Chapter 3: Synthesis and Study of aza[*n*]helicenes, with more than one hetero atom:

Heterohelicenes with nitrogen as hetero atom, are referred as aza[*n*]helicene, where "n" stands for the number of rings making the helical framework. Nitrogen is electronegative in nature, causes changes in the chemical reactivity and physical properties of helical molecules. Understanding the effect of position and number of nitrogens on the helical backbone is therefore necessary to tune the properties of helical molecules. After the successful synthesis of functionalized and non functionalized mono aza[*n*] helicenes we decided to prepare and study aza[*n*]helicenes containing more than one *N* atom in helical framework.

3.1 Synthesis and properties of bis aza[*n*]helicenes:

In 2005, Caronna *et al.* used the classical oxidative photocyclization of stilbene derivatives using visible light to obtain diaza[5]-helicenes similar to mono aza[*n*]helicene.[1] The key intermediates, ethylenes substituted at the 1- and 2-positions with quinoline or isoquinoline, were synthesized using a Wittig condensation between the corresponding aldehydes and phosphonium salts. Finally oxidative photocyclization was carried out to get aza helicenes in moderate to good yield. (**Figure 3.1**)

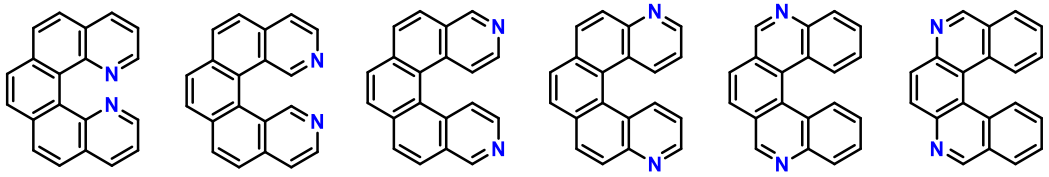
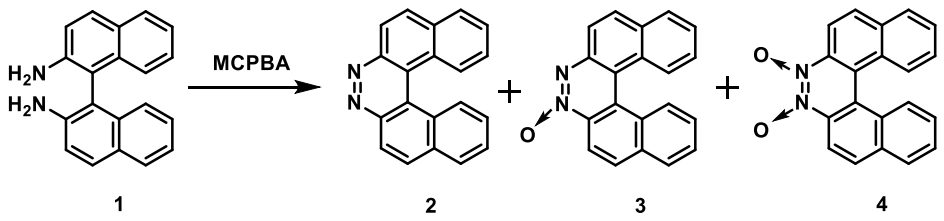


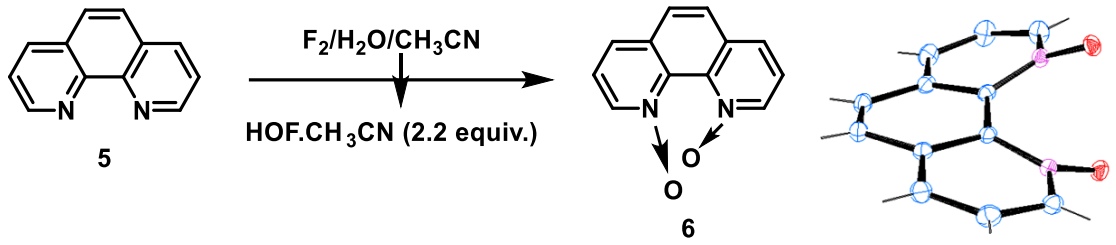
Figure 3.1: Synthesis of various di aza[5]helicenes using oxidative photocyclization or by Acid mediated cyclization process.

Synthesis of 7,8 -diaza[5]helicene **2** was easily achieved by a simple oxidation of 2,2`-diamino 1,1`-binaphthyl **1** using meta chloro perbenzoic acid (*m*-CPBA). Some side products such as *N*-oxide **3** and *N*, *N*-dioxide **4** were also formed during this reaction which was easily reduced by $LiAlH_4$.[2] (**Scheme 3.1**)



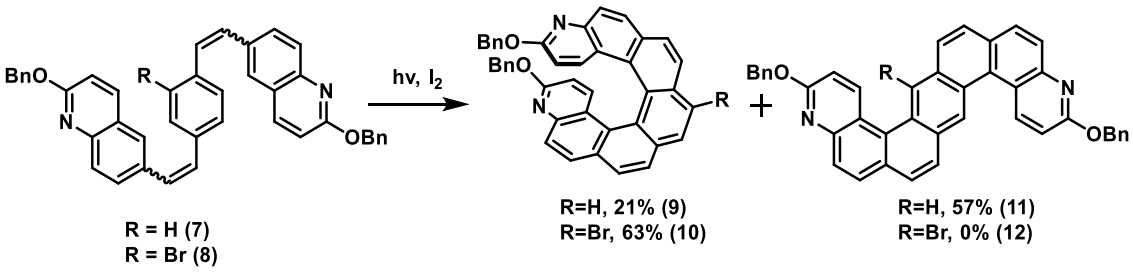
Scheme 3.1: Synthesis of 7,8-diaza[5]helicene (**Compound 2**)

Rozen and Dayen synthesized the smallest bi-aza helicene **6** (*N*,*N*,-phenanthrolinium dioxide)[3] Many attempts were made to synthesize this simple molecule. Various routine oxidizing agents have been employed but only mono *N*-oxidation took place. It was believed that it is very difficult to accommodate two oxygen atoms in the bay region of flat phenanthroline **5** moiety. Complex HOF.CH_3CN which is a strongest oxygen transfer agent did the trick; giving the desired *N*,*N*-phenanthrolinium dioxide in more than 60% yield. The structure was unambiguously confirmed by single crystal analysis. (**Scheme 3.2**) The torsion angle between the nitrogen atoms in the bay region, as measured by X-ray diffraction techniques, has a very high value of over 30 degrees



Scheme 3.2: Synthesis of smallest bis-aza helicene (**compound 6**).

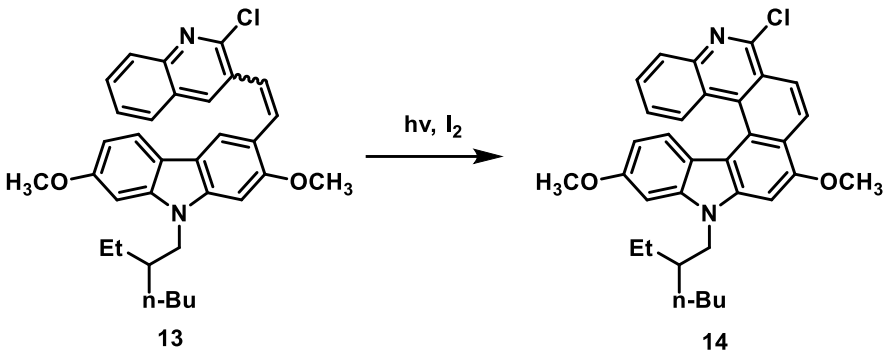
Branda *et al*.[4] prepared the substituted 4,15-diaza[7]helicenes **9** and **10** utilising double photodehydrocyclisation (**Scheme 3.3**). This study adequately demonstrates the directing role of the bromine auxiliary in the regioselective photosynthesis of helicenes.



Scheme 3.3: Synthesis of bi-aza helicene **10** using photocylizaion.

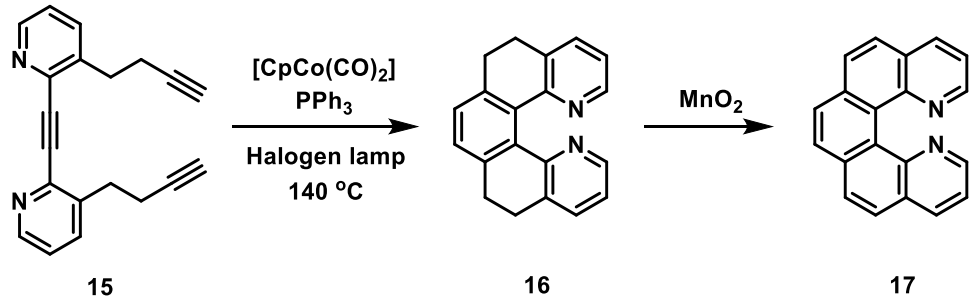
While in the absence of bromine, bis-stilbene precursor **7** affords the undesired S-shaped double aza[4]helicene molecule **11** along with minor desired 4,15-diaza[7]helicene **9**, the presence of the bromine atom in the precursor **8** directs photocyclisation away from its *ortho* position to provide exclusively the desired angularly fused azahelicene **10**.

Employing the photocyclisation strategy,Dehaen *et al*. developed an easy synthesis of the pyrido-pyrrolo[6]helicene[5] **14** from **13.**



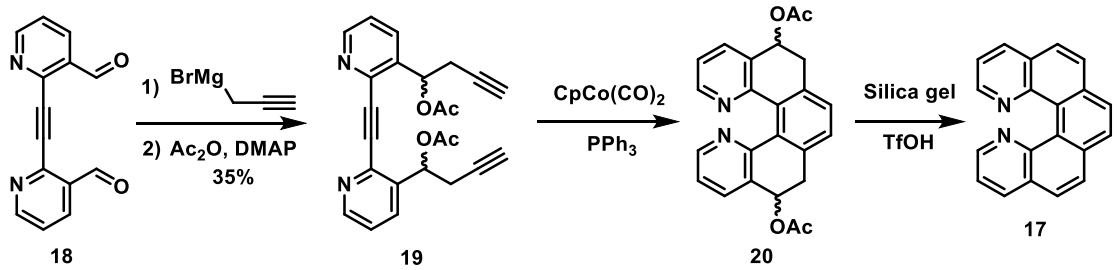
Scheme 3.4: Synthesis of compound **14**.

In 2008, Stary and Stara[6] reported a convenient synthesis of 1,14-diaza[5]helicene **17** by using a cobalt-catalyzed [2+2+2] cyclotrimerization as the key step, followed by aromatization using MnO_2 under microwave irradiation (**Scheme 3.5**). This method is very much useful for introducing one or more *N* atoms.



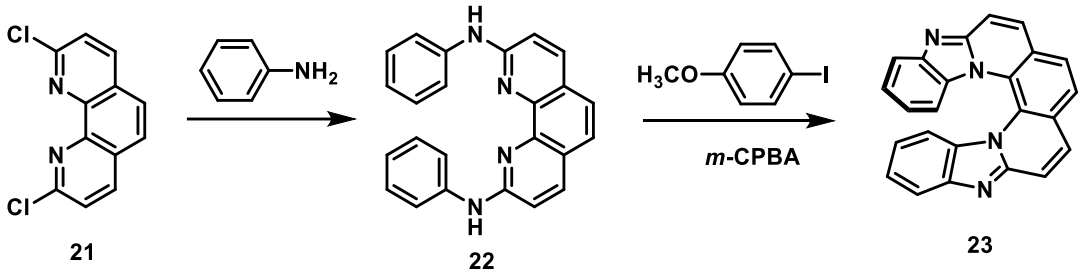
Scheme 3.5: Synthesis of 1,14-Diaza[5]helicene by [2+2+2] Alkyne Cyclotrimerization.

A similar synthetic methodology for the preparation of 1,14-diaza[5]helicene **17** has reported by Stará, Starý *et al.*[6b] (**Scheme 3.6**). It employs the sequence of a double propargyl magnesium bromide addition to a 2,2'-dialdehyde-type intermediate **18**, a cobalt-mediated [2+2+2] cycloisomerisation of a triyne intermediate **19** and a double silica gel-assisted acetic acid elimination to get bis aza helicene.



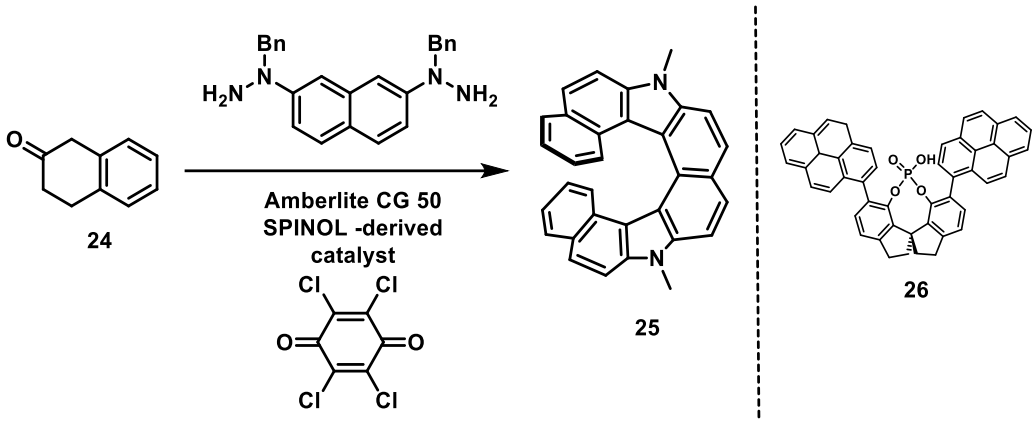
Scheme 3.6: Synthesis of racemic pyridohelice based on alkyne [2+2+2] cycloisomerisation.

Recently, a breakthrough in the step-economy of the synthesis of azahelicenes was reported by Otani, Shibata *et al.*[7] (**Scheme 3.7**). They successfully minimized the number of steps necessary to build up the azahelicene backbone by a facile two-step synthesis of polyaza[7]helicenes from a commercially available 2,9-dichloro-1,10-phenanthroline **21**. By employing double amination with various aniline derivatives followed by a hypervalent iodine reagent-mediated intramolecular double C-N oxidative coupling , various tetraaza and hexaaza[7]helicenes were synthesized in moderate to good yields.



Scheme 3.7: Synthesis of racemic polyazahelicenes using C-N oxidative coupling.

List *et al.*[8] reported on the asymmetric organocatalytic approach to indole/carbazole-derived azahelicenes (**Scheme 3.8**). They employed enantioselective Fischer indolisation reaction catalysed by a chiral SPINOL-derived phosphoric acid (*S*)-**26** to form the helical backbone in good yield.



Scheme 3.8: Asymmetric Fischer indole synthesis of compound **25**.

3.2 Properties of inserting multiple *N* atoms in helical framework:

The Nitrogen atoms help in the supramolecular self assembly process, thereby assisting in construction of supramolecular ordered structures. Few illustrative examples are,

Two pyridin-2(*1H*)-one units were fused to the skeleton of helicenes **27** by Branda group.[4] Both in solution and crystals, chiral discrimination was observed that only homochiral dimers were formed via the hydrogen bonds (**Figure 3.2**). The driving force for self-assembly behavior was the cooperative hydrogen bonds. More importantly self-assembly process was enantiospecific in solution and diastereotopic in the solid (crystal). Moreover, Takeuchi and colleagues reported the hierarchical assembly of phthalhydrazide-functionalized helicene **28** (**Figure 3.3**).[9] Helicenes first self-assembled into trimer disks by hydrogen bonds. Then, in nonpolar solvents, the disks would aggregate to form screw-shaped fibrous assemblies, which exhibited excellent CPL properties with the dissymmetric factor (g_{lum}) of 0.035.

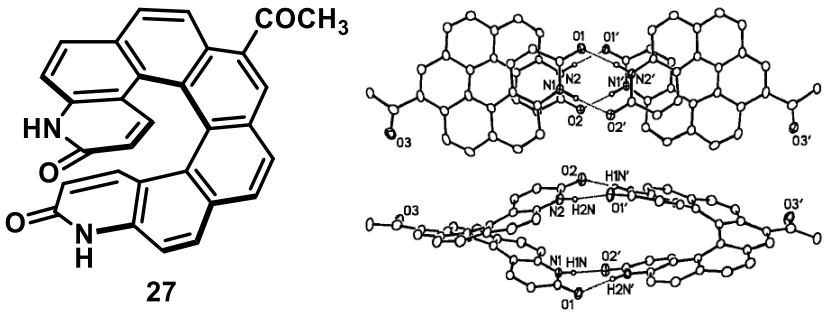


Figure 3.2: Structure of **(*P*)-27** and its crystal packing (*top-view and side-view*).

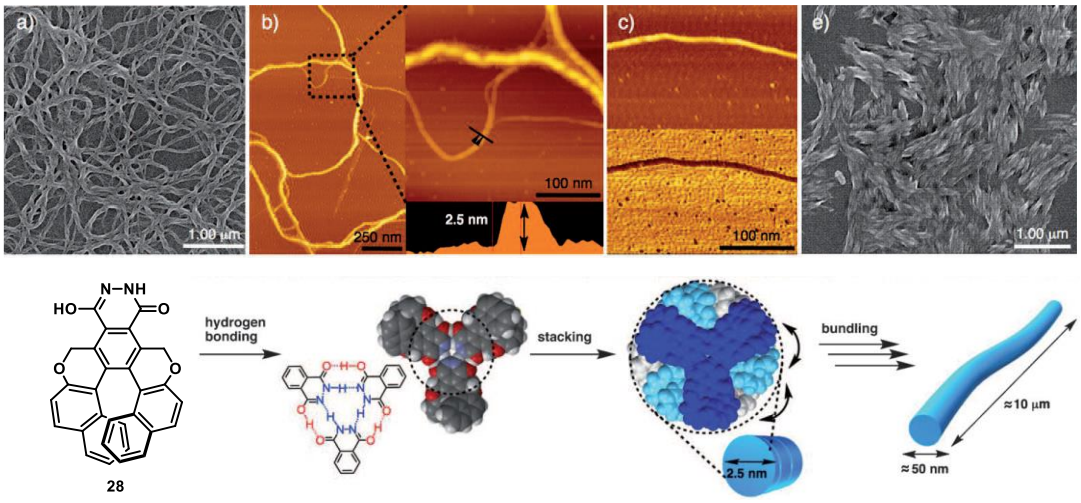


Figure 3.3: a) SEM image of **(*M*)-28** (0.5 mm) prepared in toluene; b, c) AFM images of **(*M*)-28** prepared in toluene, (c) is the (lower) phase image; d) plausible mechanism for the formation of fibrous aggregates from the trimeric disk of **(*M*)-28**; and e) SEM image of **(*rac*)-28** (0.5 mm) prepared in toluene.

Recently Wang *et. al.*[10]synthesized two helical molecules (nanographenes), one containing entirely of carbon atoms (**N-H7H**) **29** and other having *N* atoms in its core

(**C-H7H**) **30** for understanding the differeance in their optical properties. They found the presence of *N* atom drastically changes the photophysical properties.

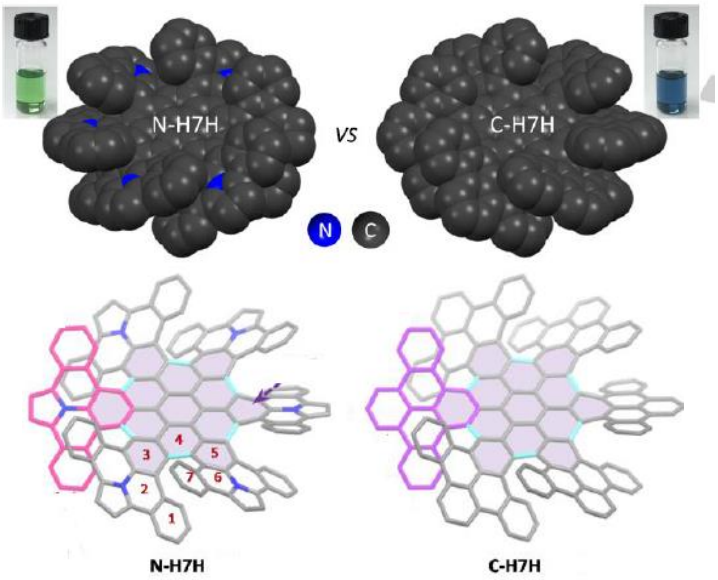
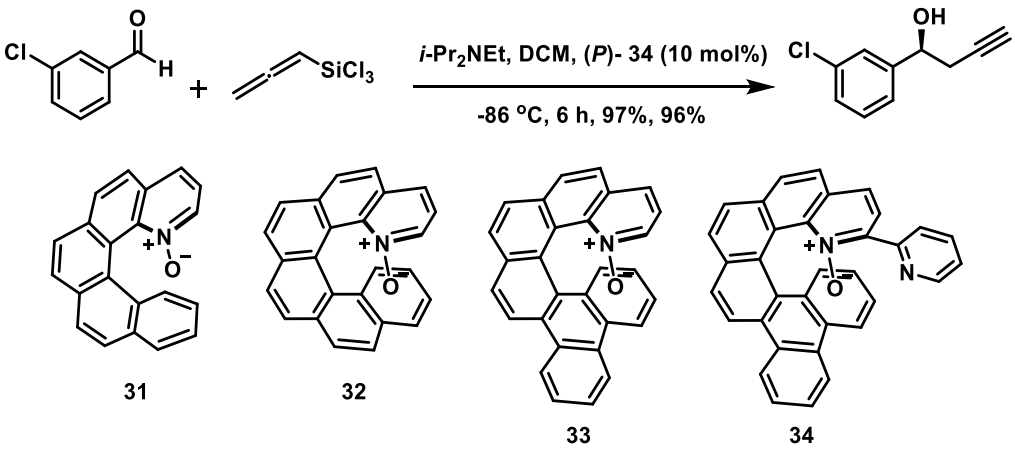


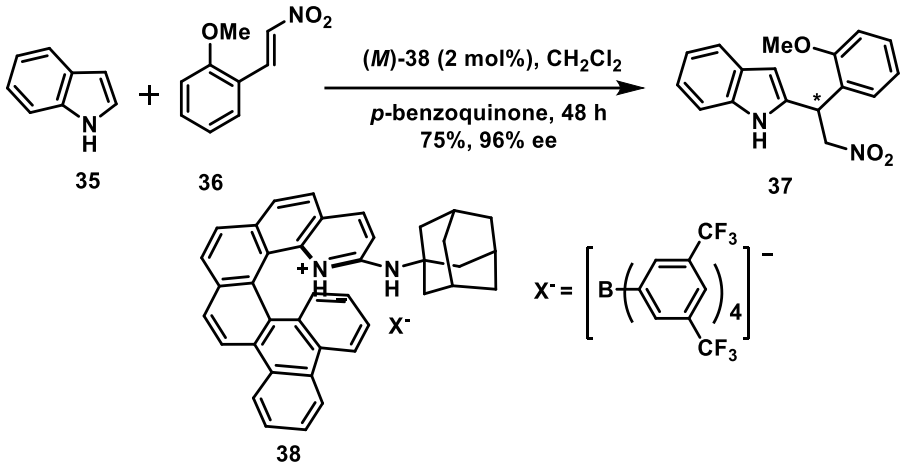
Figure 3.4: effect of *N* on photophysical properties.

Sharp contrasts in absorption ($abs_{\lambda max}$, 683 vs 593 nm), emission ($em_{\lambda max}$, 894 vs 777 nm),and electrochemical behaviour ($^{ox}E_1$, 0.28 vs 0.53 V) between **N-H7H 29** and **C-H7H 30** were observed. These shows remarkable effects of *N*-doping on nanographene`s physical properties. Takenaka's group developed series of bidentate ligands. Compared with monodentate ligands **(*P*)-31**, **32** and **33**; **(*P*)-34** showed higher efficiency for the asymmetric propargylation of aldehyde with up to 96 % ee (**Scheme 3.9**).[11]



Scheme 3.9: Asymmetric propargylation of aldehyde using **(*P*)-34**.

The protonated 2-amino-1-aza[1]helicenes were proved to be excellent dual hydrogen bonding donor catalysts. For example, in the presence of **(*M*)-38**, the stereoselectivity could be promoted up to 96 % ee for the addition reaction between dihydroindole **35** and nitroalkene **36** (**Scheme 3.10**) [12]



Scheme 3.10: Asymmetric addition reaction catalyzed by **(*M*)-38**.

The proton affinities (PAs) of 1-aza[6]helicene **39**, was determined using mass spectrometry and DFT calculations and value of its proton affinity was around 1000 kJ mol^{-1} which is less in comparison of bis aza pentahelicene **40** (1064 mol^{-1})[13] showing that these azahelicenes are chiral superbases with affinities similar to "proton sponge" 1,8- bis(dimethylamino)-naphthalene **41**. The combination of helical topology and high PAs are important in making helicene based chiral ligands for enantioselective reactions as evidenced by Takenaka's achievements.

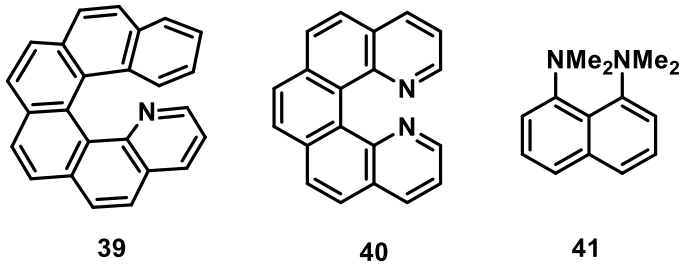


Figure 3.5: Strucure of various aza[*n*]helicenes.

3.3 Chapter 3 Part A: Synthesis and Study of Bis Aza[5] and bis aza[6]helicenes (Bihelicenes)

Bihelicenyls involve two distinct helicene moieties connected by a single bond. To study the role of steric hindrance on the second position of Hexahelicene, Laarhoven *et al.*[14] synthesized 2,2`Bis-hexahelicenyl **42**. The mixture of meso and *P*/*M* isomers were separated by column chromatography. Both the isomers have marked difference in their solubility and melting points.

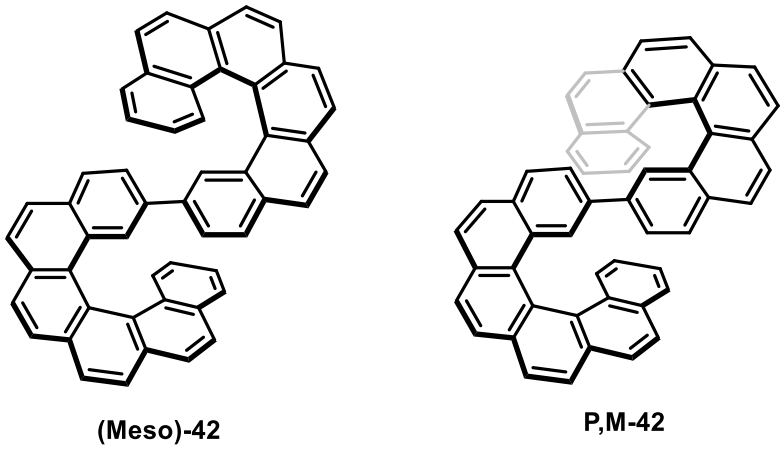
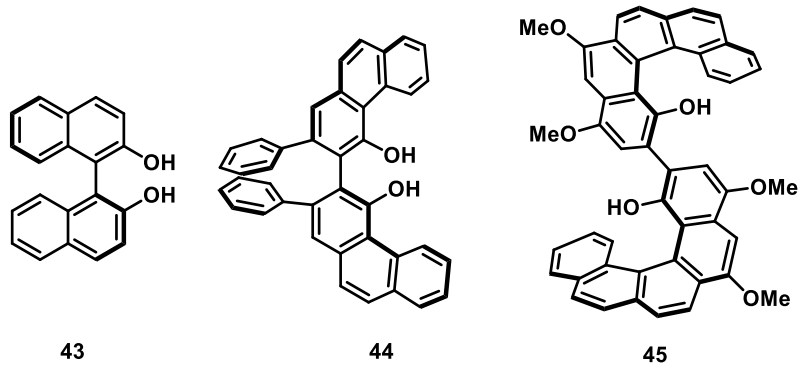


Figure 3.6: Isomers of Hexahelicenyl **42**.

The meso compound prefers a planar conformation at the central C-C single bond. For the *P*/*M* conformation such arrangement is sterically unfavorable and to overcome this, two hexahelicyl units are twisted around the central single bond. The *P*/*M* isomer at its melting point rearranges to more stable meso isomers.

1,1`-Binaphthalene-2,2`-diol (BINOL) **43** is frequently used ligand for asymmetric catalysis, and the much advanced versions of such type of ligands, VAPOL **43** having suitable chiral pockets are successfully employed for variety of asymmetric reactions. The success achieved with substituted BINOLS and VAPOL, inspired Katz *et al* [15] to design a bis-helicene diphenolic ligand **44**, because it should form a larger chiral pockets around the catalytic metal center, may enhance the ability to achieve even better asymmetric catalyst. A noteworthy feature of **44** structure is that the stereochemistry of the single bond uniting the two helicene moieties is constrained, but not by the bulk of adjacent substituent's, as in biaryls such as **1** and **2**, but by the bulk of the distant helicene rings. The bis[5]helicenediol ligand **44** is termed as [5]HELOL. This diol catalyzes the addition of diethylzinc to aldehydes and gives nonracemic

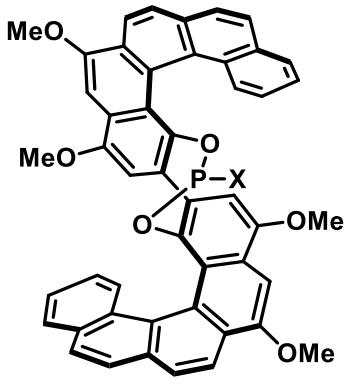
alcohols with enantiomeric excesses as high as 81%. The stereoselectivities and yields are much greater than when the reactions were performed when diol is BINOL. A dimeric helicene's chiral pocket can surround a metal center more effectively and therefore can act as more effective catalyst than the monomeric helicene.



43 44 45

Figure 3.7: Various dihydroxy ligands.

Same group explored the applications [5]HELOL Phosphite[16] as a helically grooved sensor for remote chirality. Even if the chiral center of analyte is far from the helicene moiety, it can be detected using ^{31}P NMR spectroscopy with the baseline resolution, although proper solvent needs to be chosen for better separation. The sensitivity to remote chiral centers of the moieties analyzed is attributed to their confinement to the helical groove.

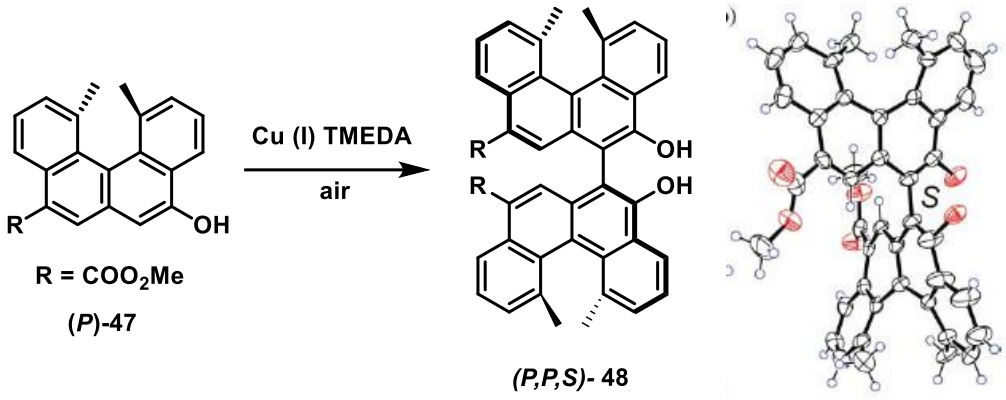


46

Figure 3.8: Structure of [5]HELOL phosphite **46**.

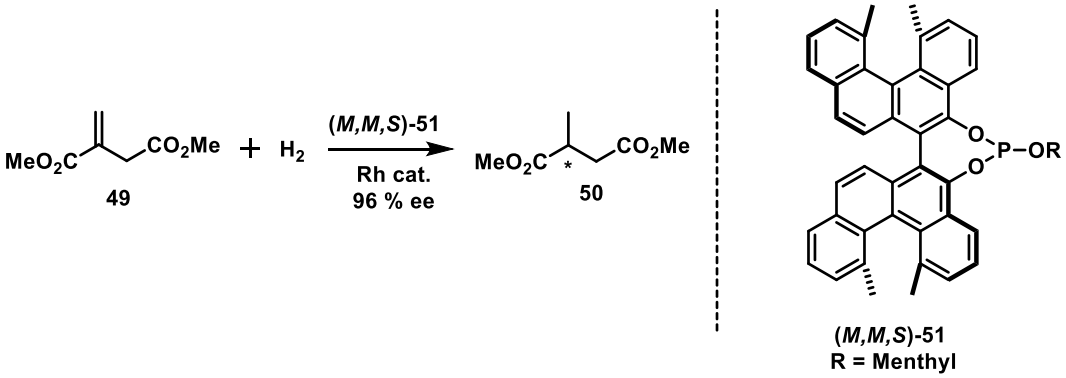
Yamaguchi *et al.*[17]synthesized another bishelicenol. They successfully resolved the bishelicenol compound. All the possible six isomers (*P,P,S*), (*P,P,R*), (*M,M,S*),

(*M,M,R*), (*P,M,S*) and (*P,M,R*) were synthesized using oxidative coupling strategy. (**Scheme 3.11**)



Scheme 3.11: Synthesis and ORTRP plot of compound **48**.

These ligands have both axial as well as helical chirality. Yamaguchi *et al.*[18] in a different piece of work converted bishelicenol in to bishelicenol phosphite **51**, which formed a complex with rhodium and used in enantioselective hydrogenation of dimethyl itaconate **49** with 96 % ee.



Scheme 3.12: Application of bihelicenol phosphite **51** in asymmetric hydrogenation.

Matched/mismatched effect was observed between helical and axial chirality. The stereochemistry at the helicene moiety plays an important role in the asymmetric induction, and (*M*) helical /(*S*) axial chirality combination found to be the matched pair. It should be noted that the substitution of achiral naphthalene moiety of binol with the chiral helicene provides a method to fine-tune chiral environment of metal center for asymmetric catalysis.

Recently Jean *et al.*[19] synthesized enantiopure Bis-4-aza[6]helicene **52** and studied the involvement of nitrogen lone pair on protonation and coordination processes and

thereby studied its impact on chiroptical properties. They addressed its chiroptical triggered switching activity chemically by (i) Zn II coordination/decoordination and (ii) protonation/deprotonation processes. The signals were studied using UV/Vis, ECD, OR, and luminescence techniques.

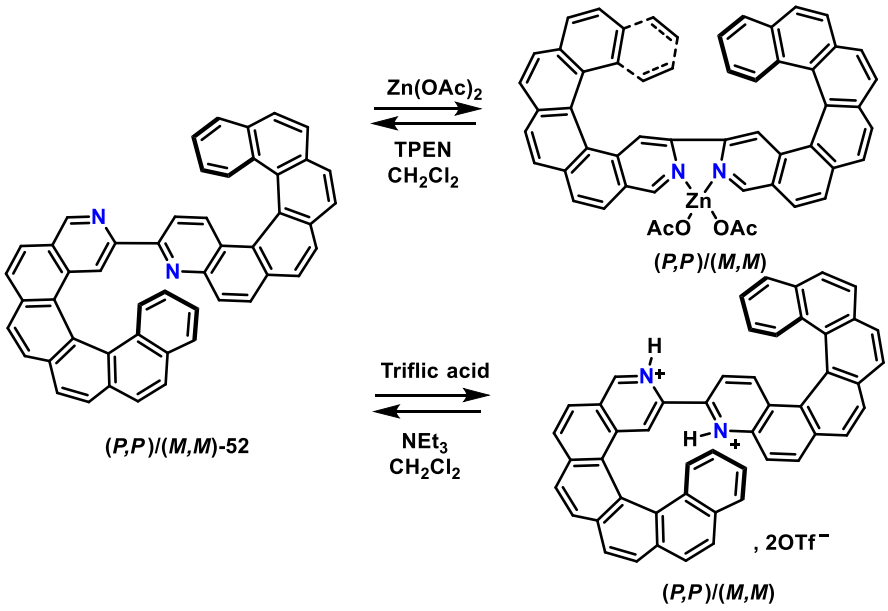


Figure 3.9: Chiroptical triggered switch **52**.

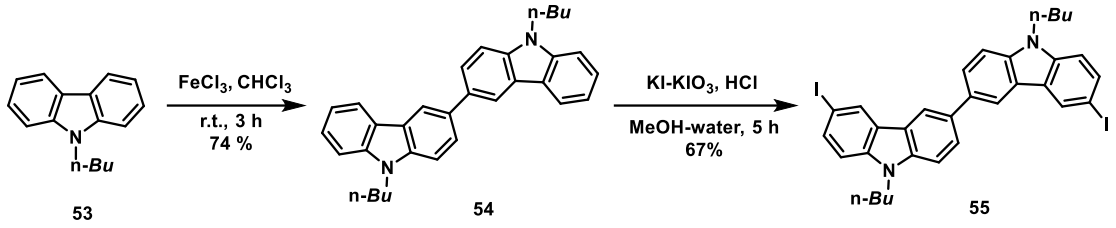
They established reversible transformation from cisoid to transoid by Zn(II) coordination/decordination. These reversible processes were found to be activation prone by π–π*-type and CT-types of excitations that leads to efficient changes of the spectral properties. Accordingly, a new example of versatile molecular chiroptical switch emerges, behaving like a chiral dye. Finally, the $1/1 \cdot 2H^{+}$, $2OTf^{-}$ switching system emits a CPL in the red region, which may be of interest in the field of bioimaging.

3.4 RESULTS AND DISCUSSION

3.4.1 Synthesis of bis-aza[5] and [6]helicenes:

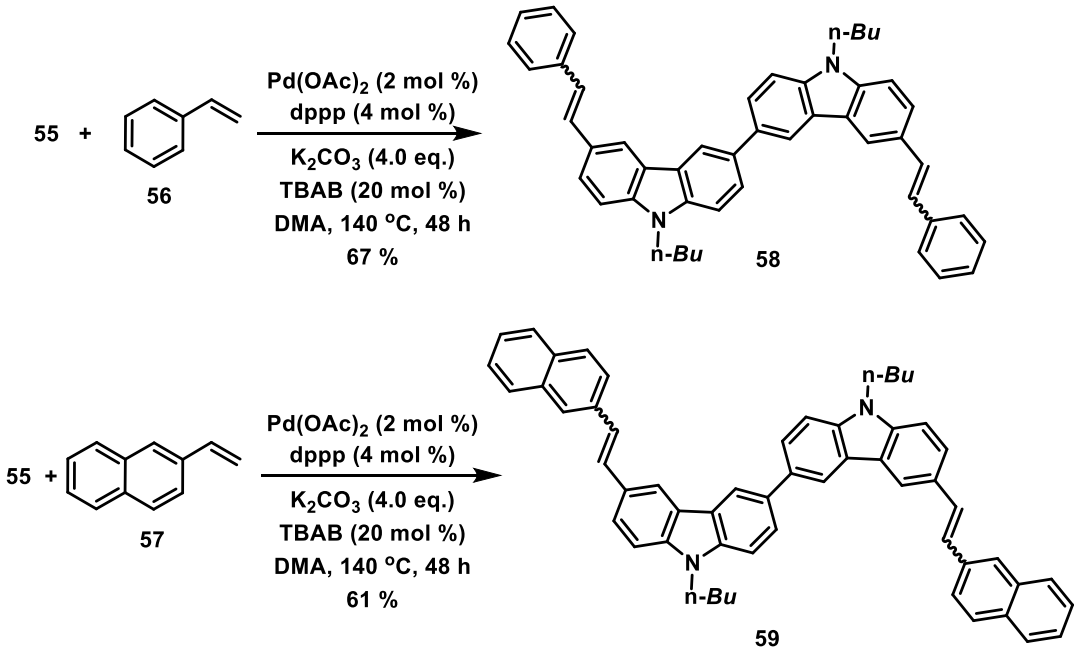
The synthesis of Bis-aza[*n*]helicene unit can be achieved by oxidative photocyclization of suitable bis-styryl derivative of alkyl carbazole moiety. We have chosen to attach n-butyl group on the nitrogen of carbazole in order to achieve reasonable solubility to the final azahelicenes and the intermediates. Accordingly *N*-butyl carbazole **53**, prepared by alkylation of carbazole, was subjected to the dimerization reaction with ferric

chloride to obtain **54** in good yields (**Scheme 3.13**). The bi-carbazole **54** was subjected to slightly modified conditions of regioselective diiodination to afford the required precursor **55** in satisfactory yield and purity.[20]



Scheme 3.13: Synthesis of compound **55**.

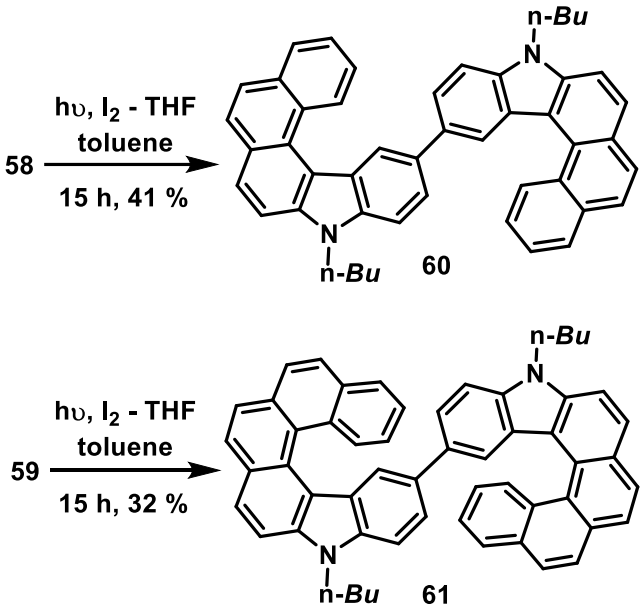
The diiodo carbazole **55** was subjected to palladium catalyzed Mizoroki-Heck reaction with styrene **56** and 2-vinylnaphthalene **57** under the suitable conditions (**Scheme 3.14**). Corresponding bis-styryl derivative **58** and **59** were obtained with styrene and 2-vinylnaphthalene in good yields mostly as the *E*-isomers.



