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A

THE EFFECTS OF MULTIPLE-BENZANNELATION ON AROMATIC/ANTIAROMATIC METHANO-BRIDGED ANNULENES

by

SHU-YA HSU

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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Abstract

THE EFFECTS OF MULTIPLE-BENZANNELATION ON AROMATIC/ANTIAROMATIC METHANO-BRIDGED ANNULENES

by

Shu-Ya Hsu

Adviser: Professor Klaus G. Grohmann

In order to assess the effect of benzannelation on the aromaticity/antiaromaticity of methano-bridged [10], [12] and [16] annulenes, compounds **I** through **IV** were targeted. Several routes including Diels-Alder cyclization, Wittig olefination, McMurry reaction and Ring Closing Metathesis (RCM) were investigated for the synthesis of compounds **I** to **IV**.

Compound **I**: 3,4-benzo-1,6-methano[10]annulene
Compound **II**: 3,4,8,9-dibenzo-1,6-methano[10]annulene
Compound **III**: 3,4-benzo-1,6-methano[12]annulene
Compound **IV**: 3,4,11,12-dibenzo-1,6:9,14-bismethano[16]annulene

In this dissertation, I will present the synthesis of **III** and **IV** as well as our attempts to obtain **I** and **II**. The generation of 8,10-

dimethylene-bicyclo[5,4,0]undeca-2,4,6,11-tetraene **65** and its Diels-Alder reaction will also be presented.

Ring Closing Metathesis (RCM) of the protected alcohols **100a** and **100b** led to a new approach towards 3,4-benzo-1,6-methano[12]annulene **III**. The scope and limitation of this new general synthesis have been investigated. This new method in essence is also an efficient synthesis of the parent 1,6-methano[12]annulene, previously obtained by Vogel et. al. through an elegant but lengthy synthesis.

The starting material in all cases is 3,4-benzcycloheptatriene-1,6-dialdehyde **63**, prepared via a one step aldol-cyclization from glutaraldehyde and o-phthalaldehyde.

The results of our comparative structural, chemical and spectroscopic investigation of these benzannelated systems with respect to their aromaticity/antiaromaticity will be presented.

Acknowledgments

First, I immensely thank my mentor Prof. Klaus Grohmann for his assistance in my research and fatherly guidance during my years at Hunter. Prof. Grohmann's graciousness and help abound above and beyond his duties as a mentor. I also thank my committee members Prof. Neil McKelvie from City College and Prof. Richard Franck from Hunter College for their valuable suggestions, advice, and guiding light in successfully directing my research. My special thanks also go Dr. Cliff Soll (GC-MS Facility director), Dr. Louis Todaro (X-ray Facility director) and Dr. Michael Blumenstein (NMR Facility director) for their valuable assistance in their respective areas of expertise. Without their help I would not have been able to achieve my graduate goals. Furthermore, I extend my thanks to all my colleagues, especially Dr. Ronnie Benshafrut, graduate students Jelena Zivkovic, Ghislain Mandouma and Kai Fan Cheng, and undergraduate students Tomoko Hagane, Jenia Myagkov, Roger Lefort and John Zambrano for their scientific and personal support. Finally and most importantly, I am indebted to my parents, my sisters, and brother for always standing behind me and encouraging me to overcome the many obstacles and challenges of graduate school.

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Chapter 1 Introduction

1.1 History

The history of aromaticity began with the discovery of benzene by Faraday(1) in 1825 which was isolated from the pyrolysis of whale oil. Millions of aromatic compounds have been discovered and synthesized since then, the notion of aromaticity inspired both synthetic and theoretical chemists for well over a century and a half and probably will continue to do so.

In 1865, Kekulé(2) proposed his formula for benzene. Not only is it famous historically for being the first cyclic formula, but its fame also opened up the vista of deeper understanding of the largest class of chemical compounds. Even though the number of isomers, such as di-substituted isomers, did not agree with a Kekulé formula with localized double bonds, Kekulé therefore introduced the concept of oscillating double bonds thus explaining the existence of only one ortho-disubstituted benzene. Initial attempts after Kekulé's benzene formula to synthesize the lower and higher analogues, cyclobutadiene and cyclooctatetraene respectively, led to Willstätter's synthesis of cyclooctatetraene in 1914. Cyclooctatetraene was found to behave much like a cyclic polyolefin – very unlike benzene. This leading to the conclusion that a cyclic conjugated set of double bonds is not sufficient for aromaticity.

Later in 1931, Hückel(3) proposed his theory of cyclic conjugated π systems. The Hückel Rule predicts that planar, cyclic, conjugated polyenes containing $[4n+2]\pi$ electrons are characterized by a closed shell configuration (aromatic) and those containing $[4n]\pi$ electrons are characterized by an opened shell configuration (antiaromatic). A cyclic compound which is either not planar, or has one or more points of saturation in the ring preventing cyclic conjugation of all π electrons is defined as non-aromatic. In addition, the Hückel rule has been applied not only to planar continuous conjugated systems, but also to homoaromatic systems where one or more out-of-plane methylene groups are intercalated(4).

Pauling(5) developed a semi-classical theory to explain the diamagnetic anisotropy in some aromatic molecules. An external magnetic field causes a flow of the π electrons around the ring.

Using a quantum mechanical treatment and the earlier observations of Hückel and Pauling, in 1937, London(6) developed a theory to explain the high diamagnetism in [4n+2] systems which gave good correlation with experimental observation. In qualitative terms London's theory concluded that for molecules possessing $[4n+2]\pi$ electrons in a planar cyclic conjugated array, a negative contribution to the diamagnetic susceptibility was predicted. Jackman and Elvidge used the term "diamagnetic ring current" to describe this phenomena(7) and explain the observed chemical shifts in [4n+2] system as a result of this diamagnetic ring current.

In 1951, Berthier, Mayot and Pullman(8) showed that application of the London theory to certain hydrocarbons of the [4n] type led to a positive contribution to the diamagnetic susceptibility. As a consequence of this positive contribution to the diamagnetic susceptibility, the [4n] system experiences in an applied magnetic field induction of a paramagnetic ring current.

Later, Pople et al.(9) correlated the ring current effects with NMR chemical shifts which turned out to be a very important discovery for the classification of aromatic and antiaromatic systems. The strong diamagnetism or paramagnetism of annulenes, resulting from the ability of annulenes in an applied magnetic field to sustain a ring current of circulating electrons in their π systems, is easily detected by NMR (Nuclear Magnetic Resonance) spectroscopy. An induced diamagnetic [4n+2] ring current causes deshielding of protons in the molecular plane outside the ring and shielding of protons inside or above the molecular plane. On the other hand, for a paramagnetic [4n] ring current, there is considerable shielding in the outside of molecular plane and deshielding inside or above the molecular the molecular plane. Therefore, NMR has become an important tool for the classification of cyclic conjugated π systems as aromatic (diatropic) or antiaromatic (paratropic).

A brief summary of the history of aromaticity is shown below.

1825	The discovery of benzene, aromaticity based on the distinctive "aromatic" smell of benzene like compounds (Faraday)(1)
1865	Benzene structure (Kekule)(2)
1866	Substitution is more favorable than addition (Erlenmeyer)(10)
1910	Aromatic compounds have exalted diamagnetic susceptibility (Pascal)(11)
1925	Electron sextet and heteroaromaticity (Armit-Robinson)(12)
1931	Theory of cyclic π systems (Huckel)(3)
1936	Ring current theory- free electron circulation around the benzene ring (Pauling)(5)
1937	London diamagnetism- π current contribution to magnetic susceptibility(6)
1956	Ring current effects on NMR chemical shifts (Pople)(9)
1961	Introduction of the term: "diamagnetic ring current" (Jackman)(7)
1969	Modern study of diamagnetic susceptibility exaltation (Dauben)(13)
1970	Magnetic susceptibility anisotropy (Flygare)(14)
1980	IGLO quantum chemical calculation of magnetic properities: chemical shifts, magnetic susceptibilities and magnetic susceptibility anisotropies (Kutzelnigg)(15)
1995	Linear relationships between energy, geometry and magnetism (Schleyer)(16)

1.2 The definition and criteria of aromaticity

The concept of "aromaticity" is very important for both the research and teaching practice of organic chemistry. It is a concept that is still in debate regarding its cause, whether it is driven by the hexagonal geometry of benzene or the delocalization and so on. A wide variety of criteria have been proposed for the assessment of aromaticity ranging from the purely qualitative to the virtually quantitative(17). Therefore, below is a summary of the current ideas of aromaticity according to recent papers(18).

a. Chemical behavior: Electrophilic aromatic substitution

Unlike alkenes, aromatic compounds undergo substitution reactions rather than addition reactions with electrophiles. For example, benzene does not undergo electrophilic addition as shown below.

Table 1 Chemical reactions of benzene

Reagent	Expected reaction in unsaturated compound	Observation
Br_2/ CCl_4	Addition of Br_2	N.R.
$KMnO_4$/ H_2O	Oxidation	N.R.
H_2/ Ni	Hydrogenation	Reacted at high temp. and high pressure
H_2O/ cat.	Addition of H_2O	N.R.

But not all of aromatic systems react like benzene, favor substitution over addition. Therefore; this criteria is not satisfactory for all aromatic systems.

b. Geometry: Bond length equalization due to cyclic delocalization

In 1971, Julg(19) applied the C-C bond length to be a criterion of aromaticity in annulenes. Aromatic system should have equal bond lengths, which should be the average between carbon-carbon single bonds and double bonds (ca. 1.39 Å in benzene) whereas nonaromatic or antiaromatic annulenes should have alternating single and double bond lengths.

However, the geometric criterion is not general applicable. For example, borazine, according to magnetic susceptibility exaltation Λ, is defined to be non-aromatic, but it sustains six electrons and equalized bond length. Therefore, bond length variations in the absence of other considerations can not be used characterize aromaticity uniquely.

c. Energy: Enhanced stability (large resonance energy)

According to the simple Hückel theory, the annulenes, if planar, should have their total π-energy smaller than m times that of the the ethylene molecule. The resulting stability gain, delocalization energy (DE), defined by

$$DE = -(E_{\pi\ \mathrm{total}} - mE_{\pi\ \mathrm{ethylene}})$$

where $E_{\pi\ total}$ is the total π-energy and $E_{\pi\ ethylene}$ is the π-energy in the ethylene. Based on this theory, delocalization energy should increase with increasing size and should be greater for annulenes with [4n+2]π electrons than for annulenes with [4n]π electrons.

In addition, annulenes with [4n+2]π electrons have a non-degenerate electronic ground state in contrast to symmetric annulenes with [4n]π electrons which have a degenerate ground state. This degeneracy is actually removed for several reasons, either the ring is not planar, or if planar, its symmetry is reduced with respect to that of the idealized Hückel perimeter ($D_{2m,h}$ symmetry) because of angle-strain relaxation or simply because of bond alternation (Jahn-Teller effect).

Although the Hückel rule is found to be surprisingly well verified, it must be pointed out that the predicted stabilization energies of the [4n]annulenes (DE>0) are in contradiction to the observed instability of these compounds. More elaborate π-energy calculations have been made by Dewar et al.(20), using a combination of the perturbational molecular orbital theory (PMO) of Longuet-Higgins(21) and the self-Consistent Field Molecular orbital method of Pople(22). These calculations indicate that the resonance energy (RE) is positive for the [4n+2]annulenes and negative for the [4n]annulenes and this qualitative difference between the two classes of annulenes will disappear for large rings.

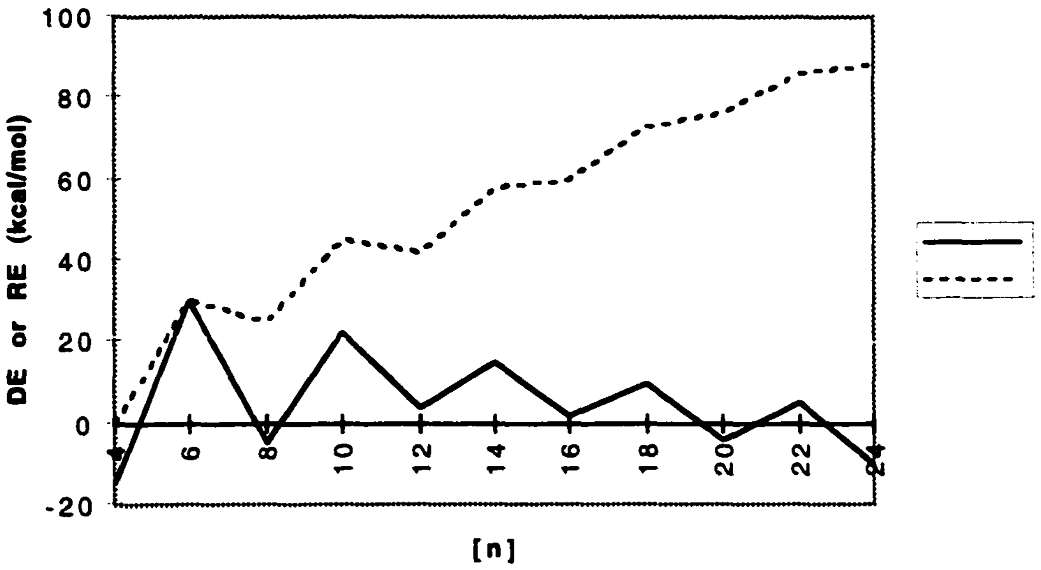


Figure 1 Delocalization (HMO) and resonance (PPP) energy of [n]annulenes

Unfortunately, the determination of aromaticity or antiaromaticity can not be solely based on the number of π electrons and resonance energy. Other factors which are important include the strain energy associated with the molecule, especially when considered in its planar conformation and the degree of bond alternation.

d. Magnetism: "Ring current" effects

The ring current effects is perhaps the most often used criteria for characterizing the given system as aromatic or antiaromatic. Experimentally, when a molecule of the [4n+2] type, like benzene, is placed in a magnetic field, a diamagnetic ring current is induced in the benzene π system to create its own magnetic field. The direction of the induced magnetic field outside the ring is parallel to the applied magnetic field, so the protons are deshielded in this area. In contrast, the direction of the induced magnetic field inside the ring is opposite to the applied magnetic field, so inside of the ring or above the ring, the protons are shielded.

However, in [4n] systems, the opposite shielding/deshielding effects are observed (paramagnetic anisotropy). In other words, outside protons are shielded and inside protons are deshielded in [4n] systems.

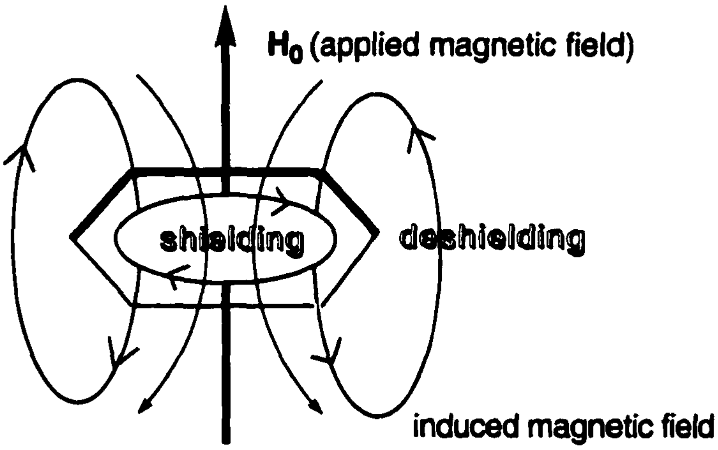
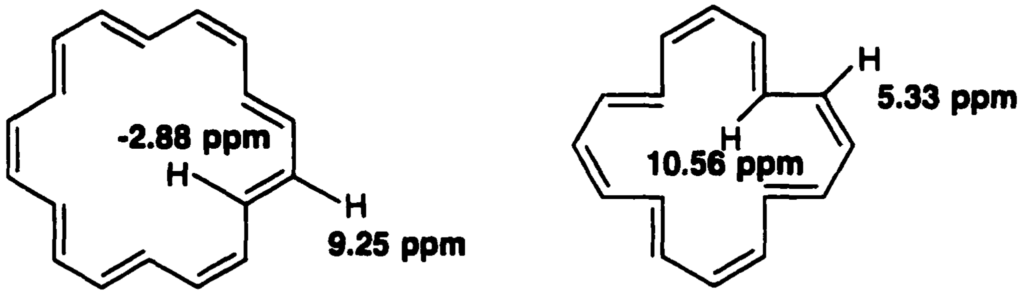


Figure 2 Representation of an induced ring current and induced magnetic field of a benzene by an applied magnetic field

Table 2 The shielding effects for aromatic and antiaromatic systems

	π electron	inner proton	outer proton
Aromatic	[4n+2]	upfield (shielding)	downfield (deshielding)
Antiaromatic	[4n]	downfield (deshielding)	upfield (shielding)

[18] and [16]annulene, which are [4n+2] and [4n] systems respectively, are two examples. The [18]annulene **1** was synthesized by Sondheimer, Wolovsky and Amiel in 1962(23). The proton NMR of [18] annulene is temperature dependent(24). At -60°C, two kinds of peaks were observed, one is the outer protons at 9.25 ppm and another is the inner protons at -2.88 ppm. This clearly reflects the diamagnetic current induced in the ring. Because protons interchange through rotation, upon heating these two signals become broader, then at 41°C coalescence is observed. Finally at 121°C, the spectrum showed a sharp single line at 5.44 ppm. [16]annulene **2** was synthesized for the first time by Sondheimer and Gaoni(25) and later by Schroder et al.(26). Below -90°C, the proton NMR showed a triplet located at a low field of 10.56 ppm, and a multiplet centered at 5.33 ppm. The very low field signal (10.56 ppm) is attributed to protons pointing inside the ring that are experiencing the paramagnetic ring current induced in the 4n π-electron system. The high field signal (5.33 ppm) is attributed to outer protons. At temperature above -50°C, all protons of [16]annulene become equivalent and give one single line located at 6.74 ppm.



1 2

Figure 3 Shielding and deshielding effects of [4n+2] and [4n]annulenes

e. The relationship of classical and magnetic criteria of aromaticity

Aromaticity and antiaromaticity are well characterized by a combination of geometric, energetic and magnetic criteria. An analytic relationship between the ring current (RC) and the resonance energy (RE) was proposed by Haddon(27) in 1978.

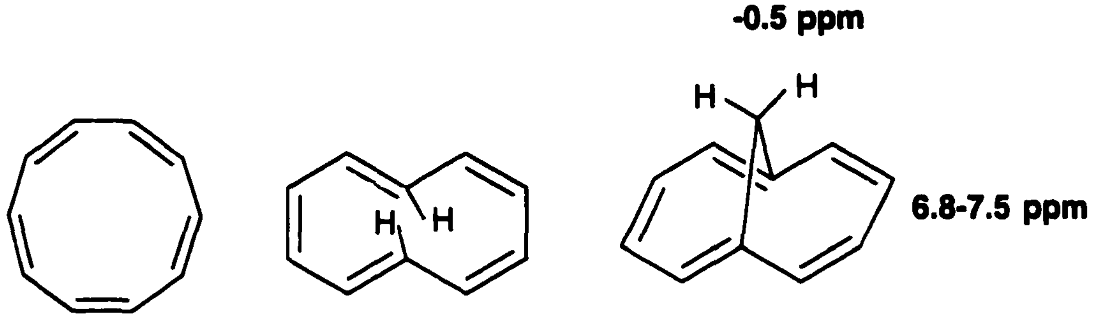
$$RC = 3S\ RE/\pi^2$$

Where S is the area of the ring and RE is the Dewar resonance energy.

In 1995, Schleyer(16) claimed to have demonstrated that linear relationships exist among the energetic, geometric and magnetic critera of aromaticity and these relationships even extend to antiaromatic systems. Later, Birds(28) claimed that good linear relationships exist between experimental diamagnetic susceptibility enhancements and the corresponding resonance energies or aromaticity indices for some 50 aromatic and heteroaromatic ring systems. Both groups concluded that they had demonstrated that there was no justification for separate classical and magnetic concepts of aromaticity(29). Aromatic compounds are stabilized energetically and exhibit diamagnetic susceptibility exaltations and negative anisotropies as well as equalized bond lengths. In contrast, antiaromatic systems are destabilized and exhibit paramagnetic susceptibility exaltations, and the single and double bond lengths are localized.

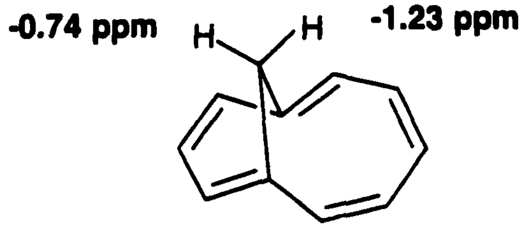
1.3 [10]annulenes

[10]annulene is the next higher homologue of benzene (n=2). Although all [4n+2] annulenes are predicted to be aromatic, the all-cis-[10]annulene **3** suffers from too much angle strain energy (bond angle of 144°) and is found to have properties similar to a polyolefin. The proton NMR showed a temperature independent singlet at 5.67 ppm over a range of -40 to -160°C. Di-trans[10]annulene **4** reduces the angle strain but appears to have severely steric interaction between two internal hydrogen atoms by there forcing the ring out of planarity. For this reason, it has never been observed. In order to reduce conformational mobility and to force π system into planarity, the internal H-H repulsion in the di-trans[10]annulene can be eliminated by placing a methano group above the plane of the ring. 1,6-Methano[10]annulene **5**, discovered by Vogel et. al.(30) is the first stable [10]annulene. The proton NMR showed a A_4B_4 system of external protons in the range of 6.8-7.5 ppm and a sharp singlet of the bridged protons at -0.5 ppm. The upfield shift for the interior protons and downfield shift for the outside protons indicate that this molecule gains aromatic character. Later, the less stable 1,5-methano[10]annulene **6** was prepared by Masamune et al.(31) and Scott et al.(32) which also shows a diamagnetism presence in the ring current.



3 **4** **5**

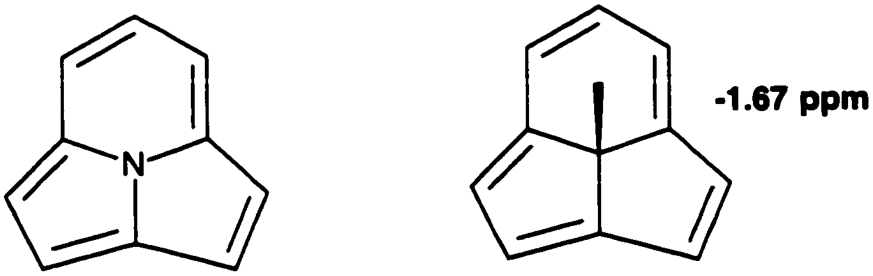
Figure 4 Comparison of isomers of [10]annulene with bridged [10]annulene



6

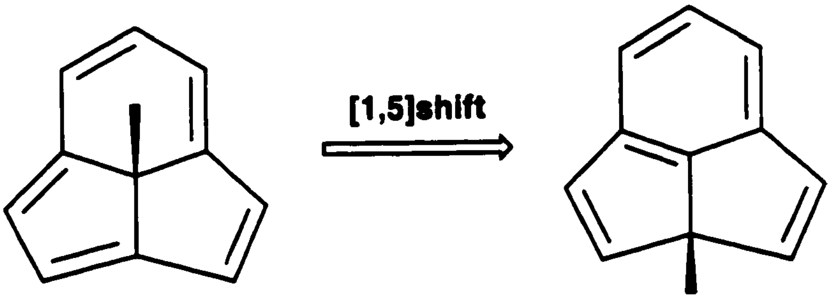
Figure 5 The structure of 1,5-methano[10]annulene

Two other bridged [10]annulenes have been reported. Cyclo[3,2,2]azine **7** (Boekelheide 1959)(33) is diatropic, the protons resonating downfield at 7.9-7.2 ppm in the proton NMR spectrum. 11-Methyl-1,4,7-methano[10]annulene **8** (Rees 1981)(34) exhibits the central methyl group at -1.67 ppm and the external protons at 7.53-7.92 ppm in the proton NMR spectrum which indicates that a diamagnetic ring current is present. The low reactivity with dienophiles also suggests that **8** is aromatic. This annulene thermally rearranges to **9** by a 1,5-methyl sigmatropic shift. The activation energy was found to be 32.7 kcal/mole. This ease of migration is presumably due to the driving force caused by the formation of benzene ring.



7 **8**

Figure 6 Nitrogen and methine bridged [10]annulenes

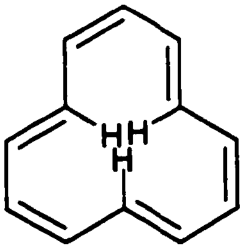


8 **9**

Figure 7 1,5-methyl sigmatropic shift of 8

1.4 [12]annulenes

[12]annulene **10**$^{(35)}$, a [4n]annulene (n=3), suffers from severe deviation from planarity caused by internal H-H repulsion. This annulene has been prepared at -100°C and is stable at low temperature only. The ^{1}H NMR of [12]annulene was found to be temperature dependent between -170 and -80°C. At -170°C, the spectrum exhibited two signals at 7.83 ppm and 5.88 ppm with the intensities in the ratio of 3:9. The low field signal (7.83 ppm) is assigned to the internal protons of a cyclic molecule which sustains a paramagnetic ring current. At higher temperature -80°C, the spectrum showed two peaks of equal intensities at 6.88 ppm (cis protons) and 5.97 ppm (trans protons).



10

Figure 8 The structure of 10

The configuration is also supported by the analysis of the temperature dependent ^{1}H NMR. [12]annulene undergoes an isodynamical conformational motion; this reversible process occurs through simultaneous rotations around all single bonds, and the protons are exchanged between magnetic sites A and B as shown below. This implies that the trans double bonds are not perpendicular to the mean plane of the ring and the whole molecule is contorted from planarity due to a torsional strain angle of 50-60° caused by the three internal protons.

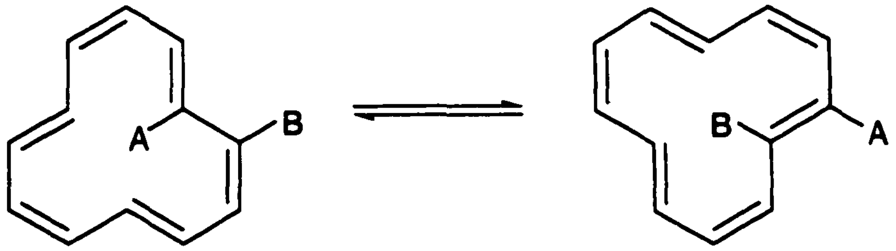
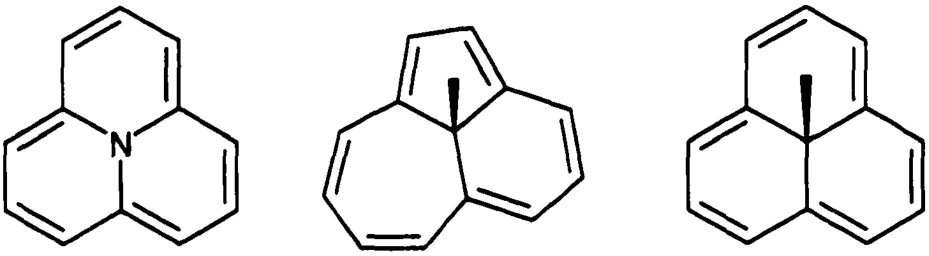


Figure 9 The isomerism of 10

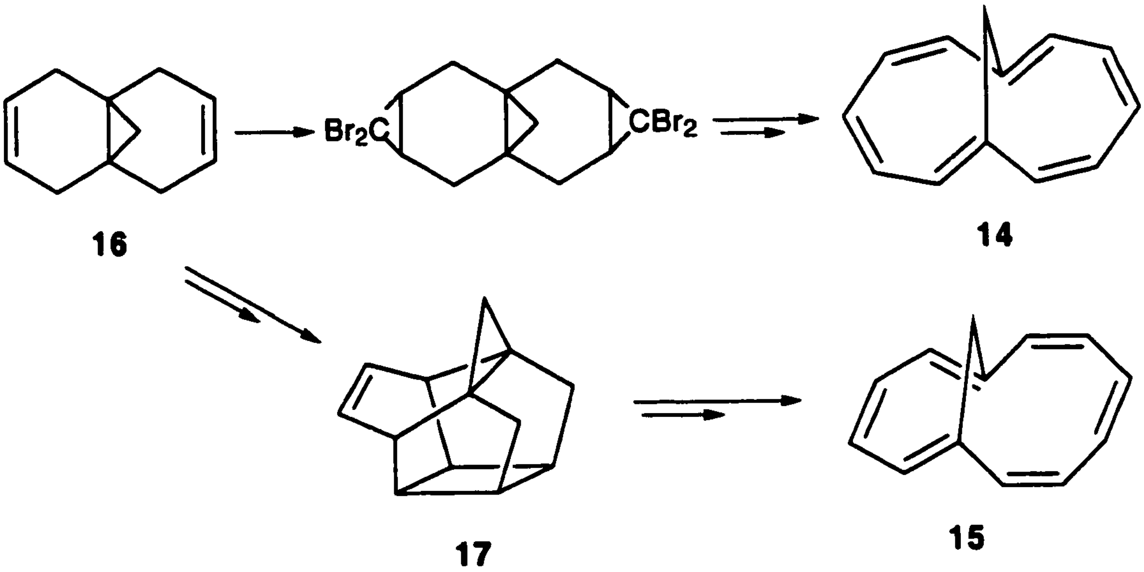
Bridging of an annulene-perimeter with carbon and hetero-atoms to reduce the conformational mobility and to force the π system into planarity has also been very successful with [12]annulene. Cyclo[3,3,3]azine **11** (Leaver 1989)(36), a nitrogen bridged [12]annulene and [4n] homologue of cyclo[3,2,2]azine **7**, exhibit NMR proton resonance at 3.65 ppm (3H) and 2.07 ppm (6H). Even though this compound showed extensive conjugation between the nitrogen lone pair and the π system, the upfield shift of the external protons demonstrated the presence of an induced paramagnetic circuit in the ring. 9b-methyl-9bH-benzo[cd]azulene **12**(37) has been synthesized by Hafner et. al. and has been proven to be paratropic by NMR criteria. The ^{1}H NMR spectrum exhibited a downfield shift at 4.57 ppm for the internal methyl group, and the external perimeter protons are shifted upfield at 3.88-4.69 ppm. This compound undergoes a [1,5] sigmatropic methyl shift while refluxing in xylene. Research in our group is continuing towards the synthesis of 13-methylphenalene **13** and its benz-derivatives. Compound **13** would be highly symmetric, rigid and planar, and would allow degeneracy of the HOMO to prohibit pseudo Jahn-Teller distortion and is therefore expected to exhibit extremely strong paratropicity.



11 **12** **13**

Figure 10 Selected bridged [12]annulenes 11,12,13

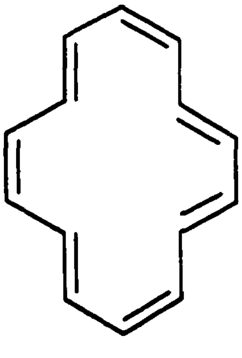
Both 1,7-methano[12]annulene **14**(38) and 1,6-methano-[12]annulene **15**(39) have been synthesized by Vogel et. al. and are found to be paratropic. Both compounds were prepared from **16**, the precursor of 1,6-methano[10]annulene, the former by dibromocarbene addition and ring expansion and the latter by thermolysis of the polycyclic system **17**, itself a product of a putative ring expansion.



Scheme 1 The synthesis of 14 and 15

1.5 [14]annulenes

The [14]annulene **18** was reported in 1960 by Sondheimer et al.(40). and was found to have a temperature-dependent NMR spectrum. The [14]annulene exists as the two conformational isomers **18A** (major) and **18B** (minor). Both isomers possess the hydrogens labeled H_u in one plane while H_d are in another plane. The two signals of the two conformers in equilibrium are clearly separated in the proton NMR spectrum at 25°C, a multiplet at 5.57 ppm of the conformer **A** and a multiplet at 6.09 ppm of conformer **B**. At -126°C, the ^1H NMR of the major conformational isomer **A** showed two signals located at -0.61 ppm (4H) and at 7.88 ppm (10H). The position of these signals clearly reveals the diamagnetic ring current induced in the 14π system.



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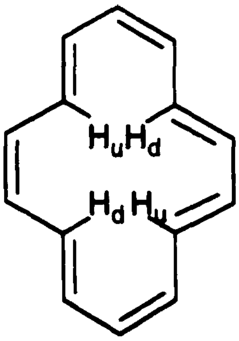
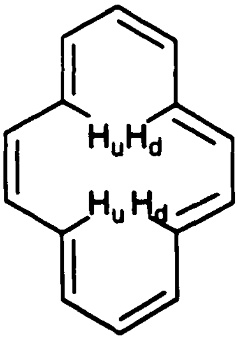


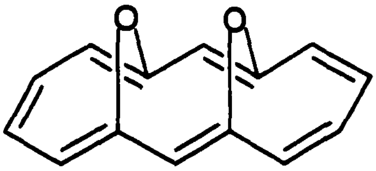
18A



18A

Figure 11 The structure of 18 and its two conformers A and B

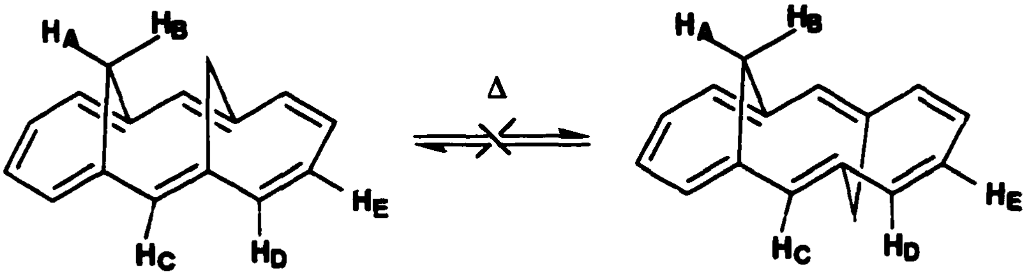
In addition, three types of bridged [14]annulenes have been reported, one based on anthracene, one on pyrene, and the third on the dicyclopentaheptalene structure. Vogel and his co-worker have made a variety of molecules based on the anthracene type. Syn-1,6:8,13-bisoxido[14]annulene **19**(41) was obtained in 1966, prepared by the synthetic sequence based on the devise used for the synthesis of 1,6-methano[10]annulene. It is a thermally stable red solid. The ^1H NMR(42) showed eight outer perimeter protons at 7.67 ppm and two central perimeter protons at 7.94 ppm. An X-ray crystallographic analysis(43) has shown that the molecule has a reasonablely planar perimeter with a nearly equal aromatic C-C distance throughout the perimeter.



19

Figure 12 The structure of syn-1,6:8,13-bisoxido[14]annulene

The synthesis of 1,6-methano[10]annulene and its proven aromatic character raised the question of whether a generalized homologous series of bridged [4n+2] annulenes formally derived from the acene series can be explored. 1,6:8,13-bismethano [14]annulene could exist in two forms, one with the bridges on the same side, syn-1,6:8,13-bismethano[14]annulene **20** and the other with the bridges on opposite sides, anti-1,6:8,13-bismethano [14]annulene **21**. Both isomers were separately synthesized by Vogel, and have strikingly different structures and magnetic properties. The syn isomer was prepared in 1975, following a new synthetic concept(44). The proton NMR spectrum of **20** shows that the signal of methano bridge protons have upfield chemical shifts at -1.20 and 0.90 ppm, while the signals of the perimeter protons are shifted downfield at 7.90 and 7.00 ppm. Furthermore, syn isomer **20** possess a nearly planar carbon perimeter and the C-C bonds are nearly equal in length(45) which is a clear demonstration of its aromatic character. On the contrary, anti isomer **21**(46) is an atropic system and has alternating single and double C-C bonds around the perimeter, presumably because it is prevented from having any orbital overlap in this configuration. No ring current is apparent from the proton NMR shifts of anti isomer **21**, perimeter protons at 6.20-6.33 ppm and methano bridge protons at 2.48 and 1.88 ppm.



20 **21**

Table 3 Chemical shifts (δ values in $CDCl_3$) of the protons of 20,21

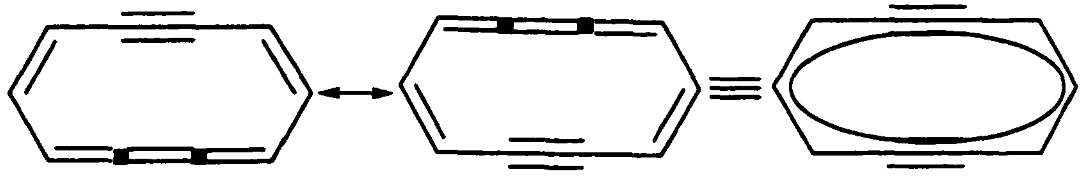
	H_A	H_B	H_C	$H_{D,E}$	
20	-1.20	0.90	7.90	7.00-7.80	diatropic
21	1.88	2.48	6.33	6.20	polyolefin

1.6 Dehydroannulenes

Dehydroannulenes are cyclic systems that are continuously conjugated double and triple bonds, or in some cases, cumulated double bonds. According to the IUPAC nomenclature rule, the number of hydrogen pairs which have to be removed from the annulene to afford the specified dehydroannulene is indicated in the prefix mono, di and tri. The triple bonds contribute two electrons to the out-of-plane π system, the other two electrons being in an orthogonal in-plane orbital. Consequently, even though the σ framework is much more rigid due to triple bonds, the dehydroannulenes exhibit the same type of magnetic behavior as the annulene of the same ring size and are even more strongly diatropic in the [4n+2] systems or paratropic in the [4n] systems.

1.6.1 Dehydro[10]annulene

1,6-didehydro[10]annulene **22** has been recognized as an interesting organic molecule for more than 40 years(47), because it posesses two equivalent Kekule structures. Its synthesis was attempted by Sondheimer et. al.(48) unsuccessfully, then it was first prepared by Myers(49).



22A **22B** **22C**

Figure 13 Representations of 22

The ^1H NMR spectrum of **22** at -75°C exhibited a triplet at 8.45 ppm (2H, J=8.3 Hz) and a doublet at 7.81 ppm (4H, J=8.3Hz) which show clear evidence of a diamagnetic ring current, supporting the notion that **22** is a aromatic compound. The proton-decoupled ^{13}C NMR spectrum at -90°C consists of three singlets at 137.1, 125.1, 107.5 ppm whose chemical shifts are approximated by averaging the anticipated chemical shifts for corresponding carbons in the two canonical resonance structures. Compound **22** is stable for extended periods at -90°C but a higher temperatures cyclized readily to form naphthalene. In deuterated solvents, incorporation of deuterium was evident at the 1 and 5 positions of naphthalene.

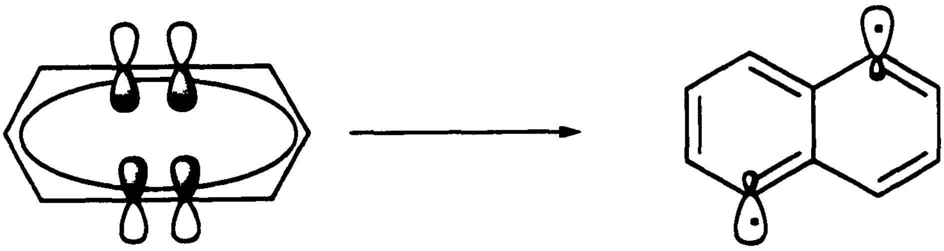
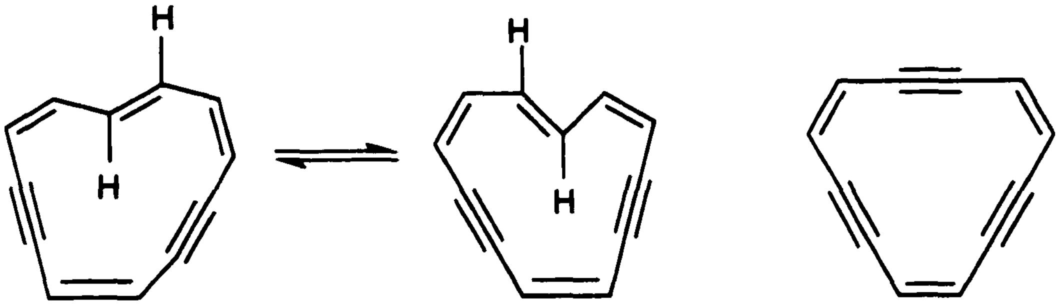


Figure 14 The cyclization of 1,6-didehydro[10]annulene 22

1.6.2 Dehydro[12]annulene

1,5-didehydro[12]annulene **23** and 1,5,9-tridehydro [12]-annulene **24** were first prepared by Sondheimer et al.(50) in low yield. The latter product was obtained in higher yield by Untch et al.(51). Both of the compounds are strongly paratropic, and this is dramatically illustrated by the ^1H NMR spectrum. The inner proton of **23** and its transoid proton appear around 11 ppm as a quartet, while the outer protons appear at 4-5 ppm. The ^1H NMR spectrum of **24** showed a singlet at 4.42 ppm. This structure is interesting with two nonequivalent Kekulé structures, one with three cumulenic systems, the other with three triple and three double bonds.

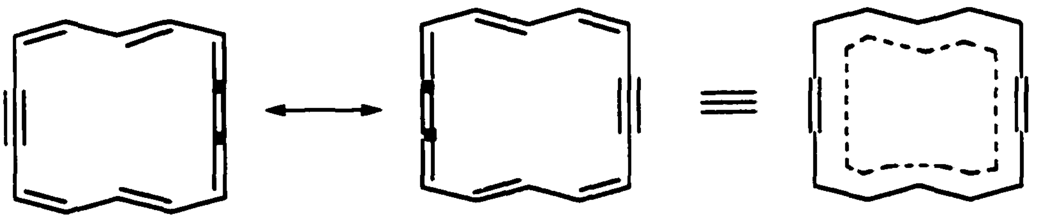


23A **23B** **24**

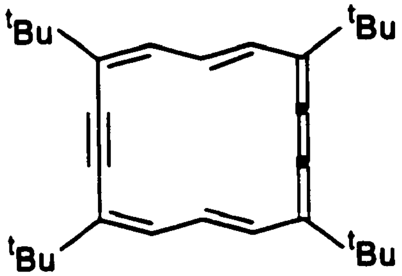
Figure 15 The structure of 23 and 24

1.6.3 Dehydro[14]annulene

According to Huckel's rule,1,8-didehydro[14]annulene **25** is expected to be aromatic. The unsubstituted system was prepared by Sondheimer et al.(52), while tetrasubstituted derivatives were prepared by Nakagawa and co-worker(55). Compound **25** is unusually stable and the ^{1}H NMR spectrum is temperature independent. The inner protons exhibited a triplet at -5.54 ppm (2H, J=13.3 Hz), while the outer protons at 8.43 ppm (d, 4H, J=13.3 Hz) and 9.55 (dd, 4H, J=13.3 Hz, 8.0 Hz). Two equivalent Kekulé structures may be written as **25A** and **25B**, and one expects complete electronic delocalization which may be written as **25C**. Interestingly, the ^{13}C NMR spectrum of tetrasubstituted derivative **25D** presents only one signal for the sp-hybridized carbons at 116.7 ppm, indicating complete electronic delocalization.



25A **25B** **25C**

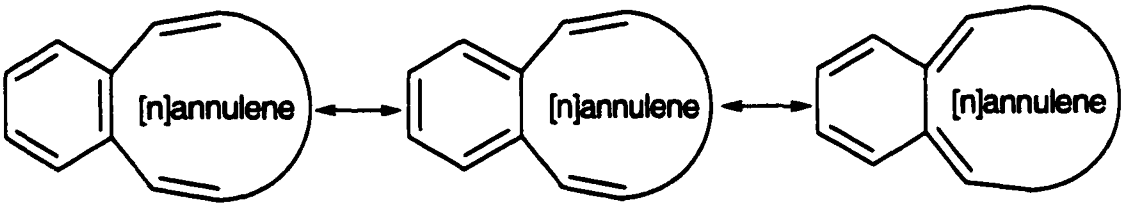


25D

Figure 16 The structure of 25

1.7 Benzannelated Annulenes

The chemistry of annulenes has received considerable attention over the past decade and there is now major interest in the related annulenoannulenes. An annulenoannulene results from the fusion of two annulene rings to form a π system with one or more bonds in common. According to the work of Haddon(27), Aihara(54) and Verbruggen(55), there is no doubt that the ring current in the annulene is related directly to the aromaticity of the annulene. The question then is whether the ring current in one annulene can give information about the aromaticity of another that is fused to the first. In our investigation, we focus on benzannelated methano-bridged annulenes. For any of the benzannelated annulenes, there are three possible resonance Kekulé structures as shown below.

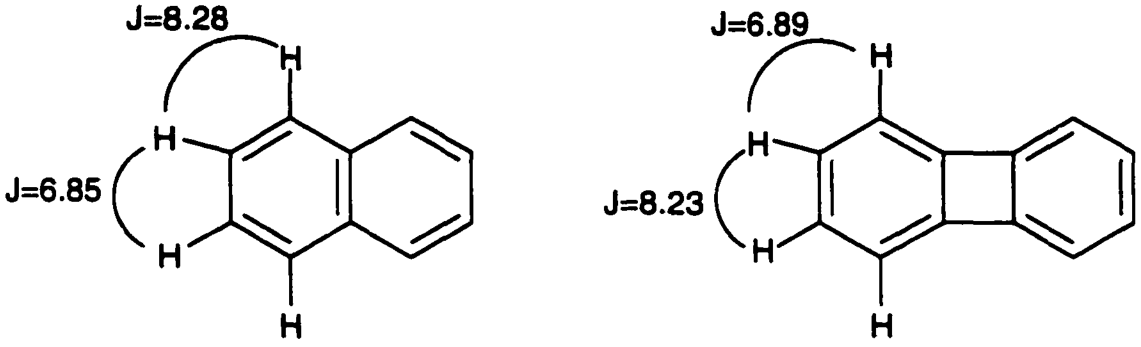


According to PPP-type SCF calculation, the ratio of the π-bond orders in the six membered ring of benzo[n]annulene, the Gunther alternance parameter Q, can be used to determine the electronic ground state properties of [n]annulene. The π-bond orders and the Q-value for a given system are obtained experimentally from the vicinal H,H coupling constants $^3J(H,H)$, measured in the ^1H-NMR spectrum by the equation$^{(56)}$:

$$P_{\mu,\gamma} = 0.104\ {}^3J_{\mu,\gamma} - 0.120$$

where $P_{\mu,\gamma}$ is the bond order between H atoms μ, γ, and $Q = P_{23}/P_{34}$. Delocalized [4n+2] and [4n] systems are characterized by Q-values >1.10 and <1.04, respectively, whereas localized olefinic systems show Q-values of 1.04-1.10.

The investigation of the π-electronic structure of benzo-annulenes from the observation of different vicinal coupling constants of aromatic protons in naphthalene and biphenylene is a typical example. Günther proposed a quantitative index, Q, which allows the differentiation between aromatic [4n+2] systems and [4n] systems. This parameter can be considered as an electronic probe for the π-electron structure of [n]annulenes and can be calculated theoretically using SCF methods.



$$Q_{exp} = \frac{8.28 \cdot 0.104 - 0.12}{6.85 \cdot 0.104 - 0.12} = 1.252 \qquad Q_{exp} = \frac{6.89 \cdot 0.104 - 0.12}{8.23 \cdot 0.104 - 0.12} = 0.811$$

Figure 17 Q-value for benzo[6]annulene and benzo[4]annulene

The prediction made on the basis of Q-values agree with the result of SCF calculation performed by Dewar and Gleicher(20). The superiority of Günther's model over the more popular ring current model is due to a smaller solvent dependence of J values and to the independence from neighboring group effects. The Q value of benzo[4n+2]annulenes decrease, whereas those of benzo[4n]-annulenes increase with increasing n values.

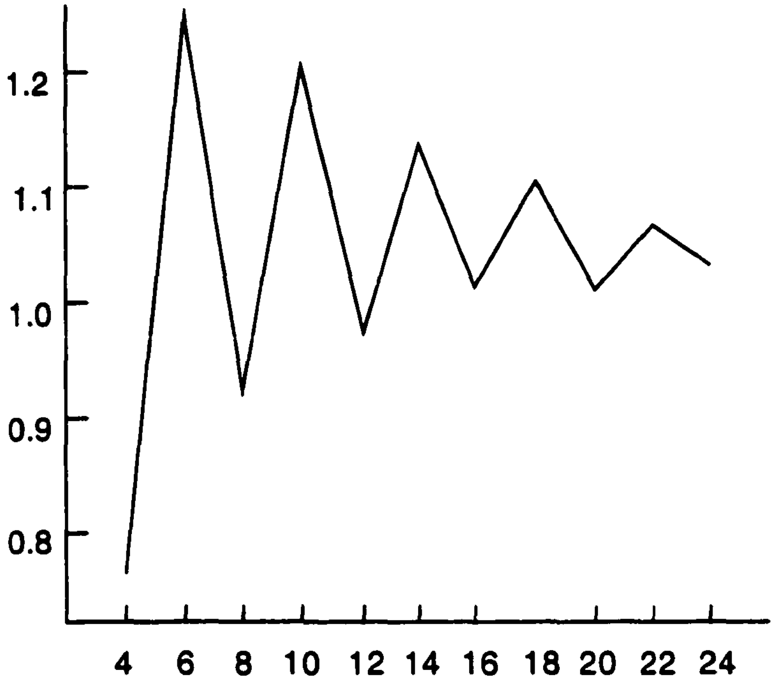


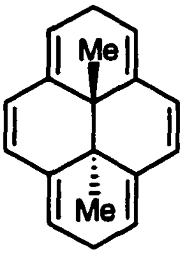
Figure 18 Variation of Q vs the n value for benzo[n]annulenes

1.7.1 Benzannelated 15,16-dimethyldihydropyrenes

The most detailed studied example of benzannelated annulenes is the series of reports by Mitchell and his coworkers(57) investigating the effect of benzannelation at different positions of the [14]annulene. Trans-15, 16-dimethyldihydropyrenes is planar and the internal methyl groups are rigidly close to the center of the strongly shielding zone of the ring current, which make them extremely sensitive probes for changes in ring current and aromaticity. Therefore, the chemical shift of the methyl protons mainly depends on the ring current around the macrocyclic ring. The chemical shifts of the internal methyl groups in **27** is -4.25 ppm, while for the mono- benzene fused annulene **28** is -1.85 ppm, and **29** at -1.60 ppm, a shift of 2.40 and 2.65 ppm respectively. This indicates that the fusion of a benzene ring could dramatically change the delocalization in the macrocyclic ring and the ring current. The chemical shift of methyl groups in dibenzene fused annulene **28** exibited even stronger change in its diamagnetic ring current, a large downfield shift at 0.02 ppm. In the following table, the residual ring current in percentage of mono and dibenzo derivatives to their parent ring have been estimated, based on the comparison of the difference of the upfield shifts of the central methyl groups relative to that of a model compound model **26**, $\delta=0.97$ ppm, summarized by the following equation:

$$\text{Residual ring current} = \frac{\delta_{\text{model}} - \delta}{\delta_{\text{model}} - \delta_{\text{parent}}} \times 100\%$$

The studies showed a steady reduction of diamagnetic ring current due to the bond localization effect of the fused benzene ring.



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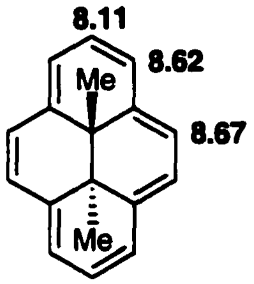

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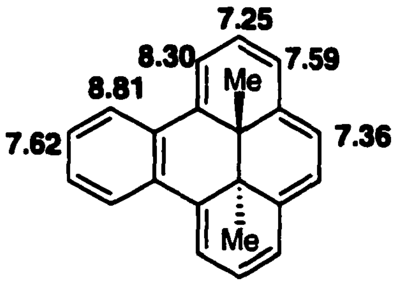

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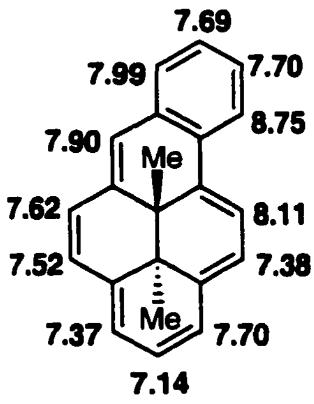

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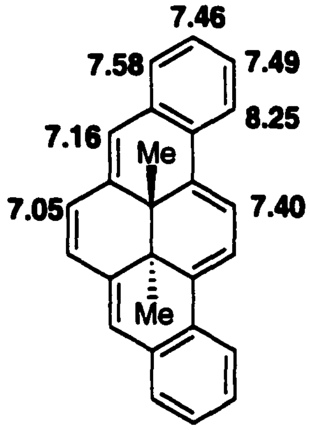

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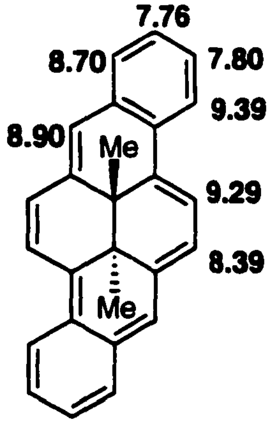
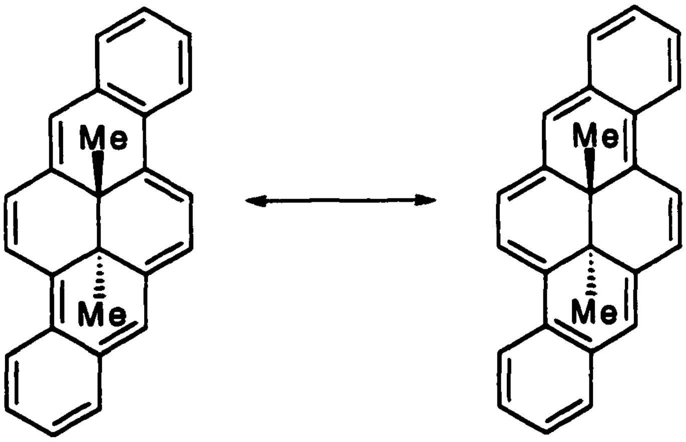


31

Table 4 Chemical shift data (δ ppm in $CDCl_3$) of ^1H NMR of 26-31

	Me (ppm)	$\Delta\delta = \delta_{model} - \delta$	%Δδ* of parent
26 (model)	*0.97*		
***27* (parent)**	*- 4.25*	5.22	100%
28	*- 1.85*	2.82	54%
29	*- 1.60*	2.57	49%
30	*0.02*	0.95	18%
31	*- 3.58*	4.55	87%

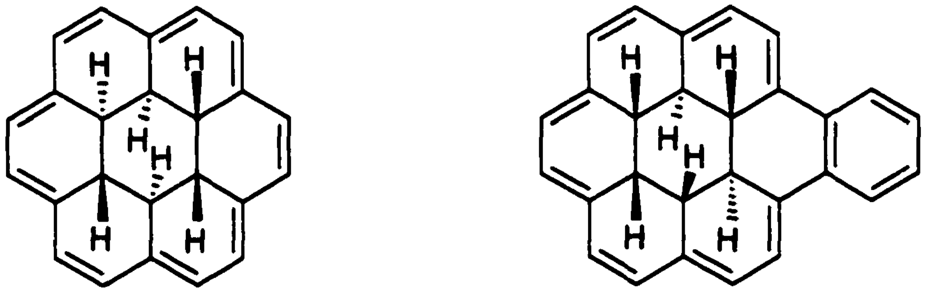
Unlike cisoid-dibenzo derivative **30**, the transoid-dibenzo derivative **31** does not show a significant change in its parent ring current with the chemical shift of methyl groups at -3.58 ppm. The difference can be explained in terms of bond localization as predicted by consideration of the Kekulé structures. In cisoid- **30**, two benzene delocalizations are always present and regardless of the benzene ring, the macroring is always localized which results in only a small ring current in the macroring. Otherwise, in case of transoid- **31**, the Kekulé structures of **31A** and **31B** are equivalent and always contain one delocalization benzene ring and one ortho-quinoid, indicating the macroring ring in **31** is more delocalized than in **30**.



31A **31B**

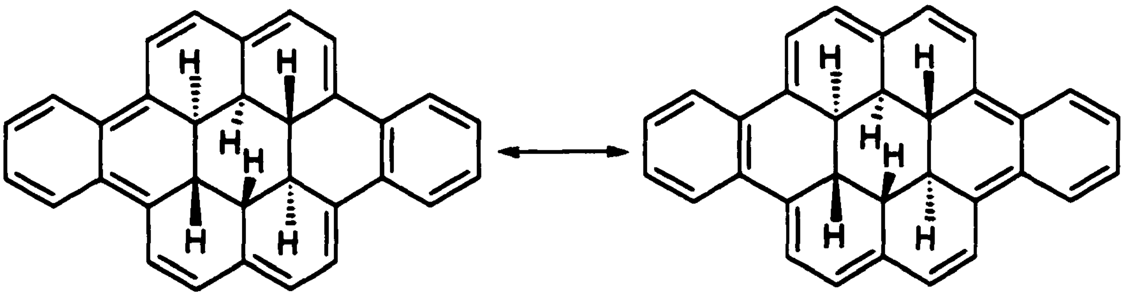
Figure 19 The resonance structures of 31

Similar dependence is clear with hexahydrocoronene **32** and its mono and dibenzo derivatives, **33** and **34**, investigated by Boekelheide(58). The chemical shift of the internal protons in monobenzo **33** appear at -1.0 to -2.6 relative to its parent **32** at -6.5 to -8.0, indicating the reduction of diatropicity in the parent ring. On the other hand, the chemical shift of the internal protons in dibenzo **34** appear at -3.5 to -5.3 ppm, indicating the ring current in the macroring to be less affected by the fused benzenes and more diatropic.



32 **33**

Figure 20 The structures of 32, 33

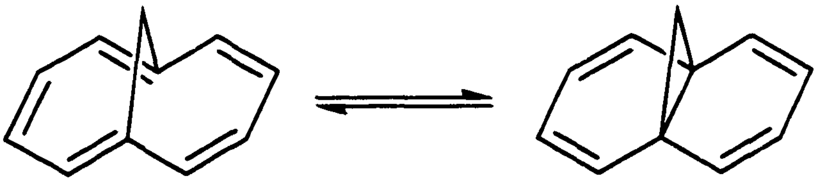


34A **34B**

Figure 21 The resonance structures of 34

1.7.2 Bridged benzo[10]annulenes

1,6-methano[10]annulene **5** was the first stable aromatic cyclodecapentaene to satisfy the Hückel [4n+2] requirement. Although the bridge slightly distorts the skeleton from planarity, sufficient π overlap remains to provide an aromatic 10-membered ring that shows clear evidence of delocalization in the ^{1}H NMR (59) (AA'BB' system at 7.0 ppm with shielded bridge protons at -0.5 ppm). The equilibrium between 1,6-methano[10]annulene **5** and its valence tautomer bisnorcaradiene **5a** lies on the side of **5**. Compound **5a** has never been detected in the equilibrium as a separable species. Tautomer **5** is only slightly more stable than **5a**. From ab initio calculations(60), the enthalpy difference was determined to be 4.5-6.3 Kcal/mol , with the barrier for conversion of **5a** to **5** at only 1.2-2.3 Kcal/mol .



5 **5a**

Figure 22 The equilibrium between 5 and 5a

With [10]annulene **5** being delocalized, both bridge protons are shielded. Compound **35**(61), however, exhibits shielding of only one of its bridge proton due to the presence of localized π conjugation in one side of the ten carbon skeleton. This level of shielding is smaller than that observed in **5** due to lack of a diamagnetic ring current. The equilibrium between structure **36** and its valence tautomer **36a** lies toward norcaradiene **36a**$^{(62)}$. Structure **36** is of higer energy than its corresponding tautomer **36a** due to the higher strain involved in the bicyclo[4,3,1]deca-1,3,5-triene system. With the six membered ring, strain is reduced and thus the equilibrium is shifted back toward cycloheptatriene type isomer **35**.

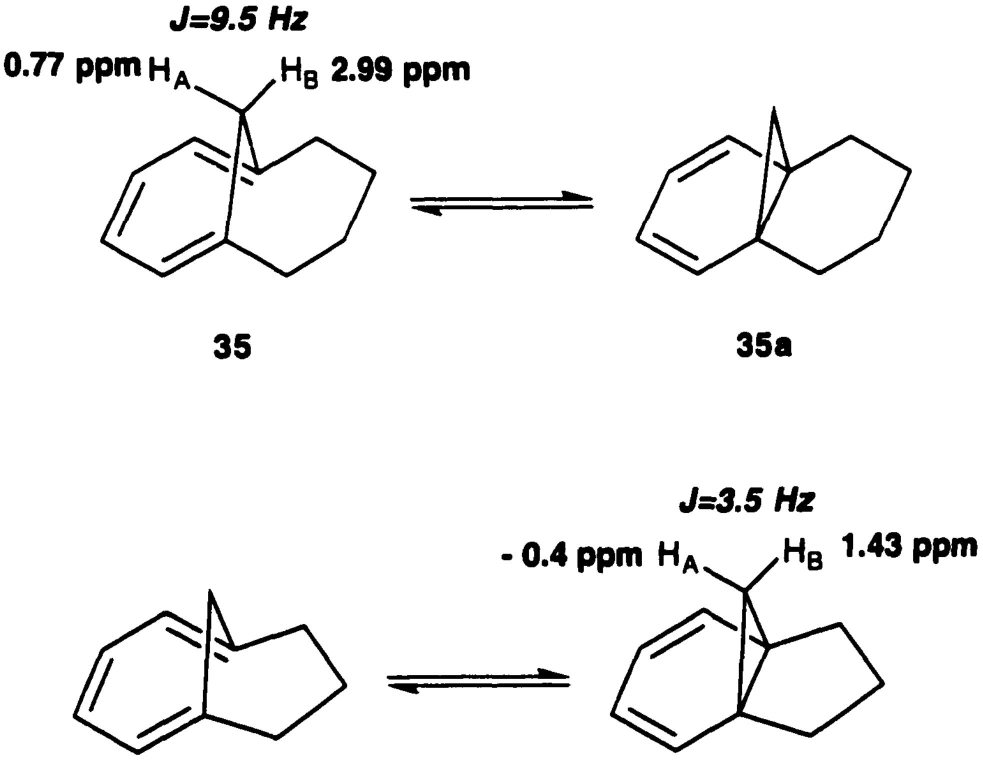
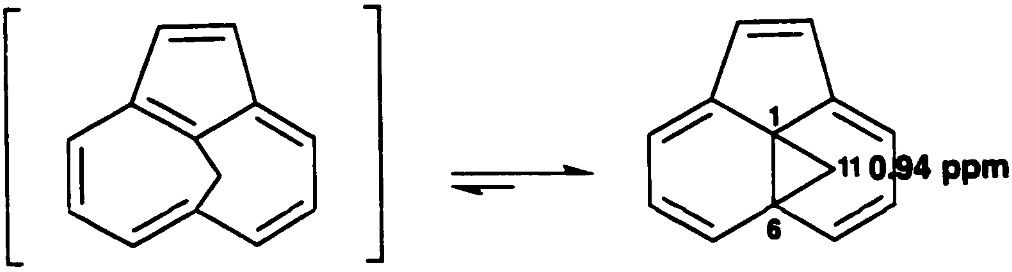
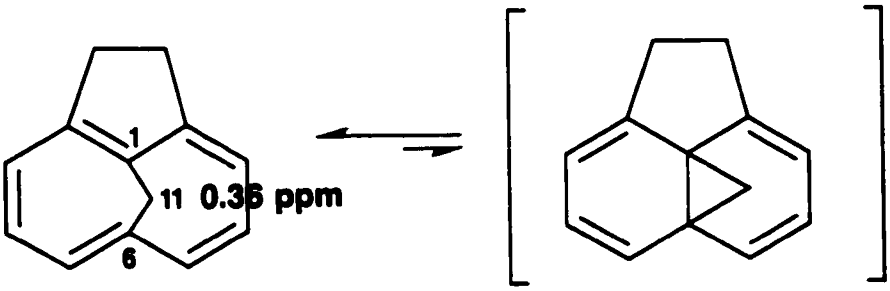


Figure 23 The equilibriums of compound 35 and 36

In order to explore the limits of existence of 1,6-methano [10]annulene, Vogel et al.(63) had examined what influence a peri-CH_2-CH_2 or peri-CH=CH bridge has on equilibrium between annulene and bisnorcaradiene. The position of the equilibrium between **37** and **37a** as well as between **38** and **38a** follows from their ^{13}C NMR spectra, 2,10-etheno-1,6-methano[10]annulene **37** exists as the norcaradiene valence tautomer **37a**; while 2,10-ethano-1,6-methano [10]annulene **38**, exists as its tautomer **38**, with total exclusion of **38a**. ^{13}C NMR proved to be decisive and highly sensitive in establishing the position in the valence tautomer equilibrium. ^1H NMR data for the bridge protons are not conclusive. The ^{13}C NMR data are listed in **Table 5**. For comparison, tricyclo[4,3,1]deca-2,4-diene **36a** and 1,6-methano[10]annulene **5** serve as reference compounds for the norcaradiene valence tautomers and [10]annulene. It is found that **37a** compares very well with **36a** regarding to the C_1 and C_6 signals and shows a ^{13}C-^1H coupling constant for C_{11} which is typical for cyclopropane C-atoms (160-170 Hz). On the other hand, comparing **38** to **5**, the position of C_1 and C_6 signals are more than 100 ppm which indicates C_1 and C_6 are vinylic carbons.

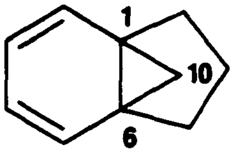


37 37a

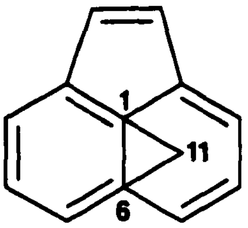


38 38a

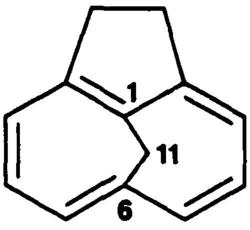
Figure 24 The equilibra of 37 and 38



36a



37a



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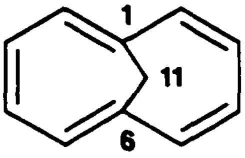


5

Table 5 ^{13}C NMR data (ppm) of 36a, 37a, 38 and 5

	C-1	C-6	C-11	$^{1}J_{C\text{-}11,H}$ (Hz)
36a	37.7	37.7	15.4*	*161**
37a	51.1	39.6	16.7	*167*
38	115.4	109.5	31.9	*146*
5	114.6	114.6	38.4	*142*

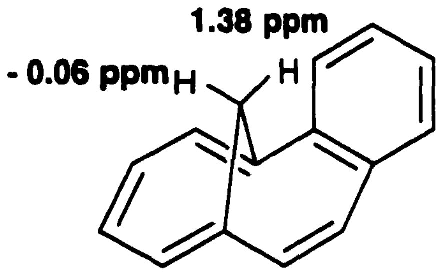
* For C_{10} in compound 36a

(A) Statement of project

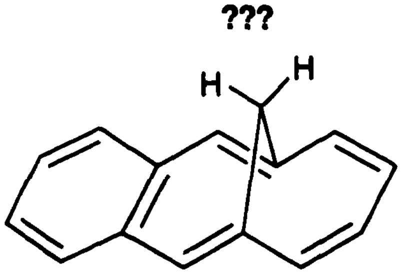
Part one of this investigation concentrated on the effects of benzannelation on the aromaticity of 1,6-methano[10]annulene. For that reason, the molecules subject to this study we first examined are compounds **40** and **44**, and the comparison of known compounds **39** and **41**. Our interest is to study the effect of benzannelation at different positions of 1,6-methano[10]annulene in order to examine the aromaticity changes in a bridged [10]annulene upon benzannelation. Fusion of a benzene ring onto one bond of a [4n+2] annulene causes bond length alternation, weakens the ring current and reduces the resonance energy in the annulene ring. Especially relevant are a series of reports by Mitchell et. al. which we described earlier, investigating the effect of benzannelation at different position of 15,16-dimethyl-dihydropyrene. The studies showed a reduction in the diamagnetic ring current due to the bond localization effect of the fused benzene ring. Similar dependence is clearly possible with 1,6-methano[10]annulene. Valence tautomerization of 1,6-methano[10] annulene **5** results in the formation of the nonaromatic bisnorcaradiene **5a**, and this equilibrium will be effected by benzannelation.

2,3-Benz-1,6-methano-[10]annulene **39** has been reported by Vogel ed. al.(64). On the basis of similar reasoning described earlier, this benzannelation reduces the aromaticity of the parent ring, as measured by the reduction of diatropicity in the NMR spectrum. The ^{1}H NMR and ^{13}C NMR spectra provide no indication of an equilibrium between **39** and its norcaradiene valence tautomer. The weakening of the diamagnetic ring current in the 1,6-methano[10]annulene of **39** expected as a result of benzannelation is most clearly manifested in the resonance signals of the bridge protons for they are shifted 1.88 and 0.44 ppm respectively, downfield relative to those in 1,6-methano[10]annulene. The isomeric 3,4-benz-1,6-methano-[10]-

annulene **40** appears to be unknown and is one of our targets in this investigation. When compared with 1,6-methano[10]annulene **5**, compound **40** is predicted to have a reduced diamagnetic ring current and thus exhibit its bridge protons at lower field.



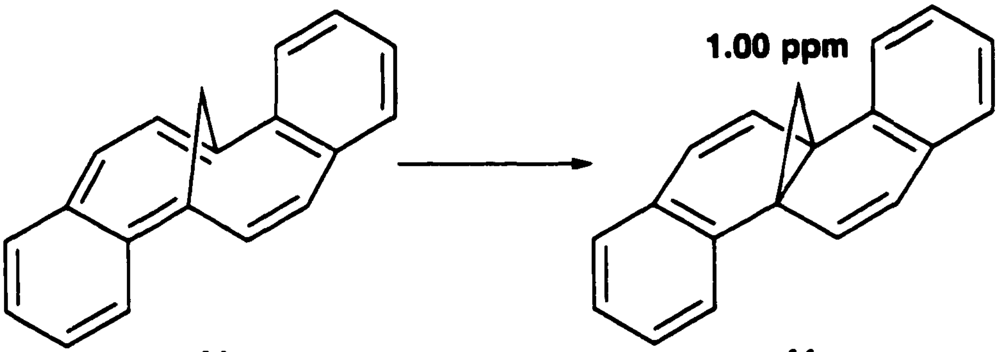
39



40

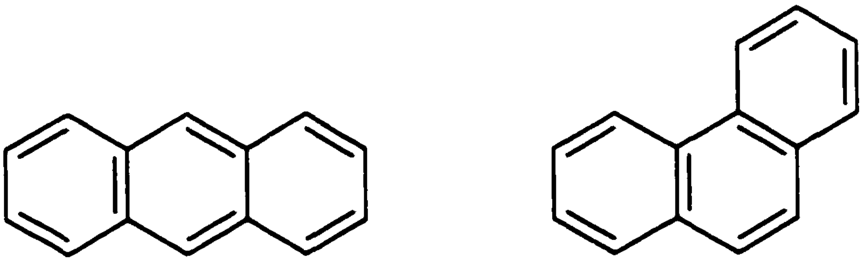
Figure 25 Monobenzo-1,6-methano[10]annulene, 39 and 40

2,3,7,8-dibenz-1,6-methano-[10] annulene **41** has been synthesized by Hill et al.(65).This molecule was found to give up its aromaticity and apparently exists exclusively as the non-aromatic norcaradiene **41a**. The energy of the system will be lowest if maximun delocalization of the benzene rings are maintained as in **41a**. Norcaradiene **41a** is known to be more stable, because the delocalization energy of 1,6-methano[10]annulene **5** is less than that of benzene. For example, it is known that anthracene **42** is higher in energy than phenanthrene **40** because phenanthrene **43** at any point maintains up to two fully aromatic benzene rings among three rings, while in anthracene there is a maximum of only one fully aromatic benzene ring. This was first described in quantitative quantum-mechanical terms by Polansky and Derflinger(66) and later by several other authors(67). It has also been demonstrated through calculations that the aromaticity of benzoannulenes is characterized more by the separate contributions of each ring rather than that of the entire π system periphery(68).



41 **41a**

Figure 26 2,3,7,8-dibenzo-1,6-methano[10]annulene 41



42 **43**

Figure 27 Anthracene 42 and phenanthrene 43

We are interested in the synthesis and investigation of the "anthra" fused 3,4,8,9-dibenz-1,6-methano[10]annulene **44**, to compare and measure the reduction in diatropicity of the [10] annulene skeleton. The reduction in diatropicity in **44** is expected relative to 1,6-methano[10]annulene **5** just on the basis of bond fixation. However, since at anytime a full benzene ring and an ortho-quinoid form are present in conjugation, the system may be described as **44b** where aromaticity is maintained. According to the reason we described earlier in Mitchell's case, compound **44** is expected to be more diatropic than 2,3,7,8-dibenzo-1,6-methano[10]-annulene **41**. In contrast to the valence tautomerizing structures **41**, **41a**, compound **44** should not be in equilibrium with its norcaradiene **44a**.

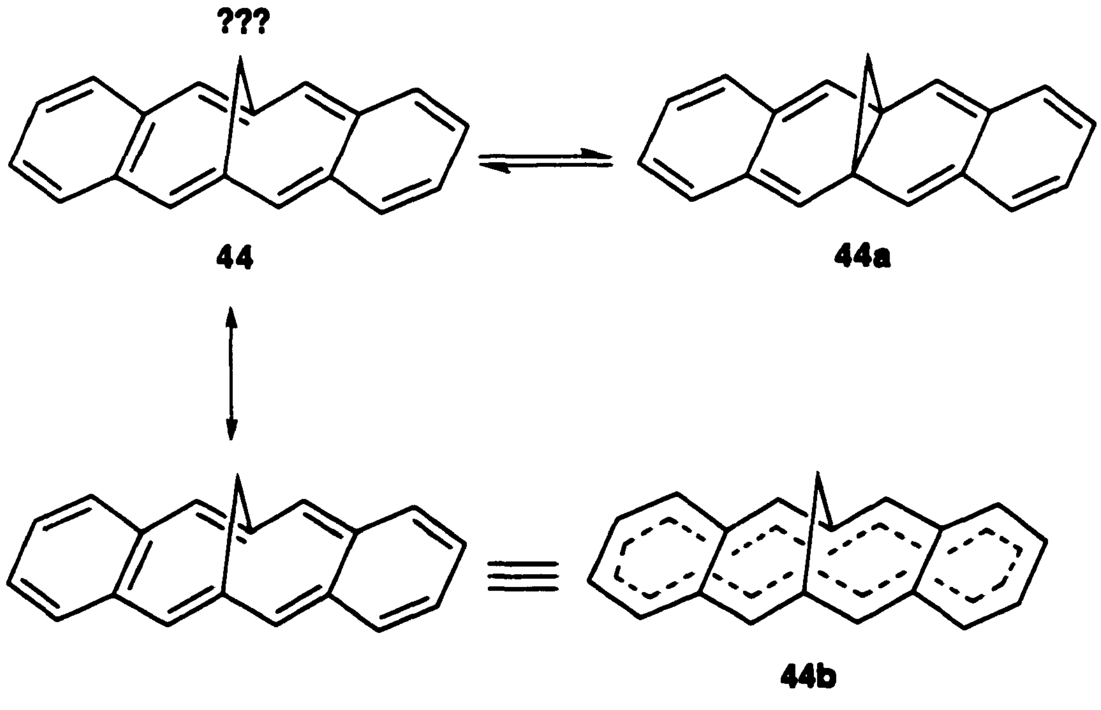
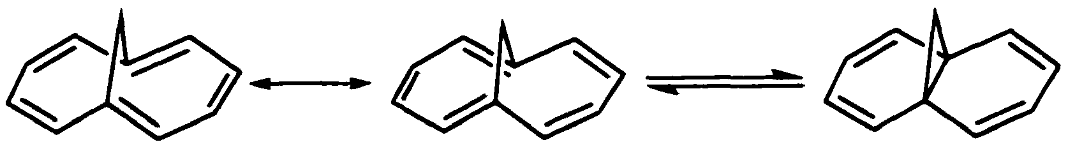


Figure 28 anthra-dibenzo-1,6-methano[10]annulene 44

(B) Semiempirical calculation- AM1

The theoretical studies of the 1,6-methano[10]annulene system are interesting in that it can, in principle, exist in either one of two valence isomers which we will refer to as "annulenic" or "norcaradienic". Using AM1 we calculated the heat of formation and optimized geometry for 1,6-methano[10]annulene and its mono- and di-benz derivatives. The 10π structures **5/5'** were compared with the respective bisnorcaradiene **5a**. The results of 1,6-methano[10]-annulene showed that the heat of formation is 80.79 kcal/mole which is 7.05 kcal/mole less than its valence tautomer norcaradiene **5a**, indicating the annulenic structure **5/5'** is more stable than its norcaradienic structure **5a**. According to ^{13}C NMR data, $C_{1,6}$ and C_{11} resonate at 114.6 ppm and 38.4 ppm respectively, and thereby clearly verify the structure of **5**. Morover, the X-ray crystal structure determination revealed that the bridgehead C_1-C_6 distance is 2.235 Å which is close to our calculation (2.30 Å) and it was found that the predicted form of lower energy agree in the study with the observed crystal structure. Therefore, there is again satisfactory agreement between theoretical and experimental structures.



5' **5** **5a**

ΔHf= 80.79 kcal/mol ΔHf= 87.84 kcal/mol

Figure 29 AM1 calculation for 1,6-methano[10]annulene

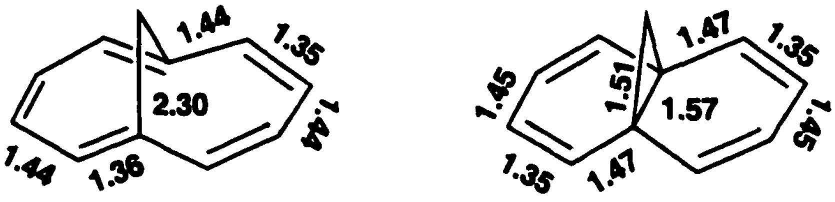


Figure 30 The geometrical parameters for 5 and 5a from AM1 calculation

In order to support our assumption for mono- and di-benzannelated 1,6-methano[10]annulenes, the heat of formation for a series of benzannelated 1,6-methano[10]annulene have been calculated using AM1 method in semiempirical techniques. The theoretical results for the known compound **39**, **41** are in good agreement with reported experimental data. Therefore, we believe these calculations support our predictions for the unknown compounds **40**, **44**, **45**.

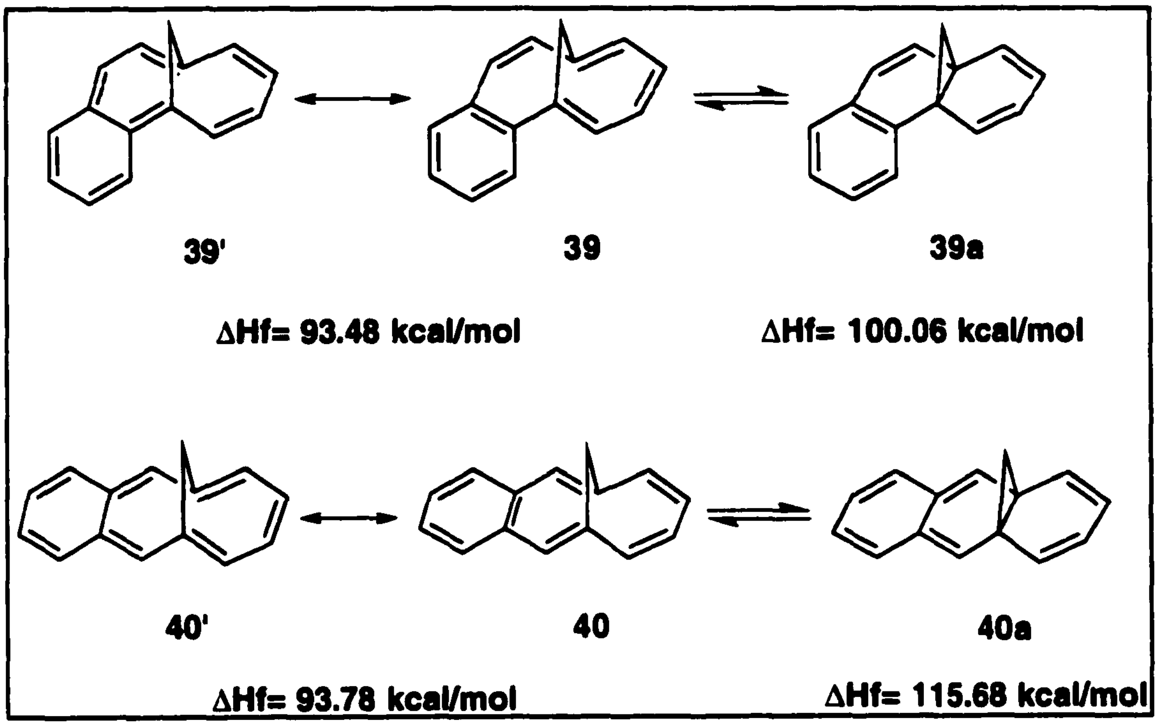
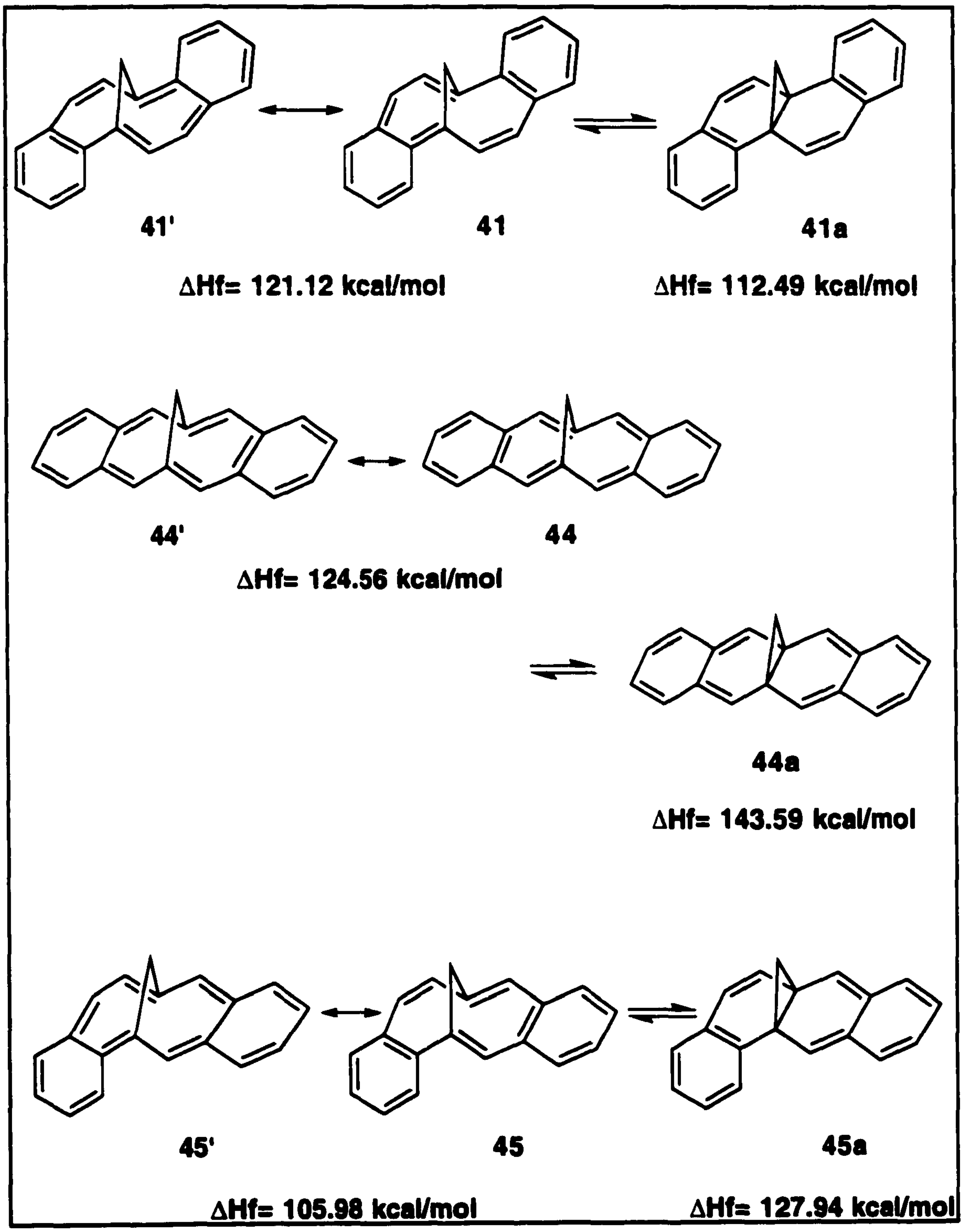


Figure 31 AM1 calculation for monobenzannelated 39 and 40



41'

41

41a

ΔHf= 121.12 kcal/mol

ΔHf= 112.49 kcal/mol

44'

44

ΔHf= 124.56 kcal/mol

44a

ΔHf= 143.59 kcal/mol

45'

45

45a

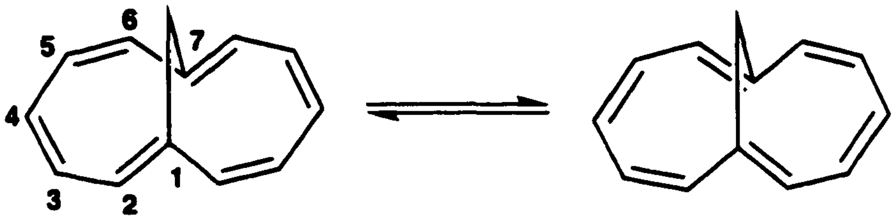
ΔHf= 105.98 kcal/mol

ΔHf= 127.94 kcal/mol

Figure 32 AM1 calculation for dibenzannelated 41, 44 and 45

1.7.3 Bridged benzo[12]annulenes

1,7-methano[12]annulene **14**(38) can be considered the 12π analog of 1,6-methano[12]annulene and is found to be paratropic. The room temperature ^1H NMR spectrum of **14** revealed that a singlet for the methylene bridge protons resonate at abnormally low field (6.16 ppm), whereas two multiplets for the ring protons resonate at relatively high field (5.5 and 5.2 ppm). Ring puckering and bond alternation undoubtedly reduce the ring current to a level below that in a pure [12]annulene, as predicted by theory(69). Analysis of spectrum, a temperature dependent ^1H NMR indicates a rapid dynamic process is occuring. This process is the isodynamic valence bond isomerization(70) as shown below. On lowering the temperature the multiplets of the annulene protons broaden below -60 °C and ceases at -135 °C, while the singlet of the bridge protons remains unchanged. On the other hand, the ^{13}C NMR spectrum shows only four signals for the annulene C atoms, indicating a rapid π-bond shift around the ring. Freezing of the π-bond shift leads to loss of magnetic equivalence of C-2 and C-6 and of C-3 and C-5. Therefore, at -40 to -120 °C, the C-2/C-6 and C-3/C-5 signals broaden and split into a six-line spectrum. Homoheptalene is undergoing rapid bond alternating between the equivalent structures **14a** and **14b**, and this process is slow on the NMR time scale at low temperature.



14a **14b**

Figure 33 The equilibrium between 14a and 14b

The synthesis of 3,4-benzo-1,7-methano[12]annulene **46**(71) provided an opportunity for a NMR comparison between a paratropic 1,7-methano[12]annulene and its monobenzo derivative **46**. One important aspect of this comparison concerns the effect of benzannelation on the dynamic π-bond shift observed previously in the parent compound. Of the two valence isomers **14a** and **14b**, the first is now highly favored, as can be seen by examining the vicinal H, H coupling constant.

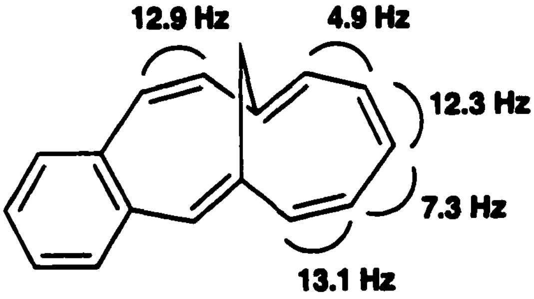
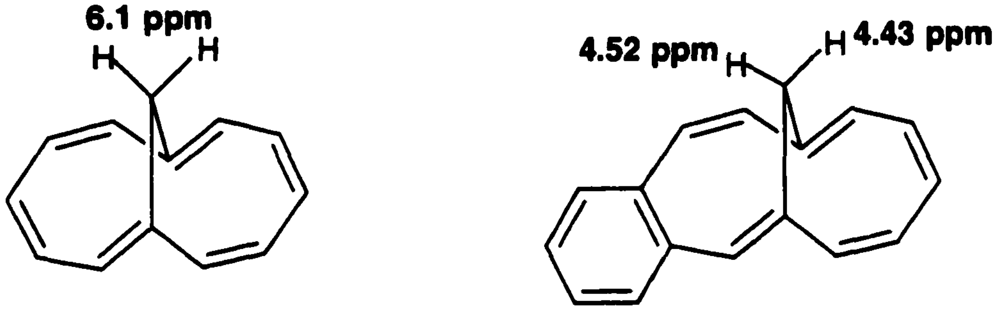


Figure 34 The vicinal H,H coupling constant of 46

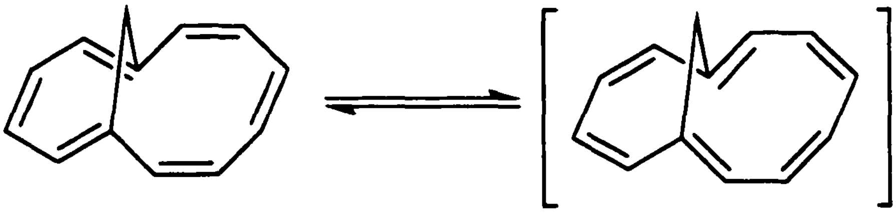
According to the NMR spectrum, the benzene ring in **46** has caused a marked reduction of the paramagnetic ring current in the 12π system relative to that in the parent ring **14**. The bridge protons in **46** resonate at 4.52 and 4.43 ppm which shift upfield from those in **14** by ca. 1.6 ppm. And the olefinic protons in **46** resonate at lower field than those in **14** by ca. 0.4 ppm.



14 **46**

Figure 35 The chemical shifts of ^{1}H NMR for 14 and 46

1,6-methano[12]annulene **15**(39) may exist as one of the valence tautomers **15** and **15a**, or there could be an equilibrium between **15** and **15a**. It can easily be seen that the case of equilibrium corresponds to a π-bond shift, which as distinguished from that observed in 1,7-methano[12]annulene, is a non-isodynamic process(70). According to the molecular models, **15** is more energetically favored than **15a**. Therefore, it should exist exclusively as **15** and does not show bond alternation to the tautomer **15a**.



15 **15a**

Figure 36 The equilibrium between 15 and 15a

The geometry of compound **15** possesses the relatively rigid preferred conformations **A** and **B**. Despite the lack of planarity, this compound is still quite strongly paratropic which can be clearly verified by proton NMR. The ^1H NMR spectrum of 1,6-methano[12]-annulene **15** is temperature independent with an AA'BB' system at 6.17, 5.63 and a multiplet at 5.73 for annulene protons, and with an AB system at 2.29 and 7.00 with J=11.5 Hz for the two bridge protons.

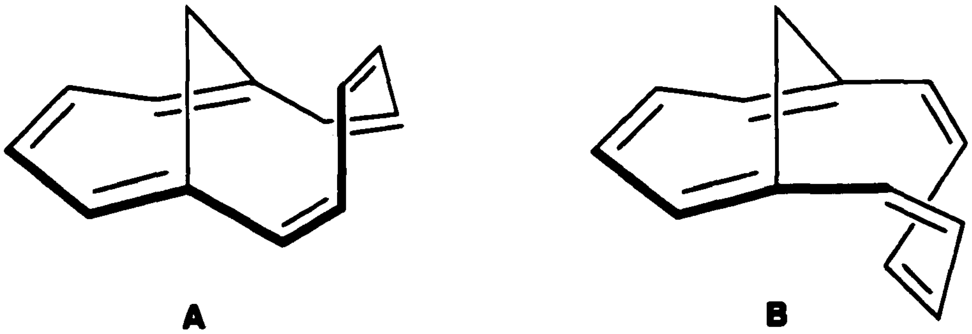
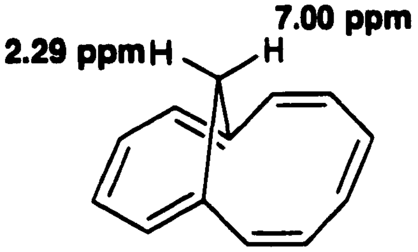
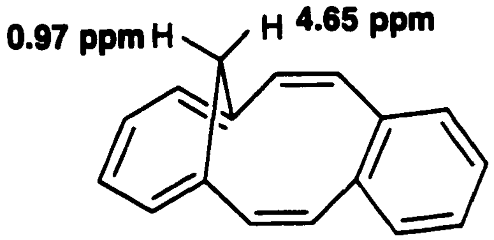


Figure 37 The conformation of 15

In the case of the [4n] annulenes, Vogel et. al. have shown that benzannelation reduces the paramagnetic ring current of the [4n] annulenes the same as the [4n+2] annulenes. The NMR comparison between a paratropic [4n] annulene **15**(39) and its benzo-derivative **47**(72), are presented as follows.



15



47

Figure 38 The chemical shift of 15 and 47

1.8 Bridged annulene ions

The area of bridged annulenes was developed in connection with that of related ionic species. The discovery and prediction of ionic aromatic species are the most significant achievements of the Hückel theory. The reduction and oxidation of annulenes have proven model experiments for bond theory and spectroscopy since they allow the ready interconversion of [4n] and [4n+2] π-systems.

1.8.1. Bicyclo[5,4,1]dodecapentaenylium ions

The bicyclo[5,4,1]dodecapentaenylium cation **50** was prepared by Vogel et al. in 1965(73), starting with olefin **48** or **49** and triphenylmethyl fluoroborate which abstracts a hydride ion and forms triphenylmethane. The starting material **48** was synthesized directly from 1,6-methano[10]annulene via the reaction of diazomethane(74), whereas **49** was obtained via a bis-Wittig reaction of cycloheptatriene-1,6-dialdehyde with trimethylene-1,3-bis(triphenyl phosphonium) bromide. The ^{1}H NMR spectra of **50** (CD_2HCN, δ ppm) showed two bridge protons at -0.25 (H-12a), -1.74 (H-12b), and nine periphery protons at 8.9 (H-9), 8.96 (H-8,10), 9.41(H-7,11), 8.73 (H-2,5), 8.47 (H-3,4), and the coupling constant (Hz) $J_{10,11}$=9.0, $J_{3,4}$=$J_{2,3}$=9.46, $J_{12a,12b}$=10, indicating a diamagnetic ring current; thus identifying it as a perturbed [11]annulenium cation.

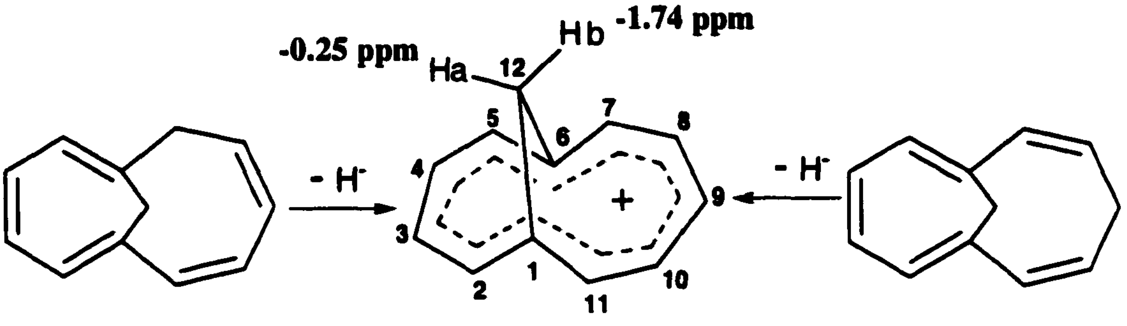
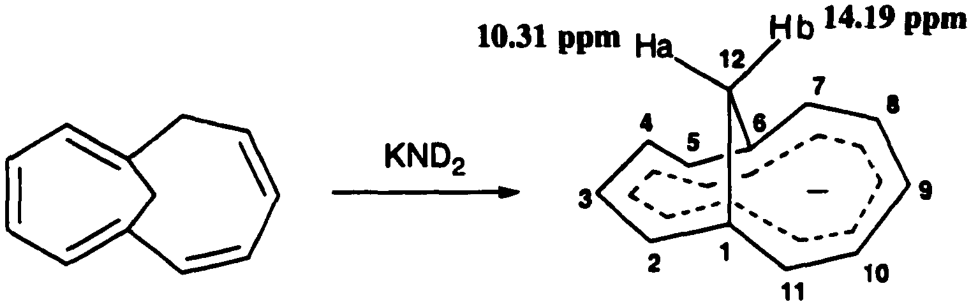


Figure 39 The formation of cation 50

The bicyclo[5,4,1]dodecapentaenyl anion **51** was obtained in 1973 by treatment of the above mentioned olefin **48**$^{(75)}$ with potassium amide in liquid ammonia. Quenching of **51** with water affords a mixture of **48** and **49**. The ^{1}H NMR (ND_3, δ ppm) of **51** exhibited the downfield shift of bridgehead protons at 10.31(H-12a), 14.19(H-12b), and the upfield shift of perimeter protons at 1.21(H-9), 2.31(H-7,11), 2.99(H-8,10), 3.16(H-2,5), 3.92(H-3,4), and the coupling constant (Hz) $J_{10,11}$=10.4, $J_{9,10}$=10.2, $J_{3,4}$=9.0, $J_{2,3}$=4.7, $J_{2,12b}$=1.3, $J_{12a,12b}$=9.6. The small value of $J_{2,3}$= $J_{4,5}$= 4.7 Hz revealed that the anion **51** is twisted about the C-2 to C-3 and C-4 to C-5 bonds, whereas in the more planar diatropic 10 π-electron analogous cation **50**, the $J_{2,3}$= $J_{4,5}$= 9.5 Hz and ^{1}H NMR signal of H-12a is about 16 ppm upfield relative to **51**.

