# SYNTHETIC STUDIES TOWARDS POLYCYCLIC AROMATIC HYDROCARBON PRECURSORS RELATED TO FULLERENES

A THESIS SUBMITTED FOR THE DEGREE OF

**DOCTOR OF PHILOSOPHY**

R 53.00

BY

*K. Venkateswara Rao*




SCHOOL OF CHEMISTRY

**UNIVERSITY OF HYDERABAD**

HYDERABAD 500 046

INDIA

JUNE 1995

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**Dedicated**
**To**
**My Parents**

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# STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, India, under the supervision of **Professor Goverdhan Mehta**.

In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever the work described is based on the findings of other investigators.



K. Venkateswara Rao

# Certificate

Certified that the work contained in the thesis entitled **"Synthetic Studies Towards Polycyclic Aromatic Hydrocarbon Precursors Related to Fullerenes"** has been carried-out by Mr. K. Venkateswara Rao, under my supervision and the same has not been submitted elsewhere for any degree.

**Goverdhan Mehta**

**(Thesis Supervisor)**

**Dean**

**School of Chemistry**

## Acknowledgements

It is with great pleasure that I acknowledge my profound gratitude to my teacher **Professor Goverdhan Mehta** for suggesting this interesting problem and for his inspiring guidance

I also thank

- All the faculty members of the School
- All the previous and present lab colleagues
- All the non-teaching staff for their cooperation
- U G C and University authorities for their support

Words would be insufficient to say a few words about my friends who made my stay pleasant and for their association

I am also indebted to my parents, brother and sisters for their love, affection and encouragement

# Abbreviations

| | | |
|---|---|---|
| AIBN | : | azobisisobutyronitrile |
| DCM | : | dichloromethane |
| DDQ | : | 2,3-dichloro-5,6-dicyano-1,4-benzoquinone |
| digol | : | diethylene glycol |
| DMF | : | N,N-dimethylformamide |
| FABMS | : | fast atom bombardment mass spectroscopy |
| FVP | : | flash vacuum pyrolysis |
| hν | : | photoirradiation |
| LAH | : | lithium aluminium hydride |
| LDA | : | lithium diisopropylamide |
| LHMDS | : | lithium hexamethyldisilazide |
| NBS | : | N-bromosuccinimide |
| PCC | : | pyridinium chlorochromate |
| PPA | : | polyphosphoric acid |
| r.t. | : | room temperature |
| THF | : | tetrahydrofuran |
| TMSCl | : | chlorotrimethylsilane |
| )))) | : | ultrasound |
| Δ | : | thermolysis |

# Preface

Fullerenes, molecular allotropes of carbon, are composed of fused hexagons and pentagons. The smallest and the most abundantly available fullerene is the $I_h$-symmetry buckminster fullerene, which obeys the "isolated pentagon rule" and has the shape of a soccer ball (football). With ready availability in macroscopic quantities and $C_{60}$ having been proclaimed as the molecule of the year in 1991, research in fullerene chemistry has attracted world-wide attention While every physical measurement and chemical reaction is being attempted on fullerenes to unravel its rich and intriguing chemistry, a no less exciting but more demanding and difficult problem of *de novo* synthetic design of these molecules has been relegated to back waters. This is hardly surprising because assembling a fullerene like $C_{60}$, a macrocycle of high symmetry, composed of 32 rings (20 six- and 12 five- membered rings), in a rational manner is a challenge of extraordinary proportion. However, a beginning has been made in this direction and initial synthetic efforts of several research groups around the world have been directed towards the design of 'bowl-shaped' hydrocarbons and their precursors, whose

carbon framework constitutes cross sections/fragments of $C_{60}$ and other fullerenes.

The present thesis entitled "**Synthetic Studies Towards Polycyclic Aromatic Hydrocarbon Precursors Related to Fullerenes**" describes our attempts towards the synthesis of three 'bowl-shaped' aromatic hydrocarbons: $C_{48}H_{12}$, $C_{36}H_{12}$ and $C_{21}H_{12}$, whose structural presence can be readily recognized in the [60]-fullerene framework. The thesis has been organized under six main sections I. Introduction, II. Results and Discussion, III. Summary, IV. Experimental, V. Spectra and VI. References. An appendix to the thesis entitled "**A Synthetic Approach Towards Cedranoid Sesquiterpens**" describes our efforts during the formative years of this research project.

In the 'Introduction' section, a brief review and schematic survey of the contributions of some of the researchers active in this area is given. The attention is mainly focused on the synthesis of the curved fragments of [60]-fullerene.

In the 'Results and Discussion' section, we describe our efforts towards the synthesis of the 'bowl-shaped' fragments, $C_{48}H_{12}$, $C_{36}H_{12}$ and $C_{21}H_{12}$ of [60]-fullerene. Our results have been discussed under two sub-headings: Synthetic Studies Towards $C_{48}H_{12}$ and $C_{36}H_{12}$ fragments and Synthetic Studies Directed Towards Sumanene and its Derivatives.

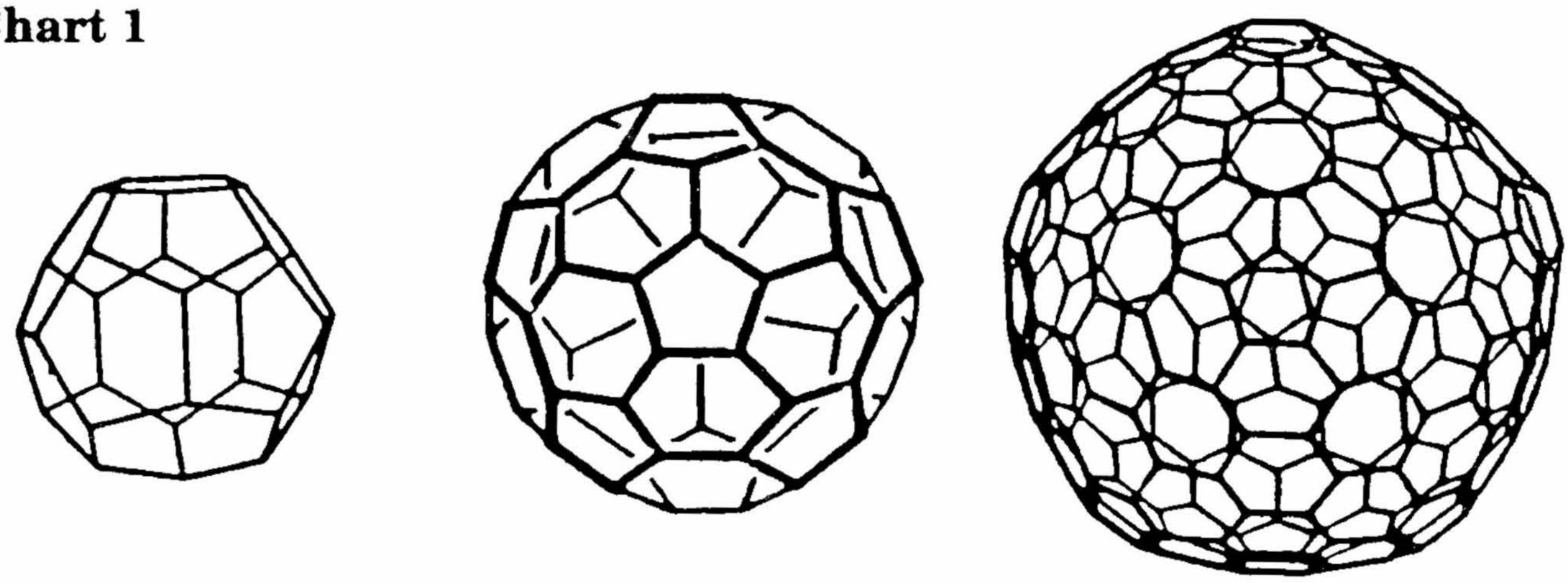
The sections III, IV, V and VI provide a brief summary, detailed experimental procedures, spectra of some of the important compounds and appropriate literature citations, respectively.

The appendix of the thesis describes our efforts towards the synthesis of cedranoid sesquiterpenes and in this context, we describe a general methodology for the construction of bicyclo[3.2.1]moiety through $Pd^{+2}$ promoted cyclization of regioselectively generated trimethylsilyl enolethers of β-alkenylated cyclopentanones.

# Introduction

Fullerenes, the newly discovered molecular allotropes of carbon, are built up of fused hexagons and pentagons. These are spherical molecules, quite unlike diamond and graphite, and are soluble in many organic solvents.[1] The building principle of fullerenes is a consequence of Euler's theorem, which says that for the ring closure of each spherical network of hexagons, 12 pentagons are required. Thus, each fullerene ($C_n$) consists of 12 pentagonal and any number of hexagonal rings (m), such that m=($C_n$-20)/2.[2] Thus, fullerenes of unlimited range in terms of shape, size and structure are possible.[3] As illustrative examples, the structures of $C_{28}$-'bucky baby', $C_{60}$-'bucky ball' and $C_{240}$-'giant bucky' are shown in Chart 1.

**Chart 1**



$C_{28}$
"Bucky-baby"

$C_{60}$
"Bucky-ball"

$C_{240}$
"Giant-bucky"

While Nature probably harboured fullerenes from time immemorial trapped inside the rock samples or accumulated elsewhere, as molecular entities they were first conceptualized by Osawa in 1970 as potential three dimensional 'superaromatic' species and he proposed the spherical $I_h$-symmetric "football-like" structure for the $C_{60}$ molecule.[4] However, this observation lay dormant for over a decade until it resurfaced in an entirely different context. In 1984 Rohlfing et al. observed that upon laser vaporization of graphite, large 'carbon-only' clusters $C_n$ with n=30-190 can be produced.[5] In 1985, Kroto and Smalley, in a great feat of intuition, assigned the persistent presence of m/z 720 peak in the mass spectra, obtained when pulsed laser was focused on graphite to $C_{60}$.[6] However, complete characterization of $C_{60}$ still proved elusive. The major breakthrough in this context was achieved by Kratschmer and Huffman[7] in 1991, who produced fullerenes in macroscopic quantities through arcing graphite rods in helium atmosphere. Since then, fullerene mixtures have been produced employing several convenient procedures using the principle of graphite vaporization. It is no longer a specialist's job and bench-top fullerene generators can now be readily assembled.[1] Fullerenes can now be

produced by i) resistive heating of graphite[7] ii) arc vaporization of graphite[8] iii) evaporation of graphite by sunlight using "Solar 1" fullerene generator[9] iv) direct inductive heating of a carbon sample in a boron nitride support[10] v) optimizing sooting flames[11] and vi) pyrolysis of naphthalene at 1000 °C in an argon stream, etc.[12] The raw product obtained by different methods is a mixture of fullerenes predominant in $C_{60}$, with $C_{70}$ being the next abundant compound. Several protocols involving sublimation, column chromatography (various adsorbents), soxhlet extraction, complexation, fractional crystallization, etc., have been developed for the purification/isolation of individual fullerenes. While many fullerenes have been isolated and characterized, so far structures of only five fullerenes *viz*. $C_{60}$, $C_{70}$, $C_{76}$, $C_{2v}$-$C_{78}$ and $D_3$-$C_{78}$ have been determined.[13]

The most abundantly available $C_{60}$ fullerene, commonly known as buckminsterfullerene, belongs to the highest known point group ($I_h$) with 60 carbon atoms arranged in such a way that each carbon is attached to three neighbouring carbons. $C_{60}$, popularly described as a 'foot ball' or a 'soccer ball', has a geometry of truncated icosahedron, a

polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal.[14] The arche type $C_{60}$, the stable and the roundest molecule that can possibly exist,[3] exhibits many interesting properties.

The structure of $C_{60}$ has been firmly established by spectroscopic properties and X-ray analysis The molecular ion peak at 720 a.m.u. in FABMS[15] clearly indicates the presence of 60 carbon atoms. Only one signal at δ 142.68 ppm in the $^{13}C$ NMR spectrum of $C_{60}$ shows that all 60 carbon atoms are equivalent.[15,16] Out of 174 vibrational modes of $C_{60}$ only four are IR active (1400, 1190, 600, 510 $cm^{-1}$) and ten are Raman active.[17] X-ray data showed bond distances of 1.388 Å and 1.432 Å for the six-six and five-six ring junctions, respectively.[18]

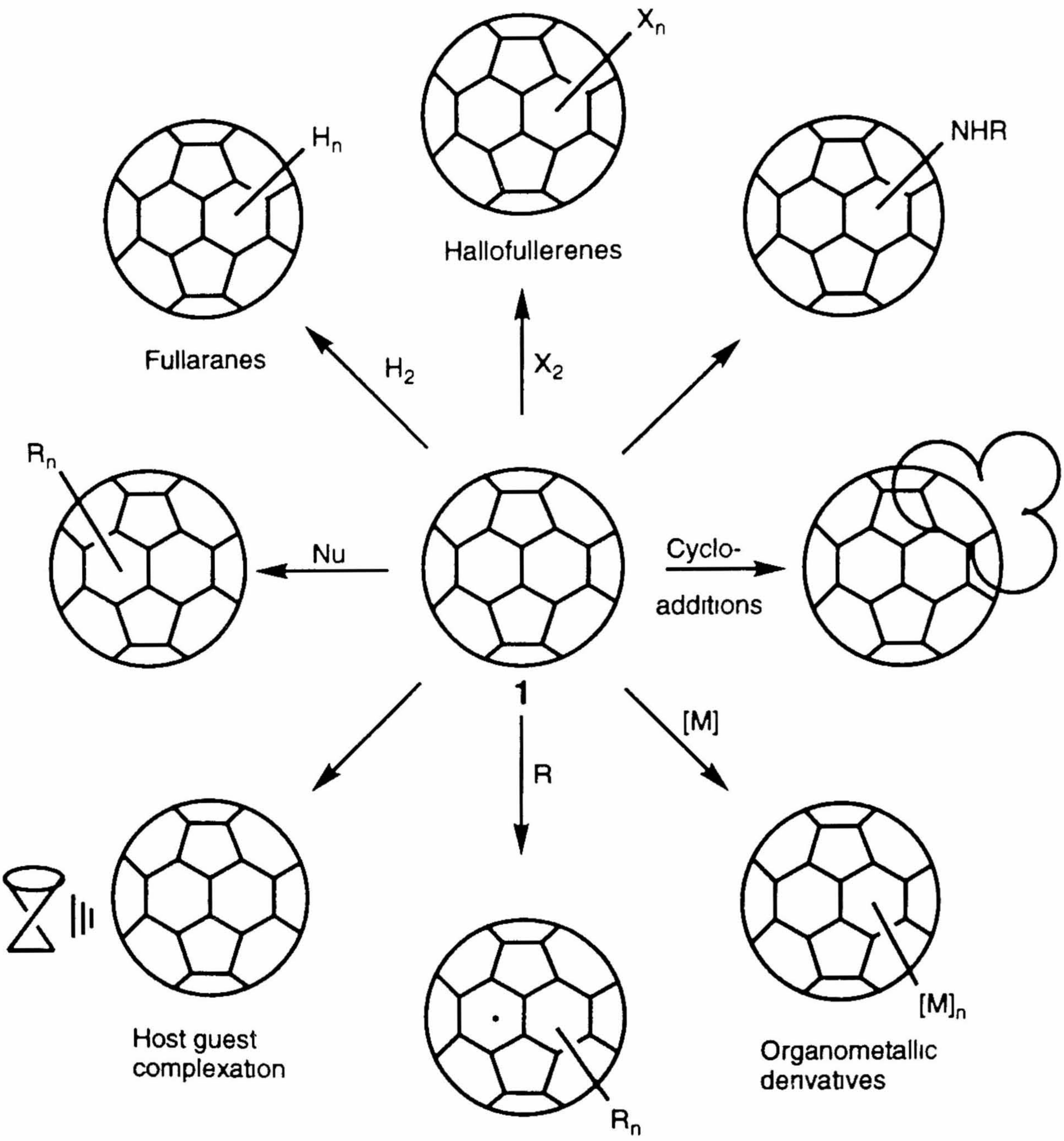
Initially, $C_{60}$ was expected to be a very stable aromatic species. Indeed, calculations showed that as many as 12,500 resonance structures are possible for the molecule.[19] However, the double bonds avoid placement in the pentagonal rings due to strain considerations. Thus, there is only one structure for $C_{60}$. As a consequence, there is little delocalization of electrons and $C_{60}$ behaves more like a giant caged alkene rather than a 'superaromatic' entity. Fullerenes, particularly

$C_{60}$, undergo reactions that are characteristic of alkenes. The diverse range of their reactions can be summarized under three broad heads: (i) electron-transfer reactions resulting in the formation of fullerene salts, (ii) addition reactions and (iii) ring opening and degradation reactions. Chart 2 summarizes some of the typical reactions of $C_{60}$.[13] Of particular interest are the cycloaddition reactions of $C_{60}$ with a range of dienes[20] and 1,3-dipoles as well as 2+2-photocycloadditions.[21] Addition of hydrogen, halogens, amines, carbanions and electrons on the surface of [60]-fullerene also provide intriguing structures, whose structure determination constitutes a formidable challenge. With transition metals, $C_{60}$ gives either hydrometalations or form $\eta^2$ or $\eta^6$ $\pi$-complexes.[22]

A fascinating feature of fullerenes is the cavity they hold within their carbon framework. The inner and outer surfaces are covered with a sea of $\pi$-electrons. These cavities can encapsulate an atom or an ion or even a molecule to form 'inclusion compounds'. The diameter of $C_{60}$ molecule is $\approx$ 7Å, providing an internal cavity which appears to be capable of holding a variety of atoms.[6] There is an evidence that an

atom, such as lanthanum or oxygen, can be placed in the interior producing molecules which may exhibit unusual properties. Endohedral

**Chart 2**




Some general reactions of fullerene

fullerene complexes can also be produced by arc vaporization of graphite impregnated with a variety of metal oxides[23] or rare earth metal carbides.[24] Metallofullerenes encaged by $C_{60}$ are unstable, destroyed upon exposure to air and are insoluble in organic solvents.[25]

Regarding the applications of fullerenes, there seems to be no particular use at present, but a lot of important applications, like superconductivity, molecular magnetism as well as catalytic and biological activity, can be expected in future. Already many $M_xC_{60}$ derivatives have been shown to exhibit high $T_c$.[26] The hydrophobic exterior and spherical shape of $C_{60}$ can be exploited through molecular recognition phenomenon. Certain derivatives and hybrid molecules, e.g., amino acid derivatives of $C_{60}$ have already exhibited inhibition of HIV Protease (HIVP) activity.[27] The ability of the fullerene core to efficiently photosensitize the conversion of triplet oxygen to singlet oxygen, which can be used for DNA cleavage[28] is another significant biological property exhibited by $C_{60}$. A variety of catalytic activities of $C_{60}$ have been discovered[29] and selective impact is expected from fullerene derivatives. Thus, synthetic pursuit of variably functionalized derivatives of [60]-

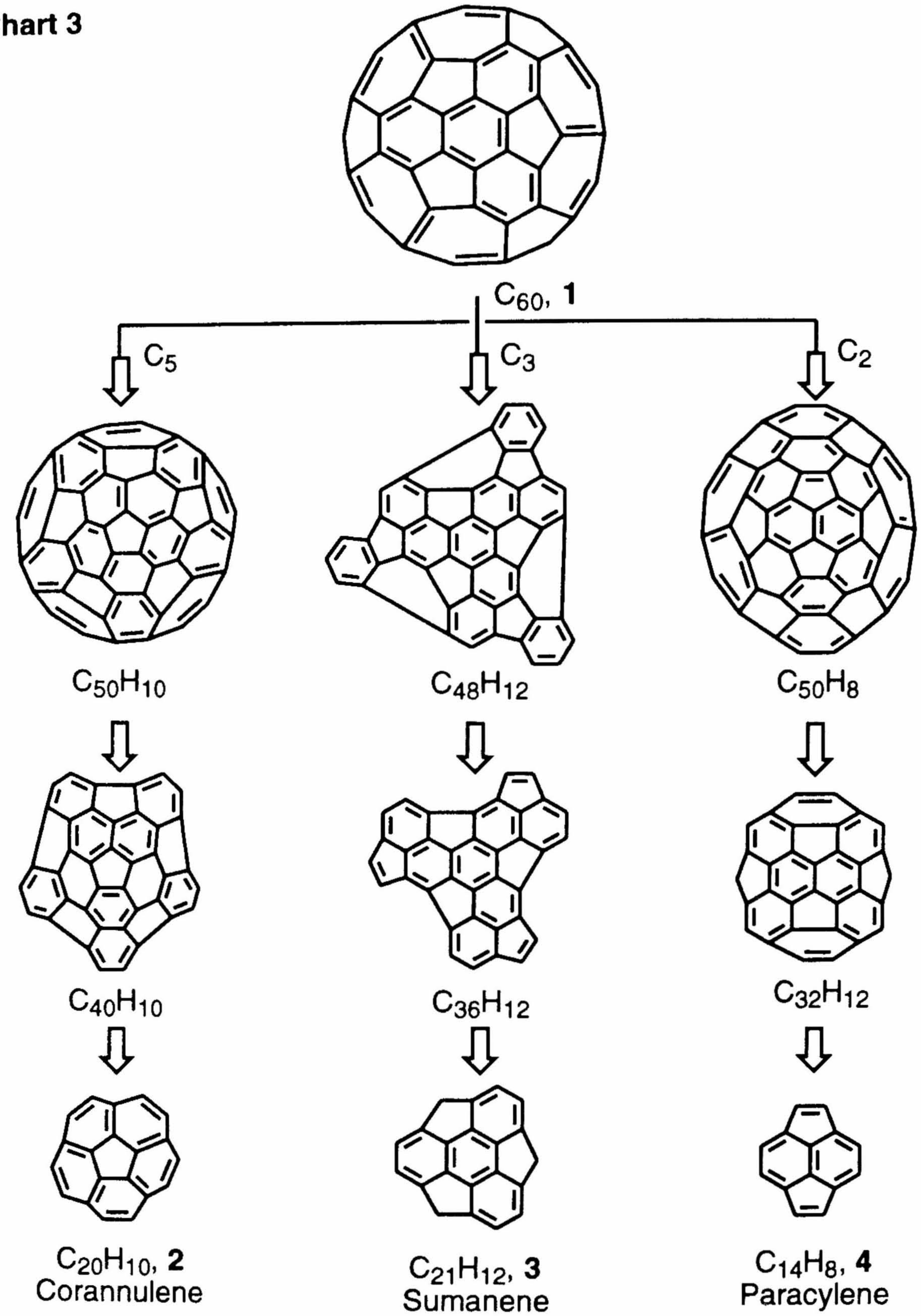
fullerene offer a large number of interesting possibilities and hence many synthetic chemists have been lured into this arena.

Although, [60]-fullerene can be readily accessed *via* arc vaporization of graphite, and also prepared through pyrolysis of benzene, naphthalene, camphor etc. and even macrocylic acetylenes,[30] synthesis of this molecule through "classical" protocols constitutes a formidable intellectual and experimental challenge. Thus, "classical" total synthesis of $C_{60}$ is a major challenge in organic chemistry today. In this quest, bowl-shaped polycyclic aromatic hydrocarbons whose carbon framework constitutes cross-sections of buckminsterfullerene, are also attractive synthetic pre-targets. Several such fragments have been identified/ recognized and many research groups around the world have been pursuing their synthesis. Some progress has been made and reports on these efforts have surfaced in the literature only during the last two or three years. Before elaborating on our own endeavours towards the synthesis of some of the bowl-shaped fragments of $C_{60}$, a brief summary of efforts and accomplishments of various research groups in this area is described below.

The synthetic routes to $C_{60}$ can be generated through geometric partitioning of the carbon sphere. The $C_{60}$, can be dismantled in a retrosynthetic sense through three conceptually different routes among others, which retain $C_5$, $C_3$ and $C_2$ symmetries, Chart 3.[31] The structural fragments are treated as hydrocarbons obtained by adding hydrogens at the perimeter to saturate the valency at the rim carbon atoms. Each of the structural fragments is having a bowl-shaped geometry and, in its own right, a fascinating target for synthetic pursuits. The important substructures at the end of $C_5$, $C_3$ and $C_2$ symmetry routes are $C_{20}$-'corannulene' **2**, $C_{21}$-'sumanene' **3** and $C_{14}$-'paracylene' **4**, Chart 3. Synthetic studies so far have focused mainly on these bowl-shaped hydrocarbons and related siblings of $C_{60}$.

Formation of $C_{60}$ through graphite arcing and combustion, clearly indicates that flash vacuum pyrolysis (FVP) should be an important technique that should prove useful for the synthesis of sub-structures of $C_{60}$, and ultimately of $C_{60}$ itself.[32] High temperature gas phase pyrolysis, with a short contact time in the hot zone, provides polycyclic aromatic hydrocarbon substrates with a large activation

**Chart 3**


C60, 1
C5
C3
C2
C50H10
C48H12
C50H8
C40H10
C36H12
C32H12
C20H10, 2
Corannulene
C21H12, 3
Sumanene
C14H8, 4
Paracylene

ıergy which is needed to effect the endothermic cyclization reactions rming a strained polycyclic carbon framework. In the context of ›rannulene and other bowl-shaped hydrocarbon synthesis, four types of yclizations under FVP conditions can be envisaged. i) an lectrocyclization followed by loss or migration of hydrogen or loss of ydrogen halide, ii) cyclization of benzylic radical, benzylic carbene or inylic carbene iii) cyclization of an aryl radical and iv) intramolecular oupling of two benzylic, benzylic and aryl or two aryl radicals. In almost ll the work related to $C_{60}$ reported so far, FVP has been attempted as a ›ivotal step.

## Corannulene and Related Compounds

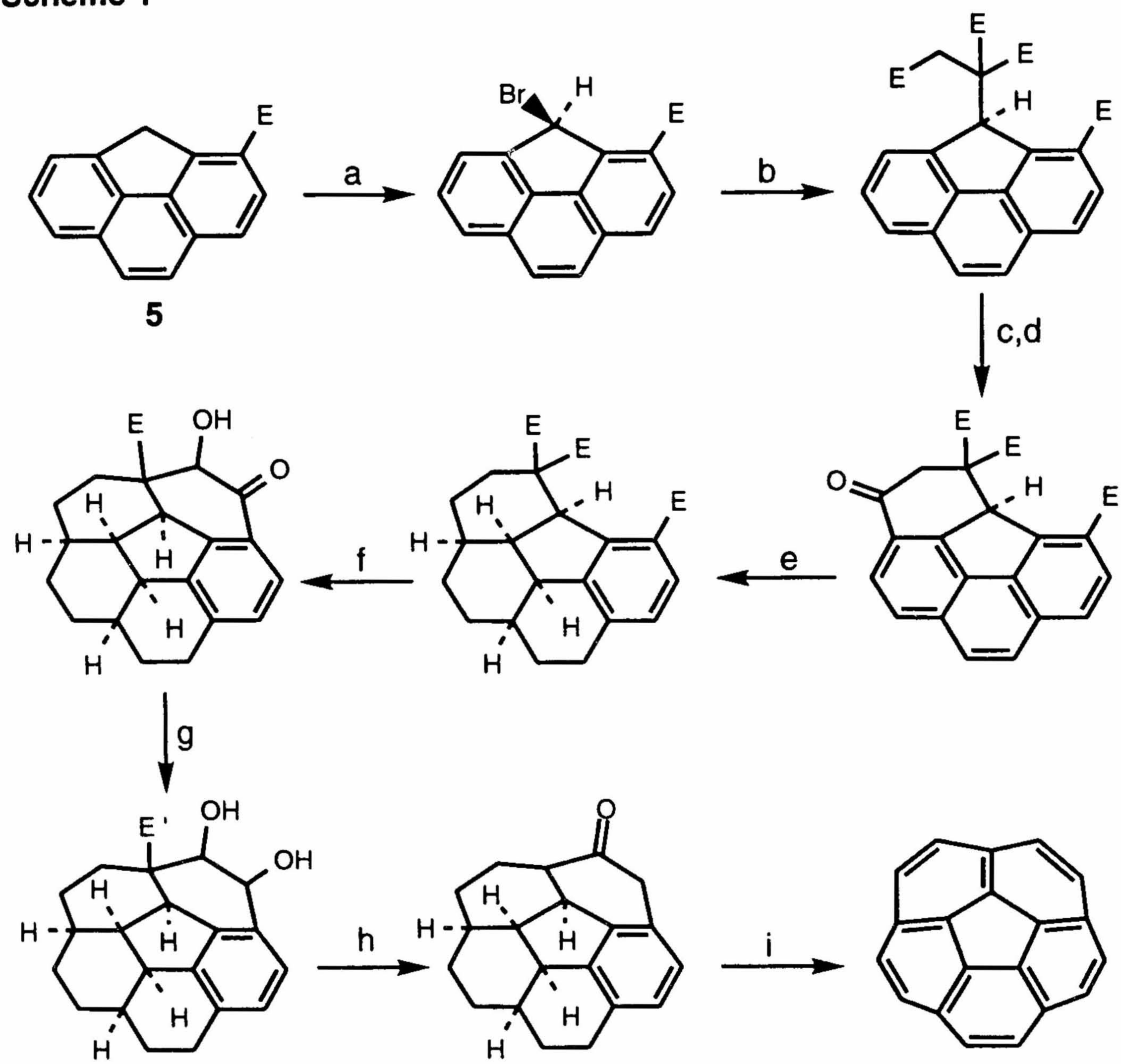
Even before the advent of fullerenes, hexacyclic bowl-shaped, $C_{20}$-corannulene **2**, composed of a five-membered ring, surrounded by ive six-membered rings, had attracted attention as a non-planar olycyclic aromatic hydrocarbon. Many interesting spectroscopic and chemical properties were anticipated of this novel hydrocarbon. Corannulene is bowl-shaped with a bowl-depth of 0.89 Å.[33] As expected, the bowl-to-bowl inversion barrier is rather modest and calculated to be

8.3 kcal/mole at MNDO and 8.8 kcal/mole at *ab initio* (STO-3G) level. Recently experimental support for bowl-to-bowl inversion has been provided on a derivative of **2** and the observed value is 10.2 kcal/mole.[34]

The first synthesis of corannulene by Barth and Lawton[35] in 1966 was hailed as a landmark synthesis of that era, Scheme 1. Their synthesis, emanating from 3-carbomethoxy-4H-cyclopenta[def]-phenanthrene **5**, was accomplished in 18 steps. The assignment of structure of corannulene followed from the single sharp peak at δ 7.81 in the $^1$H NMR spectrum and the mass peak at 250 a.m.u. The structure of corannulene was further confirmed by its X-ray crystal structure determination. The Barth and Lawton synthesis demonstrated that, given the right precursors in appropriate circumstances, curved aromatic structures can be preferred over the planar alternatives. The spontaneous creation of $C_{60}$ from graphite indicates that complete closure is also favoured.

Scott et al. have reported the synthesis of corannulene (Scheme 2) using FVP as the key technique, almost 20 years after the first synthesis of corannulene appeared in the literature.[36]

**Scheme 1**



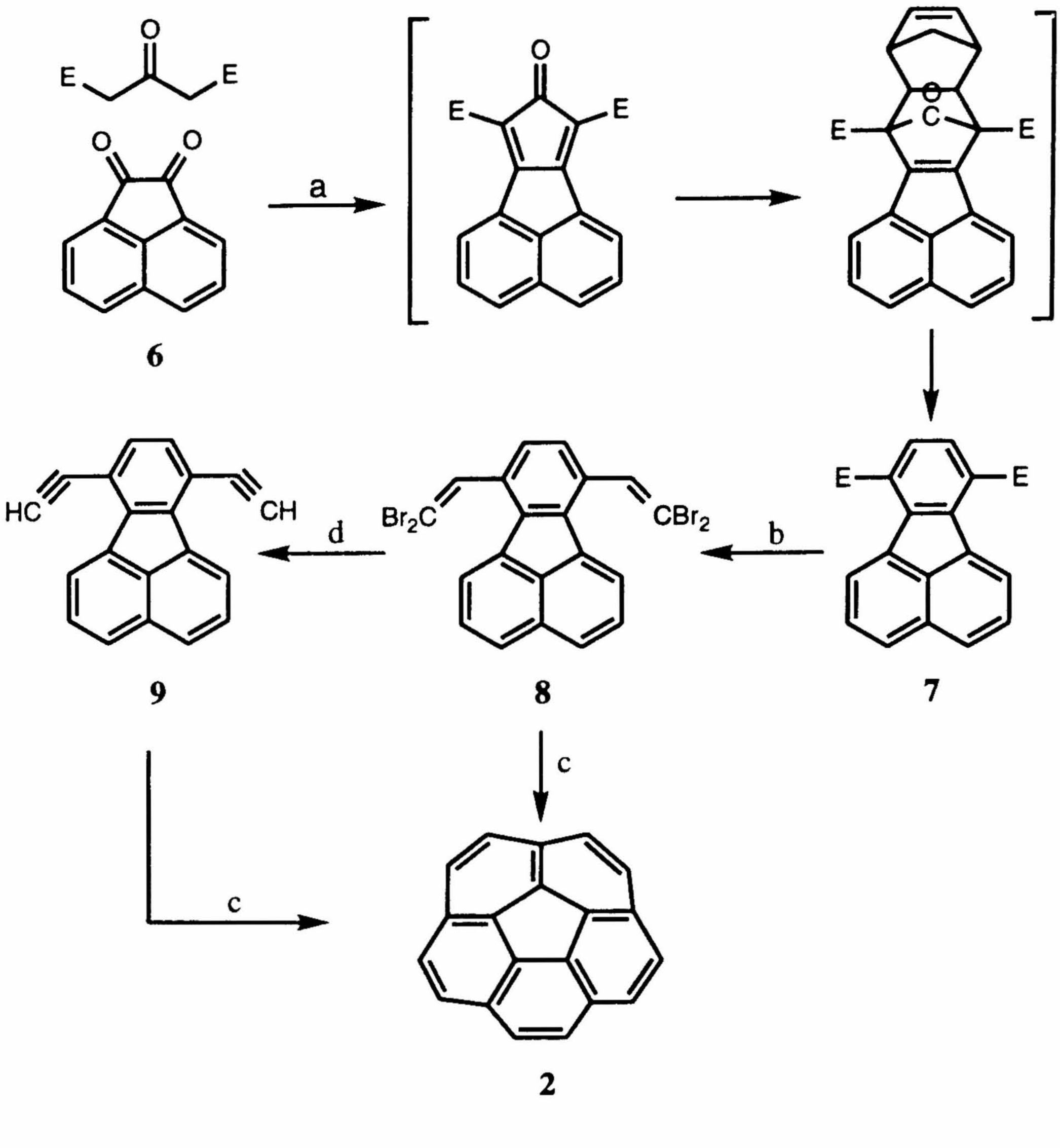

**5**

**2**

E ' = COOH, E = $COOC_2H_5$

**Reagents & Conditions:** a) NBS; b) $(COOEt)_2CHCH_2COOEt$, t-$BuO^-$ $K^+$; c) KOH; d) i. PPA, ii. $CH_2N_2$; e) 5% Pd-C, $H_2$, $CH_3COOH$; f) Na, liq. $NH_3$; g) i. $NaBH_4$, ii. KOH, n-propyl alcohol; h) 220°C; i) Pd/C, 240°C.

## Scheme 2



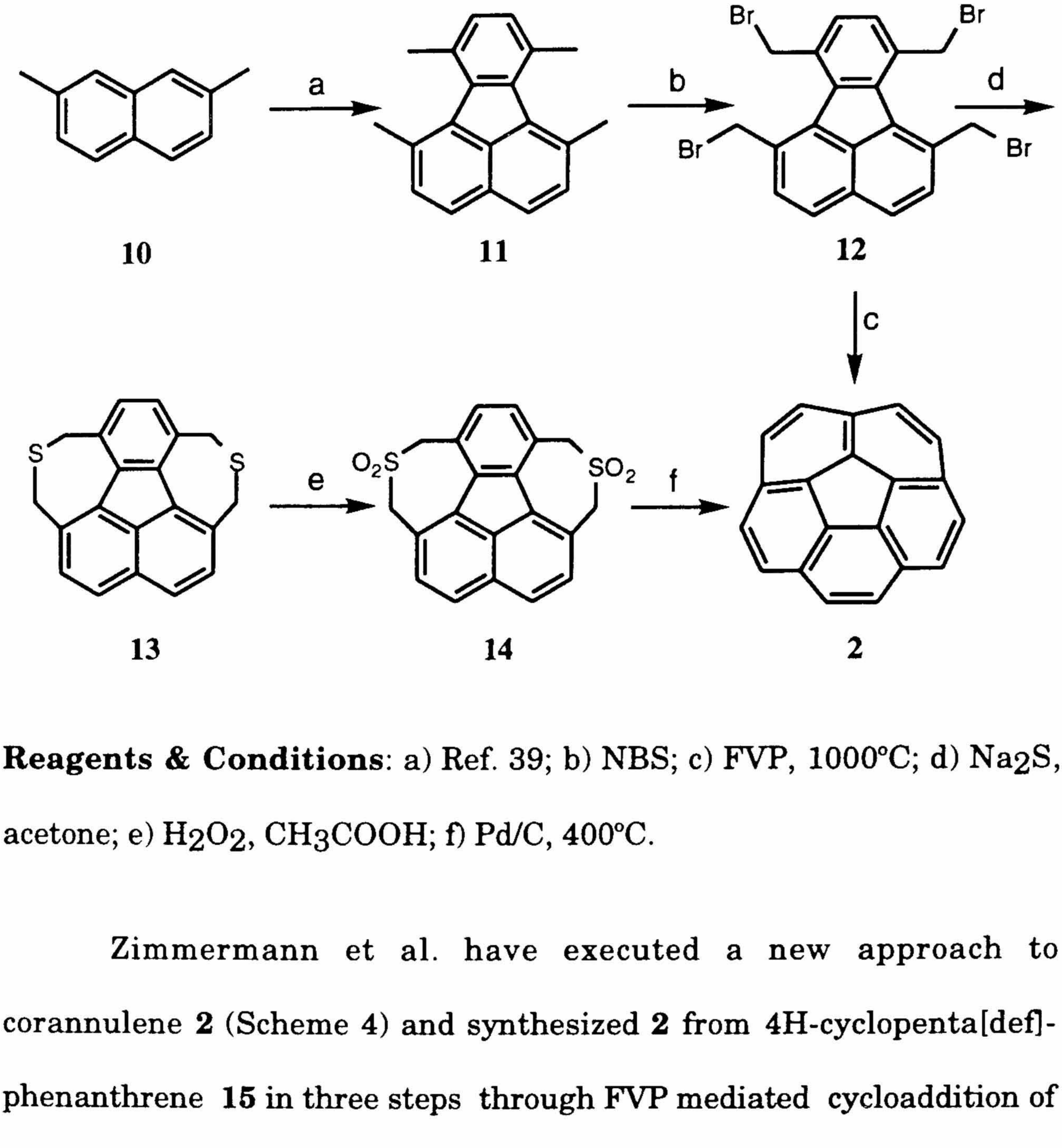

**Reagents & Conditions**: a) glycine, norbornadiene, 120°C; b) i. LAH, ii. PCC, iii. $CBr_4$, $PPh_3$, Zn; c) FVP, 1000°C; d) LDA

They prepared *bis*-acetylene **9** from 7,10-fluoranthene-dicarboxylic ester **7**,[37] a key compound prepared from acenaphthene-quinone **6**, acetonedicarboxylic ester and norbornadiene *via* the intermediacy of **8**. FVP of **9** at 1000°C furnished corannulene **2** through trapping of transient carbene *via* intramolecular C-H insertion. The tetrabromide **8** could also be converted into **2** under FVP conditions *via* electrocyclic ring closure followed by aromatization and pyrolytic loss of bromine atoms. It was also observed that when **8** was pyrolyzed under modest vacuum mono-bromocorannulene and 1,6-dibromo corannulene were also obtained along with corannulene **2**.[34]

Siegel et al. almost concurrently with Scott, reported the preparation of corannulene **2** in a short sequence[38] from 2,7-dimethyl-naphthalene **10**, Scheme 3, wherein 1,6,7,10-tetramethyl fluoranthene **11**[39] served as the key intermediate. Bromination of **11** with NBS resulted in a tetrabromo compound **12**, which on flash vacuum pyrolysis at 1000°C furnished corannulene **2**. They also synthesized **2**, using a tactic often employed in cyclophane synthesis, by displacing bromides in **12** with sodium sulfide, leading to *bis*-sulfide **13**. Further oxidation of

*bis*-sulfide **13** to the sulfone **14**, pyrolytic extrusion of $SO_2$ at 400°C, and Pd/C mediated aromatization resulted in the formation of corannulene **2**.

**Scheme 3**

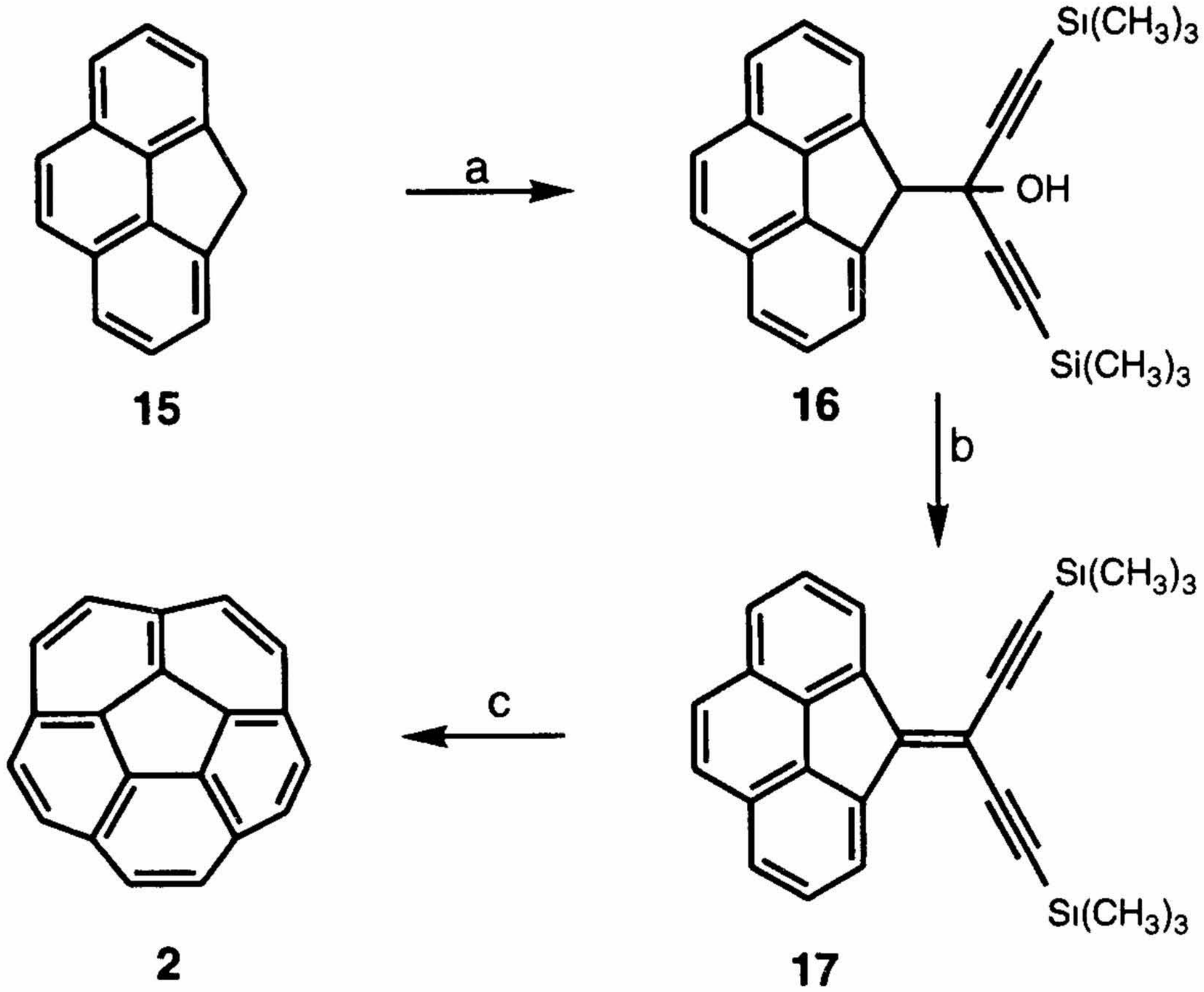



**10** **11** **12** **13** **14** **2**

**Reagents & Conditions**: a) Ref. 39; b) NBS; c) FVP, 1000°C; d) $Na_2S$, acetone; e) $H_2O_2$, $CH_3COOH$; f) Pd/C, 400°C.

Zimmermann et al. have executed a new approach to corannulene **2** (Scheme 4) and synthesized **2** from 4H-cyclopenta[def]-phenanthrene **15** in three steps through FVP mediated cycloaddition of

**Scheme 4**




**15** **16** **17** **2**

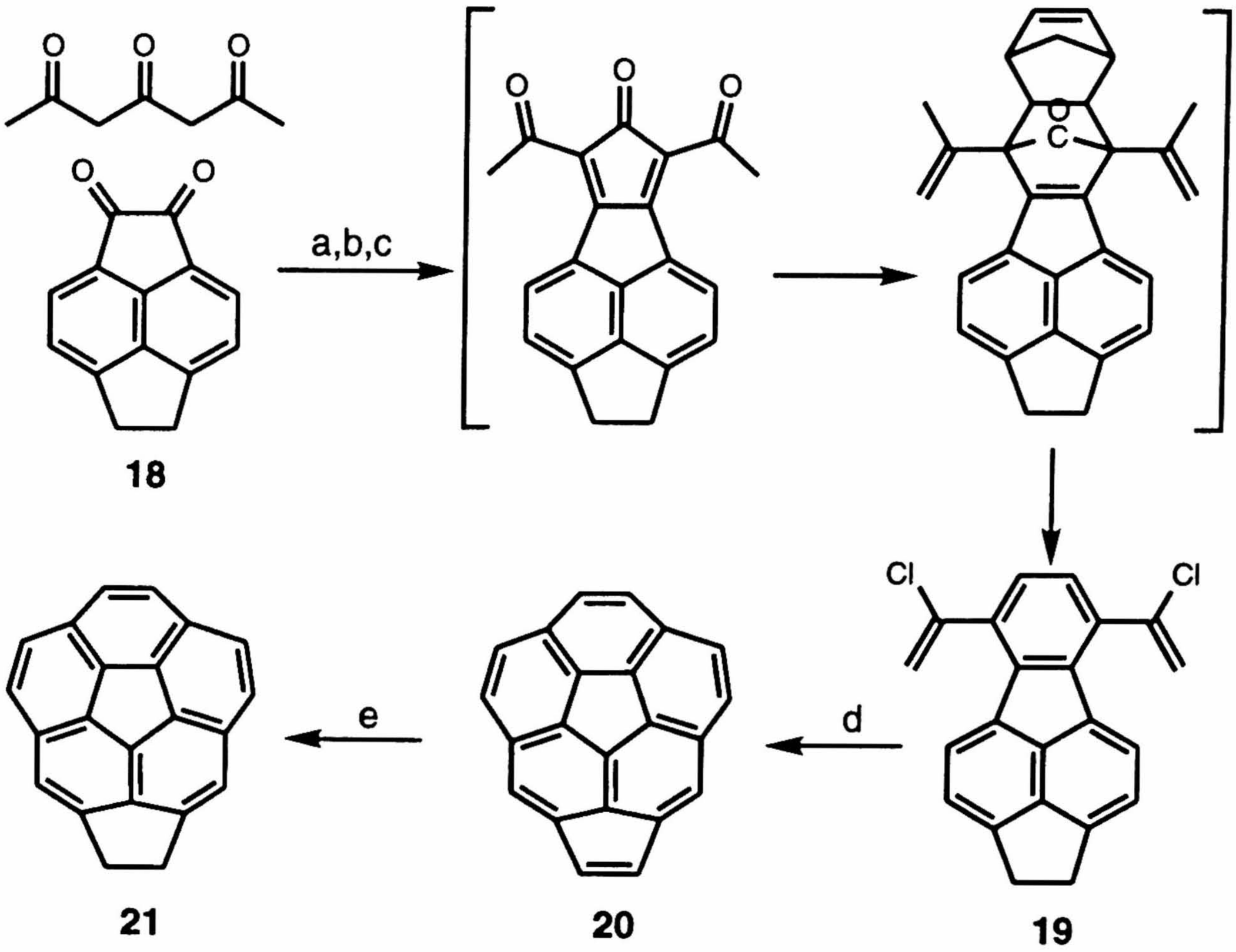
**Reagents & Conditions**: a) n-BuLi, $CO[C{\equiv}CSi(CH_3)_3]_2$; b) PTS; c) FVP

vinyl-type radicals.[40] Treatment of **15** with n-BuLi and 1,5-*bis*-(trimethylsilyl)-1,4-pentadiyn-3-one gave **16**, which on dehydration furnished 3-(4H-cyclopenta[def]phenanthrylidene)-1,5-*bis*(trimethylsilyl)-1,4-pentadiyne **17**. Flash vacuum pyrolysis of **17** in a tubular flow system using hydrogen as carrier gas at 900°C, furnished **2** along with

other PAH's like pyrene, cyclopenta[cd]pyrene, benzo[e]pyrene and benzo[ghi]fluoranthene.

To Rabideau et al. goes the credit for providing the first access to an annulated corannulene **21**, with an additional five-membered ring on

**Scheme 5**




**18** **21** **20** **19**

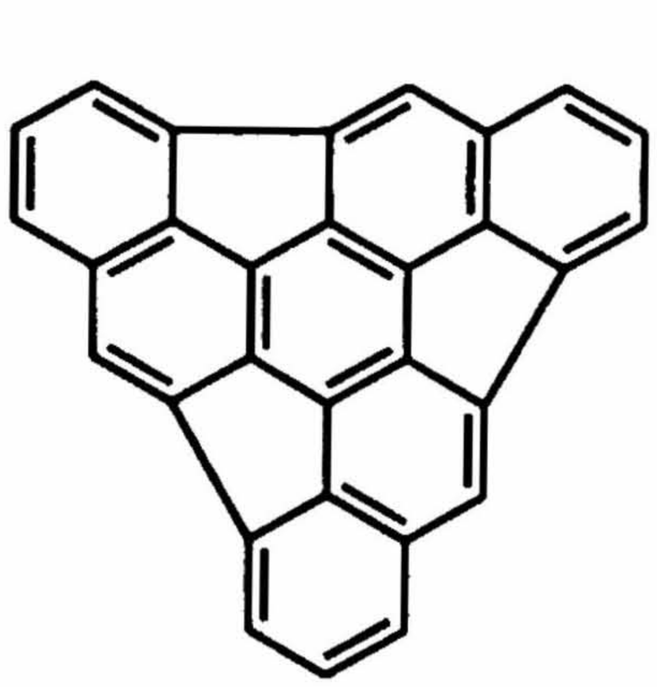
**Reagents & Conditions**: a) 2,4,6-heptatrione, MeOH, $Et_3N$; b) norbornadiene, n-BuOH; c) $PCl_5$; d) FVP, 1000°C; e) P-2 Nickel, $H_2$.

the rim.[41] Their approach is conceptually similar to Scott's and is detailed in Scheme 5. Sequential reaction between 1,2-diketopyracene **18** and 2,4,6-heptatrione followed by 4+2-cycloaddition with norbornadiene, cycloreversion (retro-Diels-Alder reaction), CO extrusion and reaction with $PCl_5$ gave **19**, in which two chlorovinyl groups were properly positioned on the fluoranthene unit. Pyrolysis of **19** was accompanied by dehydrogenation as well as fragmentation of the ethano unit, producing a mixture of **20** and corannulene. Further hydrogenation of **20** furnished cyclopentacorannulene **21**. In spite of its substantial curvature, corannulene has been shown by Scott et al. and Siegel et al. to undergo bowl-to-bowl inversion in solution. However, the work of Rabideau has shown that addition of one fused five-membered ring on to the corannulene framework raises the barrier for bowl-to-bowl inversion to 31.8 kcal/mole (calculated at HF/3-12G level) and this has not been observed experimentally for **21**.

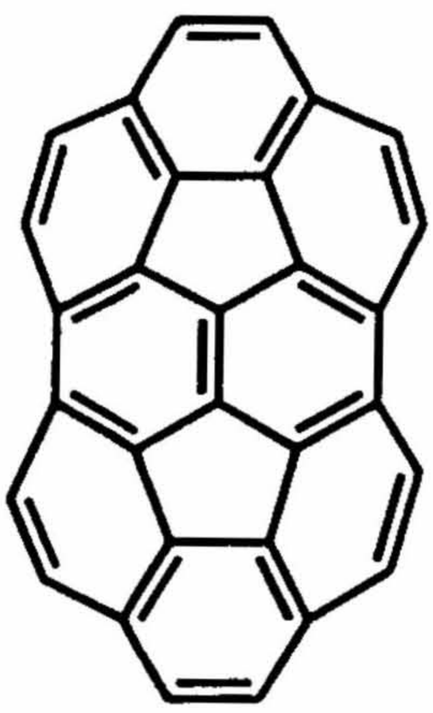
## Towards Semibuckminsterfullerenes and Related Compounds

Semibuckminsterfullerenes represent half the carbon content of $C_{60}$ and can be regarded as not only attractive pre-targets for [60]-fullerene but also interesting objectives in their own right.[42] Thus, $C_{30}H_{12}$ hydrocarbons like triindanotriphenylene **22** and 5,5-circulene **23** share common characteristics: i) 30 $sp^2$ carbon frameworks consisting of multiple fused five-membered rings that may be identified on the surface of buckminsterfullerene and ii) bowl-shaped geometries. Both **22** and **23** have received attention from theoreticians (semi-emperical and *ab initio* level calculations) as well as experimentalists. Both **22** and **23**

**Chart 4**



$C_{30}H_{12}$, **22**



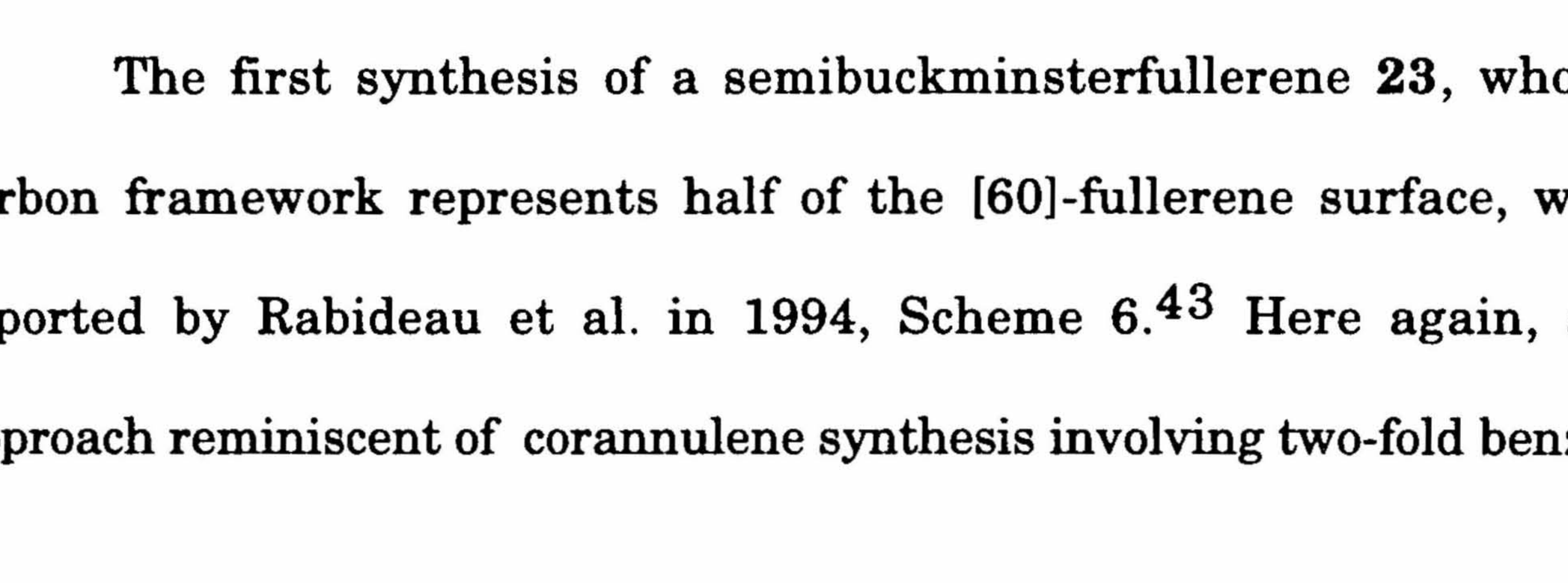
$C_{30}H_{12}$, **23**

**Semibuckminsterfullerenes**

are deep bowls and the bowl depth of **23** found to be 2.7 Å (cf. 0.89 Å in corannulene). Both of them are substantially more stable than their corresponding planar forms and are thus expected to occur exclusively in the 'bowl' form.

The first synthesis of a semibuckminsterfullerene **23**, whose carbon framework represents half of the [60]-fullerene surface, was reported by Rabideau et al. in 1994, Scheme 6.[43] Here again, an approach reminiscent of corannulene synthesis involving two-fold benzo-

**Scheme 6**



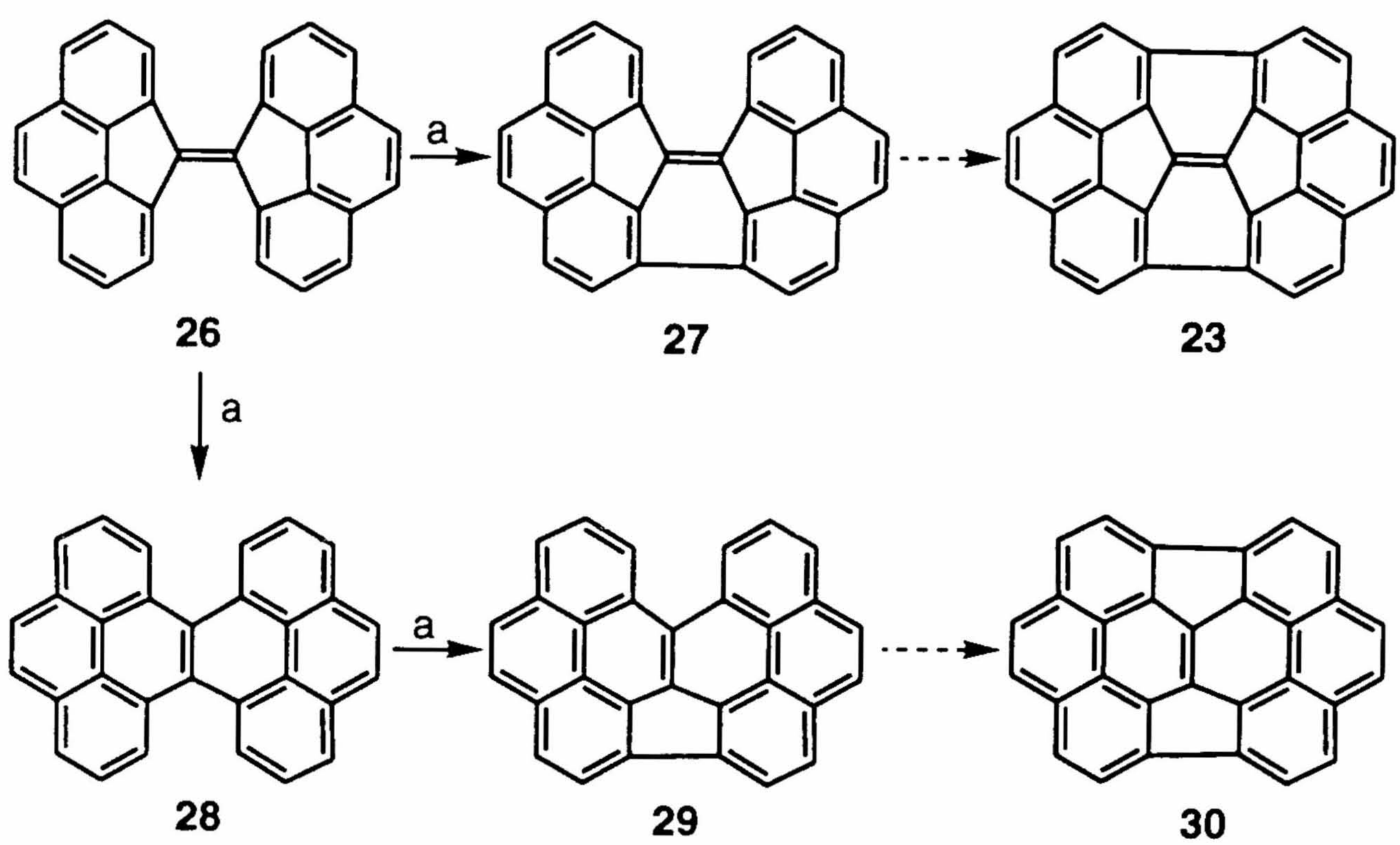

**24** **25** **23**

**Reagents & Conditions**: a) 2,4,6-heptatrione, glycine, norbornadiene; b) $PCl_5$; c) FVP.

annulation and four-fold FVP mediated cyclization proved to be rewarding

Zimmermann et al.[44] have attempted to synthesize $C_{30}H_{12}$ semibuckminsterfullerene (5,5-circulene) **23** *via* a double thermal dehydrocyclization of 4,4'-bi-4H-cyclopenta[def]phenanthrenylidene **26**,[45] Scheme 7. However, **26** showed a marked tendency to isomerize to

**Scheme 7**




**26** **27** **23**

**28** **29** **30**

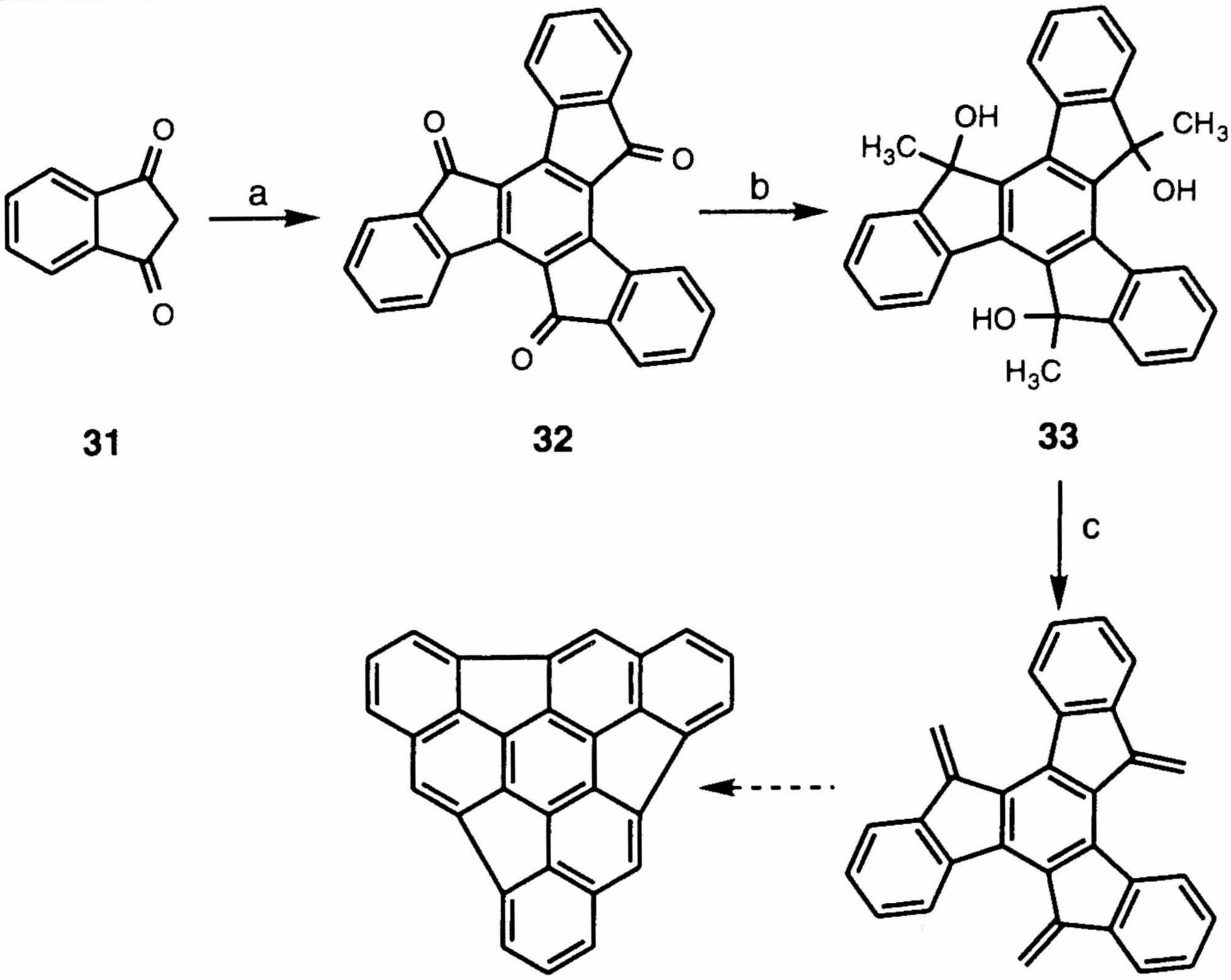
**Reagents & Conditions**: a) FVP, 850°C.

tetrabenzo[de,hi,mn,qr]naphthacene **28** *via* a homoallyl-cyclopropyl carbinyl rearrangement on heating. Thus, pyrolysis of **26** furnished **27** and **28** in 4.4% and 15%, respectively, and traces of **29**. Further attempts to cyclize **27** and **29** to **23** and **30** respectively, were not successful, since the distance between the carbon atoms is large, in the rigid frameworks of **27** and **29**.

In an effort to develop synthetic routes to cup-shaped semibuckminsterfullerene $C_{30}H_{12}$ **22** and polycyclic aromatic compounds related to fullerenes, De Lucchi et al. considered the synthesis of truxenene **34** and its derivatives, Scheme 8.[46]

Tribenzo[afk]triindenone **32** (truxenone) obtained by sulfuric acid treatment of 1,3-indanedione **31** was reacted with $CH_3Li$ to afford a mixture of two possible isomeric alcohols **33**. Dehydration of **33** by simple heating furnished the dehydrated product **34**.. However, efforts towards the ring closure of vinyl groups on to the aromatic ring in **34** by thermal and photochemical methods to yield **22** have failed.

**Scheme 8**



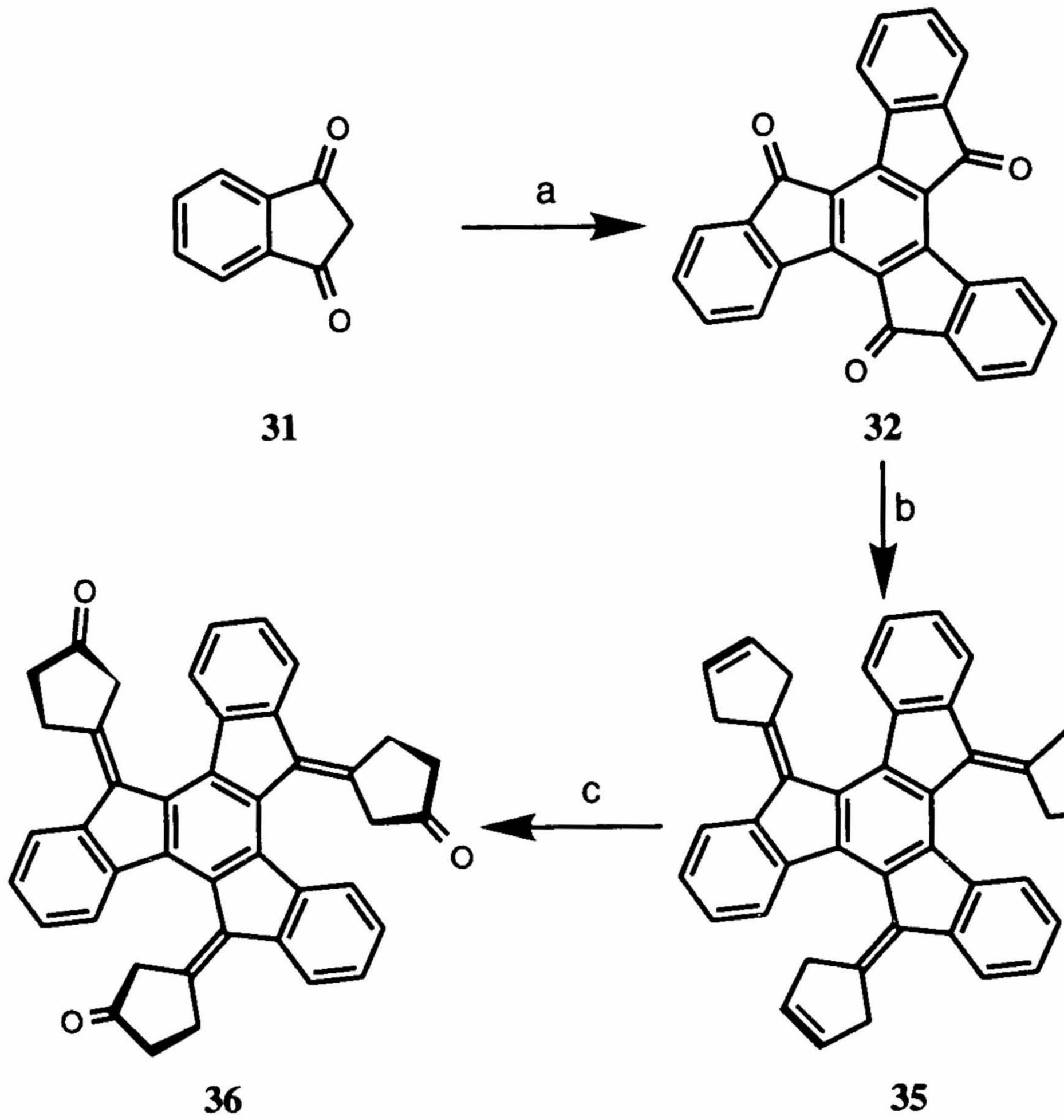

**31** **32** **33**

**22** **34**

**Reagents & Conditions**: a) $H_2SO_4$; b) $CH_3Li$; c) Δ, neat.

In their efforts to make a possible precursor of $C_{60}$ *via* a [30C+30C] route, Chapman and his group have prepared the $C_{30}$-compound **36** as shown in the Scheme 9.[47] The triketone **36**, containing six of 12 five-membered rings in $C_{60}$, was synthesized from 1,3-indane-

**Scheme 9**



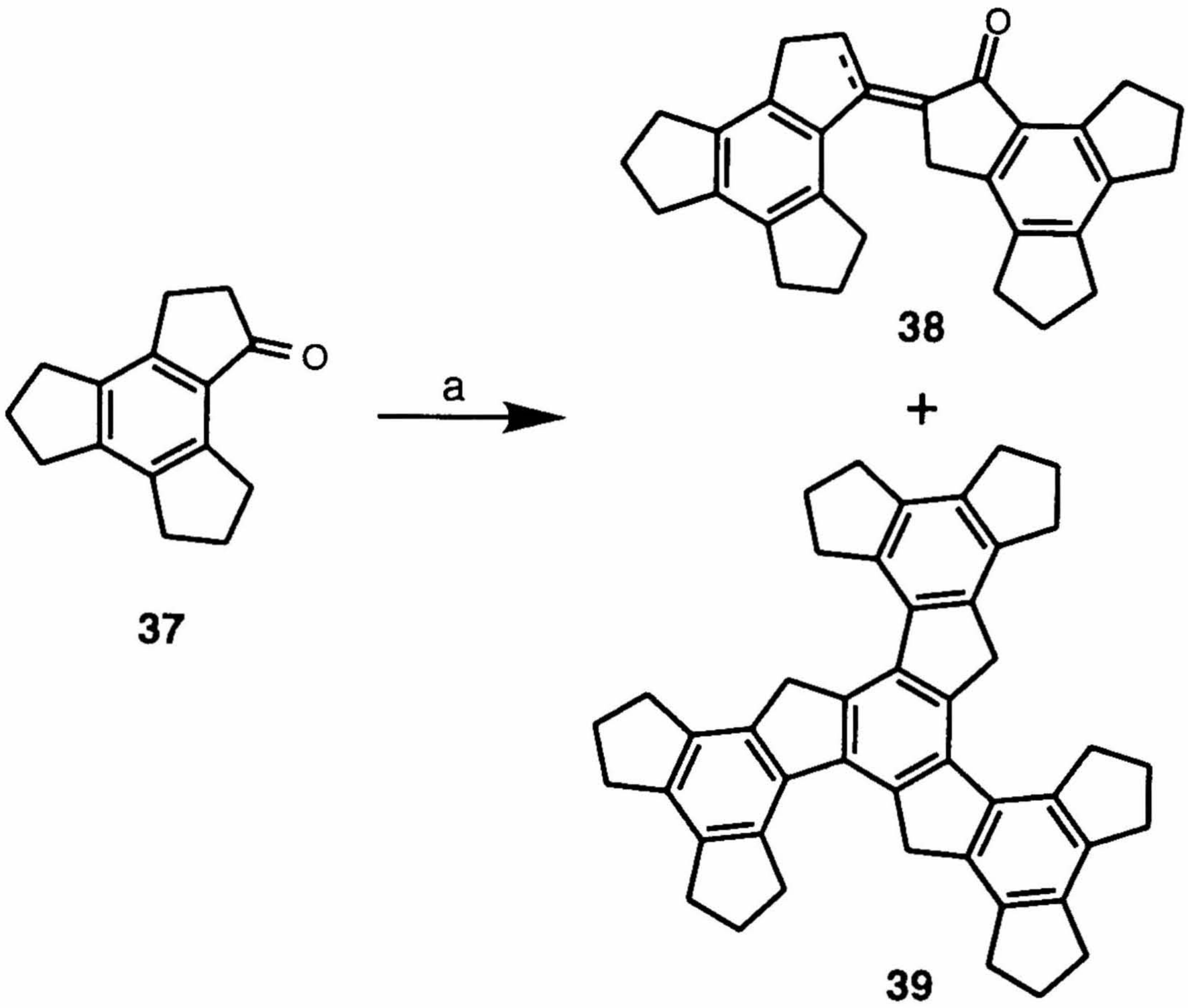

**Reagents & Conditions**: a) $H_2SO_4$; b) RMgBr, $H_2SO_4$/AcOH; c) $RBH_2$, $H_2O_2$/NaOH.

dione **31** in only a few steps *via* the novel hydrocarbon **35**, a severely distorted nonplanar molecule according to X-ray crystallographic studies.

The triketone **36** could yield a spherical structure with 60 carbon atom correctly positioned for $C_{60}$ closure, through a three- fold McMu coupling.

In one of the early approaches to $C_{60}$, Rassat et al. have follow the [45C+15C] approach and the fragment **39** was prepared through condensation reaction, Scheme 10.[48] When 1-triindanone **37** (prepare

**Scheme 10**



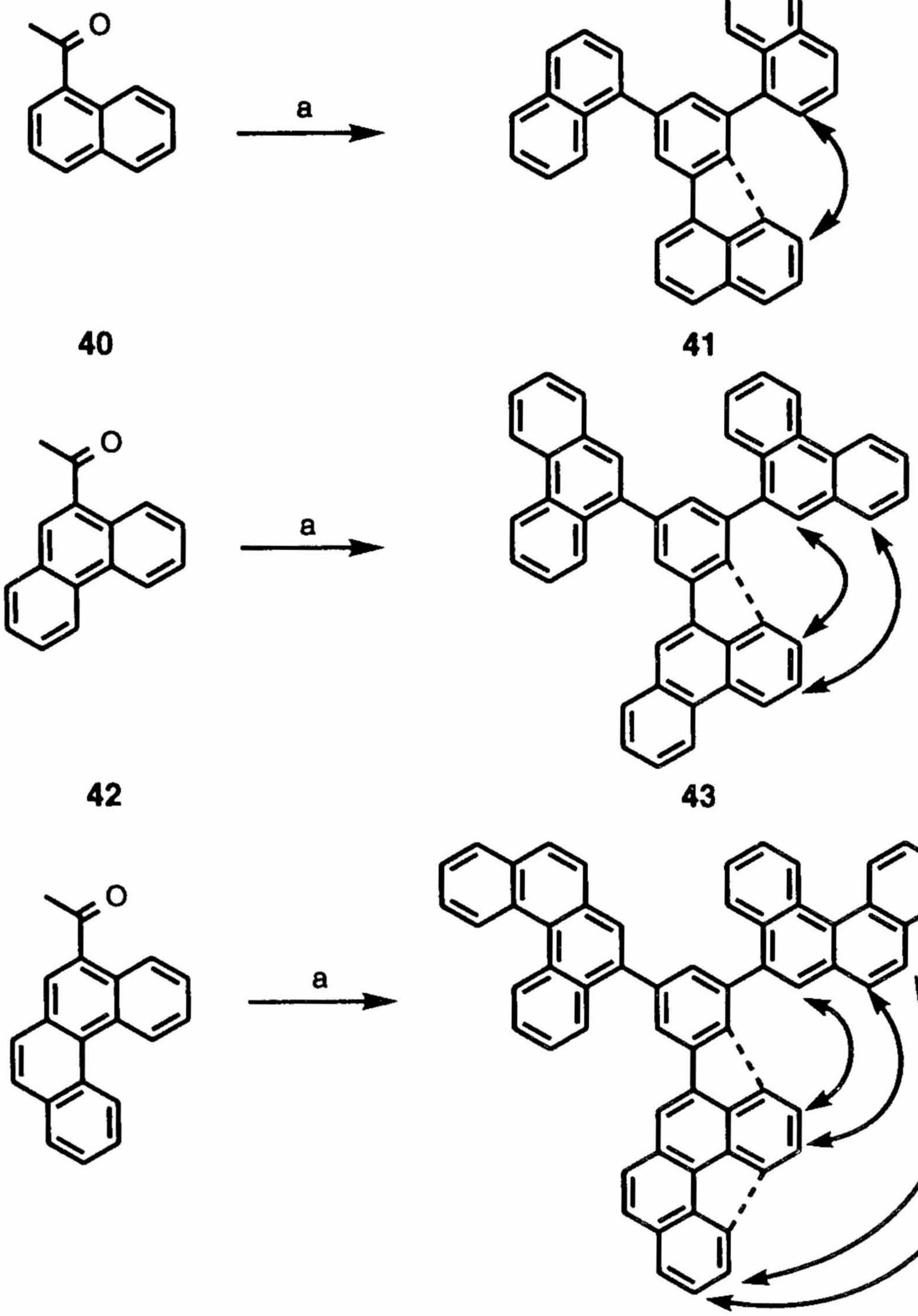

**37**

**38**

**39**

**Reagents & Conditions**: a) p-toluenesulfonic acid, reflux

**Scheme 11**

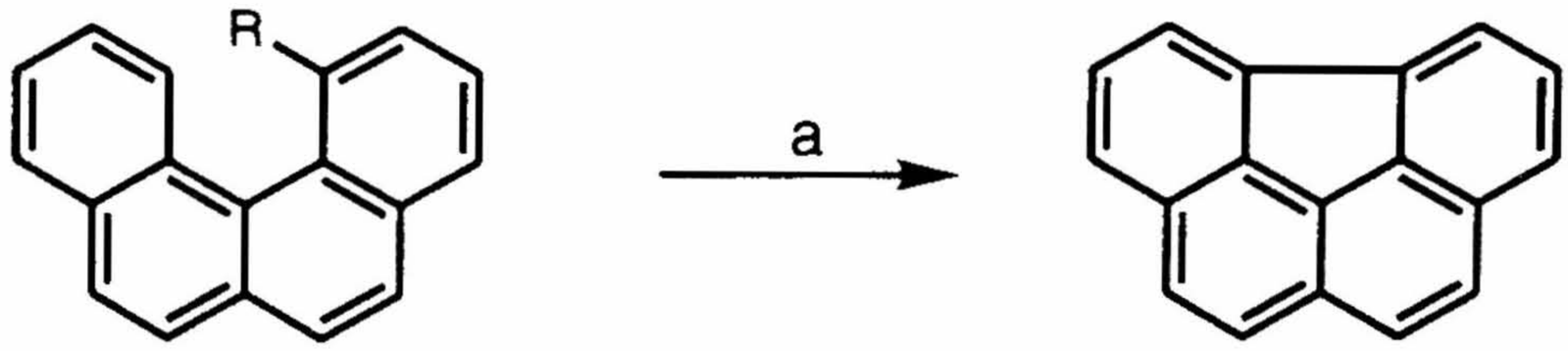



**Reagents & Conditions**: a) $SiCl_4$, EtOH, reflux

by oxidation of triindane) was treated with p-toluenesulfonic acid, two related condensation products, a dimer $C_{30}H_{30}O$ **38** and a trimer $C_{45}H_{42}$ **39** were obtained having connectivities present in $C_{60}$. However, further elaboration of either **38** or **39** could not be achieved.

