CHAPTER - 3B

Synthesis and study of pyrrolo[7]helicenes with unsymmetrical functionalization

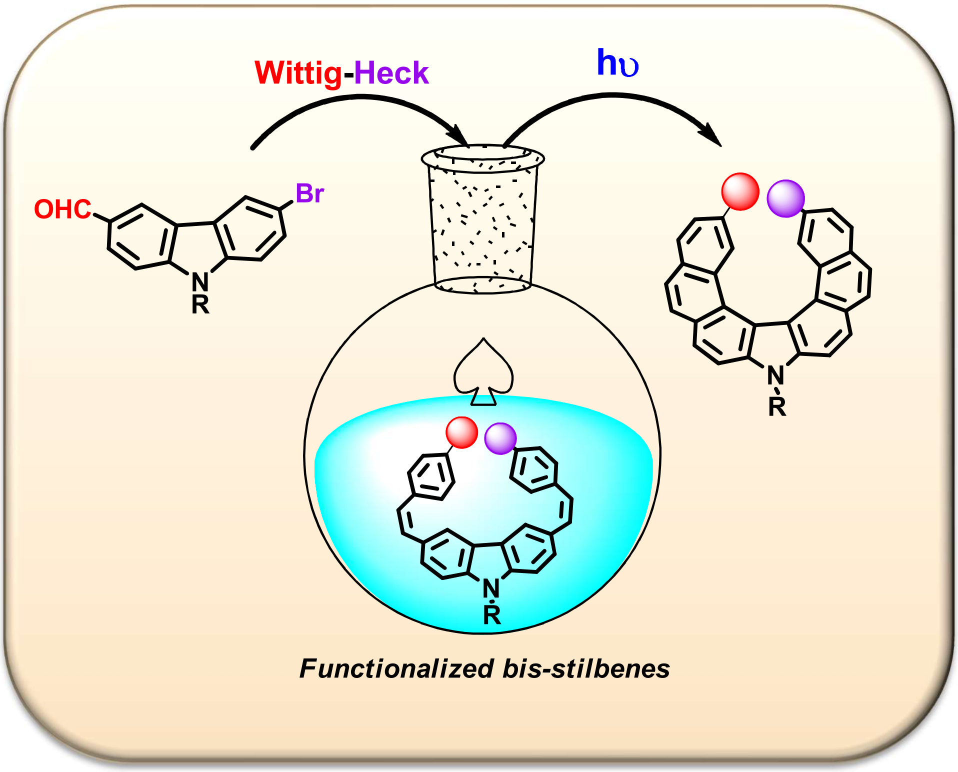
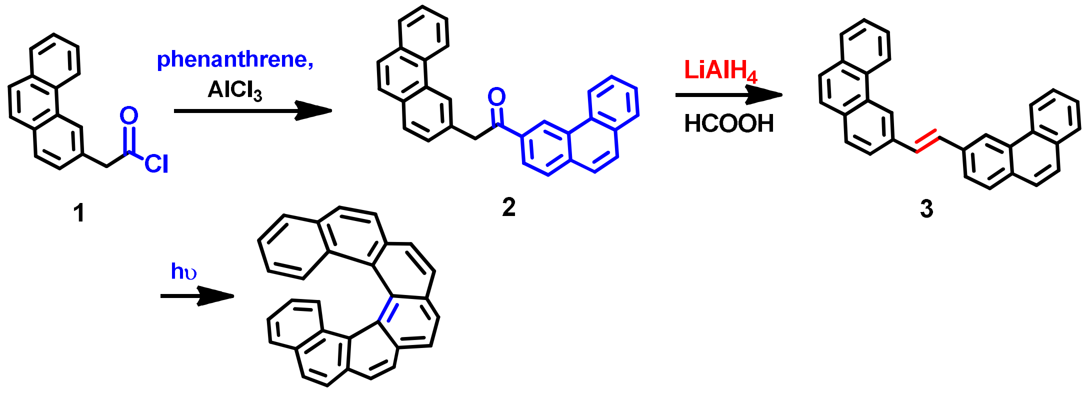


Table of Contents

3.2.1 Introduction

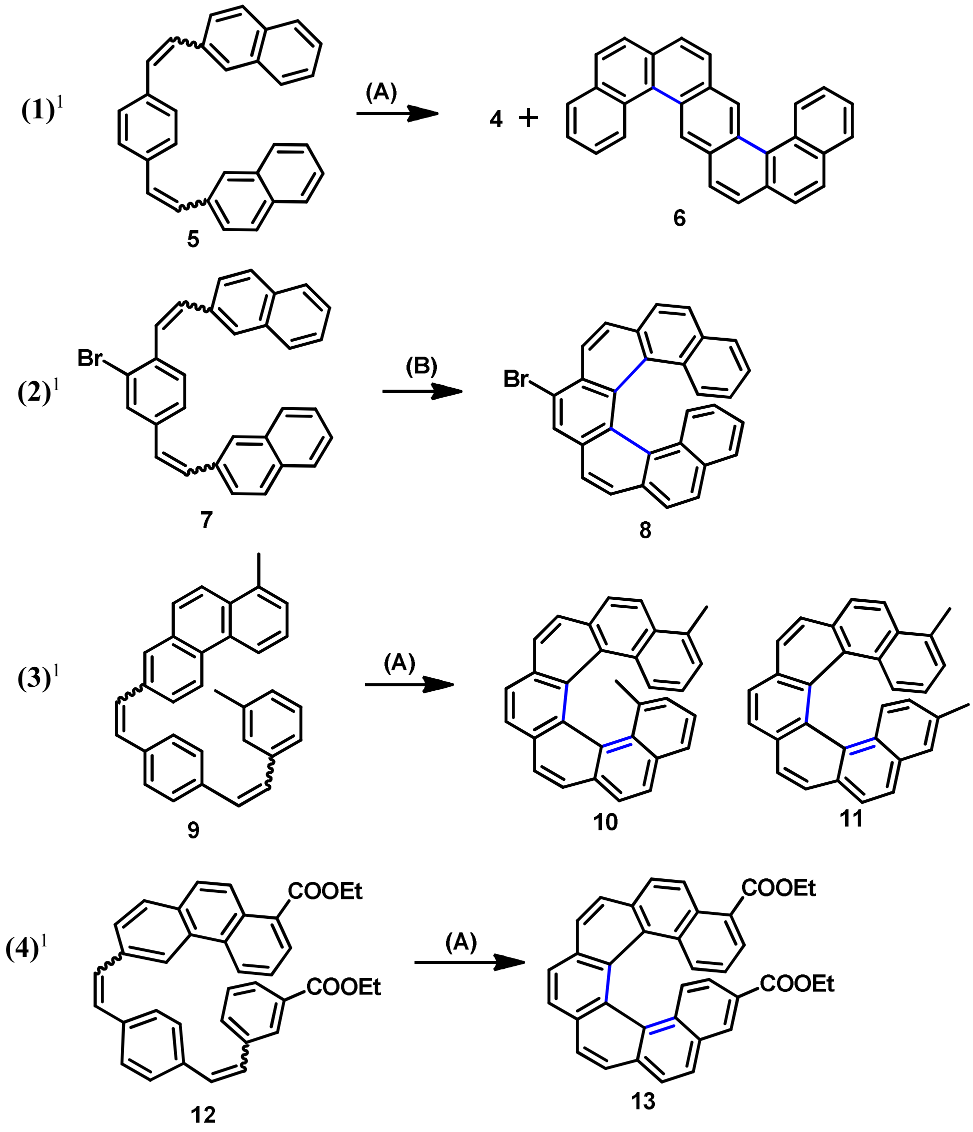
The first report of the synthesis of a seven-membered helicene was given by Martin and group in 1967.[1] They reported the synthesis of heptahelicene by photoinduced cyclization of 1,2-bis(3-phenanthryl)ethylene as shown in **Scheme 3.2.1**. The precursor for cyclization was obtained by condensation of 3-phenanthrylacetyl chloride with phenanthrene to render the corresponding ketone derivative which was then reduced in the presence of Lithium Aluminium Hydride to give the ethylene after dehydration. The cyclisation was carried out in benzene solution under irradiation with a 450 W medium pressure mercury lamp.



