SYNTHESES OF POLYPHENYL PYRENOPHANES AND PYRENYLENE-ETHYNYLENE NANORINGS

BAOZHONG ZHANG

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Syntheses of Polyphenyl Pyrenophanes and Pyrenylene-Ethynylene Nanorings

By

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Abstract

This thesis mainly describes the application of the valence isomerization-dehydrogenation (VID) reaction in the syntheses of cyclic pyrene-containing molecules.

The pyrene-containing nanorings described in Chapter 2 are named pyrenophynes, which consist of ethylene bridges between each of the two aromatic units. These nanorings are analogs to Oda's *para*-phenylene-ethynylene derivatives. Several synthetic methods have been attempted. Although the final pyrenylene-ethylnylene nanorings have not been synthesized yet, the formation of a key intermediate tetrathiacyclophyne has been verified by experiment evidence and will be instructive to future research.

In Chapter 3, the syntheses of pyrenophanes are made up of all aromatic units are described, including the pyrenophane with central *para*-phenylene, *meta*-phenylene, and 2,5-thienylene units. Müllen's methodology of building nanographitic sheets was adopted to construct the skeleton of these pyrenophanes.

In Chapter 4, synthetic investigation focuses on extremely distorted aromatic systems. In order to achieve a more distorted (2,7)pyrenophane than all the previously synthesized ones in the Bodwell group, a series of octaphenyl pyrenophanes with a central aliphatic bridge were synthesized, and the most distorted (2,7)pyrenophane that has only 6 carbon atoms in the bridge was generated using the VID methodology.

Acknowledgements

First of all, I would like to thank my supervisor Dr. Graham J. Bodwell for providing me such a great opportunity to study in his group during the past years. His enthusiasm and encouragement deeply benefits me as a growing organic chemist. Along with Dr. Graham J. Bodwell I would also express my gratitude to Dr. Paris E. Georghiou and Dr. Sunil Pansare for their interesting and instructive courses I have received.

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List of Abbreviations and Symbols Used

α	bend angle (in cyclophanes)
Å	Ångstrom
Abs.	Absolute (with ethanol)
Ac	acetyl
Anal.	Analysis (combustion)
AM	Austin Model
APCI	atmosphere pressure chemical ionization
β	bend angle (in cyclophanes)
Borch reagent	dimethoxycarbonium tetrafluoroborate
b.p.	boiling point
br	broad (in NMR)
Bu	butyl
BuLi	*n*-butyllithium
calc'd	calculated
cat.	catalytic
COSY	correlation spectroscopy
δ	chemical shift in ppm downfield from tetramethylsilane
Δ	heat
Δδ	difference in chemical shift values (in ppm)
Δν	difference in chemical shift values (in Hz)
D	deuterium (in structural formulae)

d	doublets (in NMR)
DAD	Diode array detector
dd	doublet of doublets (in NMR)
ddd	doublet of doublet of doublets (in NMR)
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DDQ	2,3-dichloro-5,6-dicycano-1,4-benzoquinone
dec.	decomposition (with melting point)
DIBAL-H	diisobutylaluminum hydride
DMSO	dimethyl sulfoxide
DNMR	dynamic nuclear magnetic resonance (spectroscopy)
dt	doublet of triplets (in NMR)
EI-MS	electron impact-mass spectrum
Et	ethyl
FT-ICR LD MS	Fourier transform ion cyclotron resonance mass spectrometry
HRMS	high-resolution mass spectrum
h	hour(s)
HMBC	heteronuclear multiple bond correlation (spectroscopy)
HMQC	heteronuclear multiple quantum correlation (spectroscopy)
hv	light
HPLC	high performance liquid chromatography
Hz	hertz
IR	infrared (spectroscopy)

J	coupling constant (Hz)
K	kelvin
kcal	kilocalorie(s)
kJ	kilojoule(s)
LDTOF MS	laser-desorption time-of-flight mass (spectroscopy)
lit	literature
m	multiplet (in NMR)
m	medium (in IR)
M^+	molecular ion
Me	methyl
MHz	megahertz
min	minute(s)
mM	millimolar
mp	melting point
MSD	Mass spectrometry detector
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance (spectroscopy)
NOESY	nuclear Overhauser effect spectroscopy
obs	observed
PAHs	polycyclic aromatic hydrocarbons
Ph	phenyl
ppm	parts per million
pyr	pyridine

q	quartet (in NMR)
R_f	retention factor (in TLC)
rt	room temperature
s	singlet (in NMR)
s	strong (in IR)
sat'd	saturated
θ	bend angle (in pyrenophanes)
t	triplet (in NMR)
t-BuLi	*tert*-butyllithium
Tc	coalescence temperature
TCNE	tetracyanoethene
Tf	trifluoromethylsulfonyl, CF_3SO_2-
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	tetramethylsilane (in NMR), trimethylsilane (in structures)
TMSA	trimethylsilyl acetylene
Ts	p-toluenesulfonyl
UV-vis	ultraviolet-visible (spectroscopy)
VID	valence isomerization-dehydrogenation
vs	very strong (in IR)
vs.	*versus*
w	weak (in IR)

Chapter 1

Introduction

1.1 Molecules with Radially Oriented p-Orbitals

1.1.1 Carbon Nanotubes

In 1991, Iijima and coworkers reported the discovery of several hollow, cylinder-shaped, one-atom thick rolled graphene sheets that consisted purely of carbon atoms.[1,2,3] These molecules are now widely known as single-walled carbon nanotubes (SWNTs).

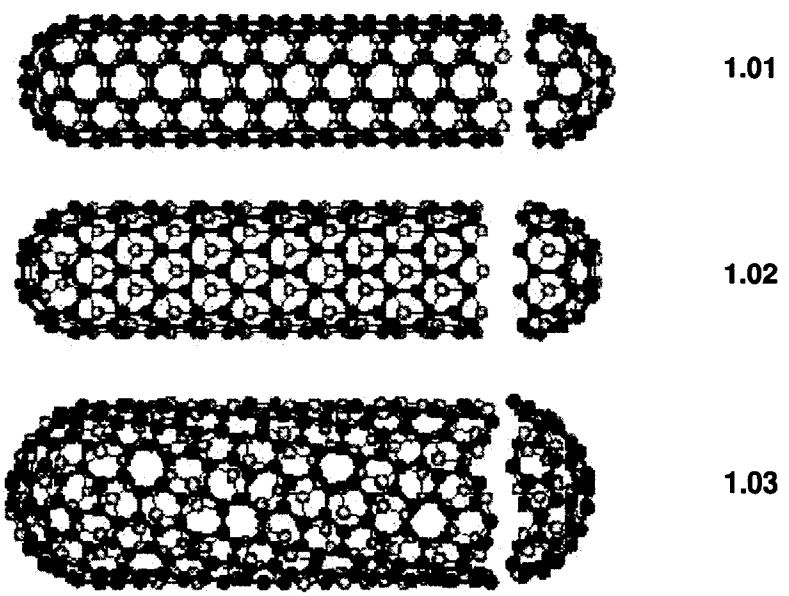


Figure 1.01. SWNTs (zigzag, armchair, chiral).[4]

Carbon nanotubes can be prepared by various methods including arc discharge, laser ablation, and chemical vapor deposition (CVD). Carbon nanotubes vary structurally in terms of length, diameter, roll-up motif (zigzag, armchair, chiral), and the number of "walls" (*i.e.* concentric tubes). Single-walled carbon nanotubes have unique electrical, physical and chemical properties, which render them excellent candidates for application in materials and optoelectronic devices. However, the low solubility of carbon nanotubes

makes them difficult to study, manipulate and process.[4] In order to gain information about carbon nanotubes, a variety of model systems have been established, a key feature of which is the presence of radially oriented *p*-orbitals. Belt- or bracelet-shaped aromatic systems are prime examples.

1.1.2 Aromatic Belts

Conjugated belt- or bracelet-shaped molecules have been synthetic targets for a long time. In this thesis, the term "belt" refers to cyclic systems, in which there are two continuous edges with no intersection between them. The discovery of fullerenes and carbon nanotubes in the past two decades initiated a great passion to synthesize conjugated belt and bracelet-shaped systems such as cyclacenes **1.04** (the shortest possible zigzag SWNTs), cyclophenacenes **1.05** (the shortest possible armchair SWNTs), cyclic phenylene-ethynylenes (Section 1.2.3), cyclocarbons (later in Section 1.1.2), and cyclophynes (Section 1.2.2).

[*n*]Cyclacenes **1.04** are benzenoid belt-shaped molecules that correspond to zigzag SWNTs. There is some computational evidence to suggest that odd numbered members of this series (having 4n+2 π electrons around each edge) will be more stable than their even congeners (4n π electrons around each edge). Some attempts have been made toward the total synthesis of cyclacenes, but the conversion of advanced intermediates, eg. **1.06**,[5] **1.07**[6] and **1.08**,[7] into the desired belts has failed in every case.

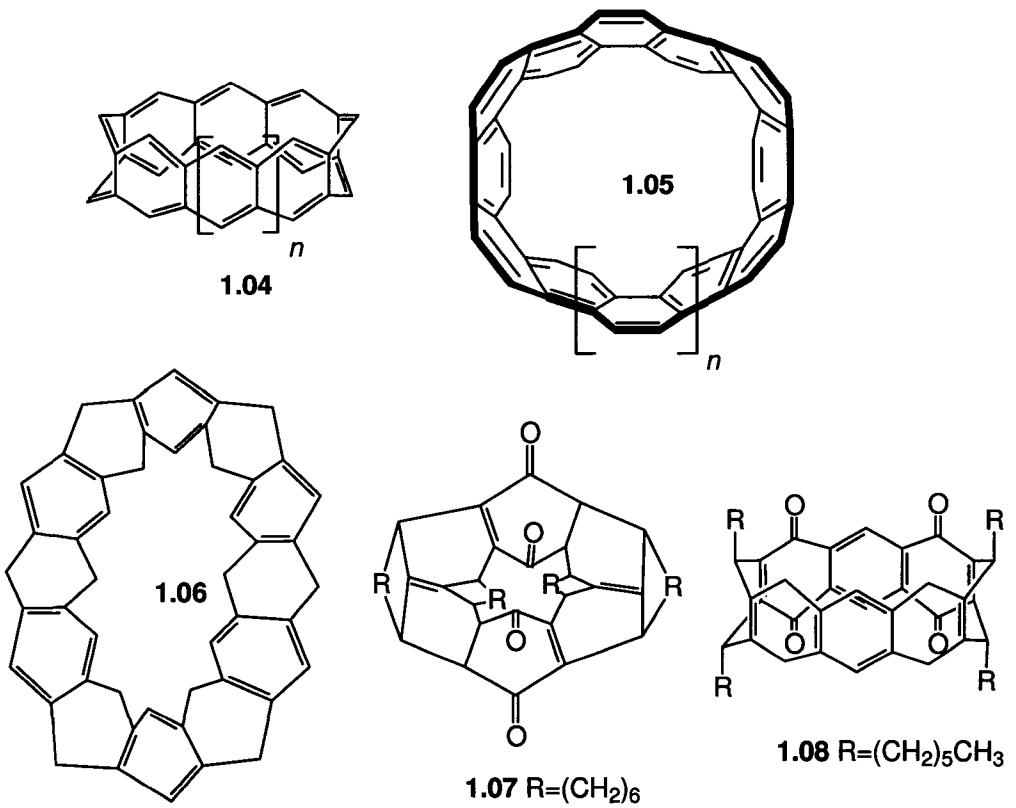
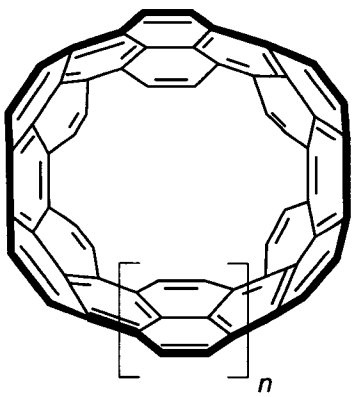
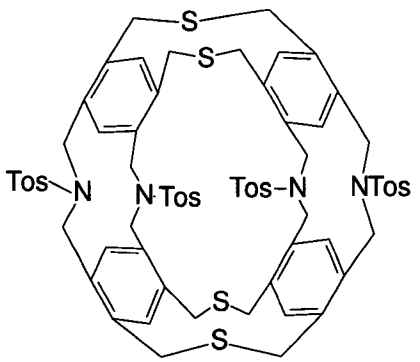


Figure 1.02. Cyclacenes, cyclophenacenes and cyclacene precursors.

Cyclophenacenes are another class of belt-shaped molecules. These aromatic belts correspond to armchair SWNTs. Vögtle and co-workers proposed a family of target molecules **1.09**, which have been referred to as "Vögtle belts". These systems are also substructures of armchair SWNTs.[8] Vögtle obtained a cyclophane **1.10**, which could be potentially converted into the belt **1.09** (n = –1) via extrusion of the sulfur and nitrogen atoms.[9] However, no successful conversion has been reported.



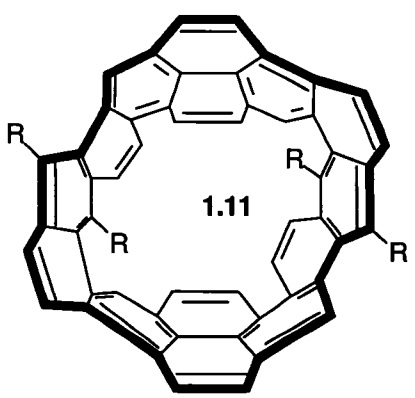
1.09

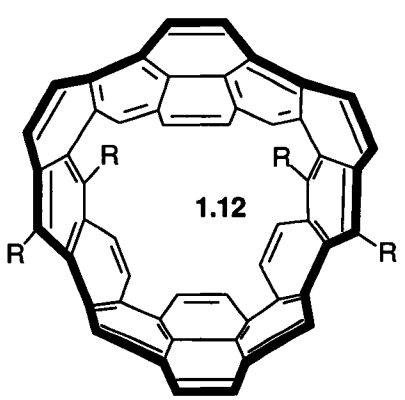


1.10

Figure 1.03. "Vögtle belt" and a potential precursor.

Bodwell and co-workers have been working on the chemical synthesis of armchair SWNT substructure as well. After some unsuccessful attempts to obtain a "Vögtle belt",[10] targets **1.11** and **1.12** were designed.[11] These have also proved to be challenging targets.[12]



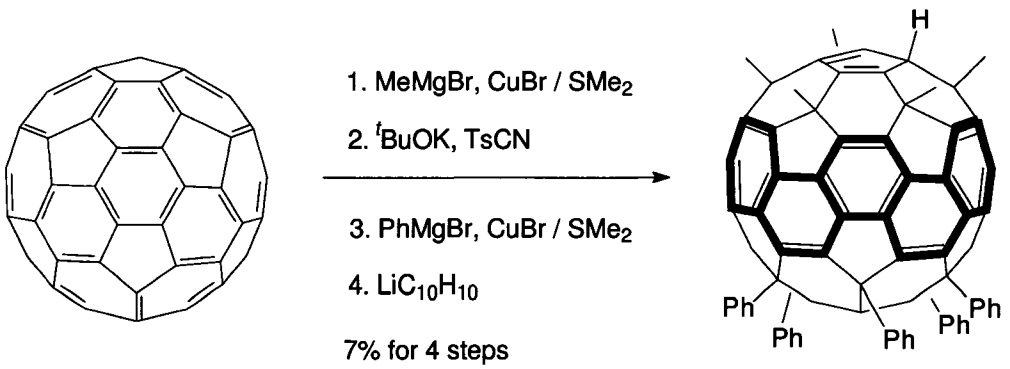


R=H, Me, decyl

Figure 1.04. Bodwell's target aromatic belts **1.11** and **1.12**.

In 2003, Nakamura and co-workers reported the first successful synthesis of a cyclophenacene.[13] Differently from conventional synthetic methods, they used C_{60} as the starting material, which already contains a [10]cyclophenacene structure within its

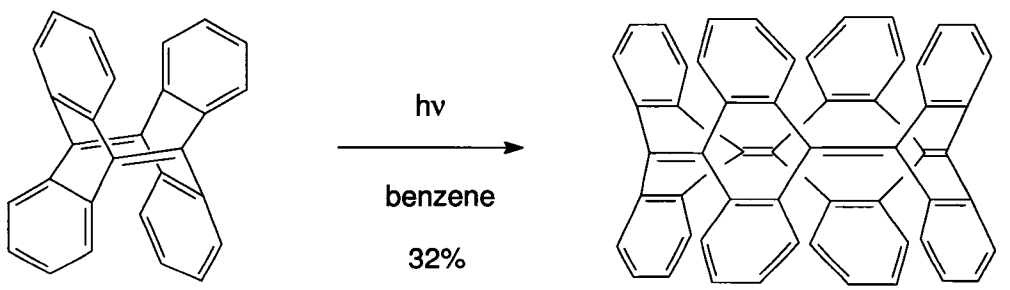
polycyclic framework. By carefully reducing the "top" and "bottom" parts of a C_{60}, the functionalized cyclophenacene belt was revealed. Of course, this approach cannot be applied beyond this specific system.



1.13 **1.14**

Scheme 1.01. Nakamura's synthesis of a [10]cyclophenacene derivative **1.14**.

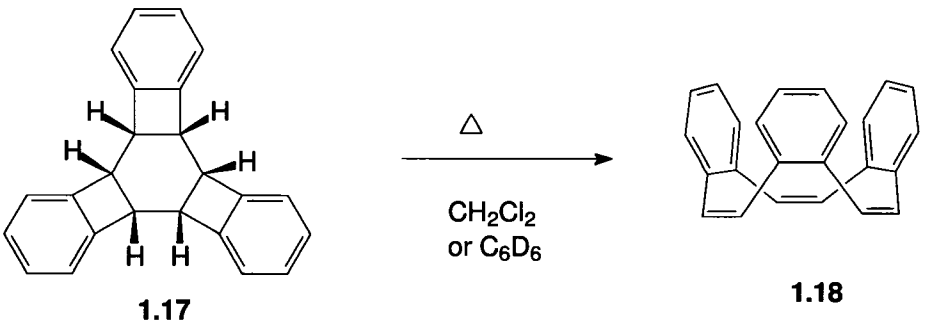
Another conjugated cyclic system with radially-oriented p orbitals is Herges and coworkers' "picotube" **1.16** (Scheme 1.02).[14] This is a potential precursor to a short (4,4)armchair nanotube, but the cyclodehydrogenation (even FVP-induced dehydrocyclization) of **1.16** has been reported to be unsuccessful.[15]



1.15 **1.16**

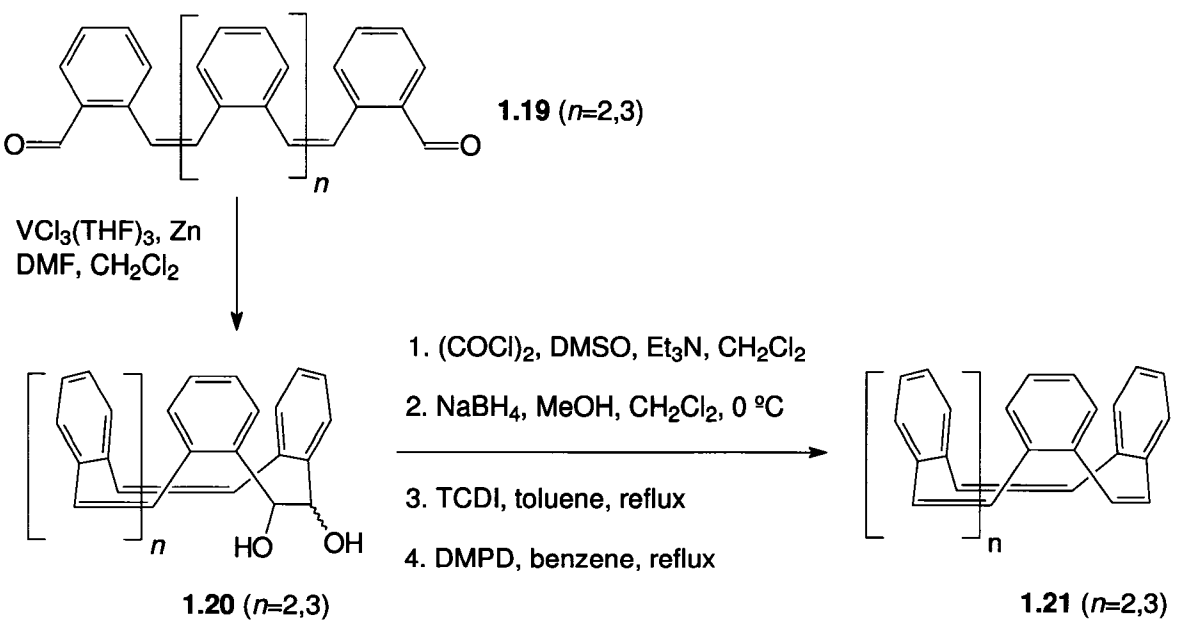
Scheme 1.02. Herges's synthesis of "picotube" **1.16**.

All-(Z)-benzannulenes are also potential precursors to cyclophenacenes. Iyoda and Vollhardt have independently reported the synthesis of an *all-Z*-tribenzo[12]annulene **1.18**.[16] However, as expected for such a small system, there has been no report of its conversion to [6]cyclophenacene.



1.17 **1.18**

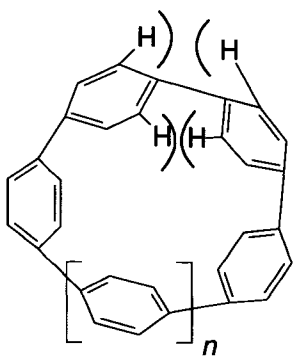
Scheme 1.03. Iyoda's and Vollhardt's synthesis of *all-(Z)*-tribenzo[12]annulenes **1.18**.



Scheme 1.04. Iyoda's synthesis of larger benzannulenes **1.21**.

Syntheses of larger *all-Z*-benzannulenes were also reported by Iyoda *et al.*, such as *all*-(*Z*)-tetrabenzo[16]annulene **1.21a** (n=2) and *all*-(*Z*)-pentabenzo[20]annulene **1.21b** (n=3).[17] *Cis*-and *trans* mixtures **1.20** were first synthesized by a transition metal catalyzed pinacol-type coupling of dialdehyde **1.19**. This was followed by a conversion to *cis*-**1.20**, and then a Corey-Winter olefination to afford **1.21**.[18] As before, the conversion of these systems to the corresponding cyclophenacenes has not been reported.

[0_n]Paracyclophanes are a family of aromatic bracelets. They also map onto the surface of armchair SWNTs, but the multiple intersection of the two edges disqualify them as belts. In addition to strain energy resulting from nonplanar benzene rings, nonbonding interactions all around the cycles would be expected to be present (Figure 1.05). As such, the syntheses of these cyclophanes will be very challenging. Nevertheless, several synthetic approaches toward [0_n]paracyclophanes have been reported.[18] These were based upon the cyclohexane hinges, butenyne hinges, sulfide and sulfur oxide hinges and 9,9',10,10'-tetradehydrodianthracene hinges, but none of them were successful.

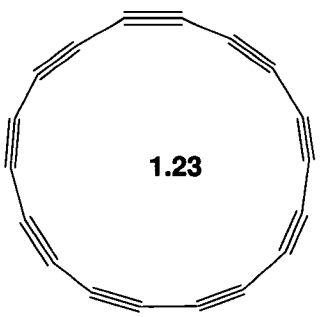


1.22

Figure 1.05. [0_n]paracyclophane.

The introduction of alkynes between adjoining rings in the [0_n]paracyclophanes should fully relieve the nonbonding interactions. The resulting systems fall under the broad heading of molecular bracelets and the more specific heading of cyclophynes. These systems are discussed in Section 1.2.2.

Cyclo[*n*]carbons (Figure 1.06), also known as cyclic carbon clusters, refer to those cyclic polyethynylenes, which also have conjugated loop-shaped structures. They have been classified as a fourth carbon allotrope besides diamond, graphite, and the fullerenes.[19] These nanorings are believed to have important functions in the formation of fullerenes.[20] Although calculations predicted that cyclic carbon clusters might exist in a polyyne form,[21] only mass spectroscopic evidence of the formation of cyclocarbons has been reported so far.[22]

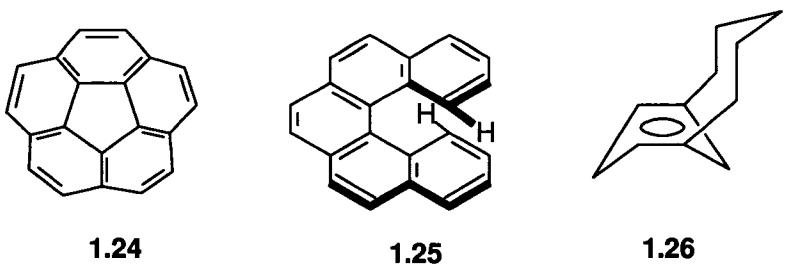


1.23

Figure 1.06. Cyclo[18]carbon.

1.2 Nonplanar Aromatics

It has been known for a very long time that an aromatic system is most stable in its planar conformation. However, examples of nonplanar aromatic systems have also been known for a very long time. Interest in such systems has skyrocketed since the discovery of fullerenes and carbon nanotubes. As discussed by Hopf, [23] there are three general ways of generating nonplanar aromatic systems (Figure 1.07).



1.24 **1.25** **1.26**

Figure 1.07. Examples of nonplanar aromatic systems.

Fullerene fragment **1.24**, named "corannulene", or [5]circulene, is a nonplanar aromatic compound because a non-six-membered ring is embedded within five six-membered rings. The planar conformation is disfavored because it requires bond length distortions, which require much energy. Bond angle distortions (pyramidalization in this case) of the five central carbon atoms require considerably less energy and this affords the molecule its bowl-shaped structure. [5]Helicene **1.25** is another example of a nonplanar aromatic system. It is nonplanar because the planar conformation requires that nonbonded atoms occupy the same space. To avoid this very high energy situation, the molecular framework twists into a helical conformation. When an aromatic system is bridged at nonadjacent positions (*i.e.* a cyclophane **1.26**, see following section), a nonplanar conformation can also be enforced. In such cases, the planar conformation

would require bond length elongation in the bridge. As above, the energy cost of deforming bond angles is much less than that of deforming bond lengths, so the aromatic systems adopt bent (or sometimes twisted) conformations.

1.2.1 Cyclophanes

Cyclophanes are a very large class of molecules. Generally speaking, a cyclophane is a system in which one or more aromatic moieties are connected by bridges. The bridges in the cyclophanes were originally aliphatic, and this is reflected in the word "cyclophane" (cyclo + phenyl + alkane).[24] Of course the bridges in cyclophanes are not limited to being purely aliphatic, and can consist of unsaturated units, such as alkenes, alkynes and arenes. Some examples of cyclophanes are shown in Figure 1.08.

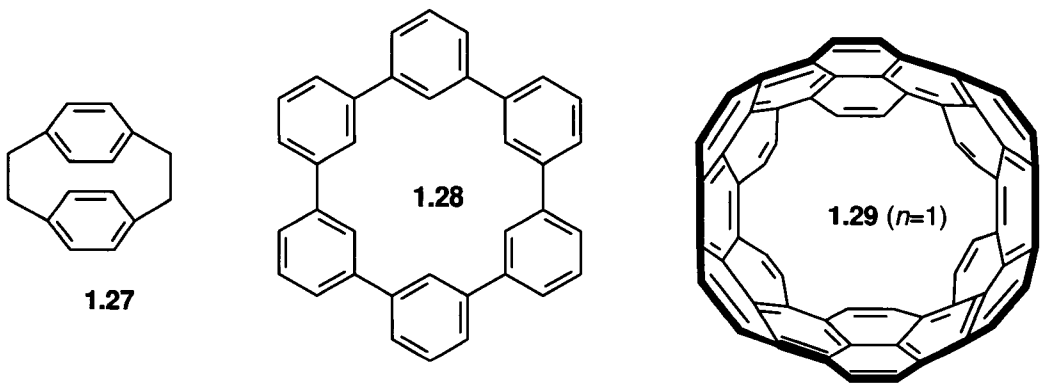


Figure 1.08. Examples of cyclophanes.

Compound **1.27**, [2.2]paracyclophane, was the first cyclophane to be reported and characterized and is the most extensively studied and recognizable cyclophane.[25] This is a typical cyclophane because it contains aromatic units and aliphatic bridges. Compound **1.28**, which is commonly viewed as a cyclic oligoarylene,[26] is not a typical cyclophane,

since it does not contain any aliphatic moieties. However, if one or more of the *meta*-phenylene groups are considered to be tethers linking other parts of the molecule, it can be viewed as a cyclophane. Alternatively, it can be considered to be a "[0]cyclophane", in which the aromatic moieties are connected by 0 atom aliphatic bridges. Compound **1.29** is a belt-shaped molecule, which was proposed by Vögtle as an "interesting target", but has not yet been synthesized.[8] This molecule could also be viewed as an aromatic moiety (a rylene) tethered to itself by 0 atom bridges. As such, it could also be called a cyclophane, although the term "aromatic belt" or "beltene" is usually applied to systems of this type. Clearly, there is considerable overlap between cyclophanes and other classes of structurally interesting molecules. The point at which a cyclophane stops being a cyclophane and starts to be something else is, like beauty, in the eye of the beholder.[27] Ultimately, cyclophane nomenclature is so broad that virtually any molecule can be considered a cyclophane.[28]

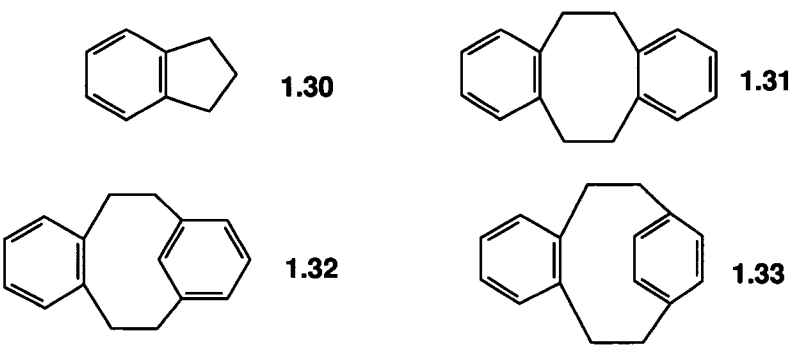


Figure 1.09. Examples of bridged aromatics.

A case in point, and also a somewhat controversial issue, is whether *ortho*-bridged aromatics are real cyclophanes or not. Some cases are more clear cut than others. Whereas indan **1.30** is never referred to as [3]othocyclophane, 1,5-dibenzocyclooctadiene

and related systems **1.31**, **1.32** and **1.33** have been treated as [2.2]orthocyclophane, [2.2] orthometacyclophane and [2.2]orthoparacyclophane, respectively. More complicated systems, such as **1.34**, are typically viewed as dehydrobenzannulenes (DBAs). When a DBA has at least one non-ortho-substituted ring, it is more often referred to as a cyclophane, *e.g.* **1.35** and **1.36** (or even the ring-opened valence isomer of **1.34**).[29]

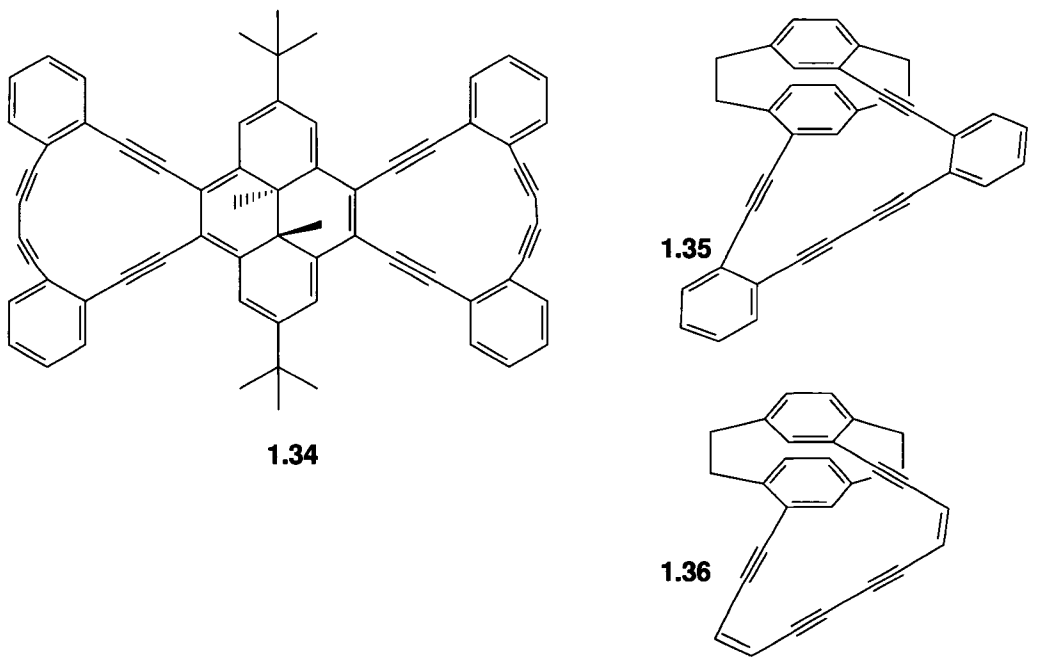


Figure 1.10. Examples of orthocyclophanes and cyclophane-DBA hybrids.

Given the diffuse boundaries that exist, the term "cyclophane" will be used broadly throughout this thesis.

1.2.2 Cyclophynes

Cyclophynes are a small subclass of cyclophanes. If the bridges in a cyclophane consist solely of ethynylene groups, the molecule is called a "cyclophyne". Cyclophyne is

a term that was first used by Hopf in 1982, when the intermediacy of [2.2]paracyclophyne **1.37** was reported.,[30] and this term is now usually referred to the systems consisting of only ethynylene bridges. As with any cyclophanes, the aromatic components of a cyclophyne could be benzenes, PAHs, heterocyclic aromatic units, or even nonbenzenoid aromatic units, and the tether could consist of any number of ethynylene units.

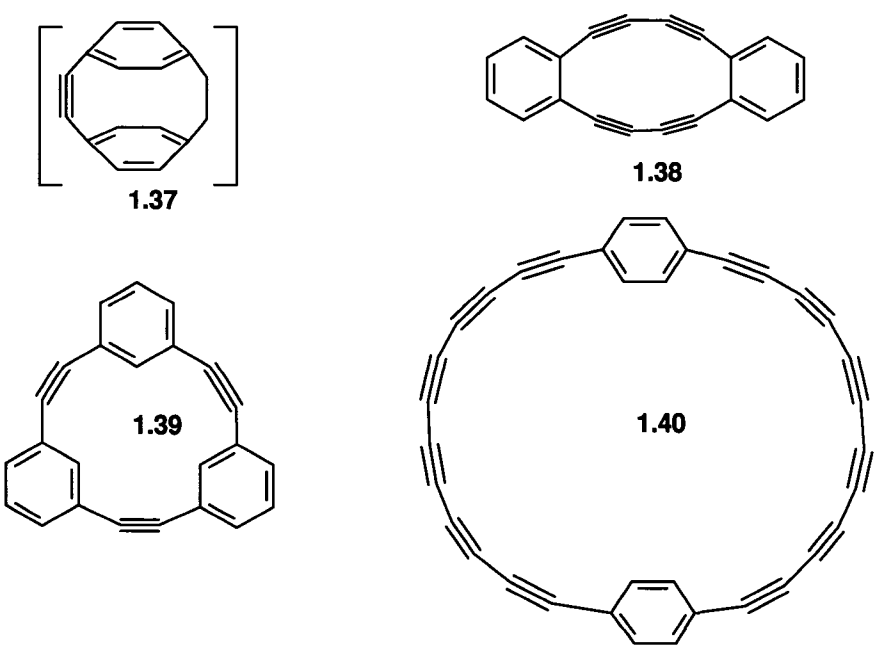


Figure 1.11. Examples of cyclophynes.

Since the generation of the first cyclophyne by Hopf, many stable cyclophynes have been reported. A few examples (**1.38-1.40**), which vary in their shape and size, are shown in Figure 1.11.[31] Cyclophynes have attracted interest because they are highly carbon-rich materials and, in some cases, they are potential precursors to fullerenes.[32]

Since the majority of cyclophynes contain benzene moieties, cyclophynes could be divided into several groups according to their substitution patterns,[33] *i.e. ortho-, meta-, para-,* and / or more highly-substituted. Aromatic moieties other than benzene could also be classified under these headings according to the substitution pattern. Depending upon the molecular architecture, cyclophynes can have planar aromatic structures as well as nonplanar ones. *Ortho-, meta-* and *para*-cyclophynes as well as other more complicated structures are described in the following sections. Cyclophynes containing PAHs are described in Chapter 2.

1.2.2.1 Orthocyclophynes (Dehydrobenzannulenes)

Orthocyclophynes, which consist of *ortho*-substituted benzenes as their aromatic units, are often referred to as dehydrobenzannulenes.[34] Many orthocyclophynes have conformations with planar aromatic units and linear ethylene groups, such as **1.41** [35] (Figure 1.12). Some orthocyclophynes are structurally planar, but with nonlinear ethynylene groups, *i.e.* **1.42**.[36] The angle about the sp-hybridized carbon atoms in **1.42** is reported to be 155.8 °. Cyclophyne **1.43**,[37] as another example, adopts a nonplanar structure because its ideal bond angles cannot be achieved in the planar conformation.[37] Larger orthocyclophynes, such as **1.44** and **1.45**, have also been reported,[38] and they can also be viewed as substructures of the postulated carbon allotropes, graphyne and graphdiyne[29,33] (Figure 1.13). Since these cyclophynes are highly unsaturated, they have been used in attempts to make carbon-rich materials, such as charged carbon clusters and nanotubes.[33]

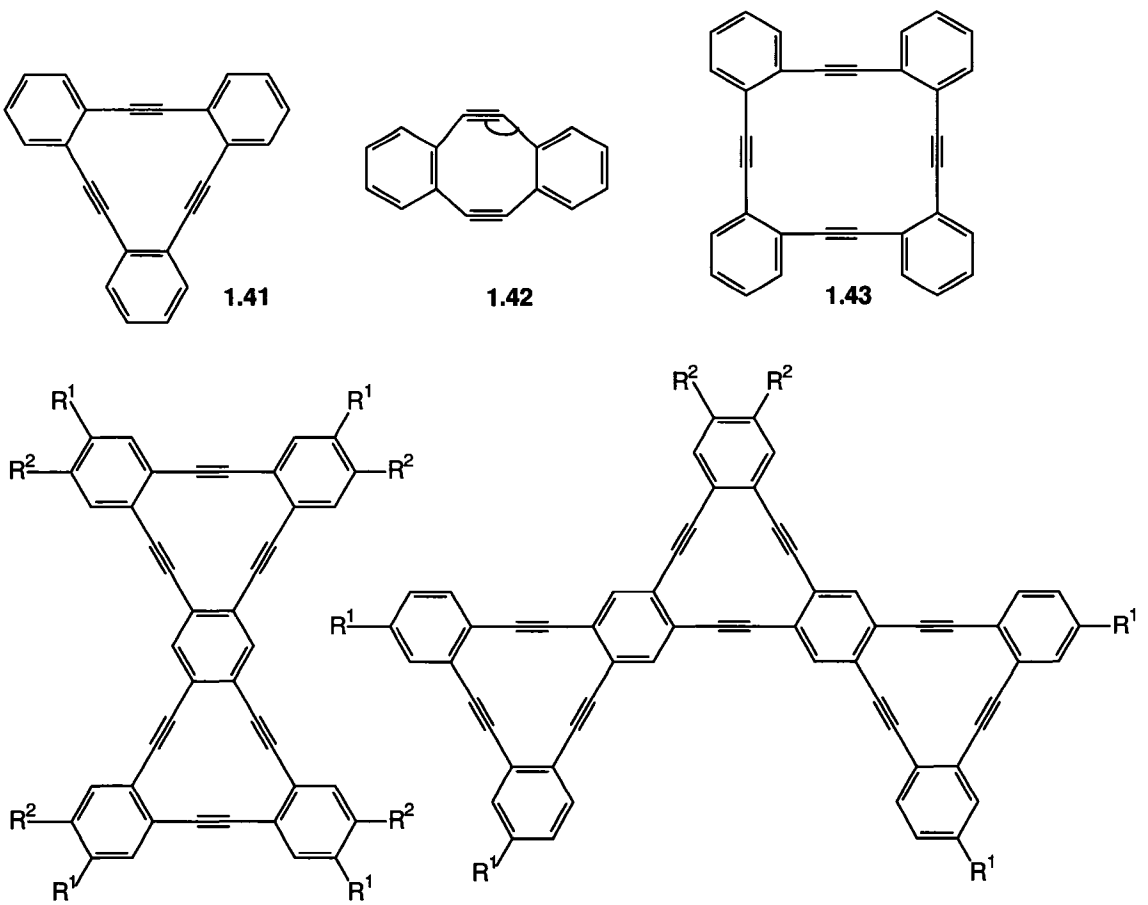
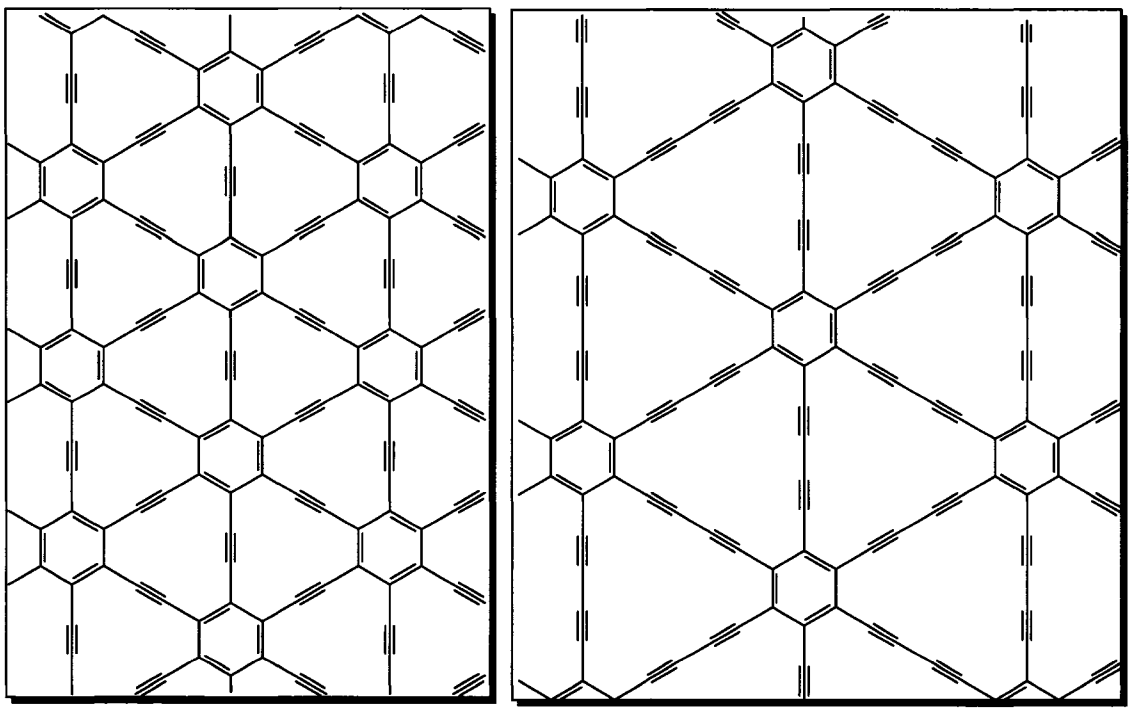


Figure 1.12. Examples of reported orthocyclophynes.



"Graphyne" **"Graphdiyne"**

Figure 1.13. Graphyne and graphdiyne.

The bridges of cyclophynes can also be polyethynylenes or even aromatic units. For instance, compound **1.46** was synthesized by Haley and co-workers, and was proved to possess a saddle-like conformation.[39] Compound **1.47**, bearing a *para*-phenylene between the two *ortho*-phenylenes, have their ethynylene groups distorted (163.5-163.7° bond angles in the alkynes), and this was proved by X-ray analysis.[40]

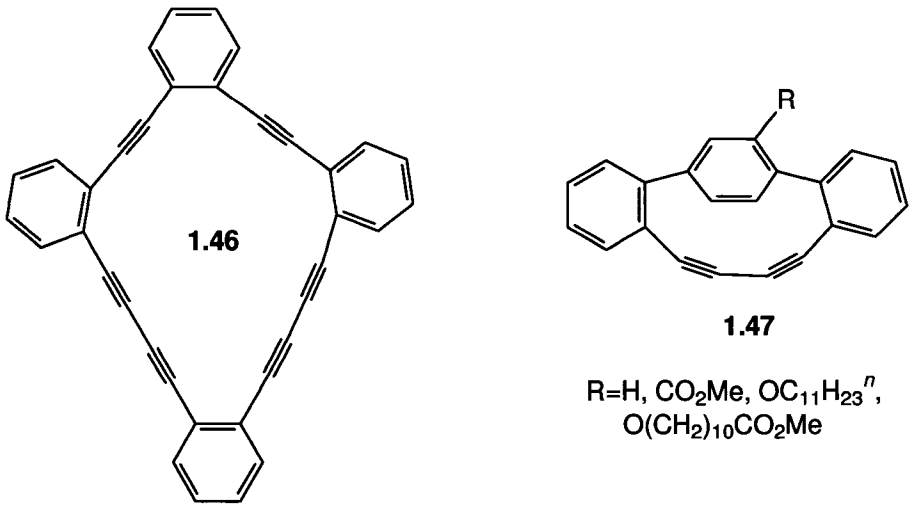


Figure 1.14. Examples of orthocyclophynes.

1.2.2.2 Metacyclophynes

The two most common classes of metacyclophynes are represented by the general structures **1.48** and **1.49**. However, these compounds are rarely referred to as metacyclophynes but are usually categorized as shape-persistent macrocycles. (Figure 1.15).[33]

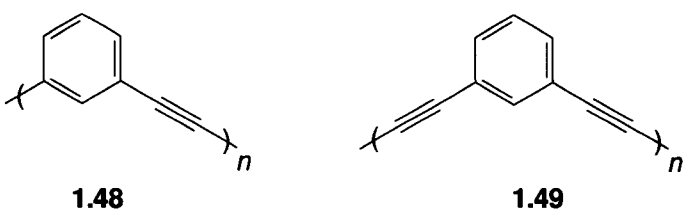


Figure 1.15. General structures of metacyclophynes.

By elongation of the bridges in a metacyclophyne, very large systems can be synthesized. For example, compound **1.50**, a planar, shape-persistent metacyclophyne,

was reported by Moore and co-workers in 1992.[41] The diameter of this macrocycle is 22 Å.

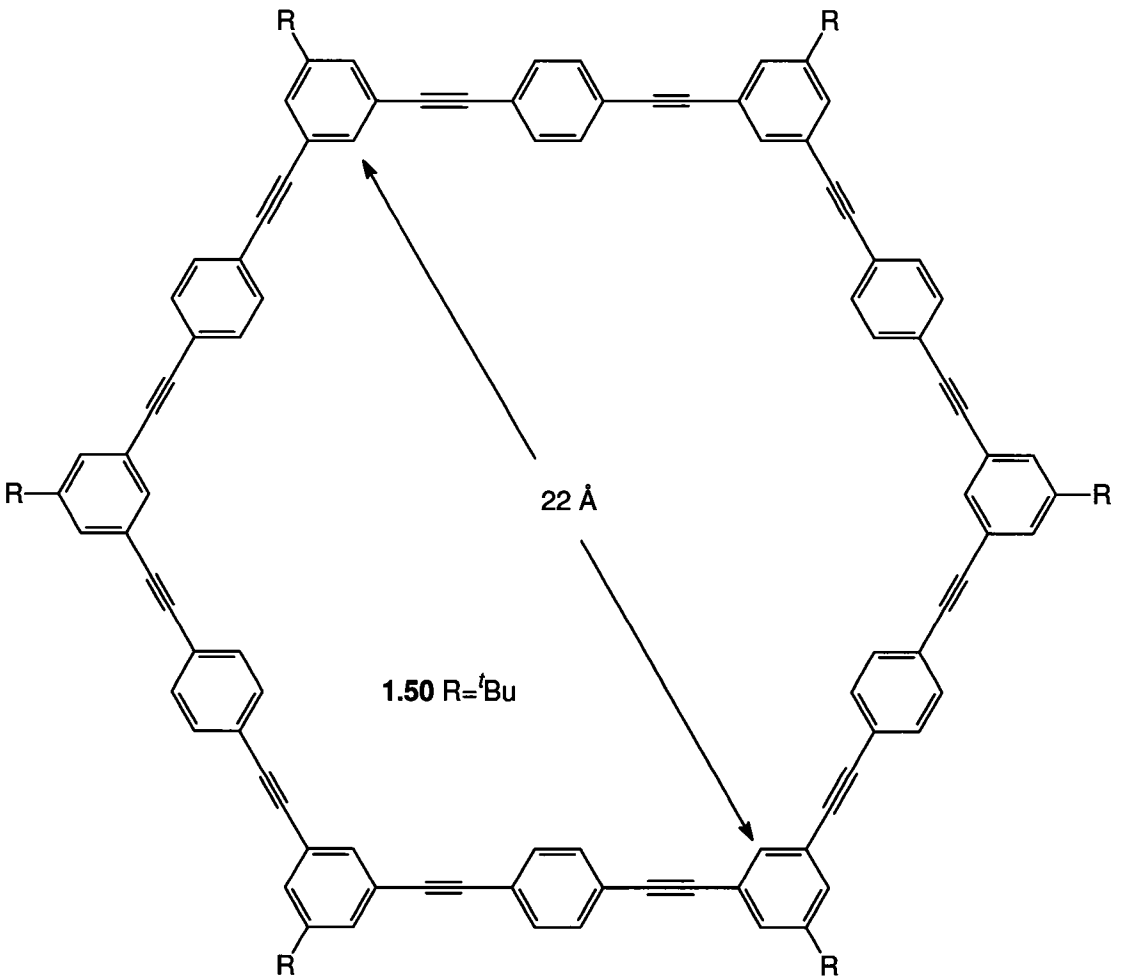


Figure 1.16. Moore's metacyclophyne **1.50**.

Although they do not have meta-substituted benzene rings, the systems shown in Figure 1.17 can be classified as metacyclophynes due to their 1,3- (or geometrically analogous) substitution patterns. These compounds have all been synthesized and studied.[42]

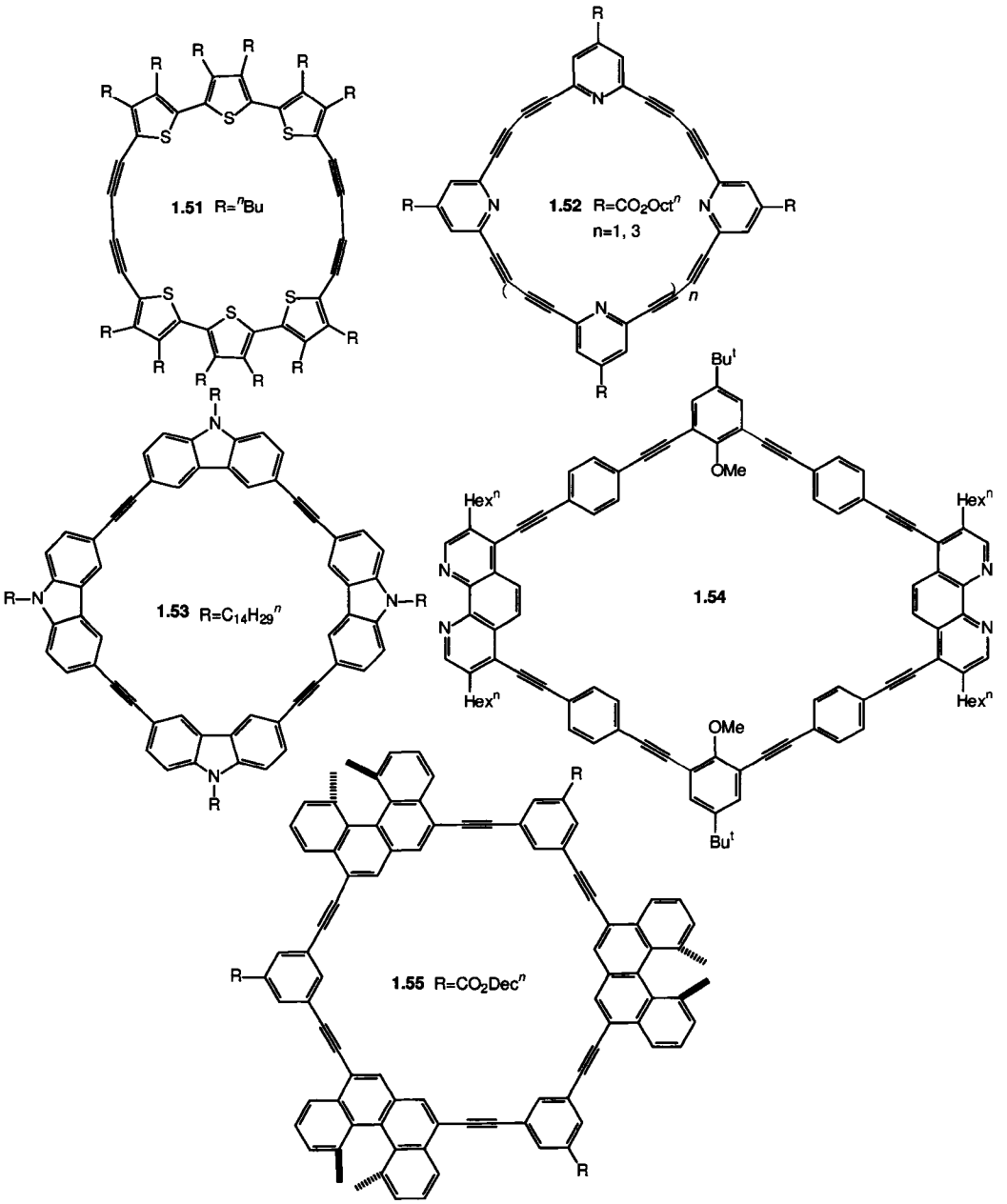


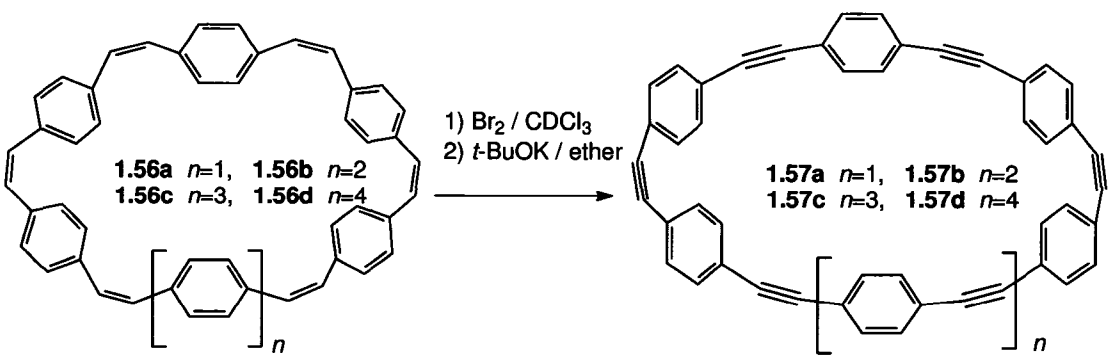
Figure 1.17. Examples of metacyclophanes with other aromatic moieties.

1.2.2.3 Paracyclophynes

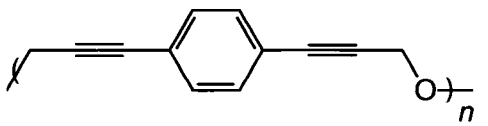
The most common class of paracyclophynes are Oda and Kawase's paraphenylene-acetylene derivatives (CPPAs) **1.56**. Because both the *p*-phenylene unit and the

ethynylene unit have "linear" structures, *i.e.* the pendant bonds form an angle of 180° in their lowest energy conformations, paracyclophynes contain both bent aromatic units and bent alkynes. This is in contrast to orthocyclophynes and metacyclophynes, in which structural distortions (if any) are located primarily in the ethynylene units. A major consequence of this is that the synthetic methodology used for the synthesis of ortho- and metacyclophynes (*e.g.* Sonogashira coupling, Glaser coupling, and oxidative coupling) fails for paracyclophynes and new / alternative methodology has been required.[33]

Oda, Kawase and their co-workers reported the synthesis of [2_n]paracyclophynes (**1.57**), also referred to as cyclic paraphenylene-acetylenes (CPPAs) and "nanorings".[43] Alkene-containing paracyclophanes **1.56** (mixtures of geometric isomers) were first generated using a McMurry reaction, and the triple bonds were then installed by applying a bromination / dehydrobromination protocol. The diameters of these nanorings vary from 13.1 Å to 17.4 Å, which makes them suitable hosts for some guest molecules, such as C_{60}.[44] Another similar molecule **1.58** was synthesized by Yoshida and co-workers, and supramolecular complex formation of **1.58** with C_{60} was also observed.[45] Although the bridges in these molecules are not solely ethynylenes, due to the structural similarity, they can still be reasonably considered as cyclophynes.[33]



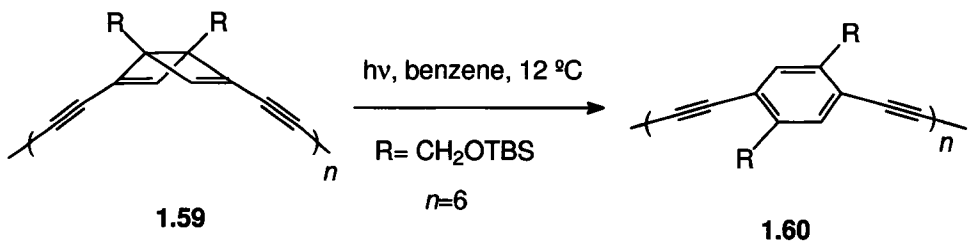
Scheme 1.05. Oda and Kawase's synthesis of [*n*]CPPAs.



1.58 n= 4

Figure 1.18. Yoshida's nanoscale oxaarenecyclynes.

From a strategic perspective, Oda, Kawase, and Yoshida's syntheses all involved the installation of the ethynylene bridges after that of the aromatic units ("alkynes last"). A complementary strategy ("arenes last"), which involves the generation of the aromatic moieties after the formation of the ethynylene bridges, has also been applied to the synthesis of paracyclophynes. In 2001, the synthesis of [4$_6$]cyclophyne **1.60** was reported by Tsuji, Ohkita and co-workers.[46] In their synthesis, a Dewar benzene derivative **1.59** was first prepared, and then a photo-induced valence isomerization converted **1.59** to cyclophyne **1.60**[46] (Scheme 1.06). This protocol was also used by the same group to synthesize related cyclophynes, such as metaparacyclophyne **1.61** and orthoparacyclophyne **1.62** (Figure 1.19).[47]



1.59 **1.60**

Scheme 1.06. Tsuji and Ohkita's synthesis of paracyclophynes.

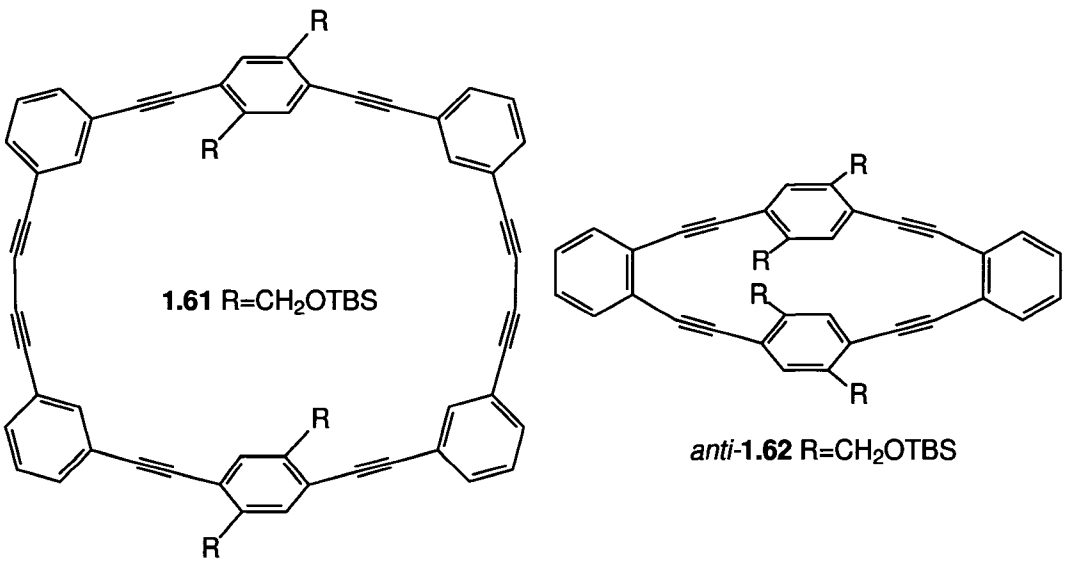


Figure 1.19. Other cyclophynes synthesized *via* photolysis.

The same strategy (but a different methodology) was used by Tobe and co-workers to prepare [6$_3$]paracyclophyne **1.63**.[48,33] Although the formation of the paracyclophyne could be detected by laser-desorption time-of-flight mass spectroscopy, the product could not be isolated due to its instability. It was also reported that the ions of **1.63** underwent the loss of 12 H atoms in the mass spectrometer to afford C_{36} clusters.[33]

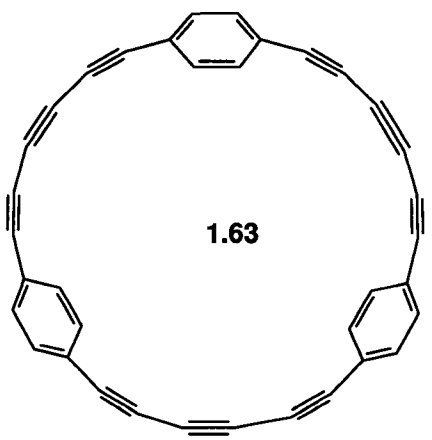
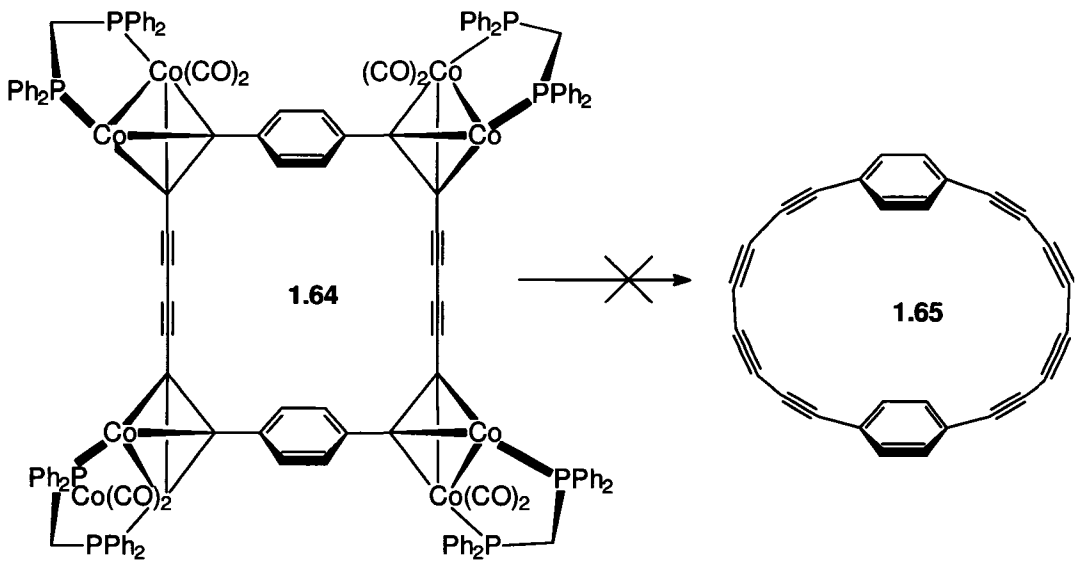


Figure 1.20. Cyclophyne with hexatriyne bridges.

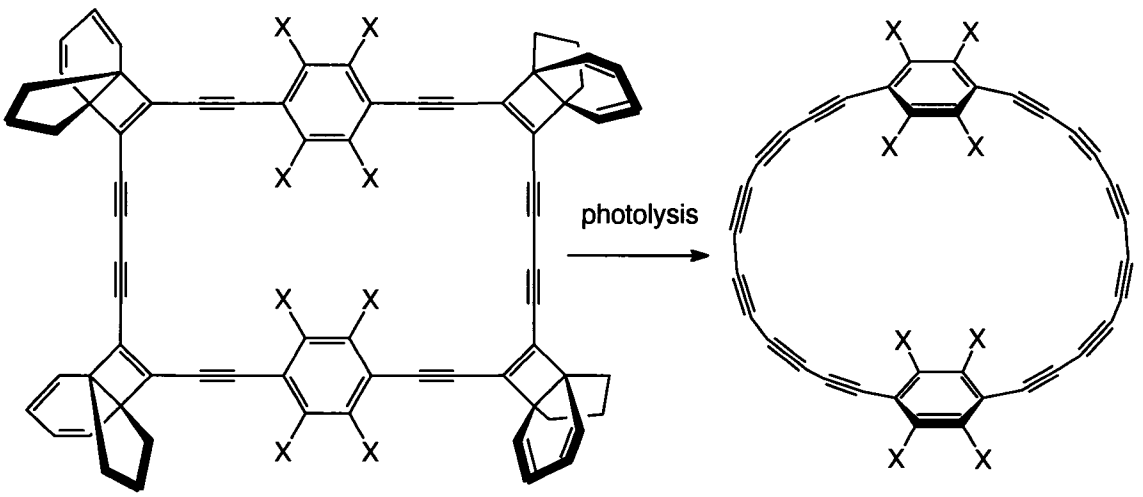
It is known that linear polyyne systems become less stable as they become larger.[23,49] An alkyne can also be destabilized through distortion from its ideal geometry (linear). In cyclophynes, these two effects can work against one another. Increasing the number of consecutive ethynylene units in a cyclophyne would, as in linear systems, be expected to be destabilizing, but average distortion per alkyne necessarily decreases, because the cycle is larger. The overall stability of a cyclophyne will be strongly influenced by the interplay of these two effects.



Scheme 1.07. Haley's attempt to prepare cyclophyne **1.65**.

For example, Haley and co-workers reported an attempted synthesis of paracyclophyne **1.65** in 1997.[50] This system is smaller than **1.63** (one *p*-phenylene and one ethynylene unit less) and has 8-atom instead of 6-atom bridges. One would therefore expect significantly lower stability than **1.63**. The "alkynes last" strategy was employed. This involved the synthesis of cobalt complex **1.64** and its subjection to an iodine-

promoted decomplexation in order to obtain **1.65**. However, not surprisingly, this reaction failed to provide any evidence of the formation of **1.65**.



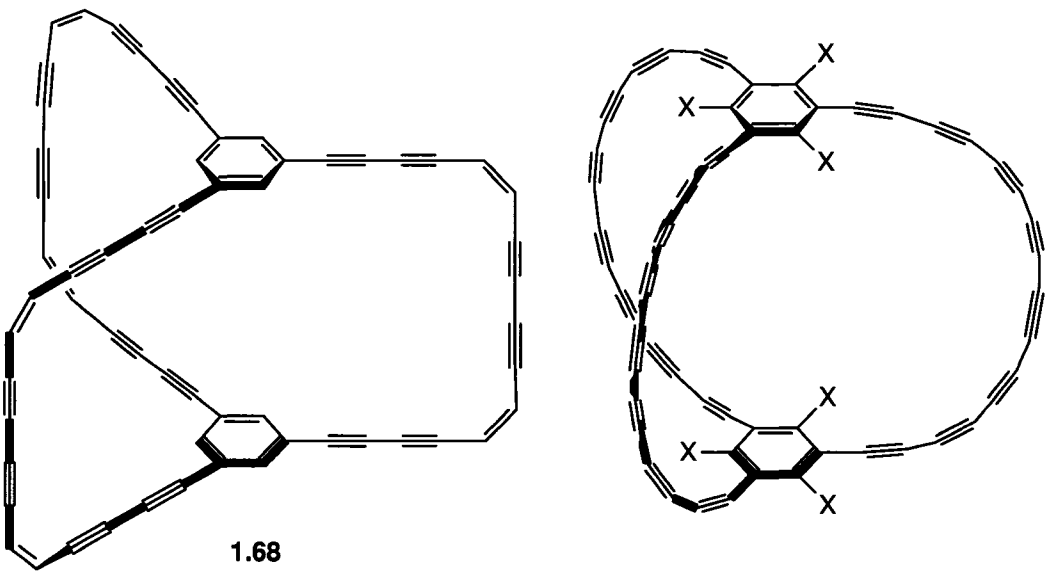
Scheme 1.08. Tobe's synthesis of paracyclophynes.

Using a similar strategy, Tobe and co-workers applied a different methodology (Scheme 1.08) to synthesize paracyclophynes with longer polyyne bridges (**1.67a** and **1.67b**).[51] The precursors **1.66a** and **1.66b**, each of which contained four [4.3.2]propellatriene moieties, were synthesized and then subjected to photolysis to obtain the desired paracyclophynes through the loss of four molecules of indan. It was observed that these reactions occurred in a stepwise fashion, and the [12.12]paracyclophanedodecaynes **1.67a** and **1.67b** were indeed formed, as supported by laser-desorption time-of-flight (LD TOF) mass spectrometry. However, no products were isolated. When **1.67b** was subjected to LDTOF MS, besides the molecular ion peak for **1.67b**, a peak for C_{36}^- was also observed, which was significantly more abundant than the

peaks corresponding to the partial loss of chlorine. The inference is that this may correspond to a C_{36} fullerene.

1.2.2.4 Three-dimensional Cyclophynes

Besides *ortho-*, *meta-* and *para*-cyclophynes, those having more complicated substitution patterns have also been designed. If there are more than two polyethylene bridges between two aromatic moieties, a 3D structure is generated. The most frequently studied systems are based on 1,3,5-trisubstituted benzene rings, which impart cage-like structures to the cyclophynes. These reactive carbon-rich materials, once synthesized, might be expected to rearrange to fullerenes. With this in mind, chlorine atoms, which are more easily lost than H atoms, were also introduced.[33]



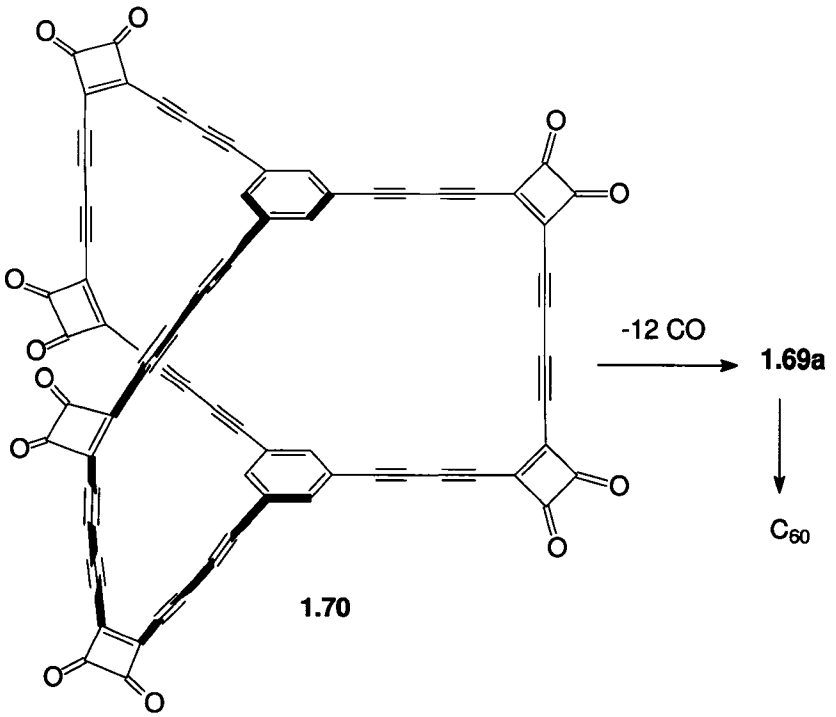
1.68

1.69a X=H
1.69b X=Cl

Figure 1.21. Structures of 1,3,5-bridged cyclophynes.

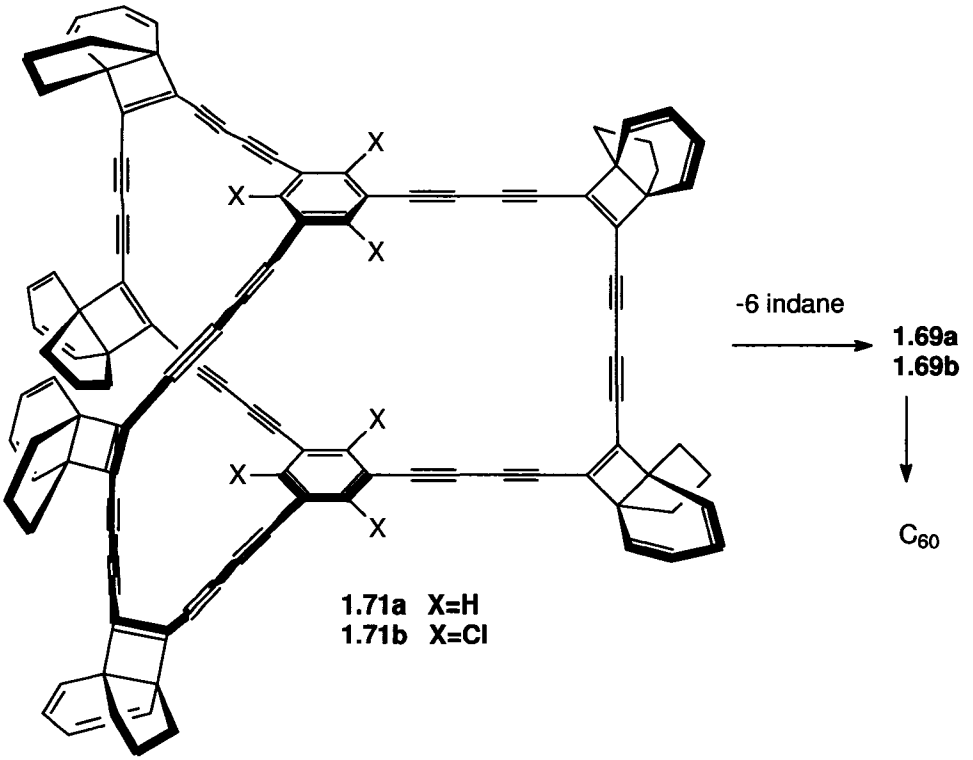
The first 1,3,5-bridged cyclophyne, [16.16.16](1,3,5)cyclophanehexaene-ocatadecayne **1.68**, was reported by Rubin and coworkers in 1996.[52] Although each of

the bridges contained two alkene groups, this molecule underwent a loss of 4 H atoms in the mass spectrometer, it was considered the first three dimensional 1,3,5-trisubstituted cyclophyne,[33] (Figure 1.21). Rubin and Tobe then reported the synthesis of **1.69a** and **1.69b** independently in 1998 (Scheme 1.09).[53] These systems contain sixty carbon atoms and were reported to rearrange to C_{60} species, presumably C_{60} fullerene, in the mass spectrometer.



Scheme 1.09. Rubin's synthesis of C_{60} *via* cyclophyne **1.69a**.

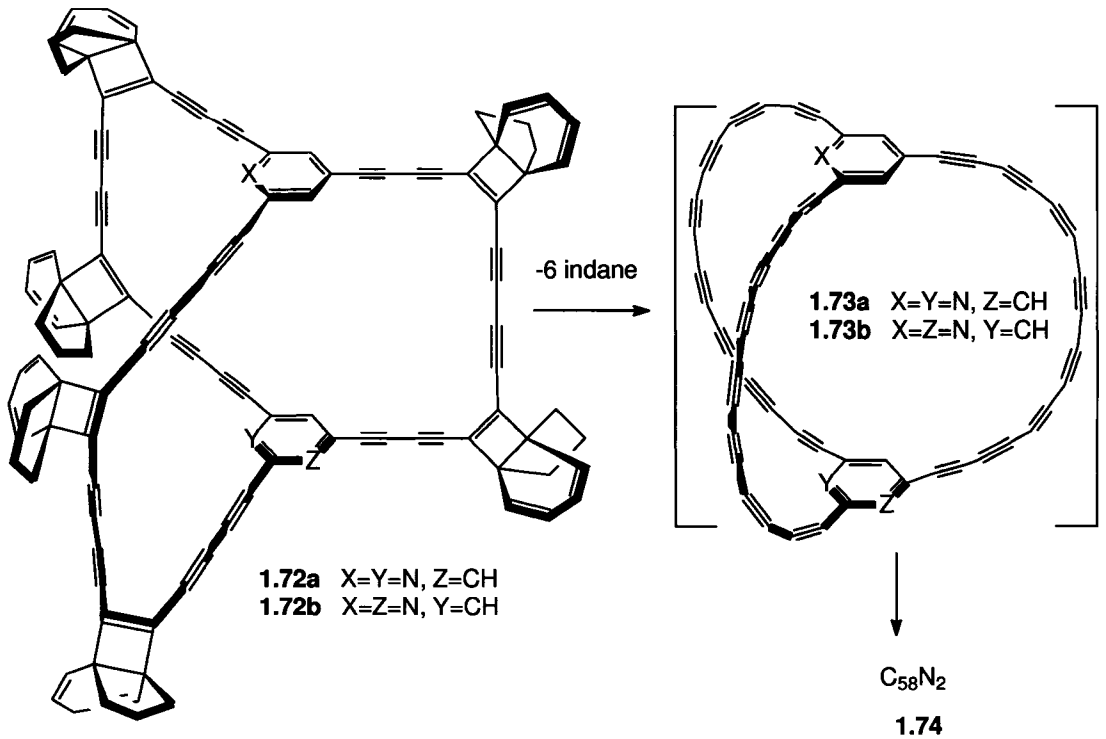
Both Rubin's (Scheme 1.09) and Tobe's (Scheme 1.10) syntheses use the "alkynes last" strategy. In Rubin's case, alkynes are revealed by the loss of CO during a FT-ICR LD MS experiment.[53a] As with the synthesis of **1.67**, Tobe's synthesis relied upon a [2+2] cycloreversion reaction. [53b-53c]



Scheme 1.10. Tobe's synthesis of C_{60} *via* cyclophyne **1.69a** and **1.69b**.

Assuming that the C_{60}^{+} signal in the mass spectrum of **1.69a** and **1.69b** was indeed C_{60} fullerene, Tobe reasoned that the heterocyclophynes **1.72a** and **1.72b** should serve as precursors to diazafullerenes (Scheme 1.11). As expected, the laser desorption mass spectra of **1.72a** and **1.72b** exhibited peaks for **1.72a**, **1.72b**, **1.73a**, **1.73b** as well as $C_{58}N_2$, which corresponds to diazafullerenes.[54]

Another cage-like cyclophyne reported by Tobe is **1.75** (Figure 1.22). This was postulated by Tobe to be a possible precursor to C_{78} fullerenes.[55,33]



Scheme 1.11. Tobe's synthesis of diazafullerene **1.74**.

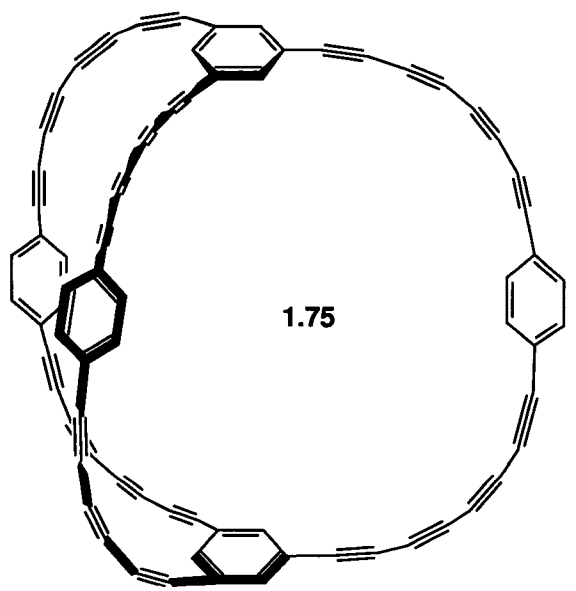


Figure 1.22. Tobe's cyclophyne **1.75**, a possible precursor to C_{78} fullerene.

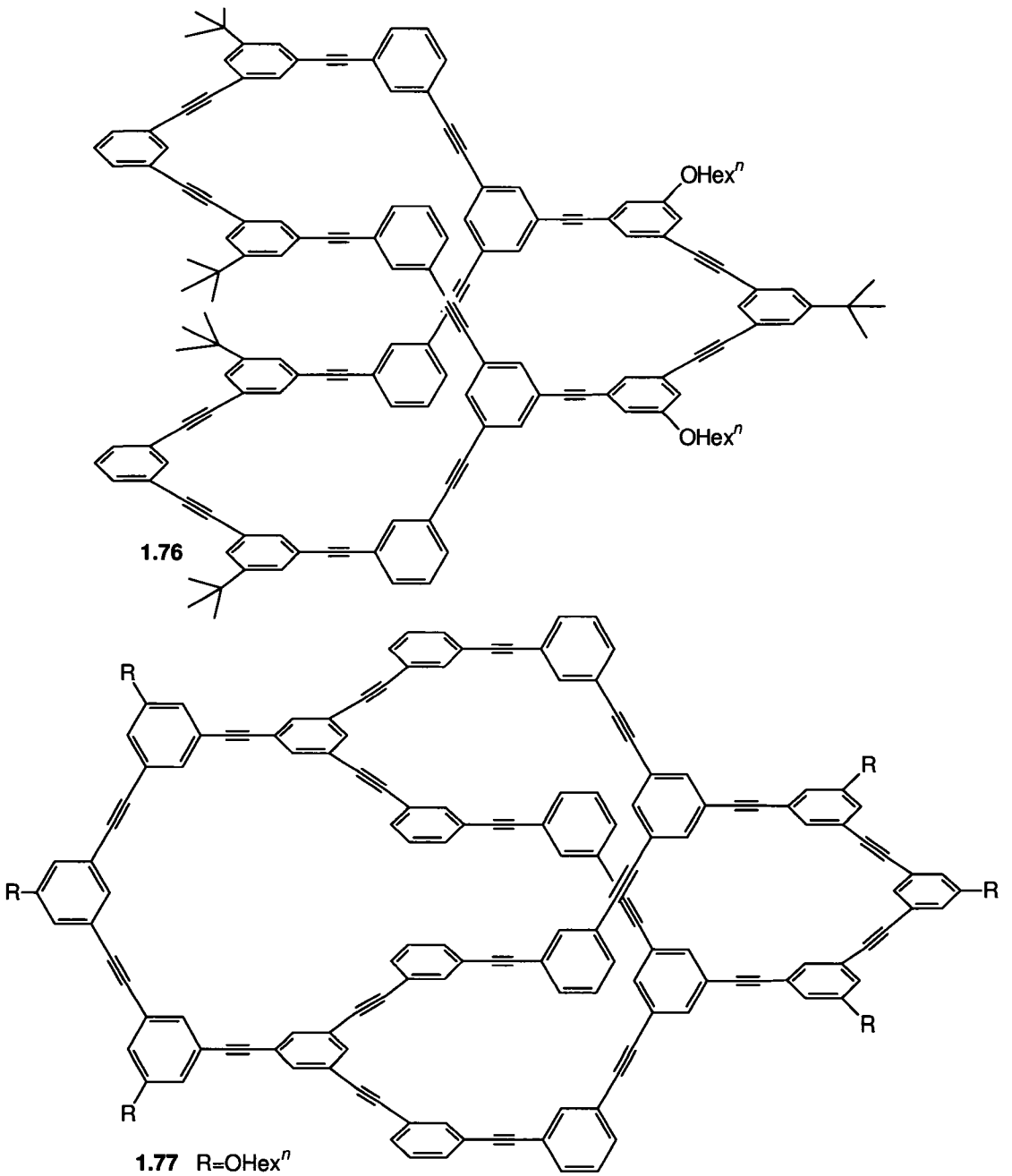


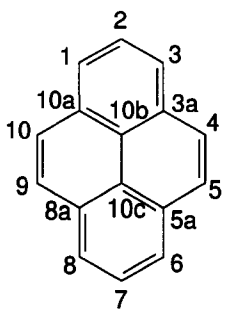
Figure 1.23. Moore's large 3D cyclophynes.

More complicated cyclophynes, such as the examples shown in Figure 1.23, have been reported. Molecules **1.76** and **1.77** were synthesized by Moore and co-workers by a

series of Sonogashira coupling reactions.[56] A remarkable feature of these syntheses was their high yields (60-65%) in the last step, which was a palladium-catalyzed double cyclization.

1.2.3 (2,7)Pyrenophanes

Pyrenophanes are, of course, pyrene-containing cyclophanes and they have been of the subjects of some interest since the 1970s.[57] Of the positions available for bridging, examples of (1,3)-, (1,6)-, (1,8)-, (2,7)-, and (4,9)pyrenophanes[57-58] have been reported. Several other bridging motifs are available, but the rather restricted substitution chemistry of pyrene (compared to that of benzene) makes the synthesis of precursors to several types of pyrenophanes a real challenge.



1.78

Figure 1.24. Numbering of Pyrene.

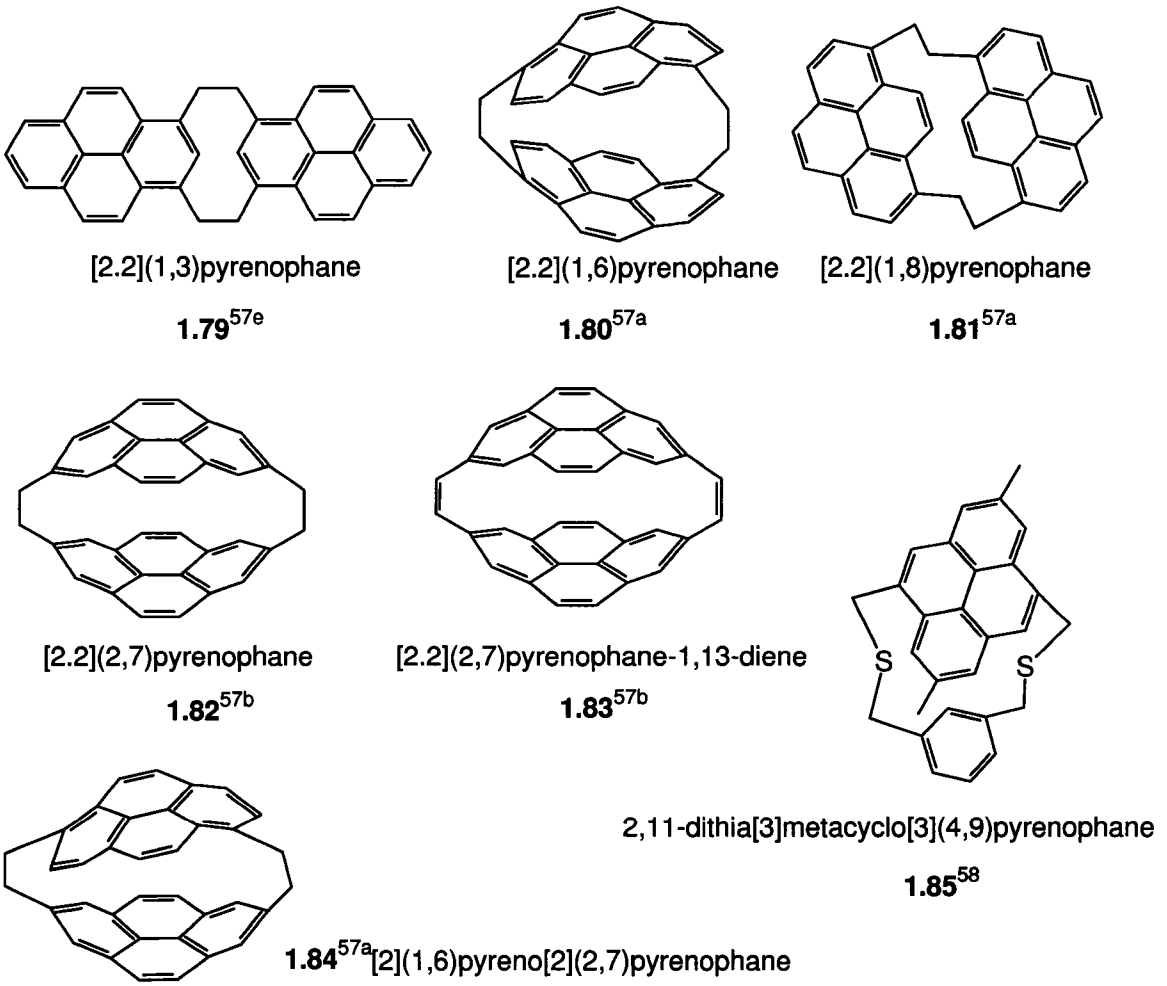
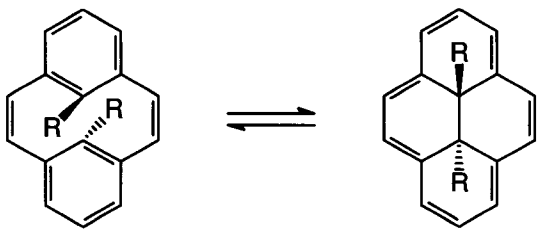


Figure 1.25. Examples of pyrenophanes.

1.2.4 VID Reaction

The Bodwell group has been interested in synthesizing (2,7)pyrenophanes, and the key methodology to gain access to these compounds is a valence isomerization / dehydrogenation (VID) reaction. The valence isomerization between [2.2]metacyclophanedienes and the 10b,10c-dihydropyrenes was first reported by Boekelheide[59] (Scheme 1.12). With internal methyl groups, the system is a stable

photochromic switch. However, when R=H, H_2 is lost easily to afford pyrene irreversibly.[59e-f]



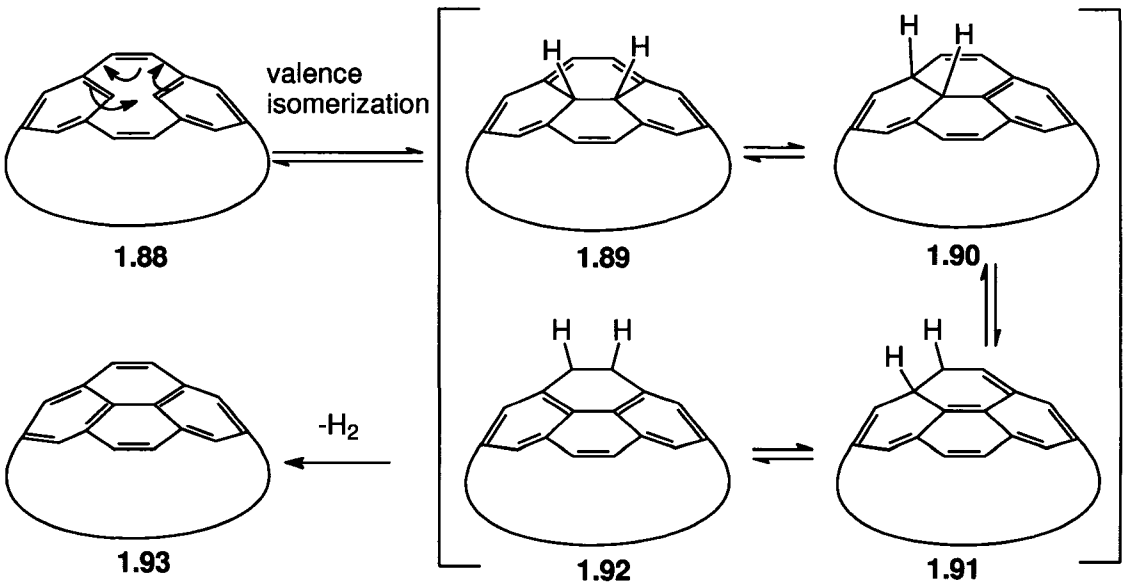
1.86 colorless ⇌ **1.87** colored

R=CH_3 photochromic switch

R=H facile loss of H_2 to afford pyrene

Scheme 1.12. Valence isomerization between cyclophanedienes and dihydropyrenophanes.

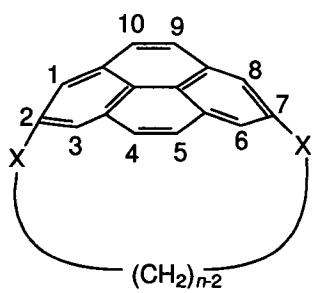
The Bodwell group has exploited this "undesirable" reaction to synthesize a range of (2,7)pyrenophanes. In general, this involves the synthesis (see below) of a tethered [2.2]metacyclophanediene **1.88** followed by a one-pot valence isomerization and dehydrogenation to afford a (2,7)pyrenophane (Scheme 1.13). The first step is a valence isomerization to give a 10b,10c-dihydropyrenophane **1.89**, which in some cases rearranges to a 4,5-dihydropyrenophane **1.92**. This product, which can be observed spectroscopically in crude reaction mixtures yet has never been isolated, presumably forms through **1.90** and **1.91** *via* 1,5-hydrogen shifts. Loss of H_2 from any of the isomers **1.89-1.92** affords pyrenophane **1.93**. The presence of a dehydrogenating reagent, such as DDQ facilitates the dehydrogenation step. Assuming that the aromatic stabilization energy (ASE) of pyrene is greater than that of the preceding10b,10c-dihydropyrene (a 14π electron system),[60] it would appear that the build-up of strain associated with the generation of a nonplanar pyrene system can be offset, at least partially, by the increase in ASE.



Scheme 1.13. Possible mechanism for VID reaction.

1.2.5 Synthesis of [*n*](2,7)Pyrenophanes

A number of [*n*](2,7)pyrenophanes have been synthesized by the Bodwell group, including 1,*n*-dioxa[*n*](2,7)pyrenophanes **1.94** and [*n*](2,7)pyrenophanes **1.95** (Figure 1.26).[61] Overall, the value of *n* has spanned the range of 7-12. Attempts to synthesize pyrenophanes with shorter tethers (*n*=6) resulted either in no reaction or the formation of unidentified material. [61f]

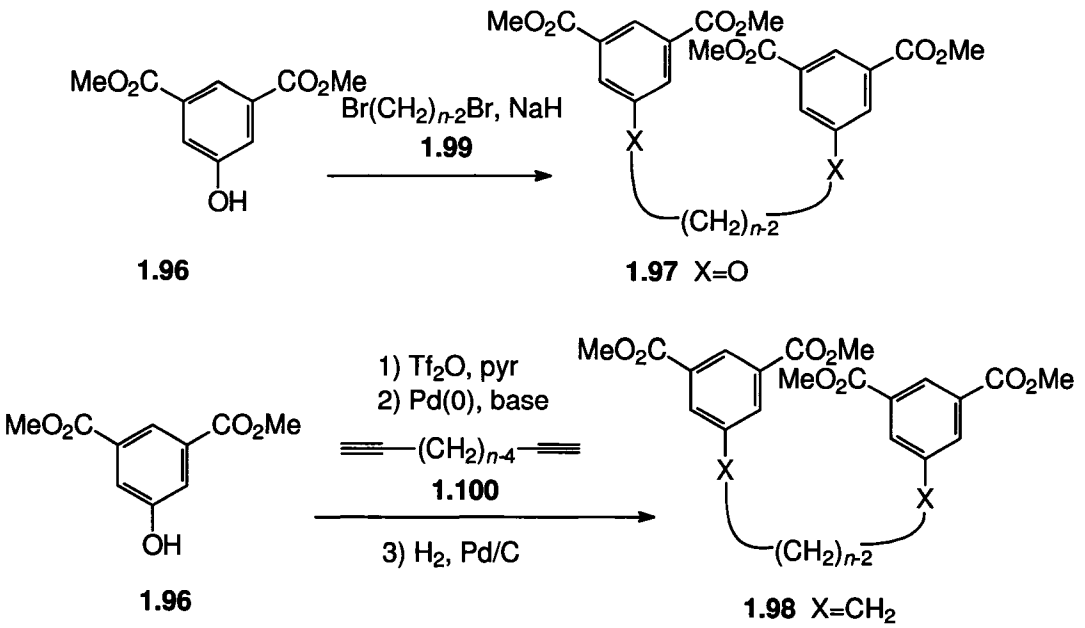


1.94 X=O, *n*=7-12
1.95 X=CH_2, *n*=7-12

For all pyrenophanes in this chapter	
a	*n*=6
b	*n*=7
c	*n*=8
d	*n*=9
e	*n*=10
f	*n*=11
g	*n*=12

Figure 1.26. [*n*](2,7)pyrenophanes investigated by the Bodwell group.

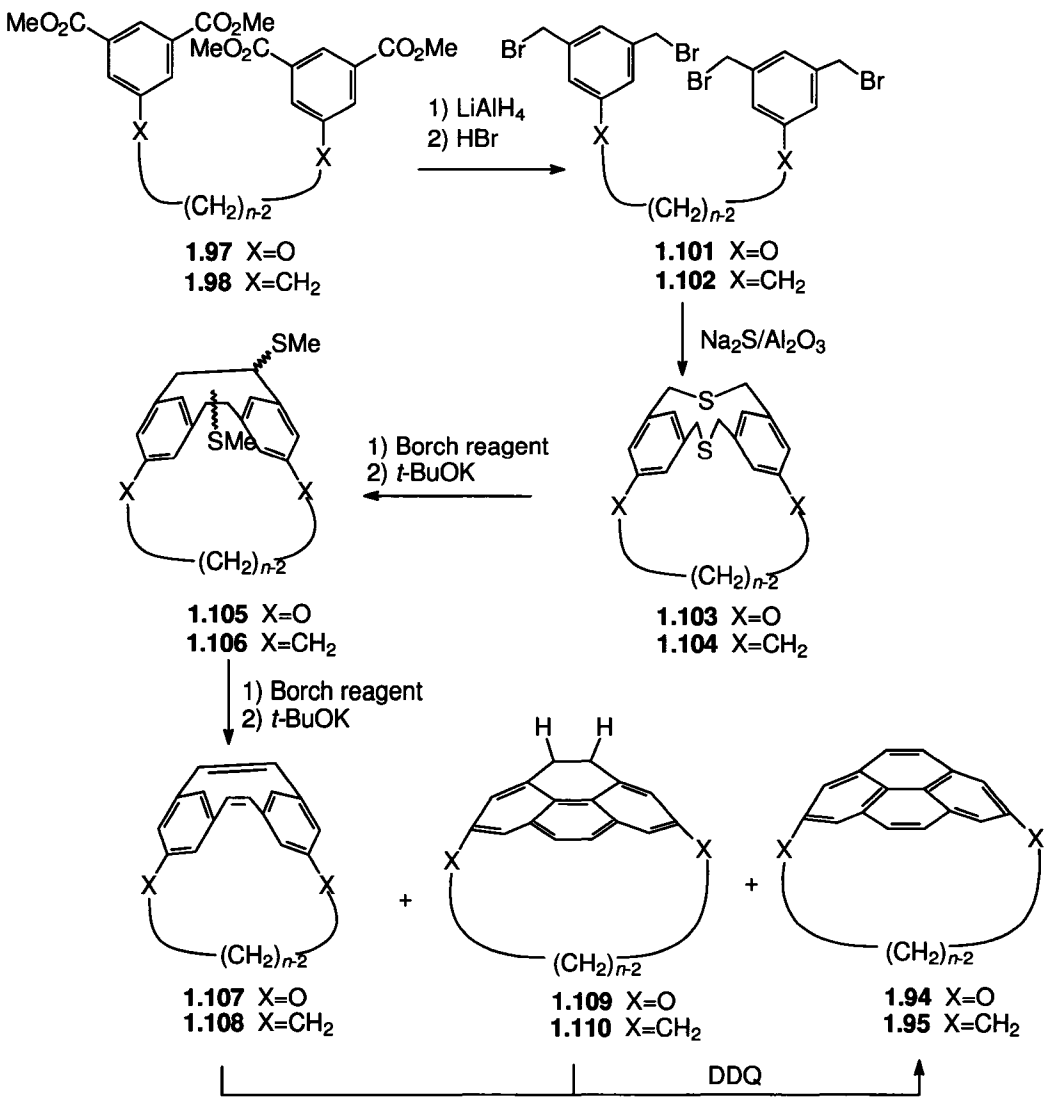
The synthesis of pyrenophanes **1.94** and **1.95** started with commercially available 5-hydroxy-isophthalic acid dimethyl ester **1.96**. An etherification of **1.96** with a series of α,ω-dibromides **1.99** provided tetraesters **1.97**. In order to obtain tetraesters **1.98**, **1.96** was first converted to the corresponding triflate and then a Sonogashira coupling with a series of terminal diynes **1.100** was performed, followed by catalytic hydrogenation (Scheme 1.14).



Scheme 1.14. Synthesis of tetraesters **1.97** and **1.98**.

Tetraesters **1.97** and **1.98** were reduced by $LiAlH_4$ and then brominated by HBr. The resulting tetrabromides **1.101** and **1.102** were treated with Na_2S/Al_2O_3 to afford dithiacyclophanes **1.103** and **1.104**. Methylation of the sulfur atoms in **1.103** and **1.104**, followed by a Stevens rearrangement furnished mixtures of isomers **1.105** and **1.106**. Without any further purification, **1.105** and **1.106** were bis(*S*-methylated) and then reacted with *t*-BuOK to initiate a Hofmann elimination to give cyclophanedienes **1.107** and **1.108** (Scheme 1.15). When the tethers are long (*nf*9), the Hofmann elimination

resulted in the formation of a mixture of varying proportions of the cyclophanediene **1.107** or **1.108**, rearranged dihydropyrenophane **1.109** or **1.110** (see also **1.92** in Scheme 1.13) and pyrenophane **1.94** or **1.95**. In cases where the product was not exclusive pyrenophane, it was treated with DDQ and this led to the formation of pyrenophanes **1.94** and **1.95**.



Scheme 1.15. Synthesis of pyrenophanes **1.94** and **1.95**.

An important structural parameter of a pyrenophane is its bend angle θ, which describes the degree of deviation from planarity of the pyrene system. It is defined as the smallest angle formed by the planes determined by C(1)-C(2)-C(3) and C(6)-C(7)-C(8)[61d] (Figure 1.26). The θ values for pyrenophanes **1.94** and **1.95** were calculated at the AM1 level of theory. Experimentally determined values came from single crystal X-ray structure analyses (Table 1.01).

Table 1.01. Calculated (AM1) and experimental θ values for pyrenophanes **1.94** and **1.95**.

Tether length	**1.94**		**1.95**	
(Series member)	$\theta_{X\text{-}ray}$	θ_{calcd}	$\theta_{X\text{-}ray}$	θ_{calcd}
6 (a)		132.1°		122.9°
7 (b)	109.2°	113.3°		104.5°
8 (c)	87.8°	94.9°	80.8°	87.0°
9 (d)	72.9°	77.8°	62.4°	70.3°
10 (e)	57.7°	61.2°	46.6°	54.4°
11 (f)	39.9°	46.6°		
12 (g)	34.6°	33.1°		

With the exception of **1.94g**, which has the least bent pyrene system, the calculated θ value overestimates the experimental derived bend angle by 4-8° The most bent pyrenophane that has been isolated in pure form is **1.94b**, which has five methylene groups as well as two oxygen atoms in the bridge. The AM1-calculated bend angle θ is 113.3°, and the experimental value is 109.2°. The pyrenophanes with shorter bridges (n=6), which have not yet been isolated, have calculated bend angles θ of 132.1° for

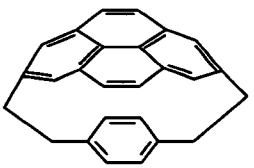
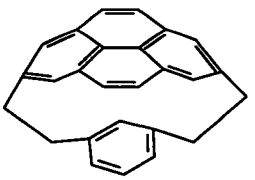
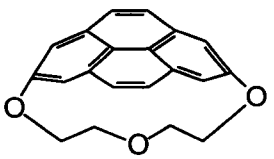
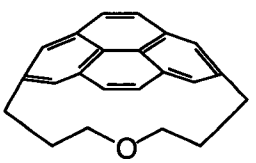
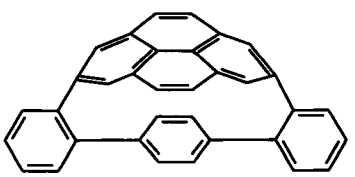
1.94a and 122.9° for **1.95a**. The consistency of the overestimation of the AM1 calculations has led to the routine use of calculated θ values in the Bodwell group as indicators of the synthetic feasibility of newly designed pyrenophanes. As a rough guide, a pyrenophane with a calculated θ value of <110° is expected to be a viable target. A θ value of 110-120° indicates a more challenging target and a value in excess of 120° is taken as an omen of likely failure.

Several other pyrenophanes have also been synthesized. In all these cases, the bend angles were calculated before the syntheses were initiated. Pyrenophanes **1.111**,[10] **1.112**[10] and **1.114**,[61d] which all have $\theta_{calc} < 110°$, were all successfully synthesized and fully characterized. On the other hand, pyrenophane **1.113** (θ_{calc} =117.2°) was only observed as a minor contamination in the ^{1}H NMR spectrum of recovered cyclophanediene precursor.

In comparing pyrenophanes **1.113**, **1.114**, **1.94b** and **1.95b**, which all have 7 atom bridges, but different numbers of oxygen atoms, the replacement of a carbon atom by an oxygen atom results in a small (4-5°) increase in θ. This is because a C(sp^3)-O(sp^3) single bond (1.41 Å)[62,63] is shorter than a C(sp^3)-C(sp^3) single bond (1.54 Å).[63,64] The amount of bend in the pyrene system can thus be fine-tuned through the judicious choice of both the length and the constitution of the tether.

Pyrenophanes **1.111** and **1.112** are no longer simple [*n*](2,7)pyrenophanes. Here, the calculated bend angles overestimated the experimental ones by about 10°. This may indicate that the rule-of-thumb described above may only be applicable to simple [*n*](2,7)pyrenophanes, in spite of the fact that it was successfully applied for both **1.111** and **1.112**.

Table 1.02. Other highly distorted pyrenophanes.

Structure of pyrenophane	Number	θ_{calcd}	$\theta_{X\text{-}ray}$
	**1.111**	100.4°	89.7°
	**1.112**	106.6°	97.1° and 96.9°
	**1.113**	117.2°	
	**1.114**	108.3°	102.9°
	**1.115**	100.7°	

The more recently synthesized pyrenophane **1.115**[65] (θ_{calc} =100.7°) differs from the other pyrenophanes synthesized in the Bodwell group in that it does not have any aliphatic atoms in its bridge. Unfortunately, crystals suitable for X-ray crystal structure

determination could not be obtained. This basic structure forms the basis of a major part of this thesis and is reintroduced in Chapter 4.

1.3 Outline of This Thesis

In this chapter, two linked areas of study are briefly reviewed: cyclophynes (nanorings), and pyrenophanes (nonplanar aromatics). The Bodwell group is actively interested in the application of VID methodology in these areas, and this thesis describes work aimed at achieving these goals. In the following chapters, the synthetic work and characterization of the products is described in detail. Pyrenylene-ethynylene nanorings are the subjects of Chapter 2. In this chapter, the synthetic approach toward these nanorings is described. Chapter 3 deals with the synthesis of a new series of (2,7)pyrenophanes, which culminated in the generation of the most distorted (2,7)pyrenophane prepared to date. Chapter 4 describes the syntheses and study of several polyphenyl pyrenophanes based on structure **1.115**. In summary, the aims and main contributions of this thesis involve: achievements in the synthesis of structurally challenging materials, improvement of the understanding of aromaticity of nonplanar aromatics, and the laying of groundwork for subsequent approaches to more complicated aromatic systems and novel materials with interesting and potentially exploitable properties.

1.4 References

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Chapter 2

Attempted Synthesis of Pyrenophyne-Type Nanorings

2.1 Introduction

The target molecules in this chapter are pyrenophynes and nanorings *e.g.* **2.01-2.03** (Fig. 2.01), each of which contains two pyrene moieties linked by different numbers of ethynylene and *p*-phenylene groups. These molecules are bracelet-shaped shape-persistent macrocycles.[1] Long alkyl groups were incorporated in the design of **2.03** in order to increase the solubility.

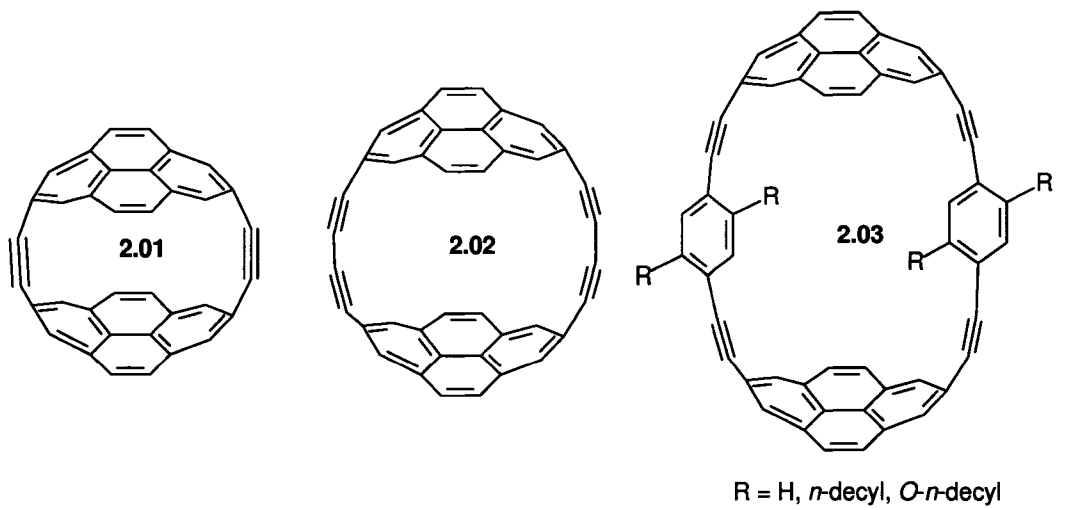


Figure 2.01. Target molecules **2.01-2.03**.

These pyrenophynes, which are related to Oda and Kawase's phenylene ethynylene nanorings (Fig. 2.02),[2] have radially-oriented *p* orbitals. One of the most interesting properties of this kind of molecules, as mentioned in Chapter 1, is their ability to form complexes with fullerenes, such as C_{60} and C_{70}.[3] It was reported that the inner cavity of **2.04a** is slightly smaller than the diameter of C_{60}, if the electron clouds are considered. As a consequence, in the complex formed by **2.04a** and C_{60}, the ball-shaped C_{60} is situated on one side of **2.04a**, with a small part inside the cavity of the nanoring. In order to obtain better complexation, similar nanorings containing larger aromatic units, *i.e.*

naphthalenes, have also been synthesized by the same group. As expected, these nanorings (**2.05** to **2.07**) form much stronger complex with C_{60} and C_{70} fullerenes.[2]

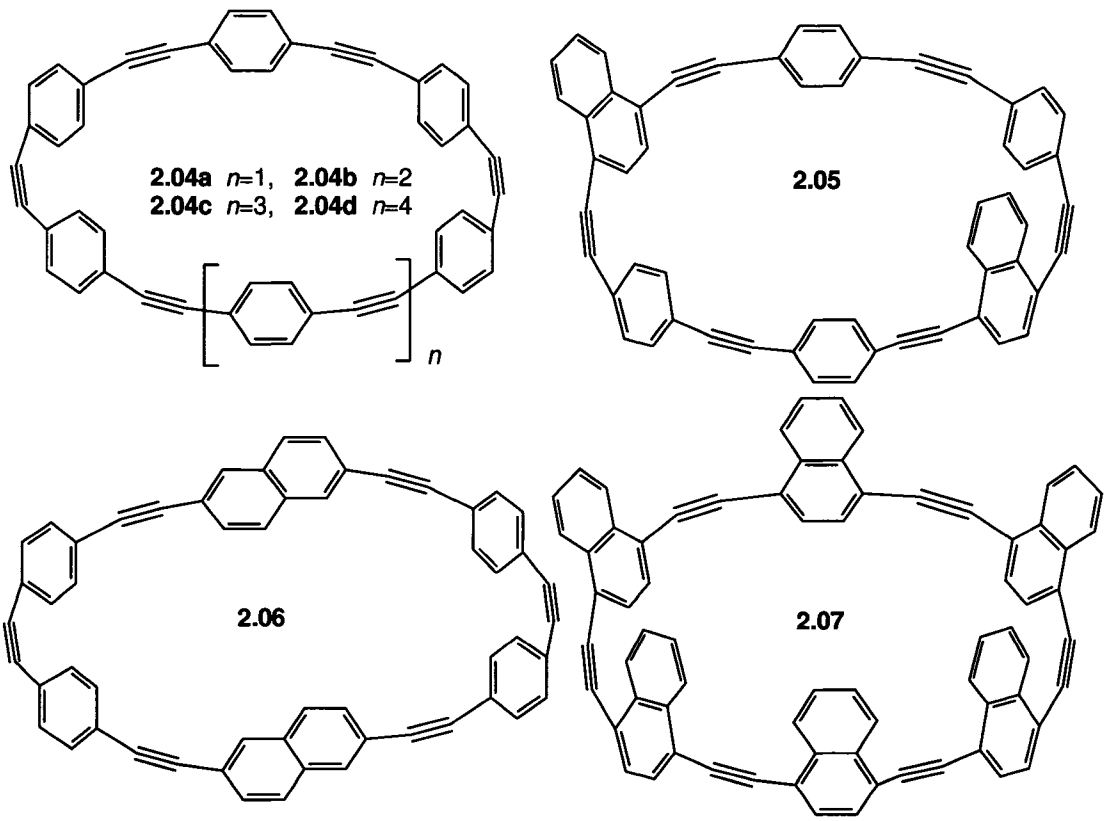


Figure 2.02. Oda and Kawase's nanorings.

The proposed pyrenophyne-type nanorings (**2.01**-**2.03**), having larger aromatic units (pyrene) than naphthalene, can be reasonably anticipated to have the ability to form even stronger complexes with fullerenes. Based on calculations at the AM1 level of theory, the diameters (distances between centers of the pyrene units) of these pyrenophyne-type nanorings are about 6.2 Å (**2.01**), 7.8 Å (**2.02**) and 10.5 Å (**2.03**). The latter value is similar to that of Oda and Kawase's [6]CPPAs, so **2.03** should be a suitable host for C_{60}

fullerene and derivatives thereof. Targets **2.01** and **2.02**, being smaller nanorings, may possibly be able to accommodate smaller guest molecules.

AM1 calculations predict that the bend angles (θ) for the targeted nanorings are 85.4° (**2.01**), 67.0° (**2.02**), and 49.9° (**2.03**), so even the smallest nanoring **2.01** has a bend angle similar to [8](2,7)pyrenophane, which means that it should not be a problem synthetically. The average bond angles about the *sp*-hybridized carbons are 153.7° (**2.01**), 160.6° and 159.2° (**2.02**), and 164.6° (**2.03**). To date, the most distorted alkyne observed in a cyclophyne (compound **1.38** in Chapter 1) has a bond angle about its *sp*-hybridized carbon atoms of 155.8°. As such, nanoring **2.01** may be expected to be a more challenging target than the θ angle would suggest. The bend angle α of the benzene rings[4] in cyclophyne **2.03** is calculated to be 10.6°, which compares to 12.6° in [2.2]paracyclophane,[5] 28.6° (calculated) in a [4]paracyclophane derivative (**2.08**),[6] and 25.6° or 24.3° (experimental) in a [1.1]paracyclophane derivative (**2.09**).[7]

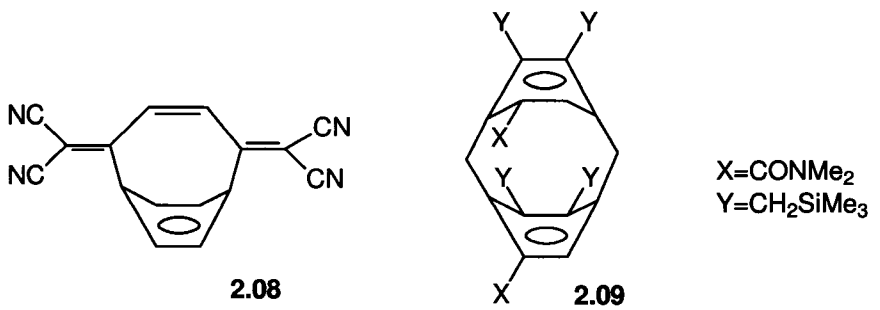


Figure 2.03. Extremely strained paracyclophanes.