Plater, in his work towards the synthesis of the bowl-shaped sub-units of $C_{60}$, has considered the intramolecular dehydrogenative aryl-aryl coupling reactions, Scheme 11.[49] The ketones **40**, **42** and **44** when treated at room temperature or under reflux in $SiCl_4$-EtOH milieu furnished the tricyclized products **41**, **43** and **45**, respectively. Compound **45** is a unimolecular precursor, which under suitable gas phase dehydrogenation conditions, could close like the petals of a flower to form $C_{60}$.

**Scheme 12**



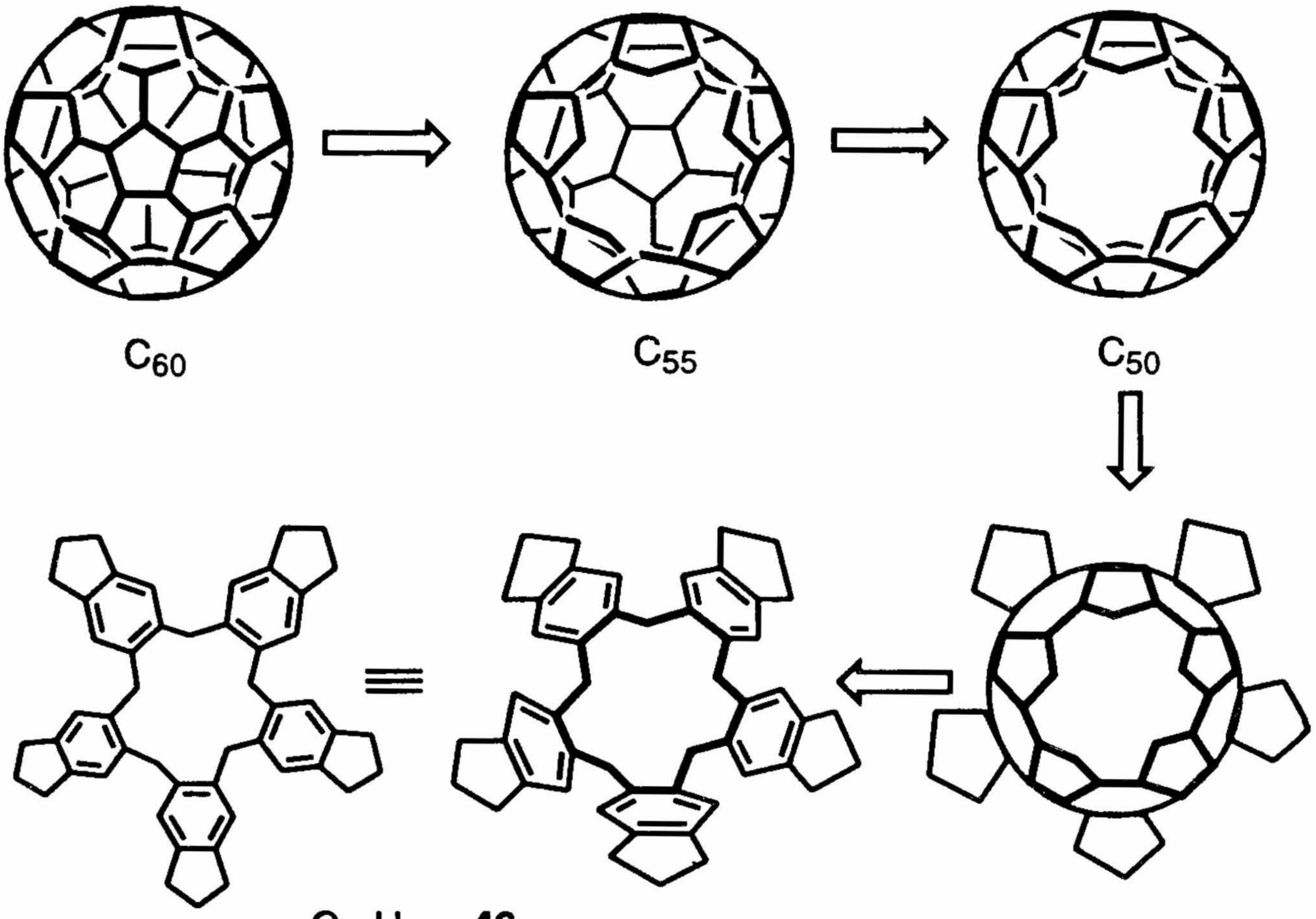

R = F, Cl

**Reagents & Conditions**: a) Flash vacuum pyrolysis, 1000°C

In the above context, to promote thermal aryl-aryl coupling, Plater has demonstrated the utility of halogen functionality, particularly the fluoro group, Scheme 12.[50]

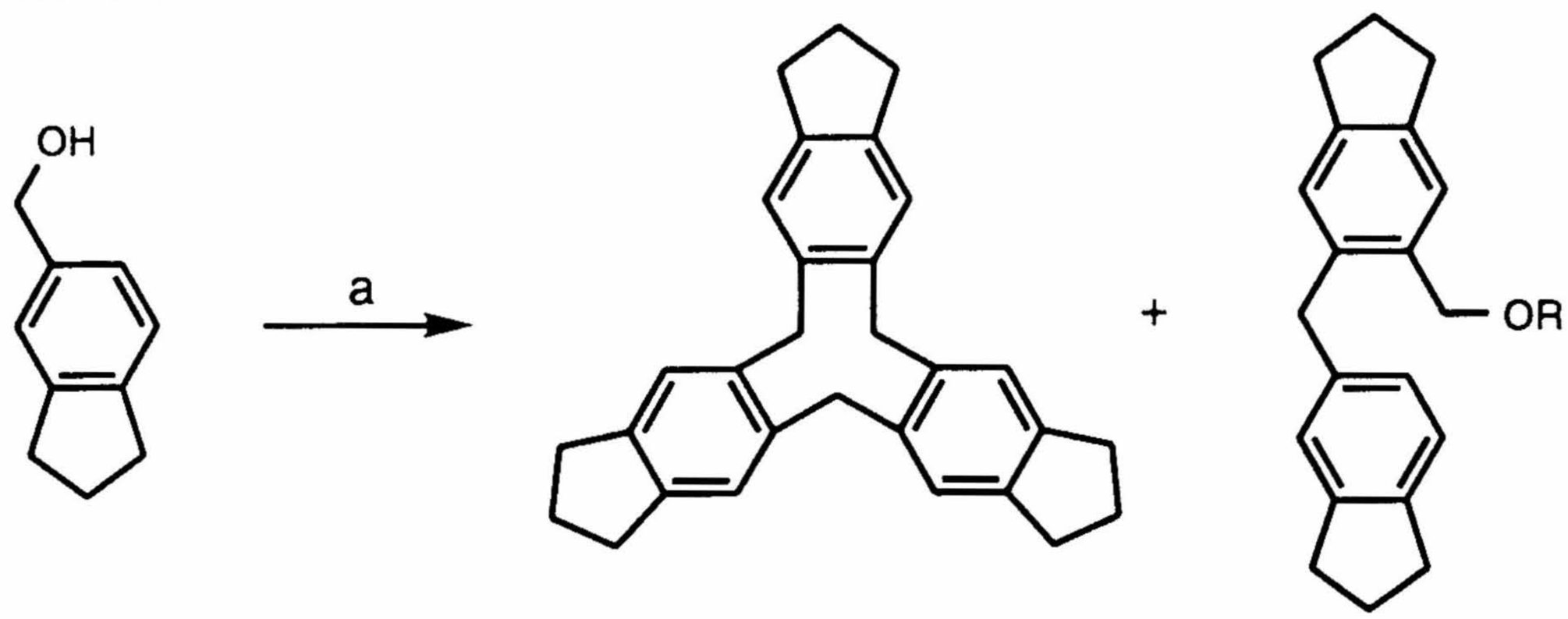
Magnus et al. have considered the ortho-cyclophanes with indanyl systems, as the potential precursors to fullerenes, Scheme 13.[51] They considered the synthesis of a cyclophane **46** (having a molecular formula $C_{50}H_{50}$), in which five-indanyl moieties are attached in a cyclic

**Scheme 13**



fashion. While this approach looks impressive in terms of retrosynthetic analysis shown in Scheme 13, in practice, very little could be accomplished and the results of the initial study leading to the formation of cyclo[3]$CH_2$-[3]indane **48** *via* a cyclic oligomerization of indane-5-carbinol **47** is shown in Scheme 14.[51]

**Scheme 14**




**47** **48** **49**

**Reagents & Conditions**: a) p-toluenesulfonic acid, reflux

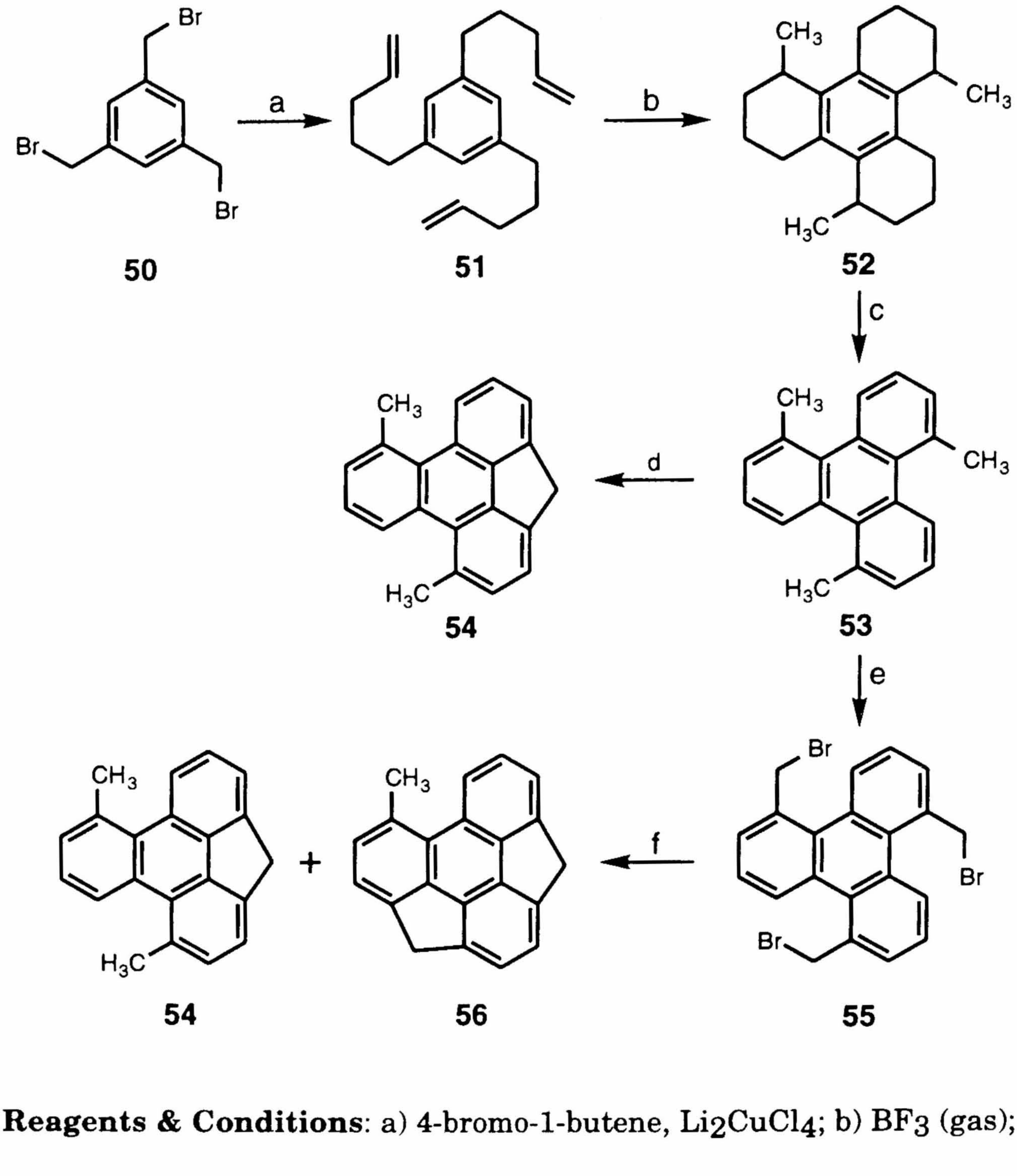
## Sumanene and Related Compounds

An alternative building block for [60]-fullerene, consisting of a central hexagon surrounded by alternate pentagons and hexagons has been considered by Mehta et al. wherein the presence of pentagons

would ensure the curling up of the molecule. Models reveal that this molecule is shaped like a flower, with the rings forming the petals. With a typical organic chemists's penchant for inventing colorful trivial names, the $C_{21}$ hydrocarbon has been christened 'sumanene' (derived from suman, meaning flower in Hindi and Sanskrit).[52] Sumanene **3**, like corannulene **2** and paracylene **4**, is an attractive synthetic target. It has a bowl-shaped geometry with a bowl depth of 1.15 Å which is more than 0.89 Å of corannulene.[31] Mehta et al. have reported their efforts towards the synthesis of sumanene maintaining $C_3$-symmetry throughout and using flash vacuum pyrolysis as the key step, Scheme 15.[52]

Dilithium tetrachlorocopper catalyzed reaction between 1,3,5-*tris*(bromomethyl)benzene **50** and the Grignard reagent (prepared from 4-bromo-1-butene) furnished the 1,3,5-tripentenylated benzene **51**, which on exposure to gaseous $BF_3$ smoothly cylized to tetracycle **52**. DDQ dehydrogenation of **52** furnished 1,5,9-trimethyltriphenylene **53**. Pd/C mediated dehydrogenation of **53** furnished the mono-bridged compound **54** but further cyclo dehydrogenation under FVP conditions was not successful. Alternately, the three methyls were converted to bromo-

## Scheme 15




**50** **51** **52** **53** **54** **55** **56**

**Reagents & Conditions**: a) 4-bromo-1-butene, $Li_2CuCl_4$; b) $BF_3$ (gas); c) DDQ; d) Pd/C, 400°C; e) NBS; f) FVP, 900°C.

methyl functionality and the flash vacuum pyrolysis of tribromomethyl derivative **55** furnished the di-bridged compound **56** along with mono-bridged compound **54**. The failure of the third cyclization leading to sumanene **3** was attributed to the large distance between the carbon atoms which are thought to participate in the formation of the supplementary C-C bond and the high strain involved in the last ring closure because of rigid framework. The synthesis of sumanene **3**, remains elusive.

Having given a brief review of the work of various researchers in this area, it is now time for us to unravel our efforts towards the bowl-shaped fullerene fragments.

We have attempted to synthesize higher fullerene fragments which are deep bowls of $C_3$-symmetry and bear close resemblance to $C_{60}$. Since the work on synthesis of sumanene was in progress in our laboratory, we have also made an attempt towards supplementing these ongoing efforts. Our efforts towards these objectives forms the main body of this thesis and the results are discussed in detail in the following section.

# Results and Discussion

Synthetic routes to architecturally complex polycyclic molecules are commonly delineated through retrosynthetic analysis based on logical bond disconnections.[53] Therefore, as a first step towards unraveling a synthetic route to **1**, we subjected it to a retrosynthetic operation, keeping in mind two important considerations

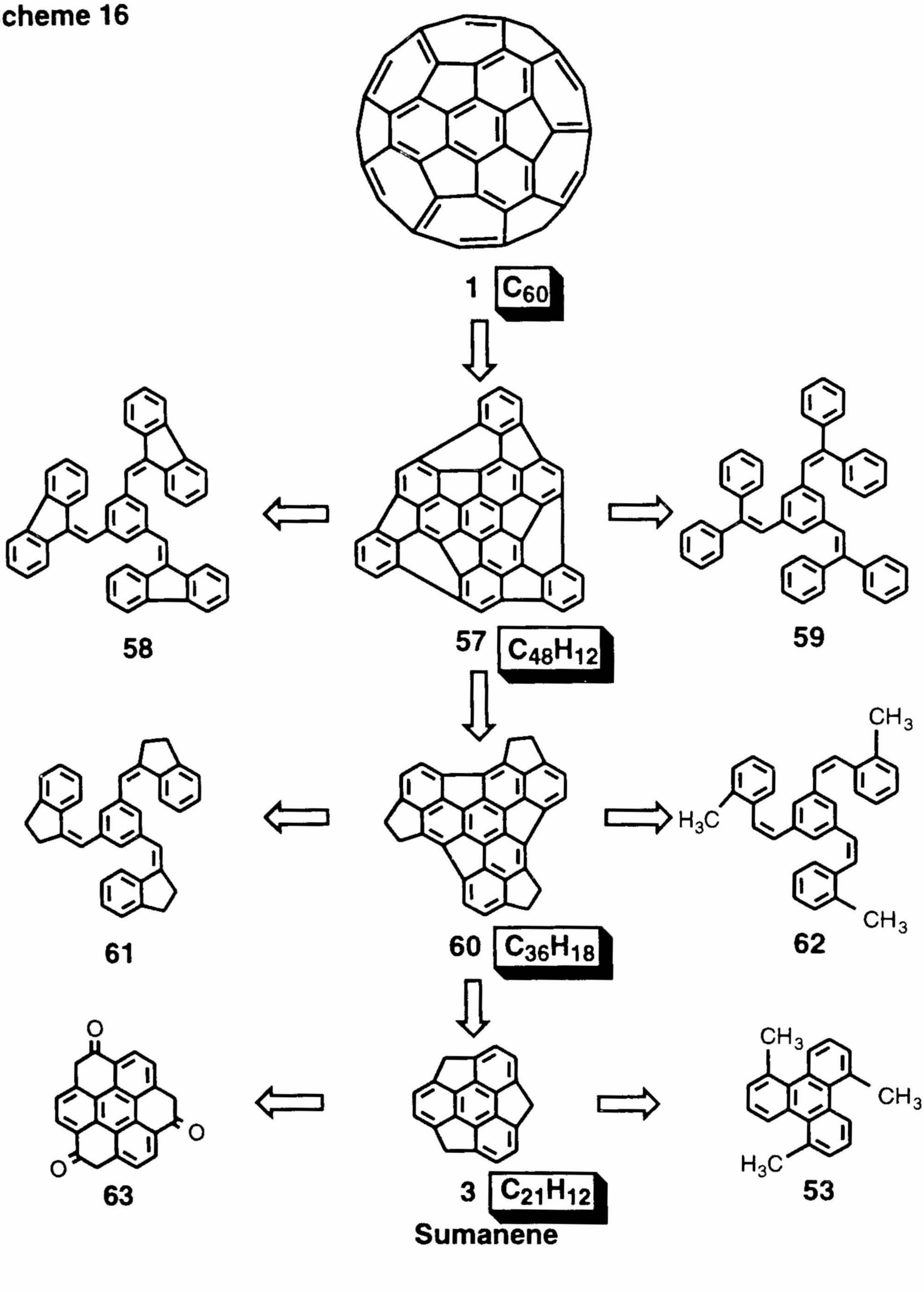
In view of the highest possible symmetry ($I_h$) present in buckminsterfullerene **1**, the symmetry element of the precursors generated through 'bond-disconnections' was a major concern. It was deemed essential to identify the main building block of high symmetry and to maintain its symmetry profile in advanced intermediates *en route* to **1**. This was expected to be of immense help in the firm characterization of intermediates in smaller quantities by imparting definitive spectroscopic behaviour. The other important consideration in delineating a retrosynthetic theme to **1** was to ensure that all chemical operations be performed in manifold manner. Simultaneous, identical manipulations at several different sites in the intermediates would render the synthesis short and greatly reduce the total number of steps

Needless to add that this factor would only supplement the earlier symmetry-based considerations.

The primary task in the synthetic endeavour towards [60]-fullerene is the identification and assembly of smaller, readily recognizable structural fragments that can be further built upon. The retrosynthetic analysis of [60]-fullerene along different symmetry pathways is depicted in Scheme 1. Retrosynthetic analysis of **1** along $C_3$-symmetry route led to the identification of three major 'bowl-shaped' fragments, $C_{48}H_{12}$ **57**, $C_{36}H_{18}$ **60** and $C_{21}H_{12}$ **3**, containing 19, 13 and 7 rings respectively, whose structural presence can be readily recognized in the [60]-fullerene framework, Scheme 16.

The $C_{48}H_{12}$ hydrocarbon **57**($C_{60}$-$C_{12}$+$H_{12}$, 19 rings), a tri-benzo-fenced, deep-bowl of $C_3$-symmetry attracted our immediate attention. Its MMX energy minimized structure is shown in Fig. 1. Further bond disconnections in fragment **57** along the $C_3$-symmetry route led to the key precursors **58** and **59** which appeared much less formidable. In a similar manner retrosynthesis of the shallow "bowl" **60** (MMX energy minimized structure, Fig. 2) along the $C_3$-symmetry route

**Scheme 16**



led to the identification of the key precursors **61** and **62**. Once again **61** and **62** could be recognized in terms of more familiar structural entities We have ventured to explore routes to both **57** and **60**.

Earlier studies from our research group had identified sumanene **3** (MMX energy minimized structure in Fig. 3), a $C_{21}H_{12}$ hydrocarbon, as an important structural fragment of [60]-fullerene. A facile route to this hydrocarbon *via* a $C_3$-symmetry triphenylene has been explored earlier.[52] As a continuation of this theme we have attempted to synthesize functionalized triphenylene derivatives *en route* to functionalized sumanene derivatives.

While formulating and evaluating the retrosynthetic theme in Scheme 16, we also addressed ourselves to the key issue of transforming the pivotal and largely of planar precursors **53**, **58**, **59**, **61**, **62** and **63** to their cyclized and non-planar, 'bowl-like' structures like **57**, **60** and **3**. Such a prospect did look formidable and awesome, but we hoped that photochemical electrocyclizations and thermal cyclizations would prove effective at least in some cases. We derived encouragement from the success of FVP technique[54] in the case of corannulene and our own positive results in the context of sumanene.

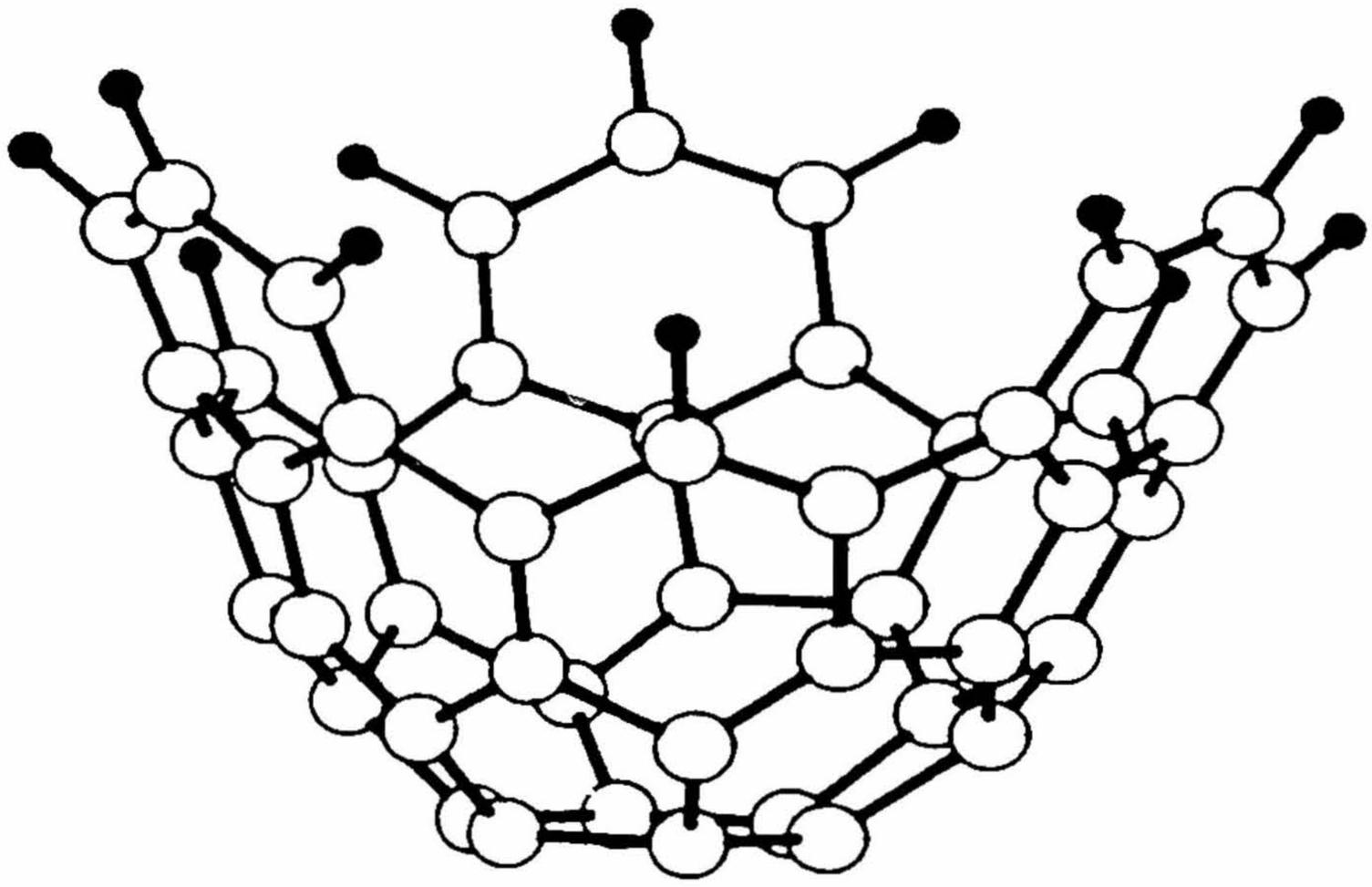


**Figure 1. MMX energy minimized structure of $C_{48}H_{12}$**

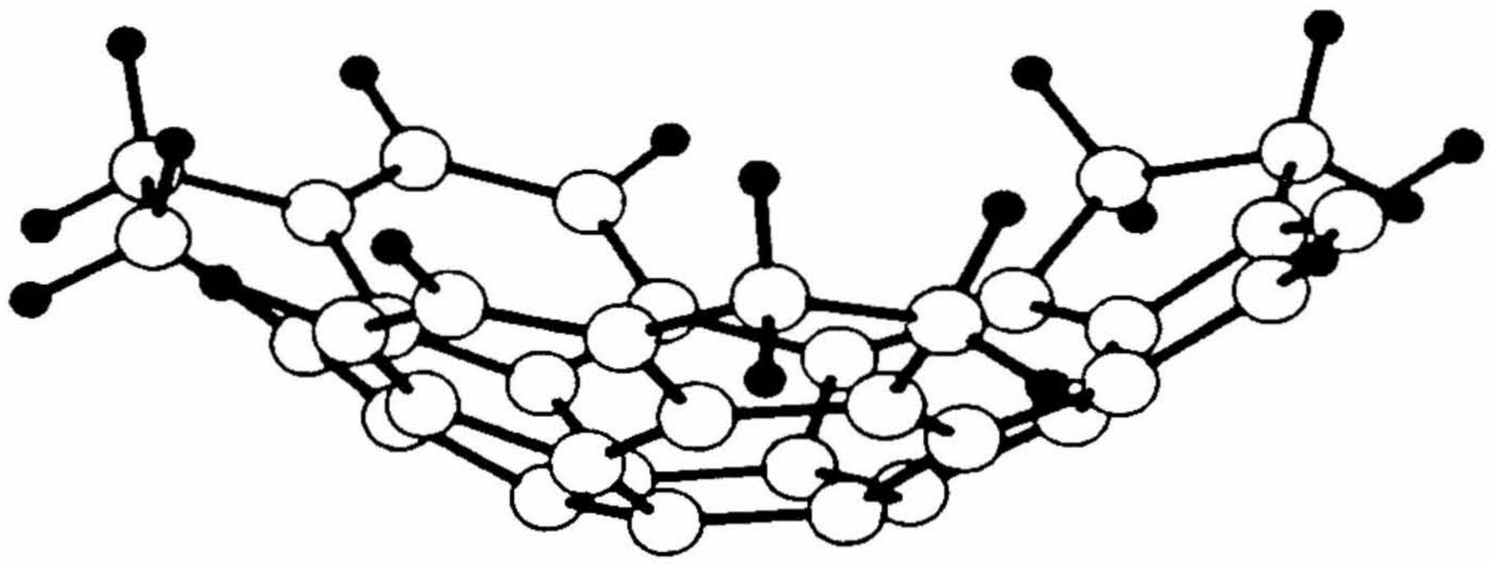


**Figure 2. MMX energy minimized structure of $C_{36}H_{18}$**

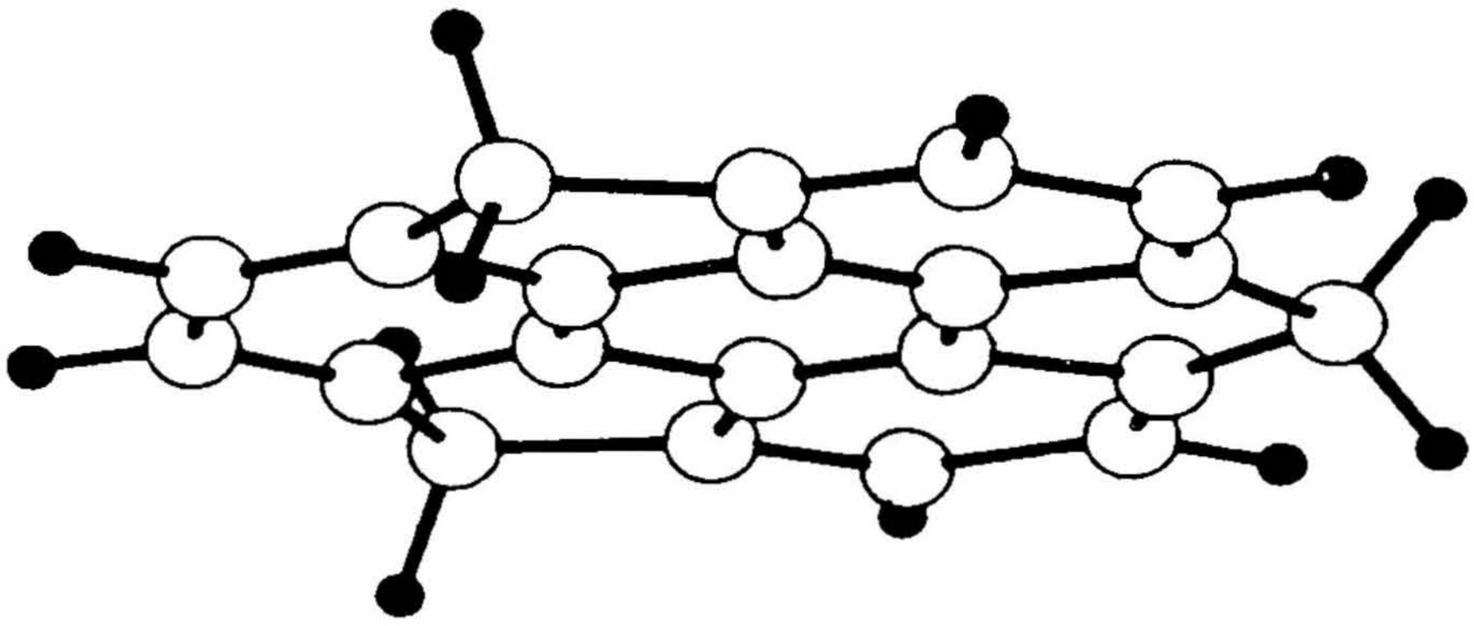
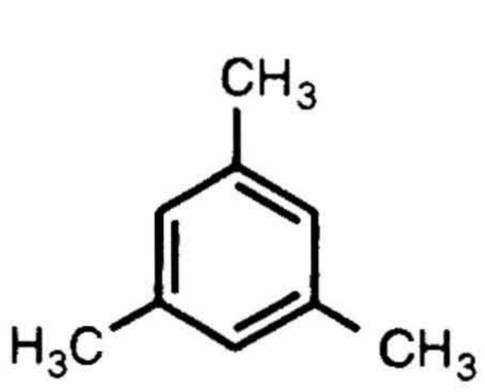


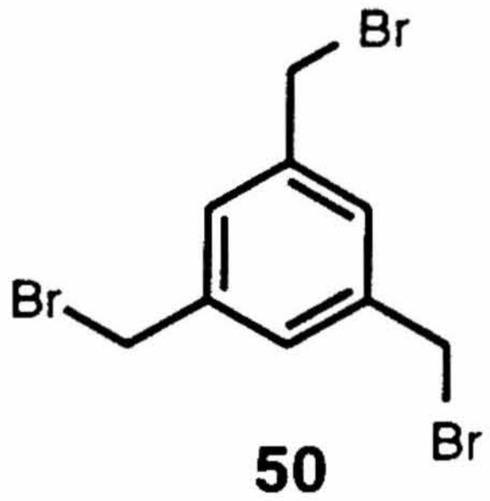
**Figure 3. MMX energy minimized structure of $C_{21}H_{12}$**

Since the intent was to explore a $C_3$-symmetry route to fullerenes as per the retrosynthetic protocol, manipulation at three different positions was simultaneously required. Hence, it was considered appropriate to employ symmetrically substituted benzene derivatives, having $C_3$-symmetry, as synthons. Consequently, mesitylene **64**, 1,3,5-*tris*(bromomethyl)benzene **50** and 1,3,5-triformylbenzene **65** were identified as starting materials (Chart 5), which were either commercially available or could be prepared through straightforward literature procedures.

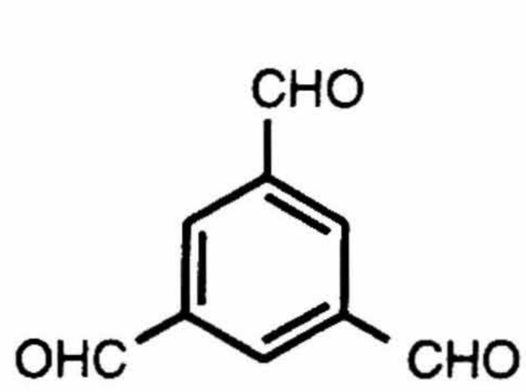
**Chart 5**



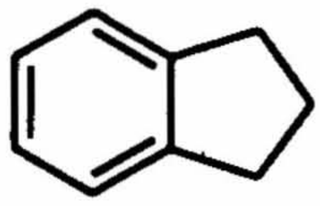
**64**



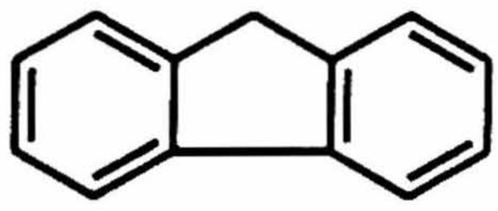
**50**



**65**



**66**



**67**

Similarly, the structural features of **57** and **60** indicate the persistent presence of aromatic 6,5-fused moieties. Thus, it appeared

most appropriate to deploy indane **66** and fluorene **67** derived derivatives as reaction partners for **50, 64** and **65**. An advantageous factor of **66** and **67** is that they can be readily activated to reactive nucleophilic species

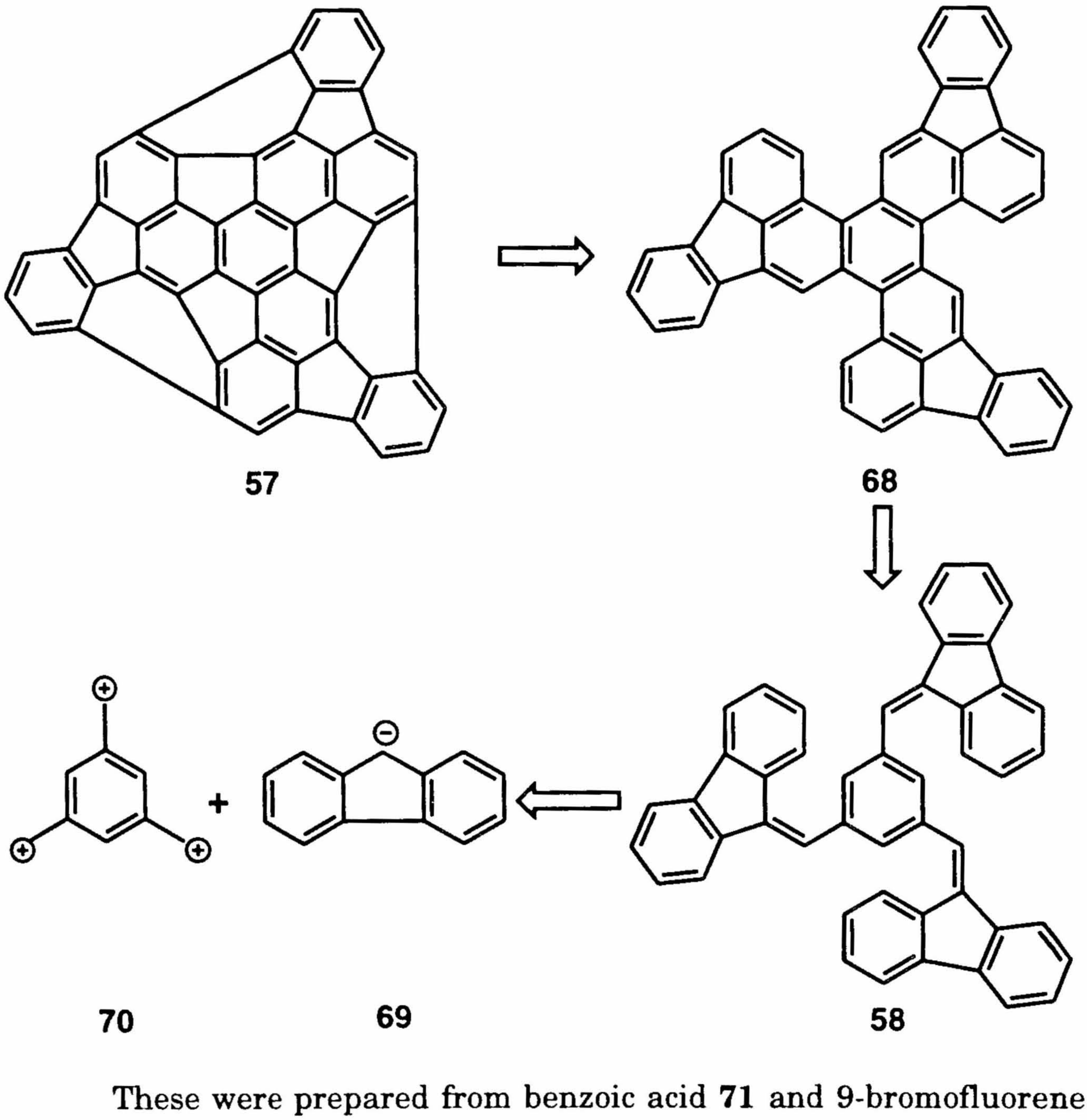
While aiming at the key precursors **57**, **60** and **3** we identified **53**, **58**, **59**, **61**, **62** and **63** as important and substantial sub-goals. To an extent, these projected subgoals *en route* to **57**, **60** and **3** have been realized However, the target molecules **57**, **60** and **3** have eluded us so far due to many unforeseen deviations arising out of the unpredictable and devious behaviour of intermediates. The execution of the synthetic strategies delineated through retrosynthetic theme depicted in Scheme 16, is described herein

## Synthetic Studies Towards $C_{48}H_{12}$ (57) and $C_{36}H_{18}$ (60) Fragments

The $C_{48}H_{12}$ fragment **57** of [60]-fullerene, which is a tribenzo-fenced 'deep-bowl' of $C_3$-symmetry, was chosen as our initial and most formidable objective. Retrosynthetic analysis of fragment **57** along $C_3$-symmetry route led to the precursors **68** and **58**, Scheme 17.[55] As a result of this retrosynthesis, an exceptionally short route to the fragment **57** was envisioned in which its 48 carbons were sought to be assembled in one step from commercially available starting materials, like fluorene **67** and mesitylene **64** through pre-installed complementary functionalities **69** and **70**, Scheme 17. While several options were considered for generating species equivalent to **69** and **70**, the Wittig reaction between 1,3,5-triformylbenzene **65** and the ylide **75** prepared from fluorene was considered to be most convenient, for directly delivering **58**.

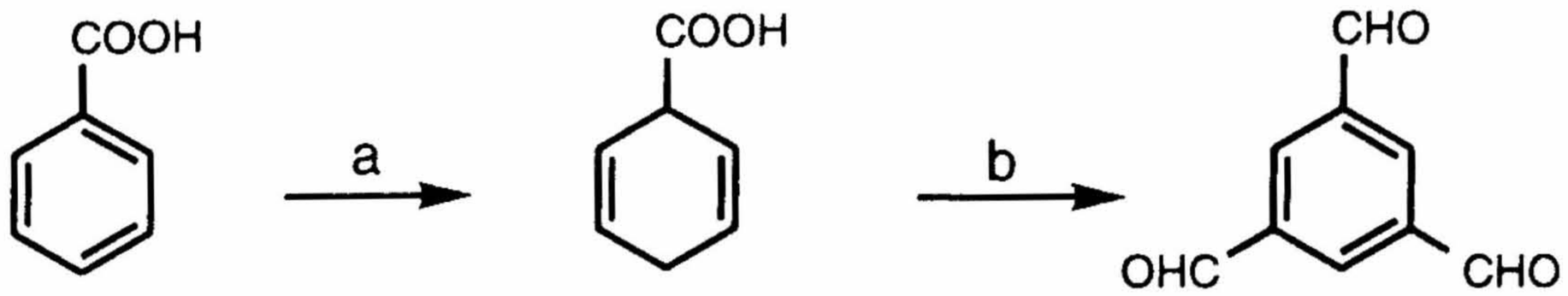
To realize the hydrocarbon **58** *via* the proposed Wittig stratagem, the two starting materials 1,3,5-triformylbenzene **65** and triphenyl-phosphonium fluorenylide **75** were required in some quantity.

**Scheme 17**




These were prepared from benzoic acid **71** and 9-bromofluorene **73**, respectively. Birch reduction of benzoic acid **71** gave 1,4-dihydrobenzoic acid **72**, which on Vilsmeier-Haack formylation furnished the trialdehyde **65**, Scheme 18.[56]

**Scheme 18**

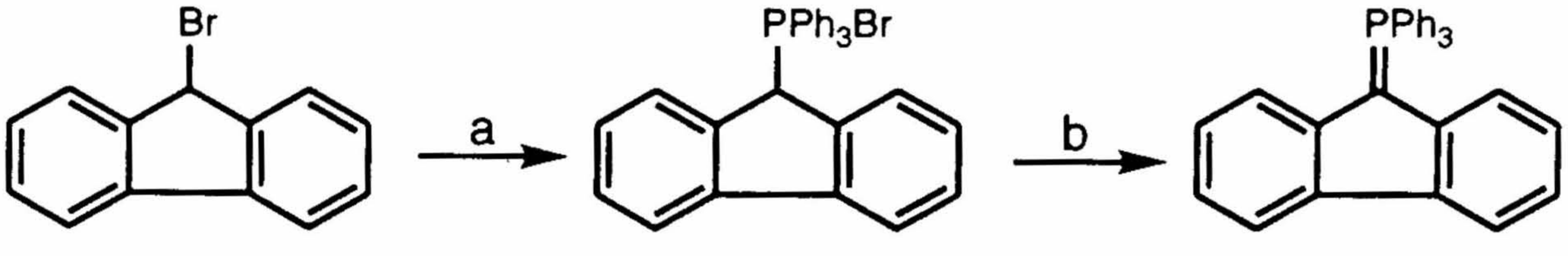



**71** **72** **65**

**Reagents, Conditions & Yields:** a) sodium, EtOH, liq. ammonia; b) $POCl_3$, DMF (35% after two steps).

For the preparation of the ylide **75**, 9-bromofluorene **73** was treated with triphenylphosphine in nitromethane to furnish fluorenyl-9-triphenylphosphonium bromide **74**, which on abstraction of hydrobromic acid with ammonium hydroxide yielded triphenylphosphonium fluorenylide **75** as yellow crystalline plates, Scheme 19.[57]

**Scheme 19**

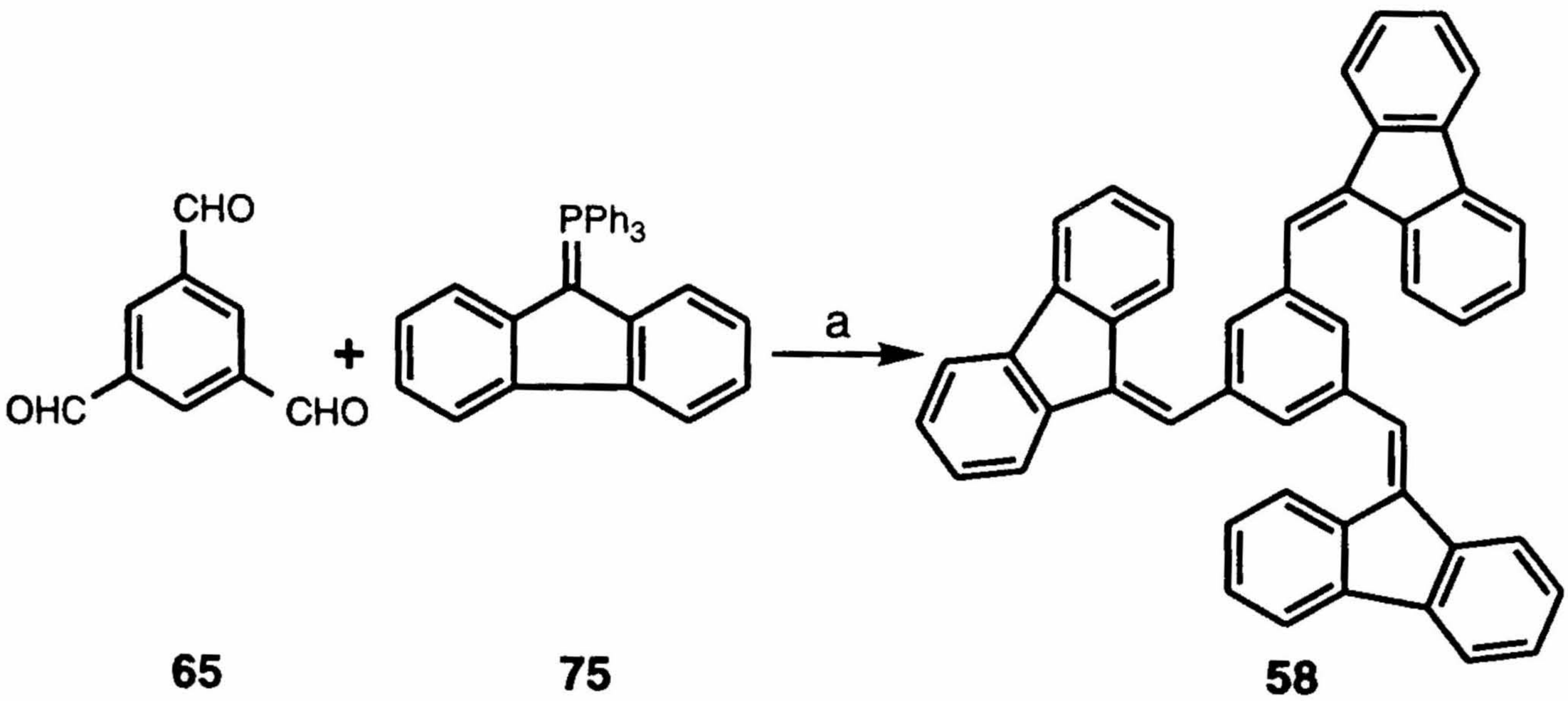



**73** **74** **75**

**Reagents, Conditions & Yields**: a) $PPh_3$, nitromethane, r.t.; b) EtOH, Δ, $NH_4OH$ (80% after two steps).

Having obtained the trialdehyde **65** and the ylide **75**, attention was turned towards effecting the Wittig coupling. Gratifyingly, a three-fold stereoselective Wittig reaction between the trialdehyde **65** and the ylide **75** could be carried out through simple heating in chloroform to furnish the crystalline hydrocarbon 1,3,5-*tris*(fluorenylidenemethyl)-benzene **58** in one step in 30% yield, Scheme 20.

**Scheme 20**




**65** **75** **58**

**Reagents, Conditions & Yield**: a) $CHCl_3$, Δ, 30%.

Structure of **58** was deduced from its analytical and spectral data (*vide experimental*). The $^1H$ NMR (Spectrum 1) and $^{13}C$ NMR (Spectrum

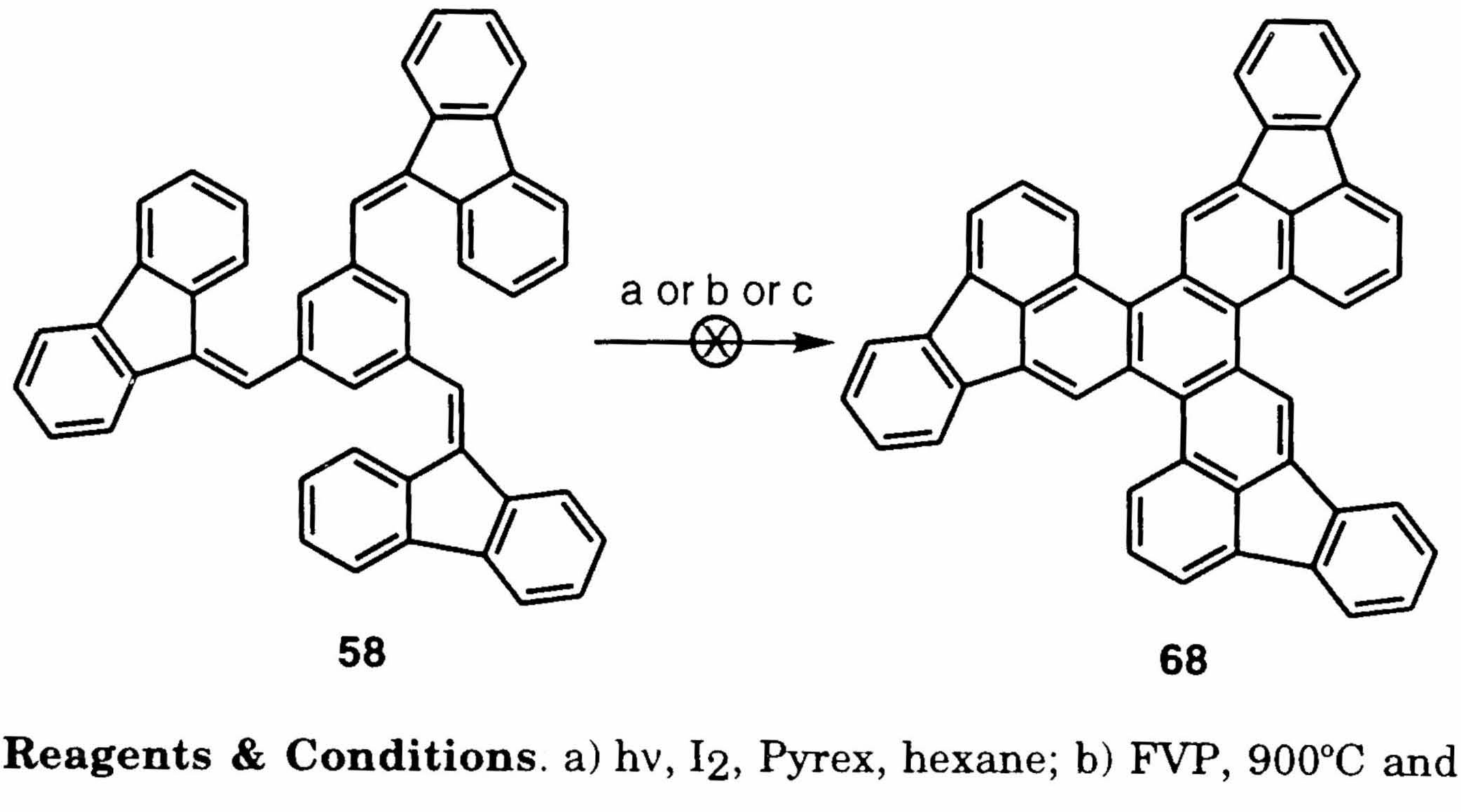
2) are in agreement with the structure **58** and, in particular, the 16-line $^{13}C$ NMR spectrum δ 141.5, 139.4, 138.1, 137.6, 136.6, 129.3, 128.8, 128.6, 128.4, 127.2, 126.9, 126.0, 124.6, 120.5, 119.9 and 119.7 revealed its $C_3$-symmetry. Thus, the 48 carbon atoms present in fragment **57** were established in a single reaction from readily available **65** and **75**.

Elated by the ready access to the $C_{48}$-compound **58** in one step, attempts were made to photocyclize **58** to obtain the cyclized product. It was anticipated that there would be some difficulties in the photocyclization on account of the deviation from planarity of the fluorenyl sheets, but this was not considered to be insurmountable.[58]

When the hydrocarbon **58** was subjected to photocyclization using 450W Hanovia medium pressure mercury vapour lamp using a quartz vessel in the presence of iodine, there was no indication of any cyclized product - even after prolonged irradiation. Despite many trials and variations in reaction conditions (temperature, solvent, filters), it was not possible to effect the **58** → **68** transformation. Disappointed by this outcome, we took recourse to thermal aryl-aryl coupling, even though such systems are known to be recalcitrant towards such

processes in the absence of appropriate substitutions like halogen on the coupling carbons of one of the aryl rings.[59] Attempted flash vacuum pyrolysis of **58** at different temperatures (900°C and 1000°C) resulted only in the sublimation of **58**.[60] Experiment to cyclize **58** through palladium-carbon mediated dehydrogenation under static conditions were also not successful, Scheme 21.

**Scheme 21**




**58** **68**

**Reagents & Conditions**. a) hν, $I_2$, Pyrex, hexane; b) FVP, 900°C and 1000°C, 0.3 mm of Hg; c) Pd/C, 400°C, 2h.

At this stage, a crystal structure of **58** was undertaken to know the spatial orientation of the fluorenyl units with respect to the central

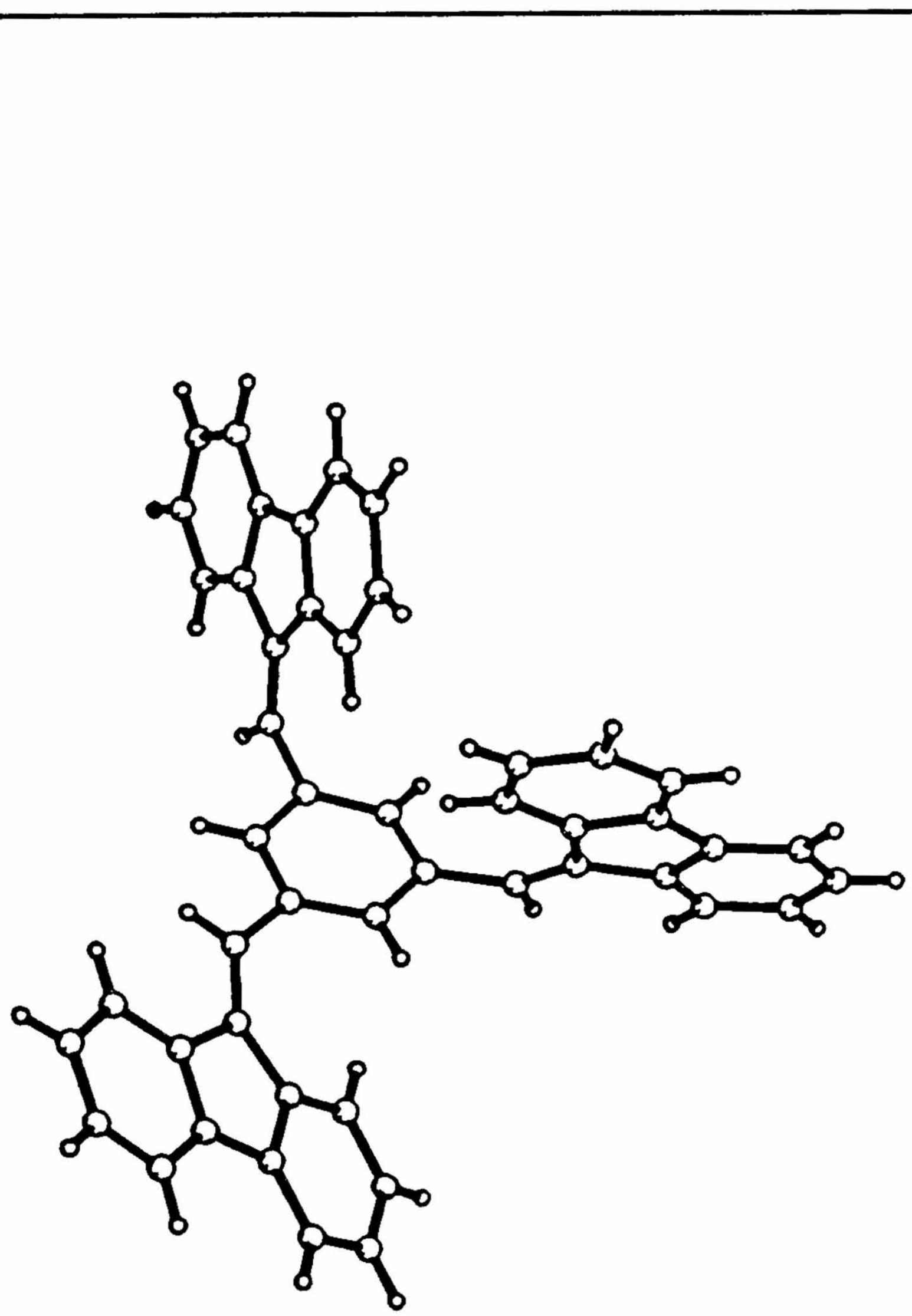
benzene ring and was found to be quite interesting on several counts.¶ The structure of **58** turned out to be "propeller shaped" with the dihedral angle between the central benzene ring and the three fluorenylidene moieties being 40.0(2)°, 72.3(2)° and 106.3(2)°, Fig. 4. The bond lengths and bond angles were found to be generally within the expected ranges. There was no evidence of any twisting, folding or pyramidalization at the fluorenylidene double bonds. Such structural deviations have been observed in related systems.[61]

The arrangement of the molecules in the unit cell is as shown in Fig 5 and the crystal structure of **58**, therefore, appears to be stabilized through -CH---π interactions between the fluorenylidene moieties in a T-shaped geometry. The angle between the orthogonally positioned fluorene moieties was ≈ 81°. There are several contacts (≈ 3 Å) between aromatic carbons and the hydrogen atoms of orthogonally positioned and partly off-set fluorenylidene sheets. Despite the presence of many aromatic rings in the molecule, there is hardly any face-to-face π—π stacking.[62]

---

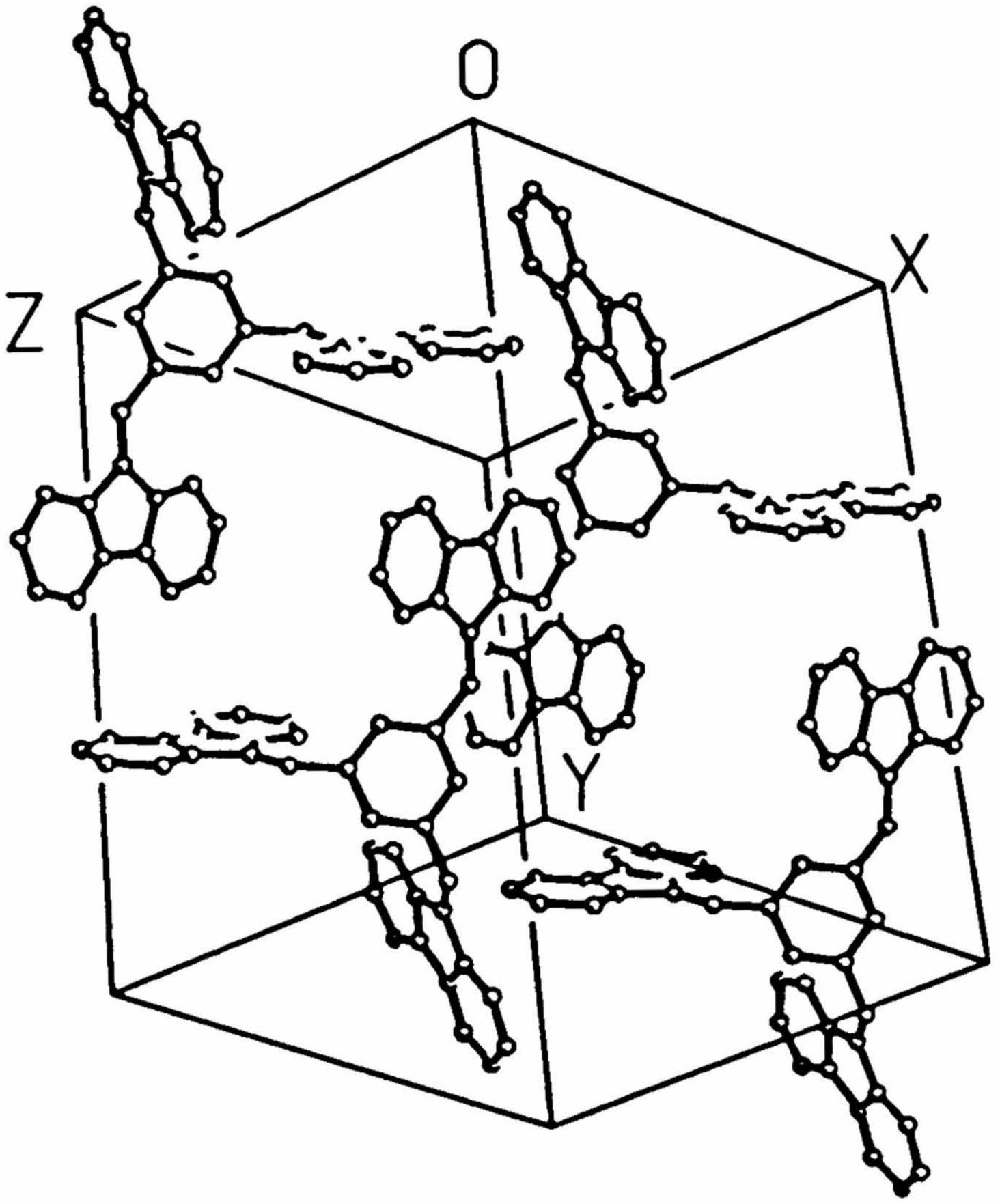
¶ We thank Dr. K. Ravikumar of IICT for this determination.

**Figure 4**



**X-ray Crystal Structure of 58**

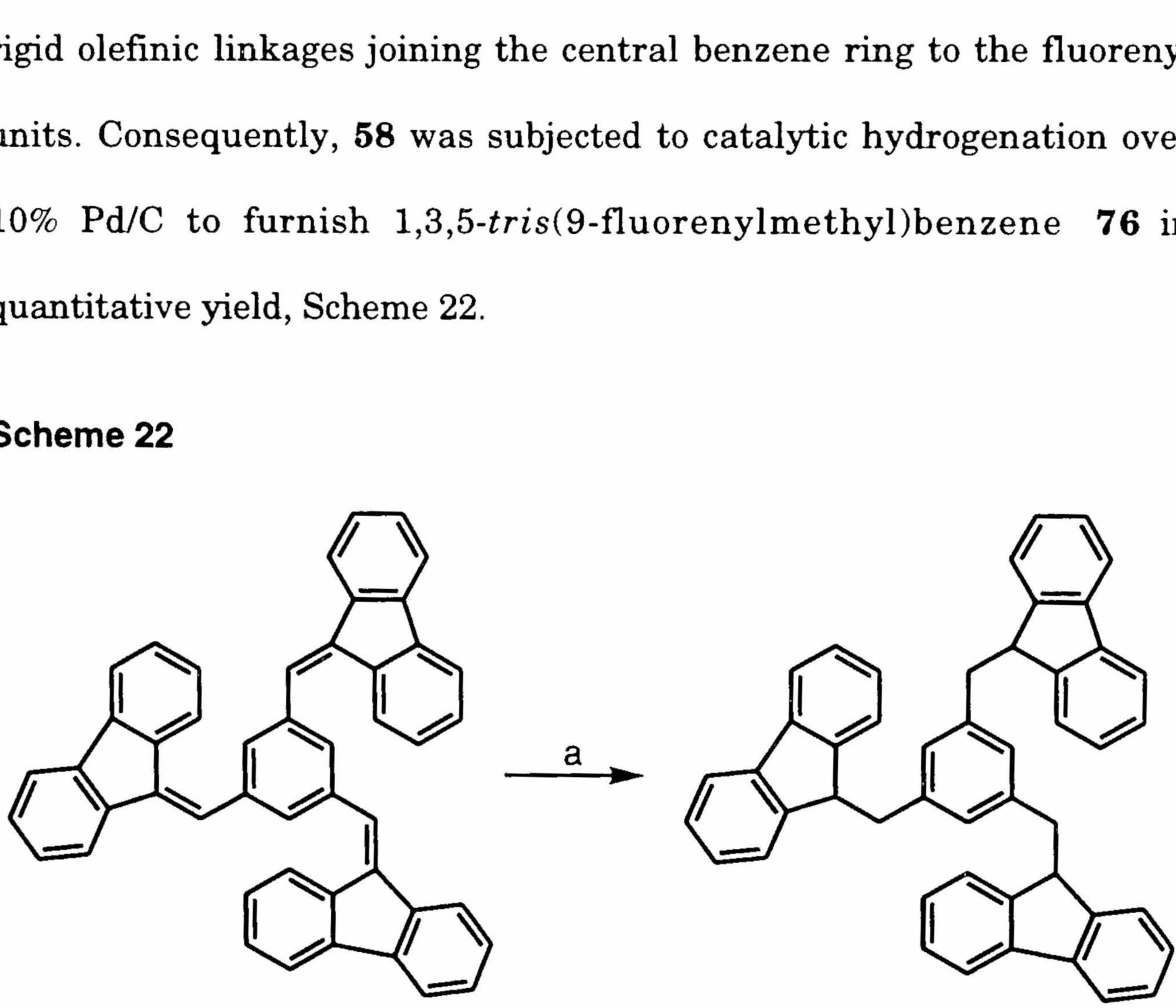
**Figure 5**




**Molecular Crystal Packing in 58**

With the X-ray crystal structure of **58** reaffirming that the non-planar, 'propeller shape' (Fig. 4) was not well constituted for the contemplated photo- or thermal-cyclization, we sought to transform **58** to a more flexible framework The simplest expedient was to remove the rigid olefinic linkages joining the central benzene ring to the fluorenyl units. Consequently, **58** was subjected to catalytic hydrogenation over 10% Pd/C to furnish 1,3,5-*tris*(9-fluorenylmethyl)benzene **76** in quantitative yield, Scheme 22.

**Scheme 22**




**58** **76**

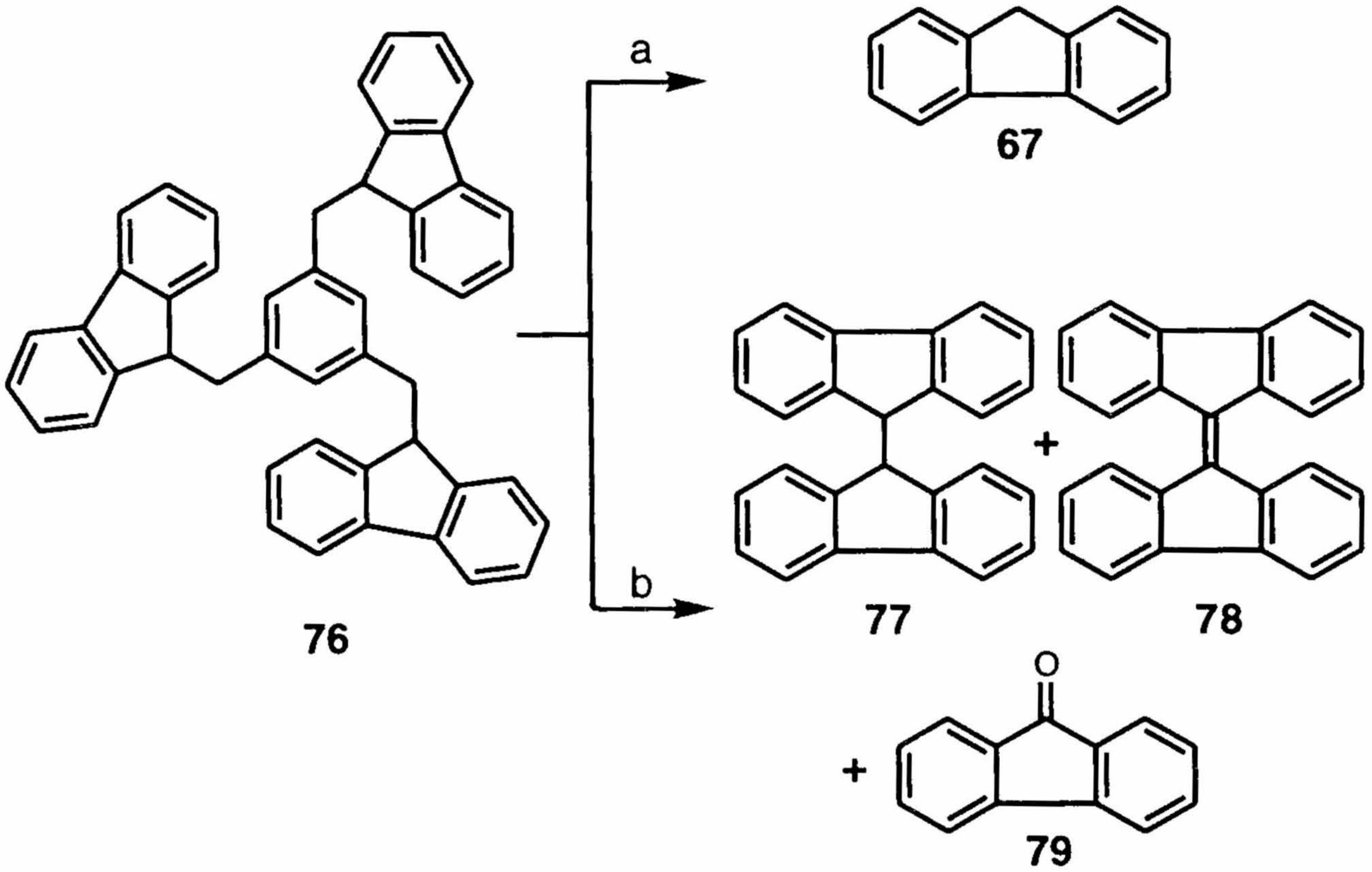
**Reagents, Conditions & Yield**: a) 10% Pd/C, $H_2$, EtOAc, 94%.

The $^{1}H$ NMR (Spectrum 3) resonances at δ 6.87 (singlet, 1H), δ 4.07 (triplet, 1H, $J_1=J_2=7.2$ Hz) and at δ 3.03 (doublet, 2H, J=7.3 Hz) indicated the presence of symmetrically substituted central benzene ring and fluorenyl moieties attached through a $-CH_2-$ group, respectively. The 10-line $^{13}C$ NMR (Spectrum 4) resonances at δ 147.0, 141.0, 139.6, 128.9, 127.2, 126.7, 125.0, 119.9, 48.7 and 40.0 confirmed the $C_3$-symmetry of **76**, especially the two aliphatic signals at 48.7 and 40.0 indicated the nature of the union between the central benzene and the fluorenyl units.

At this stage attempts were made to induce **76** to cyclize under conditions of thermal activation. Thus, FVP of **76** at 800°C was carried out. However, the outcome was the isolation and characterization of only fragmented products, 9,9'-bifluorene **77**, 9,9'-bifluorenylidene **78** and fluorenone **79**, Scheme 23, which could be easily identified through comparison with authentic samples. We also attempted cyclo-dehydrogenation of **76** over Pd/C catalyst under static conditions at 400°C - a standard requirement for such cyclizations. However, only fluorene **67** could be isolated from the reaction mixture, Scheme 23.

Our inability to induce the key cyclizations **58** → **68** and **76** → **68** were grave forebodings that alerted us to the unforeseen complexities

**Scheme 23**

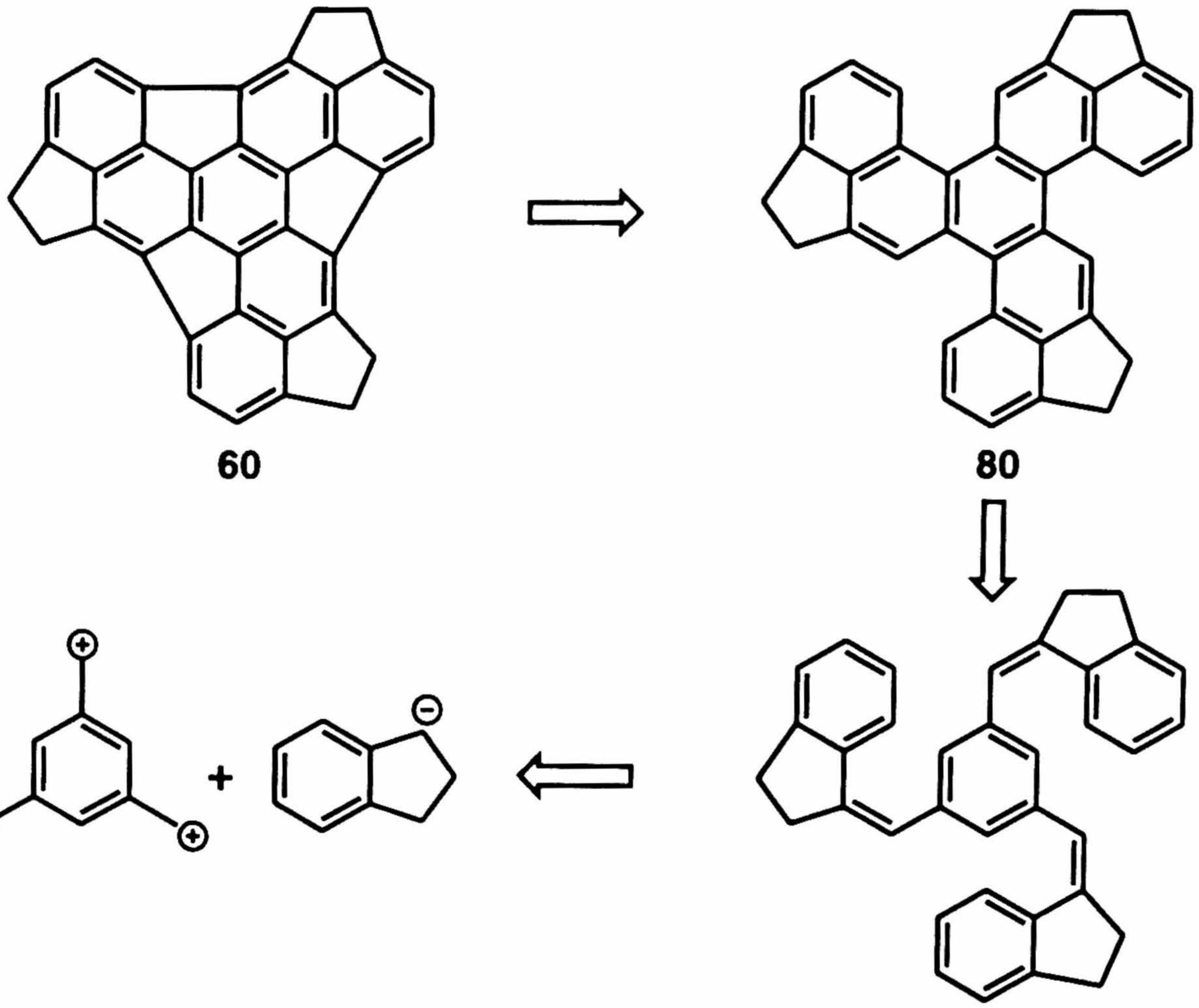



**Reagents & Conditions** a) Pd/C, 400°C, 2h; b) FVP, 800°C, 0.3 mm

involved and the hard torturous journey that lay ahead. We, therefore, concurrently began to explore alternative methodologies and strategies. Recognizing the deviation from planarity and steric overcrowding within the molecule **58**, due to the presence of three fluorenyl sheets as the

causative factor for its failure to undergo photocyclization, an alternative strategy by replacing the three fluorenyl moieties with indanyl units was considered. This was expected to lead to another fragment **60** of [60]-fullerene (as shown in the retrosynthetic Scheme 16), after appropriate cyclizations. Retrosynthetic analysis of **60** along $C_3$-symmetry route led to the precursors **80** and **61**, Scheme 24.

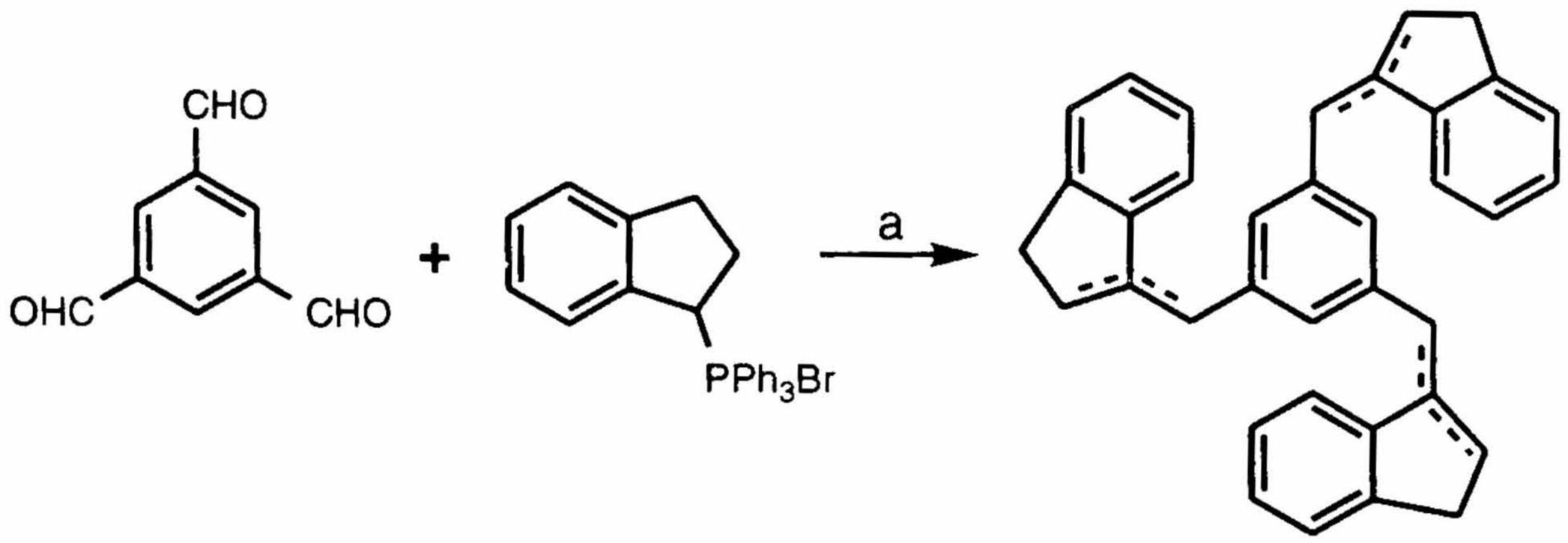
**Scheme 24**



The 36 carbon atoms present in **61** were sought to be assembled in one step from commercially available starting materials like mesitylene **64** and indane **66**, through pre-installed complementary functionalities **70** and **81**, Scheme 24.

