SYNTHESIS AND INVESTIGATION OF BIPHENYLENE PLANARIZED AROMATIC AND ANTI-AROMATIC SYSTEMS

by

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A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

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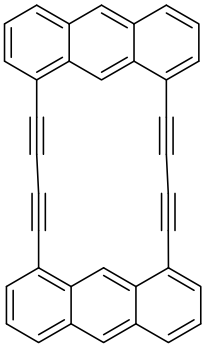
The aim of the dissertation was to develop synthetic routes to biphenylene planarized aromatic and anti-aromatic systems such as bis(diacetylene)biphenylene **109**, and 4,5,6,7-dibenzocyclobutathionin(biphenylenothionin) **110**. Bis(diacetylene)anthracene **209** was prepared by Nakagawa by dimerization of 1,8-diethynylanthracene **208**.

In the first part of this dissertation, biphenylene systems were synthesized by different methods: by aryne generation, coupling a biphenyl and by extrusion of gas. Key intermediate 1, 8-diacetylene biphenylene **114** was synthesized successfully by coupling dihalo substituted biphenylene and alkyne.

Nucleophilic addition of sulfide ion to 1, 8-diacetylene biphenylene **114**, instead of an expected nine-membered ring compound 4,5,6,7-dibenzocyclobutathionin **110**, gave an unexpected eight-membered ring compound (*Z*)-1-methylene-1*H*-biphenyleno[1,8-*cde*]thiocine **189**, with structure confirmed by DEPT ^{13}C NMR, IR , X-ray and GC-MS.

Two comparisons of 4,5,6,7-dibenzocyclobutathionin **110**, (*Z*)-5, 6-dihydrodibenzo[*d*,*f*]thionine **111** and dibenzo[*d*,*f*]thionine **112**, were synthesized and NMR data were analyzed and compared.



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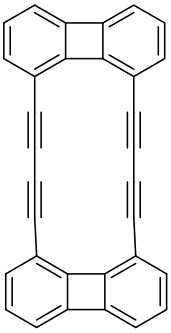

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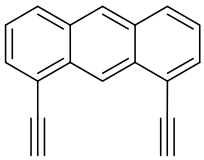

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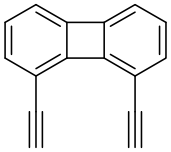

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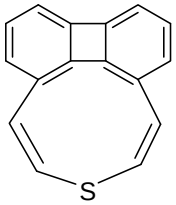

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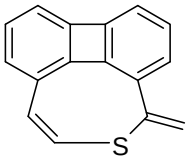

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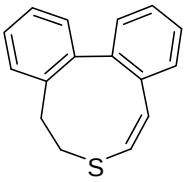

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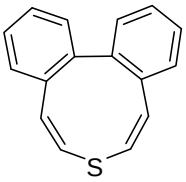

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1.1 Aromaticity

1.1.1 History

The history of "aromaticity", a fundamental chemical concept [1-6], began with the isolation of benzene by Michael Faraday in 1825[7]. Many definitions or criteria for characterizing aromaticity have been considered subsequently. Some milestones are:

Before 1825 distinctive "aromatic" smell

Before 1865 high carbon-hydrogen ratios - stable despite considerable unsaturation

1865 benzene structure (Kekulé) [8]

1866 substitution is more favorable than addition (Erlenmeyer) [9]

1910 aromatic compounds have exalted diamagnetic susceptibilities (Pascal) [10]

1925 electron sextet and heteroaromaticity (Annit-Robinson) [11]

1931 theory of cyclic $(4n+2)$ π systems (Huckel) [12]

1936 ring current theory - free electron circulation around the benzene ring (Pauling) [13]

1937 London diamagnetism - π electron current contribution to magnetic susceptibility [14]

1956 ring currents effects on NMR chemical shifts (Pople) [15]

1969 modem study of diamagnetic susceptibility exaltation (Dauben) [16]

1970 magnetic susceptibility anisotropy (Flygare) [17]

1980 IGLO quantum chemical calculation of magnetic properties: chemical shifts, magnetic susceptibilities and magnetic susceptibility anisotropies (Kutzelnigg)[18]

1.1.2 What is Aromaticity

The concept of aromaticity is still rather fuzzy, despite it has been being taught in general chemistry classrooms for a long time. It is one of the most discussed concepts in the chemical literature. Many books[19-23] and reviews[24-30] have been published, and several conferences[31-34] have been dedicated to interpret this concept.

Boldyrev and Wang[35] adopt a view of aromaticity. They believe that aromaticity is a qualitative concept that allows chemists to assign a large number of molecules to a certain class in which all species have specific and similar molecular properties. These specific molecular properties should be different from standard molecular properties observed in classical molecules. A molecule is classical if its chemical bonding could be assigned using one Lewis structure with two-center two-electron (2c-2e) bonds and lone pairs. Correspondingly, a molecule could be aromatic or antiaromatic if it cannot be characterized by this model and if it also satisfies most of the criteria for aromaticity or antiaromaticity.

For example, propylene (CH_3-CH=CH_2), benzene (C_6H_6), and cyclobutadiene (C_4H_4) are considered to be classical, aromatic, and antiaromatic, respectively. As one can see, propylene can be easily described by the 2c-2e model, whereas benzene cannot. Many criteria have been proposed in the literature for aromaticity and antiaromaticity. Boldyrev and Wang adopt a list of properties proposed by Krygowski et al. with some small modifications and additions, which are summarized in Table 1-1.[35]

Table 1. Criteria for π-Aromaticity and π-Antiaromaticity (Adapted from Reference 96)

property	aromatic	olefinic/classical	antiaromatic
(i) electronic nature	$(4n + 2)$ π-electron cyclic conjugation	no cyclic conjugation	$4n$ π-electron cyclic conjugation
(ii) energy			
cyclic conjugation	stabilization	standard	destabilization
delocalization	enhanced	standard	decreased
HOMO−LUMO gap	large	standard	small
(iii) geometry			
bond lengths	equalization	alternation	alternation
(iv) magnetic properties			
anisotropy of diamagnetic susceptibility	enhanced		small
susceptibility exaltation	high		low
^{1}H NMR shifts	diatropic (low-field shift)		paratropic (high-field shift)
NICS (nucleus independent chemical shift)	large negative		large positive
(v) reactivity			
chemical structure	e.g., benzene	e.g., cyclohexadiene	e.g., cyclooctatetraene
retention of structure	electrophilic substitution	electrophilic addition	addition
(vi) spectroscopy			
UV spectra	high energy	standard	low energy
IR/Raman spectra	high symmetry		low symmetry
photoelectron spectra	high electron detachment energies	standard	low electron detachment energies

Table 1-1 Criteria for π-Aromaticity and π-Antiaromaticity

1.1.3 Characterization of aromaticity

NMR spectroscopy is one of the most commonly used qualifiers for aromaticity. Due to the magnetic field generated by the circulating electrons, hydrogens which lie in the plane of the ring experiences a deshielding effect as shown below (Figure 1-1). At the same time those lie above and below the plane experience shielding, as the magnetic lines of force are opposite in direction with respect to the applied field.

Aromatic systems have the ability to sustain a diamagnetic ring current in an applied magnetic field and are classified as diatropic [36a]. Conversely, anti-aromatic systems sustain a paramagnetic ring current in an applied magnetic field and are classified as paratropic [36b].

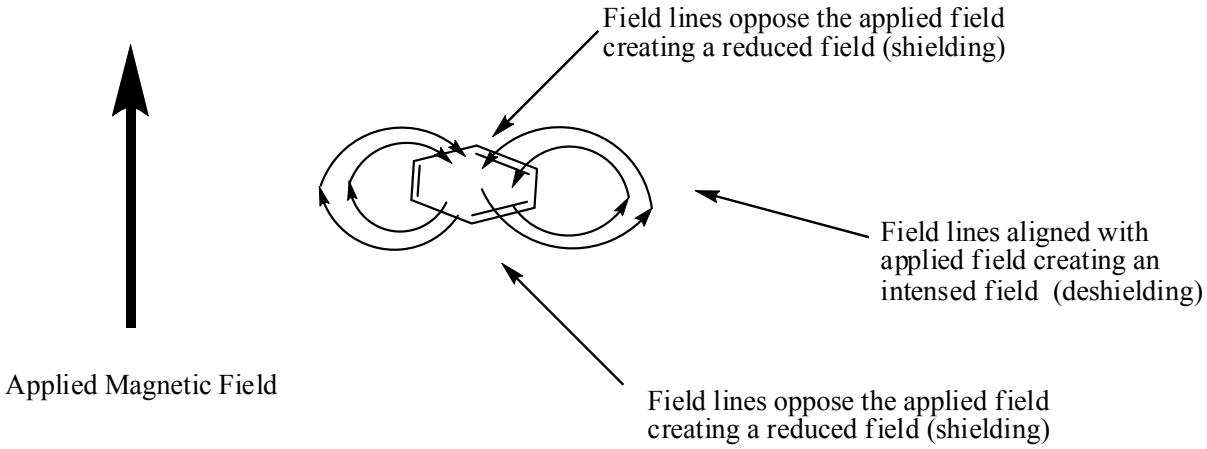


Figure 1-1 Shielding and Deshielding

Because of different local chemical environment, different protons in a molecule resonate at slightly different frequencies. Since both this frequency shift and the fundamental resonant frequency are directly proportional to the strength of the magnetic field, the shift is converted into a field-independent dimensionless value known as the chemical shift. The chemical shift

is reported as a relative measure from some reference resonance frequency. The nuclei ^{1}H, ^{13}C, and ^{29}Si, TMS (tetramethylsilane) is commonly used as a reference. This difference between the frequency of the signal and the frequency of the reference is divided by frequency of the reference signal to give the chemical shift. The frequency shifts are extremely small in comparison to the fundamental NMR frequency. A typical frequency shift might be 100 Hz, compared to a fundamental NMR frequency of 100 MHz, so the chemical shift is generally expressed in parts per million (ppm). Table 1-2a [37] and 1-2b[37] list proton and carbon chemical shifts of some organic compounds. Samples were prepared in $CDCl_3$ solution and the δ scale is relative to TMS at $\delta = 0$.

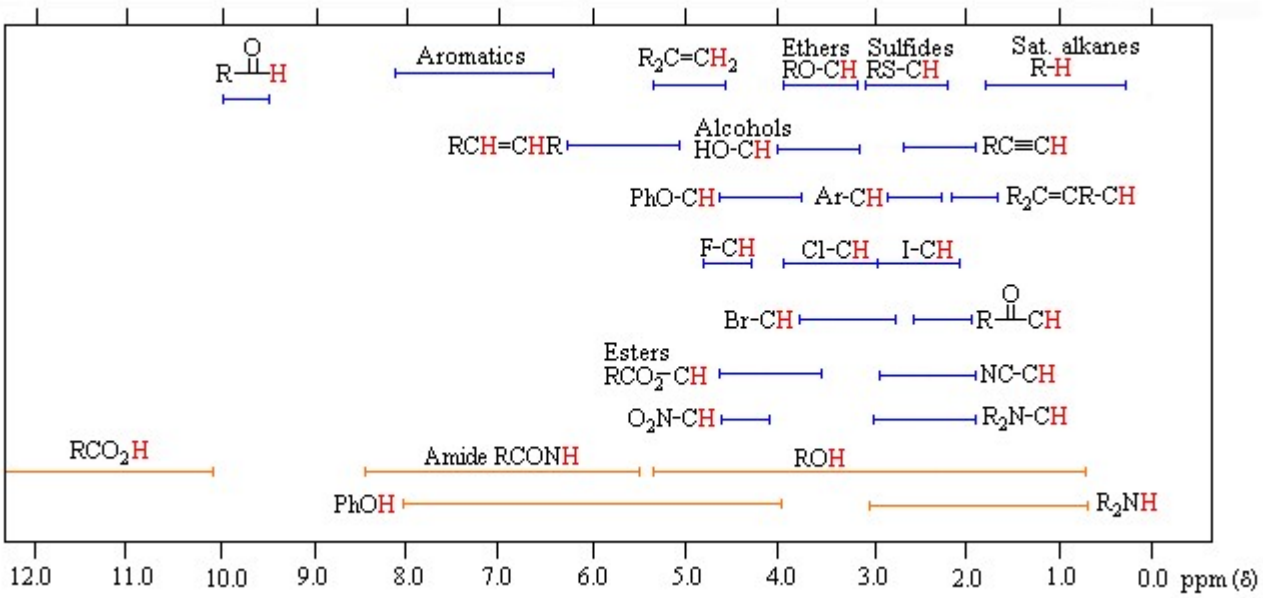


Table 1-2a Proton Chemical Shifts of Organic Compounds[37]

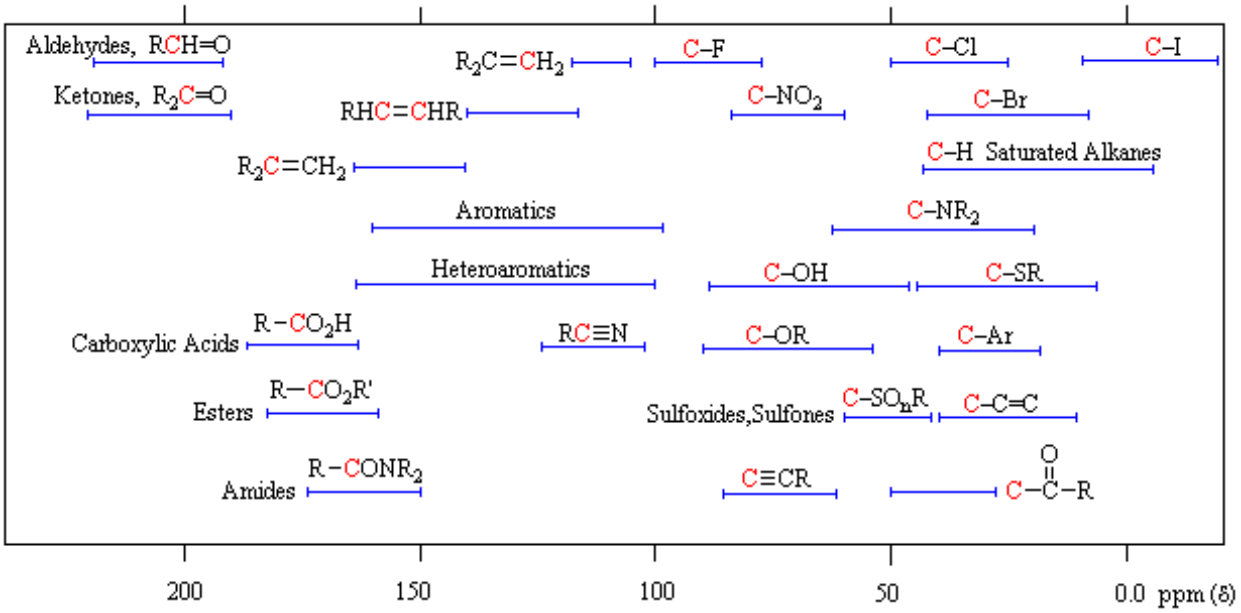


Table 1-2b Carbon Chemical Shifts of Organic Compounds[37]

In benzene **1**, the ring protons experience deshielding because the induced magnetic field has the same direction as the external field and their chemical shift is 7.3 ppm compared to 5.6 ppm to the vinylic proton in cyclohexene **2**.

Benzene
([6]annulene)

1

δ =7.3 ppm

Cyclohexene

2

δ =5.6 ppm

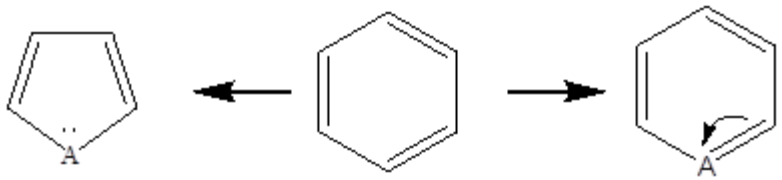
Figure 1-2 Benzene and Cyclohexene

Besides NMR spectroscopy, there is some other Characteristic Criteria[38] for aromaticity.

- Reactivity criteria: Predominance of substitution versus addition reactions; thermal stability; stabilizing ability for aryl- or heteroaryl-substituted free radicals, anions, or cations (such as carbenium, halonium, oxonium, diazonium cations);
- Bond equalization, planarity;
- Resonance energy;
- Prefixed aromaticity types (homo, bis/tris-homo, pseudo-, anti-, quasi-) and the criticisms thus engendered.

1.2 Heteraromaticity

Heterocycles with five- and six-membered rings have been considered as modified benzenes, where a pair of carbon atoms (for five-membered systems) plus any number of carbon atoms is substituted with a heteroatom. Hence, most heterocycles could be classified as π -excessive[39a] or π -deficient[39b] (Scheme 1-1).



3 1 4

replace CH=CH by A=O, S, NR or N^- — can be done only once — π-excessive heterocycles (electron-rich rings)

replace CH by $A=O^+$, S^+, N or NR^+ — can be done repeatedly — π-deficient heterocycles (electron-deficient rings)

Scheme 1-1 Heteroaromatic Compounds as Modified Benzenes

Various methods to quantify the aromaticity of heterocycles and the interrelationship between different scales are controversial and have been covered in a recent article.[40] In heterocyclic chemistry a quantitative evaluation of the aromaticity is very necessary because new heterocyclic systems are designed and synthesized and need to be evaluated with proper predictions. There are three major approaches[38] to the quantization of aromaticity:

(a) The increased thermodynamic stability of aromatic compounds.

(b) The geometry of the ring. Today inter and intra molecular bond length data could be easily collected by routine X-ray measurements. On the basis of X-ray measurements, the harmonic oscillator model of aromaticity (HOMA) concept has been used as evidence of the aromatic character. This model relates the decrease of aromaticity to two geometric/energetic factors: one describing the bond length alternation (GEO term) and the other describing the extension of the mean bond length (EN term).

(c) Magnetic property measurements. Diamagnetic susceptibility was the first magnetic property studied in connection with the concept of resonance energy. More recently, ^{1}H NMR spectroscopy has become a tool in the study of ring currents in cyclic π -conjugated systems.

1.3. Annulenes

1.3.1 History

Originally defined by Sondheimer in the early 1960s,[41] an [*n*]annulene is a monocyclic

hydrocarbon comprised of alternating single and double bonds where the number in brackets denotes the number of contiguous sp^2 carbon centers. By definition, cyclobutadiene **5** is therefore considered as [4] annulene (Figure 1-3), benzene **1** as [6] annulene (Figure 1-2), etc.

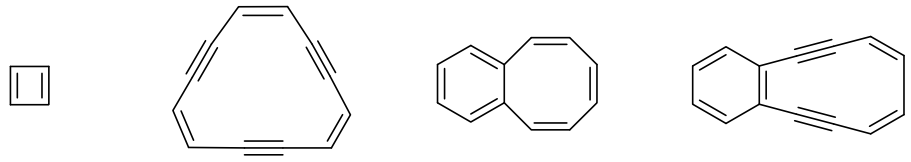


Figure 1-3 Annulenes

Replacement of one or more of the double bonds with an acetylene unit affords a dehydroannulene (e.g., **6**). An unfortunate side effect of installing triple bonds in the hydrocarbon skeleton could be compound instability. But fusion of one or more benzene rings to furnish a benzoannulene (e.g., **7**) or dehydrobenzoannulene (e.g., **8**) could increase the macrocycle stability in general.

Throughout the 1960s and 1970s, the research groups of Nakagawa,[42] Staab,[43]and Sondheimer[44] prepared an impressive array of annulene structures and showed that these hydrocarbons possess a fascinating wealth of chemistry, such as Bergman cyclization of **8** to give anthracene.[45] The main factor driving annulene research was: whether planar examples of such macrocycles were able to strengthen those ring currents? From compounds produced, the main conclusion was that ring currents in these systems became progressively weaker upon benzannulation by inclusion of triple bonds, and/or with increasing ring size. The studies of these annulenes languished in the 1980s because of lacking more impetus even

they validated theoretical conclusions based on the Huckel rule for annulenes.

The last decade of the 20th century revived annulene chemistry. A number of synthetic discoveries like Pd-mediated cross-coupling reactions between sp and sp^2 carbon centers[46] were adopted from other areas of organic chemistry. These improvements made the previous macrocycle assembly now a quick and efficient process. The ability and efficiency to create new annulenes allowed chemists to functionalize the hydrocarbon backbone easily and thus investigate the chemical reactivity and physical properties of the macrocycles.

1.3.2 (4*n*+2) π Annulenes

For annulenes containing (4*n*+2) π electrons, all of them would be aromatic according to (4*n*+2) rule. But actually not all of them are aromatic because such aromaticity requires a planar conformation.

1.3.2.1 10 π Annulenes

[10] annulene is the next higher homologue of benzene (*n*=2). Although all [4*n*+2] annulenes are predicted to be aromatic, all cis-[10]annulene **9** suffers from too much angle strain energy (bond angle of 144^0) and is found to have prosperities similar to a polyolefin. The proton NMR showed a temperature independent singlet at 5.67ppm over a range of -40 to -160^0C. Di-trans[10]annulene **10** reduces the angle strain but appears to have severely steric interaction between two internal hydrogen atoms by forcing the ring out of planarity.

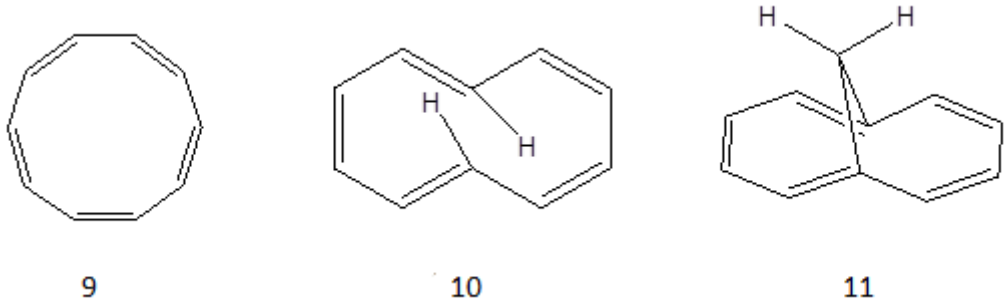
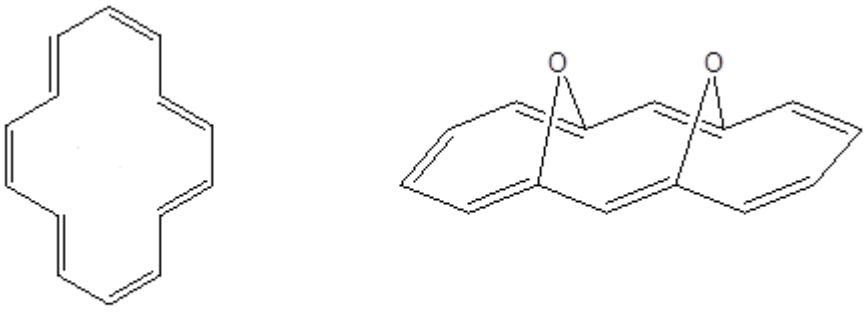


Figure 1-4 [10]Annulenes

In order to reduce conformational mobility and to force π-system into planarity, the internal H-H repulsion in the di-trans[10]annulene **10** can be eliminated by placing a methano group above the plane of the ring. 1, 6-Methano [10]annulene **11**, discovered by Vogel et. al [47] is the first stable [10]annulene. The proton NMR showed an A_4B_4 system of external protons in the range of 6.8-7.5 ppm and a sharp singlet of the bridged protons at -0.5 ppm. The upfield shift for the interior protons and the downfield shift for the outside protons indicate that this molecule is aromatic.

1.3.2.2 14π Annulenes

As to the [14] annulene **12**, the computational and experimental studies showed that the molecular adopts a non-planar conformation.



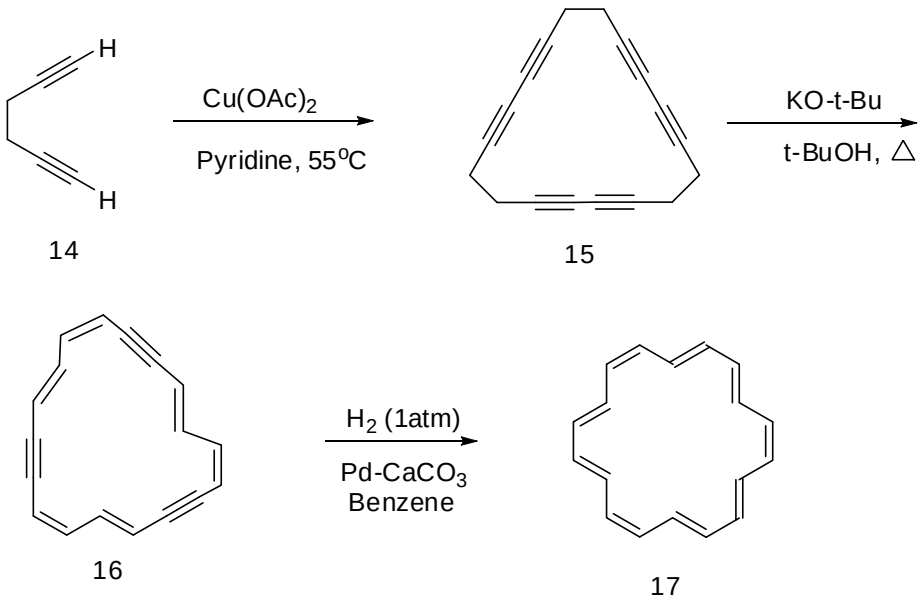
12 13

Figure 1-5 [14]Annulenes

Three types of bridged [14] annulene have been reported： one based on anthracene, one on pyrene and the third on dicyclophentaheptalene structure.Vogel and his co-worker [48] have made a variety of molecules based on the anthracene type. Syn-1, 6, 8, 13-bisoxido [14] annulene **13** was obtained in 1966. It is a thermally stable red solid. The ^{1}H NMR[49] showed eight outer perimeter protons at 7.67 ppm and the two central perimeter protons at 7.94 ppm. An X-ray crystallographic analysis[50] has shown that the molecule has a reasonable planar perimeter with a nearly equal aromatic C-C distance throughout the perimeter.

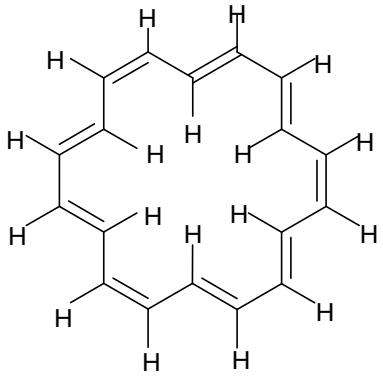
1.3.2.3 18π Annulenes

Compare with [14] annulene, [18] annulene is large enough to minimize the internal protons strain and could be qualified as aromatic. The compound was first synthesised by Franz Sondheimer.[51] The original synthesis started by the Eglinton reaction of the di-alkyne1,5-hexadiyne **14** with copper(II) acetate in pyridine to give the trimmer; deprotonation and isomerization with potassium *tert*-butoxide in *ter*t-butanoland followed by hydrogenation with the Lindlar catalyst[52, 53] gave [18] annulene **17**.



Scheme 1-2 Synthesis of [18]Annulene by Franz Sondheimer

The twelve outer proton NMR signal shift downfield to 9.3 ppm due to a more effective π-orbital overlap, and the inner protons experienced an upfield shift to -3.0 ppm, consistent with increased diatropictiy.



17

δ =9.3 ppm (12H, outer)

δ = -3.0 ppm (6H, inner)

Figure 1-6 [18]Annulene

1.3.3 4*nπ* Annulenes

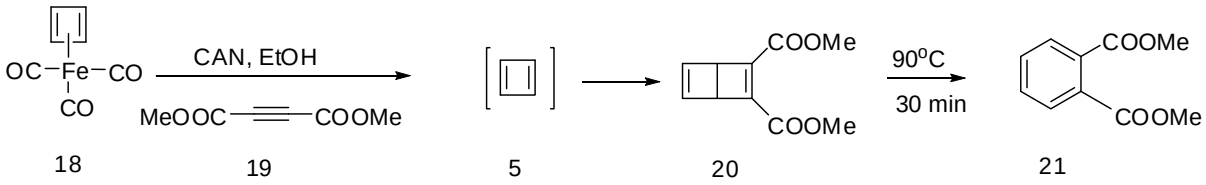
1.3.3.1 4π Annulenes

Cyclobutadiene **5** is the smallest [*n*]-annulene, which has a lifetime shorter than five seconds in the free state and is extremely unstable due to its antiaromaticity. Some cyclobutadiene-metal compounds are stable because the metal atom provides 2 more electrons to the system.

5

Figure 1-7 [4]Annulene

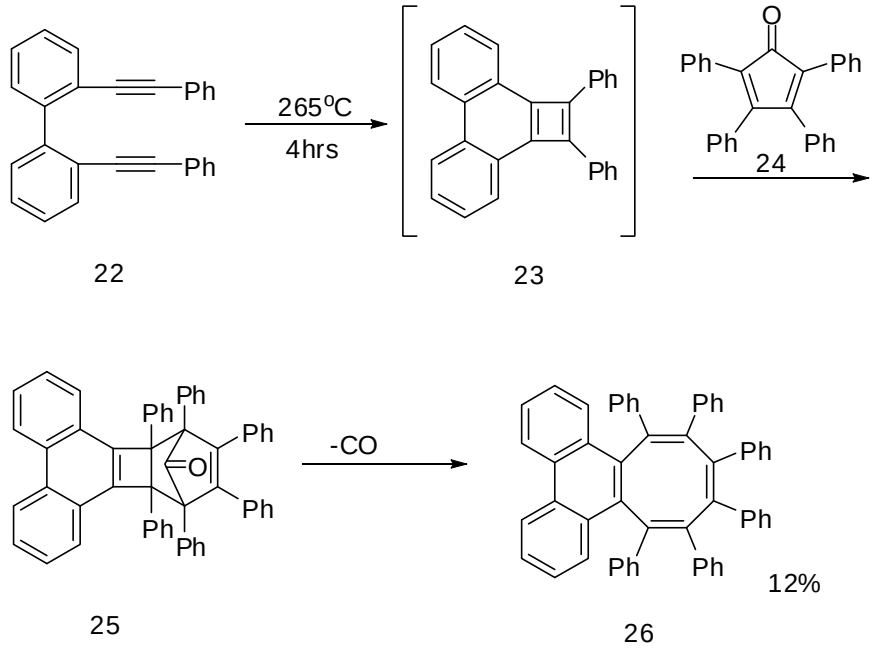
Cyclobutadiene **5** was first synthesized in 1965 by Rowland[54], although he could not isolate it. Cyclobutadiene can be generated through degradation from a cyclobutadiene metal compound for example $C_4H_4Fe(CO)_3$ with ammonium cerium(IV) nitrate (Scheme 1-3). This cyclobutadiene iron tricarbonyl complex was prepared from $Fe_4(CO)_9$ and cis-dichlorocyclobutene in a double dehydrohalogenation.[54b, 55] When liberated from the iron complex, Cyclobutadiene **5** reacts with electron-deficient alkynes **19** to form a Dewar benzene **20**.[56] The Dewar benzene converts to dimethyl phthalate **21** on heating at 90°C.



18 19 5 20 21

Scheme 1-3 Cyclobutadiene-Dewar Benzene Conversion

One cyclobutadiene derivative is also accessible through a [2+2]cycloaddition of a di-alkyne. In this particular reaction the trapping reagent is 2,3,4,5-tetraphenylcyclopenta-2,4-dienone **24** and one of the final products (after expulsion of carbon monoxide) is a cyclooctatetraene derivative **26** (Scheme 1-4).[57]



22 23 25 26

Scheme 1-4 Trapping of Cyclobutadiene Derivative Using 2,3,4,5-Tetraphenylcyclopenta-2,4-dienone

1.3.3.2 12π Annulenes

The first [12]annulene **27a** with sym-tri-trans configuration was synthesized in 1970 from a tricyclic precursor by photolysis at low temperatures (Scheme 1-5). Upon on heating **27a** rearranges to a bicyclic [6,4,0] isomer **29**. Reducing of **29** at low temperatures allowed analysis of the dianion by proton NMR with the inner protons resonating at - 4.5 ppm relative to TMS, evidence of an aromatic diamagnetic ring current[58].

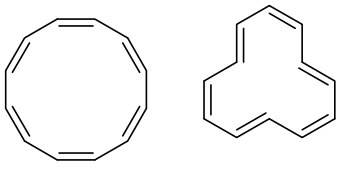
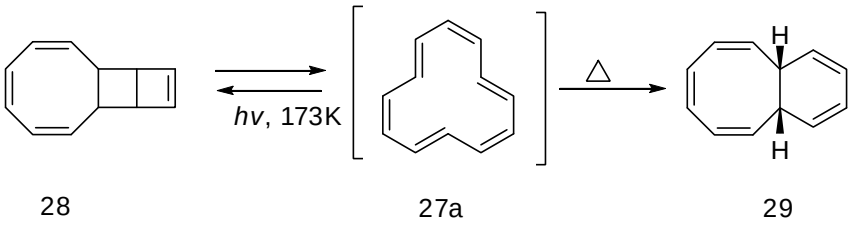


Figure 1-8 [12] Annulene



Scheme 1-5 Synthesis of [12] Annulene by Photolysis at Low Temperatures

Low temperature NMR spectroscopy showed that **27a** was significantly distorted from planarity due to steric crowding by the internal protons and that it readily underwent cis/trans isomerization through intermediate **30** (Figure 1-9). The isolated electrocyclic ring-closure products **31** and **32** suggested a very low (4.1-4.5 kcal mol^{-1}) tautomerization energy barrier[58].

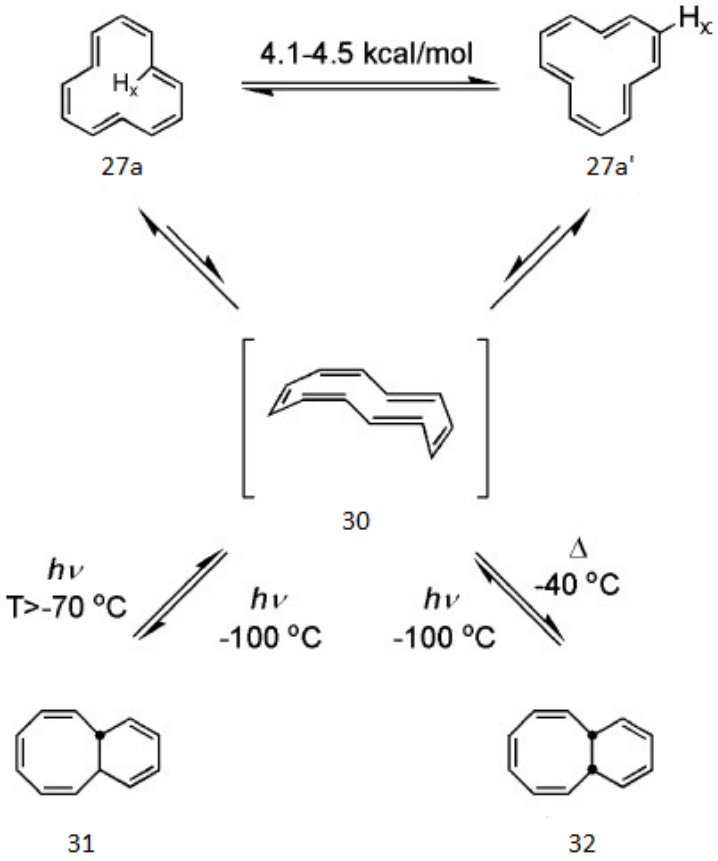
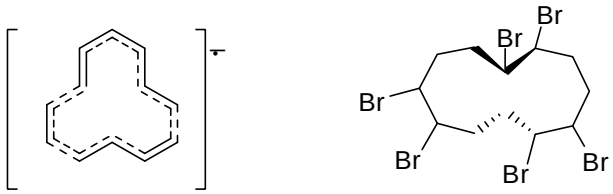


Figure 1-9 The Isomerism of [12] Annulene[58]

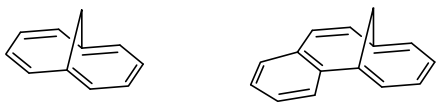
The anion radical of [12]annulene **33**(Figure 1-10) has been shown to be stable enough for spectroscopic characterization[59] and can be generated from either exposure of neutral [12]annulene to alkali metals or dehydrohalogenation of 1,2,5,6,9,10-hexabromocyclododecane **34**, a fire retardant. The anion assumes a "half-planar" conformation wherein seven carbons lie in plane and consequently contain most of the spin density with the other five atoms twisted out of the plane with rapid ($k=10^6$-10^7 s^{-1}) rearrangement between degenerate conformations .



33 34

Figure 1-10 The Anion Radical of [12]Annulene

Bridged [12]annulene (Figure 1-11), like bridged [10]-annulene, exhibits much greater stability than the parent annulene. 1, 7-Methano[12]annulene **35** was first prepared by Vogel in 1974[60] and found to be nonplanar with significant bond length alternation. It is stable and has a weak but still significant cyclic conjugation, which makes it a good candidate for electron delocalization studies.[61] For example, fusion of a benzene ring onto the 4n π - electron system to make **36** results in a reduction of the paramagnetic ring current.[62]



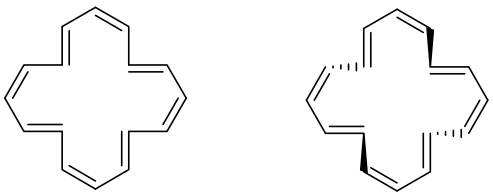
35 36

Figure 1-11 Bridged [12]Annulenes

1.3.3.3 16π Annulenes

The 4nπ system [16]annulene **37** (Figure 1-12) was first synthesized in 1961 by Sondheimer and Gaoni.[63] Since then a variety of conformations have been found to be stable either through computation or X-ray crystallography.[64,65] The annulene exists predominantly in the

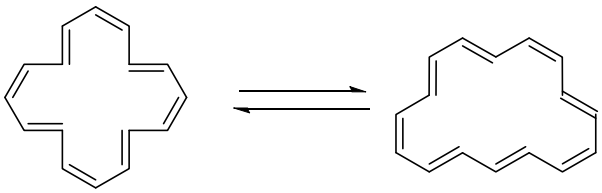
alternating cis/trans configuration with four internal protons that cause the considerable planarity distortion (**38**, Figure 1-12).



37 38

Figure 1-12 [16]Annulene

A minor (12%) isomer **39** with five internal protons is believed to exist in equilibrium with the major isomer (Figure 1-13).[66] Recently, several new conformations in which some have Moebius topography have been predicted computationally.[67] The geometry of the annulene shows significant temperature dependence in the NMR spectrum: as the temperature is decreased, the molecule becomes more planarized and antiaromatic character increases.

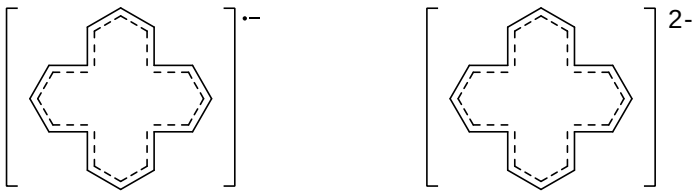


37 39

Figure 1-13 [16]Annulene

Despite the classic hypothesis that 4nπ electron systems are inherently destabilized relative to their acyclic analogues, recent work has shown that larger 4*n*π systems such as [16]annulene are only slightly destabilized by π -electron interactions. [68]

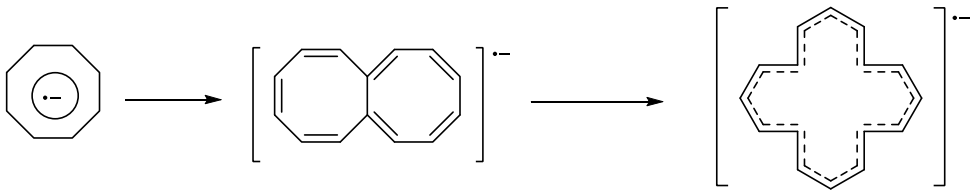
The anion radical and dianion species of [16]annulene (**40** and **41**, respectively) have been easily made by reduction of the neutral molecules with alkali metals.[69]



40 41

Figure 1-14 The Anion Radical and Dianion Species of [16]Annulene

Anion **40** could be generated by reduction of the [2+2] dimer of cyclooctatetraene(COT), or equimolar reaction of COT anion radical with neutral COT (Scheme 1-6).[70] The second method shows the synthetic potential of anion radical-neutral molecule combination reactions.



42 43 40

Scheme 1-6 Synthesis of Anion Radical of [16]Annulene

The dianion **41** is a $(4n + 2)$ π electron system and displays an even greater diatropicity than [18]annulene and is believed to be significantly more stable than neutral [16]annulene. Isotopic perturbation studies of **41** provide results directly opposite the neutral molecule: deuteration causes a pronounced increase in diatropicity, shifting the internal protons upfield

from -8.03 to -8.11 ppm. But the shifting of the external protons is "not larger than experimental error". [71]

1.3.3.4 8π Annulenes

[8]Annulene (**44**, Figure 1-15), or cyclooctatetraene (COT), was first isolated in 1911[72] and caused a fair amount of confusion because it didn't display properties like benzene. This was prior to publication of Huckel's rule that only conjugated systems with $(4n + 2)$ π electrons would exhibit what is now called aromaticity.[73] The $4n\pi$ electron [8]annulene also exhibits higher reactivity.[74] Actually [8]annulene exists in a tub conformation (Figure 1-16), which undergoes rapid interconversion, and thus is considered nonaromatic.[75] . It behaves as normal, non-conjugated alkenes, and the chemical shift of the vinyl proton is 5.777 ppm, which is in the range of normal, non-conjugated alkenes.

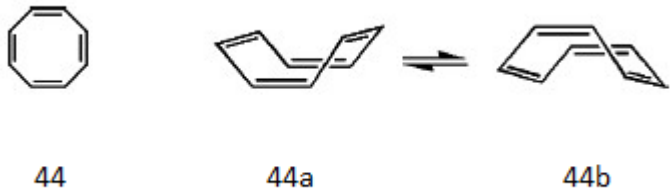


Figure 1-15 [8]Annulene[75]

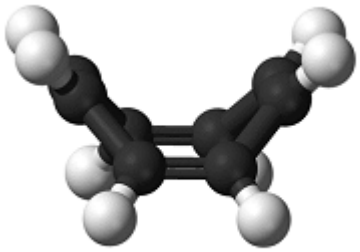
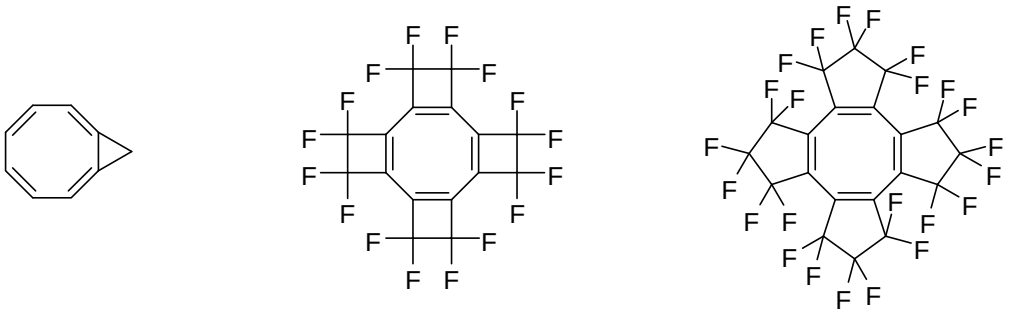


Figure 1-16 Tub Conformation of [8]Annulene

Much of the recent work that has been done with [8]annulene involves the anion radical **42** and dianion,[75b, 76] both of which are planar and much more stable. The majority of work by Stevenson involves [8]annulene anion radical, which has been shown to dimerize to **43**, followed by ring opening to [16]annulene anion radical **40** (Scheme 1-6).[76a]

Stevenson also prepared the highly strained, high-energy cycloprop[8]annulene **45**,[76g] the second known cyclopropannulene (cyclopropabenzene being the first[77]).



45 46 47

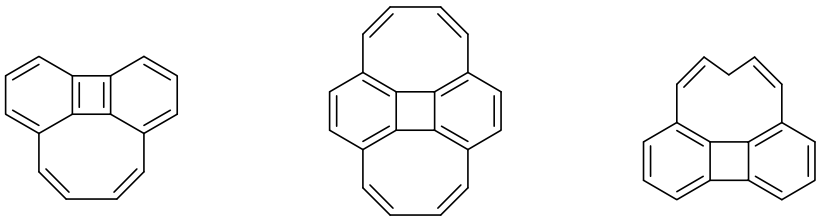
Figure 1-17 Substituted [8]Annulenes

Perfluorinated tetrakis(cyclobuta)COT **46** was synthesized by Soulen et al[78]. It is planar because of the highly strained bicyclohexene units. But perfluorinated tetrakis(cyclopenta)COT **47** prepared by Gerson and Wirz[79] is tub-shaped.

1.3.4 Biphenylene Planarized Annulenes

Cycloocta[defl biphenylene **48** was synthesized and investigated by Wilcox's group in 1974.[81] The NMR spectrum of this compound shows two groups of peaks in the ratio of 6:4 assignable to the aromatic and olefinic protons, respectively. The aromatic protons gave a complex ABC pattern with chemical shifts from 5.6 to 6.4 ppm, and the olefinic protons gave a doublet at 4.62 ppm. The result shows this compound has a planar conformation and simultaneously olefinic, aromatic, and antiaromatic properties.

In 1983 Wilcox's group synthesized and investigated made dicycloocta[def,jkl]biphenylene **49** which was found to display strong antiaromaticity.[80] Later (1*Z*,4*Z*)-3H-cyclonona[*def*]biphenylene **50**, a potentially homoantiaromatic neutral hydrocarbon, was synthesized and characterization data of **50** all point to a significant neutral homoantiaromaticity. [81]



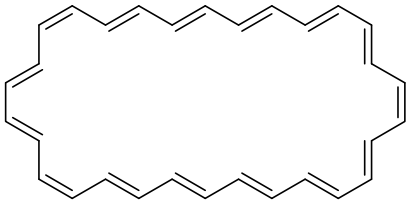
48 49 50

Figure 1-18 Biphenylene Planarized Annulenes

Our project is inspired by the results of Wilcox's group. If we could annulate dehydro parts to biphenylene core, the resulting compounds must be planarized. This suggests the idea that how some new aromatic and anti-aromatic systems could be approached.

