

# Synthesis of Rigidly Linked Polychromophores for Intramolecular Energy Transfer Study

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## Abstract

Intramolecular energy transfer is reviewed from several perspectives, such as the generally accepted mechanism and molecular structure dependence. Some unique molecules with bichromophores or trichromophores linked by rigid bridges were designed to serve as models for studying the intramolecular triplet-triplet energy transfer.

Bichromophoric molecules containing an anthracene donor and phenanthrene or diphenylpolyene acceptors linked by linearly fused norbornane units were synthesized. Approaches to the analogous compounds with anthracene as the donor and benzophenone or *p*-terphenyl as acceptors are presented.

Synthetic approaches to *cis*, *exo*-1, 4-dihydro-1, 4-methanotriphenylene, a precursor to the polynorbornyl-linked polychromophore, and trichromophoric compounds linked by adamantane spacers were explored.

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## **Chapter 1 Introduction**

### **1.1 Research Goal**

Molecular photonic devices have attracted intense attention in the community of chemists, physicists, and materials scientists. They have the advantage of fast response on the femtosecond time scale, based upon rapid energy and electron transfer processes. With microelectronics approaching the nanoscale level, metal-oxide-semiconductor (CMOS) based integrated circuits are predicted to be confronted with technical dilemmas in the near future. On the other hand, molecular photonic devices that feature rapid, controllable energy and electron transfer promise to be capable of breaking through the limitations and reaching an unparalleled level of computing efficiency. So the ultimate goal of this project is to design and synthesize polychromophoric molecules that would function as molecular photonic or electronic wires, charge-coupled devices, shuttles and other molecular-scale data-handling components.<sup>[1]</sup> For the short-term goal, we planned to synthesize various bichromophores or trichromophores linked by rigid spacers as models for studying the intramolecular triplet-triplet energy transfer.

### **1.2 Photoinduced Electron Transfer and Energy Transfer**

The absorption of ultraviolet or visible light by a molecule causes the excitation of an electron from the ground state to the excited state. Energy and electron transfer are two general nonradiative pathways in the quenching process of the excited state. As

shown in the simplified molecular orbital picture (Figure 1-1), quenching by electron transfer can be described as a one-electron reaction in which an electron jumps from an occupied orbital of one reactant to an unoccupied orbital of another reactant. The excited molecule can be either an electron donor or an acceptor. In either case, quenching by electron transfer between uncharged species leads to a radical ion pair or a charge-transfer complex.

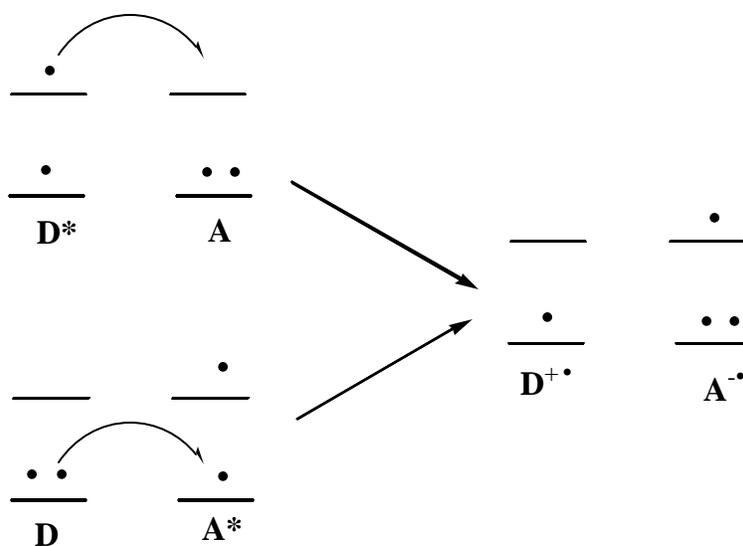


Figure 1-1. Schematic description of electron motion in electron transfer quenching mechanism: D = donor, A = acceptor, and the solid circles represent electrons.

Electron transfer through space requires a close approach of donor and acceptor for effective orbital overlap. The effective range of electron transfer is usually limited to distances of less than 10 Å.

Energy transfer can take place by two classical mechanisms: electron-exchange and dipole-dipole interaction (Figure 1-2). In the electron-exchange mechanism, two

single electron transfers – one in each direction – result in the excited state donor returning to the ground state and the acceptor being raised to the excited state. Energy transfer by the dipole-dipole mechanism operates by Coulombic resonance interactions, in which the oscillating electrons of an excited state donor are coupled with those of the acceptor by an induced dipole interaction.<sup>[2]</sup>

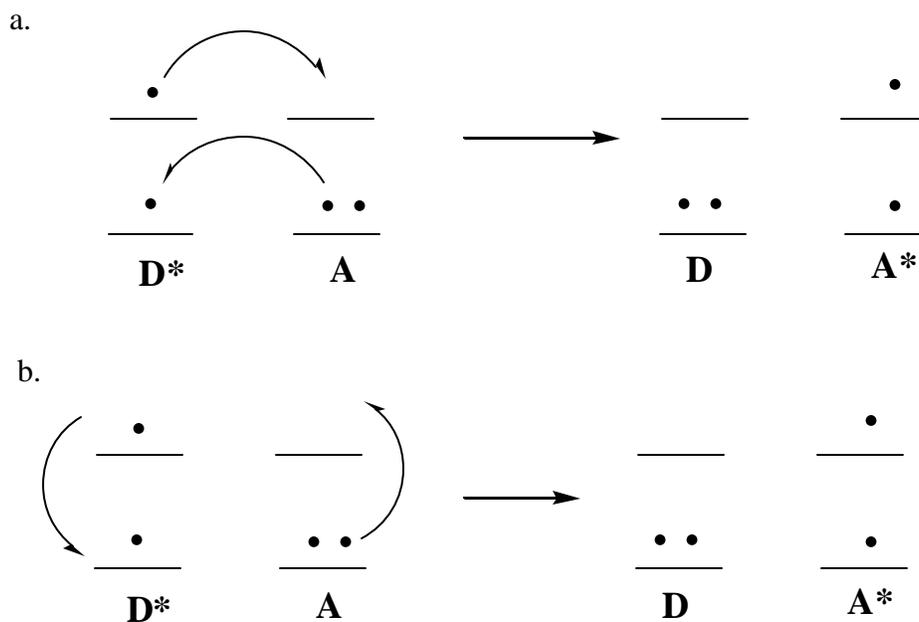


Figure 1-2. Schematic description of electron motion in energy transfer quenching mechanism: D = donor, A = acceptor, and the solid circles represent electrons: a. electron exchange mechanism; b. dipole-dipole mechanism.

Energy transfer by electron exchange requires effective orbital overlap. It can operate through space as well as through bond. However, as the distance between donor and acceptor increases, only the through-bond mechanism can provide orbital overlap over distances of greater than 10 Å. In contrast, Coulombic energy transfer does not

involve orbital overlap and can be effective from collision distances of less than 10 Å and up to separation distances as large as 100 Å.

Singlet-singlet energy transfer (SSET, eq.1-1) is spin-allowed for both the Coulombic and exchange interactions.



Triplet-triplet energy transfer (TTET, eq. 1-2) is spin-forbidden by the dipole-dipole mechanism and is only allowed by the electron exchange mechanism.



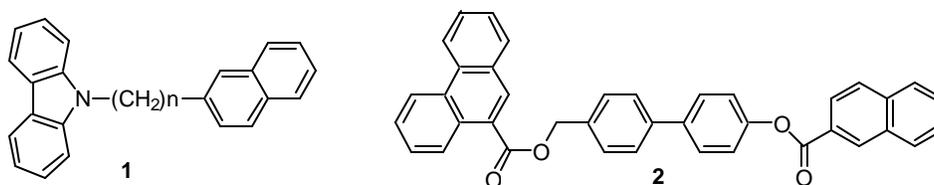
Intramolecular triplet-triplet energy transfer is the focus of most of the photochemical studies in our lab because the average lifetime of the triplet state is much longer than the singlet state, allowing the use of dye lasers with long pulse widths.

### **1.3 Molecular Structure Control of Intramolecular Energy Transfer**

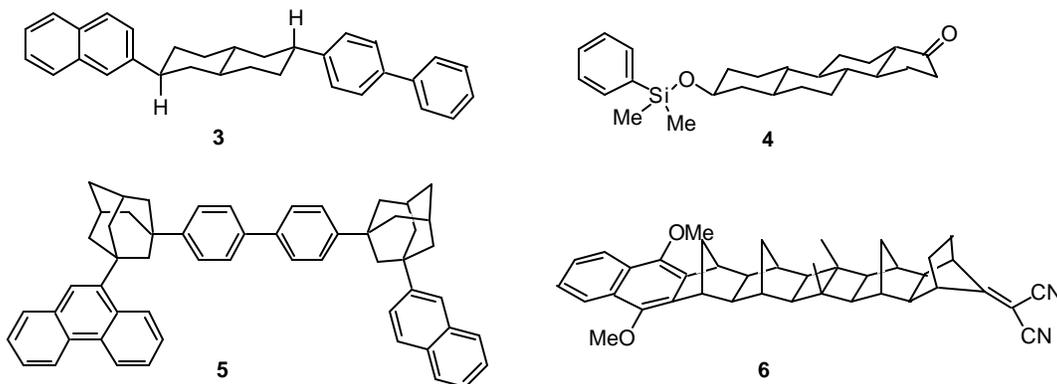
From mechanistic studies of the intramolecular energy transfer process, it has been clearly demonstrated that factors at the molecular level, such as the nature of the spacers and chromophores, the interchromophoric distance and orientation, and so on, play important roles in affecting the energy transfer process.

### 1.3.1 Flexible and rigid spacers

Molecules with flexible spacers, such as methylene-linked **1**<sup>[3]</sup> and ester-linked **2**,<sup>[4]</sup> can adopt many conformations so the measured rate constant for intramolecular energy transfer is an average over many conformations. Another disadvantage associated with flexible spacers is that several mechanisms can be operating at the same time.



By contrast, better models for quantitative study of energy transfer are provided by rigid covalently linked donor-bridge-acceptor systems in which the chromophores are held with well-defined distances and orientation by bridges that generally consist of saturated hydrocarbon units or protein backbones. The different types of saturated hydrocarbon bridges that have been employed include decalin (**3**),<sup>[5]</sup> the steroidal 5 $\alpha$ -androstanyl system (**4**),<sup>[6]</sup> adamantane (**5**),<sup>[7]</sup> and norbornylogous bridges (**6**).<sup>[8]</sup>



### 1.3.2 All-*trans* rule

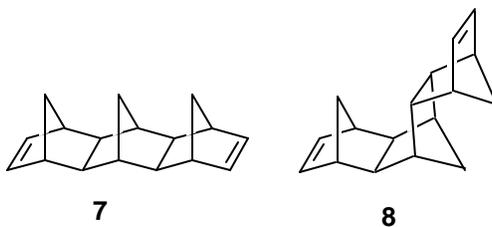
Recent work showed that rigid spacers can facilitate long-range intramolecular electron transfer over distances substantially larger than the sum of the van der Waals radii of the chromophores by a superexchange mechanism; to put it crudely, the spacer provides “orbitals” ( $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ , etc.) which the migrating electron can use to tunnel between the chromophores. When the spacer is saturated and only  $\sigma$  and  $\sigma^*$  orbitals are available for coupling with the chromophores, the superexchange mechanism is then often referred as a through-bond coupling mechanism.<sup>[9]</sup> A systematic study of this phenomena was undertaken by Paddon-Row and co-workers. They examined intramolecular electron transfer in series of bichromophores, mostly containing a rigid polynorbornyl bridge. The general conclusion that could be made is that the long-range intramolecular electron transfer is primarily mediated by through-bond coupling.<sup>[8, 10]</sup>

It is also reported that long-range intramolecular triplet-triplet energy transfer in rigid systems operates by this mechanism. Closs first demonstrated the utility of a  $\sigma$  bond spacer in promoting long distance intramolecular triplet energy transfer. He measured the rates of triplet-triplet energy transfer in series of compounds containing a 4-biphenyl donor, a 2-naphthyl acceptor, and cyclohexane or decalin (**3**) spacers. The rate decreased by 1 order of magnitude in going from equatorial-equatorial substitution to equatorial-axial. This rate dependence on the conformation of connecting bonds is known to be indicative of through-bond mediated coupling.<sup>[5, 11]</sup> Morrison and coworkers reported that selective excitation of dimethylphenylsiloxy chromophore in compound **4** led to reduction of the C17 keto group, indicating an intramolecular triplet energy transfer

process. Since the energy transfer via a through-space exchange process would be quite inefficient over the 11.6 Å separating the chromophores,<sup>[12]</sup> a through-bond mechanism was proposed to explain the energy migration.<sup>[6]</sup> A conclusion drawn from these results is that the factors important for the through-bond coupling would also play crucial roles in the triplet-triplet energy transfer process.

It is well known that the through-bond coupling greatly depends on the length and the configuration of the bridge. An important rule about the dependence of through-bond interactions on the bridge configuration is the all-*trans* rule, which states that through-bond coupling is sensitive to the configuration of the bridge and is maximized for an all-*trans* (antiperiplanar) arrangement of relaying  $\pi$  bonds.

Jordan and Paddon-Row demonstrated the all-*trans* rule through calculations and experimental measurements of the splittings between the  $\pi$  orbitals for a series of dienes with the ethylenic groups separated by polynorbornyl bridges. They found, for example, that the  $\pi_+$ ,  $\pi_-$  and  $\pi_+^*$ ,  $\pi_-^*$  splitting for the all-*trans* diene **7** is much larger than for compound **8**, which contains a gauche arrangement of  $\pi$  bonds. The result was explained by the extended McConnell model, which states that 3 major pathways, T, T' and t



interactions, contribute to the through-bond coupling. For an all-*trans* arrangement (Figure 1-3a) in which t and T' are negative and T is positive, all three contributions enhance the  $\pi_+$ ,  $\pi_-$  splitting. When a gauche configuration is introduced in the molecule (Figure 1-3b), the positive T' interaction leads to a diminished splitting.<sup>[8]</sup>

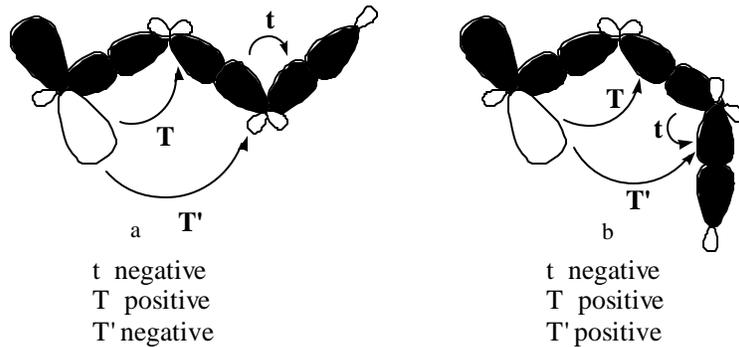


Figure 1-3. McConnell models for through-bond interaction between a chromophore ?

orbital and spacer ? orbitals.

### 1.3.3 Choice of chromophores

In order to achieve high quantum efficiency in the triplet-triplet energy transfer process, some factors must be taken into consideration for the choice of donor and acceptor chromophores.

1. There should be little electronic interaction in the ground state between donor and acceptor chromophores. However, the absorption spectra of the chromophores should be easily distinguishable and the  $S_0 \rightarrow S_1$  transition of the donor should be lower than that of the acceptor so that the donor chromophore could be the principal light absorbing species under selective UV excitation.
2. Once the donor  $S_1$  state is formed, its intersystem crossing (ISC) to the triplet manifold should be efficient with respect to other donor  $S_1$  decay pathways.
3. Triplet donor and acceptor chromophores should have distinct T-T absorptions and/or high phosphorescence quantum yields because the measurement of T-T

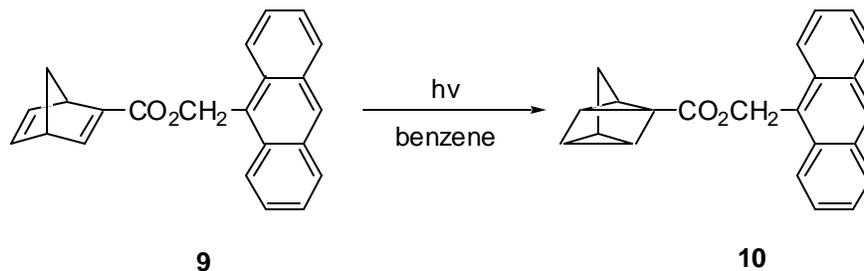
absorption or phosphorescence from donor or acceptor  $T_1$  state is often used in the study of the rate and efficiency of intramolecular triplet-triplet energy transfer.

4. The lifetime of the donor triplet excited states must be relatively long.
5. The acceptor  $T_1$  state must lie sufficiently below that of the donor triplet excited state so that the transfer process is energetically favorable.

In summary, when we decided which chromophores to be used in our study, we mainly considered the excited state characteristics of the chromophores such as the absorptions of their ground state and triplet state, the ISC yield, and the energies and lifetimes of the excited state.

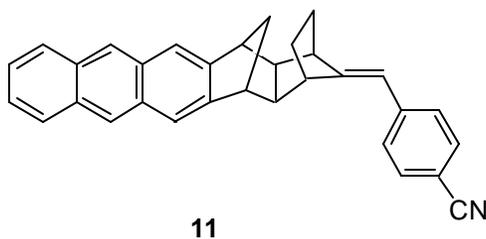
The second triplet state ( $T_2$  state) of anthracene has been demonstrated to be a good triplet donor. It can be formed efficiently by a second laser excitation of the anthracene  $T_1$  state formed via ISC from anthracene  $S_1$ .<sup>[13]</sup> The  $T_1$  and  $T_2$  energies of anthracene are  $\sim 40$ <sup>[14]</sup> and  $\sim 74$ <sup>[15]</sup> kcal/mol respectively, and this large energy gap contributes to a relatively long  $T_2$  lifetime ( $\sim 200$  ps).<sup>[16]</sup> There are some examples in the literature that demonstrate that triplet-triplet energy transfer from the anthracene  $T_2$  state to an acceptor can occur. Early spectroscopic studies at low temperature involving the excitation of anthracene in the presence of naphthalene showed that an intermolecular energy transfer from anthracene  $T_2$  to the naphthalene  $T_1$  state resulted in the naphthalene phosphorescence emission.<sup>[4]</sup> Okada reported an intramolecular energy transfer from the anthracene  $T_2$  state to the norbornadiene triplet state leading to the valence isomerization of norbornadiene to quadricyclane (as shown in Scheme1-1).

### Scheme 1-1

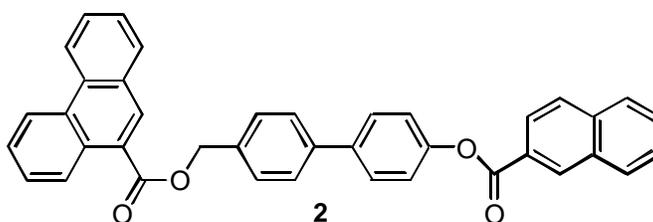


Since the  $T_2$  and  $T_1$  energies of norbornadiene are  $\sim 72$  and  $61$  kcal/mol, respectively, energy transfer from the  $T_1$  state of the anthracene ( $42$  kcal/mol) would be highly endothermic. The energy transfer from the anthracene  $S_1$  state is also highly endothermic ( $> 19$  kcal/mol). The conceivable electron transfer process is also highly endothermic. So it was proposed that the reaction might proceed via the  $T_2$  state of the anthracene because the  $T_2$  energy transfer is exothermic ( $2 \sim 7$  kcal/mol). Flash photolysis experiments with stepwise two-laser excitation confirmed that the energy transfer from the  $T_2$  state of anthracene did occur efficiently.<sup>[17]</sup>

Previous studies in our lab also showed that in compound **11**, a rapid energy transfer ( $k \sim 10^{10} \text{ s}^{-1}$ ) was observed from the  $T_2$  state of anthracene, formed by a two-laser excitation, to alkene acceptors such as *p*-cyanostyrene.<sup>[18]</sup>



We thus became interested in phenanthrene as a donor chromophore. Preliminary results in our lab showed that laser flash excitation of the phenanthrene triplet in compound **2** resulted in the production of the naphthalene triplet. It was suggested that the process occurred via a pathway in which the formation of the upper excited triplet state of phenanthrene was followed by intramolecular energy transfer to the central biphenyl moiety and further energy transfer from it to the naphthalene chromophore.<sup>[3]</sup>



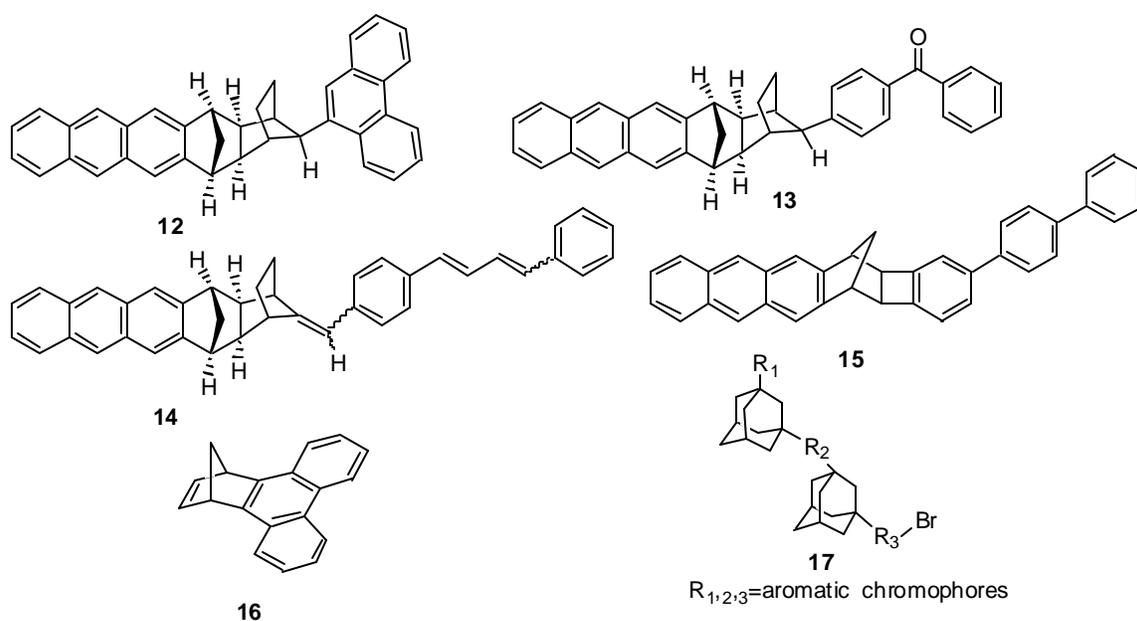
We chose benzophenone, *p*-terphenyl, and 1,4-diphenyl-1,3-butadiene (DPB) as acceptor chromophores because of the energies and the distinct T-T absorption spectra of their excited states.

#### 1.4 Molecular Design

Taking those factors into consideration, we proposed the target compounds **12** to **17** as good models for studying intramolecular energy transfer (Scheme 1-2). The common feature of these compounds is that they all contain rigid hydrocarbon bridges, either linearly fused norbornylogous units or adamantanyl rings. Based on the unique characteristics of anthracene and phenanthrene mentioned above, we decided to use them as donor chromophores and introduce various acceptor chromophores into the molecules.

Compounds **12-15** all contain linearly fused norbornylogous units and anthracene as a donor group and are expected to be useful models for studying the dynamics of energy transfer processes between anthracene and various acceptors under spatially controlled conditions.

**Scheme 1-2**

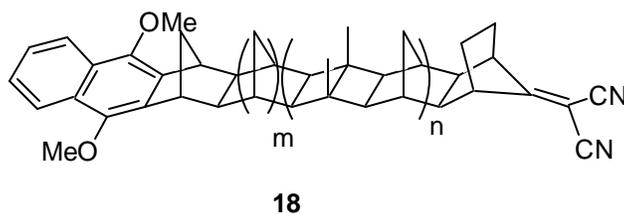


Previous studies in our lab showed that compound **5** could undergo efficient electron transfer.<sup>[7]</sup> We tried to expand the application of this useful system by exploring a more general methodology to synthesize a similar type of compound, **17**. We were also very interested in the energy transfer process of polychromophoric compounds with phenanthrene as donor chromophore. So we started out to make compound **16**, a precursor to phenanthrene-containing polychromophores.

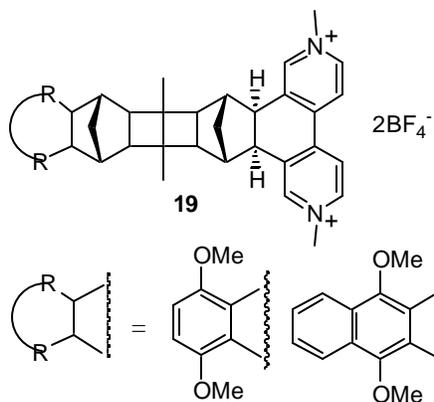
Before we discuss the synthetic strategy, it is necessary to discuss the prior work that has been done in this area.

### 1.4.1 Previous studies

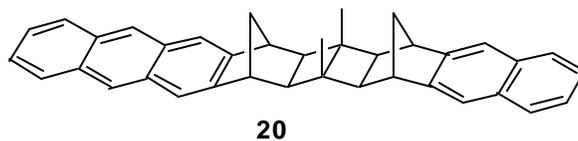
The rigid norbornylogous bridge system, comprising a mixture of linearly fused norbornyl and bicyclo[2.2.0]hexyl groups, was first synthesized by Paddon-Row and co-workers. They studied intramolecular electron transfer in systems such as **18** ( $m = 0-1$ ,  $n = 0-2$ ) where the donor group is dimethoxynaphthalene and the acceptor is a dicyanovinyl group. Their studies revealed that the norbornylogous bridge strongly mediates both electron and energy transfer by a through-bond coupling mechanism over distances exceeding 12 Å.<sup>[20]</sup>



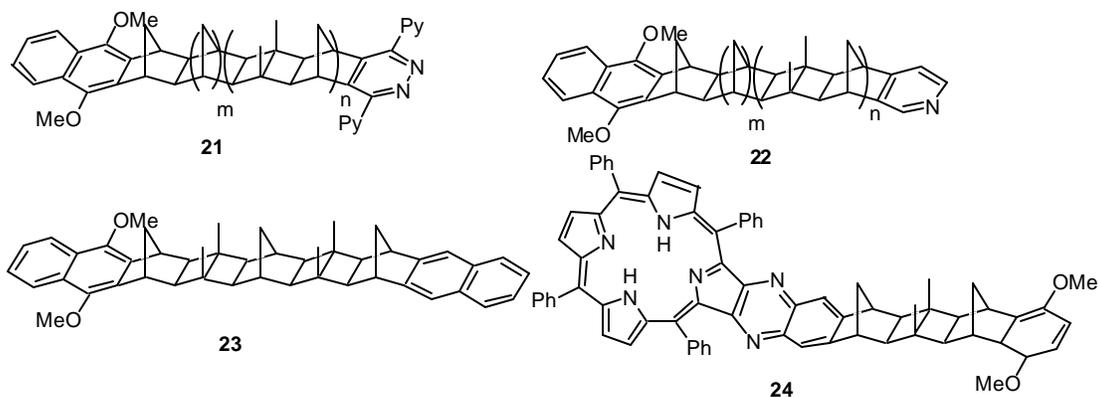
In 1997 Craig and co-workers reported the use of the bichromophoric system **19**, consisting of either a dimethoxybenzene or dimethoxynaphthalene unit, each covalently linked through a six-bond norbornylogous bridge to a methyl viologen unit for the study of long-range intramolecular energy and/or electron transfer.<sup>[21]</sup>



Scholes measured the rate of intramolecular SSET between the naphthalene and anthracene chromophores that are linked by a rigid bis(norbornyl)bicyclo[2.2.0]hexane bridge (compound **20**).<sup>[22]</sup>



So far most research has focused on the norbornylogous bridges bearing the dimethoxynaphthalene unit as donor chromophore. Examples of the acceptor chromophores that were investigated include 3,6-di(2'-pyridyl)pyridazino,<sup>[23]</sup> pyridine,<sup>[23]</sup> naphthalene and a porphyrin (compounds **21-24**).<sup>[24]</sup>

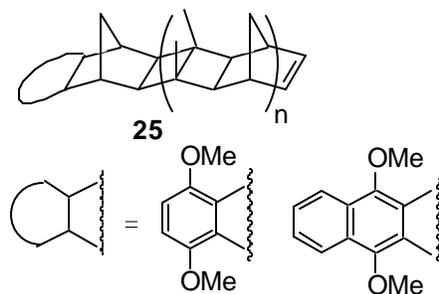


### 1.4.2 Proposed Research

Our approach is based on these literature results and has some new ideas. First, we intended to use the  $T_2$  state of either anthracene or phenanthrene as the triplet energy donor. Second, the chromophores used so far in the norbornylogous system are fused to the rigid framework. In compounds **12-14** and **17** that we planned to synthesize, however, the acceptor chromophores are connected to the bridge via a  $\sigma$ -bond or a double bond, thus providing us an opportunity to study how the energy transfer is affected by the change in the donor-acceptor orientation.

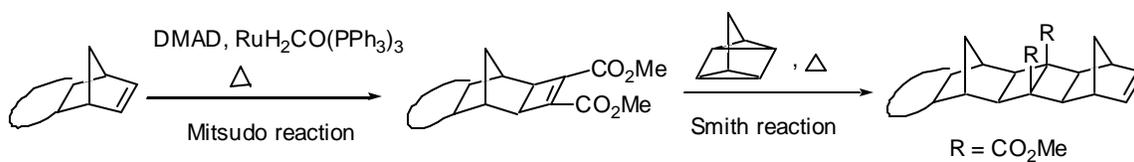
### 1.5 Synthetic Strategies for Bridge Construction

One of the key intermediates in the synthesis of the norbornylogous system used in most of the cited literature is compound **25**.



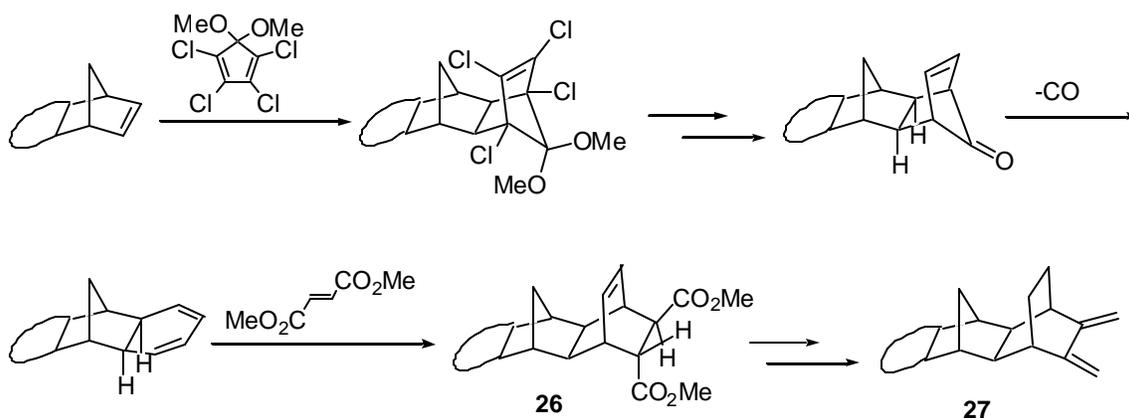
The linearly fused bridges were extended through execution of the tandem Mitsudo<sup>[25]</sup> and Smith<sup>[26]</sup> reactions (Scheme 1-3).

**Scheme 1-3**



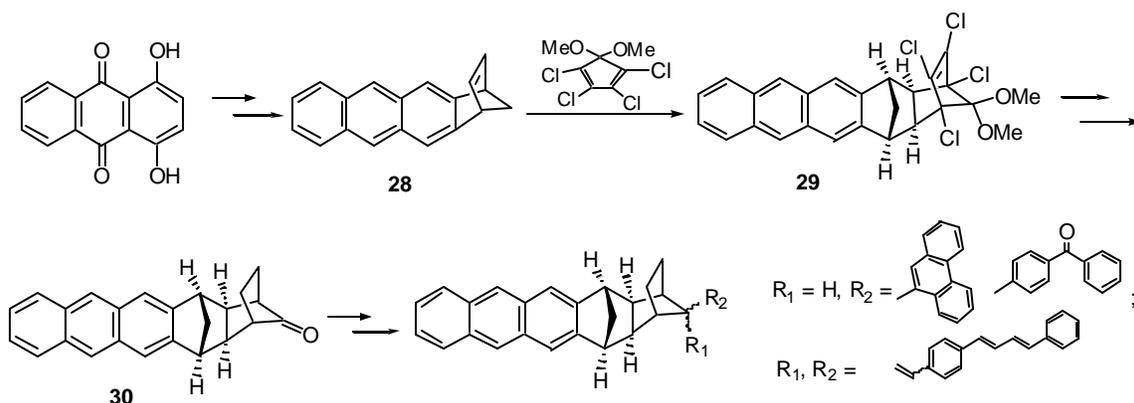
Another key intermediate is compound **27** (Scheme 1-4). Its synthesis involves the Diels-Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with the terminal double bond of the bridge. Reductive dechlorination followed by deketalization gives the thermally labile 7-norbornenone system, which readily lose carbon monoxide to give the 1,3-cyclohexadiene system. Further Diels-Alder reaction with dimethyl fumarate forms adduct **26**, from which the bis(methylene) functionality may be obtained via reduction of the ester groups, bistosylation of the resulting bis(hydroxymethylene) compound and subsequent bisdehydratosylation.

**Scheme 1-4**



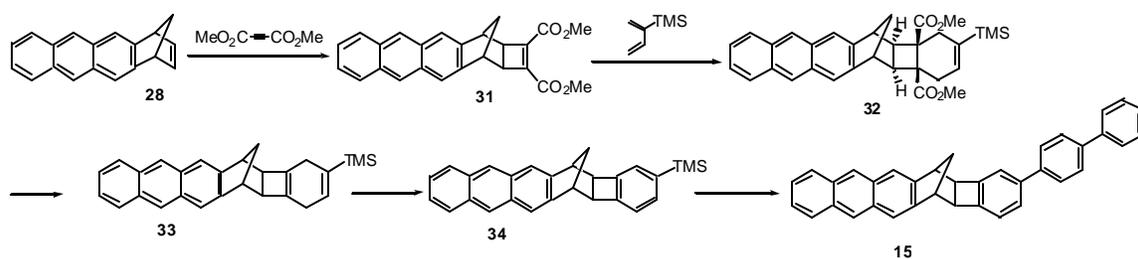
For the norbornyl bridge system that I worked on, the key intermediate is **28** (Scheme 1-5). It can be synthesized from commercially available quinizarin through several steps. Diels-Alder reaction of **28** with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene gives the adduct **29**. Reductive dechlorination followed by hydrogenation and deketalization forms compound **30**. For the phenanthrene or benzophenone chromophores, the corresponding target compounds can be obtained by a Grignard reaction and the subsequent reduction of the hydroxyl group to hydrogen. The polyphenylene chromophore can be attached to the bridge framework by a Horner-Wittig reaction.

### Scheme 1-5



In the target compound **15** (Scheme 1-2), the *p*-terphenyl chromophore is connected to anthracene through a different bridge system. To synthesize this compound, we devised another strategy. A [2+2] cycloaddition intermediate **31** could be obtained from the reaction of **28** with dimethyl acetylenedicarboxylate (Scheme 1-6). It could then undergo Diels-Alder reaction with 2-trimethylsilyl-1,3-butadiene. Subsequent hydrolysis of the ester, bisdecarboxylation and aromatization would give compound **34** which could then couple with *p*-bromobiphenyl to give the target product **15**.

### Scheme 1-6



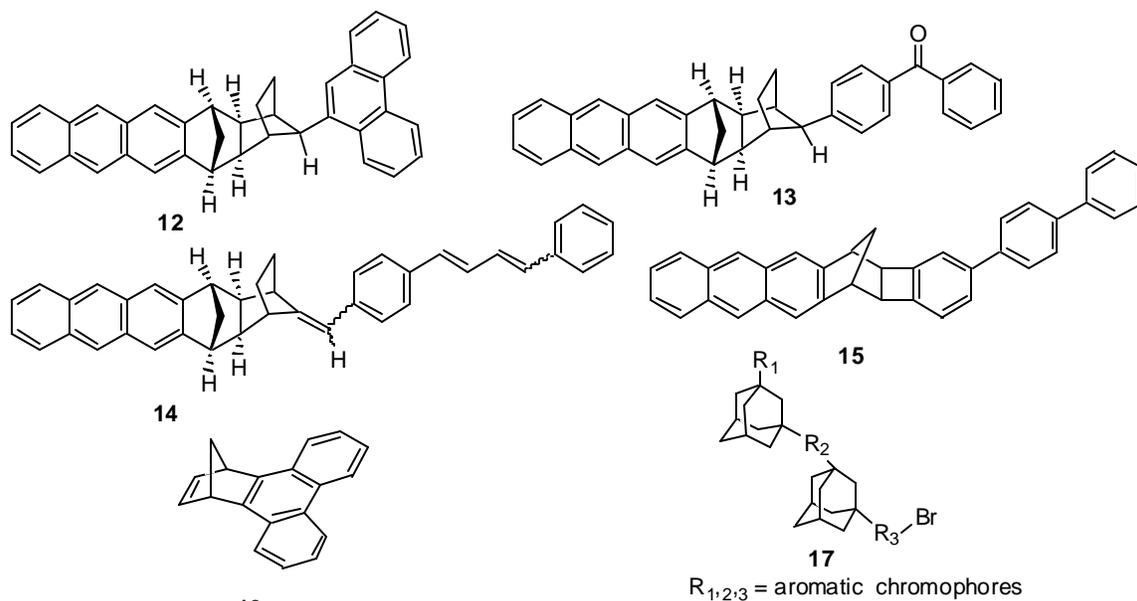
The above-mentioned synthetic strategies were used to obtain the target bichromophores **12-15** linked by linearly fused norbornyllogous units. Meanwhile, other

synthetic methodologies to make trichromophores **17** with adamantane linkages were studied. The results will be presented and discussed in the following chapter.

## Chapter 2 Syntheses of Rigidly Linked Polychromophores

The target compounds were put forward based on the rational design discussed in chapter 1. Their structures are listed in Scheme 2-1. The synthetic efforts to make these compounds are discussed in this chapter, arranged by the type of bridges connecting the chromophores.

Scheme 2-1



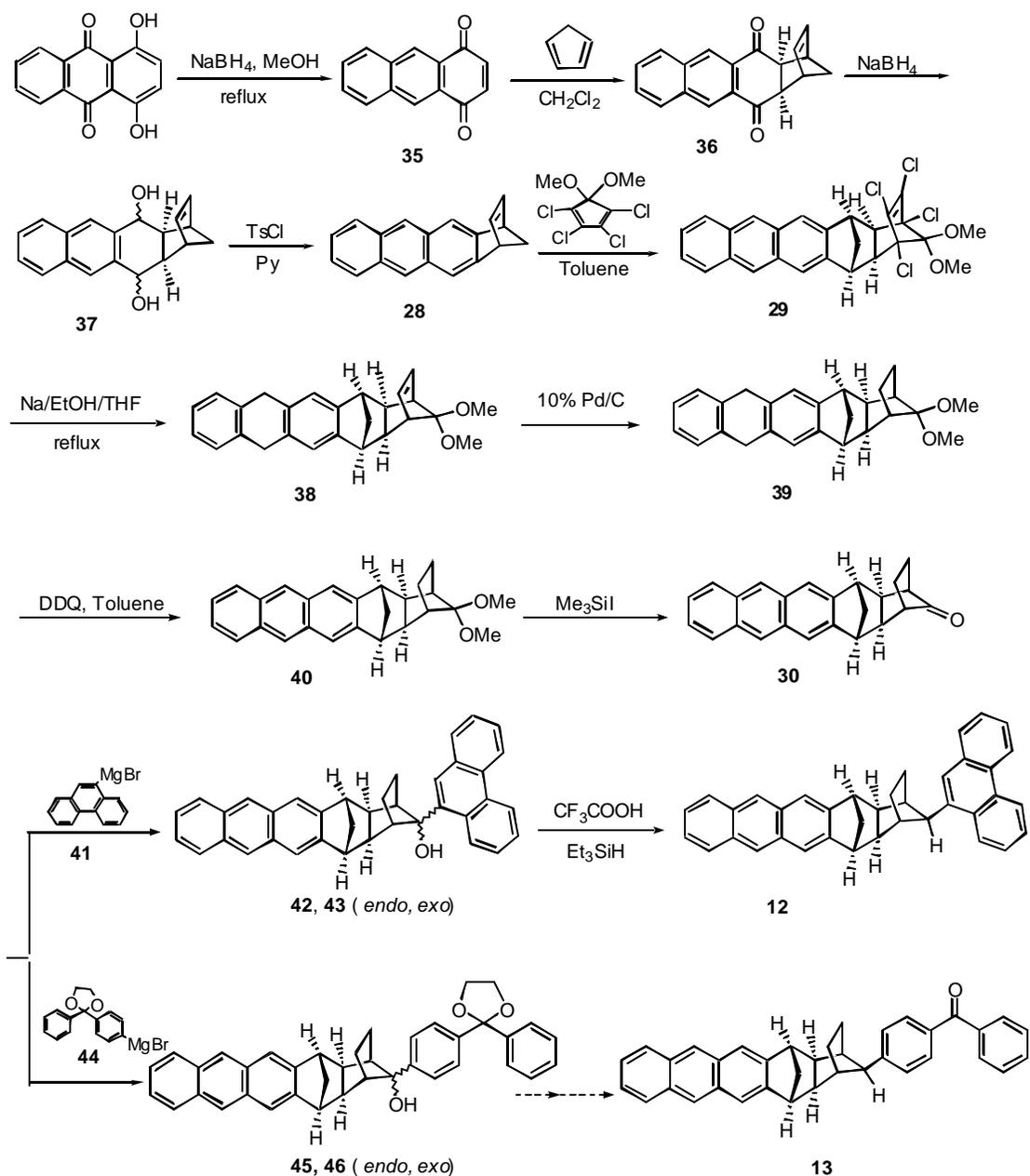
### 2.1 Syntheses of Bichromophores with Norbornylogous Bridges

The common feature of compounds **12-15** is that they all contain norbornylogous bridges. Their syntheses are described in the following sections.