Towards the preparation of **61** (as shown in Scheme 24), a three-fold stereoselective Wittig reaction between 1,3,5-triformylbenzene **65** and 1-indanyltriphenylphosphonium bromide **82** (prepared from 1-bromoindane by refluxing with triphenylphosphine in benzene) was executed in the presence of $Cs_2CO_3$ and isopropanol, which furnished the tri-Wittig compound 1,3,5-*tris*(1-indanylidenemethyl)benzene **61** as a

**Scheme 25**

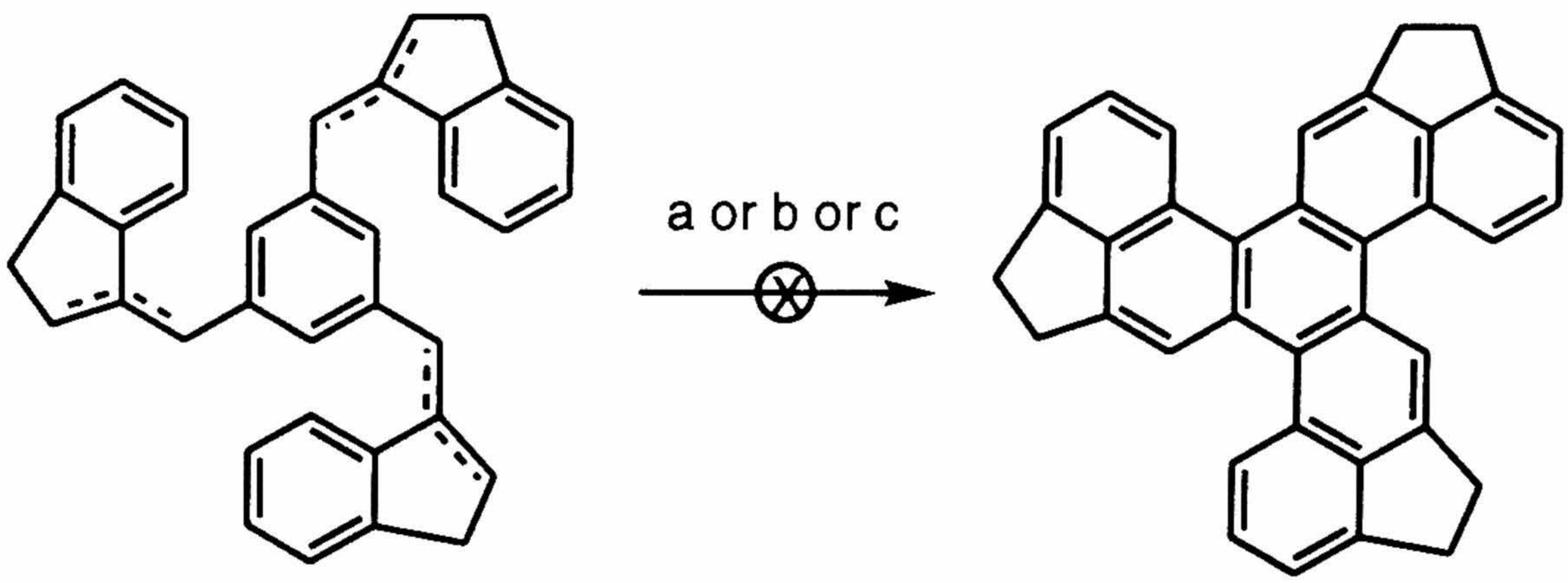



**65** **82** **61**

**Reagents, Conditions & Yield**: a) $Cs_2CO_3$, $(CH_3)_2CHOH$, 3h, r.t, 30%

mixture of double bond isomers in 30% yield, Scheme 25. The presence of two regioisomers could be established by $^{1}H$ NMR (Spectrum 5) resonances and the two sets of $^{13}C$ NMR lines (Spectrum 6). It was neither possible nor was considered necessary to separate the mixture and it was carried as such to the next step. None the less, the 36 carbon atom present in **60** were assembled in a single step from easily available starting materials.

**Scheme 26**




**61** **80**

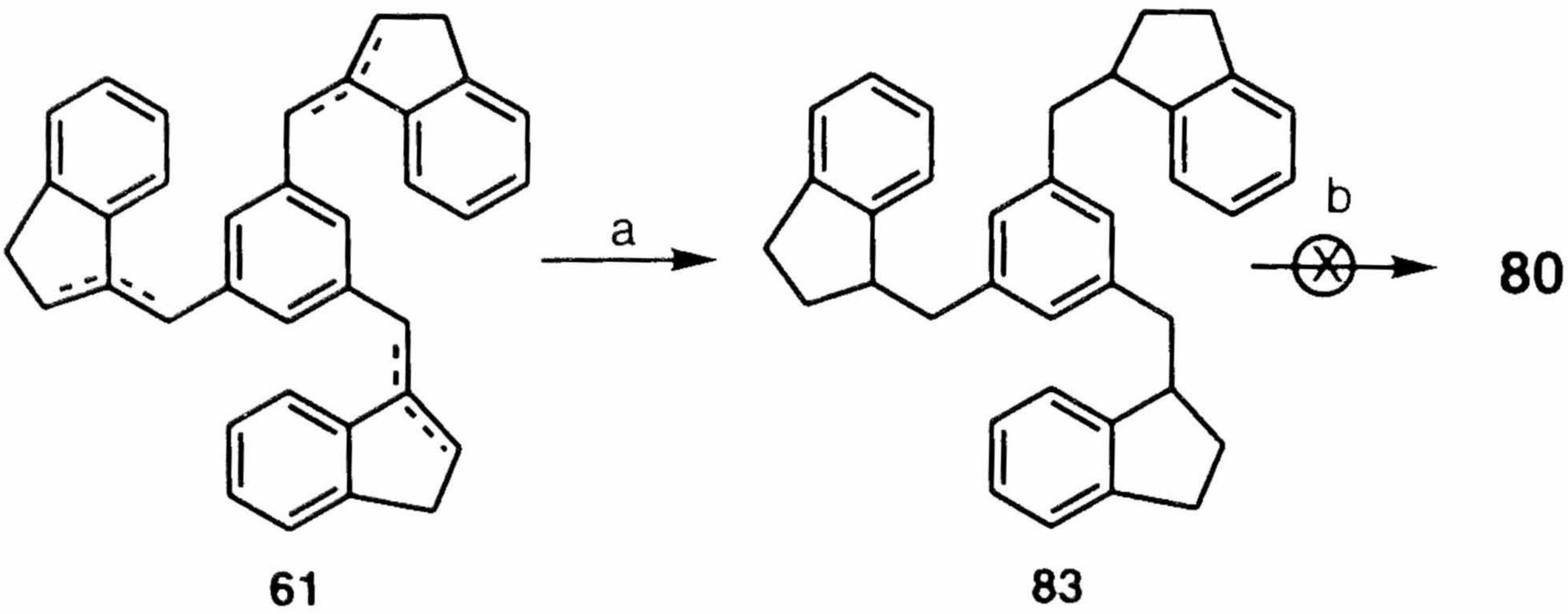
**Reagents & Conditions**: a) hν, $I_2$, Pyrex, hexane; b) FVP, 900°C and 1000°C, 0.3 mm; c) Pd/C, 400°C, 2h.

Having obtained the $C_{36}$-compound **61**, attempts were made to cyclize it by photochemical and thermal methods. Irradiation of **61** using

450W Hanovia medium pressure mercury vapour lamp in the presence of cat $I_2$ did not yield the desired cyclization Even the flash vacuum pyrolysis or Pd/C dehydrogenation methods proved futile, Scheme 26.

As an alternative, **61** was hydrogenated over 10% Pd/C catalyst to furnish 1,3,5-*tris*(1-indanylmethyl)benzene **83** as a single compound in quantitative yield (Scheme 27) ,whose analytical and spectral data were in full agreement with its structure In particular, a 12-line $^{13}C$ NMR

**Scheme 27**



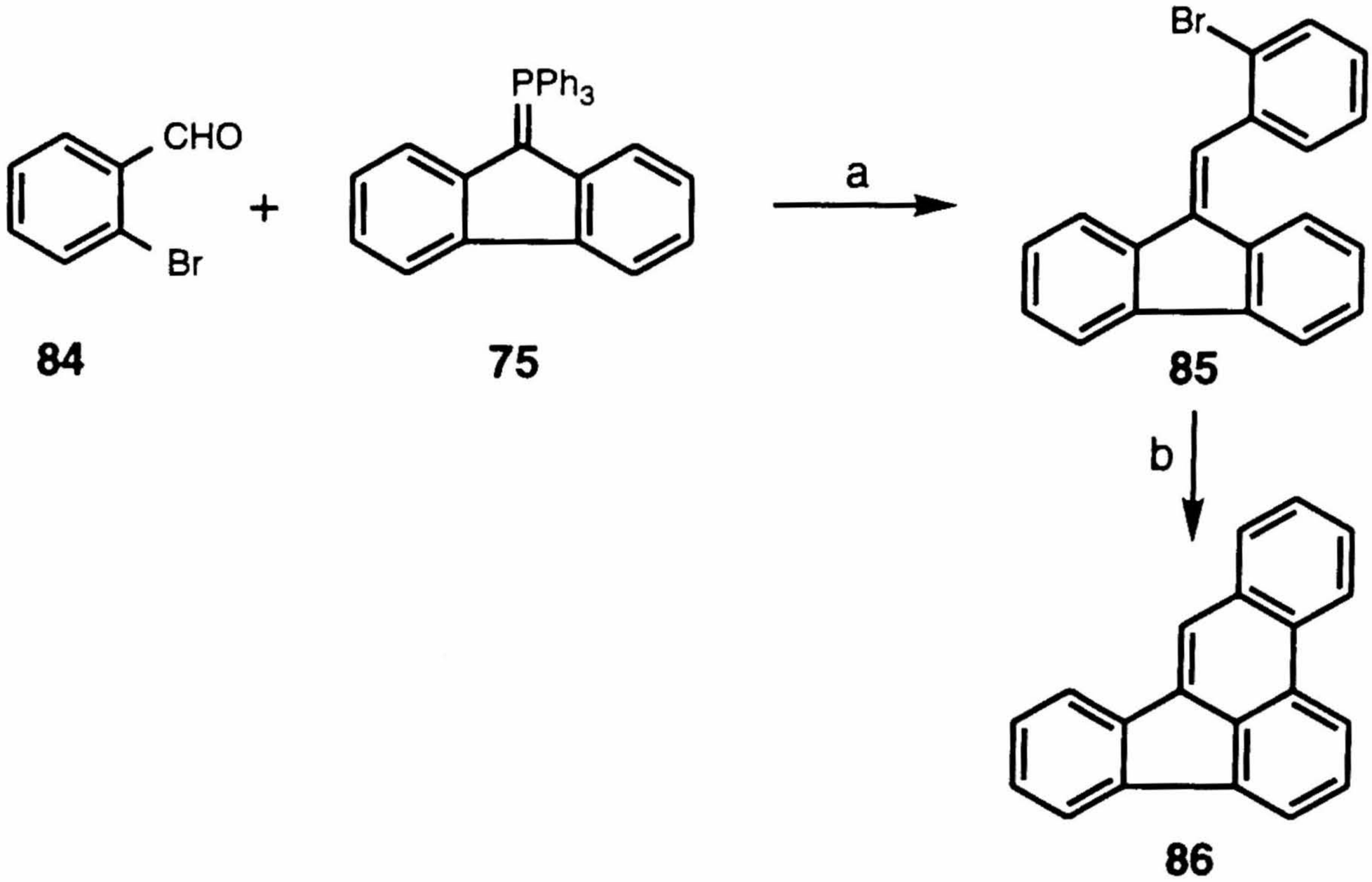

**Reagents, Conditions & Yield** a) 10% Pd/C, $H_2$, EtOAc, 90%, b) FVP, 900°C, 0 3 mm

(Spectrum 8) δ 147 1, 144 2, 140 6, 127 8, 126 5, 126 0, 124 6, 124 0, 46 5, 41 4, 31 8 and 31 1 revealed its $C_3$-symmetry and the four signals at δ

46.5, 41.4, 31.8 and 31.1 confirming the presence of an indanyl moiety were diagnostic. Attempts to cyclodehydrogenate **83** *via* flash vacuum pyrolysis were in vain.

It is known that the presence of a halogen on the benzene nucleus induces the cyclization during flash vacuum pyrolysis.[50] Before elaborating such a strategy, a model study was performed to see the viability of such a sequence. When o-bromo benzaldehyde **84** was treated

**Scheme 28**

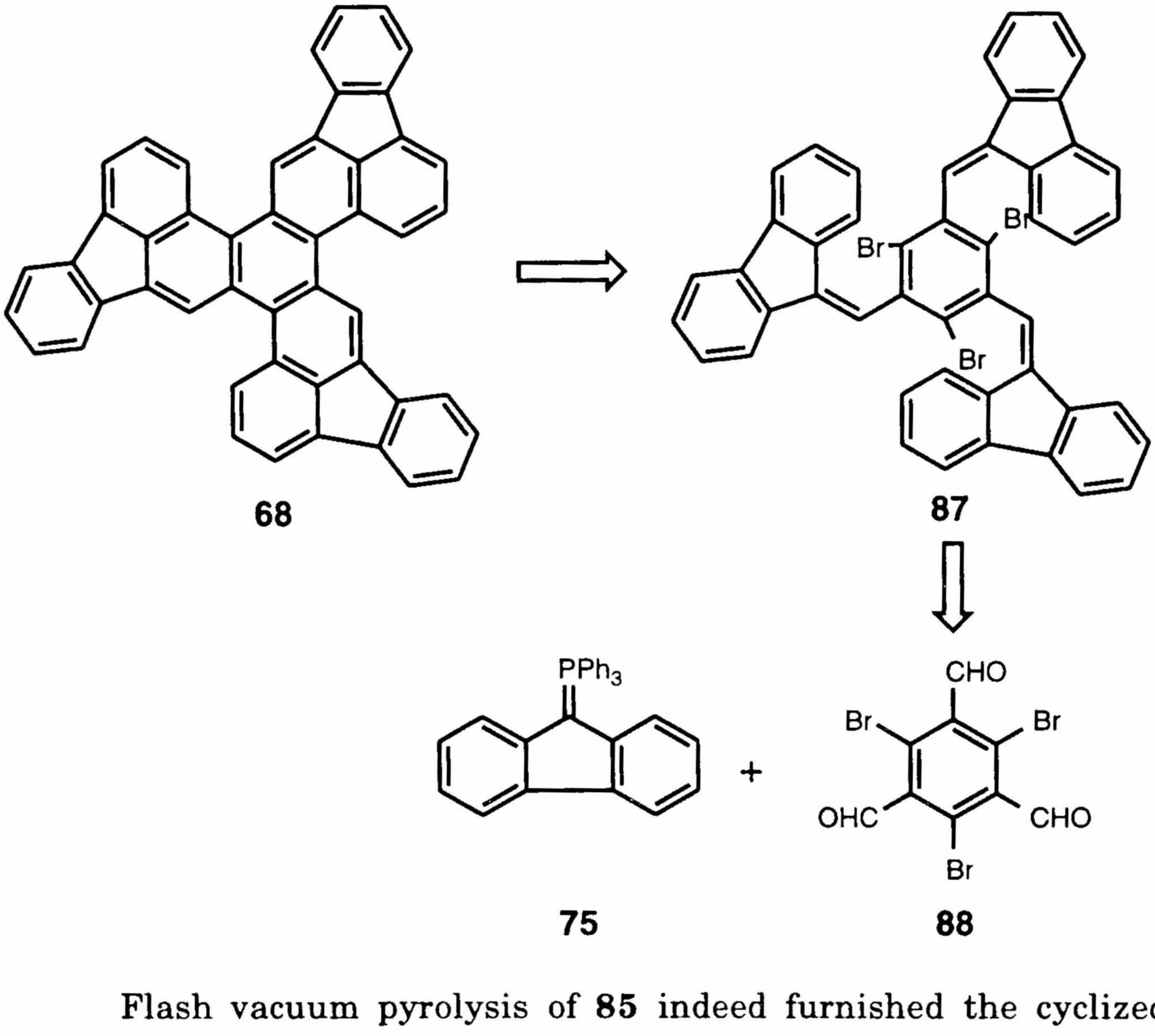



**84** **75** **85** **86**

**Reagents, Conditions & Yields**: a) $CHCl_3$, Δ, 55%; b) FVP, 900°C, 0.3 mm, 65%.

with triphenylphosphonium fluorenylide **75** in refluxing chloroform, the Wittig product o-bromophenylidene-9-fluorene **85** was readily formed.

**Scheme 29**



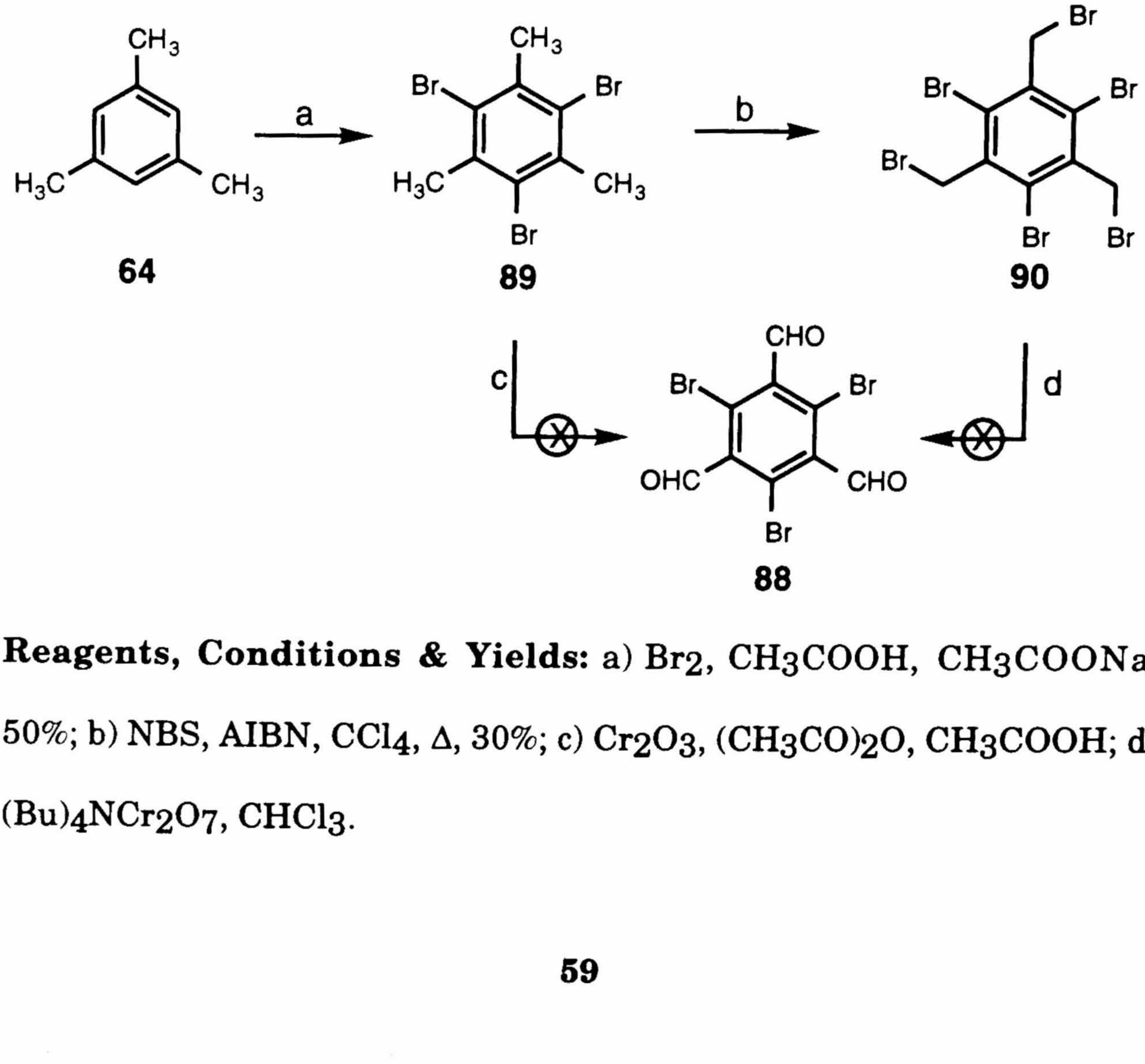

**68** **87** **75** **88**

Flash vacuum pyrolysis of **85** indeed furnished the cyclized product benzo[b]fluoranthene **86**, Scheme 28. This clearly indicated that the presence of halogen, on the benzene nucleus, facilitates the cyclization during flash vacuum pyrolysis.

Encouraged by the ready access to benzo[b]fluoranthene **86**, in a two-step sequence from 2-bromobenzaldehyde **84** *via* Wittig olefination and flash vacuum pyrolysis reactions, another route to the fragment **68** was envisaged through the retrosynthetic protocol, Scheme 29.

For this purpose, an attempt was made to prepare 2,4,6-tribromo-1,3,5-triformylbenzene **88**, Scheme 30.

**Scheme 30**



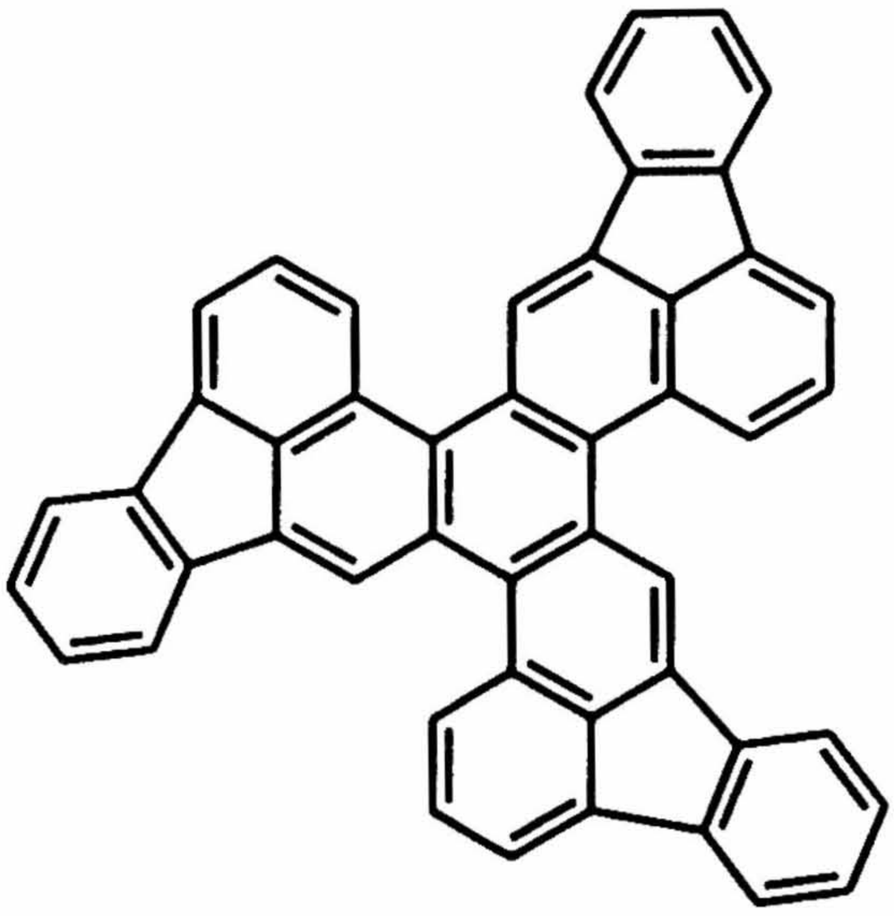

**88**

**Reagents, Conditions & Yields:** a) $Br_2$, $CH_3COOH$, $CH_3COONa$, 50%; b) NBS, AIBN, $CCl_4$, Δ, 30%; c) $Cr_2O_3$, $(CH_3CO)_2O$, $CH_3COOH$; d) $(Bu)_4NCr_2O_7$, $CHCl_3$.

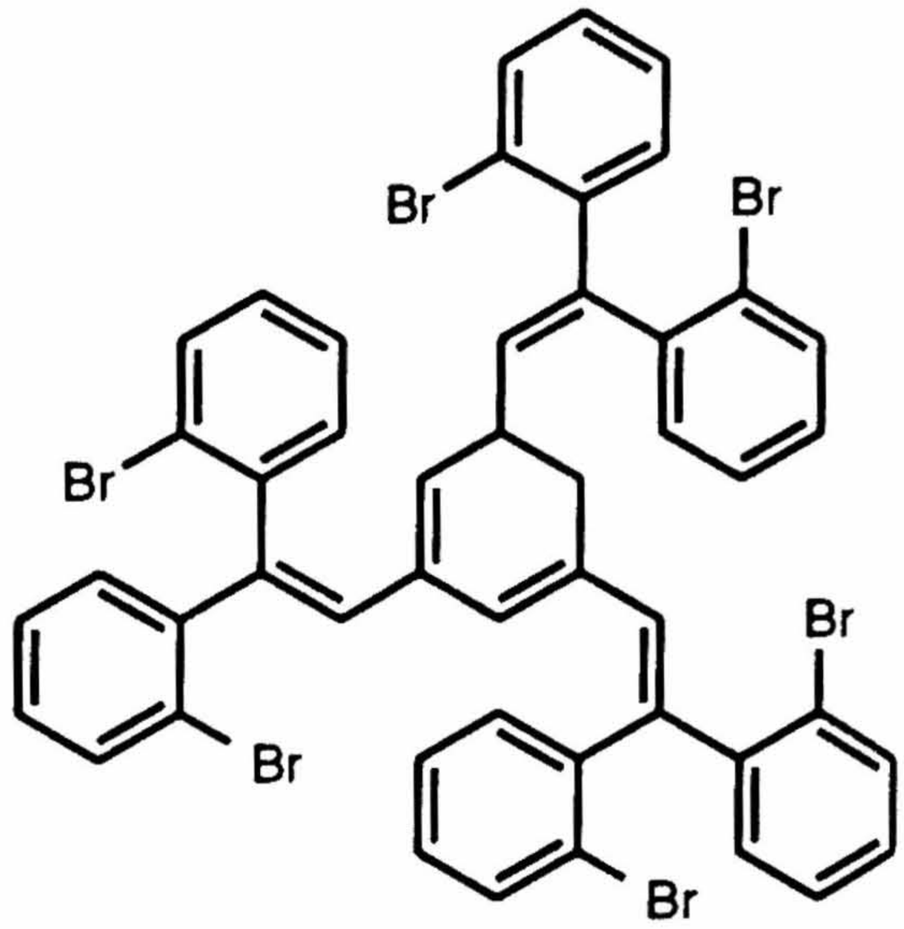
Consequently, mesitylene **64** was treated with $Br_2/CH_3COOH$ in the presence of sodium acetate to furnish 2,4,6-tribromomesitylene **89**.[63] Attempts to convert the three methyl groups to formyl functionality using various oxidizing agents led to uncharacterizable products. Therefore, the three methyl groups were converted to bromomethyl moieties using NBS in $CCl_4$ in the presence of AIBN. This readily led to 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene **90**. Attempts to either directly oxidize the bromomethyl groups to formyl groups or to solvolyze them to the corresponding alcohol and oxidize to **88** by well-known methods have been unsuccessful. Since it was not possible to prepare the required starting material **88**, another route to **68** had to be considered.

The failure of photocyclization in **58** and **61** was most likely due to steric crowding and the presence of an exocyclic olefin moiety on a five-membered ring, which is a part of the planar rigid framework, forced us to consider accessing a more flexible framework, which in principle, is equivalent to a fluorene unit (as shown in the retrosynthetic Scheme 31).

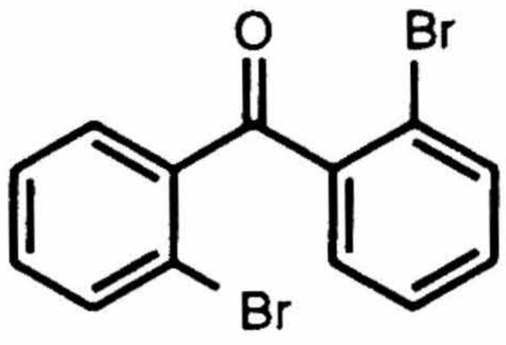
**Scheme 31**



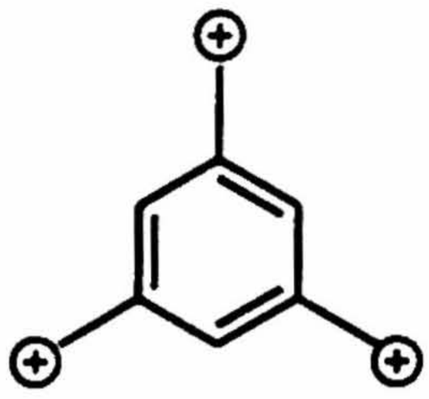
**68**



**91**



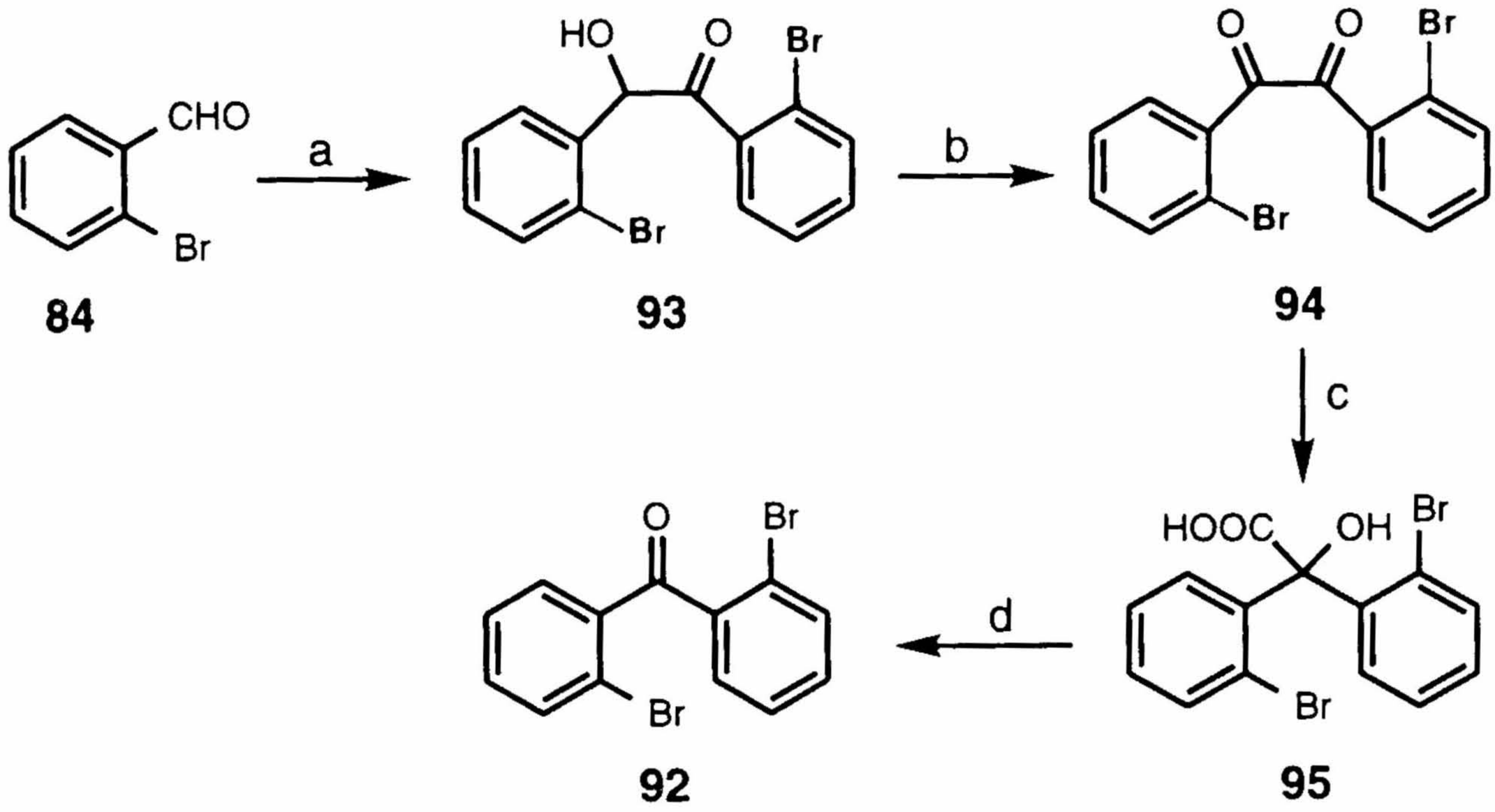
**92**



**70**

In this context, 2,2'-dibromo benzophenone **92** was prepared starting from 2-bromobenzaldehyde **84**, Scheme 32.[64] The benzoin condensation of 2-bromobenzaldehyde yielded the hydroxy ketone **93**, which was further oxidized with nitric acid to 2,2'-dibromobenzanil **94**, followed by a rearrangement with base to get **95**. Treatment of this hydroxy acid **95** with sodium bismuthate and phosphoric acid gave 2,2'-

**Scheme 32**

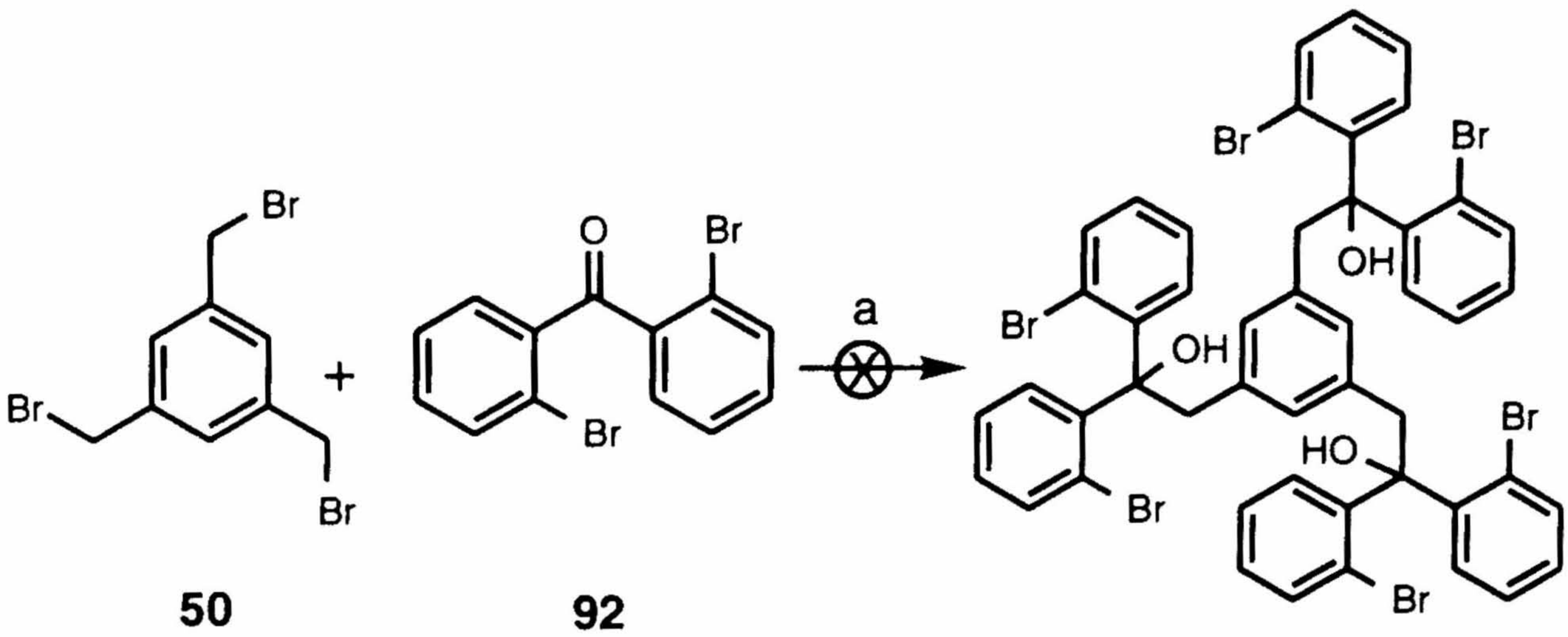



**84** **93** **94** **95** **92**

**Reagents, Conditions & Yields:** a) NaCN, EtOH, $H_2O$; b) Conc. $HNO_3$, 100 °C (60% after two steps); c) KOH, EtOH, $H_2O$, Δ, 70%; d) $NaBiO_3$, AcOH, 60 °C, $H_3PO_4$, 85%.

dibromobenzophenone **92**. In order to access **91** (as shown in the retrosynthetic Scheme 31), 1,3,5-*tris*(bromomethyl)benzene **50** and 2,2'-dibromobenzophenone **92** were treated, under Barbier-type reaction conditions,[65] but the products obtained were unseparable and uncharacterizable, Scheme 33.

**Scheme 33**

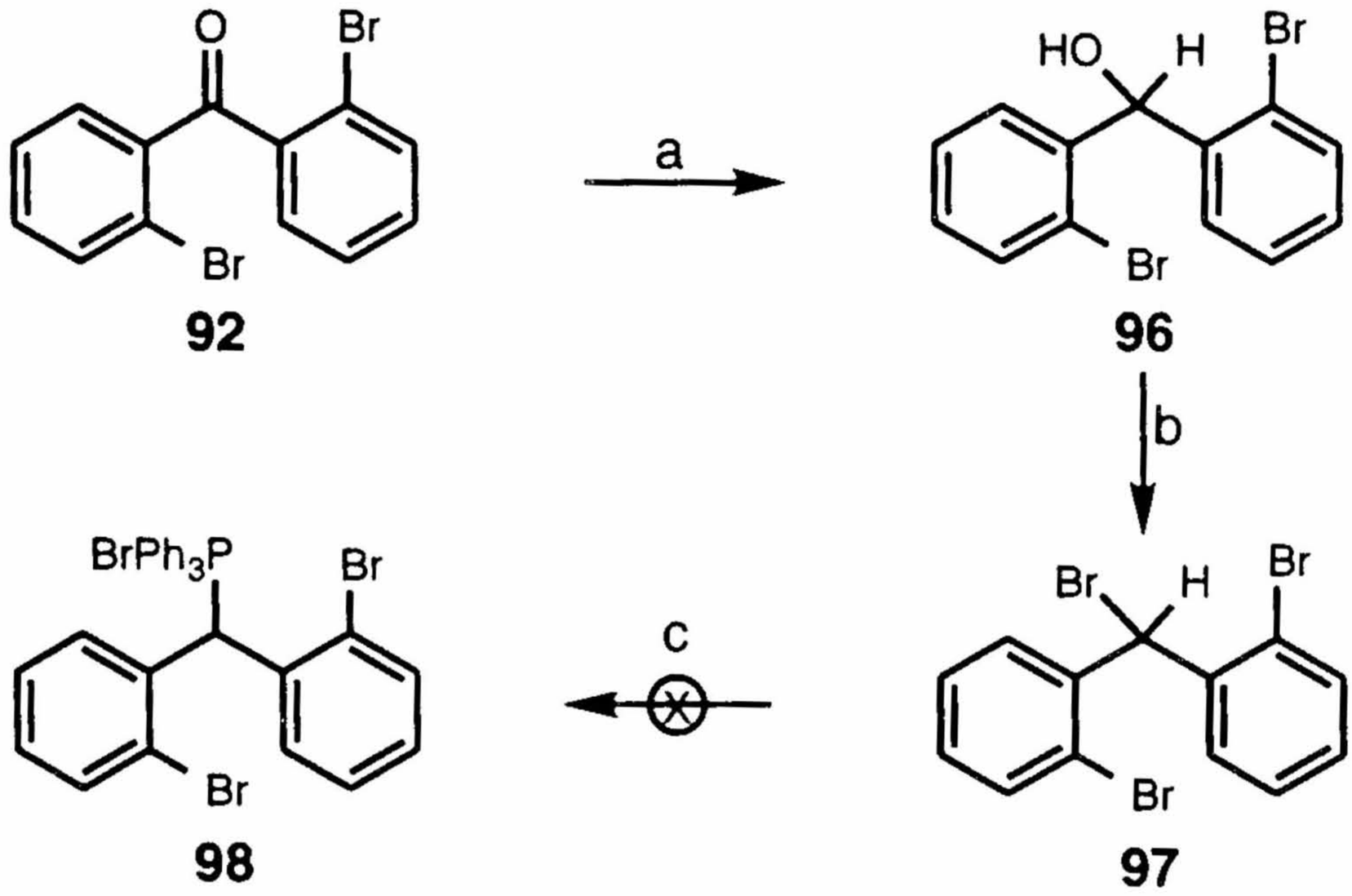



**50** **92**

**Reagents & Conditions**: a) Li, ))))), THF

The bromine substituents present on the aromatic nuclei of 2,2'-dibromobenzophenone **92** were thought to be interfering in the Barbier-type reaction and, therefore, as an alternative, the Wittig olefination was considered. Attempts were made to prepare Wittig salt of 2,2'-dibromobenzophenone by reducing it with sodiumborohydride to the alcohol **96** and further transforming it by phosphorous tribromide to the tribromide **97**, Scheme 34. Treatment of the tribromide **97** with triphenylphosphine under different conditions, did not yield the Wittig salt **98** and hence, it was not possible to continue with this theme either.

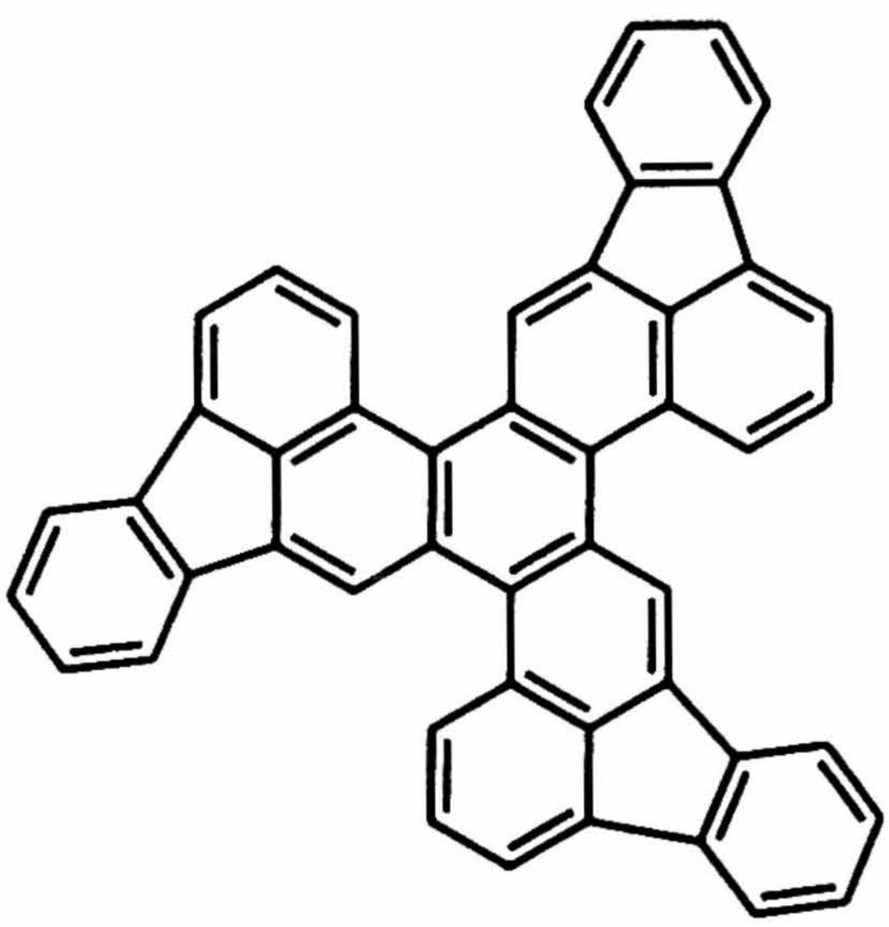
**Scheme 34**



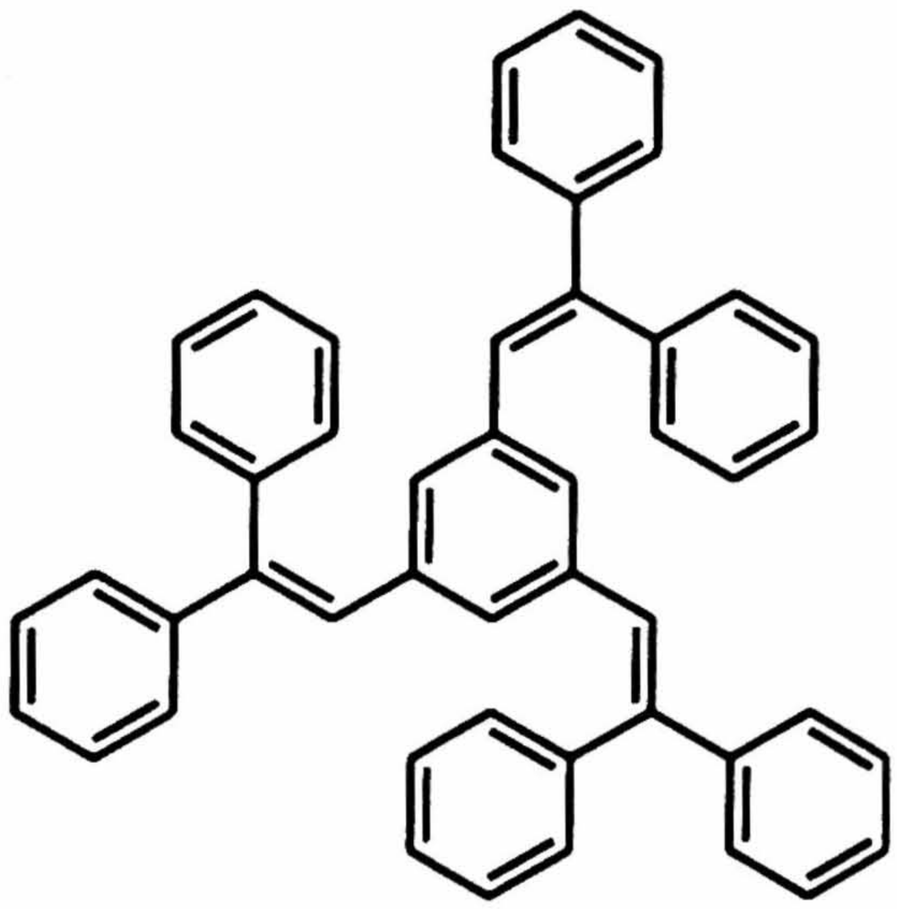

**Reagents, Conditions & Yields**: a) $NaBH_4$, MeOH, 0 °C, 90%; b) $PBr_3$, ether, 0 °C, 60%; c) $PPh_3$, ($C_6H_6$ or $CH_3NO_2$) , r.t.

Since oxidative photocyclization of stilbenes to phenanthrenes is a well established process,[66] the key precursor **59** (shown in the retro-synthetic Scheme 16) was considered as a substituted stilbene derivative and could be accessed as shown in Scheme 35.[67] The expectation was that in the absence of rigid sheets and bromo substituents, the stilbene-like subunits in **59** would readily undergo phenanthrene-type photocyclizations.

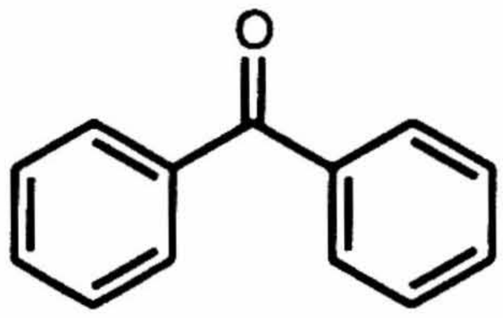
**Scheme 35**



**68**

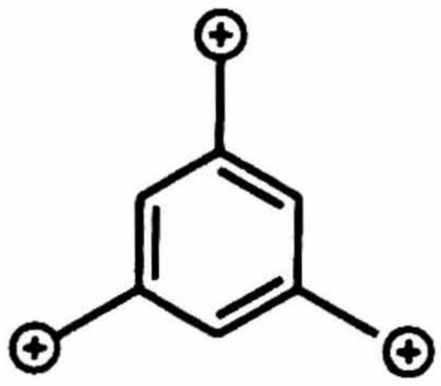


**59**



**99**

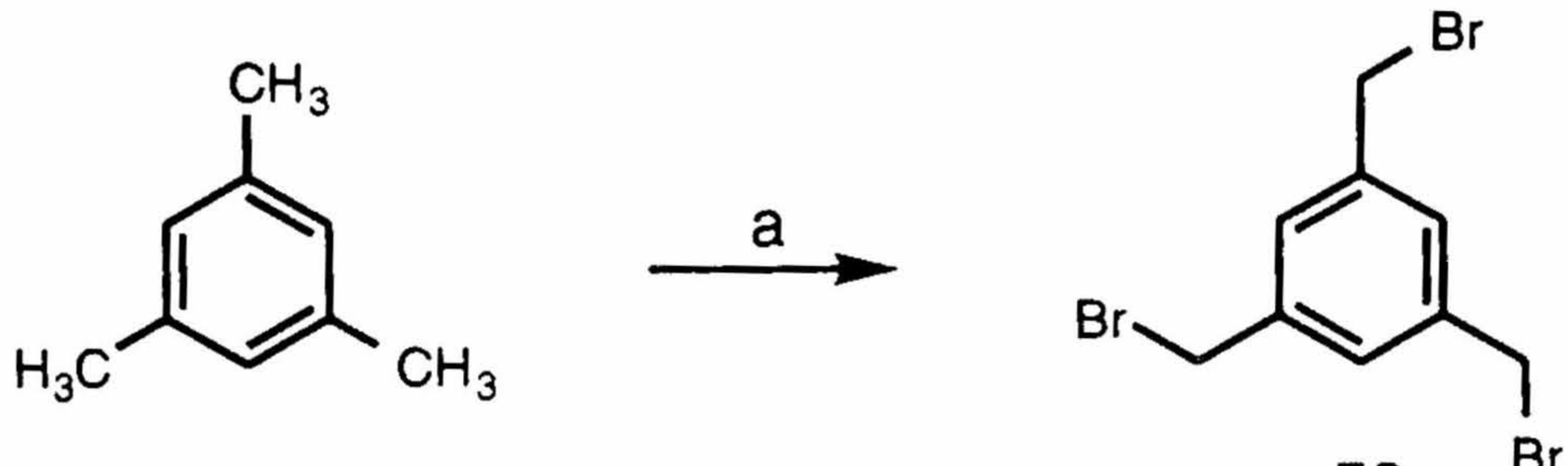
\+



**70**

To implement Scheme 35, 1,3,5-*tris*(bromomethyl)benzene **50** was prepared through radical bromination of mesitylene **64** with NBS in the presence of AIBN, Scheme 36. The other component **99** is, of course, readily and commercially available.

**Scheme 36**

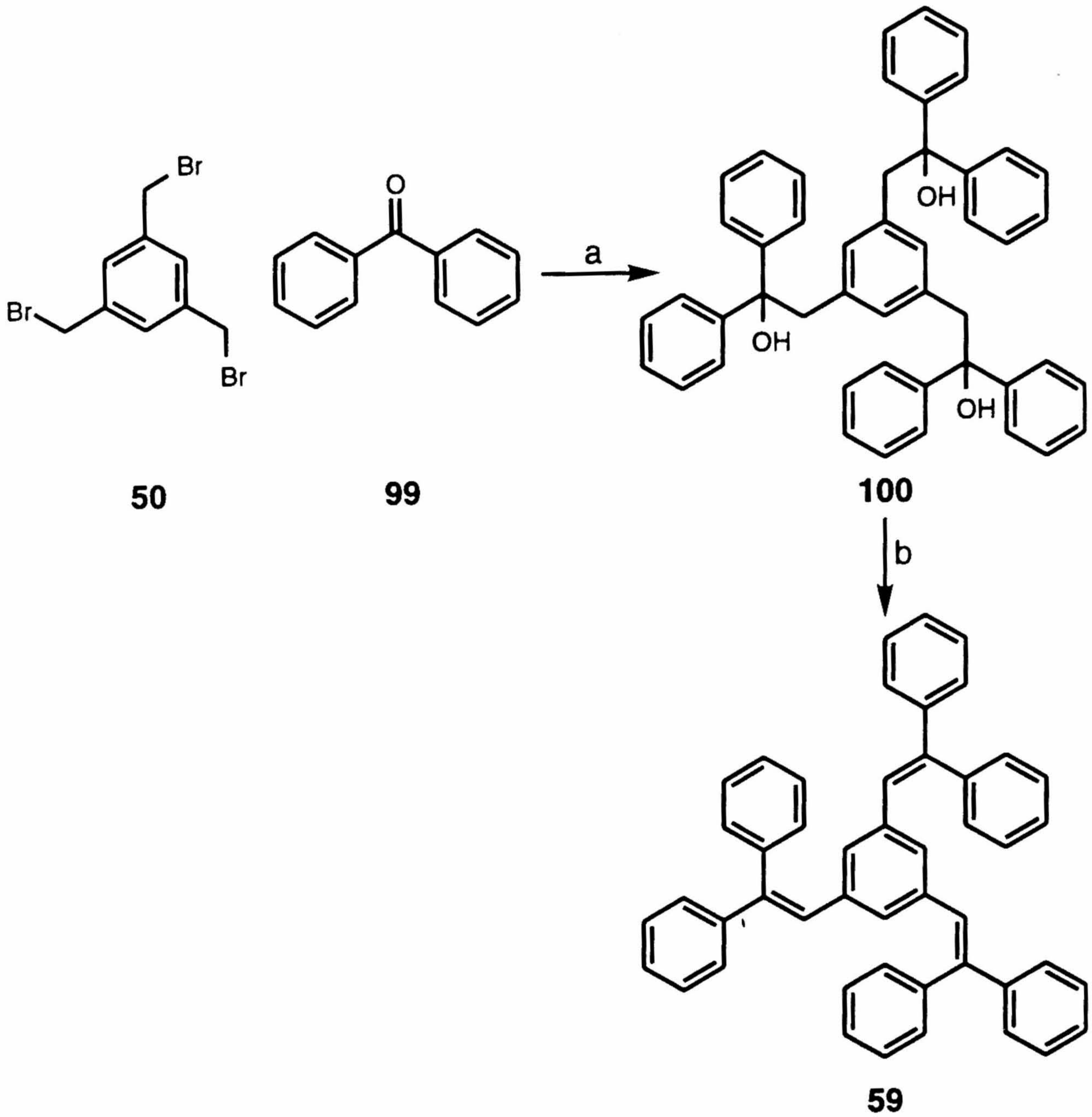



**64** **50**

**Reagents, Conditions & Yield**: a) NBS, AIBN, $CCl_4$, Δ, 30%.

Barbier-type reaction between 1,3,5-*tris*(bromomethyl)benzene **50** and a three-fold access of benzophenone **99** in the presence of lithium, under sonication, was attempted and led smoothly to the assembly of $C_{48}$-triol 1,3,5-*tris*(2',2'-diphenyl-2'-hydroxyethyl)benzene **100** in one step, Scheme 37. The structure of **100** was in full agreement with its analytical and spectral data with the IR frequency at 3586 $cm^{-1}$ indicating the presence of hydroxyl group. The $^1H$ NMR (Spectrum 13) resonances at δ 6.48 (singlet, 3H), at δ 3.40 (singlet, 6H) indicating the presence of symmetrically substituted central benzene ring and benzophenyl moieties attached through a $-CH_2-$ group, respectively. In particular, the 8-line $^{13}C$ NMR (Spectrum 14) δ 146.5, 135.6, 131.7, 128.0, 126.9, 126.2, 77.9 and 47.6 confirmed its $C_3$-symmetry. Further,

**Scheme 37**




**50** **99** **100**

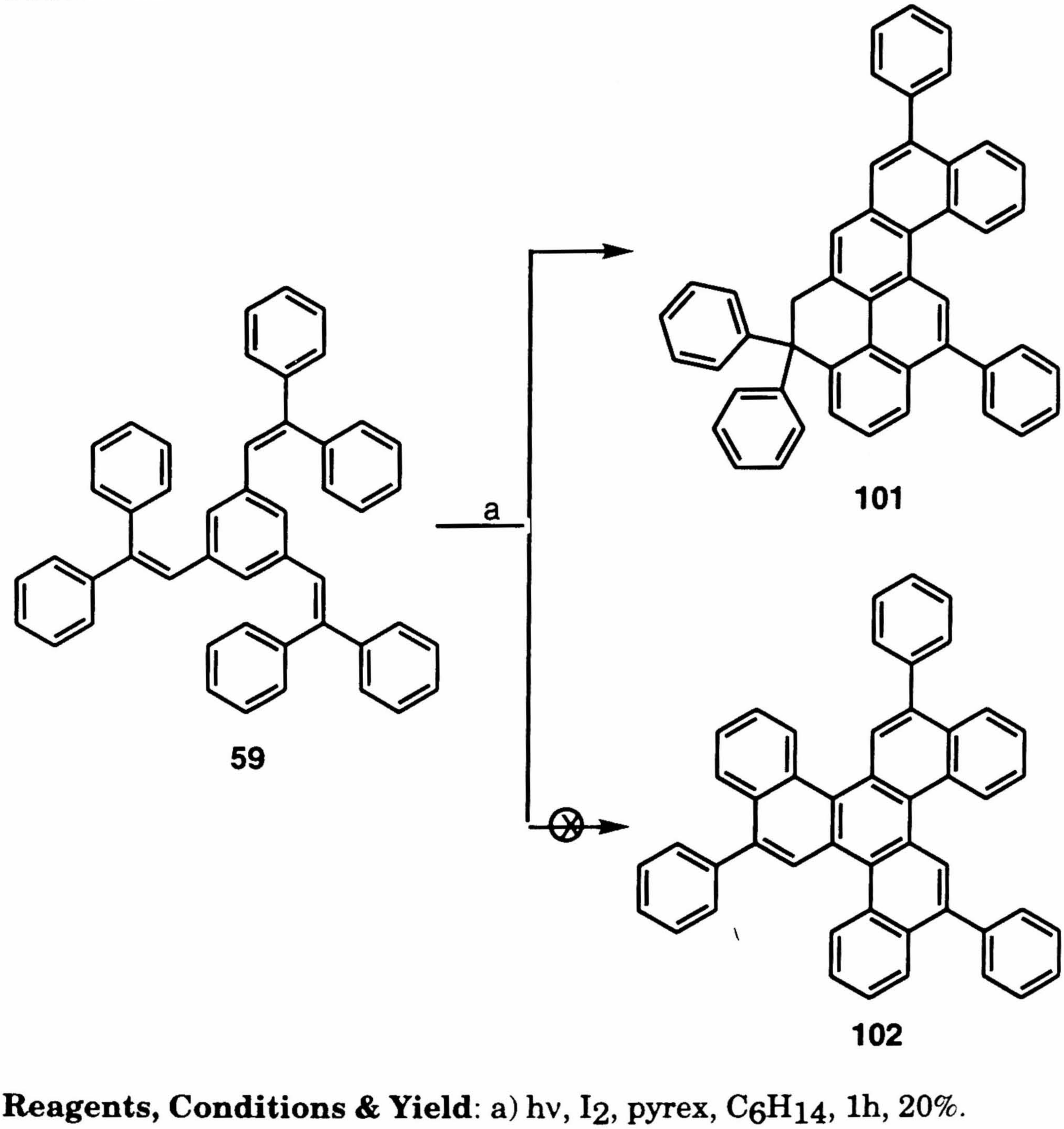
**59**

**Reagents, Conditions & Yields:** a) Li, )))), THF, 4h, 35%; b) 20% $H_2SO_4$, THF, Δ, 6h, 65%.

dehydration of **100** with 20% $H_2SO_4$ readily furnished 1,3,5-*tris*(2',2'-diphenylethenyl)benzene **59** in 65% yield, which had been identified as a key precursor in Scheme 16. The $^1H$ NMR (Spectrum 15) resonance at δ 6.50 (singlet, 3H) showed the presence of an olefinic moiety and the 12-line $^{13}C$ NMR (Spectrum 16) δ 143.3, 142.5, 140.2, 136.9, 130.5, 129.5, 128.5, 128.2, 128.0, 127.6, 127.4 and 127.3 confirmed the retention of $C_3$-symmetry of **59**. Thus, the $C_{48}H_{36}$ **59**, which is a potential precursor of the target $C_{48}$-fragment **57** was prepared in two steps from readily available starting materials in good yield.

Having obtained the precursor **59** in a short sequence, the key step, i.e. the three-fold stilbene type of photocyclization was envisaged in order to obtain the condensed aromatic product **102**. Consequently, **59** was irradiated with 450W Hanovia medium pressure mercury vapour lamp in the presence of cat. $I_2$ in a pyrex vessel The photocyclization chartered an unexpected course and the photocyclized product turned out to be **101** rather than the expected and desired product **102**, (Scheme 38) whose structure was deduced from its spectral and analytical data.

**Scheme 38**




**59** **101** **102**

**Reagents, Conditions & Yield**: a) hν, $I_2$, pyrex, $C_6H_{14}$, 1h, 20%.

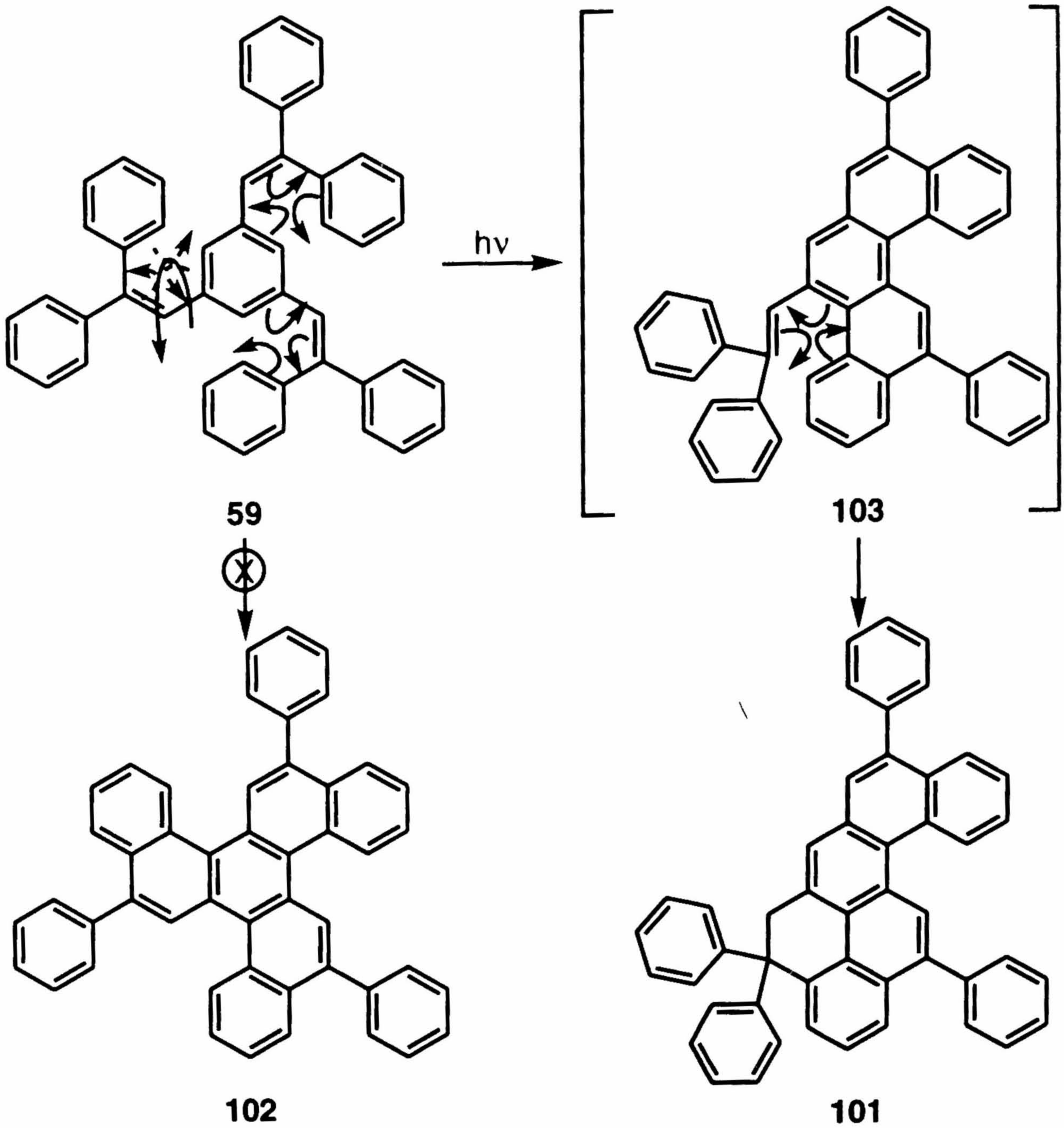
The molecular ion peak in the FABMS of **101** at 608 a.m.u. clearly indicated the loss of only four protons during photocyclization,

whereas structure **102** would have exhibited a molecular ion peak at 606 a.m.u. The $^{1}H$ NMR (Spectrum 17) resonance at δ 4.29 (singlet, 2H) indicated the presence of a methylene moiety and the resonances at δ 9.06 (doublet, 1H, J=8.0Hz) and at δ 8.98 (singlet, 1H) indicated the presence of the 'bay' region in the molecule. The $^{13}C$ NMR (Spectrum 18) clearly indicated that the molecule was completely devoid of any symmetry (cf. $C_3$-symmetry of **102**). Further, the two aliphatic signals in the $^{13}C$ NMR clearly indicate the presence of a quartenary carbon at δ 53.4 and methylene carbon at δ 43.5 confirming the structure of **101**. The unexpected formation of **101** could be rationalized as shown in Scheme 39. While the first two photo cyclizations proceed in the expected stilbene → phenanthrene type mode, the third cyclization deviates to produce **101** instead of **102**.[68]

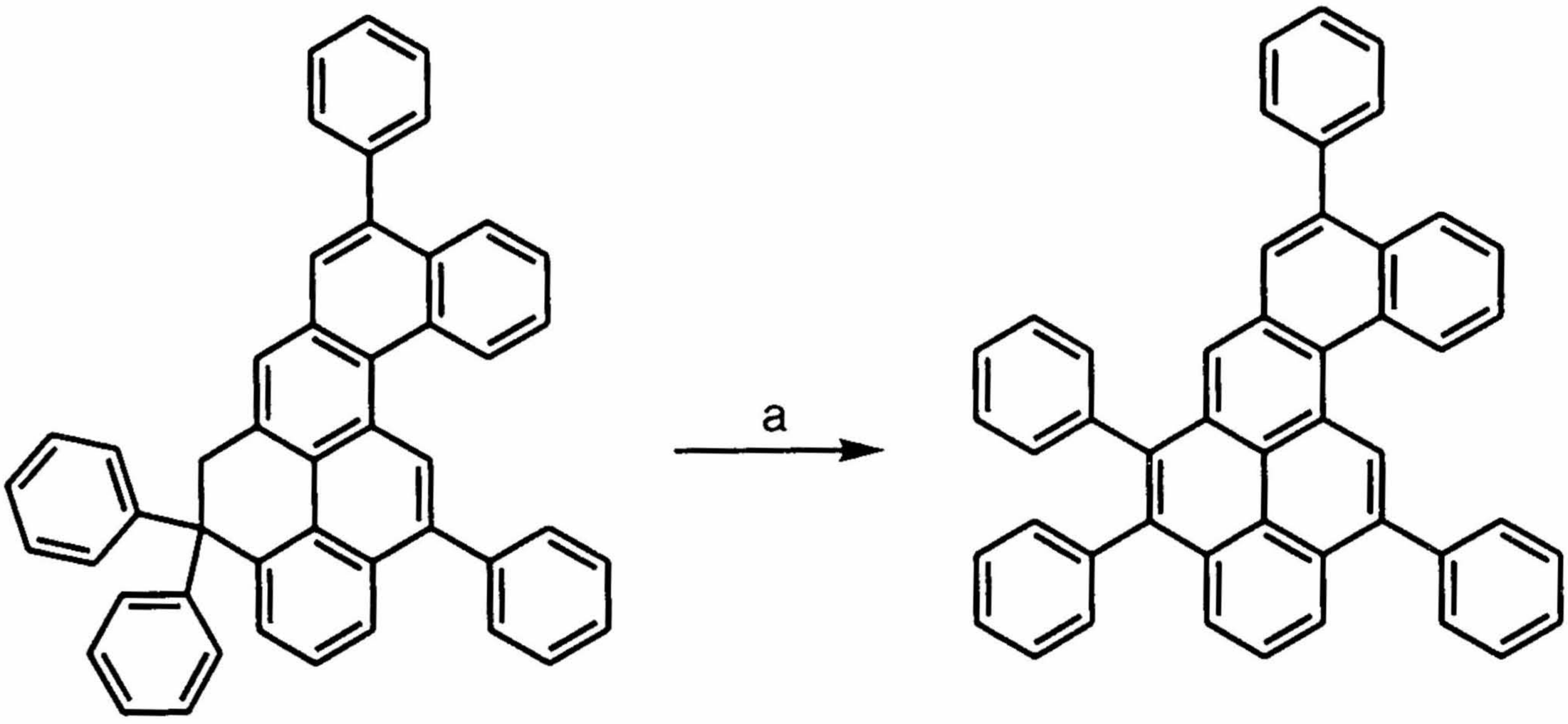
Although **101** was clearly an undesired product, we still felt that it could be serviceable for the limited purpose of demonstrating aryl-aryl connectivity under thermal activation. Thermolysis of **101** over Pd/C under static conditions at 400 °C resulted in the rearrangement and

aromatization of **101** through 1,2-phenyl migration, to furnish **104** in 80% yield, Scheme 40.

**Scheme 39**



**Scheme 40**

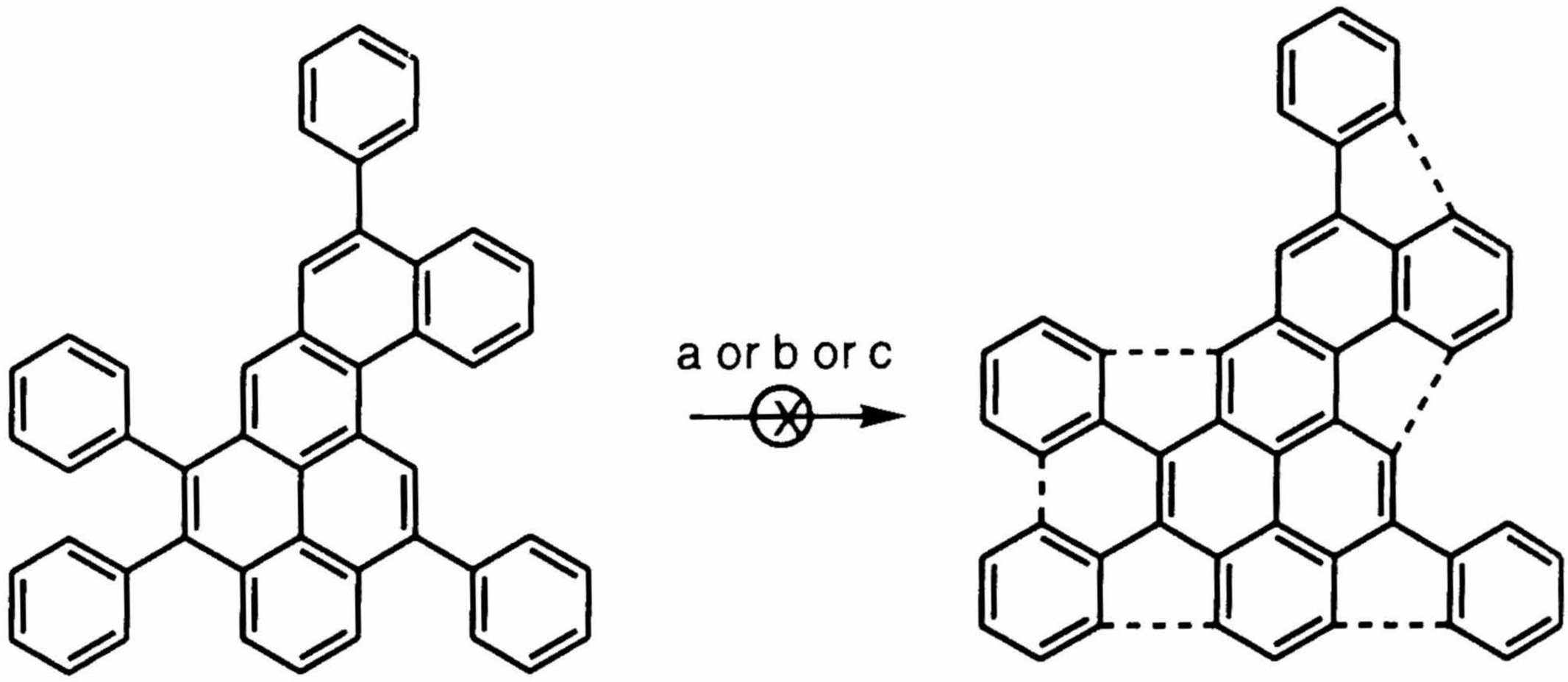



**101** **104**

**Reagents, Conditions & Yield**: a) Pd/C, 400 °C, 2h, 80%.

The structure of **104** was confirmed by analytical and spectral data with the molecular ion peak indicating the loss of two protons. The absence of $^{1}H$ NMR (Spectrum 19) resonance at δ 4.29 and $^{13}C$ NMR (Spectrum 20) resonances at δ 53.4 and 43.5 clearly indicated complete aromatization. However, the structure of **104** was further confirmed by X-ray crystal structure determination.[69] A perspective is shown in Fig. 6. FVP of **104** was also attained to establish transannular bridging as shown in **105**. However, this objective has remained unattainable. Even

**Scheme 41**



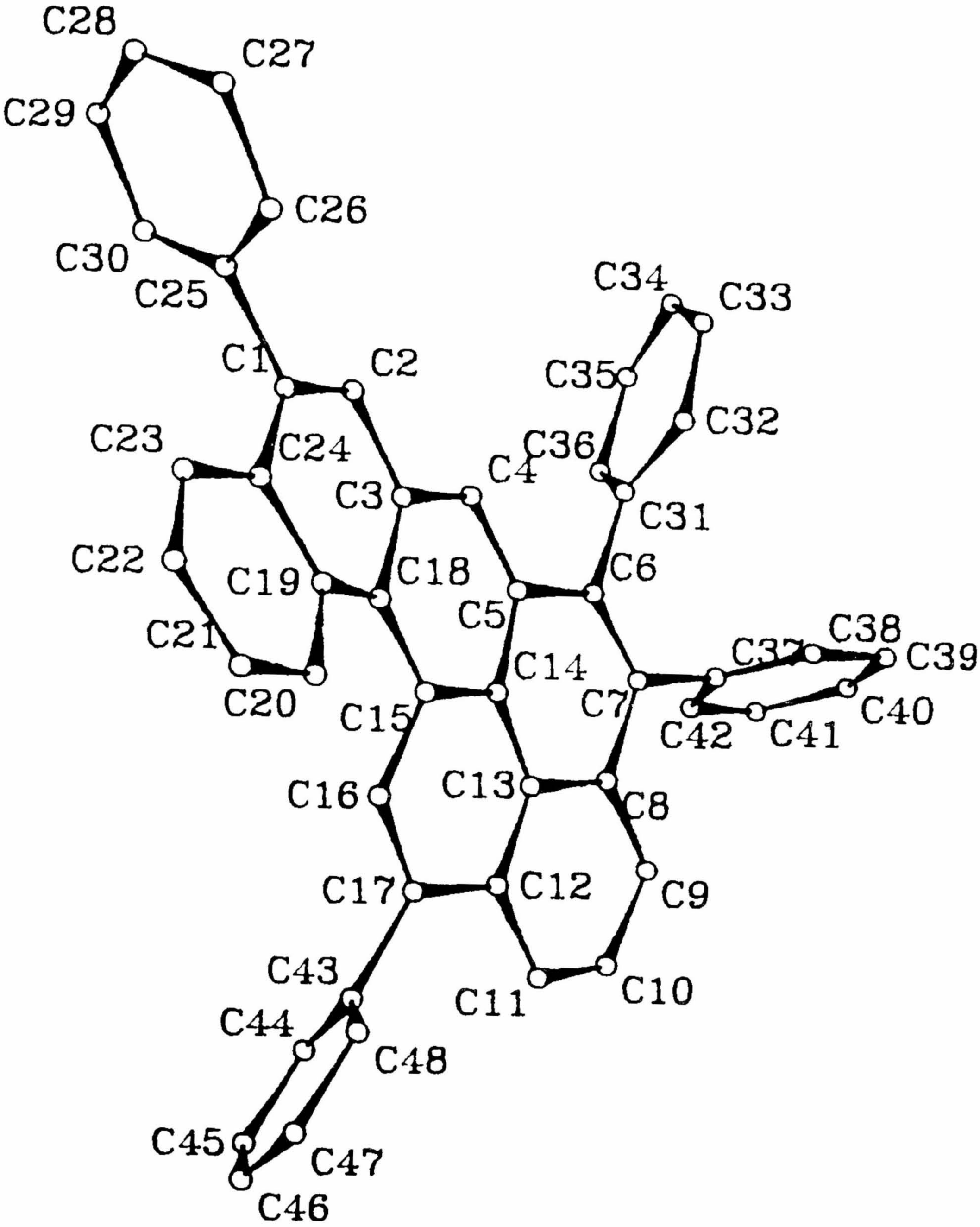

**104** **105**

**Reagents & Conditions**: a) hν, $I_2$, Pyrex, hexane; b) FVP, 900 °C and 1000 °C, .0.3 mm; c) Pd/C, 400 °C, 2h.

the irradiation of **104**, to attain the triphenylene moiety, was not possible and, therefore, we did not proceed further with this compound, Scheme 41

As an alternative, the compound **59** was hydrogenated using 10% Pd/C to get 1,3,5-*tris*(2',2'-diphenylethyl)benzene **106** (Scheme 42) whose analytical and spectral data were fully consonant with its structure. The $^1$H NMR (Spectrum 21) resonances at δ 3.18 (doublet, 2H, J=8.0 Hz) at δ

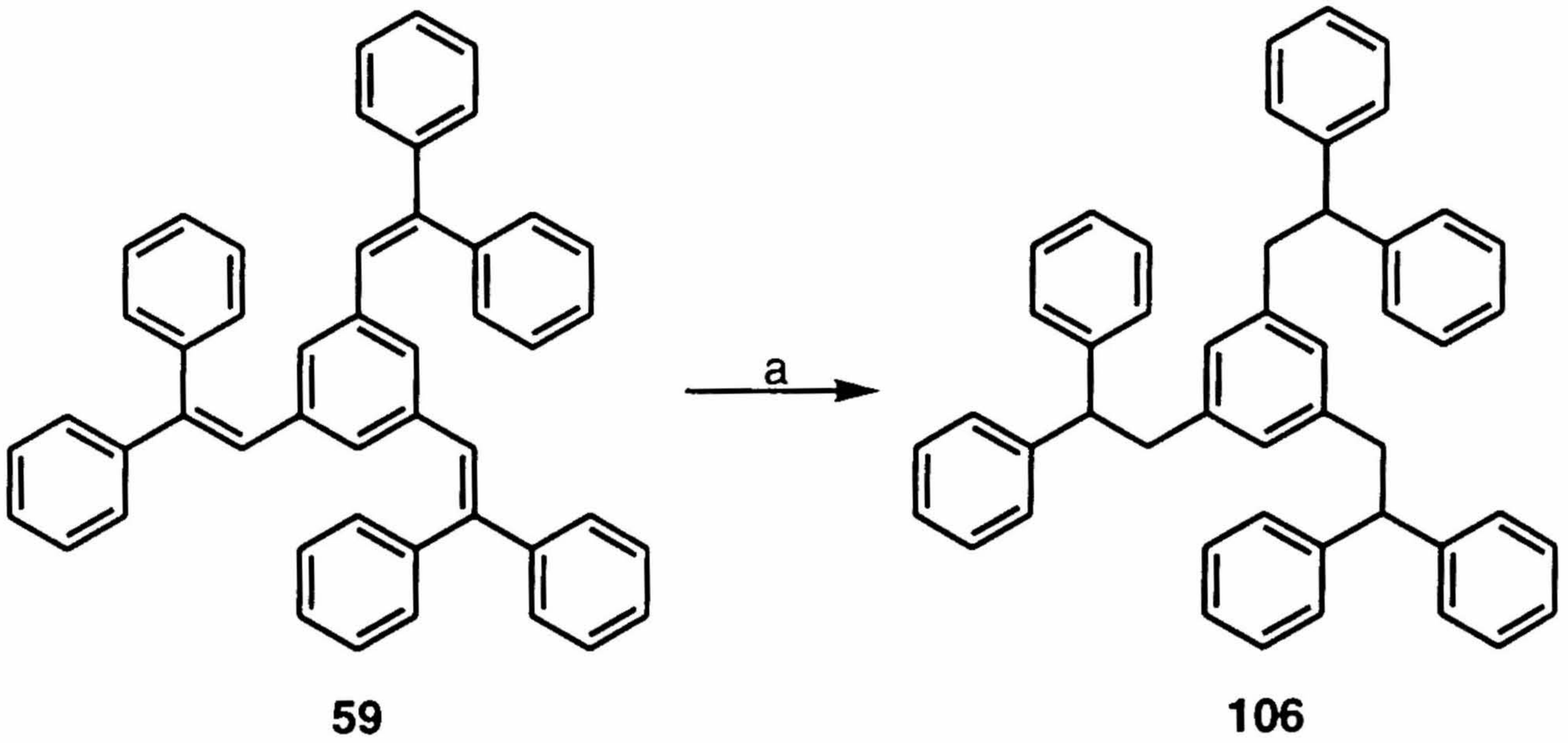
**Figure 6**




**X-ray Crystal Structure of 104**

3.88 (triplet, 1H, $J_1=J_2=6$ 0 Hz) indicated the presence of the benzylic moiety with the $^{13}C$ NMR (Spectrum 22) clearly showing the retention of $C_3$-symmetry.