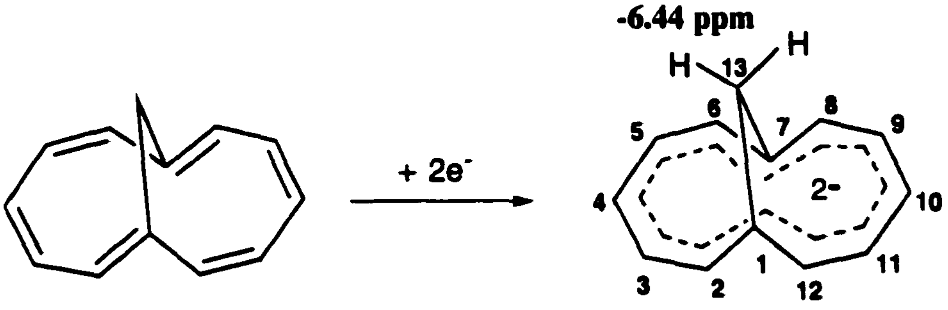


48 **51**

Figure 40 The formation of anion 51

1.8.2 Bridged 14π-annulene ions

The dianions **52** and **53** of 1,7-methano[12]annulene and 1,6-methano[12]annulene were obtained by treating the corresponding hydrocarbons with lithium or potassium in 0.02 M tetrahydrofuran-d_8 solution at -80 °C[76]. Both the lithium salts and the potassium salts of **52** and **53** are completely stable at room temperature in THF. The aromatic character of the dianions **52** and **53** supported by the comparison of their ^{1}H NMR spectra with those of neutral **14** and **15**. The transition from **14** and **15** to **52** and **53** exhibited a downfield shift of about 1-2 ppm of the annulene proton resonances, while the bridge protons are shifted upfield about 10-12 ppm. These shifts can be regarded as proof of the existence of a diamagnetic ring current. The conversion of **14** and **15** into the dianions results not only in changes of chemical shifts, but also in extensive equalization of the originally strongly alternating vicinal coupling constants. The temperature independent ^{1}H NMR shows that ther is no rapid π-bond shift in the dianions.

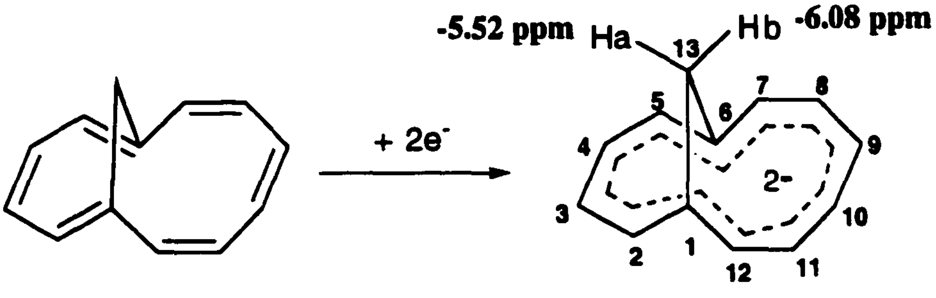


14 **52**

Figure 41 The formation of dianion 52

Table 6 ^{1}H chemical shifts and H,H coupling constants of 14 and 52

	6-H	2-H	5-H	3-H	4-H	13-H	$J_{5,6}$	$J_{2,3}$	$J_{4,5}$	$J_{3,4}$
14 -135 °C	5.47	5.61	5.20	5.18	5.12	5.98	*5.3*	*12.5*	*12.2*	*6.0*
14 25 °C	5.54		5.19		5.12	6.04	*9.0*		*9.2*	
52 -80 °C	7.16		6.28		6.41	-6.44	*8.4*		*10.7*	



15 **53**

Figure 42 The formation of dianion 53

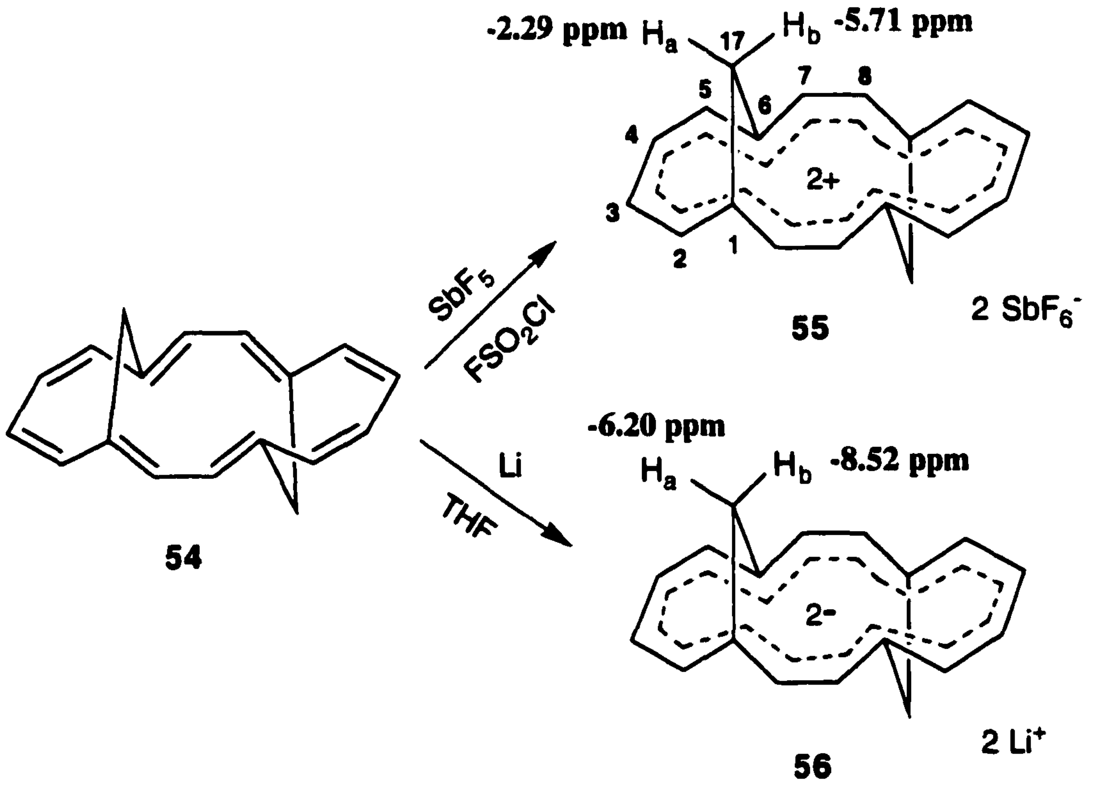
Table 7 ^{1}H chemical shifts and H,H coupling constants of 15 and 53

	2-H	3-H	7-H	13-Ha	13-Hb	$J_{2,3} = J_{4,5}$	$J_{3,4}$
15 25 °C	5.73	6.17	5.5	2.29	7.00	*5.5*	*10.8*
53 -80 °C	7.56	6.51		-5.52	-6.08	*8.3*	*8.5*

1.8.3 1,6:9,14-bismethano[16]annulenium ions

The doubly charged ion of bridged 1,6:9,14-bismethano[16]-annulene has been generated by Vogel(77) in 1985. The dication **55** was obtained by oxidation of 1,6:9,14-bismethano[16]annulene **54** with antimony pentafluoride (SbF_5) in fluorosulfurylchloride at -80°C. The dianion **56** was prepared by reacting solutions of **54** in

THF with highly active lithium in vacuo. The violet needle crystals were crystallized from solvent and are stable at room temperature in THF solution under exclusion of air.



Scheme 2 The generation of dication 55 and dianion 56

The most remarkable spectroscopic result is the large upfield shift observed for the resonances of the bridge protons upon going from the neutral compound **54** to the dication **55** or the dianion **56**. The signals of the ring protons in **55** are markedly downfield from those in **54** and are at much lower field than predicted from the charge effect alone. Similarly, the analogous signals of **56** showed expected charge-induced deshielding. The ^{1}H NMR revealed that both the dication and dianion are strongly diatropic [4n+2]π systems.

Table 8 Chemical shifts of protons of 54-56

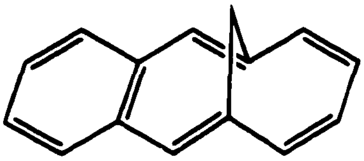
	2-H	3-H	7-H	17-H_a	17-H_b	$J_{2,3}$	$J_{3,4}$
54	5.09	5.03	4.77	5.68	8.30	*10.73*	*8.74*
55	11.02	10.56	11.81	-2.29	-5.71	*9.45*	*9.99*
56	8.24	6.93	7.92	-6.20	-8.52	*8.94*	*8.71*

Table 9 Chemical shifts of carbons of 54-56

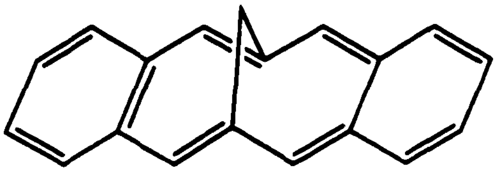
	1-H	2-H	3-H	7-H	17-H_a	17-H_b
54	140.3	135.8	126.6	131.4	39.0	
55	154.3	154.3	148.8	164.2	24.8	
56	114.1	115.7	103.5	107.7	21.3	

Chapter 2 Synthetic and Investigated Approaches

In order to investigate the effect of benzannelation on [4n+2] and [4n] methano-bridged annulenes, we were interested in studying the yet unknown 3,4-benzo-1,6-methano[10]annulene **I**, 3,4,8,9-dibenzo-1,6-methano[10]annulene **II**, 3,4-benzo-1,6-methano[12]-annulene **III** and 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]-annulene **IV**.



I



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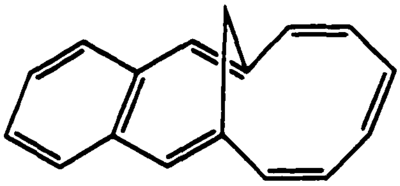
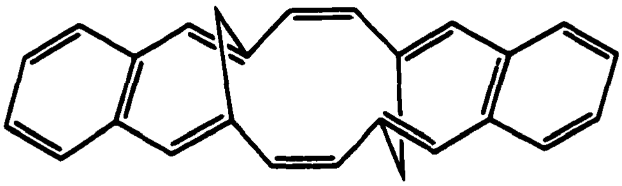
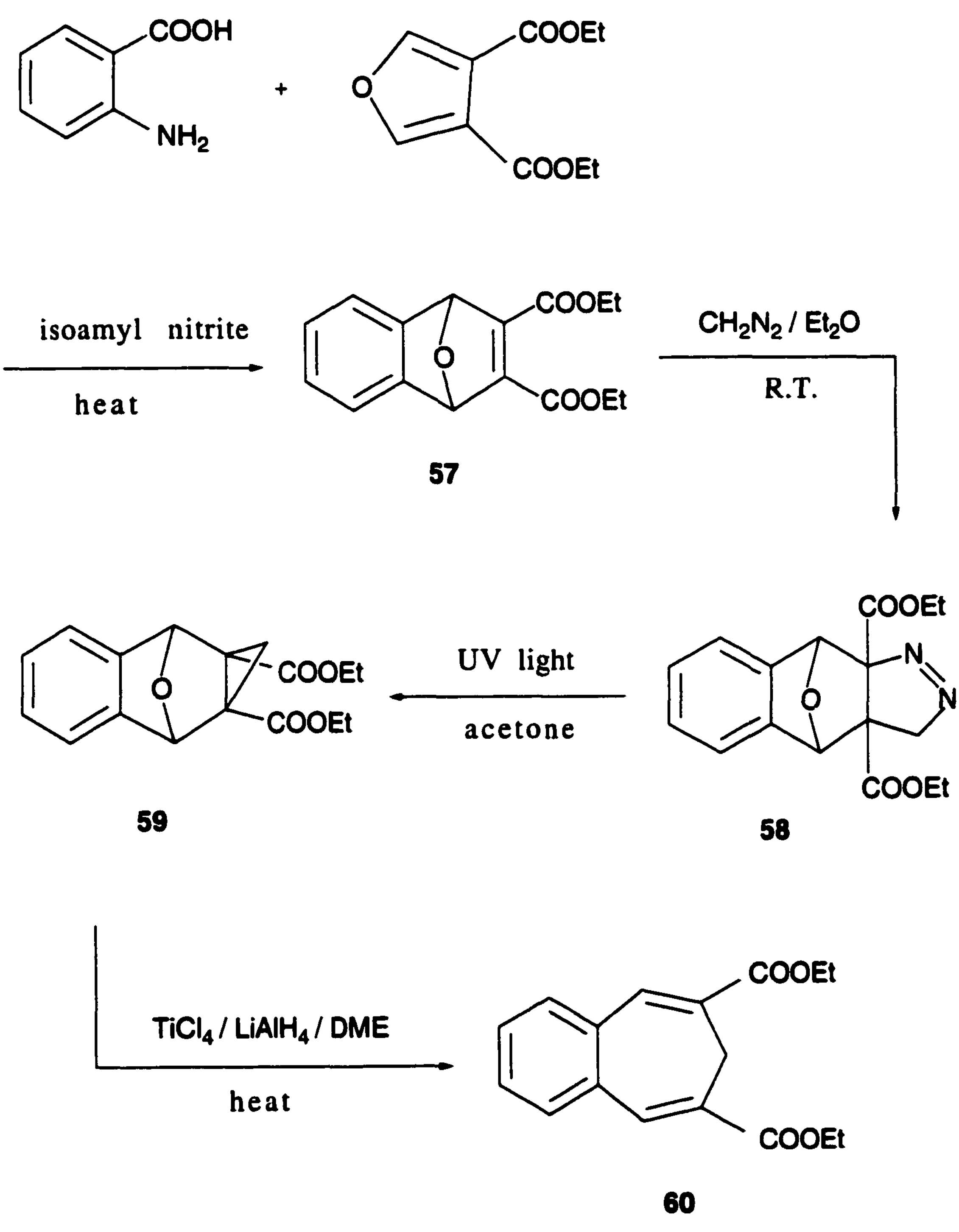


III



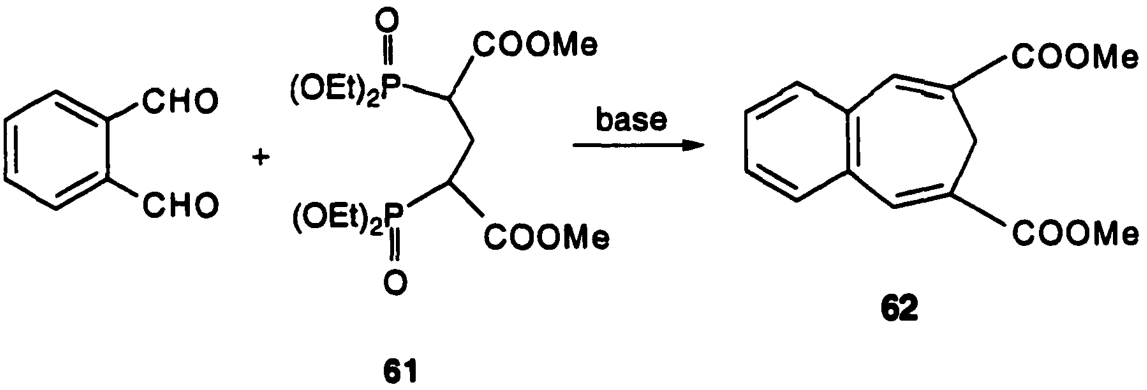
IV

Unlike the large number of benzannulated dihydropyrenes that have been investigated by Mitchell et al.(57), only a small number of benzo-fused methano-bridged annulenes have been synthesized and studied(78). The difficulty of the investigations to be performed was due to the lack of an appropriate synthetic precursor. Therefore, research efforts in our group concentrate in the research for suitable starting material enabling the synthesis of benzannelated methano-bridged annulenes. Earlier studies yielded in synthesis of 1,6-dicarbo ethoxy-3,4-benz-1,3,5-cycloheptatriene via four steps starting with anthranilic acid and 3,4-dicarboethoxy furan as below **(scheme 3)**. This method is essentically a modification of Vogel's initial synthetic approach to cycloheptatriene-1,6-dialdehyde(74). Aprotic diazotization of anthranilic acid generated the correspoonding benzenediazonium-2-carboxylate which decomposed in situ to give benzyne(79), then underwent Diels-Alder cycloaddition with diethyl-3,4-furandicarboxylate to obtain the oxygen-bridged six-membered carbocycle **57**. Subsequently, compound **57** was reacted with diazomethane(80) and the intermediate pyrazoline **58** was irradiated with a 500W medium pressure Hg-lamp to give **59**. The deoxygenation(81) of compound **59** with titanium tetrachloride / lithium aluminum hydride yielded the 1,6-dicarboethoxy-3,4-benz-1,3,5-cycloheptatriene **60** in 12% overall yield.



Scheme 3 The synthesis of 1,6-dicarboethoxy-3,4-benz-1,3,5-cycloheptatriene 60

The Bis-Wittig-Horner cyclization of o-phthalaldehyde with bisphosphonate **61** was attempted but without success(82).

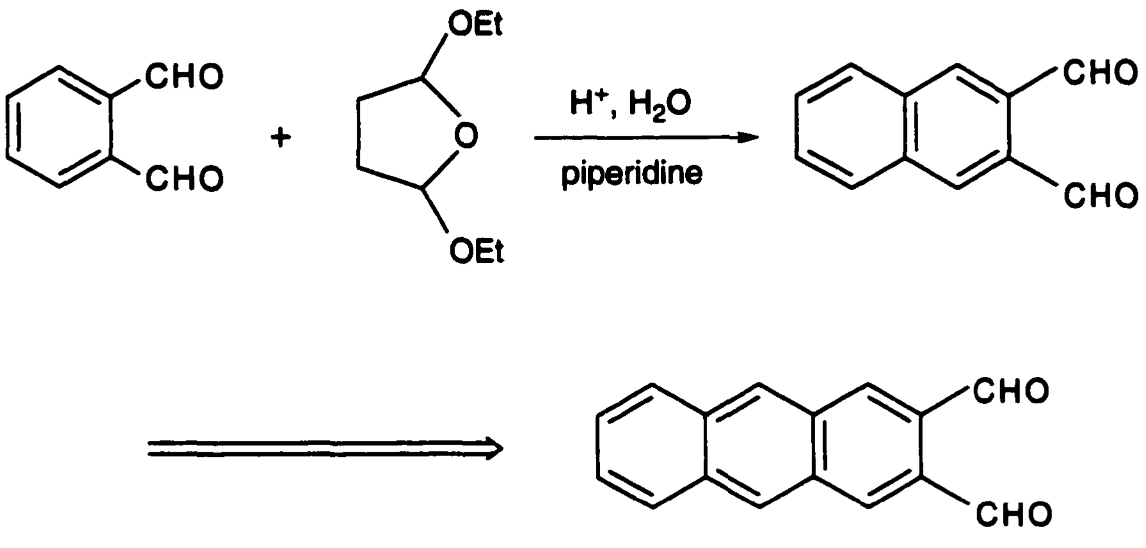


61

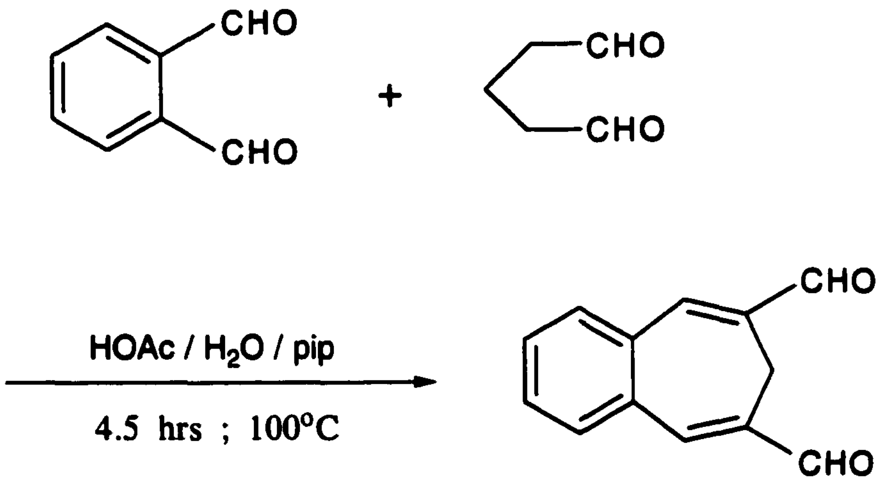
62

Scheme 4 The attempted synthesis of 1,6-dicarbomethoxy-3,4-benz-1,3,5-cycloheptatriene 62

In order to convert diester **60** into the dialdehyde **63**, the ideal building block for the synthesis of benzannelated methano-bridged annulenes, two further steps would be required. Fortunately, the extension of Lepage's elegant one-pot synthesis of naphthalene-2,3-dialdehyde(83) from phthalaldehyde and succinaldehyde, utilizing glutaraldehyde led to a one-pot synthesis of 3,4-benz-1,3,5-cyclo heptatriene-1,6-dialdehyde(84). In contrast to Lepage's synthesis which yielded in addition to naphthalene-2,3-dialdehyde significant amounts of anthracene-2,3-dialdehyde, our synthesis of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde did not yield any higher homologes.



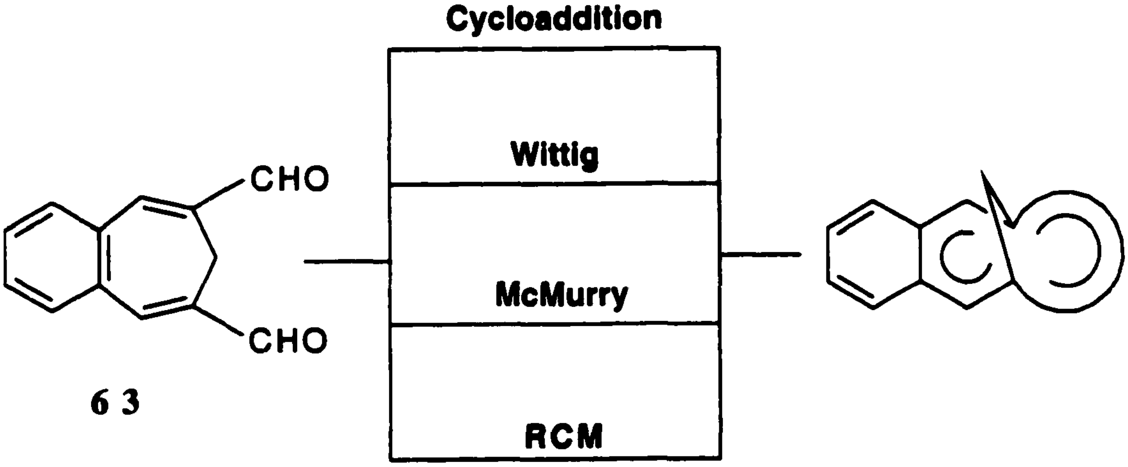
Scheme 5 Lepage's synthesis of naphthalene-2,3-dialdehyde



63

Scheme 6 The synthesis of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde 63

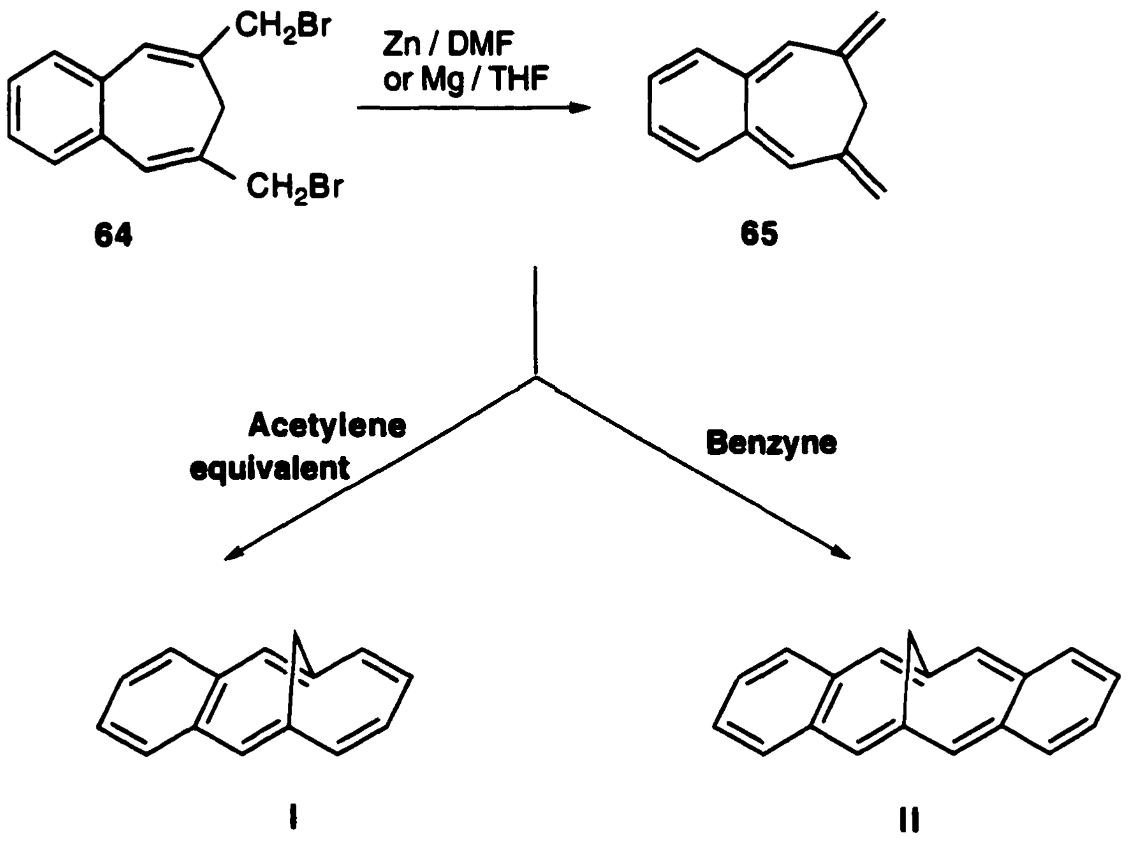
3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde **63** is valuable versatile building block for the synthesis of benzannelated bridged-methano annulenes and has been used in this study to synthesize compound **I** through **IV**. Several routes such as the Diels-Alder reaction, Wittig olefination, McMurry reaction and ring closing olefin metathesis have been explored and will be discussed below.



Scheme 7 Synthetic approach in this investigation

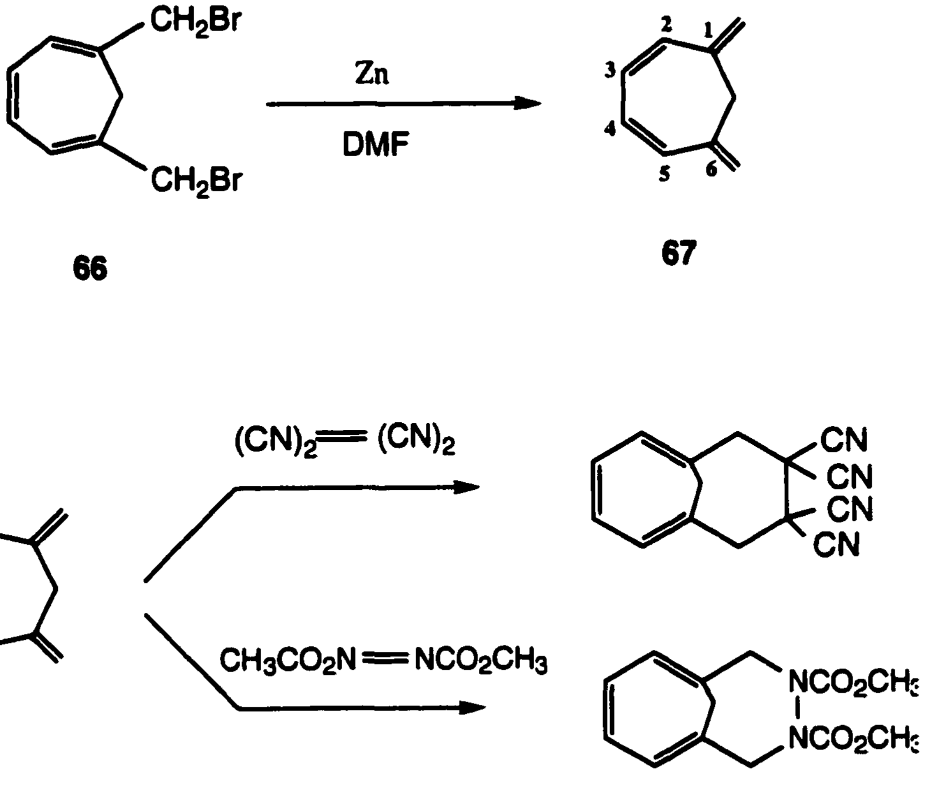
2.1 Diels-Alder reaction approach to benzannulenes

Cycloadditions in their many variations represent one of the most powerful methods in organic chemistry for making cyclic structures. Five and six membered ring are typically made by the well-known 1,3-dipolar and Diels-Alder cycloaddition reactions. Moreover, the Diels-Alder reaction has been applied to a number of synthetic objectives with notable success. Respectively, higher order cycloaddition processes have emerged recently as useful methodology for the synthesis of medium sized carbocycles(85). Therefore, a proposed study of the Diels-Alder reaction involving the highly reactive key intermediate polyene **65**, derived from the dibromide **64** might result in a direct synthesis of monobenzo and dibenzo-1,6-methano[10]annulenes, **I** and **II**.



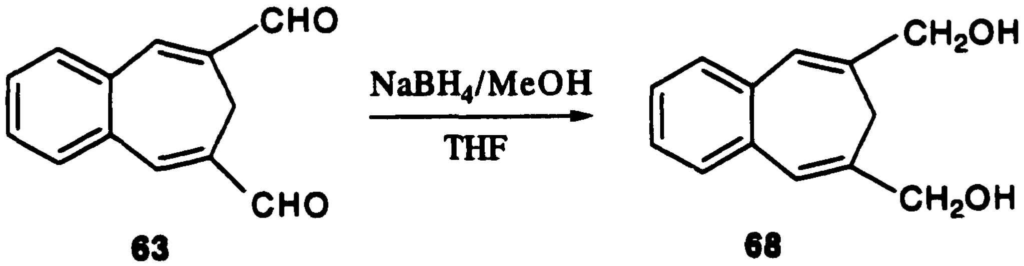
Scheme 8 The Diels-Alder approach towards I and II

In 1970, Feldmann was successful in obtaining the tetraene **67** from the 1,6-bis(bromomethyl)-1,3,5-cycloheptatriene **66**; which then underwent an [8+2] cycloaddition as shown below(86). This inspired us to obtain our desired compounds in a similar fashion.



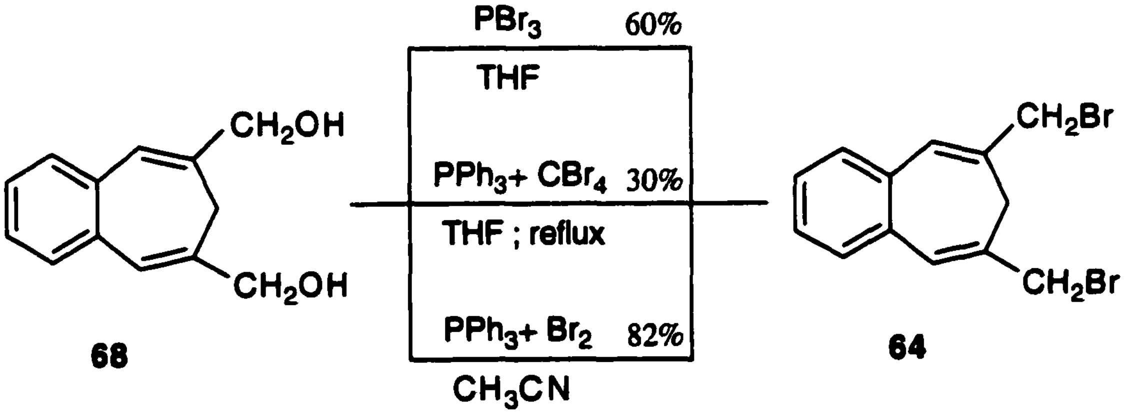
Scheme 9 Feldmann's approach towards Diels-Alder adducts

The strategy started with the reduction of dialdehyde **63** by sodium borohydride in methanol(87) / THF to obtain diol **68** in 96% yield, followed by reaction with PBr_3.



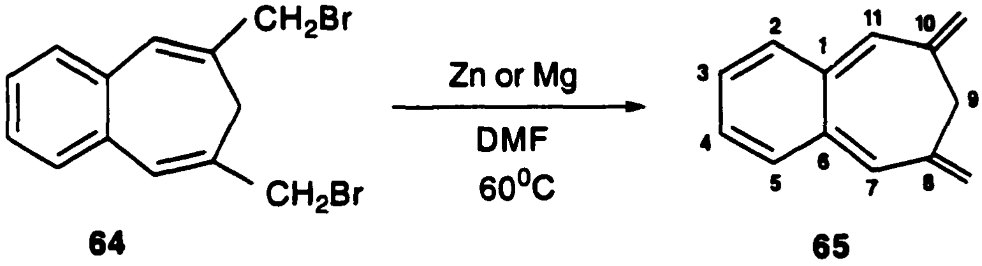
Scheme 10 The synthesis of 68

The first attempt for bromination which is a commonly used method for this preparation was the reaction of diol **68** with phosphorus tribromide in THF at room temperature. It gave dibromide **64** in 60% yield. In order to improve the yield, another method was used. The second attempt was the treatment of diol **68** with (tribromomethyl)phosphonium bromide(88) which was prepared from triphenylphosphane and tetrabromomethane in THF. Then, the reaction mixture was refluxed for 20 minutes. But this method did not reach the expected higher yield. The yield was even lower than the first at 30%. Finally, the third attempt was based on Machinek and Luttkes' work(89). Bromination with triphenylphosphine dibromide, generated in situ from triphenylphosphine and bromine, yielded dibromide **64** in 82% yield.



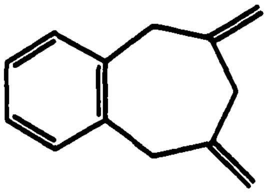
Scheme 11 Three approaches to 64

This type of dimethylenecyclopolyene, representing an extended o-quinodimethane, is a very reactive intermediate. Cycloadditions of o-quinodimethane intermediates are well document(90). In our case, the 8,10-dimethylene-bicyclo[5,4,0]undeca-2,4,6,11-tetraene **65**, was generated as shown in **scheme 12**. Treatment of the dibromide **64** with zinc in DMF at 60°C gave a hydrocarbon mixture **69**, **70**, **71**.

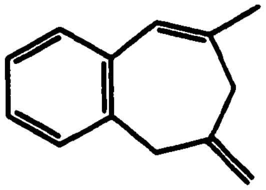


Scheme 12 The approach towards diene 65

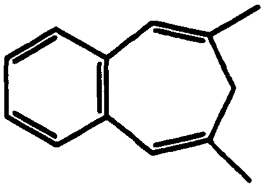
In the same way, dehalogenation of dibromide **64** with Mg in THF gave the hydrocarbon mixture **69**, **70**, **71** according to GC-MS and NMR spectra. In all cases the GC-MS showed the exclusive presence of three compounds with molecular ions of 170 (trace amounts of three compounds with molecular ions of 338 were detected). They correspond to the dimethyl compounds as shown below, most likely resulting from elimination followed by hydrogen abstraction.



69

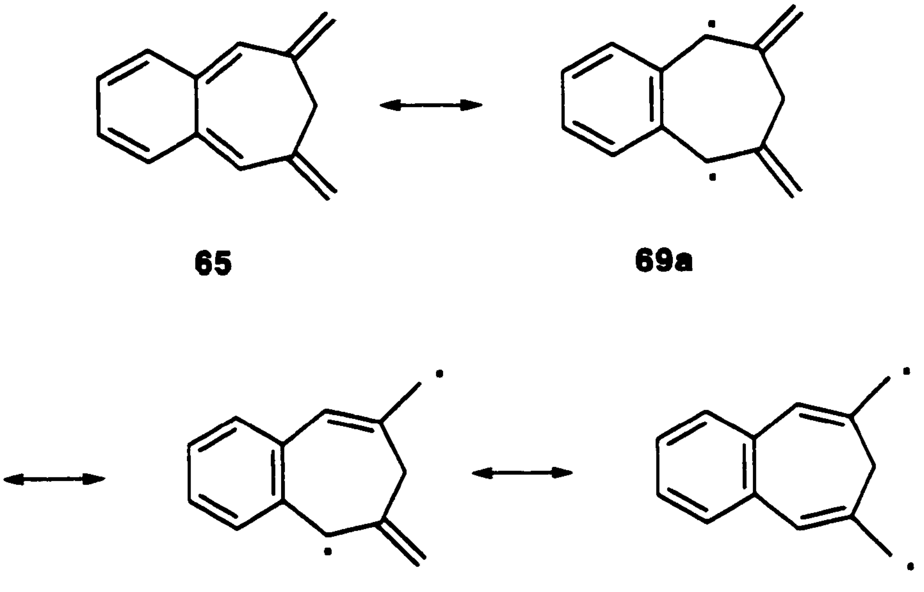


70

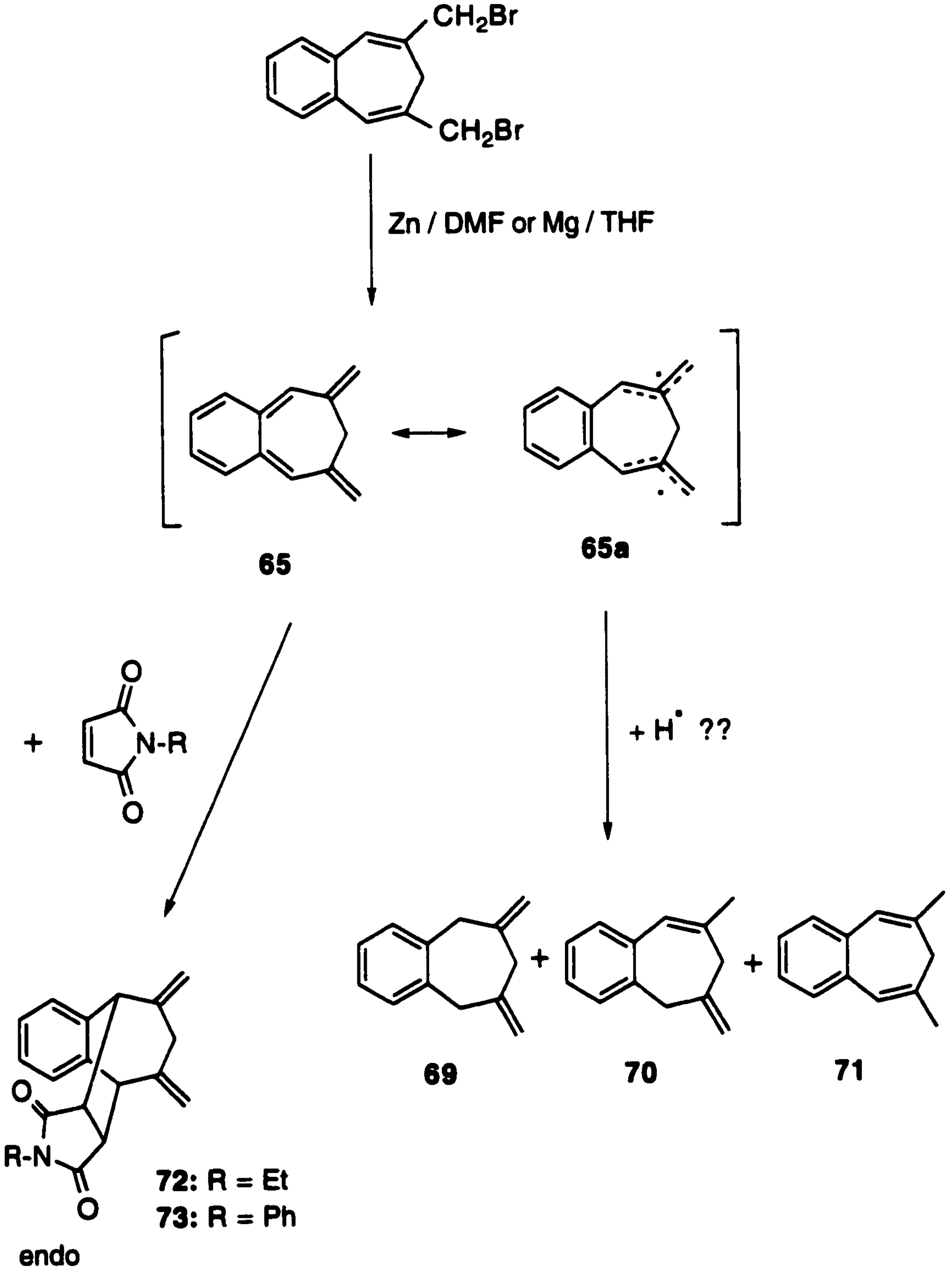


71

In an attempt to trapp the reactive intermediate **65**, we carried out the dehalogenation of **64** in the presence of dienophiles. Treatment of dibromide **64** with zinc in DMF under nitrogen in the presence of equimolar amounts of N-ethylmaleimide and N-phenylmaleimide at room temperature, reacting for 5 hours, yielded the corresponding compounds **72**, **73**. Unfortunately, the products of this reaction indicated that the Diels-Alder reaction did not occur at the ends C-8 and C-10 of **65**. Instead, the dienophiles only reacted at positions C-7 and C-11. In addition, we detected and isolated the same mixture of three compounds with molecular ions of 170 according to the GC-MS. The results are summarized in **Scheme 13**. A most likely intermediate accounting for the formation of **69**, **70**, **71** might be the diradical **69a**, **70a**, **71a**. The results of these experiments indicate that contrary to the case of **67** which could be isolated and reacted at the terminal positions C-1 and C-6, intermediate **65** could not be isolated and unfortunately did not react at the terminal position C-8 and C-10.



65 **69a** **70a** **71a**



Scheme 13 Diels-Alder reaction approach

The structure of the Diels-Alder adducts could be either endo or exo. The proton NMR ($CDCl_3$,ppm) of the N-ethylsuccinimide Diels-Alder adduct **72** exhibited a multiplet for the benzene ring at 7.20-7.10 (m, 4H), one singlet and one doublet for the diene part at 5.05 (s, 2H) and 4.84 (d, 2H, J=1.2 Hz), two singlets for the CH at 4.19 (s, 2H) and 3.27 (s, 2H), a quartet for the ethyl CH_2 at 3.23 (q, 2H, J=7.2 Hz), an AA'BB' pattern for the bridgehead protons at 3.01 (d, 1H, J=15.6 Hz) and 2.80 (dt, 1H, J=15.3 Hz, J=1.2 Hz), and a triplet for the methyl group at 0.54 (t, 3H, J=7.2 Hz). The proton decoupled ^{13}C NMR displayed the carbonyl carbon at 177.9, aromatic and olefinic carbons at 146.4, 136.3, 128.3, 127.6, 111.5, two CH and bridgehead carbons at 49.1, 47.4, 41.7, and ethyl group at 33.8 and 12.4. The mass spectrum exhibited a molecular ion m/e 293 (100%) which matched to ^1H and ^{13}C NMR.

The N-phenylsuccinimide Diels-Alder adduct **73** showed similar results in its ^1H NMR spectrum: 7.31-7.17 (m, 7H), 6.68-6.65 (m, 2H) for the benzene ring, 5.10 (s, 2H), 4.88 (d, 2H, J=0.9 Hz) for the diene part, 4.29 (s, 2H), 3.49 (s, 2H) for the CH and 3.06 (d, 1H, J=15.3 Hz), 2.85 (dt, 1H, J=15.9 Hz, J=1.5 Hz) for the bridgehead protons. The proton decoupled ^{13}C NMR displayed the carbonyl carbon at 177.1, aromatic and olefinic carbons at 146.1, 136.3, 129.2, 128.8, 128.5, 127.6, 126.5, 111.7, two CH and bridgehead carbon at 49.4, 47.8, 41.8. The mass spectrum exhibited a molecular ion m/e 341 (100%). In both cases the ^1H NMR data suggested that both adducts **72** and **73** are endo based on the rather upfield shift in the methyl group at 0.54 ppm of **72** and the two ortho protons with benzene ring of **73** at 6.68-6.65 ppm. This indicates that they are located above the benzene ring in each case. The X-ray structural determination of **73** revealed that two independent molecules A and B existed in the unit cell, and it also verified their endo configuration. The difference between A and B is the configuration in CH_2 group of C1. In molecule A, the CH_2 group points towards the benzene ring ("endo") while in molecule B, the CH_2 group points away from the benzene ring ("exo").

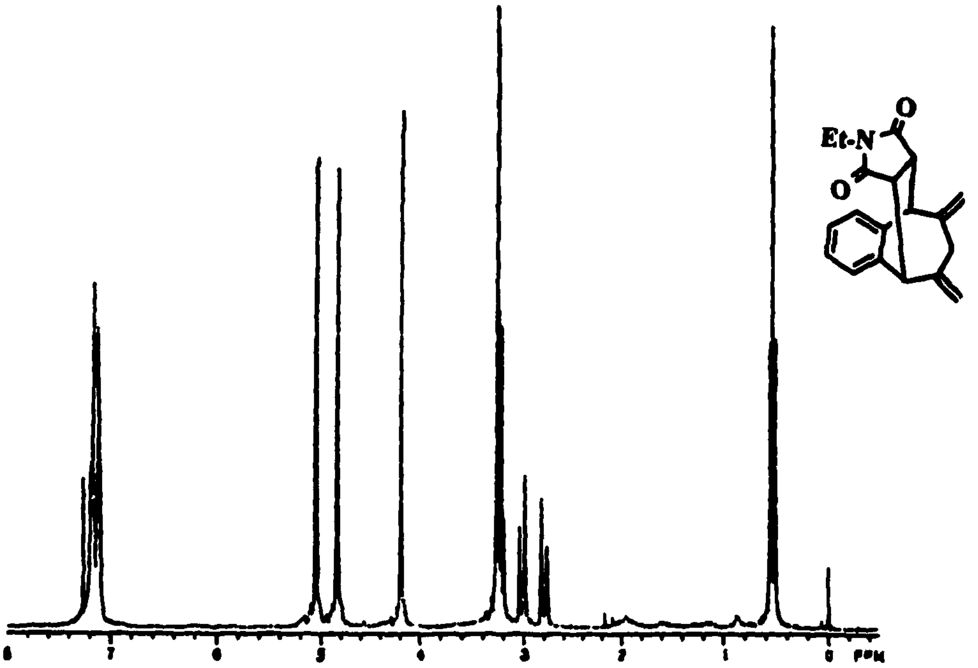


Figure 43 ^{1}H NMR of 72

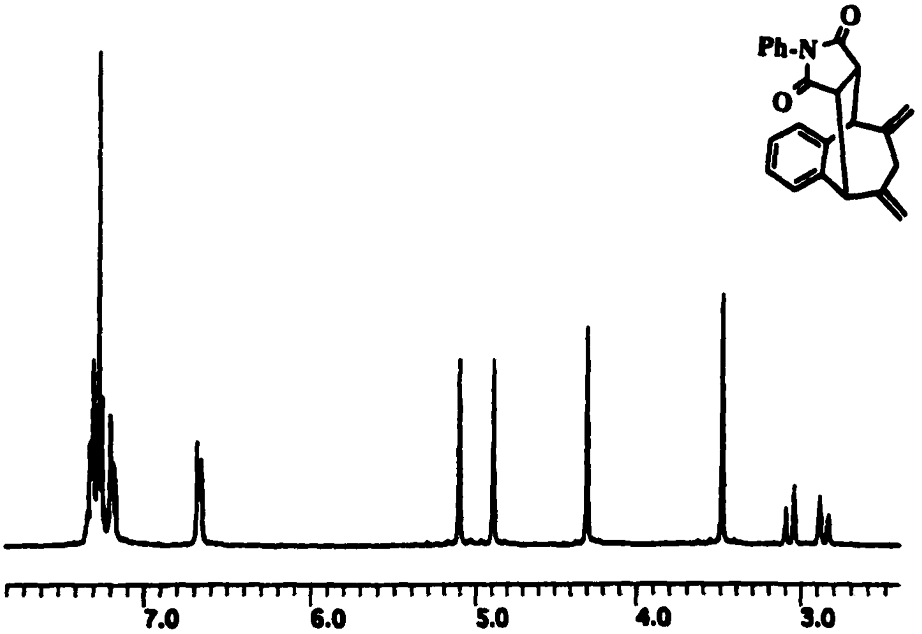


Figure 44 ^{1}H NMR of 73

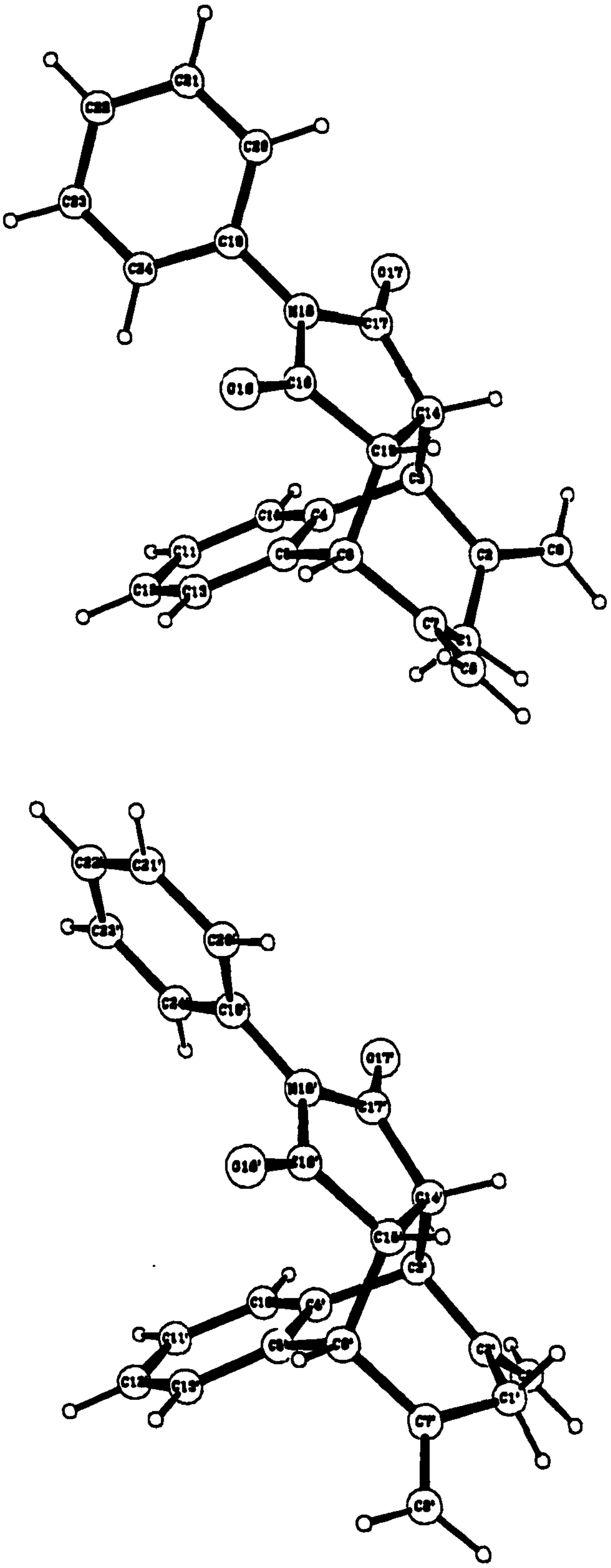
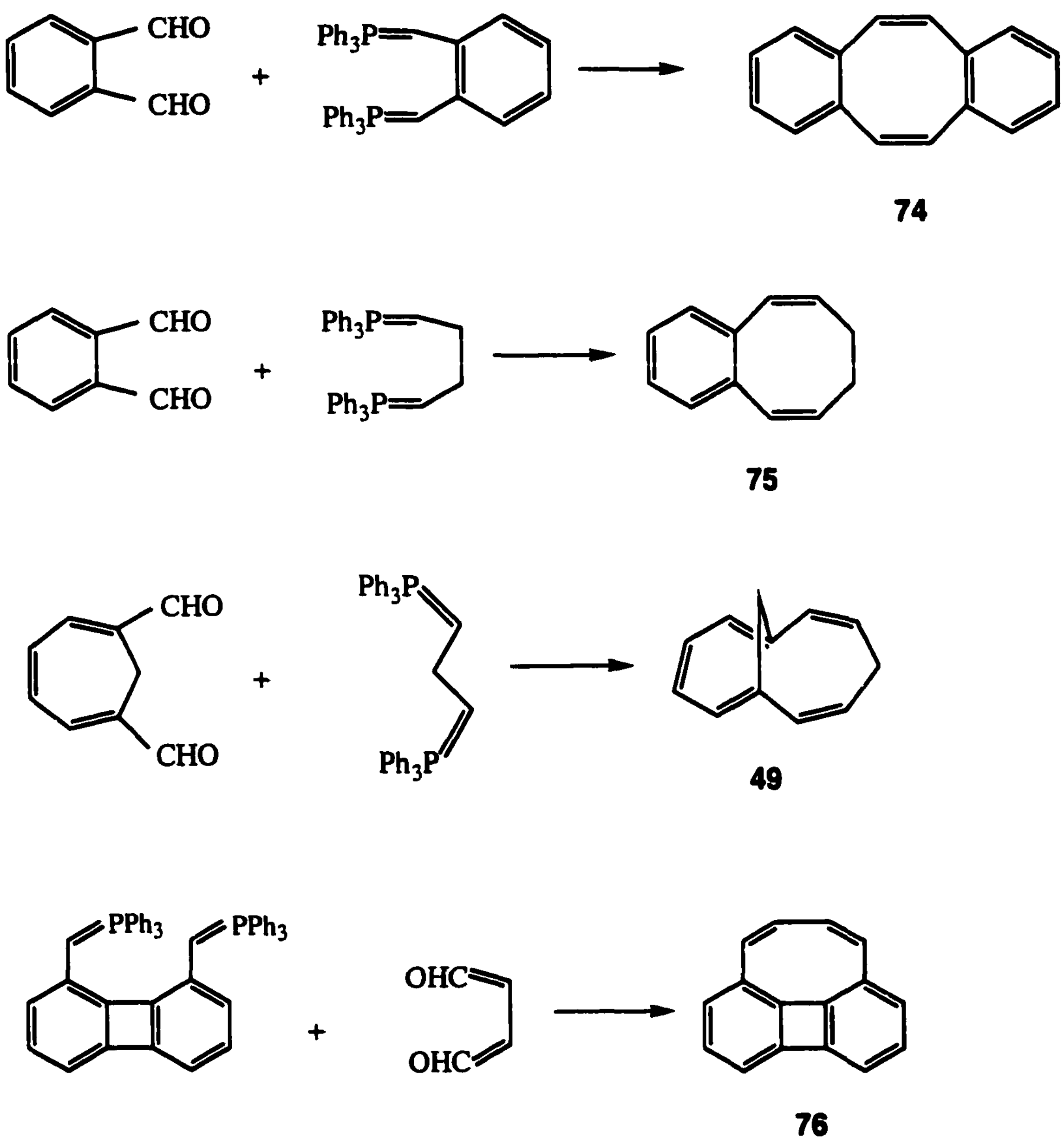


Figure 45 X-ray structure of N-phenyl succinimide Diels-Alder adduct 73 (Independent molecules A & B)

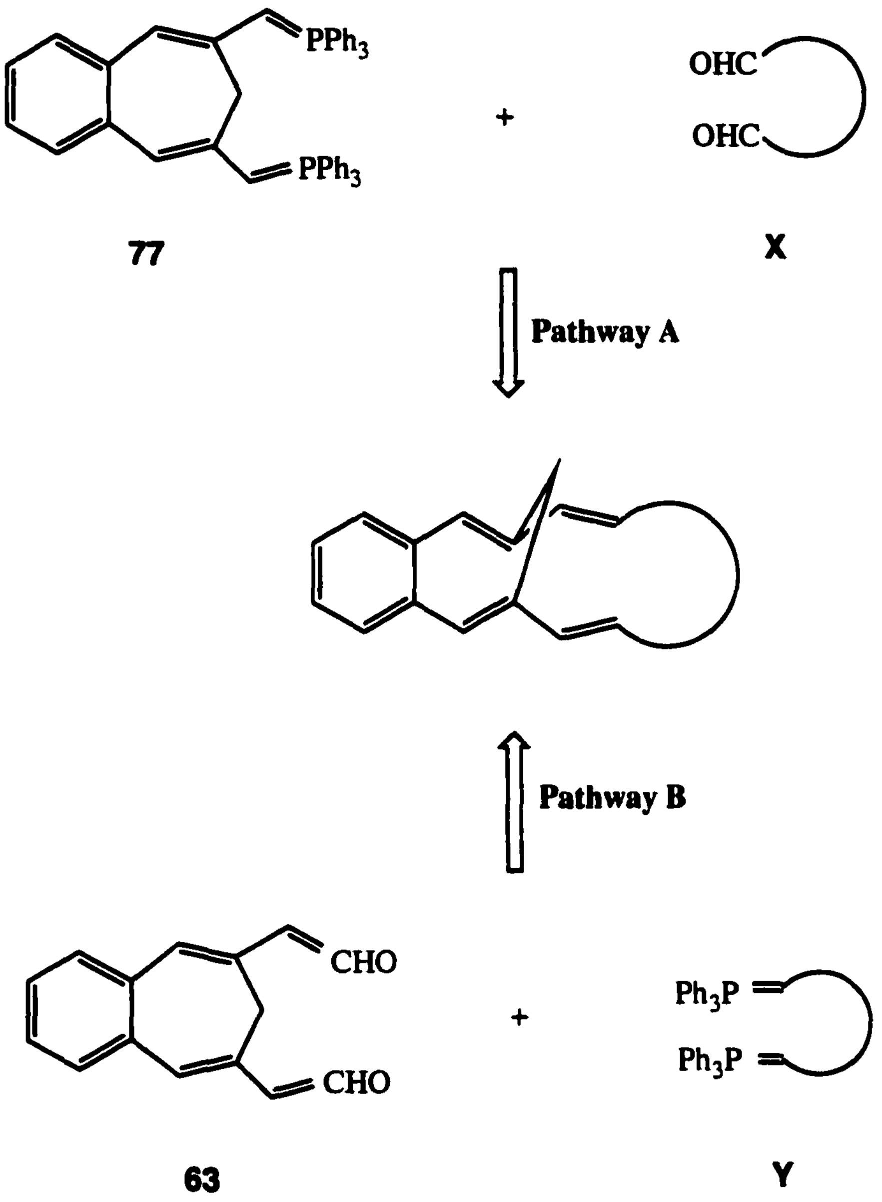
2.2 Bis-Wittig cyclization approach to benzannulenes

In 1953 Wittig and Geiser discovered that methylenetriphenyl phosphorane reacted with benzophenone to yield 1,1-diphenyl ethene and triphenylphosphine oxide, leading to the discovery of a new olefination methodology well known as the Wittig reaction(91). Since then, the universally known Wittig olefination which involves the nucleophilic attack by a phosphorus ylide into carbonyl group of an aldehyde or ketone followed by the elimination of $Ph_3P=O$, has been used extensively in synthetic organic chemistry. Systems such as compound **74**(92), **75**(93), **49**(74), **76**(94) are representative examples that use the cyclizing bis-Wittig reactions.



Scheme 14 Bis-Wittig approach towards 74, 75, 49, 76

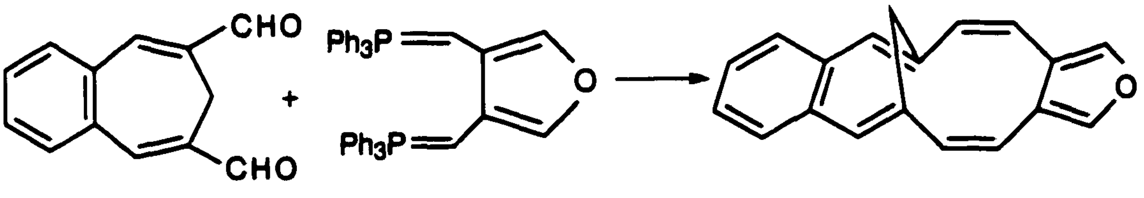
Since the Diels-Alder reaction of compound **64** with N-ethylmaleimide or N-phenylmaleimide did not proceed at the desired position, we decided to investigate the cyclizing bis-Wittig reaction as an alternative. The typical Wittig reaction requires three steps, preparation of the phosphonium salts, ylide formation, and reaction of the ylide with carbonyl compounds. Two possible pathways can be considered for the synthesis of benzannelated 1,6-methano-annulenes using the cyclizing bis-Wittig reaction. Bis-ylide **77** is reacted with dialdehyde **X** or dialdehyde **63** is reacted with bis-ylide **Y** (see **Scheme 15**). Reaction of both types are well documented in the literature(95). Two reviews on the cyclizing bis-Wittig reaction have been published by Vollhardt(96)and Becker(97).



Scheme 15 Two pathways using the Wittig olefination

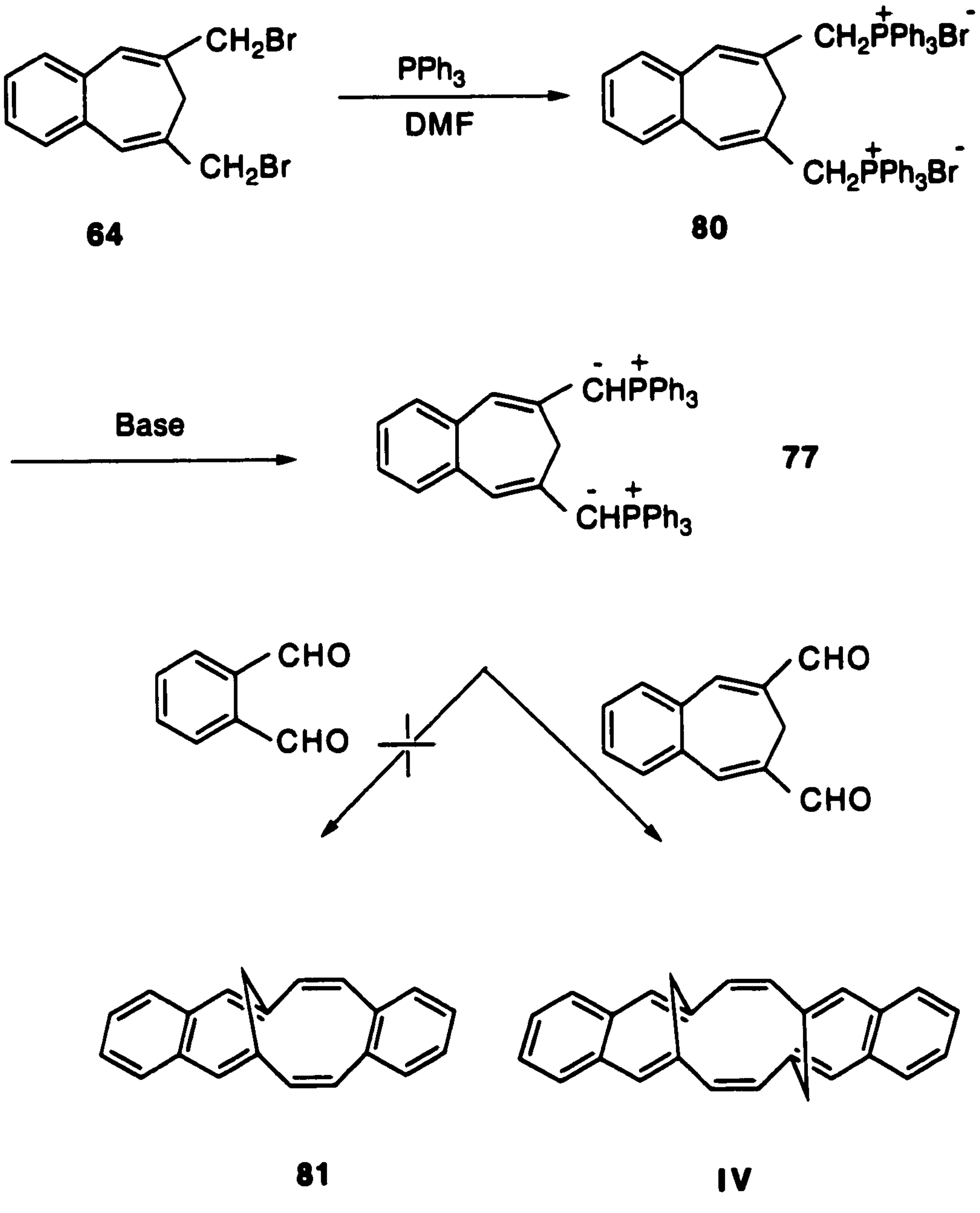
Previous work in our group(98) had shown that when dialdehyde **63** was reacted with o-xylene bisphosphonium salt (pathway B) in DMF, using EtOLi as a base, only a very small amount (<1%) of the dibenz-1,6-methano[12]annulene **81** was isolated.

Several attempts using the same condition, did not succeed in repeating those results. In all runs, the acyclic compounds **82**, **83** were obtained as the major product. However, when the dialdehyde **63** was reacted with the furan-3,4-bisphosphonium salt **78** using LiOEt in DMF, compound **79** was obtained in 6-7% yield(99). Furthermore, we were able to use the cyclizing bis-Wittig reaction (pathway A) to synthesize dibenz-bismethano[16]annulene **IV** in 2-3% yield. Bisphosphonium salt **80** was prepared from the dibromide **64** with triphenylphosphine in DMF in 89% yield, and reacted with dialdehyde **63** in DMF using EtOLi as base at 90° C. Although the Wittig approach towards benz-1,6-methano-[12]annulene **81** was similar, the reaction of the salt **80** and phthalaldehyde in DMF under the same conditions failed. When the addition of phthalaldehyde to bisphosphonium salt **80** in THF (t-BuOK) was carried out at 0°C, again, the desired compound **81** could not be detected.



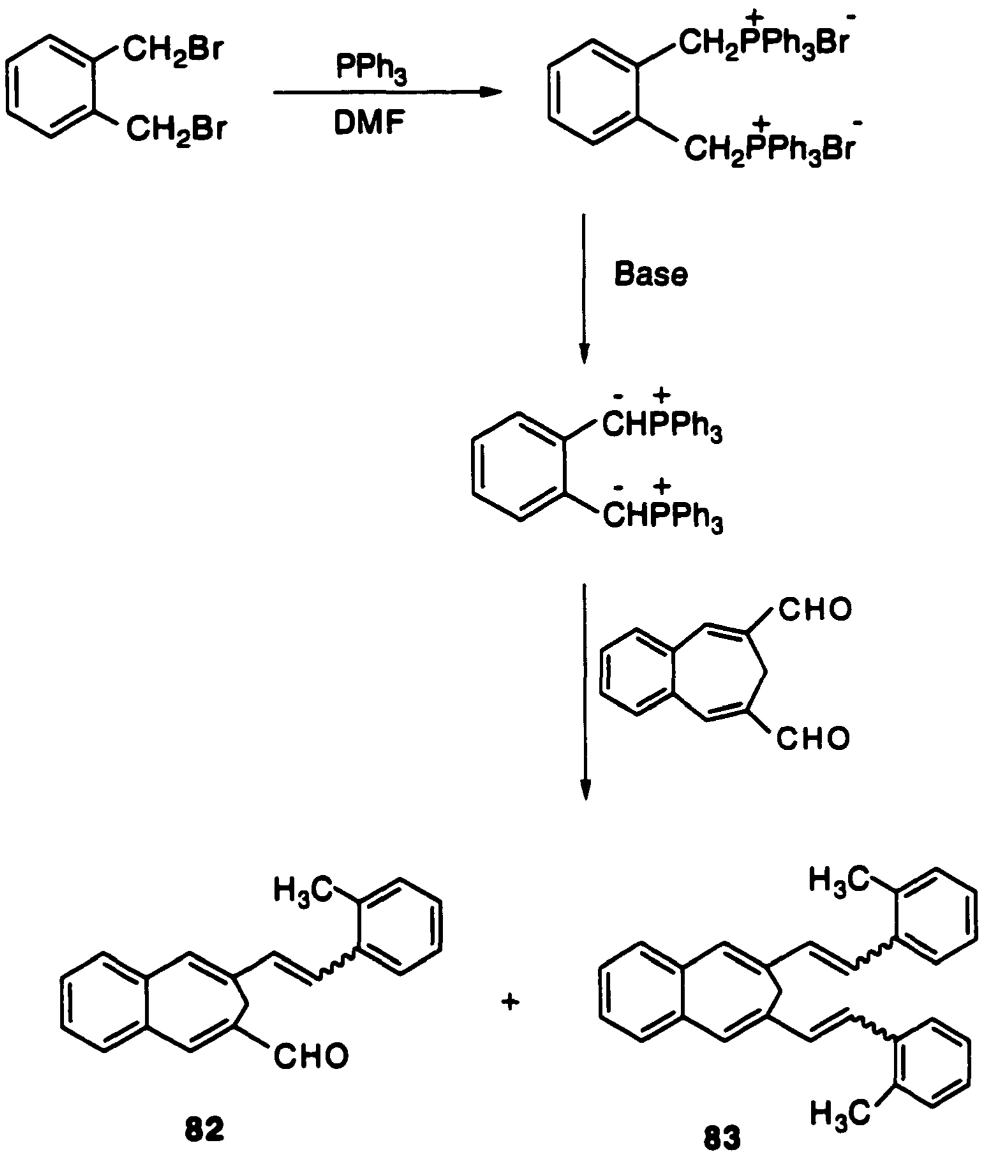
63 **78** **79**

Scheme 16 The bis-Wittig approach towards 79



Scheme 17 The Wittig approach towards 81 and IV

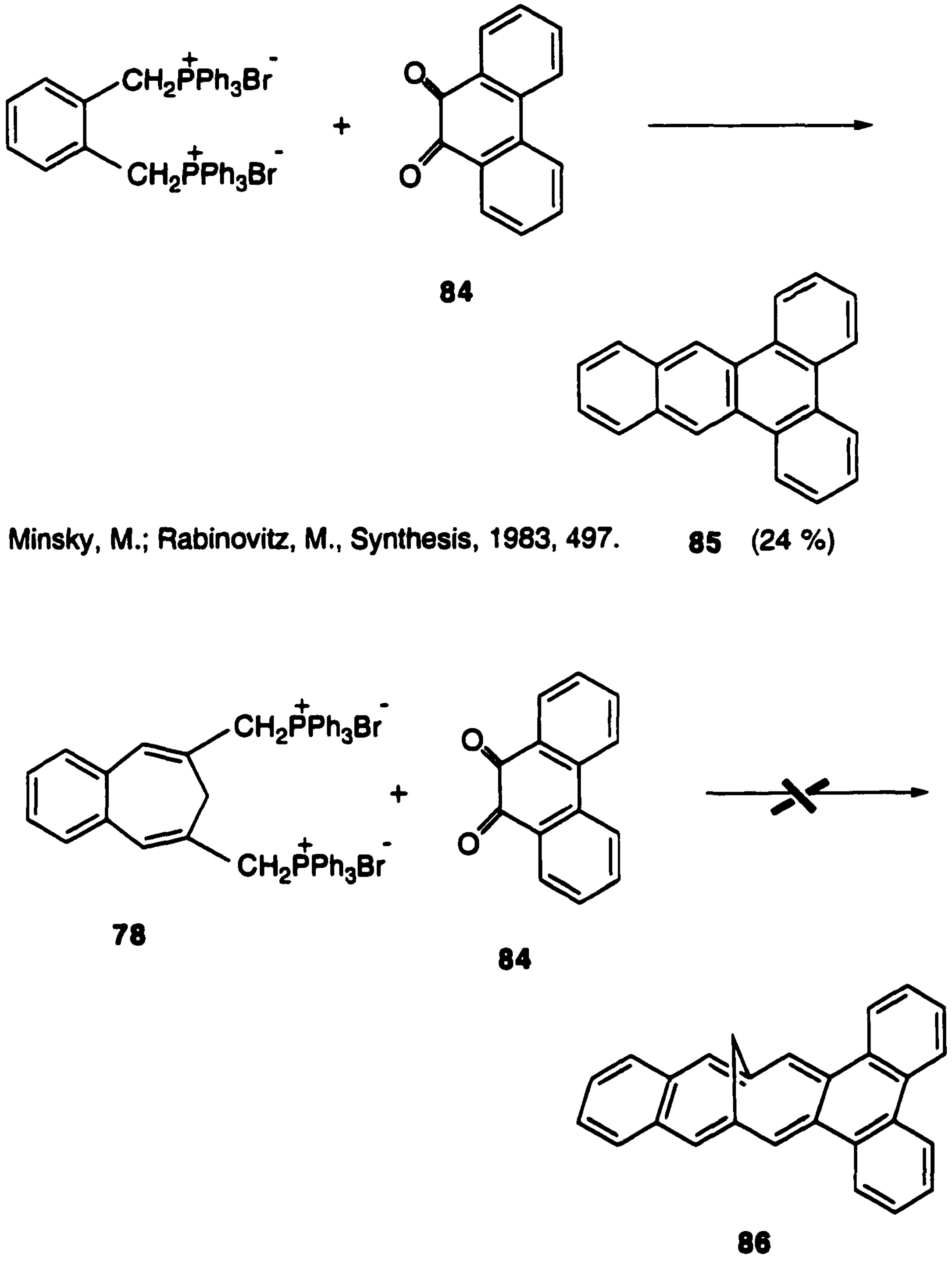
Varying the reaction conditions using the phase transfer method as reported(100) did not succeed in preparing compound **81**. When dialdehyde **63** and o-xylene bisphosphonium salt in CH_2Cl_2 were treated with different bases, such as K_2CO_3, LiOH, KOH at R.T., the desired compound **81** was not detected. Instead, we obtained acyclic mono-**82** and di-**83** adducts as major products.



Base	**82** (cis:trans)	**83**
K_2CO_3	51.2% (1:1)	-
LiOH	8.3% (1:1)	-
KOH	34.9% (1:2)	2.7%

Scheme 18 The investigation of the phase-transfer Wittig reaction

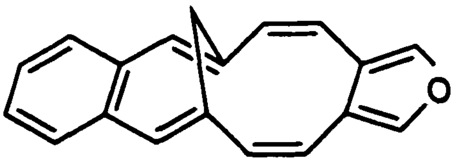
The synthesis of benzenoid systems by using a modified bis-Wittig method under phase-transfer catalysis (PTC) has been reported by Rabinovitz et al.(101). The reaction was carried out by stirring a heterogeneous mixture of o-xylenebis(triphenyl phosphonium)dibromide and 1,2-diketone **84** in lithium hydroxide solution. The bis-phosphonium salt acts as a reagent as well as a PTC catalyst. Similarily, treatment of the bis-phosphonium salt **78** with 1,2-diketone **84** under the same condition did not yield **86**.



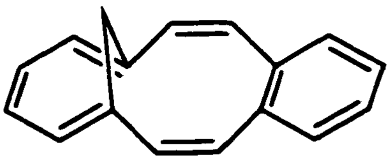
Minsky, M.; Rabinovitz, M., Synthesis, 1983, 497.

Scheme 19 The PTC approach towards 85 and 86

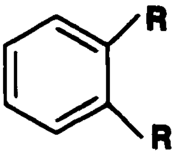
Several reasons could be accountable for our failure to obtain compounds **81** and **86**. One of the reason may be due to the considerable distance between the two phosphonium groups and the two carbonyl groups in the starting materials. Therefore, in order to find out why these Wittig reactions were not successful, we calculated the distances between two functional groups using AM1. The results of those calculations may indicate if the distance is a factor respect for the lack of success of these experiments. In our group, we had synthesized the furan-fused annulene **79**(99) via the bis-Wittig reaction. According to our result, the distance between two phosphonium groups in the furan ring is larger than the one in the benzene ring. In other words, the difference in the distances between the two aldehydes in benzene and between the two phosphonium groups in 3,4-benzcycloheptatriene is large. However Vogel et. al. had synthesized benzo[12]annulene **47** by using o-xylene bisphosphonium salt with cycloheptatriene-1,6-dialdehyde via Bis-Wittig reaction and the difference between the distance of their two reactants is similar to ours. Therefore, we think that we just did not discover the right conditions for the reaction to occur.



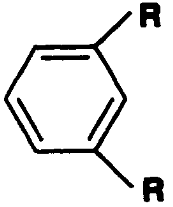
79



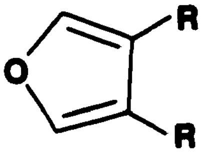
47



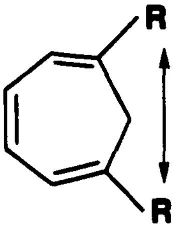
I



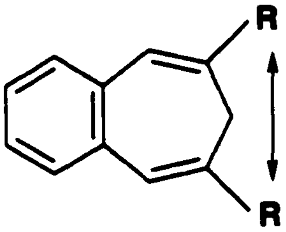
II



III



IV

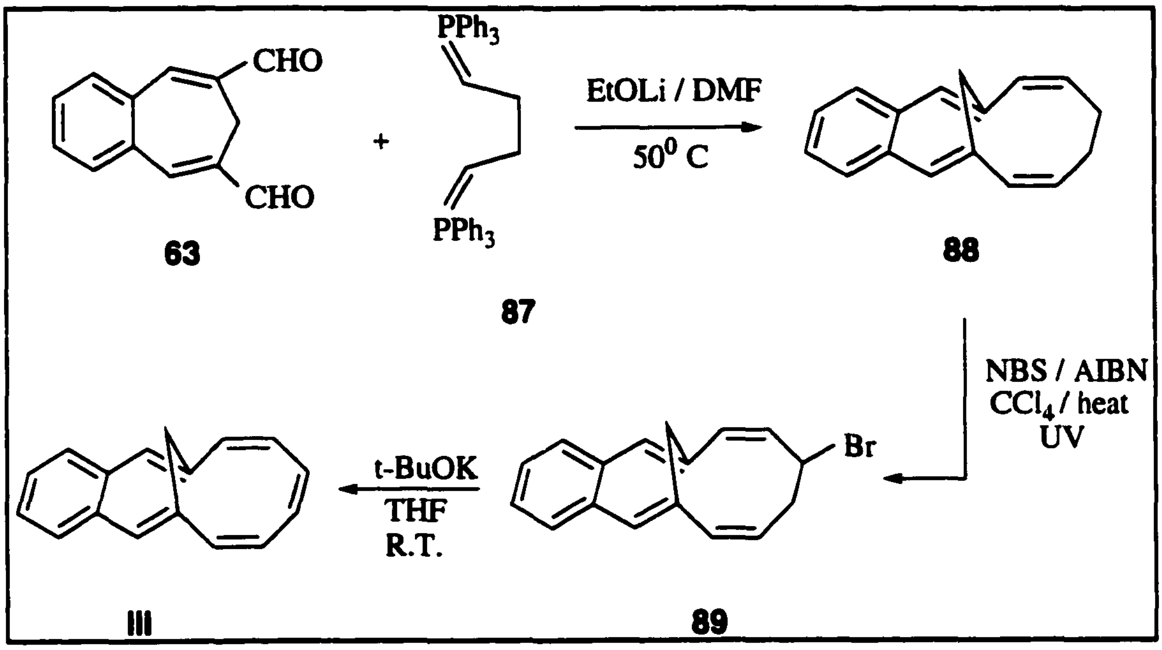


V

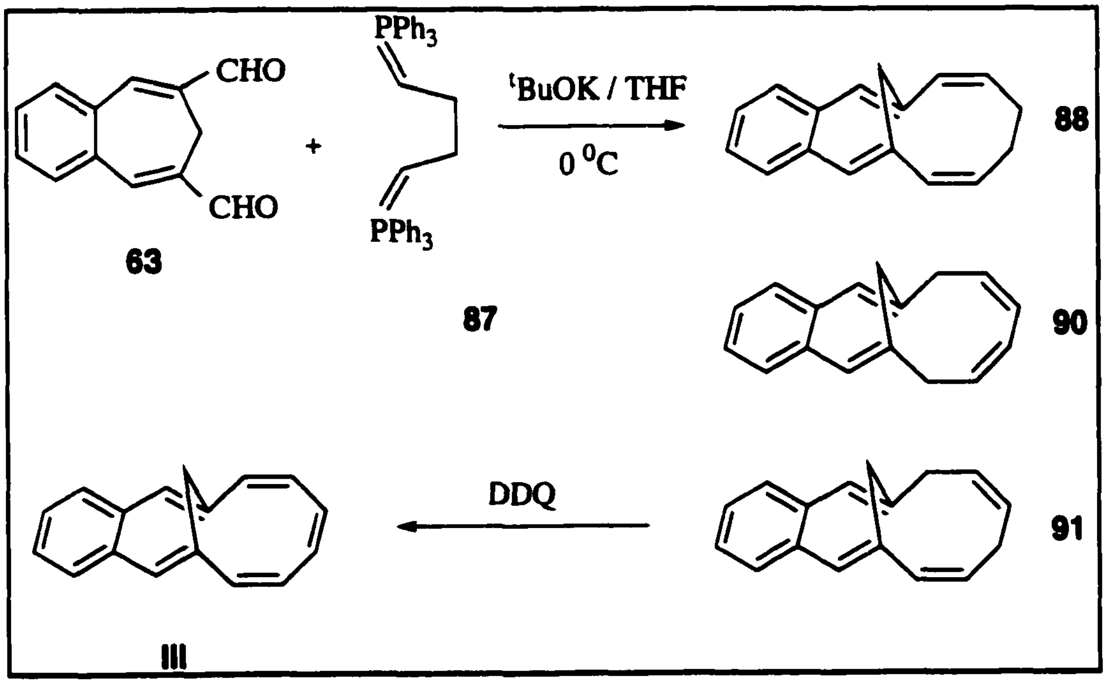
Table 10 AM1 calculation for the distance between two substituents

	I	*II*	*III*	*IV*	*V*
R: CHO	3.06	4.97	3.21	4.35	4.31
R: CH=PPh_3	3.00	4.95	3.10	4.32	4.29

Initial studies in our group using the Wittig reaction had made 3,4-benzo-1,6-methano[12]annulene **III** accessible, starting with 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde **63** and the corresponding bisphosphonium salt, followed by further functionalization(98). First, the slow addition of EtOLi, made from lithium metal and ethanol, into a dilute solution of dialdehyde **63** and bisphosphonium salt **87** in dry DMF at 50°C under nitrogen, yielded compound **88** in 15%. Introduction of the addition double bond was achieved using NBS, followed by t-BuOK. The overall yield was only 1.5%. Varying the conditions for the Wittig reaction by performing the bisylide with t-BuOK in THF, followed by slow addition of aldehyde **63** gave **88** in up to 45% yield together with varying amounts of the isomeric products **88, 90, 91**. Treatment of the hydrocarbons with DDQ in boiling anisole for 5 hours gave a complex mixture from which 3,4-benzo-1,6-methano[12]annulene **III** could be isolated in 10% yield. The overall yield in this route was 4.5%.



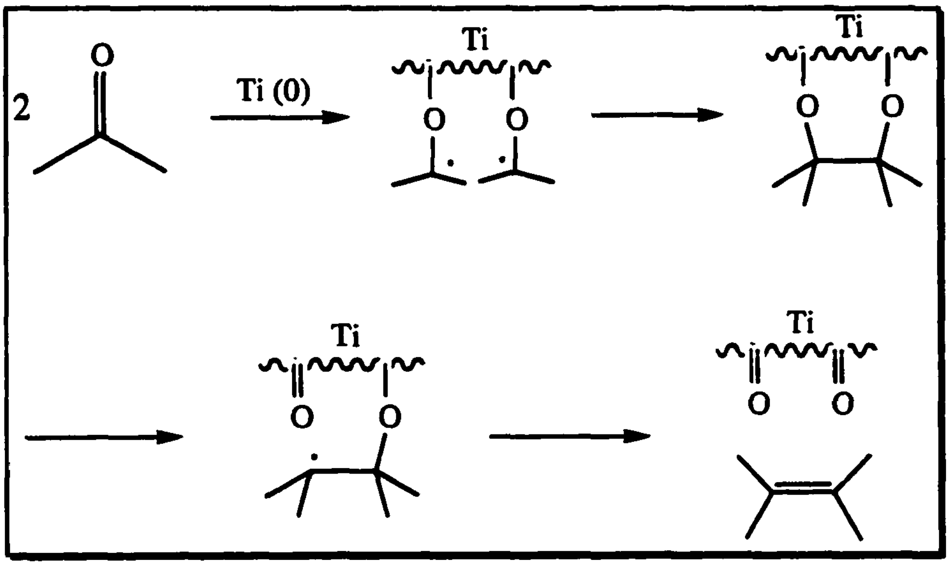
Scheme 20 Bis-Wittig approach A towards III



Scheme 21 Bis-Wittig approach B towards III

2.3 The McMurry approach to benzannulenes

The reductive coupling by low-valent titanium species of aldehydes and ketones to give alkenes , generated in situ, was first reported independently in 1973 by Tyrlik et al.(102) and Mukaiyama et al.(103) and in 1974 by McMurry et al.(104). Low-valent titanium, formed from $TiCl_x$(x=3,4) and various reducing agents, exhibits a high oxophilicity and a strong reducing ability. This particular combination of properties provides the driving force for the reductive coupling of carbonyl compounds to alkenes, generally referred to as the "McMurry olefin synthesis"(105). Recently, the reaction conditions have also been modified, for example $TiCl_4$/Zn/pyridine has been developed as a reagent and is now widely used(106). Study of the mechanism of the reaction has been reported by Geise et al.(107). The mechanism of the carbonyl-coupling reaction is considered to proceed in two steps: (a) reductive dimerization of the starting carbonyl compound to form the carbon-carbon bond and (b) deoxygenation of the 1,2-diolate intermediate to yield the alkene.

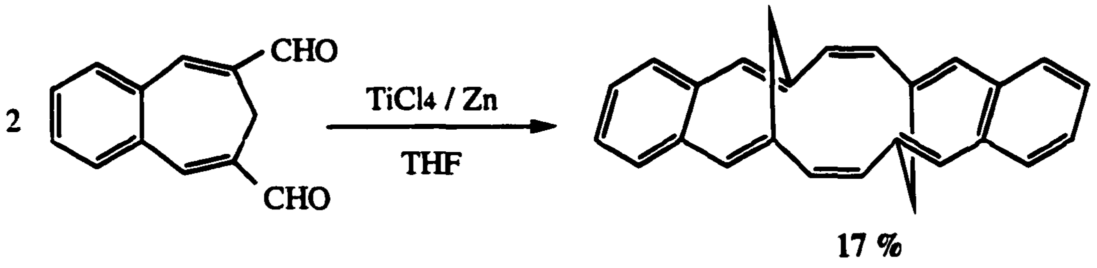


Scheme 22 The mechanism of McMurry Reaction

In the first step, an electron is transferred from titanium to the carbonyl group generating an anion radical that dimerizes to the corresponding pinacol. The intermediate pinacols can be isolated in high yields, if the carbonyl coupling reaction is carried out at 0°C rather than at solvent reflux temperature. This result strongly supports the step one of the mechanism. Deoxygenation by a cis-type concerted mechanism of the pinacol occurs readily leading to alkenes, due to the high oxygen affinity of titanium, These reactions all occur on the surface of the titanium.

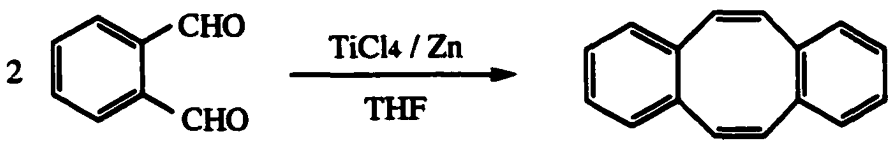
2.3.1 The synthesis of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene IV

The experimental procedure for McMurry reactions generally involves two steps, consisting in the preparation of the active titanium slurry by reducing $TiCl_x$(x=3,4) with strong reducing agents (K, Li, Na, Zn, C_8K, $LiAlH_4$), followed by the addition of the respective carbonyl compound. Since traces of oxidation and hydrolysis products can interfere with the reaction and reduce the yield, the reagents and solvents must be pure and absolutely dry. In our series of experiments, a 500 ml three-necked flask fitted with a reflux condenser, dropping funnel and a nitrogen inlet was charged with dry THF (250ml) and cooled to -78°C. $TiCl_4$ (40mmole) was then added slowly, followed by zinc powder (80mmole) and dry pyridine (1ml). The resultant black mixture was refluxed under nitrogen for one hour. To the stirred Ti^0 mixture at room temperature, a solution of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde (5mmole) **63** in dry THF (200ml) was added slowly (precision addition funnel) over 24 hrs. After an additional 12 hrs reflux , the gray reaction mixture was cooled with ice water and quenched by the addition of 200 ml of 10% K_2CO_3. The gray precipitate was filtered off and the filtrate extracted thoroughly with dichloromethane. The combined organic phases were washed with water, dried over $MgSO_4$, and evaporated to get an orange semi-solid residue. The residue was purified by flash chromatography (hexane/methylene chloride 1/1) affording orange-red crystals in 17% yield. **mp:** 237°C (dec.); **IR** (KBr, cm^{-1}): 3009, 2837, 1481, 1439, 1430, 1414, 952, 900, 872, 756, 732; **UV** (cyclohexane): λ_{max}(nm): 323 (149,778), 330 (152, 212), 390 (7,373), 755 (3,170), 765 (3,034); **MS** (CI) m/z: $(M+1)^+$ 333 (100%).



Scheme 23 The synthesis of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene IV

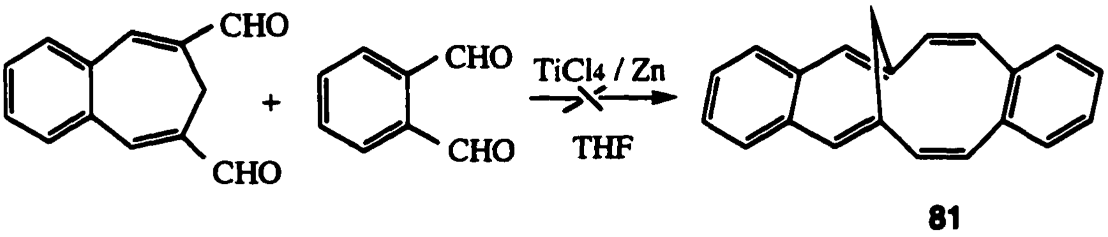
Dibenzo-bismethano[16]annulene **IV** was thus successfully obtained through the McMurry coupling of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde (THF , $TiCl_4$/Zn) in 17% isolated yield. Vogel et. al. had obtained the parent non-annelated system similarily(108) in 2-5% yieldand an X-ray structure determination showed the bridge CH_2 groups to be anti. Treatment of phthalaldehyde under the same conditions gave dibenzocyclooctatetraene **74** in 6% yield.



74

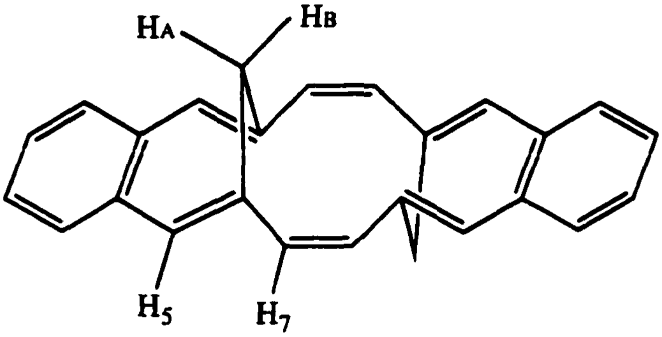
Scheme 24 The synthesis of dibenzocyclooctatetraene via the McMurry reaction

However, the attempt to approach benzo-1,6-methano[12] annulene **81** by a mixed McMurry coupling between 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde **63** and o-phthalaldehyde under the same conditions failed. Instead, we obtained dibenzo[16]annulene **IV** in 6% and dibenzocyclooctatetraene **74** in 3% yield. One possible explanation for this somewhat unexpected result might be the difference in the distances between the two aldehydes in both reactants is too large for a succesful McMurry cyclization.



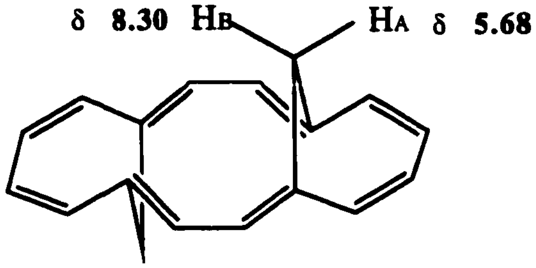
Scheme 25 The mixed McMurry reaction to synthesize dibenzo-1,6-methano[12]annulene 81

2.3.2 Spectra and structural calculation of IV



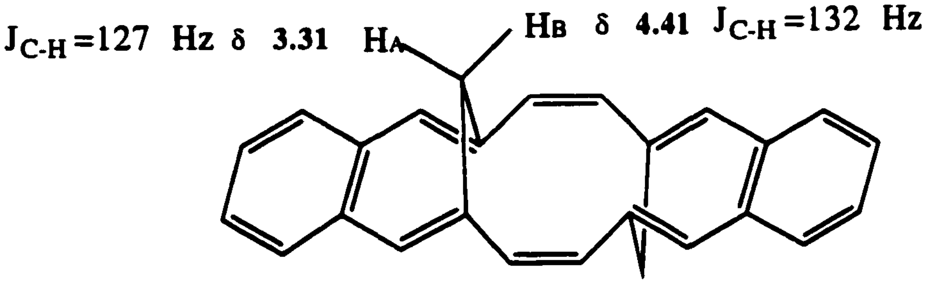
IV

The ^{1}H NMR spectrum of **IV** exhibits well defined sets of resonances due to symmetry in the system. The bridge protons H_A and H_B showed an AB system at 4.41 ppm (d, 2H, J=15.3 Hz) and 3.31 ppm (d, 2H, J=15.6 Hz). In addition, an AA'BB' system at 7.16-7.08 ppm is assigned to the protons of the benzene rings. The remaining two singlets could not be easily assigned by 1D NMR alone. However, a 2D NOESY experiment allowed the clear assignment of each set of singlets. NOE experiments showed a strong positive NOE between the α-protons on the benzene ring at 7.16-7.08 ppm and the resonance at 6.47 ppm, therefore assigned as H_2, H_5. Furthermore, a NOE between the signal at 6.47 ppm (H_2, H_5) and the signal at 6.03 ppm, therefore assigned as H_7, H_{16}. But NOE measurements could not help us to distinguish between H_A and H_B. According to the non-annulated system **54** reported by Vogel, et al.(109), the inner bridge protons appeared more downfield than the outer bridge protons. Therefore, in analogy to **54** we assigned δ 3.31 ppm as H_A and δ 4.41 ppm as H_B.



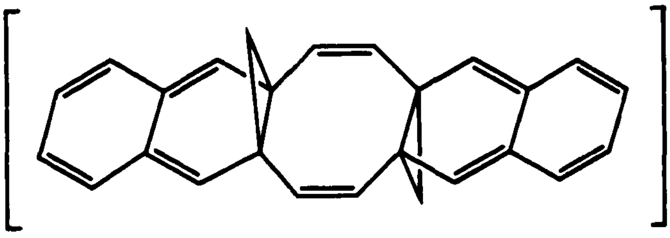
54

Comparison



IV

Furthermore, we determined the ^{13}C-H coupling constants at the bridge CH_2 groups using a 1D HSQC (Heteroneuclear Single Quantum Correlation) experiment at 500 MHz ^1H NMR. The values of J_{C-HA}= 127 Hz and J_{C-HB}= 132 Hz clearly establish the open methano annulene structure for 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano [16]annulene **IV** as opposed to the unlikely cyclopropane structure **92**.



