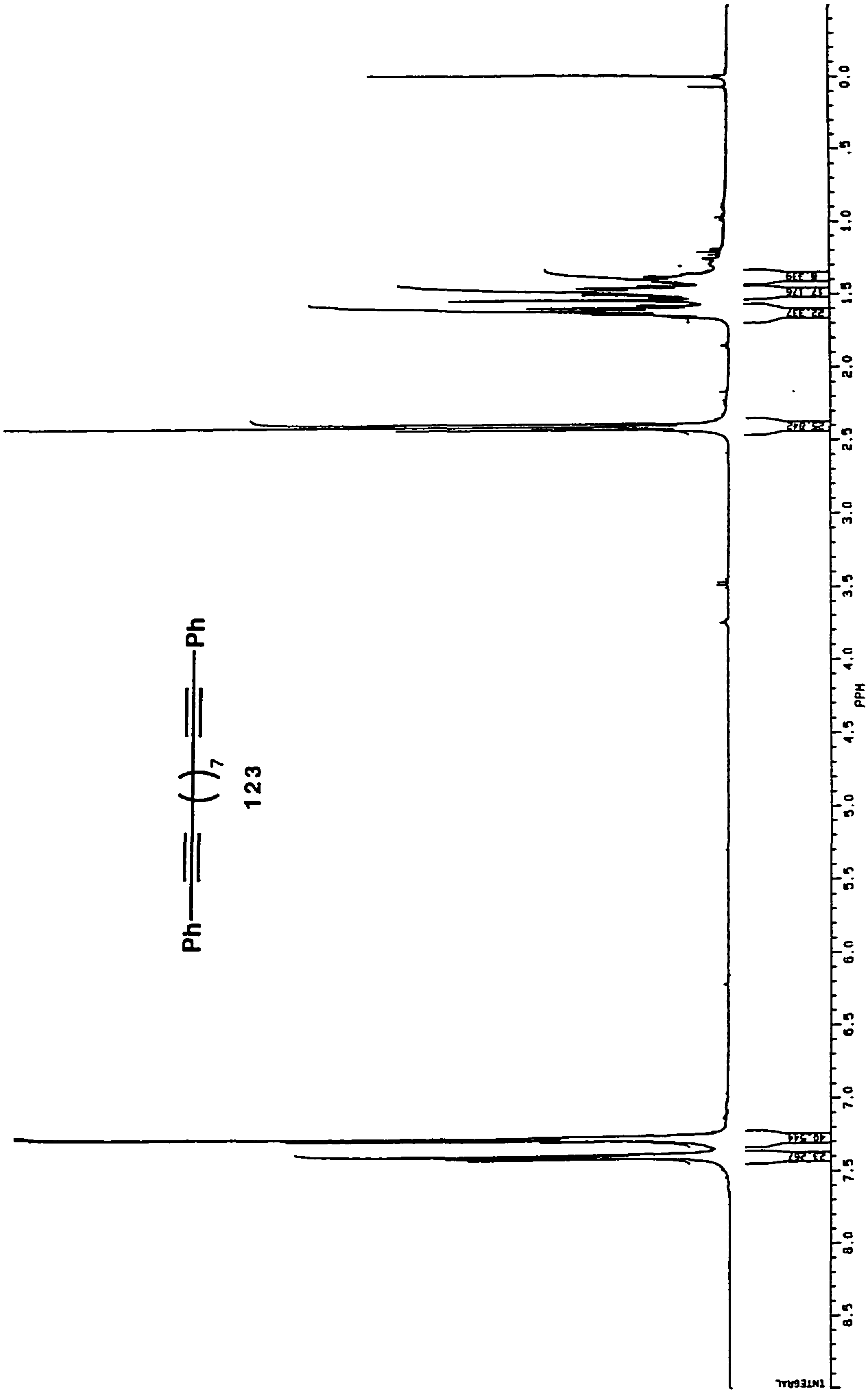
160
170

Br
Br
Br
Br
Ph
Ph
(CH2)7
122
169.06
63.72
62.20
90.73
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
PPM
INTEGRAL

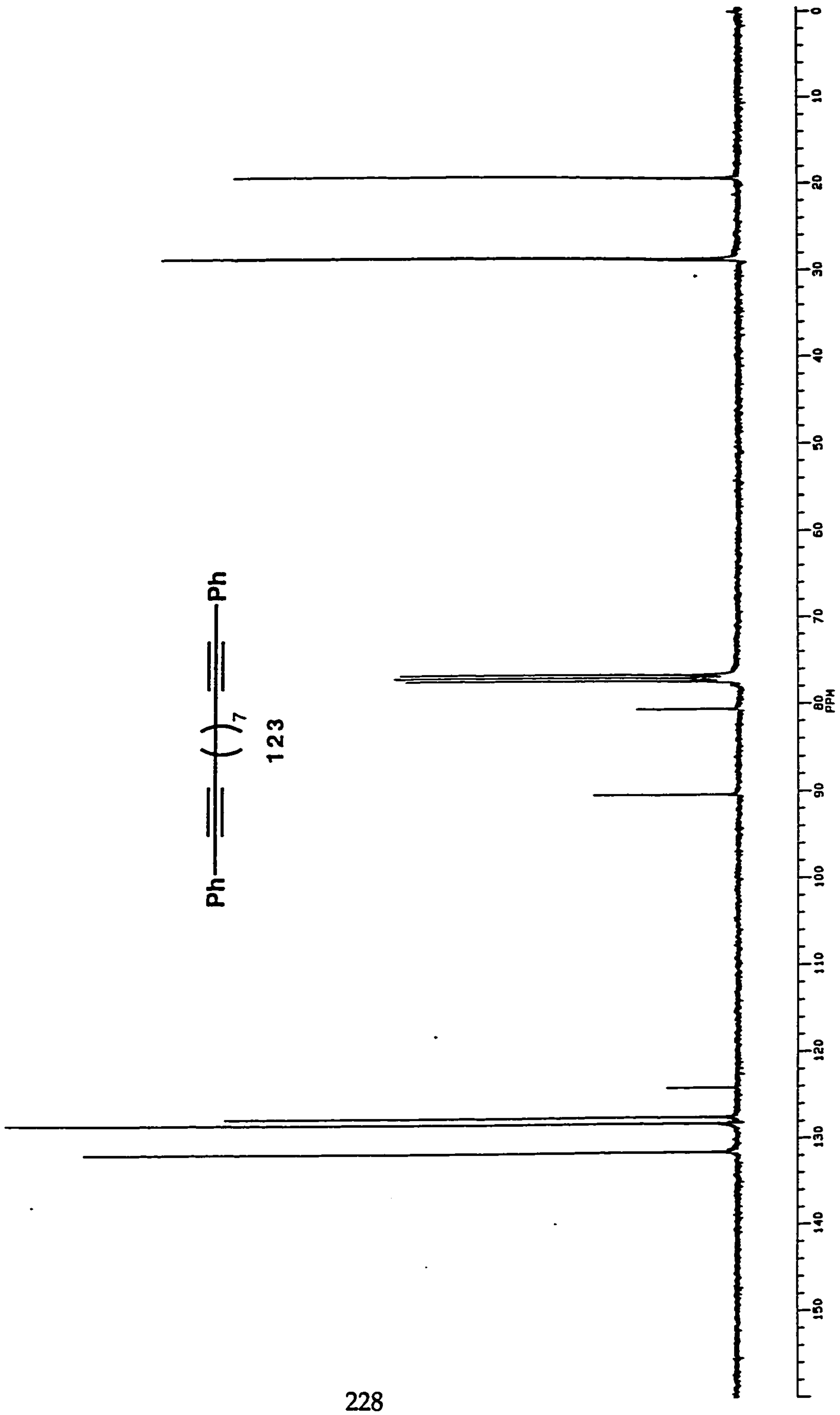


Br
Br
Br
Br
Ph
Ph
$(CH_2)_7$
30
40
50
60
70
80
90
PPM
100
110
120
130
140
150

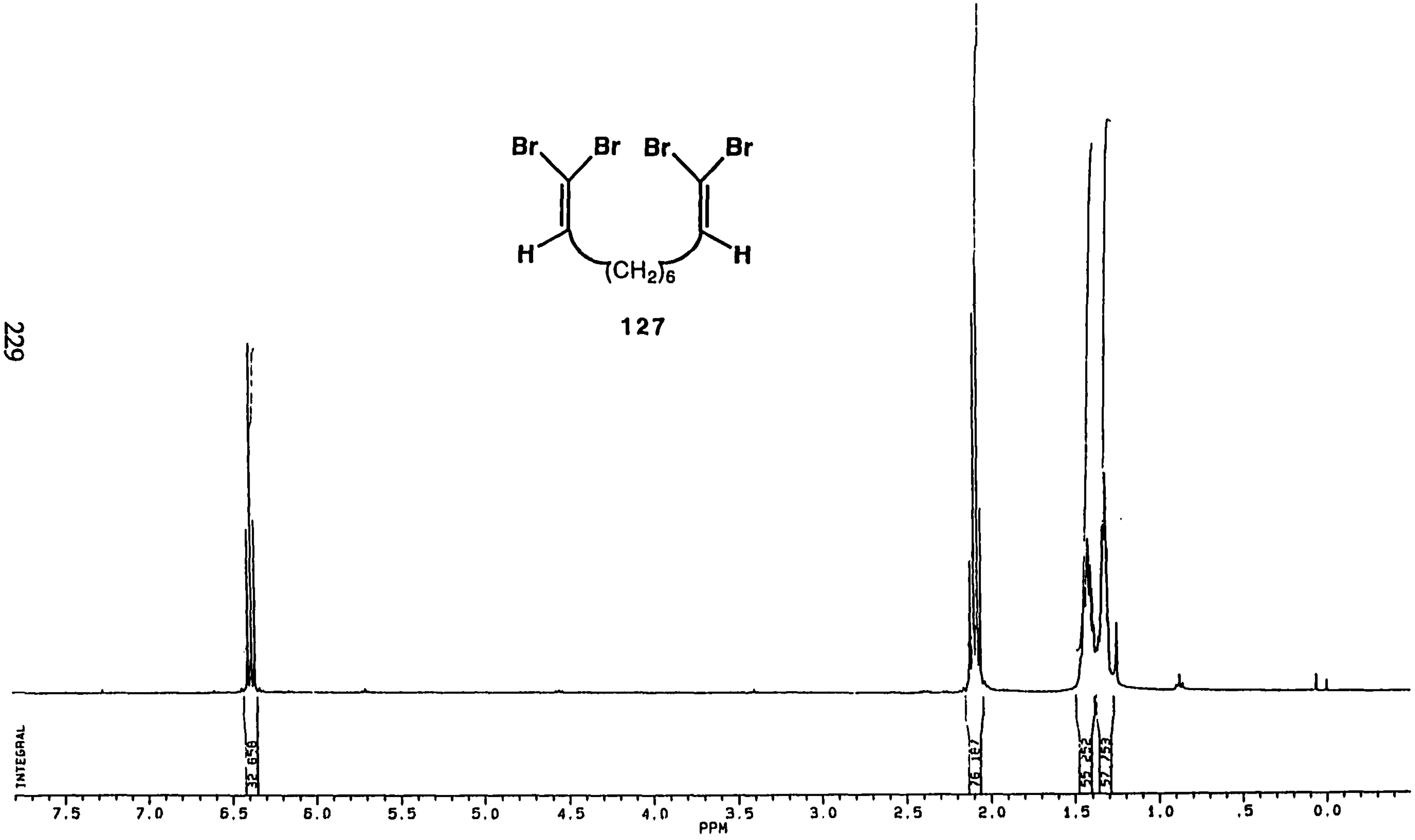
122


Ph
Ph
7
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
PPM
INTEGRAL
8.339
17.176
22.337
25.042
40.544
23.267

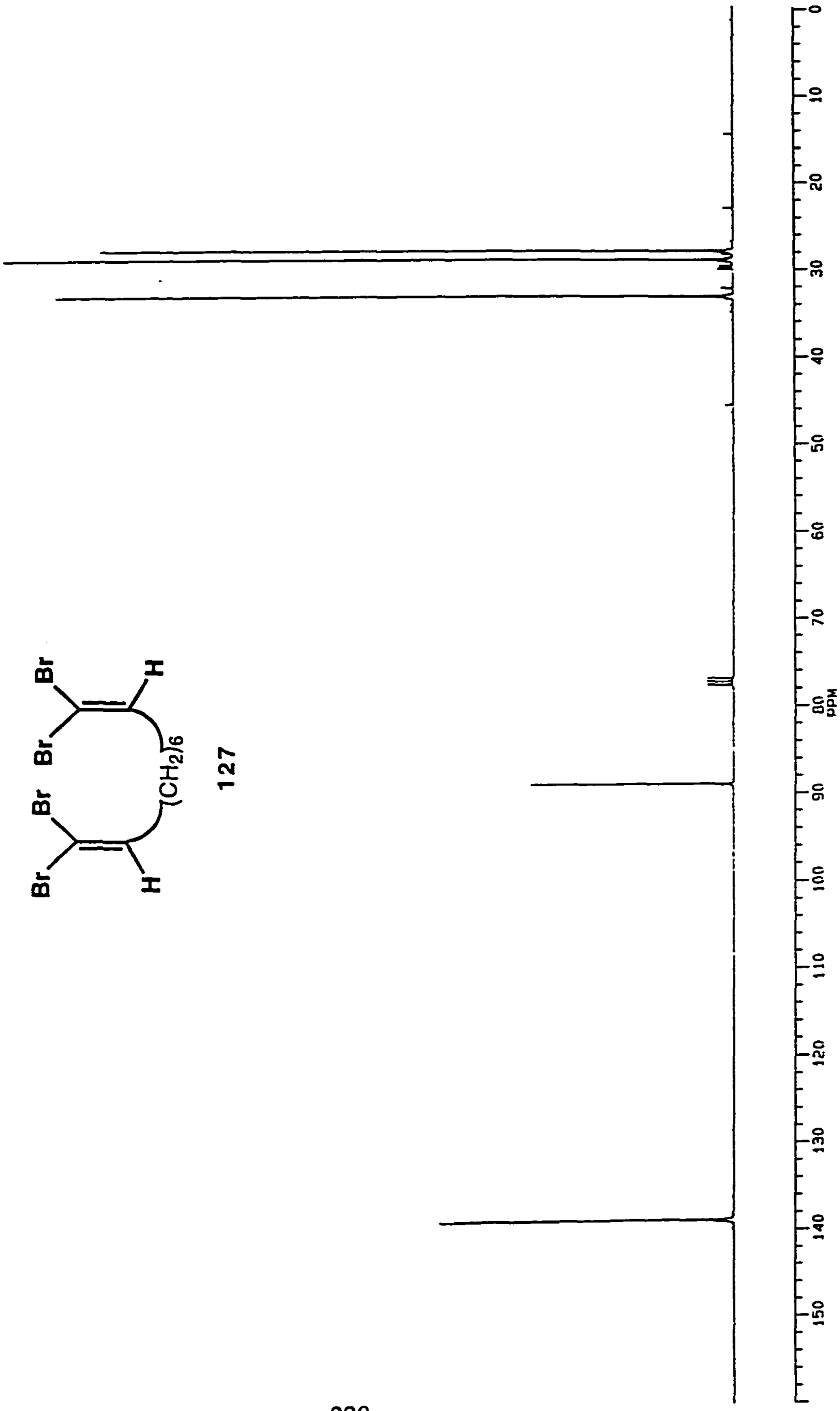
123



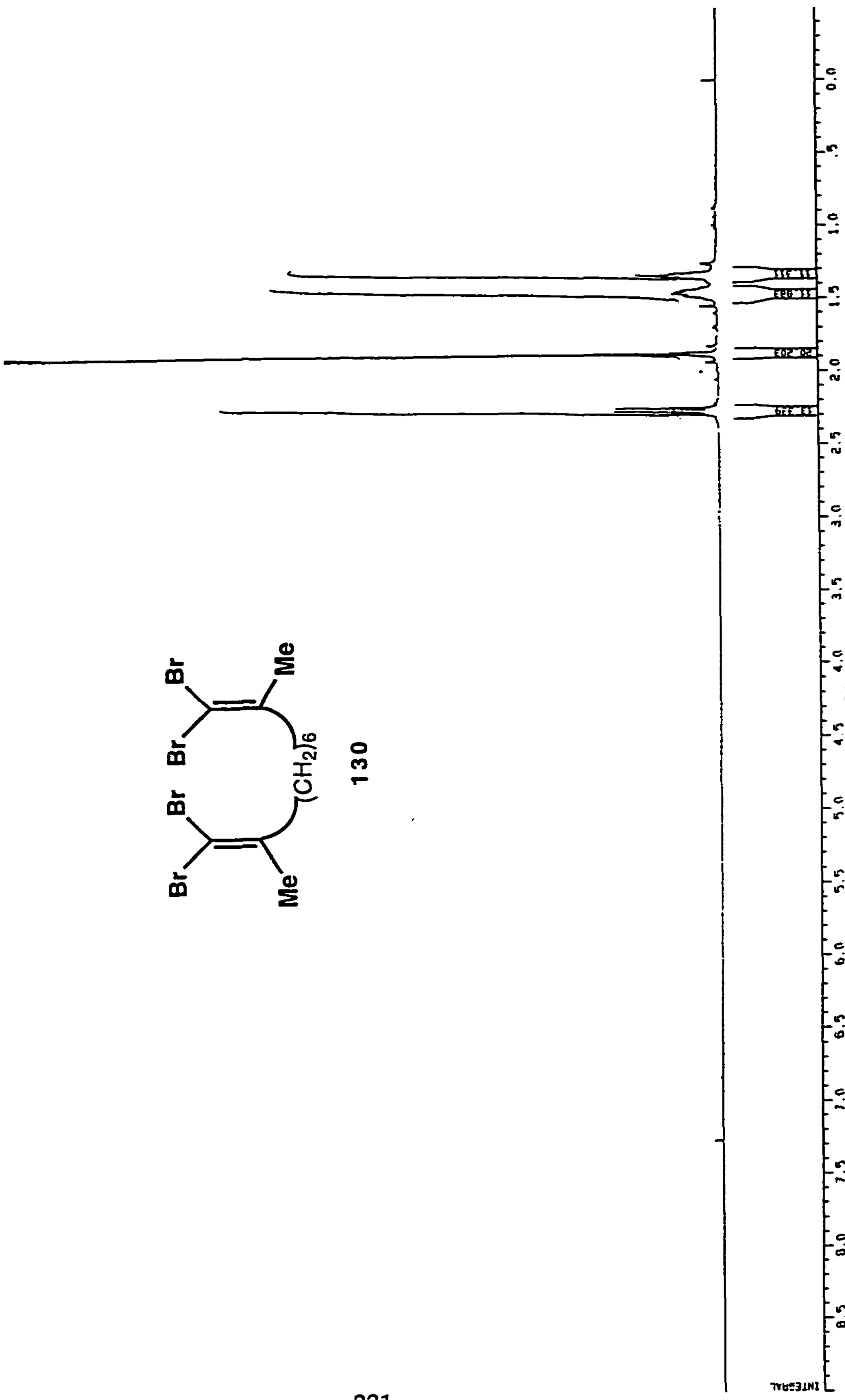
123


Br
Br
Br
Br
H
H
(CH$_2$)$_6$
INTEGRAL
32.658
76.167
55.252
57.753
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