## 2.1.1 Syntheses of Anthracene Annulated Norbornyl Compounds with Polynorbornyl Bridges

In compounds **12** and **13**, the acceptor chromophores are connected to the bridge via a  $\sigma$  bond. The synthesis routes to **12** and **13** is shown in Scheme 2-2.

Scheme 2-2



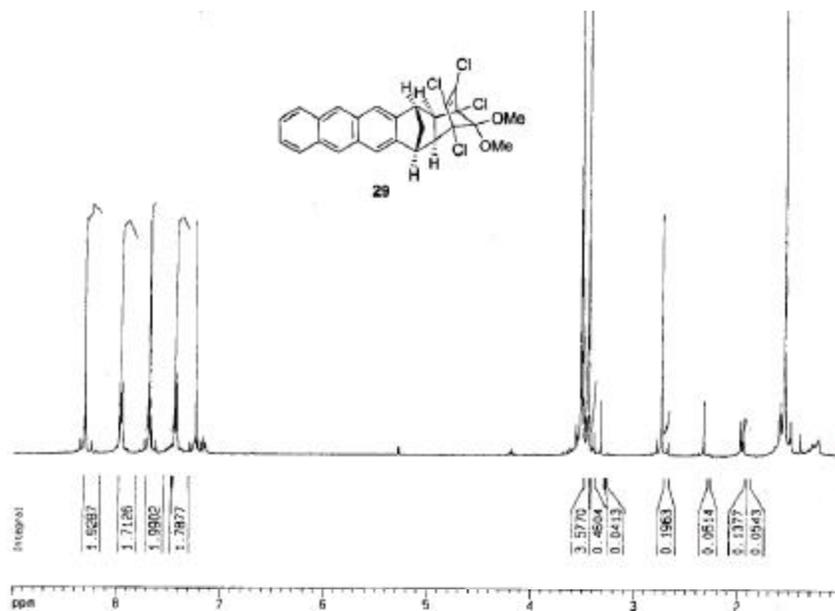
1,4-Anthraquinone (**35**) was made from quinizarin according to the literature procedure.<sup>[27]</sup> When quinizarin and NaBH<sub>4</sub> were heated to reflux in MeOH for 24 h, **35** was obtained in a yield of 85%. Diels-Alder reaction with cyclopentadiene gave **36** as the product. The reaction was first tried in EtOH. The whole system was a suspension due to the low solubility of the starting material **35** in EtOH. The reaction did not go to completion after being stirred at 0 °C for 2 days. When CH<sub>2</sub>Cl<sub>2</sub> was used as solvent, a clear solution was formed, and the reaction was complete in 7 h with a yield of 72%. The reaction was stereoselective, the endo-addition product being the major product according to NMR analysis.

Reduction of **36** with NaBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> and MeOH went smoothly to give **37** in 100% yield. It has been reported that *p*-TsCl can be used to dehydrate the alcohol to the aromatic product.<sup>[28]</sup> By heating **37** with *p*-TsCl in dry pyridine at 70 °C for 24 h, **28** was obtained in a yield of 80%. Compound **28** is an important intermediate for all three bichromophores with norbornylogous bridges described below.

When **28** was refluxed with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene in toluene in the presence of a small quantity of hydroquinone, compound **29**, which was shown by NMR to be an *endo*-addition product, was obtained in a yield of 64%. The following dechlorination step was achieved by treating **29** with sodium metal in EtOH and THF.<sup>[29]</sup> The NMR spectra of compound **29** and the dechlorination product **38** are given in Figure 2-1. It clearly shows that a new peak at 6.06 ppm in **38** represents the double bond protons of the norbornene ring. Also, the singlet peak at 8.30 ppm corresponding to the protons at C-9 and C-10 of the anthracene ring in **29** disappears in

the spectrum of **38**. This indicates that under the reaction conditions, not only the chlorine atoms were removed but also that the anthracene ring had been reduced at C-9 and C-10.

(a)



(b)

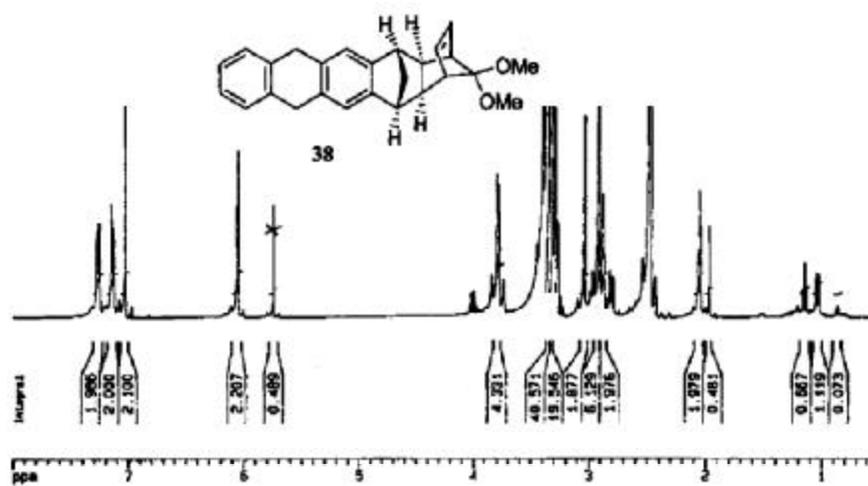


Figure 2-1. (a)  $^1\text{H}$  NMR of compound **29**; (b)  $^1\text{H}$  NMR of compound **38**.

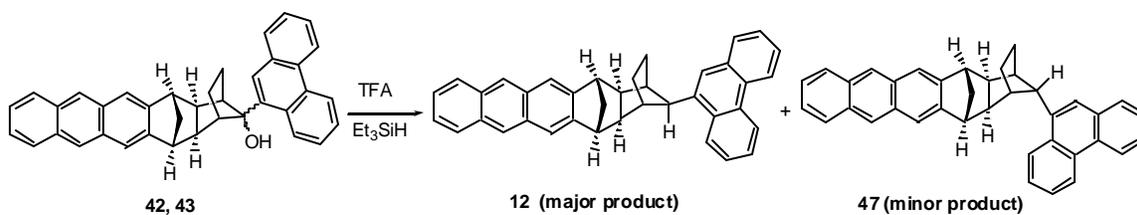
Reduction of the double bond of **38** with 10% Pd/C followed by treatment of the product with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene gave the intermediate **40**. Then the ketal group was removed with iodotrimethylsilane in  $\text{CHCl}_3$ <sup>[30]</sup> to give **30** in 88% yield. An alternative deketalization process used 96% formic acid in THF,<sup>[31]</sup> which didn't give as good a conversion of the starting material.

The intermediate **30** could undergo Grignard reaction with various aromatic halides to give the bichromophores with different aromatic groups, such as phenanthrene or a protected benzophenone, attached to the polynorbornyl framework via a  $\sigma$  bond.

To make alcohols **42** and **43**, a 1 M solution of phenanthrylmagnesium bromide **41** in diethyl ether/benzene (1:1) was first made according to the literature procedure.<sup>[32]</sup> Although this reagent is moisture sensitive, we found that it could be stored under  $\text{N}_2$  at rt for up to a week. The reaction of phenanthrylmagnesium bromide with **30** went smoothly at 55°C overnight. Two product isomers, **42** and **43**, with the hydroxyl group *endo* or *exo* position, were obtained in a 3:1 ratio. The overall yield was 87%. However, it is hard to assign the *endo* and *exo* configuration to the isomers from the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra.

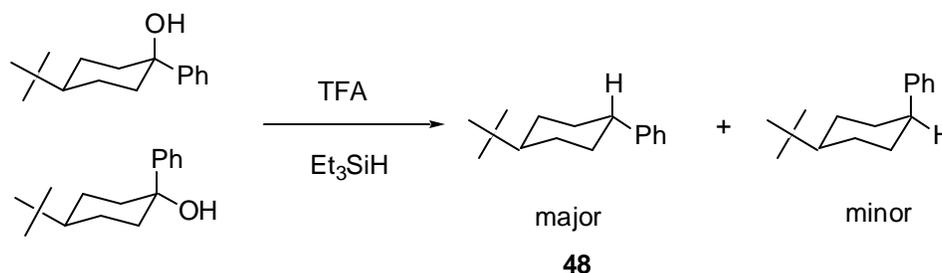
One of the most commonly used conditions for direct reduction of the hydroxyl group is to use TFA and  $\text{Et}_3\text{SiH}$ .<sup>[33]</sup> When TFA was added to the suspension of **42** and  $\text{Et}_3\text{SiH}$  in  $\text{CH}_2\text{Cl}_2$ , the color of the system quickly changed from pale yellow to pink. The color was discharged after 5 min. Only one isomer **12** was obtained as the major product. The reduction of the mixture containing both isomers (**42** and **43**) was also carried out under the same conditions, with the same isomer **12** being the major product (Scheme 2-3).

### Scheme 2-3



These results suggested that the product distribution is independent of the configuration of the starting alcohols. Similar results were reported by Carey and Tremper when they investigated the reduction of *cis*- and *trans*-4-butyl-1-phenylcyclohexanol with TFA and Et<sub>3</sub>SiH. Starting with either *cis*- or *trans*-alcohol, the major product is the thermodynamically favored *exo* isomer **48** in both cases (Scheme 2-4).<sup>[33]</sup>

### Scheme 2-4



The stereochemistry of the major product **12** was assigned from the <sup>1</sup>H NMR data. The <sup>1</sup>H NMR spectra of the major isomer **12** and the mixture of both isomers are very similar. The biggest difference in the two isomers is the chemical shift for the most downfield proton H<sub>a</sub> in the phenanthrene ring. Table 2-1 gives the chemical shift of H<sub>a</sub> in the major isomer **12**, minor isomer **47** and a model compound **49**.

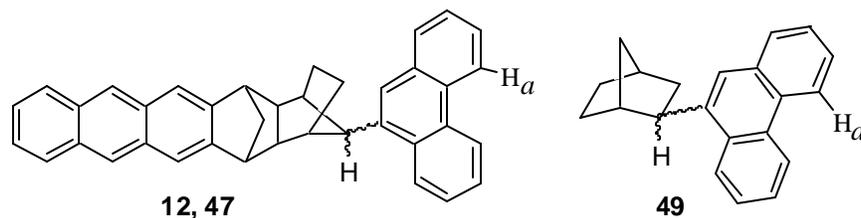


Table 2-1. Chemical Shifts of  $H_a$  (ppm) in Compounds **12**, **47** and **49** Obtained From

$^1\text{H}$  NMR Data

Compound	$H_a$ (ppm)
<b>12</b>	8.64
<b>47</b>	8.24
<b>49</b>	8.78

As shown in Table 2-1, in the major isomer **12**, the chemical shift of  $H_a$  (8.64 ppm) is within the normal range, compared to the model compound **49** (8.78 ppm). In the minor isomer **47**, however, it moves far upfield to 8.24 ppm. These results suggested that the  $H_a$  of the phenanthrene ring in the minor isomer might be located in the shielding region of the anthracene. The ring-current effect would then cause the  $H_a$  signal to move upfield. This analysis would be reasonable if the two aromatic rings are close to each other in the space. So the structure of the minor isomer **47** was tentatively assigned to be *endo*. The major isomer **12** was then assigned to be *exo*, and its spectrum is shown in Figure 2-2.

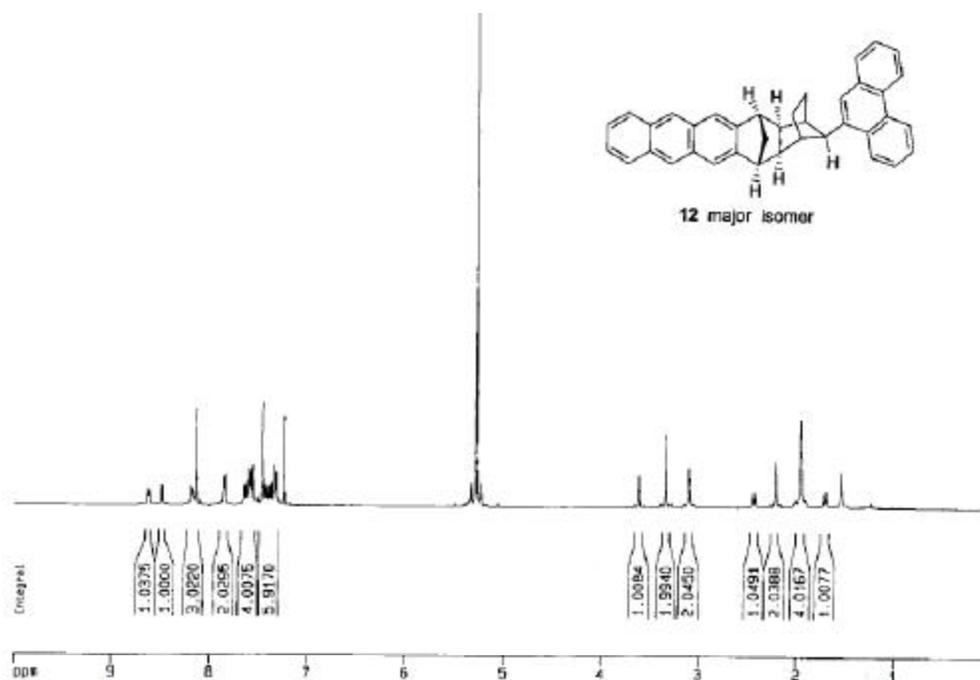
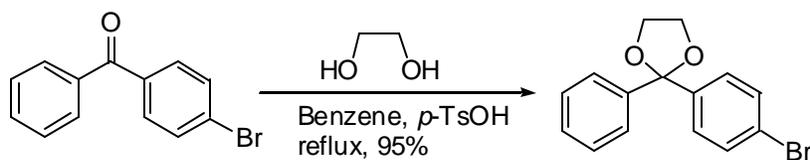


Figure 2-2.  $^1\text{H}$  NMR spectrum of compound **12**.

To synthesize **13**, we need to protect the carbonyl group in the 4-bromobenzophenone first. Ethylene glycol was chosen as the protecting group and the protection was carried out using the literature procedure.<sup>[34]</sup> The water formed was removed by azeotropic distillation. 2-(4-Bromophenyl)-2-phenyl-1,3-dioxolane was obtained in a yield of 95% (Scheme 2-5).

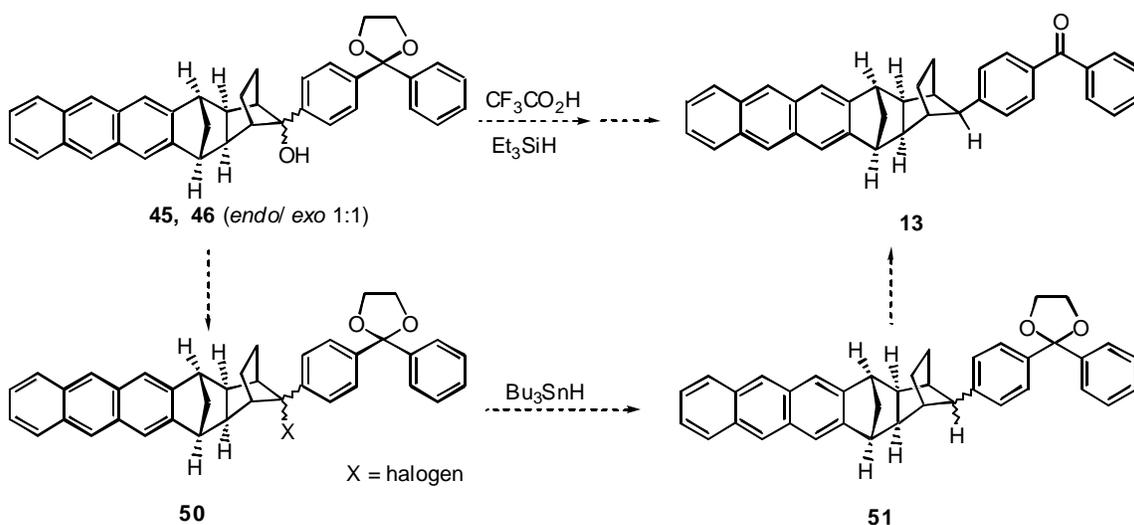
#### Scheme 2-5



The corresponding Grignard reagent **44** was synthesized using the literature method.<sup>[35]</sup> Its reaction with **30** gave the two product isomers **45** and **46** in a ratio of about 1:1. But we were not able to assign the stereochemical structures based on <sup>1</sup>H NMR and <sup>13</sup>C NMR data.

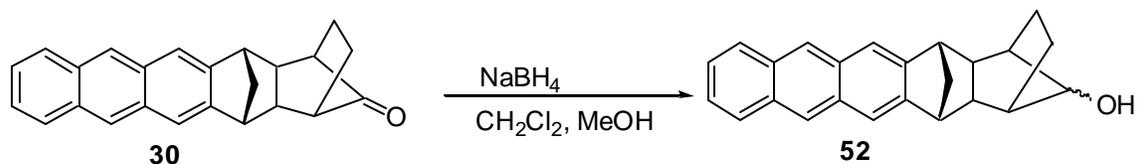
When TFA and Et<sub>3</sub>SiH were used for the direct reduction of **45** or **46**, almost all the starting material was recovered. An alternative way to make **13** is shown in Scheme 2-6. The hydroxyl group could be converted to a halogen and the halogen replaced by hydrogen using tributyltin hydride as the reducing reagent to give compound **51**. The ketal group could then be deprotected using standard methods.<sup>[36]</sup> Unfortunately we were not able to try this route (Scheme 2-6).

Scheme 2-6



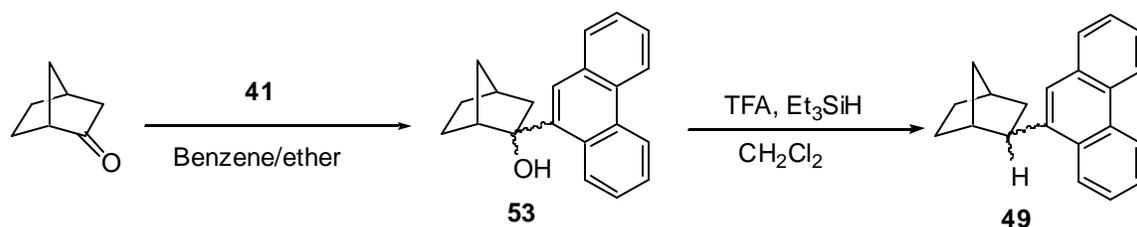
Two monochromophoric model compounds were synthesized for comparison with the bichromophores in the photochemical study. Compound **52** was obtained by reduction of the carbonyl group in **30** with NaBH<sub>4</sub> (Scheme 2-7).

Scheme 2-7



Compound **49** was made from the direct reduction of **53**, which was synthesized from the Grignard reaction of 9-phenanthrylmagnesium bromide **41** and norcamphor (Scheme 2-8).

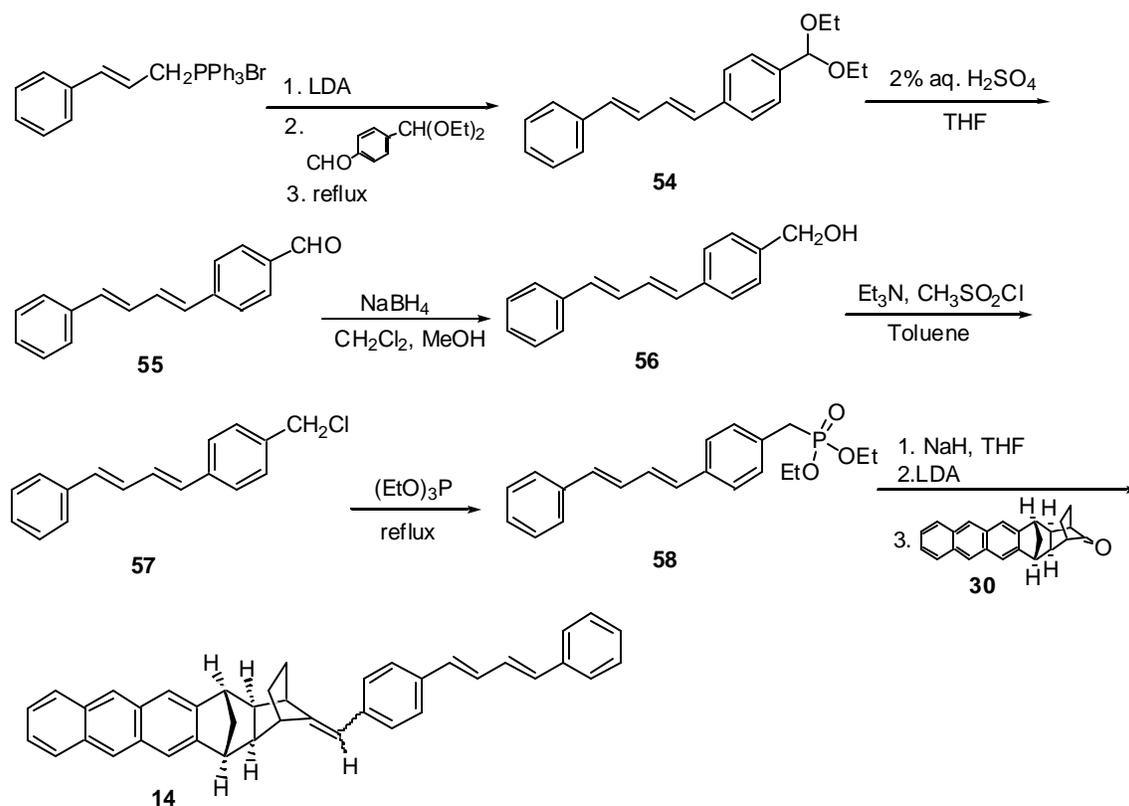
Scheme 2-8



### 2.1.2 Synthesis of a Bichromophore Containing a Polynorbornyl Bridge

The synthesis route to compound **14** is shown in Scheme 2-9.

### Scheme 2-9



Compound **54** was obtained in a yield of 42% by treating cinnamyltriphenylphosphonium bromide with LDA, followed by 36 h of heating to reflux with 4-(diethoxymethyl)benzaldehyde. Removal of the ketal group with 2% aq. H<sub>2</sub>SO<sub>4</sub> gave **55** in 99% yield. Aldehyde **55** was then treated with NaBH<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> and MeOH to give **56**. The yellow suspension of **56** in toluene was heated with CH<sub>3</sub>SO<sub>2</sub>Cl and Et<sub>3</sub>N at 70 °C for 24 h to give **57** in a yield of 84%. After the solution of **57** in triethyl phosphite was heated to reflux for 26 h, compound **58** was obtained in a yield of 45%.

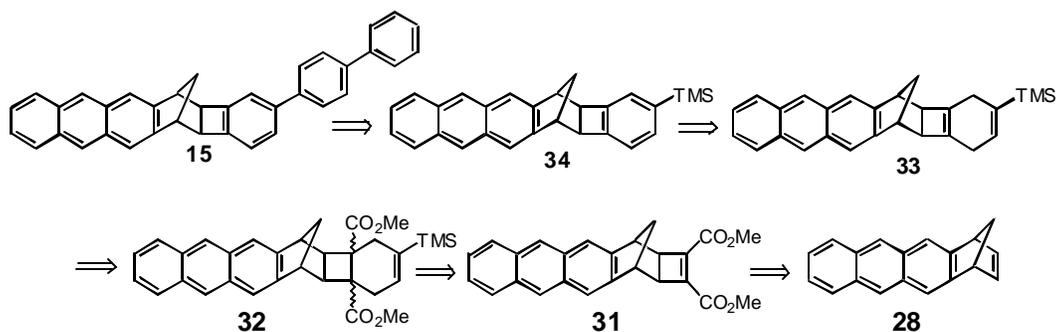
The final step was a Horner-Wittig reaction. The ylide intermediate was formed by treating **58** with NaH in THF followed by stirring with LDA. Compound **30** was then

added and the mixture was slowly warmed up to rt. The reaction was complete after 14 h of heating to reflux. The target product **14** was obtained in a yield of 95%.

### 2.1.3 Partial Syntheses of An Anthracene Annulated Chromophore with a Norbornane-Cyclobutane Bridge and a *p*-Terphenyl Acceptor

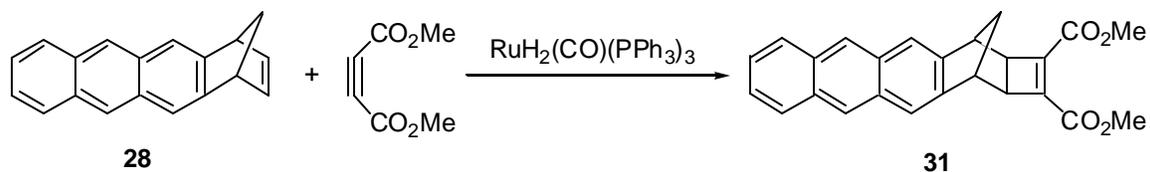
We were also interested in making bichromophores **15** with anthracene as the energy donor and *p*-terphenyl as the energy acceptor. The bridge used in this molecule is different from the linearly fused polynorbornyl units we synthesized before. A retrosynthetic analysis is presented in Scheme 2-10.

Scheme 2-10



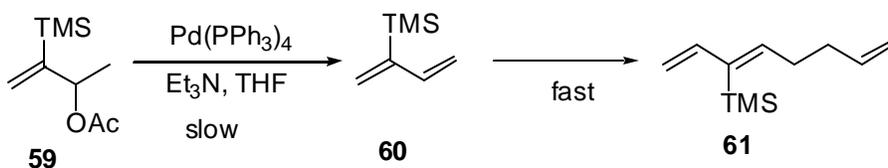
When the intermediate **28** was treated with dimethyl acetylenedicarboxylate in the presence of carbonyldihydridotris(triphenylphosphine)ruthenium, it underwent the [2+2] cycloaddition shown in Scheme 2-11.<sup>[37,38]</sup>

### Scheme 2-11



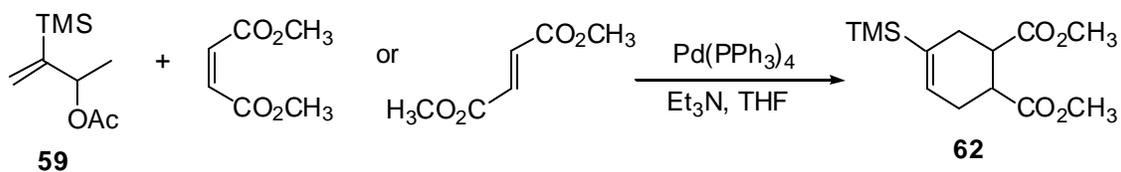
The next step was Diels-Alder reaction of **31** with 2-trimethylsilyl-1,3-butadiene. 2-Trimethylsilyl-1,3-butadiene is a useful reagent in the construction of functionalized six-membered rings. However, it is not commercially available, and is not stable enough for long term storage. It is usually synthesized under quite harsh conditions.<sup>[39-41]</sup> In 1986, when Trost and coworkers attempted to generate 2-trimethylsilyl-1,3-butadiene by palladium-catalyzed elimination from **59**, they obtained product **61** from dimerization of the desired diene (Scheme 2-12). It was suggested that the desired diene **60** was formed but its conversion to **61** occurred faster than its formation under the reaction conditions.<sup>[42]</sup>

### Scheme 2-12



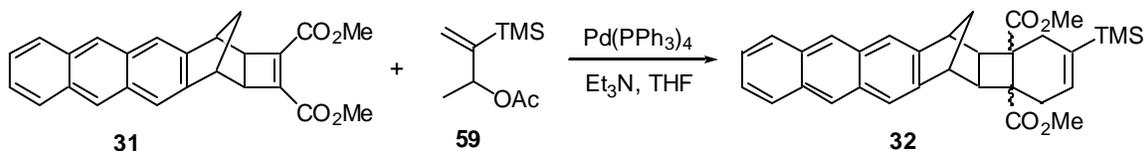
However, the intermediate diene could be smoothly intercepted by an equivalent amount of a dienophile during the elimination reaction to give a good yield of the desired Diels-Alder adduct **62** (Scheme 2-13).<sup>[42]</sup>

### Scheme 2-13



Using this method, we synthesized the key intermediate **32** (Scheme 2-14).

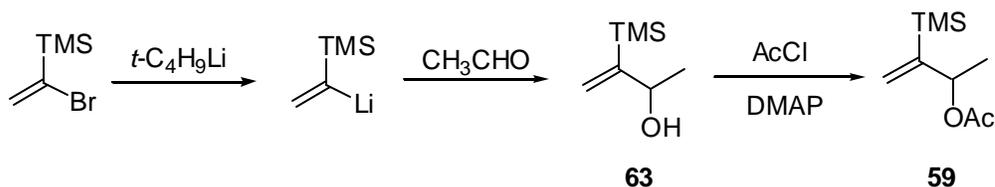
### Scheme 2-14



Compound **59** was synthesized using the literature method.<sup>[42]</sup> 1-

Trimethylsilylvinyllithium, generated from (1-bromovinyl)trimethylsilane by metal-halogen exchange, easily added to acetaldehyde to give compound **63**. Acetylation proceeded smoothly to give the allyl acetate **59** (Scheme 2-15). Its good stability permits it to be stored for long times and used as needed.

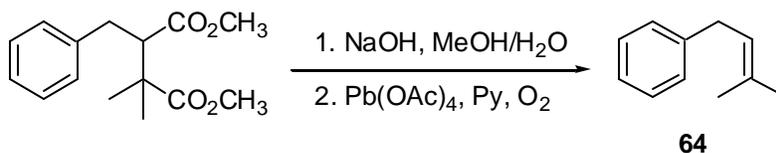
### Scheme 2-15



The following tandem palladium-catalyzed elimination-cycloaddition reaction to synthesize **32** was achieved by heating a mixture of **31** and **59** with 5 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> (generated in situ by reduction of palladium acetate with BuLi in the presence of PPh<sub>3</sub>) and Et<sub>3</sub>N in refluxing dioxane (Scheme 2-14). However, the conversion was low, probably because the dienophile was highly hindered. The yield was 30% based on the starting material consumed. The yield could probably be improved by switching to a solvent with a higher boiling point.

In 1992 Strunz and Ya reported that hydrolysis of a dimethyl 3-benzyl-2,2-dimethylsuccinate to the corresponding dicarboxylic acid, followed by bisdecarboxylation with lead tetraacetate, afforded the 1-phenyl-3-methyl-2-butene **64** (Scheme 2-16).<sup>[43]</sup>

**Scheme 2-16**



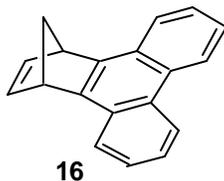
So we planned to synthesize compound **33** in a similar way (Scheme 2-10). Once **33** was made, we could use DDQ to establish the aromaticity of the benzene ring to synthesize **34**. The final step would be achieved by the coupling reaction of the phenyltrimethylsilane derivative **34** with 4-iodobiphenyl. Recent literature describes the coupling reaction of arylsiloxanes<sup>[44]</sup> and arylfluorosilanes.<sup>[45]</sup> Mowery and Deshong reported an alternative to Stille and Suzuki coupling, Pd(dba)<sub>2</sub>-catalyzed cross-coupling of phenyltrimethoxysilane with 4-iodotoluene in the presence of TBAF

(tetrabutylammonium fluoride) in DMF gave 40% of 4-methylbiphenyl.<sup>[44]</sup> This method might have been useful in our synthetic approach to the target compound **15**.

Unfortunately, we were only able to proceed as far as compound **32**.

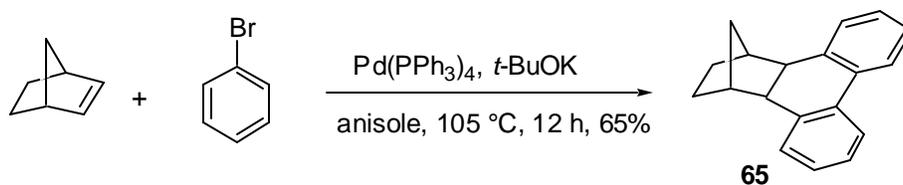
## 2.2 Attempted Syntheses of a Precursor to Phenanthrene-Containing Polychromophores

The target compound, 1,4-dihydro-1,4-methanotriphenylene, **16**, is a potentially versatile intermediate that can function as a building block for polychromophores containing a phenanthrene chromophore.



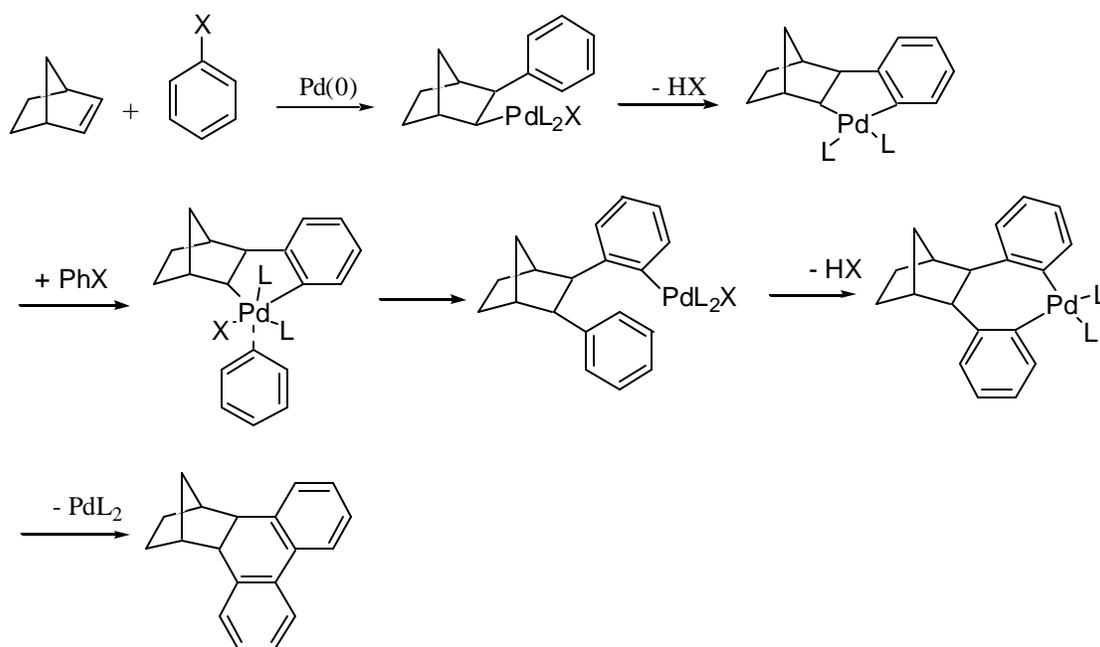
In 1985, Catellani and co-workers studied a palladium-catalyzed Heck-type coupling reaction that led to the formation of compound **65** (Scheme 2-17). They reported that when bromobenzene was treated with bicyclo[2.2.1]hept-2-ene in dry anisole in the presence of Pd (PPh<sub>3</sub>)<sub>4</sub> and *t*-BuOK at 105 °C, reaction took place readily to give *cis*, *exo*-1,2,3,4,4a,12b-hexahydro-1,4-methanotriphenylene **65** in 65% yield.<sup>[42]</sup>

### Scheme 2-17



The mechanism suggested is shown in Scheme 2-18.

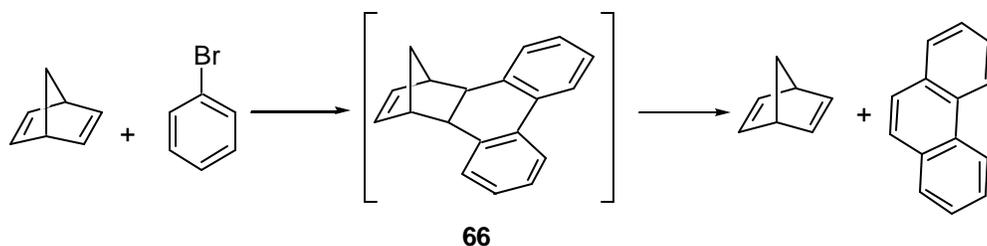
### Scheme 2-18



However, when we applied the same conditions to the reaction of bicyclo[2.2.1]hepta-2,5-diene with bromobenzene, we didn't obtain the target product **66**. The only product obtained was phenanthrene. The postulation was that compound **66** did

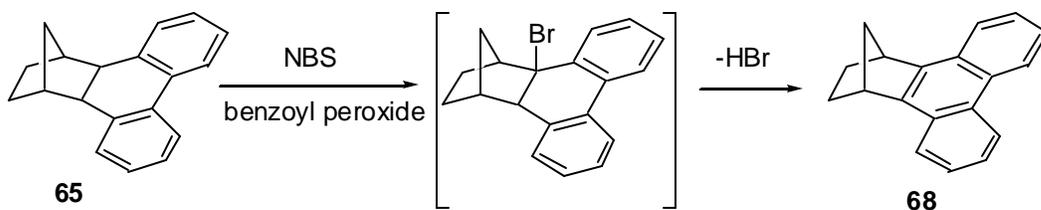
form in the reaction but it rapidly underwent retro-Diels-Alder reaction (Scheme 2-19). The entropy increase and the high stability of phenanthrene would have provided the driving force. We tried conducting the reaction at lower temperature but that still didn't permit us to isolate the desired product.

**Scheme 2-19**



We also tried to brominate the 2- or 3-position of **65**, intending to introduce the double bond by elimination of HBr. After being heated with NBS and benzoyl peroxide in  $\text{CCl}_4$  for 2 h, compound **65** was completely converted to a new product. The NMR spectrum suggested that the product was **68** (Scheme 2-20).

**Scheme 2-20**

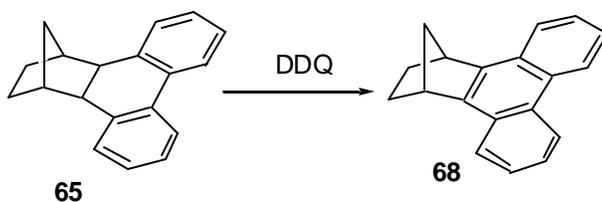


It was rationalized that instead of substituting at 2 or 3-position of **65**, the bromine radical attacked the benzyl position of the hydrophenanthrene, and then HBr was eliminated to give **68**. The stability of the intermediate radical would have provided the driving force.

Based upon the above results, we turned to the strategy of establishing the phenanthrene ring first. Once the phenanthrene ring had been formed, the molecule should have been relatively stable and we could then try to introduce the bromine atom as the precursor to the double bond in the norbornene ring.

DDQ has been reported to be a good reagent for the establishment of aromaticity. When **65** was heated to reflux with DDQ in benzene, compound **68** was obtained in a yield of 42% (Scheme 2-21).

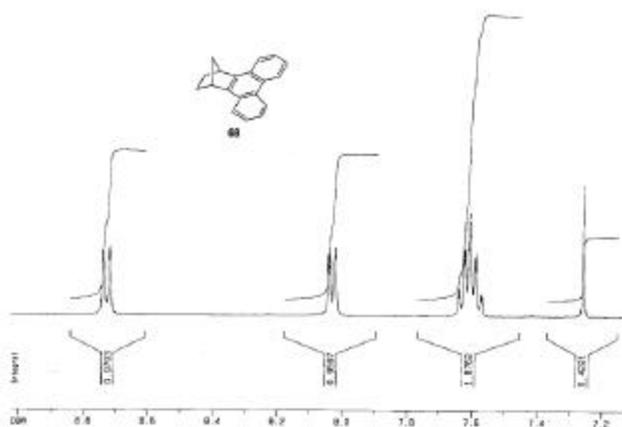
**Scheme 2-21**



We then tried both thermal and photochemical methods to introduce the bromine atom into the norbornene part of **68**. For the thermal reaction, a solution of **68**, NBS and benzoyl peroxide in  $\text{CCl}_4$  was heated to reflux. There was only little conversion of **68** after 18 h, judging from TLC. The  $^1\text{H}$  NMR spectrum of the reaction mixture shows distinct changes in the aromatic region (Figure 2-3). It seemed that the symmetry of the

phenanthrene ring had been affected in the product, probably due to the bromination in the phenanthrene ring; the NMR spectrum suggested the presence of more than one product. However, due to the difficulty of the separation, we were not able to isolate a pure product from the reaction mixture and determine its structure.

(a)



(b)

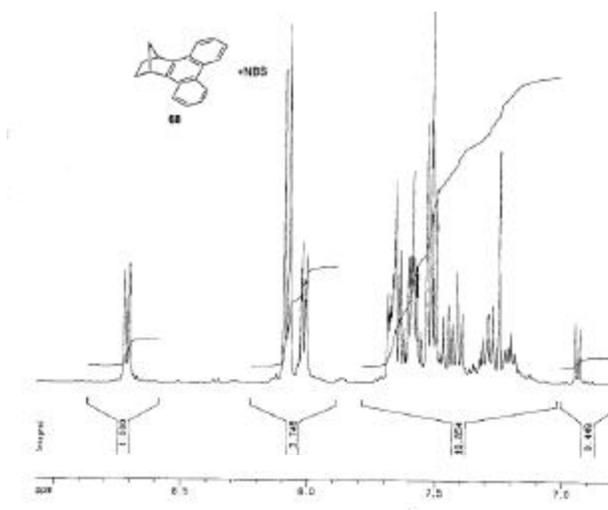


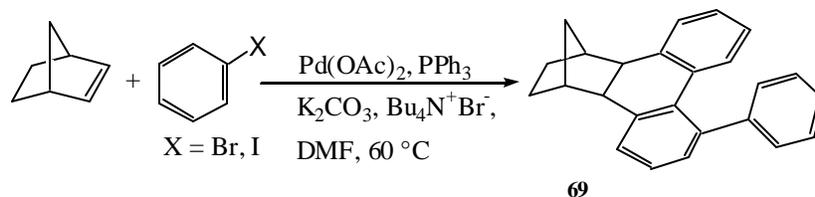
Figure 2-3. (a) Aromatic region of the  $^1\text{H}$  NMR spectrum of compound **68**; (b) Aromatic region of the  $^1\text{H}$  NMR spectrum of the reaction mixture after 18 h under thermal conditions, indicating that bromination has taken place in the aromatic ring.