4

Scheme 3.2.1: *The first heptahelicene synthesis*

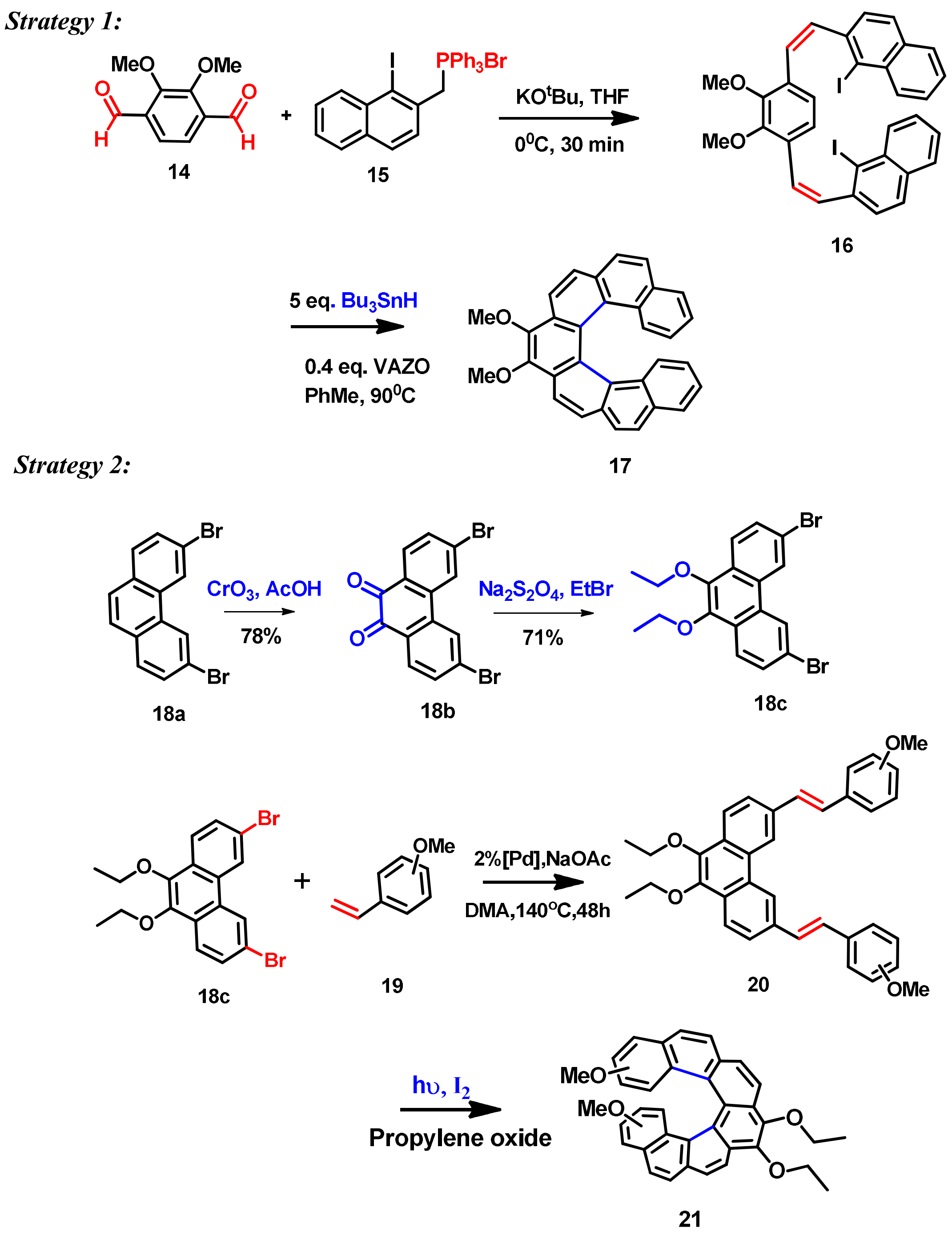
Since the first report, oxidative photocyclization has become the most common method for the synthesis of larger helicenes. It generally involves a two-step procedure: (1) the synthesis of stilbene precursors (2) irradiation of the stilbene solution in the presence of oxidants. Some representative examples of heptahelicenes synthesized by oxidative photocyclization are shown below in **Scheme 3.2.2**. Harroween and group[2] in 2006 reported a concise and efficient route to synthesize helicenes with the use of halo and alkoxy substituents to control the stereochemical outcome of Wittig reaction and the regioselectivity of homolytic aromatic substitution reaction. This strategy was first applied for the synthesis of aza[5]helicene and then extended to heptahelicenes. Thus, phosphonium salt **15** and bis-aldehyde **14** were first condensed under standard Wittig conditions to give stilbene **16** as a 3:1 mixture of *Z,Z* and *E,Z* isomers. *Z,Z* isomer was then exposed to five equivalents of tributyltin hydride and 0.4 equivalents of VAZO(1,1'-azobis-(cyclohexanecarbonitrile)) to induce selective homolysis of the carbon–iodine bond to give 9,10-dimethoxy[7]helicene in 75% yield.



***Conditions*: (A) hυ, benzene, I_2 (B) hυ, benzene, I_2 (0.2 eq)**

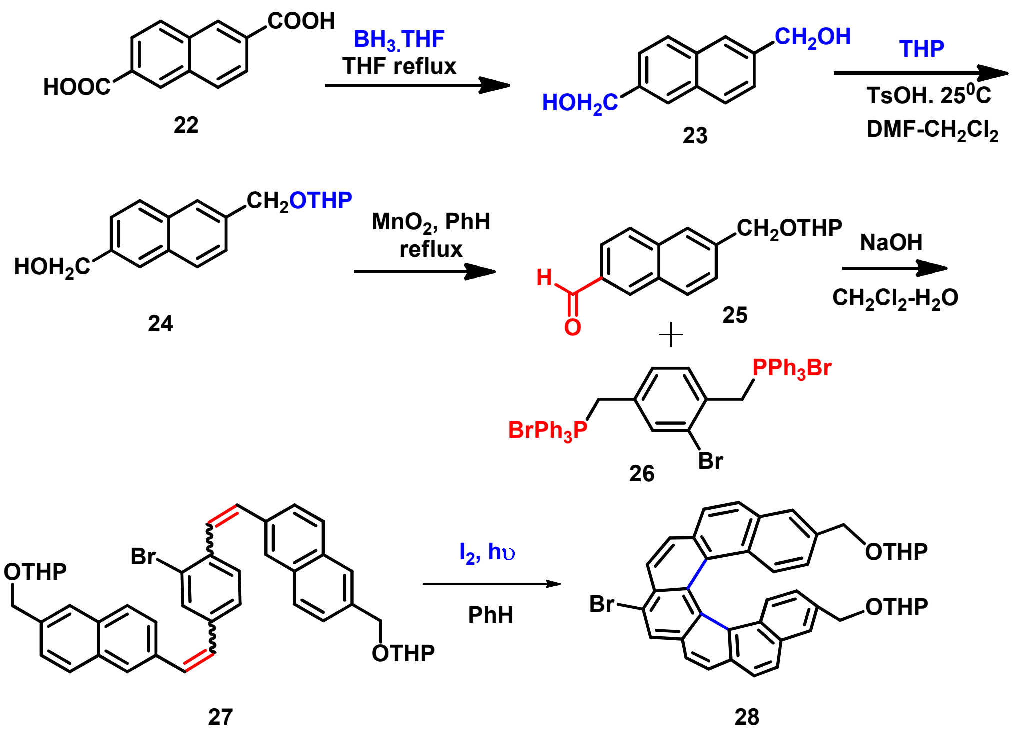
Scheme 3.2.2: Some representative examples of synthesis of heptahelicenes by photocyclization

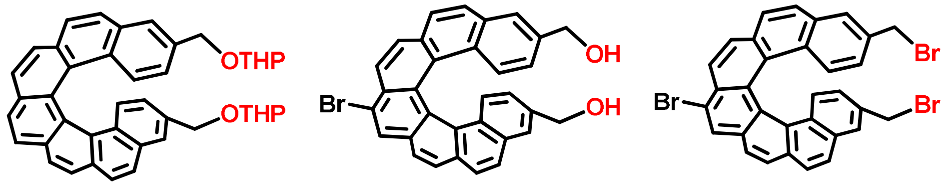
In continuation of this work, H. Guédouar and group[3] designed similar helically chiral heptacyclic system with alkoxy substituents. One of the key features of the synthesis was the utilization of a tricyclic system to serve as a building block for helicene. The alkoxy group was selected to improve the solubility of the helical molecules in common organic solvents. The synthesis was performed as shown in **Scheme 3.2.3.** Here the starting material 3,6-dibromophenanthrene was synthesised by photocyclization of the corresponding styrene which was obtained after Wittig reaction. The phenanthrene derivative was then oxidized in the presence of chromium trioxide to yield 3,6-dibromo-9,10-phenanthroquinone and later reduced with sodium dithionite to render 3,6-dibromo-9,10-diethoxyphenanthrene after in situ *O*-ethylation in bromoethane. This phenanthrene derivative with dibromo substitution was used as the key building block for the synthesis of styryl derivatives by Mizoroki-Heck coupling reaction as shown in **Scheme 3.2.3.**



Scheme 3.2.3: Synthesis of dimethoxy heptahelicene using different strategies.

In an independent study, Gingras and Collet emphasized the importance of synthesizing functionalized seven-membered helicoids.[4] They reported the synthesis of bidentate ligands for the first time in the heptahelicene series as shown in **Scheme 3.2.4**. In this work they also gave their rationale for choosing heptahelicene as the perfect scaffolds for the synthesis of helicoidal ligands. The reasons listed by Gingras and group for choosing heptahelicenes are: (a) High optical rotation values ($[a]^{25}$ +6200 for heptahelicene) which would allow a better precision in evaluating enantio- and diastereopurities. (b) Due to good π-donor abilities they can form charge transfer complexes with many π-acceptors which will aid in the optical resolution of helicenes. Besides, $\pi-\pi$ interactions play significant role in determining both the properties as well as self-assembling behaviour of helicenes. (c) The solubility of such compounds is usually better than their polyaromatic linear analogues. (d) Unlike smaller helicenes, the stereochemical stability of heptahelicene is relatively good even at higher temperatures without the fear of racemization. (e) Their helicoidal nature could serve as a large chiral template for molecular recognition, chiral induction, and molecular assemblies in supramolecular chemistry.