127

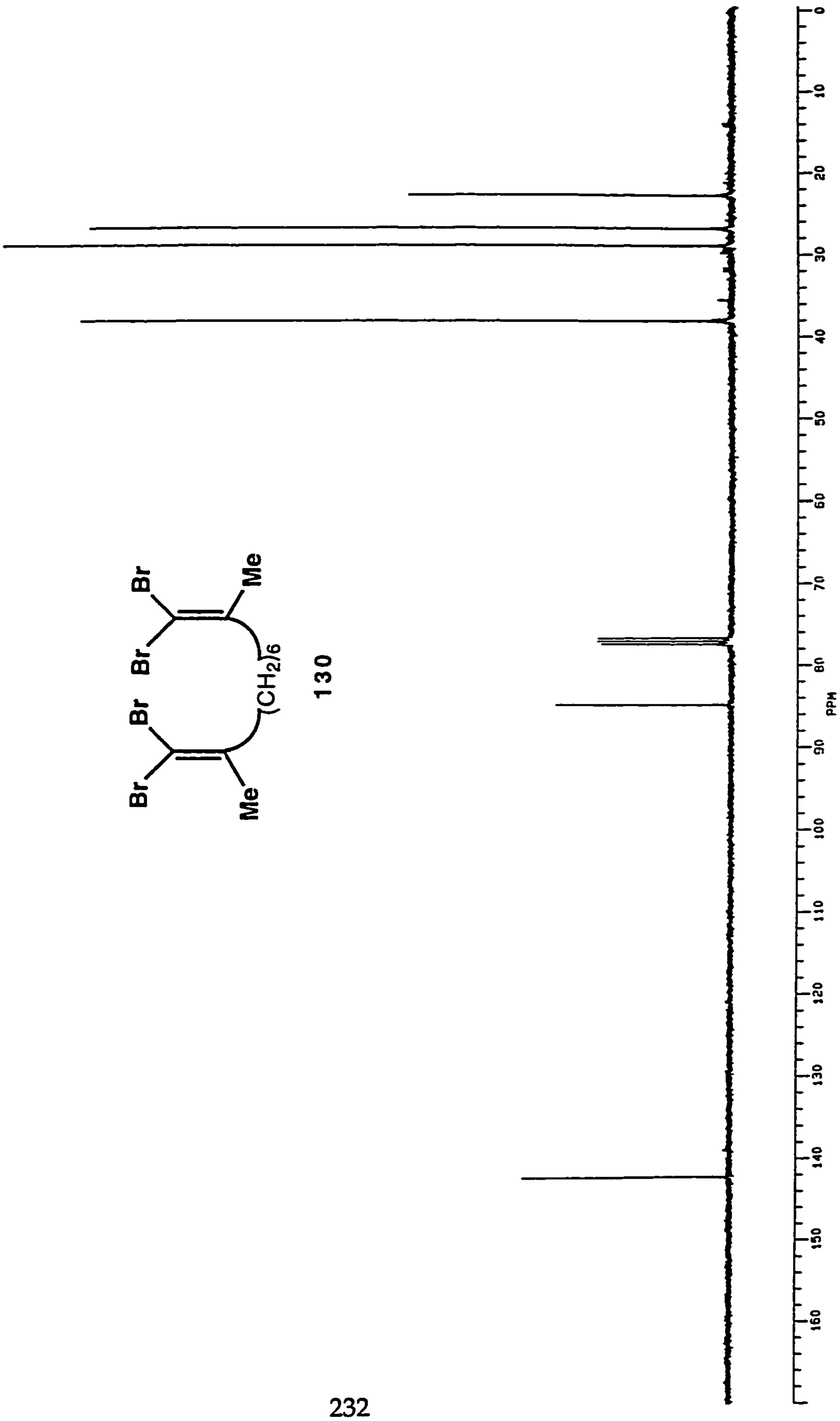

Br
Br
Br
Br
H
H
(CH2)6
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

127

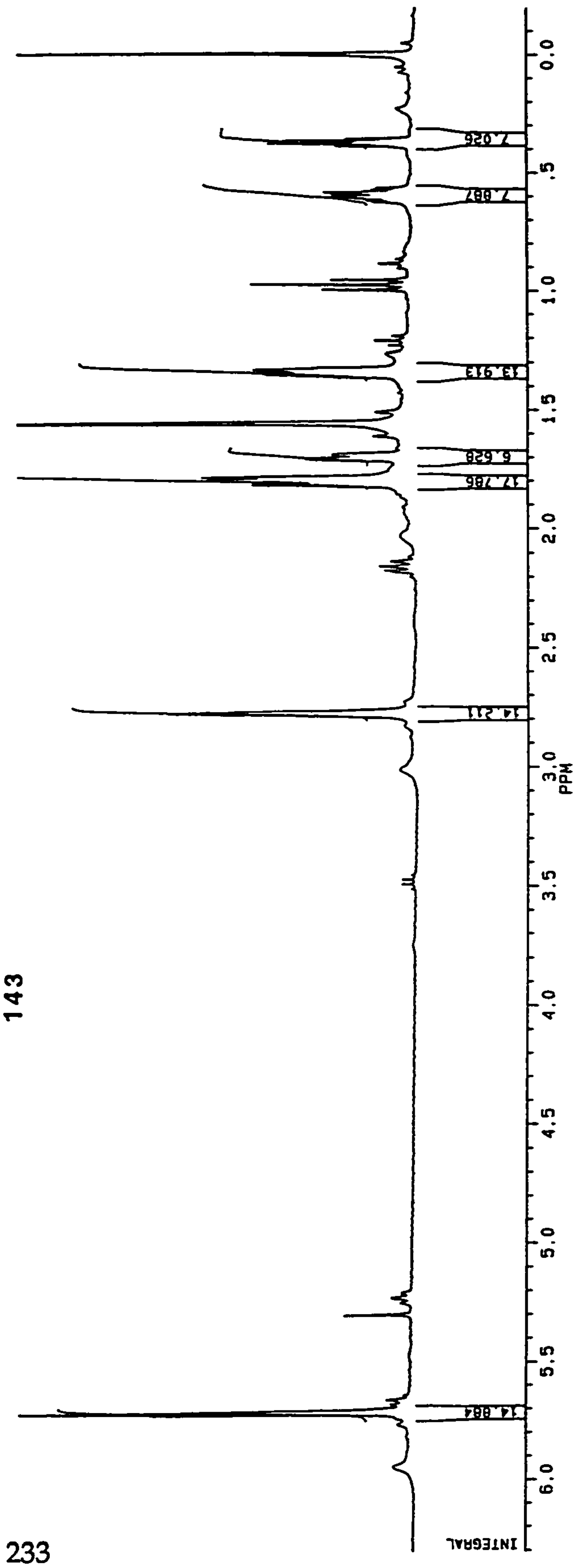


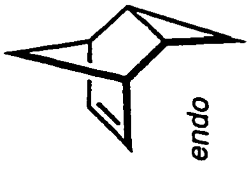
Br
Br
Br
Br
Me
Me
(CH2)6
PPM
INTEGRAL
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5

130


Br
Br
Br
Br
Me
Me
(CH2)6
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
PPM

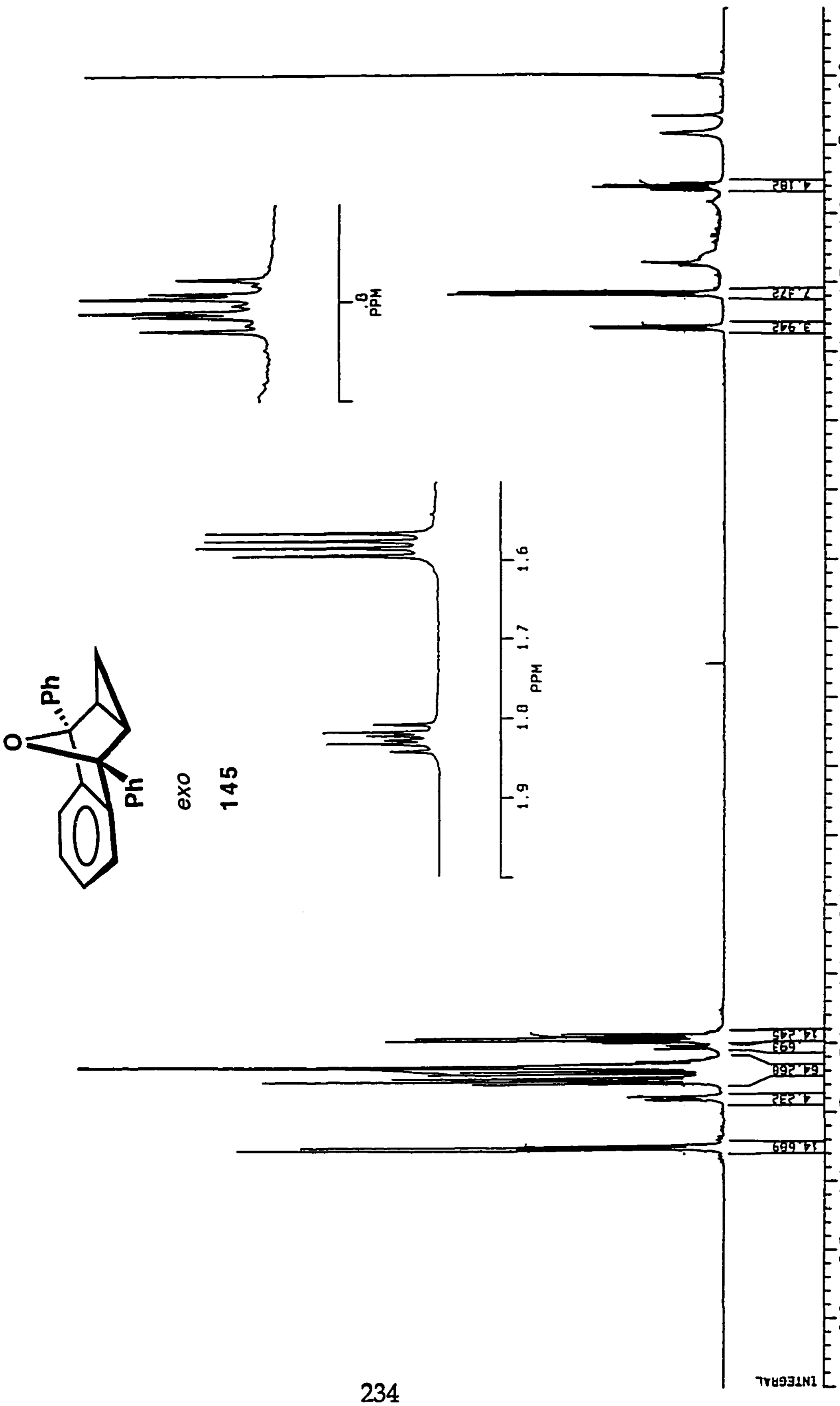
130


7.026
7.087
13.913
6.628
17.786
14.211
14.884
0.0
.5
1.0
1.5
2.0
2.5
3.0
PPM
3.5
4.0
4.5
5.0
5.5
6.0
INTEGRAL



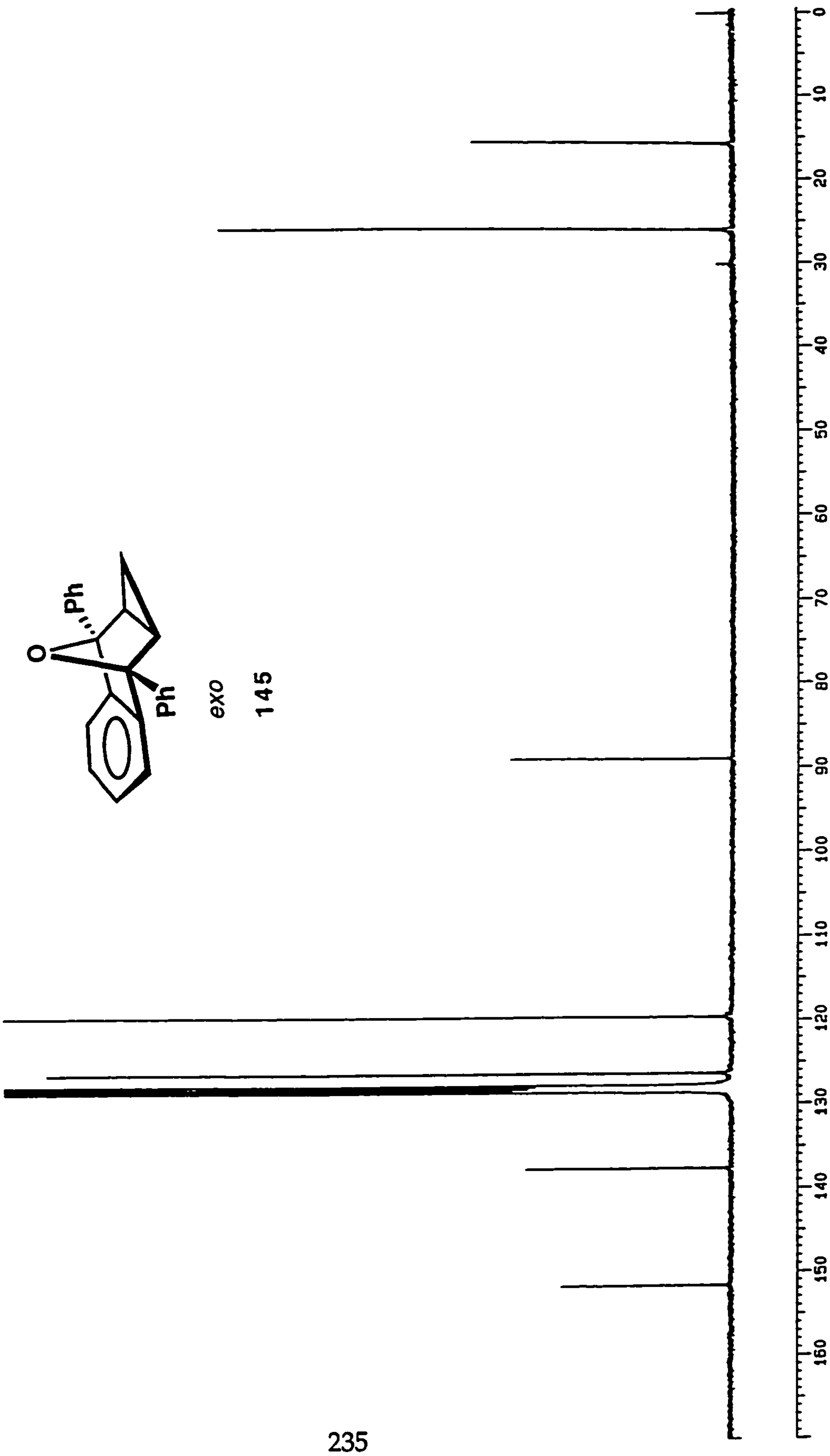
endo

143


O
Ph
Ph
1.6
1.7
1.8
1.9
PPM
.8
PPM
4.182
7.372
3.942
14.245
.693
64.268
4.232
14.689
INTEGRAL
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
PPM