Scheme 3.14: Synthesis of 3,6-distyryl-9-butyl-9*H*-carbazoles **58** and **59** by Mizoroki-Heck reaction.

We have developed a one-pot procedure to synthesize stilbene derivatives by combination of Wittig Heck reaction on appropriate aldehydes.[21] We also performed the synthesis of **59** by adopting this procedure on 2-naphthalene carboxaldehyde to in situ obtain 2-vinylnaphthalene for further olefination reaction with diiodo derivative **55**.

The desired bis-olefin **59** was obtained in comparable yields. Having synthesized the required stilbene derivatives, they were subjected to oxidative photocyclization reaction with high pressure mercury vapour lamp in presence of iodine and tetrahydrofuran as the acid scavenger. The product of the expected angular cyclization was isolated to moderate yields. We attempted to study the stereochemistry of the products by injecting the samples in chiral HPLC but due to very poor solubility in isopropanol *n*-hexane mobile phase we couldn't establish types of stereoisomers formed during photocyclization.



Scheme 3.15: Synthesis of bis-aza[5]helicene **60** and bis-aza[6]helicene **61**.

The styryl derivative of bi-carbazole **58** furnished the angular-angular bi-aza[5]helicene **60**, while the vinylnaphthyl derivative **59** furnished similarly cyclized bi-aza[6]helicene **61 (Scheme 3.15)** . Both the title compounds were purified by careful column chromatography over silica gel and the structure of the products were established by ^{1}H NMR, ^{13}C NMR and HRMS analysis.

3.4.2 X-ray structure:

The structure of the bi-aza[6]helicene **61** was further established by its single crystal X-ray diffraction analysis (**Figure 3.10**). The analysis indicated few interesting features of the compound and its crystal packing. The most striking aspect was the observed dihedral angle between C′13-C′14-C14-C15 to be only 0.51° which indicates almost a

perfect planner arrangement of the two central phenyl rings of the carbazole units. This is quite unexpected as the biphenyl unit of similar systems has been reported to show a dihedral angle of about 25° for similar compounds due to the twist caused between the two carbazole moieties.[22] This observation confirms the *meso* conformation as it is more stable and make the central C-C bond planar.

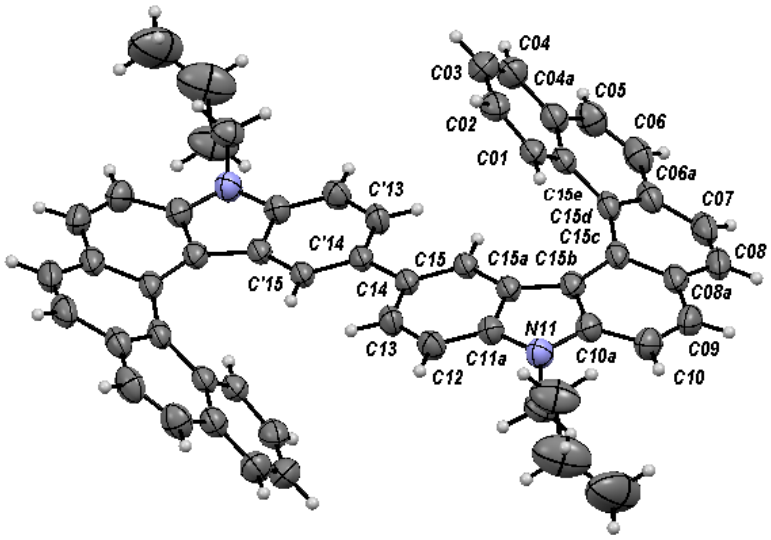


Figure 3.10: X-ray structure of compound **61**. (CCDC No. 1058514)

The other important details of the crystal structure are presented in **Table 3.1**. As it is commonly observed the internal carbon-carbon bond lengths of the helicene twist were found in the order of 1.401 to 1.456 Å, which were slightly elongated as compared to the normal carbon-carbon bonds of aromatic systems (1.39 Å). Similarly the outside carbon-carbon bonds were observed to be on shorter side than the expected values, except the C02-C03 bond. The distance between C06-C07 and C08-C09 were observed to be 2.469 and 2.458 Å, respectively as compared to the similar bond C01-C10 of phenanthrene unit (2.473 Å). The torsion angles of the inner twist of helicene were seen in the range of 15.26 to 32.49°, which is a typical characteristic of helical compounds. The sum of the torsion angles φ 1+ φ 2+ φ 3 in bi-aza[6]helicene **61** was observed to be 65.93°, while the dihedral angle which is an angle created by the bisecting planes passing through C1-C2-C3-C4-C4a-C15e & C11a-C12-C13-C14-C15-C15 was 56.14°.

Inner carbon-carbon bond lengths (Å)		Outer carbon-carbon bond length (Å)		Torsion angle (°)	
C01-C15e	1.401	C01-C02	1.372	φ 1 = C15a-C15b-C15c-C15d	18.18
C15d-C15e	1.456	C02-C-03	1.399	φ 2 = C15b-C15c-C15d-C15e	32.49
C15c-C15d	1.442	C03-C-04	1.361	φ 3 = C15c-C15d-C15e-C01	15.26
C15b-C15c	1.429	C05-C06	1.346	Distortion of the molecular structure (°)	
C15a-C15b	1.455	C07-C08	1.346	φ 1 + φ 2 + φ 3	65.93
C15-C15a	1.402	C09-C10	1.353	Dihedral angle θ (°)[a]	56.14

[a]Angle between planes passing through C1-C2-C3-C4-C4a-C15e & C11a-C12-C13-C14-C15-C15a rings.

Table 3.1: Some important crystallographic parameters of compound **61**.

Both these values auger well with the distortion created due to the helicity of such structures. This also indicates a quite rigid helical framework of the synthesized new bi-aza[6]helicene **61** structure. The stereochemical information of the two helicenes units in **61** indicates the presence of '*P*' and '*M*' conformation. The crystal analysis clearly indicates meso orientation and it is the only isomer isolated during the purification.

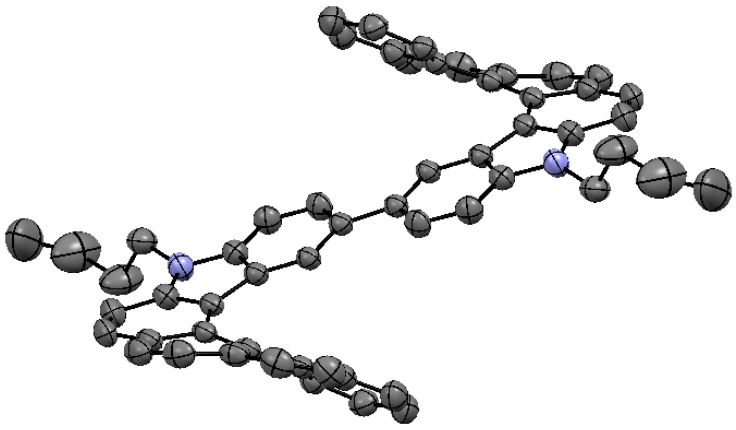


Figure 3.11: Side view of compound **61**. (CCDC No. 1058514).

The unit cell has only one molecule crystallized in *P*-1 space group. The side view of the crystal structure is presented in **Figure 3.11**. The planarity of the central biphenyl

portion is clearly visible in this diagram. The planes passing through the two terminal rings C01-C02-C03-C04-C04a-C15e and C′01-C′02-C′03-C′04-C′04a-C′15e are nearly parallel to each other.

The crystal packing of the compound **61** is presented in **Figure 3.12**. The intramolecular distance between two molecules stacked due to the π-π interaction is an important parameter. The distance between C09 of one molecule and C12 of other molecule was measured to be 3.327 Å. This distance is also the effective separation between the two layers of crystal packing.

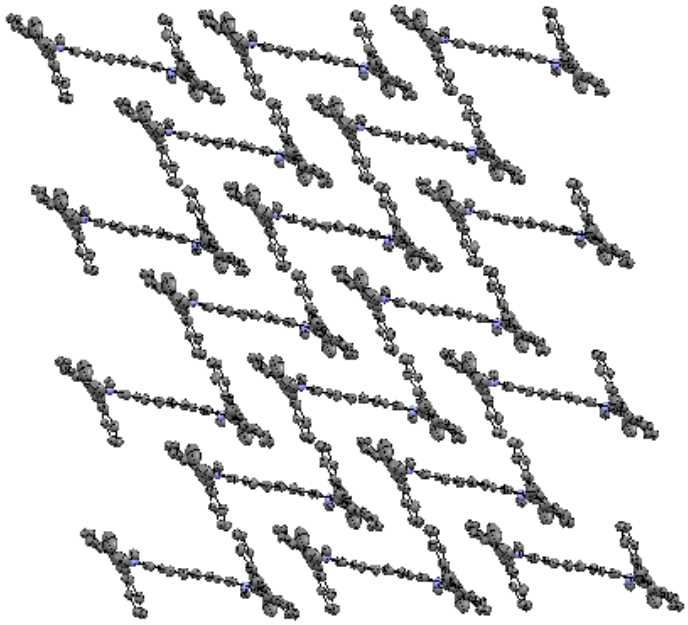


Figure 3.12: Crystal packing in compound **61**.

3.4.3 Photophysical properties:

The optical properties of bi-aza[*n*]helicenes, **60** and **61**, were studied by UV/Vis and fluorescence spectroscopy (**Figure 3.13**) and the results are presented in **Table 3.2**. The pyridine type aza[*n*]helicenes[23] and pyrrolohelicenes type aza[*n*]helicene[24] have been characterized by such spectral techniques. The effective overlap of orbitals and hence the optical properties are related to the structure of aromatic systems. Aromatic systems with extended π-conjugation and with flat structure show different optical properties as compared to the similar systems with twisted structures. In the present study we have also compared these properties with structurally similar aza[7]helicene **62** synthesized earlier. The UV-Vis spectra of bi-aza[5]helicene **60** and bi-aza[6]helicene **61**, along

with **62,** in dichloromethane exhibit absorption bands in the range of 262 to 337 nm. The three compounds showed blue emission in the range of 437 to 458 nm. The present bi-aza[n]helicenes **60**, **61** did not exhibit a distinct shoulder peak, while aza[7]helicene **62** showed it at 430 nm. On the other hand compound **61** showed small red shift (21 nm) compared to **60**, probably due to increase in π-conjugation. The absorption bands in the region 250nm to 350nm ranges are associated with the π–π* and n-π* electronic transitions. (**Table 3.2**)

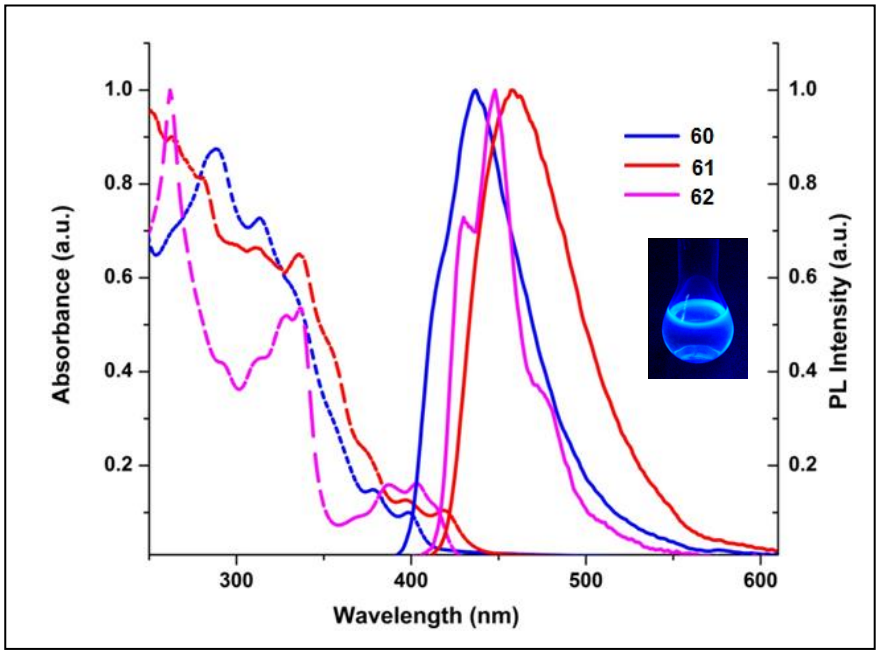
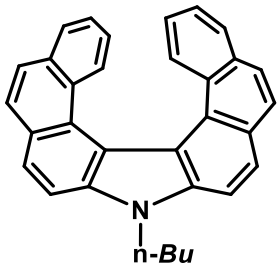


Figure 3.13: UV/Vis absorption and fluorescence spectroscopy of compound **60** and **61**. Blue emission behavior of compound **61**.



62

Figure 3.14: Structure of compound **62**.

Compound	Absorption λ_{abs} [nm]	Fluorescence λ_{em} [a] [nm]	Stokes shift/nm
60	288, 313	437	149
61	263, 311, 336	458	195
62	262, 329, 337	430, 448	186

UV VIS (1.0 X 10^{-5} M; dichloromethane) & Fluorescence (1.0 X 10^{-6} M; dichloromethane) at room temperature. [a]Excited at the longest absorption maxima.

Table 3.2. Optical properties of bi-aza[n]helicenes and aza[7]helicene in dichloromethane.

Optical measurements of compound **61** were measured in different solvents and plotted in **Figure 3.15**. There is no significant solvatochromism observed. In the polar solvent dichloromethane and acetonitrile a shift in fluorescence in longer wavelength and a loss of the structured fluorescence were observed in other solvents. This might be due to stabilization of polarized excited state more effectively in polar solvents.

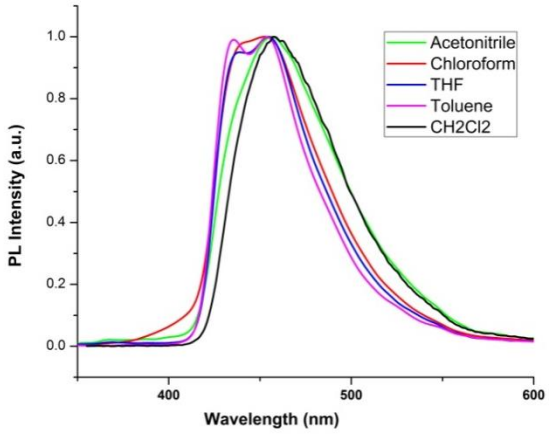
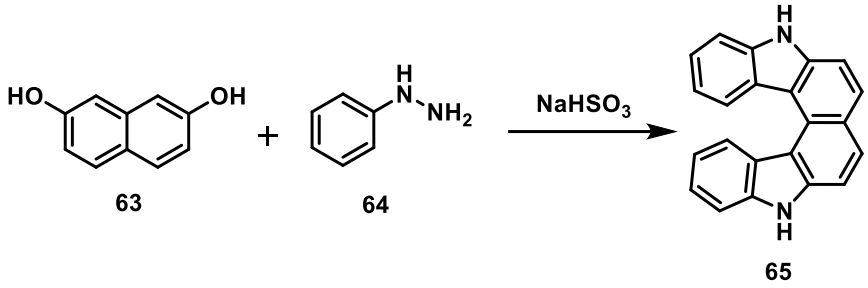


Figure 3.15. Fluorescence spectra of bi-aza[6]helicene **61** in different solvents.

The observed optical properties of the three helical structures provide interesting conclusions. The overall effect on the λ_{em} is due to the combination of π-conjugation and effective overlap of orbital of the aromatic rings. The observed highest λ_{em} and Stokes shift for **61** could be due to most number of aromatic rings as well as the flatness of the central biphenyl moiety, resulting in most efficient delocalization.

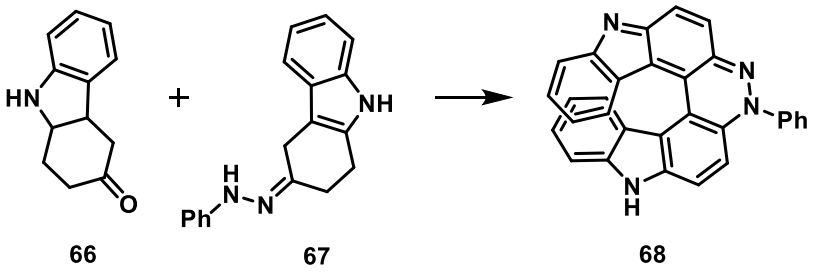
3.5 Chapter 3 Part B Synthesis and study of bis-carbazole based aza helicenes:

Introduction of two or more nitrogen atoms in helical skeleton using carbazole moiety is an interesting strategy. The first ever azahelicene containing bis carbazole moiety **65** (although no use of carbazole as starting material) was synthesized by Fuchs and Niszel in 1927 by heating 2,7 dihydroxy naphthalene **63** with phenylhydrazine **64** and sodium hydrogen sulphite (**Scheme 3.16**).[25]



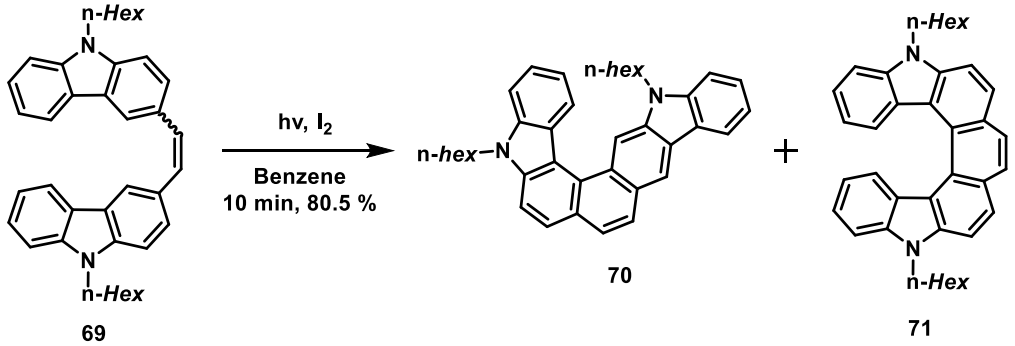
Scheme 3.16: Synthesis of compound **65**.

Vogel *et al.*[26] synthesized similar type of helical framework **68** by utilizing hydrazine derivative. (**Scheme 3.17**)



Scheme 3.17: Synthesis of compound **68**.

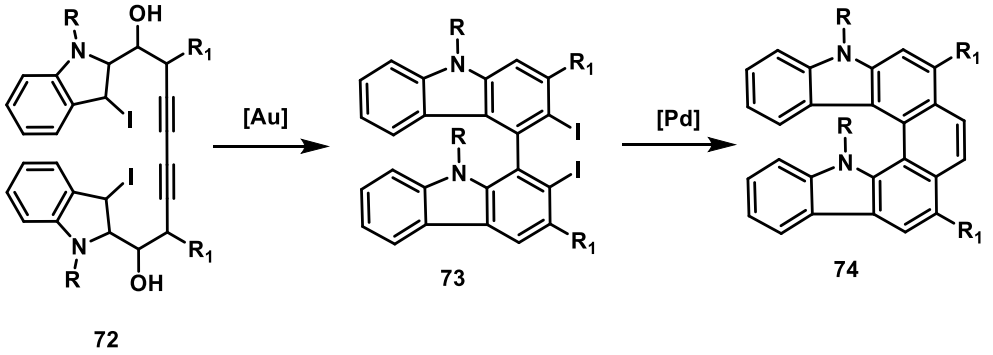
Liu *et al* [27] has attempted the synthesis of bis aza[7]helicene using carbazole as the primary starting material. The required olefin precursor **69** was synthesized using McMurry coupling of 3-formyl *N*-hexyl carbazole which was then subjected to photocyclization. Instead of symmetrically cyclized bis aza[7]helicene **71**, an unsymmetrical partial angularly cyclized [5]helicene **70** was obtained as an exclusive product (**Scheme 3.18**). The compound exhibited good thermal and photophysical properties, and found to be a potential candidate for blue light emitting OLED material.



Scheme 3.18: Synthesis of compound **70**.

List *et. al.*[8] synthesized bis aza helicene using asymmetric Bronsted acid catalyzed Fischer indole reaction. A SPINOL-derived chiral phosphoric acid has been designed and utilized for asymmetric induction. (**Scheme 3.8**)

Alcaid *et. al.*[28] attempted the synthesis of bis carbazole aza[7]helicene using the gold catalyzed rearrangement iodonium migration of C_2-symmetrical bis(indole)-1,3-diynes **72**, giving unsymmetrical bis iodo carbazole **73**. Bis-iodo carbazole derivatives were then subjected to variety of boronic acid derivatives under Suzuki-Miyaura benzannulation reaction condition to give unsymmetrical bis aza[7]helicenes **74**.



Scheme 3.19: Synthesis of compound **74**.

These [7]helicenocarbazoles are efficient blue luminophores and paving the way for the preparation of novel fluorescence sensory materials.

3.6 RESULTS AND DISCUSSION

3.6.1 Synthesis of Bis carbazole based aza[*n*]helicene:

The retro synthetic plan to access bis carbazole based helicene indicates two different possible options of introducing furan, pyrrole and benzene ring in the bis-carbazole

unit. The basic idea was to make the 3-hydroxy carbazole **75**, followed by oxidative coupling to prepare dihydroxycarbazole **76**. The central naphthofuran ring can be built by acid catalyzed ether formation from the corresponding dihydroxy carbazole or by other transition metal mediated Buchwald Harwig C-O and C-N coupling. (**Figure 3.16**)

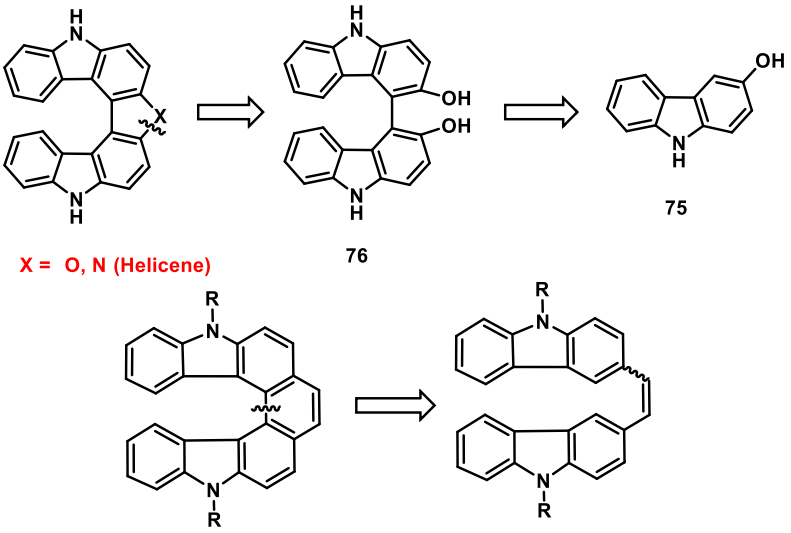
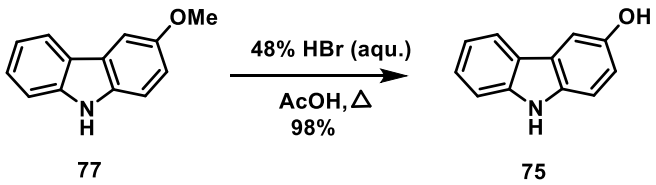


Figure 3.16: Retro synthetic analysis for the introduction of pyrrole, furan and benzene ring in bis carbazole moiety.

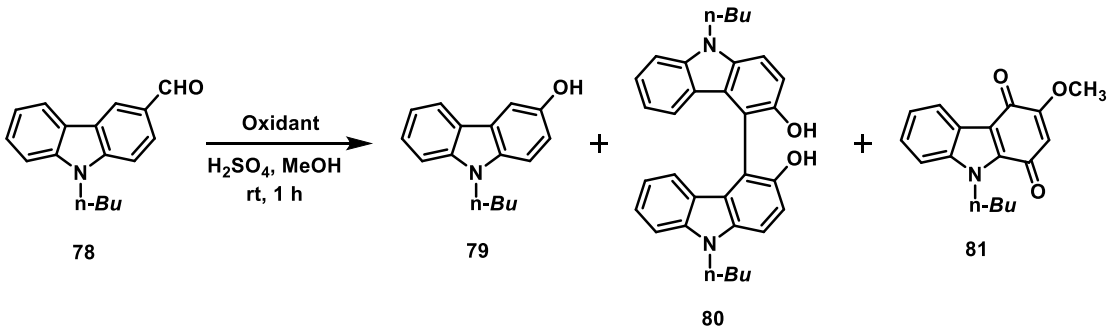
We started this work by digging the literature for the methodology to synthesize 3-hydroxyl carbazole **75**. Majority of the reported cases 3-hydroxy carbazole **75** was synthesized by demethylation of 3-methoxy carbazole **77** using acidic conditions such as aq. HBr/AcOH[29a] or BCl_3/Bu_4NI in dichloromethane.[29b] (**Scheme 3.20**)



Scheme 3.20: Synthesis of 3-hydroxy carbazole **75**.

One of the references suggests using hydrogen peroxide with catalytic sulfuric acid for converting 3-formyl *N*-methyl carbazole to 3-hydroxy *N*-methyl carbazole.[30] As we had enough of 3-formyl *N*-butyl carbazole **78** in hand we decided to explore this method for the desired target molecule. The plan moving forward was to make the desired dihydroxy carbazole **80** from 3-hydroxy *N*-butyl carbazole **79** by oxidative coupling using any one of the reported coupling methods such as $(t\text{-BuO})_2$, *p*-chloranil,

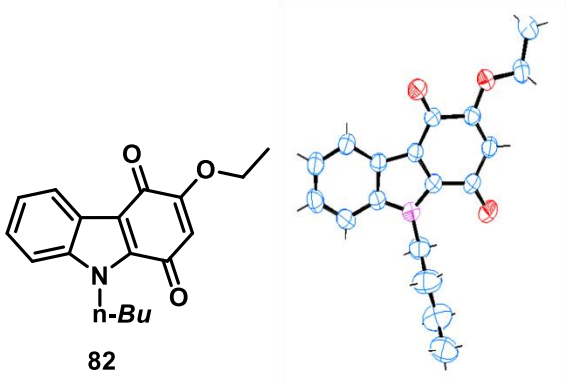
$(PhCO_2)_2$, $CuSO_4/Al_2O_3$, $CuCl_2$/TMEDA, $K_3Fe(CN)_6$,MnO_2, Ag_2CO_3 or vanadium complexes. The journey began with the synthesis of 3-hydroxy *N*-butyl carbazole **79** using Dakin reaction; *N*-butyl 3-formyl carbazole **78** was treated with 1.1 equivalents of aqueous solution of hydrogen peroxide and one drop of concentrated sulfuric acid in methanol (**Scheme 3.21**). The reaction was very fast and majority of starting material got consumed as per TLC within an hour, two spots were observed, which were separated using column chromatography. The non polar spot was identified as the desired 3-hydroxy carbazole **79** by ^{1}H NMR and mass spectral analysis, while the second and more polar spot had one hydrogen less than the 3-hydroxy carbazole. The HRMS of the polar spot was found to be 499.2356 $[M+Na]^+$ which to our surprise corresponds to the coupling product (dihydroxy carbazole) **80**.



Scheme 3.21: Synthesis of dihydroxycarbazole **80**.

Having access to both the standards, we undertook rapid screening of reaction optimization. In the second attempt we increased the amount of hydrogen peroxide from 1.1 to 2.2; TLC indicates increase in the conversion to the polar product. Disappointingly, further extension in the reaction time (up to 24 h), increase in the equivalents of hydrogen peroxide (5.0 equiv.) or high temperature (reflux) did not change the outcome in yield of dihydroxy carbazole **80**. After identifying the optimized conditions, we next explored the effect of different oxidizing agent on this transformation. It was found that with *meta* chloro perbenzoic acid (*m*-CPBA), only the mono hydroxyl carbazole **79** was formed, no coupling product was observed in this condition. When tertiary butyl hydroperoxide (TBHP) was used in the similar conditions, an entirely different oxidized product **81** was formed ^{1}H NMR and ^{13}C NMR suggests addition of methoxy moiety of methanol on the carbazole skeleton. We were not able to get X-ray of the product and hence uncertain about the structure of compound **81**. However, the structure of similar compound **82** was unambiguously

confirmed by X-ray analysis of product (**Figure 3.17**), when reaction was performed in ethanol instead of methanol, a crystalline orange colored compound was formed with addition of ethoxy moiety. Same product was formed with benzoyl peroxide as an oxidant, but under reflux temperature.



82

Figure 3.17: Structure and ORTEP plot of compound **82**.

With sterically hindered di-tert butyl peroxide (DTBP) oxidant no conversion was observed, which may be attributed to the bulkier nature of reagent which possibly prevent the nucleophilic attack of peroxide oxygen on the carbonyl carbon of 3-formyl *N*-butyl carbazole **78** (**Table 3.3**).

We next explored different organic acids such as trifluoromethanesulfonic acid, *para*-toluenesulfonic acid in the similar reaction conditions same outcome was observed as with using sulfuric acid.

After the preliminary optimization was established, we focused on understanding the reaction mechanism. Although our main focus was limited only to synthesize the desired bis hydroxyl carbazole, but to broaden the scope and to test the validity of this conditions on making very useful molecules such as BINOL, we tried one reaction with 2-formyl naphthalene under optimized reaction conditions. Unfortunately no BINOL formation was observed, possibly restricting this method of coupling to highly electron rich substrates only. No further attempts were made to test this reaction on different substrates.

Sr.No.	Oxidant (equ.)	Temp (^oC)	Time (h)	Yield (79)	Yield (80)	Yield (81)
1.	H_2O_2 (2.0)	RT	1	42	21	0
2.	m-CPBA (2.0)	RT	8-10	93	0	0
3.	TBHP (2.0)	RT	8.-10 h	Trace	Trace	25
4.	DTBP (Up to 10.0)	RT to reflux	24 h	0	0	0
5.	Benzoyl Peroxide (Up to 10.0)	RT to Reflux	24 h	0	0	30

Table 3.3: Effect of various oxidants on oxidation of **78**.

Initially it was assumed that the reaction proceed through ionic mechanism by the trace transition metal impurities present in the aqueous solution of hydrogen peroxide. To test this hypothesis, we deliberately added $FeCl_3.6H_2O$ (10 mol %) and $CuCl_2.2H_2O$ (2.0 mol %) and run the reaction keeping the similar reaction conditions. In both the cases, the starting material decomposed within 15 minutes giving polymeric polar compound, additionally with $CuCl_2.2H_2O$, less than 10 % of dihydroxy carbazole was isolated with majority of unidentified polymeric compound. These transition metal salt spiking experiments did not clarify the ionic mechanism hypothesis. The second thought was, the reaction proceeded through radical mechanism. The mechanism for this conversion is still unclear. Based on literature reports and our present experimental results, a plausible reaction mechanism has been proposed in **Figure 3.18**. First step is the acid catalyzed Dakin reaction, in methanol, hydrogen peroxide and catalytic sulfuric acid, the carbonyl oxygen of 3-formyl *N*-butyl carbazole **78** gets protonated to give **I**. After which hydrogen peroxide adds as a nucleophile (by the lone pairs of oxygen) to the carbonyl carbon, forming a tetrahedral intermediate **II**. Following an intramolecular proton transfer, the tetrahedral intermediate collapses, [1,2]-aryl migration occurs forming an ester **III**. Finally, upon hydrolysis of ester yields the hydroxyl product **IV** and regenerates the acid catalyst. Second step of mechanism is the oxidative coupling of hydroxyl carbazole to dihydroxy carbazole by homolytic coupling of two radicals **V** In the radical–radical coupling process, formation of a diketone intermediate is expected through dimerization of a carbon-centred radicals of the 3-hydroxy carbazole radical **VI** forming a dearomatized 1,4-diketone **VIII**. The 1,4-

diketone rapidly undergoes tautomerization to the more stable enol form to yield dihydroxy carbazole **80** (BICOL).

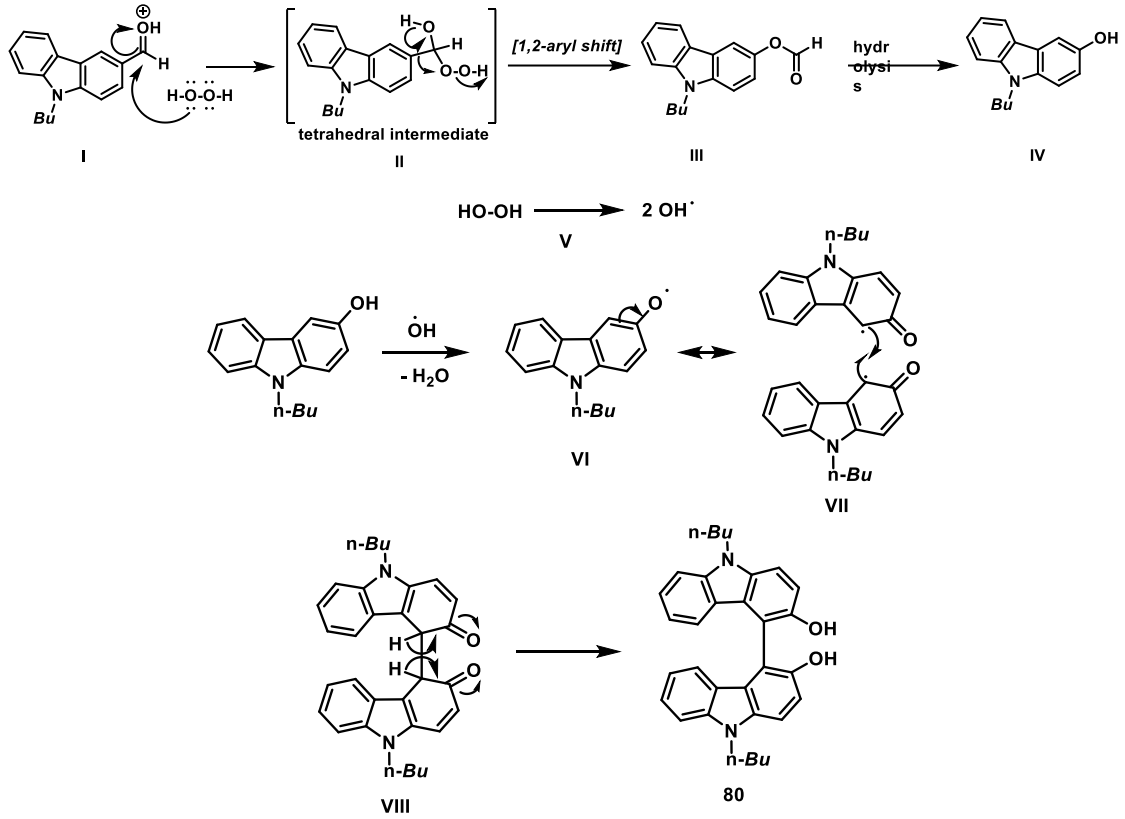
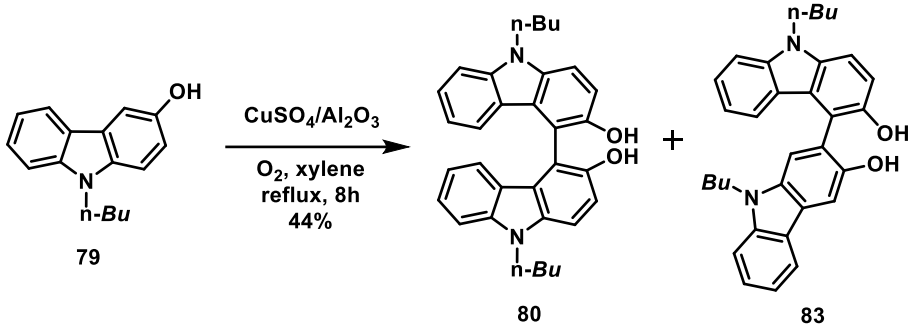


Figure 3.18: Possible mechanism for the formation of dihydroxy carbazole **80**.

In the presence of radical scavengers 2,6-di-tert-butyl-4-methyl phenol (2.0 equiv.), under standard conditions sharply lowered the yields of **80**, (TLC only) which showed that a radical mechanism was involved. In another experiment, we attempted coupling of isolated 3-hydroxy carbazole **79** under similar conditions. To our surprise, not coupling product **80** was detected.

Few of the striking features of this reaction are; the reaction is mild, performed at room temperature, environmentally benign as no metal catalyst was used, no dry or inert conditions are required and in a single step aldehyde functionality can be converted to dihydroxy carbazole without isolating the intermediate product. Most astonishing feature is very high regioselectivity, only the desired symmetrical coupling product is formed. When we carried out the coupling of 3-hydroxy carbazole under Botman's condition by using $CuSO_4$ supported over alumina under oxygen atmosphere, a non separable mixture of symmetrical **80** and unsymmetrical bis-carbazol diol **83** were formed.

One major limitation of this reaction is the incomplete conversion of hydroxyl carbazole **79** to biscarbazole **80**. Attempts in the direction of proper understanding and quantification of products are currently under progress.



Scheme 3.22: Synthesis of compound **80** using Botman's conditions.

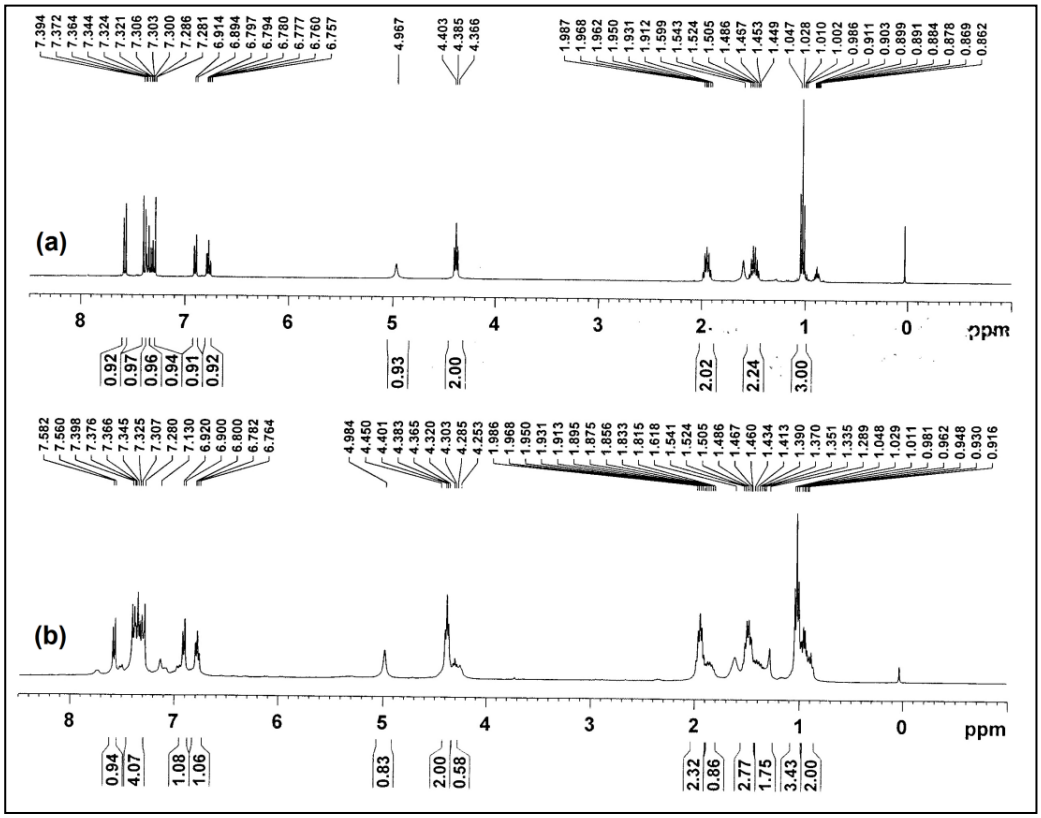
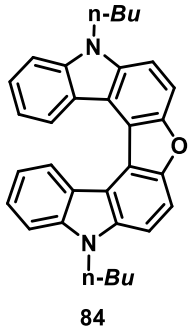


Figure 3.19: Comparison of ^{1}H NMR showing regioselectivity for compound **80**. (**a**) with H_2O_2/H^+ (**b**) with Al_2O_3 loaded on silica (Botman's conditions) In condition **b** ^{1}H NMR indicates the desired product **80** is contaminated with unwanted regiomer **83**.

After the successful but serendipitous formation of desired bis-hydroxy carbazole **80**, we began utilizing it for the construction of various helical frameworks.

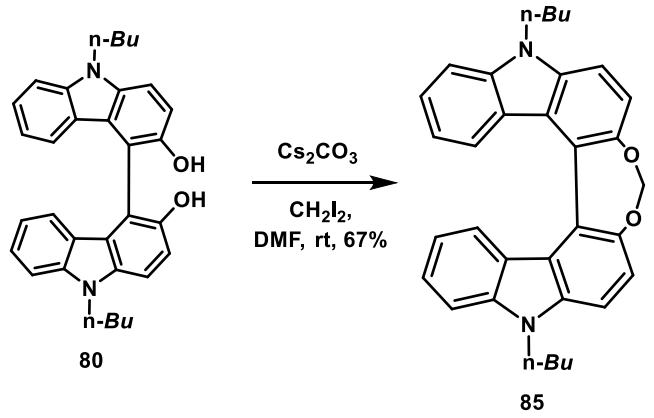
First type of bis carbazole based helical target molecule was diazaoxa[7]helicene **84**.



84

Figure 3.20: Structure of First type of bis carbazole based target molecule.