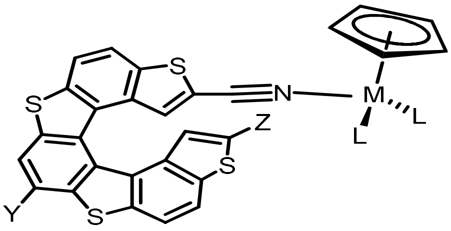




29 **30** **31**

Scheme 3.2.4: Scheme for the synthesis of bidentate heptahelicenic ligands

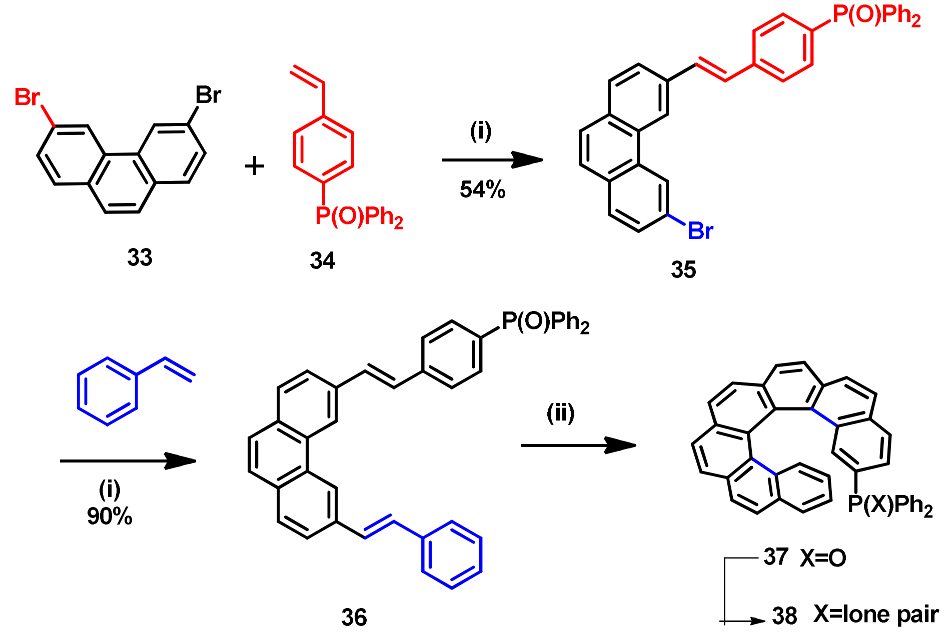
In 2009, Garcia and group[5] gave their contribution in synthesizing few heptahelicenic ligands based on thiophene moiety through functionalization of one terminal thiophene with a nitrile group (L1), two terminal thiophene rings with two nitrile groups (L2) and one terminal thiophene group with one nitrile group followed by nitration in the benzene rings (L3). The derivatives were used as ligands for the synthesis of a new family of η^5-monocyclopentadienyl ruthenium(II) and iron(II) organometallic complexes represented by the general formulation [MCp(PP)(NC{TH-[7]-Y} Z)] [PF_6] (M = Ru(II), Fe(II), P–P = DPPE, Y = H, NO_2, Z =H, CN; M = Ru(II), L–L = $2PPh_3$, Y =H, Z = H).



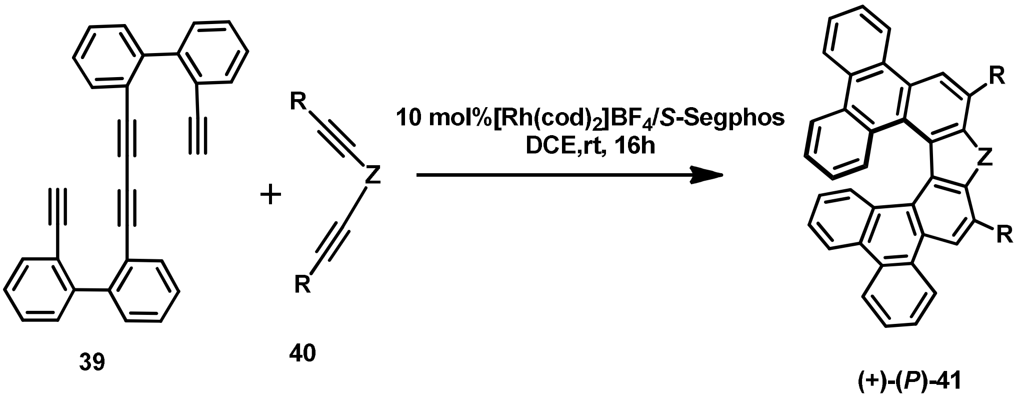
32

Figure 3.2.1: Tetrathia[7]helicene Ru/Fe derived complexes

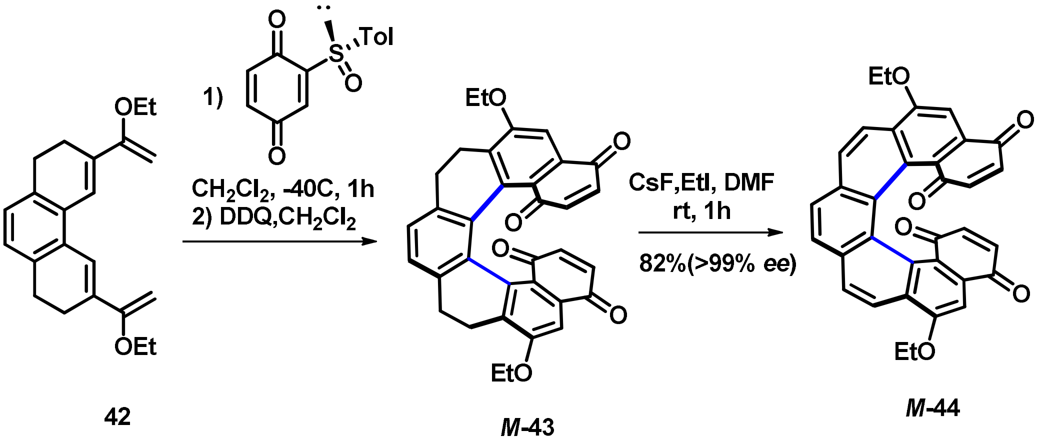
R.El Abed *et al.*[6] developed a synthetic approach and enantiomeric resolution of [7]helicene based phosphine ligands. They showed that the cyclopalladated a-naphthylethylamine complex is a suitable resolving agent for helical phosphine. The synthetic approach is based on the easy preparation of stilbene derivatives using Mizoroki-Heck reactions followed by oxidative photocycization. There are numerous reports of asymmetric synthesis of heptahelicenes using chiral ligands. Tanaka group developed Rh-catalyzed [2+2+2] cycloisomerization to build helical skeletons via intermolecular cycloaddition.[7] By changing the diyne precursor, carbo-,phospha-, and silahelicenes could be synthesized up to 93 % ee with the help of (S)-Segphos ligands in reasonable yields (**Scheme 3.2.6**).[8] A direct and easy access to enantioenriched helicenebisquinones was reported by Urbano group utilizing chiral *p*-benzoquinone.[9] **(Scheme 3.2.7)**



Scheme 3.2.5 : Synthesis of helical phosphine ligands

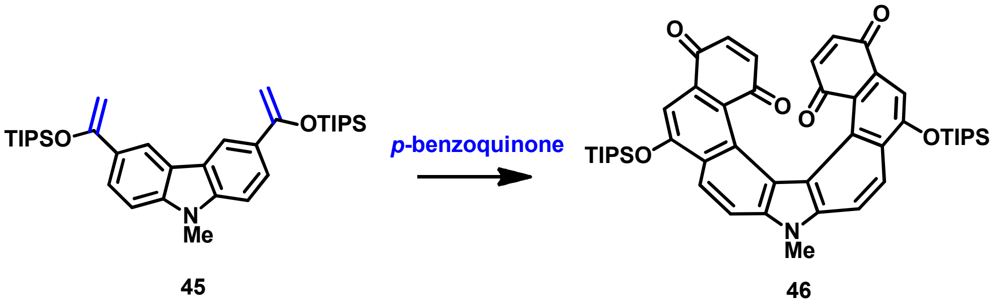


Scheme 3.2.6: Asymmetric synthesis of heptahelicene by Rh-catalysed [2+2+2] cycloisomerization



Scheme 3.2.7: Asymmetric synthesis of [7]helicene bisquinone

Amongst the nitrogen containing helicenes, aza[n]helicenes, two major types possessing the pyrrole or pyridine are known in the literature. Pyrrolohelicenes possessing the carbazole group is a well-known moiety in conjugated systems owing to its good planarity and N-H bond, which can be easily substituted for other functional groups. The first carbazole derived azahelicene was synthesized using double Diels-Alder reaction by Katz and group.[10] The aza[7]helicenebisquinone was synthesized by utilizing the bis-diene with *p*-benzoquinone as dienophile (**Scheme 3.2.8**). The rate of reaction was much faster than the synthesis of carbohelicenes.



Scheme 3.2.8: Synthesis of carbazole based helicene bisquinones by Katz and group

In 2012, Liu and group synthesized di-aza[7]helicene **47** by photo-induced cyclization. The helicene was found to be a potential candidate for deep blue emitting OLED devices with good thermal and chemical stability.[11] In 2013, Moorthy and group[12] reported the synthesis of some azahelicene based chromenes **48** showing photo-responsive behaviour, sensitive towards external stimuli like acid, heat, and visible radiation. The same group in

2016, reported few derivatives of aza[5]helicene diamines[13] **49** which rendered good hole transporting properties useful for application as OLEDs. In the same year, M.Tounsi and group[14] reported dibromo aza[7]helicene **50** and screened it for K^+ ion detection. It was for the first time that a capacitive field-effect sensor was fabricated using helicene as a carrier for K^+ detection.

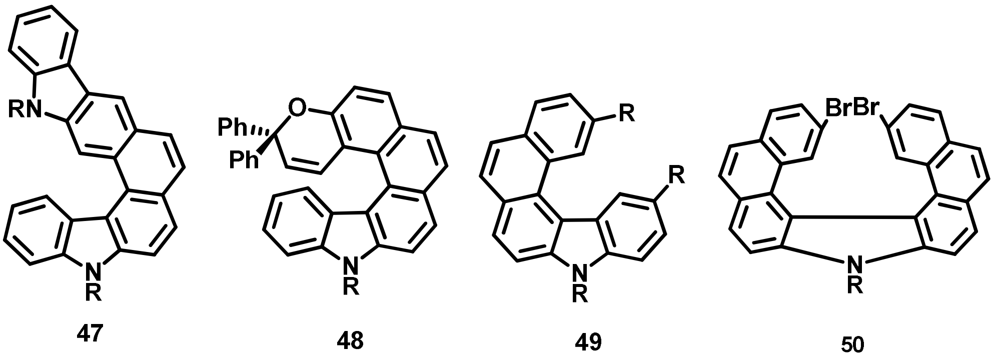


Figure 3.2.2: Some examples of pyrrrolo[7]helicenes explored for various applications

Thus, pyrrolohelicenes show promising applications in various fields like optical devices, for enantioselective transformations, as chiral inducers and in the fields of asymmetric catalysis. However, it is important to have easy access to functionalized helicenes to explore application of these compounds in various areas. So, in this chapter, we discuss the synthesis of unsymmetrically functionalized seven-membered pyrrrolohelicenes by photocyclization strategy. The facile synthesis of variably functionalized helical molecule by easy access of the stilbene precursors using one-pot reaction is the main crux of this chapter.