92

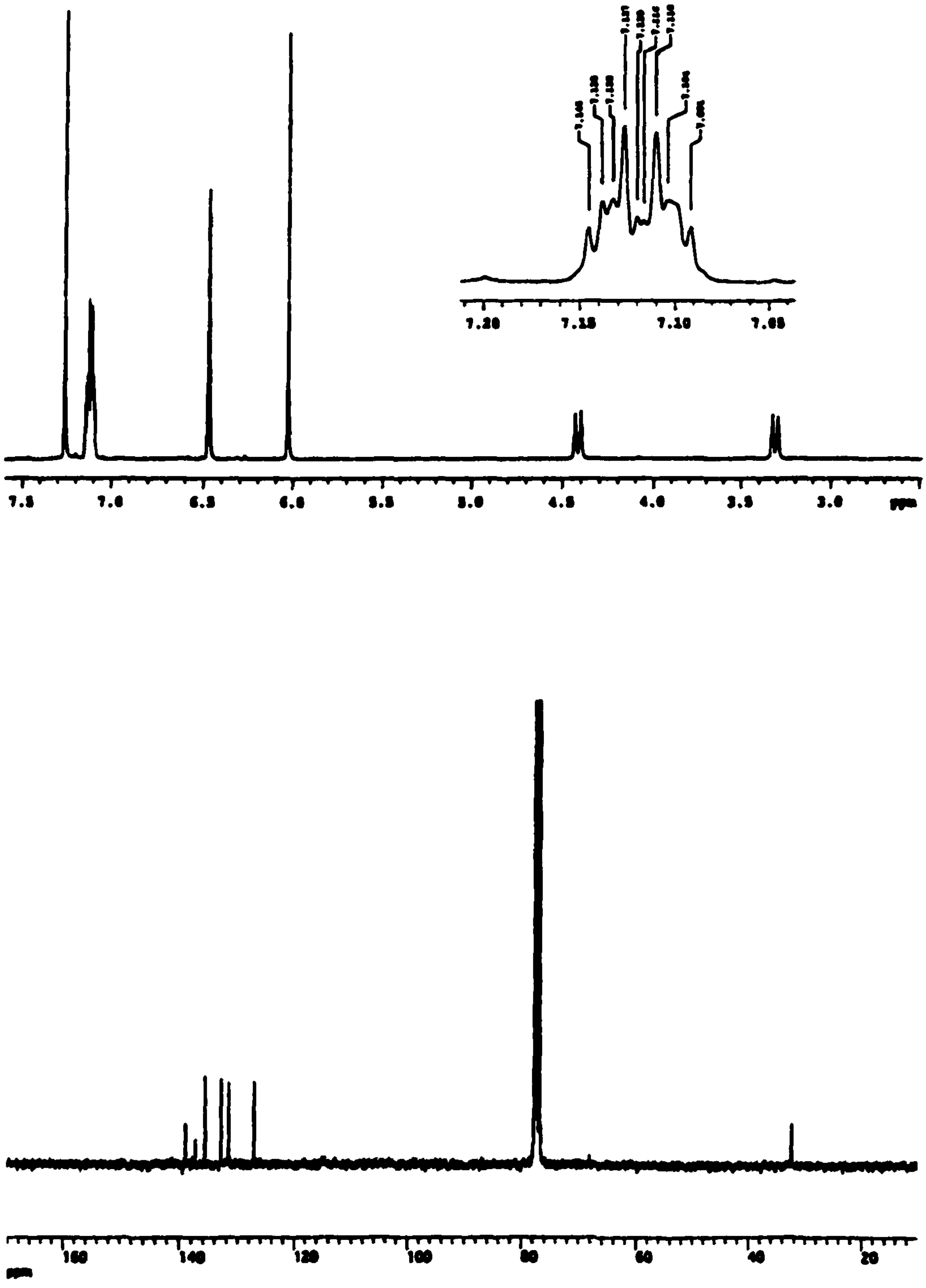
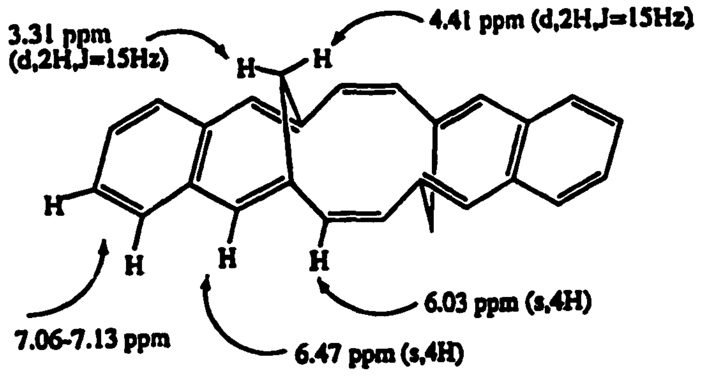


Figure 46 ^{1}H NMR and ^{13}C NMR of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene IV



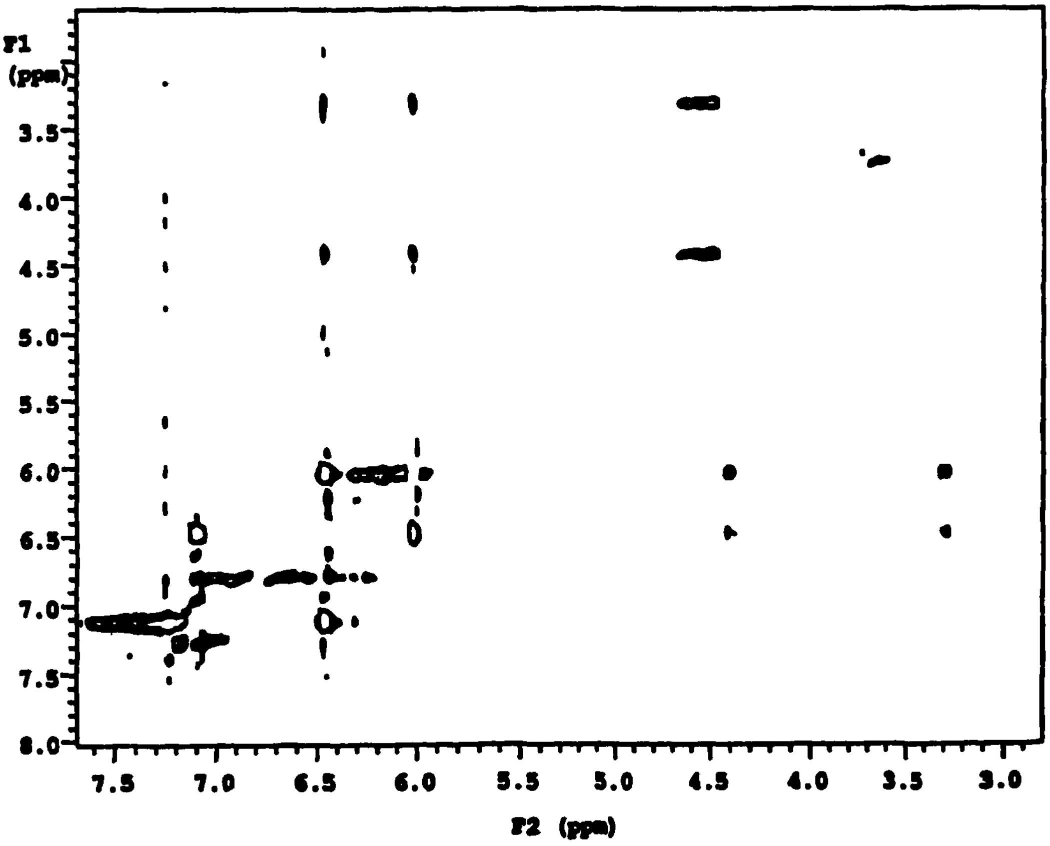
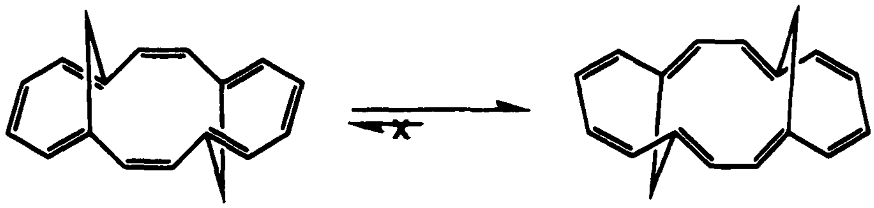
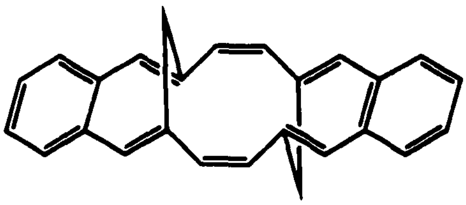


Figure 47 2D-NOSY spectrum of IV

The X-ray structure obtained for **IV** is the strongest physical evidence for the anti conformation with alternating single and double bond on the ring in the crystalline state. From the X-ray analysis, the inner protons reside directly above the center of the annulene ring whilst the outer bridge protons pointed 2.502 Å away from the center of the annulene ring and the whole molecule is quite planar. Based on this, the inner protons are supposed to show more deshielding than outer protons. Compared to its parent non-annulated analogue **27**, the chemical shift of bridge protons are shifted more upfield which indicates that the addition of benzene ring on the parent ring reduces the paramagnetic ring current on the parent ring. The difference in chemical shift between H_A and H_B in **IV** is only 1.1 ppm, which is smaller than 2.62 ppm, the chemical shift difference in **54**. It is no doubt that the upfield shift observed for bridged protons of **IV** resulted from shielding of the fused benzene ring. Futhermore, the outer proton H_A did not shift upfield as much as we expected from the reduction of paramagnetic ring current on annulene due to its position on the side of benzene ring cone.

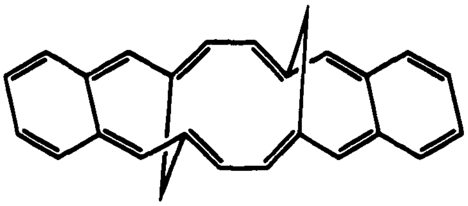


27 A **27 B**



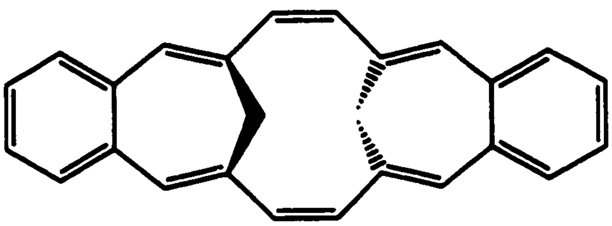
A

or



B

There are two possible forms, **A** and **B**, for compound **IV**. These two may exist in equilibrium, or one form may not exist at all. To determine the actual form of **IV**, we used the measurement of the bond distances which indicate the placement of the double bonds from the X-ray data. From the following information, we concluded that the structure was in the form of **A**. It is interesting to know that the non-annulated analogue **27** from its X-ray structure exists exclusively as form **B**. The reason for this is not known.



3,4:11,12-dibenzo-anti 1,6:9,14-bismethano[16]annulene

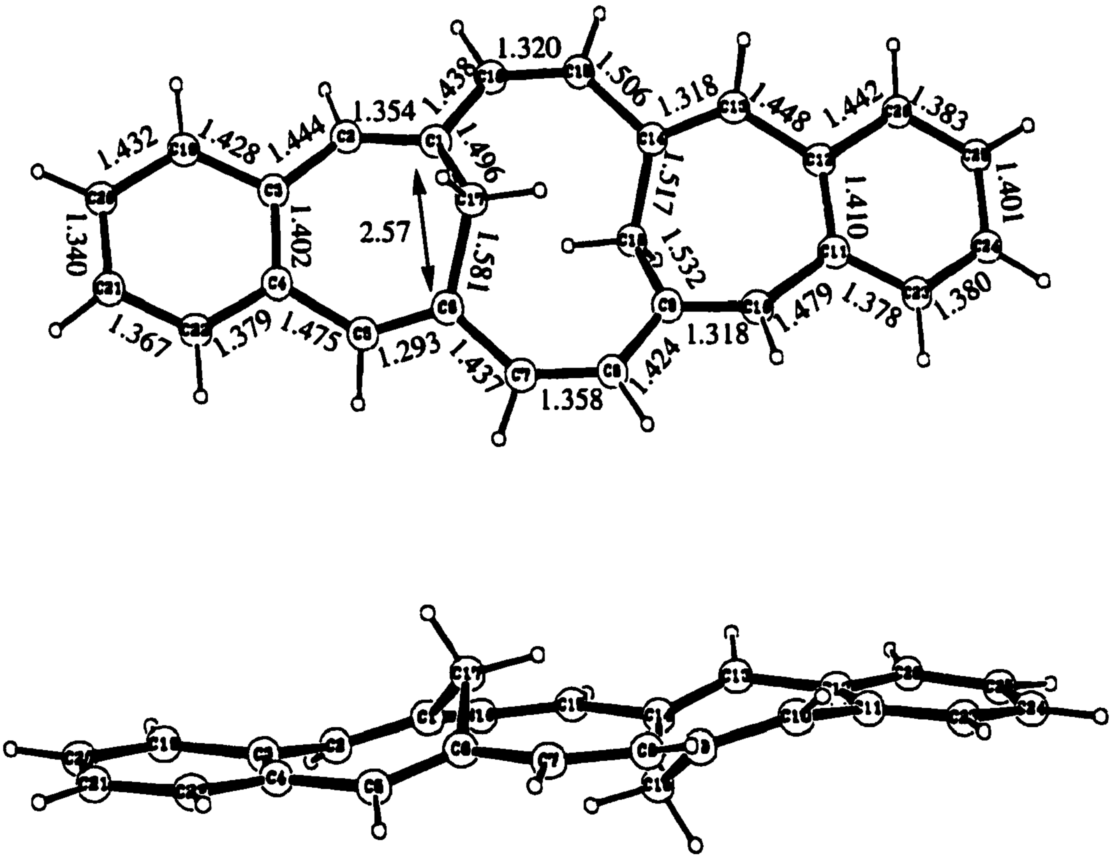


Figure 48 X-ray structure of 3,4:11,12-dibenzo-anti 1,6:9,14-bismethano[16]annulene IV

Variable temperature (dynamic) ^{1}H NMR(400 MHz, C_6D_5Br) of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene **IV** from 21°C to 145°C shows coalescence of the four bridged protons at about 98°C. As the temperature increased, two doublets emerged at δ 3.46 and 4.66 ppm as well as the broadened original. The appearance of the two doublets were observed to be their sharpest and overlapped to be a singlet at δ 4.0 ppm at 145°C. On the other hand, the observation in lower temperature from 21°C to -7.5°C did not show any significant change. Estimated free energy of activation is based on the equation(110).

$$\Delta G_{act.}^{\#} = 4.57\ T_c\ [9.97 + \log(T_c/\Delta\delta)]$$

Where T_c is the coalescence temperature (371 ± 2 °K), Δδ is the frequency separation of the two doublets (441.6 Hz), and 4.57 is the gas constant. $\Delta G_{act.}$ is calculated here to be 16.8 ± 0.1 kcal/mol. All variable temperature ^{1}H NMR analyses were kindly performed by Dr. Mike Blumenstein, Hunter College.

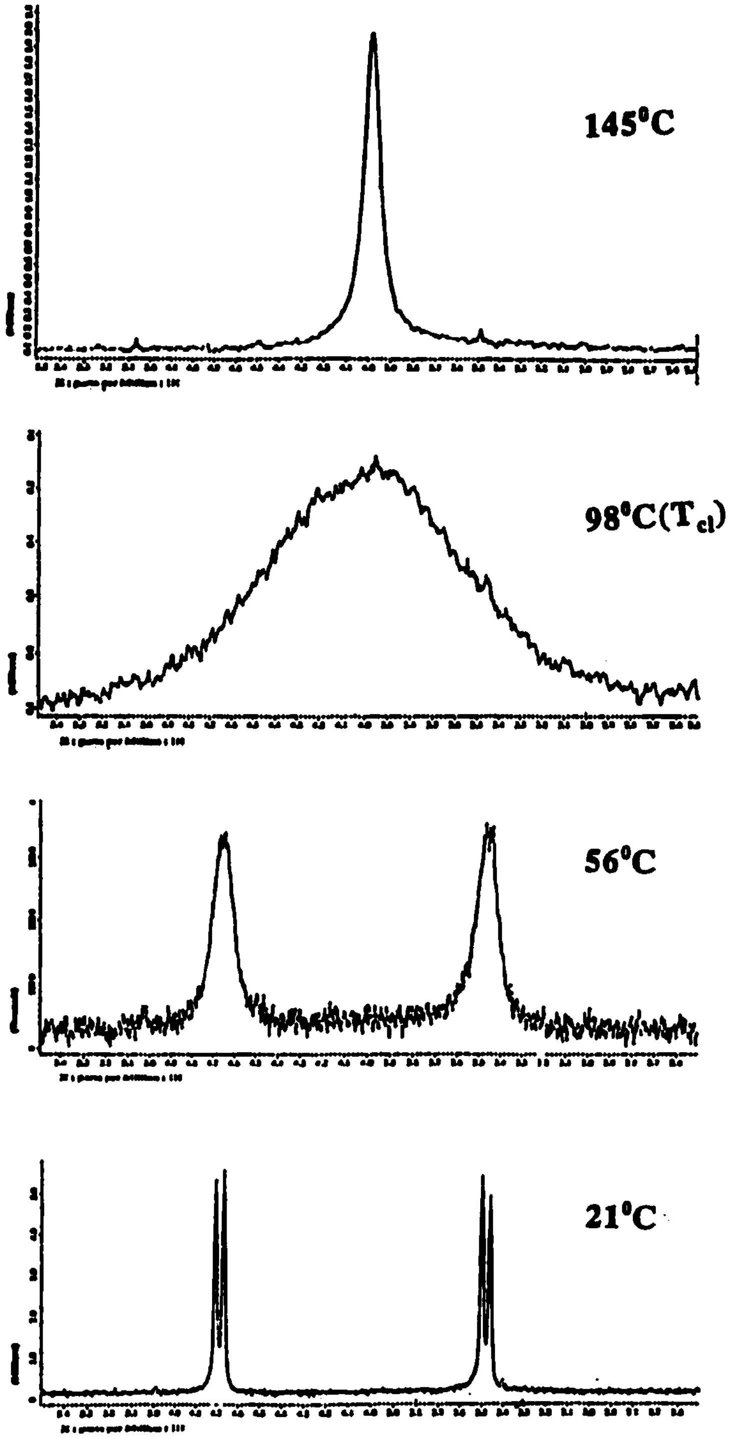
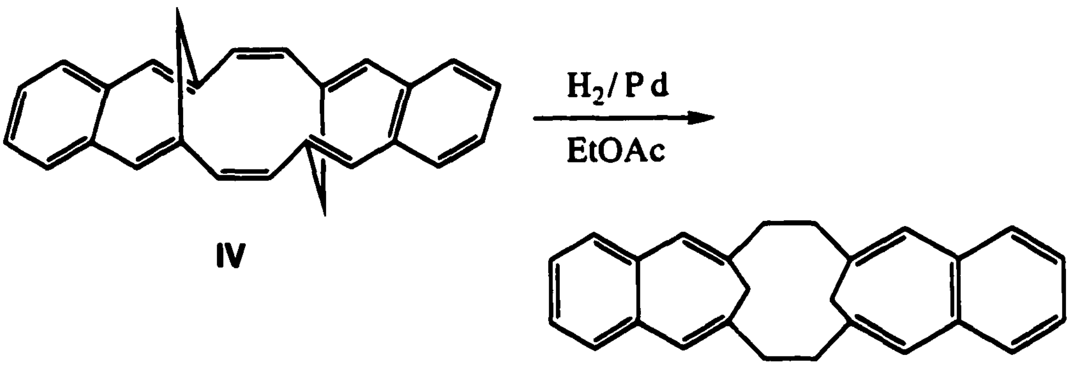


Figure 49 Variable-temperature ^{1}H NMR spectrum of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene IV in C_6D_5Br

2.3.3 The synthesis of 7,8,15,16-tetrahydro-3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene

In order to assess the antiaromaticity in 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene **IV**, we synthesized and investigated the tetrahydro compound **93**. Compound **93** was prepared by hydrogenation of **IV** with $H_2/Pd/C$ in EtOAc as described below.



Scheme 26 The hydrogenation of IV

20 mg (0.06 mmole) of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene **IV** were dissolved in 70 ml of ethylacetate to form an orange solution. The system was filled with nitrogen and a small amount of 5% palladium in charcoal was then added to the

solution. After one evacuation/N_2 flushing cycle, hydrogenation was conducted at R.T.. After absorption of the calculated amount of H_2 (9 ml), the catalyst was removed by filtration. The colorless solution was evaporated and chromatography on SiO_2 gel obtaining a white solid in 32.6% yield.

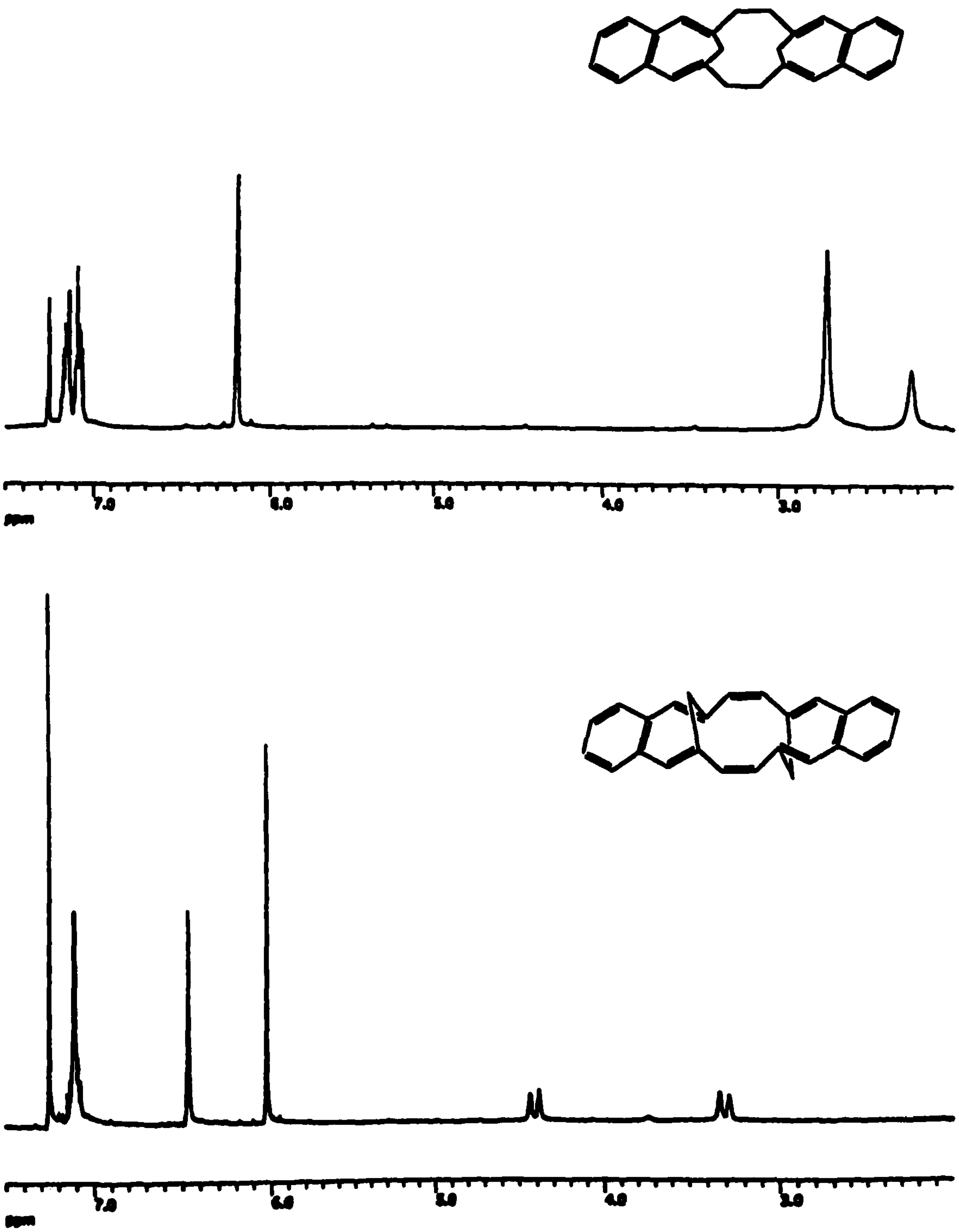
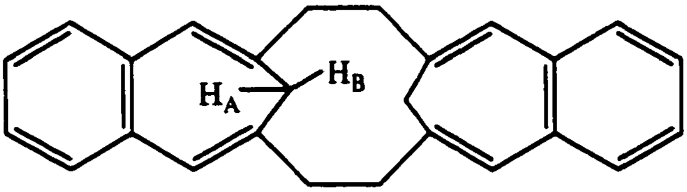


Figure 50 ^{1}H NMR comparative study of 93 and IV

The NMR spectra of **93** and **IV** are shown on **Figure 50**. Noticable is a 1-2 ppm upfield shift for the bridge protons in **93** relative to **IV**. Of interest is the observation that the signals for bridge protons and for the four CH_2 groups appear as broad singlets at 2.24 ppm and 2.74 ppm. This indicates a rapid flipping through the flexible 16 membered ring. A variable temperature dynamic ^1H NMR study confirmed our assumption.



93

As can be seen from **Figure 51**, the brcad singlet at 2.24 ppm has changed at -31°C into an AB system at (2.38, d, 2H, J=12.2 Hz ; 2.00, d, 2H, J=12.7 Hz) for the bridge protons. Lowering the temperature to -41°C caused decoalescense of the signal for the four CH_2 groups into an AA'BB' system at 2.83 and 2.60 ppm. Using a decoalescence temperature of 273.3 ± 2 °K (0.3 ± 2 °C) for the δ=2.24 ^1H NMR signal and a chemical shift difference between the H_A/H_B of $\Delta\delta$= 149.7 Hz, a free energy of activation for **93**, $\Delta G_{act}^{\#}$= 12.8 ±0.1 kcal/mole, was obtained. When the temperature increased to 48 °C, the two broad peaks at 2.74 ppm and 2.24 ppm changed into sharp singlets.

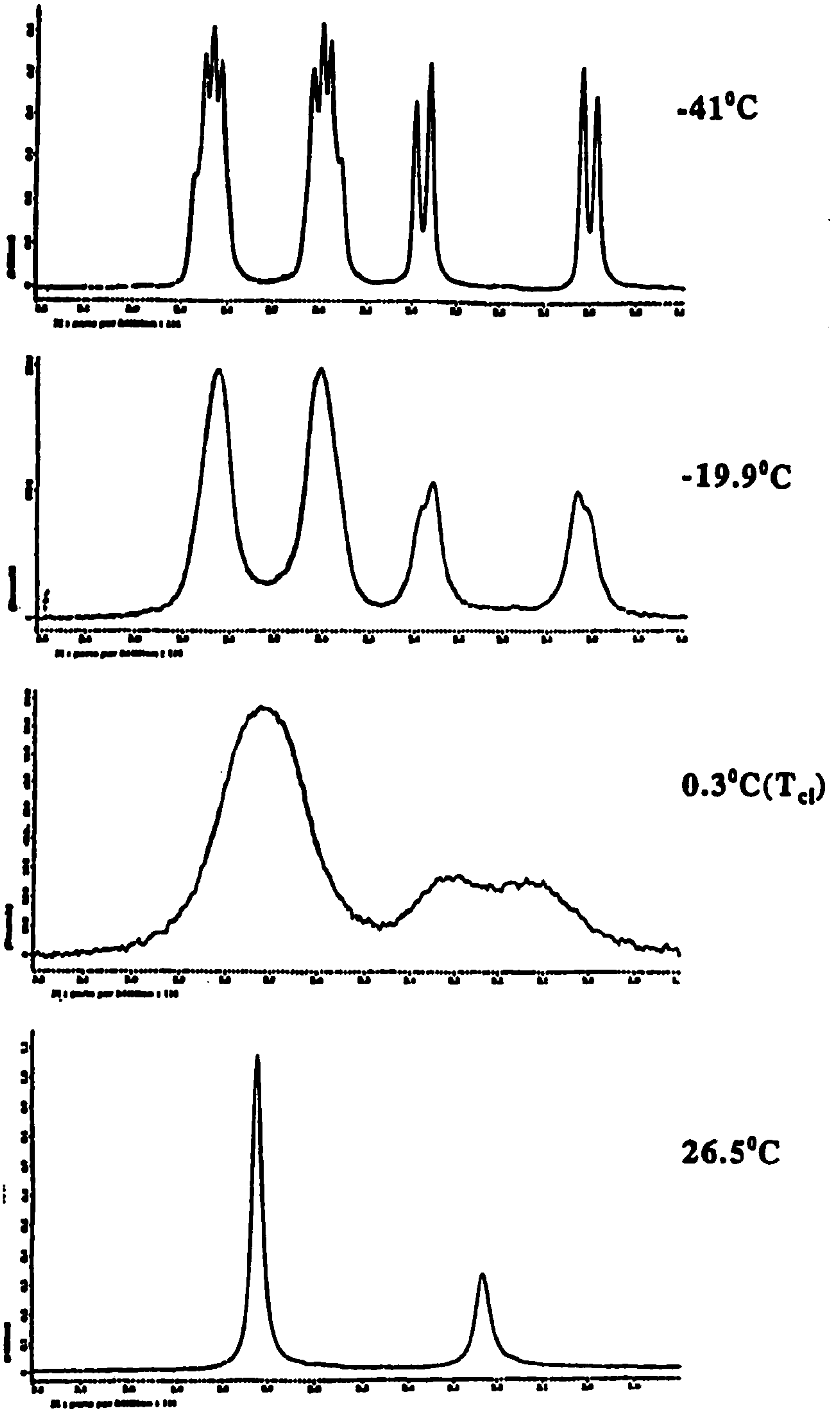
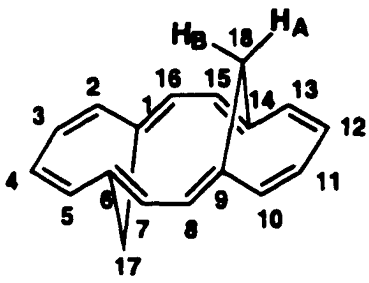
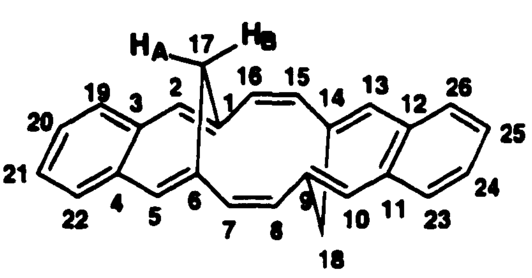


Figure 51 Variable-temperature ^1H NMR spectrum of 3,4:11,12-dibenzo-7,8,15,16-tetrahydro-anti-1,6:9,14-bismethano[16]annulene **93** in $CDCl_3$

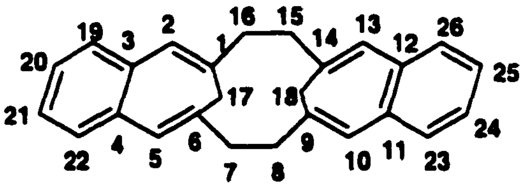
In order to verify our assumption about the ring current effects in **IV**, we not only compared the bridge protons in **IV** and **93**, but also the external protons on the ring, 2-H and 7-H, both of which in dibenzo[16]annulene **IV** shift downfield relative to the parent system **54**. The comparison is shown in the following table.



54



IV



93

Table 11 Chemical shifts (δ ppm in $CDCl_3$) of ^1H NMR for 54, IV, 93

	2-H	3-H	7-H	$17\text{-}H_A$	$17\text{-}H_B$	19-22 H
54	5.09	5.03	4.77	*5.58*	*8.20*	-
IV	6.47	-	6.03	*3.31*	*4.41*	7.08-7.16
93	6.19	-	2.74	*2.24*	*2.24*	7.07-7.18

There are two methods of determining the degree of paratropicity. One method was reported by Mitchell et. al. This method uses the information from models to estimate the percent $\Delta\delta$ of the parent [$\Delta\delta = \delta_{annulene} - \delta_{model}$]. Such a change in $\Delta\delta$ indicates a paramagnetic shielding by the added benzene rings and presents a real reduction in ring current. The other method uses the percent $\Delta\delta$ of the parent [$\Delta\delta = \delta_{annulene} - \delta_{parent}$]. The change in $\Delta\delta$ indicates the amount of reduction in its parent ring. In both calculations, a decrease in paratropicity of [16]annulene is observed on passing from the parent compound **54** to our dibenzo[16]annulene **IV**.

Table 12 Chemical shift data (δ ppm in $CDCl_3$) for 54, IV, 93

	17-H_A $\Delta\delta = \delta - \delta_{model}$			$\%\Delta\delta^*$ of parent	17-H_B $\Delta\delta = \delta - \delta_{model}$			$\%\Delta\delta^*$ of parent
54	5.58			*100%*	8.20			*100%*
IV	3.31		3.34	*32%*	4.41		5.96	*36%*
		1.07				2.17		
93 (model)	2.24				2.24			

* The method was reported by Mitchell "J. Am. Chem. Soc. 1982, 104, 2544"

	17-H_A	$\Delta\delta$	$\Delta\delta/\delta_{parent}$	*paratropicity**	17-H_B	$\Delta\delta$	$\Delta\delta/\delta_{parent}$	*paratropicity**
54	5.58		*1*	100%	8.20		*1*	100%
		2.27				3.79		
IV	3.31		*0.41*	59%	4.41		*0.46*	54%

* paratropicity relative to the parent compound

Based on the results of the NMR investigation of annulenes and benzoannulenes (including naphthalene and biphenylene). Günther proposed a quantitative index, the alternance parameter, Q, which allows one to differentiate between aromatic cyclic conjugated $(4n+2)\pi$ systems ($Q > 1.10$) and anti- or non-aromatic $4n\pi$ systems ($Q < 1.04$). This parameter can be considered as an electronic probe for the π electron structure of [n]annulenes and benzoannulenes(56).

In order to assess the aromaticity change in the fused benzene ring of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene **IV**, the Q value was determined by analysizing the vicinal $^3J_{H\text{-}H}$ coupling constants in the benzene ring at 500 MHZ ^1H NMR. The analysis of the proton NMR of **IV** was carried out analogously to the reported spectral analysis of naphthalene(111). The ^1H NMR spectrum of **IV** was analyzed and its benzene ring was treated as an A_2B_2 system. (Strictly speaking, the protons of benzene rings in **IV** can be considered as A_4B_4, but they can be dealt with approximately as a superposition of two A_2B_2 sets if the spin coupling between protons in different rings is neglected.) The 500 MHz ^1H NMR spectrum of **IV** in $CDCl_3$ is shown in **Figure 52**.

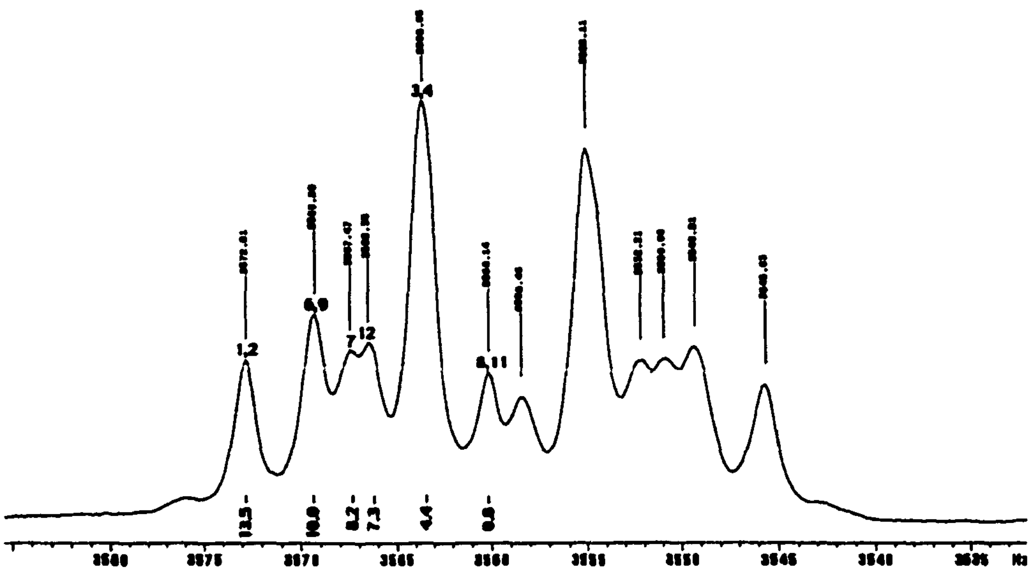


Figure 52 Proton resonance spectrum and assignment of A lines of IV at 500 MHz NMR

On the basis of the assignments below, we are able to obtain numerical values for the parameters from the positions of lines 1,3,9,11 and 12. The assignments were carried out by using the following expressions.

$N = E_1 - E_3 = 9.15$ Hz

$[(\gamma_o\delta)^2 + N^2]^{1/2} = E_1 + E_3 = 17.85$ Hz

$(M^2 + L^2)^{1/2} = E_9 - E_{11} = 9.16$ Hz

$[(\gamma_o\delta + M)^2 + L^2]^{1/2} = E_9 + E_{11} = 10.84$ Hz

To get a complete set of constants, we also need the K value. It cannot be obtained directly, it is usually assumed that K= -M. This corresponds to $J_A = 0$, which is reasonable because the A protons are far apart.

$N = J + J' = 9.15$ Hz

$L = J - J' = 6.38$ Hz

$M = J_A - J_B = -6.57$ Hz

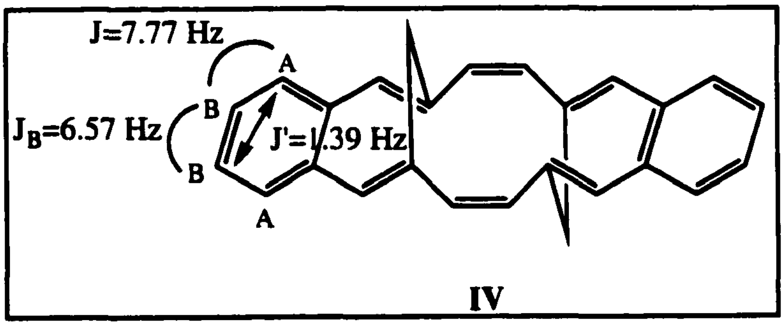
$K = J_A + J_B$

The complete set of basic parameters is then as shown below

$J = 7.77$ Hz (J: the coupling constant between H_A and H_B)

$J' = 1.39$ Hz (J: the long distance coupling constant between H_A and H_B)

$J_B = 6.57$ Hz(J: the coupling constant between H_B and H_B)



IV

As a result of this analysis a Q value was calculated according to the following equation.

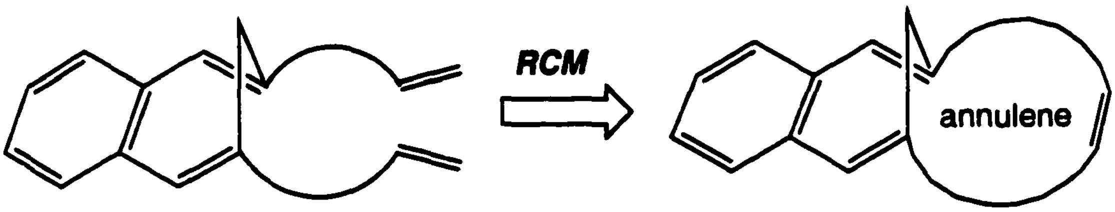
$$Q_{exp} = \frac{7.77 \cdot 0.104 - 0.12}{6.57 \cdot 0.104 - 0.12} = 1.22$$

The Q-value of 1.22 indicates that the aromaticity of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene can be characterized more by the separate contributions of each ring rather than that of the entire π-system periphery.

2.4 The RCM approach to benzannulenes

2.4.1 Introduction

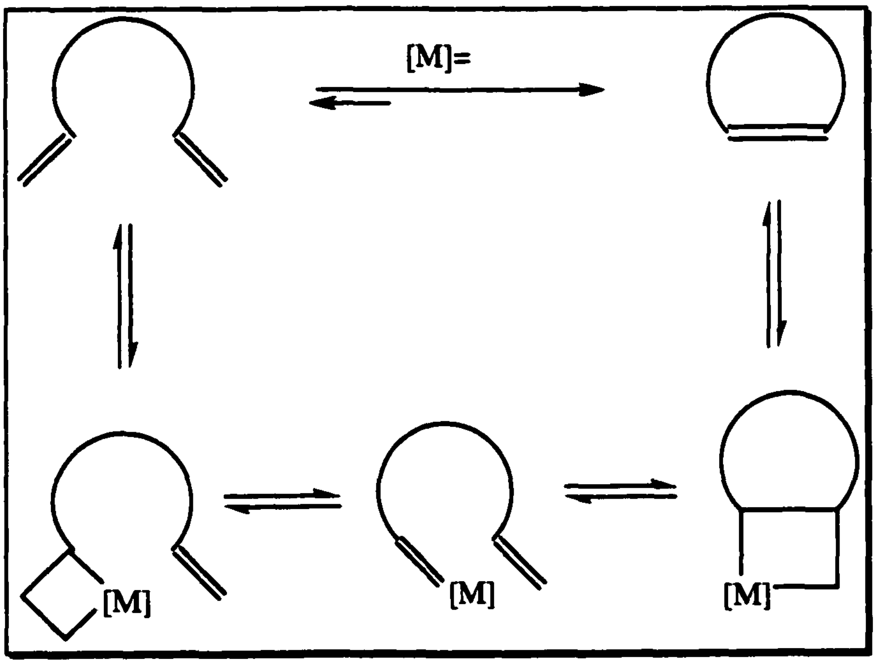
In view of the modest yields obtained for 3,4-benzo-1,6-methano[12]annulene **III** in the cyclizing bis-Wittig reaction, we investigated the feasability of the Ring Closing Metathesis(RCM) approach as a new general efficient synthesis for methano-bridged [10], [12] and [16]annulenes.



Scheme 27 The RCM approach to annulenes

Catalytic Ring Closing Metathesis(RCM) as well as Ring Opening Metathesis(ROM) have emerged over the past 10 years as two of the most promising synthetic methods for carbon-carbon bond formation under very mild conditions(112)(113). Over the last six years, the use of olefin metathesis in synthesis has grown considerably(114) with the availability of well characterized relatively stable catalysts. Ring-Closing Metathesis (RCM) has provided the organic community with new powerful tools for the construction of diversely functionalized complex molecules.

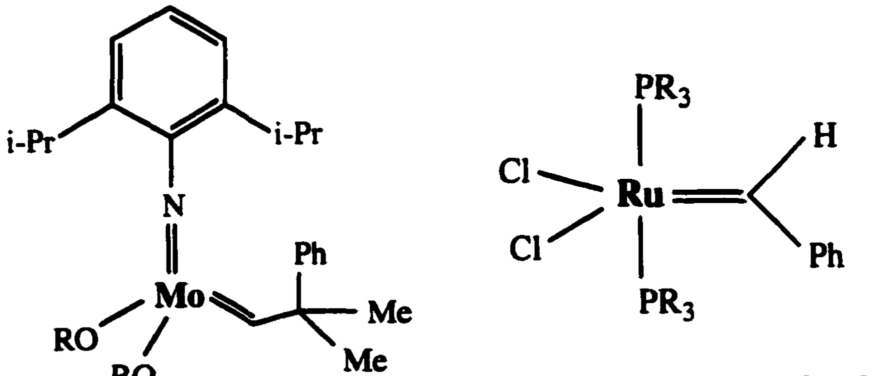
The mechanism(115) now generally accepted for the RCM, based on studies reported by Katz, Schrock, Grubbs and others, involves the reaction of a transition metal carbene complex with the alkene to form a metallacyclobutane. Subsequent bond cleavage leads to an alkene and a new transition metal carbene complex as summarized on **Scheme 28**.



Scheme 28 The mechanism of RCM

In the case of olefin metathesis, a [2+2] cycloaddition occurs between the metal alkylidene and the olefin substrate to produce a metallacyclobutane intermediate. The steps are reversible and the reaction can be characterized as thermodynamically controlled.

Several early transition metal based catalysts and catalytic systems have been utilized such as the tungsten-based reagents (WCl_6-$EtAlCl_2$ or WCl_6-$SnMe_4$)(116)(117) and the titanium-based Tebbe reagent(118) (Cp_2Ti-Me,Cl-$AlMe_2$) and others. But due to the limitation of functional group tolerance in early reports, advances in catalyst design have focused on increasing the functional group tolerance. Two well-defined and highly active catalysts that have higher tolerance for functional groups were developed. One is the molybdenum-based(119) catalyst, developed by Schrock et al. and the other is the ruthenium-based(120) catalyst, developed by Grubbs and his coworkers. Both catalysts are now commercially available(121).



RO= $(CF_3)_2(CH_3)CO$

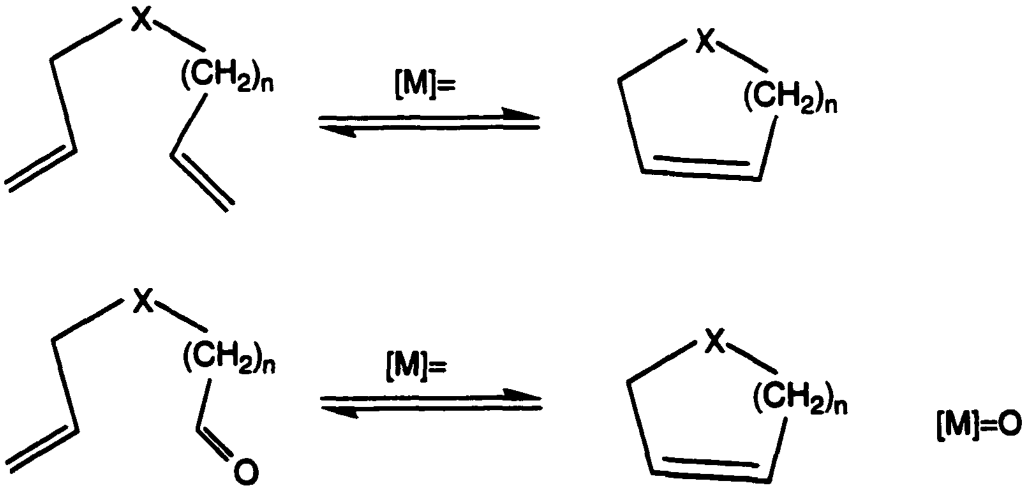
R= Ph, Cy, Cp

Schrock's catalyst

Grubbs' catalyst

Figure 53 Two well-defined catalysts

In general, RCM has found the widest use in the metathesis of carbon-carbon double bond forming strategies that result from olefins or olefinic ketones. For example, this method is employed in the syntheses of carbo- and heterocyclic products containing five to seventeen membered rings by using di-, tri- and tetra- substituted olefins(122)(123). In addition, RCM has been used to prepare numerous heterocyclic systems(124), enol ethers, catenanes, crown ethers, biologically active alkaloids and complex polycyclic systems(125). Furthermore, a large number of natural products(126) and optically active compounds(127) of general interest have been reported by using RCM as one of the key steps.

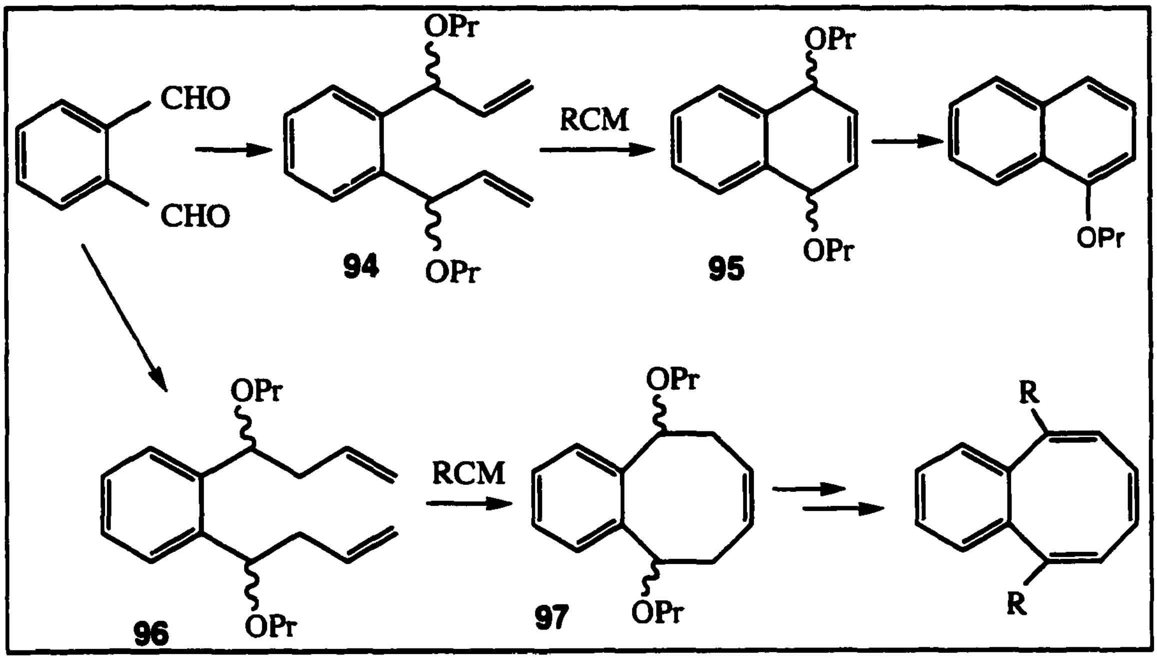


Scheme 29 The two general representatives for RCM

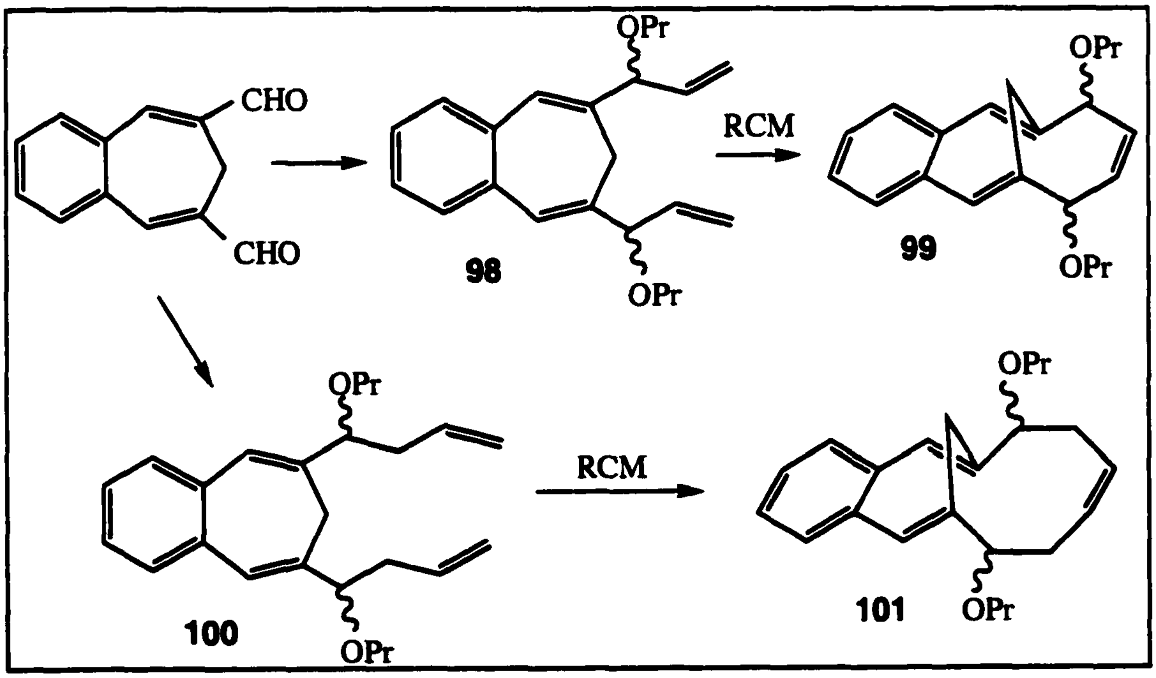
By comparison, the molybdenum-based catalyst is less tolerant towards different functional groups and more sensitive to O_2, H_2O, alcohols and carboxylic acids than the ruthenium complex. The ruthenium complex is also more readily available than the molybdenum-based catalyst and has therefore found a wider range of application. For that reason, the major part in our investigation on the Ring Closing Metathesis (RCM) was carried out by using the Grubbs' catalyst.

The RCM strategy towards 3,4-benz-1,6-methano[10]annulene **I** and 3,4-benz-1,6-methano[12]annulene **III** is outlined below. As mentioned before, RCM has emerged as one of the most powerful new method for the formation of carbo and heterocycles. But to the best of our knowledge, application of this valuable new method towards the synthesis of annulenes has not been reported.

The extension of this new approach to other systems is currently under investigation in our laboratory. The sequence can be summarized as shown in **Schemes 30 & 31**:
O-protected dialcohols **94, 96, 98, 100** readily available from the corresponding dialdehydes and Grignard reagents, are subjected to the Ring Closing Olefin Metathesis (RCM) using the ruthenium carbene complex reported by Grubbs. Subsequent functionalization leads to the corresponding fully conjugated systems.

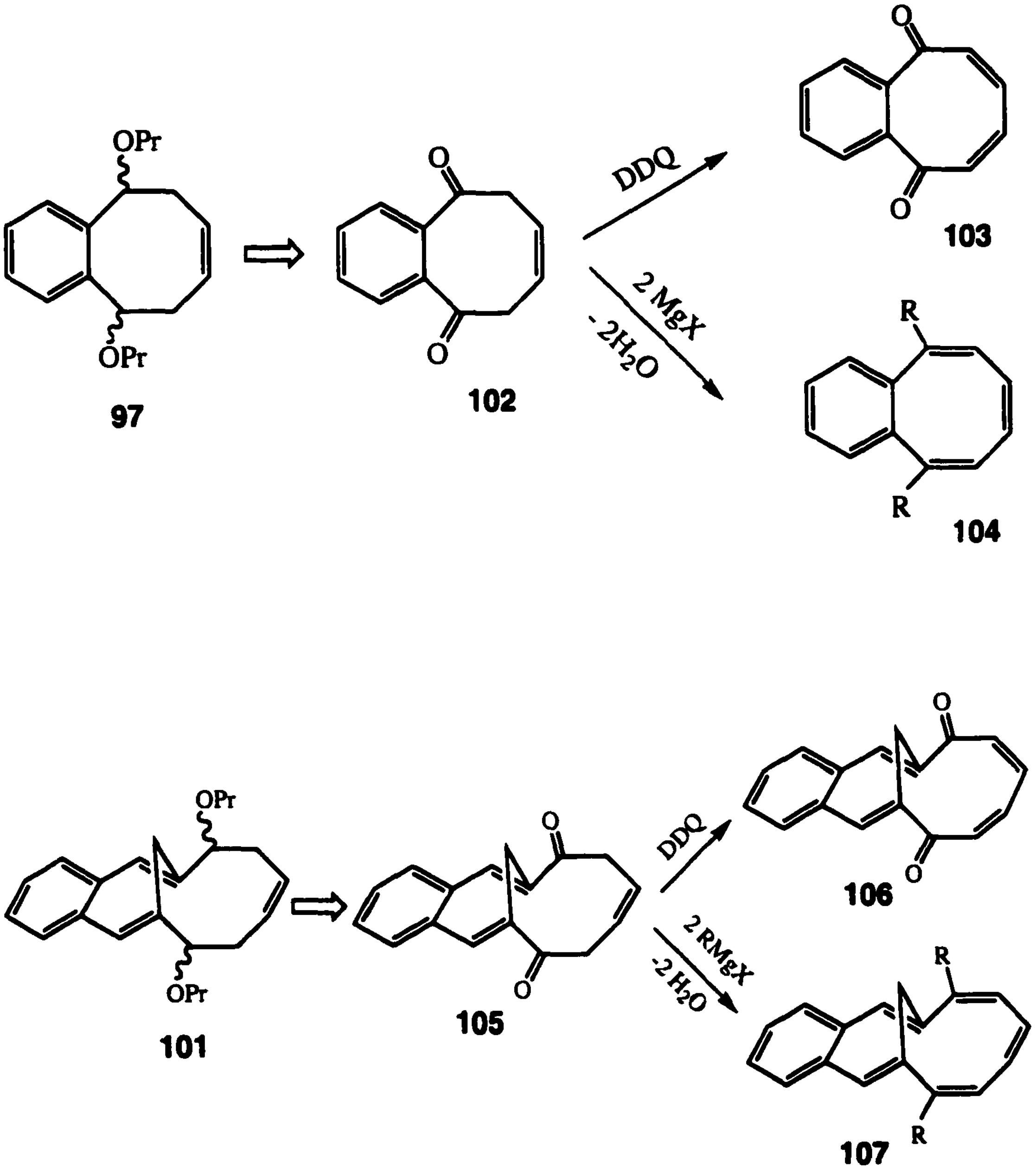


Scheme 30 The Ring Closing Metathesis (RCM) approach A



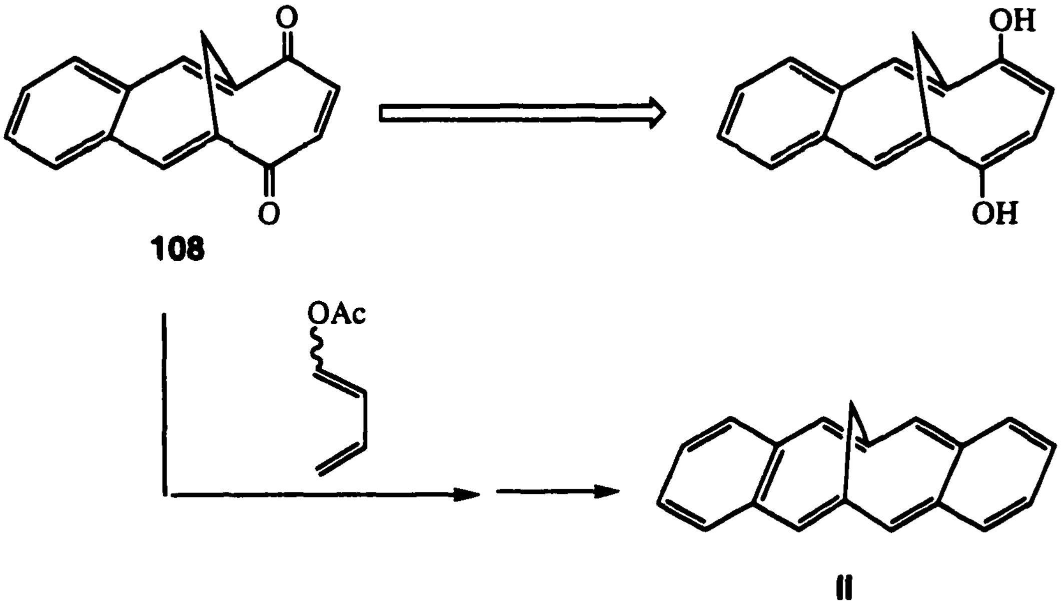
Scheme 31 The Ring Closing Metathesis (RCM) approach B

As part of this thesis, we investigated the RCM, starting with the protected alcohols such as **94**, **96**, **98** and **100** to form the cyclic olefins **95**, **97**, **99** and **101**. The advantage of this strategy is that the starting materials are readily available from o-phthalaldehyde or 3,4-benzcycloheptatriene-1,6-dialdehyde **63** and vinyl- or allyl-magnesium halide. In addition, The RCM products **97**, **99** and **101** can in principle be converted into the respective diketones **102**, **108** and **105**. These ketones are valuable intermediates for the formation of the quinones or the 7,12-disubstituted 3,4-benzo-1,6-methano [12]annulene **107** and 3,8-disubstituted benzocyclooctatetraene **104**. Compounds **103** and **106** allow us to investigate the effect of benzannelation on the quinone / hydroquinone redox equilibrium in these systems.



Scheme 32 The applications for the RCM approach

Moreover, diketone **108** is not only used for the investigation of the equilibrium between quinone and hydroquinone, but also is expected to undergo Diels-Alder reaction then further functionalization to obtain the yet unknown 3,4,8,9-dibenzo-1,6-methano[10]annulene **II**.

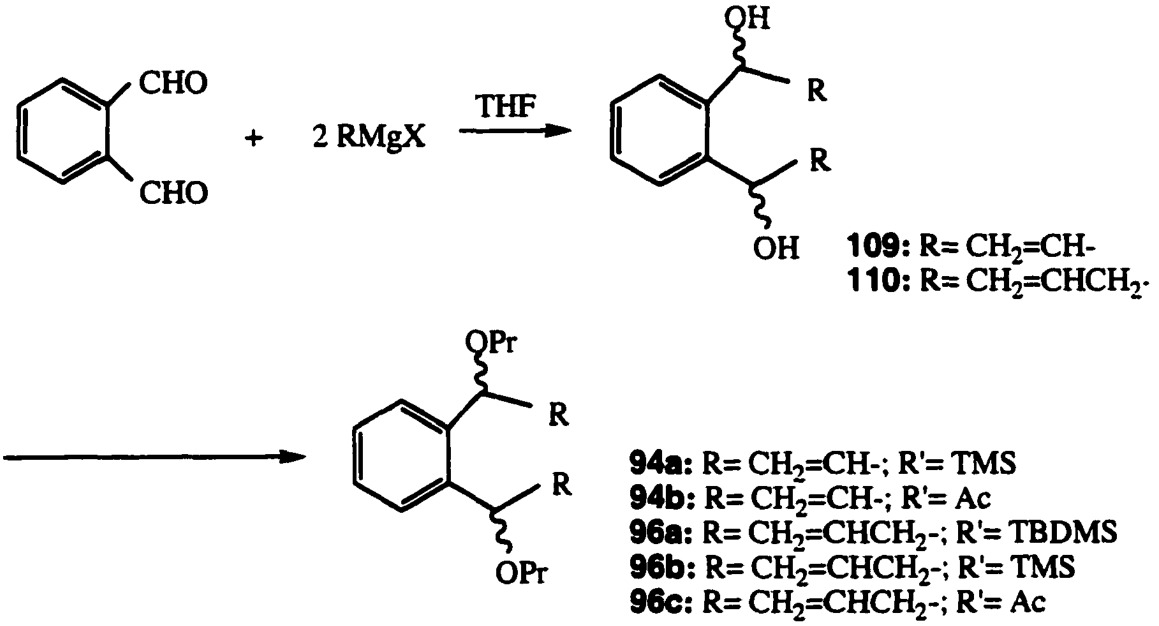


Scheme 33 The approach towards 3,4,8,9-dibenzo[10]annulene II

2.4.2 Results and Discussion

I. O-Phthalaldehyde series

The reaction of o-phthalaldehyde with excess vinylmagnesium bromide in THF(128) gave the diols **109** as a mixture of diastereomers. For the RCM reaction, the diol mixture **109** was converted into its trimethylsilyl ether **94a** and acetate **94b** using standard procedures(129). Analogously, the reaction of o-phthalaldehyde with allylmagnesium chloride in THF gave the diallyl alcohol **110** in 74% yield. The OH groups in the mixture of diastereomers were protected by t-butyldimethylsilyl chloride to give **96a**, trimethylsilyl chloride to give **96b** and acetic anhydride to give **96c** using standard procedures(129).



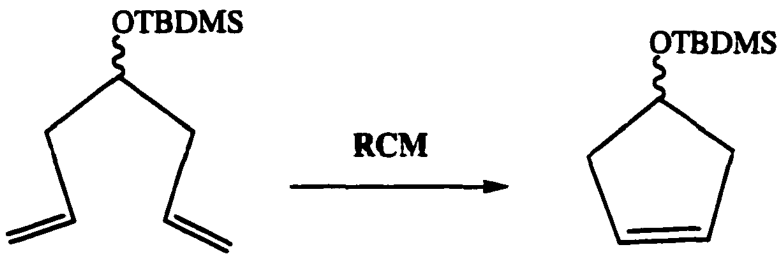
109: R= CH_2=CH-
110: R= CH_2=$CHCH_2$-

94a: R= CH_2=CH-; R'= TMS
94b: R= CH_2=CH-; R'= Ac
96a: R= CH_2=$CHCH_2$-; R'= TBDMS
96b: R= CH_2=$CHCH_2$-; R'= TMS
96c: R= CH_2=$CHCH_2$-; R'= Ac

Scheme 34 The preparation of the precursors 94 and 96

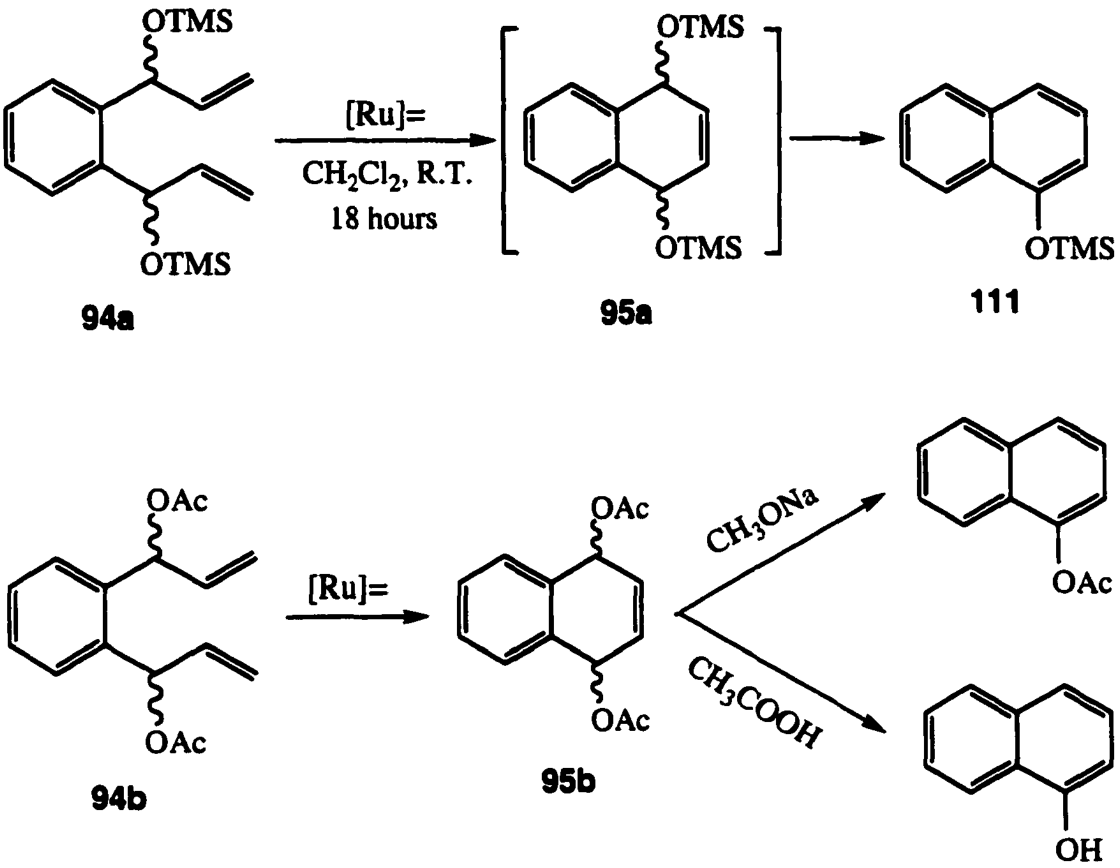
For the RCM reaction with the ruthenium catalyst, the protected alcohols were dissolved in CH_2Cl_2 (0.02M) under N_2 and 5 mole% of Ru catalyst were added. The reaction was monitored by TLC and ^1H NMR.

In order to test the reactivity of the catalyst each time before using it for the main reaction, we used the following synthesis to see if the catalyst was still active(130). The reaction was monitored by GC/MS and TLC.



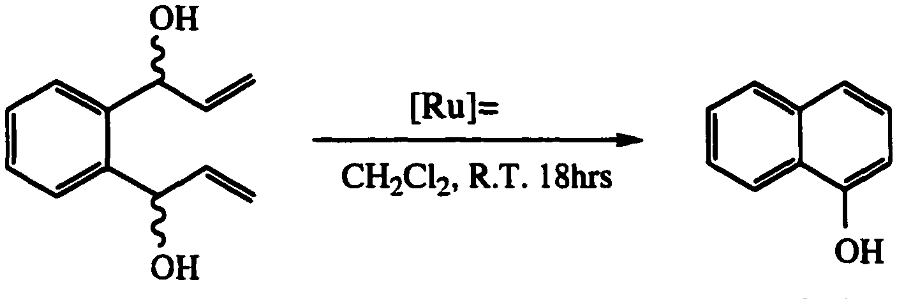
Scheme 35 Testing the reactivity of the catalyst

In the series of reacting of phthalaldehyde with vinylmagnesium bromide. Compound **95a**, the expected product of the RCM derived from **94a**, could not be observed by ^1H NMR. Instead the aromatized 1-protected naphthol **111** was obtained. However, the RCM of the diacetoxy compound **94b** gave an excellent 98% yield of the 1,4-diacetoxy-1,4-dihydronaphthalene **95b**. Acid or base treatment of **95b** lead to aromatization as expected.



Scheme 36 The RCM approach in the phthalaldehyde series I

In view of the good yield in the Ring Closing Olefin Metathesis step, we used the unprotected diol **109** with the Ru catalyst. Surprisingly, we obtained 1-naphthol in good yield. This result was somewhat unexpected since in all other cases OH groups had to be protected before the RCM reaction. This appears to be the only case known to us where a free OH was compatible with the Ru catalyst.



109

Scheme 37 The RCM based synthesis of 1-naphthol

The reaction of allylmagnesium chloride with o-phthalaldehyde gave the known diol **110** in 74% yield. Protection of the diol **110** by t-butyldimethylsilyl chloride, trimethylsilyl chloride and acetic anhydride gave the protected diols **96a, 96b** and **96c** respectively. Ring Closing Olefin Metathesis yielded the t-butyldimethylsilyl protected cyclic diol **97a** in 64% yield (84% conversion yield), the trimethylsilyl protected cyclic diol **97b** in 66% yield (85% conversion yield) and acetate protected cyclic diol **97c** in 55% yield (88% conversion yield). Deprotection of compounds **97a** and **97b** with 1M tetrabutylammonium floride in THF and of compound **97c** with 3N NaOH in MeOH gave the cyclic diol **112** in good yield. The cyclic diol **112** was converted into benzocyclooctatetraene in 81% yield by treating it with thionyl chloride in pyridine followed by potassium tert-butoxide in THF.

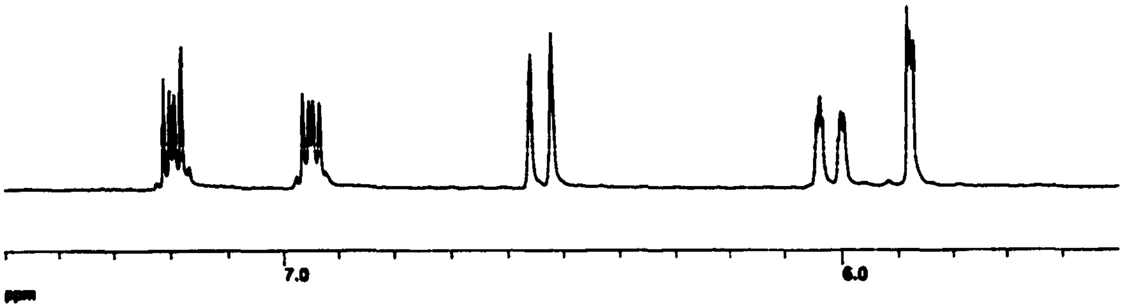
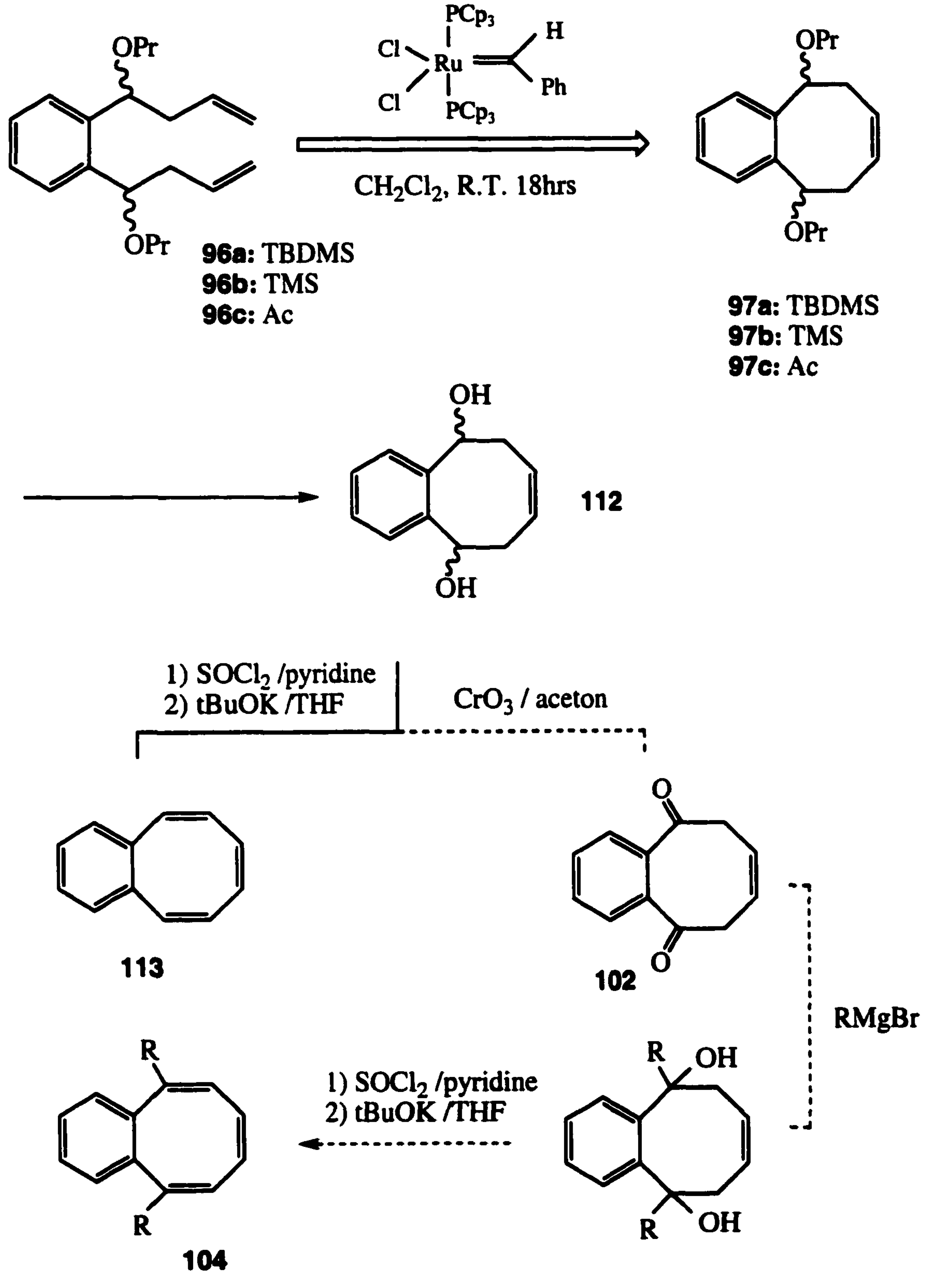
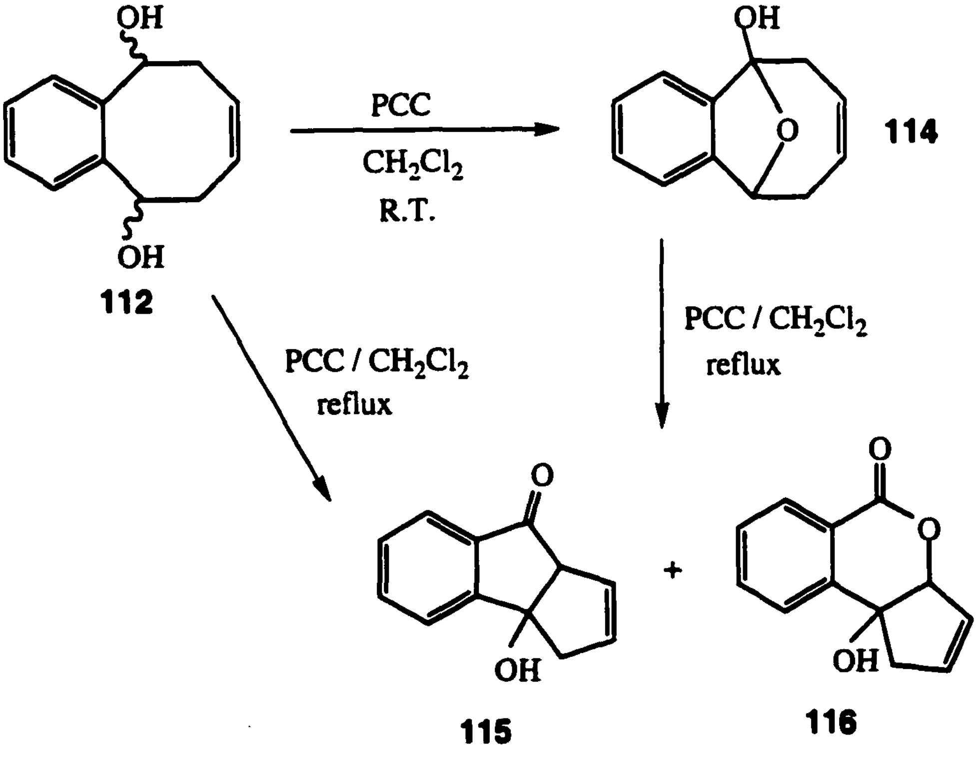


Figure 54 ^{1}H NMR of benzocyclooctatetraene



Scheme 38 The RCM approach in the phthalaldehyde series II

In order to obtain 3,8-disubstituted-benzocyclooctatetraenes, we attempted to oxidize the cyclic diol **112** to the diketone **102** by CrO_3 followed by further functionalization. To our surprise, normal oxidation of the cyclic diol **112** with PCC in CH_2Cl_2 at R.T. gave only hemiketal **114** in 77% yield. We further treated the hemiketal **114** with 5 equiv of PCC and refluxed the mixture for two days in methylene chloride in an attempt to obtain the desired dione **102**. But instead, we only isolated the major compound **115** caused by an apparent intromolecular aldol addition. A small amount of compound **116** resulting from Baeyer-Villiger oxidation was also observed.



Scheme 39 The oxidation of diol 112

Streitwieser's group at Berkeley have reported the preparation of 1,5-cyclooctandione(131) from 1,5-cyclooctandiol and 7 equiv of PCC (3.5 equiv per alcohol functionality) in refluxing methylene chloride for 3 days. With this in mind, we applied the same conditions to oxidize diol **112** in order to get the desired dione **102**. Unfortunately, again, we only isolated compounds **115** and **116**.

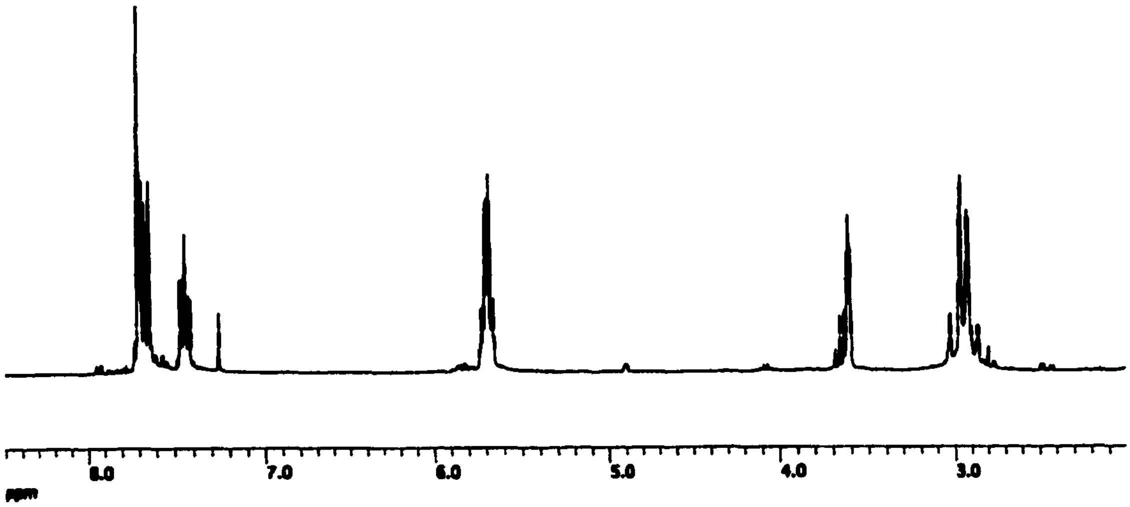


Figure 55 ^{1}H NMR of 115

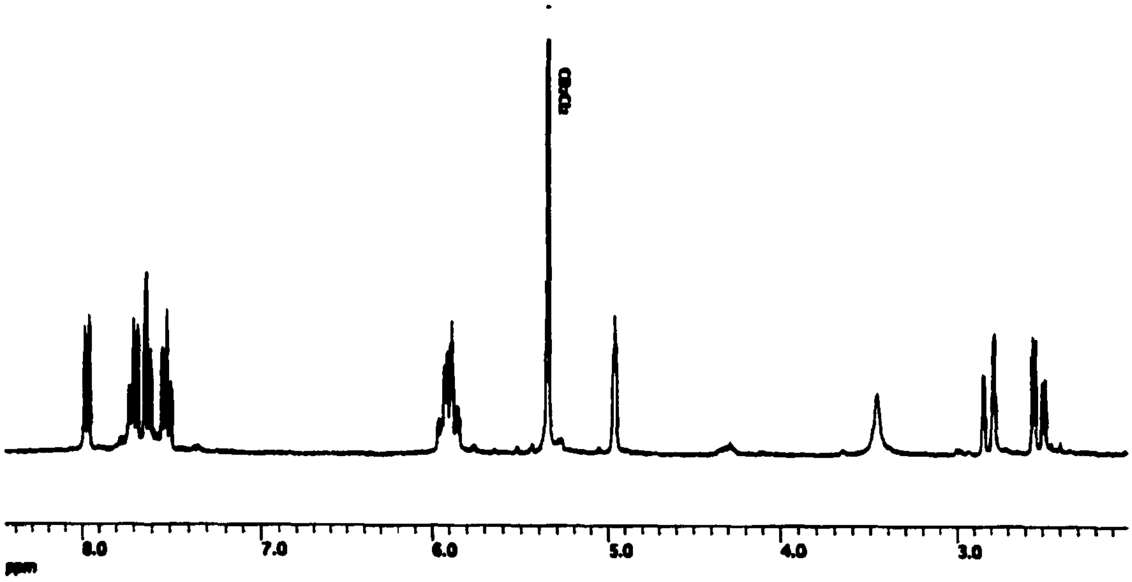
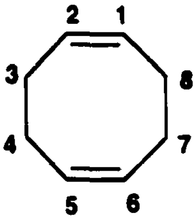
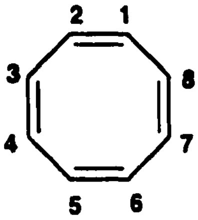


Figure 56 ^{1}H NMR of 116

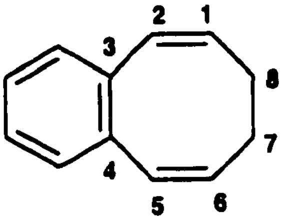
As part of our investigation regarding the effect of benzannelation on the antiaromaticity of cyclooctatetraene, we measured and compared the ^{1}H NMR spectra for compounds **117**, **118**, **75**, **113**$^{(132)}$. The following table indicates that the fusion of a benzene ring results in a downfield shift of the proton NMR signals on cyclooctatetraene, but it does not show a significant change in the ring current of cyclooctatetraene.



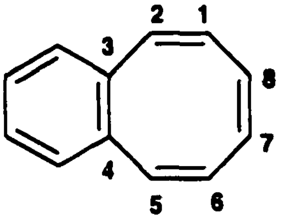
117



118



75



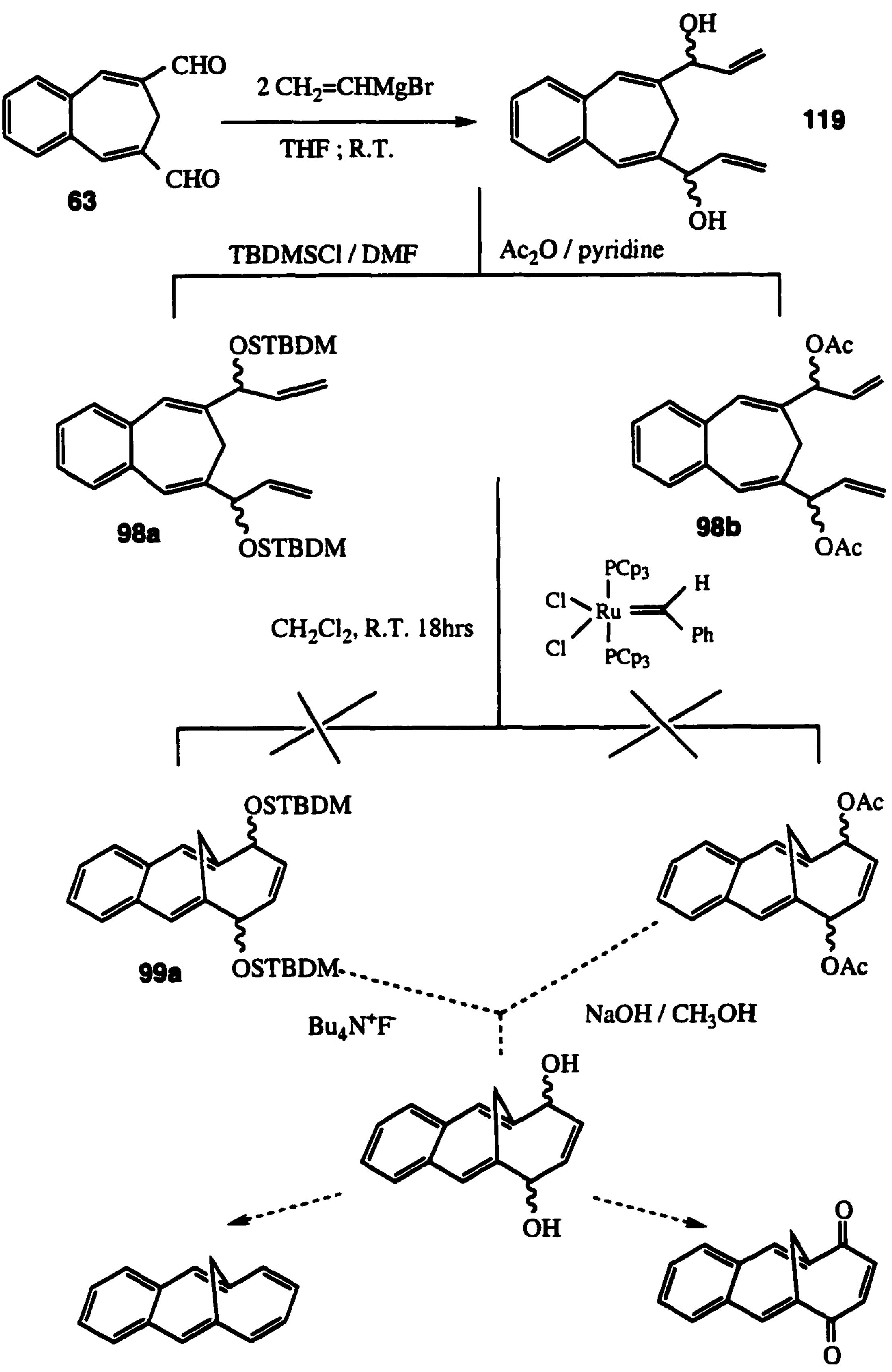
113

Table 13 Chemical shifts (δ values in $CDCl_3$) of the protons of 117, 118, 75, 113

	5-H	6-H	7-H	benzene
117	5.58	5.58	2.37	-
118	5.79	5.79	5.79	-
75	6.55	5.94	2.33	7.22-7.11
113	6.54	6.02	5.88	7.21-6.94

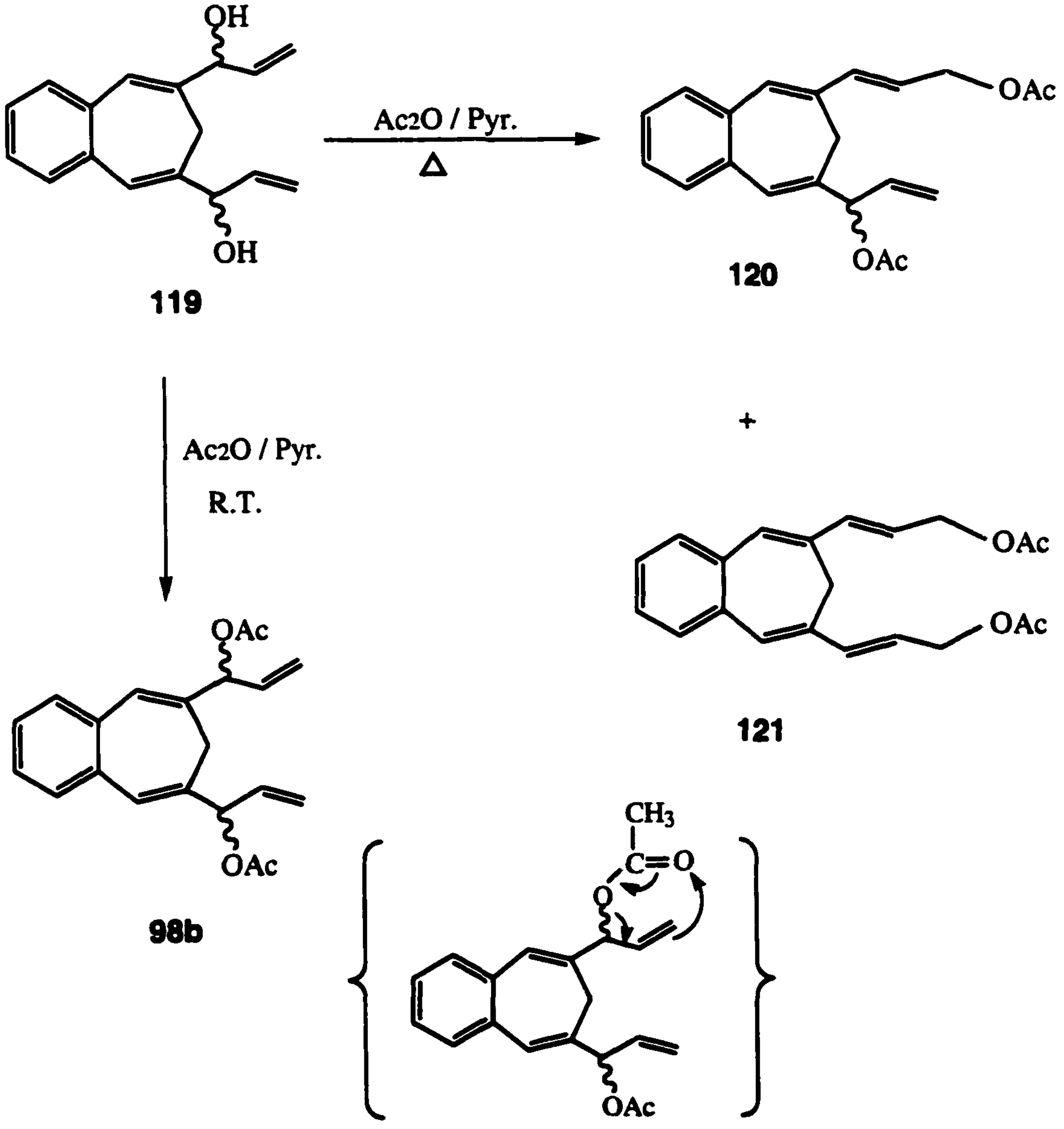
II. 3,4-benzcycloheptatriene-1,6-dialdehyde Series

The treatment of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde with vinyl magnesium bromide, yielded the diol **119** as a mixture of diastereomers in 86% yield. The diol **119** was then converted into the protected diols **98a** and **98b** by using the t-butyldimethylsilyl chloride and acetic anhydride respectively. Unfortunately, the RCM of t-butyldimethylsilyl ether protected diol **98a** and the RCM of the acetate protected diol **98b** did not yield any cyclic compound (only in one case did we observe the t-butyl dimethylsilyl ether protected cyclic diol **99a** in the reaction mixture according to the GC-MS). Each time we only recovered the starting material back. The ruthenium-based catalyst is selective for less hindered and less strained olefins. Therefore, we believe that the molecule of benzo[10]annulene **I** could be too strained and rigid to obtain. Attempting the RCM with the more reactive molybdenum-based catalyst did not yield any cyclic product.



Scheme 40 The RCM approach towards I

As described before, treatment of the diol **119** with acetic anhydride in pyridine at room temperature gave the diacetate **98b**. But when the reaction was carried out at 45°C, the desired compound **98b** was not detected. Instead, we only observed compounds **120** and **121** caused by a hetero-Cope rearrangement of **98b**.



Scheme 41 The hetero-Cope rearrangement of 98b

However, we successfully developed a new synthesis for 3,4-benzo-1,6-methano[12]annulene **III** using RCM methodology. Treatment of dialdehyde **63** with excess allyl magnesium chloride gave the diol **122** in 96% yield. The RCM of diol **63** did not succeed, so we protected the dihydroxy groups with t-butyldimethylsilyl chloride to give **100a** and with acetic anhydride to give **100b**. The RCM was then run in methylene chloride by using 5 mole% of Ru catalyst, reacting overnight at room temperature. The RCM products of t-butyldimethylsilyl protected cyclic diol **101a** was obtained in 88% yield and of the acetate protected cyclic diol **101b** was obtained in 81% yield. After deprotection we isolated two isomers of the cyclic diol **123** as white solids by flash chromatography (hexane/ethyl acetate=1/1). The mp of isomer A is 168-169 ^{0}C and IR (KBr, cm^{-1}) showed that two hydroxy groups are at 3336 and 3215 ; the mp of isomer B is 188-189 ^{0}C and IR showed that two hydroxy groups are at 3565 and 3368. The comparison of ^{1}H NMR spectra for two isomers is shown below.

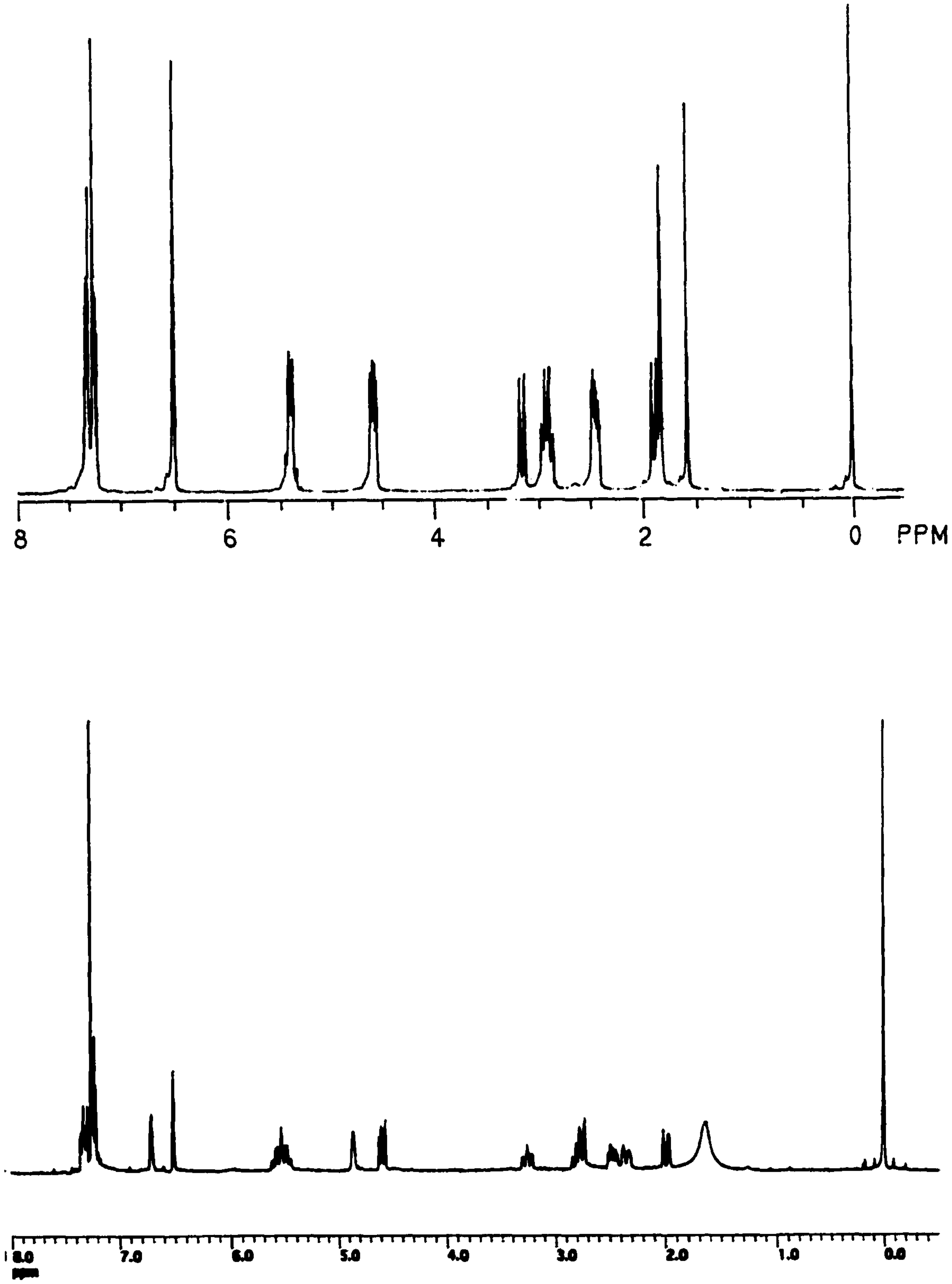
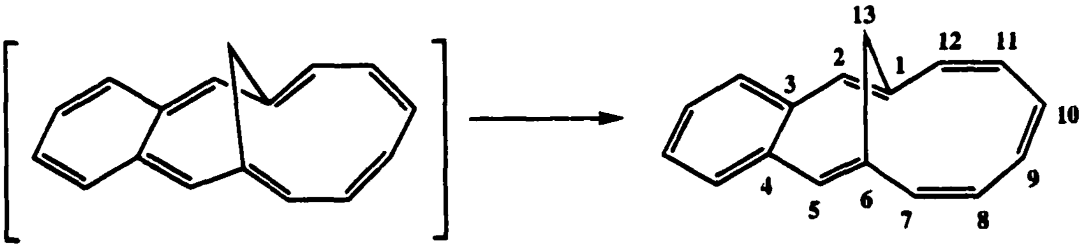


Figure 57 ^{1}H NMR comparative study of two isomers of cyclic diol **123**

Conversion of the diols **123** into 3,4-benzo-1,6-methano [12]annulene **III** was accomplished by treating the OH groups with thionyl chloride, followed by t-BuOK in THF for four hours at reflux. Flash chromatography yielded pale yellow crystals of 3,4-benzo-1,6-methano[12]annulene **III** in 73% yield. **mp:** 105-106°C; **^{1}H NMR** (300 MHz, CD_2Cl_2): δ(ppm)= 7.22-7.13 (AA'BB', 4H), 6.36 (s, 2H), 6.02 (dt, 1H, J= 12 Hz, J= 1.4 Hz), 5.87 (d, 2H, J= 12 Hz), 5.78 (d, 2H, J= 3.9 Hz), 5.69 (dt, 2H, J= 13.1 Hz), 2.37 (d, 1H, J= 11.7 Hz); **^{13}C NMR**: δ= 138.6, 138.1, 130.9, 130.7, 130.5, 130.4, 129.1, 126.4, 26.9; **M S** (EI/70 eV) m/z: M$^+$ 218(100%).



III

Figure 58 3,4-benzo-1,6-methano[12]annulene III

The ^{1}H NMR spectrum of 3,4-benzo-1,6-methano[12]annulene **III**, similar to that of the nonannelated 1,6-methano[12]annulene **15**$^{(39)}$, is indicative of the presence of a paramagnetic ring current. The resonances of the annulene protons occur at relatively high field [5.87 ppm(H-7,12), 5.69 ppm(H-8,11) and 5.78 ppm(H-9,10)] with $J_{7,8}$=12 Hz, $J_{8,9}$=3.9 Hz, whereas those of the bridge protons appear at relatively low field (AX-system at 2.37 ppm and 6.01 ppm) with the rather large $\Delta\delta$=3.64 ppm. By an examination of the vicinal coupling constant $J_{7,8}$ and $J_{8,9}$, the alternation of these couplings not only demonstrates the presence of localized π-bonds, but due to the relationship $J_{7,8} > J_{8,9}$, also clearly indicates the hydrocarbon must be present almost exclusively as the valence tautomer **III**.