For the photochemical reaction, a solution of **68** and NBS in  $\text{CDCl}_3$  was irradiated at 300 nm under Ar. The reaction was carried out at rt in a Pyrex NMR tube and was monitored by  $^1\text{H}$  NMR. The choice of the wavelength was based on the UV absorption spectra of **68** and NBS. As a control, **68** was first irradiated overnight in Pyrex in the absence of NBS at 300 nm. No change occurred, judging from the  $^1\text{H}$  NMR spectrum. Then **68** and NBS were irradiated at the same conditions. No detectable change occurred after 14 h, judging from the  $^1\text{H}$  NMR spectrum.

We then tried to introduce a hydroxyl group as a precursor for the double bond. 5-Norbornen-2-ol was allowed to react with bromobenzene under Catellani conditions. In order to see if 5-norbornen-2-ol was stable in the presence of *t*-BuOK, the two compounds were mixed and stirred at 70 °C for 1 h. No detectable change occurred. So bromobenzene and  $\text{Pd}(\text{PPh}_3)_4$  were added. Both starting materials disappeared after 7 h at 70 °C. However, the compound we got was not the desired one. We were not able to assign the structure from the NMR spectra alone.

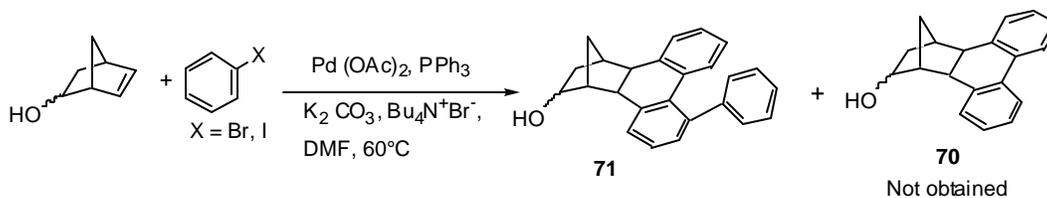
Alternative conditions for this type of coupling reaction were reported by Jeffery (Scheme 2-22). However, when  $\text{Pd}(\text{OAc})_2$  was used as the catalyst,  $\text{K}_2\text{CO}_3$  as the base in DMF or N-methylpyrrolidone (NMP) at 60-100 °C, and  $\text{Bu}_4\text{N}^+\text{Br}^-$  as a phase transfer catalyst, the reaction of norbornene with bromobenzene or iodobenzene gave only the 3:1 coupling product **69**.<sup>[48]</sup>

### Scheme 2-22



We tried to apply these conditions to make the target 2:1 coupling product **70** by maintaining the ratio of the halobenzene to 5-norbornen-2-ol at 2:1. No 2:1 coupling product was detected under these conditions (Scheme 2-23).

### Scheme 2-23



From NMR analysis it seemed that what we got was a 1:1 mixture of the *endo* and *exo* isomers of the 3:1 coupling product **71**. The 1:1 ratio of the mixture was derived from <sup>1</sup>H NMR. The two bridge protons in **71** are chemically nonequivalent and show up at very different chemical shifts as doublet signals with a typical geminal spin-coupling constant (*J*) of 10 Hz. As shown in Figure 2-4, one isomer of **71** has bridge protons that show up at 3.01 and 1.24 ppm with *J* = 10.4 Hz. The bridge protons of the other isomer

show up at 2.90 and 1.17 ppm with  $J = 9.4$  Hz. The relative integration for the bridge protons in two isomers is 1:1 (Figure 2-4).

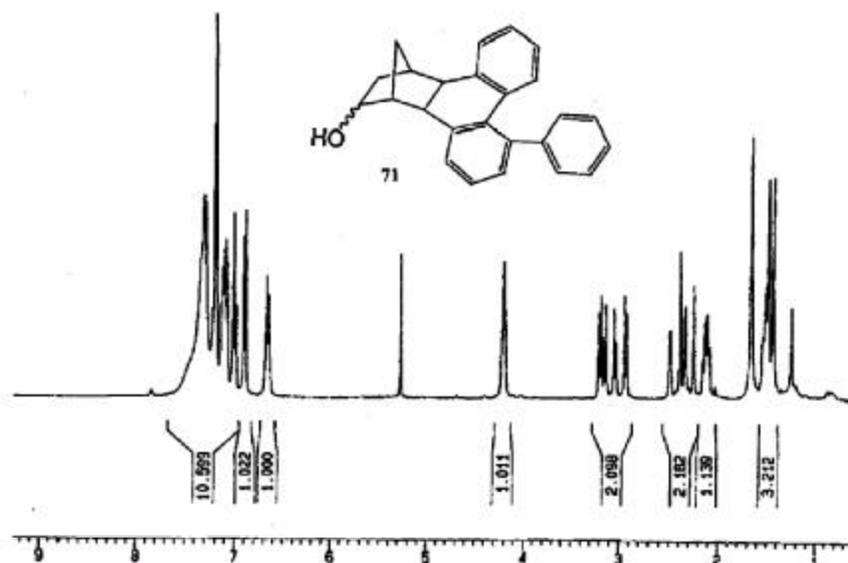
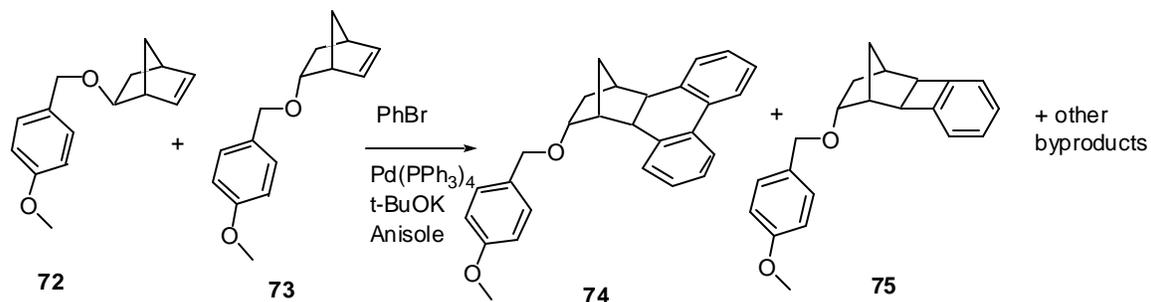


Figure 2-4. <sup>1</sup>H NMR spectrum of compound **71**.

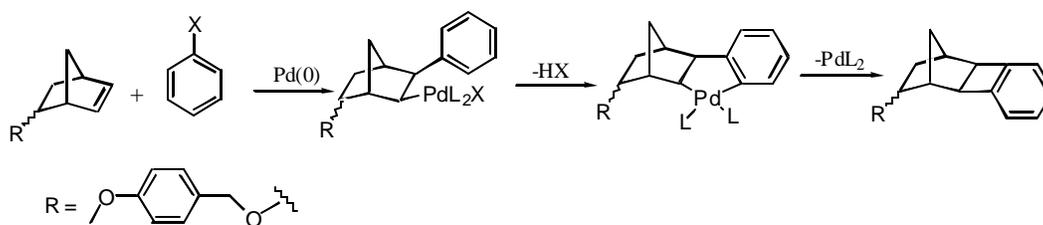
Since the reactivity of 5-norbornene-2-ol might be affected by the free hydroxyl group, we decided to protect it. A benzyl ether type of protecting group caught our attention because of its stability under basic conditions. Among the benzyl ethers, *p*-methoxybenzyl ether was chosen for our system because it can be easily removed by treatment with DDQ due to its low oxidation potential.<sup>[49]</sup> The commercially available 5-norbornene-2-ol is a mixture of *exo* and *endo* isomers (1:3.5). After being treated with *p*-methoxybenzyl chloride, it gave a mixture of the protected isomers **72** and **73** in the same ratio of 1:3.5 (Scheme 2-24). As shown in Scheme 2-24, the mixture of **72** and **73** underwent a quite complicated reaction when treated with bromobenzene under Catellani conditions.

### Scheme 2-24



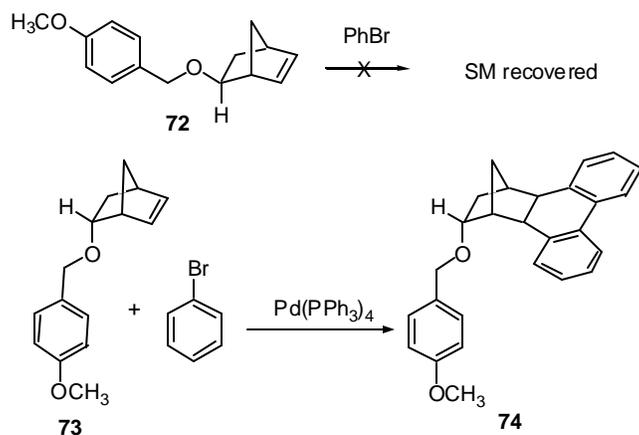
The target compound was isolated in 20% yield. Three main byproducts were also isolated from the reaction mixture. One was identified as the 4-membered ring derivative **75**; a possible pathway to it is suggested in Scheme 2-25.

### Scheme 2-25



We interpreted the low yield as being due to the poor reactivity of the *endo* isomer resulting from the steric hindrance. In order to make a comparison, the reaction of **72** and **73** were each tried separately. Surprisingly, we found out that the *exo* isomer **72** didn't react at all, even at different temperatures. The starting material was recovered. The *endo* isomer **73** could be converted completely under optimal conditions. So the stereochemistry of the product **74** was assigned to be *endo* (Scheme 2-26).

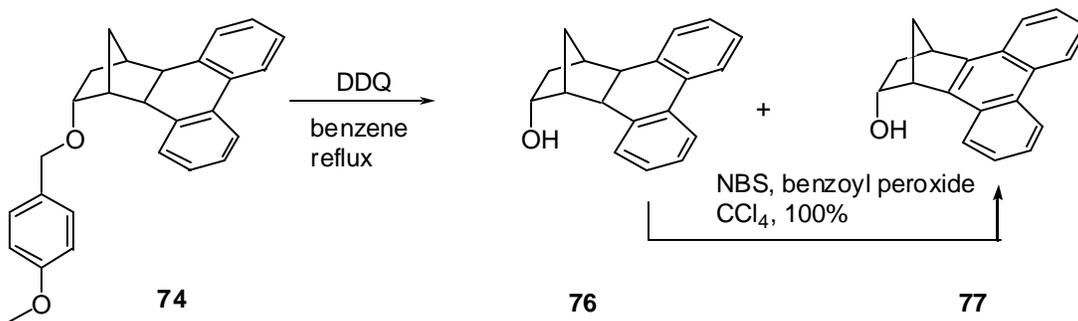
### Scheme 2-26



However, the reaction was still not clean or reproducible; a maximum yield of 58% was obtained after dozens of trials. We tried other protecting groups such as methoxymethyl ether (MOM) or ethoxymethyl ether (EOM), hoping the reaction could be improved by changing to different protecting groups. But that didn't help.

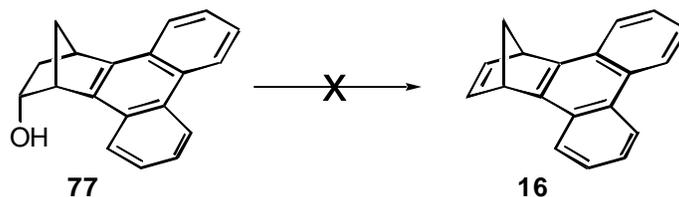
When **74** was treated with DDQ, two products (**76** and **77**) were obtained in a ratio of 1:1 (Scheme 2-27). That indicated that the cleavage of the *p*-methoxyphenyl ether was a faster process than the oxidation of the dihydrophenanthrene ring. However, **76** can be quantitatively converted to the desired product **77** simply by treatment with NBS and benzoyl peroxide under thermal conditions.

### Scheme 2-27



The final step, dehydration, turned out to be a big challenge (Scheme 2-28). The conditions we tried are shown below.

**Scheme 2-28**



Conditions tried:

- ? 85% H<sub>3</sub>PO<sub>4</sub>
- ? concentrated H<sub>2</sub>SO<sub>4</sub>, toluene
- ? 85% H<sub>3</sub>PO<sub>4</sub>, toluene
- ? *p*-TsCl, pyridine, rt  $\nrightarrow$  80 °C  $\nrightarrow$  reflux

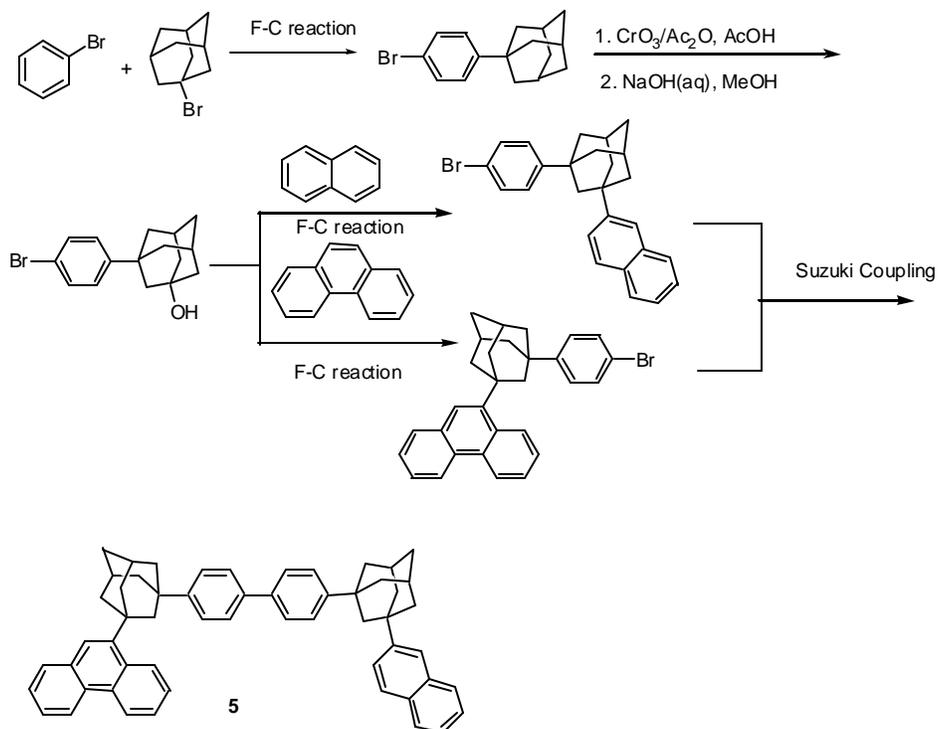
Under the acidic conditions, the starting material **77** usually was gone after being heated at 110 °C from a few min to 1 h. But the compound we obtained was not the desired one. It was hard to assign the structure simply based on the NMR data. Under *p*-TsCl and pyridine condition, no detectable change occurred even at various temperatures. The starting material **77** was recovered.

### 2.3 Preliminary Study of the Syntheses of Adamantane-Linked Trichromophores

Previous research done in our lab showed that compound **5**, a trichromophore linked by adamantane bridges, is a useful model for the photochemical study of intramolecular triplet-triplet energy transfer.<sup>[7]</sup> It was synthesized from 4-bromophenyl-

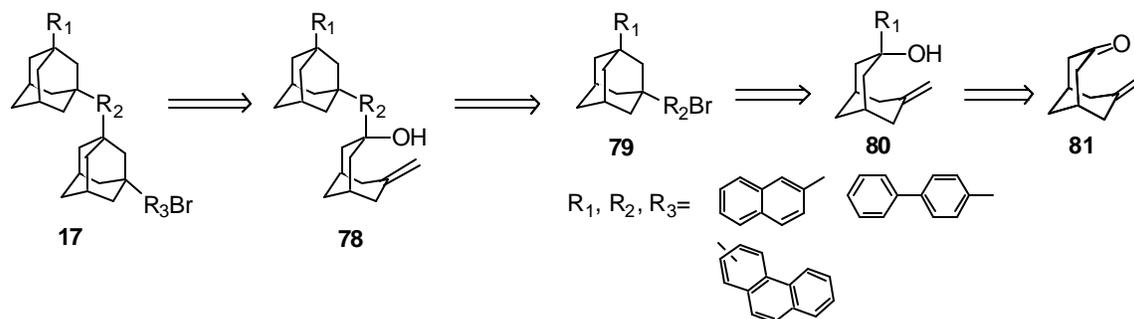
substituted adamantanol (Scheme 2-29). However, the methodology restricted the chromophore sandwiched between two adamantane rings to the biphenyl group only.

**Scheme 2-29**



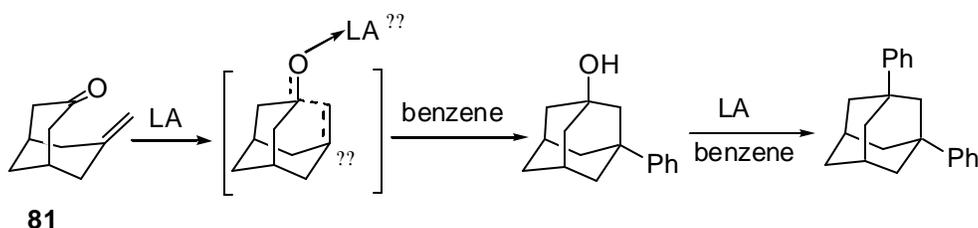
We explored a possible general method to synthesize trichromophores **17**, where  $\text{R}_1, \text{R}_2, \text{R}_3$  may be various aromatic rings. The proposed retrosynthesis is shown in Scheme 2-30. The key reactions are a Grignard reaction and a tandem transannular cyclization/Friedel-Crafts reaction.

### Scheme 2-30



The intermediate **81** is well known to undergo transannular cyclization and can react with various nucleophiles such as amines, phenols, and thiols to afford the adamantane derivatives.<sup>[50]</sup> Olah reported in 1990 that the Lewis acid mediated reaction of **81** in the presence of benzene gave 1,3-diphenyladamantane as the major product (Scheme 2-31; LA stands for Lewis acid).<sup>[51]</sup>

### Scheme 2-31

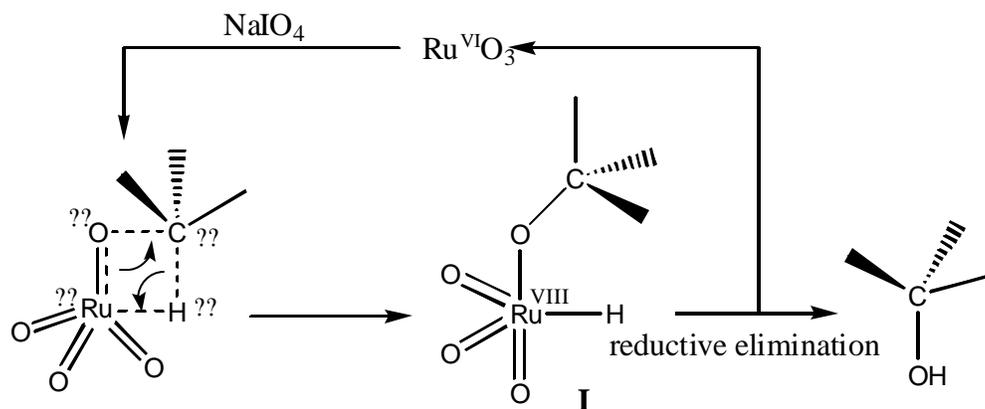


This methodology was used in our retrosynthetic design. Reaction of **81** with a Grignard reagent or organolithium reagent derived from  $R_1Br$  would give the intermediate **80**, which would then undergo the tandem transannular cyclization/ Friedel-Crafts reaction with  $R_2Br$  to give **79**. Different  $R_2$  group could be attached to the

adamantane ring in this way. Repeating the above two steps would lead to the target trichromophores. The advantage of this design is that we would have more flexibility in putting different R groups into the trichromophores.

We started with the synthesis of 1,3-adamantanediol. In 1992, Tenaglia reported the oxyfunctionalization of nonactivated C-H bonds using  $\text{RuO}_4$  as catalyst, which was generated in situ by oxidation of ruthenium chloride hydrate with  $\text{NaIO}_4$  as the oxidizing agent in the solvents mixture  $\text{CH}_3\text{CN}/\text{CCl}_4/\text{H}_2\text{O}$  (2:2:3). A concerted mechanism was suggested (Scheme 2-32).<sup>[52]</sup>

**Scheme 2-32**

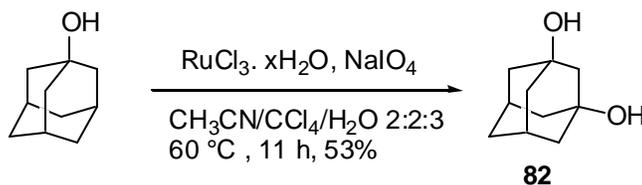


As shown in scheme 2-32, the C-H bond was first polarized by the electrophilic ruthenium tetroxide so that a partial positive charge developed on the carbon, which favored the insertion of the oxoruthenium group into the C-H bond. The alkoxyhydridotrioxoruthenium intermediate **I** thus formed underwent a reductive

elimination to yield the corresponding alcohol and ruthenium trioxide, which was reoxidized back to RuO<sub>4</sub> by NaIO<sub>4</sub>.

We applied this method to synthesize 1,3-adamantanediol **82** from adamantanol (Scheme 2-33). In the first trial, we obtained a very low yield of the target compound. It was found later that the product was much more soluble in water than in many organic solvents. After modification of the aqueous layer workup, compound **82** was obtained in 53% yield.

**Scheme 2-33**



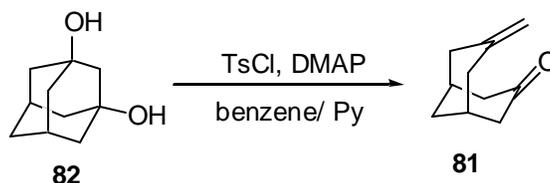
The reaction was carried out under mild conditions and was regioselective. Only the oxidation of the tertiary carbon was observed. This result was explained by the known order of the relative reactivity of C-H bonds to RuO<sub>4</sub>: CH > CH<sub>2</sub> > CH<sub>3</sub>.<sup>[53]</sup> However, increasing the reaction time led to a higher percentage of 1,3,5-adamantanetriol in which two tertiary C-H bonds were oxidized.

Compound **81**, a versatile intermediate for the synthesis of the functionalized adamantanes,<sup>[51, 54]</sup> is usually synthesized from 1,3-dibromoadamantane in a steel bomb under harsh conditions.<sup>[55]</sup>

A Japanese research group reported in 1996 that when 1,3-adamantanediol was heated with *p*-TsCl in benzene and Py, it gave **81** in 88% yield.<sup>[56]</sup> However, when we tried the same reaction several times, no desired compound was detected. Since 4-

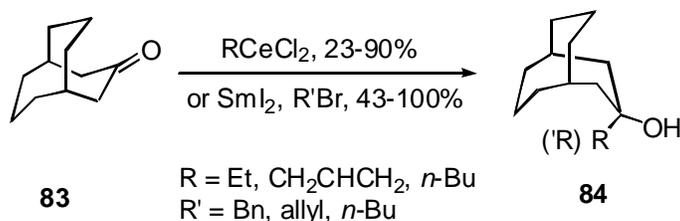
dimethylaminopyridine (DMAP) is widely used to accelerate the acylation reaction, we used it as a catalyst and obtained the target compound in a yield of 60% (Scheme 2-34).

**Scheme 2-34**



We were confronted with difficulty in introducing the R group into **81** by means of a Grignard reaction. It was reported that the ‘fork head ketone’ (C-3 ketone) in bicyclo[3.3.1]nonan-3-one was quite inert to the nucleophilic attack of several kinds of organometallic reagents due to backside steric hindrance.<sup>[57]</sup> Momose reported that in the presence of  $\text{CeCl}_3$  or  $\text{SmI}_2$ , the fork head ketone could react with organohalides to afford  $\alpha$ -alcohols **84** (Scheme 2-35).<sup>[58]</sup>

**Scheme 2-35**



However, only Grignard reagents derived from alkyl halides or allyl bromides were reported in the literature. No example was reported for aryl halides. In fact, Girard

reported that aromatic halides are inactive in the presence of SmI<sub>2</sub> and a ketone.<sup>[59]</sup> So we decided to mainly focus on using CeCl<sub>3</sub> to improve the reactivity of **81** with aryl halides.

There are many examples in the literatures showing that the organocerium (III) reagents, generated by the reaction of organolithium<sup>[60]</sup> or Grignard<sup>[58]</sup> reagents with CeCl<sub>3</sub>, can undergo efficient carbonyl addition due to the strong oxophilicity and the weak basicity of the cerium reagent.

However, when we tried the reaction of **81** with phenylmagnesium bromide in the presence of CeCl<sub>3</sub>, very little conversion was observed. For comparison, when benzophenone was used instead of **81** under the same conditions, triphenylmethanol was formed in 20 min in 100% yield. So **81** has a very low reactivity towards nucleophilic attack.

When phenyllithium and CeCl<sub>3</sub> were reacted with **81** in THF at -78 °C, about 40% conversion was observed. But the reaction was very complicated, and the major products that were isolated by column chromatography only gave upfield <sup>1</sup>H NMR signals. A trace amount of compound with aromatic protons was obtained but the structure could not be determined based on NMR analysis.

The commercial phenyllithium reagent we used exists as a tetramer in cyclohexane/ether. That may result in a high energy, bulky transition state, which may make the nucleophilic attack unfavorable. So we tried HMPA as the deaggregation reagent<sup>[61]</sup> but that didn't produce any improvement.

The reaction of **81** with 2-naphthyllithium, which was made from 2-bromonaphthalene and BuLi,<sup>[62]</sup> was also tried. Similar results were observed as with phenyllithium.

$\text{LiClO}_4$  is another commonly used additive in Grignard reactions.<sup>[63]</sup> It was also reported that  $\text{LiClO}_4$  could form a complex with the carbonyl group and phenyllithium in  $\text{Et}_2\text{O}$ <sup>[64, 65]</sup> and thus increase the rate of the nucleophilic addition of phenyllithium with various ketones (Figure 2-5).<sup>[66]</sup> However, it failed to solve the problem in our case. Only the starting material **81** was recovered.

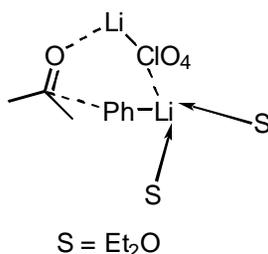


Figure 2-5.  $\text{LiClO}_4$  as Lewis acid catalyst for the nucleophilic addition of phenyllithium to a ketone in  $\text{Et}_2\text{O}$ .

Other catalysts we tried included trimethylaluminum, magnesium iodide and iron (III) chloride. None of them improved the yield. We also tried aluminum chloride. In this case, the starting material **81** was consumed completely and the major product was 3-chloro-1-adamantanol. The mechanism remains unclear.

In summary, the carbonyl group in **81** is very inert toward nucleophilic attack because the carbonyl group and the double bond are located at the ‘fork head’ positions, which puts them very close to each other. The  $^1\text{H}$  NMR data shows that the chemical shift of the protons in the double bond moves upfield ( $\delta = 4.73$  ppm) due to the shielding effect of the neighboring carbonyl group (Figure 2-6).

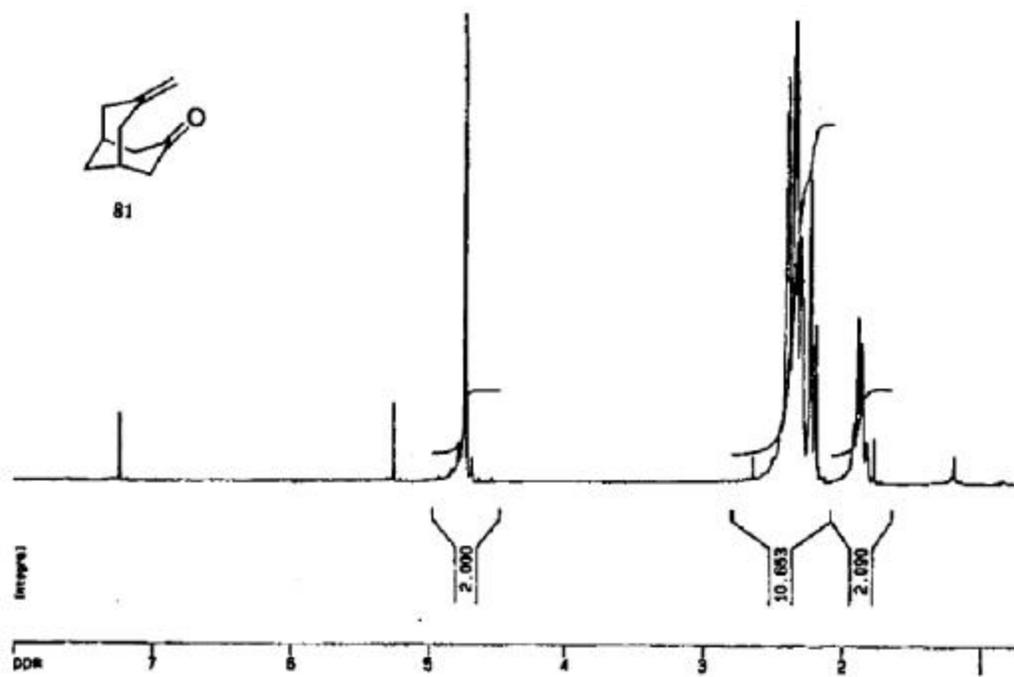


Figure 2-6.  $^1\text{H}$  NMR spectrum of compound **81**.

## Chapter 3 Experimental Section

### 3.1 General Methods

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded at 400 and 100.66 MHz, respectively, using a Bruker Avance 400 NMR Spectrometer. Chemical shifts are reported in ppm ( $\delta$ ). Abbreviations used are s, singlet; d, doublet; t, triplet; dd, doublet of doublets; q, quintet; m, multiplet; and br, broad.  $\text{CDCl}_3$  was generally employed in obtaining the NMR spectra unless specified otherwise. Ultraviolet spectra (UV) were recorded on a Hitachi U2000 UV-Vis Spectrometer. Melting points were determined on a Thomas Hoover Capillary melting point apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on silica gel 60F-254 plates with 254 nm fluorescence indicator and was visualized under a UV lamp and/or PMA stain. Flash column chromatography was performed on J.T. Baker 40  $\mu\text{m}$  diameter silica gel under a positive pressure of air. THF was distilled under nitrogen from sodium/benzophenone just prior to use. Toluene, EtOH and  $\text{CH}_2\text{Cl}_2$  were refluxed with  $\text{CaH}_2$  and distilled under nitrogen immediately prior to use. HMPA was purified by distillation from  $\text{CaH}_2$  at reduced pressure and stored over 4  $\text{\AA}$  molecular sieves.

### 3.2 Syntheses

Cyclopentadiene was distilled from dicyclopentadiene just prior to use. 2-(4-Bromophenyl)-2-phenyl-1,3-dioxolane was synthesized according to the literature

procedure.<sup>[34]</sup> All other commercial reagents were used directly without further purification unless otherwise specified.

**2, 3, 4a, 9a-Tetrahydro-anthracene-1,4-dione (35).**<sup>[27]</sup> NaBH<sub>4</sub> (10 g, 260 mmol) was added in portions over 20 min to a vigorously stirred dark red solution of quinizarin (20 g, 83 mmol) in MeOH (400 mL). After being heated to reflux for 24 h, the mixture was cooled to rt and poured into 1 L of H<sub>2</sub>O. The red solution was acidified with conc. HCl. The precipitate was isolated by filtration, washed with water, and dried in air overnight. Recrystallization from EtOH gave **35** as a red solid (14.7 g, 85%); mp 199-210 °C (lit.<sup>[27]</sup> 216-218 °C); <sup>1</sup>H NMR ? 8.57 (s, 2H), 8.02 (dd, J = 6.2, 3.0 Hz, 2H), 7.65 (dd, J = 6.5, 3.2 Hz, 2H), 7.19 (s, 2H); <sup>13</sup>C NMR ? 140.5 (CH), 130.7 (CH), 130.0 (CH), 129.3 (CH).

**1,4,4a, 5, 12, 12a-Hexahydro-1,4-methanonaphthacene-5,12-dione (36).**<sup>[38]</sup> To a solution of **35** (14.7 g, 71 mmol) in EtOH (270 mL) and CH<sub>2</sub>Cl<sub>2</sub> (310 mL) was added freshly distilled cyclopentadiene (8.9 mL, 130 mmol) and the mixture was stored in the refrigerator for 7 h. After removal of the solvents in vacuo, the residue was recrystallized from EtOAc to give **36** as a red solid (14 g, 72%); mp 163-165 °C (lit.<sup>[38]</sup> 167-168 °C); <sup>1</sup>H NMR ? 8.54 (s, 2H), 8.01-7.98 (dd, J = 6.1, 3.3 Hz, 2H), 7.64-7.62 (dd, J = 6.3, 3.2 Hz, 2H), 5.94 (s, 2H), 3.67 (s, 2H), 3.51 (s, 2H), 1.54 (s, 2H); <sup>13</sup>C NMR ? 198.0 (C), 135.5 (CH), 135.1 (C), 131.6 (C), 129.9 (CH), 129.3 (CH), 128.8 (CH), 50.0 (CH), 49.8 (CH), 49.5 (CH<sub>2</sub>).

**1,4,4a,5,12,12a-Hexahydro-1,4-methanonaphthacene-5,12-diol (37).**<sup>[38]</sup> To a solution of **36** (2.22 g, 8 mmol) in anh. CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added NaBH<sub>4</sub> (48 mg, 1.26 mmol) followed by anh. MeOH (16 mL) at 0 °C. Bubbles were formed gently. The mixture was then allowed to warm to rt. After being stirred for 14 h, it was neutralized with 10% aq. HCl to pH 7. The solvents were removed in vacuo and the residue was extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with water (1 × 10 mL) and brine (1 × 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give **37** as a red solid (2.5 g, 100%); mp 190-192 °C (lit.<sup>[38]</sup> 198-199 °C); <sup>1</sup>H NMR δ 7.81 (d, J = 3.5 Hz, 2H), 7.78 (s, 2H), 7.39 (d, J = 3.6 Hz, 2H), 5.52 (s, 1 H), 4.90 (s, 2H), 4.84 (s, 2H), 2.91 (s, 2H), 1.20 (dd, J = 1.9 Hz, 1H); 1.1 (d, J = 1.9 Hz, 1H); <sup>13</sup>C NMR δ 139.8 (C), 133.5 (CH=), 132.3 (C), 127.6 (CH), 125.0 (CH), 120.2 (CH), 67.1 (CH), 49.6 (CH<sub>2</sub>), 44.9 (CH), 44.5 (CH).

**1,4-Dihydro-1,4-methanonaphthacene (28).**<sup>[67]</sup> A mixture of **37** (2.4 g, 8.6 mmol) and *p*-TsCl (4.9 g, 25.9 mmol) in anh. pyridine (27 mL) was heated at 70 °C for 24 h and then poured into 1 L of H<sub>2</sub>O. The aqueous layer was extracted with Et<sub>2</sub>O (3 × 50 mL). The organic layers were combined, washed with 10% aq. HCl, 10% aq. NaHCO<sub>3</sub> and brine respectively, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 10:1), yielding **28** as a white solid (1.7 g, 80%); mp 227-229 °C (lit.<sup>[67]</sup> 233-234 °C); <sup>1</sup>H NMR δ 8.21 (s, 2H), 7.94-7.92 (dd, J = 6.4, 3.3 Hz, 2H), 7.66 (s, 2H), 7.41-7.39 (dd, J = 6.5, 3.2 Hz, 2H), 3.97 (s, 2H), 2.35 (d, J = 7.7 Hz, 2H), 2.21 (d, J = 7.7 Hz, 2H); <sup>13</sup>C NMR δ 147.4 (C), 141.3 (CH), 131.5 (C), 131.0 (C), 127.9 (CH), 125.5 (CH), 124.7 (CH), 118.8 (CH), 64.2 (CH<sub>2</sub>), 49.2 (CH).

**(1,4,4a,5,14,14a)-1,2,3,4-Tetrachloro-1,4,4a,5,14,14a-hexahydro-16,16-dimethoxy-1,4:5,14-dimethanopentacene (29).**<sup>[68]</sup> To a solution of **28** (0.9 g, 3.71 mmol) in anh. toluene (72 mL) containing hydroquinone (20 mg, 0.18 mmol), 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (1.2 mL, 7.42 mmol) was added via syringe. The mixture was then heated at 110 °C for 72 h. The brown solid obtained after the removal of the solvents was recrystallized from EtOAc/hexane to yield **29** as a pale yellow solid (1.2 g, 64%); mp 216-218 °C (lit.<sup>[68]</sup> 219.5-200.5 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.30 (s, 2H), 7.97-7.94 (dd, J = 6.4, 3.3 Hz, 2H), 7.67 (s, 2H), 7.44-7.42 (dd, J = 6.5, 3.2 Hz, 2H), 3.52 (s, 3H), 3.51 (s, 2H), 3.45 (s, 3H), 2.74 (s, 2H), 1.97 (d, J = 11.6 Hz, 1H), 1.58 (d, J = 12 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 146.7 (C), 131.5 (C), 131.1 (C), 128.9 (C), 127.9 (CH), 126.0 (CH), 125.1 (CH), 118.3 (CH), 114.5 (C), 55.4 (CH<sub>3</sub>), 52.5 (CH<sub>3</sub>), 51.4 (CH), 42.1 (CH), 40.7 (CH<sub>2</sub>).

**(1,4,4a,5,14,14a)-1,4,4a,5,14,14a-Hexahydro-16,16-dimethoxy-1,4:5,14-dimethanopentacene (38).** A solution of **29** (1 g, 2.0 mmol) in anh. EtOH (50 mL) and anh. THF (50 mL) was heated to 50-60 °C. Sodium metal (4.6 g, 200 mmol) was added as small pieces. After being heated to reflux for 30 h, the reaction mixture was cooled to rt and poured into 150 mL of ice water and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo to a brown oil, which was further purified by column chromatography (hexane/EtOAc, 10:1) to give **38** as a white solid (0.6 g, 81%); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.29-7.26 (dd, J = 5.4, 3.4 Hz, 2H), 7.17-7.15 (dd, J = 5.5, 3.3 Hz, 2H), 7.04 (s, 2H), 6.06 (s, 2H), 3.79 (s,

4H), 3.15 (s, 3H), 2.92 (s, 3H), 2.85 (s, 2H), 2.81 (d, J = 9.3 Hz, 1H), 2.06 (s, 2H), 1.04 (d, J = 9.2 Hz, 1H).

**(1?, 4?, 4a?, 5?, 14?, 14a?) -1,2,3,4,4a,5,7,12,14,14a-Decahydro-16,16-dimethoxy-1,4:5,14-dimethanopentacene (39).** To a solution of **38** (0.6 g, 1.62 mmol) in EtOAc (48 mL) was added 5% Pd/C (200 mg). The mixture was flushed with H<sub>2</sub> and was kept under a positive pressure of H<sub>2</sub> from a balloon. After being stirred at rt for 57 h, the reaction mixture was diluted with EtOAc (30 mL) and filtered through Celite. The solvent was removed in vacuo to give **39** as white crystals (0.56 g, 93%), which were used for the next step without further purification; <sup>1</sup>H NMR  $\delta$  7.22-7.20 (dd, J = 5.5, 3.3 Hz, 2H), 7.11-7.10 (dd, J = 5.5, 3.3 Hz, 2H), 7.01 (s, 2H), 3.81 (s, 4H), 3.17 (s, 3H), 3.03 (s, 3H), 2.10 (d, J = 8.2 Hz, 1H), 1.98 (s, 2H), 1.87 (s, 2H), 1.65-1.51 (m, 7H).

**(1?, 4?, 4a?, 5?, 14?, 14a?) -1,2,3,4,4a,5,14,14a-Octahydro-16-dimethoxy-1,4:5,14-dimethanopentacene (40).**<sup>[68]</sup> To a solution of **39** (560 mg, 1.51 mmol) in dry toluene (56 mL) was added DDQ (490 mg, 2.16 mmol). The red mixture was stirred at 65 °C for 24 h. After being cooled to rt, the reaction mixture was filtered. The filtrate was washed with 10% aq. NaOH (1  $\times$  15 mL) and brine (1  $\times$  15 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a brown residue. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yield **40** as a white solid (470 mg, 84%); mp 236-239 °C; <sup>1</sup>H NMR  $\delta$  8.29 (s, 2H), 7.97-7.94 (dd, J = 6.4, 3.3 Hz, 2H), 7.62 (s, 2H), 7.43-7.41 (dd, J = 6.5, 3.2 Hz, 2H), 3.35 (s, 2H), 3.26 (s, 3H), 3.13 (s, 3H), 2.44 (d, J = 9.5 Hz, 1H), 2.26 (s, 2H), 2.14 (s, 2H), 1.77 (d, J = 9.6 Hz, 1H), 1.72-1.68 (m, 4H); <sup>13</sup>C NMR  $\delta$

149.4 (C), 131.2 (C), 131.1 (C), 127.8 (CH), 125.5 (CH), 124.6 (CH), 117.0 (CH), 116.8 (C), 50.4 (CH), 44.9 (CH), 43.2 (CH<sub>2</sub>), 40.9 (CH), 29.6 (CH<sub>2</sub>), 22.0 (CH<sub>2</sub>).

**(1?, 4?, 4a?, 5?, 14?, 14a?) -1,2,3,4,4a,5,14,14a-Octahydro-1,4:5,14-**

**dimethanopentacene-16-one (30).**<sup>[68]</sup> To a solution of **40** (3 g, 8.1 mmol) in anh. CH<sub>2</sub>Cl<sub>2</sub> (150 mL) at 0 °C was added iodotrimethylsilane (2 mL, 13.8 mmol). Then the mixture was allowed to warm to rt. After being stirred for 3 h, the pink solution was washed with 5% aq. NaHCO<sub>3</sub> (3 × 20 mL). The organic layer was washed with H<sub>2</sub>O (1 × 20 mL) and brine (1 × 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. After removal of the solvent in vacuo, the residue was coated onto silica gel (60-200 mesh, 5 g) and the coated gel loaded onto a filled chromatographic column. Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 200:1) gave **30** as a white solid (2.3 g, 88%); mp > 300 °C; <sup>1</sup>H NMR δ 8.29 (s, 2H), 7.96-7.93 (dd, J = 6.4, 3.3 Hz, 2H), 7.66 (s, 2H), 7.42-7.40 (dd, J = 6.5, 3.2 Hz, 2H), 3.57 (s, 2H), 2.48 (d, J = 10.8 Hz, 1H), 2.24 (s, 2H), 2.10 (s, 2H), 1.98 (d, J = 8.2 Hz, 2H), 1.85 (d, J = 9.7 Hz, 2H), 1.78 (d, J = 10.7 Hz, 1H); <sup>13</sup>C NMR δ 211.9 (C=O), 148.3 (C), 131.7 (C), 131.5 (C), 128.3 (CH), 126.2 (CH), 125.3 (CH), 118.1 (CH), 44.8 (CH), 43.5 (CH), 43.5 (CH<sub>2</sub>), 39.9 (CH), 30.1 (CH<sub>2</sub>), 18.7 (CH<sub>2</sub>).