1.3.5 Higer Annulenes

The higher annulenes (n > 18) present less synthetic interest, mostly due to their significant bond alternation, asymmetry, and conformational flexibility. All annulenes up to n =30 (**51**, Figure 1-19) have been synthesized except n =26 and 28.



51

Figure 1-19 [30]Annulenes

1.4 Dehydroannulenes

The dehydroannulenes are also of theoretical interest because the criteria for aromaticity discussed for the annulenes apply also to the dehydro compounds as far as the out-of-plane π electrons are concerned. Research on dehydroannulenes in the 60s and 70s encouraged interest in cyclic conjugated alkadinyes.[171] 1, 8-dehydro [14] annulene **52** [172] and 5,6,11,12,17,18-hexadehudrotribenzo [α, e, i]cyclododecene **53** [173] are among the first studied compounds. Spectroscopic study and results from X-ray structures confirmed that a triple bond could function as part of an aromatic polyene1. For example, in pericyclyne **54** [174], the possible homoconjugation of triple bonds is known.

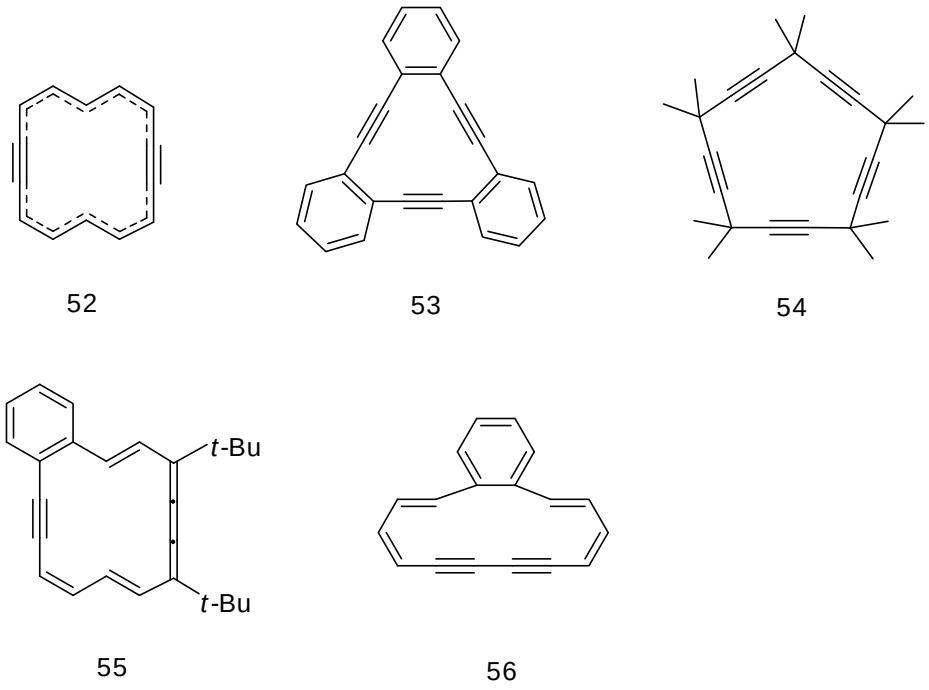


Figure 1-20 Dehydroannulenes

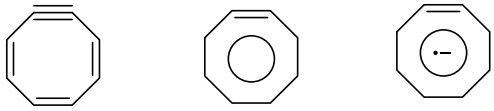
From a synthetic standpoint, replacement of one or more of the double bonds of an annulene with triple bonds is a fairly straightforward process. The resultant dehydroannulene often is considerably less stable than its annulene counterpart and thus prone to undergo side reaction, decomposition, etc. Moleculars **55**, **53** and **56** are representative examples from the groups of Nakagawa, Staab and Sondheimer, respectively. [174]

1.4.1 Dehydro 4*n*π Annulenes

1.4.1.1 Dehydro 8π annulenes

Dehydro[8]annulene, or [8]annulyne **57**, (Figure 1-21), was first prepared by Krebs in 1965.[82a,b] Huang and Sondheimer published a thorough review of work up to 1980,[82c] and

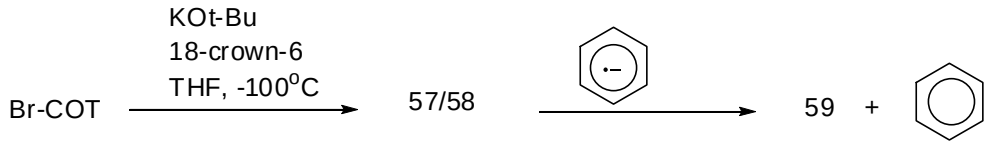
later work has focused mostly on the anion radical.[83] Wenthold and Lineberger[83a,b] measured the photoelectron spectrum of $C_8H_6^-$ and reported that it very closely resembled that of the COT anion (C_8H_8-) with similar structures. There are two observed electronic states for [8]annulyne: the lowest described as a singlet 1,3,5-cyclooctatrien-7-yne **57** and a higher triplet dehydrocyclooctatetraene state **58**.



57 58 59

Figure 1-21 Dehydro[8]annulenes

Stevenson and co-workers[83c] developed a one-step entrapment protocol for [8]annulyne anion radical **59** using dehydrohalogenation of Br-COT **60** by t-BuOK in THF solution containing an equimolar amount of 18-crown-6 (Scheme 1-7). Observation of the anion radical is allowed by the presence of the crown ether, which prevents spin delocalization into the K cation.

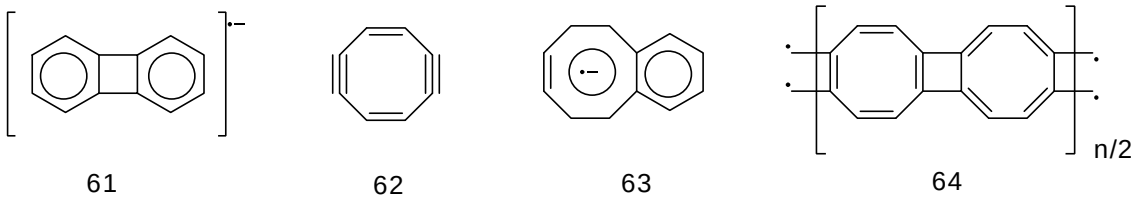


60

Scheme 1-7 Synthesis of [8]Annulyne Anion Radical **59**

[8]Annulyne also undergoes [2+2] dimerization when kept below 173 K without exposure to an electron source. Subsequent exposure would generate the corresponding dimeric anion radical **61** (Figure 1-22). Fusion of sym-[8]annuldiyne **62** to a cyclobutadiene unit leads to the benzannelated anion radical **63**, which undergoes polymerization via extended [2+2]

cycloaddition to form a solid **64** that is insoluble in THF. The cross-linking is believed to take place via suprafacial [2 + 2] cycloadditions of the cyclobutadiene units.



61 62 63 64

Figure 1-22 Dehydro[8]annulenes

1.4.1.2 Dehydro 12π annulenes

Mono-trans structure **65b** has been known since the early 1960s (Figure 1-23), but the all-cis geometry of 1,2,5,6-tetradehydro[12]- annulene **65a** has remained elusive.[84] 1,2,7,8-Tetradehydro[12]annulene **66** is believed to adopt a D2-symmetric twist boat conformation **66b** based on the NMR data. Compound **66** is calculated[85] to be 34.47 kcal mol^{-1} more stable than **65**, and their antiaromatic character causes the energy of the planarized structures to be relatively high.

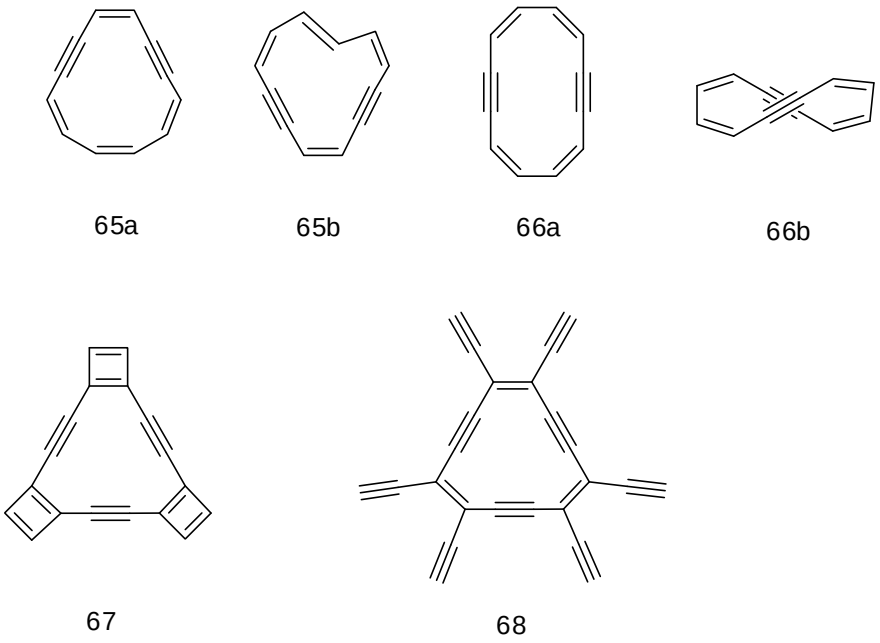
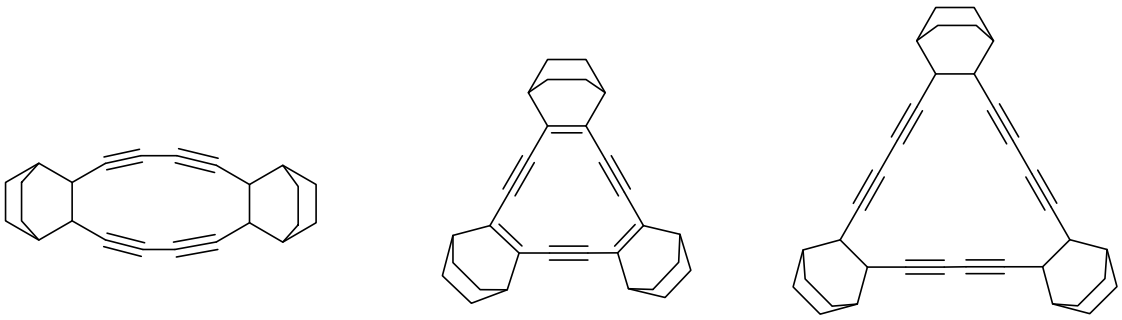


Figure 1-23 Dehydro[12]annulenes

Additional calculations suggest that fusion of cyclobutadiene units onto hexadehydro[12]annulene **67** effectively destroys the antiaromaticity of the 12-membered ring,[86] in contrast to hexadehydrohexaethynyl[12]annulene **68**, which has only slightly attenuated antiaromaticity.

Komatsu and co-workers prepared several dehydro[12]-, [18]-, [24]-, and [30]annulenes fused with bicyclo[2.2.2]-octene (BCO) frameworks[87]. Compound **69** is unstable and decomposes upon concentration without deaeration, while compound **70** decomposes even in deaerated solution over several days at room temperature. The signals for the bridgehead protons on the dehydro[12]annulenes are shifted significantly upfield from their aromatic-fused counterparts **71**.

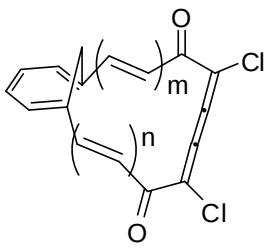


69 70 71

Figure 1-24 BCO Fused Dehydroannulenes

1.4.1.3 Dehydro 16π Annulenes

Ojima, Yamamoto, and co-workers[88] prepared several unique methanodehydro[16]-, [20]-, and [24]annulenedione structures (**72-74**, Figure 1-25) with an unusual 1,4-dichlorobutatriene moiety. A crystal structure of **72** revealed significant distortions from the expected Cs geometry, believed to be due to ring strain and transannular repulsion. The system is "fairly planar", but the dihedral angle between the two ring systems separated by the methano bridge deviates from planarity by ca. 30.



72 m=n=1

73 m=n=2

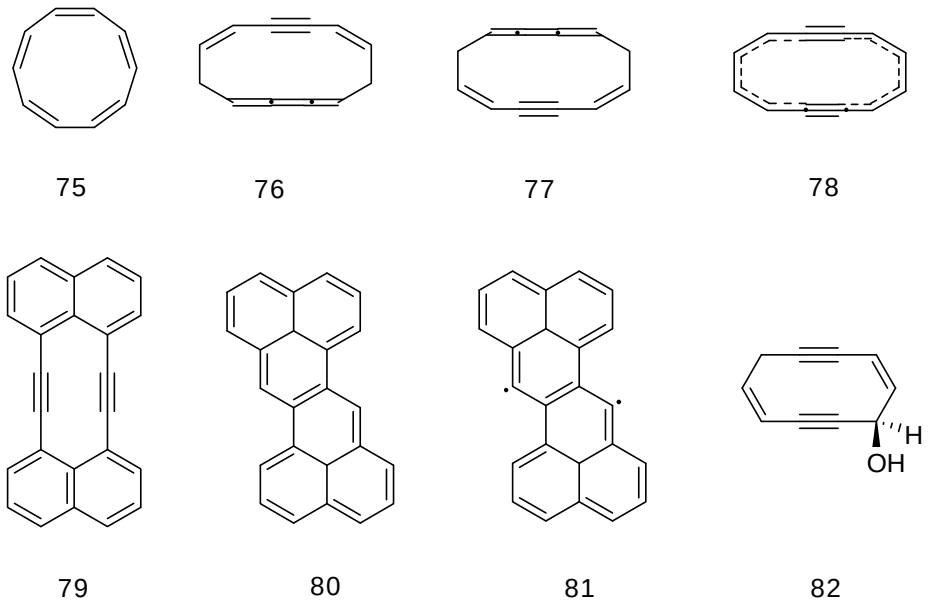
74 m=n=3

Figure 1-25 Methanodehydro[16]-, [20]-, and [24]annulenedione

1.4.2 Dehydro (4*n*+2)π Annulenes

1.4.2.1 Dehydro 10π Annulenes

Didehydro[10]annulene **75** (Figure 1-26) with its (4*n* + 2) **π** electrons, it should exhibit aromaticity in the planar geometry. The bond localized configuration is expected to have C_2 symmetry with a tub shape similar to COT. This conformation is found to be more stable than the localized flat (C_{2V}) geometry, but the energetic differences between the two are smaller than for COT, apparently due to aromatic stabilization. The ease with which the bond angles are distorted reduces ring strain in the planar geometry.[88]



75 76 77 78

79 80 81 82

Figure 1-26 Dehydro [10]annulenes

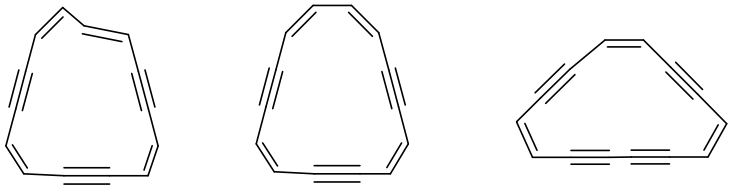
The first tetradehydro[10]annulene (Figure 1-26, various representations, **76**, **77**, **78**) was synthesized in 1992 by Myers and Finney.[89] The authors were interested in its potential thermal rearrangement to the biradical 1,5-dehydronaphthalene and noted previous attempts by Sondheimer and Staab to prepare similar benzannelated hydrocarbon **79**, which instead

lead to zethrene **80** presumably through a zethrene biradical **81**. Successful synthesis of tetradehydro[10]annulene proceeded from dehydration of the acetylenic alcohol **82**.

1.4.2.2 Dehydro 14π Annulenes

Although mono-trans-hexadehydro[14]annulene **83a** (Figure 1-27) was prepared in the mid-1960s,[90] the all-cis isomer **83b** is as yet unknown. Calculations suggest it adopts a tub-shaped conformation similar to didehydro[10]annulene **75** (Figure 1-26). Haley and Boydston synthesized the all-cis octadehydro- [14]annulene **84** and used ^{1}H NMR shifts to infer its diatropicity.[91] This parent compound was compared to various benzannelated analogues and it was found that fusion of benzene rings to the systems causes upfield shifts, implying a gradual reduction in diatropicity.

This lends support to the computational results described in the previous section concerning fusion of cyclobutadiene units to dehydro[12]annulene reducing its antiaromaticity.

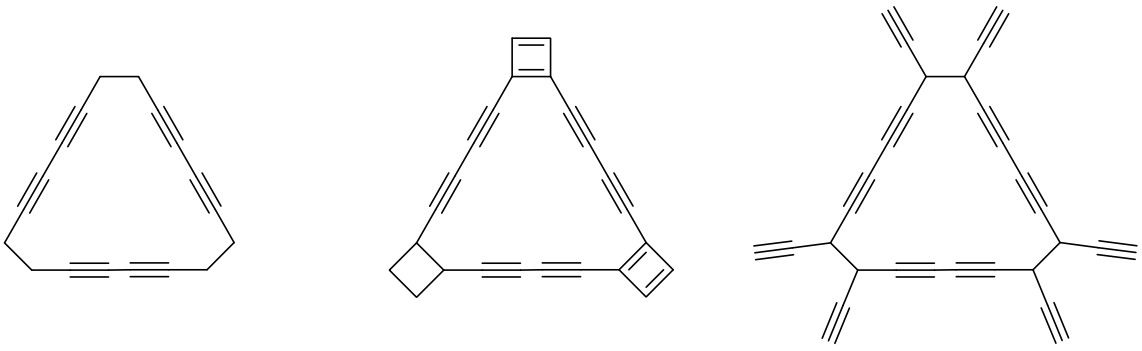


83a 83b 84

Figure 1-27 Dehydro [14] annulenes

1.4.2.3 Dehydro 18π Annulenes

Unsubstituted dodecadehydro- [18]annulene **15**[92] is unstable and potentially explosive even it decidedly aromatic. As in the case of hexadehydro[12]annulene **67** (Figure 1-23), fusion of cyclobutadiene rings **85** (Figure 1-28) is calculated to interrupt the ring current, which destroys the aromaticity,[93] while fusion of ethynyl units **86** only slightly reduces it. In the case of **85**, it was calculated that the bond lengths of the formal single bonds are significantly shortened to 1.34Å, but it was1.39-1.43Å in the other molecules studied. This means that the cyclobutadiene rings are "connected by cumulative double bonds yielding an allene structure".[93]



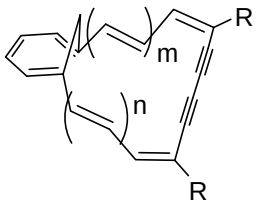
15 85 86

Figure 1-28 Dehydro [18] annulenes

1.4.3 Higher Dehydroannulenes

Ojima and co-workers[94] synthesized a series of 1,6-methanotetradehydro[n]annulenes (Figure 1-29), where *n* =18, 20, 22, 24, 26, 28, 30, 32, 34, 36, and 38. Each system was studied in order to determine the upper limit of ring current as a function of size.

Hexadehydro[24]annulene had been one of the largest 4n annulenes known to be paratropic.[95] Ojima and co-workers synthesized each annulene in the same manner and used the ^{1}H NMR shifts, as well as comparisons to their respective acyclic analogues, to assign the annulene's character as diatropic, paratropic, or atropic. It was found that diatropicity persists up to *n* =34 but paratropicity only up to *n* =28. The *n* =32, 36, and 38 annulenes are found to be atropic, with the conformational freedom that comes with their size overcoming any aromatic stabilization or antiaromatic destabilization. [94]



R=Me, *t*-Bu

m=n=1 [18] 87	m=2, n=1 [20] 93
m=n=2 [22] 88	m=3, n=2 [24] 94
m=n=3 [26] 89	m=4, n=3 [28] 95
m=n=4 [30] 90	m=5, n=4 [32] 96
m=n=5 [34] 91	m=6, n=5 [36] 97
m=n=6 [38] 92	

Figure 1-29 Higher Dehydroannulenes

1.5 Dehydrobenzoannulenes

In the 1960s and 1970s the chemistry of dehydrobenzoannulenes (DBAs) was explored by the groups of Nakagawa, Staab and Sondheimer. Molecules, **55**, **53** and **56** are representative examples from each group, respectively [174]. It is know that the induced ring current effects will be changed because of the participation of benzenoid π electrons in the macrocyclic π-

electron system and the inclusion of triple bonds. So the most interesting thing in the DBA macrocyclic systems is the ring current. How diatropic, paratropic, or atropic are the DBA macrocyclic systems?

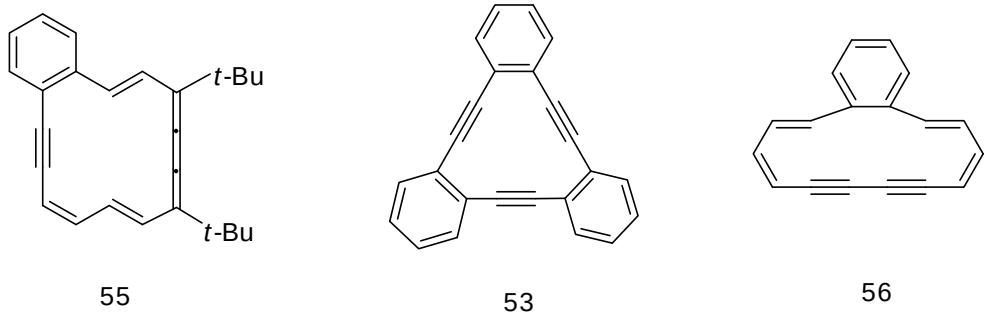


Figure 1-30 Dehydrobenzoannulenes

A key reason for this renaissance was isolation of the fullerenes[96] and several other theoretical studies that proposed unique thermal, optical, and electronic properties for highly unsaturated, nonnatural carbon allotropes such as graphyne **98** and graphdiyne **99** (Figure 1-31)[97].

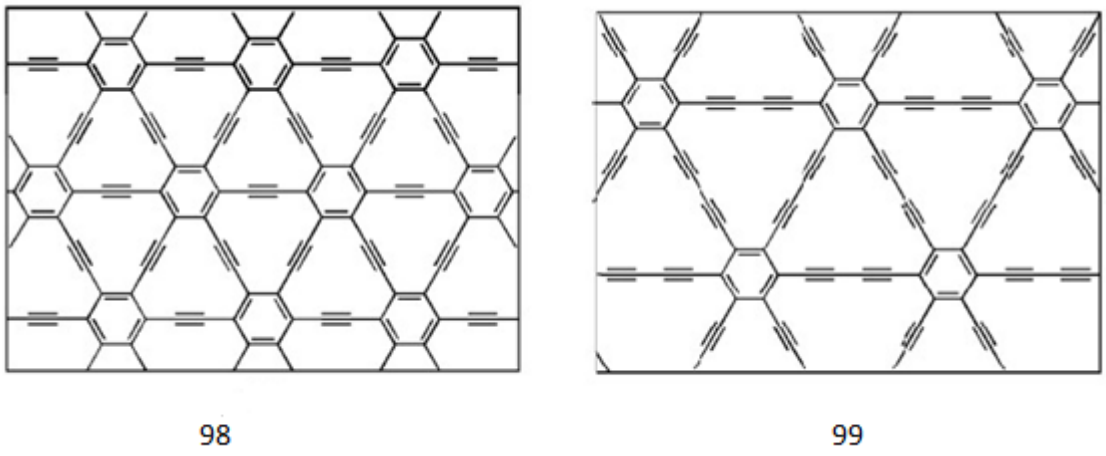
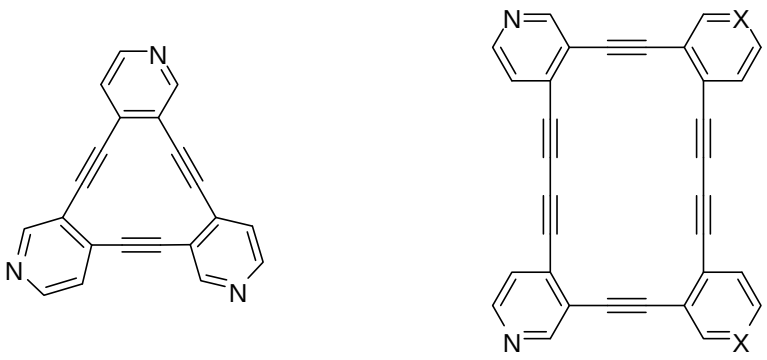


Figure 1-31 Graphyne and Graphdiyne[97]

1.6 Heterocycle-Fused Annulenes

1.6.1 Pyrido-Annulenes

Baxter and Dali-Youcef recently synthesized the first all nitrogen heterocyclic o-fused dehydroannulenes (**100** and **101a**, Figure 1-32) as well as an additional hybrid cycle containing both pyridine and benzene rings **101b**.[98] [20]Annulene systems **101a** and **101b** were constructed in a stepwise intra molecular fushion by selective alkynylation of 3-bromo-4-iodopyridine, whereas tripyrido[12]cyclyne **100** was obtained via intermolecular 3-fold coupling of 4-ethynyl-3- iodopyridine. Compound **100** possessed a selective photoluminescent quenching sensory response for Pd(II) and was precipitated as a coordination polymer upon high Ag(I) concentrations.



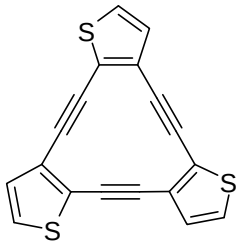
100

101a X=N
101b X=C

Figure 1-32 Pyrido-Annulenes

1.6.2 S-Based Heteroannulenes

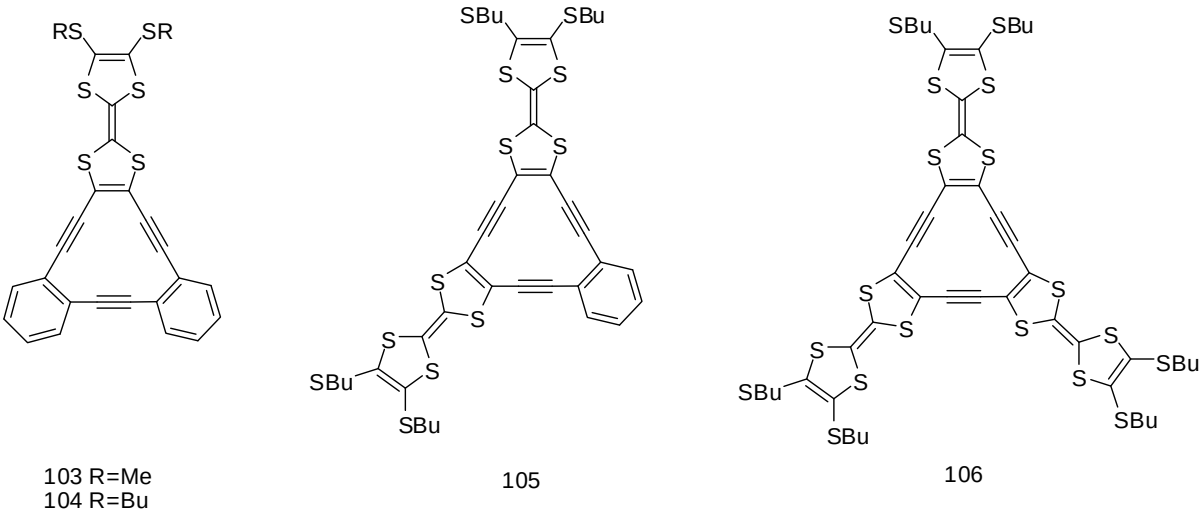
Youngs reported the first thienocyclyne **102** (Figure 1-33) in 1990 from cyclotrimerization of 3-ethynyl-2-iodothiophene via Stephens-Castro conditions in 20% yield.[99] Four years later its organometallic complex was isolated, which exhibited significant distortion of the cyclyne core since Co complex with only two alkyne groups.[100]



102

Figure 1-33 Dehydrothieno[12]annulene

Mono- **103**, **104**, bis- **105**, and tristetrathiofulvalenylacetylene **106** macrocycles were reported by Iyoda et al. in 2004[101] (Figure 1-34). The solid-state **103** displayed a slipped-stack dimeric association with a staggered co-facial array in addition to boat conformations for the TTF moieties. CV studies indicated a four-step redox process for the hybrid cycles **103, 104** and **105** with oxidation potentials for being as conducting radical salts.



103 R=Me
104 R=Bu

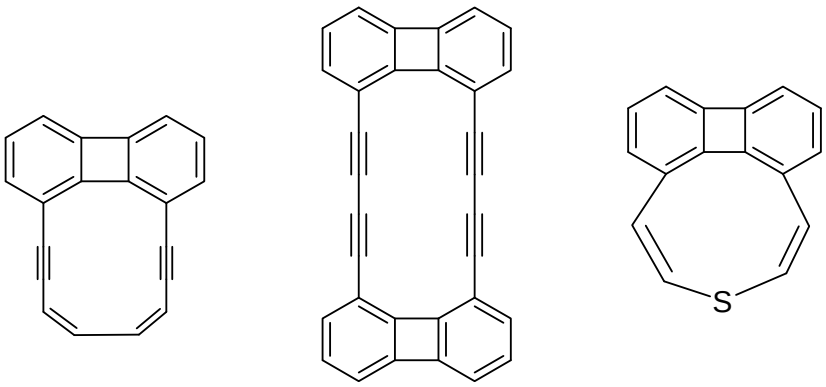
105

106

Figure 1-34 Tetrathiafulvaleno[12]annulenes

1.7 Our targets

Inspired by the result of planarization ability of biphenylene by Wilcox's group and interest on dehydrobenzoannulene and S-based heteroannulenes, we decided to attempt to annelate biphenylene to dehydrobenzoannulene cores and study the properties of such systems. Compound **108**, **109** and **110** are biphenylene [12], [16] and [10] annulenes from biphenylene annelation.

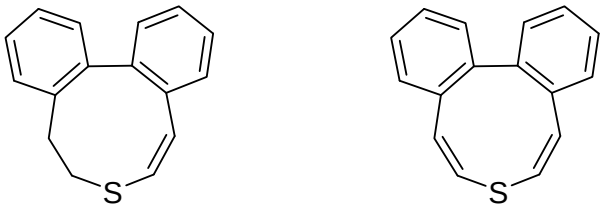


[12] [16] [10]

108 109 110

Figure 1-35 Our Targets

Moreover, after 4,5,6,7-dibenzocyclobutathionin(biphenylenothionin) **110** was approached, we'd better compare it with the according biphenyl systems. So biphenyl systems (*Z*)-5, 6-dihydrodibenzo[d,f]thionine **111** and dibenzo[d,f]thionine **112** would be synthesized and investigated as comparisons (Figure 1-36).



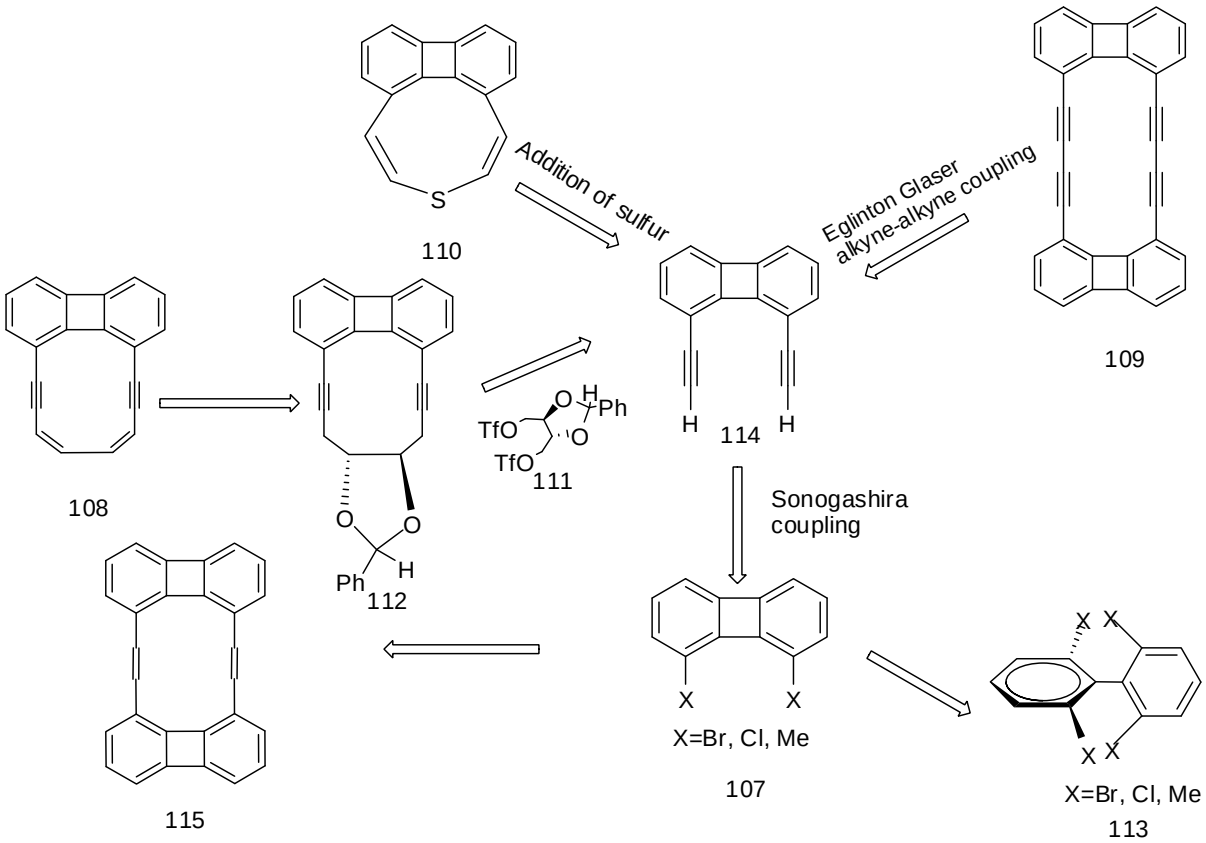
111 112

Figure 1-36 Comparisons

Chapter 2 Retro synthetic Analysis

Biphenylenothionine **110** and bis(diacetylene)biphenylene **109** would be prepared from 1,8-diacetylenebiphenylene **114** by addition of Sulfur and Eglinton-Glaser alkyne-alkyne coupling respectively.

Mono biphenylene planarized antiaromatic system **108** could be approached by addition of compound **111** to 1,8-diacetylenebiphenylene **114** followed by deprotection and elimination. 1,8-Diacetylenebiphenylene **114** would be prepared from Sonogashira coupling reaction[175] of 1,8-dihalobiphenylene and trimethylsilylacetylene. Compound **115** could be prepared from 1, 8-dimethyl biphenylene. So the key intermediates in this project are 1, 8-diacetylenebiphenylene **114** and 1, 8-disubstitued biphenylenes **107**.



Scheme 2-1 Retro Synthetic Analysis

Chapter 3 Preparation of Disubstituted Biphenylene 107

3.1. Biphenylene

3.1.1 Biphenylene

Biphenylene is one of the more interesting aromatic hydrocarbons because it contains the skeletons of the prototypes of both “aromatic” and “anti-aromatic” hydrocarbons, benzene and cyclobutadiene. Within biphenylene can be seen 4 π, 6 π, 8 π, and 12 π circuits so the overall aromaticity is not obvious.

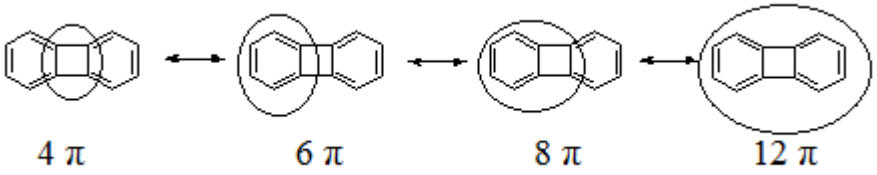
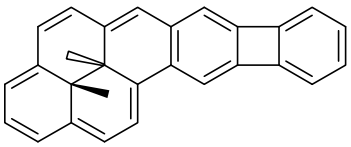


Figure 3-1 Biphenylene

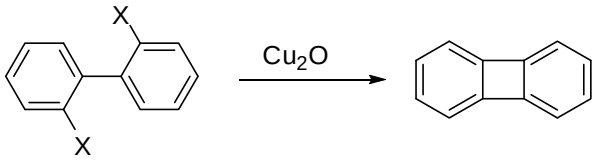
Estimates of the resonance energy of biphenylene relative to that of benzene, range from 0.43 to 1.78 in the literature.[102] In 1996, Mitchell synthesized biphenylene fused dihydropyrene **116** by cycloaddition of dibromobenzocyclobutadiene with the oxa[17]annulene and deoxygenation of the adduct with Ti(0). Analysis of the NMR data indicates that biphenylene has about 55% of the relative bond fixing ability of benzene, which is equated to relative aromaticity. The experimentally determined Dewar resonance energy is 1.59 times that of benzene and Dewar calculates 1.55 times benzene.[103]



116

Figure 3-2 Biphenylene Fused Dihydropyrene

Biphenylene **118** was prepared by Lothrop[104] in 1941 by an Ullman reaction (Scheme 3-1) and was the only known derivative of cyclobutadiene fused to benzene for many years.



117a X=Br
117b X= I

118

Scheme 3-1 Synthesis of Biphenylene by Lothrop

There are five canonical uncharged structures (**118a-e)** for biphenylene, two of which contain a cyclobutadiene ring and three which do not; the X-ray crystallographic structure shows that biphenylene is best represented by the structure shown in Figure 3-3.[105] The bonds between the 6-membered rings approximate to single bonds in length and there is some bond alternation in the 6-membered rings, indicating that the canonical structure **118a** containing the tetrakis(methylene) cyclobutane moiety is the major contributor.

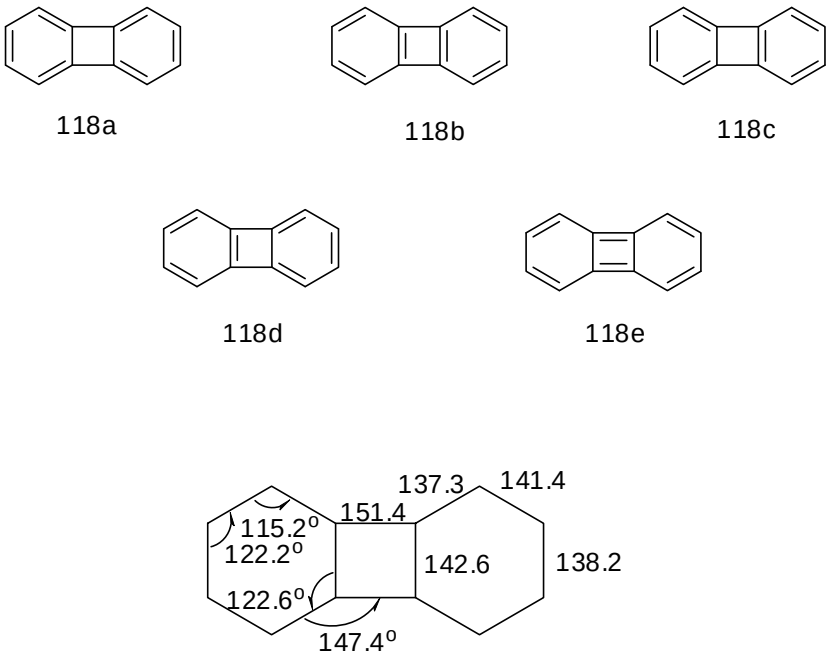


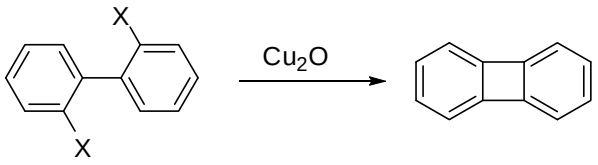
Figure 3-3 Canonical Structures and X-ray Crystallographic Structure of Biphenylene.

3.1.2 Preparative Methods of Biphenylene

The preparation of interesting hydrocarbon biphenylene encountered repeated failures and only one isolated and irreproducible success. The earliest report is that of Hosaeus[106] who carried out a Wurtz reaction with o-dibromobenzene but obtained biphenyl as the only hydrocarbon. An internal Ullmann reactions[107] in which 2, 2'-diaminobiphenyl was diazotized and treated with copper, gave carbazole, while attempted dehydration of 2-hydroxybiphenyl not unexpectedly also failed.[108]

3.1.2.1 By Coupling a Biphenyl

Lothrope [104] eventually succeeded in obtaining traces of biphenylene using a partially oxidized sample of copper as the dehalogenating agent. They found pure copper metal likewise was without effect, but some old copper powder which had been partially oxidized by long standing gave a small quantity of the compound.



117a X=Br
117b X= I

118

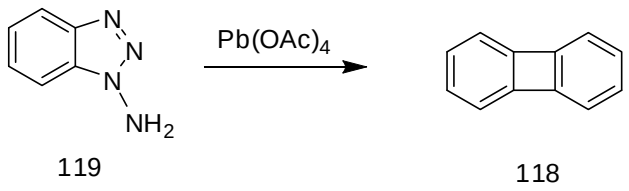
Scheme 3-1 Synthesis of Biphenylene by Lothrop

Based on Lothrop's original synthesis, preparing by coupling a biphenyl at the *ortho* positions of the two rings has been used to prepare a large variety of biphenylenes.[109] Copper powder appears preferable to the copper (I) oxide originally used as the cyclizing agent.

3.1.2.2 By Dimerization of Benzyne

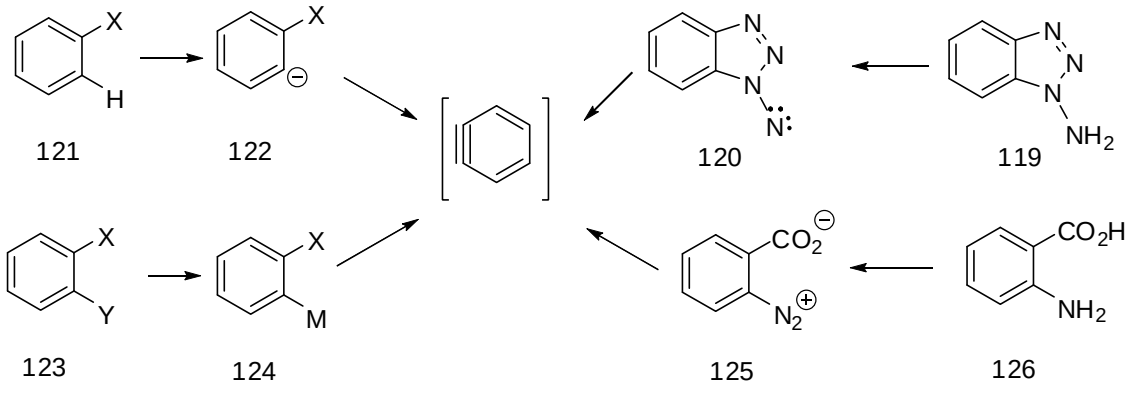
This method involves the dimerization of benzyne and the yield of biphenylene depends on the method of generation of the benzyne. For example the oxidation of l-aminobenzotriazoles

119 with lead tetraacetate produces high yields of biphenylene,[110] but substituted benzotriazoles are rather inaccessible.



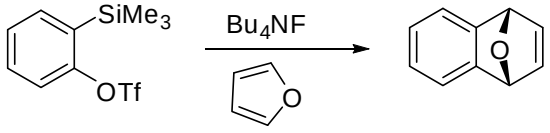
Scheme 3-2 Synthesis of Biphenylene by Rees

Many methods of generating benzyne from a variety of precursors such as *o*-halogenophenyl anions **122** and benzenediazonium-2-carboxylate **125** have been reported and summarized in Scheme 3-3.[132] A halide can be treated with a strong base such as an amide to remove the o-aromatic proton and generate benzyne via an anion.[133-135] Alternatively, treating o-dihalosubstituted benzenes with a metal (lithium or magnesium) can give the desired aryne by elimination.[132]



Scheme 3-3 General Methods for Generation of Benzyne

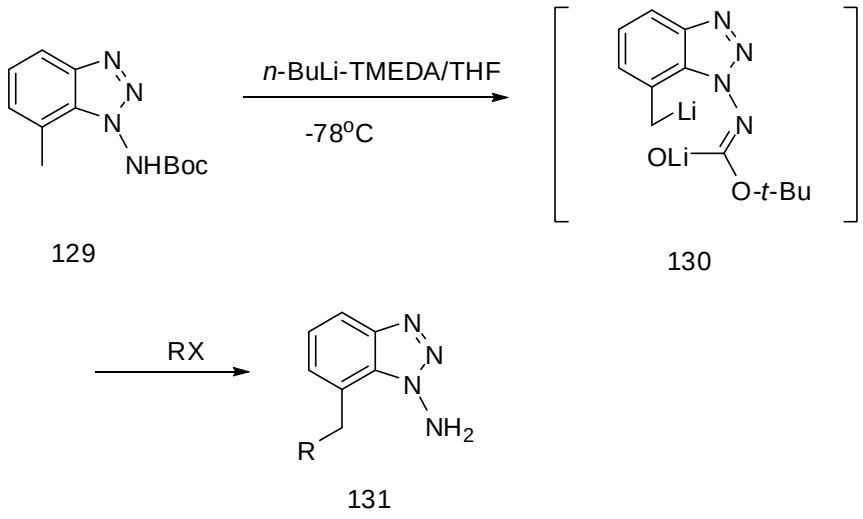
Aryl triflates have been used to generate arynes via other routes than metal – halogen exchange. For example, fluoride ion displacement of the trimethylsilyl group provides a convenient route to benzyne under mild conditions (Scheme 3-4).[132]



127 128

Scheme 3-4 Generation of Benzyne from Triflates

Oxidation of aminotriazole usually produces good yields, but has the disadvantage of requiring the presence of an oxidant such as lead tetraacetate in the reaction medium.[132] Deprotonation of 7-methyl-1-aminobenzotriazole derivatives **129** leads to 7-substituted-1-aminobenzotriazoles **131**, precursors of o-substituted benzynes (Scheme 3-5).