As mentioned in Chapter 1, the synthetic methodology employed for paracyclophynes (the class that includes **2.01-2.07**) is usually different from that for meta- and orthocyclophynes for geometric reasons. To date, only a few examples of cyclophynes

containing PAHs (aromatic systems with ≥ 3 rings) have been reported, but none of them contains radially oriented *p* orbitals. These systems incorporate phenanthroline (**2.10**[8]and **2.13**[9]), [4]helicene (**2.12**[10]) and [6]helicene (**2.11**[11]), Moreover, these PAH-containing cyclophynes can all be categorized as meta- or orthocyclophynes, and their syntheses are all based on transition metal-catalyzed coupling reactions as key cyclization steps. However, as described in Chapter 1, these methodologies are not generally suitable for the synthesis of paracyclophynes. For the syntheses of *p*-phenylene-ethynylene nanorings, which are structurally analogous to the targets in this chapter, both the "alkynes last" and "arenes last" strategies have been used. Oda and Kawase's syntheses are based on the "alkynes last" strategy, which involves the conversion of alkene-containing cyclophanes to the products (see Scheme 1.05, Chapter 1). The "arenes last" strategy was applied by Tsuji and co-workers to afford their *p*-phenylene-ethynylene nanoring (see Scheme 1.06, Chapter 1).[12] The synthesis of the target molecules **2.01**-**2.03** could, therefore follow either of these two strategies. However, the "arenes last" strategy was adopted because the power of the VID reaction of [2.2]metacyclophanedienes to afford severely distorted pyrenes has already been demonstrated numerous times by the Bodwell group.

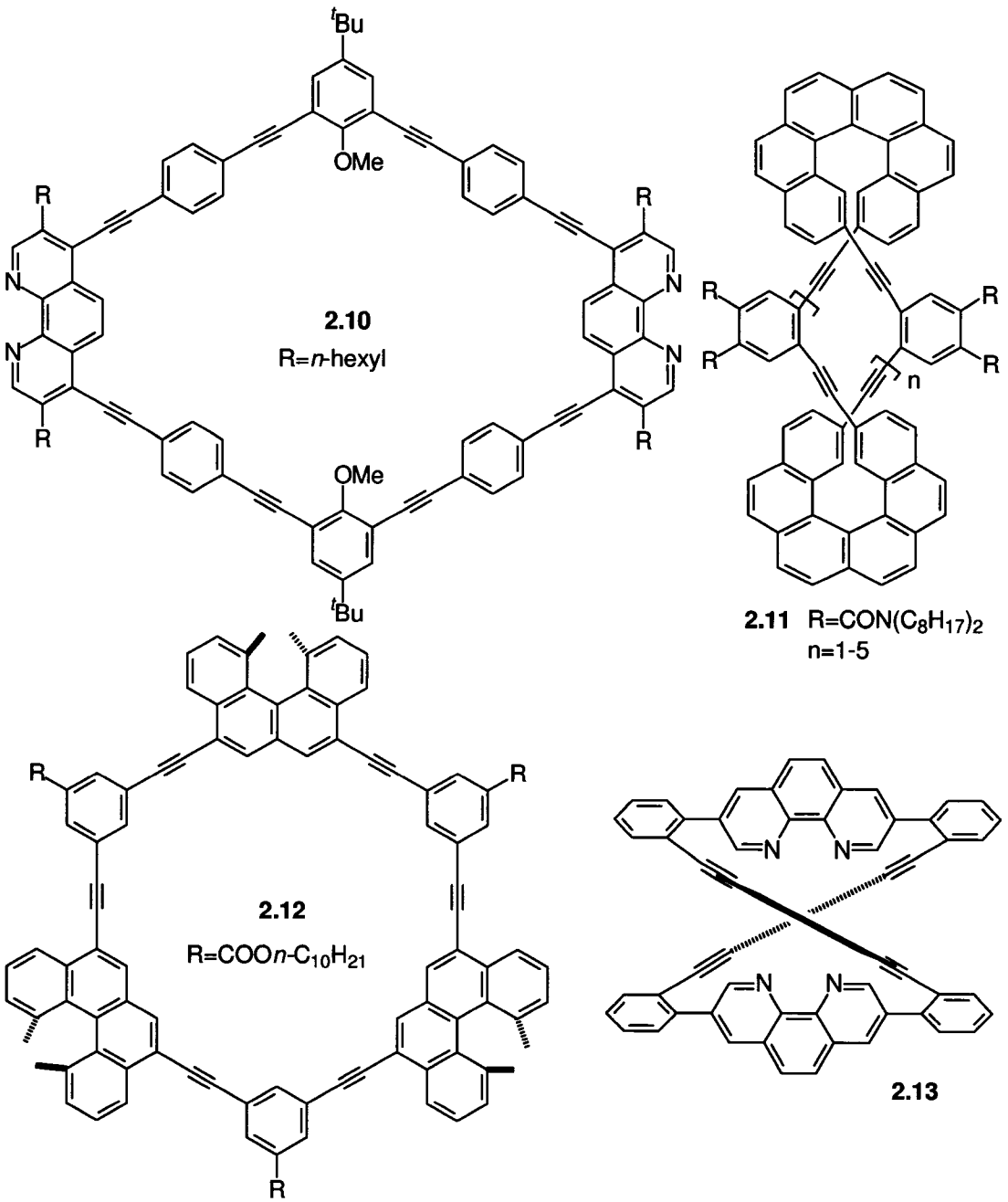
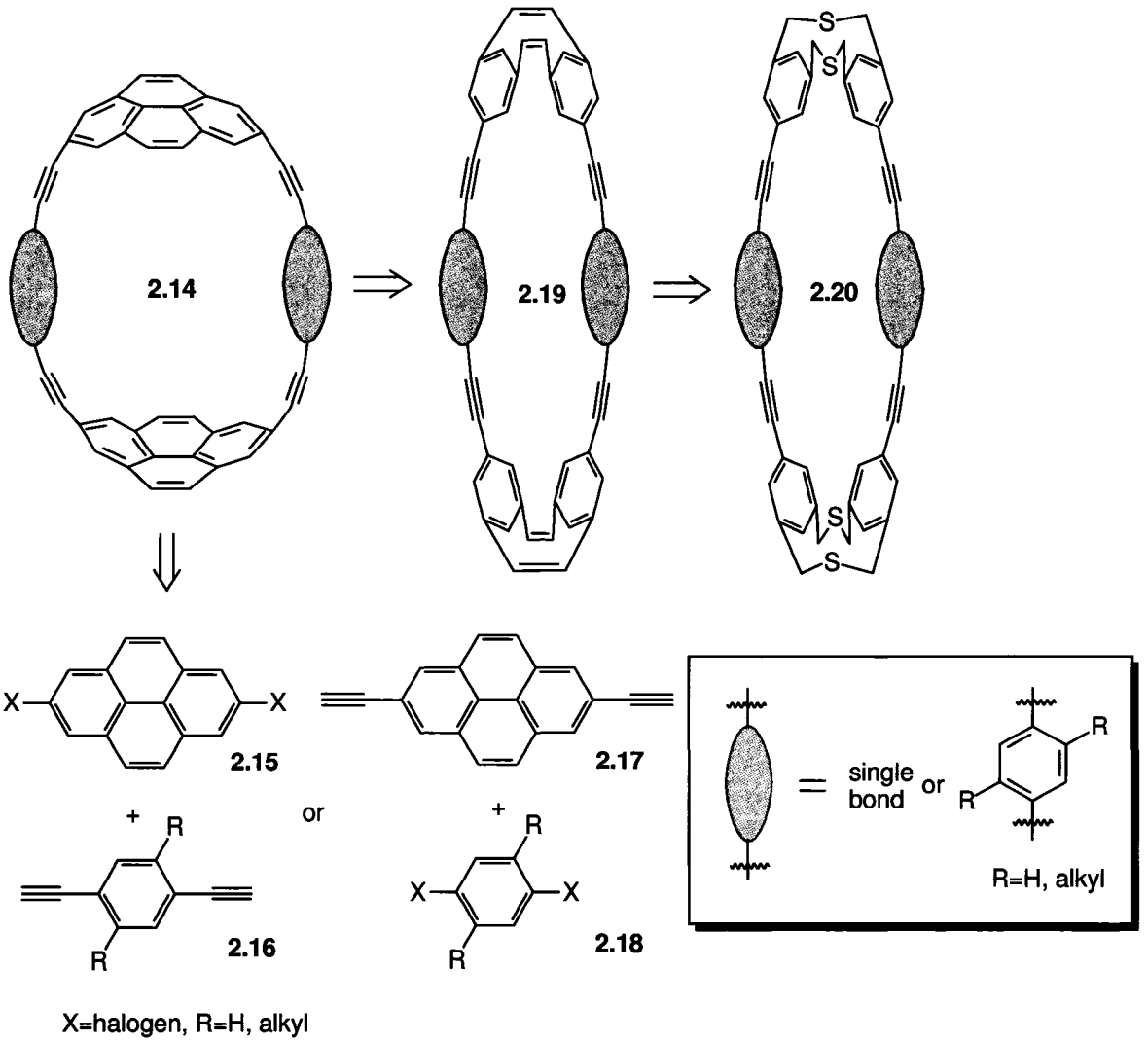


Figure 2.04. Examples of cyclophynes containing PAHs.

2.2 Retrosynthetic Analysis

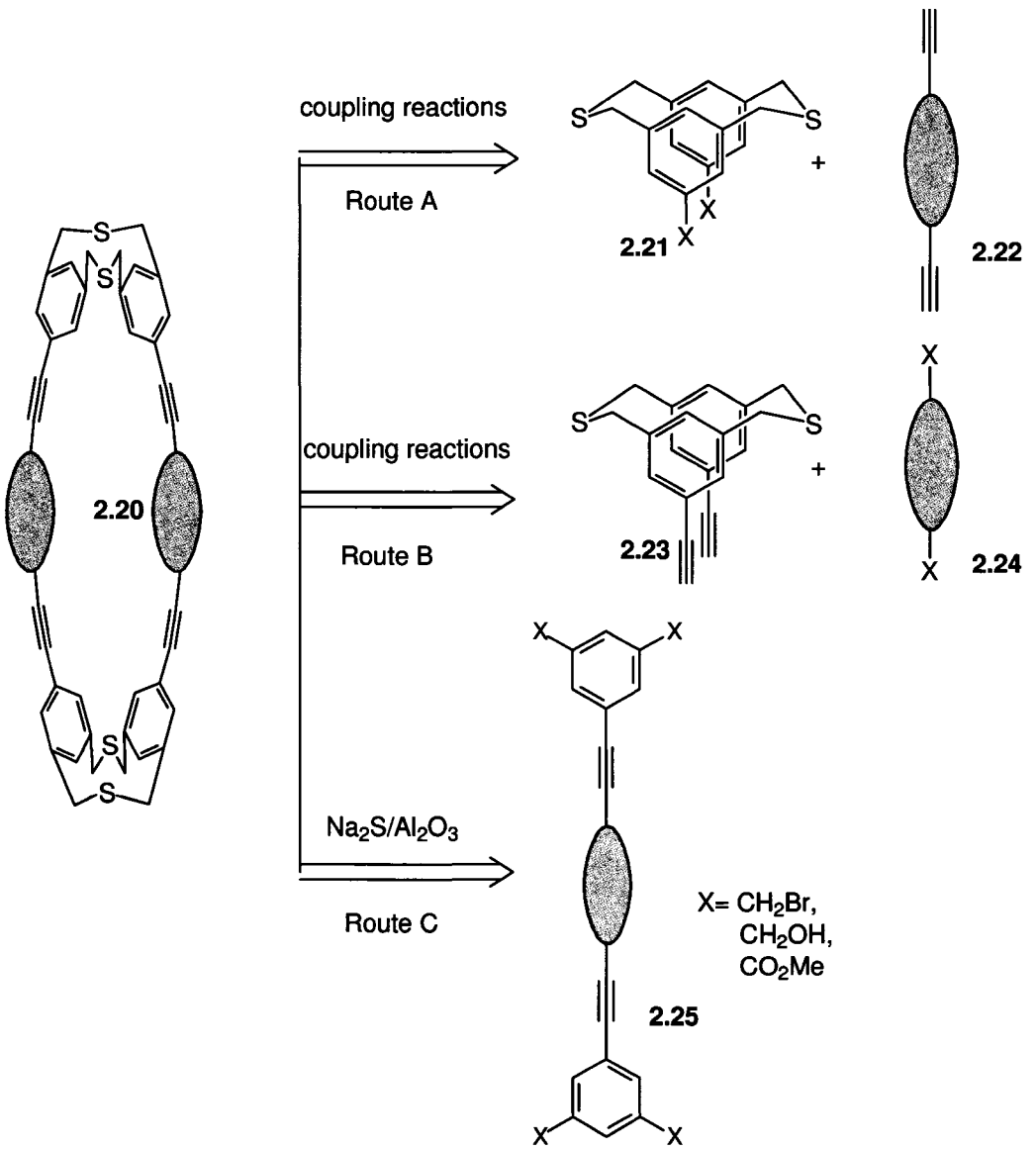
The pyrenophyne targets **2.01**-**2.03** all have two key structural features at which appropriate retrosynthetic bond scissions can be performed: the pyrene system, and the ethynylene units. A pyrene moiety could be generated from a cyclophanediene *via* a VID reaction according to the previous work in our group. Alkynes are, of course, retrons for metal-catalyzed cross-coupling reactions, such as Sonogashira coupling and Glaser coupling. Cuts along these lines lead back to 2,7-dibromopyrene and 2,7-diethylnylpyrene, which are both known compounds.[13] However, their planar structures are better suited to the formation of linear oligomers or polymers. On the other hand, pyrene formation through the VID reaction, which is now a mature methodology, leads back to a *syn*-cyclophanediene and, ultimately, a *syn*-2,11-dithia[3.3]metacyclophane, *e.g.* **2.20**. The most advantageous aspect of the dithia[3.3]cyclophane moiety is that it prefers a conformation with a 15-25° angle[14] between the planes of the two phenyl rings. As such, very little distortion of the ethynylene groups will be required in **2.20**. In other words, with the [*n*](2,7)pyrenophanes, the strain in the final (pyrene-containing) product is introduced only during the pyrene-forming reaction (VID) and the build-up of strain at this stage is counteracted by an increase in ASE.

Tetrathiacyclophyne **2.20** has two general ways back to simpler systems: metal catalyzed reaction of the disubstituted dithiacyclophanes **2.21** and **2.23**, or sulfide coupling reactions of the tetrabromides **2.25** (Scheme 2.02). In the former case, there are two complementary ways of moving backwards, which are designated as Route A and Route B. The two diethynyl species **2.22** and **2.23** could be synthesized by Sonogashira coupling from the corresponding dihalo- analogs **2.21** and **2.24**.



Scheme 2.01. Retrosynthetic analysis of pyrenophyne-type nanorings.

Alternatively, the first retrosynthetic step from **2.20** could be sulfide coupling, which leads back to tetrasubstituted phenylene-ethynylene assemblies **2.25** (Route C). Structures such as these have been reported in the literature[15] and the diynetetraester **2.25** (R = CO_2Me) has even been synthesized in our group.[16]

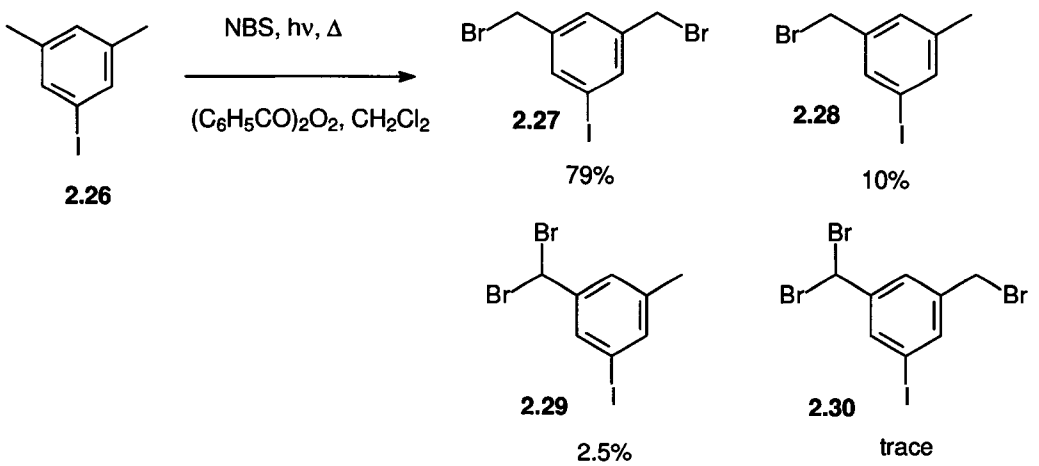


Scheme 2.02. Retrosynthetic analysis: Routes A, B and C.

2.3 Results and Discussion

2.3.1 Attempted Syntheses of 2.01-2.03 *via* Routes A and B

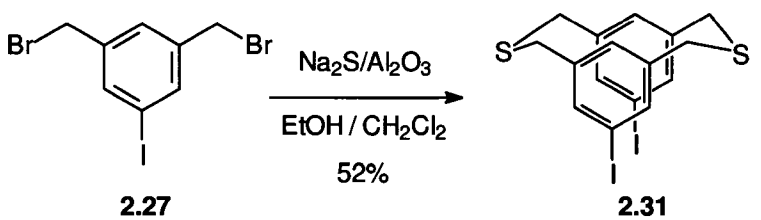
The synthetic work commenced with the free radical bromination of 5-iodo-*m*-xylene (**2.26**) by NBS. This type of bromination is notorious for giving product mixtures[17] and, not surprisingly, the reaction with **2.26** provided a mixture of bromides **2.27** (79%), **2.28** (10%), **2.29** (2.5%) and **2.30** (trace amount). What was surprising was that the desired dibromide **2.27** was obtained initially in an extraordinarily high yield (79%). However, numerous subsequent attempts to repeat this result gave **2.27** in a more typical yield of 45-55%. The initial result is difficult to explain. However, it is worth noting that radical benzylic brominations are very sensitive to the initiator (presumably its identity and the amount used) and the solvent.[18] It may be that a "sweet spot" was fortuitously struck in the initial reaction.



Scheme 2.03. Preparation of 1,3-bis(bromomethyl)-5-iodobenzene **2.27**.

Dibromide **2.27** was then subjected to reaction with Na_2S/Al_2O_3 to afford the diiododithiacyclophane **2.31** (52%), which was envisioned as a starting point for the

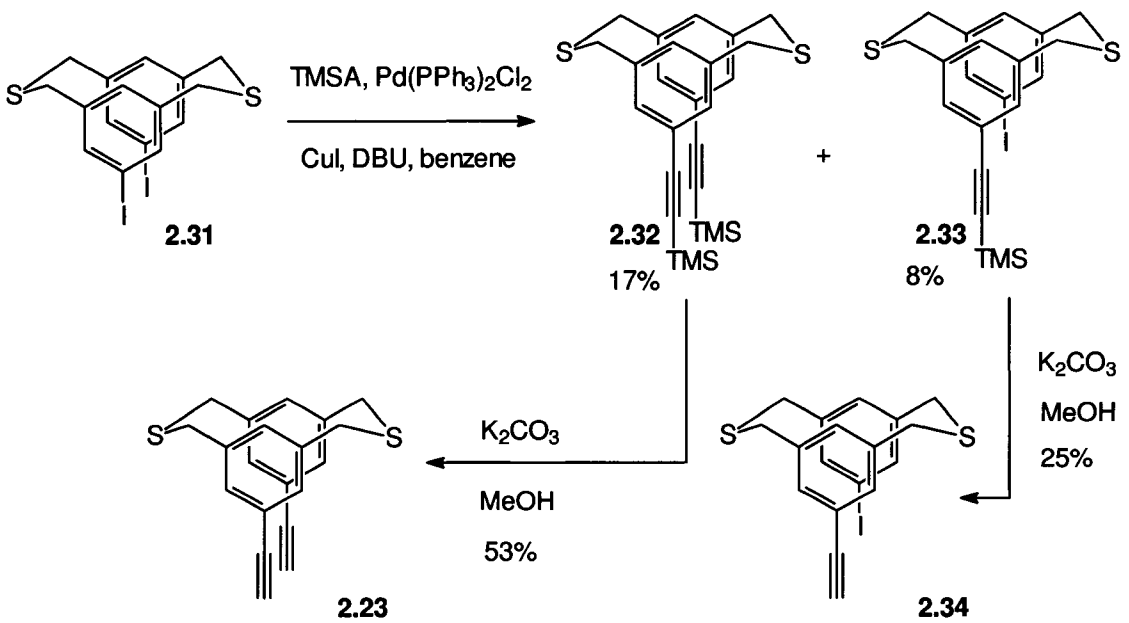
synthesis of tetrathiacyclophynes **2.20** *via* route A (Scheme 2.02). To prepare the analogous material for route B, a Sonogashira coupling reaction of **2.31** with TMSA produced bis(trimethylsilyl)cyclophane **2.32** (originally 17%, then improved to 63%), which could then be converted to *syn*-6,15-diethynyl-2,11-dithia[3.3]metacyclophane **2.23** in 53% yield by way of a standard protodesilylation using K_2CO_3 / MeOH. The observation of the internal protons of **2.31** at δ 7.01 ppm indicated that the expected (and required) *syn* conformation had been adopted.[19] This product exhibited a $2M^+$ peak and no M^+ peak in its APCI mass spectrum, which caused some concern that the Na_2S / Al_2O_3 reaction had, very unusually, given a tetrameric product and not the expected dimer.[20] That **2.31** was indeed the desired dimer was confirmed by its conversion into subsequent compounds, where there was no doubt.



2.27 **2.31**

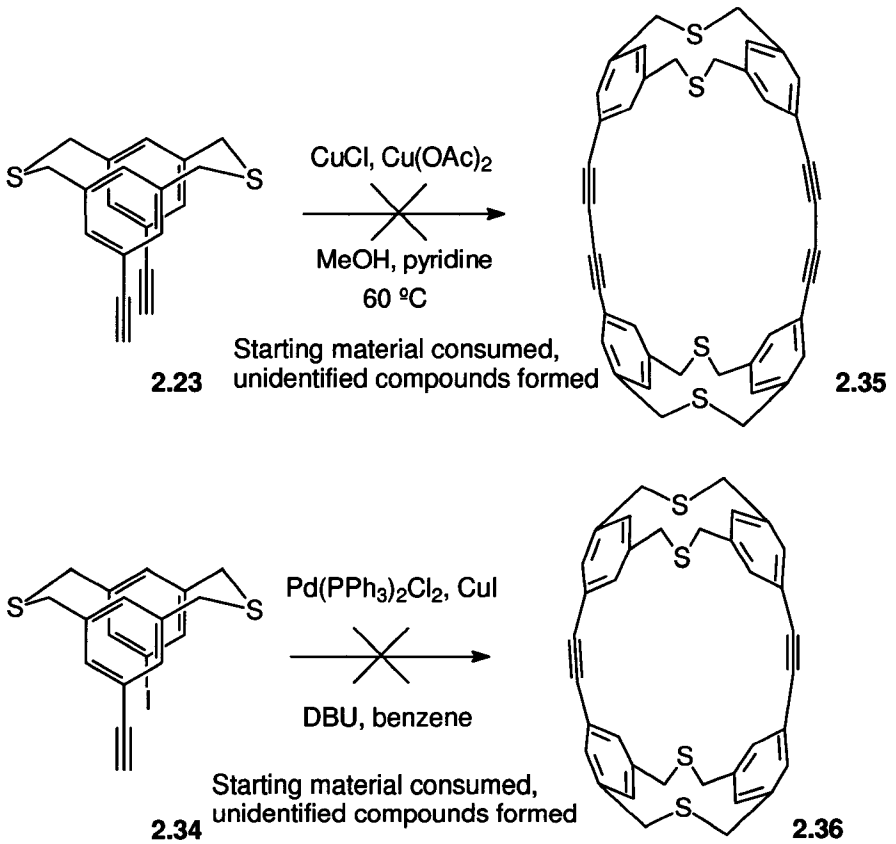
Scheme 2.04. Preparation of *syn*-6,15-diiodo-2,11-dithia[3,3]metacyclophane (**2.31**).

A by-product of the Sonogashira coupling of **2.31** with TMSA was the monoreacted product **2.33**, which could be further converted to **2.34** in 25% yield. The low yields for this protodesilylation and also the previous one (**2.32** → **2.23**) may be indicative of some degree of instability.

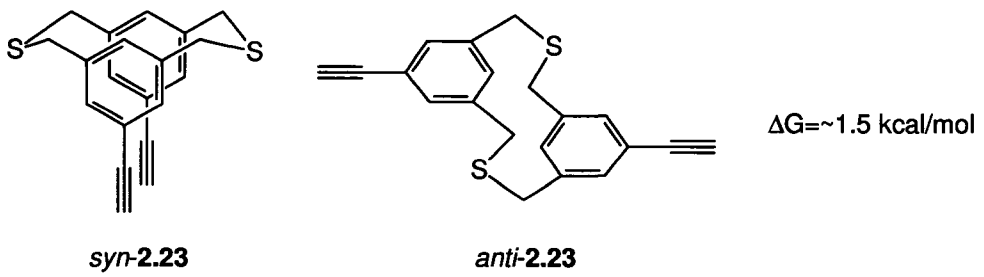


Scheme 2.05. Sonogashira coupling of *syn*-6,15-diiodo-2,11-dithia[3,3]metacyclophane (**2.31**).

With dithiacyclophane derivatives **2.31**, **2.23** and **2.34** in hand, attempts to synthesize tetrathiacyclophyne nanorings were initiated. Diyne **2.23** was treated with CuI and $Cu(OAc)_2$ in order to prepare macrocycle **2.35** *via* a Glaser coupling reaction. Unfortunately, after the starting material was consumed, none of the desired product was detected, but only some unidentified product was formed. A Sonogashira homo-coupling of **2.34**, which was expected to give structure **2.36**, was also attempted. Disappointingly, the result was similar to that of the Glaser coupling of **2.23** in that an intractable product was generated.



Scheme 2.06. Attempted syntheses of tetrathiacyclophynes **2.35** and **2.36**.

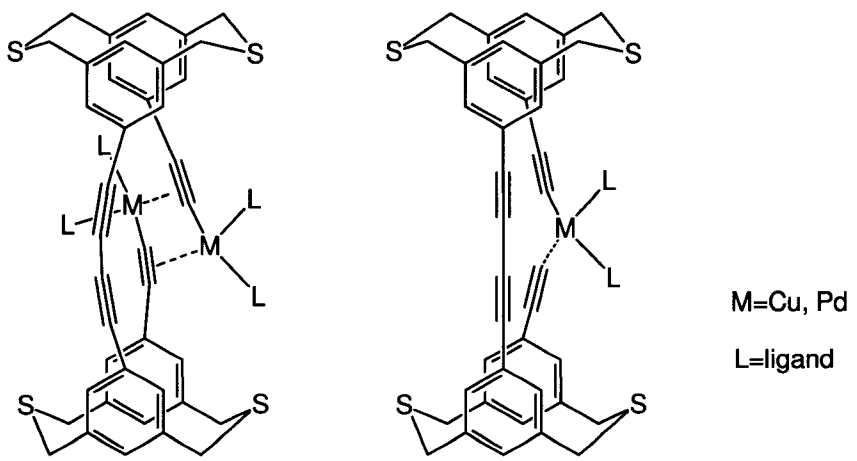


Scheme 2.07. *Syn* and *anti* conformers of **2.23**.

The failures of these reactions may have their origins in one or more of the following factors. First, it is imperative that the *syn* conformation of the 2,11-

dithia[3.3]metacyclophane **2.23** units remains accessible (and preferably highly populated) throughout the reaction, because the corresponding *anti* conformers are not geometrically disposed to macrocycle formation. Although the NMR data for **2.23** strongly suggest the *syn* conformation is preferred in solution and AM1 calculations predict that *syn*-**2.23** is ~1.5 kcal / mol more stable than *anti*-**2.23**, it should not be overlooked that thiophilic Cu species are present during the reaction. Complexation of a sulfur atom to a copper atom may (or may not) affect the conformational preference of the cyclophane. While this is an unprecedented phenomenon, it is not beyond the realm of possibilities.

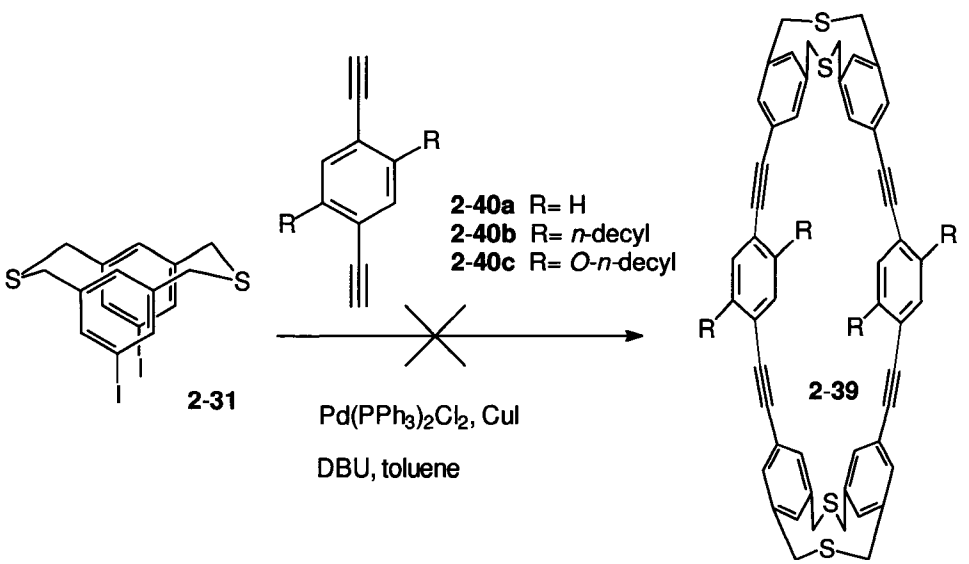
Second, although it is still not clear, the mechanism of Cu-catalyzed Glaser coupling is believed to proceed through a *pseudo-trans* Cu(I)-acetylide intermediate (π complex) **2.37** (Fig. 2.05).[21] Examination of simple molecular models clearly indicates that the *pseudo-trans* intermediate **2.37** should be difficult to form. On the other hand, a *pseudo-cis* intermediate **2.38** appears to be less strained. However, most Cu-catalyzed Glaser coupling reactions are through the *pseudo-cis* Cu acetylide species,[22] so the formation of **2.38** would rule out the subsequent formation of **2.35**. Interestingly, it has been reported that the application of Pd catalysis instead of Cu catalysis can possibly solve this problem, since the Pd-catalyzed Glaser reaction supposedly proceeds through a *pseudo-cis* intermediate.[23] This would be a worthwhile subject of future work.



pseudo-trans-**2.37** *pseudo-cis*-**2.38**

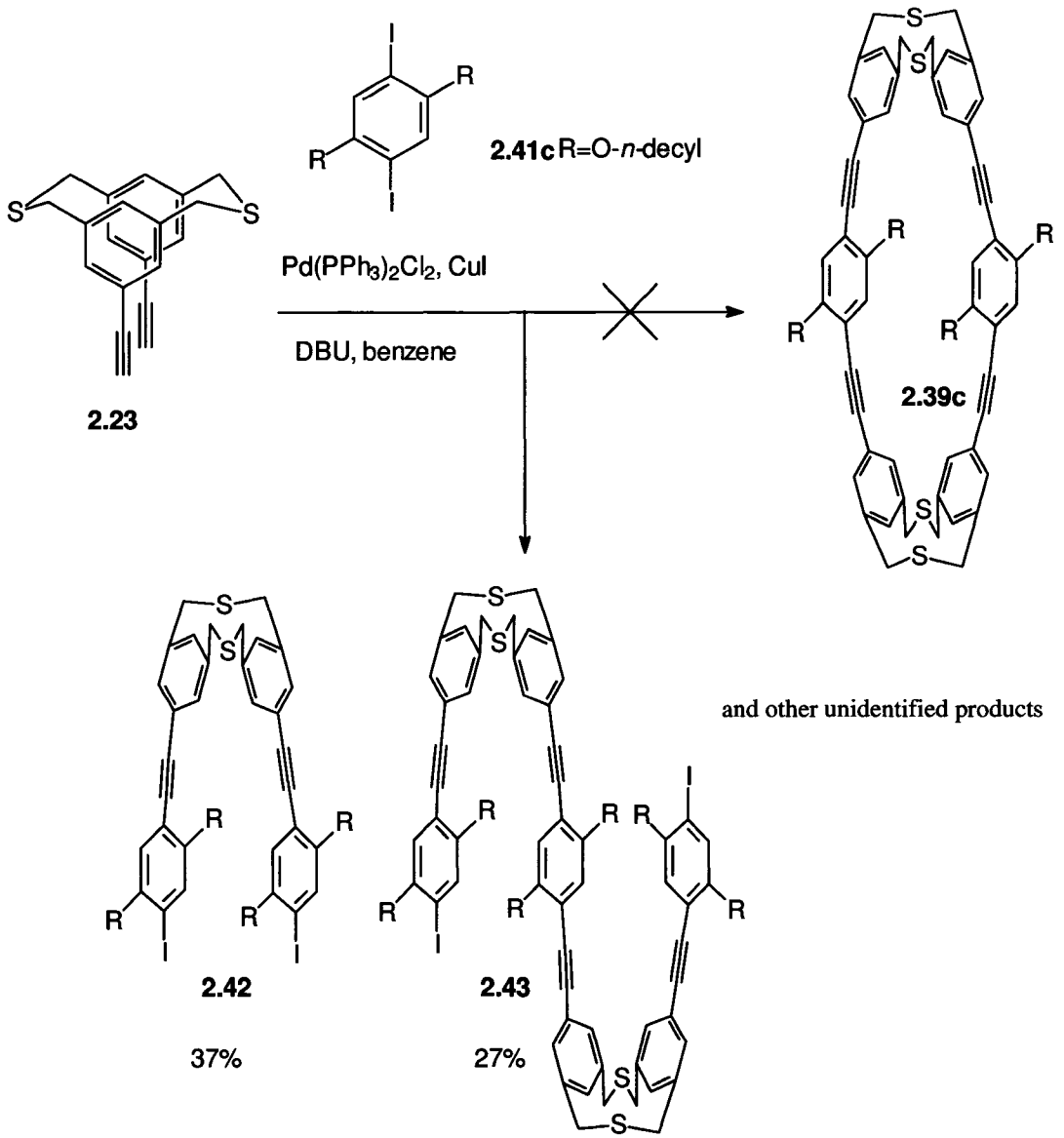
Figure 2.05. Possible intermediates in the Glaser coupling of *syn*-**2.23**.

Attempts were also made to synthesize larger nanorings, *i.e.* **2.39a-c** (Scheme 2.08), each of which has a *para*-phenylene group situated between the pyrenylene groups. Long aliphatic chains were incorporated on the *para*-phenylene units to maintain solubility, because many reported phenylene-ethynylene derivatives suffer from poor solubility.[2,24] The desired reaction (Scheme 2.08) is, in general terms, a [2A+2B] cyclization, but this is clearly not the only possible product from a reaction between two starting materials A and B. In the case at hand, Sonogashira chemistry was to be used and the key step (macrocyclization) of this multistep reaction is an intramolecular Sonogashira reaction, which will have competition from a variety of intermolecular reactions, leading to higher oligomers and then polymers [25] or, less likely, larger macrocycles. However, tetrathiacyclophanes **2.39a-c** appear to possess very little strain, so the desired intramolecular Sonogashira reaction was not expected to be unduly disfavored.



Scheme 2.08. Attempted synthesis of tetrathiacyclophyne **2.39**.

Sonogashira reaction of **2.31** with **2.40a** resulted in the consumption of the starting materials, but only material that was insoluble in common organic solvents was formed. Whether or not any of the desired cyclophyne was formed was unclear. Diyne **2.40b**, which bears two *n*-decyl groups, was synthesized according to published procedures[26] and then used instead of **2.40a** to address the solubility problem. In this case, homocoupling of **2.40b** appeared to be faster than the desired Sonogashira coupling with **2.31**. After the diyne **2.40b** had been consumed, a large amount of the diiodide **2.31** remained in solution and could be recovered (46%). Small quantities of other materials were separated, but they could not be identified. The diyne **2.40c**, which was also synthesized according to literature procedures,[27] was then reacted with **2.31**. After the consumption of the starting materials, many spots appeared on the TLC plate. However, LC- and/or MALDI MS analysis of all the products did not provide any evidence for the formation of the desired cyclophyne.



Scheme 2.09. Attempted synthesis of tetrathiacyclophyne **2.39c**.

Due to the problems encountered along Route A, Route B was investigated. Accordingly, the reaction of **2.41c** with **2.23** (1:1 ratio) was investigated (Scheme 2.05, Table 2.01). It took only 5 minutes for diyne **2.23** to be completely consumed, whereby two major new spots appeared on the TLC plate. Column chromatography led to the

recovery of the other starting material **2.41c** (41%), as well as the isolation of two new compounds. NMR and LC-MS analysis indicated that they were **2.42** (2.5%) and **2.43** (2.6%). Small amounts of other products (as mixtures) were isolated, but it was not possible to identify them. No sign of any cyclized products was observed by mass spectrometry. By changing the ratio of **2.41c** : **2.23** to 1 : 1.75 and extending the reaction time to 16 h, the yields of **2.42** and **2.43** decreased to 1.2% and 1.1%, respectively. This, combined with the low recovery of **2.41c** (1.2%) suggested that shorter reaction times be necessary. The ratio between **2.41c** : **2.23** was then held constant at 2.2 : 1 and the reaction time was varied (Entries 3-5, Table 2.01). For the 5 min reaction, **2.42** and **2.43** were isolated in 22% and 23% yields (based on **2.23**), respectively, and **2.41c** was recovered in 53% yield. Extension of the reaction time to 10 min afforded better yields of **2.42** (37%) and **2.43** (27%), along with slightly less (51%) of recovered **2.41c**. Performing the reaction for 3 h led to a significant decrease in the yields. Whether the optimal yield for **2.42** occurs at a reaction time before or after 10 min, it is clear that these reactions must be carefully monitored.

In the case of Entry 4 in Table 2.01, small quantities of some other products (1-7 mg) were isolated by column chromatography. LC- or MALDI-MS analysis suggested that they are possibly structures **2.44** (1.3%) (calcd = 834.3, obs. 811.5, possibly M^+-ethynyl) and **2.45** (0.2%) (calcd = 1540.7, obs. 1540.4, M^+) (Fig. 2.06). However, the ^1H NMR spectra, although quite encouraging, did not provide unambiguous support for the proposed structures.

Table 2.01. Results of Sonogashira coupling of **2.41c** and **2.23**.

Number	Ratio (**2.41c** : **2.23**)	Time	Recovery of **2.41c**	Yield [(a)] of **2.42**	Yield [(a)] of **2.43**
1	1 : 1	2 h	41%	2.5%	2.6%
2	1 : 1.75	16 h	1.2%	1.2%	1.1%
3	2.2 : 1	5 min	53%	22%	23%
4	2.2 : 1	10 min	51%	37%	27%
5	2.2 : 1	3 h	39%	5.9%	17%

(a) Yields are based on the limiting agent.

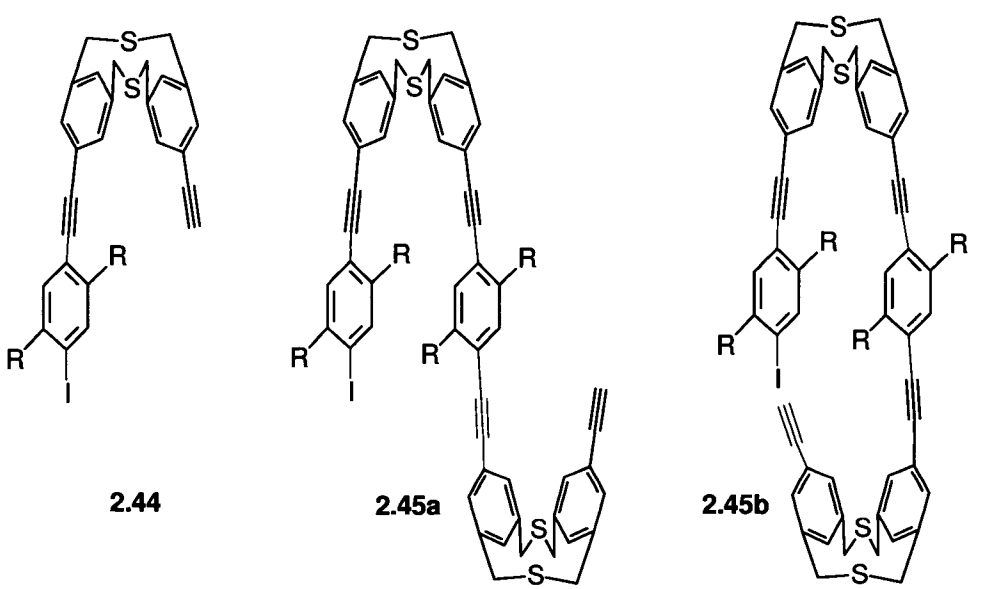


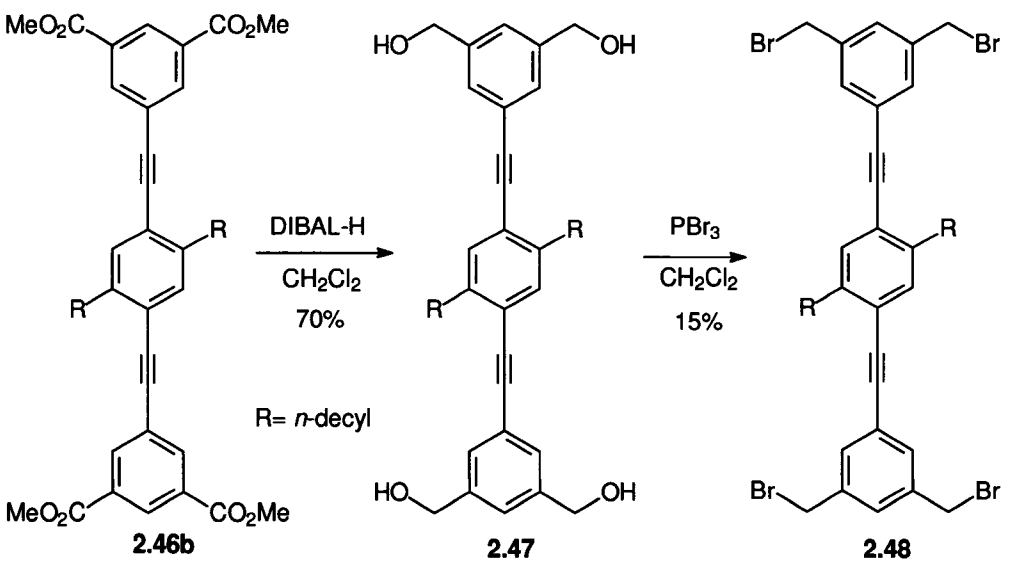
Figure 2.06. Possible by-products for the reaction in Entry 4 in Table 2.01.

The observation of the series of compounds (**2.44** → **2.42**→ **2.45** → **2.43**) and the absence of cyclized products (especially **2.39c**) indicates that, under these reaction conditions, linear oligomers are more easily formed than the cyclized ones. Beyond the entropic disadvantage associated with macrocycle formation, conformational issues are probably important too. First, a conformation resembling **2.45b** must be accessible at some intermediate stage of its intramolecular Sonogashira reaction (leading to **2.39c**) and a *cis*-Pd species must also be able to form. Since rotation around the C(sp)-C(sp^2) bonds should have a very low barrier,[28] the conformational requirement should not be difficult to fulfill. The examination of molecular models indicates that the fulfillment of the geometric requirement (*cis*-Pd species) involves some strain, but does not appear to be unattainable. A second conformational issue is the possibility of *anti* conformations existing in the [3.3]metacyclophane units. For cyclization to occur, both cyclophane systems must be *syn*. This also does not appear to be a major problem. The internal H signals of **2.42** and **2.43** appear at δ 6.77 and 6.69 / 6.70 ppm, respectively, which are consistent with the maintenance of the necessary *syn* conformation. It is therefore probably that the stumbling block is either the geometric requirements of the intramolecular Sonogashira reaction or simply entropy. A high dilution reaction between **2.42** and **2.23** may shed more light on this question.

2.3.2 Attempted Synthesis *via* Route C

Route C (see PP 56), which is based on a sulfide coupling methodology to form a macrocyclic precursor to nanoring **2.03**, was investigated next. A major advantage of this approach has to do with the key step (macrocyclization), which is a fourfold thioether

formation between two identical components. All of the thioether forming reactions are expected to occur *via* S_N2 reactions between a thiolate anion and a primary benzylic halide, both of which are highly reactive participants in S_N2 reactions.[29] Moreover, once the first sulfide coupling has occurred, the others become intramolecular. Indeed, each successive thioether formation should serve to entropically favor the subsequent reactions through increased rigidity (lower flexibility).



Scheme 2.10. Synthesis of tetrabromide **2.48**.

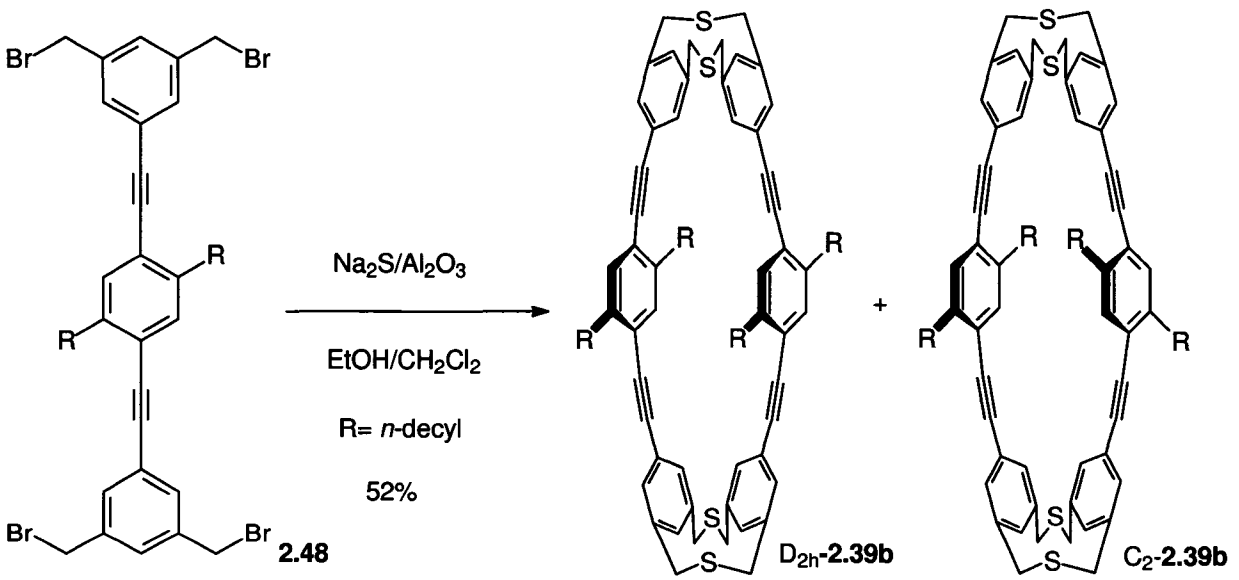
The synthetic work commenced with the preparation of the macrocyclization precursor tetrabromide **2.48** (Scheme 2.10). The choice of using two *n*-decyl groups as solubilizing group was made because its synthetic precursor, diynetetraester **2.46b**, was more easily prepared than the related tetraester **2.46c** (R=decyloxy). Reduction of tetraester **2.46b** with DIBAL-H afforded tetraol **2.47** in 70% yield. Despite the presence of the two *n*-decyl groups, the solubility of **2.47** was observed to be low in several

common organic solvents (dichloromethane, chloroform, THF, ether, benzene, methanol, hexanes). However, upon addition of PBr_3 to a suspension of **2.47** in dichloromethane, a 15% yield of tetrabromide **2.48** could be achieved. This reaction was originally performed on a small scale (20 mg), and only 4.0 mg of the product **2.48** were obtained. Attempts were made to scale-up the reaction, but a sharp decrease in both yield and purity was observed. Based on the ^1H NMR spectrum of the crude reaction mixtures, the impurities appeared to be partially brominated products. A possible reason for this is that the starting material **2.47**, being amphiphilic and capable of adopting a planar conformation, is favorably disposed to self-association. In the solid state, **2.47** is a powder, but when slurried in dichloromethane, the particles came together to form larger "chunks". If the bromination reactions are occurring on the surface of the particles, then the rate will be related to the surface area. The larger particles that formed in the larger scale reaction would therefore react more slowly. Other reagents were also tried, *i.e.* PPh_3Br_2 (in THF), CBr_4/PPh_3 (in THF), NBS/PPh_3 (in CH_2Cl_2),[30] but higher yields could not be obtained under these conditions than with the original PBr_3 condition.

Although only 4.0 mg of tetrabromide **2.48** was obtained, the subsequent sulfide coupling was investigated. After the consumption of **2.48**, a single new spot appeared on the TLC plate. Column chromatography furnished 1.5 mg of a material that, according to its ^1H NMR spectrum, contained substantially more grease than products derived from **2.48**. Encouragingly, LC-MS analysis showed the presence of a peak corresponding to the molecular ion of tetrathiacyclophyne **2.39b** (calcd = 1348.8, obs. 1350.8, M^++2). The ^1H NMR spectrum, although dominated by grease signals, contains two groups of peaks centered at 3.84 and 4.10 ppm, which may be due to the benzylic protons of the *syn*-2,11-

dithia[3.3]metacylophane moieties. A complicated spectrum is expected for these protons because each of the two expected diastereomeric forms of **2.39b** (having D_{2h} and C_2 symmetry, respectively) should have four unique nuclei (CH-S), each of which is strongly coupled to one other proton. Indeed, two broad multiplets centered at δ 3.84 and 4.10 were observed, which may be taken as evidence, albeit very shaky, for the formation of **2.39b**. The aromatic region also showed features that may be consistent with **2.39b**, but was not clean enough to provide clear evidence. Whether or not the two diastereomers of **2.39b** interconvert cannot be discussed meaningfully until sufficiently pure samples of **2.39b** are prepared.

Despite some promise in Route C, the prospects of synthesizing enough **2.39b** to carry through to the corresponding nanoring seemed bleak. Work in this area was therefore discontinued.

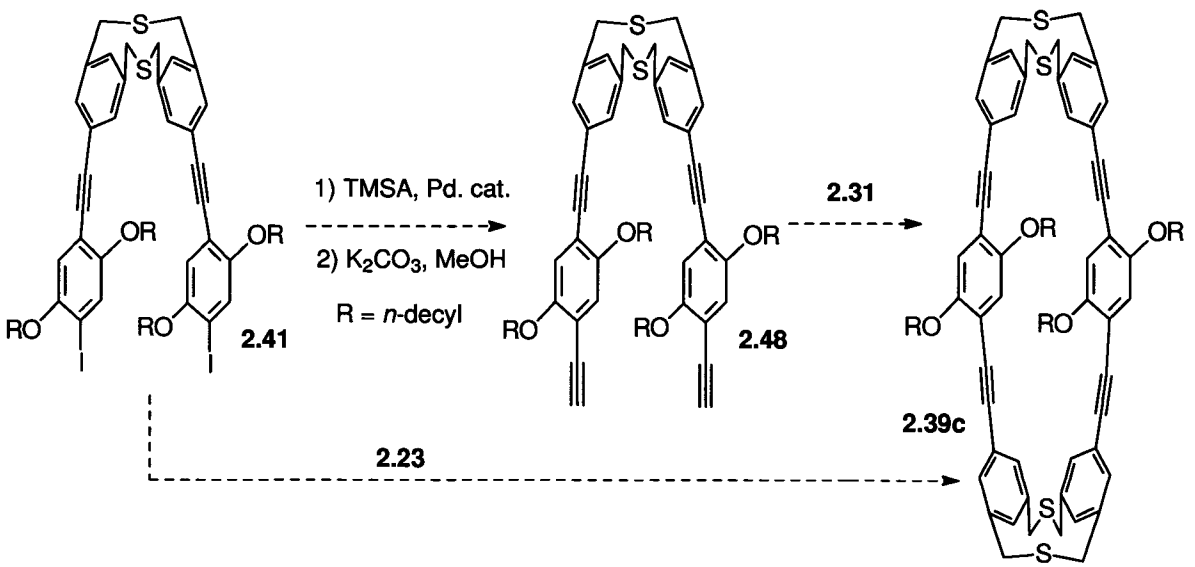


Scheme 2.11. Sulfide coupling of **2.48** to synthesize tetrathiacyclophyne **2.39b**

2.4 Conclusion and Future Work

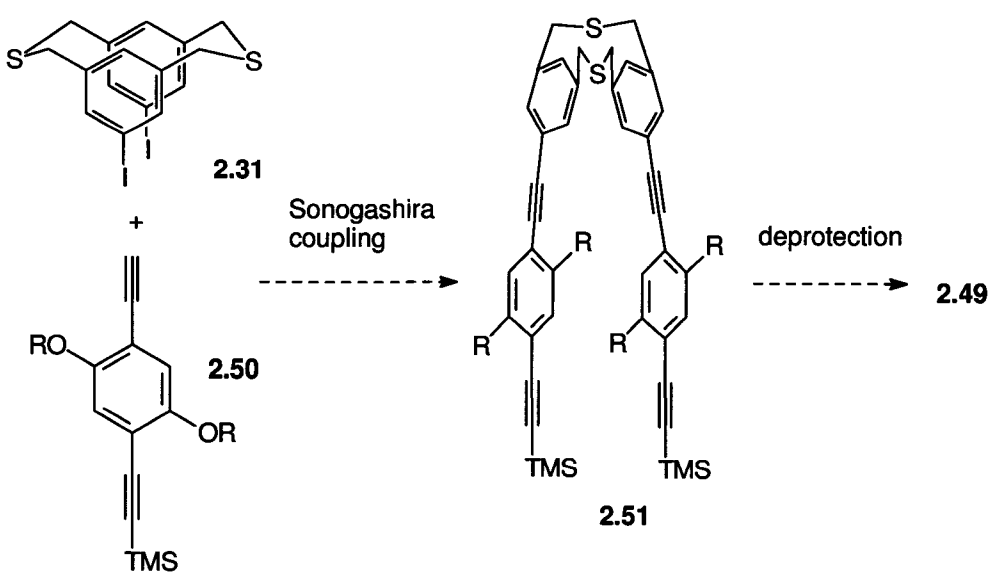
In this chapter, attempts to synthesize the first pyrenophyne type nanoring are described. Three routes were investigated, two of which were based on transition metal catalyzed coupling reactions, *i.e.* Glaser coupling and Sonogashira coupling. The other one was based on sulfide coupling of a diynetetrabromide **2.48**. The most encouraging result was for the sulfide coupling of the tetrabromide **2.48**, which produced a very small amount of material that could possibly be tetrathiacyclophyne **2.39b**.

The route *via* transition metal-catalyzed reactions can also be improved in several ways. First, as mentioned earlier, a Sonogashira coupling of **2.41** and **2.23** (Scheme 2.12) should be investigated under high dilution condition. Alternatively, **2.41** could be converted into **2.49** using Sonogashira chemistry, followed by protodesilylation. Reaction of **2.49** with **2.31** to give **2.39** could then be attempted. If this is successful, the use of similar chemistry to make larger nanorings could be investigated.



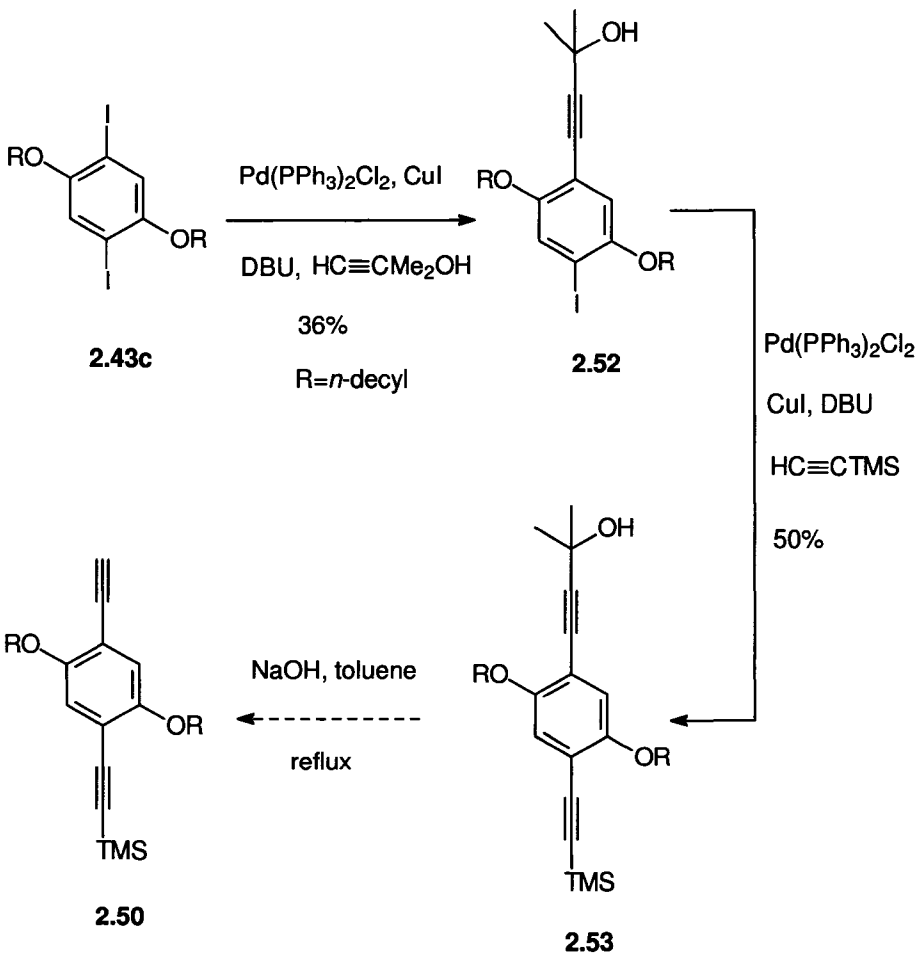
Scheme 2.12. Future work starting from **2.41**.

One of the disadvantages of the route shown in Scheme 2.08 was that the 1,4-diethylnylbenzene derivatives presumably underwent Glaser coupling in competition with intermolecular Sonogashira coupling. The use of a mono-protected 1,4-diethylnylbenzene derivative such as **2.50** may solve this problem (Scheme 2.13).



Scheme 2.13. Another route to synthesize **2.49**.

This work would start with a Sonogashira coupling reaction of diiodide **2.31** with a monoprotected diethynylbenzene derivative **2.50** to produce compound **2.51**. Deprotection would then afford compound **2.49**. Compound **2.50** could be prepared using the methodology Bryce and co-workers described in their synthesis of arylene-ethynylene molecular wires.[31]



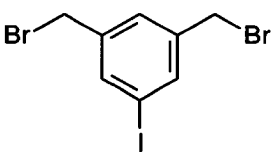
Scheme 2.14. Attempts to synthesize **2.50**.

To this end, cursory experiments were performed on a small scale (Scheme 2.14). This proceeded as far as dialkyne **2.53**, but the deprotection of **2.53** has not yet been achieved.

2.5 Experimental

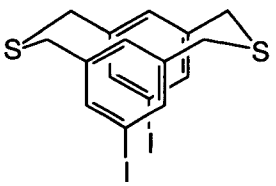
General. All chemicals mentioned in this chapter were used as received from commercial sources unless indicated, and were reagent grade. Merck silica gel 60 (particle size 40-63 μm, 230-400 mesh) was used for all the column chromatography. The dimensions of the columns were recorded as "height" % "diameter", and all solvent mixtures given for TLC retention factors were the same as those used for column chromatography unless specially mentioned. TLC spots were visualized with a 254 nm UV lamp. Melting points were measured on a Fisher-Johns apparatus and are uncorrected. X-ray crystallography was performed using an AFC8-Saturn 70 single crystal x-ray diffractometer from Rigaku/MSC, equipped with an X-stream 2000 low temperature system. Mass spectrometric data were determined on an Agilent 1100 series LC/MSD instrument. ^{1}H NMR (500.13 MHz) and ^{13}C NMR (125.76 MHz) were recorded on a Bruker AVANCE instrument. IR spectra were obtained on a Bruker TENSOR 27 infrared spectrometer. HRMS was measured on a GCT Premier instrument (Waters Micromass technologies). All reactions mentioned in the chapter were performed under the protection of nitrogen gas unless indicated. THF was freshly distilled from sodium benzophenone ketyl. Dichloromethane was freshly distilled from calcium hydride. Hexanes were distilled before use. Benzene was spectroscopic grade, and was degassed before use.

1,3-Bis(bromomethyl)-5-iodobenzene (2.27).



To a solution of 5-iodo-*m*-xylene (**2.26**) (0.50 g, 2.15 mmol) and NBS (0.88 g, 5.0 mmol) in dichloromethane (10 mL) was added dibenzoyl peroxide (5 mg, 0.02 mmol), and the reaction mixture was stirred under visible light irradiation (100 W) for 5 h. The mixture was concentrated *in vacuo* and purified by column chromatography (20 × 3.3 cm, 20% dichloromethane/hexanes) to yield 5-iodo-1,3-bis(bromomethyl)benzene (**2.27**) (0.40 g, 1.0 mmol, 48%) as a white solid; R_f (20% dichloromethane/hexanes) = 0.50, mp: 77-81 °C, lit.[32] 75-80 °C; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.67 (s, 2H), 7.37 (s, 1H), 4.38 (s, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 140.5, 138.0, 129.1, 94.5, 31.5; LC-MS (APCI) *m/z* (%): 391 (M^+, 17), 214 (70), 191 (100).

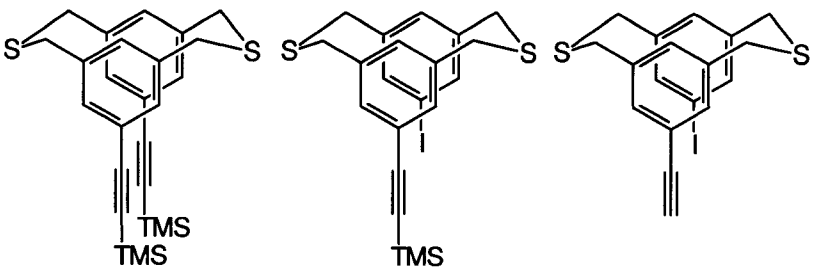
Syn-6,15-Diiodo-2,11-dithia[3.3]metacyclophane (2.31).



To a well stirred solution of 1,3-bis(bromomethyl)-5-iodobenzene (**2.27**) (1.00 g, 2.57 mmol) in 10% ethanol/dichloromethane (167 mL) was added in two portions at 15 min intervals Na_2S/Al_2O_3 (1.89 g, 5.13 mmol). The reaction was stirred at room temperature for 45 min and then filtered through a short plug of Celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (19 × 3.3 cm, 50% dichloromethane/hexanes) to yield *syn*-6,15-diiodo-2,11-dithia[3.3]metacyclophane (**2.31**) (0.35 g, 1.34 mmol, 52%) as a white solid; R_f (50% dichloromethane/hexanes) = 0.45; mp: 78-80 °C (chloroform); IR (powder): 2913 (w), 1653 (m), 1593 (s), 1560 (m), 1507 (s), 1430 (m), 1283 (m), 1249 (m), 1182 (m), 995 (m), 915 (s), 867 (m), 831 (m), 812 (m), 698 (vs) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 4H), 7.01 (s, 2H), 3.71 (s,

8H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 139.7, 135.2, 130.7, 94.0, 36.3; LC-MS (APCI) *m/z*: 1049 (100, $2M^+$), 913 (15), M^+ not observed; HR-MS *m/z* Calcd for $C_{16}H_{14}S_2I_2$ 523.8626, found 523.8652.

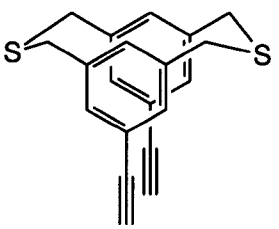
Syn-6,15-Bis(trimethylsilylethynyl)-2,11-dithia[3.3]metacyclophane (2.32), and by-products _syn_-6-iodo-15-trimethylsilylethynyl-2,11-dithia[3.3]metacyclophane (2.33) and _syn_-6-ethynyl-15-iodo-2,11-dithia[3.3]metacyclophane (2.34).



To a well stirred solution of *syn*-6,15-diiodo-2,11-dithia[3.3]metacyclophane (**2.31**) (0.98 g, 1.9 mmol), $Pd(PPh_3)_2Cl_2$ (39 mg, 0.056 mmol), CuI (37 mg, 0.19 mmol) in degassed benzene (90 mL) was added a solution of trimethylsilylacetylene (0.46 g, 4.7 mmol) and DBU (0.854 g, 5.61 mmol) in benzene (10 mL). The mixture, which turned black within 30 min, was then stirred at rt for 4 d. The mixture was concentrated *in vacuo*, and the residue was dissolved in dichloromethane (200 mL), washed with saturated aqueous ammonium chloride solution (100 mL), washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$, concentrated *in vacuo*, purified by column chromatography (20 × 3.3 cm, 50% dichloromethane/hexanes) to yield *syn*-6,15-bis(trimethylsilylethynyl)-2,11-dithia[3.3]metacyclophane (**2.32**) (0.15 g, 0.32 mmol, 17%) as a colorless oil; R_f (50% dichloromethane/hexanes) = 0.60; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.10 (d, *J*=1.5 Hz, 4H), 6.69 (s, 2H), 3.68 (s, 8H), 0.24 (s, 18H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 137.2, 132.2, 130.9, 123.6, 104.9, 94.3, 37.3, 0.2; LC-MS

(APCI-) *m/z* (%): 504 (29), 479 (62), 464 (100, M^-), 434 (23), 407 (33); HR-MS *m/z* Calcd for $C_{26}H_{32}Si_2S_2$ 464.1484, found 464.1483. Eluted next was 6-iodo-15-trimethylsilylethynyl-2,11-dithia[3.3]metacyclophane (**2.33**) (0.070g, 0.15 mmol, 8%) as a white solid; R_f (50% dichloromethane/hexanes) = 0.38; ^{1}H NMR (500.13 MHz, $CDCl_3$) 7.09 (s, 2H), 7.04 (d, *J*=0.5 Hz, 2H), 6.90 (br, s, 1H), 6.84 (br, s, 1H), 3.72 (s, 4H), 3.71 (s, 4H), 0.28 (s, 9H). To a solution of 6-iodo-15-trimethylsilylethynyl-2,11-dithia[3.3]metacyclophane (**2.33**) (66 mg, 0.13 mmol) in methanol (6 mL) was added K_2CO_3 (24 mg, 0.17 mmol). The reaction was stirred at rt for 24 h and concentrated *in vacuo*. The residue was purified by column chromatography (15 × 1.9 cm, 50% dichloromethane/hexanes) to yield *syn*-6-ethynyl-15-iodo-2,11-dithia[3.3]metacyclophane (**2.34**) (14 mg, 0.033 mmol, 25%) as an unstable white solid; R_f (50% dichloromethane/hexanes) = 0.23; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.07 (s, 2H), 7.05 (s, 2H), 6.98 (br, s, 1H), 6.97 (br, s, 1H), 3.74 (s, 8H), 3.06 (s, 1H).

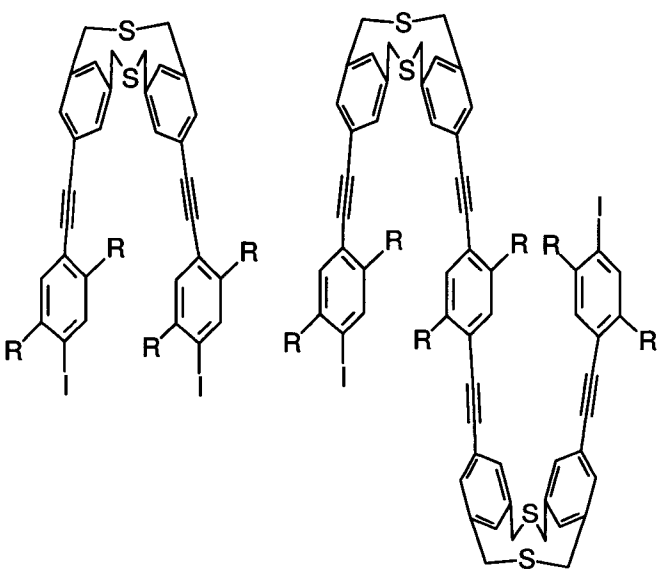
Syn-6,15-Diethynyl-2,11-dithia[3.3]metacyclophane (2.23).



A solution of *syn*-6,15-bis(trimethylsilylethylnyl)-2,11-dithia[3.3]cyclophane (**2.32**) (52 mg, 0.11 mmol) and K_2CO_3 (40 mg, 0.29 mmol) in methanol (8 mL) was stirred at rt for 2 h. The reaction mixture was poured into ice-cold water (40 mL), and extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with water (10 mL) washed with saturated aqueous sodium chloride solution (10 mL), dried over

$MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (10 × 1.4 cm, 50% dichloromethane/hexanes) to yield *syn*-6,15-diethynyl-2,11-dithia[3.3]metacyclophane (**2.23**) (19 mg, 0.059 mmol, 54%) as a colorless liquid, which solidified after 2 h to yield a white solid; (50% dichloromethane/hexanes) = 0.35; mp: 133-136 °C (chloroform); IR (powder): 3927 (w), 3278 (w), 1787 (w), 1594 (m), 1496 (s), 1447 (m), 1416 (m), 1224 (m), 1179 (w), 959 (w), 912 (s), 884 (m), 808 (s), 733 (s), 713 (s), 662 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.06 (d, *J*=2.0 Hz, 4H), 6.91 (s, 2H), 3.72 (s, 8H), 2.99 (s, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 137.5, 132.2, 131.1, 122.5, 83.4, 77.3, 37.7; LC-MS (APCI) *m/z* (%): 355 (14), 335 (21), 319 (100, M^+-1), 212 (15); HR-MS *m/z* Calcd for $C_{20}H_{16}S_2$ 320.0693, found 320.0696.

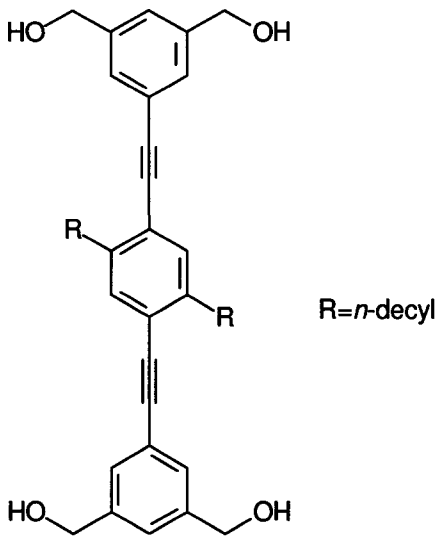
Syn-6-15-Bis((2,5-didecyloxy-4-iodophenyl)ethynyl)-2,11-dithia[3.3]metacyclophane (2.42) and by-product (2.43).



To a well stirred solution of 1,4-didecyloxy-2,5-diiodobenzene (**2.41c**) (0.88 g, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (4.3 mg, 0.0062 mmol, 0.4 mol %), CuI (4.8 mg, 0.025 mmol, 1.8

mol %) in degassed benzene (50 mL) was added a solution of *syn*-6,15-diethynyl-2,11-dithia[3.3]metacyclophane (**2.23**) (0.20 g, 0.62 mmol) and DBU (0.25 g, 1.6 mmol) in benzene (5 mL). The mixture was stirred at rt for 10 min, concentrated *in vacuo*, and purified by column chromatography (17 × 3.3 cm, 40% dichloromethane/hexanes) to yield *syn*-6,15-bis((2,5-didecyloxy-4-iodophenyl)ethynyl)-2,11-dithia[3.3]metacyclophane (**2.42**) (0.31 g, 0.23 mmol, 37%) as a colorless oil which then solidified to afford a white solid; mp: 22-25 °C; R_f (40% dichloromethane/hexanes) = 0.33; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.16 (s, 4H), 6.79 (s, 2H), 6.77 (br, 2H), 3.91 (t, *J*=6.8 Hz, 4H), 3.81 (t, *J*=6.3 Hz, 4H), 3.73 (s, 8H), 1.82-1.76 (m, 8H), 1.51-1.46 (m, 8H), 1.29-1.26 (m, 56H), 0.90-0.86 (m, 12H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.4, 152.0, 137.3, 130.6, 130.5, 124.0, 123.9, 113.9, 94.2, 87.6, 85.8, 69.6, 38.0, 37.4, 37.0, 36.4, 32.1, 30.2, 30.1, 29.8, 29.8, 29.6, 29.4, 26.3, 22.9, 14.4, 14.3; LC-MS (APCI) *m/z*: 1409.4 (17), 1349.4 (37, M^++1), 1222.5 (100), 1082.3 (73); Anal. Calcd for $C_{72}H_{102}S_2O_4I_2$: C, 64.07; H, 7.63. Found: C, 64.31; H, 7.95. Eluted next was **2.43**; R_f (40% dichloromethane/hexanes) = 0.21, which was obtained as a yellow oil (0.17 g, 0.083 mmol, 27%); ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.24 (s, 2H), 7.21-7.19 (m, 8H), 6.86 (s, 2H), 6.81 (s, 2H), 6.70 (br, 2H), 6.69 (br, 2H), 3.91 (t, *J*=6.9 Hz, 4H), 3.83 (t, *J*=6.5 Hz, 8H), 3.73 (s, 16H), 1.89-1.72 (m, 12H), 1.51-1.48 (m, 12H), 1.26-1.25 (m, 72H), 0.88-0.86 (m, 18H); MALDI-MS *m/z*: 1798 (100, M^+-2HI), 1661 (57, M^+-2HI-$C_{10}H_{21}$), 1520 (21, M^+-2HI-2$C_{10}H_{21}$), 1380 (17, M^+-2HI-3$C_{10}H_{21}$), 1255 (20), 1222 (33); Anal. Calcd for $C_{118}H_{160}I_2O_6S_4$: C, 68.90; H, 7.86. Found: C, 68.70; H, 7.92.

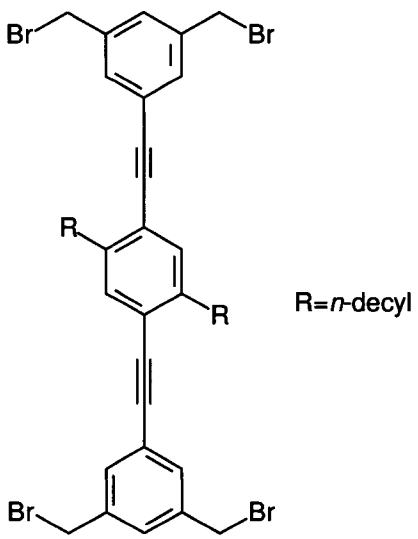
1,4-Bis(2-(3,5-bis(hydroxymethyl)phenyl)ethynyl)-2,5-didecylbenzene (2.47).



R=*n*-decyl

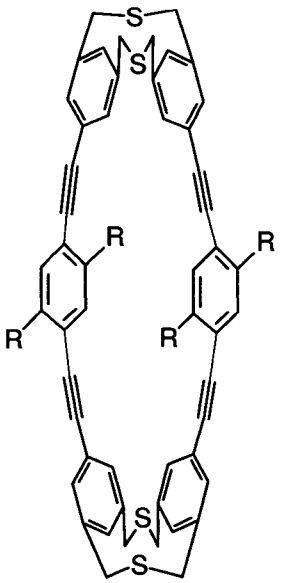
To a 0 °C well-stirred solution of 1,4-bis(2-(3,5-bis(methoxycarbonyl)phenyl)ethynyl)-2,5-didecylbenzene (**2.46b**) (0.22 g, 0.28 mmol) in dichloromethane (22 mL) was added dropwise 1M DIBAL-H solution in dichloromethane (1 M, 4.4 mL, 4.4 mmol). The mixture was stirred at room temperature for 14 h and cooled to rt. Water (1 mL) was then added followed by addition of 6 M aqueous hydrochloric acid until pH=1. The mixture was then suction filtered to yield 1,4-bis(2-(3,5-bis(hydroxymethyl)phenyl)ethynyl)-2,5-didecylbenzene (**2.47**) (0.18 g, 0.27 mmol, 95%) as a faint yellow solid; mp: 132-134 °C (chloroform); IR (powder): 3283 (br, vs), 2921 (s), 2849 (s), 1598 (w), 1466 (m), 1053 (s), 888 (m), 853 (m), 776 (m), 725 (s), 697 (vs) cm^{-1}; ^{1}H NMR (500.13 MHz, DMSO-d6) δ 7.43 (s, 2H), 7.35 (s, 4H), 7.33 (s, 2H), 4.51 (s, 8H), 2.78 (t, *J*=7.3 Hz, 4H), 1.66-1.64 (m, 4H), 1.33-1.20 (m, 28H), 0.82 (t, *J*=6.7 Hz, 6H); ^{13}C NMR (125.76 MHz, DMSO-d_6) δ 143.1, 141.8, 127.3, 127.3, 124.9, 122.0, 121.7, 94.3, 87.4, 62.3, 33.3, 31.3, 28.9, 28.9, 28.8, 28.7, 28.6, 22.0, 17.0, 13.8; LC-MS (APCI) *m/z*: 713 (100, MCl^{-}); HR-MS *m/z* Calcd for $C_{46}H_{62}O_4$ 678.4648, found 678.4651.

1,4-Bis(2-(3,5-bis(bromomethyl)phenyl)ethynyl)-2,5-didecylbenzene (2.48)



To a well-stirred suspension of 1,4-bis(2-(3,5-bis(hydroxymethyl)phenyl)ethynyl)-2,5-didecylbenzene (**2.47**) (20 mg, 0.0295 mmol) in dichloromethane (5 mL), was added PBr_3 (10 mg, 0.039 mmol). The reaction was stirred at room temperature for 14 h, concentrated *in vacuo*, and purified by column chromatography (17 × 1.9 cm, dichloromethane) to give 1,4-bis(2-(3,5-bis(bromomethyl)phenyl)ethynyl)-2,5-didecylbenzene (**2.48**) (4 mg, 0.004 mmol, 15%) as a pale yellow solid; R_f (dichloromethane) = 0.90; mp: >300 °C (chloroform); ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.48 (s, 4H), 7.37 (s, 4H), 4.47 (s, 8H), 2.80-2.75 (m, 4H), 0.89-0.87 (m, 50H); LC-MS (APCI) *m/z*: 934 (27, M^++4), 933 (68, M^++3), 932 (47, M^++2), 931 (100, M^++1), 930 (29, M^+), 929 (66, M^+-1), 867 (22).

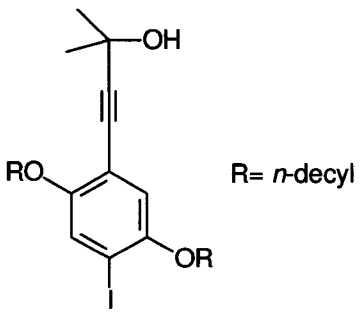
Tetrathiacyclophyne nanoring (2.39b)



R=*n*-decyl

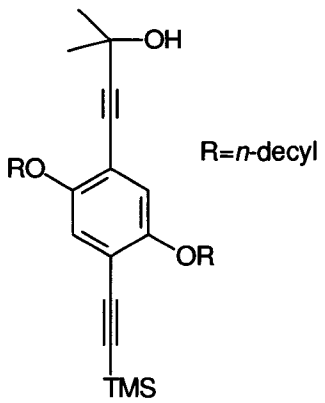
To a vigorously stirred solution of 1,4-bis(2-(3,5-bis(bromomethyl)phenyl)ethynyl)-2,5-didecylbenzene (**2.48**) (4.0 mg, 0.0043 mmol) in 10% ethanol/dichloromethane (2 mL) was added Na_2S/Al_2O_3 (6.3 mg, 0.017 mmol). The reaction mixture was stirred at room temperature for 16 h, filtered through a short plug of celite, concentrated *in vacuo* and purified by column chromatography (6 × 1.2 cm, dichloromethane) to give tetrathiacyclophyne (**2.39b**) (1.5 mg, 0.0022 mmol, 52%) as a colorless oil; R_f (dichloromethane) = 0.95; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.13 (br, 2H), 7.12 (br, 2H), 7.00-6.96 (m, 2H), 6.82 (br, 2H), 6.80 (br, 2H), 4.13-4.08 (m, 2H), 3.85-3.81 (m, 2H); LC-MS (APCI) *m/z*: 1367 (5), 1351 (9, M^++2), 1195 (100).

1,4-didecyloxy-2-(3-hydroxy-3-methyl)butynyl -5-iodobenzene (2.52)



To a well-stirred solution of 1,4-didecyloxy-2,5-diiodobenzene (**2.43c**) (50 mg, 0.078 mmol), $Pd(PPh_3)_2Cl_2$ (0.5 mg, 0.0078 mmol), CuI (0.6 mg, 0.0031 mmol) in degassed benzene (5 mL) was added a solution 2-methyl-3-butyn-2-ol (7.2 mg, 0.086 mmol) and DBU (16 mg, 0.11 mmol) in benzene (1 mL). The mixture turned light green in 5 min and then was left stirring for 2 h. The crude reaction mixture was concentrated *in vacuo*, and the residue was purified by column chromatography (7 × 1.9 cm, dichloromethane) to yield 1,4-didecyloxy-2-(3-hydroxy-3-methyl)butylnyl-5-iodobenzene (**2.52**) (17 mg, 0.028 mmol, 36%) as a colorless liquid; R_f (dichloromethane) = 0.33; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.80 (s, 1H), 3.93 (t, *J*=6.6 Hz, 4H), 2.04-2.02 (m, 1H), 1.81-1.76 (m, 4H), 1.62 (s, 6H), 1.49-1.48 (m, 4H), 1.34-1.28 (m, 24H), 0.88 (t, *J*=6.8 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.6, 152.0, 124.0, 116.4, 113.2, 98.8, 87.7, 78.4, 70.4, 70.0, 66.0, 32.1, 32.1, 31.7, 29.9, 29.8, 29.8, 29.6, 29.5, 29.5, 29.4, 26.3, 26.2, 22.9, 14.3, 0.2; LC-MS (APCI) *m/z*: 598 (10, M^+), 581 (100); HR-MS *m/z* Calcd for $C_{31}H_{51}IO_3$ 598.2883, found 598.2888.

1,4-Didecyloxy-2-(3-hydroxy-3-methyl-1-butynyl)-5-trimethylsilylethylnylbenzene (2.53)



To a well-stirred solution of 1,4-didecyloxy-2-(3-hydroxy-3-methyl)butylnyl-5-iodobenzene (**2.52**) (36 mg, 0.060 mmol), $Pd(PPh_3)_2Cl_2$ (0.4 mg, 0.0006 mmol), CuI (0.5 mg, 0.002 mmol) in degassed benzene (4 mL) was added a solution trimethylsilylacetylene (6.5 mg, 0.066 mmol) and DBU (12 mg, 0.082 mmol) in benzene (0.6 mL). The mixture was stirred at reflux for 48 h, cooled to rt, concentrated *in vacuo,* and purified by column chromatography (10 × 1.9 cm, dichloromethane) to yield 1,4-didecyloxy-2-(3-hydroxy-3-methyl-1-butynyl)-5-trimethylsilylethylnylbenzene (**2.53**) (17 mg, 0.030 mmol, 50%) as a colorless oil; R_f (dichloromethane) = 0.25; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.85 (s, 1H), 3.95-3.92 (m, 4H), 2.02 (s, 1H), 1.79-1.77 (m, 4H), 1.51-1.46 (m, 4H), 1.34-1.27 (m, 24H), 0.88 (t, *J*=6.5 Hz, 6H), 0.25 (s, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 154.3, 153.7, 117.4, 117.3, 113.9, 113.8, 101.3, 100.1, 99.4, 78.7, 69.7, 69.6, 66.0, 32.1, 31.6, 29.9, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.6, 26.2, 22.9, 14.3, 0.2; LC-MS (APCI) *m/z*: 659 (5), 576 (5), 569 (13, M^+), 552 (100), 479 (29); HR-MS *m/z* Calcd for $C_{36}H_{60}O_3Si$ 568.4312, found 568.4316.

2.6 Reference

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4. α is an "envelope flap angle", *i.e.* the smallest angle formed by the planes defined by C(1)-C(2)-C(3) and C(1)-C(3)-C(4)-C(6) of a benzene ring that it bridged at C(2) and C(5).
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Chapter 3

Synthesis of Polyphenyl Pyrenophanes with a Central Aromatic Moiety

3.1 Introduction

The series of pyrenophanes shown in Fig. 3.01 can be used to illustrate how the field of cyclophanes overlaps with other areas. The [*n*](2,7)pyrenophanes **3.01**[1] are simple cyclophanes consisting of one aromatic unit and one aliphatic bridge. Pyrenophanes **3.02** and **3.03** are mixed cyclophanes,[2] *i.e.* they are comprised of two different aromatic systems. Although they are more complex, they fall squarely under the cyclophane umbrella. Benzannulation of the bridges of the cyclophanediene derived from **3.03** gives rise to structure **3.04**, which can now be viewed either as a cyclophane or a cyclic oligoarylene.[3]

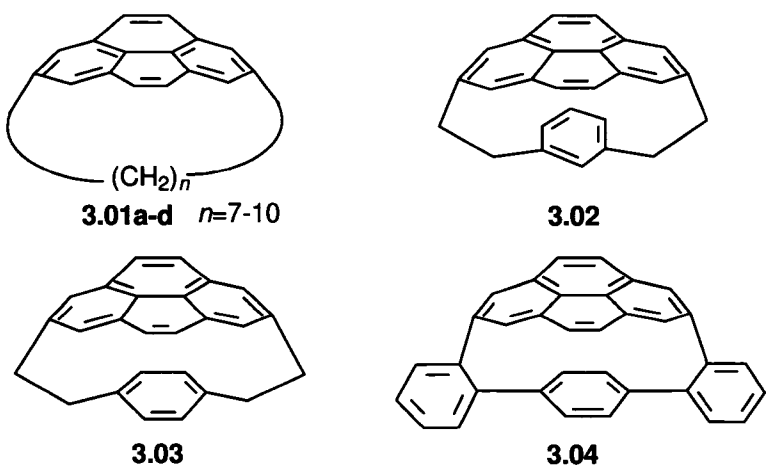
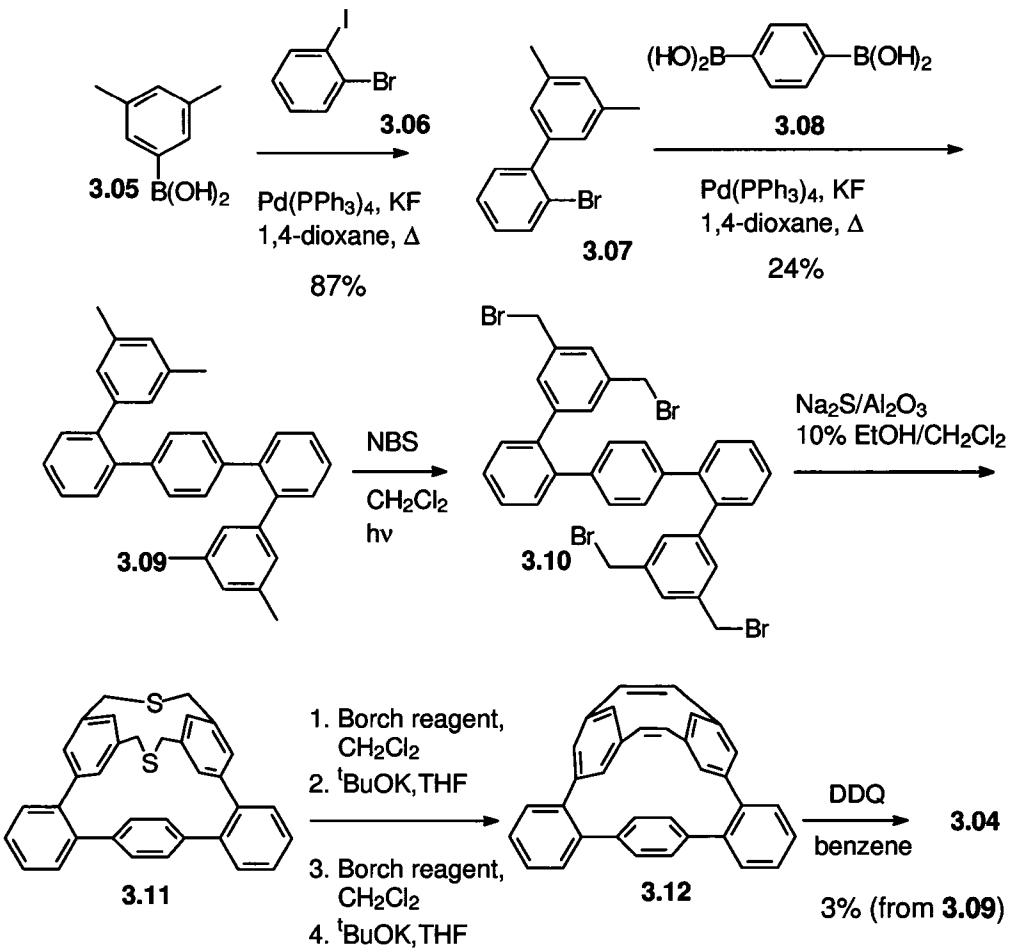


Figure 3.01. Previously synthesized pyrenophanes.

Whatever the viewpoint, compound **3.04** is structurally interesting. It is a shape-persistent assembly of orthogonally linked aromatic systems. Although there is no appreciable cavity within the cycle (see Fig. 3.01), it provides the basis for the construction of a family of structurally unique systems, in which sets of arenes that vary in their size, shape, planarity and electronic nature are held together. As such, there is

potential for the development of compounds having unusual and/or exploitable optoelectronic properties.

In 2003, pyrenophane **3.04** was synthesized in the Bodwell group (Scheme 3.01).[4] Owing to the absence of sp^3-hybridized carbon atoms in its structure, the strategies that had been so successfully applied to the syntheses of **3.01**-**3.03** could not be employed for **3.04**. The presence of 4 biaryl bonds in **3.04** strongly suggested that the Suzuki-Miayura cross-coupling reaction[5] would be effective and this was indeed the case (Scheme 3.01). Suzuki-Miayura coupling of **3.05** and **3.06** afforded biphenyl **3.07**, which was subjected to Suzuki-Miayura coupling with 1,4-phenylenebisboronic acid (**3.08**) to give quinquephenyl derivative **3.09**. Free radical benzylic bromination showed excellent selectivity, giving tetrabromide **3.10** in ~80% yield.[6] Reaction of the crude tetrabromide with Na_2S/Al_2O_3 gave dithiacyclophane **3.11**, which was brought without purification through a sequence of methylation, Stevens rearrangement, methylation, Hofmann elimination sequence to deliver cyclophanediene **3.12**. Again, this compound was not isolated in pure form. However, its reaction with DDQ at room temperature afford **3.04**, which could be purified chromatographically. Although it was ultimately successful, the synthetic route suffered from a few problems. The second Suzuki-Miayura coupling reaction was very low-yielding and the radical bromination, although relatively high-yielding, produced several by-products that were difficult to remove from the desired product. This mixture was then carried through the following six steps, which prevented characterization of all of the synthetic intermediates.

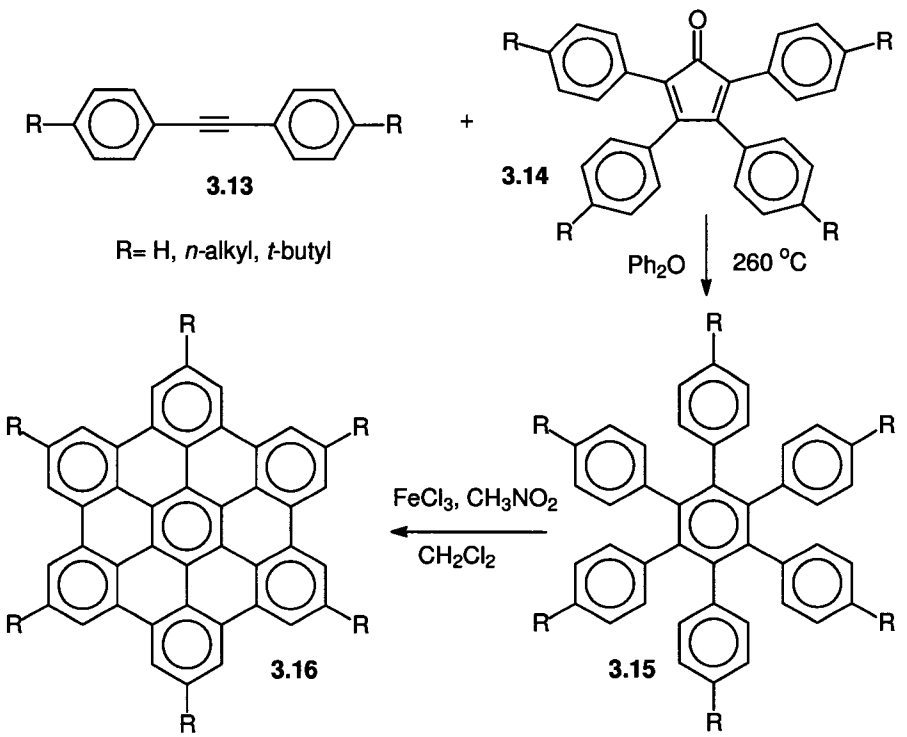


Scheme 3.01. Synthesis of pyrenophane **3.04**.

In light of the problems described above, other strategies for the construction of the core skeleton of **3.04** were sought. Upon focusing on the *ortho*-substituted aromatic rings, Müllen's approach to polyphenylene systems (oligomers, polymers and dendrimers) and then nanographitic sheets was identified as being especially promising.[7]

Müllen's methodology is based on a Diels-Alder reaction between a diphenylacetylene **3.13** and a tetraphenylcyclopentadienone **3.14** followed by an *in situ* decarbonylation reaction to yield a hexaphenylbenzene derivative **3.16**.

Cyclodehydrogenation by way of a Scholl reaction affords a hexabenzocorenene derivative **3.16**. Compound **3.15** contains 6 *ortho*-diphenylbenzene units, which is a structural element that appears twice in compound **3.09**. A limitation of this approach is that cyclopentadienone, which is a very reactive compound,[8] would be required to synthesize pyrenophane **3.04**. The use of the standard (and much more stable) diene tetraphenylcyclopentadienone **3.14** (R=H) necessarily brings some extraneous Ph substituents (see structures **3.17-3.19** below) into play. Instead of being a disadvantage, however, this may eventually prove to be beneficial.



Scheme 3.02. Müllen's Synthesis of hexabenzocorenene derivative **3.16**.

Pyrenophanes **3.17a**, **3.18**, and **3.19** were identified as targets. These compounds each contain a bent pyrene unit, two hexasubstituted benzenes and eight peripheral phenyl groups. They differ in the nature of the "central" aromatic system. The *meta*-phenylene-

and 2,5-thienylene-containing systems **3.18** and **3.19** will have lower symmetry than pyrenophane **3.17a**, which should allow conformational processes to be probed by NMR.

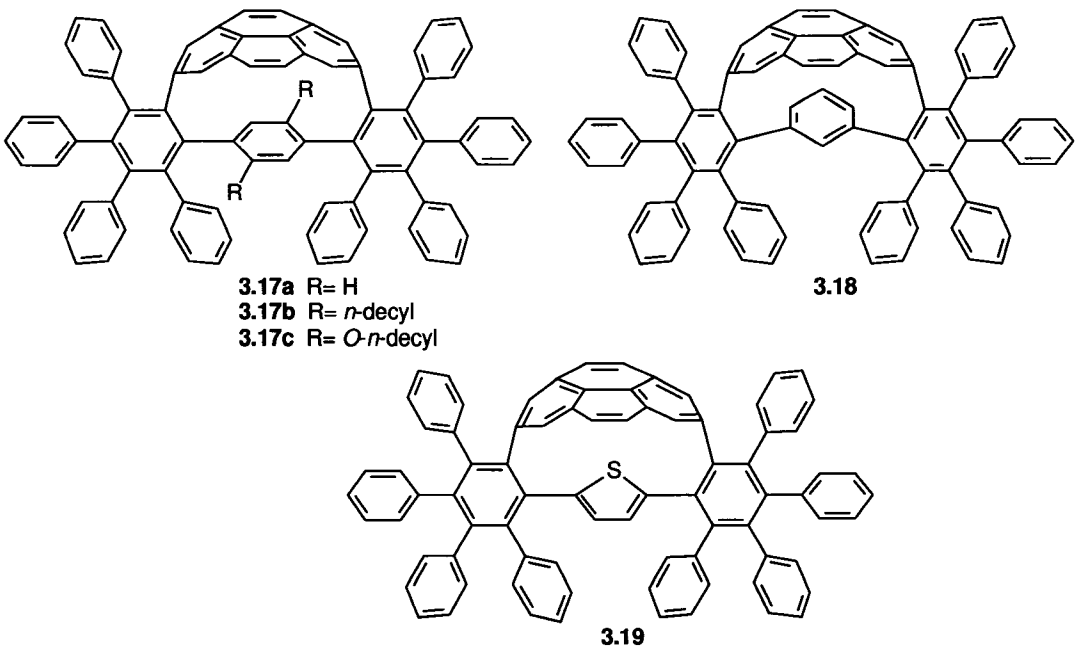
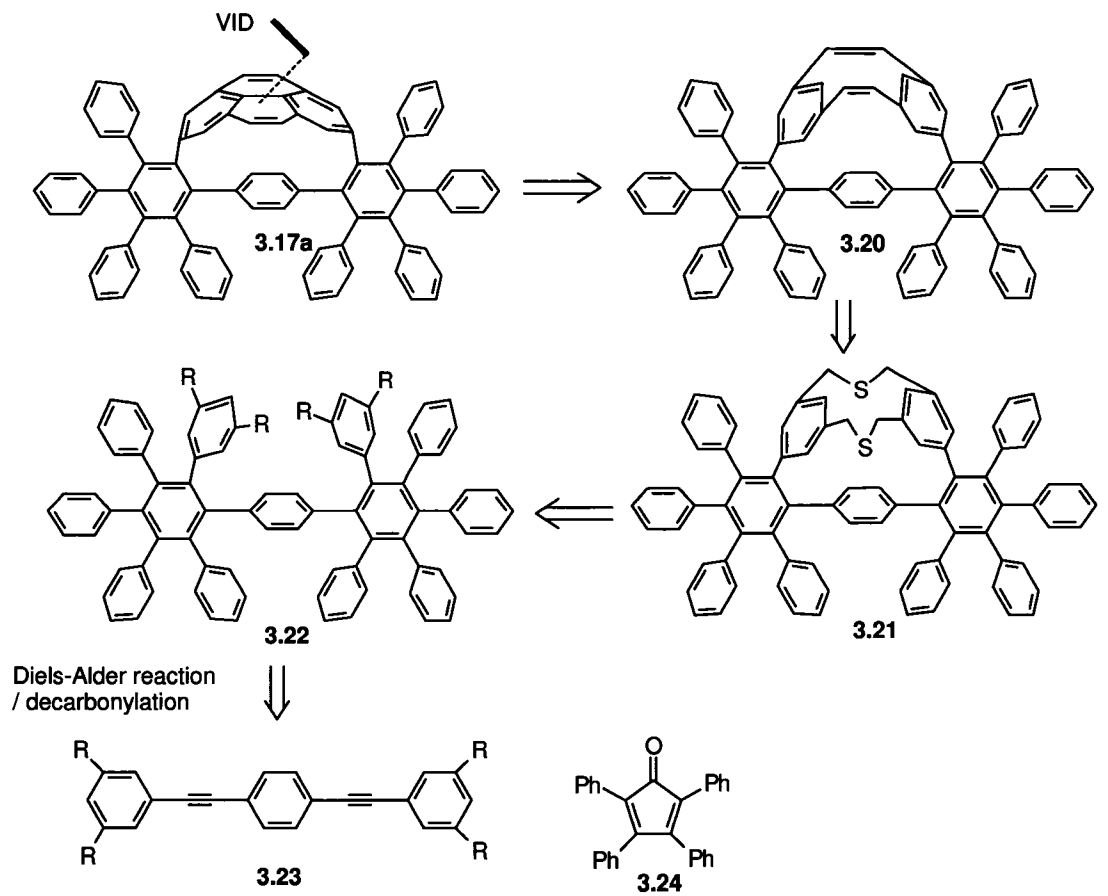


Figure 3.02. Target pyrenophanes **3.17a-c**, **3.18**, and **3.19**.

Targets **3.17a**, **3.18** and **3.19** all contain a plane of symmetry, which make them achiral. However, appropriate substitution of the central aromatic unit will destroy the plane of symmetry, and result in chiral compounds (Fig. 3.02). Accordingly, C_2-symmetric targets **3.17b** and **3.17c**, which come from the addition of two long aliphatic chains to **3.17a** were chosen for investigation.

3.2 Retrosynthetic Analysis



Scheme 3.03. Retrosynthesis of pyrenophane **3.17a**.

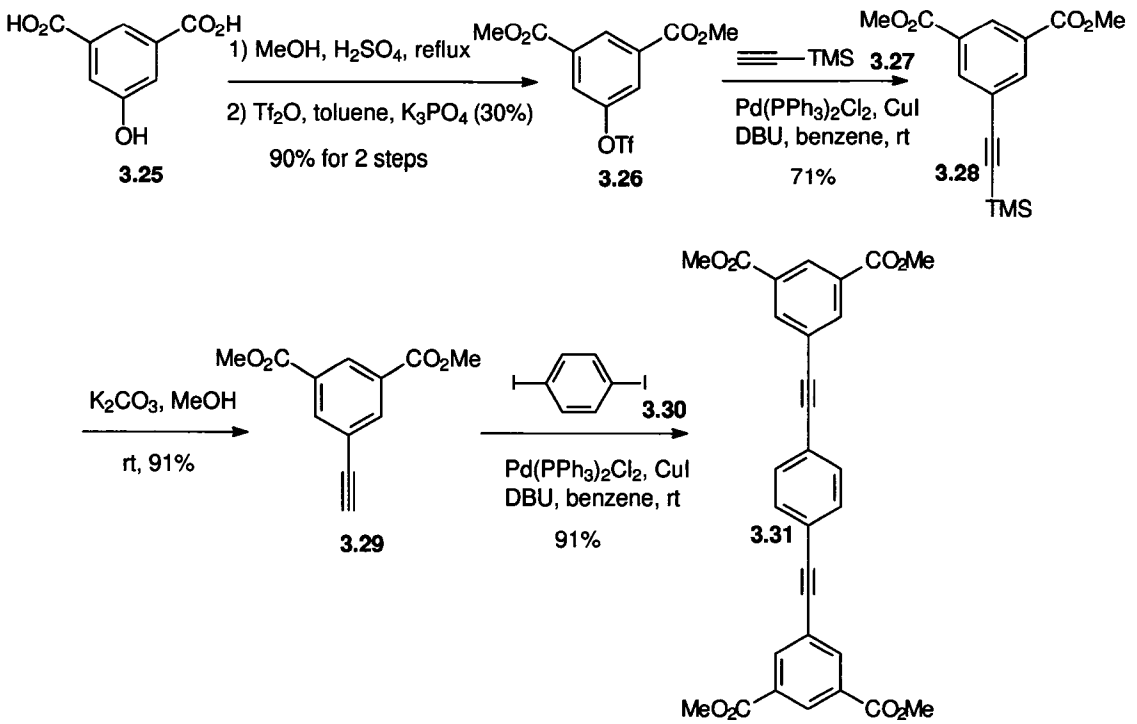
As with all other (2,7)pyrenophanes synthesized in the Bodwell group, the first retrosynthetic step back from the target molecule **3.17a** was one of the key steps, namely the VID reaction, which led back to cyclophanediene **3.20**. Cyclophanediene **3.20** was envisioned as coming by way of established cyclophane chemistry. Cleavage of the C-S bonds brought the synthesis back to "acyclic" precursor **3.22**. Structure **3.22**, which still contains all of the carbon atoms that appear in the final target **3.17a**, is ready for a highly productive disconnection. It has two retrons for a Diels-Alder/decarbonylation transform,

application of which affords linear phenylene-ethynylene species **3.23** and tetraphenylcyclopentadienone **3.24**. Compound **3.23** (R=CO_2Me) was previously synthesized in the Bodwell group and compound **3.24** is both commercially available and easily synthesized. The retrosynthetic analyses of **3.17b-c**, **3.18** and **3.19** are the same, and they lead back to analogs of **3.23** that differ in the nature of the central arylene unit.

3.3 Results and Discussion

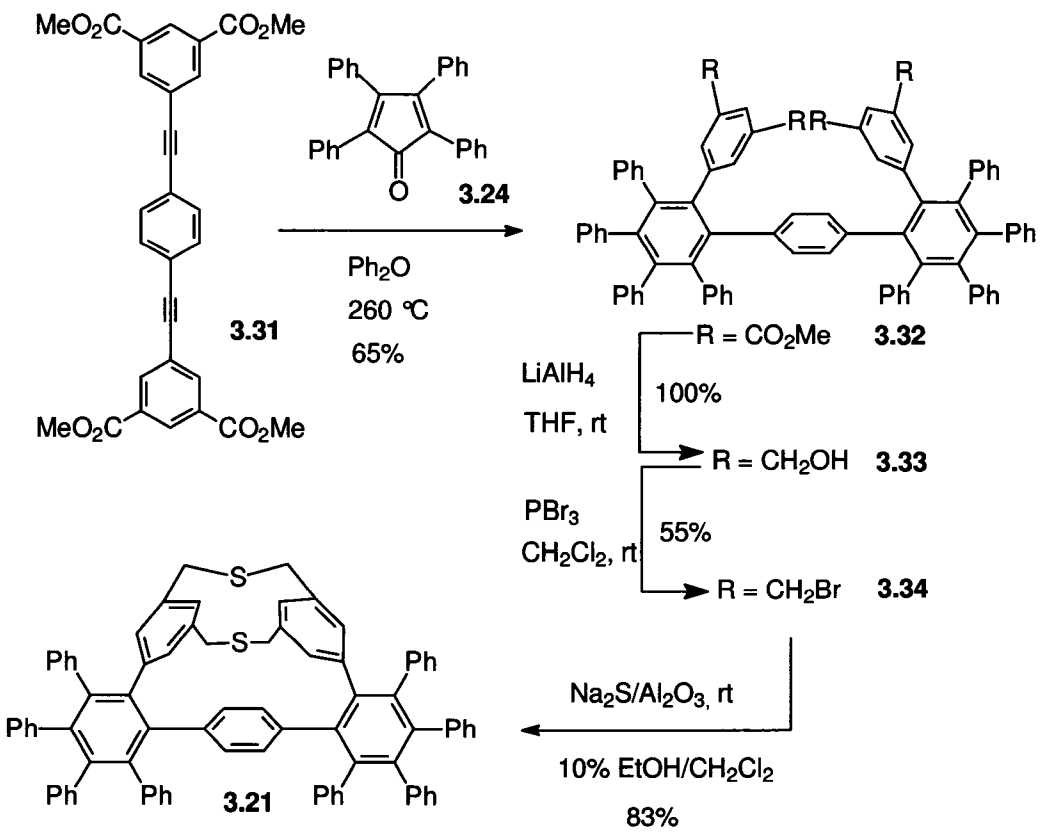
3.3.1 Synthesis of Pyrenophanes with a Central *para*-Phenylene Unit

The synthesis of pyrenophane **3.17a** commenced with the esterification of a commercially available material, 5-hydroxyisophthalic acid (**3.25**), followed by triflation, which effectively produced triflate **3.26** (90%). Triflate **3.26** was then reacted with trimethylsilylacetylene (**3.27**) (TMSA) under Sonogashira conditions to yield **3.28** (71%). Protodesilylation of **3.28** using potassium carbonate in methanol afforded terminal alkyne **3.29** (91%). Upon reaction of **3.29** with 1,4-diiodobenzene under Sonogashira conditions, diynetetraester **3.31** was formed in 91% yield. The conversion of **3.26** to **3.31** was first developed by Vermeij in 2001,[2] and the yields reported here are comparable to those of Vermeij.



Scheme 3.04. Synthesis of diynetetraester **3.31**.

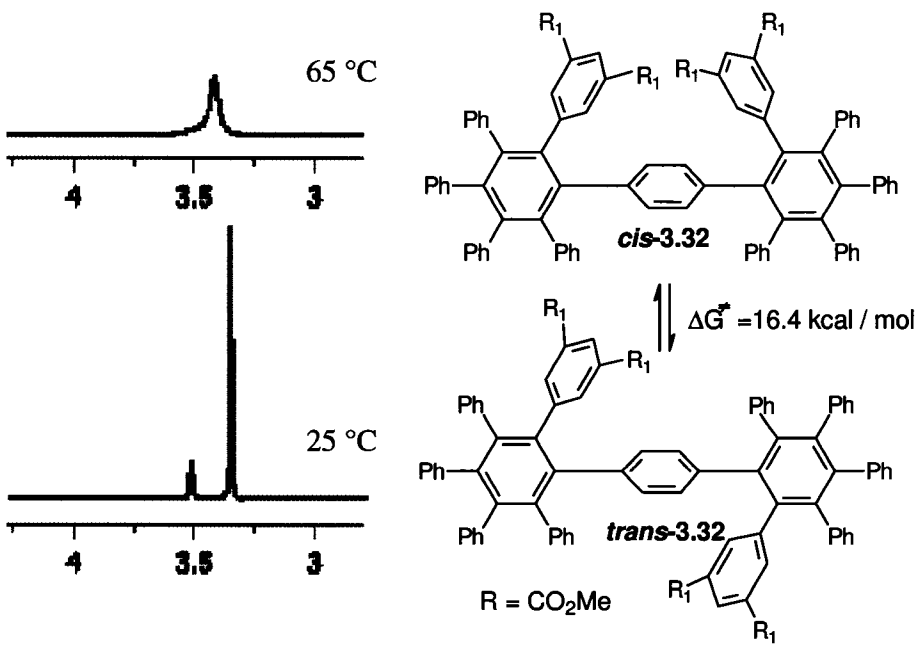
Heating tetraphenylcyclopentadienone **3.24** (3.0 eq.) with diynetetraester **3.31** in diphenyl ether at 260 °C brought about the desired twofold Diels-Alder / decarbonylation reaction and the octaphenyl tetraester **3.32** was isolated in 65% yield.



Scheme 3.05. Synthesis of dithiacyclophane **3.21**.

The ^{1}H-NMR spectrum of **3.32** shows two rather broad signals in a *ca.* 6.0:1 ratio for the methyl esters (Fig. 3.06). This is consistent with the presence of conformers, *cis*-**3.32** and *trans*-**3.32**, which interconvert by rotation about one of the biaryl bonds (see Scheme 3.06). A DNMR experiment was performed to measure the activation barrier for this process (Appendix B). At 65±5 °C, the two peaks merged into one broad peak, which indicated that the coalescence has been reached. An approximate energy barrier of

16.4±0.3 kcal/mol for the interconversion the two isomers was then calculated using the Eyring equation.[9] The Eyring equation should, strictly speaking, be applied to 1:1 mixtures. However, the 6.0:1 ratio corresponds to a ΔG of only 1.07 kcal/mol, which is small in comparison to $\Delta G^{\neq}$ (16.4 kcal/mol). Even considering the approximate nature of the $\Delta G^{\neq}$ value, it is well below the standard value of 22.4 kcal/mol that is required for the term "atropisomers"[10] to be applied to these conformers. Attempted separation of *cis*- and *trans*-**3.32** by column chromatography was, of course, not worth performing. Based solely on steric grounds, it would seem more likely that *trans*-**3.32** is the major isomer.

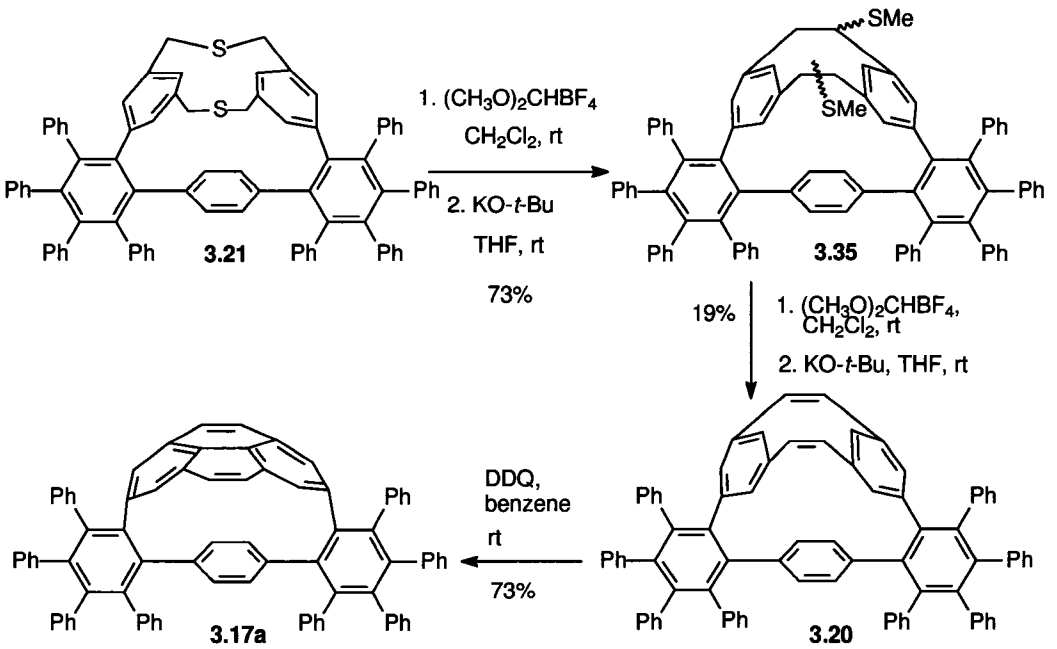


Scheme 3.06. DNMR experiment of **3.32**.

Reacting the mixture of *cis*- and *trans*-**3.32** with $LiAlH_4$ afforded tetraol **3.33** in quantitative yield. Like its precursor, its ^1H NMR spectrum exhibited broad peaks in the aromatic region, which may also indicate conformational mobility. However, the

benzylic region, which consisted of a somewhat broad AB system with a broad shoulder, was ambiguous, so no firm conclusion could be drawn. Benzylic bromination of tetraol **3.33** using phosphorous tribromide afforded tetrabromide **3.34** (55%). This compound again shows two broad singlets in a 1.7:1 ratio, which translates into ΔG=0.32 kcal/mol. Reaction of the two isomers of **3.34** with Na_2S/Al_2O_3 afforded dithiacyclophane **3.21** in 83% yield. The yield for this reaction was the highest yet obtained in the Bodwell group for the formation of any dithiacyclophane using the Na_2S/Al_2O_3 reagent. The relatively rigid structure of the tetrabromide **3.34** probably benefits the reaction entropically. In *cis*-**3.34**, the reaction sites (bromomethyl groups and thiolate anion derived from them) are not only situated close to one another, but can also easily adopt a favorable geometry for an S_N2 reaction. That the yield of the reaction exceeds the proportion of *cis*-**3.34** in the starting material (whether it is the major or minor component) is consistent with the reactive isomer being replenished by a *trans*-**3.34**→*cis*-**3.34** isomerization during the course of the reaction (12 h).

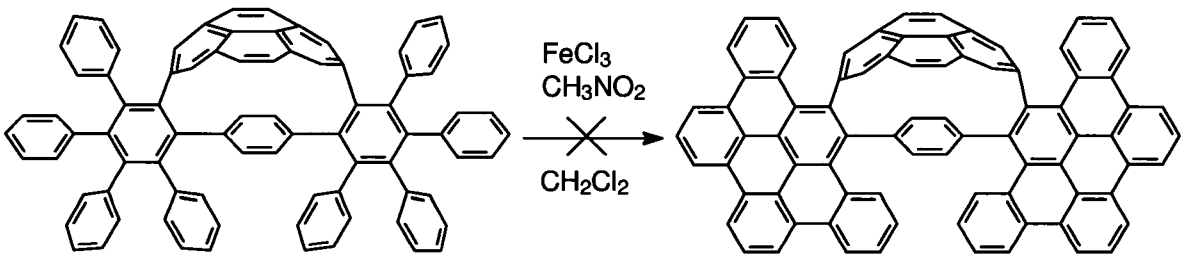
After methylating the sulfur atoms on **3.21** using Borch reagent, the resulting bis(methylsulfonium) salt was treated with *t*BuOK to initiate a Stevens rearrangement that produced a mixture of isomers **3.35** (73%, 2 steps). Without further purification, **3.35** was treated with Borch reagent again to methylate the sulfur atoms, and then *t*BuOK to initiate a Hofmann elimination, which resulted in the formation of cyclophanediene **3.20** in 19% yield (2 steps). The final step of the synthesis, as with all other (2,7)pyrenophane syntheses in the Bodwell group, was a VID reaction. Upon reaction with DDQ in benzene at room temperature, cyclophanediene **3.20** was converted to the corresponding pyrenophane **3.17a** in 73% yield.