**9-Phenanthrylmagnesium Bromide (41).**<sup>[32]</sup> 9-Bromophenanthrene (5.1 g, 20 mmol) was put in a dropping funnel and melted with a heat gun. In a three-neck round bottom flask, Mg (0.5 g, 20mmol) and 2 drops of 1,2-dibromoethane in anh. Et<sub>2</sub>O (1 mL) were stirred under N<sub>2</sub> until the reaction was initiated. 9-Bromophenanthrene and anh. Et<sub>2</sub>O (9 mL) were added separately and the addition rate was adjusted so that the two funnels

were emptied at the same time. After the addition, 10 mL of anh. benzene was added. The solution was heated to gentle reflux at 55 °C for 4 h, at which time the Mg was almost all consumed. The resulting solution of **41** in benzene/diethyl ether was cooled to rt and stored under N<sub>2</sub>.

**(1,4,5,14-dimethanopentacene-16-yl)-1,2,3,4,4a,5,14,14a-Octahydro-16-phenanthren-9-yl-1,4:5,14-dimethanopentacene-16-ol (42)**. To a suspension of **30** (750 mg, 2.25 mmol) in anh. benzene (75 mL) was added **41** (1.0 M, 2.25 mL, 2.25 mmol) in benzene/diethyl ether. The clear solution was heated at 55 °C overnight. After removal of the solvent in vacuo, the residue was coated onto silica gel (60-200 mesh, 5 g) and the coated gel loaded onto a filled chromatographic column. Purification by column chromatography (hexane/EtOAc, 20:1) gave **42** as a pale yellow solid (1.0 g, 87%); mp > 300 °C; <sup>1</sup>H NMR δ 8.84 (d, J = 8.1 Hz, 1H), 8.78 (d, J = 7.7 Hz, 1H), 8.64 (d, J = 7.9 Hz, 1H), 8.43 (s, 2H), 8.04 (d, J = 5.7 Hz, 3H), 7.97 (s, 1H), 7.76 (d, J = 6.8 Hz, 2H), 7.64 (d, J = 7.9 Hz, 4H), 7.49-7.46 (dd, J = 6.3, 2.9 Hz, 2H), 5.49 (s, 1H), 3.55 (s, 2H), 3.08 (s, 1H), 2.96 (s, 1H), 2.75-2.71 (dd, J = 8.8, 4.2 Hz, 1H), 2.45 (m, 2H), 1.99 (t, J = 10.4 Hz, 1H), 1.65-1.74 (m, 2H), 1.48 (m, 1H), 0.83 (t, J = 10.2 Hz, 1H).

**(1,4,5,14-dimethanopentacene-16-yl)-1,2,3,4,4a,5,14,14a-Octahydro-16-phenanthren-9-yl-1,4:5,14-dimethanopentacene (12)**. To a suspension of **42** (50 mg, 0.1 mmol) and Et<sub>3</sub>SiH (30 μL, 0.18 mmol) in anh. CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added TFA (30 μL, 0.4 mmol). The color of the system quickly changed from pale yellow to pink to white. After being stirred at rt for 24 h, the mixture was diluted with 30 mL of CH<sub>2</sub>Cl<sub>2</sub>, washed with 10 %

aq. NaHCO<sub>3</sub> (1 ? 20 mL) and brine (1 ? 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvent was removed in vacuo to give a yellow solid, which was further purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to give **12** as a white solid (46 mg, 96%); mp > 300 °C; <sup>1</sup>H NMR ? 8.64-8.61 (dd, J = 6.2, 3.4 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.19-8.17 (dd, J = 6.2, 3.1 Hz, 1H), 8.14 (s, 2H), 7.87-7.84 (dd, J = 6.4, 3.3 Hz, 2H), 7.65-7.56 (m, 4H), 7.46-7.32 (m, 5H), 3.61 (s, 1H), 3.33 (s, 2H), 3.10 (s, 2H), 2.44 (d, J = 10.5 Hz, 1H), 2.22 (s, 2H), 1.97 (s, 4H), 1.72 (d, J = 10.5 Hz, 1H); <sup>13</sup>C NMR ? 149.5 (C), 133.5 (C), 131.7 (C), 131.3 (C), 130.6 (C), 129.4 (C), 128.3 (CH), 127.7 (CH), 126.3 (CH), 125.9 (CH), 125.8 (2 ? CH), 125.7 (CH), 125.3 (CH), 125.1 (CH), 124.5 (CH), 123.1 (CH), 122.0 (CH), 117.0 (CH), 59.3 (CH), 53.4 (CH<sub>2</sub>), 45.9 (CH), 43.9 (CH), 43.6 (CH), 43.2 (CH<sub>2</sub>), 25.1 (CH<sub>2</sub>).

**(1? ,4? ,4a? ,5? ,14? ,14a? )-1,2,3,4,4a,5,14,14a-Octahydro-16? -[4-(2-phenyl-[1,3]dioxolan-2-yl)-phenyl]-1,4:5,14-dimethanopentacene-16-ol (45)**. A solution of 2-(4-bromophenyl)-2-phenyl-1,3-dioxolane<sup>[34]</sup> (1.53 g, 5 mmol) and bromoethane (1.09 g, 10 mmol) in dry THF (5 mL) was added dropwise to a mixture of Mg (0.42 g, 18 mmol) in dry THF (1 mL) until the reaction started. The rest of the solution was added at a rate that maintained reflux. After the addition was complete, the mixture was heated to reflux at 65 °C for 0.5 h.<sup>[35]</sup>

To a suspension of **30** (500 mg, 1.5 mmol) in dry benzene (5 mL) was added the Grignard reagent described above (1.0 M, 2.3 mL, 2.3 mmol) in THF at rt. The mixture was stirred at rt for 24 h. After the reaction was quenched with 10 mL of ice water, saturated aq. NH<sub>4</sub>Cl solution was added and the aqueous layer was extracted with EtOAc

(3 x 25 mL). The combined organic layer was dried over MgSO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a brown oil, which was purified by column chromatography (hexane/EtOAc 5:1) to give **45** as a pale yellow solid (100 mg, 40%); mp > 300 °C; <sup>1</sup>H NMR δ 8.31 (s, 2H), 7.99 (dd, J = 6.4, 3.2 Hz, 2H), 7.67 (s, 2H), 7.57-7.28 (m, 11H), 4.13-4.07 (d, J = 11.9 Hz, 4H), 3.46 (s, 2H), 2.60 (m, 4H), 2.47 (d, J = 10.3 Hz, 1H), 1.78 (d, J = 10.5 Hz, 1H), 1.67-1.41 (m, 4H); <sup>13</sup>C NMR δ 149.9 (C), 142.2 (C), 142.1 (C), 141.7 (C), 131.5 (C), 131.4 (C), 128.3 (2 × CH), 128.1 (CH), 127.1 (CH), 126.7 (CH), 126.3 (CH), 125.7 (CH), 124.8 (CH), 117.3 (CH), 109.4 (C), 92.4 (C), 65.1 (CH<sub>2</sub>O), 46.5 (CH), 45.1 (CH), 43.9 (CH), 43.5 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>).

**(1?, 4?, 4a?, 5?, 14?, 14a?) -1,2,3,4,4a,5,14,14a-Octahydro-1,4:5,14-**

**dimethanopentacene-16-ol (52).** To a suspension of **30** (50 mg, 0.15 mmol) and NaBH<sub>4</sub> (18 mg, 0.46 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL), anh. MeOH (1 mL) was added dropwise. After being stirred at rt overnight, the mixture was diluted with 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and neutralized to pH 7 with 10% aq. HCl. The organic layer was separated, washed with brine (1 × 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvent was removed in vacuo to give an yellowish oil, which was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to yield **52** as a white solid (100 mg, 99%); mp > 300 °C; <sup>1</sup>H NMR δ 8.25 (s, 2H), 7.93 (dd, J = 6.4, 2.5 Hz, 2H), 7.61 (s, 2H), 7.39 (dd, J = 6.4, 3.0 Hz, 2H), 4.16 (s, 1H), 3.37 (s, 2H), 2.27 (s, 4H), 2.17 (s, 3H), 1.74 (d, J = 10.0 Hz, 1H), 1.64 (d, J = 8.2 Hz, 2H), 1.23 (m, 1H); <sup>13</sup>C NMR δ 149.6 (C), 131.2 (C), 131.1 (C), 127.8 (CH), 125.5 (CH), 124.6 (CH), 117.1 (CH), 85.0 (CHOH), 45.7 (CH), 43.6 (CH<sub>2</sub>), 43.2 (2 × CH), 21.5 (CH<sub>2</sub>).

**2-(9-Phenanthrenyl)bicyclo[2.2.1]heptan-2-ol (53).** To a solution of bicyclo[2.2.1]heptan-2-one (0.37 g, 3.3 mmol) in dry benzene (3 mL) was added **41** (1.0 M, 5.0 mL, 5.0 mmol) in benzene/Et<sub>2</sub>O. After the clear solution had been stirred at rt for 5 min, a solid precipitated. The suspension was then stirred overnight. After being quenched with H<sub>2</sub>O (2 mL), the mixture was concentrated to ca. 1 mL of brown oil, which was purified by column chromatography (hexane/EtOAc 30:1) to yield **53** as a white solid. (440 mg, 46%); mp 120-121 °C; <sup>1</sup>H NMR ? 8.72 (d, J = 8 Hz, 1H), 8.62 (dd, J = 8.0, 3.1 Hz, 2H), 7.85 (dd, J = 7.8, 1.3 Hz, 1H), 7.80 (s, 1H), 7.65-7.55 (m, 4H), 2.37-2.28 (m, 3H), 1.99 (dd, J = 12.7, 3.2 Hz, 1H), 1.84-1.49 (m, 6H); <sup>13</sup>C NMR ? 141.5 (C), 132.4 (C), 131.3 (C), 130.4 (C), 130.3 (C), 129.4 (CH), 128.8 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 126.3 (CH), 123.6 (CH), 123.2 (CH), 122.7 (CH), 81.4 (COH), 48.3 (CH<sub>2</sub>), 46.8 (CH), 39.2 (CH<sub>2</sub>), 37.9 (CH), 29.6 (CH<sub>2</sub>), 22.4 (CH<sub>2</sub>).

**9-(2-Bicyclo[2.2.1]heptyl)phenanthrene (49).** To a stirred solution of **53** (106 mg, 0.37 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added Et<sub>3</sub>SiH (118 μL, 0.74 mmol) followed by TFA (0.28 mL, 3.7 mmol). After being stirred overnight at rt, the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), washed with 10 % aq. NaHCO<sub>3</sub> (1 ? 20 mL) and brine (1 ? 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvent was removed in vacuo to give a white solid, which was purified by column chromatography (hexane) to give **49** as a white solid (80 mg, 80%); mp 112-115 °C; <sup>1</sup>H NMR ? 8.78 (dd, J<sub>1</sub> = 7.4, 5.2 Hz, 1H), 8.70 (dd, J<sub>1</sub> = 7.3, 6.4 Hz, 1H), 8.32-8.30 (m, 1H), 7.94-7.91 (m, 1H), 7.76 (s, 1H), 7.73-7.59 (m, 5H), 2.71 (s, 1H), 2.51(s, 1H), 2.14-2.08 (m, 1H), 1.91-1.86 (m, 2H), 1.67-1.25 (m, 5H); <sup>13</sup>C NMR ? 137.0 (C), 132.8 (C), 132.0 (C), 131.2 (C), 129.9 (C), 128.8 (CH),

127.0 (CH), 126.8 (CH), 126.4 (CH), 125.0 (CH), 124.3 (CH), 123.6 (CH), 122.8 (CH), 42.9 (CH), 42.4 (CH), 41.7 (CH<sub>2</sub>), 38.1 (CH), 34.0 (CH<sub>2</sub>), 30.3 (CH<sub>2</sub>), 23.8 (CH<sub>2</sub>).

**1-(4-Diethoxymethylphenyl)-4-phenyl-1,3-butadiene (54).**<sup>[68]</sup> To a solution of diisopropylamine (1.13 mL, 8 mmol) in dry THF (5 mL) at -20 °C, a solution of BuLi (1.6 M, 5 mL, 8 mmol) in hexane was added dropwise over 20 min. The light yellow solution was then cooled to -78 °C and dry THF (40 mL) was added. Then cinnamyltriphenylphosphonium bromide was added directly as a solid under N<sub>2</sub>. After standing for 1 h at -78 °C, the mixture was allowed to warm to rt. A solution of 4-(diethoxymethyl)benzaldehyde (1.2 mL, 7 mmol) in dry THF (10 mL) was added via syringe. After being heated to reflux for 36 h, the mixture was cooled to rt and concentrated to ca. 3 mL. The resulting oil was purified by column chromatography (hexane/EtOAc 20:1) to give a yellow solid **54** (1 g, 46%); mp 125-128 °C (lit.<sup>[68]</sup> 134-137 °C); <sup>1</sup>H NMR  $\delta$  7.78 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.41-7.19 (m, 5H), 7.01-6.47 (m, 4H), 5.45 (s, 1H), 3.66 (q, J = 3.6 Hz, 4H), 1.19 (t, J = 3.4 Hz, 6H); <sup>13</sup>C NMR  $\delta$  137.2 (C), 135.6 (C), 135.5 (C), 133.1 (CH), 131.6 (CH), 130.6 (CH), 129.1 (CH), 128.9 (CH), 128.5 (CH), 127.1 (CH), 127.0 (CH), 66.5 (CH), 58.9 (CH<sub>2</sub>), 18.8 (CH<sub>3</sub>).

**4-(4-Phenyl-1,3-butadienyl)benzaldehyde (55).**<sup>[69]</sup> To a solution of **54** (200 mg, 0.65 mmol) in THF (30 mL) was added 2% aq. H<sub>2</sub>SO<sub>4</sub> (27 mL). The reaction mixture was stirred at rt for 96 h, and was neutralized with 10 % aq. NaHCO<sub>3</sub> solution to pH 8. The aqueous layer was extracted with Et<sub>2</sub>O (4  $\times$  30 mL). The combined organic layer was

washed with brine (1 ? 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo, yielding **55** as a yellow solid. (150 mg, 99%); mp 120-123 ?C (lit.<sup>[69]</sup> 128 ?C); <sup>1</sup>H NMR ? 10.1 (s, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.67-7.63 (m, 3H), 7.48-7.45 (m, 4H), 7.40 (d, J = 7.0 Hz, 1H), 6.71 (d, J = 7.0 Hz, 1H).

**[4-(4-Phenyl-1,3-butadienyl)phenyl]methanol (56)**. To a solution of **55** (115 mg, 0.49 mmol) in 2 mL anh. CH<sub>2</sub>Cl<sub>2</sub> was added NaBH<sub>4</sub> (19 mg, 0.5 mmol). The yellow suspension was stirred at rt for 25 h. The mixture was then neutralized with 10% aq. HCl to pH 7, and extracted with Et<sub>2</sub>O (2 ? 10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvent were removed in vacuo to give **56** as a yellow solid (80 mg, 70%); mp 175-178 ?C; <sup>1</sup>H NMR ? 7.44-7.23 (m, 9H), 6.95 (d, J = 11.0 Hz, 2H), 6.66 (d, J = 12.3 Hz, 2H), 4.69 (s, 2H); <sup>13</sup>C NMR ? 133.3 (CH), 132.7 (CH), 129.7 (CH), 129.5 (CH), 129.1 (C), 128.0 (C), 127.7 (CH), 126.9 (CH), 126.7 (CH), 65.5 (CH<sub>2</sub>).

**1-(4-Chloromethylphenyl)-4-phenyl-1,3-butadiene (57)**. To a yellow suspension of **56** (125 mg, 0.53 mmol) and Et<sub>3</sub>N (0.18 mL, 1.32 mmol) in dry toluene (6 mL) was added CH<sub>3</sub>SO<sub>2</sub>Cl (0.08 mL, 1.06 mmol). The mixture was heated to 70 ?C and stirred at this temperature for 24 h. After being cooled to rt the mixture was neutralized with 10% aq. HCl to pH 7 and extracted with Et<sub>2</sub>O (3 ? 10 mL). The combined organic layer was washed with H<sub>2</sub>O (1 ? 5 mL) and brine (1 ? 5 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a yellow oil, which was purified

by column chromatography (hexane) to yield **57** as a yellow solid (114 mg, 84%);  $^1\text{H}$  NMR  $\delta$  7.44-7.24 (m, 9H), 6.96-6.92 (m, 2H), 6.69-6.66 (m, 2H), 4.57 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  133.7 (CH), 132.3 (CH), 130.3 (CH), 129.4 (CH), 129.0 (CH), 128.1 (C), 127.0 (CH), 126.8 (CH), 67.8 (CH<sub>2</sub>).

**Diethyl [4-(4-phenyl-1,3-butadienyl)phenyl]methylphosphonate (58).** A mixture of **57** (300 mg, 1.18 mmol) in triethyl phosphite (8 mL) was heated to reflux for 26 h and, after being cooled, concentrated in vacuo to ca. 1 mL. The residue was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 200:1), yielding **58** as a yellow solid (190 mg, 45%);  $^1\text{H}$  NMR  $\delta$  7.41-7.23 (m, 9H), 6.94-6.91 (m, 2H), 6.75-6.64 (m, 2H), 4.01 (q, J = 6.4 Hz, 4H); 3.16 (s, 2H), 1.25 (t, J = 6.6 Hz, 6H);  $^{13}\text{C}$  NMR  $\delta$  137.7 (C), 135.3 (CH), 133.2 (C), 132.7 (C), 131.3 (CH), 130.5 (CH), 130.1 (CH), 129.5 (CH), 128.1 (CH), 126.9 (CH), 126.9 (2  $\times$  CH), 125.5 (CH), 62.6 (CH<sub>2</sub>), 34.6 (CH<sub>2</sub>), 16.8 (CH<sub>3</sub>).

**16-*p*-(4-Phenyl-1,3-butadienyl)phenylmethylene-(1?, 4?, 4a?, 5?, 14?, 14a? )-**

**1,2,3,4,4a,5,14,14a-octahydro-1,4:5,14-dimethanopentacene (14).**<sup>[68]</sup> A mixture of **58** (41 mg, 0.12 mmol) and NaH (60% oil dispersion, 10 mg, 0.25 mmol) in dry THF (4 mL) was stirred at -40  $^\circ\text{C}$  for 15 min before a solution of LDA (2.0 M, 0.4 mL, 0.8 mmol) in THF was added dropwise. The red solution was stirred at -40  $^\circ\text{C}$  for 40 min and was further cooled to -78  $^\circ\text{C}$ . A solution of **30** (25 mg, 0.08 mmol) in dry THF (4 mL) was added dropwise at this temperature. After being stirred at -78  $^\circ\text{C}$  for 3 h, the mixture was allowed to warm to rt, and then heated to reflux for 14 h. The reaction was quenched with water and neutralized with 10% aq. HCl to pH 7. The aqueous layer was extracted with

EtOAc (2 ? 10 mL) and toluene (2 ? 10 mL). The combined organic layers were washed with H<sub>2</sub>O (1 ? 10 mL) and brine (1 ? 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a yellow oil which was purified by column chromatography (hexane/CH<sub>2</sub>Cl<sub>2</sub> 10:1) to yield **14** as a yellow solid (39 mg, 95%); mp > 300 ?C (lit.<sup>[68]</sup> > 280 ?C); <sup>1</sup>H NMR ? 8.20 (s, 2H), 7.87 (d, J = 9.6 Hz, 2H), 7.54 (d, J = 4.2Hz, 2H), 7.34-7.10 (m, 11H), 6.86 (m, 2H), 6.60 (m, 2H), 5.93 (s, 1H), 3.36 (s, 2H), 3.21 (m, 1H), 2.59 (m, 1H), 2.16-1.50 (m, 8H); <sup>13</sup>C NMR ? 154.7 (C), 149.2 (C), 149.2 (C), 137.8 (C), 137.3 (C), 135.0 (C), 132.6 (CH), 132.4 (CH), 131.1 (C), 129.3 (CH), 128.6 (CH), 128.1 (CH), 127.8 (CH), 127.4 (CH), 126.2 (CH), 126.2 (CH), 125.5 (CH), 124.6 (CH), 117.1 (CH), 111.9 (CH), 46.2 (CH), 45.9 (CH), 45.7 (CH), 43.9 (CH), 42.2 (CH<sub>2</sub>), 39.7 (CH), 31.9 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 30.9 (CH), 29.6 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 14.1 (CH).

**Dimethyl 1,4,4a,4c,5,14,14a,14c-octahydro-1,4,5,14-**

**dimethanobenzo[3',4']cyclobuta[1',2',3,4]cyclobuta[1,2-b]tetracene-4b,14b-**

**dicarboxylate (31).**<sup>[34]</sup> A solution of **28** (1.5 g, 6.2 mmol), dimethyl acetylenedicarboxylate (1.5 g, 10.5 mmol), and RuH<sub>2</sub>CO(PPh<sub>3</sub>)<sub>3</sub> (0.1 g, 0.083 mmol) in dry benzene (10 mL) was heated to reflux for 24 h. The mixture was concentrated to ca. 4 mL and the residue was recrystallized from CHCl<sub>3</sub>, yielding **31** as a yellow solid (2.4 g, 100%); mp 260-262 ?C (lit.<sup>[34]</sup> 237-239 ?C); <sup>1</sup>H NMR ? 8.30 (s, 2H), 7.95 (dd, J = 6.4, 3.3 Hz, 2H), 7.73 (s, 2H), 7.42 (dd, J = 6.5, 3.2 Hz, 2H), 3.85 (s, 6H), 3.45 (s, 2H), 2.89 (s, 2H), 1.88 (m, 2H); <sup>13</sup>C NMR ? 210.0 (C=O), 161.5 (C), 144.4 (C), 142.7 (C), 131.3

(C), 131.3 (C), 127.9 (CH), 125.7 (CH), 125.0 (CH), 119.2 (CH), 52.1 (OCH<sub>3</sub>), 46.3 (CH), 40.1 (CH), 38.6 (CH<sub>2</sub>).

**3-(Trimethylsilyl)-3-buten-2-ol (63).**<sup>[42]</sup> A solution of *tert*-BuLi (1.7 M, 16.4 mL, 27.8 mmol) in pentane was added slowly to a solution of 1-bromovinyltrimethylsilane (5 g, 27.8 mmol) in 110 mL of anh. Et<sub>2</sub>O at -78 °C under N<sub>2</sub>. The solution was left for 2 h at -78 °C, then acetaldehyde (1.56 mL, 27.8 mmol) was added, and the mixture was allowed to warm to rt. The reaction was quenched with 50 mL of H<sub>2</sub>O, and the aqueous layer was extracted with Et<sub>2</sub>O (3 × 15 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, isolated by filtration, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc 1:1) to give **63** as a colorless oil (1.6 g, 41%); <sup>1</sup>H NMR δ 5.77 (s, 1H), 5.36 (s, 1H), 4.47 (m, 1H), 1.43 (br s, 1H), 1.27 (s, 3H), 0.12 (s, 9H); <sup>13</sup>C NMR δ 157.2 (C=), 123.3 (CH<sub>2</sub>=), 72.4 (CHOH), 24.7 (CH<sub>3</sub>).

**2-Acetoxy-3-trimethylsilyl-3-butene (59).**<sup>[38]</sup> Acetyl chloride (9.4 mL, 0.13 mmol) was added very slowly to a mixture of **63** (5.42 g, 0.037 mmol) and DMAP (0.46 g, 0.0038 mmol) in dry pyridine (90 mL). After being stirred overnight at rt, the solution was poured into a mixture of 300 mL of H<sub>2</sub>O and 270 mL of Et<sub>2</sub>O. The organic layer was isolated and washed with 3M HCl (3 × 30 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, isolated by filtration, and concentrated to an oil. Purification by column chromatography (hexane) gave **59** as a colorless oil (4.8 g, 88%); <sup>1</sup>H NMR δ 5.72 (d, J = 2.0 Hz, 1H), 5.48-5.42 (q, J = 6.5 Hz, 1H), 5.38 (d, J = 2.1 Hz, 1H), 2.01 (s, 3H), 1.28 (d, J = 6.6 Hz, 3H), 0.10 (s, 9H).

**Compound 32.**<sup>[42]</sup> Stirring a mixture of Pd(OAc)<sub>2</sub> (30 mg, 0.13 mmol), PPh<sub>3</sub> (180 mg, 0.67 mmol), and a solution of BuLi (1.6 M in hexane, 0.17 mL, 0.27 mmol) in dry dioxane (25 mL) for 1 h generated a yellow solution of the palladium catalyst. At rt a solution of **59** (460 mg, 2.47 mmol) in dry dioxane (1 mL), **31** (0.95 g, 2.47 mmol) in dry dioxane (10 mL) and Et<sub>3</sub>N (0.4 mL, 2.47 mmol) were added sequentially. The mixture was heated to reflux for 20 h and diluted with 40 mL of Et<sub>2</sub>O. After filtration, the organic layer was washed with H<sub>2</sub>O (2 × 10 mL) and brine (2 × 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a yellow solid, which was purified by column chromatography (hexane/EtOAc 10:1) to yield **32** as a white solid (100 mg, 30% based on the consumed starting material); mp 110 °C (sublimes); <sup>1</sup>H NMR δ 8.28 (d, J = 2.4 Hz, 2H), 7.94 (dd, J = 6.4, 3.2 Hz, 2H), 7.62 (s, 2H), 7.41 (dd, J = 6.5, 3.2 Hz, 2H), 6.26-6.22 (m, 1H), 3.81 (s, 8H), 2.63-2.42 (m, 4H), 2.35 (d, J = 10.9 Hz, 1H), 1.83-1.66 (m, 3H), 0.03 (s, 9H); <sup>13</sup>C NMR δ 174.1 (C=O), 173.8 (C=O), 146.3 (C), 146.3 (CH), 140.9 (C), 136.2 (CH), 131.4 (C), 131.3 (C), 131.1 (C), 131.0 (CH), 127.8 (CH), 125.6 (CH), 125.5 (CH), 124.7 (CH), 117.9 (CH), 117.9 (CH), 51.6 (CH<sub>3</sub>), 51.6 (OCH<sub>3</sub>), 50.8 (C), 50.7 (CH), 47.6 (CH), 46.9 (CH), 44.7 (CH), 44.6 (CH), 43.3 (CH<sub>2</sub>), 35.9 (CH<sub>2</sub>), 34.9 (CH<sub>2</sub>), 21.0 (CH), 14.1 (CH<sub>3</sub>).

**cis, exo-1,2,3,4,4a,12b-Hexahydro-1,4-methanotriphenylene (65).**<sup>[46]</sup> To a solution of bicyclo[2.2.1]hept-2-ene (0.65 g, 6.9 mmol) and bromobenzene (1.1 mL, 10.6 mmol) in dry anisole (20 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.57 g, 0.49 mmol) and *t*-BuOK (1.2 g, 10.6 mmol) were added under N<sub>2</sub>. After being stirred at 130 °C for 12 h, the mixture was diluted with anisole (20 mL) and filtered through Celite. The filtrate was washed with H<sub>2</sub>O (2 × 10

mL) and brine (1 ? 10 mL). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration, and concentrated. The solvents were removed in vacuo to give a yellow oil which was purified by column chromatography (hexane) to yield **65** as a white solid (1.01 g, 77%); mp 120-121 ?C (lit.<sup>[46]</sup> 139-141 ?C); <sup>1</sup>H NMR ? 7.85-7.82 (m, 2H), 7.24-7.16 (m, 6H), 3.21 (s, 2H), 2.38 (s, 2H), 1.71-1.62(m, 4H), 1.40 (d, J = 10.0 Hz, 1H), 1.03 (d, J = 10.0 Hz, 1H); <sup>13</sup>C NMR ? 130.6 (CH), 129.1 (CH), 128.0 (CH), 127.7 (CH), 126.6 (CH), 125.3 (CH), 122.4 (CH), 50.0 (CH), 46.3 (CH), 33.6 (CH<sub>2</sub>), 30.7 (CH<sub>2</sub>).

***cis, exo-1,2,3,4-Tetrahydro-1,4-methanotriphenylene (68).***<sup>[70]</sup> A solution of **65** (200 mg, 813 mmol) and DDQ (221 mg, 976 mmol) in anhydrous benzene (5 mL) was heated to reflux for 4.5 h. The mixture was diluted with benzene (25 mL) and filtered through Celite. The filtrate was washed with 0.3 M aq. NaOH until the color of the organic layer changed to yellow. Then the organic layer was washed with H<sub>2</sub>O (1 ? 10 mL ) and brine (1 ? 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a brown oil, which was purified by column chromatography (hexane) to give **68** as a white solid (83.8 mg, 42.2%); mp 165-170 ?C (lit.<sup>[70]</sup> 164 ?C); <sup>1</sup>H NMR ? 8.73 (dd, J = 8.4, 1.7 Hz, 2H), 8.03 (dd, J = 8.1, 1.9 Hz, 2H), 7.64-7.57 (m, 4H), 4.03 (s, 2H), 2.06 (d, J = 8.9 Hz, 2H), 1.91 (d, J = 8.4 Hz, 1H), 1.71 (d, J = 7.2 Hz, 1H), 1.20 (d, J = 7.2 Hz, 1H); <sup>13</sup>C NMR ? 141.5 (C), 129.5 (C), 127.6 (C), 126.4 (CH), 125.1 (CH), 124.0 (CH), 123.3 (CH), 49.1 (CH<sub>2</sub>), 41.9 (CH), 27.2 (CH<sub>2</sub>).

**Tetrakis(triphenylphosphine)palladium(0).**<sup>[71]</sup> A mixture of PdCl<sub>2</sub> (1.77 g, 10 mmol), PPh<sub>3</sub> (13.1 g, 50 mmol) and 120 mL of DMSO was placed in a 250 mL three-necked

round bottom flask equipped with a reflux condenser, a magnetic stirring bar and a rubber septum. The system was placed under a N<sub>2</sub> atmosphere. The yellow mixture was heated in an oil bath until it became homogeneous (140 °C). The oil bath was then taken away and the solution was stirred rapidly for 15 min. Hydrazine hydrate (2 mL, 40 mmol) was then added rapidly from a syringe. A vigorous reaction took place with evolution of N<sub>2</sub>. The dark solution was cooled to rt and filtered under N<sub>2</sub>. The filtration was washed with EtOH (2 × 5 mL) and Et<sub>2</sub>O (2 × 10 mL) to yield a yellow solid, which was dried by passing a slow stream of N<sub>2</sub> over it overnight, and stored under N<sub>2</sub> (9.9 g, 86%).

***cis, exo-1,2,3,4,4a,12b-Hexahydro-8-phenyl-1,4-methanotriphenylen-3-ol (71)***. To a mixture of iodobenzene (0.4 mL, 3.6 mmol), Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup> (1.14 g, 3.6 mmol), K<sub>2</sub>CO<sub>3</sub> (0.98 g, 7.2 mmol) and Pd(OAc)<sub>2</sub> (25 mg, 0.11 mmol) in 7 mL of dry DMF, a solution of bicyclo[2.2.1]hept-5-en-2-ol (130 mg, 1.2 mmol) in dry DMF (2 mL) was added at 65 °C over a 25 min period. The mixture was further heated at 65 °C for 5 h and then diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic layer was washed with water (5 × 50 mL), dried over MgSO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give a brown oil, which was purified by column chromatography (hexane/EtOAc 6:1) to yield **71** as a white solid (170 mg, 42%, mixture of two isomers); mp 181-185 °C; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ 7.34-6.98 (m, 20H), 6.74 (d, J = 8.2 Hz, 2H), 6.63-6.58 (m, 2H), 4.68 (t, J = 5.3 Hz, 2H), 4.00 (br s, 2H), 3.19-3.12 (m, 2H), 3.01 (d, J = 10.4 Hz, 1H), 2.90 (d, J = 9.7 Hz, 1H), 2.34 (s, 1H), 2.17 (s, 2H), 2.02 (s, 1H), 2.00-1.96 (m, 2H), 1.41-1.35 (m, 4H), 1.24 (d, J = 10.1 Hz, 1H), 1.17 (d, J = 9.4 Hz, 1H); <sup>13</sup>C NMR δ 131.1 (CH), 130.9 (CH), 130.4 (CH), 130.1 (CH), 130.0 (CH), 129.9 (CH), 129.4 (CH), 129.0 (CH), 127.4 (CH), 127.3

(CH), 127.1 (CH), 125.4 (CH), 125.3 (CH), 75.7 (CHOH), 75.3 (CHOH), 58.3 (CH), 57.2 (CH), 48.6 (CH), 48.1 (CH), 45.6 (CH), 45.4 (CH), 43.4 (CH<sub>2</sub>), 42.4 (CH<sub>2</sub>), 42.2 (CH), 30.0 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>).

***endo*- and *exo*-Bicyclo[2.2.1]hept-5-en-2-ol.** *endo*- and *exo*-Bicyclo[2.2.1]hept-5-en-2-ol were isolated by column chromatography (hexane/EtOAc 20:1) from the commercial reagent from Aldrich that contains a mixture of both isomers. *Endo* isomer: <sup>1</sup>H NMR ? 6.45 (dd, J = 5.7, 3.0 Hz, 1H), 6.06 (dd, J = 5.7, 2.8 Hz, 1H), 4.50-4.45 (m, 1H), 3.00 (s, 1H), 2.82 (s, 1H), 2.13-2.05 (m, 1H), 1.48(d, J = 10.6 Hz, 1H), 1.29 (d, J = 8.9 Hz, 1H), 1.12 (d, J = 8.9 Hz, 1H), 0.76 (d, J = 12.3 Hz, 1H); <sup>13</sup>C NMR ? 140.9 (CH=), 131.2 (CH=), 72.9 (CHOH), 48.7 (CH), 48.5 (CH<sub>2</sub>), 43.3 (CH), 38.2 (CH<sub>2</sub>). *Exo* isomer: <sup>1</sup>H NMR ? 6.16 (dd, J = 5.7, 2.8 Hz, 1H), 5.93 (dd, J = 5.6, 3.2 Hz, 1H), 3.89 (s, 1H), 2.80 (s, 1H), 2.70 (s, 1H), 1.71 (d, J = 8.5 Hz, 1H), 1.66-1.61 (m, 1H), 1.55 (d, J = 12.4 Hz, 1H), 1.46 (d, J = 3.9 Hz, 1H), 1.25 (d, J = 12.5 Hz, 1H).

***exo*-5-(4-Methoxybenzyloxy)bicyclo[2.2.1]hept-2-ene (72).** A solution of *exo*-bicyclo[2.2.1]hept-5-en-2-ol (100 mg, 0.91 mmol) in dry THF (1 mL) was added to a suspension of NaH (44 mg, 1.83 mmol) in dry DMF (0.6 mL) under N<sub>2</sub>. After this mixture was stirred at rt for 2 h, a solution of *p*-methoxybenzyl chloride (0.25 mL, 1.83 mmol) in dry THF (1 mL) was added. After being stirred for another 2.5 h, the mixture was quenched with H<sub>2</sub>O (2 mL) and concentrated in vacuo to ca. 2 mL. The residue was poured into 10 mL of H<sub>2</sub>O and extracted with EtOAc (3 ? 10 mL). The combined organic layer was washed with H<sub>2</sub>O (1 ? 10 mL) and brine (1 ? 10mL), dried over Na<sub>2</sub>SO<sub>4</sub> and

isolated by filtration. The solvents were removed in vacuo to give an oil, which was purified via column chromatography (hexane/EtOAc 100:1) to give **72** as a white solid (140 mg, 88%); mp 102-106 °C; <sup>1</sup>H NMR  $\delta$  7.25 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.16 (dd, J = 5.7, 2.8 Hz, 1H), 5.89 (dd, J = 5.5, 2.8 Hz, 1H), 4.44 (d, J = 7.4 Hz, 2H), 3.78 (s, 3H), 3.55 (d, J = 6.1 Hz, 1H), 2.91 (s, 1H), 2.79 (s, 1H), 1.71 (d, J = 8.0 Hz, 1H), 1.55-1.51 (m, 2H), 1.40 (d, J = 11.9 Hz, 1H).

**endo-5-(4-Methoxybenzyloxy)bicyclo[2.2.1]hept-2-ene (73).** A solution of *endo*-bicyclo[2.2.1]hept-5-en-2-ol (100 mg, 0.91 mmol) in dry THF (1 mL) was added to a suspension of NaH (44 mg, 1.83 mmol) in dry DMF (0.6 mL) under N<sub>2</sub>. After this mixture was stirred at rt for 2 h, a solution of *p*-methoxybenzyl chloride (0.25 mL, 1.83 mmol) in dry THF (1 mL) was added. After being stirred for another 2.5 h, the mixture was quenched with H<sub>2</sub>O (2 mL) and concentrated in vacuo to ca. 2 mL. The residue was poured into 10 mL of H<sub>2</sub>O, and extracted with EtOAc (3  $\times$  10 mL). The combined organic layer was washed with H<sub>2</sub>O (1  $\times$  10 mL) and brine (1  $\times$  10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and isolated by filtration. The solvents were removed in vacuo to give an oil, which was purified via column chromatography (hexane/EtOAc 100:1) to yield **73** as a white solid (130 mg, 80%); mp 121-124 °C; <sup>1</sup>H NMR  $\delta$  7.23 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.31 (dd, J = 5.5, 2.9 Hz, 1H), 6.00 (dd, J = 5.5, 2.8 Hz, 1H), 4.40 (d, J = 6.0 Hz, 2H), 4.21-4.17 (m, 1H), 3.78 (s, 3H), 3.06 (s, 1H), 2.77 (s, 1H), 1.97-1.91 (m, 1H), 1.40 (d, J = 8.7 Hz, 1H), 1.19 (d, J = 8.7 Hz, 1H), 0.91 (d, J = 12.1 Hz, 1H).

***cis, exo-1,2,3,4,4a,12b-Hexahydro-3-endo-(4-methoxy-benzyloxy)-1,4-methanotriphenylene (74), and compound 75.*** To a solution of **73** (340 mg, 1.48 mmol) and bromobenzene (0.24 mL, 2.28 mmol) in dry anisole (7 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (160 mg, 0.14 mmol) and *t*-BuOK (260 mg, 2.32 mmol) were added under N<sub>2</sub>. After being stirred at 105 °C for 4.5 h, the mixture was diluted with Et<sub>2</sub>O (50 mL) and filtered. The filtrate was concentrated and purified by column chromatography (hexane/EtOAc 100:3) to give **74** as a white solid (196 mg, 58%); mp 158-160 °C; <sup>1</sup>H NMR δ 7.85-7.82 (m, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.19-7.17 (m, 5H), 7.12-7.10 (m, 1H), 6.91 (d, J = 8.6 Hz, 2H), 4.65 (d, J = 11.2 Hz, 1H), 4.49 (d, J = 11.2 Hz, 1H), 4.04-3.99 (m, 1H), 3.88 (d, J = 10.0 Hz, 1H), 3.80 (s, 3H), 3.34 (d, J = 10.0 Hz, 1H), 2.53 (d, J = 2.5 Hz, 1H), 2.33 (d, J = 4.2 Hz, 1H), 2.13-2.06 (m, 1H), 1.48-1.42 (m, 2H), 1.11 (d, J = 10.5 Hz, 1H); <sup>13</sup>C NMR δ 148.9 (C), 140.7 (C), 130.3 (CH), 130.2 (CH), 129.8 (CH), 129.7 (C), 128.2 (C), 128.1 (CH), 128.0 (CH), 126.7 (CH), 126.5 (CH), 122.6 (CH), 122.4 (CH), 114.2 (CH), 80.3 (OCH<sub>3</sub>), 71.5 (CH<sub>2</sub>O), 55.7 (CHOH), 53.4 (CH), 49.3 (CH), 46.1 (CH), 38.0 (CH<sub>2</sub>), 36.3 (CH), 32.5 (CH<sub>2</sub>), and **75** (40 mg) as a byproduct: <sup>1</sup>H NMR δ 7.30 (d, J = 8.5 Hz, 2H), 7.19-7.17 (m, 2H), 7.02-6.96 (m, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.51 (d, J = 11.2 Hz, 1H), 4.38 (d, J = 11.2 Hz, 1H), 4.04-3.99 (m, 1H), 3.85 (d, J = 3.5 Hz, 1H), 3.80 (s, 3H), 3.33 (d, J = 3.6 Hz, 1H), 2.53 (d, J = 2.9 Hz, 1H), 2.24 (d, J = 4.6 Hz, 1H), 2.02-1.94 (m, 1H), 1.23 (s, 1H), 1.05-1.01 (m, 2H), 0.89 (d, J = 10.8 Hz, 1H).

***cis, exo-1,2,3,4,4a,12b-Hexahydro-1,4-methanotriphenylene-endo-3-ol (76), and 1,2,3,4-tetrahydro-1,4-methanotriphenylene-endo-3-ol (77).*** Compound **74** (56 mg, 0.15 mmol) and DDQ (66 mg, 0.29 mmol) in dry benzene (4 mL) were heated to reflux

for 2 h. The mixture was diluted with benzene (20 mL) and filtered. The filtrate was concentrated to a dark green oil, which was purified by column chromatography ( $\text{CH}_2\text{Cl}_2$ ) to give **76** (14 mg) and **77** (12 mg) (combined yield 68%); **76**: mp 164-166 °C;  $^1\text{H NMR}$   $\delta$  7.84 (d,  $J = 2.9$  Hz, 2H), 7.20-7.19 (m, 6H), 4.38-4.30 (m, 1H), 3.93 (d,  $J = 10.0$  Hz, 1H), 3.34 (d,  $J = 10.0$  Hz, 1H), 2.35 (s, 2H), 2.21-2.14 (m, 1H), 1.45 (d,  $J = 10.4$  Hz, 1H), 1.29 (d,  $J = 9.8$  Hz, 1H), 1.14 (d,  $J = 10.5$  Hz, 1H), 0.95 (d,  $J = 7.4$  Hz, 1H); **77**: mp 186-189 °C;  $^1\text{H NMR}$   $\delta$  8.75-8.71 (m, 2H), 8.07-8.01 (m, 2H), 7.66-7.58 (m, 4H), 4.90-4.86 (m, 1H), 4.15 (d,  $J = 2.6$  Hz, 1H), 3.95 (d,  $J = 1.9$  Hz, 1H), 2.53-2.47 (m, 1H), 2.01 (d,  $J = 9.1$  Hz, 1H), 1.85 (d,  $J = 9.1$  Hz, 1H), 0.89 (dt,  $J = 12.6, 3.1$  Hz, 1H).