3.2.2 Results and Discussion

In the present study, our target was to synthesize funcionalized heptahelicenes. As studied from the literature review, it is clear that in order to explore the utility of these molecules as asymmetric inducers, helical ligands or catalyst, apical functionalization was important and owing to the easier functionalization of heterohelicenes for introduction of various substituents like formyl, ester, trifluoromethyl, amide, acid halides etc., we decided to synthesize a series of apically functionalized mono and di-substituted aza[7]helicenes. A previous study from our group involves the synthesis of aza[7]helicenes[15] of type I and III and aza[9]helicenes[16] of type II as shown in **figure 3.2.3,** where the helical framework is symmetrically substituted. In this work, our aim is to synthesize a series of unsymmetrically substituted aza[7]helicenes with mono and di-substitution in the terminal ring.

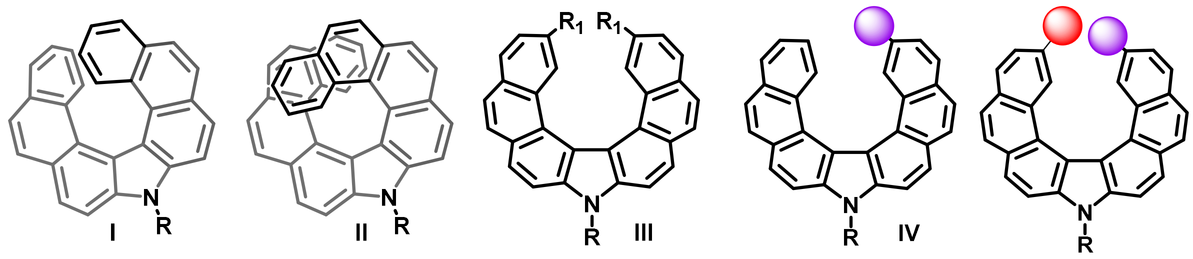
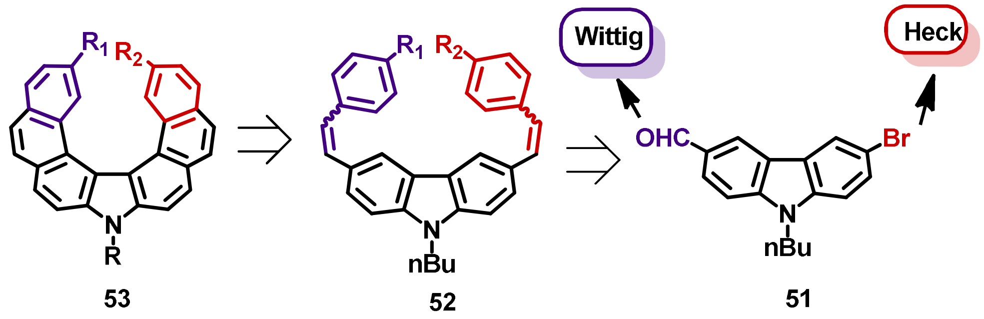


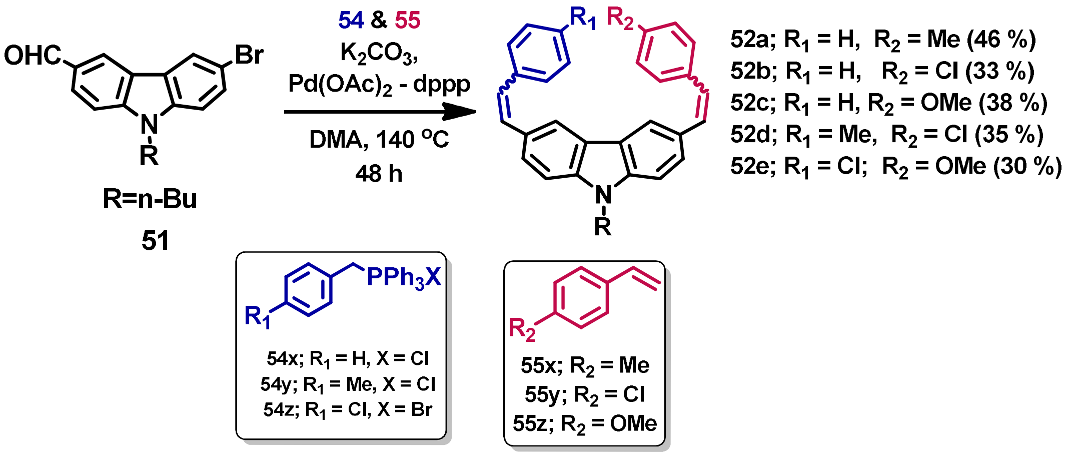
***Figure 3.2.3**: Symmetrical and Unsymmetrically substituted azahelicenes*

Retrosynthetic analysis suggests that introduction of different functional group in the olefin precursor can be achieved by a combination of Wittig and Heck reaction on the formyl and bromo group respectively of the building block. So, 3-formyl-6-bromo-9-butyl carbazole was synthesized to solve this purpose. However, the synthesis of the olefin precursor can be achieved by a one-pot reaction or by step-wise method. So in this work we had synthesized a series of bis-olefin derivatives by both the methods and compared their overall chemical yield followed by photocyclization of the olefins to afford the corresponding mono and di-funtionalized unsymmetrical aza[7]helicene. We have developed one-pot synthetic protocol for efficient preparation of derivatives of styrene involving both these reactions. Accordingly, we began the synthesis from readily available 6-bromo-3-carbaldehyde-9-butyl-9*H*-carbazole **51**, which was protected with n-butyl group to give suitable solubility in organic solvents (**Scheme 3.2.10**).



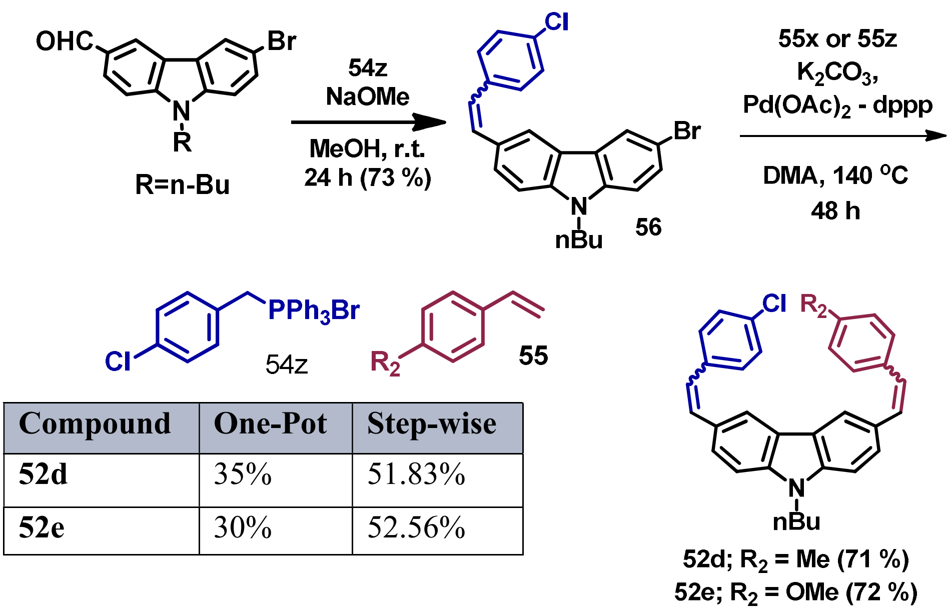
Scheme 3.2.9: Retrosynthesis of bis-stryryl type derivatives

The derivative of carbazole **51** was subjected to one-pot Wittig-Heck reaction with suitable combination of triphenyl phosphonium salt **54** ($ArCH_2PPh_3X$), styrene **55** ($ArCH{=}CH_2$) suitable catalyst and base. It is envisaged that the phosphonium salt **54** will *in situ* generate the reactive Ylide intermediate ($ArCH{=}PPh_3$) to react with the aldehyde group of **51**, while the styrene will undergo Mizoroki-Heck reaction with its halogen substituent in presence of palladium catalyst and the same base. We selected two sets of phosphonium salts and styrene derivatives to generate different bis-styryl derivatives **52a-52e** in moderate yield, but in a single convenient operation. The bis-styryl derivatives were purified by careful column chromatography over silica gel, although isolated as major *E*,*E* isomer. The same intermediates were also synthesized by stepwise reaction sequence (**Scheme 3.2.11**).



Scheme 3.2.10: Synthesis of bis-styryl derivatives by one-pot methodology

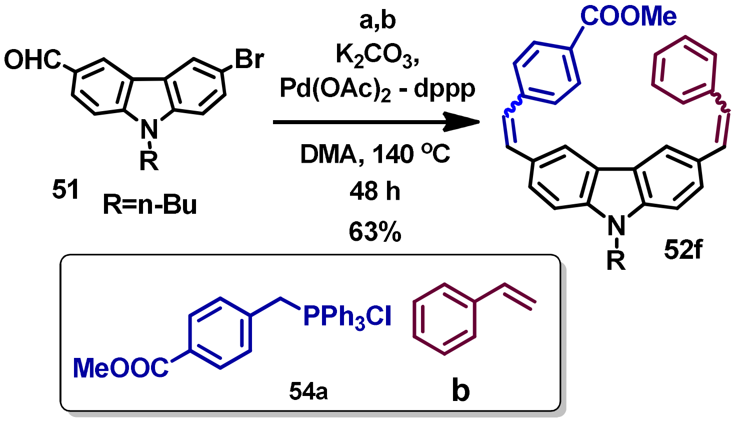
The carbazole derivative **51** was subjected first to Wittig reaction with phosphonium salt **54z** ($4\text{-}ClC_6H_4CH_2PPh_3Br$), and sodium methoxide under more classical condition of Wittig reaction to afford mono-styryl derivative **56** in much improved yield. This was then subjected separately for Mizoroki-Heck conditions to afford two derivatives of **52d** and **52e** in overall higher conversion. The synthesized bis-styryl derivatives of carbazole **52** were then subjected to photocyclization reaction in presence of iodine as an oxidizing agent and THF as scavenger of hydrogen iodide formed as byproduct (**Scheme 3.2.12**).