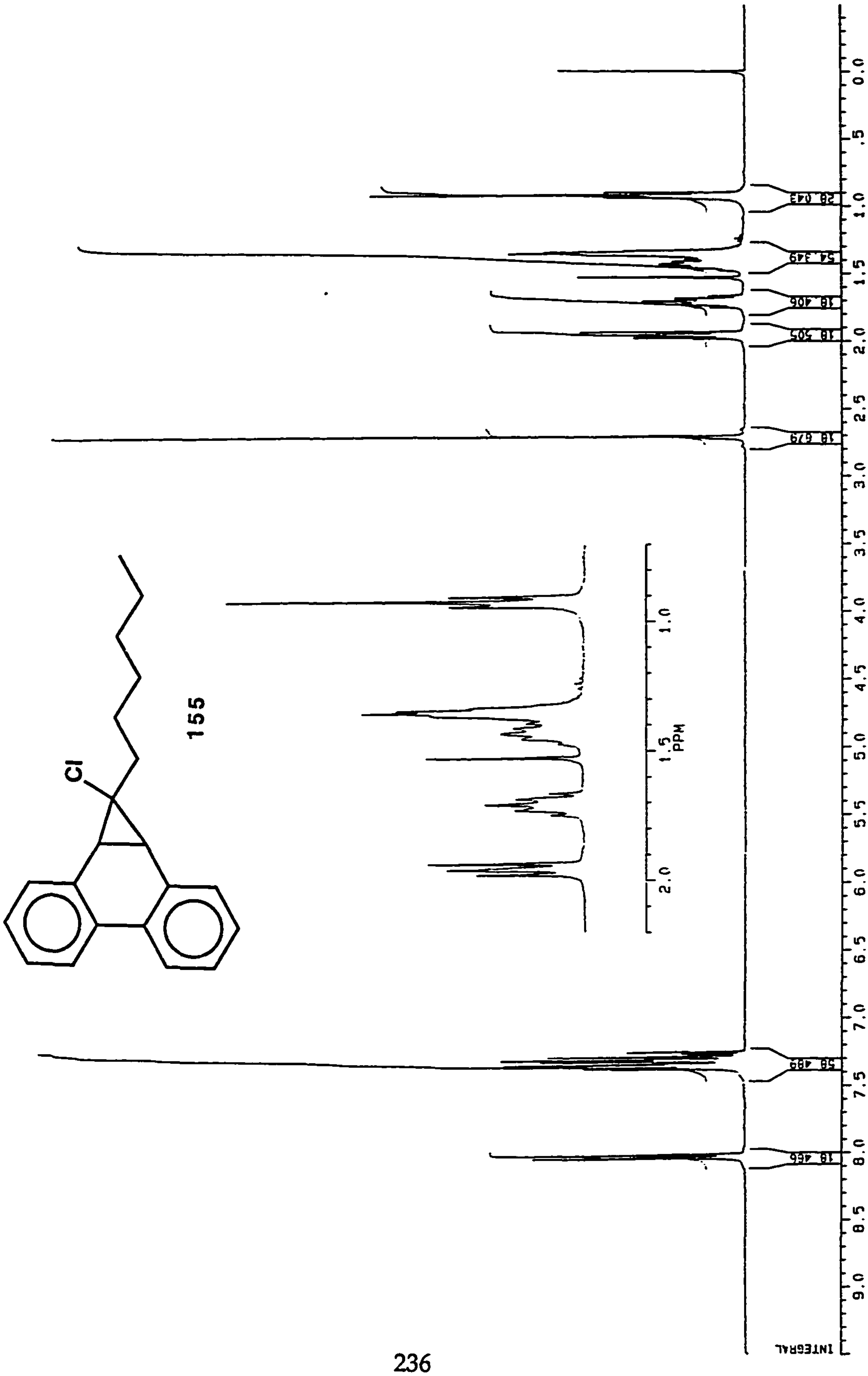
exo

145

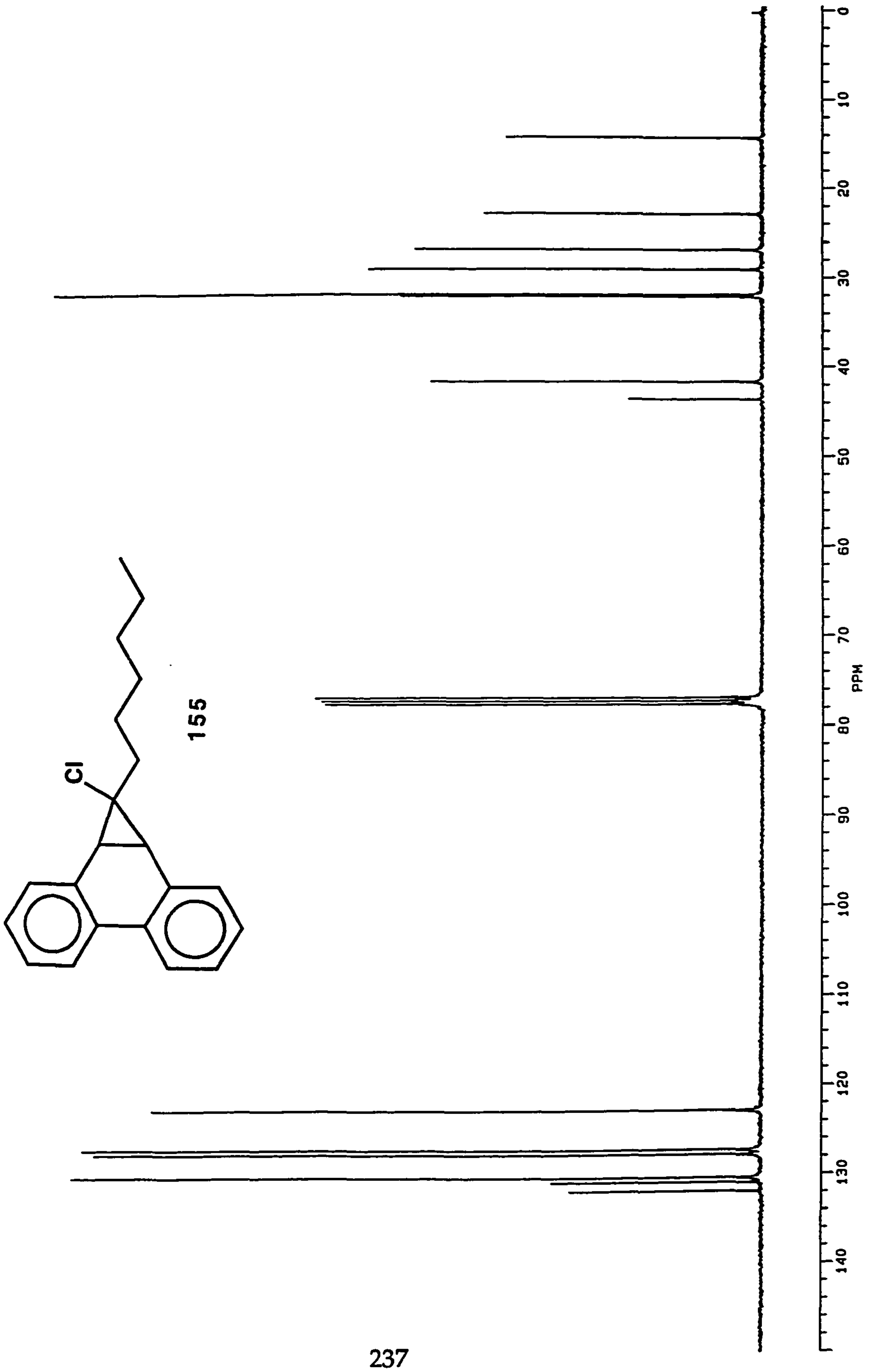


exo

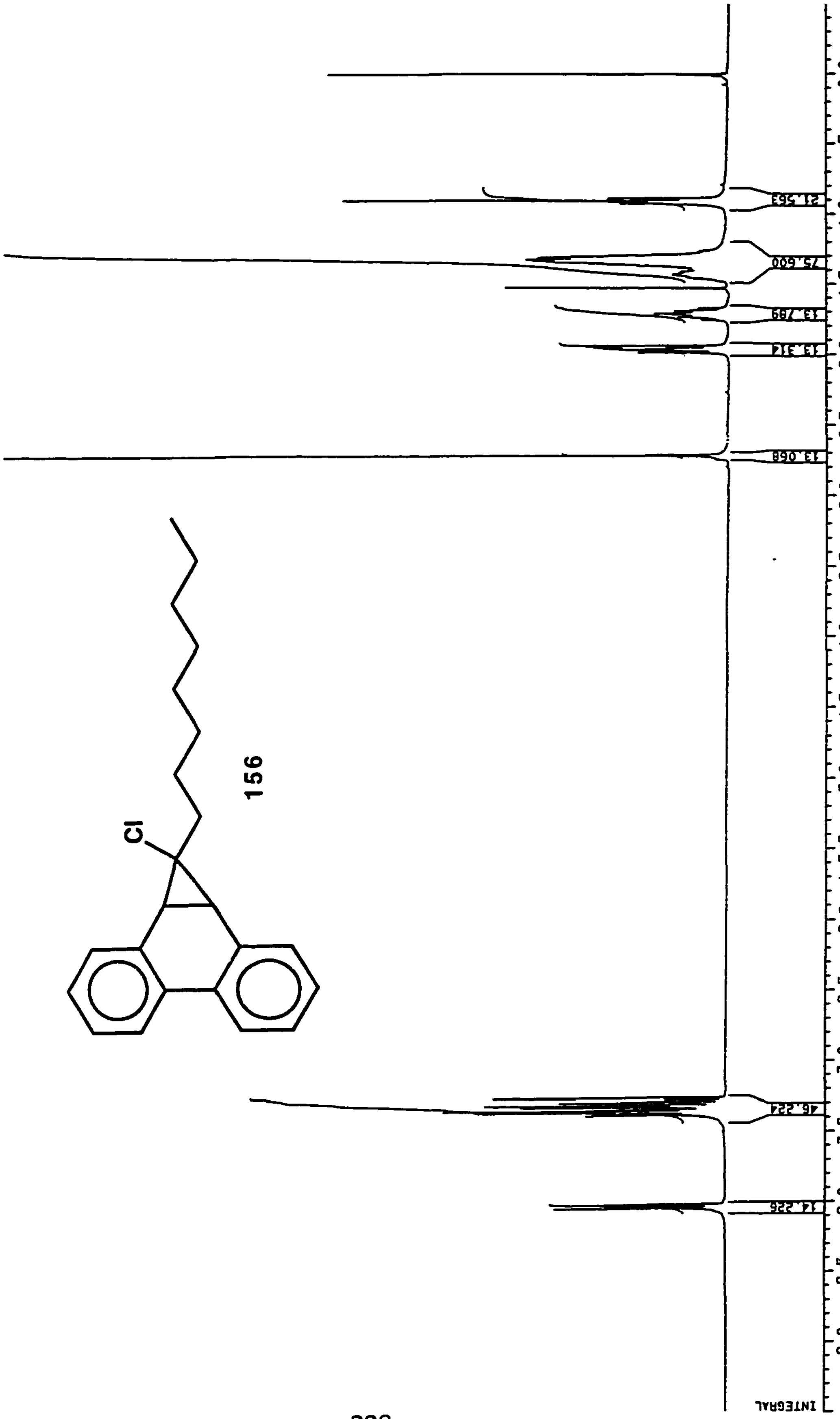
145


Cl
INTEGRAL
28.043
54.349
18.406
18.505
18.679
58.483
18.466
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
PPM
1.0
1.5
2.0
PPM

155

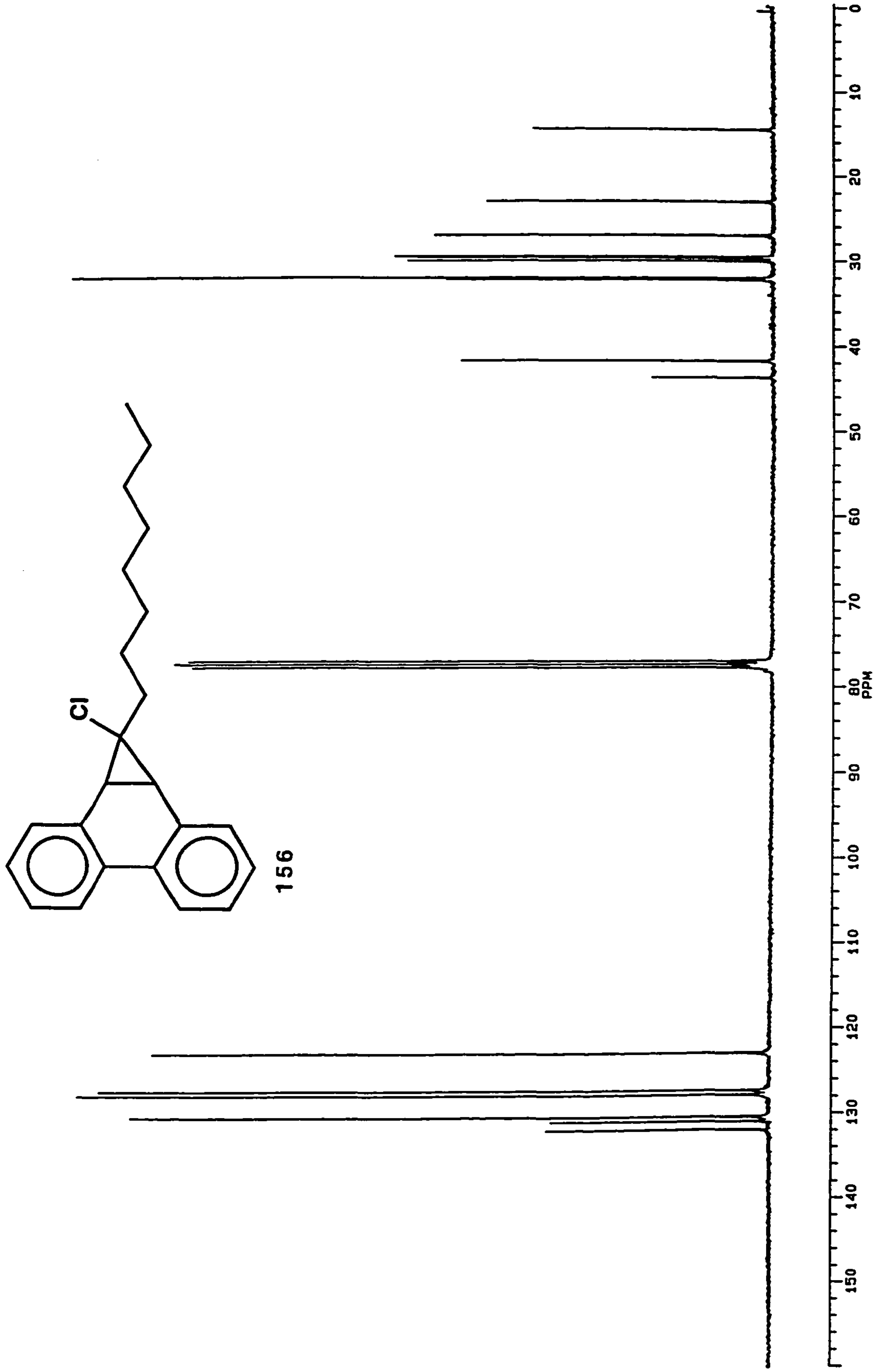


155

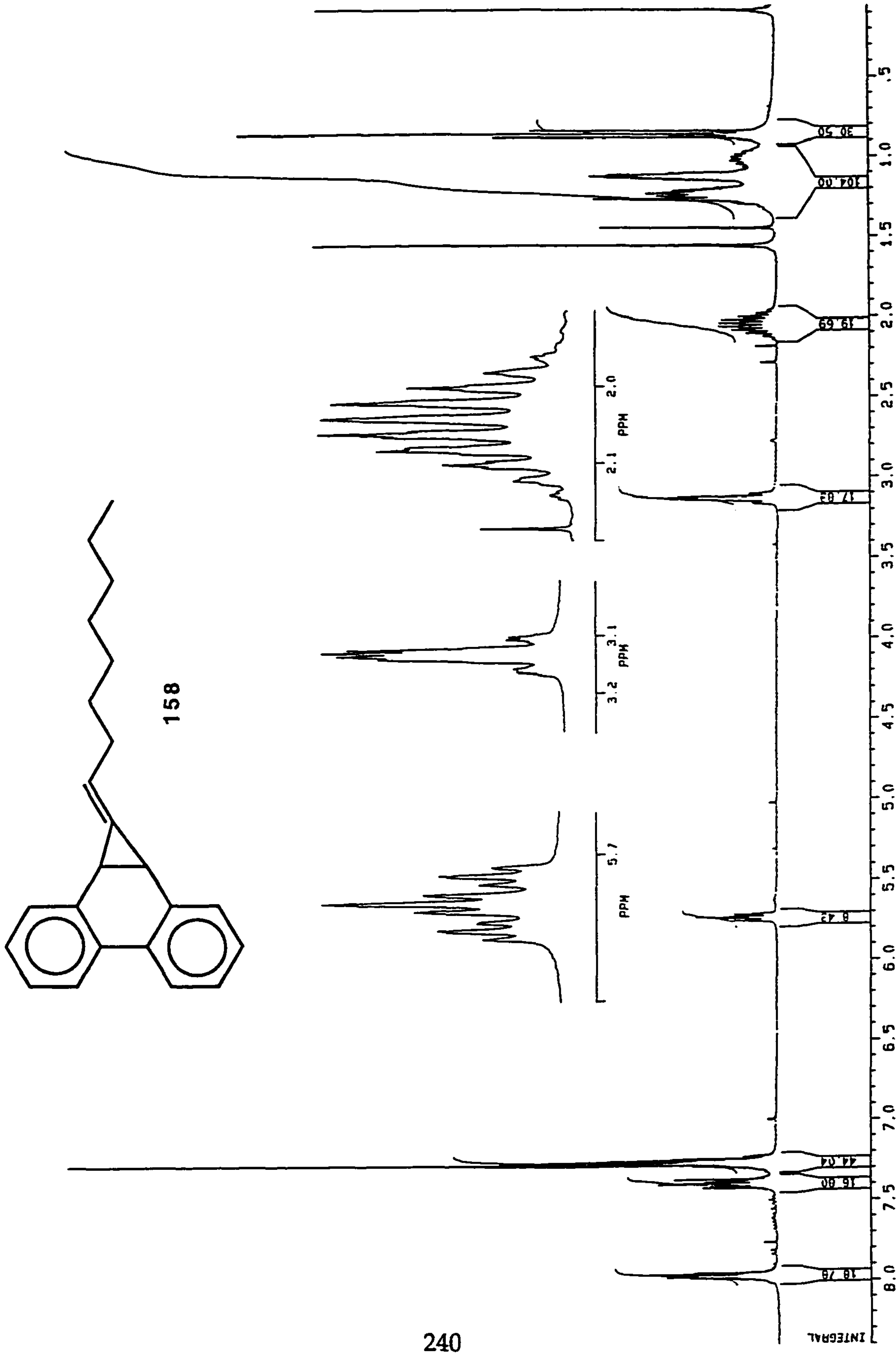


Cl
PPM
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
21.563
75.600
13.789
13.314
13.068
46.224
14.226
INTEGRAL