**1,3-Adamantanediol (82).**<sup>[48]</sup> A mixture of 1-adamantanol (5 g, 32 mmol), sodium metaperiodate (16g, 74 mmol) and  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  (200 mg, 0.96 mmol) in  $\text{CCl}_4/\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (20/30/30 mL) was stirred vigorously at 60 °C for 11 h. The reaction mixture was diluted with 300 mL of MeOH and filtered. Removal of the solvents yielded a yellow solid, which was recrystallized from  $\text{CH}_2\text{Cl}_2$  to give **82** as a yellow solid (2.9 g, 53%); mp 252 °C (sealed) (lit.<sup>[48]</sup> 315-317 °C);  $^1\text{H NMR}$   $\delta$  2.39 (s, 2H), 1.72-1.30 (m, 10H), 0.92 (m, 2H);  $^{13}\text{C NMR}$   $\delta$  70.8 (COH), 53.2 ( $\text{CH}_2$ ), 44.3 ( $\text{CH}_2$ ), 34.9 ( $\text{CH}_2$ ), 31.6 (CH).

**7-Methylenebicyclo[3.3.1]nonan-3-one (81).**<sup>[55]</sup> To a solution of **82** (185 mg, 1.1 mmol) and 4-dimethylaminopyridine (34 mg, 0.278 mmol) in dry pyridine (2 mL), *p*-TsCl (250 mg, 1.31 mmol) was added quickly as solid. After being stirred at 75 °C for 10.5 h, the reaction mixture was quenched by 10% aq. HCl cooled in ice. The mixture was then

extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, isolated by filtration, and concentrated to an oil, which was purified by column chromatography (hexane/EtOAc 5:1) to give **81** as white needles (100 mg, 60%); mp 165-170 °C (lit.<sup>[55]</sup> 158-161 °C); <sup>1</sup>H NMR δ 4.73 (t, J = 1.8 Hz, 2H), 2.45-2.20 (m, 10H), 1.94-1.83 (m, 2H); <sup>13</sup>C NMR δ 211.5 (C=O), 142.1 (C=), 115.1 (CH<sub>2</sub>=), 47.7 (CH<sub>2</sub>), 41.8 (CH<sub>2</sub>), 32.4 (CH<sub>2</sub>), 31.2 (CH), 31.0 (CH).

**Failed reaction of **81** and phenylmagnesium bromide.** To a suspension of CeCl<sub>3</sub> (330 mg, 1.34 mmol) in dry THF (4 mL) at 0 °C was added a solution of phenylmagnesium bromide (1.0 M, 1.34 mL, 1.34 mmol) in dry THF under N<sub>2</sub>. The mixture was stirred at 0 °C for 1.5 h, then a solution of **81** in dry THF (2 mL) was added dropwise and the mixture was stirred at rt overnight. TLC showed that no new product had formed.

**Failed reaction of **81** and phenylmagnesium bromide in the presence of MgI<sub>2</sub>.** To a cooled suspension of **81** (100 mg, 0.67 mmol) and MgI<sub>2</sub> (186 mg, 0.67 mmol) in anh. Et<sub>2</sub>O (10 mL) at -78 °C was added a solution of phenylmagnesium bromide (1.0 M, 1.3 mL, 1.3 mmol) in dry THF under N<sub>2</sub>. After being stirred at -78 °C for 5 h, the mixture was allowed to slowly warm to rt and stirred overnight. TLC showed that no new product had formed.

**Failed reaction of **81** and phenyllithium.** To a cooled solution of **81** (54 mg, 0.36 mmol) in dry THF (5 mL) at -78 °C was added HMPA (0.13 mL, 0.72 mmol) followed by a solution of PhLi (1.8 M, 0.3 mL, 0.54 mmol) in cyclohexane/ Et<sub>2</sub>O under N<sub>2</sub>. After

being stirred at  $-78\text{ }^{\circ}\text{C}$  for 2 h, the mixture was allowed to slowly warm to rt and stirred overnight. TLC showed that no new product had formed.

**Failed reaction of **81** and phenyllithium in the presence of  $\text{LiClO}_4$ .** A mixture of **81** (45 mg, 0.3 mmol),  $\text{LiClO}_4$  (80 mg, 0.71 mmol) in anh.  $\text{Et}_2\text{O}$  (1 mL) was stirred at rt for 30 min and then cooled to  $-78\text{ }^{\circ}\text{C}$ . A solution of PhLi (1.8 M, 0.2 mL, 0.36 mmol) in cyclohexane/  $\text{Et}_2\text{O}$  was added dropwise and the mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 3h. After being quenched with  $\text{H}_2\text{O}$ , the reaction mixture was extracted with  $\text{Et}_2\text{O}$  (3 ? 10 mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , isolated by filtration. Removal of the solvents gave a white solid. NMR and TLC showed that it was the starting material **81**.

**Failed reaction of **81** and  $\beta$ -naphthyllithium.** To a cooled solution of  $\beta$ -naphthalene (308 mg, 1.48 mmol) in dry THF (20 mL) at  $-78\text{ }^{\circ}\text{C}$  was added a solution of BuLi (1.6 M, 1 mL, 1.6 mmol) in hexane under  $\text{N}_2$ . The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, then a solution of **81** (171 mg, 1.1 mmol) in dry THF (5 mL) was added dropwise. The mixture was allowed to slowly warm to rt and stirred overnight. TLC showed that no new product had formed.

## References

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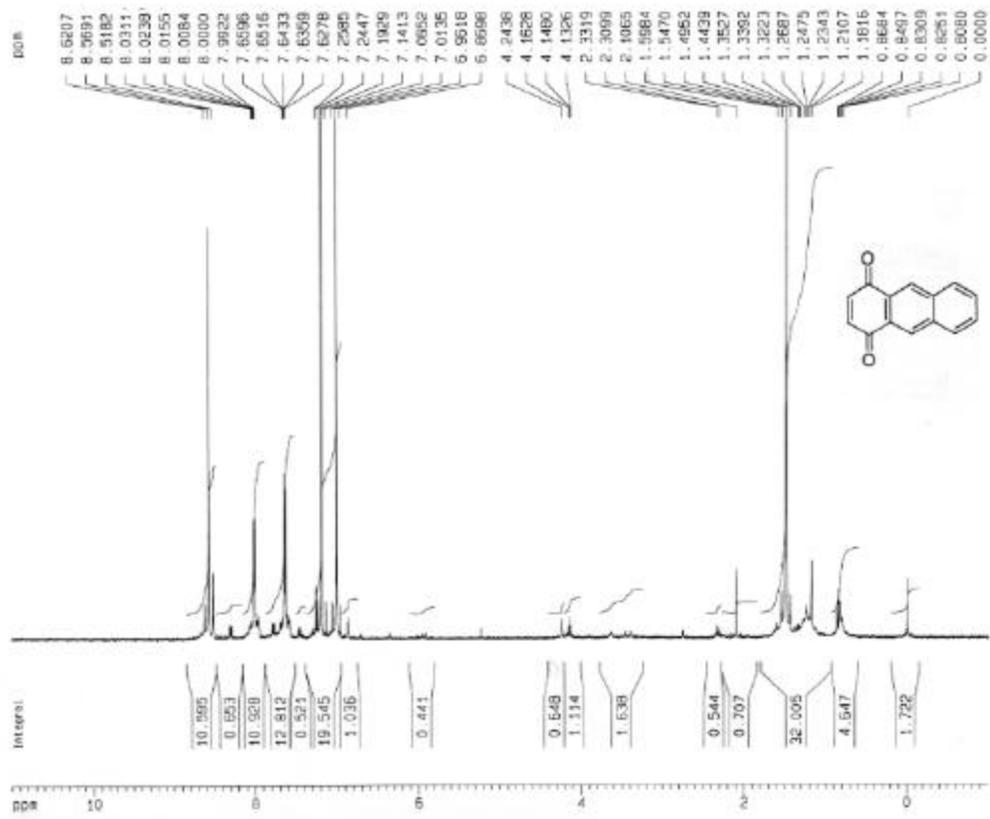


Figure A-1. <sup>1</sup>H NMR spectrum of 35.

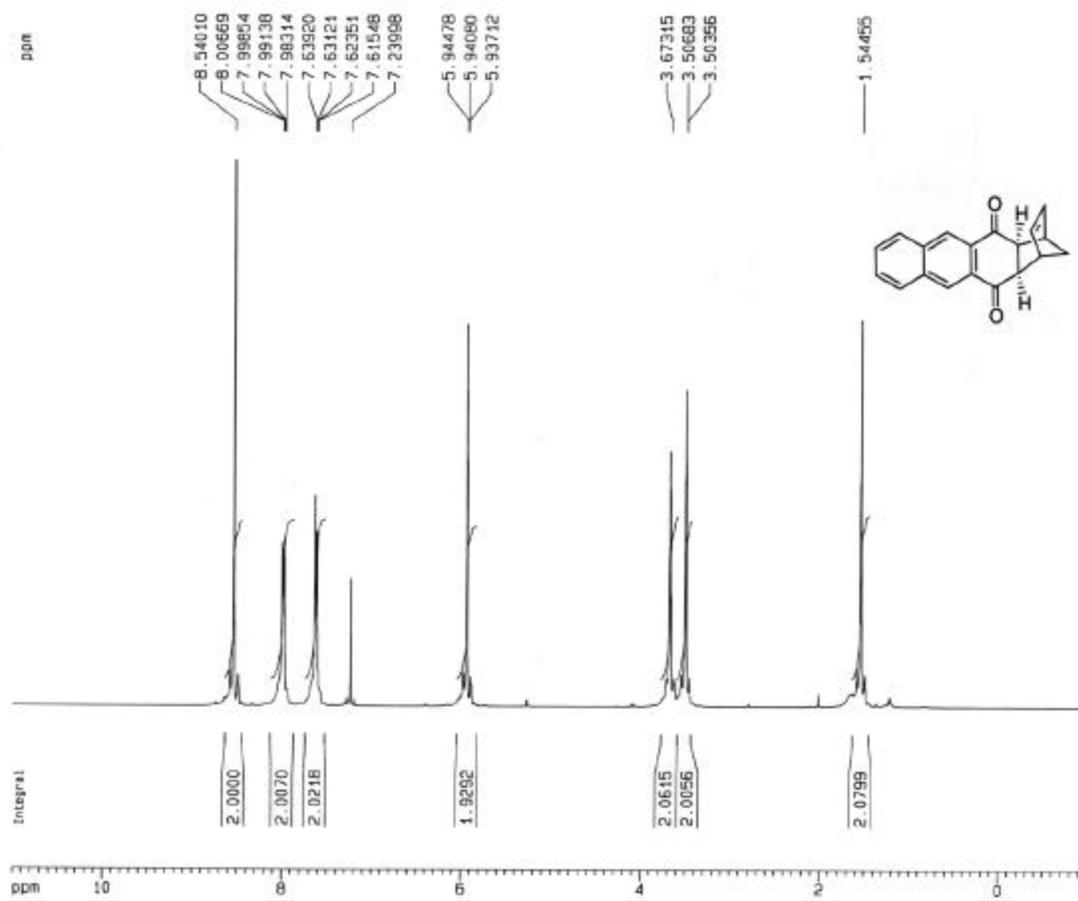


Figure A-2.  $^1\text{H}$  NMR spectrum of **36**.

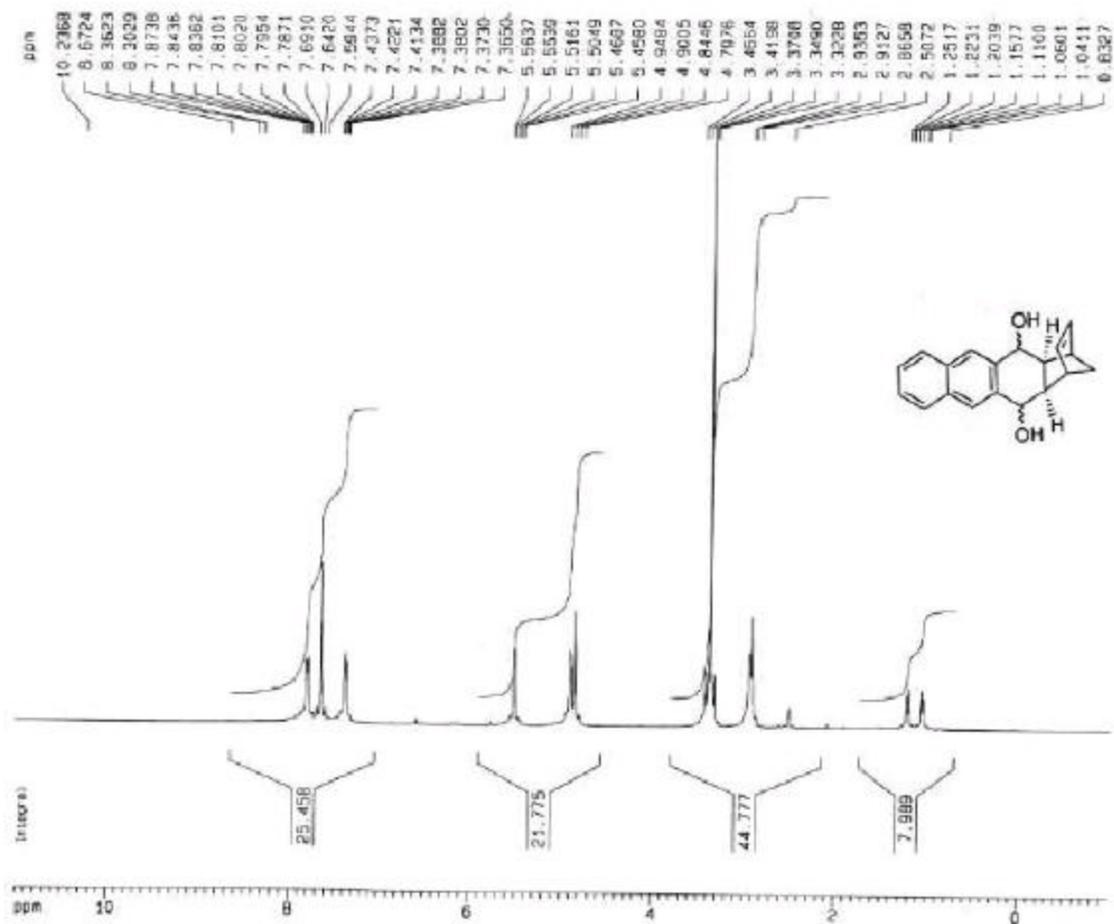


Figure A-3.  $^1\text{H}$  NMR spectrum of **37**.

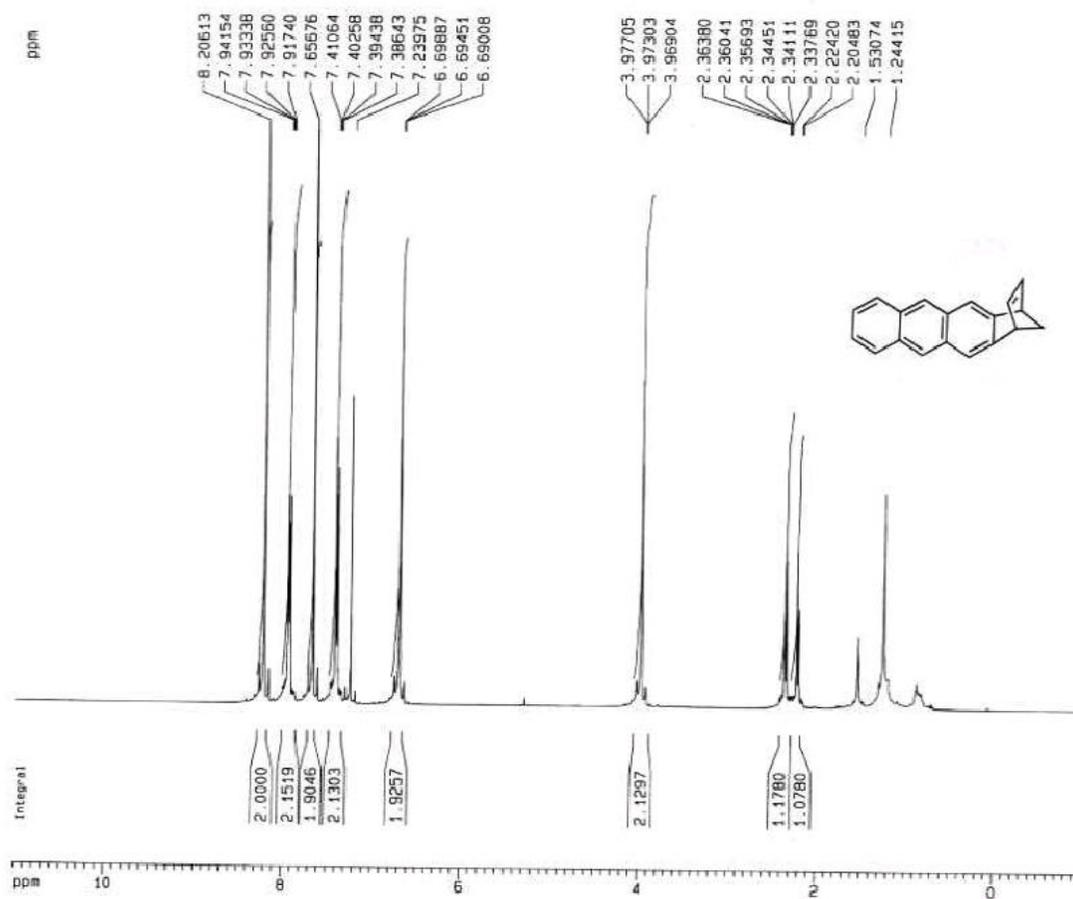


Figure A-4.  $^1\text{H}$  NMR spectrum of **28**.

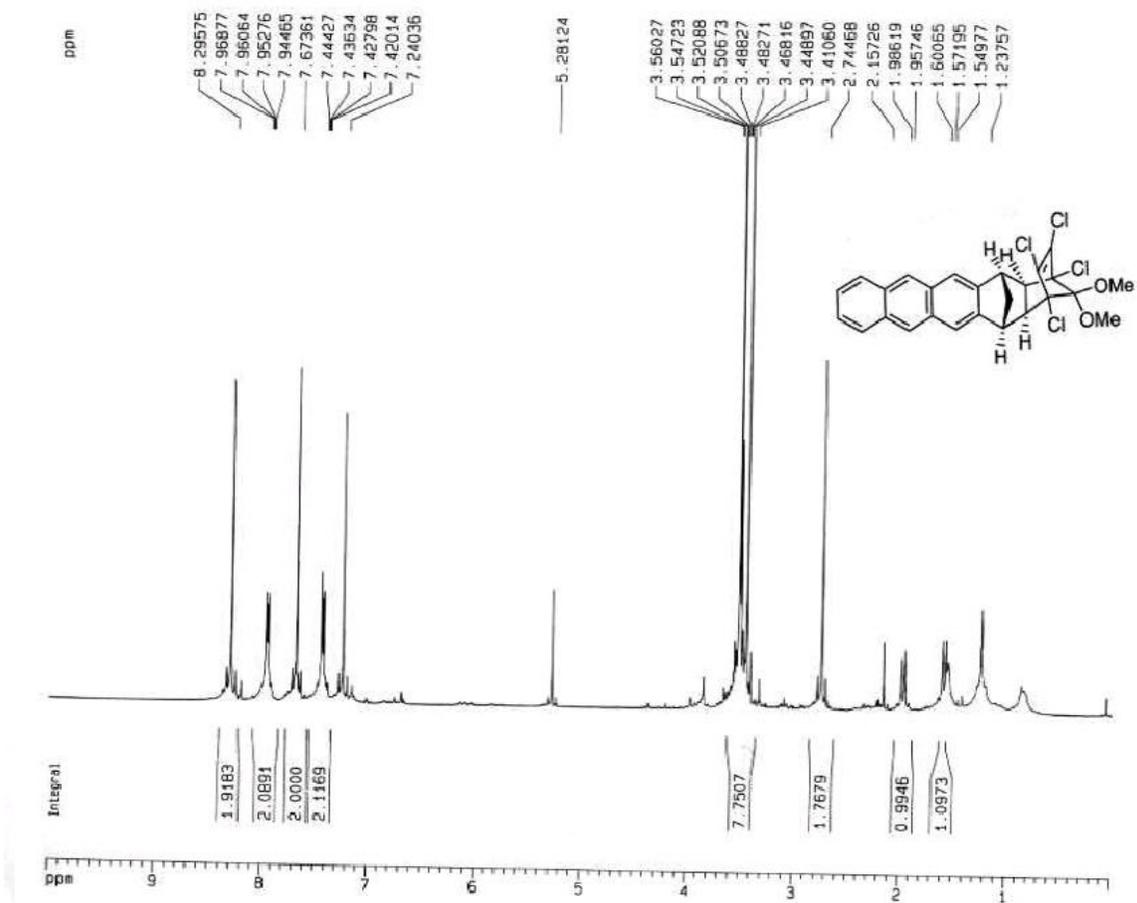


Figure A-5. <sup>1</sup>H NMR spectrum of **29**.

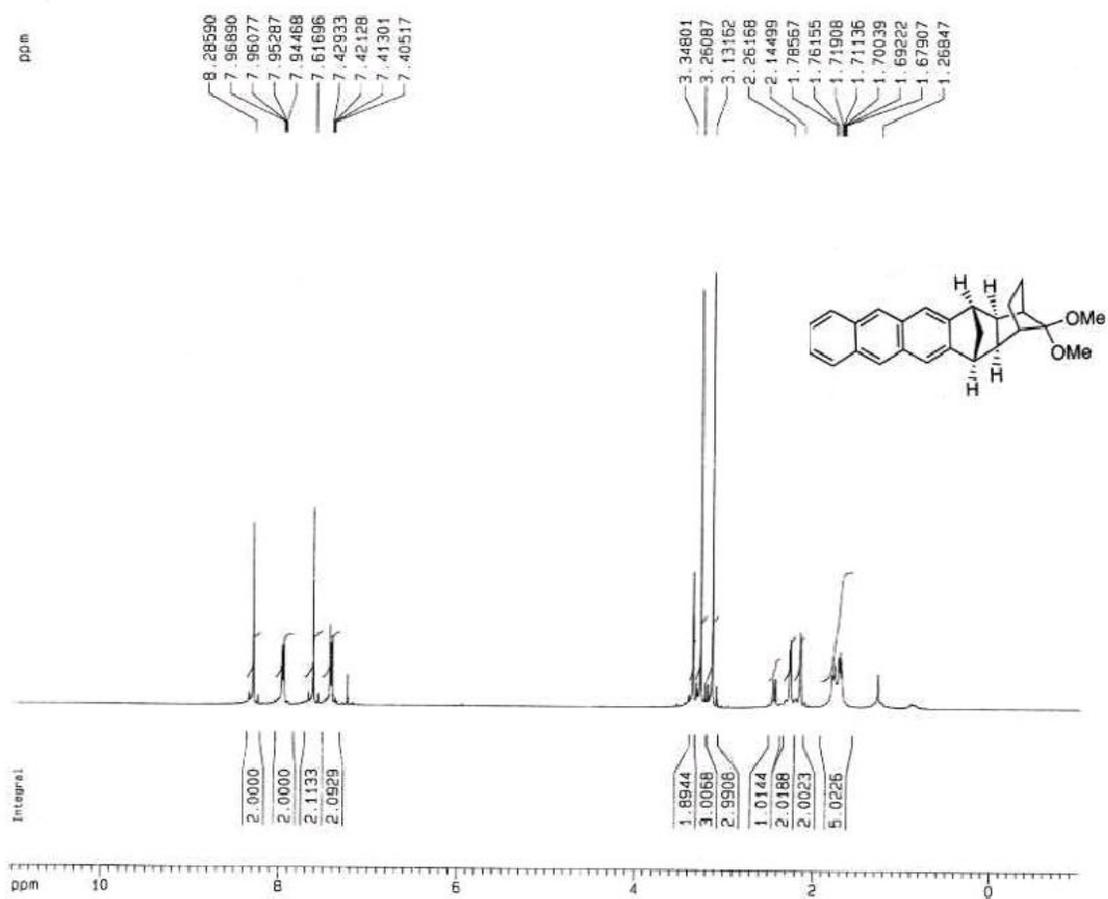


Figure A-6.  $^1\text{H}$  NMR spectrum of **40**.



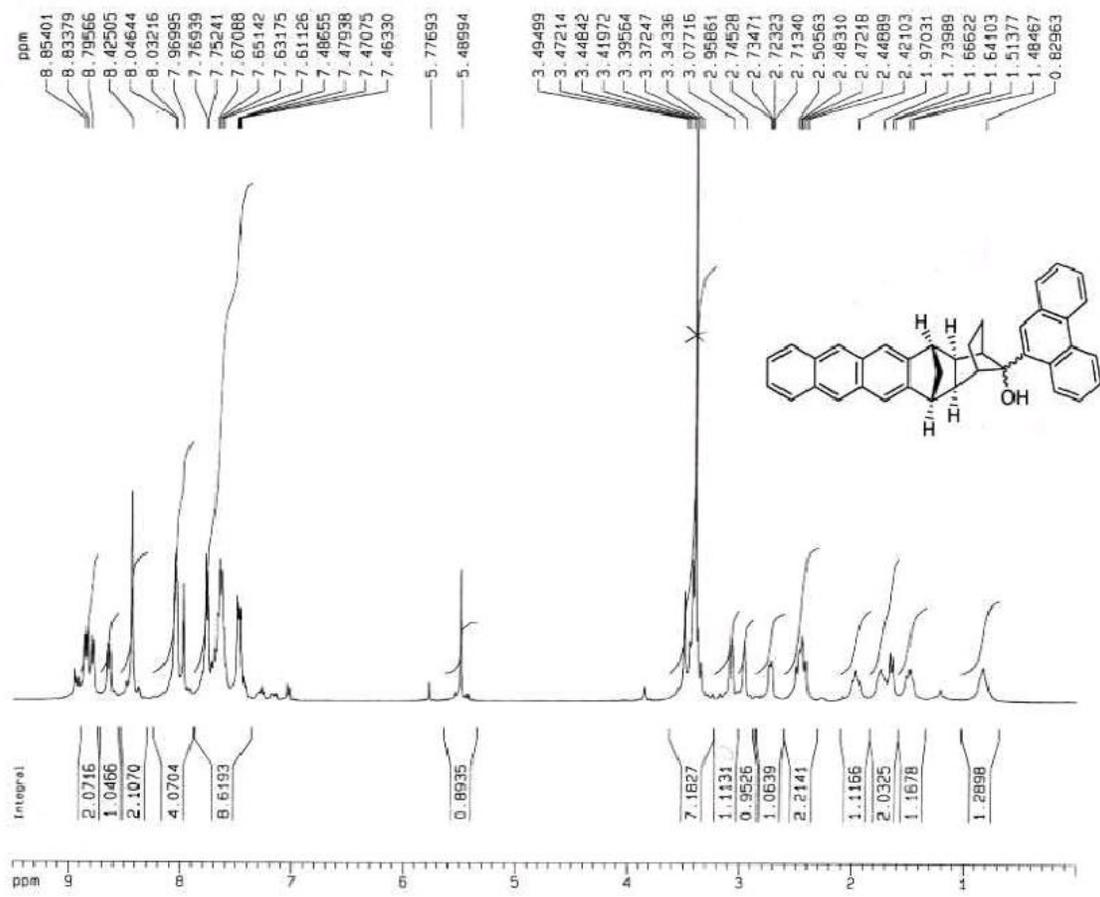


Figure A-8.  $^1\text{H}$  NMR spectrum of **42**.

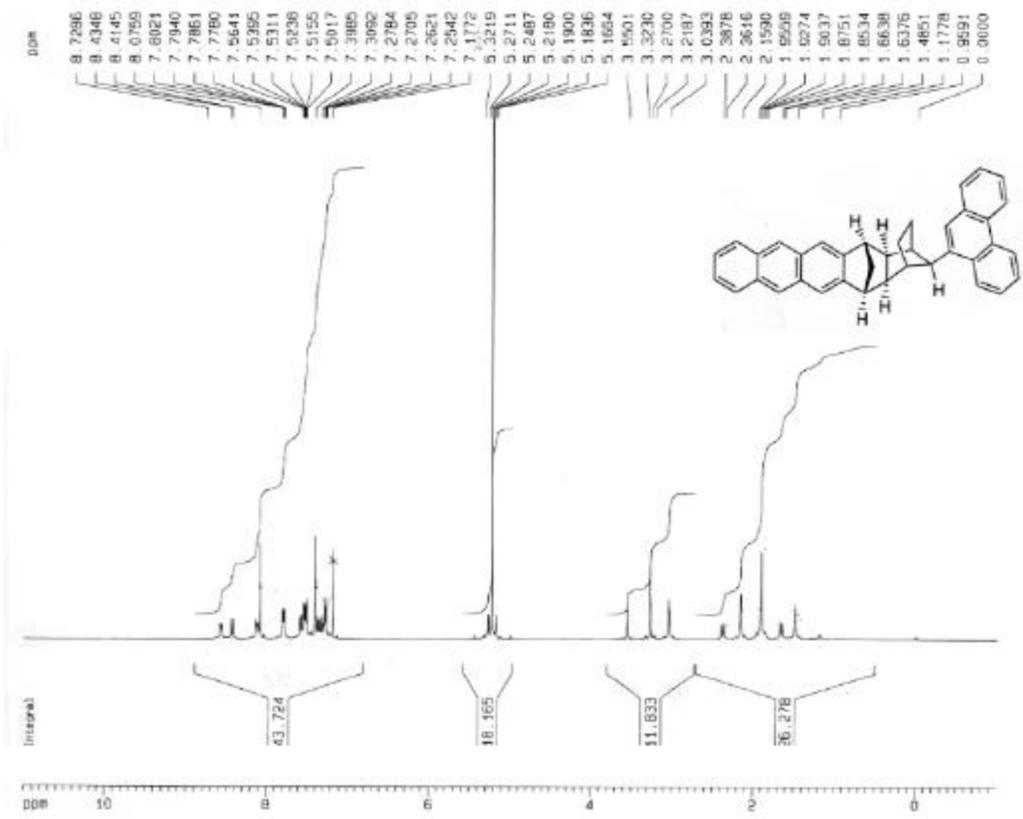


Figure A-9.  $^1\text{H}$  NMR spectrum of **12**.

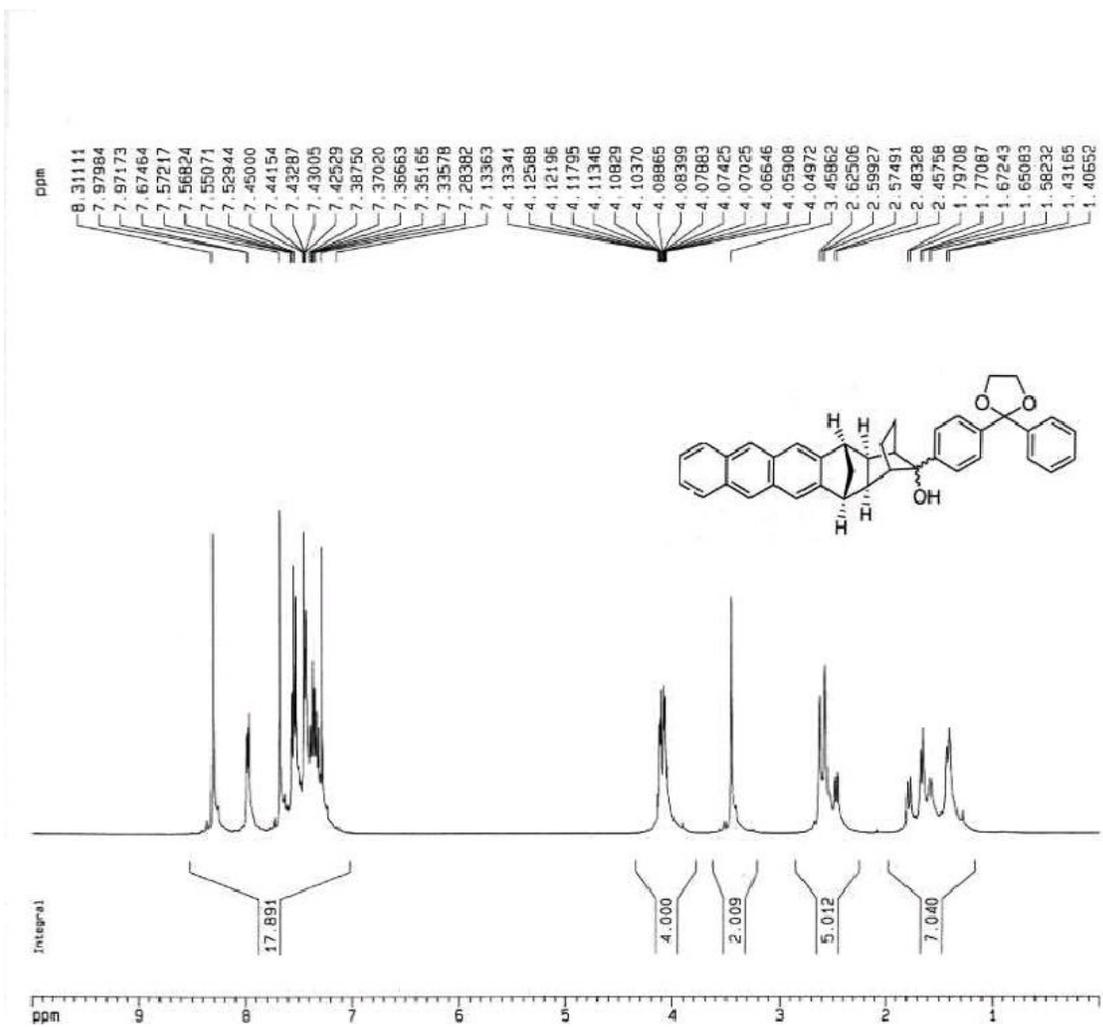


Figure A-10. <sup>1</sup>H NMR spectrum of 45.

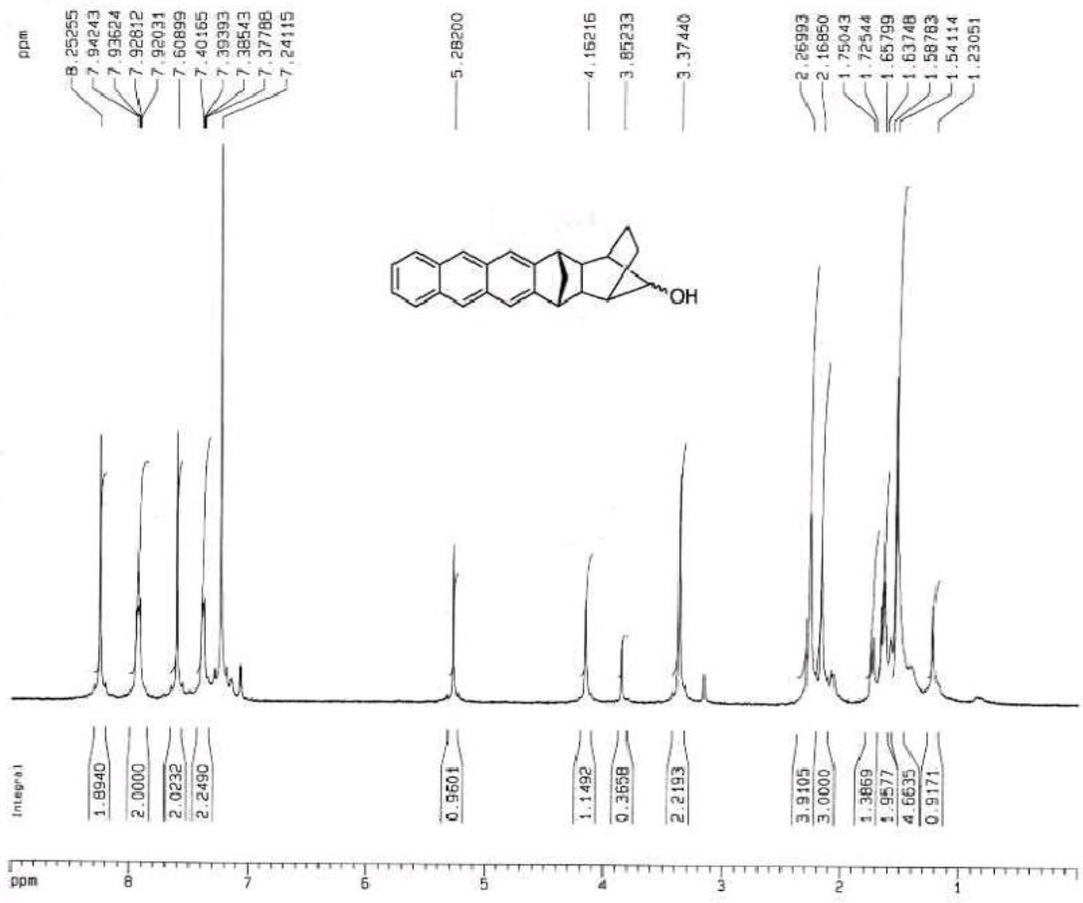


Figure A-11.  $^1\text{H}$  NMR spectrum of **52**.

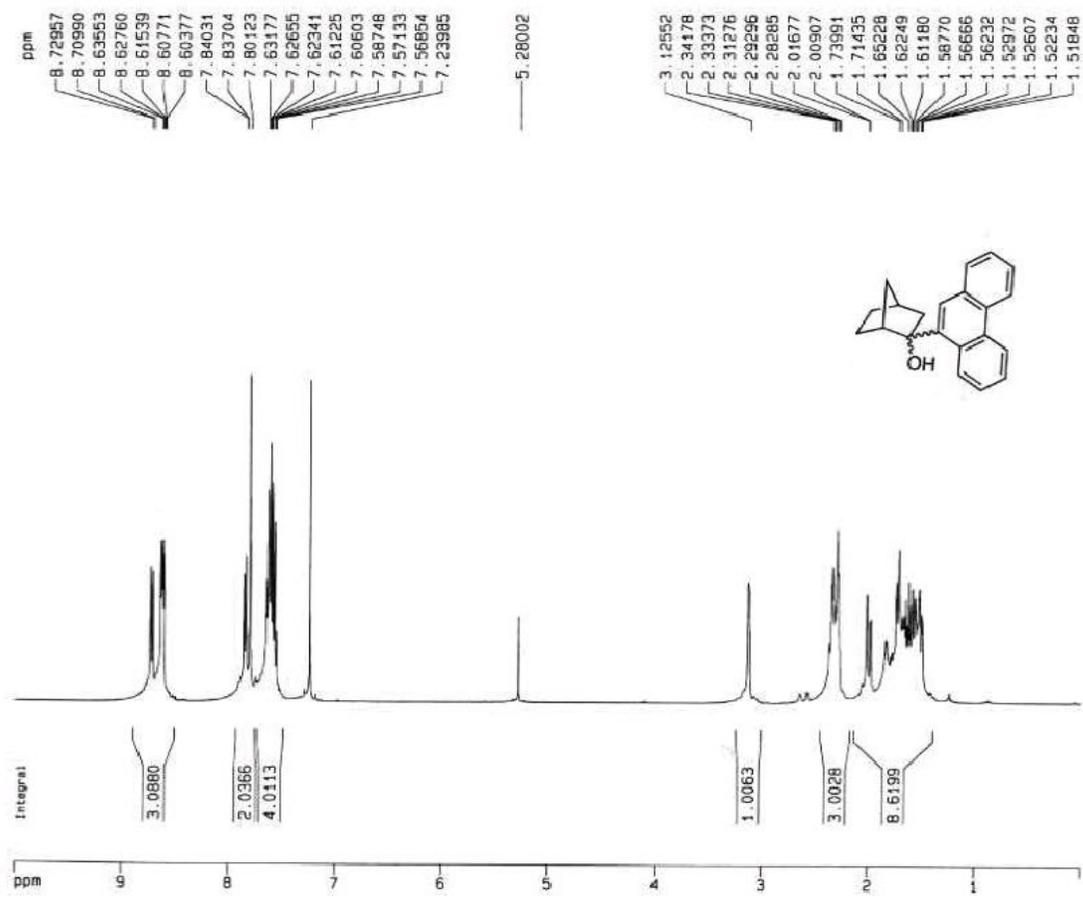


Figure A-12. <sup>1</sup>H NMR spectrum of **53**.