**Scheme 42**



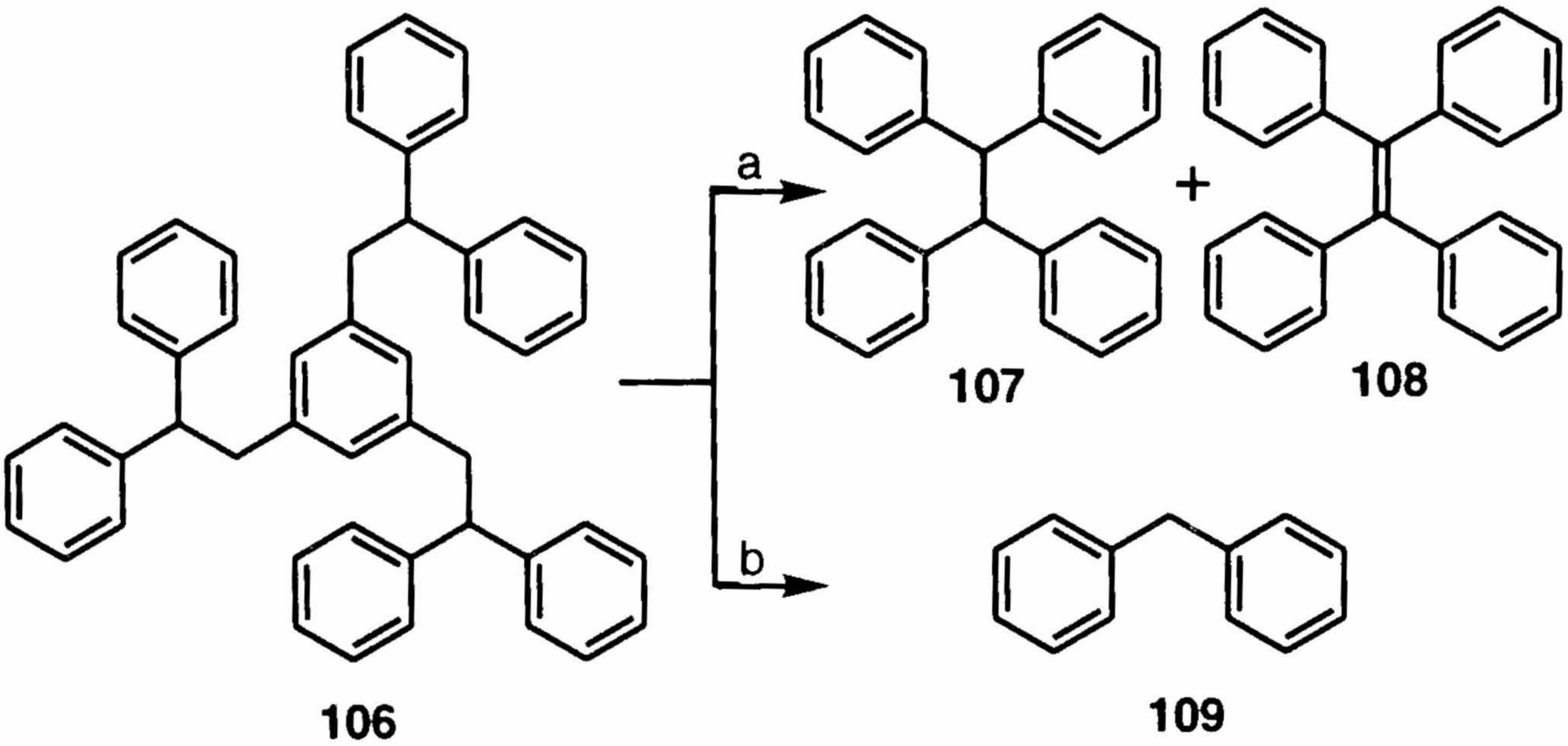

**59** **106**

**Reagents, Conditions & Yield**: a) Pd/C, $H_2$, EtOAc, 95%.

Attempts to cyclize **106** by FVP furnished 1,1,2,2-tetraphenylethane **107** and 1,1,2,2-tetraphenylethylene **108**. On the other hand, treatment of **106** with Pd/C under static conditions yielded only diphenylmethane **109**, Scheme 43.

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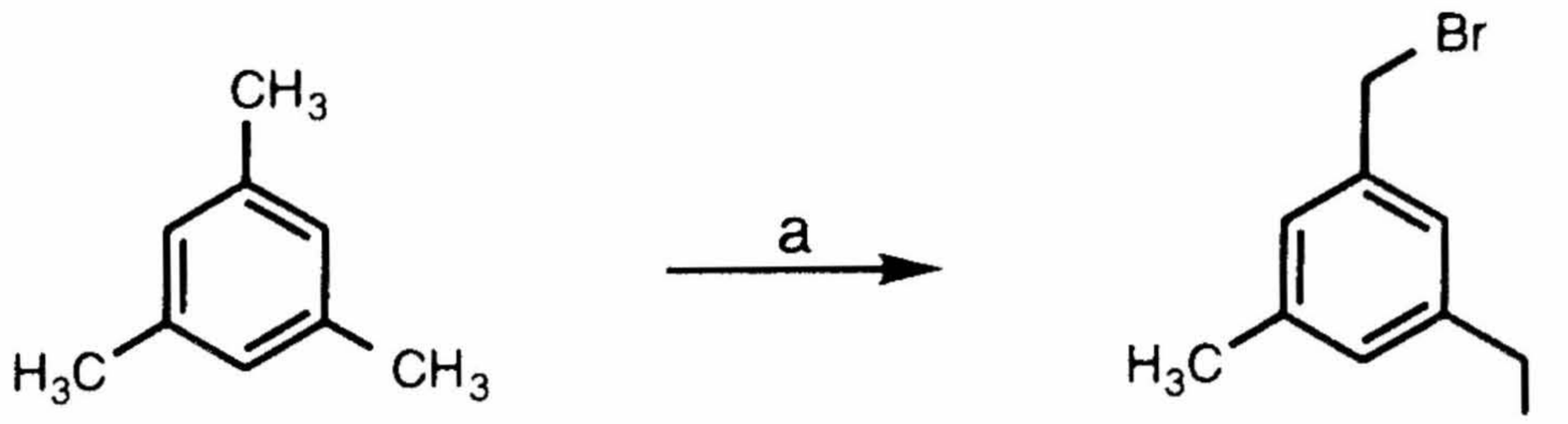
**Scheme 43**




**Reagents & Conditions** : a) FVP, 900°C, 0.3 mm; b) Pd/C, 400°C, 2 h.

Since the unexpected mode of photocyclization (**59** → **101**) was leading to an unwanted skeleton and consequent loss of C3-symmetry, it was decided to circumvent this cyclization by blocking the unwanted photocyclization site. For this purpose, 1,3-*bis*(bromomethyl)-5-methylbenzene **110** was prepared by bromination of mesitylene **64** using two equivalents of NBS in the presence of AIBN, Scheme 44.

**Scheme 44**

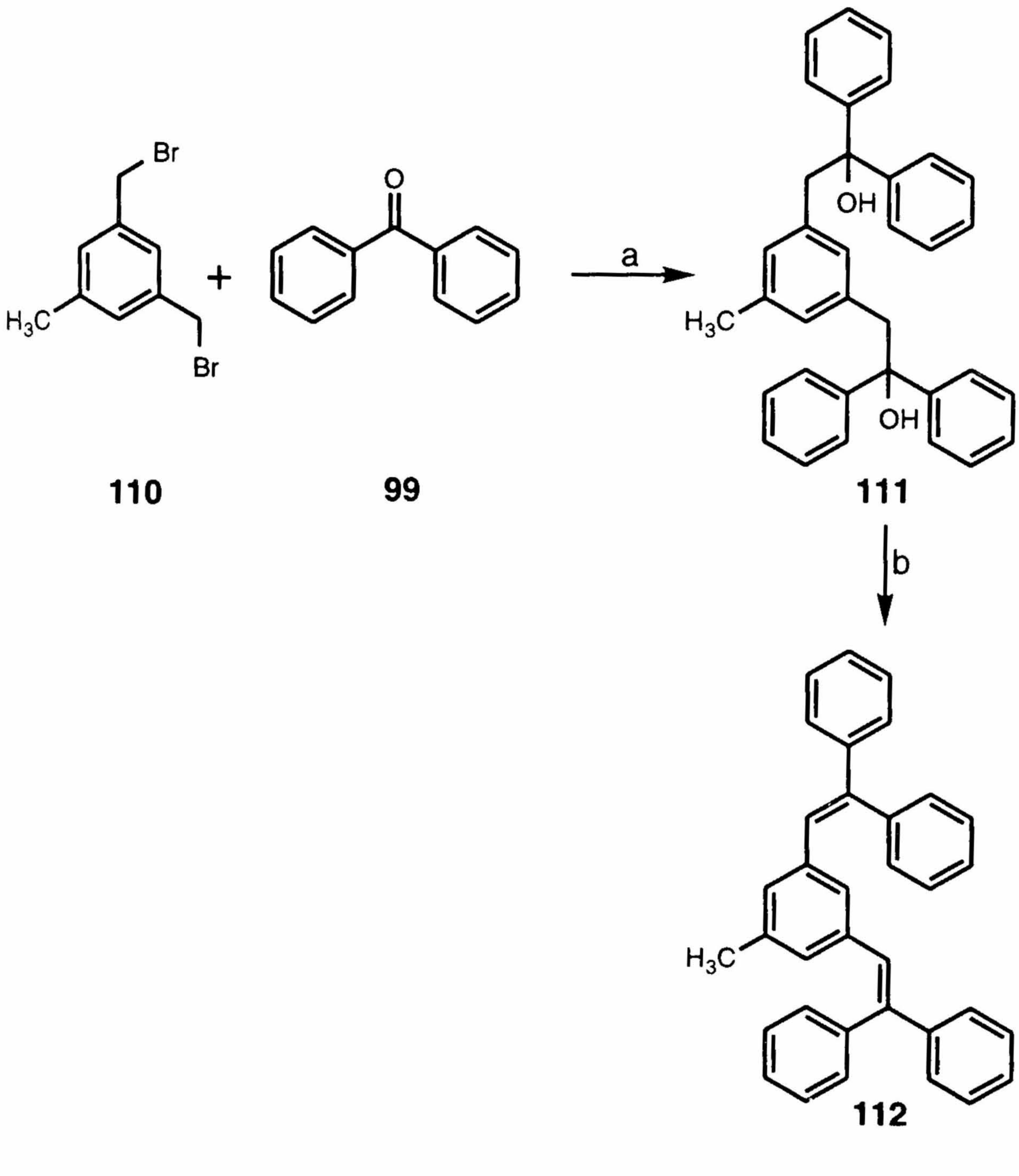



**64** **110**

**Reagents, Conditions & Yield** a) NBS, AIBN, $CCl_4$, Δ, 30%.

Barbier-type reaction between 1,3-*bis*(bromomethyl)-5-methyl-benzene **110** and two moles of benzophenone **99** in the presence of lithium, under sonication, furnished the dihydroxy compound 1,3-*bis*(2',2'-diphenyl-2'-hydroxyethyl)-5-methylbenzene **111** in 30% yield, Scheme 45 The IR spectrum with absorption at 3531 $cm^{-1}$ showed the presence of hydroxyl group The $^1H$ NMR (Spectrum 23) resonance at δ 3.50 (singlet, 4H) indicated the presence of two benzylic methylene groups. Dehydration of **111** with 20% $H_2SO_4$ smoothly furnished the dehydrated compound 1,3-*bis*(2',2'-diphenylethenyl)-5-methylbenzene **112** in 75% yield, with the analytical and spectral data confirming its structure The $^1H$ NMR (Spectrum 25) resonances at δ 6.65 (singlet, 2H), 6.50 (singlet, 1H) indicated the substitution pattern on the central

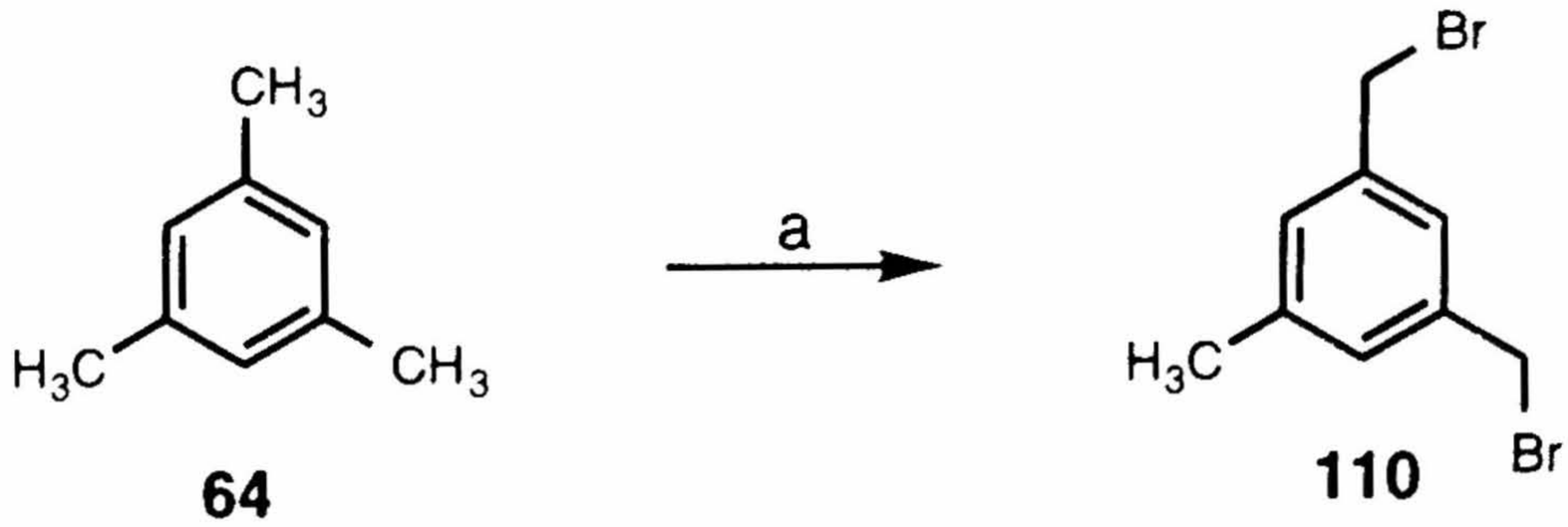
**Scheme 45**




**110** **99** **111** **112**

**Reagents, Conditions & Yields:** a) Li, ))))), THF, 30%; b) 20% $H_2SO_4$, THF, Δ, 75%.

**Scheme 44**

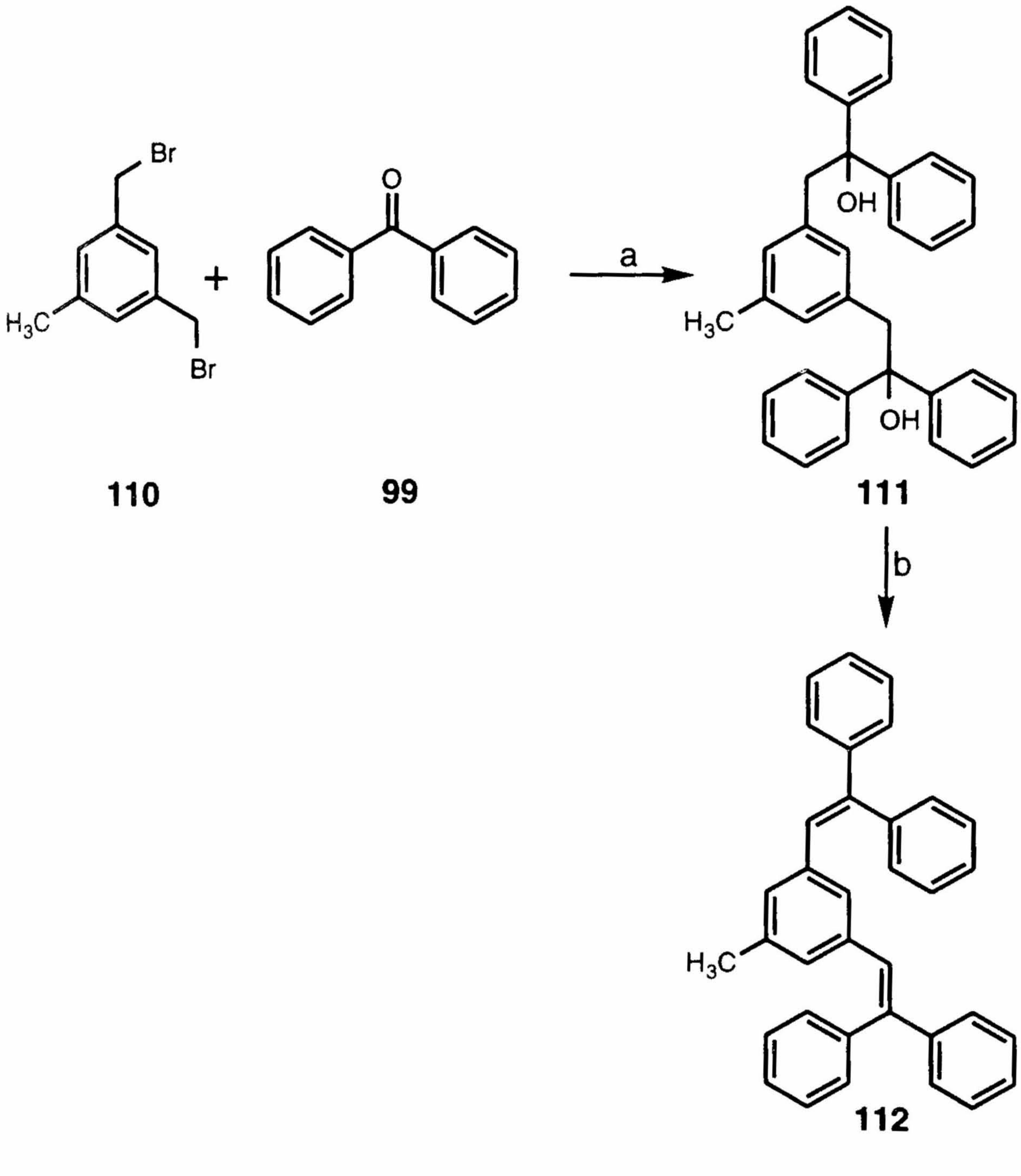



64 110

**Reagents, Conditions & Yield** a) NBS, AIBN, $CCl_4$, Δ, 30%.

Barbier-type reaction between 1,3-*bis*(bromomethyl)-5-methyl-benzene **110** and two moles of benzophenone **99** in the presence of lithium, under sonication, furnished the dihydroxy compound 1,3-*bis*(2',2'-diphenyl-2'-hydroxyethyl)-5-methylbenzene **111** in 30% yield, Scheme 45 The IR spectrum with absorption at 3531 $cm^{-1}$ showed the presence of hydroxyl group The $^1H$ NMR (Spectrum 23) resonance at δ 3 50 (singlet, 4H) indicated the presence of two benzylic methylene groups Dehydration of **111** with 20% $H_2SO_4$ smoothly furnished the dehydrated compound 1,3-*bis*(2',2'-diphenylethenyl)-5-methylbenzene **112** in 75% yield, with the analytical and spectral data confirming its structure The $^1H$ NMR (Spectrum 25) resonances at δ 6.65 (singlet, 2H), 6.50 (singlet, 1H) indicated the substitution pattern on the central

**Scheme 45**



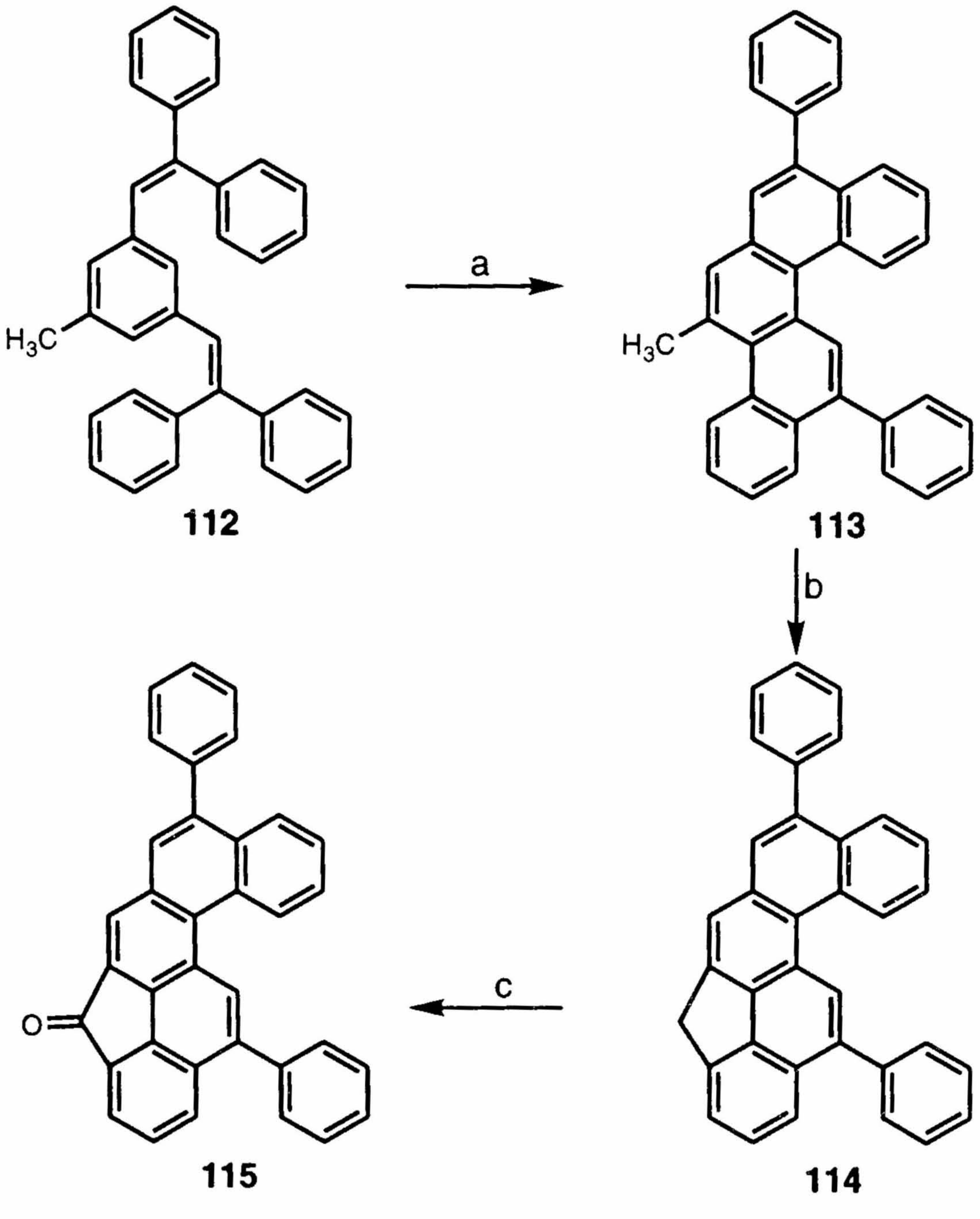

**110** **99** **111** **112**

**Reagents, Conditions & Yields:** a) Li, ))))), THF, 30%; b) 20% $H_2SO_4$, THF, Δ, 75%.

benzene ring and the resonance at δ 6.42 (singlet, 2H) showed the presence of the olefinic moiety present in the structure **112**. The $^{13}C$ NMR spectrum (Spectrum 26) of **112** had 16-lines in confirmity with its symmetry.

Now the key photocyclization step was expected to proceed smoothly. Irradiation of **112** in the presence of cat.$I_2$, using 450W Hanovia medium pressure mercury vapour lamp in a pyrex vessel, furnished the cyclized product **113**, whose structure was in full agreement with its $^{1}H$ NMR and $^{13}C$ NMR spectral data, Scheme 46. The $^{1}H$ NMR (Spectrum 27) resonances at δ 9.07 (doublet, 1H, J=9.0 Hz) and δ 8.94 (singlet, 1H) clearly indicated the presence of the 'bay' region and the formation of the condensed polycyclic aromatic structure. The $^{13}C$ NMR spectrum (Spectrum 28) had 24 lines shows the loss of symmetry. In **113**, we wished to demonstrate the formation of transannular methylene bridge under thermal activation. Cyclodehydrogenation of **113** over Pd/C furnished **114**, which exhibited the characteristic methano-bridge resonances at δ 4.55 (singlet, 2H) in the $^{1}H$ NMR (Spectrum 29) and δ 36.9 in the $^{13}C$ NMR (Spectrum 30). The methano

**Scheme 46**




**112** **113** **114** **115**

**Reagents, Conditions & Yields:** a) hν, $I_2$, pyrex, $C_6H_{14}$, 1h, 80%; b) Pd/C, 400 °C, 2h, 57%; c) $Cr_2O_3/H_2SO_4$, 0 °C, 73%.

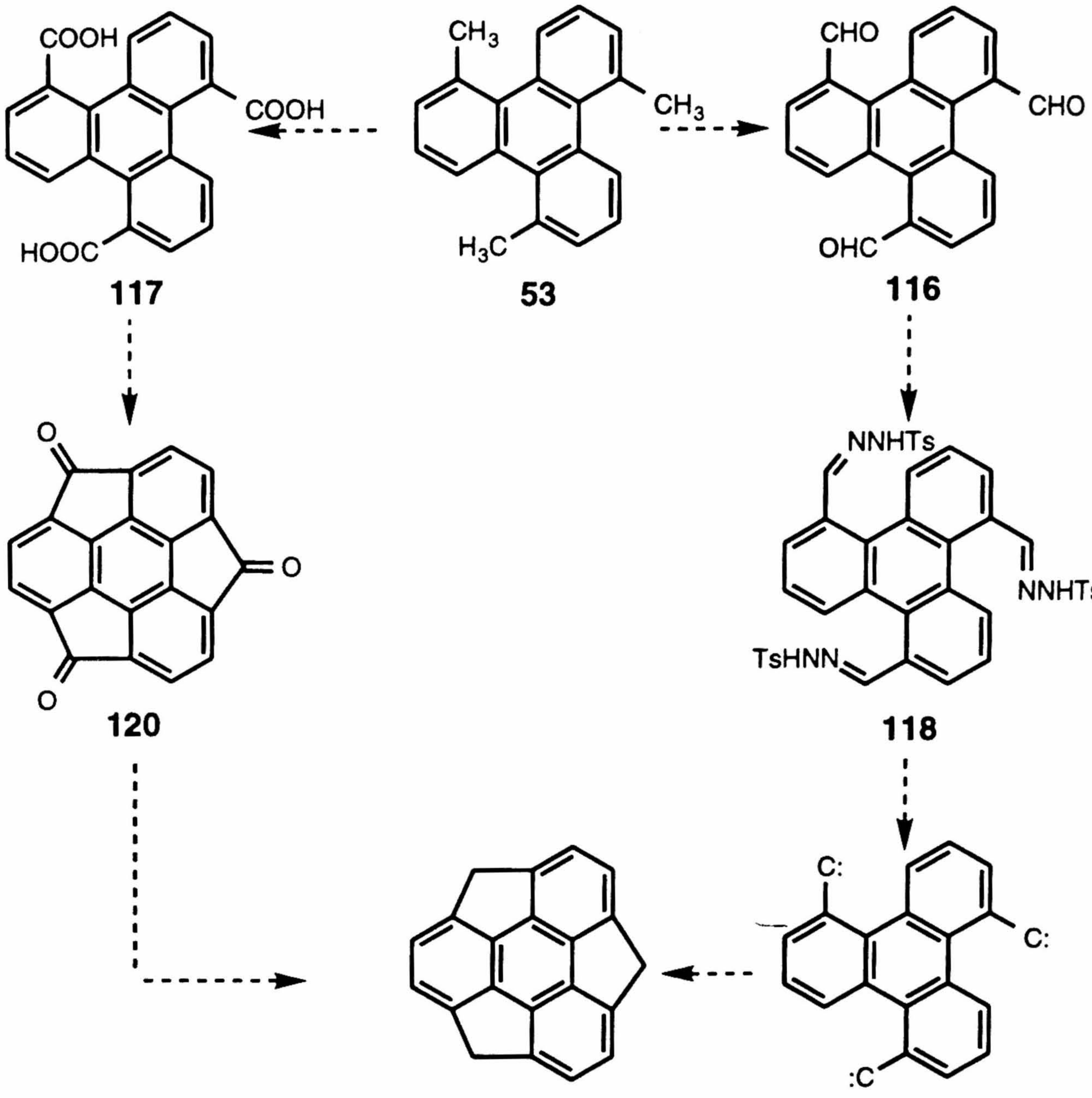
bridge in **114** was readily functionalized to **115** through Jones oxidation for further elaboration. The molecular ion peak at 456 a.m.u., the IR frequency at 1717 $cm^{-1}$ the absence of methylene resonance in the $^{1}H$ NMR (Spectrum 31) and $^{13}C$ NMR (Spectrum 32) resonance at δ 189.9 confirmed the presence of a carbonyl group in **115**. The carbonyl group in **115** can be an effective handle for further elaboration. Eventhough, further cyclodehydrogenation of **114** and **115**, under FVP conditions has not been successful, the $C_{35}$-motif of **114** and **115** represents a segment of [60]-fullerene.

## Synthetic Studies Directed Towards Sumanene $C_{21}H_{12}$ (3) and its Derivatives

In the introductory section we have shown that at the University of Hyderabad we reposed our faith in a $C_3$-symmetry route to $C_{60}$ and identified the heptacyclic $C_{21}$-hydrocarbon, 'sumanene' **3**, both as an attractive target in its own right as well as a launching pad for $C_{60}$. In this context, $C_3$-symmetric 1,5,9-trimethyl triphenylene **53** served as the key precursor in which we attempted to establish three methylene bridges in the quest for **3**. However, in practice only mono-bridged product **54** was obtained from **53** on either FVP or Pd/C mediated cyclo-dehydrogenation. Recourse to a tribromomethyl precursor **55** proved more promising and the doubly bridged compound **56** was obtained on FVP and fully characterized. However, the third methylene bridge could not be established, Scheme 15.[52]

Since we had better success with **55** compared to **53**, we reasoned that embellished derivatives of **53** may provide better avenues for the ring closure. Among the various possibilities, the two that appeared worth attempting were *via* the trialdehyde **116** and the triacid **117**,

**Scheme 47**



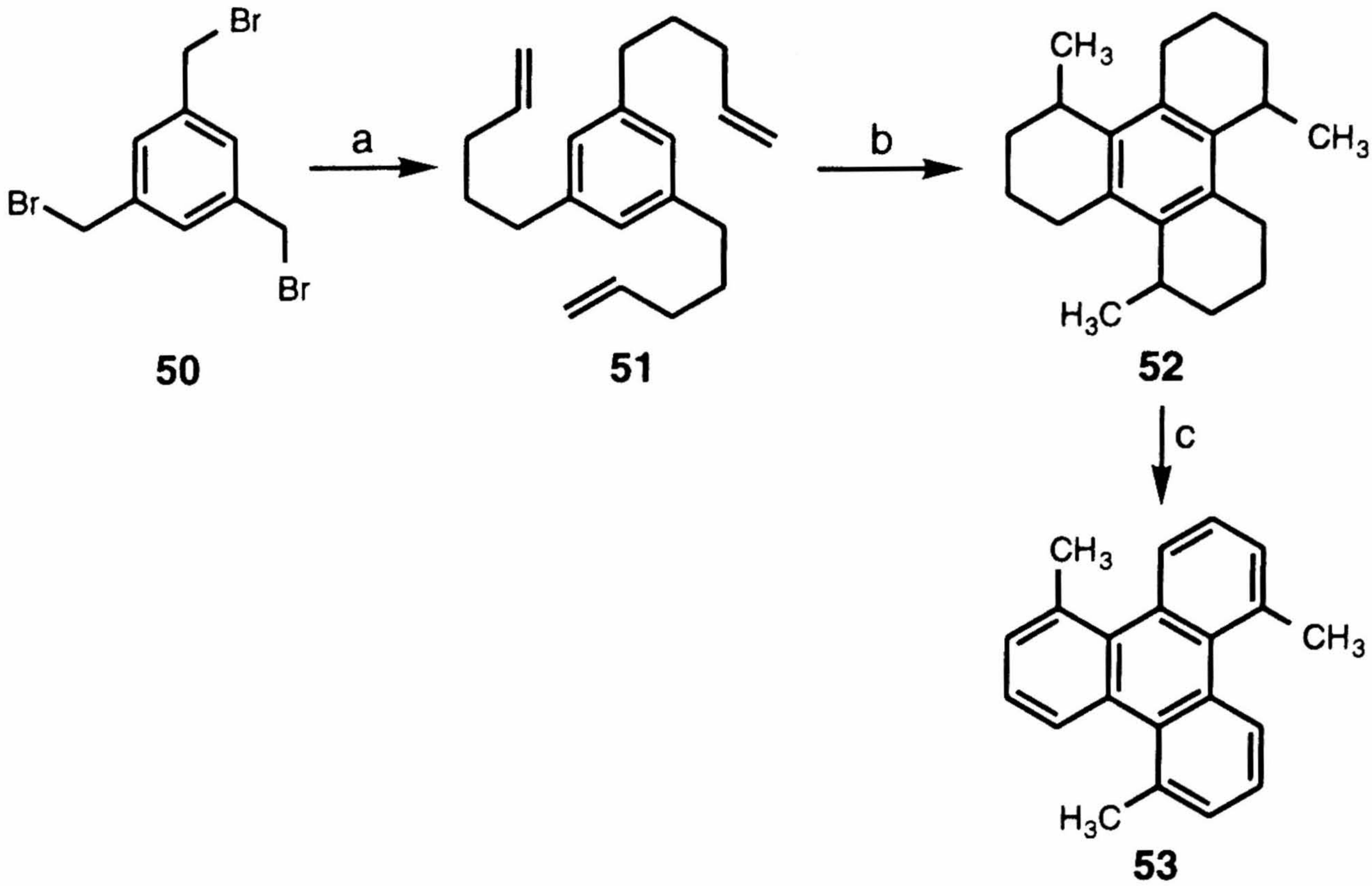

Scheme 47. It was envisaged that the trialdehyde could be transformed to the *tris*-tosylhydrazone **118** from which a *tris*-carbeniod species **119** could be generated. A species like **119** formed directly or sequentially

from **116**, was expected to insert into the neighbouring transannular aromatic ring[70] and establish crucial bridging leading to sumanene. Alternatively, the tricarboxylic acid **117** was expected to undergo transannular cyclization to furnish the triketone **120**.[71] There is considerable literature precedence for both the types of contemplated reactions on **116** and **117**.

Thus, 1,5,9-trimethyltriphenylene **53** was synthesized as shown in Scheme 48. Initial attempts to directly oxidize the methyl groups in **53** to either **116** or **117**, employing various oxidizing agents, were not successful. Recourse was therefore taken to an alternative strategy.

Consequently, 1,5,9-*tris*(bromomethyl)triphenylene **55** was prepared by NBS mediated bromination of 1,5,9-trimethyl triphenylene **53**. Oxidation of **55** with *bis*-tetrabutylammoniumdichromate[72] furnished the 1,5,9-triformyl triphenylene **116**, Scheme 49. The structure of **116** was in full agreement with its $^{1}H$ NMR (Spectrum 33) and $^{13}C$ NMR (Spectrum 34) spectral data. The $^{1}H$ NMR resonances at $\delta$ 10.4 (singlet, 1H) indicated the presence of the aldehyde functionality,

**Scheme 48**

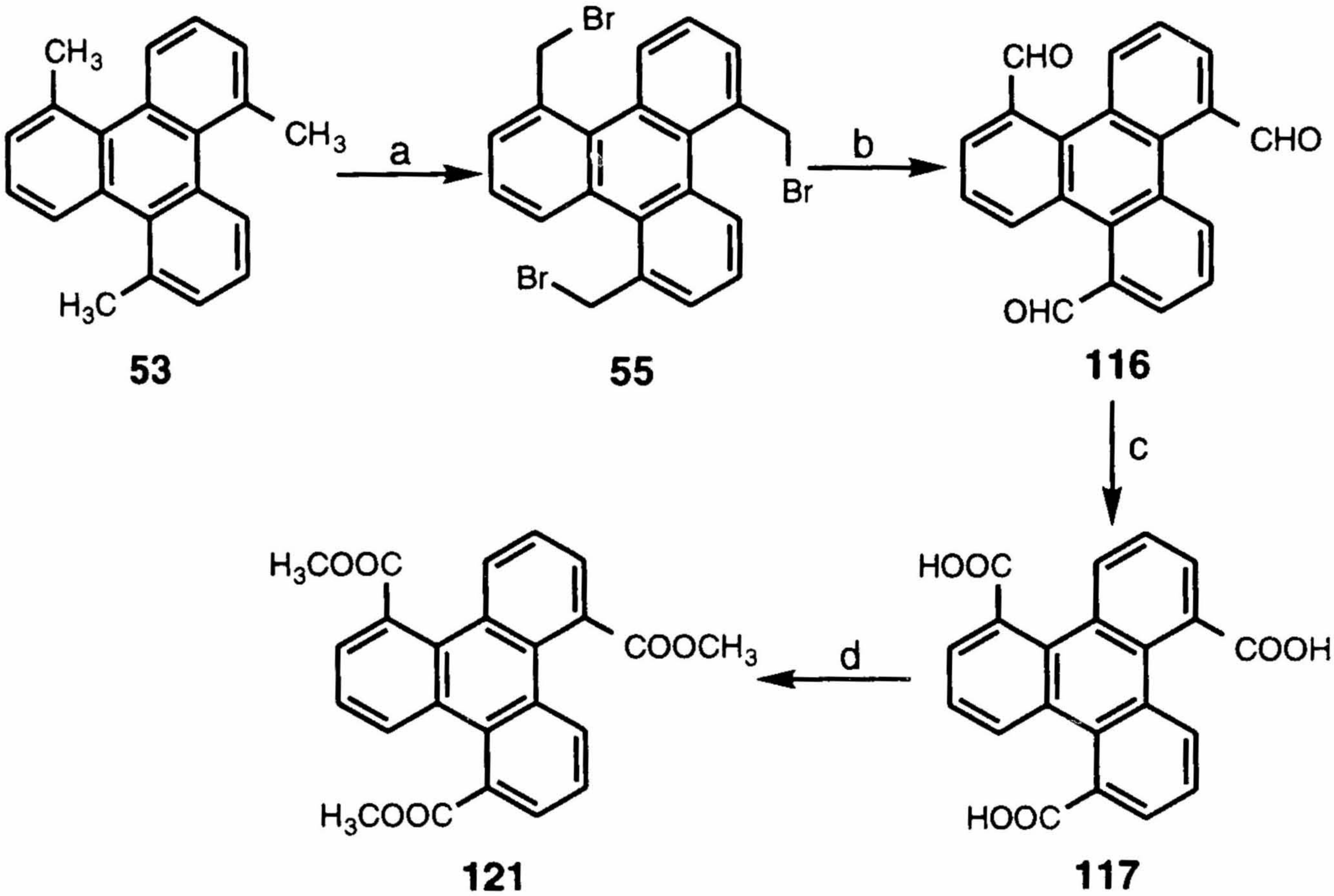



**50** **51** **52** **53**

**Reagents, Conditions & Yields:** a) $CH_2$=CH-$CH_2CH_2MgBr$, THF, $Li_2CuCl_4$, -10 → 25 °C, 3h, 45%; b) $BF_3$ (gas), $C_6H_6$, 25 °C, 2h, 55%; c) DDQ, $C_6H_6$, 95 °C, 2h, 46%.

with the 7 line $^{13}C$ NMR clearly showing the $C_3$-symmetry. Attempts were made to transform the trialdehyde **116** to the *tris*-tosylhydrazone **118**. However, despite many trials, a well characterizable material could not be obtained from this reaction. Possibly, strong *peri*-interaction inhibit the reactivity of the aldehyde functionality in **116**.

**Scheme 49**



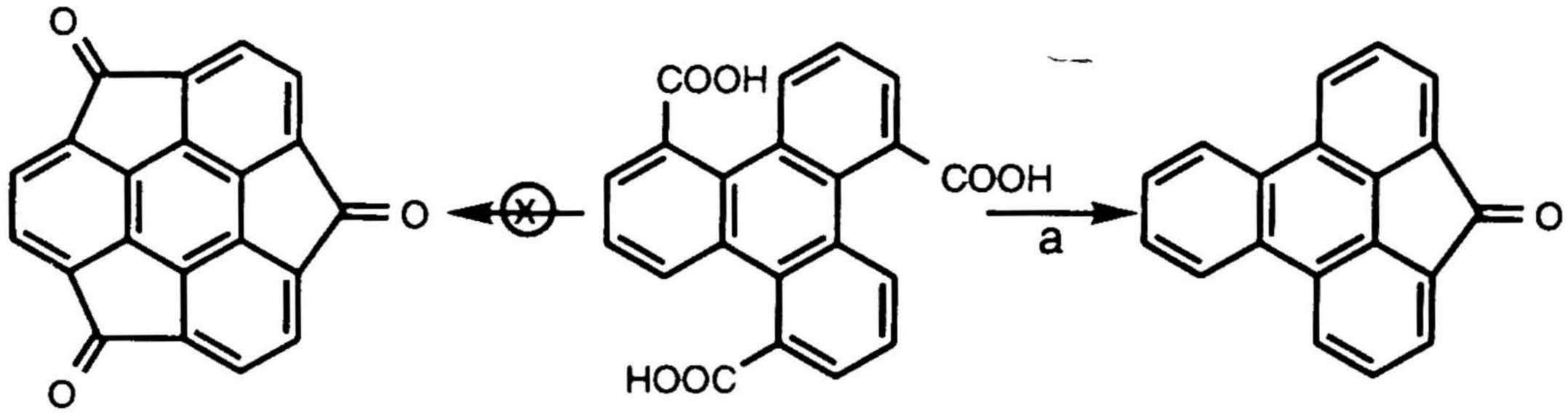

**Reagents, Conditions & Yields**: a) NBS, AIBN, $CCl_4$, 95 °C, 2h, 60%; b) $(n\text{-}Bu_4)_2NCr_2O_7$, $CHCl_3$, Δ, 2h, 45%; c) $n\text{-}Bu_4NMnO_4$, Pyridine, 3 h, r.t., d) $CH_2N_2$, ether, 48%.

We, therefore, switched to exploring the route *via* the triacid **117**. The aldehyde groups in **116** were oxidized with tetra-n-butylpermanganate[73] resulting in the formation of tricarboxylic acid **117**. The structure of the triacid was confirmed by converting it into its

triester **121** with diazomethane. The structure of triester **121** was in full agreement with its analytical and spectral data, in particular, its 8-line $^{13}C$ NMR (Spectrum 36) revealing its $C_3$-symmetry.

Now, the key step was the cyclization of the triacid **117** to get the tri-oxosumanene **120**. Heating the triacid **117** neat at 400 °C furnished only mono-cyclized product **122** in which the remaining two carboxylic acid groups had decarboxylated, Scheme 50. The structure was established by the presence of a carbonyl peak at 1720 $cm^{-1}$ and the molecular ion peak at 254 a.m.u. Attempted cyclization of the triacid with polyphosphoric acid, $P_2O_5$-methanesulfonic acid milieu and conc. $H_2SO_4$ gave the same product **122** in relatively poor yield.

**Scheme 50**

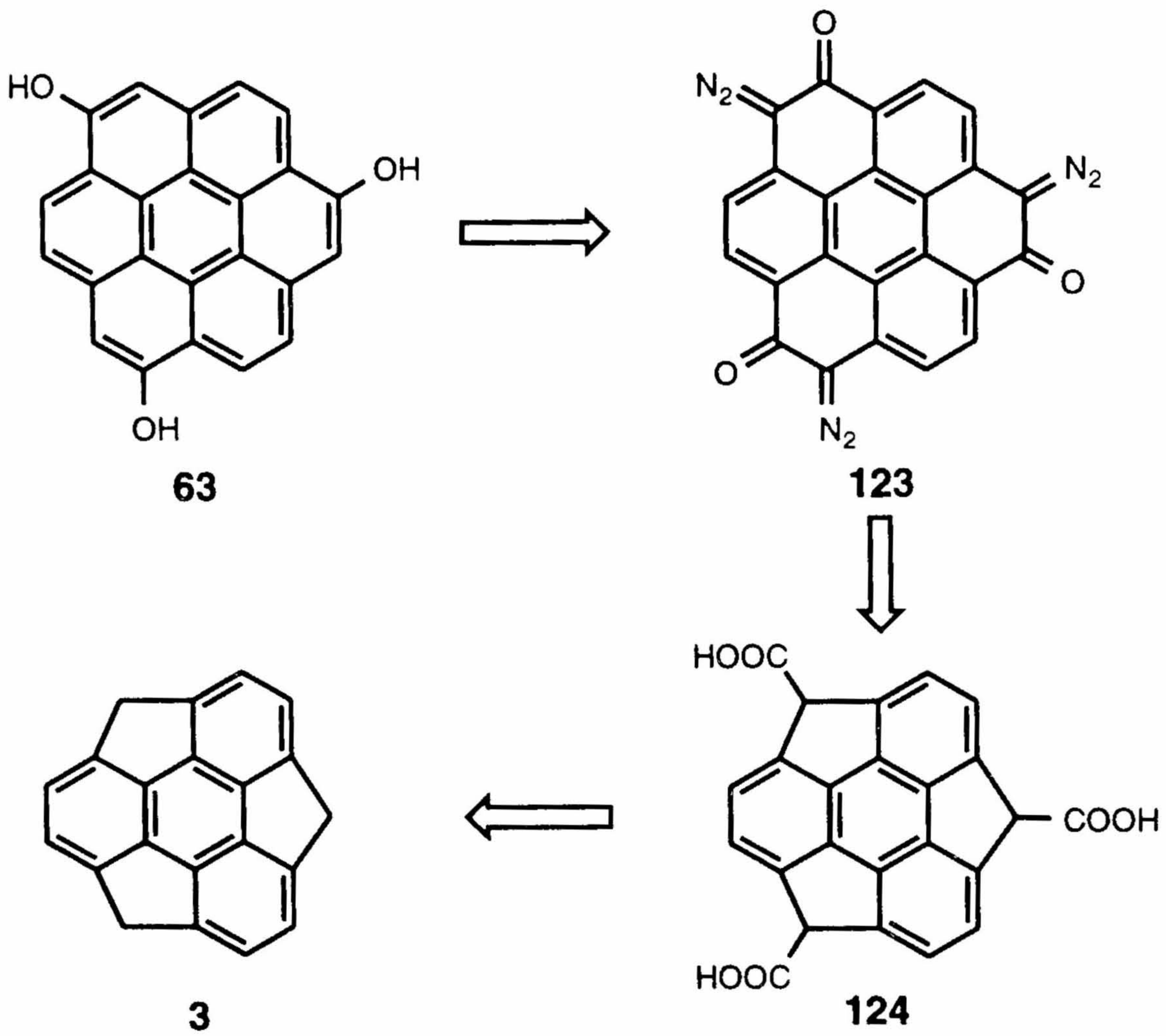



**120** **117** **122**

**Reagents, Conditions & Yield**: a) i. 400°C, 2h, 15%; or ii. PPA, 110°C, 15%.

Disappointed by the observation that only monocyclization product **122** was obtained and that decarboxylation became a major impediment, we considered another approach to sumanene system. We considered preparing a fuctionalized coronene derivative **63**, which

**Scheme 51**

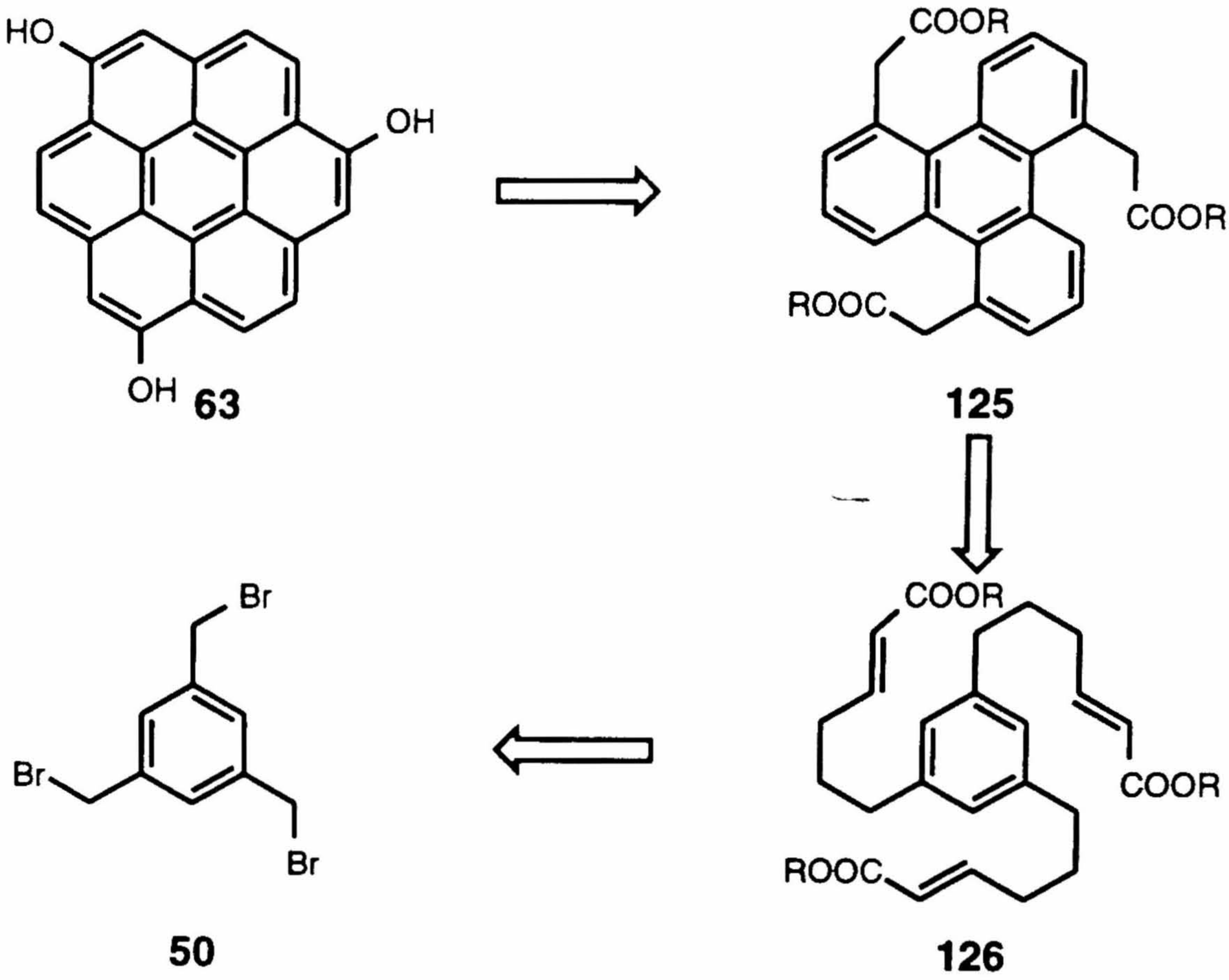



through diazo transfer, could be transformed to the *tris*-diazoketone **123**. Photochemically or thermally induced three fold Wolff rearrangement of

**123** was expected to deliver the sumanene tricarboxylic acid **124**, Scheme 51.

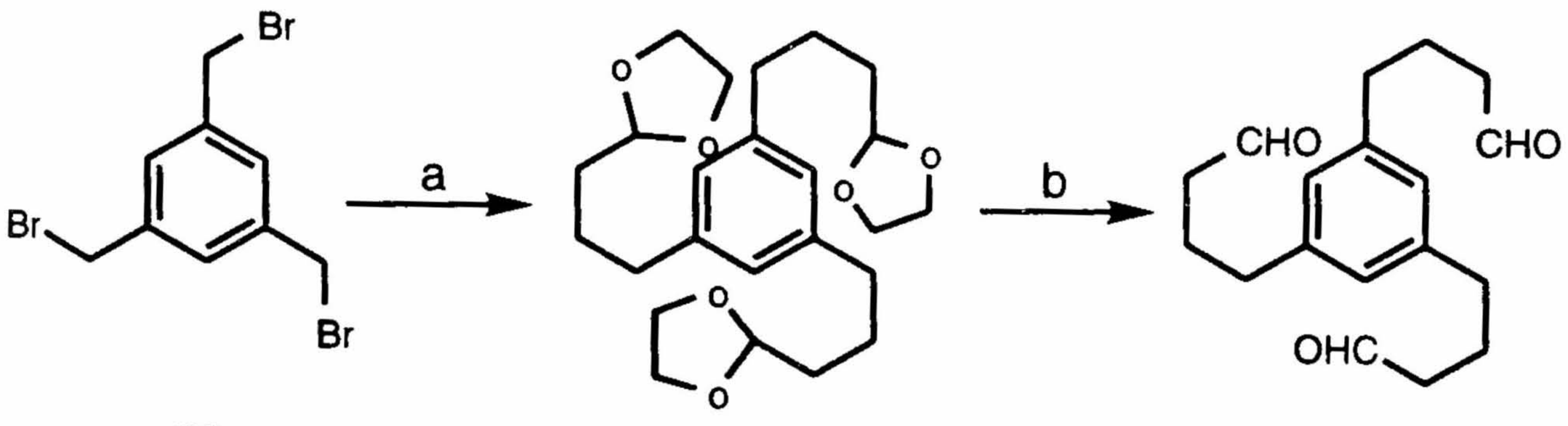
To realize **63**, tricarboxylic acid **125** was identified as the key intermediate as shown in Scheme 52. We felt that **125** could be obtained from **126** through three-fold cyclization. In turn, **126** could be accessed from 1,3,5-*tris*(bromomethyl)benzene **50**.

**Scheme 52**



Treatment of 1,3,5-*tris*(bromomethyl)benzene **50** with the Grignard reagent [prepared from 2-(2-bromomethyl)1,3-dioxalane],[74] in the presence of catalytic amount of dilithium coppertetrachloride[75] furnished the cross-coupled product **127** in 45% yield whose analytical and spectroscopic data were in full agreement with the structure **127**. The $^{1}H$ NMR (Spectrum 38) resonances at δ 6.82 (singlet, 1H) indicated the central benzene ring, at δ 4.86 (triplet, 1H, $J_1=J_2=4.0$ Hz) and the resonance at δ 3.90 (multiplet, 4H) indicated the 1,3-dioxalane group. In particular, the 7-line $^{13}C$ NMR (Spectrum 39) δ 142.1, 126.0, 104.5, 64.8, 35.7, 33.6, 25.8 revealed its $C_3$-symmetry, Scheme 53.

**Scheme 53**



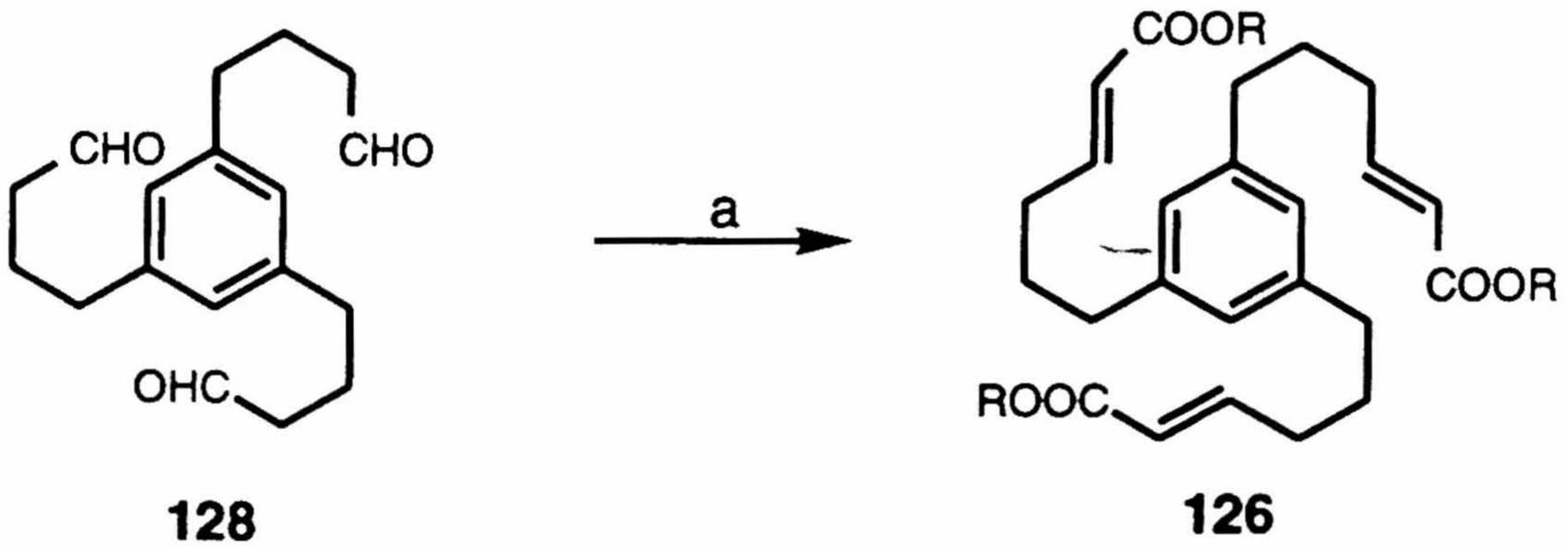

**50** **127** **128**

**Reagents, Conditions & Yield:** a) (-$OCH_2CH_2O$-)$CHCH_2CH_2MgBr$, THF, $Li_2CuCl_4$, -10 → 25 °C, 4 h, 45%; b) 0.5 N HCl, THF, 50%.

The *tris*-homologated compound **127** was carefully hydrolyzed to the trialdehyde **128** in 50% yield. The $^{1}H$ NMR (Spectrum 40) and $^{13}C$ NMR (Spectrum 41) confirmed the presence of the aldehyde functionality with $^{1}H$ NMR resonance at δ 9.75 and $^{13}C$ NMR resonance at δ 202.4. Further, the 6-line $^{13}$ C NMR confirmed the retention of $C_3$-symmetry.

The trialdehyde **128** was now sought to be converted to the α, β-unsaturated esters **126** through Horner-Wittig reaction. Treatment of trialdehyde **128**, with triethylorthophosphonoacetate using $Cs_2CO_3$ as a base, furnished the desired product **126** in 30% yield, Scheme 54.

**Scheme 54**



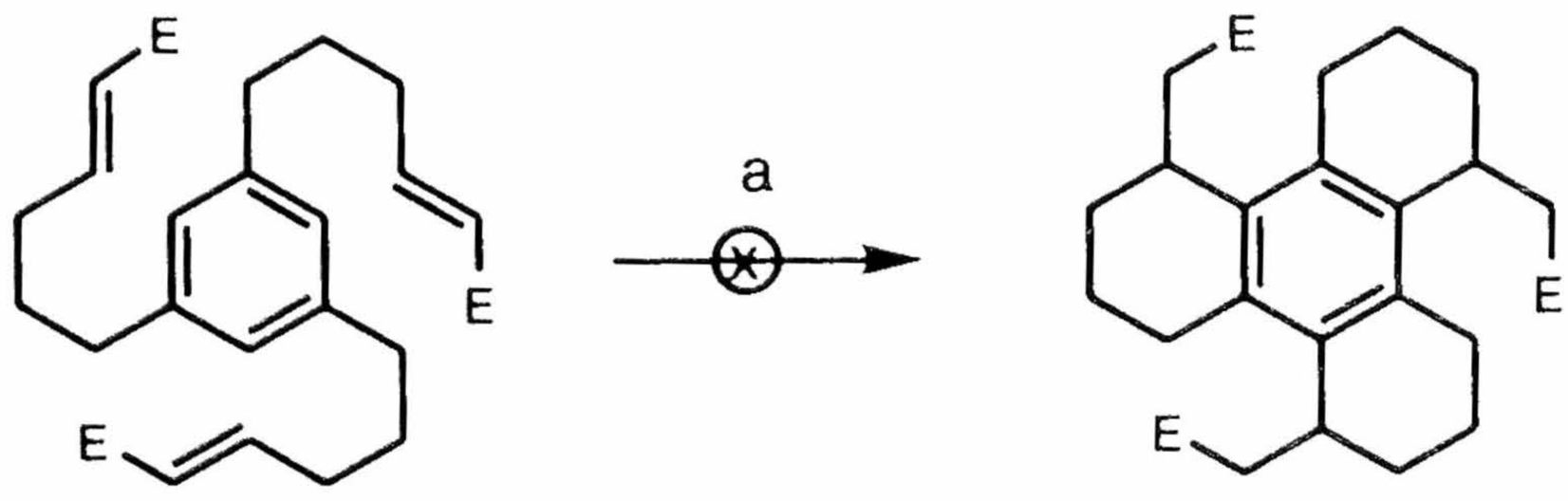

**128** **126**

**Reagents, Conditions & Yield**: a) $(EtO)_3POCH_2COOEt$, NaH, THF, 30%.

The structure of **126** was in full agreement with its spectral data and its 10-line $^{13}C$ NMR (Spectrum 43) showed that $C_3$-symmetry had been maintained throughout. Now, the key reaction was the cyclization of α, β-unsaturated esters

Taking the precedence from our laboratory, that when 1,3,5-tripentenylbenzene **51** is exposed to gaseous $BF_3$, furnishes the tetracycle **52** (Scheme 15), we attempted to convert **126** → **129** using gaseous $BF_3$ but our efforts were in vain Treatment of the tri-ester **126** with several Lewis acids failed to effect the cyclization, Scheme 55

**Scheme 55**



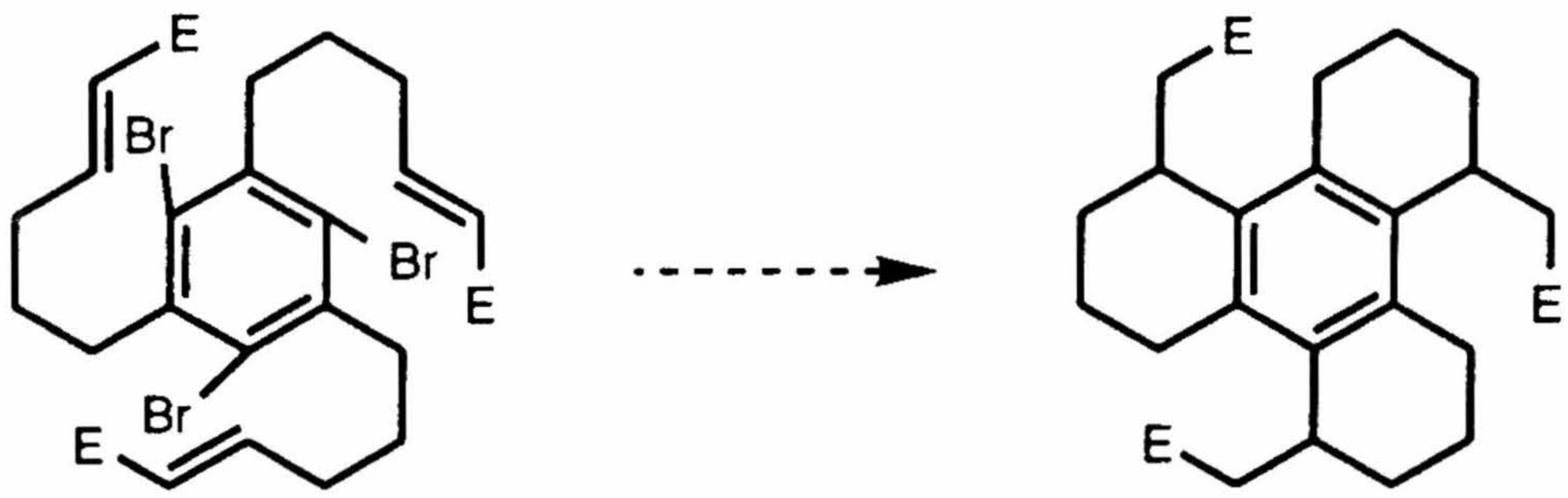

**126** **129**

**Reagents & Conditions** a) $BF_3$ (gas), $C_6H_6$, r t

The failure of **126** → **129** cyclization indicated that perhaps a better option would be to prepare **130** and attempt radical addition to

the α, β-unsaturated esters, Scheme 56. However, preparation of **130** presented unsurmountable problems.

**Scheme 56**.




**130** **129**

At this stage, the coronene based approach (Scheme 51) to sumanene was abandoned. However, a variation of this scheme could be a viable proposition and efforts along this direction are recommended.

# Summary

In summary, we have conceived a short approach to the polycyclic aromatic hydrocarbon fragments **3**, **57** and **60** *en route* to [60]-fullerene. The retrosynthetic theme depicted in Scheme 16, is notable for its brevity and novelty. The key precursors **53**, **58**, **59** and **61** shown in the Scheme 16, were prepared in a short sequence from readily available starting materials. We could assemble all the 48 carbon atoms present in **57** and 36 carbon atoms present in **60** in a single step. The $C_{35}$-motif of **114** and **115** (Scheme 46) represents a segment of [60]-fullerene and these fragments can be elaborated further to the $C_{48}$-fragment **57**. In our efforts towards sumanene **3**, we have synthesized many functionalized derivatives of 1,5,9-trisubstituted triphenylenes.

In the introduction to the thesis, we had emphatically drawn attention to the fact that synthesis of [60]-fullerene and its 'bowl-like' fragments along 'classical' synthetic route constitutes a formidable challenge. Indeed, our quest for **1** and its siblings like **3**, **57** and **60** had not only proved very difficult but met with

unexpected difficulties right from the beginning. None the less, it has been a worth while journey, full of hope, but more often than not eventuating in failure. But, we have learnt important lessons and believe that firm ground work has been laid for future assaults on these challenging and pleasing molecules.

# Experimental

**Melting points** : Melting points were recorded on Buchi SMP - 20 apparatus and are uncorrected.

**Boiling points** : Bulb to bulb distillations were carried out using oil bath for all liquid samples and boiling points refer to oil bath temperatures.

**Infrared spectra** : Infrared spectra were recorded on JASCO FT-IR 5300 or Perkin-Elmer 1310 spectrophotometers. Spectra were calibrated against the polystyrene absorption at 1601 $cm^{-1}$. Solid samples were recorded as KBr wafers and liquid samples as thin films between NaCl plates.

**Nuclear Magnetic Resonance spectra** : Proton magnetic resonance ($^{1}H$ NMR) spectra were generally recorded on Bruker AC 200 (200 MHz) or JEOL FX-100 (100 MHz) spectrophotometer. Carbon magnetic resonance ($^{13}C$ NMR) spectra were recorded on Bruker AC 200 (50 MHz) or JEOL FX-100 (25 MHz). $^{1}H$ and $^{13}C$ NMR samples were generally made in chloroform-D solvent and chemical shifts are

reported in δ scale using tetramethylsilane ($Me_4Si$) as the internal standard. The standard abbreviations s,d,t,q and m refer to singlet, doublet, triplet, quartet and multiplet, respectively. $^{13}C$ NMR assignments differing by only 2-3 ppm can, in some cases, be interchanged.

**Mass Spectra** : Mass spectral measurements were carried out on JEOL, JMS DX-303 spectrophotometer. FABMS were taken on JEOL SX-102.

**Elemental analysis**: Elemental analysis were performed on a Perkin-Elmer 240C-CHN analyzer.

**Chromatography** : Analytical thin layer chromatographies (tlc) were performed on (10 x 5 cm) glass plates coated with (250 μm) Acme's silica gel G or $GF_{254}$ (containing 13% calcium sulphate as binder). Visualization of the spots on tlc plates was achieved either by exposure to iodine vapour or UV light or by spraying sulphuric acid

and heating at 120 °C. Column chromatography was performed using Acme's silica gel and the amount of silica gel used is approximately in the ratio of 1:25 and the column was usually eluted with ethyl acetate - hexane, unless mentioned otherwise.

**Photochemical reactions** : All photochemical reactions were carried out using a 450W Hanovia medium pressure mercury vapour lamp in a quartz immersion well with either vycor or pyrex filters.

**FVP reactions** : All flash vacuum pyrolysis (FVP) reactions were carried out using a home-built setup. The temperature in the hot-zone was maintained at 800 - 1000 °C and the pressure at 0.3 mm of Hg During the reaction a slow flow of nitrogen is maintained.

**Cyclodehyro-genation reactions** : All the cyclodehydrogenation reactions were carried out using Pd/C in a sealed tube in a furnace maintained at 400 °C.

**General** : All reactions were monitored by employing tlc technique using appropriate solvent system for development. Moisture sensitive reactions were carried out by using standard syringe-septum techniques. Petroleum ether refers to the fraction boiling between 60-80 °C. Dichloromethane was distilled over $P_2O_5$. Benzene was distilled over sodium and stored over pressed sodium wire. Ethyl acetate was distilled over potassium carbonate. Dry ether and dry THF were made by distilling them from sodium benzophenone ketyl. Hydrogenations were carried out on a Parr-hydrogenation apparatus in 250 mL pressure bottles and in some cases using the hydrogen balloon. Sonochemical experiments were carried out using a Julabo USR - 3 ultrasonic instrument. All solvent extracts were washed with water, brine, dried over anhydrous $Na_2SO_4$ and

concentrated at reduced pressure on a Buchi-El rotary evaporator. Yields reported are isolated yields of materials judged homogeneous by tlc and NMR spectroscopy.

**1,3,5-Triformylbenzene (65):**[56]

To a stirred solution of benzoic acid **71** (10.0 g, 0.82 mol) in 100 mL of ethanol and 600 mL of liq.$NH_3$, 6.2 g of sodium was added in small portions and the stirring was continued for 1 h. Ammonium chloride (14.6 g, 0.27 mol) was added to the above solution and the solid thus obtained was dissolved in ice-water, acidified with 10% HCl and extracted with ether (2 x 200 mL). The ethereal layer was washed with water, brine and dried. Evaporation of ether gave a pale yellow solution of 1,4-dihydrobenzoic acid **72**.

Phosphorous oxychloride (49.5 g, 0.32 mol) was added dropwise under stirring to dimethyl formamide (59 g, 0.80 mol) and the stirring was continued for 1 h at room temperature. To the Vilsmeier reagent thus prepared, the above obtained dihydrobenzoic acid (10.0 g, 0.08 mol)

was added in one portion and the reaction mixture was cooled stirred for 2 h and then poured into 20% aq. sodium acetate (100 mL). The complex was decomposed by heating it on a water bath for 20 min. The reaction mixture was extracted with ether (2 x 200 mL) and the organic layer was washed with water, $NaHCO_3$, brine and dried. Removal of solvent gave 1,3,5-triformylbenzene **65** and was crystallized from water (5 g, 35% yield).

mp : 160 °C (lit.[56] 161 °C)

$^1$H NMR : δ 10.19 (s, -C<u>H</u>O, 3H), 8.63 (s, ø -<u>H</u>, 3H)

**Triphenylphosphonium fluorenylide (75):**[57]

To a solution of 9-bromofluorene **73** (3.0 g, 12.3 mmol) in 40 ml of nitromethane was added triphenylphosphine (3.21 g, 12.3 mmol) portion wise. As the last portion was added, fluorenyl-9-triphenyl-phosphoniumbromide **74** began to crystallize. After 2 h, 5.75 g of fluorenyl-9-triphenylphosphoniumbromide **74** was collected through filtration.

mp : 300 °C (dec.) (lit.[57] 303 °C dec.)

The above salt fluorenyl-9-triphenylphosphoniumbromide **74** (3g) was dissolved in 150 ml of boiling ethanol and the solution was made alkaline by adding 8 mL of ammonium hydroxide. As the solution cooled, yellow glistening crystals of triphenylphosphonium fluorenylide **75** were formed. Filtration gave 2.0 g (80% yield) of **75**.

mp : 251 °C (lit.[57] 253 °C)

**1,3,5-Tris(fluorenylidenemethyl)benzene (58):**

To a suspension of triphenylphosphonium fluorenylide **75** (4.33 g, 10.18 mmol) in 75 mL of chloroform was added 1,3,5-triformylbenzene **65** (500 mg, 3.08 mmol) in 15 mL of chloroform. The contents of the flask were refluxed for 4 h and then chloroform was removed under reduced pressure. The crude material was charged on a silica gel column and eluted with 5% ethyl acetate-hexane, which afforded the tri-Wittig product **58** (575 mg, 30% yield) as a solid residue. Recrystallization from chloroform and hexane gave fine crystals of 1,3,5-tris(fluorenylidenemethyl)benzene **58**.

mp : 246 °C

IR (KBr) : 1600, 1440, 770, 720 $cm^{-1}$

$^{1}H$ NMR : δ 7.85 - 7.65 (m, 18H), 7.45 - 7.25 (m, 9H), 7.05 - 6.95

(Spectrum 1) (m, 3H)

$^{13}C$ NMR : δ 141.5, 139.4, 138.1, 137.6, 136.6, 129.3, 128.8, 128.6,

(Spectrum 2) 128.4, 127.2, 126.9, 126.0, 124.6, 120.5, 119.9, 119.7

Analysis : $C_{48}H_{30}$ Calcd. : C, 95.02; H, 4.98

Found : C, 94.98; H, 4.95

**Crystal Data**

$C_{48}H_{30}$, colorless crystal, monoclinic, space group $P2_1/c$, a = 13.377(2), b = 21.595(4), c = 12.337(2) Å units , β = 111.78(2)°, Volume = 3309(1) $Å^3$, Z = 4, $D_{cal}$=1.218 $g/cm^3$, T=293K, crystal dimensions 0.12 x 0.20 x 0.17 $mm^3$. 4745 reflections measured, range ($3 \leq 2\theta \leq 45$) and $0 \leq h \leq 16$, $0 \leq k \leq 25$, $-16 \leq l \leq 16$; 4353 unique reflections ($R_{int}$=0.028), and 1221 observed with $I \geq 3\sigma(I)$, μ=0.64 $cm^{-1}$. Final R=0.053 and $R_w$=0.059 ($w=1/\sigma^2(F_0)+0.0002|F_0|^2$, Goodness of fit = 1.08); maximum shift/ error=0.001, $\Delta\rho_{max}$=0.21e$Å^{-3}$, $\Delta\rho_{min}$ = -0.17e$Å^{-3}$. X-ray experimental procedure: Mo Kα radiation (λ=0.71073Å), graphite crystal monochromator, Siemens R3m/v diffractometer (ω-2θ scan technique).

Data corrected for Lorentz and polarization correction but not for absorption. The structure was solved by direct methods (SHELXTL-Plus 4.11/v) and anisotropically refined. H-atoms were included in the refinement as riding model with fixed isotropic temperature factor. Drawing made using SHELXTL-Plus graphics package.

**General method for flash vacuum pyrolysis (FVP)**

Our flash vacuum pyrolysis apparatus is similar to that described by Stabbe et al.[60] The flash vacuum pyrolysis was carried out in a horizontal tube (30 cm x 1.5 cm) connected to a vacuum line and adapted with a cold finger and a liquid nitrogen trap The quartz tube was heated with a nichrom coil wound around it and insulated by asbestos padding. The temperature of the tube was controlled by a variac and measured by a thermocouple (Chromel-Alumel). The heating portion was divided into two zones, one of high temperature zone (13 cm x 1.5 cm) that can go up to 1000 - 1200 °C and the second one, a sublimation zone (5 cm x 1.5 cm) that can go up to 400 °C. A continuous flow of nitrogen was maintained throughout the reaction.

**FVP of 1,3,5-tris(fluorenylidenemethyl)benzene (58):**

The flash vacuum pyrolysis tube was pre-heated to the requisite temperature of 1000 °C and 1,3,5-tris(fluorenylidenemethyl)-benzene **58** (20 mg, 0.03 mmol) was kept in a sample boat and placed in the sublimation zone. The compound **58** was sublimed through the quartz tube at a pressure of 0.3 mm of Hg under nitrogen flow. The sample deposited at the cold finger was collected and found to be the starting material.

**Attempted thermal cyclization of (58):**

A mixture of 1,3,5-tris(fluorenylidenemethyl)benzene **58** (20 mg, 0.3 mmol) and 5 mg of 10% Pd/C was sealed in a pyrex tube under nitrogen. The sealed tube was heated at 400 °C for 2 h in a furnace. The material was collected by dissolving in dichloromethane and was found to be recovered starting material.

**1,3,5-Tris(9-fluorenylmethyl)benzene (76):**

A solution of 1,3,5-tris(fluorenylidenemethyl)benzene **58** (100 mg, 0.16 mmol) in 15 mL of dry ethyl acetate was hydrogenated

over 5 mg of 10% Pd/C at atmospheric pressure for 2 h. The catalyst was filtered-off and ethyl acetate was removed under reduced pressure. The remaining crude material was charged on a silica gel column and elution with 3% ethyl acetate-hexane afforded 1,3,5-tris(9-fluorenylmethyl)-benzene **76** (95 mg, 94% yield), which was recrystallized from dichloro-methane-pet ether.

mp : 210 °C

IR (KBr) : 3000, 2900, 1600, 1440, 780, 760, 740 $cm^{-1}$

$^1H$ NMR : δ 7.67 (d, J=7.4 Hz, 6H), 7.40 -7.10 (m, 18H), 6.87 (s, ϕ-

(Spectrum 3) H, 3H), 4.07 (t, $J_1=J_2$=7.2 Hz, $-CH_2-CH$, 3H), 3.03 (d,

J=7.3 Hz, $-CH_2-CH-$, 6H)

$^{13}C$ NMR : δ 147.0, 141.0, 139.6, 128.9, 127.2, 126.7, 125.0, 119.9,

(Spectrum 4) 48.7, 40.0

Analysis : $C_{48}H_{36}$ Calcd : C, 94 08; H, 5.92

Found : C, 93.95; H, 5.89

**FVP of 1,3,5-tris(fluorenylmethyl)benzene (76)**:

The flash vacuum pyrolysis tube was pre-heated to the requisite temperature of 800 °C and 1,3,5-tri(fluorenylmethyl)benzene

**76** was kept in a sample boat and the boat was placed in the sublimation zone. The compound **76** was sublimed through the quartz tube at a pressure of 0.3 mm of Hg under nitrogen flow. The sample deposited at the cold finger was collected and the crude material was charged on a silica gel column. Elution with 5% ethyl acetate - hexane furnished the fragmented products 9,9'-bifluorene **77**, 9,9'-bifluorenylidene **78** and fluorenone **79** and are identified through the comparison with the authentic samples.

**Attempted thermal cyclization of 1,3,5-tri(fluorenylmethyl)benzene (76):**

A mixture of 1,3,5-tri(fluorenylmethyl)benzene **76** (50 mg, 0.08 mmol) and 5 mg of 10% Pd/C was sealed in a pyrex tube under nitrogen. The sealed tube was heated at 400 °C for 2 h in a furnace. The material was collected by dissolving in dichloromethane. The crude material obtained, after removing the solvent was charged on a alumina column and elution with 2% ethyl acetate - hexane furnished only the fragmented product fluorene **67** and is compared with the authentic sample.