129 130 131

Scheme 3-5 Generation of Benzyne from Aminobenzotriazoles

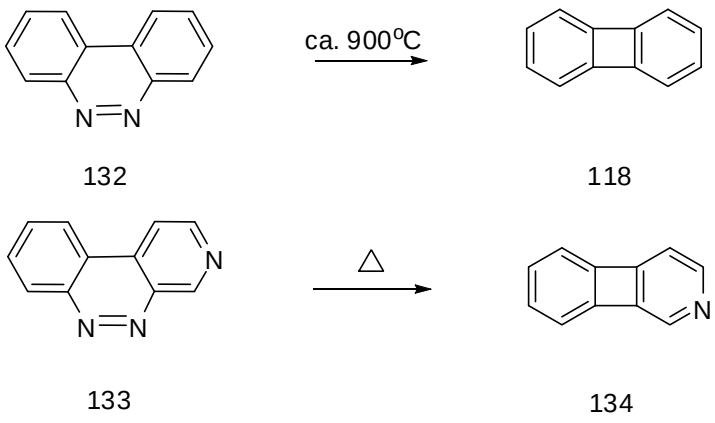
To have synthetic and mechanistic use, the benzyne precursors should fulfill the following requirements: (i) practical facility in their synthesis; (ii) formation of only one aryne for a

given precursor; (iii) relative stability and safe ease of handling and (iv) the absence of a requirement to use a strong base or high temperature in the generation of benzyne.

3.1.2.3 By Extrusion of Gas

This method, by extrusion of nitrogen or carbon dioxide and carbon monoxide from benzo-[*c*]cinnolines or phthalic anhydrides, utilizes flash vacuum pyrolysis and is only suitable for small amount. It is a highly versatile method, however, and a variety of biphenylenes and heterobiphenylenes have been prepared by this route.[111-114]

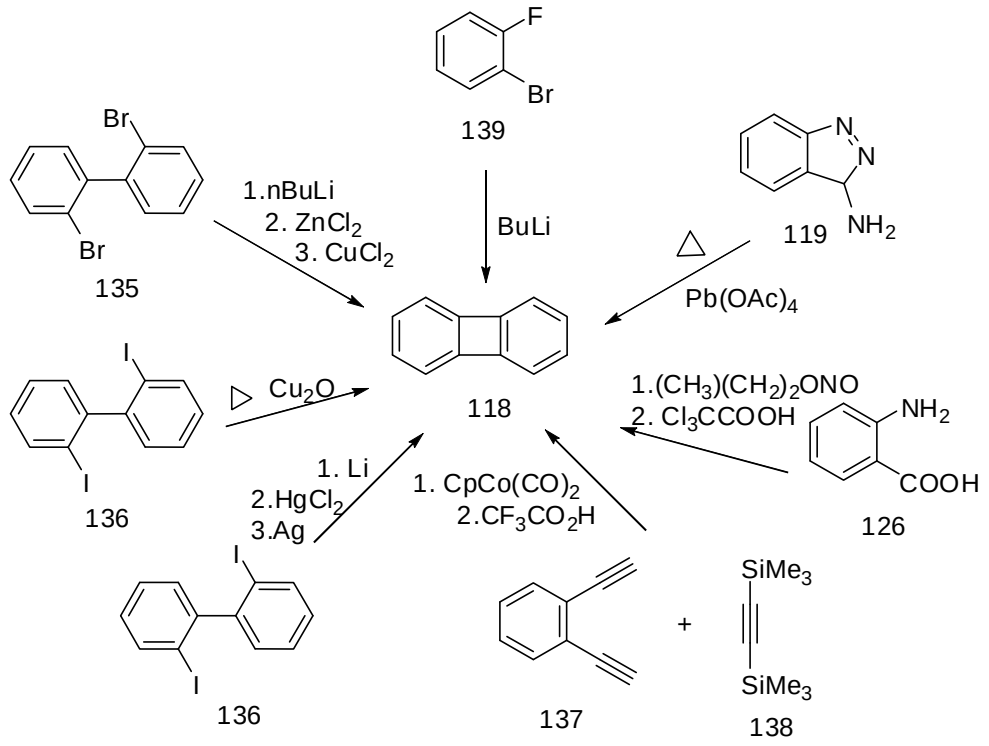
Analogues of biphenylene in which one of the benzene ring has been replaced by another heterocyclic ring have also been prepared. Pyrolysis of the appropriate N-substituted benzocinnoline **133** thus gives the pyridino biphenylene **134**.[115-122]



Scheme 3-6 Synthesis of Biphenylene and its Analogue by Pyrolysis

Many alternative protocols have been developed for its synthesis, but the known procedures for the preparation of biphenylene are unsatisfactory because they either use expensive starting materials or they afford biphenylene only in small amounts.[123]

A summary of the known, preparative useful synthetic routes which are not based on vacuum-pyrolysis is given in Scheme 3-7.



Scheme 3-7. Synthetic Routes to Biphenylene Not Based on Vacuum-pyrolysis Methods.

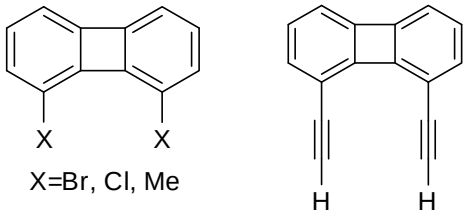
Starting from **139**, **119**,[124] and **126**,[125] an aryne intermediate would be formed via elimination reactions, which dimerizes to biphenylene. With the exception of the procedure starting from **119**, the yields of biphenylene formation are generally low and compound **119** has to be prepared in four steps from o-nitroaniline in approximately 54% yield. [124]

Nowadays the standard method for the synthesis of biphenylene is from commercially available anthranilic acid **126**, which leads to 76 in 21%–30% yield.[125] However, explosive benzenediazonium-2-carboxylate is an intermediate. Although it is not necessary to isolate this substance, it is a hazardous material which should be a driving force to replace it in the laboratory.

Other preparations starting from [1]**135** [28] and **136** [126,127] employ transition metal mediated coupling reactions of 2, 2'- dihalogenated derivatives of biphenyl. A method mainly developed by Vollhardt and co-workers [129] uses a cobalt mediated alkyne coupling reactions of o-diethynylbenzene **137** with other alkynes. This procedure is valuable for substituted biphenylene derivatives, but maybe too expensive for the synthesis of the parent biphenylene. Other ways to synthesize biphenylene rely on vacuum-pyrolysis, [130,131] with the typical drawbacks of an often troublesome preparation of starting materials, low yields, and the problem to synthesize larger amounts of the desired product.

3.2 Preparation of Disubstituted Biphenylene

Retrosynthetic analysis (Scheme 2-1) shows the key intermediate are 1, 8-diacetylenebiphenylene **114** and 1, 8-disubstitued biphenylenes **107.** The method of making disubstituted biphenylene is similar to methods of making biphenylene that we discussed above.



107 114

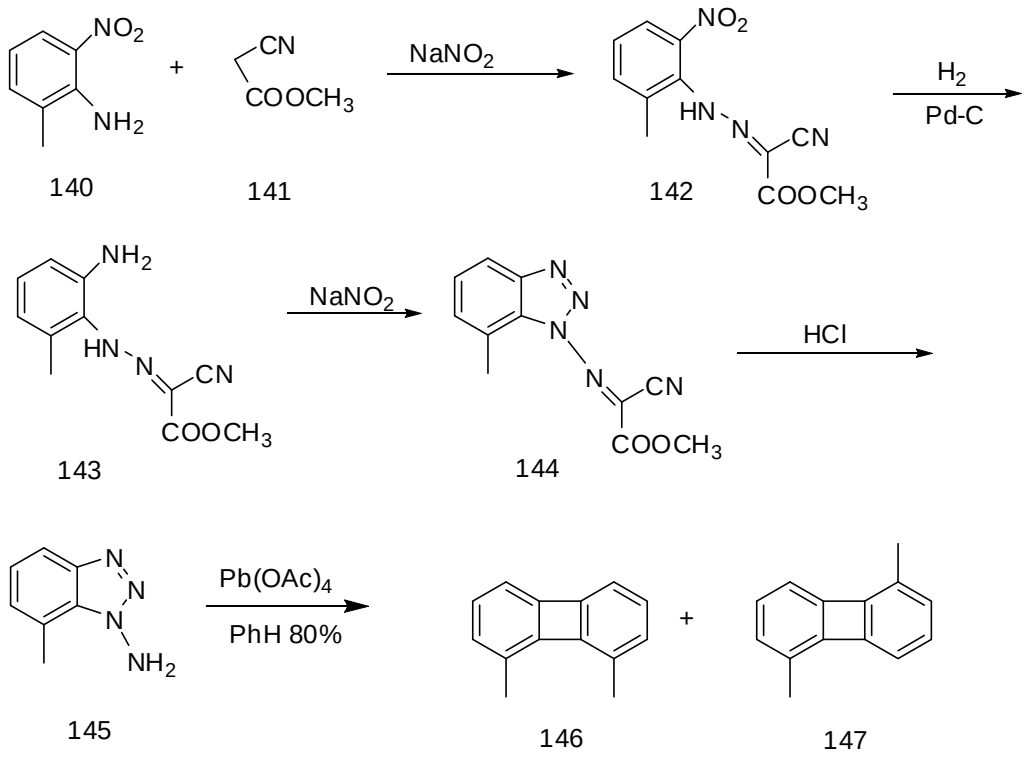
Figure 3-4 Disubstituted Biphenylenes

3.2.1 By Aryne Generation

Likewise with benzyne, methylbenzynes (toluynes) are generated in high yield in mild condition (room temperature, benzene or methylene chloride). But the method has been limited by the unavailability of the *ortho* methyl substituted 1-aminobenzotriazole.

Synthesis of dimethylbiphenylene has been done by former students [164] in our group by lead tetraacetate oxidation of 4-methyl-1-aminobenzotriazole **145**. 1, 5 and 1, 8 dimethylbiphenylene mixtures (**147** and **146**) were the final products and the ratio of these two dimethylbiphenylene was 1:1. 1-amino-7-methylbenzotriazole **145** was prepared in four steps from 2-methyl-6-nitroaniline **140** by the procedure outlined below (scheme 3-8).

Coupling of the diazotized amine with methylcyanoacetate **141** in an acetate buffered aqueous solution produced the hydrazone **142**. Catalytic hydrogenation of the hydrazone converted the nitro group into the more versatile amino compound **143** which was isolated pure prior to further diazotization. Hydrolysis of the obtained intermediate **144** afforded the free amine **145**, which on oxidation by lead tetraacetate gave 1,5- and 1,8-dimethylbiphenylenes **147** and **146** (1:1 ratio) in high yield and equal ratio.



Scheme 3-8 Synthesis of Dimethylbiphenylene by Aryne Generation

As shown in the GC spectrum (Figure 3-6), the two isomers (m/z 180) have a similar fragmentation pathway. Consecutive loss of methyl groups (m/z 165 and m/z 152, +2Hs) to afford the parent biphenylene.

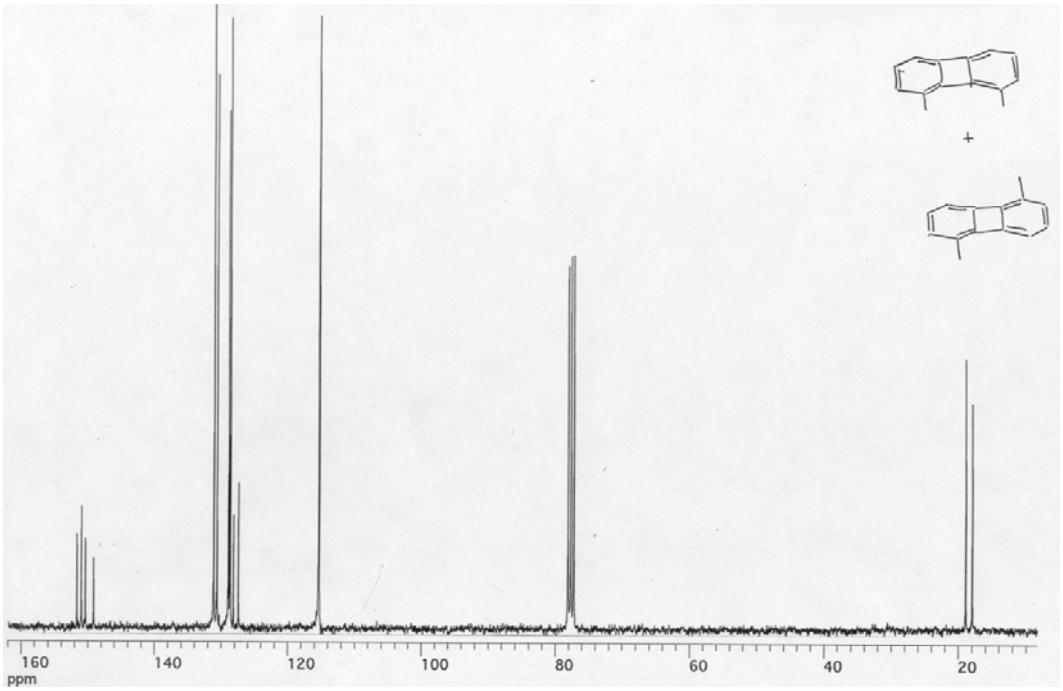


Figure 3-5 NMR of the mixture of 1,5- and 1,8- Dimethylbiphenylene (1:1)

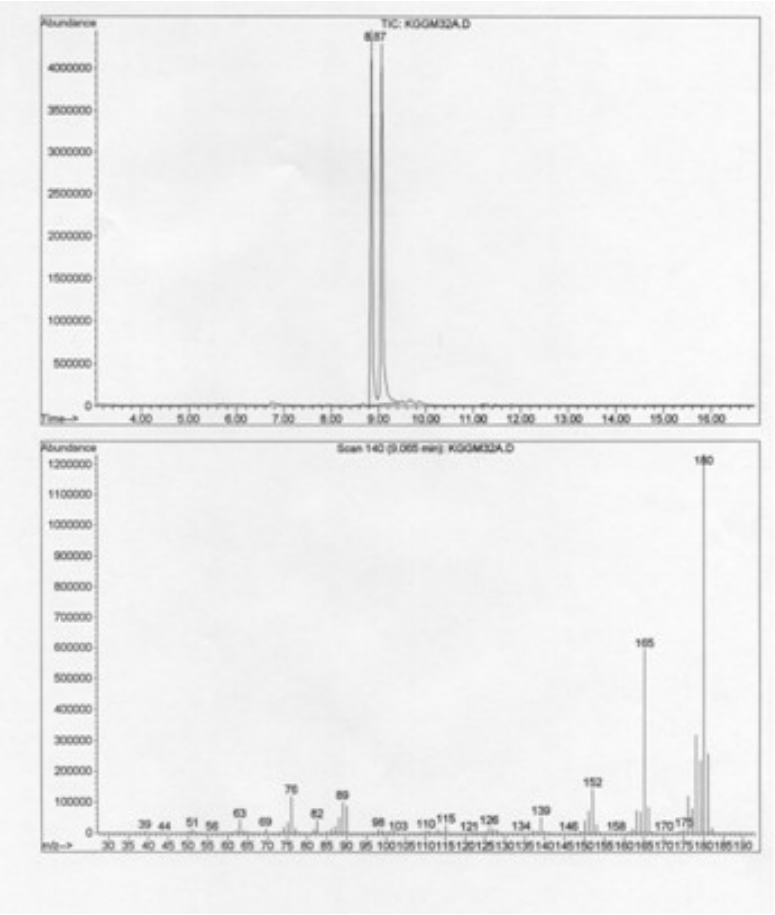
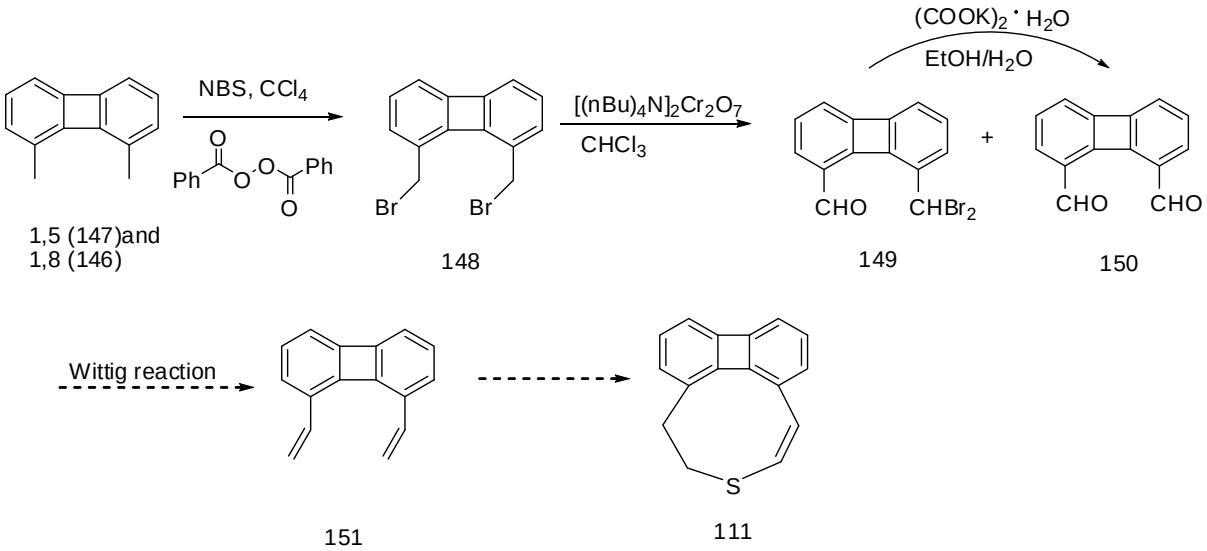


Figure 3-6 GC-MS of the Mixture of 1,5- and 1,8- Dimethylbiphenylene (1:1)

1,5- and 1,8-Dimethylbiphenylenes **147** and **146** (1:1 ratio) were treated with NBS in CCl_4 and benzoyl peroxide to get the corresponding bromo-substuited compounds. The resulting were mixing compounds of mono-bromo substituted, di-bromo substituted and tri-bromo substituted 1,5 and 1,8 dimethylbiphenylenes. The three bromo-substituted dimethylbiphenylene's yield was 2.4%, 27% and 14.7% respectively. Oxidation of the dibromo compounds **148** resulted in corresponding mono-aldehyde and di-aldehyde substituted 1,5 and 1,8 dimethylbiphenylenes. The mono-aldehyde substituted 1,5 and 1,8 dimethylbiphenylenes **149** could be converted to di-aldehyde substituted 1,5 and 1,8 dimethylbiphenylenes **150** by treating with potassium oxalate in ethanol and water. The overall yield of converting di-bromo substituted 1,5 and 1,8 dimethylbiphenylenes**148** to di-aldehyde substituted 1,5 and 1,8 dimethylbiphenylenes **150** was 22%.



Scheme 3-9 Synthesis of 111 from Dimethylbiphenylene

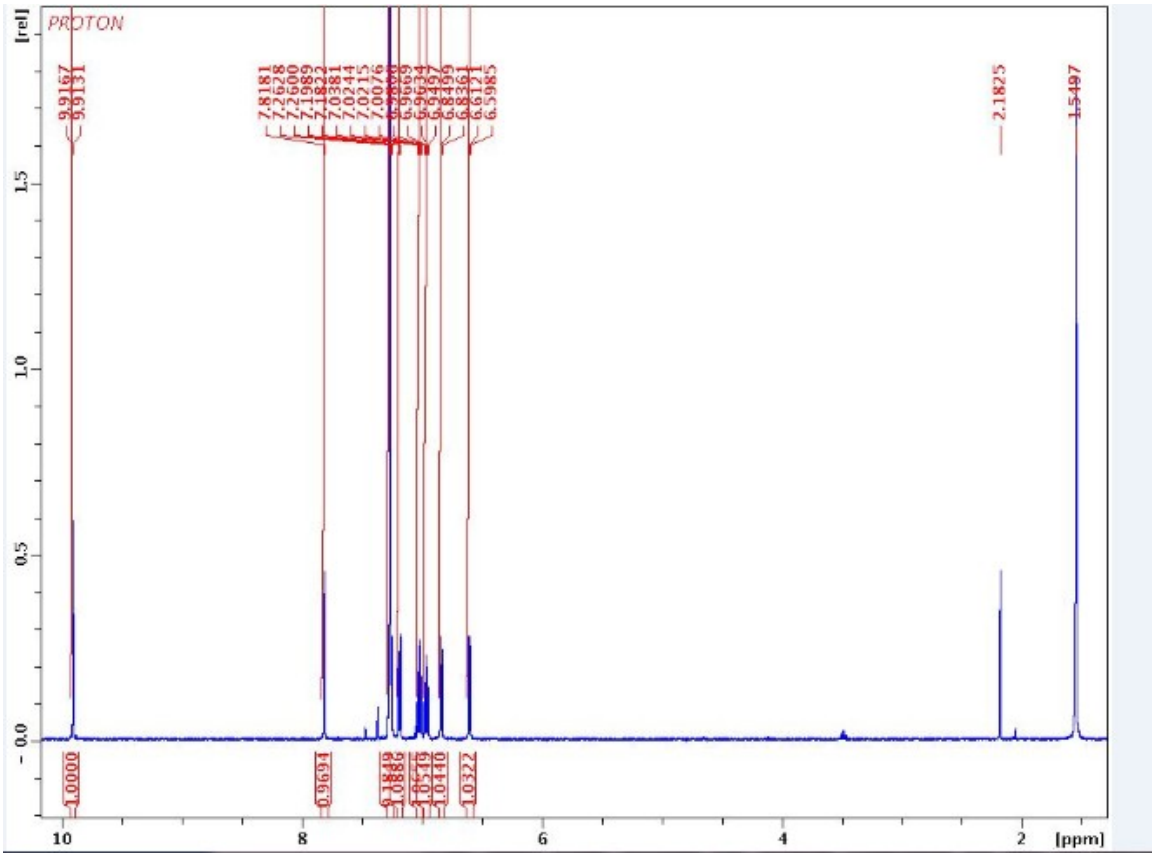


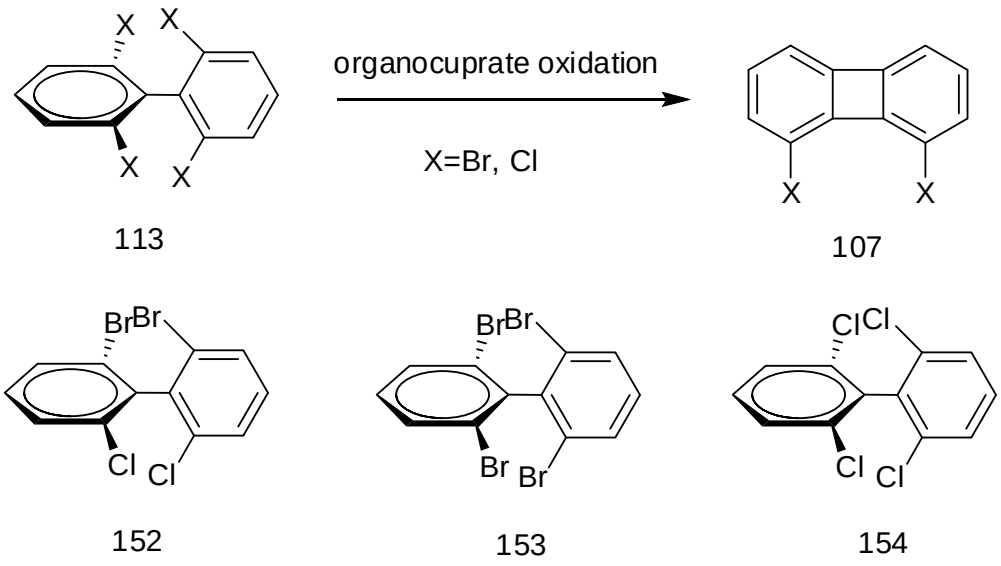
Figure 3-7 ^{1}H NMR Spectrum of the Mixture of 1,5- and 1,8- Dialdehydebiphenylene

The next step would be Wittig reaction of the di-aldehyde substituted 1,5 and 1,8 dimethylbiphenylenes **150** to get di-vinyl substituted 1,5 and 1,8 dimethylbiphenylenes **151** and then covert them to biphenylene planarized aromatic system's comparison **111**.

But **148**, **149** and **150** are all 1, 5 and 1, 8 mixtures, and we found it was very hard to separate those two isomers even at the aldehyde stage. So the trial of preparing key intermediate 1, 8-disubsituted biphenylene from aryne generation was not a good choice. Other methods to reach the key intermediate would be considered.

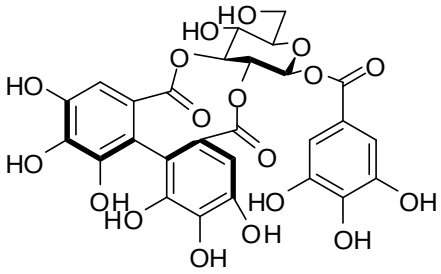
3.2.2 By Coupling a Biphenyl

The second method of preparing disubstituted biphenylene would be coupling a biphenyl (organocuprate oxidation) from tetrahalosubstituted biphenyl. The tetrahalosubstituted biphenyl could be 2,2'-dibromo-6,6'-dichlorobiphenyl **152**, 2,2',6,6'-tetrabromobiphenyl **153**, or 2,2',6,6'-tetrachlorobiphenyl **154**.

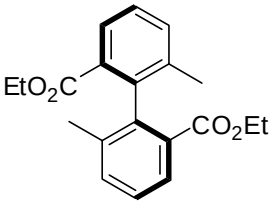


Scheme 3-10 Synthesis of Disubstituted Biphenylene by Organocuprate Oxidation

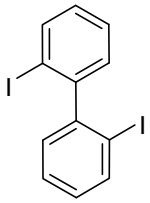
There are many ways to construct biaryls,[136] mostly through palladium-,[137,138] nickel-,[139] or copper-mediated processes.[140] Unfortunately, only a limited number is suitable for the synthesis of medium-ring compounds such **155**,[141,142] sterically hindered systems such as **156**, and iodinated biaryls such as **157** (Figure 3-8). Biaryl-containing medium-ring compounds are difficult to synthesize using existing methodology because of their associated torsional, transannular, and large angle strain.



155



156



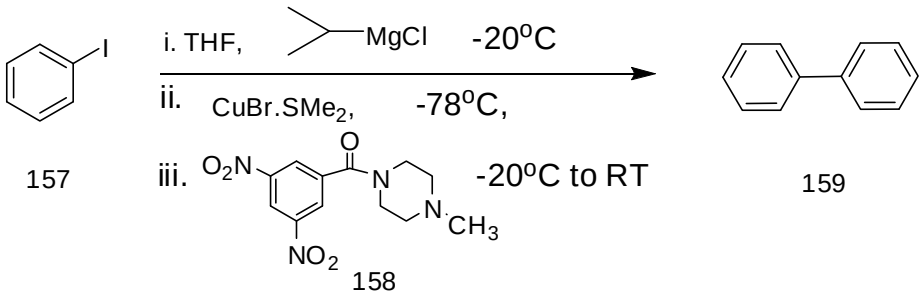
136

Figure 3-8 Biaryl-containing Medium-ring Compound, Sterically Hindered Biaryl, and Iodinated Biaryl

In addition, the synthesis of biaryls that contain four *ortho* substituents is often challenging, and palladium-catalyzed reactions of synthesizing four *ortho* substituted biaryls have only recently been developed.[143] Moreover, iodinated biaryls are only formed by a relatively small number of reactions.[144]

Besides, oxidation of organocuprates allows the formation of both intermolecular[145] and intramolecular[146] biaryl bonds; however, extreme reaction conditions and poor functional-group tolerance means that this reaction is not seen as being widely useful.

In 2005, Spring[149] group reported a general, efficient and functional group tolerant method to synthesize biaryl compounds. In this method, the aryl Grignard reagents was treated with copper bromide dimethyl sulfide and then oxidized with 3, 5-dinitrobenzo-1-methylpiperazine **158** at room temperature and an excellent yield of the biaryl could be obtained.



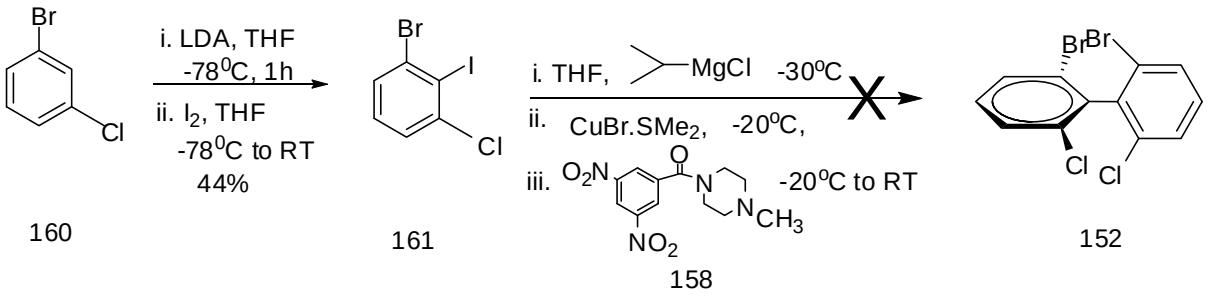
Scheme 3-11 Synthesis of Biaryl Compounds by Spring

The optimized methodology can be used for the preparation of a wide range of functionalized biaryls. The reaction does not seem to be significantly influenced by steric interactions, thus allowing the synthesis of a biaryl bond with multiple *ortho* substituents. Iodinated aromatic heterocycles are also suitable substrates, which makes the synthesis of the corresponding dimer possible.[147] The iodine–magnesium exchange can be performed in the presence of an aryl bromide,[148] which allows the formation of brominated biaryls. Furthermore, the ability to regioselectively perform a single iodine–magnesium exchange on multiply iodinated substrates permits the synthesis of iodinated biaryls which are often extremely difficult to form directly by other methods because of oligomerization. The reaction is also successful when performed intramolecularly so that strained medium-ring compounds with ten- and eleven-membered rings can be constructed without the need for high dilution conditions. Also, the success of this cyclization allows cross-coupling of different aryl units.

3.2.2. 1 Synthesis of 2, 2'-dibromo 6, 6'-dichlorobiphenyl 152

a. From 1-bromo-3-chloro-2-iodobenzene

Iodination[150] of 3-chloro-bromobenzene **160** by treating with LDA at -78°C for 1h and then with I_2 afforded the resulting iodo compound **161**, namely 1-bromo-3-chloro-2-iodobenzene and the yield was 44% after chromatography. Isopropyl magnesium chloride was added to the THF solution of the iodole compound **161** and organocuprate oxidation[149] of the resulting solution with copper (I) bromide dimethyl sulfide and 3,5-dinitrobenzo-1-methylpiperazine **158** gave no 2,2'-dibromo 6,6'-dichlorobiphenyl **152**.



Scheme 3-12 Synthesis of 2, 2'-Dibromo 6, 6'-dichlorobiphenyl from 1-Bromo-3-chloro-2-iodobenzene

Two sets of doublet-doublet, doublet-doublet and triplet peaks were found in the ^{1}H NMR spectrum of 1-bromo-3-chloro-2-iodobenzene, and the integration ratio was about 1:6. So the white crystal obtained contained two compounds that couldn't be separated by chromatography. GC-MS gave the idea that the major compound was 1-bromo-3-chloro-2-iodobenzene and the minor compound was 1-chloro-2, 3-diiodobenzene.

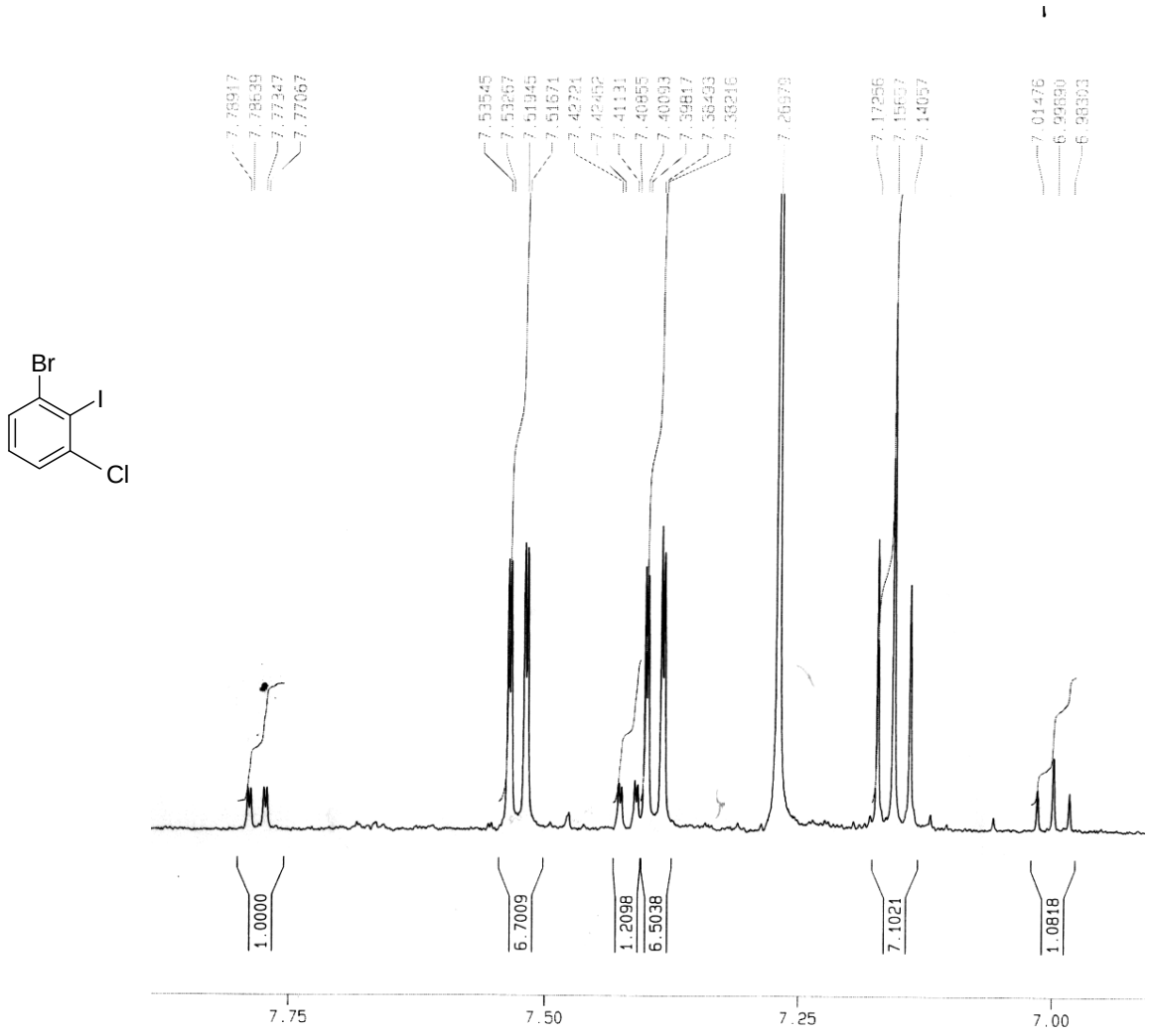


Figure 3-9 NMR Spectrum of 1-Bromo-3-chloro-2-iodobenzene

Later on we tried to use isopropyl magnesium bromide instead of isopropyl magnesium chloride, 2,2'-dibromo 6,6'-dichlorobiphenyl was obtained successfully and the yield was 28%.

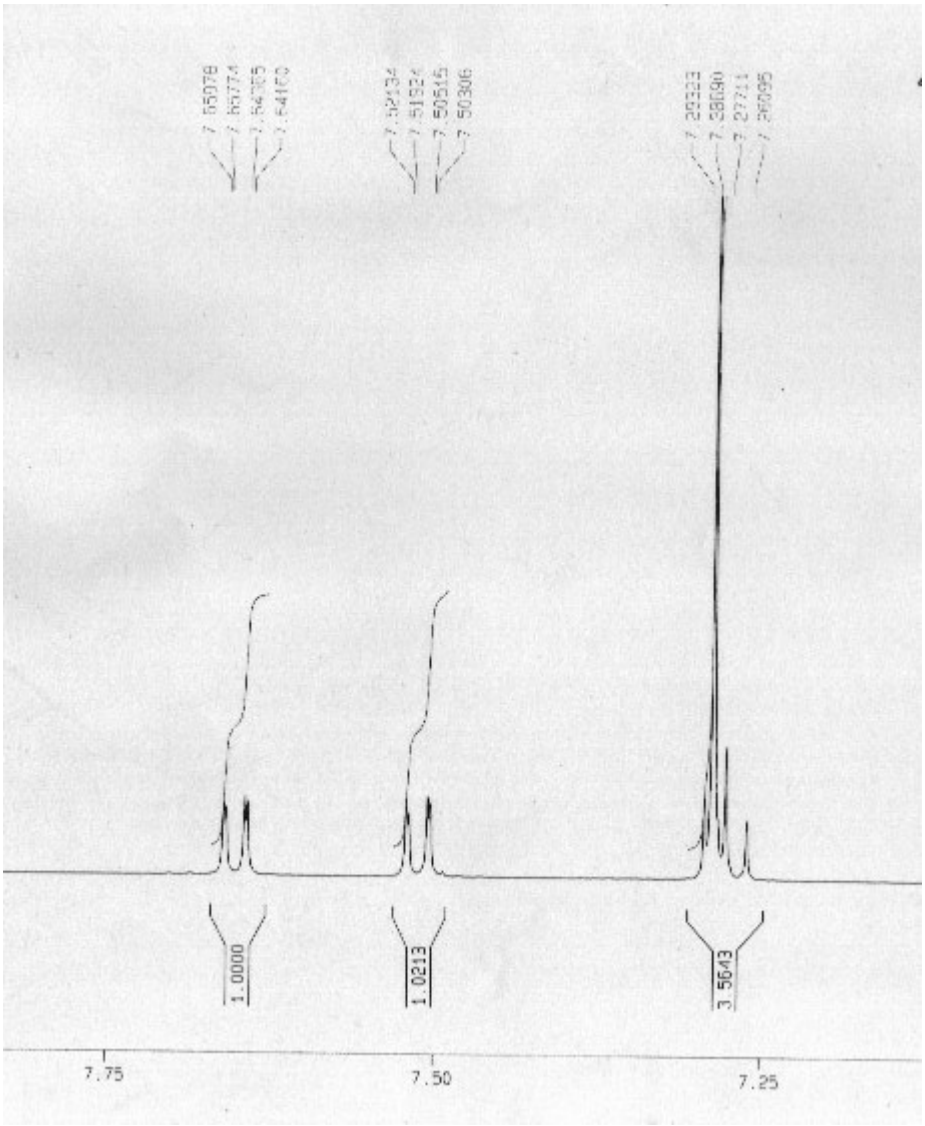
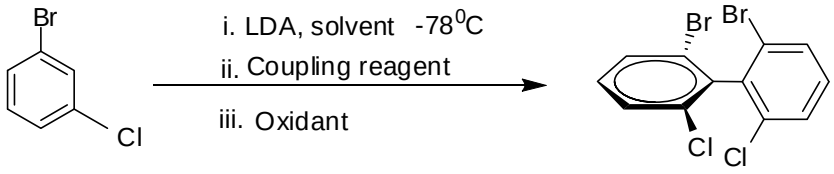


Figure 3-10 NMR Spectrum of 2,2'-Dibromo 6,6'-dichlorobiphenyl

b. From 3-chloro-bromobenzene

Starting from 3-chloro-bromobenzene **160** solution, regioselective lithiation with LDA at –78^{0}C gave 1-bromo-3-chlorophenyllithium, which was treated with coupling reagent and the temperature was allowed to warm up to –30^{0}C while stirring. Organocuprate oxidation[149] of the resulting solution with oxidant afforded 2, 2'-dibromo 6, 6'-dichlorobiphenyl **152**. We've

tried 3-chloro-bromobenzene in different solvents, and used different coupling reagents and different oxidants. The results are shown in table 3-1.

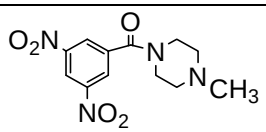


160 152

Scheme 3-13 Synthesis of 2, 2'-Dibromo 6, 6'-dichlorobiphenyl from 3-Chloro-bromobenzene

Table 3-1 Results of Synthesis 2, 2'-Dibromo 6, 6'-dichlorobiphenyl from 3-Chloro-bromobenzene

Entry	Solvent	Coupling reagent	Oxidant	Yield (%)c
1	THF	$CuBr{\cdot}SMe_2$	**158**[a] in THF	20%
2	Ether/Hexane (3:1)	$CuBr{\cdot}SMe_2$	O_2	1.3%
3	Ether/Hexane (3:1)	$CuBr{\cdot}SMe_2$	**158** in THF	1.3%
4[b]	Ether	$CuBr_2$	$CuBr_2$	0
5	THF/Hexane (3:1)	$CuBr{\cdot}SMe_2$	**158** in THF	0



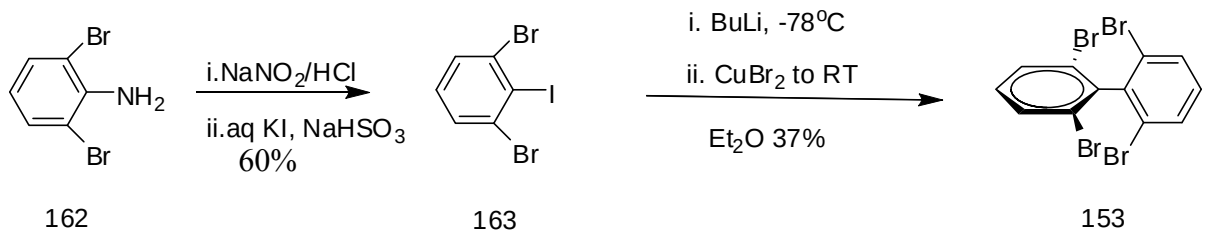
Note. a. 3, 5-dinitrobenzo-1-methylpiperazine **158** b. In entry 4, Copper (II) Bromide was coupling reagent and oxidant and was added into reaction at one time. c. In entry 1, the yield was after treatment with cold hexane, and in entry 2-5, it was after chromatograph (Petroleum ether).

It was very clear to know that so far the best condition to get 2, 2'-dibromo 6, 6'-dichlorobiphenyl is using THF as a solvent, $CuBr{\cdot}SMe_2$ as a coupling reagent and 3, 5-dinitrobenzo-1-methylpiperazine **158** as an oxidant.

3.2.2.2 Synthesis of 2, 2', 6, 6'-tetrabromobiphenyl 153

a. From 2, 6-dibromoaniline

Starting from 2, 6-dibromoaniline **162**, diazotization in cold hydrochloric acid using sodium nitrite gave the diazonium salt, which was converted to the corresponding iodo compound **163** when it was poured into a cold aqueous solution of potassium iodide. Aryl coupling occurred when the copper salt obtained by lithiation **163** and treatment with cupric bromide at low temperature was allowed to warm to RT. The tetrasubstituted biaryl, namely 2, 2', 6, 6'-tetrabromobiphenyl **153** was obtained and the yield was 37%.

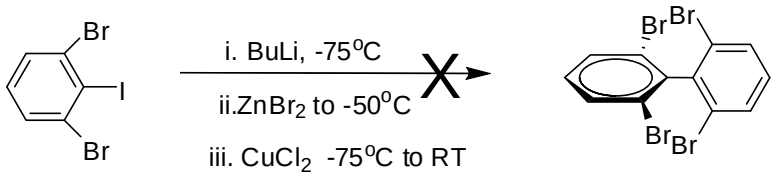


162 163 153

Scheme 3-14 Synthesis of 2, 2', 6, 6'-Tetrabromobiphenyl from 2, 6-Dibromoaniline

b. From 1-iodo-2, 6-dibromobenzene

Starting from 1-iodo-2, 6-dibromobenzene **163**, regioselective lithiation with BuLi in THF at –75^{0}C gave 2,6-dichlorophenyllithium, which was treated at –70^{0}C with solid zinc bromide then temperature was increased to –50^{0}C. Organozinc oxidation of the resulting solution with copper (II) chloride at–75^{0}C gave no product.



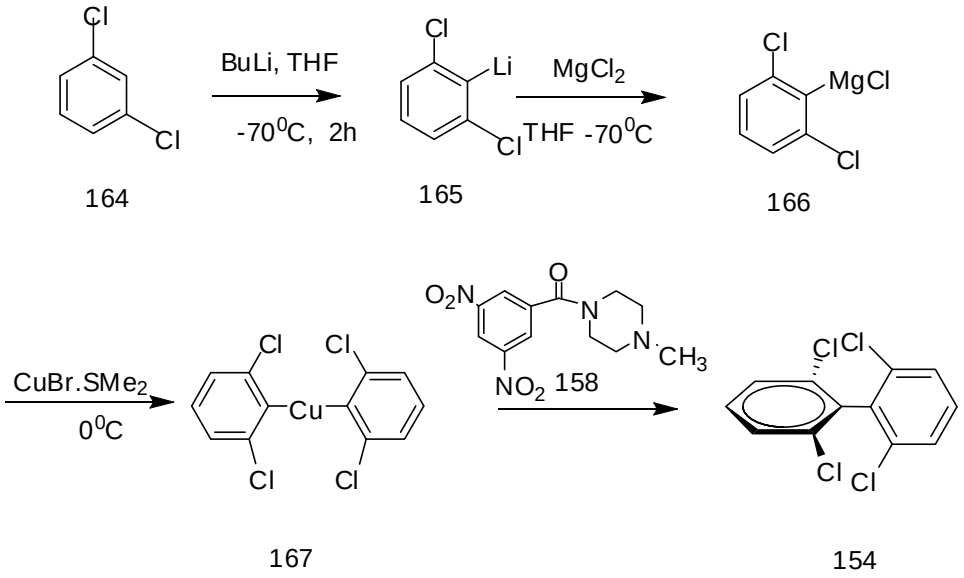
163 153

Scheme 3-15 Synthesis of 2, 2', 6, 6'-Tetrabromobiphenyl from 1-Iodo-2, 6-dibromobenzene

3.2.2.3 Synthesis of 2, 2', 6, 6'-tetrachlorobiphenyl 154

a. From 1, 3-dichlorobenzene

Starting from 1,3-dichlorobenzene **164**, regioselective lithiation with BuLi in THF at -70^0C gave 2,6-dichlorophenyllithium **165**, which was treated at -70^0C with freshly prepared $MgCl_2$ (from 1:1 equiv 1,2-dichloroethane and Mg powder in THF at room temperature) [151]. Organocuprate oxidation of the resulting solution with copper (I) bromide/dimethyl sulfide and 3,5-dinitrobenzo-1-methylpiperazine **158** gave 2, 2', 6, 6'-tetrachloro –biphenyl **154** . The yield was 53%.