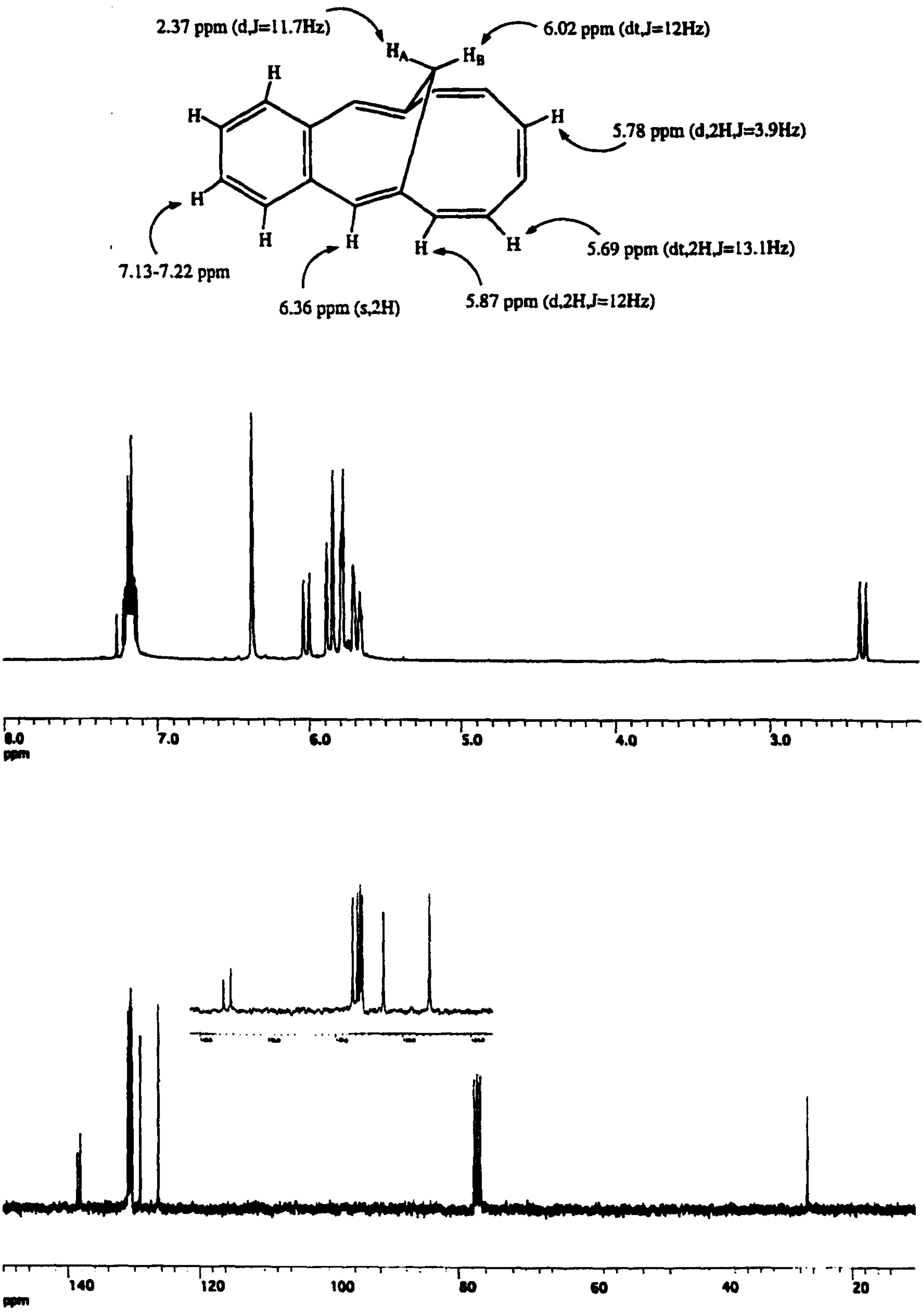


Figure 59 ^{1}H and ^{13}C NMR of III

In order to obtain 7,12-disubstituted-3,4-benzo-1,6-methano [12]annulene (by Grignard reagent) and also to study the effect of benzannelation on the hydroquinone/quinone redox equilibrium, the diketone **105** has been synthesized in 31% isolated yield by treating the cyclic diol **123** with chromic acid in acetone. **mp:** 202 (decomp.); **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm) indicated that four benzene protons at 7.60-7.42 (m), olefinic protons at 7.58 (s, 2H) and 5.58 (t, 2H, J= 6 Hz), aliphatic protons at 4.26 (t, 2H, J= 10.9 Hz) and 3.16 (dd, 2H, J= 11.9 Hz, J= 4.7 Hz), the bridged protons at 3.73 (d, 1H, J=14.7 Hz) and 2.16 (d, 1H, J= 15 Hz); **^{13}C NMR** indicated that the peak of carbonyl groups at 198.8, six peaks of olefinic carbon at 136.2, 136.0, 135.5, 132.3, 128.4, 126.7 and two peaks of aliphatic carbon at 41.4, 27.0; **IR** (KBr, cm^{-1}) indicated that the C=O and C=C stretching in α,β-unsaturated ketones at 1673.2 and 1588.1.

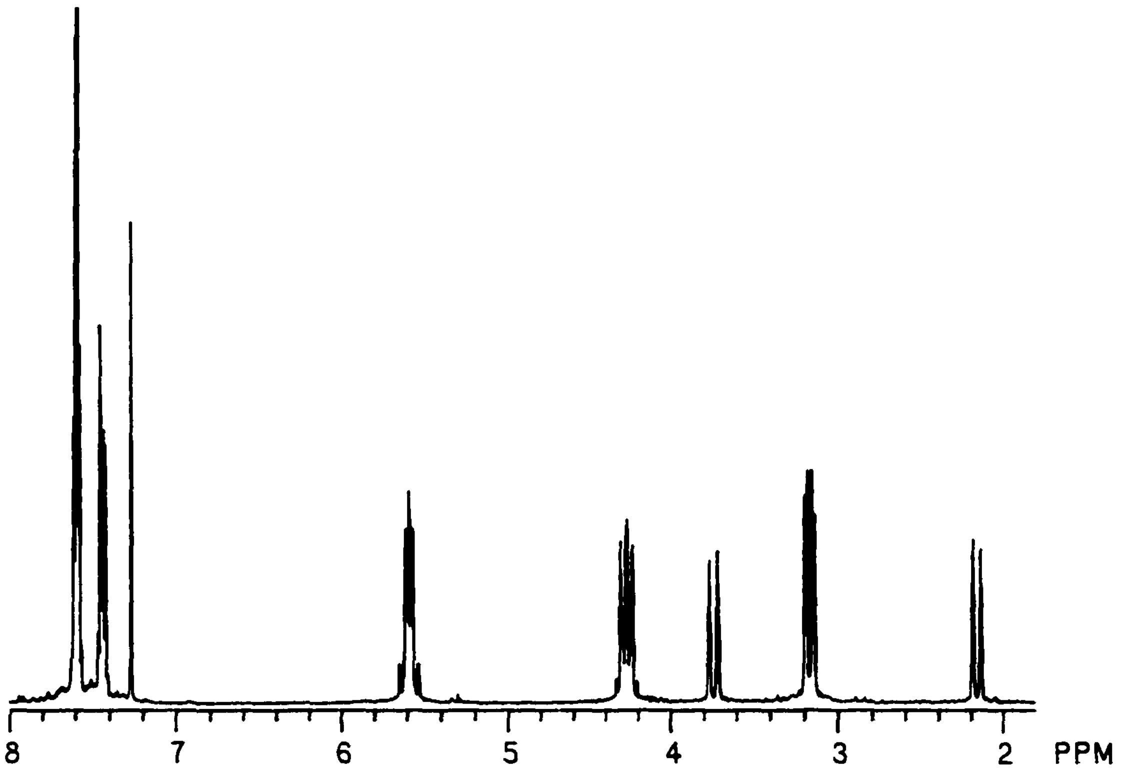
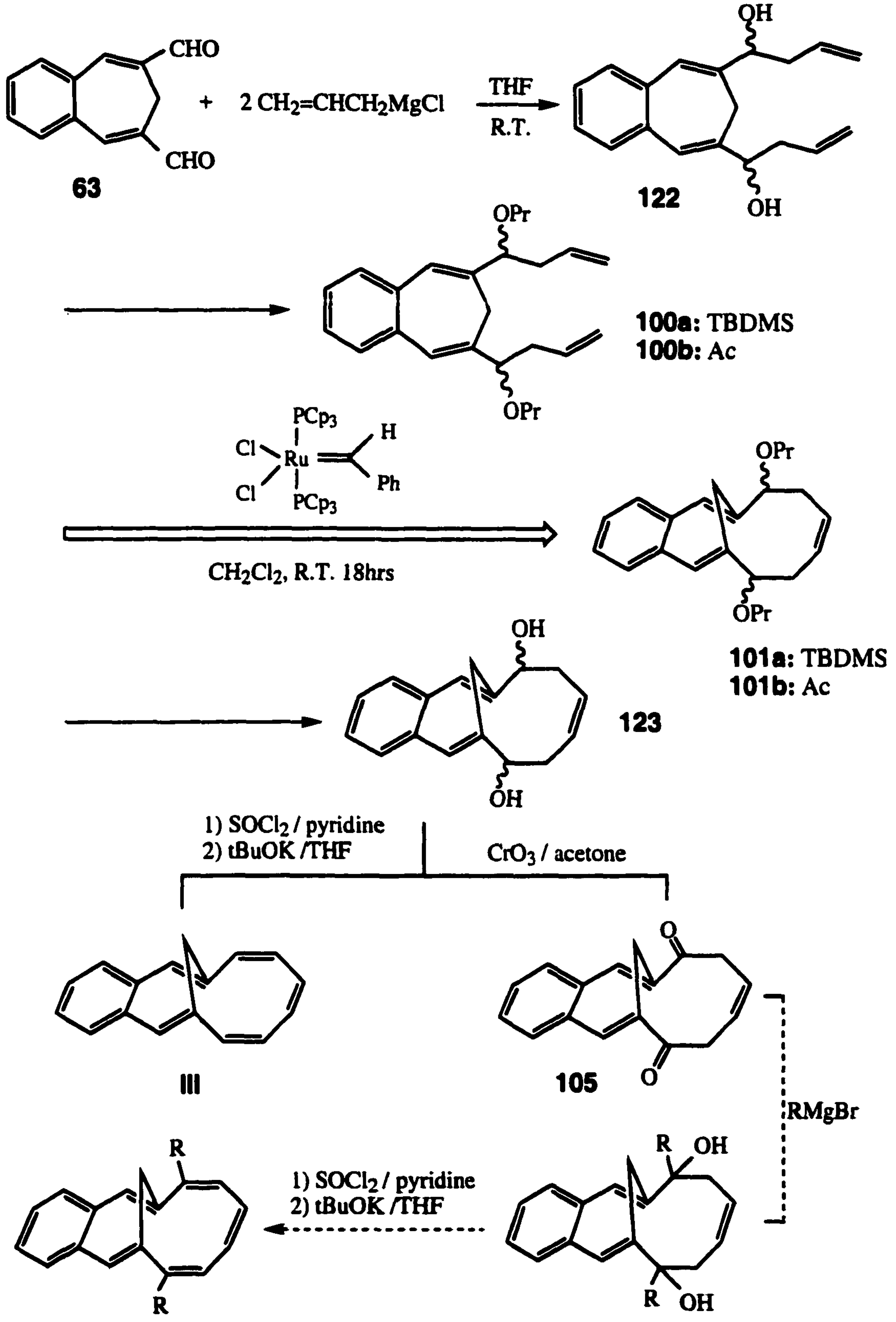
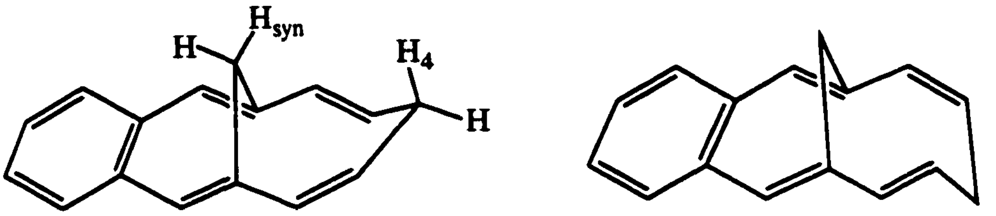


Figure 60 ^{1}H NMR of 105



Scheme 42 The RCM approach towards III

Current research efforts in our group are aimed at obtaining suitable crystals of **III** in order to have an X-ray structure determinated. Initial AM1 calculations for the geometry of benzo[12]annulene **III** show a very interesting unexpected result. The calculation for compound **124** which had been synthesized by our group(98) showed the heat of formation for the syn conformation **A** is 13.77 kcal/mole lower than that for the anti conformation **B** which indicates that the syn conformation **A** is more stable. The X-ray determination also confirmed the structure of compound **124** as syn conformation **A** in the solid state. A NOE experiment also supported the syn conformation **A** by the observation of a 5% NOE between H_{syn} and H_4. On the other hand, AM1 calculations of compound **III** showed the heat of formation for the syn conformation **A** is 1.38 kcal/mole higher than that for the anti conformation **B** which indicates that the anti conformation **B** in this system appears to be more stable than the syn conformation **A**. Since the difference in the heats of formation for each isomer is so close, we predict that our crystal may contain both conformations or the ^1H NMR of **III** would be temperature dependent. Therefore, an X-ray structure determination will very informative with regard to the exact geometry of 3,4-benzo-1,6-methano[12]annulene **III** espically in comparison to compound **124**.



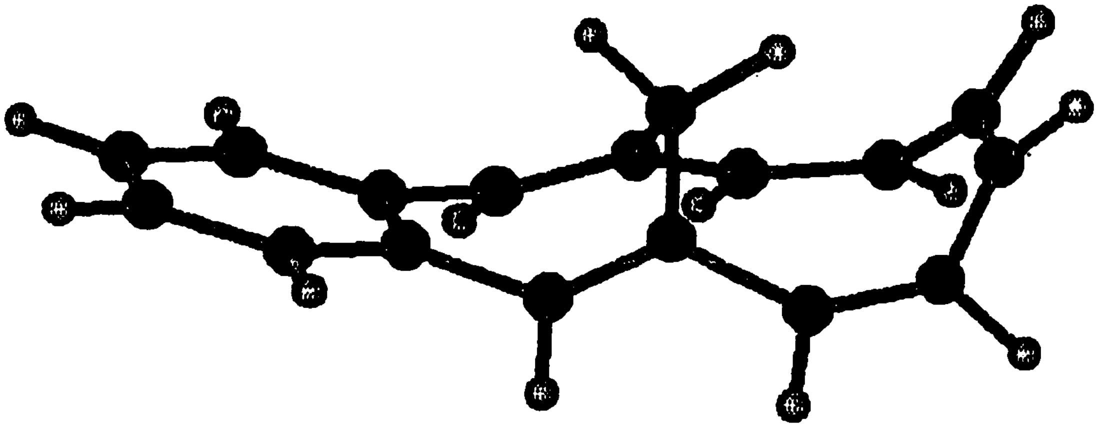
124-A

ΔHf= 87.82 kcal/mole

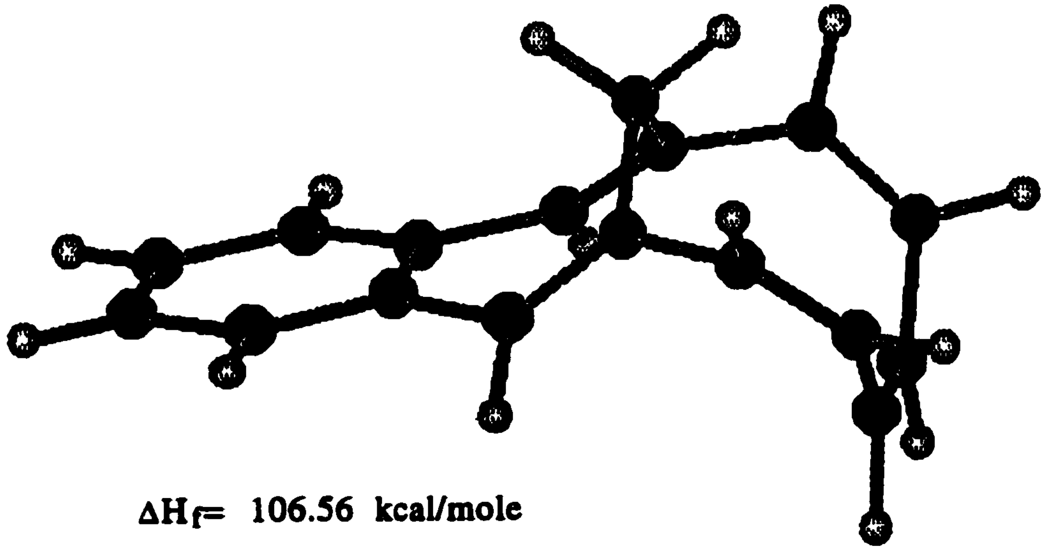
124-B

ΔHf= 101.59 kcal/mole

Figure 61 AM1 calculation for the geometry of compound 124



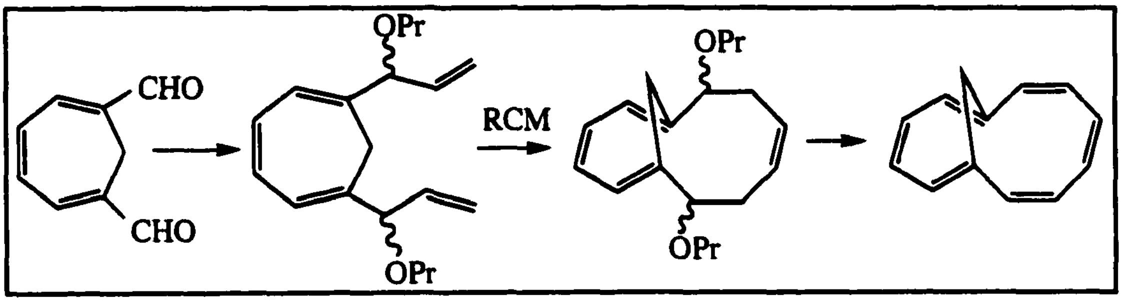
ΔH$_f$= 107.94 kcal/mole



ΔH$_f$= 106.56 kcal/mole

Figure 62 AM1 caculation for the geometry of 3,4-benzo-1,6-methano[12]annulene III

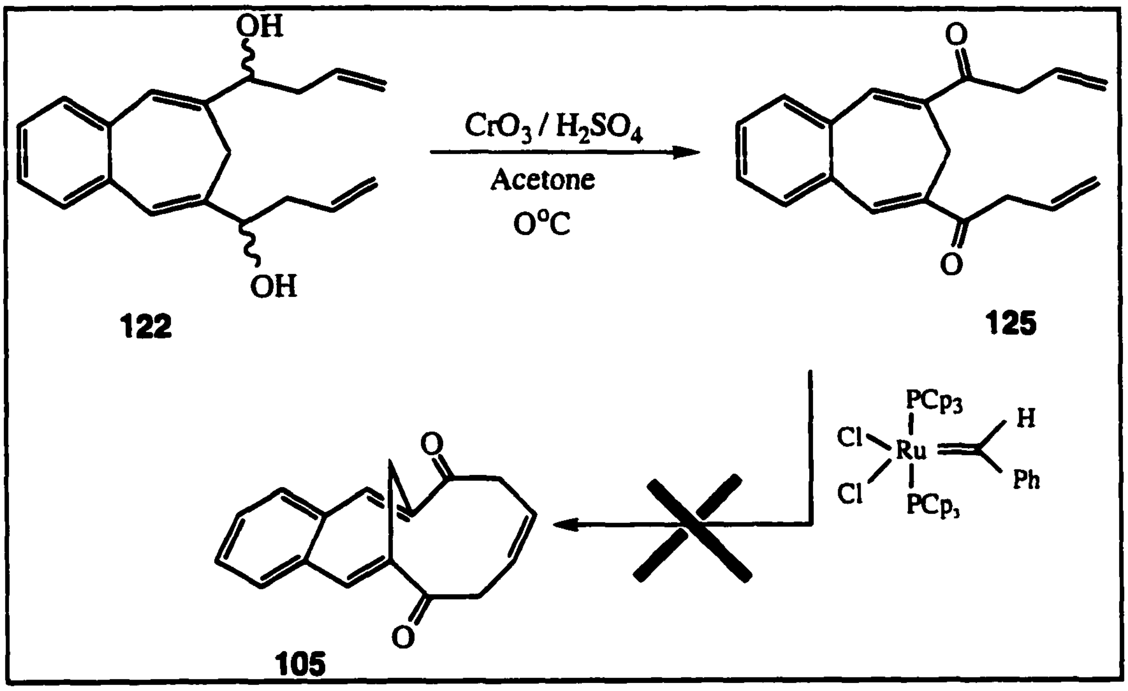
The extension of this general method based on the Ring Closing Olefin Metathesis would lead to an efficient synthesis of 1,6-methano [12]annulene, starting with 1,3,5-cycloheptatriene-1,6-dialdehyde and allylmagnesium bromide and the same sequence of steps. This compound had been reported by Vogel et al.(39) who obtained it by an elegant but lengthy route involving many steps in a low overall yield.



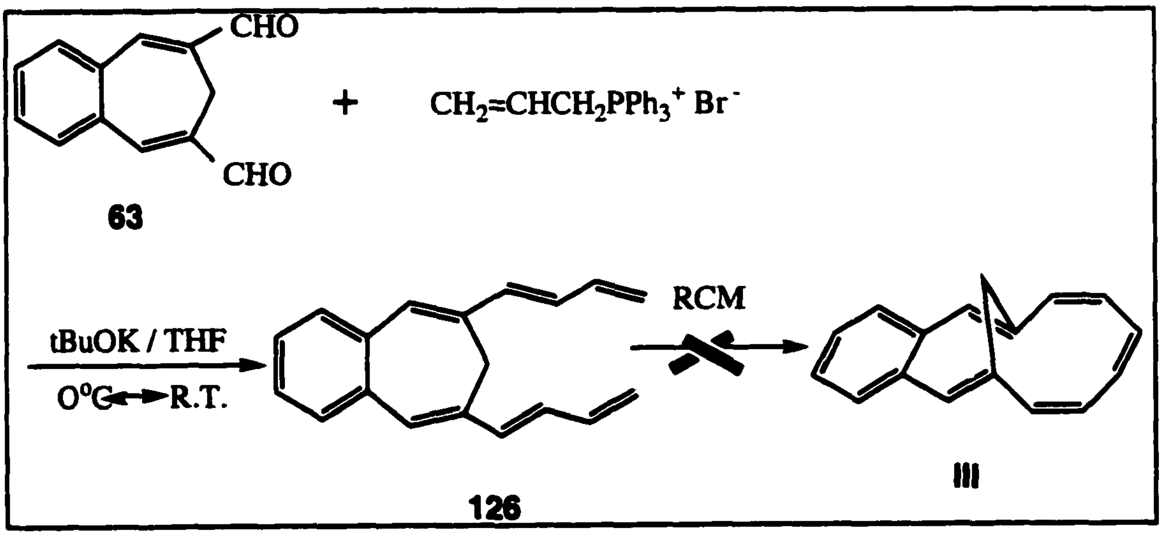
Scheme 43 A proposal towards 1,6-methano[12]annulene

Even though the ruthenium carbene catalyst has a broad tolerance toward various functional groups, we observed some limitations in the RCM synthesis of compounds **125** and **126**. The unsaturated ketone **125** was prepared by oxidation of the secondary alcohol **122**, but the following Ring Closing Olefin Metathesis failed. Only the starting material **125** was recovered. Compound **126** was prepared by Wittig reaction, starting with 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde and the allyl phosphonium salt. Unfortunately, RCM to compound **III** led to decomposition.

Compound **III** could not be detected. One reason for this might be the sensitivity of compound **126** and its tendency to polymerize.

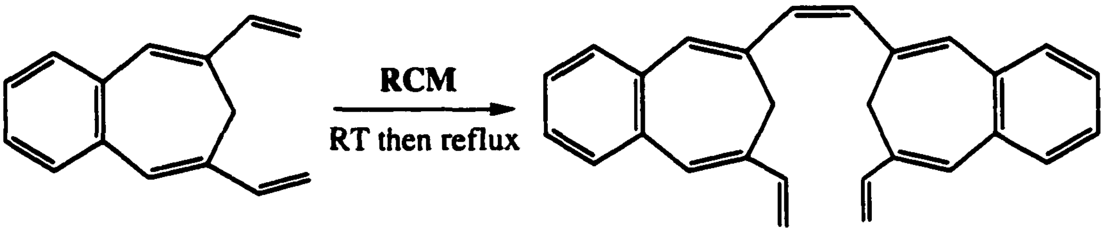


Scheme 44 Unsuccessful RCM reaction A



Scheme 45 Unsuccessful RCM reaction B

We also tried to synthesize dibenzo[16]annulene **IV** based on the Ring Closing Olefin Metathesis. In this approach, the starting material **127** was prepared by Wittig reaction, but the expected double bismolecular RCM reaction did not yield the desired compound **IV**. Instead, we obtained an open dimer **128** (5.4%) of unknown stereochemistry in the newly formed double bond.

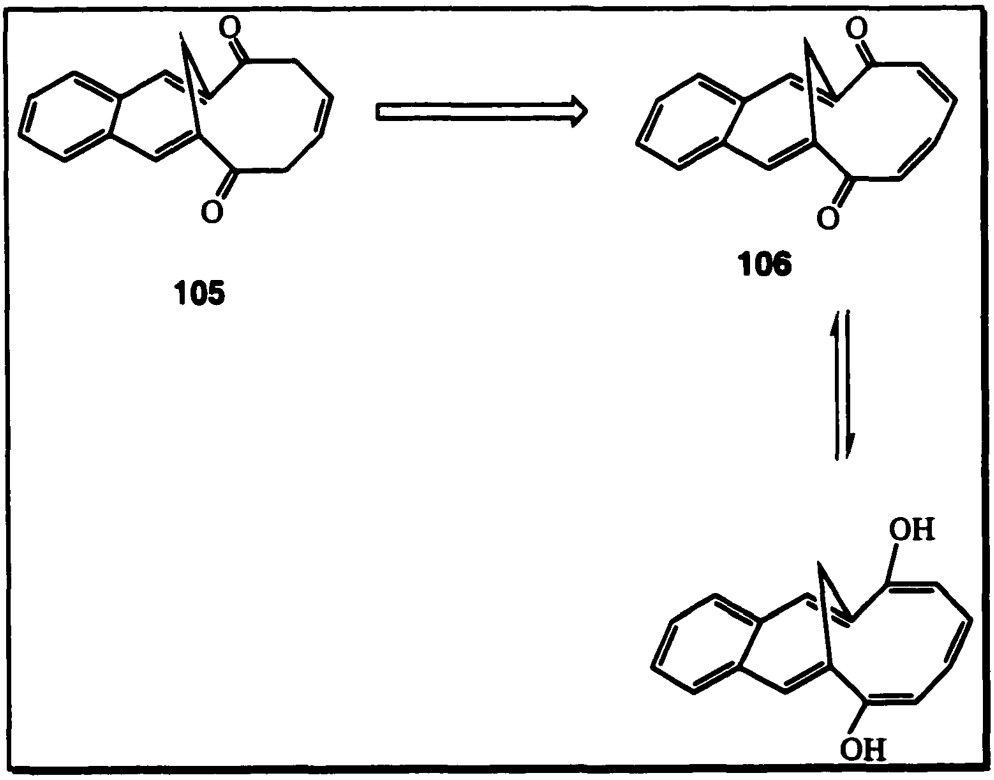


127

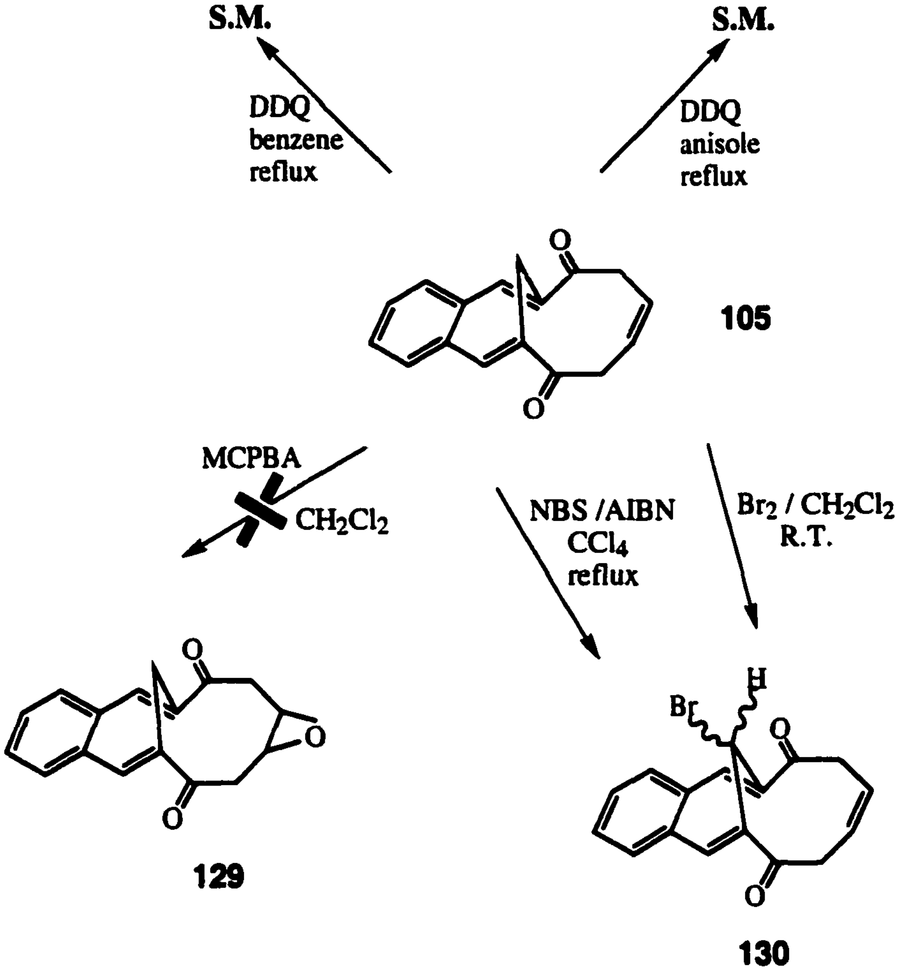
128

Scheme 46 The RCM approach towards 128

Continuing this investigation, we attempted to approach the synthesis of compound **106** in order to study the effect of benzannelation on the quinone / hydroquinone redox equilibrium in the 1,6-methano[12]annulene series. First, we reacted diketone **105** with DDQ in benzene under reflux, but only starting material was recovered. To improve the reaction condition, we changed the solvent to anisole in order to run this reaction at a higher temperature, but again, the starting material was recovered and some anisole coupling products were observed by GC-MS. We then tried the treatment of compound **105** with MCPBA to get the epoxide **129**, followed by subsequent hydrolysis and elimination to give the desired compound **106**, but instead it appeared, based on the ^{1}H NMR and GC-MS indicated that the reaction probably went through Baeyer-Villiger oxidation. In a third attempt to introduce the additional double bond, **105** was treated with NBS / AIBN under reflux as well as with Br_2 / CH_2Cl_2 at R.T.. Both reactions gave a brominated compound tentatively assigned to be the compound **130** of unknown stereochemistry.

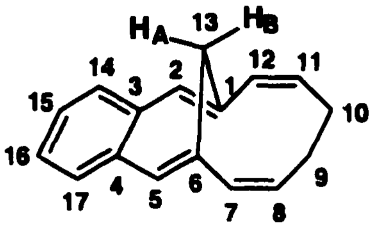


Scheme 47 The quinone/hydroquinone redox equilibrium

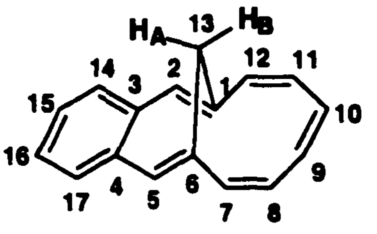


Scheme 48 Some reactions of 105

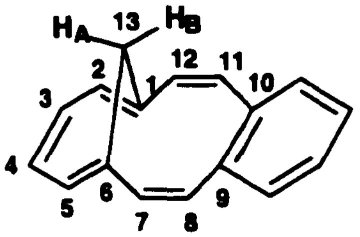
In order to document the effect of benzannelation in 1.6-methano[12]annulene **III** on the ring current, we undertook a detailed comparative ^{1}H NMR study as summarized in **Table 14**. Compounds **88**, **III** and **81** were prepared in our group and compounds **47**$^{(72)}$, **15**$^{(39)}$ and **131**$^{(133)}$ were synthesized and reported by Vogel et al.. All NMR samples were prepared in $CDCl_3$ at the same concentration . When we compared monobenzo **III** and **47** and dibenzo **81** with the nonannelated 1,6-methano[12]annulene **15**, the proton NMR showed that the bridge protons are shifted upfield and the external protons are shifted downfield relative to the nonannelated system **15**. This indicates that the fusion of the benzene rings on the parent ring reduces the paratropicity in the 12π system. The only exception is that the chemical shift of H_A in compound **III** didn't show any significant change. By comparing the chemical shift for H_A in the monobenzene fused polyolefin **88** with the bicyclo[6,4,1]trideca-1,3,5,7,11-pentaene **131**, we observe that H_A in **88** (δ=1.99 ppm) is further downfield relative to H_A in **131** (δ=1.57 ppm). This 0.42 ppm downfield shift is most likely caused by the effect of the benzene ring in **88** where H_A is positioned in the deshielding area of the benzene ring. Therefore in comparing **III** and **15**, we observed in **III** (a) the effect of the 12π antiaromatic system (paramagnetic ring current) and (b) the before mentioned deshielding effect of the benzene ring. These effects apparently cancel each other out as observed with the small change of only 0.08 ppm.



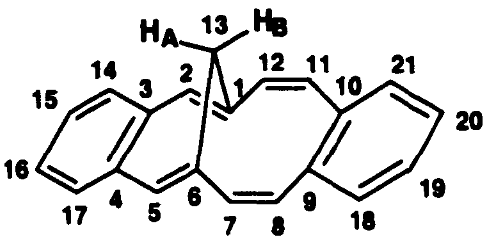
88



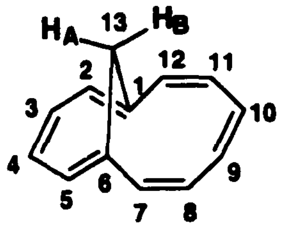
III



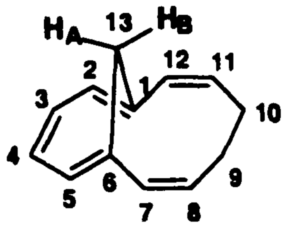
47



81



15



131

Table 14 Chemical shifts (δ values in $CDCl_3$) of the protons of 88, III, 47, 81, 15, 131

	2-H	3-H	7-H	8-H	13-H_A	13-H_B	benzene
88	6.65	–	6.53	5.93	*1.99*	*3.20*	7.25-7.45
III	6.36	–	5.87	5.69	*2.37*	*6.01*	7.13-7.22
47	6.10	6.50	6.02	6.48	*0.97*	*4.65*	6.90-7.20
81	6.53	–	5.83	6.04	*1.50*	*4.37*	7.30-7.55
15	5.73	6.17	5.50	5.50	*2.29*	*7.00*	–
131	6.30	6.70	–	–	*1.57*	*3.13*	–

We calculated the degree of reduction of paratropicity relative to the parent ring by using the same methods as described previously (page 115). Both methods gave us the same tendency of decrease in paratropicity from the parent to the monobenzo and the dibenzo compounds as shown below.

Table 15 Chemical shift data (δ ppm in $CDCl_3$) of the protons of III, 47, 81, 15, 131

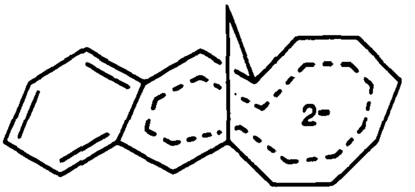
	$13\text{-}H_B$	$\Delta\delta = \delta - \delta_{model}$	%Δδ* of parent	$\Delta\delta = \delta - \delta_{parent}$	$\Delta\delta / \delta_{parent}$	Paratropicity*
III	*6.01*	**2.88**	**74%**	**0.99**	**0.14**	**86%**
47	*4.65*	**1.52**	**39%**	**2.35**	**0.34**	**66%**
81	*4.37*	**1.24**	**32%**	**2.63**	**0.38**	**62%**
15 (parent)	*7.00*	**3.87**	**100%**	–	**1**	**100%**
131 (model)	*3.13*	–	–			

* The method was reported by Mitchell "J. Am. Chem. Soc. 1982, 104, 2544"

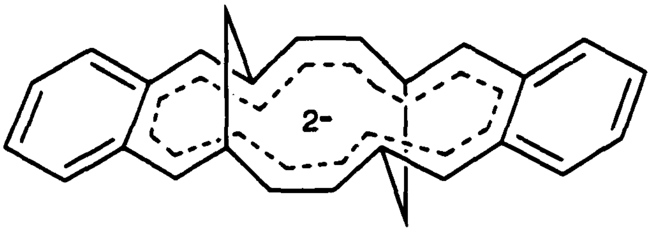
* Paratropicity relative to the parent compound

2.5 Bridged benzoannulene ions

In order to assess the effects of benzannelation on aromatic/ antiaromatic methano bridged annulene ions, research efforts in our group are directed toward the generation of [12] and [16] annulene dianions, **132** and **133**.

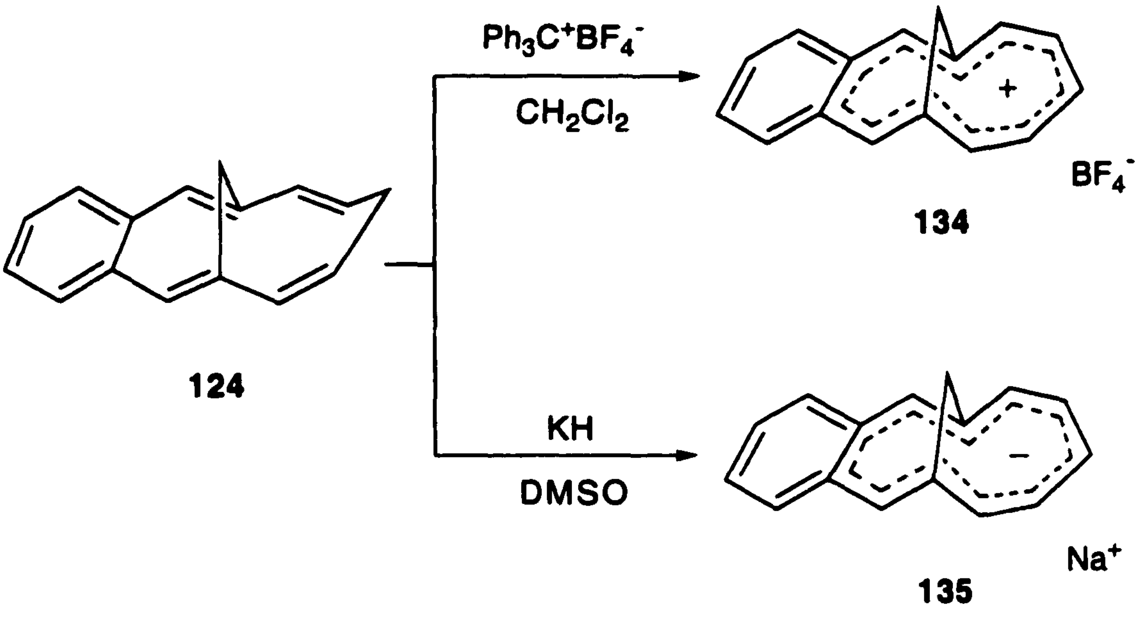


132



133

Previous work by us had resulted in the synthesis of the cation and anion derived from benzbicyclo[5,4,1]dodeca-2,5,7,9,11-pentaene **124**(98). The formation of the aromatic cation **134** was achieved by treatment of **124** with equimolar trityl fluoroborate in methylene chloride at room temperature, resulting in a deep green solution. Compound **134** was precipitated by the addition of anhydrous ether forming green crystals. On the other hand, treatment of **124** with KH in deuterated dimethyl sulfoxide resulted in a proton abstraction and the formation of a black solution containing anion **135**.



Scheme 49 The formation of cation 134 and anion 135

The ^1H NMR spectrum of cation **134** convincingly indicated the presence of a diamagnetic ring current. A downfield shift of ca. 4 ppm (δ values of the peripheral protons between 8-10 ppm) as compared with the corresponding protons of the atropic compound **124**, and a 2.40-5.80 ppm upfield shift of the bridge protons (singlet at -1.20 ppm). A comparison with Vogel's bridged 10π aromatic bicyclo[5,4,1]dodecapentaene cation **50**(73), reveals that benz-annelation does not appear to effect the ring current in this system. Similar chemical shift differences for all ring protons are observed in **50** relative to **124**. The bridge protons of **134** resonate at a higer field than the averaged chemical shift of the bridge protons of **50** (H_A=-0.25 ppm, H_B=-1.74 ppm). ^{13}C NMR of the aromatic cation **134** does not reveal any overwhelming chemical shift differences. Many studies have shown that ^{13}C resonances are influenced by conformation, ring size, strain and conjugation, but to a lesser extent by ring currents. A distinct 1 ppm shift in ^{1}H NMR which results from altered ring current, can be attributed in the corresponding ^{13}C NMR to one of many other effects, or may be ignored as unindicative(134).

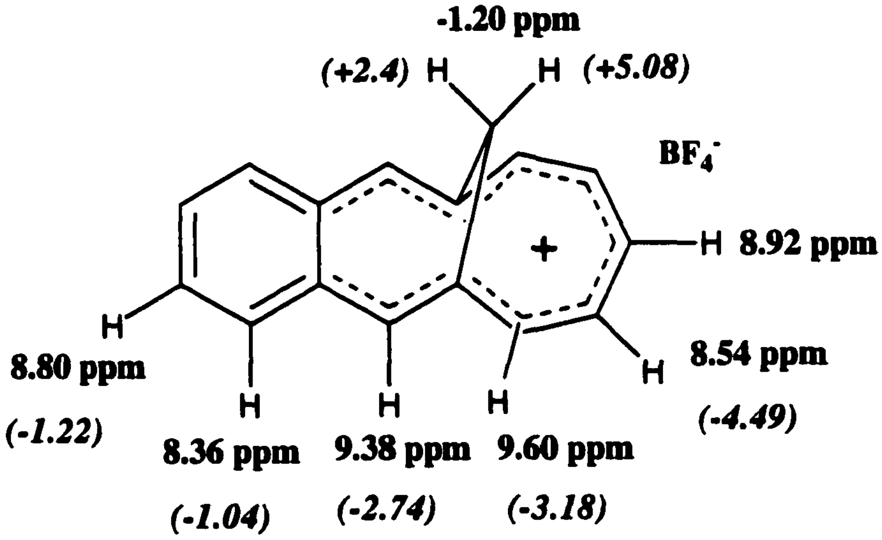


Figure 63 **The ^{1}H NMR chemical shift for cation 134**
(in bracket are for comparison the observed chemical shift change relative to **124**)

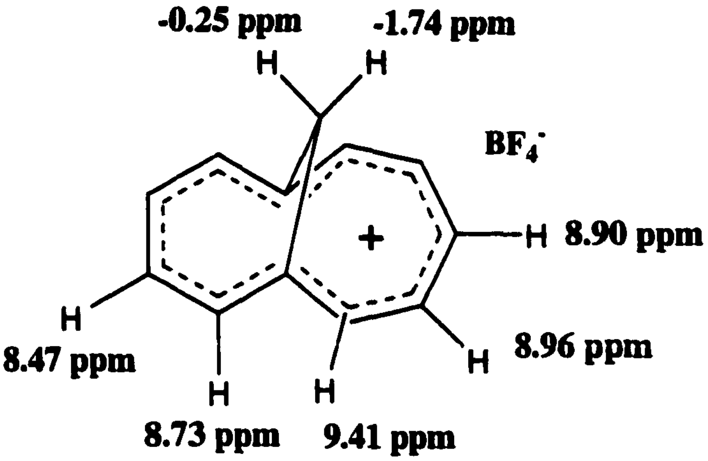


Figure 64 The ^1H NMR chemical shift for bicyclo[5,4,1]dodecapentaene cation 50

The peripheral protons in anion **135** appear at 2.57-5.87 ppm while the bridge protons appear at 6.68 ppm and 8.80 ppm. These chemical shifts indicate the presence of a strong paramagnetic ring current in **135**. Relative to starting material **124** the peripheral protons show 2-3 ppm upfield shift while the bridge protons show ca. 5 ppm downfield shift. Of interest in connection with this investigation was the comparison of the ^1H NMR spectrum of **135** with that of the anion **51**(75) derived from bicyclo[5,4,1] dodeca pentaene. One notices a definite reduction in the paratropicity due to benzannelation. The ^1H NMR of **51** exhibits the bridge protons at 10.31 and 14.19 ppm (ca. 5 ppm lower field as compared with **135**) and ring protons of **51** is positioned at 1-2 ppm higer field than those in **135**.

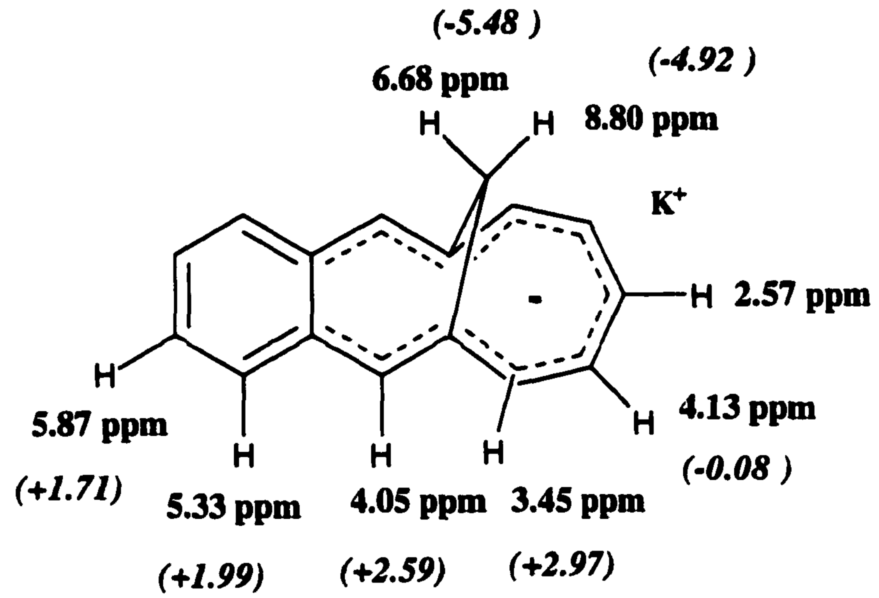


Figure 65 The ^{1}H NMR chemical shift for cation 135
(in bracket are for comparison the observed chemical shift change relative to 124)

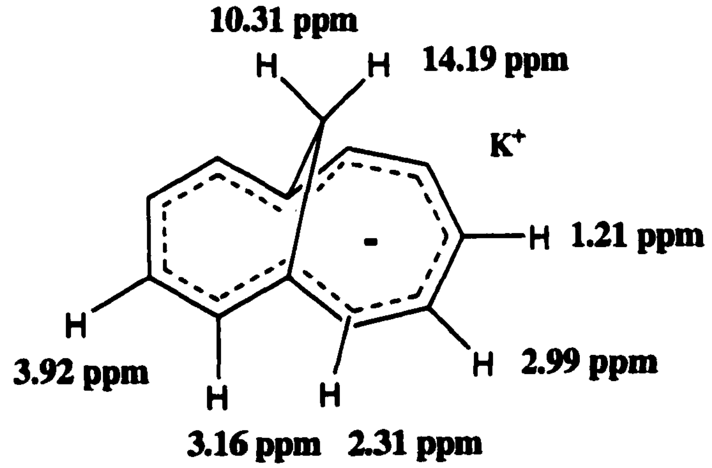
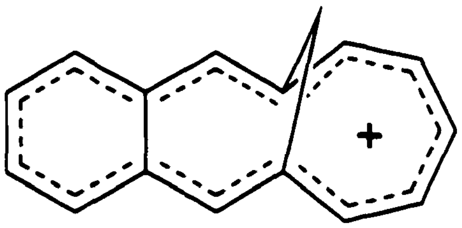
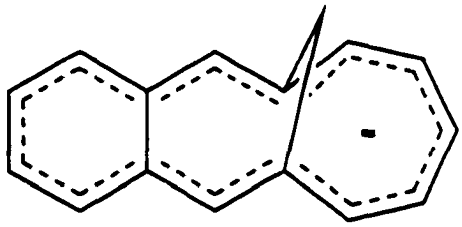


Figure 66 The ^{1}H NMR chemical shift for bicyclo[5,4,1]dodecapentaene anion 51

Of interest are the observed chemical shift changes for the benzene protons upon going from hydrocarbon **124** to the respective cation **134** and anion **135** (downfield shift from **124** to **134** and upfield shift from **124** to **135**). A possible interpretation for these chemical shift change could be the representation of **134** as an extended 14π system and **135** as an extended 16π system as shown below.



134



135

Continuing the above studies we were interested in generating and characterizing the 14π aromatic dianion **132** by treatment of **III** with potasium or lithium metal in deuterated THF, or treatment of **88** with DMSO-Na in DMSO. Reacting solutions of **III** in THF-d_8 with K or Li at RT under Ar in a special NMR tube as shown below gave dark red solution but no satisfactory ^1H NMR could be observed. Ultra-sound was used to facilitate the reaction of the metal with **III**. Hydrolysis of the solution from the NMR tube gave a mixture of dihydro isomers according to GC/MS data. An indication for the intermediate existence of the dianion **132** was the observation that the Wittig reaction of 3,4-benzcycloheptatriene-1.6-dialdehyde **63** with the bisphosphonium salt derived from 1,4-dibromobutane gave isomers **90** and **91**.

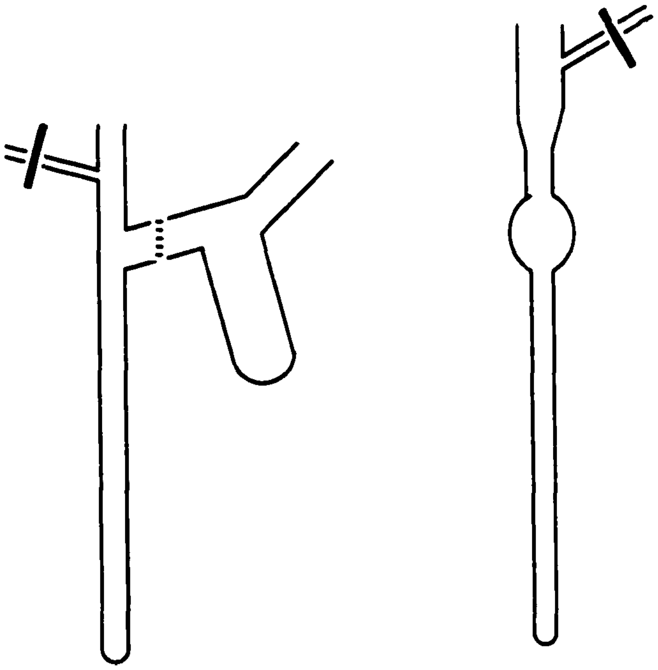
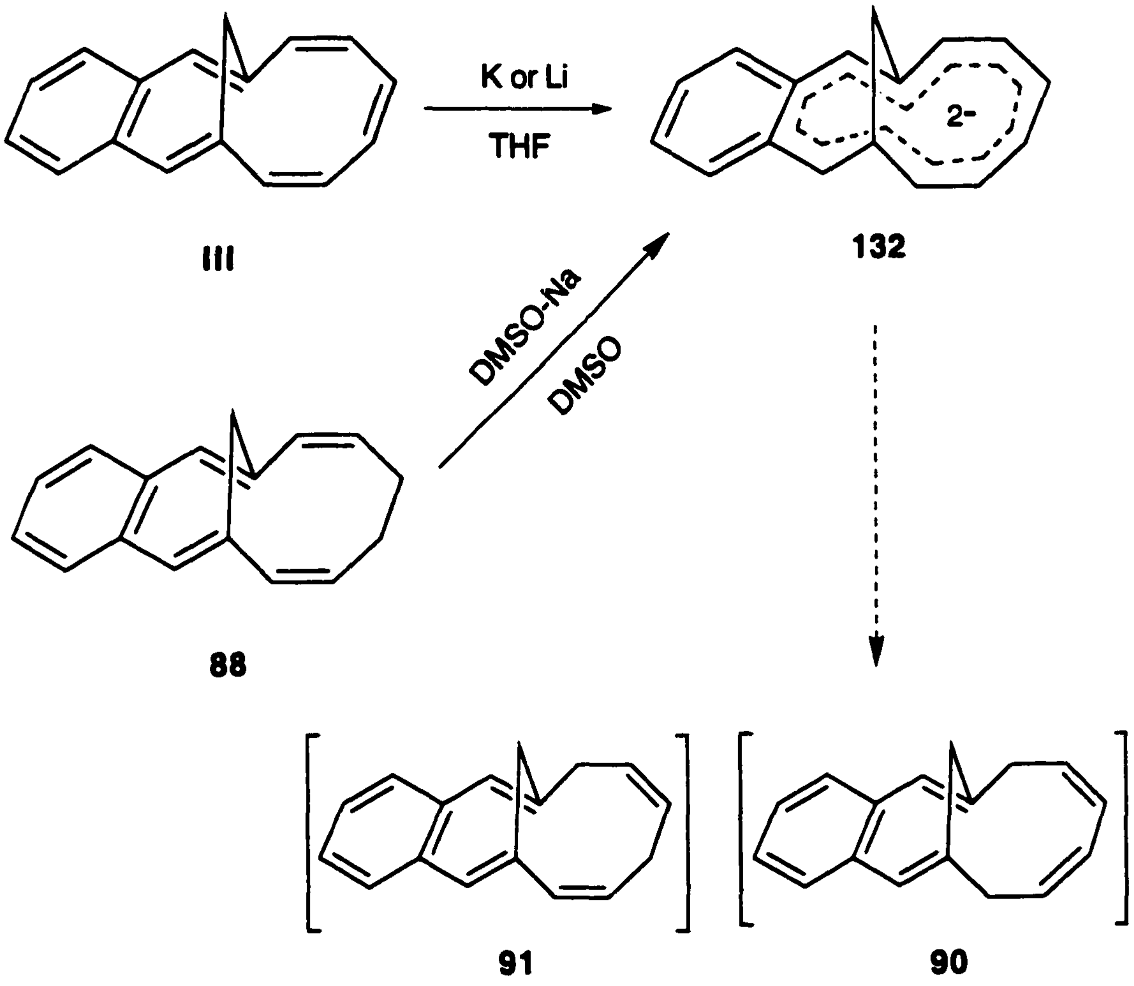
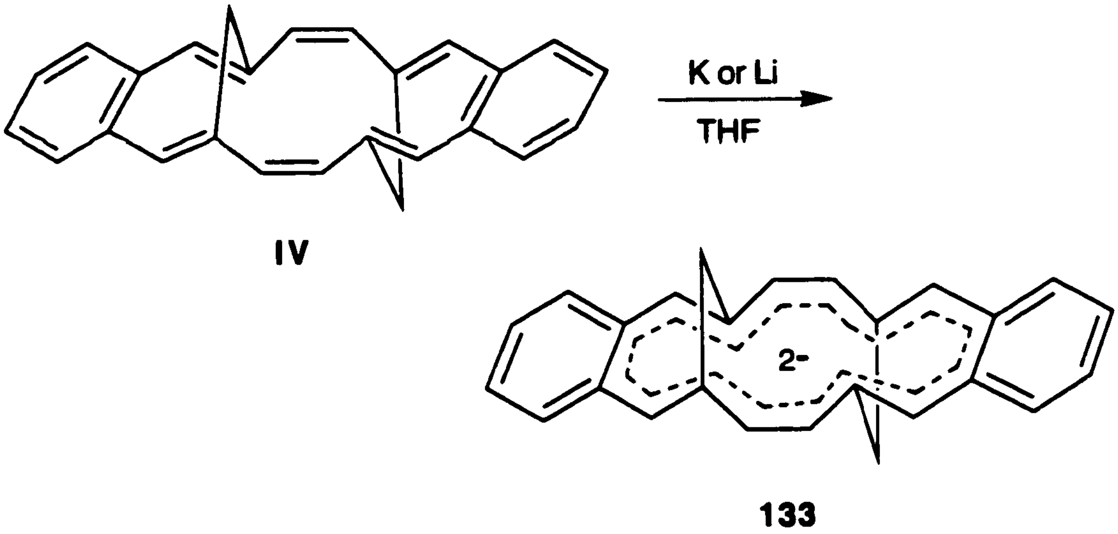


Figure 67 Two special NMR tubes for the generation of dianions 132 and 133



Scheme 50 Attempts to generate dianion 132

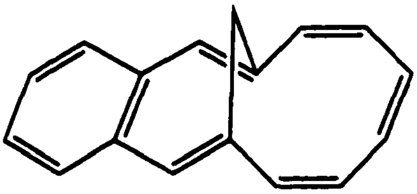
Treatment of **IV** with K or Li in THF-d_8 and sonification in an apparatus described below led to a deep dark red solution. Again, we were unable to obtain good ^{1}H NMR spectra. Hydrolysis of this solution and subsequent analysis by GC/MS gave ions with m/z= 336, 338, 340 corresponding to tetra, hexa and octahydro compounds. Research in our group is continuing to work out the generation and characterization of dianions **132** and **133**.

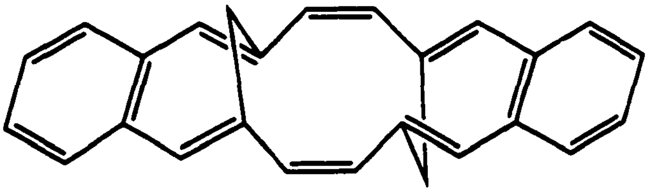


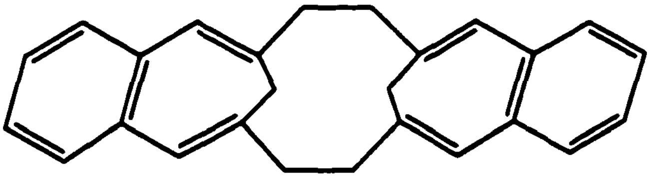
Scheme 51 The formation of dianion 133

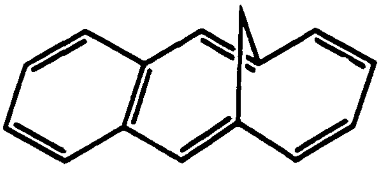
2.6 Summary

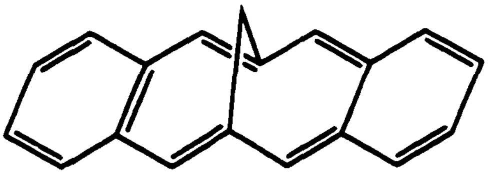
In this project, the unknown compounds **III, IV** and **93** have been synthesized and fully characterized. Synthetic efforts toward the yet unknown benzannelated 1,6-methano[10]annulenes **I** and **II** have been investigated.


III


IV

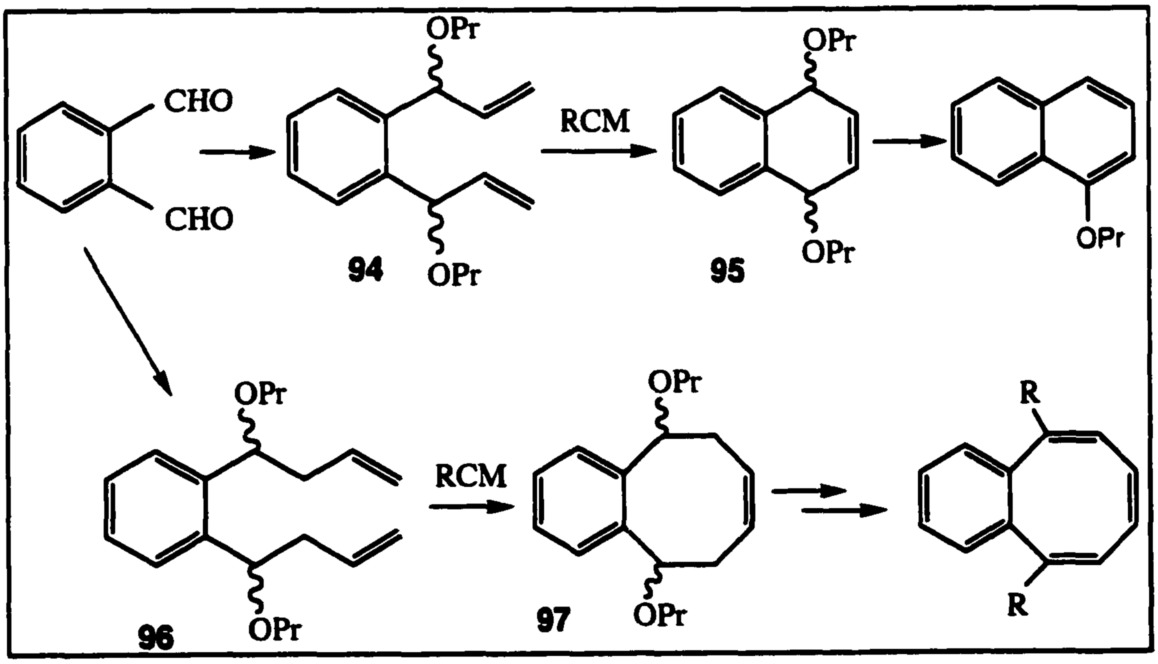

93

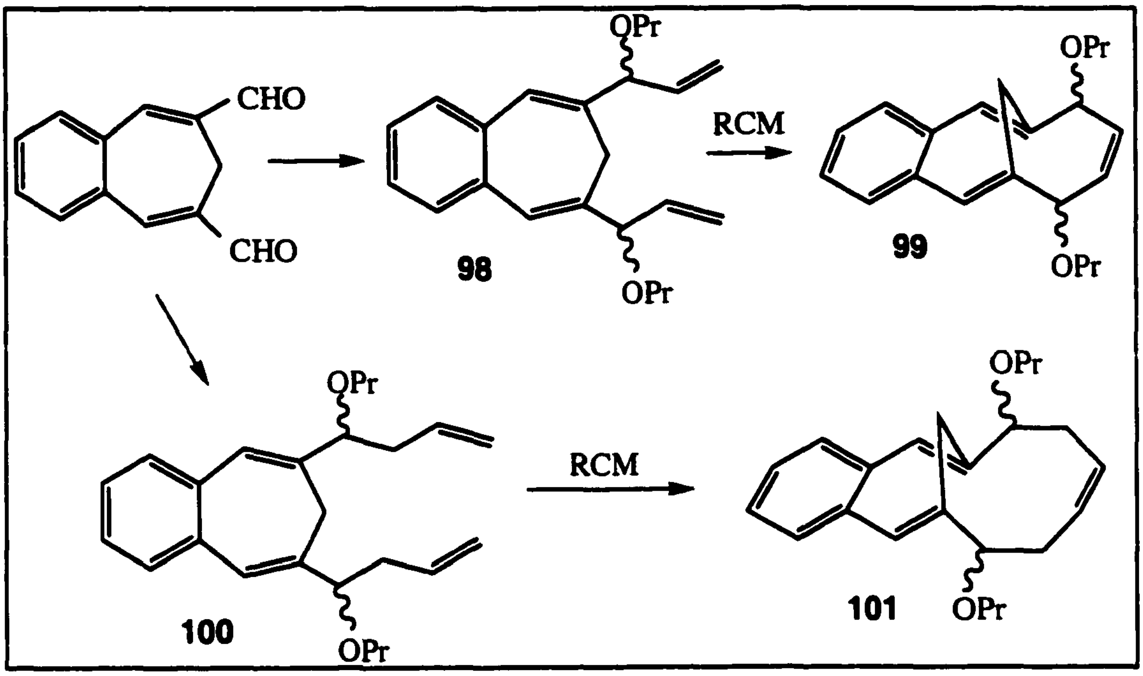

I


II

A detailed comparative NMR study on the benzannelated [10], [12] and [16] annulenes was carried out in order to evaluate quantitatively the effect of multiple benzannelation on the paratropicity and diatropicity of the given [10], [12] and [16] π systems.

In addition, we developed a new general method for the synthesis of 3,8-disubstituted benzocyclooctatetraenes and 3,4-benzo-1,6-methano[12]annulene based on the ring closing olefin metathesis (RCM). This valuable method can also be extended to the synthesis of the parent system (1,6-methano[12]annulene).





The results of this investigation can be summarized as follows:

(1) The protected dialcohol **94** under RCM conditions formed the corresponding cyclic compound **95**, which readily aromatized to give the 1-substituted naphthalene.

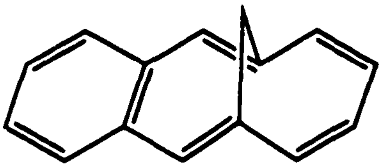
(2) The protected dialcohol **96** by the same sequence of steps gave the benzcyclooctatetraene in good yield.

(3) The protected dialcohol **98** was prepared by the reaction of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde with vinylmagnesium bromide. However, the RCM of compound **98** to generate compound **99** did not succeed so far. The reason might be that the distance between carbons 8 and 9 is larger than the distance of the reacting carbons in phthalaldehyde, therefore making the compound **99** somewhat strained.

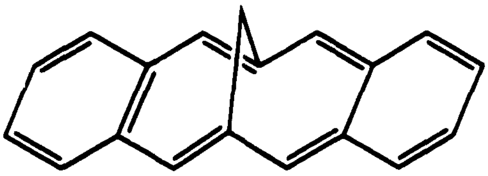
(4) The protected dialcohol **100** was prepared by the reaction of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde with allylmagnesium chloride, followed by protection of the hydroxy groups. The RCM of this compound generated compound **101**. Deprotection, reaction with $SOCl_2$ and subsequent elimination converted compound **101** into the fully conjugated 3,4-benzo-1,6-methano[12]annulene **III**.

2.7 A glance to the future

From the results of this investigation as well as from earlier studies in our group(98), it became clear that different approaches towards **I** and **II** had to be considered.



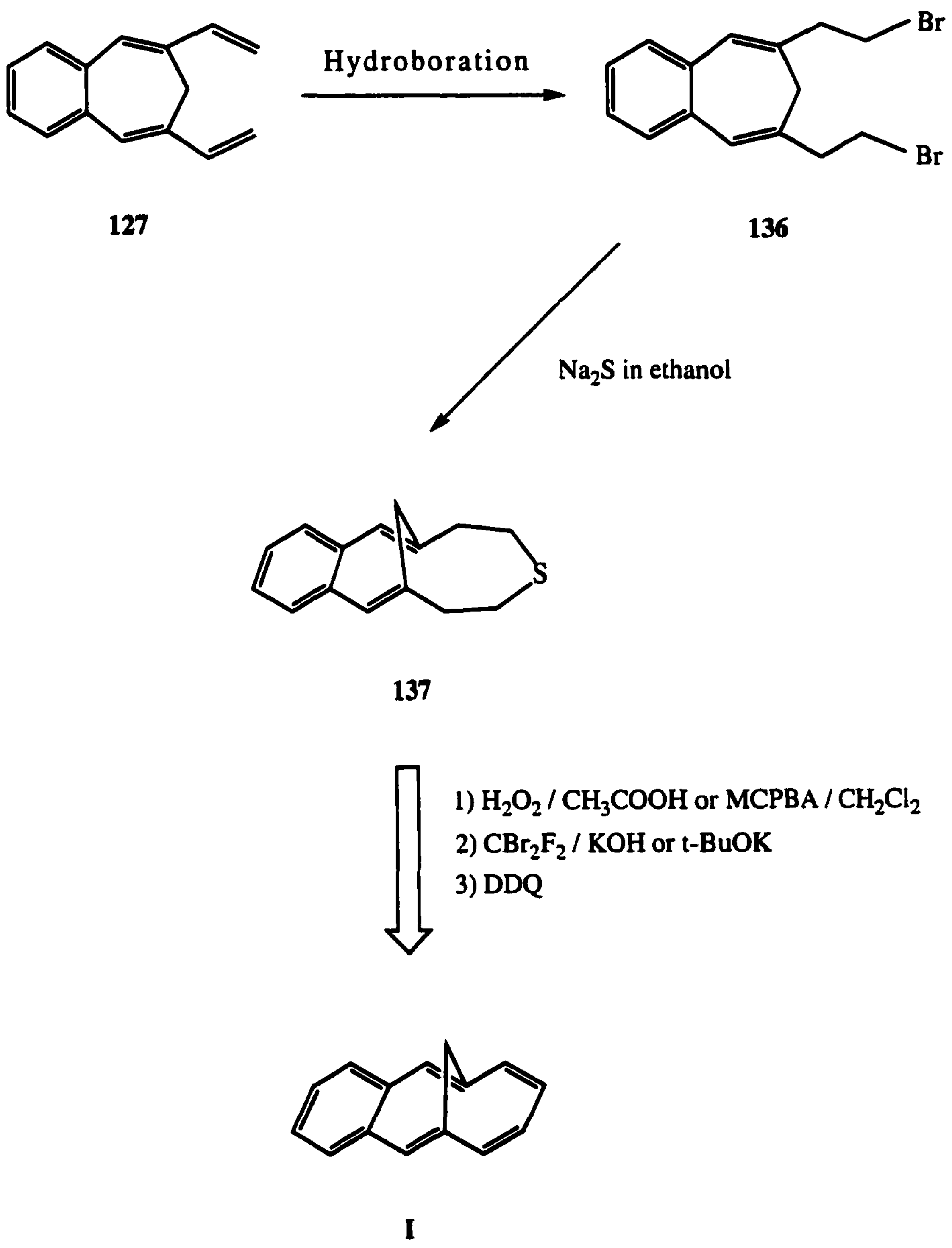
I



II

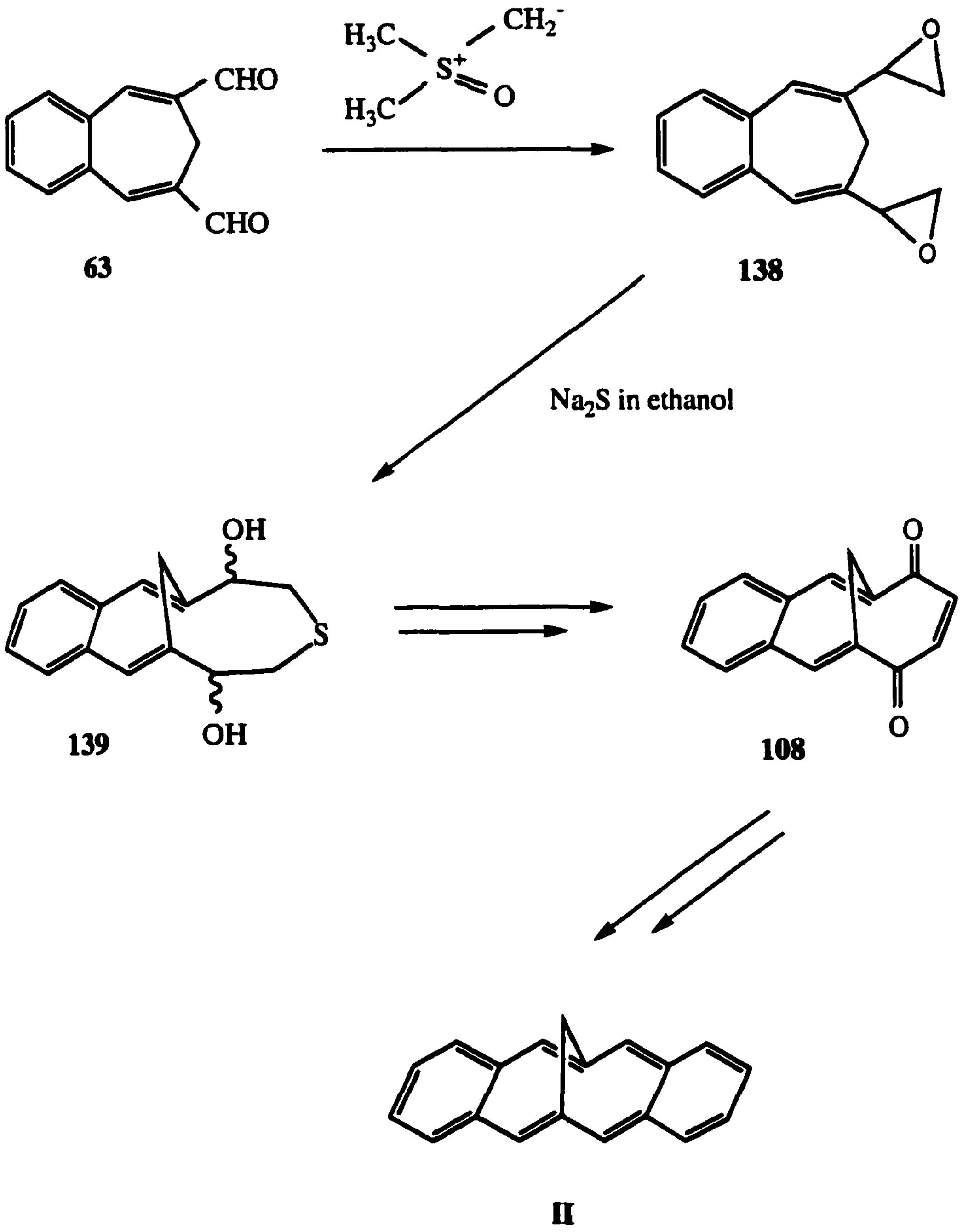
The use of the Ramberg-Bäcklund reaction(135) as shown on **Schemes 52** and **53** looks very promising. Furthermore, in particular compound **108** formally a quinone of **I** is very promising for the annelation of the second benzene ring via a Diels-Alder addition leading to compound **II**.

The approach towards 3,4-benzo-1,6-methano[10]annulene **I**, starting with 3,4-benz-1,6-divinyl-1,3,5-cycloheptatriene **127**. Hydroboration and cyclization is expected to yield compound **137**, followed by Ramberg-Bäcklund and oxidation to approach desired compound **I**.



Scheme 52 The Ramberg-Bäcklund approach towards I

On the other hand, a promising approach towards 3,4,8,9-dibenzo-1,6-methano[12]annulene **II**, starting with dialdehyde **63** is described below.



Scheme 53 The Ramberg-Bäcklund approach towards II

Chapter 3 Experimental Section

3.1 General Procedure

All glassware used in moisture or air sensitive reactions was oven-dried at over 100 °C overnight, then assembled as described in each individual experiment and flushed with nitrogen or argon. A common set-up consisted of a three-necked round bottom flask fitted with a pressure equalizing dropping funnel and or a condenser attached to a three-way connecting tube for inert atmosphere inlet and a calcium dichloride or potassium hydroxide drying tube. Stirring was achieved by the use of a magnetic stirrer. Acid or basic neutralization was accomplished by the addition of a suitable aqueous solution, usually saturated sodium bicarbonate for acid neutralization and dilute hydrochloric acid or saturated ammonium chloride for basic neutralization. Standard work-up included quenching with a suitable cold aqueous solution, extraction with a suitable organic solvent, such as diethyl ether or methylene chloride, drying the organic solvent over magnesium sulfate or sodium sulfate and removal of organic solvent by rotary evaporation in vacuo at a water aspiration pressure of about 11 torr.

3.2 Spectroscopy

Proton and carbon magnetic resonance spectra (^{1}H and ^{13}C NMR) were collected by a 300 MHz General Electric QE-300 nuclear magnetic resonance spectrophotometer with Tecmaq Aquerius data system. Variable temperature proton NMR were performed by a JEOL 400 MHz nuclear magnetic resonance spectrophotometer. 2D-NOESY experiments were all performed on a Varian Unity Plus 500 MHz spectrometer. All samples were prepared by dissolving a suitable amount of compound in a properly deuterated solvent, usually $CDCl_3$ (99.8% D, 0.03% V/V tetramethylsilane). Chemical shifts are reported in parts per million (ppm) downfield from the TMS internal standard, $\delta=0$, and are expressed in the following order: Chemical Shift (ppm); Multiplicities (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, b=broad); Coupling Constant (J in Hz).

Infrared spectra were recorded on Perkin-Elmer 1310 IR spectrophotometer and are reported in wave numbers (γ = cm^{-1}). Solid samples were recorded by preparing KBr pellets. Liquid samples were examined by placing them between sodium chloride plates.

Gas Chromatography / Mass spectra were determined by either electron impact (EI) ionization or chemical ionization (CI) using methane as the carrier gas on a Hewlett-Packard 5890 Series II GC/5989A mass spectrometer. Some samples of high molecular weights (>400-600 amu) were analyzed by direct probe inlet. The data presented shows the parent ion (M^+), and base peak(s) (100%).

Ultraviolet Spectra were measured with a Cary UV-VIS-NIR spectrophotometer between 500 and 250 nm using either methylene chloride or cyclohexane as the solvent. UV bands are reported by the maximum wavelength and the absorbance intensity.

X-ray crystal structure determinations were measured on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation, ω-2θ scans). The size of the crystal of N-phenylsuccinimide Diels-Alder adduct **73** used for data collection was approximately 0.64 x 0.64 x 0.64 mm. The data were not corrected for absorption. Of the 8408 unique reflections for $\theta<28^o$, 3560 were considered observed $[I>3.0\sigma(I)]$. The structure was solved by a multiple-solution procedure and was refined by full-matrix least squares. In the final refinement, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices are $R=0.050$ and $R_w=0.056$ for the 3560 observed reflections. The final difference map has no peaks greater than ±0.23 $e\text{Å}^{-3}$. The size of the crystal of 3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene **IV** used for data collection was approximately 0.02 x 0.40 x 0.80 mm. The data were not corrected for absorption. Of the 839 unique reflections for $\theta<20^o$, 355 were considered observed $[I>3.0\sigma(I)]$. The structure was solved by a multiple-solution procedure and was refined by full-matrix least squares. In the final refinement, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices are R=0.056 and R_w=0.055 for the 355 observed reflections. The final difference map has no peaks greater than $\pm$0.21 eÅ^{-3}. The coordinates, the thermal parameters, bond distances and bond angles for **73** and **IV** are listed in appendix.

Melting points were determined using a Büchi Schmelzpunk-bestimmungs instrument in soft-glass capillaries and are uncorrected

Thin-layer Chromatography was performed using pre-coated plastic sheets of silica gel, with a thickness of 0.25 mm, supplied by Macherey-Nagel. UV-active compounds were observed by 254 nm UV lamp. Non UV-active compounds were observed by phospho-molybdic acid in ethanol (0.5 g/100 ml).

Column Chromatography was performed using silica gel 60 or aluminum oxide (80-200 mesh) for either regular or flash chromatography. A separation by a Rf difference of 0.1 units required 40-60 g of gel per gram of residue to be purified.

Solvents were ACS reagent grade and purified as follows:

Hexane	distilled over calcium hydride
Ethyl Acetate	distilled over calcium hydride
Dichloromethane	distilled over calcium hydride
Methanol	distilled over calcium hydride
Acetonitrile	distilled over calcium hydride
Tetrahydrofuran	distilled over calcium hydride, then under nitrogen over potassium metal
Triethylamine	distilled under nitrogen over sodium metal
Toluene	distilled over calcium hydride
Pyridine	distilled over calcium hydride
N,N-Dimethylformamide	distilled over calcium hydride under vacuo

3.3 Experimental Procedure

3.3.1 Diels-Alder reaction approach to benzannulenes

3,4-benz-1,6-bis(hydroxymethyl)-1,3,5-cycloheptatriene (68)

1.98 g (10 mmole) of 3,4-benz-1,3,5-cycloheptatriene **63** was dissolved in 40 ml of THF and cooled to 0°C. 1 g (26 mmole) of $NaBH_4$ and 3 ml of MeOH were added into the solution, followed by two hours of stirring at room temperature. Then the reaction mixture was quenched by 80 ml of sat. NaCl solution and extracted with diethyl ether. The organic layer was washed with water and dried. Then, the solvent was evaporated to obtain white solid in 96% yield. The product was recrystalized from chloroform affording white needle crystals. **mp:** 124.5-125 °C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.34-7.23 (m, 4H), 6.60 (s, 2H), 4.33 (s, 4H), 2.57 (s, 2H), 1.70 (s, 2OH).

3,4-benz-1,6-bis(bromomethyl)-1,3,5-cycloheptatriene (64)

Method A: 2.02 g (10 mmole) of 3,4-benz-1,6-bis(hydroxymethyl)-1,3,5-cycloheptatriene **68** was dissolved in 40 ml of THF at room temperature under nitrogen. 1 ml of distilled pyridine was then added under ice bath and the solution which was prepared by adding 2ml (21 mmole) of phosphorus tribromide in 10 ml of THF was then added dropwise while stirring at 0°C. After stirring overnight at room temperature, TLC indicated the absence of all starting material. The reaction mixture was then quenched by ice water and extracted with diethyl ether. The organic layer was washed with 10%

$NaHCO_{3(aq)}$ and dried over $MgSO_4$. Then, the organic solvent was evaporated to obtain white solid in 60% yield. The product was recrystalized from hexane affording white crystals.

Method B: 0.98 g (4.85 mmole) of 3,4-benz-1,6-bis(hydroxymethyl) -1,3,5-cycloheptatriene **68** was dissolved in 20 ml of THF. Then, 4.02 g (12 mmole) of carbon tetrabromide and 3.82 g (15 mmole) of triphenylphosphine were added while stirring at room temperature. After 30 mins of stirring, the reaction mixture was then refluxed for 20 mins. Then, the solvent was evaporated to attain yellow residue. After chromatography in hexane to ethyl acetate 4:1, an yellow solid which consisted of the product and bromoform was obtained. Then, the yellow solid was kept inside of hood for few days to get rid of bromoform. The white product was obtained in 30% yield.

Method C: Bromine was added to the suspension of 27.86 g (0.1 mole) of triphenylphosphine in 220 ml anhydrous acetonitrile in the ice bath at such a rate that the mixture remained colorless. After the addition was completed, the supernatant solution should be at most slightly yellow. Then, the ice bath was removed and a solution of 9.33 g (0.05 mole) of 3,4-benz-1,6-bis(hydroxymethyl)-1,3,5-cycloheptatriene **68** in 130 ml of anhydrous acetonitrile was added over a period of 15 mins while stirring. After 4 hours of stirring, the solution became clear. The solvent was evaporated and the dark brown residue was dissolved in minimum amount of methylene chloride, followed by chromatography in hexane to ethyl acetate 6:1 to obtain white solid in 82% yield. **mp:** 70.5-71°C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.29-7.28 (m, 4H), 6.71 (s, 2H), 4.28 (s, 4H), 2.73 (s, 2H) ; **^{13}C NMR**: δ= 137.8, 136.0, 131.1, 130.0, 127.5, 39.6, 32.5; **IR** (KBr, cm^{-1}): 3016, 2958, 1483, 1430,1224, 1200, 1114, 863; **MS** (EI/70 eV) m/z: M^+ 326/328/330, 247/249 (100%).

N-ethylsuccinimide Diels-Alder adduct (72)

1.64 g (5 mmole) of 1,6-bis(bromomethyl)-3,4-benz-1,3,5-cyclo heptatriene **64** was dissolved in 20 ml of DMF under nitrogen at room temperature. 0.70 g (11 mmole) of zinc and 0.63 g (5 mmole) of N-ethylmaleimide were added into the solution while stirring. After reacting for 5 hours, TLC showed that there is no more starting material left. Then the reaction mixture was quenched with water. The precipitate was filtered out and washed with diethyl ether. The organic layer was then separated from the filtrate. After the organic layer was evaporated, chromatography was run on silica gel in 5 to 1 hexane/ethyl acetate mixture. A white solid was obtained in 4.8 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.20-7.10 (m, 4H), 5.05 (s, 2H), 4.84 (d, 2H, J=1.2 Hz), 4.19 (s, 2H), 3.27 (s, 2H), 3.23 (q, 2H, J=7.2 Hz), 3.01 (d,1H, J=15.6 Hz), 2.80 (dt, 1H, J=15.3 Hz, J=1.2 Hz), 0.54 (t, 3H, J= 7.2 Hz); **^{13}C NMR:** δ= 177.9, 146.4, 136.3, 128.3, 127.6, 111.5, 49.1, 47.4, 41.7, 33.8, 12.4; **MS** (EI/70eV) m/z: M^+ 293 (100%).

N-phenylsuccinimide Diels-Alder adduct (73)

2.74 g (8.35 mmole) of 1,6-bis(bromomethyl)-3,4-benz-1,3,5-cycloheptatriene **64** was dissolved in 20 ml of DMF under nitrogen at room temperature. 1.65 g (25.23 mmole) of zinc and 1.45 g (8.35 mmole) of N-phenylmaleimide were added into the solution while stirring. After 5 hours of reacting, TLC showed no sign of the starting material. Then the reaction mixture was quenched with water. The precipitate was filtered out and washed with diethyl ether. The organic layer was then separated from the filtrate. After the organic layer was evaporated, chromatography was run on silica gel in 5 to 1 hexane/ethyl acetate mixture. A white solid was obtained and recrystalized using ethyl acetate and hexane to get colorless crystals in 6.2 % yield. ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.31-7.17 (m, 7H), 6.68-6.65 (m, 2H), 5.10 (s, 2H), 4.88 (d, 2H, J=0.9 Hz), 4.29 (s, 2H), 3.49 (d, 2H, J=0.6 Hz), 3.06 (d,1H, J=15.3 Hz), 2.85 (dt, 1H, J=15.9 Hz, J=1.5 Hz); ^{13}**C NMR**: δ= 177.1, 146.1, 136.3, 129.2, 128.8, 128.5, 127.6, 126.5, 111.7, 49.4, 47.8, 41.8; **MS** (EI/70eV) m/z: M^+ 341 (100%).

3.3.2 Bis-Wittig cyclization approach to benzannulenes

3,4-benz-1,3,5-cycloheptatriene-1,6-bis(methyltriphenyl phosphonium bromide) (80)

11.62 g (35 mmole) of 3,4-benz-1,6-bis(bromomethyl)-1,3,5-cycloheptatriene **64** and 18.58 g (71 mmole) of triphenylphosphine were dissolved in 50 ml of dry DMF. The solution was then heated to 60°C under nitrogen overnight. Next day, the reaction mixture was poured into 400 ml of anhydrous diethyl ether. A white precipitate was obtained by filtration in 98% yield. Recrystallization with ethyl acetate afforded white crystals in 90% recovery. ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.92-7.70 (m, 30H), 7.16-7.14 (m, 2H), 6.75-6.72 (m, 2H),6.15 (d, 2H, J= 6.3 Hz)), 4.90 (d, 4H, J= 15.6 Hz), 2.37 (s, 2H).

The phase transfer Wittig reactions

A solution of the 3,4-benzcycloheptatriene-1,6-dialdehyde **63** (5.05 mmole) and xylene bisphosphonium salt (6.09 mmole) in methylene chloride was stirred under nitrogen at room temperature. 20.3 mmole of ground $K_2CO_{3(s)}$ powder were then added into the solution. The reaction was monitored by TLC. After 16 hours of stirring, the reaction mixture was quenched with water and extracted with diethyl ether. After the evaporation of the solvent, the residue was purified by chromatography (hexane/ethyl acetate 5/1) affording the mixture of cis/trans isomers **82** in 51.2% yield (cis/trans=1/1). Cis and trans isomers were separated by recrystallization from hexane. Using $LiOH_{(s)}$ instead of $K_2CO_{3(s)}$, we obtained the mixture of cis/trans isomers **82** in 8.3% (cis/trans=1/1). When using $KOH_{(s)}$, not only mono-adduct **82** was obtained in 34.9% but also di-adduct **83** was obtained in 2.7%. **MS** (EI/70 eV) m/z: M^+ 286 (100%).

3.3.3 The McMurry approach to benzannulenes

3,4:11,12-dibenzo-anti-1,6:9,14-bismethano[16]annulene (IV)

A 500 ml three-necked flask fitted with a reflux condenser, dropping funnel and a nitrogen inlet was charged with dry THF (250ml) and cooled to -78°C. $TiCl_4$(40mmole). Then, zinc powder (80mmole) and dry pyridine(1ml) were added slowly. The resultant black mixture was refluxed under nitrogen for one hour and a solution of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde (5mmole) **63** in dry THF (200ml) was then added dropwise to the stirred mixture over 24 hrs. After being refluxed for further 12 hrs, the reaction mixture was ice-cooled and quenched by 10% K_2CO_3. The gray precipitate was filtered out and the filtrate extracted thoroughly with dichloromethane. The combined organic phases were washed with water, dried over with $MgSO_4$ and evaporated to get a orange semi-solid residue. The residue was purified by flash chromatography (hexane/methylene chloride 1/1) affording orang-red crystals in 17% yield. **mp:** 237^{0}C (dec.); **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.16-7.08 (AA'BB', 8H), 6.47 (s, 4H), 6.03 (s, 4H), 4.41 (d, 2H, J=15.3 Hz), 3.31 (d, 2H, J=15.6 Hz); **^{13}C NMR**: δ= 138.9, 137.2, 135.6, 132.9, 131.6, 127.2, 32.4; **IR** (KBr, cm^{-1}): 3009, 2837, 1481, 1439, 1430, 1414, 952, 900, 872, 756, 732; **UV** (cyclohexane): λ_{max}(nm): 323 (149,778), 330 (152, 212), 390 (7,373), 755 (3,170), 765 (3,034); **MS** (CI) m/z: M$^+$ 333 (100%); calc. for $C_{26}H_{20}$ 332.444.

3,4:11,12-dibenzo-7,8,15,16-tetrahydro-anti-1,6:9,14-bismethano[16]annulene (93)

20 mg (0.06 mmole) of 3,4:11,12-dibenzo-anti-1,6:9,14-bis-methano[16]annulene **IV** were dissolved in 70 ml of ethyl acetate to form an orange solution. The system was filled with nitrogen and a small amount of palladium in charcoal was then added to the solution. The solution was then cooled to 0^{o}C. After introduction of hydrogen into the hydrogenation system, the ice bath was removed and 9 ml of hydrogen were determined to have reacted in the process at room temperature. Platinum/charcoal was then filtered

out and the solution became colorless. The ethyl acetate was then evaporated to get semi-solid residue. The residue was purified by flash chromatography (hexane/ethyl acetate 30/1) affording white solid in 32.6% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.18-7.07 (AA'BB', 8H), 6.19 (s, 4H), 2.74 (s, 8H), 2.24 (s, 4H) ; **^{13}C NMR**: δ= 138.7, 136.9, 129.3, 126.1, 124.9, 36.8, 36.1; **MS** (EI/70 eV) m/z: M^+ 336 (100%).

3.3.4 The RCM approach to benzannulenes

I. O-Phthalaldehyde series

1,2-bis(1-hydroxybutenyl)benzene (110)

4.02 g (30 mmole) of o-phthalic dicarboxyaldehyde was dissolved in 80 ml of dry THF. 50 ml (100 mmole) of 2.0 M allyl magnesium chloride solution in THF were then added while stirring under nitrogen at 0°C. After stirring overnight at room temperature, the reaction mixture was quenched by sat. ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with water, dried and evaporated to obtain pale yellow residue. Chromatography was run on silica gel in hexane to ethyl acetate 4:1 affording a mixture of two isomers in 74 % yield and cope rearrangement compound **C**.

Isomer A: ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm)= 7.50-7.46 (m, 2H), 7.33-7.29 (m, 2H), 5.92-5.78 (m, 2H), 5.22-5.15 (m, 4H), 5.04 (td, 2H, J= 6.5 Hz, J= 2.6 Hz), 2.59-2.54 (m, 4H), 2.24 (s, 2OH); **^{13}C NMR**: δ=

140.7, 134.9, 128.1, 126.4, 118.6, 69.9, 43.3; **MS** (EI/70 eV) m/z: M^+ 218, 236 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.51-7.48 (m, 2H), 7.34-7.31 (m, 2H), 5.93-5.79 (m, 2H), 5.22-5.15 (m, 4H), 5.07 (t, 2H, J= 6.6 Hz,), 2.60-2.55 (m, 4H), 2.41 (s, 2OH); ^{13}**C NMR**: δ= 140.9, 135.0, 128.2, 126.3, 118.6, 69.2, 42.6; **MS** (EI/70 eV) m/z: M^+ 218, 236 (100%).

Compound C: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.56 (d, 1H, J=7.2 Hz), 7.29-7.22 (m, 2H), 5.91-5.80 (m, 1H), 5.75-5.61 (m, 2H), 5.53 (t, 1H, J= 6.6 Hz), 5.20 (t, 1H, d=1.7 Hz), 5.11 (d, 6H, J= 12 Hz), 2.95 (s, 2OH), 2.85-2.73 (m, 2H), 2.67-2.56 (m, 4H); ^{13}**C NMR**: δ= 142.7, 142.1, 135.9, 133.8, 128.4, 127.5, 127.3, 127.2, 119.7, 119.5, 117.9, 77.4, 70.8, 47.3, 43.1; **MS** (EI/70 eV) m/z: M^+ 276, 258, 199 (100%).

1,2-bis(1-tert-butyldimethylsilyloxybutenyl)benzene (96a)

4.20 g (19.3 mmole) of 1,2-bis(1-hydroxybutenyl)benzene **110** was dissolved in 15 ml of dry DMF under nitrogen. 7.35 g (48.8 mmole) of tert-butyldimethylsilyl chloride and 3.46 g (50.8 mmole) of imidazole were added into the solution. After the reaction mixture was stirred at R.T. overnight, the reaction was quenched with sat. $NaCl_{(aq)}$ in ice water and extracted with diethyl ether. After the organic layer was washed with sat. $NaHCO_{3(aq)}$ and water, the organic solvent was evaporated. Chromatography was run on silica gel in 50 to 1 hexane/ethyl acetate mixture to afford colorless liquid mixture of two isomers in 67% yield. **MS** (EI/70 eV) m/z: M^+ 405.

1,2-bis(1-trimethylsilyloxybutenyl)benzene (96b)

1.51 g (6.9 mmole) of 1,2-bis(1-hydroxybutenyl)benzene **110** was dissolved in 15 ml of dry DMF under nitrogen. THe solution was cooled under ice bath. Then, 3.5 ml (27.7 mmole) of chlorotrimethylsilane and 4.1 ml (29.1 mmole) of triethylamine were separately added into the solution. After the reaction mixture was stirred at R.T. overnight, the solution was deep color. Then, the reaction was quenched with sat. $NaHCO_{3(aq)}$ in ice water and extracted with diethyl ether. After the organic layer was washed with water, the organic solvent was evaporated. Chromatography was run on silica gel in 20 to 1 hexane/ethyl acetate mixture to afford colorless liquid mixture of two isomers in 56% yield, but 77% conversion. **MS** (EI/70 eV) m/z: M^+ 321, 231 (100%).

1,2-bis(1-acetoxybutenyl)benzene (96c)

1.09 g (5 mmole) of 1,2-bis(1-hydroxybutenyl)benzene **110** was suspended in 10 ml of acetic anhydride and cooled to 0°C. After 1 ml of pyridine were added slowly into the solution, the ice bath was removed and the reaction mixture was stirred at R.T. overnight. Then the reaction was quenched by 120 ml of dil. $HCl_{(aq)}$ and extracted with diethyl ether. After the organic layer was washed with sat. $NaHCO_{3(aq)}$ and water, the organic solvent was dried and evaporated to obtain colorless residue. The residue was purified by chromatography (hexane/ethyl acetate 8:1) affording a mixture of two isomers in 86 % yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.39-7.34 (m, 2H), 7.31-7.26 (m, 2H), 6.10 (dd, 2H, J=8.7 Hz, J=4.5 Hz), 5.89-5.76 (m, 2H), 5.17-5.06 (m, 4H), 2.74-2.56 (m, 4H), 2.06 (s, 6H); ^{13}C **NMR**: δ= 170.4, 137.8, 133.9, 128.2, 126.0, 118.1, 71.9, 40.8, 21.3; **MS** (EI/70 eV) m/z: M$^+$ 302, 261, 159 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, CDCl$_3$): δ(ppm)= 7.41-7.37 (m, 2H), 7.32-7.28 (m, 2H), 6.17 (dd, 2H, J=8.3 Hz, J=5.6 Hz), 5.80-5.66 (m, 2H), 5.14-5.04 (m, 4H), 2.76-2.54 (m, 4H), 2.06 (s, 6H); ^{13}C **NMR**: δ= 170.2, 137.8, 133.8, 128.3, 127.5, 118.2, 72.5, 40.8, 21.3; **MS** (EI/70 eV) m/z: M$^+$ 302, 261, 159 (100%).

1,4-bis(tert-butyldimethylsilyloxy)-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene (97a)

0.89 g (2 mmole) of 1,2-bis(1-tert-butyldimethylsilyloxy-butenyl) benzene **96a** was dissolved in 50 ml of methylene chloride at R.T. under nitrogen and 29 mg (0.04 mmole) of bis(tricyclopentyl-phosphine) benzylidene ruthenium(IV) dichloride were added into the solution while stirring. After reacting for 48 hours, the reaction mixture was refluxed for 24 hours. Then, the organic solvent was evaporated, and chromatography on silica gel was run in 100 to 1 hexane/ethyl acetate mixture to obtain a mixture of two isomers in 41% yield, 84% conversion.

Isomer A: ^{1}**H NMR** (300 MHz, CDCl$_3$): δ(ppm)= 7.25-7.23 (m, 2H), 7.20-7.17 (m, 2H), 5.36-5.31 (m, 4H), 2.79-2.70 (m, 2H), 2.38-2.27 (m, 2H); ^{13}C **NMR**: δ= 141.3, 128.9, 127.6, 127.4, 97.6, 74.1, 40.8, 26.2, 18.4; **MS** (EI/70 eV) m/z: M$^+$ 364 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, CDCl$_3$): δ(ppm)= 7.55-7.52 (m, 2H), 7.26-7.23 (m, 2H), 5.34 (t, 2H, J=3.9 Hz), 5.20 (dd, 2H, J=7.8 Hz, J=5.7 Hz), 2.82-2.74 (m, 2H), 2.35-2.25 (m, 2H); ^{13}C **NMR**: δ= 140.7, 126.9, 126.6, 123.9, 69.9, 42.9, 26.1, 18.6; **MS** (EI/70 eV) m/z: M^+ 364 (100%).

1,4-bis(trimethylsilyloxy)-1,4,5,8-tetrahydro-2,3-benzo-cyclooctatetraene (97b)

0.18 g (0.5 mmole) of 1,2-bis(1-tert-butyldimethylsilyloxy-butenyl) benzene **96b** was dissolved in 15 ml of methylene chloride at R.T. under nitrogen and 9 mg (0.0125 mmole) of bis(tricyclopentyl- phosphine) benzylidine ruthenium(IV) dichloride was added into the solution while stirring. After reacting for 48 hours, the reaction mixture was refluxed for 24 hours. Then, the organic solvent was evaporated, and chromatography on silica gel was run in 60 to 1 hexane/ethyl acetate mixture to obtain a mixture of two isomers in 66% yield, 85% conversion.

MS (EI/70 eV) m/z: M+ 334, 280 (100%).

1,4-diacetoxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetra-ene (97c)

0.16 g (0.53 mmole) of 1,2-bis(1-acetoxybutenyl)benzene **96c** was dissolved in 20 ml of methylene chloride at R.T. under nitrogen and 19.6 mg (0.026 mmole) of bis(tricyclopentylphosphine) benzylidine ruthenium(IV) dichloride was added into the solution while stirring. After 48 hours, the reaction mixture was refluxed for 24 hours. Then, the organic solvent was evaporated, and chromatography on silica gel was run in 8 to 1 hexane/ethyl acetate mixture to obtain a mixture of two isomers in 55% yield, 88% conversion.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.38-7.33 (m, 2H), 7.31-7.26 (m, 2H), 6.44 (dd, 2H, J= 10.4 Hz, J= 7.9 Hz), 5.44 (t, 2H, J= 4.4 Hz), 3.00-2.91 (m, 2H), 2.57-2.45 (m, 2H), 2.10 (s, 6H); **^{13}C NMR**: δ= 170.1, 137.3, 128.4, 128.1, 128.0, 74.3, 35.8, 21.5; **MS** (EI/70 eV) m/z: M^+ 214.

Isomer B: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.38-7.35 (m, 2H), 7.31-7.26 (m, 2H), 6.36 (t, 2H, J= 6.8 Hz), 5.45 (t, 2H, J= 4.5 Hz), 3.03-2.95 (m, 2H), 2.47-2.34 (m, 2H), 2.17 (s, 6H); **^{13}C NMR**: δ= 170.0, 136.9, 127.9, 127.1, 124.7, 72.2, 37.3, 21.5; **MS** (EI/70 eV) m/z: M^+ 214.

1,4-dihydroxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene (112)

method A: 0.24 g (0.88 mmole) of 1,4-diacetoxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene **97c** was suspended in 15 ml of methanol, and 2 ml of 3N $NaOH_{(aq)}$ was added into the solution under ice bath. After one and half hours of stirring, the reaction mixture was quenched by sat. $NaCl_{(aq)}$ in ice water and extracted with diethyl ether. The organic layer was then washed with $NaCl_{(aq)}$ and water, dried and evaporated to obtain white solid products. The product was recrystallized from methylene chloride affording two isomers in 84% combined yield.

method B: 0.14 g (0.33 mmole) of 1,4-bis(tert-butyldimethyl silyloxy)-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene **97a** was dissolved in 5 ml of THF, and 1 ml of tetrabutylammonium fluoride (1 M in THF) was added to the solution, turning it yellow. After stirring at room temperature for 30 mins, the organic solvent was evaporated and the residue was purified and isolated by flash chromatography (hexane: ethyl acetate 1/1) affording two solid isomers in 63% combined yield. The two isomers were then recrystallized from methylene chloride to obtain white crystals.