**1,3,5-tris(1-indanylidenemethyl)benzene (61):**

To a suspension of 1-indanyltriphenylphosphonium bromide **82** (1.388 g, 3.08 mmol) in 20 mL of isopropanol was added $Cs_2CO_3$ (1.0 g, 3.08 mmol) in 5 mL of isopropanol. The resulting yellow coloured ylide was stirred at room temperature for 30 min. and 1,3,5-triformylbenzene **65** (100 mg, 0.61 mmol) in 5 mL of isopropanol was added at 0 °C and stirring was continued for another 1 h. The reaction mixture was quenched with water and extracted with ether (2 x 75 mL). The combined ethereal extracts were washed with dil. HCl, water, brine and dried. The resulting crude mixture after the evaporation of the solvent was charged on a silica gel column and elution with 5% ethyl acetate-hexane afforded the tri-Wittig product **61** (90 mg, 30% yield) as a mixture of double bond isomers.

IR (neat) : 3010, 2900, 1595, 1460, 1260, 895, 770 $cm^{-1}$

$^1H$ NMR : δ 7.60 - 6.95 (series of m, 15H), 6.20 - 6.00 (m, 1H),

(Spectrum 5) 4.00 - 3.80 (m, 2H), 3.40 - 3.32 (m, 2H), 3.06 (s, 4H)

$^{13}C$ NMR : δ 145.9, 145.3, 144.7, 144.2, 143.7, 142.7, 139.5, 138.5,

(Spectrum 6) 130.2, 130.1, 128.2, 127.6, 127.2, 126.7, 126.1, 125.4,

124.7, 123.8, 120.3, 119.5, 119.3, 37.7, 34.5, 30.7.

**1,3,5-Tris(1-indanylmethyl)benzene (83):**

A solution of 100 mg of the tri-Wittig product **61** in ethyl acetate was hydrogenated using 5 mg of 10% Pd-C as a catalyst at room temperature and at atmospheric pressure for 1 h. The catalyst was filtered-off and ethyl acetate was removed under reduced pressure. The resulting material was charged on a silica gel column and eluted with 5% ethyl acetate-hexane, to furnish 1,3,5-tris(1-indanylmethyl)benzene **83** as a viscous liquid (90 mg, 90% yield).

IR (neat) : 3025, 2920, 1600, 1490, 1470, 750 $cm^{-1}$

$^1H$ NMR : δ 7.21 (m, 12H), 6.86 (s, ϕ-H, 3H), 3.45-3.35 (m, 3H),

(Spectrum 7) 3.11 -3 .10 (m, 3H), 2.84 - 2.59 (m, 9H), 2.21 - 2.05 (m, 3H), 1.83-1.70 (m, 3H)

$^{13}C$ NMR : δ 147.1, 144.2, 140.6, 127.8, 126.5, 126.0, 124.6, 124.0,

(Spectrum 8) 46.5, 41.4, 31.8, 31.1

Analysis : $C_{36}H_{36}$ Calcd. : C, 92.25; H, 7.74

Found : C, 92.13; H, 7.70

**o-Bromo-benzylidene-fluorene (85):**[57]

A solution of o-bromo benzaldehyde **84** (100 mg, 0.54 mmol) and triphenylphosphonium fluorenylide **75** (254 mg, 0.59 mmol) was refluxed for 4 h in 25 mL of chloroform. The reaction mixture was concentrated and the resulting material was charged on a silica gel column. Elution with hexane furnished the Wittig product **85** (100 mg, 55% yield) as a crystalline material.

IR (KBr) : 3025, 1440, 1020, 770, 720 $cm^{-1}$

$^1H$ NMR : δ 7.85 - 7.80 (m, 1H), 7.73 - 7.62 (m, 3H), 7.55 (s, 1H),

(Spectrum 9) 7.40 - 7.24 (m, 7H), 7.05 - 6.98 (m, 1H)

$^{13}C$ NMR : δ 141.5, 139.5, 139.1, 137.4, 137.3, 136.5, 132.9, 131.5,

(Spectrum 10) 129.7, 128.9, 128.6, 127.3, 127.2, 126.8, 126.0, 124.5,

124.2, 120.7, 119.9, 119.7

**Benzo[b]fluoranthene (86):**

Flash vacuum pyrolysis of o-bromobenzylidene-fluorene **85** (30 mg, 0.09 mmol) at 800°C, and 0.3 mm furnished the dehydro-halogenated compound along with some starting material. The crude material was charged on a silica gel column and elution with hexane

afforded the cyclized compound, benzo[b]fluoranthene **86** as a crystalline material (15 mg, 65% yield based on the recovery of starting material).

mp : 167 °C (lit.[76] 168 °C)

IR (KBr) : 3025, 1440, 1020, 770, 720 $cm^{-1}$

$^1H$ NMR : δ 8.63 (d, J=8Hz, 1H), 8.43 (d, J=8Hz, 1H), 8.19 (s, 1H), 8.05 - 7.89 (m, 4H), 7.77 - 7.60 (m, 3H), 7.43 - 7.38 (m, 2H)

(Spectrum 11)

$^{13}C$ NMR : δ 141.3, 140.8, 138.6, 137.1, 135.2, 134.1, 130.8, 130.3, 128.3, 128.2, 127.6, 127.5, 127.1, 126.9, 123.2, 122.0, 121. 7, 121.6, 121.5, 119.6

(Spectrum 12)

**1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene (90)**

A solution of 1,3,5-tribromo-2,4,6-trimethyl-benzene **89** (2.0 g, 5.6 mmol) , N-bromosuccinimide (3.3 g, 18.48 mmol) and AIBN (25 mg) in 50 mL of carbontetrachloride was refluxed for 4 h. The insoluble succinimide was removed by filtration and the filtrate was washed successively with 10% HCl, water, $NaHCO_3$, brine and dried. Carbon-tetrachloride was concentrated, hexane was added and cooled to 0 °C.

The solid that separated was recrystallized from hexane to get 1,3,5-tribromo-2,4,6-tris(bromomethyl)benzene **90** (1.0 g, 30% yield).

IR (neat) : 2920, 1590, 1460, 740, 720 $cm^{-1}$

$^{1}H$ NMR : δ 4.94 (s, -C$\underline{H_2}$-Br, 6H)

$^{13}C$ NMR : δ 138.1, 128.6, 35.5.

**2,2'-Dibromobenzoin (93)**:[77]

To a solution of o-bromo benzaldehyde **84** (10 g, 0.05 mmol) in 96% ethanol (25 mL) was added sodium cyanide (2 g) in water (20 ml) and the contents of the flask were refluxed for 30 min. After the completion of the reaction, ethanol was removed under reduced pressure and the residue extracted with ether. The ethereal layer was washed with water and dried. Evaporation of ether gave 2,2'-dibromobenzoin **93** as an oily substance which was used as such for the next step.

**2,2'-Dibromobenzil (94)**:[64]

To a stirred solution of dibromobenzoin **93** (10 g, 0.02 mmol), conc. $HNO_3$ was added dropwise at 100 °C. The reaction mixture was

stirred for 6 h and the contents of the flask were poured into water. The resulting precipitate was filtered and crystallized from ethanol to get fine crystals of 2,2'-dibromobenzil **94** (6 g, 60% yield).

mp : 126 °C (lit.[64] 127-128 °C)

**2,2'-Dibromobenzilic acid (95):**[64]

A mixture of 2,2'-dibromobenzil **94** (10 g, 0.027 mmol), 96% ethanol (20 mL), potassium hydroxide (6 g) and water (10 mL) was refluxed for 30 min. The reaction mixture was diluted with water and on acidification with dil.HCl gave a precipitate which was filtered and crystallized from benzene to give 2,2'-dibromobenzilic acid (7.3 g, 70% yield).

mp : 151 °C (lit.[64] 152-154 °C)

**2,2'-dibromobenzophenone (92):**[64]

A solution of 2,2'-dibromobenzilic acid **95** (5 g, 12.95 mmol) in glacial acetic acid (20 mL) was stirred vigorously with sodium bismuthate (4.5 g, 16.26 mmol) at 60 °C for 5 h. After the addition of a

mixture of 85% phosphoric acid (3 mL) and water (4 mL) the reaction mixture was allowed to stand overnight at room temperature. Ether was added, the organic layer was separated, washed successively with water, $NaHCO_3$ and dried. Removal of solvent gave a residue which was crystallized from ethanol to get 2,2'-dibromobenzophenone **92** (3.3 g, 85% yield) .

| | | |
|---|---|---|
| mp | : | 85 °C (lit.[78] 86 °C) |
| IR (KBr) | : | 3024, 1680, 1597, 1440, 740, 720 $cm^{-1}$ |
| $^1H$ NMR | : | δ 7.65-7.60 (m, 2H), 7.47-7.35 (m, 6H) |
| $^{13}C$ NMR | : | δ 195.3, 139.3, 134.1, 132.5, 131.3, 127.3, 121.2 |

**2,2'-Dibromodiphenylmethanol (96):**

To a solution of 2,2'-dibromobenzophenone **92** (5 g, 14.7 mmol) in methanol (50 mL) was added sodium borohydride (300 mg, 8.10 mmol) portion wise. After the completion of the reaction, methanol was removed and the residue was extracted with ether. The ethereal layer was washed with water, brine and dried. Removal of solvent gave 2,2'-dibromodiphenylmethanol **96** (4.5 g, 90% yield) as an oily material.

IR (KBr) : 3300, 1580, 1430, 1000, 900, 720 $cm^{-1}$

$^{1}H$ NMR : δ 7.59 - 7.55 (m, 2H), 7.33 - 7.30 (m, 6H), 6.48 (s, 1H, ϕC<u>H</u>(OH)ϕ), 2.70 (brs, 1H, O<u>H</u>)

$^{13}C$ NMR : δ 141.0, 133.0, 129.5, 128.8, 127.7, 123.9, 74.3.

**2,2'-dibromodiphenylmethylbromide (97):**

To a solution of 2,2'-dibromodiphenylmethanol **96** (1.0 g, 2.9 mmol) in ether (25 mL) at 0 °C, phosphorous tribromide (260 mg, 1.0 mmol) was added dropwise. After the addition was over, the mixture was stirred for 2 h at 0 °C and allowed to come to room temperature. The reaction mixture was quenched with water and extracted with ether (2 x 100 mL). The ethereal layer was washed with water, $NaHCO_3$ and dried. Removal of ether gave bis(2-bromophenyl)bromomethane **97** as an oily material (550 mg, 60% yield).

IR (KBr) : 3050, 2930, 1440, 1000, 740, 720 $cm^{-1}$

$^{1}H$ NMR : δ 7.60-7.50 (m, 4H), 7.34-7.08 (m, 4H), 6.87 (s, 1H)

$^{13}C$ NMR : δ 139.1, 133.3, 131.3, 129.8, 127.9, 123.9, 53.5

**1,3,5-tris(bromomethyl)benzene (50):**[79]

To a stirred solution of mesitylene **64** (10.0 g, 0.08 mol) in 150 mL of carbon tetrachloride, N-bromosuccinimide (45.6 g, 0.256 mol) and 20 mg of AIBN were added and the contents were refluxed for 4 h under nitrogen. The insoluble succinimide was filtered-off and the filtrate was washed successively with 10% HCl, $NaHCO_3$, water, brine and dried. The volume of carbon tetrachloride was reduced to 50 mL and 20 mL of hexane was added. On cooling to 0 °C a solid began to crystallize. The crude solid was filtered and recrystallized from hexane to give the 1,3,5-tris(bromomethyl)benzene **50** in 30% yield.

mp : 97 °C, (lit[79] 96-99 °C)

$^1$H NMR : δ 7.35 (s, ϕ-H, 3H), 4.45 (s, -C$H_2$-Br, 6H)

**1,3,5-Tris(2',2'-diphenyl-2'-hydroxyethyl)benzene (100):**

Into a dry 100 mL RB flask were introduced 1,3,5-tris(bromomethyl)benzene **50** (500 mg, 1.4 mmol), benzophenone **89** (840 mg, 4.62 mmol) and lithium pieces (50 mg) under nitrogen atmosphere in dry THF (25 mL). The reaction flask was sonicated in a cleaning bath (60 W,

50 KHz) for 2 h. After the completion of the reaction, THF was removed under reduced pressure, diluted with water and extracted with ethyl acetate (2 x 75 mL). The combined organic extracts were washed with dil. HCl, water, brine and dried. Evaporation of the solvent under reduced pressure gave crude material which was charged on a silica gel column. Elution with 10% ethyl acetate-hexane gave the trihydroxy compound **100** (340 mg, 35% yield) as a fluffy material which was recrystallized from dichloromethane-hexane.

mp : 125 °C

IR (KBr) : 3586, 3414, 3024, 2930, 1597, 1446, 775, 746 $cm^{-1}$

$^1H$ NMR : δ 7.34 (s, 30H), 6.48 (s, ϕ-H, 3H), 3.40 (s, -$CH_2$-C(OH)-,

(Spectrum 13) 6H), 1.91 (br s, 3H)

$^{13}C$ NMR : δ 146.5, 135.6, 131.7, 128.0 (2C), 126.9, 126.2 (2C),

(Spectrum 14) 77.9, 47.6

Analysis : $C_{48}H_{42}O_3$ Calcd. : C, 86.45; H, 6.34

Found : C, 86.35; H, 6.32

**1,3,5-Tris(2',2'-diphenylethenyl)benzene (59):**

To a stirred solution of triol **100** (1.0 g, 1.5 mmol) in 25 mL of THF was added 25 mL of 20% $H_2SO_4$ and the contents were refluxed for 4 h. After the completion of the reaction, THF was removed under reduced pressure and the residue was diluted with water and extracted with ether (2 x 150 mL). The combined ethereal layer was washed with water, $NaHCO_3$, brine and dried. Ether was removed and the crude material was charged on a silica gel column. Elution with 5% ethyl acetate-hexane yielded 1,3,5-*tris*(2',2'-diphenylethenyl)benzene **59** (600 mg, 65% yield) which was crystallized from dichloromethane-hexane to afford a nice crystalline product.

| | | |
|---|---|---|
| mp | : | 183 °C |
| IR (KBr) | : | 3016, 1577, 1489, 1442, 760, 694 $cm^{-1}$ |
| $^1H$ NMR | : | δ 7.40 - 7.20 (m, 24H), 7.15 - 7.00 (m, 6H), 6.57 (s, ϕ-H, |
| (Spectrum 15) | | 3H), 6.50 (s, -C<u>H</u>=C-, 3H) |
| $^{13}C$ NMR | : | δ 143.3, 142.5, 140.2, 136 9, 130.5 (2C), 129.5, 128.5 |
| (Spectrum 16) | | (2C), 128.2 (2C), 128.0, 127.6 (2C), 127.4, 127.3 |
| Analysis | : | $C_{48}H_{36}$ Calcd. : C, 94.08; H, 5.92 |
| | | Found : C, 93.98; H, 5.92 |

**1-hydro-4,10,14,14-tetraphenyl-[1,2-b]naphtha-pyrene (101):**

A solution of 1,3,5-tris(2',2'-diphenylethenyl)benzene **59** (200 mg, 0.32 mmol) in 800 mL of hexane was purged with a slow stream of nitrogen and was irradiated using a 450W medium pressure mercury vapour lamp in a quartz immersion vessel using a pyrex filter for 1 h in the presence of catalytic amount of iodine. The solvent was removed and the crude product was charged on a silica gel column. Elution with 2% ethyl acetate-hexane furnished the cyclized product **101** (40 mg, 20% yield) which was crystallized from dichloromethane-hexane.

| | | |
|---|---|---|
| mp | : | 249 °C |
| IR (KBr) | : | 3057, 1599, 1444, 1265, 773, 738, 700 $cm^{-1}$ |
| $^1H$ NMR (Spectrum 17) | : | δ 9.06 (d, J=8Hz, 1H), 8.98 (s, 1H), 7.96 (d, J=8Hz, 2H), 7.76 (d, J=4.4Hz, 2H), 7.68 (d, J=7Hz, 2H), 7.65-7.40 (m, 12H), 7.18 (s, 10H), 4.29 (s, 2H) |
| $^{13}C$ NMR (Spectrum 18) | : | δ 146.2, 142.5, 140.7, 139.1, 138.6, 133.7, 132.0, 131.3, 130.7, 130.3, 130.1, 129.3, 128.4, 128.2, 127.9, 127.6, 127.4, 127.1, 126.8, 126.4, 126.0, 125.7, 125.0, 124.7, 53.4, 43.5 |

FAB MS : 608 ($M^+$)

Analysis : $C_{48}H_{32}$ Calcd. : C, 94 74, H, 5.29

Found : C, 94.40, H, 5 05

**3,9,13,14-Tetraphenyl-[1,2-b]naphthapyrene (104):**

A mixture of 25 mg of the photo-cyclized compound **101** and 3 mg of Pd-C was sealed under nitrogen in a pyrex glass tube The sealed tube was heated at 400°C in a furnace for 2 h The black tarry material was extracted with dichloromethane (2 x 25 mL) and removal of solvent gave a crude material which was charged on a silica gel column Elution with 1% ethyl acetate-hexane furnished the rearranged compound **104** (20 mg, 80% yield) which was crystallized from hexane

mp : > 300 °C

IR (KBr) : 3059, 1599, 1440, 1265, 771, 734, 702 $cm^{-1}$

$^1H$ NMR : δ 9.47 (s, 1H), 9 37 (d, J=8Hz, 1H), 8 38 - 8 30 (m, 1H),

(Spectrum 19) 8 23 (s, 1H), 8 12 - 8.04 (m, 1H), 7 92 (s, 1H), 7 90 -

7 74 (m, 4H), 7 70 -7 44 (m, 10H), 7 40 - 7 26 (m, 10 H)

$^{13}C$ NMR : δ 146.2, 141.5, 140.5, 139.6, 139.5, 139.3, 139.0, 138.2,

(Spectrum 20) 137.7, 132.4, 132.2, 131.3, 131.2, 130.4, 130.0, 129.2,

128.5, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 126.7,

126.3, 126.0, 125.8, 125.4, 124.8, 124.0

FAB MS : 606 ($M^+$)

Analysis : $C_{48}H_{30}$ Calcd. : C, 95.02; H, 4.98

Found : C, 95.15; H, 5.02

**1,3,5-Tris(2',2'-diphenylethyl)benzene (106):**

A solution of 1,3,5-tris(2',2'-diphenylethenyl)benzene **59** (100 mg, 0.16 mmol) in dry ethyl acetate was hydrogenated at room temperature and at atmospheric pressure for 1h using 5 mg of 10% Pd/C. The catalyst was filtered and ethyl acetate was removed under reduced pressure to give the trihydrogenated compound as an oily material which was charged on a silica gel column. Elution with 3% ethyl acetate-benzene afforded 1,3,5-tris(2',2'-diphenylethyl)benzene **106** (95 mg, 95% yield) .

IR (neat) : 3026, 2926,1601, 1493, 1450, 1080, 1032, 740, 700$cm^{-1}$

$^{1}$H NMR : δ 7.40 -7.12 (m, 30H), 6.45 (s, 3H), 3.88 (t, $J_1$=$J_2$=6Hz,

(Spectrum 21) -$CH_2$-C<u>H</u>, 3H), 3.18 (d, J=8Hz, 6H)

$^{13}$C NMR : δ 144.5, 139.5, 128.2, 128.1, 127.7, 126.0, 53.2, 41.9

(Spectrum 22)

Analysis : $C_{48}H_{42}$ Calcd. : C, 95.81; H, 4.01

Found : C, 95.30; H, 3.93

**1,3-bis(bromomethyl)-5-methyl-benzene (110):**

A mixture of mesitylene **64** (3.0 g, 25 mmol), N-bromo-succinimide (9.8 g, 55 mmol) and 10 mg of AIBN was heated under reflux for 3 h. The floating succinimide was filtered and the organic layer was washed successively with dil. HCl, $NaHCO_3$, water, brine and dried. The organic layer was concentrated and the crude material was charged on a silica gel column. Elution with hexane to gave the dibromo compound **110** (2.0 g, 30% yield).

IR (neat) : 3020, 2930, 1600, 1440, 760 $cm^{-1}$

$^{1}$H NMR : δ 7.39 (s, 1H), 7.16 (s, 2H), 4.46 (s, -C<u>H</u>$_2$Br, 4H), 2.36

(s, -C<u>H</u>$_3$, 3H)

**1,3-bis(2',2'-diphenyl-2'-hydroxyethyl)-5-methylbenzene (111):**

Into a dry 100 mL RB flask 1,3-bis(bromomethyl)-5-methylbenzene **110** (3.0 g, 10.8 mmol), benzophenone **99** (4.27 g, 32.37 mmol) and 150 mg of lithium metal were introduced in dry THF (25 mL) under nitrogen atmosphere. The reaction flask was sonicated using ultrasound laboratory cleaner (60 W, 50 KHz) for 2 h. After the completion of the reaction, THF was removed under reduced pressure, diluted with water and extracted with ethyl acetate (2 x 150 mL). The organic layer was washed with dil. HCl, water, brine and dried. Evaporation of the solvent gave a gummy material which was chromatographed on a silica gel column using 10% ethyl acetate-hexane as eluent to afford the dihydroxy compound **111** (1.60 g, 30% yield) as a viscous liquid.

| | | |
|---|---|---|
| IR (neat) | : | 3551, 3447, 3059, 1600, 1493, 1050, 758, 700 $cm^{-1}$ |
| $^{1}H$ NMR | : | δ 7.50 - 7.20 (m, 20H), 6.53 (s, 2H), 6.45 (s, 1H), 3.50 |
| (Spectrum 23) | | (s, 4H), 2.50 (br s, 1H), 2.30 (br s, 1H), 2.08 (s, 3H) |
| $^{13}C$ NMR | : | δ 146.6, 143.9, 137.2, 135.5, 130.3, 130.2, 128.5, 128.0, |
| (Spectrum 24) | | 127.6, 126.9, 126.6, 126.3, 77.9, 76.2, 47.8, 21.1 |

**1,3-bis(2',2'-diphenylethenyl)-5-methylbenzene (112):**

To a solution of diol **111** (2.0 g, 4.13 mmol) in 30 mL of THF was added 20 mL of 25% $H_2SO_4$ and the reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure, diluted with water and extracted with ether (2 x 100 mL). The combined ethereal extract was washed with $NaHCO_3$, water, brine and dried. Removal of solvent gave the crude product as a gummy material which was charged on a silica gel column. Elution with 3% ethyl acetate-hexane afforded the dehydrated product, 1,3-bis(2',2'-diphenylethenyl)-5-methylbenzene **112** (1.4 g, 75% yield) as a thick liquid.

| | | |
|---|---|---|
| IR (neat) | : | 3050, 3024, 1597, 1493, 1444, 908, 763, 730, 700 $cm^{-1}$ |
| $^1H$ NMR | : | δ 7.30 - 7.10 (m, 16H), 7.10 - 6.90 (m, 4H), 6.65 (s, 2H), |
| (Spectrum 25) | | 6.50 (s, 1H), 6.42 (s, 2H), 1.81 (s, 3H) |
| $^{13}C$ NMR | : | δ 143.5, 142.4, 142.3, 140.5, 137.1, 136.7, 130.4, 128.8, |
| (Spectrum 26) | | 128.7, 128.5, 128.4, 128.2, 127.6, 127.4, 127.3, 21.3 |
| Analysis | : | $C_{35}H_{28}$ Calcd. : C, 93.71; H,6.29 |
| | | Found : C, 93.68; H, 6.26 |

**5,14-diphenyl-8-methyl-[1,2-a]naphthaphenanthrene (113):**

A solution of dehydrated compound **112** (500 mg, 1.12 mmol) in 125 mL of hexane was purged with a slow stream of nitrogen for 20 min. and the solution was irradiated using a 450 W Hanovia medium pressure mercury vapour lamp for 1 h in a quartz immersion vessel using a pyrex filter in the presence of catalytic amount of iodine. The solvent was removed under reduced pressure and the residue was charged on a silica gel column. Elution with 2% ethyl acetate-hexane gave the cyclized compound **113** which was crystallized from dichloromethane-hexane mixture (400 mg, 80% yield).

| | | |
|---|---|---|
| mp | : | 225 °C |
| IR (KBr) | : | 3020, 1597, 1440, 775, 761, 733, 702 $cm^{-1}$ |
| $^1H$ NMR | : | δ 9.07 (d, J=8.3Hz, 1H), 8.94 (s, 1H), 8.89 (d, J=8Hz, |
| (Spectrum 27) | | 1H), 8.15 - 8.00 (m, 2H), 7.85 (s, 1H), 7.80 - 7.50 (m, |
| | | 15H), 3.26 (s, 3H) |
| $^{13}C$ NMR | : | δ 140.9, 140.7, 139.4, 137.1, 133.8, 133.2, 131.9, 131.7, |
| (Spectrum 28) | | 130.7, 130.4, 130.1 (4C), 129.7, 128.8, 128.5, 128.4 |

(2C), 128.1, 128.0, 127.4, 126.8, 126.5, 126.2, 125.9, 125.8, 124.8, 26.6

MS : 444 ($M^+$)

Analysis : $C_{35}H_{24}$ Calcd. : C, 94.56; H, 5.44

Found : C, 94.45; H, 5.38

**8H-5,12-diphenyl-[1,2-a]-naphthacyclopenta[def]phenanthrene (114):**

A mixture of the cyclized compound **113** (100 mg, 0.22 mmol) and 10 mg of 10% Pd/C was sealed under nitrogen in a pyrex glass tube. The sealed tube was heated at 400 °C in a furnace for 2 h. The black tarry material was extracted with dichloromethane (2 x 50 mL) and concentrated to give a black residue which was charged on a silica gel column. Elution with 10% benzene-hexane gave the methylene bridged compound **114** (56 mg, 57% yield) as a fluffy material which was recrystallized from hexane.

mp : 210 °C

IR (KBr) : 3042, 1597, 1440, 777, 729, 700 $cm^{-1}$

$^1H$ NMR : δ 9.48 (d, J=8.4 Hz, 1H), 9.18 (s, 1H), 8.15 - 8.00 (m,

(Spectrum 29) 2H), 7.97 (s, 1H), 7.90 - 7.50 (m, 15H), 4.56 (s, 2H)

| | | |
|---|---|---|
| $^{13}C$ NMR (Spectrum 30) | : | δ 142.5, 141.0, 140.8, 139.4, 139.0, 138.5, 138.3, 132.9, 131.8, 131.7, 130.2 (2C), 130.0 (2C), 129.3, 128.6 (2C), 128.4 (2C), 127.8, 127.5 (2C), 127.3 (2C), 126.8, 126.4, 126.1, 125.8, 125.3, 124.6, 122.5, 121.5, 121.2, 36.9 |
| MS | : | 442 ($M^+$) |
| Analysis | : | $C_{35}H_{22}$ Calcd : C, 94.98; H, 5.01<br>Found : C, 95.00; H, 4.98 |

**8-oxo-5,12-diphenyl-[1,2-a]-naphthacyclopenta[def]phenanthrene (115):**

To an ice-cold stirred solution of compound **114** (15 mg, 0.034 mmol) in 5 mL of acetone was added Jones reagent drop by drop till the colour of the reagent persisted. Stirring was continued for another 15 min. at 0 °C, and the chromium salts were filtered-off. Acetone was removed under reduced pressure, diluted with water and extracted with ether (2 x 20 mL). Usual work-up and removal of solvent gave the crude product which was charged on a silica gel column. Elution with hexane gave the ketone **115** in pure form which was crystallized from hexane (11 mg, 73% yield).

| | | |
|---|---|---|
| mp | : | 250 °C |
| IR (KBr) | : | 3050, 2926, 1716, 1612, 765, 696 $cm^{-1}$ |
| $^{1}H$ NMR | : | δ 9.36 - 9.32 (d, J=8Hz, 1H), 8.98 (s, 1H), 8.24 (s, 1H), |
| (Spectrum 31) | | 8.06 (d, J=8Hz, 1H), 7.90 (d, J=6Hz, 1H), 7.89 (s, 1H), |
| | | 7.75 - 7.50 (m, 14H) |
| $^{13}C$ NMR | : | 189.9, 140.0, 139.6, 134.4, 133.5, 133.1, 132.1, 131.4, |
| (Spectrum 32) | | 130.0, 129.8, 129.1, 128.8, 128.5, 127.9, 127.7, 127.5, |
| | | 127.3, 127.1, 126.7, 126.3, 125.0, 124.5, 122.5 |
| MS | : | 456 ($M^+$) |
| Analysis | : | $C_{35}H_{20}O$ Calcd. : C, 92.08; H, 4.42 |
| | | Found : C, 92.20; H, 4.45 |

**1,3,5-tri(pent-1-en-5-yl)benzene (51):**

The Grignard reagent 4-butenylmagnesium bromide (2.7 g, 0.017 mmol) in THF was prepared by adding 4-bromo-1-butene (2.3 g, 0.017 mmol) in 20 mL of dry THF to a stirred suspension of magnesium (500 mg, 0.021 g. atom) in 5 mL of dry THF. To the pre-cooled solution of this Grignard reagent 0.1 M solution of dilithium coppertetrachloride $Li_2CuCl_4$ [75] in THF was added with stirring and the mixture was cooled

in an ice-salt bath 1,3,5-tris(bromomethyl)benzene **50** (1.0 g, 2.8 mmol) in THF (10 mL) was added to the above solution in one lot with vigorous stirring and the stirring was continued for another 3 h during which period it was allowed to come to room temperature. The reaction mixture was quenched with aq.$NH_4Cl$ and extracted with hexane (2 x 100 mL). After removing the solvent, the crude material was charged on a basic alumina column and eluted with hexane to furnish 1,3,5-tri(pent-1-en-5-yl)benzene **51** (360 mg, 45% yield).

IR(KBr) : 2900, 1635, 1595, 1435, 980 $cm^{-1}$

$^1H$ NMR : δ 6.8 (s, 3H), 6.08-5.56 (m, 3H), 5.16-4.8 (m, 6H), 2.72-2.32 (t, 6H), 2.32-1.90 (m, 6H), 1.9-1.5 (m, 6H)

$^{13}C$ NMR : δ 142.5, 138.9, 126.2, 114.8, 35.3, 33.5, 30.7

Analysis : $C_{21}H_{30}$ Calcd. : C, 89.29; H, 10.71

Found : C, 89.13; H, 10.81

**1,5,9-Trimethyldodecahydrotriphenylene (52)**:

Into a stirred solution of 1,3,5-tris(pent-1-en-5-yl)benzene **51** (500 mg, 1.7 mmol) in dry benzene (25 ml) was bubbled borontrifluoride

gas for 3 min. and the stirring was continued for another 2h. The reaction mixture was quenched with water and extracted with hexane (2 x 75 mL). The crude material obtained after removing the solvent was charged on an alumina column. Elution with hexane gave the tricyclized product **52** and was crystallized to furnish a white solid (270 mg, 55% yield).

mp : 159 °C

IR (KBr) : 2900, 1460, 1420, 1375, 1300, 1200, 1000 $cm^{-1}$

$^1H$ NMR : δ 3.32-2.92 (m, 3H), 2.92-2.4 (m, 6H), 2.1-1.6 (m, 12H), 1.24 (dd, $J_1$=7Hz, $J_2$=2Hz, 9H)

Analysis : $C_{21}H_{30}$ Calcd. : C, 89.24; H, 10.75

Found : C, 89.28; H, 11.06

**1,5,9-Trimethyltriphenylene (53):**

To a solution of 1,5,9-trimethyldodecahydrotriphenylene **52** (500 mg, 1.7 mmol) in benzene was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (2.7 g, 11.9 mmol) and the mixture was refluxed for 3h. The reaction mixture was cooled and the residual hydroquinone was

filtered off. The filtrate was concentrated and the residue was chromatographed on a silica gel column and eluted with 10% benzene - hexane to afford 1,5,9-trimethyltriphenylene **53** (215 mg, 46% yield) as a white solid.

| | | |
|---|---|---|
| mp | : | 123 °C |
| IR (KBr) | : | 2950, 1590, 1455, 1415, 735 $cm^{-1}$ |
| $^{1}H$ NMR | : | δ 8.20 (m, 3H), 7.46-7.26 (m, 6H), 2.92 (s, 9H, ø-C$\underline{H}_3$) |
| $^{13}C$ NMR | : | δ 134.3, 132.3, 132.0, 131.0, 125.7, 124.8, 26.0 |
| Analysis | : | $C_{21}H_{18}$ Calcd. : C, 93.29; H, 6.71 |
| | | Found : C, 92.85; H, 6.62 |

**1,5,9-Tris(bromomethyl)triphenylene (55)**:

A mixture of 1,5,9-trimethyltriphenylene **53** (150 mg, 0.55 mmol), N-bromosuccinimide (325 mg, 1.83 mmol) and AIBN (10 mg) in 40 mL of carbontetrachloride was refluxed for 1.5 h. The residual succinimide was filtered-off and the removal of solvent furnished the crude material which was charged on silica gel column. Elution with 2% ethyl acetate - hexane furnished 1,5,9-tris(bromomethyl)triphenylene **55** (230 mg, 82% yield).

mp : 179-180 °C

IR (KBr) : 1440, 1415, 1200, 825, 760, 640 $cm^{-1}$

$^1H$ NMR : δ 8..50-8.30 (m, 3H), 7.80-7.44 (m, 6H), 4.96 (s, 6H ø-$C\underline{H}_2Br$)

$^{13}C$ NMR : δ 134.2, 133.1, 131.8, 130.6, 128.4, 126.7, 36.9

Analysis : $C_{21}H_{15}Br_3$ Calcd. : C, 71.47; H, 4.50

Found : C, 71.85; H, 4.53

**1,5,9-Triformyltriphenylene (116):**

1,5,9-*tris*(bromomethyl)triphenylene **55** (25 mg, 0.049 mmol) and *bis*-tetrabutylammonium dichromate[72] (210 mg, 0.30 mmol) were dissolved in 5 ml of chloroform and the mixture was refluxed for 2h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered through fluorosil pad and washed with diethyl ether. The combined washings were concentrated and the residue was chromatographed over silica gel column using 25% ethyl acetate - hexane as eluent to yield 1,5,9-triformyltriphenylene **116** (7 mg, 45% yield).

mp : 187 °C

IR (KBr) : 1680, 1570, 1200, 1180, 860, 760 $cm^{-1}$

$^1H$ NMR : δ 10.47 (s, 3H, -C<u>H</u>O), 8.32 - 7.70 (m, 9H)

(Spectrum 33)

$^{13}C$ NMR : δ 191.9, 135.3, 134.0, 132.1, 130.4, 128.9, 127.4

(Spectrum 34)

MS : 312 ($M^+$)

**Methyl-1,5,9-triphenylenetricarboxylate (121):**

Into a solution of 1,5,9-triformyltriphenylene **116** (40 mg, 0.128 mmol) in 1 mL of pyridine was added tetrabutyl ammonium permanganate[73] (115 mg, 0.318 mmol) in 2 mL of pyridine dropwise and the mixture was stirred at room temperature for 3 h. The reaction mixture was poured into cold dilute 4N HCl and was extracted with ethyl acetate (2 x 25 mL). Removal of solvent gave crude 1,5,9-triphenylenetricarboxylic acid **117** which was dissolved in methanol and ethereal diazomethane was added until the reaction mixture was light yellow. Excess diazomethane was destroyed by carefully adding acetic acid and the solvent was removed. The residue was charged on a silica gel column and elution with 15% ethyl acetate - hexane furnished methyl-1,5,9-triphenylene tricarboxylate **121** (25 mg, 48% yield).

mp : 162 °C

IR (KBr) : 1710, 1430, 1260, 1130, 745 $cm^{-1}$

$^1H$ NMR : δ 8.16 - 7.96 (m, 3H), 7.88 - 7.40 (m, 6H), 3.90 (s, 9H)
(Spectrum 35)

$^{13}C$ NMR : δ 172.0, 131.0, 130.0, 129.5 (2C), 128.9, 126.0, 52.6
(Spectrum 36)

MS : 402 ($M^+$)

Analysis : $C_{24}H_{18}O_6$ Calcd. : C, 71.47; H, 4.50

Found : C, 71.85; H, 4.53

**Thermal cyclization of the triacid (117): 4-oxo-[l]-benzocyclopenta[def]-phenanthrene (122)**:

The triacid **117** (20 mg) was placed in a small sublimation apparatus and heated in a metal nitrate bath kept at ~400 °C for 5 minutes. After cooling, the material deposited on the cold finger was removed with dichloromethane. Removal of solvent furnished the ketone **122** (2 mg, 15% yield).

mp : 224 °C

IR (KBr) : 1715, 1410, 1390, 930, 740 $cm^{-1}$

$^1$H NMR : δ 8.60 - 8.26 (m, 4H), 7.85 - 7.52 (m, 6H)
(Spectrum 37)

MS : 254 ($M^+$)

**1,3,5-Tris(3(1,3-dioxalanylpropyl))benzene (127):**

A solution of the Grignard reagent was prepared by the addition of 2-(2-bromoethyl)-1,3-dioxalane[80] (1.52 g, 8.4 mmol) in 15 mL of dry THF to magnesium turnings (220 mg, 9.24 mmol) under nitrogen and stirring for 1 h at room temperature. The Grignard reagent was cooled to 0 °C and $Li_2CuCl_4$[75] in 5 mL of THF followed by 1,3,5-tris(bromomethyl)benzene **50** (500 mg, 1.4 mmol) in 5 mL of dry THF were added at 0 °C. The reaction mixture was allowed to come to room temperature slowly and was quenched with ammonium chloride and extracted with ether (2 x 100 mL). The ethereal layer was washed with dil. HCl, water, brine and dried. Evaporation of the solvent gave a crude material which was charged on a silica gel column. Elution with 10% ethyl acetate-hexane to gave the tricoupled product **127** (260 mg, 45% yield).

IR(neat) : 2920, 1600, 1410, 1130, 1040, 940 $cm^{-1}$

$^{1}$H NMR : δ 6.82 (s, ϕ-H, 3H), 4.86 (t, $J_1$=$J_2$=4.0 Hz, CH(OCH$_2$)$_2$, (Spectrum 38) 3H), 4.00-3.77 (m, 12H), 2.58 (t, $J_1$=$J_2$=7.8 Hz, 6H), 1.77-1.64 (m, 12H)

$^{13}$C NMR : δ 142.1, 126.0, 104.5, 64.8 (2C), 35.7, 33.6, 25.8 (Spectrum 39)

Analysis : $C_{24}H_{36}O_6$ Calcd. : C, 68.64; H, 8.62

Found : C, 68.39; H, 8.55

**1,3,5-Tris(4-oxo-butyl)benzene (128):**

To a stirred solution of **127** (500 mg, 1.19 mmol) in 25 mL of acetone was added 20 mL of 0.5 N HCl[80] and stirring was continued for another 10 h at room temperature. Acetone was removed under reduced pressure, diluted with water and the product was extracted with ether (2 x 75 mL). The ethereal layer was washed with $NaHCO_3$, brine and dried. The crude material obtained after removing the solvent was charged on a silica gel column. Elution with 10% ethyl acetate-hexane afforded the trialdehyde **128** (170 mg, 50% yield ) as an oily substance.

IR (neat) : 2920, 2720, 1715, 1600, 1400 cm$^{-1}$

$^1$H NMR : δ 9.75 (s, -C<u>H</u>O, 3H), 6.83 (s, ϕ-<u>H</u>, 3H), 2.60 (t,

(Spectrum 40) $J_1=J_2$=8.0 Hz, ϕ-C<u>H</u>$_2$- , 6H), 2.46 (t, $J_1=J_2$=8.0 Hz,

-C<u>H</u>$_2$-CHO, 6H), 1.94 (m, -C<u>H</u>$_2$-CH$_2$-CHO, 6H)

$^{13}$C NMR : δ 202.4, 141.6, 126.4, 43.2, 34.9, 23.7

(Spectrum 41)

Analysis : $C_{18}H_{24}O_3$ Calcd. : C, 74.96; H, 8.38

Found : C, 74.84; H, 8.32

**1,3,5-Tris(5-ethoxycarbonyl-pent-4-enyl)benzene (126):**

To a stirred solution of triethyl orthophosphonoacetate (770 mg, 3.47 mmol) in 20 mL of isopropanol was added $Cs_2CO_3$ (1.13 g, 3.47 mmol) and the stirring was continued for another 30 min. The trialdehyde **128** (200 mg, 0.7 mmol) in 10 mL of isopropanol was added to the yellow coloured ylide and the reaction mixture was quenched with water after 60 min. and extracted with ether. The ethereal layer was washed with dil. HCl, brine and dried. Ether was evaporated and the crude product was charged on a silica gel column. Elution with 15% ethyl acetate-hexane furnished the tri-Wittig product **126** (110 mg, 30% yield) as a thick liquid.

IR (neat) : 2925, 1715, 1650, 1600, 1270, 1190, 1040, 980 $cm^{-1}$

$^1H$ NMR : δ 6.98 (dt, -$CH_2$-C<u>H</u>=CH-, 3H), 6.81 (s, ϕ-<u>H</u>, 3H), 5.82

(Spectrum 42) (d, -CH=C<u>H</u>-COOEt, 3H), 4.18 (q, -COOC<u>$H_2$</u>$CH_3$, 6H),
2.58 (t, $J_1$=$J_2$=8.0 Hz, ϕ-C<u>$H_2$</u>-, 6H), 2.26-2.20 (m, 6H),
1.80 - 1.60 (m, 6H), 1.28 (t, $J_1$=$J_2$=7.5 Hz, -$COOCH_2$-
C<u>$H_3$</u>, 9H)