Scheme 3-16 Synthesis of 2, 2', 6, 6'-Tetrachlorobiphenyl from 1, 3-Dichlorobenzene

This method was successful but the yield was rather low. We found 1, 2, 3-trichlorobenzene was one of the byproducts and its yield was 7.4%, which was probably from reaction of 2, 6-dichlorophenyllithium and unreacted 1, 2-dichloroethane in $MgCl_2$. So if we use excess Mg powder when preparing $MgCl_2$, the yield of 2, 2', 6, 6'-tetrachlorobiphenyl might be increased.

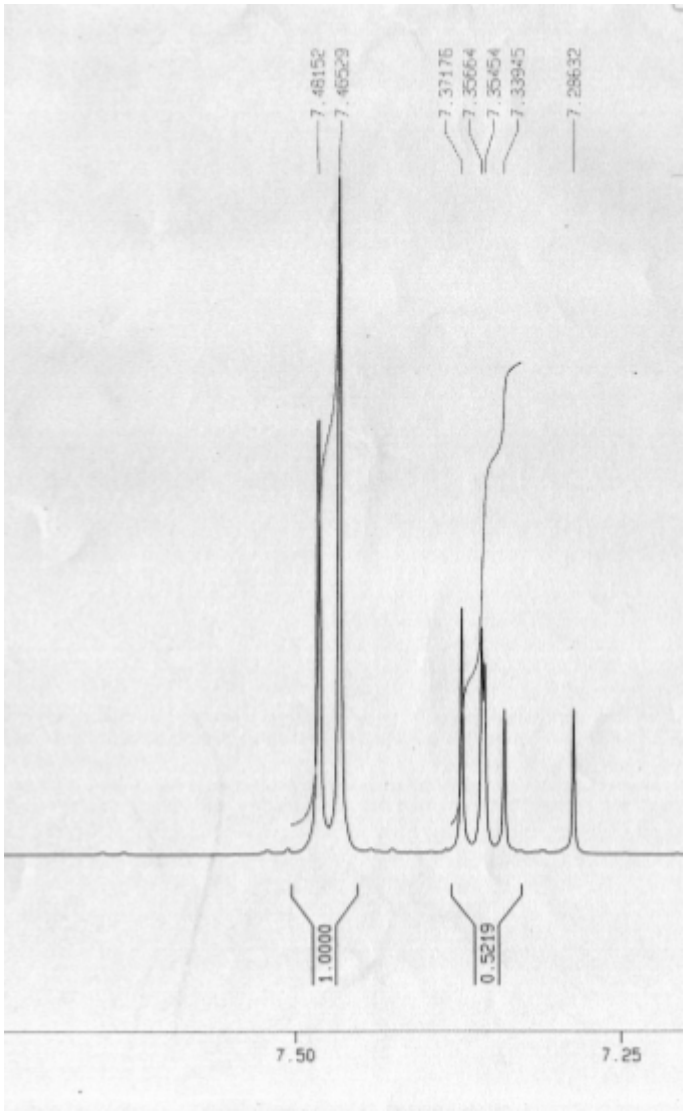
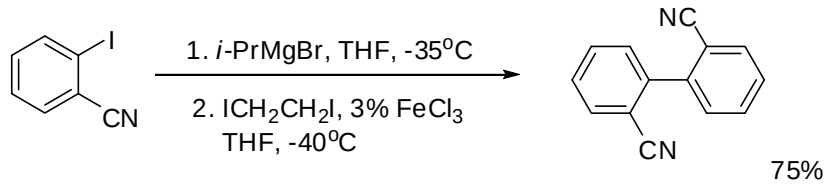


Figure 3-11 NMR Spectrum of 2, 2', 6, 6'-Tetrachlorobiphenyl

b. From 1, 3-dichloro-2-iodobenzene

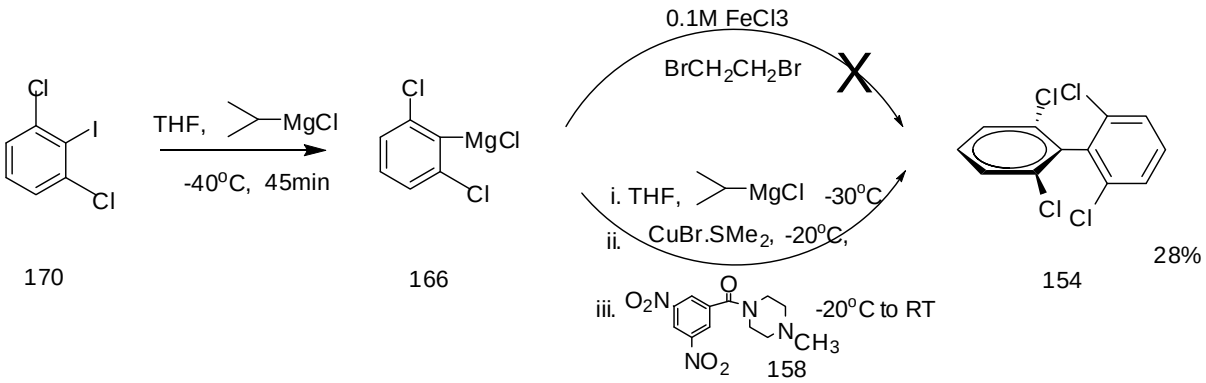
Recently G Cahiez[152] reported a successful iron-catalyzed homo coupling of aryl Grignard reagents. The reaction was highly chemoselective (CN,COOEt, NO_2 groups are tolerated), where iron is a catalyst and alkyl halides act as stoichiometric reoxidants.



168 169

Scheme 3-17 Iron-catalyzed Homo Coupling of Aryl Grignard Reagents by Cahiez

We tried this homo-coupling method with 1, 3-dichloro-2-iodobenzene **170** as starting material. The resulting 1, 3-dichloromagnesium chloride **166** was treated with 0.1M $FeCl_3$ in THF[153] and 1, 2-dibromoethane. Unfortunately we got 1/3 starting material back and no 2, 2', 6, 6'-tetrachlorobiphenyl **154**. Instead applying Organocuprate oxidation method to the resulting 1,3-dichloro benzene magnesium chloride with copper (I) bromide/dimethyl sulfide and 3,5-dinitrobenzo-1-methylpiperazine **158** gave 2, 2', 6, 6'-tetrachlorobiphenyl **154** successfully and the yield was 28%.



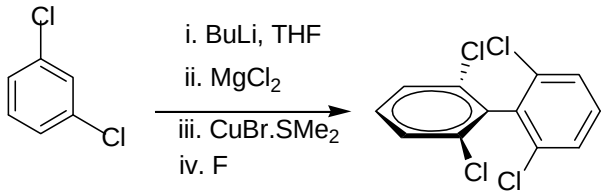
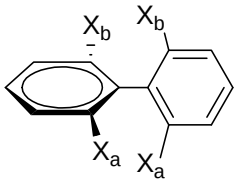
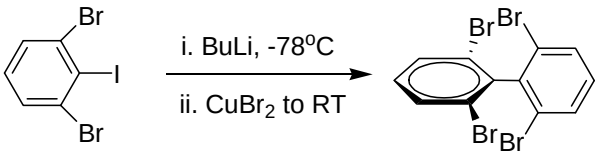
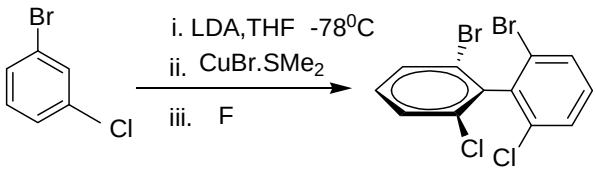
170 166 154

Scheme 3-18 Synthesis of 2,2',6,6'-Tetrachlorobiphenyl from 1, 3-Dichloro-2-iodobenzene

3.2.2.4 Conclusion of Synthesis of Tetrahalobiphenyl

Three different tetrahalobiphenyls have been achieved and the best result of each compound is listed in table 3-2.

Table 3-2 Conclusion of Synthesis of Tetrahalobiphenyl

Product	a	b	Yield (%)	Reaction
	Cl	Cl	53	
	Br	Br	37	
	Cl	Br	20	

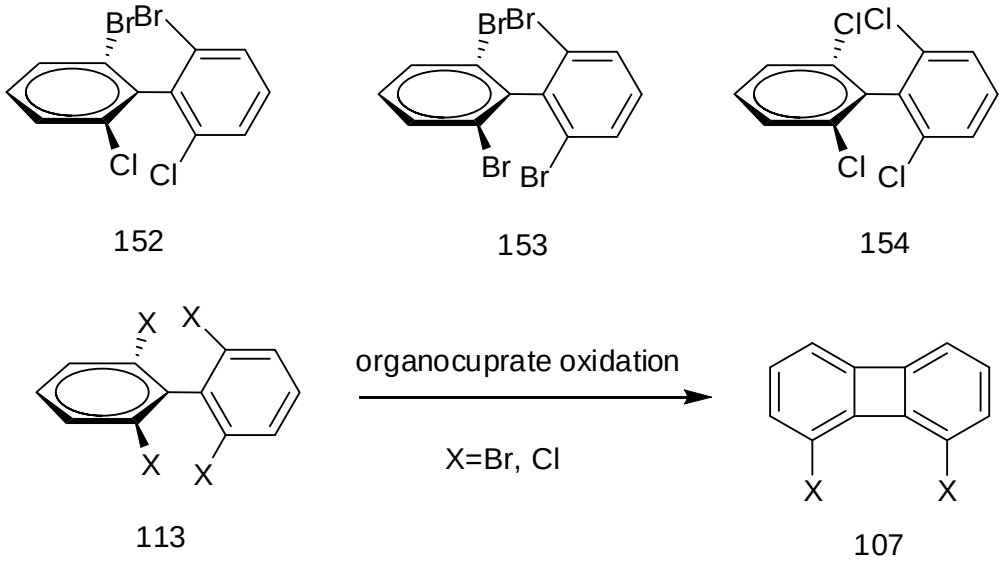
Among these three reactions, the highest yield was the synthesis for 2, 2', 6, 6'-tetrachlorobiphenyl, which was 53%. For 2, 2', 6, 6'-tetrabromobiphenyl, the best yield was 37%. But it would not be a good precursor for the next step because of its solubility and none selectivity of these four Brs.

In the 2, 2', 6, 6'-tetrachlorobiphenyl synthesis, 1, 2, 3-trichlorobenzene was found as one of the product and its yield was 7.4%. 1, 2, 3-trichlorobenzene might be from reaction of 2, 6-

dichlorophenyllithium and unreacted 1, 2-dichloroethane in $MgCl_2$. So if excess Mg powder could be used when preparing $MgCl_2$, the yield might be increased.

3.2.2.5 From Biphenyl to Biphenylene

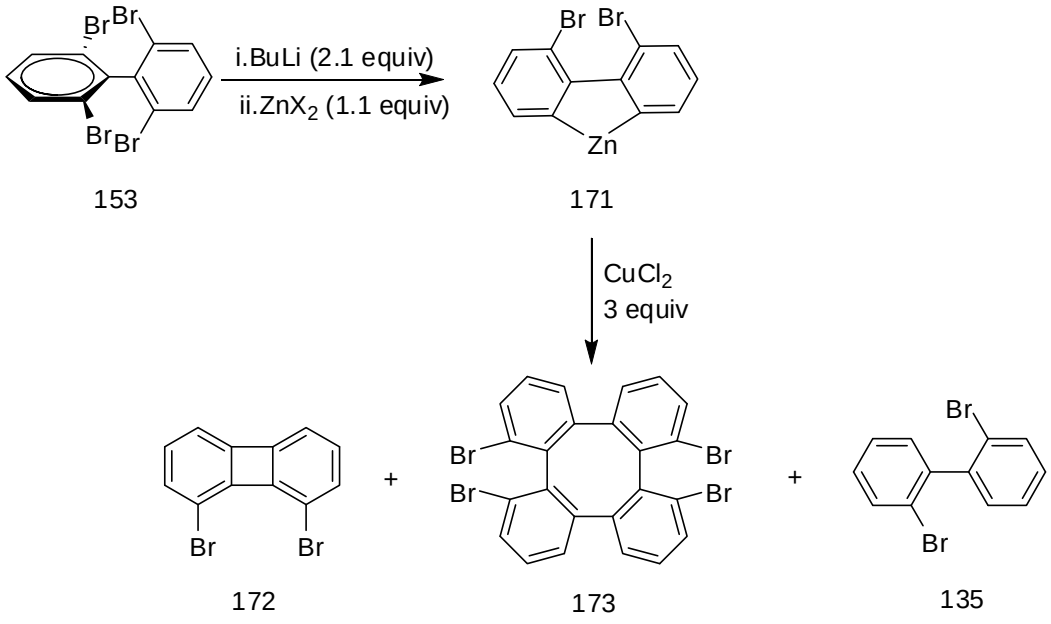
Three biphenyl compounds, 2, 2'-dibromo 6, 6'-dichlorobiphenyl **152**, 2, 2', 6, 6'-tetrabromobiphenyl **153**, and 2, 2', 6, 6'-tetrachlorobiphenyl **154**, were achieved. The next step would be conversion of biphenyl compounds into biphenylene compounds, which are the key intermediates in our project.



Scheme 3-19 Synthesis of Disubstituted Biphenylene from Tetrasubstituted Biphenyl

a. Synthesis of 1, 8-dibromobiphenylene

Conversion of 2, 2', 6, 6'-tetrabromobiphenyl **153** into 1,8-dibromobiphenylene **172** was published by Iyoda group[154] in 2001. 2, 2', 6, 6'-tetrabromobiphenyl **153** was treated with 2.1 equiv. BuLi and then 1.1 equiv. zinc chloride or zinc bromide, followed by 3 equiv. copper chloride. When zinc chloride was used, the result were 40% 1, 8-dibromobiphenylene **172**, trace amount of biphenyl dimmer **173** and 20% 2, 2'-dibromobiphenyl **135**. When zinc bromide was used, the results were 72% 1, 8-dibromobiphenylene **172** and trace amount of biphenyl dimmer**173**.

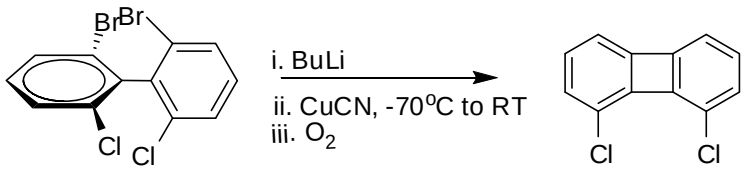


Scheme 3-20 Synthesis of 1, 8-Dibromobiphenylene

But no expected1, 8-dibromobiphenylene **172** was formed when attempts were made to repeat this reaction.

b. Synthesis of 1, 8-dichlorobiphenylene

To 2, 2'-dibromo 6, 6'-dichlorobiphenyl **152**, BuLi was added and then copper cyanide, followed by oxidation using Oxygen as the oxidant; 1,8-dichlorobiphenylene **174** was obtained in 31% yield.



152 174

Scheme 3-21 Synthesis of 1, 8-Dichlorobiphenylene from 2, 2'-dibromo 6, 6'-dichlorobiphenyl

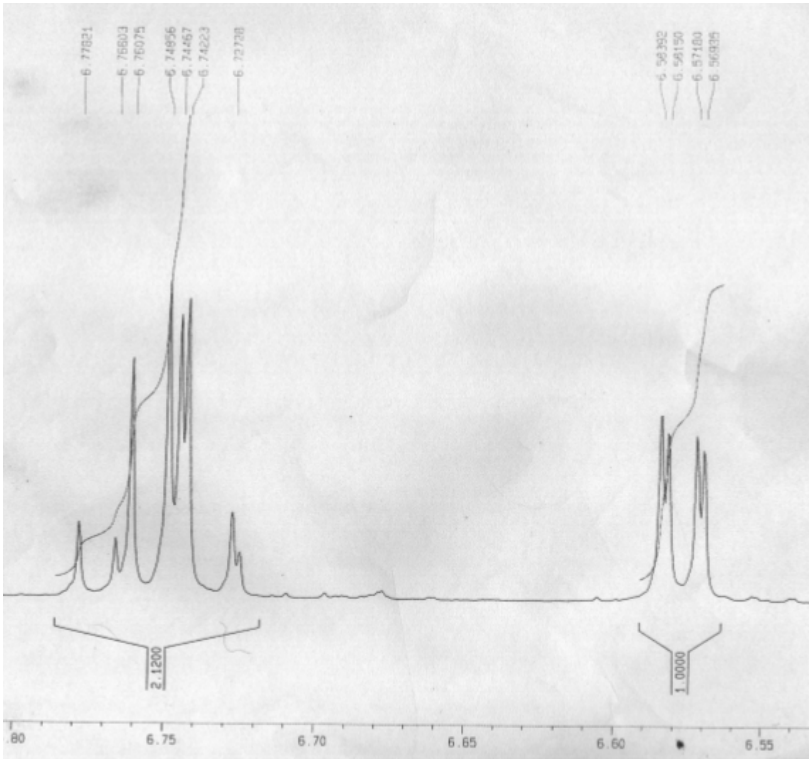
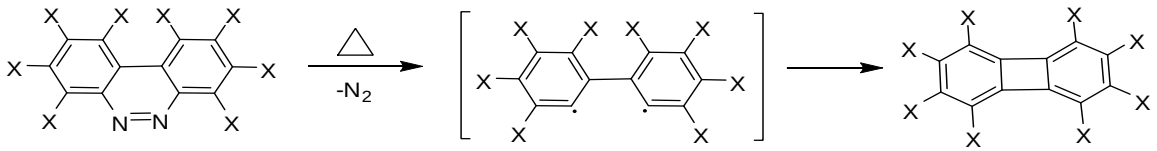


Figure 3-12 NMR Spectrum of 1, 8-Dichlorobiphenylene

3.2.3 By Flash Vacuum Pyrolysis

Flash vacuum pyrolysis (FVP) of benzo[*c*]cinnoline at around 800°C offers a good synthetic procedure for the generation of biphenylene.

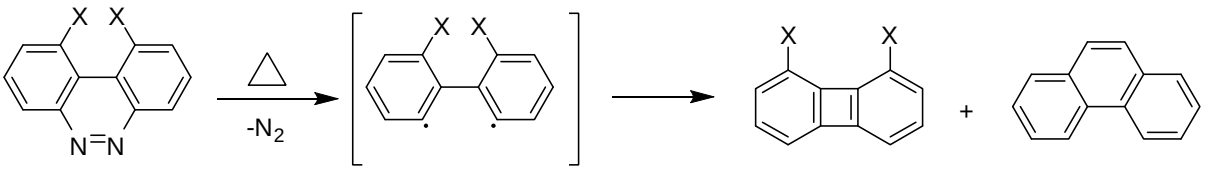
In 1972, Macbride[155] reported that vacumm pyrolysis of benzo[*c*]cinnoline or its octachloro-derivative gave the corresponding biphenylene in high yield. The pyrolysis yield of benzo[*c*]cinnoline was 70%, and the yield was 80% when the starting material was octachloro benzo[*c*]cinnoline.



X= H, ca. 870^{0}C, 0.2 torr 70%
X= Cl, ca. 700^{0}C, 0.2 torr 80%

Scheme 3-22 Flash Vacumm Pyrolysis of Benzo[*c*]cinnoline and Its Octachloro-derivative

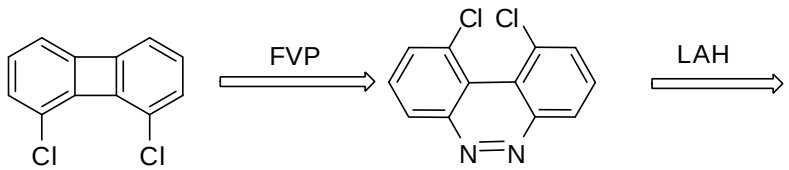
In 1987, Wilcox group reported preparation of akyl-substituted biphenylenes by pyrolytic extrusion of nitrogen from benzo [*c*]cinnnolines.[156] Fvp of 1,10- dimethylbenzo[*c*]cinnoline at 730°C and 0.12 Torr provide 1,8 dimethylbiphenylene in 71% yield, but pyrolysis of diethylbenzo[*c*]cinnoline provide a complex mixture containing 11.3% of diethylbiphenylene but more phenanthrene.



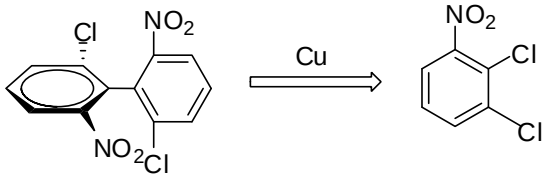
X= Me, ca. 730°C, 0.12 torr 71% 0%
X= Et, ca. 730°C, 0.12 torr 11.3% 12.9%

Scheme 3-23 Flash Vacumm Pyrolysis of Akyl-substituted Biphenylenes by Wilcox

So we attempt to get 1,8-dichlorobihphenylene **174** by flash vacumm pyrolysis. Retrosynthetic analysis (Scheme 3-24) shows that in order to using flash vacumm pyrolysis to make 1,8-dichlorobihphenylene **174**, the 1,10- dichlorobenzo[*c*]cinnoline **175** would be required, and 1,10- dichlorobenzo[*c*]cinnoline **175** could be achieved by LAH reduction of 2, 2'-dichloro-6, 6'-dinitrobiphenyl **176**. Ullmann coupling using Cu powder could be used to synthesize 2, 2'-dichloro-6, 6'-dinitrobiphenyl **176** from 2, 3-dichloro-nitrobenzene **177**.



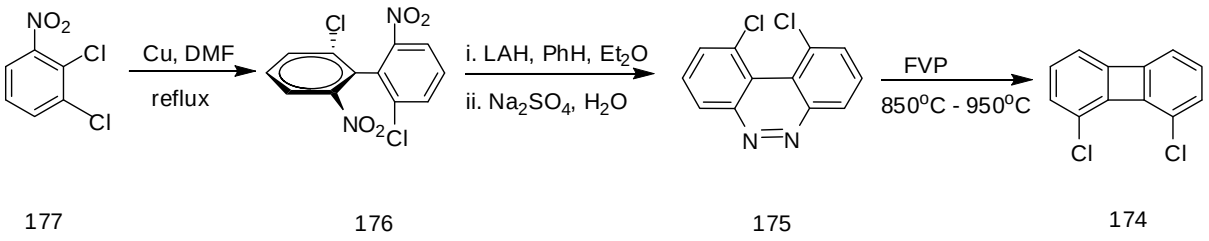
174 175



176 177

Scheme 3-24 Retro Synthesis of 1,8- Dichlorobihphenylene by Flash Vacumm Pyrolysis

Starting from 2, 3-dichloro-nitrobenzene **177**, ullmann coupling[157] using Cu powder in DMF gave us 2, 2'-dichloro-6, 6'-dinitrobiphenyl **176** in 54%. LAH reduction of 2, 2'-dichloro-6, 6'-dinitrobiphenyl **176** produced 1, 10-dichlorobenzo[*c*]cinnoline **175** in very good yield, which was the precursor for 1,8-dichlorobihphenylene **174** in FVP reaction. Flash Vacuum Pyrolysis of 1, 10-dichlorobenzo[*c*]cinnoline **175** under 730°C and 0.1 Torr provide 1,8-dichlorobihphenylene **174** in 80%.



177 176 175 174

Scheme 3-25 Synthesis of 1, 8-Dichlorobiphenylene

We also tried solid-state reaction of Ullmann coupling to synthesize 2, 2'-dichloro-6, 6'-dinitrobiphenyl **176** and the yield was 67%.

The mass spectrum of 1, 10-dichlorobenzo[c]cinnoline **175** predicted a facile loss of dinitrogen (Figure 3-14). Indeed, as found by Baker *et al.*, flash vacuum pyrolysis of this benzocinnoline at *ca.* 800°C went smoothly and 'completely' in that no starting material was left unconverted. NMR spectrum of 1,8-dichlorobiphenylene **174** is characteristic of biphenylene derivatives (Figure 3-15) in that the chemical shifts are in the region around 6.7 – 7.0 ppm and the effect of the chlorine substituent is noticeable in the chemical shift of the neighboring H atom (*ortho*) and the H atom (*para*) to the chlorine substituents. The remaining H atoms are typical doublet of doublet, being located between two H atoms.

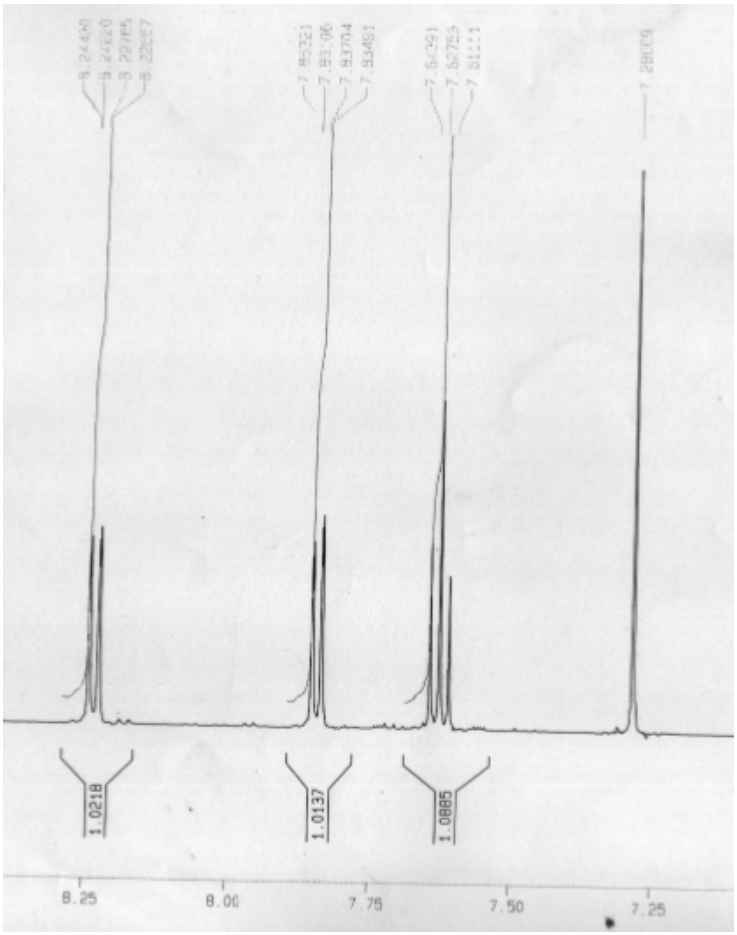


Figure 3-13 NMR Spectrum of 2, 2'-Dichloro-6, 6'-dinitrobiphenyl

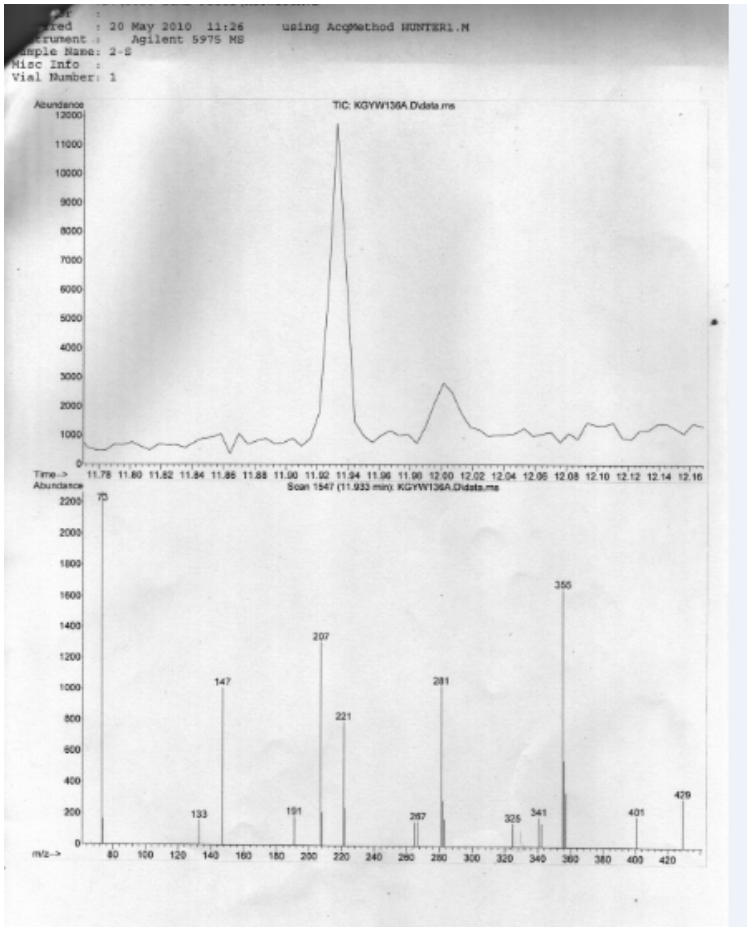


Figure 3-14 GC-MS of 1, 10-Dichlorobenzo[*c*]cinnoline

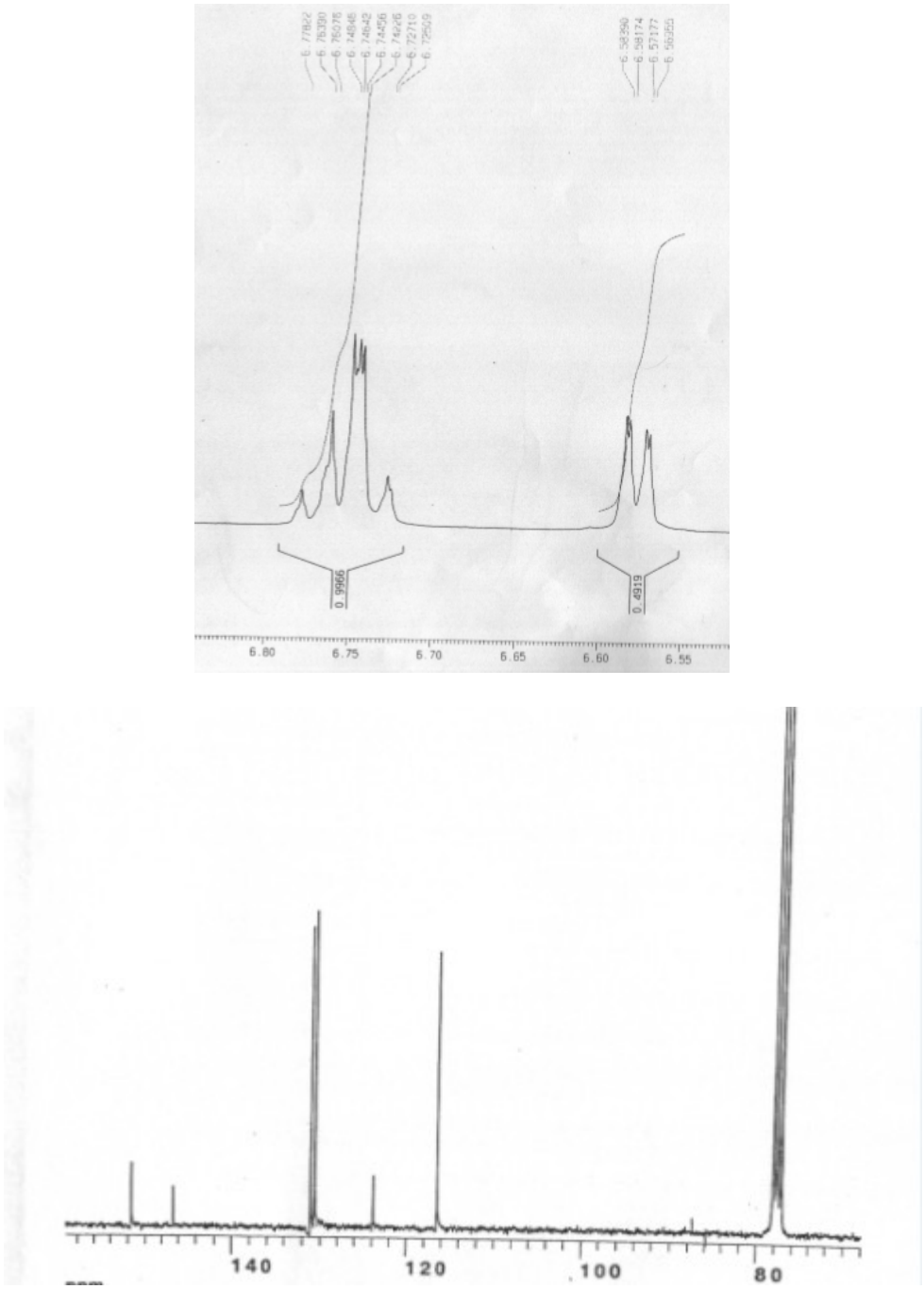


Figure 3-15 NMR Spectrum of 1, 8-Dichlorobiphenylene

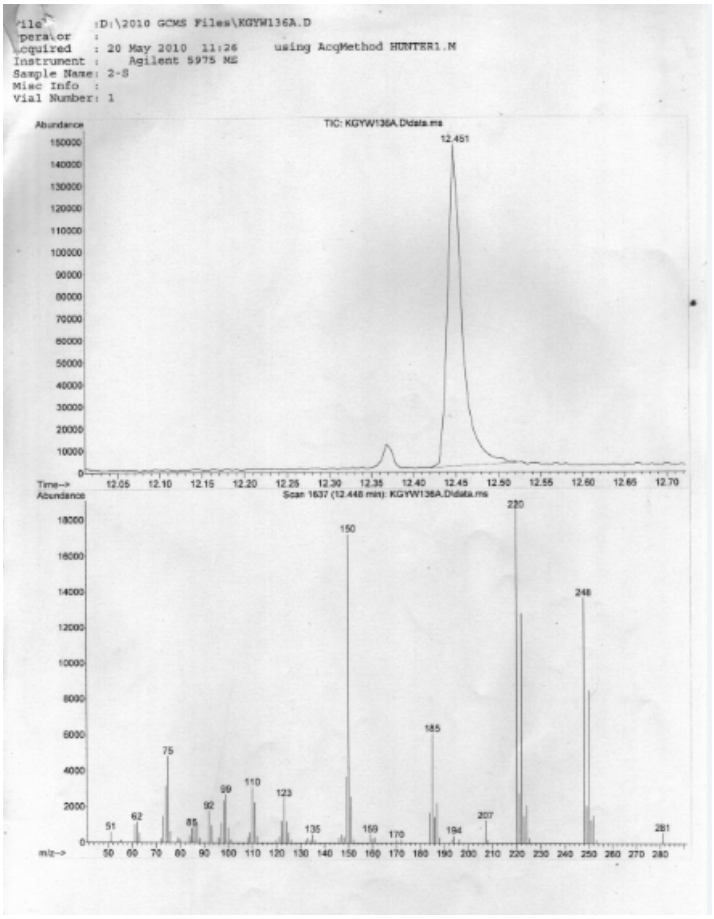


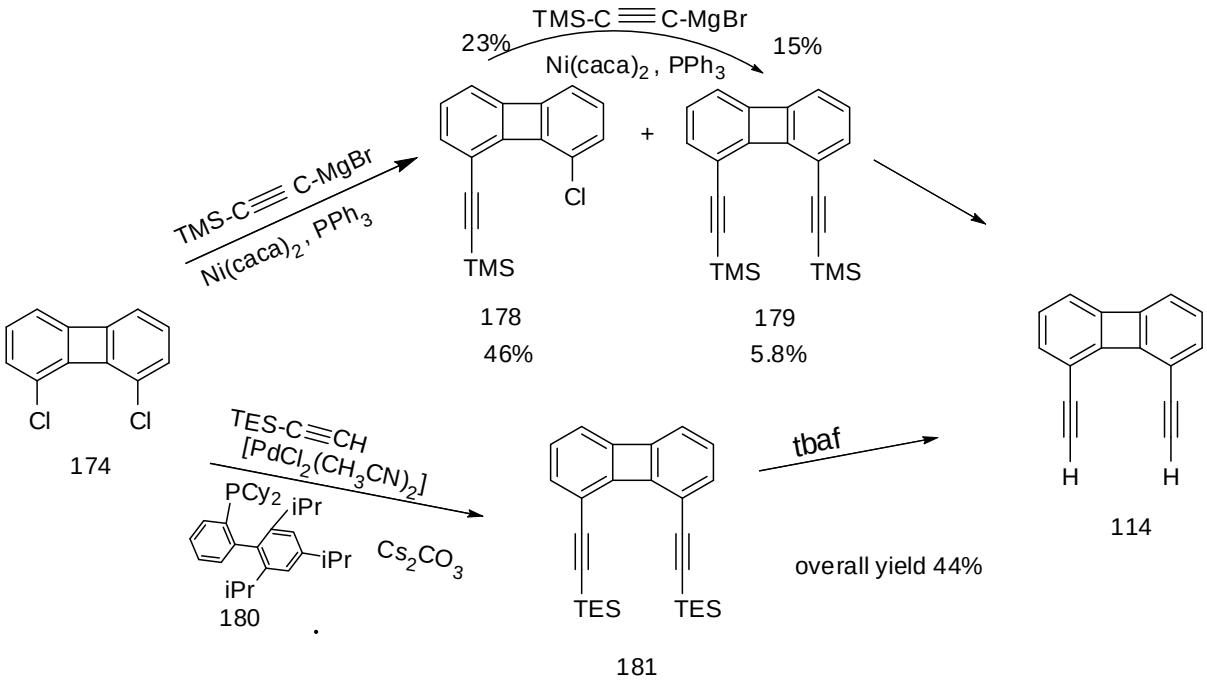
Figure 3-16 GC-MS of 1, 8-Dichlorobiphenylene

3.3 Synthesis of 1, 8-Diacetylenebiphenylene 114

1,8-Diacetylenebiphenylene **114** would be prepared from Sonogashira coupling reaction[175] of 1, 8-dichlorobiphenylene **117**.

The trimethylsilylacetylene magnesium bromide[158] was generated in situ by the reaction of trimethylsiylacetylene and ethylmagnesium bromide. Addition of this solution to a solution of dichlorobiphenylene, $Ni(acac)_2$ and $Pd(Ph_3)_4$ in THF gave TMS-protected mono- acetylene

substituted **178** and TMS-protected di- acetylene substituted biphenylene **179**. The TMS-protected mono- acetylene substituted **178** yield was 46%, and the TMS-protected di-acetylene substituted biphenylene **179** yield was only 5.8%. The TMS-protected mono-acetylene substituted **178** could be converted to TMS-protected di- acetylene substituted biphenylene **179** by repeating the Sonogashira coupling. The converting yield was only 15% and 23% **178** was recovered.



Scheme 3-26 Synthesis of 1, 8-Diacetylenebiphenylene

We also tried Buchwald catalyst[159] and triethylsiylacetylene to do the coupling, and the coupling underwent very well. We got 1, 8-diacetylene-biphenylene **114** in 44% overall yield.

The proton NMR spectrum of 1, 8-diacetylenebiphenylene **114** shows that the aromatic peaks on the biphenylene ring shift upfield from the normal position of benzene proton.

The IR spectrum shows absorption at 3284.03 cm^{-1} indicating the presence of terminal acetylene and absorption at 1679.57 cm^{-1} indicating that of acetylene.

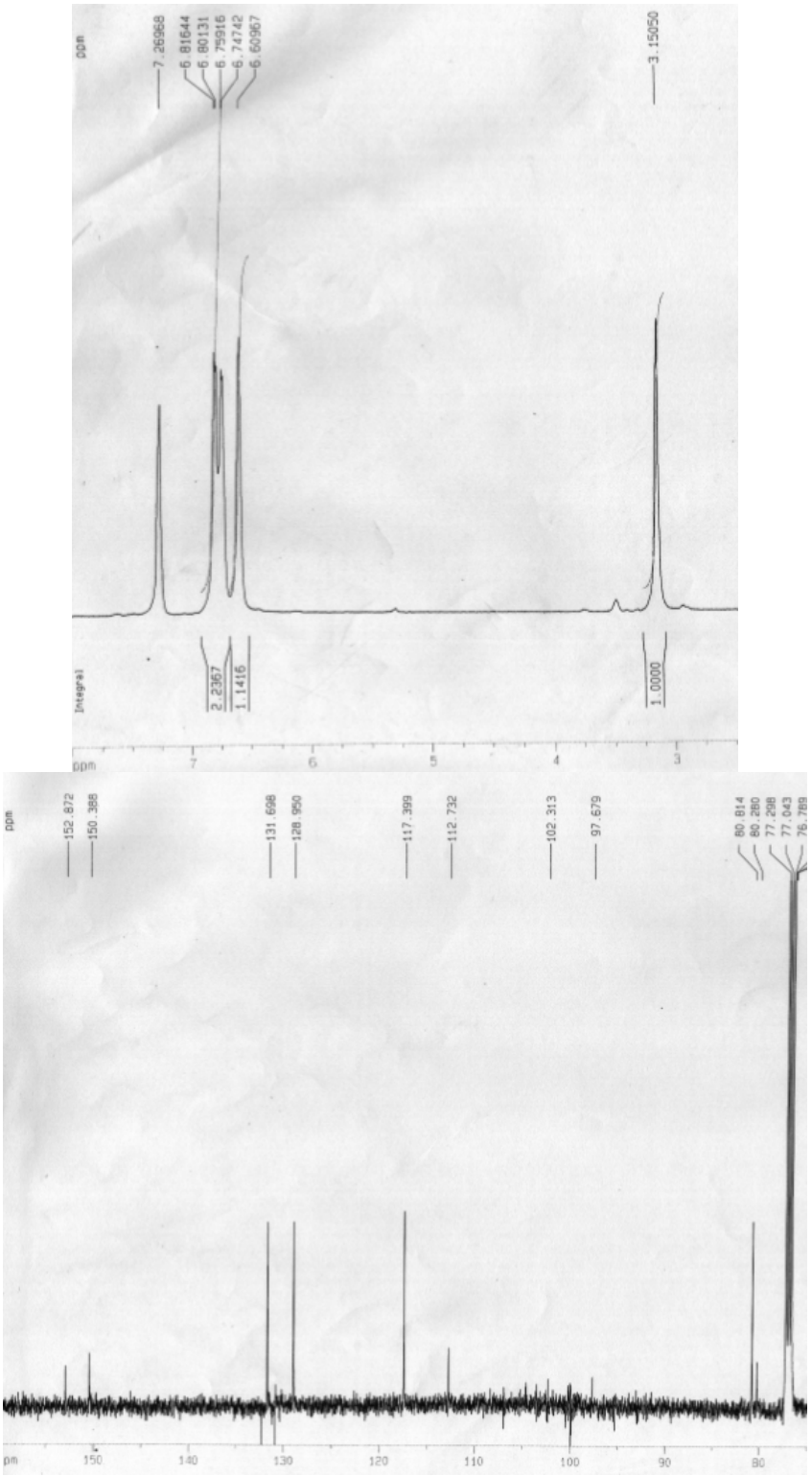


Figure 3-17 NMR Spectrum of 1, 8-Diacetylenebiphenylene

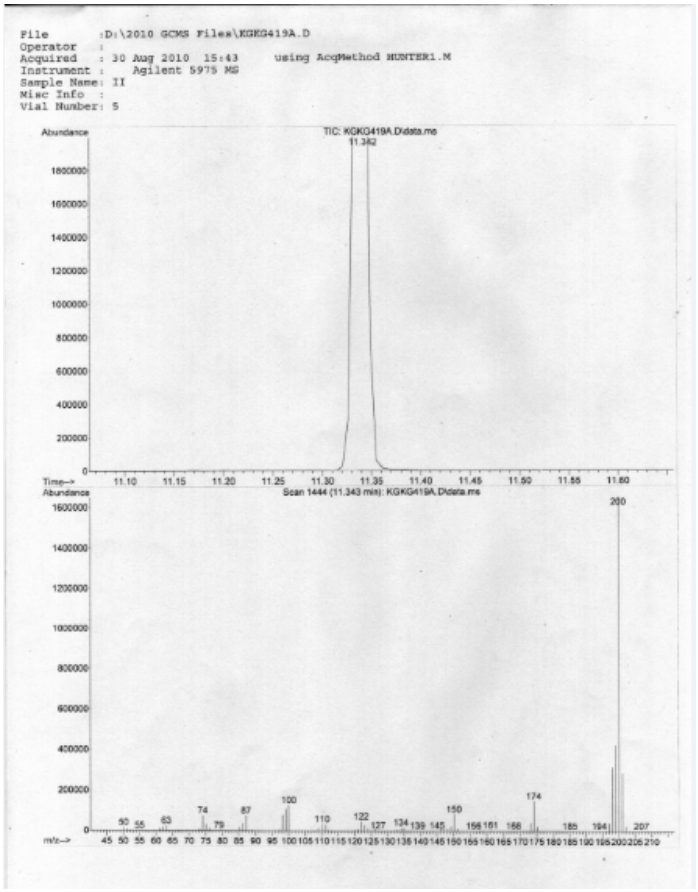


Figure 3-18 GC-MS of 1, 8-diacetylenebiphenylene

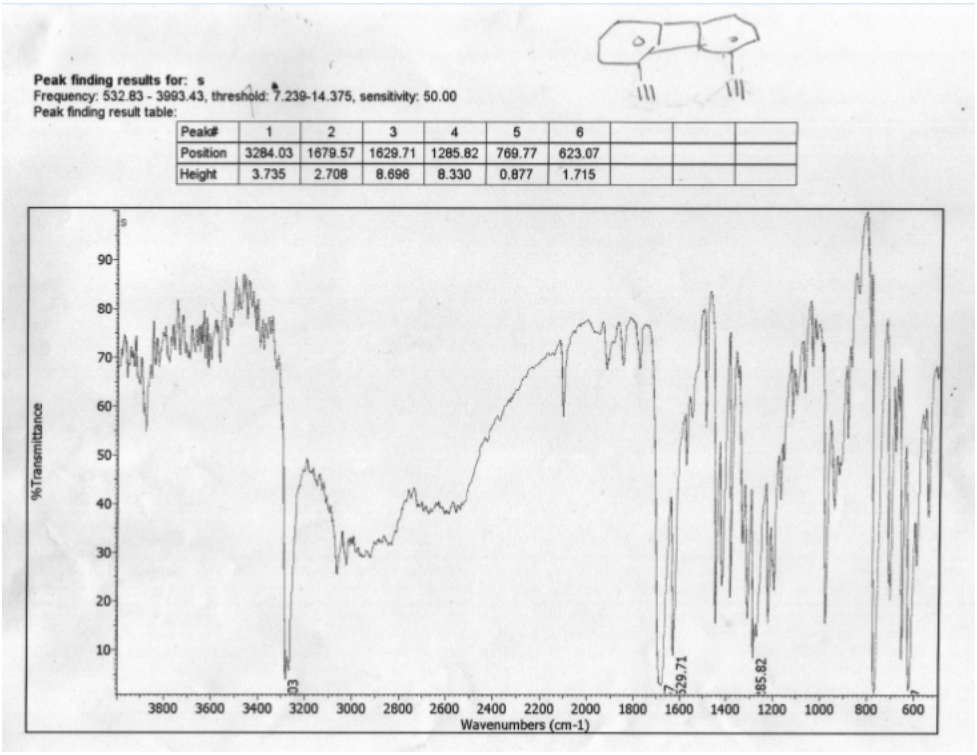


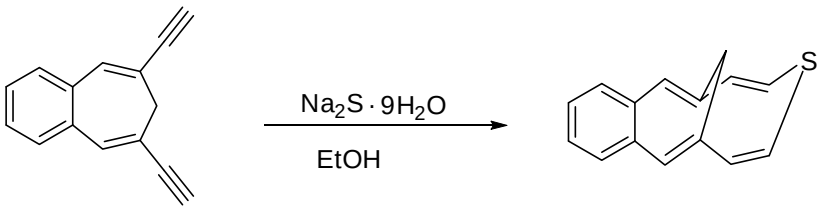
Figure 3-19 IR Spectrum of 1, 8-Diacetylenebiphenylene

Chapter 4 Preparation of Biphenylene Planarized Hetero-aromatic Systems, Anti-aromatic Systems and Comparisons

4.1 Sulfur Addition

4.1.1 Possibility 1

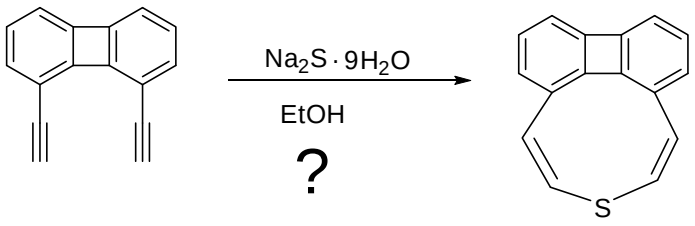
Grohmann and Benshafrut[160] synthesized the thiepin by addition of sodium sulfide nonahydrate to 1,6-diacetylene-3,4-benzocycloheptatriene **182**. The resulting thiepin **183** was found to be stable and was not planar because the inclusion of the sulfur's long pair electrons in the conjugated system would result in a high-energy antiaromatic system. And they were able to show that the syn-conformation was more stable than the anti-conformation.