Scheme 3.07. Synthesis of pyrenophane **3.17a.**

In Müllen's many syntheses of nanographitic sheets (Scheme 3.02), a multifold cyclodehydrogenation was investigated to produce hexabenzocorenene derivatives, *e.g.* **3.16** (Scheme 3.02). This cyclodehydrogenation, which is also known as the intramolecular Scholl reaction,[11] was also attempted on pyrenophane **3.17a** in order to obtain a pyrenophane with two graphene substructures, *e.g.* **3.36** (Scheme 3.08). Addition of $FeCl_3$ to a solution of **3.17a** resulted in the consumption of the starting material and the appearance of several brightly colored fluorescent spots on the tlc plate, the R_f values of which were very close to one another. Column chromatography resulted in a partial separation of these components. Under long-wave length UV-lamp irradiation, they showed strong orange, yellow or green fluorescence, while the starting material **3.17a** only showed a much weaker purplish blue fluorescence. Based on this observation, it can

be tentatively concluded that some cyclodehydrogenation occurred. However, LC MS and MALDI MS analysis failed to provide useful information about the identity of the products, presumably because these components are difficult to ionize. The ^{1}H NMR spectra of these products showed some aromatic signals, but were very difficult to interpret. The failure of this reaction to provide a clear result may also have its origin in intermolecular reactions, which have been reported for the systems containing no substituents on the phenyl groups.[12]



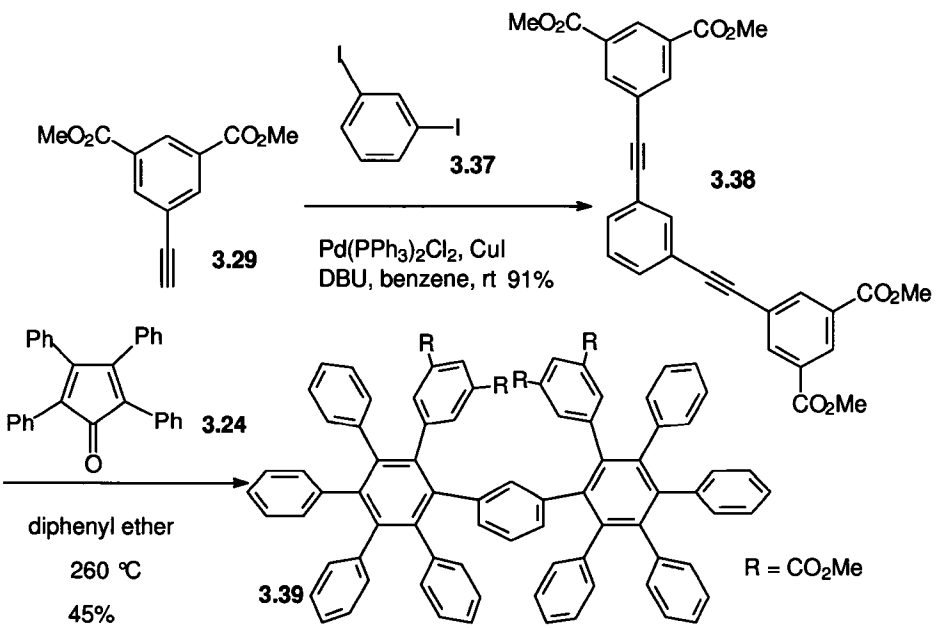
3.17a **3.36**

Scheme 3.08. Attempted cyclodehydrogenation (Scholl reaction) of **3.17a**.

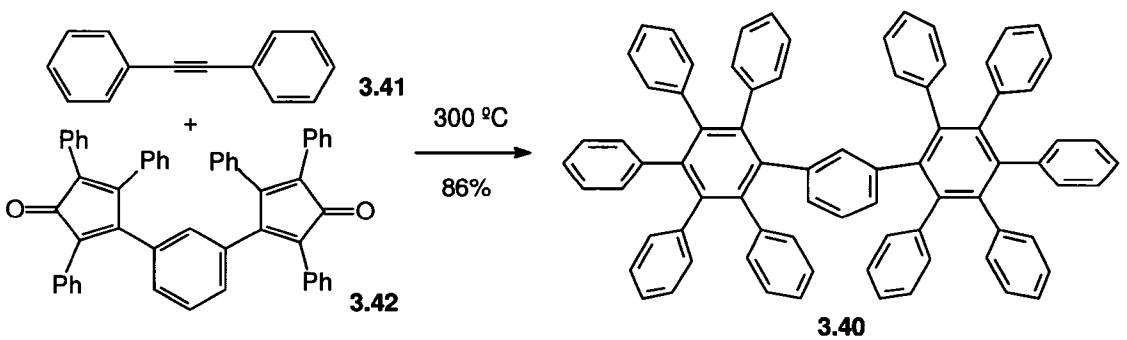
3.3.2 Synthesis of Pyrenophane 3.18 with a Central *meta*-phenylene Unit

Pyrenophane **3.18** is structurally similar to **3.17a**, differing only in the substitution pattern of the central benzene ring. The synthesis of **3.18** followed the same route as **3.17a**, but started with a Sonogashira coupling between alkyne **3.29** and 1,3-diiodobenzene **3.37** instead of 1,4-diiodobenzene **3.30** (Scheme 3.09). This Sonogashira reaction was also performed previously by Vermeij.[2] The resulting diynetetraester **3.38** (91%) was then reacted with tetraphenylcyclopentadienone **3.24** (Diels-Alder / decarbonylation reaction) to afford tetraester **3.39** in 45% yield. In its ^{1}H NMR spectrum (room temperature, $CDCl_3$), two sharp singlets were observed at δ 3.83 and 3.79 ppm, which correspond to the methyl groups of **3.39**. In the aromatic region, the main group of

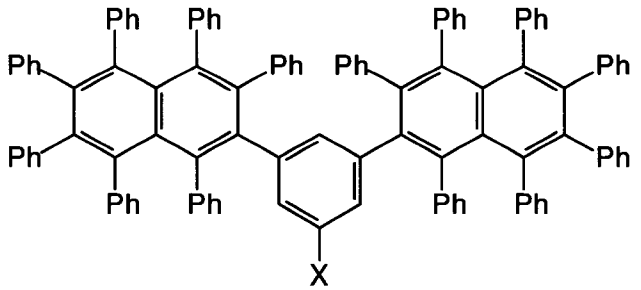
signals appeared at δ 7.00-6.23 (42H), many of which overlapped. These features are consistent with the ^{1}H NMR spectrum of the parent polyphenylene species **3.40**, which has aromatic signals in the range of δ 7.00-6.15.[13] Pascal's synthesis of **3.40** was also accomplished using a Diels-Alder approach, but it differed from the synthesis of **3.39** in that it proceeded through the bis(cyclopentadienonediene) (**3.42**) instead of a bis(dienophile) (**3.38**).



Scheme 3.09. Synthesis of **3.39**.



Scheme 3.10. Pascal's synthesis of polyphenylene species **3.40**.

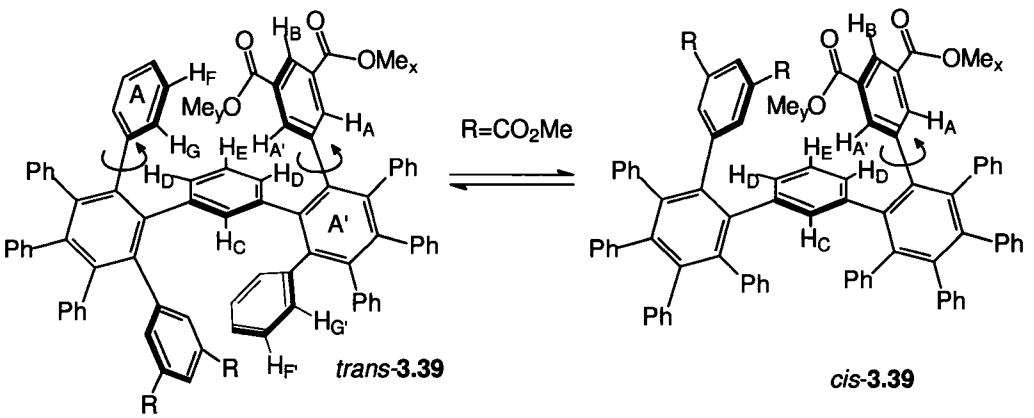


3.43 X=H
3.44 X=Br

Figure 3.03. Pascal's polyphenyl aromatic compounds **3.43** and **3.44**.

Some clear differences were observed between the ^{1}H NMR spectrum of **3.39** and that of **3.40**. The first difference was the presence in the spectrum of **3.39** of three low field 2H singlets at δ 8.42, 7.99 and 7.87 ppm, which are attributed to the protons on the ester-bearing phenyl groups. The fact that three signals are observed indicates that the rotation of the ester-bearing phenyl groups, which would produce a simpler spectrum (see discussion below), is slow on the NMR time scale. This is consistent with studies on hexaphenylbenzenes, which concluded that the energy barrier for rotation of *meta*-substituted phenyl groups in hexaphenylbenzene systems is *ca.* 17 kcal/mol.[14] A second, yet unexpected, major difference was a 2H doublet (J=7.4 Hz) at δ 5.16 ppm, which was shown to be correlated with a 2H triplet at δ 6.32 ppm in a ^{1}H,^{1}H-COSY experiment. It is due to one of the "*ortho*" H's on one of the phenyl groups and its symmetry-related partner on another (symmetry-related) phenyl ring. Exactly which proton this is could not be determined unambiguously. However, it is tentatively assigned to H_G and $H_{G'}$ (Scheme 3.11). The superficial explanation is that the addition of four ester groups to **3.40** causes a distortion in the geometry toward an "edge-to-face" orientation of the rings A with respect to the ester bearing groups. As such, the "*ortho*" protons of ring A sit in the shielding cone of the ester-bearing rings and consequently appear at high field. A

similar argument was used by Pascal to explain the anomalously high field signals observed in the ^{1}H NMR spectra of **3.43** (especially δ 4.99, d, *J*=7 Hz) and **3.44** (especially δ 5.02, br, s) (Fig. 3.03).[13]



Scheme 3.11. Conformers of **3.39**.

The 1H triplet observed at δ 6.24 must be H_E. In the ^{1}H,^{1}H-COSY spectrum, this signal showed a strong cross peak to the 2H doublet at δ 6.35, which must therefore be due to H_D. The "internal" proton, H_C, could not be found and presumably lies under the 33H multiplet at δ 6.87-6.63 ppm. All of the above observations are consistent with the presence of a single observable rotamer (either *cis*-**3.39** or *trans*-**3.39**, see Scheme 3.11) and a slow rotation of the peripheral aryl units. Based on steric arguments, *trans*-**3.39** would be expected to be a lower energy species than *cis*-**3.39**, which has proximate ester groups. A DNMR experiment (toluene-d_8, 5 °C to 75 °C) was then performed (Appendix B) to obtain information about the conformational behavior of **3.39**. Surprisingly, the presence of a second rotamer was immediately apparent. At 5 °C, two 6H sharp singlets were observed at δ 3.47 and 3.42 ppm, but they were accompanied by a smaller broad singlet at δ 3.60 ppm. In the aromatic region, a set of three 2H singlets at δ 8.85, 8.36 and

8.33 ppm was observed, which correspond to H_A, $H_{A'}$ and H_B, along with a set of three smaller signals at δ 8.50, 8.22 and 7.60 ppm (Fig. 3.04). The integral ratio of the major and minor signals of the aromatic protons was *ca.* 6:1 in every case. In contrast, the methyl signals have an approximate ratio of 1:6:6 (δ 3.60:3.47:3.43). However, upon closer inspection, the integration of the signal at δ 3.43 ppm is larger than that of the one at δ 3.47 ppm, the difference being roughly equal to the integral value of the minor signal at δ 3.60 ppm. Assuming that the partner to the signal at δ 3.60 ppm is underneath the signal at δ 3.43 ppm, the isomer ratio is 6:1, which is consistent with the ratio exhibited by the integrals of the aromatic signals. Perhaps coincidentally, this 6:1 ratio is the same as that observed for the *para*-phenylene analog (*cis* and *trans*-**3.32**). As in $CDCl_3$, an upfield aromatic signal was observed (δ 5.72, d, J=7.5 Hz, 2H). Assuming it is due to the same protons that give the high field signals in **3.39**, there is a *ca.* 0.6 ppm change in chemical shift upon changing solvents. This is either a solvent shift or an indication of a structural change. The observation that the minor conformer is more highly populated in toluene-d_8 than in $CDCl_3$ is difficult to explain.

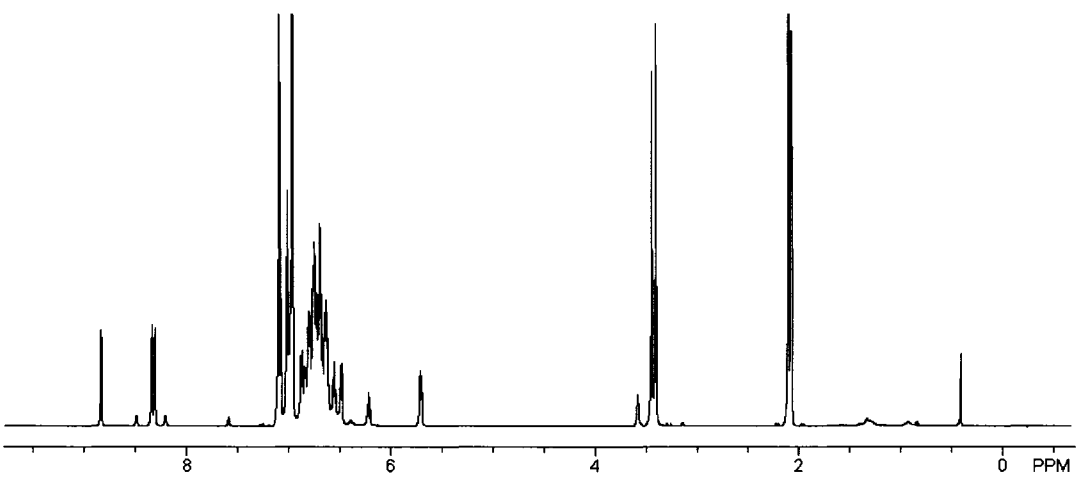


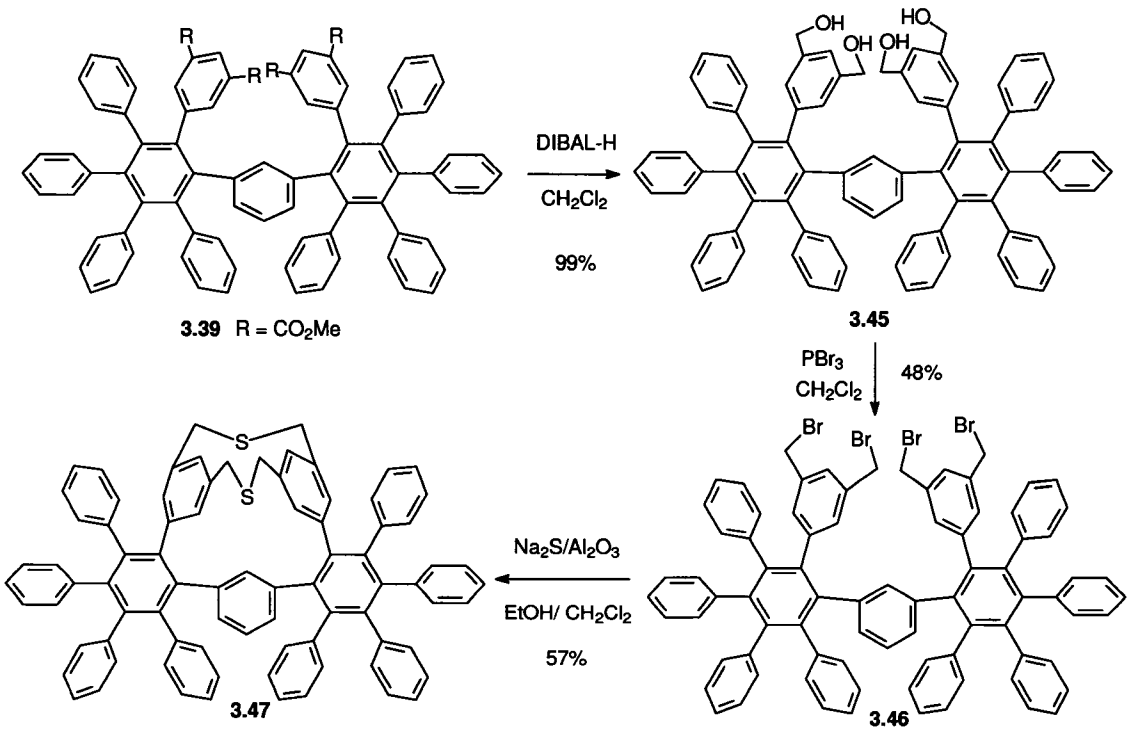
Figure 3.04. ^{1}H NMR spectrum of **3.39** (toluene-d_8, 5 °C).

Upon warming to 25 °C, the minor signals in the aromatic region are barely discernable and the major signals at δ 8.36 and 8.33 ppm have either overlapped (temperature shift) or coalesced. The minor signal at δ 3.60 ppm has broadened to the point that it is almost a shoulder on the peak at δ 3.47. This supports the notion that the partner to the signal at δ 3.60 ppm is underneath the major signal at δ 3.43 ppm. At 35 °C, the minor signals are no longer observable and the major signals are all relatively broad. Assuming a chemical shift of δ 3.43 for the presumed hidden signal of the minor isomer and a coalescence temperature of 27±5 °C (300±5 K), $\Delta G^{\neq}$ for the rotation of the bis(methoxycarbonyl)phenyl groups in this isomer is 14.4±0.3 kcal/mol. The two major isomer signals at δ 3.47 and δ 3.43 ppm coalesce at 50±5 °C (323±5 K), from which $\Delta G^{\neq}$ = 16.5±0.3 kcal/mol can be calculated. These observations are consistent with the minor isomer being *cis*-**3.39**, in which two ester-bearing aryl groups are oriented toward one another. One would expect this conformer to be geometrically distorted to some degree, most likely in the direction of the geometry of the transition state for aryl group rotation. Consequently, $\Delta G^{\neq}$ value for aryl group rotation in the minor isomer (*cis*-**3.39**) should be lower than that for the major isomer (*trans*-**3.39**).

Upon warming to 75(±5) °C, which was the temperature limit imposed by the NMR facility at the time, the signal for H_G (δ 5.72) had broadened into the baseline, which indicated that the coalescence temperature with its exchange partner $H_{G'}$ (somewhere in the multiplet δ 7.00-6.68). The energy barrier for the rotation of A ring is then calculated to be 15.6±0.3 kcal/mol, and this number is within the normal range for a biphenyl rotation of hexaphenylbenzenes.[15] Clear information about the *cis/trans* interconversion, which is also a biphenyl rotation, could not be extracted because, in the aromatic region,

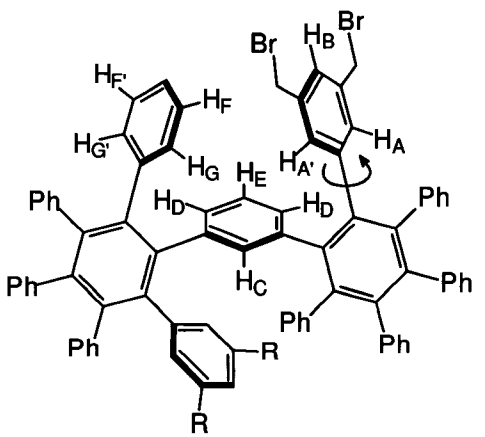
it was unclear which minor peak was coalescing with which major peak and in the aliphatic region, since the coalescing signals were very close in chemical shifts. On top of that, changes due to peripheral phenyl group rotations were occurring. However, assuming $\Delta\nu$=34.5 Hz[16] and a coalescence temperature of 60±15 °C, $\Delta G^{\neq}$=16.7±0.8 kcal/mol. It would appear as though all of the biphenyl rotations have similar activation barriers. It may well be that biaryl rotation of the peripheral phenyl groups is correlated.

Reduction of tetraester **3.39** using DIBAL-H afforded tetraol **3.45** (99%) (Scheme 3.12). The room temperature ^{1}H NMR spectrum (in $CDCl_3$) of **3.45** was complicated and many of the signals were broad. A DNMR experiment (DMSO-d_6) revealed significant changes between 25 °C and 75 °C (Appendix B), but the spectra were too complex to be meaningfully interpreted.



Scheme 3.12. Synthesis of dithiacyclophane **3.47**.

Tetraol **3.45** was reacted with PBr_3 to yield tetrabromide **3.46** (43%). Its ^1H NMR spectrum ($CDCl_3$, room temperature) contained a 4H singlet (δ 4.50 ppm) and a 4H AB system (δ 4.28, 4.18, J_{AB}=9.9 Hz, Δν=50.6 Hz) for the benzylic protons. In the aromatic region, three 2H singlets are observed (δ 7.08, 7.06 and 7.01), which correspond to H_A, $H_{A'}$ and H_B (Fig. 3.05) (in no particular order). As with tetraester **3.39**, an upfield 2H doublet (δ 5.49) was observed, which presumably corresponds to H_G. A $^1H,^1H$-COSY experiment indicated that the 2H triplet at δ 5.49 ppm is correlated to the signal at δ 6.42 ppm (t, J=8.1 Hz, 2H), which is assigned to the neighboring proton H_F. The ^1H triplet at δ 6.11 and 2H doublet δ 6.19 ppm are correlated and must correspond to the protons on the central *m*-phenylene (H_E and H_D, respectively). A low cut of the $^1H,^1H$-COSY experiment indicated that the signal for H_D is also correlated with a 1H singlet at δ 6.88 ppm (on the edge of the main group of aromatic peak (δ 6.86-6.65, 36H). Based on this evidence, it appears as though tetrabromide **3.46** is present as a single rotamer (either *cis* or *trans*-**3.46**) at room temperature in $CDCl_3$. Again, for steric reasons, this was tentatively assigned to be *trans*-**3.46**.



trans-**3.46**

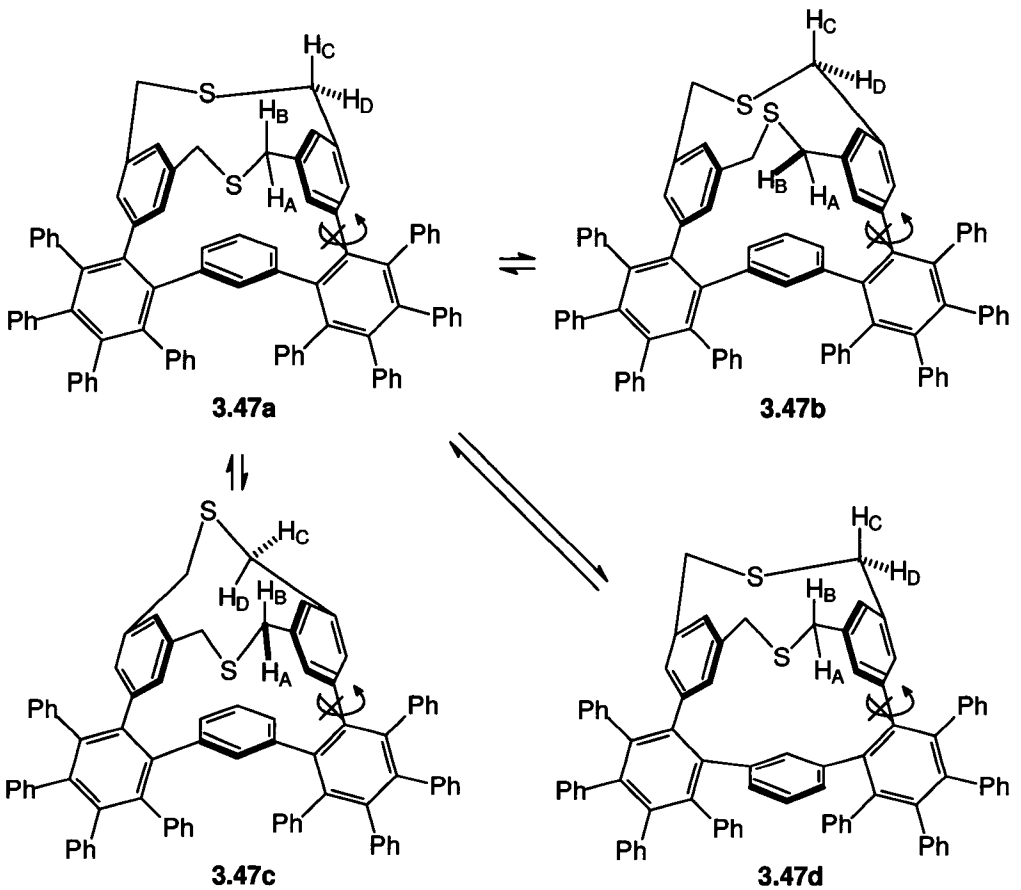
R=CH_2Br

Figure 3.05. Tetrabromide **3.46** (only the *trans* isomer is shown).

A DNMR experiment was also performed (toluene-d_8, 5 °C to 75 °C). At 5 °C, an AB system (δ 4.07, 3.96, J_{AB}=9.5 Hz, Δν=53.5 Hz) and an AX system (δ 3.89, 3.56, J_{AX}=9.8 Hz, Δν=161.2 Hz) were observed in the benzylic region, which correspond to the benzylic protons in **3.46**. Signals for H_G and H_F were observed as a 2H doublet (δ 5.65 ppm) and a 2H triplet (δ 6.27 ppm), respectively. Signals for H_A, $H_{A'}$, H_B, H_C and H_E are overlapped with other peaks and could not be identified. At the temperature limit (75 °C), the AB system is near coalescence and the AX system is broad, but not yet near coalescence. Assuming T_c=80±5 °C for the AB system, an energy barrier of $\Delta G^{\neq}$=17.5±0.3 kcal/mol can be calculated (Δν'=58.3 Hz).[17] Thus there is, if anything, only a slightly difference in the activation barrier to biphenyl rotation between **3.39** and **3.46**.

Tetrabromide **3.46** was converted to dithiacyclophane **3.47** in 57% yield using Na_2S/Al_2O_3 (Scheme 3.12). Compared to the previously discussed *para*-phenylene analog (**3.21**), this reaction was problematic. It took longer for the starting material to be consumed and the reaction afforded a number of unidentified by-products along with **3.47**. This made the isolation of **3.47** difficult and had a slightly detrimental effect on the yield. This result also provided some indirect information about the conformational behavior of **3.46**. The comparative difficulty of this reaction (*cf.* tetrabromide **3.37** to dithiacyclophane **3.21**) supports the tentative conclusion that **3.46** exists primarily in the *trans*-conformation at room temperature, which cannot lead to **3.47**. By comparison, **3.34**, which reacted rapidly and in high yield to give **3.21**, was observed to exist as a ~1.7:1 mixture of *cis* and *trans* rotamers at room temperature.

The benzylic region of the ^{1}H NMR spectrum (room temperature, $CDCl_3$) of **3.47** is similar to that of its precursor **3.46**. A 4H singlet (δ 3.55 ppm) and a 4H AB system (δ 3.22 and 2.97 ppm, J_{AB}=14.8 Hz, Δν=127.3 Hz) were observed. The aromatic region contains, as before, a large group of overlapped peaks (δ 6.89-6.62), as well as some individual peaks (1H singlet at δ 6.94, 2H singlet at δ 6.47, 2H doublet at δ 6.25 (J=7.6 Hz), 2H singlet at δ 6.18). Interestingly, the upfield doublet for H_G in **3.46** and **3.39** was absent, which indicated that the formation of the thioether bridges prevents the adoption of any "edge-to-face" orientation of the opposing phenyl groups beneath the *m*-phenylene ring (Scheme 3.13).



Scheme 3.13. Dithiacyclophane **3.47**.

A DNMR experiment was performed in toluene-d_8 from 5 °C to 75 °C, and two 4H AB systems were observed at all temperatures. This is consistent with the structure of **3.47** (Scheme 3.13), because neither the indicated rotation nor a *cis-cis* interconversion[18] is accessible. However, some clear changes were observed. At 5 °C, a broad 4H AB system appeared at δ 3.47 and 3.32 ppm (J_{AB}=13.7 Hz, Δν=75.3 Hz) and a sharper one was observed at δ 3.20 and 3.13 ppm (J_{AB}=14.7 Hz, Δν=31.2 Hz). At 25 °C, the broad AB system became sharp. At 75 °C, one 4H AB system appeared at δ 3.42 and 3.38 ppm, J_{AB}=14.7 Hz, Δν=22.2 Hz and the other one was observed at δ 3.19 and 3.09 ppm, J_{AB}=14.8 Hz, Δν=49.0 Hz). Upon warming from 5 °C to 75 °C, the value of Δν for the downfield AB system decreased steadily from 75.3 Hz to 22.2 Hz and the value of Δν for the higher field AB system increased steadily from 31.2 Hz to 49.0 Hz (Table 3.01). These changes are presumably associated with bridge wobbles (*pseudo-chair / pseudo-boat* interconversions), which do not cause exchange within pairs of geminal protons (*i.e.* H_A with H_B and H_C with H_D), but rather change the chemical environment of both. Each bridge conformer will have its own unique AB system and the observation at any given temperature will be a weighted average of these two spectra according to their relative populations, which would be expected to change with temperature ($\Delta G = \Delta H - T\Delta S = -RT\ln K$). As the rate of the bridge wobble approaches the time scale, broadening occurs, and this is what was observed at 5 °C.

Another conformational process is available to **3.47**, namely a flip of the *m*-phenylene ring (**3.47a→3.47d**). This process exchanges the environments of the two CH_2SCH_2 bridges. When this process is fast, a single AB system would be observed in the ^1H NMR spectrum. However, since two sharp AB systems were observed at 75 °C, it can be

calculated that this process is not close to its coalescence temperature. The energy barrier to this process is at least 18.2 kcal/mol and likely substantially higher.[19]

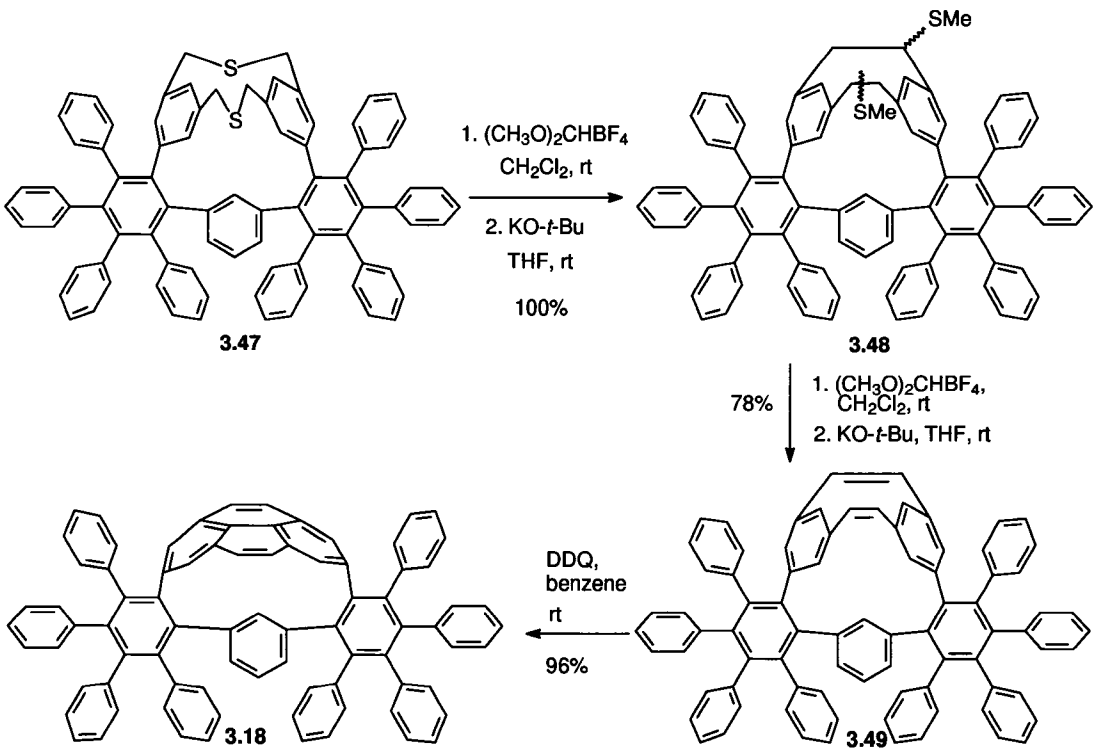
Table 3.01. Δν for AB systems in the DNMR spectra of **3.47** (appendix B)

Temperature (°C)	5	25	45	65	75
Δν (downfield) (Hz)	75.3	55.0	39.8	27.6	22.2
Δν (upfield) (Hz)	31.2	38.3	43.6	47.5	49.0

Bis(*S*-methylation) of dithiacyclophane **3.47** with Borch reagent, followed by treatment of the resulting bis(methylsulfonium) salt with *t*BuOK afforded isomer mixture **3.48** (Scheme 3.14). This was then treated with Borch reagent to remethylate the sulfur atoms and the resulting bis(dimethylsulfonium) salts were reacted with *t*BuOK to afford cyclophanediene **3.49** (78% from dithiacyclophane **3.47**).

The last step of the synthesis was a VID reaction. Cyclophanediene **3.47** was stirred in the presence of DDQ in benzene at room temperature. However, after 24 h, only a very faint new spot had appeared on the tlc plate. The mixture was then heated at reflux at 12 h, and the new spot became more intense at the expense of the spot corresponding to **3.49**. The reaction eventually took 7 days at reflux to consume the starting material **3.49** and the desired pyrenophane **3.18** was obtained in 96% yield. The difficulty of this reaction is expected, because the pyrene unit in **3.18** (θ_{calcd} = 117.2°, see section 3.3.5, page 124-126) is predicted to be significantly more distorted than that of **3.17a** (θ_{calcd} = 102.8°). The more distorted pyrene unit in **3.18** should have less ASE and more strain than the one in **3.17a**, which should diminished the energy benefit of the VID reaction.

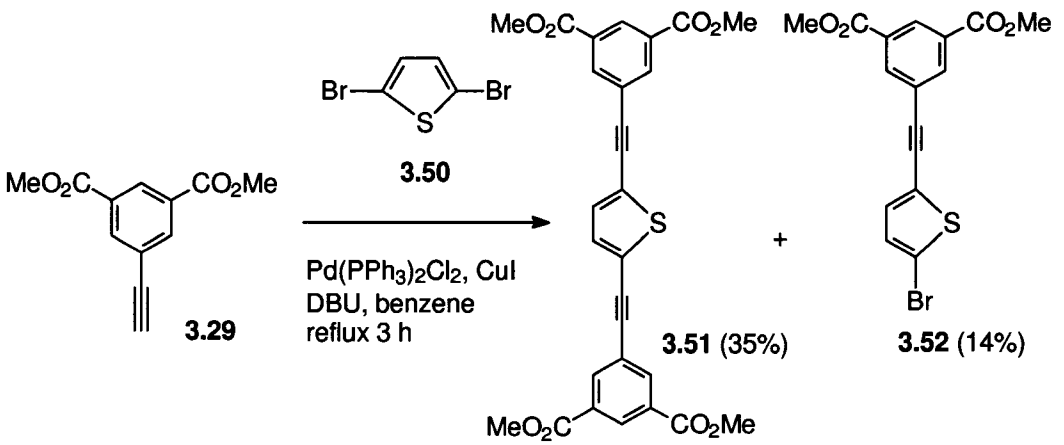
This is consistent with observations that the more distorted pyrene units are, the more difficult to prepare via the VID reaction.[1,20]



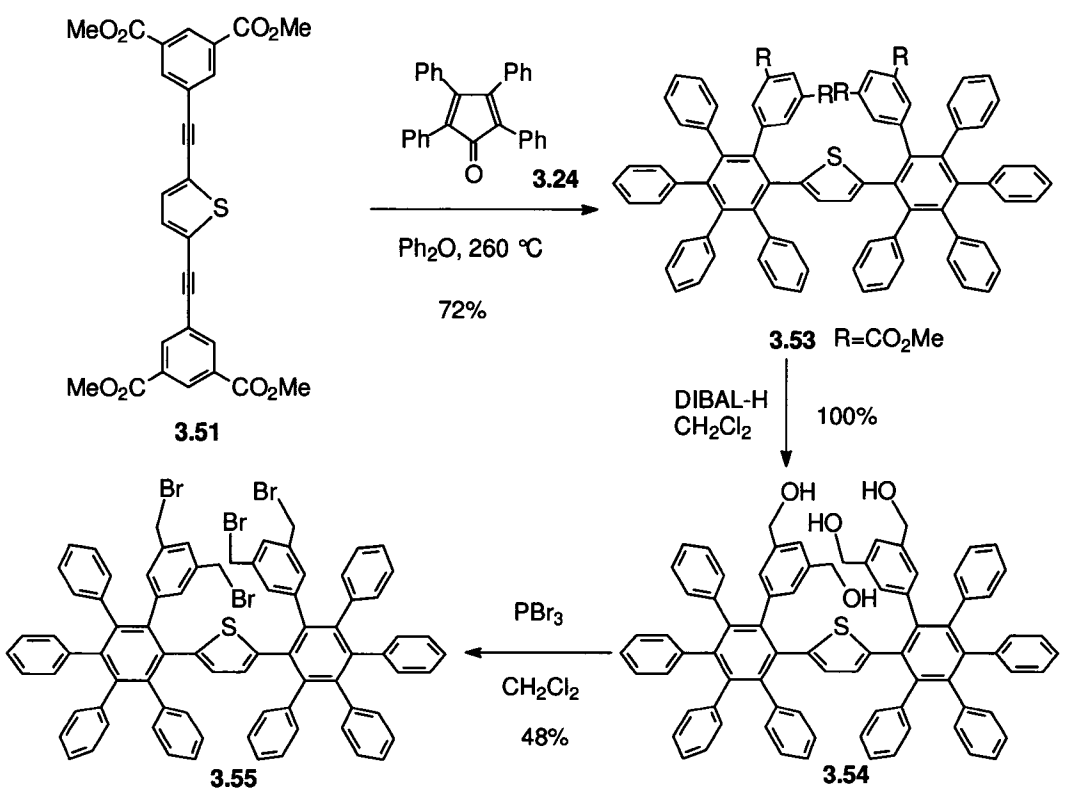
Scheme 3.14. Synthesis of pyrenophane **3.18**.

3.3.3 Synthesis of Pyrenophane 3.19 with a Central 2,5-Thienylene Unit

The synthesis of pyrenophane **3.19**, which contains a central 2,5-thienylene unit, was conducted analogously to those of pyrenophane **3.17a** and **3.18**. The first task of the synthesis was to synthesize diynetetraester **3.51**. The Sonogashira coupling between alkyne **3.29** and 2,5-dibromothiophene (**3.50**) was performed to afford **3.51** in just 35% yield (Scheme 3.15). A by-product isolated from column chromatography was a mono-reacted product. Increasing the ratio of **3.29**:**3.50** to 3:1 or elongating the reaction time resulted in the formation of complicated mixtures and decreased isolated yield.



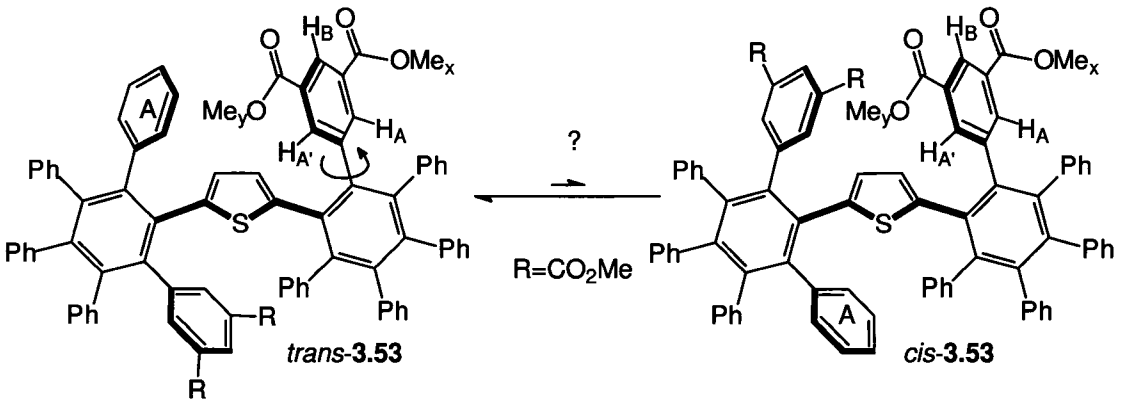
Scheme 3.15. Preparation of tetraester **3.51**.



Scheme 3.16. Synthesis of tetrabromide **3.55**.

The Diels-Alder reaction between diynetetraester **3.51** and tetraphenylcyclopentadienone **3.24**, followed by a chelotropic decarbonylation reaction, afforded tetraester **3.53** (72%) (Scheme 3.16). The ^{1}H NMR spectrum of **3.53** contains a sharp 12H singlet (δ 3.90 ppm), which corresponds to the protons on the methyl esters. This observation is consistent with the presence of a single observable rotamer (presumably *trans*) and fast biaryl rotation. Close inspection of the spectrum revealed the presence of some very small (*ca.* 1:30) signals (δ 8.56, 8.22, 7.89 and 3.83), which *may* be due to a minor rotamer. Whether or not this is the case, it is consistent with structural changes that occur upon going from **3.32** (*p*-phenylene unit: 180° angle between connecting bonds, 6:1 mixture of rotamers) to **3.53** (2,5-thienylene unit: 150° angle,[21] *ca.* 30:1 mixture of rotamers) to **3.39** (*m*-phenylene unit: 120° angle, single isomer). As the angle formed by the connecting bonds of the central arylene unit becomes smaller, the ester groups on opposing rings move closer to one another in the *cis* rotamer. This would be expected to increasingly disfavor the *cis* rotamer. The aromatic region contains several well-resolved peaks besides the main 42H multiplet at δ 6.82-6.66 ppm. The 2H triplet at δ 8.30 (J=1.6 Hz) and 4H doublet at δ 7.75 (J=1.6 Hz) correspond to the internal (H_B) and external hydrogens (H_A and $H_{A'}$) of the bis(methoxycarbonyl)phenyl groups and the 4H doublet at δ 6.53 ppm (J= 7.0 Hz) corresponds to "*ortho*" protons on one pair of symmetry-related peripheral phenyl groups, most likely on the A ring (Scheme 3.17). As with **3.39**, the high field shift may be a consequence of an edge-to-face interaction. Interestingly, the 2H singlet corresponding to the protons on the central 2,5-thienylene unit was observed at δ 5.89 ppm. By comparison, the protons of the thienylene unit in 2,5-diphenylthiophene appear at δ 7.31 ppm.[22] This pronounced shift indicates that, in

$CDCl_3$, **3.53** adopts a conformation in which the hydrogens on the thienylene unit are within the shielding cone of certain peripheral phenyl groups. The observation that biaryl rotation of the peripheral phenyl groups in **3.53** is easier than that in **3.32** and **3.39** can be explained by the absence of an *ortho*-hydrogen on one side of the 2,5-thienylene unit.

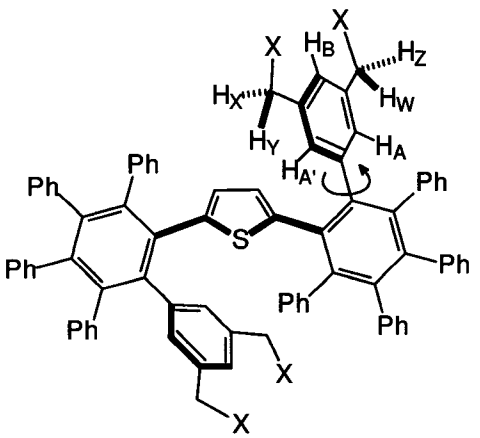


Scheme 3.17. Tetraester **3.53**.

Reduction of **3.53** using DIBAL-H afforded tetraol **3.54** in quantitative yield. In its ^1H NMR spectrum, the thienylene singlet (δ 5.75) was also observed at high field, which indicated that there is no significant conformational difference between tetraol **3.54** and its precursor **3.53**. The rest of the aromatic signals were overlapped. In the benzylic region, an 8H AB system was observed (δ 4.33 and 4.31, J_{AB}=12.8 Hz, Δν=11.1 Hz). As shown in Fig. 3.06, H_X, H_Y, H_Z and H_W should all have different chemical environments, so two 4H AB systems should be observed if biaryl rotation is slow. Barring a remarkable set of chemical shift degeneracies, it can be concluded that biaryl rotation is rapid.

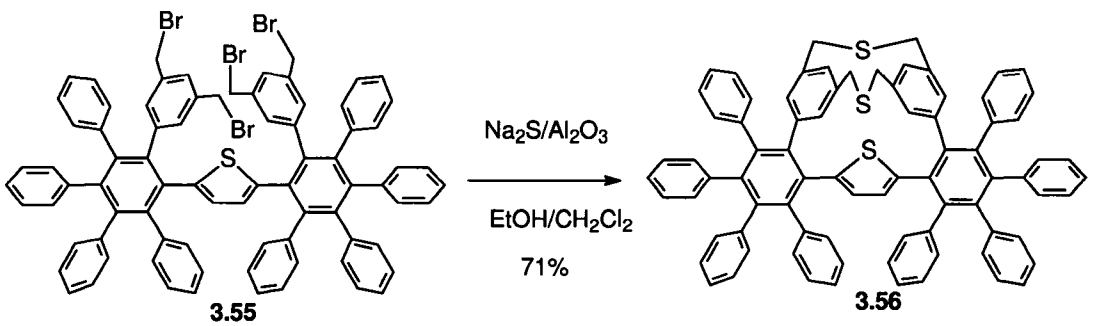
Bromination of tetraol **3.54** using PBr_3 afforded tetrabromide **3.55** in 48% yield. Its ^1H NMR spectrum is similar to that of its precursor **3.54**. Besides a large group of aromatic signals at δ 6.97-6.67 ppm, a sharp high field singlet at δ 5.75 ppm was

observed. The benzylic region contains an 8H AB system (δ 4.23 and 4.20, J_{AB}= 10.2 Hz, Δν=15.4 Hz), which is again consistent with rapid biaryl rotation (Fig. 3.06).



trans-**3.54** X=OH
trans-**3.55** X=Br

Figure 3.06. Tetraol **3.54** and tetrabromide **3.55** (*trans* conformer).



Scheme 3.18. Synthesis of dithiacyclophane **3.56**.

Reaction of tetrabromide **3.55** with Na_2S/Al_2O_3 afforded dithiacyclophane **3.56** in 71% yield (Scheme 3.18). Again, it is clear that *cis* rotamers must be accessible during this reaction. In its ^1H NMR spectrum, the signal for the hydrogens on the central thienylene group appeared at δ 6.07 ppm, which is at slightly lower field than that of **3.53-3.55** (δ 5.89-5.75 ppm). The benzylic region contains two sets of signals due to the two distinct CH_2SCH_2 bridges: a 4H singlet at δ 3.67 ppm, which is presumably a

degenerate AB system, and a 4H AB system (δ 3.33 and 3.18 ppm, J_{AB}=14.7 Hz, Δν=77.8 Hz) (Fig. 3.07). This observation is similar to that of analogous compound **3.47**.

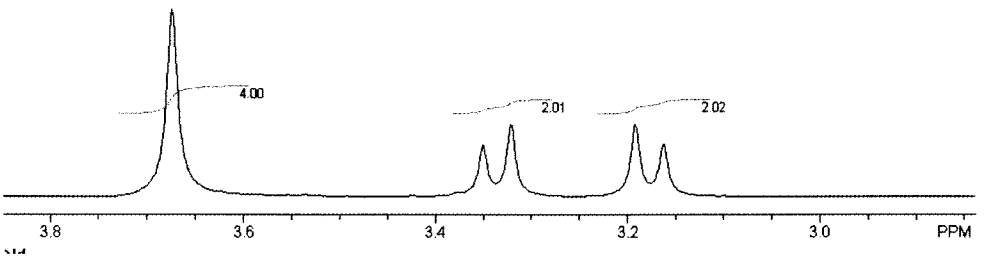
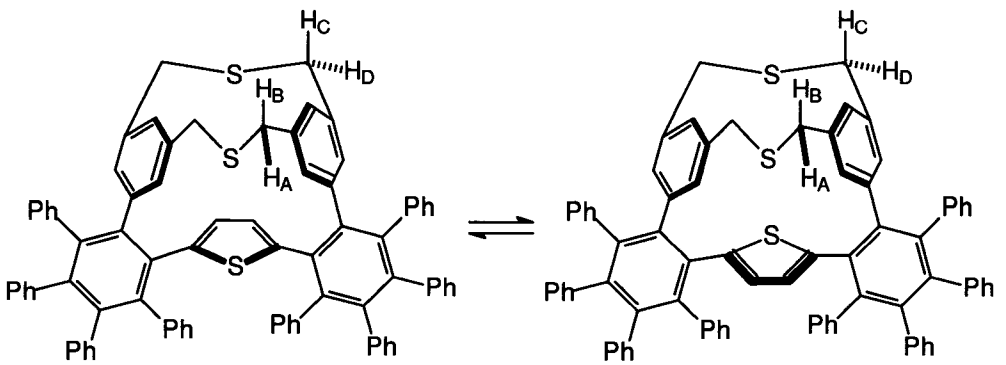


Figure 3.07. ^{1}H NMR of **3.56** (benzylic protons).

As discussed earlier in the case of **3.47**, the observed chemical shifts of benzylic protons (H_A, H_B, H_C and H_D) are weighted averages of the isomers formed by bridge wobbles (*pseudo-chair / pseudo-boat* interconversions). It can be anticipated that the values of Δν for the AB system of geminal protons will change upon temperature changes. Moreover, through a conformational flip of the 2,5-thienylene unit, *i.e.* **3.56a** to **3.56b**, H_A and H_D (or H_B and H_C) will exchange their environments. For these reasons, a DNMR experiment was performed in toluene-d_8 from 5 °C to 75 °C. At 5 °C, the aromatic region contains a sharp 2H singlet at δ 6.00 ppm, which corresponds to the protons on the thienylene unit. The rest of aromatic region consists of a set of overlapping signals together with toluene peaks and is difficult to interpret. In the benzylic region, although overlapping with some impurity peaks (δ 3.45, 3.37, 3.32), two 4H AB systems (δ 3.51 and 3.36, J_{AB}=13.7 Hz, Δν=73.2 Hz; δ 3.23 and 3.17, J_{AB}=14.6 Hz, Δν=32.0 Hz) are observed. The lower field signal is somewhat broad. As the temperature was gradually increased to 75 °C, the signals broadened, coalesced (*ca.* 55 °C) and eventually became a broad singlet. This indicated exchange between the two sets of geminal protons (Scheme

3.19). Based on this observation (T_c=55±10 °C, Δν=64.6-169.8 Hz), the energy barrier for this process was calculated to be 15.7±0.8 kcal/mol using the Eyring equation. The singlet for the thienylene protons started as a sharp singlet at 5 °C, broadened in the range 25 °C-65 °C and became sharper at 75 °C. It also moved steadily downfield over this temperature range. In comparison to the results obtained from the DNMR experiment of **3.56** and **3.47**, it is clear that the conformational flip of the 2,5-thienylene unit is easier than that of *m*-phenylene unit. It has been reported that, unlike *m*-terphenyl systems, 2,5-diphenylthiophene derivatives can adopt a coplanar geometry with the attached aryl groups.[23] This may indicate that the transition state (having a coplanar or nearly coplanar diphenylthiophene system) for the conformational flip of **3.56** is less unfavorable than that of **3.47**.

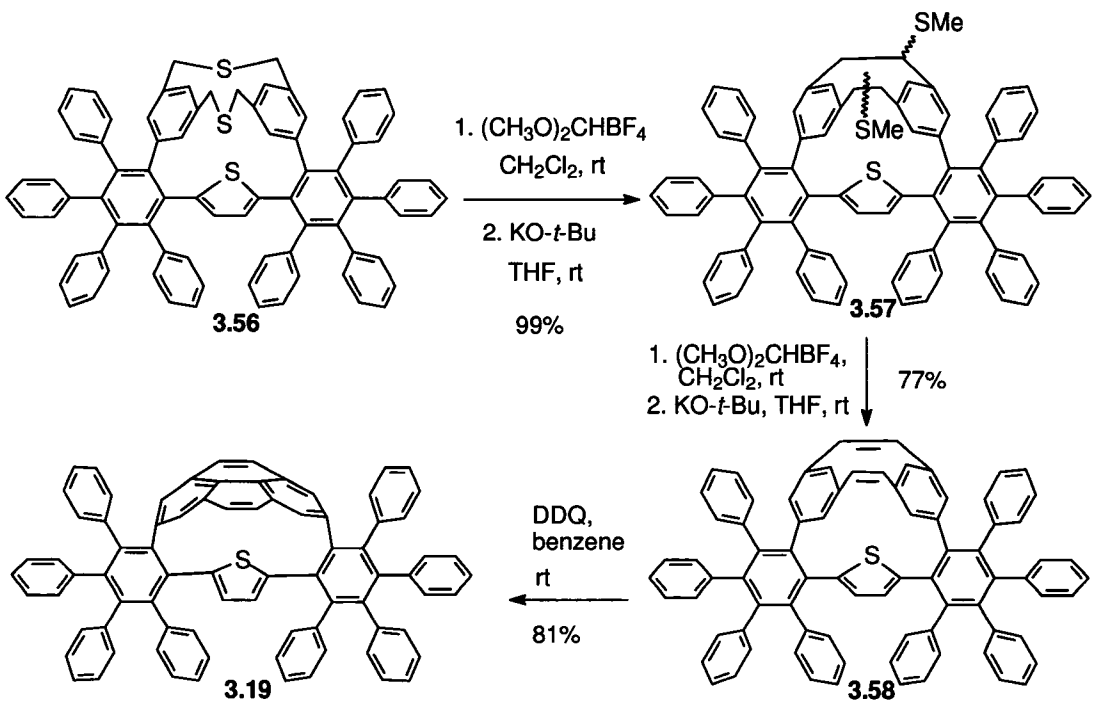


3.56a **3.56b**

Scheme 3.19. Conformational flip of dithiacyclophane **3.56**.

Bis(*S*-methylation) of dithiacyclophane **3.56** with Borch reagent, followed by treatment of the resulting bis(methylsulfonium) salt with *t*BuOK afforded isomer mixture **3.57** (Scheme 3.20). This was then treated with Borch reagent to remethylate the sulfur atoms and the resulting bis(dimethylsulfonium) salts were reacted with *t*BuOK to afford

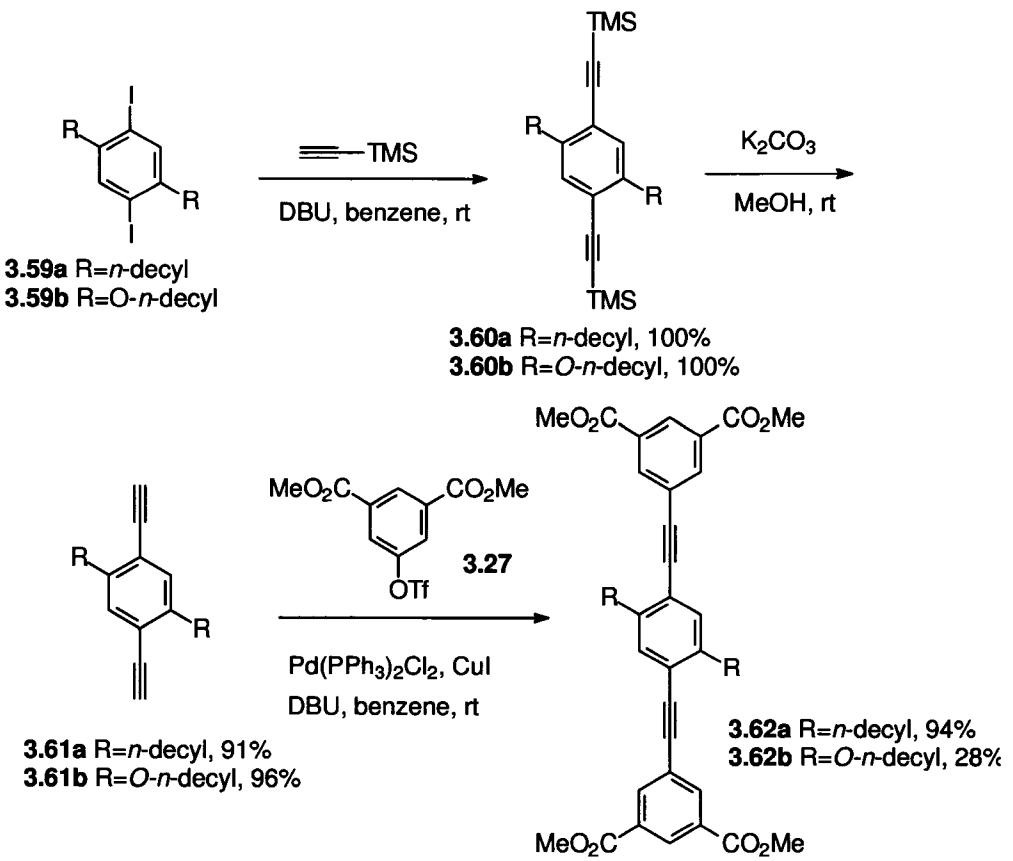
cyclophanediene **3.58** (77% from dithiacyclophane **3.56**). In its ^{1}H NMR spectrum of **3.58** ($CDCl_3$, room temperature), the thienylene unit has its signal at δ 5.90 ppm (singlet, 2H) and the alkene bridges give rise to two 2H singlets (δ 6.26 and 6.07), which are slightly broad. The internal and external proton signals for the cyclophanediene system could not be identified. A DNMR experiment was performed (toluene-d_8, 5 °C to 75 °C). At 5 °C, the two signals for alkene bridges were sharp singlets (δ 6.50 and 6.30 ppm). When the temperature was increased, these two peaks became broader. At 51 °C, these two peaks coalesced and a singlet was observed at higher temperatures. The energy barrier for the conformational flip of the thienylene unit was then calculated to be 15.6±0.3 kcal/mol using Eyring equation (T_c=55 °C, Δν=100.0 Hz), which is similar to that of dithiacyclophane **3.56** (15.7±0.8 kcal/mol).



Scheme 3.20. Synthesis of pyrenophane **3.19**.

The last step of this synthesis, the VID reaction, took only 5 minutes of stirring at room temperature to go to completion and afforded pyrenophane **3.19** in 81% yield. The quickness of this reaction compared to the one leading to pyrenophane **3.18** indicated that this product was significantly less strained than **3.18**, as was predicted by AM1-calculations (**3.18**: θ_{calcd} = 117.2°. **3.19**: θ_{calcd} = 111.4°, see Section 3.3.5, page 124-126).

3.3.4 Attempted Synthesis of Pyrenophanes 3.17b and 3.17c

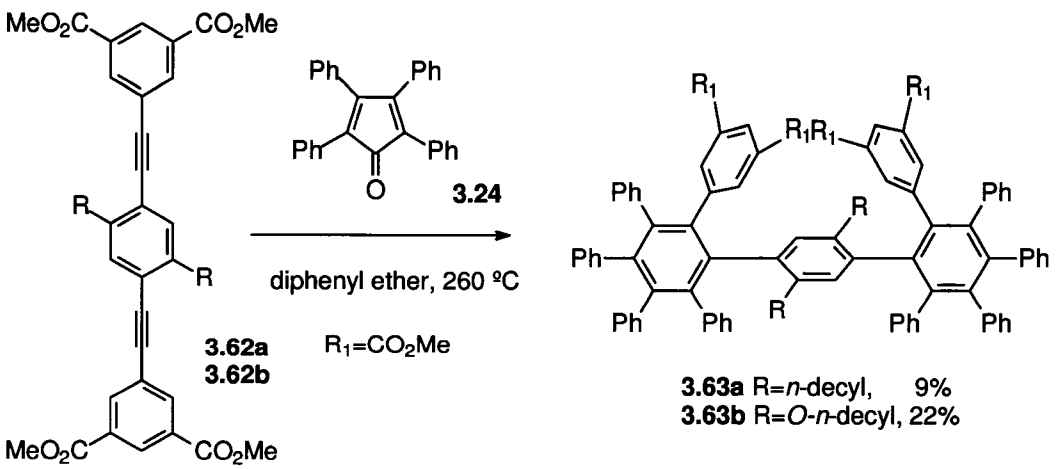


Scheme 3.21. Synthesis of diynetetraesters **3.62a** and **3.62b**.

Pyrenophanes **3.17b** and **3.17c** differ from **3.17a** in that they contain long aliphatic chains on the central benzene ring. As such, the first task for the syntheses of these targets was the preparation of requisite diynetetraesters **3.62**. Direct precursors **3.61a** and

3.61b are known compounds,[24] and the synthetic work toward **3.61a** and **3.61b** followed the published procedures.

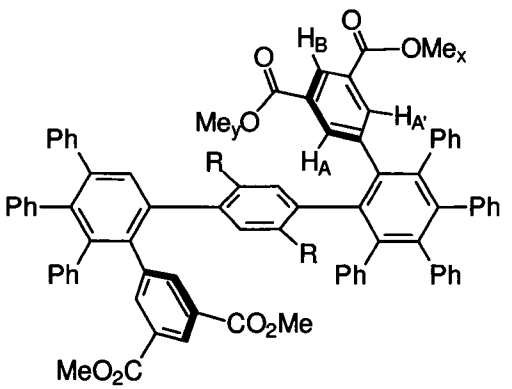
The first step of this approach was a Sonogashira cross-coupling of diiodides **3.59a** and **3.59b** with TMSA to afford **3.60a** and **3.60b**, both quantitatively (Scheme 3.21). Protodesilylation afforded terminal alkynes **3.61a** (91%) and **3.61b** (96%). Subsequent Sonogashira coupling reactions with triflate **3.27** afforded **3.62a** (94%) and **3.62b** (28%). The low yield for the formation of **3.62b** was probably due to the homocoupling of the diyne **3.61b**.[23b] The diynetetraesters **3.62a** and **3.62b** were then subjected to Diels-Alder reaction with **3.24** followed by chelotropic decarbonylation of the initial adducts to furnish **3.63a** (9%) and **3.63b** (22%) (Scheme 3.22). The better yield for **3.63b** may be due to the smaller size of O vs. CH_2 and the superior electron donating ability of decyloxy vs. decyl (the Diels-Alder reaction is an inverse electron demand Diels-Alder reaction). Furthermore, it has been reported that benzylic radicals can be generated thermally at high temperatures (*i.e.* 260 °C).[25] Whatever the case, the yields for **3.63a** and **3.63b** were too low to provide sufficient material to continue the syntheses.



Scheme 3.22. Preparation of **3.63a** and **3.63b**.

The ^{1}H NMR spectrum of the tetraester **3.63a** contains three sharp singlets at δ 8.18, 7.65 and 7.62 ppm for the protons on the ester-bearing rings (H_B, H_A and $H_{A'}$ in Fig. 3.08). Biaryl rotation is therefore slow at room temperature. The spectrum also contains two sharp 6H singlets (δ 3.90 and 3.80 ppm), which correspond to the two different ester methyl groups for a single isomer (presumably *trans*). The rest of aromatic region consists of two clusters of signals at δ 7.33-7.12 and δ 6.92-6.50, as well as a 2H triplet (J=7.6 Hz) at δ 6.35. Upon close inspection, the methyl ester signals appear to be accompanied by small peaks (≈20:1 intensity ratio) at δ 4.56 and 3.80, which might due to the minor conformer (presumably *cis*-**3.63a**). Corresponding minor peaks for the protons on the ester-bearing ring may also be present, but the presence of some impurity signals made this difficult to assess. The diastereotopic benzylic protons appear as 2H multiplet at δ 2.29-2.25 and 2.13-2.09. A DNMR experiment was performed (toluene-d_8, 25 °C -100 °C).[26] At 25 °C, all signals are sharp. Upon heating to 100 °C, no significant broadening effect was observed. This observation is not surprising because the introduction of the two long aliphatic groups on the central *p*-phenylene would be expected to raise the energy barrier to the biaryl rotation that results in *cis* / *trans* isomerization to *ca.* >30 kcal/mol.[15] Furthermore, if the biaryl rotation is correlated, then all biaryl rotations will be suppressed. The ^{1}H NMR spectrum of **3.63b** is similar to that of **3.63a**. Two sharp 6H singlets (δ 3.86 and 3.80) were observed, which correspond to the protons on the methyl ester groups. Singlets for the internal proton H_B (δ 7.94) and external protons H_A and $H_{A'}$ (δ 7.79 and 7.49) were also observed. It is interesting to note the significant differences between the chemical shifts of these protons (H_A, $H_{A'}$ and H_B) between **3.63a** and those of **3.63b**. A sharp 2H singlet was also observed (δ 6.17), which

corresponds to the protons on the central *p*-phenylene ring. Two different 2H multiplets (δ 3.64-3.59 and 3.46-3.42) were observed, which correspond to the diastereotopic protons on the benzylic OCH_2 groups. Signals attributable to a minor isomer are not clearly visible.



anti-**3.63a** R=*n*-decyl
anti-**3.63b** R=*O*-*n*-decyl

Figure 3.08. Tetraesters **3.63a** and **3.63b**.

3.3.5 Structure of Pyrenophanes 3.17a, 3.18 and 3.19

Attempts to grow crystals of pyrenophanes **3.17a**, **3.18** and **3.19** were performed and a crystal of **3.19** was obtained in good quality from a mixed solvent of chloroform and heptane. Suitable crystals of **3.17a** and **3.18** were not obtained. The crystal structure was determined in collaboration with R. Pascal (Princeton). The attempts to solve this crystal structure are still underway and a major complication is an occupational disorder in which there are two orientations of the molecule in one site in a *ca.* 5:1 ratio (See the structure in Appendix A). A preliminary bend angle (θ) of 102.8° has been determined, but the structure is still being refined.

As discussed in Chapter 1, the bend angle (θ) is an important parameter of a pyrenophane, which describes the extent to which a pyrene unit is bent. In the absence of experimentally derived data, the bend angles for pyrenophanes **3.17a-3.19** were calculated at the AM1 level of theory, and the results are listed in Table 3.02. The structures of **3.04** and **3.17a** were also calculated at the B3LYP/6-311G** level of theory in collaboration with Cyrański (University of Warsaw). The experimental (X-ray) value for the bend angles of **3.02**, **3.03** and **3.19** are also listed.

Table 3.02. Bend angle θ for pyrenophanes **3.04** and **3.17a-3.19**.

Pyrenophane	$\theta_{calcd\ (AM1)}$	$\theta_{calcd\ (DFT)}$	$\theta_{X\text{-}ray}$
3.02	106.6°		97.1° and 96.9°
3.03	100.4°		89.7°
3.04	100.7°	93.6°	
3.17a	102.8°	95.8°	
3.18	117.2°		
3.19	111.4°		102.8°

Bend angles are routinely calculated in the Bodwell group at the AM1 level of theory, knowing that these calculations tend to overestimate the degree of bend. In the case of **3.02** and **3.03**, the overestimation is relatively large (9.5-10.7°) and this is also the case for **3.19**. From the single crystal X-ray analysis of **3.19**, the bend angle is 102.8° (9.6° overestimation by the AM1 calculation). In the case of **3.04** and **3.17a**, although no x-ray

data is available, the DFT calculations predicted significantly lower (~7°) bend angles than the AM1 calculations, which means they are probably close to the actual values. In the case of **3.18**, if the AM1 calculation overestimated the bend angle by 7-10°, the actual bend angle should be 107-110°, which is on the edge of being a record number (current record holder, as discussed in Chapter 1, is 109.2° for **1.94b**).

According to AM1 calculations, for the three newly synthesized pyrenophanes (**3.17a**, **3.18** and **3.19**), **3.17a** has the smallest value of θ (102.8°) and **3.18** has the largest (117.2°). This observation is entirely consistent with their structures. As shown in Fig. 3.09, the distances between the two benzylic carbon atoms in *p*-xylene, *m*-xylene and 2,5-dimethylthiophene are 5.77 Å, 5.01 Å and 5.31 Å, respectively. According to these numbers, the bridge in **3.18** should be shortest among the three pyrenophanes, so the pyrene unit should be the most bent. Similarly, the pyrene unit in **3.17a** should be the least bent. The pyrene unit in **3.19** should be bent to an intermediate degree.

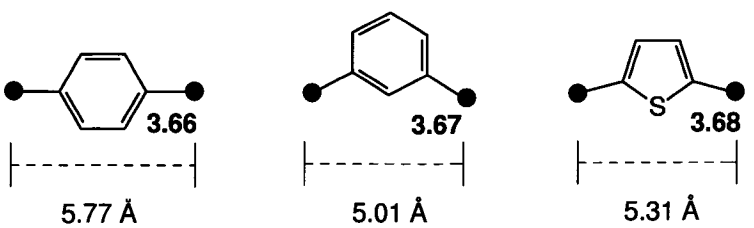


Figure 3.09. Distances between the two benzylic carbon atoms of *p*-xylene, *m*-xylene and 2,5-dimethylthiophene (AM1 calculation).

3.3.6 NMR Spectroscopy of the Pyrenophanes

3.3.6.1 ^{1}H NMR Spectrum of Pyrenophane 3.17a

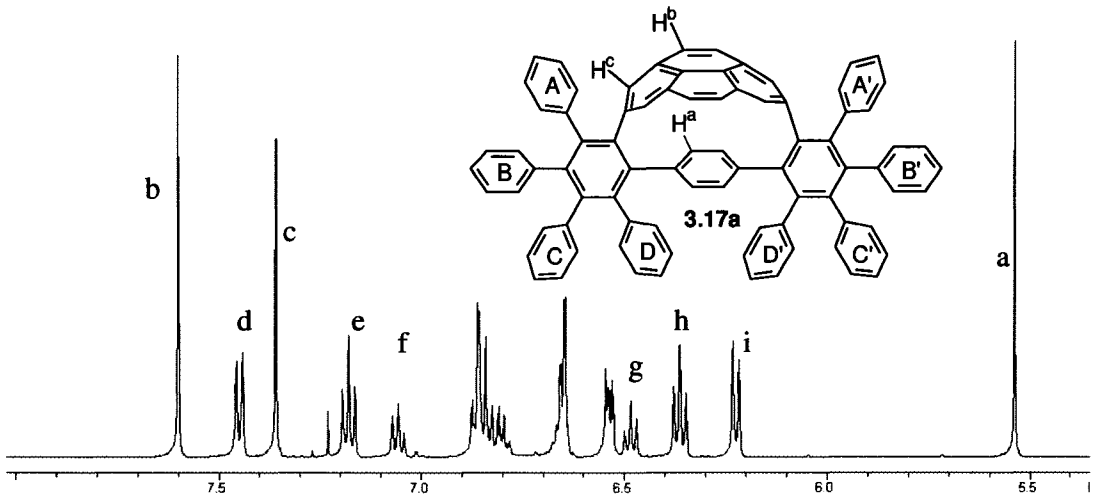


Figure 3.10. ^{1}H NMR spectrum of pyrenophane **3.17a**.

The ^{1}H NMR spectrum of pyrenophane **3.17a** contains three sharp 4H singlets at δ 7.61 (H^b), 7.36 (H^c) and 5.54 (H^a) ppm, which correspond to the protons on the pyrene moiety and the central *p*-phenylene unit. The chemical shift of H^a is at significant higher field (Δδ=2.26 ppm) than the corresponding proton in *p*-terphenyl, which resonates as δ 7.67 ppm. This is because H^a is situated within the shielding zone of the pyrene system and thus appears at high field. This is similar to the analogous protons of pyrenophane **3.04** (δ 5.67 ppm).[4] The slightly further upfield shift of H^a in **3.17a** may be due to an additional shielding effect of the two proximate phenyl groups (D and D') or simply a small change in the position of H^a in the shielding cone of the pyrene unit. The assignments of H^b and H^c were based on a NOESY experiment. When the signal for H^a was irradiated, enhancement (1.42%) was observed for the singlet at δ 7.36, which

indicated that this signal should correspond to the protons on the apical ring (H^c). (According to an AM1-calculated structure, the distance between H^a and H^c is 3.24 Å and the distance between H^a and H^b is 4.46 Å).

The remaining signals are more spread out than those of the precursor molecules **3.32**, **3.33**, **3.34**, **3.21** and **3.20**. However, it is still difficult to definitively assign any of them. A $^1H,^1H$-COSY experiment revealed that signals d (δ 7.45, d, *J*=7.1 Hz, 4H), e (δ 7.18, t, *J*=7.7 Hz, 4H) and f (δ 7.06, t, *J*= 7.0 Hz, 2H) correspond to the protons on the same phenyl group. Similarly, signals g (δ 6.49, t, *J*=7.3 Hz, 2H), h (δ 6.36, t, *J*= 7.4 Hz, 4H) and i (δ 6.22, d, *J*= 7.9 Hz, 4H) correspond to the protons on another phenyl group. Since the D ring lies beneath the pyrene and the *p*-phenylene units, its protons might be expected to appear at relatively high field. As such, signals g, h and i likely correspond to the protons on the D ring. By the same token, the lower field signals (d, e and f) are most likely due to the protons on the A ring. Here, one of the neighboring aryl groups (the pyrene system) is bent away from it, which would be expected to take any shielding effect with it. Three multiplets (22H total) appeared at δ 6.87-6.53 ppm, which presumably correspond to the protons on the B and C rings.

3.3.6.2 ^{1}H NMR Spectrum of Pyrenophane 3.18

In the ^{1}H NMR spectrum of **3.18**, the most upfield signal (δ 4.74 ppm, 1H, s) corresponds to the internal proton of the *m*-phenylene ring (H^a) (Fig. 3.10). A low cut of the $^1H,^1H$-COSY spectrum indicated that this signal is correlated with a 2H doublet (*J*=7.8 Hz) at δ 6.18 ppm, which is therefore the proton H^b ("*meta*" to H^a). It is also observed that H^b is correlated with its neighboring 1H triplet (δ 6.20 ppm, *J*=7.6 Hz),

which must correspond to H^c. Four 2H singlets (δ 7.41, 7.36, 7.17, 6.86 (overlapped with a group of multiplets at δ 6.91-6.86)) were also observed, which should correspond to the protons on the pyrene unit. The observation of four signals is expected because the replacement of the *p*-phenylene with an *m*-phenylene unit lowers the symmetry of the molecule from C_{2v} (**3.17a**) to C_s (**3.18**). In order to assign the four pyrene signals, an NOESY experiment was performed. When the 2H singlet at δ 7.41 ppm was irradiated, enhancements of the 2H singlet at δ 7.17 ppm (1.24%) and the 2H doublet at δ 6.18 ppm (H^b) (2.30%) were observed. This indicated that the signals at δ 7.41 and 7.17 ppm are due to protons H^j and H^h, respectively, which are situated over H^b. The assignment of H^h to the higher field signal was made because (1), in the AM1-calculated structure, H^h is much further from H^b (4.16 Å) than H^j (2.43 Å), and (2) an nOe between the protons analogous to H^b and H^j was also observed in **3.02**. As expected, the signals at δ 7.36 and δ 6.86 exhibited mutual enhancement (1.29%) and they were assigned to H^i and H^g, respectively. The higher field signal was assigned to H^g because H^g is correlated to H^j in the $^1H,^1H$-COSY spectrum ("*meta*"-coupling). The unusually high field chemical shift of H^g can be explained by its situation within the shielding cone of the peripheral phenyl group A in the AM1-calculated structure. The H^h resonates at higher field than H^i is consistent with the location of H^h directly above the *m*-phenylene ring, *i.e.* in its shielding cone. In contrast to what was observed for **3.02**, H^g appears at higher field than H^h. This suggests that the above-mentioned shielding effect of the peripheral phenyl group A is strong.

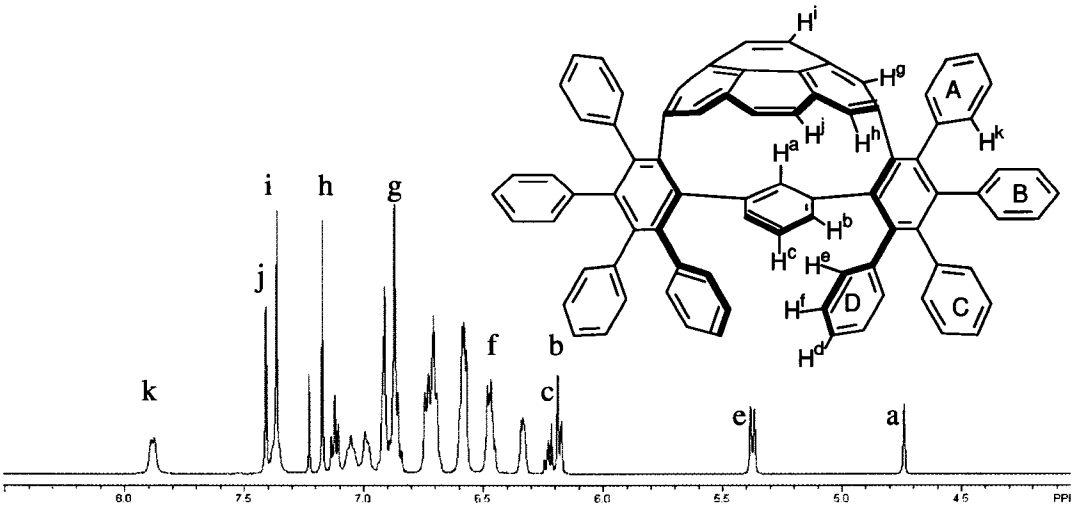


Figure 3.11. ^{1}H NMR spectrum of pyrenophane **3.18**.

The remaining signals were quite spread out, but only a few of them were not overlapped. A relatively high field signal at δ 5.38 (d, *J*=7.3 Hz, 2H) was tentatively assigned to H^e, which is situated in the shielding zone of the *m*-phenylene ring in the AM1-calculated structure. The chemical shift of H^a is at significantly higher field (Δδ=3.06 ppm) than the corresponding proton in *m*-terphenyl, which resonates at δ 7.80 ppm.[5] The signal for H^b also appears further upfield (Δδ=1.85-2.20 ppm) than the corresponding protons in *m*-terphenyl (δ 7.58-7.23 ppm), but the effect is smaller. This suggests that H^a is located more deeply within the shielding zone of the pyrene unit than H^b. Indeed this is what is expected based on simple molecular models and the AM1-calculated structure (Fig. 3.12). The most downfield signal is a 2H doublet (δ 7.87 ppm, *J*=6.8 Hz). This signal is tentatively assigned to the "*ortho*" protons on peripheral phenyl group A for the same reasons used to assign a similar signal in the spectrum of **3.17a** (page 127). This signal was somewhat broad at room temperature in $CDCl_3$, which indicates that the coalescence temperature (biaryl rotation) is not much higher than room temperature.

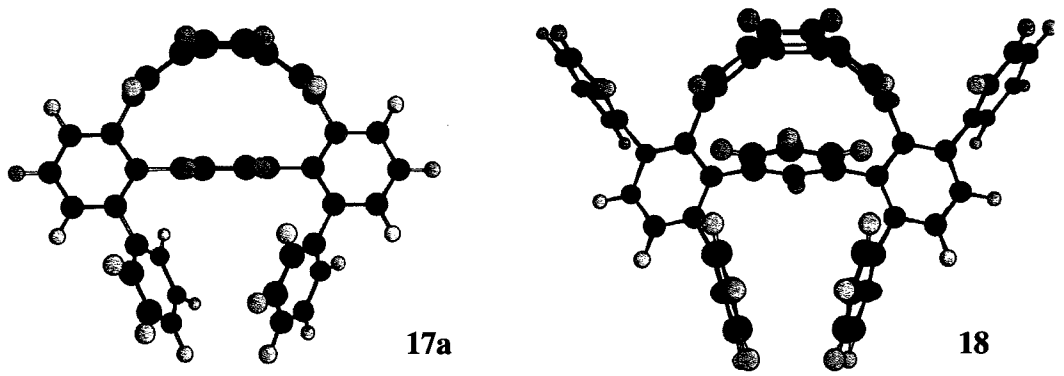


Figure 3.12. AM1-calculated structures of **3.17a** and **3.18** (some peripheral phenyl groups are omitted).

A DNMR experiment was then performed (toluene-d_8, 8 °C to 75 °C) (Fig. 3.13). At 8 °C, all of the signals were sharp. As the temperature rose, several signals gradually broadened. However, meaningful information could only be extracted from signal "m", which was assigned to H^k in Fig. 3.11 based on its downfield chemical shift. At 65 °C, this signal had broadened to the point of being almost coincident with the baseline. At 75 °C, what appears to be the beginning of an emerging singlet was observed at ~7.6 ppm. If this represents the midpoint of signal "m" and the signal it is coalescing with, then $\Delta\nu \approx 500$ Hz. Based a coalescence temperature of 65 °C, the energy barriers for the phenyl groups rotation can be calculated to be 15.1±0.5 kcal /mol. Over the entire temperature range, the signals of the pyrene protons remained sharp, which indicates that an *m*-phenylene flip has a relatively high barrier to rotation.

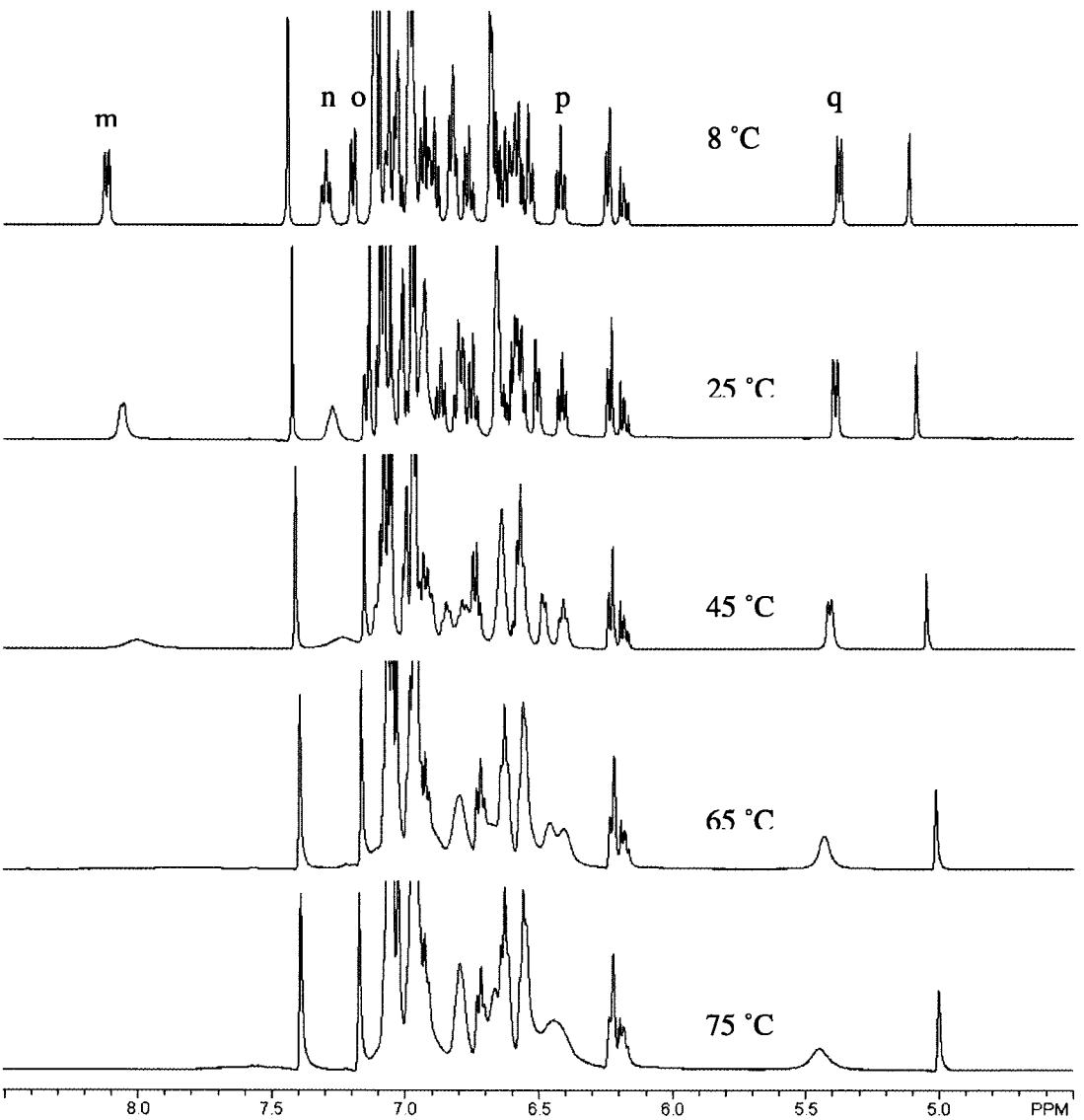


Figure 3.13. DNMR experiment of pyrenophane **3.18**.

3.3.6.3 ^{1}H NMR Spectrum of Pyrenophane 3.19

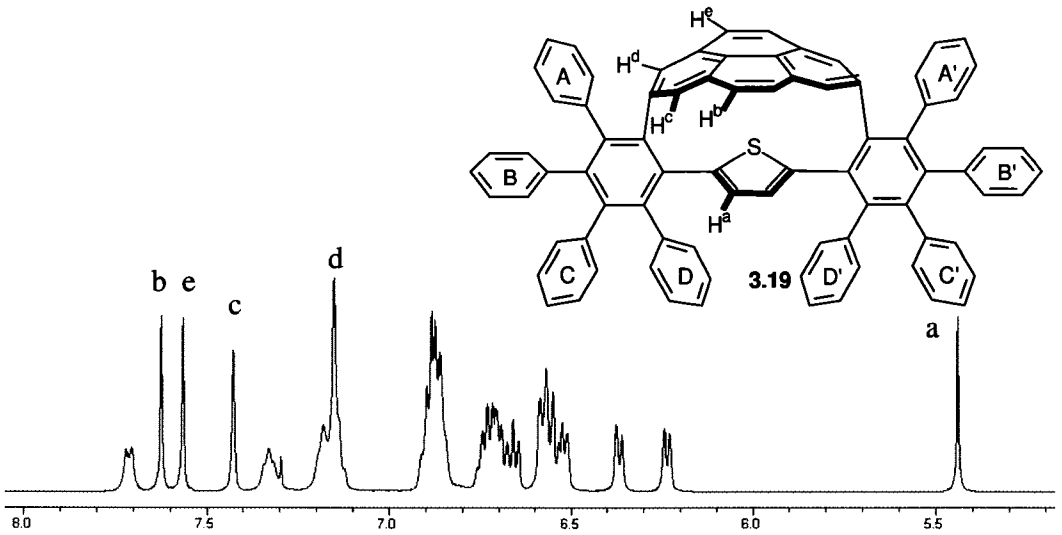


Figure 3.14. ^{1}H NMR spectrum of pyrenophane **3.19**.

As with **3.18**, the ^{1}H NMR spectrum is considerably more complicated than that of **3.17a**, because the symmetry is also lowered to C_s. The high field 2H singlet at δ 5.38 was immediately assigned to the protons on the central 2,5-thienylene unit (H^a in Fig. 3.14). This is again due to the shielding effect of the pyrene moiety. As in the case of **3.18**, four sharp 2H singlets (δ 7.57, 7.51, 7.37 and 7.09 (partially overlapped with a group of multiplets at δ 7.12-7.09)) were observed for the protons on the pyrene unit. These were assigned to protons H^b, H^e, H^c and H^d, respectively, based on the following observations. When H^a (δ 5.38) was irradiated, enhancement of the signal at δ 7.37 ppm (1.07%) was observed (H^c assigned to δ 7.37). When the signal for H^c (δ 7.37) was irradiated, enhancements were observed for the signal at δ 7.57 (1.16%) (assigned to H^b) and the signal at δ 5.38 ppm (1.88%) (H^a). In the ^{1}H,^{1}H-COSY spectrum, the signal at δ 7.37 (H^c) is correlated to the signal at δ 7.09 (assigned to H^d). Irradiation of the signal at δ

7.09 resulted in a 2.36% enhancement of the signal at δ 7.51 (assigned to H^e). A DNMR experiment (toluene-d_8, 5 °C to 75 °C) was also performed, but despite significant broadening of several signals due to protons on the peripheral phenyl groups, little useful information could be extracted. The most important observation was that the signal of the pyrene protons remained sharp up to 75 °C, indicating that the flip of the thiophene ring has a relatively high energy barrier.

3.3.7 UV-vis Spectra of the Pyrenophanes

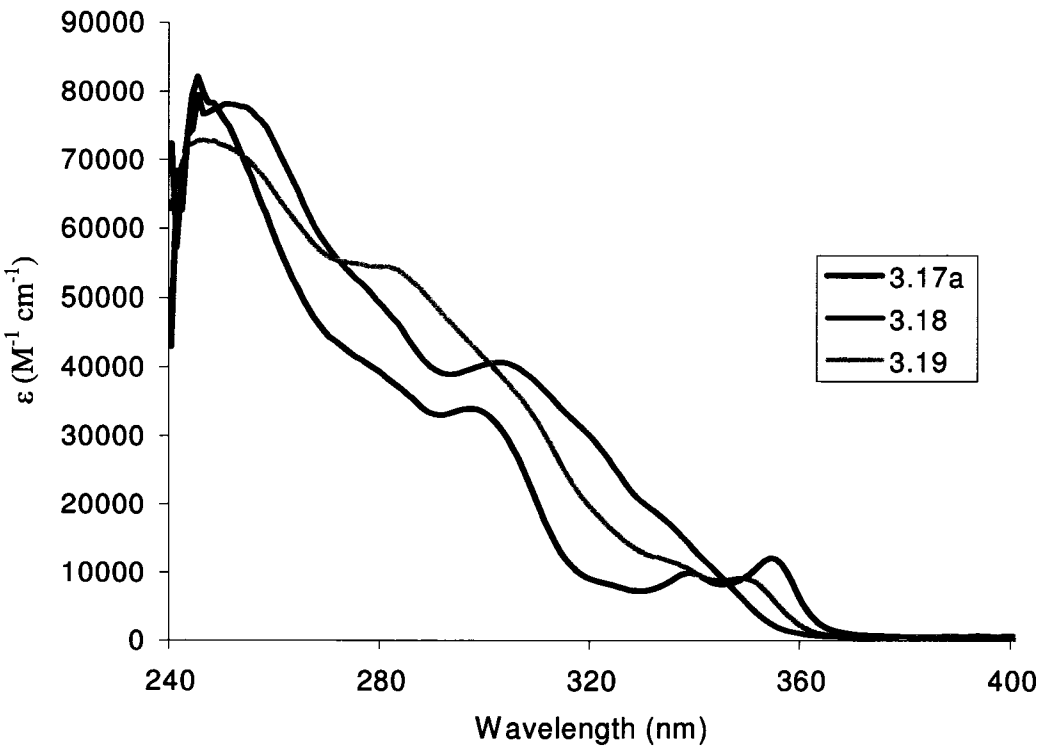


Figure 3.15. The UV-vis spectra of pyrenophanes (in chloroform).

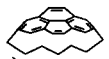
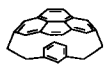
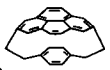
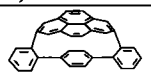
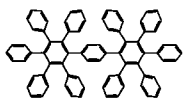
Pyrenophanes **3.17a**, **3.18** and **3.19** consist of twelve individual aromatic systems, which makes them interesting from an electronic perspective. The UV-vis spectra of

these compounds (Fig. 3.15) exhibit several absorption bands, although the features are generally broad and poorly-resolved. UV-vis data for **3.17a-3.19** and some comparison compounds are listed in Table 3.03.

Planar pyrene exhibits several bands in its absorption spectra, which are designated as β' (242 nm), β (273 nm) and *p* (306, 320 and 336 nm).[27] In the [*n*](2,7)pyrenophanes and 1,*n*-dioxa[*n*](2,7)pyrenophanes, it was observed that the β' (257τ280 nm) and β (279τ287 nm) bands moved to longer wavelength and merged as the pyrene system became more bent and that the *p* bands (all within 306-339 nm) remained stationary and became less intense.[1f] In systems with pyrene bend angles similar to those of **3.17a**, **3.18** and **3.19**, *e.g.* **3.01a** (θ_{calcd}= 104.6°), the β'/β band is observed at 277 nm and the *p* bands at 309/323/338 nm. The UV-vis spectrum of **3.04** (θ_{calcd}= 100.7°) shows clear absorption bands at 240, 290 and 322/336/352 nm. A cautious interpretation is that the band at 240 nm is due to the terphenyl unit, the band at 290 nm to the merged β' and β bands of the pyrene system and the group of 3 bands at 322/336/352 nm to the pyrene *p* bands. Unfortunately, UV-vis data are not available for **3.02** and **3.03**, so it is difficult to say to what extent the red shifts of the β'/β band (~13 nm) and the *p* band (~13 nm) relative to **3.01a** is due to a through space interaction between the pyrene system and the benzene ring situated beneath it. Finally, polyphenyl compound **3.65** exhibits absorptions at 252 and 278 nm, sh.[28] Thus, the spectrum of **3.17a** appears to be a slightly red-shifted sum of contributions from **3.04** and **3.65**. In the case of **3.19**, which has the next most distorted pyrene system (θ_{calcd}=111.4°), the UV-vis spectrum is similar, but appears broader and more poorly-resolved. Only the longest wavelength *p* band is observed (349 nm). For

3.18, which has the most distorted pyrene system (θ_{calcd}=117.2°), the *p* bands are no longer discernable and the β'/β band is even further red-shifted (302 nm).

Table 3.03. UV absorptions of pyrenophanes **3.17a**, **3.18** and **3.19**.

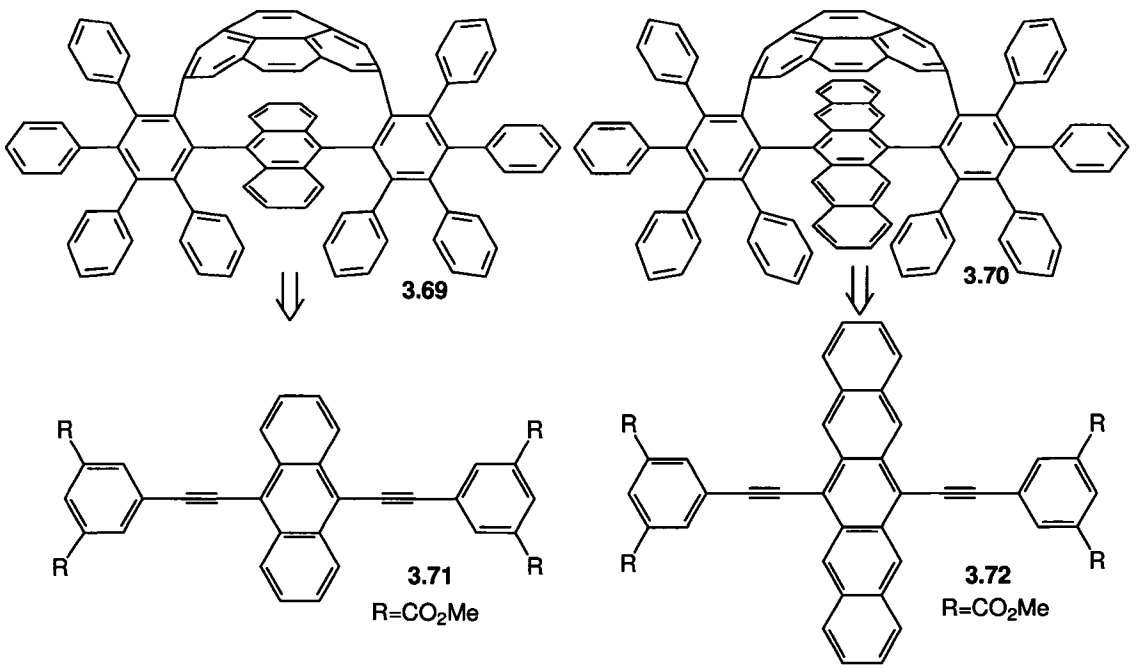
Compounds	Polyphenyl bands (nm)		Pyrene β'/β bands (nm)	Pyrene *p* bands (nm)			θ_{calcd} (°)	Lit.
Pyrene (**3.64**)	-	-	242 (88) 273 (54)	306 (13)	320 (32)	336 (56)	-	27
 (**3.01a**)	-	-	277 (62)	309 (9)	323 (10)	338 (13)	104.6	1(f)
 (**3.02**)	-	-	-	-	-	-	106.6	2
 (**3.03**)	-	-	-	-	-	-	100.4	2
 (**3.04**)	240	-	290	322	336	352	100.7	4
 (**3.65**)	252 (78)	278 (53, sh)	-	-	-	-	-	28
3.17a	245 (82)	278 (40, sh)	297 (34)	-	339 (10)	354 (12)	102.8	-
3.18	250 (78)	275 (53, sh)	302 (41)	-	-	-	117.2	-
3.19	246 (73)	279 (55, sh)	301 (40, sh)	-	-	349 (9)	111.4	-

Notes: the values in the brackets are $\varepsilon \times 10^{-3}$ (M^{-1} cm^{-1}).

3.4 Conclusion and Future Work

In this chapter, the successful syntheses of pyrenophanes **3.17a**, **3.18** and **3.19** is described. The overall yields for these three targets are 1.6% for **3.17a** (14 steps), 4.8%

for **3.18** (14 steps), and 3.1% for **3.19** (14 steps). Attempts to synthesize C_2-symmetric pyrenophanes with long aliphatic chains were made, but were not completed due to the low yields for both the formation of tetraesters **3.63a** and **3.63b**. Since **3.62b** proved to be a better substrate for the Diels-Alder/decarbonylation reaction than **3.62a**, future work in this area should focus on oxygen-based substituents.



Scheme 3.23. Future targets with central PAHs.

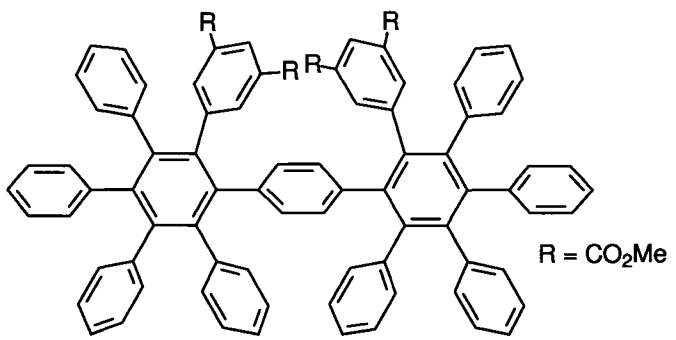
Other targets have also been identified for future investigation (Scheme 3.23). Introduction of [*n*]acene systems gives rise, for example, to structures **3.69** and **3.70**. Following the retrosynthetic route used for **3.17a**, **3.18** and **3.19**, these pyrenophanes will lead back to diyne tetraester structures **3.71** and **3.72**. It has been reported that compounds similar to **3.71** can be synthesized *via* Sonogashira coupling reactions.[29] However, pentacene-containing systems are difficult for Sonogashira coupling, and

similar systems were reported to be synthesized using organometallic additions to quinoidal precursors.[30]

3.5 Experimental

General. For general procedures please refer to the section in Chapter 2. Elemental analysis was performed by Canadian Microanalytical Service Ltd company. The values reported for the compounds with high carbon content (>85%) are usually lower than expected. Similar observation was reported by Müllen and co-workers.[31]

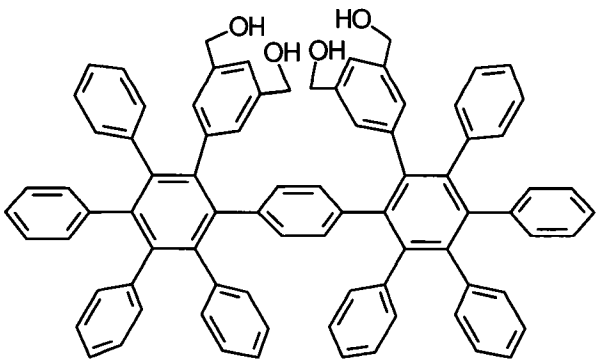
3,5,3'''',5''''-Tetrakis(methoxycarbonyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (3.32)



A solution of 1,4-bis(3,5-bis(methoxycarbonyl)phenylethynyl)benzene (**3.31**) (1.00 g, 1.96 mmol) and tetraphenylcyclopentadienone (**3.24**) (2.26 g, 5.88 mmol) in degassed diphenyl ether (30 mL) was heated at reflux (260 °C) for 48 h. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (29 cm × 3.3 cm, gradient elution: dichloromethane to 4% ethyl acetate/dichloromethane) to give 3,5,3'''',5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.32**) (1.35 g, 1.10 mmol, 57%, R_f=0.50 in 4% ethyl acetate/dichloromethane) as a white solid; mp:

>300 °C (ethyl acetate); IR (powder): 3105 (vw), 3078 (w), 3.55 (w), 3024 (w), 2942 (w), 2921 (vw), 2859 (vw), 2841 (vw), 1725 (s), 1441 (m), 1354 (w), 1299 (s), 1239 (s), 1212 (s), 1191 (m), 1147 (m), 1126 (m), 1104 (m), 1072 (m), 1054 (m), 1024 (m), 995 (m), 910 (w), 893 (w), 883 (w), 849 (w), 818 (w), 801 (m), 779 (s), 770 (s), 748 (s), 725 (s), 697 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) major isomer: δ 8.21 (s, 2H), 7.68 (s, 4H), 6.77-6.51 (m, 44H), 3.89 (s, 12H); discernable peaks for the minor isomer: δ 8.01, 7.56, 3.84; ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.4, 141.2, 140.9, 140.4, 140.0, 139.7, 139.1, 137.3, 136.4, 131.3, 131.1, 130.8, 130.2, 128.8, 128.7, 126.9, 126.7, 126.6, 126.3, 125.6, 125.5, 125.4, 125.3, 52.3; LC-MS (APCI) *m/z*: 1237 (22), 1223 (100, M^++1), 338 (9); Anal. Calcd for $C_{86}H_{62}O_8$: C, 84.43; H, 5.11. Found: C, 80.84; H, 5.35.

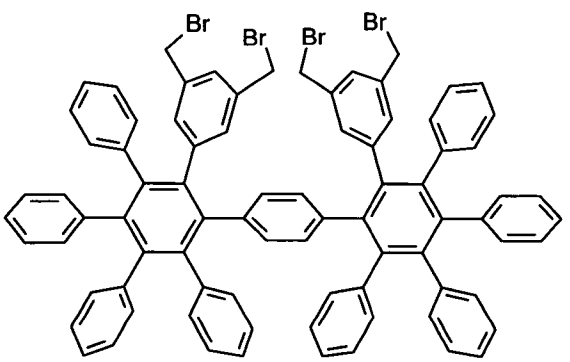
3,5,3'''',5''''-Tetrakis(hydroxymethyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (3.33).



A solution of 3,5,3'''',5''''-tetrakis(hydroxymethyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.32**) (1.30 g, 1.06 mmol) in THF (60 mL) was added dropwise to a 0 °C suspension of $LiAlH_4$ (0.32 g, 8.5 mmol) in THF (70 mL). The mixture was stirred at room temperature for 10 h and then heated at reflux for 1 h. The mixture was cooled to 0 °C and then ethyl acetate (100 mL) was added slowly and the

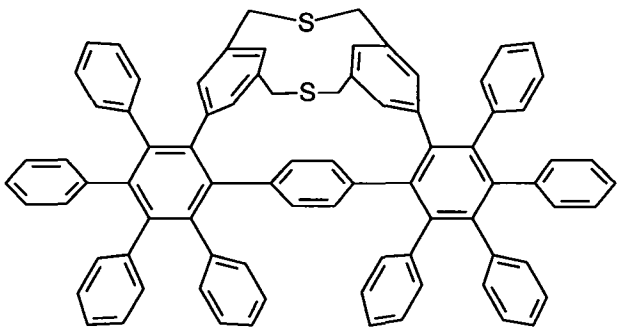
mixture was stirred for 10 min. Water (100 mL) was added slowly and the aqueous layer was extracted with ethyl acetate (3 × 300 mL). The combined organic layers were washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (10 cm × 3.3 cm, gradient elution: 4% ethyl acetate/dichloromethane to pure ethyl acetate) to give 3,5,3'''',5''''-tetrakis(hydroxymethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.33**) (1.15 g, 1.03 mmol, 97%, R_f= 0.80 in ethyl acetate) as a white solid; mp: >300 °C (ethyl acetate); IR (powder): 3334 (br, w), 3080 (w), 3056 (w), 3025 (w), 2926 (w), 2854 (w), 1734 (w), 1717 (w), 1700 (w), 1684 (w), 1669 (w), 1652 (w), 1635 (w), 1616 (vw), 1600 (w), 1576 (w), 1559 (w), 1539 (w), 1533 (vw), 1520 (vw), 1517 (vw), 1506 (w), 1496 (w), 1456 (w), 1441 (m), 1399 (w), 1071 (w), 1022 (w), 772 (w), 759 (m), 730 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.88-6.58 (m, 50H), 4.29-4.21 (m, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.6, 140.9, 140.8, 140.6, 140.3, 139.7, 138.8, 131.5, 131.44, 131.40, 130.5, 126.71, 126.67, 126.6, 125.4, 125.3, 60.6; LC-MS (APCI) *m/z*: 1110 (21, M^+) 1089 (100), 1071 (47), 1059 (21), 1039 (18), 635 (28), 163 (32), 149 (42). Anal. Calcd for $C_{82}H_{62}O_4$: C, 88.61; H, 5.63. Found: C, 87.22; H, 5.81.

3,5,3'''',5''''-Tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (3.34).



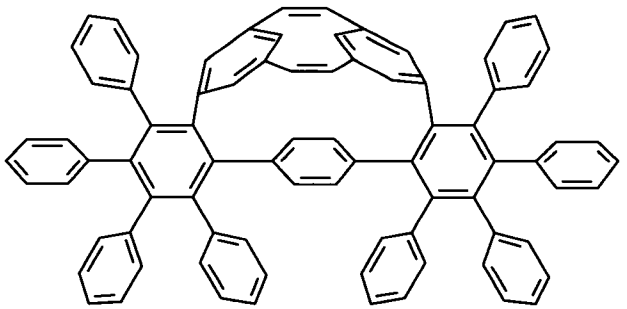
To a stirred suspension of 3,5,3'''',5''''-tetrakis(hydroxymethyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.33**) (70 mg, 0.063 mmol) in dichloromethane (10 mL) was added a solution of phosphorus tribromide (34 mg, 0.13 mmol) in dichloromethane (0.5 mL). The reaction was shielded from light by aluminum foil and stirred at room temperature overnight. The reaction mixture was heated at reflux for 10 min. Water (40 mL) was added to the reaction mixture, followed by dichloromethane (400 mL). The organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (28 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 3,5,3'''',5''''-tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.34**) (47 mg, 0.034 mmol, 55%, R_f=0.50) as a white solid; mp: >300 °C (dichloromethane); IR (powder): 3080 (w), 3054 (w), 3024 (w), 2922 (w), 2854 (w), 1274 (vw), 1210 (w), 1071 (w), 1023 (w), 849 (w), 760 (w), 734 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.85-6.57 (m, 50H), 4.18 (s, 6H), 4.08 (s, 2H); discernable peaks for the minor isomer: δ 4.08; ^{13}C NMR (125.76 MHz, $CDCl_3$): 141.0, 140.5, 140.2, 138.9, 136.4, 134.3, 131.4, 131.3, 126.9, 126.7, 126.6, 125.4, 125.4, 31.8; LC-MS (APCI-) *m/z*: 1396 (6), 603 (6), 566 (6), 528 (27), 449 (6), 419 (100), 209 (5); Anal. Calcd for $C_{82}H_{58}Br_4$: C, 72.25; H, 4.30. Found: C, 72.99; H, 4.48.

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5,6;7;8-tribenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,3,5,7-tetraene (3.21)



To a vigorously stirred solution of 3,5,3'''',5''''-tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.34**) (70 mg, 0.051 mmol) in 10% ethanol/dichloromethane (10 mL) was added Na_2S/Al_2O_3 (76 mg, 0.21 mmol). The reaction mixture was stirred at room temperature for 12 h. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (20 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5,6;7,8-tribenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,3,5,7-tetraene (**3.21**) (47 mg, 0.042 mmol, 83%, R_f=0.25) as a white solid; mp: >300 °C (chloroform); IR (powder): 3048 (w), 1600 (w), 1496 (w), 1442 (w), 1401 (w), 1072 (w), 1023 (w), 881 (w), 798 (w), 762 (w), 728 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.79-6.47 (m, 50H), 3.54 (s, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 140.9, 140.8, 140.44, 140.40, 140.11, 140.05, 140.00, 139.9, 139.7, 137.7, 135.6, 131.52, 131.46, 130.99, 130.97, 129.72, 129.67, 128.5, 126.8, 126.59, 126.56, 126.3, 125.6, 125.25, 125.20, 125.1, 40.1; LC-MS (APCI) *m/z*: 1232 (100), 1197 (63), 1107 (43, M^++1); Anal. Calcd for $C_{82}H_{58}S_2$: C, 88.92; H, 5.29. Found: C, 87.23; H, 5.22.

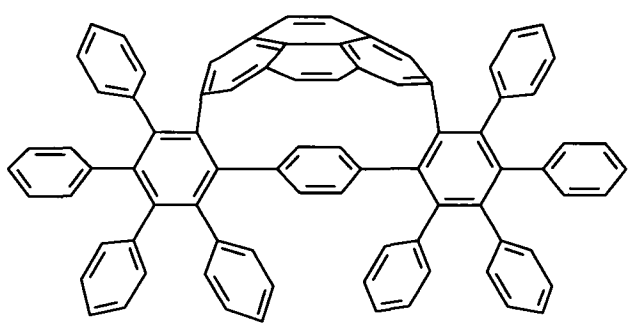
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5,6;7,8-tribenzo[8.2.2](1,3,5)cyclophane-1,3,5,7,15,23-hexaene (3.35)



To a well-stirred solution of dithiacyclophane **3.21** (0.12 g, 0.11 mmol) in dichloromethane (13 mL) was added Borch reagent[32] (53 mg, 0.33 mmol). After 1 h, the reaction mixture was concentrated *in vacuo*, quenched with ethyl acetate (1.6 mL) and suction filtered. The resulting white solid was dried *in vacuo* for 6 h and then slurried in THF (12 mL). *t*-BuOK (61 mg, 0.54 mmol) was added and the reaction mixture was stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (40 mL) and water (5 mL). The organic layer was washed with water (10 mL), washed with brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo* and passed through a short plug of silica gel (5 cm × 1.9 cm) using 50% dichloromethane/hexanes to give a mixture of isomers 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5,6;7,8-tribenzo-15/16,23/24-bis(methylthio)[8.2.2](1,3,5) cyclophane-1,3,5,7-tetraene (**3.35**) (90 mg, 0.079 mmol, 73%, R_f=0.45) as a white solid. The solid was dissolved in dichloromethane (10 mL) and Borch reagent (44 mg, 0.27 mmol) was injected. The reaction mixture turned yellow and was stirred for 2.5 h. The reaction was quenched with ethyl acetate (2 mL) and concentrated *in vacuo*. The residue

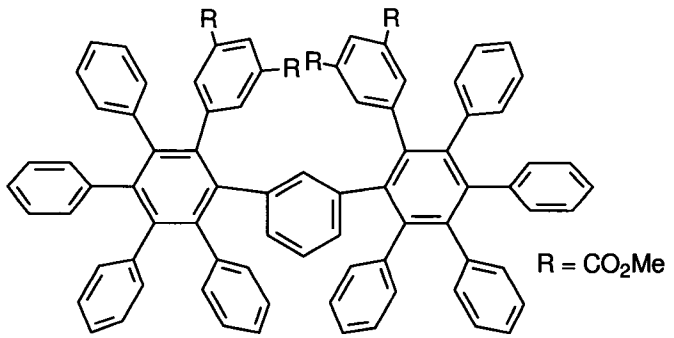
was dried under high vacuum and then suspended in THF (8 mL). *t*-BuOK (44 mg, 0.40 mmol) was added and the reaction mixture was vigorously stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (60 mL) and water (5 mL) were added to the residue. The organic layer was washed with water (5 mL), washed with brine (5 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (18 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5,6;7,8-tribenzo[*a,cde,g*][8.2.2](1,3,5)cyclophanes-1,3,5,7,15,23-hexaene (**3.20**) (16 mg, 0.015 mmol, 19%, R_f=0.70) as a white solid; mp: >300 °C (chloroform); IR (powder): 2924 (w), 2853 (w), 1630 (s), 1384 (w), 695 (s) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.28 (s, 2H), 6.94 (s, 4H), 6.79-6.70 (m, 42H), 6.46 (s, 4H), 6.23 (s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.1, 140.9, 140.8, 140.7, 140.4, 140.2, 140.1, 139.8, 139.7, 139.5, 137.9, 136.0, 135.5, 135.0, 131.6, 131.1, 130.9, 129.8, 129.4, 127.8, 126.7, 126.6, 126.5, 125.5, 125.24, 125.21; LC-MS (APCI) *m/z*: 1056 (100, M^++18), 1039 (65, M^++1); Anal. Calcd for $C_{82}H_{54}$: C, 94.51; H, 5.49. Found: C, 90.23; H, 5.65.

1',2',3',4',1",2",3",4"-Octaphenyl-1,2;13,14-dibenzo[2]paracyclo[2](2,7)pyrenophane-1,13-diene (3.17a)



To a well-stirred solution of cyclophanediene **3.20** (16 mg, 0.015 mmol) in degassed benzene (2 mL) was added a solution of DDQ (3.7 mg) in degassed benzene (0.5 mL). The reaction mixture turned green immediately, then orange within 5 min. A crystal of hydroquinone was added and the mixture was stirred for 5 min. The reaction mixture was concentrated *in vacuo*, and the resulting yellow residue was purified by column chromatography (10 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-1,2;13,14-dibenzo[2]paracyclo[2](2,7)pyrenophane-1,13-diene (**3.17a**) (11 mg, 0.011 mmol, 73%, R_f= 0.70) as a white solid; mp: >300 °C (chloroform); IR (powder): 3054 (w), 3025 (w), 2925 (w), 2854 (w), 1942 (w), 1868 (w), 1827 (w), 1794 (w), 1717 (w), 1699 (w), 1683 (w), 1576 (w), 1558 (w), 1520 (w), 1457 (w), 1441 (w), 1419 (w), 1399 (w), 1262 (w), 1142 (w), 1071 (w), 1024 (w), 951 (w), 929 (w), 871 (s), 845(w), 800 (w), 786 (w), 727 (m), 697 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.45 (d, *J*=7.1 Hz, 4H), 7.36 (s, 4H), 7.18 (t, *J*=7.7 Hz, 4H), 7.06 (t, *J*= 7.0 Hz, 2H), 6.87-6.79 (m, 12H), 6.66-6.64 (m, 6H), 6.54-6.53 (m, 4H), 6.49 (t, *J*=7.3 Hz, 2H), 6.36 (t, *J*= 7.4 Hz, 4H), 6.22 (d, *J*= 7.9 Hz, 4H), 5.54 (s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.6, 141.4, 141.3, 141.0, 140.81, 140.75, 140.5, 139.7, 139.4, 136.7, 136.5, 134.0, 131.6, 131.4, 131.3, 130.8, 130.6, 130.3, 129.6, 128.6, 127.4, 126.8, 126.4, 126.33, 126.30, 126.2, 126.0, 125.5, 124.9; LC-MS (APCI) *m/z*: 1037 (100, M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 245 (20 300), 278 sh (20 000), 297 (4000), 339 (200), 354 (200); Anal. Calcd for $C_{82}H_{52}$: C, 94.94; H, 5.06. Found: C, 86.39; H, 5.80.