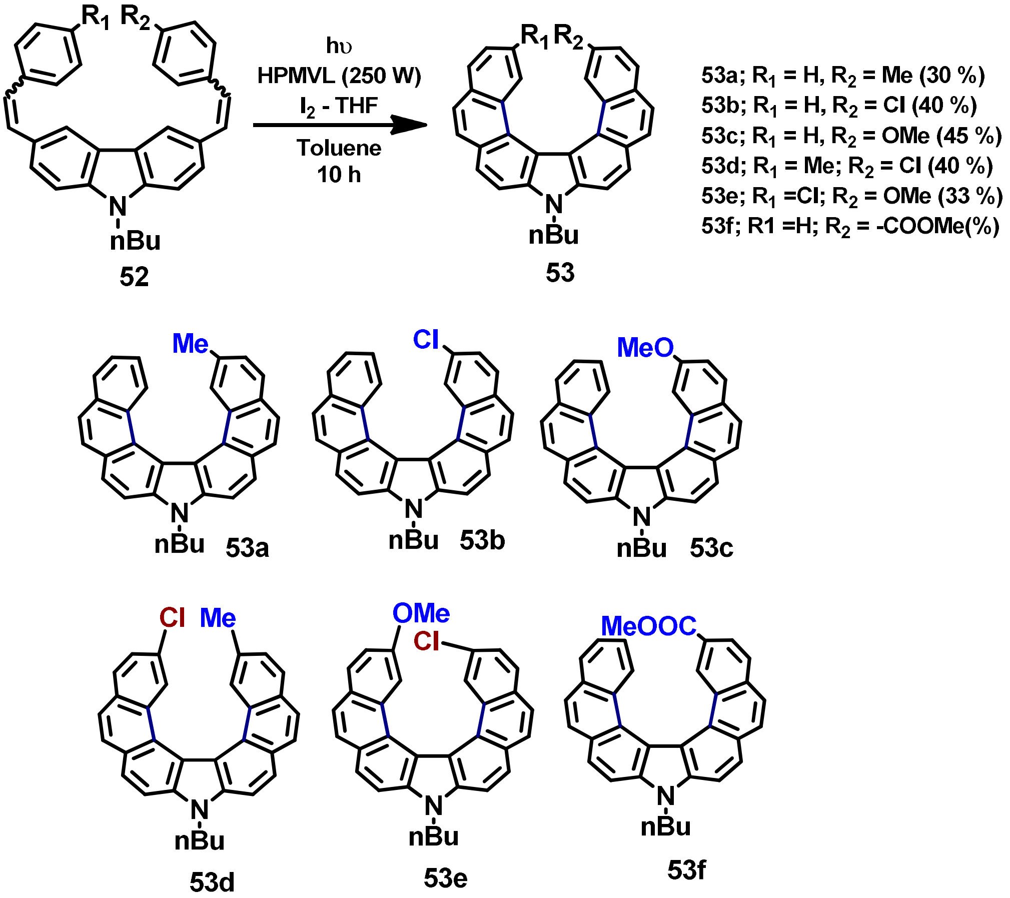
Compound	One-Pot	Step-wise
52d	35%	51.83%
52e	30%	52.56%

Scheme 3.2.11: Synthesis of bis-styryl derivatives by step-wise method

As an extension to this work, we also thought of incorporating an ester and the corresponding acid functional group to the scaffold with the objective to carry out resolution experiments. As shown in **Scheme 3.2.12**, to obtain the bis-styryl precursor, compound **51** was subjected to one-pot Wittig-Heck reaction conditions using 4-(methoxycarbonyl)benzyltriphenylphosphoniumbromide **54a**. The reaction proceeded smoothly at 140°C for 48 hours resulting in yellow solid. Purification of compound **52f** was done using column chromatography giving good yield (63 %). The cyclization proceeds through the desired angular-angular mode furnishing the unsymmetrical aza[7]helicene derivatives **53** in moderate yields. The compound **53f** with the ester functionality was then subjected to basic hydrolysis to render the corresponding acid **57.** The products were characterized by usual spectroscopic and analytical techniques

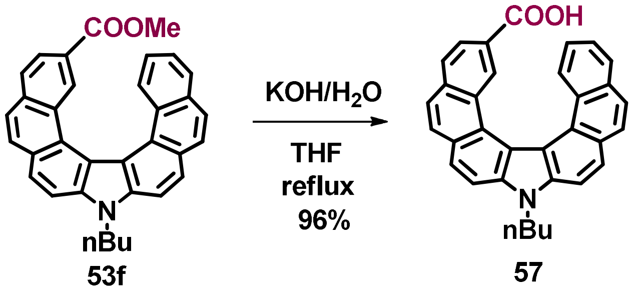


Scheme 3.2.12: Synthesis of methyl carboxylate stilbene precursor



53a; R_1 = H, R_2 = Me (30 %)
53b; R_1 = H, R_2 = Cl (40 %)
53c; R_1 = H, R_2 = OMe (45 %)
53d; R_1 = Me; R_2 = Cl (40 %)
53e; R_1 =Cl; R_2 = OMe (33 %)
53f; R1 =H; R_2 = -COOMe(%)

Scheme 3.2.13: Scheme for photocyclization for the synthesis of substituted pyrrolo[7]helicenes



Scheme 3.2.14: Synthesis of pyrrolo[7]helicene carboxylic acid

In the ^{1}H-NMR spectra(400MHz), the methyl proton of the bis-styryl derivative **52a** appears as a singlet at 2.40 ppm while the methyl proton of the butyl chain appears as a triplet at 4.32 ppm. The olefinic proton signals appear at 7.1 and 7.2 ppm with a coupling constant value of 16 MHz indicating trans proton coupling. Similarly, the methoxy proton of the bis-styryl derivative **52c** appears at 3.8 ppm. For the compound **52d** with a methyl and chloro substitution, the ^{1}H-NMR spectra showed similar signals with the methyl proton at 2.39 ppm while for the compound **52e** with a methoxy and chloro substitution the methoxy proton signal appears at 3.87 ppm. The methyl ester proton of the bis-styryl derivative **52f** appears at 3.9 ppm. In all the compounds, post-cyclization, the spectra clearly show the disappearance of the olefinic proton signals. Moreover, due to helical winding after cyclization the proton in the aromatic ring which comes in the shielding zone of the other ring is shifted relatively upfield. This upfield shift is also seen in the case of the methyl and methoxy substitution. The methyl proton signals appear at 1.4 ppm in the helicene while it appeared at 2.4 ppm in the corresponding olefin precursor. Similarly, the methoxy proton signal appears at 2.5 ppm in the helicene compared to 3.7 ppm in the precursor. In the case of the methyl ester of the helicene **53f**, the methyl proton appears at 3.4 ppm. After hydrolysis, the methyl proton signal of the ester disappears while the remaining signals of the aromatic protons remains as such indicating the formation of the carboxylic acid. This was further confirmed from FTIR analysis showing hydroxyl peak at 3434 cm^{-1}.

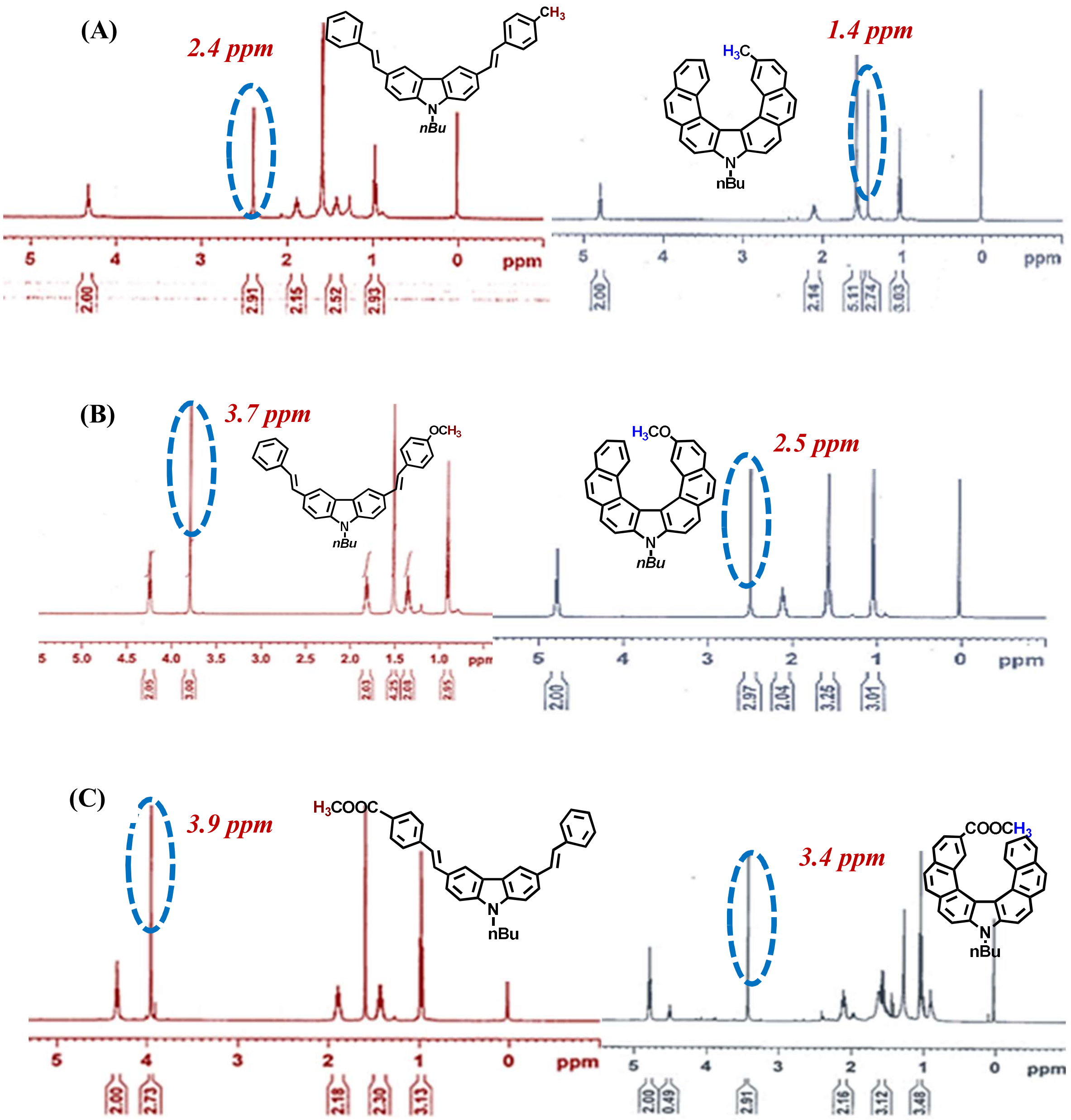


Figure 3.2.4: ^{1}HNMR spectra of compounds 52 and 53 showing upfield shift of methyl and methoxy proton signals post cyclization. (A) 52a and 53a (B) 52c and 53c (C) 52f and 53f