182 183

Scheme 4-1 Synthesis of Thiepin by Grohmann and Benshafrut

Therefore we were interested in what might happen if we did the same sulfur addition to our 1, 8-diacetylene-biphenylene **114**. If the sulfur addition was successful, because of the presence of biphenylene core, the resulting compound would be a planarized 10π aromatic system, and this aromatic heterocyclic system is totally new and never been published before.

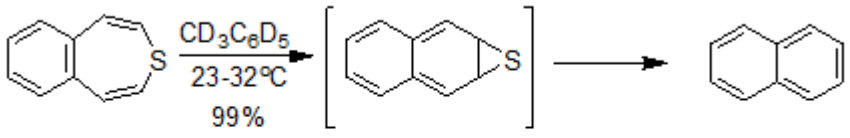


114 110

Scheme 4-2 Possibility 1

4.1.2 Possibility 2

It has been known that 3-benzothiepine **184** is too thermally unstable to be isolated. It undergoes sulfur extrusion reaction. The mechanism involves valence isomerization of the seven-membered ring to the correspongding nocaradinen intermediate **185** and following irreversible loss of sulfur[161,162] to form naphthalene **186**.

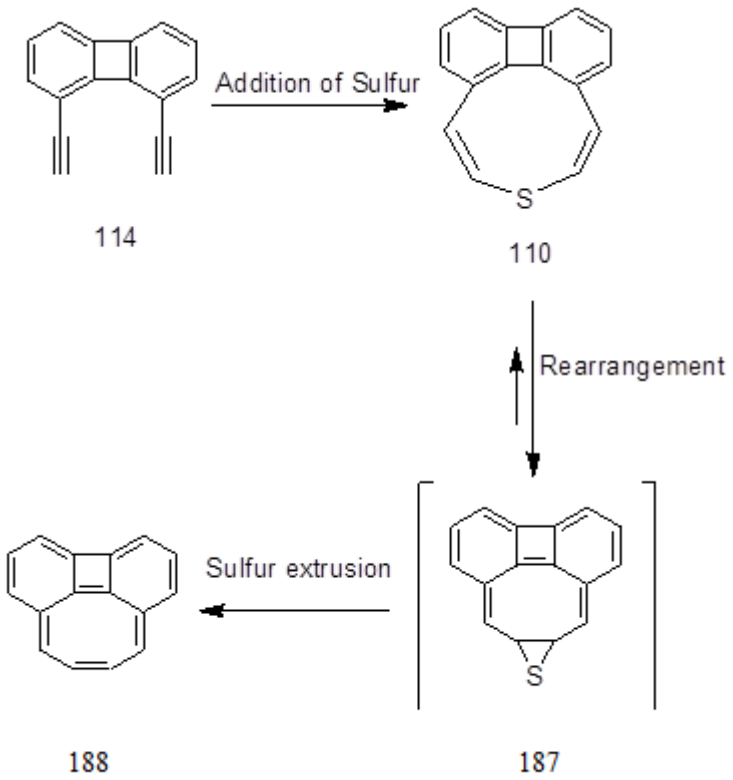


184 185 186

Scheme 4-3 Sulfur Extrusion Reaction of 3-benzothiepine

So there would be two possibilities of your sulfur addition reaction. It could be just the simple sulfur addition to 1, 8-diacetylene-biphenylene **114** and the result would be the nine-membered ring, a totally new biphenylene planarized heterocylic aromatic system **110**. Also,

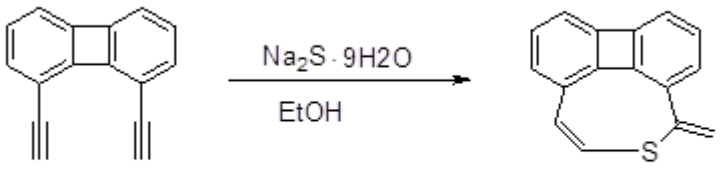
the nine-membered ring might undergo rearrangement to form this intermediate followed by irreversible loss of sulfur. Then the result would be compound **188**, cycloocta[defl biphenylene.



Scheme 4-4 Possibility 2

4.1.3 Our Sulfur Addition Result

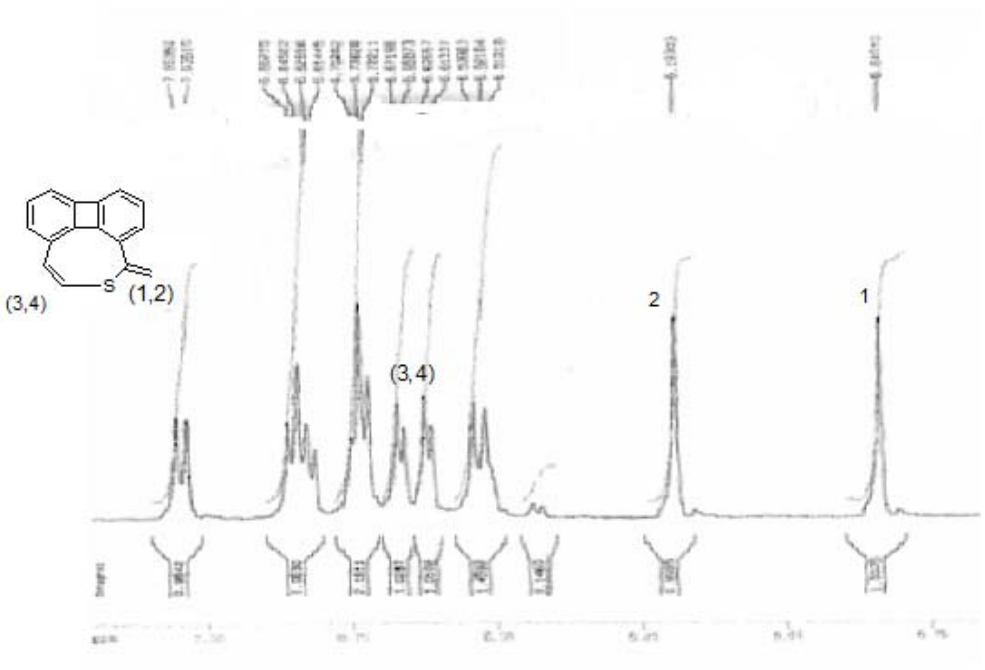
Dissolved in EtOH, 1, 8-diacetylene-biphenylene **114** was refluxed gently with Na_2S nonahydrate for 20h. To our surprise, the sulfur addition to 1, 8-diacetylene-biphenylene **114** gave us an unexpected eight-membered ring **189**, instead of the proposed nine-membered ring **110** or cycloocta[*def*l biphenylene **188**.



114 189

Scheme 4-5 Our Sulfur Addition Result

The ^{1}H NMR spectrum of the unexpected compound is shown below. The two singlet peaks reveal the terminal vinylic proton outside the ring, and these two doublet reveal the two vinylic proton on the ring.



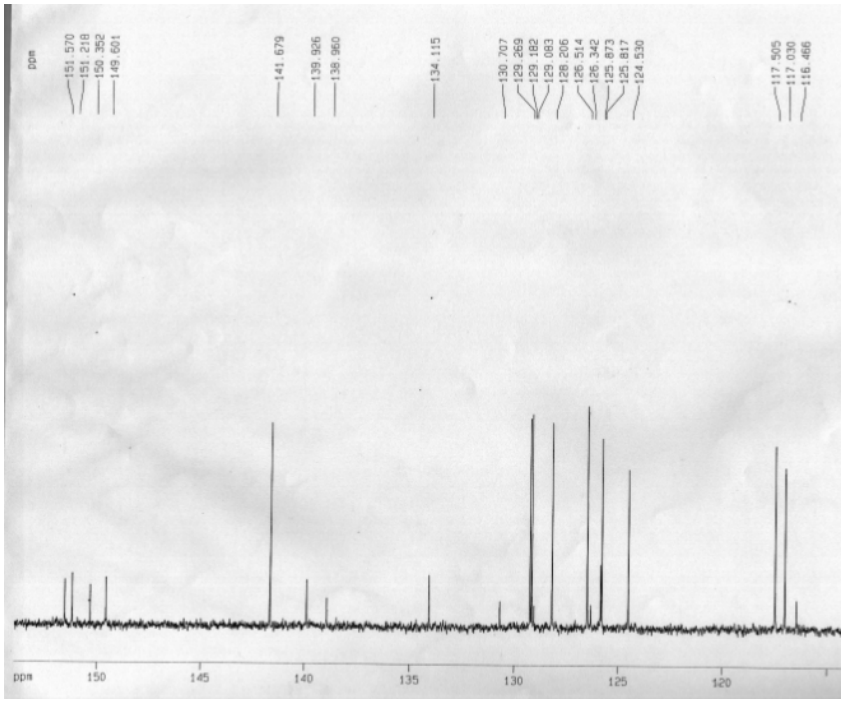


Figure 4-1 NMR Spectrum of Sulfur Addition Result

The DEPT ^{13}C NMR of the unexpected compound clearly demonstrated that the unexpected compound has one CH_2 group and eight CH groups, which proved the proposed structure of the unexpected compound is right.

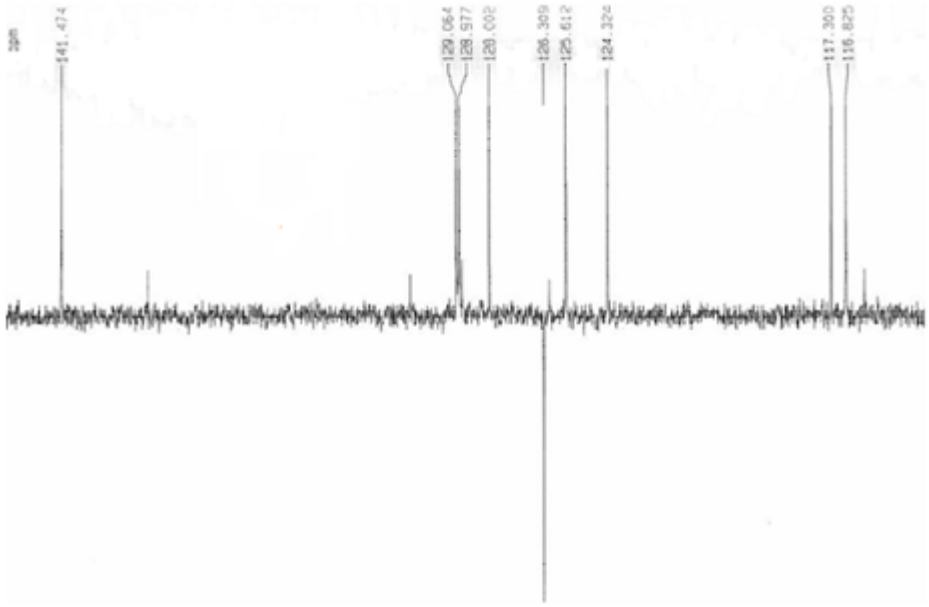


Figure 4-2a DEPT ^{13}C NMR Spectrum of Sulfur Addition Result

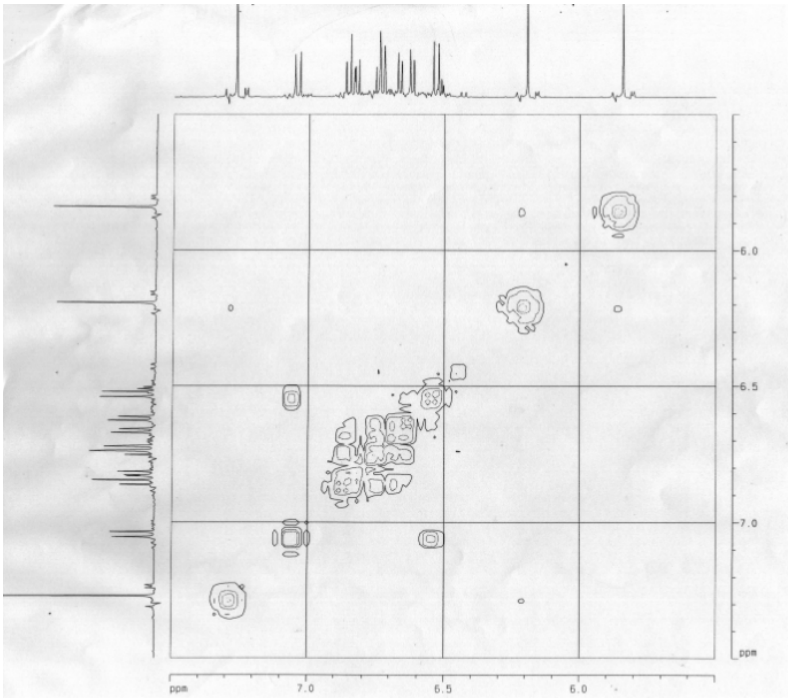
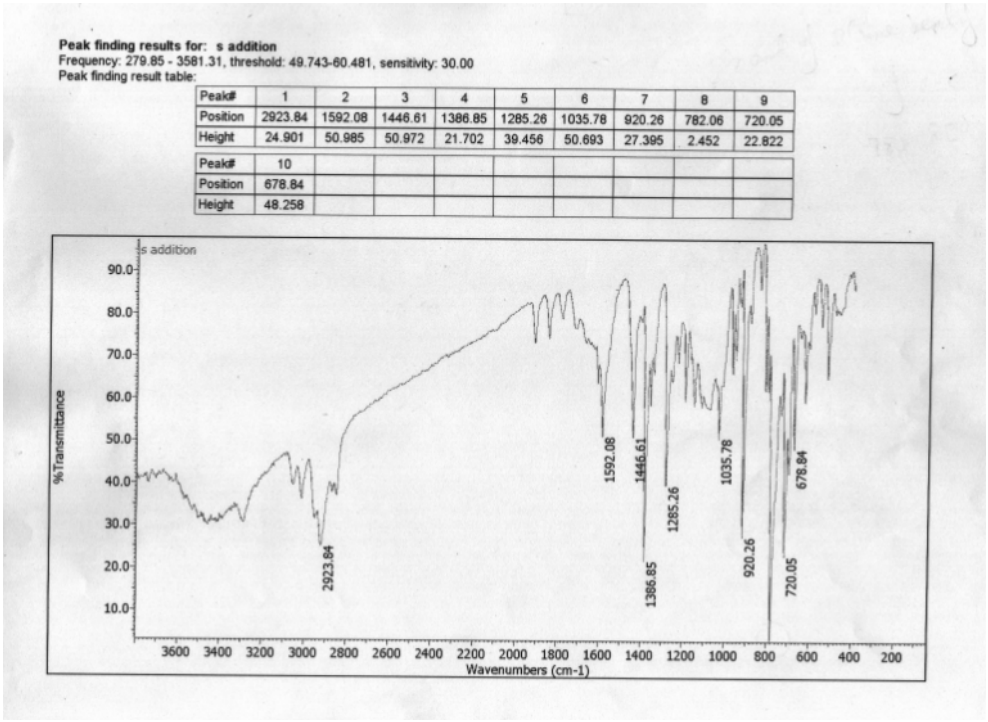


Figure 4-2b COSY NMR Spectrum of Sulfur Addition Result

In IR spectrum, the 780.06cm^{-1} absorbance revealed the out of plane bending of C=C bond.



Peak#	1	2	3	4	5	6	7	8	9
Position	2923.84	1592.08	1446.61	1386.85	1285.26	1035.78	920.26	782.06	720.05
Height	24.901	50.985	50.972	21.702	39.456	50.693	27.395	2.452	22.822

Peak#	10
Position	678.84
Height	48.258

Figure 4-3 IR Spectrum of Sulfur Addition Result

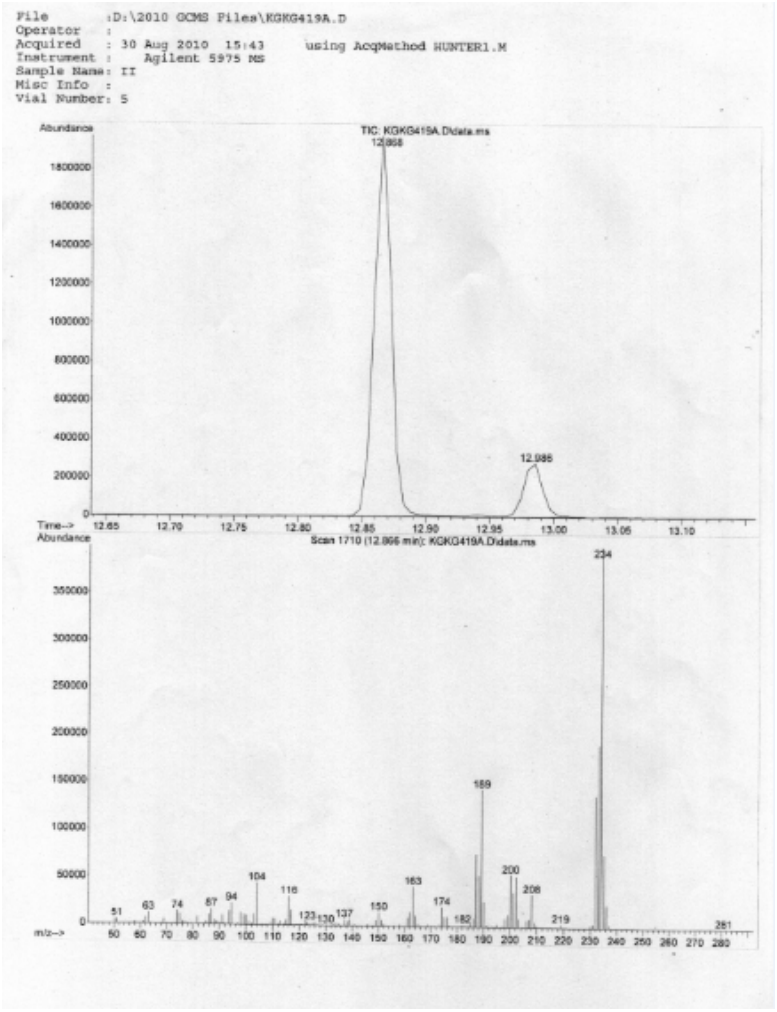


Figure 4-4 GC-MS of Sulfur Addition Result

X-ray structure confirmed the structure of compound **189**.

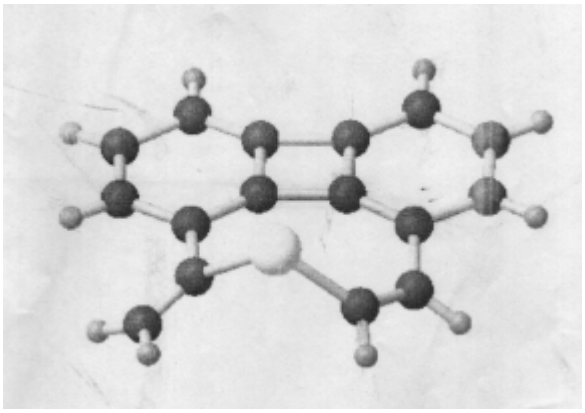


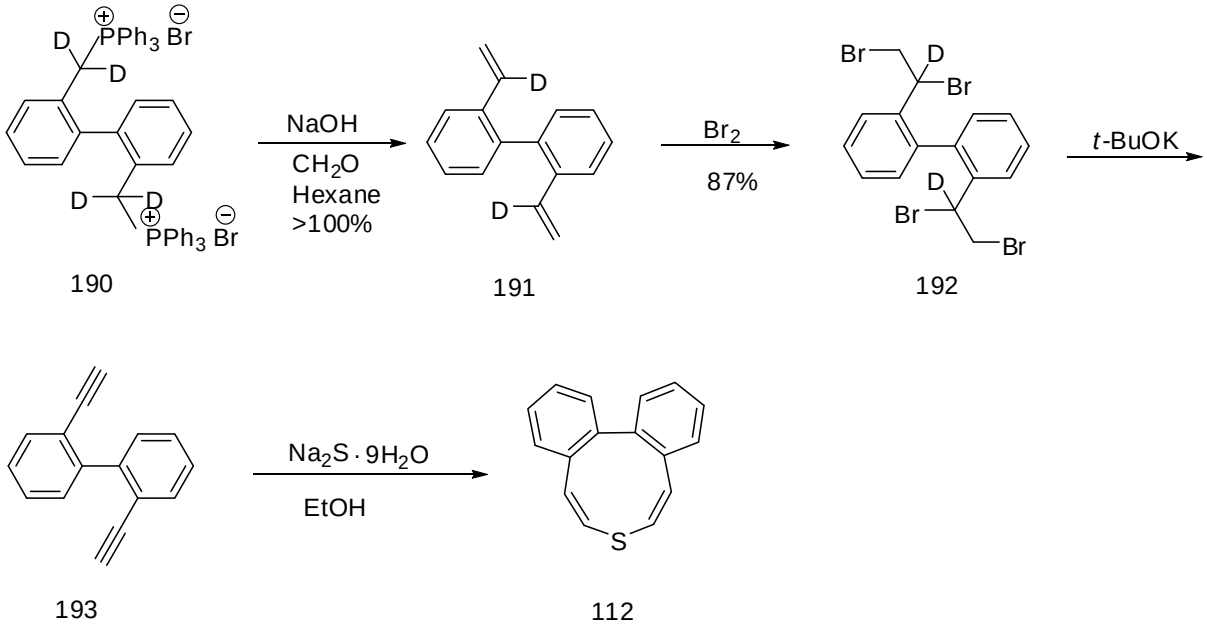
Figure 4-5 X-ray Structure of Sulfur Addition Result

4.2 Preparation of Comparisons

4.2.1 Synthesis of Comparison 1 Dibenzo[*d,f*]thionine 112

Wittig reaction ylide **190** and formaldehyde gave the corresponding alkene **191**. Bromination of **191** followed by elimination gave 2, 2'-diacetylenebiphenyl **193** in 77% yield. Sulfur addition to **193** gave 6% dibenzo[*d,f*]thionine **112**.

Sulfur addition of 2, 2'-diacetylene biphenyl **193** gave expected nine-membered ring whereas to 1, 8-diacetylene biphenylene **114** gave unexpected eight-membered ring.



Scheme 4-6 Synthesis of Dibenzo[*d,f*]thionine

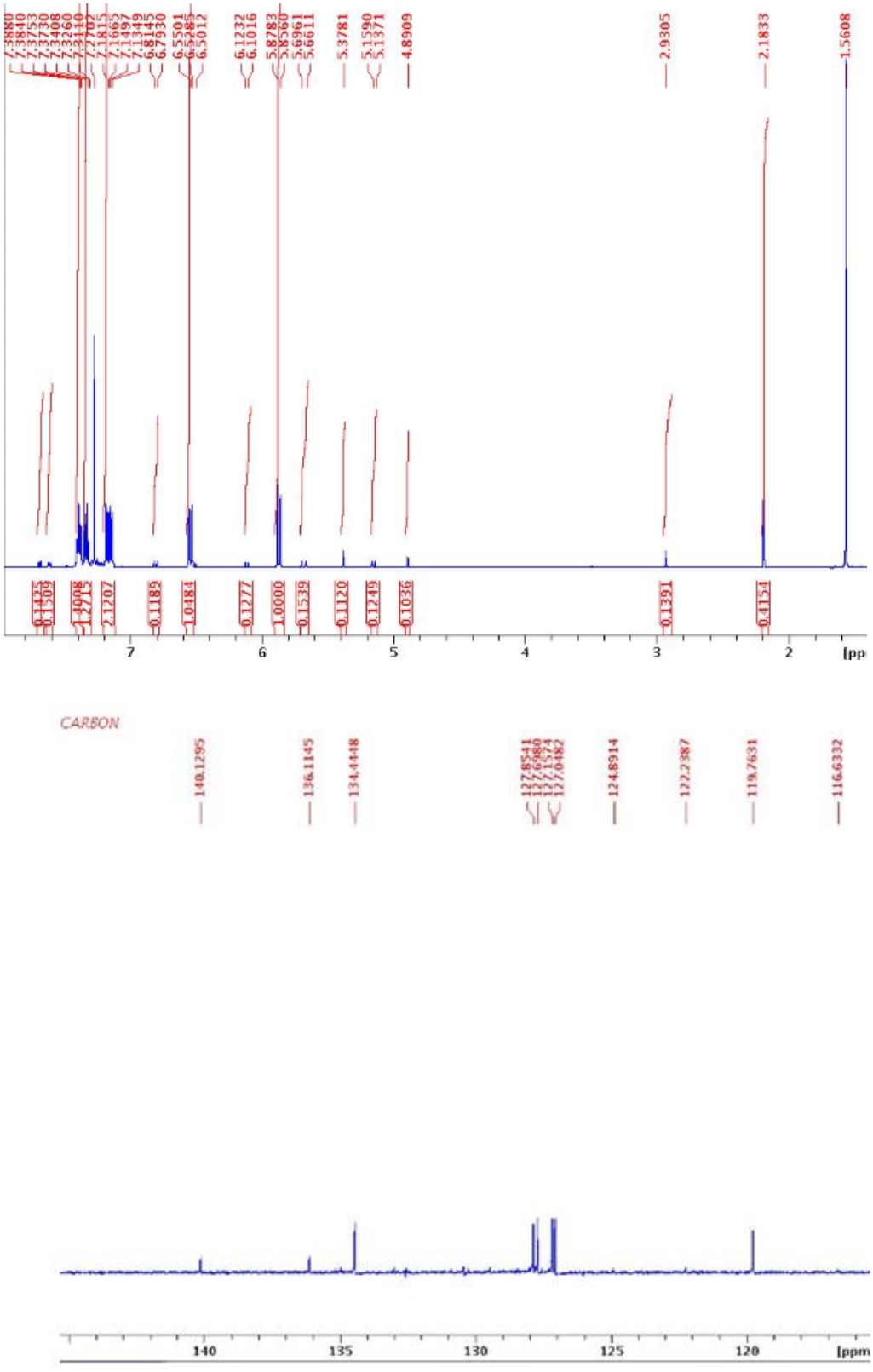


Figure 4-6 NMR Spectrum of Dibenzo[*d,f*]thionine

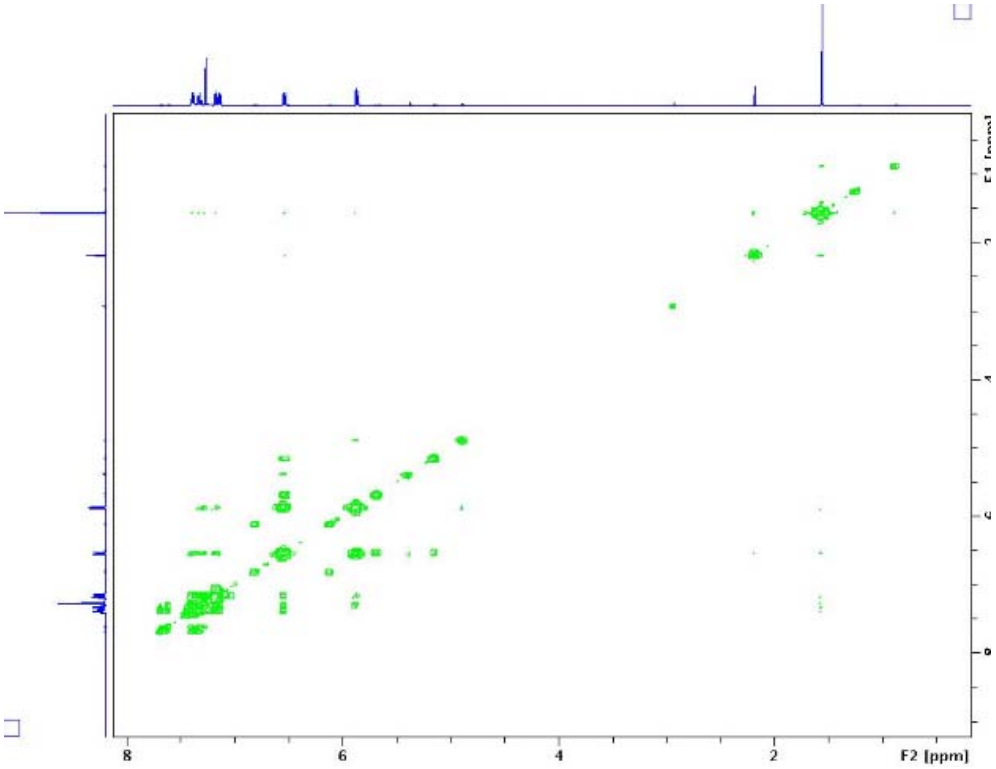
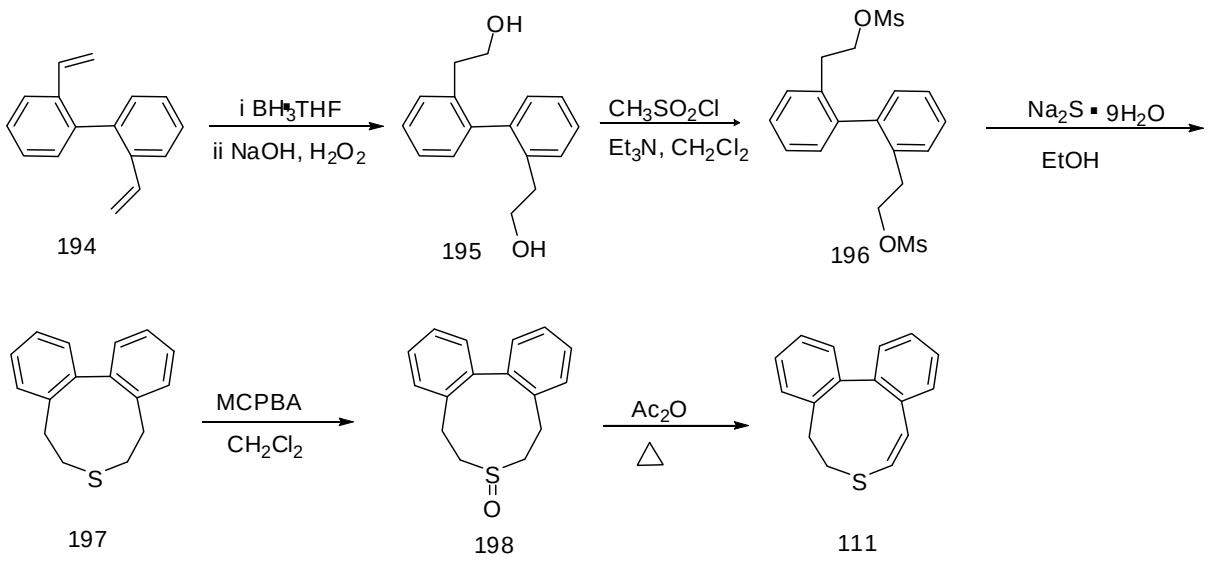


Figure 4-7 COSY NMR Spectrum of Dibenzo[*d,f*]thionine

4.2.2 Synthesis of Comparison 2 5, 6-Dihydrodibenzo[*d,f*]thionine 111

Starting with 2,2'-divinylbiphenyl **194**, treatment with Borane-THF complex and then hydrogen peroxide in sodium hydroxide gave the corresponding 2,2'-dialcoholbiphenyl **195**, conversion of **195** to a good leaving group[167] and then addition of sulfur gave us a saturated thionine **197**. Oxidation[168] of the saturated thionine followed by Pummerer rearrangement[169] gave the desired 5, 6-dihydrodibenzo[*d,f*]thionine **111**.



Scheme 4-7 Synthesis of 5, 6-Dihydrodibenzo[*d,f*]thionine

Synthesis of 5, 6-dihydrodibenzo[d,f]thionine **111** gave the idea like this: Starting with 2,2'-divinylbiphenyl **194**, after several steps sulfur additioned nine-membered ring compound with double bond could be achieved. If oxidation and Pummerer rearrangement could be performed one more time, the second double bond would be formed. If starting with 1,8-divinylbiphenylene instead of 2,2'-divinylbiphenyl, hopefully biphenylene planarized nine-membered ring with one or two double bond could be achieved.

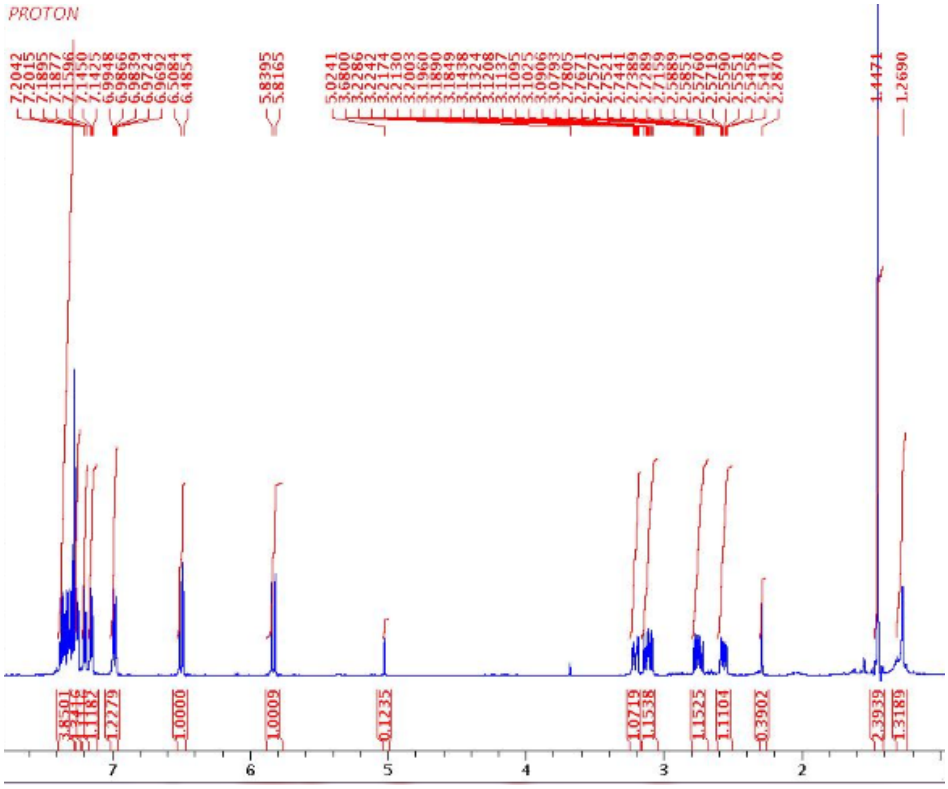
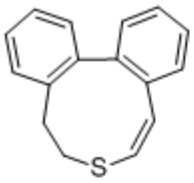


Figure 4-8 NMR Spectrum of 5, 6-Dihydrodibenzo[*d*,*f*]thionine

4.2.3 Compare of the NMR spectra of comparisons

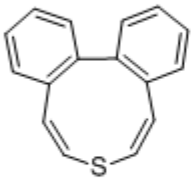
Figure 4-9 NMR data analysis of comparisons shows NMR data of these two thionines and literature value[170]. There is no big difference in NMR data between these two compounds. This is reasonable because they are all in biphenyl systems.



111

δ_a =6.49 ppm (1H,) J_{ab}=11.5 Hz

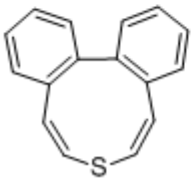
δ_b = 5.82 ppm (1H,) J_{ba}=*11.5* Hz



112

δ_a =6.38 ppm (2H,) J_{ab}=10.5 Hz

δ_b = 5.69 ppm (2H,) J_{ba}=*10.5* Hz *(By Flix)*



112

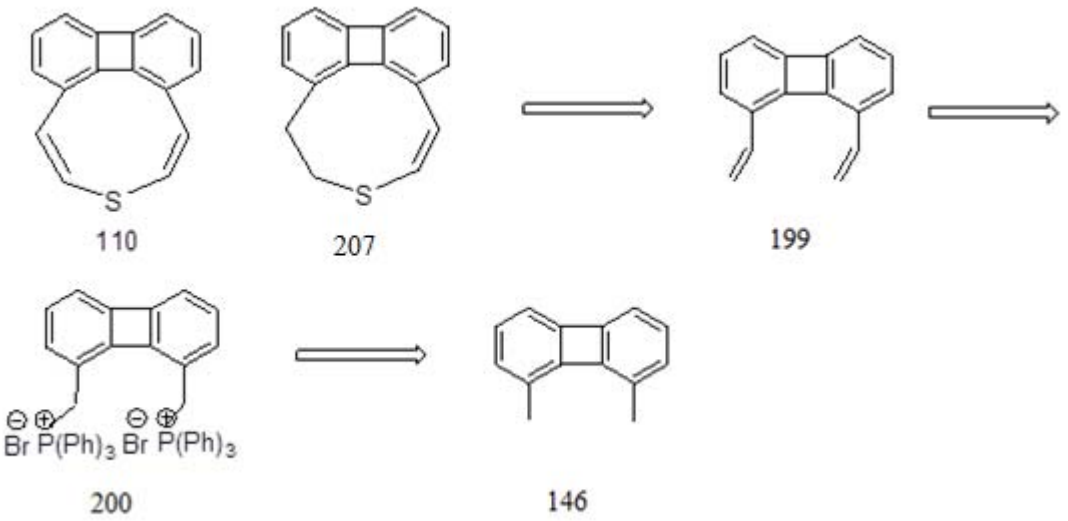
δ_a =6.54 ppm (2H,) J_{ab}=10.8 Hz

δ_b = 5.86 ppm (2H,) J_{ba}=*11.15* Hz

Figure 4-9 NMR Data Analysis of Comparisons

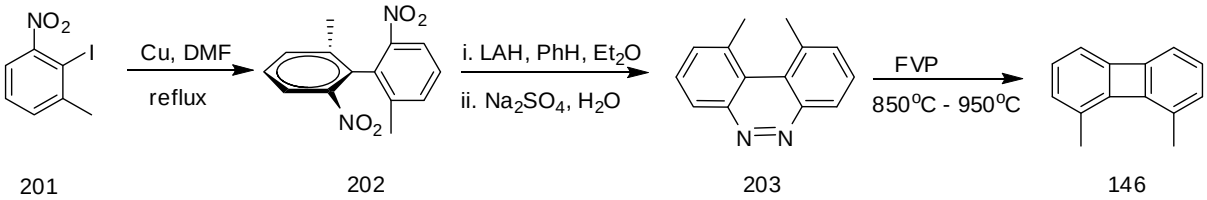
4.3 Synthesis of Biphenylene Planarized Aromatic and Anti-aromatic System Starting With Pure 1, 8- Dimethylbiphenylene

Since scheme 4-7 gave the idea of synthesizing normal sulfur additioned nine-membered ring with one or two double bonds from 2,2'-divinylbiphenyl **194**, similarly biphenyleno[1,8-def]thionine **110** and its comparison **207** can be achieved from 1,8-divinylbiphenylene **199**. Scheme 4-8 shows the retro synthesis of biphenyleno[1,8-*def]*thionine **110** and its comparison **207**.



Scheme 4-8 Retro Synthesis of Biphenyleno[1,8-*def*]thionine 110 and Its Comparison 207

Pure 1, 8-dichlorobiphenylene could by synthesized by Ullmann coupling of 2,3-dichloronitrobenzene **177**, followed by the LAH reduction and then FVP of the resulting cinnoline **175** (Scheme 3-19). So similarly, 1, 8-dimethylbiphenylene **146** could be synthesized by Ullmann coupling of 2-iodo-3-methylnitrobenzene **201**, followed by the LAH reduction and then FVP of the resulting cinnoline **203**[164].