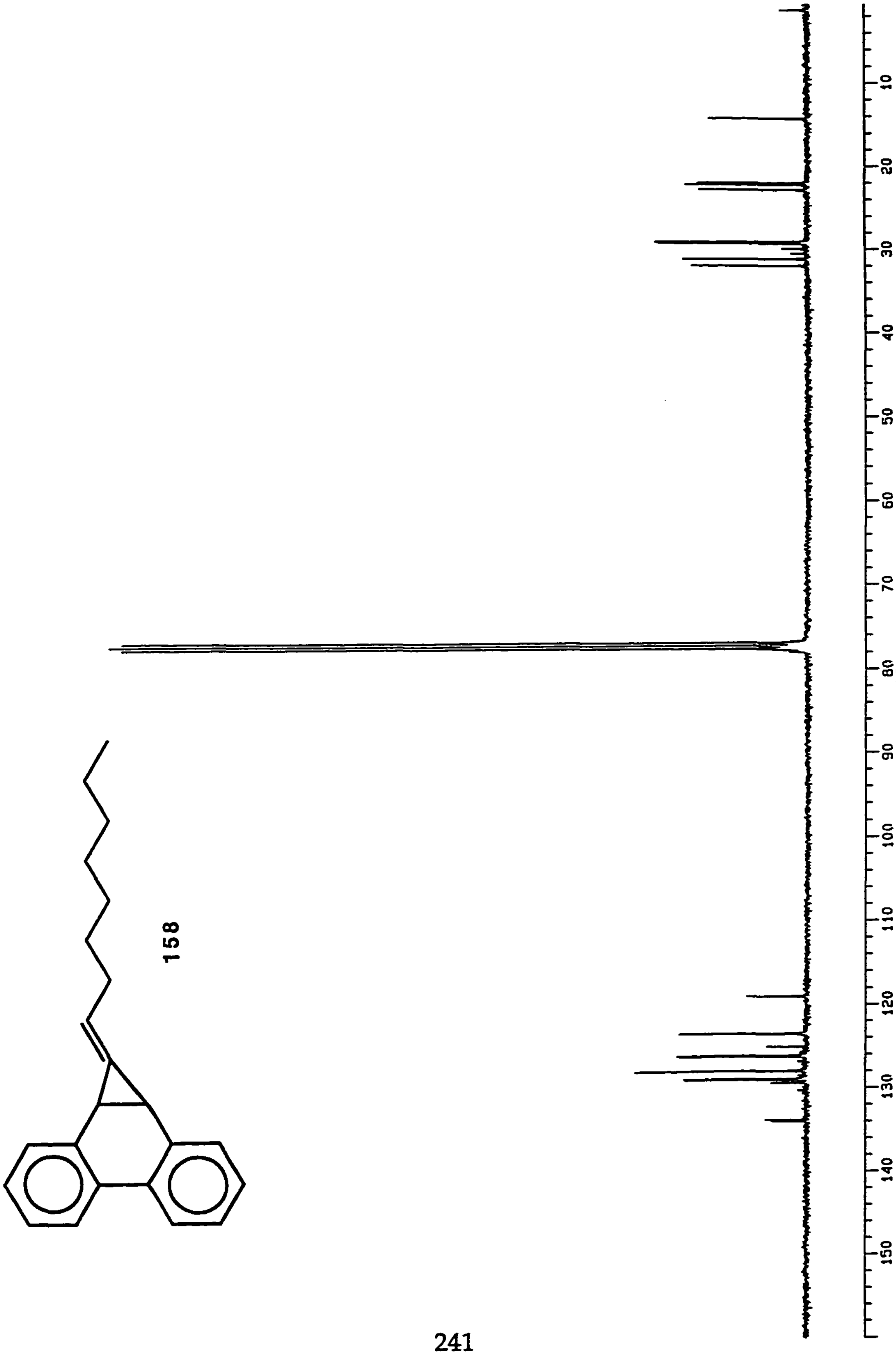
156



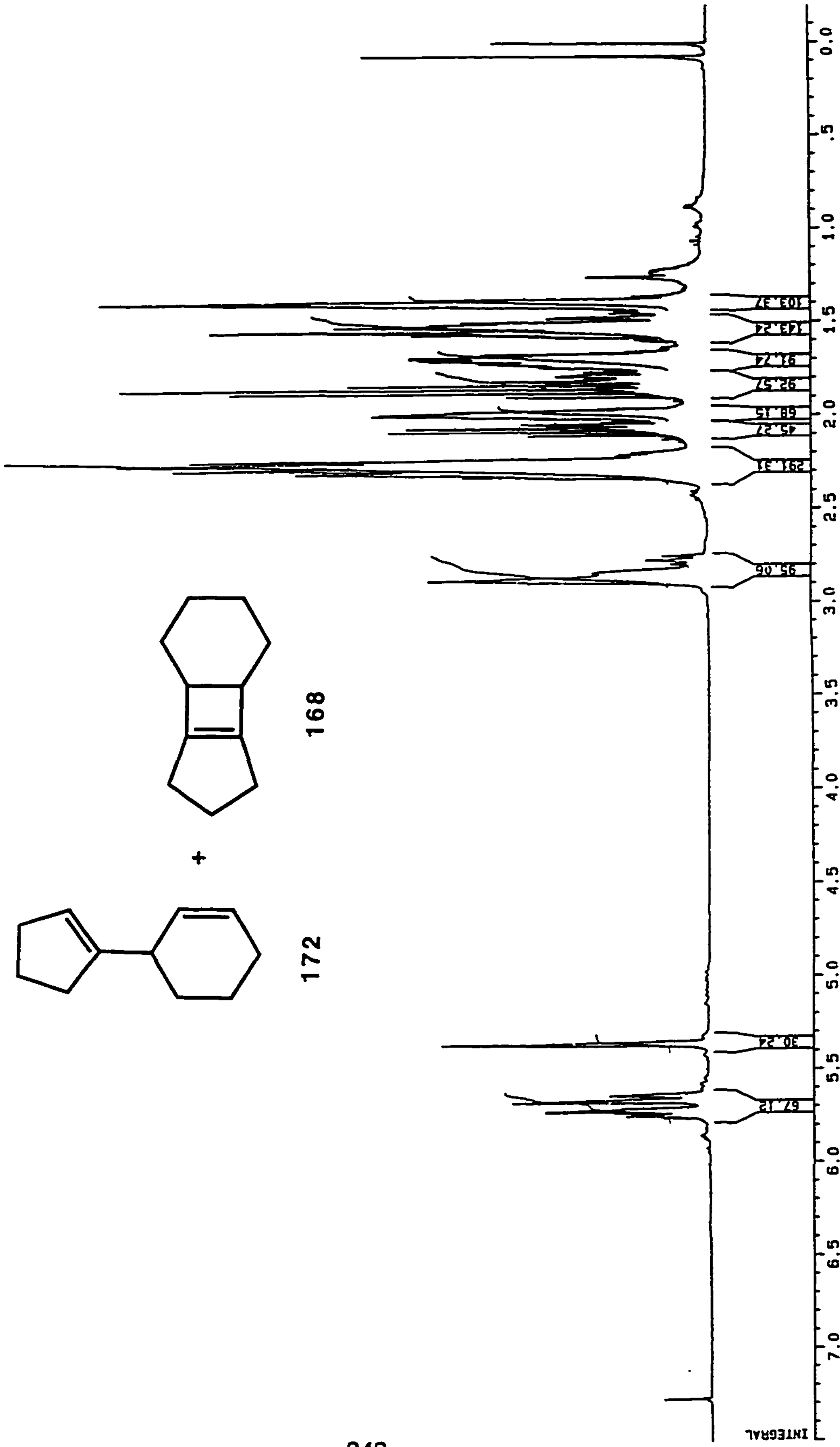
156


INTEGRAL
18.78
16.80
44.04
8.42
17.83
19.69
104.00
30.50
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
PPM
5.7
PPM
3.2
3.1
PPM
2.1
2.0
PPM

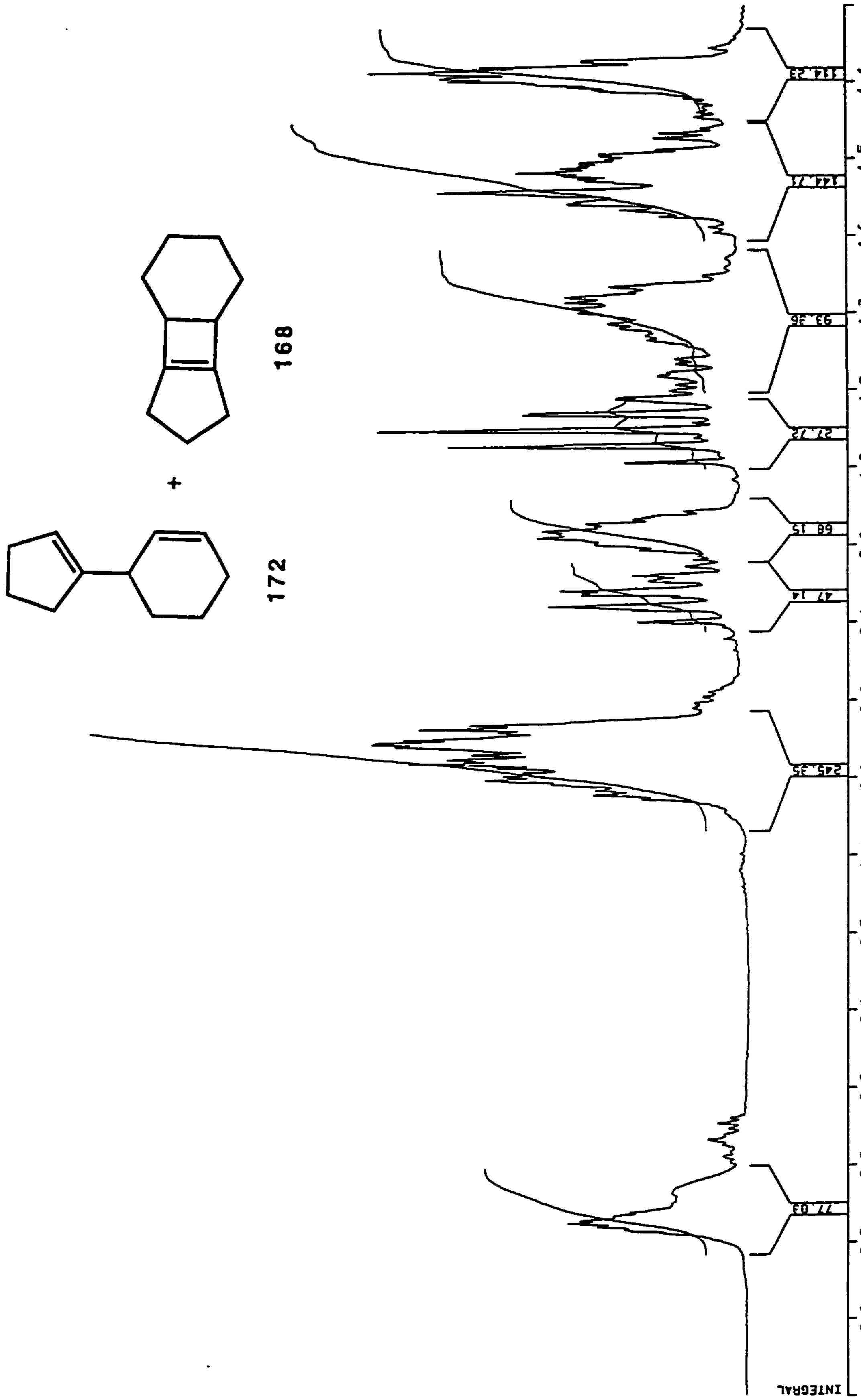
158



158

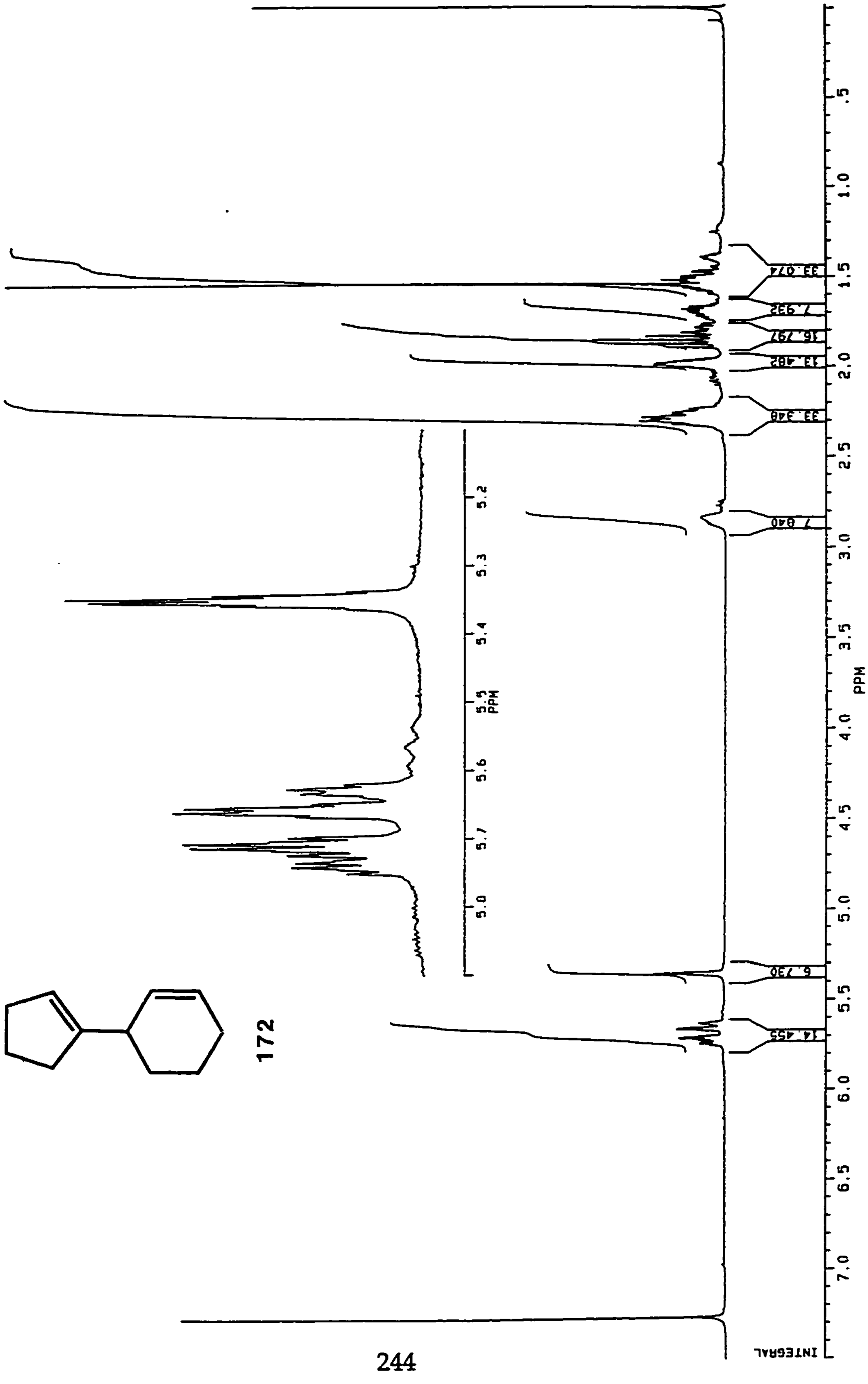


172
+
168
103.37
143.24
91.74
92.57
68.15
45.27
291.31
95.06
30.24
62.12
INTEGRAL
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
PPM



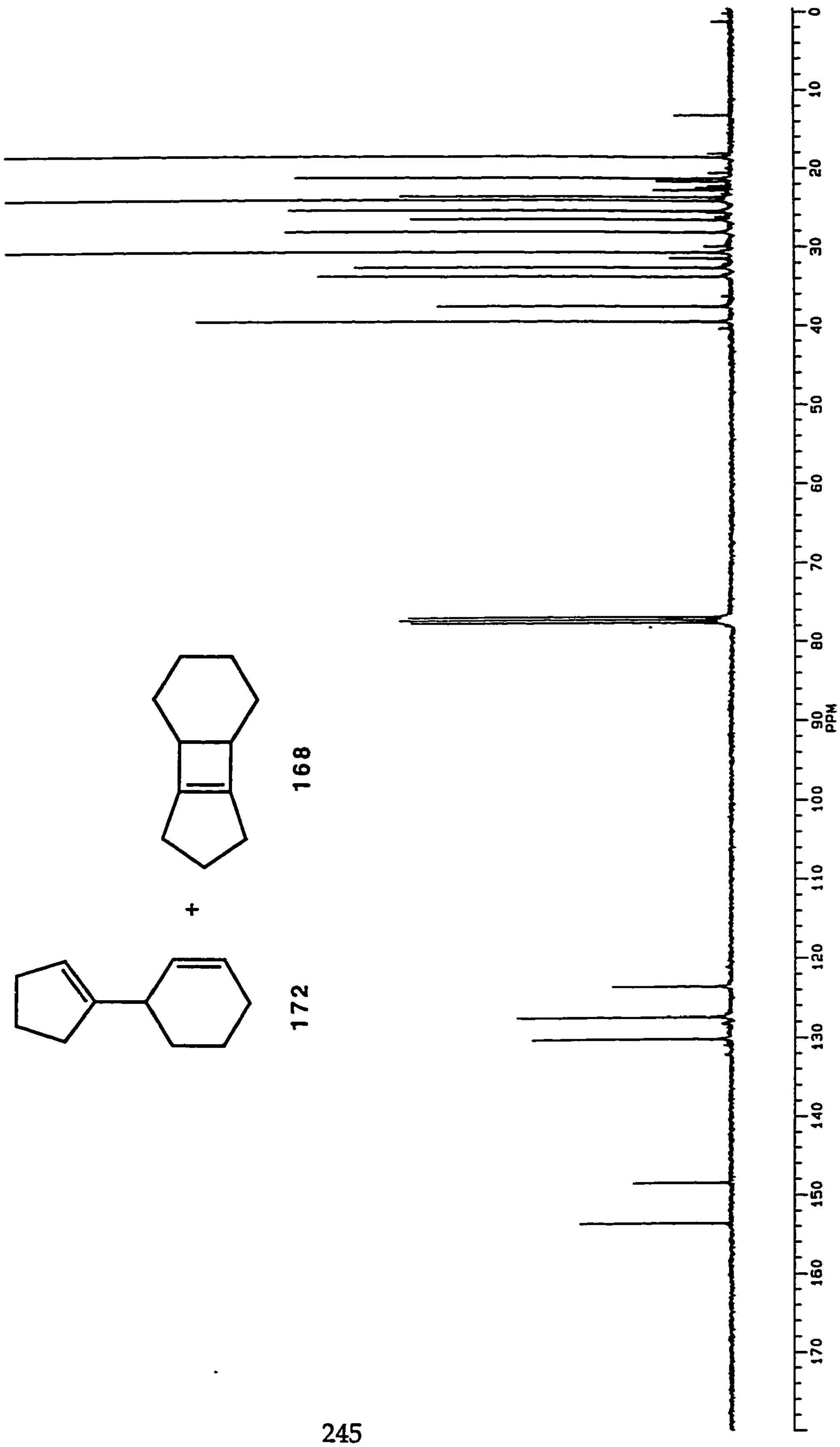
172 + 168

1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
PPM
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
INTEGRAL
114.23
144.71
93.36
27.72
68.15
47.14
245.35
77.83