3.2.3 Solid state structure analysis

A suitable crystal of **53a** was obtained from ethyl acetate-hexane and subjected to single crystal X-ray diffraction analysis (**Figure 3.2.5**). As expected for the helical compounds, the inner carbon-carbon bonds were found to be slightly elongated compared to the normal bonds (1.398 to 1.449 Å), while the outer bonds were slightly compressed (1.329 to 1.354Å). The observed torsion angles were 14.89° (φ1 = C17d-C17e-C17f-C1), 17.89° (φ2 = C17c-C17d-C17e-C17f), 19.65° (φ3 = C17b-C17c-C17d-C17e), 17.92° (φ4 = C17a-C17b-C17c-C17d) and 11.81° (φ5 = C17-C17a-C17b-C17c), while the distortion in the molecule was found to be 52.42° (φ1 + φ2 + φ3) and 49.38° (φ3 + φ4 + φ5) resulting in a dihedral angle of 42.19° (*θ*). The unit cell consists of an equal mixture of *P* and *M* isomers crystallized in space group of C 2/c. Similarly, crystal of **53d,** with a chloro and methyl substitution, was obtained from ethyl acetate-hexane and subjected to single crystal X-ray diffraction analysis (**Figure 3.2.5**). The inner carbon-carbon bonds were found to be slightly elongated compared to the normal bonds (1.398 to 1.449 Å), while the outer bonds were slightly compressed (1.329 to 1.354Å).[11a] The observed torsion angles were 14.89° (φ1 = C17d-C17e-C17f-C1), 17.89° (φ2 = C17c-C17d-C17e-C17f), 19.65° (φ3 = C17b-C17c-C17d-C17e), 17.92° (φ4 = C17a-C17b-C17c-C17d) and 11.81° (φ5 = C17-C17a-C17b-C17c), while the distortion in the molecule was found to be 52.42° (φ1 + φ2 + φ3) and 49.38° (φ3 + φ4 + φ5) resulting in a dihedral angle of 42.19° (*θ*). The unit cell consists of an equal mixture of *P* and *M* isomers crystallized in space group of C 2/c

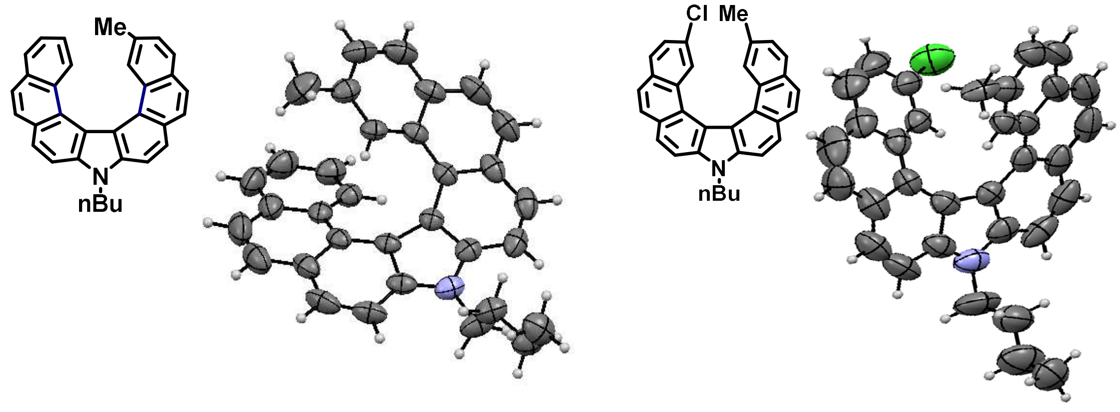


Figure 3.2.5: ORTEP plot of compound 53a and 53d

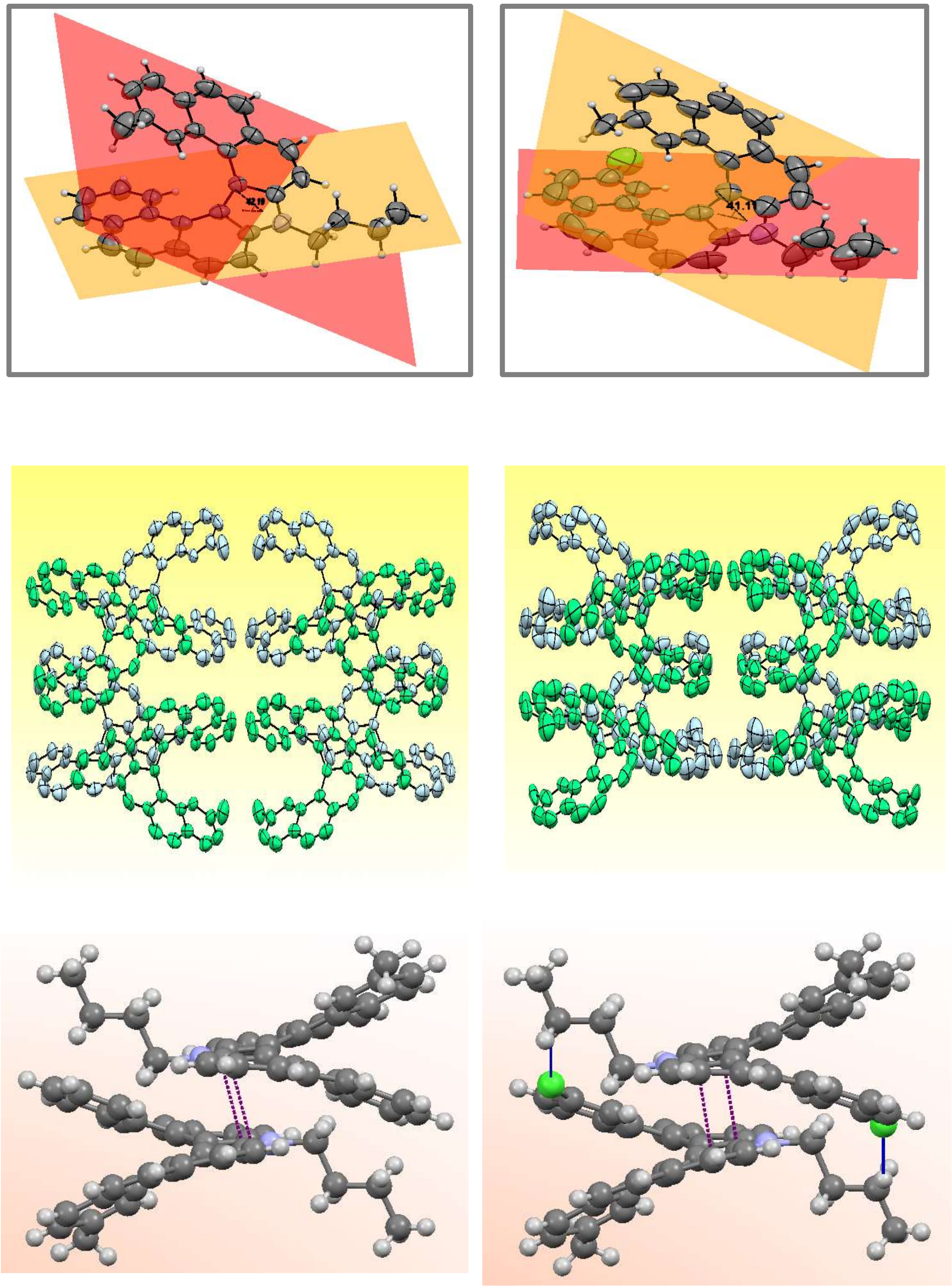


Figure 3.2.6: Crystal packing and intermolecular interactions of compound 53a and 53d

We tried to grow crystals for the ester and acid derivative of unsymmetrical pyrrolo[7]helicene, but we could not get good quality crystals for single crystal X-ray diffraction analysis. So to study the structural parameters for the acid derivative of pyrrolo[7]helicene, we carried out B3LYP/6-31G calculation for compound **57.** As estimated by the computational analysis, torsional angle along the inner helical rim varied from 14.26 to 20.35° and the sum of the torsional angles which indicates the extent of distortion from planarity was found to be 82.85° while the dihedral angle or the interplanar angle was 39.82°. The optimized geometry of **57** obtained from the theoretical calculations is shown in **Figure 3.2.7**.

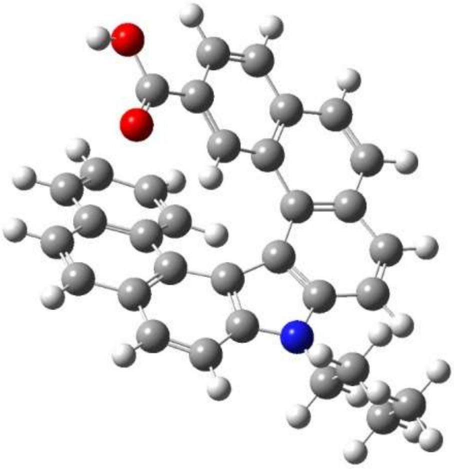


Figure 3.2.7. *Optimized geometry of 57 calculated at the B3LYP/6-31G level of theory*

3.2.4 Photophysical properties

Optical properties of aza[7]helicenes **53a** – **53e** were studied by UV-Vis and fluorescence spectroscopy (**Table 3.2.1 and Figure 3.2.8**). These compounds show spectral properties similar to the compounds of similar twisted π-conjugated structures. In chloroform these compounds exhibit absorption bands in the range of 329 - 346 nm, while show blue emission between 428 - 460 nm.