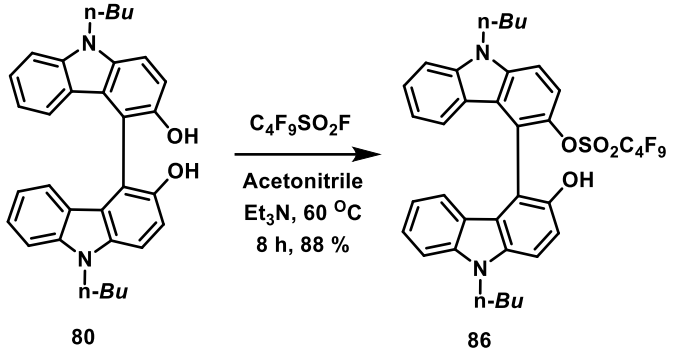
With the desired diol **80** in hand we attempted the synthesis of helicene like molecule, which may be relatively easier to synthesis than helicene molecule, which required a tougher dehydration conditions. The diol **80** was then transformed to the methylene-bridged compound **85** by reaction with diiodomethane and Cs_2CO_3 in 67% yield. (**Scheme 3.23**)



80 85

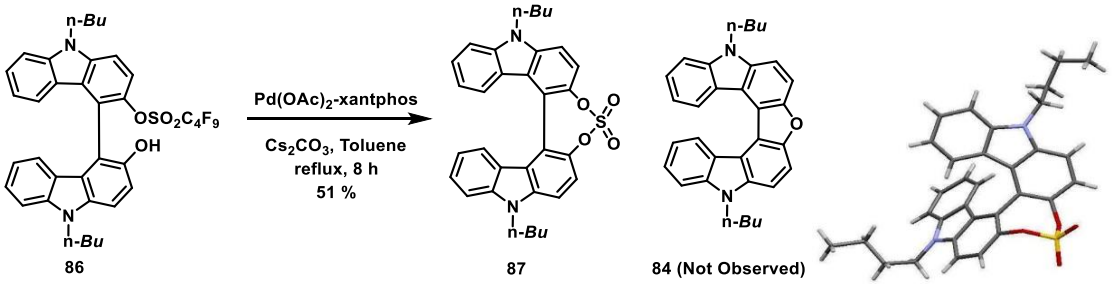
Scheme 3.23: Synthesis of helicene-like compound **85**.

Secondly we tried to synthesize central benzofuran ring by acid-catalyzed ether formation from the corresponding diol **80**. Attempts to perform acid catalyzed dehydration reaction on this diol **80** with *p*-TSA, conc. H_2SO_4, zeolite or chloranil/$BF_3.OEt_2$ ended up with uncontrolled polymerization. Hence, we resorted to the other method of palladium catalyzed intermolecular diaryl ether synthesis by Buchwald's C-O bond formation protocol.[31] Compound **80** was converted to its mono nonafluoro sulfonate **86** by refluxing with perfluorobutanesulfonyl fluoride in acetonitrile. (**Scheme 3.24**)



Scheme 3.24: Synthesis of compound **86**.

Compound **86** was than subjected to cyclization with palladium acetate-Xantphos catalyst system in presence of Cs_2CO_3 as base. A non polar compound was isolated and characterized by ^{1}H NMR and ^{13}C NMR. The number of protons and carbon signals indicated possible formation of desired compound **84** but HRMS analysis shows higher mass value than expected. So to confirm actual structure we grew single crystal of compound **87**, the crystal structure revealed that instead of desired dibenzofuran **84**, a new compound **87** has formed. In this compound a sulfonyl group has got inserted in the diol compound and helicene-like compound is formed. (**Scheme 3.25**)

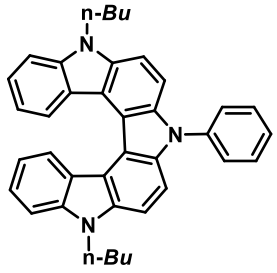


Scheme 3.25: Synthesis of compound **87** and its ORTEP plot.

Possible explanation for this product formation is discussed here. In the presence of Cs_2CO_3, free mono hydroxyl compound gets converted to phenoxide, which attacks on the sulfonate ester, leaving the perfluoro butane group, thereby inserting sulfonyl group flanked between two ether linkages. Failure of these strategy leads us back to our initial approach, the literature review suggests the 2nd and 7th positions of the carbazole must be blocked before subjecting to acidic cyclization conditions otherwise it leads to polymerization[32] this is consistent with our initial attempts to cyclized unprotected

carbazole, leading to thick black polymeric material. Attempts to block the 2 and 7 position and cyclization are currently under progress.

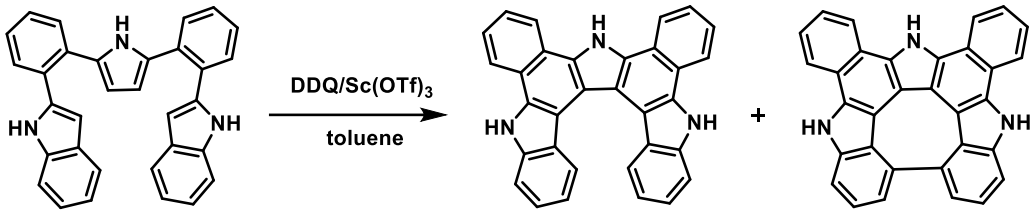
Second type of bis carbazole based helical target molecule was triaza[7]helicene **88**.



88

Figure 3.21: Structure of second type of bis carbazole based target molecule **88**.

Recently Osuka *et al.*[33] reported the synthesis of similar molecule, triaza[7]helicene **90** by oxidation of acyclic tripyrroles.



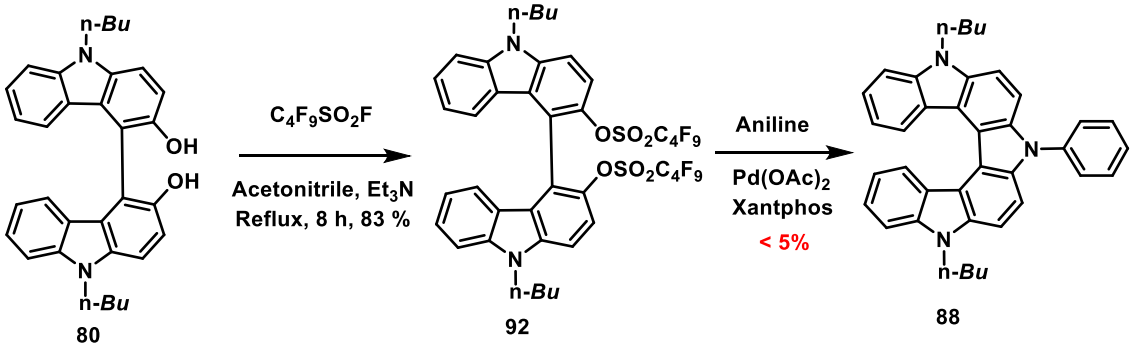
89 90 91

Scheme 3.26: Synthesis of triaza[7]helicene **90** by Osuka *et al.*

The tripyrrolic precursor **89** was subjected to oxidative fusion conditions with DDQ/$Sc(OTf)_3$ in toluene under reflux conditions gave unexpected fused product azahepta[8]circulene **91**. Under mild reaction conditions at lower equivalents of DDQ/$Sc(OTf)_3$ in toluene at 60 ^oC, they obtained the desired triaza[7helicene **90** in 32%. Further modifications of reaction conditions improved the yield up to 71 %. (**Scheme 3.26**)

This target molecule **88** can be prepared by the double *N*-arylation of primary amines with biphenylylene disulfonate.[34] the diol **80** was treated with excess of perfluorobutanesulfonyl fluoride with triethyl amine base in acetonitrile to get dinonaflate bi carbazole **92** in 83 % yield. The Compound **92** was then subjected to palladium catalyzed double *N*-arylation with aniline in presence of $Pd(OAc)_2$-Xantphos system, Cs_2CO_3 in refluxing toluene. After prolonged heating for 72 hours we observed formation of an intense blue fluorescent spot, with few decomposed products.

Gratifyingly the NMR of crude mixture showed the signals of desired triaza[7helicene **88** but unfortunately the yield was very low (less than 5%). (**Scheme 3.27**) We believe a proper combination of palladium source, catalyst and base can improve the yield of desire compound, efforts in the direction of optimization of conditions are currently under progress.



Scheme 3.27: Pd-xantphos catalyzed double *N*-arylation strategy for the synthesis of compound **88**.

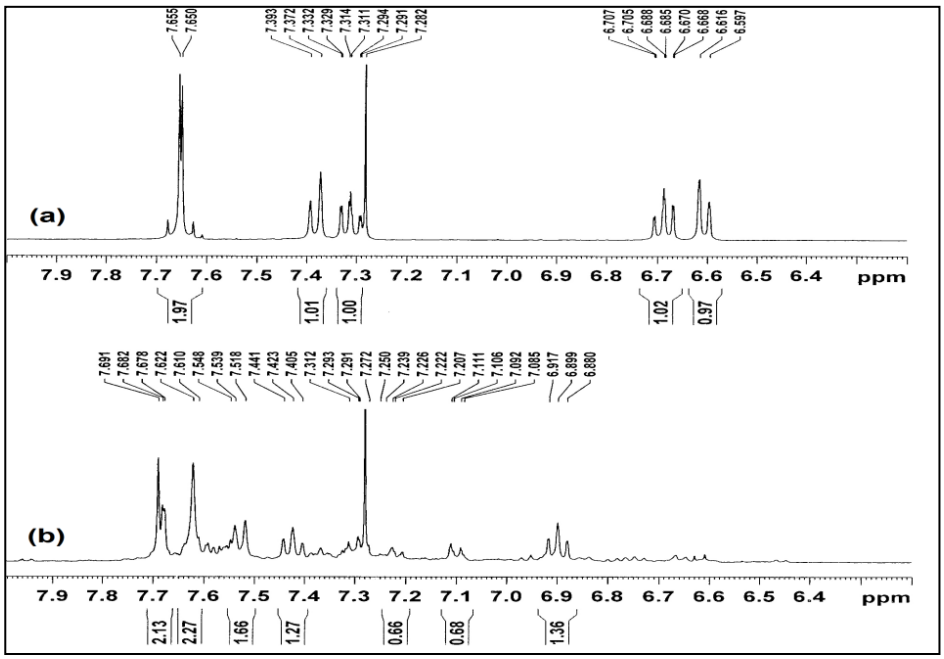


Figure 3.22: ^{1}H-NMR of aromatic region for compound **92** (a) and reaction mixture after 72 h (b) Indication of formation of desired triaza[7]helicene **88** in spectra (b)

Third type of bis carbazole based target molecule is bis aza[7]helicene **93**. Historically this type of target molecule has already been known, nevertheless, we wanted to introduce one benzene ring between two carbazole moieties. The synthetic approaches for these types of target molecules are briefly discussed in the introduction part of this chapter.

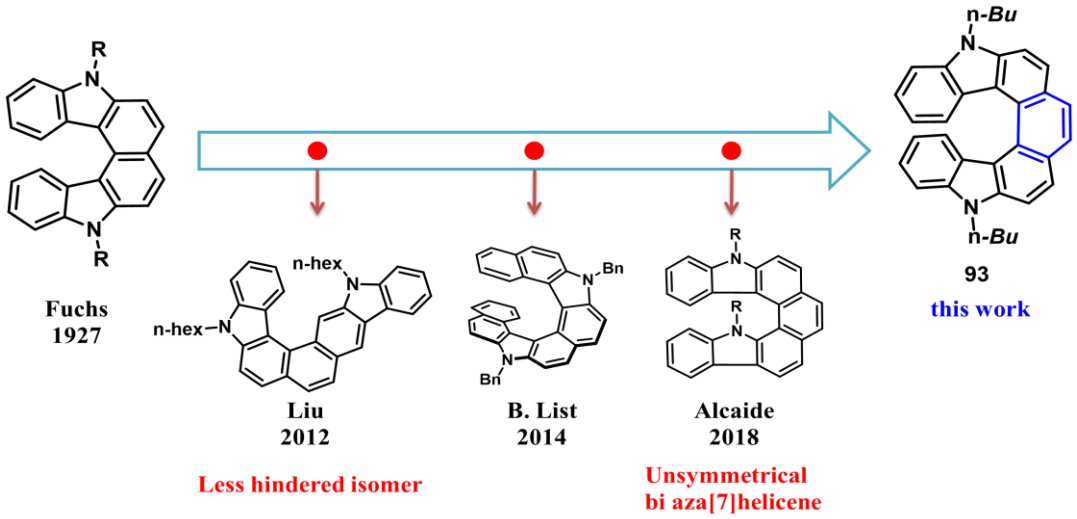
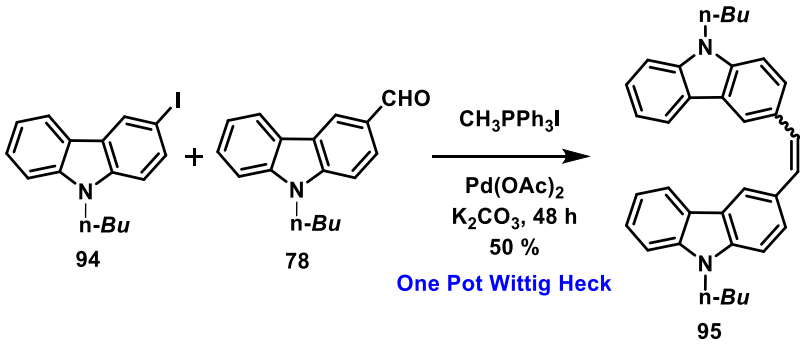


Figure 3.23: Various bis aza helicenes.

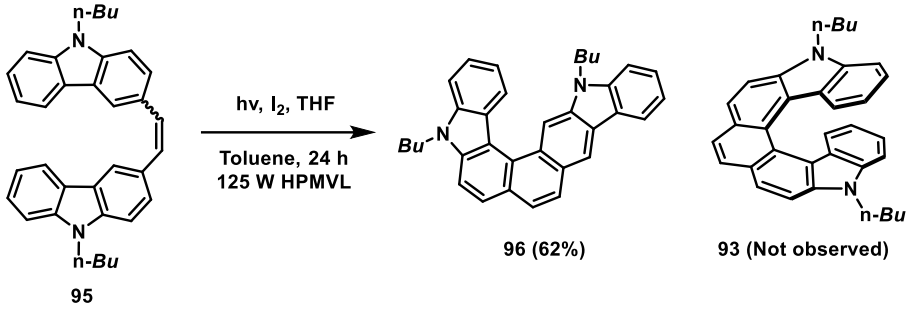
Approach 1: We begin with the classical approach of photocyclization; the requisite olefin precursor was prepared by One Pot Wittig-Heck Olefination in which 3-formyl *N*-butyl carbazole **78** was subjected to the Wittig reaction with a one carbon phosphonium salt (Ph_3PCH_3I) to generate the desired styrene derivative, which was further subjected to Mizoroki–Heck condition with 3-iodo *N*-butyl carbazole **94** in the same flask to give the stilbene derivative **95** in 50% yield. (**Scheme 3.28**)



Scheme 3.28: Synthesis of compound **95**.

Similar molecule was attempted for photocyclization by Liu *et al.*[24a] but instead of compound **93** they got only the less hindered pentahelicene **96**. We also tried to

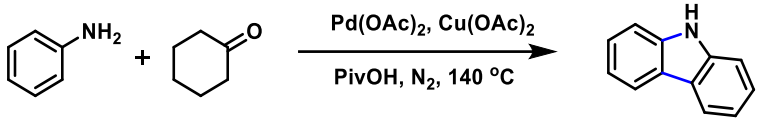
synthesize this molecule by slightly modified or rather milder photocyclization conditions such as high dilution conditions and also less power of high-pressure mercury vapor lamp (125 W instead of 500 W reported by Liu *et al*). (**Scheme 3.29**)



Scheme 3.29: Photocyclization of compound **95**.

Our attempt of using milder conditions did not change the outcome and result remained the same. We too observed formation of **96** as the sole product in 62% yield.

Approach 2: After the failure of photocyclization strategy to prepare symmetrical bis aza[7]helicene, we tried another approach. This is inspired by Wang *et al.*[35] methodology for the synthesis of carbazole; which is based on palladium catalyzed domino reaction via a dehydrogenative aromatization step followed by dehydrogenative coupling $C(sp^2)$-$C(sp^2)$ for one-pot synthesis of carbazole. (**Scheme 3.30**)



Scheme 3.30: Synthesis of carbazole by palladium catalyzed domino reaction.

In the retro synthetic plan to access desired bis aza[7]helicene **93**, key synthetic disconnection was C-C bond formation to get the desired helical framework using palladium catalyzed aromatization and Cu catalyzed oxidative coupling reaction. (**Figure 3.24**)

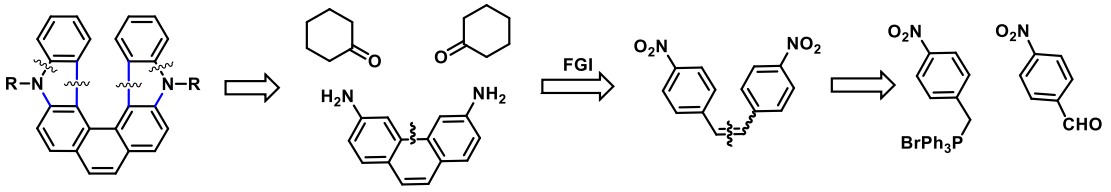
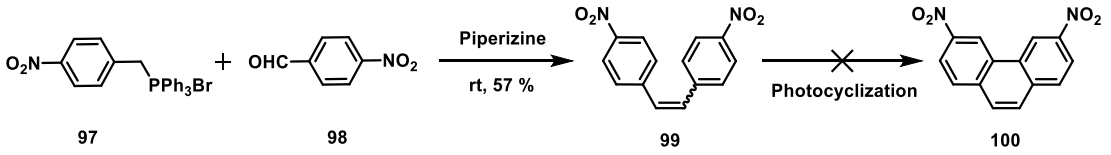


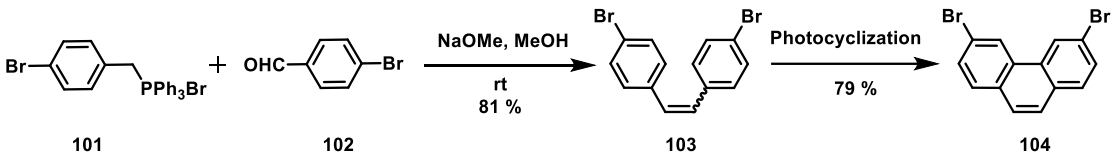
Figure 3.24: Retrosynthetic plan to synthesize bis aza[7helicene **93**.

We begin the synthesis with the Wittig Olefination of simple starting materials such as *p*-nitro benzaldehyde **98** and Wittig salt of *p*-nitro benzyl bromide **97** in presence of piperizine base at room temperature to get dinitro stilbene **99** derivative in 57% yield. The stilbene derivative was subjected to photocyclization, but even after prolonged exposure (40 hours) stilbene **99** failed to undergo photocyclization. (**Scheme 3.31**)



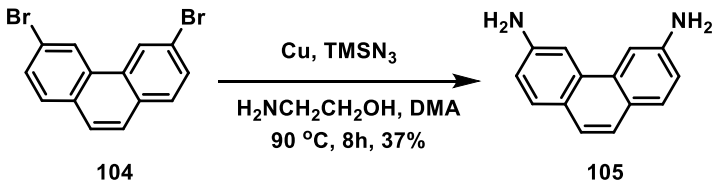
Scheme 3.31: Attempted synthesis of compound **100**.

To address this problem we adopted an alternative strategy for synthesizing diamino phenanthrene **105**, which again started with Wittig Olefination of *p*-bromo benzaldehyde **102** and Wittig salt of *p*-bromo benzyl bromide **101**. The resulted di-bromo stilbene **104** was subjected to photocyclization which smoothly furnishes desired dibromo phenanthrene **104** in 79% yield (**Scheme 3.32**).



Scheme 3.32: Synthesis of compound **104**.

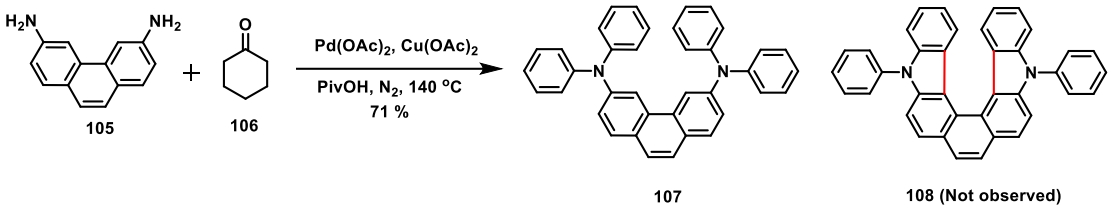
The dibromo phenanthrene **104** was then subjected to copper mediated reductive amination reaction with trimethyl silyl azide ($TMSN_3$) to get diamino phenanthrene **105** in 37% yield. (**Scheme 3.33**)



Scheme 3.33: Synthesis of compound **105**.

As as per our retro synthetic strategy diamino phenanthrene **105** was treated with cyclohexanone in excess (3.0 equiv.) in presence of palladium acetate catalyst and

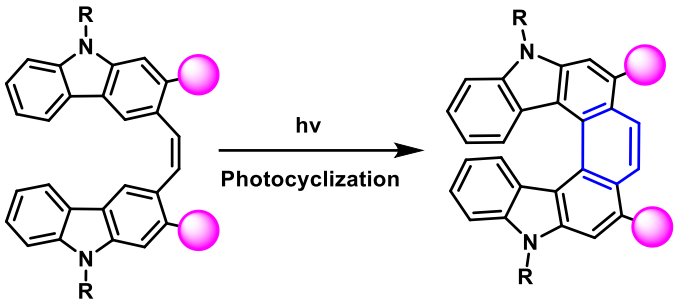
copper acetate as an oxidant. Few drops of DMF was added to ensure solubility in the reaction system.



Scheme. 3.34: Attempted synthesis of compound **108** using Wang *et al* conditions.

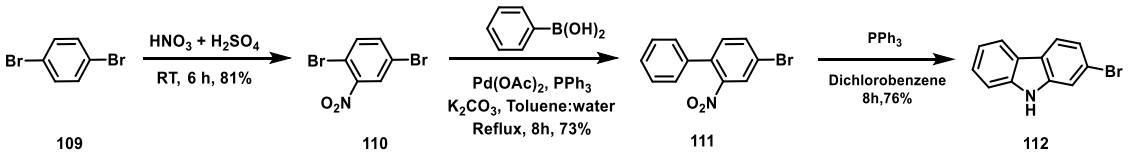
After the completion of reaction a blue fluorescent spot was isolated which was characterized as compound **107** and not the desired triaza[7]helicene **108**, this pointed that only the first step dehydrogenative aromatization took place and second step C (sp^2)-C(sp^2) coupling step did not occurred; possibly due to high steric demand of the final molecule **108**.

Approach 3: Again we considered the photocyclization to solve the desired problem with slight modification in the precursor used for photocyclization. The idea was to block the position which undergoes cyclization to give linear isomer instead of desired angularly cyclized product. (**Scheme 3.35**)



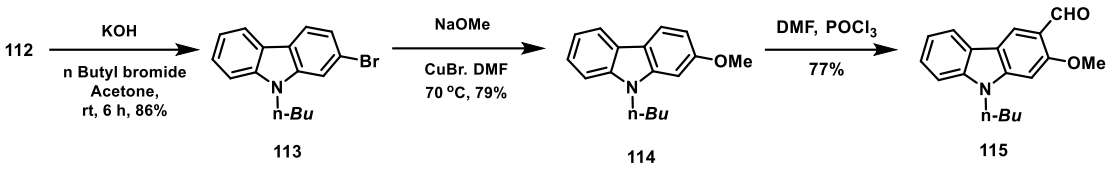
Scheme 3.35: Proposed photocyclization approach by blocking strategy.

For achieving this goal we started synthesis of carbazole having required positions substituted by some functional group. (**Scheme 3.36**)



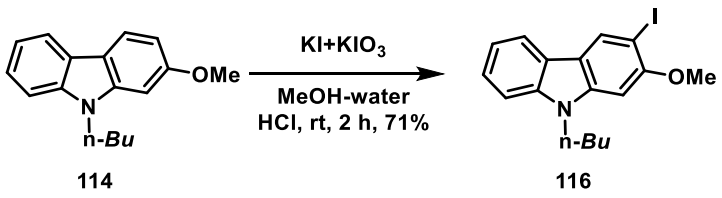
Scheme 3.36: Synthesis of 2-bromo carbazole **112**.

1,4-dibromobenzene **109** was subjected to mono nitration with nitrating mixture to get compound **110**. Compound **110** was then treated with phenyl boronic acid under Suzuki-Miyaura cross-coupling protocol conditions under standard conditions with palladium acetate and , aqueous carbonate base under reflux to give compound **111** in 73% yield, along with some product of di-Suzuki coupling was formed which was removed by column chromatography. A reductive modified Cadogan ring-closure conditions then produced the 2- bromo carbazole **112** in 76% yield. In order to have good solubility for the carbazole, *N*-butylation was carried out. (**Scheme 3.37**)



Scheme 3.37: Synthesis of compound **115**.

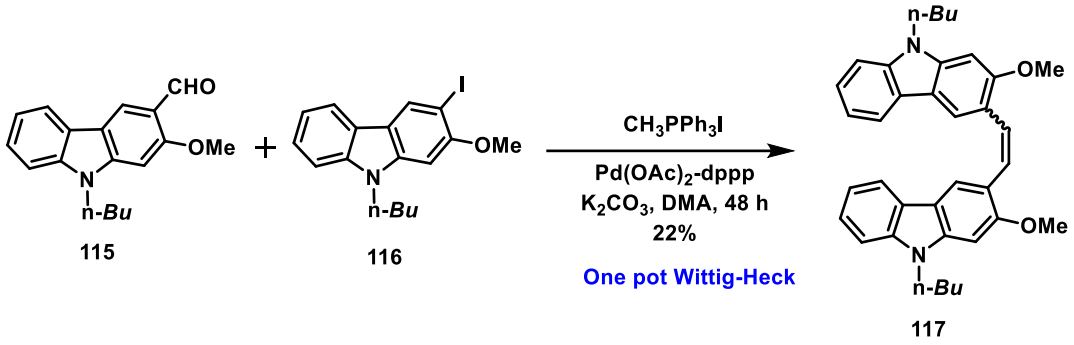
Idea to carry out formylation of 2-bromo *N*-butyl carbazole **113** was dropped, based on the report by Nagarajan *et al* [36] The formylation of 2-bromo *N*-ethyl carbazole by DMF/$POCl_3$ gave 6-formyl *N*-ethyl carbazole as the major product instead of the desired 3-formyl derivative. This can be explained by deactivating nature of bromo group. So it encouraged us to convert deactivating bromo functional group to electron releasing methoxy group in **114** by copper catalyzed reaction with NaOMe. Gratifyingly formylation of compound **114** gave the desired 2-methoxy 3-formyl *N*-butyl carbazole **115**. Its counterpart 3-iodo 2-methoxy *N*-butyl carbazole **116** was synthesized by iodination of compound **114** in 71% yield with KI and KIO_3. (**Scheme 3.38**)



Scheme 3.38: Synthesis of compound **116**.

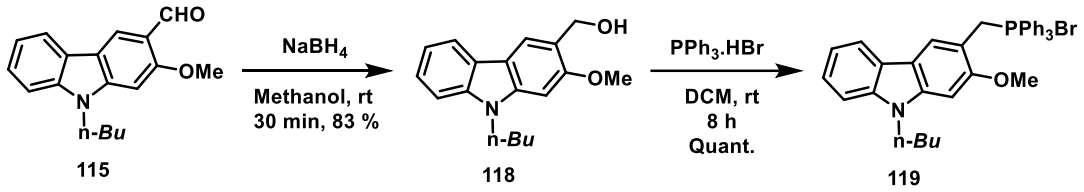
In the next step both the compounds 2-methoxy 3-formyl *N*-butyl carbazole **115** and 3-iodo 2-methoxy *N*-butyl carbazole **116** were subjected to one pot Wittig-Heck reaction

conditions to get olefin having both the positions blocked with methoxy groups in low yield of 22%. (**Scheme 3.39**)



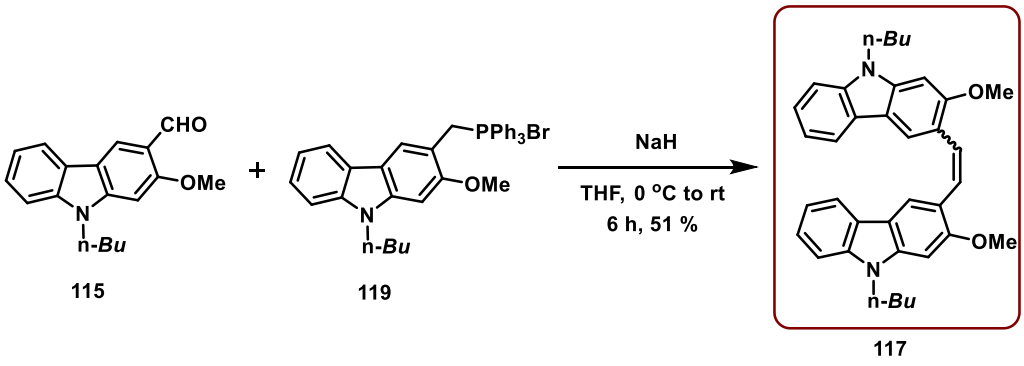
Scheme 3.39: Synthesis of compound **117**.

We attempted direct synthesis of olefin **117** from compound **115** by McMurry coupling conditions, but failed to give the desired molecule **117**. To improve the yield of target olefin molecule **117** an alternative strategy was adopted. The aldehyde **115** was reduced using $NaBH_4$ and then reacted with triphenylphosphine hydrobromide to give the Wittig salt in quantitative yield. (**Scheme 3.40**)



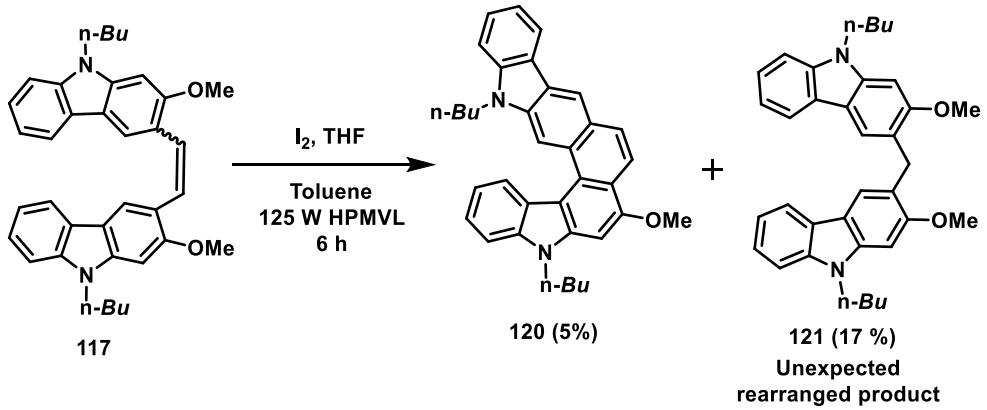
Scheme 3.40: Synthesis of compound **119**.

The aldehyde **115** and Wittig salt **119** was then subjected to Wittig Olefination with NaH as base in THF to get the desired olefin **117** in 51% yield. (**Scheme 3.41**)



Scheme 3.41: Improved synthesis of compound **117**.

With enough olefin **117** in possession we subjected it to standard photocyclization conditions (**Scheme 3.42**). After the careful column chromatography two products were isolated and characterized by ^{1}H-NMR. One was characterized as linear isomer (5% yield) in which one methoxy group was observed to have been knocked out giving us again the unwanted isomer as observed in case of **approach 1**. More surprisingly second product which was unambiguously characterized by single crystal analysis, and found to be a rearranged product **121 (Figure 3.24)**. At this point formation of this compound is not clear but initial experiments in NMR tube confirms the iodine reacted itself with the highly electron rich olefin **117** system. Further experiments to understand mechanism are currently under progress.



Scheme 3.42: Photocyclization of compound **117**.

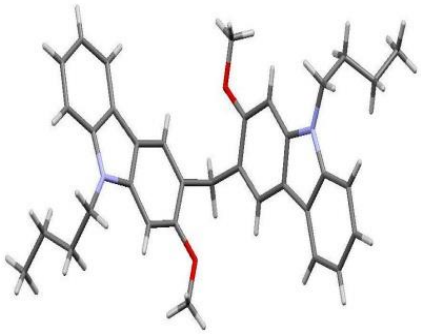


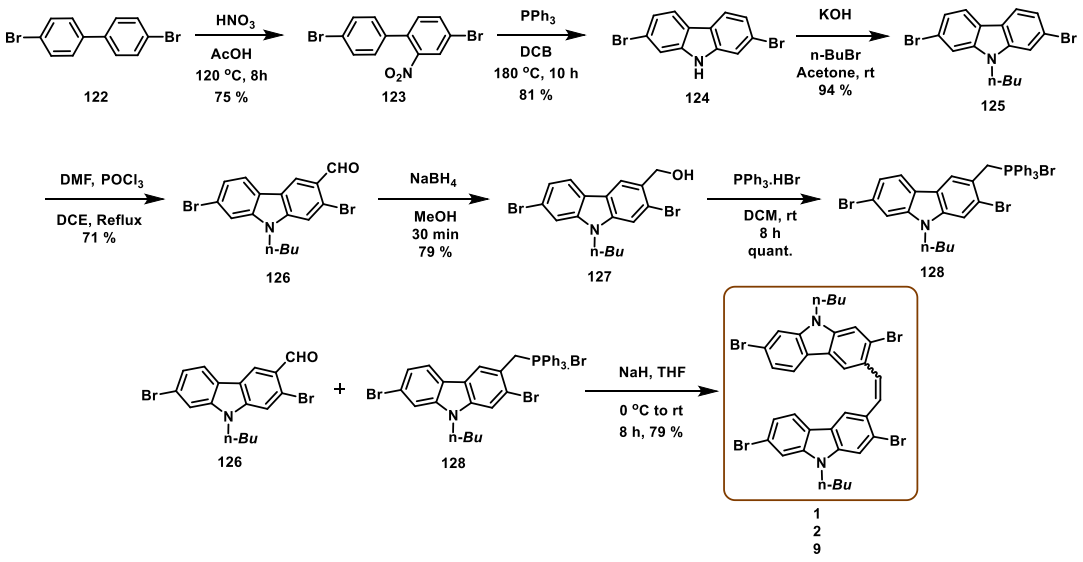
Figure 3.24: ORTEP plot of rearranged product **121**.

Initial assessment for very low overall yield of photocyclization may be attributed to attack of iodine on the electron rich double bond (as immediate brown precipitation observed during the degassing stage (sonication)), leads to fast rearrangement and decomposition. We have noticed that the solution of **117** in $CDCl_3$ upon storage gradually turns from yellow to green, which indicates its instability in solvents or its

photosensitive nature, nevertheless there was no appreciable change in the ^{1}H NMR of freshly prepared sample and dark greenish sample upon standing for few days.

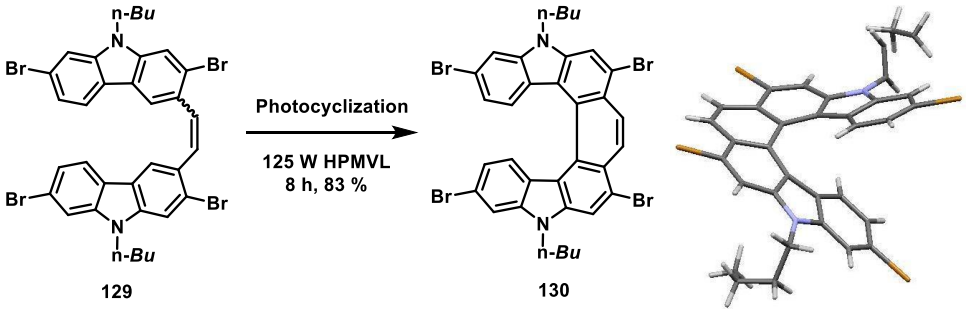
To confirm the decomposition due to iodine, we set up similar experiment with cyclohexene as an oxidizing agent in place of iodine. To our surprise no product could be isolated except the unidentifiable multiple decomposition products, this further confirms photosensitivity of olefin itself **117**. So we failed to synthesize desired bis aza[7]helicene **93** using this approach to block the positions using methoxy group.

Approach 4: As the literature suggests bromo functionality can survive photocyclization conditions and can effectively act as blocking group. It can also serve to solve the electron density problem making us to shift from bromo to methoxy group which .we faced in our approach 3. This scheme begins with the reported synthesis of 2, 7-dibromo carbazole **124**. Nitration of 4,4`-dibromobiphenyl **122** with concentrated nitric acid in glacial acetic acid gave the 2-nitro compound **123** in 75% yield. A modified reductive Cadogan ring-closure with triphenyl phosphine in high boiling point *o*-dichlorobenzene solvent then produced the 2,7-dibromo carbazole **124** in 81% yield. In order to have good solubility, compound **124** was alkylated using butyl bromide to get compound **125** in 94% yield. Compound **125** was then subjected to Vilsmeir-Haack formylation to get monoformylated derivative **126** followed by its reduction using $NaBH_4$ and passed through a filter column to get alcohol **127** in 79% yield. Similar to our approach 3 this was treated with triphenyl phosphine hydrobromide reagent in dichloromethane to get Wittig salt **128** in quantitative yield. (**Scheme 3.43**)



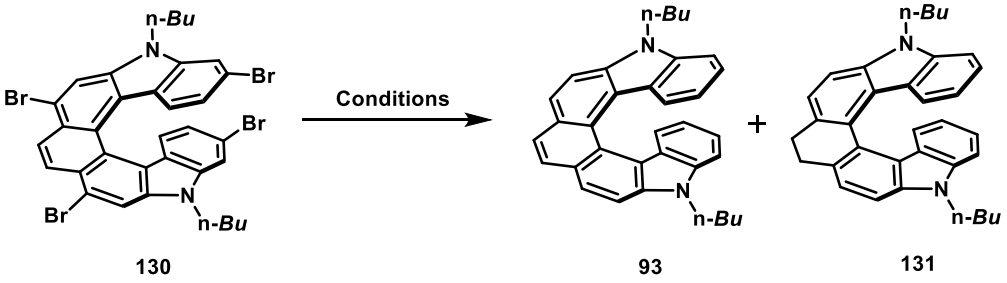
Scheme 3.43: Synthesis of tetra bromo olefin **129**.

2,7- dibromo 3-formyl *N*-butyl carbazole **126** and Wittig salt of carbazole **128** was then subjected to Wittig Olefination in THF solvent with NaH base to get tetra bromo olefin **129** in good yield of 79% which was then subjected to photocyclization. To our delight we got the desired bis aza[7]helicene **130** in an excellent yield of 83% (**Scheme 3.44**). Its structure was confirmed by spectral analysis and single crystal X-ray analysis.



Scheme 3.44: Synthesis of compound **130** and its ORTEP plot.

After the successful synthesis of desired helical framework **130** the last target was to remove the bromo functional group to get the desired target molecule **93**. First condition was simple reductive dehalogenation using palladium on charcoal in presence of hydrogen at room temperature (entry 1, table 3.3) gave us mixture of products, one the desired dehalogenated product **93** in 57% yield along with a intense blue fluorescent over saturated product **131** in which central benzene ring also hydrogenated in 17% yield. (**Scheme 3.45**)



Scheme 3.45: Synthesis of bis aza[7]helicene **93**.

Another condition for dehalogenation was tried using radical reducing agent Tributyltin hydride in high equivalents (20%) with catalytic amount of Azobisisobutyronitrile (AIBN) under reflux in toluene (entry 2, **Table 3.3**). This method gave 77% yield. Third method for debromination was palladium catalyzed dehalogenation to get 81% yield. (entry 3, **Table 3.3**)

Entry	Conditions	Yield (**93**)	Yield (**131**)
1.	Palladium on charcoal (10%), hydrogen, rt, 2-3h	57	17
2.	Bu_3SnH (20 equiv.), AIBN (10 mol%), toluene reflux, 24h	77	0
3.	$Pd(OAc)_2$ (10 mol%), PPh_3(40 mol%), K_2CO_3 (8.0 equiv.), toluene:n-butanol mixture reflux, 8h	81	0

Table 3.3: Various conditions for dehalogenation for compound **130**.

3.7 Conclusion:

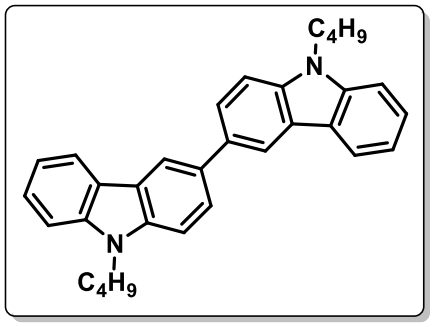
In summary bi-aza[5]helicene and bi-aza[6] helicenes have been synthesized using photocyclization. The target compounds were characterized and their photophysical properties were studied; also the effect of solvents on their photophysical properties was presented.

In another part we mainly focused on the preparation of challenging bis-carbazole based target molecules. In this course of study we found an interesting reaction of converting mono formyl carbazole directly in to dihydroxy bis-carbazole using H_2O_2 in presence of acid catalyst. Detailed mechanistic investigation is currently under progress. This strategy was utilized for synthesis of various bis aza[7]helicenes.