$^{13}C$ NMR : δ 166.5, 148.7, 141.8, 126.1, 121.6, 60.0, 35.1, 31.6,

(Spectrum 43) 28.7, 14.2

Analysis : $C_{30}H_{42}O_6$ Calcd. : C, 72.25; H, 8.49

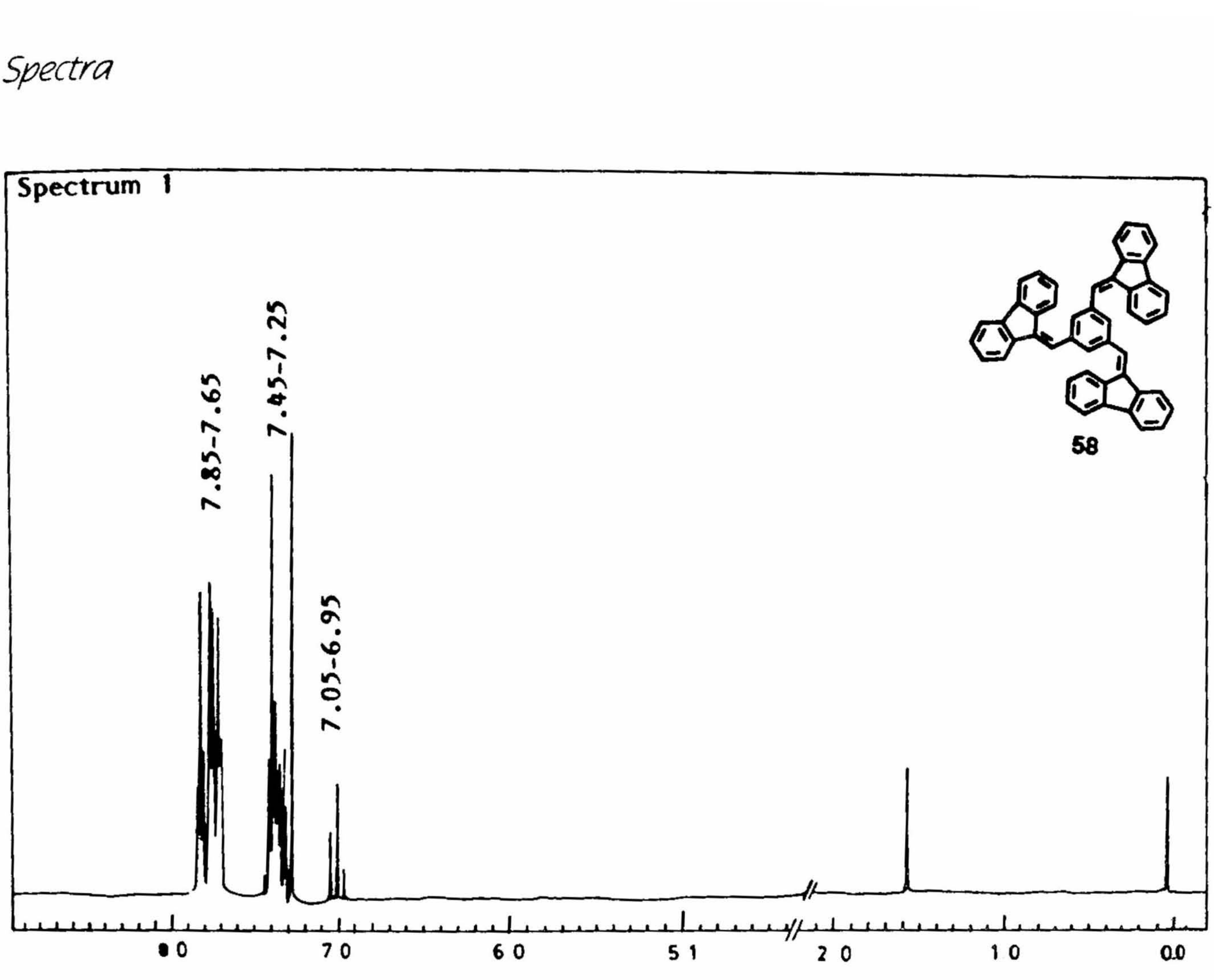
Found : C, 72.20; H, 8.45

# Spectra

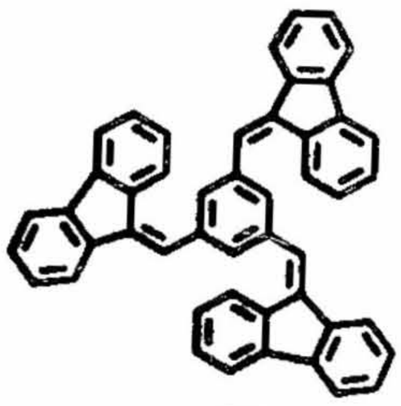
**Spectrum 1**



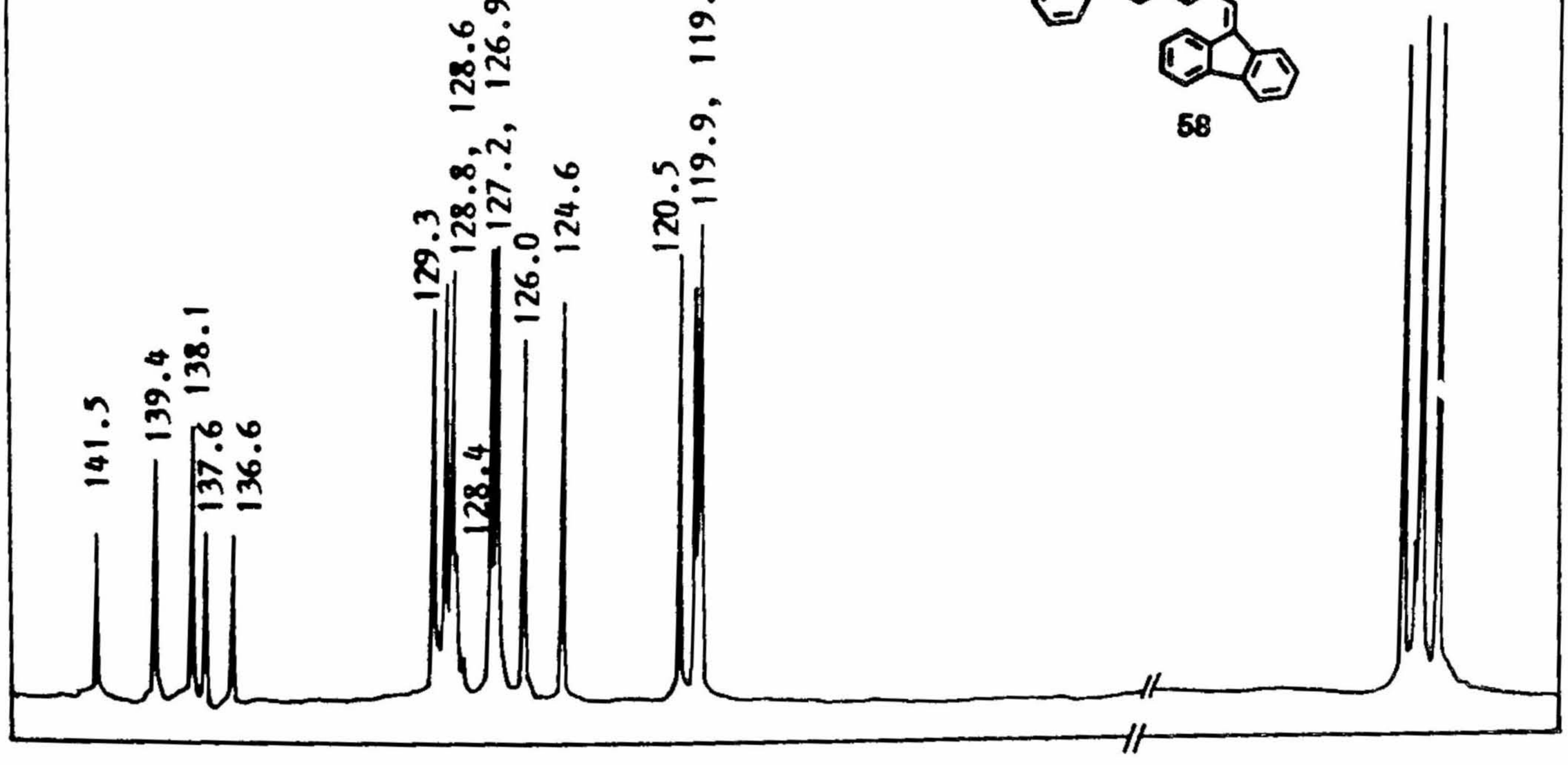
58




**Spectrum 2**



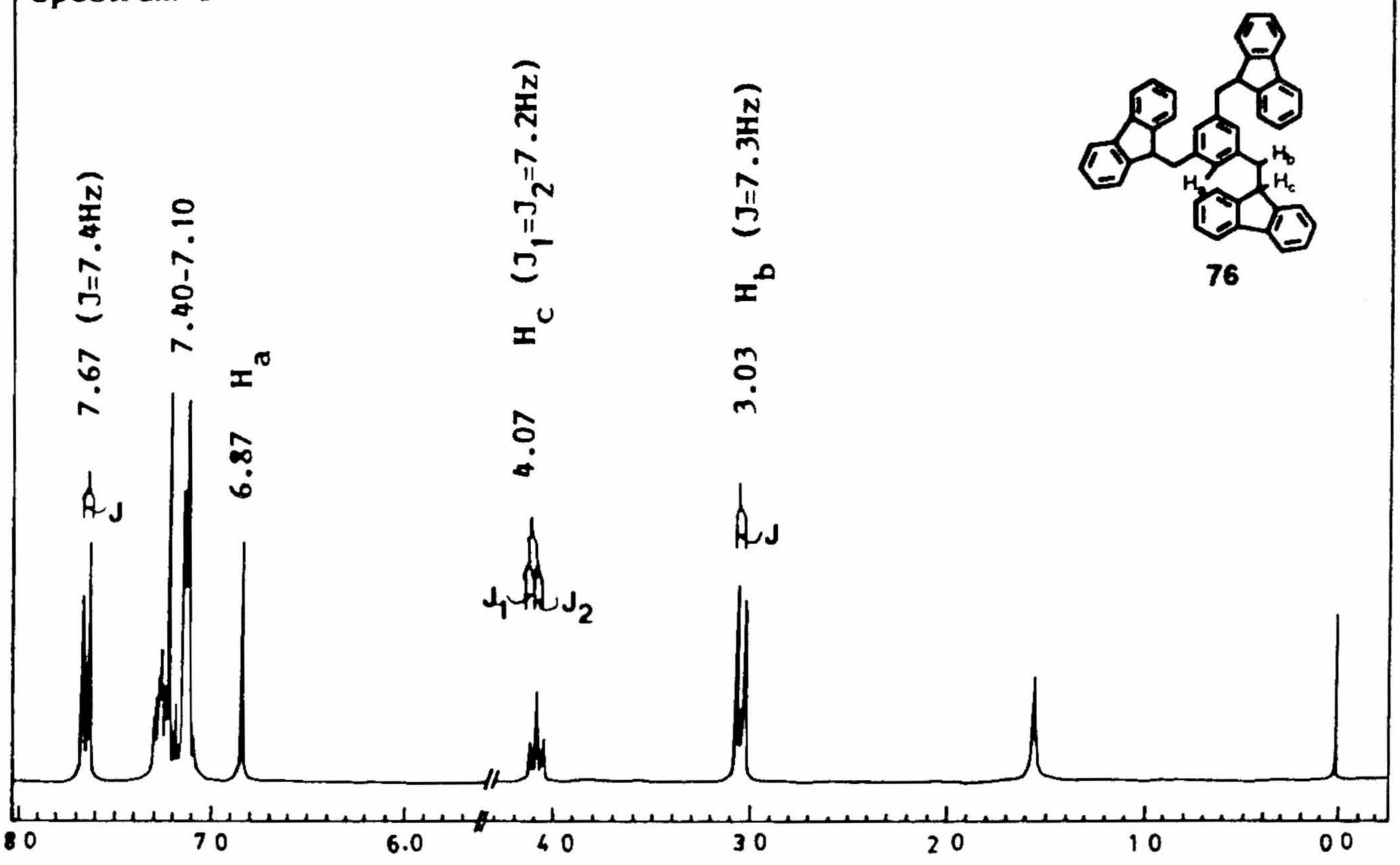
58



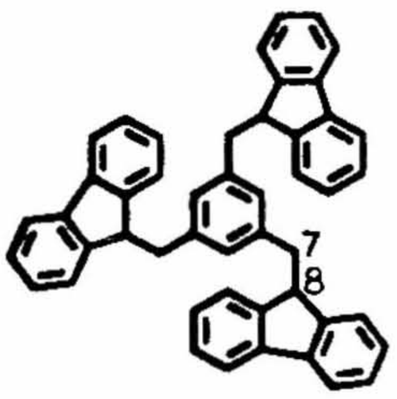
**Spectrum 3**



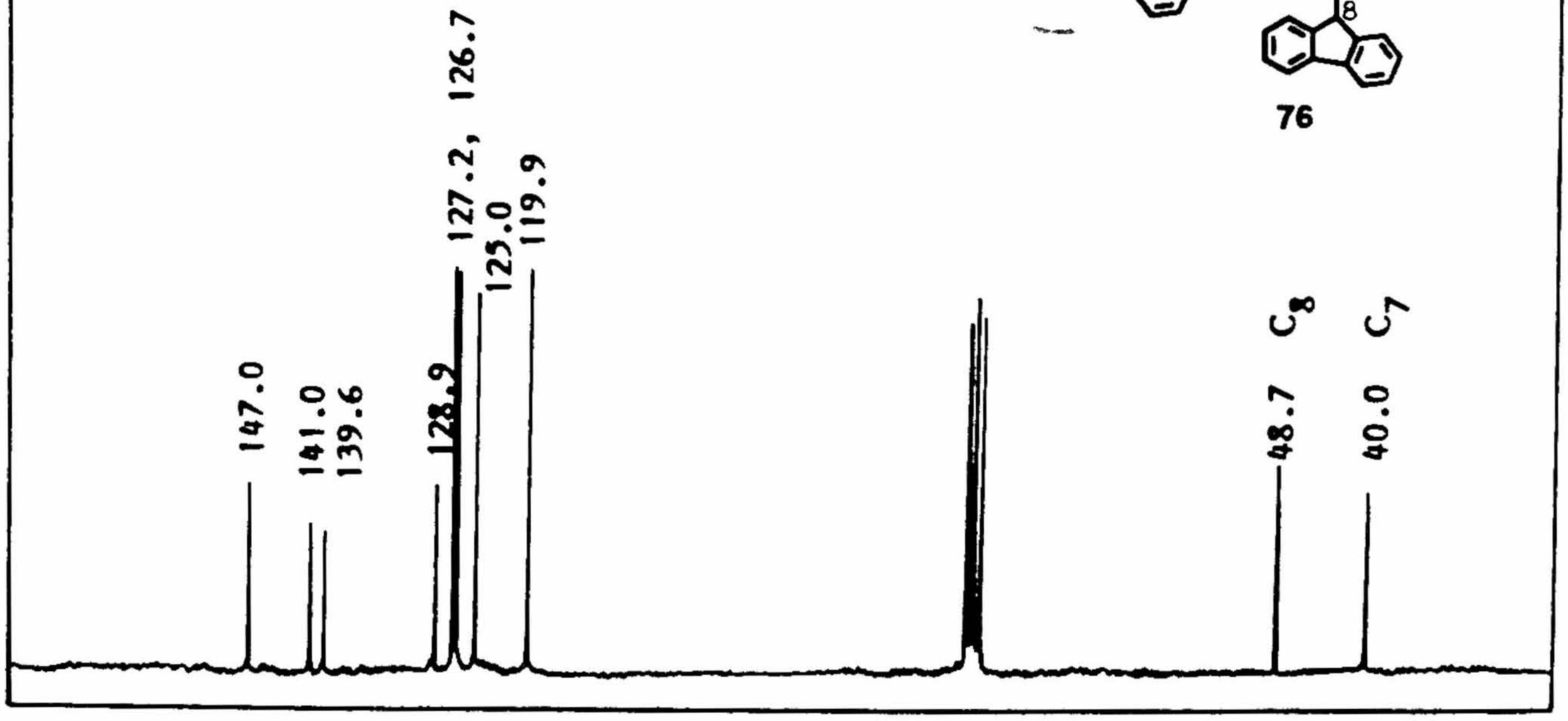
**76**




**Spectrum 4**



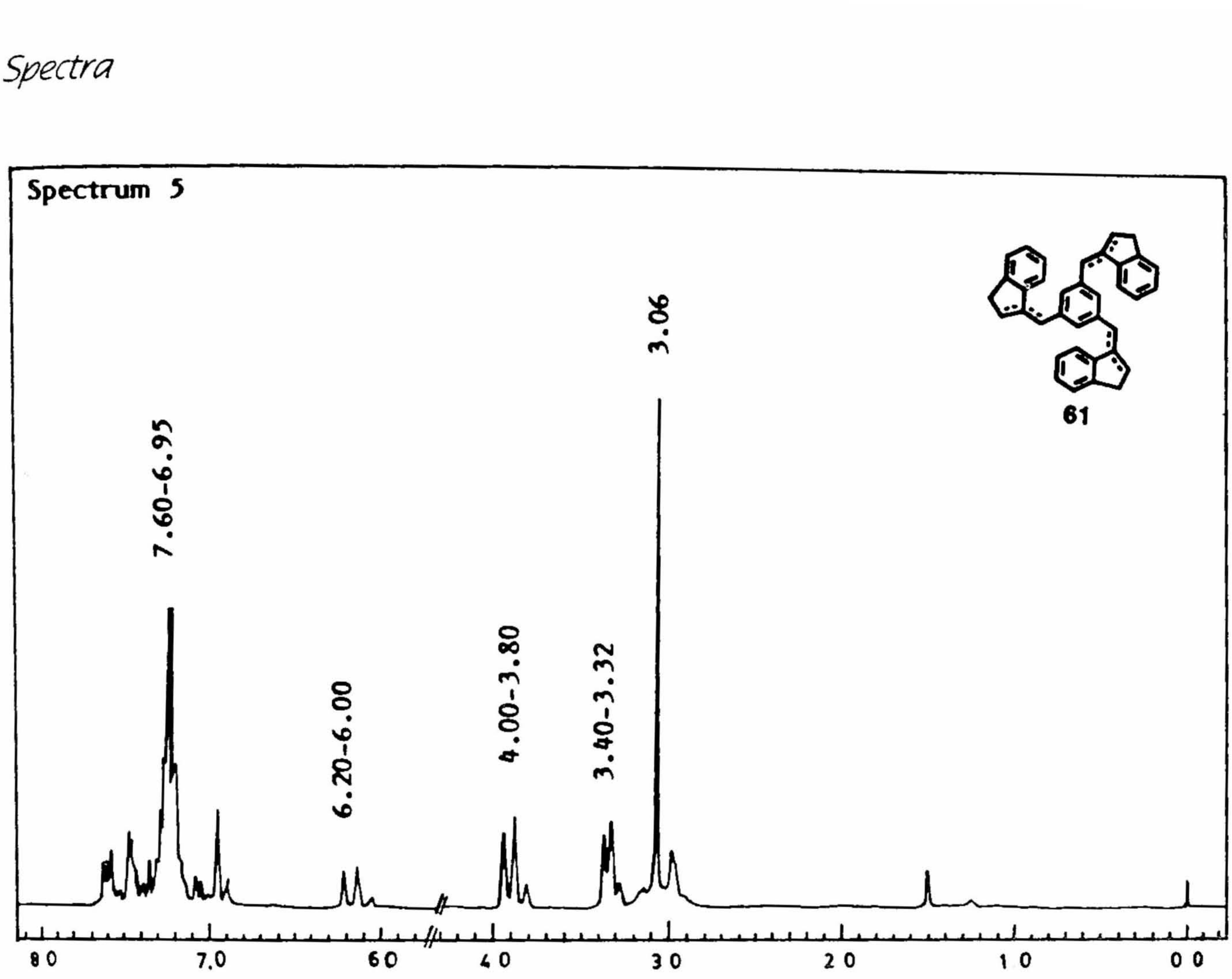
**76**



**Spectrum 5**



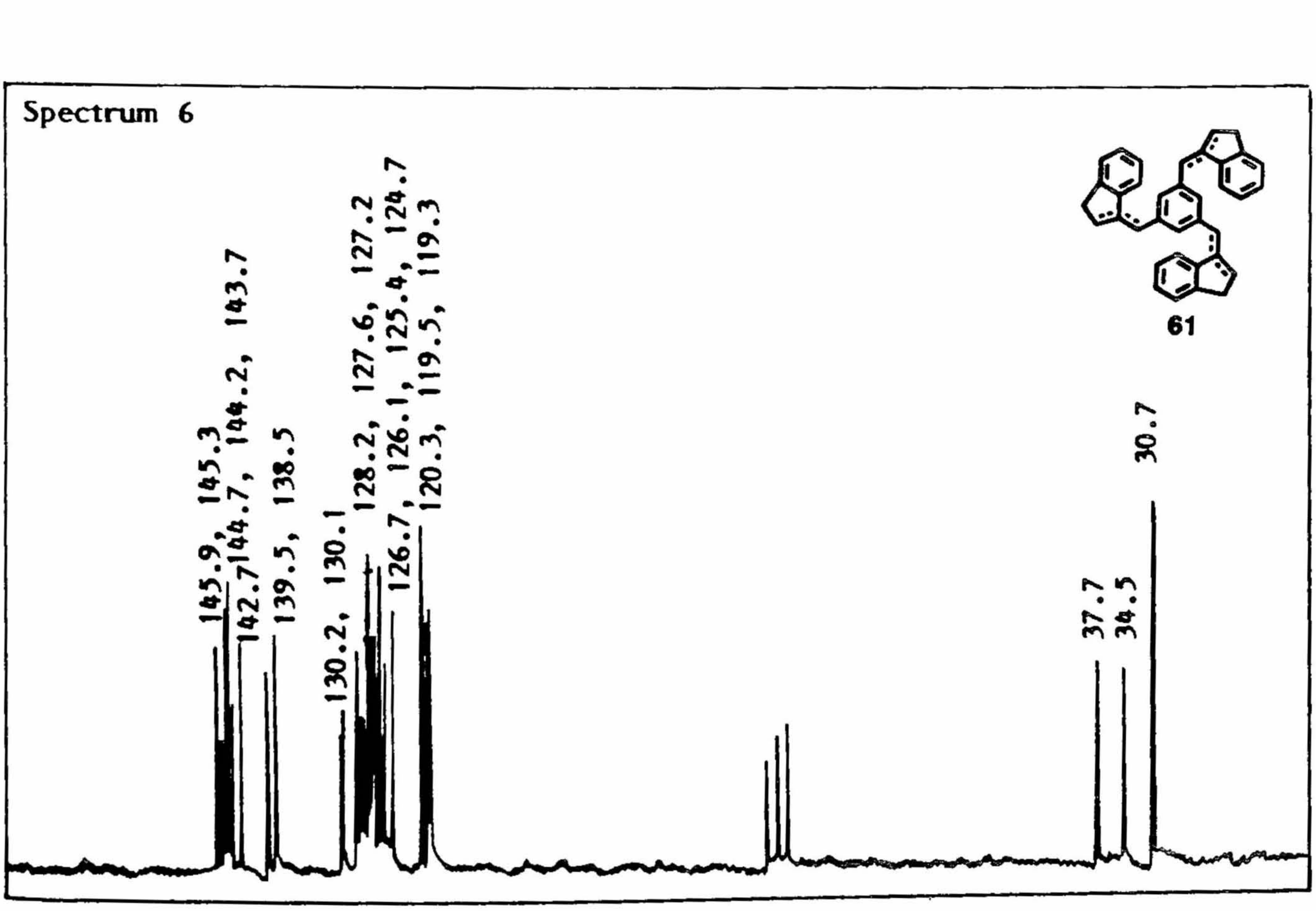
61



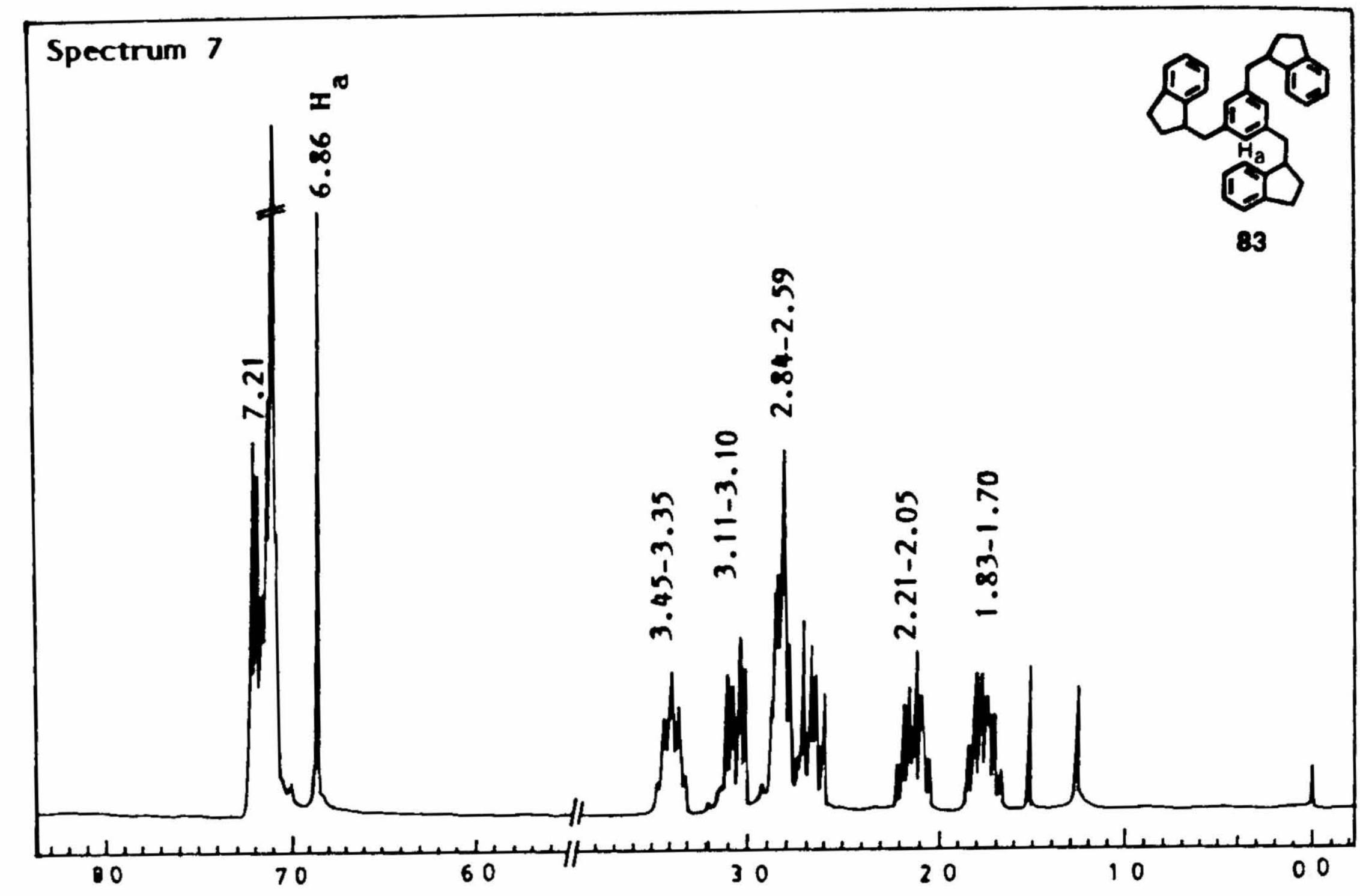

**Spectrum 6**



61



Spectrum 7

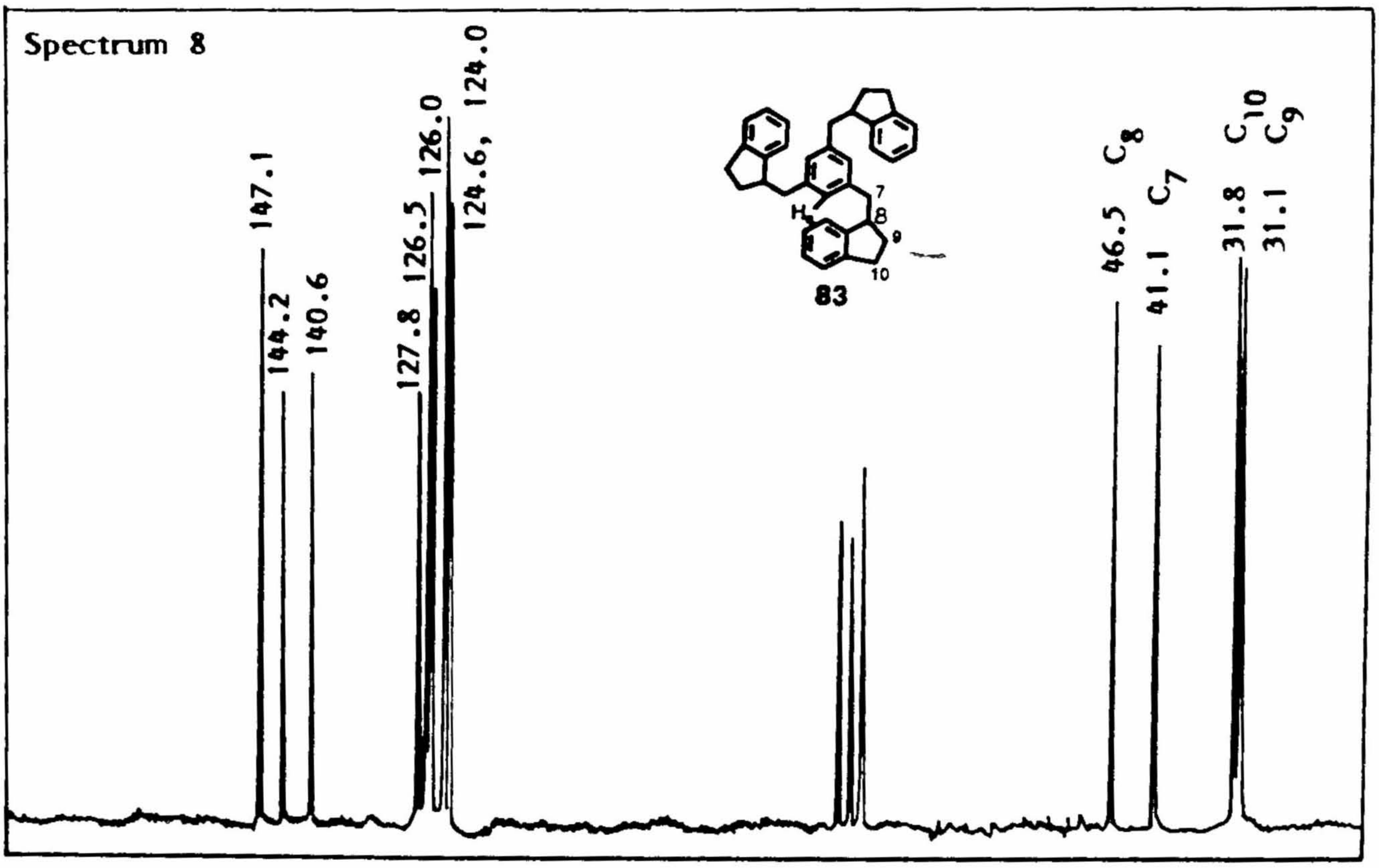






83

Spectrum 8

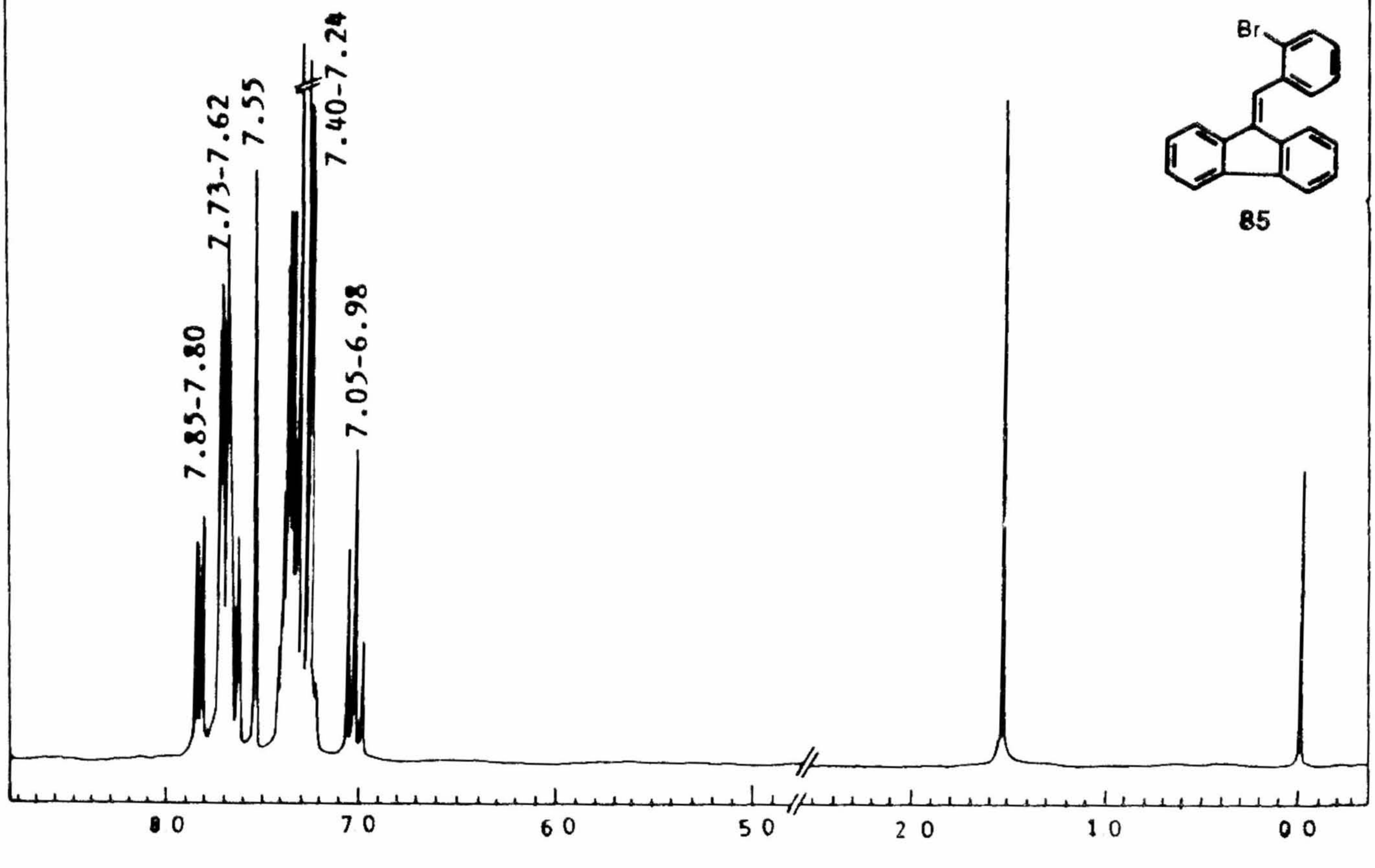




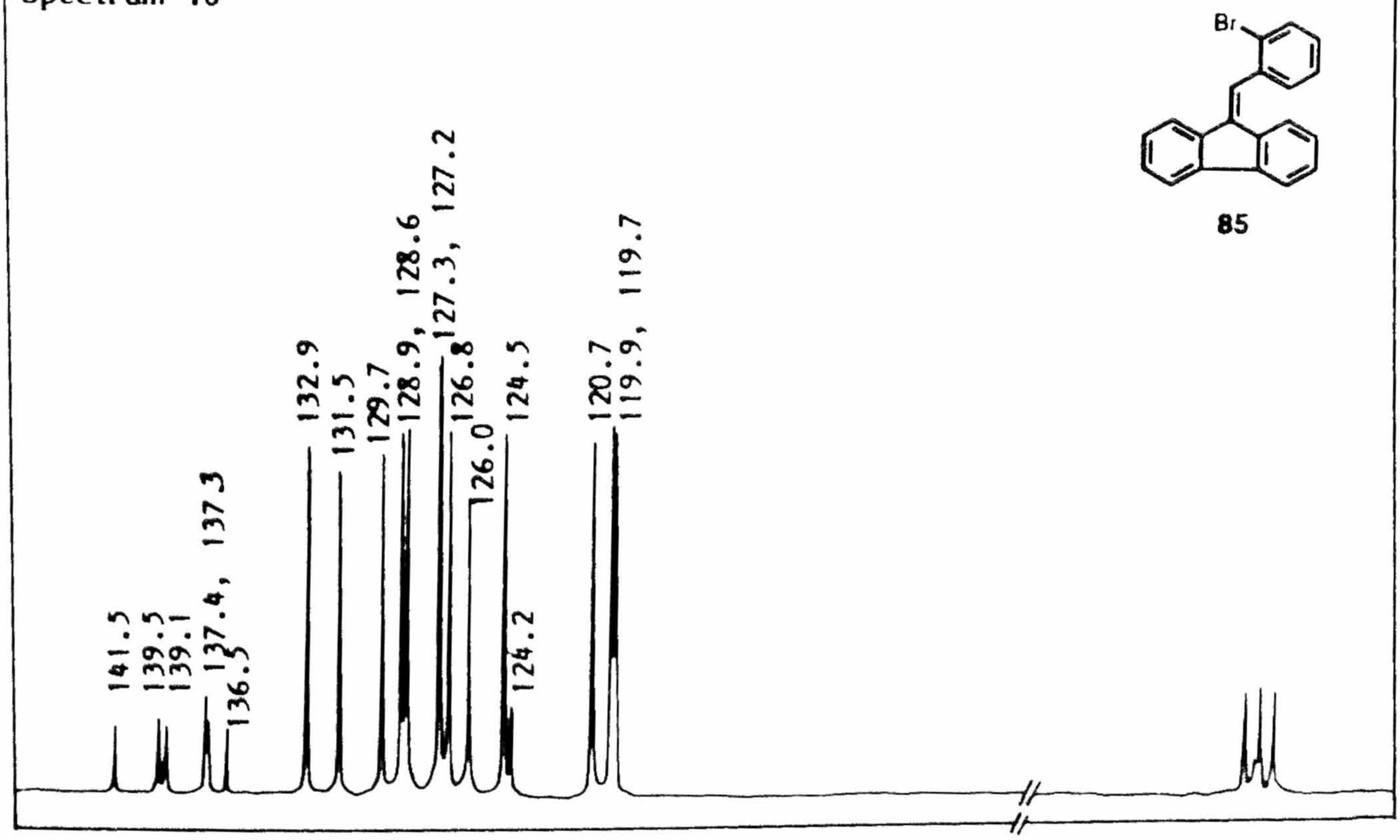


83

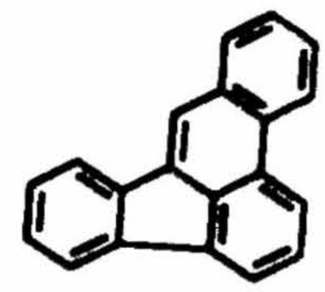
**Spectrum 9**



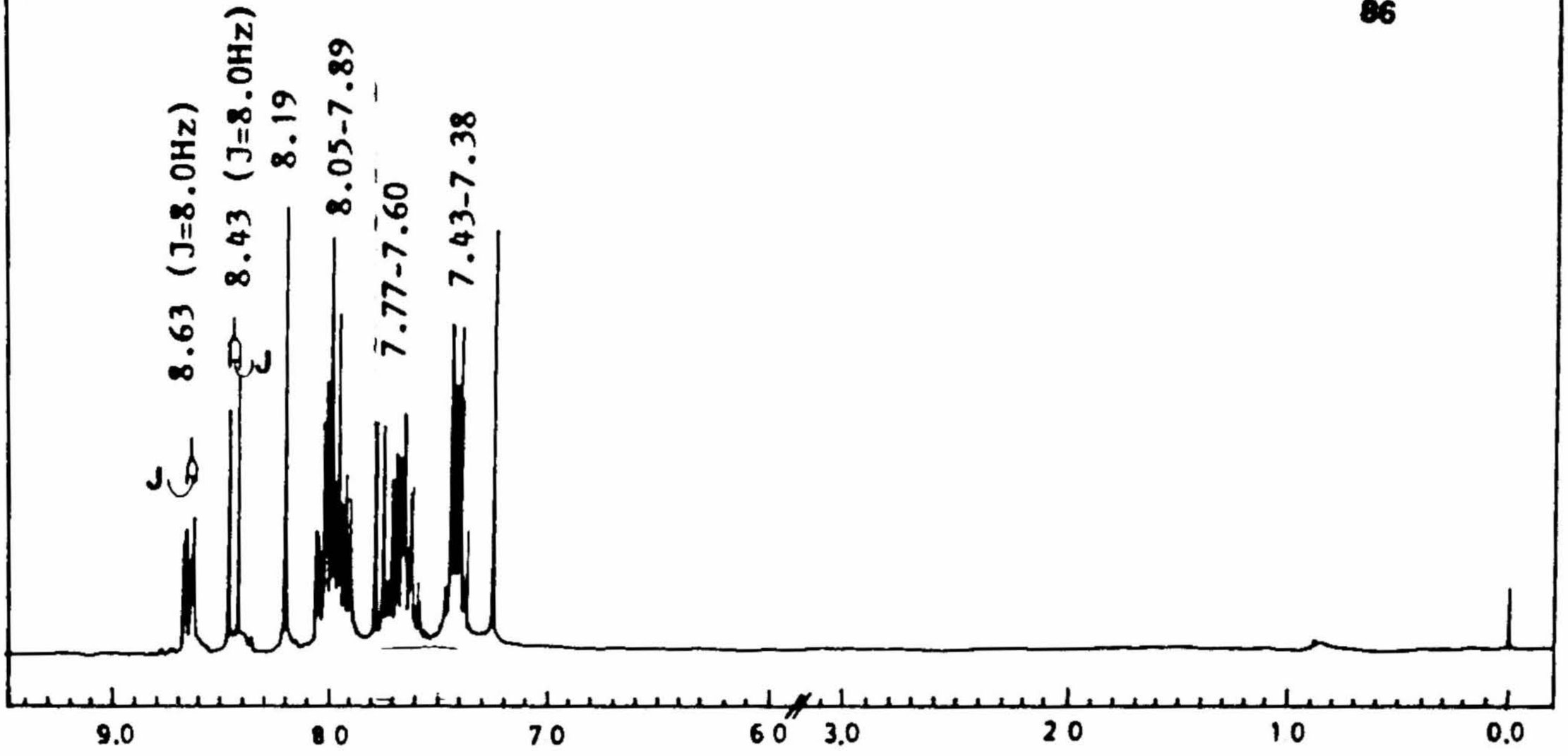

**Spectrum 10**



**Spectrum 11**



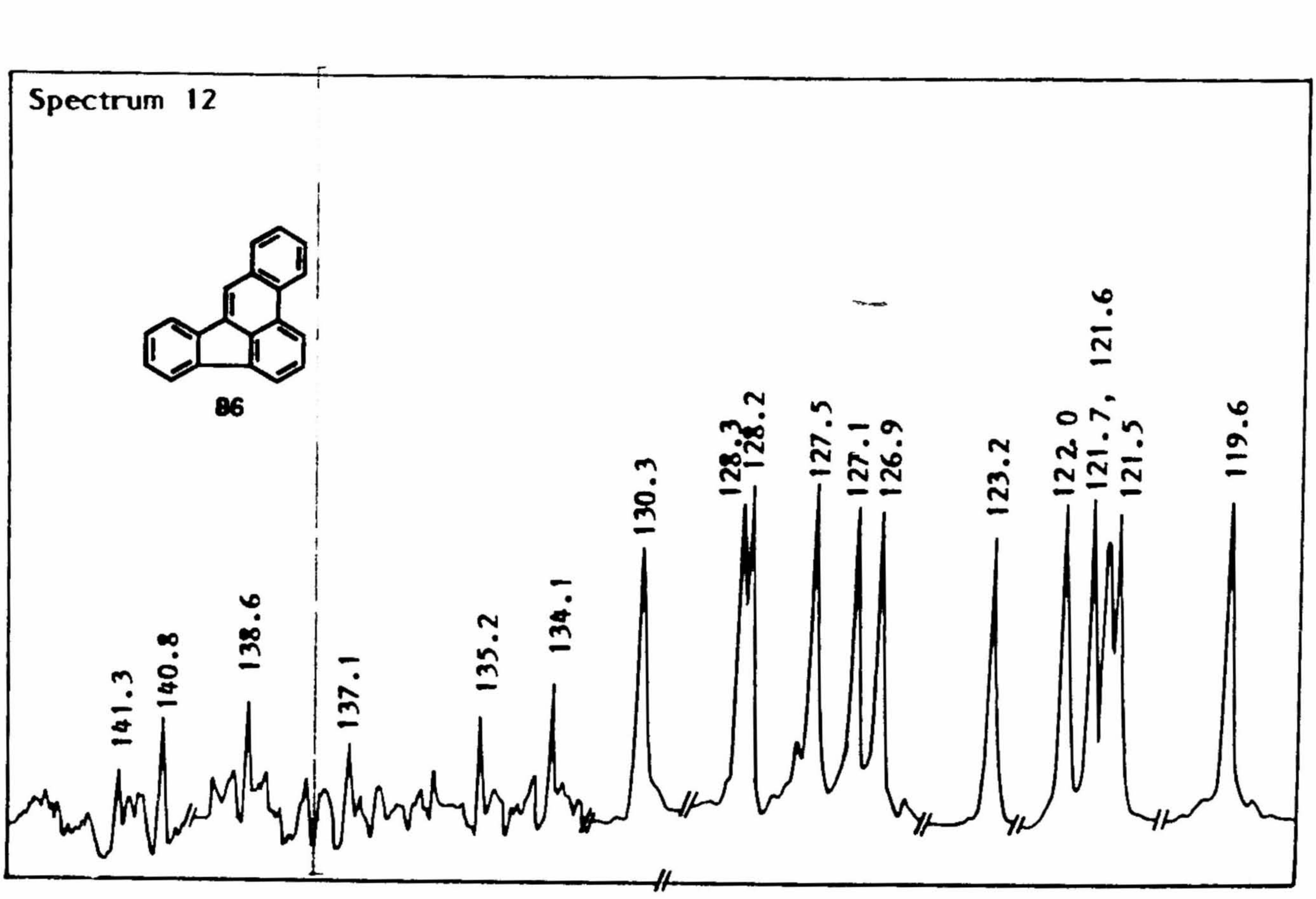
86



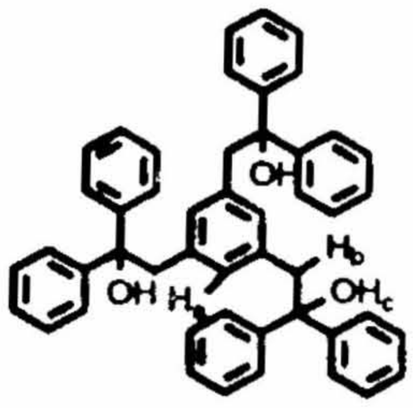

**Spectrum 12**



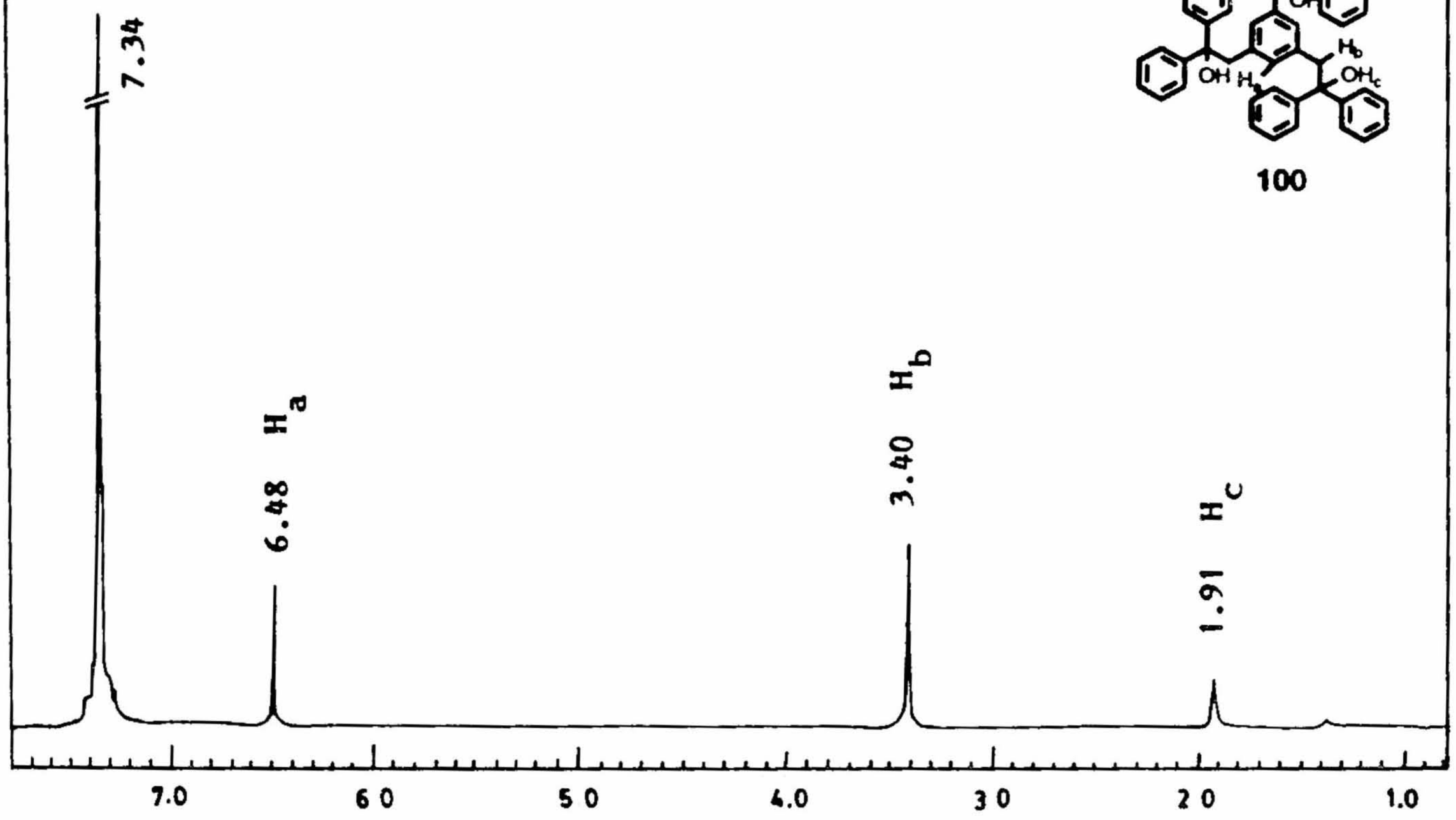
86



**Spectrum 13**



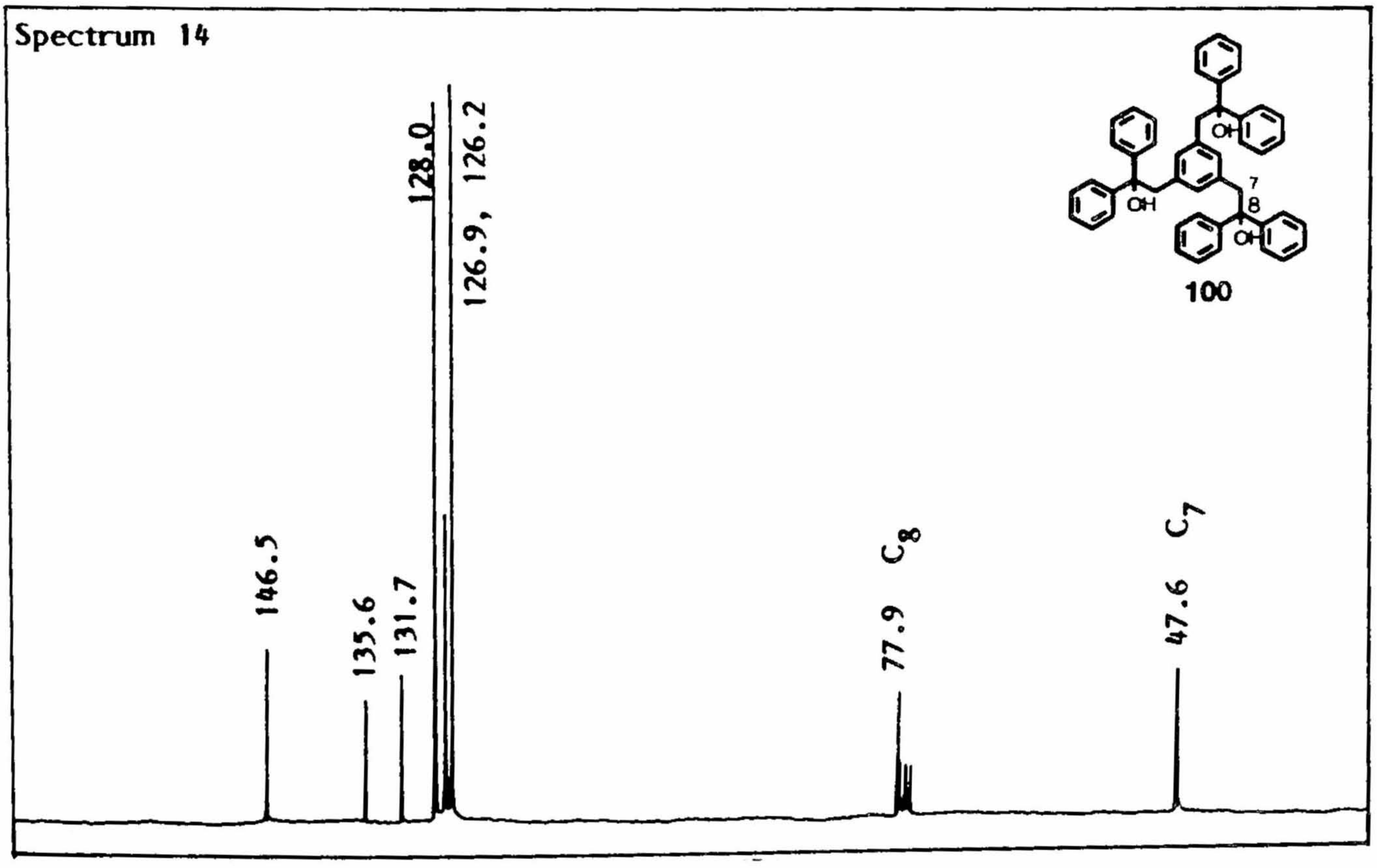

100



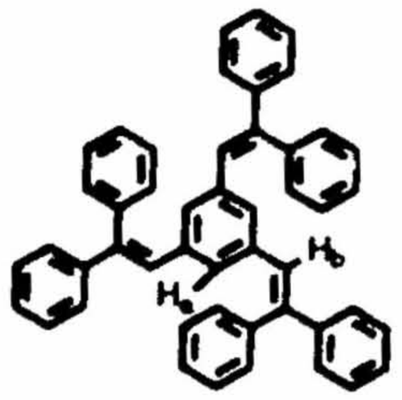

**Spectrum 14**



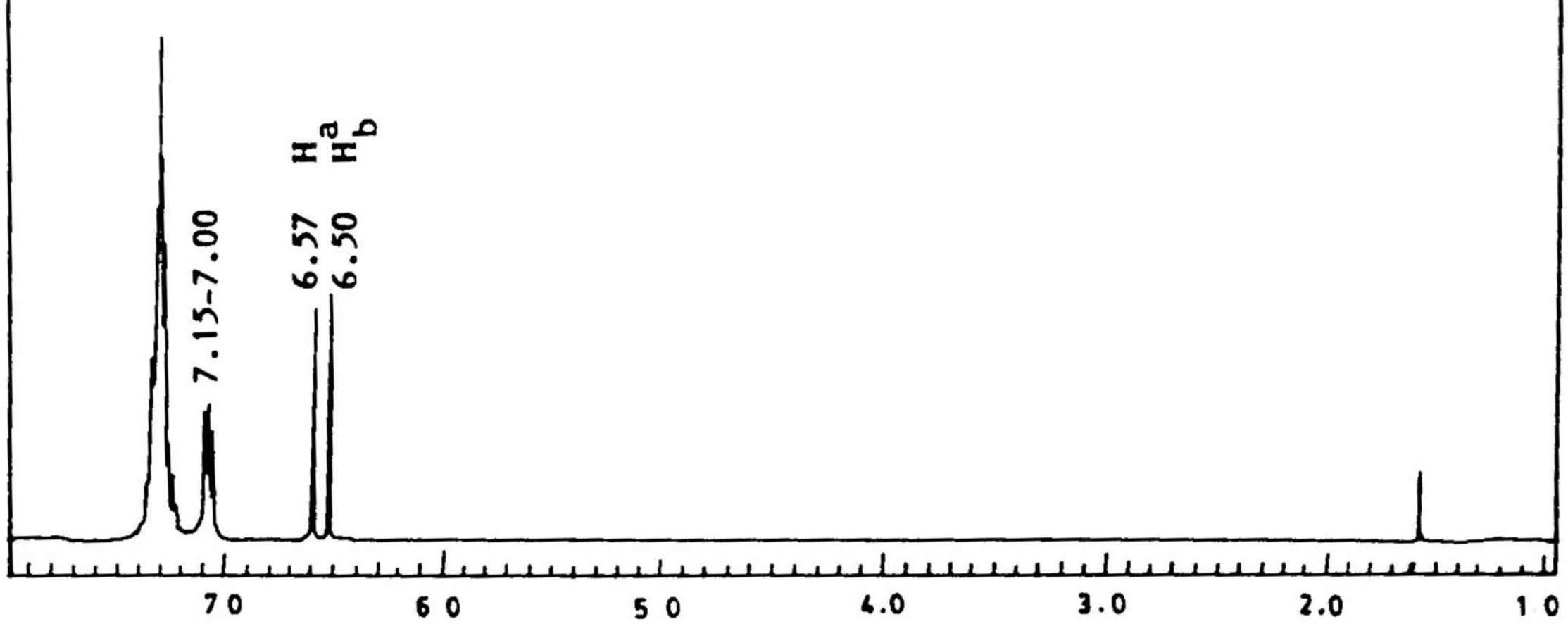

100



**Spectrum 15**



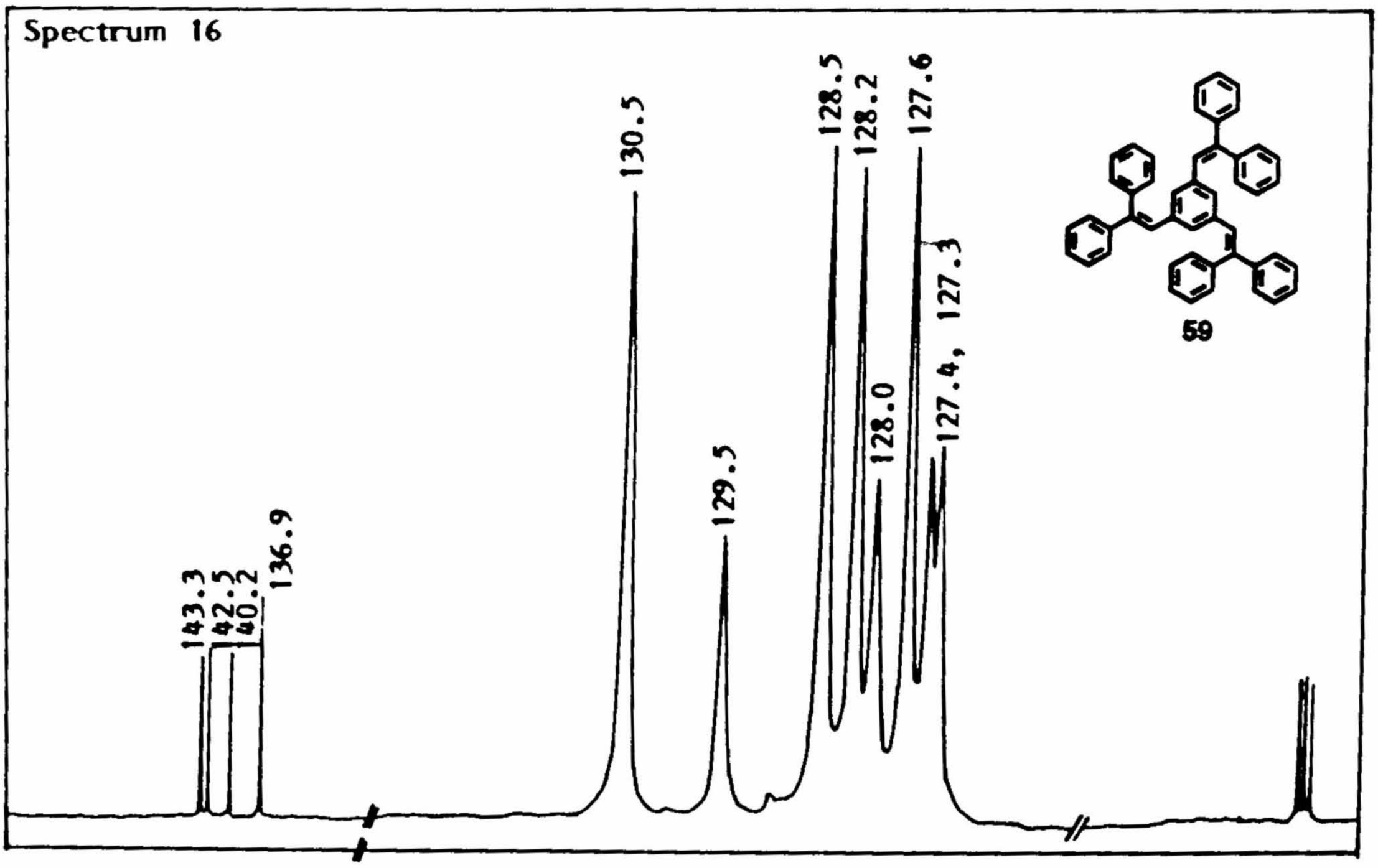

59



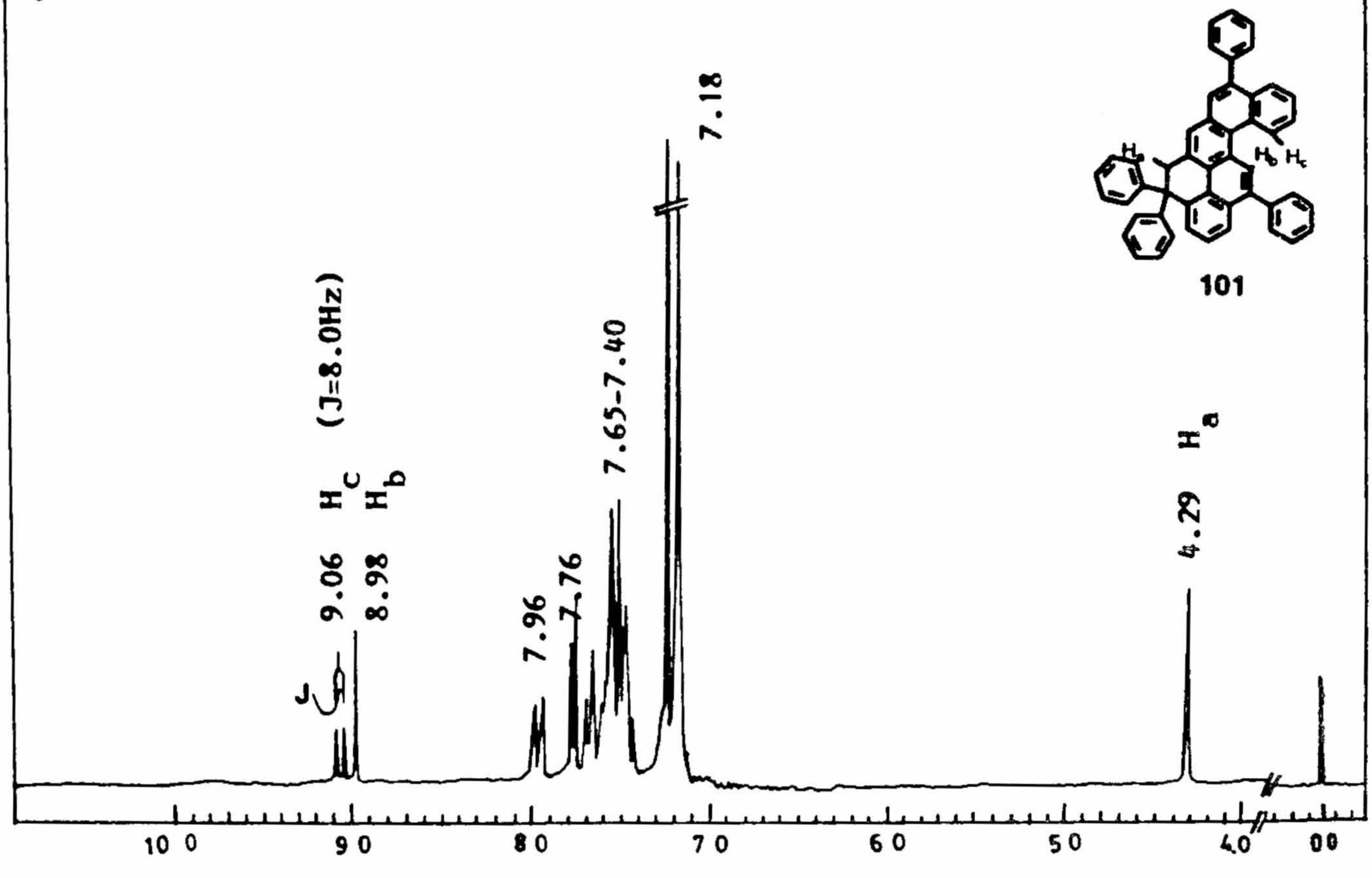

**Spectrum 16**



59



**Spectrum 17**

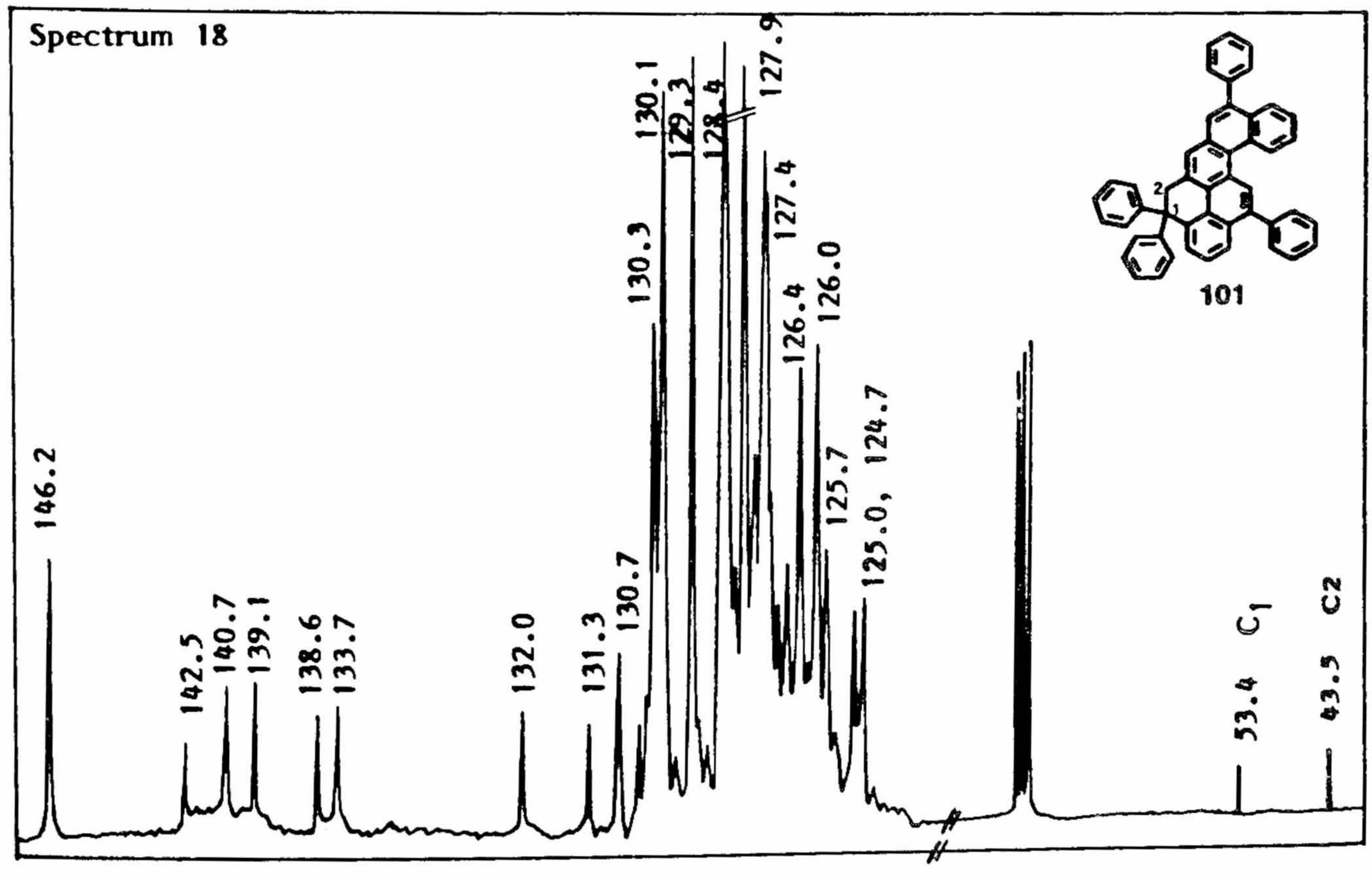






101

**Spectrum 18**

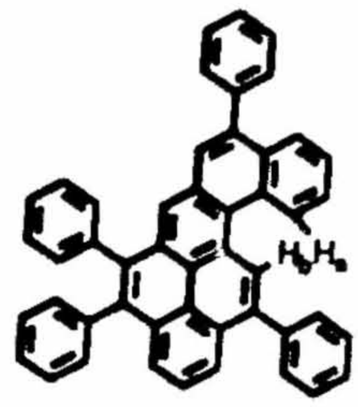




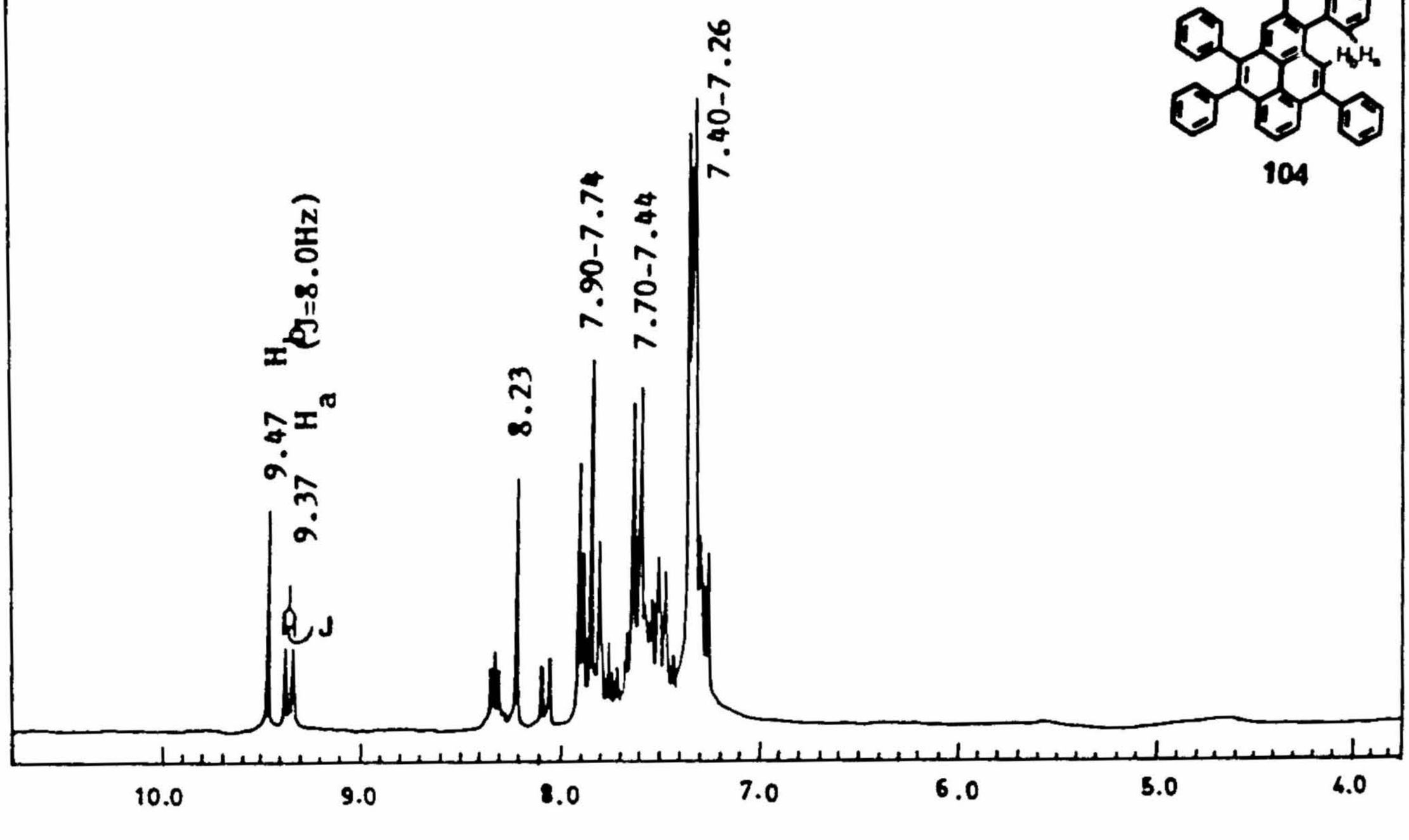


101

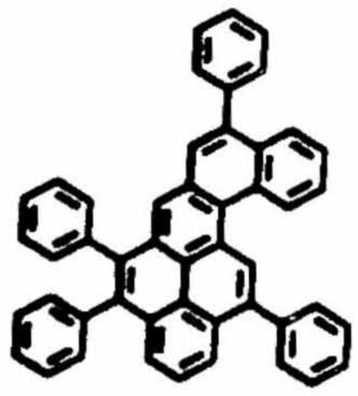
**Spectrum 19**



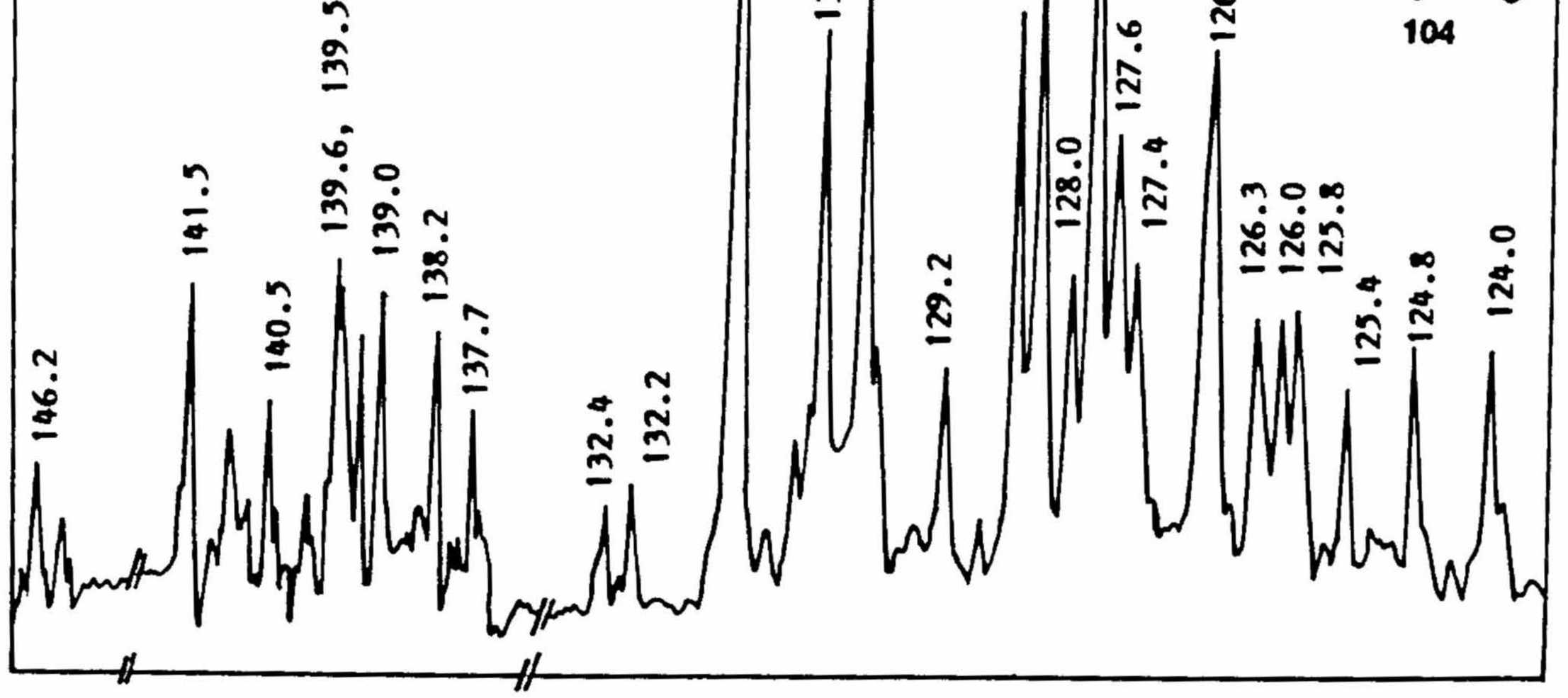
104



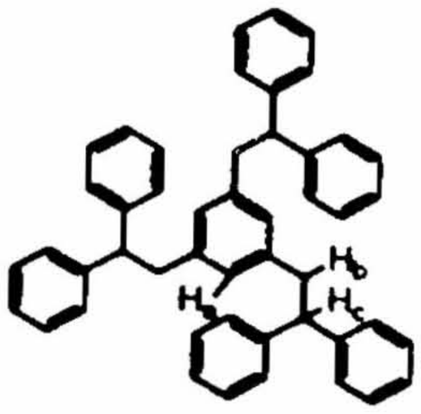

**Spectrum 20**



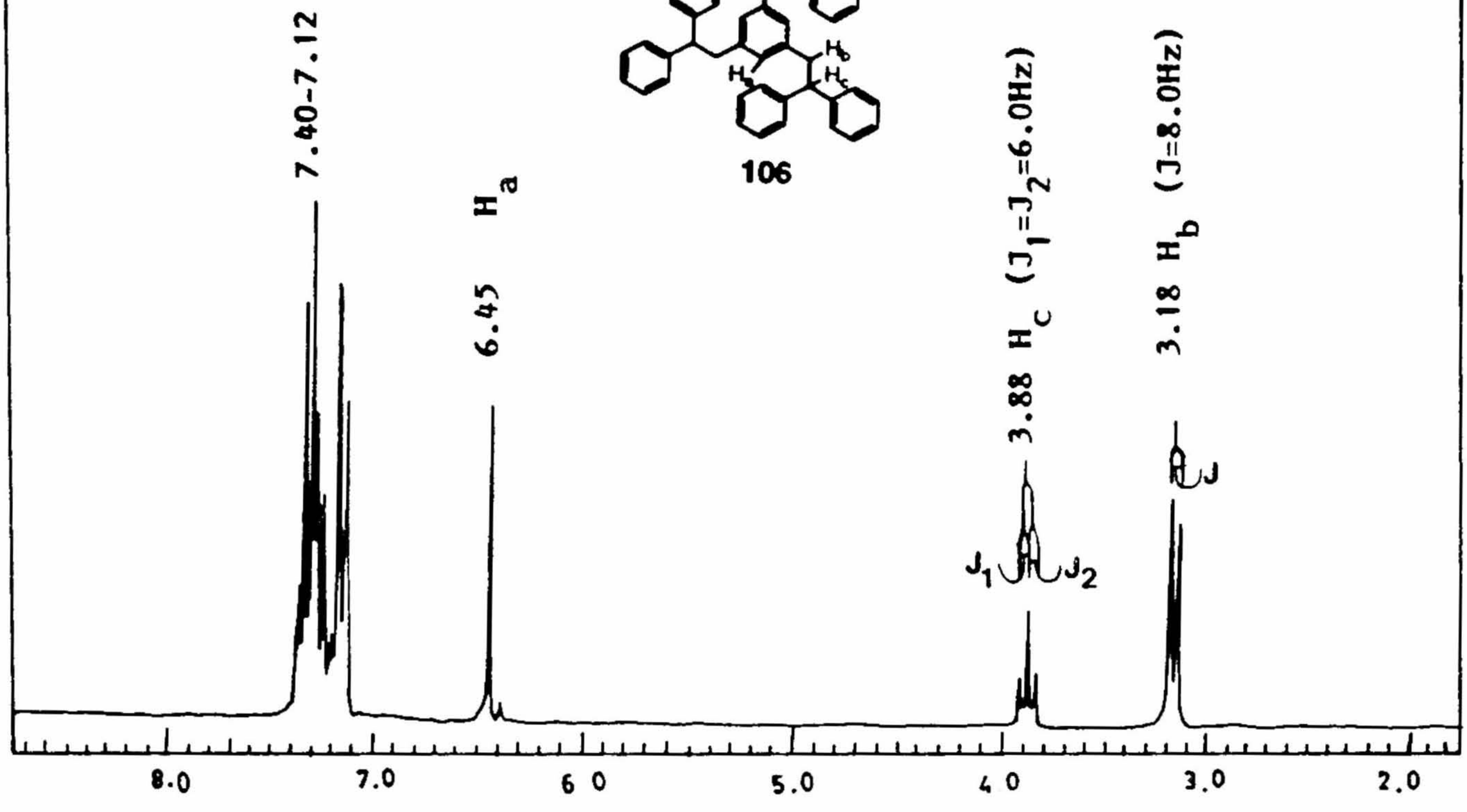
104



**Spectrum 21**



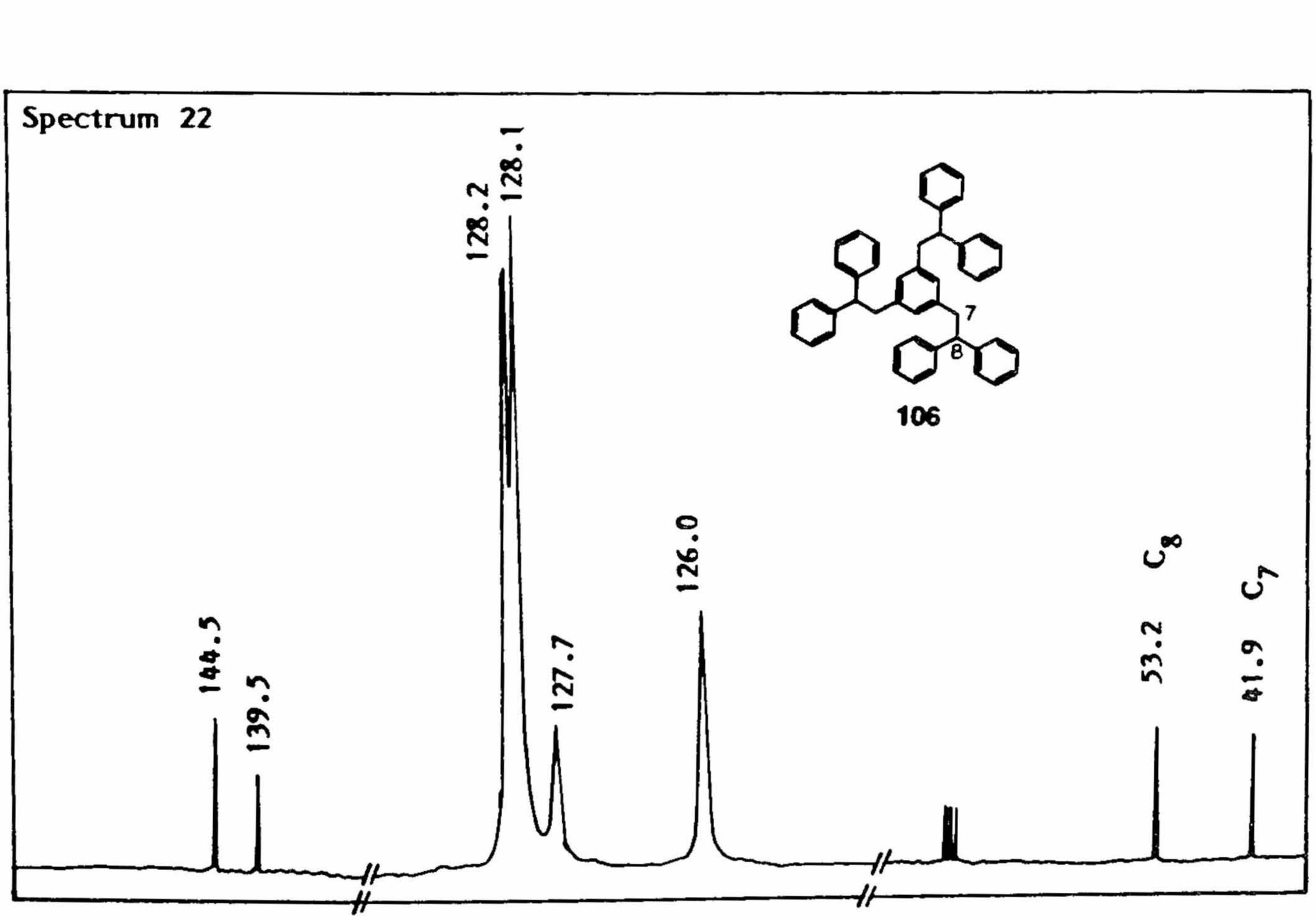
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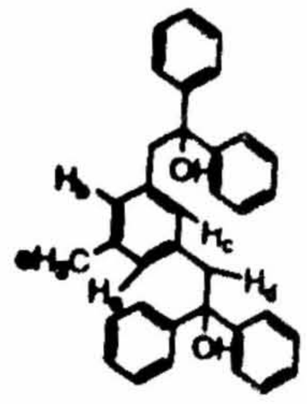