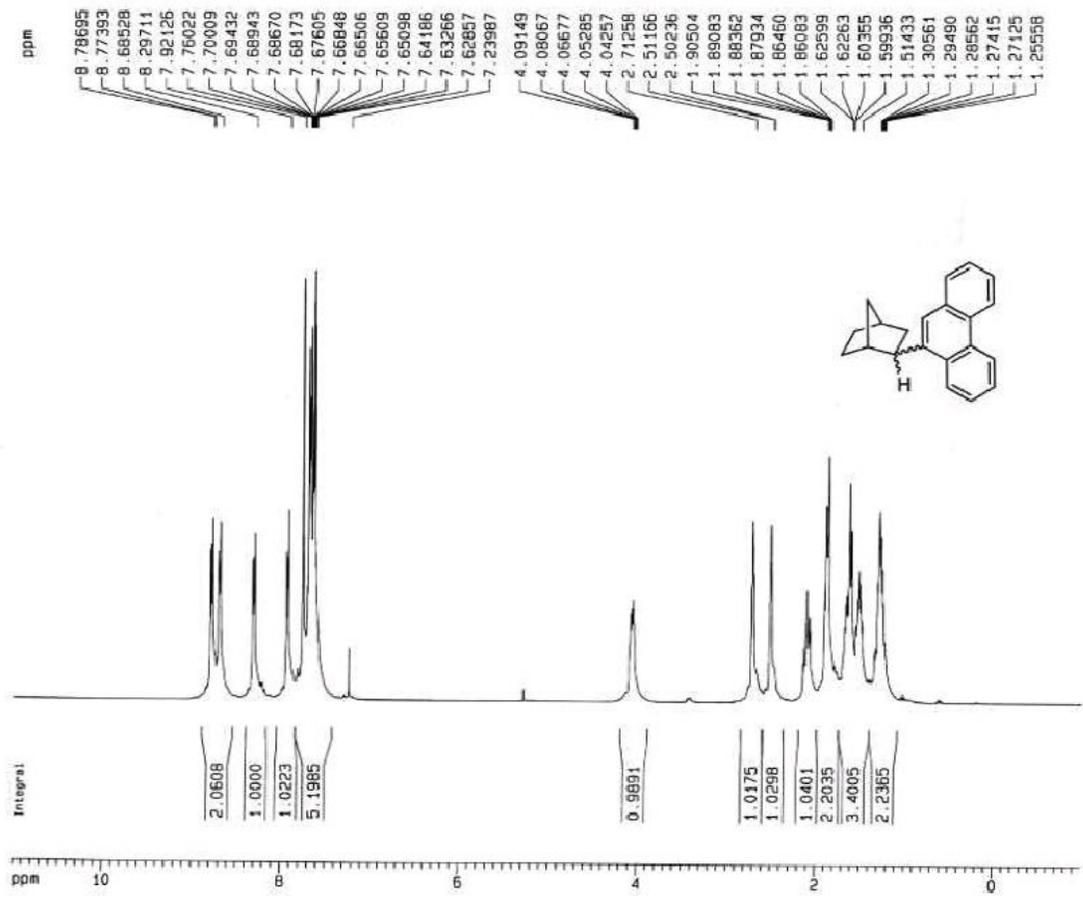


Figure A-13.  $^1\text{H}$  NMR spectrum of **49**.

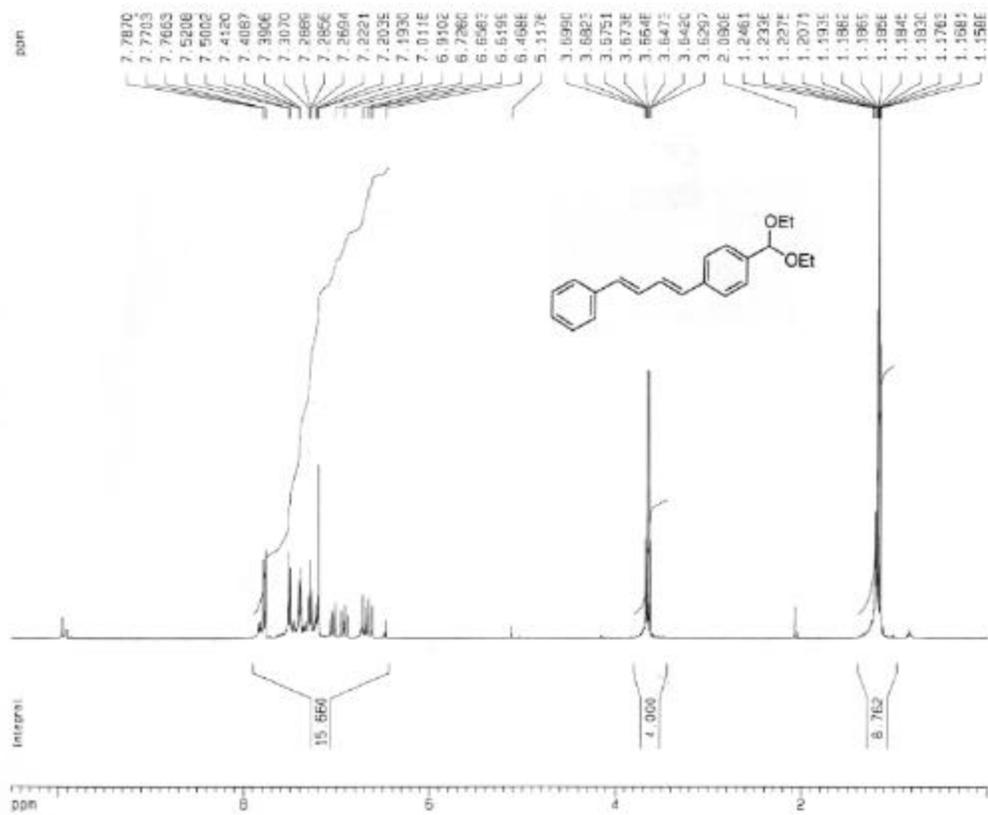


Figure A-14. <sup>1</sup>H NMR spectrum of **54**.

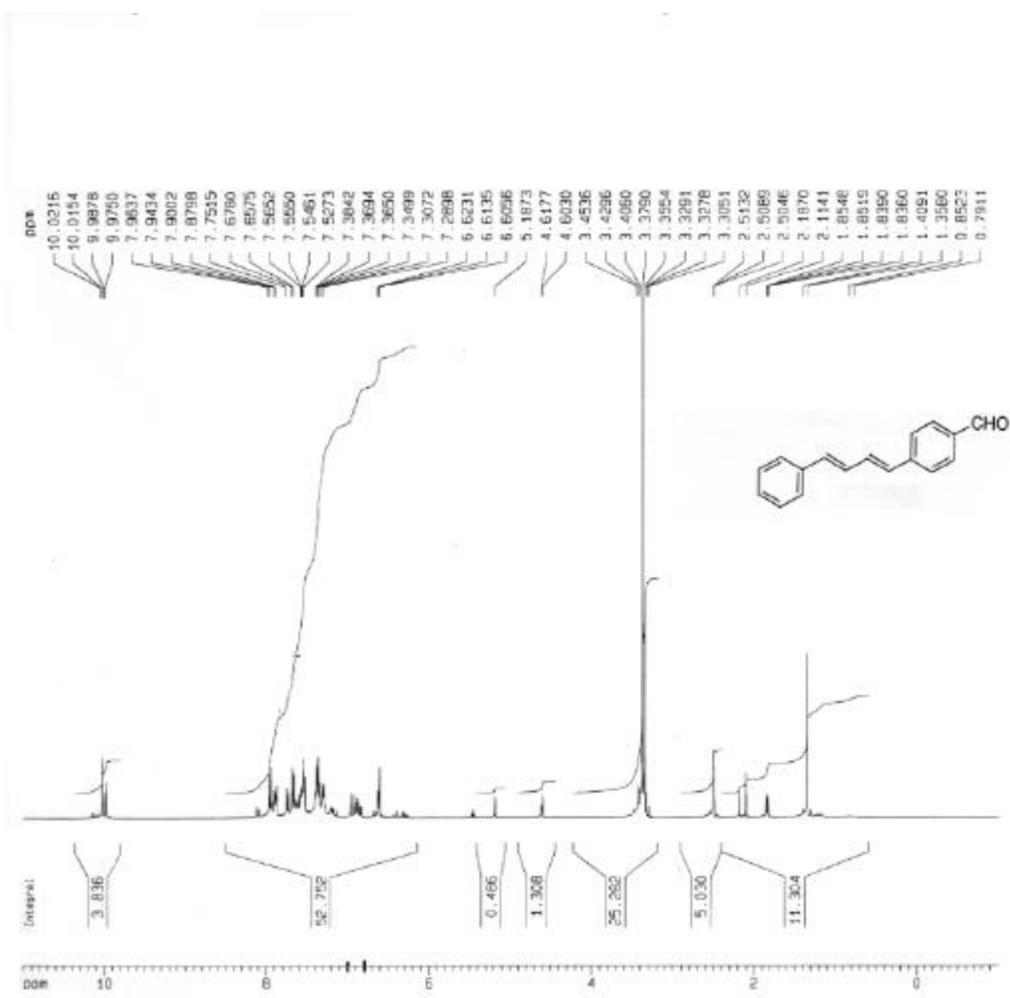


Figure A-15. <sup>1</sup>H NMR spectrum of **55**.

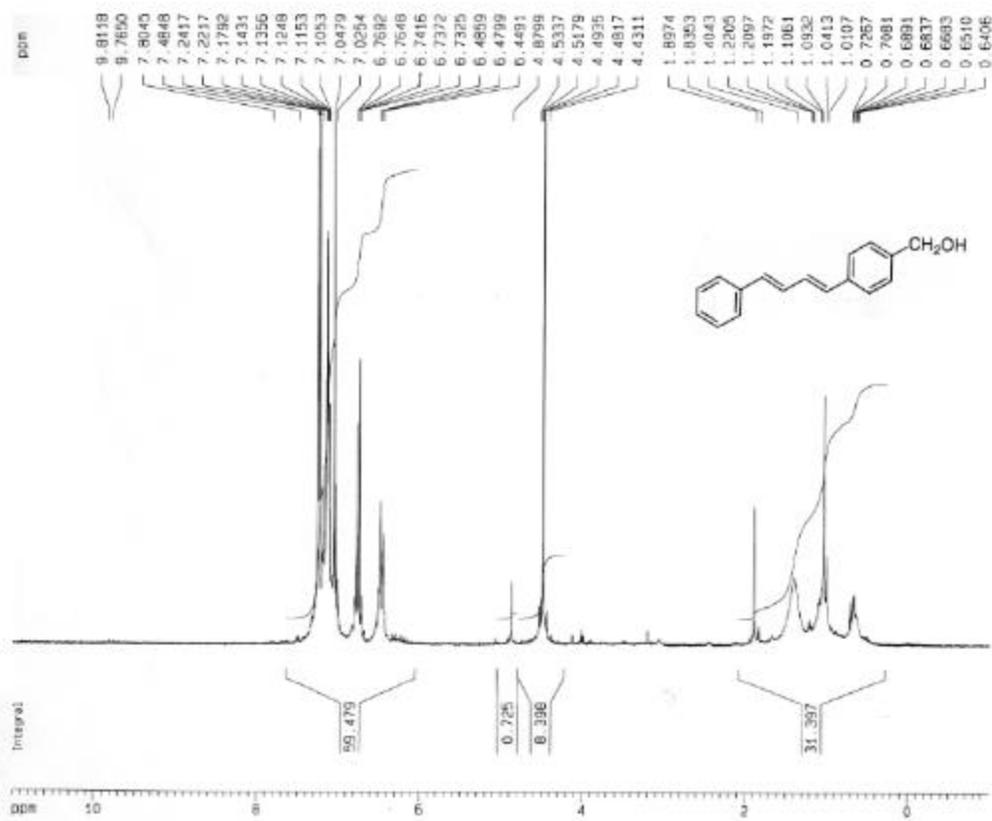


Figure A-16. <sup>1</sup>H NMR spectrum of **56**.

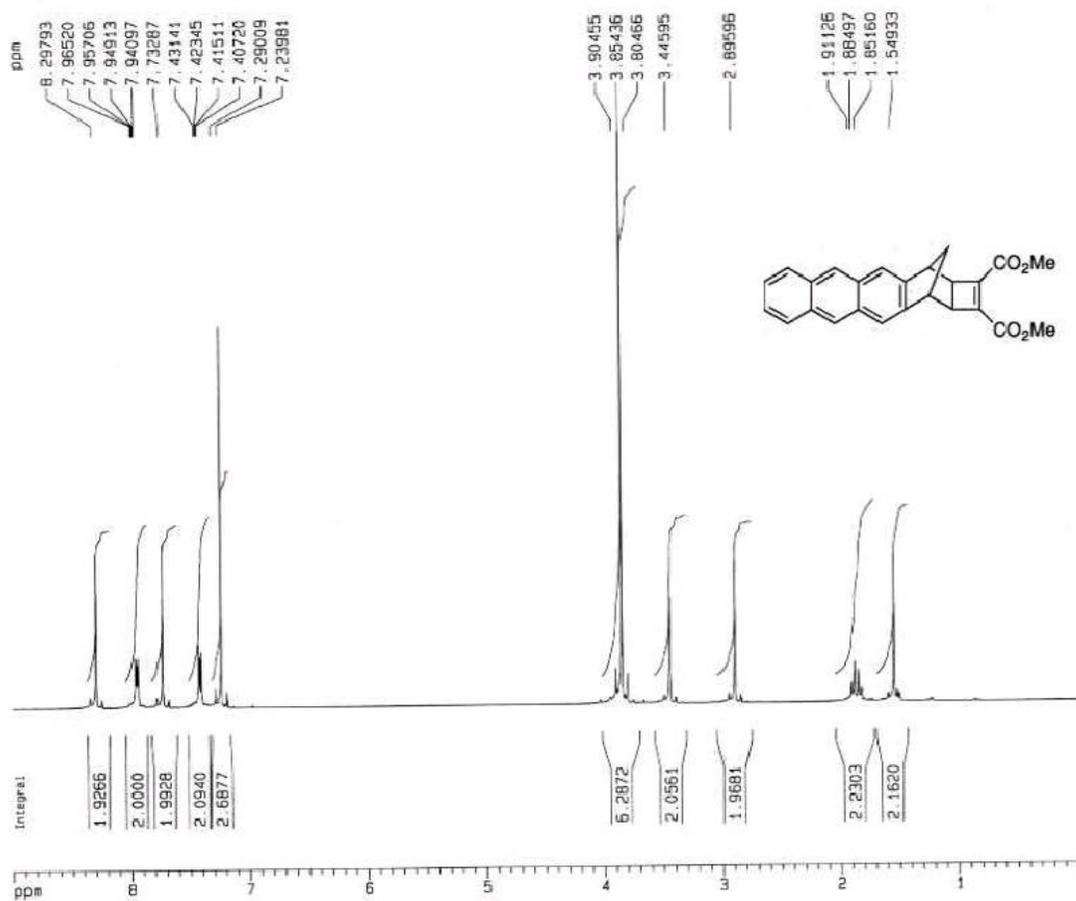


Figure A-17.  $^1\text{H}$  NMR spectrum of **31**.

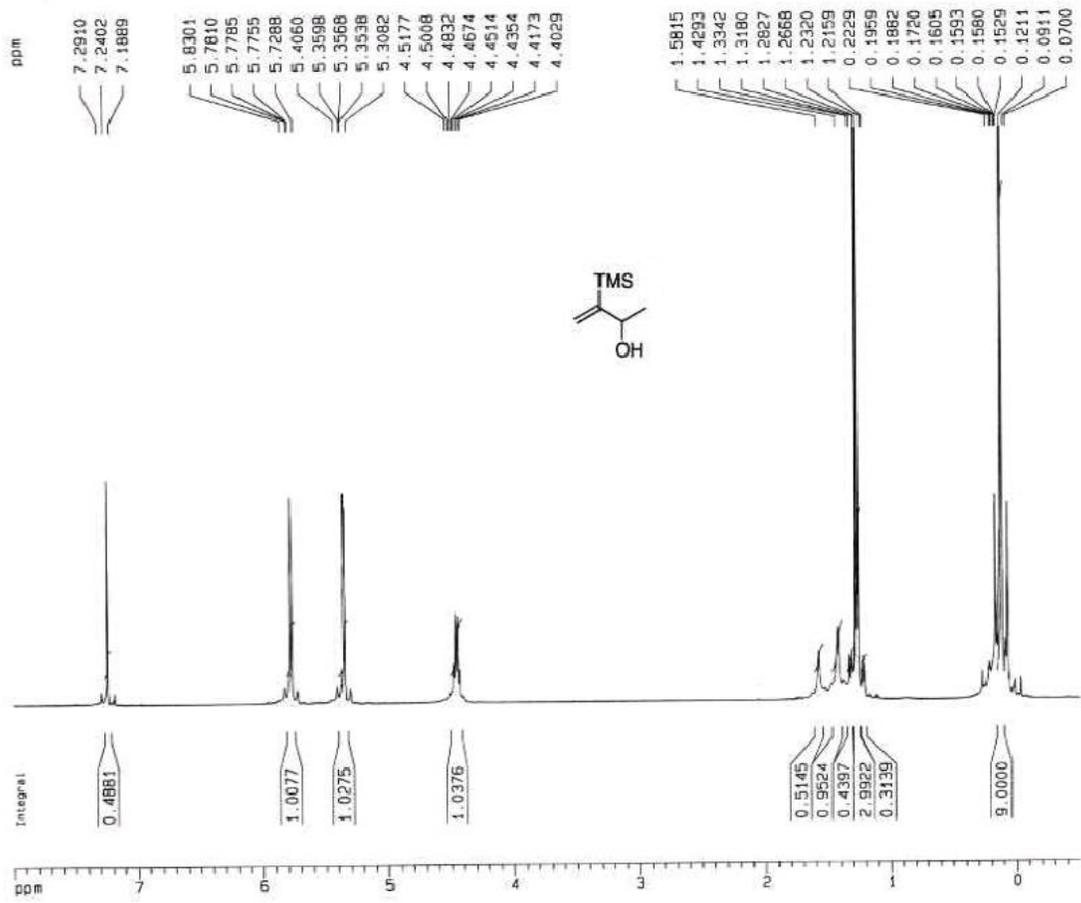


Figure A-18.  $^1\text{H}$  NMR spectrum of **63**.

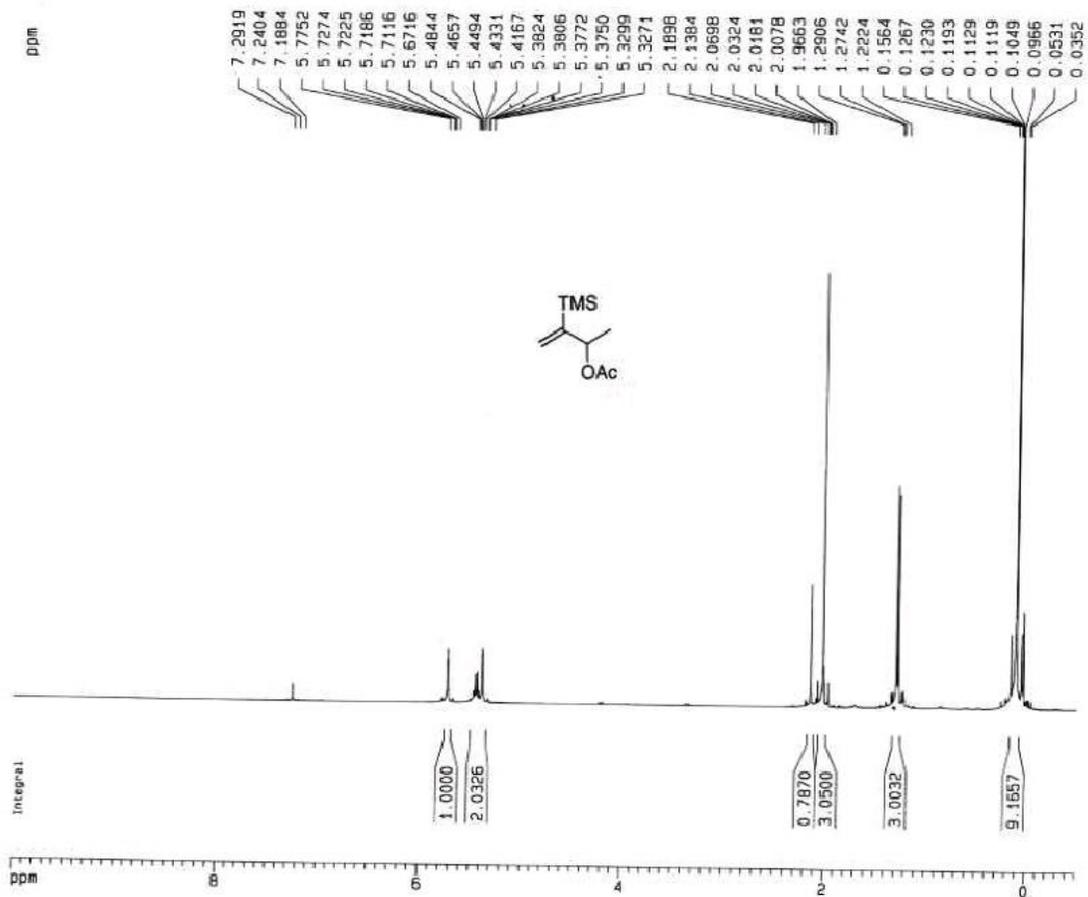


Figure A-19.  $^1\text{H}$  NMR spectrum of **59**.

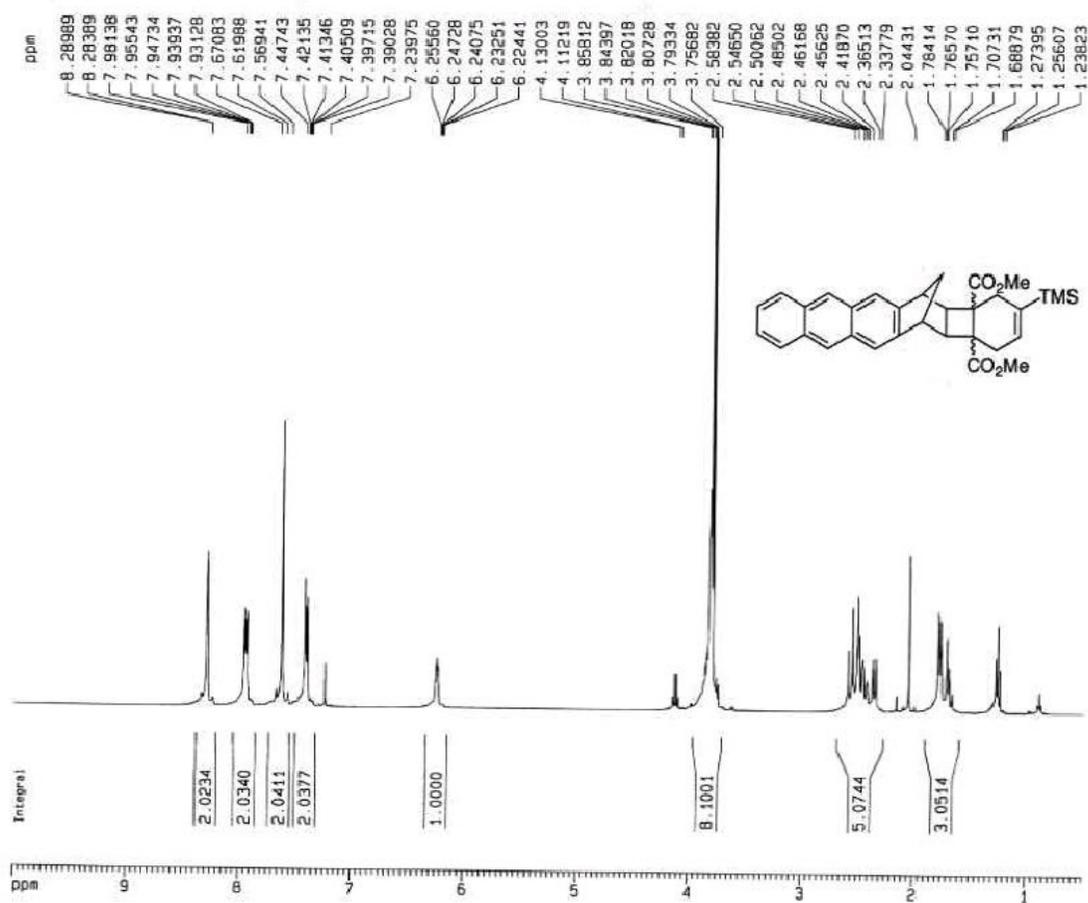


Figure A-20. <sup>1</sup>H NMR spectrum of **32**.

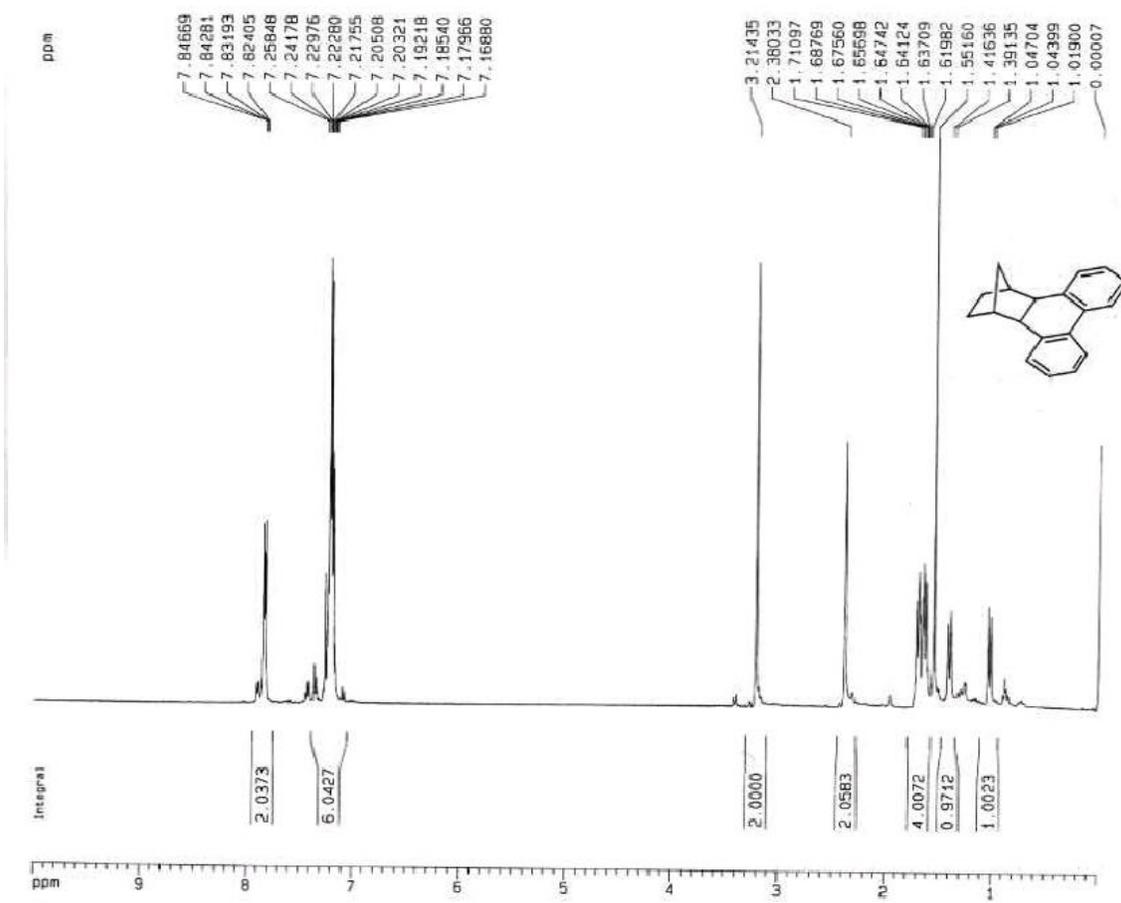


Figure A-21. <sup>1</sup>H NMR spectrum of **65**.

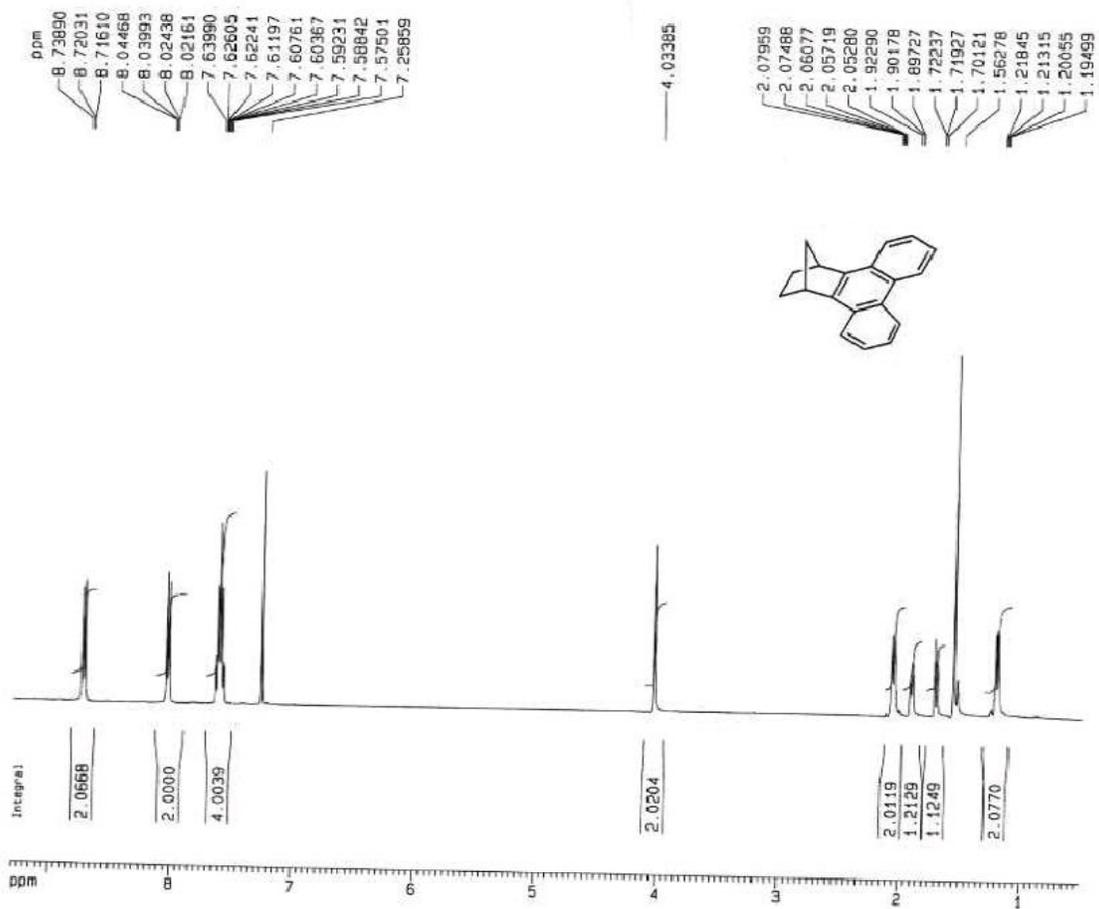


Figure A-22.  $^1\text{H}$  NMR spectrum of **68**.

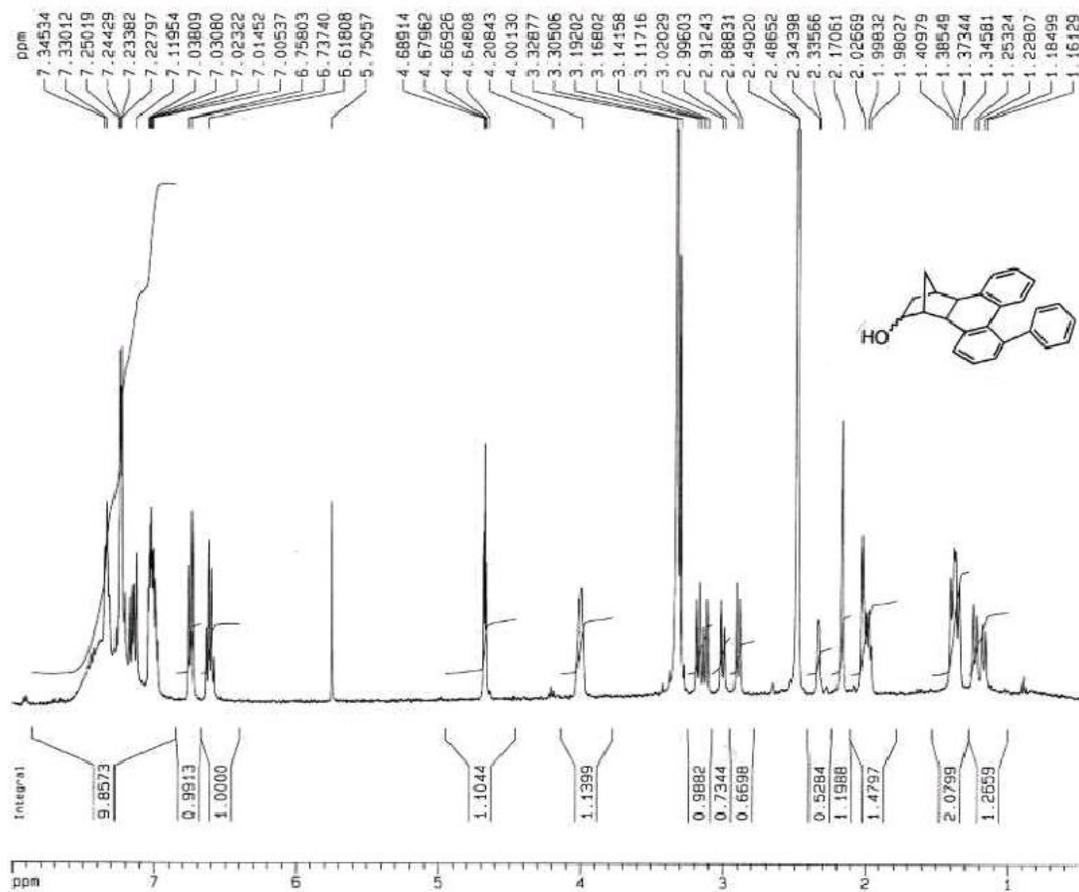


Figure A-23.  $^1\text{H}$  NMR spectrum of **71**.

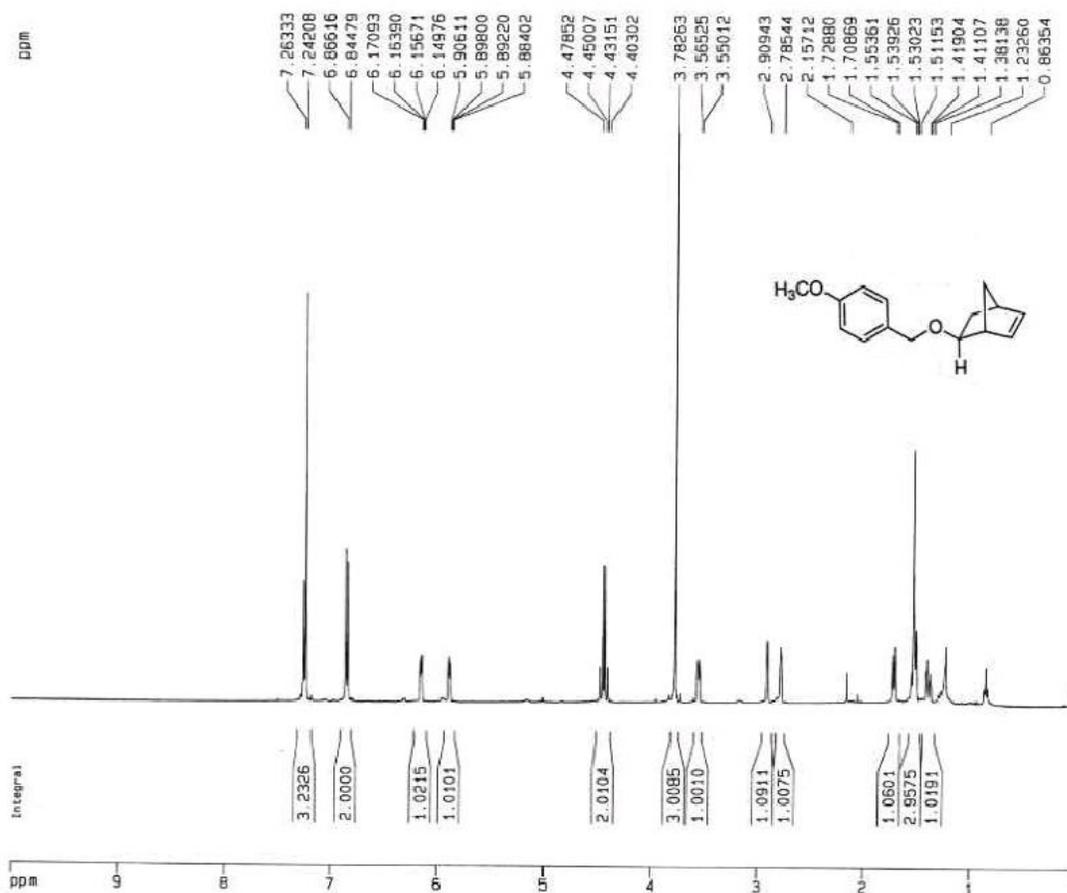


Figure A-24.  $^1\text{H}$  NMR spectrum of **72**.

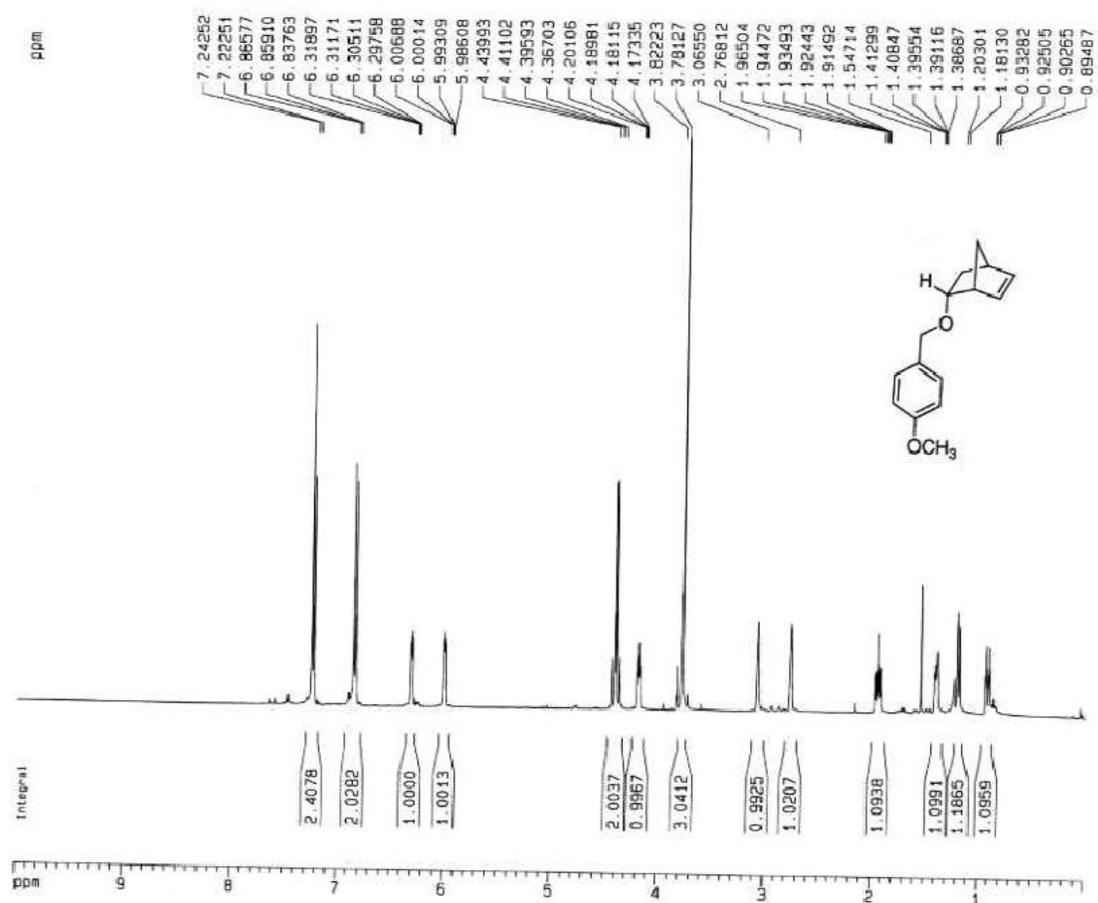


Figure A-25. <sup>1</sup>H NMR spectrum of **73**.

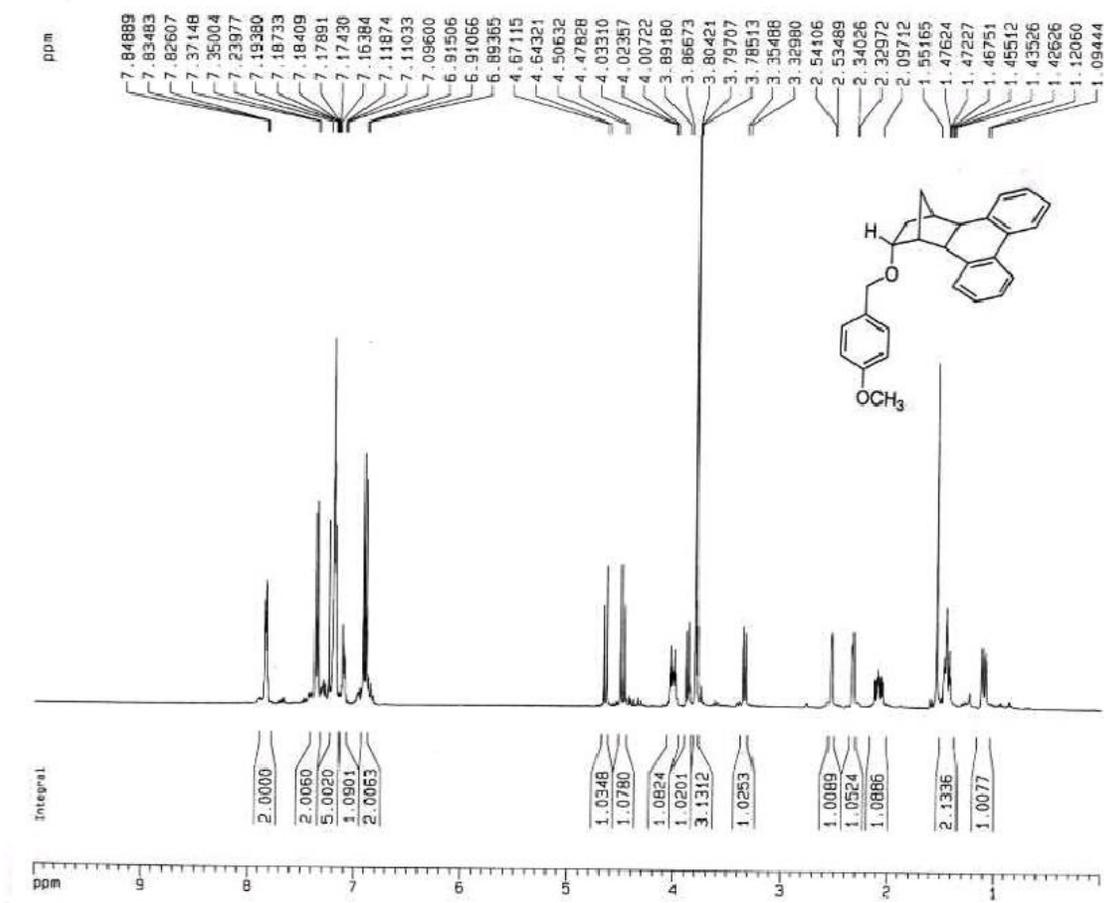


Figure A-26. <sup>1</sup>H NMR spectrum of **74**.