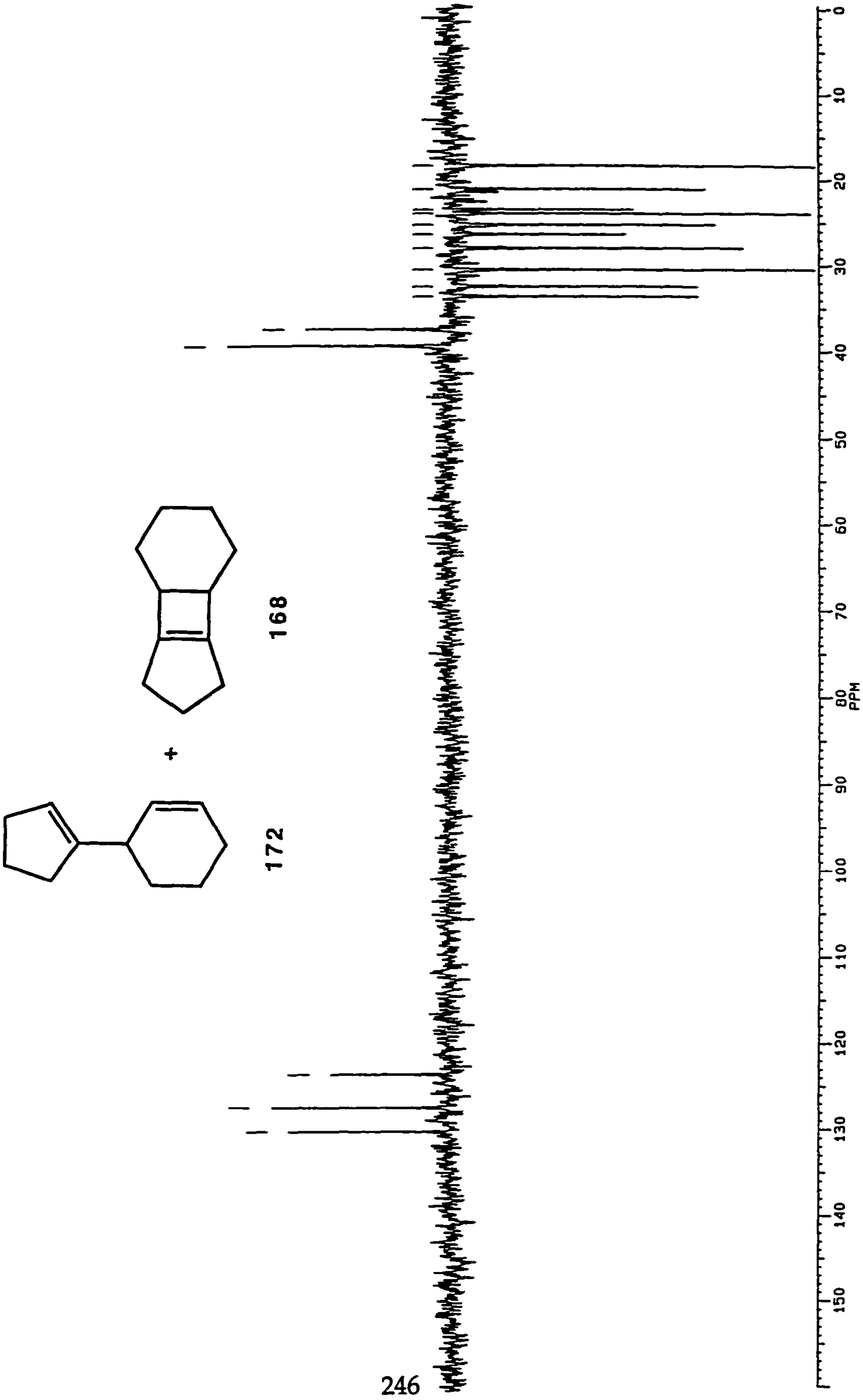


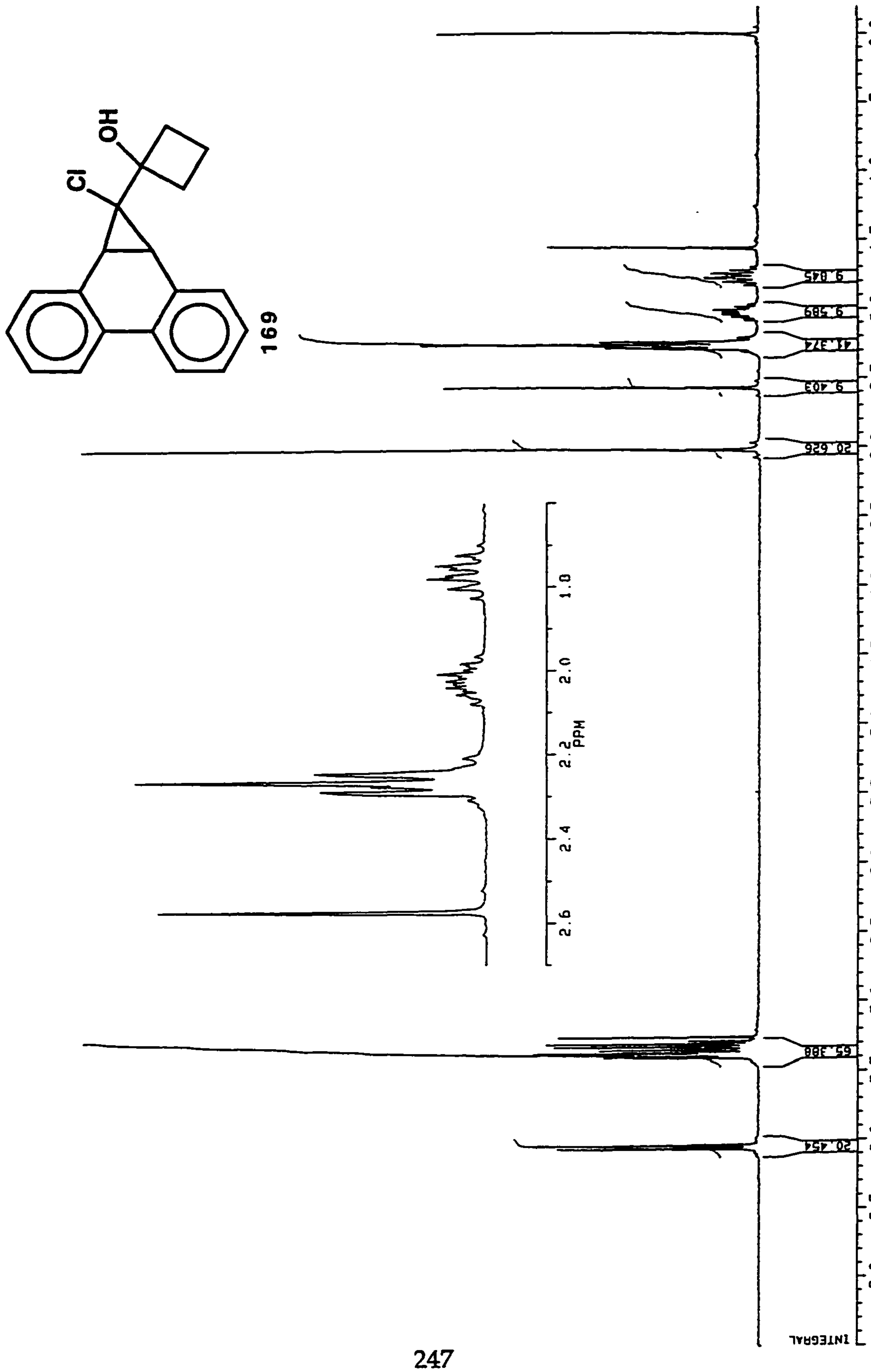
33.074
7.932
16.797
13.482
33.348
7.840
6.730
14.455
INTEGRAL
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
PPM
5.2
5.3
5.4
5.5
5.6
5.7
5.8
PPM

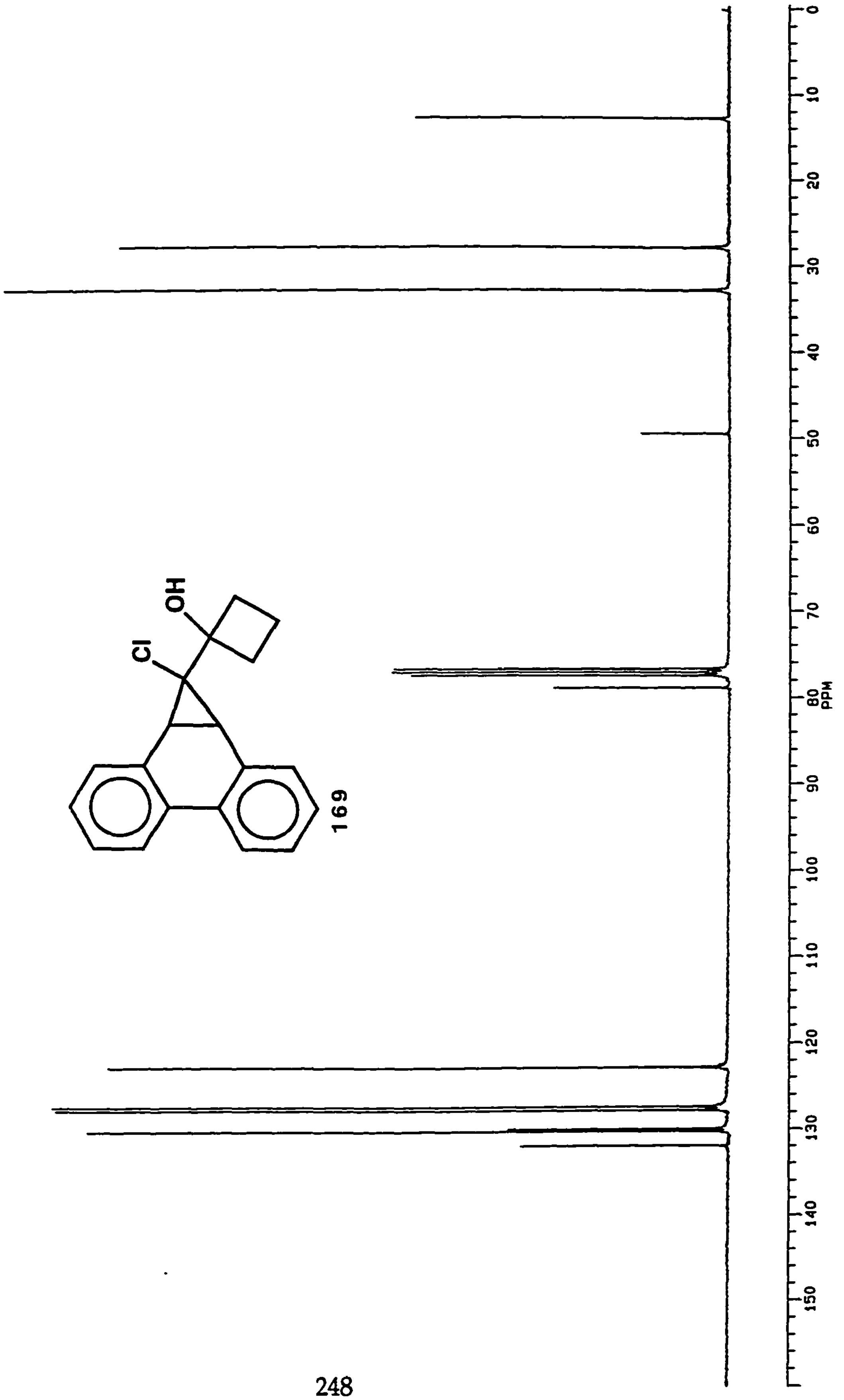
172



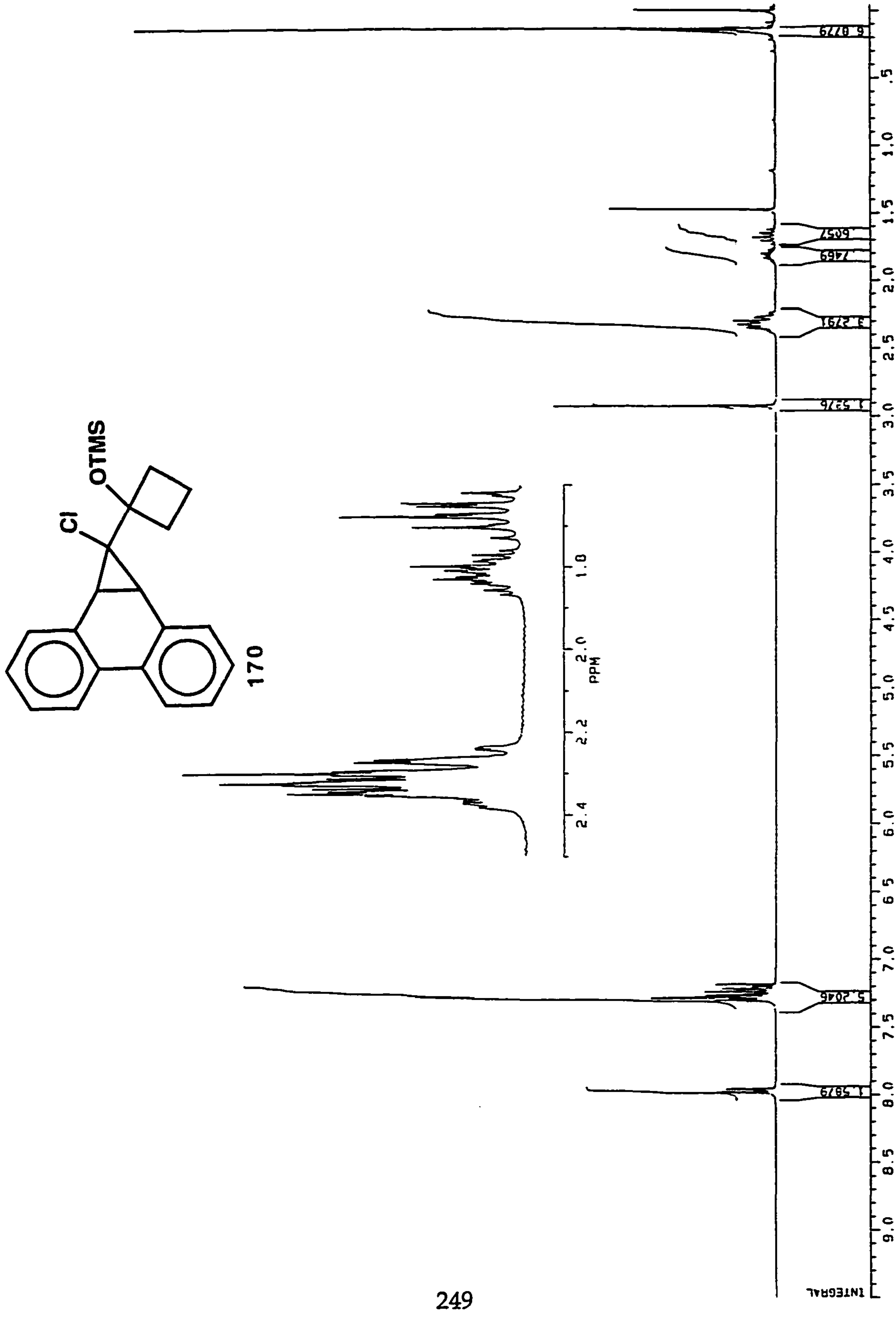
172
+
168
0
10
20
30
40
50
60
70
80
90
PPM
100
110
120
130
140
150
160
170


172
+
168
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150

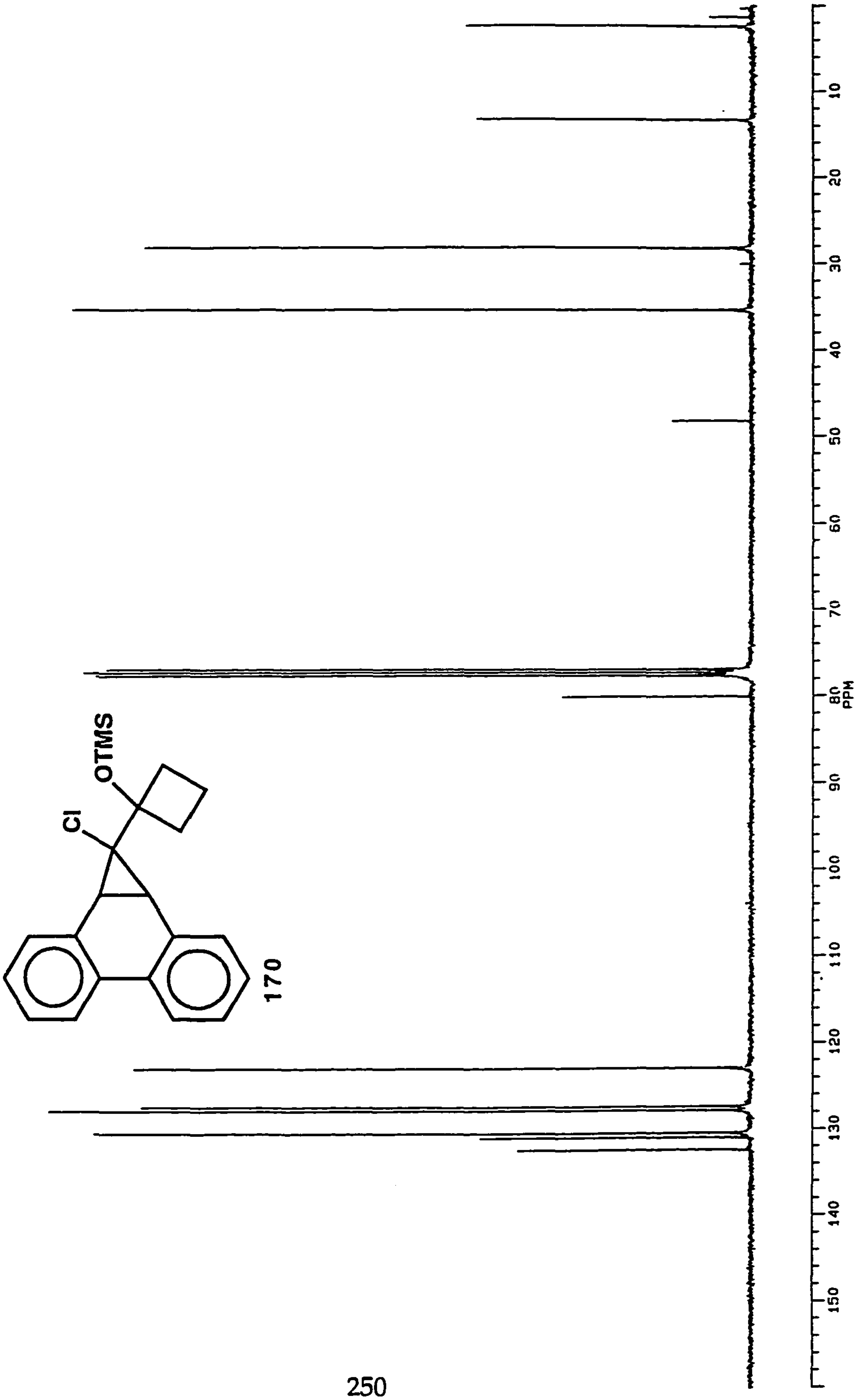

169
Cl
OH
INTEGRAL
9.845
9.589
41.374
9.403
20.626
65.388
20.454
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
PPM
1.8
2.0
2.2
2.4
2.6
PPM



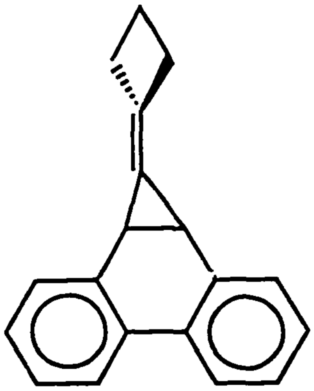
169


Cl
OTMS
6.0279
.6057
.7469
3.2791
1.5276
5.2046
1.5879
INTEGRAL
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
PPM
1.8
2.0
2.2
2.4
PPM