Isomer A: mp: 147-148 °C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.39 (dd, 2H, J=5.7 Hz, J=3.6 Hz), 7.29 (dd, 2H, J=5.4 Hz, J=3.3 Hz), 5.49-5.43 (m, 4H), 2.94-2.85 (m, 2H), 2.46-2.35 (m, 2H), 2.00 (s, 2OH); **^{13}C NMR**: δ= 141.1, 128.5, 128.3, 127.5, 73.4, 38.9; **IR** (KBr, cm^{-1}): 3281, 1036, 1024, 982, 969; **MS** (EI/70 eV) m/z: M^+ 172, 118 (100%).

Isomer B: mp: 164.5-165.5 °C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.45 (dd, 2H, J=5.9 Hz, J=3.5 Hz), 7.30 (dd, 2H, J=5.7 Hz, J=3.3Hz), 5.48 (t, 2H, J= 4.1 Hz), 5.25 (t, 2H, J=6.8 Hz), 2.94-2.84 (m, 2H), 2.61-2.52 (m, 2H), 1.92 (s, 2OH); **^{13}C NMR**: δ= 140.6, 127.9, 127.8, 126.0, 72.5, 39.6; **IR** (KBr, cm^{-1}): 3348, 1481, 1026, 770, 744; **MS** (EI/70 eV) m/z: M+ 172, 118(100%).

Benzocyclooctatetraene (113)

50 mg (0.26 mmole) of 1,4-dihydroxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene **112** and 0.32 ml of thionyl chloride were mixed in a round bottom flask under nitrogen. 0.25 ml of pyridine was then added slowly into the reaction mixture under ice bath. After 90 mins of stirring, the ice bath was removed and the reaction mixture was stirred at room temperature for further 30 mins. Then, the reaction mixture was quenched by sat. $NaCl_{(aq)}$ in ice water and extracted with methylene chloride. The organic layer was washed

with water and evaporated to obtain 1,4-dichloro-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene as a yellow oil residue.

The yellow oil residue was dissolved in 20 ml of THF and 0.12 g (1.07 mmole) of potassium tert-butoxide were added into the solution under ice bath. After 40 mins of stirring, the solution was kept in refrigerator overnight. Then, the reaction mixture was warmed to room temperature and quenched by sat. $NaCl_{(aq)}$ in ice water. After the reaction mixture was extracted with methylene chloride, the organic layer was washed with ice water and evaporated to obtain an oil residue. The residue was then purified by chromatography on aluminum oxide in hexane affording pure product. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ(ppm)= 7.20 (dd, 2H, J=5.6 Hz, J=3.5 Hz), 6.95 (dd, 2H, J=5.6 Hz, J=3.5 Hz), 6.54 (d, 2H, J=11.4 Hz), 6.02 (dt, 2H, J=11.1 Hz, J=1.7 Hz), 5.88 (dd, 2H, J=2.0 Hz, J=1.4 Hz), ; **^{13}C NMR**: δ= 138.6, 134.1, 131.7, 131.3, 130.1, 127.4; **MS** (EI/70 eV) m/z: M^+ 154, 153 (100%).

The oxidation of 1,4-dihydroxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene

Method A: 0.272 g (1.26 mmole) of pyridinium chlorochromate was dissolved in 20 ml of dry methylene chloride. To this was added the solution of 80 mg (0.42 mmole) of 1,4-dihydroxy-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene **112** in 30 ml of dry methylene chloride. The reaction mixture was stirred at R.T. for two hours. After the black residue was filtered off, the filtrate was extracted with diethyl ether and dried. The organic solvent was evaporated to obtain a yellow residue. Chromatography on silica gel [hexane:ethyl acetate 3/1] afforded hemiketal **114** in 77% yield. **^{1}H NMR** (300 MHz, CH_2Cl_2): δ(ppm)= 7.32-7.28 (m, 3H), 7.02-6.98 (m, 1H), 5.23(t, 2H, J=2.7 Hz), 5.09 (d, 1H, J=4.5 Hz), 4.07 (s, OH), 3.02-2.85 (m, 2H), 2.74-2.67 (m, 1H), 2.29-2.22 (m, 1H); **^{13}C NMR**: δ= 142.3, 142.0, 128.9, 128.0, 124.8, 124.0, 120.9, 120.4, 108.3, 78.0, 44.6, 37.8; **MS** (EI/70 eV) m/z: M^+ 188, 170, 134 (100%).

Method B: 60 mg (0.32 mmole) of 1,4-dihydro-1,4,5,8-tetrahydro-2,3-benzocyclooctatetraene was dissolved in 20 ml of dry methylene chloride in a flask adapted with a condenser. To this was added 0.55 g (2.55 mmole) of PCC with stirring. The solution became black and was refluxed for 12 hours. Then, the black mixture was cooled and filtered by celite. After the black precipitate was washed with diethyl ether, the solvent was removed from filtrate to obtain brown residue. The residue was purified and isolated by chromatography [hexane:ethyl acetate 6/1] on silica gel affording unexpected compounds **115** and **116**.

Compound 115: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.71-7.64 (m, 3H), 7.47-7.42 (m, 1H), 5.74-5.66 (m, 2H), 3.67-3.60 (m, 1H), 3.04-2.85 (m, 3H); **^{13}C NMR**: δ= 203.4, 157.4, 136.1, 135.0, 131.3, 129.7, 127.4, 124.8, 124.0, 84.9, 68.9, 47.3; **MS** (EI/70 eV) m/z: M^+ 186, 168 (100%).

Compound 116: **^{1}H NMR** (300 MHz, CD_2Cl_2): δ(ppm)= 7.97 (dd, 1H, J=8.0 Hz, J=1,4 Hz), 7.70 (td, 1H, J=7.5 Hz, J=1.2 Hz), 7.62 (dd, 1H, J=8.0 Hz, J=1.4 Hz), 7.52 (td, 1H, J=7.5 Hz, J=1.4 Hz), 5.97-5.84 (m, 2H), 4.97-4.95 (m, 1H), 3.46 (s, OH), 2.81 (dq, 1H, J=18 Hz, J=2.1 Hz), 2.52 (dd, 1H, j=17.9 Hz, J=5.0 Hz); **^{13}C NMR**: δ= 193.2, 145.6, 134.9, 129.6, 128.3, 127.6, 126.4, 125.6, 123.6, 95.3, 80.5, 37.7; **MS** (EI/70 eV) m/z: M^+ 202, 184 (100%).

II. 3,4-benzcycloheptatriene-1,6-dialdehyde series

3,4-benz-1,6-bis(1-hydroxyallyl)-1,3,5-cycloheptatriene (119)

1.98 g (10 mmole) of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde **63** was dissolved in 55 ml of dry THF. 30 ml of 1.0 M vinyl magnesium bromide solution in THF was then added while stirring under nitrogen at 0°C. After 20 mins of stirring at room temperature, the reaction mixture was quenched by sat. ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with water, dried and evaporated to obtain pale yellow residue. Chromatography on silica gel in hexane to ethyl acetate 3:1 gave a mixture of two isomers in 86 % yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.32-7.22 (m, 4H), 6.60 (s, 2H), 6.04-5.93 (m, 2H), 5.43 (dt, 2H, J= 17.1 Hz, J= 1.5 Hz), 5.25 (dt, 2H, J= 10.5 Hz, J= 1.5 Hz), 4.84 (d, 2H, J=4.2 Hz), 2.86 (s, 2OH), 2.69 (d, 1H, J= 13.8 Hz), 2.21 (d, 1H, J= 14.1 Hz); **MS** (EI/70 eV) m/z: M^+ 254, 165 (100%).

Isomer B: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.31-7.21 (m, 4H), 6.57 (s, 2H), 6.05-5.94 (m, 2H), 5.40 (d, 2H, J= 17.1 Hz,), 5.25 (d, 2H, J= 10.5 Hz), 4.82 (d, 2H, J=5.4 Hz), 3.24 (s, 2OH), 2.50 (s, 2H); **MS** (EI/70 eV) m/z: M^+ 254, 181 (100%).

3,4-benz-1,6-bis(1-acetoxyallyl)-1,3,5-cycloheptatriene (98b)

2.69 g (10.6 mmole) of 3,4-benz-1,6-bis(1-hydroxyallyl)-1,3,5-cycloheptatriene **119** was suspended in 15 ml of acetic anhydride and cooled to $0^{o}C$. After 2 ml of pyridine was added slowly into the solution, the ice bath was removed and the reaction mixture was stirred at R.T. for an hour. Then the reaction was quenched by 120 ml of dil. $HCl_{(aq)}$ and extracted with diethyl ether. After the organic layer was washed with sat. $NaHCO_{3(aq)}$ and water, the organic solvent was dried and evaporated to obtain a colorless residue. The residue was purified by chromatography (hexane/ethyl acetate 5:1) affording a mixture of two isomers in 60 % yield.

Isomer A: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.35-7.24 (m, 4H), 6.67 (s, 2H), 5.97-5.88 (m, 4H), 5.40-5.31 (m, 4H), 2.52 (d, 1H, J= 14.4 Hz), 2.30 (d, 1H, J= 14.1 Hz), 2.15 (s, 6H); ^{13}**C NMR**: δ= 169.9, 137.5. 135.8, 134.8, 130.7,127.5, 126.5, 118.0, 77.7, 27.5, 21.4. **MS** (EI/70 eV) m/z: M^+ 338.

Isomer B: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.34-7.26 (m, 4H), 6.66 (s, 2H), 5.95-5.88 (m, 4H), 5.40-5.30 (m, 4H), 2.45 (s, 2H), 2.15 (s, 6H); ^{13}**C NMR**: δ= 170.0, 137.8, 137.5, 135.8, 134.8, 130.6, 127.7, 127.5, 126.6, 118.1, 117.9, 77.5, 77.4, 27.5, 21.4; **MS** (EI/70 eV) m/z: M^+ 338.

Cope rearrangement products from 3,4-benz-1,6-bis(1-acetoxyallyl)-1,3,5-cycloheptatriene

1.41 g (5.6 mmole) of 3,4-benz-1,6-bis(1-hydroxyallyl)-1,3,5-cycloheptatriene was suspended in 20 ml of acetic anhydride and cooled to 0°C. After 1.4 ml of pyridine was added slowly into the solution, the ice bath was removed and the reaction mixture was heated to 40°C for an hour. The NMR spectrum of the mixture at this point in the procedure showed that there is no more starting material left. After one and half hours of further heating, the reaction was quenched by 100 ml of dil. $HCl_{(aq)}$ and extracted with diethyl ether. In order to remove excess acetic anhydride, the organic layer was washed with sat. $NaHCO_{3(aq)}$ and water. After the organic solvent was removed, the residue was isolated by flash chromatography(hexane/ethyl acetate 4:1) to afford compound **120** and compound **121** caused by Cope rearrangement.

Compound 120: ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm)= 7.43-7.32 (m, 4H), 6.69 (s, 1H), 6.63 (s, 1H), 6.45 (d, 1H, J= 15.6 Hz), 6.11-6.02 (m, 1H), 5.92-5.81 (m, 2H), 5.40-5.25 (m, 2H), 4.71 (d, 2H, J=6.3 Hz), 2.62 (d, 2H, J= 6.3 Hz), 2.11 (s, 3H), 2.09 (s, 3H); **^{13}C NMR**: δ= 170.9, 170.0, 137.5, 137.4, 136.6, 135.9, 135.8, 134.6, 131.7, 130.8, 130.7, 128.7, 126.7, 126.6, 123.8, 117.6, 77.9, 65.3, 25.6, 21.1, 21.3; **MS** (EI/70 eV) m/z: M^+ 338.

Compound 121: ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm)= 7.37-7.25 (m, 4H), 6.68 (s, 2H), 6.52 (d, 2H, J= 15.6 Hz), 6.13-6.04 (m, 2H), 4.72 (d, 4H, J= 6.3 Hz), 2.73 (s, 2H), 2.11 (s, 6H); **^{13}C NMR**: δ= 170.9, 136.8, 136.6, 136.4, 131.6, 130.7, 126.7, 123.0, 65.2, 25.0, 21.2; **MS** (EI/70 eV) m/z: M^+ 338.

3,4-benz-1,6-bis(1-tert-butyldimethylsilyloxyallyl)-1,3,5-cycloheptatriene (98a)

0.38 g (1.5 mmole) of 3,4-benz-1,6-bis(1-hydroxyallyl)-1,3,5-cycloheptatriene **119** was dissolved in 4 ml of dry DMF under nitrogen. 0.66 g (4.4 mmole) of tert-butyldimethylsilyl chloride and 0.3 g (4.4 mmole) of imidazole were added into the solution. After the reaction mixture was stirred at R.T. for an hour, a precipitate formed. With additional hour of stirring, the reaction was quenched with sat. $NaCl_{(aq)}$ in ice water and extracted with diethyl ether. After the organic layer was washed with saturated $NaHCO3_{(aq)}$ and water, the organic solvent was evaporated. Chromatography on silica gel in 40 to 1 hexane/ethyl acetate mixture gave a colorless liquid mixture of two isomers in 37% yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.35-7.21 (m, 4H), 6.63 (s, 2H), 5.83-5.74 (m, 2H), 5.34 (d, 2H, J= 16.8 Hz), 5.14 (d, 2H, J= 11.4 Hz), 4.68 (d, 2H, J= 5.4 Hz), 2.68 (d, 1H, J= 14.4 Hz), 1.95 (d, 1H, J=14.4 Hz), 0.91 (s, 18H), 0.08 (s, 6H), 0.03 (s, 6H); **MS** (EI/70 eV) m/z: M^+ 482, 350 (100%).

Isomer B: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.35-7.21 (m, 4H), 6.63 (s, 2H), 5.83-5.74 (m, 2H), 5.34 (d, 2H, J= 16.8 Hz), 5.14 (d, 2H, J= 11.4 Hz), 4.68 (d, 2H, J= 5.4 Hz), 2.38 (s, 2H), 0.91 (s, 18H), 0.08 (s, 6H), 0.03 (s, 6H); **MS** (EI/70 eV) m/z: M^+ 482.

3,4-benzo-7,10-bis(tert-butyldimethylsilyloxy)-7,10-dihydro-1,6-methano[10]annulene (99a)

0.26 g (0.54 mmole) of 3,4-benz-1,6-bis(1-tert-butyldimethylsilyloxyallyl)-1,3,5-cycloheptatriene **98a** was dissolved in methylene chloride under nitrogen and 7.9 mg (0.011 mmole) of bis(tricyclopentylphosphine) benzylidine ruthenium(IV) dichloride was added into the solution. Then the reaction mixture was stirred at R.T. overnight. Although the GC-MS spectrum showed a trace of product present, it was too little to isolate.

3,4-benz-1,6-bis(1-hydroxybutenyl)-1,3,5-cycloheptatriene (122)

3.96 g (20 mmole) of 3,4-benz-1,3,5-cycloheptatriene-1,6-dialdehyde **63** was dissolved in 120 ml of dry THF. 25 ml of 2.0 M allyl magnesium chloride in THF was then added while stirring under nitrogen at 0°C. After one hour of stirring, an additional 20 ml of 2.0 M allylmagnesium chloride in THF was added into the solution. Then, the ice bath was removed and the reaction mixture was stirred at room temperature for another hour. It was then quenched by saturated ammonium chloride solution and extracted with diethyl ether. The organic layer was washed with water, dried and evaporated to obtain pale yellow residue. Chromatography on silica gel in hexane to ethyl acetate 4:1 gave a mixture of two isomers in 96 % yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.27-7.19 (m, 4H), 6.48 (s, 2H), 5.86-5.73 (m, 2H), 5.16-5.08 (m, 4H), 4.29 (t, 2H, J= 6.9 Hz), 3.50 (s, 2OH), 2.83 (d, 1H, J= 13.5 Hz), 2.50 (t, 4H, J=7.0 Hz), 2.17 (d, 1H, J= 13.5 Hz); **^{13}C NMR**: δ= 143.4, 136.1, 134.6, 130.2, 126.4, 126.1, 118.0, 75.8, 40.8, 24.2; **MS** (EI/70 eV) m/z: M^+ 300, 282 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.29-7.20 (m, 4H), 6.52 (s, 2H), 5.90-5.76 (m, 2H), 5.19-5.11 (m, 4H), 4.32 (t, 2H, J= 6.5 Hz,), 3.04 (s, 2OH), 2.56-2.41 (m, 4H), 2.50 (s, 2H); ^{13}**C NMR**: δ= 143.7, 136.1, 134.7, 130.3, 126.1, 125.5, 118.1, 74.9, 40.3, 27.0; **MS** (EI/70 eV) m/z: M^+ 300, 282 (100%).

3,4-benz-1,6-bis(1-tert-butyldimethylsilyloxybutenyl)-1,3,5-cycloheptatriene (100a)

2.68 g (9.5 mmole) of 3,4-benz-1,6-bis(1-hydroxybutenyl)-1,3,5-cycloheptatriene **122** was dissolved in 10 ml of dry DMF under nitrogen. 4.3 g (28.5 mmole) of tert-butyldimethylsilyl chloride and 2.1 g (30.8 mmole) of imidazole were added into the solution. After the reaction mixture was stirred at R.T. overnight, a precipitate formed. The reaction was then quenched with saturated $NaCl_{(aq)}$ in ice water and extracted with diethyl ether. After the organic layer was washed with saturated $NaHCO_{3(aq)}$ and water, the organic solvent was evaporated. Chromatography on silica gel in 60 to 1 hexane/ethyl acetate mixture gave a colorless liquid mixture of two isomers in 62% yield.

Isomer A: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.30-7.19 (m, 4H), 6.55 (s, 2H), 5.87-5.78 (m, 2H), 5.08-5.02 (m, 4H), 4.26 (t, 2H, J= 6 Hz), 2.79 (d, 1H, J= 14.7 Hz), 2.37 (t, 4H, J= 6.5 Hz), 2.15 (d, 1H, J=14.4 Hz), 0.90 (s, 18H), 0.072 (s, 6H), -0.15 (s, 6H); **MS** (EI/70 eV) m/z: M^+ 469 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.27-7.19 (m, 4H), 6.52 (s, 2H), 5.83-5.78 (m, 2H), 5.22-5.01 (m, 4H), 4.30 (t, 2H, J= 6

Hz), 2.60 (s, 2H), 2.43 (t, 4H, J= 6.5 Hz), 0.90 (s, 18H), 0.07 (s, 6H), 0.02 (s, 6H); **MS** (EI/70 eV) m/z: M^+ 469 (100%).

3,4-benz-1,6-bis(1-acetoxybutenyl)-1,3,5-cycloheptatriene (100b)

2.22 g (7.9 mmole) of 3,4-benz-1,6-bis(1-hydroxybutenyl)-1,3,5-cycloheptatriene **122** was suspended in 14 ml of acetic anhydride and cooled to 0°C. After 1.5 ml of pyridine was added slowly into the solution, the ice bath was removed and the reaction mixture was stirred at R.T. overnight. Then the reaction was quenched by 120 ml of dil. $HCl_{(aq)}$ and extracted with diethyl ether. After the organic layer was washed with saturated $NaHCO_{3(aq)}$ and water, the organic solvent was dried and evaporated to obtain a colorless residue. The residue was purified by chromatography (hexane/ethyl acetate 8:1) affording a mixture of two isomers in 68 % yield.

Isomer A: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.32-7.22 (m, 4H), 6.60 (s, 2H), 5.82-5.69 (m, 2H), 5.48 (t, 2H, J=6.5 Hz), 5.16-5.06 (m, 4H), 2.60-2.55 (m, 6H), 2.40 (d, 1H, J= 14.1 Hz), 2.10 (s, 6H); ^{13}**C NMR**: δ= 170.3, 138.6, 135.7, 133.6, 130.7, 127.3, 126.5, 118.2, 76.6, 38.2, 27.7, 21.4; **MS** (EI/70 eV) m/z: M^+ 306, 246 (100%).

Isomer B: ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.30-7.21 (m, 4H), 6.59 (s, 2H), 5.81-5.67 (m, 2H), 5.49 (t, 2H, J=6.9 Hz), 5.16-5.06 (m, 4H), 2.60-2.54 (m, 4H), 2.53 (s, 2H), 2.09 (s, 6H); ^{13}**C NMR**: δ= 170.2, 138.5, 135.7, 133.5, 130.6, 128.1, 126.5, 118.1, 77.0, 38.1, 26.4, 21.4; **MS** (EI/70 eV) m/z: M^+ 306, 246 (100%).

3,4-benzo-7,12-bis(tert-butyldimethylsilyloxy)-7,8,11,12-tetrahydro-1,6-methano[12]annulene (101a)

0.44 g (0.86 mmole) of 3,4-benz-1,6-bis(1-tert-butyldimethyl silyloxy butenyl)-1,3,5-cycloheptatriene **100a** was dissolved in methylene chloride at R.T. under nitrogen and 31.8 mg (0.043 mmole) of bis(tricyclopentylphosphine) benzylidine ruthenium(IV) dichloride was added into the solution while stirring. After reacting overnight, the organic solvent was evaporated, and chromatography on silica gel was run in 60 to 1 hexane/ethyl acetate mixture to obtain a mixture of two isomers in 88% yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.30-7.20 (m, 4H), 6.33 (s, 2H), 5.31 (dd, 2H, J= 6.3 Hz, J= 4.2 Hz), 4.51 (dd, 2H, J= 10.2 Hz, J= 6.6 Hz), 3.08 (d, 1H, J= 14.4 Hz), 2.91 (q, 2H, J= 11.9 Hz), 2.32-2.24 (m, 2H), 1.75 (dt, 1H, J= 14.1 Hz, J= 1.5 Hz), 0.9 (s, 18H), 0.16 (s, 6H), 0.6 (s, 6H); **^{13}C NMR**: δ= 144.1, 136.7, 130.0, 128.3, 127.7, 126.0, 79.7, 34.6, 26.1, 21.7, 18.5; **MS** (EI/70 eV) m/z: M^+ 482, 428(100%).

Isomer B: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.29-7.17 (m, 4H), 6.73 (d, 1H, J= 1.5 Hz), 6.34 (s, 1H), 5.57 (td, 1H, J= 11.3 Hz, J=5.0 Hz), 5.39 (td, 1H, J= 11.3, J= 5.1 Hz), 4.80 (s, 1H), 4.51 (dd, 1H, J= 10.1, J= 6.8 Hz), 3.20 (ddd, 1H, J= 13.8Hz, J= 12.2Hz, J= 4.1 Hz), 2.79-2.68 (m, 1H), 2.66 (d, 1H, J= 13.8 Hz), 2.32 (quintet, 1H, J= 6 Hz), 2.17 (dt, 1H, J=13.5 Hz, J= 3.6 Hz), 1.90 (d, 1H, J= 13.9 Hz), 1.00 (s, 9H), 0.90 (s, 9H); 0.20 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H), 0.05 (s, 3H); **^{13}C NMR**: δ= 143.5, 143.4, 137.3, 136.1, 130.3, 129.9, 128.5, 128.4, 127.6, 125.9, 125.4, 123.7, 79.1, 75.7, 34.9, 33.7, 26.2, 26.1, 24.7, 18.6; **MS** (EI/70 eV) m/z: M^+ 482, 428(100%).

3,4-benzo-7,12-diacetoxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene (101b)

0.28 g (0.77 mmole) of 3,4-benz-1,6-bis(1-acetoxybutenyl)-1,3,5-cycloheptatriene **100b** was dissolved in methylene chloride at R.T. under nitrogen and 28 mg (0.038 mmole) of bis(tricyclopentyl-phosphine) benzylidine ruthenium(IV) dichloride was added into the solution while stirring. After reacting for 48 hours, the organic solvent was evaporated, and chromatography on silica gel was run in 10 to 1 hexane/ethyl acetate mixture to obtain a mixture of two isomers in 81% yield.

Isomer A: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.34-7.21 (m, 4H), 6.62 (s, 2H), 5.66 (dd, 2H, J= 10.7 Hz, J= 6.5 Hz), 5.40 (dd, 2H, J= 6.2 Hz, J= 4.4 Hz), 3.07 (d, 1H, J= 14.4 Hz), 2.96 (q, 2H, J= 11.1 Hz), 2.51-2.43 (m, 2H), 2.08 (s, 6H), 1.93 (d, 1H, J= 14.4 Hz); **^{13}C NMR**: δ= 170.5, 137.5, 136.3, 131.9, 130.8, 128.2, 126.9, 80.1, 30.7, 23.1, 22.1; **MS** (EI/70 eV) m/z: M^+ 338, 218(100%).

Isomer B: **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.30-7.20 (m, 4H), 6.65 (s, 1H), 6.43 (s, 1H), 5.94 (s, 1H), 5.66 (dd, 1H, J= 10.7 Hz, J=6.5 Hz), 5.60-5.42 (m, 2H), 3.20 (ddd, 1H, J= 14.9, J= 11.1 Hz, J= 3.9 Hz), 2.82 (q, 1H, J=11.7 Hz), 2.68 (d,1H, J=14.1 Hz), 2.52-2.44 (m, 1H), 2.31 (dt, 1H, J= 14.4, J= 3.2 Hz), 2.21 (s, 3H), 2.06 (s, 3H), 2.03 (d, 1H, J= 14.1Hz); **^{13}C NMR**: δ= 170.1, 169.9, 137.6, 137.1, 136.4, 135.4, 132.4, 130.4, 130.3, 128.0, 127.9, 127.5, 126.5,125.9, 123.5, 79.1, 75.9, 30.4, 25.0, 21.7, 21.5; **MS** (EI/70 eV) m/z: M^+ 338, 218(100%).

3,4-benzo-7,12-dihydroxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene (123)

Method A: 0.18 g (0.53 mmole) of 3,4-benzo-7,12-diacetoxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene was suspended in 4 ml of methanol under nitrogen. The sodium methoxide solution which was prepared by adding a small piece of sodium metal (large excess over 0.023g) in 10 ml of methanol was added dropwise into the solution under the ice bath. This addition should be done at such a rate that the solution remained colorless. After one hour of stirring, the reaction mixture was quenched by dil. $HCl_{(aq)}$ in ice water and extracted with diethyl ether. The organic layer was then washed with $NaCl_{(aq)}$ and water, dried and evaporated to obtain white solid products. The product was purified and isolated by chromatography (hexane: ethyl acetate 1/1) affording two isomers in 60% combined yield.

Method B: 0.44 g (1.3 mmole) of 3,4-benzo-7,12-diacetoxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene was dissolved in 20 ml of methanol, and 2 ml of 3N $NaOH_{(aq)}$ was added into the solution under ice bath. After one hour of stirring, the reaction mixture was quenched by dil. $HCl_{(aq)}$ in ice water and extracted with diethyl ether. The organic layer was then washed with $NaCl_{(aq)}$ and water, dried and evaporated to obtain white solid products. The product was purified and isolated by chromatography (hexane: ethyl acetate 1/1) affording two isomers in 85% combined yield.

Method C: 0.72 g (1.49 mmole) of 3,4-benzo-7,12-bis(tert-butyl dimethylsilyloxy)-7,8,11,12-tetrahydro-1,6-methano[12]annulene was dissolved in 15 ml of THF, and 3.6 ml of tetrabutylammonium fluoride (1 M in THF) was added, turning the solution yellow. After stirring at room temperature overnight, the organic solvent was evaporated and the residue was purified and isolated by flash chromatography (hexane: ethyl acetate 1/1) affording two solid isomers in 84% combined yield. The two isomers were then recrystalized from methylene chloride to obtain white crystals.

Isomer A: mp: 168-169 °C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.34-7.22 (m, 4H), 6.50 (s, 2H), 5.39 (dd, 2H, J=6 Hz, J=4.4 Hz), 4.58 (dd, 2H, J=10.5 Hz, J=6.3 Hz), 3.16 (d, 1H, J=13.8 Hz), 2.91 (q, 2H, J= 10.8 Hz), 2.48-2.40 (m, 2H), 1.89 (dt, 1H, J=13.8 Hz, J=1.4 Hz), 1.82 (s, 2OH); **^{13}C NMR**: δ= 142.8, 136.5, 130.3, 129.0, 128.2, 126.4, 78.8, 33.0, 21.4; **IR** (KBr, cm^{-1}): 3335.8, 3215.4, 1292.0, 1025.6, 979.3, 865.8, 750.2, 724.6; **MS** (EI/70 eV) m/z: M+ 272, 254, 237(100%).

Isomer B: mp: 188-189 °C; **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.36-7.21 (m, 4H), 6.72 (s, 1H), 6.52 (s, 1H), 5.59-5.49 (m, 2H), 4.86 (s, 1H), 4.59 (dd, 1H, J=10.2 Hz, J=6.3 Hz), 3.26 (ddd, 1H, J=14.8 Hz, J=11Hz, J=4.2 Hz), 2.85-2.73 (m, 2H), 2.51-2.43 (m, 1H), 2.35 (d, 1H, J= 16.1 Hz), 1.99 (d, 1H, J=15 Hz), 1.67 (s, 2OH); **^{13}C NMR**: δ= 143.2, 142.3, 136.9, 135.7, 130.4, 130.2, 129.7, 128.4, 127.1, 126.4, 125.8, 123.3, 78.3, 75.3, 33.2, 33.1, 24.7; **IR** (KBr, cm^{-1}): 3564.7, 3367.9, 2884.1, 1398.1, 1062.7, 1008.1, 877.0, 852.4,758.2; **MS** (EI/70 eV) m/z: M$^+$ 272, 254, 237(100%).

3,4-benzo-1,6-methano[12]annulene (III)

60 mg (0.24 mmole) of 3,4-benzo-7,12-dihydroxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene **123** and 0.5 ml of thionyl chloride were mixed in a round bottom flask under nitrogen. 0.3 ml of

pyridine were then added slowly into the reaction mixture under ice bath. After 40 mins of stirring, the ice bath was removed and the reaction mixture was stirred at room temperature for further 20 mins. Then, the reaction mixture was quenched by sat. $NaCl_{(aq)}$ in ice water and extracted with methylene chloride. The organic layer was washed with water and evaporated to obtain colorless oil residue in 87% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.35-7.25 (m, 4H), 6.59 (s, 2H), 5.40 (dd, 2H, J= 5.9 Hz, J= 4.1 Hz), 4.87-4.81 (m, 2H), 3.24 (q, 2H, J= 12 Hz), 3.10 (dt, 1H, J=14.4 Hz, J= 1.7 Hz), 2.68-2.61 (m, 2H), 2.05 (dt, 1H, J= 14.4 Hz, J= 1.7 Hz); **^{13}C NMR**: δ= 141.4, 138.2, 132.7, 132.3, 131.5, 129.1, 69.4, 37.8, 24.4.

40 mg (0.14 mmole) of 3,4-benzo-7,12-dichloro-7,8,11,12-tetrahydro-1,6-methano[12]annulene was dissolved in 10 ml of THF and 47 mg (0.42 mmole) of potassium tert-butoxide was added into the solution under ice bath. After the ice bath was removed, the reaction mixture was warmed up to room temperature and refluxed for four hours. Then, the reaction mixture was cooled to room temperature and quenched by sat. $NaCl_{(aq)}$ in ice water. After the reaction mixture was extracted with methylene chloride, the organic layer was washed with water and evaporated to obtain pale yellow residue. The residue was then purified by chromatography on aluminum oxide in hexane affording yellow needle crystals in 84% yield. **mp:** 105-106 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ(ppm)= 7.22-7.13 (AA'BB', 4H), 6.36 (s, 2H), 6.02 (dt, 1H, J= 12 Hz, J= 1.4 Hz), 5.87 (d, 2H, J= 12 Hz), 5.78 (d, 2H, J= 3.9 Hz), 5.69 (dt, 2H, J= 13.1 Hz), 2.37

(d, 1H, J= 11.7 Hz); ^{13}C **NMR**: δ= 138.6, 138.1, 130.9, 130.7, 130.5, 130.4, 129.1, 126.4, 26.9; **MS** (EI/70 eV) m/z: M$^+$ 218(100%).

The oxidation of diol 122 to diketone 125

1.5 g (5.32 mmole) of 3,4-benz-1,6-bis(1-hydroxybutenyl)-1,3,5-cycloheptatriene **122** was dissolved in 20 ml of acetone. The Jones reagent was prepared by dissolving 1 g of chromic oxide in 1 ml of concentrated sulfuric acid and then carefully added to 3 ml of water. 3 ml of Jones reagent were added into the solution under ice bath. After stirring for 30 mins, the reaction mixture was quenched with ice water and extracted with methylene chloride. The organic layer was washed with sat. $Na_2CO_{3(aq)}$ and water. After the evaporation of the solvent, the residue was purified by chromatography (hexane/ethyl acetate 5/1) affording white solid **125** in 41% yield. **mp:** 202 (decomp.); ^{1}**H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.62 (s, 2H), 7.56-7.45 (AA'BB', 4H), 6.11-5.97 (m, 2H), 5.23 (d, 2H, J= 0.9 Hz), 5.18 (dd, 2H, J= 8.6 Hz, J=1.4 Hz), 3.65 (d, 4H, J=6.6 Hz), 3.13 (s, 2H); ^{13}C **NMR**: δ= 197.1, 138.9, 137.4, 136.1, 132.1, 131.6, 128.8, 118.7, 43.3, 22.0; **MS** (EI/70 eV) m/z: M$^+$ 278.

3,4-benzo-7,12-dione-8,11-dihydro-1,6-methano[12]-annulene (105)

0.2 g (0.79 mmole) of 3,4-benzo-7,12-dihydroxy-7,8,11,12-tetrahydro-1,6-methano[12]annulene **123** was dissolved in 13 ml of acetone. The reagent was separately prepared by dissolving 1 g of chromic oxide in 1 ml of concentrated sulfuric acid which was carefully added to 3 ml of water. Then, 2 ml of this reagent was added into the solution under ice bath. After stirring for 30 mins, the reaction mixture was quenched by ice water and extracted with methylene chloride. The organic layer was then washed with sat. $Na_2CO_{3(aq)}$ and water. After the evaporation of the solvent, the residue was purified by chromatography (hexane/ethyl acetate 5/1) affording white solids **105** in 31% yield. **mp:** 202 (decomp.); **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.60-7.42 (m, 4H), 7.58 (s, 2H), 5.58 (t, 2H, J= 6 Hz), 4.26 (dd, 2H, J=11.7 Hz, J=9.9 Hz), 3.73 (d, 1H, J=14.7 Hz), 3.16 (dd, 2H, J= 11.9 Hz, J= 4.7 Hz), 2.16 (d, 1H, J= 15 Hz); **^{13}C NMR:** δ= 198.8, 136.2, 136.0, 135.5, 132.3, 128.4, 126.7, 41.4, 27.0; **IR** (KBr, cm^{-1}): 3020.5, 1673.2, 1588.1, 1277.0, 1254.2, 801.8; **MS** (EI/70 eV) m/z: M^+ 250(100%).

The reactions of 3,4-benzo-7,12-dione-8,11-dihydro-1,6-methano[12]annulene 105

20 mg (0.08 mmole) of 3,4-benzo-7,12-dione-8,11-dihydro-1,6-methano[12]annulene **105** was dissolved in 8 ml of CH_2Cl_2 and 41 mg (0.24 mmole) of m-chloroperoxybenzoic acid (MCPBA) was added into the solution under nitrogen. The solution was stirred for two hours at room temperature. The excess peracid was then destroyed by addition of 10% $NaHSO_{3(aq)}$ until a test with starch-iodide paper is negative. The reaction mixture was then transferred to a separatory funnel and the organic layer was washed with sat. $NaHCO_{3(aq)}$ to extract the m-chlorobenzoic acid, followed by washing with water and sat. $NaCl_{(aq)}$. The organic layer was dried and stripped of solvent to obtain semi-solid residue. Unfortunately, only starting material **105** had been isolated.

A solution of 20 mg (0.08 mmole) of 3,4-benzo-7,12-dione-8,11-dihydro-1,6-methano[12]annulene **105** in 5 ml of carbon tetrachloride was treated with 28 mg (0.16 mmole) of N-bromo-succinimide (NBS) and refluxed under irradiation for 30 minutes. After excess NBS was filtered out, the organic solvent was then evaporated to obtain bromo-compound. The compound was tentatively assigned as compound **130**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm)= 7.78 (s, 2H), 7.74-7.54 (AA'BB', 4H), 6.55 (s, 1H), 5.55 (t, 2H, J= 6 Hz), 4.22 (t, 2H, J=10.8 Hz), 3.27 (dd, 2H, J=12.9 Hz, J=4.8 Hz); **MS** (EI/70 eV) m/z: M^+ 328/330.

Appendix

X-ray Spectra and ^1H NMR, ^{13}C NMR, IR, GC-MS of Selected Compounds

Table I. X-ray Data for Compound **73** at 295 K

Book reference	SY-1
Formula	$C_{23}H_{19}NO_2$
Formula weight	341.41
Crystal size (mm)	0.64 x 0.64 x 0.64
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	16.646(2)
b (Å)	13.074(3)
c (Å)	16.805(3)
β (°)	107.20(1)
V (Å^3)	3493.9(10)
Z	8
d_{calc} (g cm^{-3})	1.298
μ(Mo $K\alpha$) (cm^{-1})	0.77
Absorption correction	none
Maximum θ (°)	28
Unique reflections	8408
Observed reflections [$I > 3.0\sigma(I)$]	3560
Number of variables	469
R	0.050
R_w	0.056
$(\Delta\rho)_{max}$ (e Å^{-3})	0.23
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.19

Table II. Final Atomic Parameters for Compound **73**

Atom	x	y	z	B(Å^2)
O16	0.4958(1)	-0.0499(1)	0.4071(1)	4.56(5)
O17	0.4506(1)	0.2927(1)	0.3901(1)	5.43(5)
N18	0.4535(1)	0.1181(2)	0.3936(1)	3.39(5)
C1	0.7484(2)	0.1735(2)	0.3363(2)	5.01(8)
C2	0.6962(2)	0.2638(2)	0.3460(2)	4.24(7)
C3	0.6026(2)	0.2466(2)	0.3299(2)	3.69(6)
C4	0.5683(1)	0.1752(2)	0.2573(2)	3.29(6)
C5	0.5880(1)	0.0715(2)	0.2706(2)	3.36(6)
C6	0.6406(2)	0.0403(2)	0.3569(2)	3.50(6)
C7	0.7314(2)	0.0764(2)	0.3775(2)	4.20(7)
C8	0.7928(2)	0.0231(3)	0.4270(2)	6.25(9)
C9	0.7290(2)	0.3564(2)	0.3628(2)	5.24(8)
C10	0.5215(2)	0.2083(2)	0.1787(2)	3.94(6)
C11	0.4933(2)	0.1385(3)	0.1143(2)	4.61(7)
C12	0.5117(2)	0.0354(2)	0.1279(2)	4.71(7)
C13	0.5589(2)	0.0025(2)	0.2064(2)	4.03(7)
C14	0.5827(2)	0.2018(2)	0.4080(2)	3.69(6)
C15	0.5988(2)	0.0865(2)	0.4197(2)	3.51(6)
C16	0.5124(2)	0.0394(2)	0.4066(2)	3.43(6)
C17	0.4897(2)	0.2142(2)	0.3969(2)	3.74(6)
C19	0.3642(2)	0.1032(2)	0.3721(2)	3.55(6)
C20	0.3201(2)	0.1424(3)	0.4228(2)	5.00(8)
C21	0.2332(2)	0.1336(3)	0.3971(2)	5.86(8)
C22	0.1922(2)	0.0857(3)	0.3245(2)	5.91(9)
C23	0.2369(2)	0.0461(3)	0.2748(2)	5.90(9)
C24	0.3237(2)	0.0551(2)	0.2987(2)	4.67(7)
O16'	0.0455(1)	0.0119(1)	0.1019(1)	4.81(5)
O17'	-0.0083(1)	0.3533(1)	0.0749(1)	4.79(5)
N18'	0.0378(1)	0.1870(2)	0.0880(1)	3.47(5)
C1'	-0.2639(2)	0.1223(3)	0.0836(2)	5.45(9)
C2'	-0.2371(2)	0.2283(2)	0.1153(2)	4.22(7)
C3'	-0.1455(2)	0.2573(2)	0.1320(2)	3.90(7)
C4'	-0.0945(2)	0.2178(2)	0.2163(2)	3.78(6)
C5'	-0.0811(2)	0.1127(2)	0.2243(2)	3.79(6)
C6'	-0.1144(2)	0.0478(2)	0.1468(2)	3.84(7)
C7'	-0.2086(2)	0.0338(2)	0.1249(2)	4.32(7)
C8'	-0.2416(2)	-0.0552(3)	0.1352(2)	6.05(9)
C9'	-0.2928(2)	0.2969(3)	0.1246(2)	5.14(8)
C10'	-0.0630(2)	0.2814(3)	0.2843(2)	4.79(7)
C11'	-0.0190(2)	0.2400(3)	0.3601(2)	5.66(8)
C12'	-0.0076(2)	0.1353(3)	0.3697(2)	5.64(9)
C13'	-0.0382(2)	0.0712(3)	0.3012(2)	4.73(7)
C14'	-0.1076(2)	0.2141(2)	0.0659(2)	3.46(6)
C15'	-0.0893(2)	0.0989(2)	0.0744(2)	3.49(6)
C16'	0.0046(2)	0.0900(2)	0.0896(2)	3.68(6)
C17'	-0.0233(2)	0.2637(2)	0.0761(2)	3.54(6)
C19'	0.1258(2)	0.2068(2)	0.1040(2)	3.76(6)
C20'	0.1698(2)	0.1609(2)	0.0561(2)	4.64(7)
C21'	0.2550(2)	0.1775(3)	0.0748(2)	5.64(8)
C22'	0.2954(2)	0.2405(3)	0.1394(2)	6.24(9)
C23'	0.2510(2)	0.2885(3)	0.1860(2)	6.33(9)
C24'	0.1656(2)	0.2715(2)	0.1684(2)	4.97(8)

Table II (cont.). Final Atomic Parameters for Compound **73**

Atom	x	y	z	B(Å^2)
H1A	0.809	0.192	0.361	6.0
H1B	0.737	0.160	0.275	6.0
H3	0.573	0.314	0.316	4.4
H6	0.640	-0.036	0.361	4.2
H8A	0.780	-0.041	0.454	7.4
H8B	0.852	0.047	0.439	7.4
H9A	0.693	0.415	0.369	6.3
H9B	0.790	0.368	0.370	6.3
H10	0.508	0.283	0.169	4.7
H11	0.460	0.163	0.058	5.6
H12	0.491	-0.015	0.081	5.7
H13	0.572	-0.072	0.217	4.8
H14	0.616	0.239	0.459	4.4
H15	0.635	0.073	0.478	4.2
H20	0.350	0.176	0.477	6.0
H21	0.200	0.163	0.433	7.0
H22	0.130	0.080	0.307	7.1
H23	0.207	0.010	0.222	7.0
H24	0.357	0.027	0.262	5.6
H1A'	-0.267	0.121	0.023	6.5
H1B'	-0.321	0.110	0.090	6.5
H3'	-0.141	0.334	0.132	4.7
H6'	-0.087	-0.021	0.158	4.6
H8A'	-0.204	-0.113	0.163	7.3
H8B'	-0.304	-0.065	0.115	7.3
H9A'	-0.274	0.367	0.146	6.2
H9B'	-0.354	0.278	0.110	6.2
H10'	-0.072	0.357	0.278	5.7
H11'	0.005	0.287	0.409	6.8
H12'	0.023	0.106	0.426	6.7
H13'	-0.030	-0.005	0.308	5.7
H14'	-0.146	0.229	0.009	4.2
H15'	-0.119	0.064	0.021	4.2
H20'	0.140	0.116	0.008	5.6
H21'	0.288	0.143	0.041	6.8
H22'	0.358	0.251	0.153	7.5
H23'	0.281	0.336	0.232	7.6
H24'	0.133	0.306	0.202	5.9

The parameters of the hydrogen atoms were not refined.

Standard deviations are in parentheses.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Table III. Final Anisotropic Thermal Parameters (U's) for Compound 73

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
O16	0.064(1)	0.034(1)	0.081(1)	-0.0046(9)	0.0319(9)	0.004(1)
O17	0.076(1)	0.039(1)	0.101(1)	0.008(1)	0.0423(9)	0.007(1)
N18	0.047(1)	0.038(1)	0.048(1)	-0.000(1)	0.0191(9)	0.002(1)
C1	0.046(2)	0.069(2)	0.076(2)	-0.007(2)	0.018(1)	0.012(2)
C2	0.051(1)	0.058(2)	0.053(1)	-0.010(1)	0.017(1)	0.008(1)
C3	0.051(1)	0.041(1)	0.052(1)	-0.003(1)	0.019(1)	0.004(1)
C4	0.035(1)	0.046(2)	0.046(1)	-0.004(1)	0.016(1)	0.002(1)
C5	0.036(1)	0.047(2)	0.048(1)	-0.003(1)	0.016(1)	-0.001(1)
C6	0.043(1)	0.042(1)	0.048(1)	0.001(1)	0.012(1)	0.002(1)
C7	0.044(1)	0.059(2)	0.058(2)	0.003(1)	0.016(1)	0.007(1)
C8	0.052(2)	0.096(3)	0.088(2)	0.004(2)	0.017(2)	0.030(2)
C9	0.066(2)	0.066(2)	0.063(2)	-0.023(2)	0.012(1)	0.010(2)
C10	0.042(1)	0.057(2)	0.054(1)	0.003(1)	0.019(1)	0.011(1)
C11	0.048(2)	0.083(2)	0.043(1)	0.003(2)	0.011(1)	0.004(2)
C12	0.056(2)	0.069(2)	0.055(2)	-0.001(2)	0.018(1)	-0.010(2)
C13	0.046(1)	0.056(2)	0.053(1)	-0.000(1)	0.018(1)	-0.006(1)
C14	0.052(1)	0.041(2)	0.048(1)	-0.007(1)	0.017(1)	-0.001(1)
C15	0.047(1)	0.042(2)	0.043(1)	-0.002(1)	0.012(1)	0.004(1)
C16	0.051(1)	0.043(1)	0.039(1)	0.000(1)	0.019(1)	0.003(1)
C17	0.063(2)	0.037(1)	0.047(1)	-0.002(1)	0.025(1)	-0.000(1)
C19	0.046(1)	0.044(2)	0.050(1)	-0.000(1)	0.022(1)	0.007(1)
C20	0.061(2)	0.076(2)	0.061(2)	0.005(2)	0.029(1)	0.000(2)
C21	0.063(2)	0.092(2)	0.080(2)	0.008(2)	0.040(1)	0.003(2)
C22	0.053(2)	0.075(2)	0.103(2)	0.002(2)	0.033(1)	0.009(2)
C23	0.052(2)	0.076(2)	0.093(2)	-0.001(2)	0.018(2)	-0.014(2)
C24	0.051(2)	0.061(2)	0.069(2)	-0.004(2)	0.022(1)	-0.011(2)
O16'	0.062(1)	0.048(1)	0.077(1)	0.006(1)	0.0279(9)	0.000(1)
O17'	0.065(1)	0.043(1)	0.078(1)	-0.006(1)	0.0285(9)	0.001(1)
N18'	0.042(1)	0.043(1)	0.050(1)	-0.006(1)	0.0184(8)	-0.001(1)
C1'	0.049(2)	0.077(2)	0.080(2)	-0.005(2)	0.019(1)	0.006(2)
C2'	0.047(1)	0.059(2)	0.055(2)	0.001(1)	0.016(1)	0.005(1)
C3'	0.048(1)	0.049(2)	0.054(1)	-0.001(1)	0.019(1)	-0.003(1)
C4'	0.041(1)	0.061(2)	0.048(1)	-0.006(1)	0.022(1)	-0.006(1)
C5'	0.039(1)	0.060(2)	0.049(1)	-0.002(1)	0.019(1)	0.004(1)
C6'	0.048(1)	0.047(2)	0.053(1)	-0.003(1)	0.017(1)	0.002(1)
C7'	0.050(1)	0.062(2)	0.055(2)	-0.010(1)	0.019(1)	0.003(1)
C8'	0.072(2)	0.074(2)	0.088(2)	-0.021(2)	0.029(2)	0.008(2)
C9'	0.055(2)	0.084(2)	0.058(2)	0.014(2)	0.019(1)	0.004(2)
C10'	0.050(1)	0.083(2)	0.055(2)	-0.008(2)	0.023(1)	-0.013(2)
C11'	0.052(2)	0.110(3)	0.057(2)	-0.014(2)	0.021(1)	-0.023(2)
C12'	0.046(2)	0.129(3)	0.042(1)	0.003(2)	0.017(1)	0.003(2)
C13'	0.045(1)	0.085(2)	0.053(2)	0.003(2)	0.021(1)	0.013(2)
C14'	0.040(1)	0.047(2)	0.045(1)	-0.003(1)	0.013(1)	-0.000(1)
C15'	0.040(1)	0.049(2)	0.044(1)	-0.006(1)	0.014(1)	-0.003(1)
C16'	0.052(1)	0.046(2)	0.045(1)	-0.003(1)	0.019(1)	-0.003(1)
C17'	0.048(1)	0.049(2)	0.039(1)	-0.001(1)	0.015(1)	-0.001(1)
C19'	0.044(1)	0.049(2)	0.053(1)	-0.006(1)	0.020(1)	-0.000(1)
C20'	0.060(2)	0.060(2)	0.065(2)	-0.002(2)	0.032(1)	-0.005(2)
C21'	0.061(2)	0.069(2)	0.098(2)	0.003(2)	0.044(1)	-0.001(2)
C22'	0.054(2)	0.075(2)	0.115(2)	-0.009(2)	0.036(2)	0.001(2)
C23'	0.054(2)	0.085(2)	0.105(2)	-0.018(2)	0.028(2)	-0.026(2)
C24'	0.048(1)	0.071(2)	0.076(2)	-0.013(2)	0.026(1)	-0.018(2)

The form of the anisotropic displacement parameter is:
exp[-2PI2{h2a2U(1,1) + k2b2U(2,2) + l2c2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3)}] where a,b, and c are reciprocal lattice constants.

Table IV. Bond Distances (A) for Compound **73**

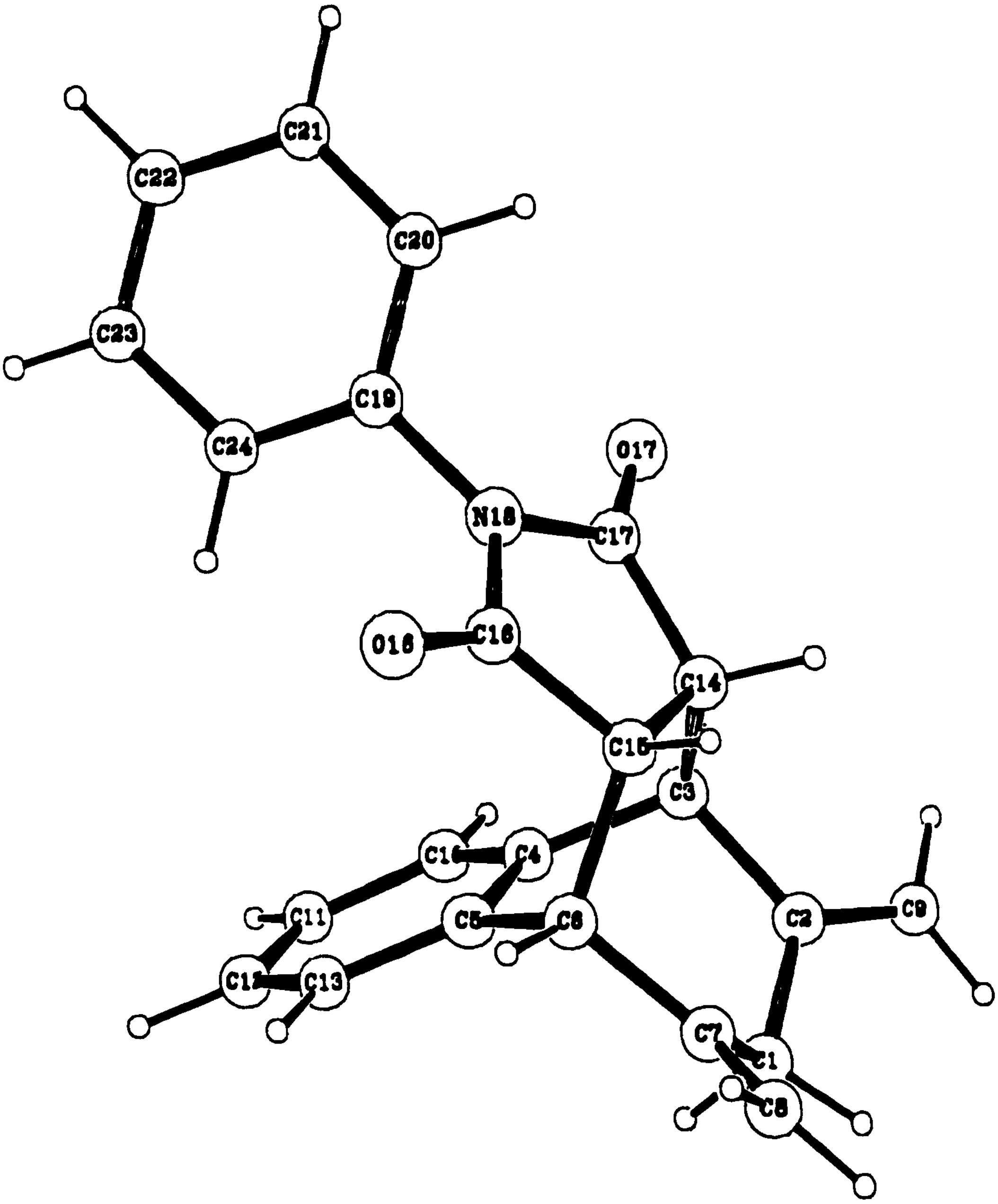
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O16	C16	1.200(3)	O16'	C16'	1.211(3)
O17	C17	1.203(3)	O17'	C17'	1.200(3)
N18	C16	1.395(3)	N18'	C16'	1.388(3)
N18	C17	1.388(3)	N18'	C17'	1.399(3)
N18	C19	1.435(3)	N18'	C19'	1.433(3)
C1	C2	1.504(4)	C1'	C2'	1.504(4)
C1	C7	1.511(4)	C1'	C7'	1.513(4)
C2	C3	1.517(4)	C2'	C3'	1.515(4)
C2	C9	1.323(4)	C2'	C9'	1.332(4)
C3	C4	1.508(3)	C3'	C4'	1.511(3)
C3	C14	1.559(4)	C3'	C14'	1.538(4)
C4	C5	1.398(4)	C4'	C5'	1.392(4)
C4	C10	1.389(3)	C4'	C10'	1.385(4)
C5	C6	1.512(3)	C5'	C6'	1.516(4)
C5	C13	1.380(4)	C5'	C13'	1.389(4)
C6	C7	1.522(4)	C6'	C7'	1.512(4)
C6	C15	1.548(4)	C6'	C15'	1.550(4)
C7	C8	1.312(4)	C7'	C8'	1.319(5)
C10	C11	1.387(4)	C10'	C11'	1.379(4)
C11	C12	1.386(4)	C11'	C12'	1.384(5)
C12	C13	1.389(4)	C12'	C13'	1.393(4)
C14	C15	1.534(4)	C14'	C15'	1.535(4)
C14	C17	1.512(4)	C14'	C17'	1.507(4)
C15	C16	1.520(4)	C15'	C16'	1.511(4)
C19	C20	1.378(4)	C19'	C20'	1.376(4)
C19	C24	1.371(4)	C19'	C24'	1.379(4)
C20	C21	1.386(4)	C20'	C21'	1.377(4)
C21	C22	1.361(4)	C21'	C22'	1.370(4)
C22	C23	1.373(5)	C22'	C23'	1.376(5)
C23	C24	1.386(4)	C23'	C24'	1.383(4)

Standard deviations are in parentheses.

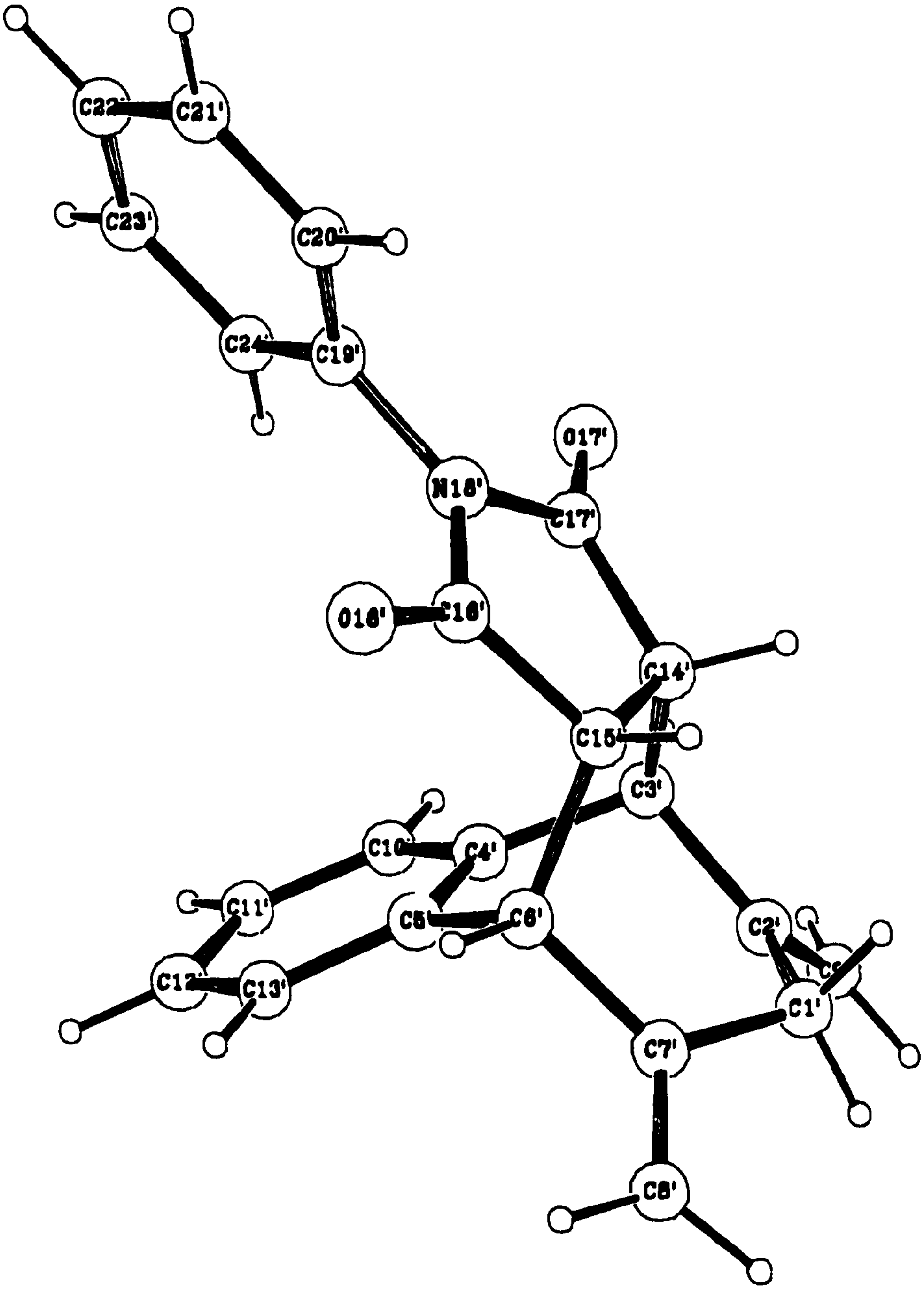
Table V. Bond Angles (°) for Compound **73**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C16	N18	C17	112.6(2)	C16'	N18'	C17'	112.4(2)
C16	N18	C19	124.6(2)	C16'	N18'	C19'	123.5(2)
C17	N18	C19	122.6(2)	C17'	N18'	C19'	123.9(2)
C2	C1	C7	114.7(3)	C2'	C1'	C7'	117.8(2)
C1	C2	C3	117.4(2)	C1'	C2'	C3'	118.2(2)
C1	C2	C9	121.7(3)	C1'	C2'	C9'	121.2(3)
C3	C2	C9	120.8(3)	C3'	C2'	C9'	120.5(3)
C2	C3	C4	111.1(2)	C2'	C3'	C4'	110.1(2)
C2	C3	C14	111.6(2)	C2'	C3'	C14'	112.3(2)
C4	C3	C14	108.9(2)	C4'	C3'	C14'	108.4(2)
C3	C4	C5	117.1(2)	C3'	C4'	C5'	117.3(2)
C3	C4	C10	123.3(2)	C3'	C4'	C10'	122.7(3)
C5	C4	C10	119.6(2)	C5'	C4'	C10'	120.1(2)
C4	C5	C6	117.2(2)	C4'	C5'	C6'	117.5(2)
C4	C5	C13	119.8(2)	C4'	C5'	C13'	120.0(2)
C6	C5	C13	123.0(2)	C6'	C5'	C13'	122.5(3)
C5	C6	C7	112.9(2)	C5'	C6'	C7'	111.5(2)
C5	C6	C15	107.4(2)	C5'	C6'	C15'	108.5(2)
C7	C6	C15	109.9(2)	C7'	C6'	C15'	111.2(2)
C1	C7	C6	117.7(2)	C1'	C7'	C6'	117.7(3)
C1	C7	C8	121.3(3)	C1'	C7'	C8'	121.0(2)
C6	C7	C8	121.0(3)	C6'	C7'	C8'	121.1(3)
C4	C10	C11	120.1(3)	C4'	C10'	C11'	119.7(3)
C10	C11	C12	120.3(2)	C10'	C11'	C12'	120.8(3)
C11	C12	C13	119.6(3)	C11'	C12'	C13'	119.7(3)
C5	C13	C12	120.6(3)	C5'	C13'	C12'	119.7(3)
C3	C14	C15	113.9(2)	C3'	C14'	C15'	113.9(2)
C3	C14	C17	108.7(2)	C3'	C14'	C17'	109.0(2)
C15	C14	C17	104.8(2)	C15'	C14'	C17'	105.1(2)
C6	C15	C14	113.1(2)	C6'	C15'	C14'	113.9(2)
C6	C15	C16	109.9(2)	C6'	C15'	C16'	109.8(2)
C14	C15	C16	104.9(2)	C14'	C15'	C16'	104.9(2)
O16	C16	N18	124.5(2)	O16'	C16'	N18'	124.5(2)
O16	C16	C15	127.2(2)	O16'	C16'	C15'	126.6(2)
N18	C16	C15	108.4(2)	N18'	C16'	C15'	108.9(2)
O17	C17	N18	123.5(2)	O17'	C17'	N18'	123.7(2)
O17	C17	C14	127.5(2)	O17'	C17'	C14'	127.6(2)
N18	C17	C14	109.0(2)	N18'	C17'	C14'	108.7(2)
N18	C19	C20	119.7(2)	N18'	C19'	C20'	120.2(2)
N18	C19	C24	119.1(3)	N18'	C19'	C24'	119.0(3)
C20	C19	C24	121.1(2)	C20'	C19'	C24'	120.7(2)
C19	C20	C21	118.3(3)	C19'	C20'	C21'	119.2(3)
C20	C21	C22	121.2(3)	C20'	C21'	C22'	120.5(3)
C21	C22	C23	120.0(3)	C21'	C22'	C23'	120.3(3)
C22	C23	C24	119.8(3)	C22'	C23'	C24'	119.8(3)
C19	C24	C23	119.5(3)	C19'	C24'	C23'	119.4(3)

Standard deviations are in parentheses.



X-ray structure of N-phenylsuccinimide Diels-Alder adduct 73
(Independent molecule *A*)



X-ray structure of N-phenylsuccinimide Diels-Alder adduct 73 (Independent molecule *B*)

Table VI. X-ray Data for Compound **IV** at 295 K

Book reference	SY-2
Formula	$C_{26}H_{20}$
Formula weight	332.45
Crystal size (mm)	0.02 x 0.40 x 0.80
Crystal system	Orthorhombic
Space group	$Pbn2_1$
a (Å)	6.0502(10)
b (Å)	15.472(3)
c (Å)	18.652(6)
V (Å^3)	1745.9(32)
Z	4
d_{calc} (g cm^{-3})	1.265
μ(Mo $K\alpha$) (cm^{-1})	0.66
Absorption correction	none
Maximum θ (°)	20
Unique reflections	839
Observed reflections [$I > 3.0\sigma(I)$]	355
Number of variables	104
R	0.056
R_w	0.055
$(\Delta\rho)_{max}$ (e Å^{-3})	0.21
$(\Delta\rho)_{min}$ (e Å^{-3})	-0.19

Table VII. Final Atomic Parameters for Compound **IV**

Atom	x	y	z	B(Å^2)
C1	0.741(3)	0.4577(9)	0.444	2.4(4)*
C2	0.787(3)	0.5399(9)	0.4632(8)	3.0(4)*
C3	0.722(3)	0.5866(9)	0.5268(8)	3.0(4)*
C4	0.528(3)	0.574(1)	0.5666(8)	3.7(4)*
C5	0.372(3)	0.503(1)	0.5500(8)	3.1(4)*
C6	0.395(3)	0.4284(9)	0.5197(8)	2.6(3)*
C7	0.216(2)	0.3669(9)	0.5198(8)	2.4(3)*
C8	0.172(3)	0.2955(9)	0.4800(8)	3.8(4)*
C9	0.261(3)	0.2644(9)	0.4141(7)	2.8(4)*
C10	0.223(3)	0.184(1)	0.3936(8)	3.5(4)*
C11	0.287(3)	0.1357(9)	0.3286(8)	3.2(4)*
C12	0.483(3)	0.1534(9)	0.2902(8)	2.7(4)*
C13	0.646(3)	0.220(1)	0.3060(9)	4.2(4)*
C14	0.611(3)	0.2947(9)	0.3372(9)	3.3(4)*
C15	0.796(3)	0.360(1)	0.3383(8)	3.9(4)*
C16	0.834(3)	0.4301(9)	0.3766(8)	3.1(4)*
C17	0.632(3)	0.3966(9)	0.4948(7)	2.9(4)*
C18	0.382(3)	0.3234(9)	0.3611(7)	2.4(4)*
C19	0.862(3)	0.655(1)	0.5508(8)	4.4(4)*
C20	0.808(3)	0.710(1)	0.6101(9)	5.2(5)*
C21	0.615(3)	0.695(1)	0.6434(9)	3.8(4)*
C22	0.481(3)	0.628(1)	0.6233(9)	3.7(4)*
C23	0.148(3)	0.0696(9)	0.3083(8)	3.1(4)*
C24	0.196(3)	0.020(1)	0.2491(9)	4.7(5)*
C25	0.391(4)	0.033(1)	0.210(1)	5.6(5)*
C26	0.539(3)	0.096(1)	0.2321(9)	3.7(5)*
H2	0.880	0.573	0.429	3.6
H5	0.219	0.516	0.566	3.8
H7	0.102	0.379	0.557	2.9
H8	0.055	0.258	0.502	4.5
H10	0.135	0.150	0.429	4.2
H13	0.803	0.207	0.292	5.0
H15	0.916	0.347	0.303	4.7
H16	0.946	0.470	0.356	3.7
H17A	0.728	0.391	0.538	3.4
H17B	0.615	0.339	0.471	3.4
H18A	0.397	0.381	0.384	2.8
H18B	0.287	0.329	0.318	2.8
H19	1.004	0.665	0.525	5.1
H20	0.911	0.757	0.625	6.2
H21	0.572	0.734	0.684	4.6
H22	0.343	0.618	0.651	4.4
H23	0.011	0.057	0.336	3.8
H24	0.092	-0.027	0.233	5.6
H25	0.427	-0.002	0.168	6.8
H26	0.685	0.103	0.207	4.6

The starred atoms were refined isotropically.
The parameters of the hydrogen atoms were not refined.
Standard deviations are in parentheses.

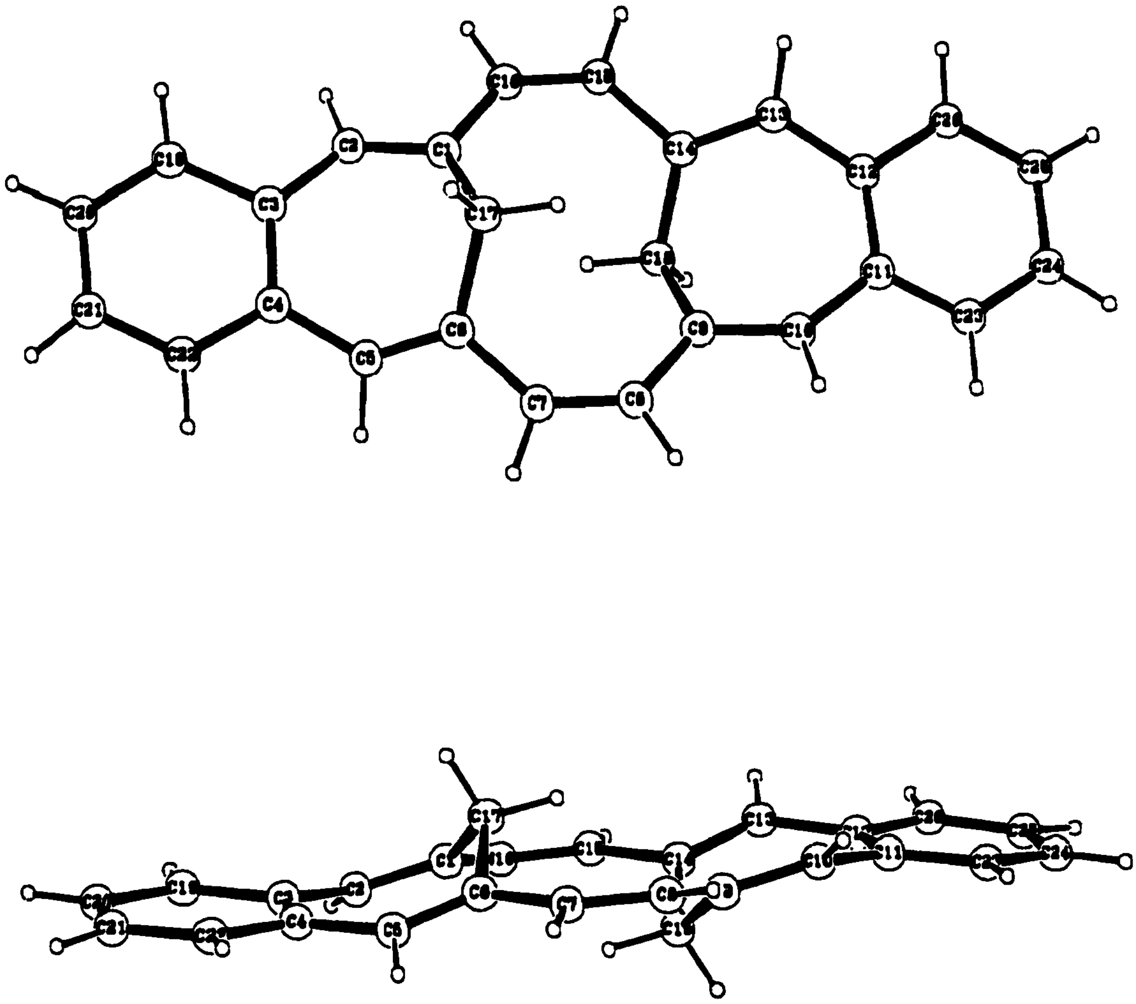
Table VIII. Distances (Å) for Compound **IV**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C1	C2	1.35(2)	C10	C11	1.48(2)
C1	C16	1.44(2)	C11	C12	1.41(2)
C1	C17	1.50(2)	C11	C23	1.38(2)
C2	C3	1.44(2)	C12	C13	1.45(2)
C3	C4	1.40(2)	C13	C14	1.32(2)
C3	C19	1.43(2)	C14	C15	1.51(2)
C4	C5	1.48(2)	C14	C18	1.52(2)
C4	C22	1.38(2)	C15	C16	1.32(2)
C5	C6	1.29(2)	C19	C20	1.43(2)
C6	C7	1.44(2)	C20	C21	1.34(3)
C6	C17	1.58(2)	C21	C22	1.37(2)
C7	C8	1.36(2)	C23	C24	1.38(2)
C8	C9	1.42(2)			
C9	C10	1.32(2)	C1	C6	2.57(2)
C9	C18	1.53(2)	C9	C14	2.60(2)

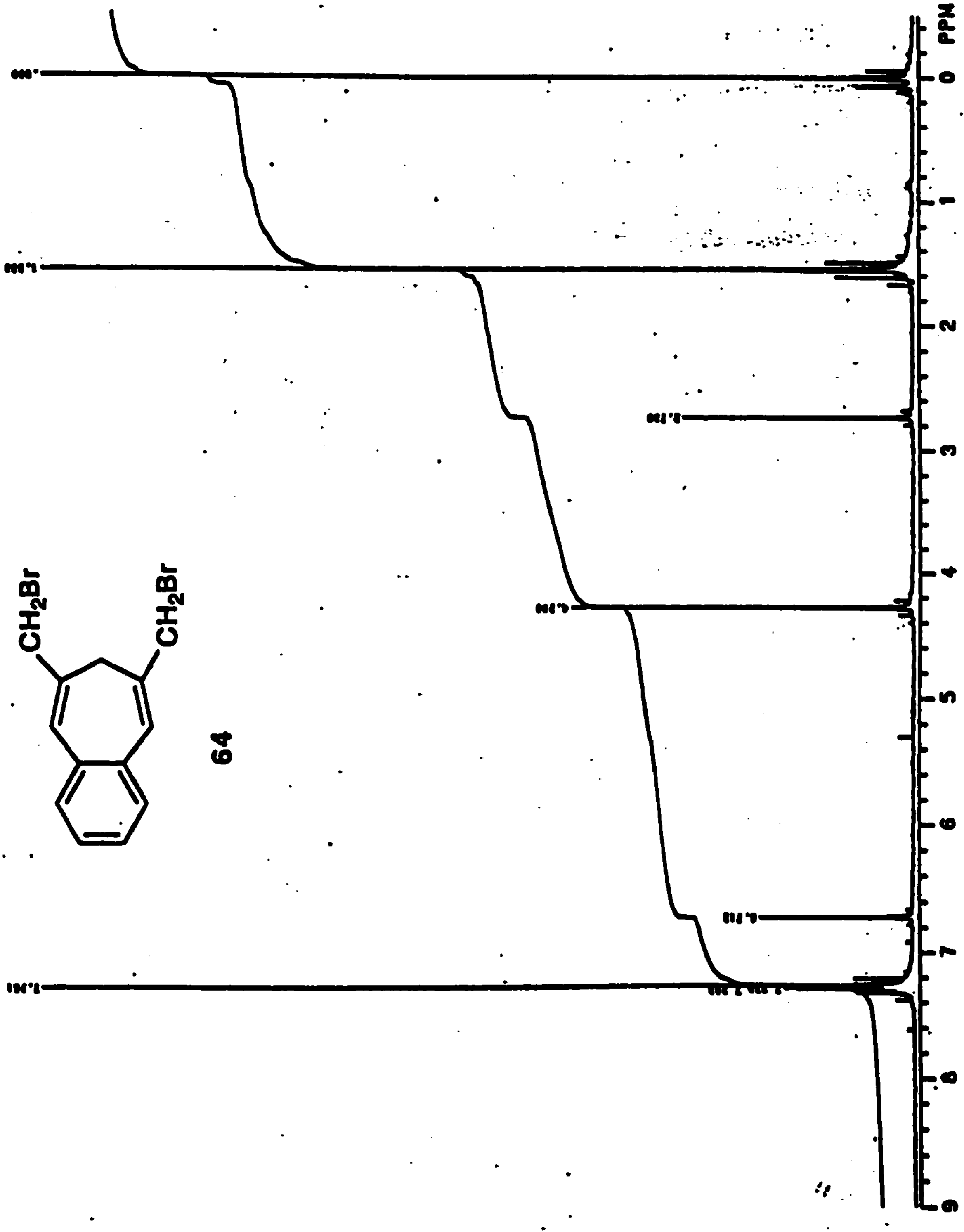
Table IX. Bond Angles (°) for Compound **IV**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C1	C16	116(1)	C9	C10	C11	132(1)
C2	C1	C17	121(1)	C10	C11	C12	122(1)
C16	C1	C17	123(1)	C10	C11	C23	116(1)
C1	C2	C3	129(1)	C12	C11	C23	121(1)
C2	C3	C4	126(1)	C11	C12	C13	127(1)
C2	C3	C19	118(1)	C12	C13	C14	127(2)
C4	C3	C19	116(1)	C13	C14	C15	119(2)
C3	C4	C5	122(1)	C13	C14	C18	122(2)
C3	C4	C22	119(2)	C15	C14	C18	118(1)
C5	C4	C22	119(2)	C14	C15	C16	133(2)
C4	C5	C6	133(2)	C1	C16	C15	130(1)
C5	C6	C7	121(2)	C1	C17	C6	113(1)
C5	C6	C17	120(1)	C9	C18	C14	117(1)
C7	C6	C17	118(1)	C3	C19	C20	123(2)
C6	C7	C8	133(1)	C19	C20	C21	117(2)
C7	C8	C9	132(2)	C20	C21	C22	121(2)
C8	C9	C10	120(1)	C4	C22	C21	123(2)
C8	C9	C18	122(1)	C11	C23	C24	120(2)
C10	C9	C18	117(1)				

Standard deviations are in parentheses.



X-ray structure of 3,4:11,12-dibenzo-anti 1,6:9,14-bismethano[16]annulene IV



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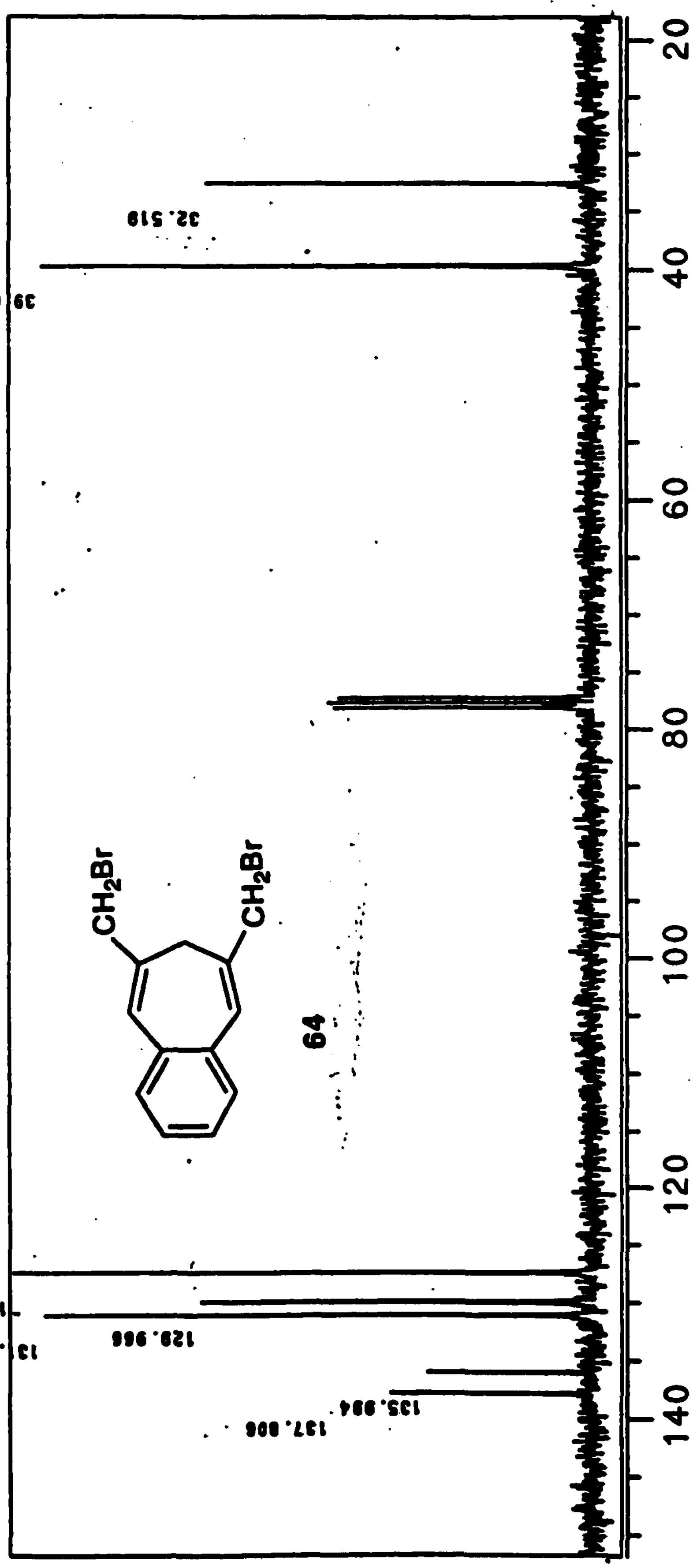
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100
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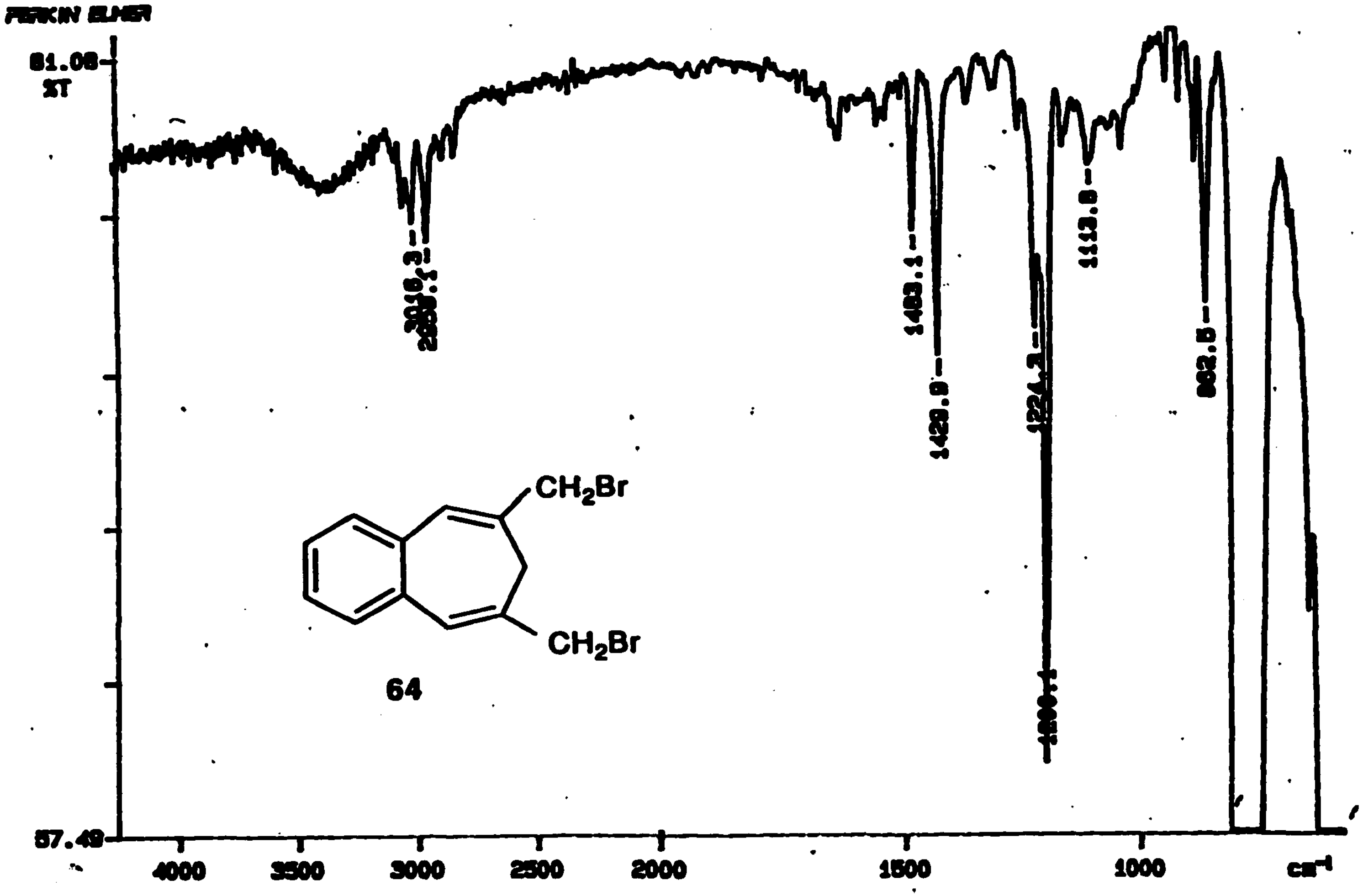
140

64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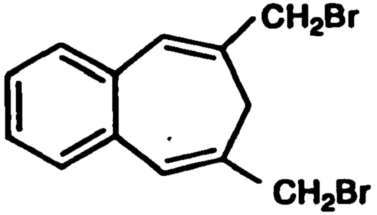
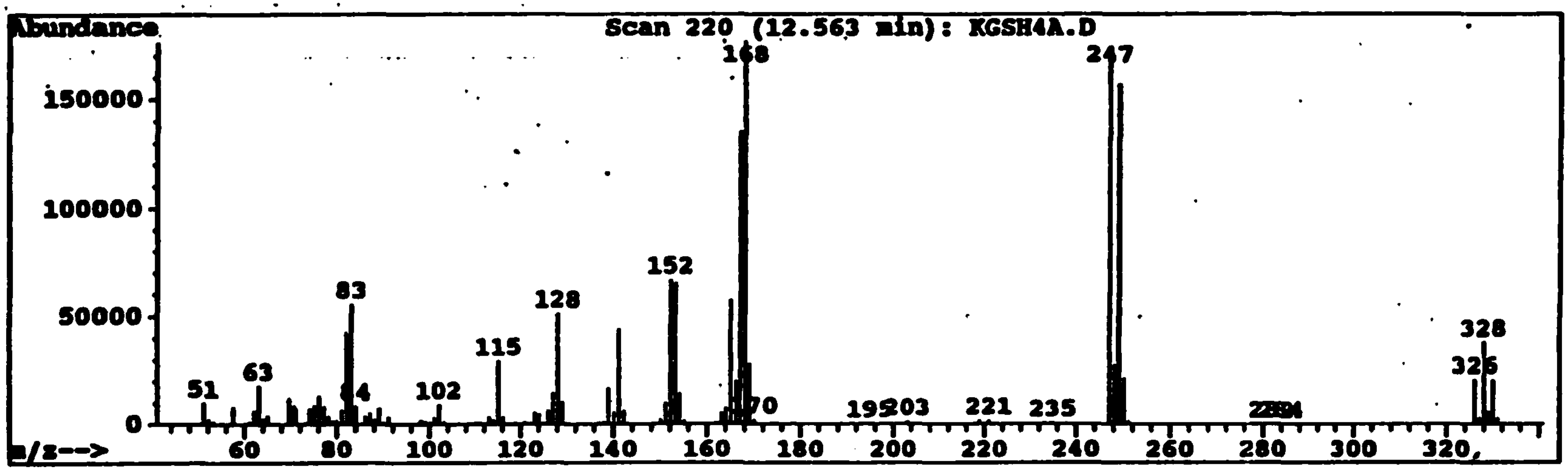
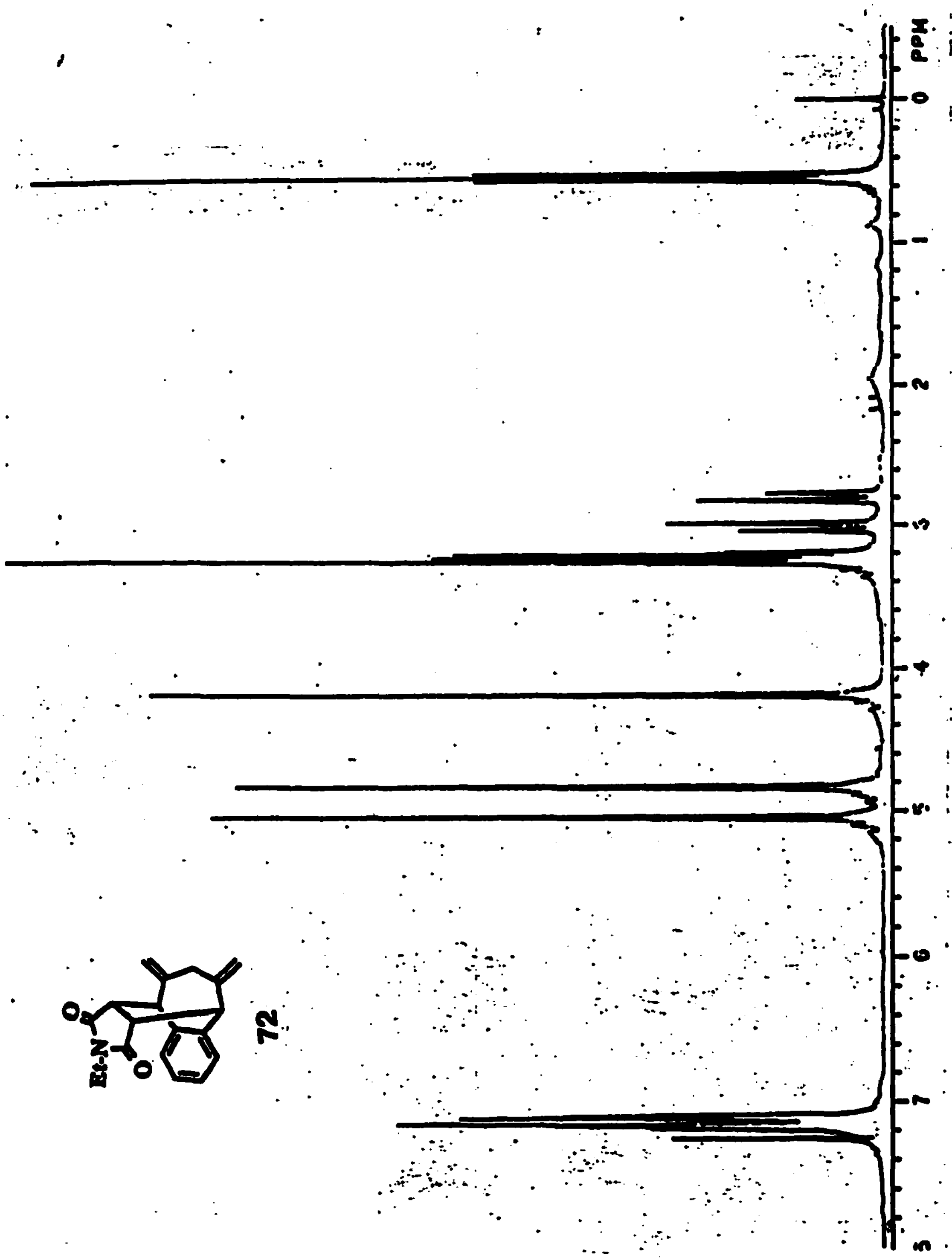
1428.9
1224.3
1200.1
1113.8
862.5
CH2Br
CH2Br
64

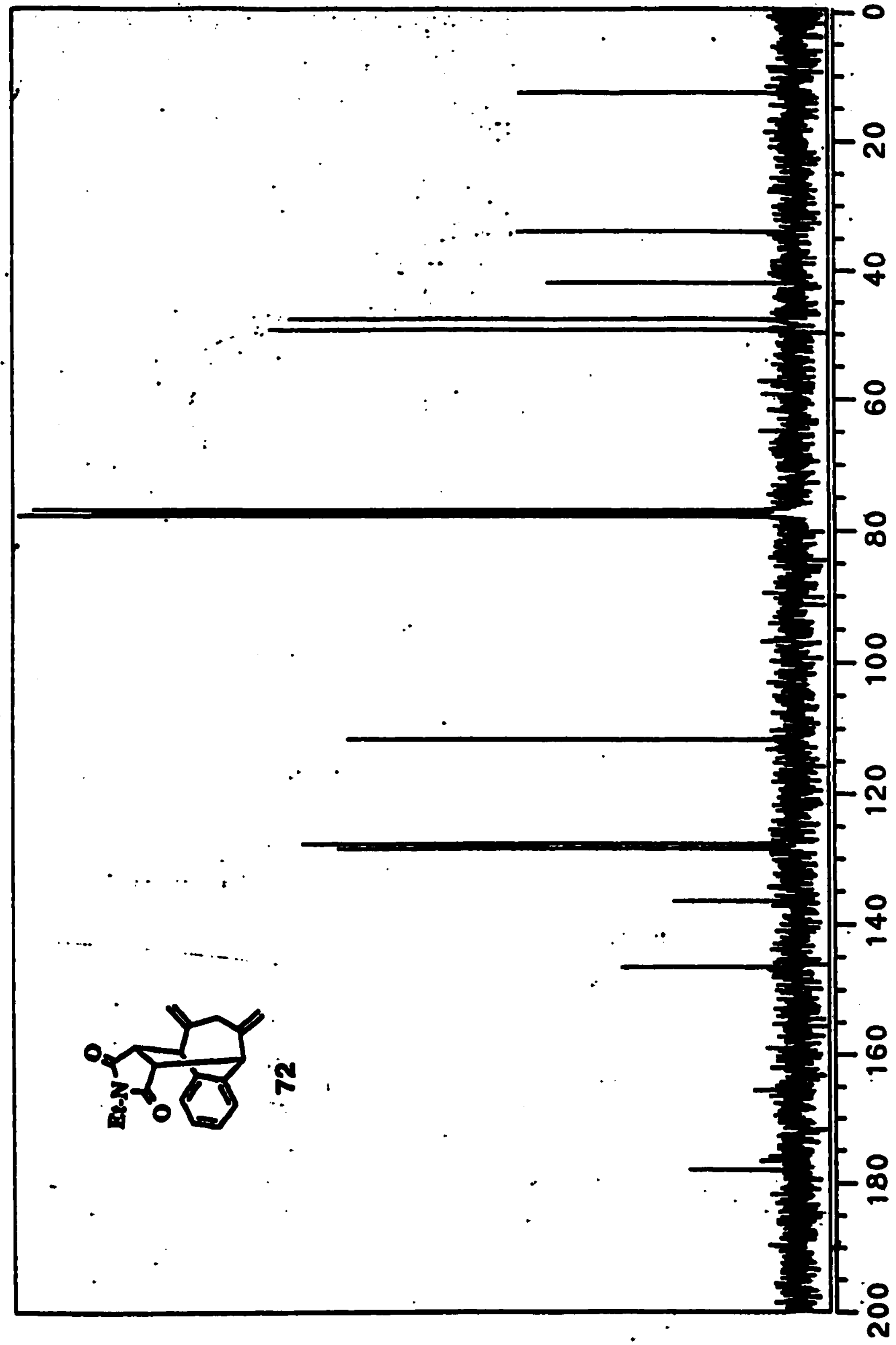

CH$_2$Br
CH$_2$Br

64

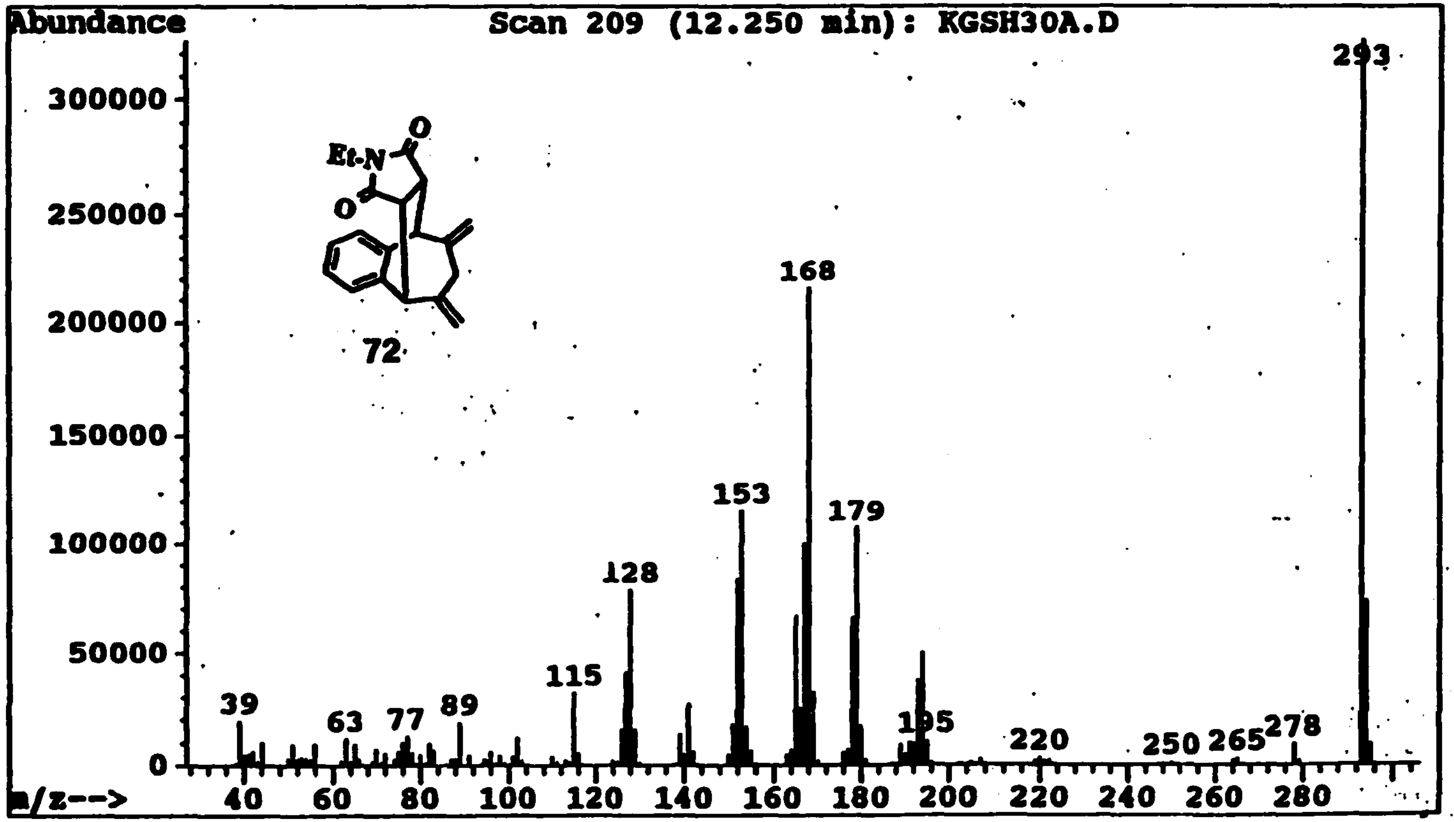

Abundance
Scan 220 (12.563 min): KGSH4A.D
150000
100000
50000
0
m/z-->
60
80
100
120
140
160
180
200
220
240
260
280
300
320
51
63
83
84
102
115
128
152
168
170
195
203
221
235
247
326
328