**Spectrum 22**



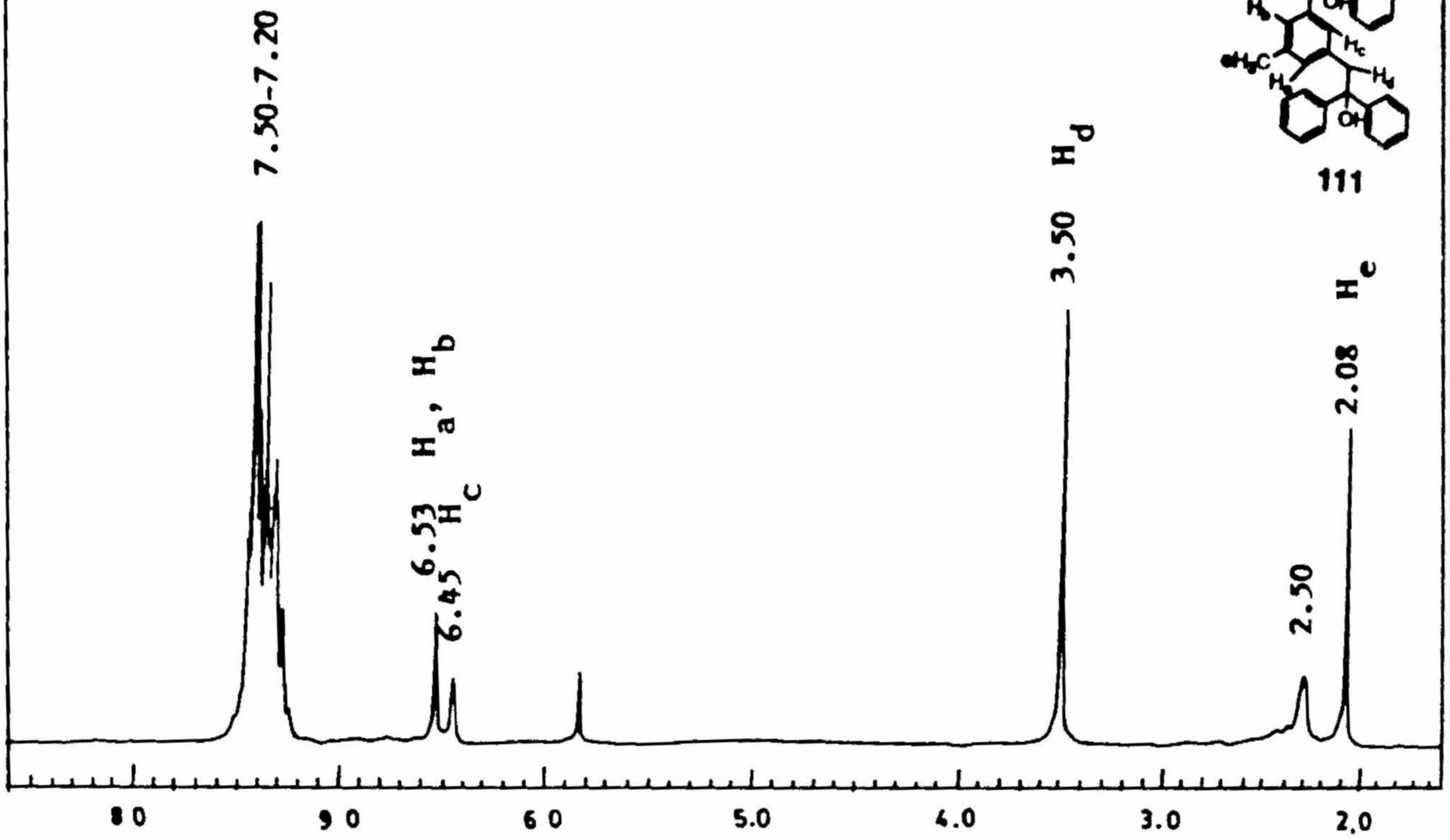
106



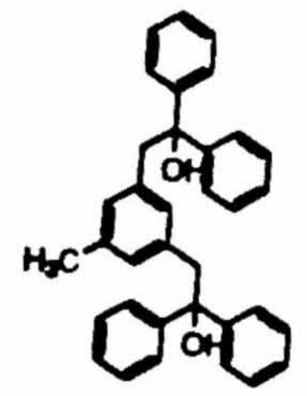
**Spectrum 23**



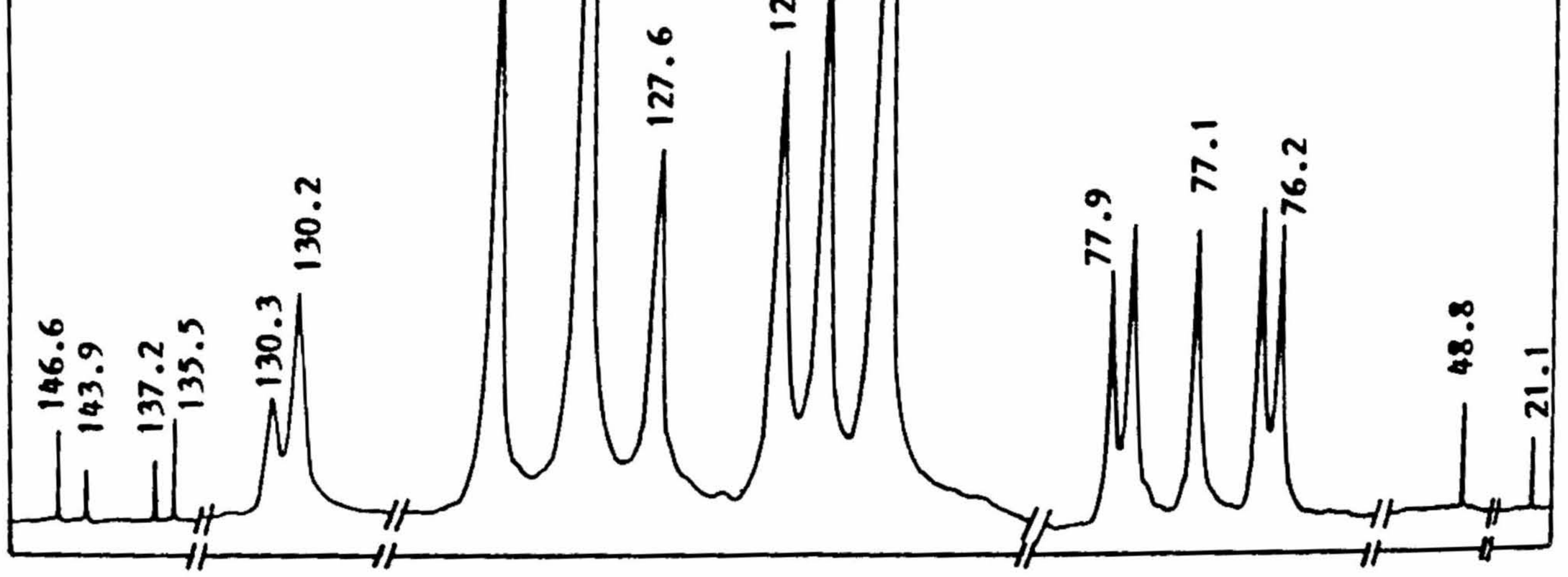
111



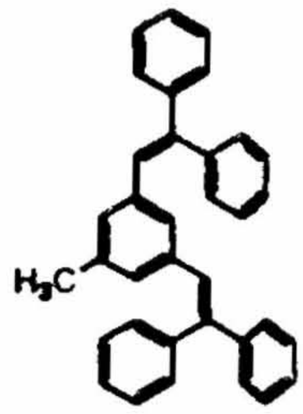

**Spectrum 24**



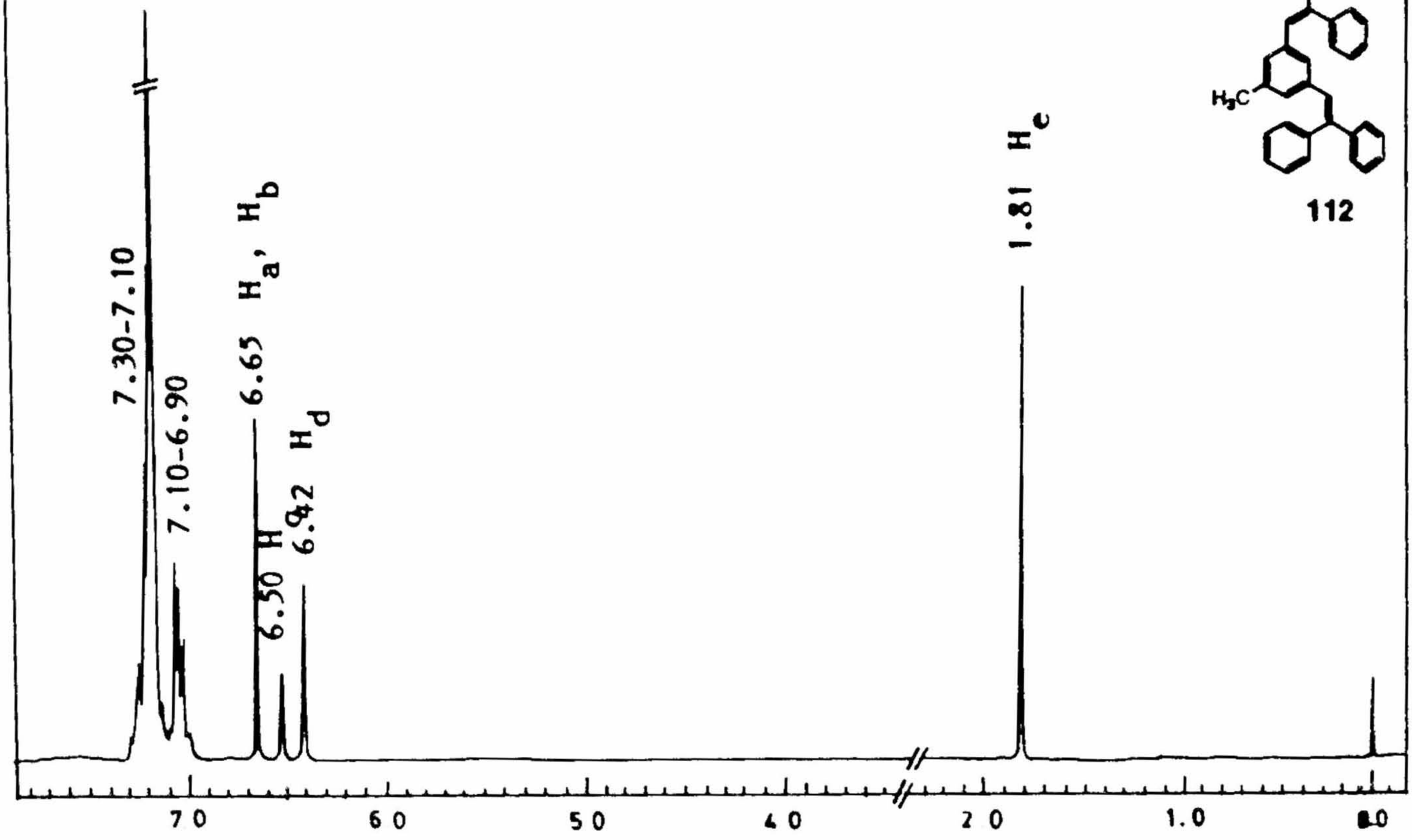
111



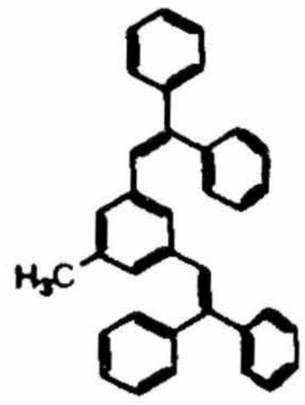
**Spectrum 25**



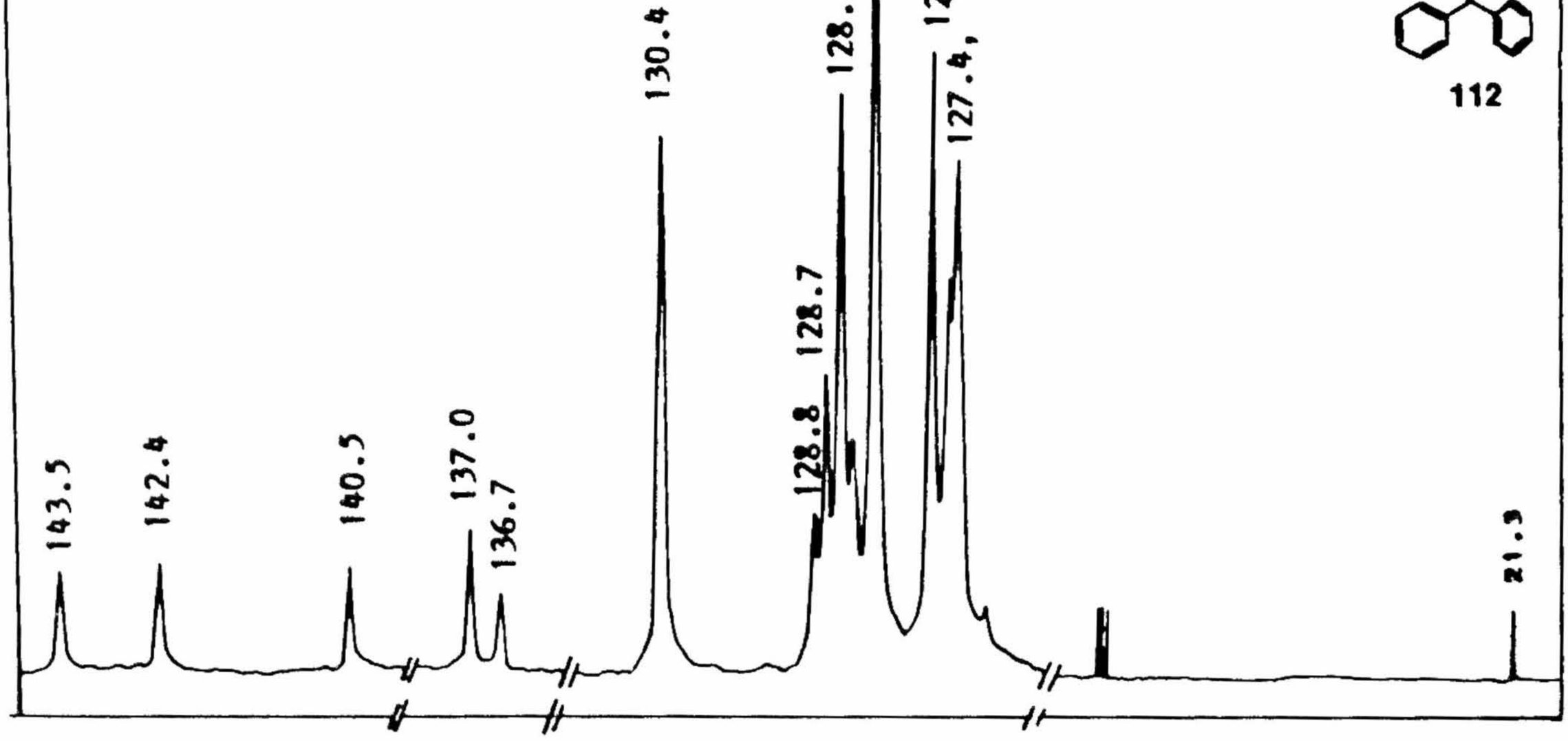

112



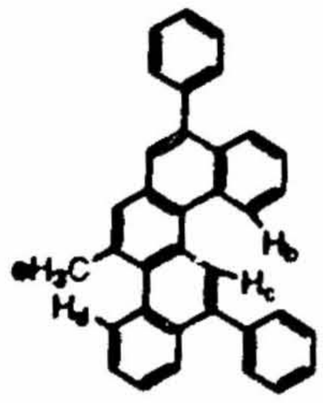

**Spectrum 26**



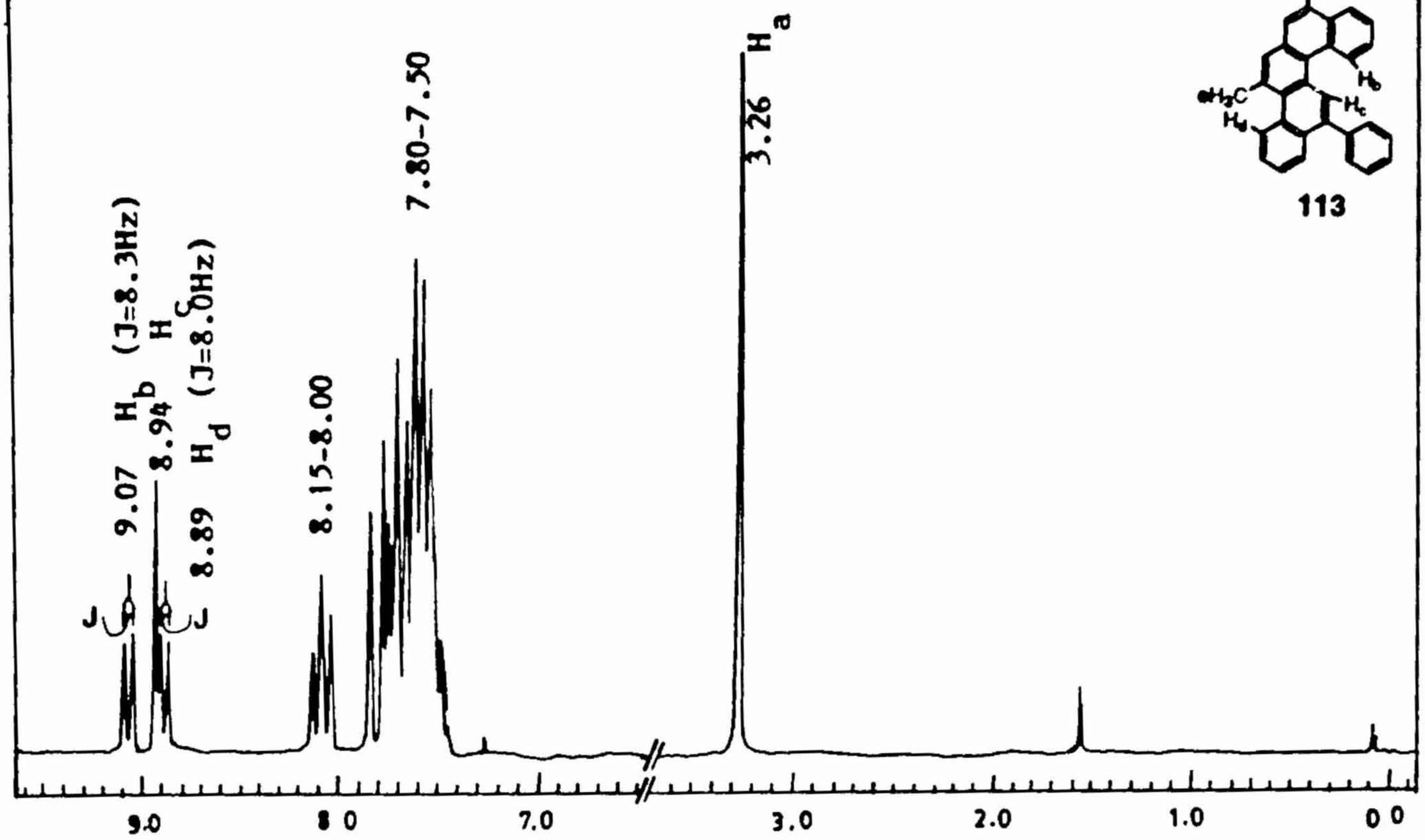

112



**Spectrum 27**



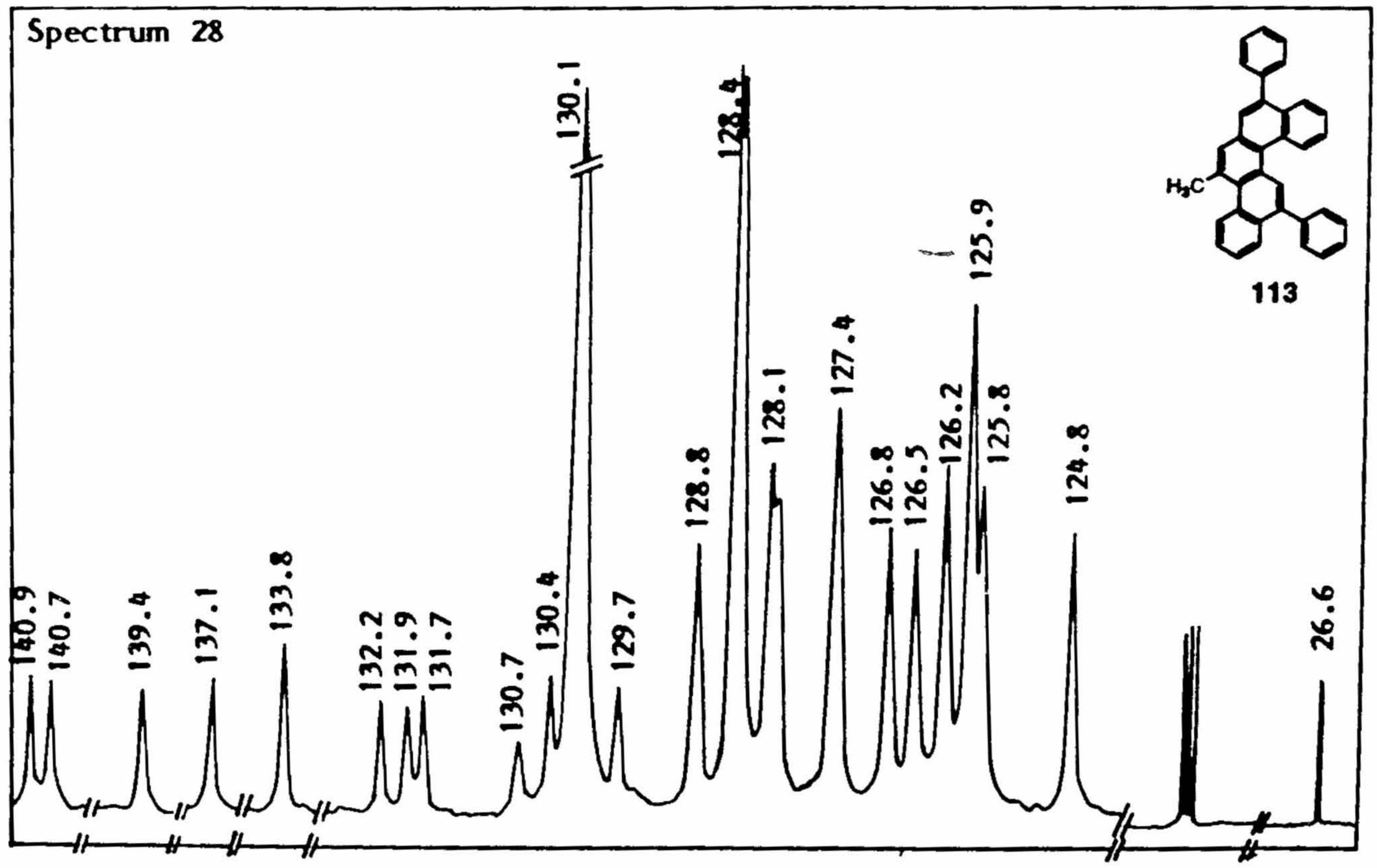
113



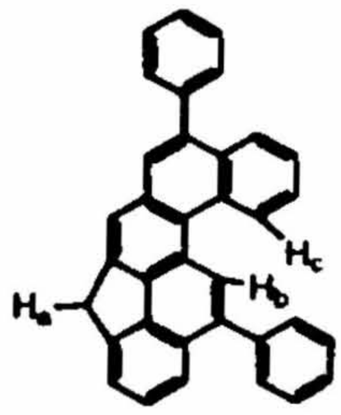

**Spectrum 28**



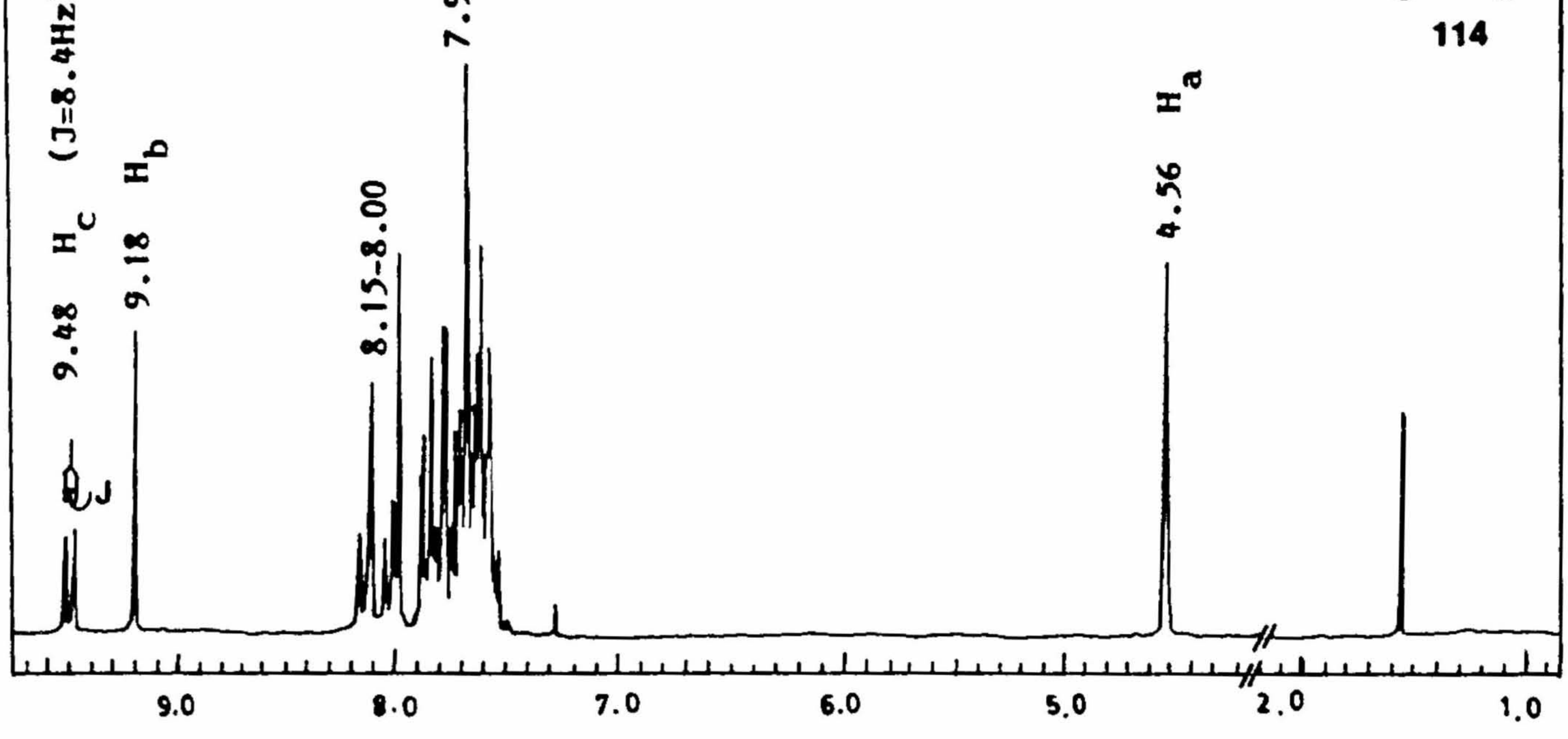
113



**Spectrum 29**



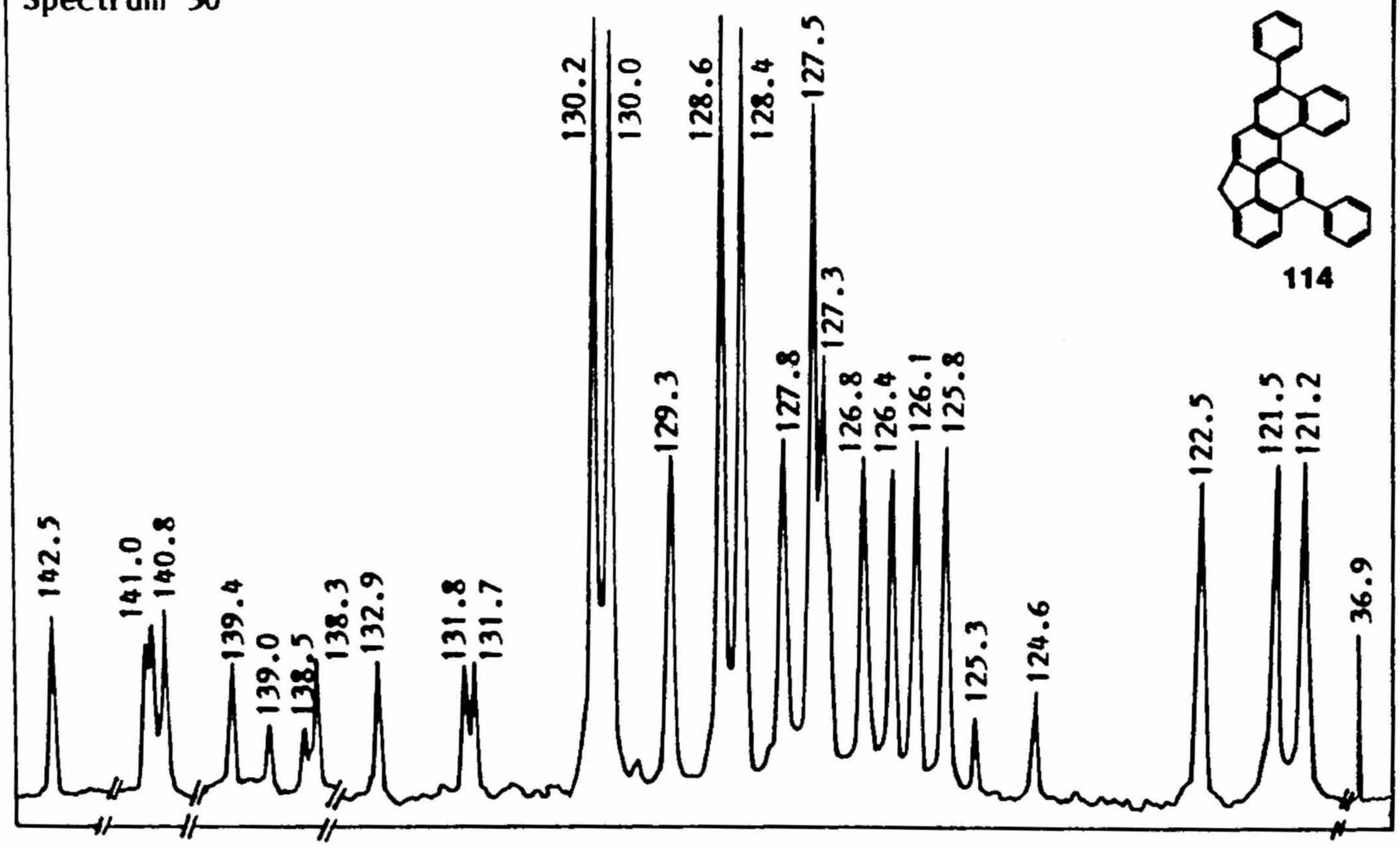

114



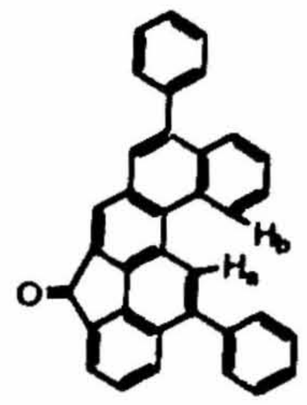

**Spectrum 30**



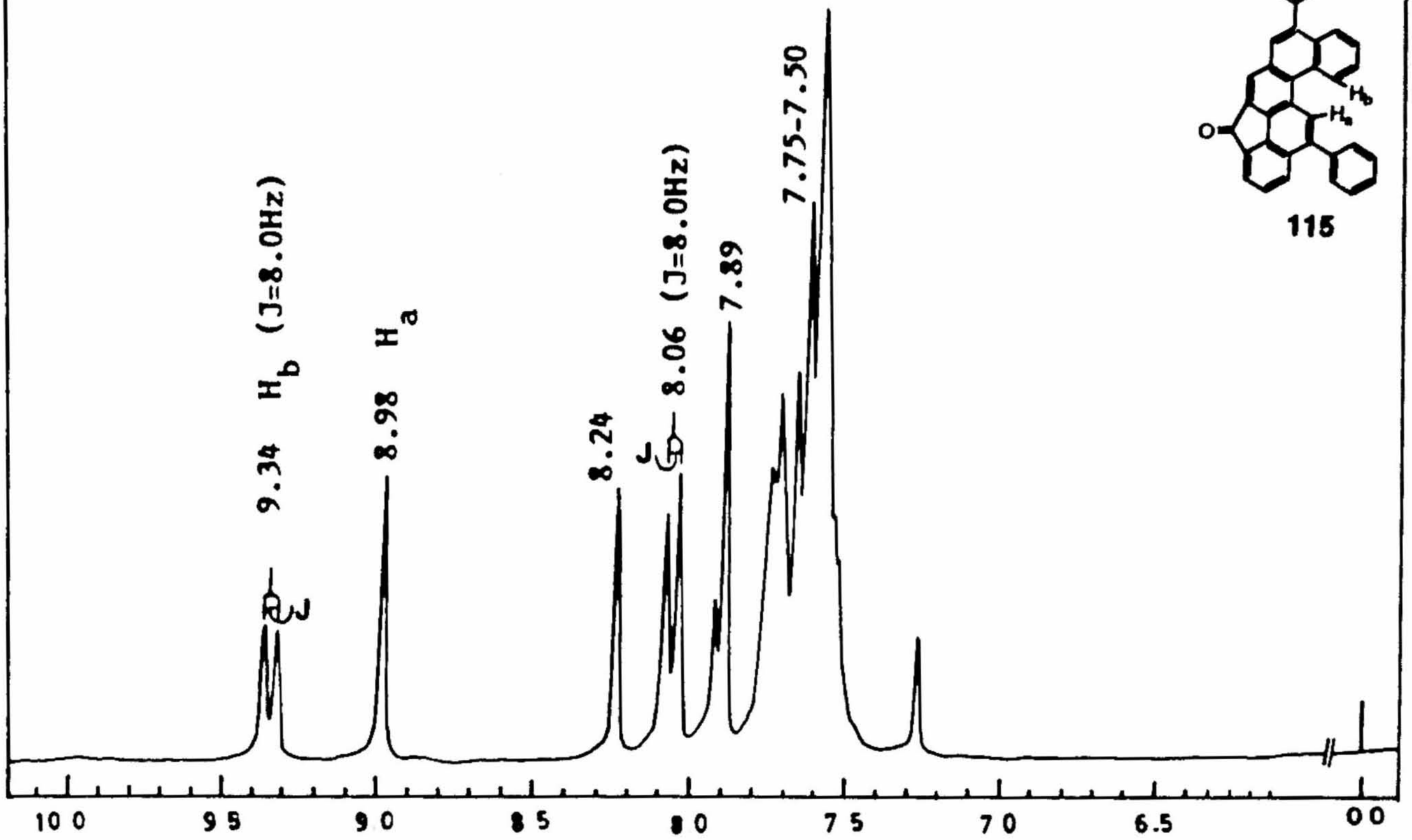
114



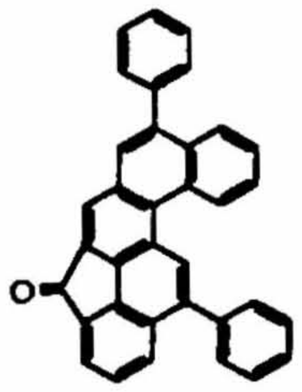
**Spectrum 31**



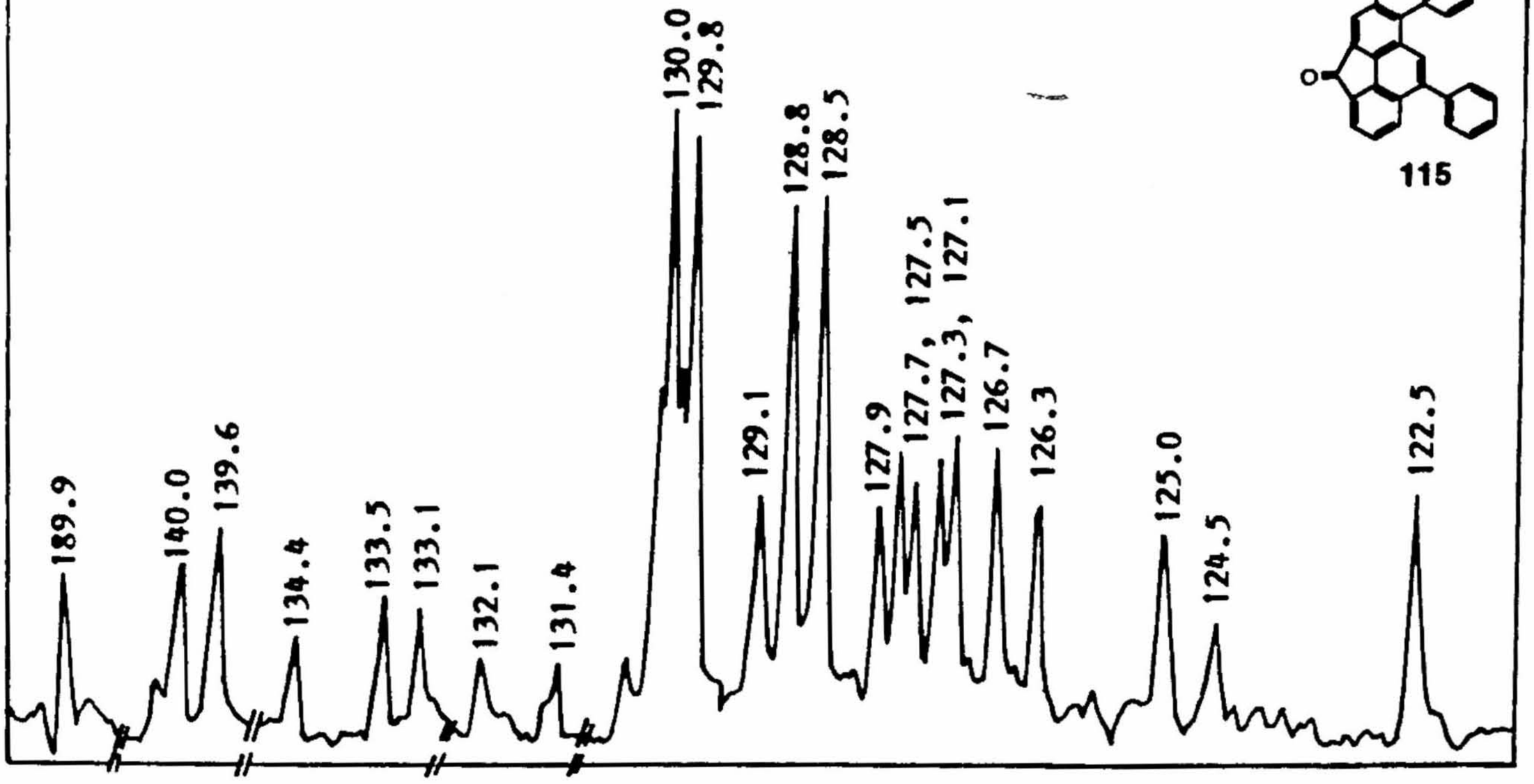
115



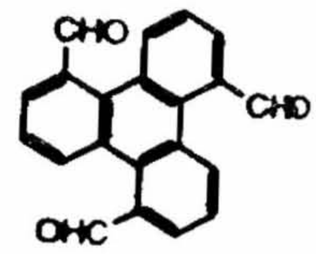

**Spectrum 32**



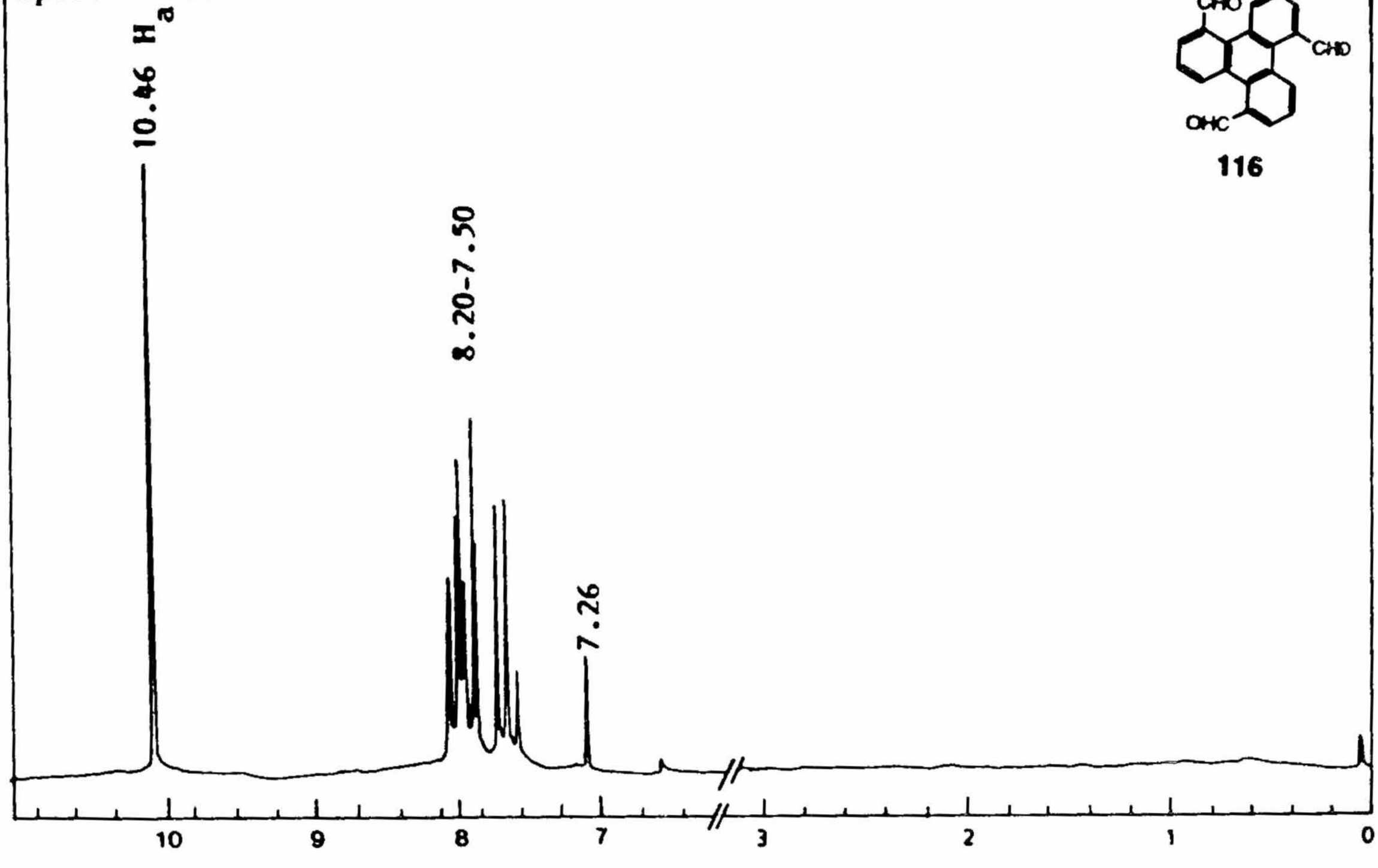
115



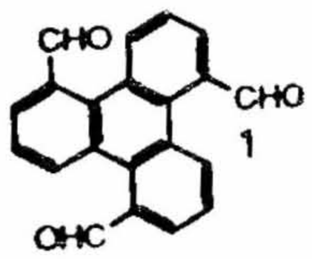
**Spectrum 33**



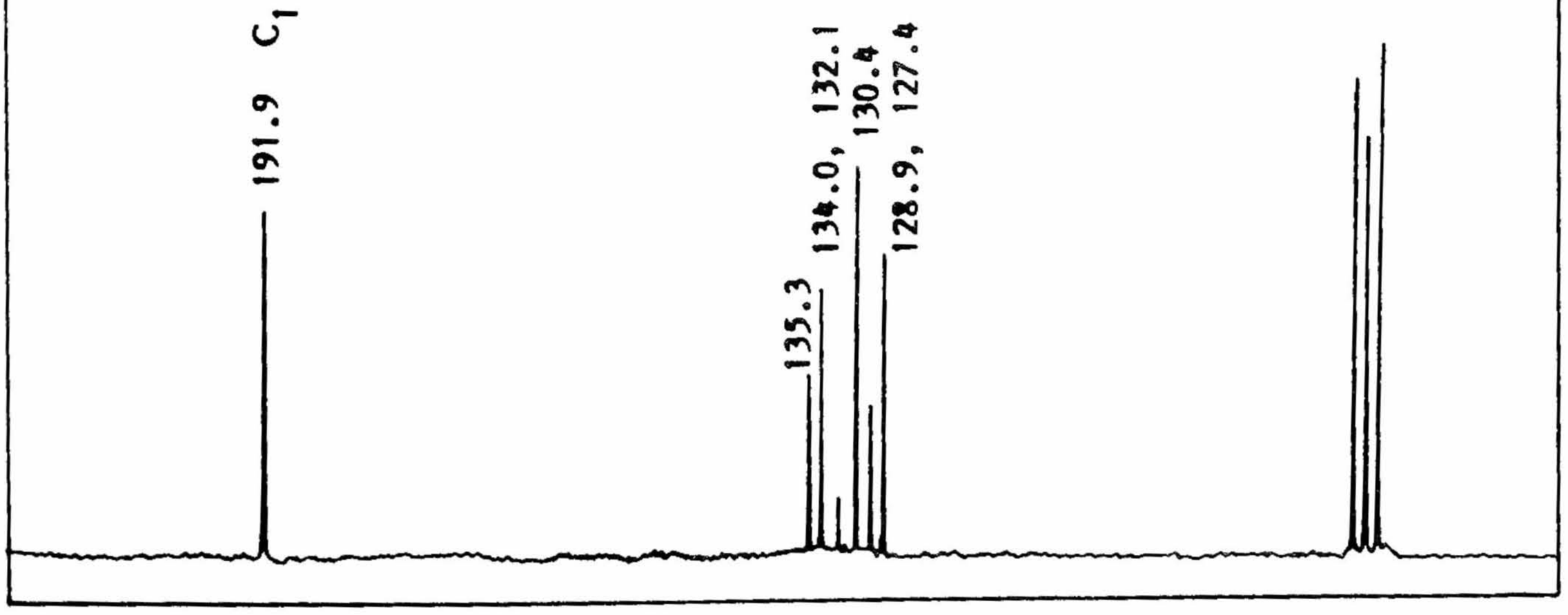

**116**




**Spectrum 34**



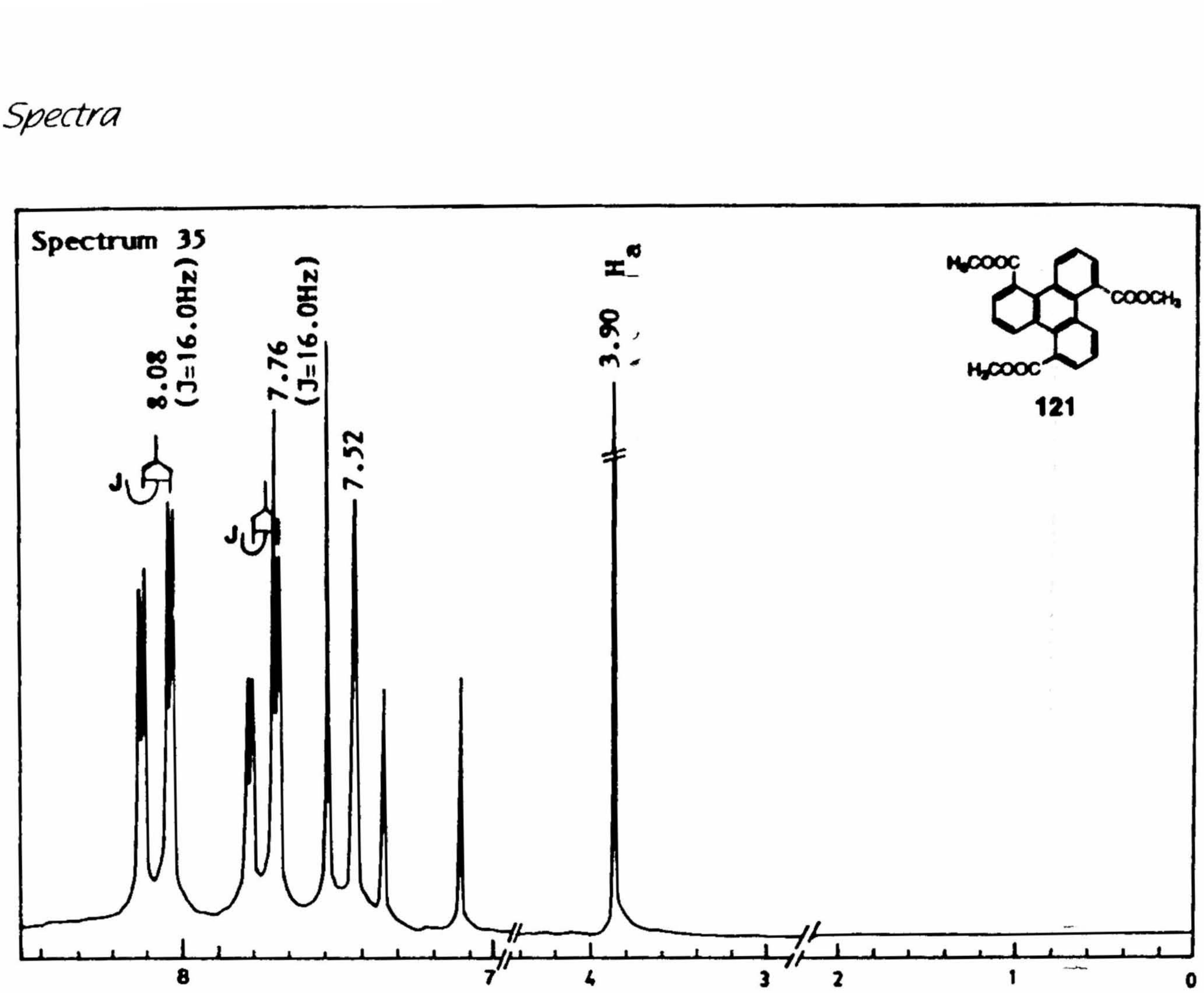

**116**



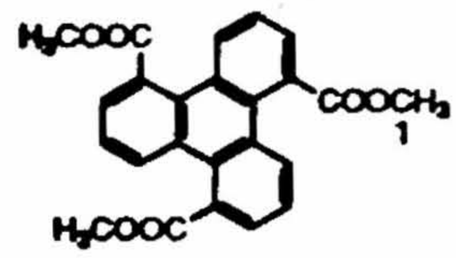
**Spectrum 35**



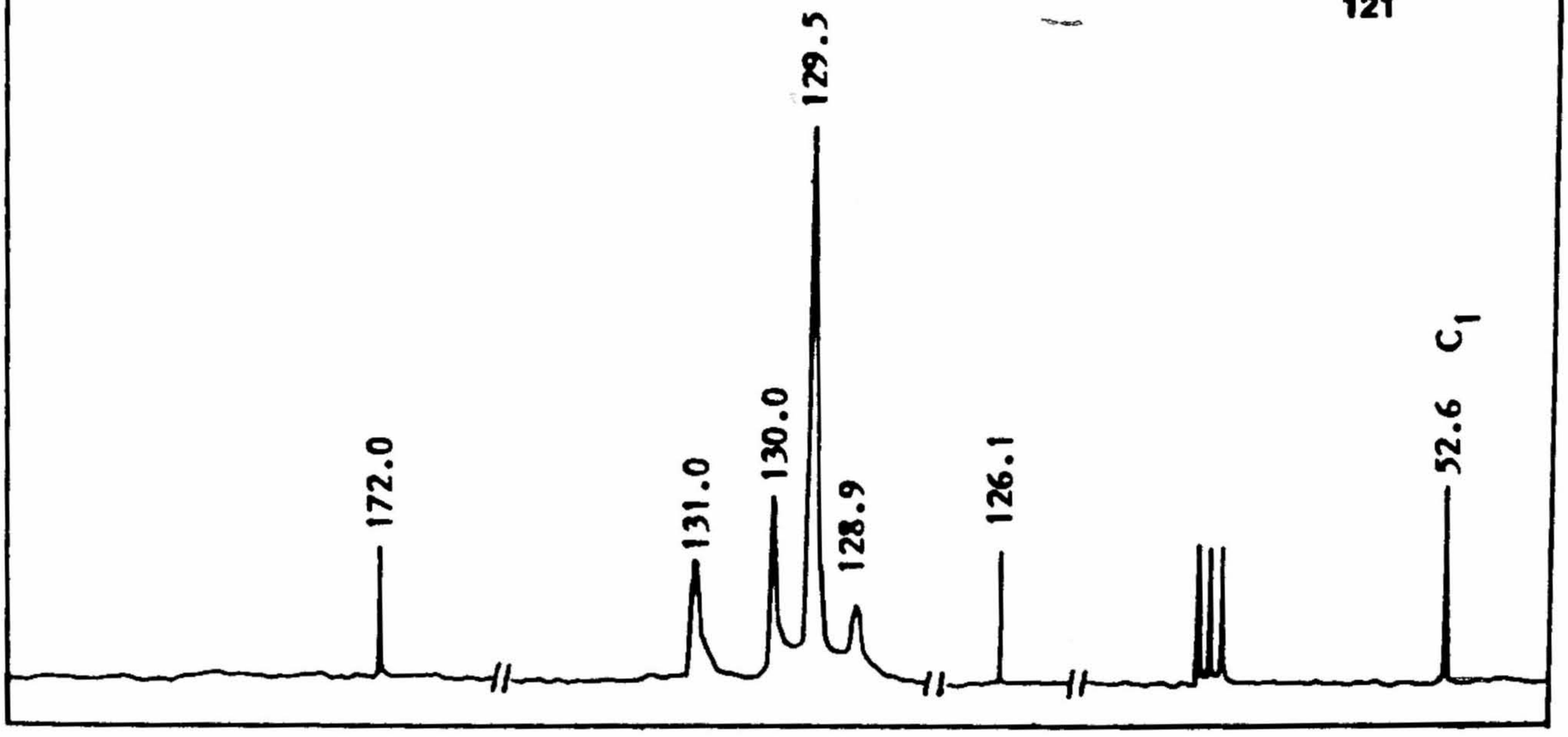

121



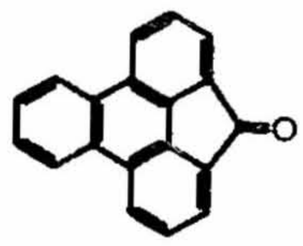

**Spectrum 36**



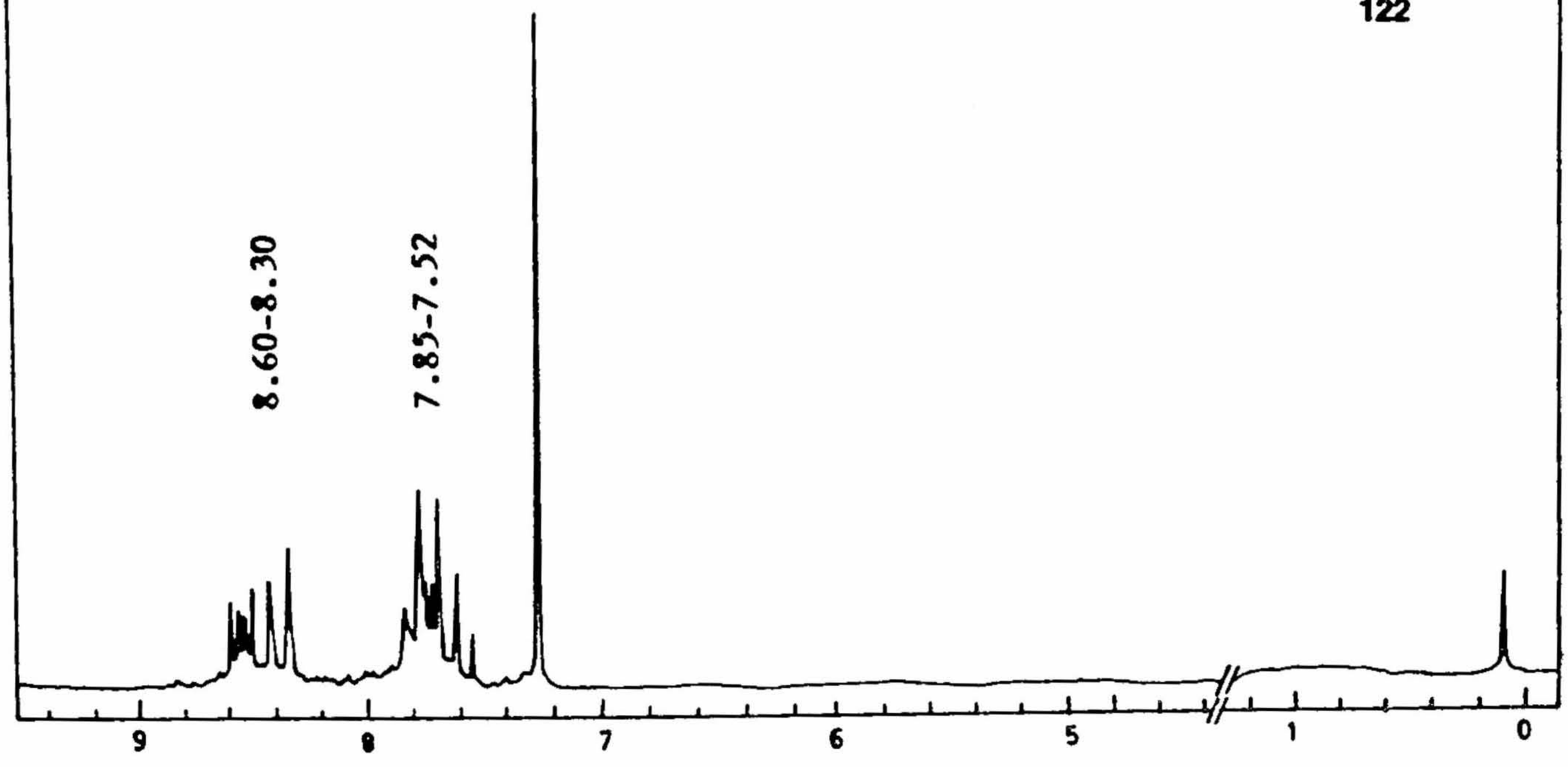

121



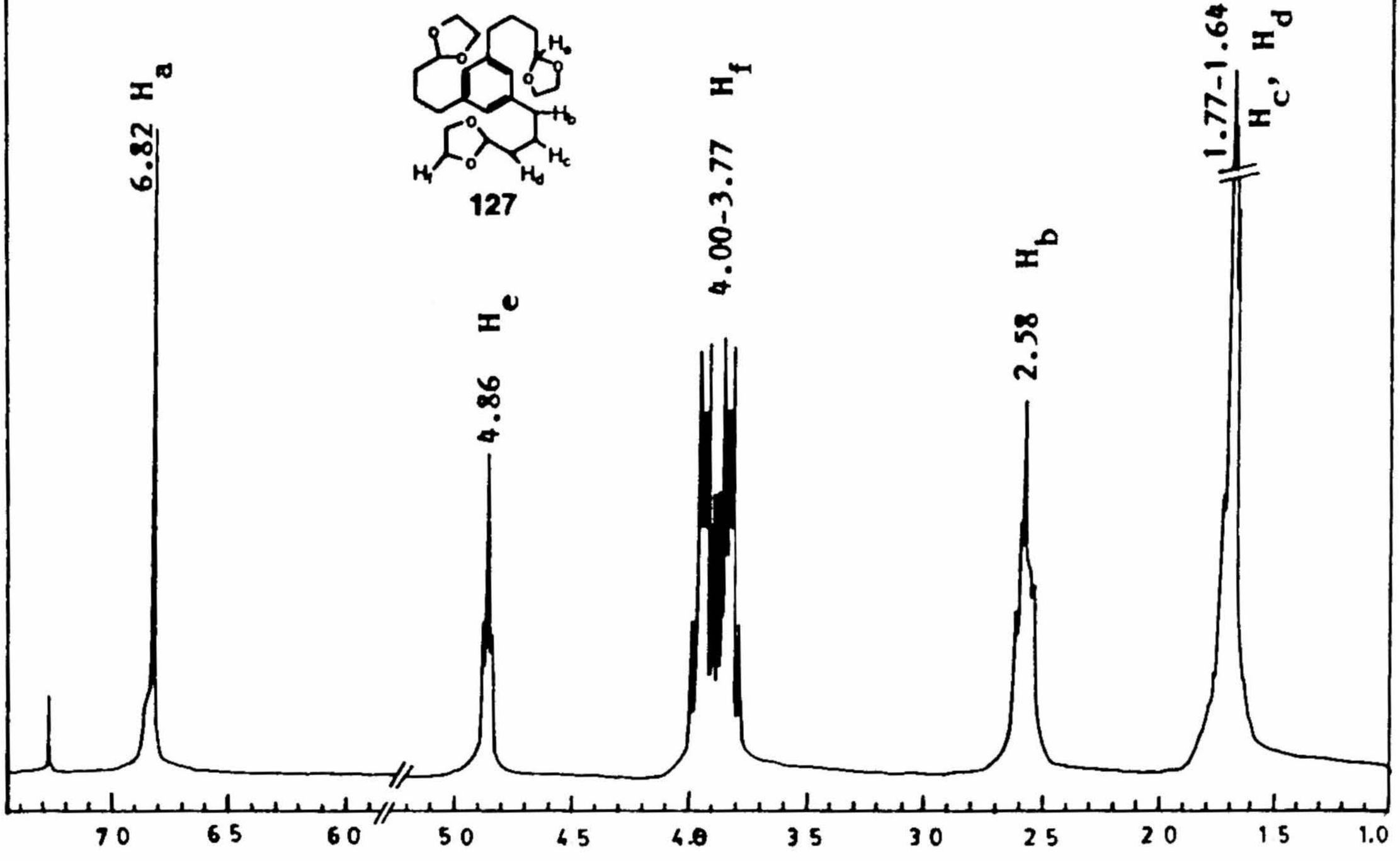
Spectrum 37



122

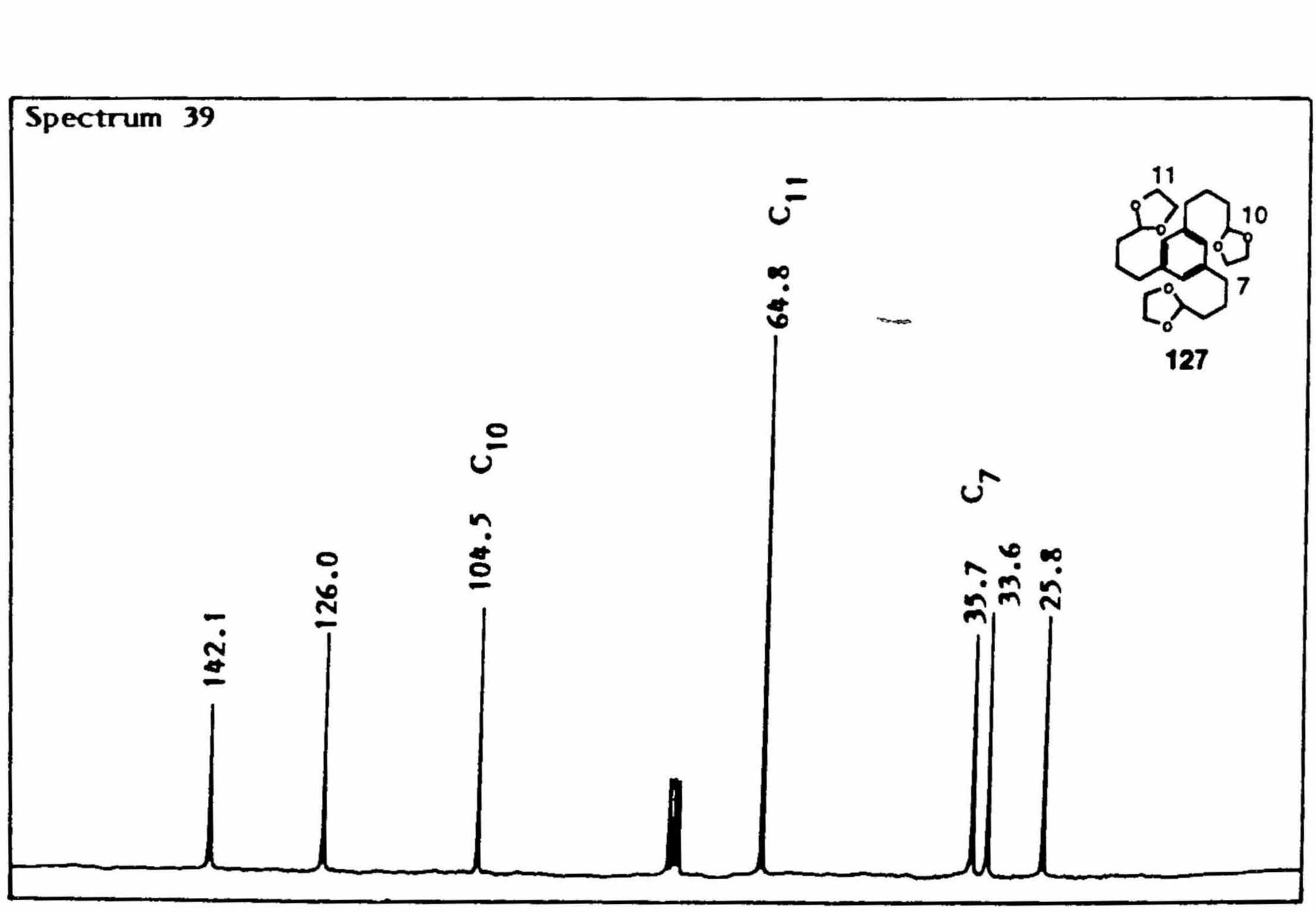


**Spectrum 38**



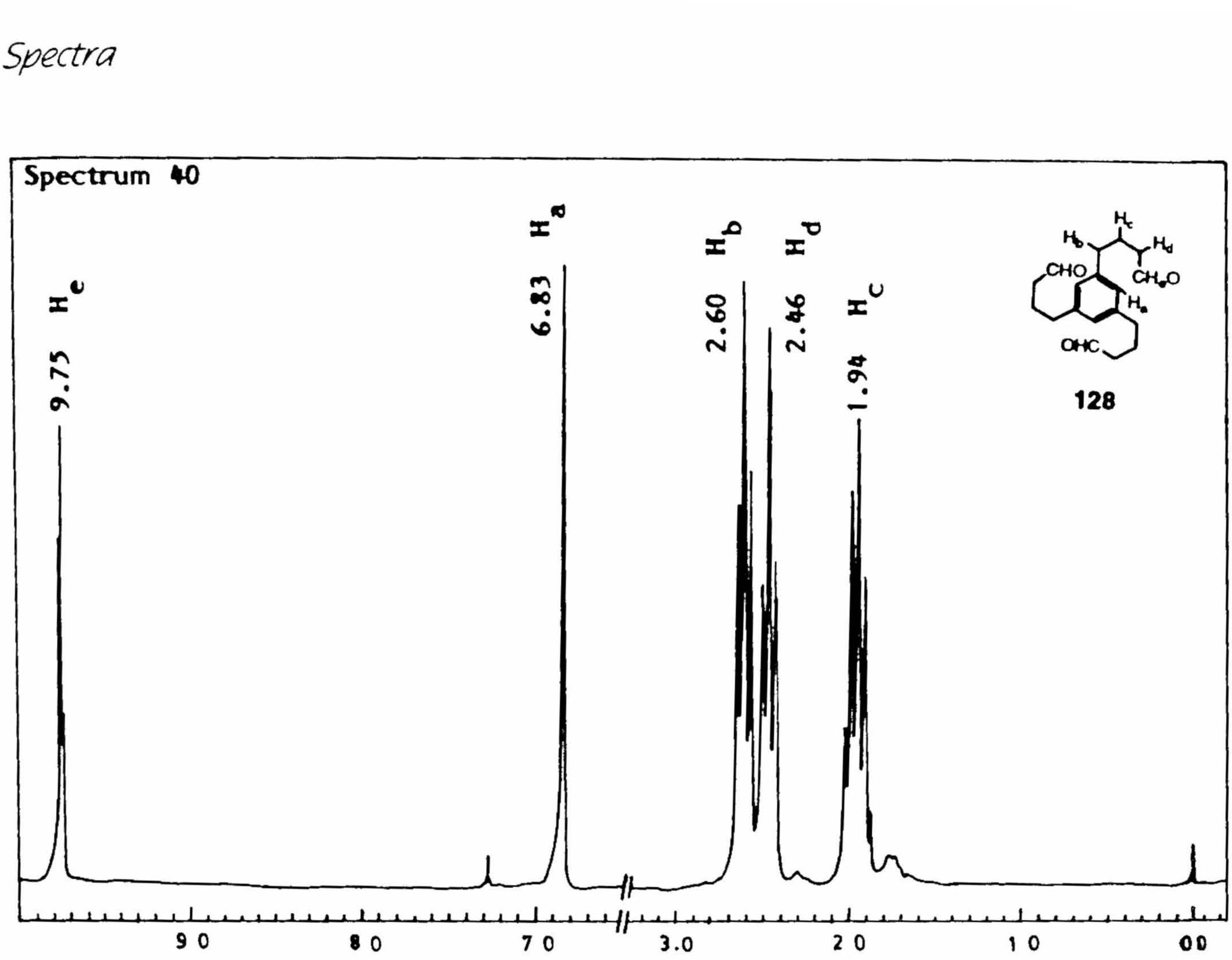

127

**Spectrum 39**




127

**Spectrum 40**

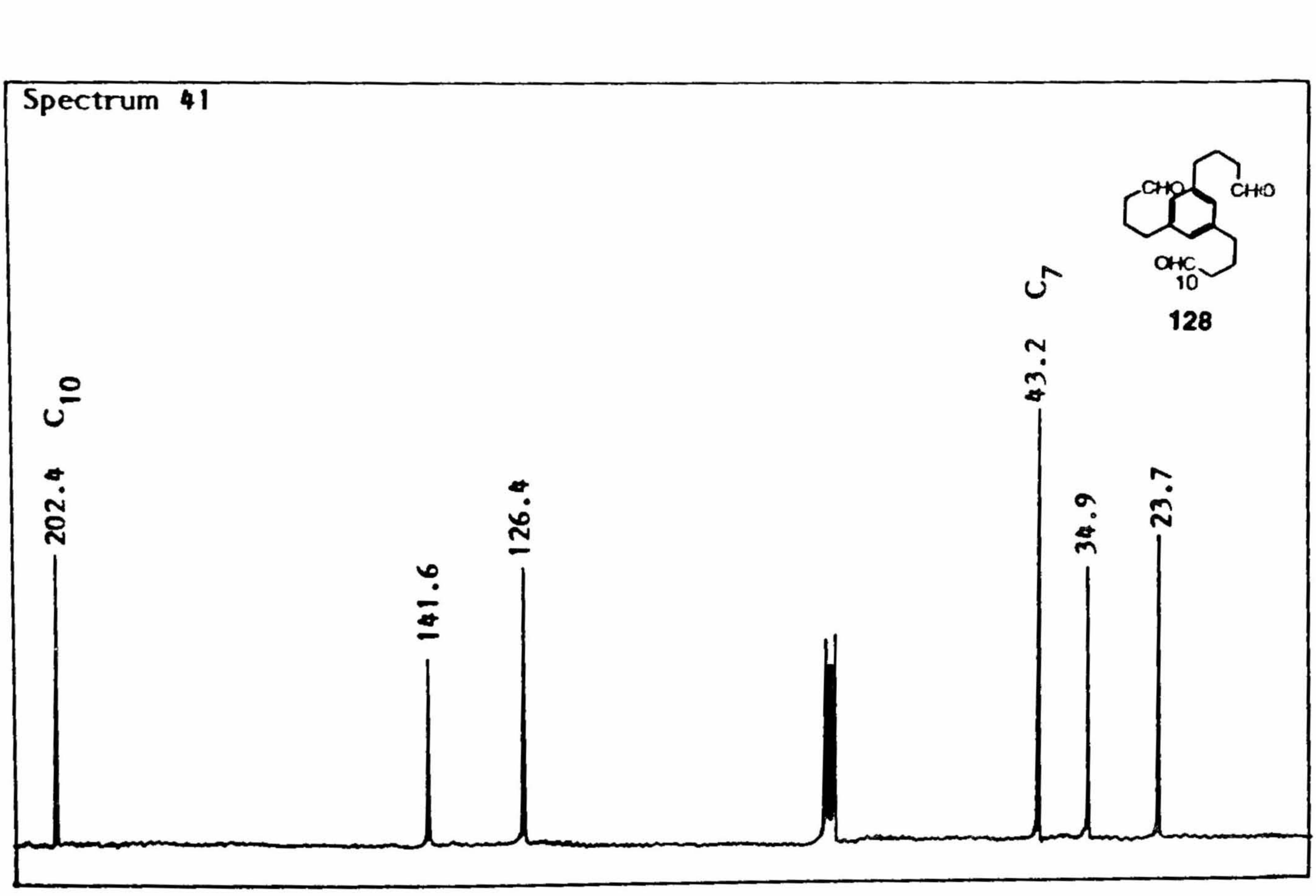






**128**

**Spectrum 41**

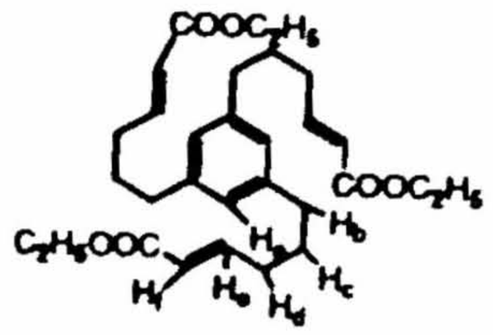




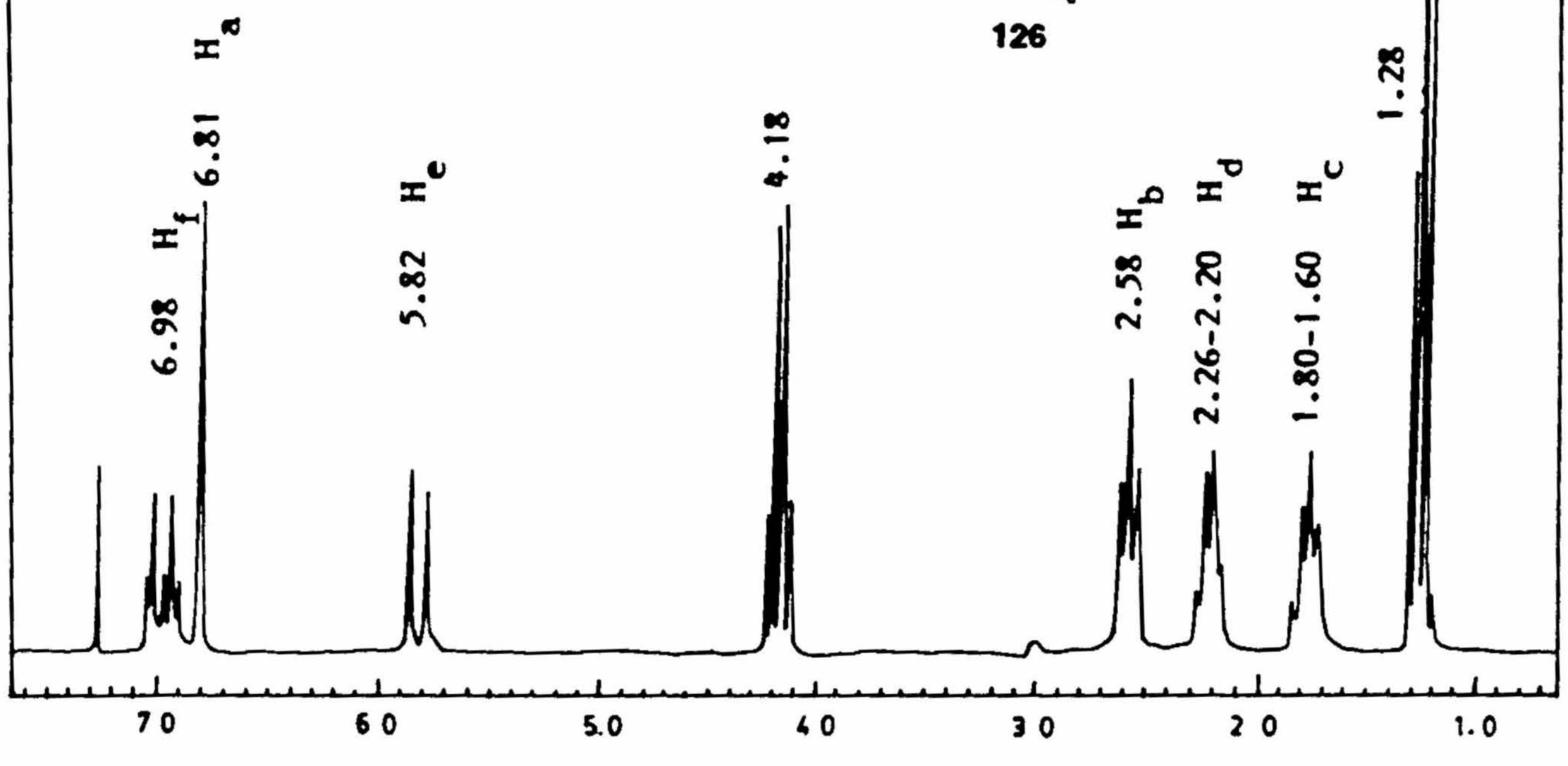


**128**

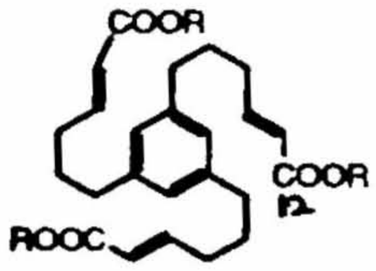
**Spectrum 42**



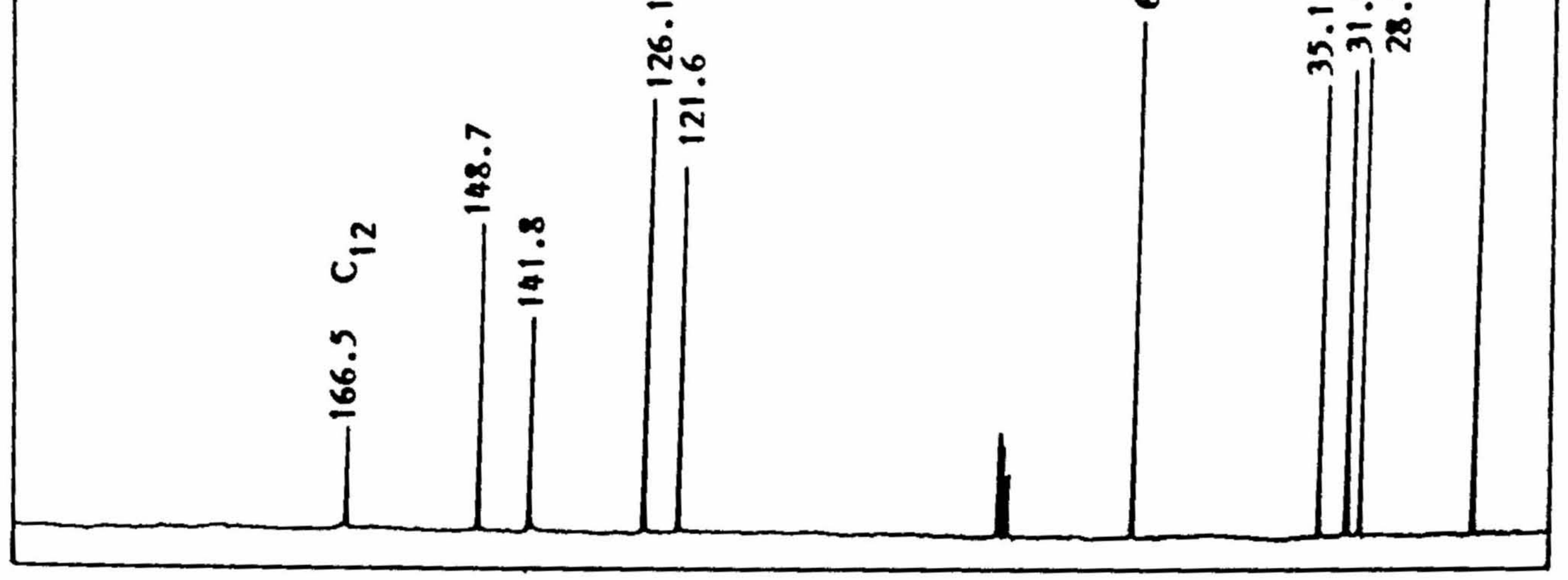

**126**




**Spectrum 43**




**126**




**160**

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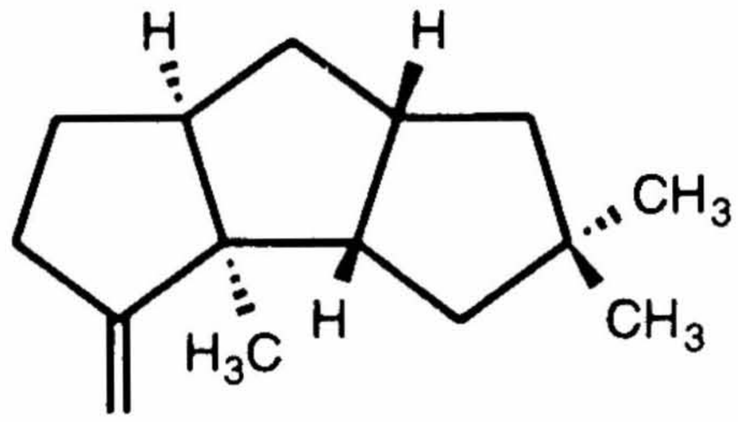
# Appendix

# A Synthetic Approach Towards Cedranoid Sesquiterpenes

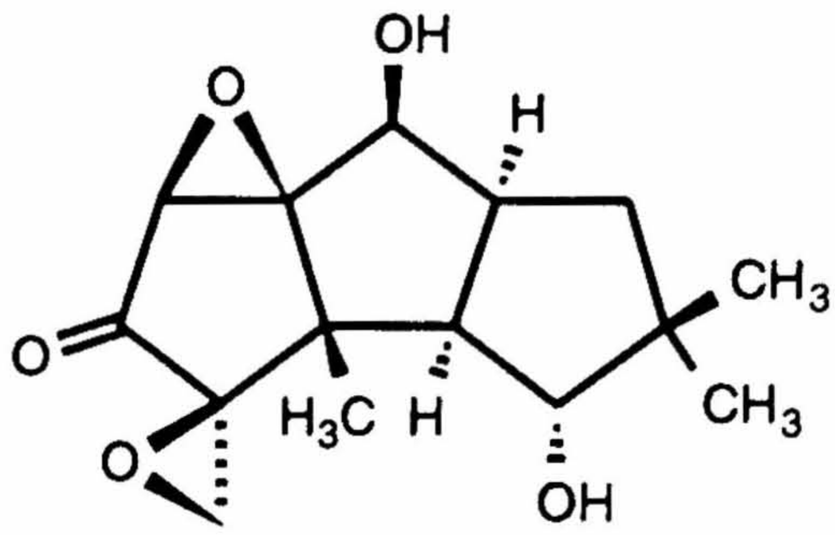
Terpenoids are among Nature's more versatile and exciting creations. In a remarkable display of synthetic ingenuity and creativity, Nature has endowed terpenes with a bewildering array of carbocyclic frameworks with unusual assemblage of rings and functionality. Because of this phenomenal structural diversity, this class of natural products hold special appeal to the synthetic chemists and provide a fertile ground for developing new synthetic strategies.

Sesquiterpenes, biogenetically derived from farnesyl pyrophosphate, are assembled in monocyclic, bicyclic, tricyclic and even tetracyclic structures containing small, medium and large rings with a wide range of functionalities.[1] Among these diverse carbocyclic assemblies those containing fused five-membered rings (generally referred to as polyquinanes) have received a great deal of attention.[1] In our research group, we have a long standing and on-going research interest in the synthesis of polyquinane natural products, Chart 1. These endeavors have culminated in the synthesis of linear triquinane bearing terpenes like (±)-hirsutene **1**[2], (±)-coriolin **2**[3], (±)-capnellene **3**[4], (-)-ceratopicanol **4**[5] and the framework of the diterpene crinipellin-A **9**.[6]

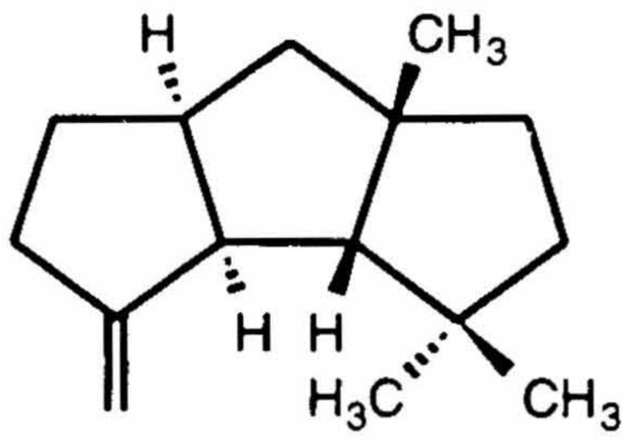
**Chart 1**



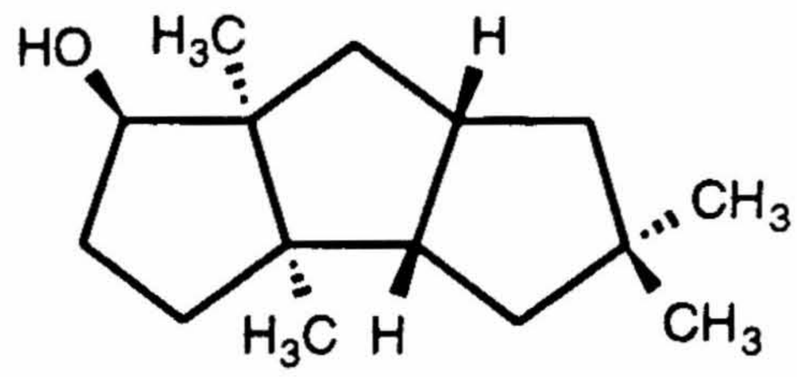
Hirsutene **1**



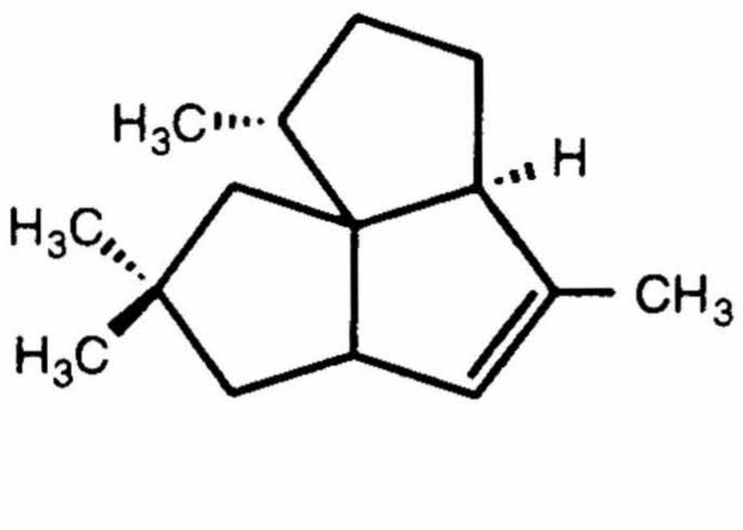
Coriolin **2**



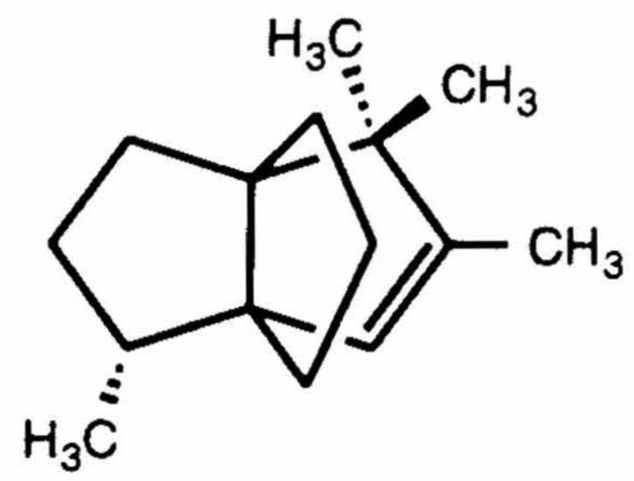
Capnellene **3**



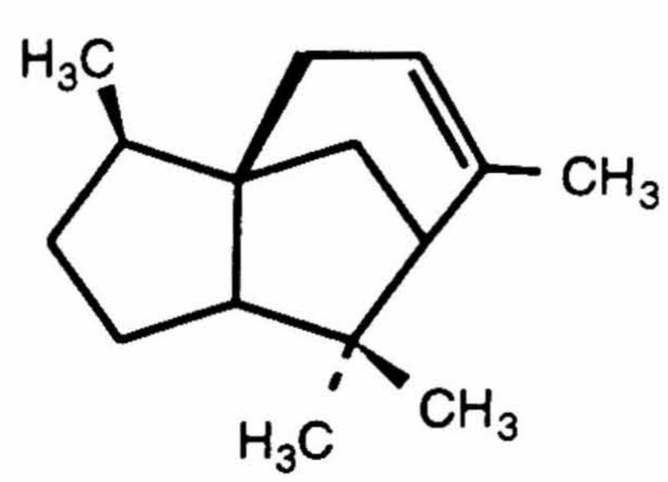
Ceratopicanol **4**



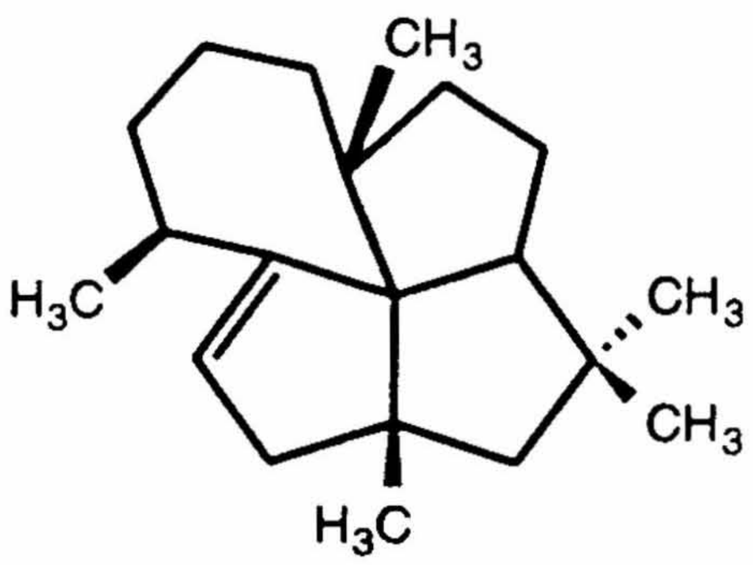
Pentalenene **5**



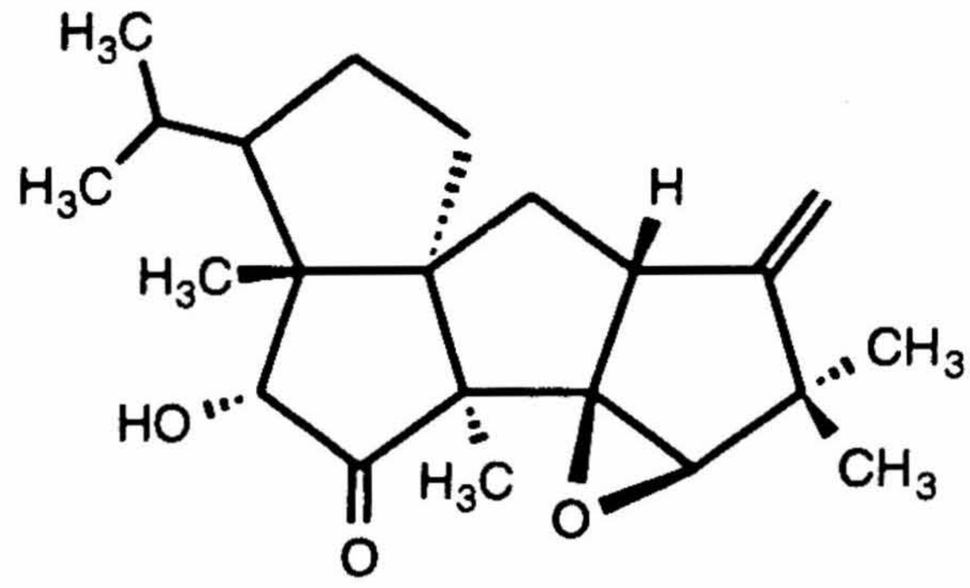
Modephene **6**



Cedrene **7**



Laurenene **8**

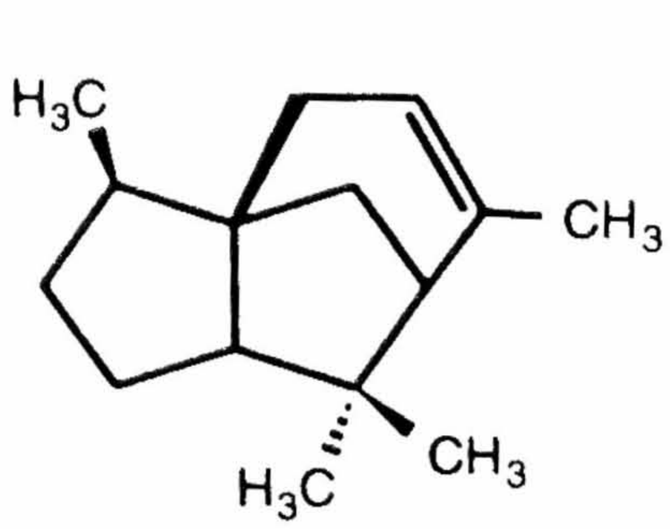


Crinipellin -A **9**

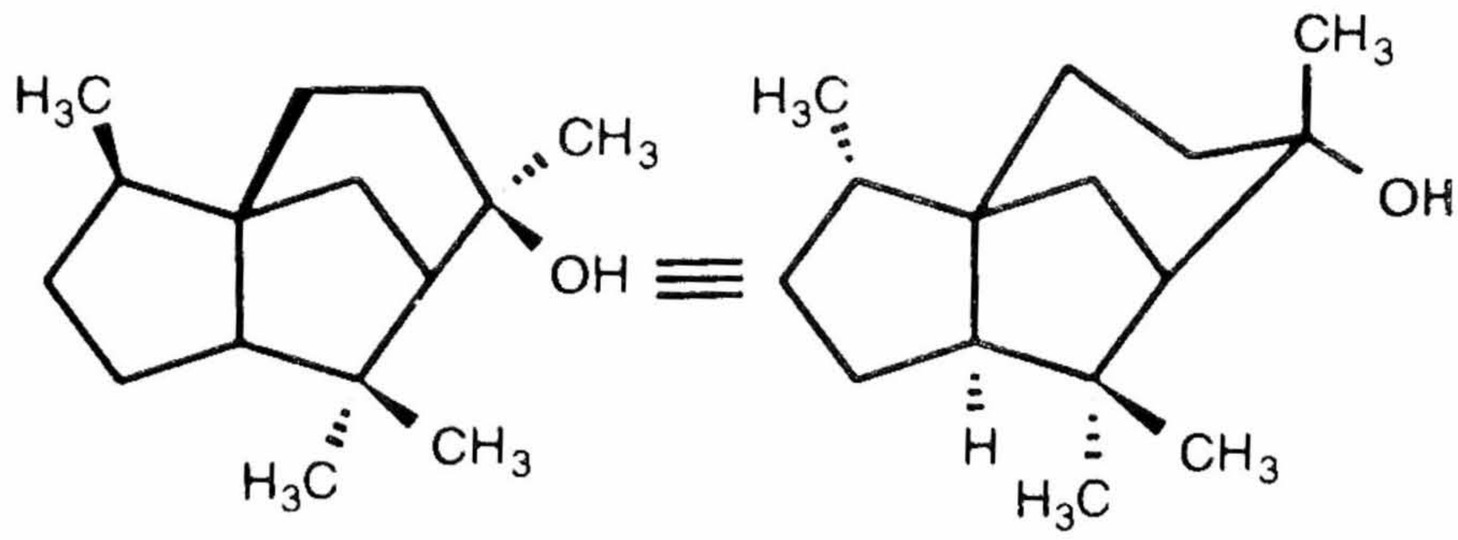
Concurrent efforts also led to the synthesis of the propellanic sesquiterpene (±)-modephene **6**.[7] In addition, transannular cyclization based strategies have been evolved for the synthesis of angular triquinane sesquiterpene (±)-pentalenene **5**[8] and the skeleton of diterpene laurenene **8**.[9]

In this context, our attention was drawn towards the tricyclic sesquiterpene hydrocarbon, cedrene **7** that co-occurs with cedrol **10** in the "cedar wood oil," the essential oil of several juniper species and possesses a diquinane based carbon skeleton, Chart 2 [10] The tricyclic framework of **7** and **10** has attracted the attention of many synthetic chemists Stork and Clarke were the first to achieve the synthesis of cedranoid sesquiterpenes[11] and their seminal synthesis has been

**Chart 2**




Cedrene **7**

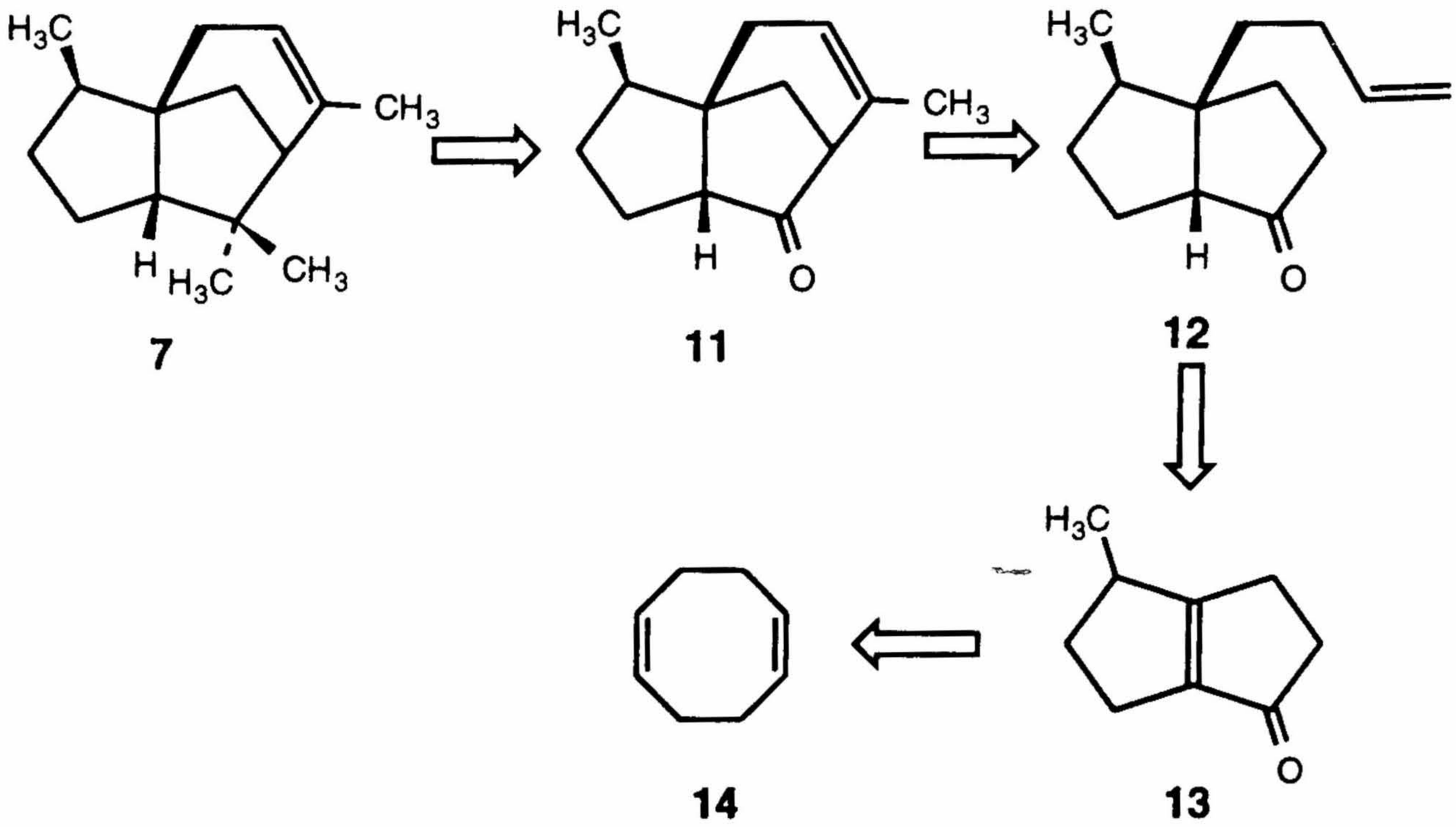



Cedrol **10**

followed by several other total syntheses of these interesting sesquiterpenes.[12]

We conceived a synthetic approach towards cedrene based on the following retrosynthetic logic starting from 1,5-cyclooctadiene **14**, a cheap, readily available starting material, Scheme 1. It was expected

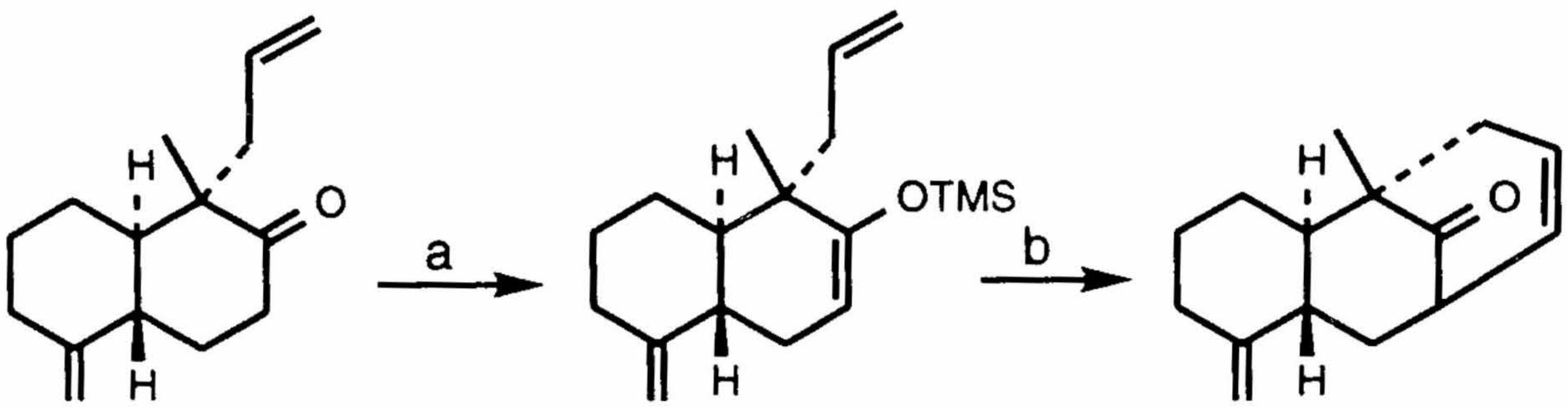
**Scheme 1**




that **14** could be transformed into the bicyclic enone **13** *via* transannular cyclization. Conjugate addition to **13** was expected to deliver the precursor **12** in which the key C-C bond was sought to be installed

through Kende cyclization.[13] Kende cyclization reaction involves Pd catalyzed cyclization of olefin to TMS enol ether to furnish key C-C bond. An example involving the cyclization of **15** → **16** is shown in Scheme 2. Once the tricyclic ketone **11** was formed, functional group transformations were expected to lead to cedrene **7**.

**Scheme 2**

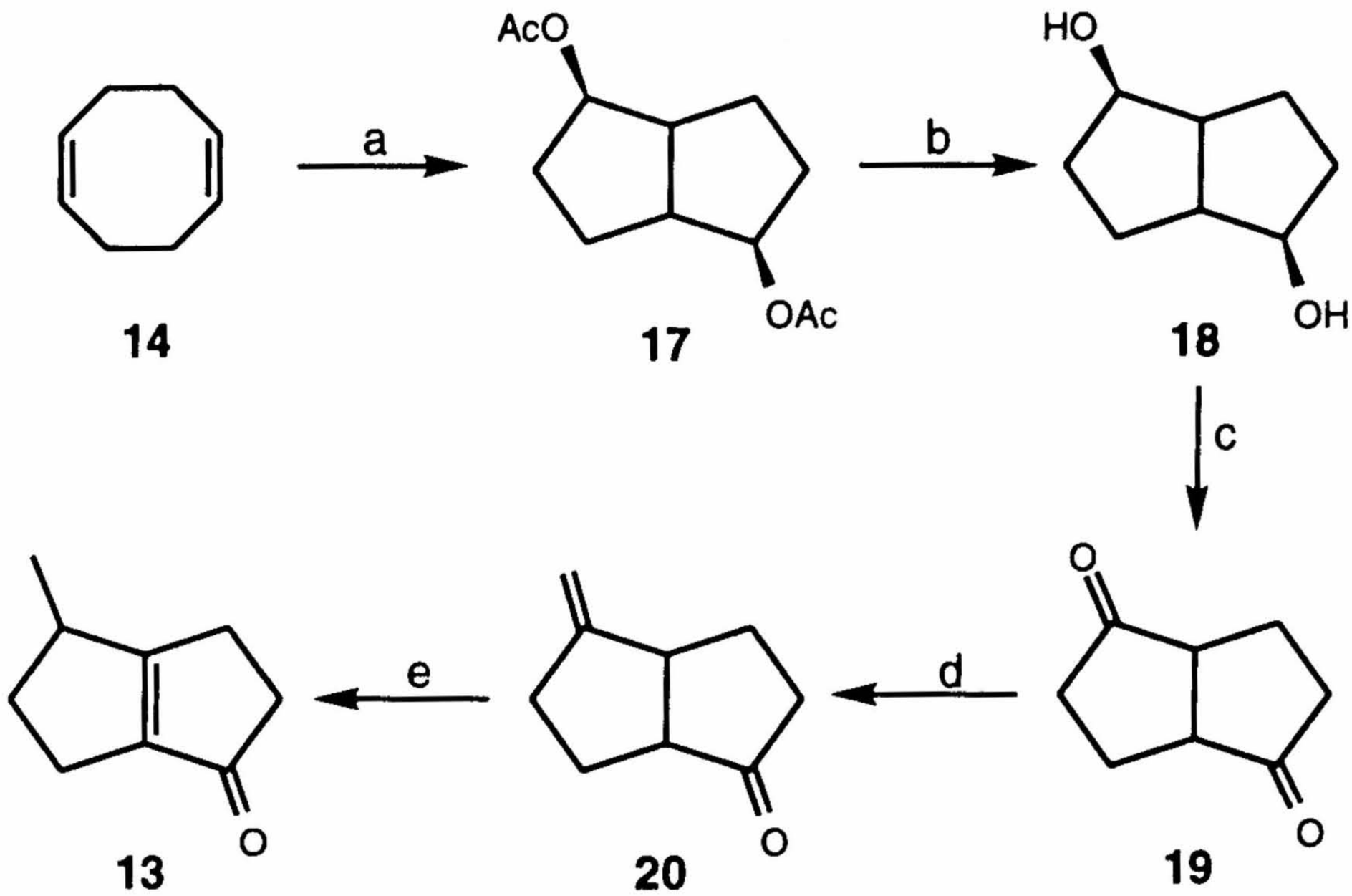



**15** **16**

**Reagents & Conditions**: a) LDA, -78°C → 0°C, TMS Chloride; b) $Pd(OAc)_2$, $CH_3CN$.

The bicyclo[3.3.0]octane-2,6-dione **19** was readily prepared from 1,5-cyclooctadiene **14**, Scheme 3. Treatment of 1,5-cyclooctadiene **14** with a mixture of $PdCl_2$, $Pb(OAc)_4$ in $CH_3COOH$ furnished the transannular cyclized product, the 2,6-diacetoxybicyclo[3.3.0]octane **17**.[14] The diacetate **17** was hydrolyzed with methanolic KOH to furnish the diol **18**.

## Scheme 3




**14** **17** **18** **19** **20** **13**

**Reagents, Conditions & Yields**: a) $Pb(OAc)_4$, $PdCl_2$, $CH_3COOH$, 30h, r.t.; b) Methanolic KOH, Δ, 6h; c) $Cr_2O_3/H_2SO_4$, acetone, 0°C (18% after 3 steps); d) $CH_3PPh_3^+ Br^-$, t-amyloxide, THF, 45%; e) p-TSA, Δ,$C_6H_6$, 75%.

Further oxidation of the diol with Jones reagent gave the diketone bicyclo[3.3.0]octane-2,6-dione **19**. The analytical and spectral data of the dione were in full agreement with the reported values.[15] The bicyclic dione **19** was converted to the enone **13** *via* selective mono-Wittig

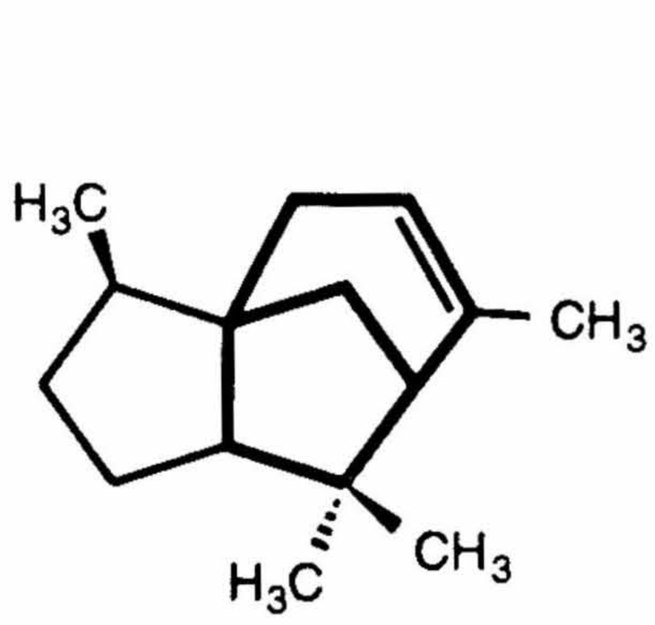
olefination and isomerization sequence. The dione was treated with one equivalent of methyltriphenylphosphonium bromide in the presence of t-amyloxide to obtain the mono-Wittig olefin **20**. The $^{1}H$ NMR resonance at δ 4.96 (singlet, 2H) and the $^{13}C$ NMR resonances at δ 155.1 and 106.3 indicated the presence of an olefinic moiety. The enone **20** was isomerized to 6-methyl bicyclo[3.3.0]oct-1-en-2-one **13** by treating it with p-toluenesulfonic acid in refluxing benzene. The analytical and spectral data of **13** confirmed its formulation.[12f] The $^{1}H$ NMR (Spectrum 1) resonance at δ 0.98 (doublet, 3H) indicated the presence of a secondary methyl group. The $^{13}C$ NMR (Spectrum 2) resonances at δ 204.3, 190.7 and 147.4 clearly showed the presence of a keto group and olefinic functionality. Thus, the bicyclic enone **13** is available in a short sequence from readily and cheaply available 1,5-cyclooctadiene **14**, Scheme 3.

The next step towards the creation of cedrene framework was the construction of the six-membered ring, utilizing the enone moiety. This represents the bicyclo[3.2.1]octane moiety present in cedrene and in many diverse terpenes like stemodin **21**[16] and quadrone **22**[17] possesing novel polycarbocyclic frameworks, Chart 3. Several interesting strategies

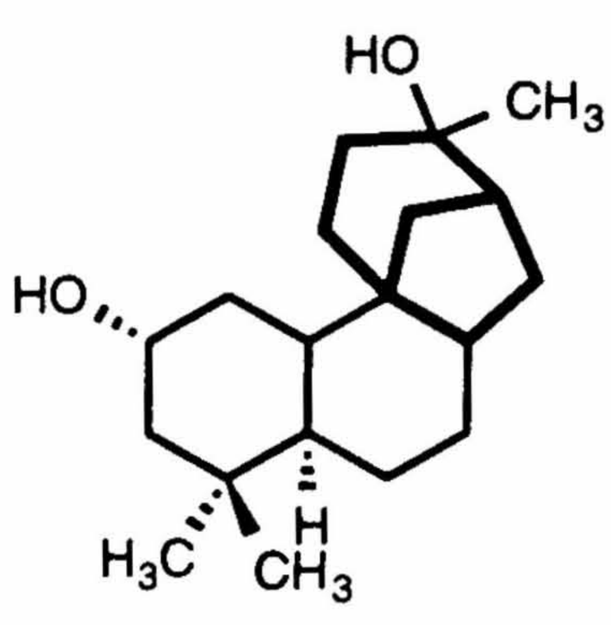
have been devised for the construction of bicylco[3.2.1]octane substructure present in these and other related natural products.