Different attempts to prepare the desired bis carbazole helicene have been presented. The study of photophysical properties of various bis-aza[7]helicene derivatives are currently under progress.

3.8 Experimental procedures:

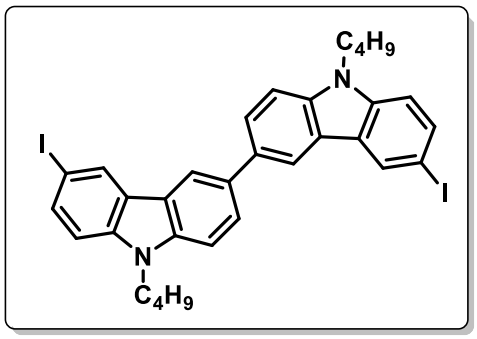
9,9'-Dibutyl-9*H*, 9'*H*-3,3'-bicarbazole (54):



In a round bottom flask 9-butyl carbazole **53** (0.5 g, 2.24 mmol) was dissolve in $CHCl_3$ (10 mL). The reaction temperature was maintained at 0°C and $FeCl_3$ (1.453 g, 8.96 mmol) was added slowly. After addition of $FeCl_3$ the reaction mixture was stirred at room temperature for further 3 h and then filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford 9 ,9'-dibutyl-9*H*, 9'*H*-3, 3'-bicarbazole **54** (0.736 g, 74%) as thick colorless liquid which solidifies under vacuum. m.p.= 116-117 °C. The analytical data were in complete agreement with the previously published data.[37a]

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 2H), 8.22 (d, *J* = 7.6 Hz, 2H), 7.86 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.54-7.45 (m, 6H), 7.30-7.26 (m, 2H), 4.38 (t, *J* = 7.2 Hz, 4H), 1.97- 1.90 (m, 4H), 1.50-1.44 (m, 4H), 1.0 (t, *J* = 7.2 Hz, 6H).

9,9'-Dibutyl-6, 6'-diiodo-9*H*,9'*H*-3,3'-bicarbazole (55)

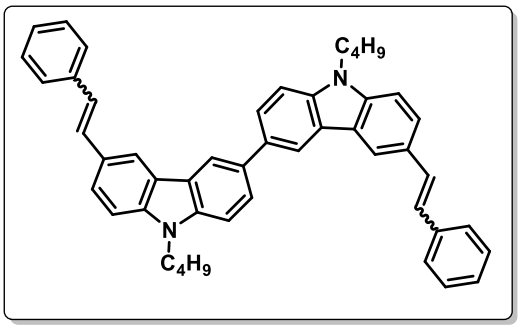


9, 9'-dibutyl-9*H*, 9'*H*-3,3'-bicarbazole **54** (1.732 g, 3.89 mmol) was dissolved in acetic acid (30 mL). To this stirred solution KIO_3 (0.549 g, 2.56 mmol) and KI (0.859 g, 5.177 mmol) was added and continued to stir at 80-90 °C for 16 h. Reaction mixture was cooled and poured into water and neutralized using $NaHCO_3$. The product was extracted in ethyl acetate and it was washed with sodium thiosulfate. Organic phase was dried over sodium sulfate and concentrated under vacuum. The crude product was purified through column chromatography on silica gel using petroleum ether as eluent to afford 9,9'-dibutyl-6,6'-diiodo-9*H*,9'*H*-3,3'- bicarbazole **55** (1.785 g, 67 %)

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, *J* = 1.6 Hz, 2H), 8.34 (d, *J* = 1.6 Hz, 2H), 7.84 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.73 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2H), 7.51 (d, *J* = 8.4

Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 4H), 1.93-1.86 (m, 4H), 1.48-1.38 (m, 4H), 1.00-0.98 (t, *J* = 7.2 Hz, 6 H).

9,9'-Dibutyl-6, 6'-di((*E*)-styryl)-9*H*, 9'*H*-3,3'-bicarbazole (58):



A solution of palladium acetate (0.0016 g, 0.00718 mmol, 2 mol%) and 1.3-bis(diphenylphosphinopropane) (0.0059 g, 0.0143 mmol, 4 mol%) was prepared in *N,N*-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until a homogeneous solution was obtained. This catalyst solution was repeatedly purged by N_2 prior to use. A two neck round bottom flask was charged with 9,9`-dibutyl-6,6`-diiodo-9*H*, 9`*H*,3,3`-bicarbazole **55** (0.25 g, 0.35 mmol), dry potassium carbonate (0.197 g, 1.43 mmol), TBAB (0.023 g, 0.0718 mmol, 20 mol%) and *N,N*-dimethylacetamide (10 mL). The solution was repeatedly purged with N_2. Styrene **56** (0.089 g, 0.089 mmol) was added at 60 °C and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added dropwise and the mixture was heated to 140 °C for 48 h. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 100 mL). The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (90:10) as eluent to afford *cis-trans* mixture of 9,9`-dibutyl-6,6`-distyryl-9*H*,9`*H*-3,3`-bicarbazole **58** as light yellow solid. Yield = 0.155g (67%). m.p. = 186-188 ºC

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 1.6 Hz, 1H), 8.37 (d, *J* = 1.2 Hz, 1H), 7.88-7.86 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.71-7.68 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.60 (d, *J* = 7.2 Hz , 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45-7.35 (m, 4H), 7.27-7.19 (m, 1H), 7.27-7.19 (m, 1), 4.40-4.37 (t, *J* = 7.2 Hz, 2H), 1.98-1.90 (m, 2H), 1.52-1.42 (m, 2H), 1.02-0.98 (t, *J* = 7.6 Hz, 3H).

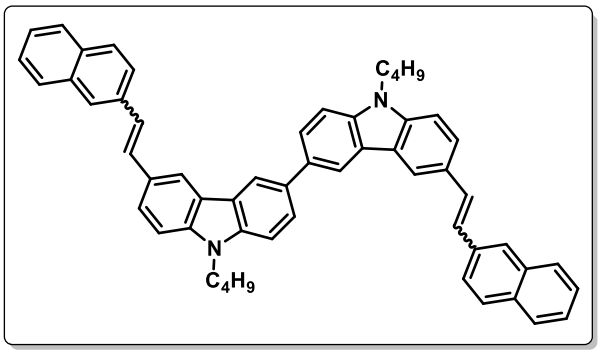
IR (KBr): 3021, 2959, 2930, 2867, 2401, 1676, 1654, 1479, 1214, 960, 885, 757, 691 $cm.^{-1}$

HRMS (TOF MS ES+): *m/z* calculated for $C_{48}H_{45}N_2$ $[M+H]^+$ 649.3579, Observed = 649.3577.

9,9'-Dibutyl-6, 6'-bis(2-(naphthalen-2-yl)vinyl)-9*H*, 9'*H*-3,3'-bicarbazole (59):

Reaction was performed in the same manner as for compound **58.**

Yield = 62%; Physical State = Light yellow solid; m.p. = 238-240 ^oC.

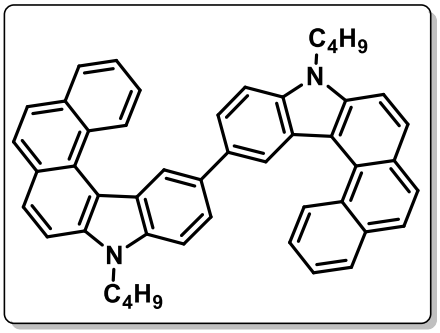


^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.51–8.40 (m, 2H), 7.93-7.61 (m, 6H), 7.56-7.39 (m, 6H), 4.41-4.38 (m, 2H), 1.97-1.59 (m, 2H), 1.48-1.46 (m, 2H), 1.03-0.98 (m, 3H).

IR (KBr): 3027, 2950, 2930, 2847, 1670, 1650, 1390, 1221, 1157, 970, 760 $cm.^{-1}$

HRMS (TOF MS ES+): *m/z* calculated for $C_{56}H_{49}N_2$ $[M+H]^+$ 749.3892, Observed = 749.3890.

9,9'-Dibutyl-bi aza[5]helicene (60):



A solution of of 9,9`-dibutyl-6,6`-distyryl-9*H*,9`*H*-3,3`-bicarbazole **58** (0.110 g, 0.169 mmol), iodine (0.094 g, 0.371 mmol), THF (1.21 g, 1.35 mL, 16.9 mmol) and toluene (610 mL) was irradiated using a 125W HMPV lamp for 15 h monitored by TLC. After the completion of reaction, the excess of iodine was removed by washing the solution with aqueous sodium thiosulfate followed by distilled water. The organic layer was concentrated under the reduced pressure to obtain the crude product. The crude product purified by column chromatography over silica gel using petroleum ether: ethyl acetate (90:10) as eluent to obtained **60** as light brown solid. Yield = 0.044 g (41%); m.p. = < 250 ^oC.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.54 (d, *J* = 8.4 Hz, 1H), 9.21 (d, *J* =1.6 Hz, 1H), 7.98-7.94 (m, 3H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.69 (d, J=8.4 Hz, 1H), 7.50-7.47 (m, 1H), 7.25-7.23 (m, 1H), 4.57-4.53 (t, *J* = 7.2 Hz, 2H), 2.07-1.98 (m, 2H), 1.57-1.52 (m, 2H), 1.06-1.02 (t, *J* = 7.6 Hz, 3H).

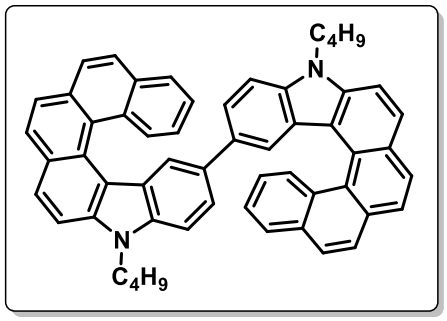
^{13}C-NMR (100 MHz, $CDCl_3$):

δ 140.6, 139.2, 133.1, 133.0, 129.4, 128.08, 128.05, 127.6, 127.4, 127, 126.7, 124.9, 12 4.3, 124.2, 123.9, 122.4, 116.8, 110.1, 109.4, 43.1, 31.4, 20.6, 13.99 (one peak was missing).

IR (KBr): ν 3042, 2954, 2864, 2384, 1701, 1608, 1523, 1469, 1338, 1274, 1212, 894, 824, 794, 752, 690, 634 cm.$^{-1}$

HRMS (TOF MS ES$^+$): *m/z* calculated for: $C_{48}H_{40}N_2Na$ $[M+Na]^+$ 667.3085, Observed: 667.3084.

9, 9`-Dibutyl-bi aza[6]helicene (61):



Reaction was performed in the same manner as for compound **60**.

Yield = 32%, Physical state = Light brown solid; m. p. = < 250 ºC.

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 8.07 (d, J=8.8 Hz, 1H), 8.06-8.04 (m, 2H), 7.99-7.96 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.33 (d, J=8.4 Hz, 1H), 7.26-7.23 (m, 1H), 6.95-6.91 (m, 1H), 6.84 (d, *J* = 1.2, 1H), 6.74 (dd, J=8.8 and 2.0 Hz, 1H), 4.54 (t, *J* = 7.2 Hz, 2H), 2.07-2.02 (m,2H), 1.58-1.55 (m, 2H), 1.08 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR(100 MHz,$CDCl_3$): δ 140.2, 138.1, 132.2, 131.6, 131.3, 130.4, 128.8, 128.4, 127.9, 127.7, 127.2, 126.6, 126.1, 125.9, 125.5, 125.1, 124.0, 123.7, 123.3, 123.2, 118.1, 110.4, 108.0, 43.2, 31.5, 20.7, 14.0 ppm (One peak was missing)

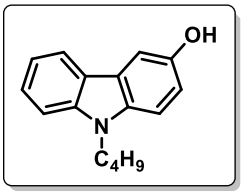
IR (KBr): ν 3043, 2957, 2901, 2857, 1691, 1600, 1527, 1341, 1275, 891, 783 cm.$^{-1}$

HRMS (TOF MS ES$^+$): *m/z* calculated for $C_{56}H_{45}N_2$ $[M+H]^+$ 745.3578, Observed=745.3577.

Dakin reaction for the synthesis of 9,9'-dibutyl-9*H*, 9'*H*-[4, 4'-bicarbazole]-3,3'-diol (80):

To a solution of 3-Formyl *N*-butyl carbazole **78** (2.0g, 7.96 mmol), in methanol (25 mL) was added aqueous solution of hydrogen peroxide (0.542 g, 1.80 mL,15.93 mmol, 30 % solution in water) and concentrated sulfuric acid (0.1 mL). After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using ethyl acetate pet ether (10:90) as eluent to obtain 3-hydroxy *N*-butyl carbazole **79** brown solid (0.8.g, 42%).

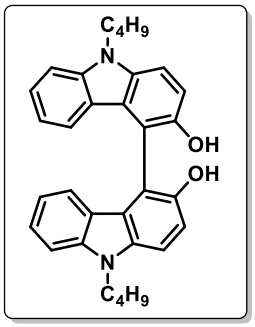
3-Hydroxy *N*-butyl carbazole (79):



^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.49-7.45 (m, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.22-7.18 (m, 1H), 7.05 (dd, *J* = 8.4 and 2.4 Hz, 1H), 4.91 (s, 1H), 4.28 (t, *J* = 7.2 Hz, 2H), 1.89-1.75 (m, 2H), 1.43-1.38 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.8, 141.0, 135.6, 125.7, 123.3, 122.3, 120.4, 118.2, 114.5, 109.2, 108.7, 105.9, 42.9, 31.1, 20.5, 13.9.

9,9'-Dibutyl-9*H*, 9'*H*-[4,4'-bicarbazole]-3,3'-diol (80):



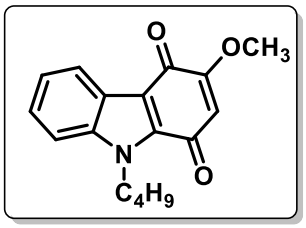
Yield = 0.4 g, 21%; Physical state = Brown solid.

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.32-7.28 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.79-6.75 (m, 1H), 4.96 (s, 1H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.98-1.91 (m, 2H), 1.52-1.44 (m, 2H), 1.02 (t, *J*=7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 147.6, 141.0, 135.8, 125.6, 121.8, 121.5, 121.0, 118.5, 114.7, 111.8, 110.5, 108.4, 43.0, 31.2, 20.6, 13.9.

HRMS: *m/z* calculated for $C_{32}H_{32}N_2O_2Na$ $[M+Na]^+$ 499.2357, Observed= 499.2356

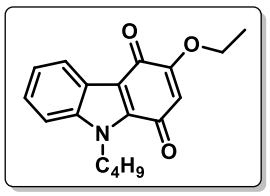
9-Butyl-3-methoxy-1*H*-carbazole-1,4-(9*H*)-dione (81):



Physical State = Orange solid.

^{1}H-NMR (400MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.46-7.37 (m, 3H), 5.73 (s, 1H), 4.61 (t, *J* =7.6 Hz, 3H), 3.89 (s, 3H), 1.85-1.77 (m, 2H), 1.46-1.36 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

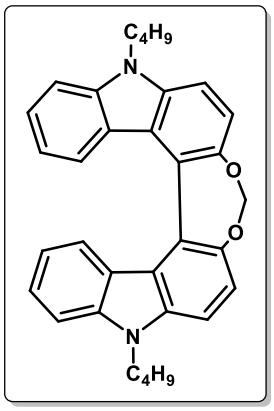
9-Butyl-3-ethoxy-1*H*-carbazole-1,4-(9*H*)-dione (81):



Physical State = Orange solid.

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.31–8.29(m, 1H), 7.47-7.45 (m, 1H), 7.44-7.40 (m, 1H), 7.39-7.35 (m, 1H), 5.73 (s, 1H), 4.63 (t, *J* = 7.6 Hz, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.85-1.81 (m, 2H), 1.55 (t, *J* = 7.2 Hz, 3H), 1.45-1.27 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H).

Helicenoid compound 85:

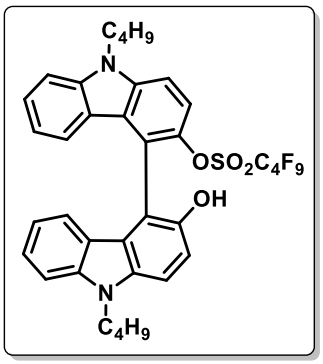


A solution of 9,9'-dibutyl-9*H*,9'*H*-[4,4'-bicarbazole]-3,3'-diol **80** (0.1 g, 0.21 mmol) in 10 mL of dry DMF were added Cs_2CO_3 (0.205 g, 0.63 mmol) and CH_2I_2 (0.085 g, 0.03 mL, 0.315 mmol), the mixture was stirred for 24 h at room temperature. After the completion of the reaction monitored by TLC the reaction mixture was poured in ice cold water. The aqueous was extracted with chloroform (3 x 50 mL) combine the extract and washed with water (2 x 50 mL) and the organic layer was dried over Na_2SO_4 and evaporated to obtained brown solid. The crude product was purified by column chromatography over silica gel using a gradient of petroleum ether/ethyl acetate (90:10) as eluent to obtain **85** as white solid (0.068 g, 67%)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.23-7.19 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.50-6.46 (m, 1H), 5.66 (s, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 2.07-1.94 (m, 2H), 1.51-1.46 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.9, 141.1, 138.3, 125.5, 125.3, 123.2, 122.2, 121.4, 118.4, 117.9, 109.0, 108.0, 103.7, 60.4, 43.0, 31.0, 20.6, 14.0.

Compound 86:

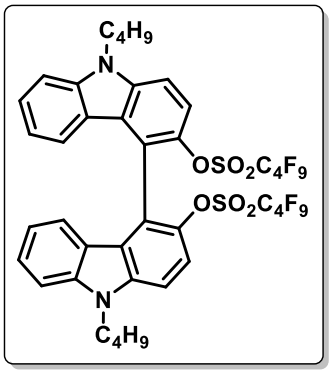


A mixture of 9,9'-dibutyl-9*H*,9'*H*-[4,4'-bicarbazole]-3,3'-diol **80** (0.2 g, 0.42 mmol) and triethylamine (0.063 g, 0.09 mL, 0.63 mmol) in acetonitrile (25 mL) was placed in a round bottom flask. To this solution was slowly added nonafluorobutanesulfonyl fluoride (0.14 g, 0.08 mL, 0.46 mmol) at room temperature. The reaction mixture was stirred at 60 ^{o}C for 8 hours. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using ethyl acetate pet ether (05:95) as eluent to obtain **86** solid brown solid (0.280.g, 88%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.41-7.38 (m, 3H), 7.36-7.33 (m, 1H), 7.30-7.26 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.89-6.85 (m, 1H), 6.75-6.70 (m, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 4.37 (t, *J* = 7.2 Hz, 2H), 1.98-1.90 (m, 4H), 1.51-1.42 (m, 4H), 1.03 (t, *J* = 7.6 Hz, 3H), 0.99 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.9, 141.5, 141.1, 141.0, 139.6, 135.8, 126.8, 125.2, 123.3, 122.4, 122.2, 122.1, 121.9, 121.1, 121.0, 119.8, 118.9, 118.0, 115.2, 113.0, 110.5, 109.7, 108.8, 108.5, 43.2, 42.9, 31.1, 20.6, 20.5, 13.9.

Compound 92:



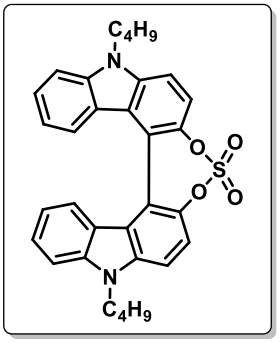
A mixture of 9,9'-dibutyl-9*H*,9'*H*-[4,4'-bicarbazole]-3,3'-diol **80** (0.2 g, 0.42 mmol) and triethylamine (0.127 g, 0.77 mL, 1.26 mmol) in acetonitrile (25 mL) was placed in a round bottom flask. To this solution was slowly added nonafluorobutanesulfonyl fluoride (0.381 g, 0.23 mL, 1.26 mmol) at room temperature. The reaction mixture was stirred at 60 ^{o}C for 8 hours. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over Na_2SO_4 and solvent removed in vacuo. The purification of compound was

performed by column chromatography over silica gel using ethyl acetate pet ether (05:95) as eluent to obtain **86** solid brown solid (0.362.g, 83%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.67–7.62 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.33-7.29 (m, 1H), 6.70-6.66 (m, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 2H), 1.96-1.92 (m, 2H), 1.59-1.39 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.4, 140.0, 139.1, 126.6, 122.1, 121.7, 121.3, 119.3, 118.4, 109.9, 108.8, 43.1, 30.9, 20.4, 13.8.

Helicenoid 87:



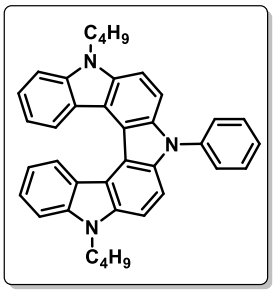
A mixture of **86** (0.25 g, 0.33 mmol), $Pd(OAc)_2$ (0.004 g, 0.016 mmol), xantphos (0.019 g, 0.033 mmol), anhydrous Cs_2CO_3 (0.215 g, 0.66 mmol) in toluene (15 mL) was placed in a 50 mL round bottom flask. The reaction mixture was refluxed for 8 hours under nitrogen atmosphere. The reaction mixture was cooled down to ambient temperature and was then diluted with toluene (10 mL). The resulting mixture was washed with water, extracted with toluene, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as an eluent to give **87** as white solid (0.09g, 51%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.70–7.65 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.31-7.26 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.56-6.52 (m, 1H) 4.46 (t, *J* = 7.2 Hz, 2H), 1.99-1.92 (m, 2H), 1.53-1.43 (m, 2H), 1.02 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 141.7, 141.3, 139.1, 126.5, 122.8, 121.6, 121.4, 121.0, 118.7, 118.6, 110.1, 108.7, 43. 2, 30.9, 20.6, 13.9.

Tri-aza[7]helicene (88):

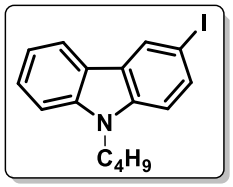


A mixture of **92** (0.5 g, 0.14 mmol), aniline (0.016 g, 0.015 mL, 0.17 mmol), $Pd(OAc)_2$ (0.002 g, 0.072 mmol), xantphos (0.008 g, 0.014 mmol), K_3PO_4 (0.092 g, 0.43 mmol) in toluene (15 mL) was placed in a 50 mL round bottom flask. The reaction mixture was refluxed for 72 hours under nitrogen atmosphere. The

reaction mixture was cooled down to ambient temperature and was then diluted with toluene (10 mL). The resulting mixture was washed with water, extracted with toluene, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude residue was roughly purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as an eluent to give **88** as brown sticky solid (0.003 g, less than 5%)

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.69-7.67 (m, 2H), 7.62-7.61 (m, 2H), 7.54-7.51 (m, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31-7.20 (m, 1H), 7.11-7.08 (m, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 4.51 (t, *J* = 6.8 Hz, 2H), 2.05-1.94 (m, 2H), 1.59-1.53 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H).

3-Iodo *N*-butyl carbazole (94):



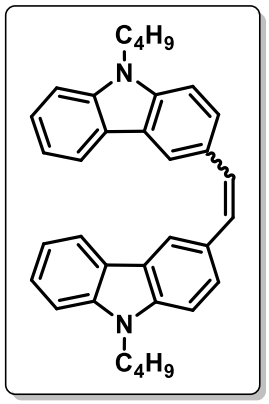
In a round bottom flask KIO_3 (0.632 g, 2.95 mmol) and KI (0.981 g, 5.91 mmol) was dissolved in 20 mL water. To this stirred mixture, solution of 9-butyl carbazole **53** (2 g, 8.96 mmol) in methanol was added slowly. After the solution became clear concentrated HCl (1.1 mL) was added dropwise and the reaction mixture was stirred rigorously. After addition of HCl oily mass was separated in the reaction mixture which was separated using separating funnel. It was washed with water and dissolved in ethyl acetate. The organic phase was washed with sodium thiosulfate and dried over sodium sulfate. Solvent was removed under vacuum and the crude product was purified through column chromatography on silica gel using petroleum ether as solvent. Pure product was isolated as brown oil (2.331 g, 74.52%). m.p.: 45 ^oC.

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.42 (d, *J* = 1.2, 1H), 8.05 (d, *J* = 7.6Hz, 1H), 7.72 (dd, *J* = 8.4Hz and *J* = 1.6Hz, 1H), 7.53-7.49 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29-7.25(m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 1.88-1.81 (m, 2H), 1.42-1.37 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

1,2-Bis(9-butyl-9H-carbazol-3-yl)ethane (95):

A solution of palladium acetate (0.004g, 0.014 mmol, 1.0 mol%) and 1.3-bis(diphenylphosphinopropane) (0.012 g, 0.028 mmol, 2 mol%) was prepared in *N,N*-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room

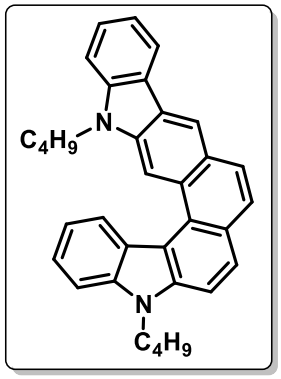
temperature until a homogeneous solution was obtained. This catalyst solution was repeatedly purged by N_2 prior to use.



A two neck round bottom flask was charged with 3-iodo-*N*-butylcarbazole **94** (0.5 g, 1.43 mmol), 3-formyl *N*-butyl carbazole **78** (0.43 g, 1.72 mmol), methyltriphenylphosphonium iodide (1.13 g, 2.8mmol), dry potassium carbonate (0.79 g, 5.7 mmol), tetrabutylammonium bromide TBAB (0.046 g, 0.14 mmol, 10 mol%) and *N,N*-dimethylacetamide (10 mL) and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether:ethyl acetate (95:5) as eluent to afford **95** as green solid (0.336 g, 50%); m.p. = 205-209 °C (Reported 207 °C)[37b]

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.30 (d, *J* = 1.2 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.75 (dd, *J* = 8.4 and 1.2 Hz, 1H), 7.50-7.38 (m, 4H), 7.33-7.26 (m, 1H), 4.34 (t, *J* = 7.2 Hz, 2H), 1.94-1.86 (m, 2H), 1.47-1.41 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

Unsymmetrical di-butyl diaza[7]helicene (96):

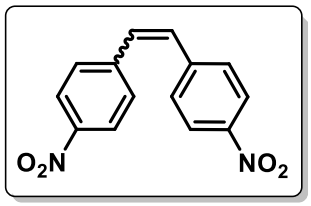


A solution of **95** (0.2 g, 0.42 mmol), iodine (0.12 g, 0.46 mmol), dry THF (1.53 g, 1.72 mL, 21.27 mmol) and toluene (350 mL) was irradiated using a 125W HMPV lamp (24 h monitored by TLC). After the completion of reaction, the excess of iodine was removed by washing the solution with aqueous $Na_2S_2O_3$ and water. The organic layer was concentrated under the reduced pressure to obtain the crude product. The crude product purified by column chromatography over silica gel using petroleum ether: ethyl acetate (95:05) as eluent to obtained a pale yellow solid (0.123 g; 62%), m. p. = 172-176 °C.

^{1}H-NMR (400MHz, $CDCl_3$): δ 9.39 (s, 1H), 9.02 (d, *J* = 8.0 Hz, 1H), 8.70 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 7.97-7.93 (m, 2H), 7.77-7.73 (m, 2H), 7.64-7.54 (m, 3H), 7.49 (d, *J*= 8.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.53 (t, *J* = 7.2 Hz, 2H), 4.44 (t, *J* = 7.2 Hz, 2H), 2.03-1.98 (m, 4H), 1.58-1.46 (m, 4H), 1.04 (t, *J* = 7.6 Hz, 3H), 0.96 (t, *J* = 7.6 Hz, 3H).

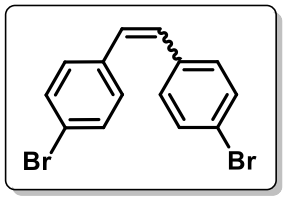
^{13}C-NMR (100 MHz, $CDCl_3$): δ 142.5, 140.2, 140.1, 139.1, 128.4, 128.0, 127.1, 127.0, 126.9, 126.6, 124.89, 124.83, 124.2, 123.8, 123.3, 122.7, 120.9, 118.7, 118.6, 117.6, 116.8, 109.5, 109.2, 108.5, 105.9, 43.3, 43.0, 31.3, 20.7, 20.6, 13.99, 13.97.

4,4'-Dinitro stilbene (99):



To a solution of *p*-nitrobenzaldehyde **98** (0.142 g, 0.95 mmol), (4-nitrobenzyl)triphenylphosphonium bromide **97** (0.5 g, 1.05 mmol) in dichloromethane (25 mL) was added piperidine (0.178 g, 0.20 mL, 2.09 mmol) drop wise at 0 ^oC. and reaction was stirred for 5 h at room temperature. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether:ethyl acetate (90:10) as eluent to afford **99** as yellow solid (0.144 g, 57%). The analytical data were in complete agreement with the previously published data.[37c]

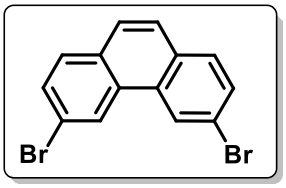
4,4'-Dibromo stilbene (103):



To a solution of p-bromobenzaldehyde **102** (0.328 g, 1.77 mmol), (4-bromobenzyl)triphenylphosphonium bromide **101** (1.0 g, 1.95 mmol) in dry methanol (25 mL) To this was added drop-wise, with stirring, a solution of (0.203 g, 8.86 mmol) sodium dissolved in 10 mL of dry methanol and the mixture was stirred for 5 hours at room temperature. After completion of reaction the methanol was evaporated under reduced pressure the mixture was poured into ice-cold water and extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with water, brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using

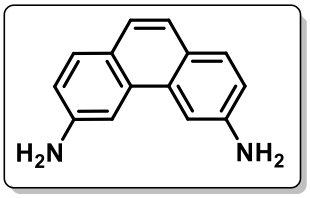
petroleum ether as eluent to afford **103** as white solid (0.485 g, 81%). m.p. = 211-214°C.

3,6-Dibromo phenanthrene (104):



A solution of 4,4'-dibromo stilbene **103** (0.4 g, 1.18 mmol), iodine (0.33 g, 1.30 mmol), dry THF (4.26 g, 4.79 mL, 59.17 mmol) and toluene (650 mL) was irradiated using a 125W HMPV lamp (24 h monitored by TLC). After the completion of reaction, the excess of iodine was removed by washing the solution with aqueous $Na_2S_2O_3$ and water. The organic layer was concentrated under the reduced pressure to obtain the crude product. The crude product purified by column chromatography over silica gel using petroleum ether as eluent to obtained **104** as white solid (0.314 g; 79%), m. p. = 188-191°C.

3,6-Diamino phenanthrene (105):

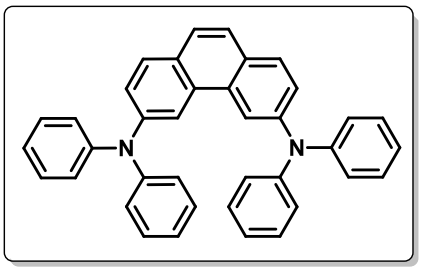


A mixture of copper powder (0.187 g, 3.0 mmol), 3,6-dibromo phenanthrene **104** (0.25 g, 0.74 mmol), 2-aminoethanol (0.226 g, 0.23 mL, 3.7 mmol), and $TMSN_3$ (0.345 g, 0.4 mL, 3.0 mmol) in DMA (10 mL) was stirred under nitrogen atmosphere at 95 °C. After complete consumption of starting material was confirmed by TLC analyses the mixture was diluted with EtOAc (10 mL) and then filtered through a Celite pad. The pad was successively washed with EtOAc (20 mL), H_2O (25 mL), and concentrated aqueous ammonia solution (5 mL). After the two layers were separated, the aqueous layer was extracted with EtOAc (3X25 mL). The combined organic phase was washed with water, brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether:ethyl acetate (50:50) as eluent to afford **10** as brown solid (0.057 g, 37%)

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.55 (d, *J* = 2.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 2H), 7.0 (dd, *J* = 8.4 and 2.4 Hz, 2H), 3.95 (s, 4H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 144.5, 130.7, 129.7, 126.0, 123.3, 116.9, 106.1.

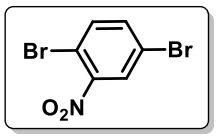
Compound 107:



To a 25 mL round bottom flask equipped with a magnetic stirrer, **105** (0.08 g, 0.38 mmol), cyclohexanone **106** (0.113 g, 0.12 mL, 1.15 mmol), $Pd(OAc)_2$ (0.017 g, 0.078 mmol, 20 mol%), $Cu(OAc)_2$ (0.455 g, 2.30 mmol) and PivOH (5 mL) and DMF (1 mL) were added.. The reaction mixture was then stirred under N2 atmosphere at 140 ^oC for 24 hours. After cooling to room temperature, the reaction mixture was diluted with saturated K_2CO_3 aqueous (30 mL), and extracted with EtOAc (3X50 mL), the combined organic layer was dried over Na_2SO_4, filtered, and evaporated under vacuum. The crude product purified by column chromatography over silica gel using petroleum ether: ethyl acetate (95:05) as eluent to obtained a greenish solid (0.140 g, 71%). The analytical data were in complete agreement with the previously published data.[37d]

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.90 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 7.33 (dd, *J* = 8.4 and 2.0 Hz, 1H), 7.28-7.21 (m, 4H), 7.12-7.10 (m, 4H), 7.05-7.02 (m, 2H).

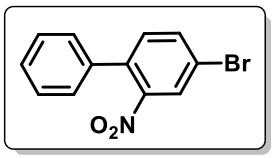
1,4-Dibromo-2-nitrobenzene (110):



1,4-Dibromobenzene **109** (10 g, 42.5 mmol) was disolved in dichloromethane (100 mL) with sulfuric acid (9.5 mL, 170 mmol) and nitration mixture (nitric acid (2.3 ml, 55.2 mmol) and sulfuric acid (4.7 mL, 63.5 mmol)) was added portion wise during 15 min. The mixture was stirred for next 6 h, quenched with 25% NaOH (5 ml) and diluted with dichloromethane (10 ml). The lower layer was separated and washed with dichloromethane (1 x 25 ml). Combined organic layers were washed with water (1 x 50 ml), brine (1 x 25 ml) and dried with sodium sulfate, filtered and concentrated in vacuo to give **110** as a yellow solid (17.0 g, 81%). The analytical data were in complete agreement with the previously published data.[37e]

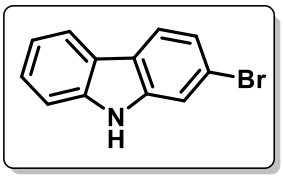
^{1}H-NMR (400MHz, $CDCl_3$): δ (d, *J* = 2.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (dd, *J* = 8.4 and 2.4 Hz, 1H).

4-Bromo-2-nitro-1,1'-biphenyl (111):



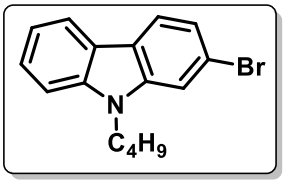
Phenylboronic acid (0.737 g, 6.05 mmol), 1,4-dibromo-2-nitrobenzene **110** (1.7 g, 6.05 mmol), $Pd(OAc)_2$ (0.027 g, 0.012 mmol), PPh_3 (0.062 g, 0.24 mmol) and K_2CO_3 (1.67 g, 12.1 mmol)were dissolved in a mixture of toluene:water (25:25 mL). The degassed mixture was refluxed for 8 h. After completion of reaction the mixture was poured into ice-cold water and extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with water, brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether as eluent to afford **111** as yellow viscous oil (1.23 g, 73%). The analytical data were in complete agreement with the previously published data.[37f]

2-Bromo-9*H*-carbazole (112):



A solution of 4-bromo-2-nitro-1,1'-biphenyl **111**(1.0 g, 3.59 mmol) and PPh_3 (2.35 g, 8.99 mmol) in *o*-dichlorobenzene (25 mL) was heated to reflux with vigorous stirring for 8 h, during which time the color changed from yellow to brown. After completion of reaction, the mixture was cooled to room temperature. The crude product was directly loaded on silica gel and purified by using column chromatography using petroleum ether:ethyl acetate (90:10) as eluent to afford **112** as yellow solid (0.672 g, 76%). The analytical data were in complete agreement with the previously published data.[37f]

2-Bromo *N*-butyl carbazole (113):



In a round bottom flask carbazole (0.6 g, 2.43 mmol) was added into the solution of KOH (0.82 g, 14.63 mmol) in 30 mL acetone at the conditions of stirring and room temperature. After 1 h 1- bromobutane (0.50 g, 0.35 mL, 3.65 mmol) was added to the reaction mixture and then maintained for 6 h. The final reaction mixture was concentrated under vacuum and then poured into 100 mL water. The product was extracted with ethyl acetate (50 x 3 mL). Ethyl acetate layer was washed with water twice, dried over sodium sulfate and concentrated under vacuum. The crude product

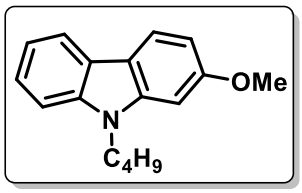
was purified by column chromatography on silica gel using petroleum ether as a eluent to afford **113** as white solid (0.63 g, 86%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.08 (dd, *J* = 8.0 and 1.2 Hz, 1H), 7.96 ((d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.53-7.48 (m, 1H), 7.42 ((d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4 and 1.6 Hz, 1H), 7.28-7.24 (m, 1H), 4.27 (t, *J* = 7.2 Hz, 2H), 1.90-1.82 (m, 2H), 1.45-1.37 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 141.2, 140.5, 126.0, 122.3, 121.8, 121.7, 121.5, 120.3, 119.3, 119.2, 111.7, 108.9, 43. 0, 31.0, 20.5, 13.9.

2-Methoxy *N*-butyl carbazole (114):

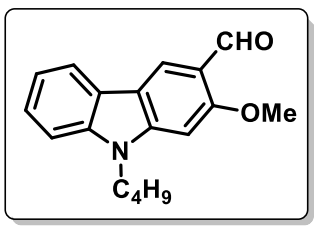


To a stirred solution of 2-Bromo *N*-butyl carbazole **113** (0.6 g, 1.98 mmol) and CuBr (0.142 g, 0.99 mmol) in dry DMF (25 mL) was added solution of sodium (0.29 g, 9.93 mmol dissolved in 10 mL in dry methanol) and the reaction mixture was stirred at 70 °C under nitrogen for 5 h. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (90:10) as eluent to afford **114** as brown viscous oil (0.397 g, 79%)

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.44-7.38 (m, 2H), 7.25-7.21 (m, 1H), 6.90-6.87 (m, 2H), 4.27 (t, *J* = 7.2 Hz, 2H), 3.97 (s, 3H), 1.91-1.84 (m, 2H), 1.49-1.39 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.9, 141.8, 140.6, 124.3, 123.0, 121.0, 119.5, 118.8, 116.8, 108.4, 106.8, 93.2, 55.7, 42.8, 31.0, 20.6, 13.9.

3-Formyl 2-Methoxy *N*-butyl carbazole (115):



In a dry two neck round bottom flask phosphoryl chloride (1.21 g, 0.73 mL, 7.90 mmol) was added slowly in DMF (1.44 g, 1.52 mL, 19.76 mmol) which was purged with nitrogen and cooled to 0 °C. The reactant was warmed to room temperature and stirred for 1 hour and cooled again to

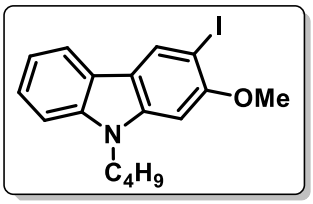
0 ºC. To this mixture was added 2-Methoxy *N*-butyl carbazole **114** (1.0 g, 3.95 mmol) in 1, 2-dichloroethane (25 mL). In 1 hour, the reaction temperature was raised to 90 ºC and then kept for 8 hours. The cooled solution was poured in to ice water and extracted with dichloromethane (3X50 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated at reduced pressure. The purification of compound was performed by column chromatography over silica gel using 20 % ethyl acetate pet ether as eluent to obtain light brown solid (0.85 g, 77%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 10.49 (s, 1H), 8.58 (s, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 1H), 6.75 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 1.91-1.83 (m, 2H), 1.48-1.38 (m, 2H), 0.99 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 189.4, 161.6, 147.7, 141.1, 125.5, 123.4, 121.7, 120.4, 120.1, 118.3, 116.9, 109.0, 90. 3, 55.9, 43.0, 30.8, 20.5, 13.8.

3-Iodo 2-Methoxy *N*-butyl carbazole (116):

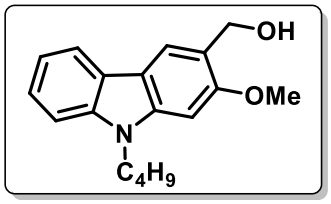


In a round bottom flask KIO_3 (0.140 g, 0.65 mmol) and KI (0.164 g, 0.98 mmol) was dissolved in 10 mL water. To this stirred mixture, solution of 2-Methoxy *N*-butyl carbazole **114** (0.5 g, 1.97 mmol) in methanol (10 mL) was added slowly and stirring was continued for 1 h at room temperature. To this reaction mixture concentrated HCl (1.1 mL) was added dropwise and the reaction mixture was stirred rigorously for 1 hour. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with sodium thiosulfate, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether: ethyl acetate (95:05) as eluent to afford **116** as light green solid (0.532 g, 71%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.45-7.41 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 1H), 6.83 (s, 1H), 4.26 (t, *J* = 7.2 Hz, 2H), 4.02 (s, 3H), 1.89-1.82 (m, 2H), 1.45-1.36 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.3, 141.7, 140.3, 130.7, 124.8, 121.7, 119.6, 119.3, 118.8, 108.6, 91.5, 75.0, 56.6, 42.8, 30.9, 20.5, 13.9.