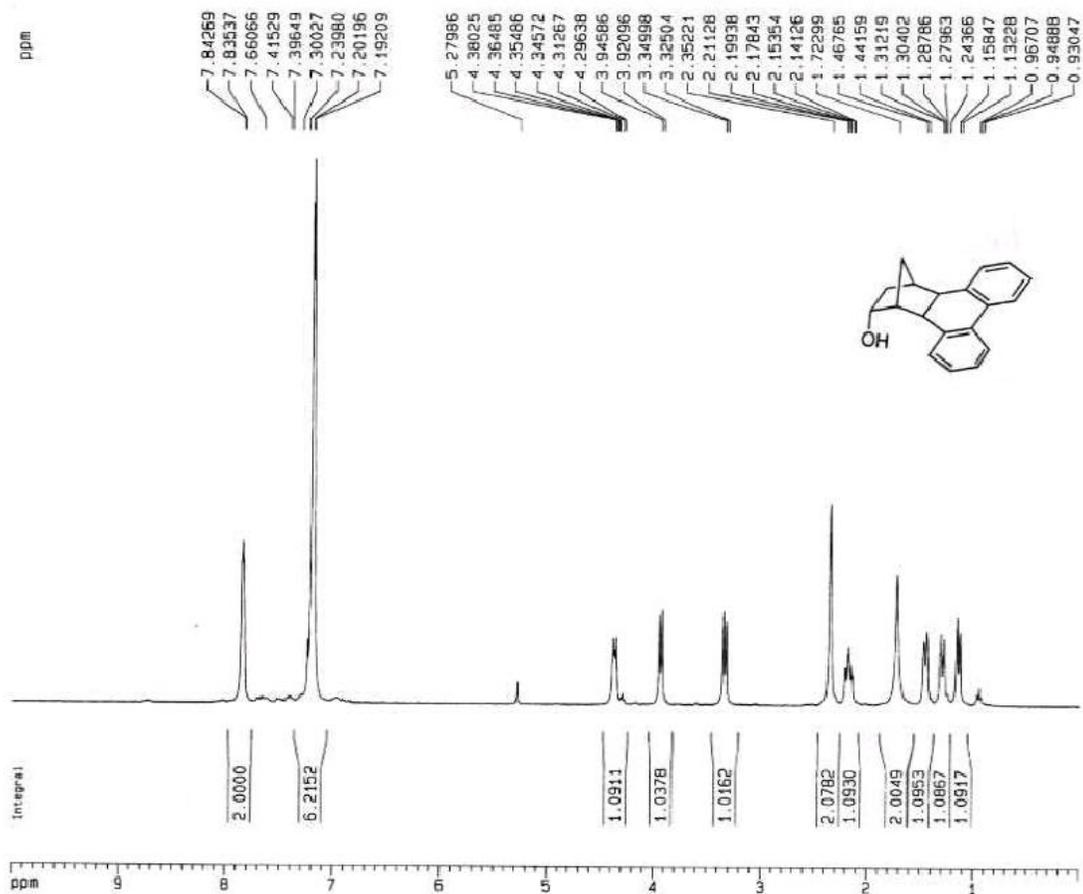


Figure A-27.  $^1\text{H}$  NMR spectrum of **76**.

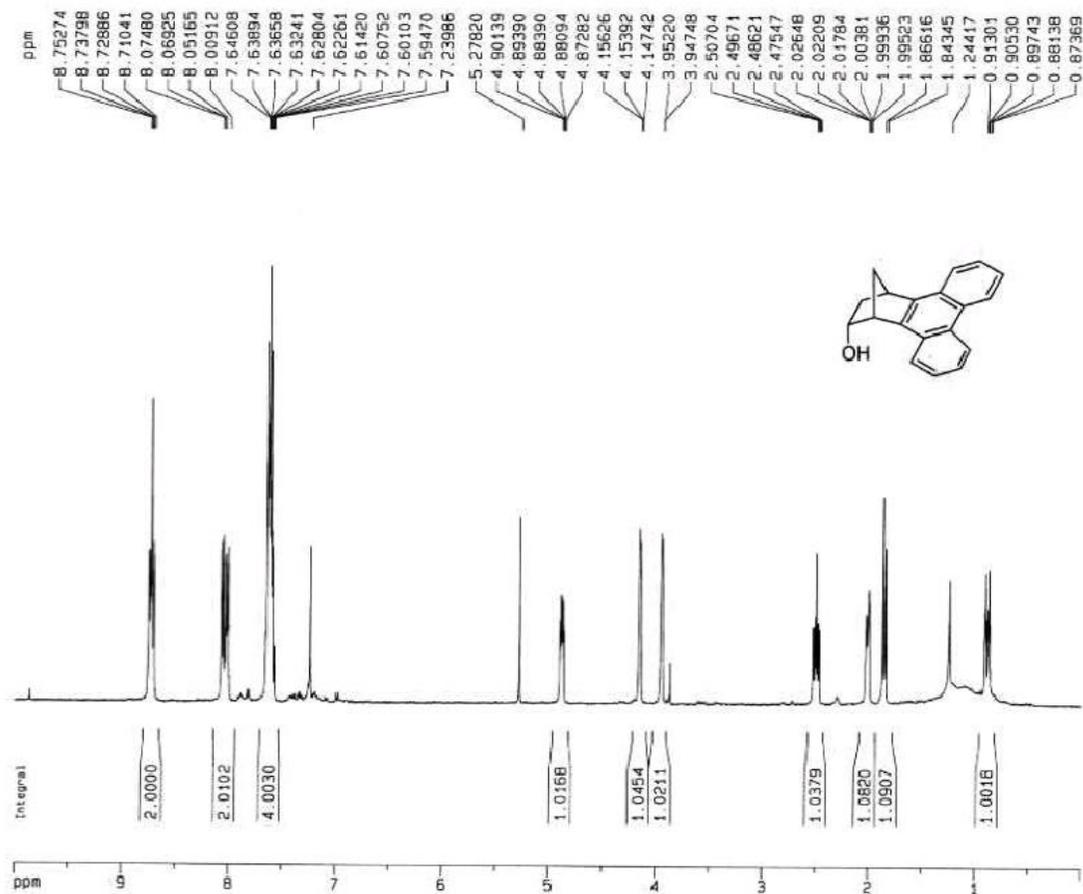


Figure A-28.  $^1\text{H}$  NMR spectrum of **77**.

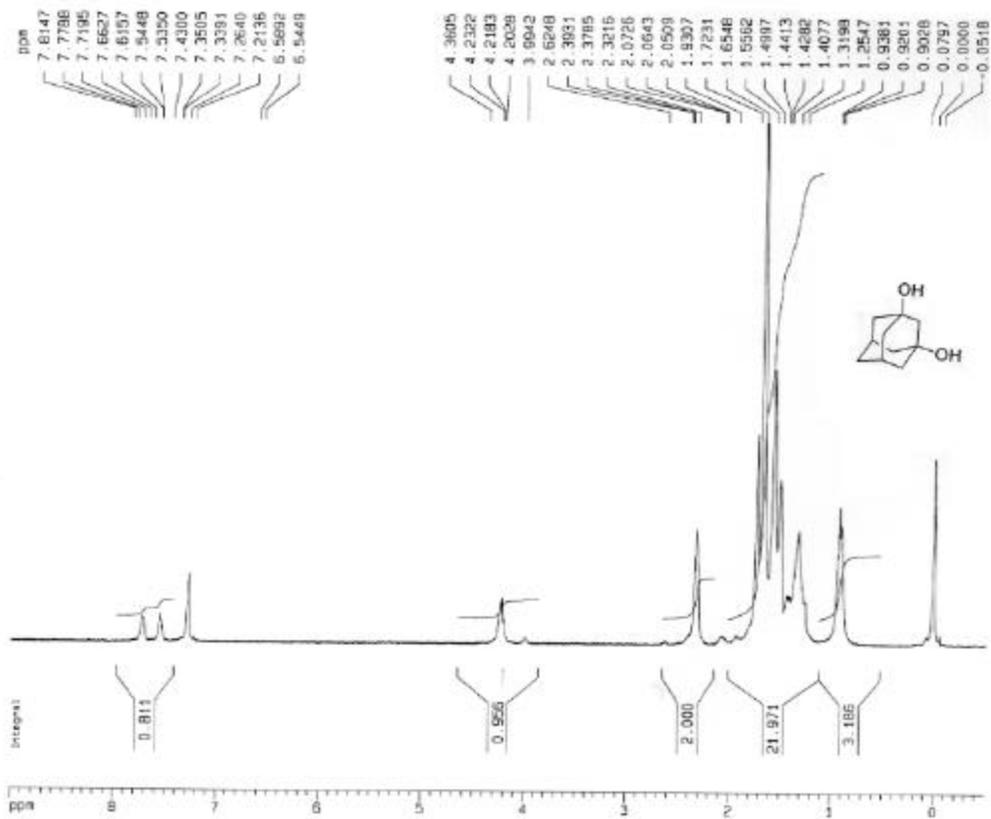


Figure A-29. <sup>1</sup>H NMR spectrum of **82**.

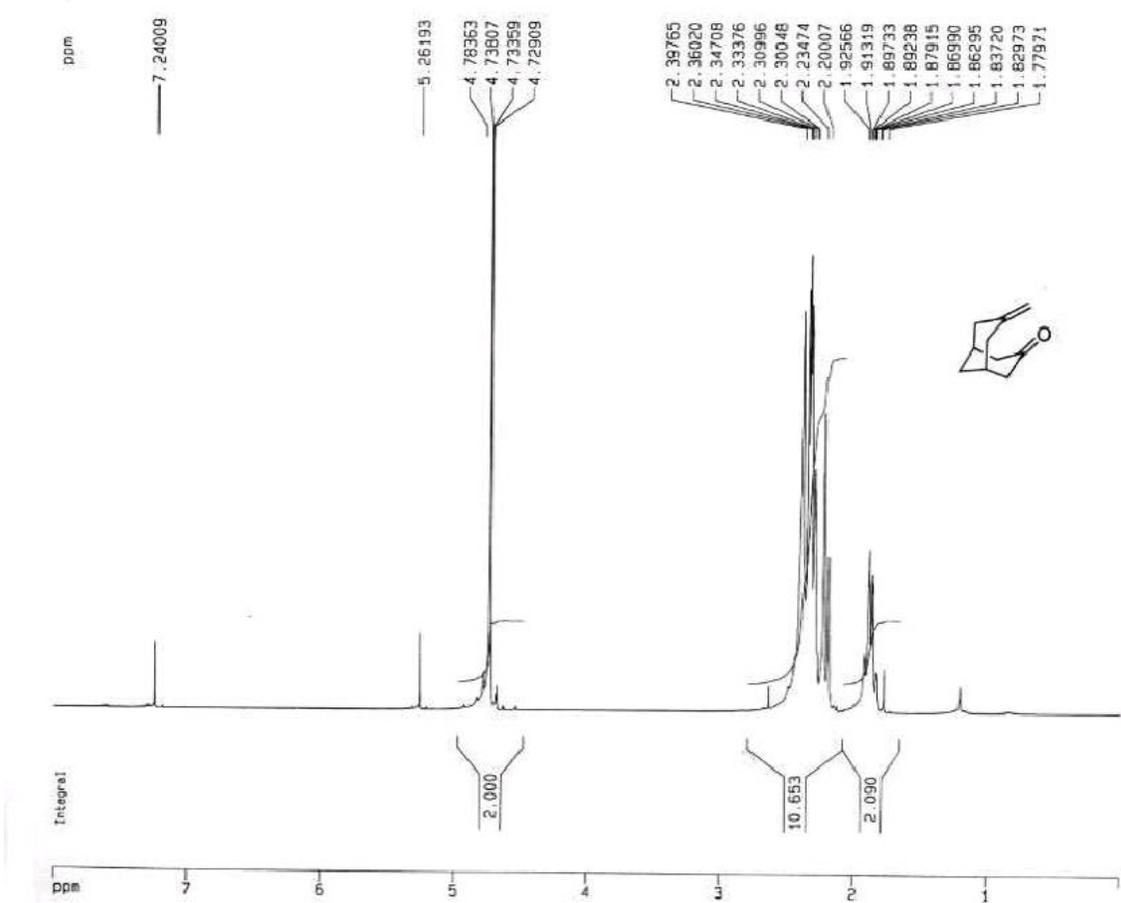


Figure A-30. <sup>1</sup>H NMR spectrum of **81**.

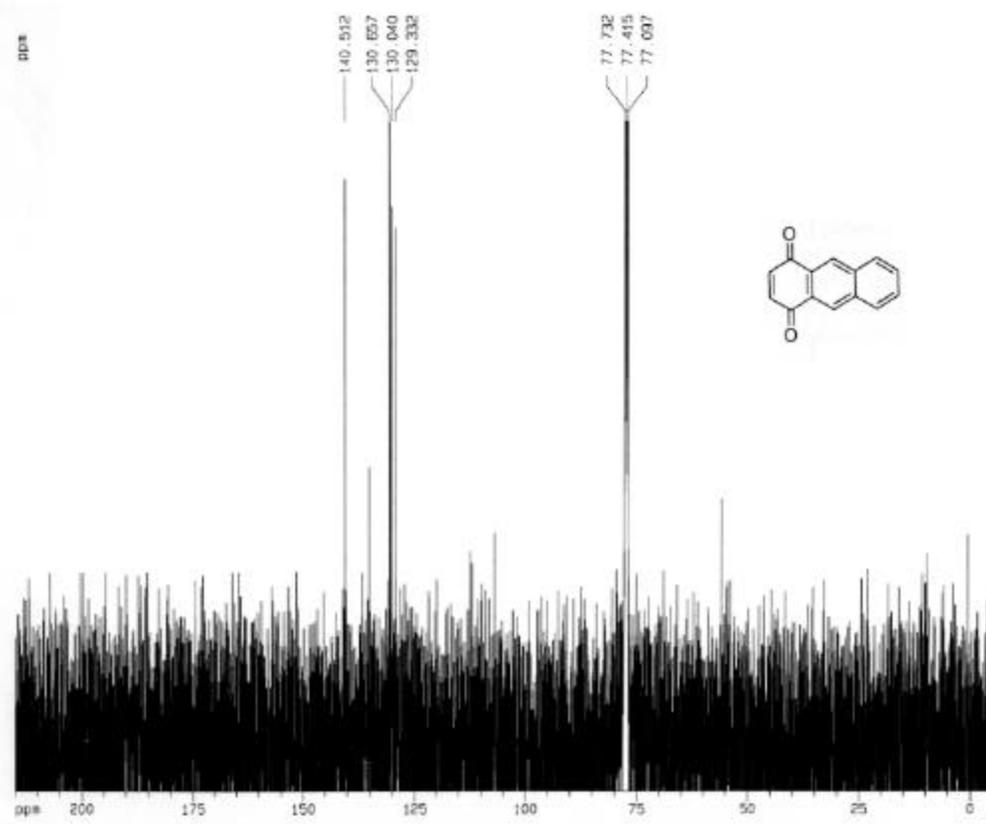


Figure B-1.  $^{13}\text{C}$  NMR spectrum of **35**.

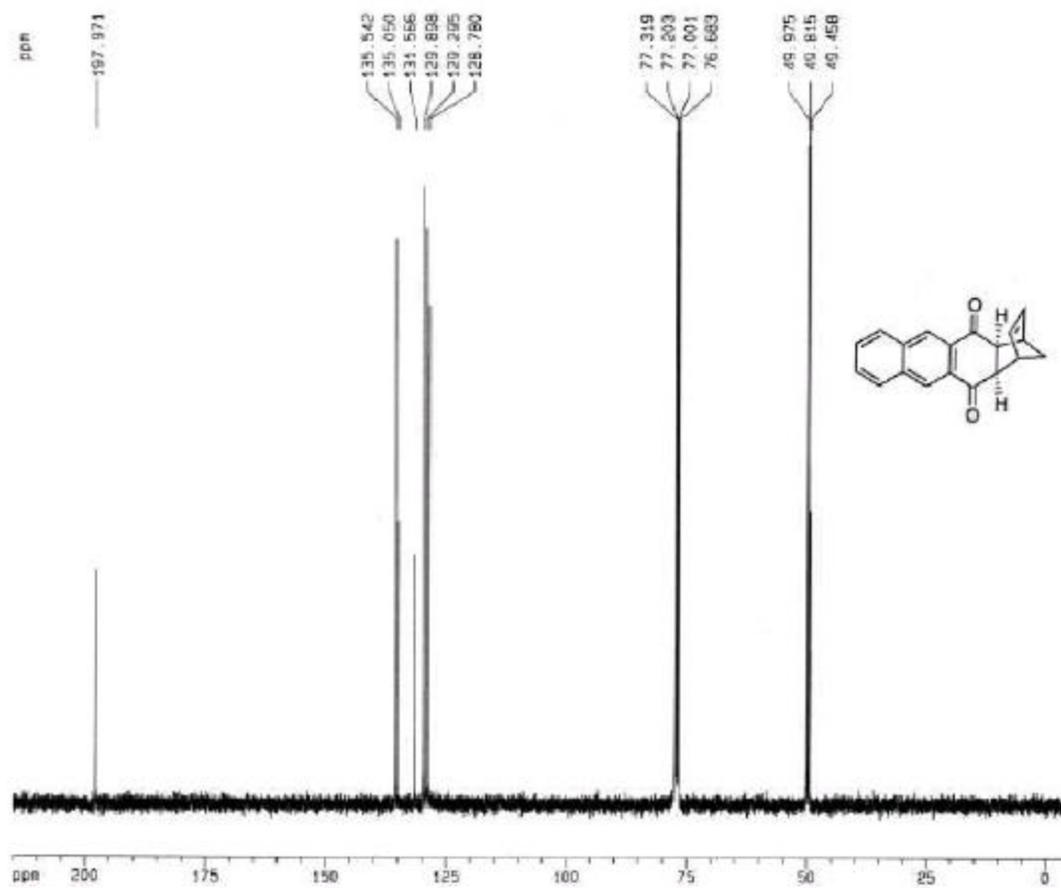


Figure B-2.  $^{13}\text{C}$  NMR spectrum of **36**.

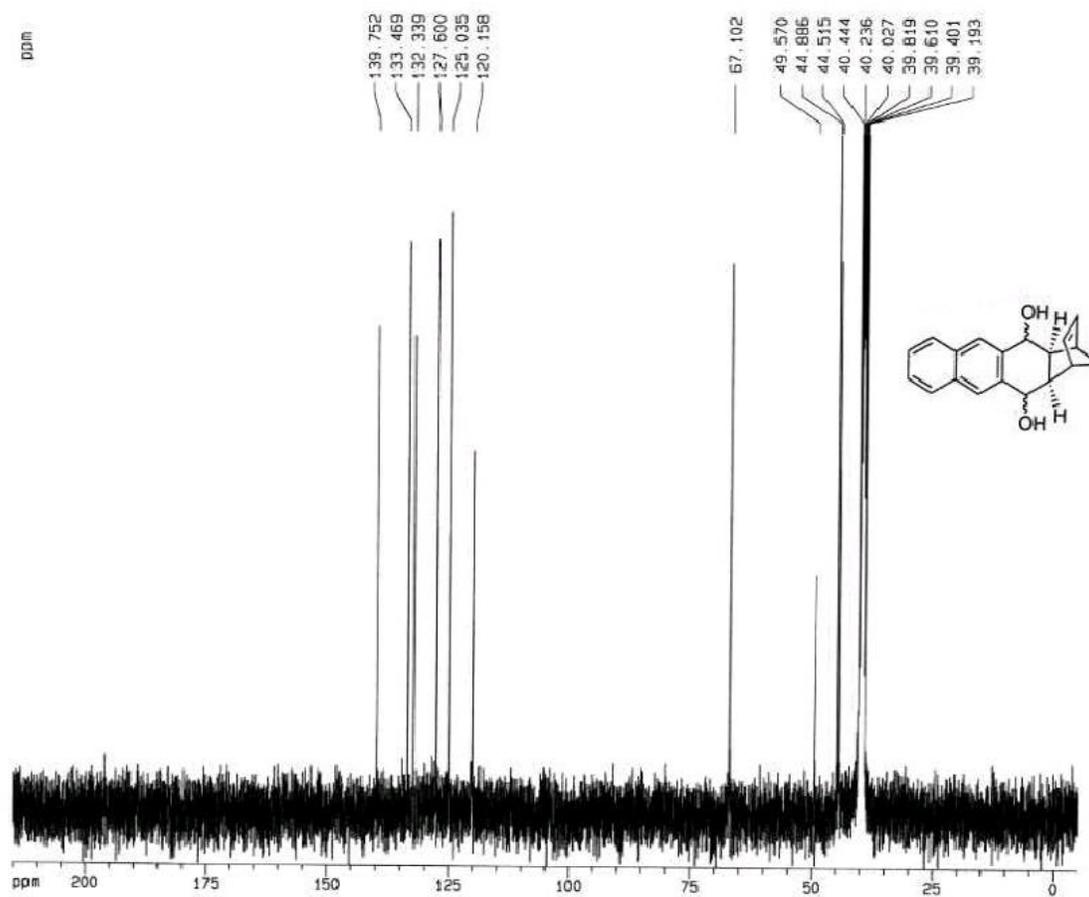


Figure B-3.  $^{13}\text{C}$  NMR spectrum of **37**.

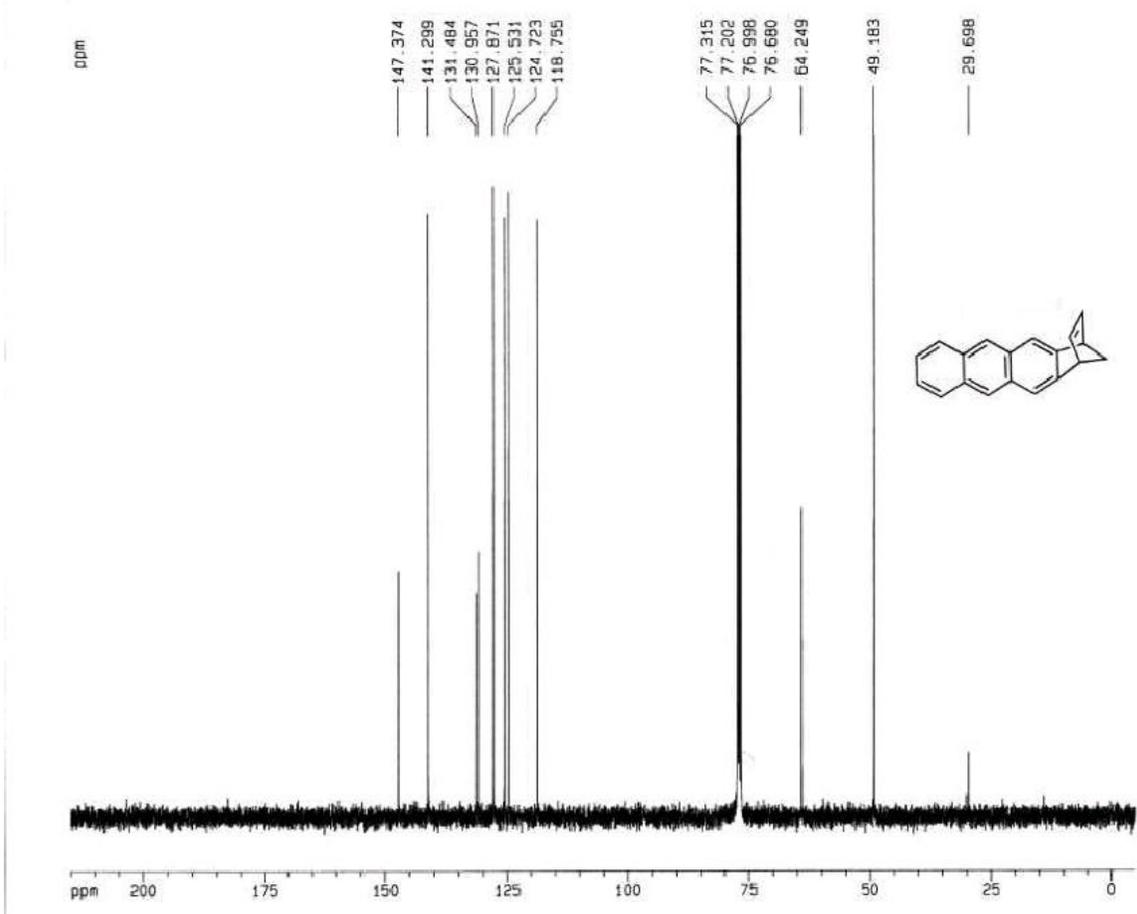


Figure B-4.  $^{13}\text{C}$  NMR spectrum of **28**.

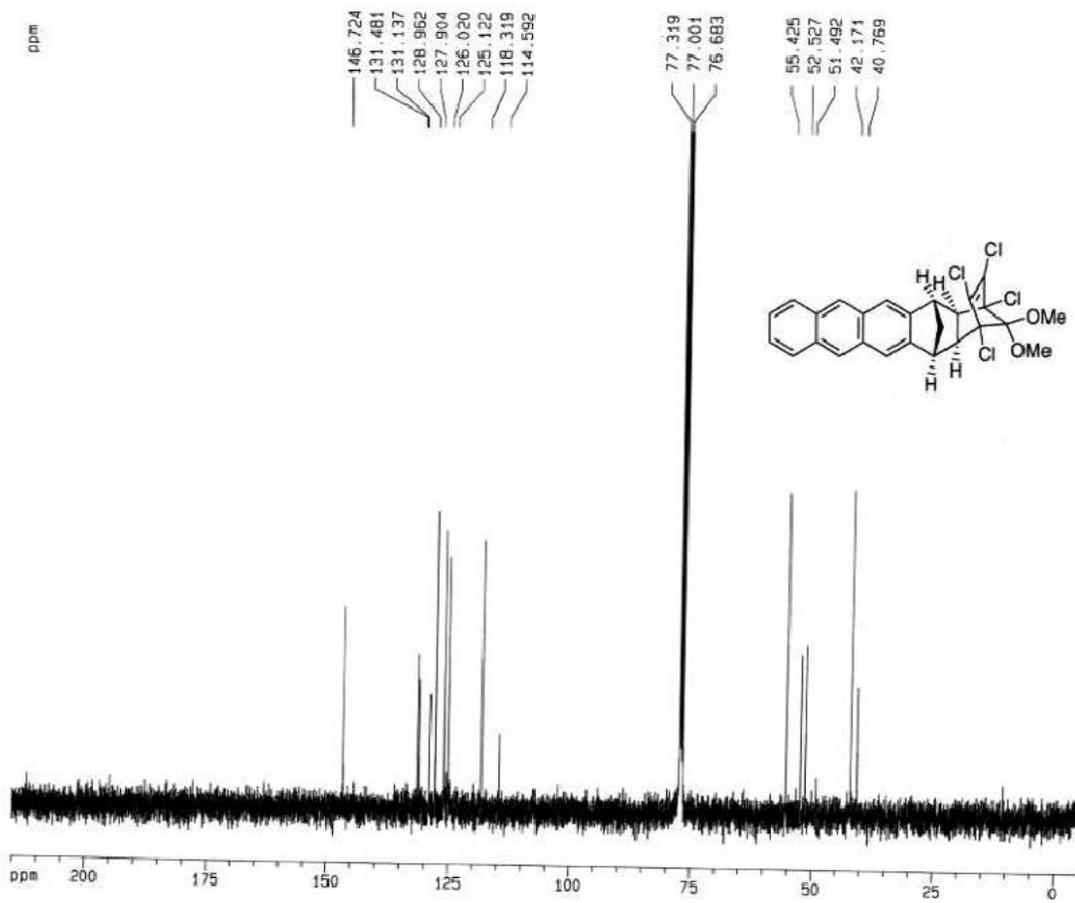


Figure B-5.  $^{13}\text{C}$  NMR spectrum of **29**.

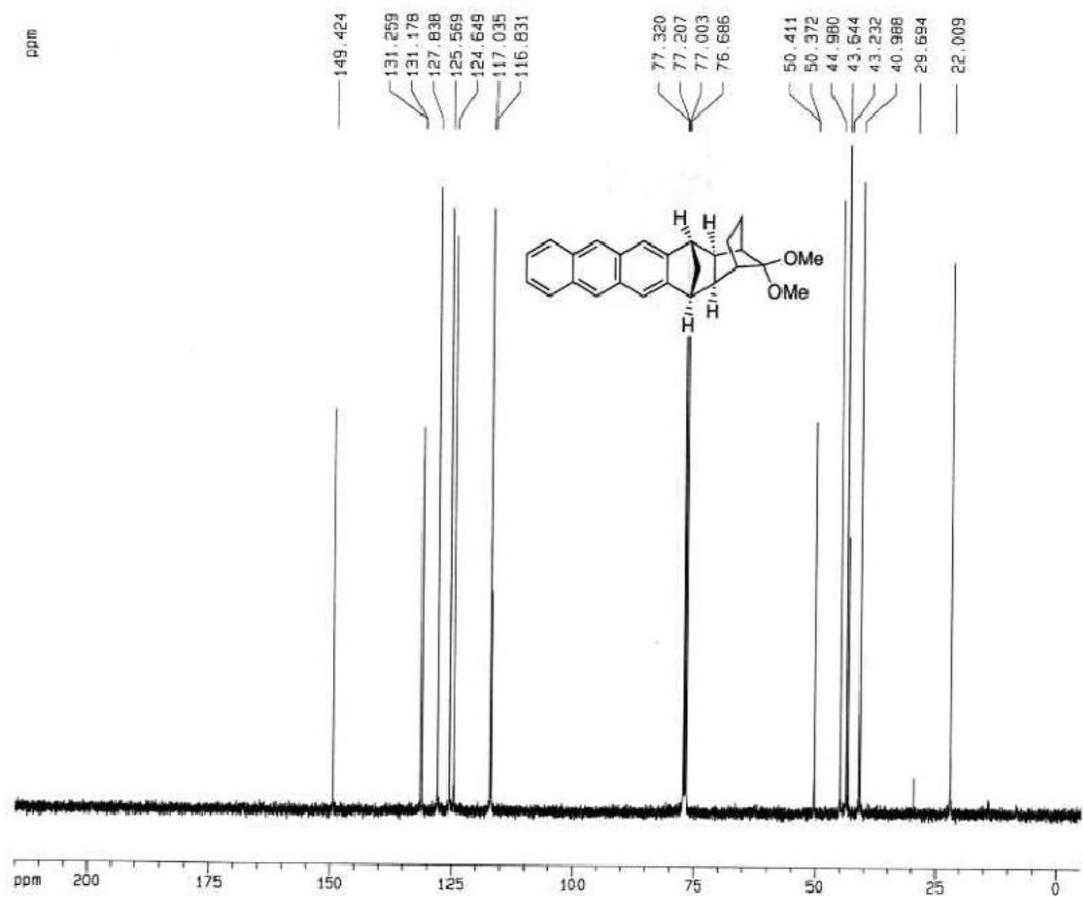


Figure B-6.  $^{13}\text{C}$  NMR spectrum of **40**.

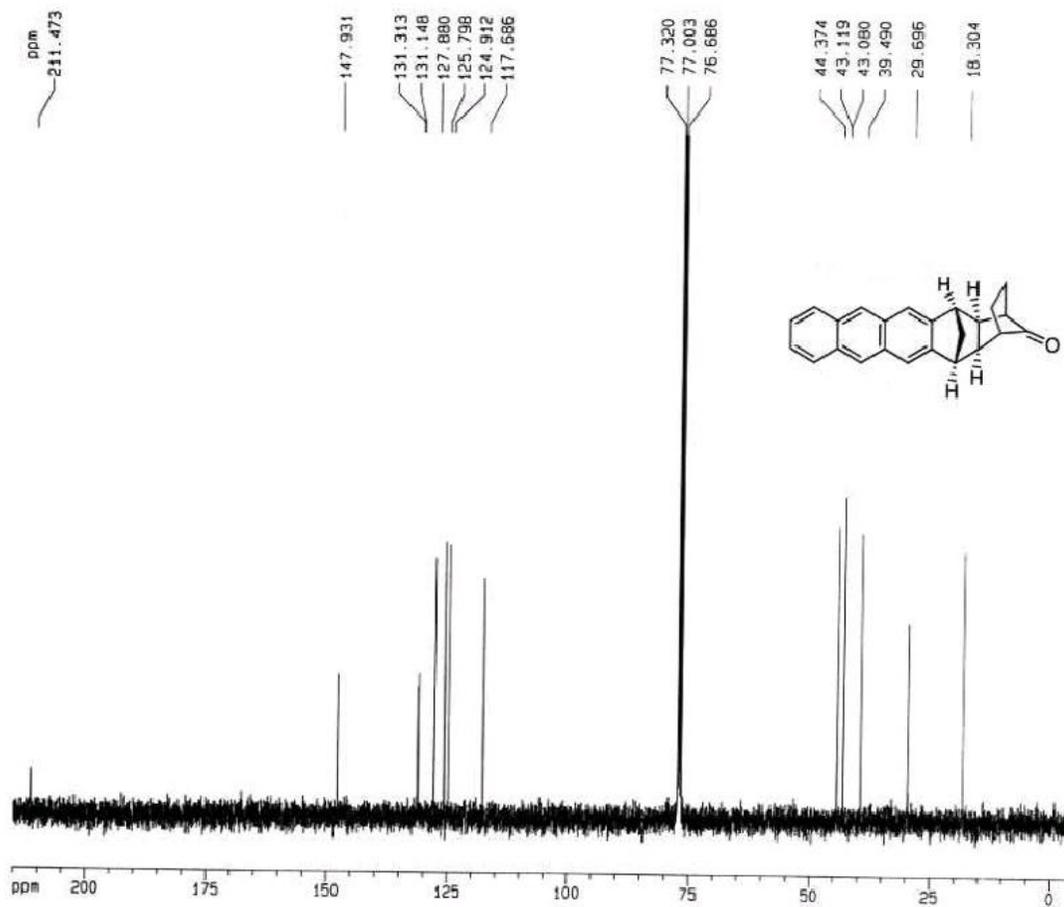


Figure B-7.  $^{13}\text{C}$  NMR spectrum of **30**.

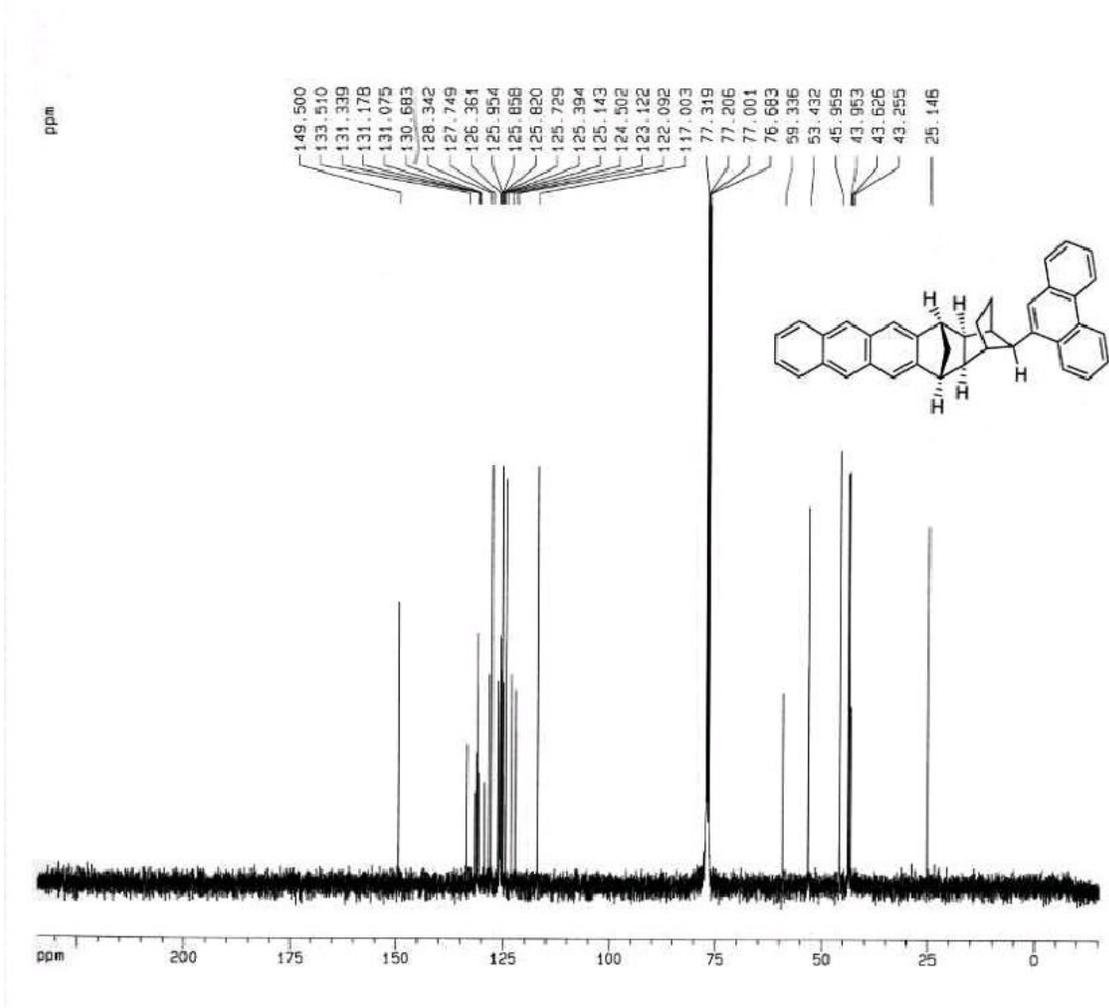


Figure B-8.  $^{13}\text{C}$  NMR spectrum of **12**.

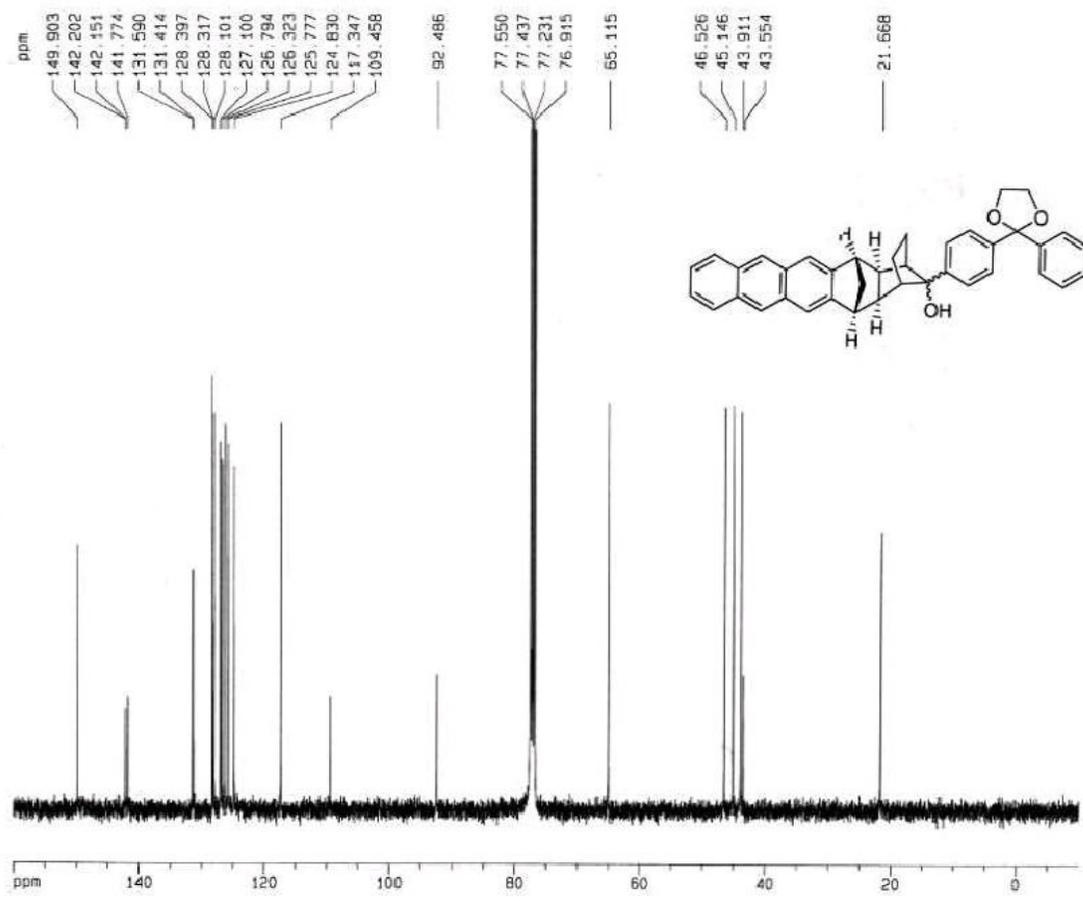


Figure B-9.  $^{13}\text{C}$  NMR spectrum of **45**.