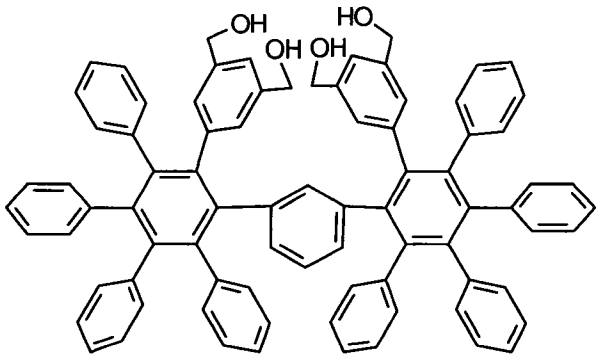
3,5,3'''',5''''-Tetrakis(methoxycarbonyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (3.39)



1,3-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)benzene (**3.38**) (2.18 g, 4.27 mmol) and tetraphenylcyclopentadienone (**3.24**) (4.93 g, 12.8 mmol) were dissolved in degassed diphenyl ether (55 mL). The reaction mixture was heated at reflux (260 °C) for 7 h. The mixture was cooled to room temperature and purified by column chromatography (29 cm × 4.2 cm, dichloromethane) to yield 3,5,3'''',5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.39**) (2.35 g, 1.92 mmol, 45%, R_f=0.15) as a yellow solid; mp: 178-180 °C (chloroform); IR (powder): 3056 (w), 3024 (w), 2948 (w), 1718 (s), 1600 (m), 1576 (w), 1496 (s), 1441 (s), 1399 (s), 1353 (s), 1325 (s), 1300 (s), 1238 (s), 1215 (m), 1203 (m), 1146 (m), 1126 (m). 1107 (m), 1073 (m), 1054 (ms), 1025 (w), 1000 (w), 908 (s), 881 (w), 830 (w), 812 (s), 791 (s), 773 (s), 763 (s), 747 (s), 731 (s), 725 (s), 715 (s), 710 (s), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.42 (s, 2H), 7.99 (s, 2H), 7.87 (s, 2H), 6.99 (d, *J*=7.6 Hz, 2H), 6.87-6.50 (m, 34H), 6.50 (d, *J*=7.2 Hz, 2H), 6.36-6.30 (m, 4H), 6.24 (t, *J*=7.7 Hz, 1H), 5.16 (d, 2H, *J*=7.4 Hz), 3.83 (s, 6H), 3.79 (s, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.20, 166.15, 142.4, 141.2, 141.0, 140.6, 140.43, 140.41, 140.2, 139.9, 139.7, 138.7, 138.4, 137.8, 137.04, 136.96, 135.8, 131.9, 131.32, 131.28, 131.2, 131.0, 130.7, 130.0, 129.4, 129.0,

128.0. 127.4, 127.0, 126.74, 126.65, 126.6, 126.5, 126.3, 125.8, 125.5, 125.4, 125.2, 125.0, 52.29, 52.26; LC-MS (APCI) *m/z*: 1224 (100, M^++1); Anal. Calcd for $C_{86}H_{62}O_8$: C, 84.43; H, 5.11. Found: C, 81.85; H, 5.19.

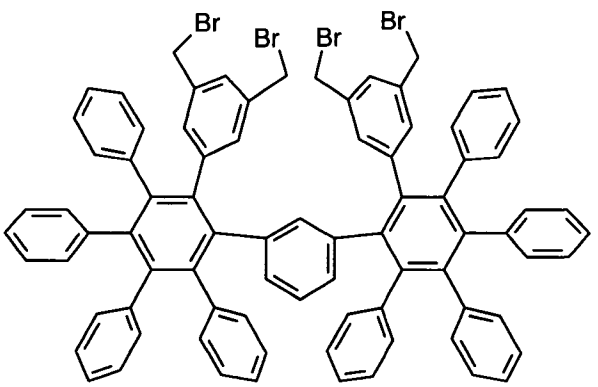
3,5,3'''',5''''-Tetrakis(hydroxymethyl)- 3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (3.45)



To a solution of 3,5,3'''',5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.39**) (2.34 g, 1.91 mmol) in dichloromethane (140 mL) was added dropwise at 0 °C to a solution of DIBAL-H (30.6 mL, 1.0 M in dichloromethane, 31 mmol). The mixture was stirred at room temperature for 16 h and quenched with 6 M aqueous hydrochloric acid. The organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (14 cm × 4.2 cm, 15% ethyl acetate/dichloromethane to ethyl acetate) to give 3,5,3'''',5''''-tetrakis(hydroxymethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.45**) (2.11 g, 1.90 mmol, 99%, R_f=0.75 in ethyl acetate) as a yellow solid; mp: 210-213 °C (chloroform); IR (powder): 3353 (br, w), 3054 (w), 3024 (w), 2879 (w), 1945 (w), 1875 (w), 1799 (w), 1600 (w), 1576 (w), 1496 (w), 1441 (w), 1396 (w),

1071 (m), 1021 (w), 914 (w), 869 (w), 812 (w), 786 (w), 752 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.02-6.70 (m, 46H), 6.58-6.57 (m, 1H), 6.47-6.46 (m, 1H), 6.30-6.21 (m, 6H), 5.49 (d, *J*=6.5 Hz, 1H), 4.53-4.36 (m, 6H), 4.27-4.16 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.3, 141.20, 141.18, 141.0, 140.9, 140.8, 140.6, 140.5, 140.43, 140.41, 140.37, 140.3, 139.8, 139.1, 138.8, 138.5, 132.0, 131.9, 131.8, 131.6, 131.5, 131.44, 131.38, 130.8, 130.2, 130.0, 129.9, 129.0, 127.1, 126.94, 126.92, 126.83, 126.81, 126.79, 126.7, 126.64, 126.56, 125.5, 125.4, 125.3, 125.2, 123.2, 122.8, 65.3, 64.9; LC-MS (APCI-) *m/z*: 1146 (100, MCl^-); Anal. Calcd for $C_{82}H_{62}O_4$: C, 88.61; H, 5.63. Found: C, 87.56; H, 5.56.

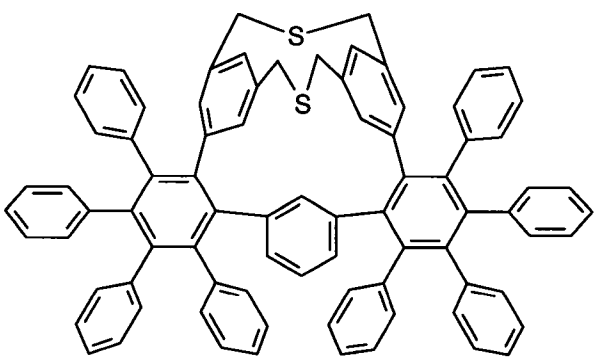
3,5,3'''',5''''-Tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (3.46)



To a well stirred suspension of 3,5,3'''',5''''-tetrakis(hydroxymethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.45**) (2.28g, 2.05 mmol) in dichloromethane (200 mL) was added phosphorus tribromide (0.739 g, 2.73 mmol) dropwise. The reaction was shielded from light by aluminum foil and stirred at room temperature overnight. Water (200 mL) was added to the reaction mixture, followed by dichloromethane (200 mL). The organic layer was washed with water (200

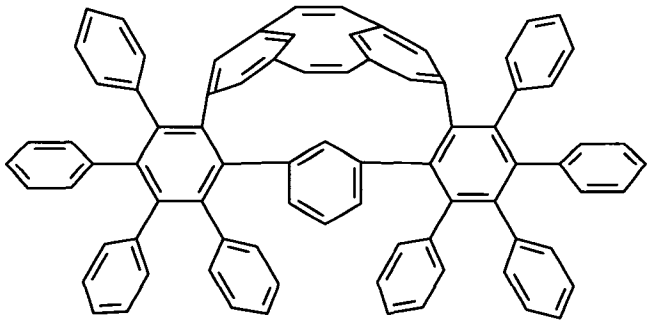
mL), washed with brine (200 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (18 cm × 4.2 cm, 60% dichloromethane/hexanes) to give 3,5,3'''',5''''-tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.46**) (1.33 g, 0.984 mmol, 48%, R_f=0.55) as a white solid; mp: 220-222°C (chloroform); IR (powder): 3055 (w), 3023 (w), 1943 (w), 1877 (w), 1802 (w), 1600 (w), 1576 (w), 1495 (w), 1441 (w), 1399 (w), 1273 (m), 1211 (w), 1071 (w), 1025 (w), 907 (w), 812 (w), 732 (s), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.07 (d, *J*=7.3 Hz, 4H), 7.01 (s, 2H), 6.88-6.65 (m, 38H), 6.42 (t, *J*= 8.1 Hz, 2H), 6.19 (d, 2H, *J*=7.4 Hz), 6.13-6.10 (m, 1H), 5.49 (d, *J*=7.6 Hz, 2H), 4.95 (s, 4H), 4.28 and 4.18 (AB system, J_{AB}=9.9 Hz, Δν=50.6 Hz, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 143.7, 140.9, 140.8, 140.7, 140.5, 140.4, 140.3, 139.8, 139.0, 138.6, 138.3, 137.8, 137.6, 136.8, 133.8, 132.20, 132.16, 131.6, 131.5, 131.3, 131.0, 129.0, 127.0, 126.7, 126.6, 126.5, 126.2, 126.1, 125.4, 125.3, 125.2, 125.0, 33.6, 33.3; LC-MS (APCI) *m/z*: 1441 (21), 1399 (100), 1355 (9); Anal. Calcd for $C_{82}H_{58}Br_4$: C, 72.26; H, 4.29. Found: C, 71.90; H, 4.00.

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,6*Z*)-1,2;3,4,5;6,7-tribenzo-15,24-dithia[7.3.3](1,3,5)cyclophane-1,3,6-triene (3.47).



To a vigorously stirred solution of 3,5,3'''',5''''-tetrakis(bromomethyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':3'',1''':2''',1''''-quinquephenyl (**3.46**) (0.52 g, 0.38 mmol) in 10% ethanol/dichloromethane (100 mL) was added Na_2S/Al_2O_3 (0.563 g, 1.53 mmol). The reaction mixture was stirred at room temperature for 20 h. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (25 cm × 3.3 cm, 65% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;3,4,5;6,7-tribenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,3,5,7-tetraene (**3.47**) (241 mg, 0.217 mmol, 57%, R_f=0.65) as a white solid; mp: >300 °C (chloroform); IR (powder): 3023 (w), 2903 (w), 1945 (w), 1874 (w), 1799 (w), 1599 (w), 1576 (w), 1494 (w), 1442 (w), 1395 (w), 1219 (w), 1073 (w), 1023 (w), 943 (w), 910 (w), 899 (w), 882 (w), 727 (s), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.90-6.61 (m, 40H), 6.47 (s, 2H), 6.25 (d, *J*=7.6 Hz, 2H), 6.17 (s, 2H), 3.55 (s, 4H), 3.22 and 2.97 (AB system, J_{AB}=14.8 Hz, Δv= 127.3 Hz, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.5, 141.4, 141.00, 140.98, 140.8, 140.7, 140.5, 140.0, 139.3, 139.0, 135.2, 135.0, 132.7, 132.4, 132.1, 132.0, 131.8, 131.6, 131.53, 131.47, 131.2, 130.59, 130.55, 129.2, 128.7, 128.4, 127.0, 126.7, 126.60, 126.57, 126.4, 125.5, 125.4, 125.2, 125.1, 125.0, 39.5, 38.5; LC-MS (APCI) *m/z*: 1188 (27), 1107 (33, M^+), 1074 (100); Anal. Calcd for $C_{82}H_{58}S_2$: C, 88.92; H, 5.29. Found: C, 83.09; H, 5.36.

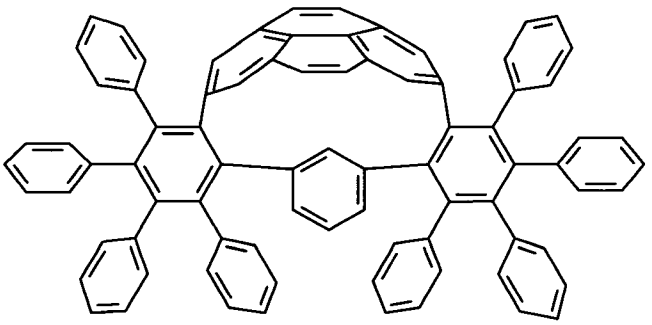
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,6*Z*)-1,2;3,4,5;6,7-tribenzo[8.2.2](1,3,5)cyclophane-1,3,6,14,22-pentaene (3.49)



To a well-stirred solution of dithiacyclophane **3.47** (110 mg, 0.099 mmol) in dichloromethane (16 mL) was added Borch reagent (48 mg, 0.30 mmol). After 12 h, the reaction mixture was concentrated *in vacuo*, quenched with ethyl acetate (1.6 mL) and concentrated *in vacuo*. The resulting brown residue was dried under high vacuum for 9 h, followed by the addition of THF (12 mL) and *t*-BuOK (56 mg, 0.50 mmol). The reaction mixture was stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (40 mL) and water (5 mL). The organic layer was washed with water (10 mL), washed with brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo* and passed through a short plug of silica (4 cm × 1.9 cm) using 50% dichloromethane/hexanes to give the isomer mixture 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,3*E*,6*Z*)-1,2;3,4,5;6,7-tribenzo-14/15,22/23-bis(methylthio)[8.2.2](1,3,5)cyclophane-1,3,6-triene (**3.48**) (113 mg, 0.099 mmol, 100%, R_f=0.20) as a white solid. The solid was dissolved in dichloromethane (18 mL), and Borch reagent (55 mg, 0.34 mmol) was injected. The reaction mixture turned yellow and was stirred for 16 h. The reaction was quenched with ethyl acetate (2 mL) and concentrated *in vacuo*. The residue was dried

over high vacuum pump and was suspended in a mixture of THF (9 mL) and *t*-BuOH (9 mL). *t*-BuOK (56 mg, 0.50 mmol) was added and the reaction mixture was vigorously stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (60 mL) and water (5 mL) were added to the residue. The organic layer was washed with water (5 mL), brine (5 mL), dried by $MgSO_4$, concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (18 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,3*E*,6*Z*)-1,2;3,4,5;6,7-tribenzo[8.2.2](1,3,5) cyclophane-1,3,6,14,22-pentaene (**3.49**) (81 mg, 0.078 mmol, 78%, R_f=0.75) as a white solid; mp: >300 °C (chloroform); IR (powder): 3020 (w), 2922 (w), 2854 (w), 1942 (w), 1869 (w), 1751 (w), 1600 (w), 1576 (w), 1496 (m), 1442 (w), 1394 (w), 1157 (w), 1072 (w), 1022 (w), 1001 (w), 988 (w), 944 (w), 916 (w), 886 (w), 786 (w), 718 (s), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.88-6.58 (m, 51H), 6.44 (d, *J*=7.1 Hz, 2H), 6.08 (s, 2H), 5.88 (s, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.6, 141.1, 141.0, 140.83, 140.79, 140.7, 140.5, 140.3, 139.6, 139.3, 136.6, 135.80, 135.78, 135.6, 132.1, 132.04, 132.01, 131.72, 131.65, 131.63, 131.59, 131.57, 131.5, 131.2, 130.9, 129.3, 128.6, 127.1, 126.8, 126.70, 126.67, 126.63, 126.60, 126.5, 125.3, 125.2, 125.11, 125.09, 124.9; LC-MS (APCI) *m/z*: 1071 (5), 1056 (47), 1039 (100, M^++1).

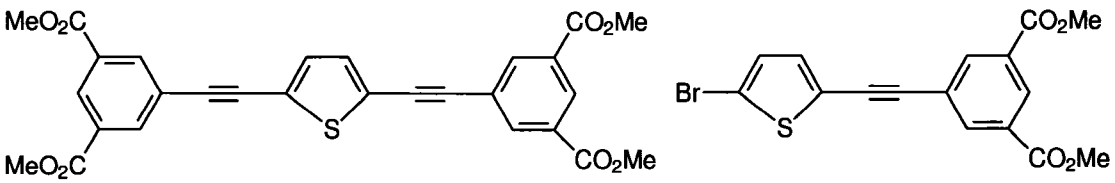
1',2',3',4',1",2",3",4"-Octaphenyl-1,2;13,14-dibenzo[2]metacyclo[2](2,7)pyrenophane-1,13-diene



To a well-stirred solution of cyclophanediene **3.49** (70 mg, 0.067 mmol) in degassed benzene (12 mL) was added a solution of DDQ (17 mg, 0.074 mmol). The reaction mixture was stirred at room temperature for 20 min and then heated at reflux for 7 d. A crystal of hydroquinone was added and the mixture was stirred for 5 min. The reaction mixture was concentrated *in vacuo*, and the resulting yellow residue was purified by column chromatography (19 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-1,2;13,14-dibenzo[2]metacyclo[2](2,7)pyrenophane-1,13-diene (**3.18**) (67 mg, 0.064 mmol, 96%, R_f=0.70) as a white solid; mp: 265-268 °C (chloroform); IR (powder): 3054 (w), 2926 (w), 2854 (w), 1942 (w), 1879 (w), 1800 (w), 1749 (w), 1600 (w), 1576 (w), 1495 (m), 1441 (w), 1384 (w), 1072 (w), 1028 (w), 720 (m), 696 (vs) cm^{-1} ; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.87 (d, *J*=6.8 Hz, 2H), 7.41 (s, 2H), 7.36 (s, 2H), 7.17 (s, 2H), 7.12 (t, *J*=7.7 Hz, 2H), 7.05 (br, t, *J*=6.5 Hz, 2H), 6.99 (br, d, *J*=6.3 Hz, 2H), 6.91-6.86 (m, 10H), 6.74-6.69 (m, 8H), 6.59-6.57 (m, 6H), 6.48-6.45 (m, 4H), 6.34-6.33 (m, 2H), 6.20 (t, *J*=7.6 Hz, 1H), 6.18 (d, *J*=7.8 Hz, 2H), 5.37 (d, *J*=7.3 Hz, 2H), 4.74 (s, 1H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.9, 142.2, 141.4, 141.0, 140.5, 140.3, 140.3, 139.6, 137.8, 137.0, 132.8, 132.4, 132.3, 131.73, 131.67, 131.6, 131.5, 131.2, 130.9, 127.8, 127.4, 126.9, 126.73, 126.67, 126.6, 126.5, 126.4, 126.3, 125.5, 125.10, 125.05, 122.6; LC-MS (APCI) *m/z*: 1127 (6), 1054 (5), 1038 (100,

M^++1); Anal. Calcd for $C_{82}H_{52}$: C, 94.95; H, 5.05. Found: C, 92.91; H, 5.58; UV-vis (chloroform) λ_{max} (ε_{max}) nm 250 (20 300), 275 sh (20 000), 302 (4000).

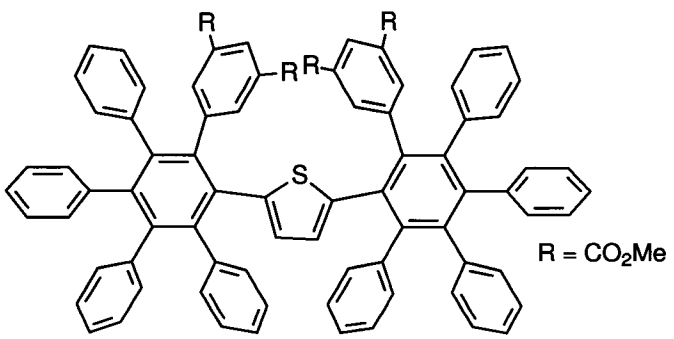
2,5-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)thiophene (3.51) and by-product 2-(3,5-bis(methoxycarbonyl)phenylethynyl)-5-bromothiophene (3.52)



To a well-stirred solution of $Pd(PPh_3)_2Cl_2$ (70 mg, 0.10 mmol) and CuI (70 mg, 0.37 mmol) in degassed benzene (48 mL) was added 2,5-dibromothiophene (**3.50**) (0.23 mL, 2.1 mmol). The reaction mixture was stirred for 5 min and then a solution of DBU (0.78 mL, 5.2 mmol) and 5-ethynylisophthalic acid dimethyl ester (**3.29**) (0.99 g, 4.55 mmol) in benzene (32 mL) was added. The mixture was stirred at room temperature for 3 h, then heated at reflux for 45 min, cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in a mixture of dichloromethane (100 mL) and saturated ammonium chloride solution (100 mL). The aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were washed with water (50 mL), washed with brine (50 mL), dried over $MgSO_4$, concentrated *in vacuo*, purified by column chromatography to yield 2,5-bis(3,5-bis(methoxycarbonyl)phenylethynyl)thiophene (**3.51**) as a yellow solid (0.38 g, 1.59 mmol, 35%) as a yellow solid; R_f (dichloromethane) = 0.20; mp: 188-189 °C (chloroform); IR (powder): 2923 (m), 2853 (m), 1723 (s), 1597 (w), 1521 (w), 1435 (s), 1345 (m), 1314 (m), 1246 (vs), 1140 (m), 1104 (m), 994 (s), 907 (s), 882 (m), 799 (m), 789 (m), 749 (vs), 725 (s), 671 (m) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.60 (s, 2H),

8.32 (d, J=1.6 Hz, 4H), 7.23 (s, 2H), 3.96 (s, 12H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 165.7, 136.5, 132.8, 131.3, 130.6, 124.7, 123.8, 92.5, 84.2, 52.8; LC-MS (APCI) *m/z*: 517 (100, M^++1); HRMS Calculated for $C_{28}H_{21}O_8S$: 516.0879, found 516.0885. By-product, 2-(3,5-bis(methoxycarbonyl)phenylethynyl)-5-bromothiophene (**3.52**) was also eluted (0.11g, 0.64 mmol, 14%) as a yellow solid; R_f (dichloromethane) = 0.60; mp: 135-138 °C (chloroform); IR (powder): 3427 (w), 3098 (w), 3040 (w), 3006 (w), 2957 (w), 2924 (w), 2852 (w), 1724 (s), 1593 (w), 1540 (w), 1436 (m), 1420 (m), 1351 (m), 1308 (m), 1244 (s), 1136 (m), 1103 (m), 992 (m), 911 (m), 874 (w), 784 (m), 789 (m), 753 (s), 722 (m), 694 (m), 671 (w) cm^{-1}; ^{1}H NMR (500.13 MHz, $CDCl_3$) 8.62 (t, J=1.6 Hz, 2H), 8.32 (d, J=1.6 Hz, 2H), 7.07 (d, J=3.9 Hz, 1H), 6.99 (d, J=3.9 Hz, 1H), 3.96 (s, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 165.7, 136.4, 133.2, 131.3, 130.55, 130.47, 124.4, 123.9, 114.3, 92.2, 83.8, 52.8; LC-MS (APCI) *m/z*: 420 (100), 378 (38, M^+); HRMS Calculated for $C_{28}H_{21}O_8S$: 377.9561, found 377.9563.

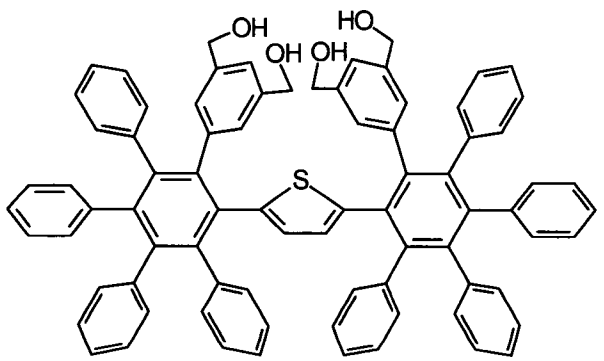
2,5-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (3.53)



2,5-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)thiophene (**3.51**) (1.00 g, 1.94 mmol) and tetraphenylcyclopentadienone (**3.24**) (2.23 g, 5.81 mmol) were dissolved in degassed diphenyl ether (40 mL). The reaction mixture was heated at reflux (260 °C) for

6 h. The mixture was cooled to room temperature and purified by column chromatography (23 cm × 3.3 cm, dichloromethane) to give 2,5-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.53**) (1.41 g, 1.14 mmol, 59%, R_f=0.25) as a yellow solid; mp: 178-180 °C (chloroform); IR (powder): 3024 (w), 2949 (w), 1725 (s), 1600 (w), 1547 (w), 1497 (m), 1441 (m), 1396 (m), 1352 (m), 1298 (m), 1329 (s), 1147 (m), 1105 (w), 1073 (w), 1055 (w), 1025 (w), 1001 (w), 909 (w), 799 (w), 750 (s), 724 (s), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.30 (t, *J*=1.6 Hz, 2H), 7.75 (d, *J*=1.6 Hz, 4H), 6.82-6.66 (m, 42H), 6.53 (d, *J*=7.0 Hz, 6H), 5.89 (s, 2H), 3.90 (s, 12H); discernable peaks for the minor isomer: δ 8.56, 8.22, 7.89, 3.83; ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 141.8, 141.7, 141.6, 141.3, 141.20, 141.16, 140.4, 140.13, 140.06, 139.8, 139.2, 136.8, 136.6, 131.6, 131.23, 131.15, 131.1, 129.3, 129.0, 128.7. 128.6, 126.9, 126.8, 126.72, 126.65, 125.6, 125.5, 125.4, 52.6; LC-MS (APCI) *m/z*: 1318 (6), 1291 (5), 1248 (20), 1229 (100, M^++1), 1215 (20), 1201 (5).

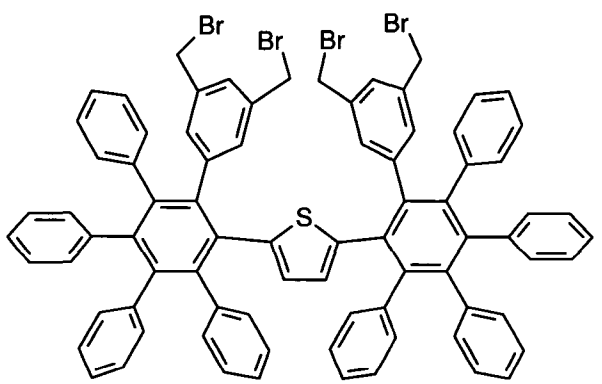
2,5-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (3.54)



To a solution of 2,5-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.53**) (1.39 g, 1.13 mmol) in dichloromethane (70 mL) was added dropwise at 0 °C a solution of DIBAL-H (18.0 mL, 1 M in dichloromethane).

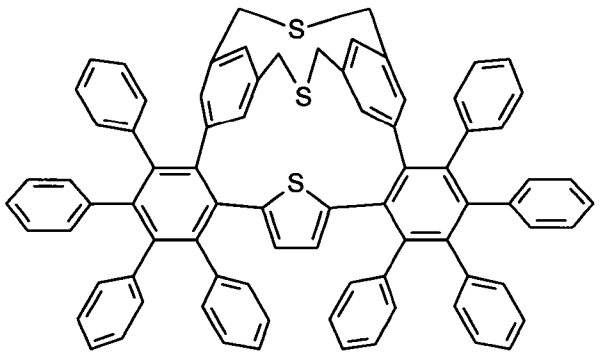
The mixture was stirred at room temperature for 16 h and quenched with 6 M aqueous hydrochloric acid solution (25 mL). The organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (10% ethyl acetate/dichloromethane to pure ethyl acetate) to give 2,5-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.54**) (1.27 g, 1.13 mmol, 100%) as a yellow solid; mp: 203-205 °C (ethyl acetate); IR (powder): 3358 (br, w), 3055 (w), 3023 (w), 1947 (w), 1877 (w), 1736 (w), 1693 (w), 1600 (w), 1546 (w), 1494 (w), 1441 (w), 1392 (w), 1239 (w), 1154 (w), 1070 (m), 1021(w), 736 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.99-6.94 (m, 6H), 6.89 (s, 2H), 6.82-6.68 (m, 36H), 5.74 (s, 2H), 4.34 and 4.31 (AB system, J_{AB}=12.8 Hz, Δν=11.1 Hz, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.8, 141.4, 141.3, 141.2, 141.13, 141.06, 140.8, 140.6, 140.4, 139.7, 139.1, 131.8, 131.5, 131.4, 131.3, 131.0, 129.6, 129.5, 129.4, 129.1, 129.0, 128.0, 126.9, 126.73, 126.65, 125.8, 122.9, 122.8, 65.0; LC-MS (APCI) *m/z*: 1152 (100, MCl^-); Anal. Calcd for $C_{80}H_{60}O_4S$: C, 85.99; H, 5.41. Found: C, 82.21; H, 5.38.

2,5-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (3.55)



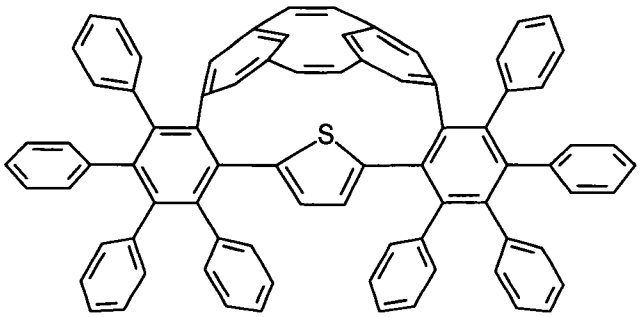
To a well stirred solution of 2,5-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.54**) (1.40 g, 1.25 mmol) in dichloromethane (120 mL) was added PBr_3 (0.451 g, 1.67 mmol) dropwise. The reaction was shielded from light by aluminum foil and stirred at room temperature overnight. Water (120 mL) was added to the reaction mixture, followed by dichloromethane (120 mL). The organic layer was washed with water (120 mL), washed with brine (120 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (20 cm × 3.3 cm, 50% dichloromethane/hexanes) to give 2,5-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.55**) (0.82 g, 0.60 mmol, 48%, R_f=0.60) as a white solid; mp: 178-181 °C (50% dichloromethane/hexanes); IR (powder): 3055 (w), 2955 (w), 1600 (w), 1576 (w), 1495 (w), 1441 (w), 1397 (w), 1271 (w), 1071 (w), 1027 (w), 790 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.97 (s, 2H), 6.94 (d, *J*=7.3 Hz, 2H), 6.89 (t, *J*= 7.4 Hz, 4H), 6.81-6.67 (m, 38H), 5.75 (s, 2H), 4.23 and 4.20 (AB system, J_{AB}=10.2 Hz, Δν=15.4 Hz, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 142.1, 141.5, 141.3, 141.3, 141.2, 141.1, 140.6, 140.5, 140.3, 140.1, 139.7, 136.7, 132.5, 131.7, 131.4, 131.31, 131.27, 129.2, 126.99, 126.95, 126.9, 126.71, 126.68, 125.7, 125.6, 125.5, 125.4, 33.4; LC-MS (APCI) *m/z*: 1460 (19), 1386 (100), 1369 (67, M^++1), 1335 (7); Anal. Calcd for $C_{80}H_{56}Br_4S$: C, 70.19; H, 4.12. Found: C, 70.34; H, 4.58.

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;7,8-dibenzo-thieno[2,3,4,5-3,4,5,6]-16,25-dithia[8.3.3](1,3,5)cyclophane-1,3,5,7-tetraene (3.56).



To a vigorously stirred solution of 2,5-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)thiophene (**3.55**) (120 mg, 0.088 mmol) in 10% ethanol/dichloromethane (15 mL) was added Na_2S/Al_2O_3 (129 mg, 0.351 mmol). The reaction mixture was stirred at room temperature for 6 h. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (18 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;7,8-dibenzo-thieno[2,3,4,5-3,4,5,6]-16,25-dithia[8.3.3](1,3,5)cyclophane-1,3,5,7-tetraene (**3.56**) (71 mg, 0.062 mmol, 71%, R_f=0.25) as a white solid; mp: >300 °C (50% dichloromethane/hexanes); IR (powder): 3054 (w), 2921 (w), 1942 (w), 1869 (w), 1747 (w), 1600 (w), 1576 (w), 1496 (w), 1441 (w), 1397 (w), 1219 (w), 1071 (w), 1027 (w), 878 (w), 732 (s), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 6.94-6.60 (m, 42H), 6.32-6.28 (m, 4H), 6.07 (s, 2H), 3.67 (s, 4H), 3.33 and 3.18 (AB system, J_{AB}=14.7 Hz, Δν=77.8 Hz, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.1, 141.0, 140.9, 140.8, 140.7, 140.6, 140.5, 140.4, 135.8, 135.3, 131.7, 131.6, 131.5, 131.4, 131.3, 130.44, 130.35, 130.1, 129.0, 128.5, 127.3, 126.61, 126.56, 126.5, 126.3, 125.6, 125.3, 125.2, 125.1, 39.6, 39.4; LC-MS (APCI) *m/z*: 1202 (30), 1193 (5), 1131 (66), 1113 (100, M^++1), 1079 (47), 1062 (8), 1046 (10); Anal. Calcd for $C_{80}H_{56}S_3$: C, 86.29; H, 5.07. Found: C, 85.39; H, 5.34.

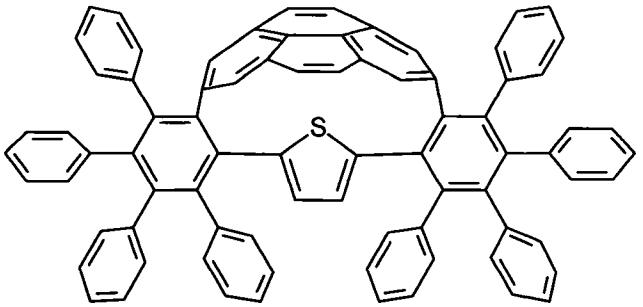
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,3*E*,5*E*,7Z,15Z,23Z)-1,2;7,8-dibenzo-thieno[2,3,4,5-3,4,5,6][8.2.2](1,3,5)cyclophane-1,3,5,7,15,23-hexaene (3.58).



To a well-stirred solution of dithiacyclophane **3.56** (70 mg, 0.063 mmol) in dichloromethane (10 mL) was added Borch reagent (30 mg, 0.19 mmol). After 20 h, the reaction mixture was concentrated *in vacuo*, quenched with ethyl acetate (1 mL) and concentrated *in vacuo*. The obtained brown residue was dried over high vacuum pump for 6 h, followed by an addition of THF (7.5 mL) and *t*-BuOK (35 mg, 0.32 mmol). The reaction mixture was stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. The residue was dissolved in dichloromethane (20 mL) and water (5 mL). The organic layer was washed with water (10 mL), washed with brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo* and passed through a short plug of silica gel (15 cm × 1.9 cm) using 50% dichloromethane/hexanes to give isomer mixture 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;7,8-dibenzo[*a*,*g*]-thieno[1,2,3,4-3,4,5,6]-15/16,23/24-bis(methylthio) [8.2.2](1,3,5)cyclophane-1,3,5,7-tetraene (**3.57**) (71 mg, 0.062 mmol, 99%, R_f=0.35) as a white solid. The solid was dissolved in dichloromethane (10 mL) and Borch reagent (34 mg, 0.21 mmol) was injected. The reaction mixture turned yellow and was stirred for 16 h. The reaction was quenched with ethyl acetate (1 mL) and concentrated *in vacuo*. The

residue was dried over high vacuum pump and was suspended in a mixture of THF (5 mL) and *t*-BuOH (5 mL). *t*-BuOK (34 mg, 0.31 mmol) was added, and the reaction mixture was vigorously stirred overnight. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (20 mL) and water (3 mL) were added to the residue. The organic layer was washed with water (5 mL), washed with brine (5 mL), dried by $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (18 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,3*E*,5*E*,7*Z*,15*Z*,23*Z*)-1,2;7,8-dibenzo-thieno[1,2,3,4-3,4,5,6][8.2.2](1,3,5)cyclophane-1,3,5,7,15,23-hexaene (**3.58**) (49 mg, 0.047 mmol, 77%, R_f=0.55) as a white solid; mp: >300 °C (50% dichloromethane/hexanes); IR (powder):3024 (w), 2923 (m), 2854 (w), 1940 (w), 1874 (w), 1745 (w), 1600 (w), 1576 (w), 1496 (w), 1442 (w), 1394 (w), 1154 (w), 1071 (w), 1027 (w), 914 (w), 729 (m), 695(vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.18 (s, 2H), 7.02 (s, 2H), 6.95-6.92 (m, 2H), 6.88-6.67 (m, 40H), 6.54 (s, 2H), 6.26 (s, 2H), 6.07 (s, 2H), 5.90 (s, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.2, 142.0, 141.1, 140.81, 140.80, 140.75, 140.7, 140.61, 140.56, 140.5, 136.5, 135.9, 135.5, 135.3, 132.3, 131.5, 131.43, 131.35, 131.2, 131.0, 130.0, 129.3, 128.3, 127.6, 127.4, 126.64, 126.60, 125.6, 125.3, 125.2; LC-MS (APCI) *m/z*: 1045 (100, M^++1), 1011 (45).

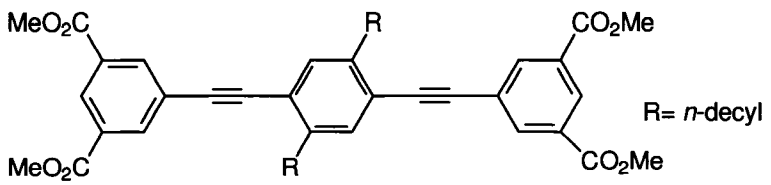
1',2',3',4',1",2",3",4"-Octaphenyl-(1*Z*,3*E*,5*E*,7*Z*)-1,2;7,8-dibenzo-thieno[1,2,3,4-3,4,5,6][8](2,7)pyrenophane-1,3,5,7-tetraene (3.19).



To a well-stirred solution of cyclophanediene **3.58** (49 mg, 0.047 mmol) in degassed benzene (12 mL) was added a solution of DDQ (12 mg, 0.052 mmol) in benzene (2.5 mL). The reaction mixture was stirred at room temperature for 20 min and then heated at reflux for 1.5 h. A crystal of hydroquinone was added and the mixture was stirred for 5 min. The reaction mixture was concentrated *in vacuo* and the resulting yellow residue was purified by column chromatography (12 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,3*E*,5*E*,7Z)-1,2;7,8-dibenzo-thieno[1,2,3,4-3,4,5,6][8](2,7)pyrenophane-1,3,5,7-tetraene (**3.19**) (40 mg, 0.038 mmol, 81%, R_f=0.50) as a white solid; mp: >300 °C (50% dichloromethane/hexanes); IR (powder): 3026 (w), 2953 (w), 2924 (w), 2857 (w), 1942 (w), 1869 (w), 1734 (w), 1600 (w), 1576 (w), 1495 (w), 1441 (s), 1378 (w), 1071 (w), 1028 (w), 780 (w), 722 (s), 654 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) 7.66 (d, *J*=7.1 Hz, 2H), 7.57 (s, 2H), 7.51 (s, 2H), 7.37 (s, 2H), 7.27-7.26 (m, 2H), 7.12-7.09 (m, 8H), 6.84-6.80 (m, 10H), 6.69-6.59 (m, 8H), 6.53-6.45 (m, 8H), 6.31 (d, *J*=7.6 Hz, 2H), 6.18 (d, *J*=7.5 Hz, 2H), 5.38 (s, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 143.7, 142.2, 141.2, 141.1, 140.7, 140.6, 140.3, 139.4, 139.2, 137.2, 134.7, 132.8, 132.0, 131.52, 131.45, 131.3, 131.2, 131.1, 130.9, 130.8, 130.7, 130.5, 129.1, 127.6, 127.4, 126.9, 126.7, 126.51, 126.45, 126.4, 126.34, 126.31, 125.7, 125.6, 125.0; LC-MS (APCI) *m/z*:1043 (100,

M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 246 (20 300), 279 sh (20 000), 301 sh (4000), 349 (200); Anal. Calcd for $C_{80}H_{50}S$: C, 92.10; H, 4.83. Found: C, 88.04; H, 5.12.

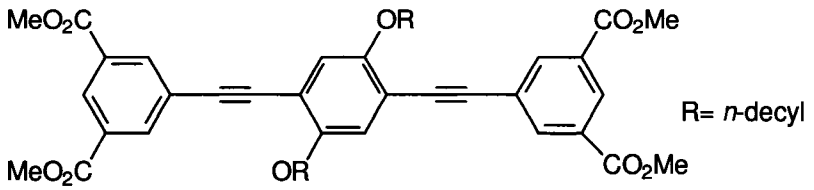
1,4-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecylbenzene (3.62a)



To a well-stirred solution of $Pd(PPh_3)_2Cl_2$ (4.5 mg, 0.0065 mmol) and CuI (4.9 mg, 0.026 mmol) in degassed benzene (7 mL) was added 1,4-didecyl-2,5-diethylnylbenzene (**3.61a**) (60 mg, 0.15 mmol). The reaction mixture was stirred for 5 min and then a solution of DBU (0.13 mL, 0.88 mmol) and triflate **3.27a** (0.22 g, 0.65 mmol) in benzene (3 mL) was added. The mixture was stirred at room temperature for 2 h, concentrated *in vacuo*. The residue was dissolved in dichloromethane (30 mL) and saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic layers were washed with water (10 mL), washed with brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (17 cm × 1.9 cm, 50% dichloromethane/hexanes) to yield 1,4-bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecylbenzene (**3.62a**) (0.11 g, 0.14 mmol, 94%, R_f=0.15) as yellow solid; mp: 80-82 °C (chloroform); IR (powder): 2951 (w), 2923 (m), 2849 (m), 2211(w), 1726(vs), 1653 (w), 1600 (w), 1594 (w), 1437 (s), 1335 (s), 1295 (w), 1286 (w), 1243 (vs), 1193 (m), 1148 (s), 1116 (w), 1104 (w), 997 (m), 912 (w), 889 (w), 752 (vs), 723 (s), 672 (w) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.64 (s, 2H), 8.35 (d, *J*= 1.3 Hz, 4H), 7.40 (s, 2H), 3.98 (s, 12H), 2.84-2.78 (m, 4H), 1.73-1.68 (m, 4H), 1.43-1.23 (m, 30H), 0.86-0.84 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.0,

142.8, 136.6, 133.0, 131.4, 130.4, 124.7, 122.7, 92.2, 90.4, 52.8, 34.1, 32.1, 30.8, 29.8, 29.8, 29.6, 22.9, 14.3; LC-MS (APCI) *m/z*: 880 (5), 808 (7), 791 (100, M^++1); HR-MS Calc for $C_{50}H_{62}O_8$: 790.4445, found 790.4459.

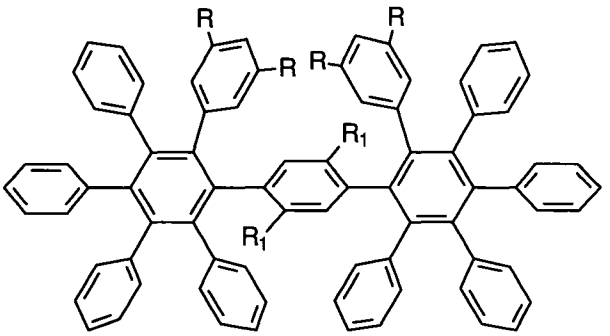
1,4-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecyloxybenzene (3.62b)



To a well-stirred solution of $Pd(PPh_3)_2Cl_2$ (5.7 mg, 0.0081 mmol) and CuI (6.2 mg, 0.033 mmol) in degassed benzene (10 mL) was added 1,4-didecyloxy-2,5-diethylnylbenzene (**3.61b**) (100 mg, 0.23 mmol). The reaction mixture was stirred for 5 min and then a solution of DBU (0.17 mL, 1.1 mmol) and triflate **3.27** (0.28 g, 0.81 mmol) in benzene (5 mL) was added. The mixture was stirred at room temperature for 18 h and then concentrated *in vacuo*. The residue was dissolved in dichloromethane (30 mL) and saturated ammonium chloride solution (10 mL). The aqueous layer was extracted with dichloromethane (3 × 10 mL), and combined organic layer was washed with water (10 mL), washed with brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography to yield 1,4-bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecyloxybenzene (**3.62b**) (54 mg, 0.067 mmol, 29%) as a yellow solid; mp: >300 °C (chloroform); ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.63 (t, *J*=1.6 Hz, 2H), 8.37 (d, *J*=1.6, 4H), 7.04 (s, 2H), 4.06 (t, *J*=6.5 Hz, 4H), 3.97 (s, 12H), 1.89-1.86 (m, 4H), 1.56-1.54 (m, 8H), 1.41-1.38 (m, 4H), 1.30-1.24 (m, 22H), 0.85 (t, *J*=7.0 Hz, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 165.8, 154.0, 136.7,

136.6, 131.2, 130.3, 130.2, 124.7, 117.2, 114.0, 93.1, 88.0, 69.9, 53.0, 52.72, 52.70, 52.40, 32.1, 29.83, 29.77, 29.5, 26.3, 22.9, 14.3.

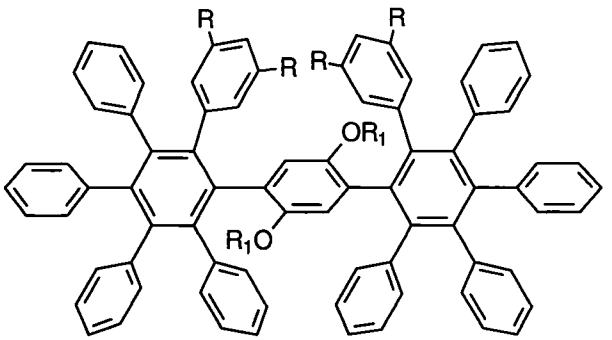
2''',5'''-Didecyl-3,3'''',5,5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (3.63a)



1,4-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecylbenzene (**3.62a**) (50 mg, 0.063 mmol) and tetraphenylcyclopentadienone (**3.24**) (73 mg, 0.19mmol) were dissolved in degassed diphenyl ether (1 mL). The reaction mixture was heated at reflux (260 °C) for 48 h. The mixture was cooled to room temperature and purified by column chromatography (25 cm × 1.9 cm, dichloromethane) to give 2''',5'''-didecyl-3,3'''',5,5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.63a**) (8.5 mg, 0.0057 mmol, 9%, R_f=0.60 in dichloromethane) as a faint yellow oil; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.65 (s, 2H), 7.62 (s, 2H), 7.33-6.50 (m, 46H), 6.35 (t, *J*= 7.6 Hz, 2H), 3.90 (s, 6H), 3.80 (s, 6H), 2.29-2.25 (m, 2H), 2.13-2.09 (m, 2H), 1.34-1.28 (m, 28H), 0.91 (t, *J*= 6.7 Hz, 6H); discernable peaks for the minor isomer: δ 4.56, 3.80; ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.4, 166.0, 141.4, 141.2, 140.84, 140.80, 140.6, 140.5, 140.3, 140.0, 139.3, 138.9, 138.7, 137.3, 136.7, 136.2, 135.3, 131.6, 131.5, 131.3, 131.24, 131.18, 131.1, 131.0, 130.8, 130.2, 130.0, 129.7, 129.24, 129.22, 129.16, 128.6, 128.52, 128.46, 128.4, 128.3, 128.2, 128.0, 127.8, 127.4,

127.3, 126.9, 126.73, 126.68, 126.62, 126.55, 126.5, 126.1, 126.00, 125.97, 125.5, 125.4, 125.2, 63.3, 57.9, 52.3, 52.1, 32.8, 32.2, 30.7, 30.2, 30.12, 30.09, 29.7, 23.0, 14.4; LC-MS (APCI) *m/z*: 1505 (100, M^++1) 1391 (5), 1051 (5).

2''',5'''-Didecyloxy-3,3'''',5,5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (3.63b)



1,4-Bis(3,5-bis(methoxycarbonyl)phenylethynyl)-2,5-didecyloxybenzene (**3.62b**) (37 mg, 0.045 mmol) and tetraphenylcyclopentadienone (**3.24**) (43 mg, 0.11mmol) were dissolved in degassed diphenyl ether (1 mL). The reaction mixture was heated at reflux (260 °C) for 60 h. The mixture was cooled to room temperature and purified by column chromatography (20 cm × 1.9 cm, dichloromethane to 10% ethyl acetate/dichloromethane) to give 2''',5'''-didecyloxy-3,3'''',5,5''''-tetrakis(methoxycarbonyl)-3',4',5',6',3''',4''',5''',6'''-octaphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (**3.63b**) (15 mg, 0.0099 mmol, 22%, R_f =0.60 in 4% ethyl acetate/dichloromethane) as a brown oil; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.79 (s, 1H), 7.49 (s, 1H), 6.82-6.67 (m, 40H), 6.52-6.49 (m, 2H), 6.17 (s, 2H), 3.86 (s, 6H), 3.80 (s, 6H), 3.64-3.59 (m, 2H), 3.46-3.42 (m, 2H), 1.67-1.66 (m, 4H), 1.37-1.27 (m, 44H), 0.90-0.87 (m, 18H). ^{13}C NMR (125.76 MHz, $CDCl_3$): insufficient amount of

material; LC-MS (APCI) *m/z*: 1636 (10), 1621 (13), 1608 (5), 1593 (37), 1581 (6), 1565 (78), 1554 (10), 1537 (100, M^++1), 1408 (5).

3.6 References

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9. Eyring equation: $\Delta G^{\neq} = 2.303RT_c\{10.319 + \log_{10}T_c - \log_{10}k_c\}$. T_c is coalescence temperature, $k_c = \pi(\Delta\nu)/\sqrt{2}$. $\Delta\nu$ is the distance between the two peaks.

For a 6.0:1 ratio, $\Delta G = -RT\ln K = 1.07$ kcal/mol ($K = [A] / [B] = 6.0$)

10. Atropisomers have been arbitrarily defined as "physically separable species when, at a given temperature, they have a half-life τ of at least 1000 s (16.7 min)". As a consequence, the free energy barrier $\Delta G^{\neq}$ required for term "atropisomers" at room temperature (300 K) is at least 22.4 kcal/mol. See Bringmann, G.; Mortimer, A. J. P.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 5384-5427.
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16. This value was calculated as follows. At 5 °C, the average chemical shift of the CH_3 signals of the major rotamer is (3.465+3.425)/2=3.445. For the minor isomer, the average chemical shift is (3.602+(presumably)3.425)/2=3.514.
17. For AB systems, $\Delta\nu' = (\Delta\nu^2+6J^2)^{1/2}$, $\Delta G^{\neq} = RT_c(22.96+\ln T_c-\ln\Delta\nu')$, see (a) Calder, I. C.; Garratt, P. J. *J. Chem. Soc. (B)* **1967**, 660-662; (b) Mannschreck, A.; Rissmann, G.; Vögtle, F.; Wild, D. *Chem. Ber.* **1967**, *100*, 335-346.
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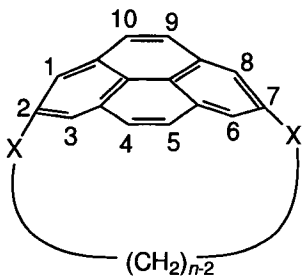
Chapter 4

Synthesis of Polyphenyl Pyrenophanes with Central Aliphatic Bridges

4.1 Introduction

As discussed in Chapter 1, pyrenophanes **4.01** and **4.02** (Fig. 4.01, also see Fig. 1.26) have been synthesized by the Bodwell group.[1] The key methodology for the syntheses of these molecules is a VID reaction of tethered [2.2]metacyclophane-1,9-diene unit.[1]



4.01 X=O, *n*=7-12
4.02 X=CH_2, *n*=7-12

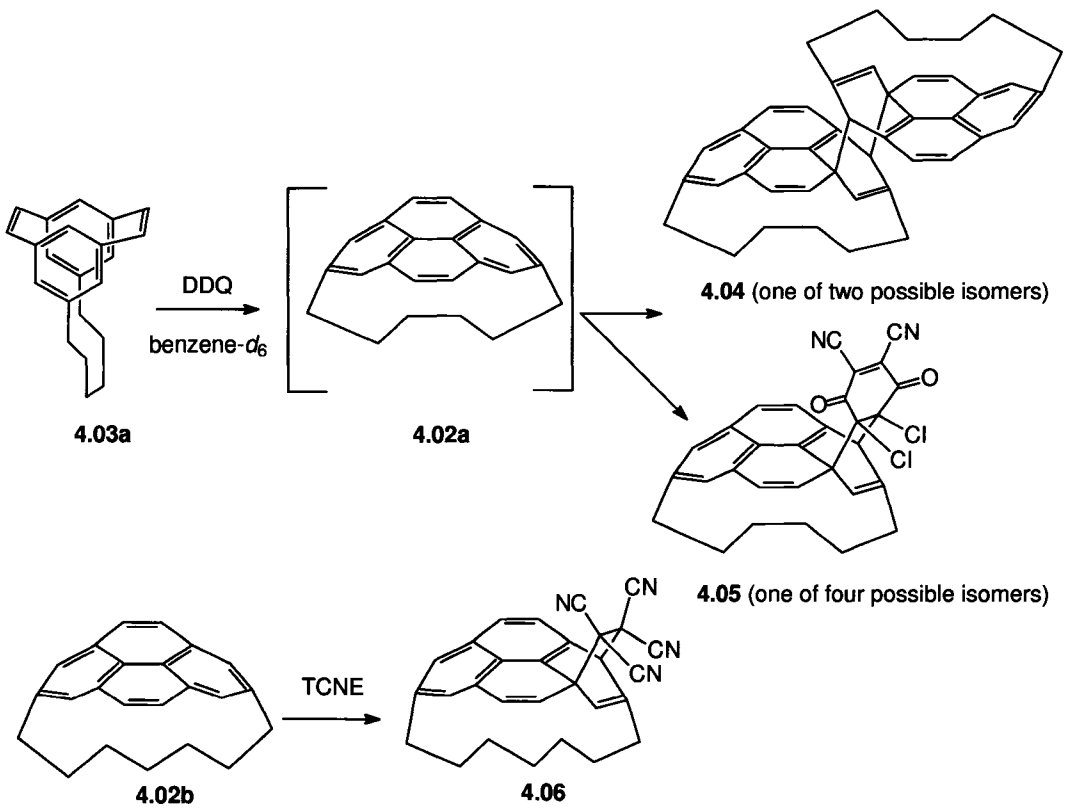
For all pyrenophanes and precursors in this chapter

a	*n*=6
b	*n*=7
c	*n*=8
d	*n*=9
e	*n*=10
f	*n*=11
g	*n*=12

Figure 4.01. Previously synthesized pyrenophanes with aliphatic bridges.

The interplay of strain and aromaticity is a crucial factor in determining the limitations of the reaction. As the number of atoms in the bridge is reduced, the ASE of the pyrene system drops off only slightly, but the strain energy increases significantly.[2] For both series of pyrenophanes, the smallest isolable homolog contained 7 atoms in the bridge (**4.01b** or **4.02b**). Attempts to synthesize pyrenophanes **4.01a** and **4.02a**, which have 6 atoms in the bridges, failed to provide the desired products. In the case of **4.01a** (θ_{calcd}=132.1°), the starting material was unreactive, even under forcing conditions. The failure to effect a VID reaction for **4.01a** was attributed to its significant strain energy. In the case of **4.02a**, the starting material was consumed, but **4.02a** was not formed. Clearly, the VID reaction has taken place, but the product was too unstable to isolate.[3] In a small scale, low-conversion experiment, a very small quantity of product was obtained. Its ^{1}H NMR spectrum resembled that of adduct **4.06** (Scheme 4.01), which was formed via an addition reaction of **4.02b** and TCNE (84%). The structure of the product formed from

the VID reaction of **4.03a** could be either a [4+4] dimer **4.04**, or DDQ adduct **4.05** (Scheme 4.01).[2]



Scheme 4.01. [4+4] and [4+2] addition of **4.02a** and **4.02b**.

The observation that **4.02a** was very likely as a short-lived intermediate provided the hope that more distorted pyrenophanes could be synthesized.[1] To achieve this goal, a new class of [2,7]pyrenophanes was designed. As was the case for [1.1]paracyclophanes, *i.e.* **4.07** and **4.08** (Fig. 4.02),[4] this relied upon kinetic stabilization of the products through multiple substitution. As discussed in Chapter 3, Müllen's methodology to synthesize hexabenzocorenene derivatives (Scheme 3.02)[5] was adopted to synthesize a series of octaphenyl[2,7]pyrenophanes, one of which was calculated to contain a near-record degree of bend in the pyrene system. Based on the same approach, a new series of

pyrenophanes **4.09** was designed (Fig 4.03). Instead of a central arylene unit, these systems contain central aliphatic bridges with variable lengths.

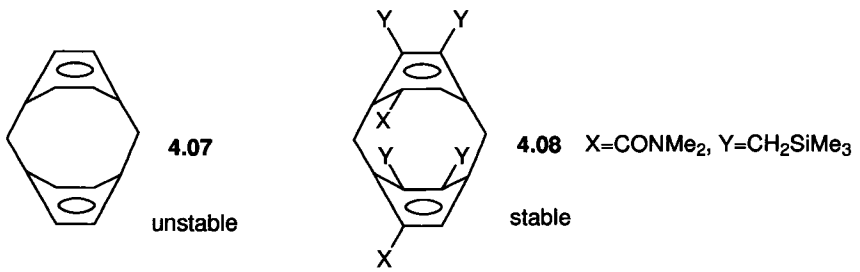


Figure 4.02. [1.1]paracyclophanes.

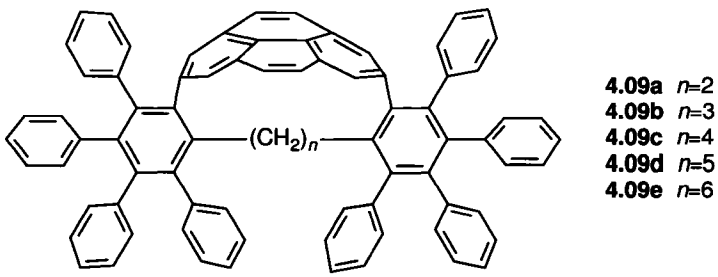


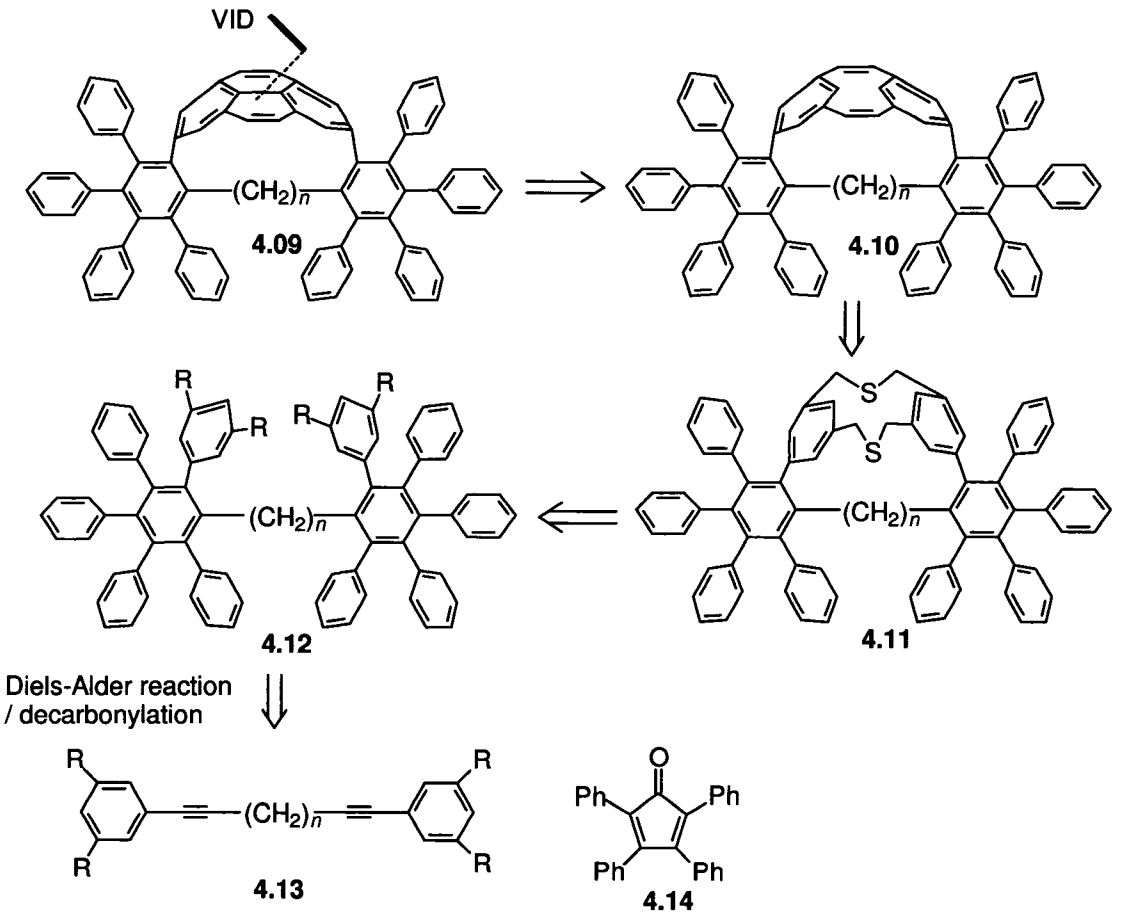
Figure 4.03. Target pyrenophanes **4.09a-e**.

AM1-calculated values of θ for pyrenophanes **4.09a-e** are listed in Table 4.01 along with calculated and experimental values for **4.01** and **4.02** (also see Table 1.01, Chapter 1). The underlined values are for those pyrenophanes that have not yet been synthesized. The current record holder for θ of a compound that has been isolated and characterized is **4.01b**, which has θ_{calcd}=113.3º, $\theta_{X\text{-}ray}$ = 109.2°. The proposed structures **4.09a-e** have θ_{calcd} values that are very similar to the corresponding dioxapyrenophanes **4.01a-1e**. As such, the synthesis of **4.09b** was expected to be challenging. Pyrenophane **4.09a** (θ_{calcd}=132.8°) is probably an unattainable product (also see PP. 37-38, Chapter 1).

Table 4.01. Calculated bend angle θ for pyrenophanes **4.01, 4.02** and **4.09a-e**.

Number of bridge atoms	θ_{calcd}(**4.09**)	θ_{calcd}(**4.02**)	$\theta_{x\text{-}ray}$(**4.02**)	θ_{calcd}(**4.01**)	$\theta_{x\text{-}ray}$(**4.01**)
6	132.8°	122.9°		132.1°	
7	116.2°	104.5°		113.3°	109.2°
8	94.8°	87.0°	80.8°	94.9°	87.8°
9	77.6°	70.3°	62.4°	77.8°	72.9°
10	62.0°	54.4°	46.6°	61.2°	57.7°

4.2 Retrosynthetic Analysis



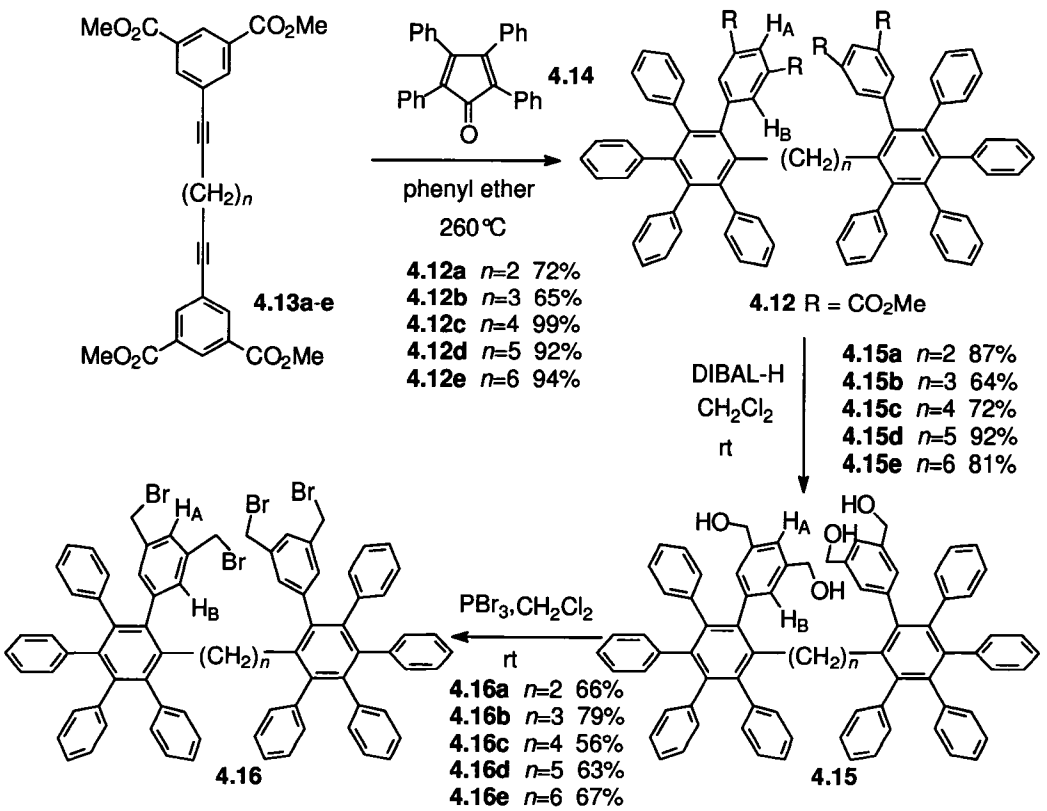
Scheme 4.02. Retrosynthesis of pyrenophane **4.09**.

Due to the structural similarity of the target pyrenophanes **4.09a-e** to the polyphenyl pyrenophanes described in Chapter 3 (**3.17a**, **3.18** and **3.19**), the retrosynthetic analysis of **4.09** is analogous to that of **3.17a-3.19**. The first retrosynthetic step from the target molecules **4.09** was the VID reaction, which led back to cyclophanedienes **4.10**. Cyclophanedienes **4.10** could then lead back to dithiacyclophanes **4.11** by established cyclophane chemistry. Dithiacyclophanes **4.11** was envisioned as coming from "acyclic" precursors **4.12**, which still contain all of the skeletal carbon atoms that appear in the

target pyrenophanes **4.09**. A highly productive Dies-Alder transform then led back to two precursors tetraphenylcyclopentadienone **4.14** and a series of linear phenylene-ethynylene compounds **4.13**, which have been synthesized in the Bodwell group previously.[2d, 2e]

4.3 Results and Discussion

4.3.1 Synthesis of Pyrenophanes with Central Aliphatic Bridges



Scheme 4.03. Synthesis of tetrabromide **4.16a-e**.

The syntheses of pyrenophanes **4.09a-e** commenced with the preparation of a series of tetraesterdiynes **4.13a-e** *via* Sonogashira coupling reactions between a series of

terminal diynes and an aryl triflate (see Scheme 1.14, Chapter 1).[2] Diels-Alder reaction between diynes **4.13a-e** and three equivalents of tetraphenylcyclopentadienone **4.14** followed by cheletropic elimination of carbon monoxide afforded the corresponding diynetetraesters **4.12a-e** in 65-99% yields. The yields for **4.12a** (n=2) and **4.12b** (n=3) are slightly lower than the other members of the series, possibly because of steric hindrance, once the first Diels-Alder/decarbonylation reaction has taken place. Each of the ^{1}H NMR spectra of **4.12a-e**, as expected, each contains overlapping multiplets at δ 6.6-7.1 ppm (40H), which correspond to the protons on the peripheral phenyl groups. They also contain well-resolved signals for internal (H_A) and external protons (H_B) on the ester-bearing phenyl groups (Scheme 4.03), the ester methyl groups (H_C) and the aliphatic bridges (H_D, H_E and H_F for the benzylic, homobenzylic and bis-homobenzylic protons, respectively), the chemical shifts of which are complied in Table 4.02. The same designations are used for **4.15, 4.16, 4.11** and **4.10** in Table 4.03-4.05. For clarity, symmetrical multiplets are represented by the chemical shift of the midpoint.

The chemical shifts of H_A and H_B are essentially invariant as n decreases from 6 to 3. In **4.12a** (n=2), H_A is observed at ~0.1 ppm higher field and H_B resonates at ~0.6 ppm higher field. The chemical shift of H_C remains constant over the full range of n. The aliphatic protons all appear at higher field than the analogous protons in the corresponding 1,n-diphenylalkanes.[6] This is presumably due to the combined shielding effect of the ester-bearing rings and the peripheral phenyl groups that are located *ortho* to the aliphatic chain. The protons H_F are shielded by ~1.1 ppm and the protons H_E are shielded by 0.71-0.94 ppm. The magnitude of these two effects increases consistently as

n decreases from 6 to 3. The protons H_D are shielded by 0.51-1.04 ppm and no clear trend was evident.

Table 4.02. Chemical shifts (δ ppm) of the protons on **4.12a-e**.

Compound	H_A	H_B	H_C	H_D	H_E	H_F
4.12a	8.29	7.34	3.87	2.41 (2.92)[a] Δδ=0.51	-	-
4.12b	8.42	7.89	3.93	1.92 (2.62) Δδ=0.70	1.02 (1.96) Δδ=0.94	-
4.12c	8.37	7.86	3.91	1.58 (2.62) Δδ=1.04	0.68 (1.59) Δδ=0.91	-
4.12d	8.39	7.96	3.89	1.96 (2.62) Δδ=0.64	0.73 (1.59) Δδ=0.86	0.15 (1.29) Δδ=1.14
4.12e	8.40	7.99	3.86	2.02 (2.62) Δδ=0.60	0.88 (1.59) Δδ=0.71	0.19 (1.29) Δδ=1.10

Notes: (a) numbers in brackets are calculated values for the corresponding protons in the analogous 1,*n*-diphenylalkanes.[5]

Reduction of tetraesters **4.12a-e** using DIBAL-H afforded tetraols **4.15a-e** (64-92%). Unlike the tetraols reported in Chapter 3, these tetraols are soluble in common organic solvents, which greatly facilitated the ensuing bromination. The ^1H NMR spectra of these compounds have overlapping multiplets in the aromatic region. In most cases, signals of the internal (H_A) and external protons (H_B) of the substituted ring can be assigned, but in a few cases they are overlapped (or partially overlapped) with other signals. In such cases, a low cut in the $^1H,^1H$-COSY spectrum was performed to determine the approximate chemical shifts. The signals for the benzylic protons (H_C) on CH_2OH appear as 8H AB systems or nearly degenerate AB systems at δ 4.3-4.5 ppm. The aliphatic region contains up to three signals, which correspond to the protons on the aliphatic bridges. The chemical shifts of H_A-H_F are listed in Table 4.03.

Table 4.03. Chemical shifts (δ ppm) of the protons on **4.15a-e**.

Compound	H_A	H_B	H_C	H_D	H_E	H_F
4.15a	6.94	6.66 (br)	4.43 (de)	2.49 (2.92)[b] Δδ=0.43	-	-
4.15b	6.97	7.08 [a]	4.36 (de)	2.05 (2.62) Δδ=0.57	1.21 (1.96) Δδ=0.75	-
4.15c	7.00	6.87	4.43	1.73 (2.62) Δδ=0.89	0.79 (1.59) Δδ=0.80	-
4.15d	7.02 *	6.90	4.35 (de)	2.05 (2.62) Δδ=0.57	0.88 (1.59) Δδ=0.71	0.22 (1.29) Δδ=1.07
4.15e	7.09 *	6.96	4.43	2.12 (2.62) Δδ=0.50	0.96 (1.59) Δδ=0.63	0.27 (1.29) Δδ=1.02

Notes: "br" denotes a broad signal; "de" denotes a degenerate AB system; (a) denotes that the chemical shifts were determined by a low cut of the $^1H,^1H$-COSY spectrum (for overlapping signals); (b) numbers in brackets are calculated values for the corresponding protons in the analogous 1,*n*-diphenylalkanes.[6]

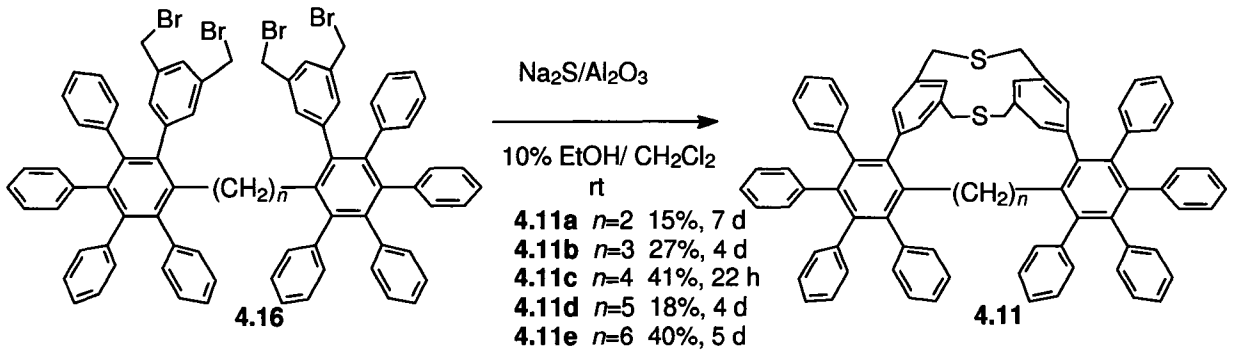
As with **4.12a-e**, the most conspicuous chemical shift is that of H_B in the smallest homolog (**4.15a**), which appears at anomalously high field. The aliphatic protons are shielded with respect to those of the corresponding 1,*n*-diphenylalkanes and the magnitude of this effect tends to increase with distance from the aromatic systems, *i.e.* $H_D<H_E<H_F$.

Table 4.04. Chemical shifts (δ ppm) of the protons on **4.16a-e**.

Compound	H_A	H_B	H_C	H_D	H_E	H_F
4.16a	-	-	4.22, 4.16 (AB)	2.46 (2.92)[a] Δδ=0.46	-	-
4.16b	7.15	7.06	4.39 (s)	1.86 (2.62) Δδ=0.76	1.21 (1.96) Δδ=0.75	-
4.16c	7.01	6.96	4.26 (s)	1.70 (2.62) Δδ=0.92	0.81 (1.59) Δδ=0.78	-
4.16d	-	-	4.26, 4.25 (AB)	2.05 (2.62) Δδ=0.57	0.88 (1.59) Δδ=0.72	0.28 (1.29) Δδ=1.01
4.16e	-	-	4.28, 4.26 (AB)	2.10 (2.62) Δδ=0.52	0.97 (1.59) Δδ=0.62	0.33 (1.29) Δδ=0.96

Note: "AB" denotes an AB system; (a) numbers in brackets are calculated values for the corresponding protons in the analogous 1,*n*-diphenylalkanes.[6]

Tetraols **4.15a-e** were reacted with PBr_3 to yield tetrabromides **4.16a-e** (56%-79%). The ^1H NMR spectra of **4.16a-e** are very similar to those of **4.15a-e**. Tetrabromides **4.16a-e** were converted to dithiacyclophanes **4.11a-e** using Na_2S/Al_2O_3 (Scheme 4.04). The yields for this reaction varied from 15% (**4.11a**) to 41% (**4.11c**). These reactions were generally quite sluggish, especially the one leading to **4.11a**. The NMR data for the well-resolved signals of **4.11a-e** are listed in Table 4.05. Protons H_A-H_F are analogous to those in **4.15a-e**.



Scheme 4.04. Synthesis of dithiacyclophanes **4.11a-e**.

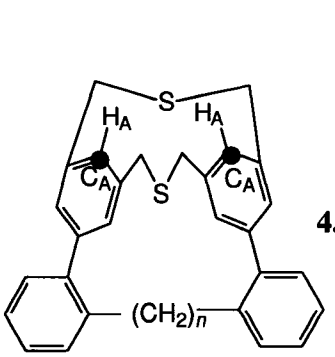
Table 4.05. Chemical shifts (δ ppm) of the protons on **4.11a-e**.

Compound	H_A	H_B	H_C	H_D	H_E	H_F
4.11a	-	-	3.59 (br, s)	2.80 (br) (2.92) [b] Δδ=0.18	-	-
4.11b	6.84	6.62	3.56, 3.49 (AB)	2.54 (2.62) Δδ=0.08	1.31 (1.96) Δδ=0.65	-
4.11c	6.72 [a]	6.64	3.66, 3.64 (AB)	2.22 (2.62) Δδ=0.40	0.78 (1.59) Δδ=0.81	-
4.11d	7.17 (br)	6.64	3.67, 3.64 (AB)	2.17 (2.62) Δδ=0.45	1.05 (1.59) Δδ=0.54	0.45 (1.29) Δδ=0.84
4.11e	7.41	6.67	3.77, 3.61 (AB)	2.15 (2.62) Δδ=0.47	1.01 (1.59) Δδ=0.58	0.25 (1.29) Δδ=1.04

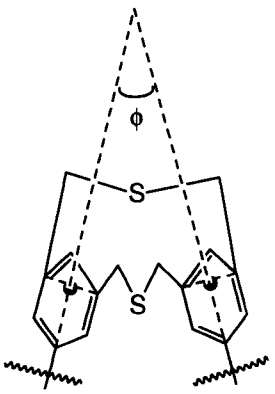
Note: "br" denotes a broad signal; "AB" denotes an AB system; (a) denotes the chemical shifts that were determined by a low cut of the $^1H,^1H$-COSY spectrum (for overlapping signals); (b) numbers in brackets are calculated values for the corresponding protons in the analogous 1,*n*-diphenylalkanes.[6]

Other than a somewhat diminished shielding of protons H_D (compared to the corresponding 1,*n*-diphenylalkanes), the only interesting feature of this set of data is the change in chemical shift of the internal protons H_A with the value of n. For *n*=6, H_A resonates at unusually low field (δ 7.41). As n decreases, H_A moves to higher field (*n*=5, δ 7.17; *n*=3-4, δ ~6.8; *n*=2, not found). This can be explained by a change in structure of the *syn*-2,11-dithia[3.3]metacyclophane unit with the changing length of the aliphatic chain. When the aliphatic chain adopts an all-anti conformation, it functions as a linear spacer. As it becomes longer, it forces to increase the angle between the two rings in the 2,11- dithia[3.3]metacyclophane unit. This has the effect of pushing the internal protons toward one another. As they move increasingly within the sum of their van der Waals radii (2.16 Å), they would be expected to sterically deshield one another and this is what is observed. The structures of cyclophanes **4.17** (octadephenylated analogs of **4.09**) were calculated at the AM1 level of theory (Table 4.06). The sulfur-containing bridges were maintained in *pseudo-chair* conformations and the aliphatic chains were maintained in *all-anti* conformations. As the value of *n* increases from 2 to 6, the angle formed by the two rings of the 2,11- dithia[3.3]metacyclophane unit increases from 32.3° (*cf.* 20.6° in the crystal structure of *syn*-2,11-dithia[3.3]metacyclophane[7]) to 84.2°. At the same time, the H_A-$H_{A'}$ distance decreases steadily from 2.43 Å to 1.89 Å. In going from *n*=3 (2.25 Å) to *n*=4 (2.09 Å), the internal protons move within the sum of their van der Waals radii, so the most pronounced changes would be expected for *n*=4-6. Unfortunately, neither H_A nor H_B could be located for **4.11a** (*n*=2).

Table 4.06. AM1-calculated structure of **4.17a-e**.

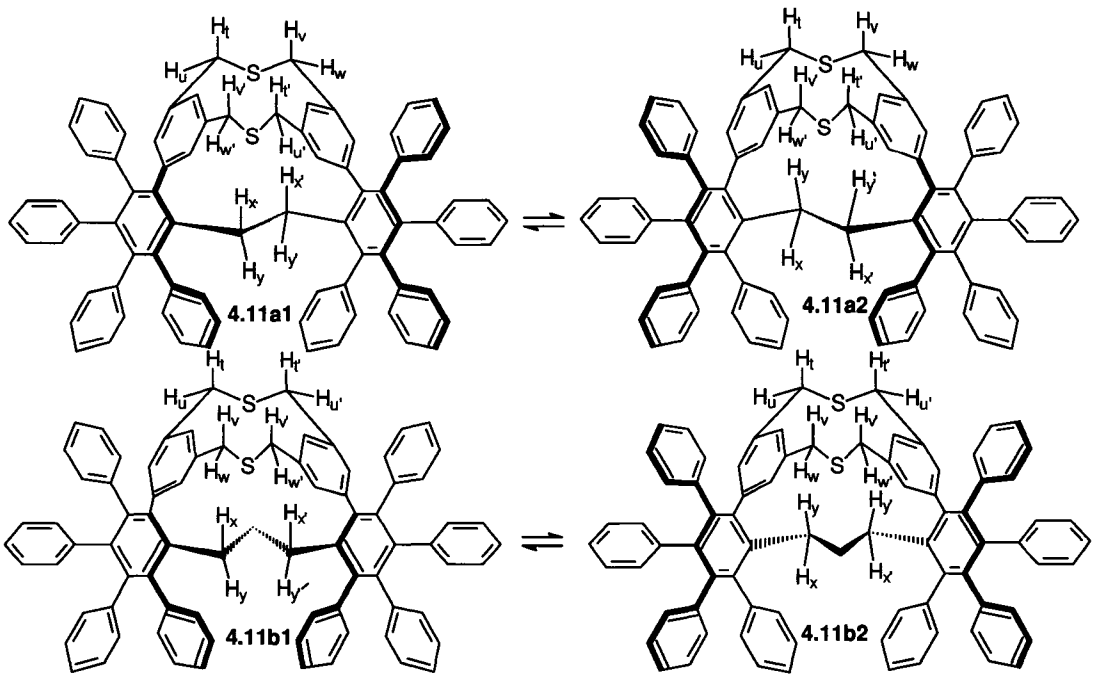


4.17a-e

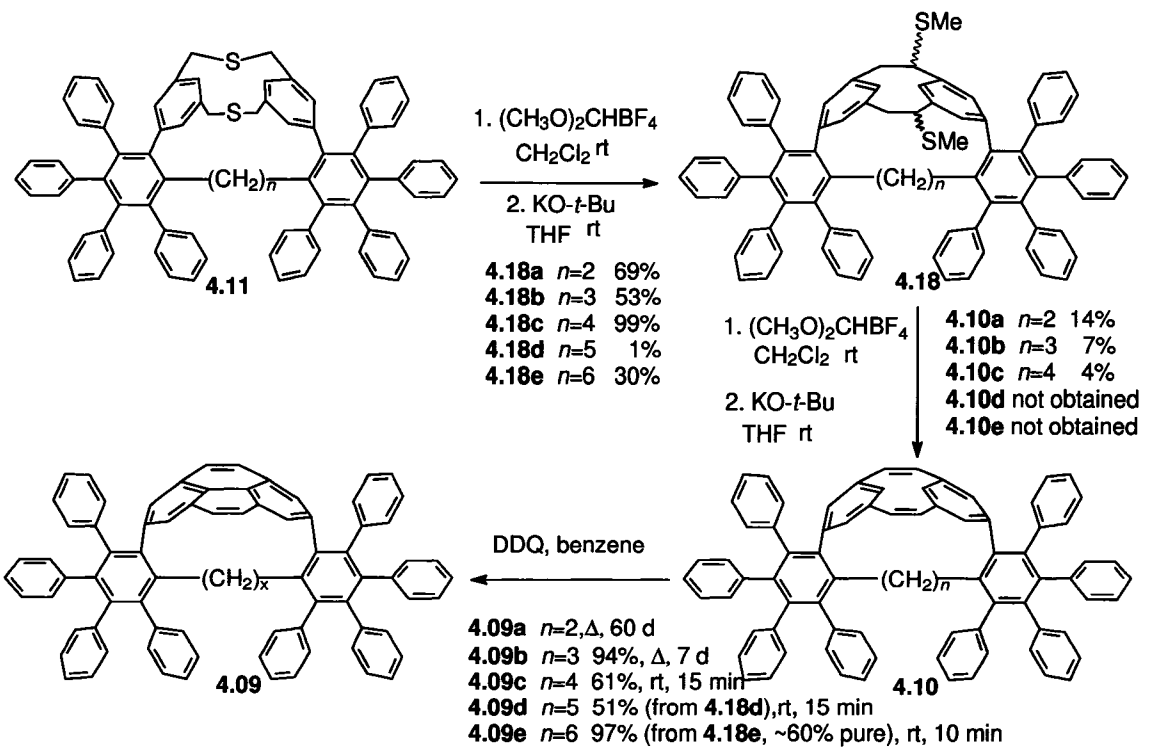


Compound	H_A-H_A (Å)	Angle ϕ (°) [a)]	C_A-C_A (Å)	δ H_A (ppm)
4.17a (*n*=2)	2.43	32.3	3.04	-
4.17b (*n*=3)	2.25	44.7	3.04	6.84
4.17c (*n*=4)	2.09	59.9	3.07	6.72
4.17d (*n*=5)	1.98	70.8	3.10	7.17
4.17e (*n*=6)	1.89	84.2	3.16	7.41

The spectrum of **4.11a** (*n*=2) stands out from the others because the signals are all broad. This is presumably due to the degenerate conformational process shown in Scheme 4.05 being near coalescence. In fact, similar conformational processes are available to all members of the series, but these are all fast on the NMR timescale, as evidenced by the observation of a single AB system for the sulfur-containing bridges. Two AB systems would be expected if these conformational processes were slow. Interestingly, due to the different symmetries, the protons that exchange when n is odd are on the same CH_2SCH_2 bridge and those that exchange when n is even are on opposite CH_2SCH_2 bridges. No DNMR experiments were performed on these systems.



Scheme 4.05. Conformational flip of dithiacyclophanes C_2-**4.11a** and C_s-**4.11b**.



Scheme 4.06. Synthesis of pyrenophanes **4.09**.

Bis(*S*-methylation) of dithiacyclophane **4.11** with Borch reagent, followed by treatment of the resulting bis(methylsulfonium) salts with *t*BuOK afforded isomer mixtures **4.18** (Scheme 4.06). These were then treated with Borch reagent to remethylate the sulfur atoms and the resulting bis(dimethylsulfonium) salts were reacted with *t*BuOK. This reaction provided different results under different situations. ^{1}H NMR study showed that for n=2-3, the desired cyclophanedienes **4.10a** and **4.10b** were obtained. For n=4, the major component of the product isolated after the reaction was cyclophanediene **4.10c**, but it was contaminated with a small portion of the pyrenophane **4.09c**. For n=5-6, the white solids obtained from the Hofmann elimination were mainly pyrenophanes **4.09d** and **4.09e** with no cyclophanediene **4.10d** and **4.10e**. This is consistent with previous observations in the synthesis of **4.01** and **4.02** that pyrenophanes rather than cyclophanedienes were obtained for Hofmann eliminations when the molecules contained relatively long bridges.[2f] Several steps were very low-yielding, such as Stevens rearrangement (n=5) and Hofmann elimination (n=3,4). The cause for these low yields is most likely the quality of the *t*-BuOK that was used. Although this was not examined methodically, it appears as though the yield of these steps (especially for the Hofmann elimination) is affected by the age of *t*-BuOK.

Treating cyclophanedienes **4.10b** and **4.10c** with DDQ resulted in the formation of pyrenophanes **4.09b** (94%) and **4.09c** (61%) (Scheme 4.06). For n=4, the VID reaction took place at room temperature, and went to completion in 15 min. For n=3, the reaction did not occur at room temperature, but went to completion after being refluxed in benzene for 7 days. This reaction was expected to be difficult because the AM1-calculated bend angle of the pyrene unit in **4.10b** is 116.2°. For n=5-6, the white solid

obtained from the Hofmann elimination were treated with DDQ in order to remove any traces of cyclophanedienes or dihydropyrenophanes. The resulting pyrenophanes **4.09d** and **4.09e** were obtained in less than satisfactory purity. The very small quantity of product thwarted attempted purification.

The most difficult VID reaction, as expected, was the conversion of **4.10a** to **4.09a**. In fact, this reaction was not expected to proceed at all, because the AM1-calculated bend angle θ is 136.6°. However, after reaction for one week under gentle reflux in benzene, a new spot could be clearly seen on the TLC plate slightly below the starting material. The appearance (color, fluorescence) of the spot under both 254 nm and 365 nm light was similar to that of the pyrenophanes **4.09b-e**. Upon continued heating, the new spot gradually became more intense at the cost of starting material. Another spot that has an even lower R_f value appeared on the tlc plate after about 3 weeks of reflux. After 4 weeks reflux, the intensities of the two new spots reached their maxima. A small portion of the crude material was subjected to HPLC analysis, and three fractions were obtained with baseline separations (Fig. 4.04). The first fraction showed a mass signal at *m/z* = 991, which corresponds to the M^++1 of the starting material, cyclophanediene **4.10a** (Fig. 4.05). The second fraction showed a mass signal at *m/z* = 989, which corresponds to the molecular ion peak (M^++1) for the product **4.09a**. The last fraction showed two groups of peaks in the MS, one at *m/z* = 989 and the other at *m/z* = 1215. The higher mass corresponds to a 1:1 adduct of **4.09a** and DDQ (Fig. 4.05). The lower mass peak again corresponds to **4.09a**. Formal [4+2] additions to pyrenophanes with more severely bent pyrene systems have been observed previously.[2] It seems very likely that the third product is either **4.19** (see Fig. 4.05, PP 188), or either of the *endo/exo* isomers due to

addition of the Cl-bearing double bond instead of the CN-bearing double bond. A mixture of isomers is also possible.

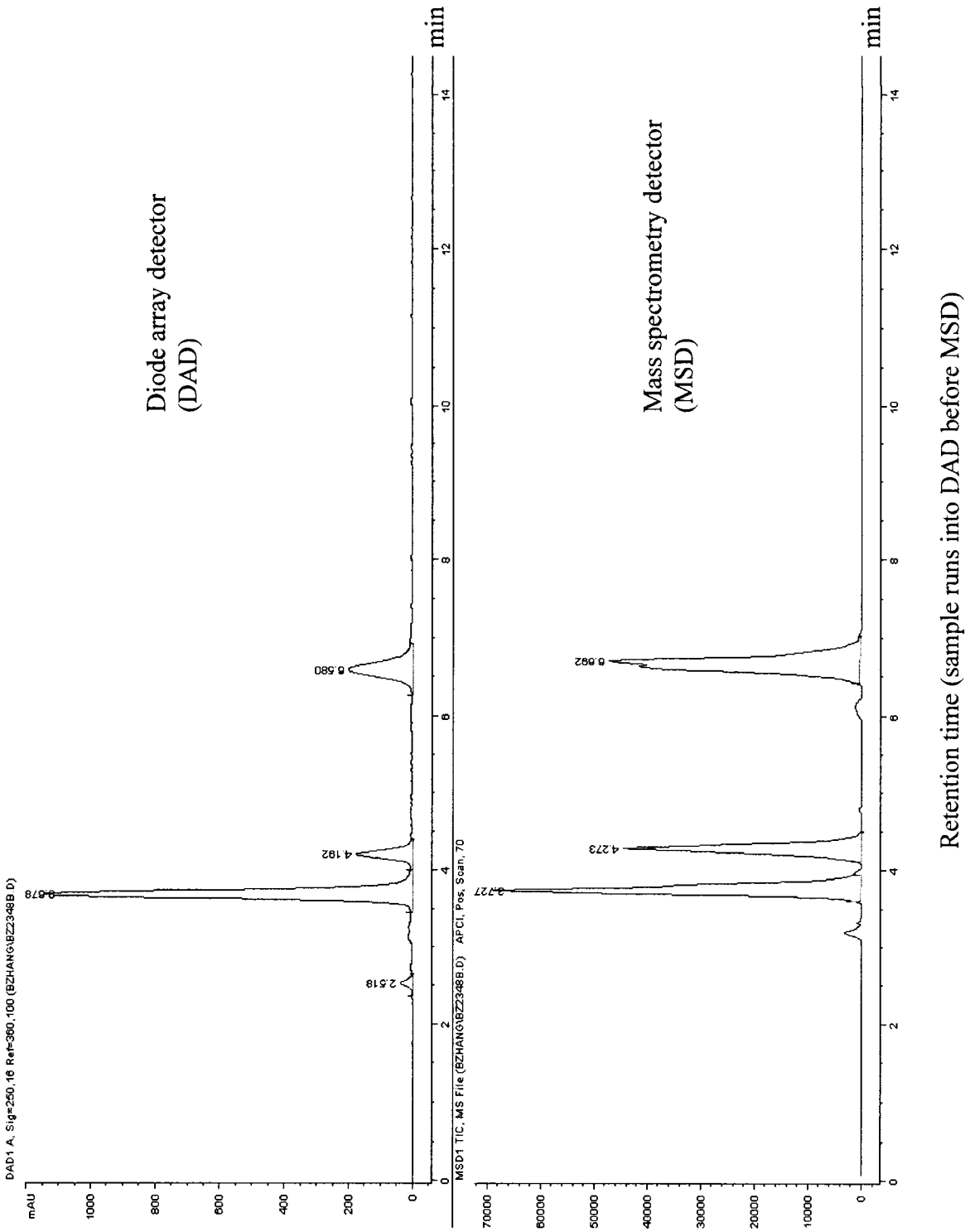


Figure 4.04. HPLC analysis of the resulting mixture of the VID reaction of **4.10a**.

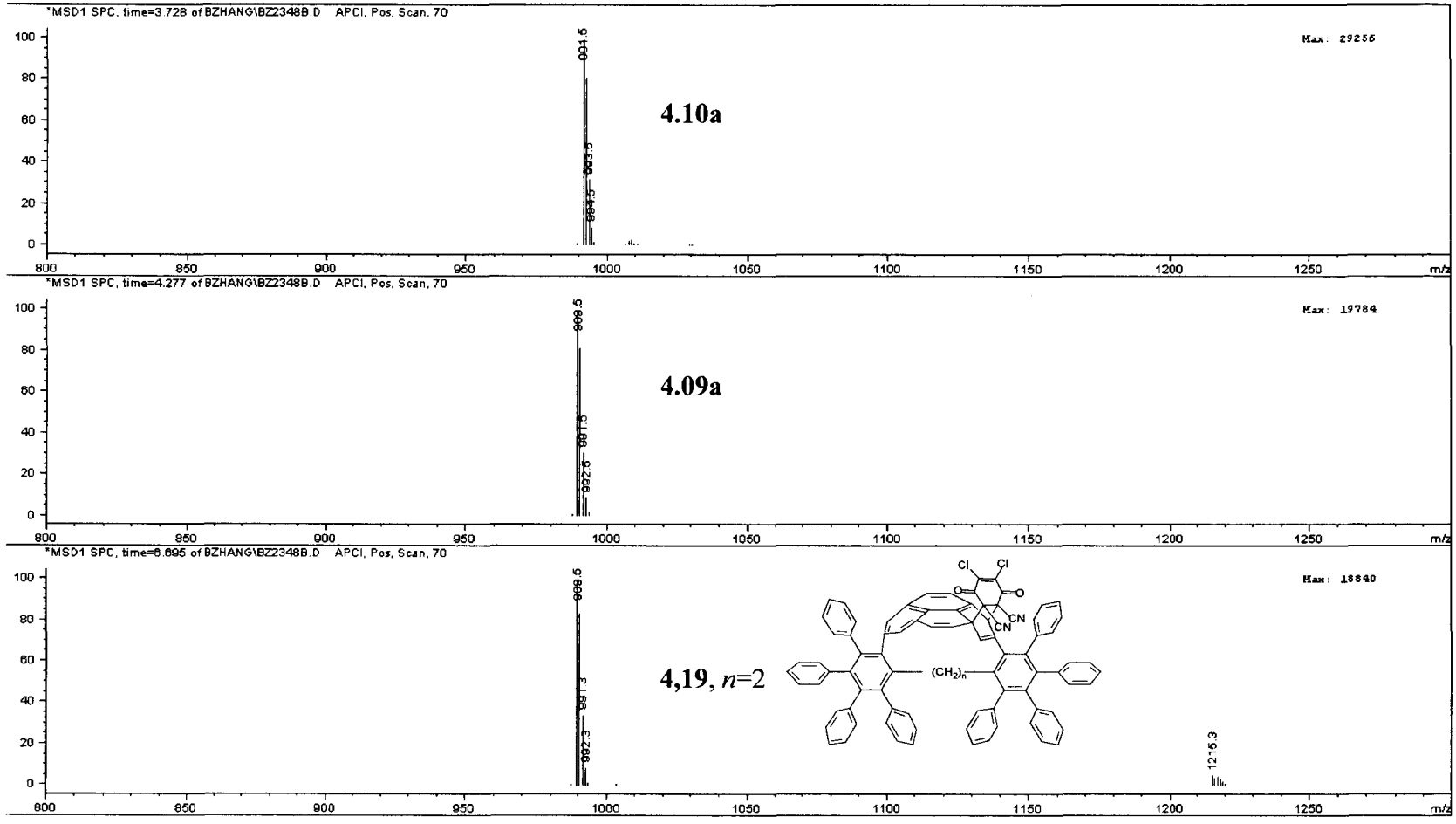
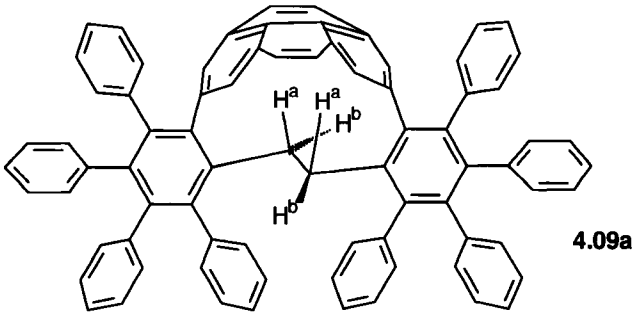


Figure 4.05. HPLC-MS analysis of the resulting mixture of the VID reaction of **4.10a**

As with the dithiacyclophanes **4.11a-e**, the bridge flip in the smallest member of the series of pyrenophanes (**4.09a**) is slower than that of the higher homologs (**4.09b-e**). Pyrenophane **4.09a** is the only member of the series for which two signals are observed for the diastereotopic CH_2 protons in the ^1H NMR spectrum. Specifically, the ^1H NMR spectrum (room temperature, $CDCl_3$) of the crude mixture contains, in addition to the relatively intense signals for the cyclophanediene, a pair of coupled (as determined by a $^1H,^1H$-COSY experiment) multiplets centered at δ −1.14 and 1.11 ppm, the latter of which was observed as a shoulder on a large hydrocarbon signal (δ1.2-1.3) (Fig. 4.07). In C_6D_6, the lower field signal was well resolved (δ 1.86 ppm) and it again showed a cross-peak to the higher field signal (δ −0.55 ppm). Examination of simple molecular models revealed that **4.09a** should adopt a conformation in which two of the bridge hydrogen atoms point into the concave face of the pyrene system (H^a), while the other two point to the side (H^b) (Fig. 4.06). Being further within the shielding zone of the pyrene moiety, H^a should have a significantly higher field chemical shift than H^b. The integration of the signal at δ −1.14 ppm is about one-fifth of the magnitude of the signal at δ 2.58 ppm (benzylic CH_2 for **4.10a**), thus the ratio of **4.09a**: **4.10a** is *ca.* 1:2.5 in the crude mixture. A sharp singlet could also be seen at δ 7.36 ppm (integration of 8, relative to the signal at δ −1.14), which was not present in the spectrum of cyclophanediene **4.10a**. This might be due to the two accidentally degenerate pyrene signals.



4.09a

Figure 4.06. Two kinds of hydrogen atoms in the central ethylene bridge.

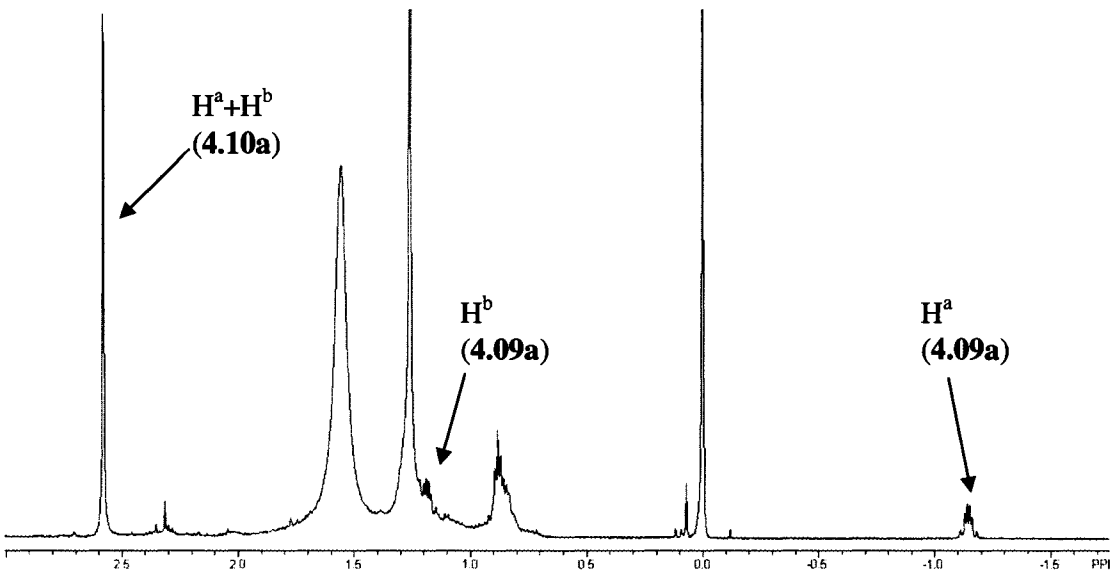


Figure 4.07. High field region of the crude reaction mixture of the VID reaction of **4.10a**.

4.3.2 Structure of Pyrenophanes 4.09a-e

Attempts to grow crystals of pyrenophanes **4.09b**, **4.09c** and **4.09e** were performed and a good quality crystal of **4.09c** was obtained from a mixed solvent of chloroform and heptane. Suitable crystals of **4.09b** and **4.09e** were not obtained. The crystal structure was determined in collaboration with R. Pascal (Princeton University). The full crystallographic details are shown in Appendix A. The β angles (Fig. 4.08)[8] of **4.09c**

(centered at 2 and 7 positions of pyrene) were found to be 12.9° and 11.8°, which are smaller than the corresponding β values of **4.20** (16.1° and 16.3°)[9], but greater than that of the [*n*](2,7)pyrenophanes (<9.0°).[1d-e]

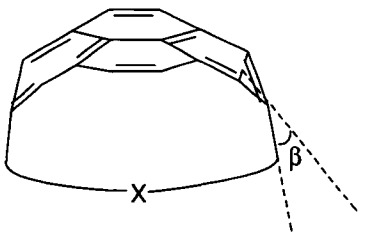
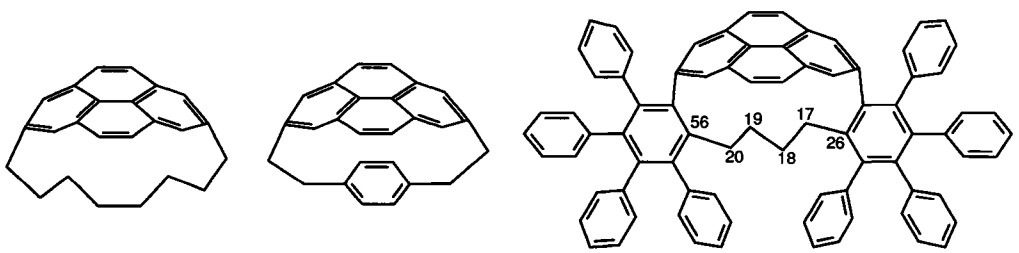


Figure 4.08. β angle of a pyrenophane.



4.02c ($\theta_{X\text{-ray}}$=80.8°) (θ_{calc}=87.0°)

4.20 ($\theta_{X\text{-ray}}$=89.7°) (θ_{calc}=100.4°)

4.09c ($\theta_{X\text{-ray}}$=87.7°) (θ_{calc}=94.8°)

Note: the numbering of the carbon atoms will follow the crystallographic numbering system, and will be different from the IUPAC numbering system.

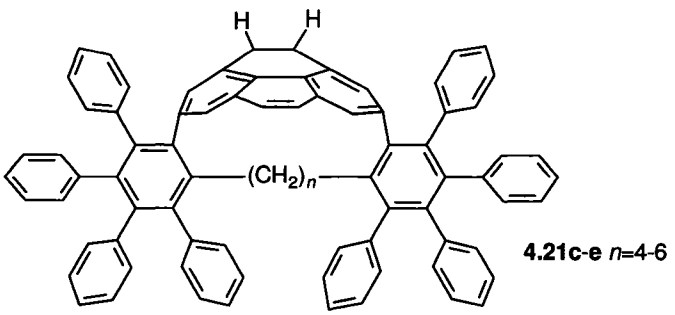
Figure 4.09. Pyrenophanes having 8 carbon atoms in the bridge.

The central butylene group is almost coplanar with torsion angles of 3.3° (C(56)-C(20)-C(19)-C(18)), 5.6° (C(20)-C(19)-C(18)-C(17)) and 1.2° (C(19)-C(18)-C(17)-C(26)) (Fig. 4.09). The C-C-C bond angles about the benzylic carbon atoms are significantly enlarged (118.5° and 119.5°), whereas those about the homobenzylic carbon atoms are close to the tetrahedral angle (111.5° and 112.2°). The bend angle θ of pyrenophane **4.09c** in the crystal is 87.7°, which is 7.1° less than the AM1-calculated value (94.8°). Pyrenophanes **4.20** and **4.09c** can be viewed as benzannulated derivatives

of **4.02c** (Fig. 4.09). An 8-carbon bridge can be identified in each case. It can be seen that in both cases "benzannulation" has the effect of shortening the bridge and thus increasing θ. The annulation of three bonds with one benzene unit (*i.e.* **4.20**) has a more pronounced effect than the annulation of two separate bonds (*i.e.* **4.09c**).

4.3.3 ^{1}H NMR Spectra of Pyrenophanes 4.09a-e

Pyrenophanes **4.09b-e** were obtained in relatively pure form, except for some hydrocarbon impurities, presumably solvent-derived, which were observed in the ^{1}H NMR spectrum. Pyrenophane **4.09e**, which was obtained in the largest quantities among all homologs, contained the least hydrocarbon impurities. Pyrenophanes **4.09b-d**, especially **4.09d**, contained relatively large quantity of hydrocarbon impurity. It is partially because the small quantities of material that were available made purification and characterization somewhat challenging. All of the pyrenophanes were dried under high vacuum for extended periods, so it may be that small alkanes somehow associate favorably with the pyrenophane structures.



4.21c-e *n*=4-6

Figure 4.10. Dihydropyrenophanes **4.21c-e**.

It was observed that the VID reactions of **4.10c-e** were incomplete at room temperature and a significant amount (*ca.* 10-35%) of 4,5-dihydropyrenophanes **4.21c-e**

were formed (Fig. 4.10), which was indicated by the existence of a pair of symmetrical multiplets centered at δ ~3.1 and 3.3 ppm. The same observation was also reported in other pyrenophane syntheses.[10] Upon reflux in benzene, these multiplets disappeared, which indicated that the reactions were complete.

The high-field (δ 0.8 to –1.8 ppm) and low-field regions (δ 8.5 to 6.0 ppm) of the ^{1}H NMR spectra of pyrenophanes **4.09a-e** are shown in Fig 4.11 and Fig. 4.12, respectively, and chemical shift data are presented in Table 4.06. As mentioned earlier, pyrenophane **4.09a** is a minor component in a mixture consisting of cyclophanediene **4.10a**, **4.09a** and DDQ-adduct **4.19**. As such, the chemical shifts, for H_A and H_B could not be identified. The assignment of H_A to the lower-field pyrene signal and H_B to the higher-field pyrene signal was made by analogy to the previously synthesized pyrenophanes **4.01** and **4.02**. The lowest-field aliphatic signals were assigned to the benzylic bridge protons H_D. H_E and H_F were assigned using ^{1}H,^{1}H-COSY experiments.

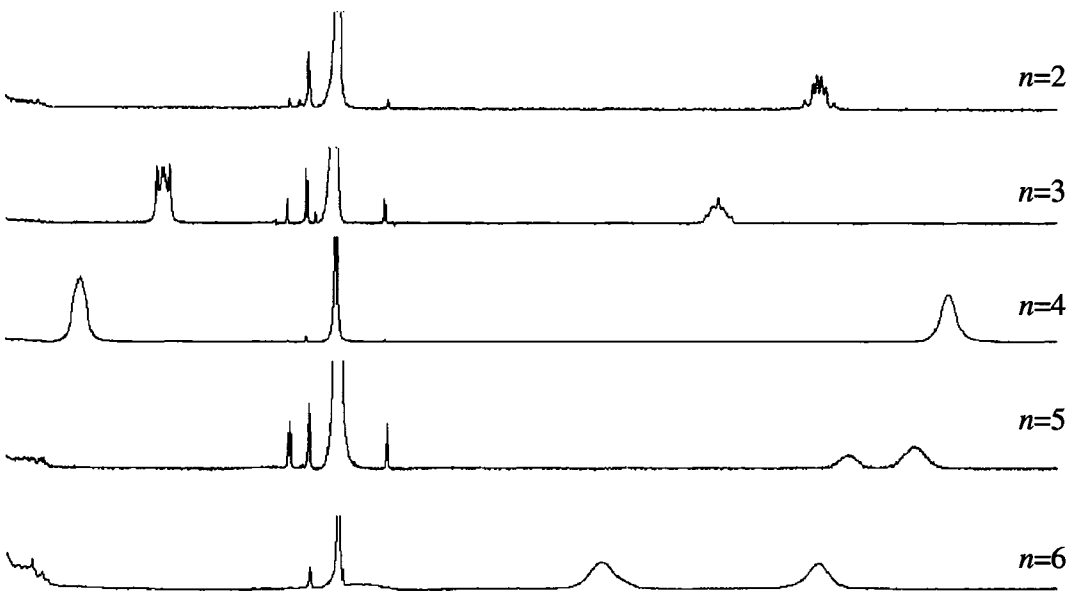


Figure 4.11. High field region of the ^{1}H NMR of pyrenophanes **4.09a-e**.

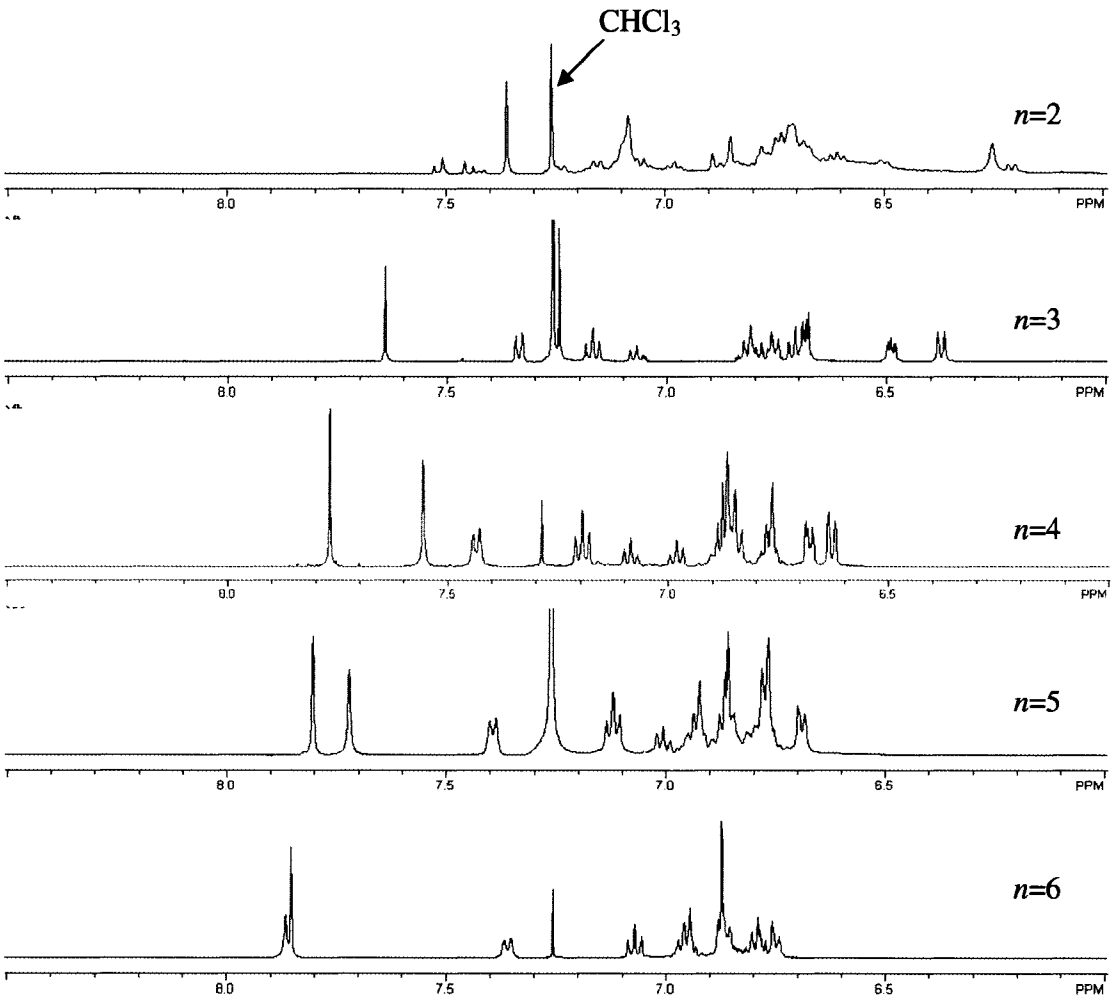


Figure 4.12. Aromatic region of the ^{1}H NMR spectra of pyrenophanes **4.09a-e**.

As observed in pyrenophanes **4.01** and **4.02**, the chemical shifts of H_A and H_B move to higher field as the bridge becomes shorter. Additionally, this effect is more pronounced for H_B. The range spanned by both H_A ($\Delta\delta$ =0.22 ppm) and H_B ($\Delta\delta$ =0.60 ppm) for **4.09b-e** is similar to the ranges spanned by the analogous protons in **4.01b-e** and **4.02b-e** (Table 4.08), which is indicative of a comparable range of structural change in the pyrene system. The signals for the benzylic bridge protons also move steadily to higher field as the bridge is shortened. Moreover, the magnitude of the upfield shift in comparison to the 1,*n*-diphenylalkanes also increases steadily. Clear trends were not

evident for H_E and H_F, but these protons appeared at very high field due to the shielding effect of the pyrene system.

Table 4.07. Chemical shifts (δ ppm) of the well-resolved signals (**4.09a-e**).

Compound	H_A	H_B	H_D	H_E	H_F
4.09a *n*=2	- [a]	- [a]	0.02 [b] (2.92) [d] Δδ=2.90	-	-
4.09b *n*=3	7.64	7.25	0.41 (2.62) Δδ=2.21	–0.93 (1.96) Δδ=2.89	-
4.09c *n*=4	7.74	7.52	0.62 (2.62) Δδ=2.00	–1.48 (1.59) Δδ=3.07	-
4.09d *n*=5	7.80	7.72	1.36 [c] (2.62) Δδ=1.26	–1.39 (1.59) Δδ=2.98	–1.24 (1.29) Δδ=2.53
4.09e *n*=6	7.86	7.85	1.85 (2.62) Δδ=0.77	–0.63 (1.59) Δδ=2.22	–1.16 (1.29) Δδ=2.45

Notes: (a) signal not observed; (b) midpoint of the signals at δ 1.11 and –1.14 ppm; (c) signal overlapped with grease peak and the chemical shift was determined by a $^1H,^1H$-COSY experiment; (d) numbers in brackets are calculated values for the corresponding protons in the analogous 1,*n*-diphenylalkanes.[6]

Table 4.08. Δδ for pyrene signals of **4.01**, **4.02** and **4.09**.

Compounds	Δδ for H_A (ppm)	Δδ for H_B (ppm)
4.09b-e	0.22	0.60
4.01b-e	0.20	0.50
4.02b-e	0.29	0.53

4.3.4 UV-vis Spectra of Pyrenophanes 4.09b-e

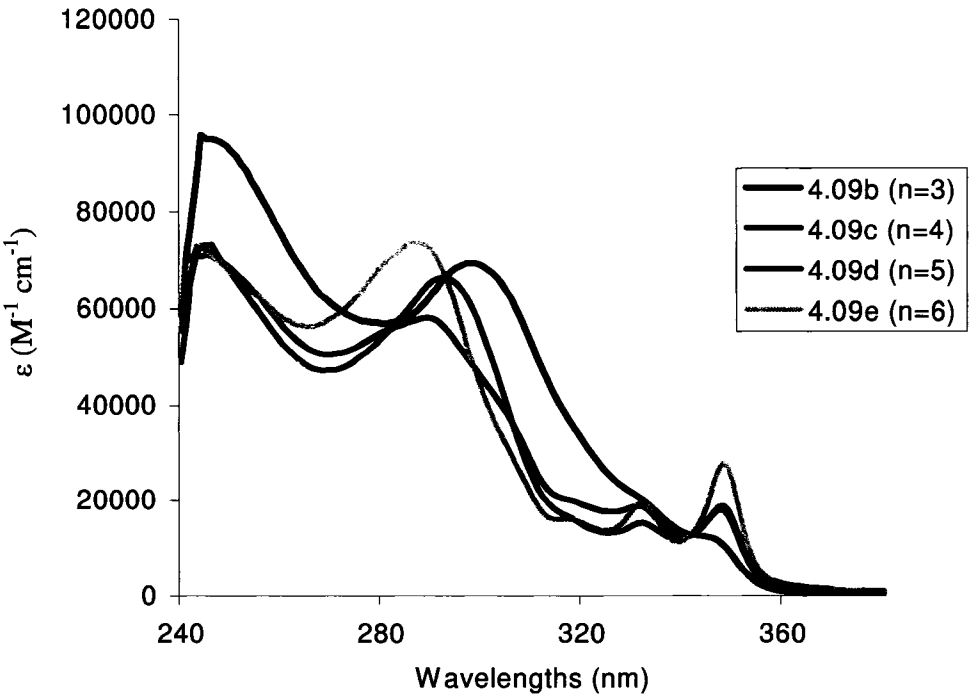


Figure 4.13. The UV-vis spectra of pyrenophanes **4.09b-e**.