Scheme 4-9 Synthesis of 1, 8- Dimethylbiphenylene

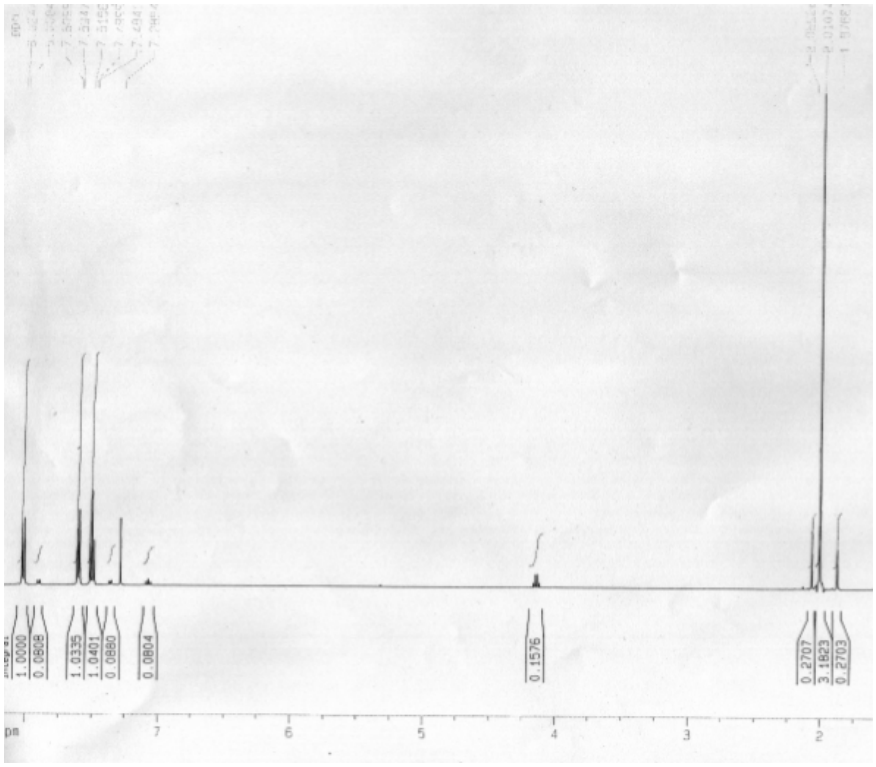


Figure 4-10 NMR Spectrum of 2, 2'-Methyl-6, 6'-dinitrobiphenyl

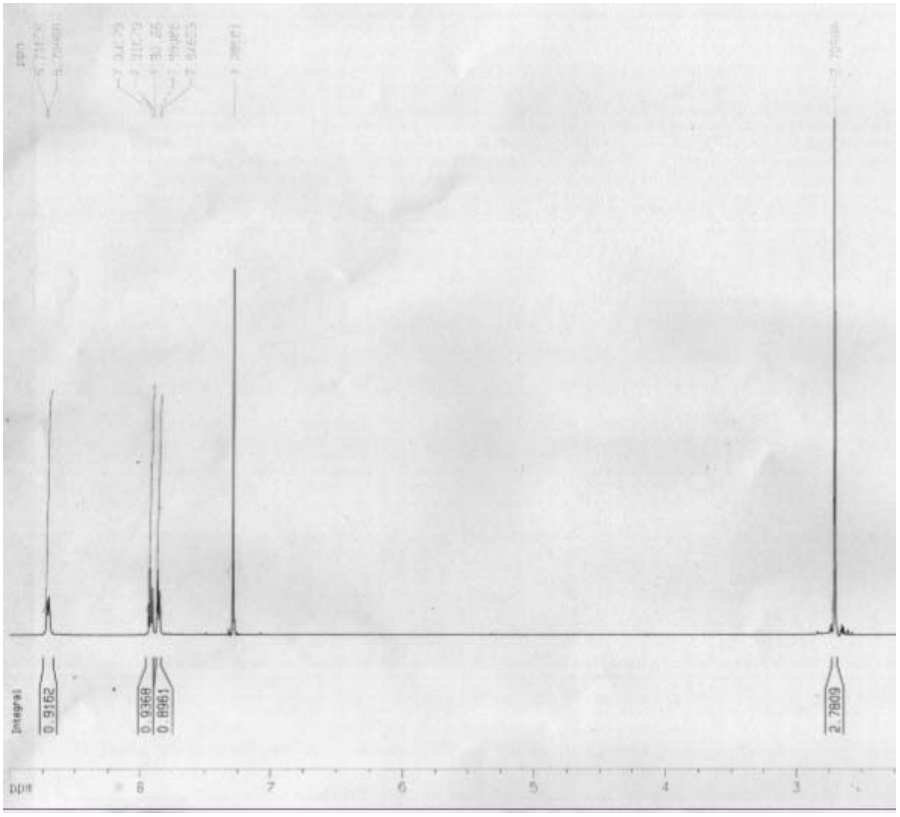


Figure 4-11 NMR Spectrum of 1, 10- Dimethylbenzo[*c*]cinnoline

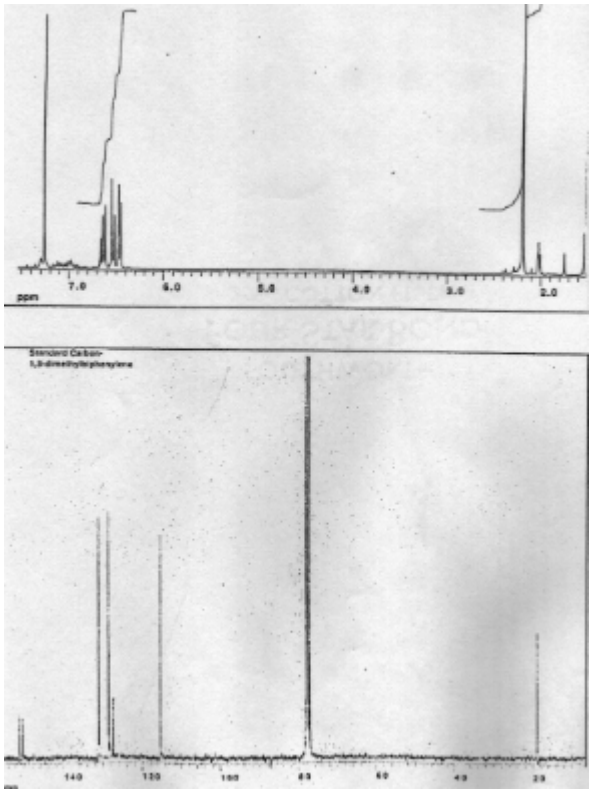
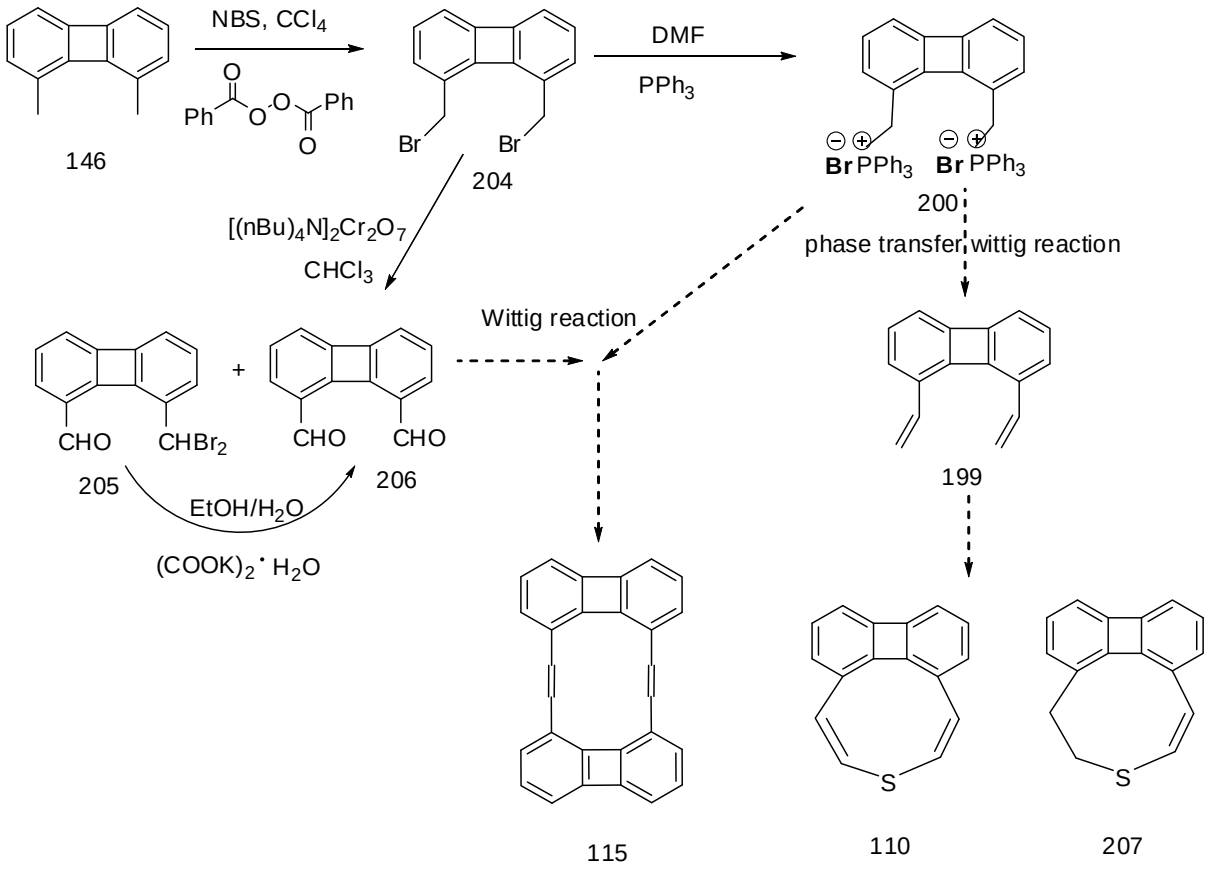


Figure 4-12 NMR Spectrum of 1, 8- Dimethylbiphenylene

1, 8- Dimethylbiphenylene **146** was treated with NBS in CCl_4 and benzoyl peroxide to get the corresponding bromo-substuited compounds (Scheme 4-10)[165]. The yield of dibromo substituted compound **204** was 25%. Oxidation[165] of the dibromo-substuited compound **204** resulted in corresponding mono-aldehyde and di-aldehyde 1,8 dimethylbiphenylenes **(205** and **206**). Compound **205** could be converted to **206** by treating with potassium oxalate in ethanol and water[166]. 1,8-Bis(bromomethyl)biphenylene **204** was also converted to phosphonium salt **200** successfully. The next step could be Wittig reaction of 1,8 dialdehydebiphenylenes **206** with the phosphonium salt **200** to get di-biphenylene planarized anti-aromatic system **115**.

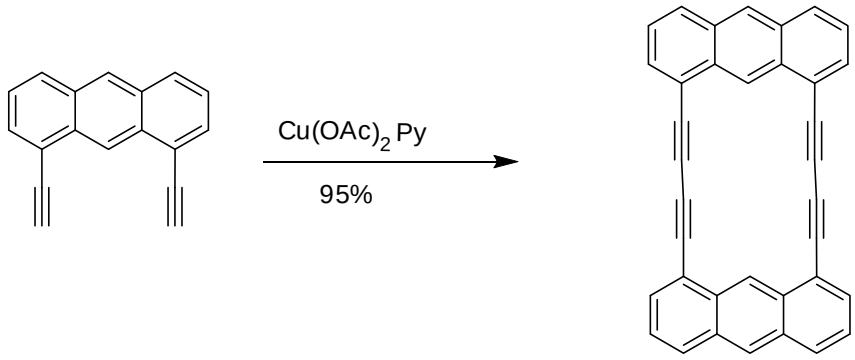


Scheme 4-10 Synthesis of Biphenylene Planarized Aromatic and Anti-aromatic System Starting with Pure 1, 8- Dimethylbiphenylene

Further, with phosphonium salt **200** we can perform phase transfer Wittig reaction to get 1,8-divinylbiphenylene **199** and subsequently convert it to biphenylene planarized aromatic system **110** and its comparison **207** (Scheme 4-11).

4.4 Synthesis of Bis(diacetylene)biphenylene 109

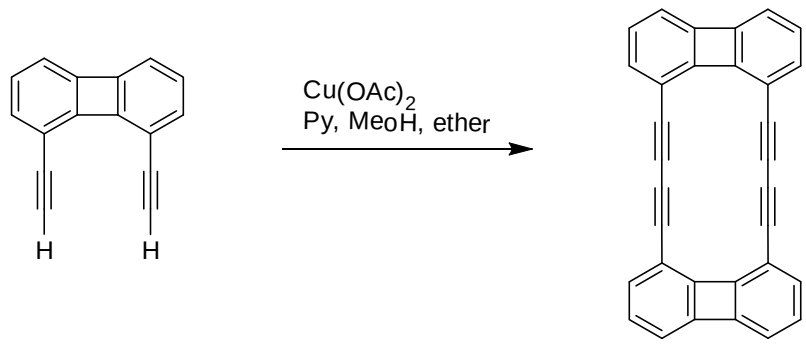
In 1960 Nakagawa[163] reported dimerization of 1,8 –diaceyteleneanthracene **208** using copper acetate in pyridine. The yield was as high as 95%.



208 209

Scheme 4-11 Synthesis of 1,8–Diaceyteleneanthracene by Nakagawa

We applied this method to our 1,8-diaceytelenebiphenylene **114 (**Scheme 4-12), but we didn't get the expected dimer **109**. We thought reason might be because of the solubility of the dimer in ether, we threw the compound away when we did the extraction. But later results confirmed that there was no right compound even if we used CH_2Cl_2 to do the extraction. Figure 4-13 shows the NMR spectrum of compounds in ether and Figure 4-14 shows spectrum of compounds in CH_2Cl_2.



114 109

Scheme 4-12 Synthesis of Bis(diacetylene)biphenylene

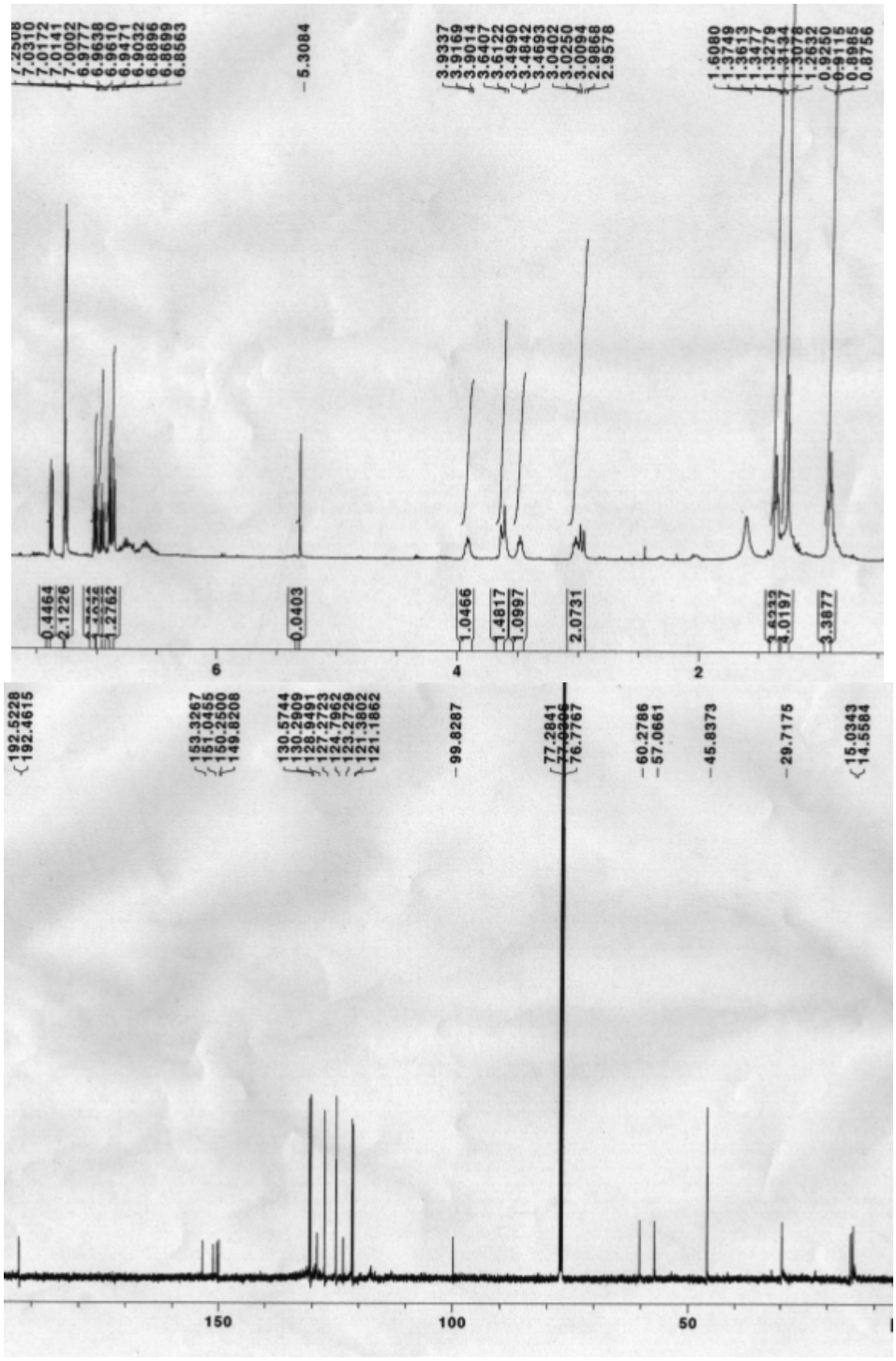


Figure 4-13 NMR spectrum of Bis(diacetylene)biphenylene in Ether

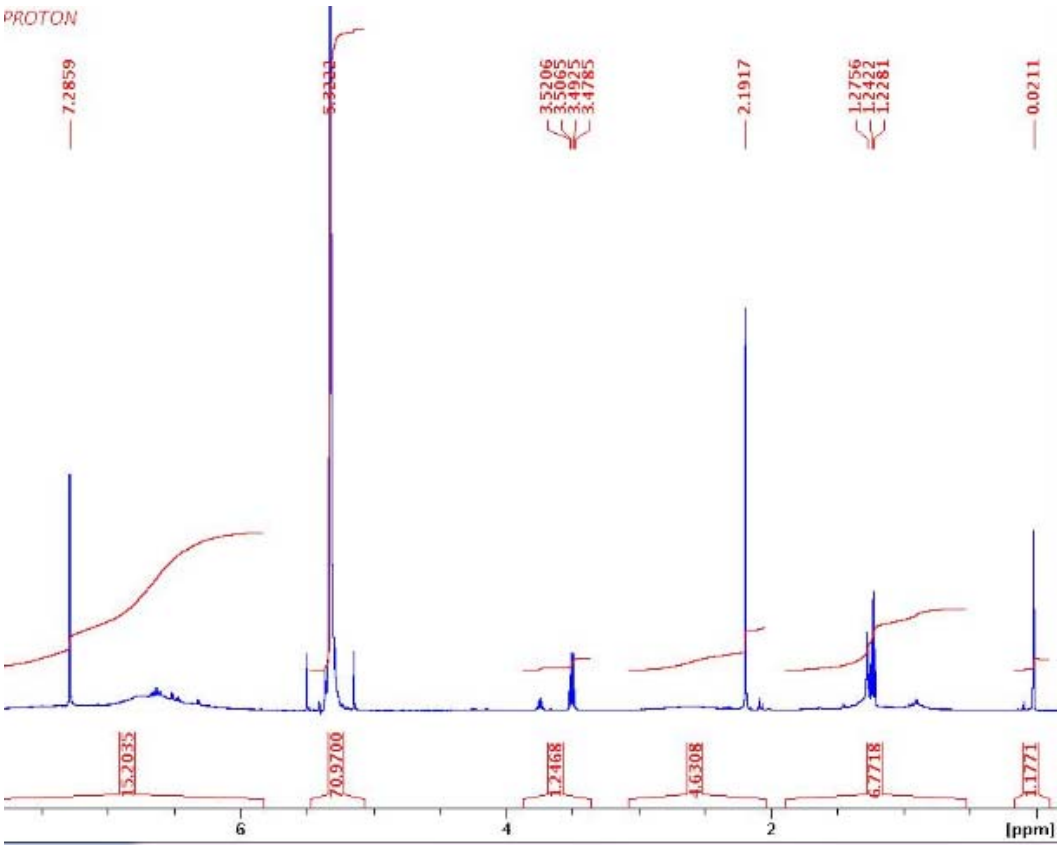
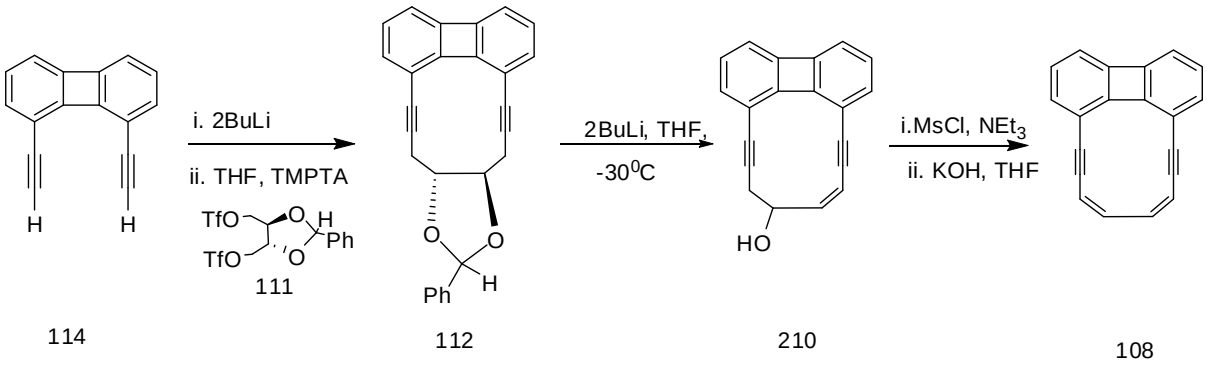


Figure 4-14 NMR spectrum of Bis(diacetylene)biphenylene in CH_2Cl_2

4.5 Synthesis of 108

We may accomplish the cyclization of 1,8-diacetylenebiphylene **114** by treating with 2 equiv BuLi and then the solution of compound **111** and TMPTA in THF. The deprotection of this kind of diol is normally difficult. Recently our group developed a new method to solve this problem. Treating the resulting compound with 2 equiv BuLi would lead to elimination and deprotection and give the corresponding allylic alcohol **210**, and the second elimination of the alcohol would give biphenylene planarized anti-aromatic compound **108**.



Scheme 4-13 Synthesis of bis(diacetylene)biphenylene

4.6 Conclusion and Future Work

1. Key intermediate disubstituted biphenylenes **114** and **117** were synthesized successfully.
2. When approaching biphenylene planarized heterocycllic aromatic system, unexpected eight-membered ring compound **189** was formed, instead of nine-membered ring **110**.
3. Comparisons **111** and **112** were synthesized successfully.
4. Synthesis of biphenylene planarized aromatic system **110**, anti-aromatic systems **108** and **115**, and comparison **207** were proposed.

Chapter 5 Experimental Section

5.1 General procedures

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

5.2 Spectroscopy

Proton and carbon magnetic resonance spectra ^{1}H and ^{13}C NMR were collected by a Bruker 500 MHz spectrometer. All samples were prepared by dissolving a suitable amount of compound in a properly deuterated solvent, usually $CDCl_3$ (99% D, 0.05%VN tetramethylsilane). Chemical shifts are reported in part per million (ppm) downfield from the TMS internal standard 0 =0, and are expressed in the following order: chemical shift (ppm); multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad); coupling constant (*J* in Hz).

Gas chromatography / mass spectra were determined by either electron impact (EI) ionization or chemical ionization (CI) using argon as the carrier gas on a Hewlett-Packard 5890 series II GC / 5989A mass spectrometer.

X-ray crystal structure determinations were measured on an Emaf-Nonius CAD4 diffractometer (graphite-monochromated M_o K^a radiation, ɯ -2^{Θ} scans).

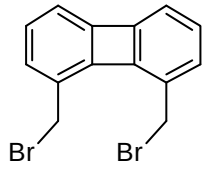
Melting points were determined by using a Melt-temp II instrument in glass capillaries to measure.

Thin-layer chromatography was performed using pre-coated glass plates of silica gel, with a thickness of 0.25mm, supplied by Merck.

Column chromatography was performed using silica gel 60 for flash chromatography.

5.3 Experimental Procedure

1, 8 (1, 5)-Bis (bromomethyl)biphenylene 148



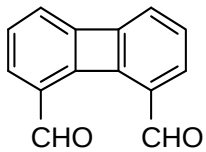
1, 8 and 1, 5

A mixture of 1,8 (1, 5) -dimethylbiphenylene (5.1g, 28.3mmol), N-bromosuccinimide (11.2g, 63mmol), benzoyl peroxide (0.24g, 100mmol), and carbon tetrachloride (125ml) in 250ml three-neck round bottom flash was stirred and refluxed for 5h. Additional benzoyl peroxide (0.24g) was added each hour. Insoluble material was removed from the mixture by gravity filtration, and most of the solvent was evaporated. The crude material was purified by flash chromatography (petroleum ether/ethyl acetate 90:10) to give 1,8 (1, 5) -bis (bromomethyl) biphenylene and some tribromo-substituted methylbiphenylene mixtures 2.61g (27.2%) which was hard to purify.

m.p. 150-176 ^{o}C, lit[81] 154-175^{o}C

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ= 6.5-7.0(m, 6H), 4.0-4.5 (m, 4H)

1,8 (1, 5)–Diformylbiphenylene 150 from 1,8 (1,5) –Bis(bromomethyl) biphenylene 148

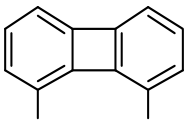


1, 8 and 1, 5

1, 8 (1, 5)-Bis (bromomethyl) biphenylene(1.47g, 4.35mmol) and tetra-n-butylammonium dichromate(5g, 7mmol) were dissolved in $CHCl_3$(70ml) and refluxed for 3h, stirred overnight under N_2. The mixtures were washed with water, dried by $MgSO_4$ and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 80:20) to give 1, 8 (1, 5) – Diformylbiphenylene 0.235g (22%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ= 9.91 (s, 1H), 7.81(s, 1H), 7.18-7.20 (m, 1H), 6.94-7.03(m, 2H), 6.83-6.84(m, 1H), 6.59-6.61(m, 1H).

1,8 (1,5)–Diformylbiphenylene 150 from 8-(dibromomethyl)biphenylene-1-carbaldehyde 149

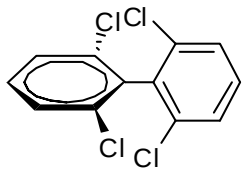


1, 8 and 1, 5

1, 8 (1, 5) -(Dibromomethyl)biphenylene-1-carbaldehyde (0.44g, 1.25mmol) and potassium oxalate (0.92g, 5mmol) were dissolved in ethanol/water mixture(1:1) and refluxed for 2h. The ethanol was distilled off and the remaining mixtures were extracted with diethyl ether, dried by $MgSO_4$ and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 80:20) to give 1,8 (1, 5) –Diformylbiphenylene 0.18g (69.3%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ= 9.91 (s, 1H), 7.81(s, 1H), 7.18-7.20 (m, 1H), 6.94-7.03(m, 2H), 6.83-6.84(m, 1H), 6.59-6.61(m, 1H).

2, 2', 6, 6'-Tetrachlorobiphenyl 154 from 1,3-dichlorobenzene



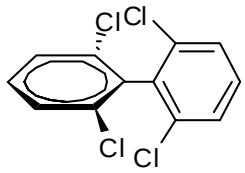
To a stirred solution of 1,3-dichlorobenzene (0.57ml, 5mmol) in THF (30ml) at -70^0C was slowly added from a dropping funnel BuLi (2ml, 5mmol, 2.5M in hexanes). The reaction mixture was stirred at -70^0C for 2h and then put in ice water, to which was added via syringe a solution of $MgCl_2$ in THF (freshly prepared from 1,2-dichloroehane (0.39ml, 495mg, 5mmol) and Mg powder (122mg, 5mmol)). Temperature of the mixture increased to 0^oC quickly. Solid $CuBr{\bullet}SMe_2$ (1.028g, 2.5mmol) was added and the mixture was stirred for 15min, to which a solution of oxidant 3,5-dinitrobenzo-1-methylpiperazinewas added and the resulting solution was warmed to ambient temperature and stir overnight. The reaction mixture was poured into an ice-cold solution of concentrated HCl (2ml) and 30% $NaHSO_3$ (30ml) in brine (100ml) and extracted with ethyl ether (3x100ml). The combined organic extracts were washed by saturated $NaHCO_3$, dried by $MgSO_4$ and concentrated in vacuo to yield a brown oil which was chromatographed (petroleum ether/ethyl acetate 95:5). The product, 109.6mg-15%, was obtained as white crystals.

m. p. 186-190^0C.

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.47 (d, J=6.15 Hz, 4H); 7.35(t, J=8.38Hz, 2H).

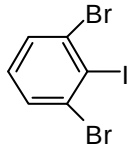
^{13}C NMR (500 MHz, $CDCl_3$, TMS)[164]: δ= 135.8, 130.1, 128.0.

2, 2', 6, 6'-Tetrachlorobiphenyl 154 from 1,3-dichloro-2-iodobenzene



To a stirred solution of 1,3-dichloro-2-iodobenzene (1.3645g, 5mmol) in THF (18ml) at –40^0C was slowly added from a dropping funnel isopropyl magnesium chloride (2.75ml, 5.5mmol, 2M in THF). After stirring at –40^0C for 45min, a solution of $FeCl_3$ in THF (0.1M, 1.5ml, 0.15mmol) and 1,2-dibromoethane (0.43ml, 5mmol) were added simultaneously and the resulting mixture was warm up to room temperature over 1h and stirred at room temperature for 15min then hydrolyzed with 1M HCl. After extraction with ethyl ether (3x100ml), the combined organic extracts were washed by 10% $NaHSO_3$ and then by brine, dried by $MgSO_4$ and concentrated in vacuo to yield a white crystal and brown oil which was chromatographed (petroleum ether). 1/3 starting material was recovered and no product was found.

1-Iodo-2, 6-dibromobenzene 163



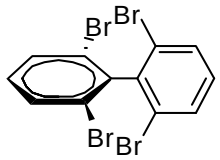
2, 6-Dibromoaniline (4.98g, 19.85mmol) was suspended in concentrated HCl (15ml) and 20ml H_2O. Stir, then add additional 10ml concentrated HCl and 20ml H_2O. The suspension was cool to 0^0C and a solution of sodium nitrite (1.725g, 25mmol) in 20ml H_2O was added slowly via dropping funnel in 30min. After the diazonium chloride formed were poured into

an ice-cold aqueous (30ml) solution of potassium iodide (4.98g, 30mmol) contained in a 1000ml beaker. Excess of sodium bisulfite was added to neutralize the excess of iodine while stirring and the mixture was extracted with ether (3x100ml). The combined organic layers were washed with 4M HCl, 10% sodium bisulfite, water and brine, then dried by $MgSO_4$ and concentrated in vacuo to yield pinkish crystals. Recrystallization in ethanol afforded 4.29g (60%) of colorless crystals.

^{1}H NMR (300MHz, $CDCl_3$, TMS) δ =7.56 (d, 2H), 7.06(t, 2H).

^{13}C NMR (300 MHz, $CDCl_3$, TMS) [164]: δ =131, 132, 132.05

2, 2', 6, 6'-Tetrabromobiphenyl 153

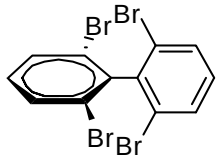


n-BuLi (6ml, 15mmol, 2.5M solution in hexanes) was added to a solution of 1-iodo-2, 6-dibromobenzene (3.617g, 10mmol) in ether (180ml) at -78^{0}C. After the solution was stirred for 2h, $CuBr_2$ (13.9g, 62.23mmol) was added and then the resulting mixture was allowed to attain ambient temperature overnight. Cold water was added to the reaction mixture, and the organic layer was separated from the mixture. The rest water layer was extracted with ether (2x100ml). The combined organic layers were dried by $MgSO_4$ and concentrated in vacuo to yield white crystals and brown oil. Treatment of the crude product with cold hexane (10ml) afforded 0.87g (37%) of a white crystal. Mp. 198-200^{0}C.

^{1}H NMR (300MHz, $CDCl_3$, TMS) δ=7.67 (d, 4H), 7.16(t, 2H)

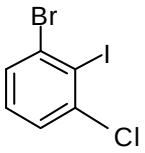
^{13}C NMR (300 MHz, $CDCl_3$, TMS) [164] δ= 142, 132.2, 131, 124.2,

2, 2', 6, 6'-Tetrabromobiphenyl 153



n-BuLi (2ml, 5mmol, 2.5M solution in hexanes) was added to a solution of 1-iodo-2, 6-dibromobenzene (0.803g, 2.22mmol) in ether (40ml) at -75^{0}C. After the solution was stirred for 2h, $ZnBr_2$ (0.55g, 2.44mmol) was added and then the resulting mixture was warmed to -50^{0}C. After stirring for 2h, $CuCl_2$ (0.908g, 6.66mmol) was added into the solution and the resulting mixture was allowed to attain ambient temperature overnight. Cold water was added to the reaction mixture, and the organic layer was separated from the mixture. The rest water layer was extracted with ether (2x75ml). The combined organic layers were dried by $MgSO_4$ and concentrated in vacuo to yield white crystals and brown oil that was chromatographed (hexane). No 2,2',6,6'-tetrabromobiphenyl was obtained.

1-Bromo-3-chloro-2-iodobenzene 161

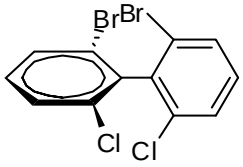


LDA (10mmol in 30ml ether) was added to a solution of 3-chloro-bromobenzene (1.2ml, 10mmol) in THF/Hexane (40ml, 3:1) slowly by dropping funnel at -78^{0}C. After the solution was stirred for 1h, I_2 (2.5g, 10mmol) was added and then the resulting mixture was warmed to ambient temperature and stir overnight. The reaction mixture was poured into an ice-cold solution of concentrated HCl (2ml) and 30% $NaHSO_3$ (30ml) in brine (100ml) and extracted with ethyl ether (3x100ml). The combined organic extracts were washed by saturated

$NaHCO_3$, dried by $MgSO_4$ and concentrated in vacuo to yield white crystals and brown oil which was chromatographed. The product, 1.405g -44%, was obtained as white crystals.

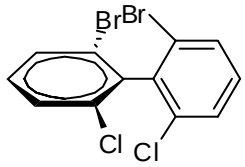
^1H NMR (500Hz, $CDCl_3$, TMS) δ=7.54(dd, J=8.5Hz, 1.37Hz, 1H), 7.41 (dd, J=8Hz, 1.37Hz, 1H), 7.17 (t, J=7.98Hz, 1H)

2,2'-Dibromo 6,6'-dichlorobiphenyl 152



To a stirred solution of 1-bromo-3-chlooro-iodobenzene (2.81g, 8.85mmol) in THF (30ml) at -30^0C was slowly added from a dropping funnel isopropyl magnesium chloride (4.43ml, 8.85mmol, 2M in THF). After stirring at -30^0C for 10min Solid $CuBr{\cdot}SMe_2$ (0.91, 4.43mmol) was added and the mixture temperature was warmed up to -20^0C. A THF solution of oxidant 3,5-dinitrobenzo-1-methylpiperazinewas added into the mixture and the resulting solution was warmed to ambient temperature and stir overnight. The reaction mixture was poured into an ice-cold solution of concentrated HCl (2ml) in brine (100ml) and extracted with ethyl ether (2x100ml). The combined organic extracts were washed by saturated $NaHCO_3$, dried by $MgSO_4$ and concentrated in vacuo to yield brown oil that was chromatographed (petroleum ether/ethyl acetate 90:10). No 2,2'-dibromo 6,6'-dichlorobiphenyl was obtained.

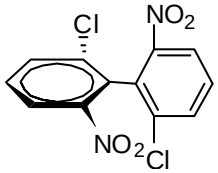
2,2'-Dibromo 6,6'-dichlorobiphenyl 152



To a stirred solution of 3-chloro-bromobenzene (1.2ml, 10mmol) in solvent (30ml) at -78^0C was slowly added from a dropping funnel LDA (10mmol in 30ml ether). Coupling reagent [$CuBr{\cdot}SMe_2$ (5mmol), or $CuBr_2$ (60mmol)] was added and the mixture temperature was warmed up to -20^0C. Oxidant was added into the mixture and the resulting solution was warmed to ambient temperature and stir overnight. The reaction mixture was poured into an ice-cold solution of concentrated HCl (2ml) and 30% $NaHSO_3$ (30ml) in brine (100ml) and extracted with ethyl ether (3x100ml). The combined organic extracts were washed by saturated $NaHCO_3$, dried by $MgSO_4$ and concentrated in vacuo to yield brown oil. Treatment of the product with cold hexane afforded white crystals.

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.65 (dd, J=8.05Hz, 1.02Hz, 1H), 7.51(dd, J=8Hz, 1.05 Hz, 1H), 7.27 (t, J=8.08Hz, 1H)

2, 2'-Dichloro-6, 6'-dinitrobiphenyl 176



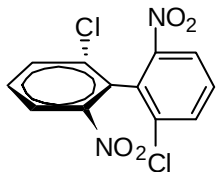
1, 2-Dichloro-3-nitrobenzene (19.2g, 100mmol) and Cu powder (20g, 310mmol) was suspended over freshly dried DMF (150ml). The mixtures were refluxed overnight before additional Cu powder (20g, 310mmol) were added and refluxed for an additional 4h. The

inorganic impurities were filtered off by vacuum filtration and the filtrate were extracted with ethyl ether, dried by $MgSO_4$ and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 90:10) to give 2, 2'-Dichloro-6, 6'-dinitrobiphenyl 8.45g (54%). Mp 155-150^{0}C

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=8.23(d, J=10.5Hz, 2H), 7.84 (d, J=8Hz, 2H), 7.62 (t, J=8.19Hz, 2H)

^{13}C NMR (500 MHz, $CDCl_3$, TMS) [164] δ= 135.8, 135.2, 131.1, 130.6, 124.0.

2, 2'-Dichloro-6, 6'-dinitrobiphenyl 176 by solid-state reaction

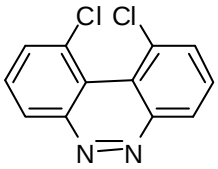


1, 2-Dichloro-3-nitrobenzene (15.36g, 80mmol) and Cu powder (16g, 250mmol) were heated at 250-260 0C for 1h. Wash the mixtures with CH_2Cl_2 and inorganic impurities were filtered off by vacuum filtration. The filtrate were extracted with ethyl ether, dried by $MgSO_4$ and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 90:10) to give 2, 2'-Dichloro-6, 6'-dinitrobiphenyl 7.46g (67%). Mp 155-150^{0}C

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=8.23(d, J=10.5Hz, 2H), 7.84 (d, J=8Hz, 2H), 7.62 (t, J=8.19Hz, 2H)

^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ= 135.8, 135.2, 131.1, 130.6, 124.0.

1,10- Dichlorobenzo[c]cinnoline 175



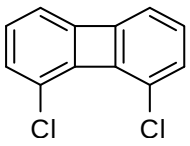
A solution of 2, 2'-Dichloro-6, 6'-dinitrobiphenyl (3.13g, 10mmol) in dry benzene (80ml) was added dropwise over a 90 min period to a suspension of $LiAlH_4$ (2g, 52.6mmol) in dry ethyl ether (60ml). The mixtures were stirred for additional 1h and Na_2SO_4 saturated solution 40ml was added carefully. Gravity filtration and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 85:15) gave 1,10- dichlorobenzo[c]cinnoline 1.77g (71%).

m.p. 106-108^{0}C

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=8.70(d, *J*=1Hz, 2H), 7.97 (d, *J*=1.23Hz, 2H), 7.62 (t, *J*=7.9Hz, 2H)

^{13}C NMR (500 MHz, $CDCl_3$, TMS) [164] *δ*= 147.6, 133.9, 131.9, 130.1, 129.3, 118.9.

1,8- Dichlorobiphenylene 174 by FVP



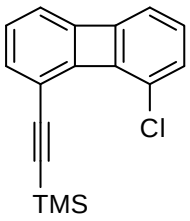
1, 8- Dichlorobenzo[c]cinnoline (1g, 4mmol) was pyrolyzed at 850-920^{0}C and 0.1 Torr. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 90:10) to give crystal 1,8-dichlorobiphenylene (0.71g, 80%). Mp 126-128^{0}C

^{1}H NMR (500MHz, $CDCl_3$, TMS): δ= 6.74(m, 4H), 6.57 (dd, *J*=5.75Hz, 1.08Hz, 2H),

^{13}C NMR (500 MHz, $CDCl_3$, TMS) [164] δ= 151.5, 146.6, 131.0, 130.6, 123.7, 116.5

MS (EI): M+ 220, 185, 150, 110, 75 (100%) m/z;

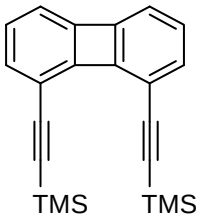
((8-Chlorobiphenylen-1-yl)ethynyl)trimethylsilane 178



To a suspension of 1,8-dichlorobiphenylene (100mg, 0.5mmol), Ni $(acac)_2$ (0.25mg) and $Pd(PPh_3)_4$ (0.55mg) in THF(10ml) was added a solution of [(trimethylsilyl)ethynyl]magnesium bromide prepared from trimethylsilyl acetylene (0.35ml, 2.5mmol) and ethylmagnesium bromide (2.5mmol, excess) in THF(25ml) at 0^0C (and let to warm to room temperature during 45 min) with vigorous gas evolution. Then the mixture was heated at refluxed for 48h. Usual aqueous workup with ether gave an oil that was chromatographed with petroleum ether to give ((8-chlorobiphenylen-1-yl)ethynyl)trimethylsilane 65mg (46%) and 1,8-bis((trimethylsilyl)ethynyl) biphenylene 10mg (5.8%).

^{1}H NMR (500MHz, $CDCl_3$, TMS): δ=6.81 (d, *J*=8.4Hz, 1H), 6.73 (m, 3H), 6.59 (d, *J*=6.76Hz, 1H), 6.54 (dd, *J*= 6.25Hz, 1.05 Hz, 1H), 0.26 (s, 9H).

1,8-Bis ((trimethylsilyl)ethynyl)biphenylene 179

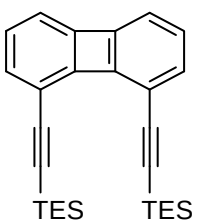


To a suspension of 1,8- ((8-chlorobiphenylen-1-yl) ethynyl)trimethylsilane (65mg, 0.23mmol), $Ni(acac)_2$ (0.25mg) and $Pd(PPh_3)_4$ (0.55mg) in THF(25ml) was added a solution of [(trimethylsilyl)ethynyl]magnesium bromide prepared from trimethylsilylacetylene (0.35ml, 2.5mmol) and ethylmagnesium bromide (2.5mmol, excess) in THF(25ml) at 0^0C (and let to warm to room temperature during 45 min) with vigorous gas evolution. Then the mixture was heated at refluxed for 48h. Usual aqueous workup with ether gave an oil that was chromatographed with petroleum ether to give ((8-chlorobiphenylen-1-yl)ethynyl)trimethylsilane 15mg (23%) and 1,8-bis((trimethylsilyl)ethynyl) biphenylene (12mg 15%)

^{1}H NMR (500MHz, $CDCl_3$, TMS): δ=6.82 (d, J=8.38Hz, 2H), 6.73 (t, J=6.84 Hz 2H), 6.55 (d, J=6.73Hz, 2H), 0.26 (s, 9H).

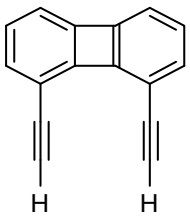
^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ= 151.7, 150.2, 135.3, 128.0, 118.2, 116.5, 104.3, 98.7.

1,8-Bis ((triethylsilyl)ethynyl)biphenylene 181



An oven-dried Schlenk tube was evacuated and backfilled with argon and then charged under a positive pressure of argon with [$PdCl_2(CH_3CN)_2$] (26mg, 0.1mmol, 1mol%), dicyclohexyl(2',4',6'-triisopropylbiphenyl-2-yl) phosphine (143mg, 0.3mmol, 3mol%), Cs_2CO_3 (8.47g, 23mmol), followed by anhydrous acetonitrile (20ml) and 1,8-dichlorobiphenylene (1.10g, 5mmol). The slightly yellow suspension was stirred for 25min at room temperature. Then triethylsilylacetylene (2.33ml, 13mmol) was injected and the mixture was stirred for 10 min, the Schlenk tube was sealed and the mixture was heated by oil bath to 90^0C for 13h. The resulting suspension was allowed to reach room temperature, diluted with ice water, and extracted with diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 90:10) to give a mixture of 1,8-bis ((triethylsilyl)ethynyl)biphenylene, 1,8-bis (ethynyl) biphenylene and 1- triethylsilylethynyl-8- ethynyl biphenylene(1.05g).

1, 8-Diacetylene biphenylene 114

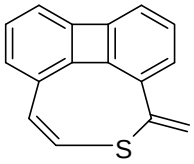


The mixture of 1,8-bis ((triethylsilyl)ethynyl)biphenylene, 1,8-bis (ethynyl) biphenylene and 1- triethylsilylethynyl-8- ethynyl biphenylene (1.05g) was stirred with *tert*-butylammonium fluoride (20ml, 1M) and water (3ml) for 3h, and then extracted with diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 90:10) to give 1,8-diacetylenebiphenylene (0.44g, 44% overall yield).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=6.78 (dd, J=27Hz, 7.5Hz, 4H), 6.61(s, 2H), 3.15 (s, 2H)

^{13}C NMR (500 MHz, $CDCl_3$, TMS): 150.3, 131.7, 128.9, 117.4, 112.7, 80.8

1-Methylene-1H-biphenyleno[1,8-*cde*]thiocine 189

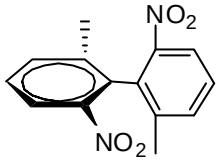


1, 8-Diacetylene biphenylene (0.44g, 2.2mmol) was dissolved in EtOH(100ml) and charged with Nitrogen. Na_2S nonahydrate (0.98g, 4.1mmol) was added and the mixture was refluxed gently for 20h to get a yellow solution. EtOH was evaporated and the residue was extracted by ice-brine and diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 95:5) to yellow crystal (0.384g, 16%) and starting material (0.37g, 84% recovered).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.04(d, J=9.2Hz, 1H), 6.84 (t, J=8.7Hz, 1H), 6.82 (d, J=8.4Hz, 1H), 6.73 (t, J=7.0Hz, 1H), 6.62 (d, J=6.7Hz, 1H), 6.51 (d, J=6.7Hz, 1H), 6.19 (s, 1H), 5.84 (s, 1H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=151.5, 151.2, 150.3, 149.6, 141.7, 139.9, 134.1, 129.2, 129.1, 128.2, 126.5, 125.9, 125.8, 124.5, 117.5, 117.

2, 2'-Dimethyl-6, 6'-dinitrobiphenyl 202

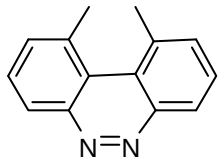


2-Iodo-1-methyl-3-nitrobenzene (19g, 72mmol) and Cu powder (20g, 310mmol) were suspended over freshly dried DMF (150ml). The mixtures were refluxed overnight before additional Cu powder (20g, 310mmol) were added and refluxed for an additional 4h. The inorganic impurities were filtered off by vacuum filtration and the filtrate were extracted with ethyl ether, dried by $MgSO_4$ and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 90:10) to give 2, 2'-dimethyl-6, 6'-dinitrobiphenyl 8.33g (85%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=8.01(d, J=8.1Hz, 2H), 7.60 (d, J=7.6Hz, 2H), 7.50 (t, J=7.9Hz, 2H), 2.01(s, 6H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS) [164]: δ=148.2, 138.5, 135.3, 131.8, 128.7, 122.8, 20.0

1,10- Dimethylbenzo[*c*]cinnoline 203

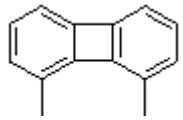


A solution of 2,2'-methyl-6,6'-dinitrobiphenyl (14.16, 52mmol) in dry benzene (400ml) was added dropwise over a 5h period to a suspension of $LiAlH_4$ (10g, 263mmol) in dry ethyl ether (300ml). The mixtures were stirred for additional 1h and Na_2SO_4 saturated solution 200ml was added carefully. Gravity filtration and concentrated in vacuo then chromatographed (petroleum ether/ethyl acetate 85:15) gave 1,10- Dimethylbenzo[*c*]cinnoline 6.33g (58%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=8.70(d, J=7.8Hz, 2H), 7.91(t, J=9.5Hz, 2H), 7.85 (d, J=7.16Hz, 2H), 2.71(s, 6H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS) [164]: δ=146.2, 134.1, 133.0, 128.5, 121.3, 22.1

1, 8- Dimethylbiphenylene 146

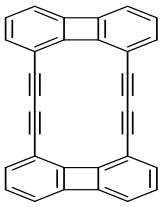


1,8- Dimethylbenzo[c]cinnoline (1g, 4.8mmol) was pyrolyzed at 850-920^{o}C and 0.1 Torr. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 90:10) to give crystal 1,8- Dimethylbiphenylene (0.71g, 80%). Mp 78^{0}C

^{1}H NMR (300MHz, $CDCl_3$, TMS) [164] δ=6.64 (t, 2H), 6.53 (d, 2H), 6.46 (d, 2H), 2.2(s, 6H).