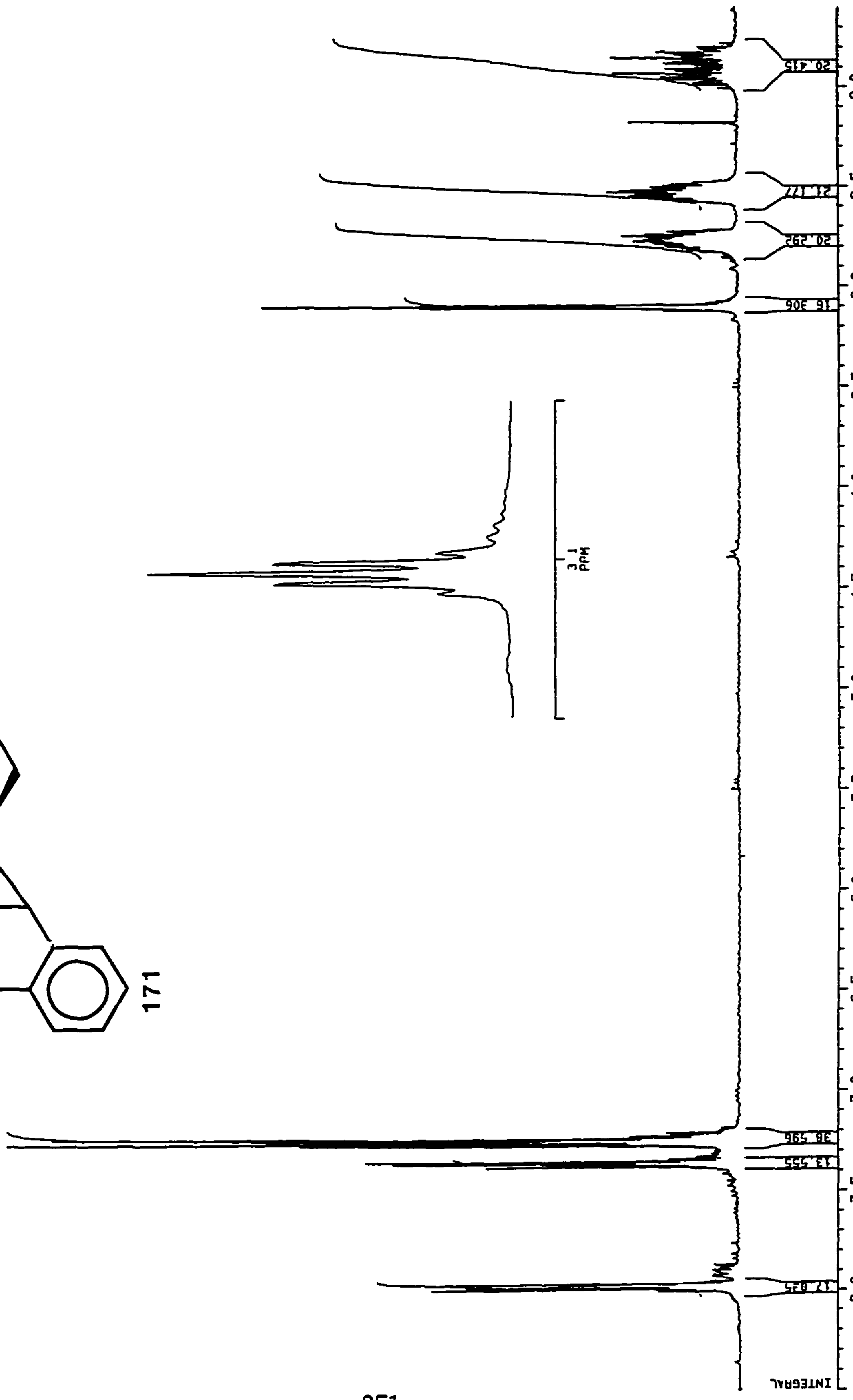
170



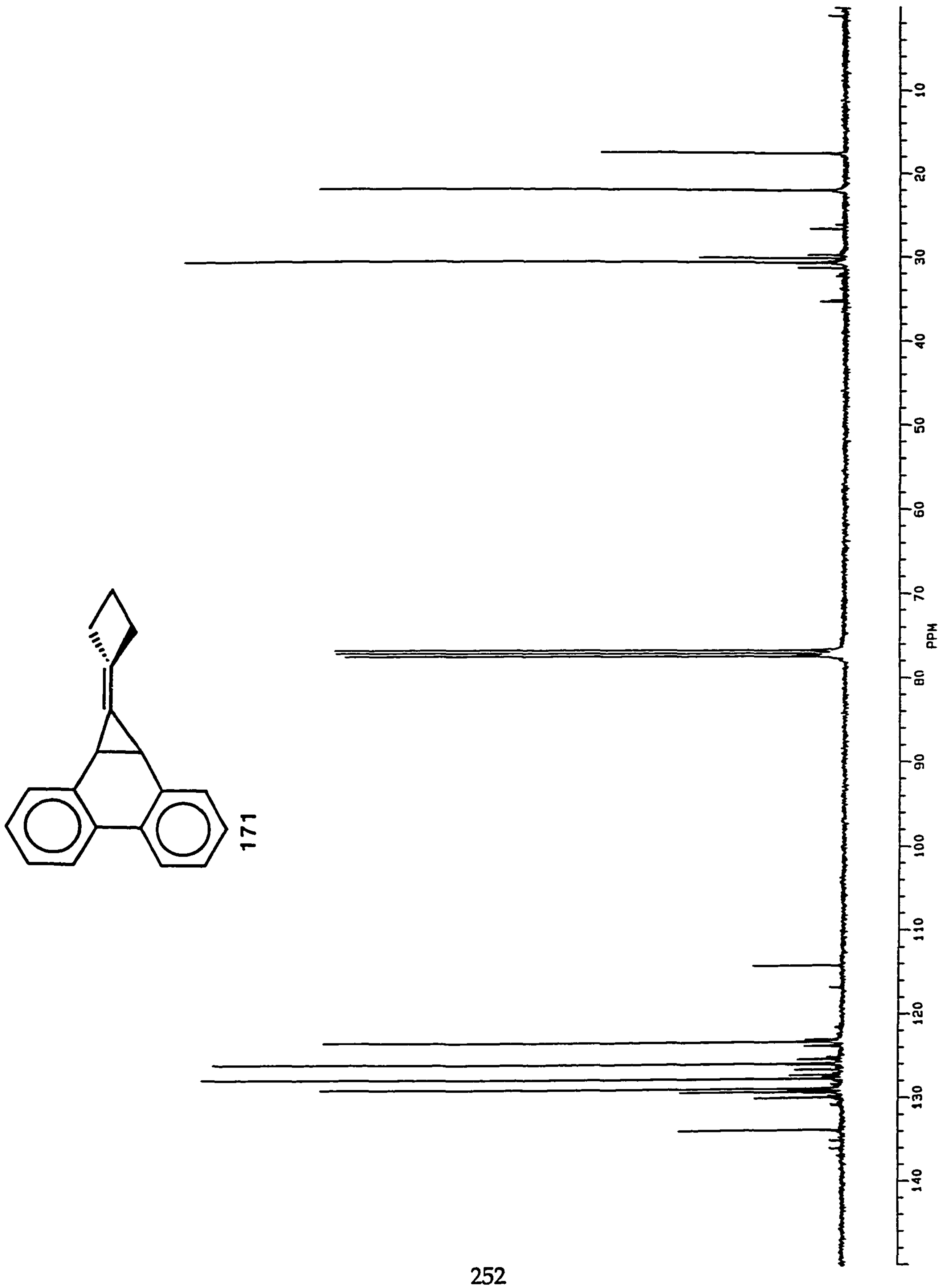
170



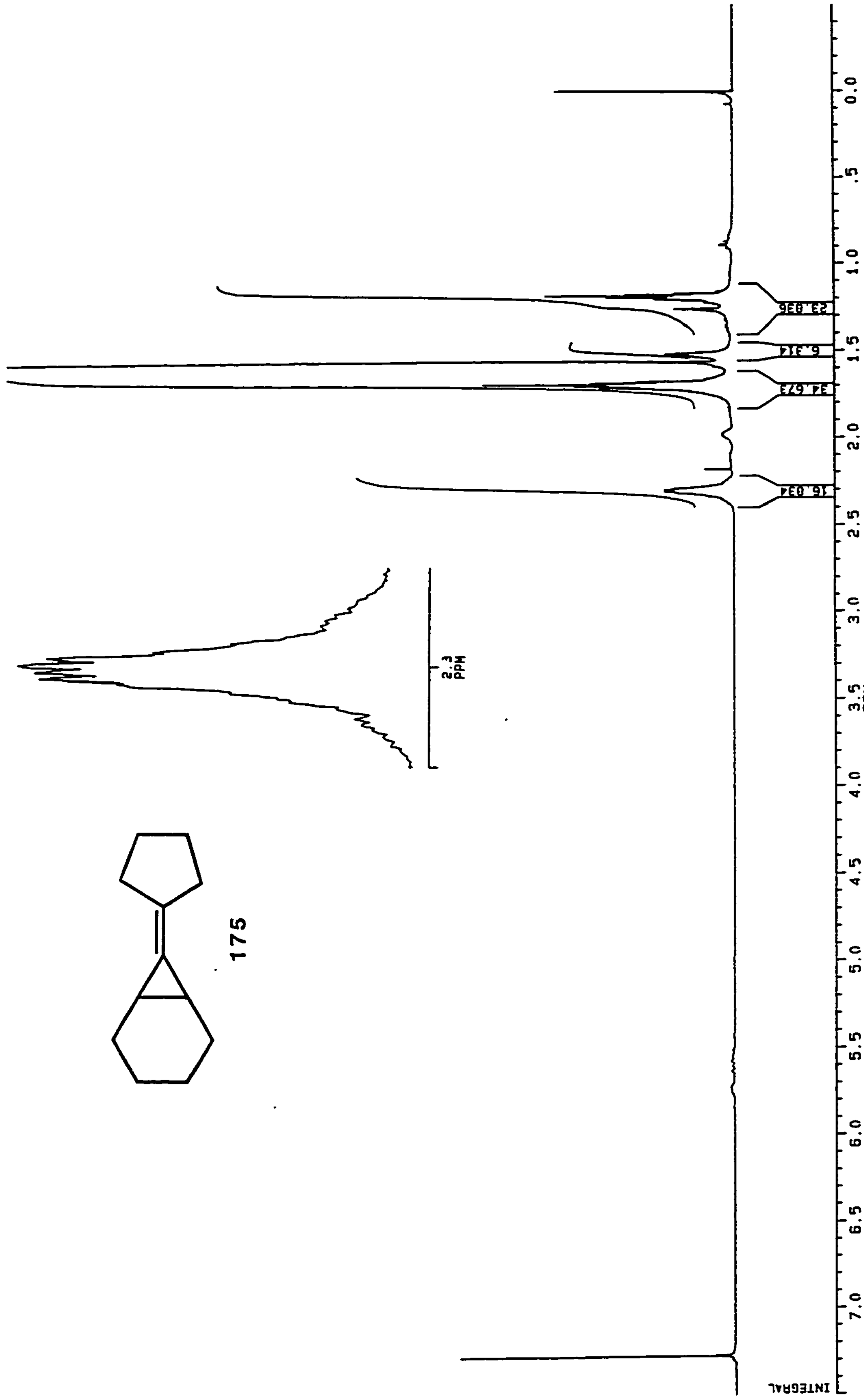
171



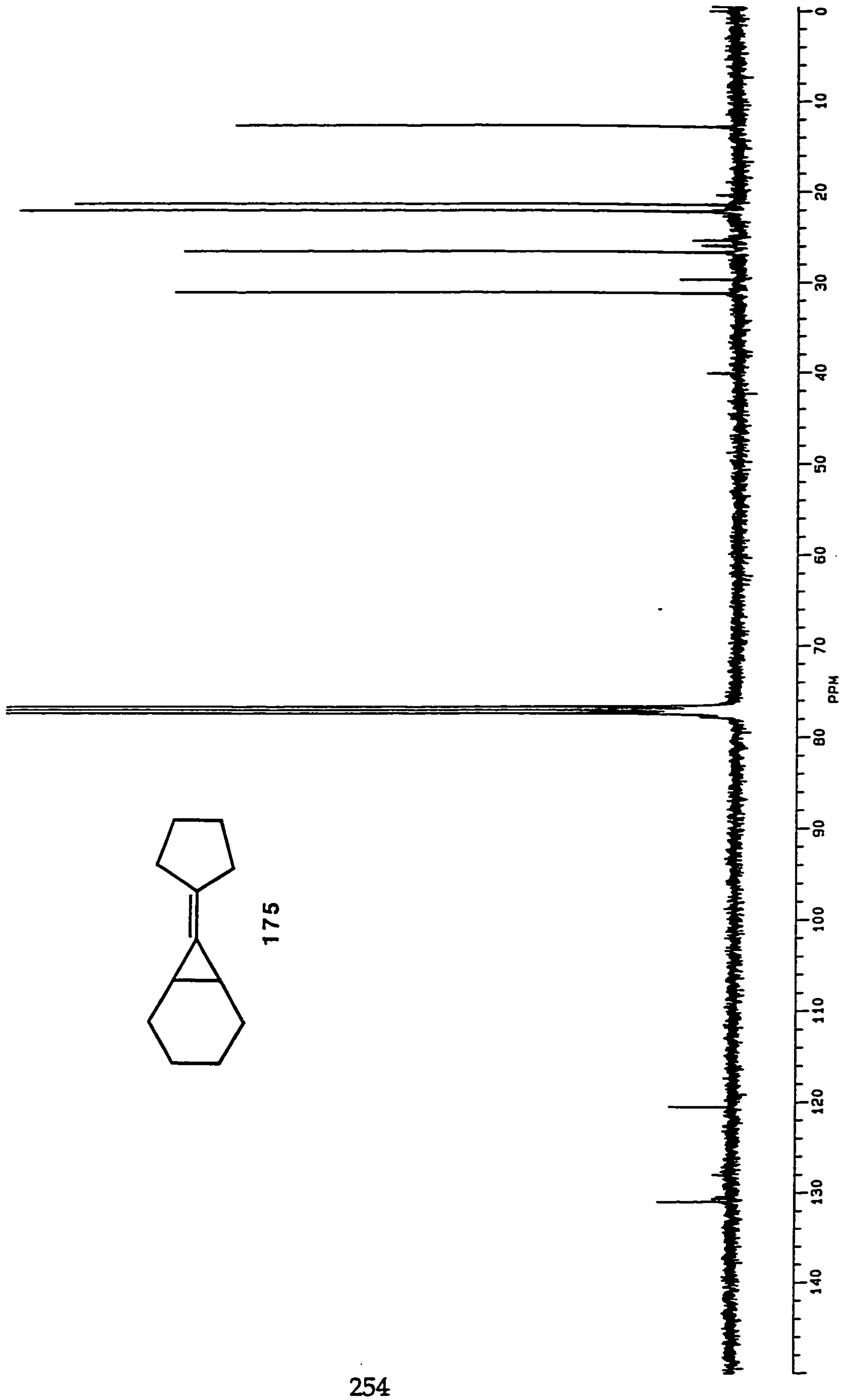
20.415
21.177
20.292
16.306
36.596
13.555
12.845
3.1
PPM
2.0
2.5
3.0
3.5
4.0
4.5
5.0
PPM
5.5
6.0
6.5
7.0
7.5
8.0
INTEGRAL



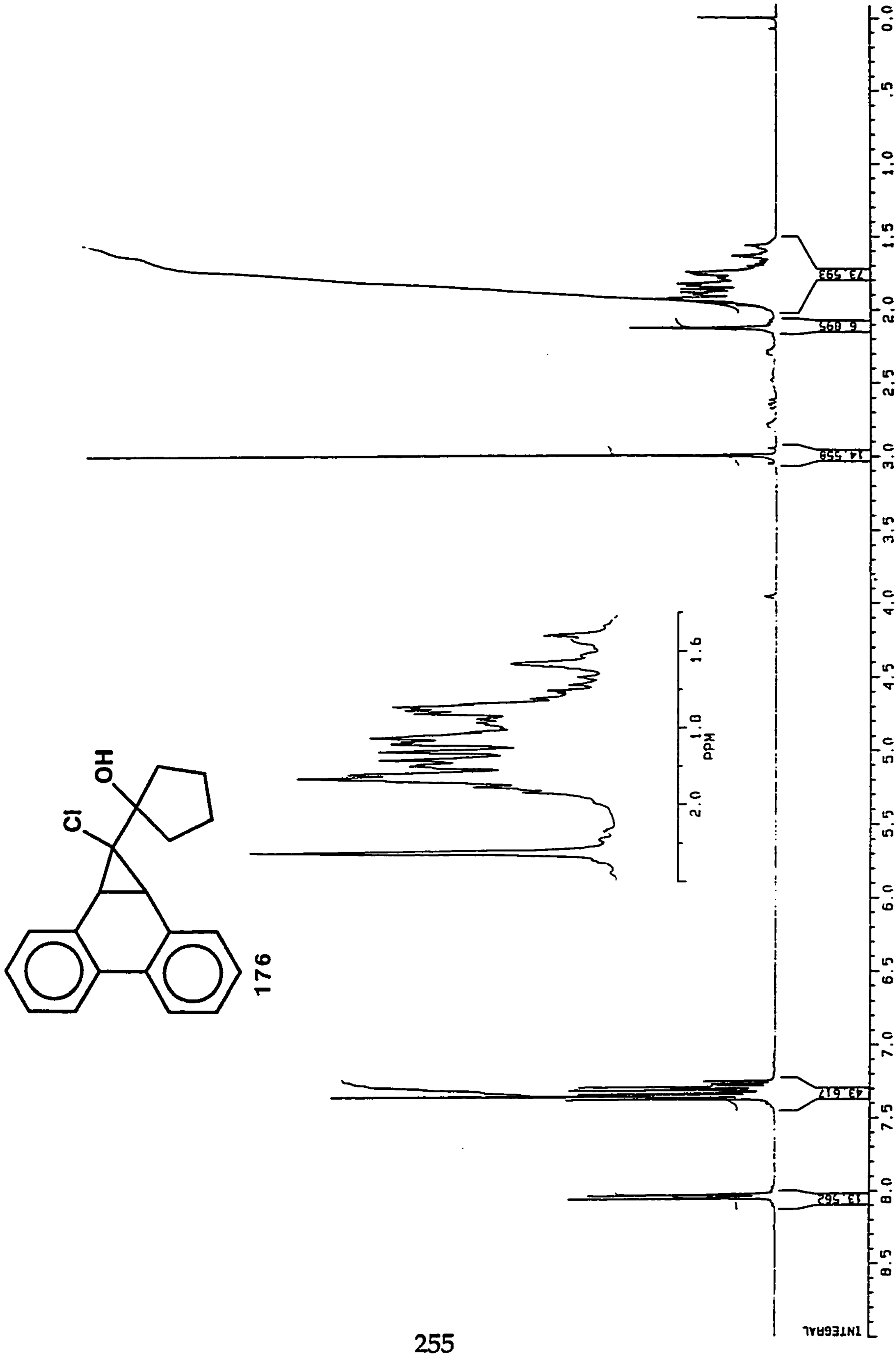
171


23.036
6.314
34.673
16.034
INTEGRAL
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
PPM
4.0
4.5
5.0
5.5
6.0
6.5
7.0
2.3
PPM