As described in Chapter 3, the UV-vis spectra of pyrene and its bridged derivatives (pyrenophanes) all contain three absorption bands, namely β' (~242 nm), β (~260-290 nm) and *p* (~300-340 nm).[11,2e] The UV-vis absorptions of 1,*n*-dioxa[*n*](2,7)pyrenophanes (**4.01**) and [*n*](2,7)pyrenophanes (**4.02**) have been studied in the Bodwell group.[2e,2g] It has been reported that, as the bridges become shorter, the β' band undergoes a significant red shift and the β band undergoes a less pronounced red shift. Consequently, in the UV-vis spectrum of the more highly distorted pyrenophanes (such as **4.01b** and **4.02b**), the β' and β bands have merged. The *p* bands usually remain stationary and became less intense as the length of the bridge decreases. The series of bis(hexaphenylbenzene)s **4.21** (Fig. 4.14) are reasonable model systems for pyrenophane **4.09a-e** and they have been reported to

have absorption maxima at 247-248 nm and 267-268 nm.[12] UV-vis data for pyrene, **4.02b-e**, **4.21b-e** and **4.09b-e** are compiled in Table 4.09.

Table 4.09. UV absorptions of pyrenophanes **4.09b-e** and related compounds.

Compounds	Polyphenyl bands (nm)		Pyrene β′/β bands (nm)	Pyrene *p* bands (nm)			θ_{calcd} (°)	Lit.
Pyrene (**3.64**)	-	-	242 (88) 273 (54)	306 (13)	320 (32)	336 (56)	-	4
4.02b	-	-	277 (62)	309 (9.0)	323 (10)	338 (13)	104.6	2d
4.02c	-	-	267 (64) 287 (30)	311 (10)	324 (16)	339 (21)	87.0	2d
4.02d	-	-	261 (57) 284 (23)	309 (9.5)	323 (19)	338 (29)	70.3	2d
4.02e	-	-				340	54.4	2e
4.21b-e	247-248 (93-99)	267-268 (51-62)	-	-	-	-	-	10
4.09b	244 (96)	-	298 (70)	-	332 (20, sh)	346 (12, sh)	116.2	-
4.09c	246 (73)	-	292 (67)	318 (16, sh)	332 (16)	348 (18)	94.8	-
4.09d	245 (71)	-	289 (58) 305 (38, sh)	317 (20, sh)	331 (19)	348 (19)	77.6	-
4.09e	243 (73)	-	287 (74) 305 (31, sh)	317 (16)	332 (20)	348 (28)	62.0	-

Notes: the values in the brackets are $\varepsilon \times 10^{-3}$ (M^{-1} cm^{-1}).

Pyrenophanes **4.09b-e** can be viewed as hybrids of simple pyrenophanes **4.02** and polyphenyl compounds **4.21** and the observed spectra (Fig. 4.13) appear to be consistent with this perspective. The most intense absorptions (243-246 nm) are presumably due to the absorption of pentaphenylbenzene units. The second intense absorption at 290 to 300

nm is likely due to the merged β'/ β bands of the pyrene system. The absorption bands at 320 to 360 nm are likely the pyrene *p* bands. As observed in **4.01** and **4.02**, the *p* bands became less intense as the bridge is shortened. All three *p* bands are discernable in the spectrum of **4.09e**, while in the case of **4.09b** and **4.09c**, only the two longer wave-length absorptions are discernable and the band at 317-318 nm appears as a shoulder. In the case of **4.09b**, none of the *p* bands is clearly discernable and only two shoulders are observed.

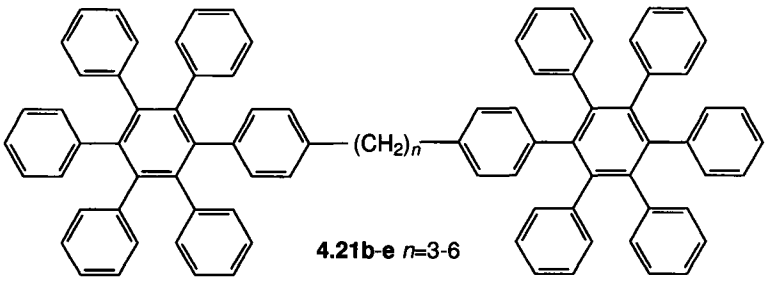


Figure 4.14. Analogous compounds **4.21b-e**.

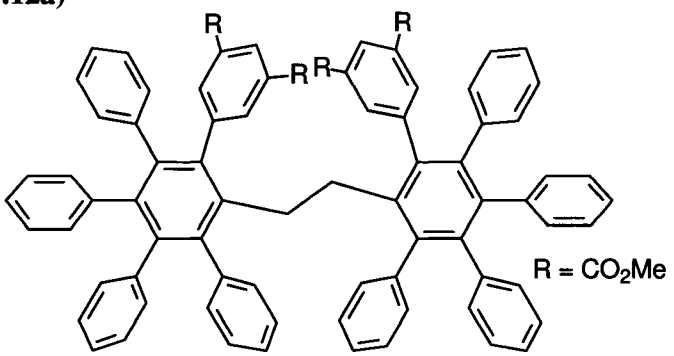
4.4 Conclusions

In this chapter, the syntheses of pyrenophanes **4.09b-e** are described. The bend angles of **4.09a-e** were calculated at the AM1 level of theory and the bend angle for **4.09b** is predicted to be the largest of any pyrenophanes isolated to date. Strong evidence was obtained for the formation of pyrenophane **4.09a**, which has a much larger calculated bend angle θ, from a very long reaction of cyclophanediene **4.10a** with DDQ. Although a complete separation of the three main components (pyrenophane **4.09a**, cyclophanediene **4.10a**, and a DDQ adduct **4.19**) was achieved using analytical HPLC, macroscopic amounts of **4.09a** have not yet been isolated.

4.4 Experimental

General. For general procedures please refer to the section in Chapter 2.

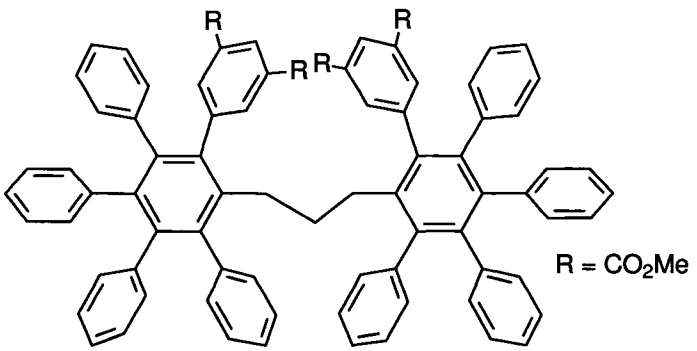
1,2-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (4.12a)



A solution of 1,6-bis(3,5-bis(methoxycarbonyl)phenyl)-1,5-hexadiyne (**4.13a**) (0.50 g, 1.08 mmol) and tetraphenylcyclopentadienone (**4.14**) (1.04 g, 2.70 mmol) in degassed diphenyl ether (60 mL) was heated at reflux for 20 h. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (36 cm × 3.3 cm dichloromethane to 10% ethyl acetate/dichloromethane) to give 1,2-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.12a**) (1.21 g, 1.03 mmol, 72%, R_f=0.20 in dichloromethane) as a yellow solid; mp: 183-185 °C (chloroform); IR (powder): 3023 (w), 2950 (m), 1724 (s), 1601 (w), 1496 (w), 1441 (m), 1240 (s), 758-742 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.34 (s, 4H), 7.28-7.27 (m, 6H), 6.88-6.72 (m, 28H), 6.67-6.63 (m, 6H), 3.87 (s, 12H), 2.41 (s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 141.6, 141.4, 141.1, 141.05, 140.98, 140.8, 140.5, 140.1, 139.9, 139.3, 136.1, 136.0, 131.4, 131.1, 130.95, 130.92, 129.6, 128.6, 127.7, 126.7, 126.6, 125.7, 125.5, 125.4, 125.3, 52.3, 30.9; LC-MS (APCI) *m/z*:

1176 (18, M^++1), 1193 (100, M^++18); Anal. Calcd for $C_{82}H_{62}O_8$: C, 83.79; H, 5.32. Found: C, 84.76; H, 5.61.

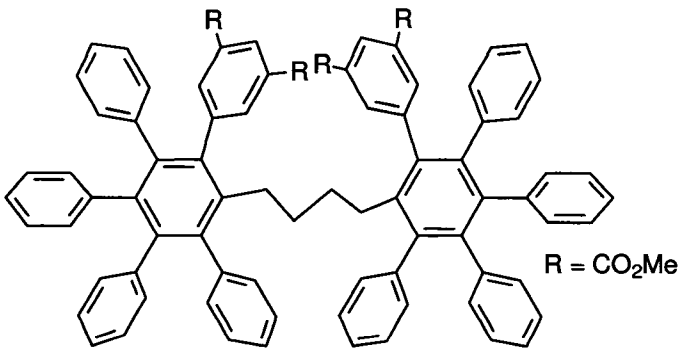
1,3-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (4.12b)



A solution of 1,7-bis(3,5-bis(methoxycarbonyl)phenyl)-1,6-heptadiyne (**4.13b**) (3.03 g, 6.36 mmol) and tetraphenylcyclopentadienone (**4.14**) (6.11 g, 15.9 mmol) in degassed diphenyl ether (60 mL) was heated at reflux for 6 d. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (30 cm × 4.2 cm, dichloromethane to 10% ethyl acetate/dichloromethane) to give 1,3-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.12b**) (5.43 g, 4.58 mmol, 72%, R_f=0.15 in dichloromethane) as a yellow solid; mp: 151-152 °C (chloroform); IR (powder): 3042 (w), 3025 (w), 2952 (w), 1724 (s), 1600 (w), 1496 (m), 1441 (w), 1240 (s), 758 (m), 743(m), 698 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.42 (t, *J*=1.6 Hz, 2H), 7.89 (d, *J*=1.6 Hz, 4H), 6.95-6.94 (m, 6H), 6.80-6.71 (m, 31H), 6.69 (d, *J*=1.6 Hz, 2H), 6.67 (t, *J*=1.4 Hz, 1H), 3.93 (s, 12H), 1.94-1.91 (m, 4H), 1.03-1.01 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 141.8, 141.3, 141.0, 140.7, 140.4, 140.21, 140.20, 139.0, 138.6, 137.3, 137.0, 136.6, 136.3, 131.5, 131.0, 130.8, 130.3,

129.5, 127.3, 127.2, 126.8, 126.6, 126.44, 126.37, 125.9, 125.1, 53.2, 52.9, 52.0; LC-MS (APCI) *m/z*: 1189 (100, M^++1), 797 (9); Anal. Calcd for $C_{83}H_{64}O_8$: C, 83.80; H, 5.43. Found: C, 81.32; H, 5.74.

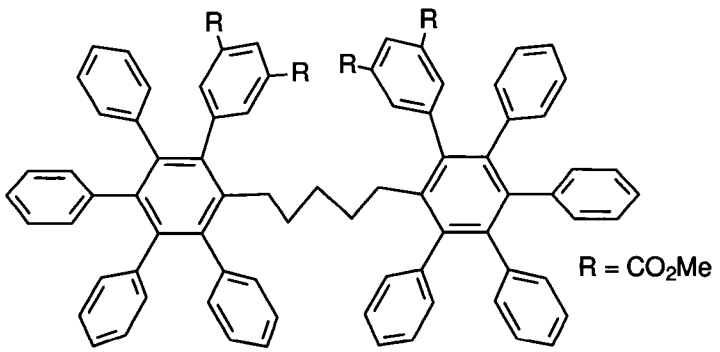
1,4-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (4.12c)



A solution of 1,8-bis(3,5-bis(methoxycarbonyl)phenyl)-1,7-octadiyne (**4.13c**) (3.03 g, 6.18 mmol) and tetraphenylcyclopentadienone (**4.14**) (6.40 g, 16.68 mmol) in degassed diphenyl ether (60 mL) was heated at reflux for 3 d. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (28 cm × 4.2 cm, dichloromethane to 14% ethyl acetate/dichloromethane) to give 1,4-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.12c**) (7.36 g, 6.12 mmol, 99%, R_f=0.20 in dichloromethane) as a yellow solid; mp: 167-169 °C (chloroform); IR (nujol): 3043 (w), 3025 (w), 2949 (w), 1725 (s), 1600 (w), 1441 (m), 1352 (w), 1240 (s), 1196 (w), 1023 (w), 745 (m), 724 (w), 698 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.37 (t, *J*=1.5 Hz, 2H), 7.86 (d, *J*=1.6 Hz, 4H), 7.00-6.98 (m, 6H), 6.87-6.71 (m, 36H), 3.91 (s, 12H), 1.59-1.57 (m, 4H), 0.69-0.67 (m, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 141.8, 141.3, 141.0, 140.6, 140.4, 140.3, 140.2, 138.8,

138.6, 138.0, 135.9, 131.4, 131.2, 131.1, 130.5, 129.5, 128.6, 127.2, 126.9, 126.7, 126.6, 126.2, 125.6, 125.4, 52.4, 34.9, 30.3; LC-MS (APCI) *m/z*: 1277 (7), 1261 (10), 1233 (45), 1204 (100, M^++1), 1189 (5); Anal. Calcd for $C_{84}H_{66}O_8$: C, 83.84; H, 5.53. Found: C, 83.68; H, 5.98.

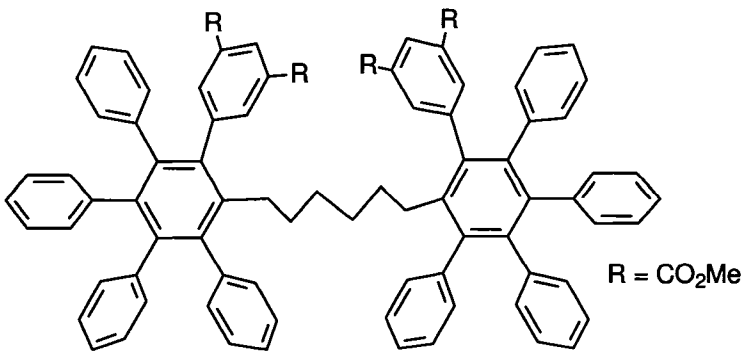
1,5-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (4.12d)



A solution of 1,9-bis(3,5-bis(methoxycarbonyl)phenyl)-1,8-nonadiyne (**4.13d**) (2.40 g, 4.76 mmol) and tetraphenylcyclopentadienone (**4.14**) (5.00 g, 12.8 mmol) in degassed diphenyl ether (45 mL) was heated at reflux for 4 d. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (31 cm × 4.1 cm, dichloromethane to 10% ethyl acetate/dichloromethane) to give 1,5-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.12d**) (3.85 g, 3.14 mmol, 66%, R_f=0.25 in dichloromethane) as a yellow solid; mp: 152-157 °C (chloroform); IR (powder): 3044 (w), 3025 (w), 2951 (m), 1724 (s), 1600(w), 1496 (m), 1441 (m), 1407 (m), 1352 (m), 1240 (s), 1072 (w), 1001 (w), 913 (w), 747 (s), 724 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.39 (t, *J*=1.6 Hz, 2H), 7.96 (d, *J*=1.6 Hz, 4H), 7.10-7.07 (m, 4H), 7.02-6.99 (m, 6H), 6.85-6.75 (m, 30H), 3.89 (s, 12H), 1.97-

1.94 (m, 4H), 0.74-0.71 (m, 4H), 0.16-0.13 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 166.3, 142.0, 141.4, 141.0, 140.7, 140.6, 140.4, 140.3, 138.8, 138.6, 138.4, 136.0, 131.4, 131.23, 131.18, 130.6, 129.6, 128.6, 127.3, 127.0, 126.9, 126.7, 126.1, 125.6, 125.4, 52.4, 31.5, 30.3, 30.1; LC-MS (APCI) *m/z*: 1275 (6), 1247 (37), 1235 (5), 1218 (100, M^++1); Anal. Calcd for $C_{85}H_{68}O_8$: C, 83.86; H, 5.63. Found: C, 83.59; H, 5.44.

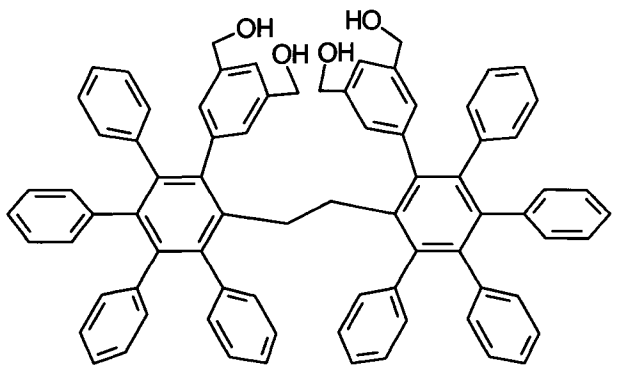
1,6-Bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (4.12e)



A solution of 1,10-bis(3,5-bis(methoxycarbonyl)phenyl)-1,9-nonadiyne (**4.13e**) (3.06 g, 5.90 mmol) and tetraphenylcyclopentadienone (**4.14**) (6.13 g, 15.93 mmol) in degassed diphenyl ether (60 mL) was heated at reflux for 2 d. The mixture was cooled to room temperature and (without removal of the solvent) purified by column chromatography (26 cm × 4.2 cm, dichloromethane to 10% ethyl acetate/dichloromethane) to give 1,6-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.12e**) (6.78 g, 5.55 mmol, 94%, R_f=0.20 in dichloromethane) as a faint yellow solid; mp: 134-135 °C (chloroform); IR (powder): 3056 (w), 3025 (w), 2950 (w), 1724 (s), 1600 (w), 1496 (m), 1441 (w), 1351 (w), 1301 (w), 1239 (s), 1001 (w), 909 (w), 746 (s), 698 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 8.40 (t, *J*=1.6 Hz, 2H), 7.99 (d, *J*=1.7 Hz, 4H), 7.06-7.02

(m, 10H), 6.84-6.75 (m, 30H), 3.86 (s, 12H), 2.03-2.00 (m, 4H), 0.88-0.84 (m, 4H), 0.19 (br, s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 142.0, 141.4, 141.1, 140.71, 140.67, 140.6, 140.4, 140.3, 138.9, 138.8, 138.5, 136.02, 136.01, 131.4, 131.3, 131.2, 130.6, 129.7, 128.7, 127.4, 127.0, 126.71, 126.66, 126.2, 125.6, 125.4, 52.4, 31.6, 30.7, 28.9; LC-MS (APCI) *m/z*: 1304 (7), 1289 (10), 1260 (40), 1232 (100, M^++1); Anal. Calcd for $C_{86}H_{70}O_8$: C, 83.88; H, 5.73. Found: C, 84.09; H, 5.81.

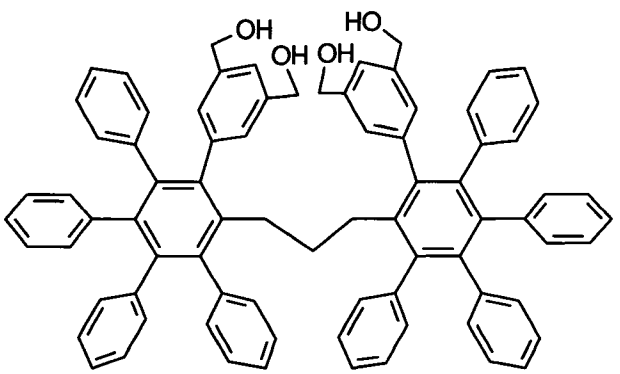
1,2-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (4.15a)



To a 0 °C stirred solution of 1,2-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.12a**) (1.20 g, 1.02 mmol) in dichloromethane (60 mL) was added dropwise DIBAL-H solution in dichloromethane (16.3 mL, 1.0 M, 16.3 mmol). The mixture was stirred at room temperature for 15 h. Aqueous 6 M hydrochloric acid (100 mL) was added and the mixture was stirred for 10 min. The aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (16 cm × 3.3 cm, 10% ethyl acetate to pure ethyl acetate) to give 1,2-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.15a**) (0.94 g, 0.89 mmol, 87%, R_f=0.45 in ethyl acetate) as a

yellow solid; mp: >300 °C (chloroform); IR (powder): 3368 (br, w), 3054 (w), 1600 (w), 1506 (w), 1441 (w), 1070 (w) 1023 (w), 736 (m), 718 (m), 697 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.19-7.18 (m, 6H), 6.94 (s, 2H), 6.87-6.72 (m, 30H), 6.66 (d, *J*=7.0 Hz, 4H), 6.34 (br, s, 4H), 4.44 and 4.42 (AB system, J_{AB}=13.1 Hz, Δν=10.4 Hz, 8H), 2.49 (s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) (low solubility, several signals not observed) δ 141.4, 140.2, 135.1, 134.9, 131.5, 131.3, 131.2, 131.1, 127.5, 126.7, 126.7, 126.5, 116.7, 65.4, 39.7; LC-MS (APCI-) *m/z*: 1098 (100, MCl^-); Anal. Calcd for $C_{78}H_{62}O_4$: C, 88.10; H, 5.88. Found: C, 85.98; H, 5.90.

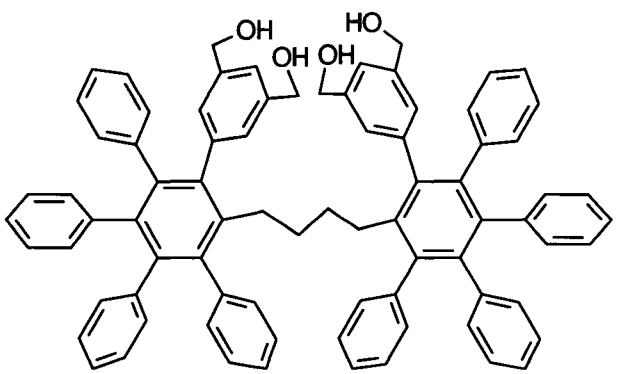
1,3-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (4.15b)



To a 0 °C stirred solution of 1,3-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.12b**) (1.29 g, 1.08 mmol) in dichloromethane (65 mL) was added dropwise DIBAL-H solution in dichloromethane (17.4 mL, 1.0 M, 17.4 mmol). The mixture was stirred at room temperature for 15 h. Aqueous 6 M hydrochloric acid (100 mL) was added and the mixture was stirred for 10 min. The aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (7 cm × 3.3 cm, 70% ethyl

acetate/dichloromethane) to give 1,3-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.15b**) (0.96 g, 0.89 mmol, 82%, R_f=0.50) as a yellow solid; mp: >300 °C (ethyl acetate); IR (powder): 3346 (br, w), 3056 (w), 1664 (w), 1600 (w), 1511 (w), 1441 (w), 1071 (w), 1019 (w), 807 (w), 761 (w), 743 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.09-7.08 (m, 6H), 6.97 (s, 2H), 6.91-6.89 (m, 4H), 6.82-6.67 (m, 36H), 4.36 (nearly degenerate AB system, J_{AB}=13.8 Hz, Δν~0 Hz, 8H), 2.07-2.03 (m, 4H), 1.24-1.19 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.4, 141.2, 140.94, 140.90, 140.86, 140.8, 140.7, 140.4, 140.2, 140.0, 138.7, 137.8, 131.5, 131.4, 131.3, 130.9, 129.1, 127.3, 126.63, 126.57, 126.55, 126.0, 125.24, 125.15, 123.2, 65.0, 32.3, 31.2, 0.21; LC-MS (APCI) *m/z*: 1111 (100, M^-) 413 (5), 369 (15); Anal. Calcd for $C_{79}H_{64}O_4$: C, 88.07; H, 5.99. Found: C, 85.16; H, 5.61.

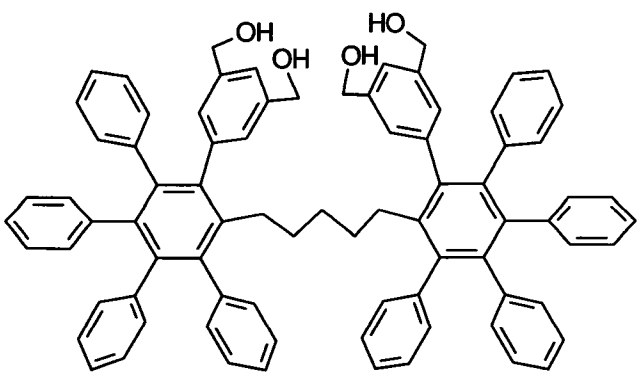
1,4-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (4.15c)



To a 0 °C stirred solution of 1,4-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.12c**) (7.50 g, 6.23 mmol) in dichloromethane (395 mL) was added dropwise DIBAL-H solution in dichloromethane (99.7 mL, 1 M, 99.7 mmol). The mixture was stirred at room temperature for 15 h. Aqueous 6 M hydrochloric acid (100 mL) was added, and the mixture was stirred for 10 min. The aqueous layer was extracted

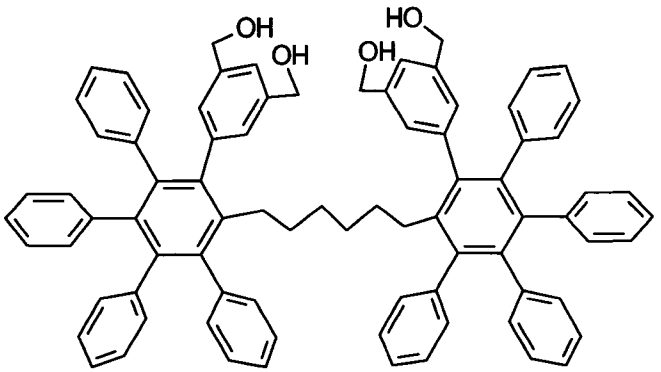
with dichloromethane (3 × 300 mL). The combined organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (15 cm × 4.2 cm, 10% ethyl acetate to pure ethyl acetate) to give 1,4-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.15c**) (4.89 g, 4.49 mmol, 72%, R_f=0.85 in ethyl acetate) as a white solid; mp: >300 °C (ethyl acetate); IR (powder): 3319 (br, w), 3056 (w), 2958 (w), 1946 (w), 1700 (w), 1601 (w), 1576 (w), 1496 (w), 1441 (w), 1405 (w), 1155 (w), 1070 (w), 909 (w), 863 (w), 762 (w), 745 (w), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) 7.08-7.07 (m, 6H), 7.00 (s, 2H), 6.95-6.94 (m, 4H), 6.87 (d, J=1.4 Hz, 4H), 6.79-6.71 (m, 30H), 4.45 and 4.41 (AB system, J_{AB}=12.8 Hz, Δν=17.9 Hz, 8H), 1.74-1.71 (m, 4H), 0.81-0.78 (m, 4H); ^{13}C NMR (125.76 MHz, DMSO-d_6) δ 140.8, 140.45, 140.42, 140.33, 140.27, 139.9, 139.8, 139.4, 138.1, 137.6, 131.0, 130.94, 130.88, 130.81, 130.77, 130.29, 130.25, 130.23, 127.1, 126.4, 125.9, 125.2, 125.15, 125.07, 121.7, 62.8, 29.64, 29.63; LC-MS (APCI) *m/z*: 1126 (100, MCl^-); Anal. Calcd for $C_{80}H_{66}O_4$: C, 88.04; H, 6.10. Found: C, 80.61; H, 5.75.

1,5-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (4.15d)



To a 0 °C stirred solution of 1,5-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.12d**) (5.36 g, 2.61 mmol) in dichloromethane (250 mL) was added dropwise DIBAL-H solution in dichloromethane (70.4 mL, 1 M, 70.4 mmol). The mixture was stirred at room temperature for 46 h. Aqueous 6 M hydrochloric acid (100 mL) was added, and the mixture was stirred for 10 min. The aqueous layer was extracted with dichloromethane (3 × 300 mL). The combined organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (12 cm × 4.2 cm, 10% ethyl acetate/dichloromethane to pure ethyl acetate) to give 1,5-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.15d**) (4.47 g, 4.05 mmol, 92%, R_f=0.85 in ethyl acetate) as a yellow solid; mp: 169-172 °C (chloroform); IR (powder): 3376 (br, w), 3042 (w), 3022 (w), 2926 (w), 1734 (w), 1600 (w), 1576 (w), 1496 (w), 1457 (w), 1411 (w), 1399 (w), 1373 (w), 1240 (w), 1154 (w), 1071 (w), 1020 (m), 1020(m), 751 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.10-7.02 (m, 12H), 6.90 (s, 4H), 6.83-6.75 (m, 28H), 6.71-6.69 (m, 2H), 4.35 (nearly degenerate AB system, J_{AB}=13.7 Hz, Δν~0 Hz, 8H), 2.07-2.04 (m, 4H), 0.88 (br, s, 4H), 0.24-0.21 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.6, 141.1, 140.9, 140.8, 140.7, 140.6, 140.3, 140.2, 138.7, 138.5, 131.5, 131.41, 131.36, 130.7, 128.7, 127.3, 126.67, 126.65, 126.6, 126.1, 125.3, 125.2, 123.2, 65.0, 31.8, 30.9, 30.5; LC-MS (APCI-) *m/z*: 1140 (5), 1104 (100, M^-) 1084 (30), 1075 (20), 1068 (16), 1056 (14), 1044 (11), 1028 (10), 1014 (5); Anal. Calcd for $C_{81}H_{68}O_4$: C, 88.01; H, 6.20. Found: C, 86.09; H, 6.47.

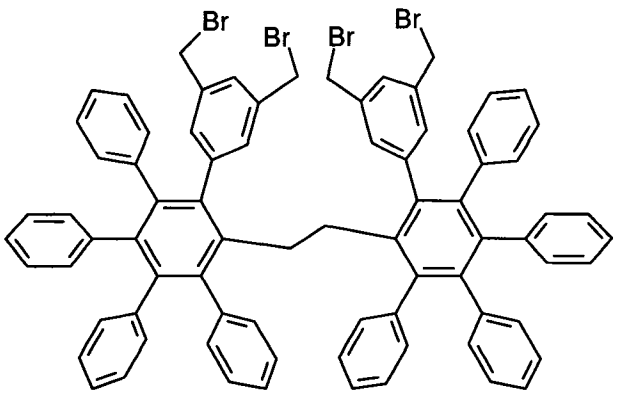
1,6-Bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (4.15e)



To a 0 °C stirred solution of 1,6-bis(2-(3,5-bis(methoxycarbonyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.12e**) (6.96 g, 5.65 mmol) in dichloromethane (350 mL) was added dropwise DIBAL-H solution in dichloromethane (90.4 mL, 1 M, 90.4 mmol). The mixture was stirred at rt for 16 h. Aqueous 6 M hydrochloric acid (100 mL) was added, and the mixture was stirred for 10 min. The aqueous layer was extracted with dichloromethane (3 × 300 mL). The combined organic layer was washed with water (200 mL), washed with brine (200 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (11 cm × 4.2 cm, 10% ethyl acetate/dichloromethane to pure ethyl acetate) to give 1,6-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.15e**) (5.19 g, 4.63 mmol, 82%, R_f=0.85 in ethyl acetate) as a light yellow solid; mp: 272-274 °C (ethyl acetate); IR (powder): 3308 (br, w), 3045 (w), 3026 (w), 2927 (w), 1700 (w), 1652 (w), 1635 (w), 1600 (w), 1676 (w), 1558 (w), 1496 (w), 1441 (w), 1070 (w), 1022 (w), 862 (w), 751 (m), 694 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.10-7.05 (m, 12H), 6.96 (s, 4H), 6.79-6.77 (m, 30H), 4.44 and 4.42 (AB system, J_{AB}=12.8 Hz, Δν=10.6 Hz, 8H), 2.14-2.11 (m, 4H), 0.96 (br, s, 4H), 0.27 (br, s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 141.05, 140.96, 140.93, 140.86, 140.8, 140.7, 140.6, 140.33, 140.28, 138.68, 138.66, 138.4, 138.4, 131.5, 131.4, 131.3, 130.7, 128.9,

127.3, 126.7, 126.6, 126.1, 125.3, 123.2, 65.3, 31.7, 31.0, 29.3; LC-MS (APCI) *m/z*: 1154 (100, MCl^-), 1118 (59, M^-), 1057 (8); Anal. Calcd for $C_{82}H_{70}O_4$: C, 87.98; H, 6.30. Found: C, 85.30; H, 6.28.

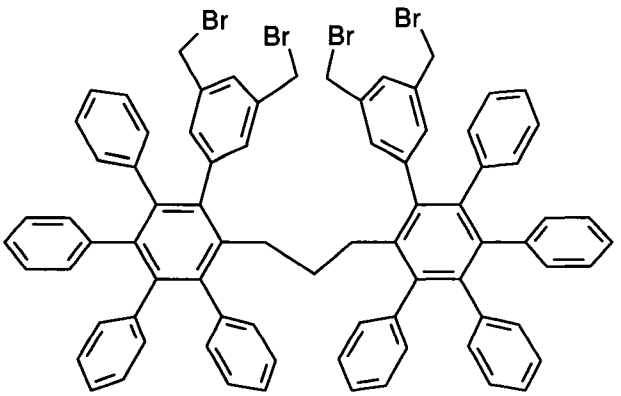
1,2-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (4.16a)



To a stirred solution of 1,2-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.15a**) (0.93 g, 0.87 mmol) in dichloromethane (84 mL) was added PBr_3 (0.31 g, 1.2 mmol). The reaction was shielded from light by aluminum foil and stirred at room temperature for 20 h. Water (70 mL) was added to the reaction mixture, followed by dichloromethane (200 mL). The layers were separated and the organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (22 cm × 3.3 cm, 60% dichloromethane/hexanes) to give 1,2-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.16a**) (0.75 g, 0.57 mmol, 66%, R_f=0.65) as a white solid; mp: >300°C (chloroform); IR (powder): 3041 (w), 3020 (w), 2922 (w), 1945 (w), 1601 (w), 1496 (w), 1399 (w), 1272 (m), 1211 (w), 1069 (w), 1024 (w), 760 (m), 747 (w), 698 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.25 (s, 6H), 6.91-6.66 (m, 36H), 4.22 and 4.16 (AB system, J_{AB}=10.1 Hz, Δν=32.8 Hz, 8H), 2.46

(s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$): 141.9, 141.4, 141.3, 141.1, 141.0, 140.91, 140.89, 140.7, 140.1, 139.1, 137.0, 136.1, 131.5, 131.2, 131.15, 131.09, 127.7, 126.8, 126.7, 125.9, 125.39, 125.36, 125.3, 33.2, 30.9; LC-MS (APCI) *m/z*: 1393 (10), 1354 (24), 1353 (44), 1352 (57), 1351 (89), 1350 (77), 1349 (100, MCl^-), 1348 (41), 1347 (55), 1305 (9); Anal. Calcd for $C_{78}H_{58}Br_4$: C, 71.25; H, 4.45. Found: C, 70.86; H, 4.49.

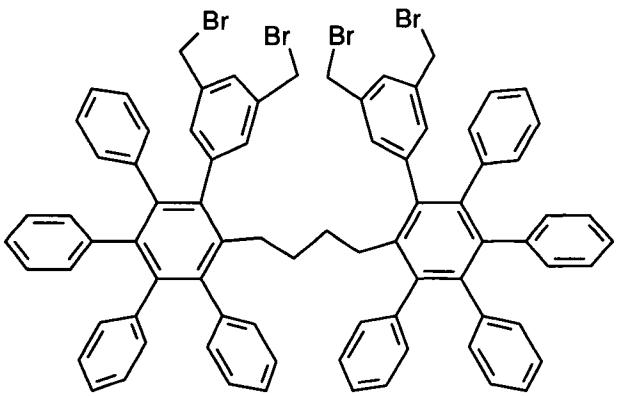
1,3-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (4.16b)



To a stirred solution of 1,3-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.15b**) (2.66 g, 2.47 mmol) in dichloromethane (300 mL) was added PBr_3 (0.89 g, 3.28 mmol). The reaction was shielded from light by aluminum foil and stirred at room temperature for 16 h. Water (200 mL) was added to the reaction mixture, followed by dichloromethane (400 mL). The layers were separated and the organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (12 cm × 3.7 cm, 50% dichloromethane/hexanes) to give 1,3-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.16b**) (2.60 g, 2.10 mmol, 79%, R_f=0.55) as a yellow solid; mp: >300 °C (dichloromethane); IR (powder): 3040 (w),

3022 (w), 2963 (w), 2922 (w), 1948 (w), 1601 (w), 1496 (w), 1407 (w), 1266 (w), 1210 (m), 1070 (w), 1027 (w), 748 (m), 735 (m), 728 (m), 697 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) 7.16 (s, 2H), 7.07 (d, *J*=1.4 Hz, 4H), 6.99 (t, *J*=7.3 Hz, 2H), 6.94 (t, *J*=7.2 Hz, 6H), 6.83-6.73 (m, 30H), 6.69 (d, *J*=6.9 Hz, 4H), 4.40 (s, 8H), 1.87-1.83 (m, 4H), 0.88-0.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): (low solubility prevented the measurement of a spectrum); LC-MS (APCI-) *m/z*: 1369 (10), 1368 (25), 1367 (43), 1366 (61), 1365 (100, MCl^-), 1364 (78). 1363 (96), 1362 (40), 1361 (53), 1319 (7); Anal. Calcd for $C_{79}H_{60}Br_4$: C, 71.40; H, 4.55. Found: C, 71.88; H, 5.44.

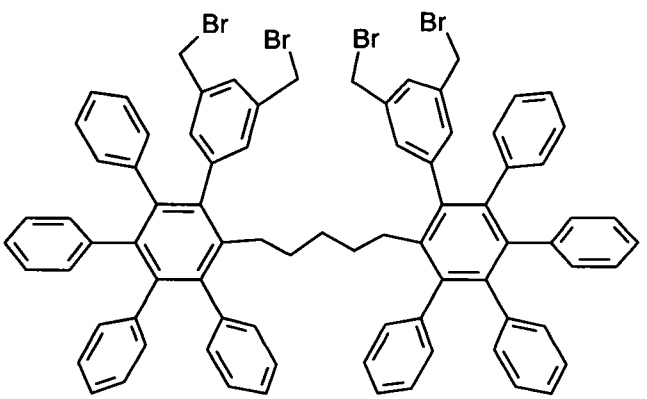
1,4-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (4.16c)



To a stirred solution of 1,4-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.15c**) (4.68 g, 4.29 mmol) in dichloromethane (300 mL) was added PBr_3 (1.54 g, 5.70 mmol). The reaction was shielded from light by aluminum foil and stirred at room temperature for 16 h. Water (200 mL) was added to the reaction mixture, followed by dichloromethane (400 mL). The layers were separated and the organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (14 cm × 4.2 cm, 80% dichloromethane/hexanes) to give 1,4-bis(2-(3,5-

bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.16c**) (3.24 g, 2.40 mmol, 56%, R_f=0.85) as a white solid; mp: 273-275 °C (dichloromethane); IR (powder): 3045 (w), 3023 (w), 2924 (w), 1805 (w), 1601 (w), 1495 (w), 1441 (w), 1407 (w), 1213 (w), 1070 (w), 1024 (w), 908 (w), 762 (w), 746 (w), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.06-7.04 (m, 4H), 7.01 (br, s, 2H), 6.96 (d, *J*=1.6 Hz, 4H), 6.94-6.92 (m, 4H), 6.81-6.71 (m, 30H), 4.26 (s, 8H), 1.72-1.69 (m, 4H), 0.83-0.80 (m, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$): 142.3, 141.0, 140.8, 140.6, 140.5, 140.4, 139.5, 138.6, 138.1, 137.1, 131.8, 131.7, 131.63, 131.56, 131.5, 131.4, 131.2, 131.0, 130.8, 130.7, 127.3, 126.8, 126.6, 126.3, 126.0, 33.2, 32.8, 32.2; LC-MS (APCI) *m/z*: 1377 (36), 1376 (52), 1375 (80), 1374 (76), 1373 (100, M^++Cl), 1372 (56), 1371 (61), 1360.2 (52), 1345.2 (10); Anal. Calcd for $C_{80}H_{62}Br_4$: C, 71.55; H, 4.65. Found: C, 70.72; H, 4.81.

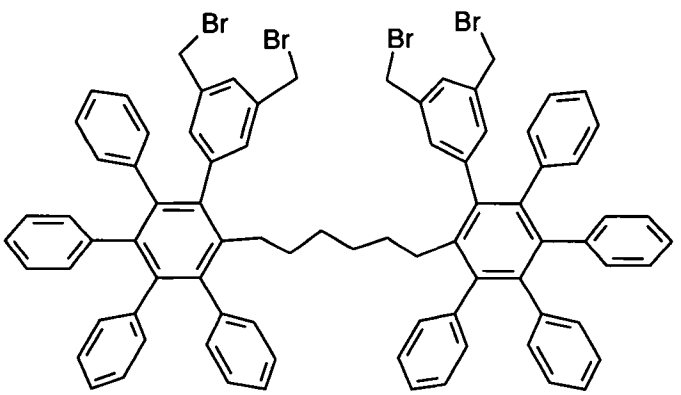
1,5-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (4.16d)



To a stirred solution of 1,5-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.15d**) (4.01 g, 3.63 mmol) in dichloromethane (280 mL) was added PBr_3 (1.31 g, 4.82 mmol). The reaction was shielded from light by aluminum foil and stirred at room temperature for 16 h. Water (200 mL) was added to the reaction mixture, followed by dichloromethane (400 mL). The layers were separated and the

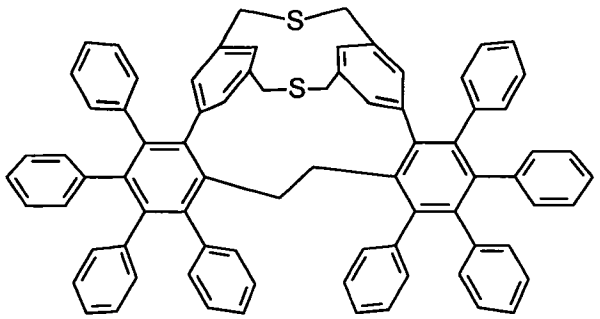
organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (14 cm × 4.2 cm, 60% dichloromethane/hexanes) to give 1,5-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.16d**) (3.11 g, 2.29 mmol, 63%, R_f=0.75) as a yellow solid; mp: 155-157 °C (chloroform); IR (powder): 3045 (w), 3024 (w), 2954 (w), 1942 (w), 1869 (w), 1799 (w), 1600 (w), 1496 (w), 1405 (w), 1275 (w), 1212 (m), 1070 (w), 1026 (w), 806 (s), 697 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.08-7.01 (m, 16H), 6.83-6.74 (m, 30H), 4.26 and 4.25 (AB system, J_{AB}=13.8 Hz, Δν=9.1 Hz, 8H), 2.07-2.04 (m, 4H), 0.88-0.87 (m, 4H), 0.30-0.27 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$): 142.5, 141.1, 140.9, 140.84, 140.82, 140.6, 140.5, 139.4, 138.7, 138.5, 137.3, 131.72, 131.70, 131.5, 131.32, 131.31, 131.0, 130.7, 127.3, 126.9, 126.7, 126.6, 126.1, 125.5, 125.3, 33.1, 31.8, 30.7, 30.3; LC-MS (APCI-) *m/z*: 1396 (20), 1395 (45) ,1394 (65), 1393 (100), 1392 (77), 1391 (100, MCl^-), 1390 (38), 1389 (43), 1356 (10, M^-); Anal. Calcd for $C_{81}H_{64}Br_4$: C, 71.69; H, 4.75. Found: C, 70.29; H, 4.83.

1,6-Bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (4.16e)



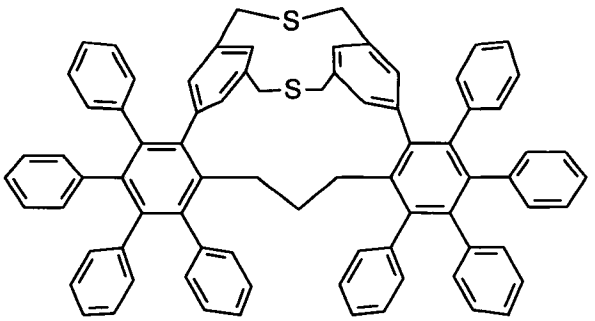
To a stirred solution of 1,6-bis(2-(3,5-bis(hydroxymethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.15e**) (5.07 g, 4.53 mmol) in dichloromethane (300 mL) was added PBr_3 (1.63 g, 6.02 mmol). The reaction was shielded from light by aluminum foil and stirred at room temperature for 16 h. Water (200 mL) was added to the reaction mixture, followed by dichloromethane (400 mL). The layers were separated and the organic layer was washed with water (100 mL), washed with brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow solid was purified by column chromatography (20 cm × 4.2 cm, 70% dichloromethane/hexanes) to give 1,6-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.16e**) (6.07 g, 4.44 mmol, 98%, R_f=0.85) as a pale yellow solid; mp: 286-288 °C (chloroform); IR (powder): 3055 (w), 3022 (w), 2927 (w), 1942 (w), 1734 (w), 1600 (w), 1576 (w), 1558 (w), 1496 (w), 1405 (w), 1271 (w), 1212 (m), 1071 (w), 1026 (w), 910 (w), 750 (s), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.10-7.03 (m, 16H), 6.84-6.73 (m, 30H), 4.28 and 4.26 (AB system, J_{AB}=10.3 Hz, Δν=12.0 Hz, 8H), 2.12-2.09 (m, 4H), 0.97 (br, s, 4H), 0.33 (br, s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): 142.4, 141.02, 140.96, 140.80, 140.78, 140.6, 140.5, 139.5, 138.6, 138.5, 137.3, 131.8, 131.7, 131.5, 131.4, 131.3, 131.05, 131.01, 130.68, 130.66, 130.6, 127.3, 126.9, 126.7, 126.4, 126.1, 34.0, 33.1, 31.8, 29.2; LC-MS (APCI) *m/z*: 1451 (12), 1410 (22), 1409 (40), 1408 (55), 1407 (82), 1406 (73), 1405 (100, MCl^-), 1404 (42), 1403 (53), 1371 (20, M^-); Anal. Calcd for $C_{82}H_{66}Br_4$: C, 71.84; H, 4.85. Found: C, 71.81; H, 5.12.

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,5*Z*)-1,2;5,6-dibenzo-14,23-dithia[6.3.3](1,3,5)cyclophane-1,5-diene (4.11a)



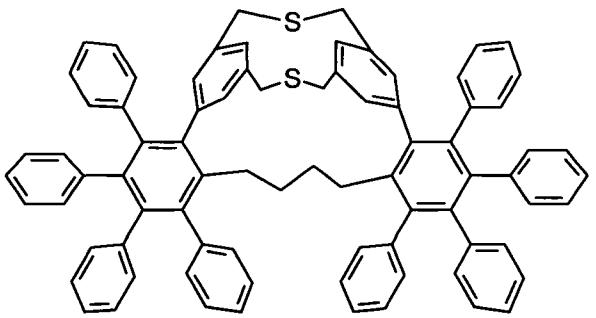
To a vigorously stirred solution of 1,2-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)ethane (**4.16a**) (0.74 g, 0.56 mmol) in 10% ethanol/dichloromethane (54 mL) was added Na_2S/Al_2O_3 (0.20 g, 0.75 mmol) in two portions with a 15 minute interval. The reaction mixture was stirred at room temperature for 7 d. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (27 cm × 3.3 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,5*Z*)-1,2;5,6-dibenzo-14,23-dithia[6.3.3](1,3,5) cyclophane-1,5-diene (**4.11a**) (0.21 g, 0.20 mmol, 35%, R_f=0.40) as a white solid; mp: >300 °C (chloroform); IR (powder): 3039 (w), 3021 (w), 2904 (w), 1940 (w), 1802 (w), 1600 (w), 1576 (w), 1496 (w), 1441 (w), 1404 (w), 1272 (w), 1072 (w), 913 (w), 879 (w), 762 (w), 745 (w), 653 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.10 (s, 8H), 6.69-6.63 (m, 36H), 3.58 (br, s, 8H), 2.80 (br, s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.13, 141.12, 141.07, 140.8, 140.74, 140.71, 140.61, 140.58, 140.5, 138.6, 137.1, 135.7, 132.2, 131.2, 130.0, 129.5, 127.9, 127.2, 126.3, 126.0, 125.8, 125.0, 124.91, 124.89, 38.7, 33.0; LC-MS (APCI) *m/z*: 1139 (56), 1098 (13), 1076 (100, M^++18), 1059 (12, M+1^+); Anal. Calcd for $C_{78}H_{58}S_2$: C, 88.43; H, 5.52. Found: C, 86.97; H, 5.72.

1',2',3',4',1",2",3",4"-Octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo-15,24-dithia[7.3.3](1,3,5)cyclophane-1,6-diene (4.11b)



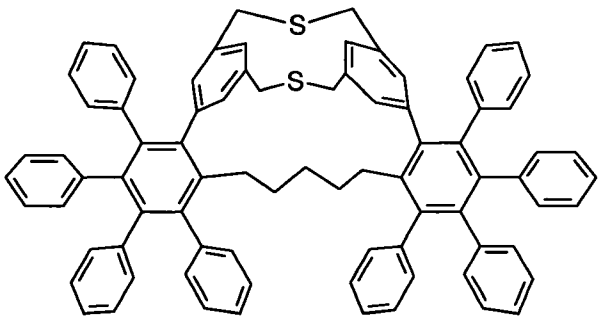
To a vigorously stirred solution of 1,3-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)propane (**4.16b**) (2.61 g, 1.96 mmol) in 10% ethanol/dichloromethane (260 mL) was added Na_2S/Al_2O_3 (2.90 g, 7.86 mmol). The reaction mixture was stirred at room temperature for 4 d. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (25 cm × 3.7 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo-15,24-dithia[7.3.3](1,3,5)cyclophane-1,6-diene (**4.11b**) (0.57 g, 0.53 mmol, 27%, R_f=0.45) as a white solid; mp: >300 °C (chloroform); IR (powder): 3054 (w), 3023 (w), 2929 (w), 1943 (w), 1872 (w), 1751 (w), 1599 (w), 1576 (w), 1495 (w), 1459 (w), 1441 (w), 1402 (w), 1072 (w), 1020 (w), 1001 (w), 910 (w), 885 (m), 760 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.05-7.04 (m, 6H), 6.93-6.91 (m, 4H), 6.84 (s, 2H), 6.80-6.66 (m, 28H), 6.62 (s, 4H), 6.53-6.51 (m, 4H), 3.56 and 3.49 (AB system, J_{AB}=14.8 Hz, Δν=36.7 Hz, 8H), 2.55-2.52 (m, 4H), 1.32-1.30 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.5, 141.3, 141.11, 141.10, 140.95, 140.92, 140.85, 140.7, 140.0, 138.9, 137.1, 136.0, 131.5, 131.38, 131.36, 130.6, 130.4, 129.3, 127.4, 126.52, 126.48, 126.4, 126.0, 125.12, 125.08, 124.9, 39.3, 32.4, 30.5; LC-MS (APCI) *m/z*: 1151 (10), 1119 (78), 1073 (100, M^++1), 1041 (65).

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1Z,7Z)-1,2;7,8-dibenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,7-diene (4.11c)



To a vigorously stirred solution of 1,4-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)butane (**4.16c**) (3.10 g, 2.31 mmol) in 10% ethanol/dichloromethane (320 mL) was added Na_2S/Al_2O_3 (3.41 g, 9.23 mmol). The reaction mixture was stirred at room temperature for 22 h. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (14 cm × 4.2 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1Z,7Z)-1,2;7,8-dibenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,7-diene (**4.11c**) (1.03 g, 0.95 mmol, 41%, R_f= 0.50) as a faint yellow solid; mp: 152-154 °C, dec. (chloroform); IR (powder): 3044 (w), 3022 (w), 2925 (w), 1725 (w), 1599 (w), 1496 (w), 1463 (w), 1441 (w), 1405 (w), 1221 (w), 1180 (w), 1072 (w), 1026 (w), 912 (w), 880 (w), 747 (m), 729 (m), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.14-7.13 (m, 6H), 7.02-7.00 (m, 4H), 6.81-6.69 (m, 28H), 6.64 (s, 4H), 6.62-6.60 (m, 4H), 3.66 and 3.64 (AB system, J_{AB}=15.0 Hz, Δν=8.5 Hz, 8H), 2.24-2.21 (br, m, 4H), 0.80-0.77 (br, m, 4H); ^{13}C NMR (125.76 MHz, DMSO-d_6) low solubility prevented the measurement of a spectrum; LC-MS (APCI) *m/z*: 1133 (37), 1117 (100), 1087 (92, M^++1), 1053 (23); Anal. Calcd for $C_{80}H_{62}S_2$: C, 88.36; H, 5.75. Found: C, 79.29; H, 5.73.

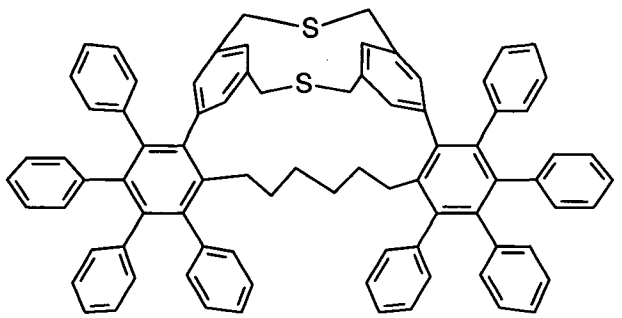
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1Z,8Z)-1,2;8,9-dibenzo-17,26-dithia[9.3.3](1,3,5)cyclophane-1,8-diene (4.11d)



To a vigorously stirred solution of 1,5-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)pentane (**4.16d**) (3.09 g, 2.28 mmol) in 10% ethanol/dichloromethane (320 mL) was added Na_2S/Al_2O_3 (3.36 g, 9.11 mmol). The reaction mixture was stirred at room temperature for 5 d and then filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (24 cm × 4.2 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1Z,8Z)-1,2;8,9-dibenzo-17,26-dithia[9.3.3](1,3,5)cyclophane-1,8-diene (**4.11d**) (0.45 g, 0.41 mmol, 18%, R_f=0.45) as a white solid; mp: >300 °C (chloroform); IR (powder): 3055 (w), 3023 (w), 2917 (w), 1942 (w), 1869 (w), 1734 (w), 1599 (w), 1495 (w), 1457 (w), 1440 (w), 1404 (w), 1274 (w), 1222 (w), 1071 (w), 1023 (w), 908 (w), 880 (w), 758 (w), 726 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.17 (s, 2H), 7.08-6.99 (m, 10H), 6.78-6.69 (m, 26H), 6.64 (d, J=1.0 Hz, 4H), 6.61-6.59 (m, 4H), 3.67 and 3.64 (AB system, J_{AB}=15.0 Hz, Δν=15.1 Hz, 8H), 2.19-2.16 (m, 4H), 1.07-1.04 (m, 4H), 0.46-0.44 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) 141.5, 141.01, 141.00, 140.9, 140.8, 140.6, 140.5, 140.1, 139.1, 138.4, 137.1, 131.7, 131.5, 131.4, 131.2, 130.9, 130.6, 129.3, 128.7, 127.4, 126.7, 126.6, 126.5, 126.4, 126.3, 126.0, 41.0, 40.6, 32.8, 31.3; LC-MS (APCI) *m/z*: 1102

(100, M^++1), 1067 (36); Anal. Calcd for $C_{81}H_{64}S_2$: C, 88.32; H, 5.86. Found: C, 83.53; H, 5.90.

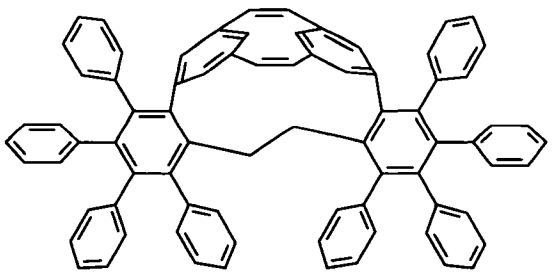
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,9*Z*)-1,2;9,10-dibenzo-18,27-dithia[10.3.3](1,3,5)cyclophane-1,9-diene (4.11e)



To a vigorously stirred solution of 1,6-bis(2-(3,5-bis(bromomethyl)phenyl)-3,4,5,6-tetraphenylphenyl)hexane (**4.16e**) (5.00 g, 3.65 mmol) in 10% ethanol/dichloromethane (550 mL) was added Na_2S/Al_2O_3 (5.38 g, 14.6 mmol). The reaction mixture was stirred at room temperature for 16 h. The mixture was filtered through a short plug of celite. The filtrate was concentrated *in vacuo* and purified by column chromatography (20 cm × 4.2 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,9*Z*)-1,2;9,10-dibenzo-18,27-dithia[10.3.3](1,3,5)cyclophane-1,9-diene (**4.11e**) (1.66 g, 1.50 mmol, 41%, R_f=0.30) as a white solid; mp: >300 °C (chloroform); IR (powder): 3051 (w), 3022 (w), 2922 (w), 1691 (w), 1599 (w), 1494 (w), 1441 (w), 1220 (w), 1071 (w), 1026 (w), 909 (w), 806 (m), 748 (m), 695 (vs); ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.41 (s, 2H), 7.09-7.00 (m, 10H), 6.79-6.66 (m, 34H), 3.77 and 3.61 (AB system, J_{AB}=15.0 Hz, Δν=75.8 Hz, 8H), 2.17-2.13 (m, 4H), 1.01 (br, s, 4H), 0.25 (br, s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) 141.0, 140.90, 140.87, 140.80, 140.75, 140.7, 140.5, 140.3, 138.6, 138.4, 131.5, 131.3, 131.1, 130.6, 129.6, 129.1, 127.2, 126.55, 126.53, 126.49, 126.0, 125.2,

125.1, 39.8, 31.1, 30.6, 27.9; ALC-MS (APCI-) *m/z*: 1162 (9), 1146 (9), 1129 (17), 1115 (100, M^-); Anal. Calcd for $C_{82}H_{66}S_2$: C, 88.29; H, 5.90. Found: C, 83.03; H, 5.89.

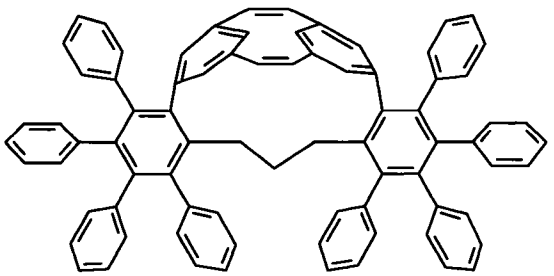
1',2',3',4',1",2",3",4"-Octaphenyl-(1Z,5Z,13Z,21Z)-1,2;5,6-dibenzo[6.2.2](1,3,5)cyclophane-1,5,13,21-tetraene (4.10a)



To a stirred solution of 1',2',3',4',1",2",3",4"-octaphenyl-(1Z,5Z)-1,2;5,6-dibenzo-14,23-dithia[6.3.3](1,3,5)cyclophane-1,5-diene (**4.11a**) (0.20 g, 0.19 mmol) in dichloromethane (30 mL) was added Borch reagent (92 mg, 0.57 mmol). The reaction mixture was stirred at rt for 18 h, concentrated *in vacuo* and quenched with ethyl acetate (2.7 mL). The obtained mixture was concentrated *in vacuo* and dried under high vacuum for 6 h, followed by an addition of THF (25 mL) and *t*BuOK (106 mg, 0.95 mmol). The reaction mixture was stirred at rt for 16 h, concentrated *in vacuo* and passed through a short plug of silica gel (5 cm × 3.3 cm) using 50% dichloromethane/hexanes to give a mixture of isomers 1',2',3',4',1",2",3",4"-octaphenyl-(1Z,5Z)-1,2;5,6-dibenzo-13/14,21/22-bis(methylthio)[6.2.2](1,3,5)cyclophane-1,5-diene (**4.18a**) (141 mg, 0.13 mmol, 69%) as a white solid (R_f=0.30). The solid was suspended in dichloromethane (23 mL) and Borch reagent (71 mg, 0.44 mmol) was injected. The reaction mixture turned pink and was then stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo* and dried under high vacuum for 20 min. The residue was suspended in THF (12 mL).

After 5 minutes stirring, *t*-BuOH (12 mL) was added. The reaction mixture was stirred at rt for 10 min and then *t*-BuOK (72 mg, 0.65 mmol) was added. The reaction mixture was vigorously stirred at rt for 16 h. Saturated aqueous ammonium chloride solution (10 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (20 mL) and water (15 mL) were added to the residue. The organic layer was washed with water (10 mL), washed with brine (5 mL), dried by $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (25 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,5*Z*,13*Z*,21*Z*)-1,2;5,6-dibenzo[6.2.2](1,3,5)cyclophane-1,5,13,21-tetraene (**4.10a**) (18 mg, 0.018 mmol, 14%, R_f=0.50) as a white solid; mp: >300 °C (50% dichloromethane/hexanes); IR (powder): 3038 (w), 3025 (w), 2924 (w), 1753 (w), 1665 (w), 1495 (w), 1441 (w), 1392 (w), 1332 (w), 1072 (w), 1024 (w), 937 (w), 743 (m), 727 (w), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.08 (s, 10H), 6.85 (s, 2H), 6.74-6.56 (m, 30H), 6.25 (s, 4H), 2.58 (s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.25, 141.21, 140.75, 140.68, 140.5, 138.6, 137.7, 137.60, 137.57, 136.9, 133.9, 132.1, 131.3, 131.0, 128.2, 127.3, 126.4, 125.8, 125.14, 125.09, 124.9, 33.1, 29.9; LC-MS (APCI) *m/z*: 991 (100, M^++1), 1008 (10, M^++18); Anal. Calcd for $C_{78}H_{54}$: C, 94.51; H, 5.49. Found: C, 91.36; H, 6.06.

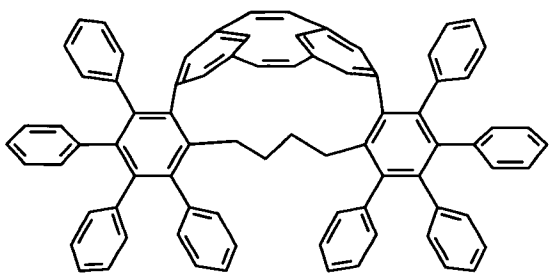
1',2',3',4',1",2",3",4"-Octaphenyl-(1*Z*,6*Z*,14*Z*,22*Z*)-1,2;6,7-dibenzo[7.2.2](1,3,5)cyclophane-1,6,14,22-tetraene (4.10b)



To a stirred solution of 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo-15,24-dithia[7.3.3](1,3,5)cyclophane-1,6-diene (**4.11b**) (0.55 g, 0.51 mmol) in dichloromethane (70 mL) was added Borch reagent (0.25 g, 1.54 mmol). The reaction mixture was stirred at rt for 16 h, concentrated *in vacuo* and quenched with ethyl acetate (7.7 mL). The obtained mixture was concentrated *in vacuo* and dried under high vacuum for 6 h, followed by an addition of THF (55 mL) and *t*BuOK (0.29 g, 2.57 mmol). The reaction mixture was stirred at rt for 6 h, concentrated *in vacuo* and passed through a short plug of silica gel (5 cm × 3.3 cm) using 50% dichloromethane/hexanes to give a mixture of isomers 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo-14/15,22/23-bis(methylthio)[7.2.2](1,3,5)cyclophane-1,6-diene (**4.18b**) (0.30 g, 0.27 mmol, 53%, R_f=0.30) as a white solid. The solid was suspended in dichloromethane (40 mL), and Borch reagent (0.15 g, 0.93 mmol) was injected. The reaction mixture turned pink immediately and was stirred at rt for 4.5 h. The reaction mixture was concentrated *in vacuo* and dried under high vacuum for 1 h. The residue was suspended in THF (15 mL). After 5 minutes stirring, *t*-BuOH (15 mL) was added. The reaction mixture was stirred at rt for 10 min and then *t*-BuOK (0.153 g, 1.36 mmol) was added. The reaction mixture was vigorously stirred at rt for 14 h. Saturated aqueous ammonium chloride solution (15 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (60 mL) and water (5 mL) were added to the residue. The layers were separated and the

organic layer was washed with water (5 mL), washed with brine (5 mL), dried by $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (12 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,6*Z*,14*Z*,22*Z*)-1,2;6,7-dibenzo[7.2.2](1,3,5) cyclophane-1,6,14,22-tetraene (**4.10b**) (20 mg, 0.020 mmol, 7.3%, R_f=0.50) as a white solid; mp: >300 °C; IR (powder): 2922 (s), 2853 (m), 1734 (w), 1496 (w), 1457 (w), 1072 (w), 1026 (w), 907 (m), 731 (s), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.02-7.00 (m, 6H), 6.97 (s, 4H), 6.92-6.90 (m, 4H), 6.78-6.73 (m, 18H), 6.69-6.67 (m, 8H), 6.58-6.56 (m, 4H), 6.35 (s, 4H), 2.34-2.31 (m, 4H), 0.86-0.83 (m, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 141.8, 141.21, 141.17, 141.1, 141.0, 140.9, 140.8, 140.1, 139.0, 137.2, 136.8, 135.9, 135.8, 131.9, 131.6, 131.5, 131.4, 130.4, 127.5, 127.3, 126.6, 126.51, 126.48, 126.0, 125.1, 124.9, 32.2, 22.9; LC-MS (APCI) *m/z*: 1005 (100, M^++1).

1',2',3',4',1",2",3",4"-Octaphenyl-(1*Z*,7*Z*,15*Z*,23*Z*)-1,2;7,8-dibenzo[8.2.2](1,3,5)cyclophane-1,7,15,23-tetraene (4.10c)

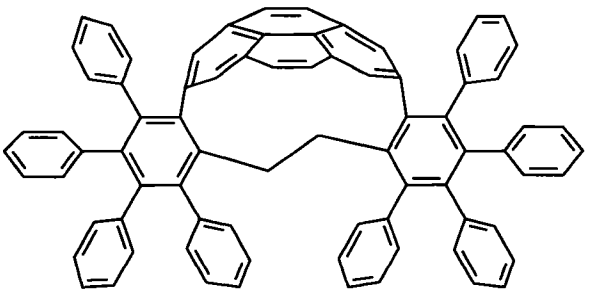


To a stirred solution of 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,7*Z*)-1,2;7,8-dibenzo-16,25-dithia[8.3.3](1,3,5)cyclophane-1,7-diene (**4.11c**) (0.90 g, 0.83 mmol) in dichloromethane (120 mL) was added Borch reagent (0.40 g, 2.48 mmol). The reaction

mixture was stirred at rt for 16 h, concentrated *in vacuo* and quenched with ethyl acetate (13 mL). The obtained mixture was concentrated *in vacuo* and dried under high vacuum for 6 h, followed by an addition of THF (90 mL) and *t*BuOK (0.47 g, 4.14 mmol). The reaction mixture was stirred at rt for 16 h, concentrated *in vacuo* and passed through a short plug of silica gel (7 cm × 3.3 cm) using 50% dichloromethane/hexanes to give a mixture of isomers 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,7*Z*)-1,2;7,8-dibenzo-15/16,23/24-bis(methylthio)[8.2.2](1,3,5)cyclophane-1,7-diene (**4.18c**) (0.92 g, 0.83 mmol, 99%, R_f=0.35) as a white solid. TLC showed this white solid contains some impurity. Without further purification, the solid was suspended in dichloromethane (120 mL) and Borch reagent (0.49 g, 3.1 mmol) was injected. The reaction mixture turned pinkish yellow immediately and was stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo* and dried under high vacuum for 6 h. The residue was suspended in THF (40 mL). After 5 minutes stirring, *t*-BuOH (40 mL) was added. The reaction mixture was stirred at rt for 10 min and then *t*-BuOK (0.153 g, 1.36 mmol) was added. The reaction mixture was vigorously stirred for 14 h. Saturated aqueous ammonium chloride solution (35 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (80 mL) and water (15 mL) were added to the residue. The organic layer was washed with water (15 mL), washed with brine (15 mL), dried by $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (12 cm × 3.3 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,7*Z*,15*Z*,23*Z*)-1,2;7,8-dibenzo[8.2.2](1,3,5) cyclophane-1,7,15,23-tetraene (**4.10c**) (37 mg, 0.033 mmol, 4%, R_f=0.30) as a white solid. NMR analysis shows it's a mixture of **4.10c** and pyrenophane **4.09c** and other

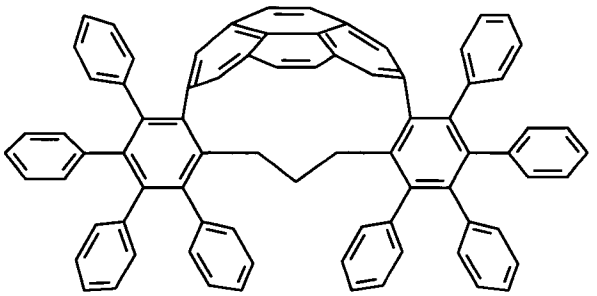
unidentifiable impurities; mp: >300 °C (chloroform); IR (powder): (not for mixtures); ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.60 (s, 4H), 7.52 (s, 2H), 7.41-7.40 (m, 2H), 7.18-7.05 (m, 10H), 7.01 (s, 4H), 6.96-6.59 (m, 50H), 6.50 (s, 8H); discernable peaks for pyrenophane **4.09c** δ –1.48; ^{1}H NMR (500.13 MHz, C_6D_6) ; ^{13}C NMR (125.76 MHz, $CDCl_3$) (not for mixtures); LC-MS (APCI) *m/z*: 1020 (100, M^++1).

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,5*Z*)-1,2;5,6-dibenzo[6](2,7)pyrenophane-1,5-diene (4.09a)



To a stirred solution of 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,5*Z*,13*Z*,21*Z*)-1,2;5,6-dibenzo[6.2.2](1,3,5)cyclophane-1,5,13,21-tetraene (**4.10a**) (18 mg, 0.018 mmol) in degassed benzene (5 mL) was added a solution of DDQ (4.5 mg) in degassed benzene (0.5 mL). The reaction was heated at reflux for 60 d. The reaction mixture was concentrated *in vacuo* with no further purifications. ^{1}H NMR (500.13 MHz, $CDCl_3$) discernable peaks for pyrenophane **4.09a**: δ 1.12-1.11 (m, 2H, sh), –1.13 - –1.16 (m, 2H); ^{1}H NMR (500.13 MHz, C_6D_6) discernable peaks for pyrenophane **4.09a**: δ 1.88-1.85 (m, 2H), –0.54 - –0.57 (m, 2H); HPLC-MS (APCI) *m/z*: first fraction: 991 (100, M^++1 for **4.10a**); second fraction: 989 (100, M^++1 for **4.09a**); third fraction: 989 (100, M^++1 for **4.09a**), 1217 (10, M+DDQ).

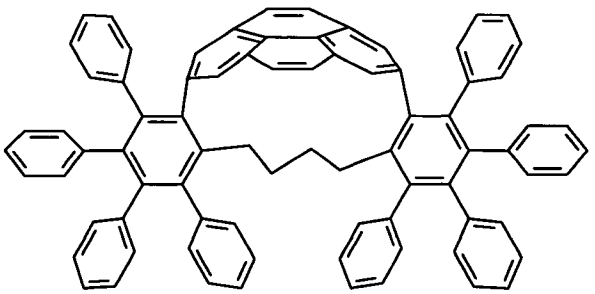
1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo[7](2,7)pyrenophane-1,6-diene (4.09b)



To a stirred solution of 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,6*Z*,14*Z*,22*Z*)-1,2;6,7-dibenzo[7.2.2](1,3,5)cyclophane-1,6,14,22-tetraene (**4.10b**) (18 mg, 0.018 mmol) in degassed benzene (5 mL) was added a solution of DDQ (4.5 mg) in degassed benzene (0.5 mL). The reaction was heated at reflux for 26 h, and then a solution of DDQ (1.5 mg) in benzene (0.5 mL) was added. The reaction was then refluxing for 4 d. A crystal of hydroquinone was added and the mixture was stirred for 5 min. The reaction mixture was concentrated *in vacuo*, and the resulting yellow residue was purified by column chromatography (12 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,6*Z*)-1,2;6,7-dibenzo[7](2,7)pyrenophane-1,6-diene (17 mg, 0.017 mmol, 94%, R_f=0.50) (**4.09b**) as a white solid; mp: >300 °C (chloroform); IR (powder): 3042 (w), 3025 (w), 2921 (m), 1734 (w), 1600 (w), 1576 (w), 1495 (w), 1441 (w), 1366 (w), 1071 (w), 1027 (w), 951 (w), 917 (w), 872 (w), 811 (w), 798 (w), 738 (w), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.34-7.33 (m, 4H), 7.25 (s, 4H), 7.17 (t, *J*=7.6 Hz, 4H), 7.07 (t, *J*=7.4 Hz, 2H), 6.82-6.68 (m, 24H), 6.50-6.49 (m, 4H), 6.38-6.37 (m, 4H), 0.43-0.40 (m, 4H), –0.94 - –0.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) (not obtained due to low solubility); LC-MS (APCI) *m/z*: 1004

(100, M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 244 (96000), 298 (70000), 332 sh (20000), 346 sh (12000); Anal. Calcd for $C_{79}H_{54}$: C, 94.57; H, 5.43. Found: C, 84.84; H, 8.83.

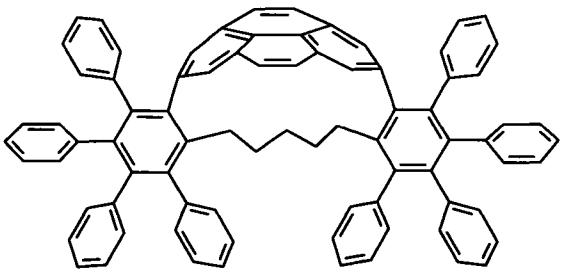
1',2',3',4',1",2",3",4"-Octaphenyl-(1Z,7Z)-1,2;7,8-dibenzo[8](2,7)pyrenophane-1,7-diene (4.09c)



To a stirred solution of 1',2',3',4',1",2",3",4"-octaphenyl-(1Z,7Z,15Z,23Z)-1,2;7,8-dibenzo[8.2.2](1,3,5)cyclophane-1,7,15,23-tetraene (**4.10c**) (37 mg, 0.036 mmol) in degassed benzene (10 mL) was added a solution of DDQ (9.1 mg) in degassed benzene (10 mL). The reaction was stirred at reflux for 20 h. A crystal of hydroquinone was added and the mixture was stirred for 5 min. The reaction mixture was concentrated *in vacuo* and the resulting yellow residue was purified by column chromatography (14 cm × 1.9 cm, 50% dichloromethane/hexanes) to give 1',2',3',4',1",2",3",4"-octaphenyl-(1Z,7Z)-1,2;7,8-dibenzo[8](2,7)pyrenophane-1,7-diene (**4.09c**) (17 mg, 0.022 mmol, 61%, R_f=0.50) as a white solid; mp: >300 °C (chloroform); IR (powder): 3044 (w), 3022 (w), 2927 (w), 1942 (w), 1733 (w), 1700 (w), 1684 (w), 1653 (w), 1635 (w), 1600 (w), 1576 (w), 1558 (w), 1539 (w), 1506 (w), 1496 (w), 1441 (w), 1399 (w), 1294 (w), 1178 (w), 1071 (w), 1027 (w), 874 (w), 790 (m), 766 (m), 695 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.74 (s, 4H), 7.52 (s, 4H), 7.40 (d, *J*=7.4 Hz, 4H), 7.16 (t, *J*=7.6 Hz, 4H), 7.05

(t, *J*=7.4 Hz, 2H), 6.95 (t, *J*=7.4 Hz, 2H), 6.84-6.80 (m, 18H), 6.74-6.73 (m, 10H), 6.66-6.64 (m, 6H), 6.60 (d, *J*=7.7 Hz, 4H), 0.62 (br, s, 4H), −1.48 (br, s, 4H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 142.5, 141.6, 141.03, 141.00, 140.9, 140.7, 140.6, 139.6, 138.6, 137.3, 135.0, 132.1, 131.9, 131.8, 131.7, 131.5, 130.7, 130.5, 129.9, 129.8, 128.6, 127.5, 127.2, 127.1, 126.8, 126.1, 125.8, 31.8, 29.5; LC-MS (APCI) *m/z*: 1018 (100, M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 246 (73000), 292 (67000), 318 sh (16000), 332 (16000), 348 (18000).

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1*Z*,8*Z*)-1,2;8,9-dibenzo[9](2,7)pyrenophane-1,8-diene (4.09d)

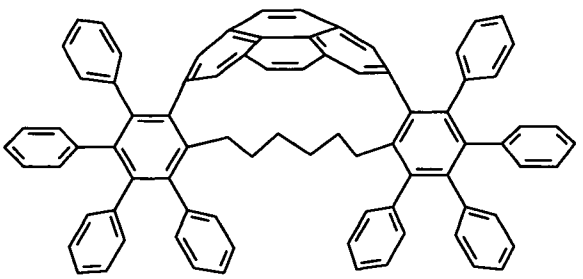


To a stirred solution of 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,8*Z*)-1,2;8,9-dibenzo-17,26-dithia[9.3.3](1,3,5)cyclophane-1,8-diene (**4.11d**) (0.32 g, 0.29 mmol) in dichloromethane (40 mL) was added Borch reagent (0.14 g, 0.86 mmol). The reaction mixture was stirred at rt for 20 h, concentrated *in vacuo* and quenched with ethyl acetate (4.5 mL). The resulting mixture was concentrated *in vacuo* and dried under high vacuum for 6 h, followed by an addition of THF (30 mL) and *t*BuOK (0.16 g, 1.44 mmol). The reaction mixture was stirred at rt for 6 h, concentrated *in vacuo* and passed through a short plug of silica (10 cm × 3.3 cm) using 50% dichloromethane/hexanes to give a mixture of isomers 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1*Z*,8*Z*)-1,2;8,9-dibenzo-

16/17,24/25-bis(methylthio)[9.2.2](1,3,5)cyclophane-1,8-diene (**4.18d**) (3.7 mg, 0.0035 mmol, R_f=0.45) as a white solid. The solid was suspended in dichloromethane (1 mL), and Borch reagent (1.5 mg, 0.0091 mmol) was injected. The reaction mixture turned pink, and was stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo* and dried under high vacuum for 1 h. The residue was suspended in THF (1 mL). After 5 minutes of stirring, *t*-BuOH (1 mL) was added. The reaction mixture was stirred at rt for 10 min and then *t*-BuOK (1.5 mg, 0.014 mmol) was added. The reaction mixture was vigorously stirred at rt for 14 h. Saturated aqueous ammonium chloride solution (1 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (6 mL) and water (5 mL) were added to the residue. The layers were separated and the organic layer was washed with water (2 mL), washed with brine (2 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (12 cm × 1.3 cm, 50% dichloromethane/hexanes) to give a white solid (3.5 mg, 0.0034 mmol, R_f=0.70). ^{1}H NMR spectrum showed that the major component in the white solid was pyrenophanes **4.09d**, and no cyclophanediene **4.10d** observed. Without further purification, the obtained white solid was stirred in benzene (1 mL) in the presence of DDQ (0.8 mg, 0.0037 mmol). The reaction was stirred at reflux for 20 h and concentrated *in vacuo*. The resulting orange residue was purified by column chromatography (7 cm × 1.3 cm, 50% dichloromethane/hexanes) to give a colorless oil, which contains 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,8*Z*)-1,2;8,9-dibenzo[9](2,7)pyrenophane-1,8-diene (**4.09d**) (2.3 mg, 0.0022 mmol, 0.8% from dithiacyclophane **4.11d**, R_f=0.65). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (s, 4H), 7.72 (s, 4H), 7.50 (s, 2H), 7.40-7.38 (m, 5H), 7.12 (t, *J*=7.7 Hz, 7H), 7.02-6.76 (m, 56H), 6.70-

6.68 (m, 6H), 1.37-1.34 (m, 4H), –1.24 (br, s, 2H), –1.39 (br, s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) insufficient amount of material; LC-MS (APCI) *m/z*: 1032 (100, M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 245 (71000), 289 (58000), 305 sh (38000), 317 sh (20000), 331 (19000), 348 (19000).

1',2',3',4',1'',2'',3'',4''-Octaphenyl-(1Z,9Z)-1,2;9,10-dibenzo[10](2,7)pyrenophane-1,9-diene (4.09e)



To a stirred solution of 1',2',3',4',1'',2'',3'',4''-octaphenyl-(1Z,9Z)-1,2;9,10-dibenzo-18, 27-dithia[10.3.3](1,3,5)cyclophane-1,9-diene (**4.11e**) (1.50 g, 1.34 mmol) in dichloromethane (200 mL) was added Borch reagent (0.65 g, 4.03 mmol). The reaction mixture was stirred at rt for 16 h, concentrated *in vacuo* and quenched with ethyl acetate (20 mL). The obtained mixture was concentrated *in vacuo* and dried under high vacuum for 8 h, followed by an addition of THF (150 mL) and *t*-BuOK (0.75 g, 6.70 mmol). The reaction mixture was stirred at rt for 16 h, concentrated *in vacuo*, and the residue was dissolved in dichloromethane (100 mL) and water (100 mL). The aqueous layer was extracted with dichloromethane (3 × 70 mL), and the combined organic layer was washed with water (70 mL), washed with brine (70 mL), dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography (15 cm × 3.3 cm, 50% dichloromethane/hexanes) to give a mixture of isomers 1',2',3',4',1'',2'',3'',4''-octaphenyl-

(1*Z*,9*Z*)-1,2;9,10-dibenzo-17/18,25/26-bis(methylthio)[10.2.2](1,3,5)cyclophane-1,9-diene (**4.18e**) (0.46 g, 0.40 mmol, R_f=0.55) as a white solid. The solid was suspended in dichloromethane (50 mL), and Borch reagent (0.22 g, 1.37 mmol) was injected. The reaction mixture turned yellow immediately and was stirred at rt for 16 h. The reaction mixture was concentrated *in vacuo* and dried under high vacuum for 1 h. The residue was suspended in THF (20 mL). After 5 minutes of stirring, *t*-BuOH (20 mL) was added. The reaction mixture was stirred at rt for 10 min, then *t*-BuOK (0.22 g, 2.00 mmol) was added and the reaction mixture was vigorously stirred for 46 h. Water (4 mL) was added and the reaction mixture was concentrated *in vacuo*. Dichloromethane (40 mL) and water (45 mL) were added to the residue. The organic layer was washed with water (20 mL), brine (10 mL), dried over $MgSO_4$, concentrated *in vacuo*. The resulting yellow residue was purified by column chromatography (19 cm × 3.3 cm, 50% dichloromethane/hexanes) to give a white solid (0.11 g, 0.10 mmol, R_f=0.70). The white solid was stirred in benzene (5 mL), at the presence of DDQ (26 mg, 0.0037 mmol) at reflux for 20 h, concentrated *in vacuo* and the resulting orange residue was purified by column chromatography (20 cm × 1.9 cm, 45% dichloromethane/hexanes) to give a white solid, the main component of which is 1',2',3',4',1",2",3",4"-octaphenyl-(1*Z*,9*Z*)-1,2;9,10-dibenzo[10](2,7)pyrenophane-1,9-diene (**4.09e**) (107 mg, 0.10 mmol, 8% from dithiacyclophane **4.11e**, R_f=0.65). mp >300 °C; IR (powder): 3054 (w), 3027 (w), 2923 (w), 1599 (w), 1495 (w), 1466 (w), 1441 (w), 1404 (w), 1220 (w), 1071 (w), 1026 (w), 914 (w), 883 (w), 814 (w), 802 (w), 748 (m), 727 (s), 696 (vs) cm^{-1}; ^1H NMR (500.13 MHz, $CDCl_3$) δ 7.86 (s, 4H), 7.84 (s, 4H), 7.50 (s, 2H), 7.41 (s, 2H), 7.36 (d, *J*=7.6 Hz, 4H), 7.14 (s, 2H), 7.08-6.75 (m, 64H), 1.64-1.61 (m, 4H), –0.63 (br, s, 4H), –1.16 (br, s,

4H); ^{13}C NMR (125.13 MHz, $CDCl_3$) 141.7, 141.5, 141.3, 141.1, 141.0, 140.8, 140.7, 139.6, 138.9, 138.6, 137.02, 137.00, 132.2, 131.7, 131.4, 131.0, 130.2, 129.1, 128.0, 127.3, 127.20, 127.18, 126.8, 126.6, 126.0, 125.4, 125.3, 33.1, 31.1, 28.6; LC-MS (APCI) *m/z*: 1046 (100, M^++1); UV-vis (chloroform) λ_{max} (ε_{max}) nm 243 (73000), 287 (74000), 305 sh (31000), 317 (16000), 332 (20000), 348 (28000).

4.6 References

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6. Chemical shift values for the 1,*n*-diphenylalkanes were predicted using ChemDraw 10.0. Reported values are all very close to the calculated values. Because the reported values of the chemical shifts of H_E and H_F are in a broad range, calculated values are used. See Ibuki, E.; Ozasa, S.; Fujioka, Y.; Okada, M. *J. Pharm. Soc. Japan*, **1980**, *100*, 718-724.
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8. The angle β are analogous to those used for smaller cyclophanes, such as the [*n*]paracyclophanes. See: (a) *Cyclophanes, Vols. 1 and 2*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983; (b) Vögtle, F. *Cyclophan-Chemie*; B. G. Teubner: Stuttgart, 1990; (c) Diederich, F. N. *Cyclophanes*; Royal Society of Chemistry: London, 1991; (d) Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000.
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10. For an explanation of the formation of these systems, see *J. Org. Chem.* **2003**, *68*, 2089-2098. A 4,5-dihydropyrenophane was recently isolated: Bodwell, G. J.; Swyers, J. Unpublished results.
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Chapter 5

Conclusions

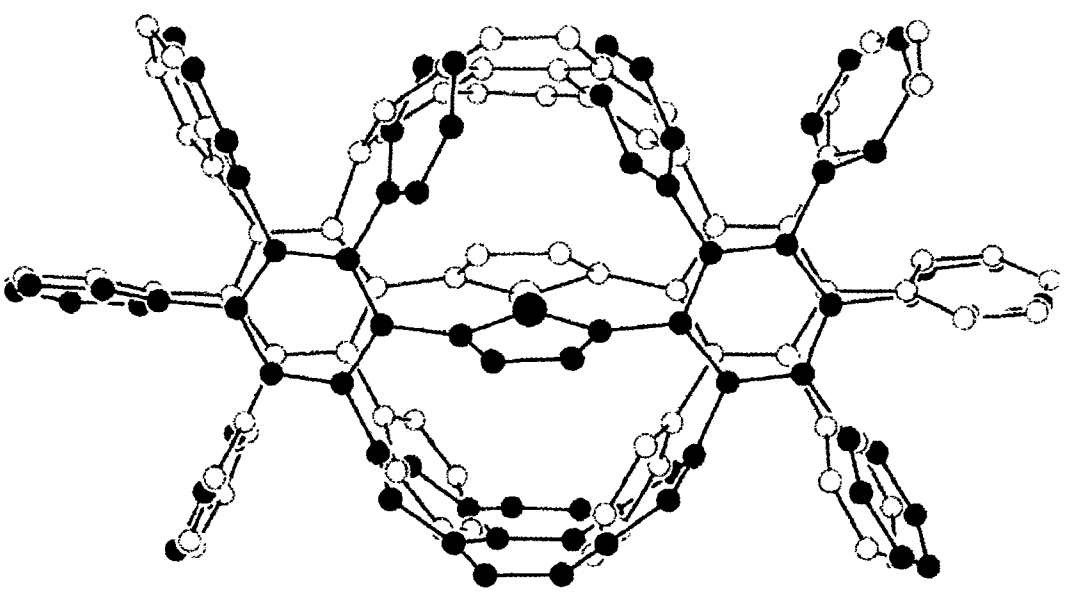
This thesis describes investigations on three research projects, which are related by the application of the valence isomerization-dehydrogenation (VID) reaction to synthesize cyclic pyrene-containing molecules, namely pyrenophanes and pyrenophynes.

Pyrenophynes, which can also be viewed as analogs of Oda and Kawase's nanorings, distinguish themselves from the previously synthesized (2,7)pyrenophanes in that they have alkyne bridges. Synthetic approaches to these synthons using transition metal-catalyzed cross-coupling reactions and sulfide coupling reactions were investigated, but none of them afforded the desired products. Some spectroscopic evidence indicated that a key intermediate to a pyrenophyne (a tetrathiacyclophyne) had been formed.

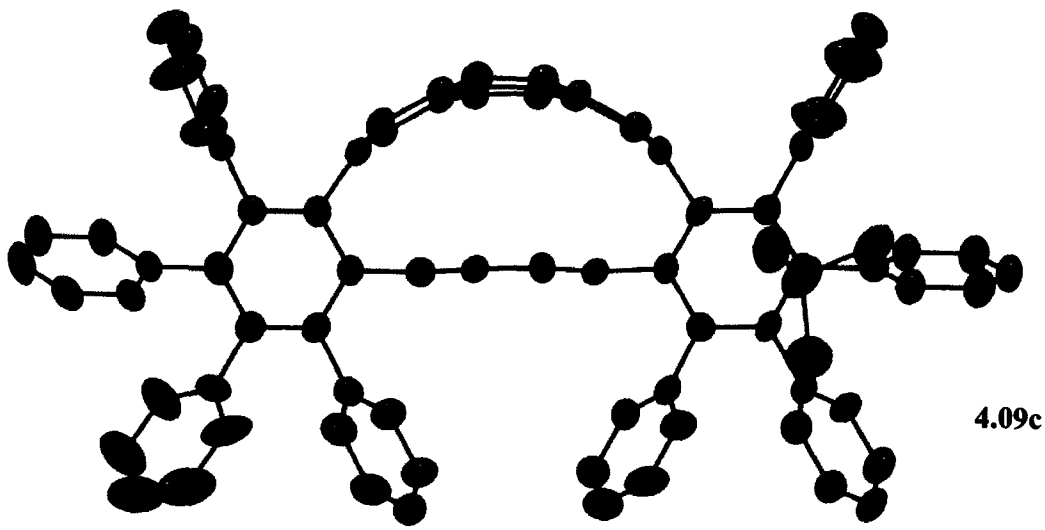
Although the VID reaction was not performed in the attempted synthesis of pyrenophynes described in Chapter 2, it was used to great effect in the syntheses of a series of octaphenylpyrenophanes. As described in Chapter 3-4, several octaphenylpyrenophanes were successfully synthesized, including pyrenophanes bearing all-aromatic bridges (Chapter 3) and aliphatic bridges (Chapter 4). The bridges of these pyrenophanes were installed by a Diels-Alder/chelotropic CO elimination reaction. One of the main contributions of this work is the synthesis of a pyrenophane that contains a 6-atom bridge. Calculations revealed that the pyrene unit contained in this product easily breaks the record for the degree of bend in a pyrenylene unit.

In these projects, several structurally unique compounds were synthesized and characterized. Some of them have interesting NMR and UV-vis properties, and these are discussed in Chapter 3-4. The conformational behavior of several cyclophanes was also investigated using DNMR experiments and this is also discussed in Chapters 3-4.

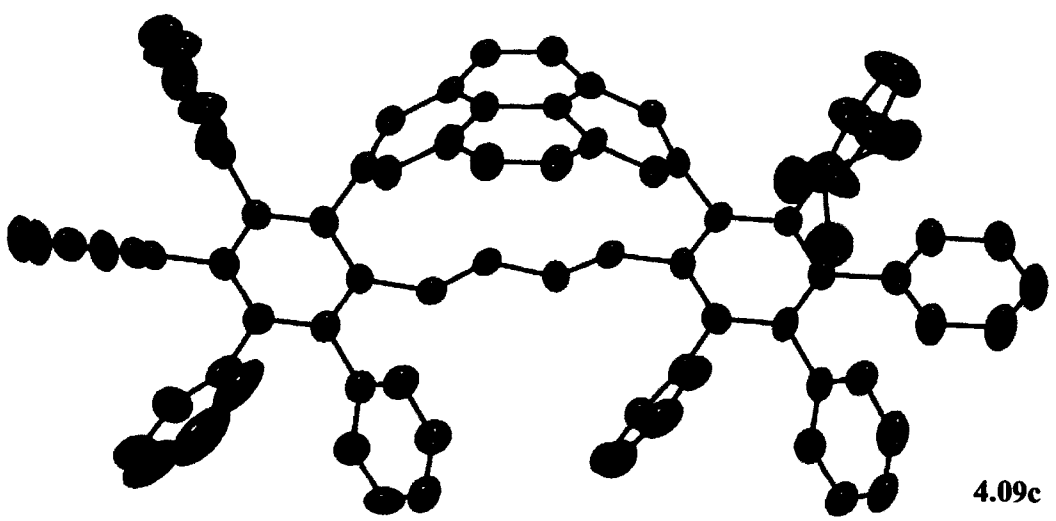
Appendix A. X-ray Structures of Pyrenophanes 3.19 and 4.09c



3.19



4.09c



4.09c

Solvent: chloroform

Crystal Data of **4.09c**

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_diffrn_measured_fraction_theta_full 0.99

_reflns_number_total 15985
_reflns_number_gt 13457
_reflns_threshold_expression >2sigma(I)

_computing_data_collection 'CrystalClear (Rigaku/MSC, 2005)'
_computing_cell_refinement 'CrystalClear (Rigaku/MSC, 2005)'
_computing_data_reduction 'CrystalClear (Rigaku/MSC, 2005)'
_computing_structure_solution 'Siemens SHELXTL (Sheldrick, 1996)'
_computing_structure_refinement 'Siemens SHELXTL (Sheldrick, 1996)'
_computing_molecular_graphics 'Siemens SHELXTL (Sheldrick, 1996)'
_computing_publication_material 'Siemens SHELXTL (Sheldrick, 1996)'

_refine_special_details

Initial solution and refinement showed that 30% of the unit cell volume is occupied by chloroform molecules (solvent of crystallization) with varying degrees of disorder. The formula of the asymmetric unit appears to be C80H56 . 2.5CHCl3. One well-defined chloroform is disordered across a center of inversion, and this was retained in the final structural model. Two other, connected areas of the unit cell held what appeared to be highly disordered chloroform molecules. These were initially described, rather poorly, with two discrete-atom, three-site disorder models. However, the poor performance of these discrete-atom solvent models led us to employ the SQUEEZE/BYPASS procedure (Van der Sluis and Spek, 1990) as implemented in PLATON-96 (Spek, 1990) to account for this part of the solvent density.

With only the title hydrocarbon and the well-defined chloroform retained in the instruction file for PLATON-96, the SQUEEZE option found a total electron count of 73.2 e in a volume of 888.9 A^3^. This electron count corresponds to 1.3 CHCl3, while the volume is that of 6.7 CHCl3 (133 A^3^each). 4.0 CHCl3 was the expected value in both cases, but experience has shown that SQUEEZE often underestimates the electron count of HIGHLY disordered solvent, and, by its very nature, disordered solvent does not completely fill the nominally available volume. The SQUEEZE-processed data was used for all subsequent refinement.

Refinement on F^2^ for ALL reflections except for 0 with very negative F^2^ or flagged by the user for potential systematic errors. Weighted R-factors wR and all goodnesses of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The observed criterion of F^2^ > 2sigma(F^2^) is used only for calculating _R_factor_obs etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

_refine_ls_structure_factor_coef Fsqd
_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc
_refine_ls_weighting_details
'w=1/[\s^2^(Fo^2^)+(0.1577P)^2^+4.9860P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary direct
_atom_sites_solution_secondary difmap
_atom_sites_solution_hydrogens geom
_refine_ls_hydrogen_treatment ?
_refine_ls_extinction_method none
_refine_ls_extinction_coef ?
_refine_ls_number_reflns 15985
_refine_ls_number_parameters 757
_refine_ls_number_restraints 1
_refine_ls_R_factor_all 0.1320
_refine_ls_R_factor_gt 0.1223
_refine_ls_wR_factor_all 0.3301
_refine_ls_wR_factor_ref 0.3226
_refine_ls_goodness_of_fit_all 1.047
_refine_ls_goodness_of_fit_ref 1.116
_refine_ls_restrained_S_all 1.047
_refine_ls_restrained_S_obs 1.116
_refine_ls_shift/su_max 0.001
_refine_ls_shift/esd_mean 0.000
_refine_diff_density_max 0.469
_refine_diff_density_min -0.386
_refine_diff_density_rms 0.080

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Bond lengths

C1 C14 1.372(4) . ? C1 C2 1.400(4) . ? C1 C21 1.505(4) . ? C2 C3 1.403(4) . ?
C2 H2 0.95 . ? C3 C15 1.419(4) . ? C3 C4 1.443(4) . ? C4 C5 1.353(4) . ?
C4 H4 0.95 . ? C5 C6 1.447(4) . ? C5 H5 0.95 . ? C6 C16 1.399(4) . ?
C6 C7 1.400(4) . ? C7 C8 1.379(4) . ? C7 H7 0.95 . ? C8 C9 1.392(4) . ?
C8 C51 1.505(4) . ? C9 C10 1.395(4) . ? C9 H9 0.95 . ? C10 C16 1.426(4) . ?
C10 C11 1.456(4) . ? C11 C12 1.336(4) . ? C11 H11 0.95 . ? C12 C13 1.431(5) . ?
C12 H12 0.95 . ? C13 C14 1.397(4) . ? C13 C15 1.432(4) . ? C14 H14 0.95 . ?
C15 C16 1.429(4) . ? C17 C18 1.533(4) . ? C17 C26 1.539(4) . ? C17 H17A 0.99 . ?

C17 H17B 0.99 . ? C18 C19 1.530(4) . ? C18 H18A 0.99 . ? C18 H18B 0.99 . ?
C19 C20 1.538(4) . ? C19 H19A 0.99 . ? C19 H19B 0.99 . ? C20 C56 1.527(4) . ?
C20 H20A 0.99 . ? C20 H20B 0.99 . ? C21 C26 1.406(4) . ? C21 C22 1.407(4) . ?
C22 C23 1.404(4) . ? C22 C27 1.490(4) . ? C23 C24 1.391(4) . ? C23 C33 1.503(4) . ?
C24 C25 1.412(4) . ? C24 C39 1.502(4) . ? C25 C26 1.411(4) . ? C25 C45 1.502(4) . ?
C27 C28 1.352(5) . ? C27 C32 1.363(5) . ? C28 C29 1.384(6) . ? C28 H28 0.95 . ?
C29 C30 1.351(6) . ? C29 H29 0.95 . ? C30 C31 1.353(7) . ? C30 H30 0.95 . ?
C31 C32 1.392(6) . ? C31 H31 0.95 . ? C32 H32 0.95 . ? C33 C38 1.373(5) . ?
C33 C34 1.386(5) . ? C34 C35 1.395(5) . ? C34 H34 0.95 . ? C35 C36 1.360(7) . ?
C35 H35 0.95 . ? C36 C37 1.363(7) . ? C36 H36 0.95 . ? C37 C38 1.404(5) . ?
C37 H37 0.95 . ? C38 H38 0.95 . ? C39 C44 1.370(5) . ? C39 C40 1.389(5) . ?
C40 C41 1.398(5) . ? C40 H40 0.95 . ? C41 C42 1.371(7) . ? C41 H41 0.95 . ?
C42 C43 1.370(7) . ? C42 H42 0.95 . ? C43 C44 1.403(5) . ? C43 H43 0.95 . ?
C44 H44 0.95 . ? C45 C50 1.382(5) . ? C45 C46 1.397(5) . ? C46 C47 1.392(6) . ?
C46 H46 0.95 . ? C47 C48 1.385(8) . ? C47 H47 0.95 . ? C48 C49 1.352(8) . ?
C48 H48 0.95 . ? C49 C50 1.394(6) . ? C49 H49 0.95 . ? C50 H50 0.95 . ?
C51 C52 1.400(4) . ? C51 C56 1.415(4) . ? C52 C53 1.405(4) . ? C52 C57 1.491(4) . ?
C53 C54 1.395(5) . ? C53 C63 1.503(4) . ? C54 C55 1.411(5) . ? C54 C69 1.484(5) . ?
C55 C56 1.395(4) . ? C55 C75 1.495(4) . ? C57 C62 1.360(5) . ? C57 C58 1.373(6) . ?
C58 C59 1.375(6) . ? C58 H58 0.95 . ? C59 C60 1.355(8) . ? C59 H59 0.95 . ?
C60 C61 1.372(7) . ? C60 H60 0.95 . ? C61 C62 1.398(6) . ? C61 H61 0.95 . ?
C62 H62 0.95 . ? C63 C68 1.373(5) . ? C63 C64 1.396(5) . ? C64 C65 1.400(5) . ?
C64 H64 0.95 . ? C65 C66 1.378(7) . ? C65 H65 0.95 . ? C66 C67 1.364(8) . ?
C66 H66 0.95 . ? C67 C68 1.393(5) . ? C67 H67 0.95 . ? C68 H68 0.95 . ?
C69 C70 1.343(9) . ? C69 C74 1.399(9) . ? C70 C71 1.465(11) . ? C70 H70 0.95 . ?
C71 C72 1.36(2) . ? C71 H71 0.95 . ? C72 C73 1.33(2) . ? C72 H72 0.95 . ?
C73 C74 1.375(8) . ? C73 H73 0.95 . ? C74 H74 0.95 . ? C75 C76 1.370(6) . ?
C75 C80 1.377(5) . ? C76 C77 1.395(5) . ? C76 H76 0.95 . ? C77 C78 1.366(7) . ?
C77 H77 0.95 . ? C78 C79 1.346(7) . ? C78 H78 0.95 . ? C79 C80 1.385(6) . ?
C79 H79 0.95 . ? C80 H80 0.95 . ? C1S Cl3S 1.753(11) . ? C1S Cl2S 1.755(8) . ?
C1S Cl1S 1.760(2) . ? C1S H1S 1.00 . ?

Bond angles_

C14 C1 C2 119.8(3) . . ? C14 C1 C21 119.6(3) . . ? C2 C1 C21 118.9(3) . . ?
C1 C2 C3 119.3(3) . . ? C1 C2 H2 120.4 . . ? C3 C2 H2 120.4 . . ?
C2 C3 C15 118.1(3) . . ? C2 C3 C4 121.1(3) . . ? C15 C3 C4 118.9(3) . . ?
C5 C4 C3 119.9(3) . . ? C5 C4 H4 120.0 . . ? C3 C4 H4 120.0 . . ?
C4 C5 C6 119.7(3) . . ? C4 C5 H5 120.1 . . ? C6 C5 H5 120.1 . . ?
C16 C6 C7 118.5(3) . . ? C16 C6 C5 119.0(3) . . ? C7 C6 C5 120.8(3) . . ?
C8 C7 C6 119.8(3) . . ? C8 C7 H7 120.1 . . ? C6 C7 H7 120.1 . . ?
C7 C8 C9 120.2(3) . . ? C7 C8 C51 118.7(3) . . ? C9 C8 C51 119.7(3) . . ?
C8 C9 C10 119.3(3) . . ? C8 C9 H9 120.4 . . ? C10 C9 H9 120.4 . . ?
C9 C10 C16 118.3(3) . . ? C9 C10 C11 121.0(3) . . ? C16 C10 C11 118.5(3) . . ?
C12 C11 C10 120.0(3) . . ? C12 C11 H11 120.0 . . ? C10 C11 H11 120.0 . . ?
C11 C12 C13 120.8(3) . . ? C11 C12 H12 119.6 . . ? C13 C12 H12 119.6 . . ?

C14 C13 C12 123.2(3) . . ? C14 C13 C15 116.3(3) . . ? C12 C13 C15 118.8(3) . . ?
C1 C14 C13 121.8(3) . . ? C1 C14 H14 119.1 . . ? C13 C14 H14 119.1 . . ?
C3 C15 C16 118.5(3) . . ? C3 C15 C13 120.7(3) . . ? C16 C15 C13 118.4(3) . . ?
C6 C16 C10 119.7(3) . . ? C6 C16 C15 119.3(3) . . ? C10 C16 C15 118.9(3) . . ?
C18 C17 C26 118.5(2) . . ? C18 C17 H17A 107.7 . . ? C26 C17 H17A 107.7 . . ?
C18 C17 H17B 107.7 . . ? C26 C17 H17B 107.7 . . ? H17A C17 H17B 107.1 . . ?
C19 C18 C17 112.2(3) . . ? C19 C18 H18A 109.2 . . ? C17 C18 H18A 109.2 . . ?
C19 C18 H18B 109.2 . . ? C17 C18 H18B 109.2 . . ? H18A C18 H18B 107.9 . . ?
C18 C19 C20 111.5(2) . . ? C18 C19 H19A 109.3 . . ? C20 C19 H19A 109.3 . . ?
C18 C19 H19B 109.3 . . ? C20 C19 H19B 109.3 . . ? H19A C19 H19B 108.0 . . ?
C56 C20 C19 119.5(2) . . ? C56 C20 H20A 107.4 . . ? C19 C20 H20A 107.4 . . ?
C56 C20 H20B 107.4 . . ? C19 C20 H20B 107.4 . . ? H20A C20 H20B 107.0 . . ?
C26 C21 C22 121.6(3) . . ? C26 C21 C1 116.2(2) . . ? C22 C21 C1 122.1(3) . . ?
C23 C22 C21 119.3(3) . . ? C23 C22 C27 121.0(3) . . ? C21 C22 C27 119.6(3) . . ?
C24 C23 C22 119.9(3) . . ? C24 C23 C33 120.0(3) . . ? C22 C23 C33 120.0(3) . . ?
C23 C24 C25 120.3(3) . . ? C23 C24 C39 120.2(3) . . ? C25 C24 C39 119.5(3) . . ?
C26 C25 C24 120.6(3) . . ? C26 C25 C45 120.6(3) . . ? C24 C25 C45 118.7(3) . . ?
C21 C26 C25 117.9(3) . . ? C21 C26 C17 122.8(2) . . ? C25 C26 C17 119.0(3) . . ?
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C27 C28 C29 122.1(4) . . ? C27 C28 H28 119.0 . . ? C29 C28 H28 119.0 . . ?
C30 C29 C28 120.0(4) . . ? C30 C29 H29 120.0 . . ? C28 C29 H29 120.0 . . ?
C29 C30 C31 118.7(4) . . ? C29 C30 H30 120.6 . . ? C31 C30 H30 120.6 . . ?
C30 C31 C32 121.2(4) . . ? C30 C31 H31 119.4 . . ? C32 C31 H31 119.4 . . ?
C27 C32 C31 120.2(4) . . ? C27 C32 H32 119.9 . . ? C31 C32 H32 119.9 . . ?
C38 C33 C34 119.1(3) . . ? C38 C33 C23 119.1(3) . . ? C34 C33 C23 121.8(3) . . ?
C33 C34 C35 119.8(4) . . ? C33 C34 H34 120.1 . . ? C35 C34 H34 120.1 . . ?
C36 C35 C34 120.5(4) . . ? C36 C35 H35 119.8 . . ? C34 C35 H35 119.8 . . ?
C35 C36 C37 120.5(4) . . ? C35 C36 H36 119.7 . . ? C37 C36 H36 119.7 . . ?
C36 C37 C38 119.6(4) . . ? C36 C37 H37 120.2 . . ? C38 C37 H37 120.2 . . ?
C33 C38 C37 120.6(4) . . ? C33 C38 H38 119.7 . . ? C37 C38 H38 119.7 . . ?
C44 C39 C40 119.9(3) . . ? C44 C39 C24 119.8(3) . . ? C40 C39 C24 120.2(3) . . ?
C39 C40 C41 119.1(4) . . ? C39 C40 H40 120.5 . . ? C41 C40 H40 120.5 . . ?
C42 C41 C40 121.1(4) . . ? C42 C41 H41 119.5 . . ? C40 C41 H41 119.5 . . ?
C43 C42 C41 119.6(4) . . ? C43 C42 H42 120.2 . . ? C41 C42 H42 120.2 . . ?
C42 C43 C44 120.2(4) . . ? C42 C43 H43 119.9 . . ? C44 C43 H43 119.9 . . ?
C39 C44 C43 120.2(4) . . ? C39 C44 H44 119.9 . . ? C43 C44 H44 119.9 . . ?
C50 C45 C46 119.2(4) . . ? C50 C45 C25 120.6(3) . . ? C46 C45 C25 120.3(3) . . ?
C47 C46 C45 119.4(5) . . ? C47 C46 H46 120.3 . . ? C45 C46 H46 120.3 . . ?
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C49 C48 C47 119.8(4) . . ? C49 C48 H48 120.1 . . ? C47 C48 H48 120.1 . . ?
C48 C49 C50 120.7(5) . . ? C48 C49 H49 119.6 . . ? C50 C49 H49 119.6 . . ?
C45 C50 C49 120.3(4) . . ? C45 C50 H50 119.9 . . ? C49 C50 H50 119.9 . . ?
C52 C51 C56 121.6(3) . . ? C52 C51 C8 121.5(3) . . ? C56 C51 C8 116.7(3) . . ?
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C54 C53 C52 120.5(3) . . ? C54 C53 C63 120.4(3) . . ? C52 C53 C63 119.1(3) . . ?
C53 C54 C55 119.7(3) . . ? C53 C54 C69 120.0(3) . . ? C55 C54 C69 120.2(3) . . ?

C56 C55 C54 120.9(3) . . ? C56 C55 C75 120.4(3) . . ? C54 C55 C75 118.7(3) . . ?
C55 C56 C51 118.3(3) . . ? C55 C56 C20 120.0(3) . . ? C51 C56 C20 121.5(3) . . ?
C62 C57 C58 118.0(3) . . ? C62 C57 C52 120.8(4) . . ? C58 C57 C52 121.2(3) . . ?
C57 C58 C59 120.4(4) . . ? C57 C58 H58 119.8 . . ? C59 C58 H58 119.8 . . ?
C60 C59 C58 121.5(5) . . ? C60 C59 H59 119.2 . . ? C58 C59 H59 119.2 . . ?
C59 C60 C61 119.3(4) . . ? C59 C60 H60 120.4 . . ? C61 C60 H60 120.4 . . ?
C60 C61 C62 118.8(4) . . ? C60 C61 H61 120.6 . . ? C62 C61 H61 120.6 . . ?
C57 C62 C61 122.0(4) . . ? C57 C62 H62 119.0 . . ? C61 C62 H62 119.0 . . ?
C68 C63 C64 119.1(3) . . ? C68 C63 C53 121.0(3) . . ? C64 C63 C53 119.8(3) . . ?
C63 C64 C65 120.1(4) . . ? C63 C64 H64 120.0 . . ? C65 C64 H64 120.0 . . ?
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C67 C66 C65 120.4(4) . . ? C67 C66 H66 119.8 . . ? C65 C66 H66 119.8 . . ?
C66 C67 C68 120.3(4) . . ? C66 C67 H67 119.8 . . ? C68 C67 H67 119.8 . . ?
C63 C68 C67 120.5(4) . . ? C63 C68 H68 119.8 . . ? C67 C68 H68 119.8 . . ?
C70 C69 C74 119.0(5) . . ? C70 C69 C54 122.7(6) . . ? C74 C69 C54 118.2(5) . . ?
C69 C70 C71 118.5(9) . . ? C69 C70 H70 120.8 . . ? C71 C70 H70 120.8 . . ?
C72 C71 C70 118.7(11) . . ? C72 C71 H71 120.7 . . ? C70 C71 H71 120.7 . . ?
C73 C72 C71 123.1(9) . . ? C73 C72 H72 118.5 . . ? C71 C72 H72 118.5 . . ?
C72 C73 C74 118.1(11) . . ? C72 C73 H73 120.9 . . ? C74 C73 H73 120.9 . . ?
C73 C74 C69 122.6(9) . . ? C73 C74 H74 118.7 . . ? C69 C74 H74 118.7 . . ?
C76 C75 C80 118.2(3) . . ? C76 C75 C55 120.2(3) . . ? C80 C75 C55 121.6(3) . . ?
C75 C76 C77 121.1(4) . . ? C75 C76 H76 119.5 . . ? C77 C76 H76 119.5 . . ?
C78 C77 C76 119.5(4) . . ? C78 C77 H77 120.3 . . ? C76 C77 H77 120.3 . . ?
C79 C78 C77 119.9(4) . . ? C79 C78 H78 120.1 . . ? C77 C78 H78 120.1 . . ?
C78 C79 C80 121.0(4) . . ? C78 C79 H79 119.5 . . ? C80 C79 H79 119.5 . . ?
C75 C80 C79 120.3(4) . . ? C75 C80 H80 119.8 . . ? C79 C80 H80 119.8 . . ?
Cl3S C1S Cl2S 110.0(6) . . ? Cl3S C1S Cl1S 108.7(15) . . ? Cl2S C1S Cl1S 110.1(19) . ?
Cl3S C1S H1S 109.3 . . ? Cl2S C1S H1S 109.3 . . ? Cl1S C1S H1S 109.3 . . ?

Dihedral angle

C14 C1 C2 C3 -18.6(4) . . . ? C21 C1 C2 C3 146.7(3) . . . ? C1 C2 C3 C15 3.4(4) . . . ?
C1 C2 C3 C4 -160.5(3) . . .. ? C2 C3 C4 C5 146.2(3) . . . ? C15 C3 C4 C5 -17.7(4) . . .. ?
C3 C4 C5 C6 1.1(5) . . . . ? C4 C5 C6 C16 17.1(4) . . . . ? C4 C5 C6 C7 -148.2(3) . . . . ?
C16 C6 C7 C8 -0.3(4) . . . . ? C5 C6 C7 C8 165.1(3) . . . . ? C6 C7 C8 C9 17.5(4) . . . . ?
C6 C7 C8 C51 -148.9(3) . . .? C7 C8 C9 C10 -18.2(4) . . . ? C51 C8 C9 C10 148.1(3) . . ?
C8 C9 C10 C16 1.9(4) . . . ? C8 C9 C10 C11 -161.1(3) . ? C9 C10 C11 C12 145.4(3) .. ?
C16 C10 C11 C12 -17.5(5) . ..? C10 C11 C12 C13 0.8(5) .. . ?
C11 C12 C13 C14 -146.9(3) . . ? C11 C12 C13 C15 17.6(5) . . . . ?
C2 C1 C14 C13 16.7(4) . . . . ? C21 C1 C14 C13 -148.5(3) . . . . ?
C12 C13 C14 C1 165.2(3) . . . . ? C15 C13 C14 C1 0.4(4) . . . . ?
C2 C3 C15 C16 -148.4(3) . . . . ? C4 C3 C15 C16 15.9(4) . . . . ?
C2 C3 C15 C13 13.8(4) . . . . ? C4 C3 C15 C13 178.1(3) . . . . ?
C14 C13 C15 C3 -15.7(4) . . . . ? C12 C13 C15 C3 178.8(3) . . . . ?
C14 C13 C15 C16 146.5(3) . . . . ? C12 C13 C15 C16 -19.0(4) . . . . ?
C7 C6 C16 C10 -15.8(4) . . . . ? C5 C6 C16 C10 178.5(3) . . . . ?