(9-Butyl-2-methoxy-9*H*-carbazol-3-yl)methanol (118):

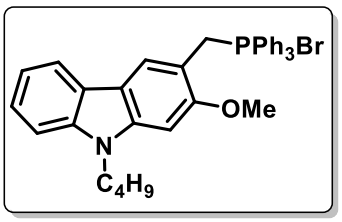


To a solution of 3-Formyl 2-Methoxy *N*-butyl carbazole **115** (0.5 g, 1.78 mmol) in methanol (10 mL) and THF (5 mL) was added $NaBH_4$ (0.067 g, 1.78 mmol), the resultant solution was stirred for 30 minutes at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over anhyd. Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 10 % ethyl acetate pet ether as eluent to obtain white solid (0.417 g, 83%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.02 (dd, *J* = 6.8 and 0.4 Hz, 1H), 7.97 (s, 1H), 7.44-7.38 (m, 2H), 7.26-7.22 (m, 1H), 6.85 (s, 1H), 4.86 (s, 2H), 4.29 (t, *J* = 7.2 Hz, 2H), 4.02 (s, 3H), 2.45 (s, 1H), 1.91-1.83 (m, 2H), 1.46-1.39 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.2, 141.3, 140.3, 124.2, 123.0, 121.2, 121.0, 119.5, 119.0, 115.7, 108.5, 90.8, 62.9, 55.6, 42.8, 31.0, 20.5, 13.9.

Wittig salt of (9-butyl-2-methoxy-9*H*-carbazol-3-yl)methanol (119):

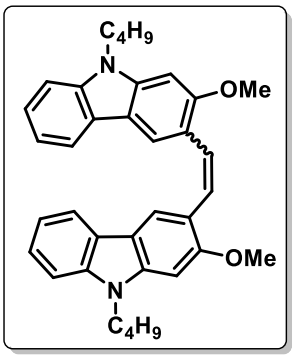


To a solution of (9-butyl-2-methoxy-9*H*-carbazol-3-yl)methanol **118** (0.4 g, 1.41 mmol) in dichloromethane (10 mL) was added triphenylphosphine hydrobromide PPh_3.HBr (0.507 g, 1.48 mmol), the resultant solution was stirred for 8 h at room temperature under nitrogen. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was washed with cold petroleum ether, dried to get light brown solid (0.85 g, quant.) which was used directly in the next step without any purification.

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.92-7.66 (m, 7H), 7.64-7.56 (m, 18H), 7.52-7.33 (m, 6H), 7.19-7.15 (m, 1H), 5.15 (d, *J* = 12.4 Hz, 2H), 4.24 (t, *J* = 7.2 Hz, 2H), 1.79-1.36 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.2, 141.3, 14.3, 124.2, 123.0, 121.2, 121.0, 119.5, 119.0, 115.7, 108.5, 90.8, 62.9, 55.6, 42.8, 31.0, 20.5, 13.9.

1,2-Bis(9-butyl-2-methoxy-9*H*-carbazol-3-yl)ethane (117):



Method A One pot Wiitig-Heck reaction: A solution of palladium acetate (0.004g, 0.018 mmol, 2 mol%) and 1.3-bis(diphenylphosphinopropane) (0.016 g, 0.037 mmol, 4 mol%) was prepared in *N,N*-dimethylacetamide (5 mL) under nitrogen atmosphere. The mixture was stirred at room temperature until a homogeneous solution was obtained. This catalyst solution was repeatedly purged by N_2 prior to use.

A two neck round bottom flask was charged with 3-iodo 2-methoxy *N*-butyl carbazole **116** (0.35 g, 0.93 mmol), 3-formyl 2-methoxy *N*-butyl carbazole **115** (0.286 g, 1.02 mmol), methyltriphenylphosphonium iodide (1.0 g, 2.55 mmol), dry potassium carbonate (0.643 g, 4.65 mmol), tetrabutylammonium bromide TBAB (0.060 g, 0.18 mmol, 20 mol%) and *N,N*-dimethylacetamide (10 mL) and the mixture was heated up to 100 °C. When the temperature reached 100 °C, the previously prepared Pd catalyst solution was added drop wise and the mixture was heated to 140 °C for 48 h. After the completion of the reaction, the mixture was poured in ice-cold water and extracted with dichloromethane (3 x 50 mL). The combined organic phase was washed with water, brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether:ethyl acetate (95:5) as eluent to afford **117** as yellow solid (0.107 g, 22%)

Method B Wittig reaction:

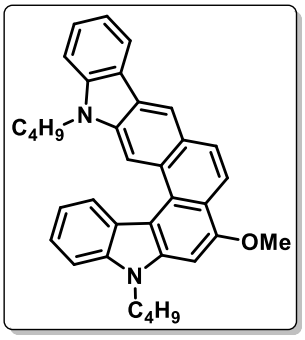
To a suspension of methyltriphenylphosponium bromide of 2-methoxy *N*-butyl carbazole **119** (0.79 g, 1.28 mmol) in dry THF (10 mL) at 0 °C under nitrogen was added NaH (0.085 g, 2.13 mmol, 60% in mineral oil) followed by 3-Formyl 2-Methoxy *N*-butyl carbazole **115 (**0.3 g, 1.06 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred for 6 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over anhydrous Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 10 % ethyl acetate pet ether as eluent to obtain **117** as yellow solid (0.214g, 51%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.43-7.37 (m, 2H), 7.26-7.22 (m, 1H), 6.86 (s, 1H), 4.30 (t, J=7.2 Hz, 2H), 4.07 (s, 3H), 1.93-1.86 (m, 2H), 1.58-1.40 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.7, 141.0, 140.6, 124.2, 123.3, 122.3, 120.5, 119.7, 118.9, 117.7, 116.5, 108.5, 90.9, 56.0, 42.8, 31.0, 20.5, 13.9.

Photocyclization of 1,2-bis(9-butyl-2-methoxy-9*H*-carbazol-3-yl)ethane (117):

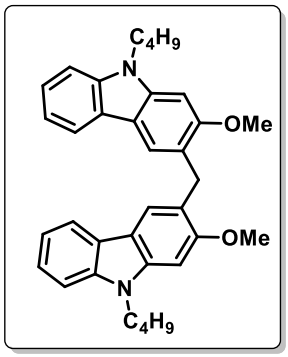
In an immersion wall photoreactor (borosilicate glass) equipped with a water cooling jacket and a stir bar, 1,2-bis(9-butyl-2-methoxy-9*H*-carbazol-3-yl)ethane **117** (0.1 g, 0.19 mmol), iodine (0.053 g, 0.20 mmol), THF (0.68 g, 0.76 mL, 9.43 mmol) were dissolved in toluene (350 mL). Nitrogen gas was bubbled through the solution within 10 minutes under sonication for removing the dissolved oxygen prior to irradiation using a 125W HPMV lamp (6 h monitored by TLC). After the completion of reaction, the excess of iodine was removed by washing the solution with aqueous sodium thiosulfate, followed by distilled water. The organic layer was concentrated under the reduced pressure to obtain the crude product. The crude product purified by column chromatography over silica gel using petroleum ether: ethyl acetate (98:2) as eluent to obtained **120** as yellow solid (0.005 g, 5%).



^{1}H-NMR (400MHz, $CDCl_3$): δ 9.34 (s, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.68 (s, 1H), 8.31 (d, *J* = 7.6 Hz, 1H), 8.22 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.59-7.56 (m, 2H), 7.49-7.45 (m, 2H), 7.33-7.29 (m, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.10 (s, 1H), 4.49 (t, *J* = 7.2 Hz, 2H), 4.43 (t, *J* = 7.2 Hz, 2H), 4.20 (s, 3H), 2.04-1.97 (m, 4H), 1.53-1.43 (m, 4H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.5, 142.6, 140.7, 139.9, 139.1, 128.9, 128.2, 127.3, 126.7, 124.4, 124.3, 124.2, 123.3, 122.7, 122.5, 120.9, 119.2, 118.7, 118.5, 117.7, 117.5, 110.5, 108.8, 108.5, 106.2, 89.8, 56.1, 43.3, 42.9, 31.31, 20.7, 20.6, 13.99, 13.94.

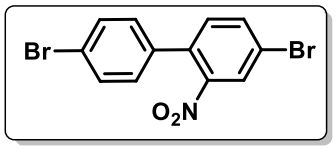
Compound 121:



^{1}H-NMR (400MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.76 (s, 2H), 7.38-7.33 (m, 4H), 7.16-7.12 (m, 2H), 4.30 (t, *J* = 7.6 Hz, 4H), 4.27 (s, 2H), 4.0 (s, 6H), 1.93-1.85 (m, 4H), 1.50-1.41 (m, 4H), 0.99 (t, *J* = 7.6 Hz, 6H).

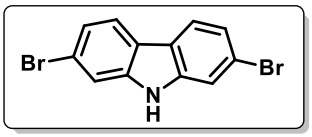
^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.3, 140.3, 140.2, 123.7, 123.1, 121.9, 121.7, 119.4, 118.4, 115.7, 108.2, 90.8, 55.8, 42.8, 31.1, 30.5, 20.6, 13.9.

4, 4'-Dibromo-2-nitrobiphenyl (123):

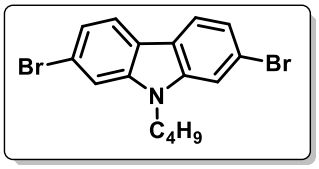


4,4'-Dibromobiphenyl **122** (5.0 g, 16 mmol) was suspended in glacial acetic acid (30 mL) and, concentrated nitric acid (20 mL, 67% w/v). The resulting mixture was refluxed for 8 h. After the completion of reaction, the mixture was cooled to room temperature and poured into ice cold water. The obtained yellow color solid crude product was filtered and washed with water and dried to obtain **123** as yellow solid (4.33 g, 75%). The analytical data were in complete agreement with the previously published data.[37g]

2, 7-Dibromo carbazole (124):



A solution of 4,4'-Dibromo-2-nitrobiphenyl **123** (3.0 g, 8.40 mmol) and PPh_3 (5.5 g, 21.0 mmol) in *o*-dichlorobenzene (30 mL) was heated to reflux with vigorous stirring for 8 h, during which time the color changed from yellow to brown. After completion of reaction, the mixture was cooled to room temperature. The crude product was directly loaded on silica gel and purified by using column chromatography using petroleum ether:ethyl acetate (90:10) as eluent to afford **124** as brown solid (02.21 g, 81%). The analytical data were in complete agreement with the previously published data.[37g]**2, 7-Dibromo *N*-butyl carbazole (125):**

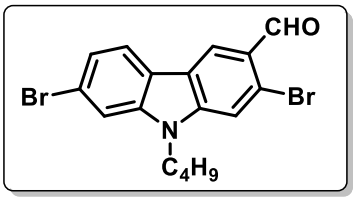


In a round bottom flask 2, 7-Dibromo carbazole **124** (2.0 g, 6.15 mmol) was added into the solution of KOH (2.0 g, 36.92 mmol) in 30 mL acetone at the conditions of stirring

and room temperature. After 1 h 1- bromobutane (1.26 g, 1.0 mL, 9.23 mmol) was added to the reaction mixture and then maintained for 6 h. The final reaction mixture was concentrated under vacuum and then poured into 100 mL water. The product was extracted with ethyl acetate (50 x 3 mL). Ethyl acetate layer was washed with water twice, dried over sodium sulfate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether as a eluent to afford **113** as white solid (2.20 g, 94%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 2H), 7.35 (dd, *J* =8.0 and 1.2 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 2H), 1.87-1.80 (m, 2H), 1.57-1.36 (m, 2H), 0.98 (t, *J* = 7.6 Hz, 3H).

2,7-Dibromo 3-Formyl *N*-butyl carbazole (126):



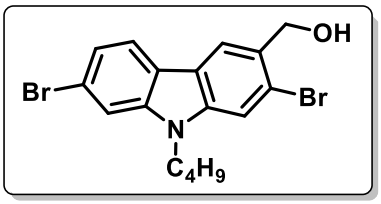
In a dry two neck round bottom flask phosphoryl chloride (2.33 g, 1.42 mL, 15.2 mmol) was added slowly in DMF (2.77 g, 2.92 mL, 38.02 mmol) which was purged with nitrogen and cooled to 0 ^{o}C. The reactant was warmed to room temperature and stirred for 1 hour and cooled again to 0 ^{o}C. To this mixture was added 2,7-Dibromo *N*-butyl carbazole **125** (2.9 g, 7.61 mmol) in 1, 2-dichloroethane (30 mL). In 1 hour, the reaction temperature was raised to 90 ^{o}C and then kept for 8 hours. The cooled solution was poured in to ice water and extracted with dichloromethane (3X100 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated at reduced pressure. The purification of compound was performed by column chromatography over silica gel using 10 % ethyl acetate pet ether as eluent to obtain light brown solid (2.2 g, 71%)

^{1}H-NMR (400MHz, $CDCl_3$): δ 10.4 (s, 1H), 8.65 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.43 (dd, *J* = 8.4 and 1.6 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.90-1.82 (m, 2H), 1.47-1.40 (m, 2H), 1.38 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 191.7, 144.3, 142.1, 125.3, 124.5, 124.0, 122.6, 122.1, 122.1, 121.7, 120.9, 113.2, 11 2.6, 43.5, 30.8, 20.5, 13.8.

(2, 7-Dibromo-9-butyl-9*H*-carbazol-3-yl)methanol (127):



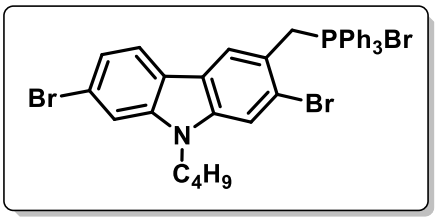
To a solution of 2,7-Dibromo 3-Formyl *N*-butyl carbazole **126** (1.0 g, 2.44 mmol) in methanol (20 mL) and THF (10 mL) was added $NaBH_4$ (0.092 g, 2.44 mmol), the resultant solution was stirred for 30 minutes at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over anhyd. Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 20 % ethyl acetate pet ether as eluent to obtain **127** as white solid (0.794 g, 79%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.91 (d, *J* =8.4 Hz, 1H), 7.61 (s, 1H), 7.54 (d, *J* = 1.2 Hz, 1H), 7.36 (dd, *J* = 8.0 and 1.6 Hz, 1H), 4.92 (d, *J* = 4.4 Hz, 2H), 4.21 (t, *J* = 7.2 Hz, 2H), 2.12-1.80 (m, 2H), 1.45-1.35 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$):

δ 141.5, 140.7, 130.3, 122.6, 121.8, 121.6, 121.2, 120.9, 120.4, 119.8, 112.9, 112.1, 65. 7, 43.2, 30.9, 20.5, 13.8.

Wittig salt of (2,7-Dibromo-9-butyl-9*H*-carbazol-3-yl)methanol (128):



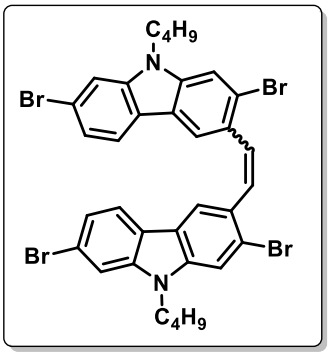
To a solution of 2,7-Dibromo-9-butyl-9*H*-carbazol-3-yl)methanol **127** (0.5 g, 1.21 mmol) in dichloromethane (10 mL) was added triphenylphosphine hydrobromide PPh_3.HBr (0.437 g, 1.27 mmol), the resultant solution was stirred for 8 h at room temperature under nitrogen. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was washed with cold petroleum ether, dried to get light brown solid (0.87 g, quant.) which was used directly in the next step without any purification.

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.22 (d, *J* = 2.8 Hz, 1H), 7.81-7.73 (m, 4H), 7.68-7.61 (m, 13H), 7.55 (dd, *J* = 7.6 and 1.2 Hz, 1H), 7.46 (d, *J* = 1.6 Hz, 1H), 7.34 (s, 1H), 7.27-7.25 (m, 1H), 5.57 (d, *J* = 13.2 Hz, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 1.79-1.72 (m, 2H), 1.36-1.32 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.5, 140.8, 135.16, 135.13, 134.5, 134.4, 134.0, 133.9, 132.1, 130.2, 130.1, 129.7, 129.6, 128.7, 128.6, 124.69, 124.64, 123.99, 123.93,

123.0, 122.4, 122.3, 120.6, 120.4, 118.0, 117.1, 116.7, 112.9, 112.0, 43.2, 30.8, 20.4, 13.9.

1,2-Bis-(2,7-dibromo-9-butyl-9*H*-carbazol-3-yl)ethane (129):

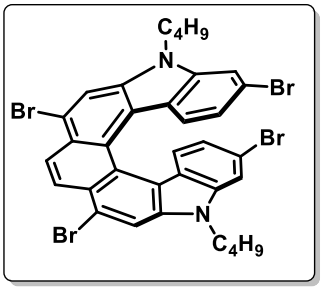


To a suspension of methyltriphenylphosponium bromide of 2,7-dibromo *N*-butyl carbazole **128** (0.59 g, 0.81 mmol) in dry THF (10 mL) at 0 °C under nitrogen was added NaH (0.058 g, 1.46 mmol, 60% in mineral oil) followed by 2,7-Dibromo 3-Formyl *N*-butyl carbazole **126 (**0.3 g, 0.73 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred for 6 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over anhydrous Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 10 % ethyl acetate pet ether as eluent to obtain **129** as yellow solid (0.455 g, 79%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.64 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.13 (dd, *J* = 8.0 and 1.6 Hz, 1H), 6.95 (s, 1H), 4.16 (t, *J* = 7.2 Hz, 2H), 1.85-1.77 (m, 2H), 1.44-1.36 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.5, 140.3, 130.3, 128.1, 122.2, 121.9, 121.8, 121.6, 121.4, 121.1, 119.6, 112.5, 111.8, 43.2, 30.9, 20.5, 13.9.

Photocyclization of 1,2-bis(2,7-dibromo-9-butyl-9*H*-carbazol-3-yl)ethane:



In an immersion wall photoreactor (borosilicate glass) equipped with a water cooling jacket and a stir bar, 1,2-bis(2,7-dibromo-9-butyl-9*H*-carbazol-3-yl)ethane **129** (0.35 g, 0.44 mmol), iodine (0.113 g, 0.49 mmol), THF (01.60 g, 1.80 mL, 22.26 mmol) were dissolved in toluene (650 mL). Nitrogen gas was bubbled through the solution within 10 minutes under sonication for removing the dissolved oxygen prior to irradiation using a 125W HPMV lamp (8 h monitored by TLC). After the completion of reaction, the excess of iodine was removed by washing the solution with aqueous sodium

thiosulfate, followed by distilled water. The organic layer was concentrated under the reduced pressure to obtain the crude product. The crude product purified by column chromatography over silica gel using petroleum ether: ethyl acetate (95:05) as eluent to obtained **130** as light yellow solid (0.289 g, 83%).

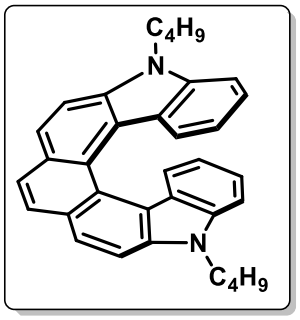
^{1}H-NMR (400MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.18 (s, 1H), 7.53 (s, 1H), 6.51-6.47 (m, 2H), 4.43 (t, *J* = 7.6 Hz, 2H), 2.01-1.94 (m, 2H), 1.58-1.46 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.0, 138.5, 126.8, 125.1, 124.3, 123.9, 122.0, 121.0, 120.6, 118.7, 117.9, 115.0, 111.6, 43.4, 31.2, 20.5, 13.9.

HRMS: *m/z* calculated for $C_{34}H_{29}N_2Br_4$ 780.9064, Observed= 780.9058.

Di aza[7]helicene (93):

Method A: To a suspension of tetra bromo di aza[7]helicene **130** (0.11 g, 0.14 mmol),



Pd/C (0.110 g, 10 wt. %), $NaHCO_3$ (0.176 g, 2.10 mmol) in methanol (5 mL) and toluene (5 mL) was attached a hydrogen filled balloon. The reaction mixture was stirred for 2 hour at room temperature. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over anhyd. Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 5 % ethyl acetate pet ether as eluent to obtain **93** as yellow solid (0.037 g, 57%).

^{1}H-NMR (400MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.90-7.88 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.38 (t, *J* = 7.6 Hz, 1H), 4.57 (t, *J* = 7.2 Hz, 2H), 2.02-1.97 (m, 2H), 1.57-1.50 (m, 2H), 1.04 (t, *J* = 7.6 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 139.2, 138.7, 128.2, 125.7, 124.6, 124.06, 124.03, 124.0, 118.7, 116.8, 110.1, 108.0, 107.9, 43.1, 31.3, 20.6, 14.0.

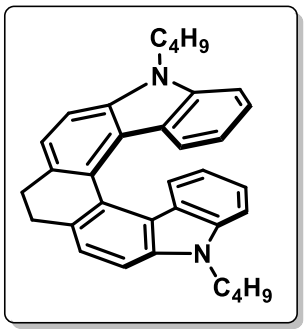
HRMS: *m/z* calculated for $C_{34}H_{32}N_2$ $[M+H]^+$469.2644, Observed= 469.2635.

Method B: Tributyltin hydride (0.74 g, 0.686 mL, 2.55 mmol) was added to a solution of tetra bromo di aza[7]helicene **130** (0.1 g, 0.127 mmol) and azobisisobutyronitrile (AIBN) (catalytic amount) in dry toluene (10 mL), under an atmosphere of nitrogen.

The mixture was refluxed for 24 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 5 % ethyl acetate pet ether as eluent to obtain **93**as yellow solid (0.046 g, 77%).

Method C: A suspension of tetra bromo di aza[7]helicene **130** (0.1 g, 0.127 mmol), K_2CO_3 (0.141 g, 1.0 mmol), $Pd(OAc)_2$ (0.003 g, 0.012 mmol, 10 mol%) and PPh_3 (0.013g, 0.051 mmol, 40 mol%) in *n*-butanol (5 mL) and toluene (5 mL) was refluxed for 8 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with water, brine, dried over Na_2SO_4 and solvent removed in vacuo. The purification of compound was performed by column chromatography over silica gel using 5 % ethyl acetate pet ether as eluent to obtain **93**as yellow solid (0.048 g, 81%).

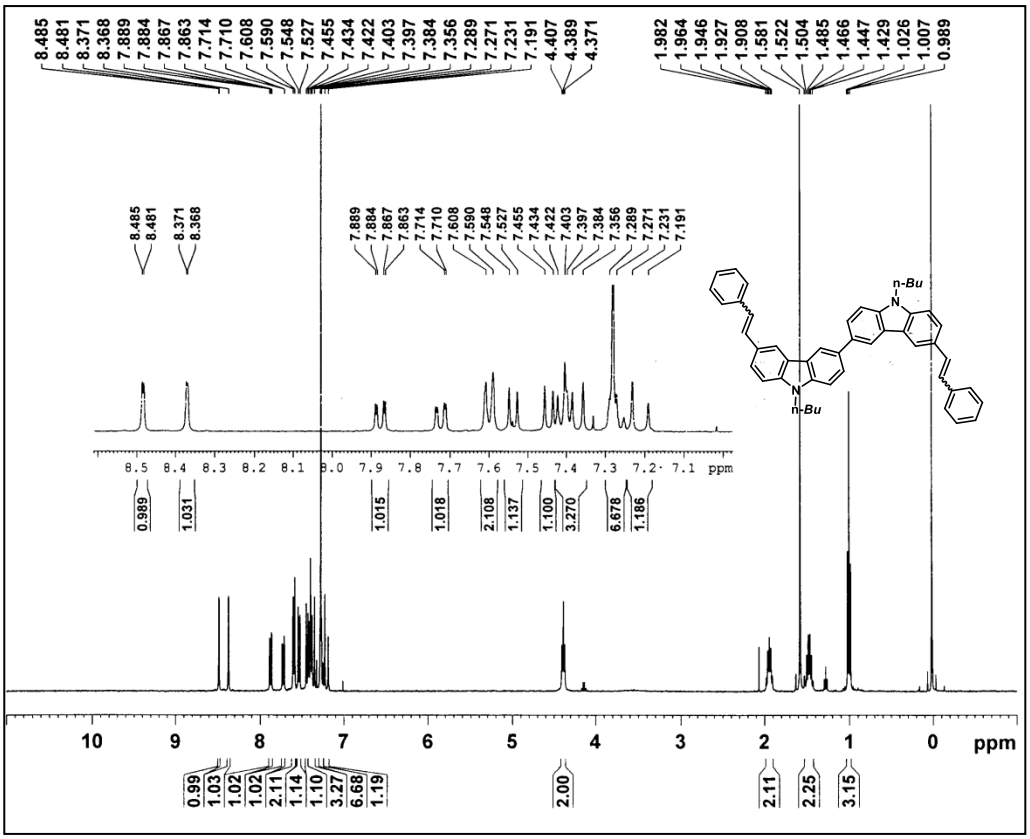
Compound 131:



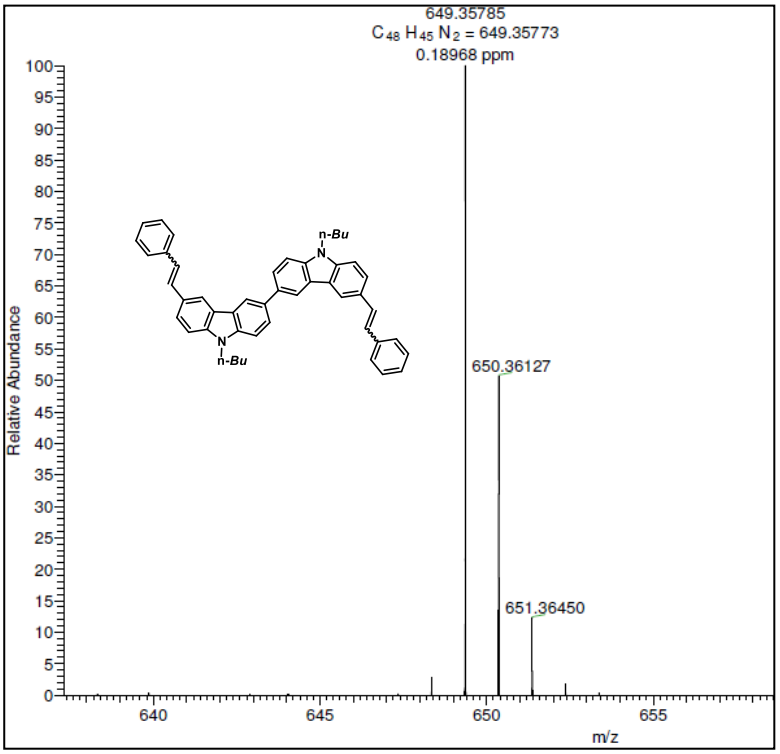
^{1}H-NMR (400MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.36 (t, *J* = 7.6 Hz, 1H), 4.41 (t, *J* = 7.2 Hz, 2H), 2.99-2.91 (m, 2H), 1.96-1.91 (m, 2H), 1.57-1.45 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.6, 140.3, 132.2, 129.7, 125.0, 124.5, 123.7, 122.6, 120.4, 117.0, 107.5, 107.3, 42.8, 30.9, 30.8, 20.6, 14.0.

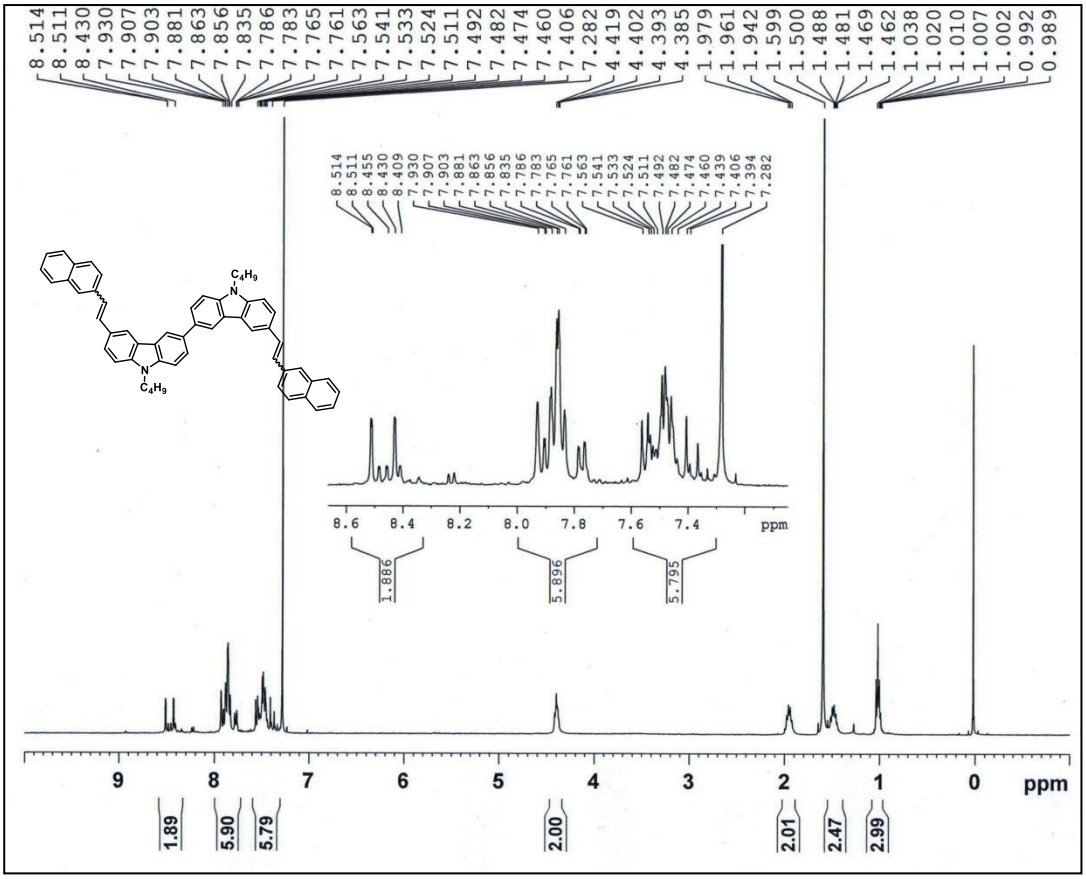
3.9 Spectral data:



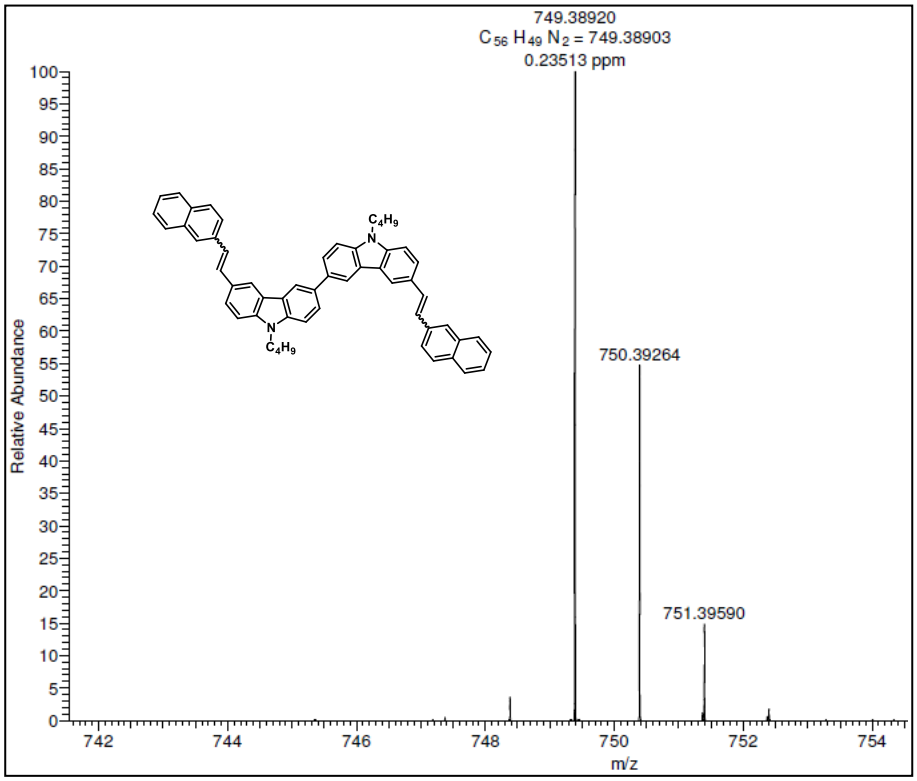
^{1}H-NMR of compound 58 ($CDCl_3$, 400 MHz)



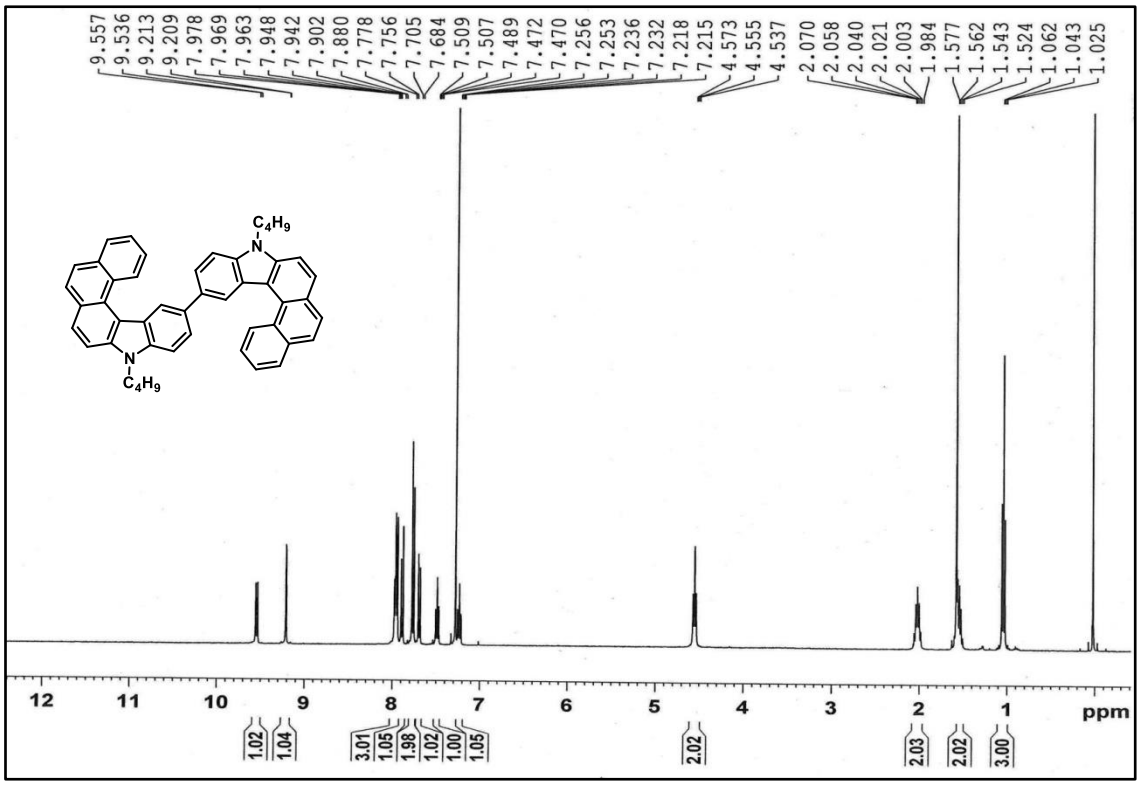
HRMS of compound 58



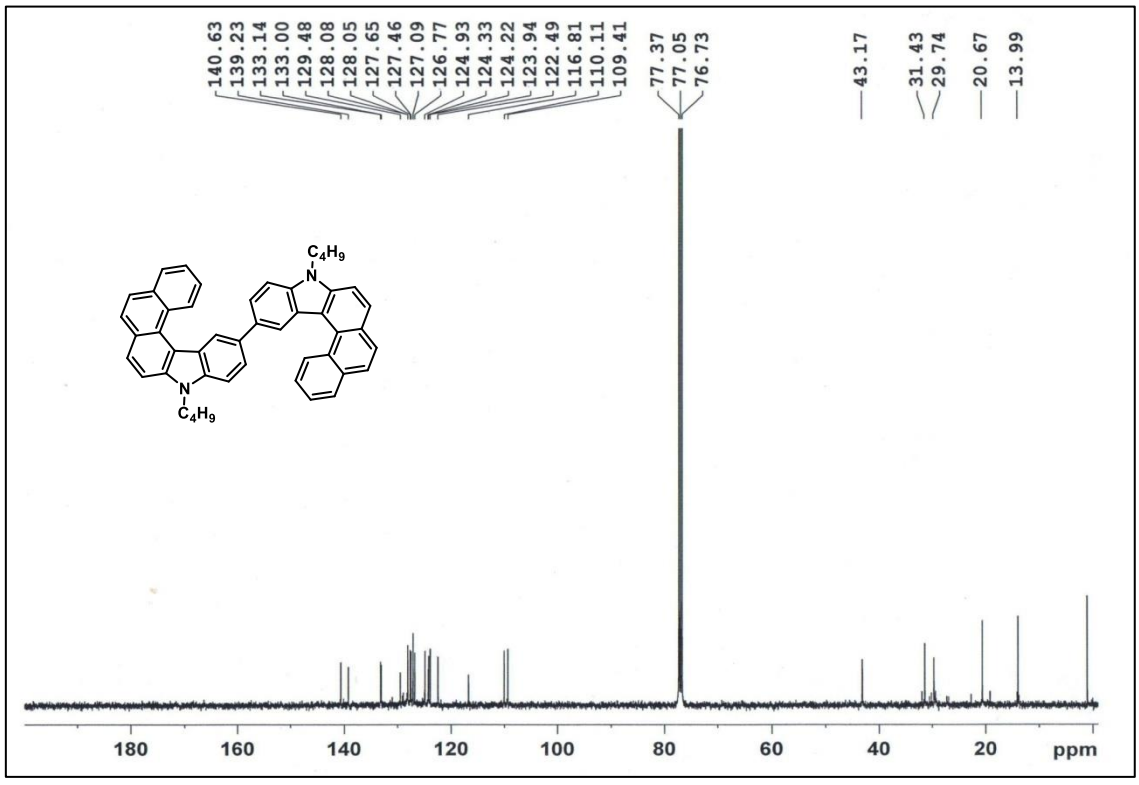
^{1}H-NMR of compound 59 ($CDCl_3$, 400 MHz)