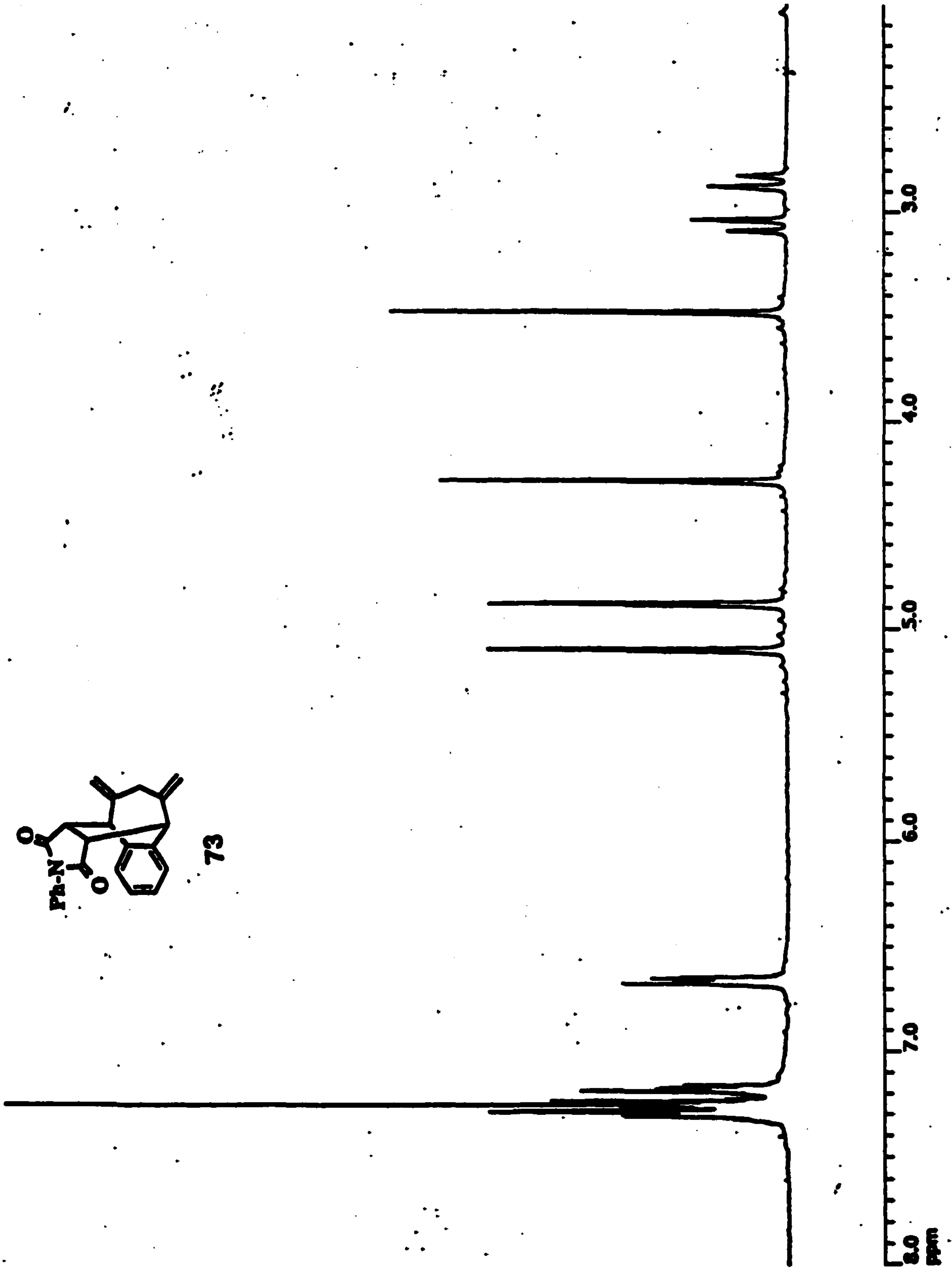


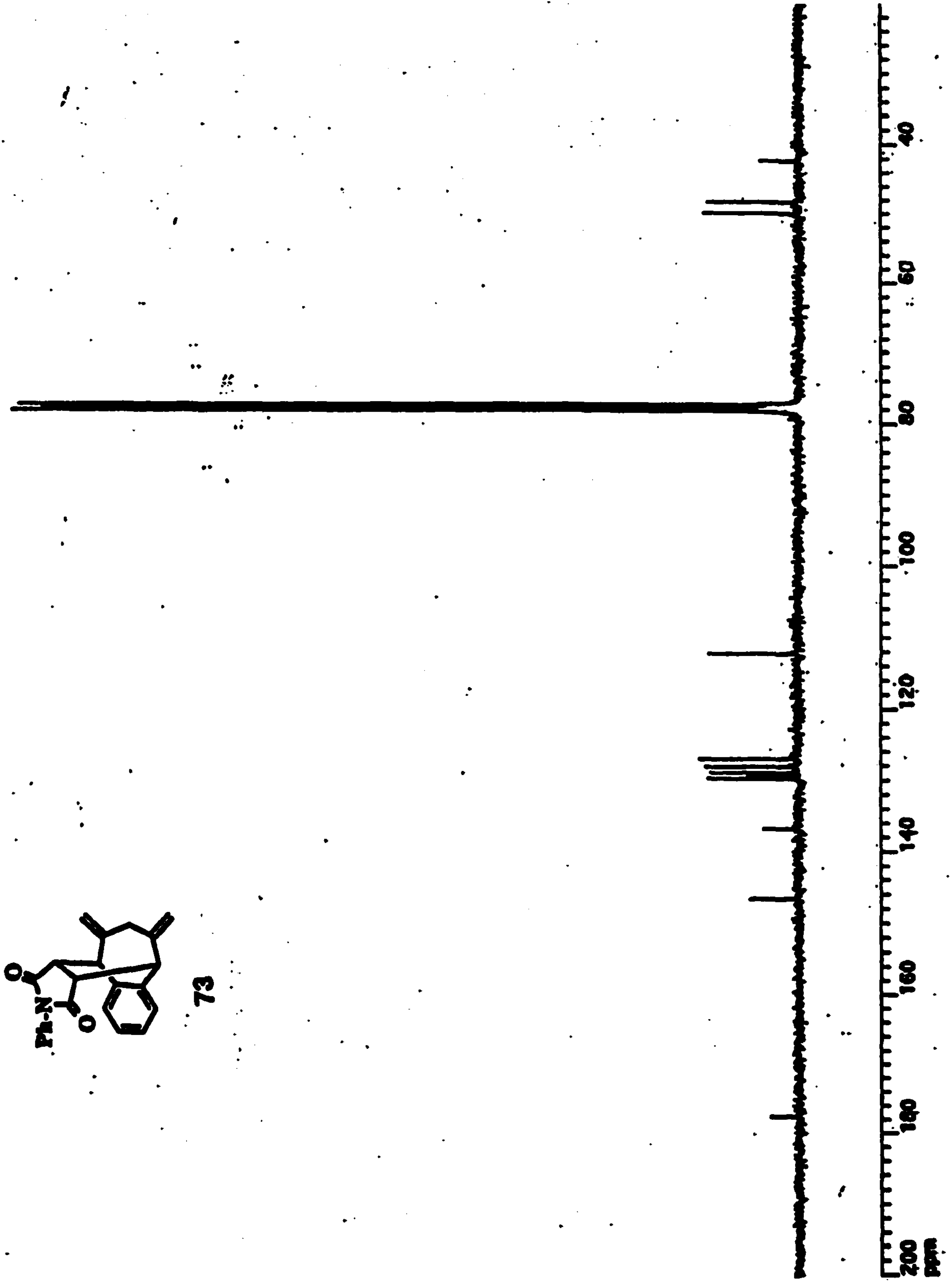
72



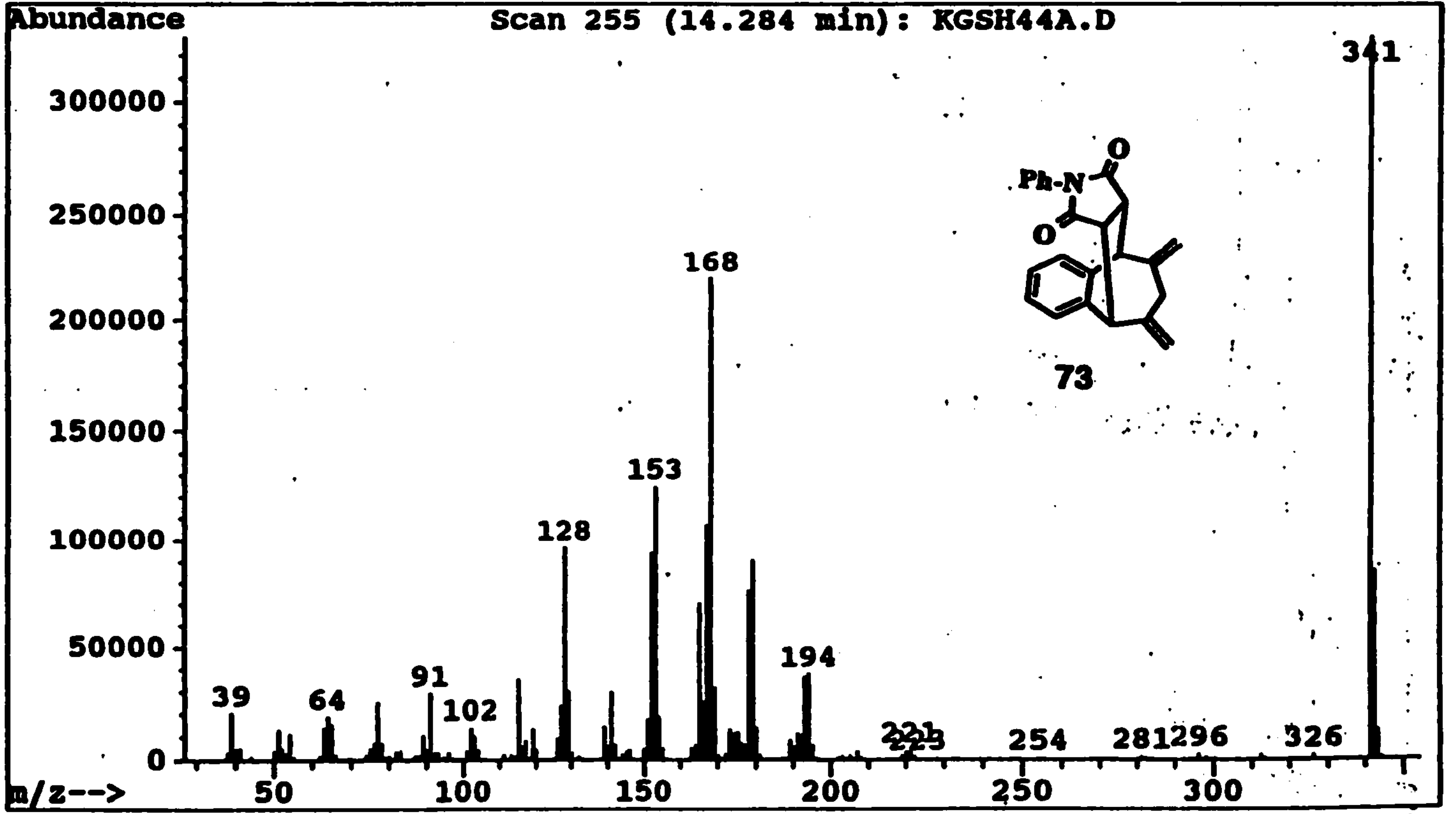
72

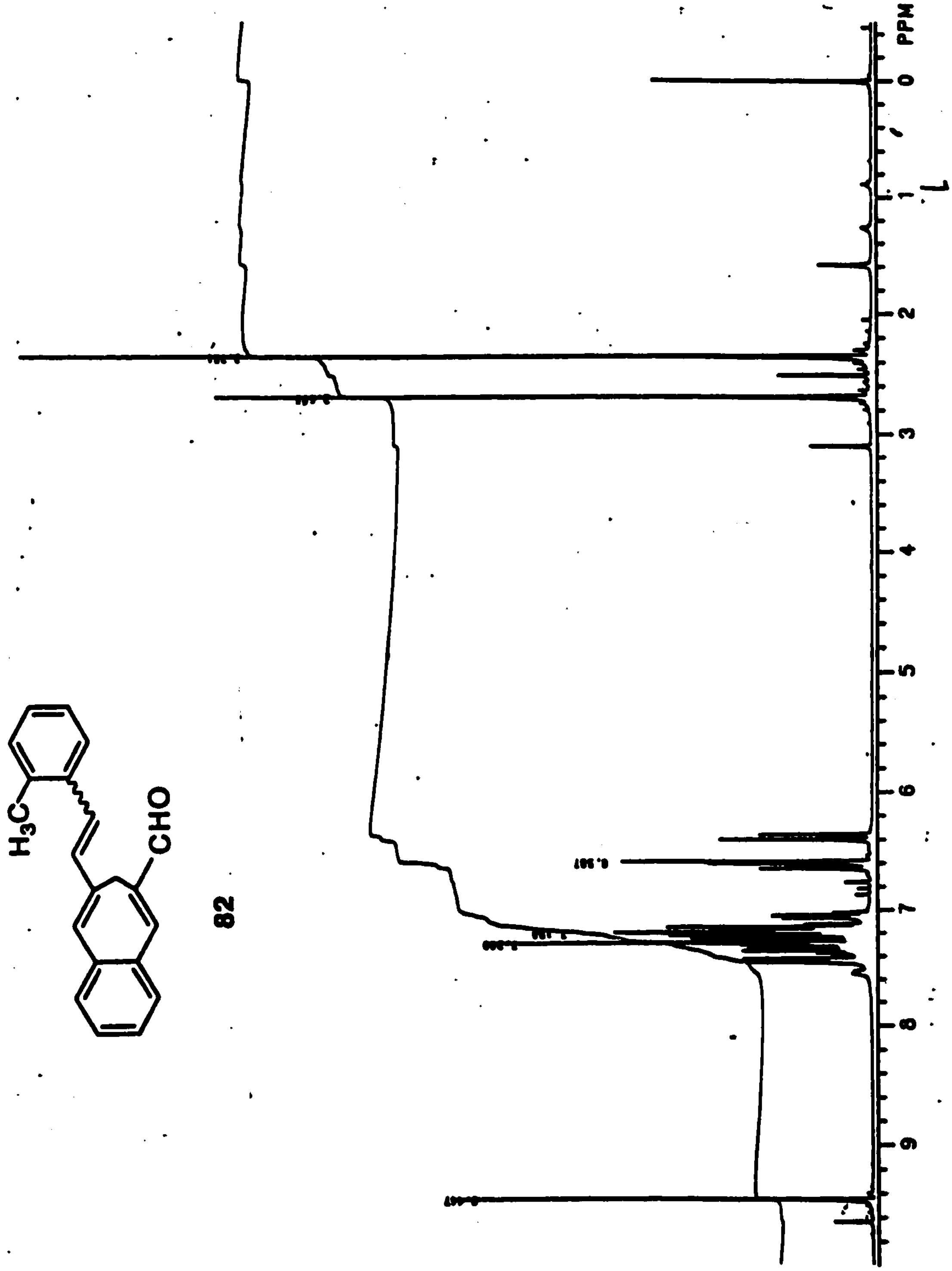

Abundance
Scan 209 (12.250 min): KGSH30A.D
300000
250000
200000
150000
100000
50000
0
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
39
63
77
89
115
128
153
168
179
195
220
250
265
278
293
Et-N
O
O
72


73
Ph-N
O
O
3.0
4.0
5.0
6.0
7.0
8.0
ppm

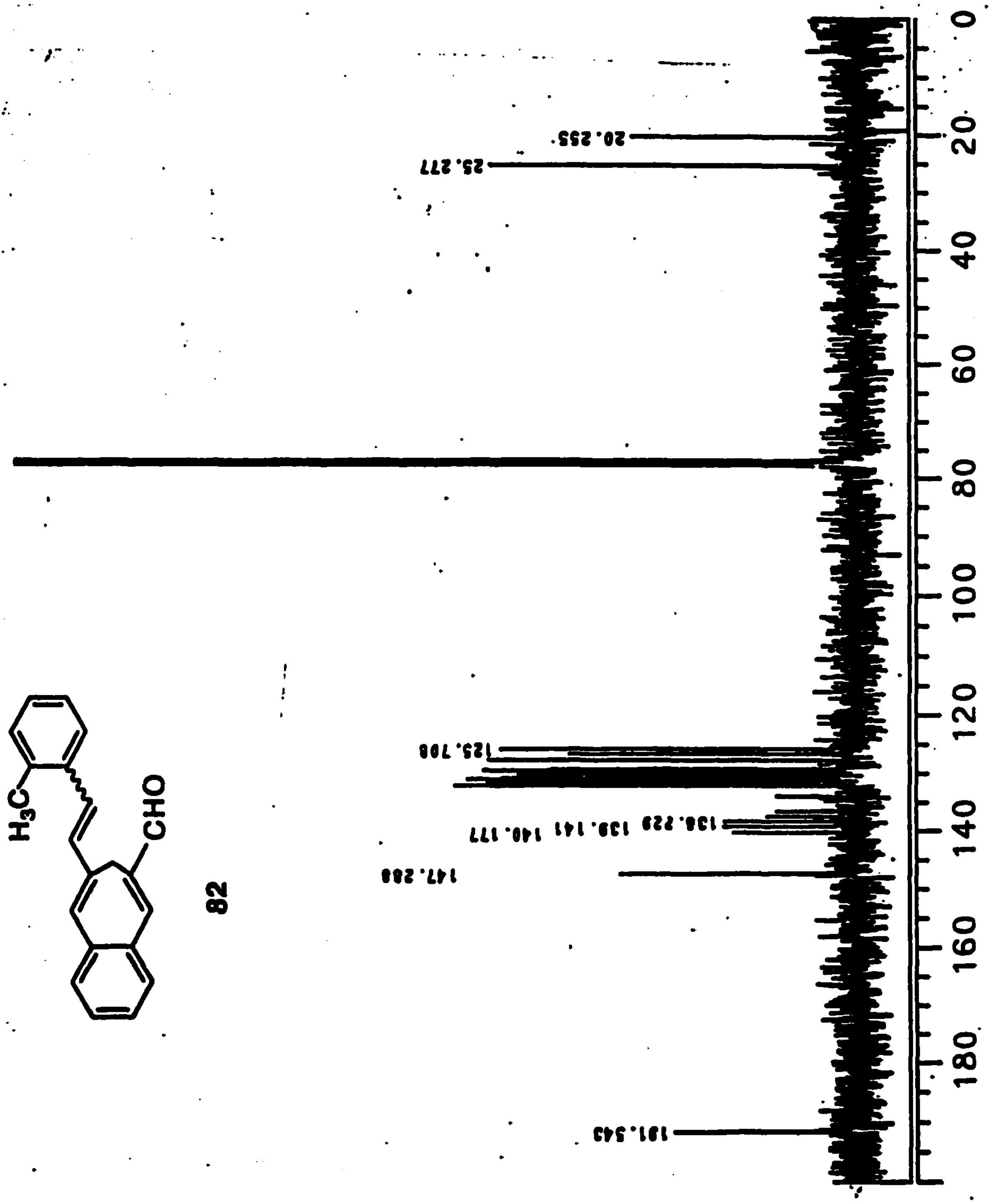


73

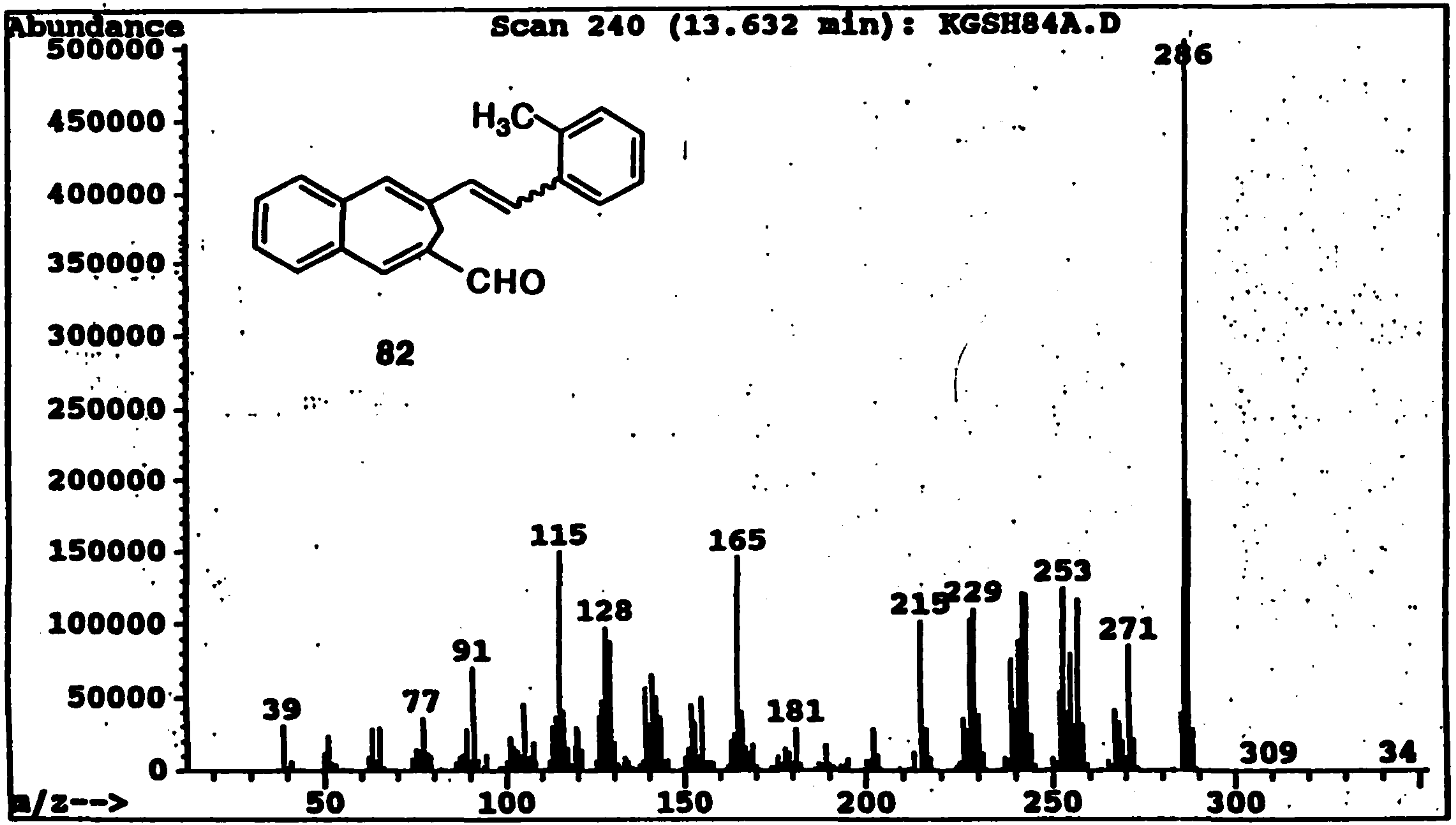

Abundance
Scan 255 (14.284 min): KGSH44A.D
300000
250000
200000
150000
100000
50000
0
m/z-->
50
100
150
200
250
300
39
64
91
102
128
153
168
194
221
223
254
281
296
326
341
Ph-N
O
O
73

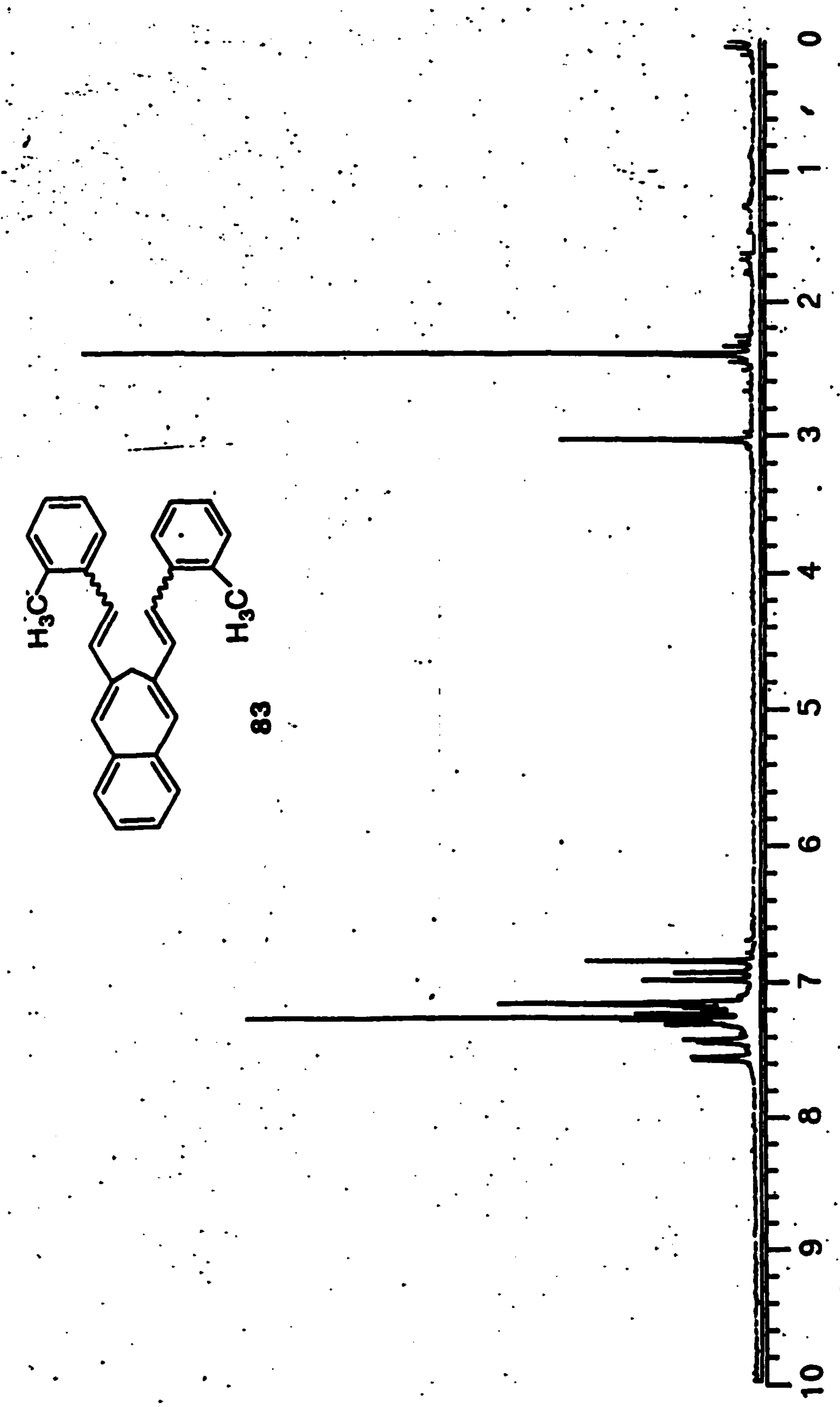


82

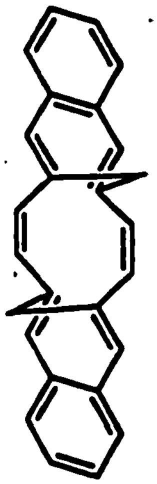

H$_3$C
CHO
20.255
25.277
125.708
138.229
139.141
140.177
147.288
181.543
0
20
40
60
80
100
120
140
160
180

82

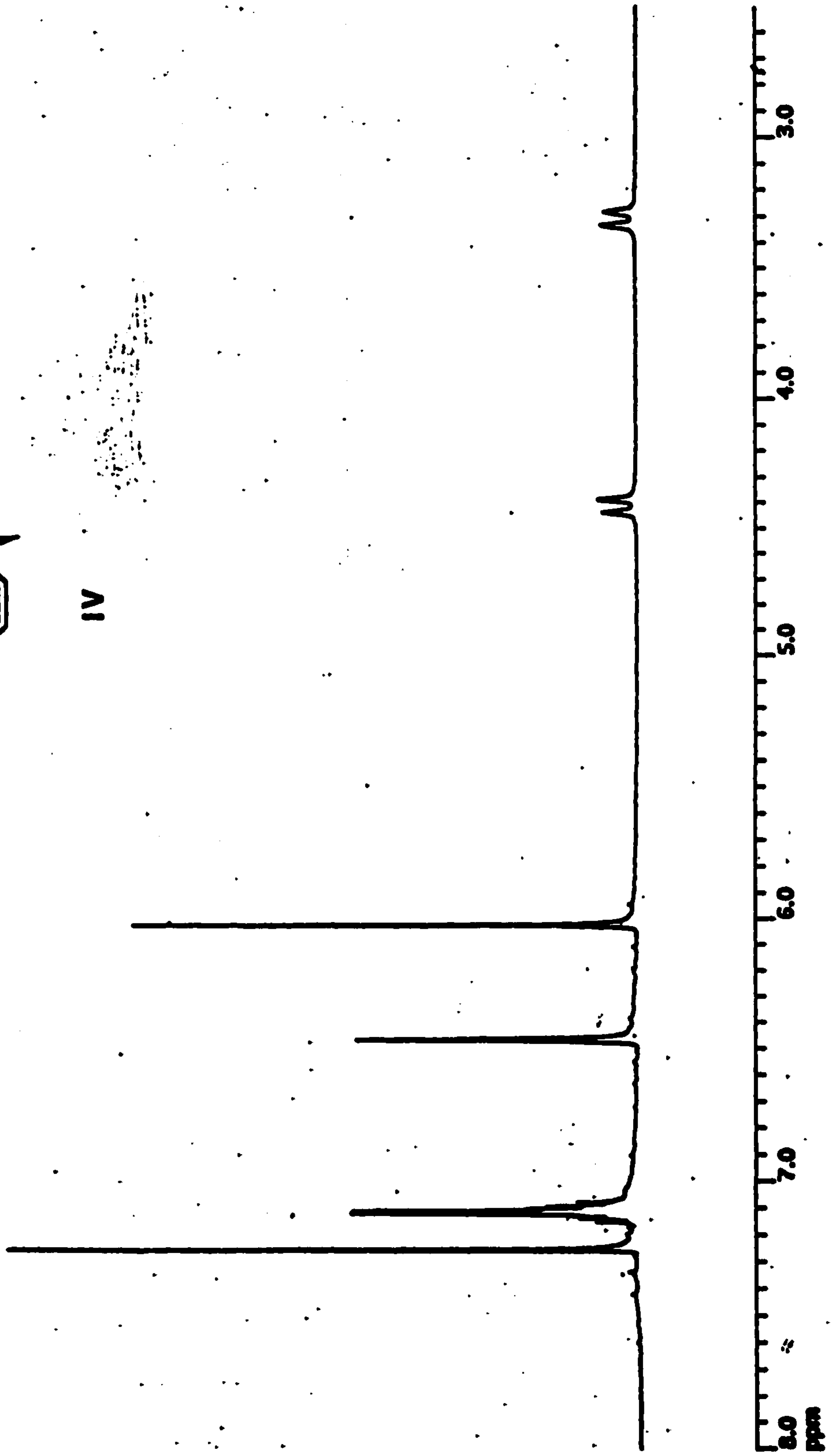

Scan 240 (13.632 min): KGSH84A.D
Abundance
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
50
100
150
200
250
300
39
77
91
115
128
165
181
215
229
253
271
286
309
34
H_3C
CHO
82

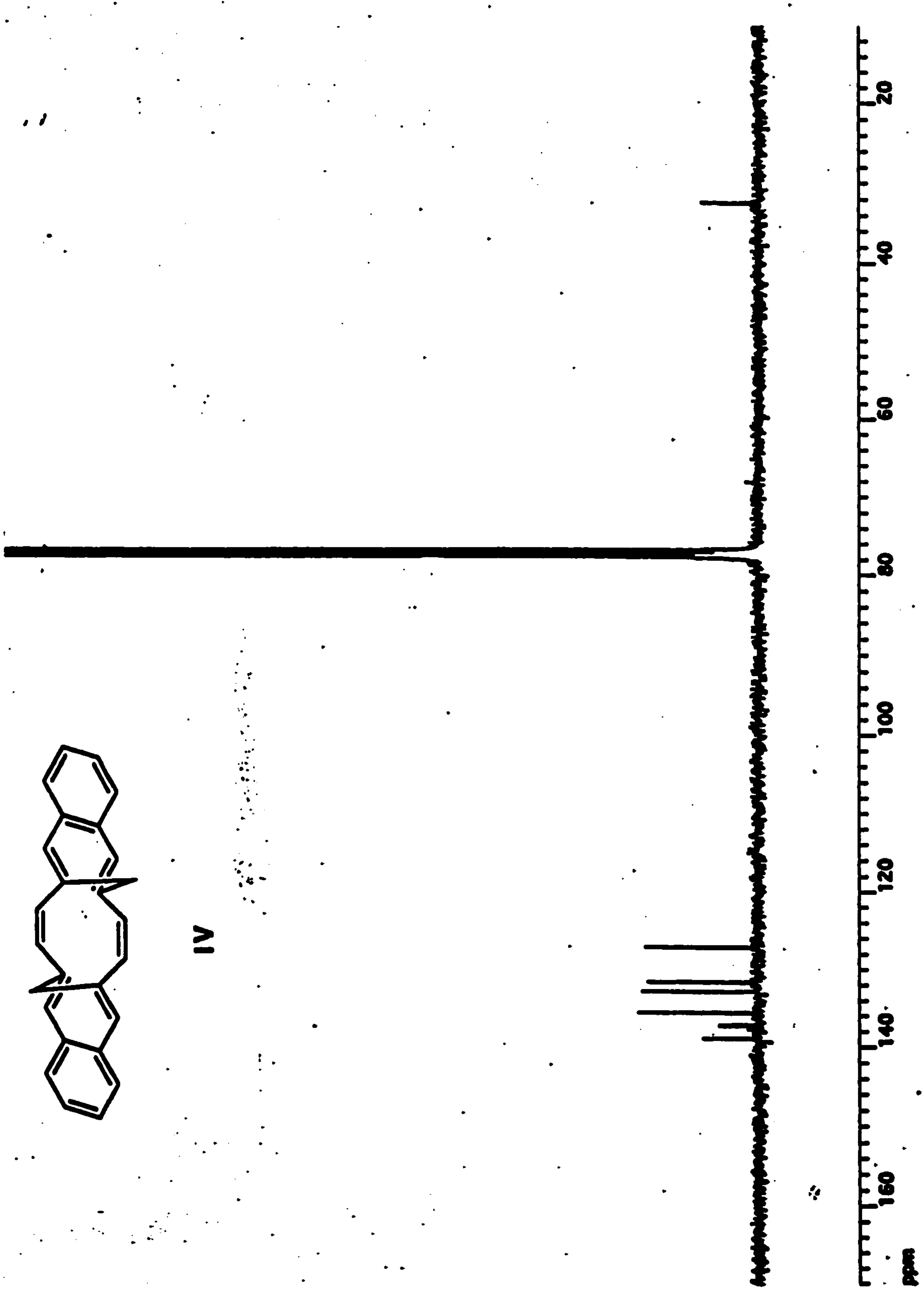


83

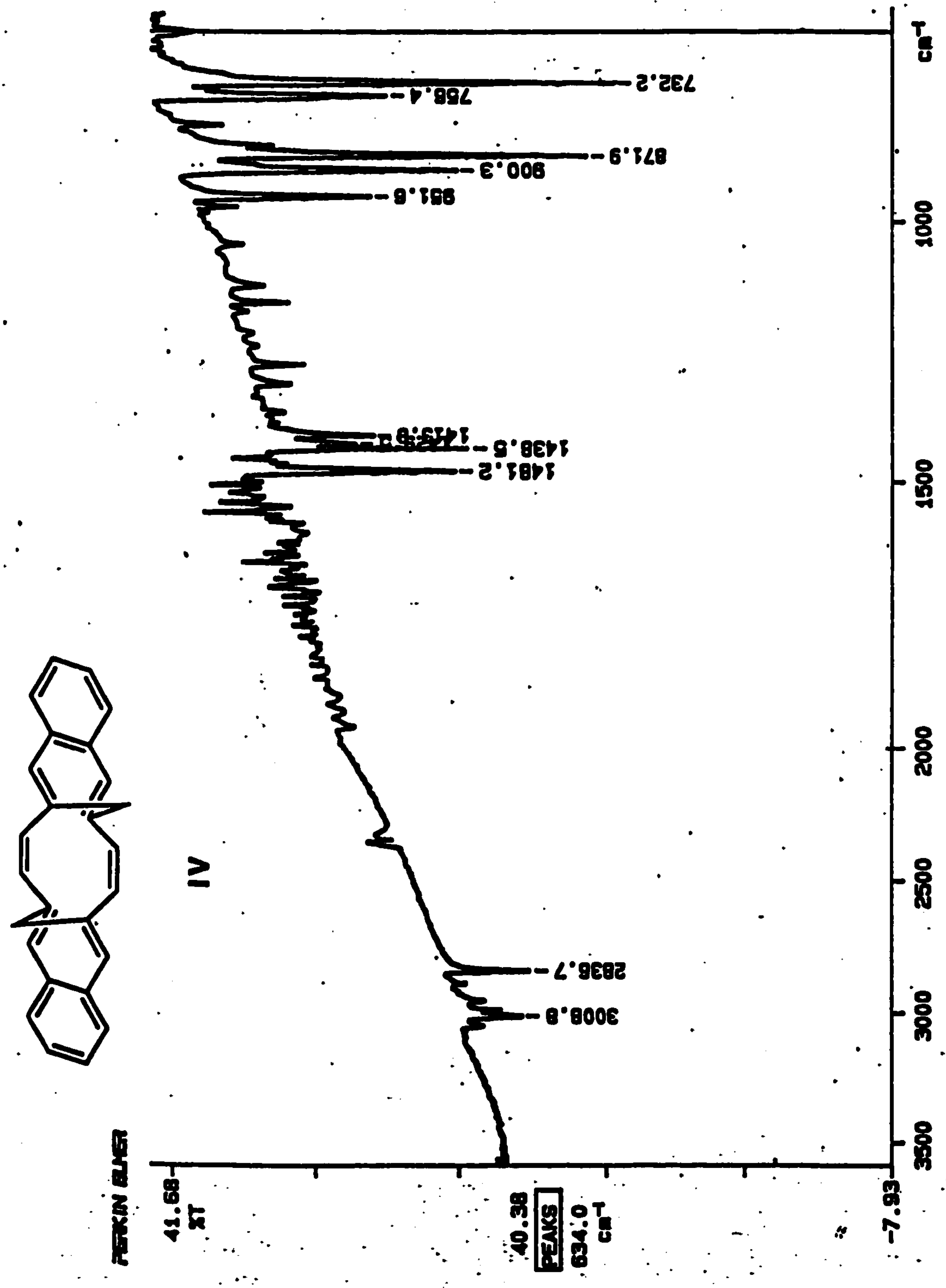


IV

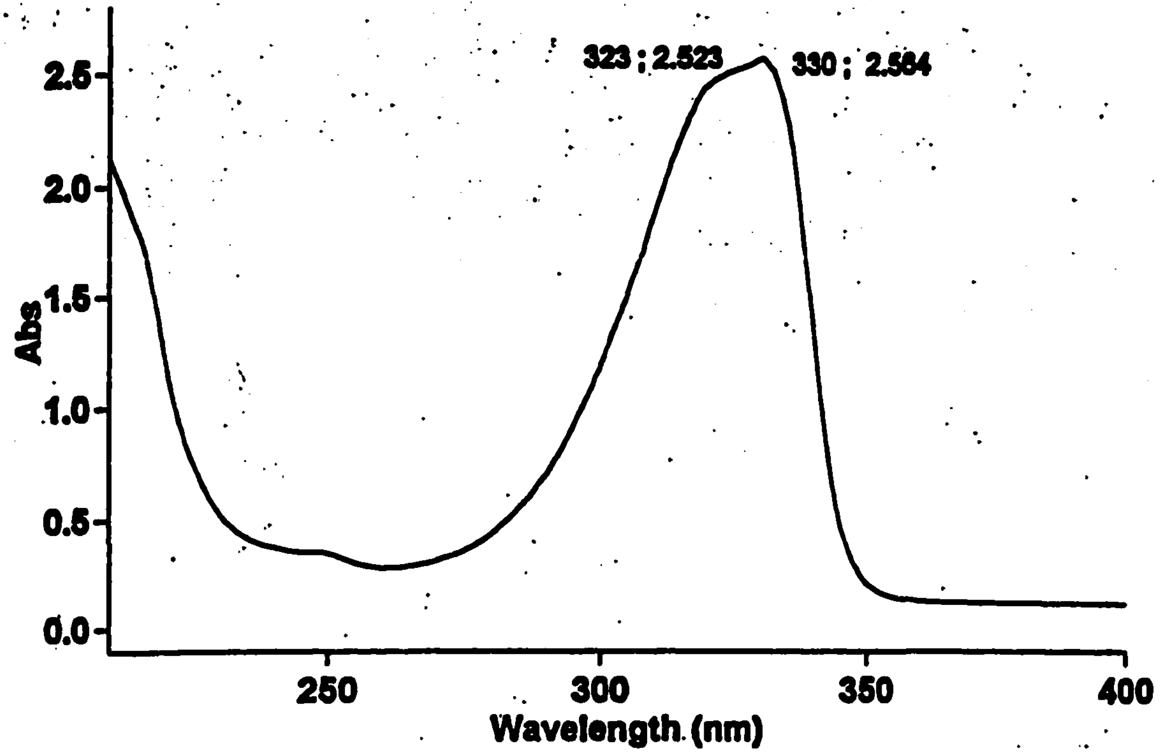


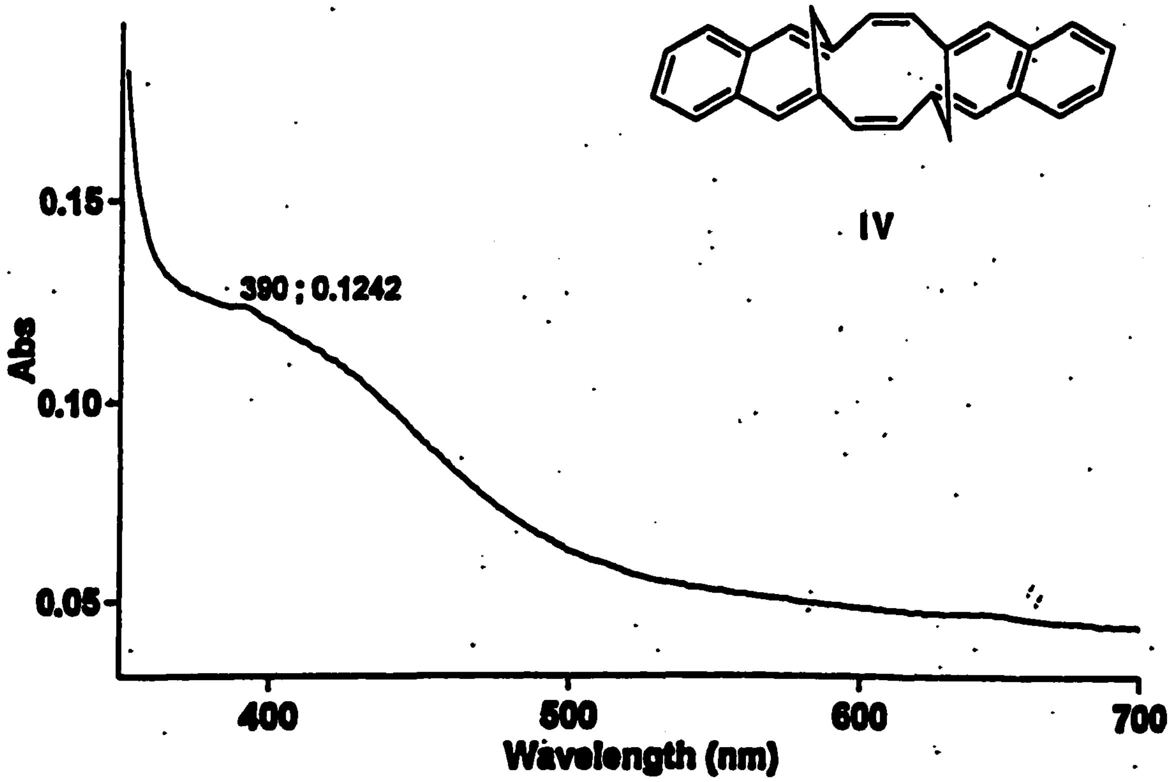


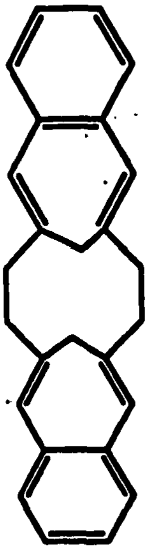
IV


PERKIN ELMER
41.68
%T
40.38
PEAKS
634.0
cm-1
-7.93
3500
3000
2500
2000
1500
1000
cm-1
3008.8
2836.7
1481.2
1438.5
1413.9
951.6
900.3
871.9
758.4
732.2

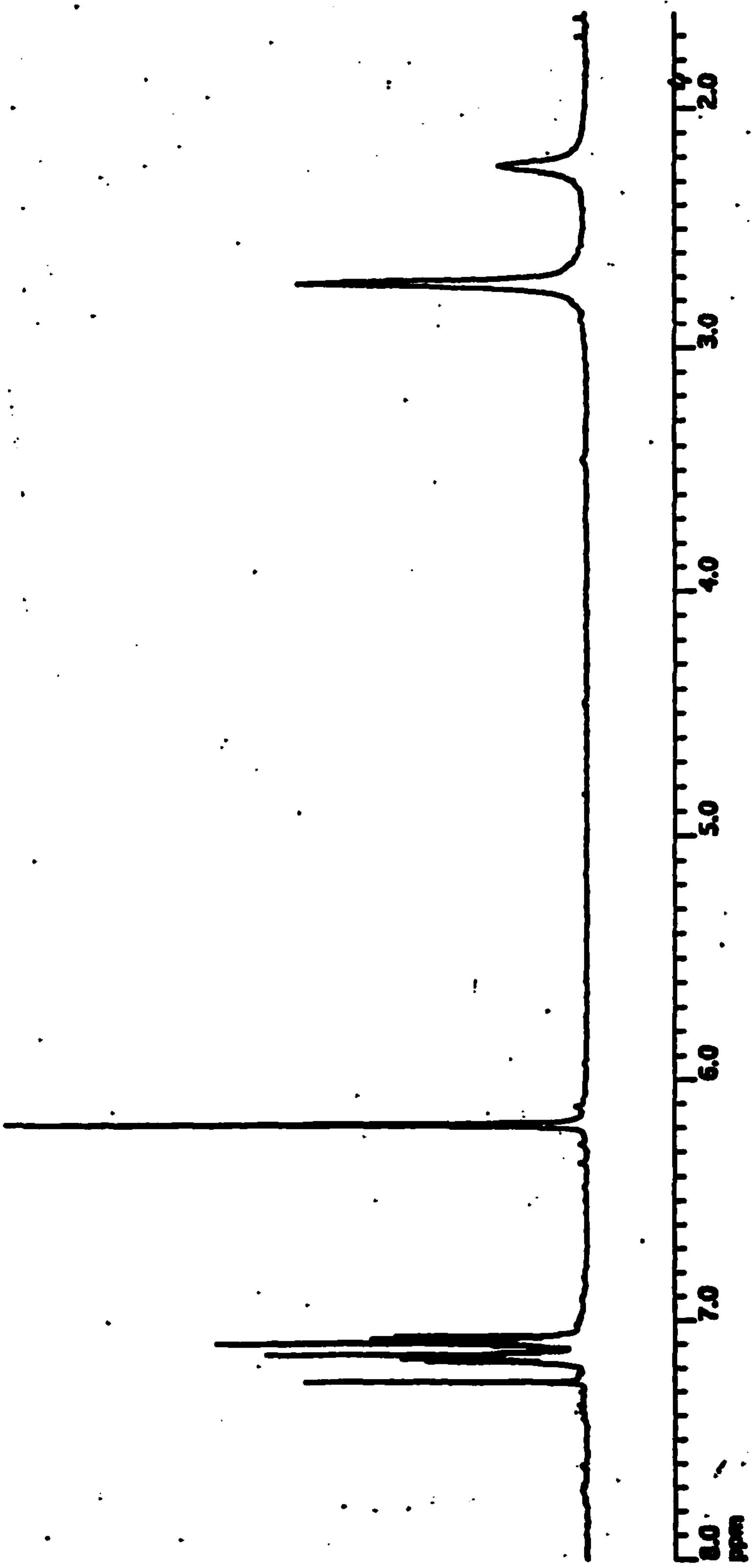
IV

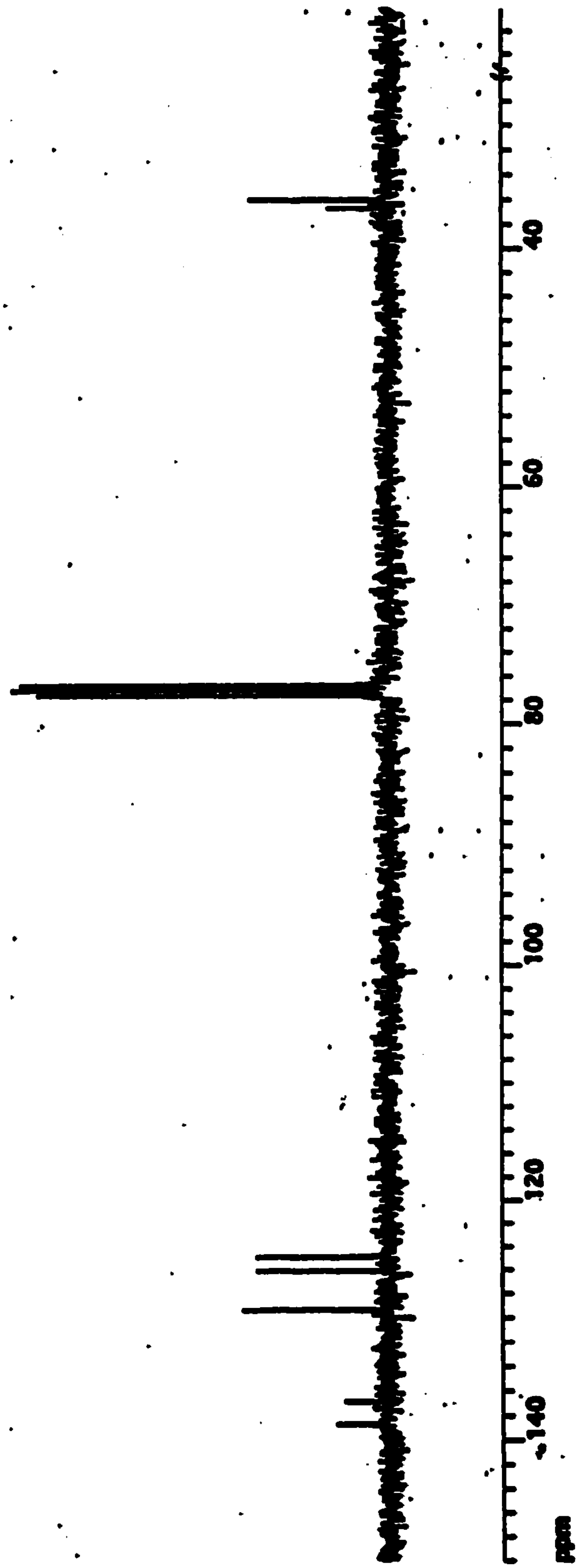

323 ; 2.523
330 ; 2.584
2.5
2.0
1.5
1.0
0.5
0.0
Abs
250
300
350
400
Wavelength (nm)

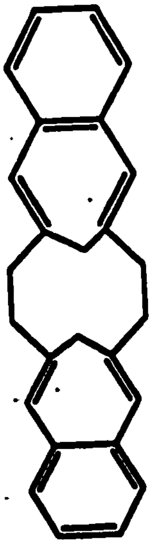

IV
390 ; 0.1242
0.15
0.10
0.05
Abs
400
500
600
700
Wavelength (nm)



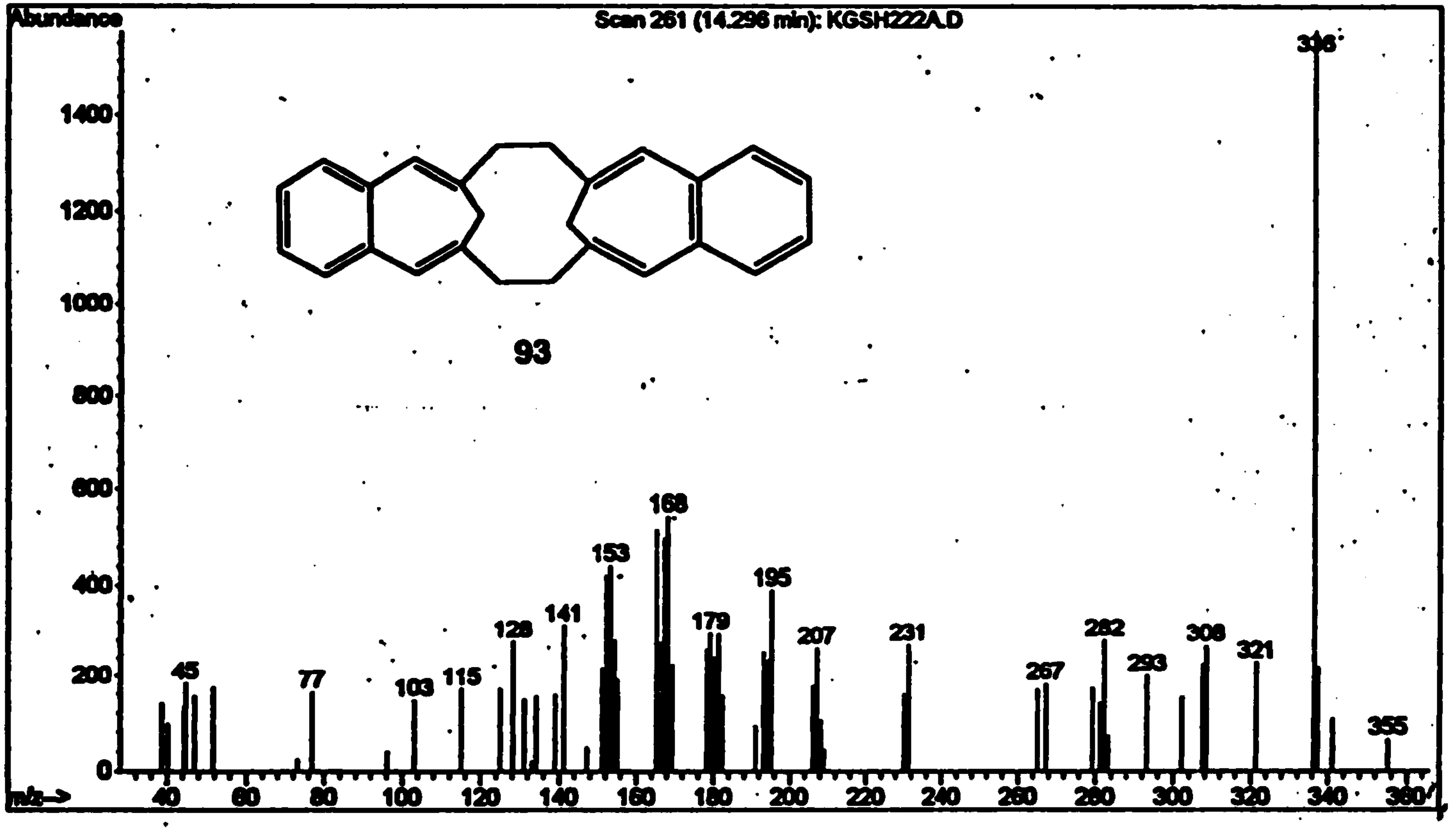
93

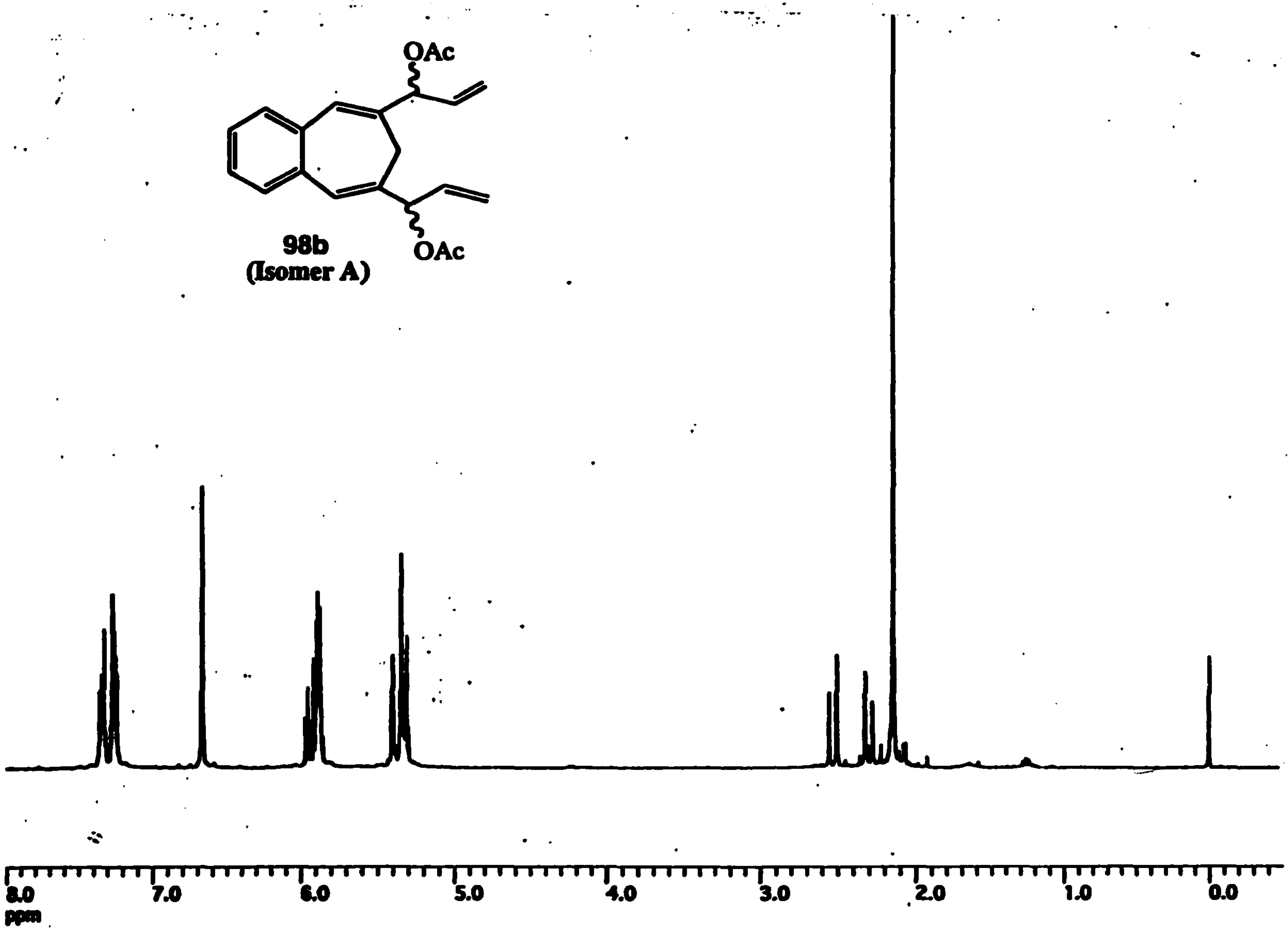




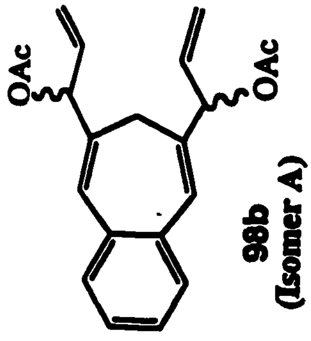


93

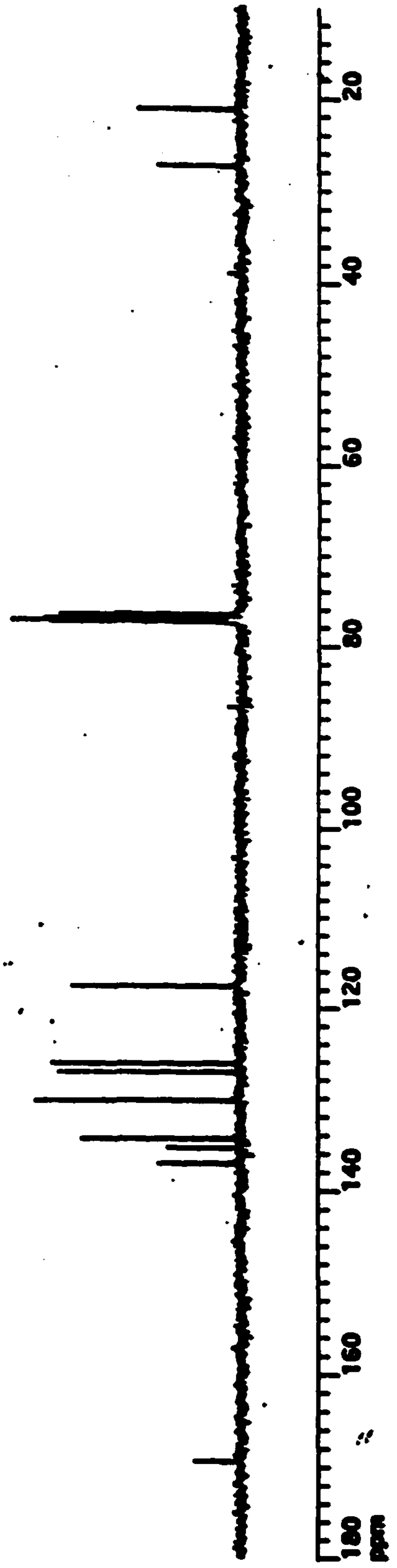

Abundance
Scan 261 (14.296 min): KGSH222A.D
93
0
200
400
600
800
1000
1200
1400
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
45
77
103
115
128
141
153
168
179
195
207
231
267
282
293
308
321
336
355

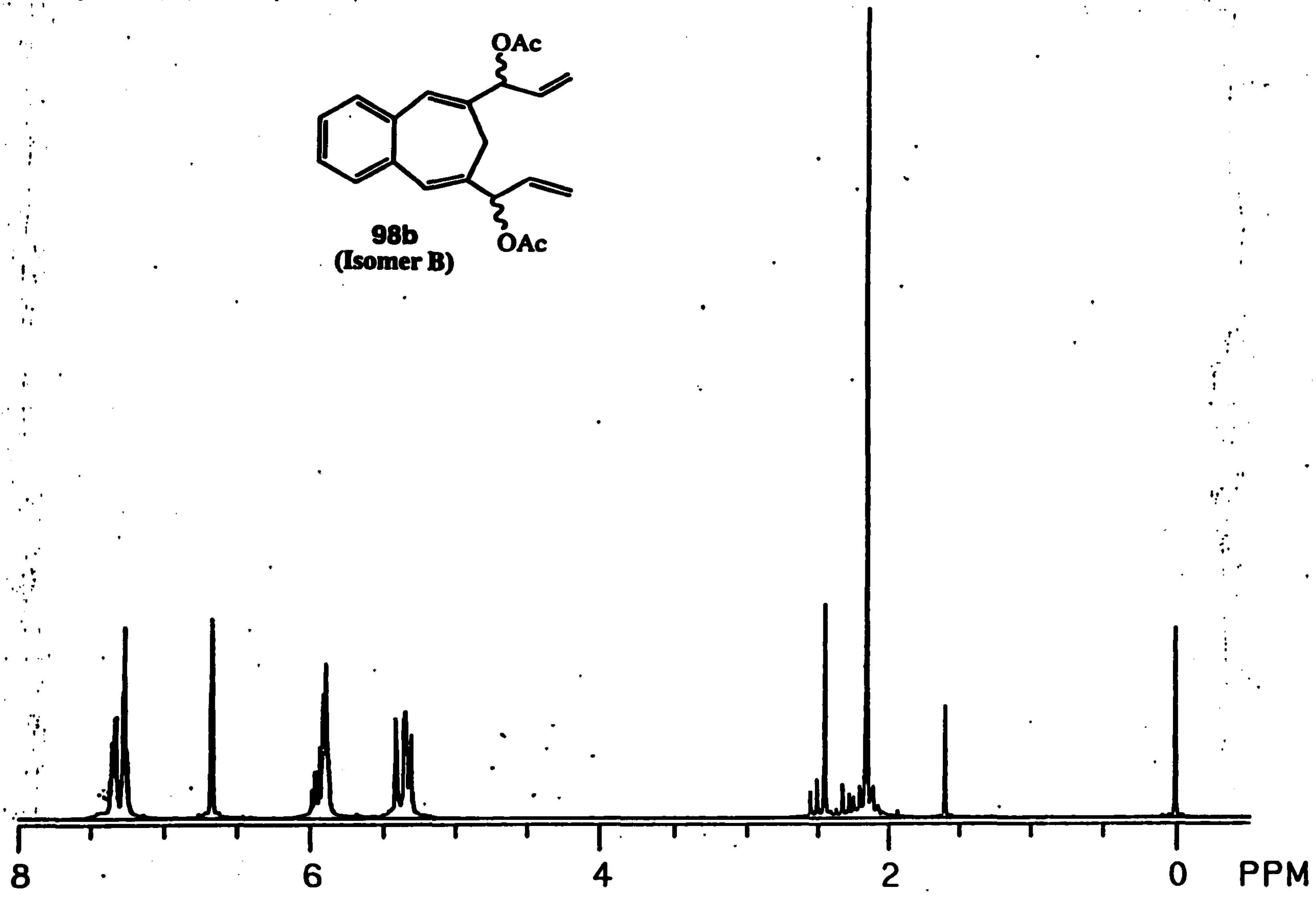


98b
(Isomer A)

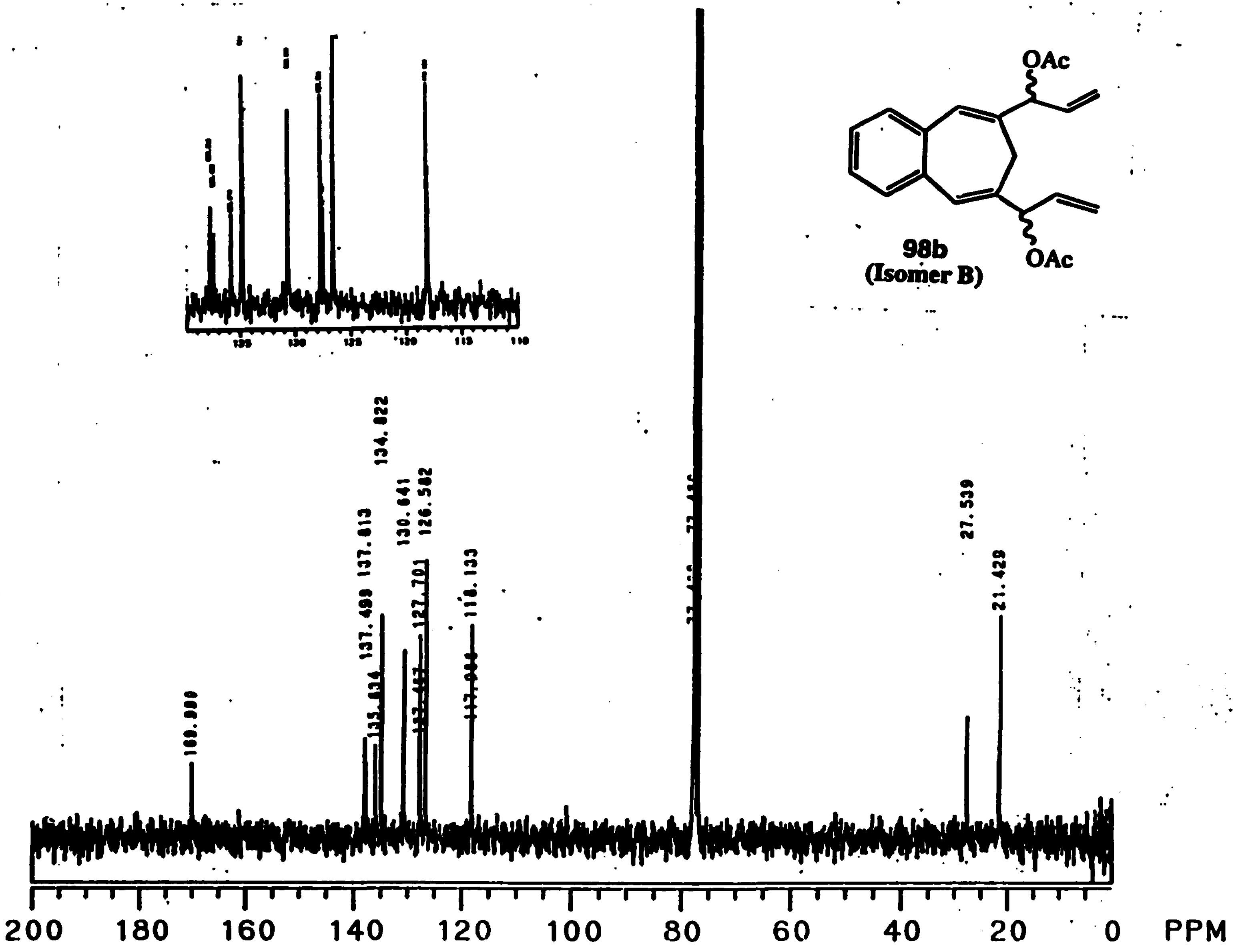


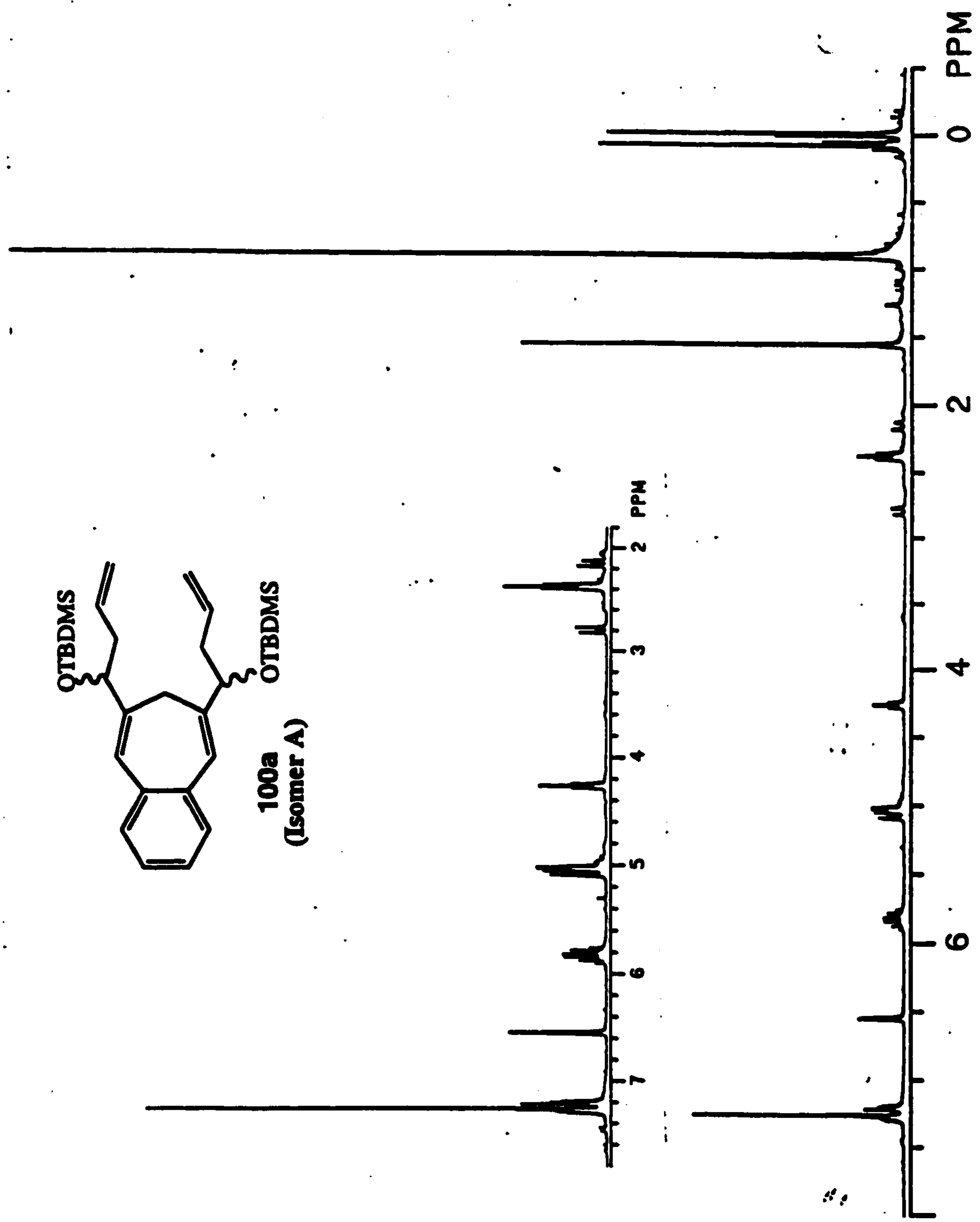
98b
(Isomer A)



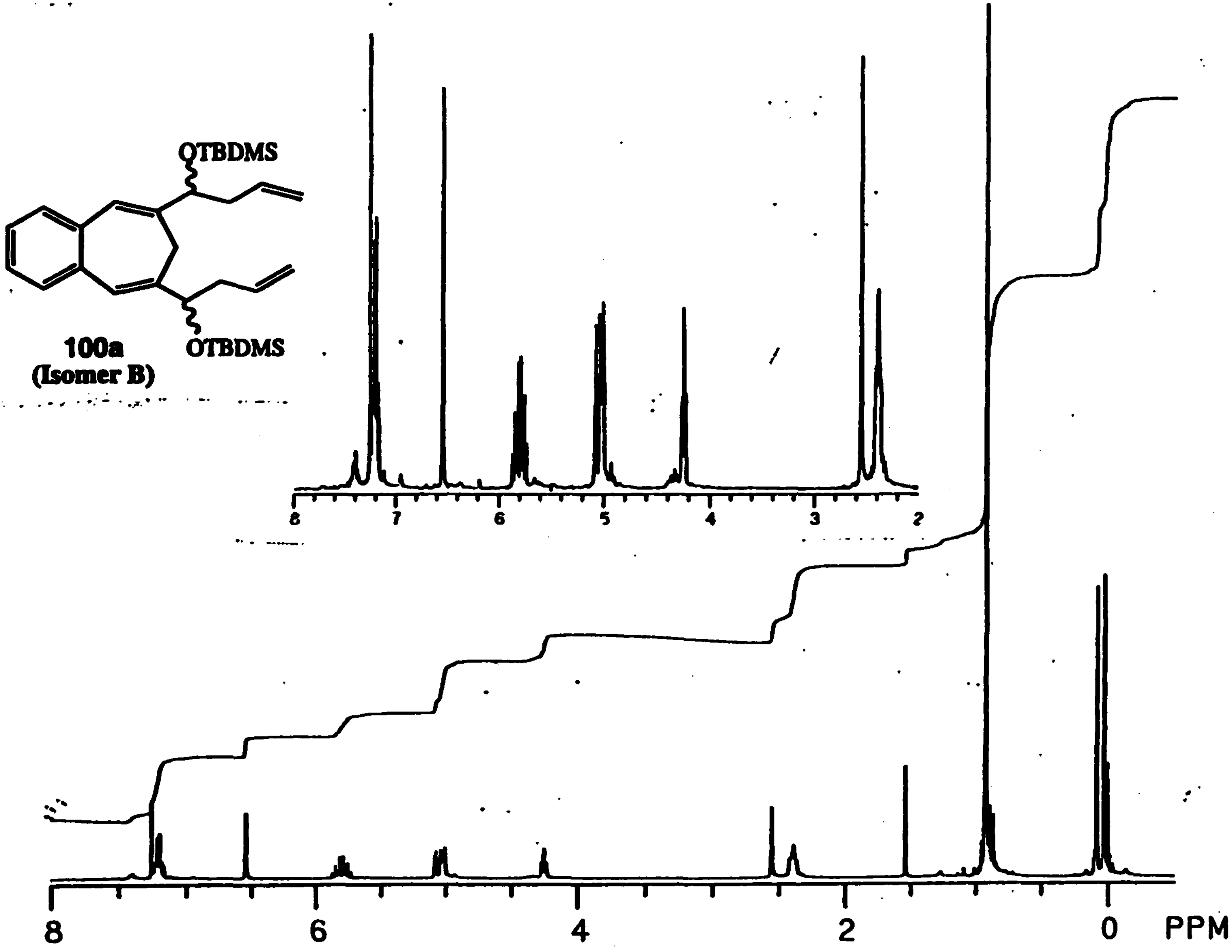


98b
(Isomer B)

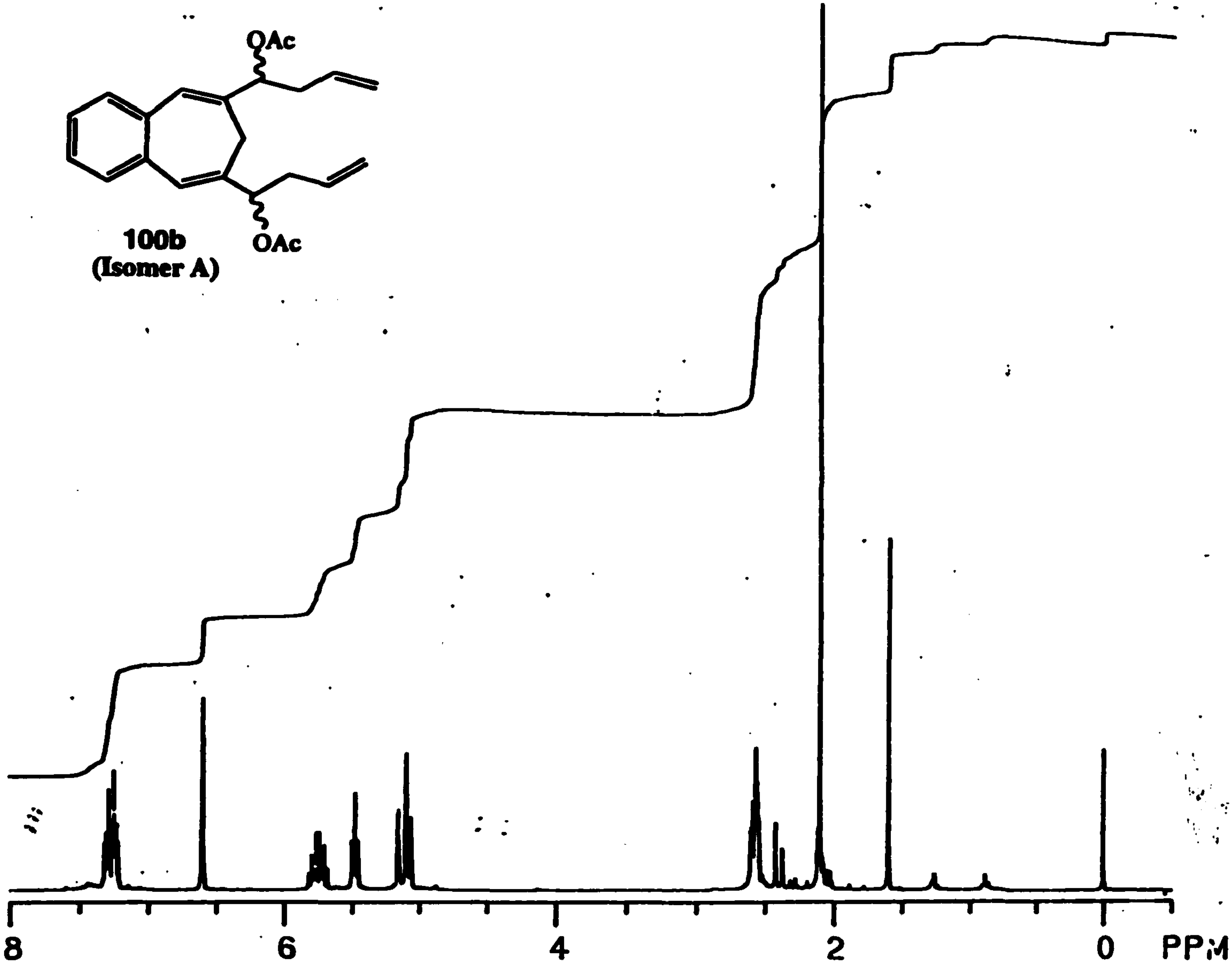

OAc
OAc
98b
(Isomer B)
169.990
137.499
137.813
134.822
130.641
126.582
127.701
118.133
27.539
21.429
200
180
160
140
120
100
80
60
40
20
0
PPM



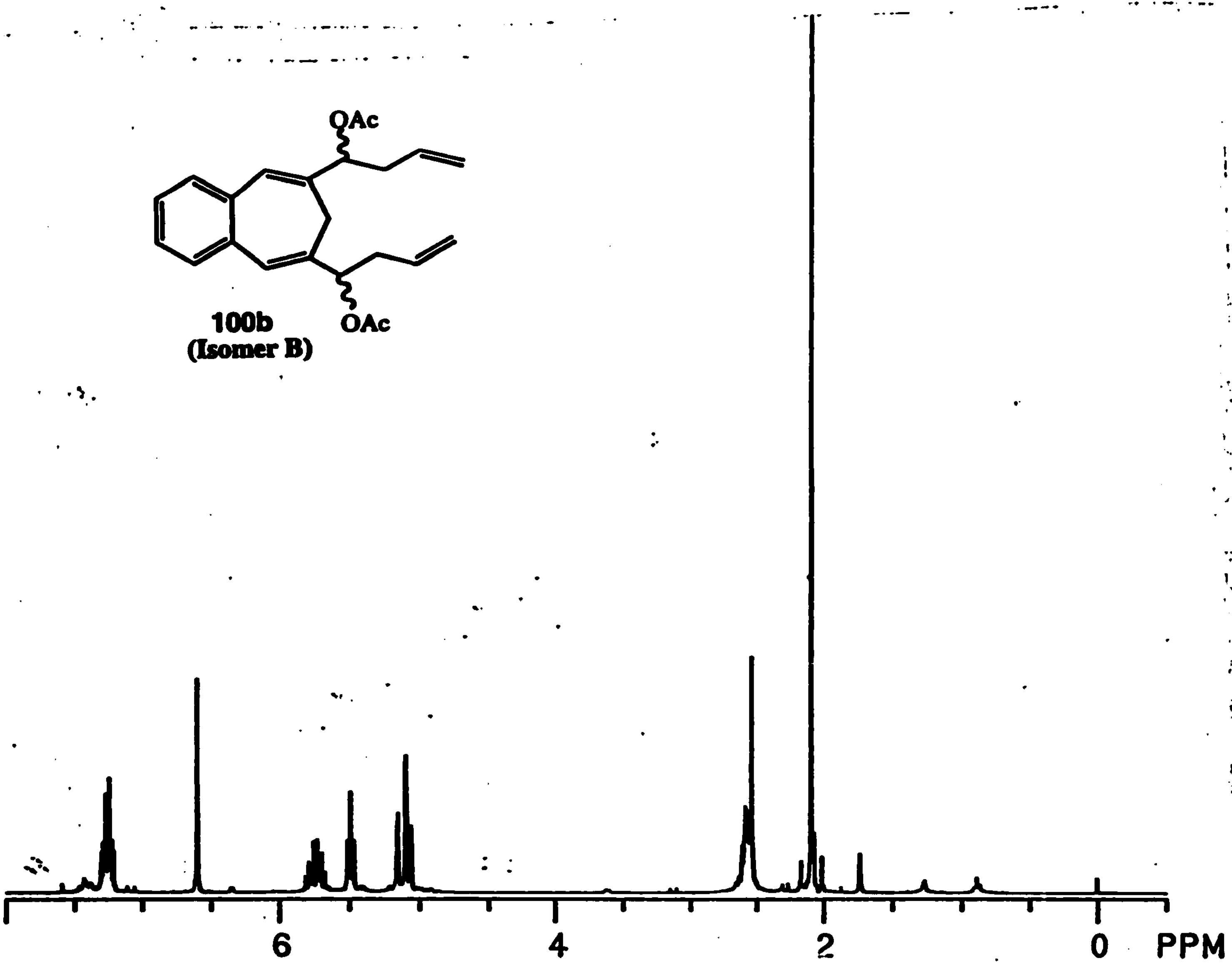
100a
(Isomer A)



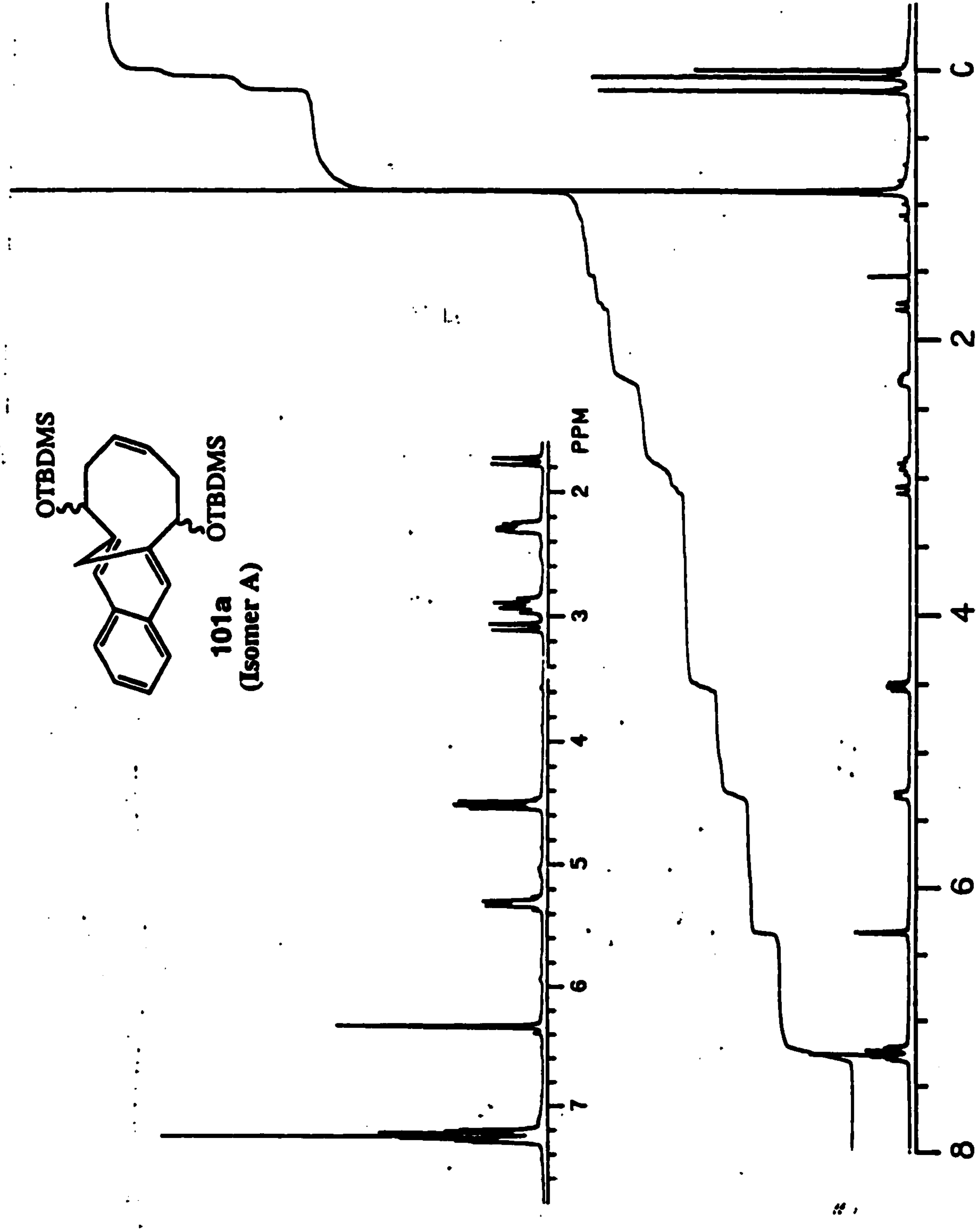
100a
(Isomer B)



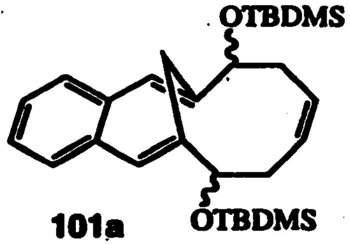
100b
(Isomer A)



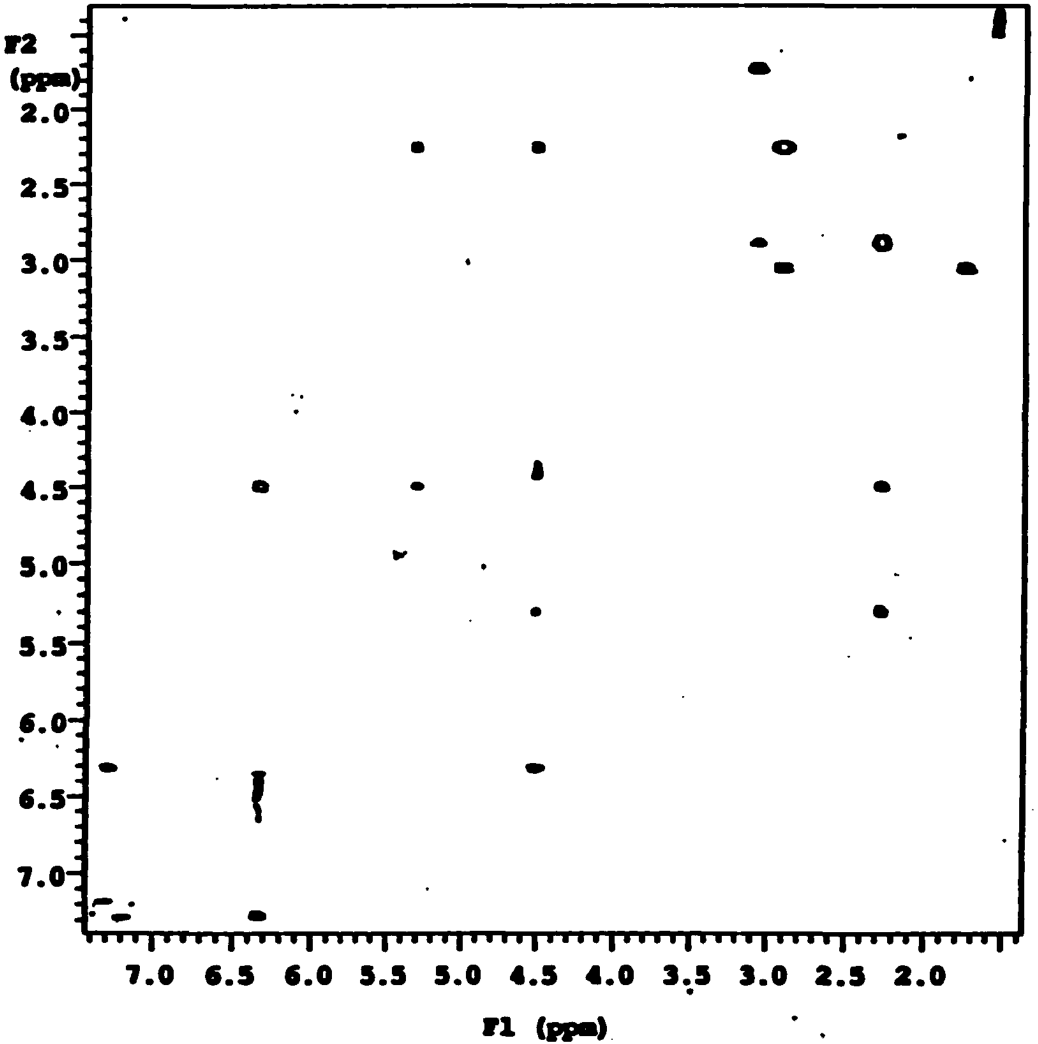
100b
(Isomer B)

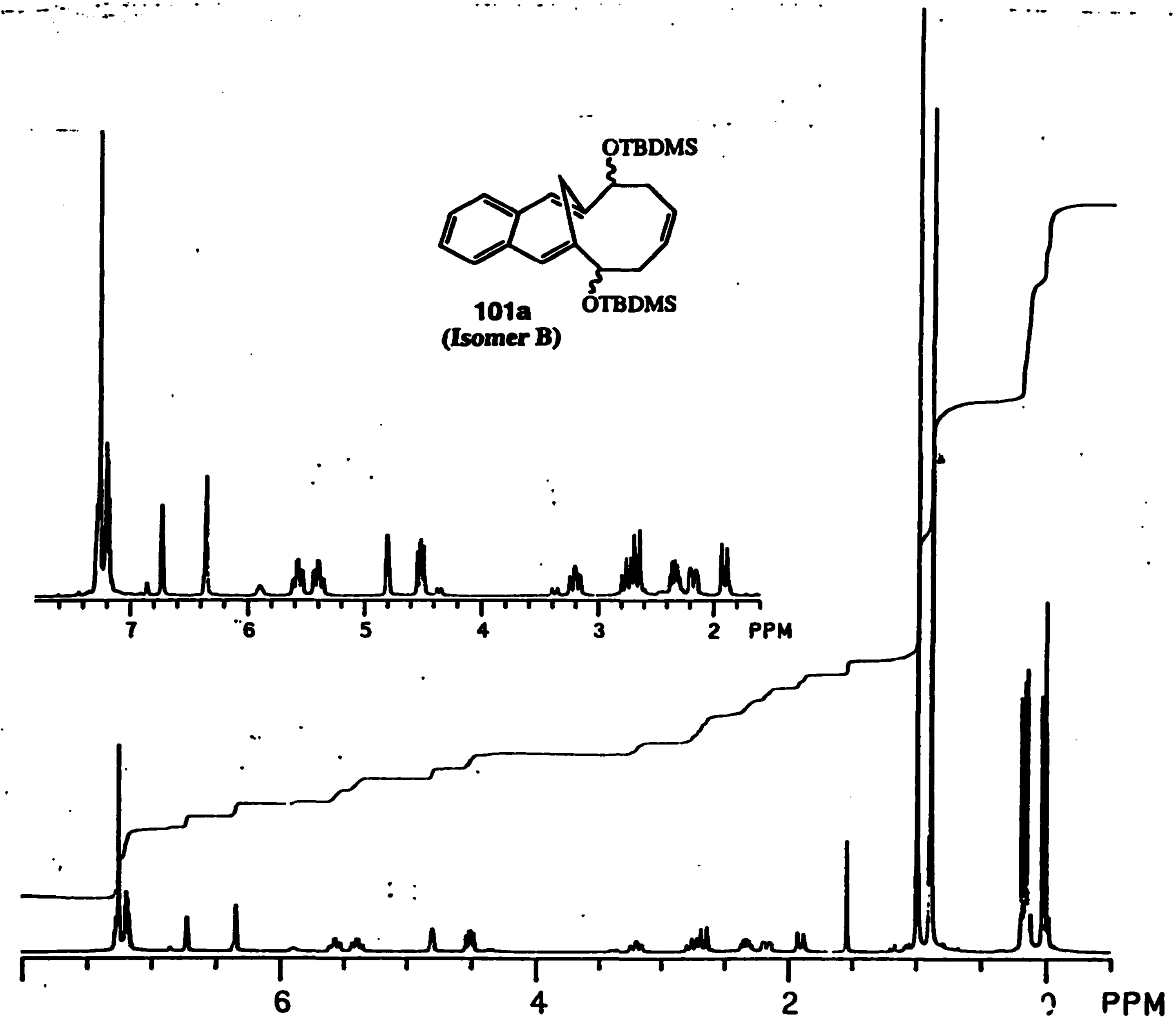


101a
(Isomer A)

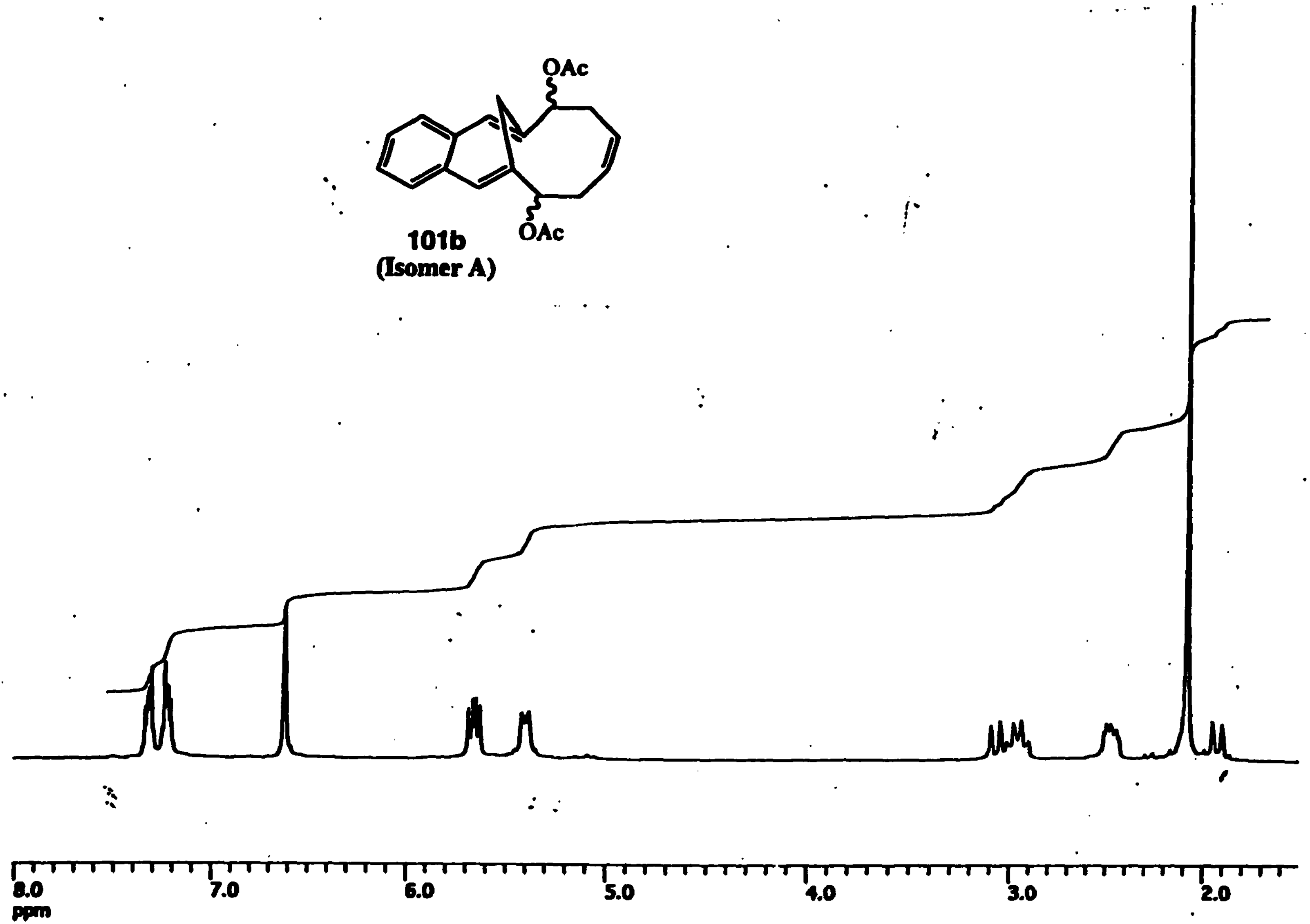


101a
(Isomer A)