C7 C6 C16 C15 147.2(3) . . . . ? C5 C6 C16 C15 -18.5(4) . . . . ?
C9 C10 C16 C6 15.1(4) . . . . ? C11 C10 C16 C6 178.4(3) . . . . ?
C9 C10 C16 C15 -148.0(3) . . . . ? C11 C10 C16 C15 15.4(4) . . . . ?
C3 C15 C16 C6 2.1(4) . . . . ? C13 C15 C16 C6 -160.5(3) . . . . ?
C3 C15 C16 C10 165.2(3) . . . . ? C13 C15 C16 C10 2.6(4) . . . . ?
C26 C17 C18 C19 178.8(2) . . . . ? C17 C18 C19 C20 174.4(2) . . . . ?
C18 C19 C20 C56 176.7(3) . . . . ? C14 C1 C21 C26 90.1(3) . . . . ?
C2 C1 C21 C26 -75.2(3) . . . . ? C14 C1 C21 C22 -86.1(3) . . . . ?
C2 C1 C21 C22 108.6(3) . . . . ? C26 C21 C22 C23 -0.7(4) . . . . ?
C1 C21 C22 C23 175.2(3) . . . . ? C26 C21 C22 C27 -179.0(3) . . . . ?
C1 C21 C22 C27 -3.1(4) . . . . ? C21 C22 C23 C24 -4.5(4) . . . . ?
C27 C22 C23 C24 173.7(3) . . . . ? C21 C22 C23 C33 175.0(3) . . . . ?
C27 C22 C23 C33 -6.7(5) . . . . ? C22 C23 C24 C25 6.0(5) . . . . ?
C33 C23 C24 C25 -173.5(3) . . . . ? C22 C23 C24 C39 -174.6(3) . . . . ?
C33 C23 C24 C39 5.9(5) . . . . ? C23 C24 C25 C26 -2.2(5) . . . . ?
C39 C24 C25 C26 178.4(3) . . . . ? C23 C24 C25 C45 174.7(3) . . . . ?
C39 C24 C25 C45 -4.7(4) . . . . ? C22 C21 C26 C25 4.4(4) . . . . ?
C1 C21 C26 C25 -171.8(3) . . . . ? C22 C21 C26 C17 -170.0(3) . . . . ?
C1 C21 C26 C17 13.8(4) . . . . ? C24 C25 C26 C21 -2.9(4) . . . . ?
C45 C25 C26 C21 -179.8(3) . . . . ? C24 C25 C26 C17 171.7(3) . . . . ?
C45 C25 C26 C17 -5.2(4) . . . . ? C18 C17 C26 C21 -87.2(4) . . . . ?
C18 C17 C26 C25 98.5(3) . . . . ? C23 C22 C27 C28 -86.8(4) . . . . ?
C21 C22 C27 C28 91.5(4) . . . . ? C23 C22 C27 C32 89.8(4) . . . . ?
C21 C22 C27 C32 -92.0(4) . . . . ? C32 C27 C28 C29 0.8(7) . . . . ?
C22 C27 C28 C29 177.5(4) . . . . ? C27 C28 C29 C30 -0.4(8) . . . . ?
C28 C29 C30 C31 -0.2(8) . . . . ? C29 C30 C31 C32 0.4(8) . . . . ?
C28 C27 C32 C31 -0.6(7) . . . . ? C22 C27 C32 C31 -177.2(4) . . . . ?
C30 C31 C32 C27 0.0(8) . . . . ? C24 C23 C33 C38 105.0(4) . . . . ?
C22 C23 C33 C38 -74.6(4) . . . . ? C24 C23 C33 C34 -71.3(4) . . . . ?
C22 C23 C33 C34 109.1(4) . . . . ? C38 C33 C34 C35 0.5(5) . . . . ?
C23 C33 C34 C35 176.8(3) . . . . ? C33 C34 C35 C36 -1.4(6) . . . . ?
C34 C35 C36 C37 1.9(6) . . . . ? C35 C36 C37 C38 -1.6(7) . . . . ?
C34 C33 C38 C37 -0.2(6) . . . . ? C23 C33 C38 C37 -176.6(3) . . . . ?
C36 C37 C38 C33 0.7(6) . . . . ? C23 C24 C39 C44 111.5(4) . . . . ?
C25 C24 C39 C44 -69.1(4) . . . . ? C23 C24 C39 C40 -67.0(4) . . . . ?
C25 C24 C39 C40 112.4(4) . . . . ? C44 C39 C40 C41 0.9(5) . . . . ?
C24 C39 C40 C41 179.4(3) . . . . ? C39 C40 C41 C42 -0.4(6) . . . . ?
C40 C41 C42 C43 0.2(7) . . . . ? C41 C42 C43 C44 -0.5(6) . . . . ?
C40 C39 C44 C43 -1.3(5) . . . . ? C24 C39 C44 C43 -179.8(3) . . . . ?
C42 C43 C44 C39 1.1(6) . . . . ? C26 C25 C45 C50 -71.7(4) . . . . ?
C24 C25 C45 C50 111.4(3) . . . . ? C26 C25 C45 C46 108.5(4) . . . . ?
C24 C25 C45 C46 -68.5(4) . . . . ? C50 C45 C46 C47 1.7(5) . . . . ?
C25 C45 C46 C47 -178.5(3) . . . . ? C45 C46 C47 C48 0.4(6) . . . . ?
C46 C47 C48 C49 -1.8(7) . . . . ? C47 C48 C49 C50 1.2(7) . . . . ?
C46 C45 C50 C49 -2.3(5) . . . . ? C25 C45 C50 C49 177.9(3) . . . . ?
C48 C49 C50 C45 0.9(6) . . . . ? C7 C8 C51 C52 -84.0(4) . . . . ?

C9 C8 C51 C52 109.5(3) . . . . ? C7 C8 C51 C56 90.1(3) . . . . ?
C9 C8 C51 C56 -76.4(4) . . . . ? C56 C51 C52 C53 -0.3(5) . . . . ?
C8 C51 C52 C53 173.4(3) . . . . ? C56 C51 C52 C57 -179.7(3) . . . . ?
C8 C51 C52 C57 -6.0(4) . . . . ? C51 C52 C53 C54 -2.2(5) . . . . ?
C57 C52 C53 C54 177.2(3) . . . . ? C51 C52 C53 C63 -179.8(3) . . . . ?
C57 C52 C53 C63 -0.4(5) . . . . ? C52 C53 C54 C55 2.8(5) . . . . ?
C63 C53 C54 C55 -179.6(3) . . . . ? C52 C53 C54 C69 178.2(4) . . . . ?
C63 C53 C54 C69 -4.2(6) . . . . ? C53 C54 C55 C56 -1.0(5) . . . . ?
C69 C54 C55 C56 -176.4(4) . . . . ? C53 C54 C55 C75 178.5(3) . . . . ?
C69 C54 C55 C75 3.1(6) . . . . ? C54 C55 C56 C51 -1.5(5) . . . . ?
C75 C55 C56 C51 179.1(3) . . . . ? C54 C55 C56 C20 174.2(3) . . . . ?
C75 C55 C56 C20 -5.2(5) . . . . ? C52 C51 C56 C55 2.1(5) . . . . ?
C8 C51 C56 C55 -171.9(3) . . . . ? C52 C51 C56 C20 -173.5(3) . . . . ?
C8 C51 C56 C20 12.5(4) . . . . ? C19 C20 C56 C55 97.0(4) . . . . ?
C19 C20 C56 C51 -87.5(4) . . . . ? C51 C52 C57 C62 -67.6(4) . . . . ?
C53 C52 C57 C62 113.0(4) . . . . ? C51 C52 C57 C58 110.7(4) . . . . ?
C53 C52 C57 C58 -68.7(5) . . . . ? C62 C57 C58 C59 0.8(7) . . . . ?
C52 C57 C58 C59 -177.6(5) . . . . ? C57 C58 C59 C60 -0.9(9) . . . . ?
C58 C59 C60 C61 0.7(9) . . . . ? C59 C60 C61 C62 -0.3(8) . . . . ?
C58 C57 C62 C61 -0.5(6) . . . . ? C52 C57 C62 C61 177.9(3) . . . . ?
C60 C61 C62 C57 0.3(6) . . . . ? C54 C53 C63 C68 120.0(4) . . . . ?
C52 C53 C63 C68 -62.4(5) . . . . ? C54 C53 C63 C64 -59.6(5) . . . . ?
C52 C53 C63 C64 118.0(4) . . . . ? C68 C63 C64 C65 1.8(5) . . . . ?
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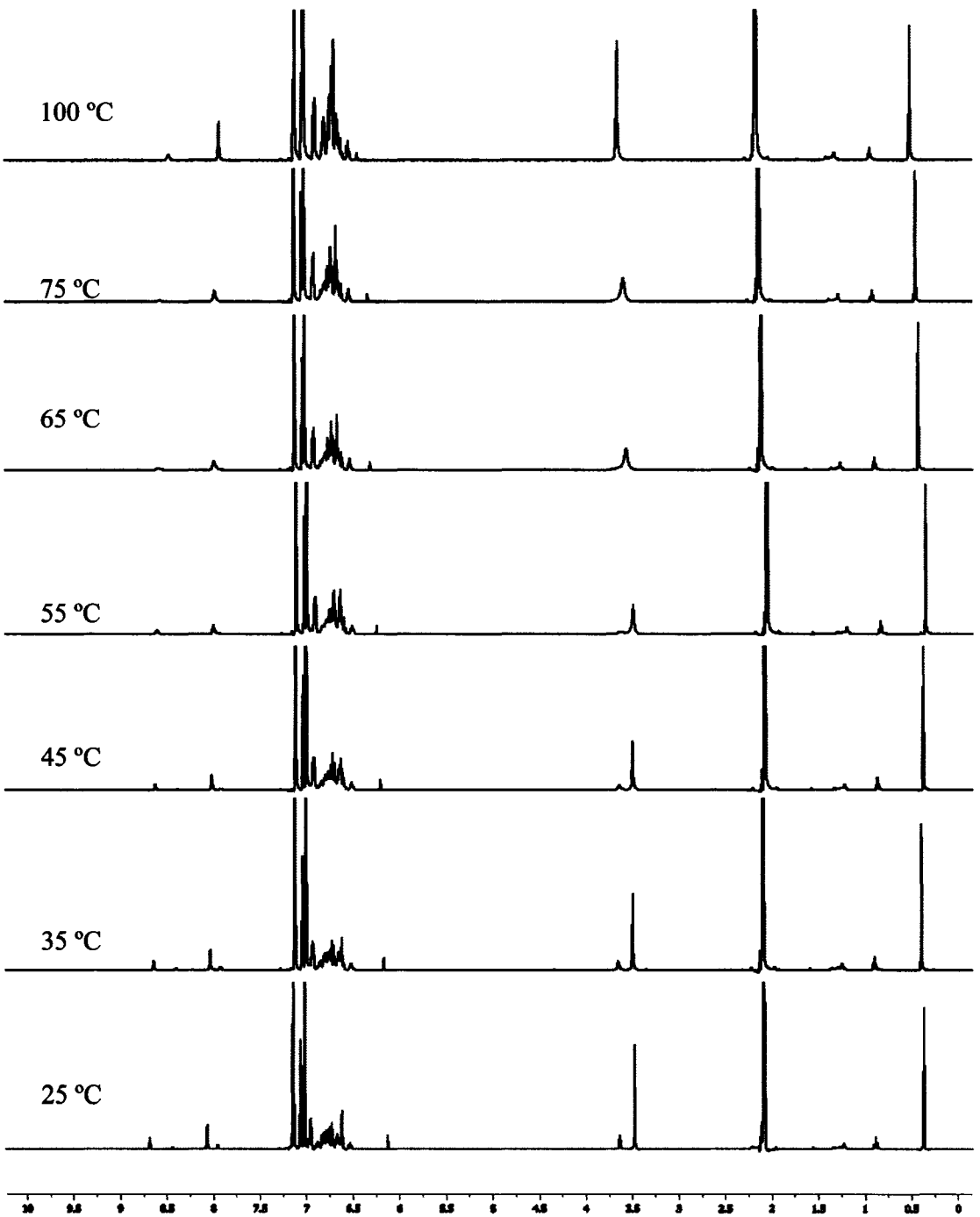
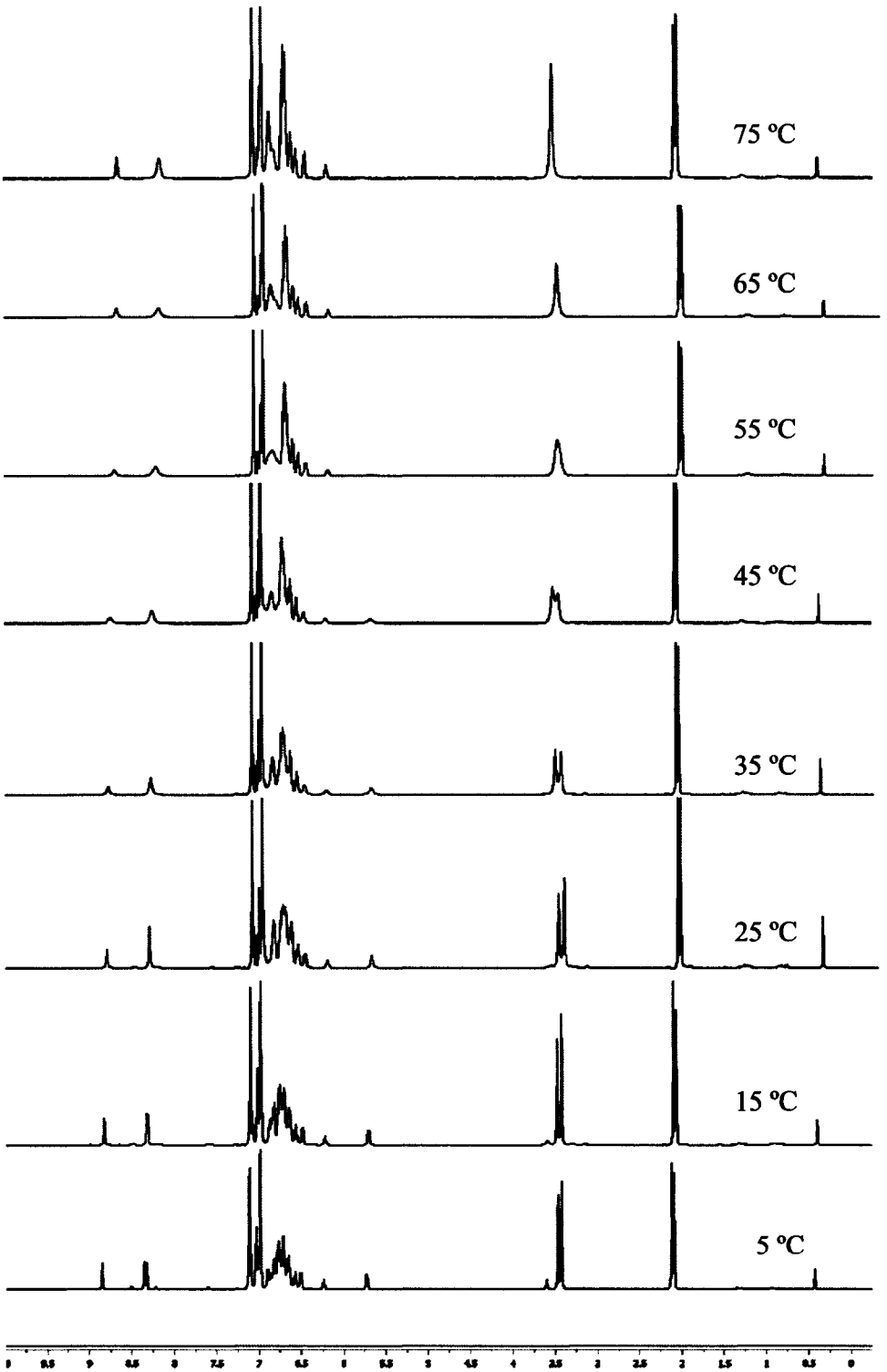
C64 C65 C66 C67 0.6(7) . . . . ? C65 C66 C67 C68 -0.1(8) . . . . ?
C64 C63 C68 C67 -1.3(6) . . . . ? C53 C63 C68 C67 179.1(4) . . . . ?
C66 C67 C68 C63 0.5(7) . . . . ? C53 C54 C69 C70 117.8(5) . . . . ?
C55 C54 C69 C70 -66.8(6) . . . . ? C53 C54 C69 C74 -60.2(6) . . . . ?
C55 C54 C69 C74 115.2(4) . . . . ? C74 C69 C70 C71 0.6(7) . . . . ?
C54 C69 C70 C71 -177.4(5) . . . . ? C69 C70 C71 C72 0.5(11) . . . . ?
C70 C71 C72 C73 -2.5(14) . . . . ? C71 C72 C73 C74 3.1(13) . . . . ?
C72 C73 C74 C69 -1.9(9) . . . . ? C70 C69 C74 C73 0.0(8) . . . . ?
C54 C69 C74 C73 178.1(5) . . . . ? C56 C55 C75 C76 -76.1(4) . . . . ?
C54 C55 C75 C76 104.4(4) . . . . ? C56 C55 C75 C80 104.3(4) . . . . ?
C54 C55 C75 C80 -75.2(5) . . . . ? C80 C75 C76 C77 -0.4(6) . . . . ?
C55 C75 C76 C77 180.0(3) . . . . ? C75 C76 C77 C78 -0.2(6) . . . . ?
C76 C77 C78 C79 0.7(7) . . . . ? C77 C78 C79 C80 -0.6(7) . . . . ?
C76 C75 C80 C79 0.6(5) . . . . ? C55 C75 C80 C79 -179.9(3) . . . . ?
C78 C79 C80 C75 -0.1(6) . . . . ?
#========== END DATA ==========

Appendix B. Selected DNMR Spectra

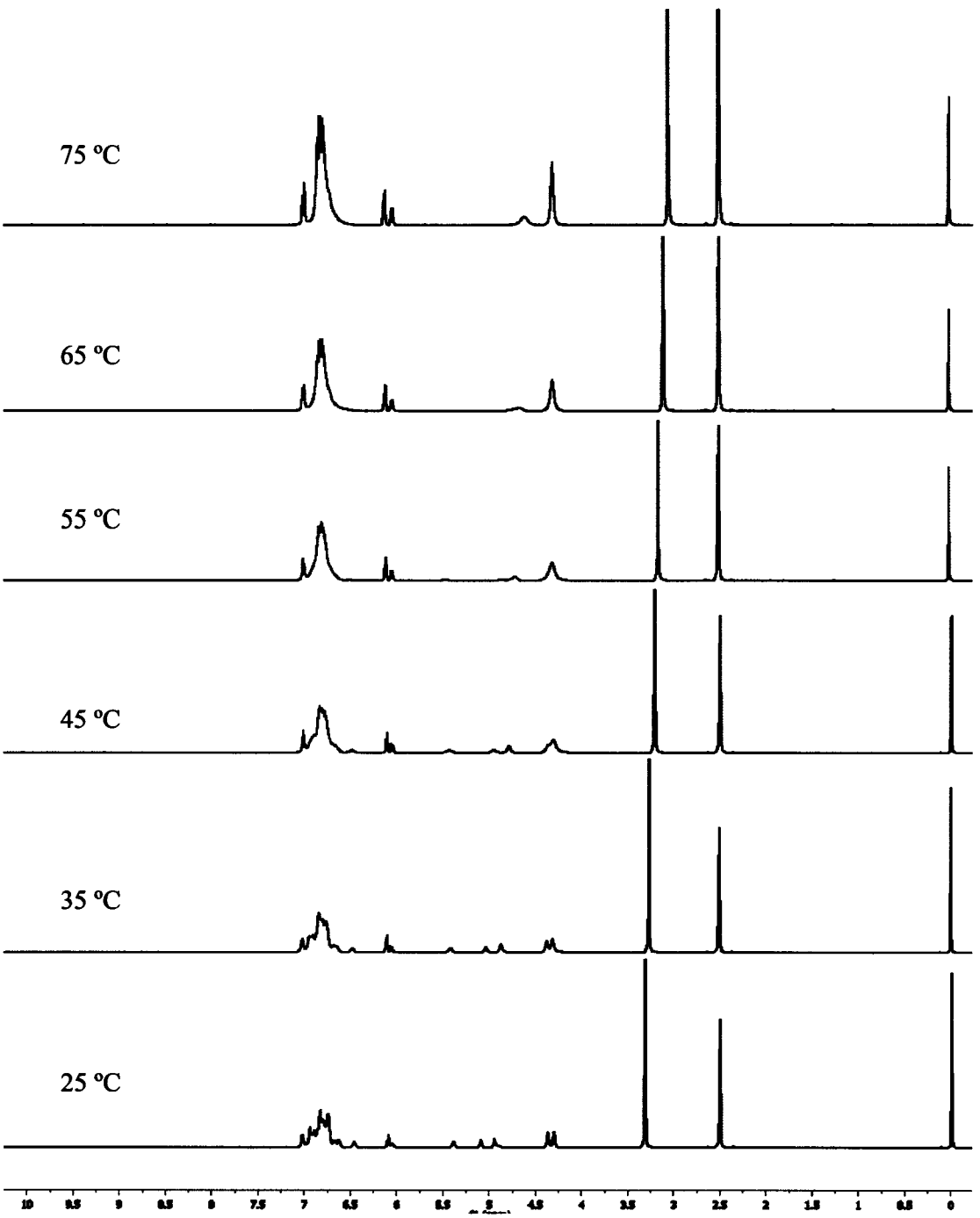
DNMR spectra of tetraester **3.32** (toluene-d_8, 25-100 °C)



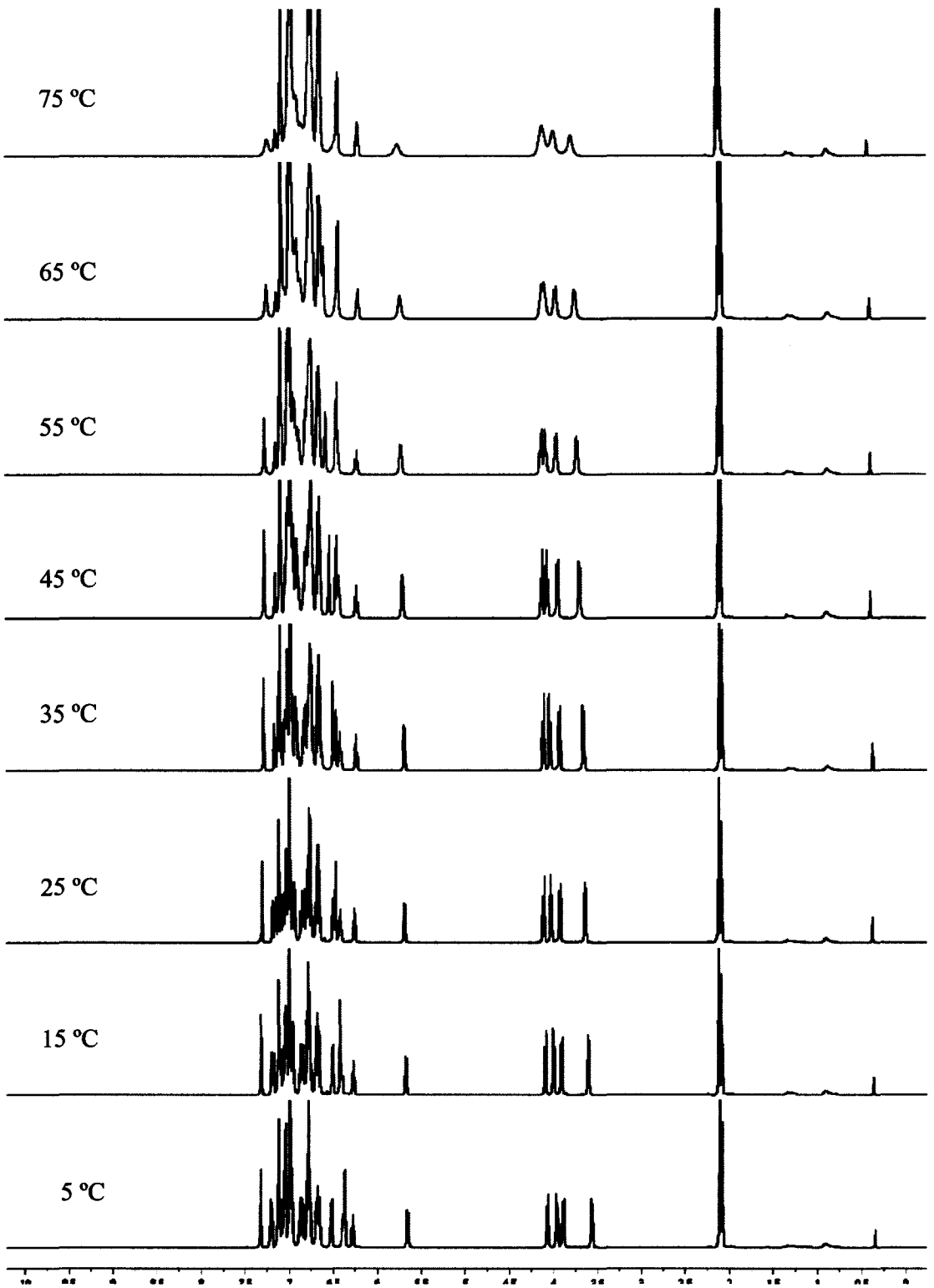
DNMR spectra of tetraester **3.39** (toluene-d_8, 5-75 °C)



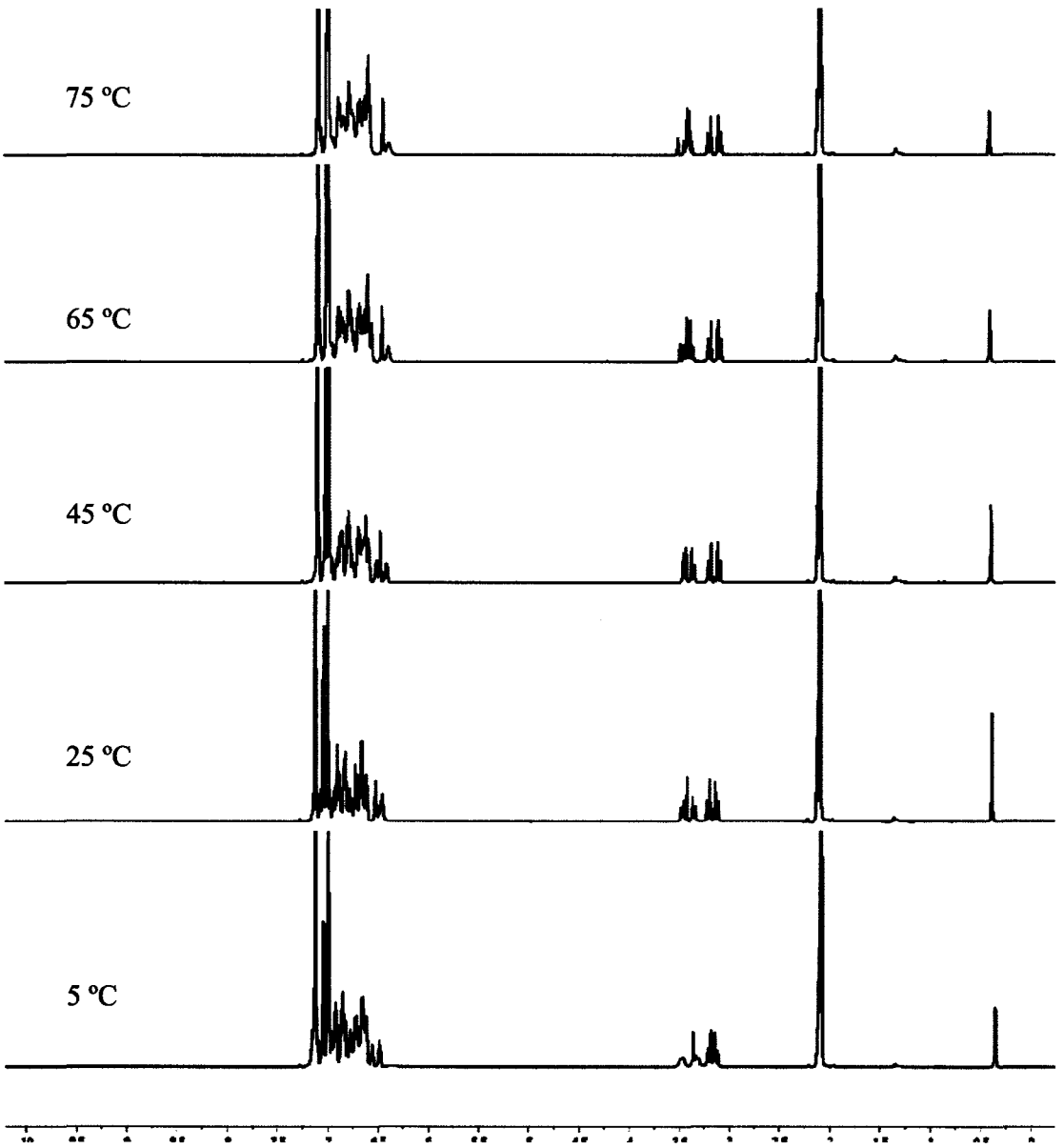
DNMR spectra of tetraol **3.45** (DMSO-d_6, 25-75 °C)



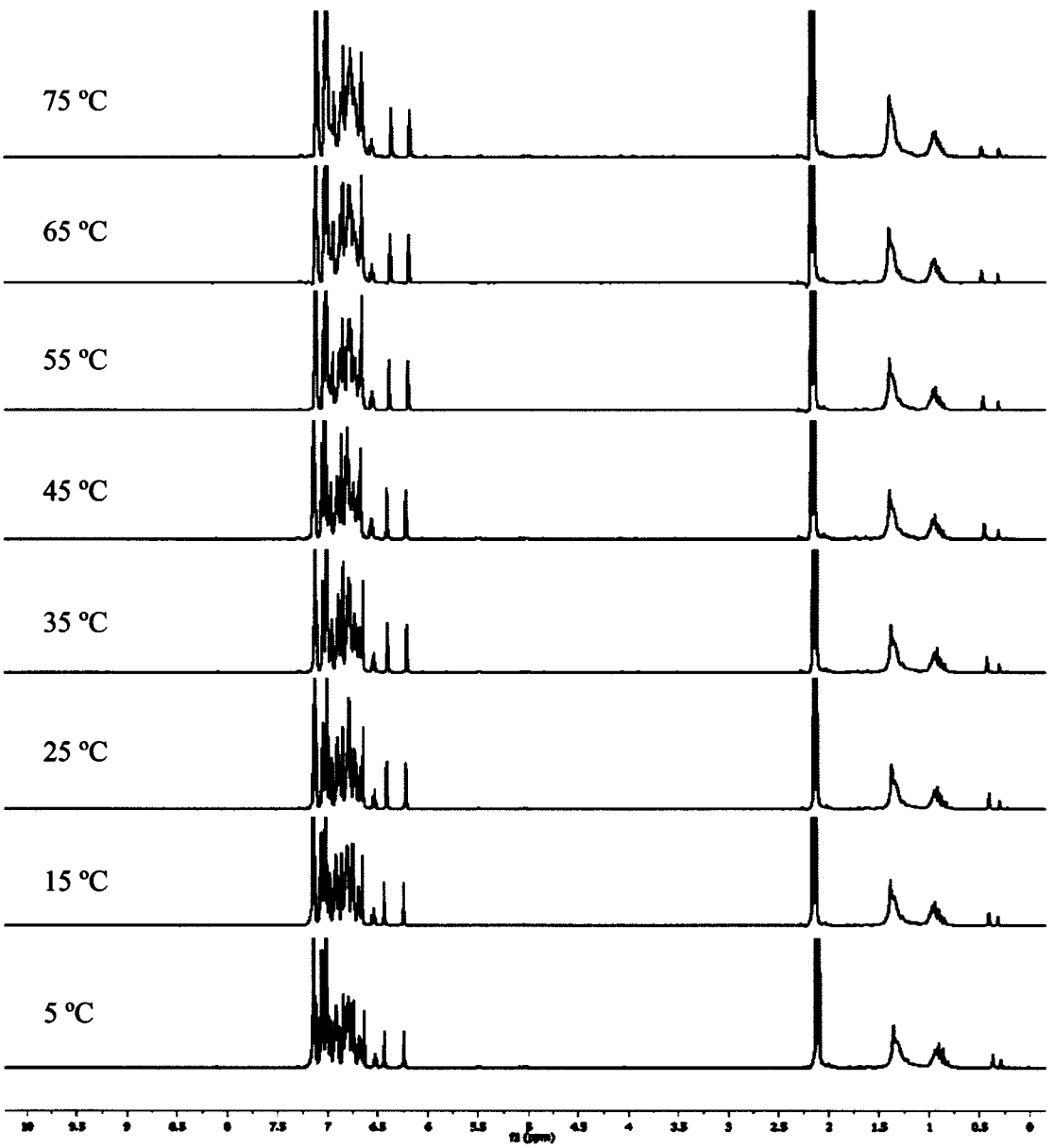
DNMR spectra of tetrabromide **3.46** (toluene-d_8, 5-75 °C)



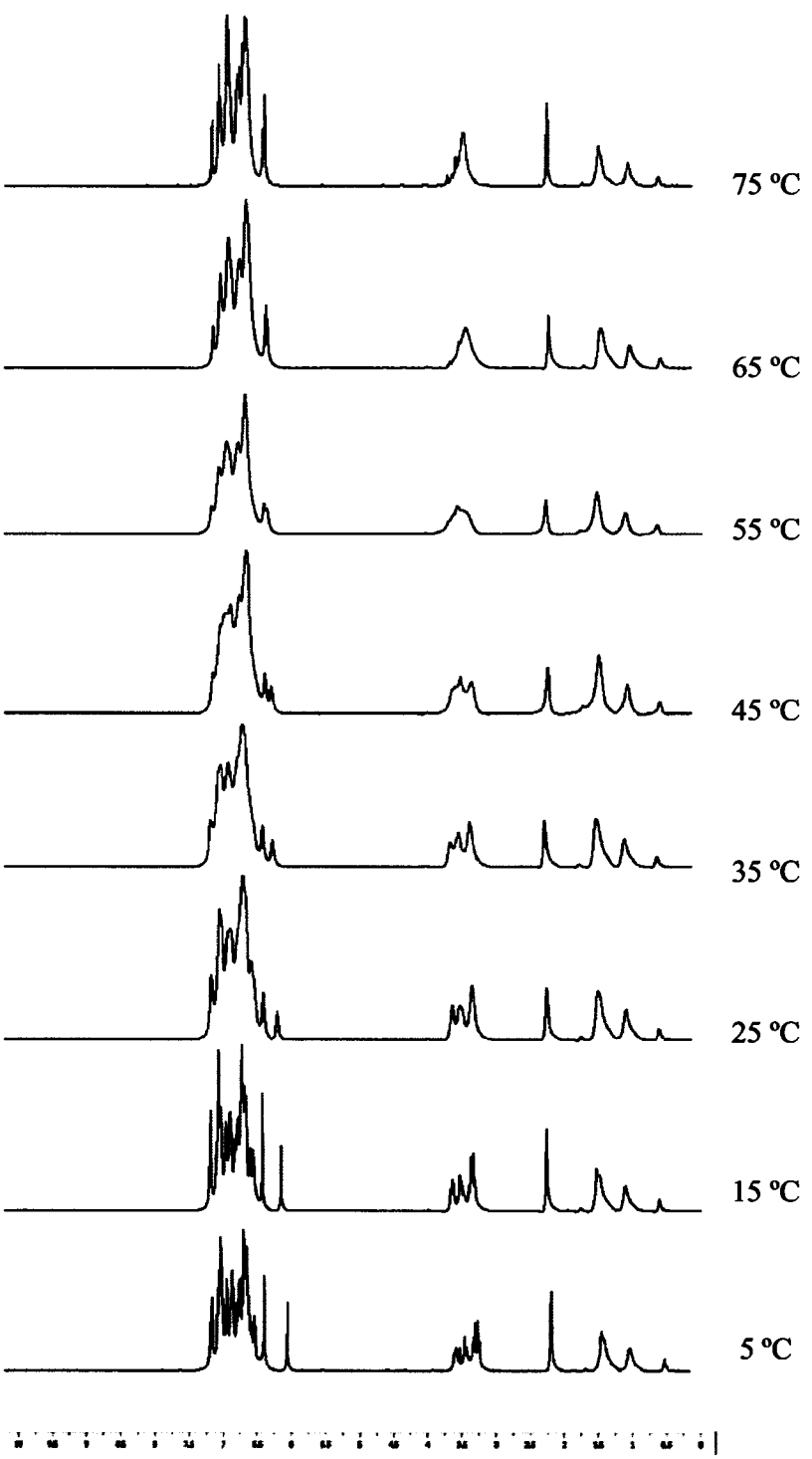
DNMR spectra of dithiacyclophane **3.47** (toluene-d_8, 5-75 °C)



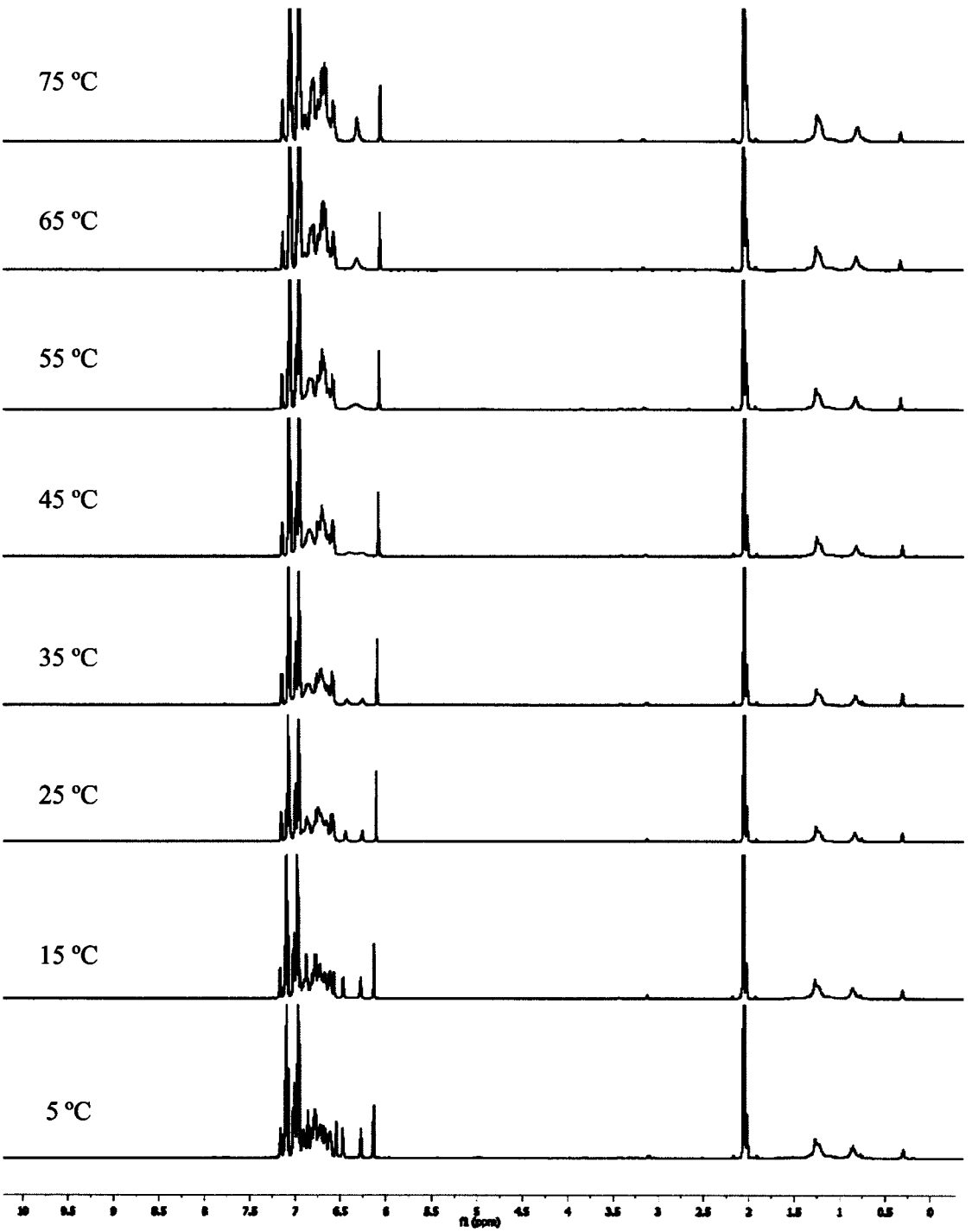
DNMR spectra of cyclophanediene **3.49** (toluene-d_8, 5-75 °C)



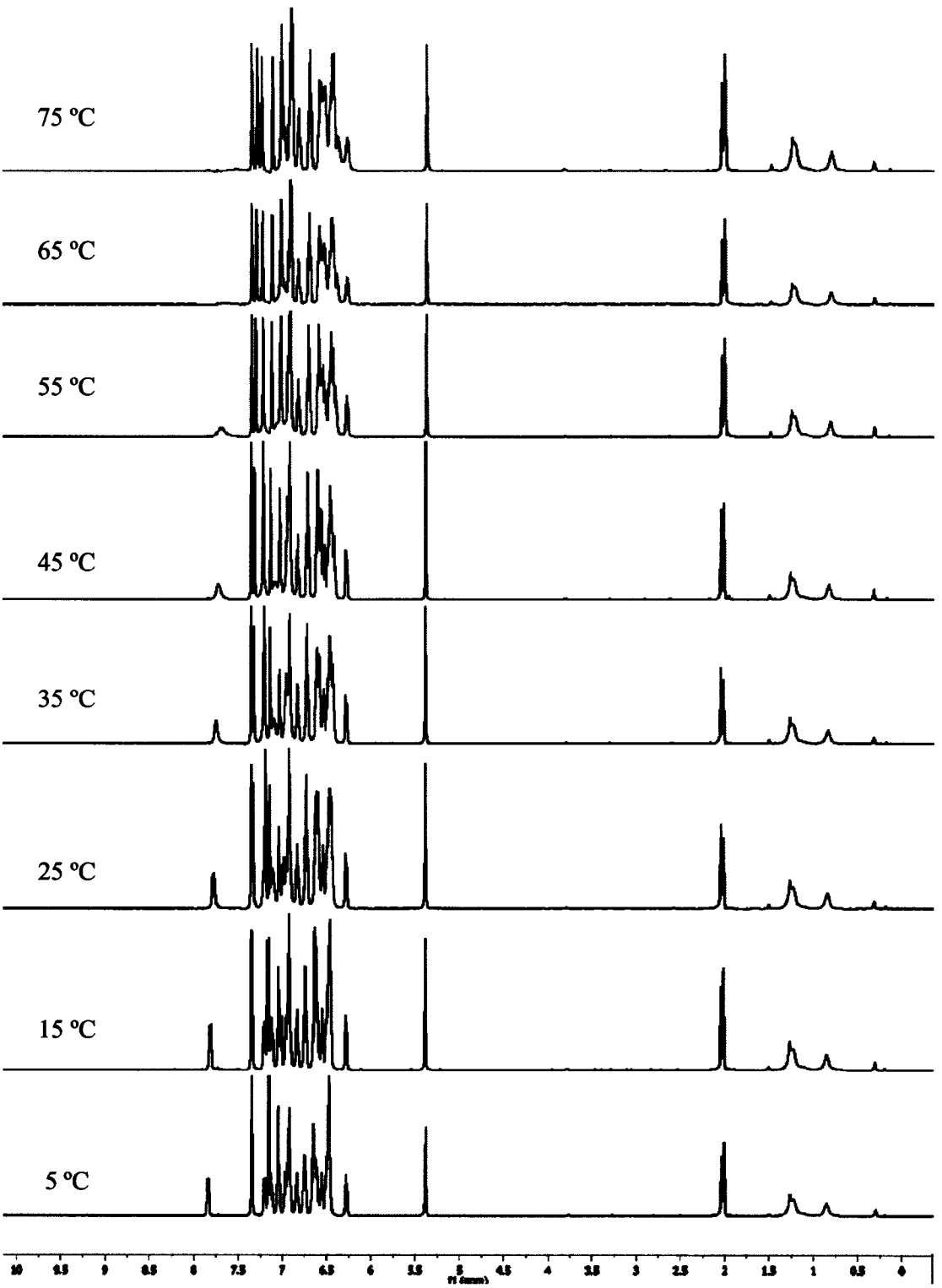
DNMR spectra of dithiacyclophane **3.56** (toluene-d_8, 5-75 °C)



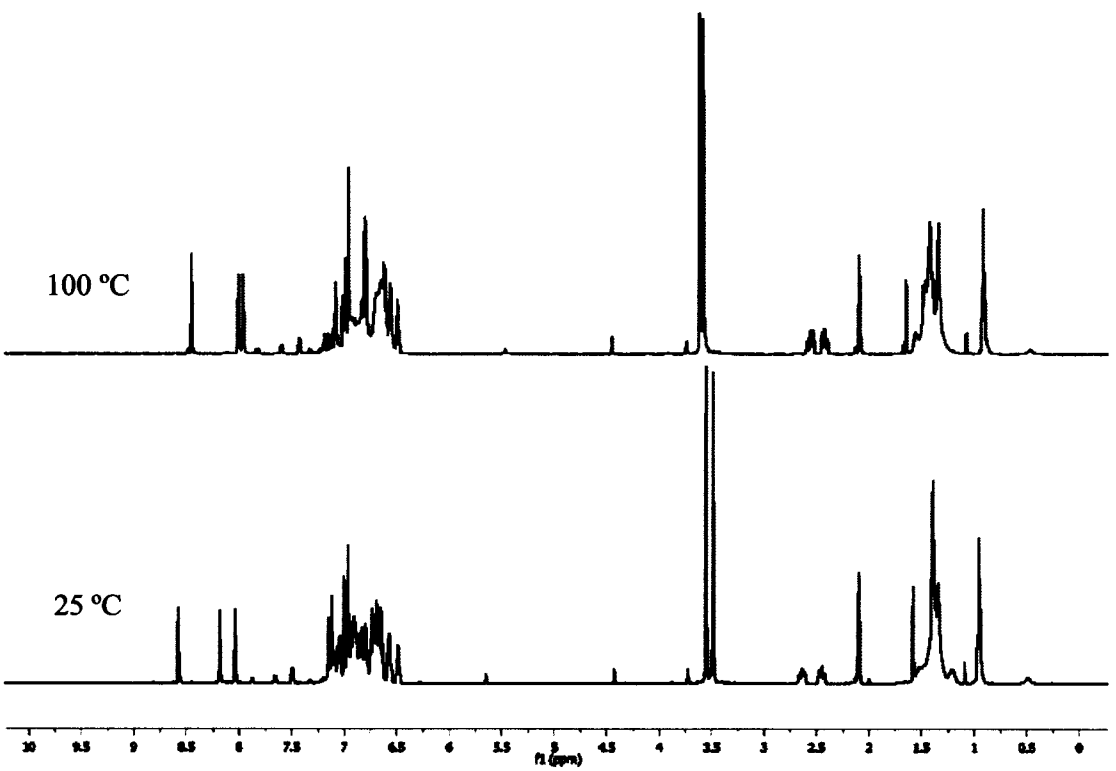
DNMR spectra of cyclophanediene **3.58** (toluene-d_8, 5-75 °C)



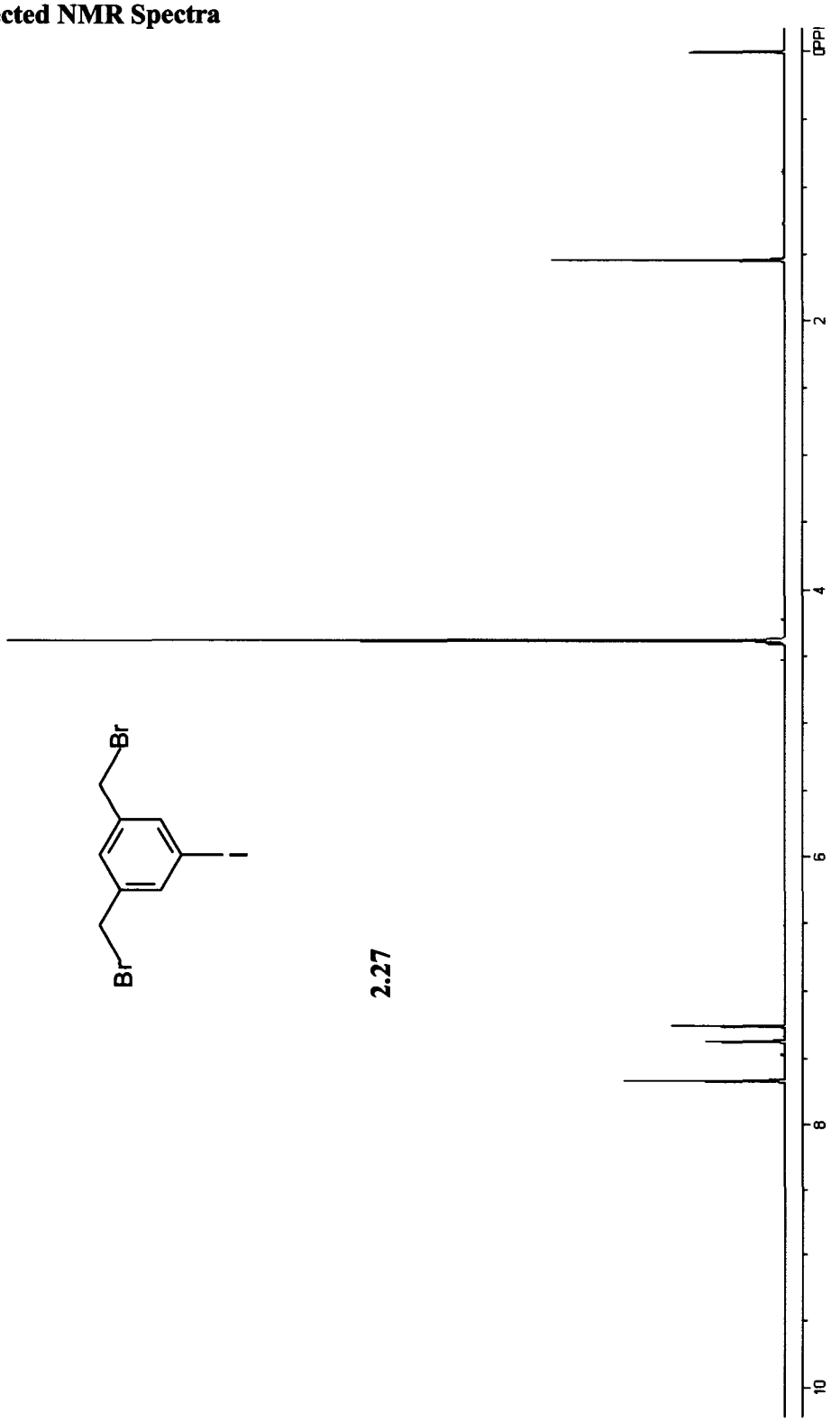
DNMR spectra of pyrenophane **3.19** (toluene-d_8, 5-75 °C)

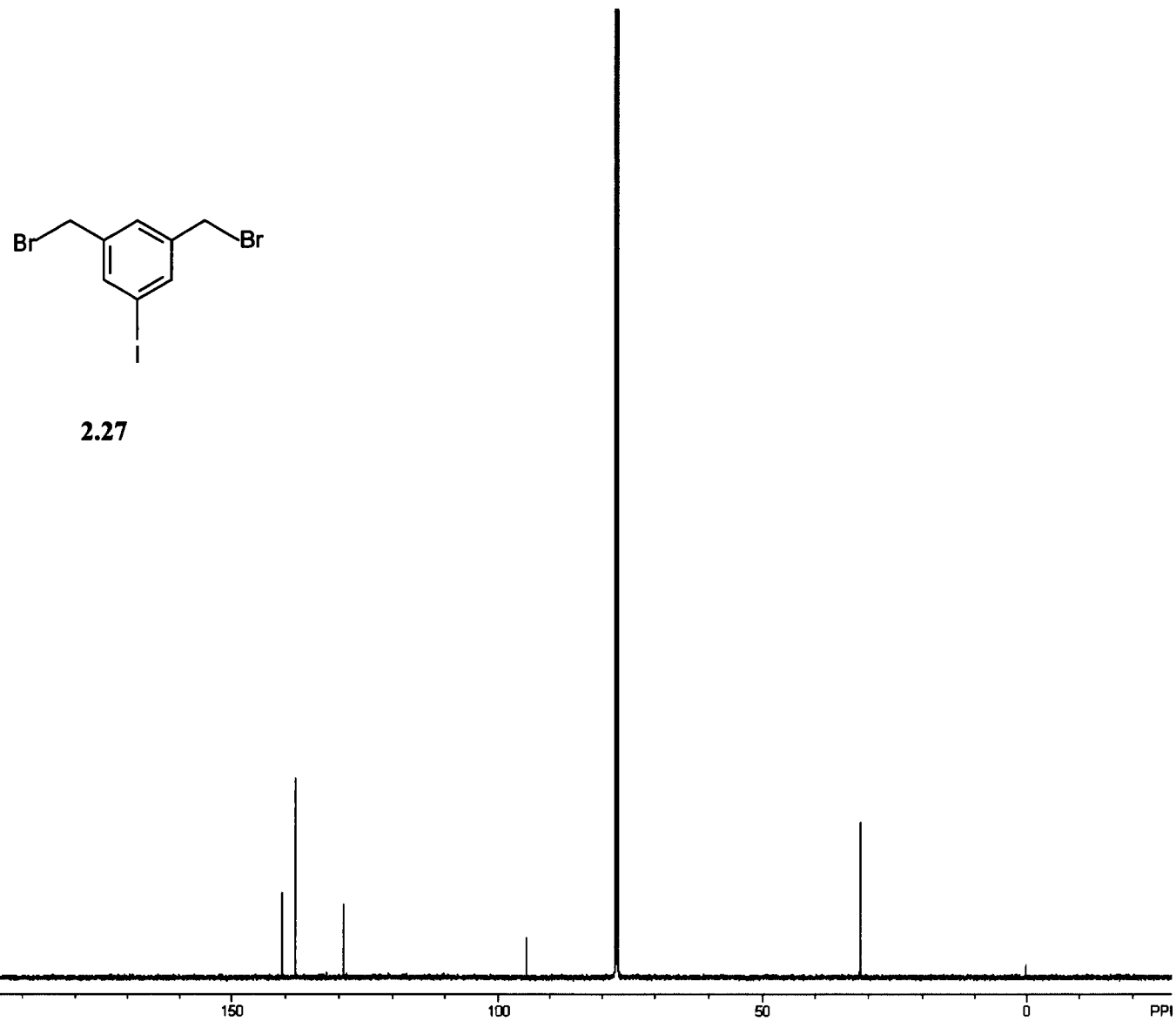


DNMR spectra of tetraester **3.63a** (toluene-d_8, 25-100 °C)

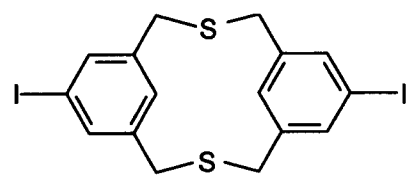


Appendix C. Selected NMR Spectra

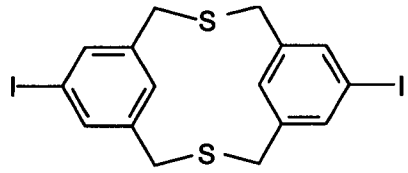




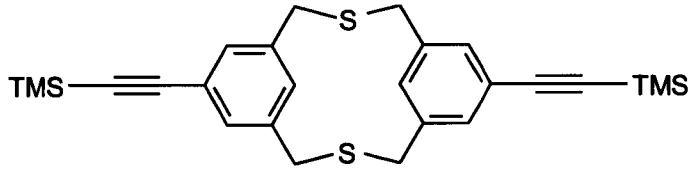
2.27



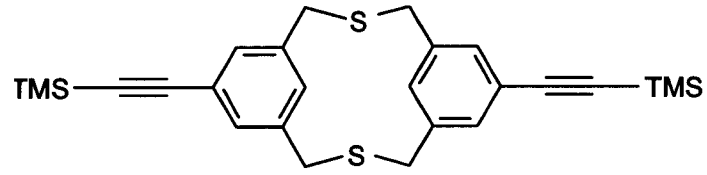
2.31



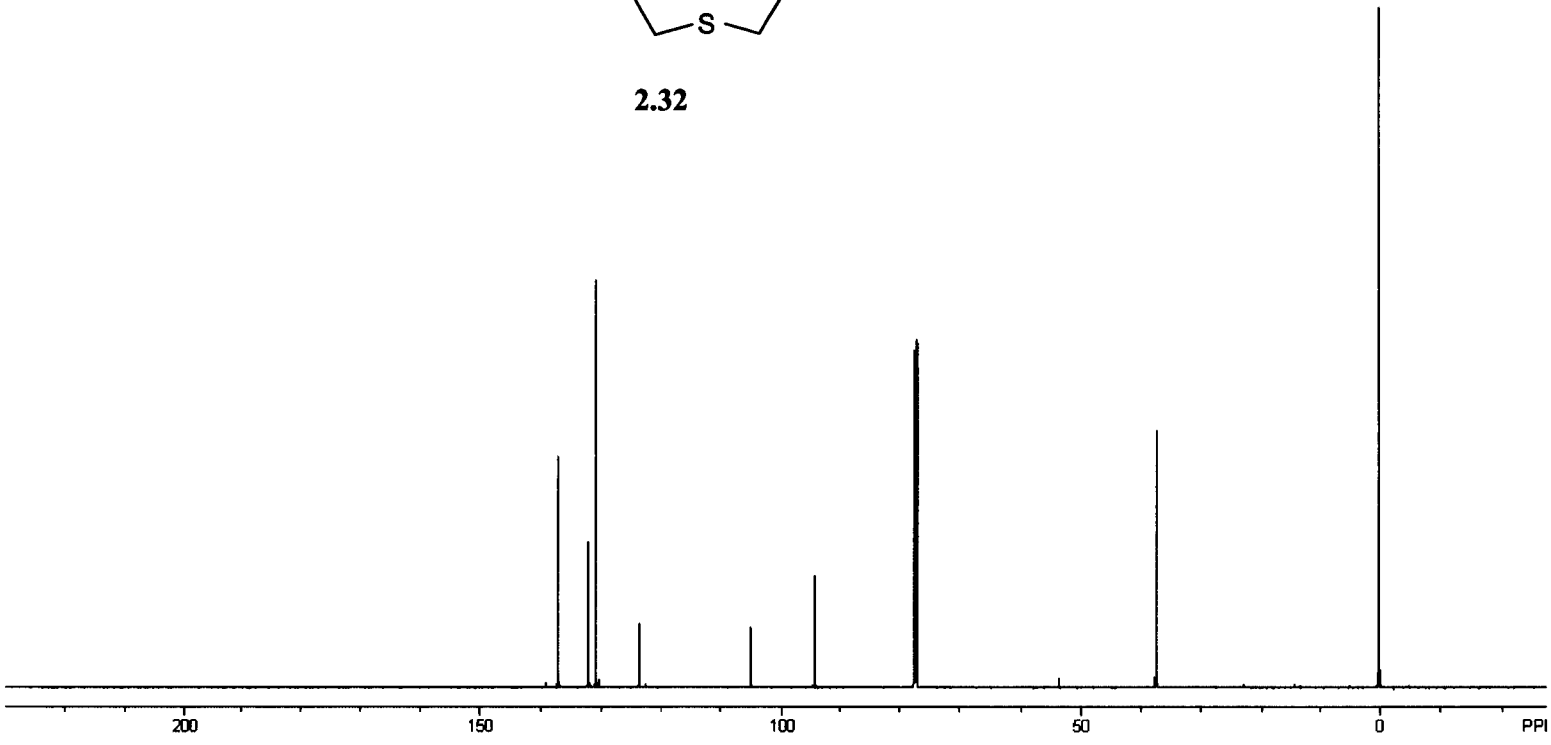
2.31

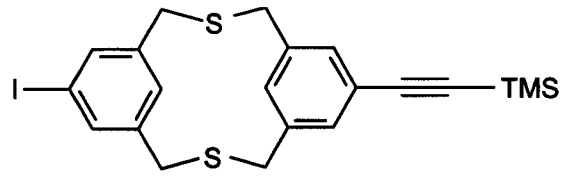


2.32



2.32





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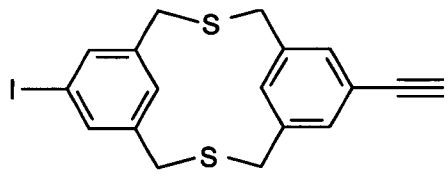
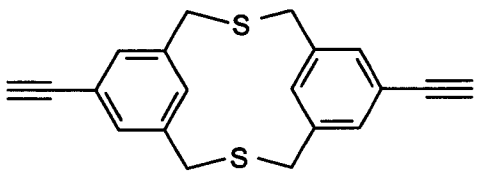
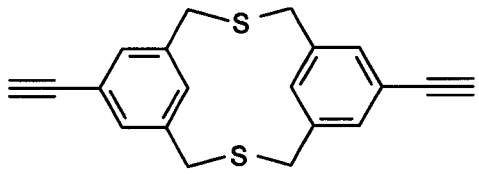


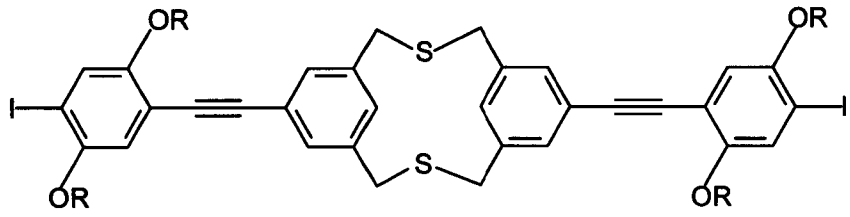
2.34



2.23



2.23



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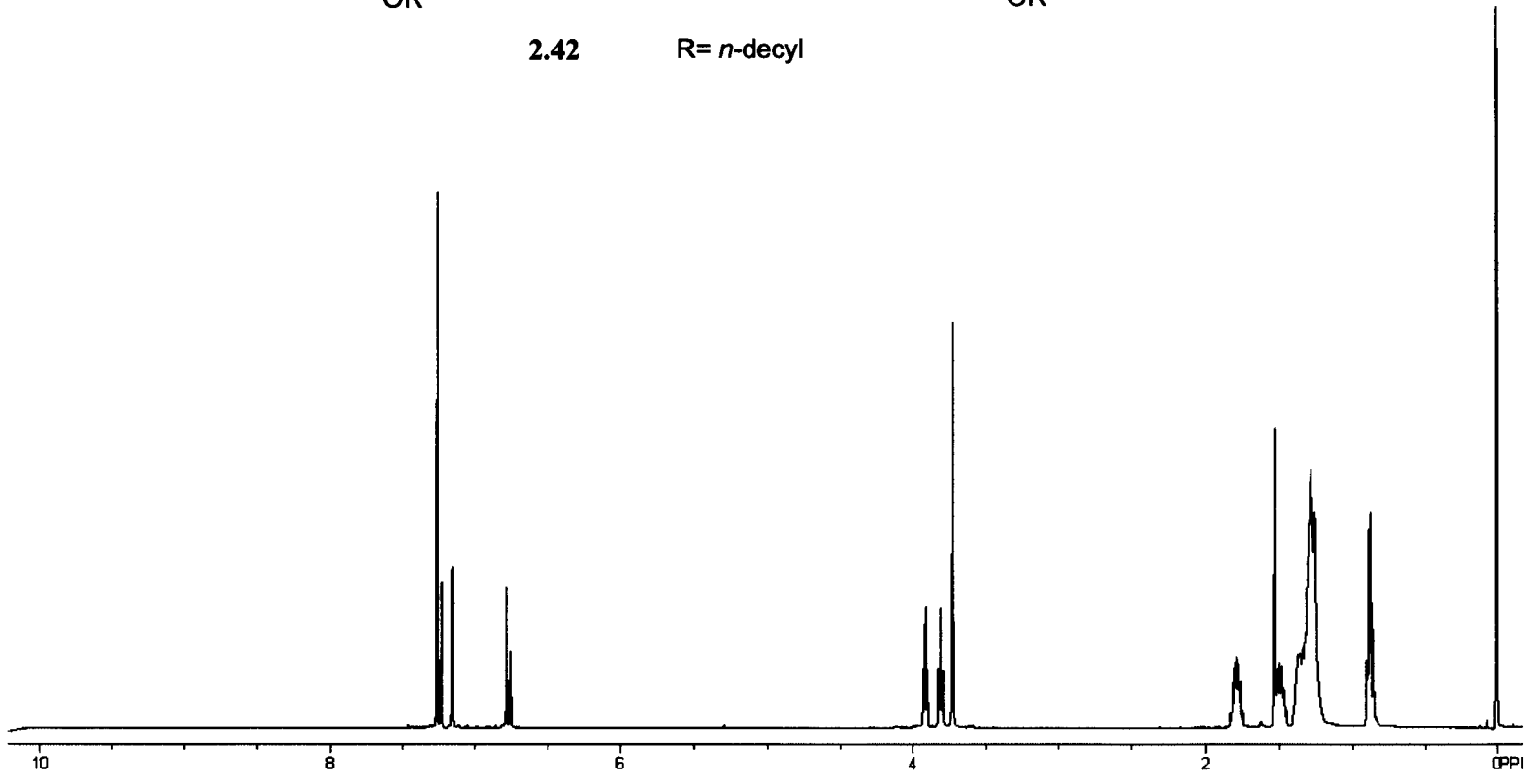
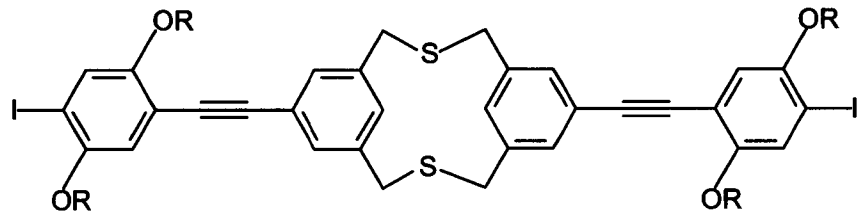
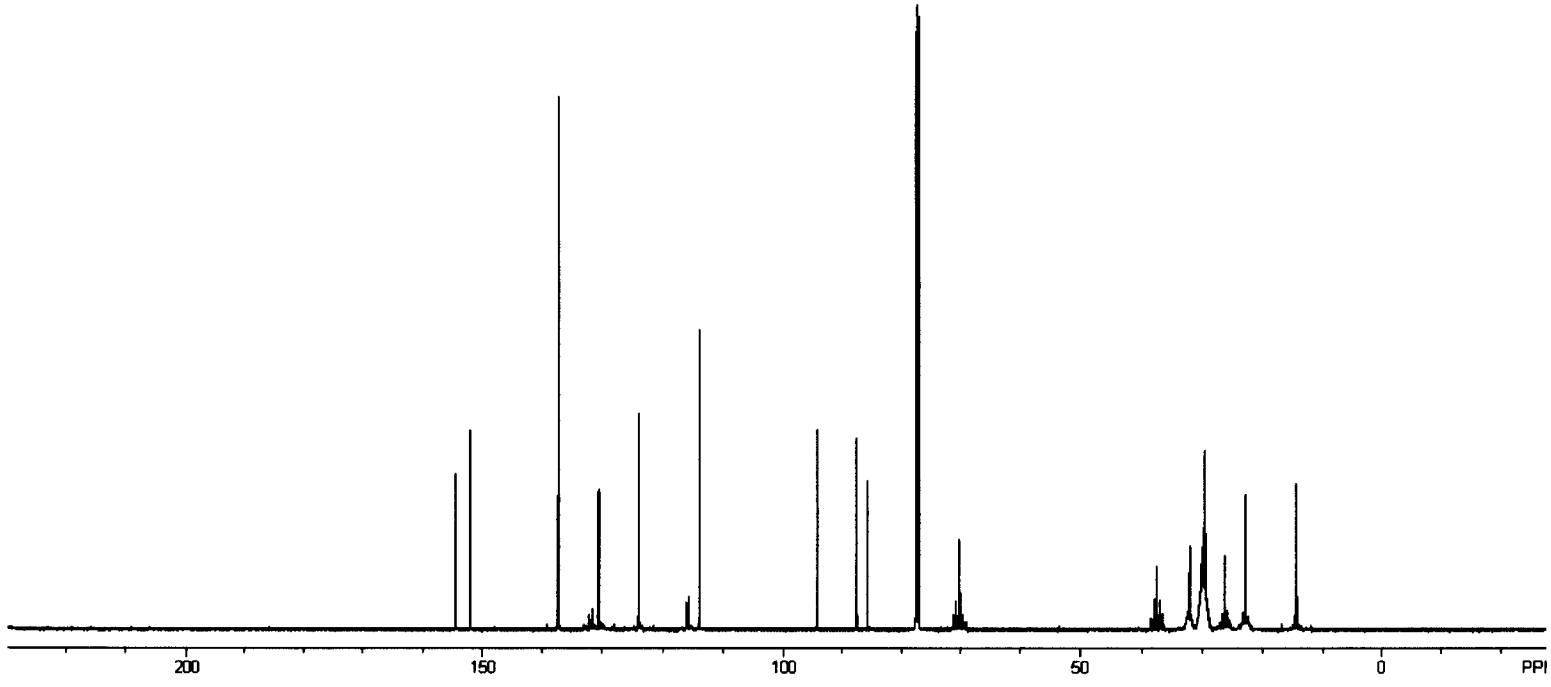
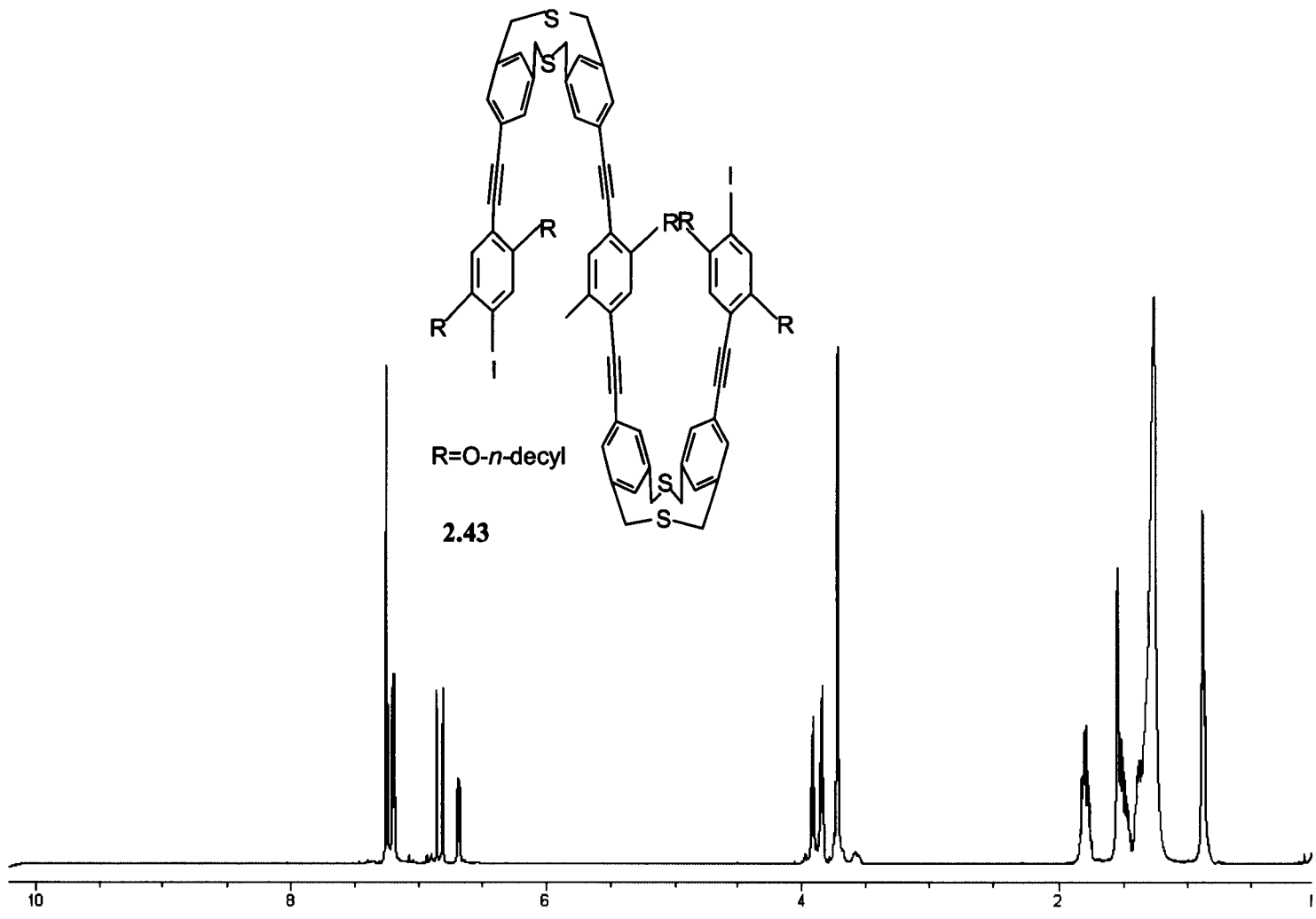
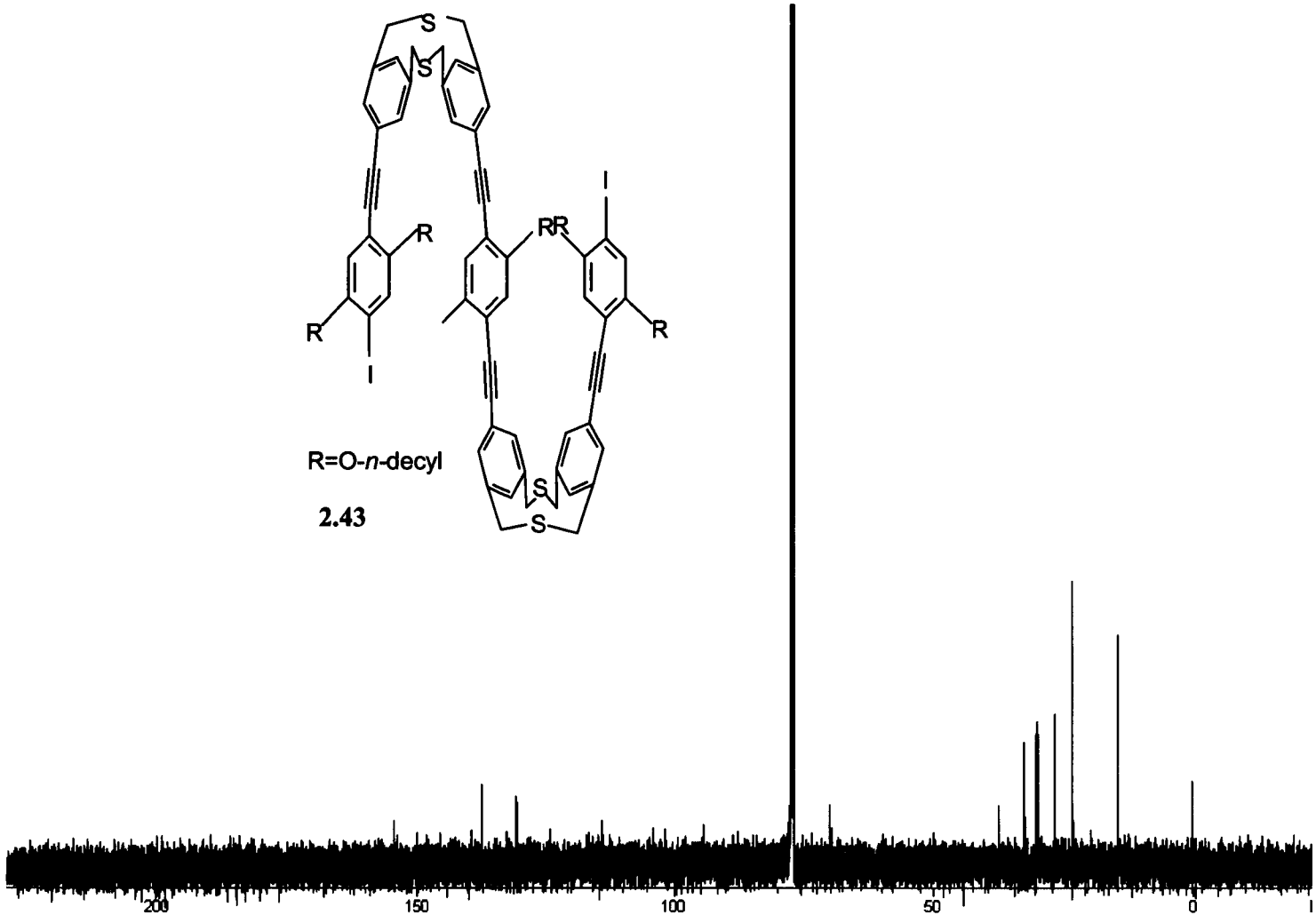


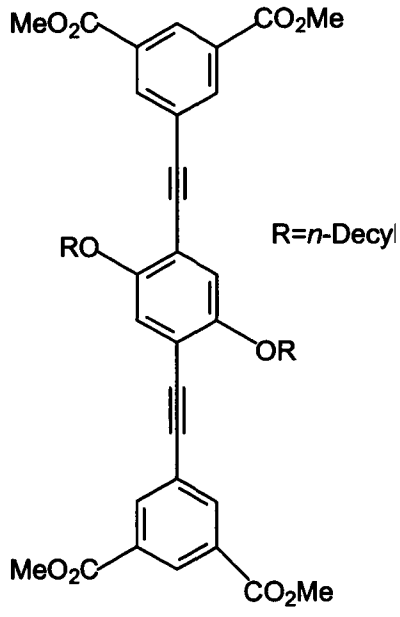


2.42 R= *n*-decyl

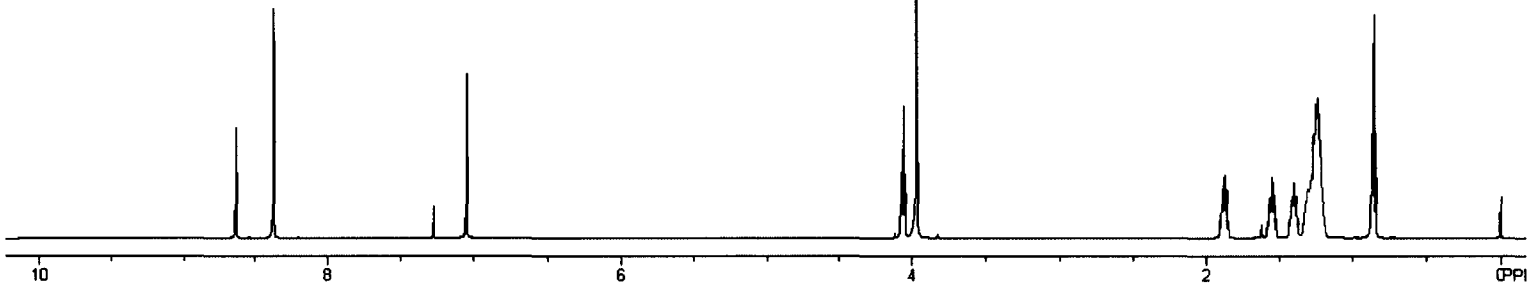


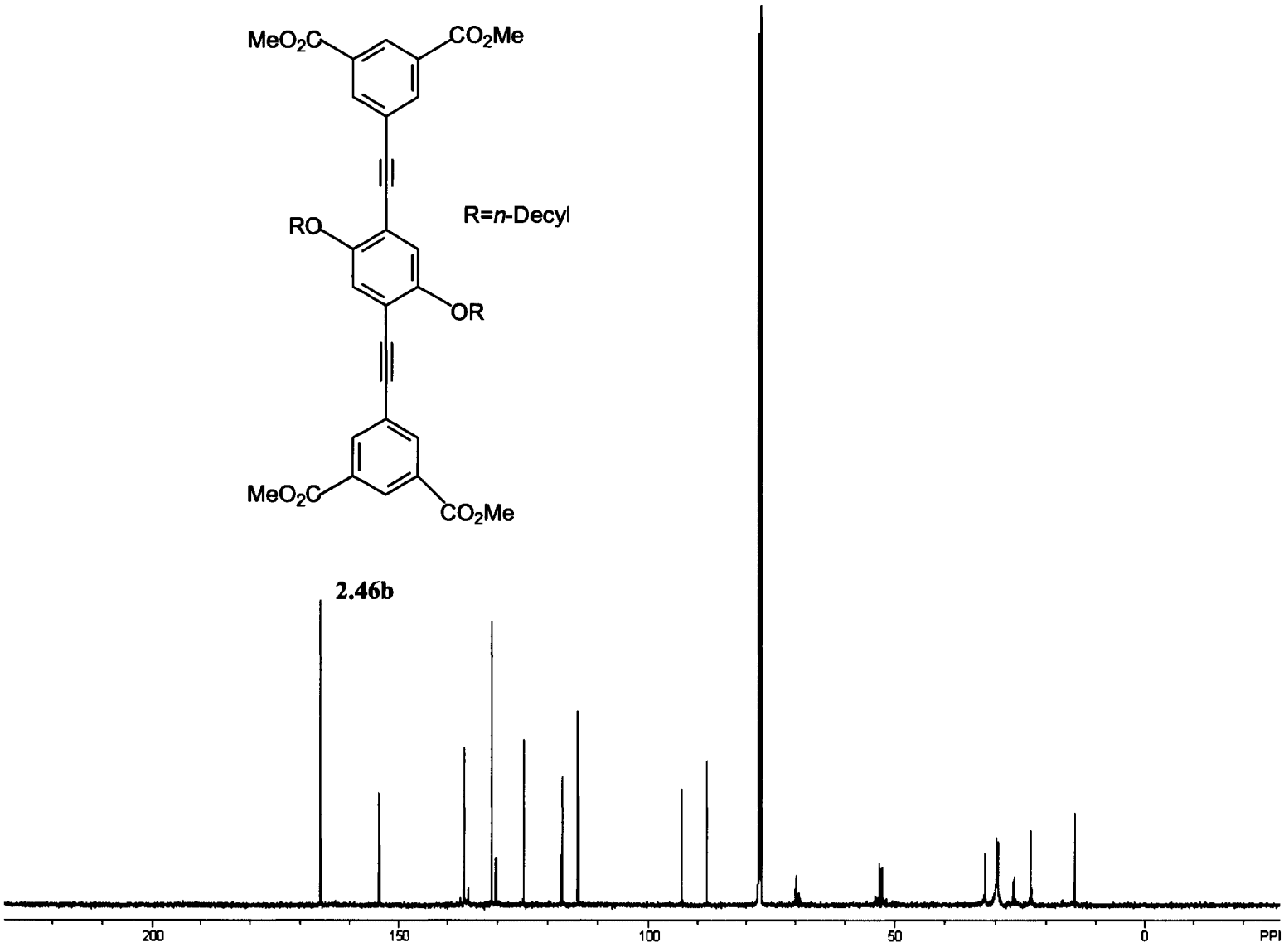

S
S
R
R
R
I
R
I
R
S
S
R=O-n-decyl
2.43
10
8
6
4
2
1

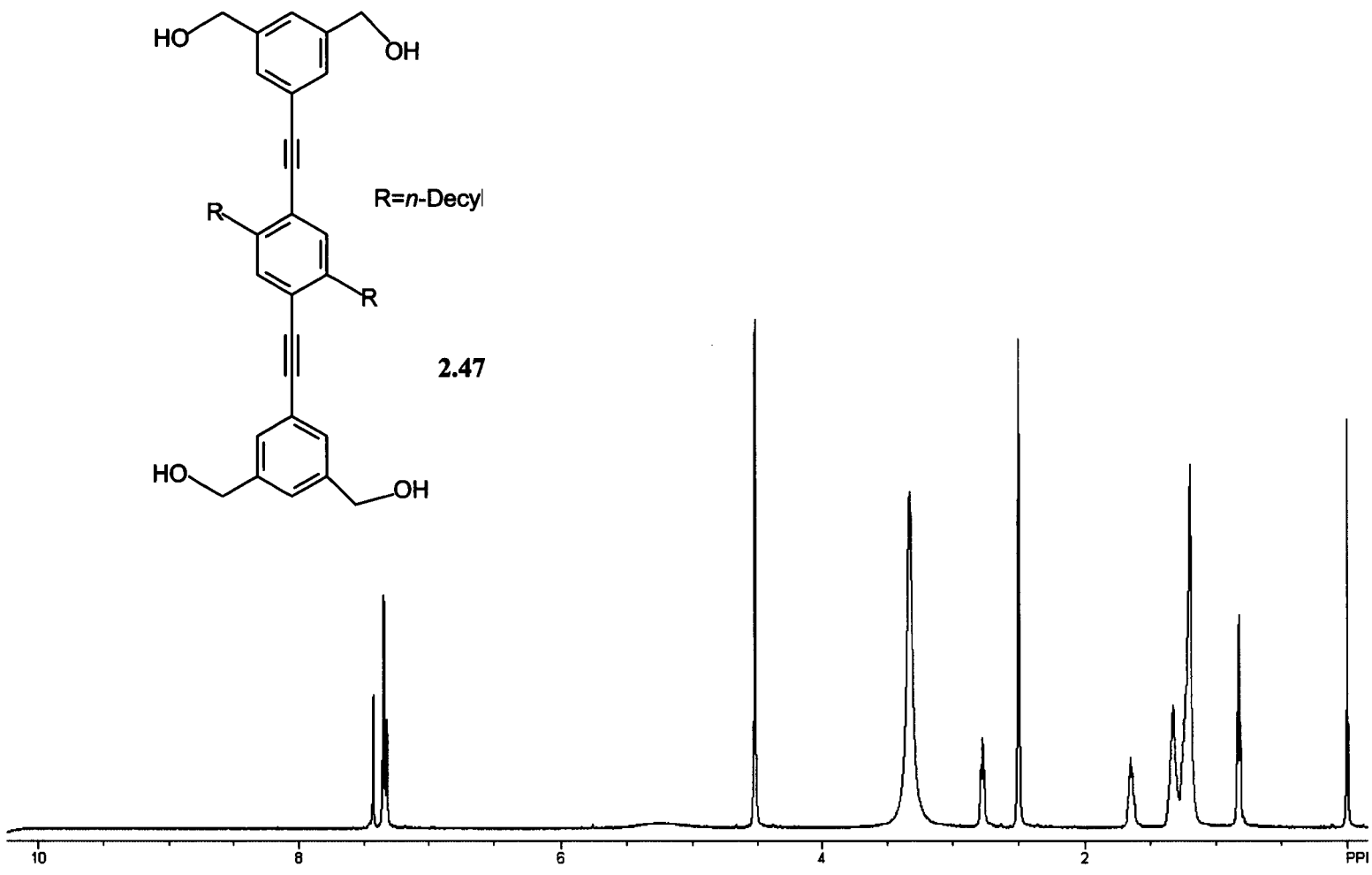

S
S
R
R
R
I
RR
I
R
S
S
R=O-n-decyl
2.43
200
150
100
50
0

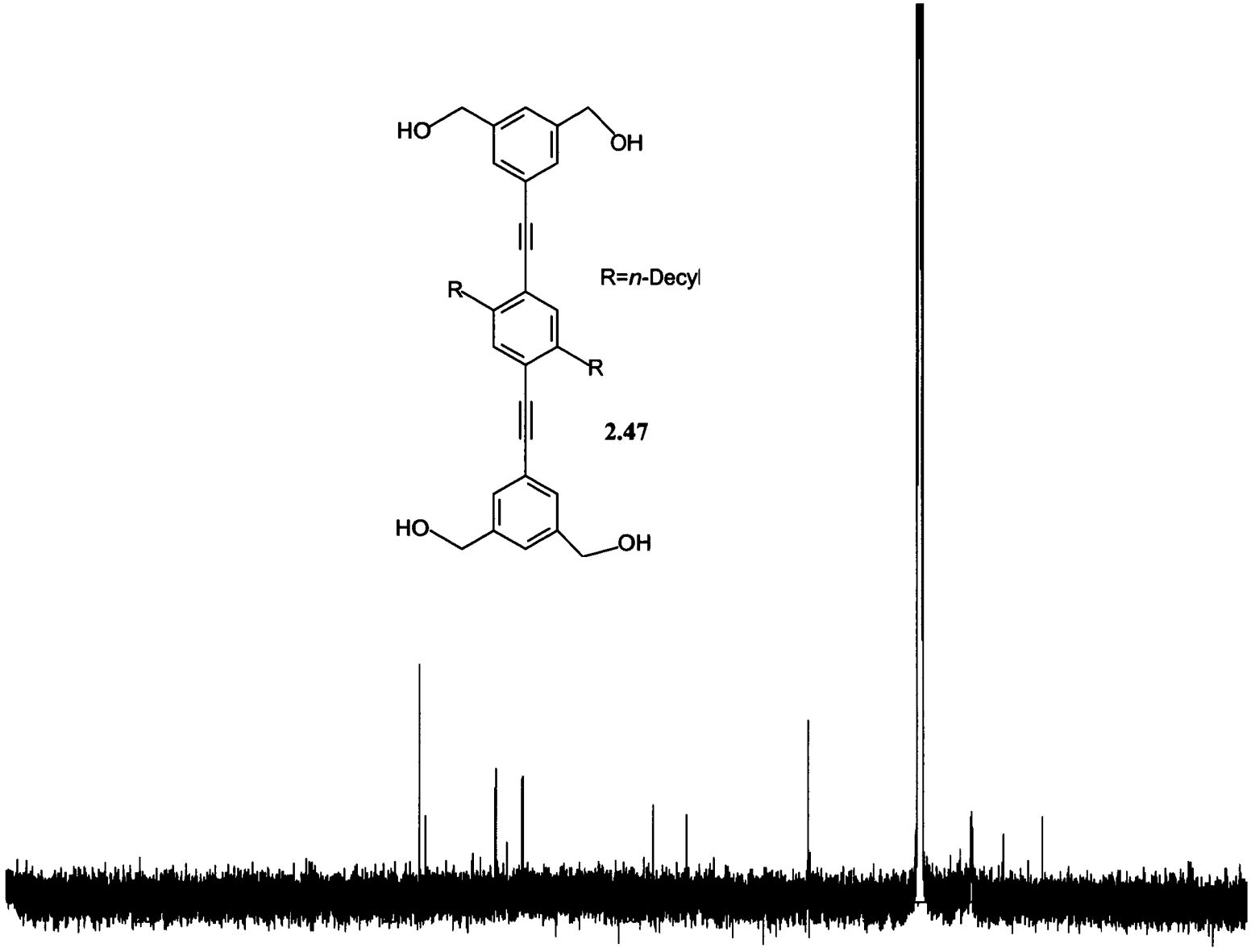


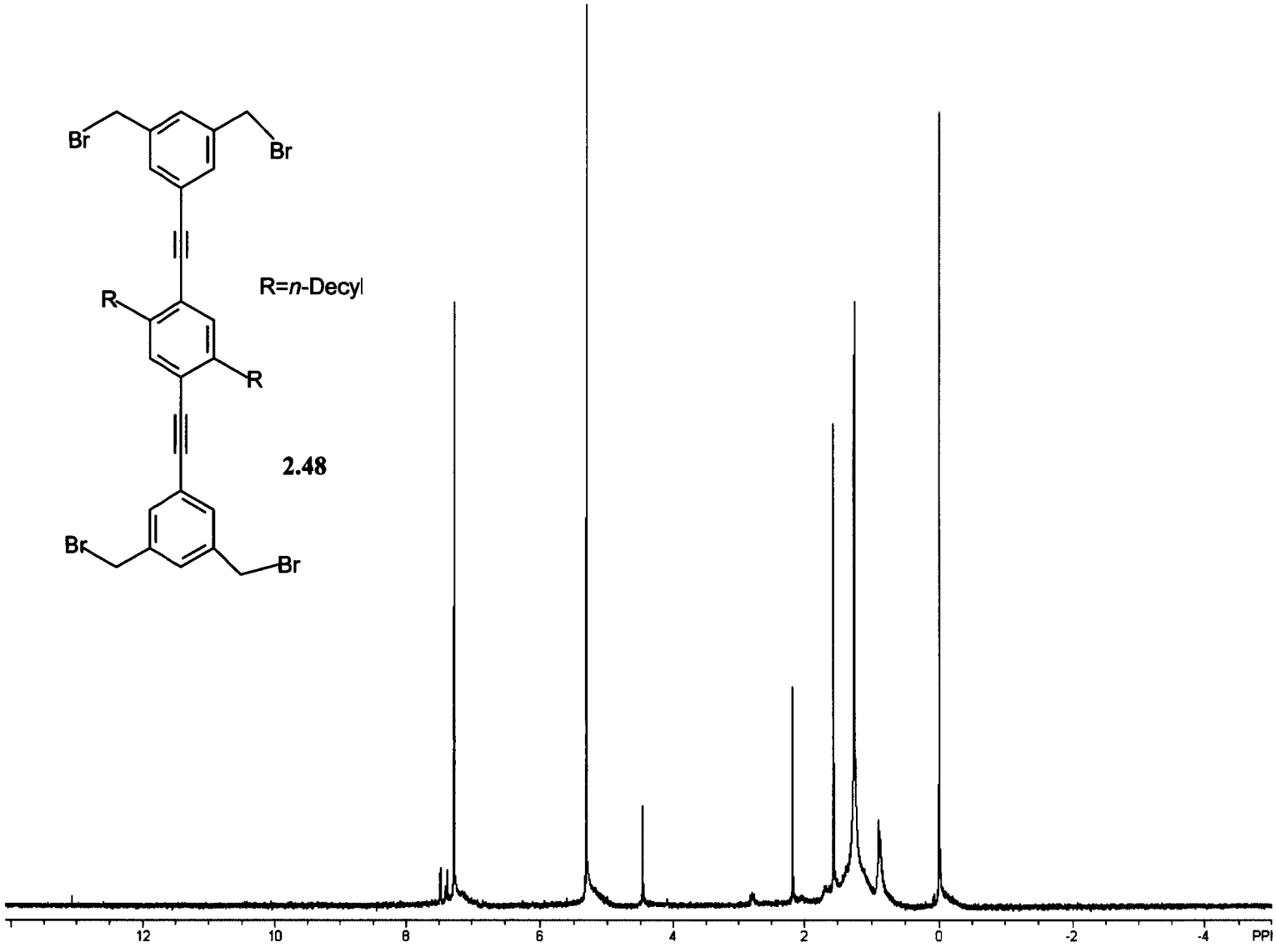
2.46b

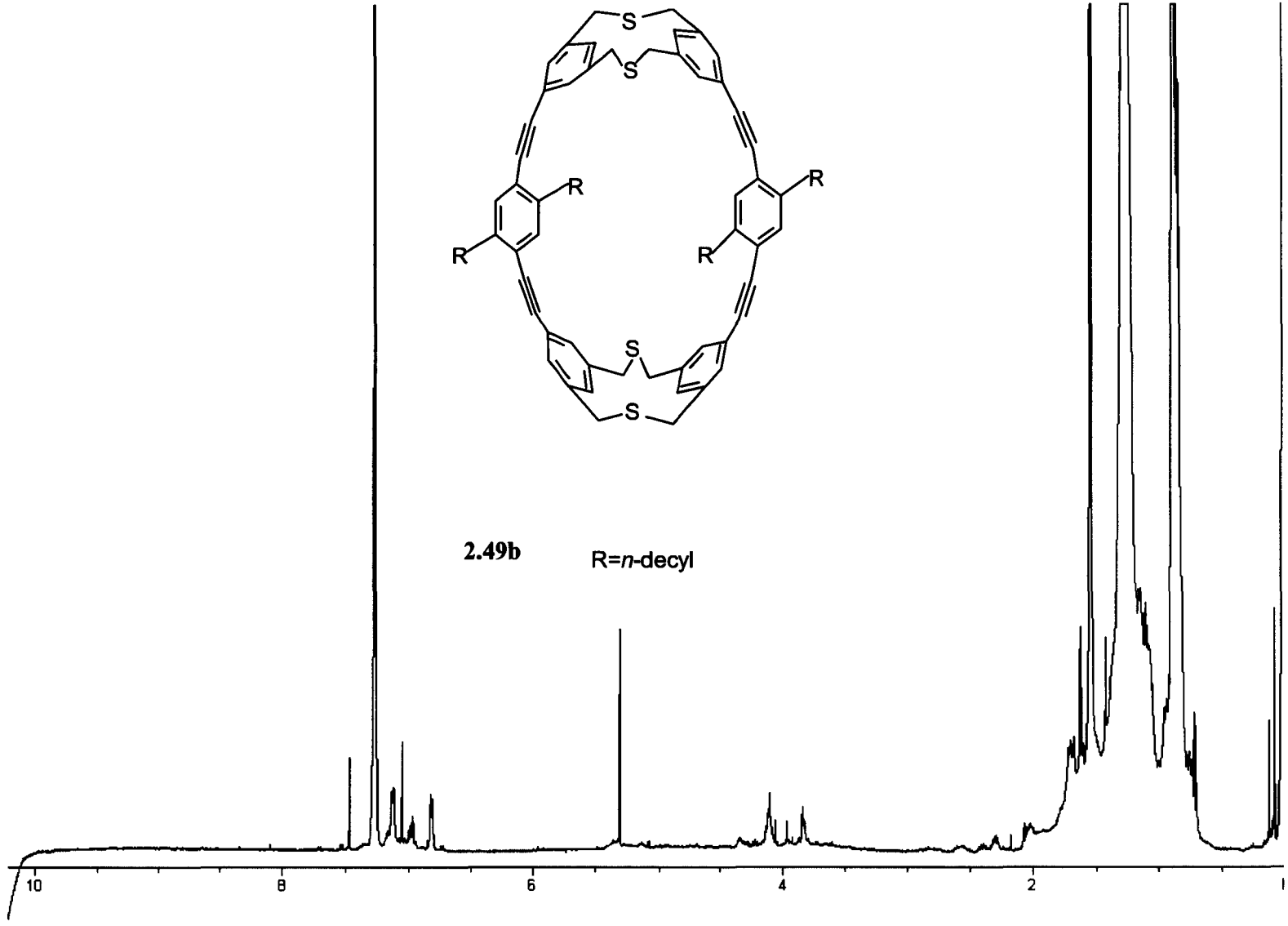


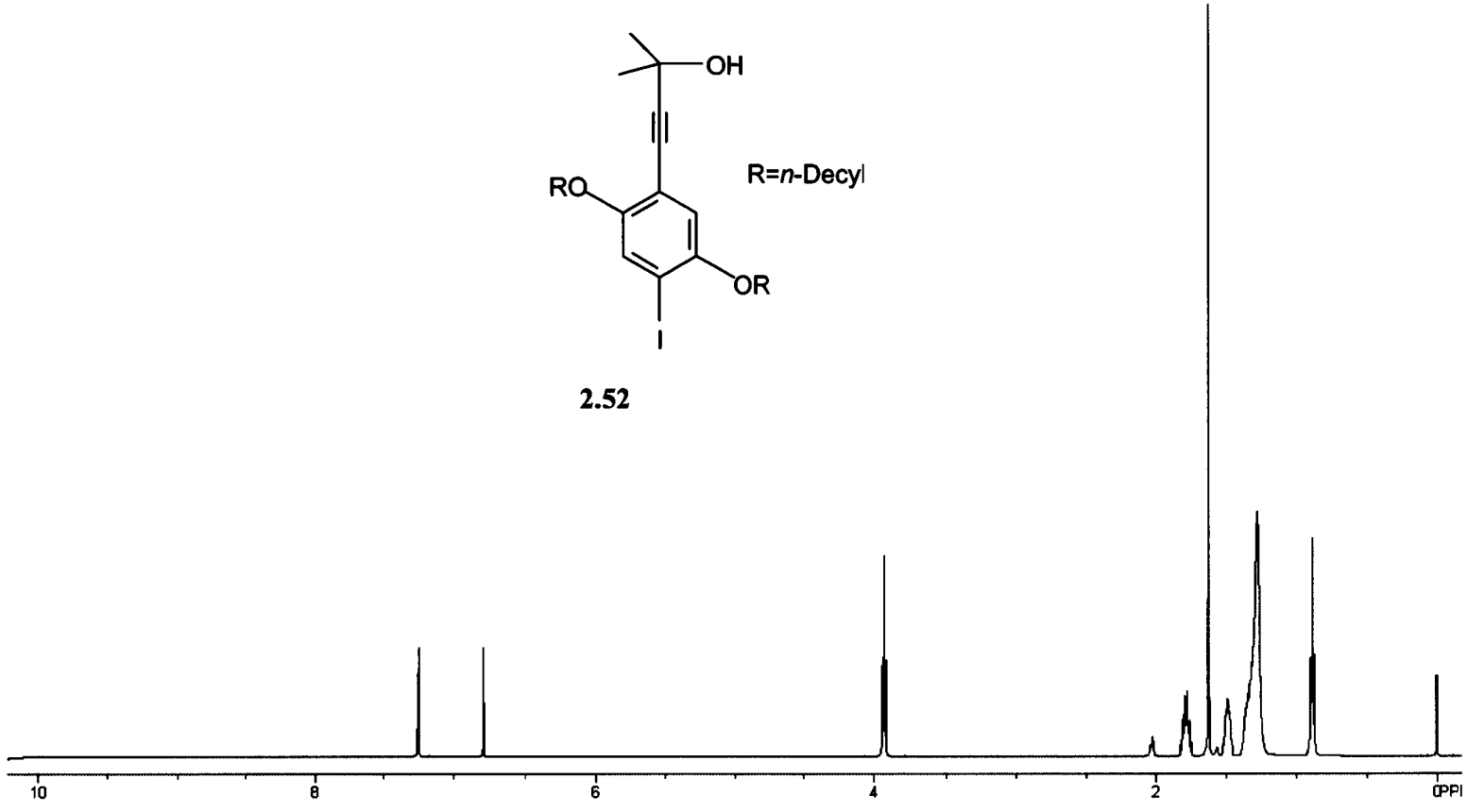

MeO2C
CO2Me
RO
R=n-Decyl
OR
MeO2C
CO2Me
2.46b
200
150
100
50
0
PPI


HO
OH
R=n-Decyl
R
R
HO
OH
2.47
10
8
6
4
2
PPI


HO
OH
R=n-Decyl
R
R
2.47
HO
OH


Br
Br
R=n-Decyl
R
R
2.48
Br
Br
12
10
8
6
4
2
0
-2
-4
PPI


S
S
R
R
R
R
S
S
2.49b
R=n-decyl
10
8
6
4
2
1



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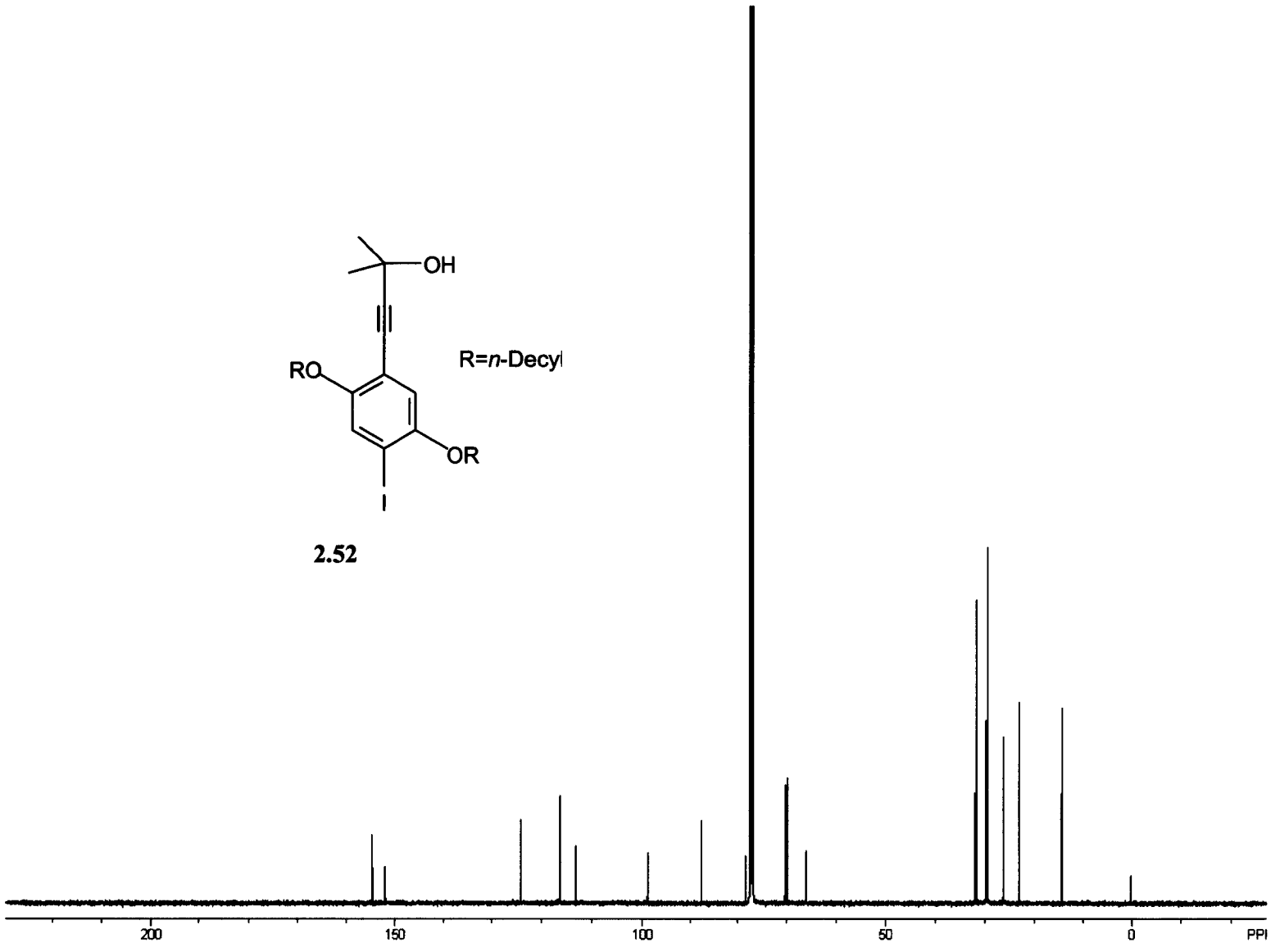
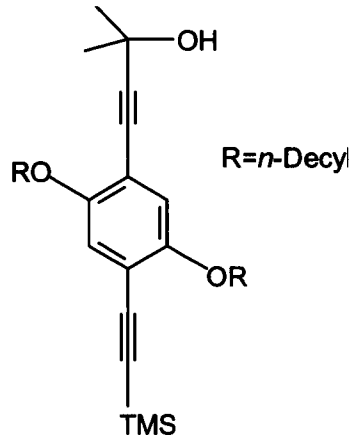


2.52



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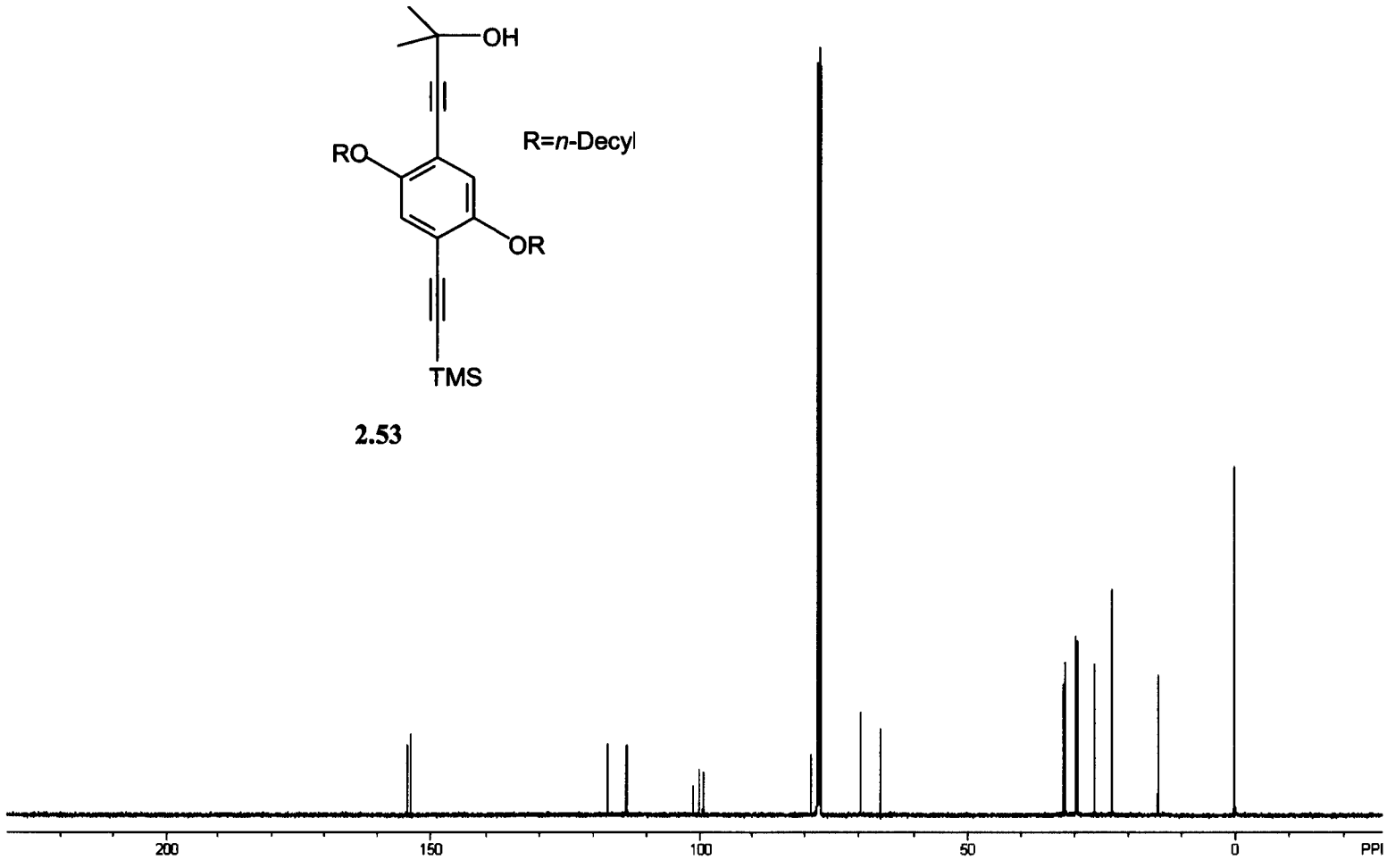

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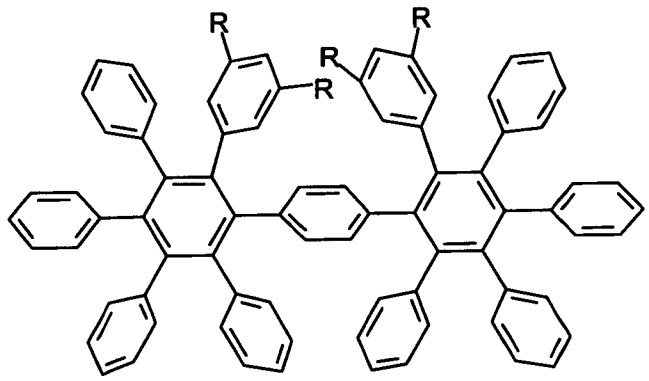
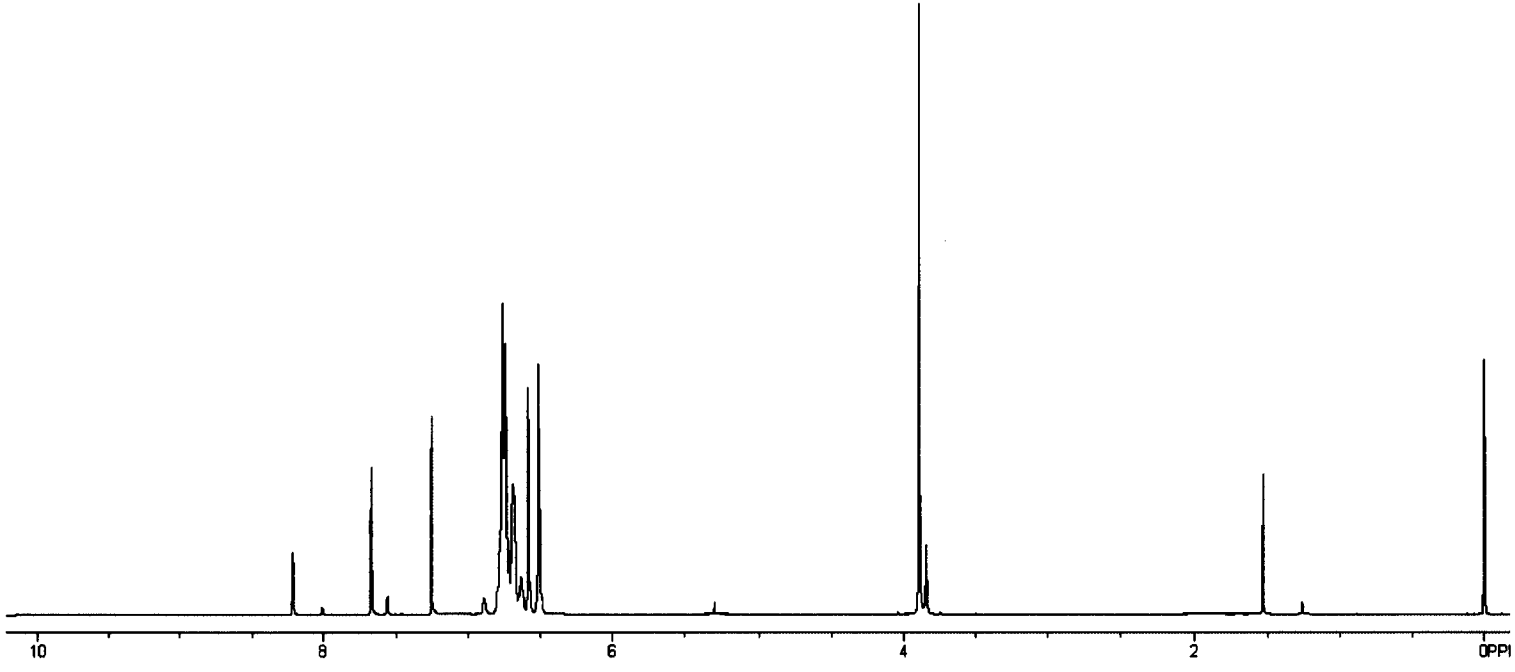
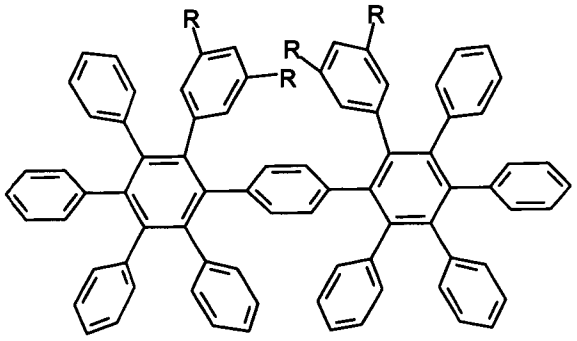
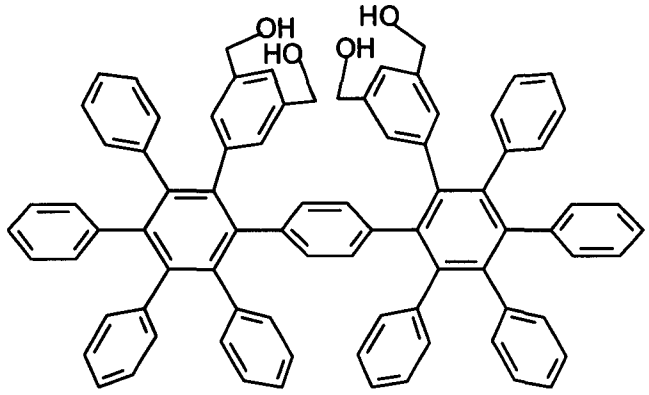


3.32 R=CO_2Me





3.32 R=CO_2Me



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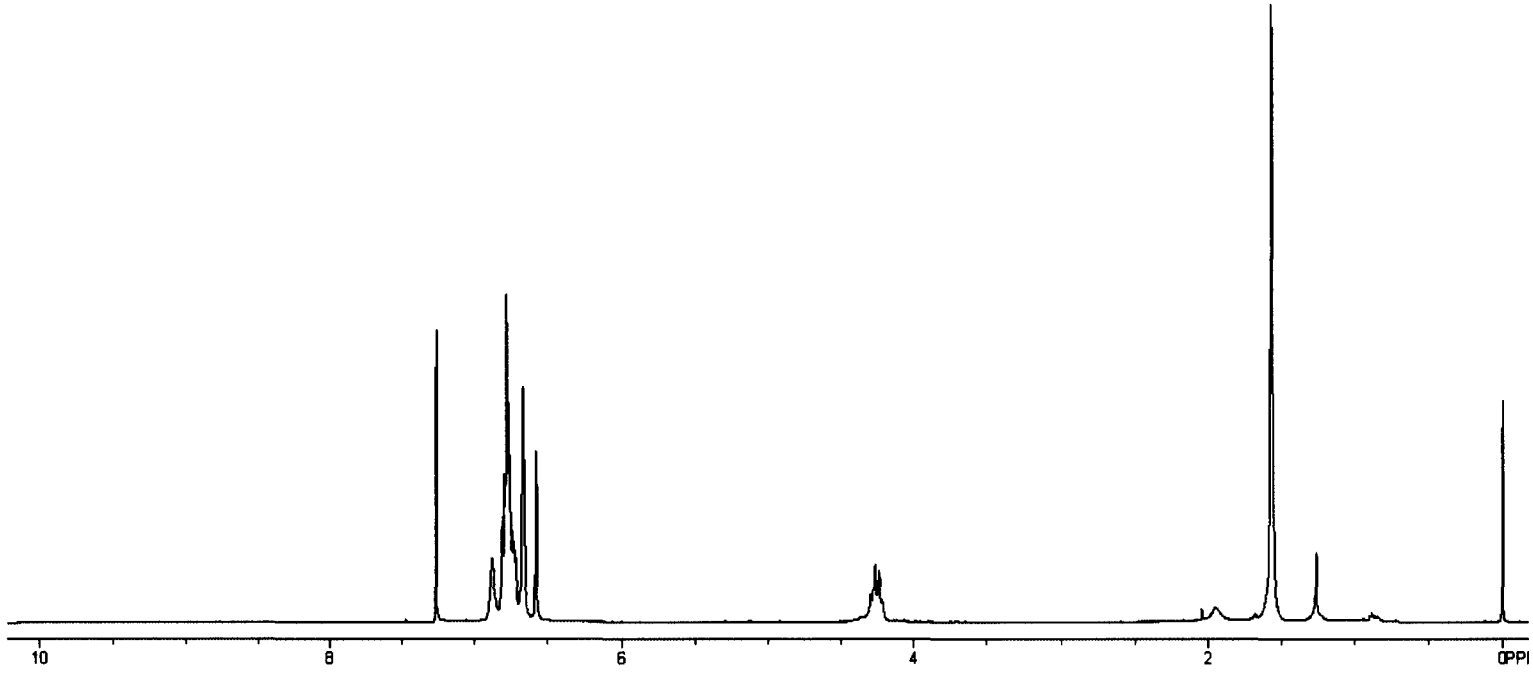