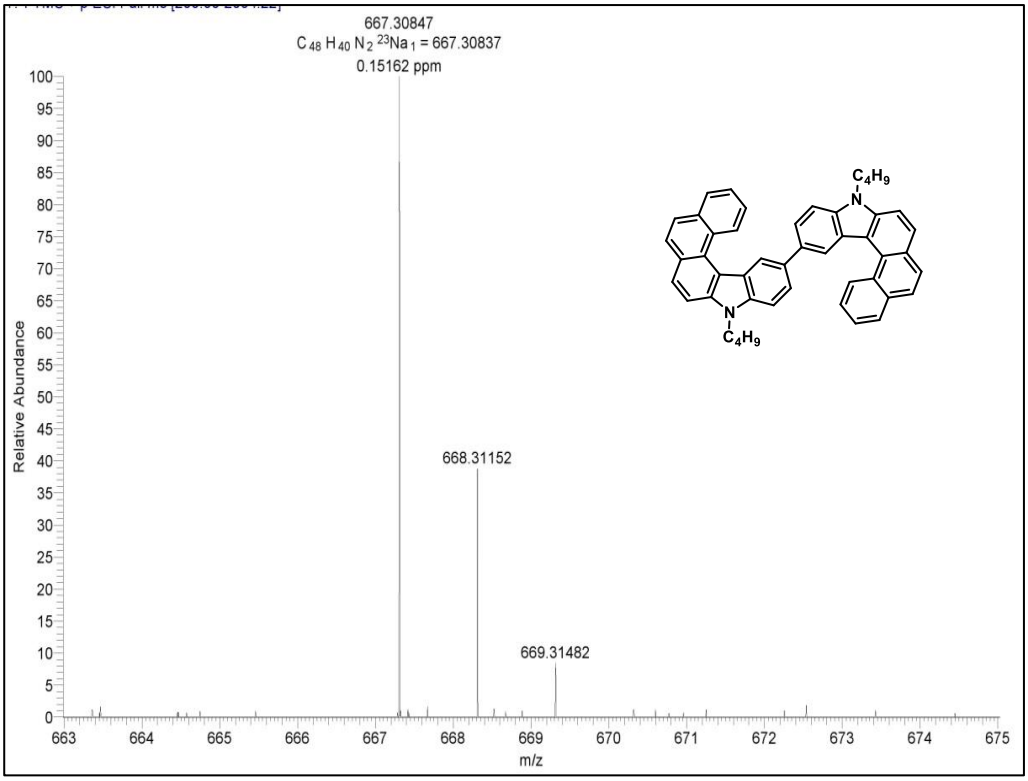
HRMS of compound 59



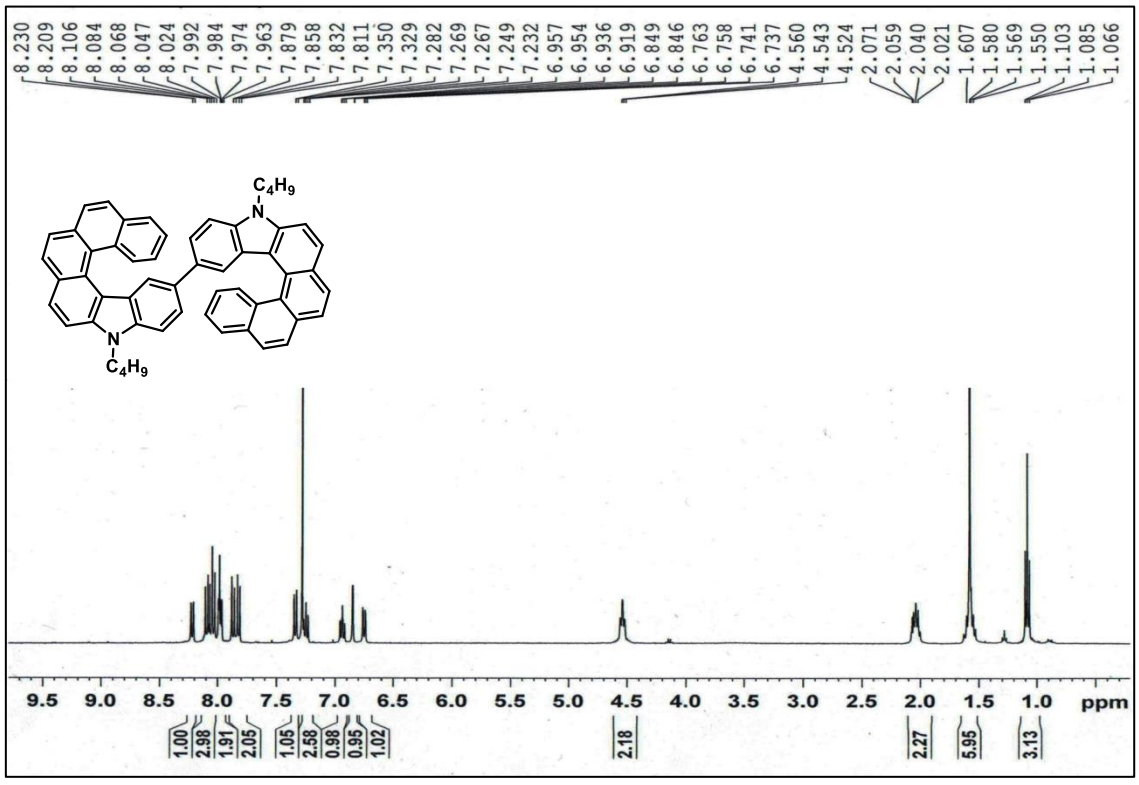
^{1}H-NMR of compound 60 ($CDCl_3$, 400 MHz)



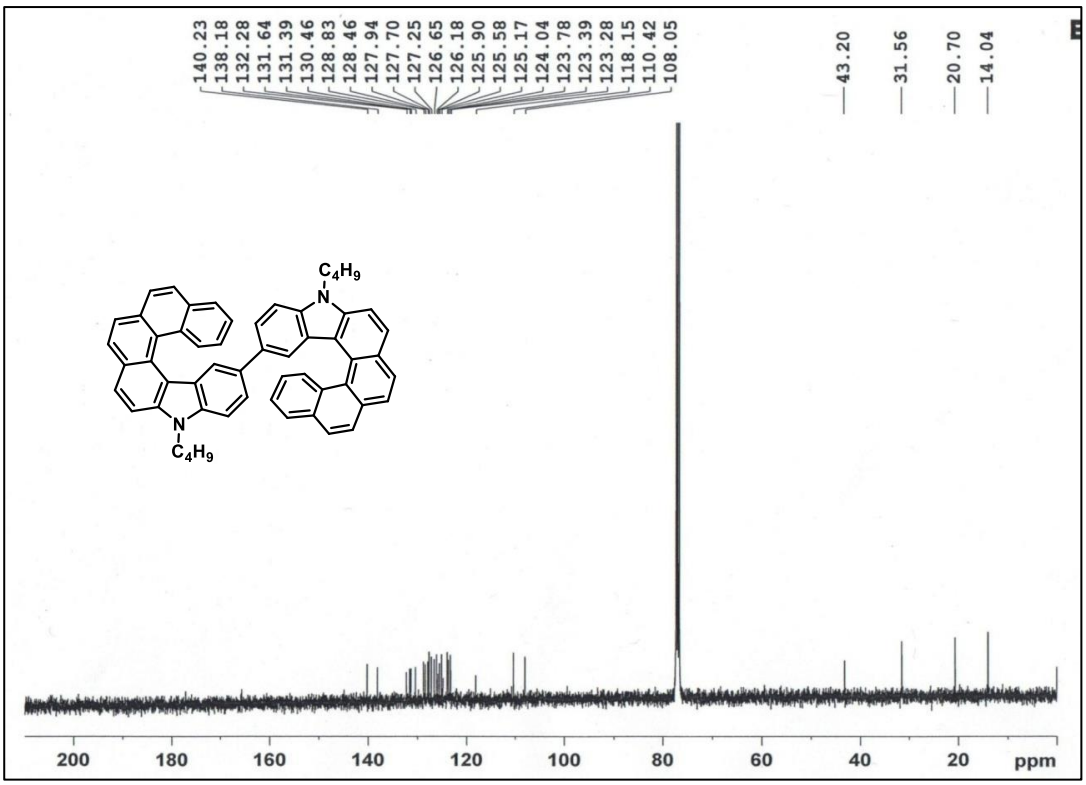
^{13}C-NMR of compound 60 ($CDCl_3$, 100 MHz)



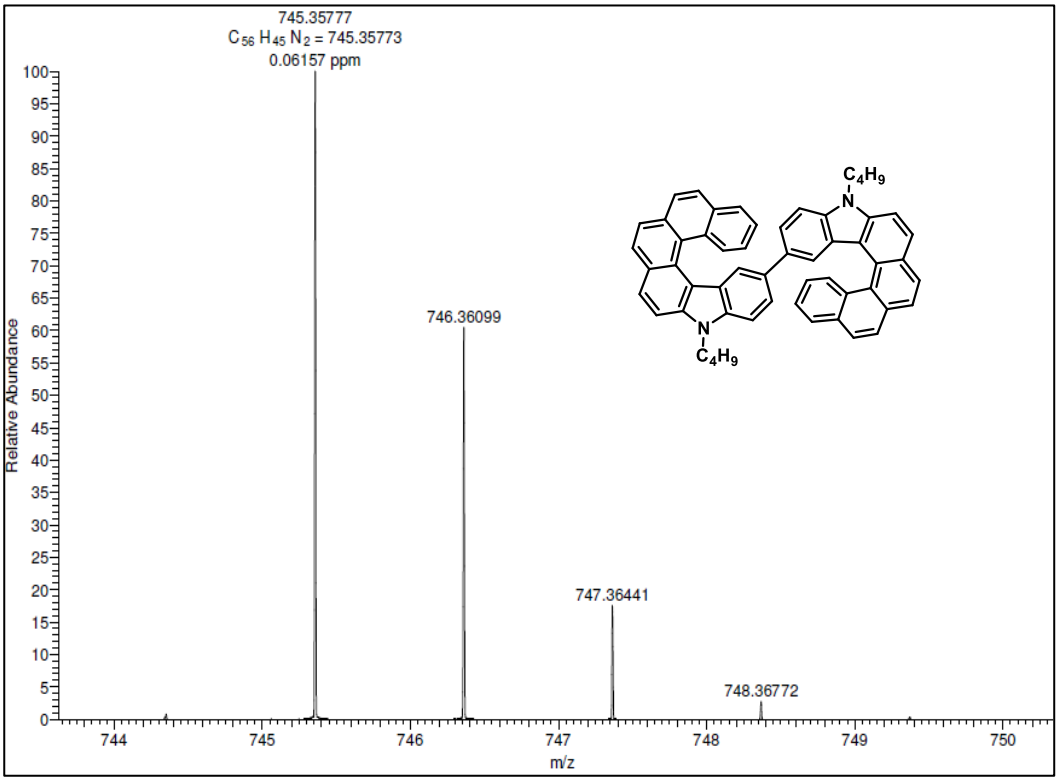
HRMS of compound 60



^{1}H-NMR of compound 61 ($CDCl_3$, 400 MHz)

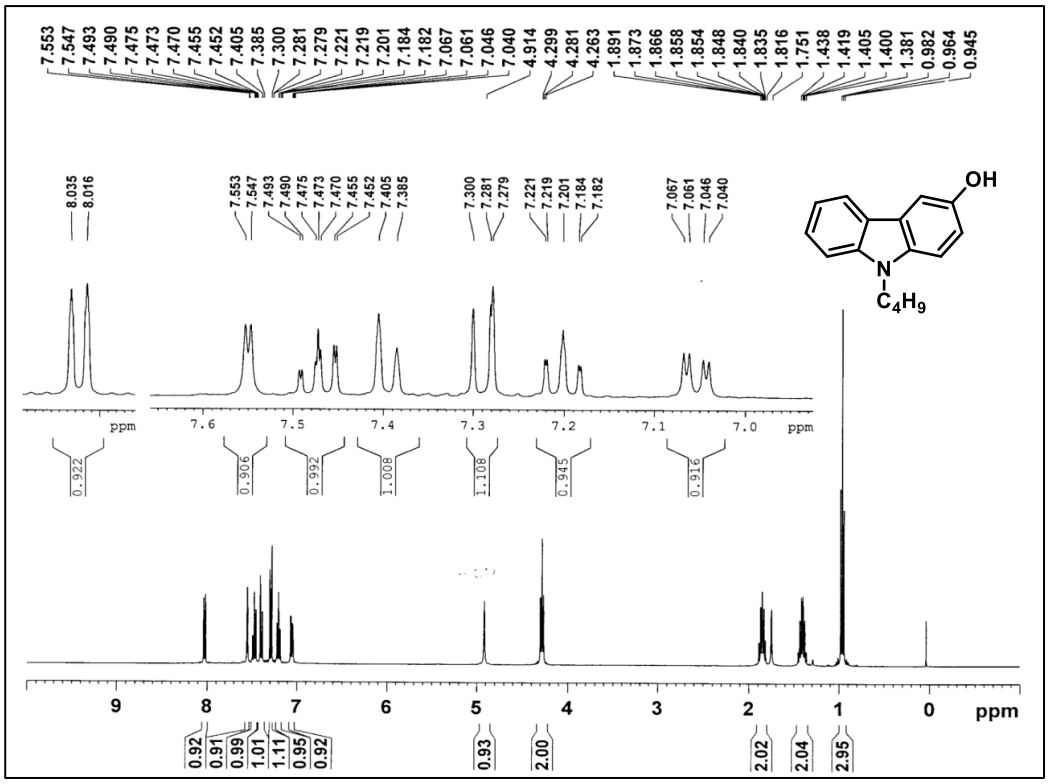


^{13}C-NMR of compound 61 ($CDCl_3$, 100 MHz)

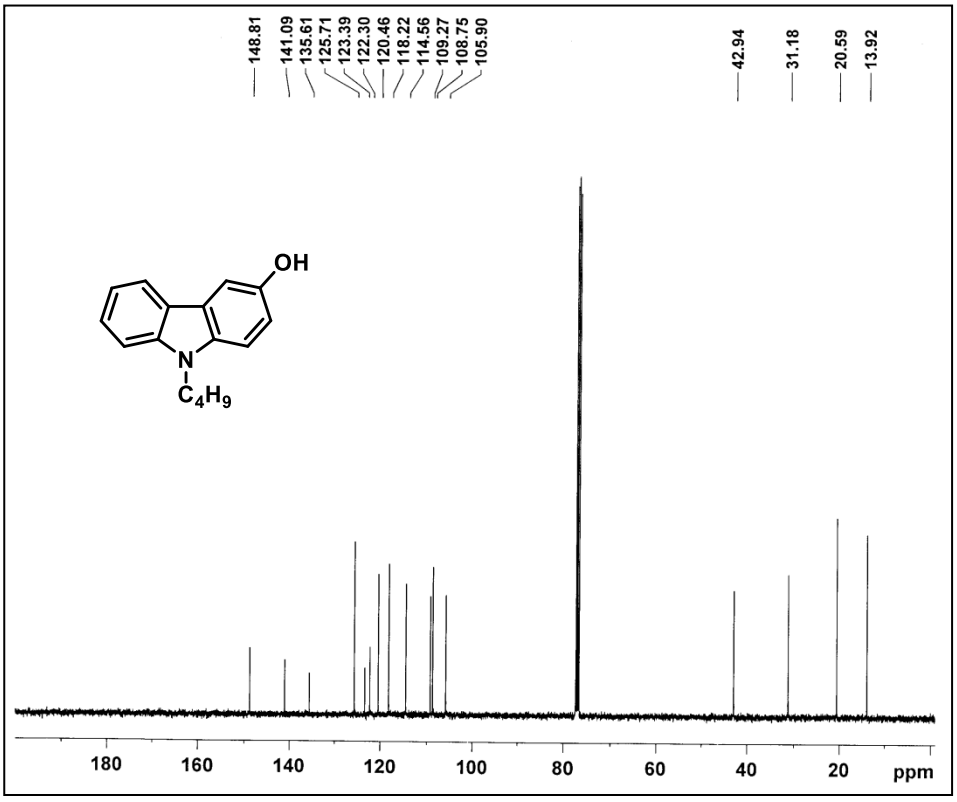


HRMS of compound 61

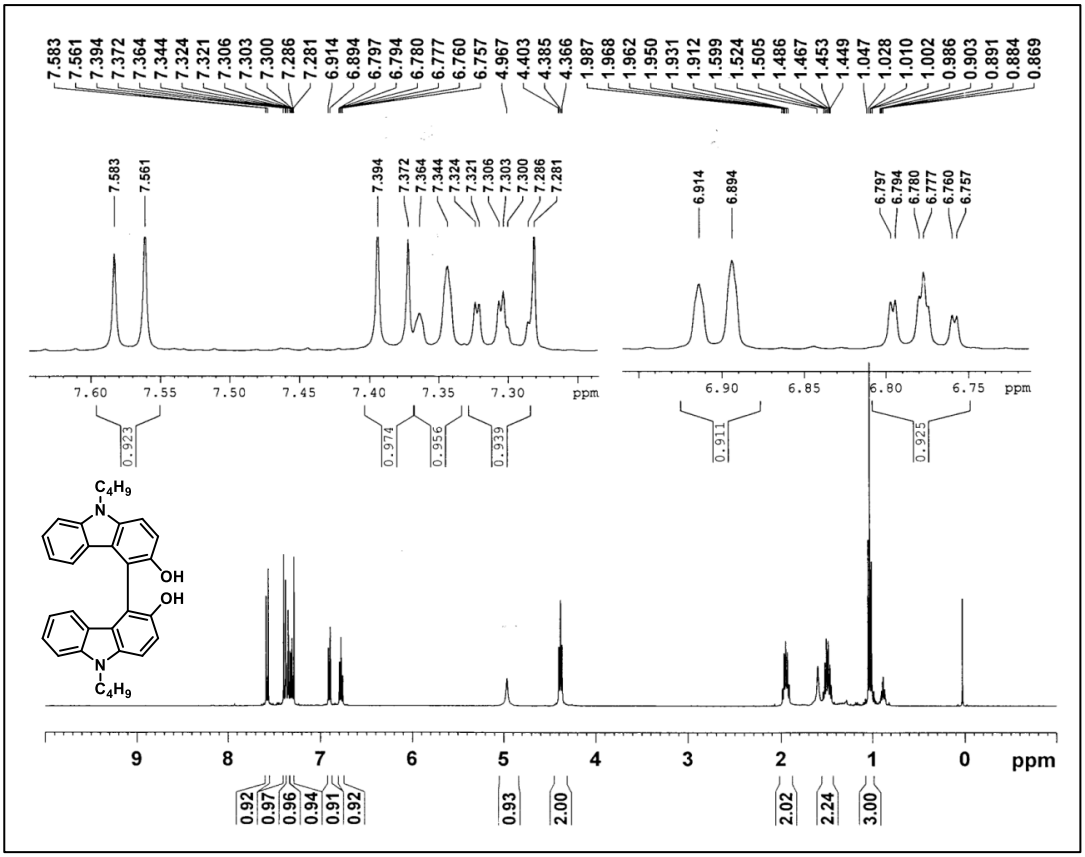
Spectra



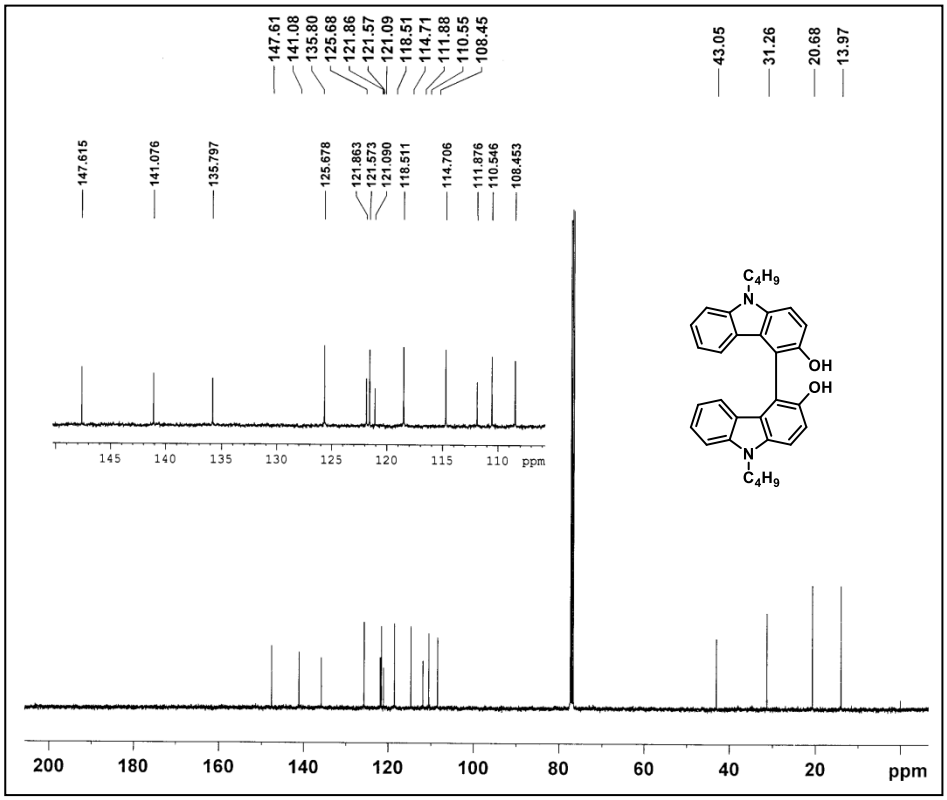
^{1}H-NMR of compound 79 ($CDCl_3$, 400 MHz)



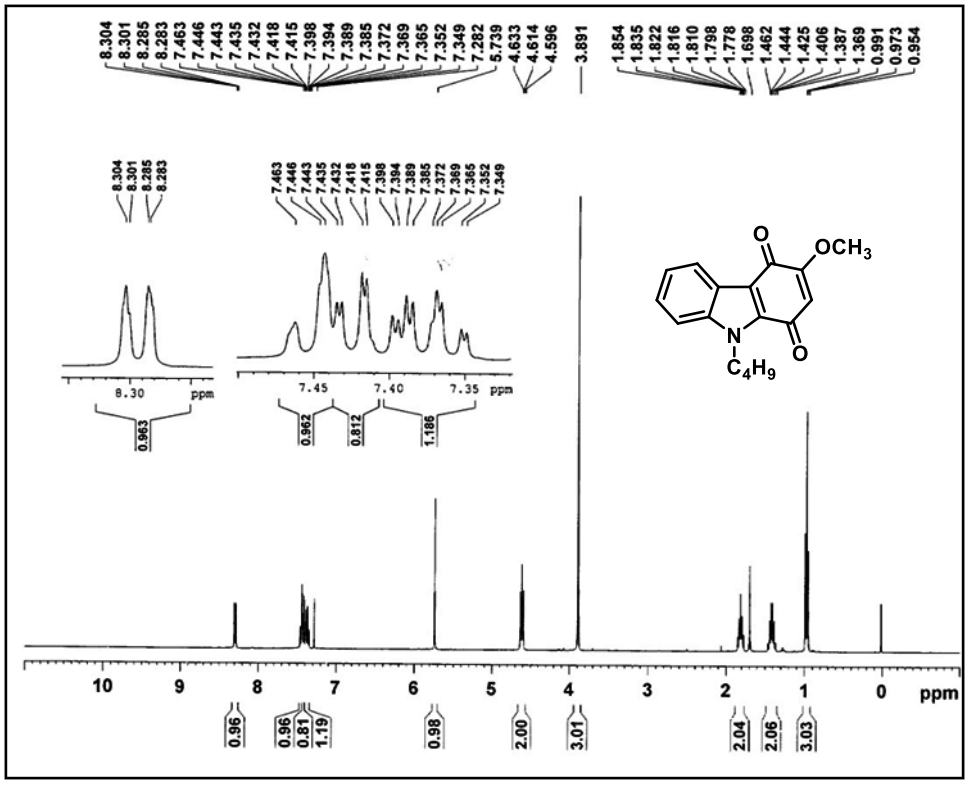
^{13}C-NMR of compound 79 ($CDCl_3$, 100 MHz)



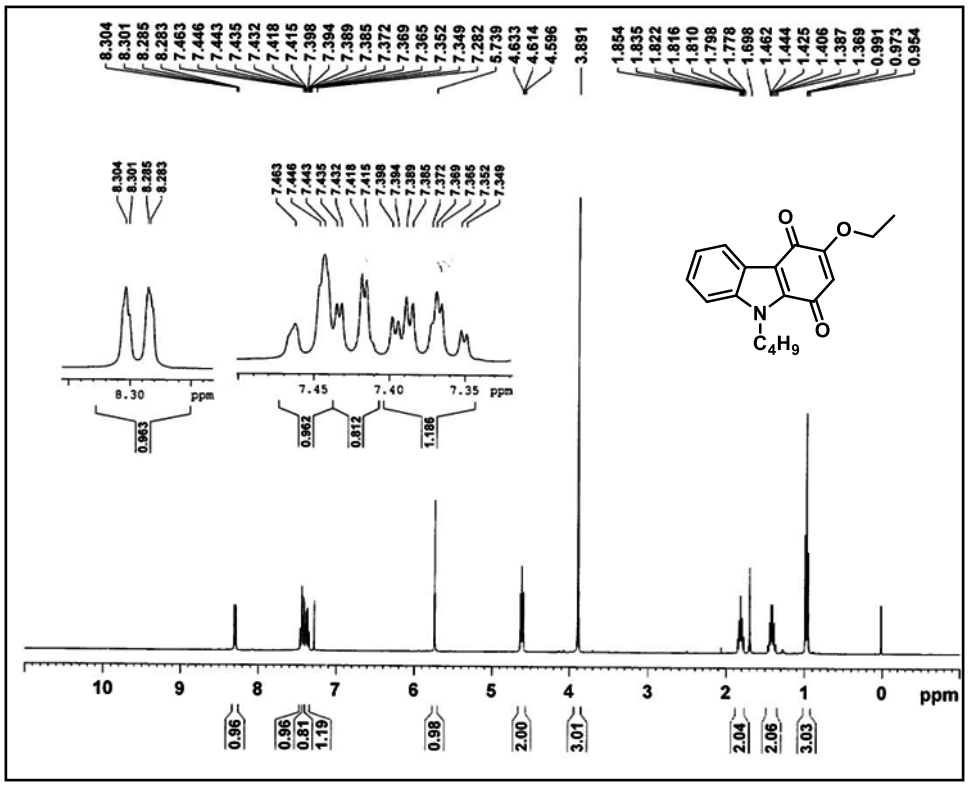
^{1}H-NMR of compound 80 ($CDCl_3$, 400 MHz)



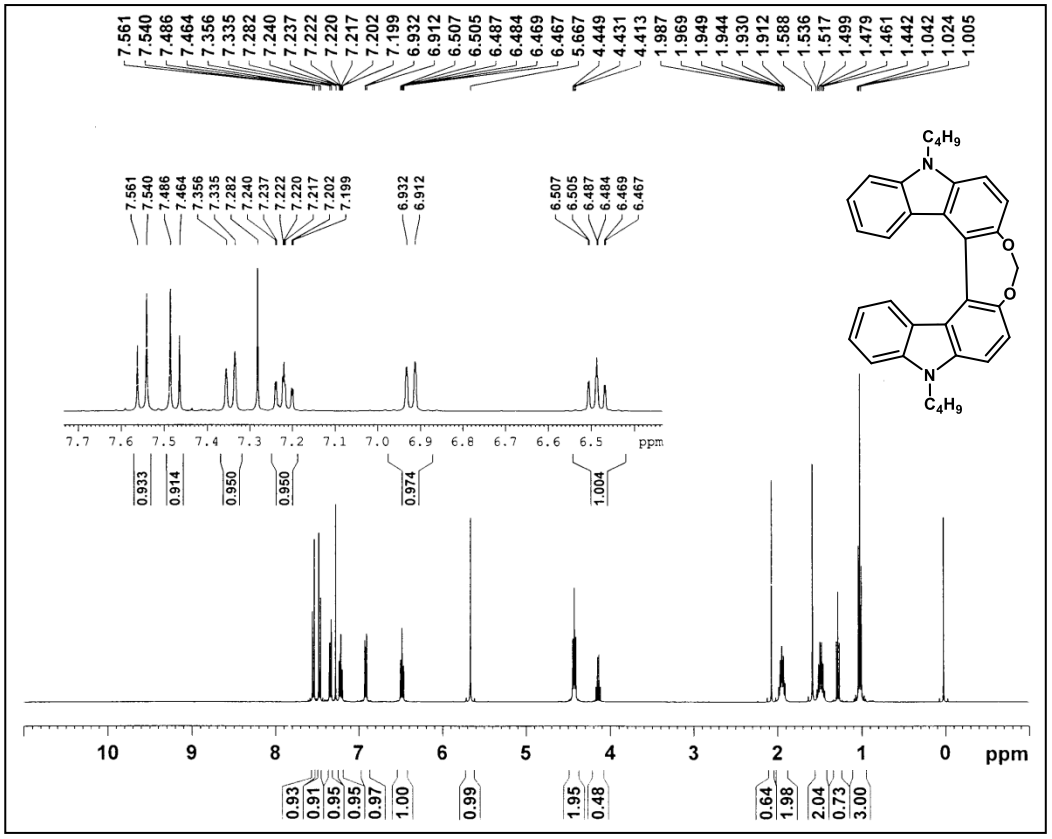
^{13}C-NMR of compound 80 ($CDCl_3$, 100 MHz)



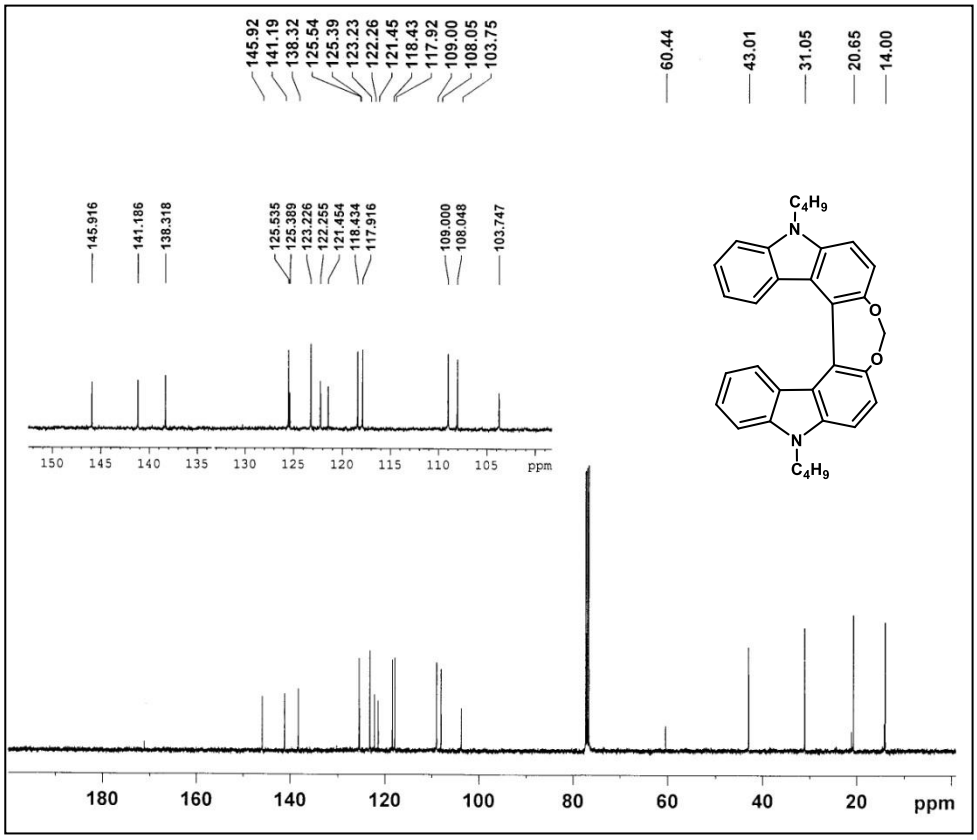
^{1}H-NMR of compound 81 ($CDCl_3$, 400 MHz)



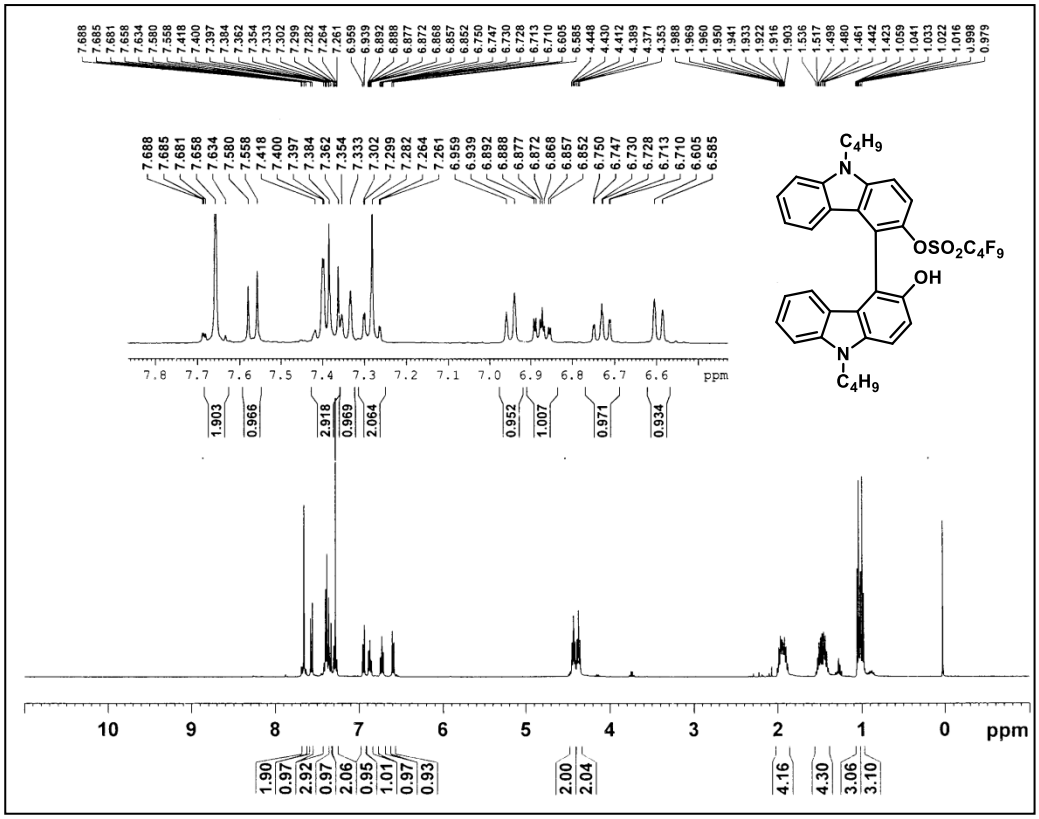
^{1}H-NMR of compound 82 ($CDCl_3$, 400 MHz)



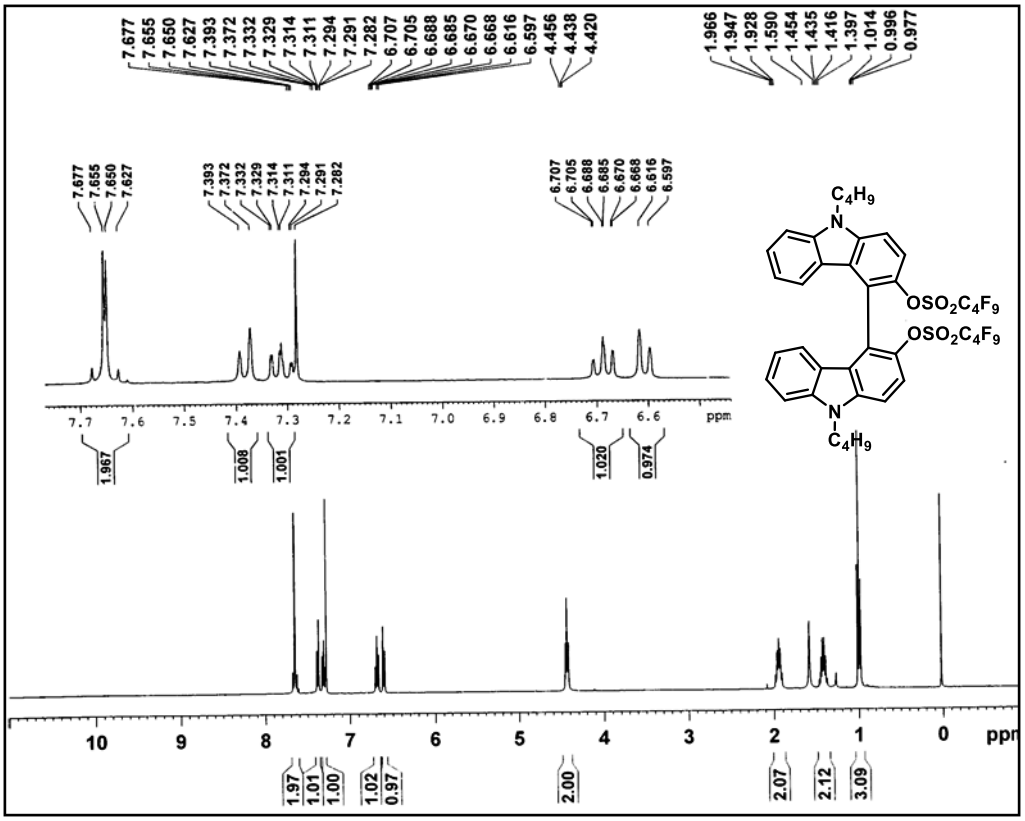
^{1}H-NMR of compound 85 ($CDCl_3$, 400 MHz)



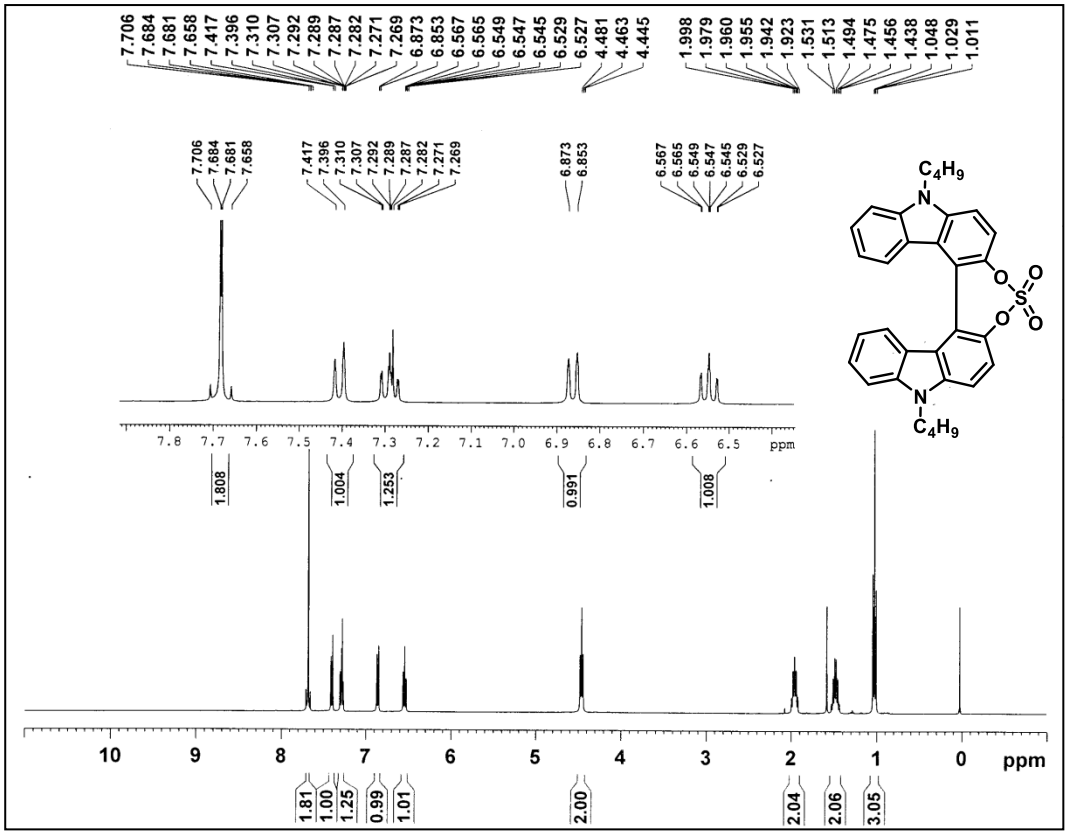
^{13}C-NMR of compound 85 ($CDCl_3$, 100 MHz)



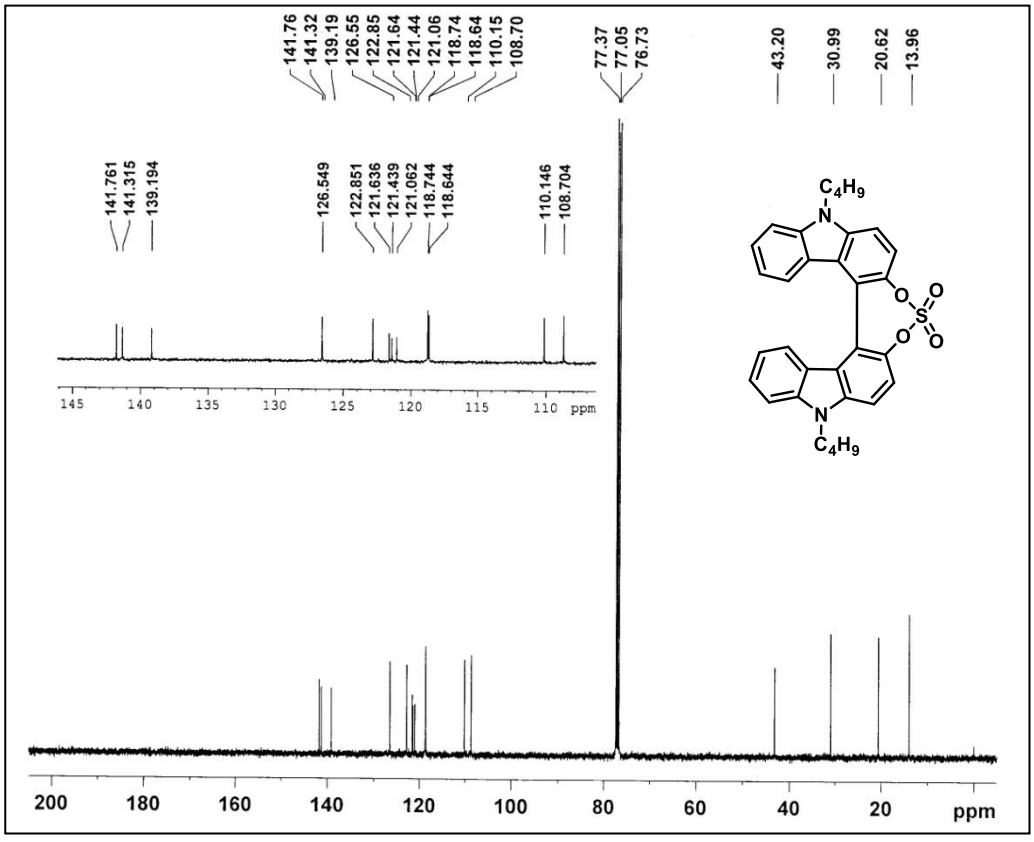
^{1}H-NMR of compound 86 ($CDCl_3$, 400 MHz)