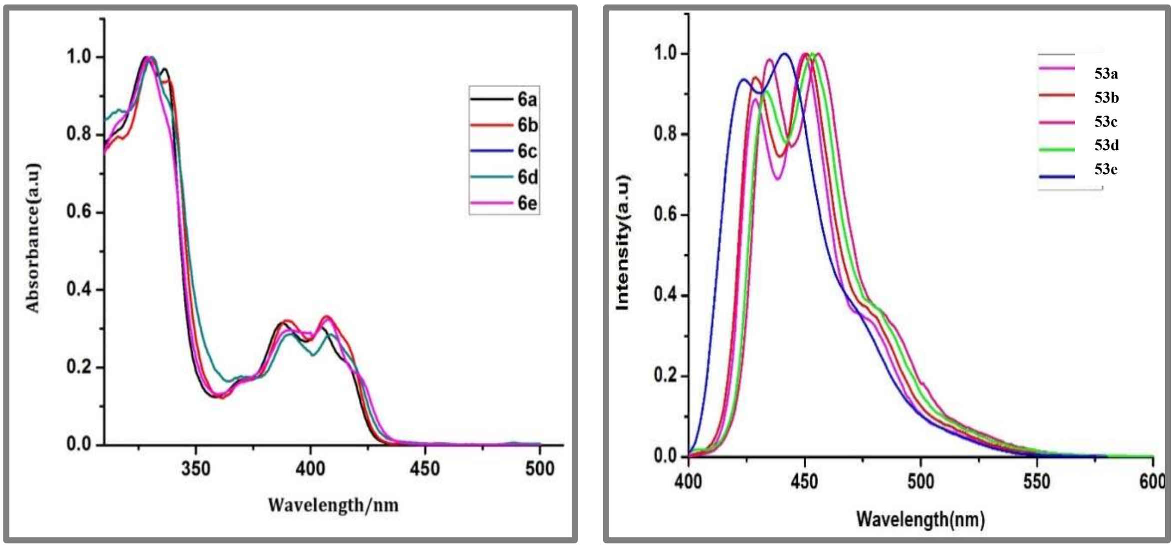


Figure 3.2.8: ***UV-Vis and Fluorescence (1.0 X 10^{-5} mol in $CHCl_3$) at room temperature***

Compound.	**Absorption λ_{abs} [nm]**	**Fluorescence λ_{em} [nm]**	**Stokes Shift/nm**
53a	**329**	**449**	**120**
53b	**331**	**428**	**97**
53c	**329**	**434**	**105**
53d	**331**	**453**	**122**
53e	**346**	**460**	**114**

***Table 3.2.1**: Optical properties of unsymmetrical pyrrolo[7]helicenes*

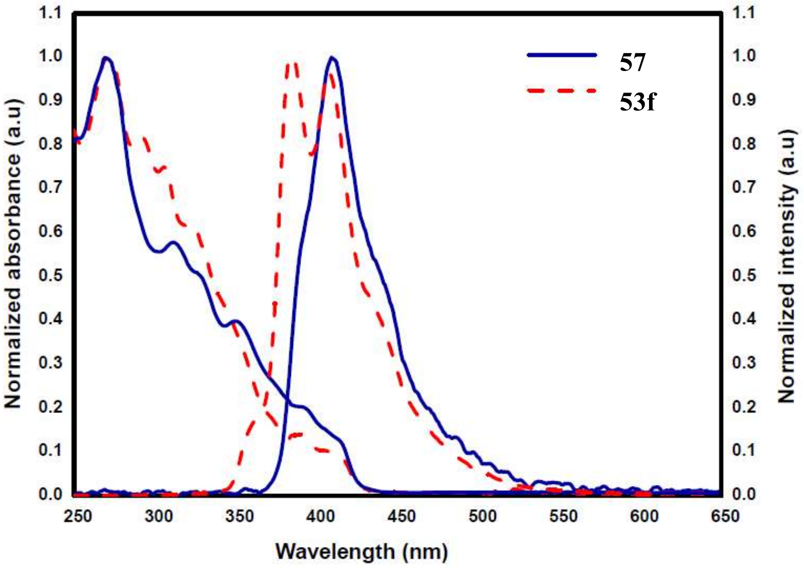


***Figure 3.2.9*: UV-vis absorption and fluorescence spectra of 57 and 53f in dichloromethane (1.0 X 10^{-5} M)**

Compound	Absorption λ_{max} (nm)	Fluorescence λ_{max} (nm)	Stokes shift (cm^{-1})	Φ_{Fl} (nm)
53f	**272**	**423**	**14903**	**0.146**
57	**269**	**449**	**9737**	**0.133**

***Table 3.2.2:* Optical properties of the ester and acid derivatives of pyrrolo[7]helicene**

The optical properties of the synthesized methylpyrrolo[7]helicene-2-carboxylate **53f** and its acid **57** derivative was evaluated using UV-visible absorption and fluorescence spectroscopy in dilute dichloromethane as shown (**Figure 3.2.9**). The UV-visible spectra of both the compounds exhibit strong absorption in the region of 260-420 nm due to π–π and n-π electronic transitions. The absorption maxima appear at around 265-272 nm. The blue emission was also observed for compounds **57** and **53f** when they were excited at 269 and 272 nm respectively.

3.2.5 Molecular recognition study

The presence of acid functional group can offer several advantages such as it can be converted to different functional groups or can be used to form diastereomeric salt with chiral amines for easy separation of its enantiomers. The two helical isomers of acid **57** exist in stable form, as their barrier of interconversion is sufficiently high. The HPLC analysis of compound **57** on chiral stationary phase column is shown in **figure 3.2.10**. It was our objective to prepare diastereomeric salts with optically pure amines or bases. The diastereomeric salts can be physically separated by fractional crystallization. However, our efforts to prepare salts with different chiral bases and their crystallization did not proceed smoothly and we were unable to resolve isomers of **57**. To investigate if the necessary salts are formed, we performed few NMR experiments with chiral amines. The ^{1}H-NMR analysis for the enantiodiscrimination of pyrrolo[7]helicene carboxylic acid **57** with different chiral amines (R^*NH_2) should form salt, and the signal of H_{16} is focussed in its ^{1}H-NMR analysis. The hydrogen attached to C_{16} of the helical framework appears shielded (6.19-6.24) as it is located underneath the acid bearing aromatic ring. The ^{1}H-NMR analysis of the acid **57** with different chiral amines is performed in $CDCl_3$ and the shift in the signal or change in the splitting behaviour of H_{16} is observed (**Figure 3.2.11**).

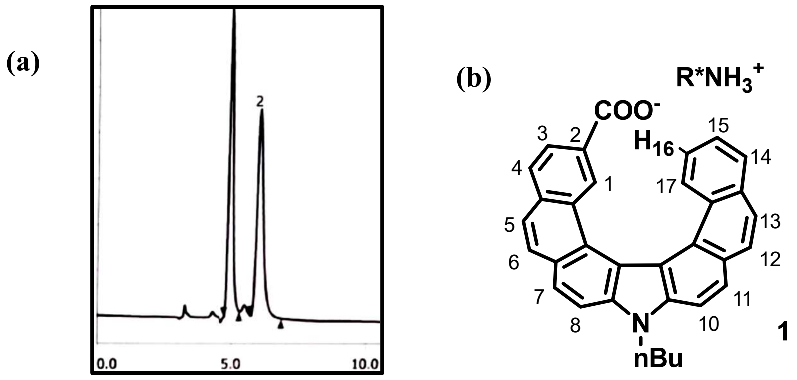


***Figure 3.2.10** (a) HPLC analysis of 57 on chiralpak-IC column with flow rate of 1 mL/min in 70:30 Hexane-Propan-2-ol, t_R = 4.9 and 5.9 min. (b) Diastereomeric salt of the helicene acid 57 and chiral amine.*

Although there was no separation of signal in either of the experiments, a considerable splitting was observed. With (*S*)-phenylethylamine used as base or as chiral solvating agent (1:1 ratio), the spectra with **57** shows negligible discrimination for the H_{16} (**figure 3.2.11b**). The splitting is enhanced when the ratio of acid and amine was increased (**figure 3.2.11c**). In the case of (L)-2-aminobutanol, there was not much splitting of signals observed (**figure 3.2.11d**). With 1:1 equivalent of acid and (*S*)-quinine a much better signal splitting was observed (**figure 3.2.11e**). However, the nature of the interactions and the position of signals in NMR scale did not result in clear separation of the signals for quantitative determination of ratio of isomers.