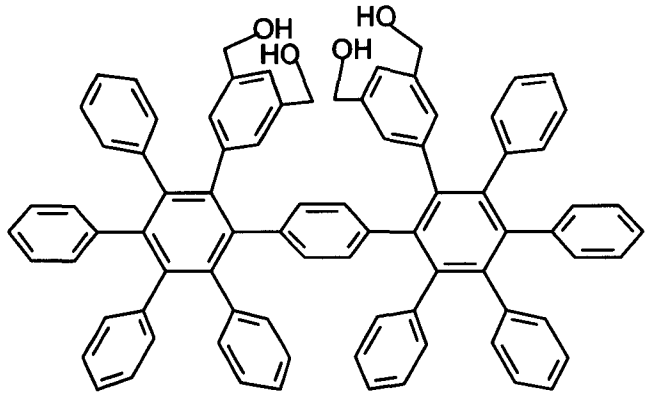

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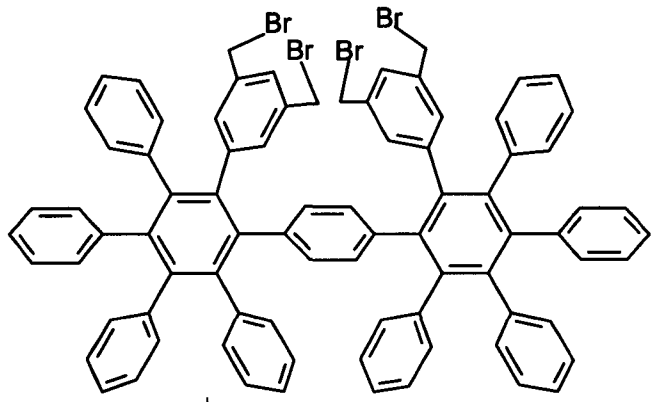

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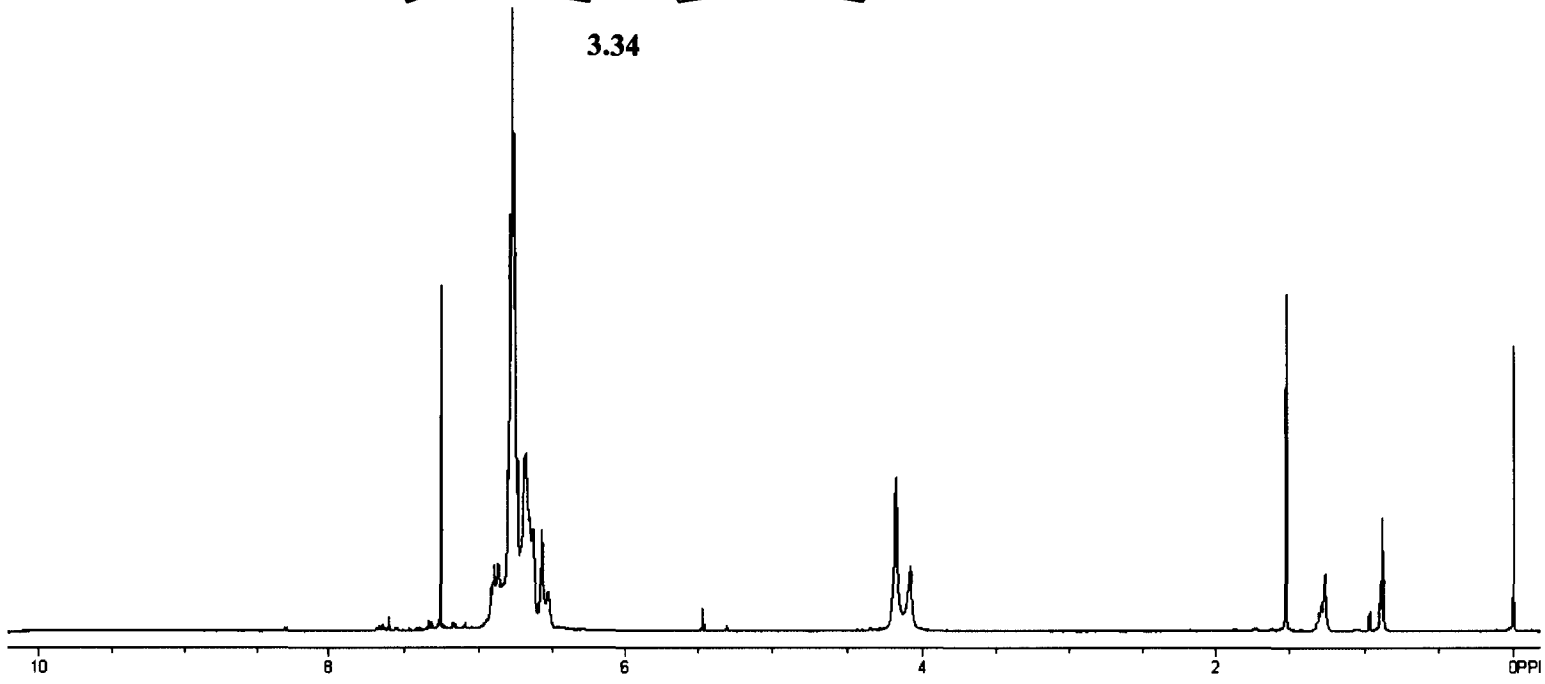

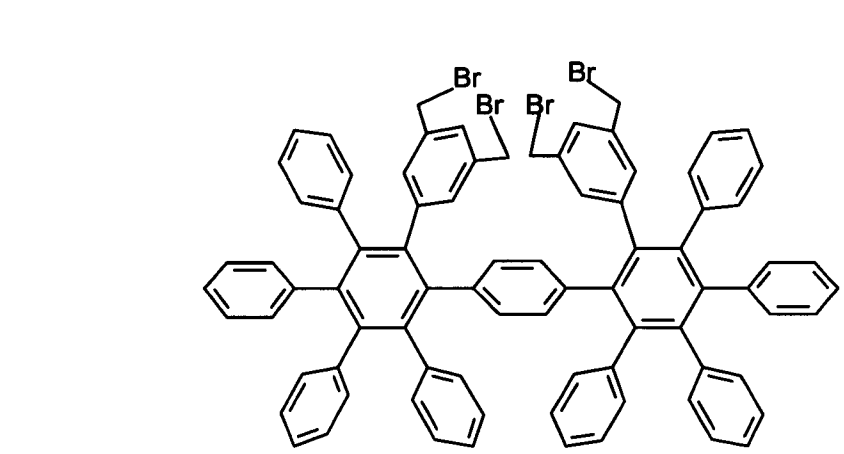

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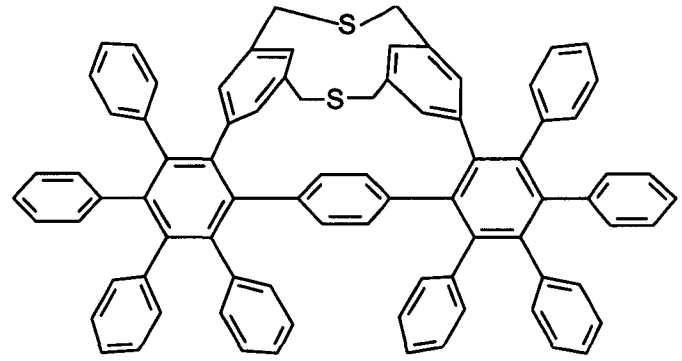

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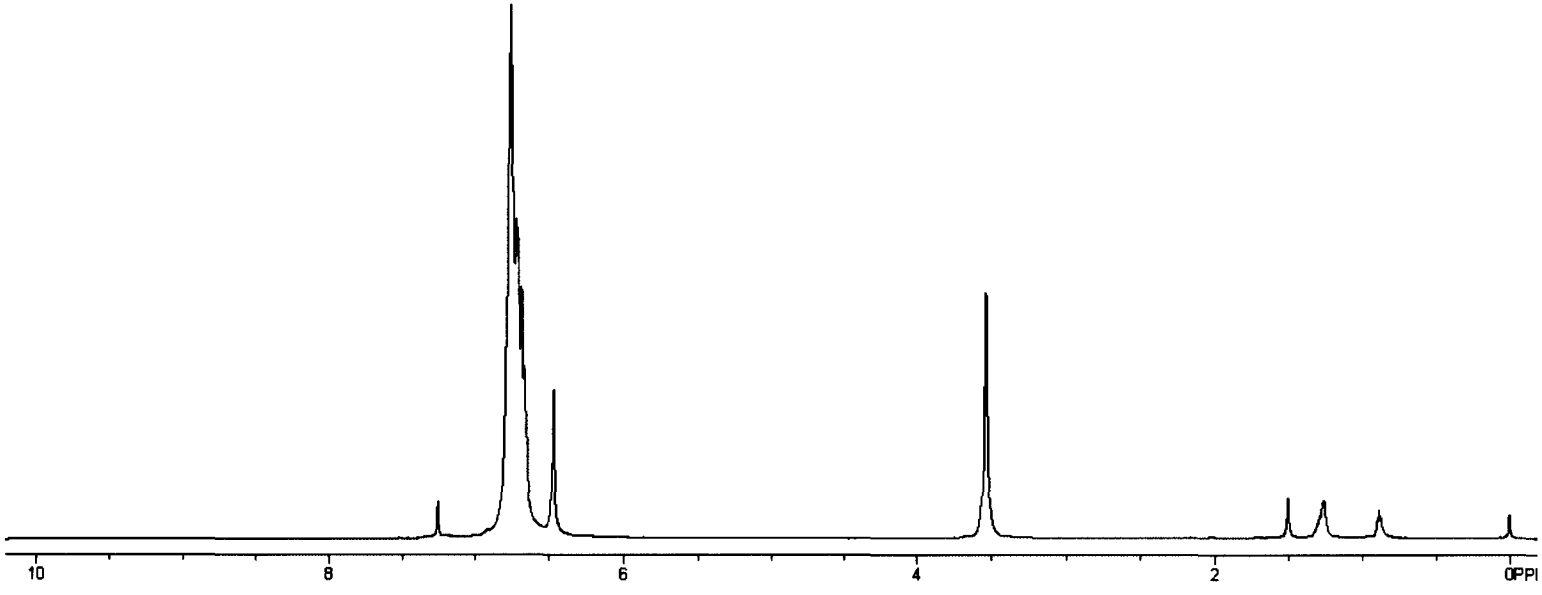

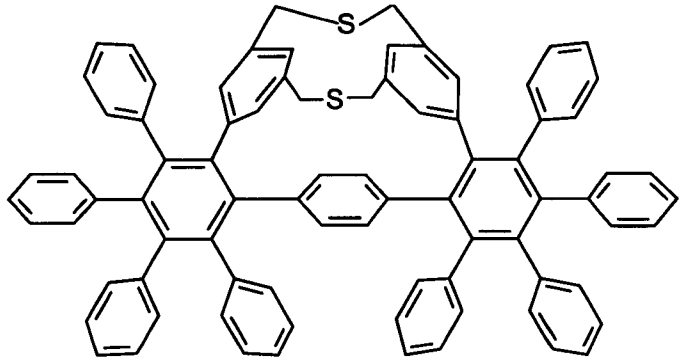

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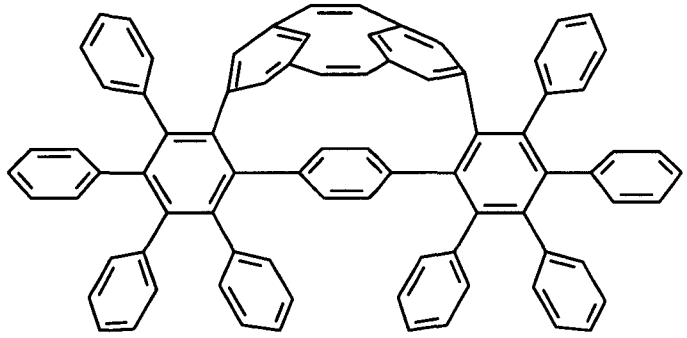

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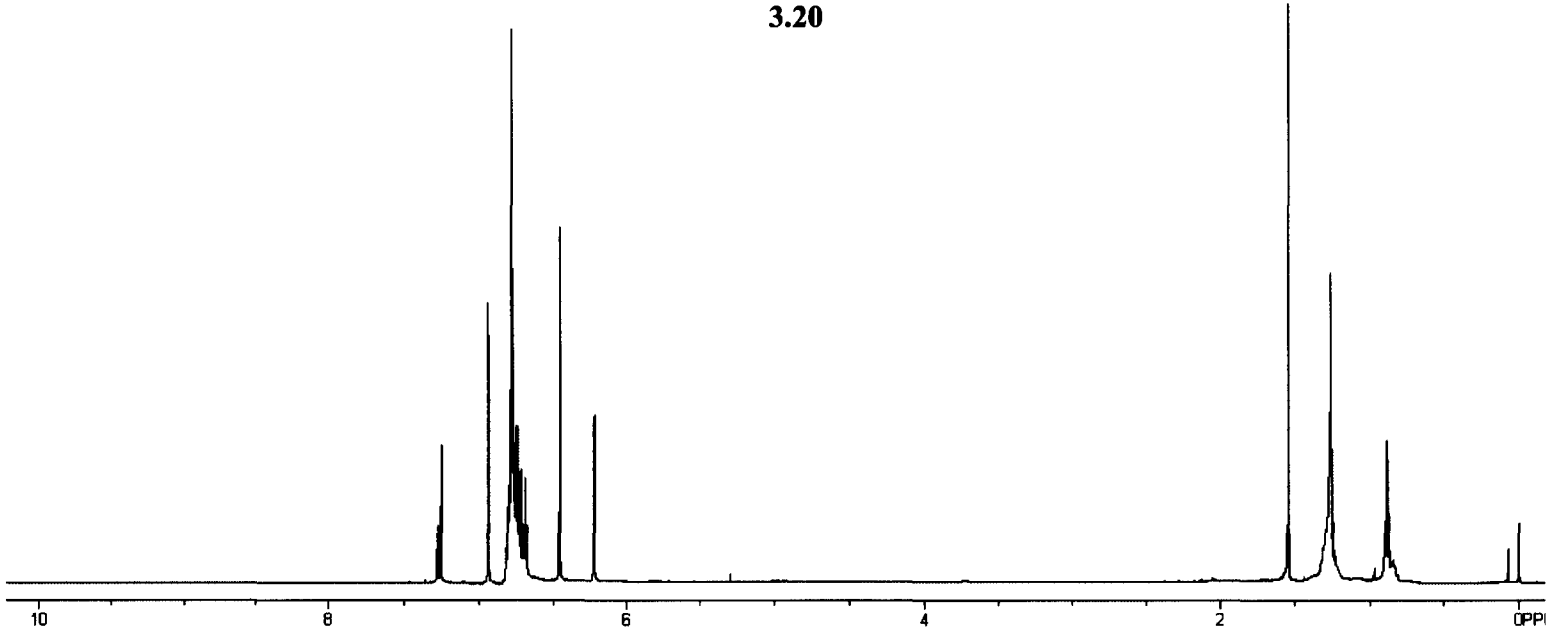

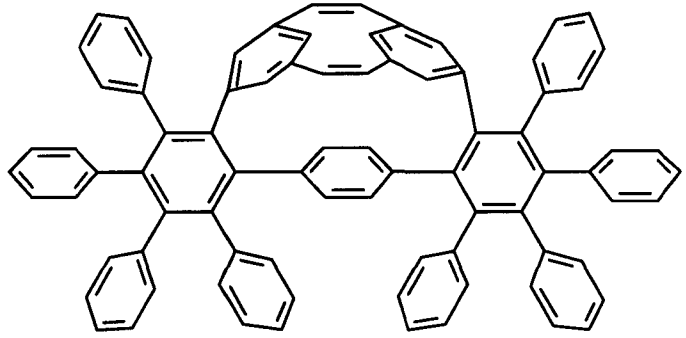

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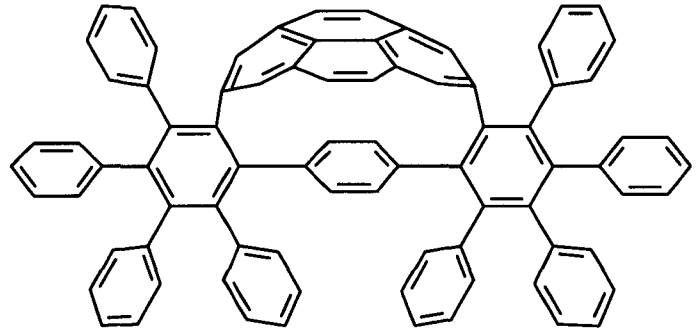

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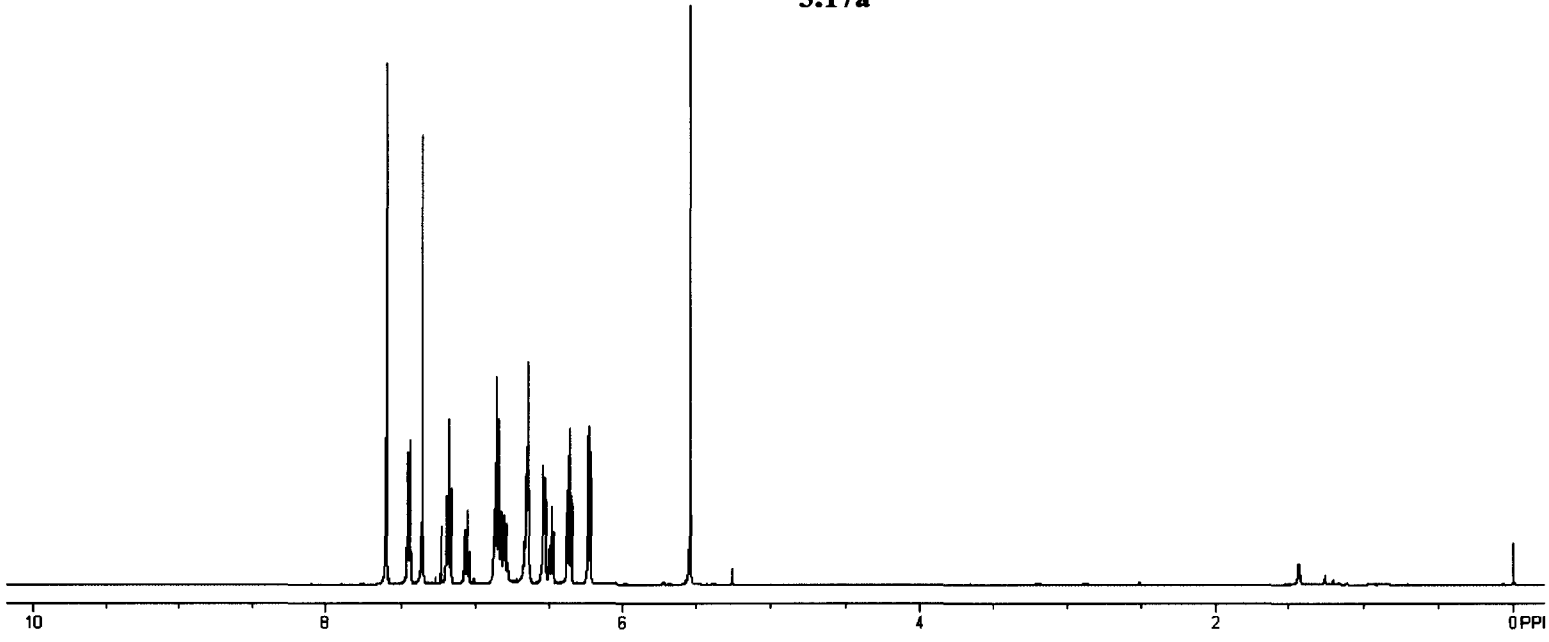

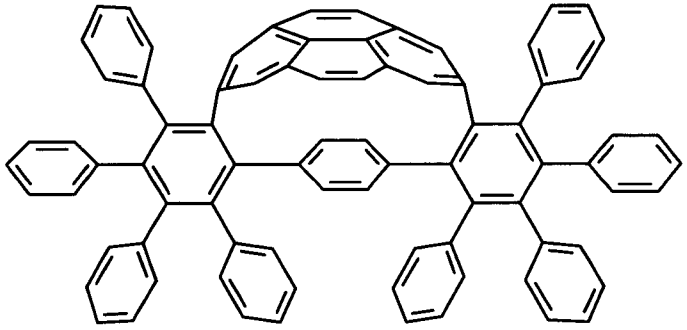

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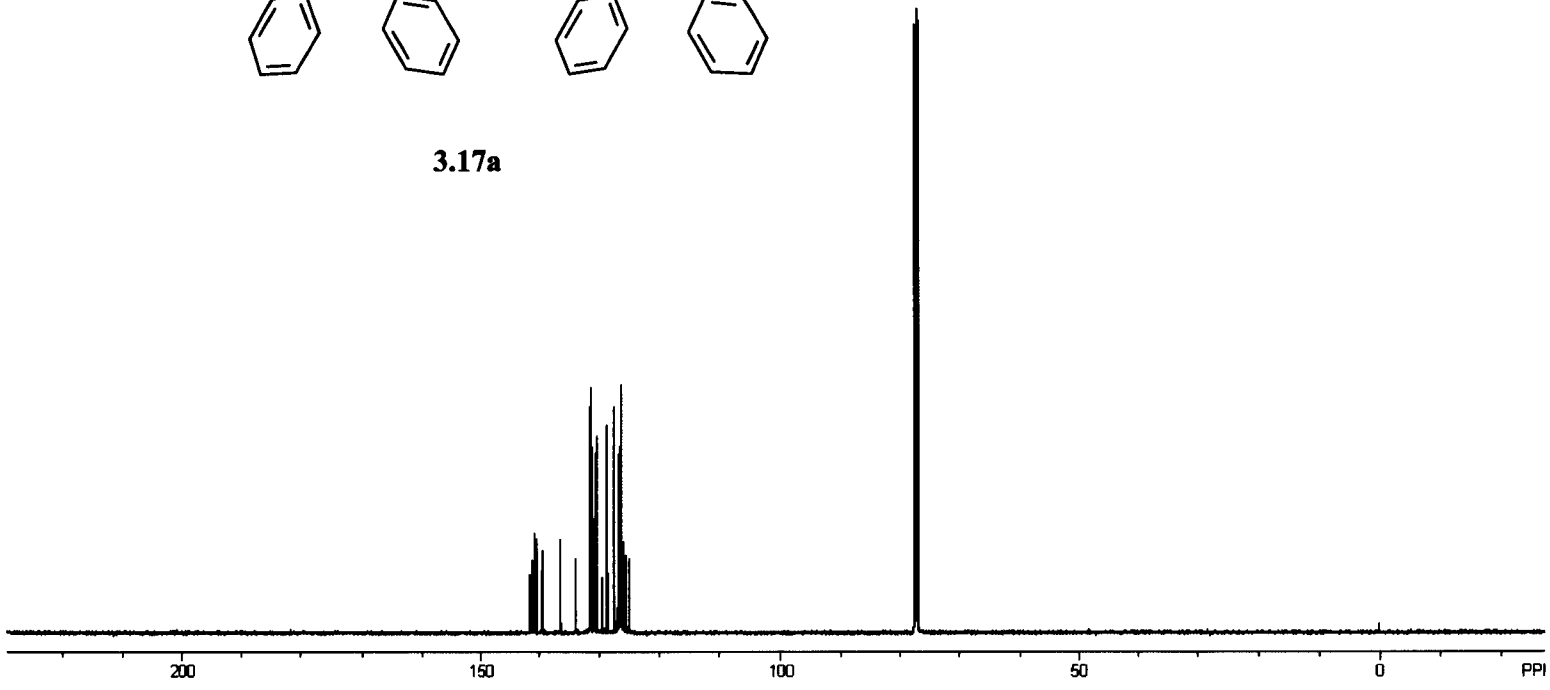
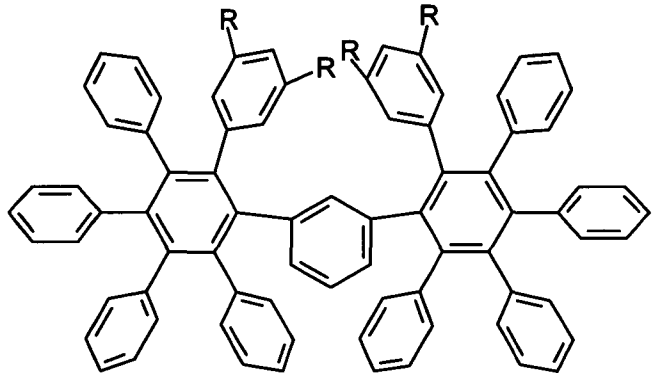
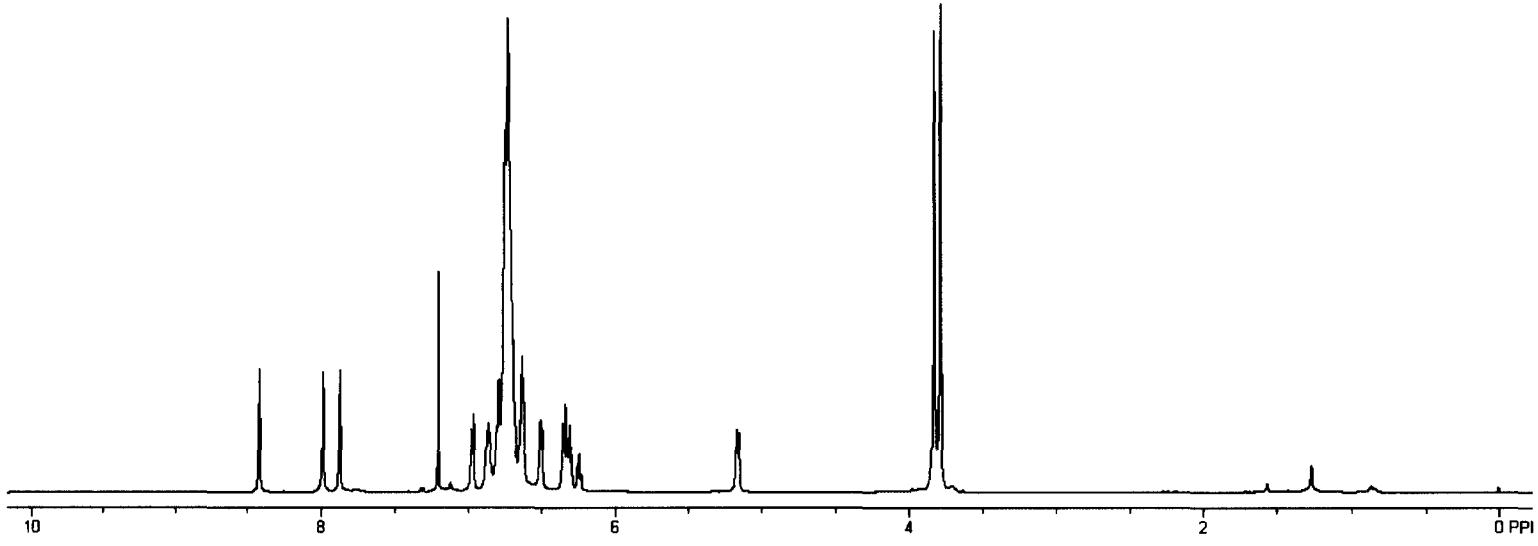
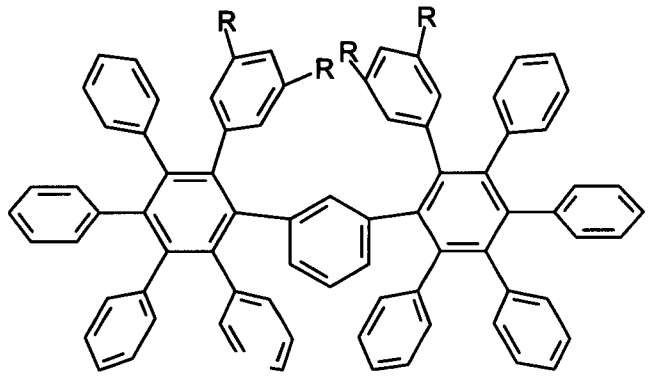


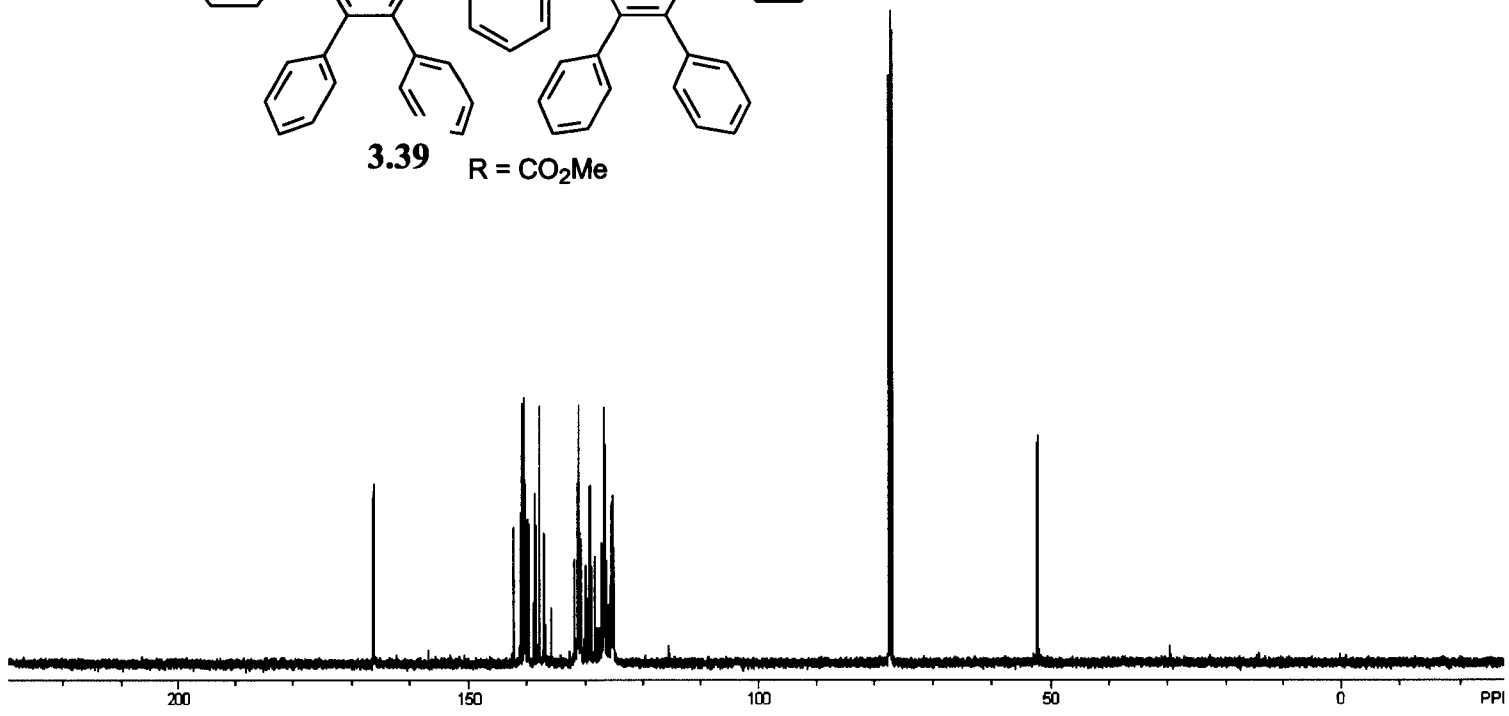


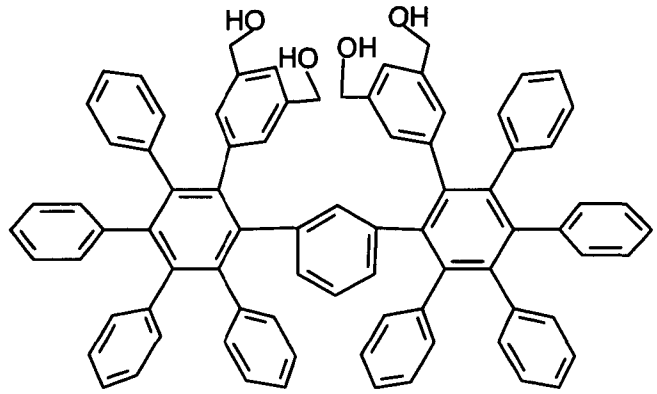
3.39 R = CO_2Me





3.39 R = CO_2Me





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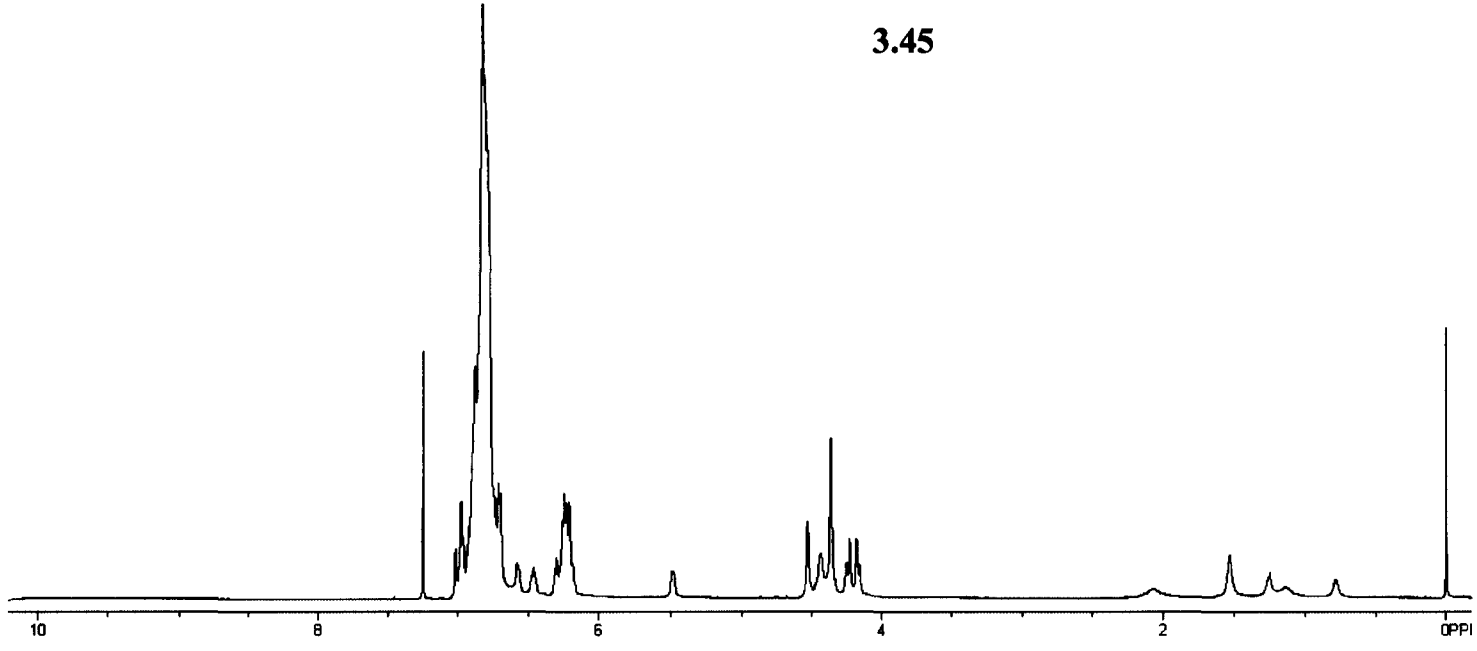

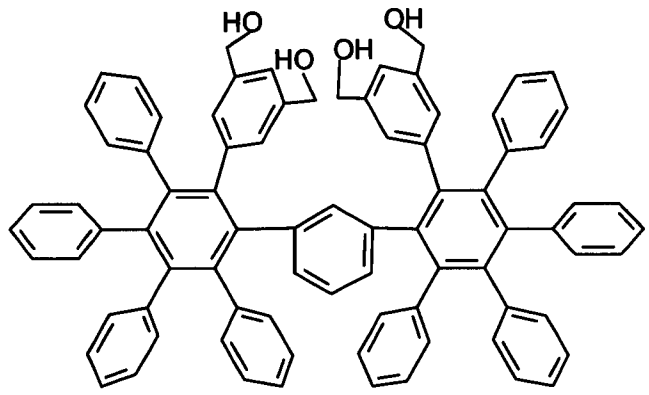

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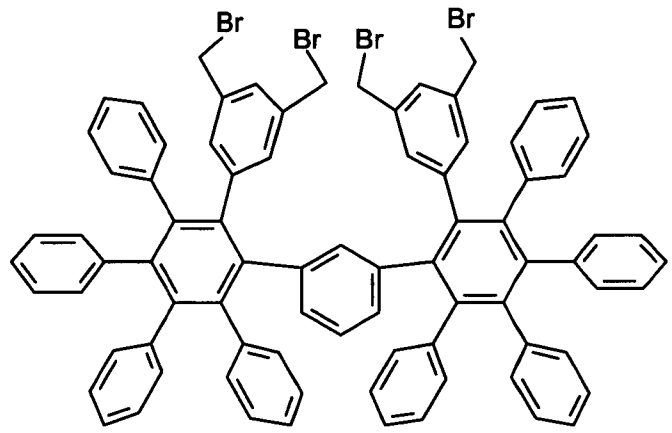

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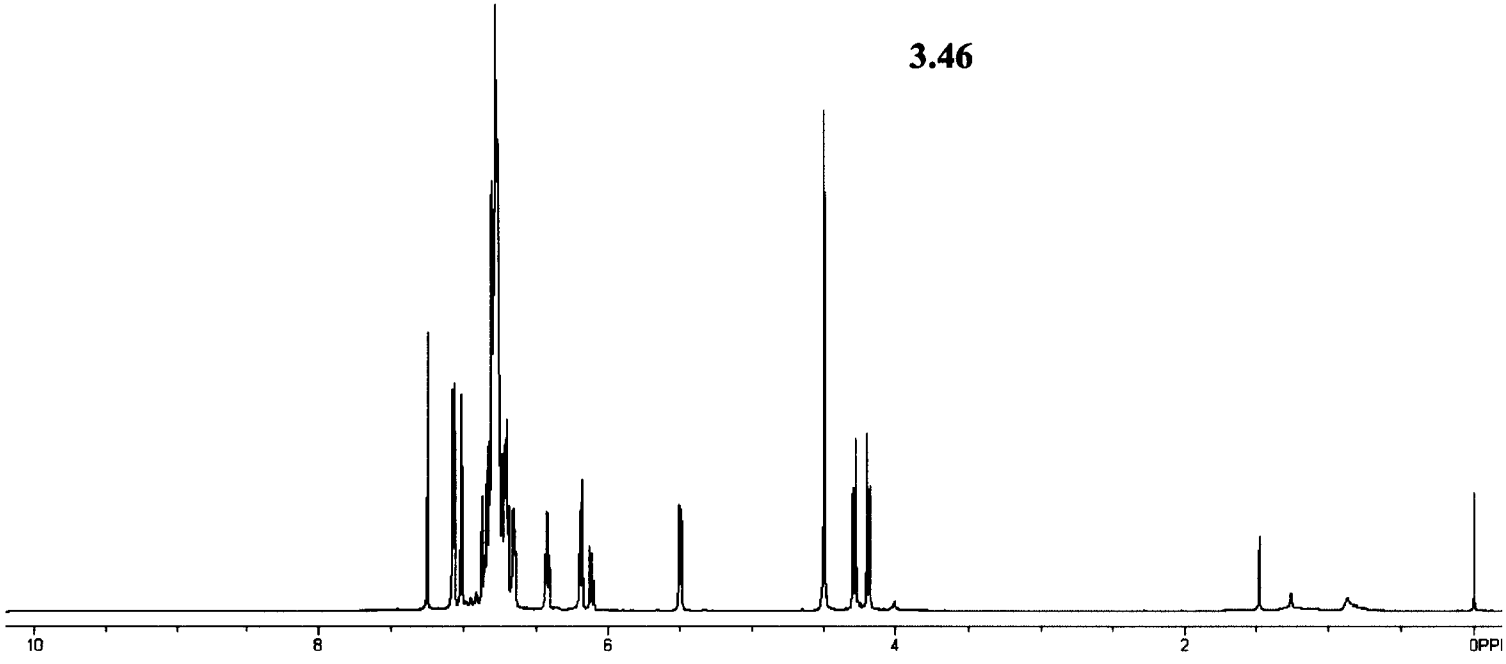

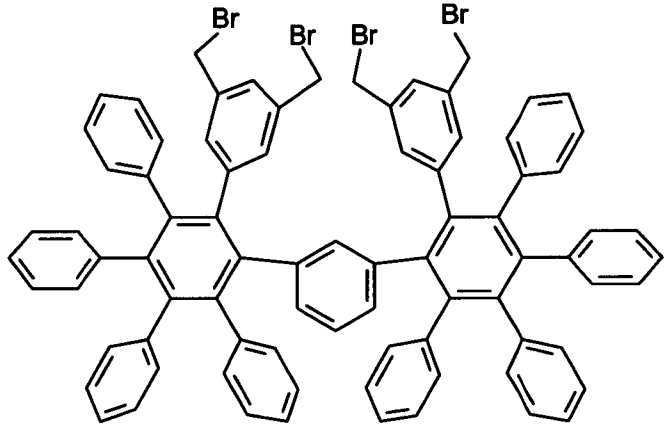

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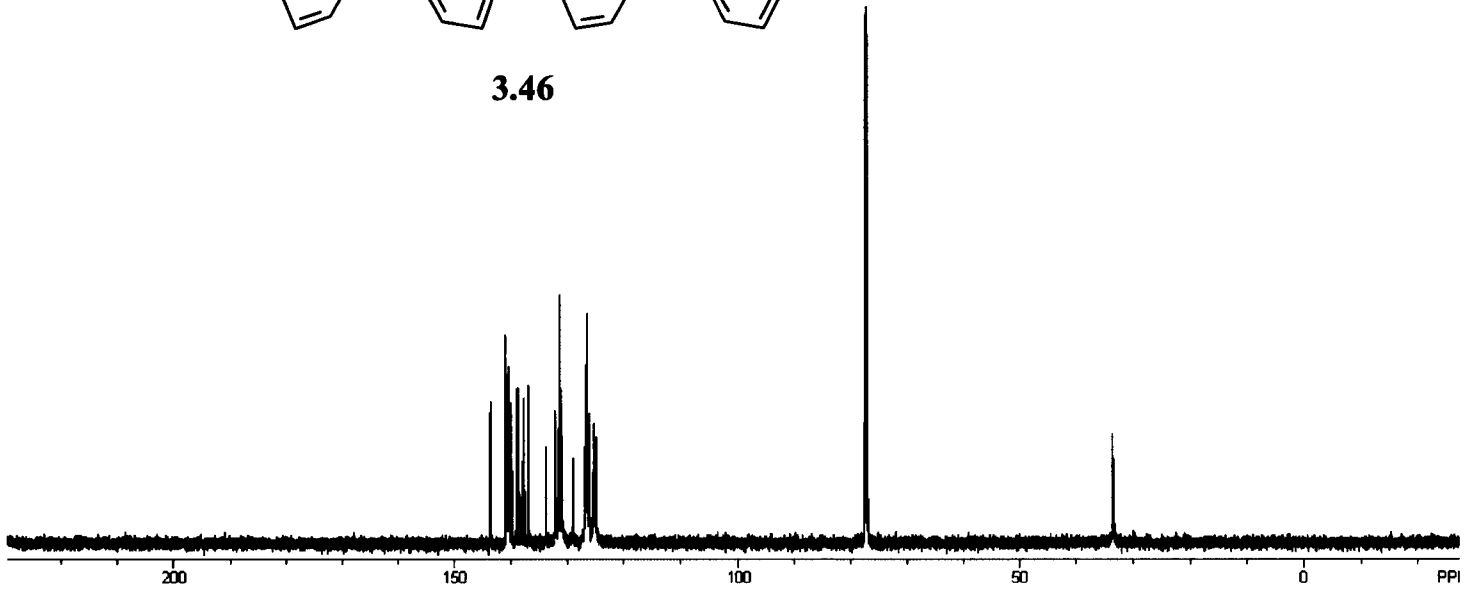

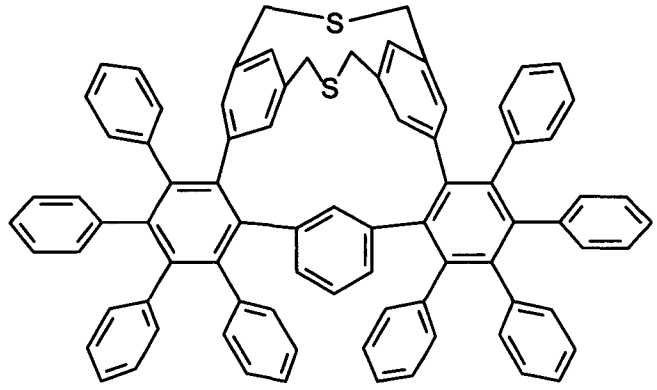

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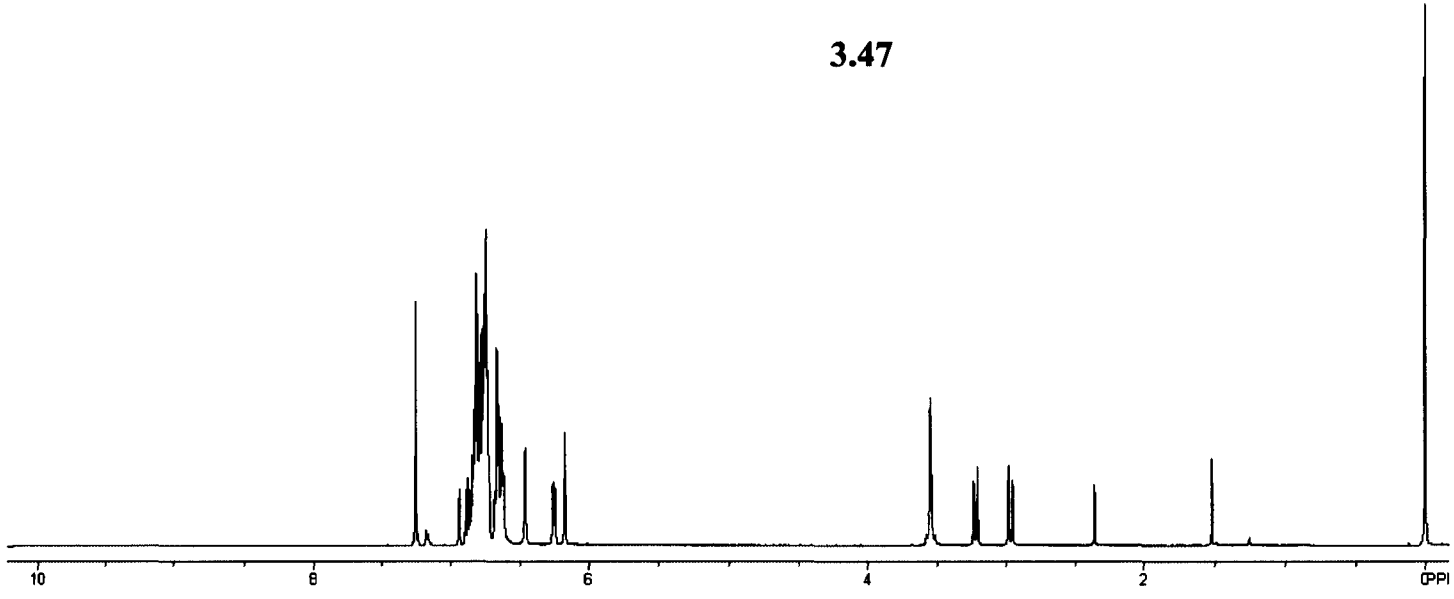

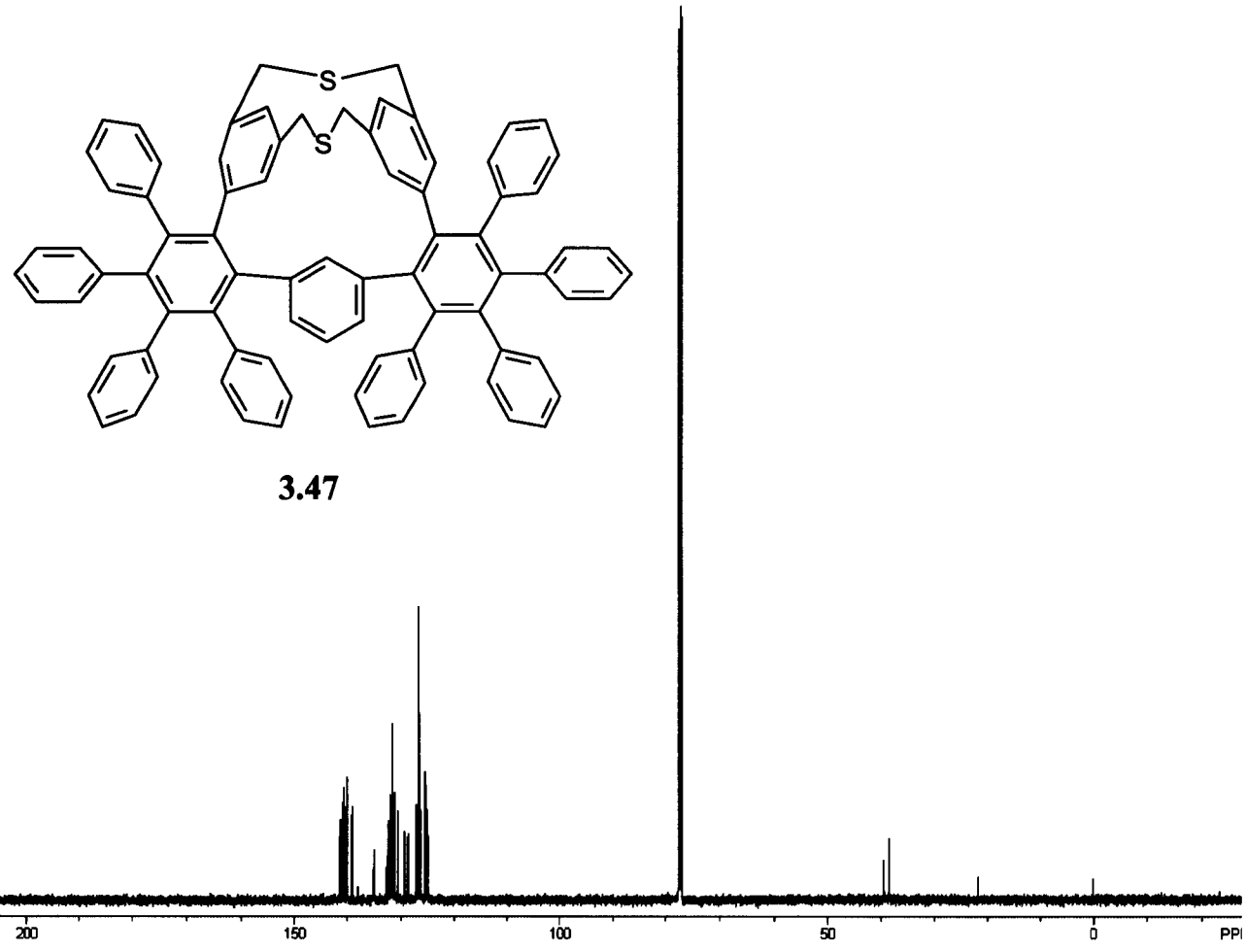

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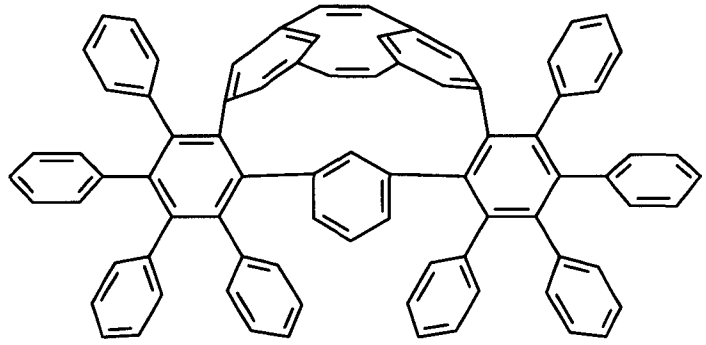

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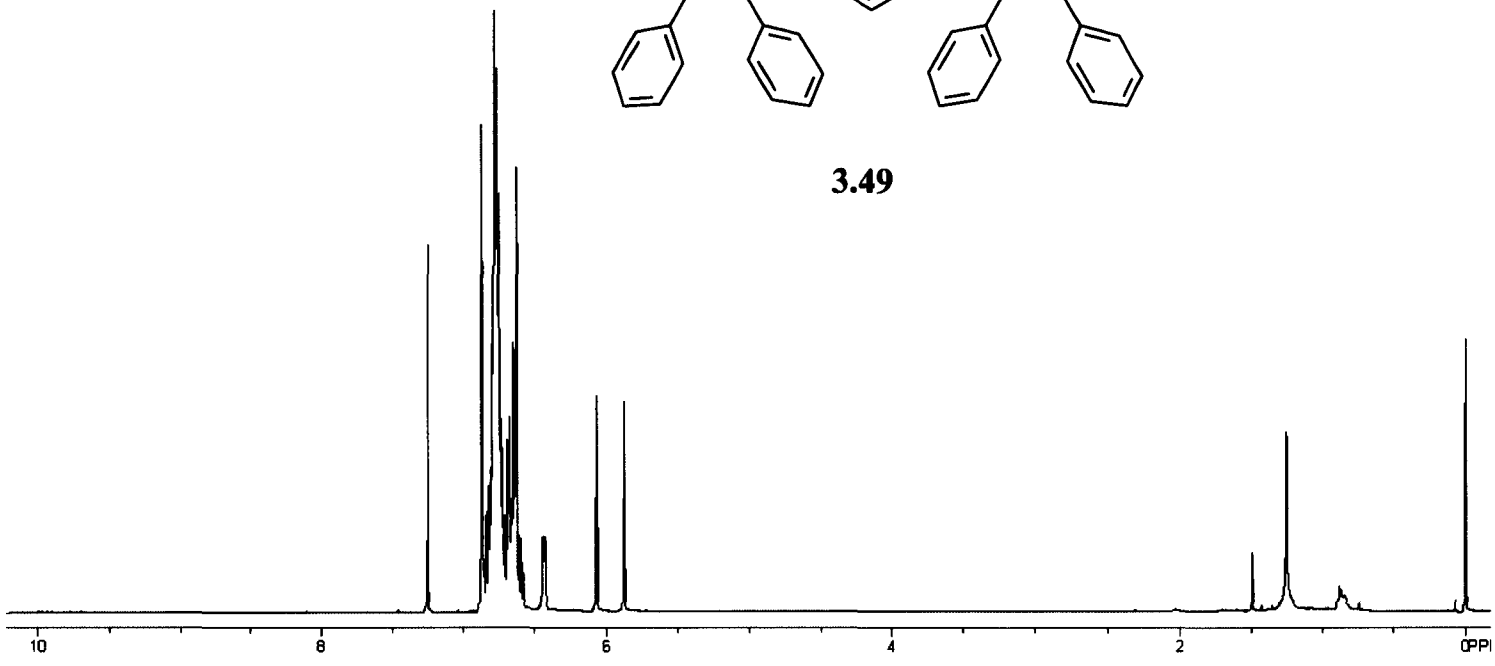

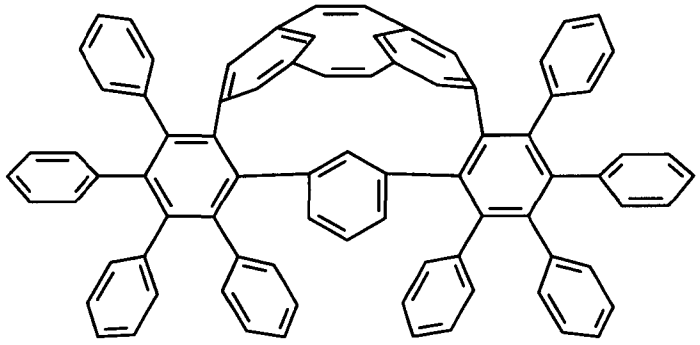

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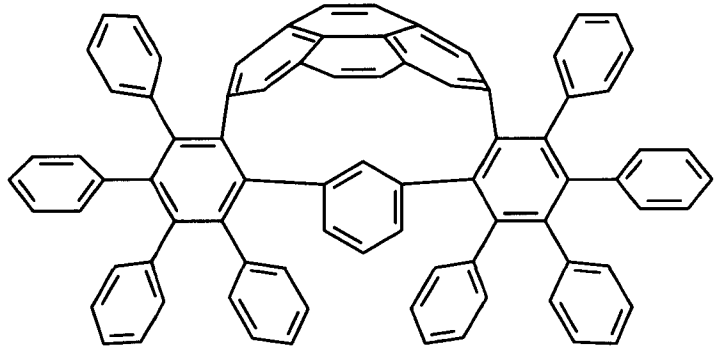

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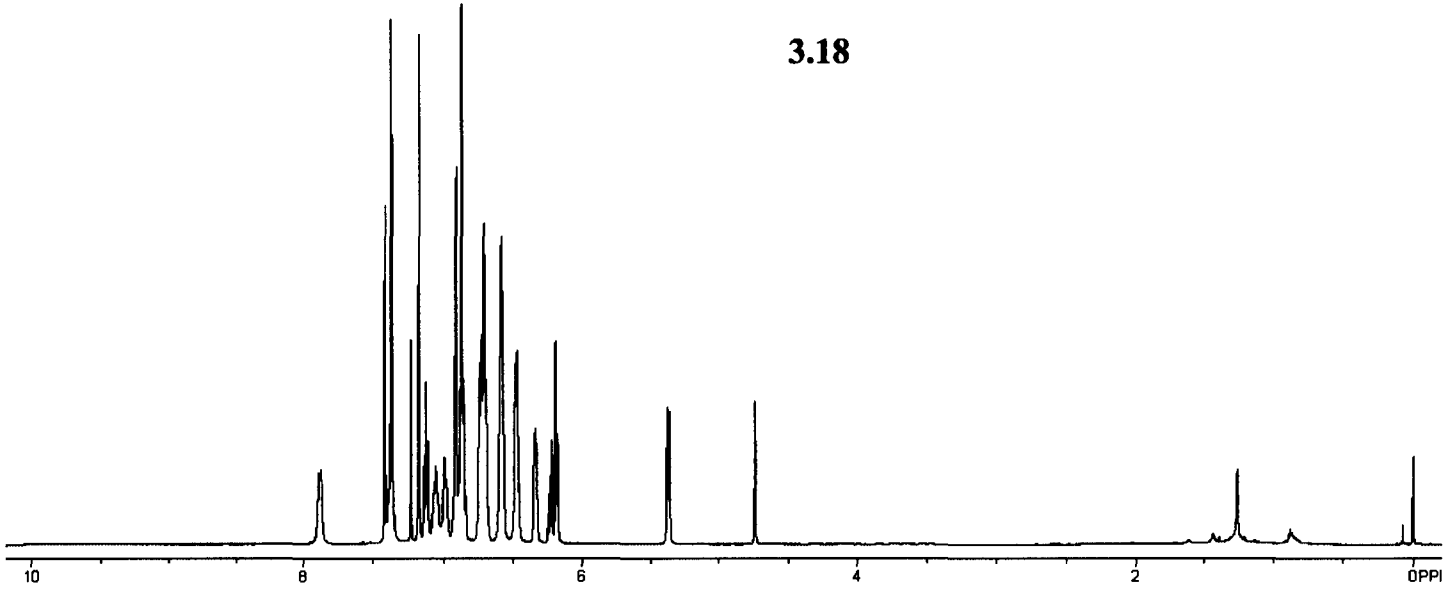

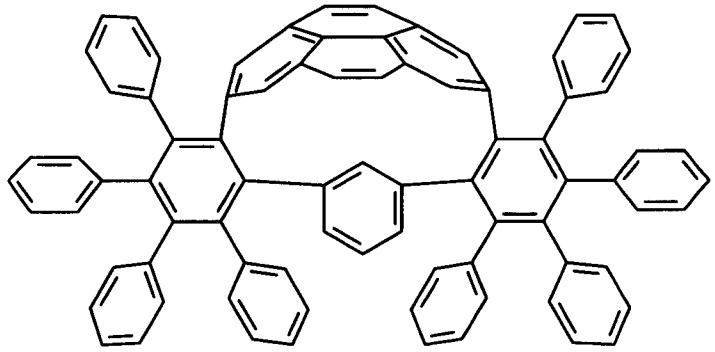

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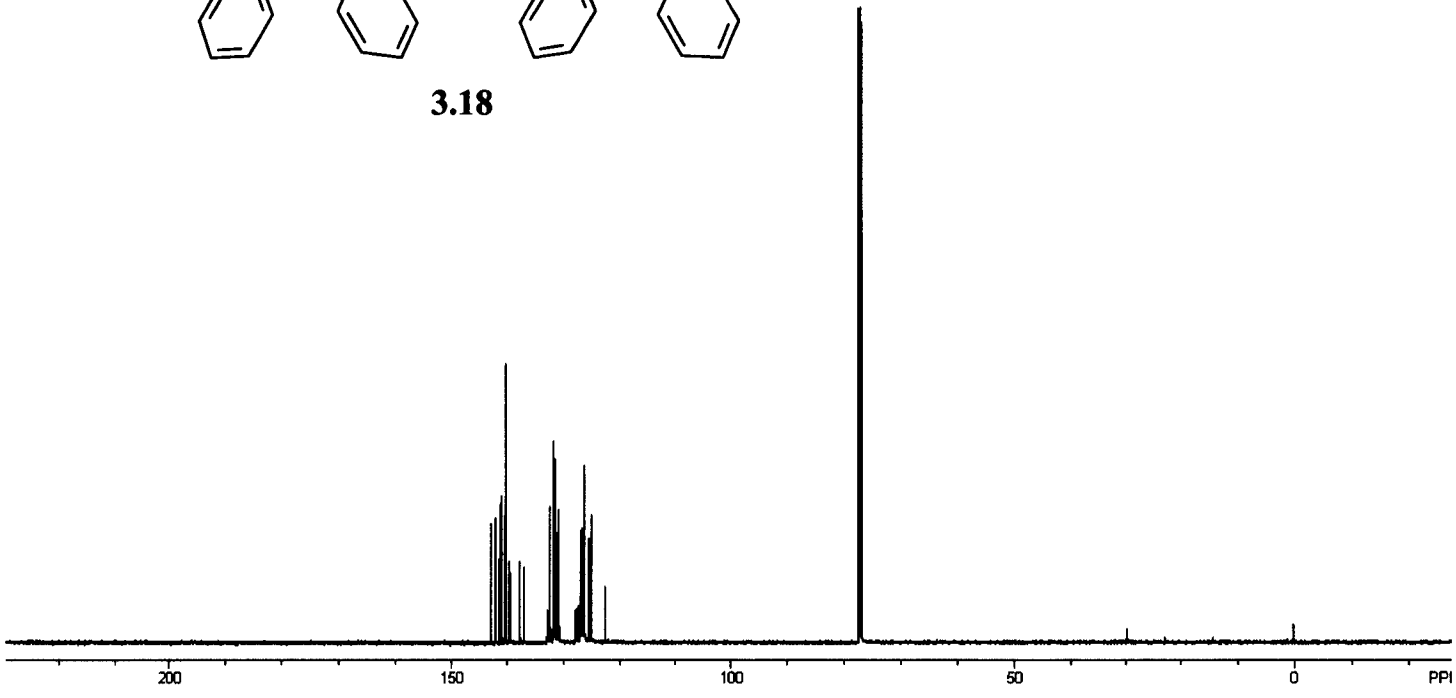

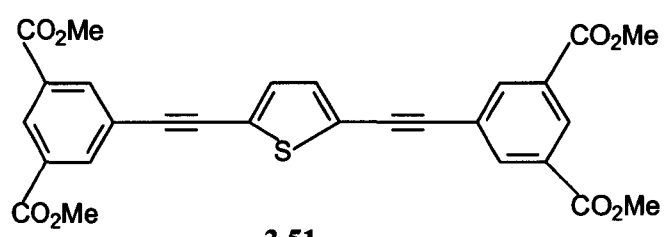

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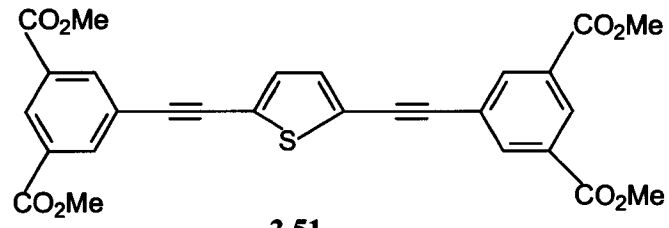

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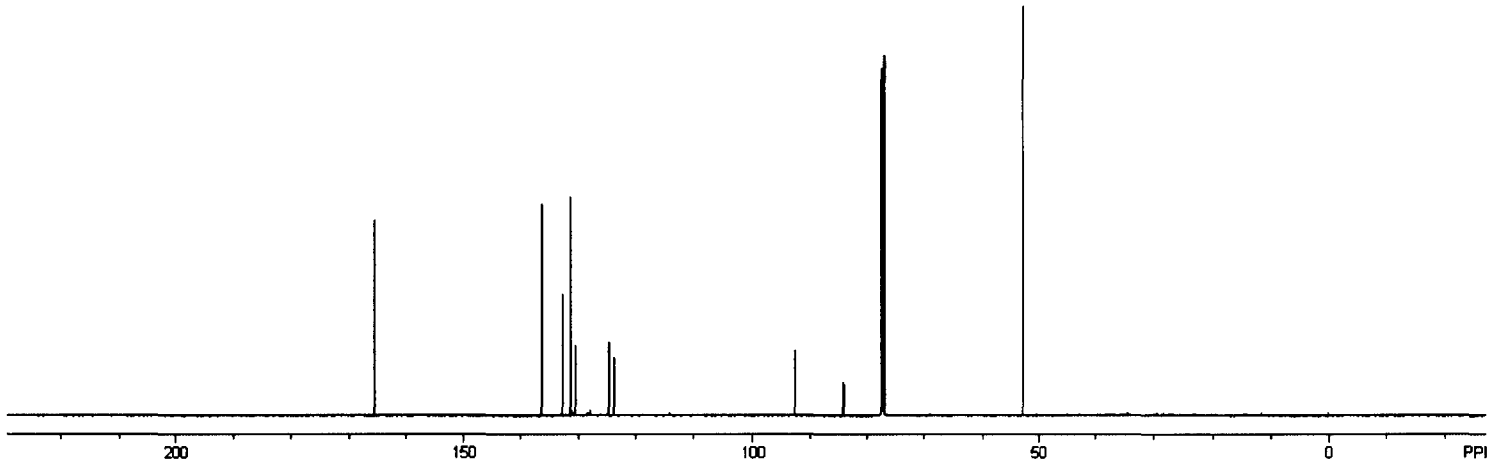

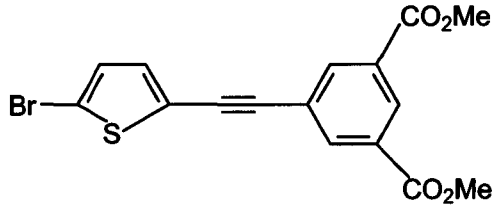

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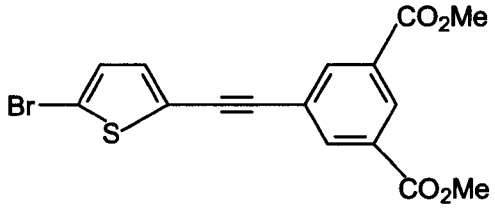

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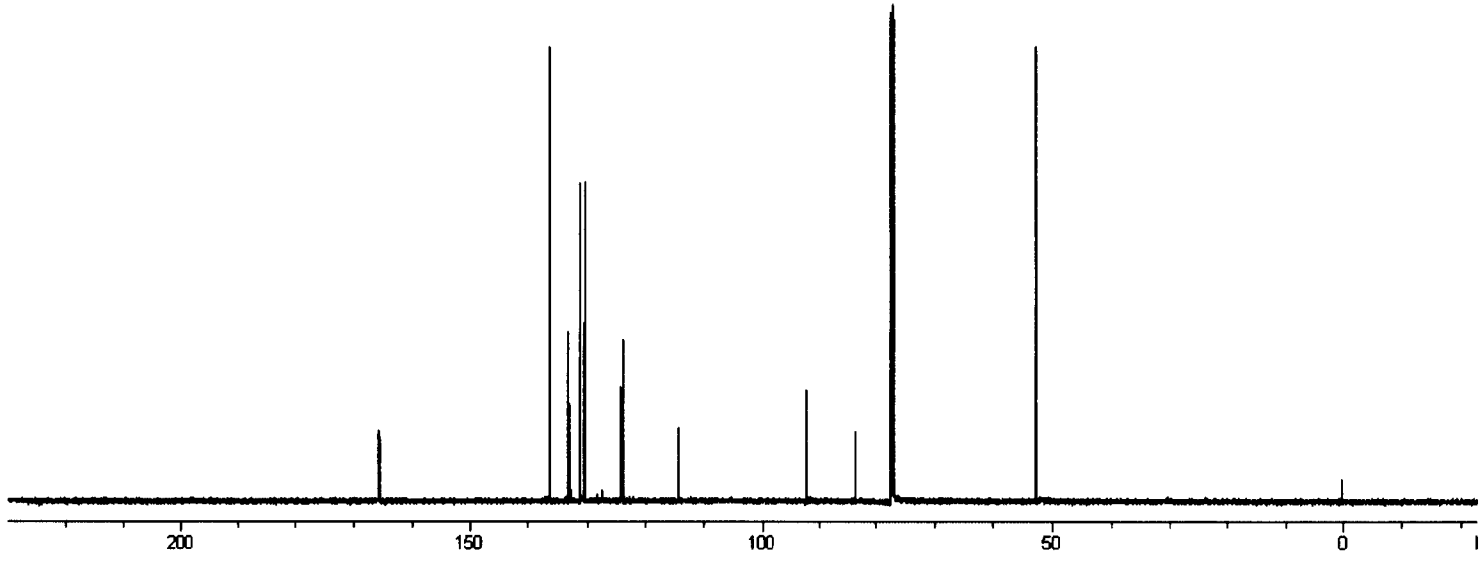
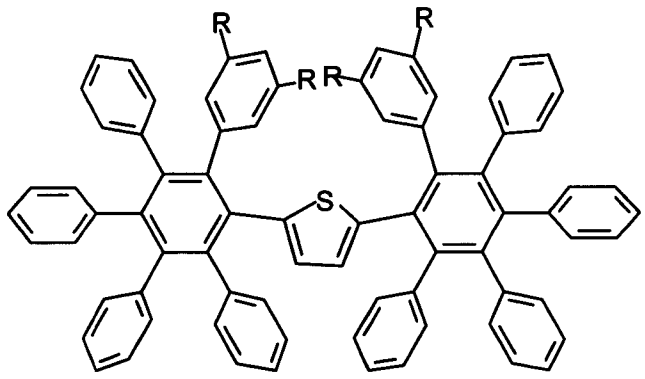
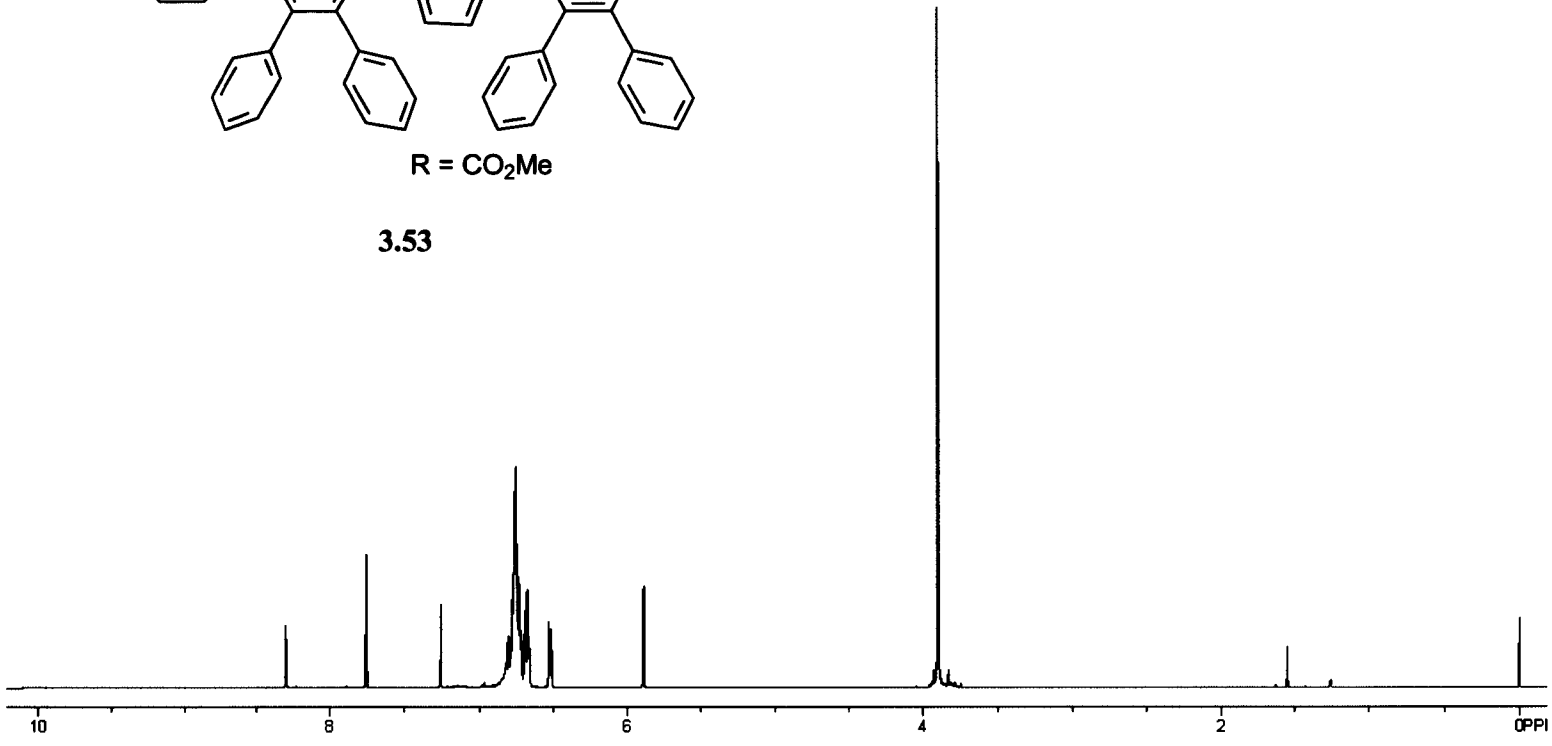
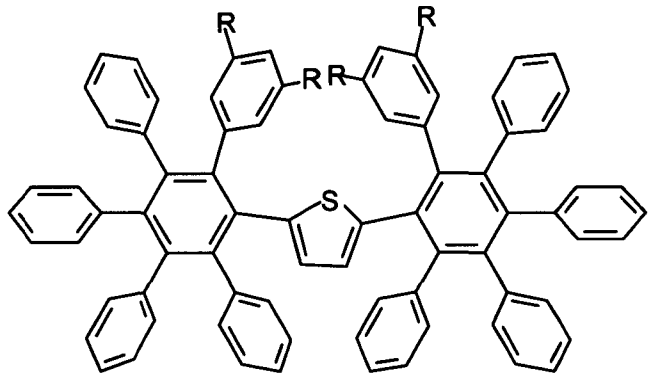




R = CO_2Me

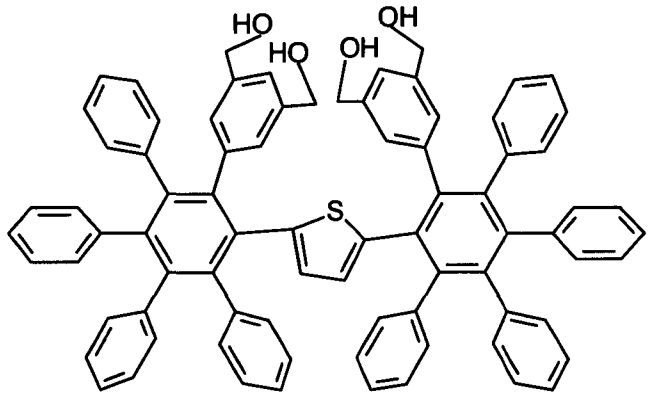
3.53





R = CO_2Me

3.53



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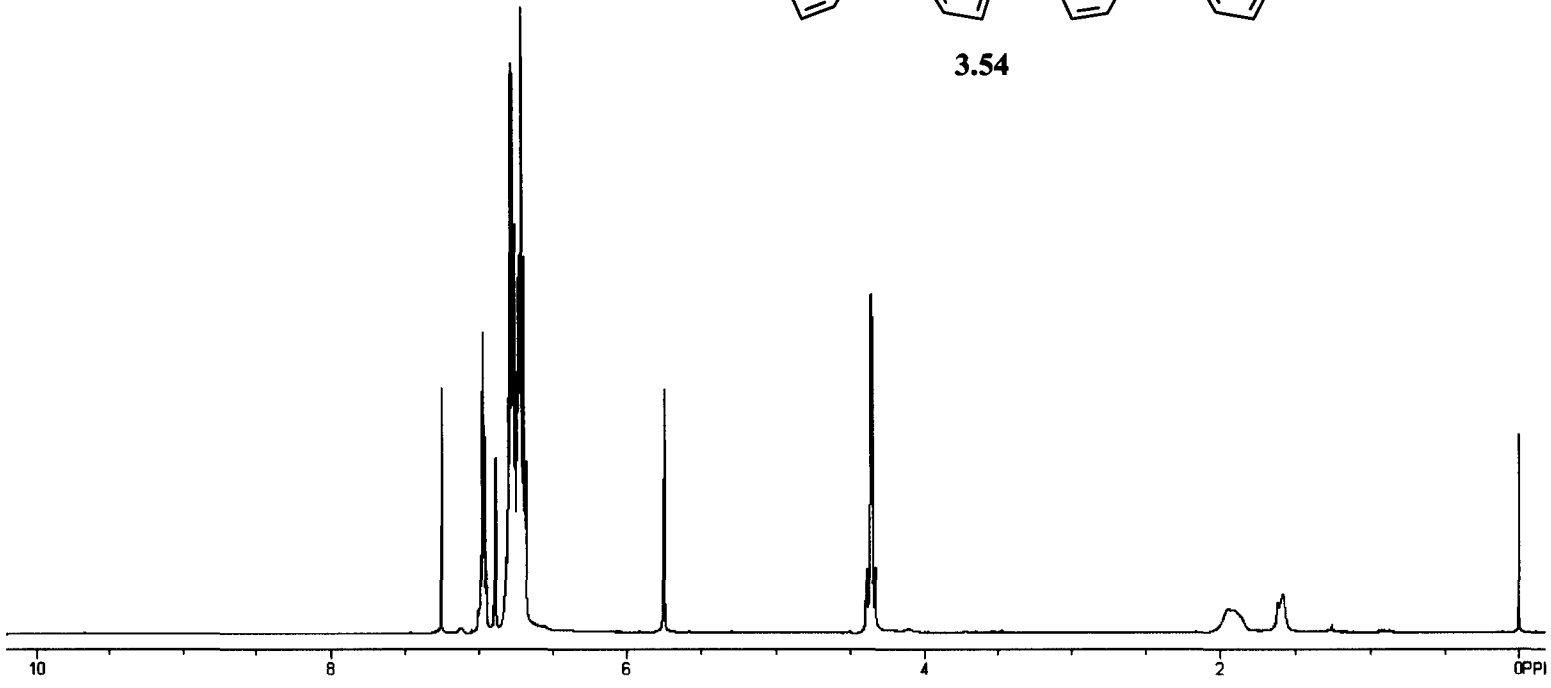

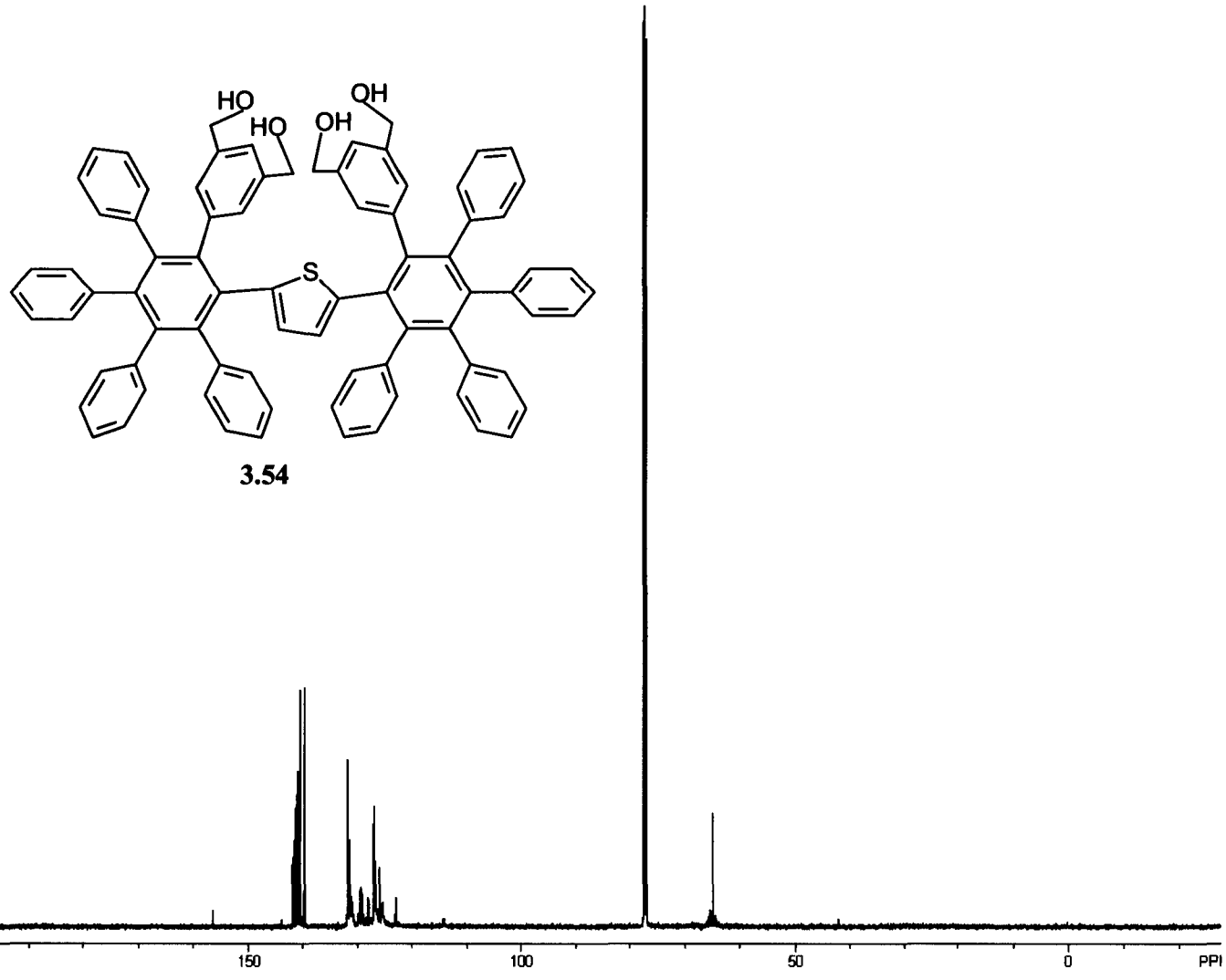

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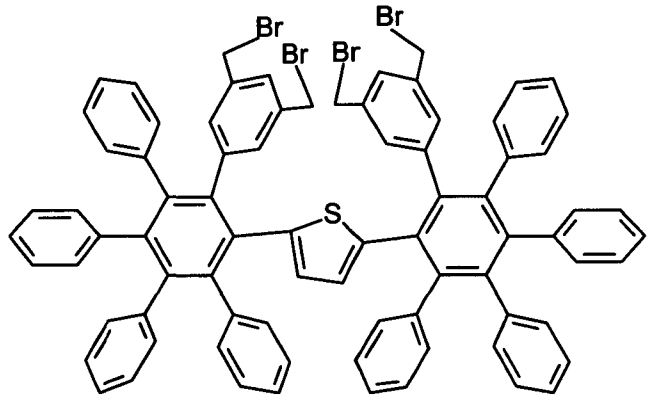

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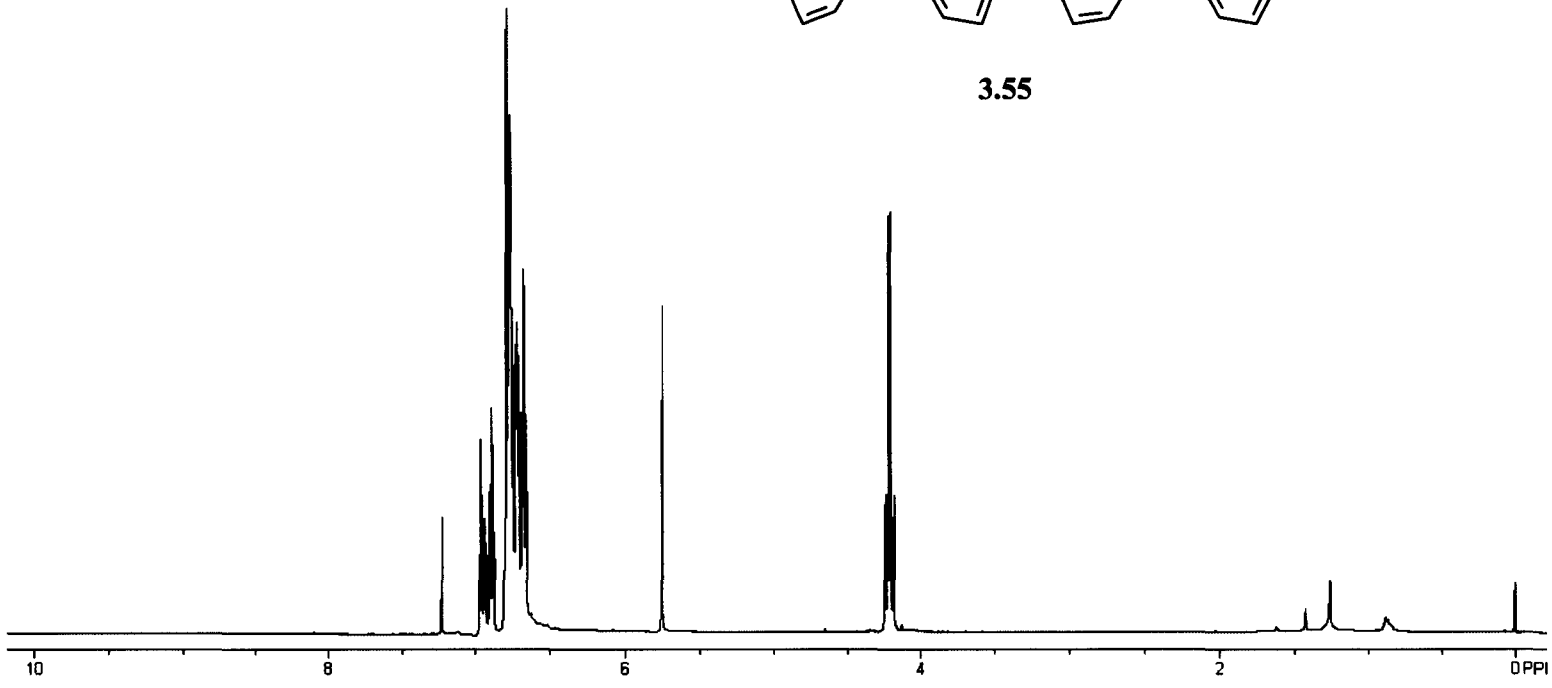

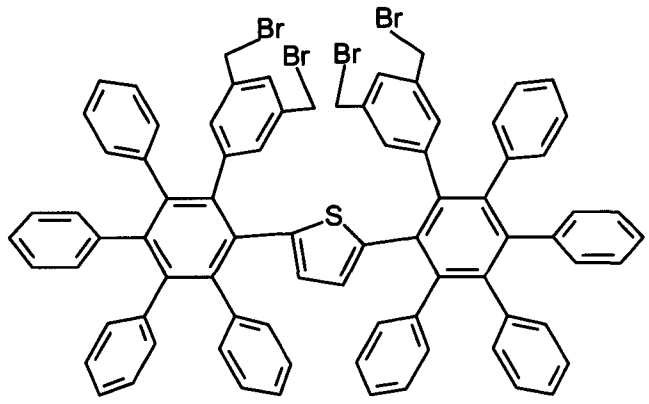

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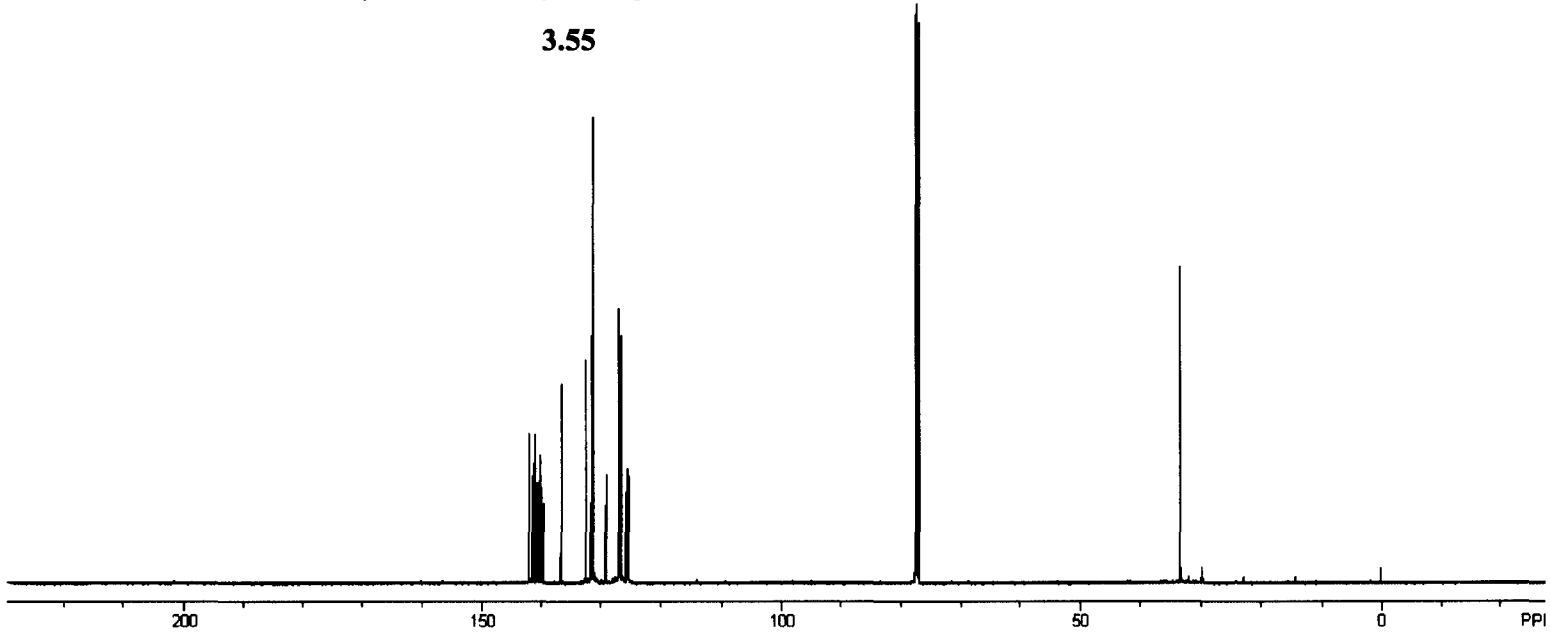

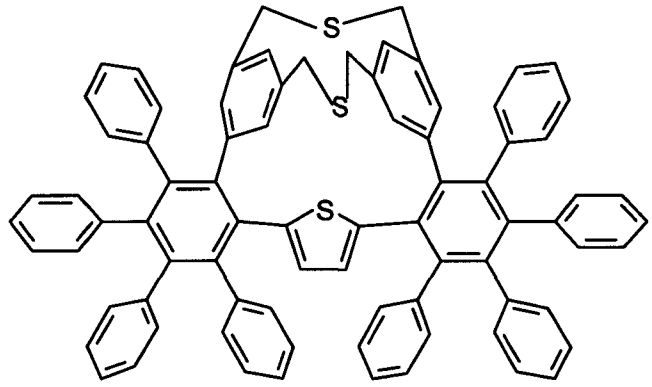

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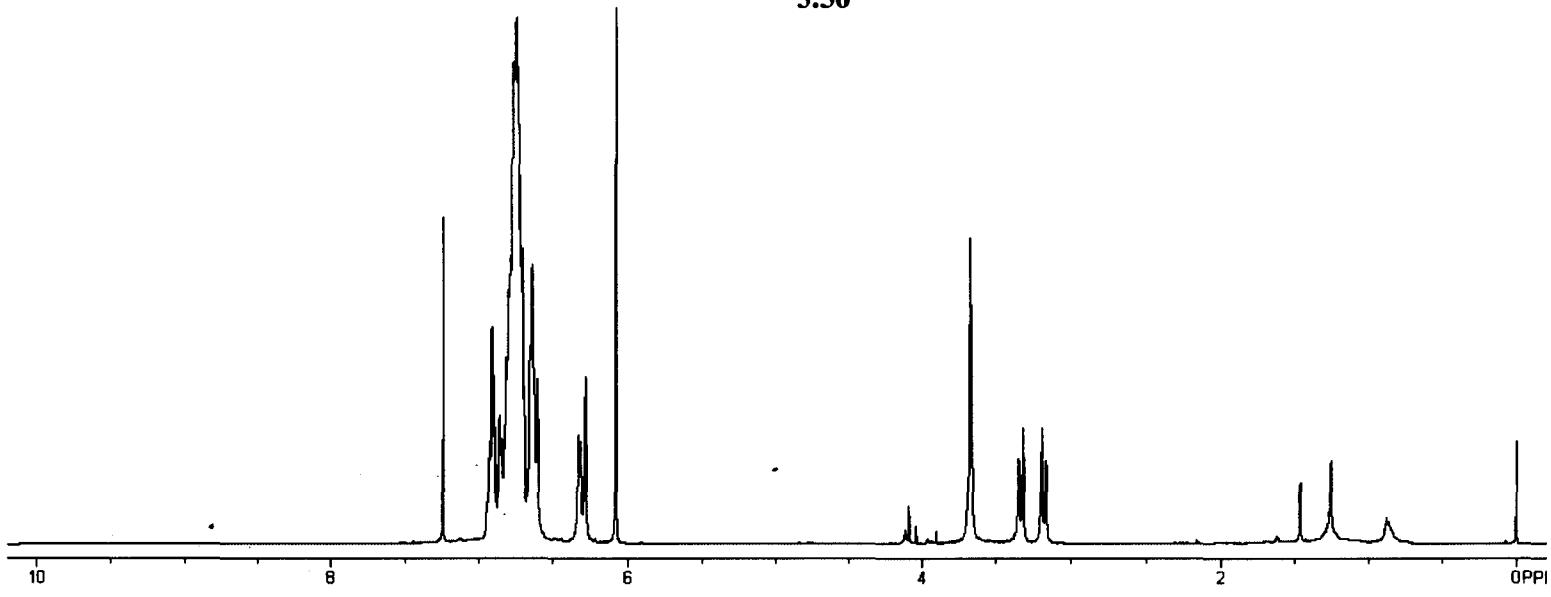

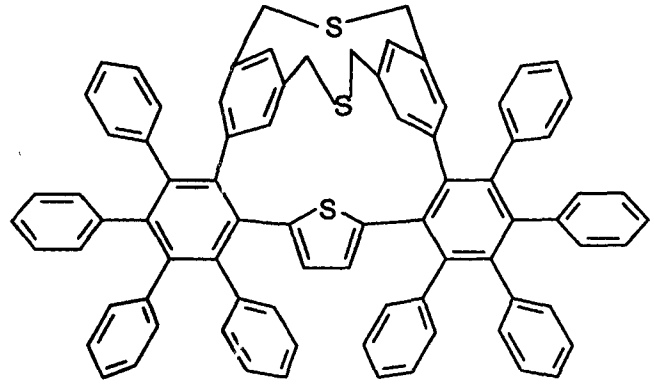

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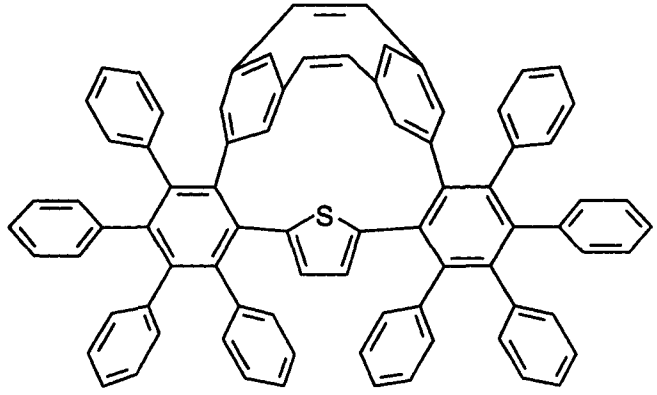

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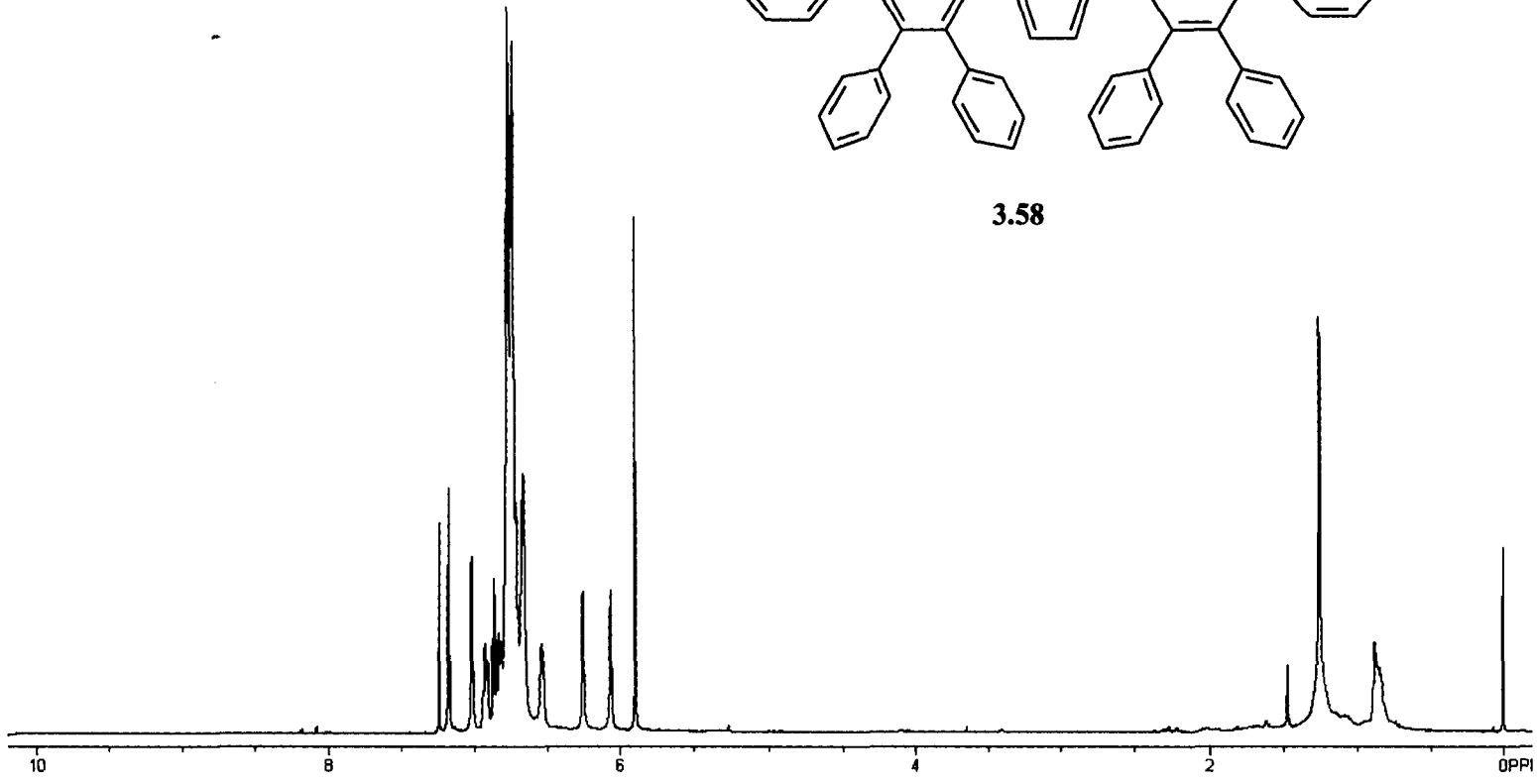

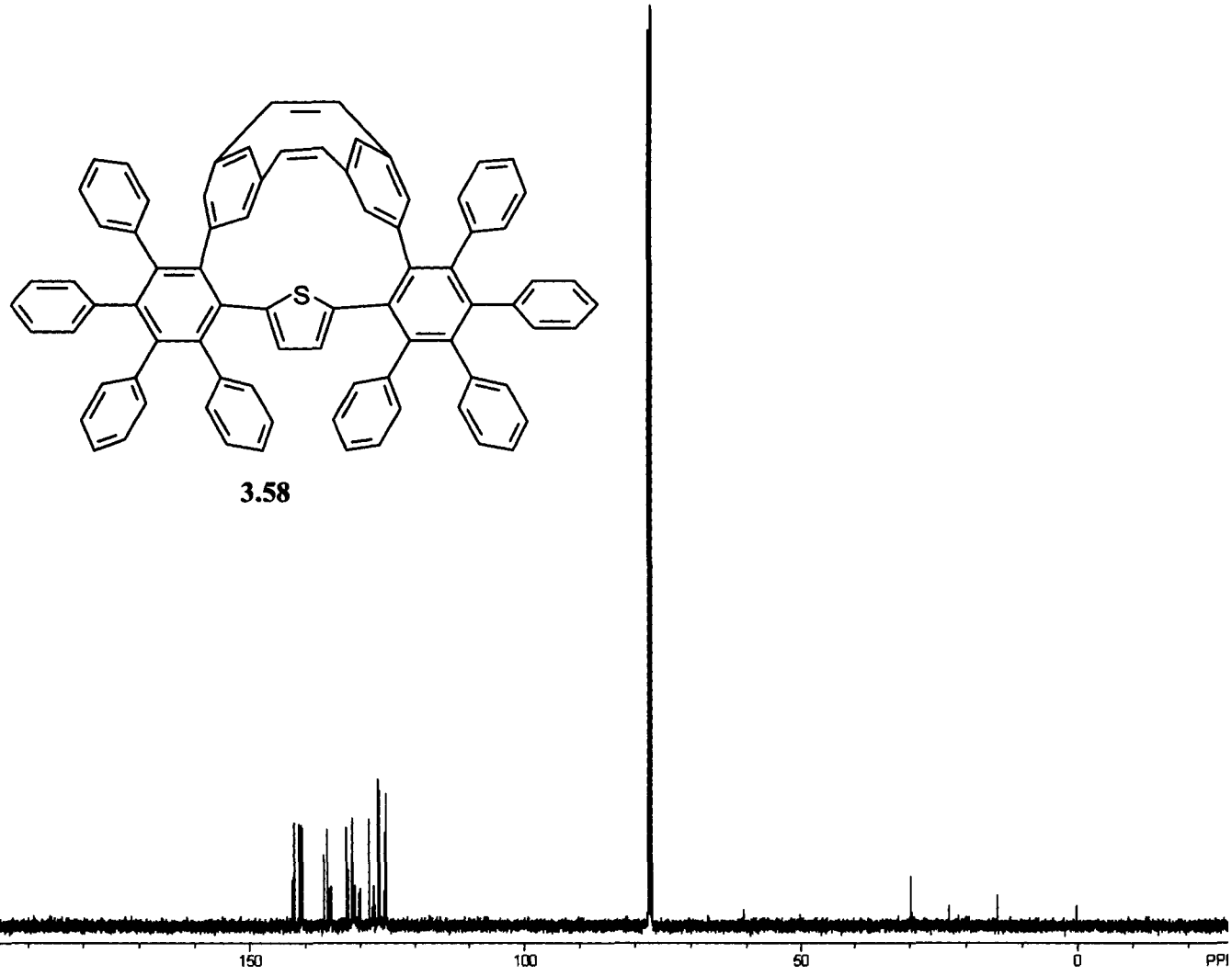

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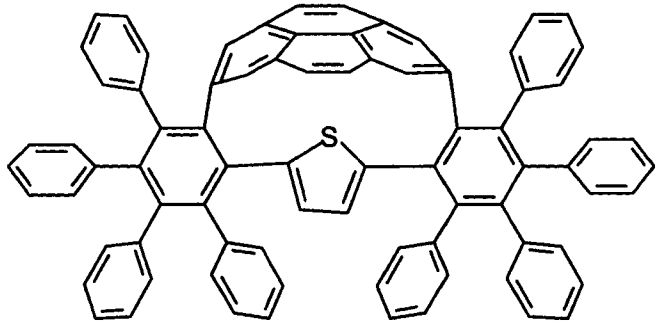

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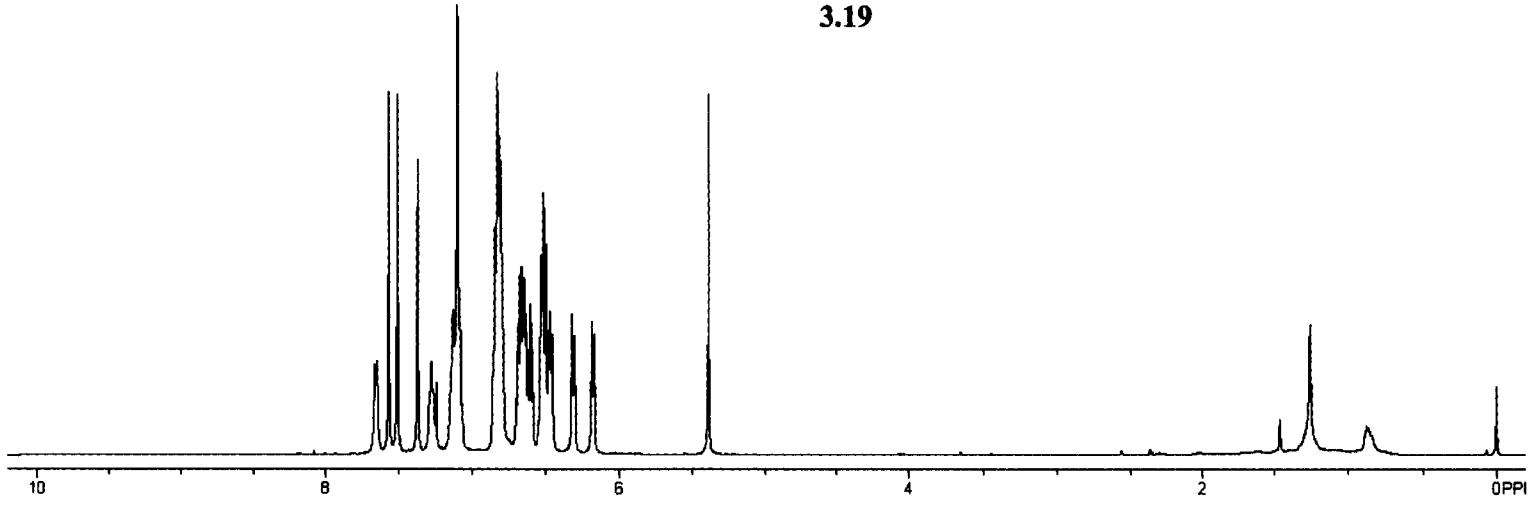

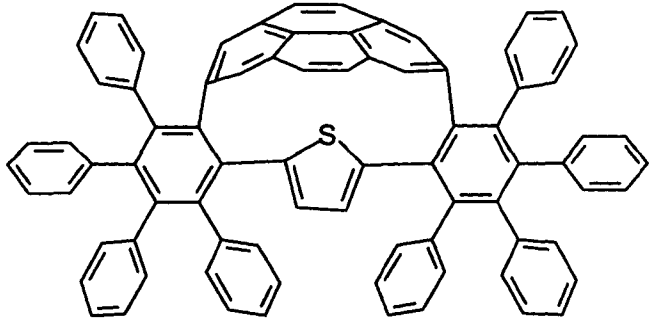

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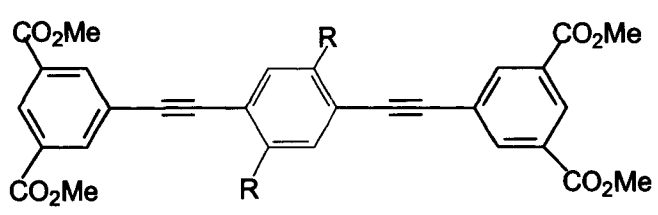
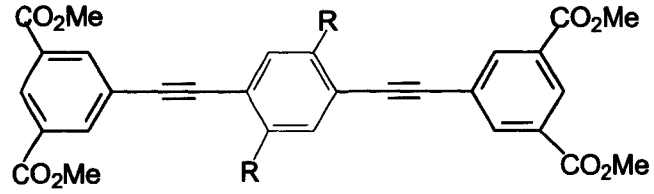
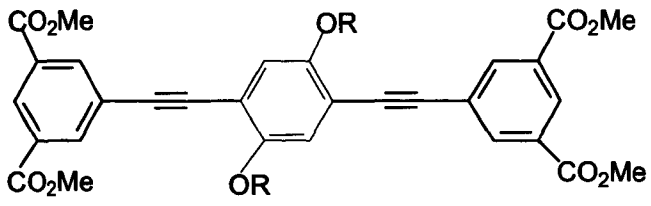


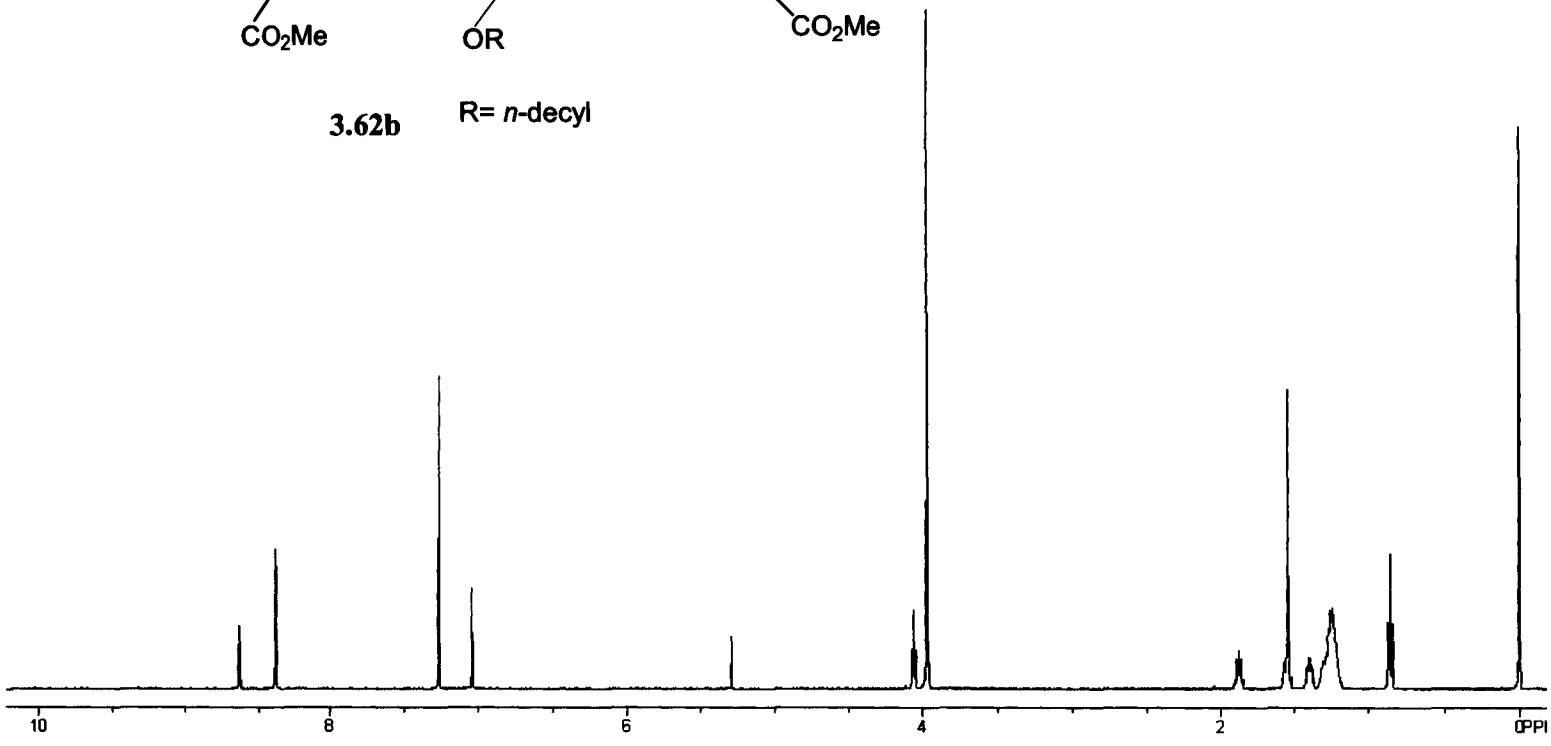
3.62a R= *n*-decyl

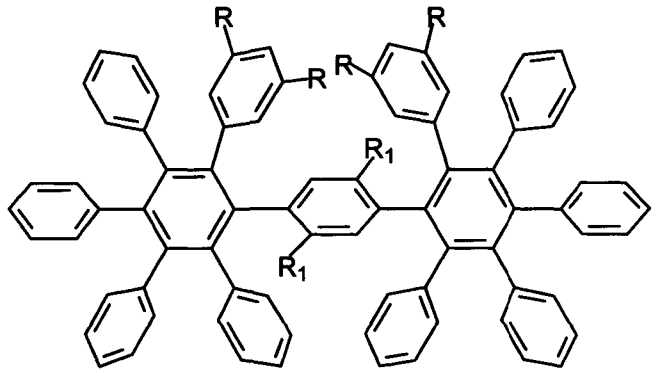


3.62a R= *n*-decyl



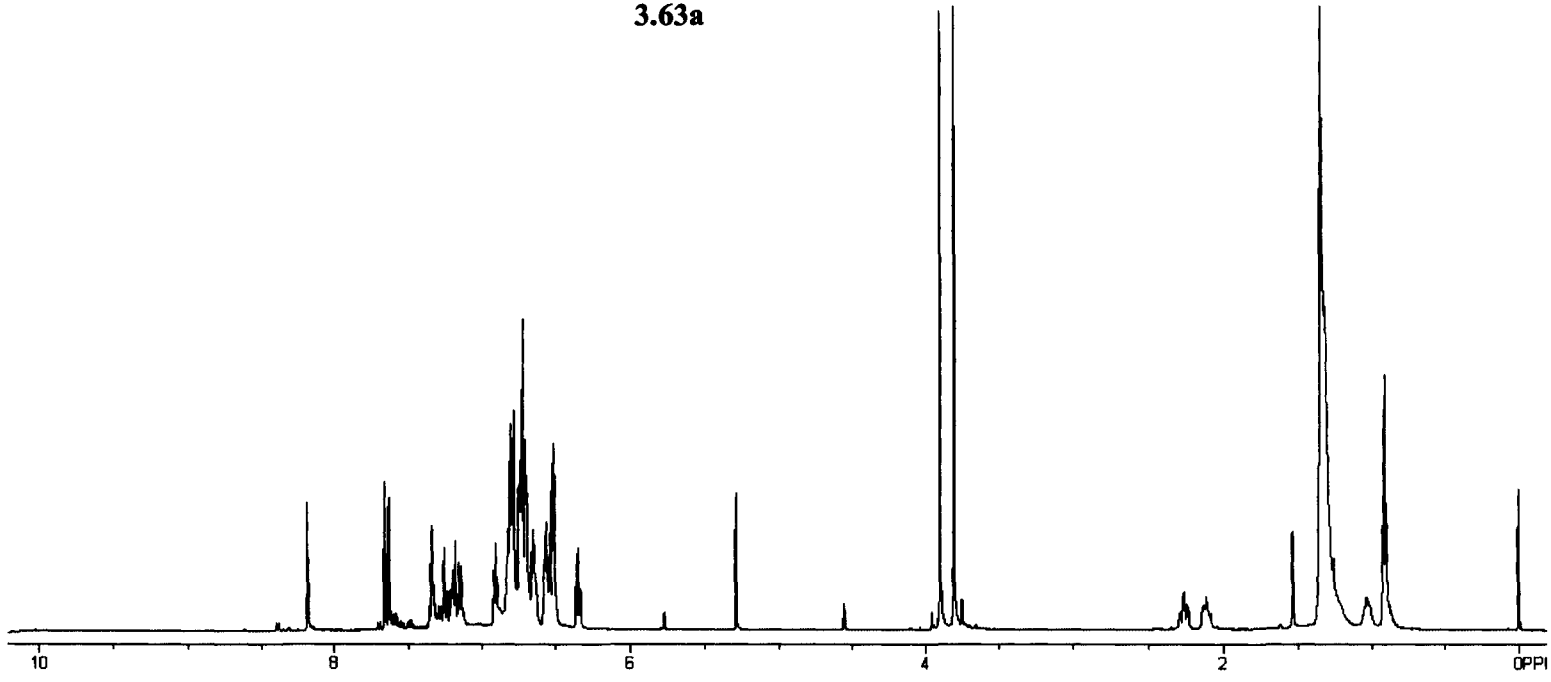
3.62b R= *n*-decyl

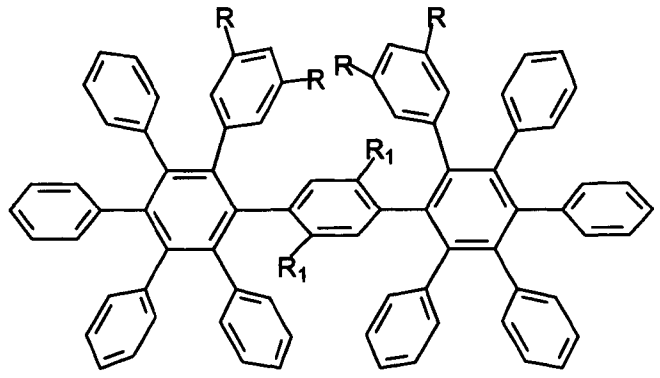




R = CO_2Me
R_1= *n*-decyl

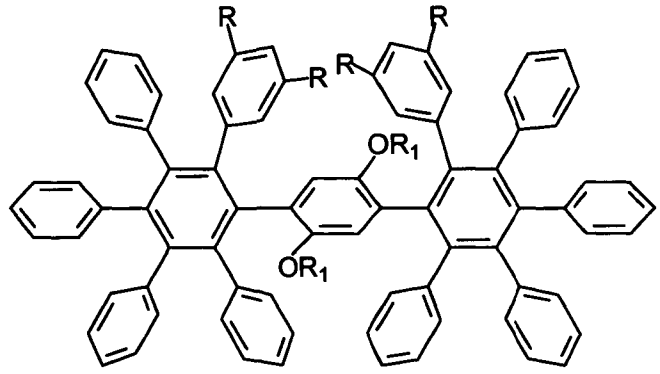
3.63a





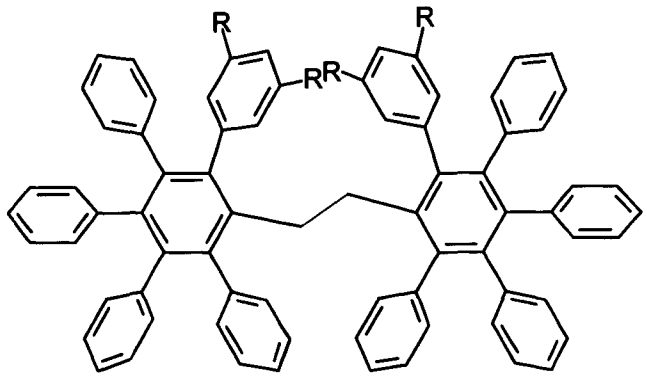
R = CO_2Me
R_1= *n*-decyl

3.63a



R = CO_2Me
R_1= *n*-decyl

3.63b



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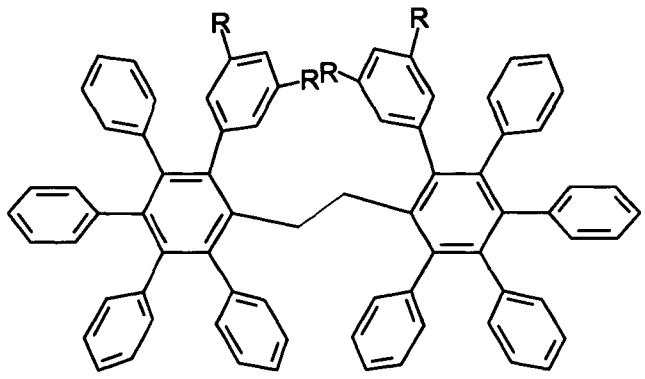