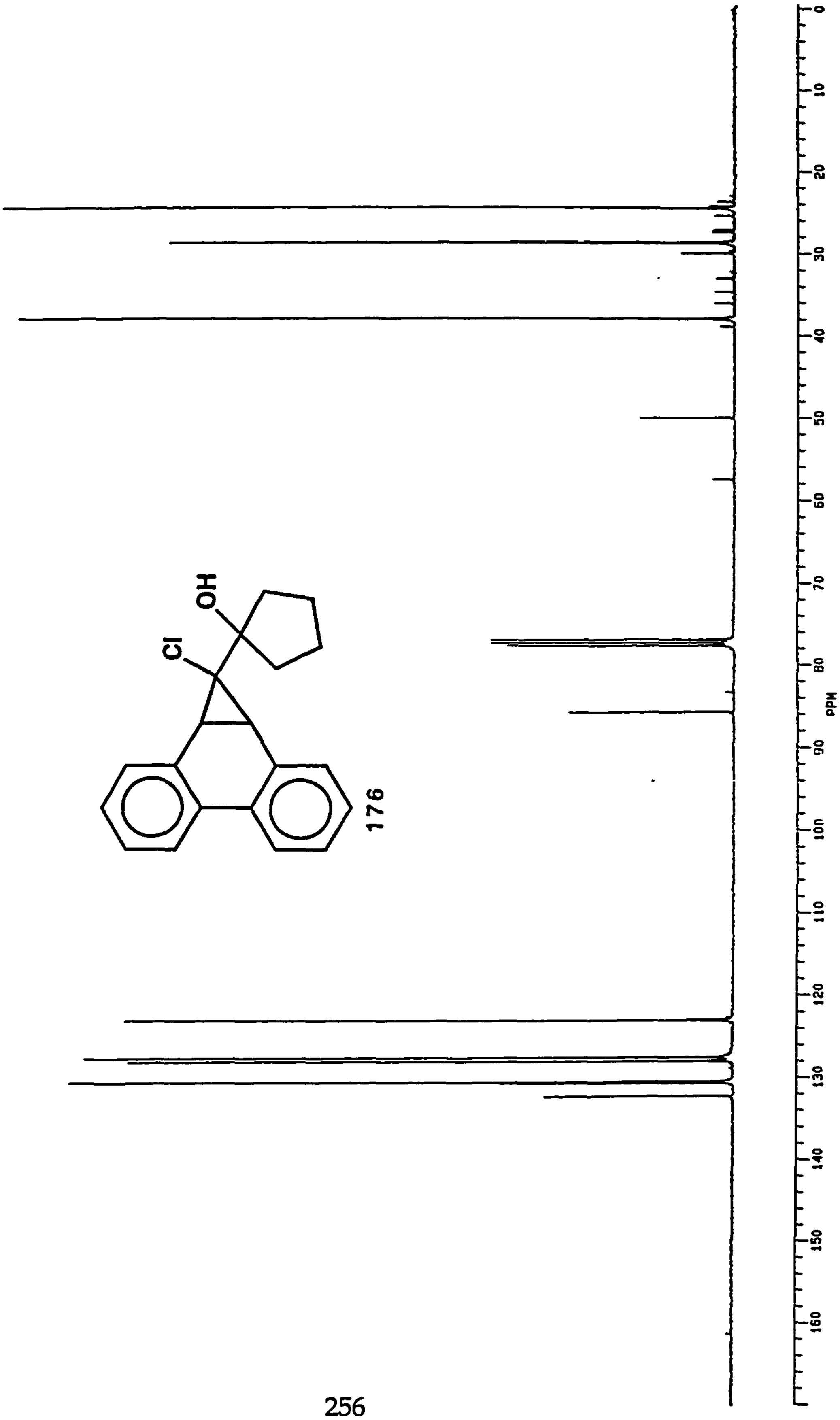
175



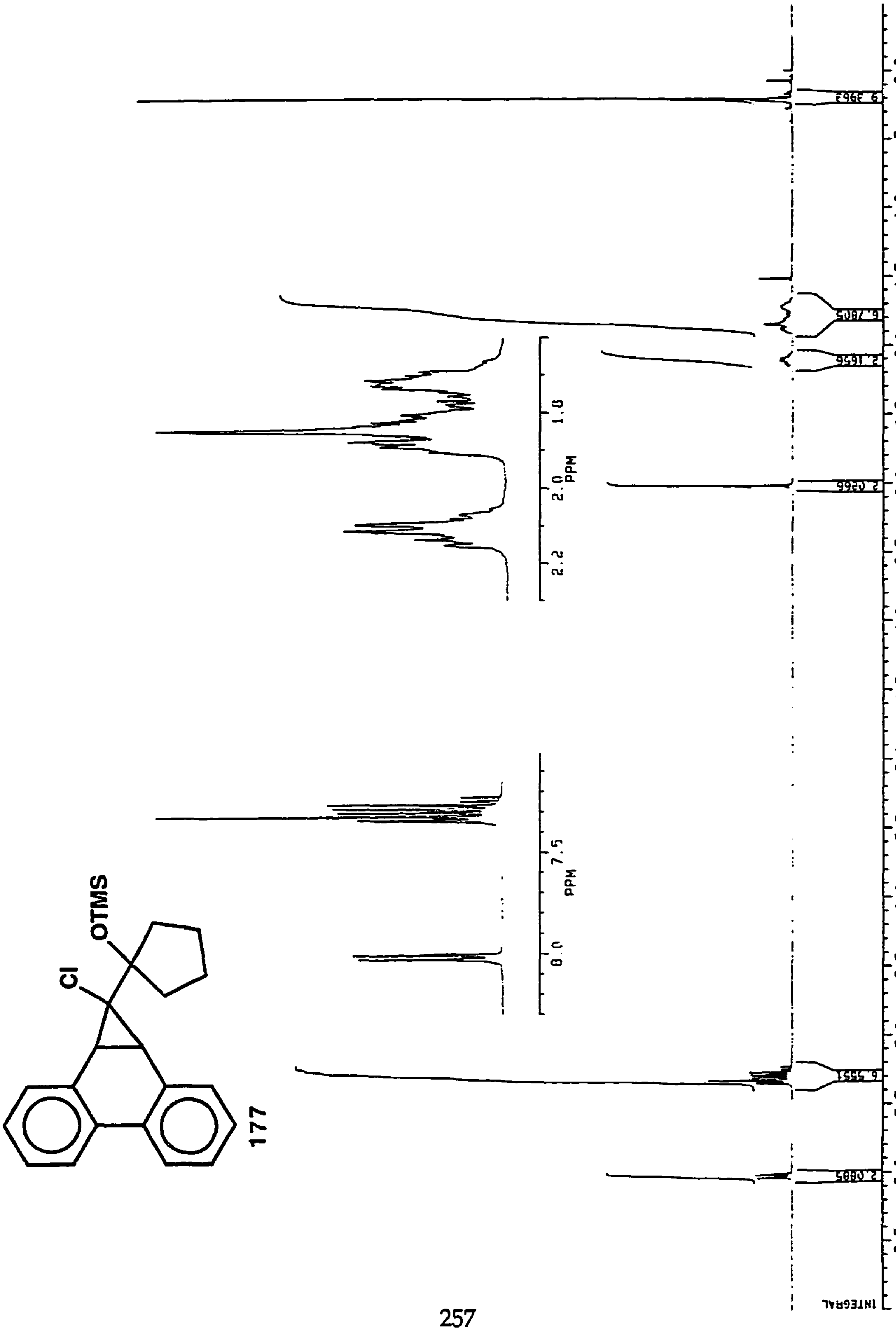
175

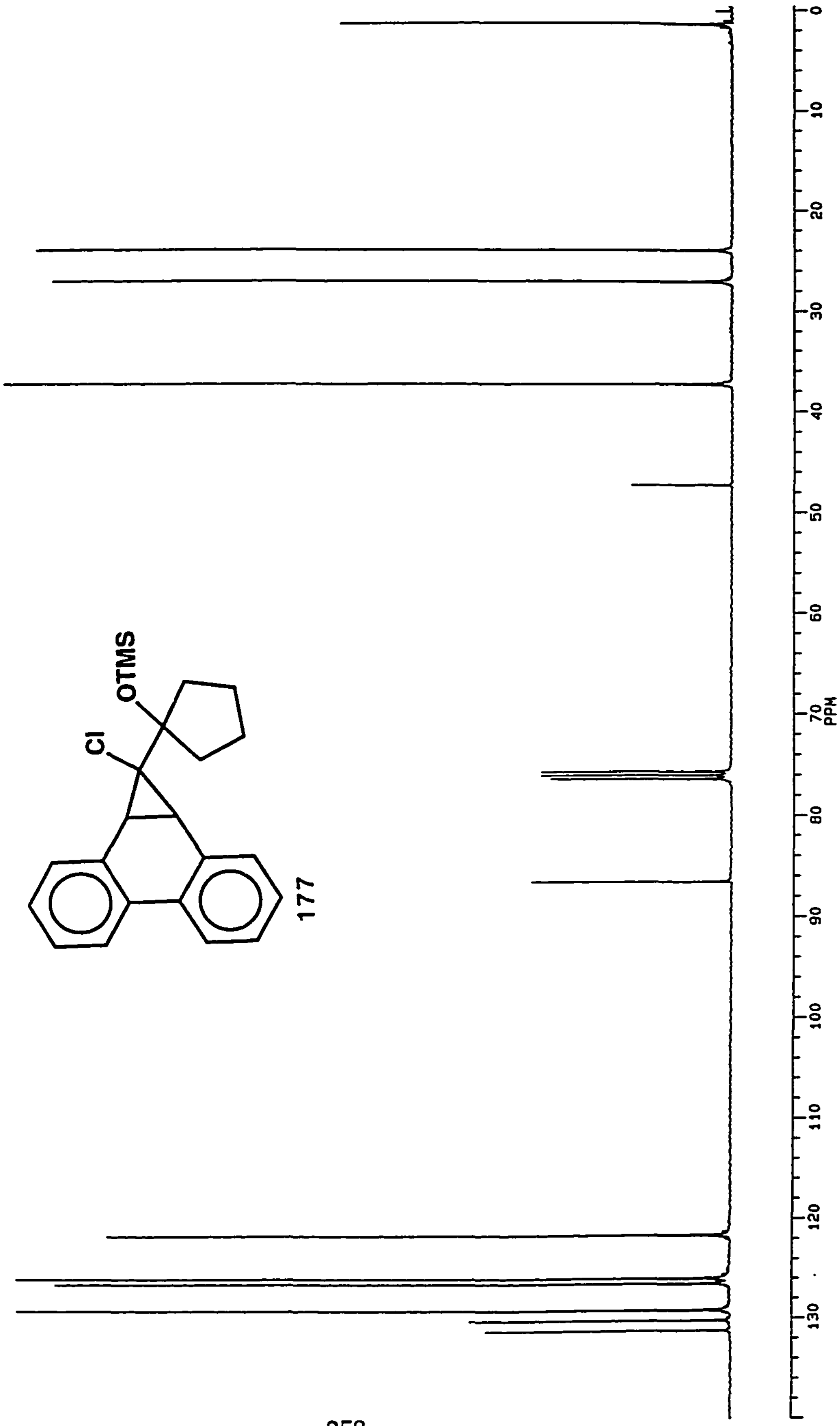

Cl
OH
INTEGRAL
73.593
6.695
14.558
43.617
13.562
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
PPM
2.0
1.8
1.6
PPM

176

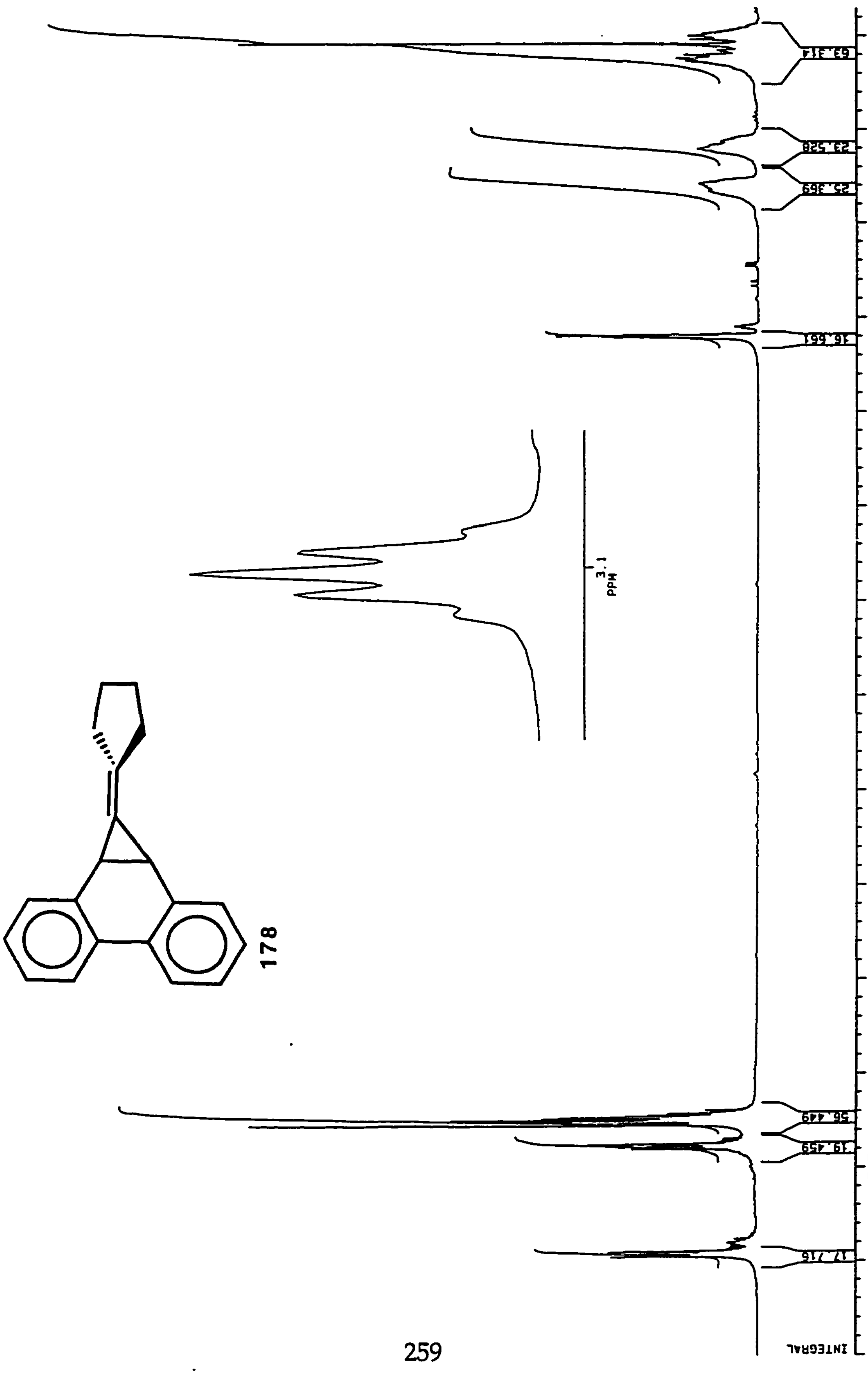


176

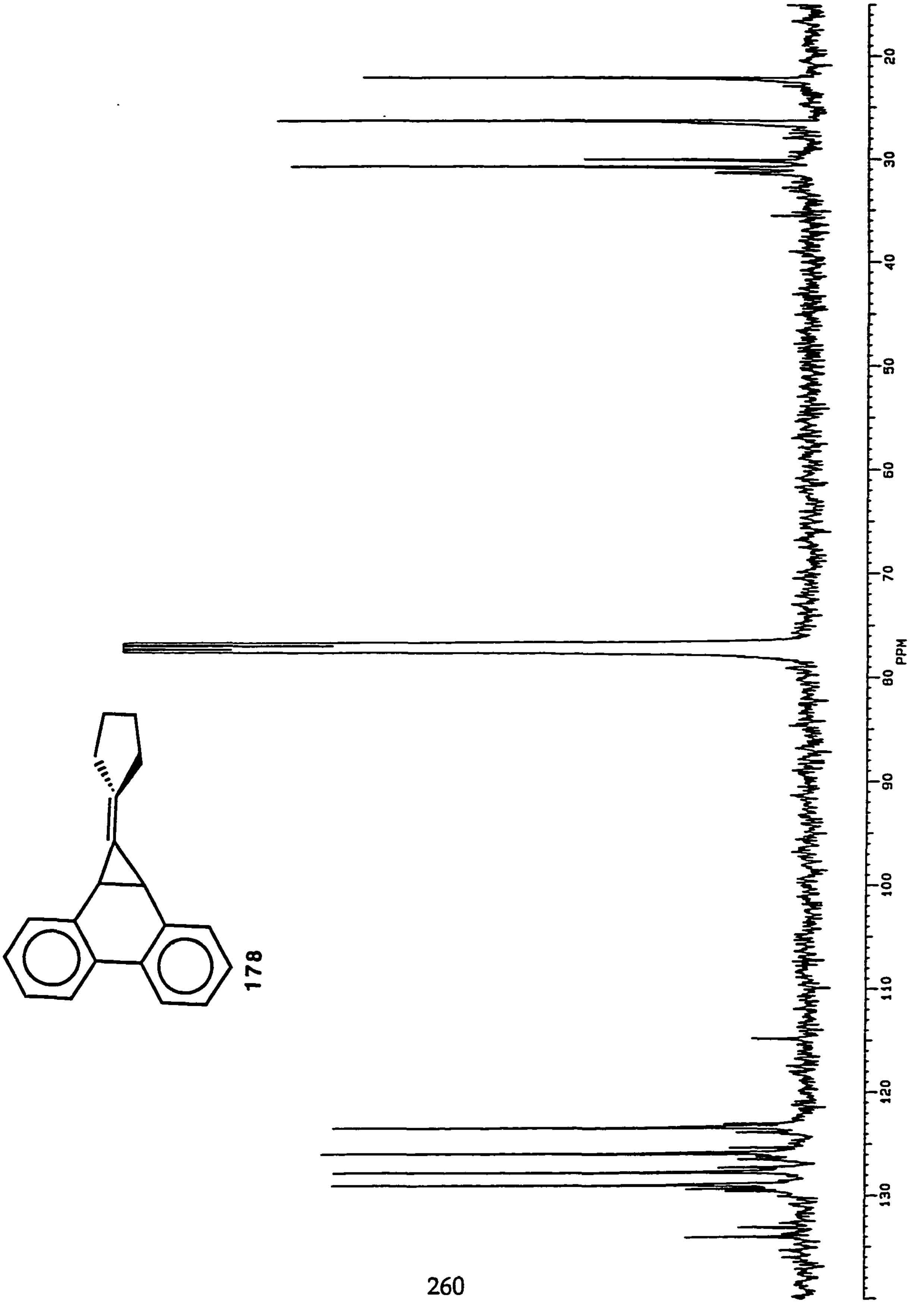

Cl
OTMS
177
INTEGRAL
9.3963
6.7805
2.1656
2.0266
6.5551
2.0885
0.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
PPM
1.0
2.0
2.2
PPM
7.5
8.0
PPM



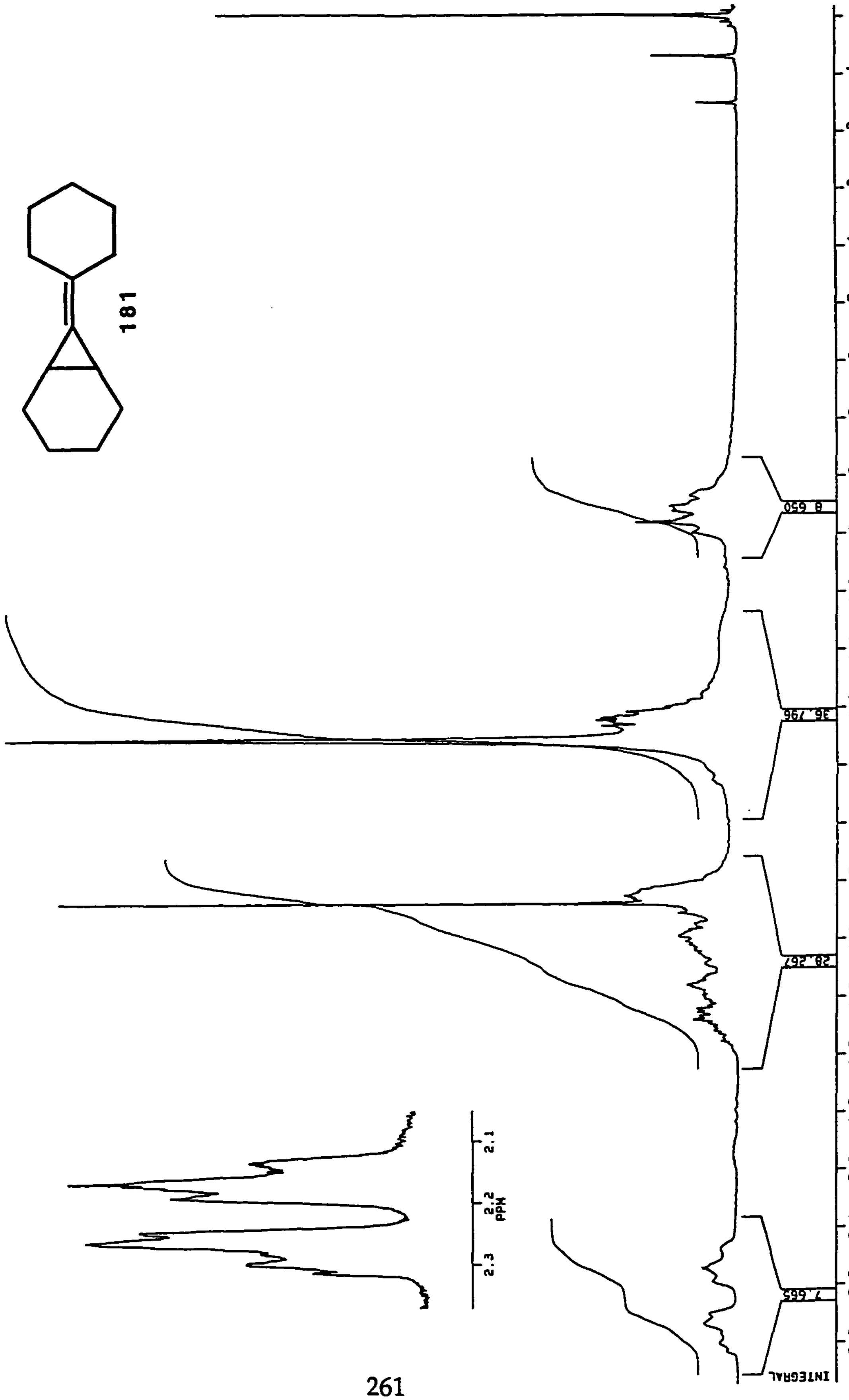
177


1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
PPM
5.5
6.0
6.5
7.0
7.5
8.0
INTEGRAL
63.314
23.528
25.369
36.661
56.449
19.459
17.716
3.1
PPM