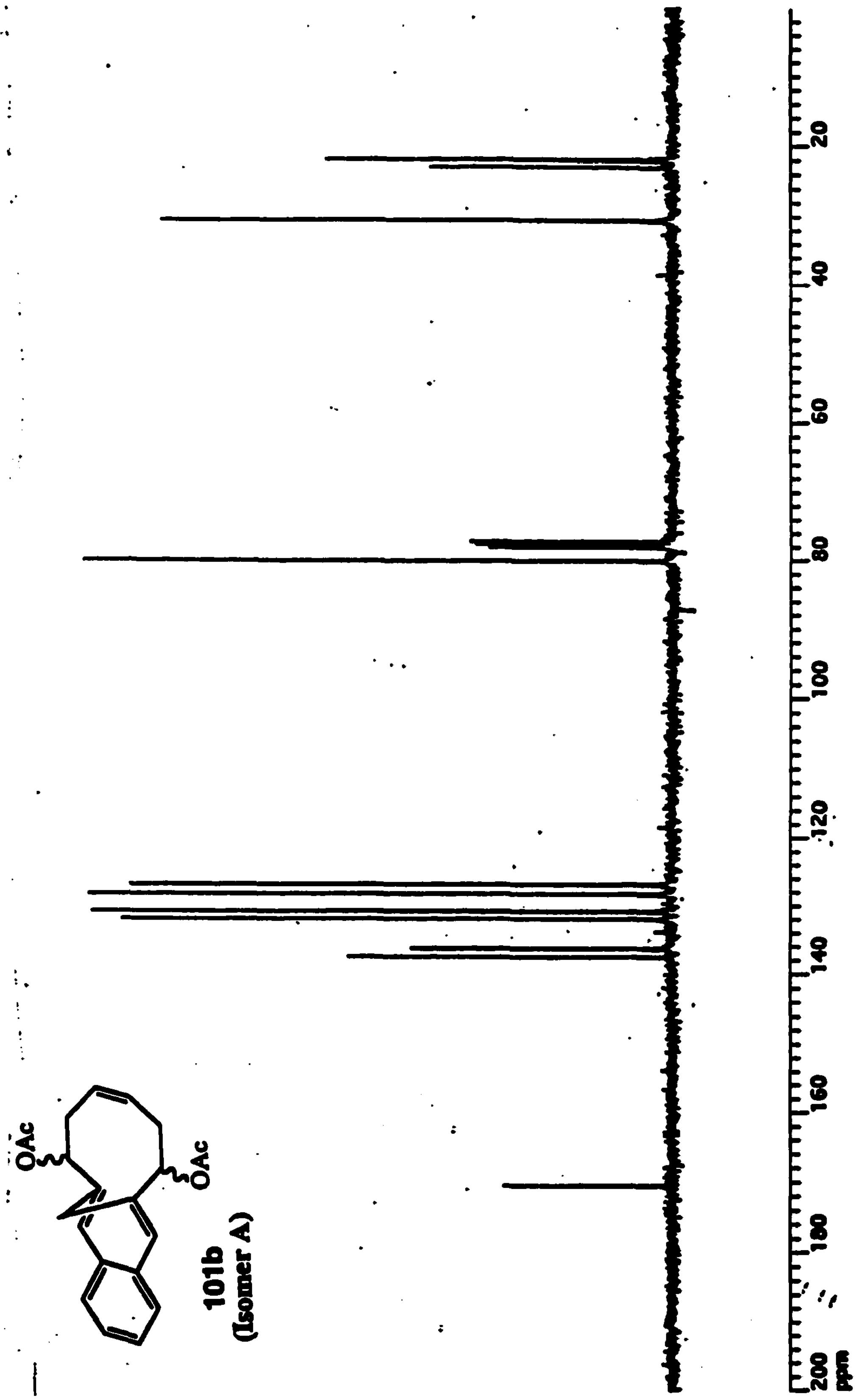




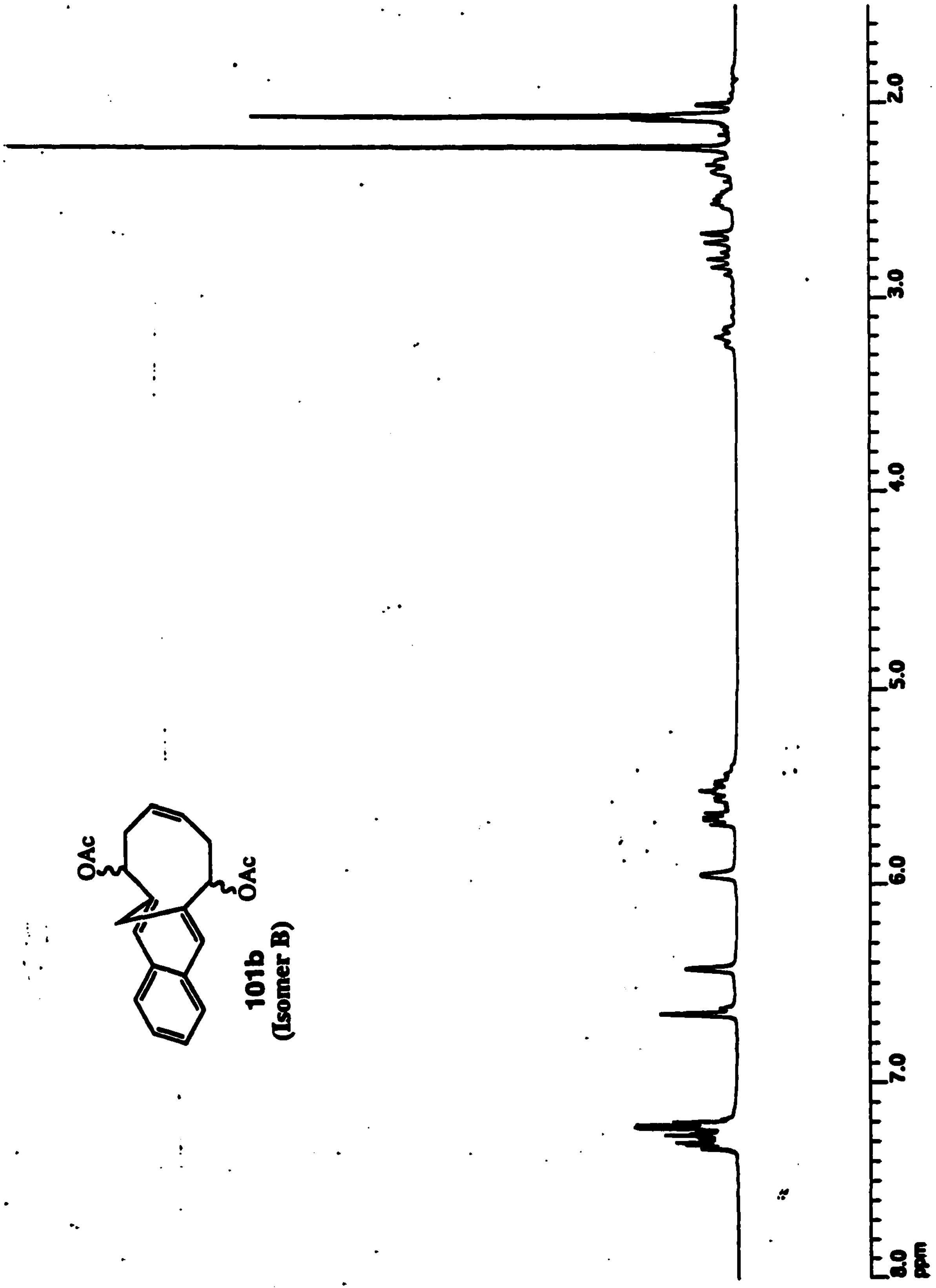
101a
(Isomer B)



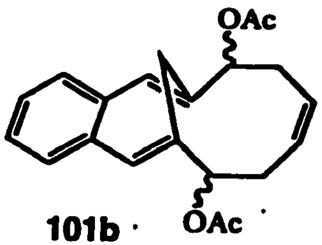
101b
(Isomer A)



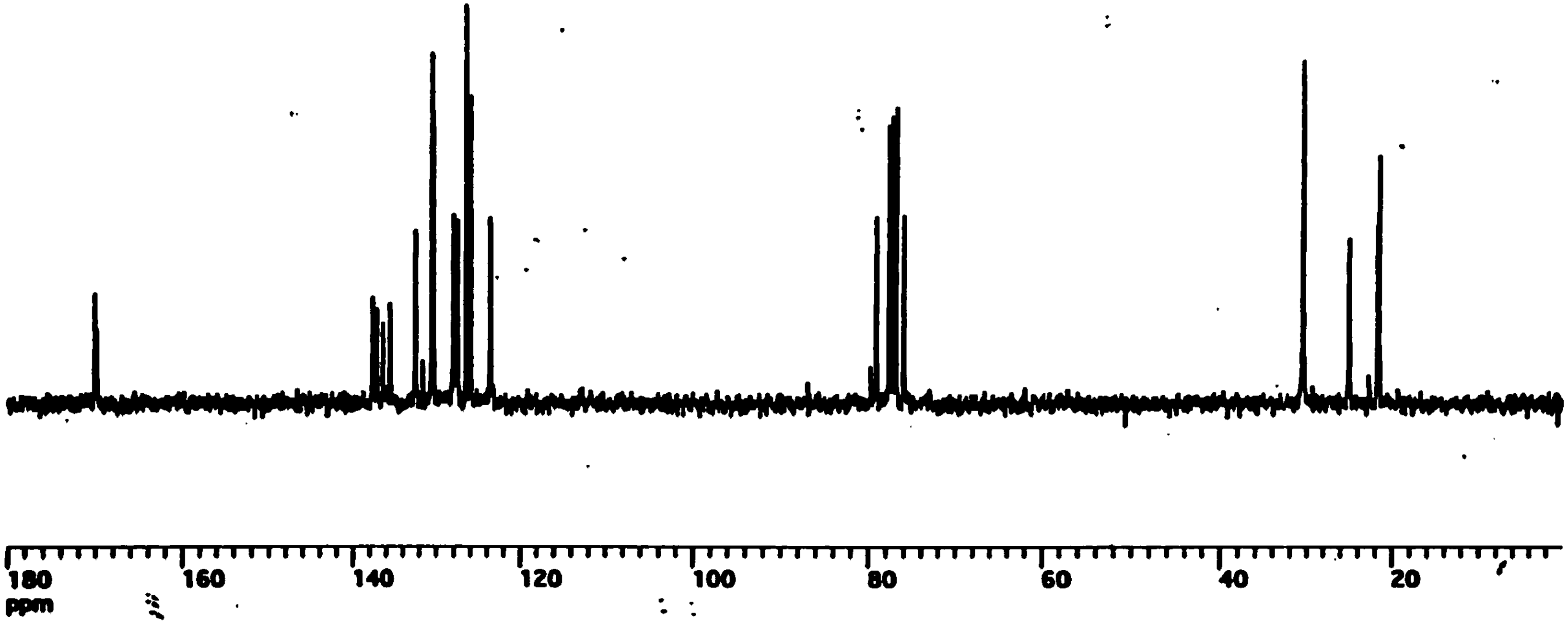
101b
(Isomer A)



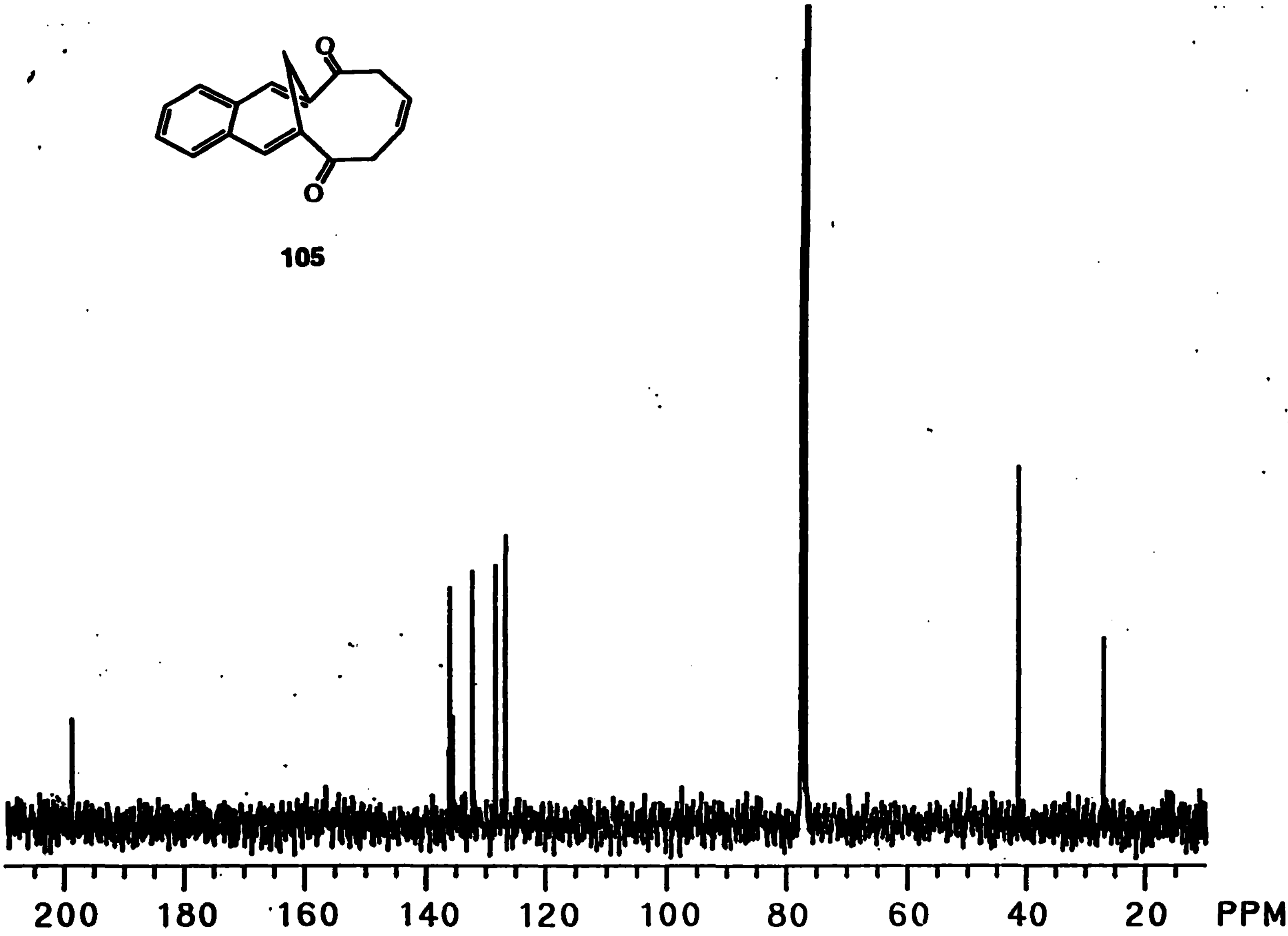
101b
(Isomer B)



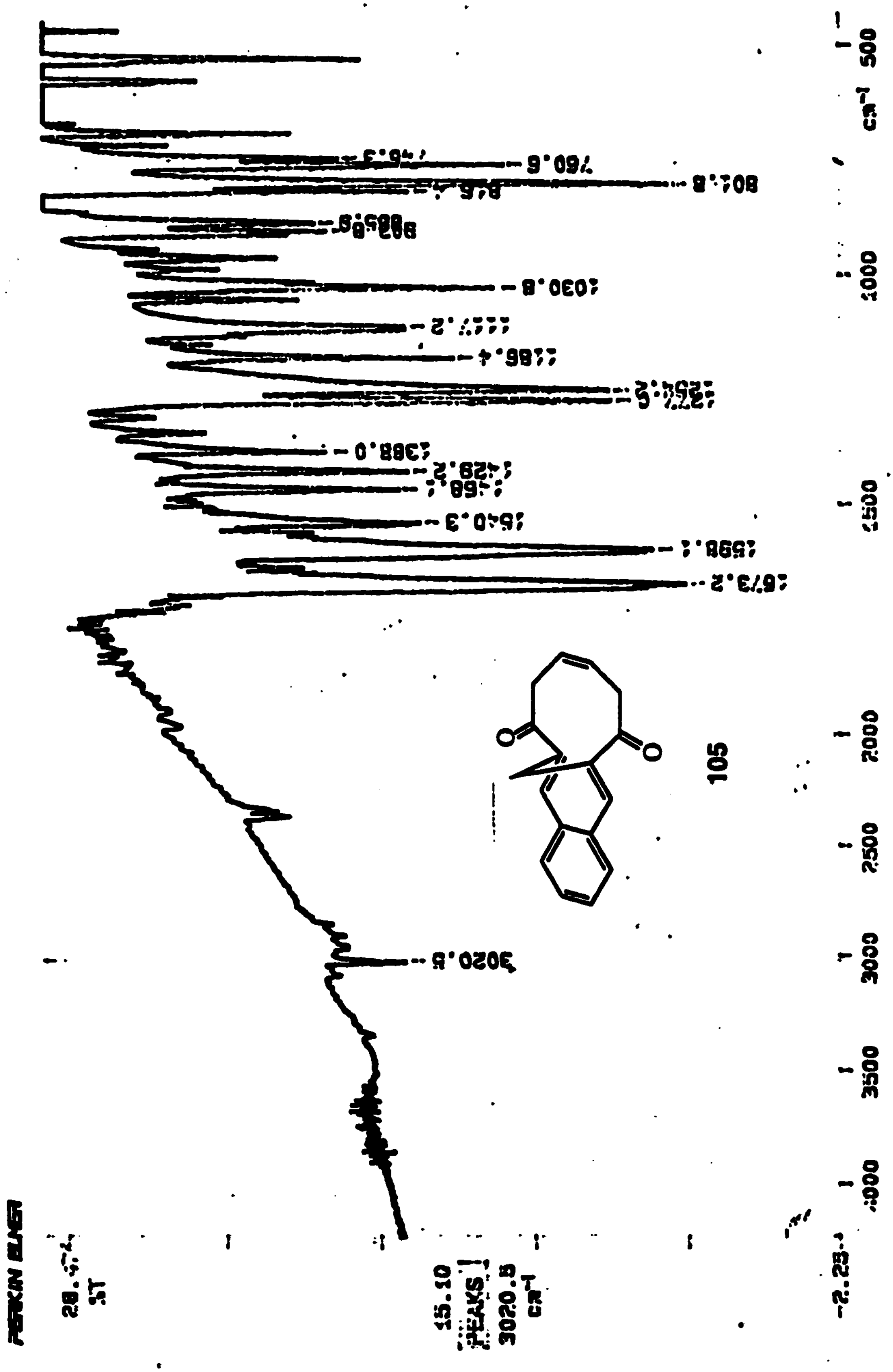
101b
(Isomer B)



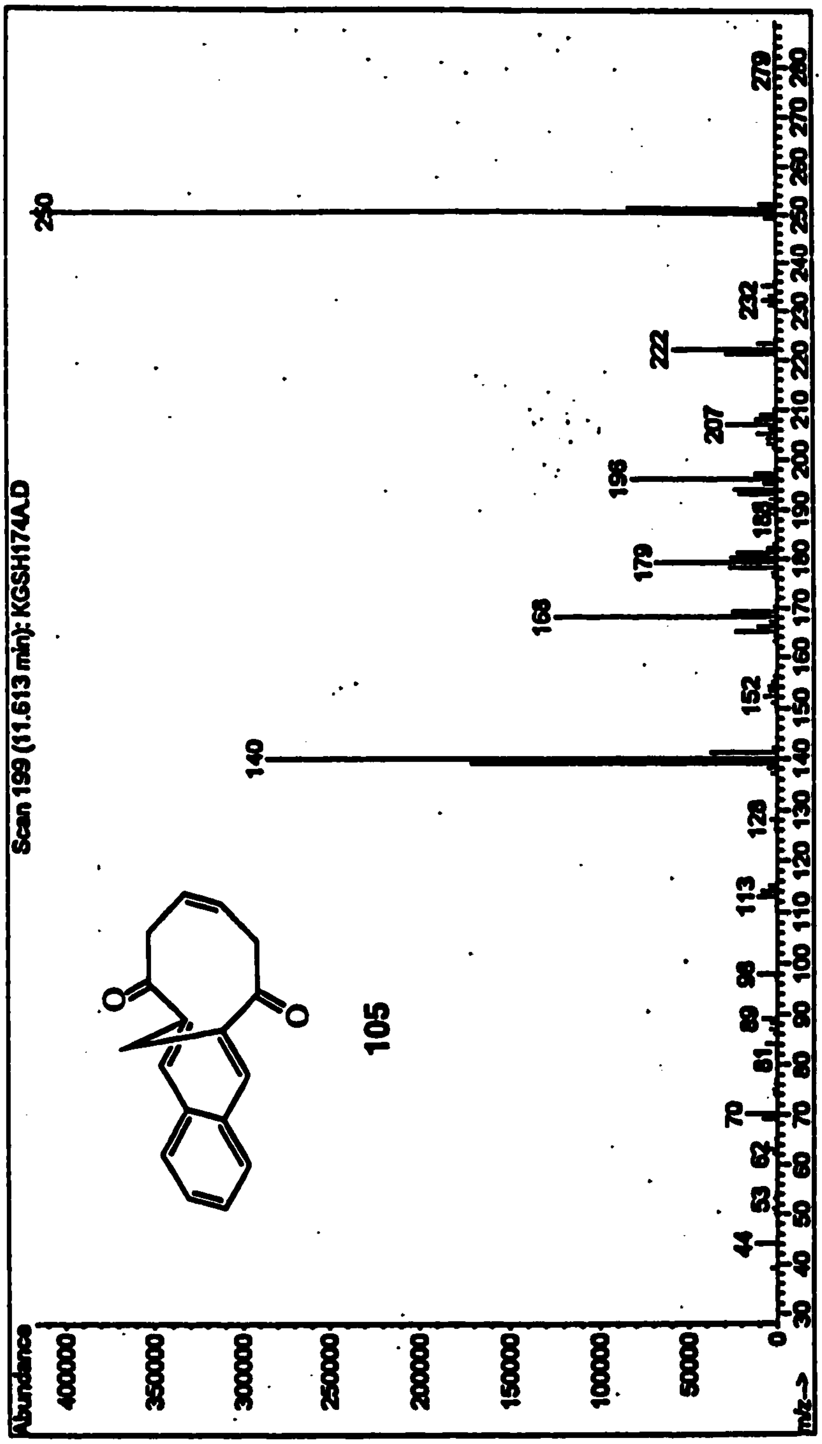
105



105

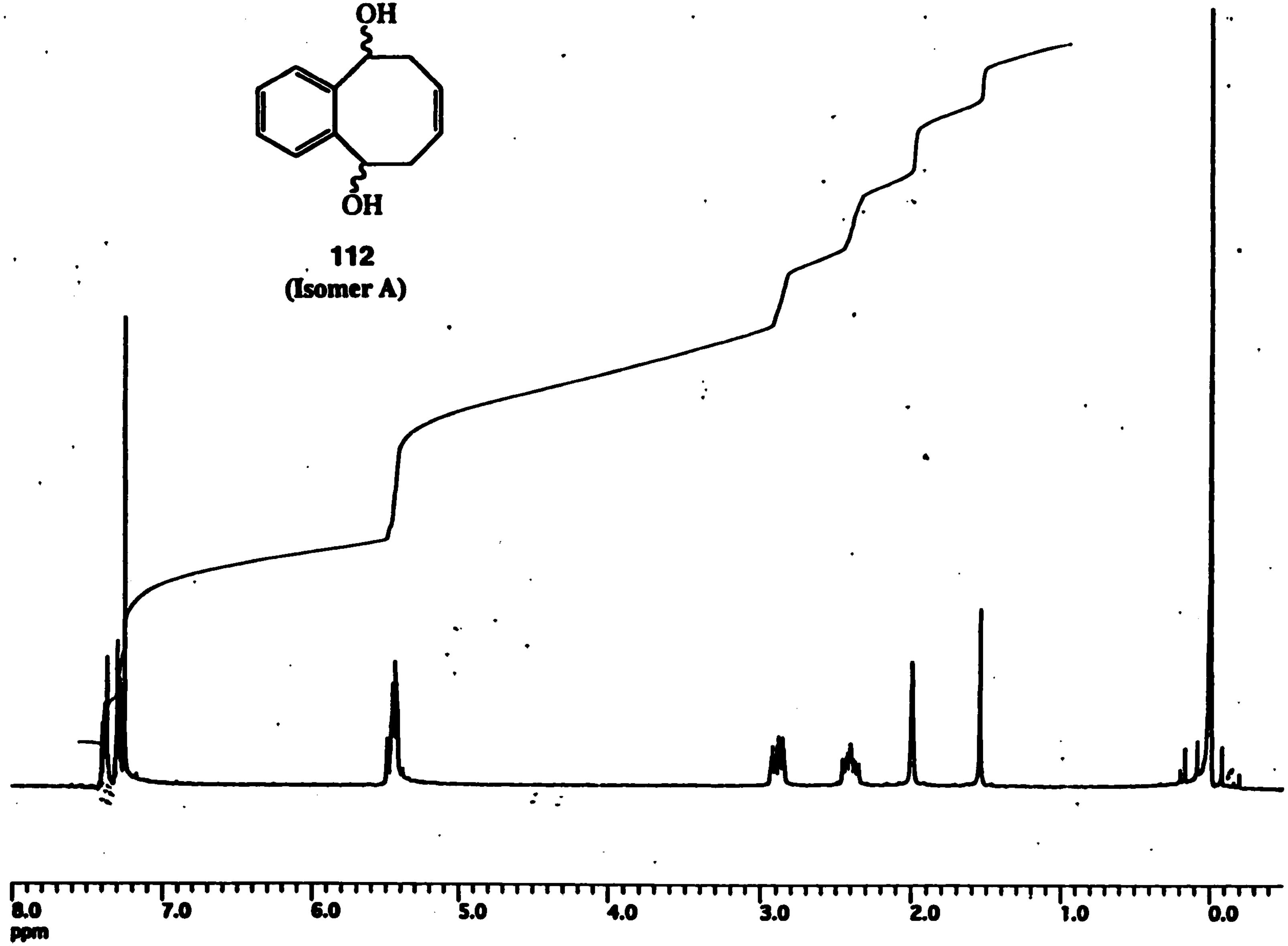

PERKIN ELMER
28.
%T
15.10
PEAKS
3020.8
cm-1
-2.25
4000
3500
3000
2500
2000
1500
1000
500
cm-1
3020.8
1673.2
1598.1
1540.3
1468.1
1428.2
1388.0
1277.6
1254.2
1186.4
1147.2
1030.8
885.8
883.6
846.7
804.8
760.6
746.3

105

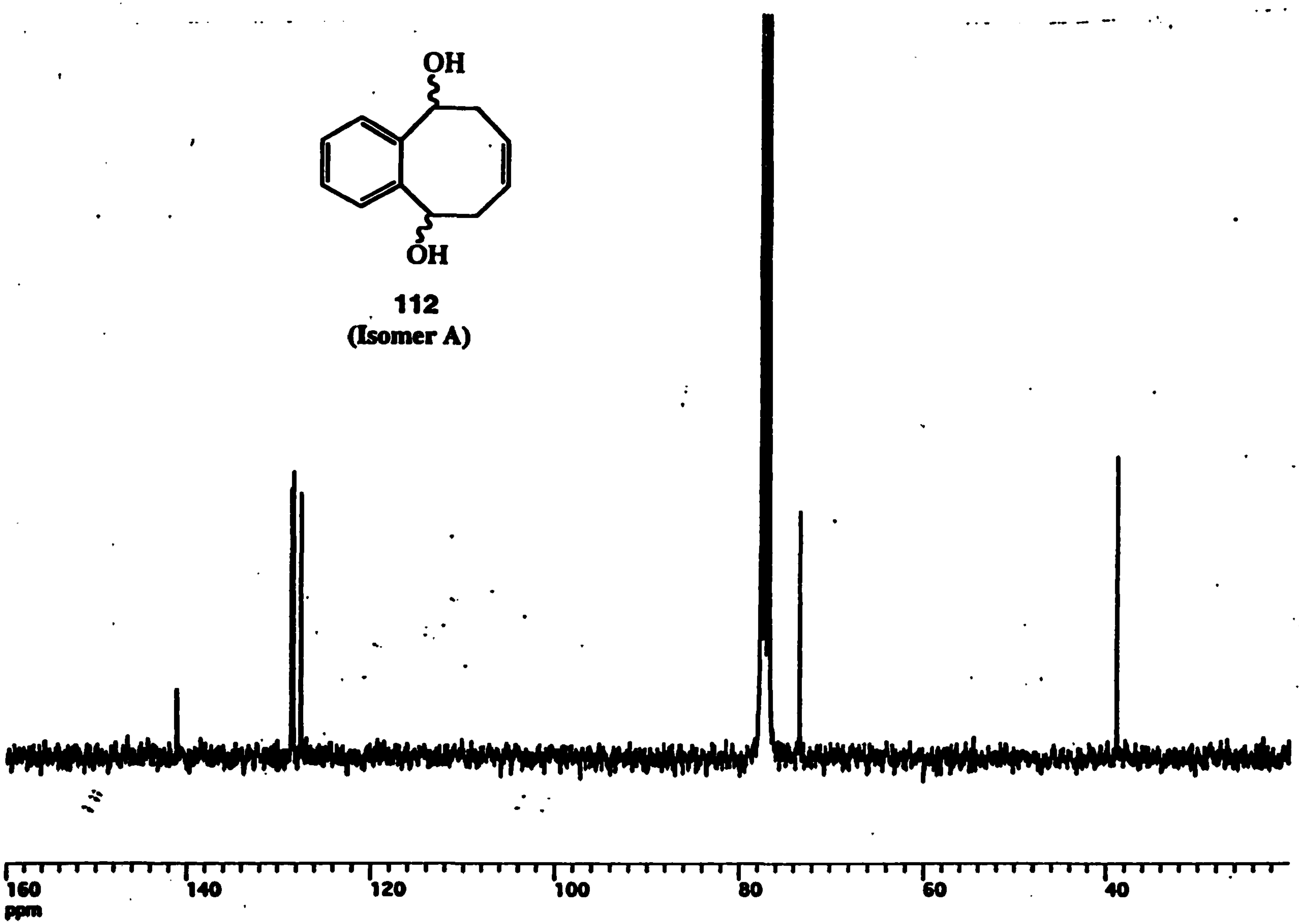


105

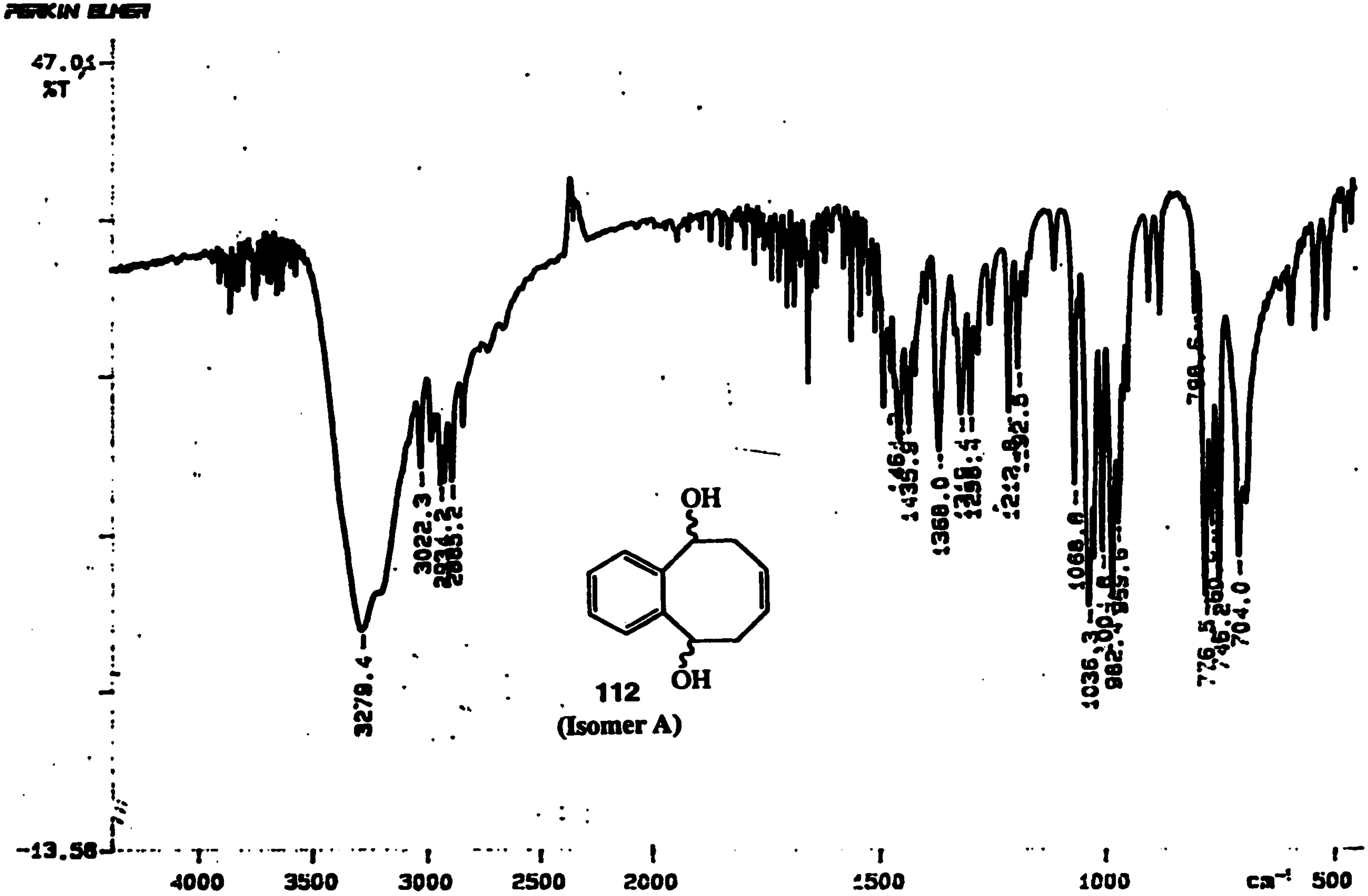
Scan 199 (11.613 min): KGSH174A.D
Abundance
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
44
53
62
70
81
89
98
113
128
140
152
168
179
188
196
207
222
232
250
279
O
O



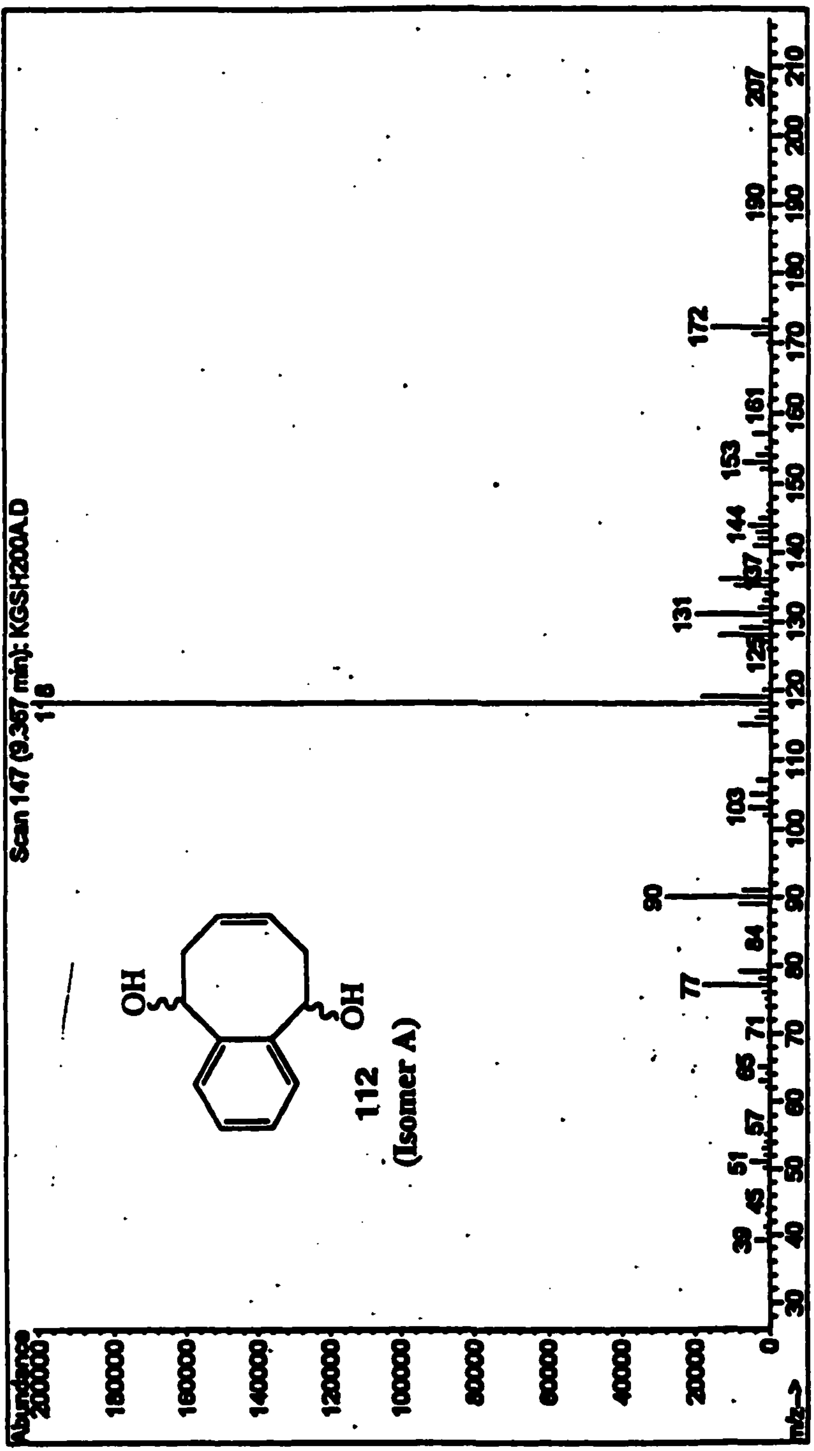
112
(Isomer A)



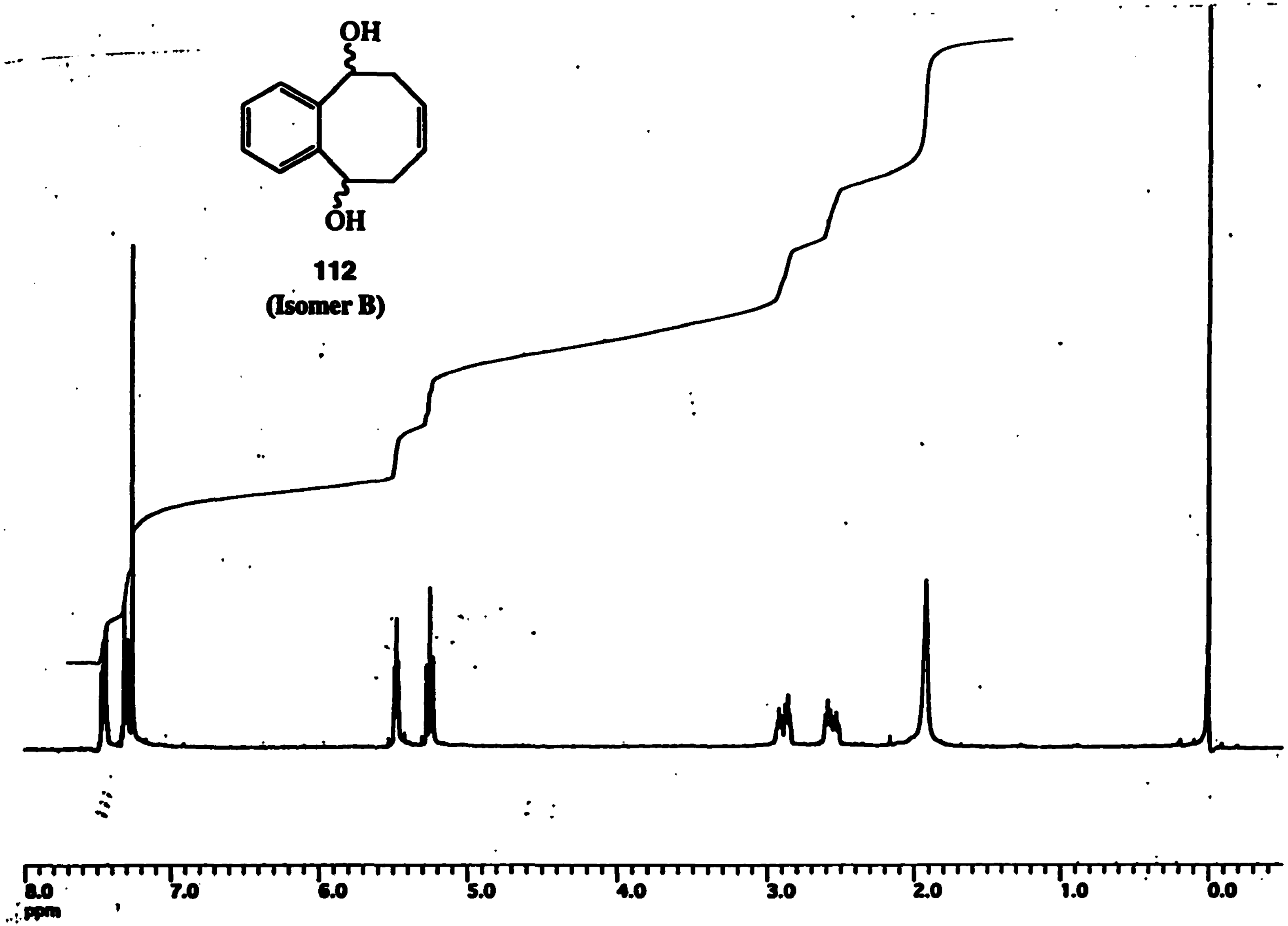
112
(Isomer A)


PERKIN ELMER
47.01
%T
-13.58
4000
3500
3000
2500
2000
1500
1000
cm⁻¹ 500
3278.4
3022.3
2934.2
2885.2
1461.2
1435.9
1368.0
1318.4
1258.4
1212.8
1192.5
1068.8
1036.3
1001.8
982.4
955.6
798.5
776.5
760
746.2
704.0
OH
OH

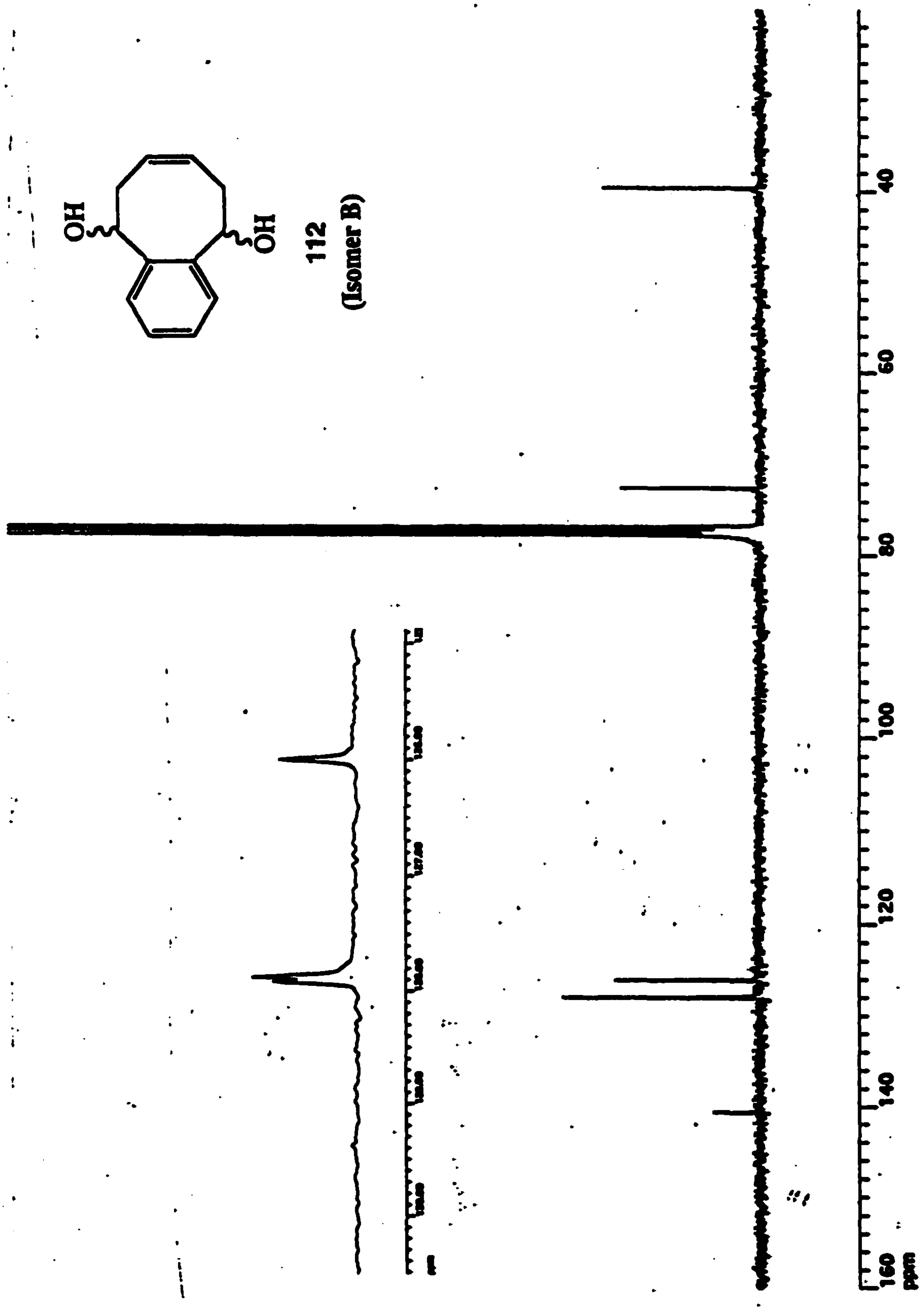
112
(Isomer A)


Scan 147 (9.367 min): KGSH200A.D
Abundance
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
39
45
51
57
65
71
77
84
90
103
118
125
131
137
144
153
161
172
190
207
OH
OH

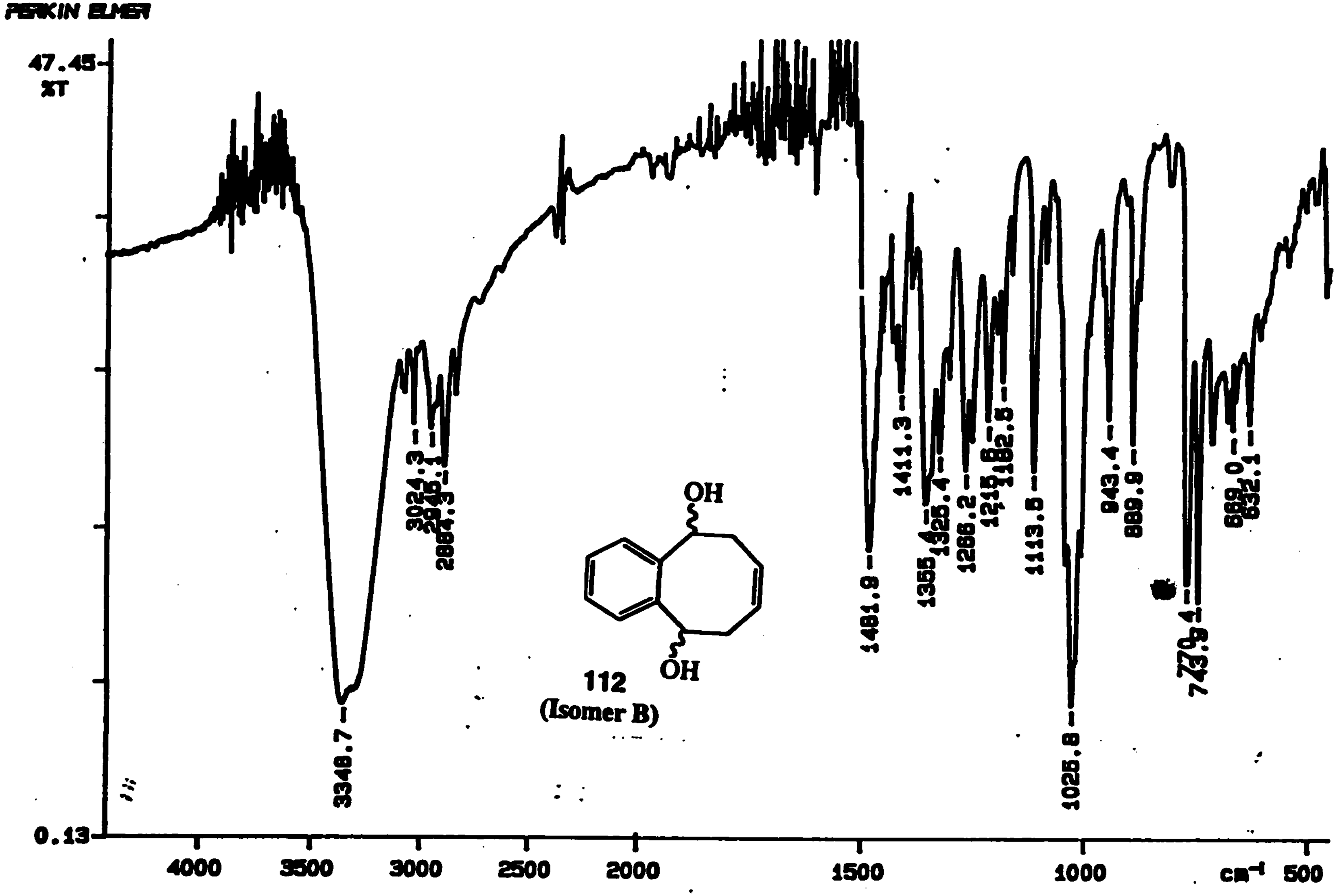
112
(Isomer A)



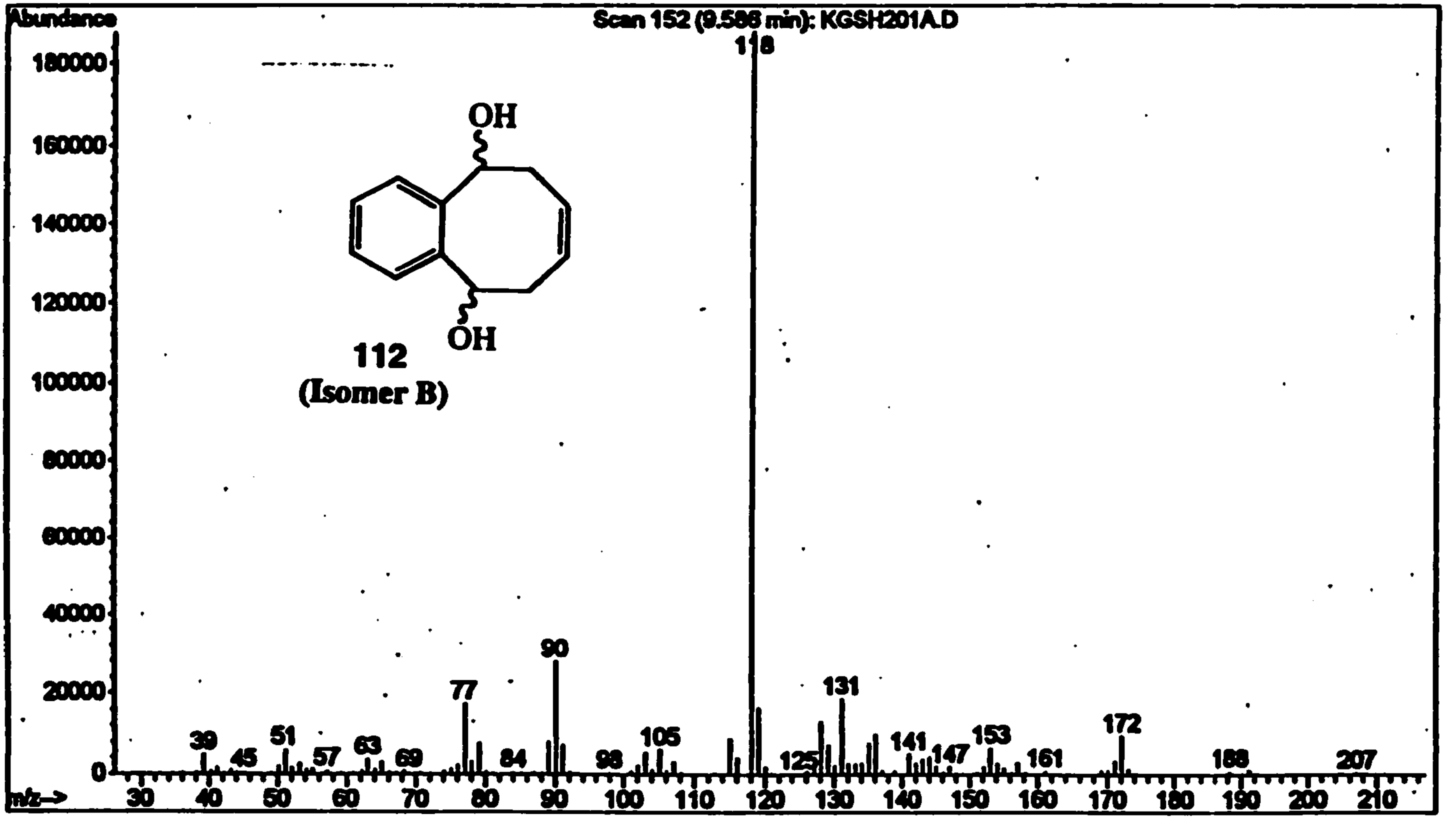
112
(Isomer B)



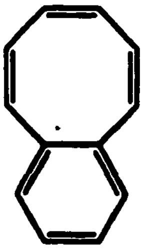
112
(Isomer B)


PERKIN ELMER
47.45
%T
0.13
4000
3500
3000
2500
2000
1500
1000
cm⁻¹ 500
3348.7
3024.3
2945.1
2884.3
1481.9
1411.3
1355.4
1325.4
1288.2
1215.8
1182.8
1113.8
1025.8
943.4
889.9
770.4
743.9
669.0
632.1
OH
OH

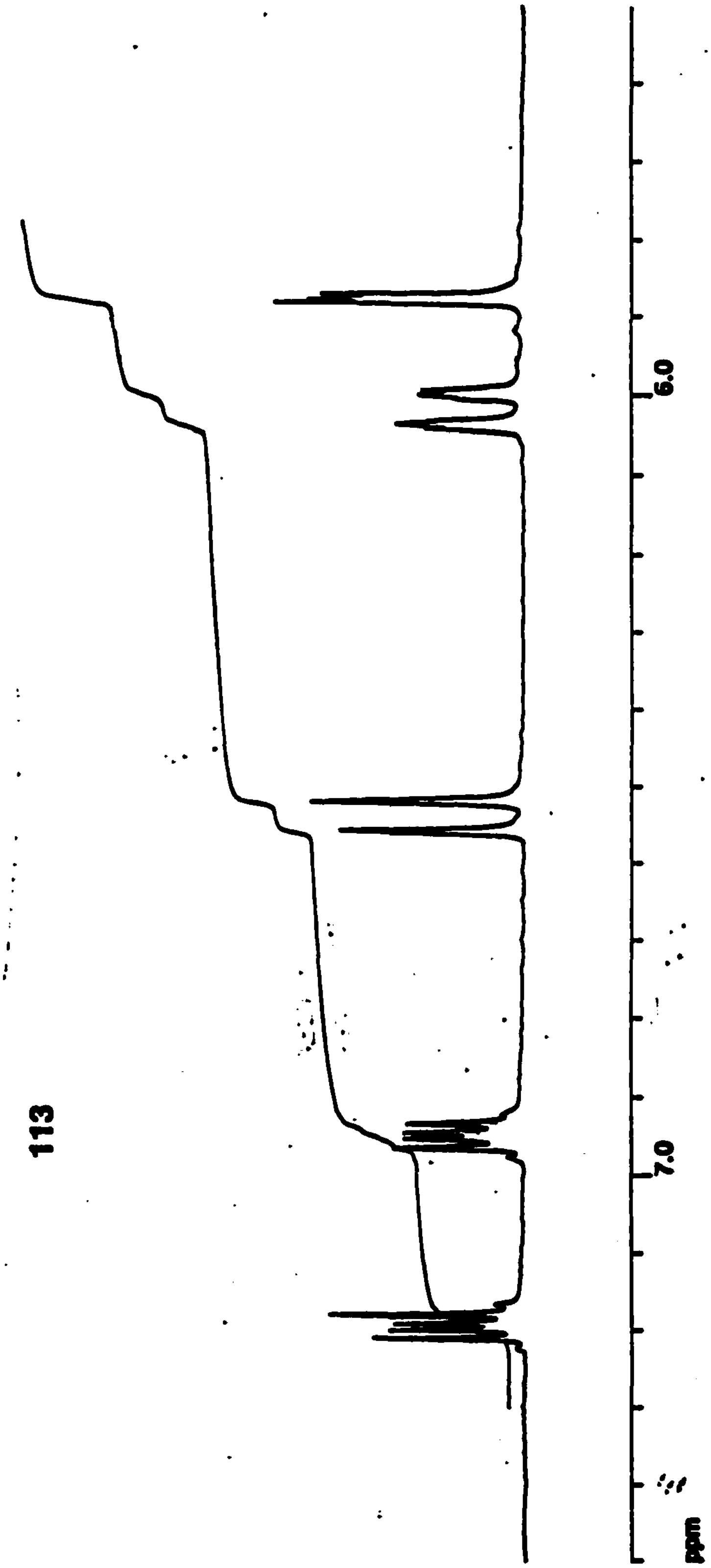
112
(Isomer B)

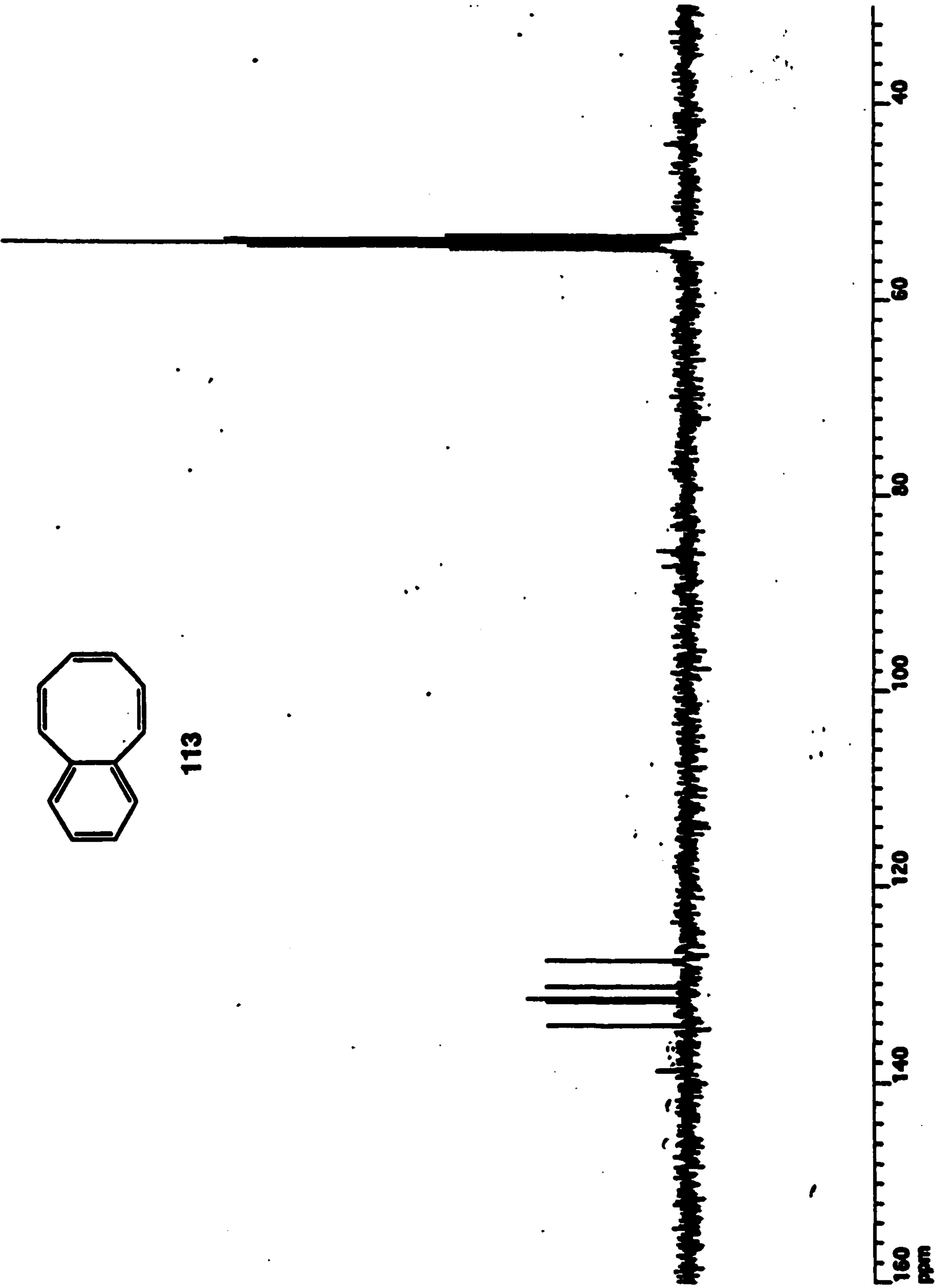

Abundance
Scan 152 (9.586 min): KGSH201A.D
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
118
90
77
131
172
105
153
141
147
51
63
39
45
57
69
84
98
125
161
188
207
OH
OH

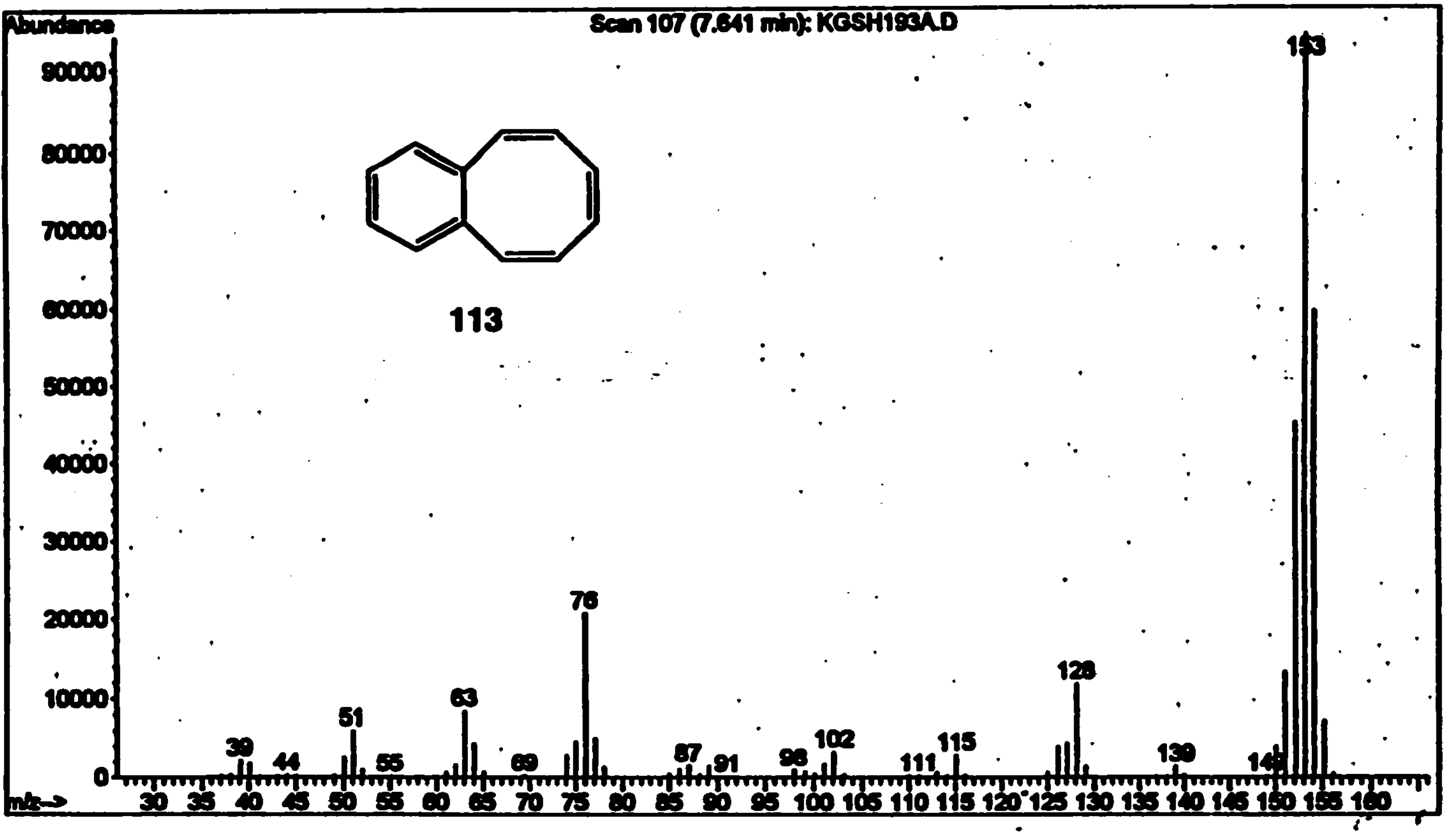
112
(Isomer B)

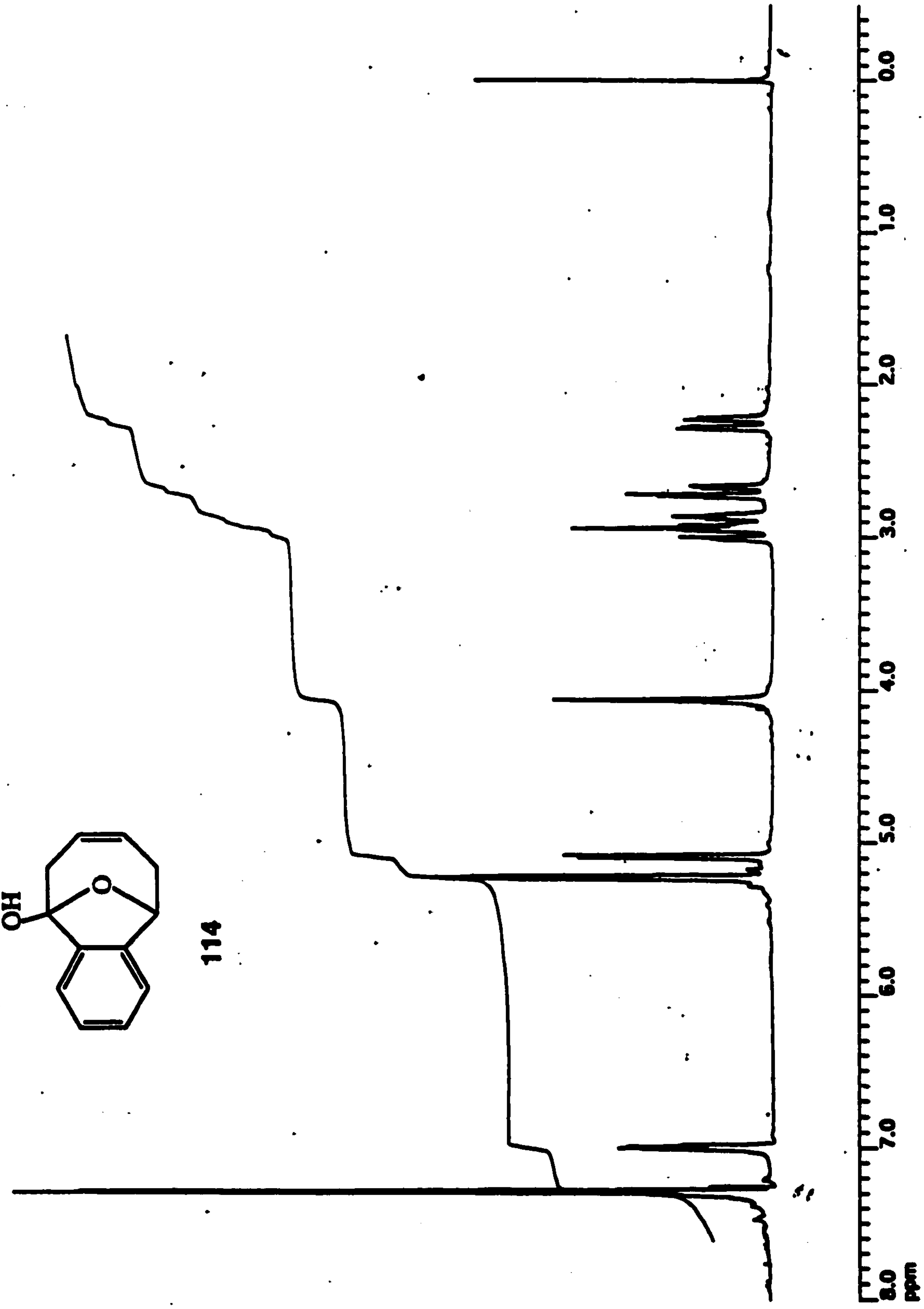


113

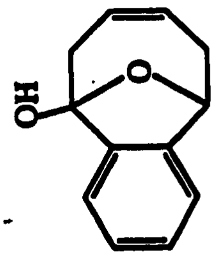



113

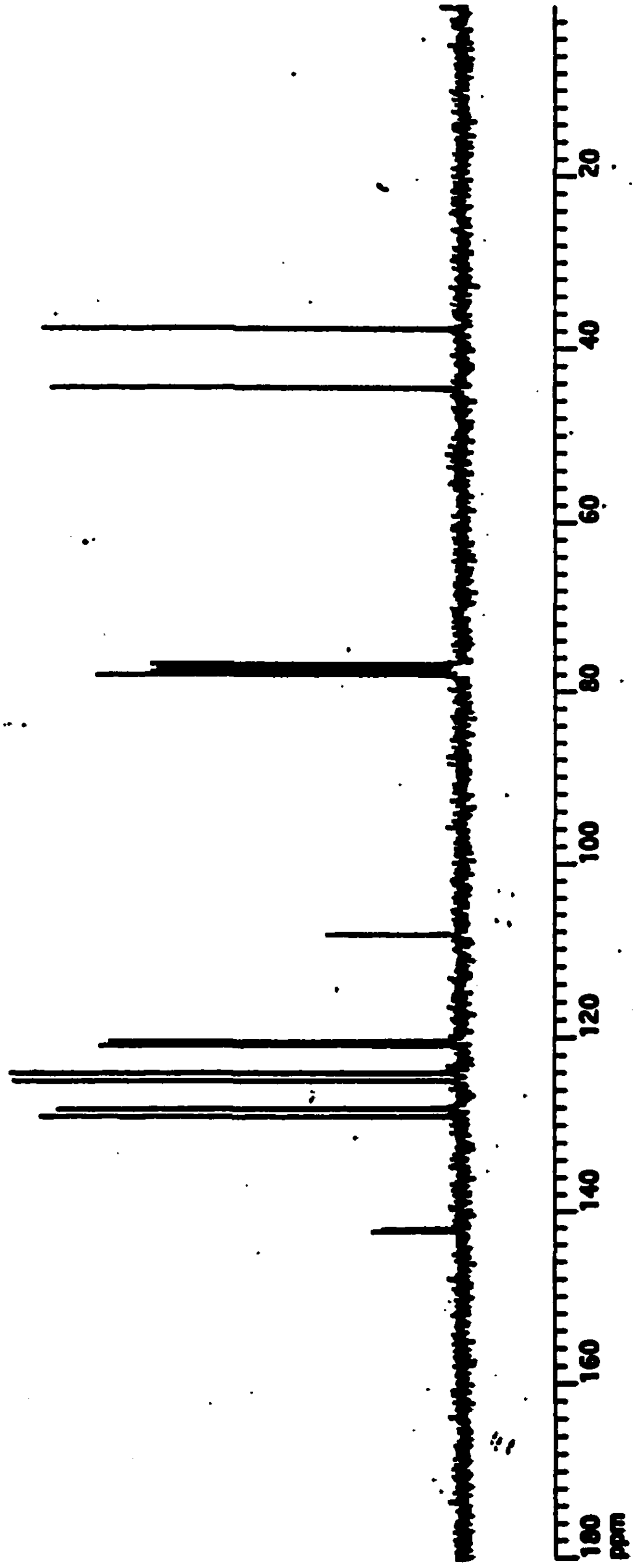

Abundance
Scan 107 (7.641 min): KGSH193A.D
113
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160
153
76
128
63
51
39
44
55
69
87
91
98
102
111
115
139
149

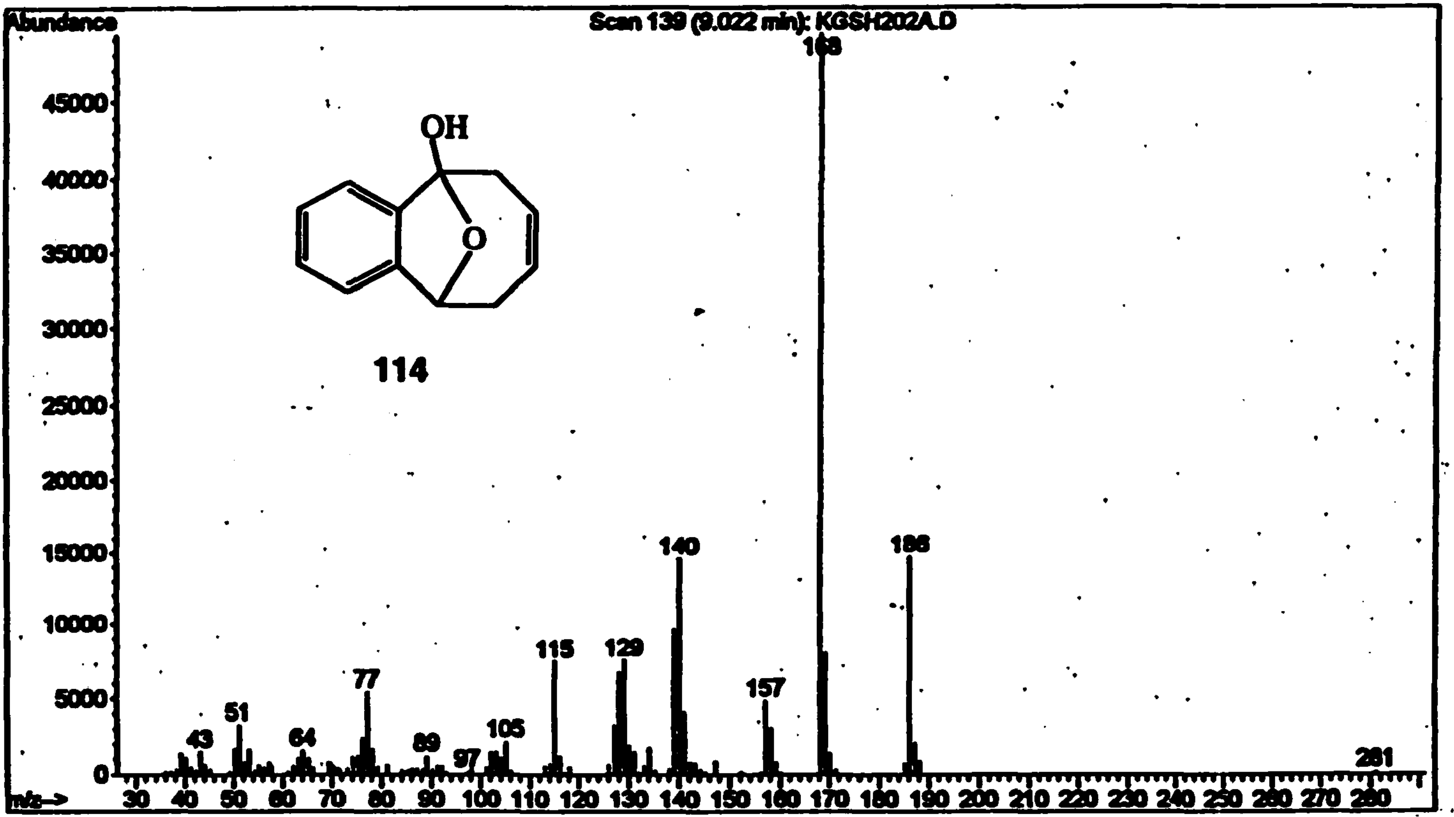


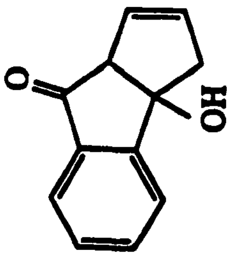
114



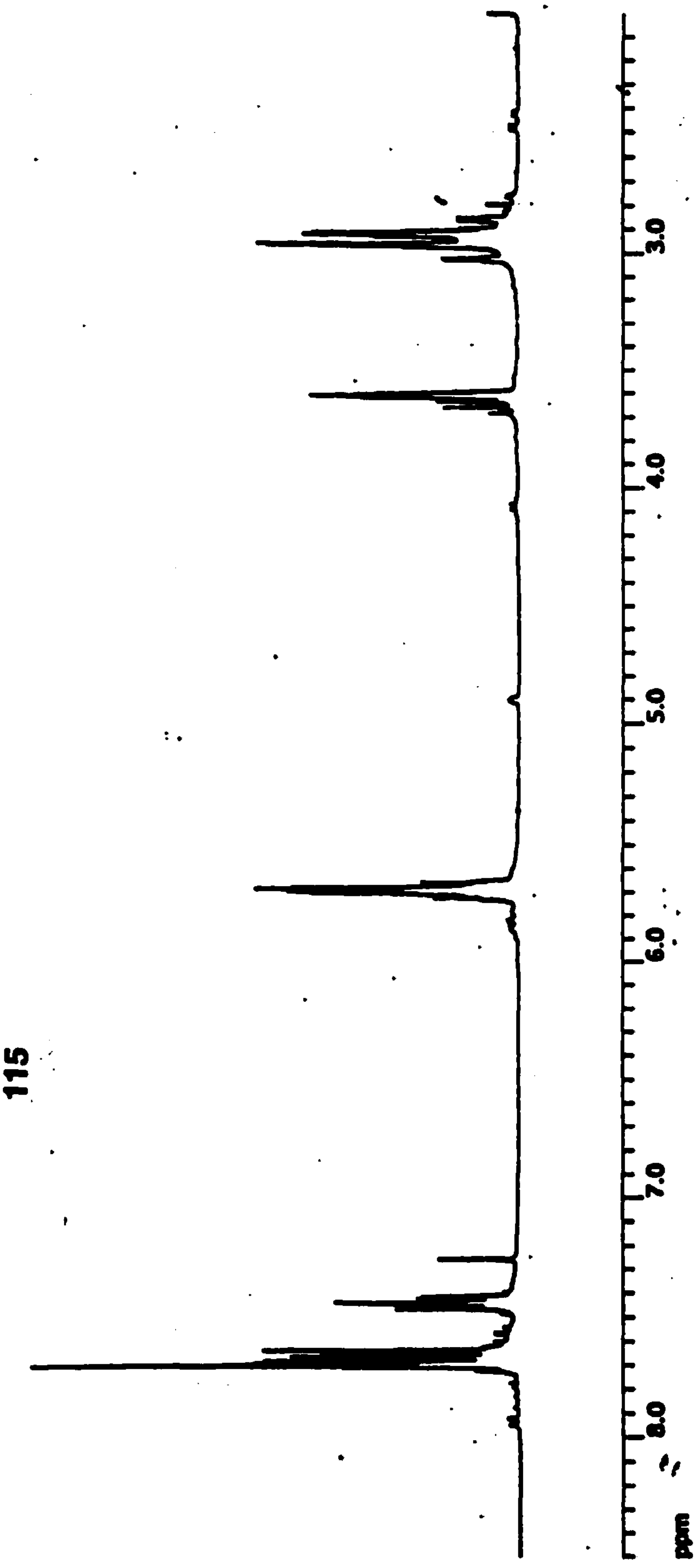
114

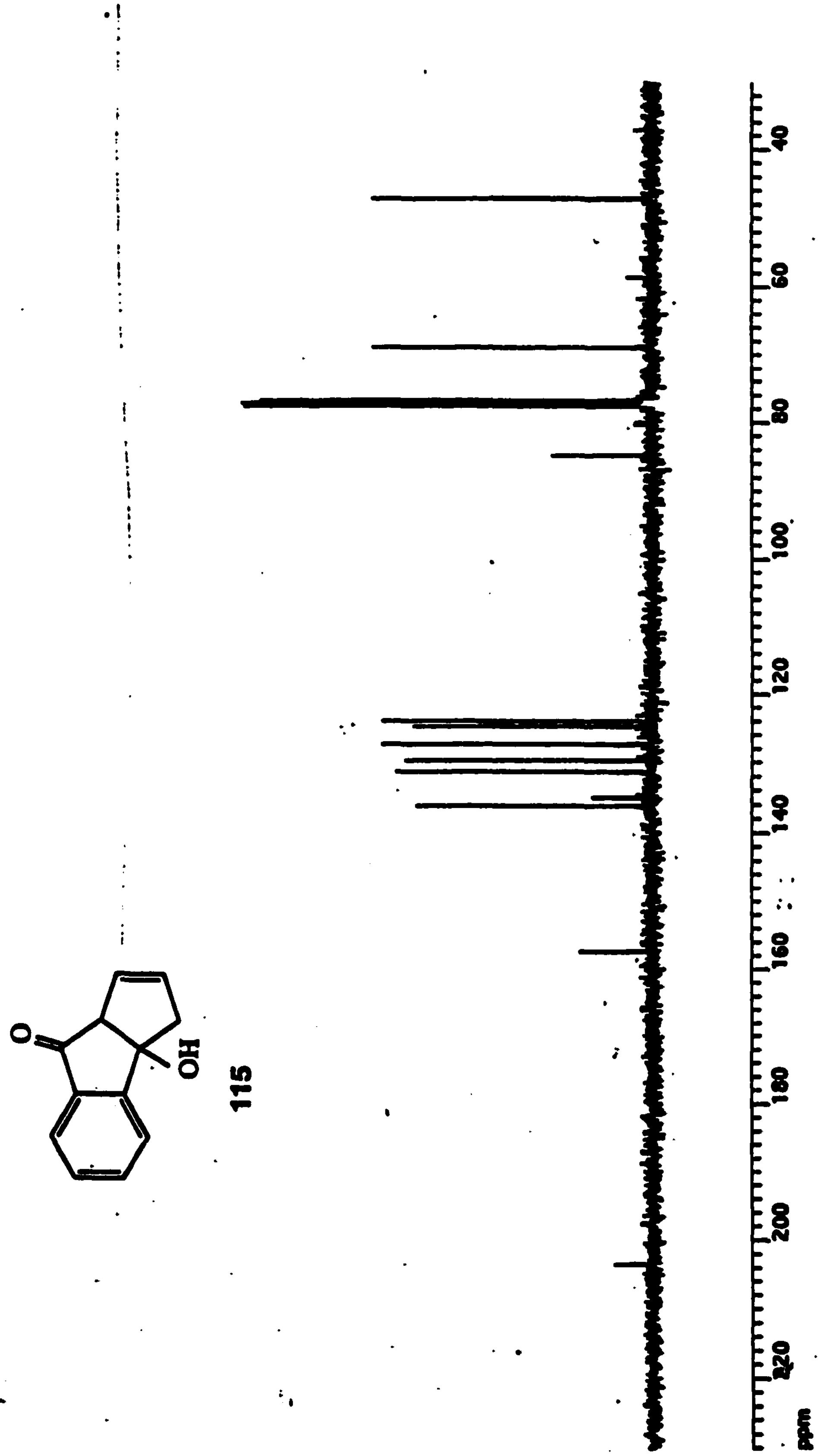



Scan 139 (9.022 min): KGSH202A.D
Abundance
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280
168
186
140
129
115
157
77
51
43
64
89
97
105
281
OH
O
114

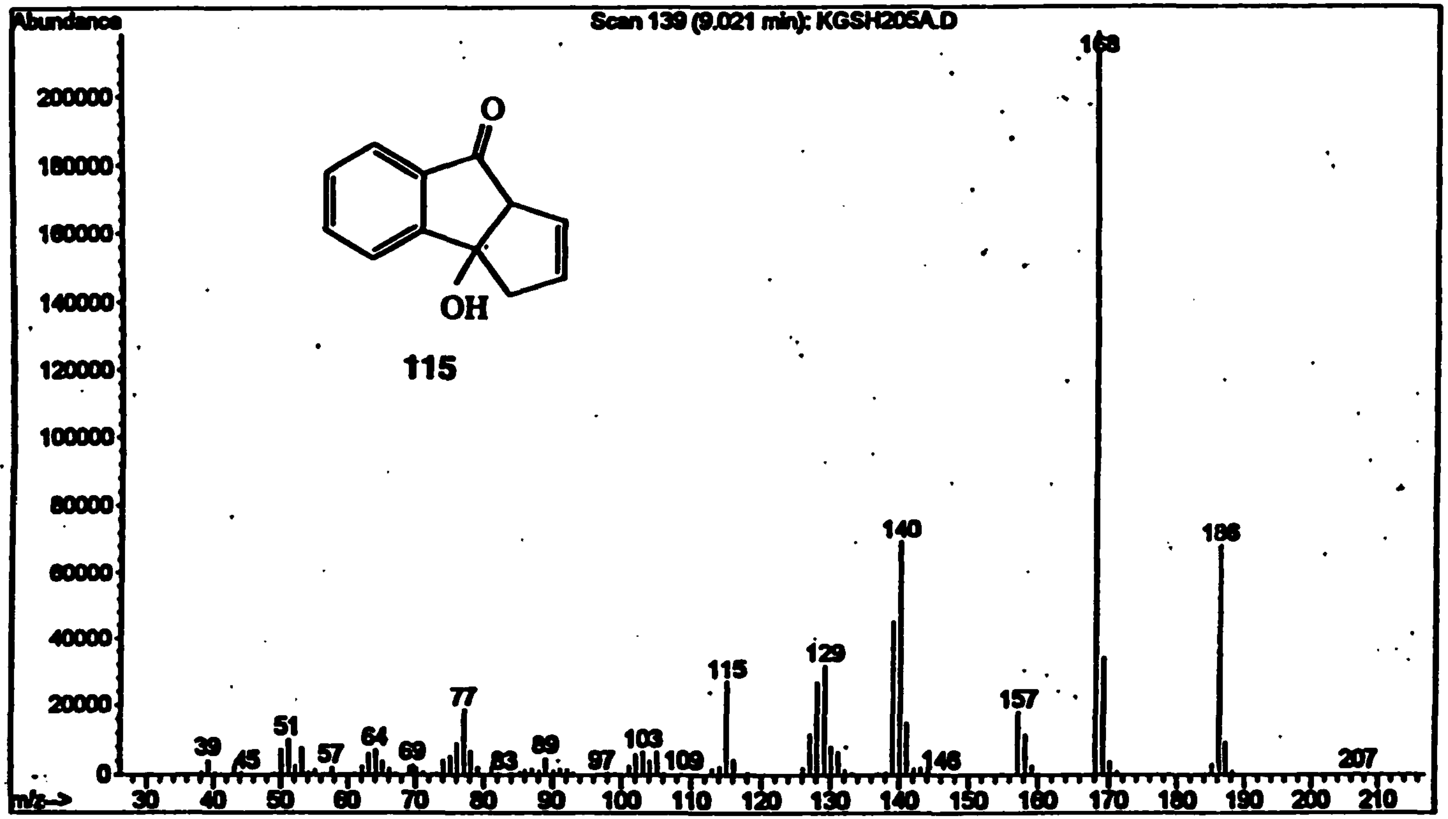


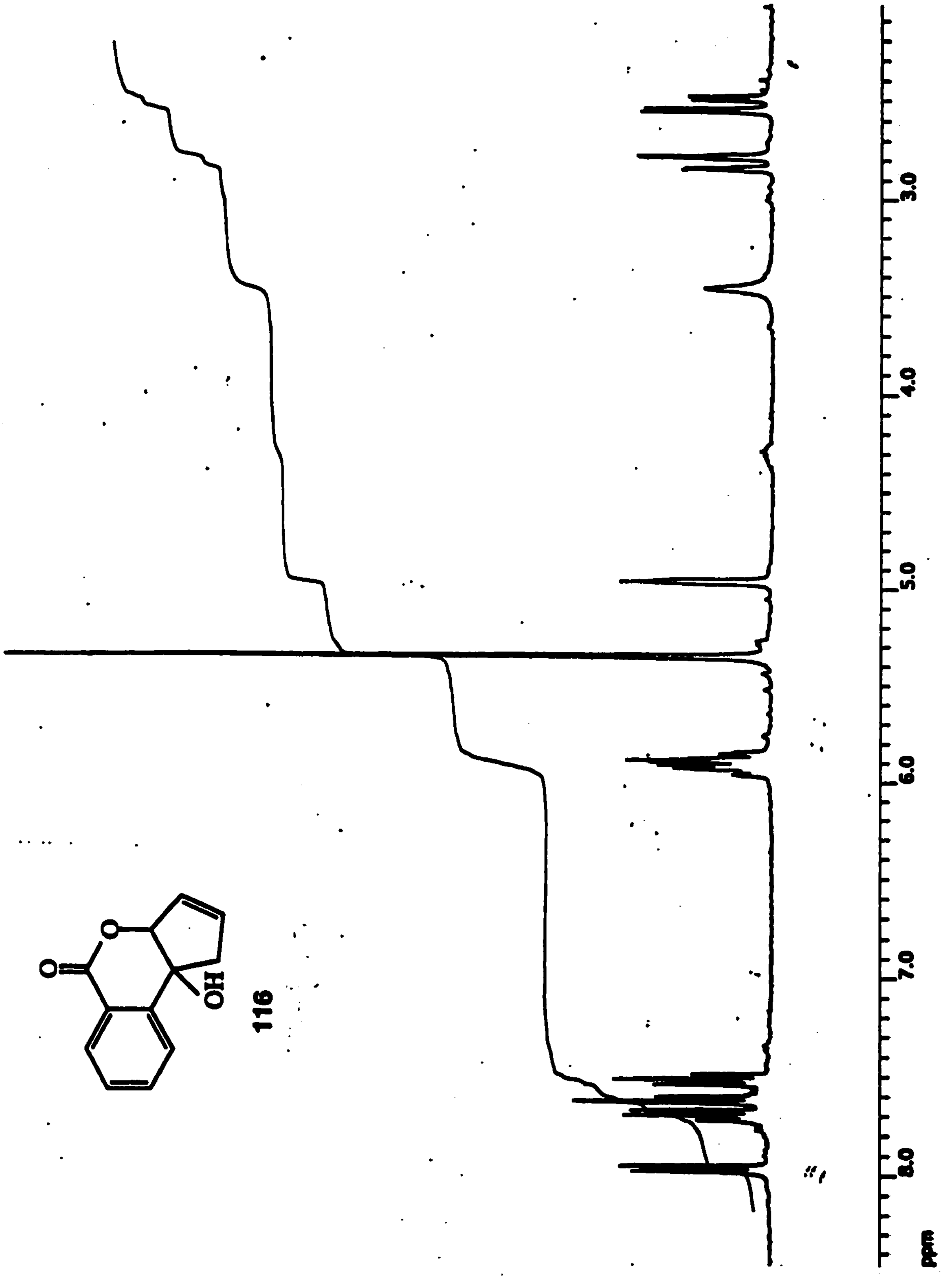
115



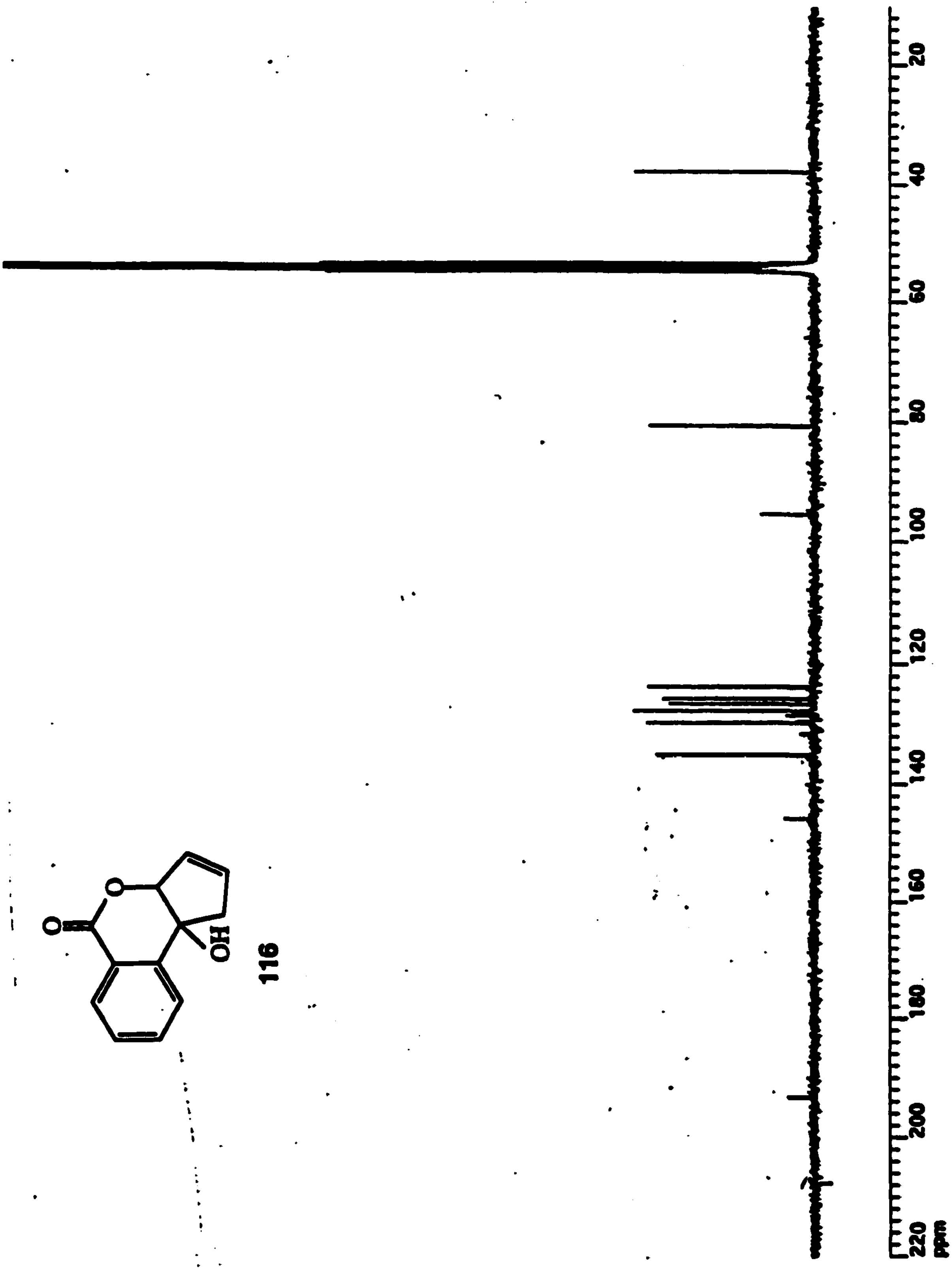


115

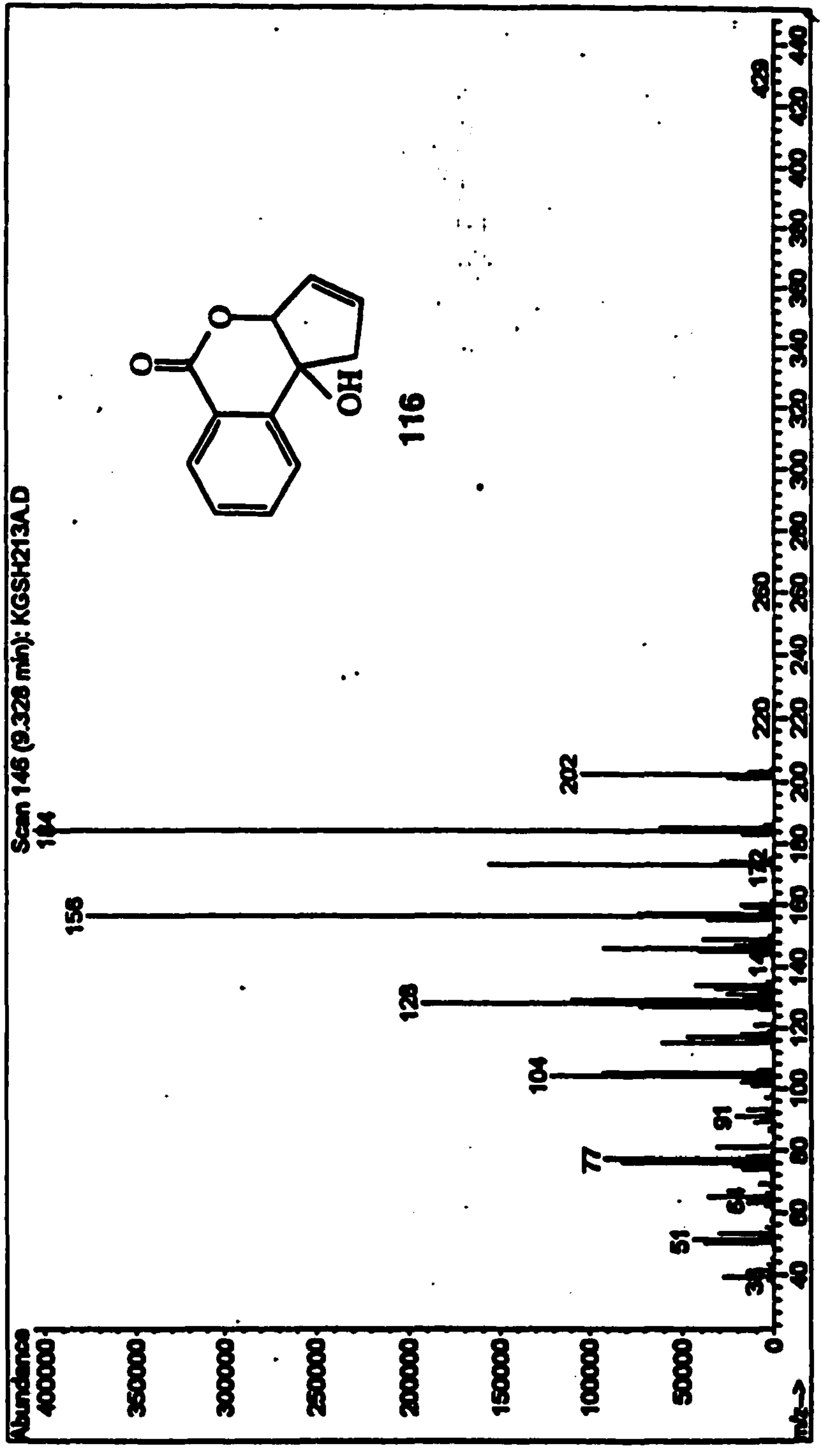

Scan 139 (9.021 min): KGSH205A.D
Abundance
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
39
45
51
57
64
69
77
83
89
97
103
109
115
129
140
146
157
168
186
207
O
OH
115