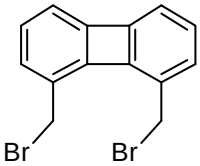
^{13}C NMR (300 MHz, $CDCl_3$, TMS) [164] δ=151.3, 150.4, 131.2, 128.7, 127.5, 115.4, 18.9.

Bis(diacetylene)biphenylene 109



A dry 3-neck 250ml round bottom flask, under an atmosphere of Nitrogen, was charged with anhydrous $Cu(OAc)_2$ (0.92g, 5.03mmol), distilled pyridine(45ml), EtOH(45ml), anhydrous diethyl ether (7.5ml). The solid was allowed to suspend while 1,8-bis (ethynyl)biphenylene (0.15g, 0.75mmol) in 38ml of 1:1 solution of pyridine and ethanol were added dropwise over a 4h period. The mixture was refluxed for 2h and then stirred overnight under room temperature. Concentrated HCl was used to neutralize pyridine and the resulting solution was extracted by diethyl ether. The combined organic layer was dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give no valuable compound.

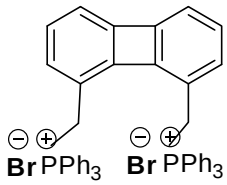
1,8 -Bis (bromomethyl)biphenylene 204



A mixture of 1,8 -dimethylbiphenylene (3.7g, 20.5mmol), N-bromosuccinimide (6.8g, 38.33mmol), benzoyl peroxide (0.24g, 100mmol), and carbon tetrachloride (100ml) in 250ml three-neck round bottom flash was stirred and refluxed for 5h. Additional benzoyl peroxide (0.24g) was added each hour. Insoluble material was removed from the mixture by gravity filtration, and most of the solvent was evaporated. The crude material was purified by flash chromatography (petroleum ether/ethyl acetate 95:5) to give 1,8 -bis (bromomethyl) biphenylene crystal 0.55g (8%). Mp 180-182^{0}C

^{1}H NMR (600MHz, $CDCl_3$, TMS) δ=6.81 (t, 2H), 6.75 (d, 2H), 6.60 (d, 2H), 4.93(s, 4H).

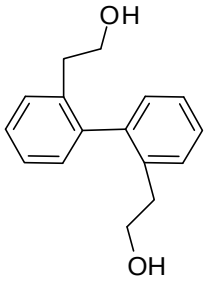
1, 8 –Bis(triphenylphosphine (bromomethyl))biphenylene Ylide 200



A dry 100ml round bottom flask, was charged with 1,8 -Bis (bromomethyl) biphenylene (2g, 5.9mmol), PPh_3 (3.5g, 13.4mmol) and anhydrous DMF(50ml). The mixture was heated at 100^{0}C overnight and then cooled to room temperature. 100ml dry ether was added to get precipitation. The resulting was recrystalized by CH_2Cl_2 to give a nice crystal (0.76g, 14%).

^{1}H NMR (600MHz, $CDCl_3$, TMS) δ=8.18 (d, J=7.75Hz, 2H), 7.50 (m, 2H), 7.30 (m, 4H), 2.65(s, 4H).

2,2'-(Biphenyl-2, 2'-diyl) diethanol 195

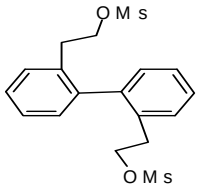


A dry 3-neck 100ml round bottom flask, under an atmosphere of Argon, was charged with 2,2'-divinylbiphenyl (1.3g, 6.3mmol), anhydrous THF (20ml) and cooled in ice bath. Borane-THF complex (4.2ml) was added dropwise into the cold mixture during 20min and the resulting mixture was removed from ice bath and stirred for 3h under room temperature. After adding NaOH (1.5ml, 3M, 4.2mmol), the flask was put into ice bath again and H_2O_2 (1.5ml, 30%, 12.6mmol) was dropwised in. After heating at 50 ^{0}C for 1h the mixture was extracted by ice brine and diethyl ether. The combined organic layer was dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 50:50) to give 2,2'-(biphenyl-2, 2'-diyl)diethanol with some impurities. (0.53g, 34.8%).

^{1}H NMR (500MHz, D_2O, TMS) δ=7.08-7.35 (m, 6H), 3.66(t, J=6.8Hz, 4H), 2.69-2.74 (m, 2H), 2.59-2.64 (m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=141.2, 136.1, 129.7, 129.3, 128.3, 127.1, 62.8, 36.3

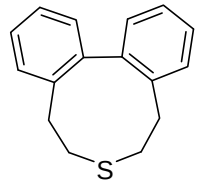
2,2'-(Biphenyl-2, 2'-diyl)bis(ethane-2,1-diyl)dimethanesulfonate 196



A dry 3-neck 100ml round bottom flask, under an atmosphere of Argon, was charged with 2,2'-(biphenyl-2, 2'-diyl) diethanol (0.53g, 2.19mmol), distilled CH_2Cl_2 (50ml), MsCl(0.3g, 0.2ml, 2.63mmol) and cooled in ice bath. Et_3N (1.52ml, 1.1g, 10.95mmol) in distilled CH_2Cl_2 (20ml) was added dropwise into the reaction and the mixture was stirred for 1h at 50^0C. The reaction was quenched by adding ice water and concentrated HCl (0.5ml) and extract by CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 50:50) to give 2, 2'-(biphenyl-2, 2'-diyl)bis(ethane-2,1-diyl) dimethanesulfonate (0.87g, 99.8%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.1-7.3(m, 6H), 4.1-4.2(m, 4H), 2.7-3.1(m, 4H), 2.79(s, 3H), 2.0(s, 3H)

5, 6, 8, 9-Tetrahydrodibenzo[*d,f*]thionine 197

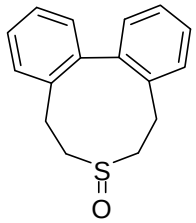


2,2'-(Biphenyl-2,2'-diyl)bis(ethane-2,1-diyl) dimethanesulfonate (0.87g, 2.19mmol) was dissolved in dry EtOH(50ml) and charged with Nitrogen. Na2S nonahydrate (1.05g, 4.38mmol) dissolved in dry EtOH (100ml) was added in and the mixture was refluxed gently overnight. EtOH was evaporated and the residue was extracted by ice-brine and CH_2Cl_2. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give crystal 5,6,8,9-tetrahydrodibenzo[*d,f*]thionine (0.06g, 12%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.19-7.38(m, 8H), 2.93(m, 2H), 2.64-2.71(m, 6H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=141.9, 139.8, 129.8, 128.9, 127.8, 126.2, 35.8, 32.1.

5, 6, 8, 9-Tetrahydrodibenzo[d,f]thionin oxide 198

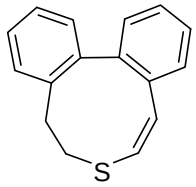


5,6,8,9-Tetrahydrodibenzo[*d,f*]thionine (0.06g, 0.25mmol) was dissolved in distilled CH_2Cl_2(5ml) and charged with Nitrogen. MCPBA (0.061g, 0.25mmol) dissolved in CH_2Cl_2 (5ml) was added dropwise in during 20min. The resulting mixture was washed by $NaHCO_3$ solution and extracted by diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give 5, 6, 8, 9-tetrahydrodibenzo[*d,f*]thionin oxide (0.06g, 94%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.11-7.36(m, 8H), 2.54-3.70(m, 6H), 1.23-1.26(m, 2H).

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=138, 130.48, 129.6, 128.7, 128.3, 127.3, 28.7, 26.7.

5, 6-Dihydrodibenzo[*d,f*]thionine 111



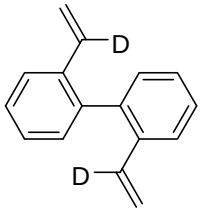
The mixture of 5, 6, 8, 9-tetrahydrodibenzo[*d,f*]thionin oxide (0.06g, 0.23mmol) and Acetic anhydride (3ml) was refluxed for 30min and then cooled down to room temperature. Enough NaOH solution was used to neutralize the mixture and the resulting mixture was extracted by diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the

residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give 5, 6-dihydrodibenzo [*d,f*]thionine (0.02g, 38%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=6.97-7.20(m, 8H), 6.49(d, *J*=11.5Hz, 1H), 5.82(d, *J*=11.5Hz, 1H), 3.18-3.22(m, 1H), 3.07-3.14(m, 1H), 2.71-2.78(m, 1H), 2.54-2.58(m, 1H),

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=142.3, 140.6, 137.5, 136.4, 131.7, 128.9, 128.7, 127.4, 127.1, 126.5, 125.7, 124.6, 104.5, 95.8, 30.5, 28.2

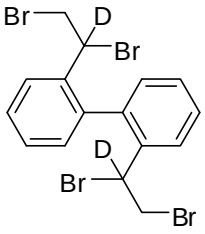
2,2'-Bis(1-deutero-vinyl)biphenyl 191



2,2'-Bis(triphenylphosphine-1-deutero-vinyl) biphenyl ylide (7.5g, 8.66mmol) formaldehyde (50ml, 37%) was dissolved in dry Hexane (50ml) and charged with Nitrogen. NaOH solution (15ml, saturated) was added dropwise during 40min. The mixture was stirred for 4h at room temperature and then quenched by using ice water, extracted by hexane. The combined organic layer were dried over $MgSO_4$, concentrated to give 2,2'-bis(1-deutero-vinyl)biphenyl (2.17g, >100%).

^{1}H NMR (500MHz, $CDCl_3$, TMS) δ=7.68 (d, *J*=7.6Hz, 2H), 7.37 (t, *J*=7.2Hz, 2H), 7.31(t, *J*=7.4Hz, 2H), 7.17(d, *J*=7.5Hz, 2H), 6.42(dd, *J*=17Hz, 11.05Hz, 2H), 5.67(d, *J*=17.5Hz, 2H), 5.11(d, *J*=11.05Hz, 2H),

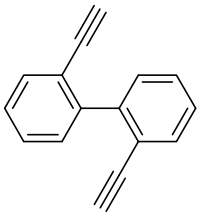
2, 2'-Bis (1,2-dibromoethyl) biphenyl 192



To an ice-salt bath cooled solution of 2,2'-bis(1-deutero-vinyl)biphenyl (1.78g, 8.66mmol) in $CHCl_3$ (50ml), the solution of Bromine (2.77g, 0.89ml, 17.32mmol) in $CHCl_3$ (20ml) was dropwised in until the mixture was colored. Added a lit excess of Bromine and then use ice water and enough $NaHSO_3$ to decolorize the solution. The resulting mixture was washed with ice water and $NaHCO_3$ saturate solution and then extracted by diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated to give crystal 2, 2'-bis(1,2-dibromoethyl) biphenyl (3.96g, 87%).

^1H NMR (500MHz, $CDCl_3$, TMS) δ=7.38-7.70(m, 8H), 4.93-5.06(m, 2H), 4.89-4.91(m, 2H), 3.66-4.01(m, 4H).

2, 2'-Diethynylbiphenyl 193

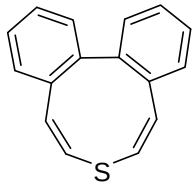


To an ice-salt bath cooled, Nitrogen charged solution of *t*-BuOK (4.5g, 40mmol) in dry THF (50ml, the solution of 2,2'-bis(1,2-dibromoethyl) biphenyl (3.96g, 7.55mmol) in dry THF

(30ml) was dropwised in and the mixture was stirred overnight under room temperature and then washed by ice brine and concentrated HCl (2ml), extracted by diethyl ether. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give 2,2'-diethynylbiphenyl (1.16g, 77%).

^{1}HNMR (500MHz, $CDCl_3$, TMS) δ=7.63(d, J=7.6Hz, 2H), 7.41(d, J=3.95Hz, 4H), 7.33-7.37(m, 2H), 2.97(s, 2H)

Dibenzo[*d,f*]thionine 112



2, 2'-Diethynylbiphenyl (0.69g, 3.4mmol) was dissolved in dry EtOH(100ml) and charged with Nitrogen. Na_2S nonahydrate (1g, 4.17mmol) was added in and the mixture was refluxed gently overnight. EtOH was evaporated and the residue was extracted by ice-brine and CH_2Cl_2. The combined organic layer were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate 80:20) to give crystal dibenzo[*d,f*]thionine (0.045g, 6%).

^{1}HNMR (500MHz, $CDCl_3$, TMS) δ=7.37-7.38(m, 2H), 7.31-7.34(m, 2H), 7.13-7.18(m, 4H), 6.53 (d, J=10.8Hz, 2H), 5.86 (d, J=10.8Hz, 2H)

^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ=140.1, 136.1, 134.3, 127.8, 127.6, 127.1, 127.0, 119.8.