Kende *et al.*, have shown that trimethylsilyl enol ether derivatives of variety of cyclopentanone and hexanones bearing unsaturated side chains α or γ to the carbonyl group can be converted to bridged and spiro-cyclic systems through $Pd^{+2}$ promoted intramolecular cycloalkenylation.[13] This reaction appeared quite suitable for the construction of bicyclo[3.2.1]moiety in the context of our cedrene synthesis.

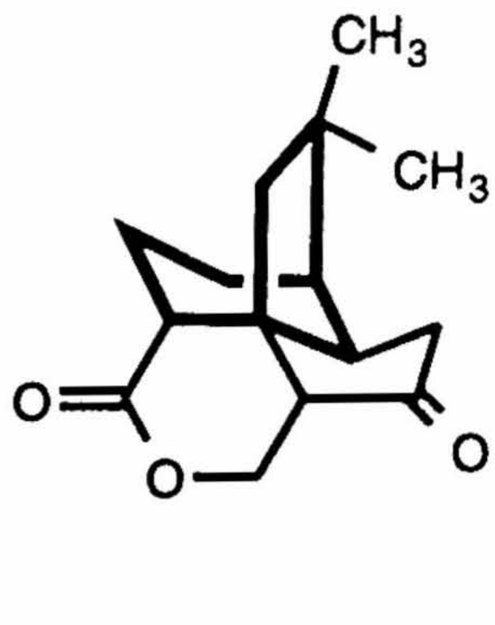
**Chart 3**




Cedrene **7**




Stemodin **21**

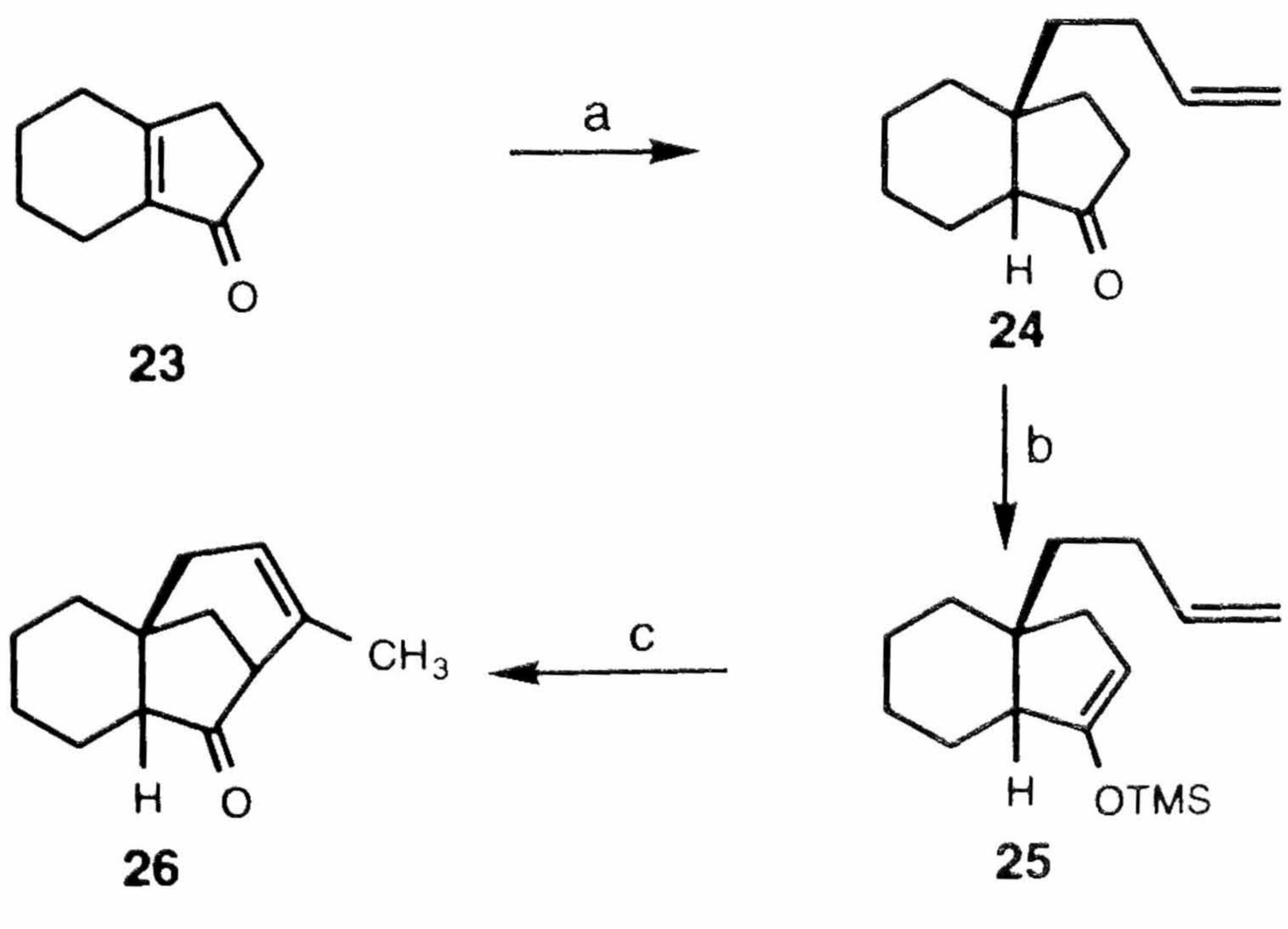



Quadrone **22**

Before, we attempted the Kende-type cyclization for the construction of cedranoid skeleton, we did a model study on

bicyclo[4.3.0]nona-1,5-en-2-one **23**[18], Scheme 4. The keto-olefin required for the study was prepared by conjugate addition of Grignard reagent prepared from 4-bromo-1-butene to bicyclic enone **23**, in the presence of dimethylsulfide-copper complex and $BF_3$-etherate, to furnish the 1,4-addition product **24** in 70% yield. The $^1H$ NMR (Spectrum 3) resonances at δ 5.88 (multiplet, 1H), at δ 5 15 (multiplet, 2H) indicated the presence

**Scheme 4**



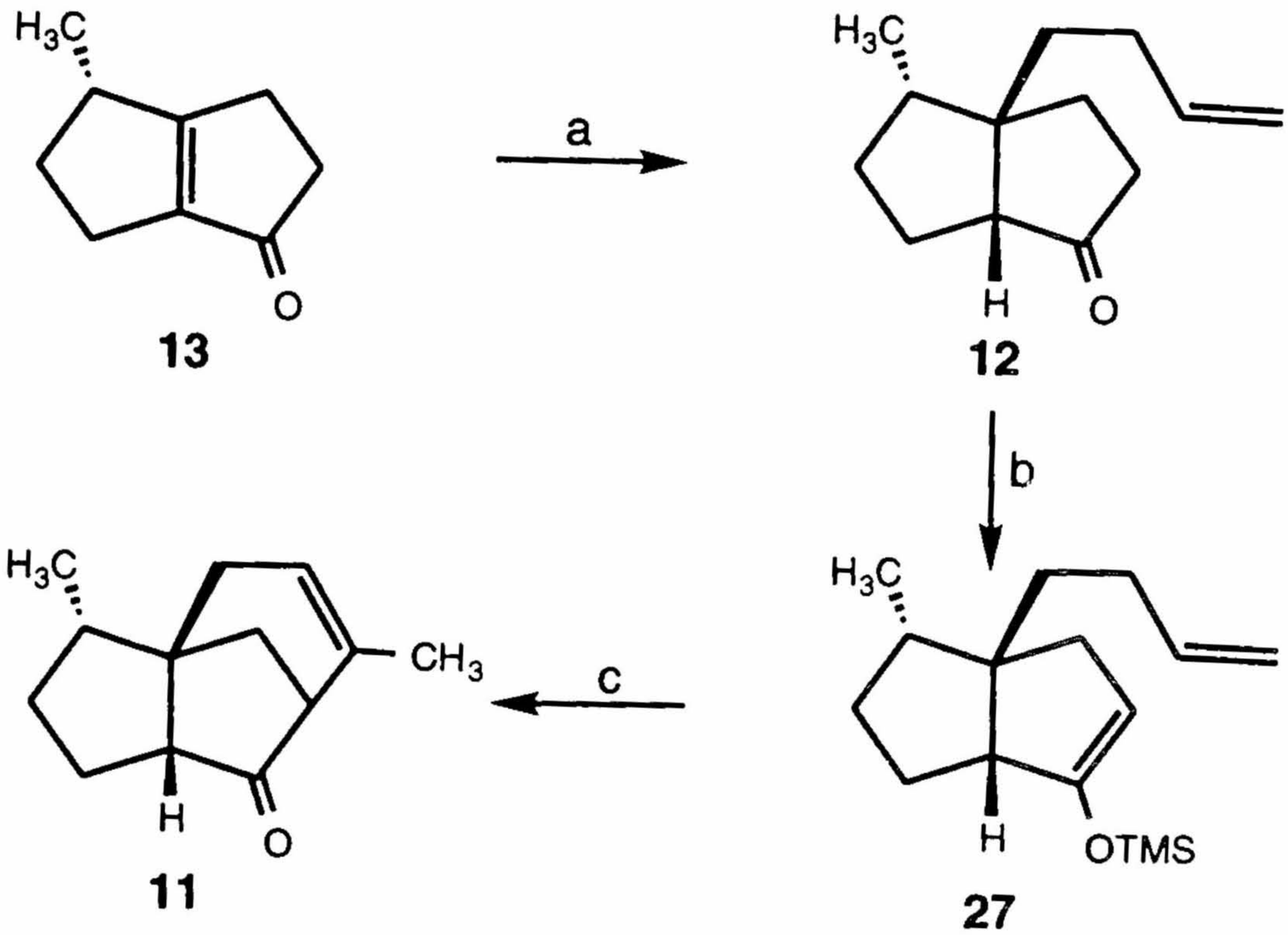

**23** **24** **25** **26**

**Reagents, Conditions & Yields:** a) 4-bromo-1-butene, $Me_2S$ CuBr, -78°C → r t , $BF_3$ $OEt_2$, 70%, b) LHMDS, TMSCl, -78°C → r t , c) $Pd(OAc)_2$, $CH_3CN$, r t , 52%

of terminal olefinic moiety. The 13 line $^{13}C$ NMR spectrum clearly indicated the conjugate 1,4-addition of butenyl side chain to the enone **23** (Spectrum 4). Kinetically controlled deprotonation of **24** and quenching of the enolate with chlorotrimethylsilane furnished the labile TMS-enol ether **25**. The crude TMS-ether was treated with $Pd(OAc)_2$ in acetonitrile under Saegusa-Kende conditions[19] to yield the tricyclic skeleton **26** in 50% yield, Scheme 4. The $^1H$ NMR (Spectrum 5) resonances at δ 5.36 (brs, 1H) and at δ 1.72 (singlet) showed the presence of a trisubstituted olefin bearing a methyl group. In addition the $^{13}C$ NMR (Spectrum 6) exhibited the expected 13 lines with three $sp^2$ carbon resonances at δ 215.9, 134.0 and 122.4. Thus, the structural moiety present in stemodin **21** was easily accessible in just two steps from bicyclic enone **23**, Scheme 4.

Encouraged by the ready preparation of bicyclo[3.2.1]moiety *via* a straightforward two step sequence, we ventured to apply this theme to the synthesis of the cedrene skeleton from bicyclic enone **13**, Scheme 5. Consequently, conjugate addition of the Grignard reagent prepared from 4-bromo-1-butene to the bicyclic enone **13** in the presence of $Cu(I)$-$Me_2S$

## Scheme 5



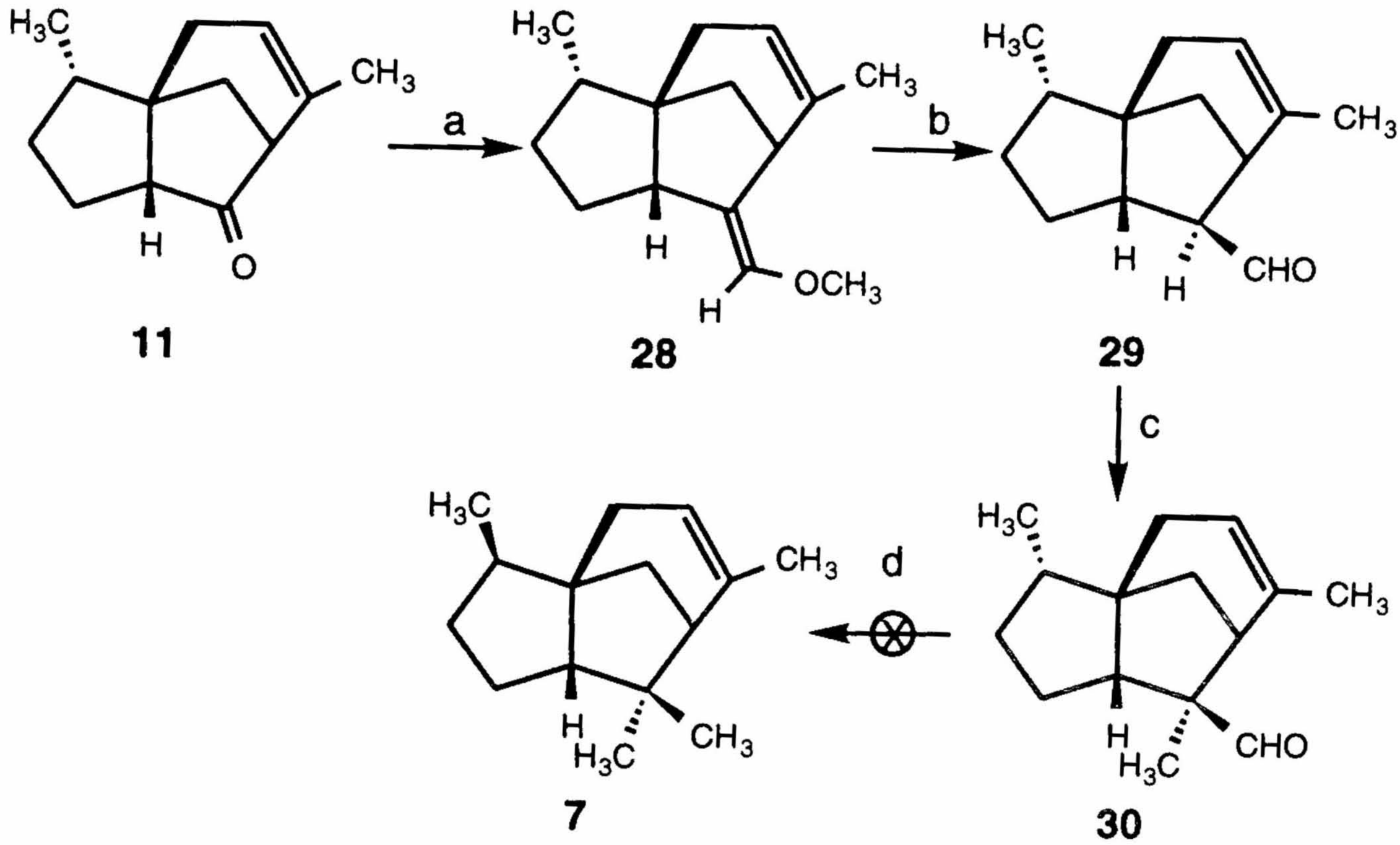

**Reagents, Conditions & Yields:** a) 4-bromo-1-butene, $Me_2S.CuBr$, THF, DMS, -78°C → r.t., $BF_3.OEt_2$, 72%; b) LHMDS, TMSCl, THF, -78°C → r.t.; c) $Pd(OAc)_2$, $CH_3CN$, r.t., 52%.

complex and $BF_3$-etherate furnished the 1,4-addition compound **12** as a single diastereomer in 72% yield. The $^1H$ NMR resonances at δ 5.80 (multiplet, 1H) and at δ 4.98 (multiplet, 2H) indicated the presence of the olefinic side chain and a signal at δ 0.96 (doublet, 3H) showed the presence of a secondary methyl group (Spectrum 7). The 13 line $^{13}C$

NMR spectrum clearly showed the addition of butenyl side chain (Spectrum 8). Kinetically controlled deprotonation in **12** and quenching of the enolate with trimethylchlorosilane furnished the TMS-enol ether **27**, which was directly subjected to reaction with $Pd(OAc)_2$ in acetonitrile under the standard Saegusa-Kende conditions to furnish tricyclic ketone **11**. The structure of **11** was in full agreement with its analytical and spectral data. The $^1H$ NMR (Spectrum 9) resonaces at δ 5.46 (multiplet, 1H) and δ 1.76 (singlet, 1H) indicated the presence of trisubstituted olefinic moiety. In addition, the $^{13}C$ NMR spectrum (Spectrum 10) exhibited the expected 13 lines, with three $sp^2$ carbon resonances at δ 216.2, 134.3 and 123.3, Scheme 5.

The tricyclic ketone **11** bearing the framework of cedranoid sesquiterpenes was thus accessible in just three steps from the readily available bicyclic enone **13**. To complete the synthesis, we now needed to convert the keto group to a gem-dimethyl group. For this purpose, the keto group in **11** was converted to the aldehyde group (Scheme 6) *via* one carbon Wittig homologation protocol. The tricyclic ketone **11** was treated with methoxymethyltriphenylphosphonium chloride in the presence of

## Scheme 6




11 28 29

7 30

**Reagents, Conditions & Yields:** a) $(OCH_3)CH_2PPh_3^+$ $Br^-$, t-amyloxide, ether, 0°C; b) 35% $HClO_4$, ether, 57%; c) KH, $CH_3I$, THF, 40%; d) $NH_2$-$NH_2$, Na, digol,

sodium-t-amyloxide to furnish a mixture of (E) and (Z) enol ethers **28** which was directly hydrolyzed with 35% $HClO_4$ to yield the tricyclic aldehyde **29**. The $^1H$ NMR resonances at δ 9.64 (singlet, 1H) showed the presence of aldehyde group and the resonances at δ 5.32 (singlet, 1H)and δ 1.64 (singlet, 3H) showed the presence of methyl group on the olefinic

moiety (Spectrum 11). The 14 line $^{13}C$ NMR spectrum confirmed the addition of one carbon to the tricyclic ketone **11** (Spectrum 12). Alkylation of **29** with potassium hydride and methyl iodide furnished the alkylated product **30**. The $^{1}H$ NMR spectrum showed the presence of a quaternary methyl group. Thus, the $C_{15}$ framework of cedranoid sesquiterpenes was attained.

Completion of the synthesis of cedrene required reductive deoxygenation of the aldehyde functionality in **30** to yield **7**. However, all our attempts to convert the aldehyde group in **30** to methyl group by Wolf-Kishner reduction[20] and other methods were unsuccessful.

**Summary**:

In summary, a facile and short route to polycyclic frameworks, embodying the bicyclo[3.2.1]octane moiety, annulated at the bridgehead position, through the $Pd^{+2}$ catalyzed cyclization of β-alkenylated cyclopentanone trimethylsilyl enol ethers is described.[21] This methodology was applied for the synthesis of the cedranoid sesquiterpene skeleton. It was also shown that the structural moiety present in stemodin diterpenes can be prepared in a short sequence.

**Experimental**:

For general write-up, see Section IV.

**2,6-Diacetoxy bicyclo[3.3.0]octane (17):**[14]

1,5-Cyclooctadiene **14** (10 g, 0.09 mol) was treated with $PdCl_2$ (655 mg, 3.70 mol, 0.04 mol equiv.) in the presence of leadtetraacetate (40 g, 100 ml of acetic acid, 1M) at room temperature for 40 h. The reaction mixture was poured into ice-cold water and extracted with hexane. The hexane layer was carefully neutralized with $NaHCO_3$, washed with water, brine, dried and concentrated under reduced pressure to give the diacetoxy compound **17** (15 g, 70% yield) and used as such for the next reaction.

IR (neat) : 2970, 1720, 1370, 1240, 1060, 1030 $cm^{-1}$

**2,6-Dihydroxy bicyclo[3.3.0]octane (18):**

The crude diacetate **17** (15 g) was dissolved in 40 ml of methanol. To this, 50 ml of 20% methanolic KOH was added and the reaction

mixture was stirred at room temperature for 20 h After completion of the hydrolysis, methanol was removed under reduced pressure, diluted with water and extracted with ether The ethereal layer was washed with dil HCl, water, brine and dried Removal of solvent furnished the crude diol, 2,6-dihydroxybicyclo[3 3 0]octane **18** (5 6 g, 60% yield) as a yellow oil and was used as such for the next step

IR (neat) 3300, 2950, 1050, 1010, 900 $cm^{-1}$

**Bicyclo[3.3.0]octane-2,6-dione (19):**[15]

The diol **18** (6 g, 0 04 mol) dissolved in acetone (distilled over $KMnO_4$) was maintained at 0 °C and Jones reagent was added dropwise with stirring The reagent was added till the colour of the reagent persisted The reaction mixture was allowed to stir at 0 °C for further 30 min and the precipitated chromium salts were filtered off Acetone was removed under reduced pressure, diluted with water and extracted with ether The ethereal layer was washed with dil HCl, water, $NaHCO_3$, brine and dried Removal of solvent furnished the diketone and was charged on a silica gel column Elution with 10% ethyl acetate-hexane

furnished the diketone, bicyclo[3.3.0]octane-2,6-dione **19** (2.3 g, 40% yield) as a yellow oil which was solidified by keeping it in the refrigerator.

IR (neat) : 2950, 1720, 1420, 1170, 1110 $cm^{-1}$

$^{1}H$ NMR : δ 2.84 (br s, 2H), 2.26 - 2.00 (m, 8H)

$^{13}C$ NMR : δ 220.5, 49.4, 37.5, 22.9.

**Bicyclo[3.3.0]oct-6-methylene-2-one (20):**

To a suspension of methyl triphenylphosphonium bromide (9.3 g, 0.026 mol) in 50 ml of dry benzene was added sodium t-amyl oxide (2.86 g, 0.026 mol) in 5 ml of dry benzene and the resulting yellow coloured ylide was stirred at room temperature for 30 min. The diketone **19** (3.0 g, 0.021 mol) was added to the ylide in 10 ml of dry benzene and the reaction mixture was allowed to stir for further 1h. The reaction mixture was quenched with brine and extracted with ether. The ethereal layer was washed with dil. HCl, water, brine and dried. Removal of solvent furnished the crude material which was charged on a silica gel column and elution with 10% ethyl acetate-hexane furnished the mono-

Wittig product, bicyclo[3.3.0]octa-6-methylene-2-one **20** (1.6 g, 55% yield) as a viscous liquid.

IR (neat) : 3050, 1735, 1650, 890 $cm^{-1}$

$^{1}H$ NMR : δ 4.96 (s, 2H), 3.32 - 3.04 (br s, 1H), 2.76 - 2.46 (m, 1H), 2.40 - 1.84 (series of m, 8H)

$^{13}C$ NMR : δ 222.2, 155.1, 106.3, 52.7, 45.5, 37.3, 32.9, 27.4, 27.0

**6-Methyl bicyclo[3.3.0]oct-1-en-2-one (13):**[12f]

A solution of bicyclo[3.3.0]oct-6-methylene-2-one **20** (1.6 g, 11.76 mmol) in 50 ml of dry benzene and a catalytic amount of p-toluene sulphonic acid was refluxed under nitrogen atmosphere using a Dean-Stark apparatus for 4 h. The reaction mixture was quenched with brine and extracted with ether. The ethereal layer was washed with $NaHCO_3$, water, brine and dried. The resulting crude material, after removing the solvent was charged on a silica gel column and elution with 15% ethyl acetate-hexane furnished the bicyclic enone, 6-methyl bicyclo[3.3.0]oct-1-en-2-one **13** (1.0 g, 62% yield) as a viscous liquid.

IR (neat) : 2925, 1680, 1630, 1010 $cm^{-1}$

$^1H$ NMR : δ 2.84 - 2.64 (m, 2H), 2.60 - 2.40 (m, 4H), 2.00 -

(Spectrum 1) 1.80 (m, 1H), 1.75 - 1.50 (m, 2H), 0.98 (d, J = 8 Hz, 3H)

$^{13}C$ NMR : δ 204.3, 190.7, 147.5, 40.9, 38.8, 36.9, 23.8, 23.7, 18.2.

(Spectrum 2)

**1,4 - addition to bicyclo[4.3.0]nona-2-one (24):**

Into a 50 ml dried two necked RB fitted with nitrogen inlet, septum and a magnetic pellet was introduced 800 mg of $Me_2S.CuBr$ complex and was dissolved in 5 ml of DMS and 5 ml of THF. It was cooled to -78 °C and the Grignard reagent, prepared from 4-bromo-1-butene and magnesium, was added dropwise. After stirring for 10 min. at the same temperature $BF_3.OEt_2$ was added and the stirring was continued for further 15 min. Then the bicyclic enone, bicyclo[4.3.0]nona-1,5-en-2-one **23** (500 mg, 3.6 mmol) in 5 ml of THF was added dropwise and stirring was continued further for 15 min. at the same temperature and was allowed to come to room temperature. The reaction mixture was quenched with $NH_4Cl$ solution and extracted with ether. The ethereal layer was washed with dil. HCl, brine and dried. Evaporation of the

solvent gave the crude material which was charged on a silica gel column and elution with 6% ethyl acetate-hexane furnished the 1,4 - addition product **24** (490 mg, 70% yield) as a viscous liquid.

| | | |
|---|---|---|
| IR (neat) | : | 3050, 2940, 1740, 1640, 1450, 910 $cm^{-1}$ |
| $^{1}H$ NMR | : | δ 6.12 - 5.64 (m, 1H), 5.40 - 4.90 (m, 2H), 2.40 - 1.00 |
| (Spectrum 3) | | (series of m, 17H) |
| $^{13}C$ NMR | : | δ 220.3, 135.0, 114.5, 55.3, 41.1, 36.6, 34.6, 31.2, 30.2, |
| (Spectrum 4) | | 28.1, 22.5, 21.0, 20.6 |

**Cyclization of keto-olefin (26):**[13]

Into a 50 ml three necked RB fitted with a magnetic pellet, dry nitrogen inlet and septum was placed n-butyl lithium (2 ml, 2 mmol) and the flask was cooled to -78 °C. Hexamethyldisilazane (1 ml, 3 mmol) was carefully injected and the resulting slurry was stirred at the same temperature for 10 min. A solution of keto-olefin **24** (100 mg, 0.52 mmol) in 2 ml of dry THF was added slowly. The resulting enolate solution was stirred for 30 min. and quenched with TMS chloride and further stirred at room temperature for 2 h. The reaction mixture was quenched with

$NaHCO_3$ and extracted with ether. Removal of ether furnished the TMS enol ether **25** which was used as such for the next step.

To the TMS enol ether **25** in dry acetonitrile, palladium acetate (10 mg) was added and the reaction mixture was stirred at room temperature for further 15 h. The reaction mixture was quenched with brine and extracted with ether. The ethereal layer was washed with dil. HCl, brine and dried. Ether was removed and the resulting material was charged on a silica gel column and eluted with 8% ethyl acetate-hexane to get the cyclized product **26** (49 mg) in 50% yield.

IR (neat) : 2920, 1738, 1450, 880 $cm^{-1}$

$^1H$ NMR : δ 5.36 (br s, 1 H), 2.66 (d, 1H), 2.40 - 1.00 (series of m,

(Spectrum 5) 13H), 1.72 (s, 3H)

$^{13}C$ NMR : δ 215.9, 134.0, 122.4, 52.9, 52.3, 43.8, 37.5, 34.5, 32.9,

(Spectrum 6) 25.5, 24.9, 22.1, 21.7

**1,4 - addition to 6-Methyl bicyclo[3.3.0]oct-1-en-2-one (12):**

Into a 50 ml dried two necked RB flask, which was equipped with nitrogen inlet, a magnetic pellet was introduced 800 mg of $Me_2S.CuBr$ complex and dissolved in 5 ml of DMS and 5 ml of THF by syringe-septum operation. It was cooled to -78 °C and the Grignard reagent, prepared from 4-bromo-1-butene and magnesium, was added to it dropwise, when the colour changed to yellow. The solution was stirred for 10 min. and then $BF_3.OEt_2$ was added and the above mixture was stirred for further 15 min. at the same temperature. Then the bicyclic enone **13** (500 mg, 3.67 mmol) in 10 ml of THF was added dropwise when colour changed to yellowish green. The above mixture was allowed to stir at the same temperature further for 15 min. and was allowed to come to room temperature. As the temperature increases, the color changed to dark blue. The reaction mixture was quenched with $NH_4Cl$ solution and extracted with ether. The ethereal layer was washed with dil. HCl, brine and dried. Evaporation of the solvent gave the crude material which was charged on a silica gel column and elution with 10% ethyl acetate-hexane afforded the 1,4 - addition product **12** (500 mg, 70% yield) as viscous liquid.

IR (neat) : 3050, 2950, 1730, 1640, 1450, 900 $cm^{-1}$

$^{1}H$ NMR : δ 6.00 - 5.60 (m, 1H), 5.16 - 4.80 (m, 2H), 2.44 - 1.40

(Spectrum 7) (series of m, 14H), 0.96 (d, J = 8 Hz, 3H)

$^{13}C$ NMR : δ 223.6, 138.9, 114.6, 57.3, 52.6, 42.5, 38.6 (2C), 33.7,

(Spectrum 8) 29.4, 28.3, 27.3, 13.3

**Cyclization of the keto-olefin (11):**[13]

Into a 50 ml three necked RB flask fitted with dry nitrogen inlet, septum and a magnetic pellet were placed n-butyl lithium (3 ml, 3 mmol) and the reaction flask was cooled to -78 °C. Hexamethyldisilazane (1 ml, 4 mmol) was carefully injected and the resulting slurry was stirred at the same temperature for 10 min. A solution of keto-olefin **12** (100 mg, 0.52 mmol) in 2 ml of dry THF was added slowly. The resulting enolate solution was stirred for 30 min., quenched with TMS chloride (0.3 ml, 1.56 mmol) and the stirring was continued for 2 h. The reaction mixture was quenched with $NaHCO_3$ and extracted with ether. The ethereal layer was dried over $Na_2SO_4$ and removal of solvent furnished the TMS enol ether **27** which was used as such for the next step.

The TMS enol ether **27** was dissolved in dry acetonitrile and palladium acetate (10 mg) was added and stirred for 24 h at room temperature. The reaction mixture was quenched with brine and extracted with ether. The ethereal layer was washed with dil. HCl, brine and dried. The resulting crude product, obtained after removing the solvent, was charged on a silica gel column and eluted with 10% ethyl acetate-hexane which furnished the cyclized product **11** (51 mg, 52% yield) as a viscous liquid.

IR (neat) : 3010, 2960, 1730, 1450, 890, 810 $cm^{-1}$

$^1H$ NMR : δ 5.46 (br s, 1H), 2.63 (m, 1H), 2.60 - 2.24 (m, 3H),

(Spectrum 9) 1.96 - 1.56 (series of m, 6H), 1.76 (s, 3H), 0.94 (d, J = 8Hz, 3H)

$^{13}C$ NMR : δ 216.2, 134.4, 123.3, 57.2, 55.3, 51.2, 41.9, 37.9, 32.4,

(Spectrum 10) 30.2, 25.2, 22.3, 12.8

**Conversion of ketone to aldehyde (29):**

To a suspension of (methoxymethyl)triphenyl phosphonium chloride (300 mg, 0.81 mmol) in 25 ml of dry ether, was added freshly

sublimed sodium t-amyl oxide (45 mg, 0.4 mmol) in 3 ml of dry ether. The resulting dark red colored solution was stirred at room temperature for 15 min. and the ketone **11** (50 mg, 0.27 mmol) in 3 ml of dry ether was introduced. The reactants were stirred for 30 min., quenched with water and extracted with ether. The ethereal layer was washed, dried and evaporated to get a mixture of the enol ethers **28**. To a solution of mixture of enol ethers **28** in 25 ml of ether, 35% perchloric acid was added at 0 °C. The reaction mixture was allowed to reach room temperature and was stirred for 8 h, and quenched with $NaHCO_3$ and extracted with ether. The ethereal layer was washed with brine and dried Removal of solvent furnished the crude aldehyde, which was charged on a silica gel column and elution with 8% ethyl acetate-hexane furnished the aldehyde **29** (25 mg, 47% yield) as an oily material.

IR (neat) : 2950, 2720, 1720, 1450, 805 $cm^{-1}$

$^1H$ NMR : δ 9.64 (d, 1H, -C**H**O), 5.32 (br s, 1H), 2.68 - 2.28 (m, 4H), 1.80 - 1.40 (m, 8H), 1.64 (s, 3H), 0.93 (d, J = 6 Hz, 3H).

(Spectrum 11)

$^{13}C$ NMR : δ 205.2, 137.0, 122.0, 70.2, 54.5, 47.9, 45.7, 41.5, 40.0, 36.2, 32.7, 29.5, 23.7, 13.6.

(Spectrum 12)

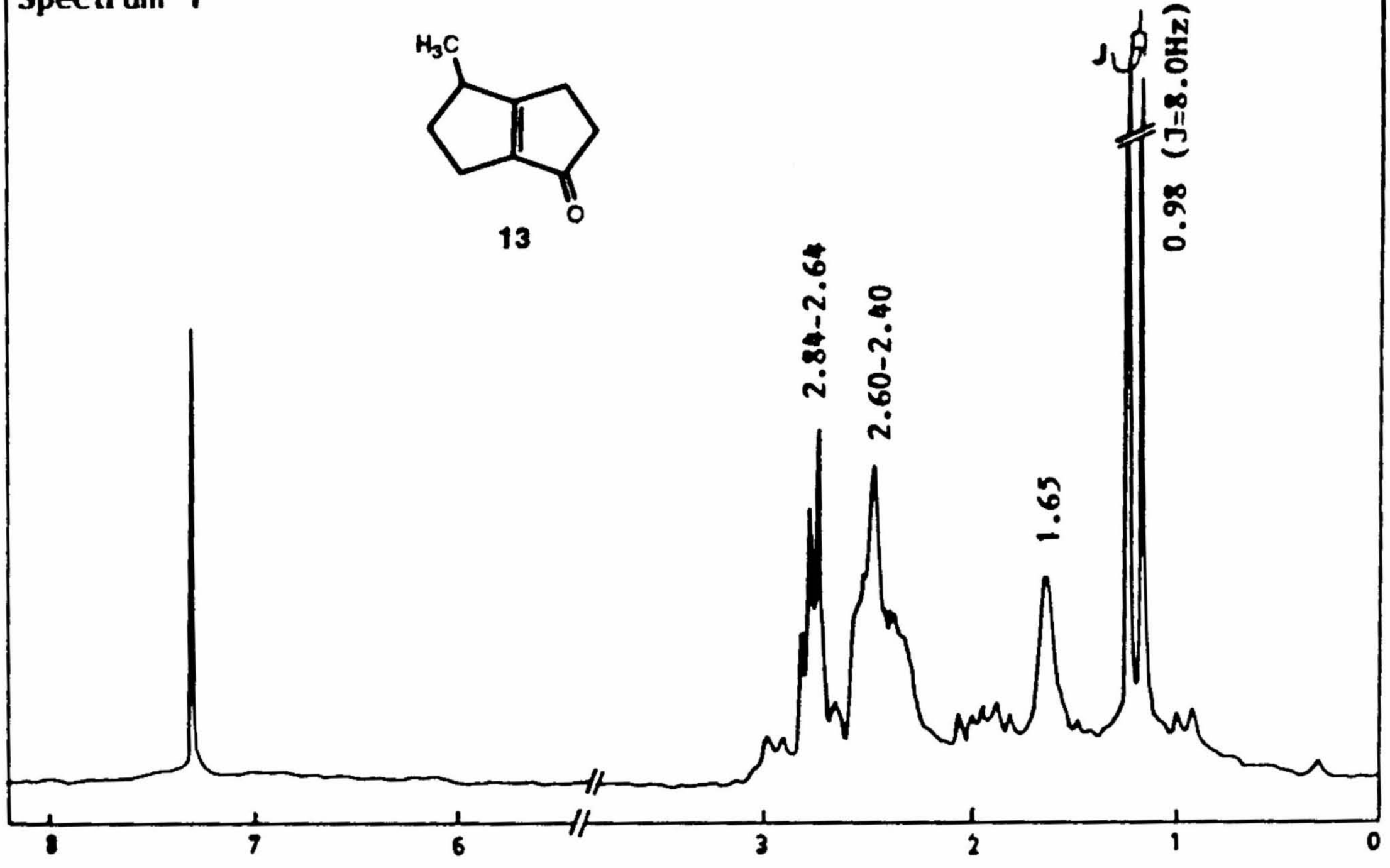
**Alkylation of 29**:

To a suspension of KH (15 mg) in dry THF (10 mL) the tricyclic aldehyde **29** (20 mg, 0.10 mmol) dissolved in 2 mL of dry THF was introduced using syringe-septum technique. The reaction mixture was allowed to stir for 10 min at room temperature and methyl iodide (0.2 mL) was introduced. After stirring for another 30 min. the reaction mixture was quenched with brine and extracted with ether. The ethereal layer was concentrated and the crude material obtained was charged on a silica gel column. Elution with 5% ethyl acetate - hexane afforded the alkylated product **30** (7 mg, 40% yield) as a oily material.

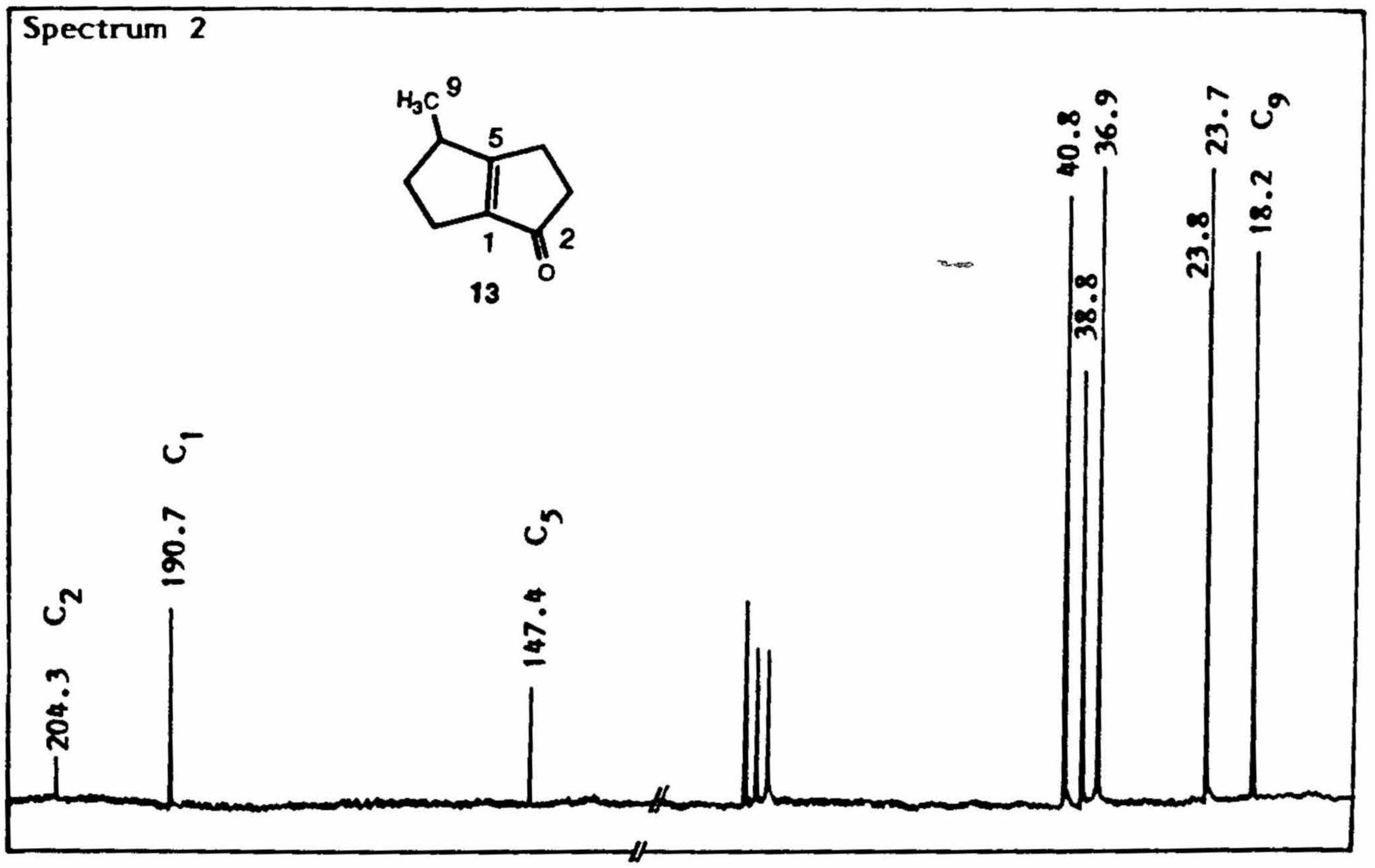
IR (neat) : 2950, 2720, 1710, 1445, 800 $cm^{-1}$

$^1H$ NMR : δ 9.38 (d, 1H, -C<u>H</u>O), 5.32 (br s, 1H), 2.68 - 2.28 (m, 4H), 1.80 - 1.40 (m, 8H), 1.64 (s, 3H), 0.93 (d, J = 6 Hz, 3H)

**Spectrum 1**



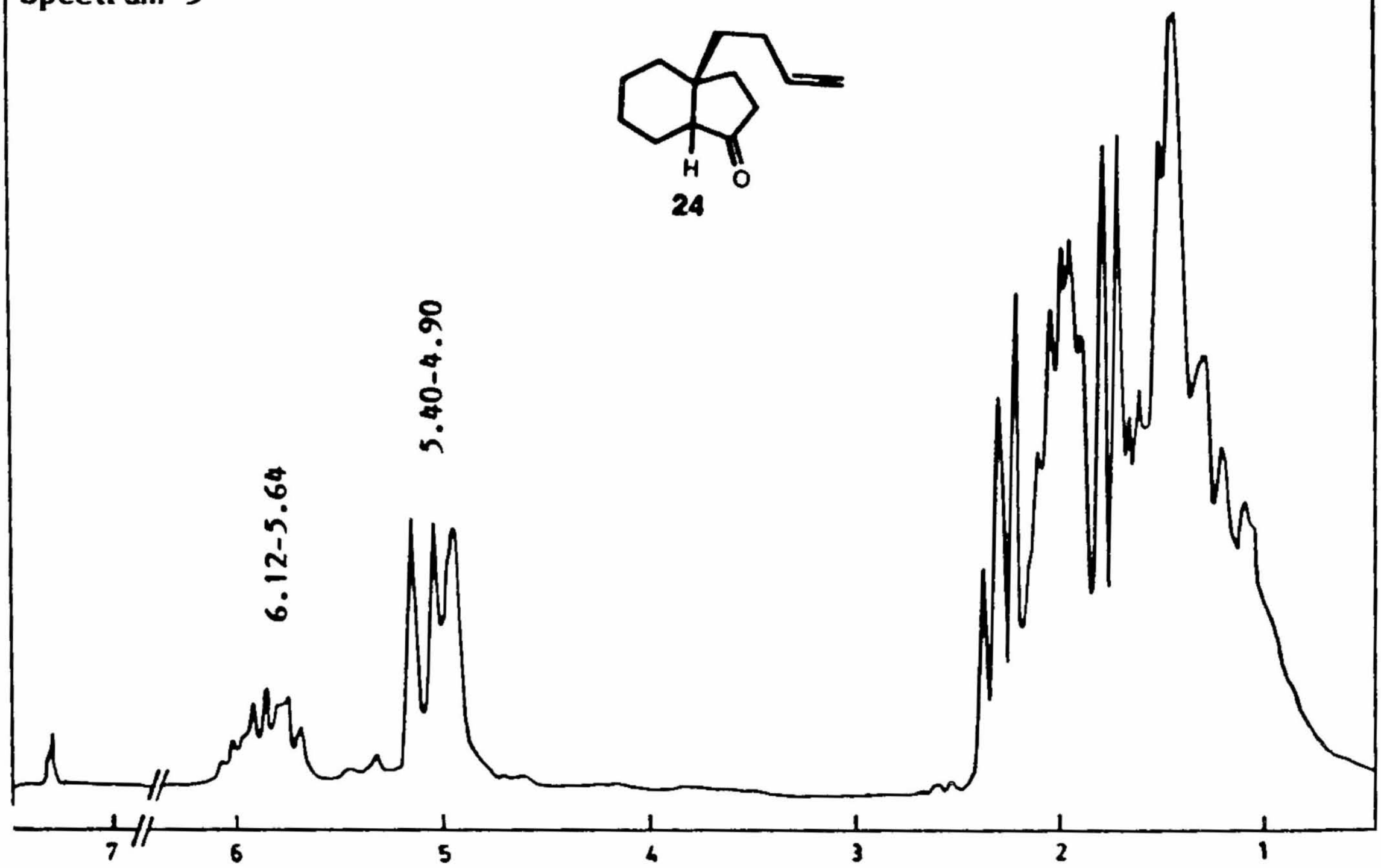

**Spectrum 2**



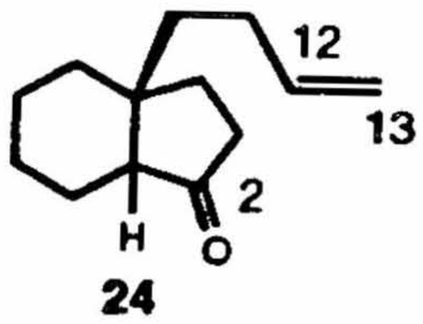
**Spectrum 3**



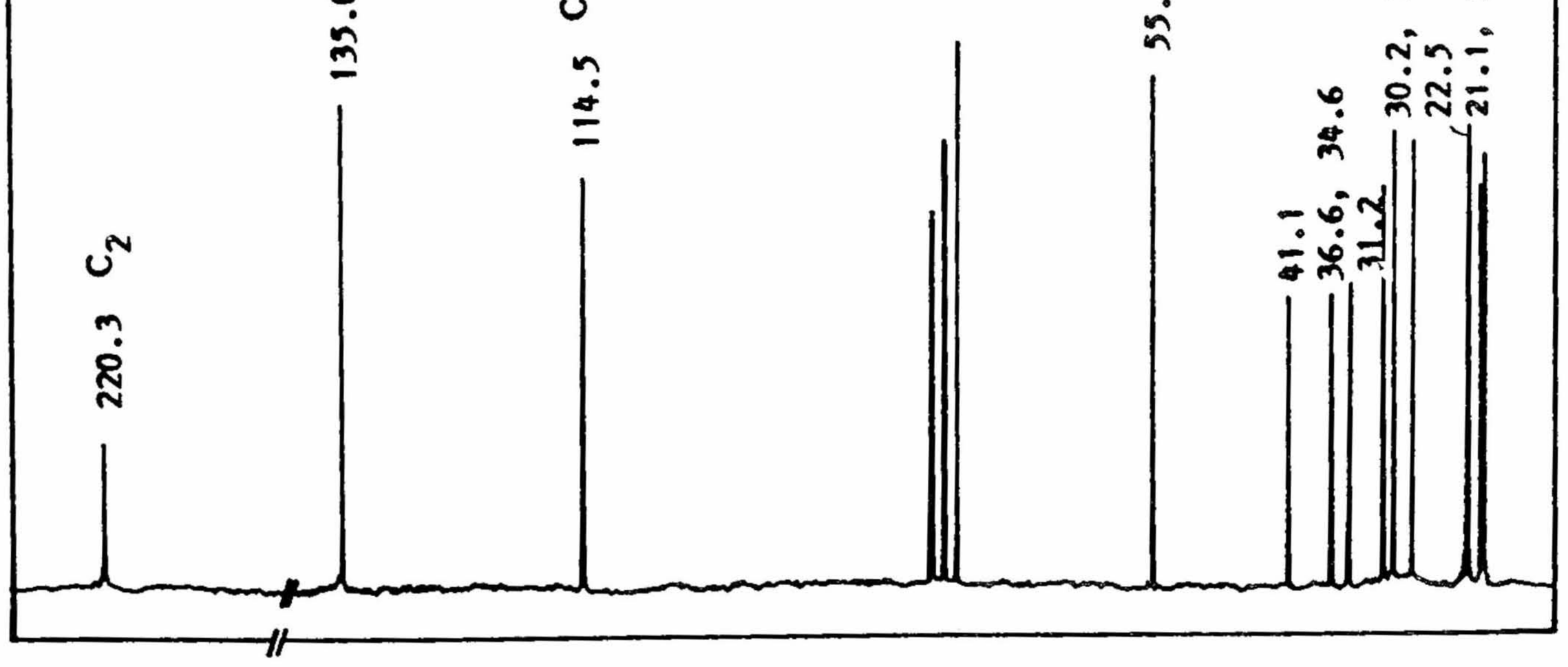

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**Spectrum 4**



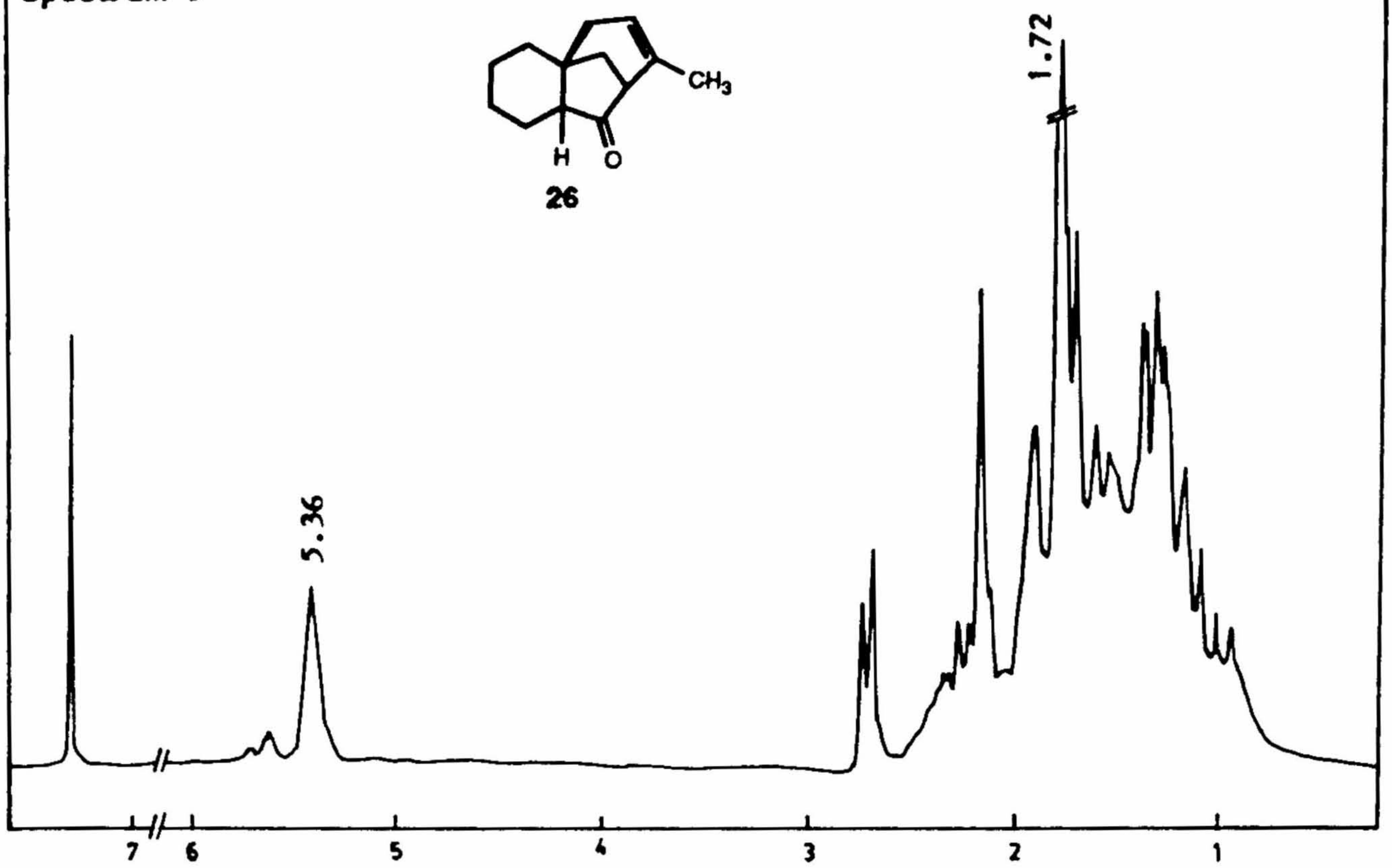

24



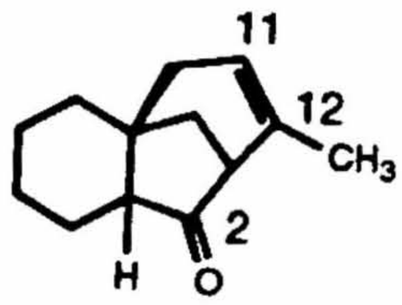
**Spectrum 5**



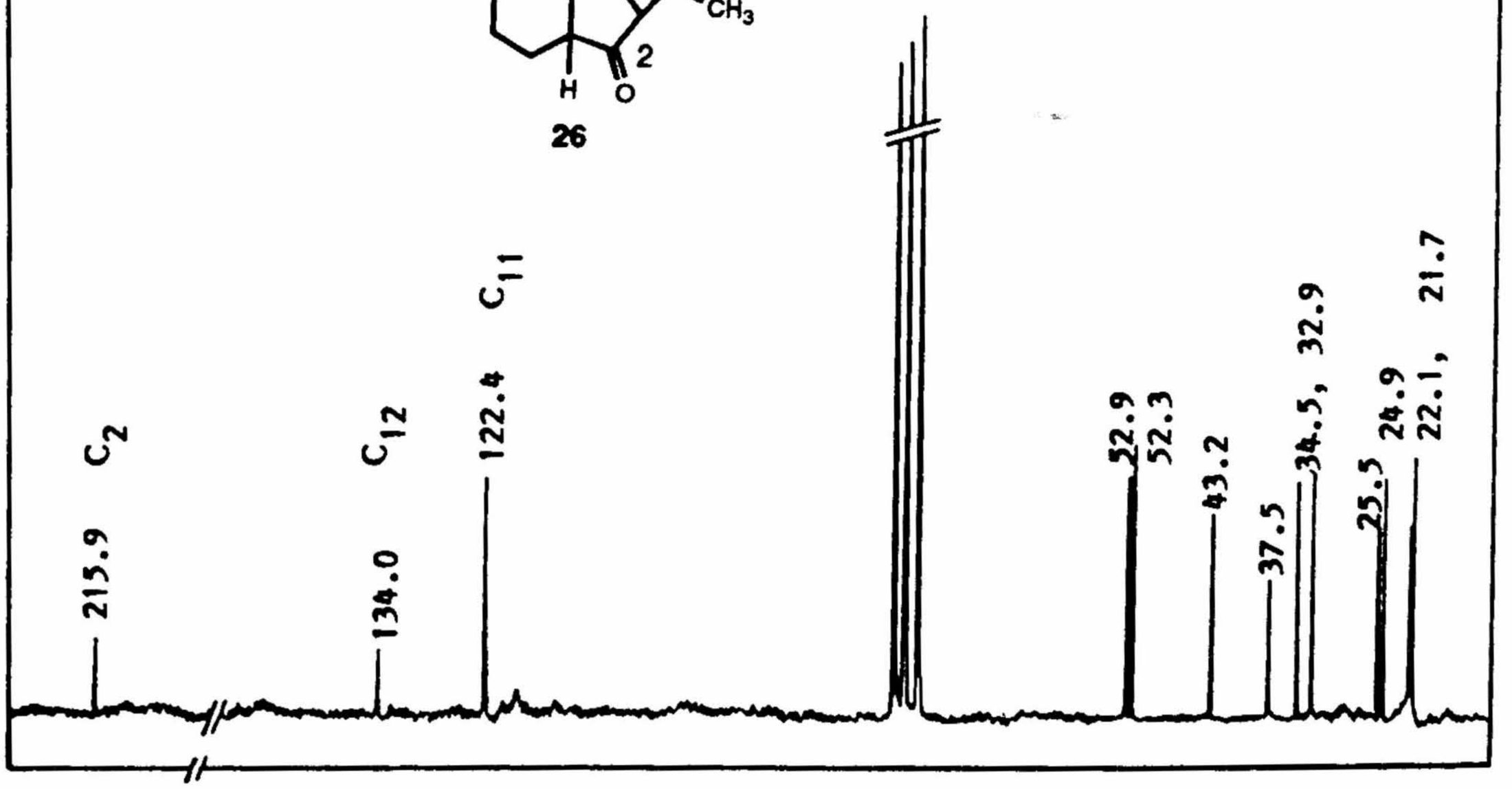

26



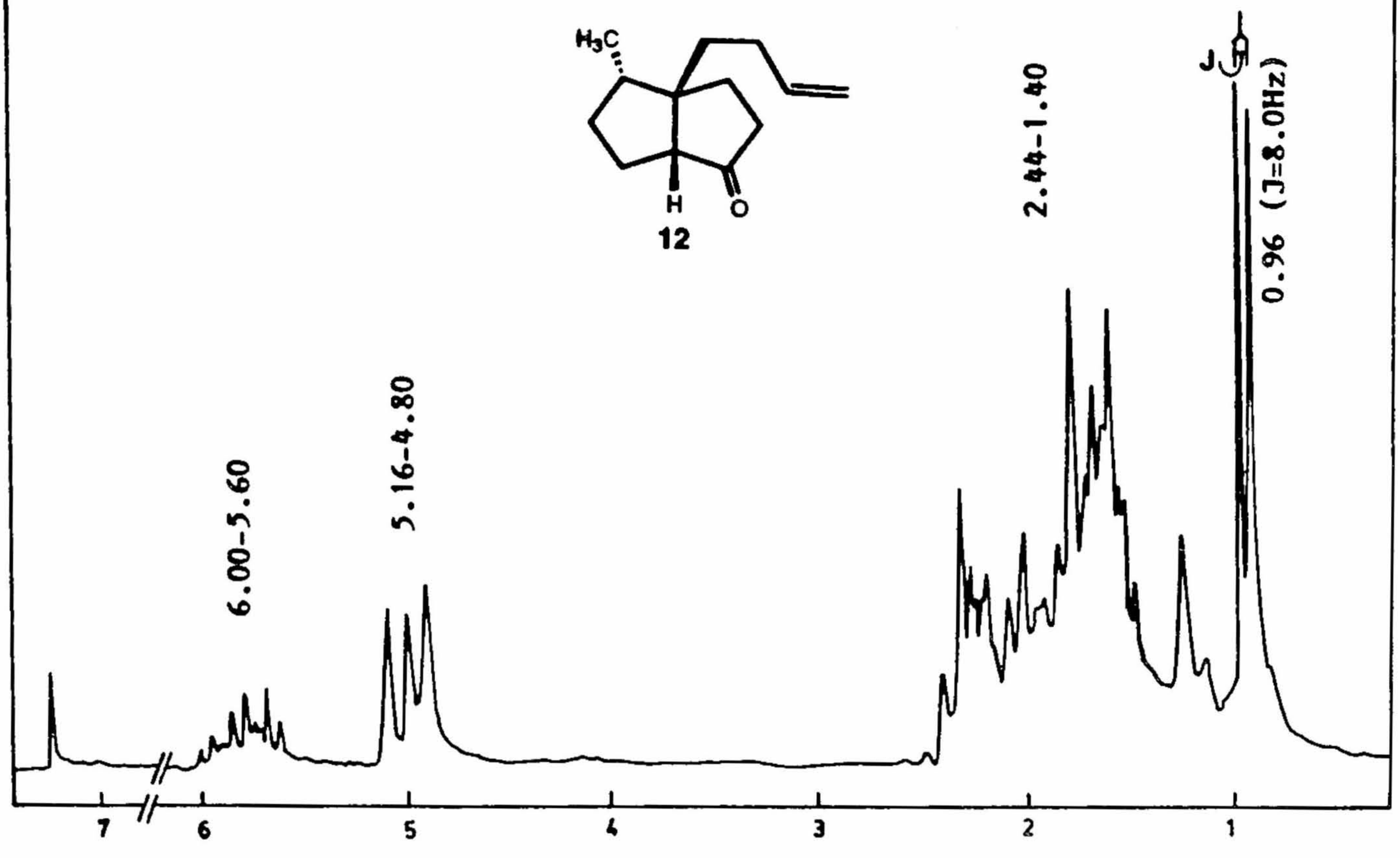

**Spectrum 6**



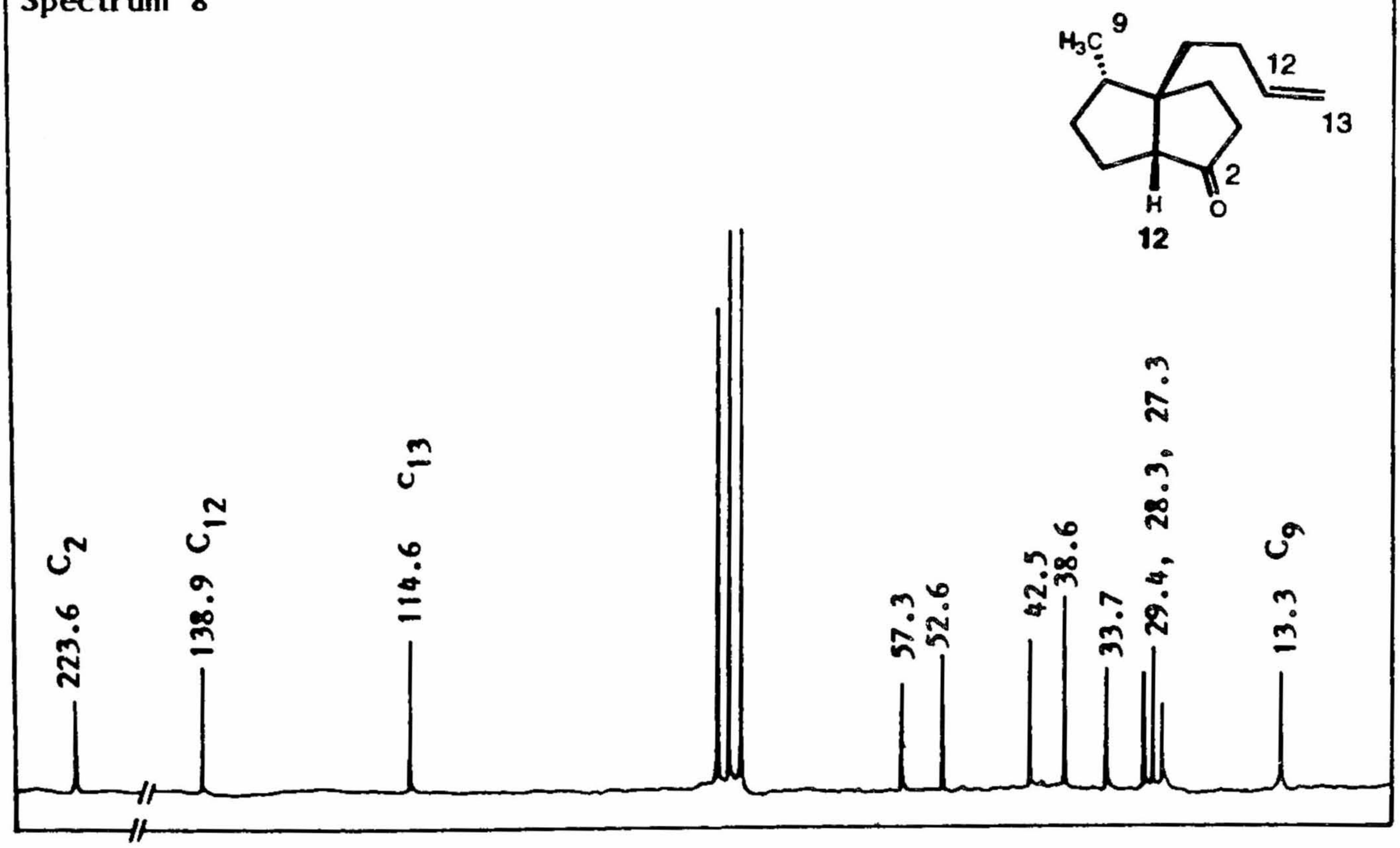

26



**Spectrum 7**



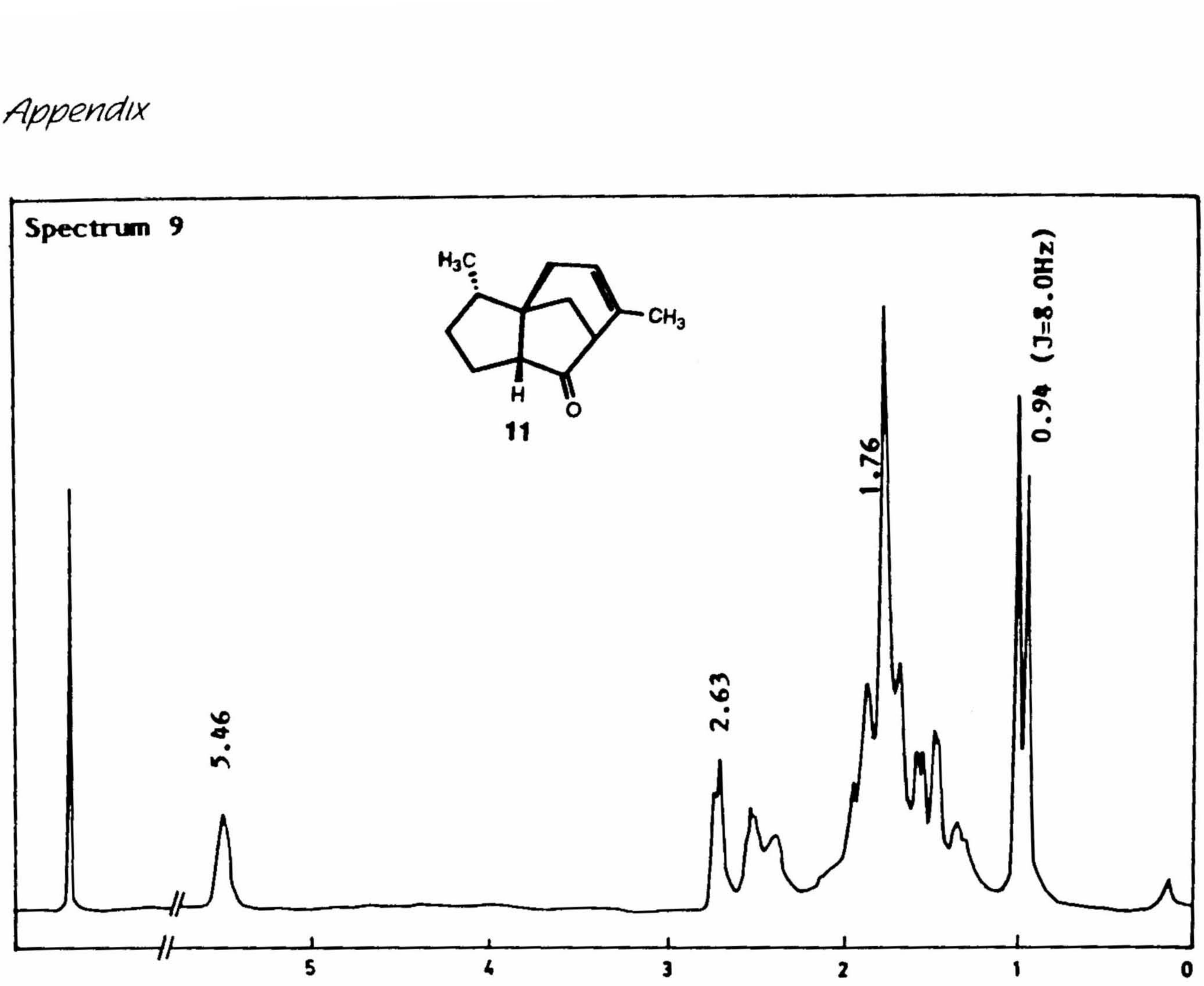

**Spectrum 8**



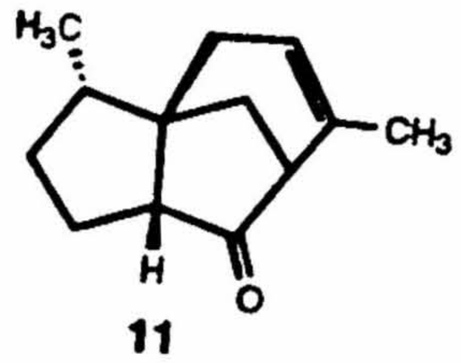
**Spectrum 9**



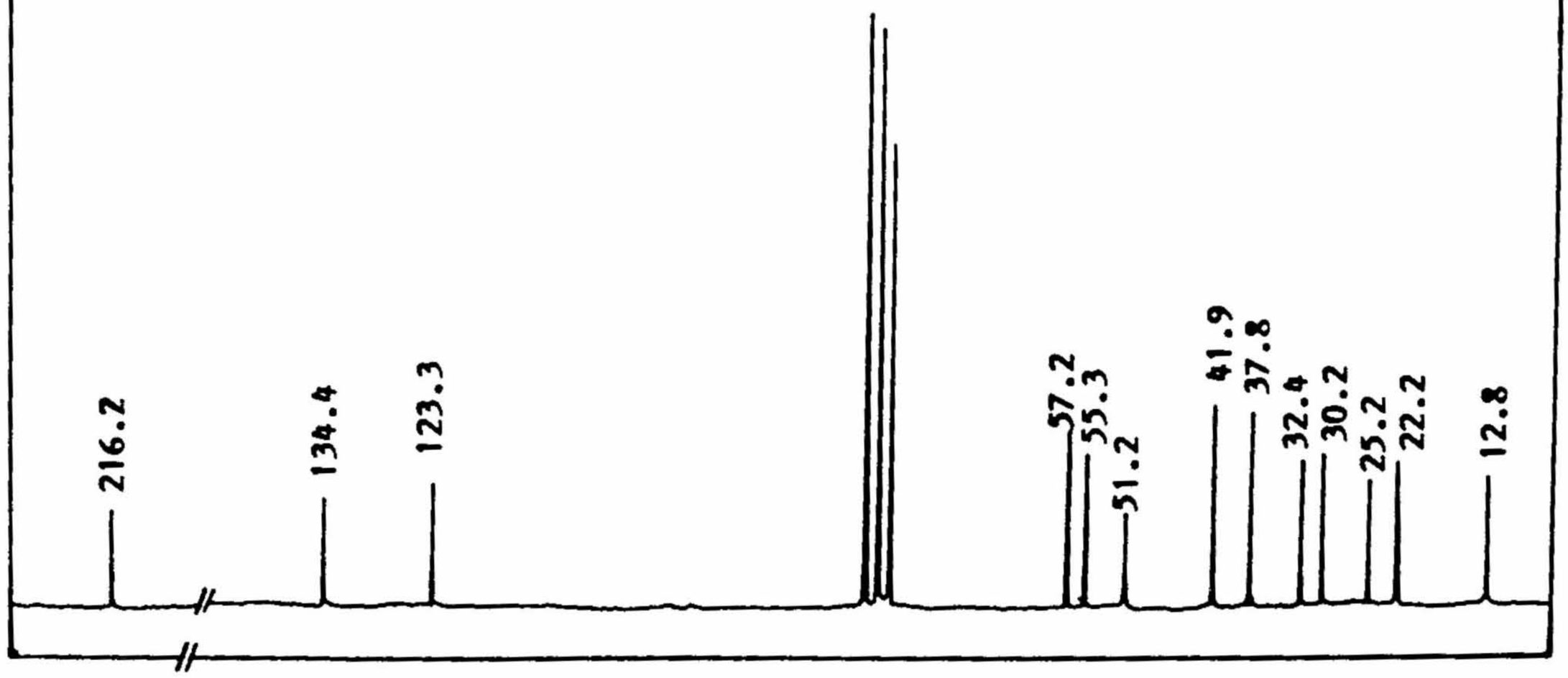

11



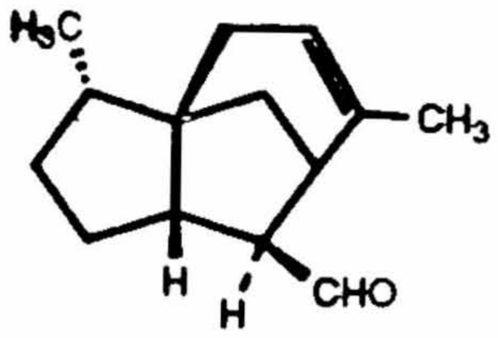

**Spectrum 10**



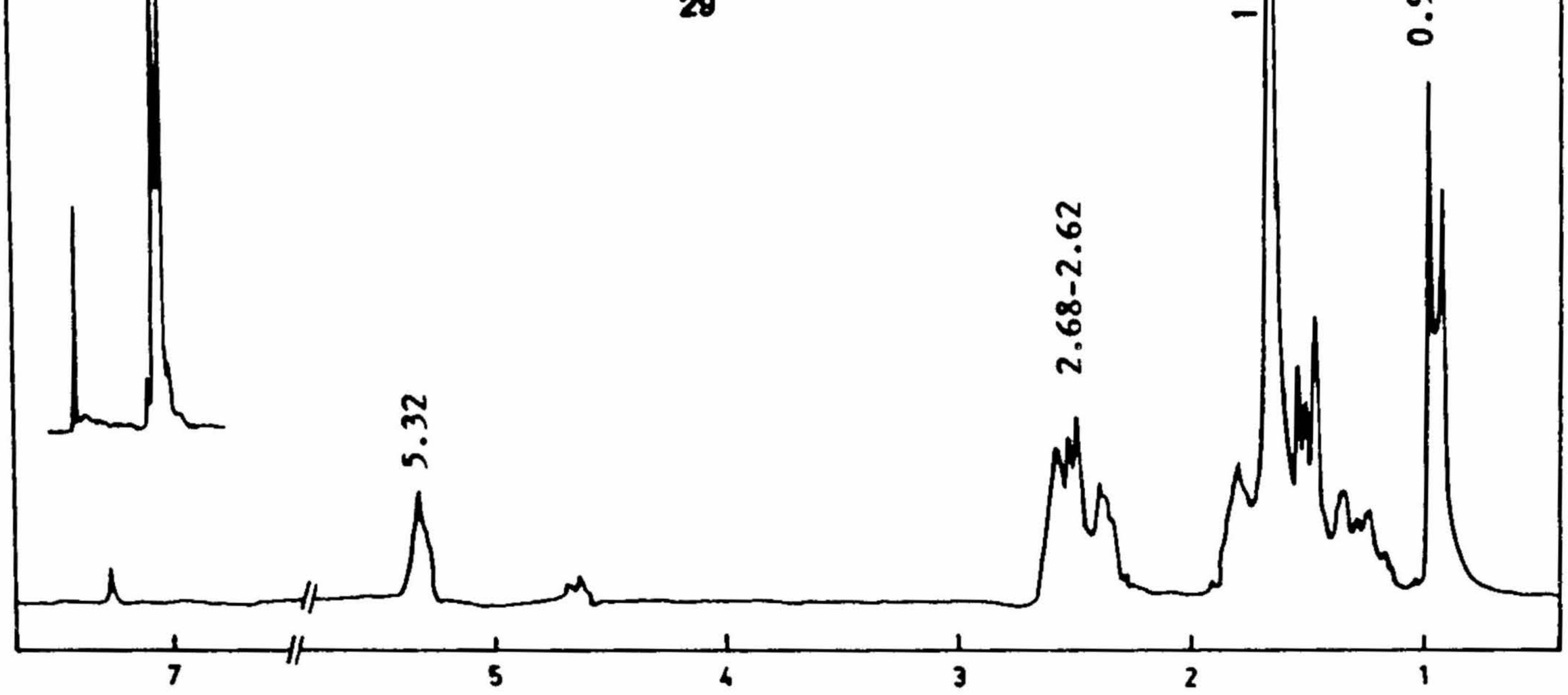

11



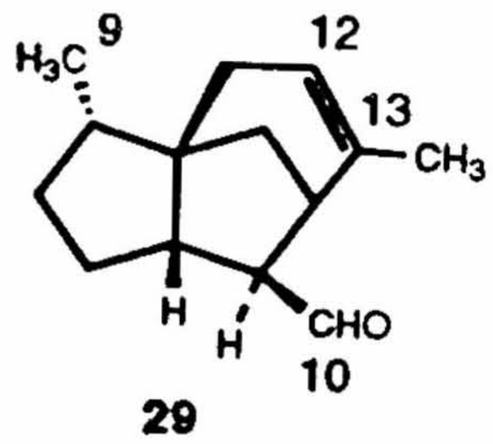
**Spectrum 11**



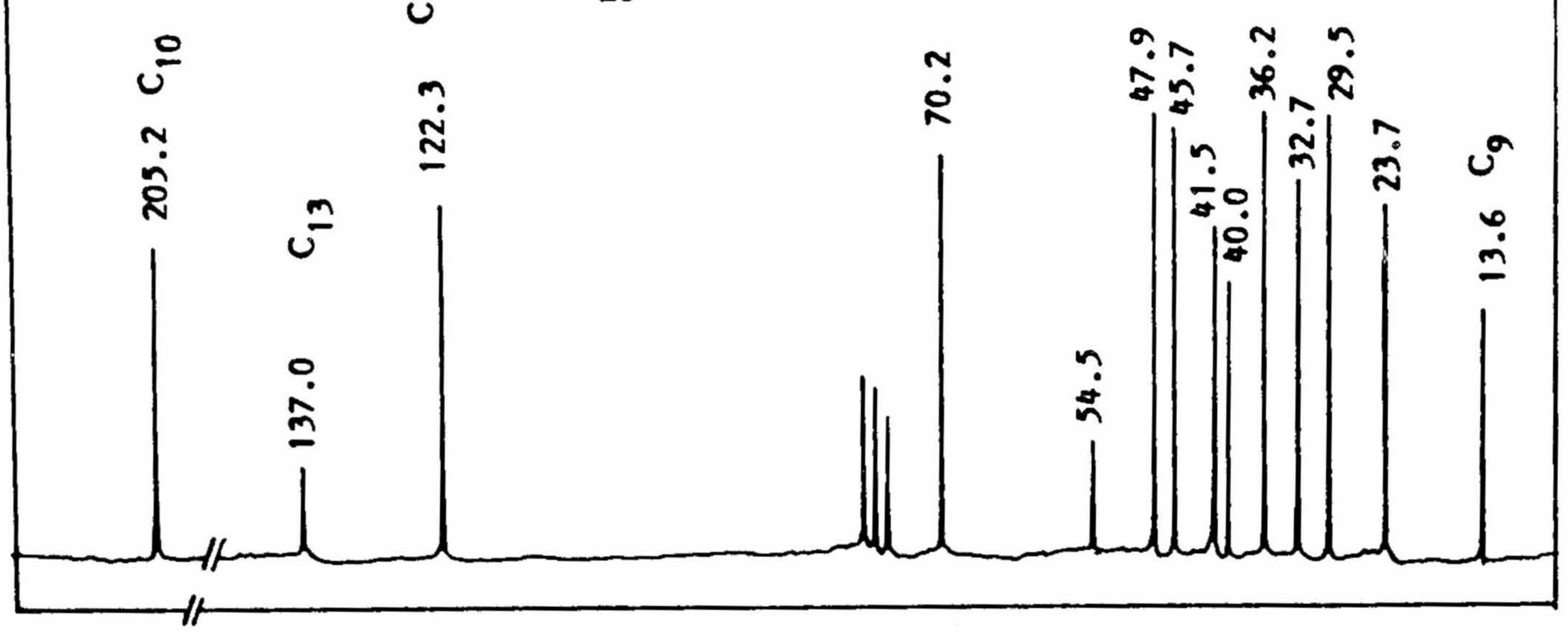

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**Spectrum 12**




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# VITAE

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**List of Publications**

1. A Short entry into annulated bicyclo[3.2.1]octanoid systems *via* palladium(II) mediated intramolecular cycloalkenylation; G. Mehta, ***K. Venkateswara Rao*** and K. Srinivasa Rao; Ind. J. Chem., **1991**, *30B*, 457-459
2. Model Studies Related to Classical Synthetic Approaches to [60]-Fullerene and its Siblings; G. Mehta and ***K. Venkateswara Rao***; Synlett. **1995**, 319-320
3. Synthesis and X-ray crystal structure of 1,3,5-*tris*(fluorenylidene-methyl)benzene: Towards a $C_{48}$-Fragment of [60]-fullerene; G. Mehta and ***K. Venkateswara Rao***, K. Ravikumar; J. Chem. Soc. Perk.Trans 1, **1995**, 0000