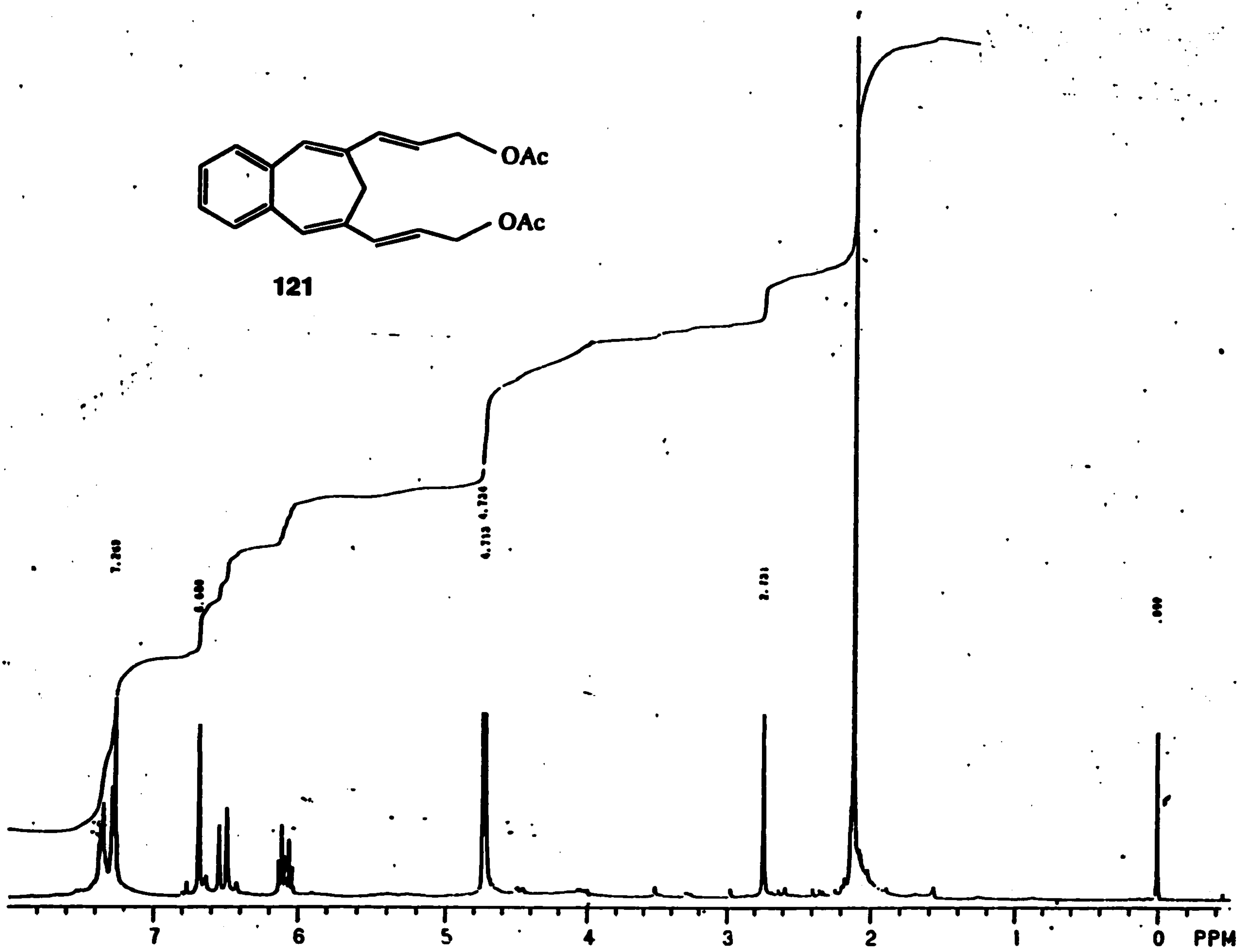
116



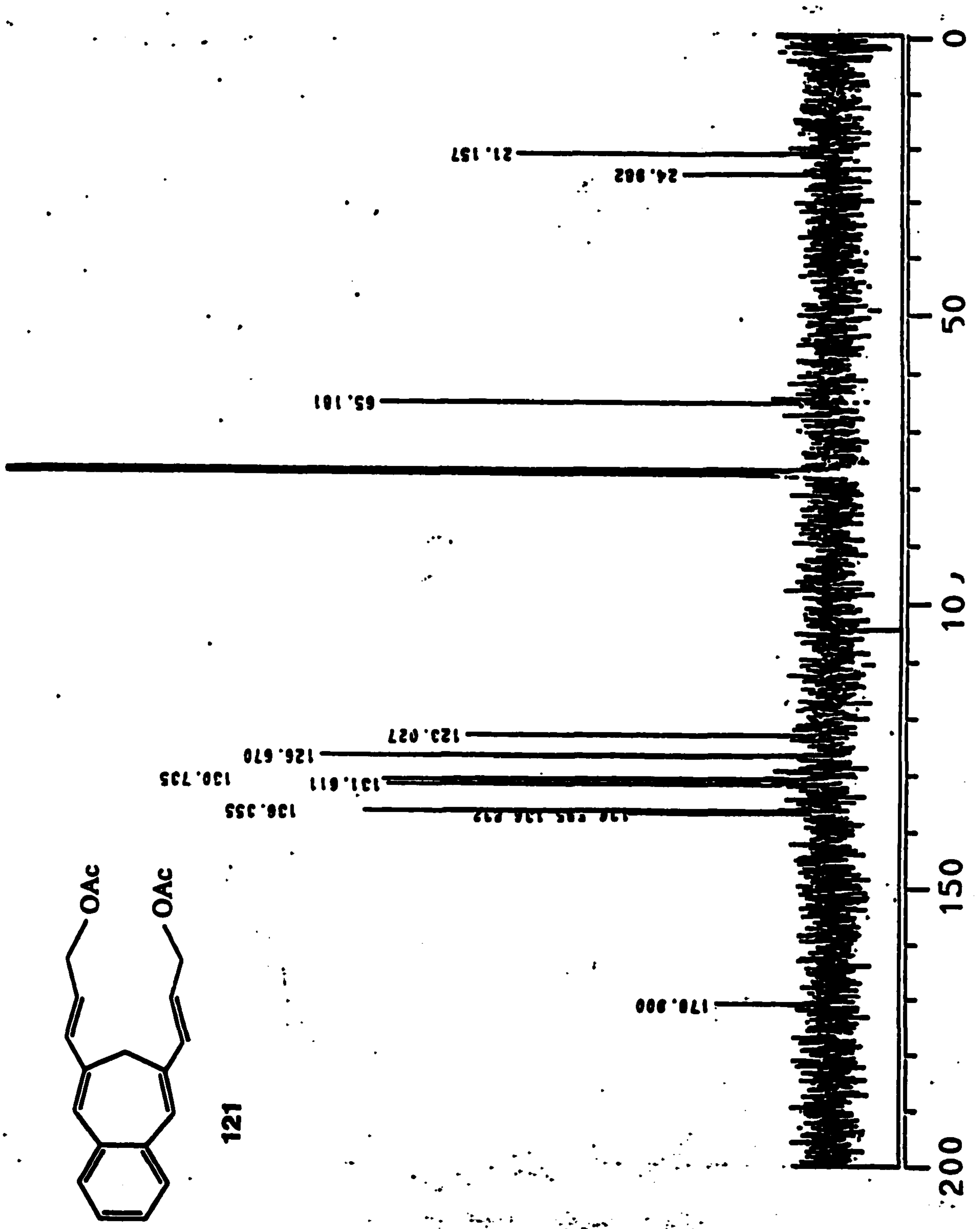
116


Scan 146 (9.328 min): KGSH213A.D
Abundance
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
184
156
128
104
77
91
51
64
39
202
172
141
260
429
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
O
O
OH

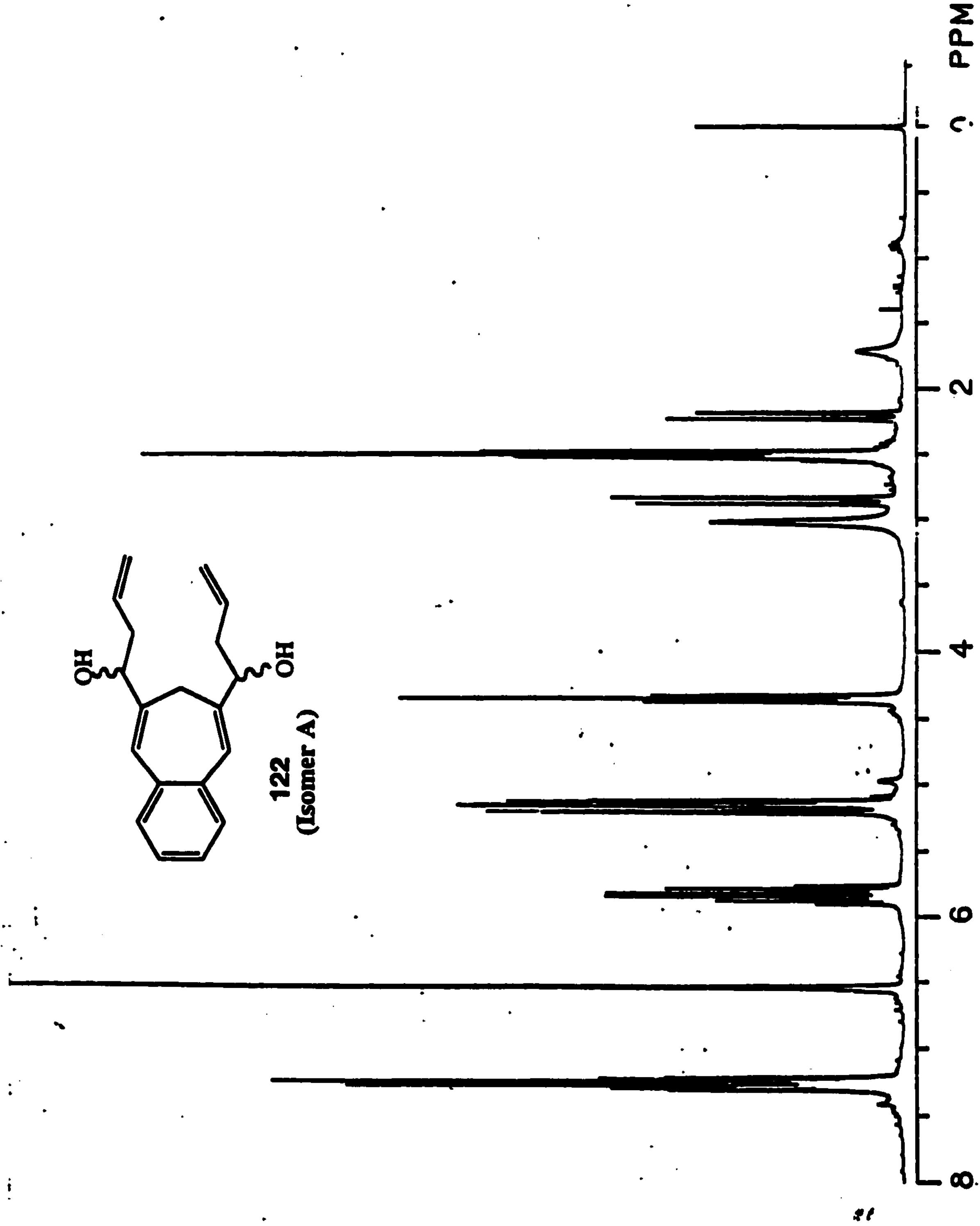
116



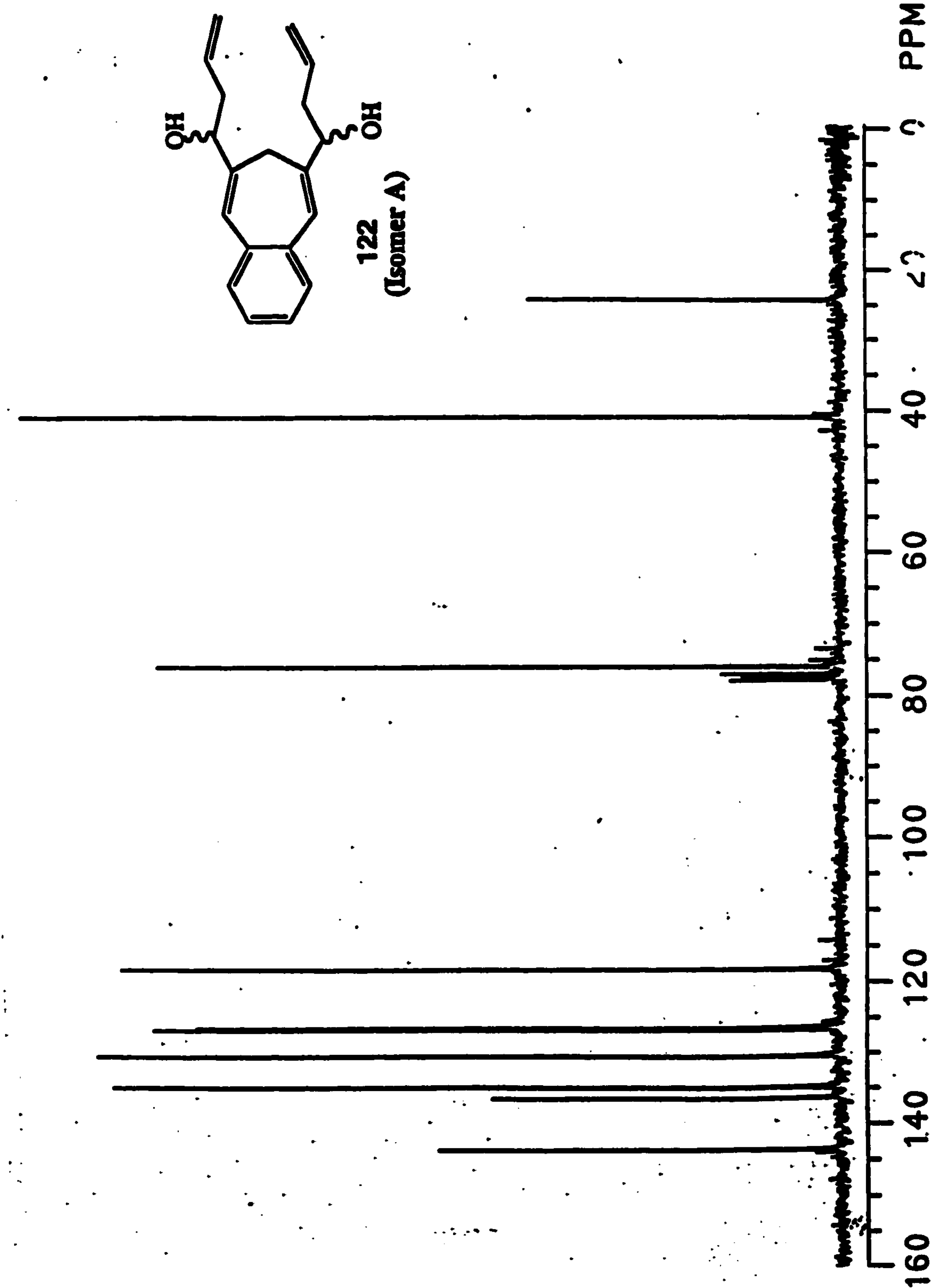
121


21.157
24.882
65.181
123.027
126.670
130.735
131.611
136.355
170.000
OAc
OAc
0
50
100
150
200

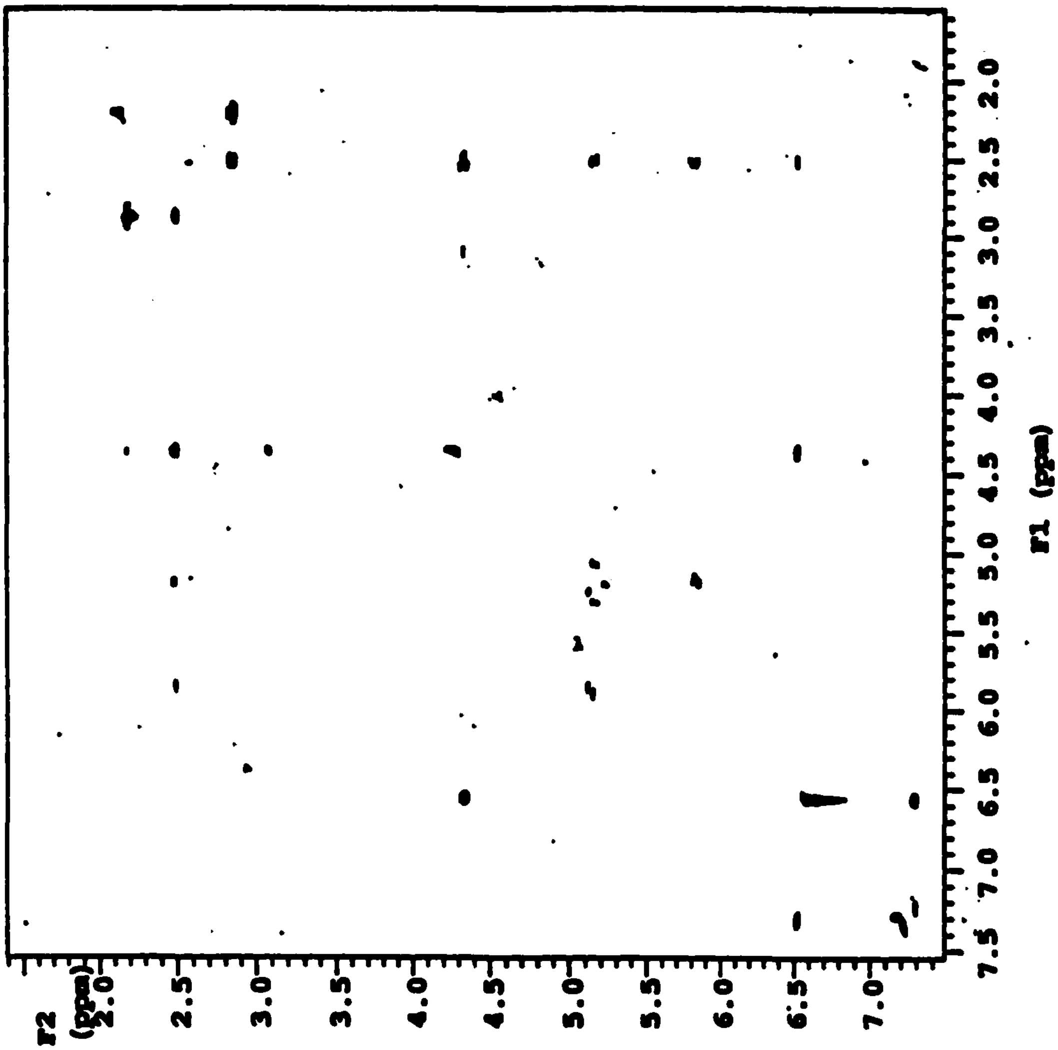
121

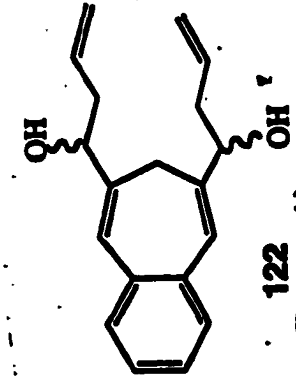


122
(Isomer A)

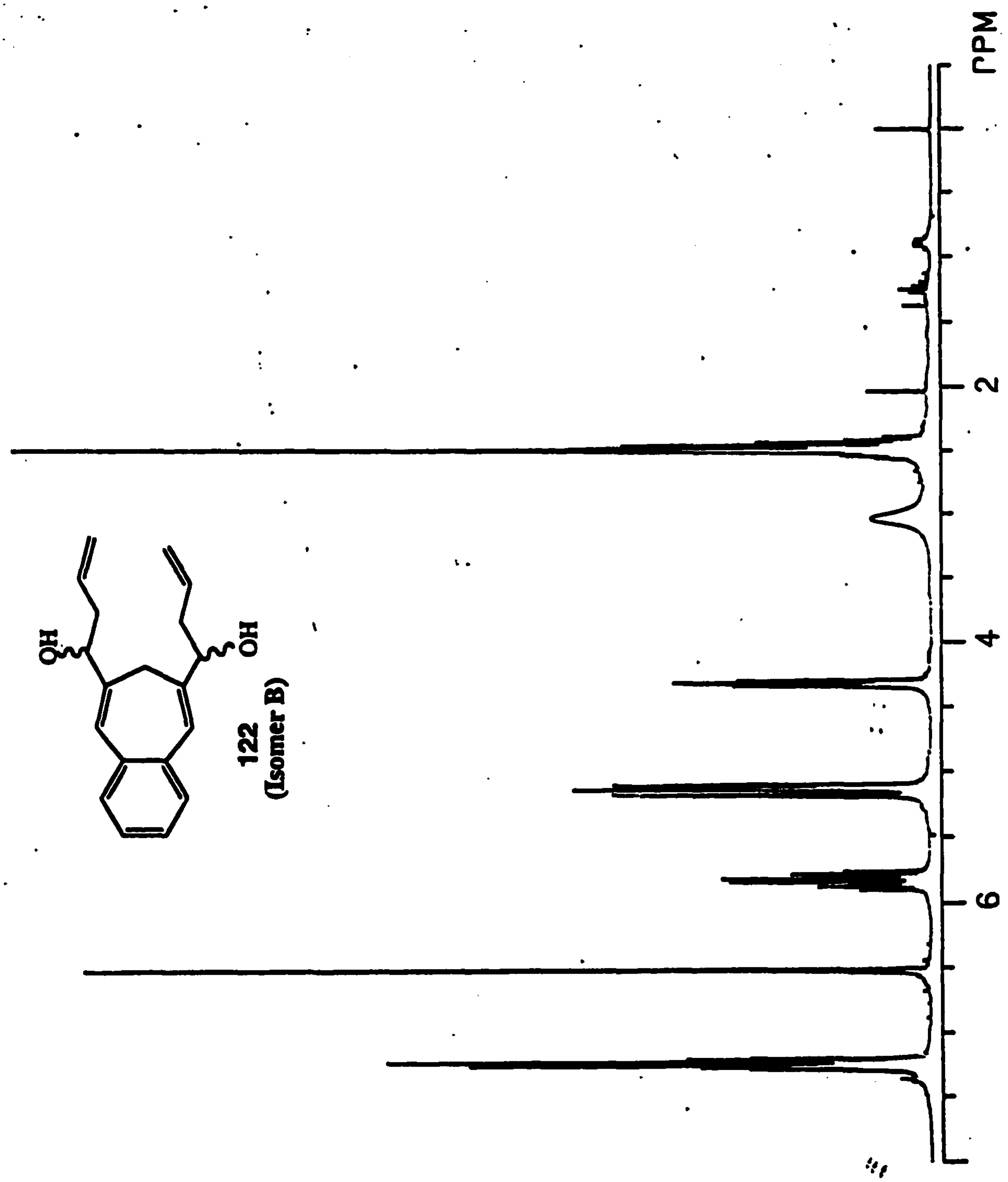


122
(Isomer A)

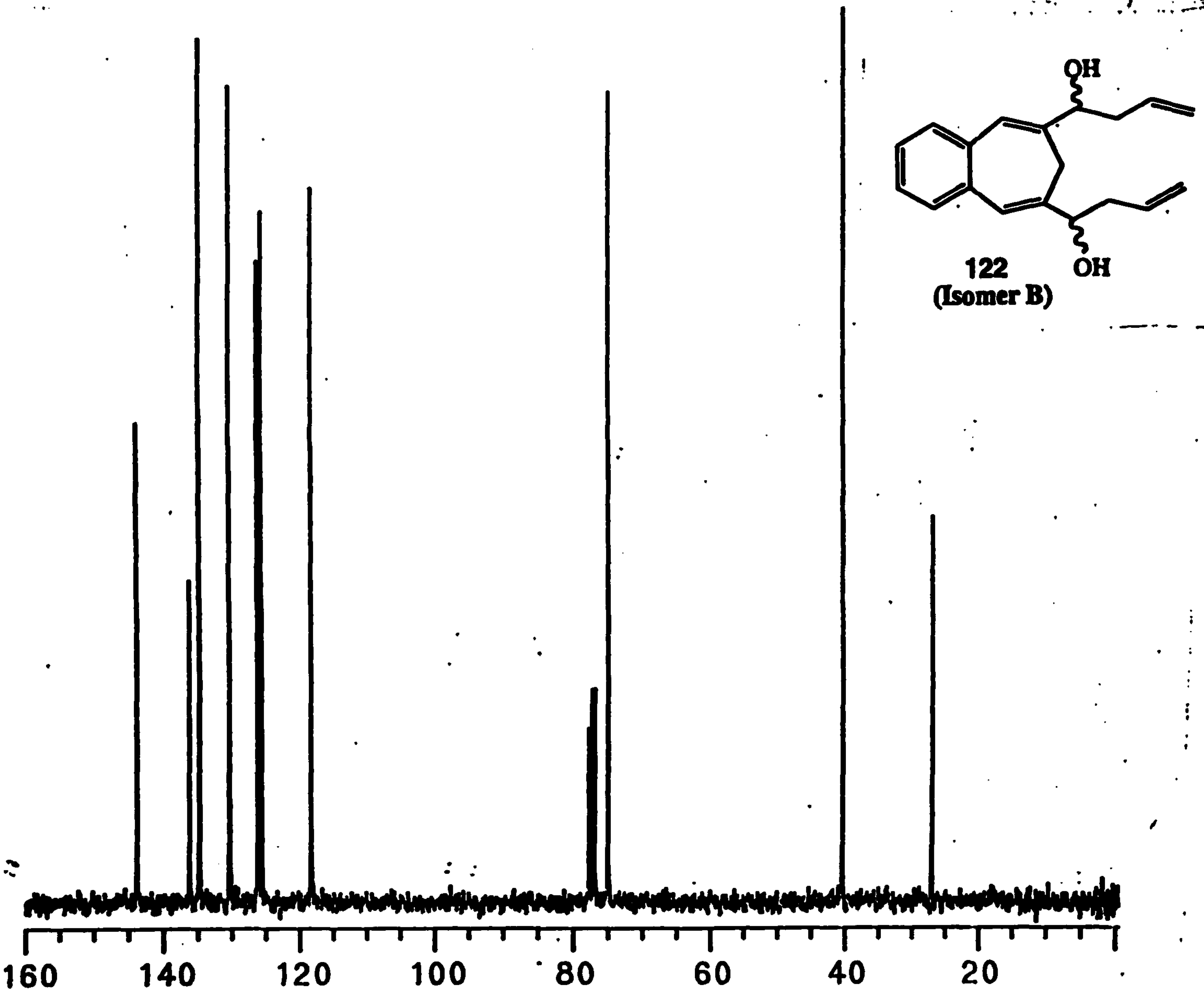

F2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
F1 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5


OH
OH

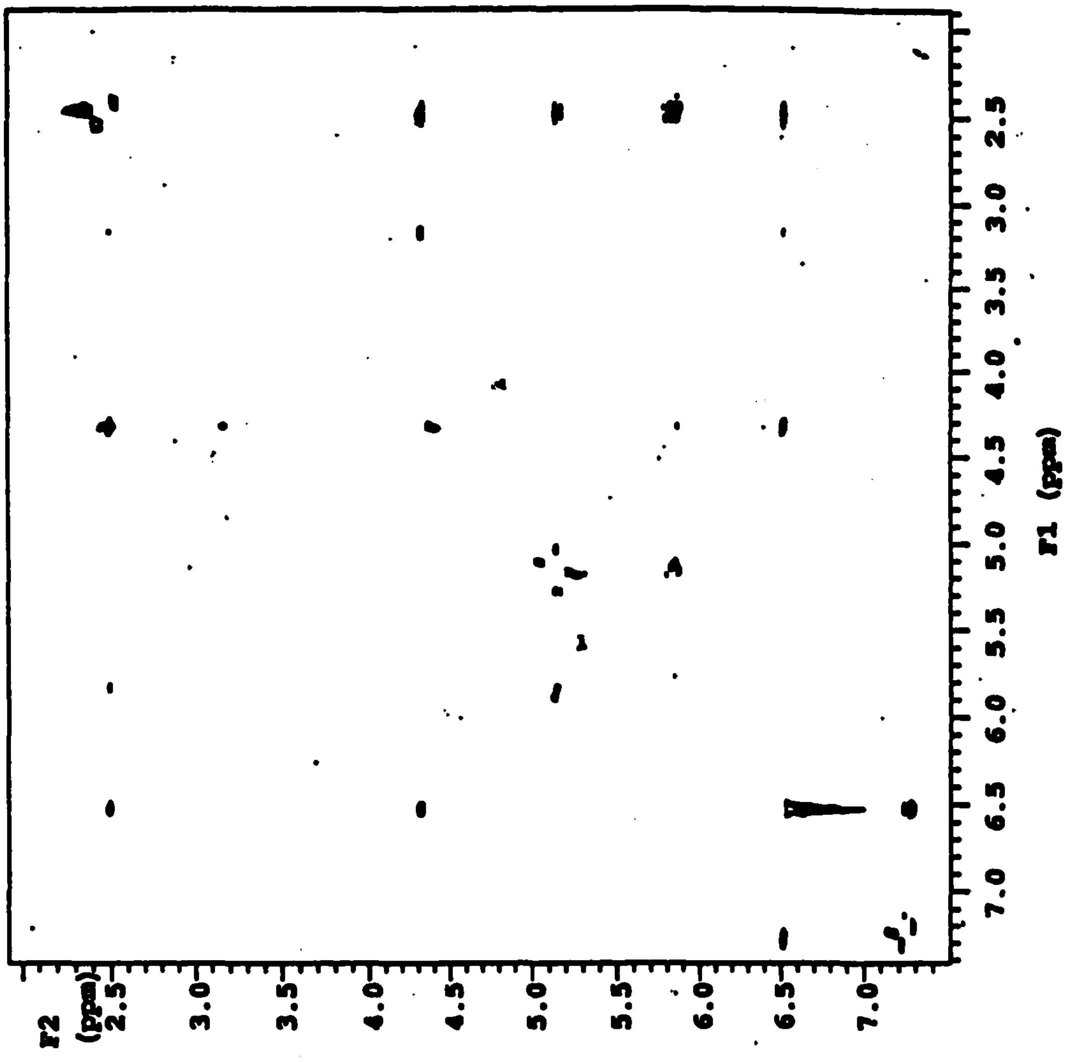
122
(Isomer A)

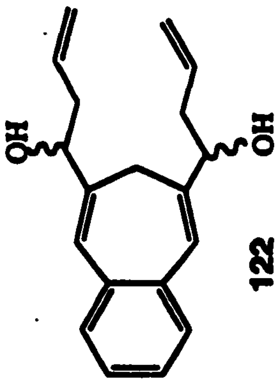


122
(Isomer B)

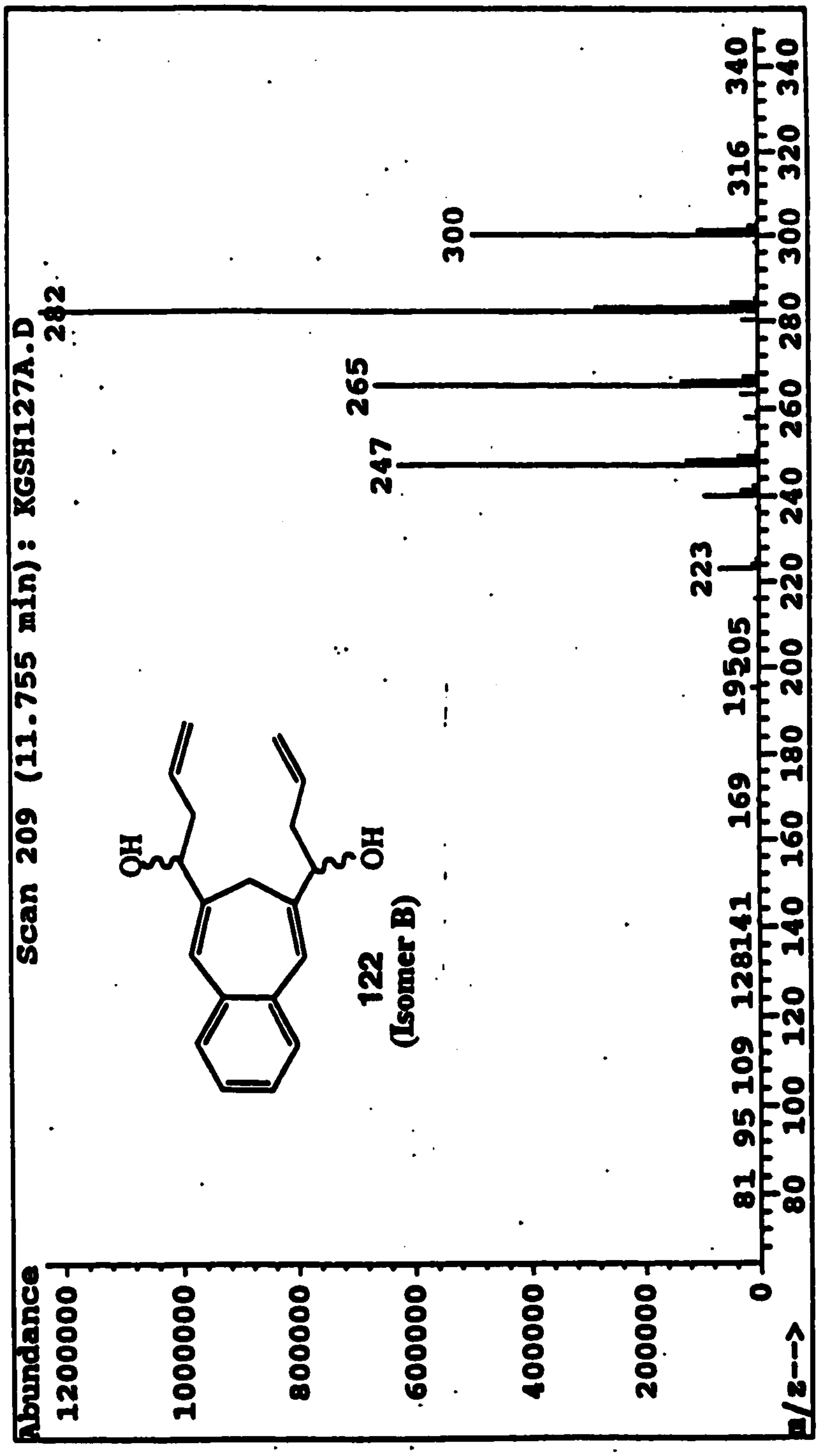


122
(Isomer B)

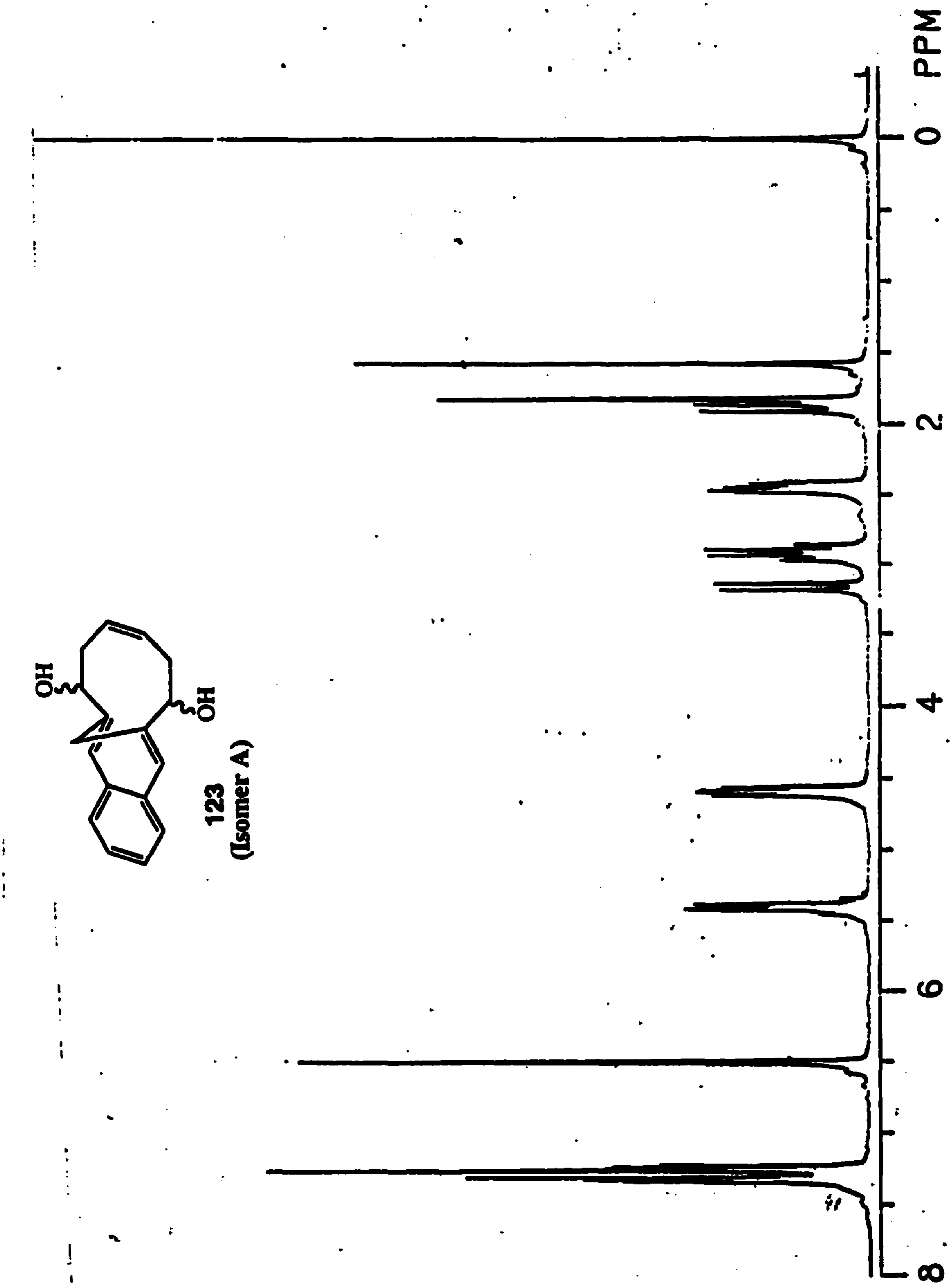

F2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
F1 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0


OH
OH

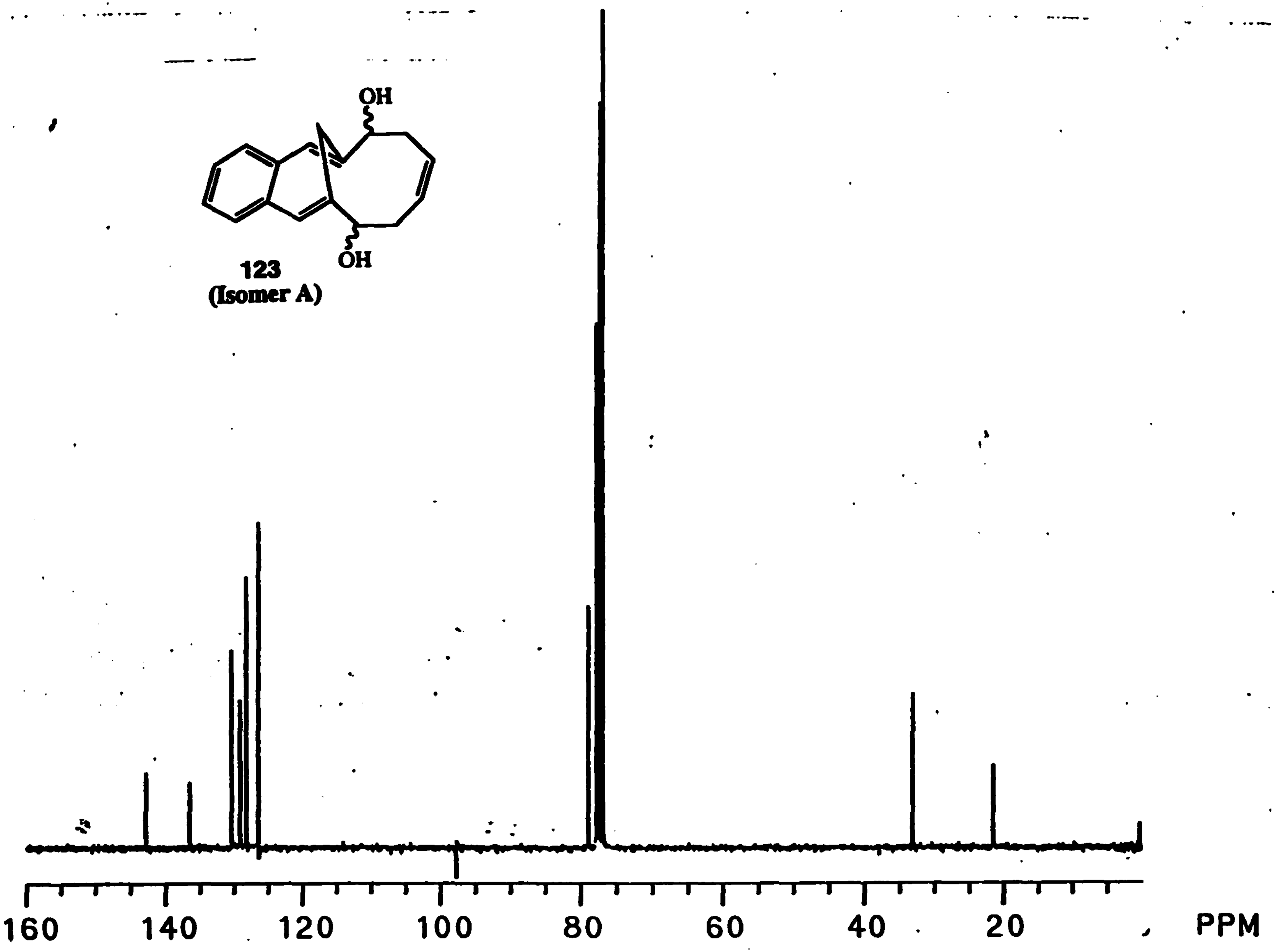
122
(Isomer B)


Scan 209 (11.755 min): KGSH127A.D
Abundance
1200000
1000000
800000
600000
400000
200000
0
m/z-->
81
95
109
128
141
169
195
205
223
247
265
282
300
316
340
80
100
120
140
160
180
200
220
240
260
280
300
320
340
OH
OH

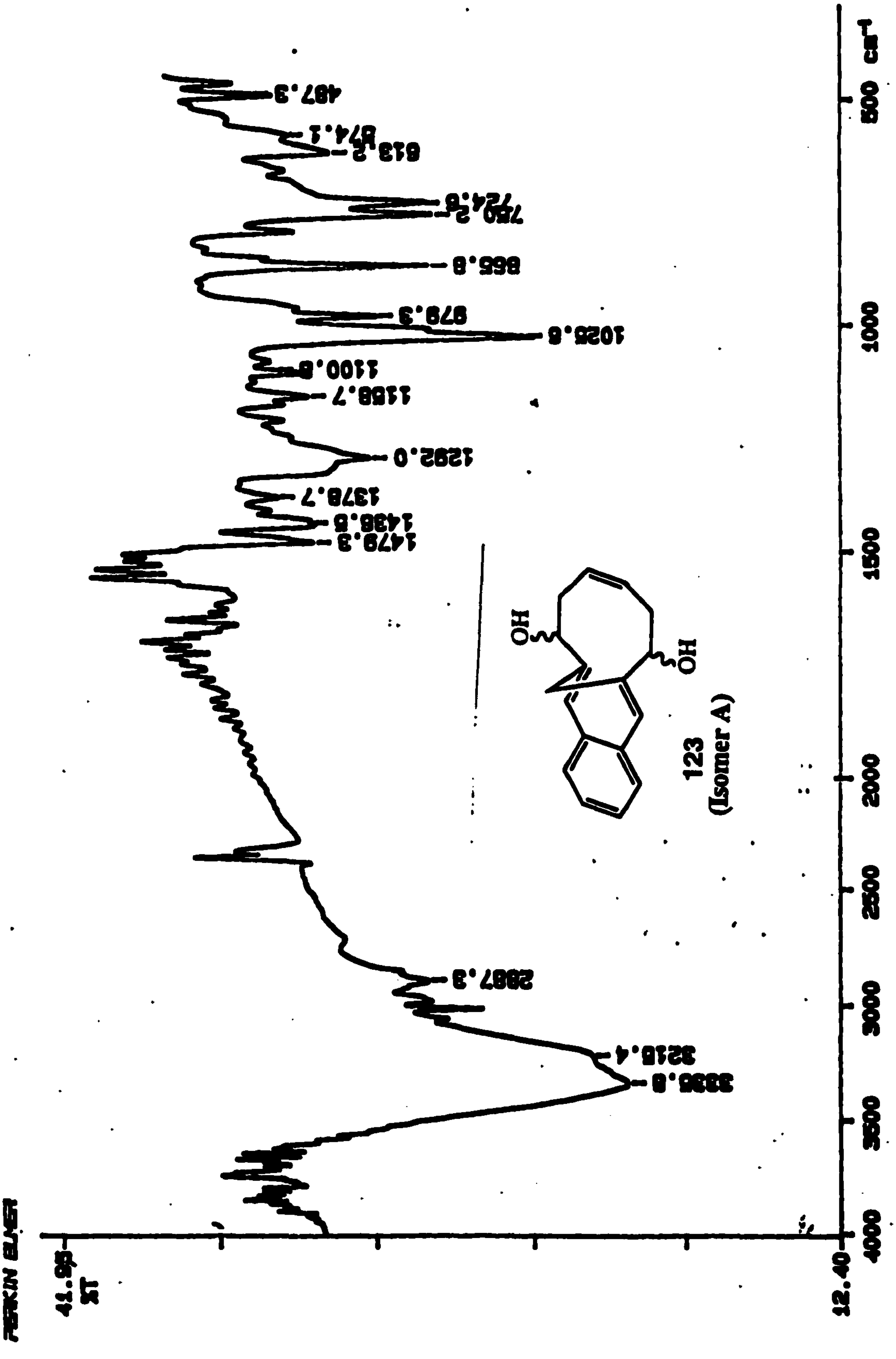
122
(Isomer B)

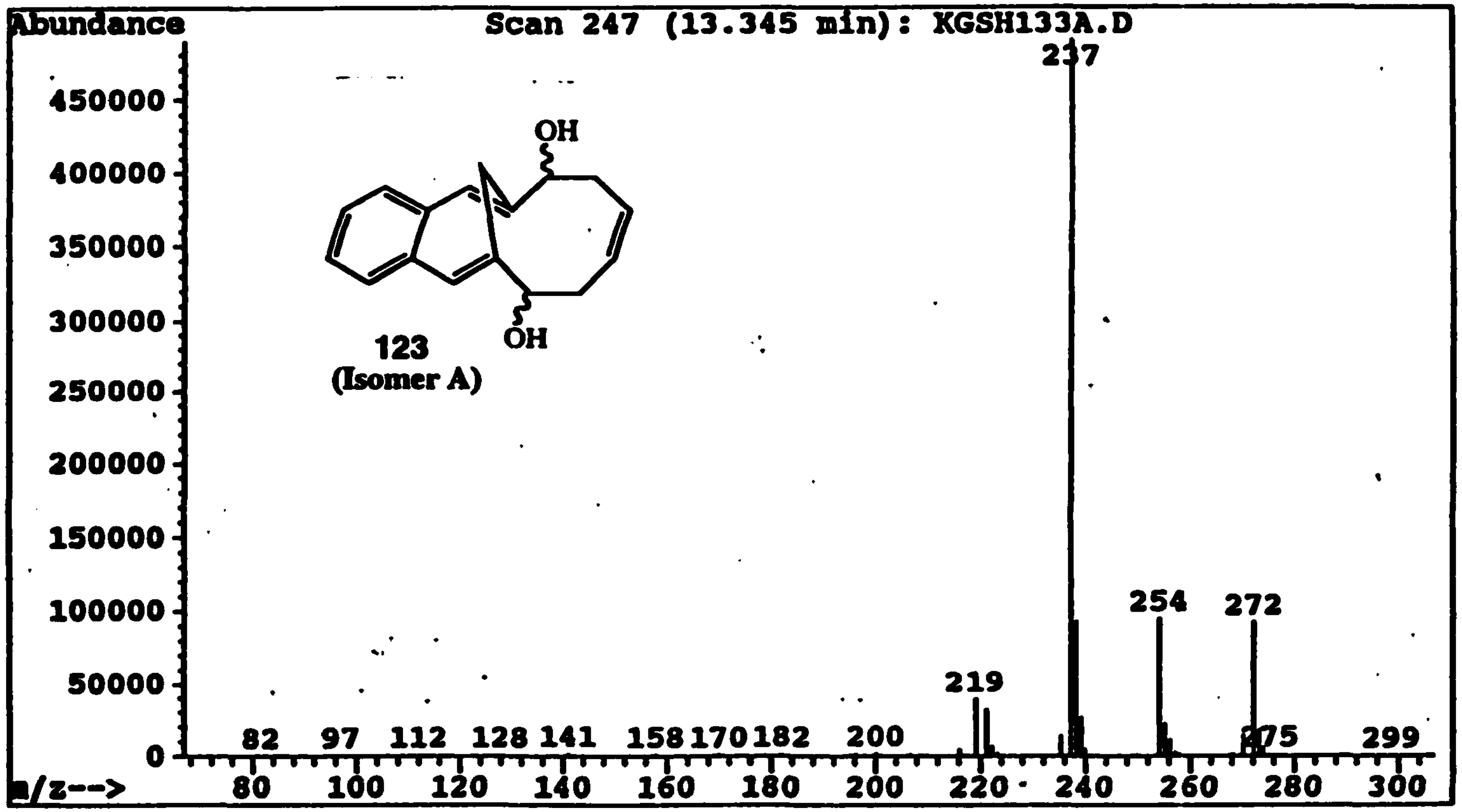


123
(Isomer A)

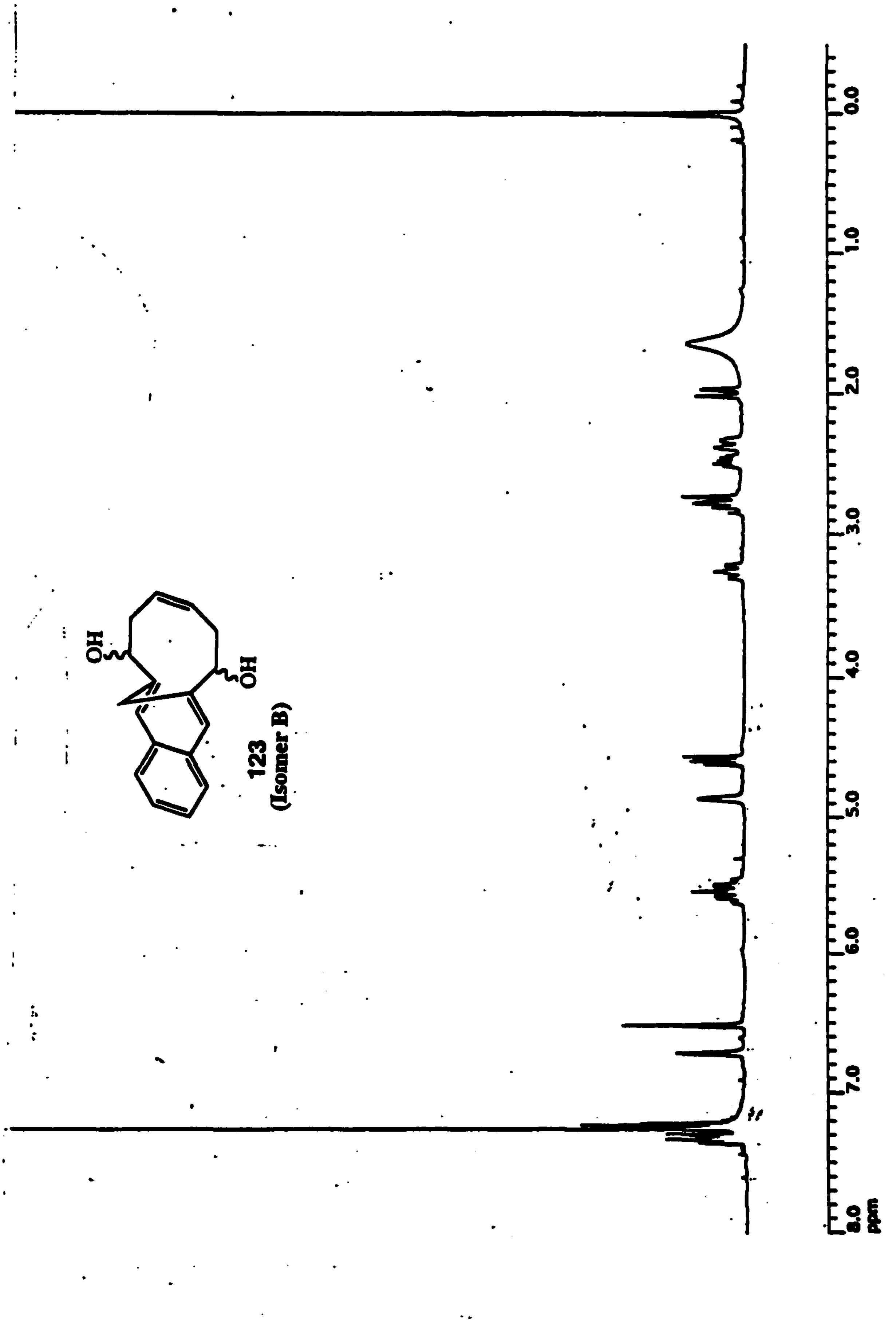


123
(Isomer A)

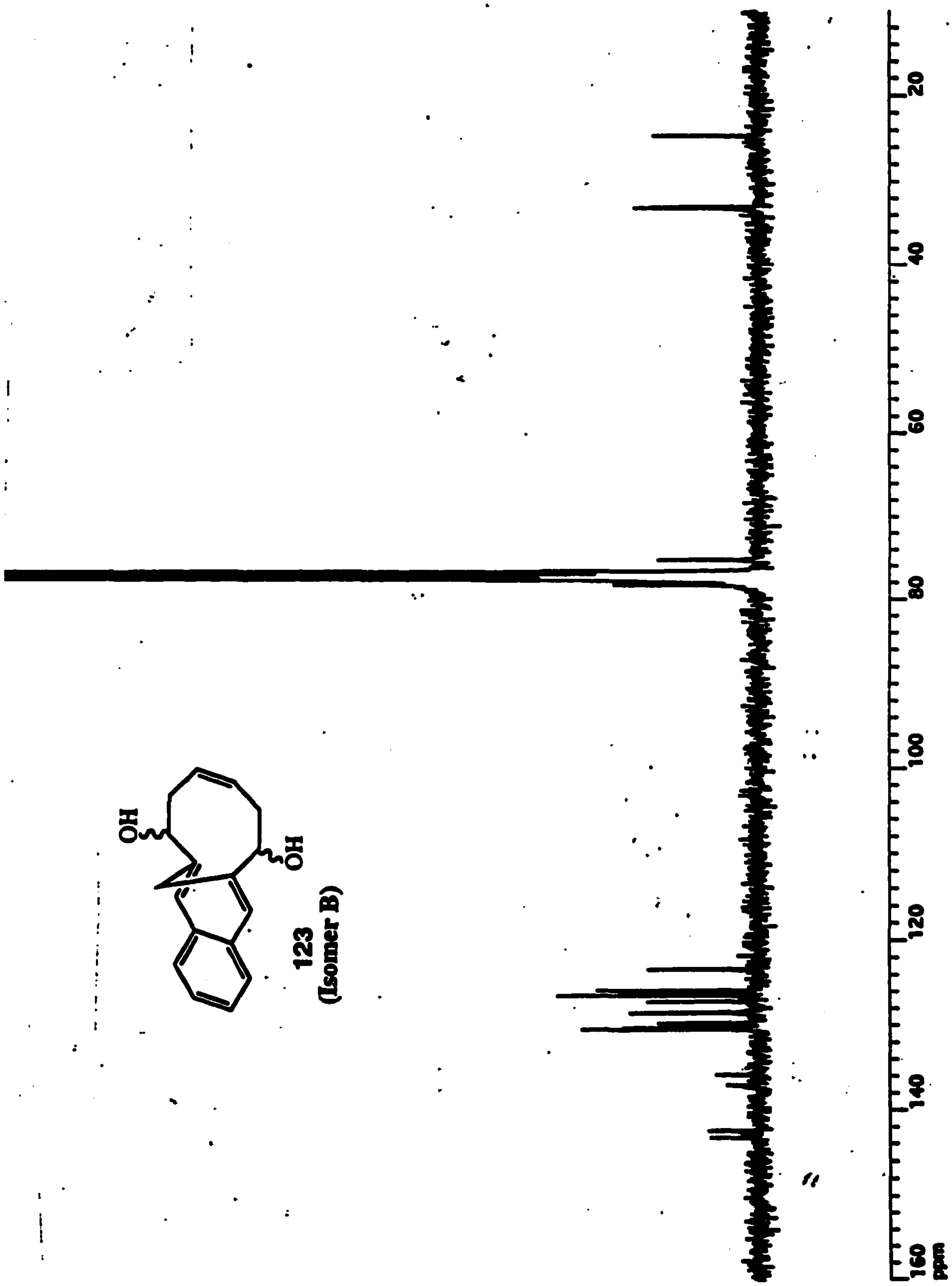

PERKIN ELMER
41.95
%T
12.40
4000
3500
3000
2500
2000
1500
1000
500 cm-1
3385.8
3218.4
2887.3
1479.3
1438.5
1378.7
1292.0
1158.7
1100.8
1025.8
979.3
865.8
750.2
724.5
613.2
574.1
487.3
OH
OH
123
(Isomer A)


Abundance
Scan 247 (13.345 min): KGSH133A.D
237
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
OH
OH
82
97
112
128
141
158
170
182
200
219
254
272
275
299
m/z-->
80
100
120
140
160
180
200
220
240
260
280
300

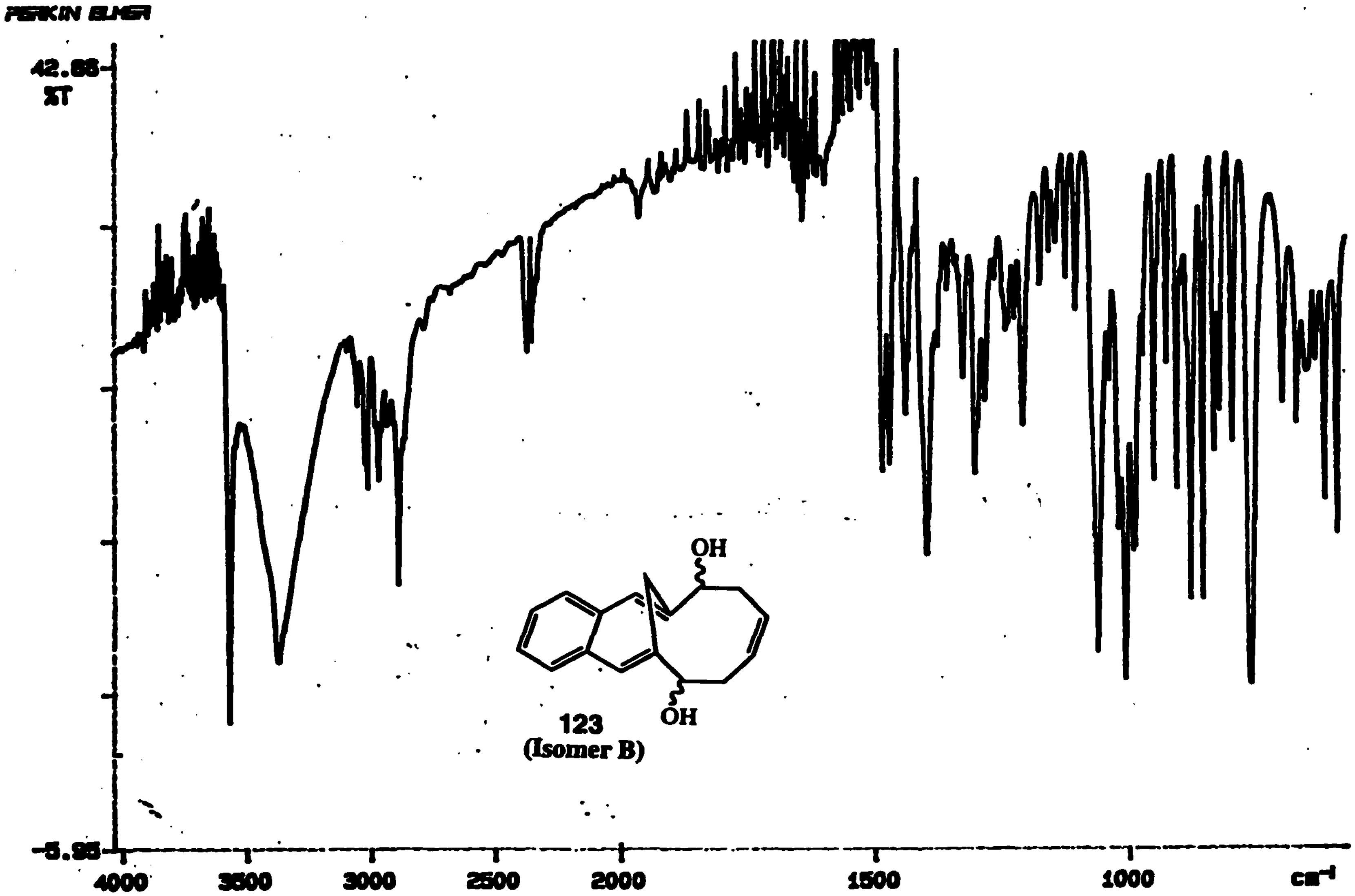
123
(Isomer A)



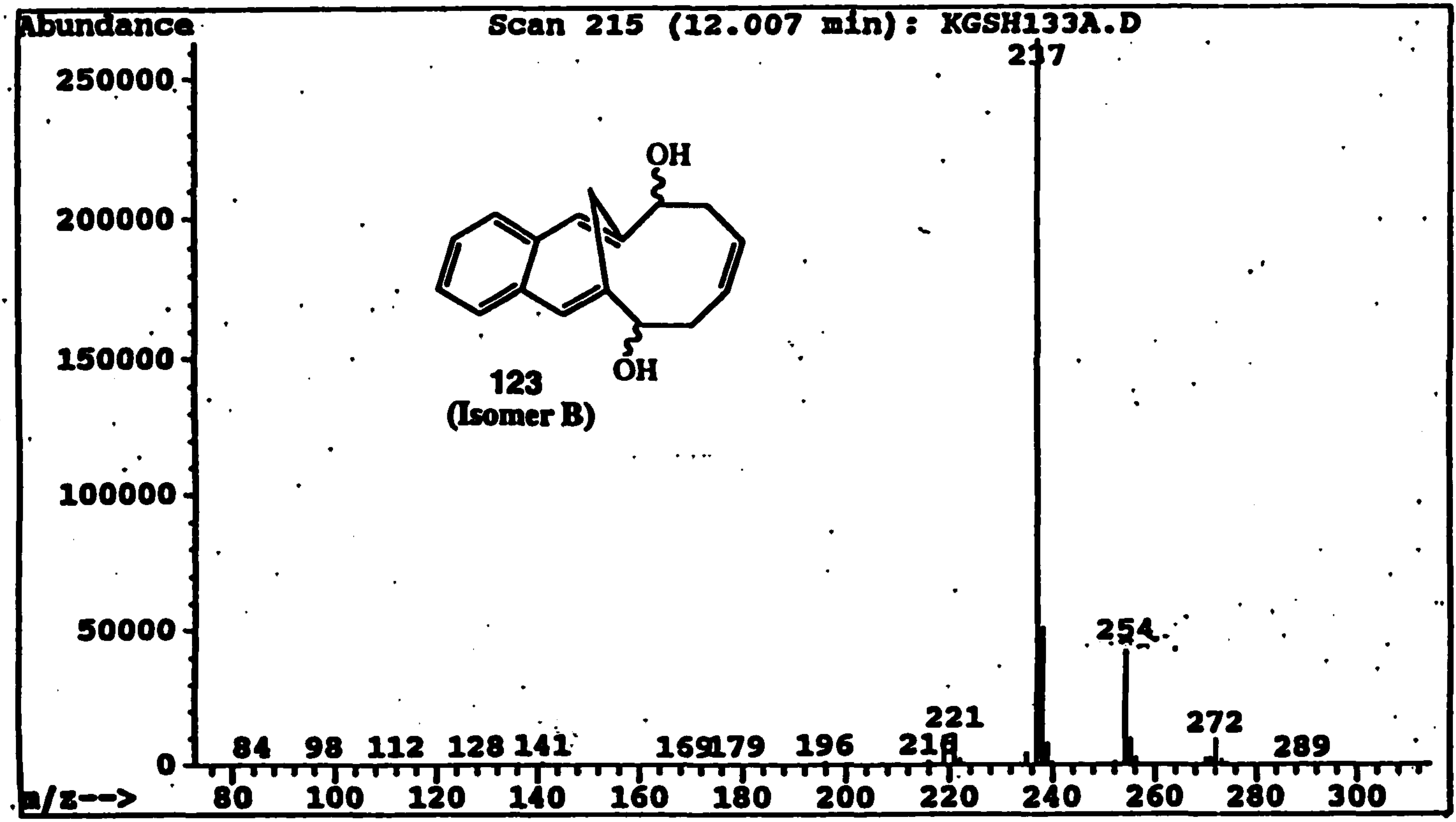
123
(Isomer B)

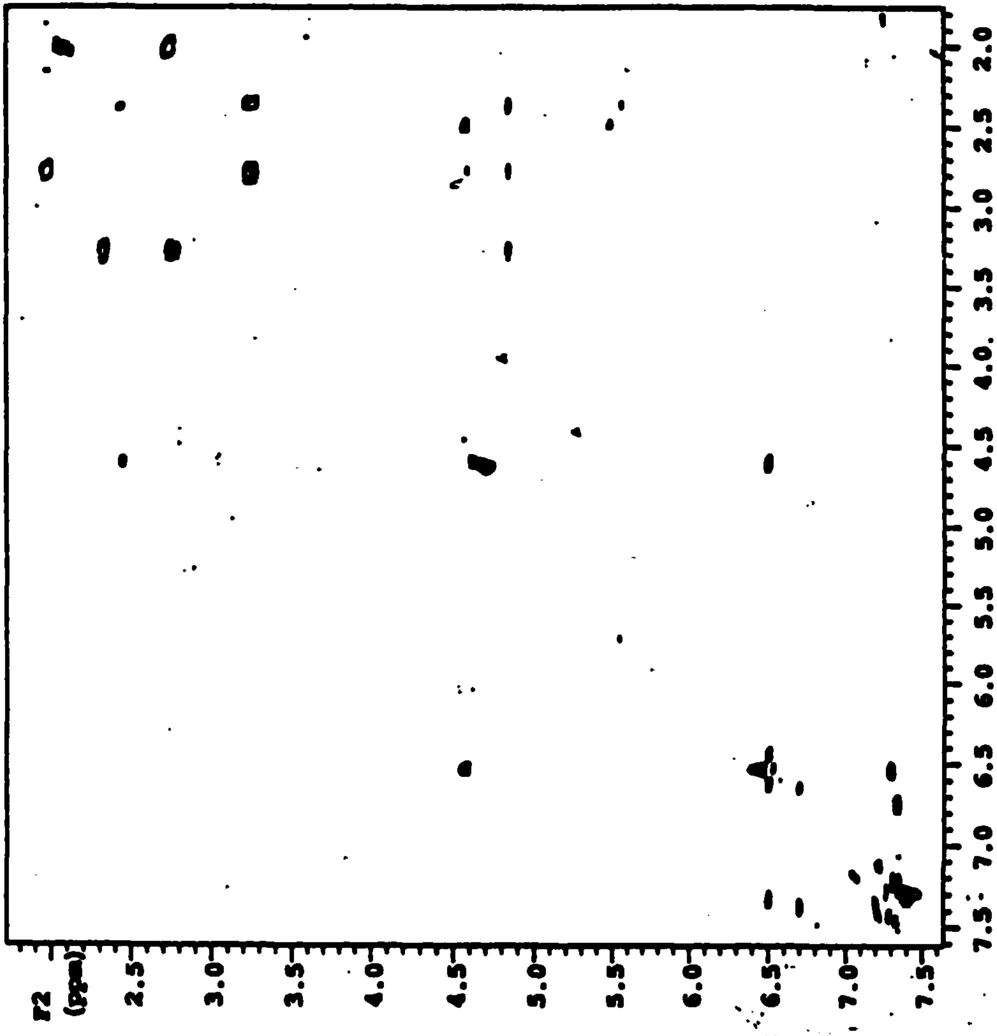


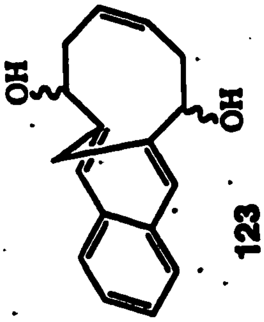
123
(Isomer B)


PERKIN ELMER
42.86
%T
-5.95
4000
3500
3000
2500
2000
1500
1000
cm⁻¹
OH
OH

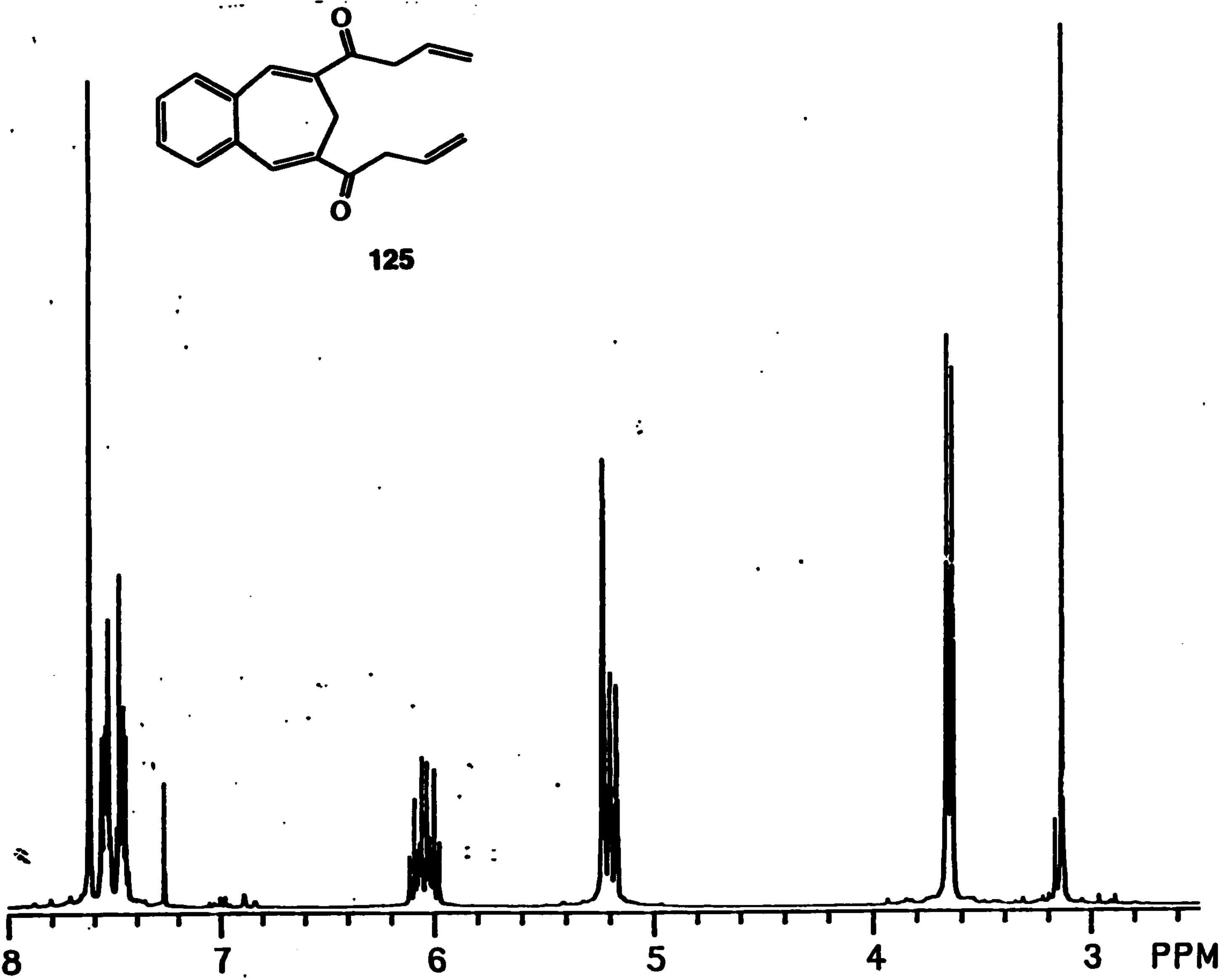
123
(Isomer B)


Abundance
Scan 215 (12.007 min): KGSH133A.D
250000
200000
150000
100000
50000
0
m/z-->
80
100
120
140
160
180
200
220
240
260
280
300
84
98
112
128
141
169
179
196
218
221
237
254
272
289
OH
OH
123
(Isomer B)

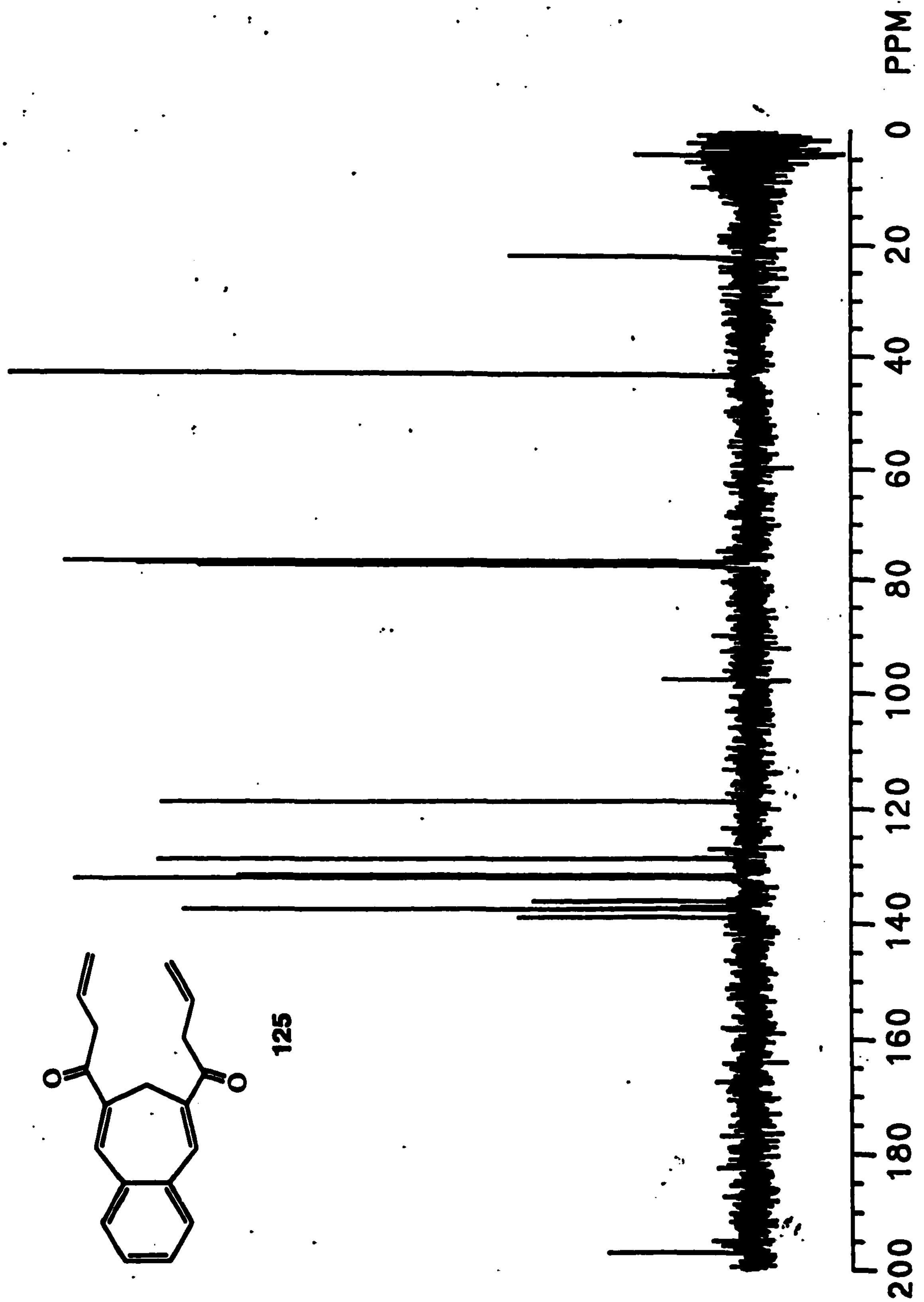

F2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
F1 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5


OH
OH

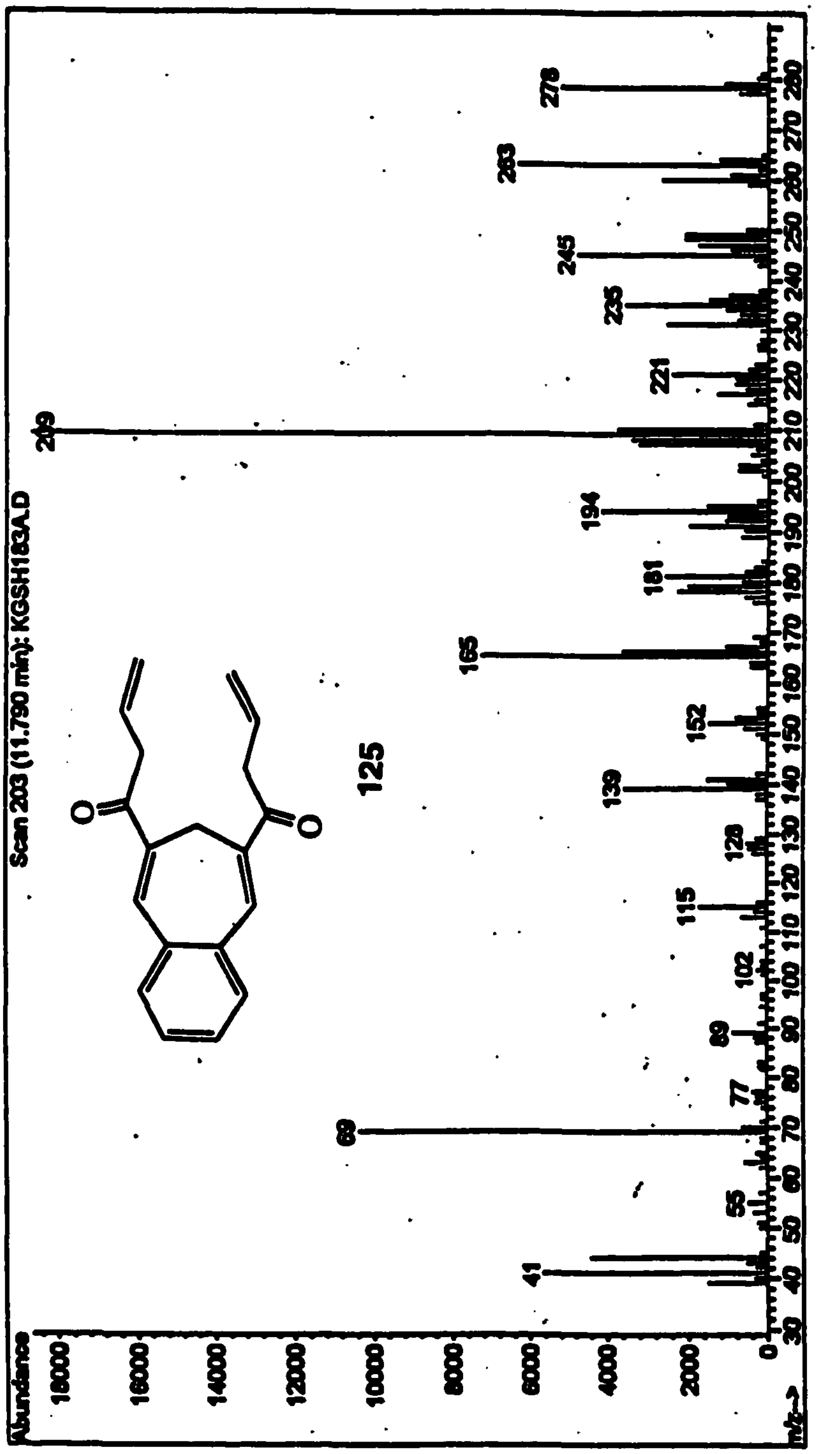
123
(Isomer B)



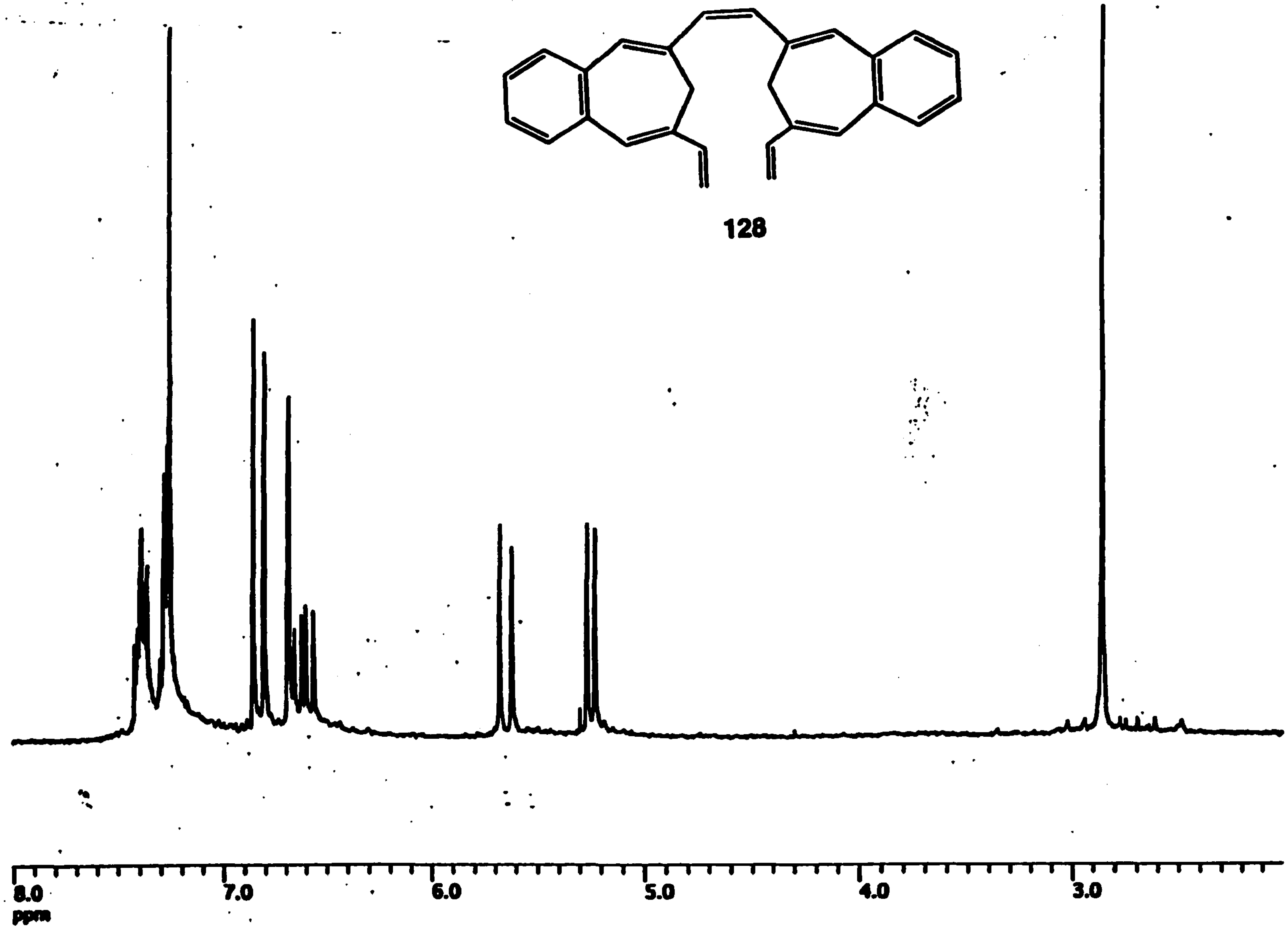
125



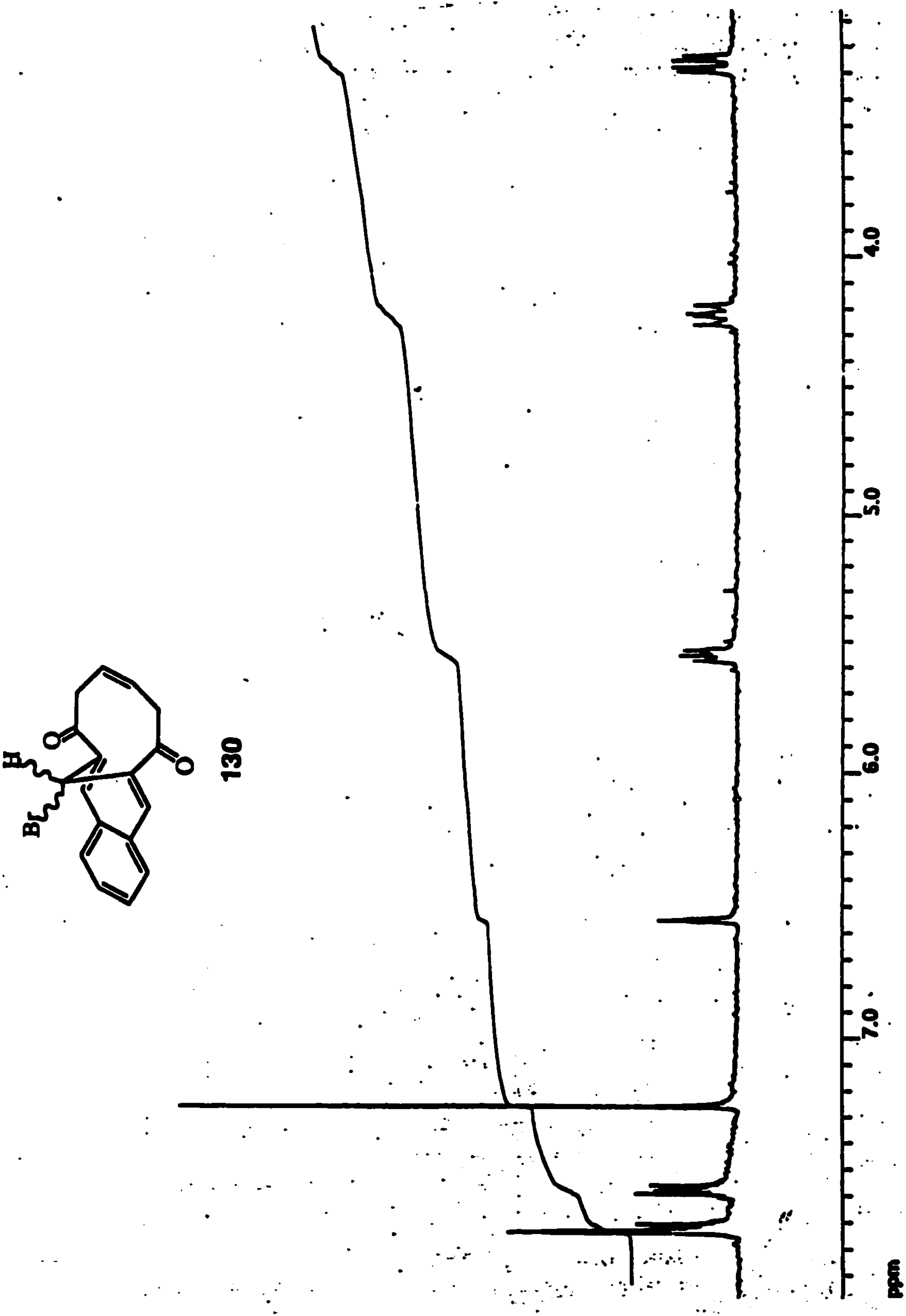
125


Scan 203 (11.790 min): KGSH183A.D
Abundance
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
41
55
69
77
89
102
115
128
139
152
165
181
194
209
221
235
245
263
278
O
O

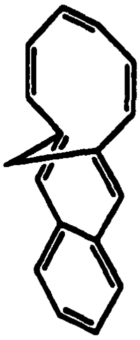
125



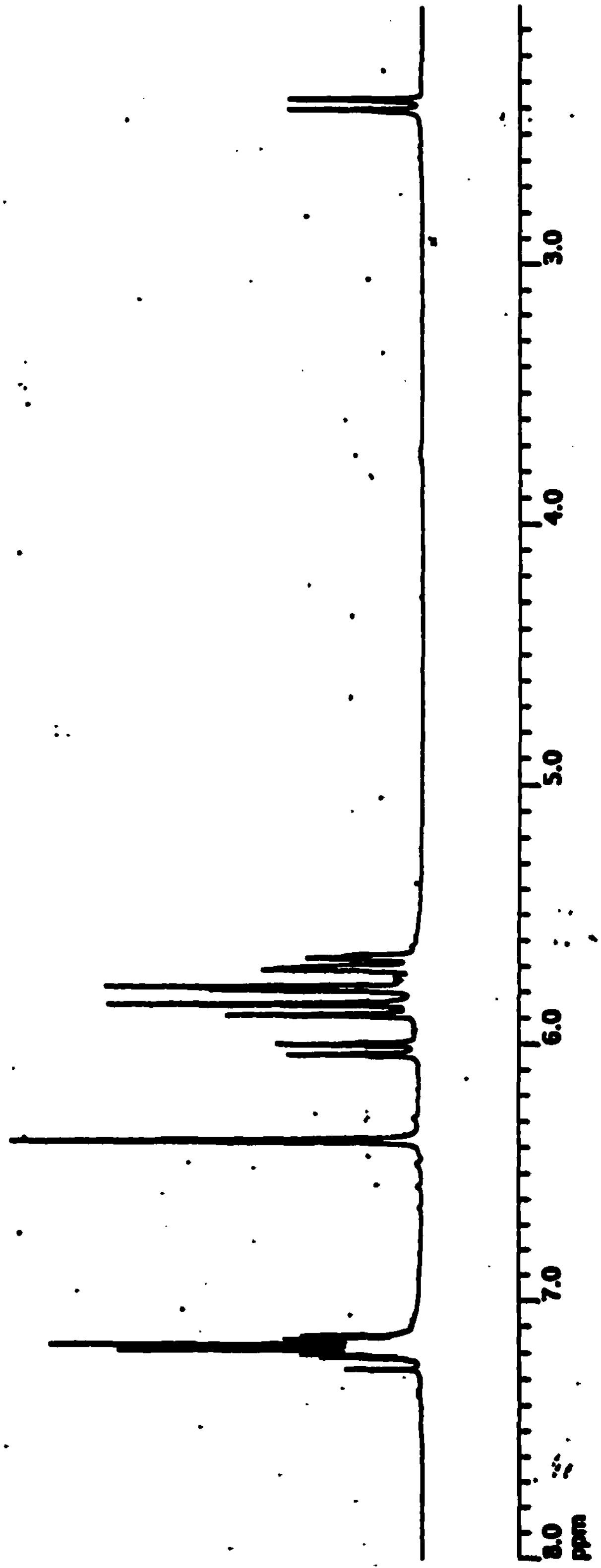
128

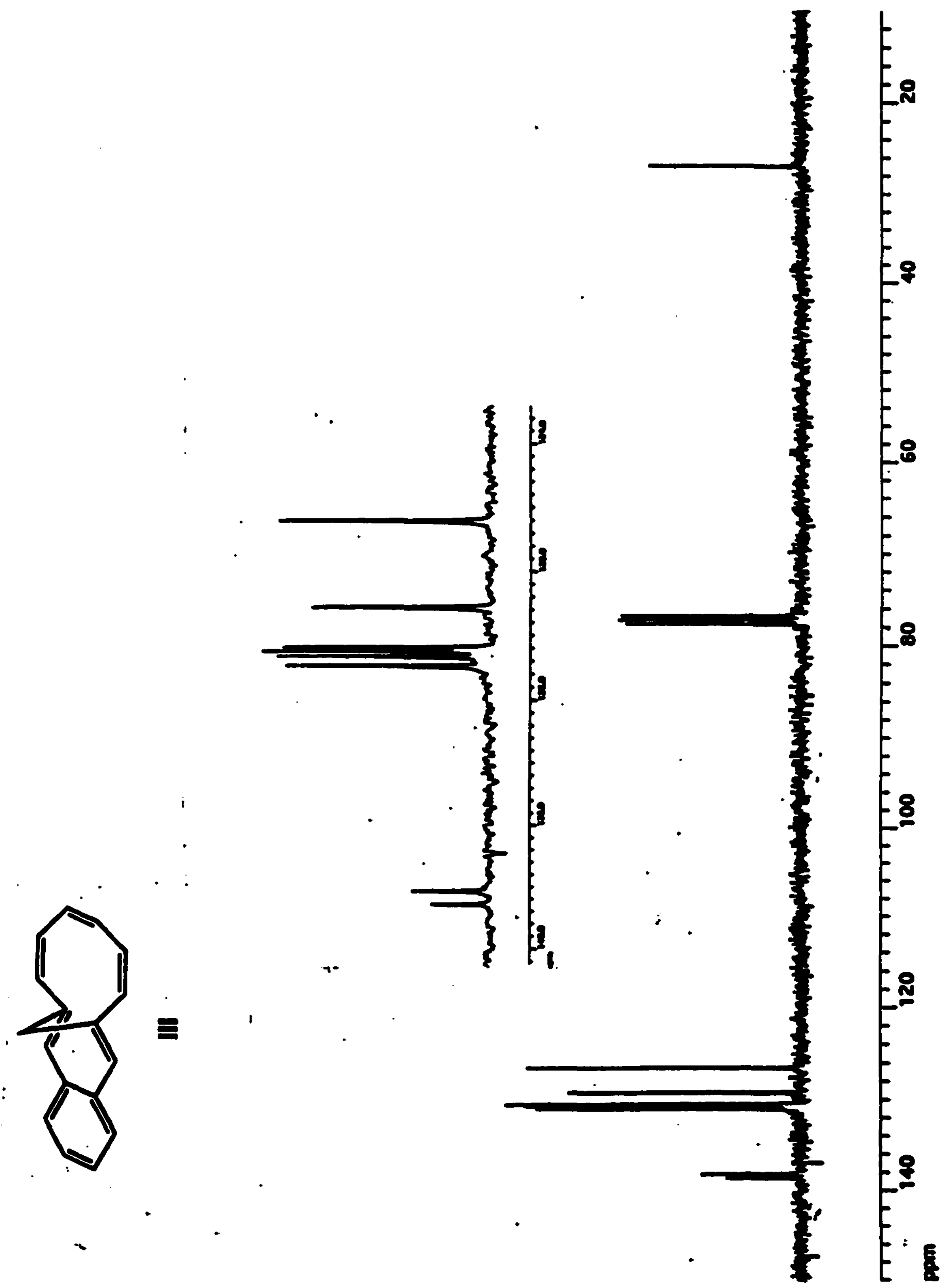


130

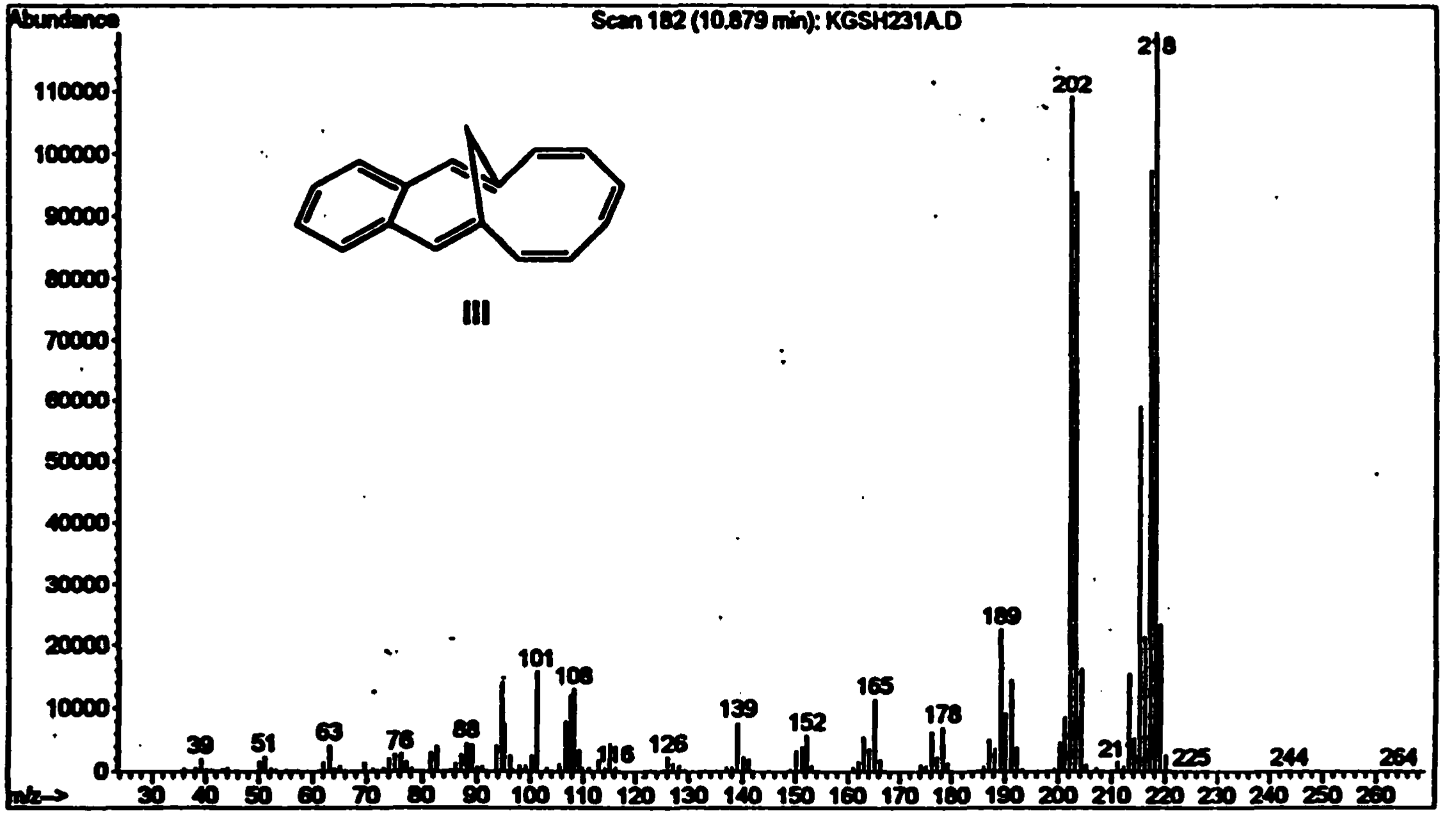


III





III


Abundance
Scan 182 (10.879 min): KGSH231A.D
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260
39
51
63
76
88
101
108
116
126
139
152
165
178
189
202
211
218
225
244
264
III

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