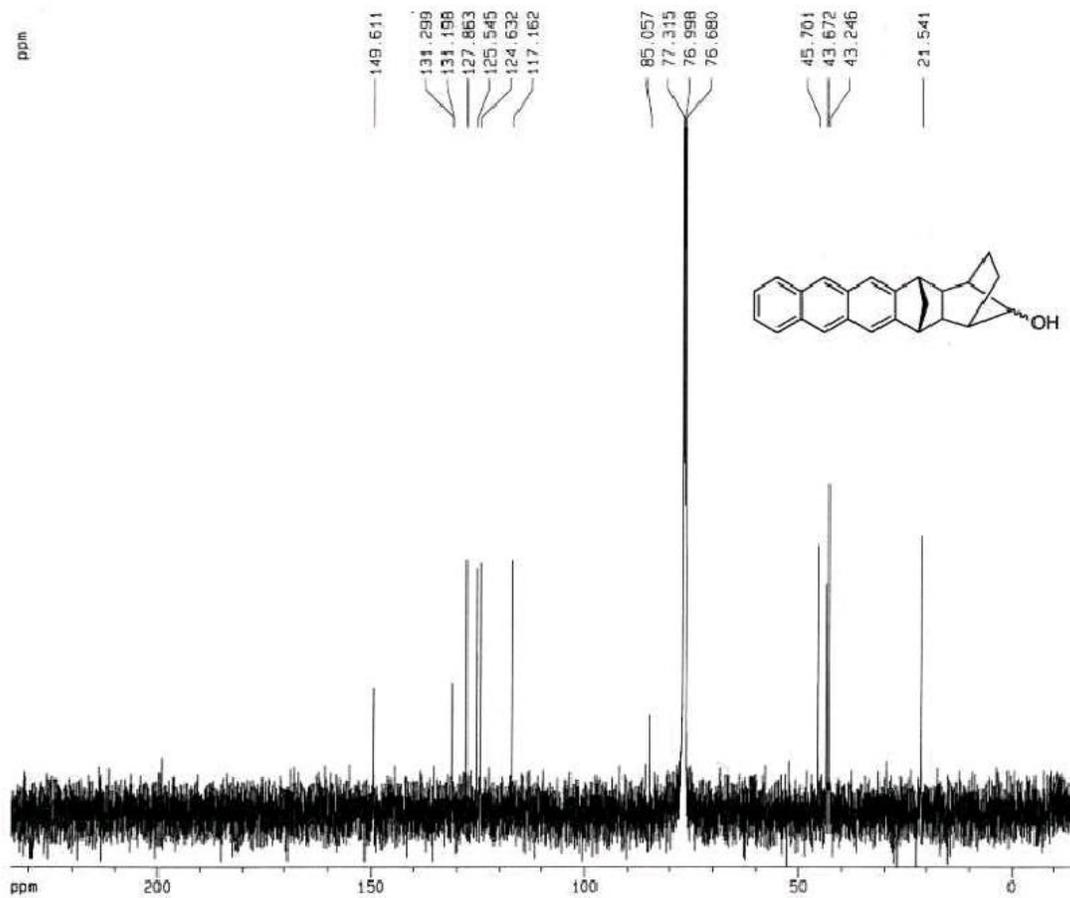


Figure B-10.  $^{13}\text{C}$  NMR spectrum of **52**.

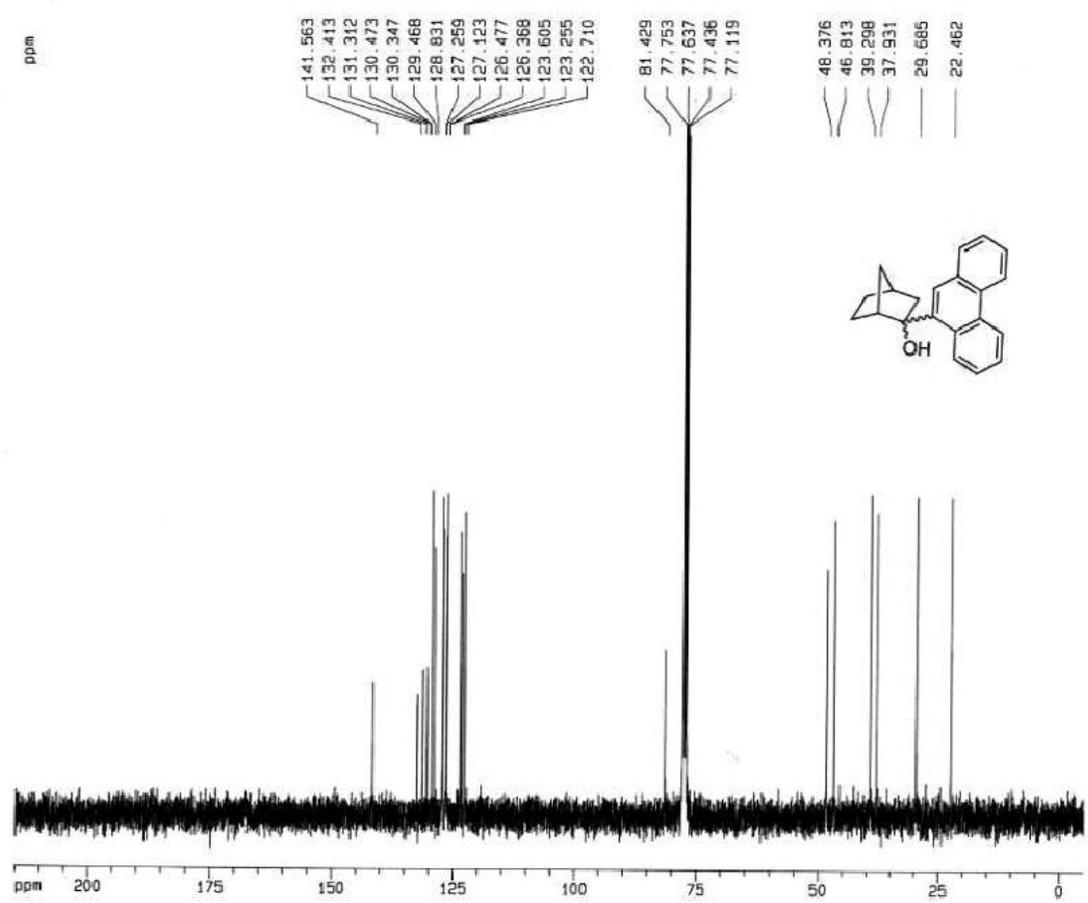


Figure B-11. <sup>13</sup>C NMR spectrum of **53**.

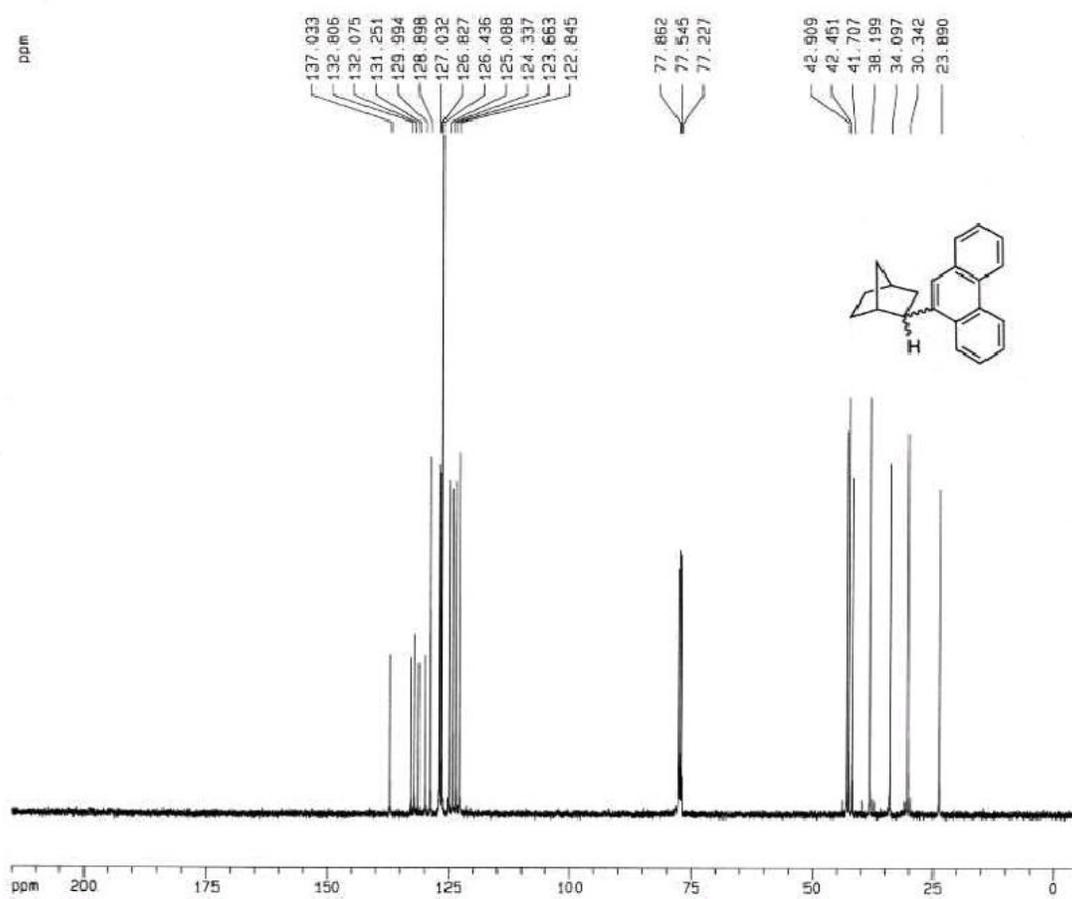


Figure B-12.  $^{13}\text{C}$  NMR spectrum of **49**.

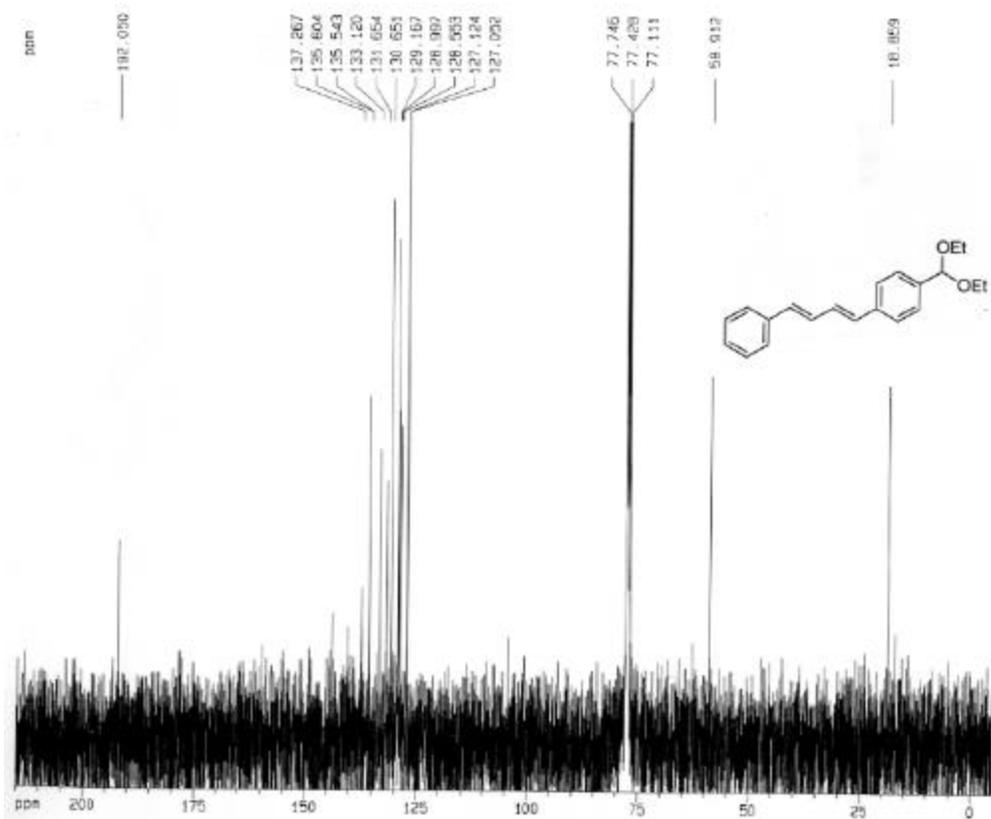


Figure B-13.  $^{13}\text{C}$  NMR spectrum of **54**.

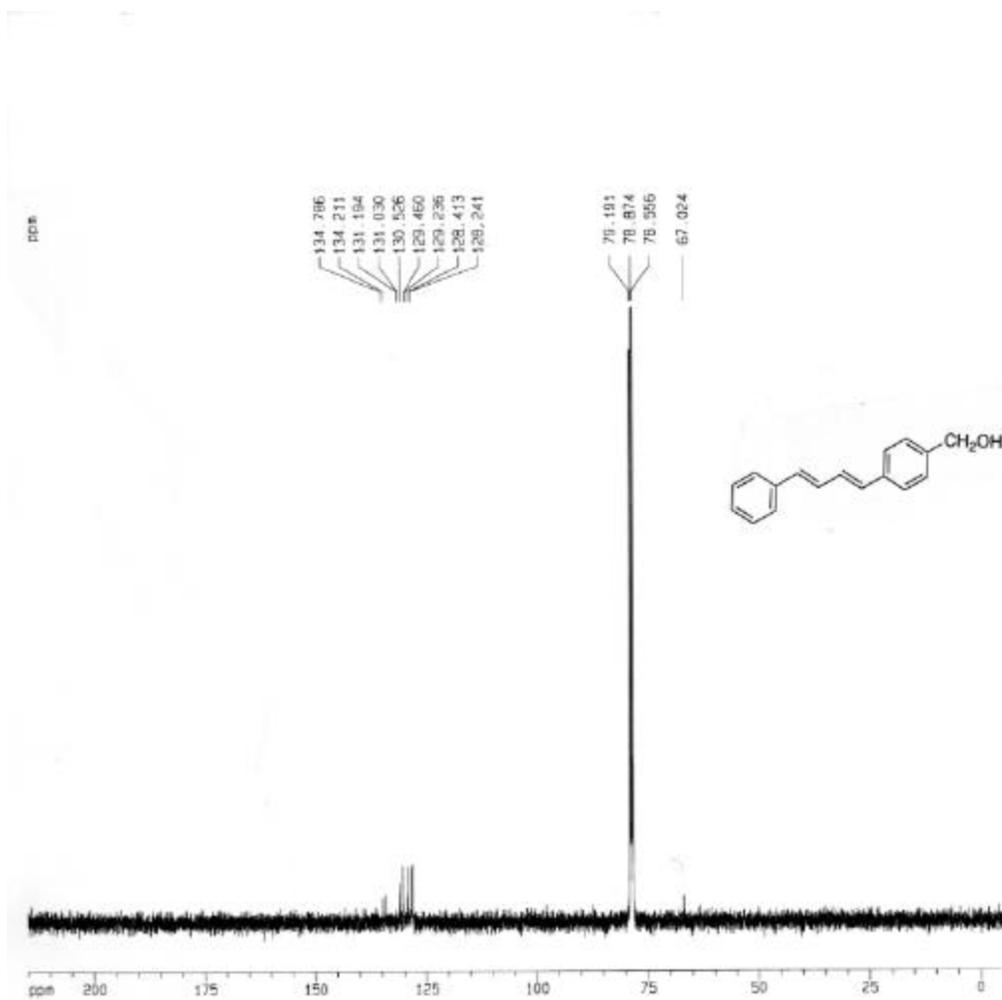


Figure B-14.  $^{13}\text{C}$  NMR spectrum of **56**.

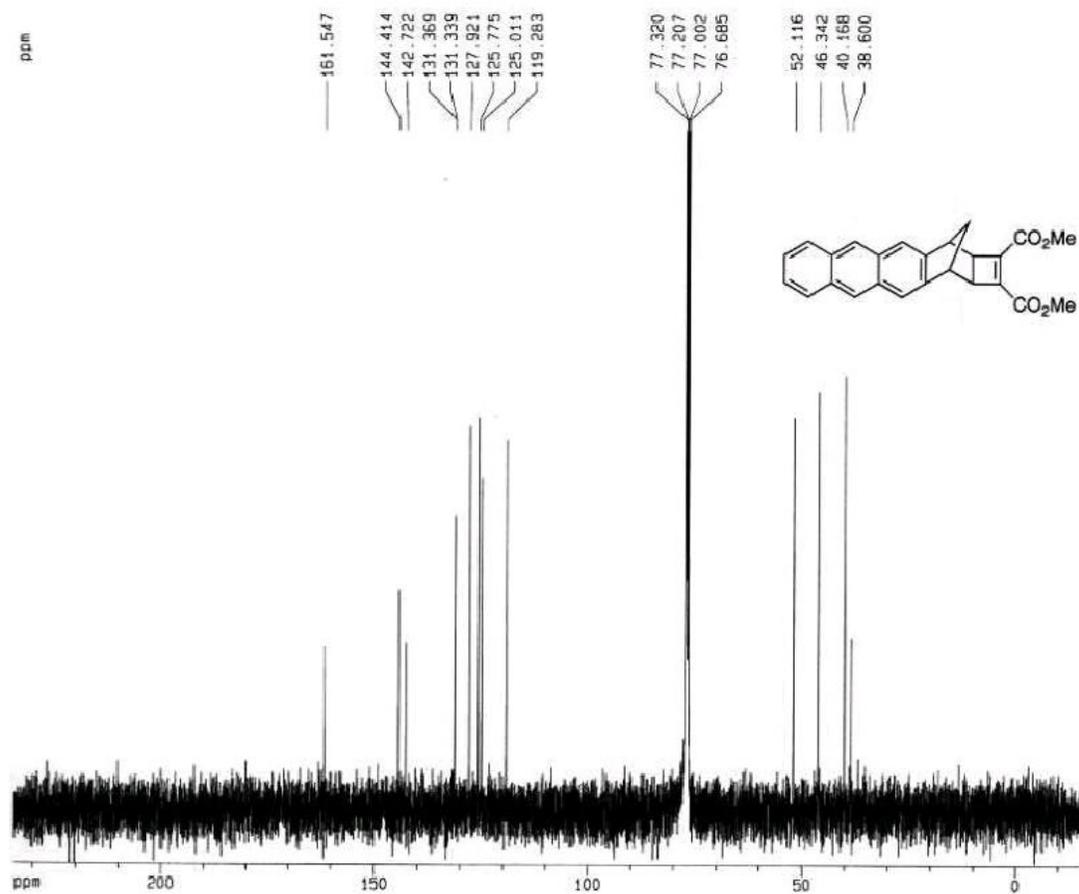


Figure B-15.  $^{13}\text{C}$  NMR spectrum of **31**.

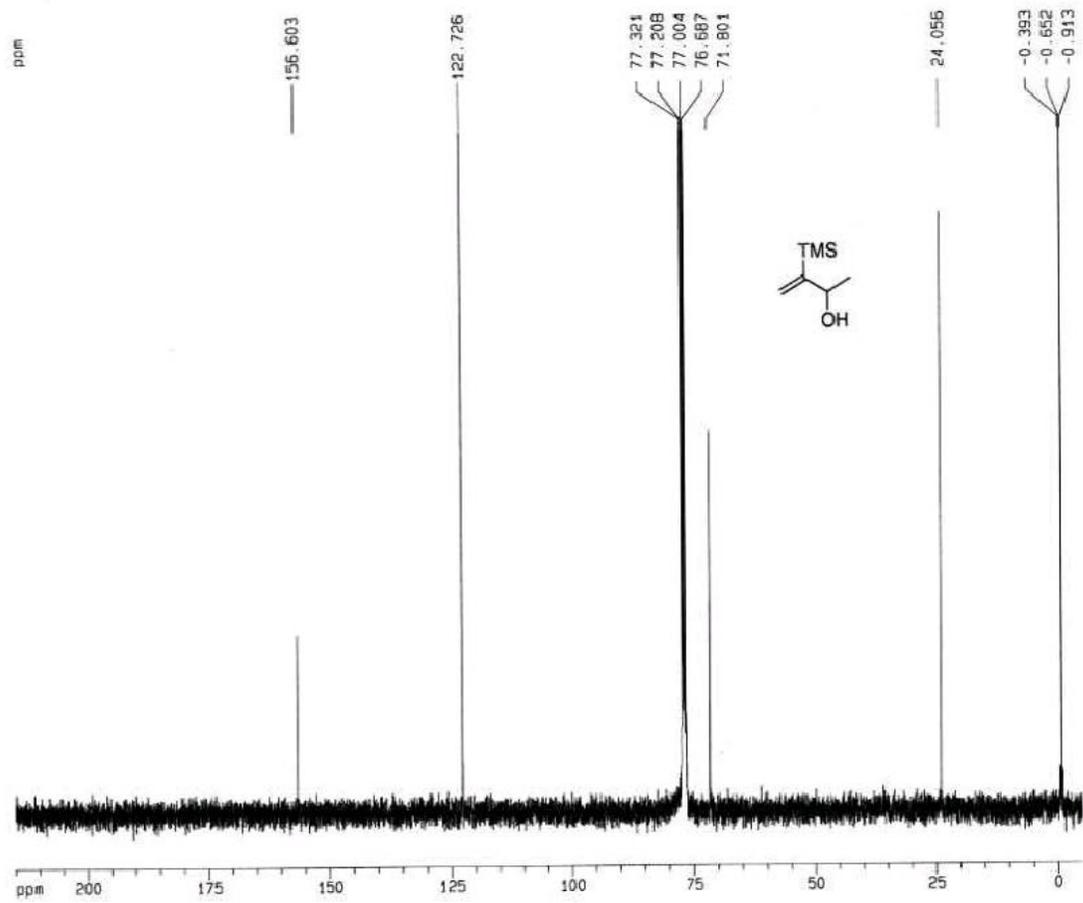


Figure B-16.  $^{13}\text{C}$  NMR spectrum of **63**.

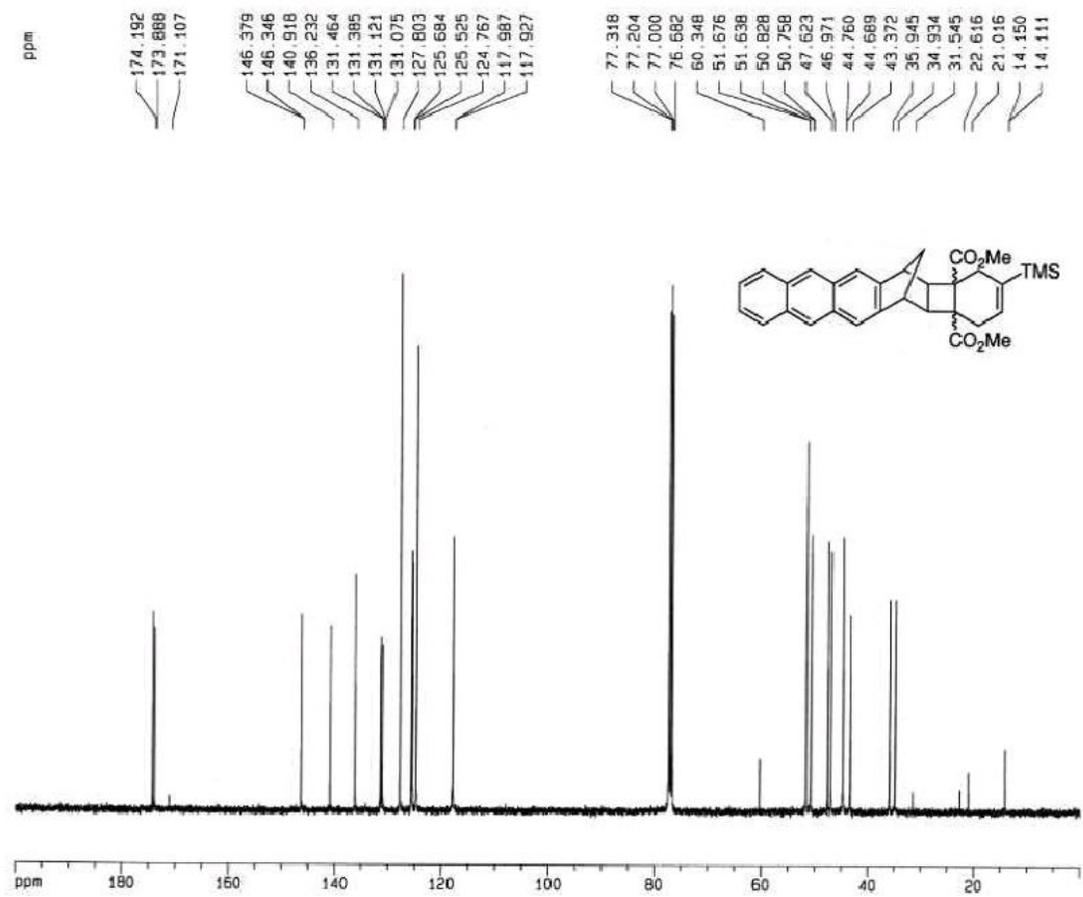


Figure B-17.  $^{13}\text{C}$  NMR spectrum of **32**.

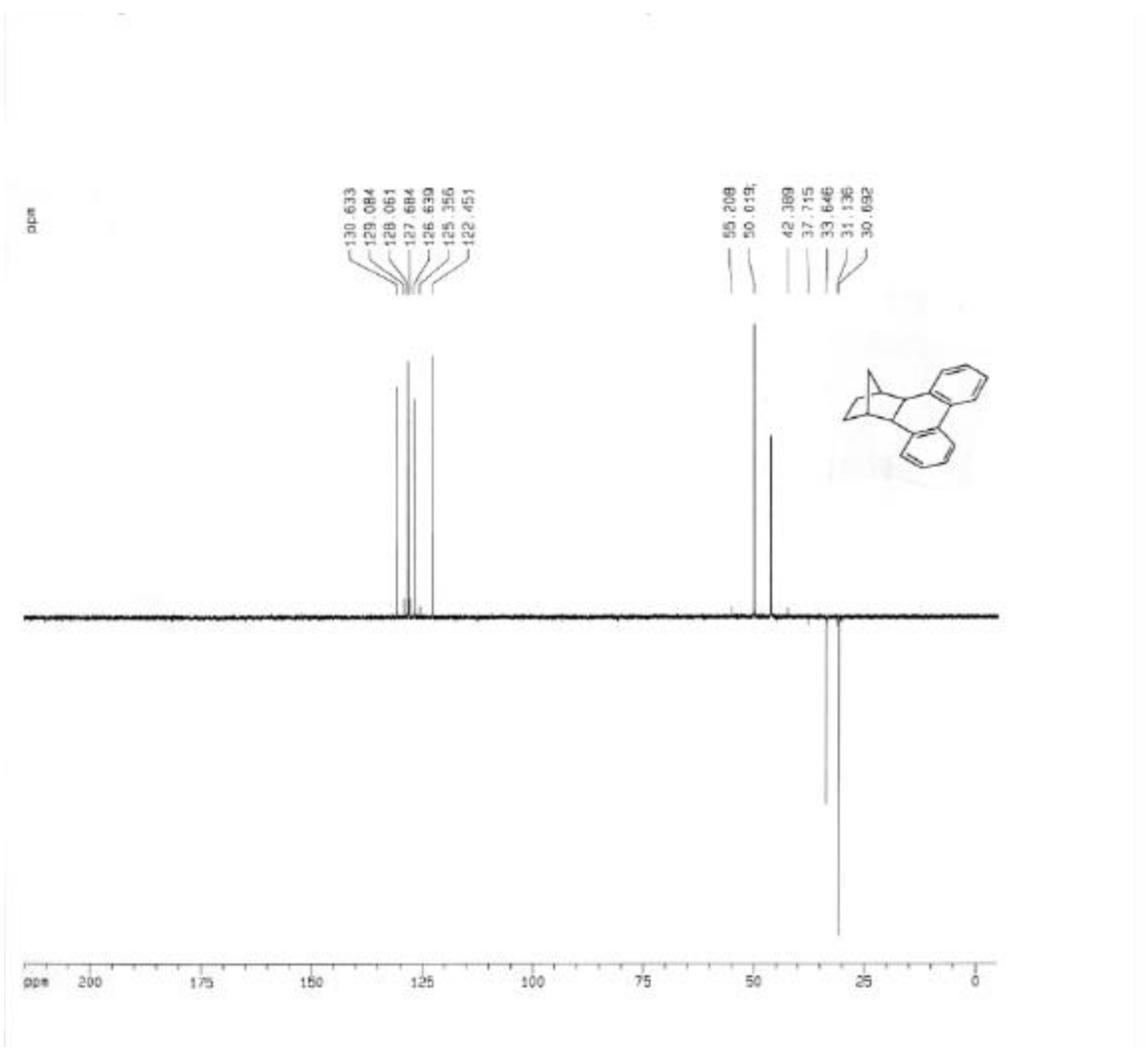


Figure B-18.  $^{13}\text{C}$  NMR spectrum of **65**.

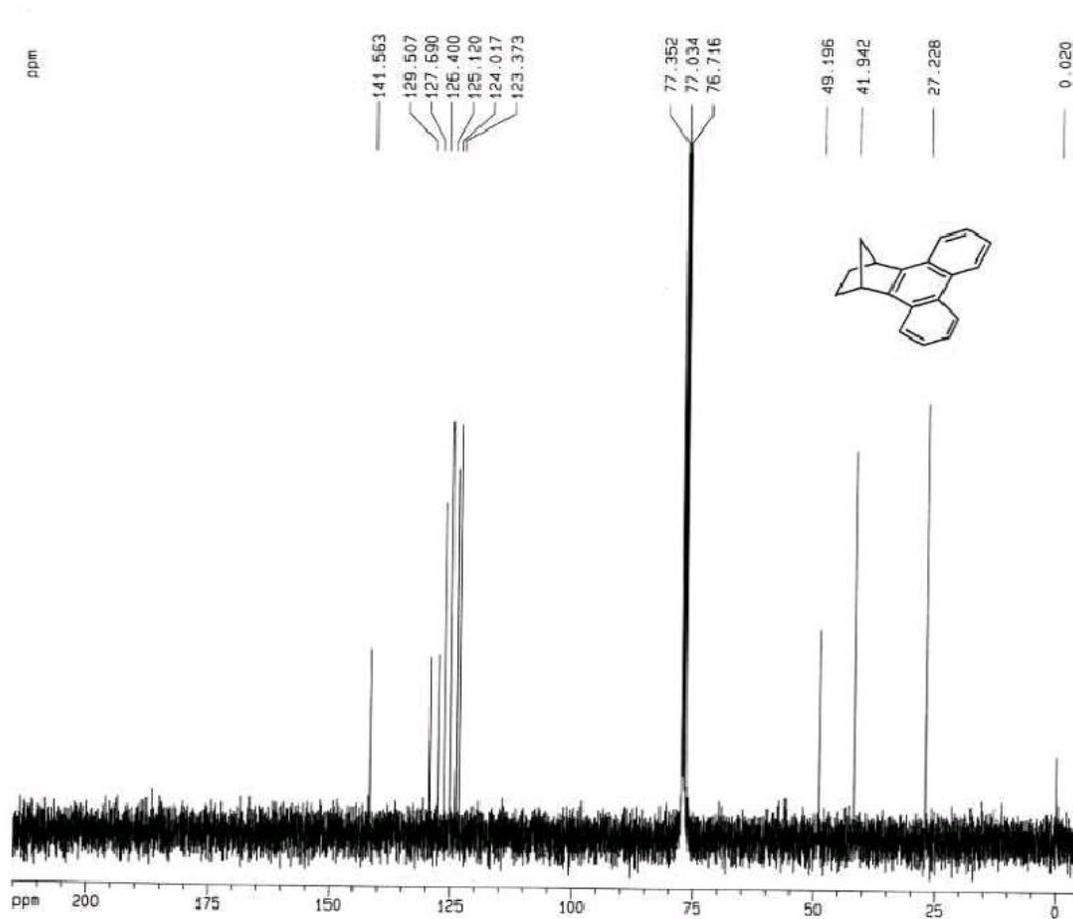


Figure B-19.  $^{13}\text{C}$  NMR spectrum of **68**.

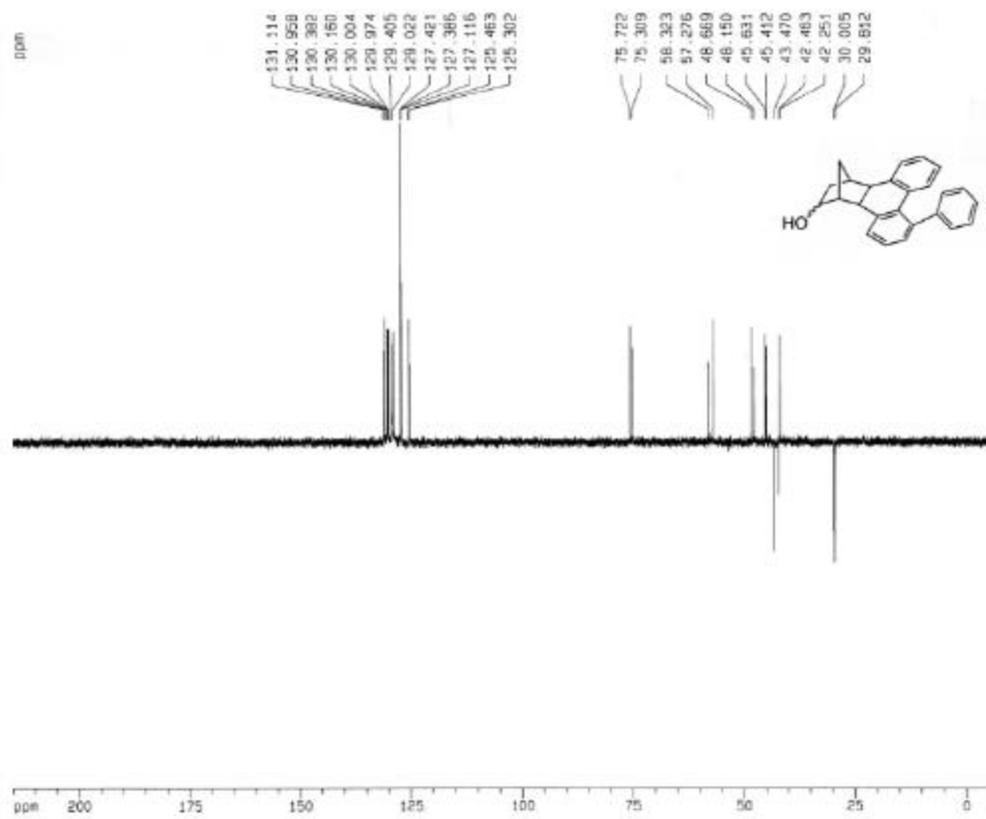


Figure B-20.  $^{13}\text{C}$  NMR spectrum of **71**.

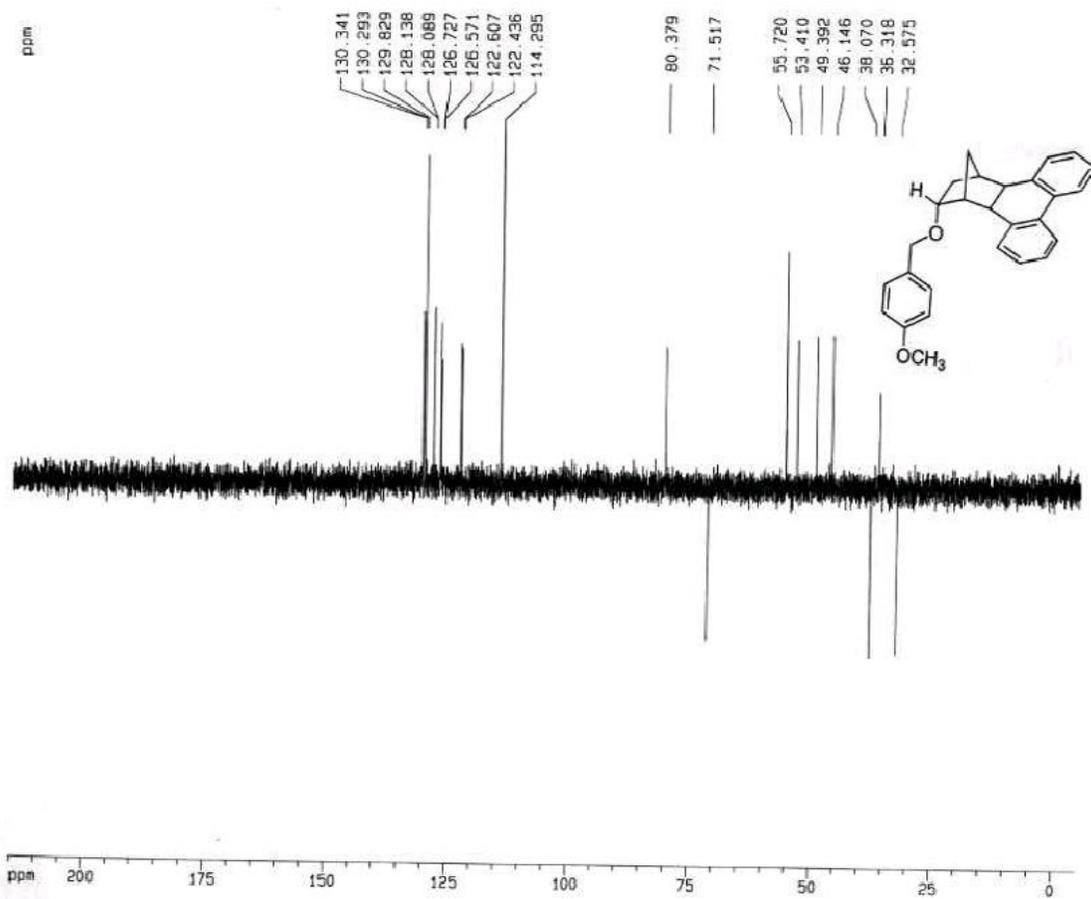


Figure B-21.  $^{13}\text{C}$  NMR spectrum of **74**.

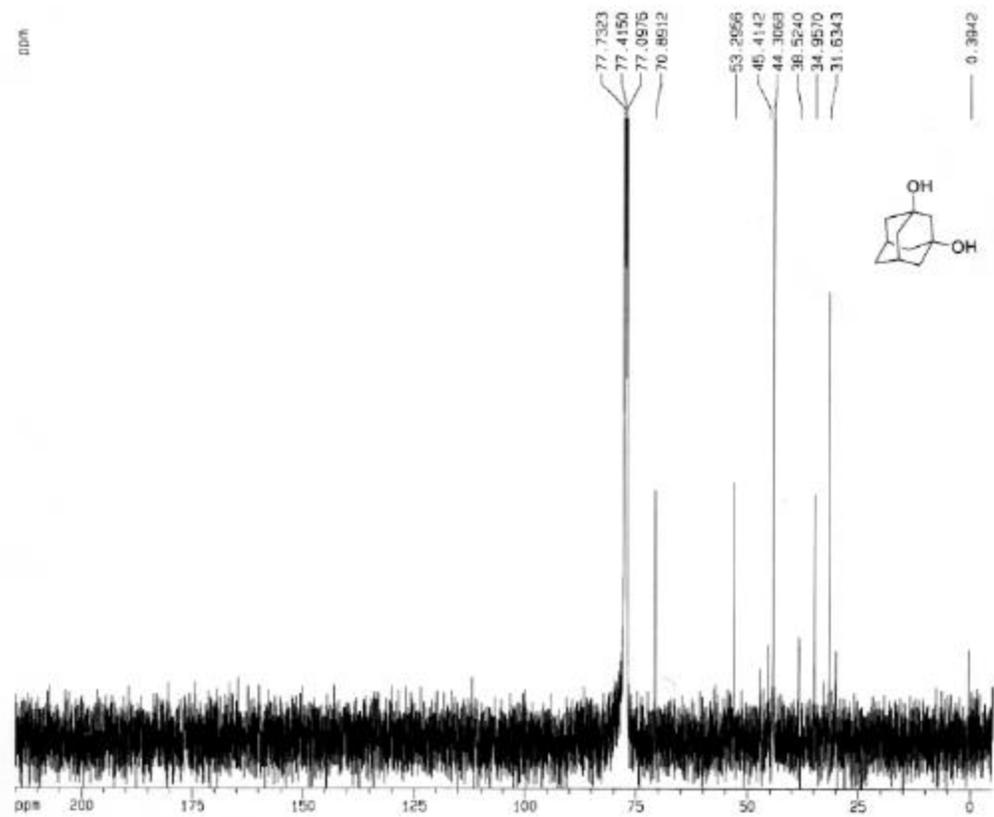


Figure B-22. <sup>13</sup>C NMR spectrum of **82**.

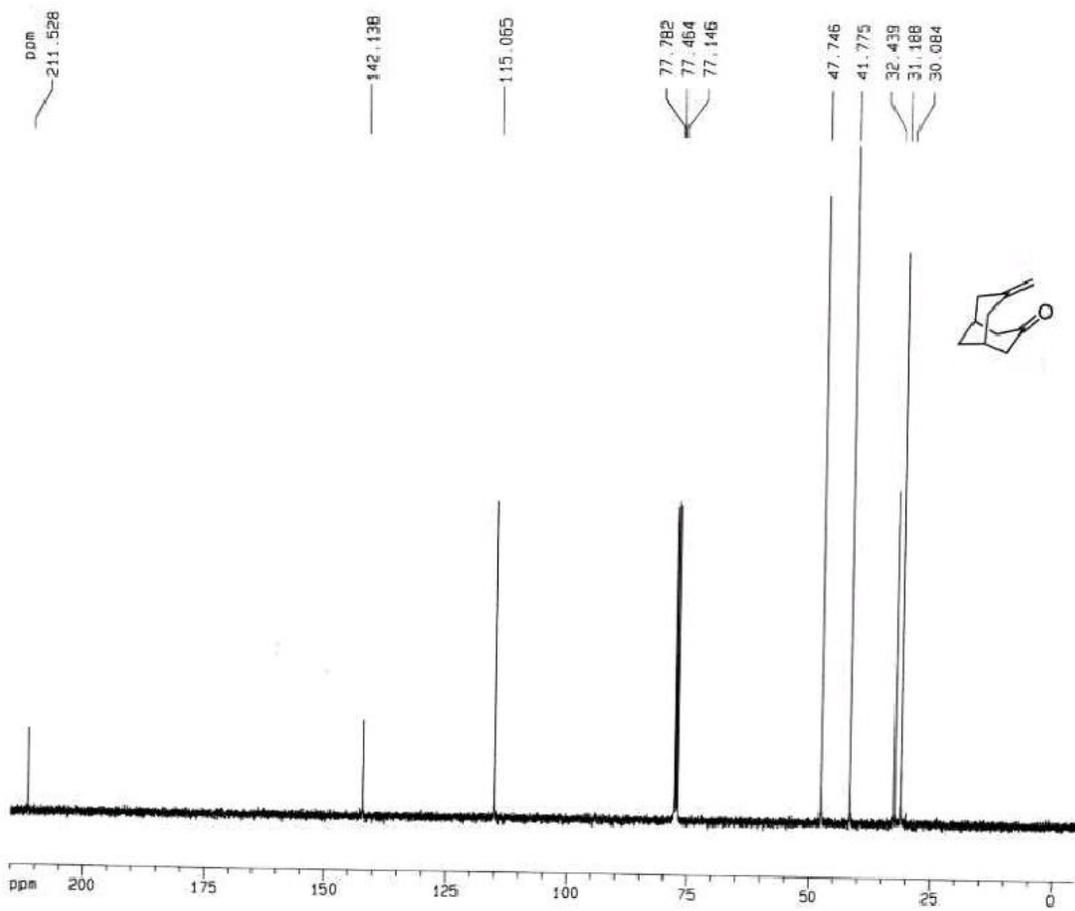


Figure B-23. <sup>13</sup>C NMR spectrum of **81**.