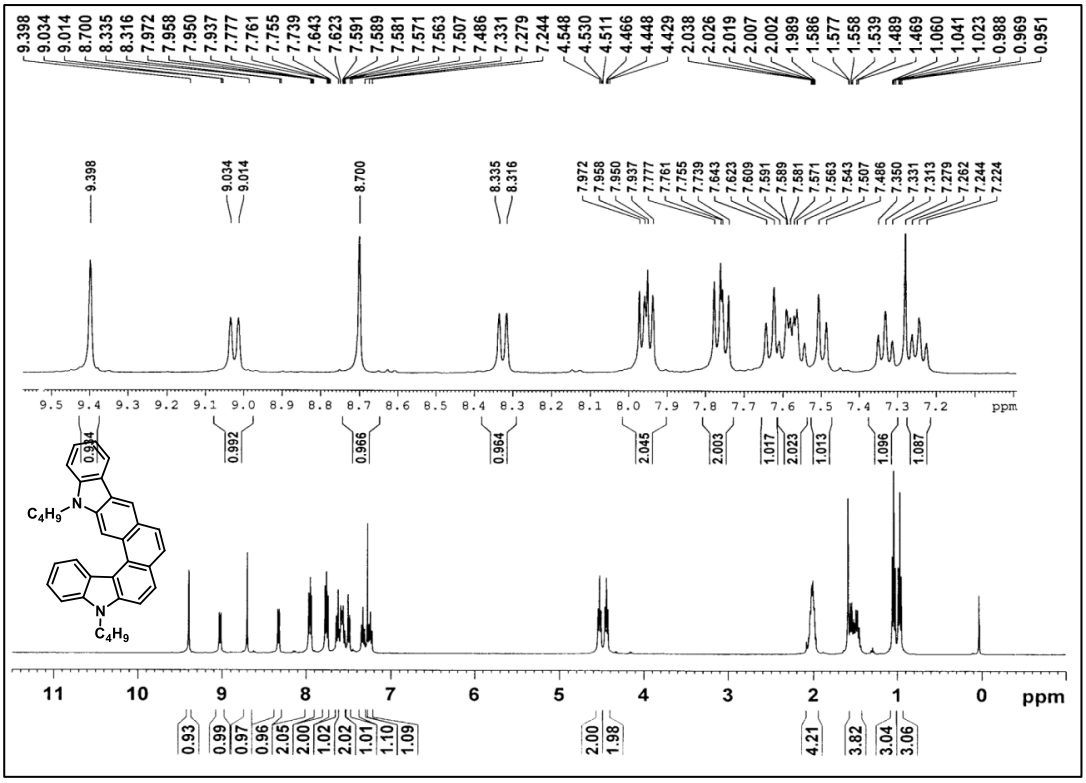
^{1}H-NMR of compound 92 ($CDCl_3$, 400 MHz)



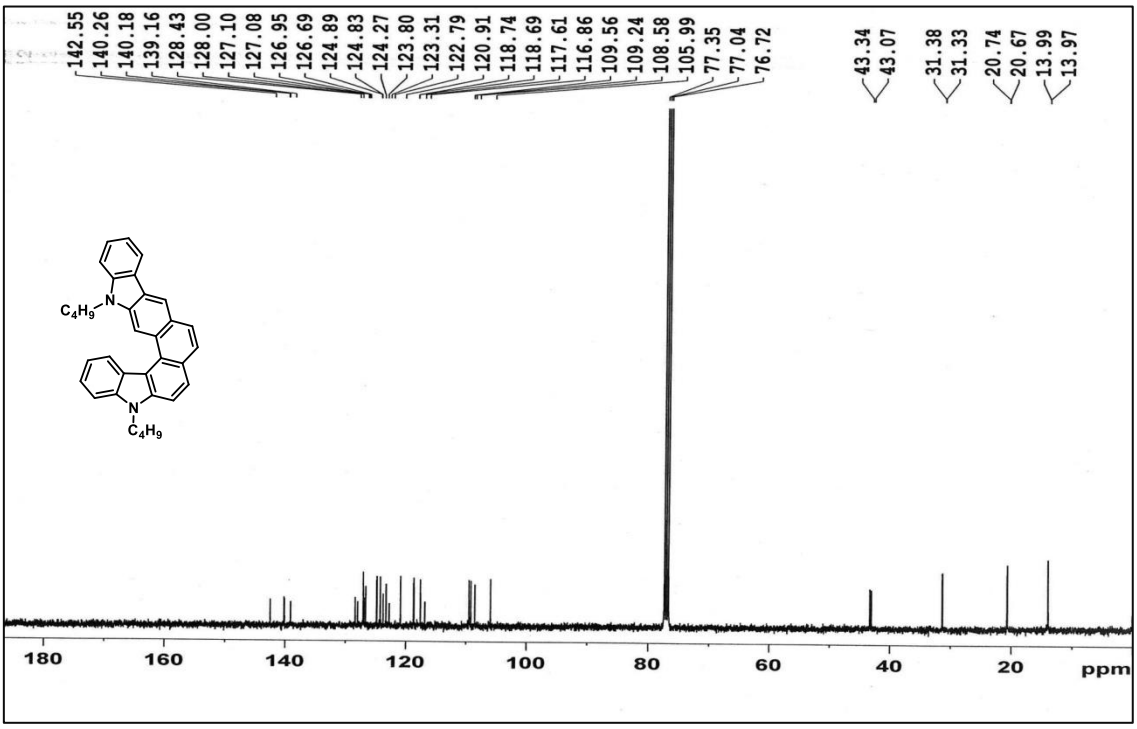
^{1}H-NMR of compound 87 ($CDCl_3$, 400 MHz)



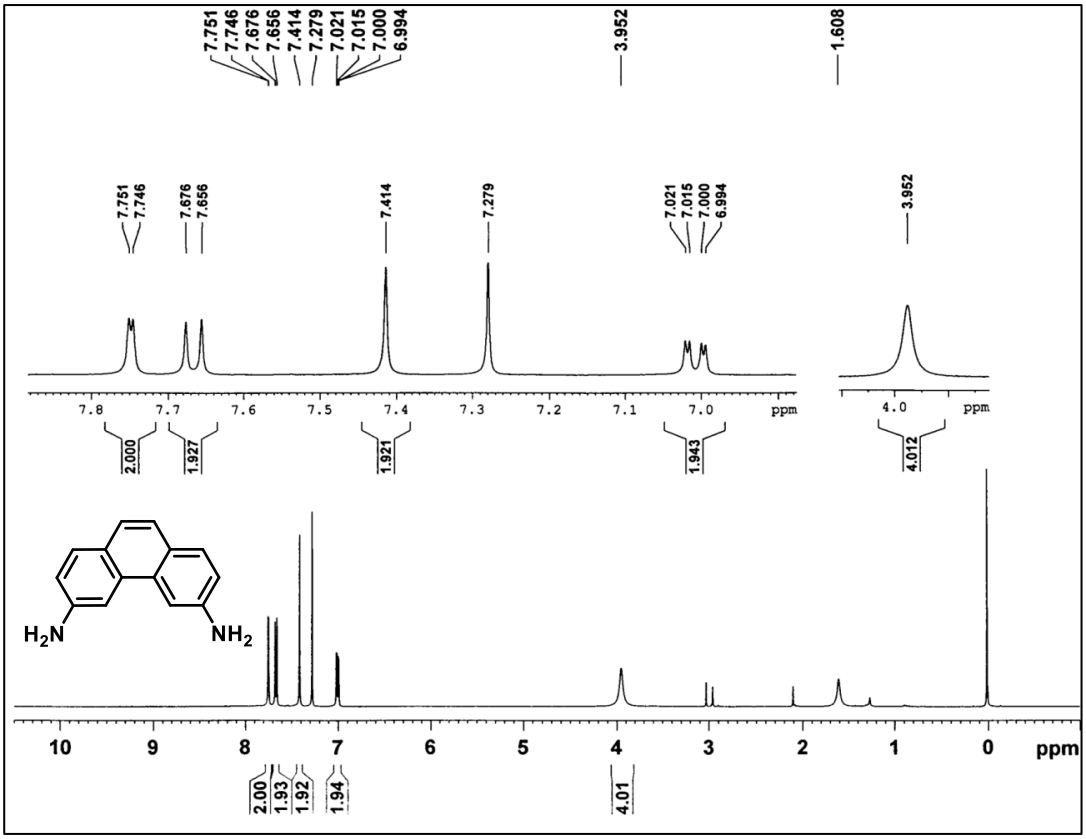
^{13}C-NMR of compound 87 ($CDCl_3$, 100 MHz)



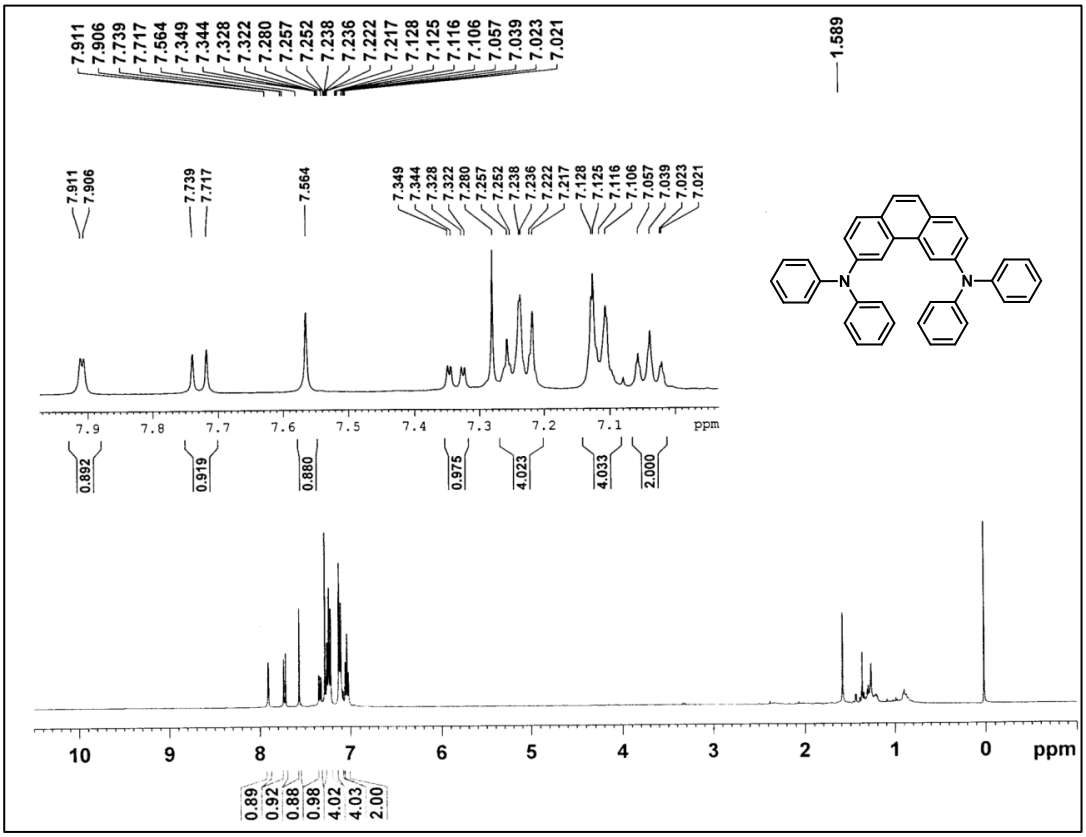
^{1}H-NMR of compound 96 ($CDCl_3$, 400 MHz)



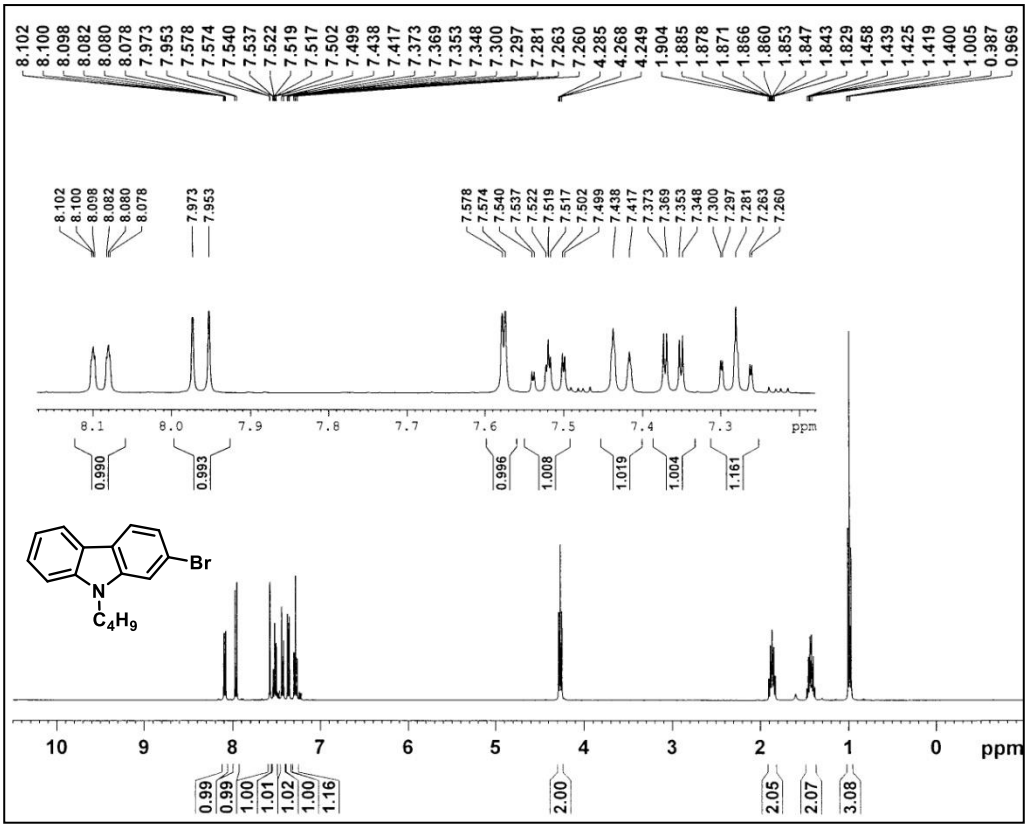
^{13}C-NMR of compound 96 ($CDCl_3$, 100 MHz)



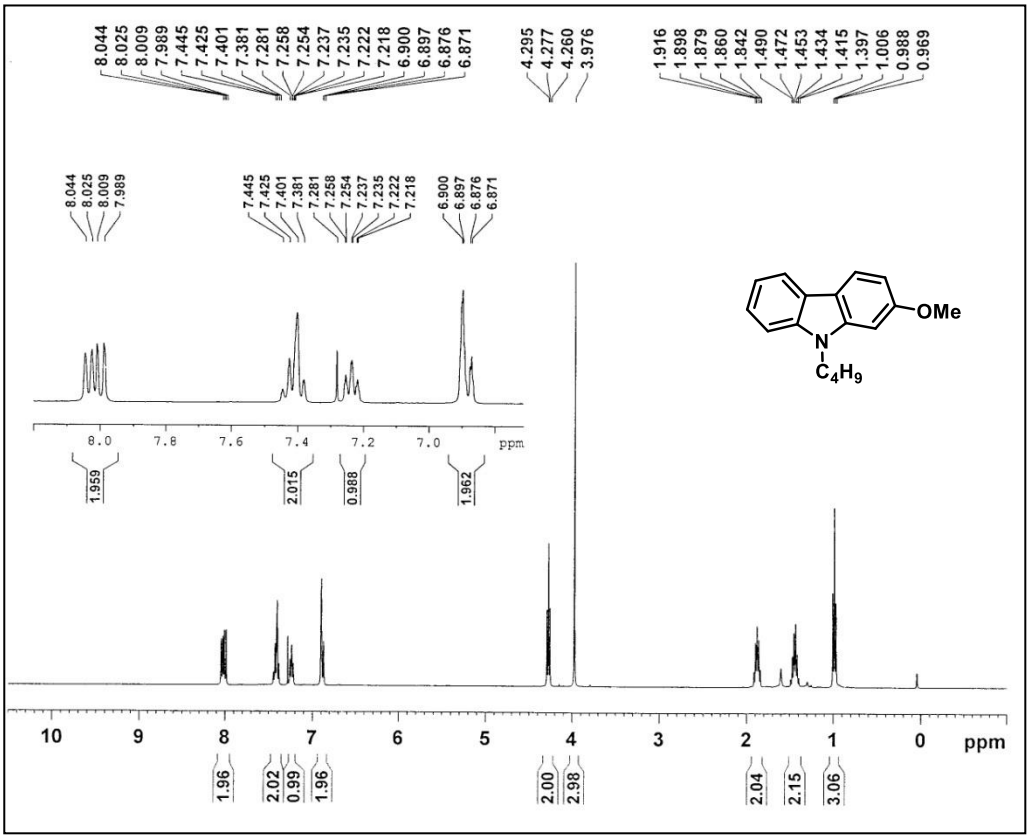
^{1}H-NMR of compound 105 ($CDCl_3$, 400 MHz)



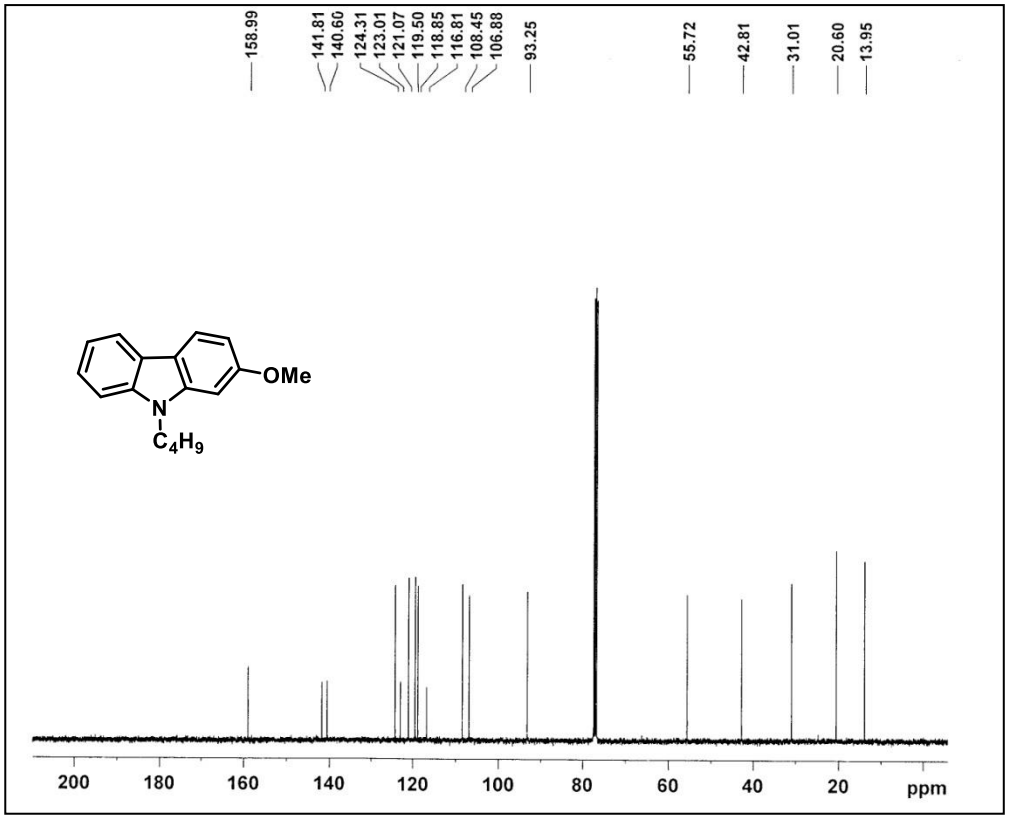
^{1}H-NMR of compound 107 ($CDCl_3$, 400 MHz)



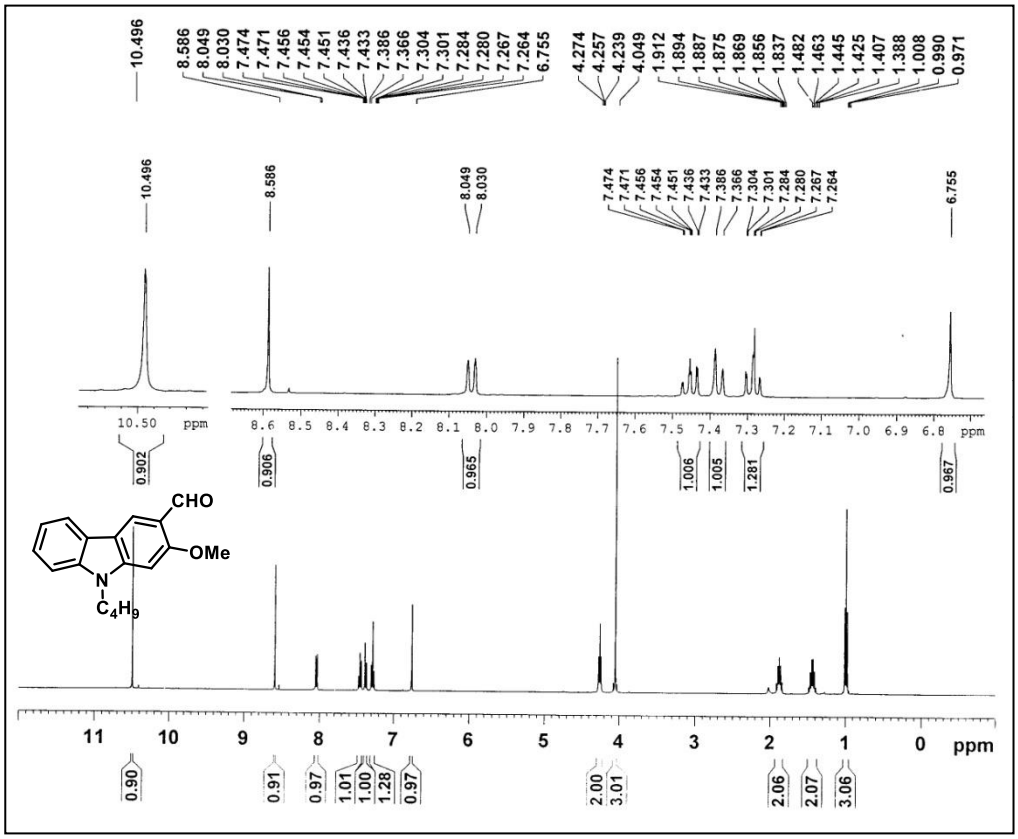
^{1}H-NMR of compound 113 ($CDCl_3$, 400 MHz)



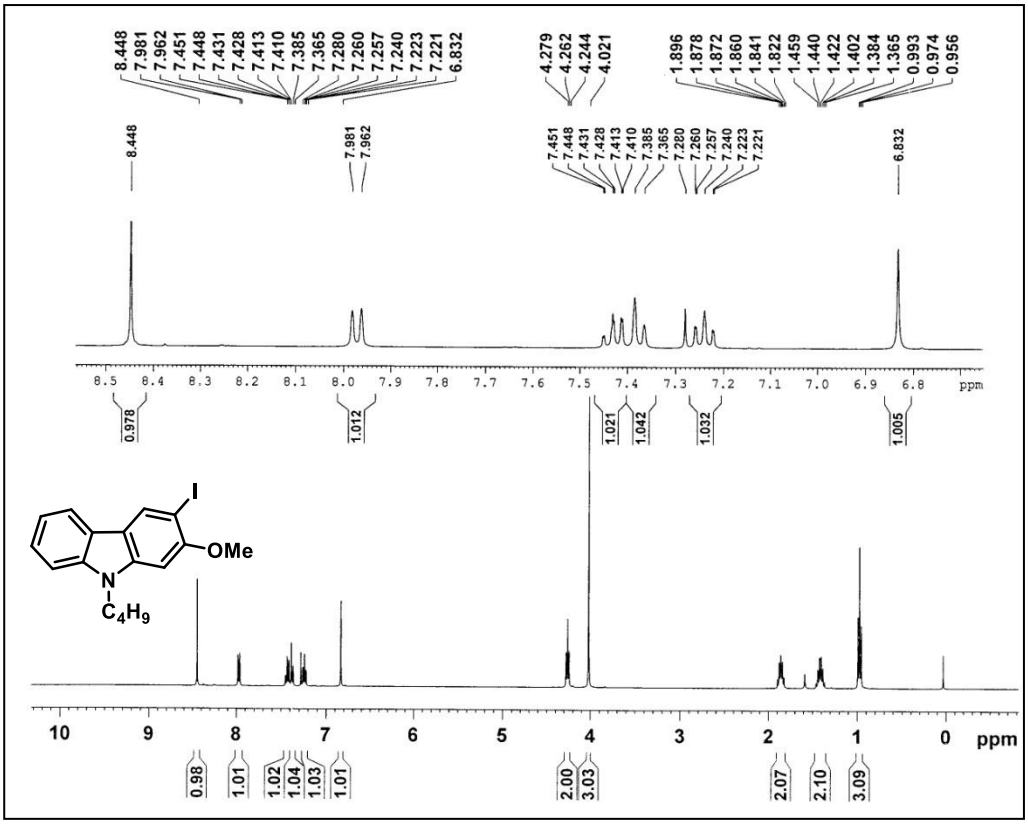
^{1}H-NMR of compound 114 ($CDCl_3$, 400 MHz)



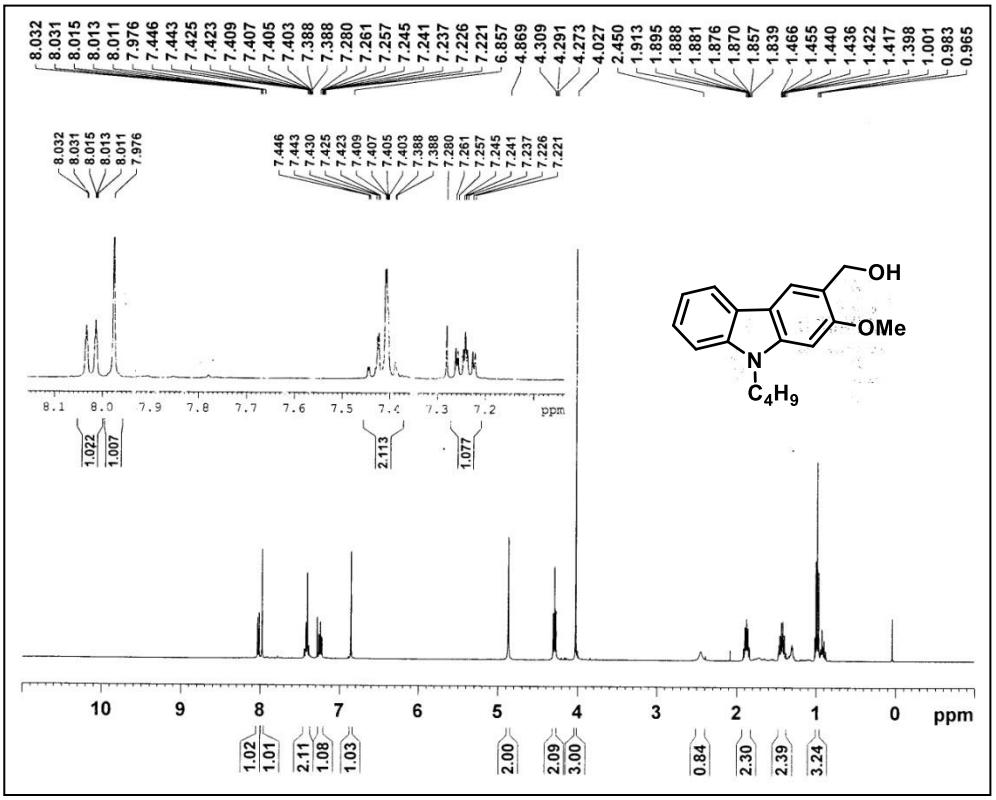
^{13}C-NMR of compound 114 ($CDCl_3$, 100 MHz)



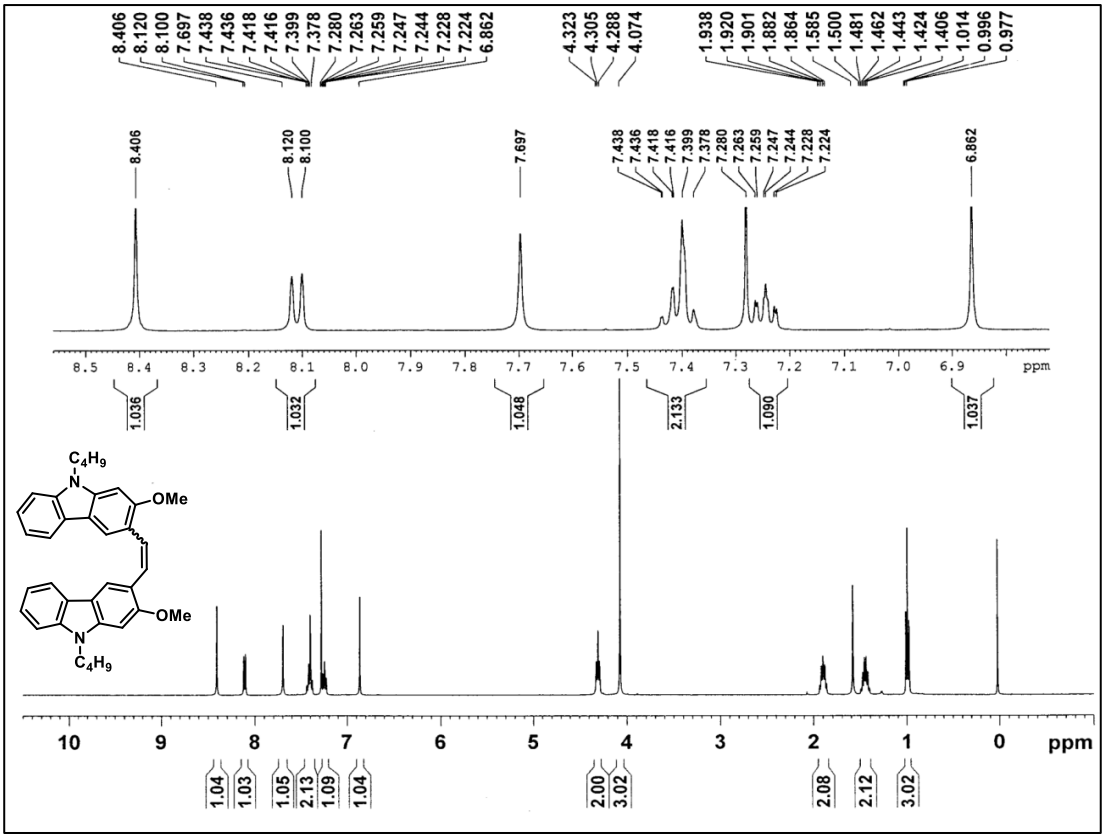
^{1}H-NMR of compound 115 ($CDCl_3$, 400 MHz)



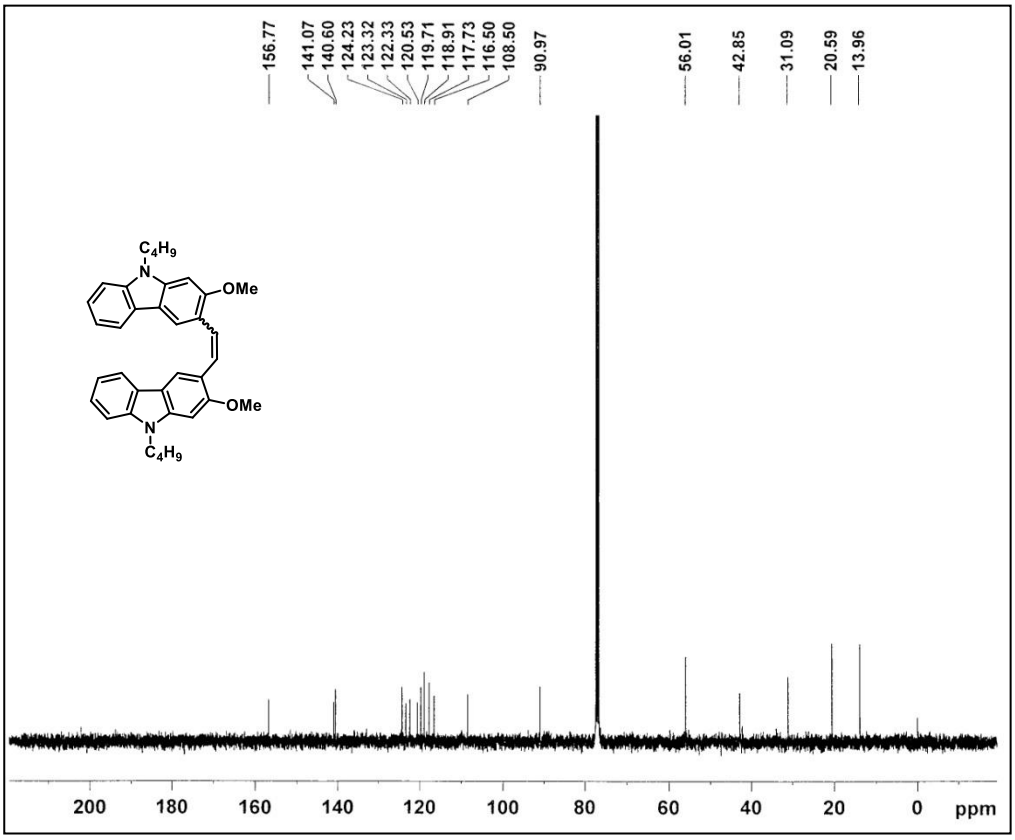
^{1}H-NMR of compound 116 ($CDCl_3$, 400 MHz)



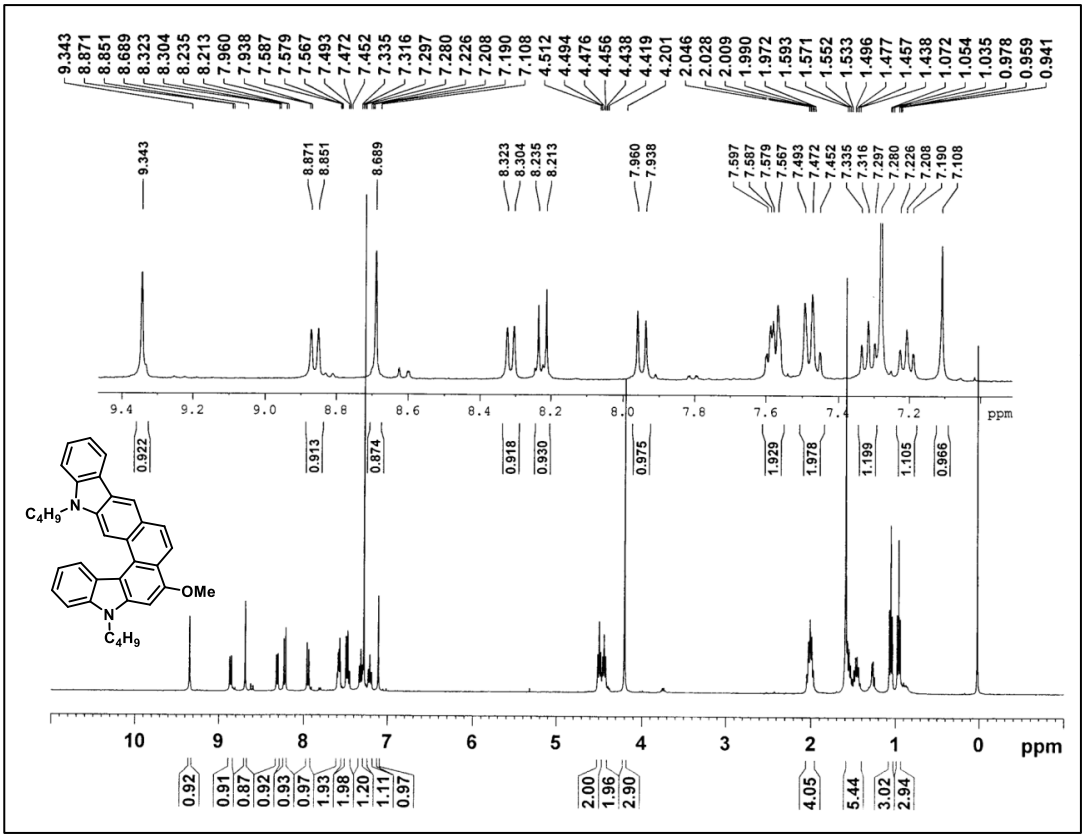
^{1}H-NMR of compound 118 ($CDCl_3$, 400 MHz)



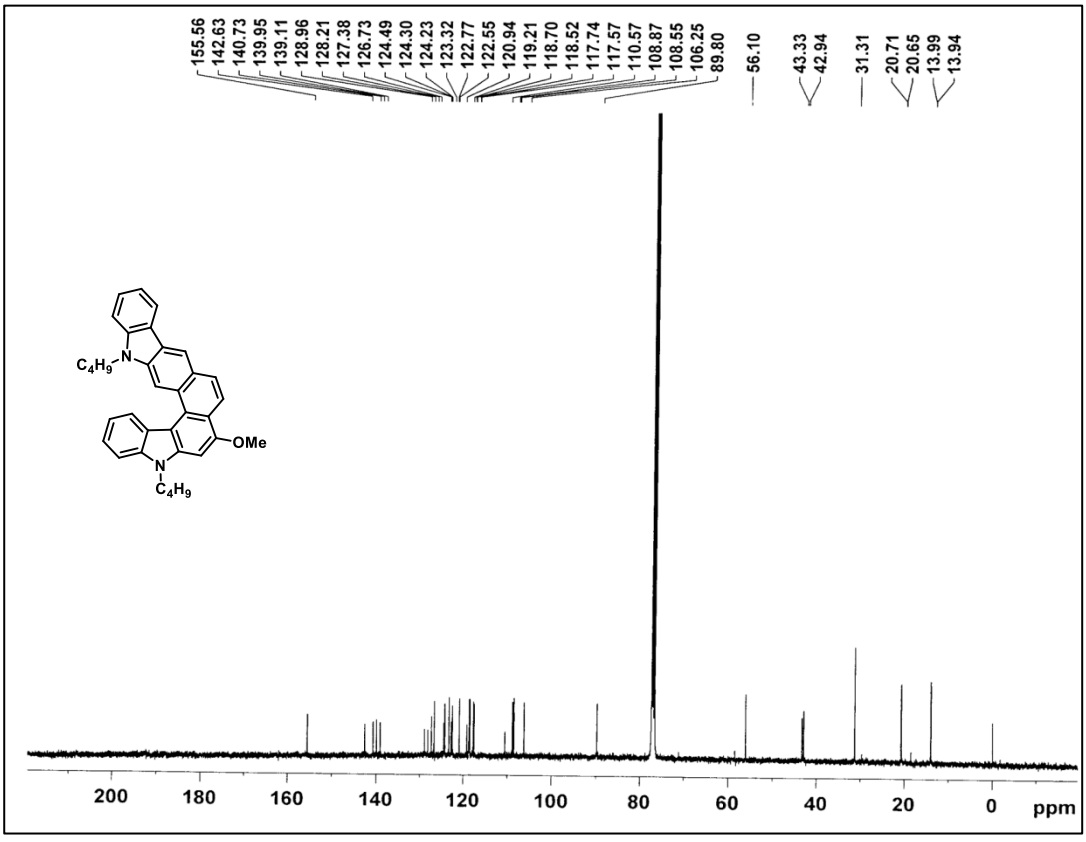
^{1}H-NMR of compound 117 ($CDCl_3$, 400 MHz)



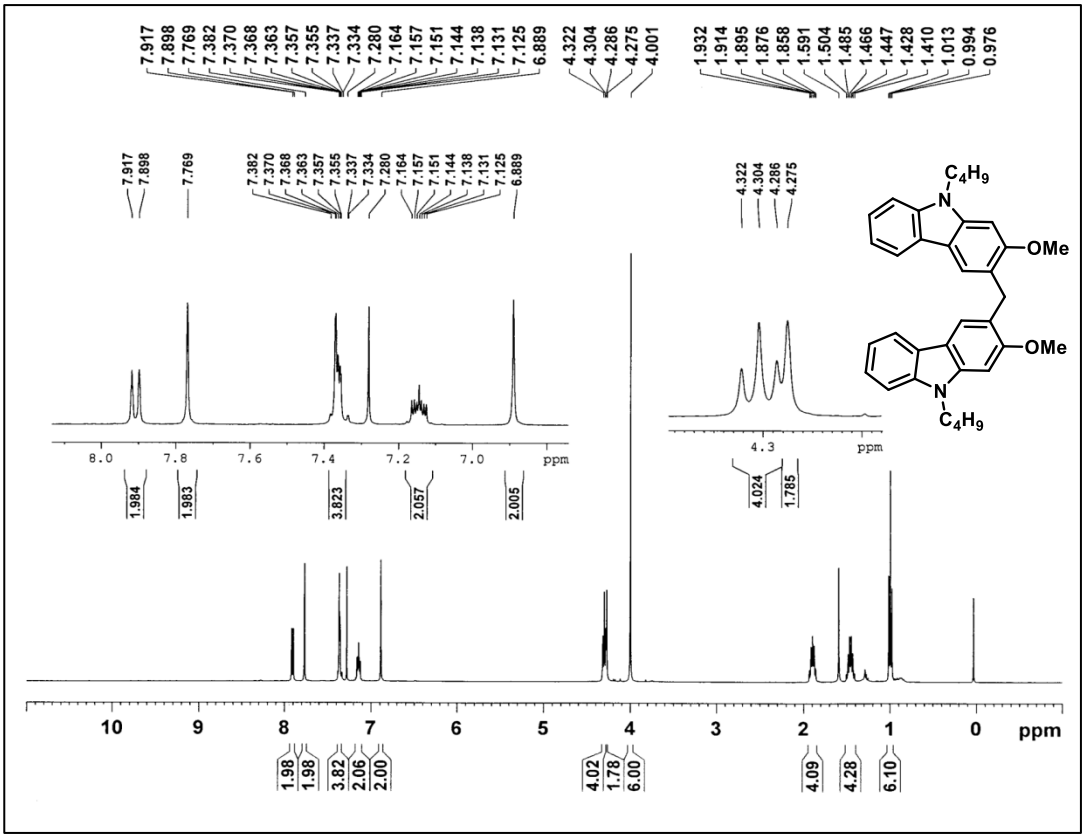
^{13}C-NMR of compound 117 ($CDCl_3$, 100 MHz)