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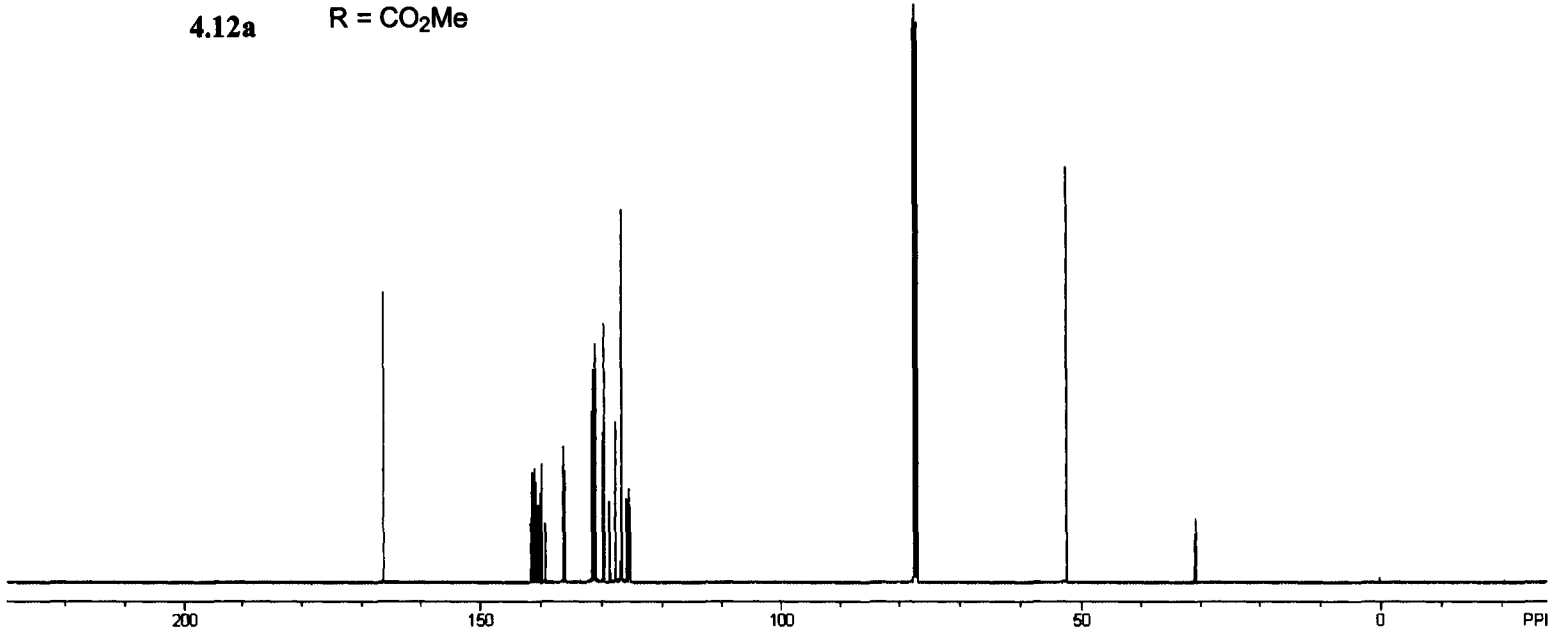
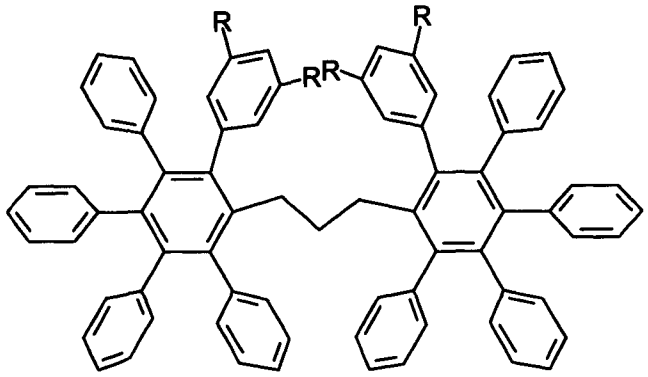
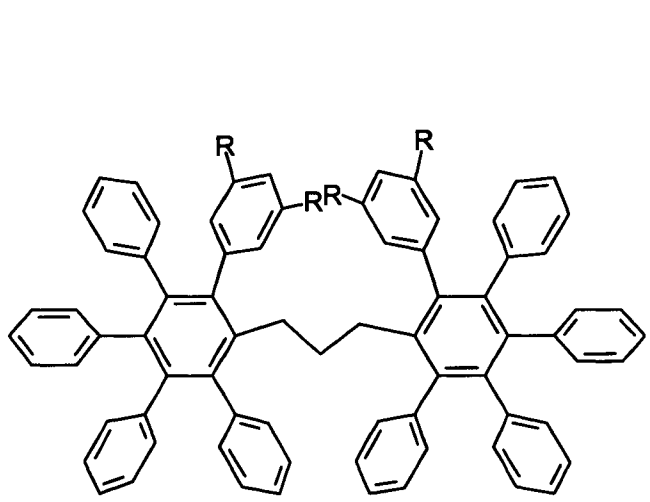




R = CO_2Me

4.12b



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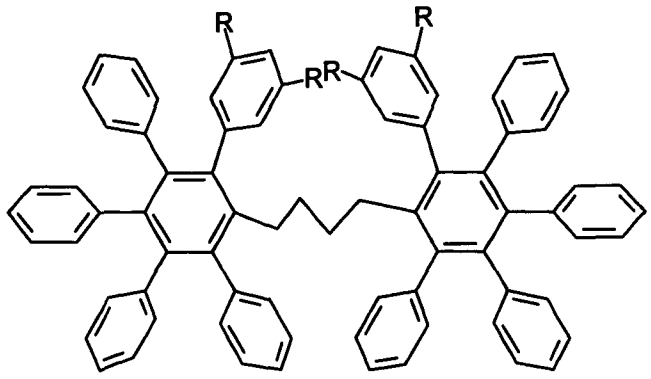

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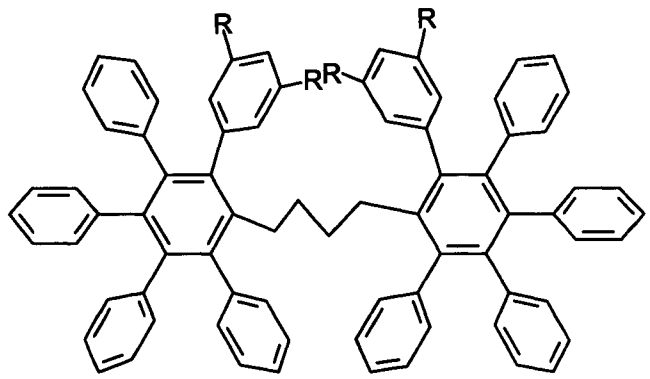

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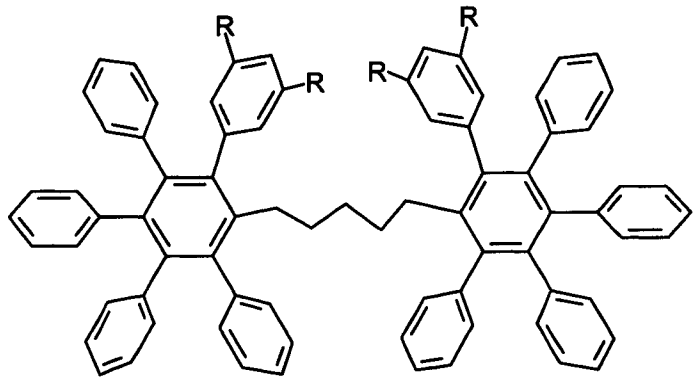

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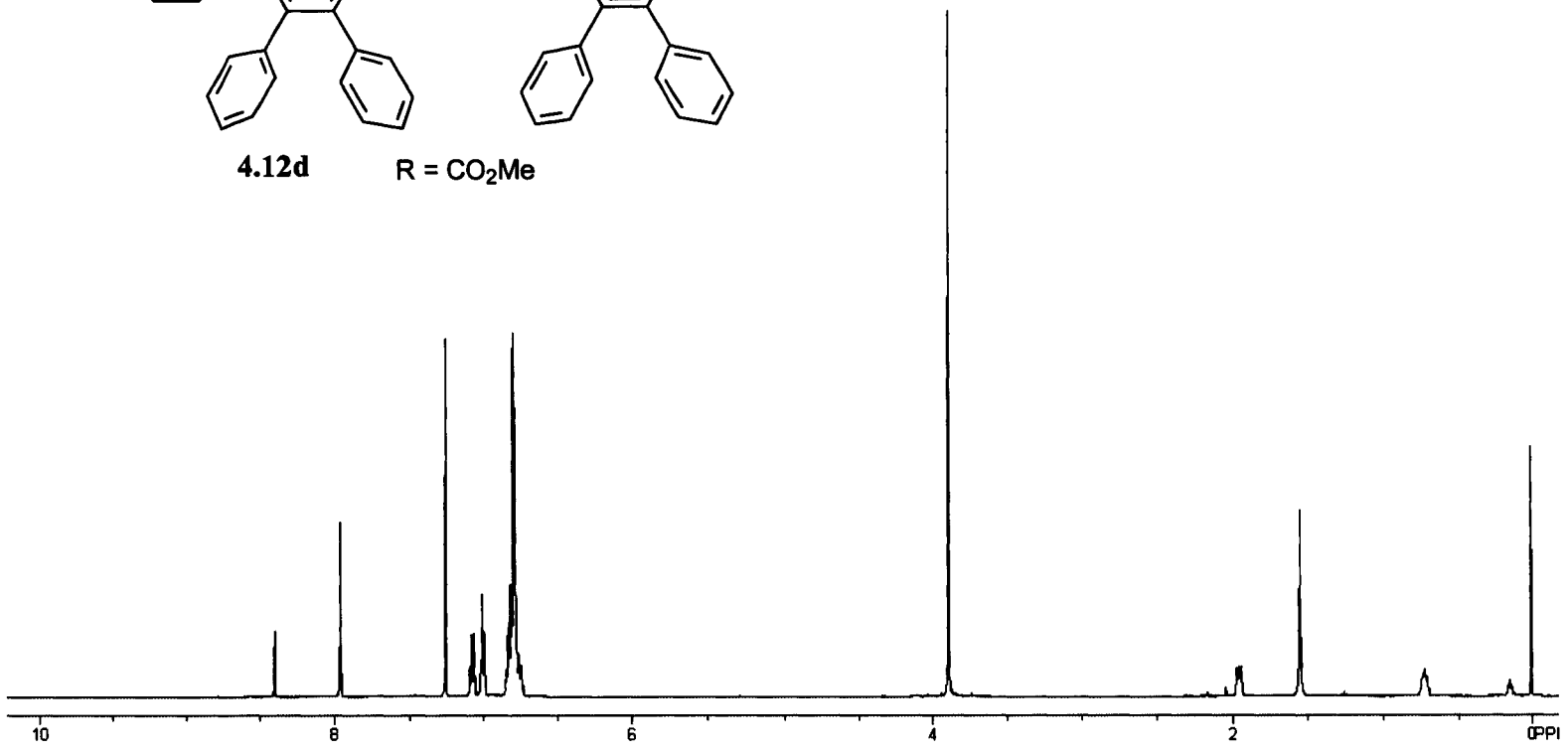
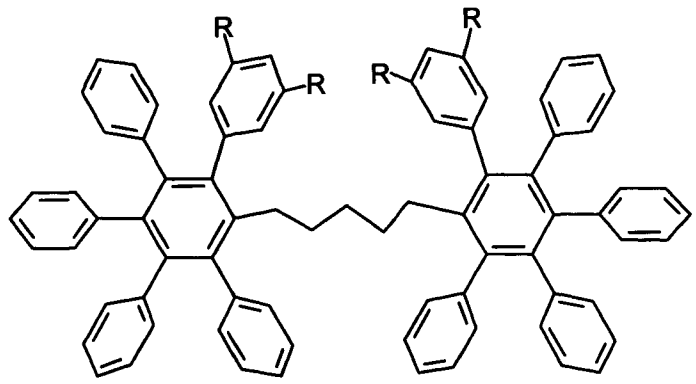
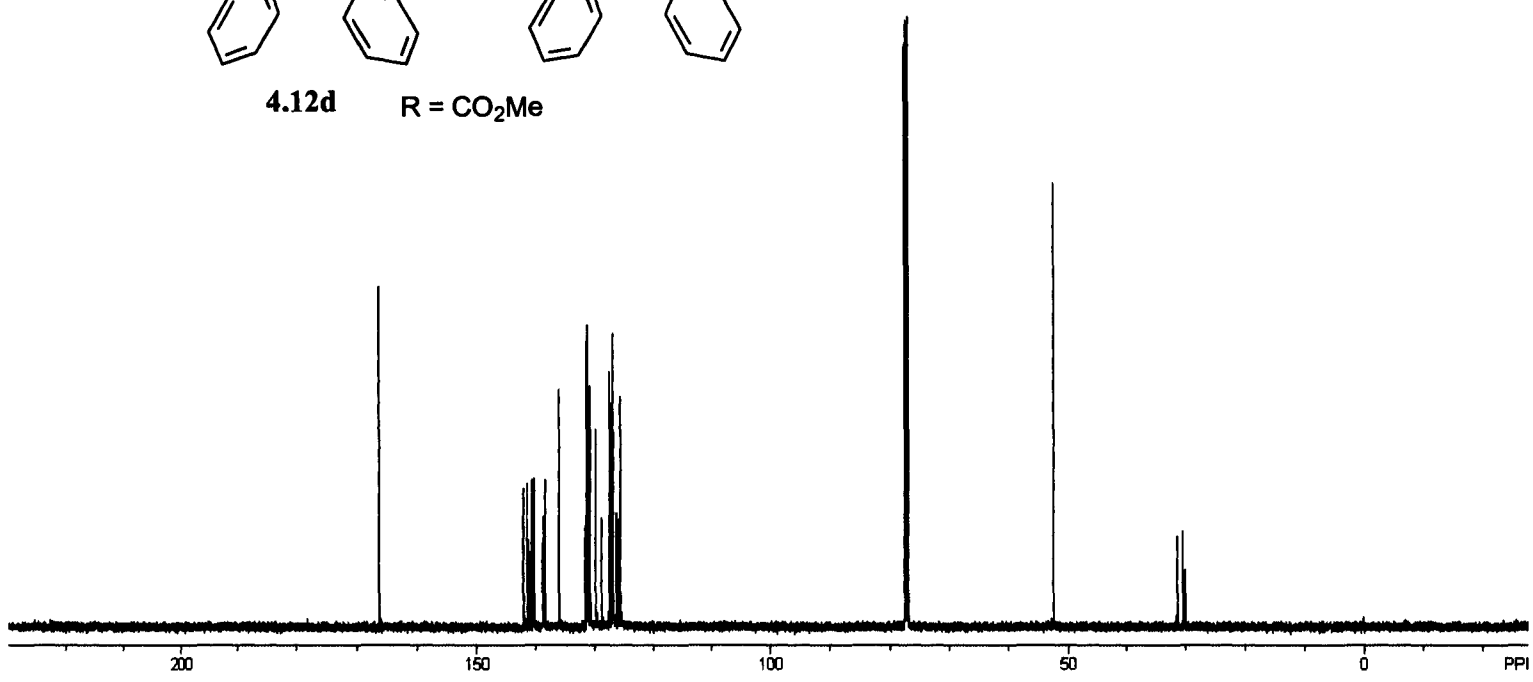
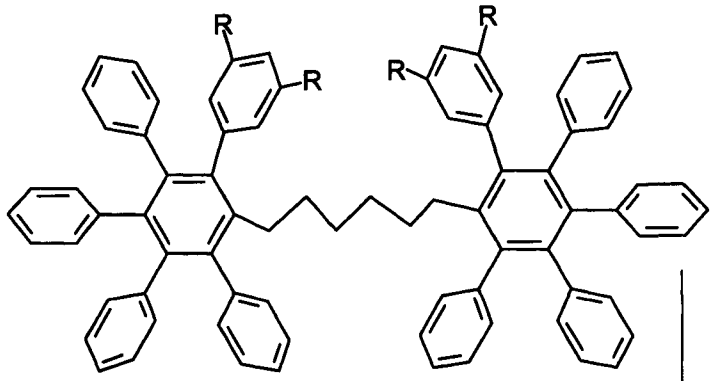




4.12d R = CO_2Me





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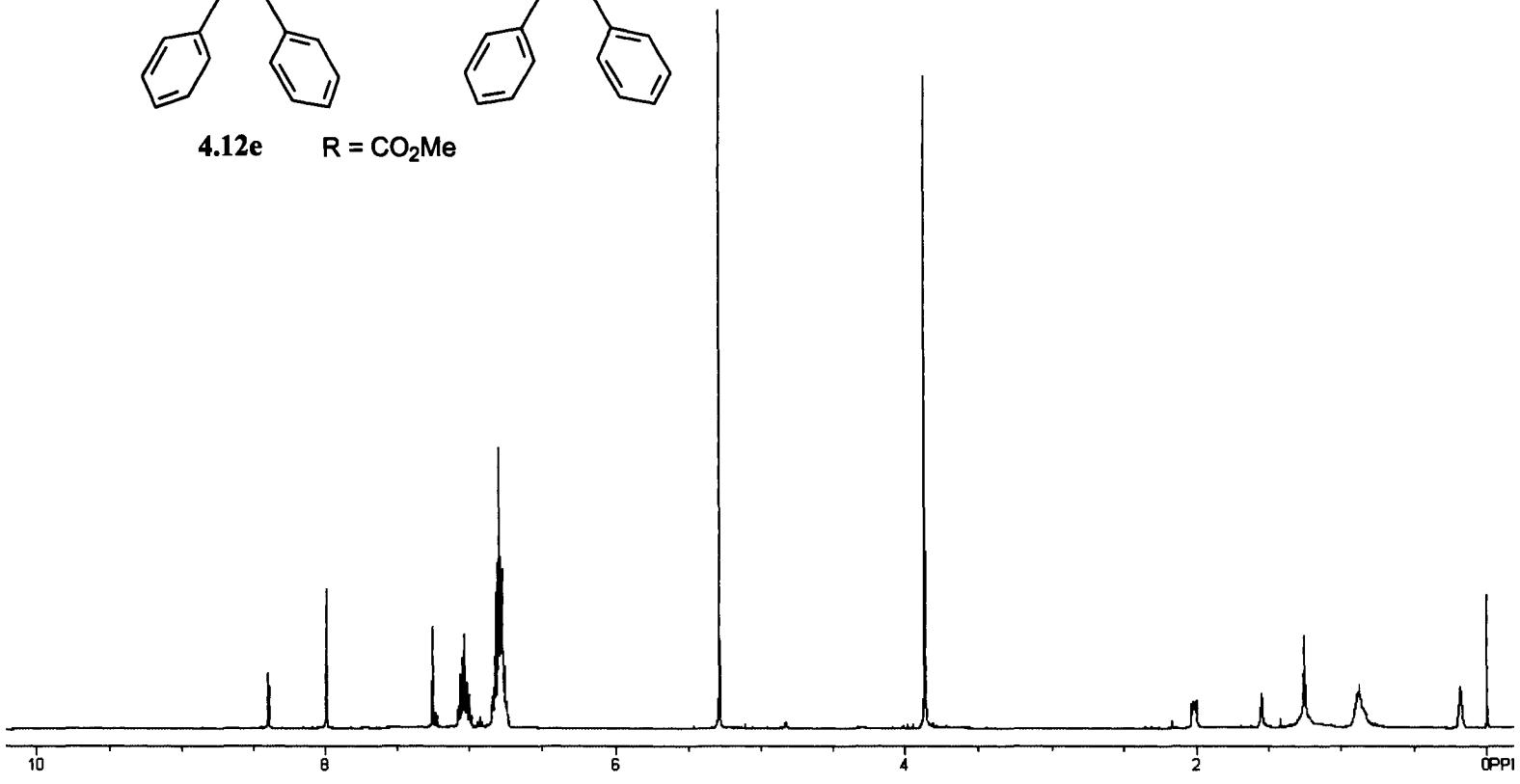

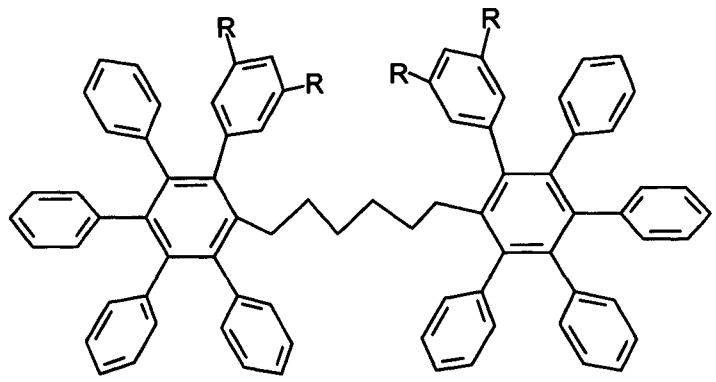

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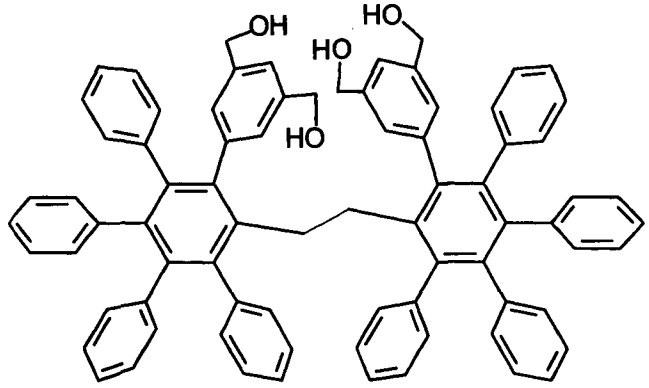
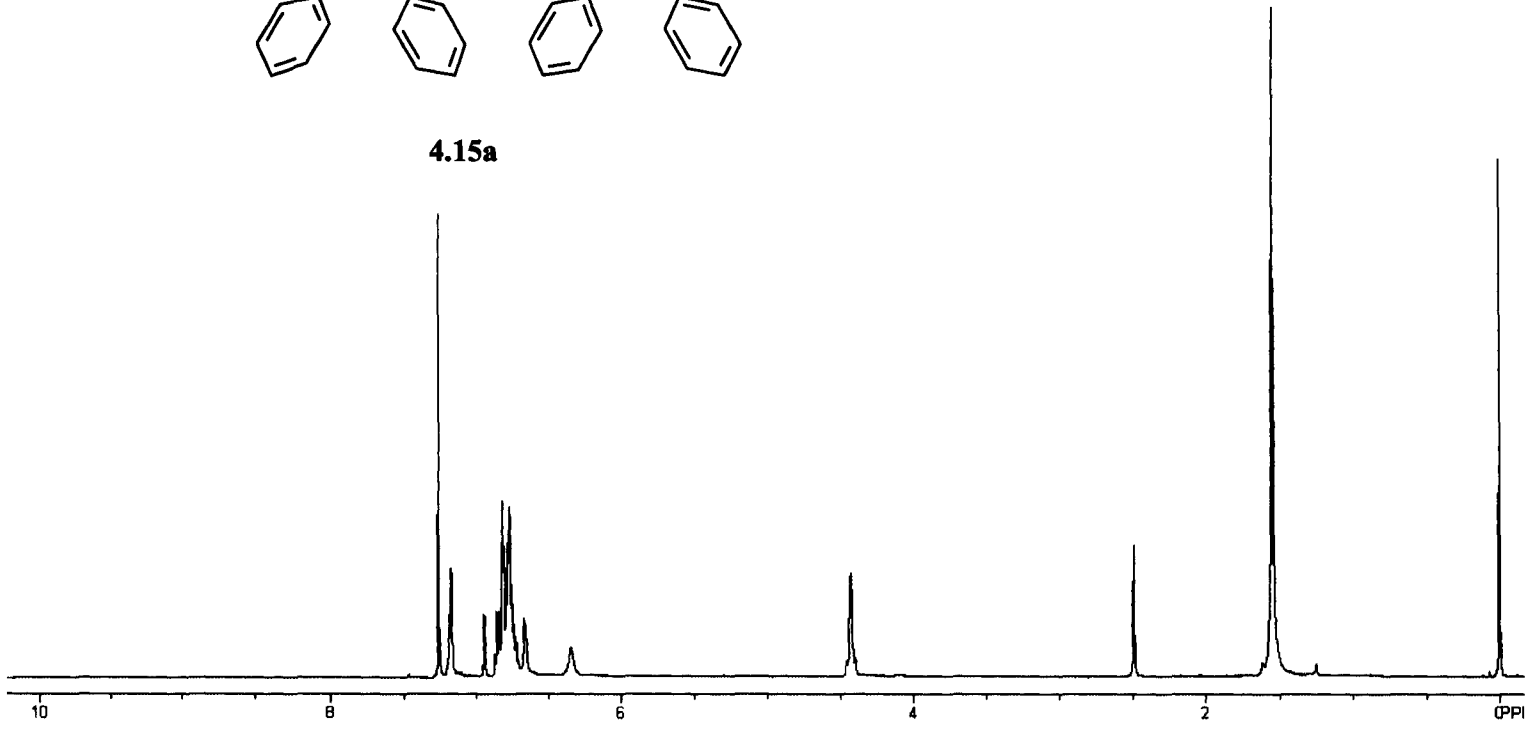
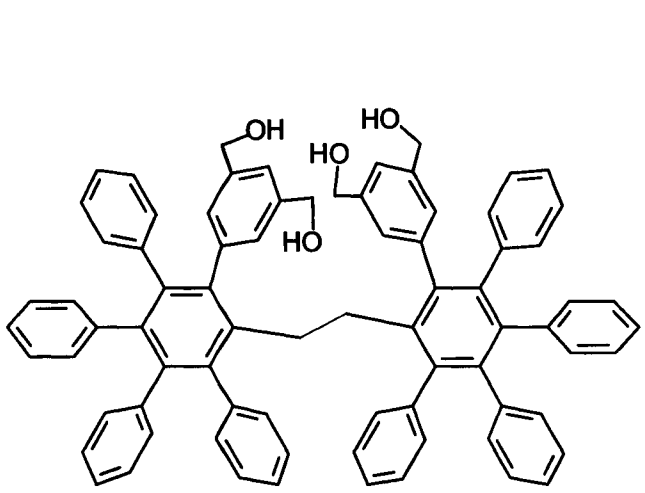
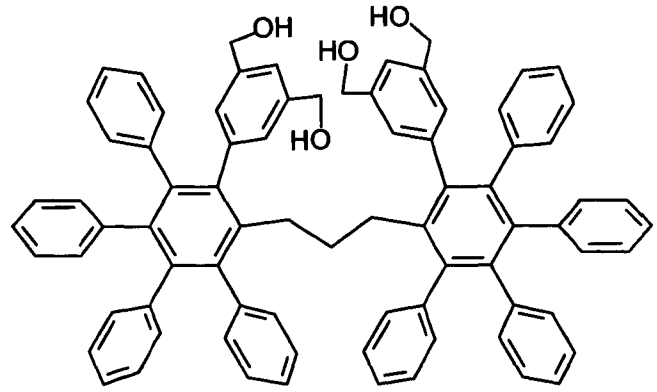


4.15a





4.15a



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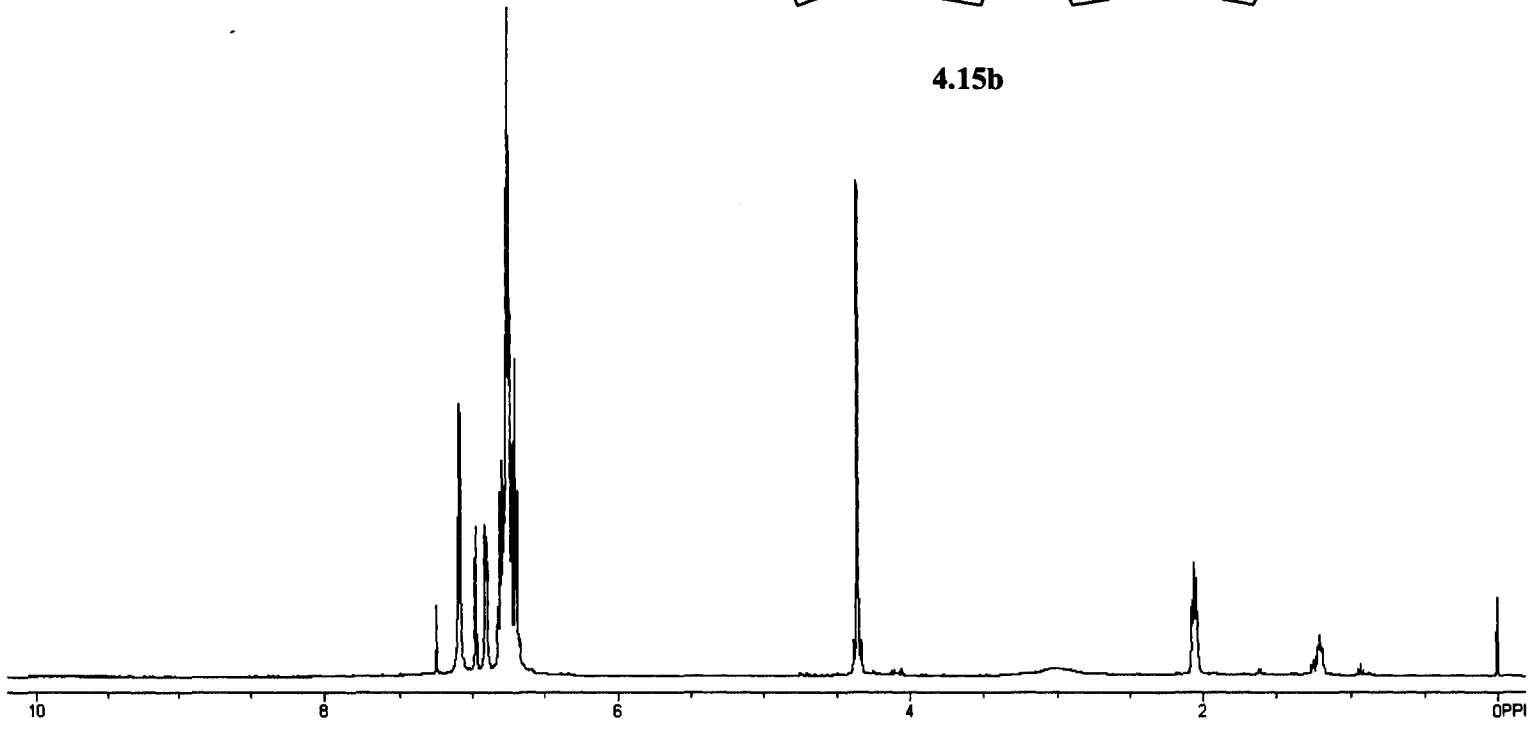

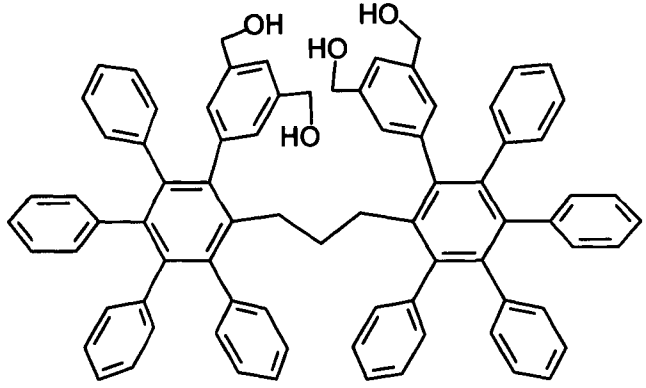

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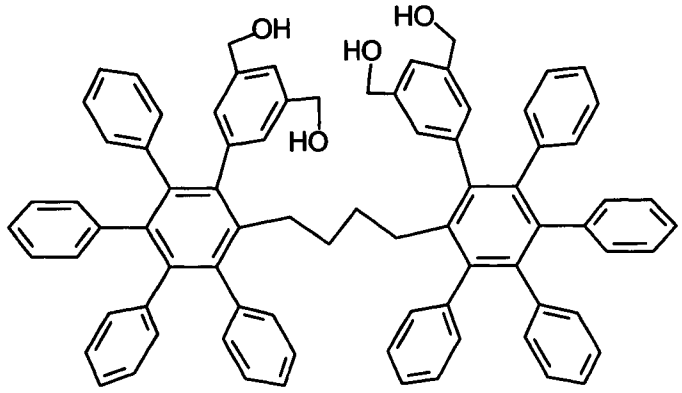

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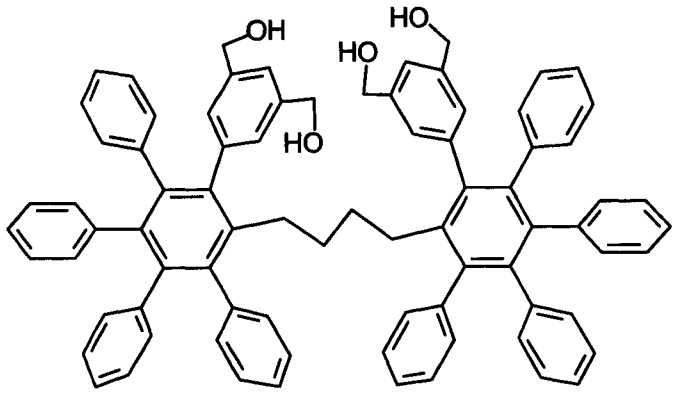

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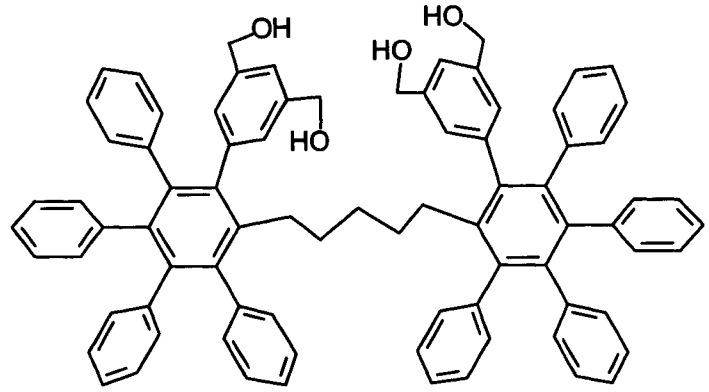

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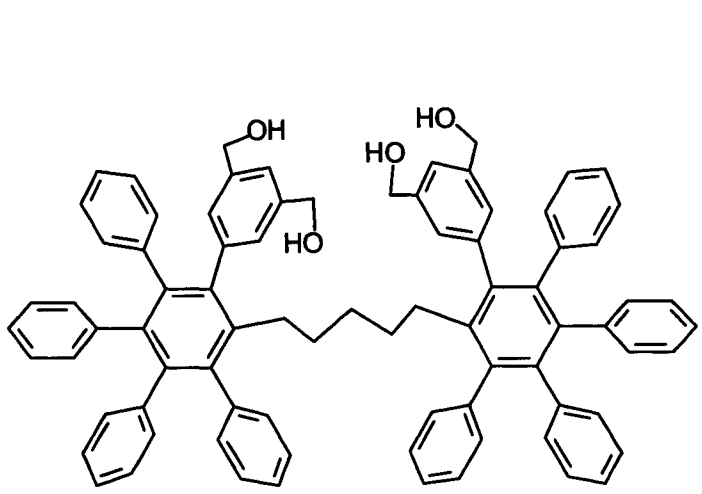

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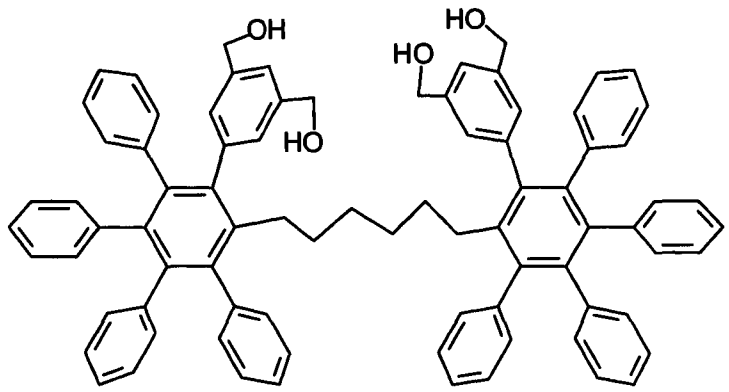

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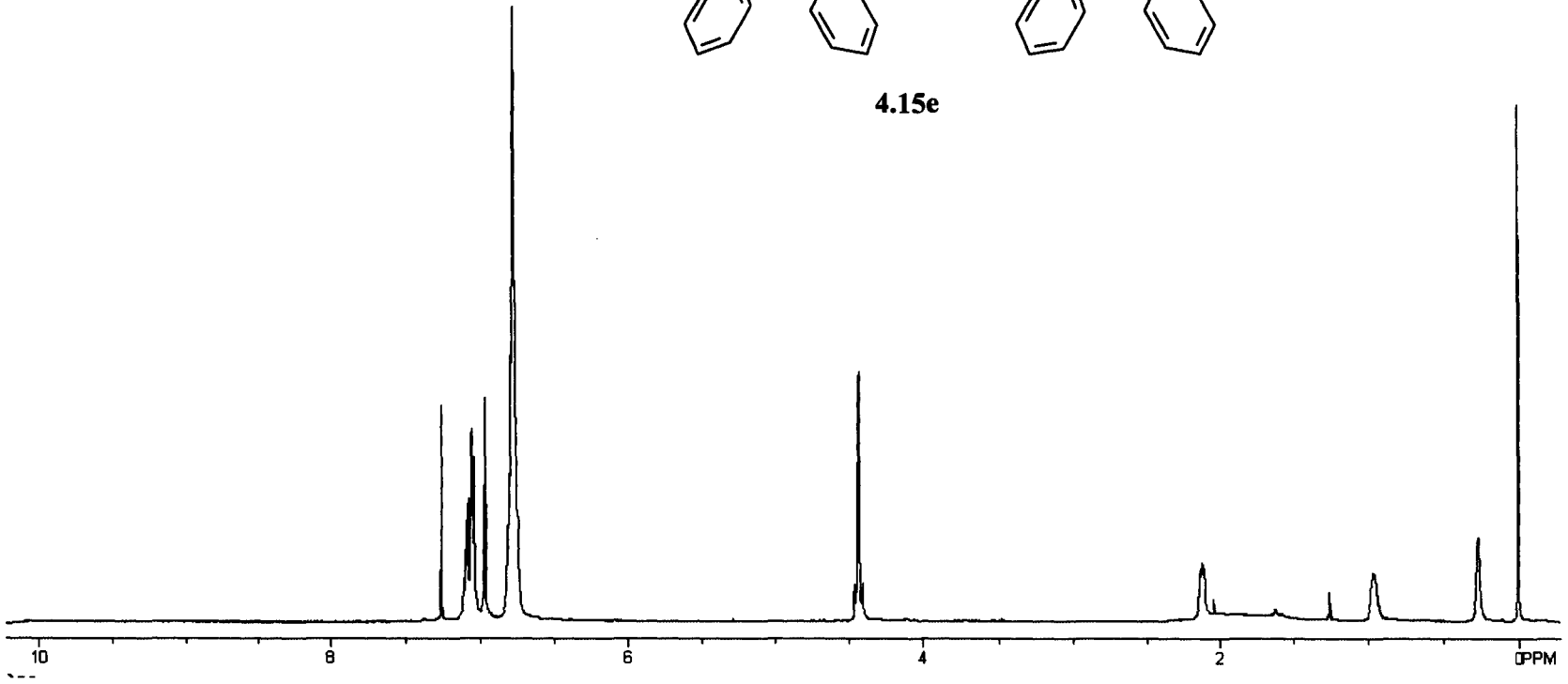

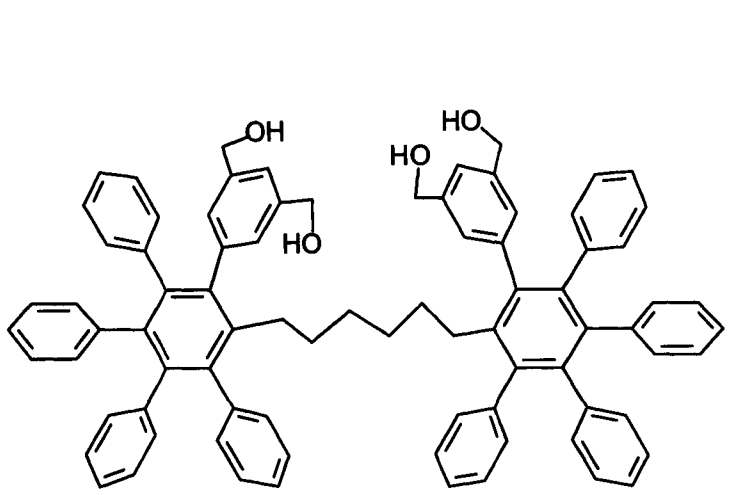

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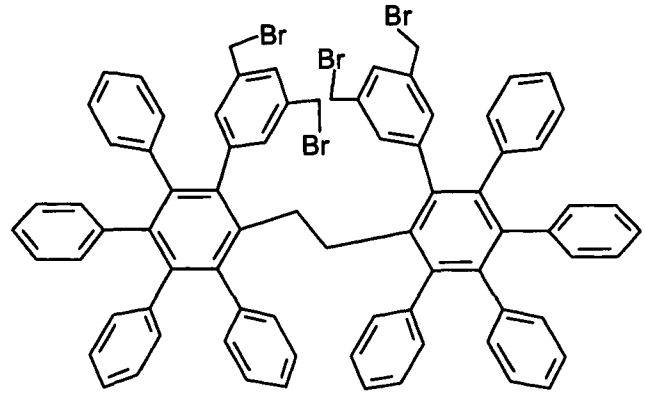

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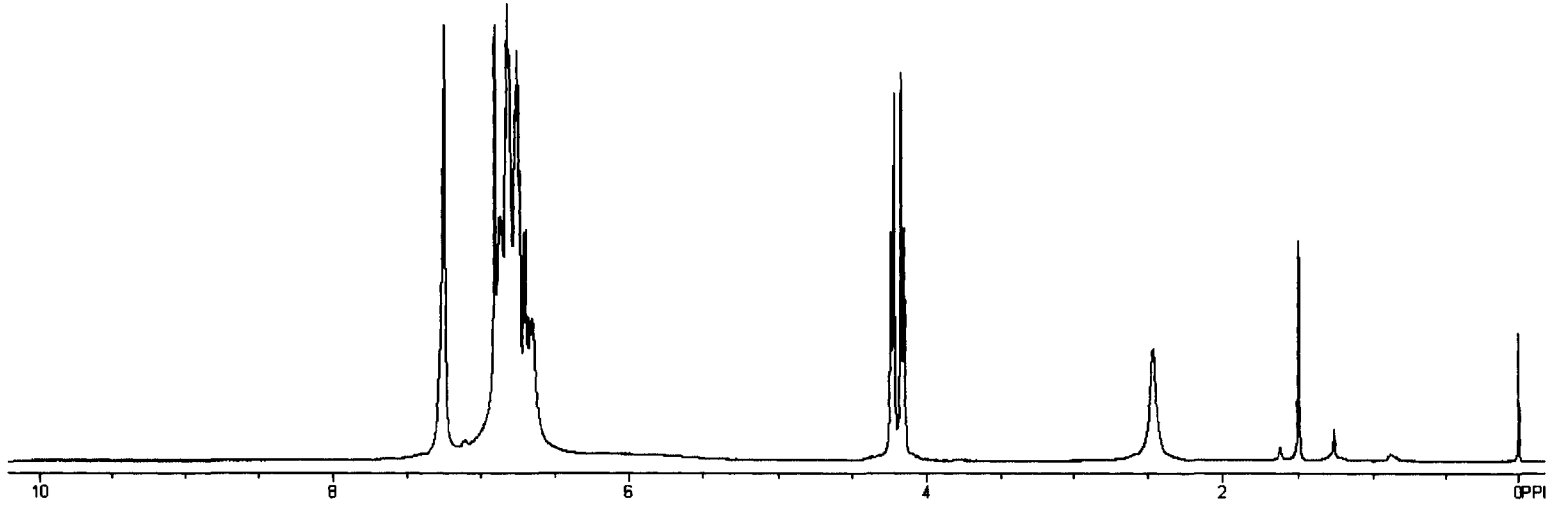

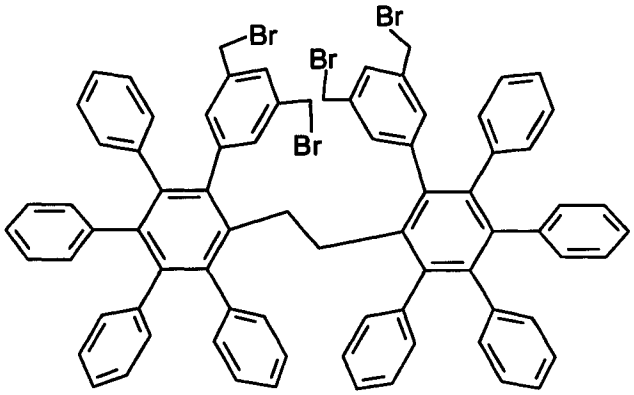

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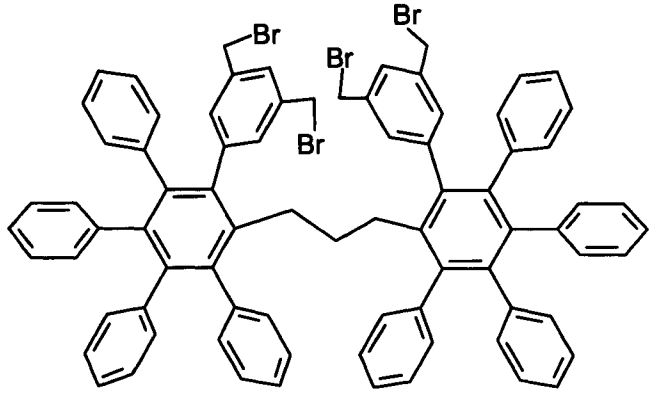

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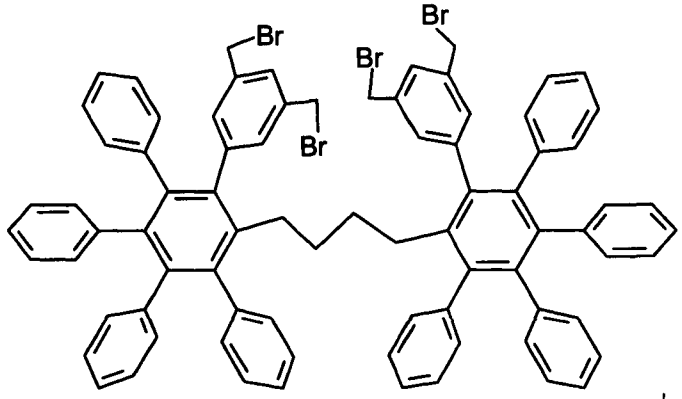

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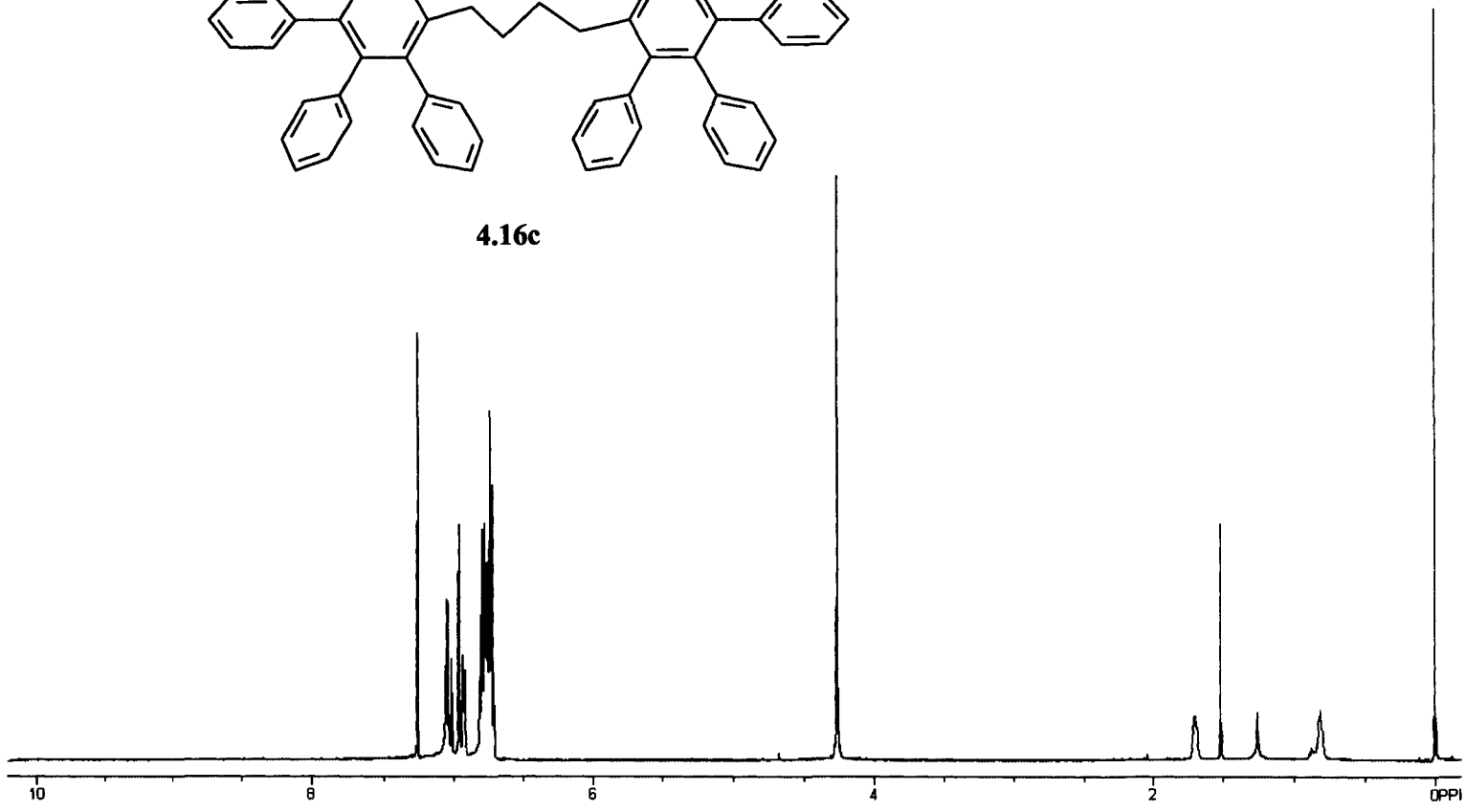

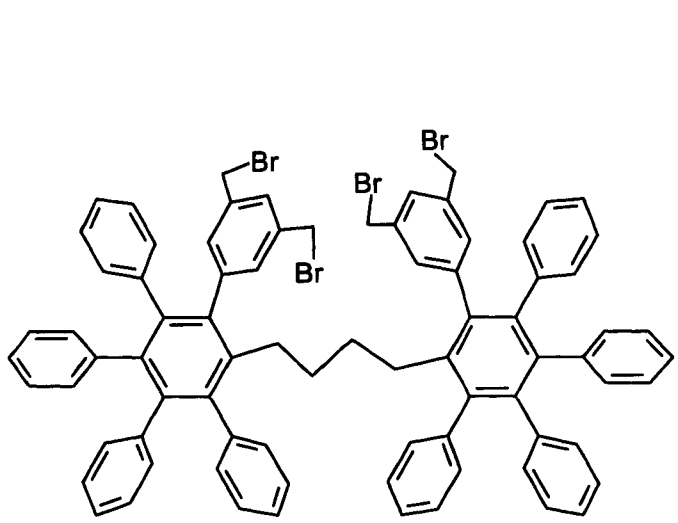

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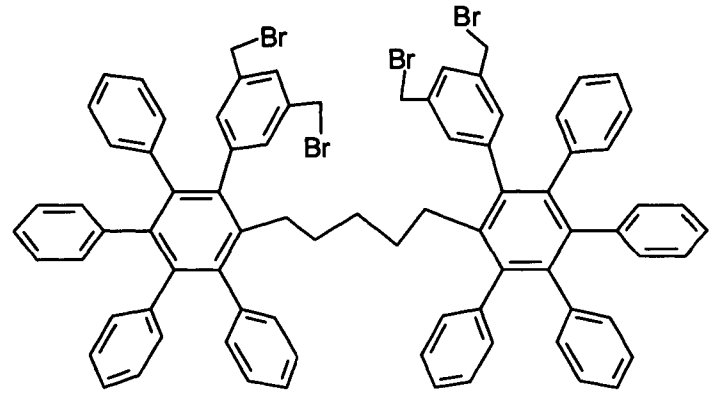

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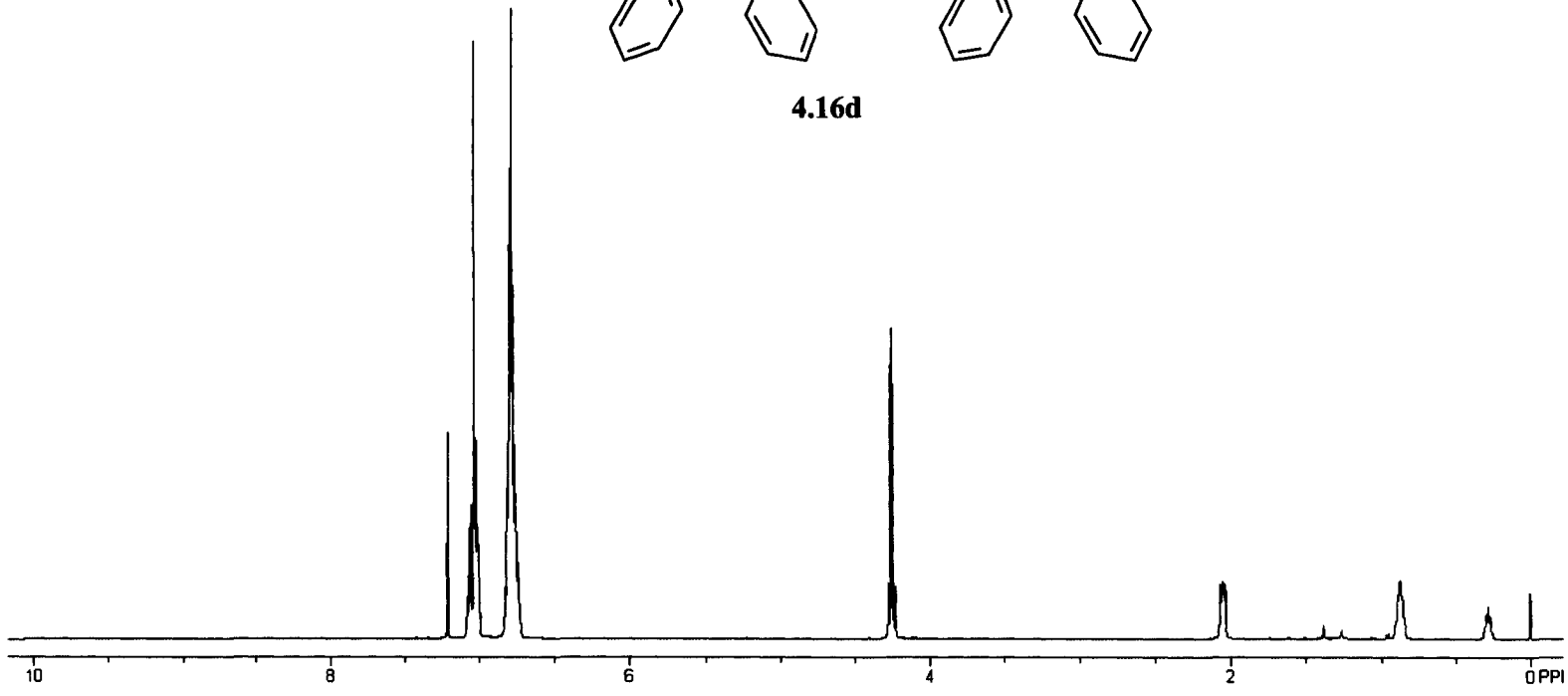

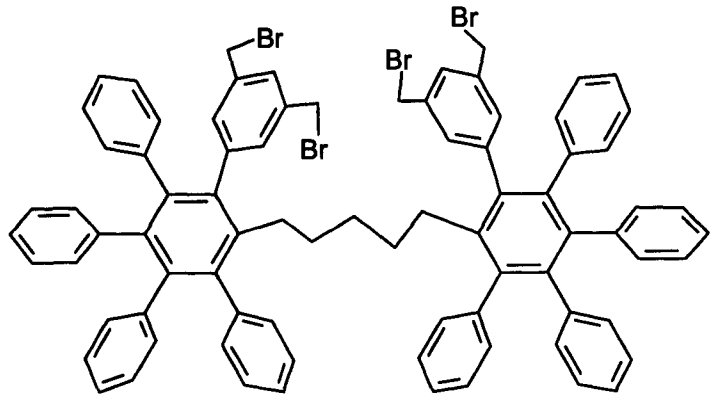

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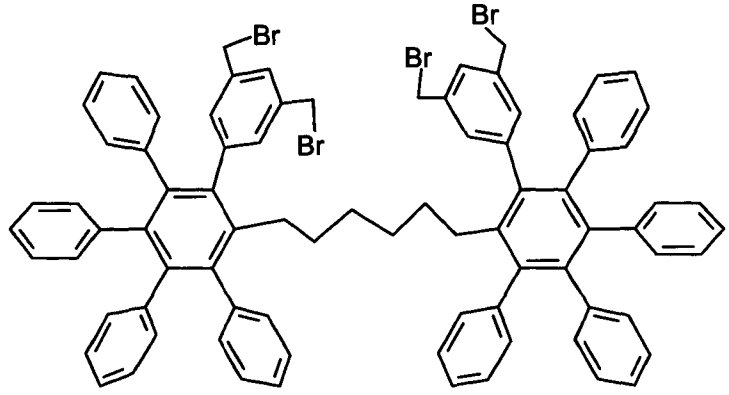

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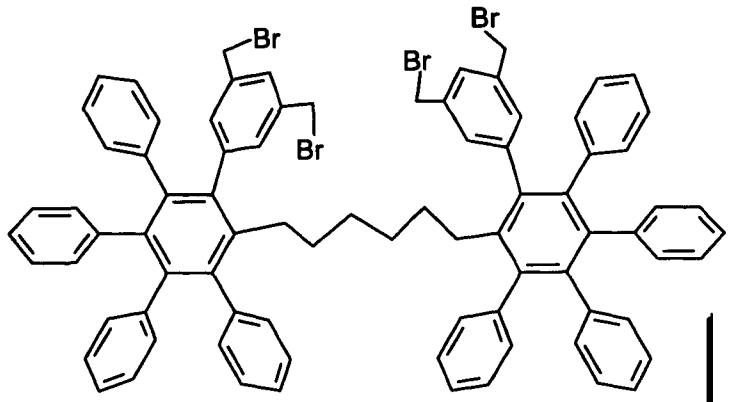

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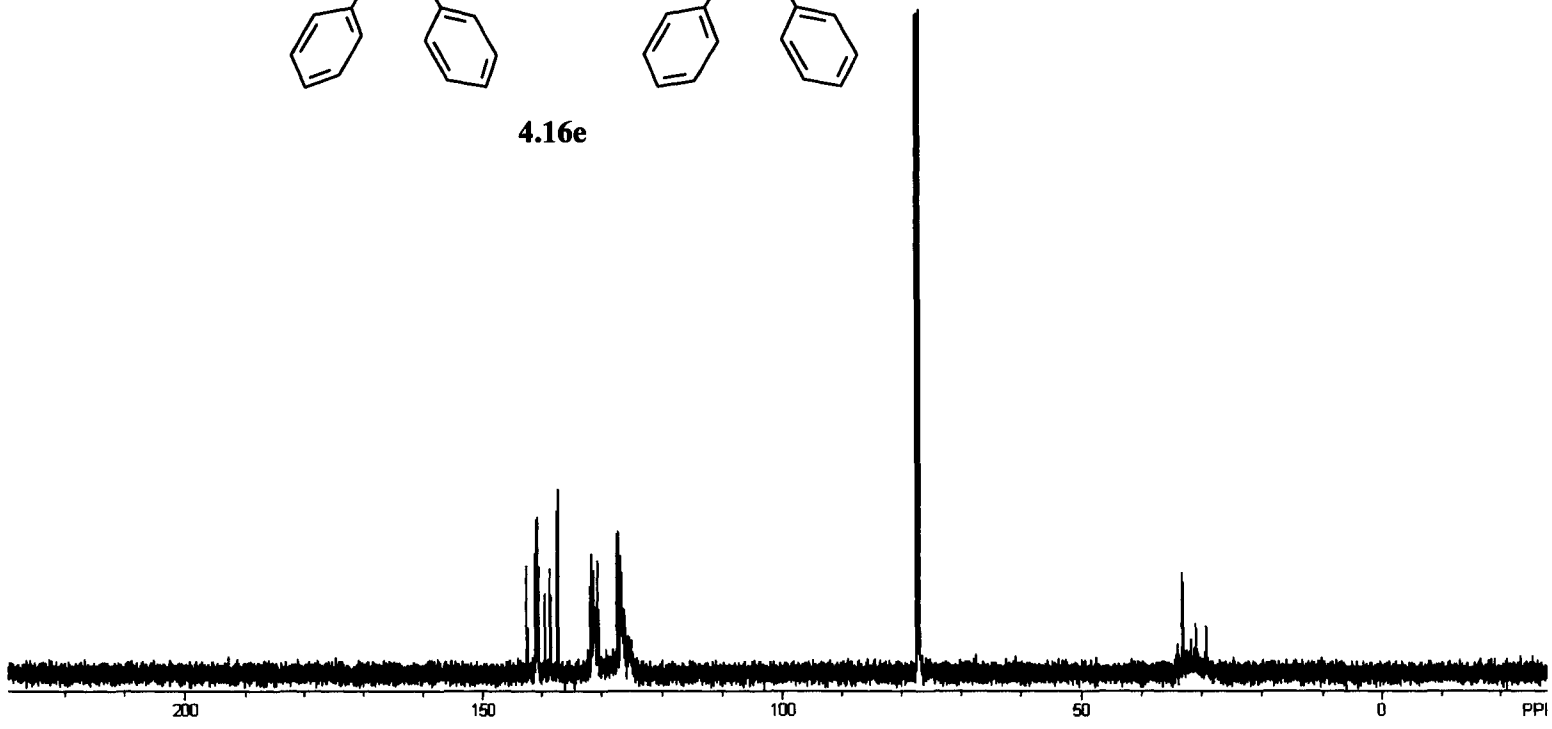

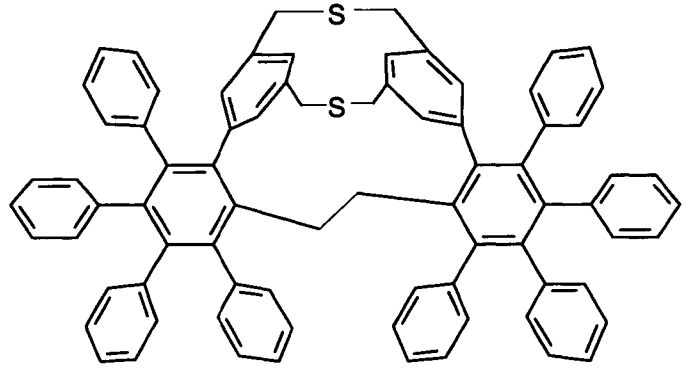

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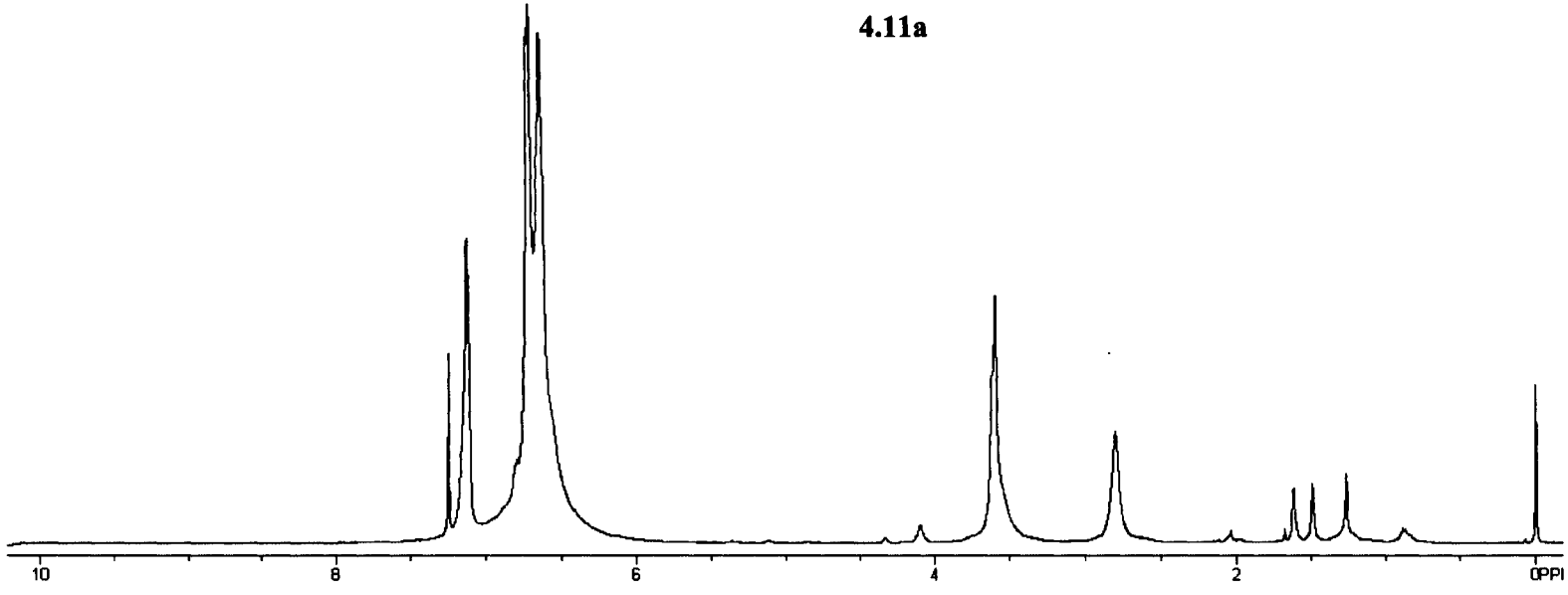

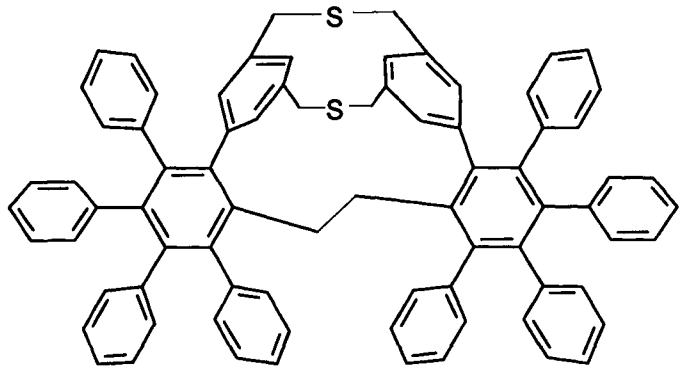

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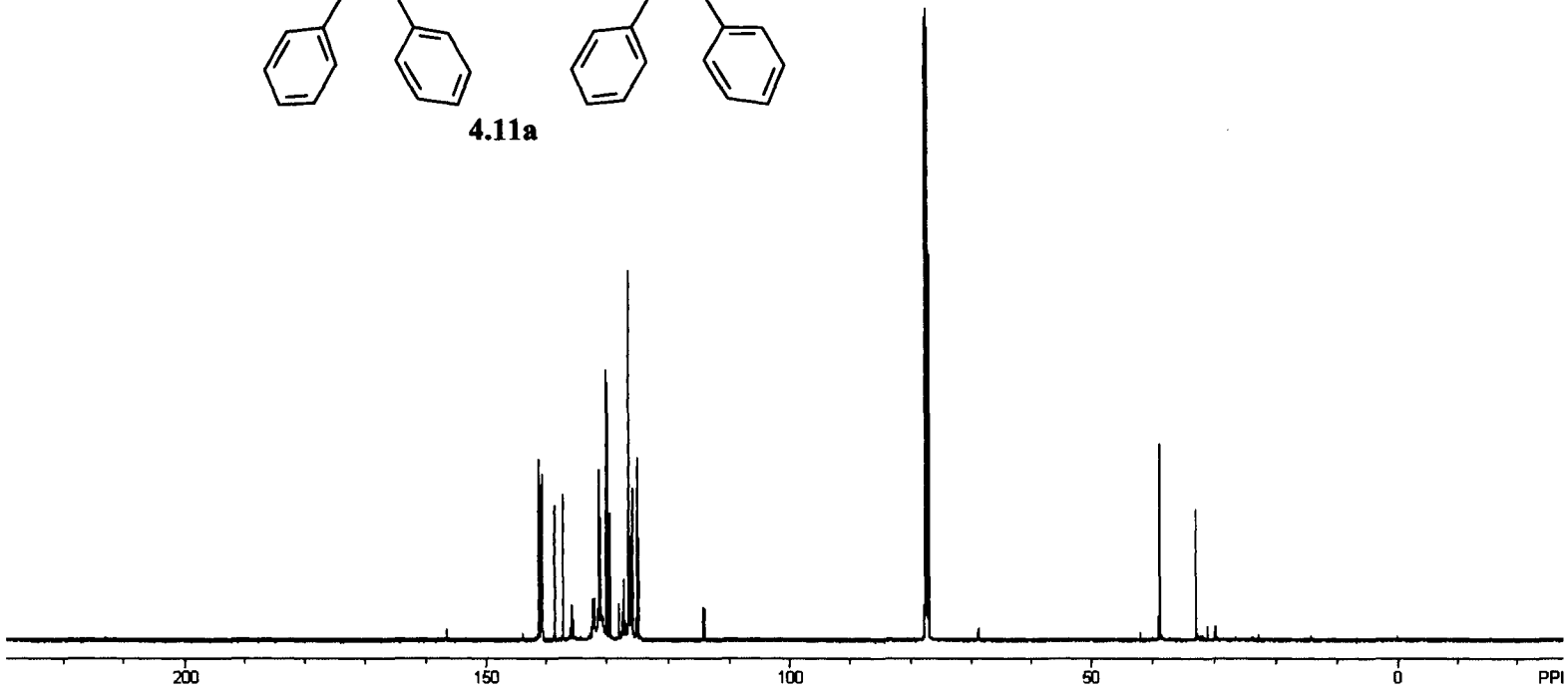

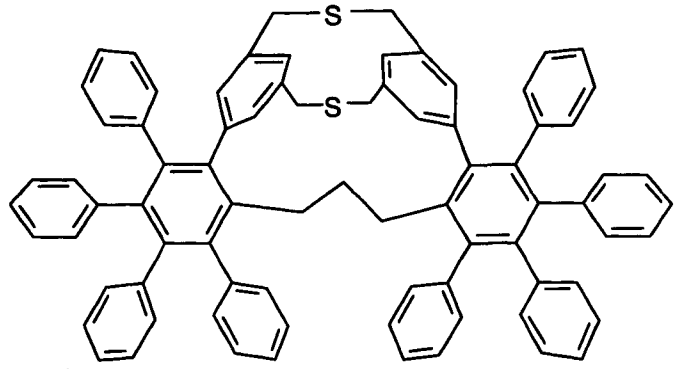

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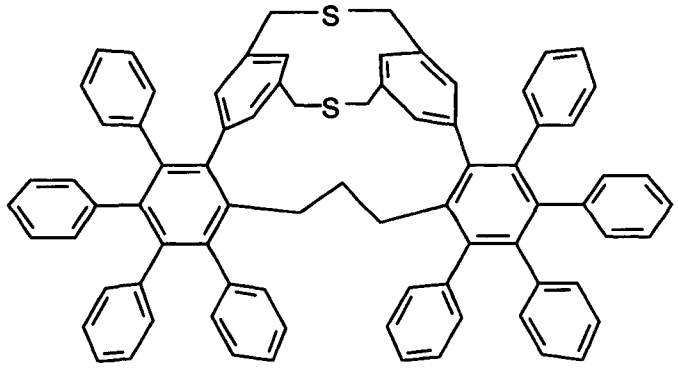

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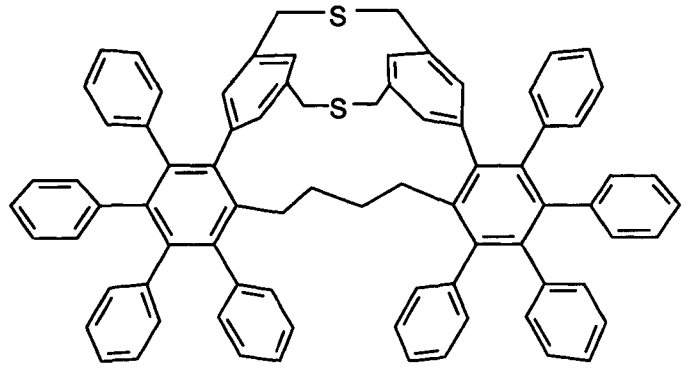

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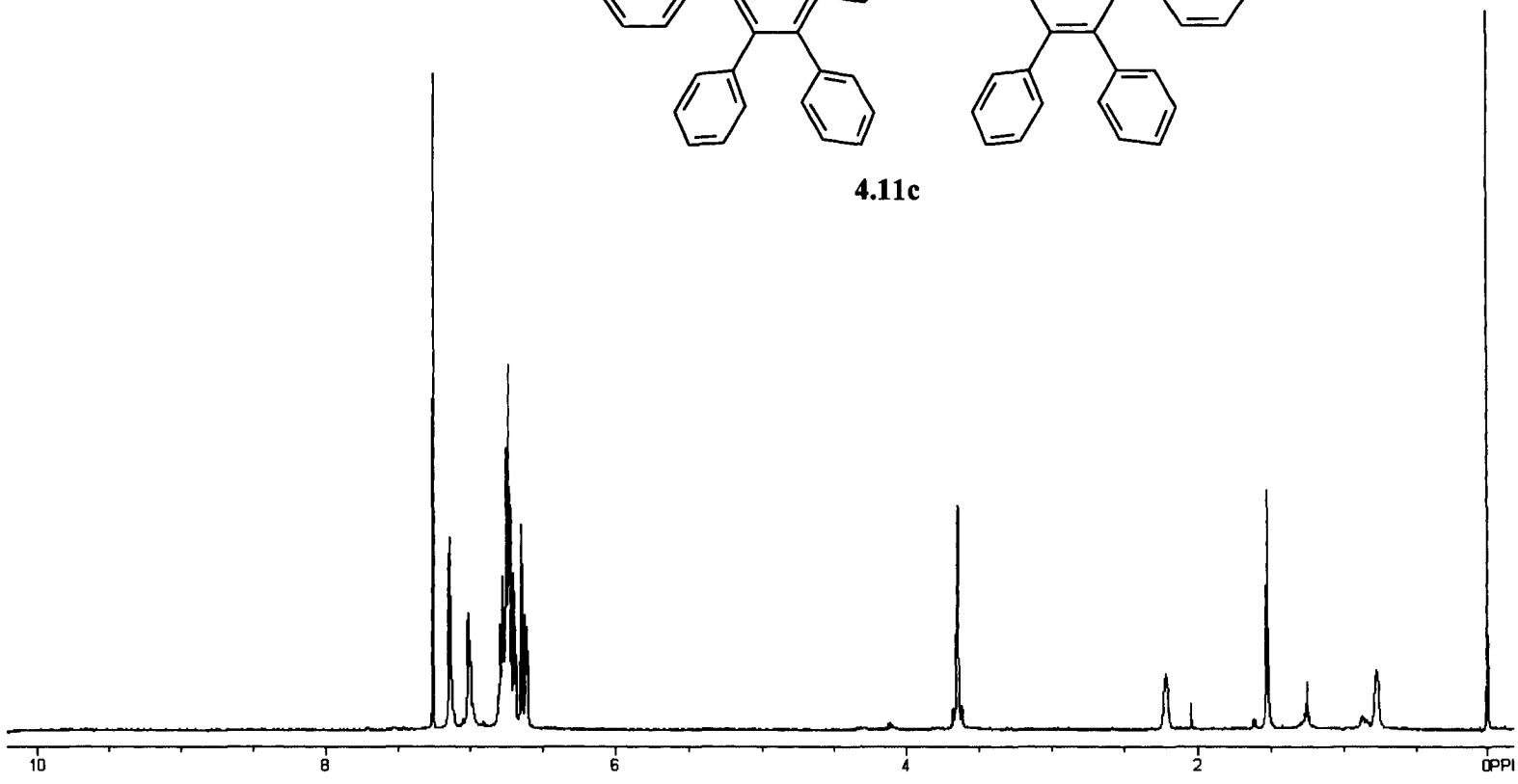

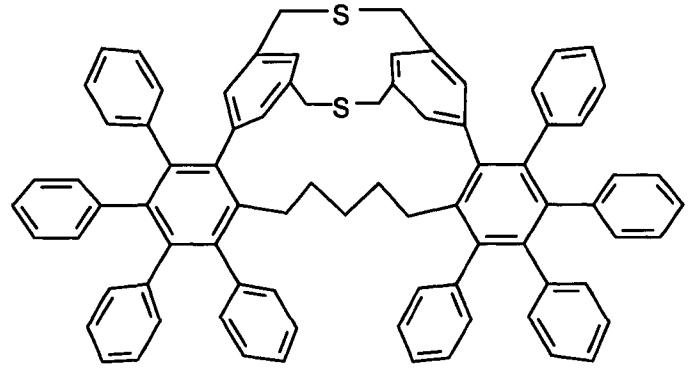

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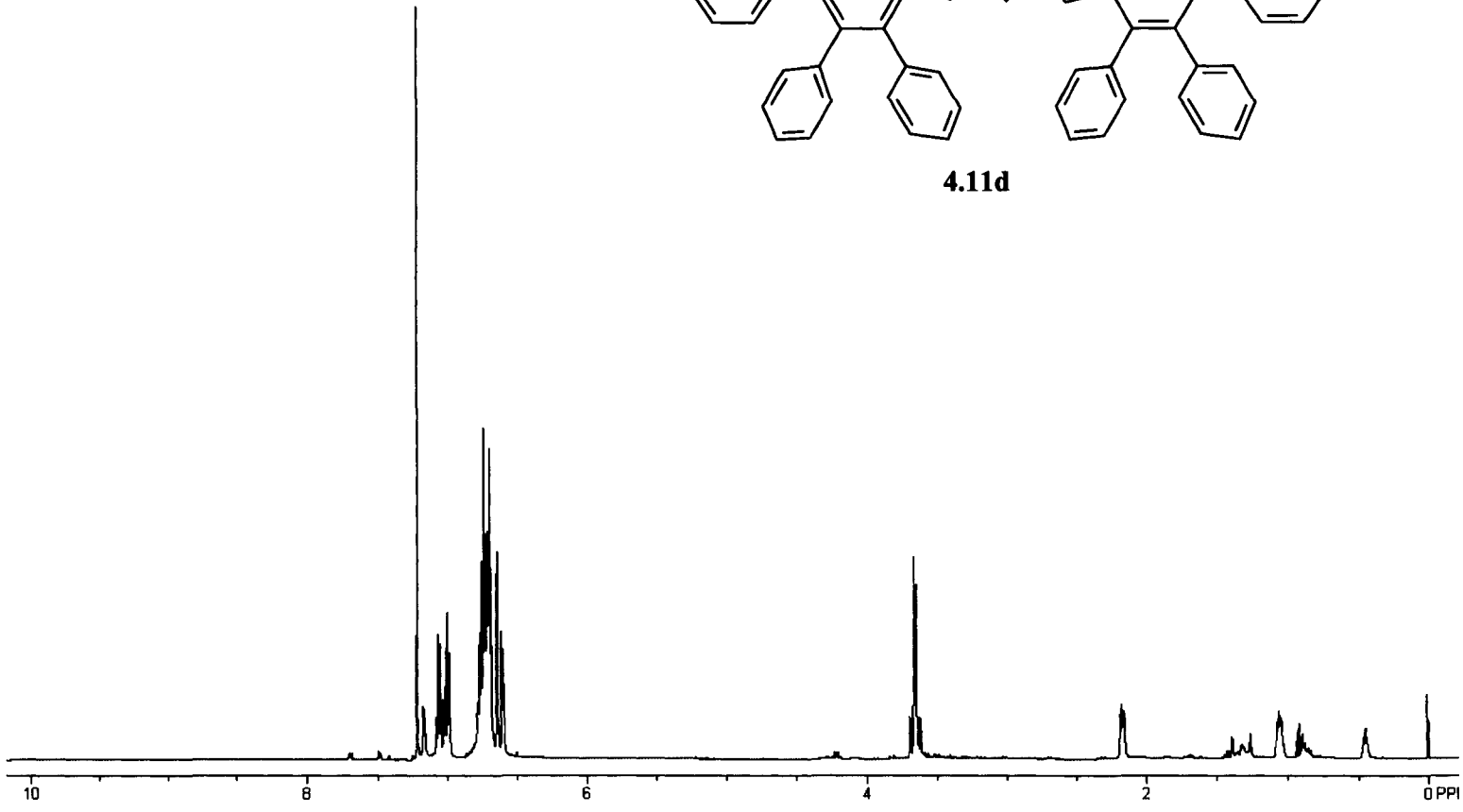

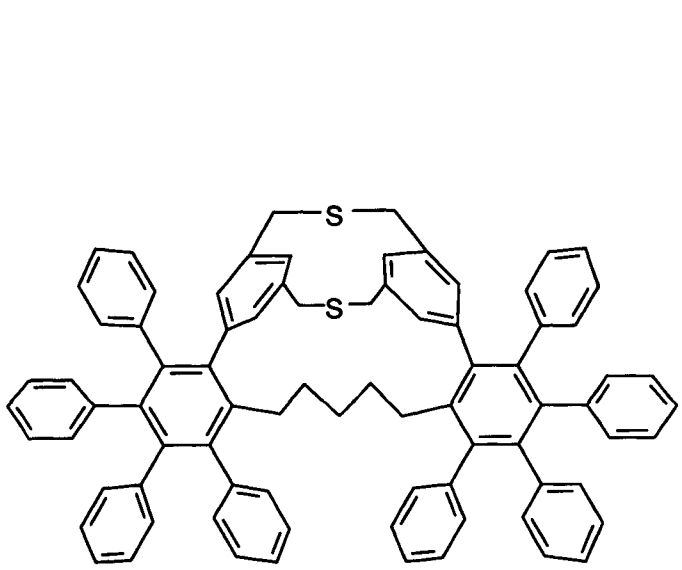

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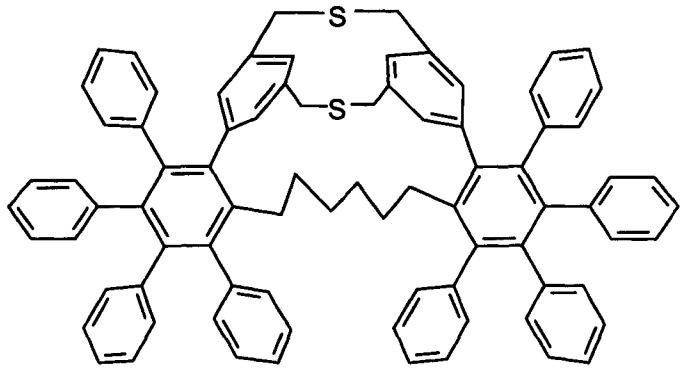

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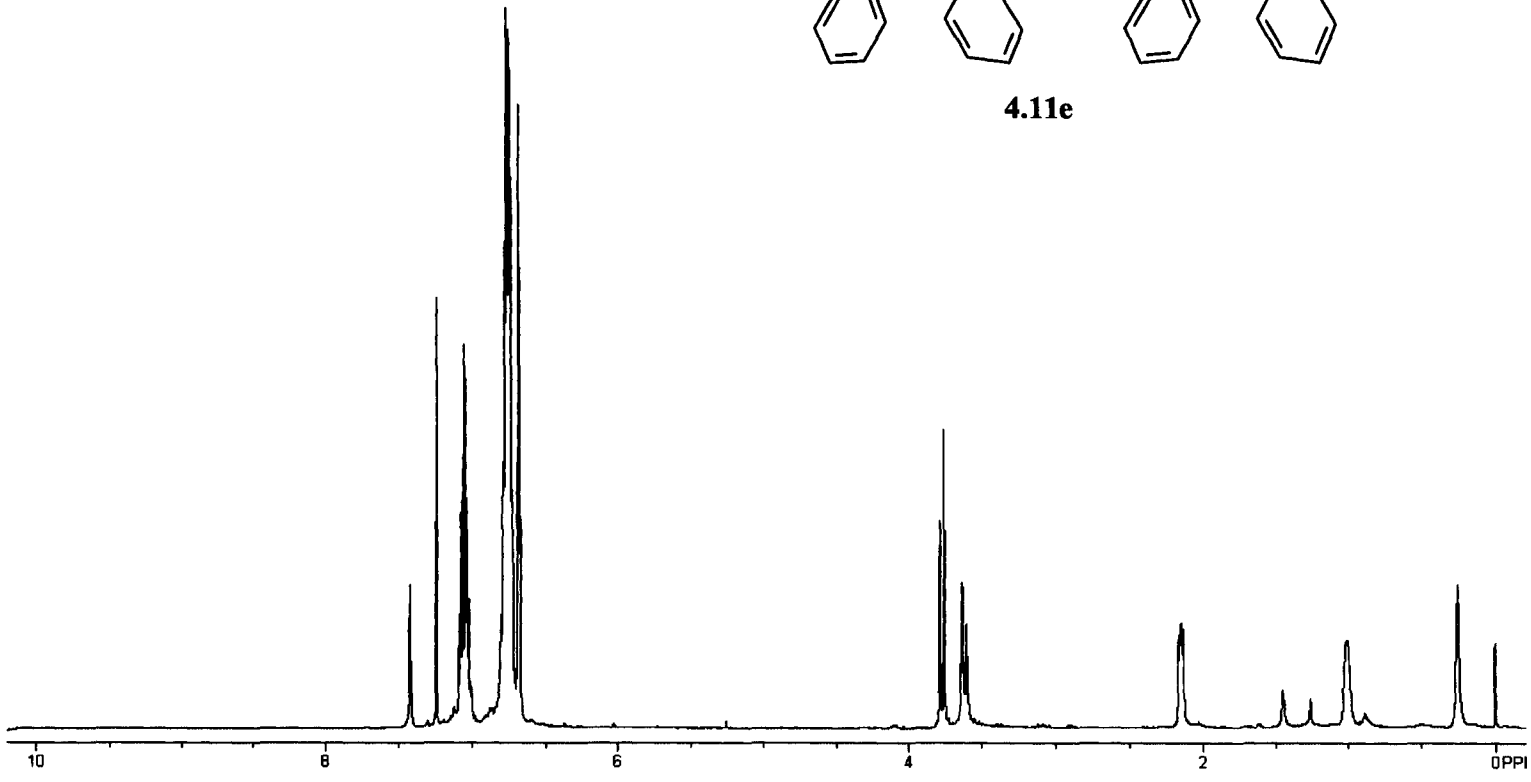

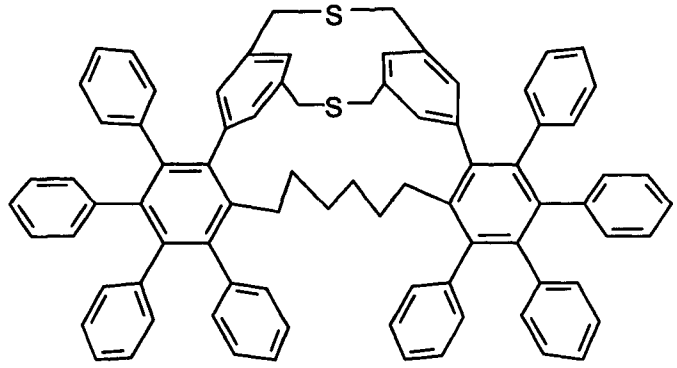

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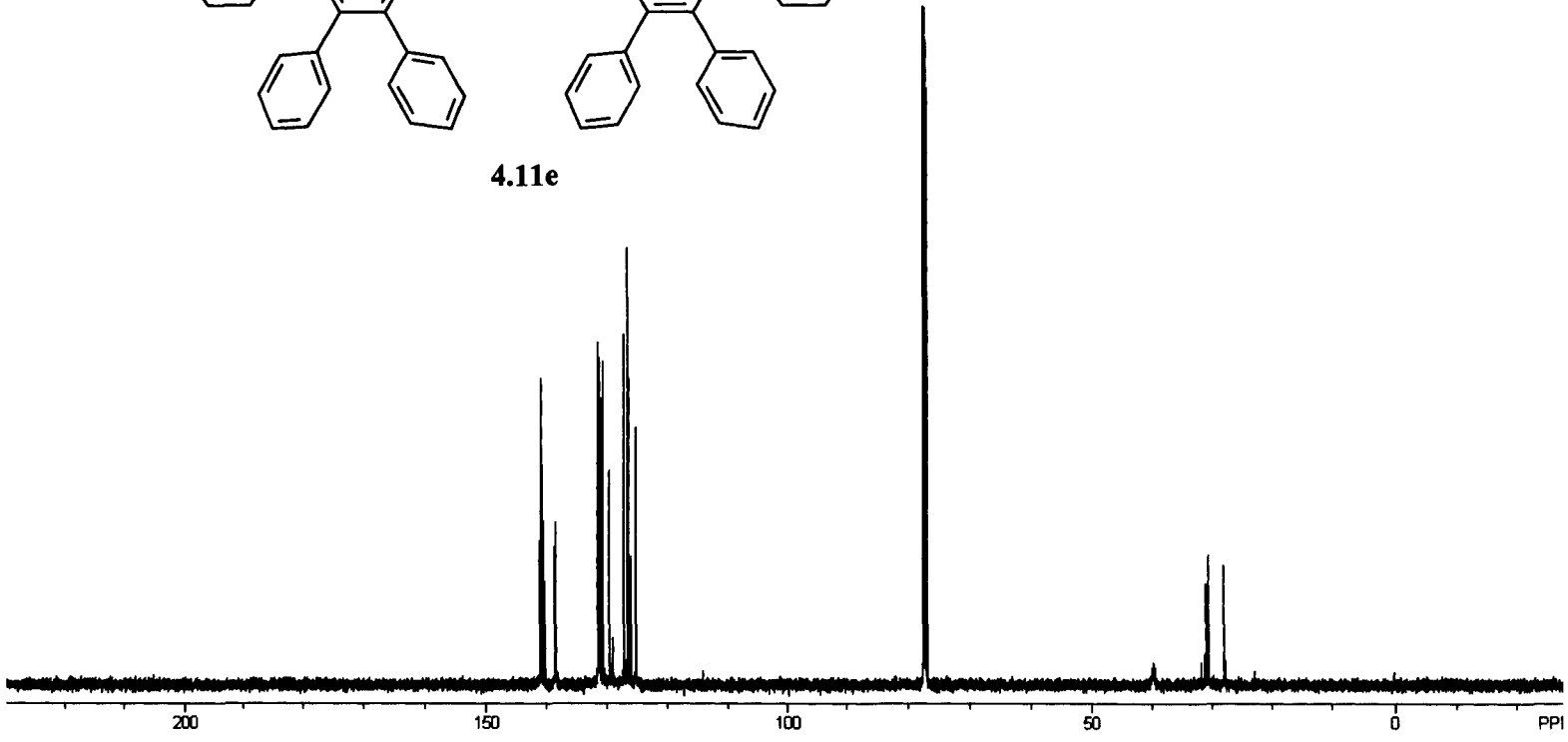

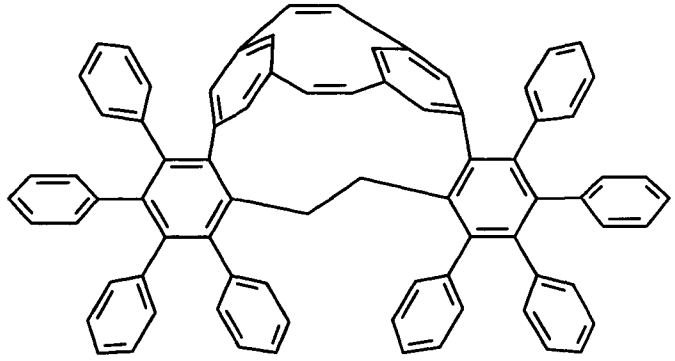

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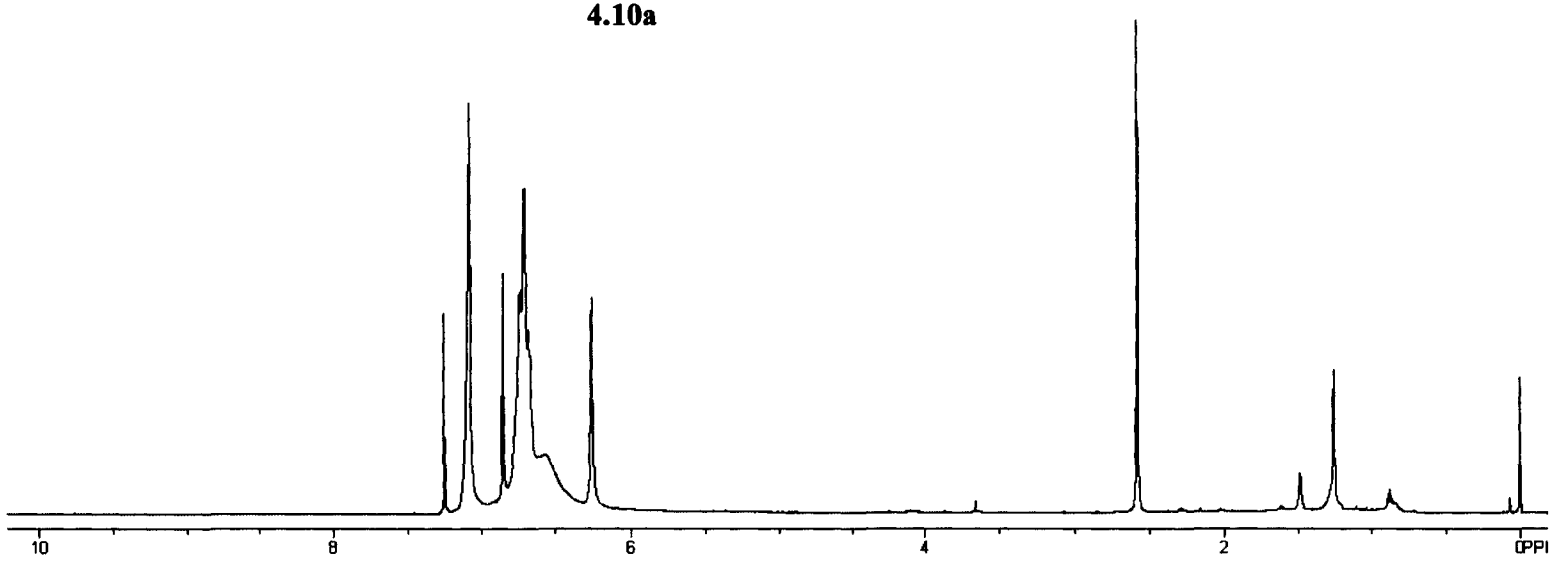

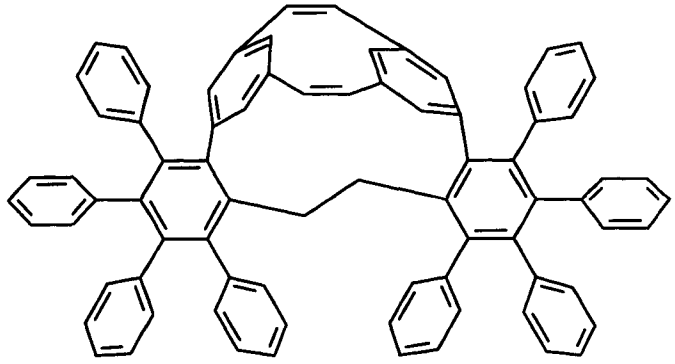

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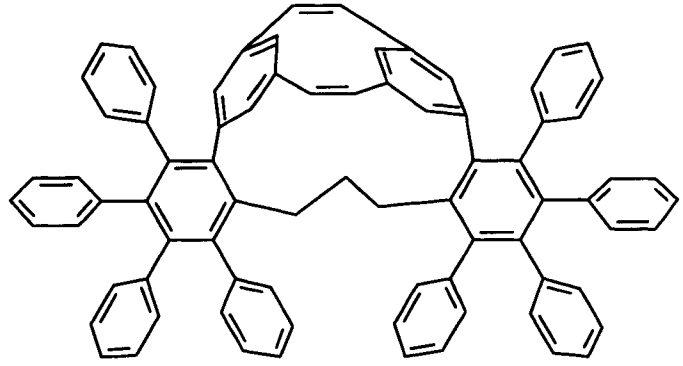

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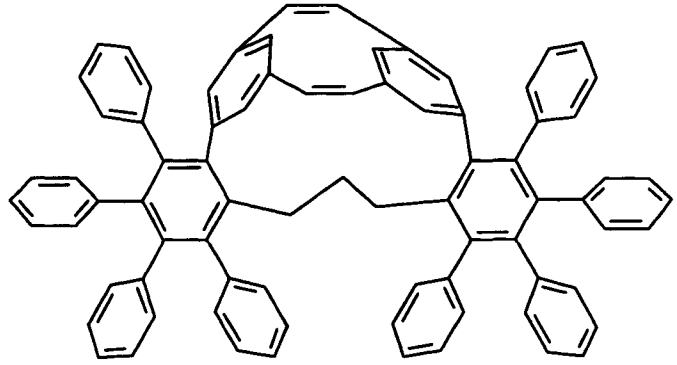

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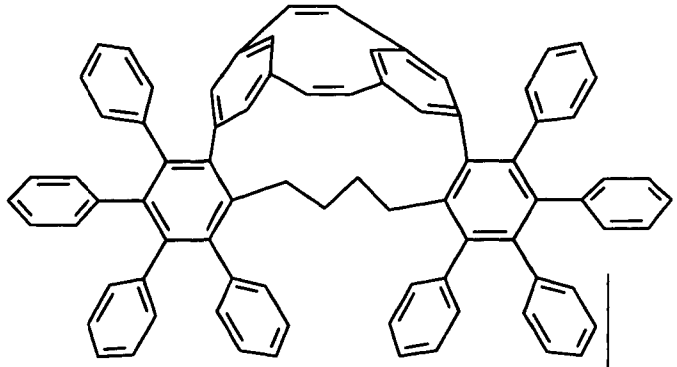

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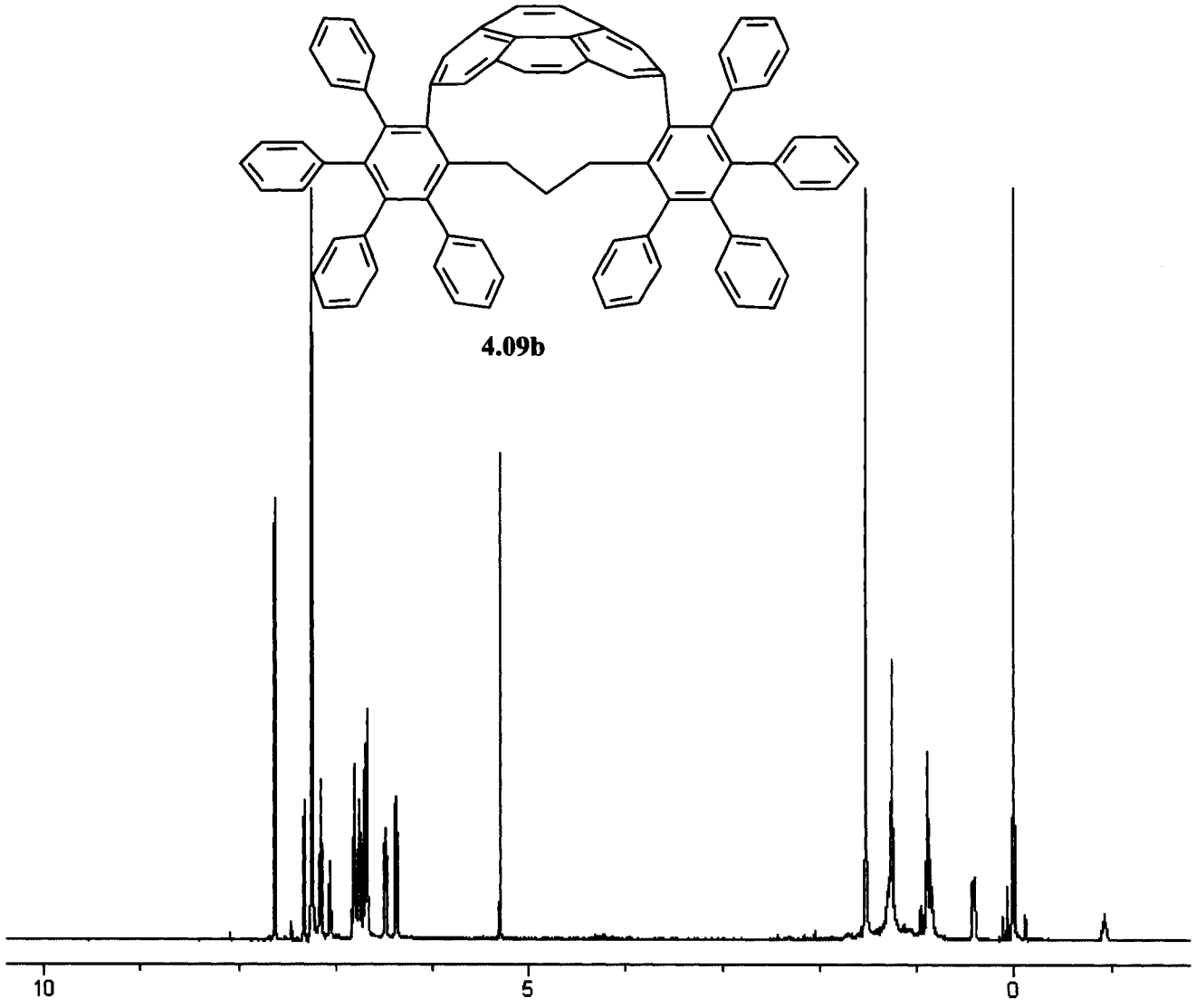

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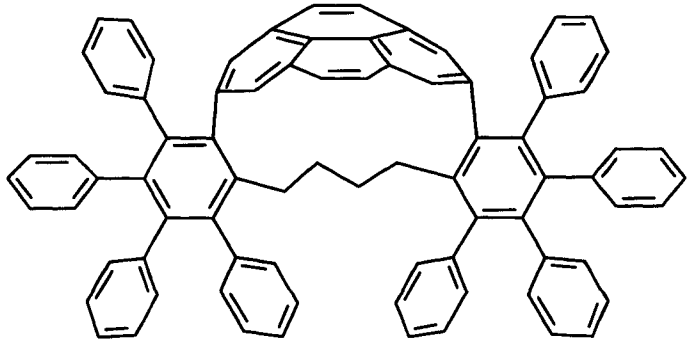

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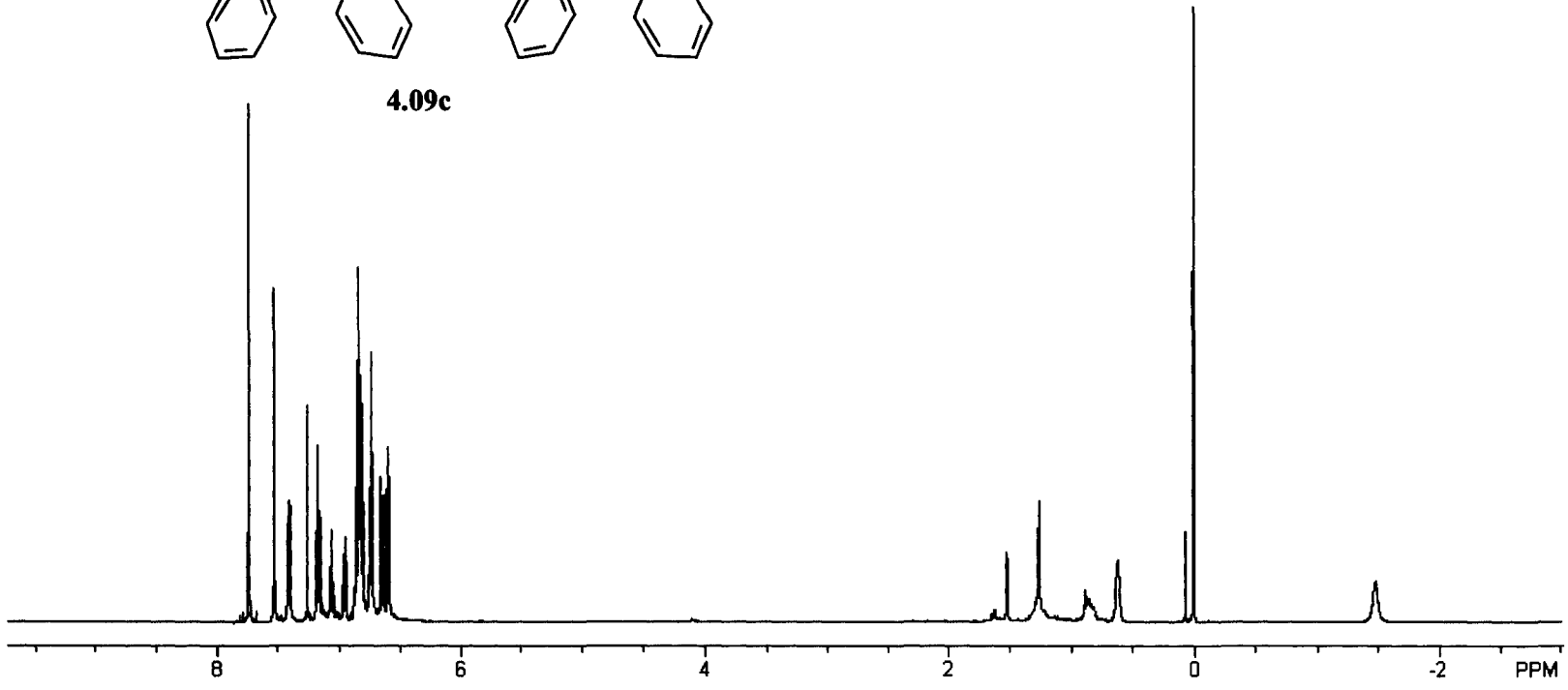

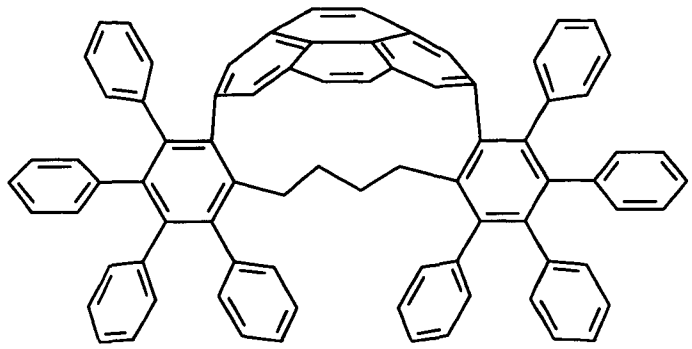

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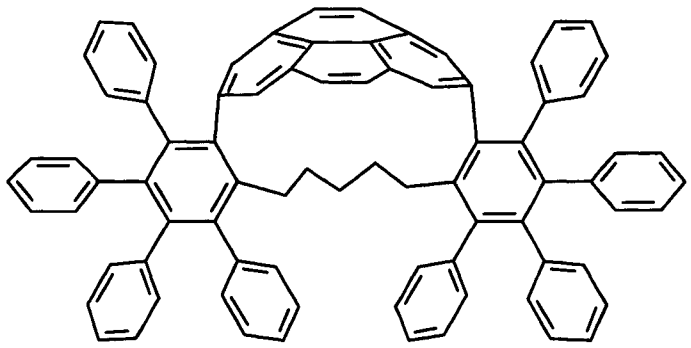

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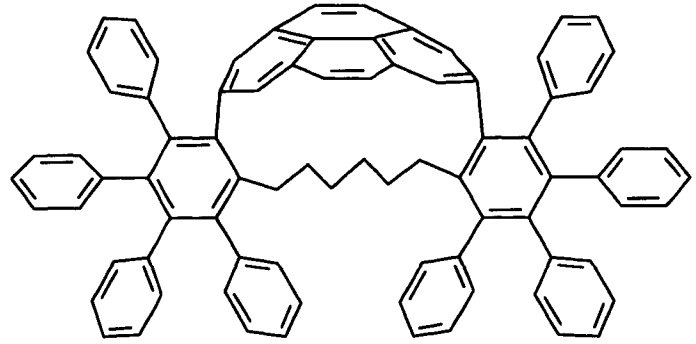

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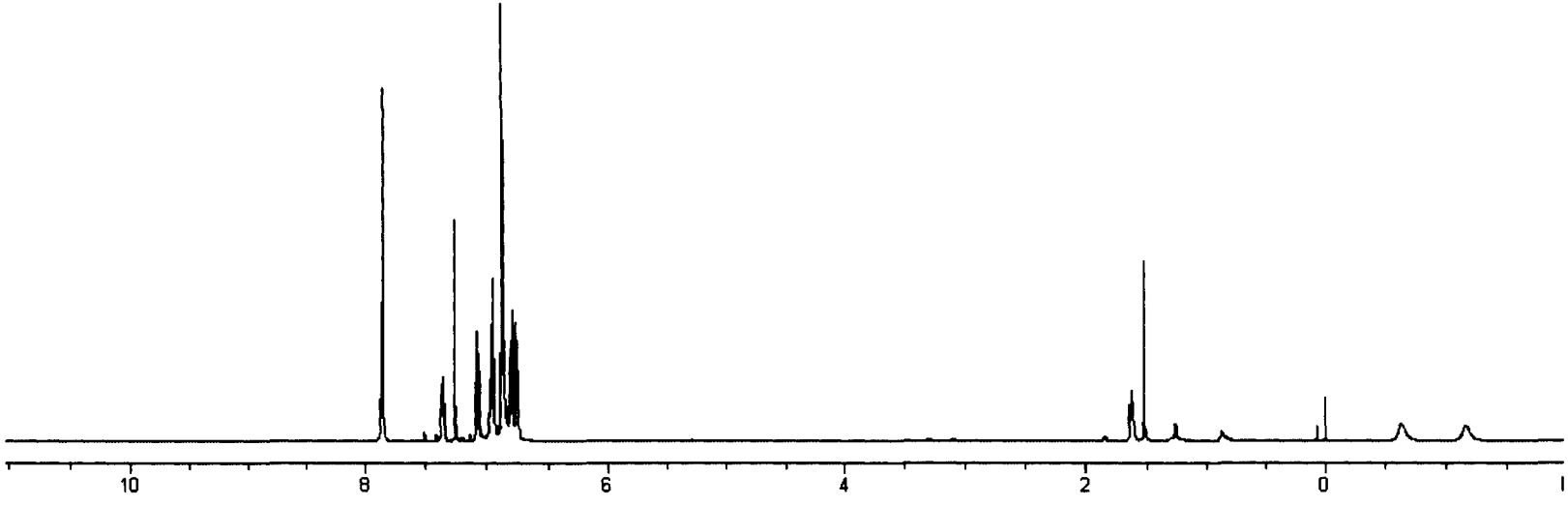

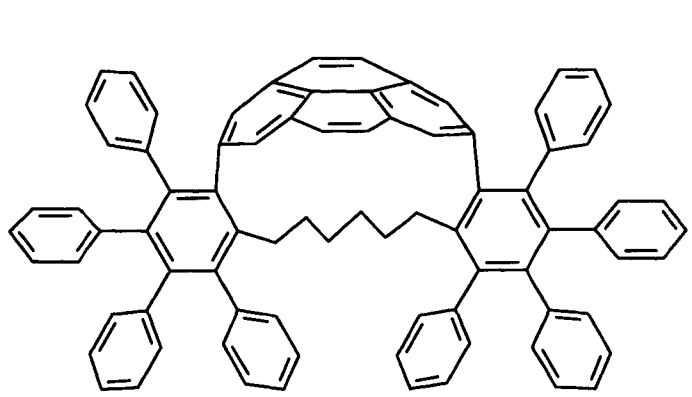

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