Appendix

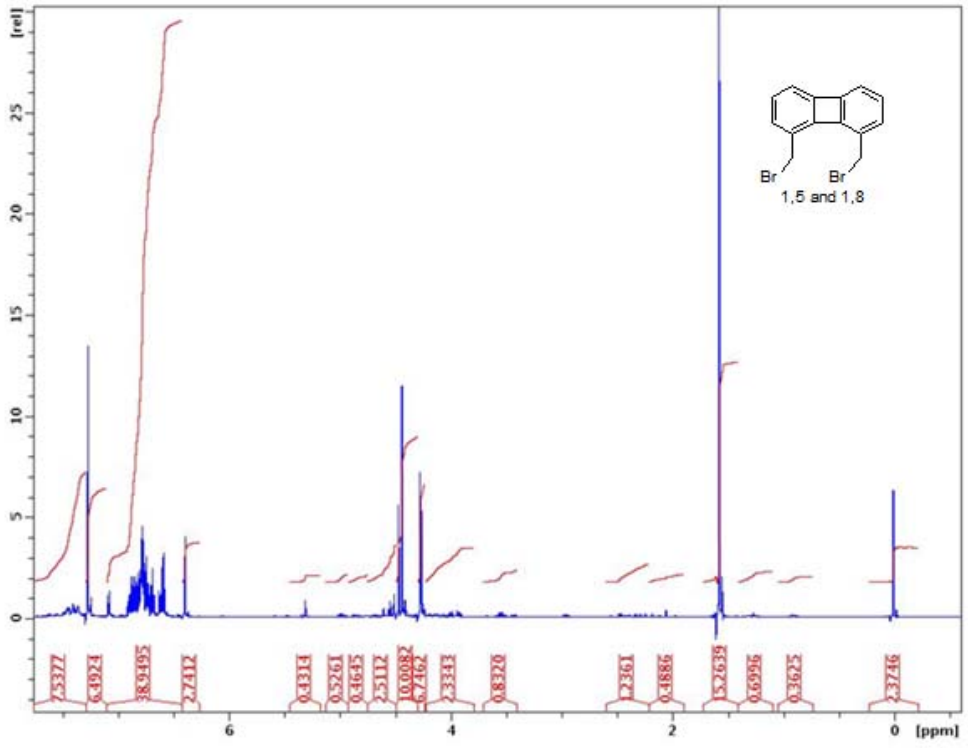


Figure 6-1 NMR Spectrum of 1, 8 (1, 5)-Bis(bromomethyl)biphenylene

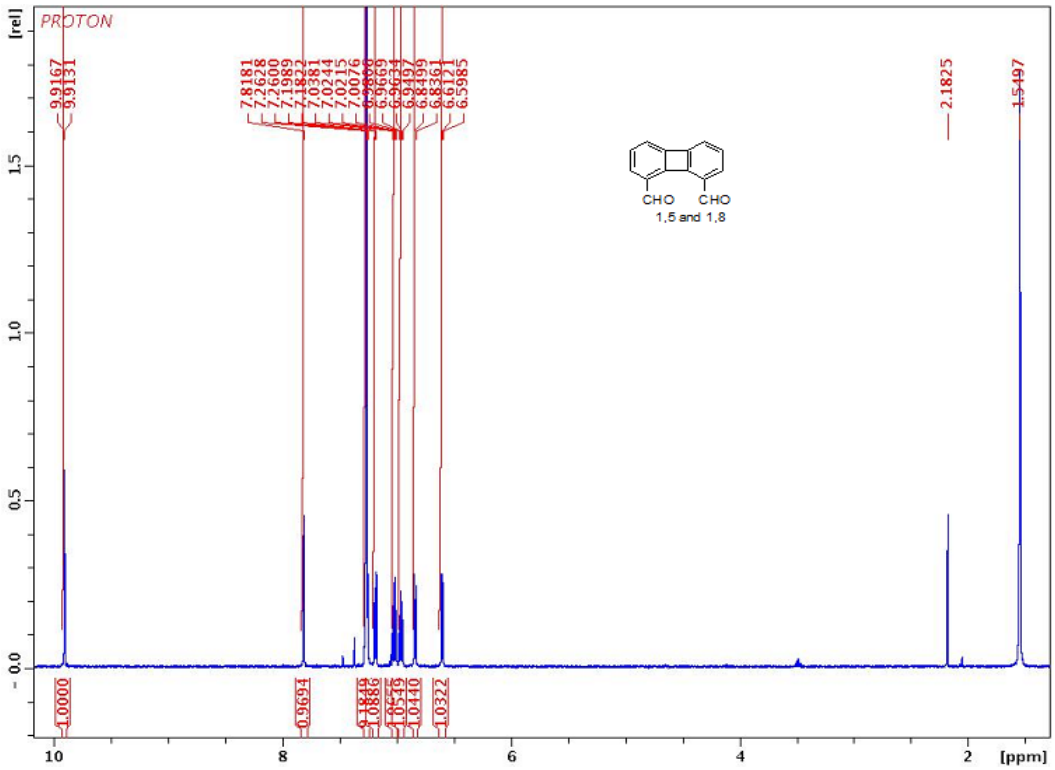


Figure 6-2 NMR Spectrum of 1,8 (1, 5)–Diformylbiphenylene

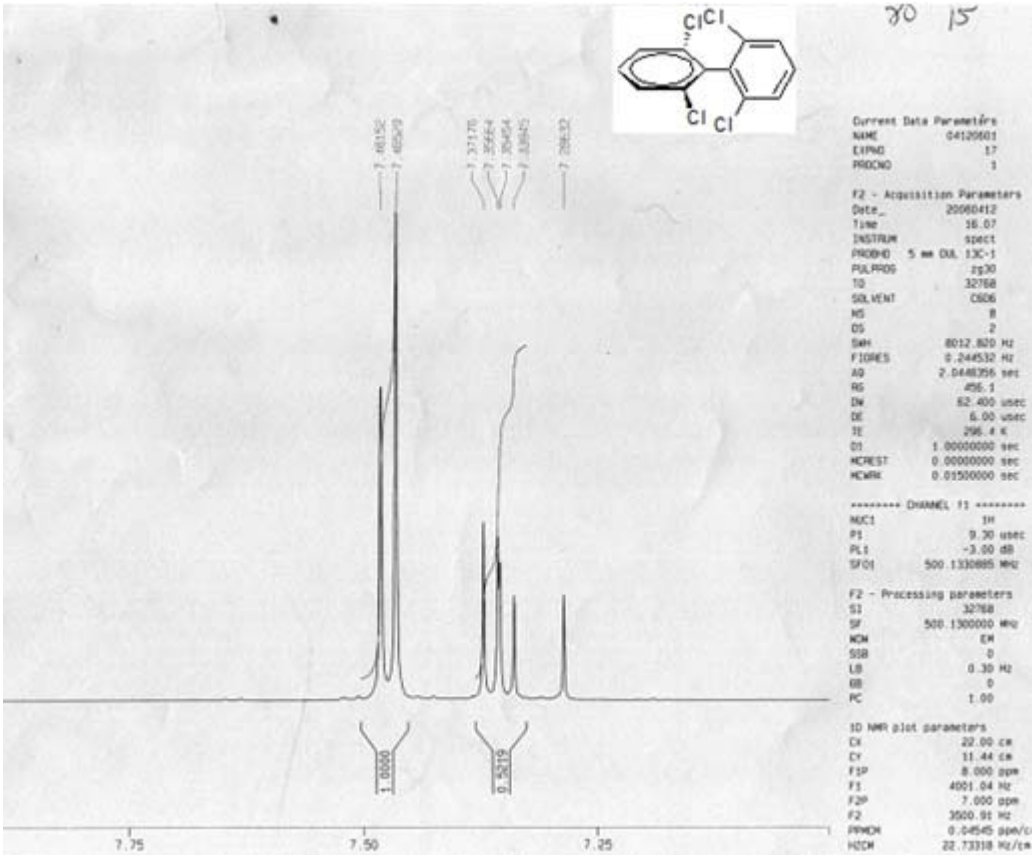


Figure 6-3 NMR Spectrum of 2, 2', 6, 6'-Tetrachlorobiphenyl

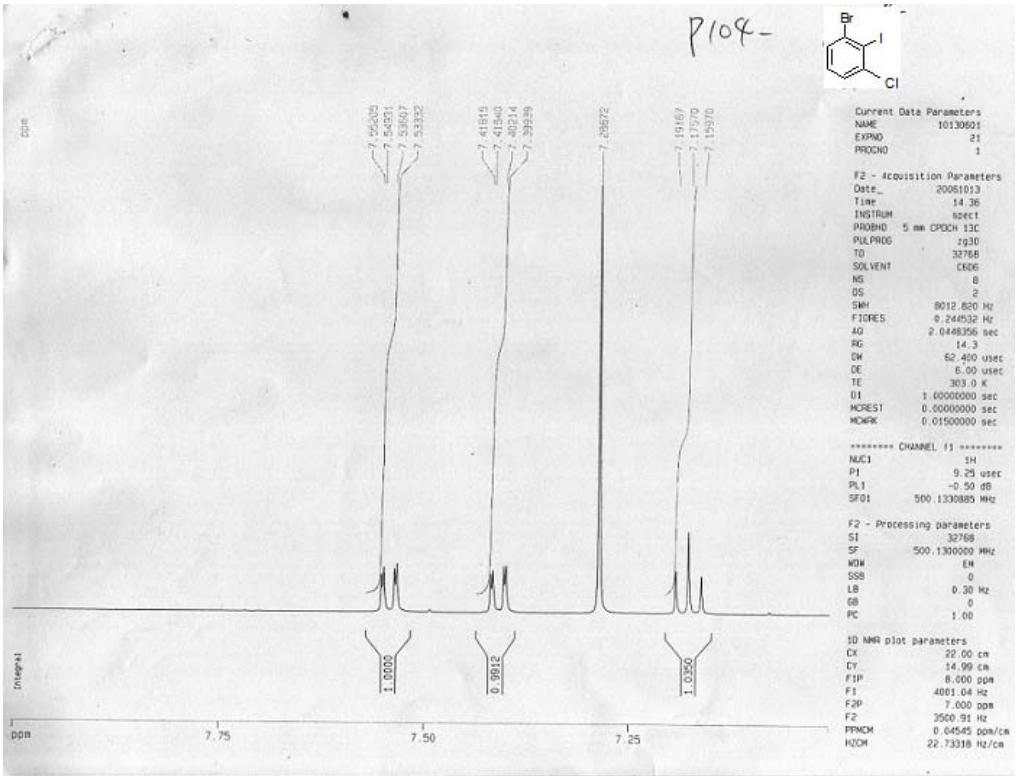


Figure 6-4 NMR Spectrum of 1-Bromo-3-chloro-2-iodobenzene

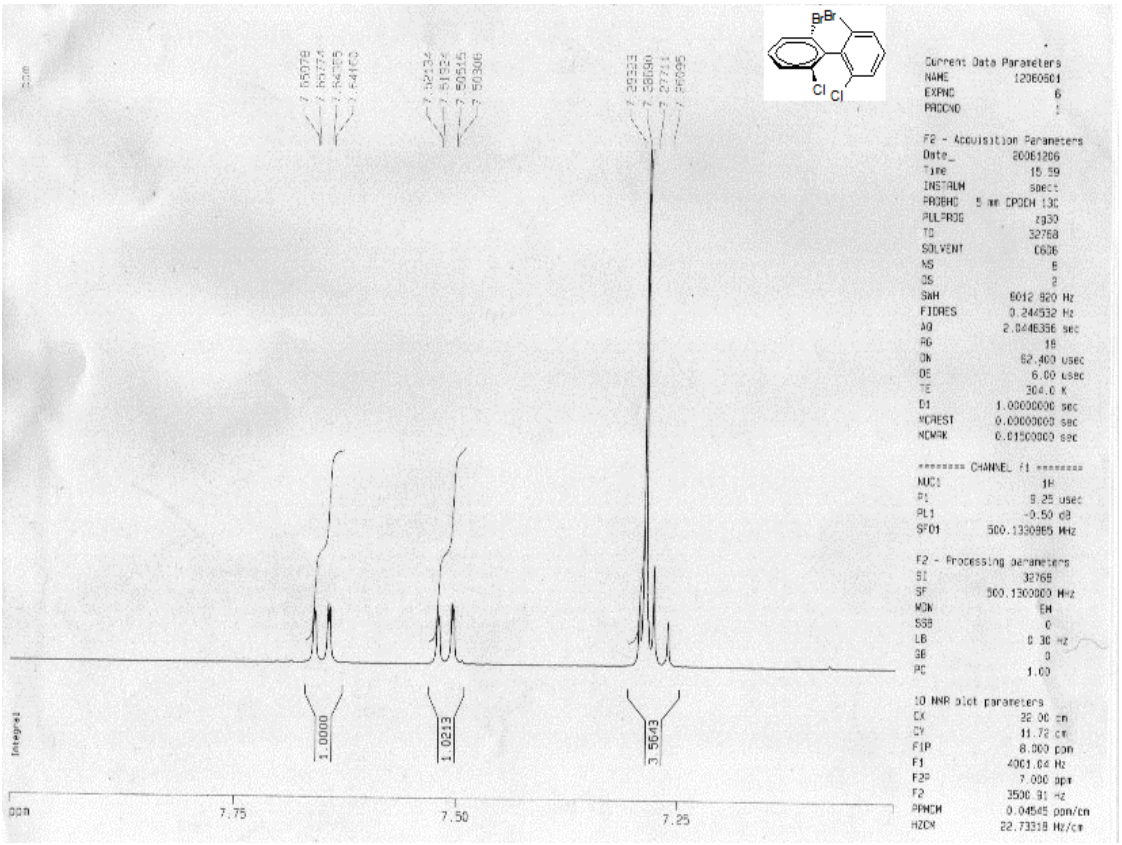


Figure 6-5 NMR Spectrum of 2,2'-Dibromo 6,6'-dichlorobiphenyl

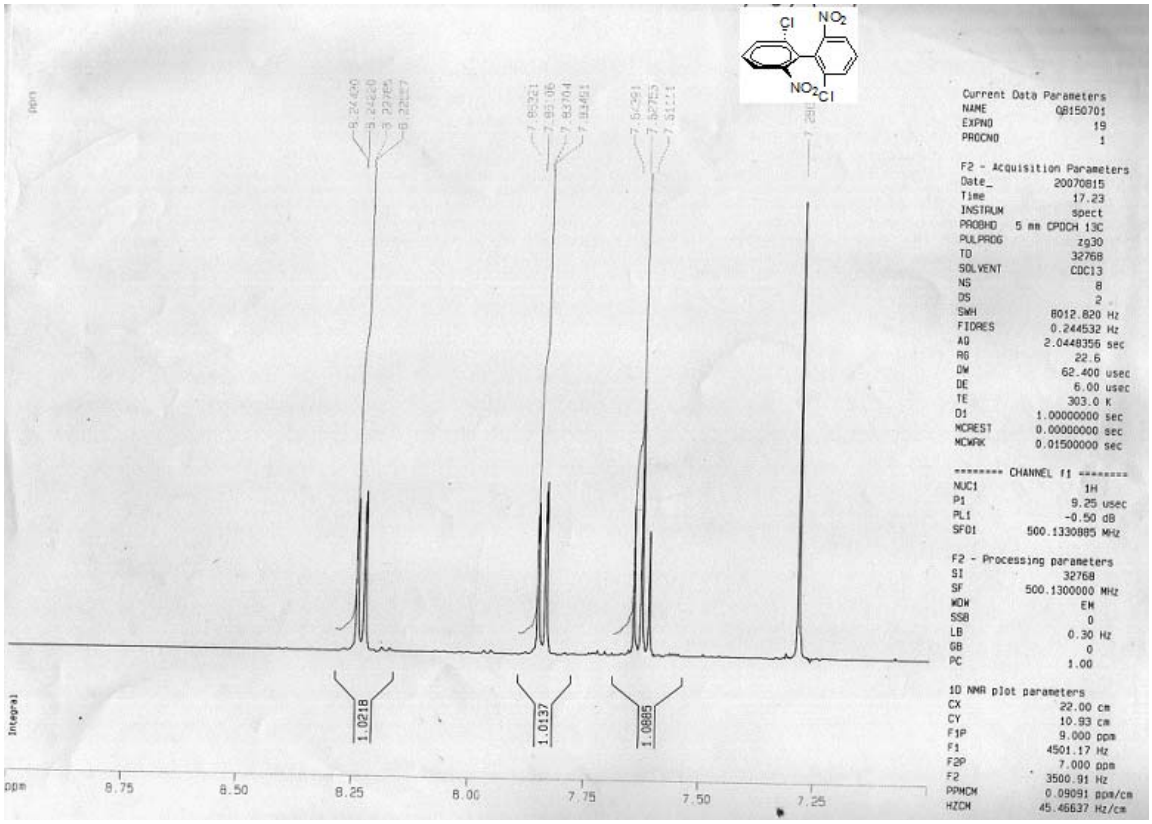


Figure 6-6 NMR Spectrum of 2, 2'-Dichloro-6, 6'-dinitrobiphenyl

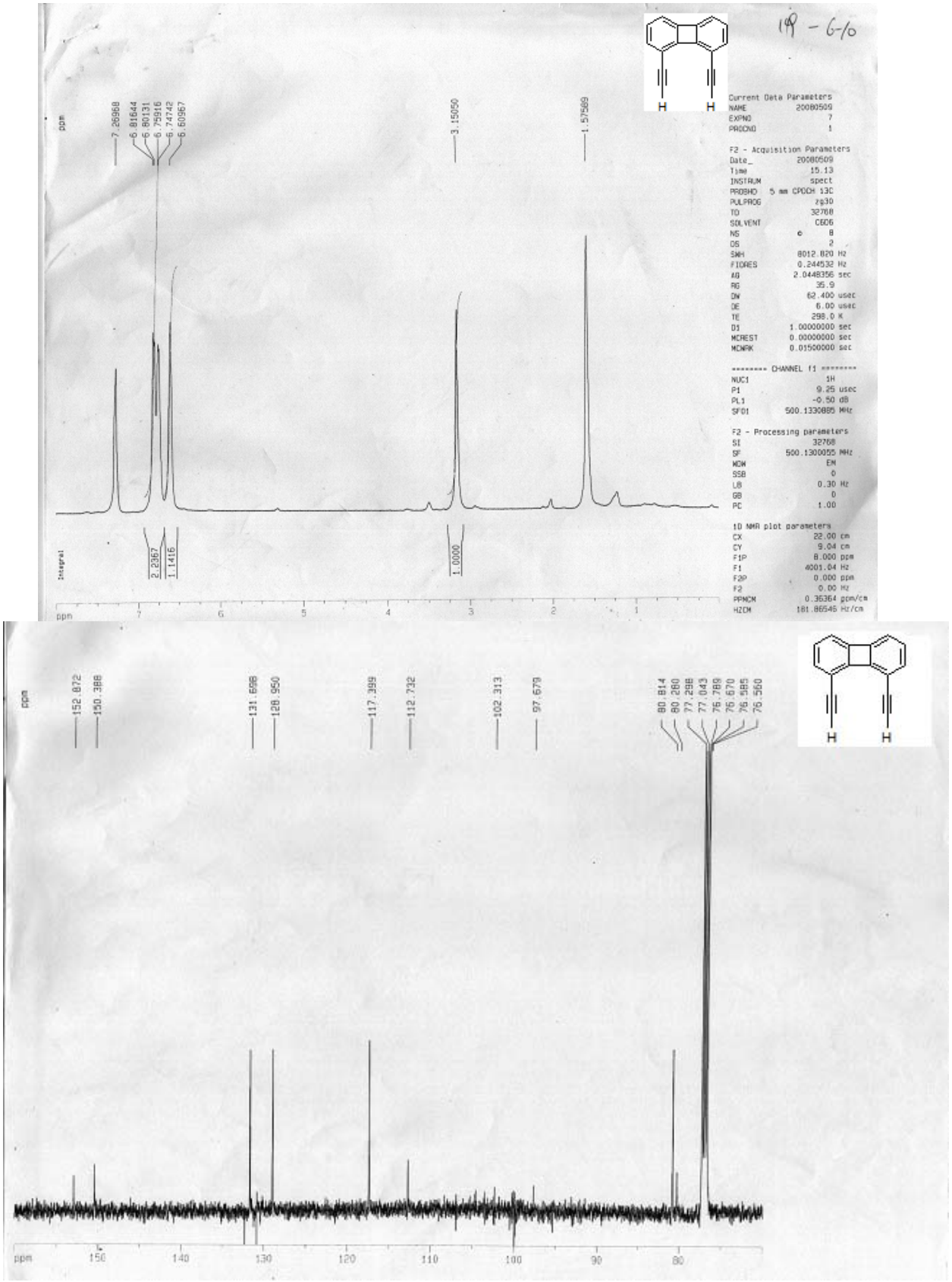


Figure 6-7 NMR Spectrum of 1, 8-Diacetylene biphenylene

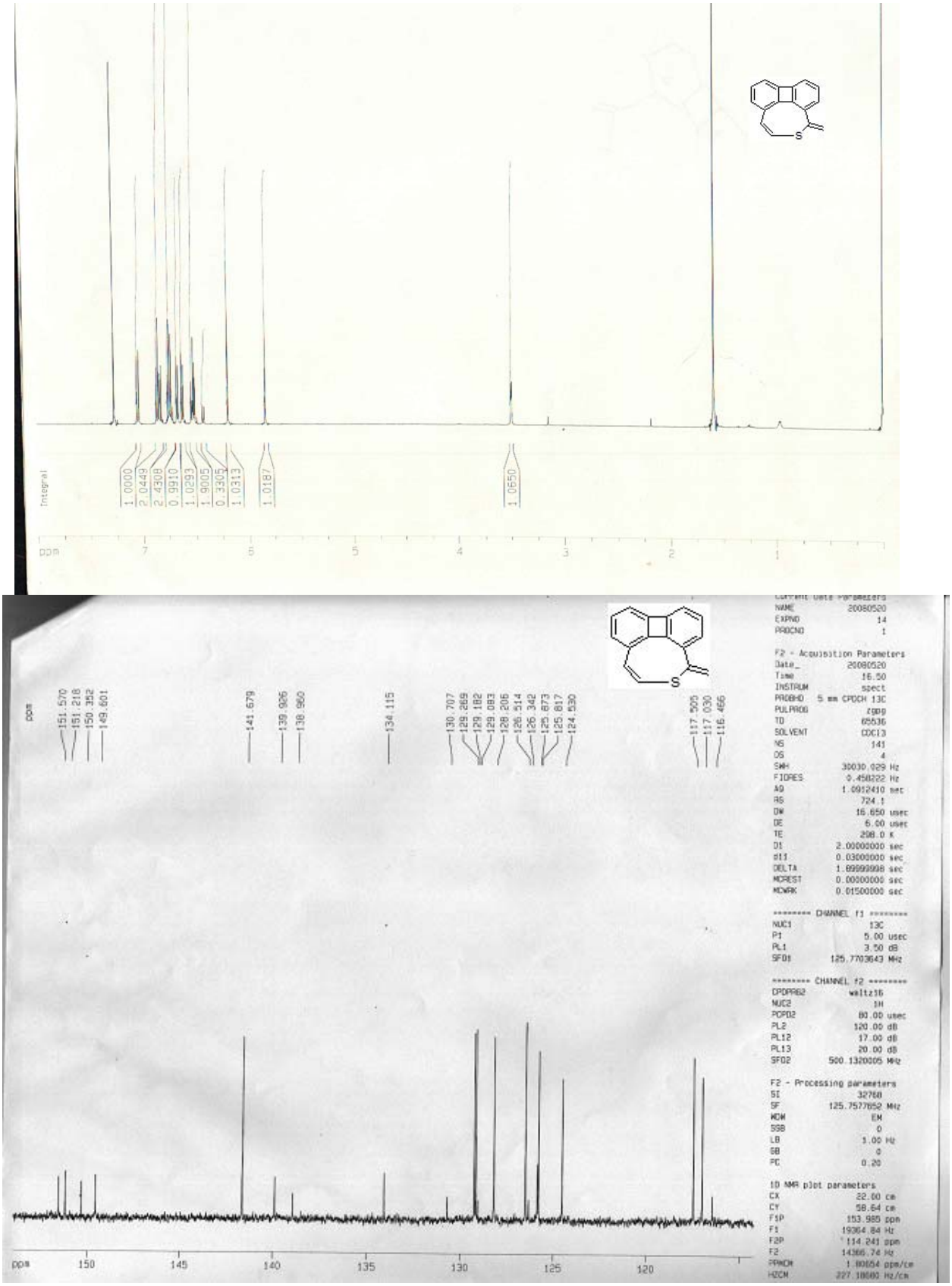


Figure 6-8 NMR Spectrum of 1-Methylene-1H-biphenyleno[1,8-*cde*]thiocine

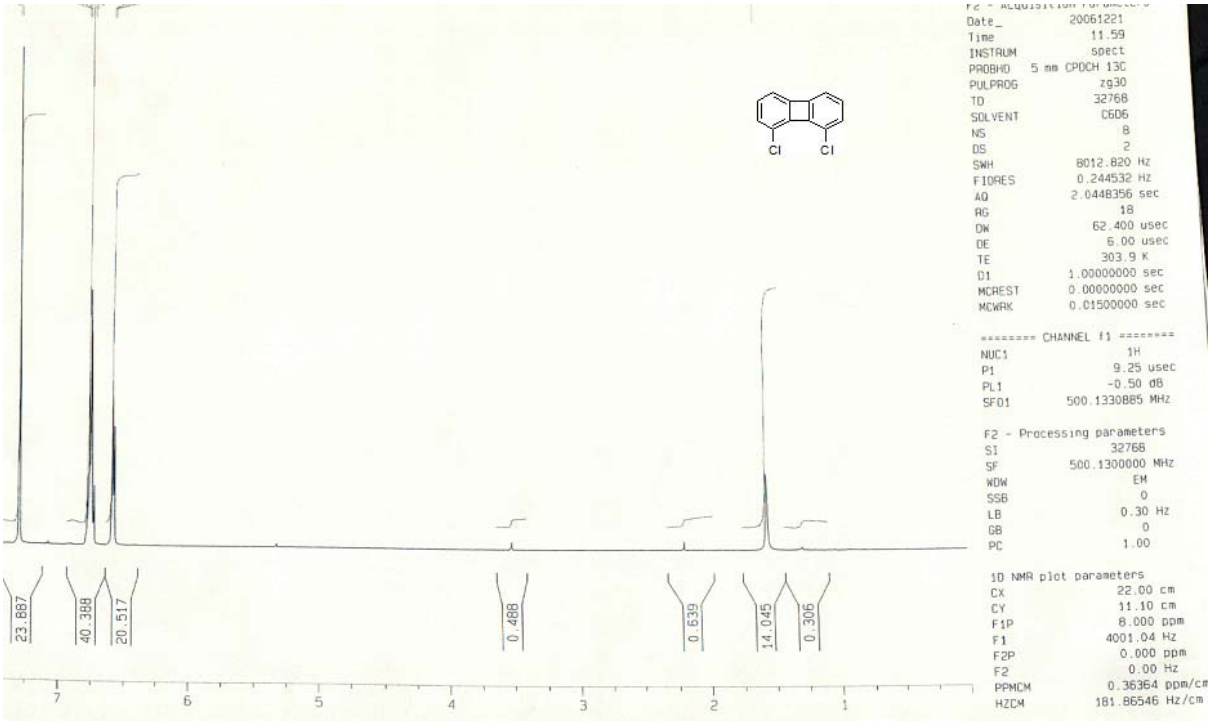


Figure 6-9 NMR Spectrum of 1,8- Dichlorobiphenylene

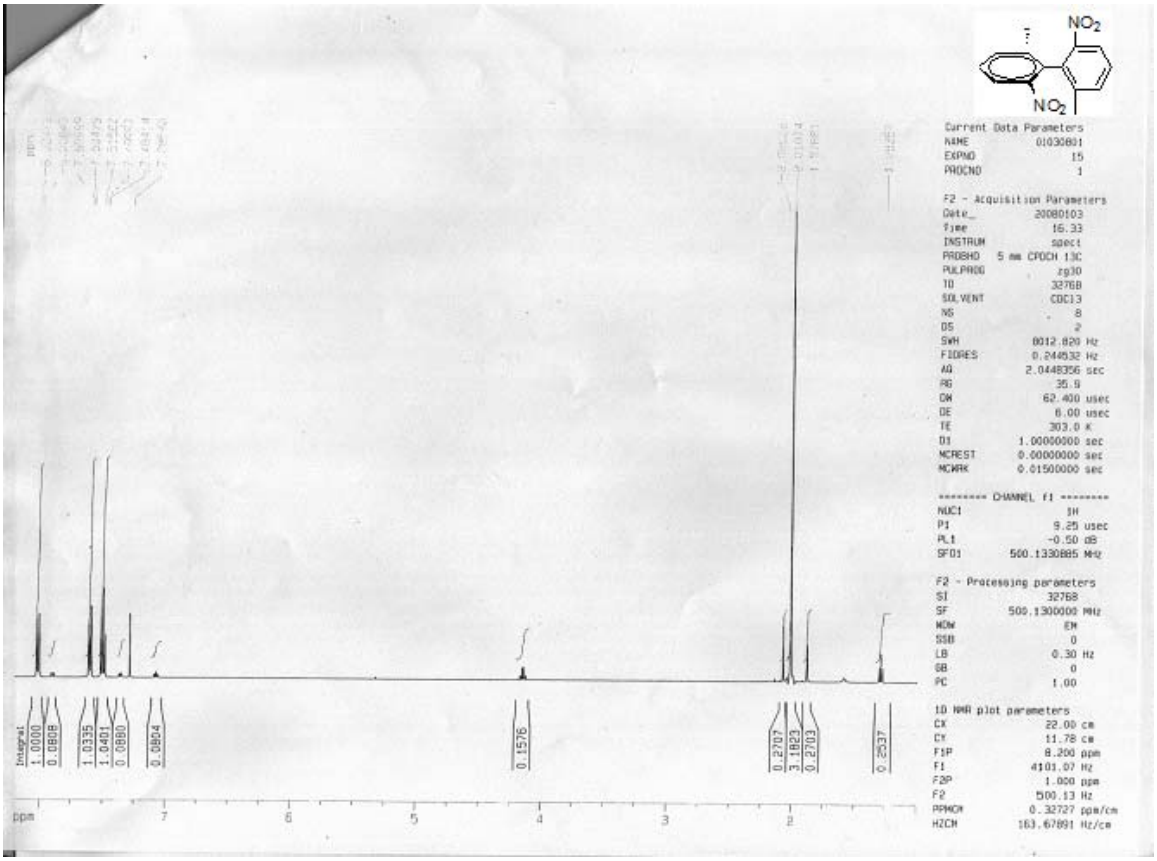


Figure 6-10 NMR Spectrum of 2, 2'-Dimethyl-6, 6'-dinitrobiphenyl

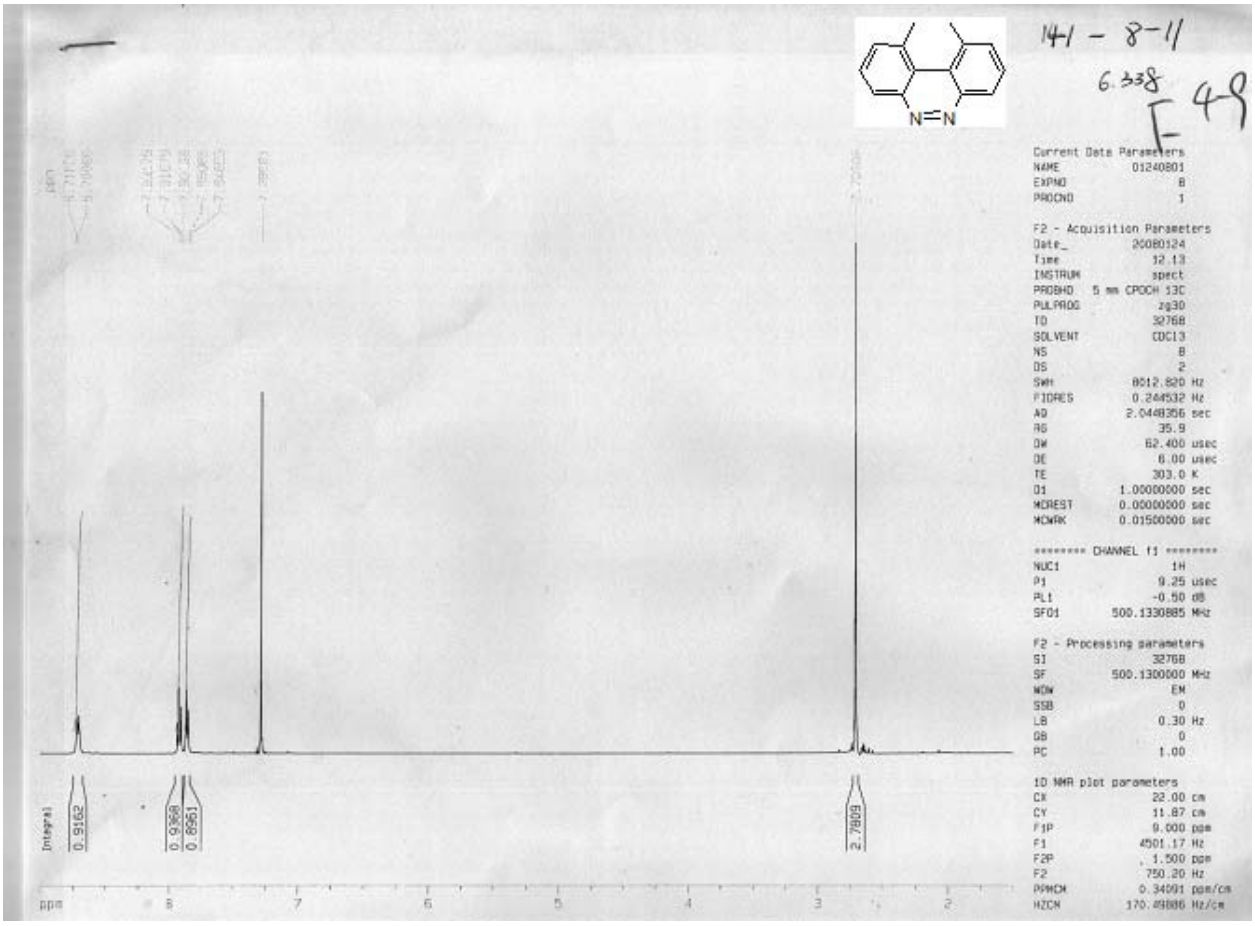


Figure 6-11NMR Spectrum of 1,10- Dimethylbenzo[*c*]cinnoline

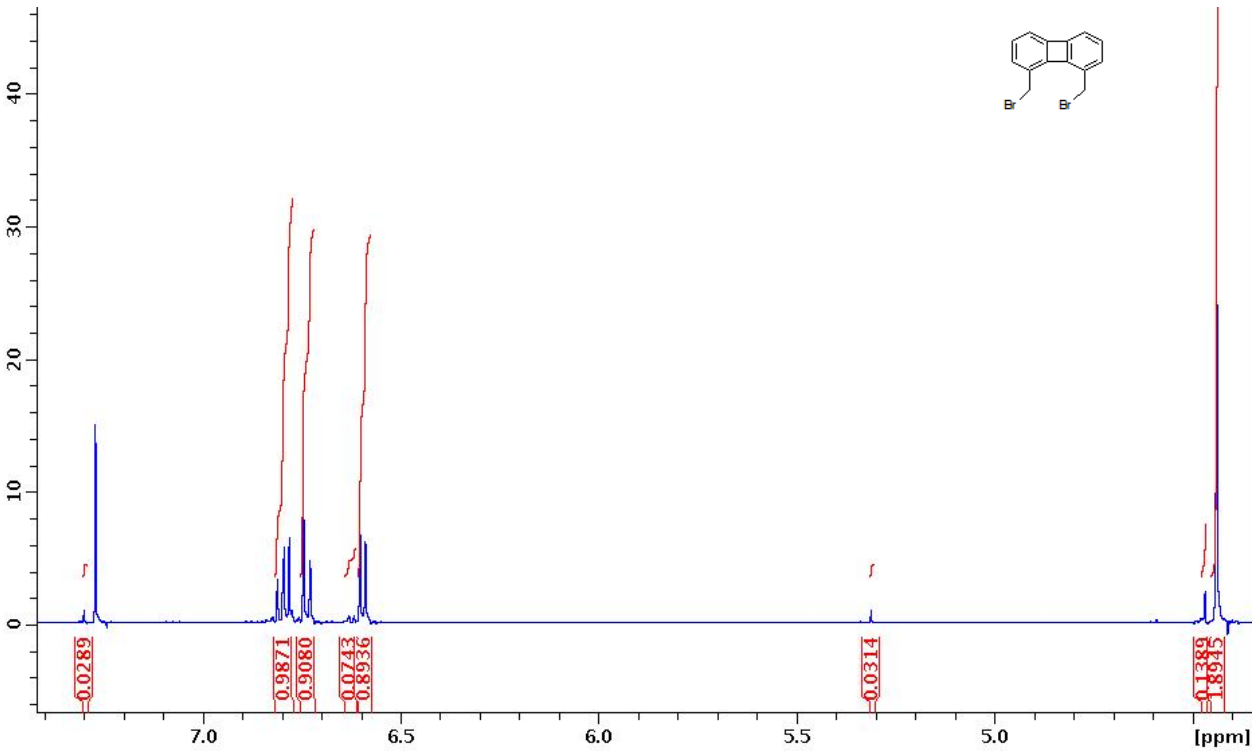


Figure 6-12 NMR Spectrum of 1,8 -Bis (bromomethyl)biphenylene

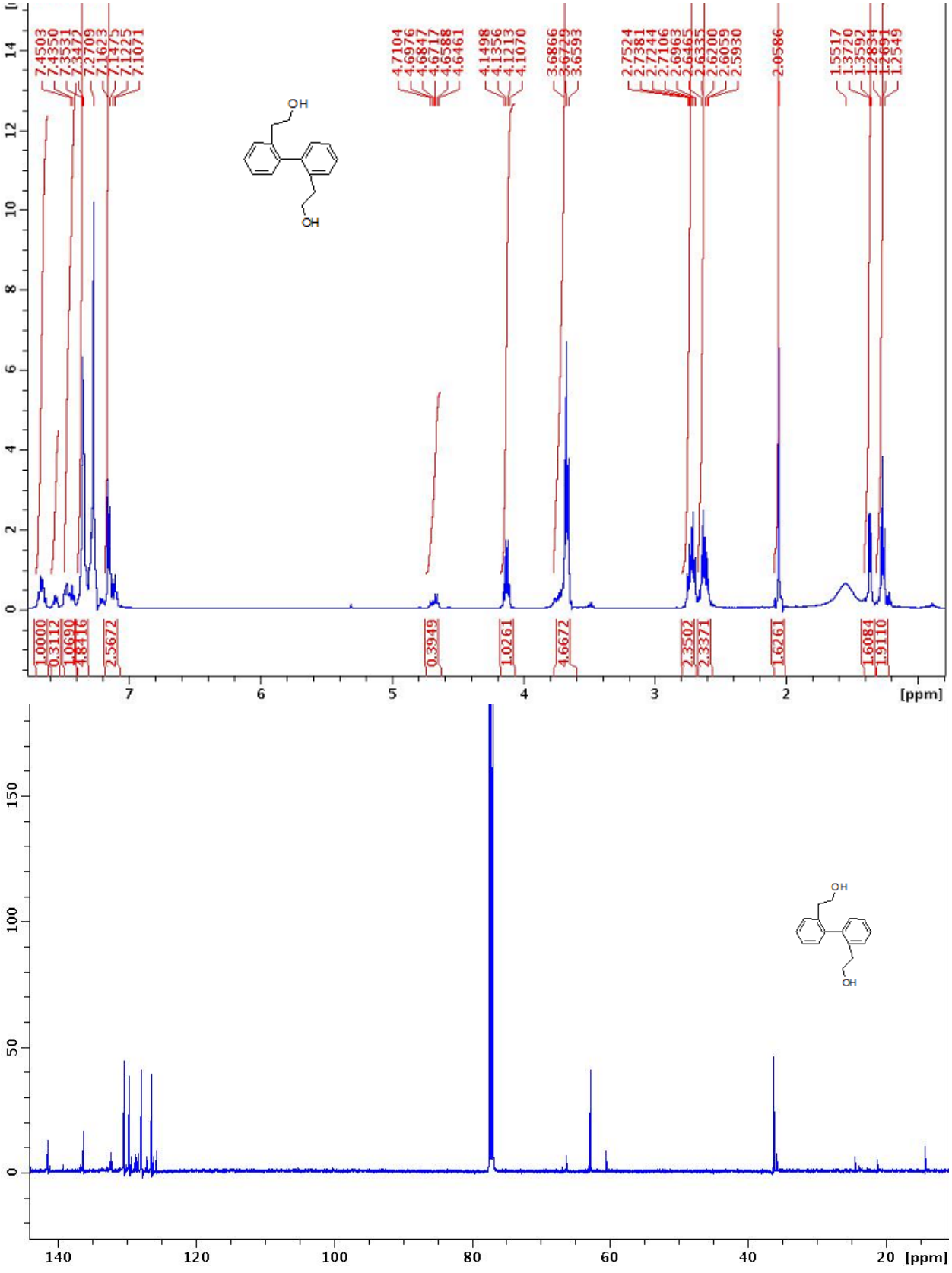


Figure 6-13 NMR Spectrum of 2,2'-(Biphenyl-2, 2'-diyl) diethanol

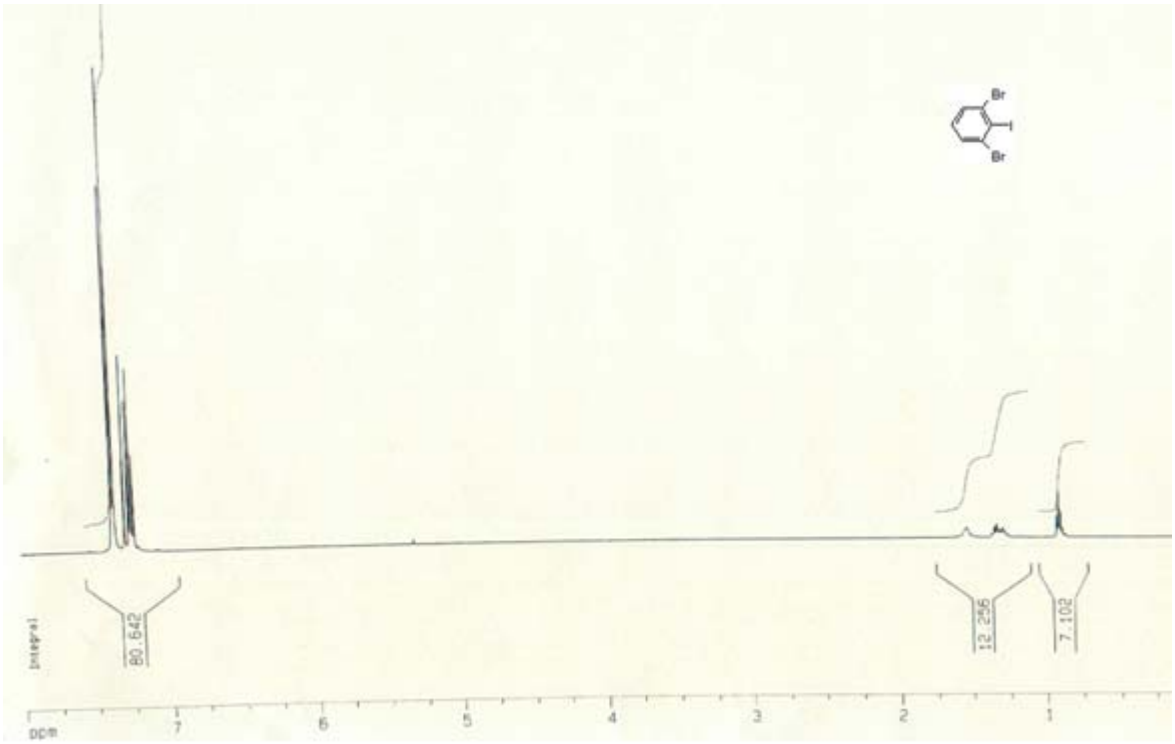


Figure 6-14 NMR Spectrum of 1-Iodo-2, 6-dibromobenzene

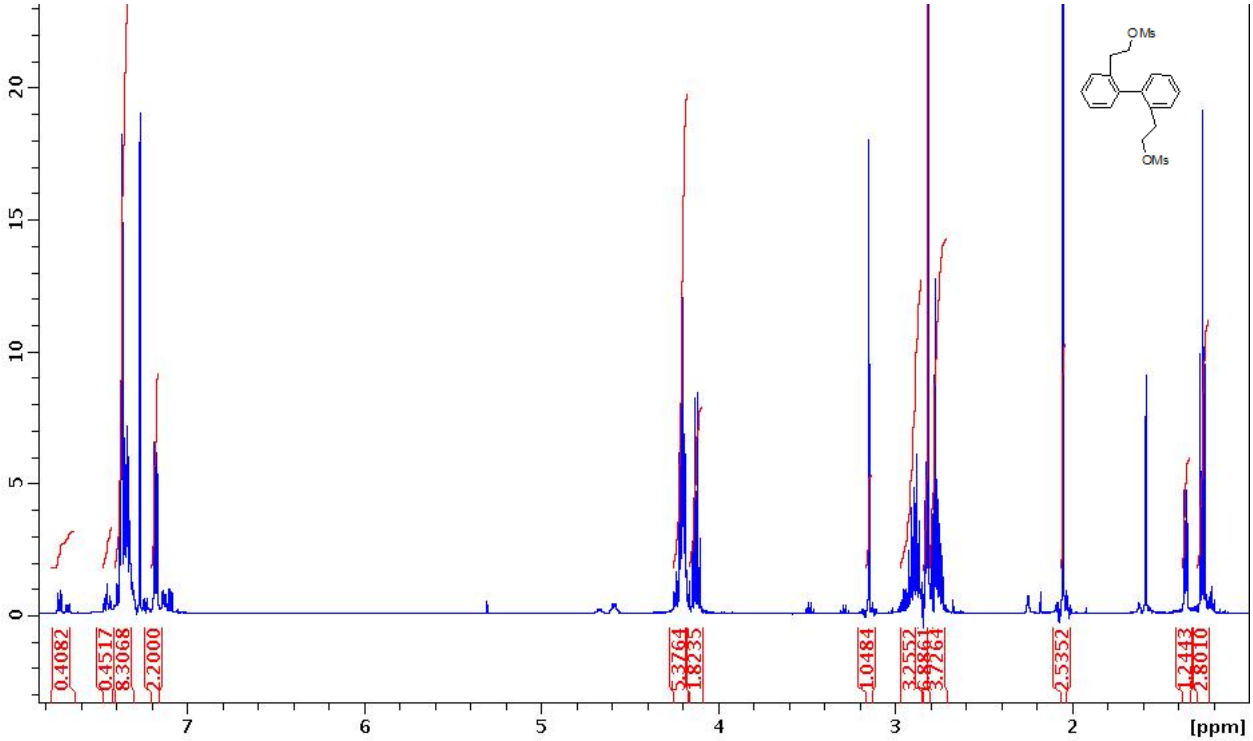


Figure 6-15 NMR Spectrum of 2,2'-(Biphenyl-2, 2'-diyl)bis(ethane-2,1-diyl)dimethanesulfonate

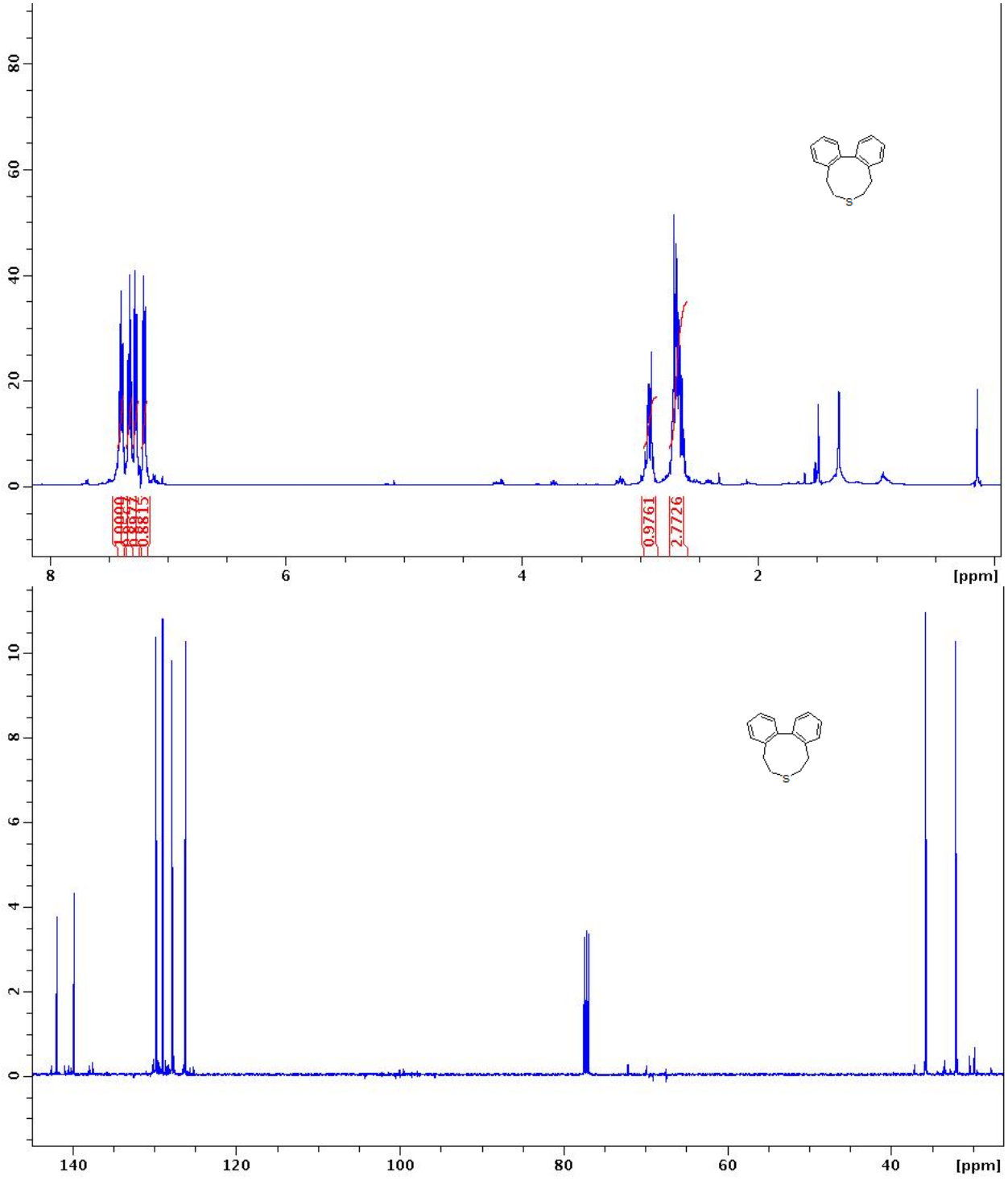


Figure 6-16 NMR Spectrum of 5, 6, 8, 9-Tetrahydrodibenzo[*d,f*]thionine

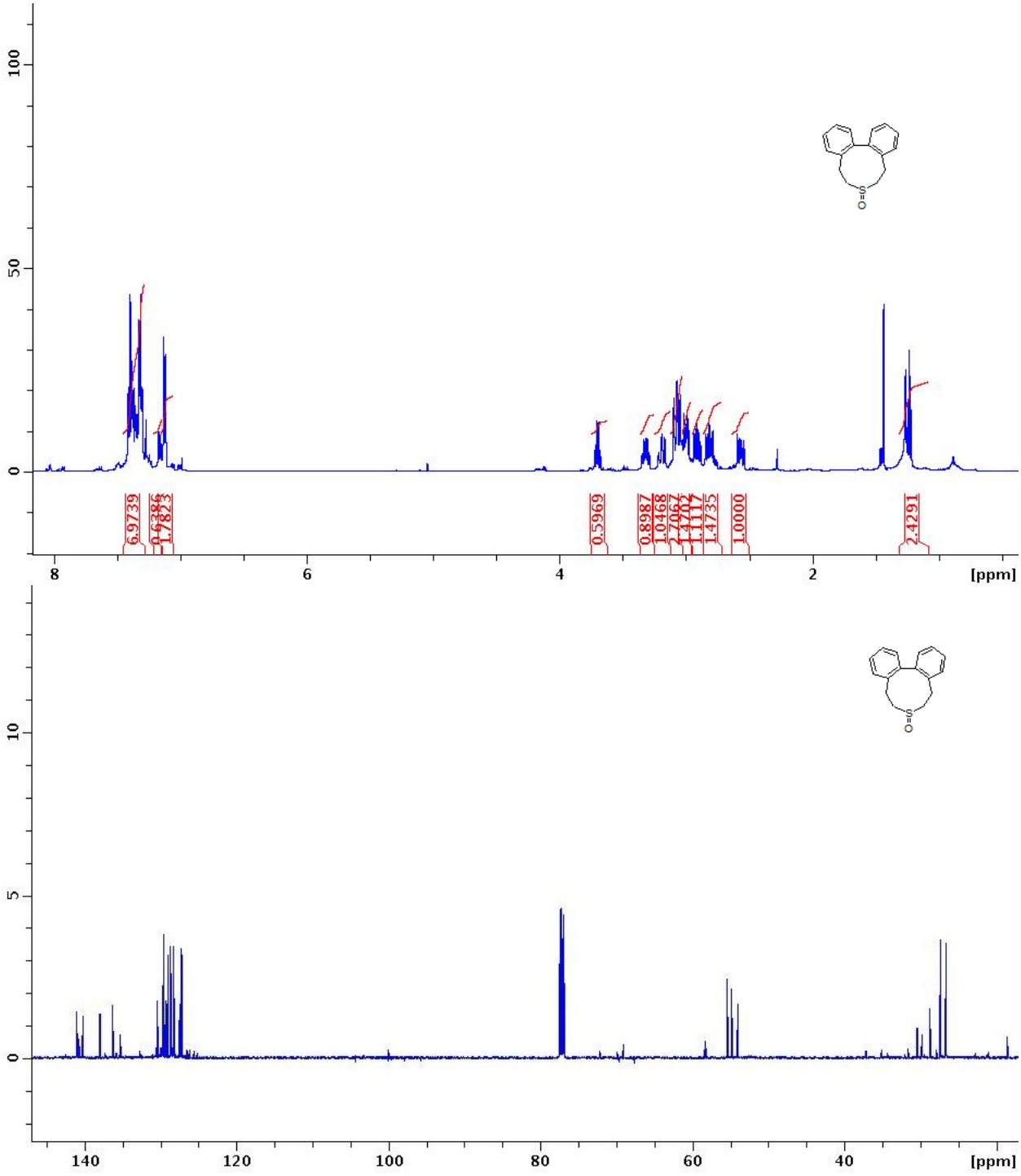


Figure 6-17 NMR Spectrum of 5, 6, 8, 9-Tetrahydrodibenzo[d,f]thionin oxide

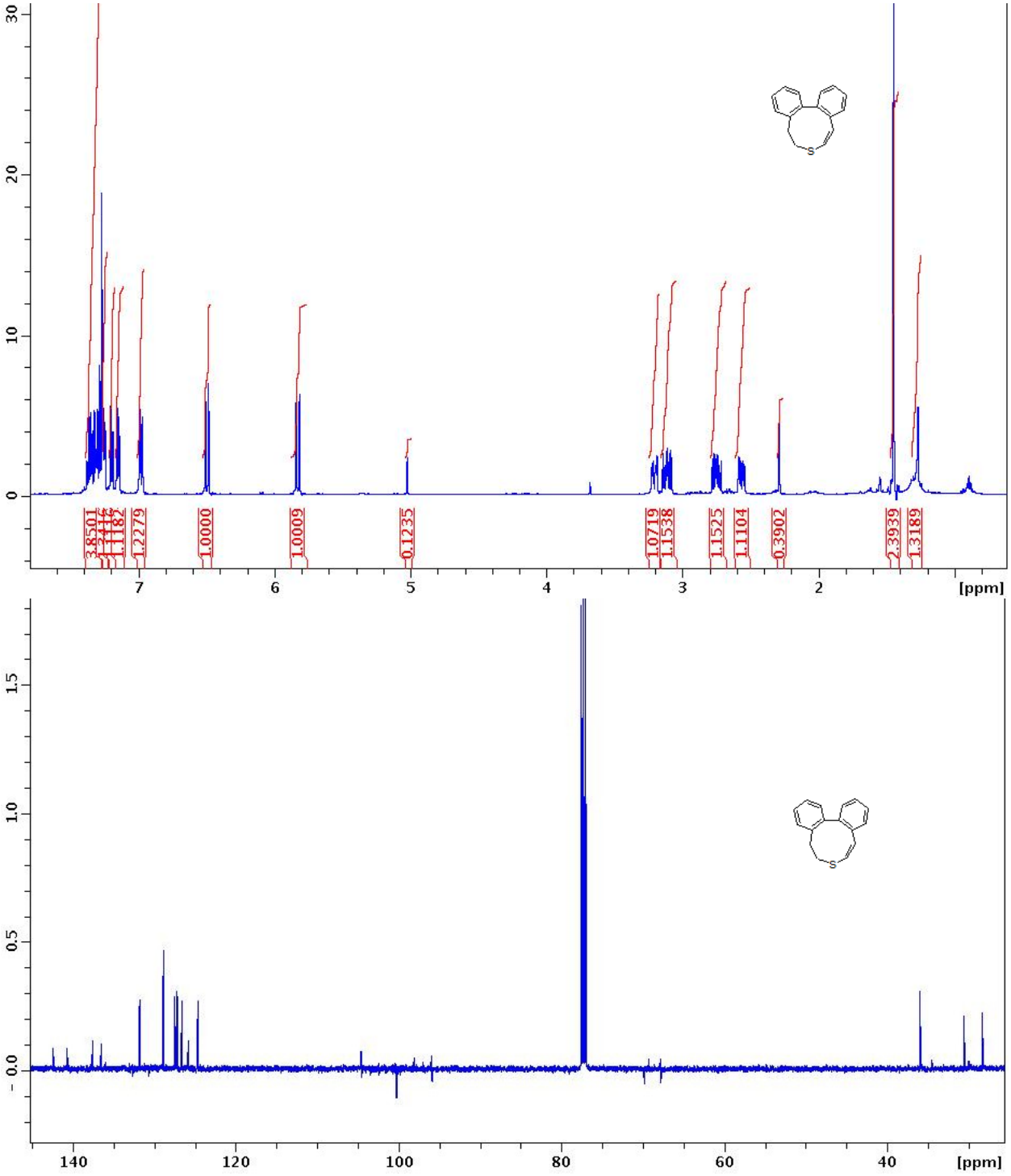


Figure 6-18 NMR Spectrum of 5, 6-Dihydrodibenzo[*d,f*]thionine

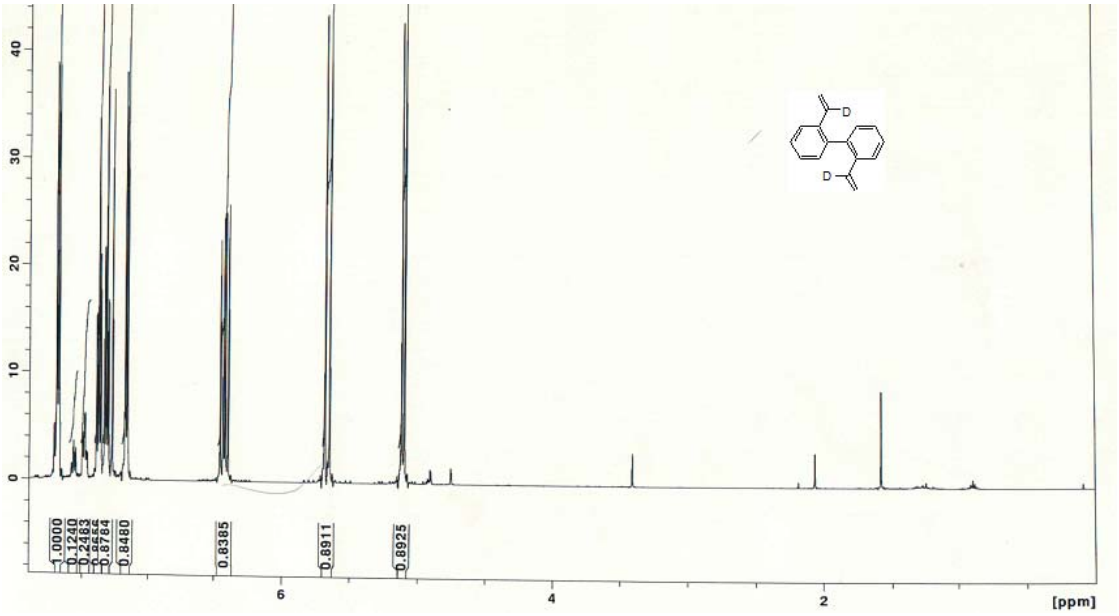


Figure 6-19 NMR Spectrum of 2,2'-Bis(1-deutero-vinyl)biphenyl

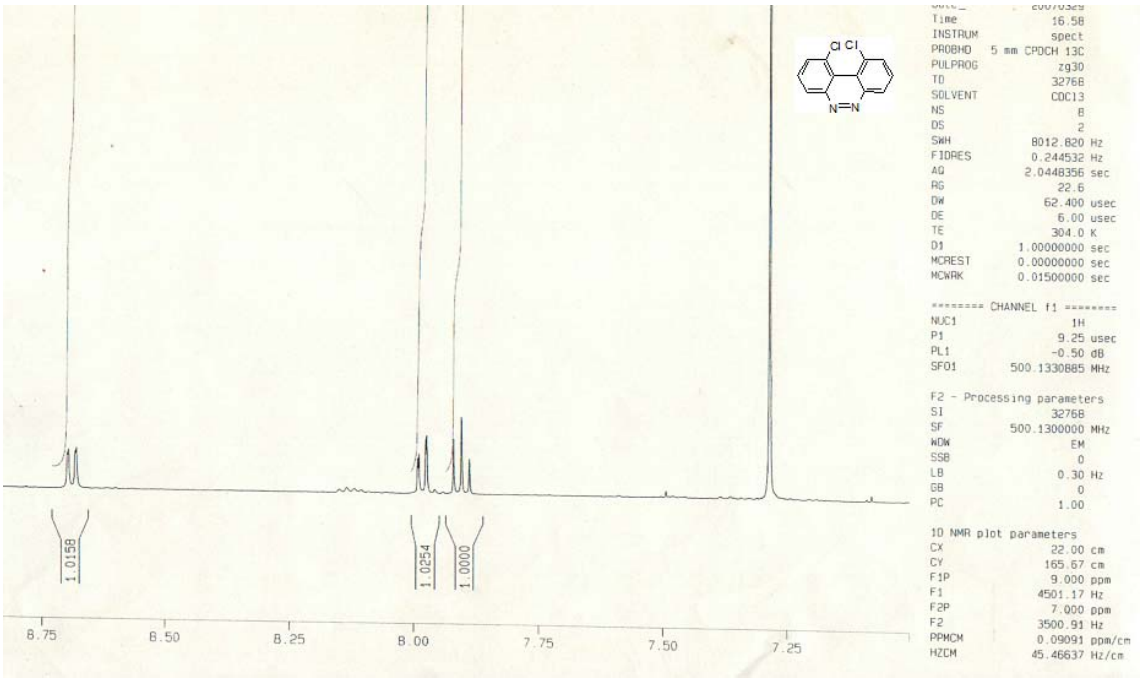


Figure 6-20 NMR Spectrum of 1,10- Dichlorobenzo[c]cinnoline

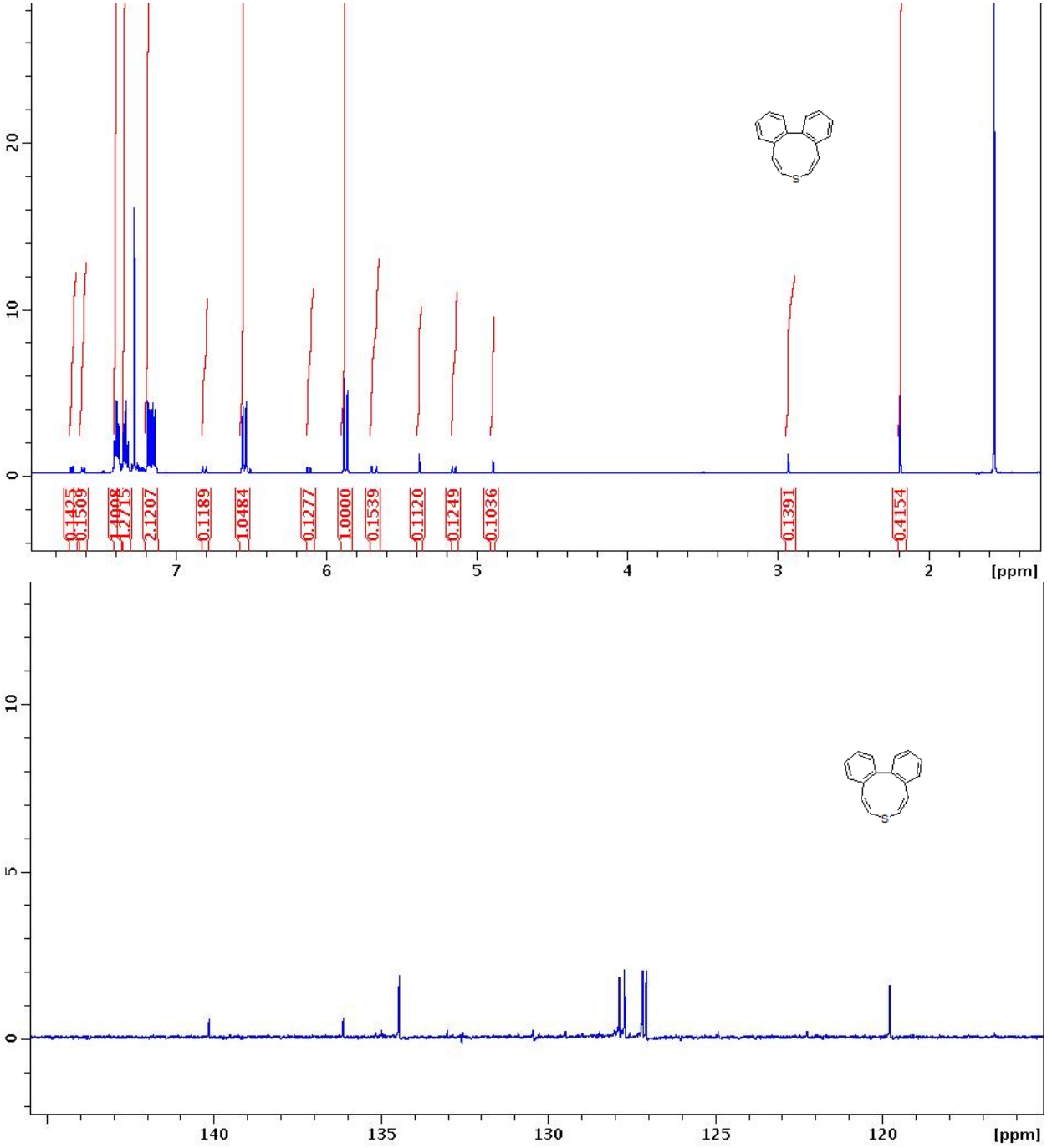


Figure 6-21 NMR Spectrum of Dibenzo[*d,f*]thionine

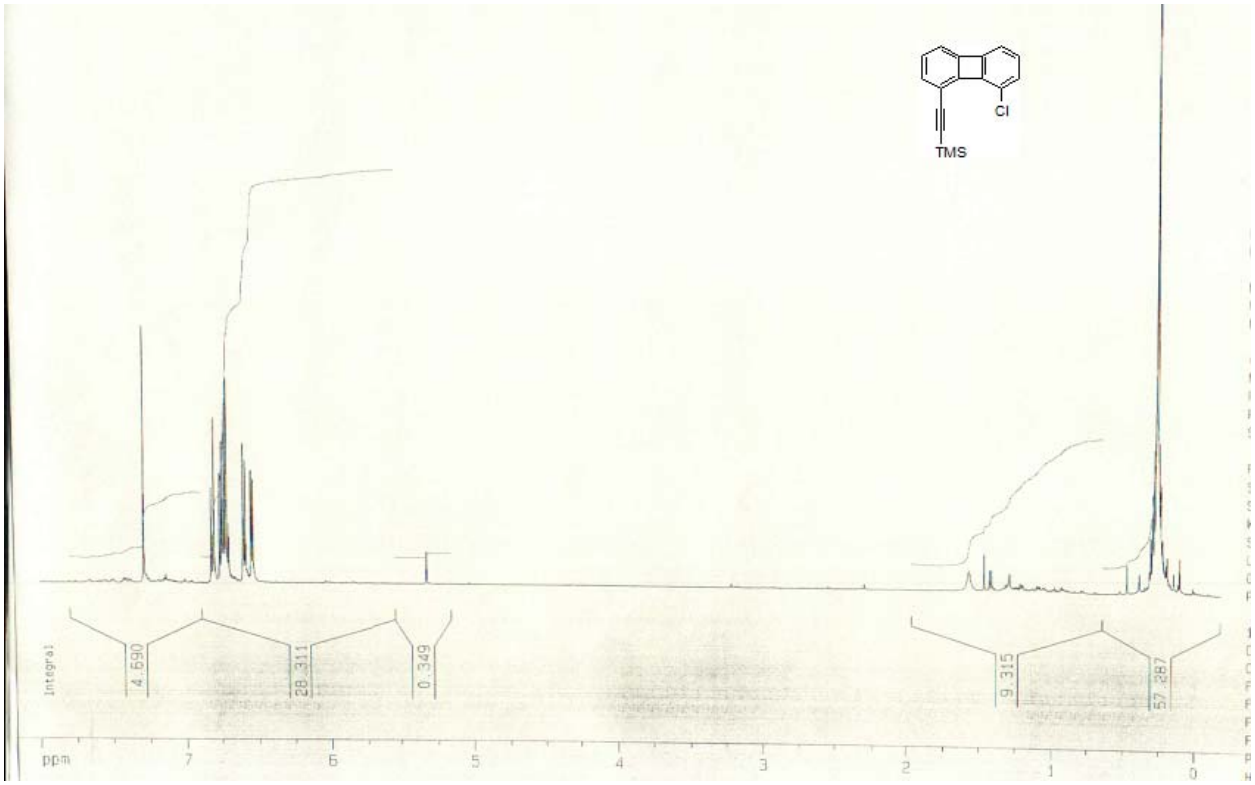


Figure 6-22 NMR Spectrum of ((8-Chlorobiphenylen-1-yl)ethynyl)trimethylsilane

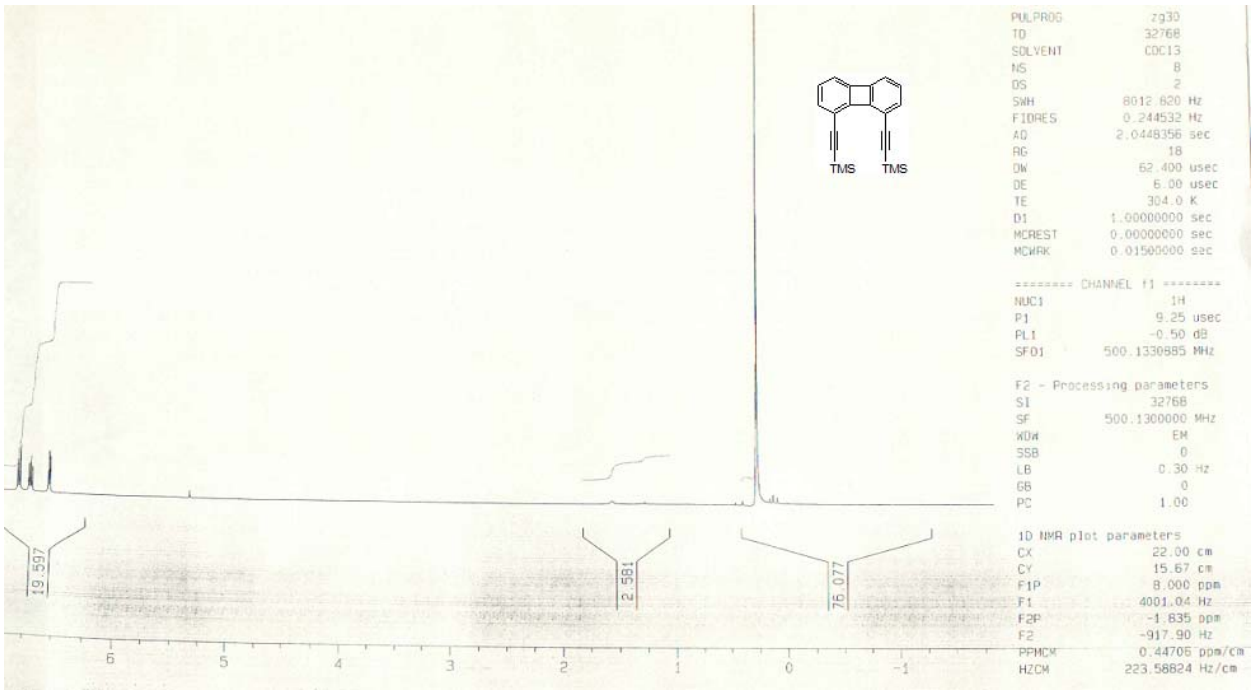


Figure 6-23 NMR Spectrum of 1,8-Bis ((trimethylsilyl)ethynyl)biphenylene

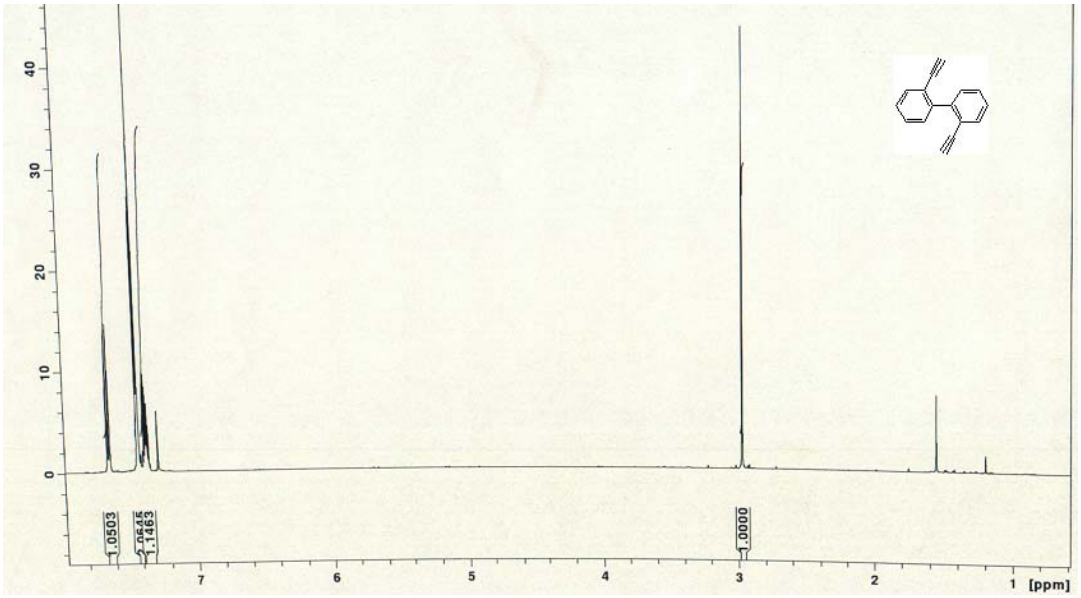


Figure 6-24 NMR Spectrum of 2, 2'-Diethynylbiphenyl

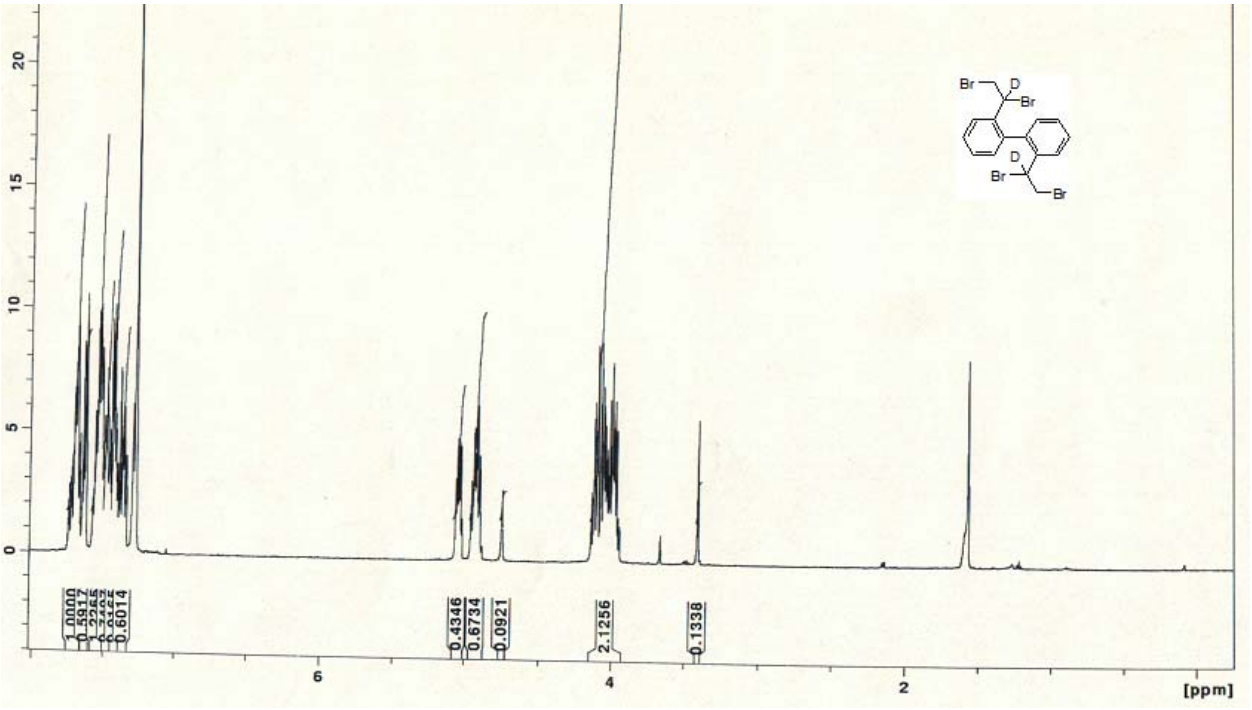


Figure 6-25 NMR Spectrum of 2, 2'-Bis (1,2-dibromoethyl) biphenyl

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