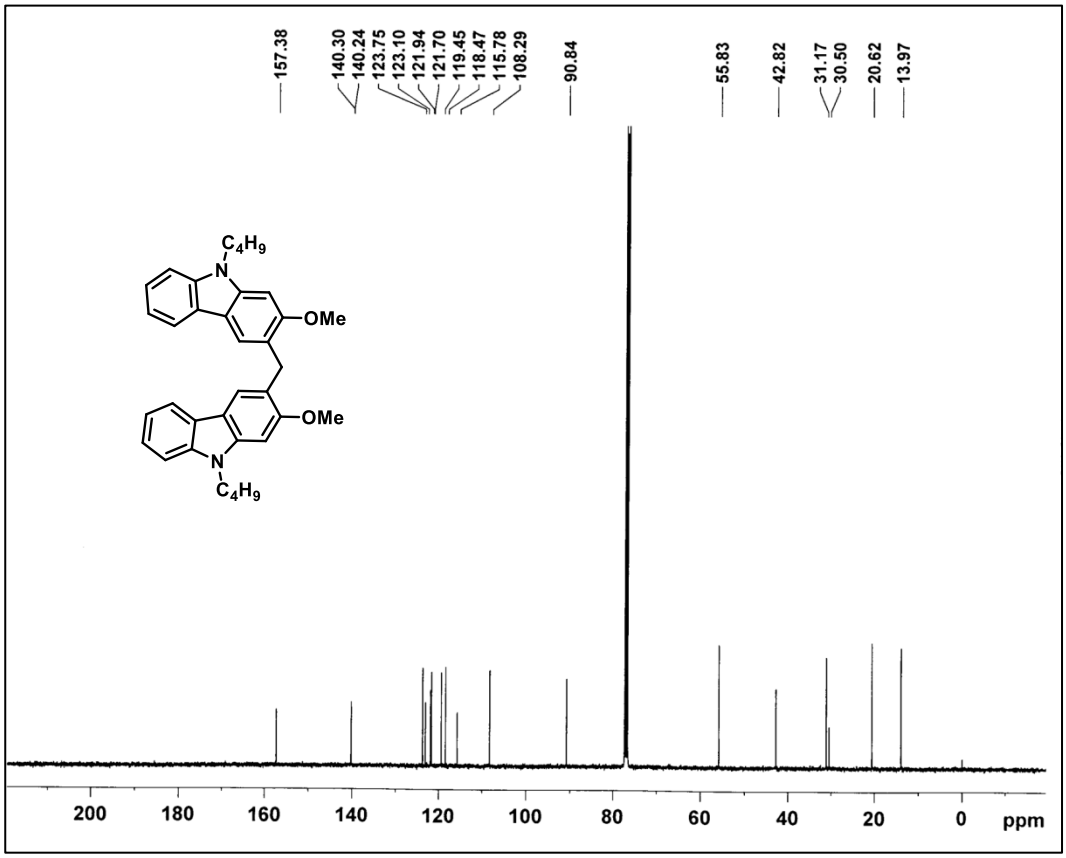
^{1}H-NMR of compound 120 ($CDCl_3$, 400 MHz)



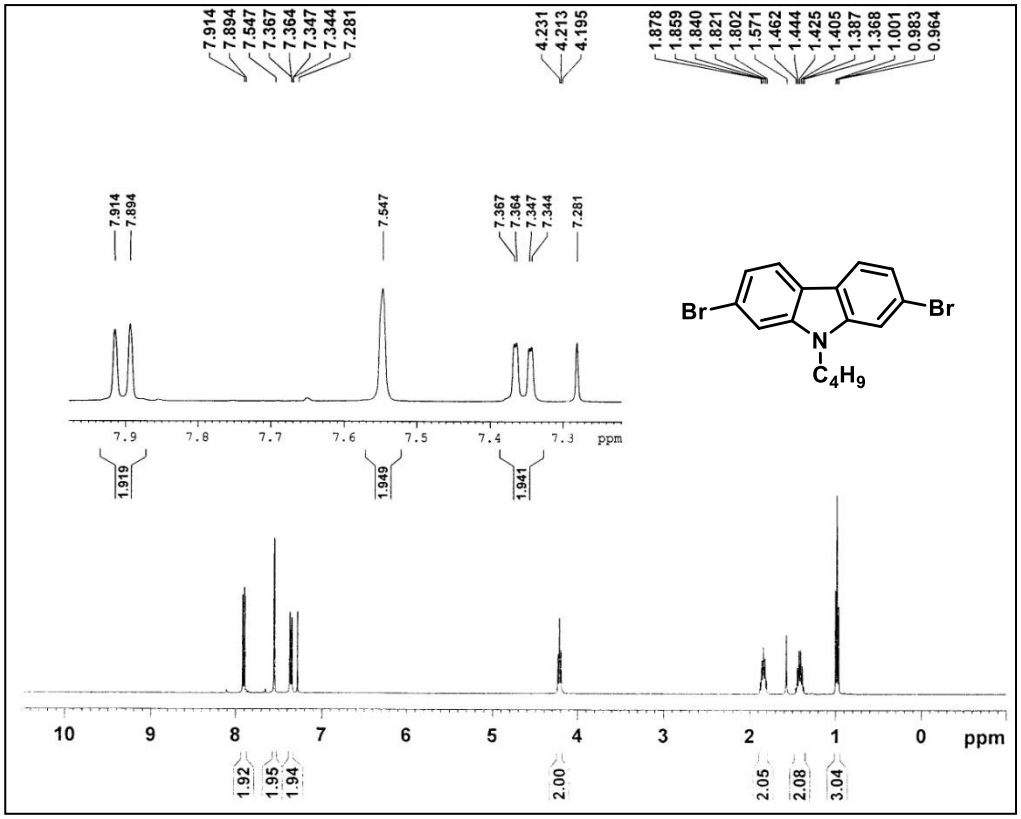
^{13}C-NMR of compound 120 ($CDCl_3$, 100 MHz)



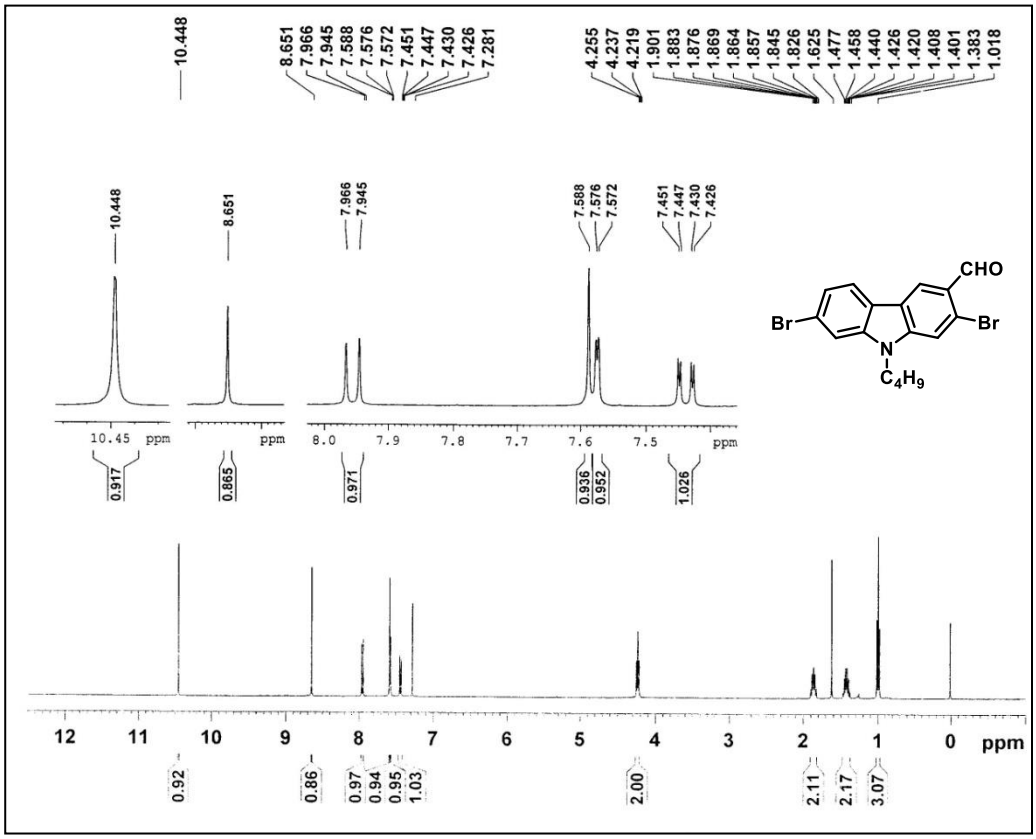
^{1}H-NMR of compound 121 ($CDCl_3$, 400 MHz)



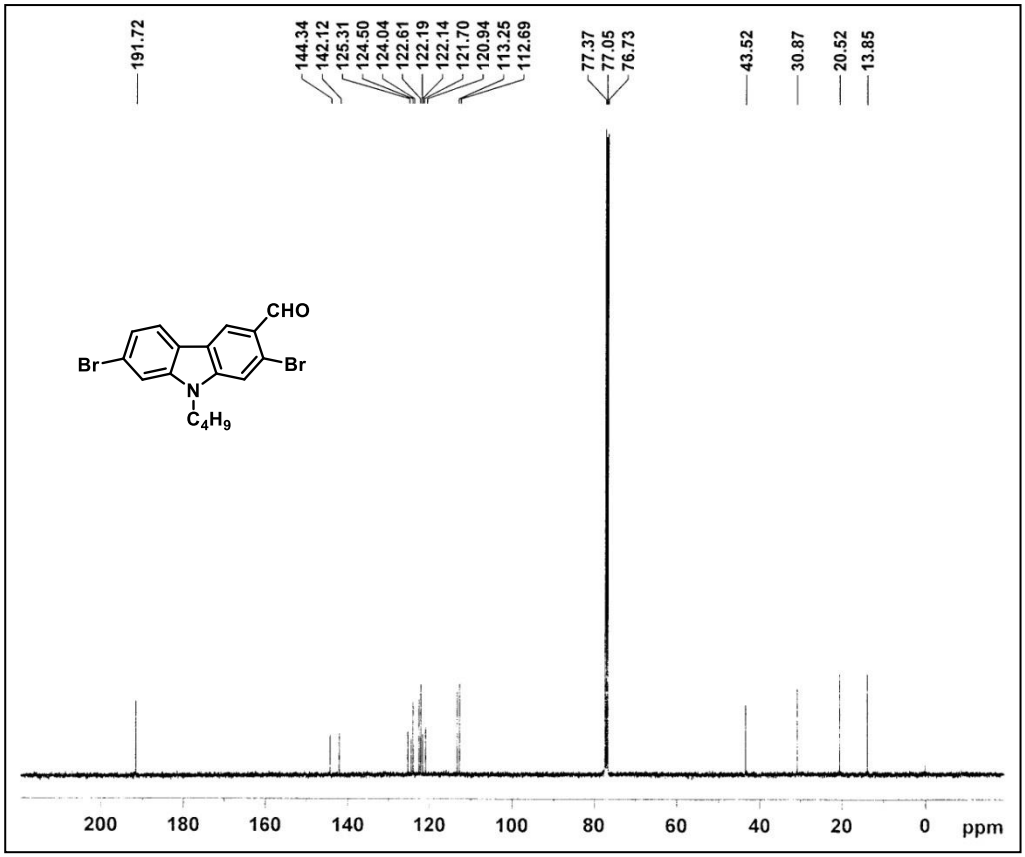
^{13}C-NMR of compound 121 ($CDCl_3$, 100 MHz)



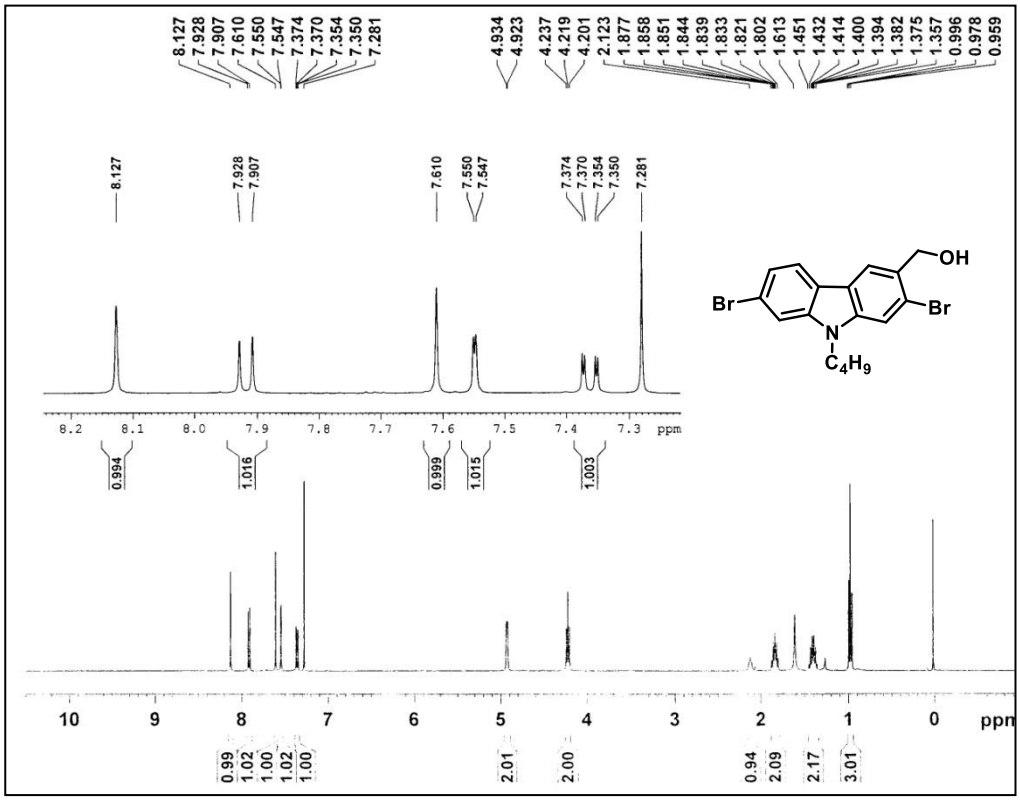
^{1}H-NMR of compound 125 ($CDCl_3$, 400 MHz)



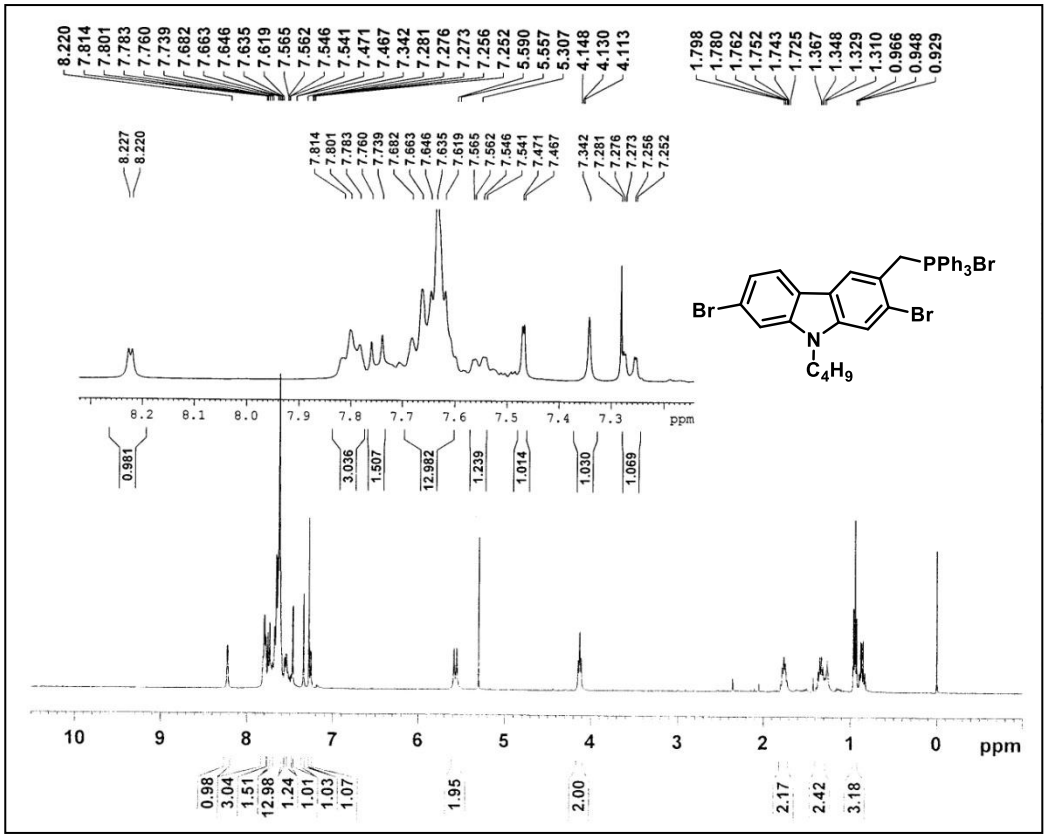
^{1}H-NMR of compound 126 ($CDCl_3$, 400 MHz)



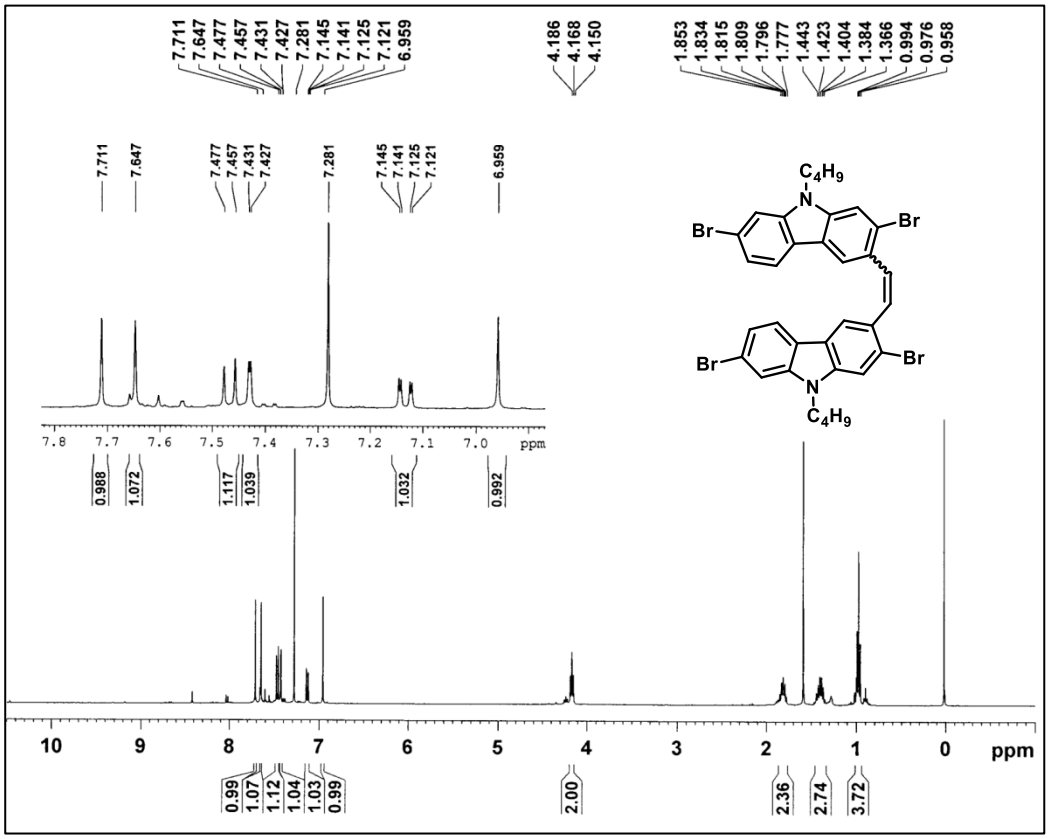
^{13}C-NMR of compound 126 ($CDCl_3$, 100 MHz)



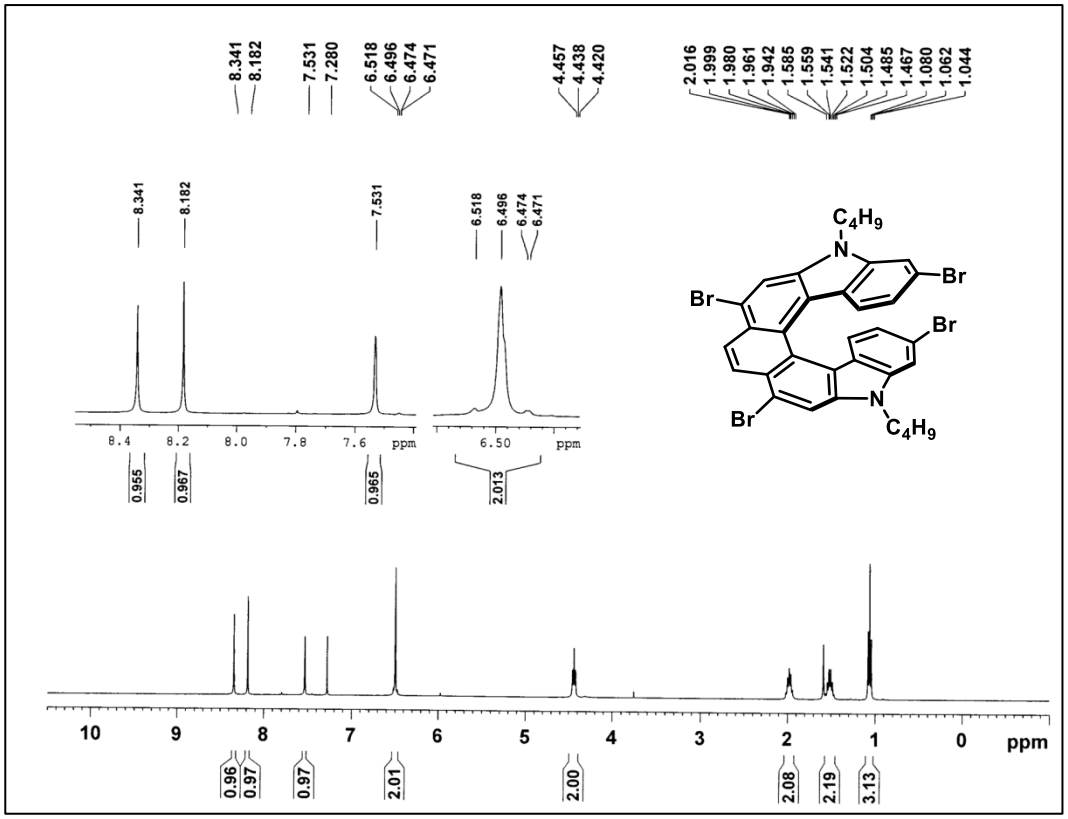
^{1}H-NMR of compound 127 ($CDCl_3$, 400 MHz)



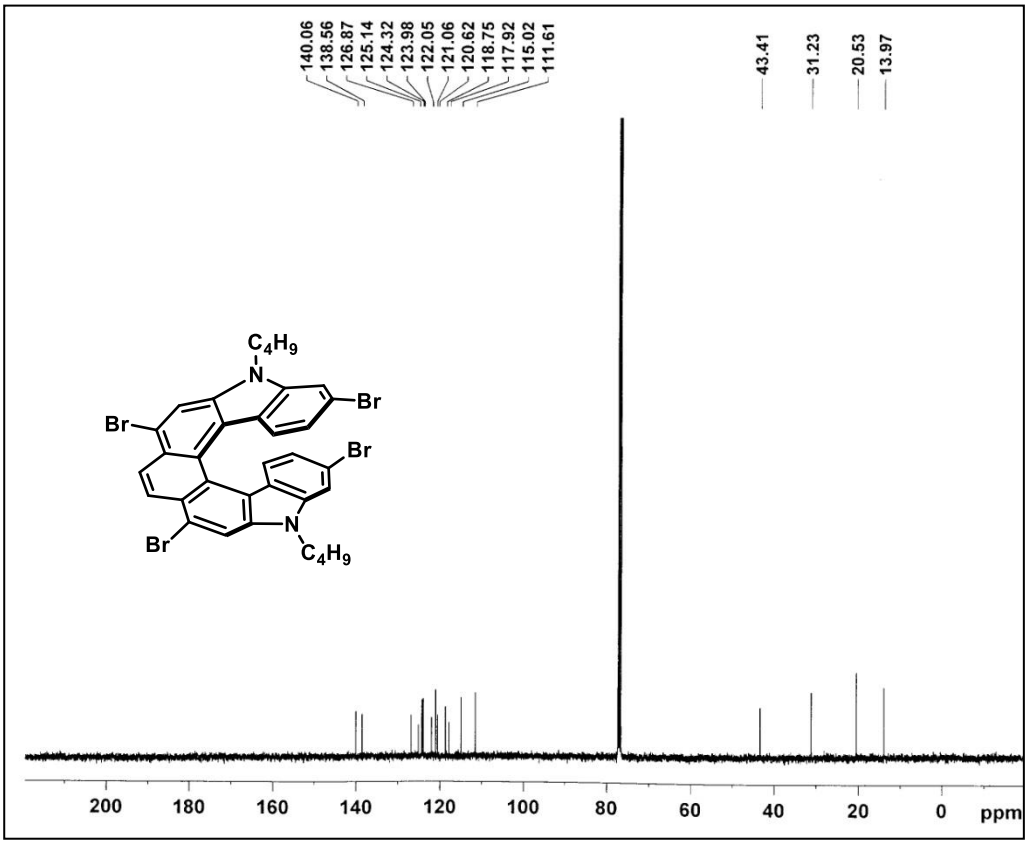
^{1}H-NMR of compound 128 ($CDCl_3$, 400 MHz)



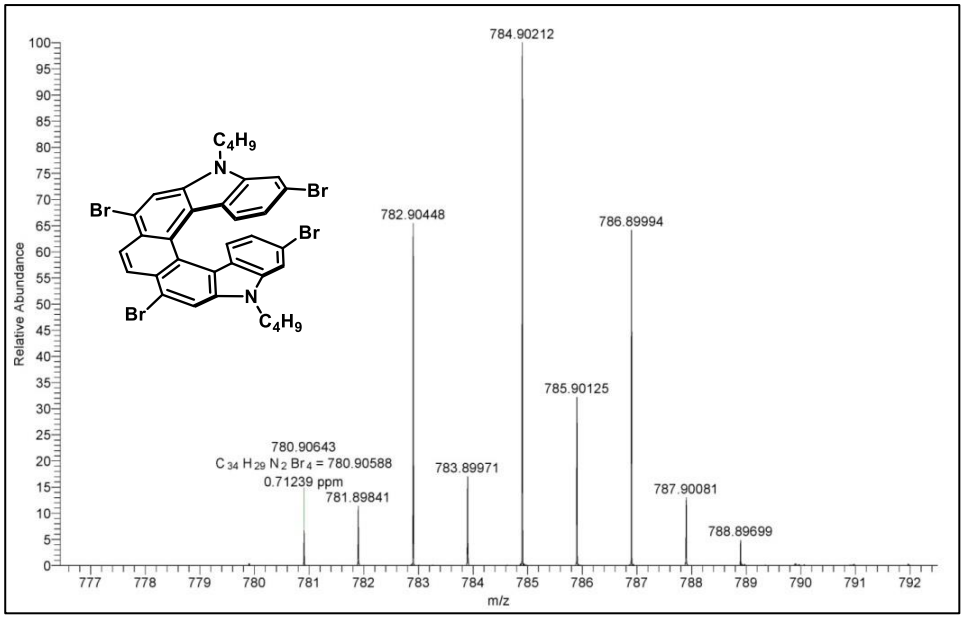
^{1}H-NMR of compound 129 ($CDCl_3$, 400 MHz)



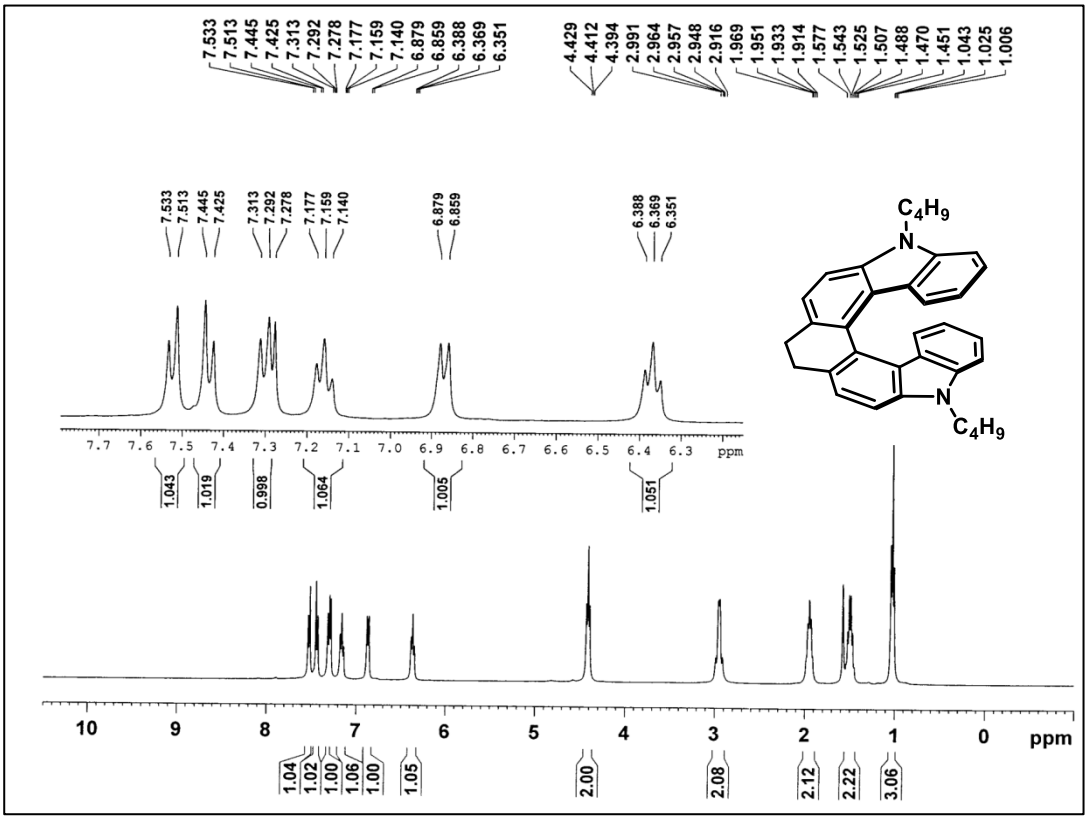
^{1}H-NMR of compound 130 ($CDCl_3$, 400 MHz)



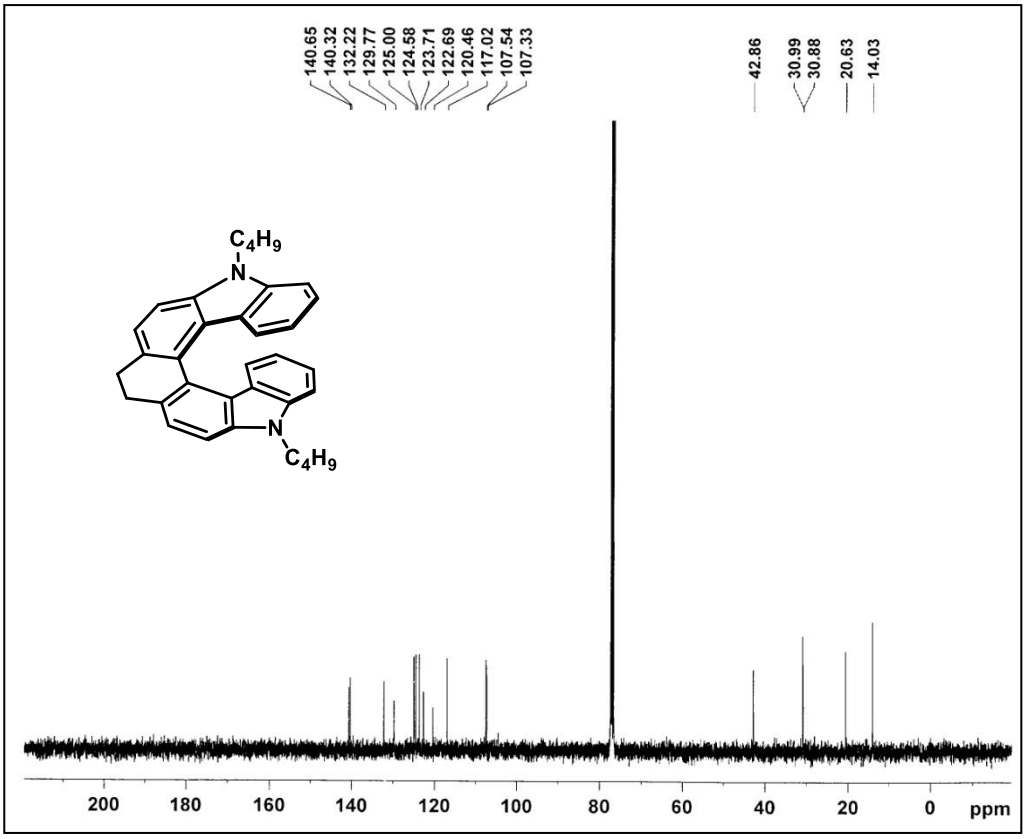
^{13}C-NMR of compound 130 ($CDCl_3$, 100 MHz)



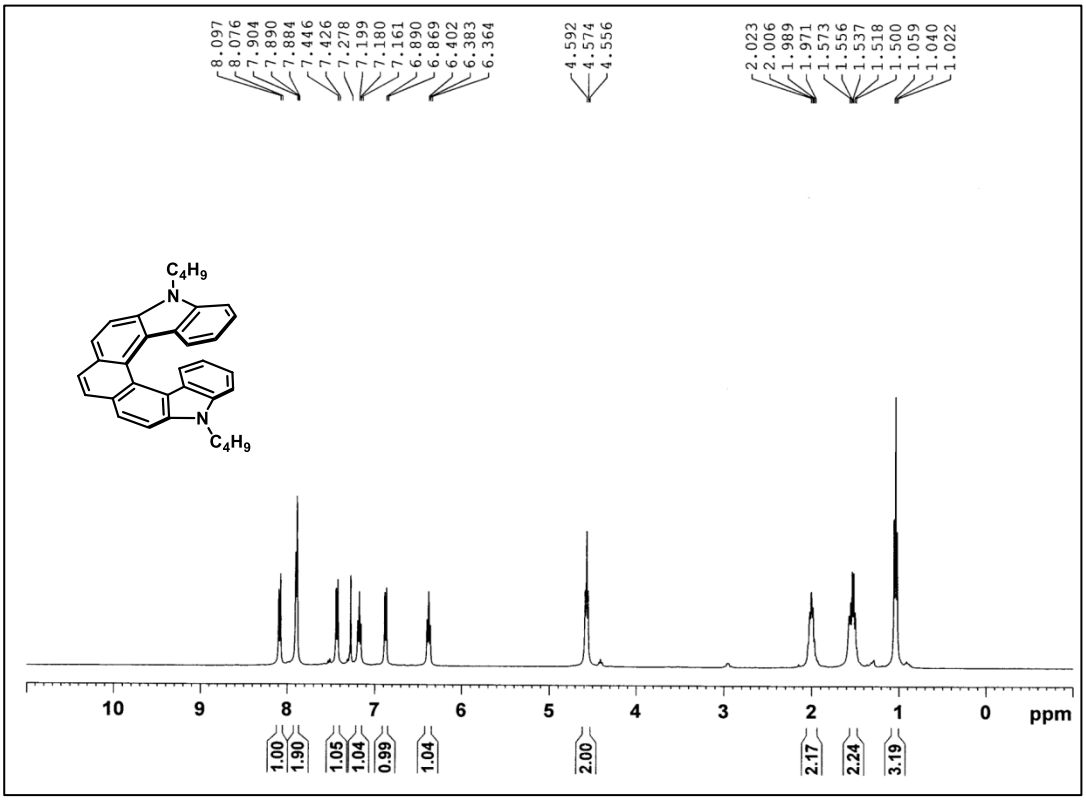
HRMS of compound 130



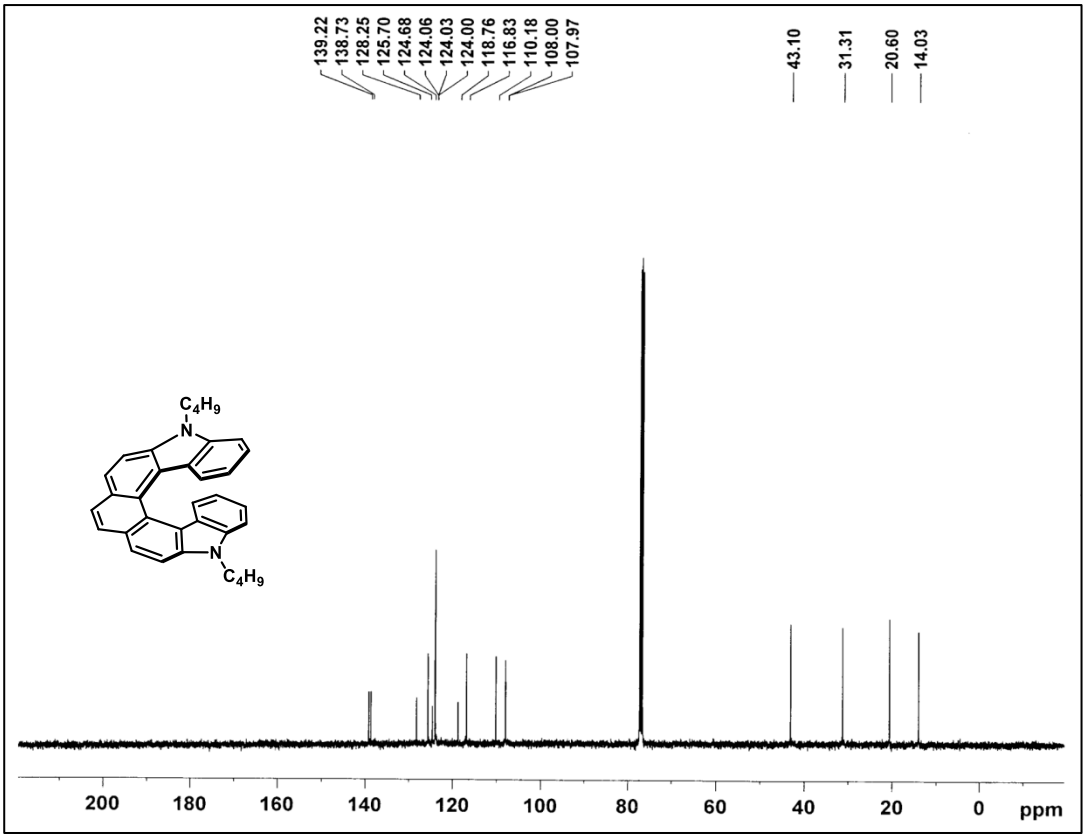
^{1}H-NMR of compound 131 ($CDCl_3$, 400 MHz)



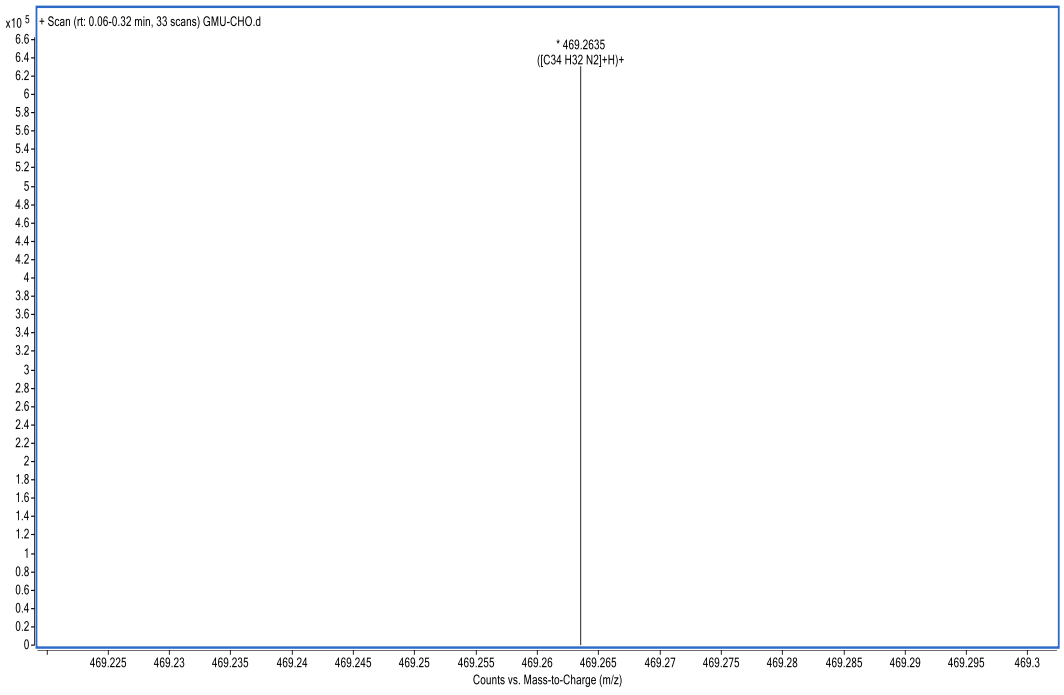
^{13}C-NMR of compound 131 ($CDCl_3$, 100 MHz)



^{1}H-NMR of compound 93 ($CDCl_3$, 400 MHz)



^{13}C-NMR of compound 93 ($CDCl_3$, 100 MHz)



HRMS of compound 93.

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