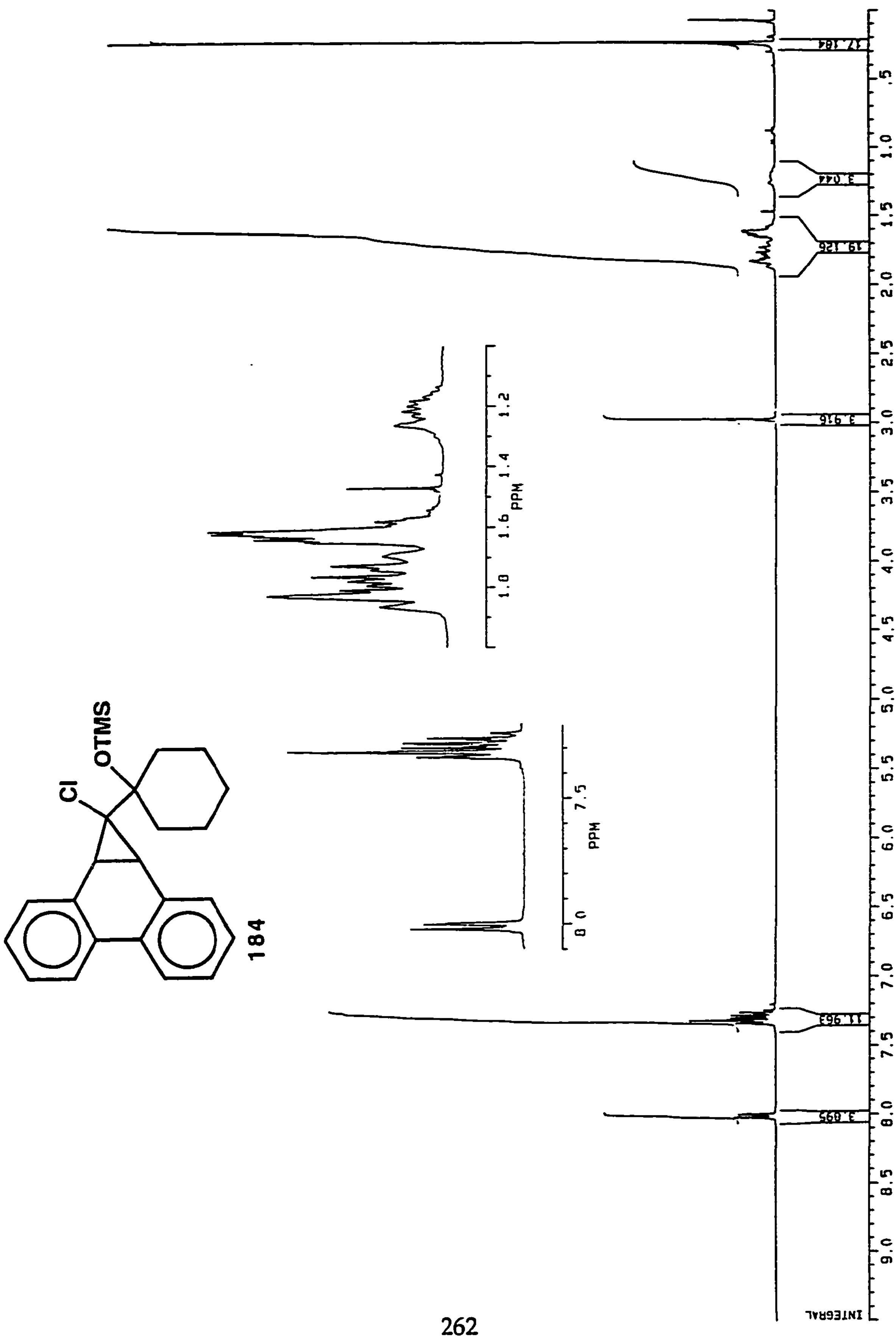
178



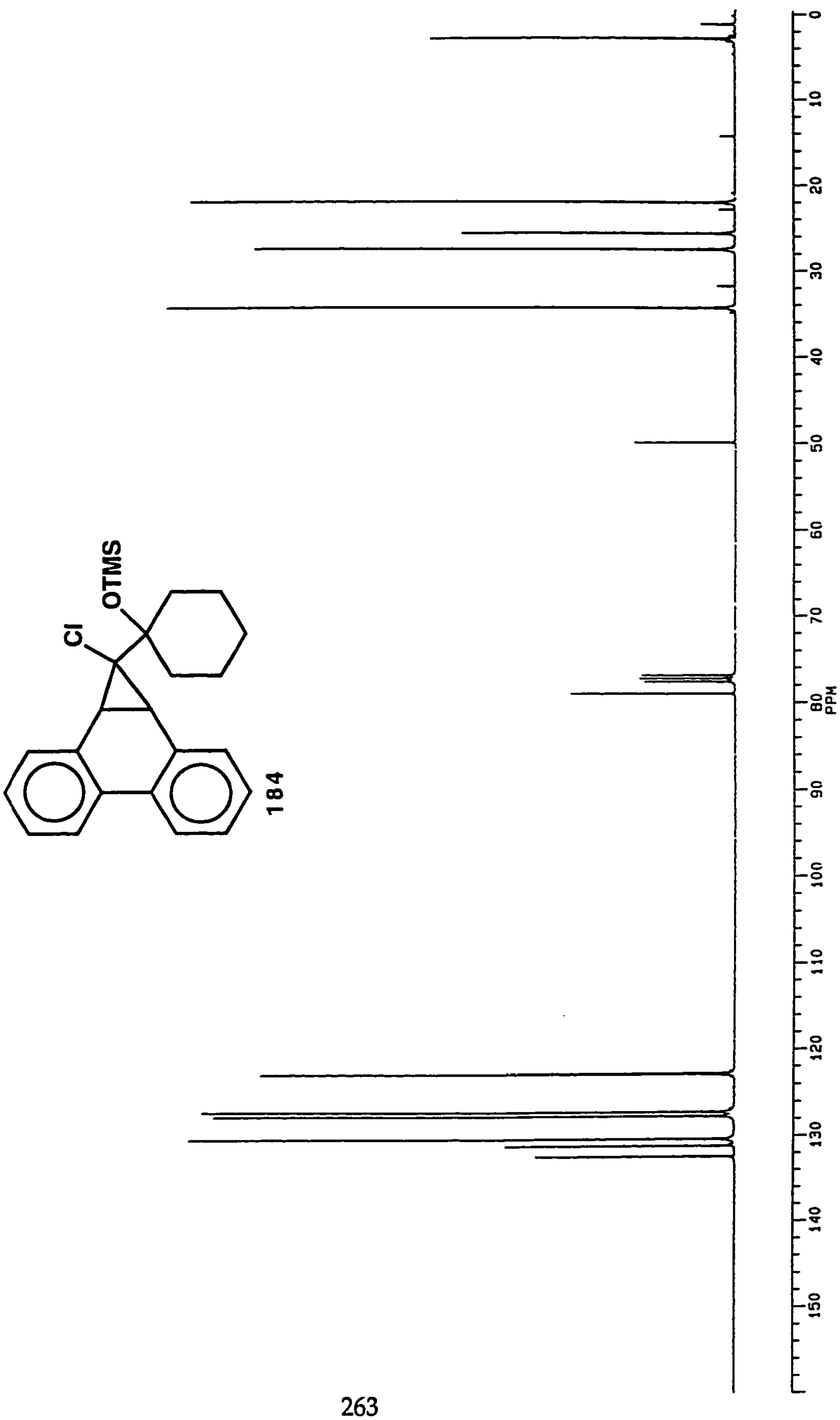
178


181

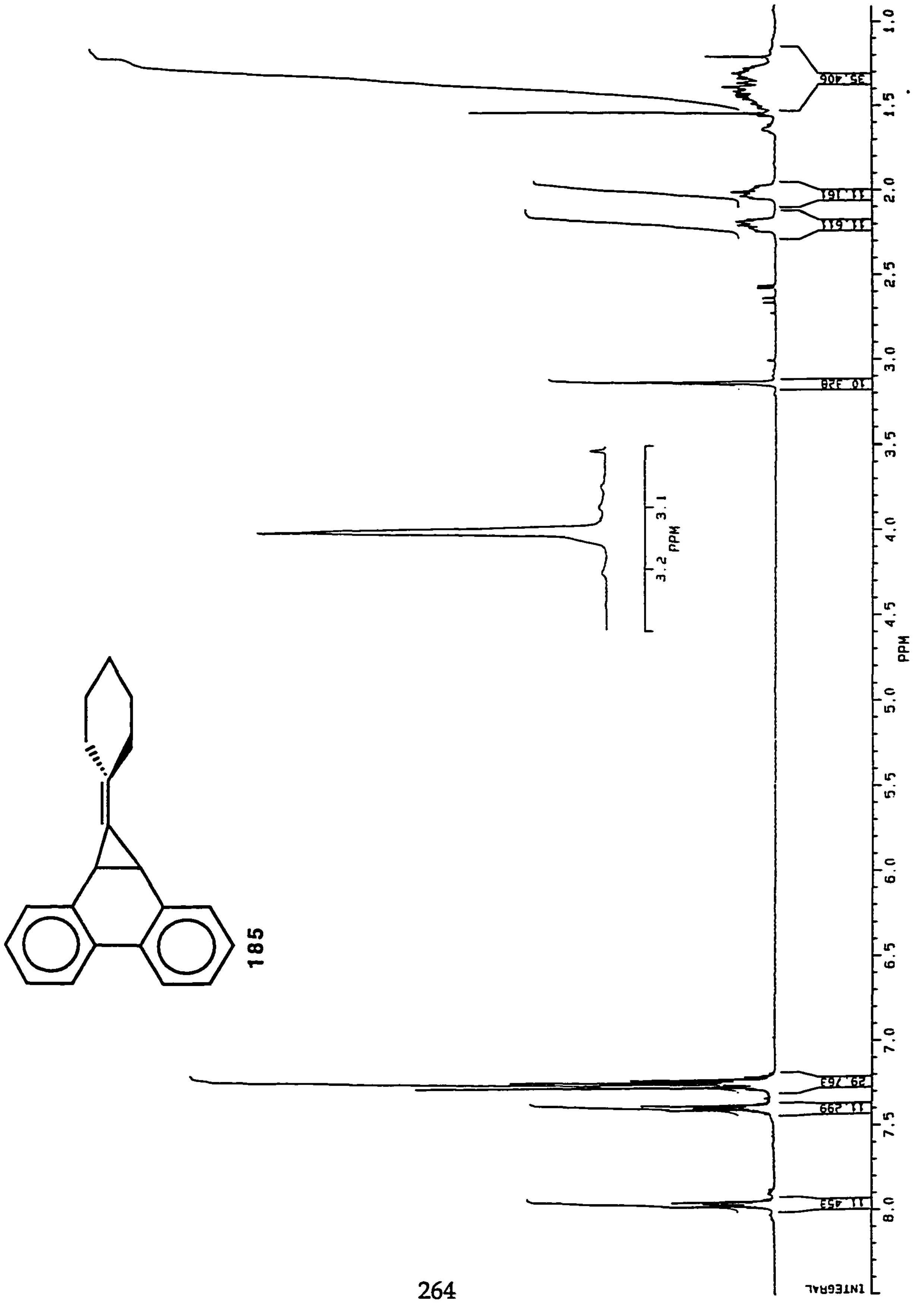
2.3
2.2
2.1
PPM
INTEGRAL
7.665
28.267
36.796
8.650
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
PPM
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1


Cl
OTMS
PPM
.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
INTEGRAL
17.184
3.044
19.126
3.916
11.963
3.695
1.2
1.4
1.6
1.8
PPM
7.5
8.0
PPM

184



184



185

35.406
11.161
11.611
10.328
29.763
11.299
11.453
INTEGRAL
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
PPM
3.2
3.1
PPM

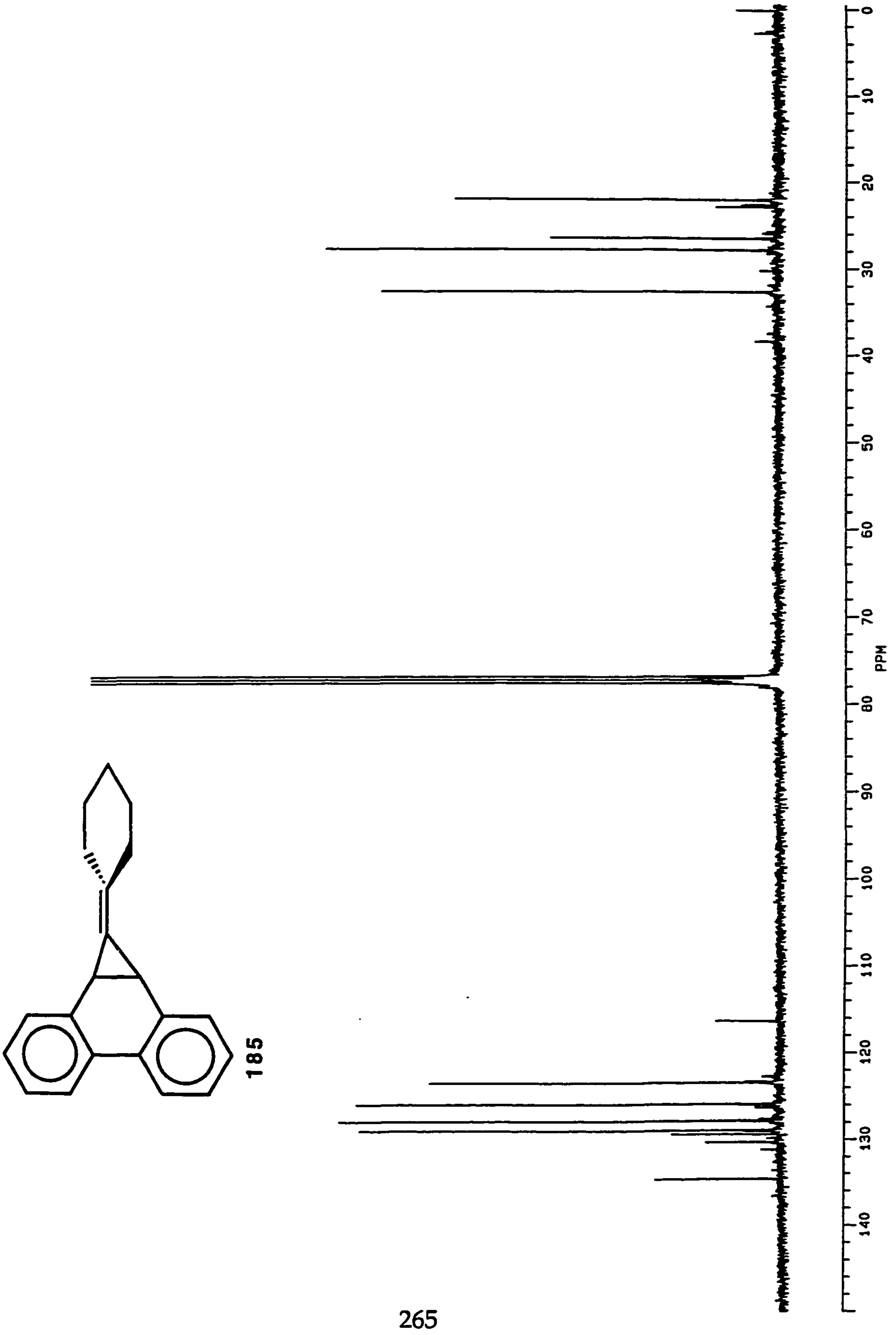


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IMAGE EVALUATION
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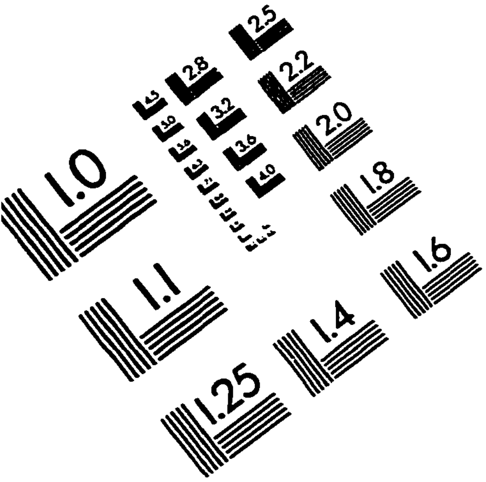

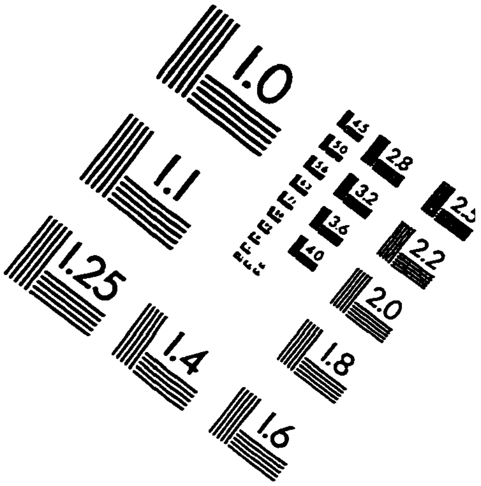

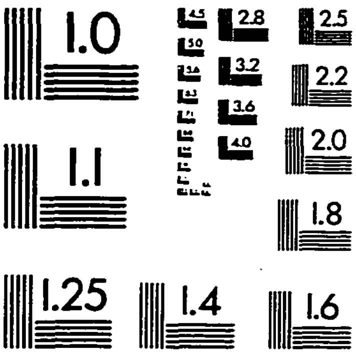

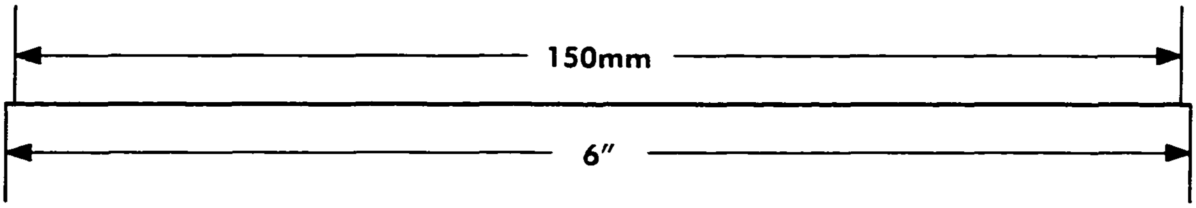

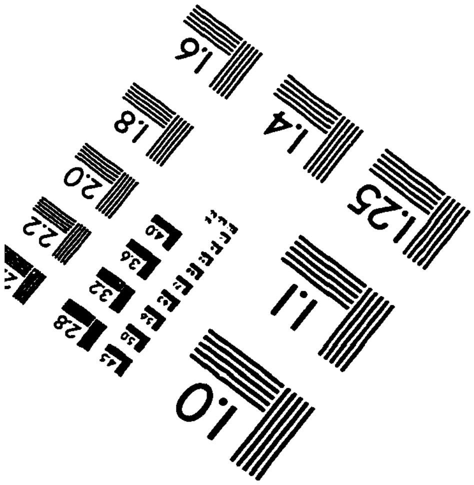

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