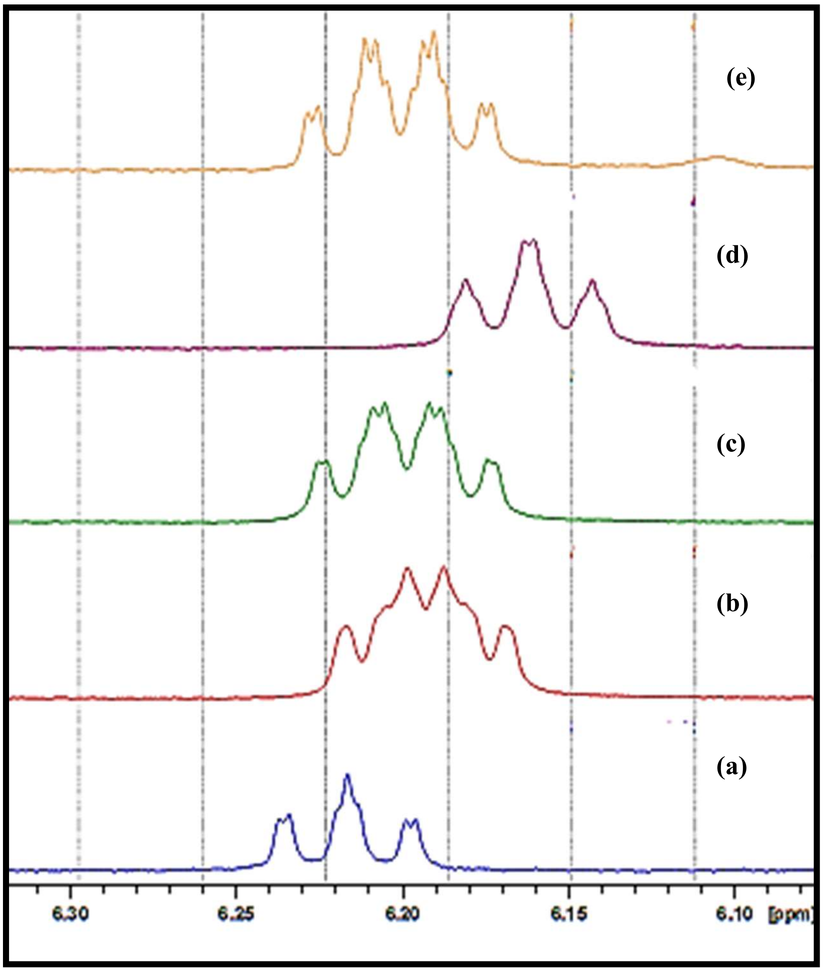


Figure 3.2.11. ***Select region of ^{1}H-NMR spectrum of compound 57. Condition: 20 mmol solution in $CDCl_3$ (a) blank 57 (b) 1:1 eq. with (S)-1-phenylethylamine (c) 1:2 eq. with (S)-1-phenylethylamine (d) 1:1 eq. with (L)-2-aminobutanol (e) 1:1 eq. with (S)-Quinine***

3.2.6 Conclusion

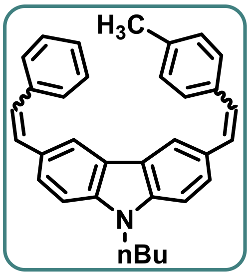
Thus, in this chapter we present the synthesis of unsymmetrically functionalized seven-membered pyrrrolohelicenes by photocyclization strategy. The synthesis of variably functionalized helical molecule was carried out by easy access of the stilbene precursors using one-pot reaction Wittig-Heck reaction and step-wise method. All the derivatives were screened for their photophysical properties. Besides, we carried out the synthesis of ester functionalized helicene using the same one-pot Wittig-Heck and photodehydrogenation sequence. This was then hydrolysed to its acid derivative and molecular recognition studies were carried out.

3.2.7 Experimental Section

All reactions were carried out in oven-dried glassware with magnetic stirring. Purification of reaction products was carried out by column chromatography using silica gel (60-120 mesh). Thin layer chromatography was performed on TLC Silica Gel 60 F254 (Merck). The spots were visualized under UV light or with iodine vapour. 1H-NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer (400 MHz) and were run in CDCl3 unless otherwise stated. Mass spectra were recorded on Thermo-Fischer DSQ II GCMS instrument; IR spectra were recorded on Perkin-Elmer FTIR RXI spectrometer as KBr pallets. UV-Visible absorption of all the compounds was measured as a solution in THF at room temperature on Perkin-Elmer Lambda 35 spectrometer and fluorescence was measured on Jasco FP-6300 spectro fluorometer. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected. Solvents were dried and purified by distillation under reduced pressure and stored on molecular sieves. All chemicals were purchased from Sigma-Aldrich Chemicals Limited, SD Fine, Sisco, Qualigens, Avara Chemicals Limited etc., and used without further purification.

Synthetic procedures and analytical data

9-butyl-3-(4-methylstyryl)-6-(styryl)-9*H*-carbazole (52a)



Molecular formula: $C_{33}H_{31}N$

Molecular weight: 441.24

Physical state: white crystalline solid

R*f* =0.5 (5:95 EtOAc/petroleum ether).

M.p = 178-180 ^{0}C.

A catalyst solution was prepared under nitrogen atmosphere using palladium acetate (0.010 g, 0.045 mmol, 1 mol %) and 1,3-bis(diphenylphosphinopropane) (0.037 g, 0.091 mmol, 2 mol %) in *N*,*N*-dimethylacetamide (5 mL) at room temperature with constant stirring until a homogenous solution was obtained. A two-necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazole-3-carbaldehyde (**51**) (1.500 g, 4.54 mmol), 4-methyl styrene (**55x**) (0.640 g, 5.450 mmol), benzyltriphenylphosphonium chloride (**54x**) (2.120 g, 5.450 mmol), dry potassium carbonate (2.510 g, 18.200 mmol), TBAB (0.290 g, 0.908 mmol, 20 mol %), and *N*,*N*-dimethylacetamide (10 mL) and the mixture was heated up to 100°C. At 100°C, the catalyst solution was added drop wise and the mixture was heated to 140^{0}C for 48

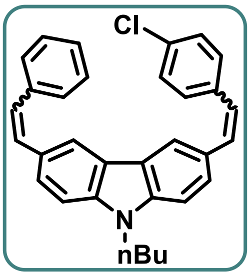
h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (3 x 100 mL). The combined organic phase was washed with water, brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (95:5) as eluent to afford *cis-trans* isomers of the compound **52a**.

IR (KBr): υ 3423, 3016, 2947, 1863, 1596, 1489, 1388, 1349, 1306, 1250, 1179, 1116, 1038, 970, 861, 823, 750 cm^{-1}

^{1}**H NMR** (400 MHz, $CDCl_3$): δ =8.28 (d, J = 3.2, 2H), 7.70–7.67 (m, 2H), 7.60–7.58 (d, J = 7.6 Hz, 2H), 7.50–7.48 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 16.4 Hz), 7.12–7.08 (d, J = 16.4 Hz, 2H), 6.93–6.91 (broad d, 4H),4.32 (t, J = 7.2, 2H), 2.4 (s, 3H), 1.93–1.86 (m, 2H), 1.47–1.38 (m, 2H),0.97 (t, *J* = 7.2 Hz,3H) ppm.

^{13}**C NMR** (100 MHz, $CDCl_3$): δ= 140.73, 140.53, 136.95, 136.48, 135.12, 132.47, 130.19, 129.43, 129.02, 128.82, 128.50, 128.32, 127.37, 126.19, 126.16, 124.74, 124.66, 124.63, 123.28, 123.19, 118.79, 118.51, 109.12, 43.08, 31.20, 21.30, 20.57, 13.93.

9-butyl-3-(4-chlorostyryl)-6-(styryl)-9*H*-carbazole (52b)



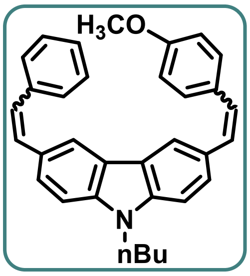
Molecular formula: $C_{32}H_{28}NCl$
Molecular weight: 461.19
Physical state: white crystalline solid
R$_f$ =0.5 (5:95 EtOAc/petroleum ether).
M.p = 156 ^{0}C.

A catalyst solution of palladium acetate (0.013 g, 0.006 mmol, 1 mol %) and 1,3-bis(diphenylphosphinopropane) (0.049 g, 0.012 mmol, 2 mol %) in *N*,*N*-dimethylacetamide (2 mL) at room temperature was prepared under nitrogen atmosphere with constant stirring until a homogenous solution was obtained. A two-necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazole-3-carbaldehyde (**51**) (0.200 g, 0.60 mmol), 4-chloro styrene (**55y**) (0.1 g, 0.72 mmol), benzyltriphenylphosphonium chloride (**54x**) (0.283 g, 0.72 mmol), dry potassium carbonate (0.33 g, 2.40 mmol), TBAB (0.039 g, 0.12 mmol, 20 mol %), and *N*,*N*-dimethylacetamide (10 mL) and the mixture was heated up to 100°C. At 100°C, the catalyst solution was added drop wise and the mixture was heated to 140^{0}C for 48 h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (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 (95:5) as eluent to afford *cis-trans* isomers of the compound **52b**.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.26 (d, J = 1.6, 2H), 7.70–7.65 (m, 2H), 7.60–7.58 (d, J = 7.6 Hz, 2H), 7.51–7.49 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 16.4 Hz), 7.12–7.08 (d, J = 16.4 Hz, 2H), 6.93–6.91 (broad d, 4H),4.32 (t, J = 7.2, 2H), 2.4 (s, 3H), 1.93–1.86 (m, 2H), 1.47–1.38 (m, 2H),0.97 (t, *J* = 7.2 Hz,3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 140.79, 140.48, 139.85, 139.45, 136.91, 136.88, 129.35, 129.00, 128.82, 128.46, 127.38, 127.35, 127.31, 127.25, 126.92, 126.68, 125.94, 125.15, 124.59, 123.21, 118.79, 111.83, 110.35, 109.22, 43.12, 31.10, 20.54, 13.89.

9-butyl-3-(4-methoxystyryl)-6-(styryl)-9*H*-carbazole (52c)



Molecular formula: $C_{33}H_{31}NO$
Molecular weight: 457.21
Physical state: white crystalline solid
R$_f$ =0.5 (5:95 EtOAc/petroleum ether).
M.p = 164-166 ^{0}C.

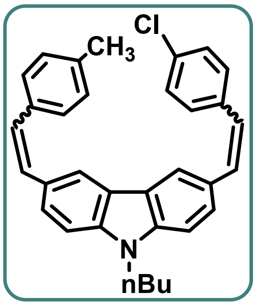
A two-necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazole-3-carbaldehyde (**51**) (0.578 g, 1.75 mmol), 4-methoxy styrene (**55z**) (0.281 g, 2.1 mmol), benzyltriphenylphosphonium chloride (**54x**) (0.816 g, 2.1 mmol), dry potassium carbonate (0.967 g, 7.00 mmol), TBAB (0.113 g, 0.35 mmol, 20 mol %), and *N*,*N*-dimethylacetamide (10 mL) and the mixture was heated up to 100°C. A catalyst solution was prepared under nitrogen atmosphere using palladium acetate (0.003 g, 0.017 mmol, 1 mol %) and 1,3-bis(diphenylphosphinopropane) (0.014 g, 0.035 mmol, 2 mol %) in *N*,*N*-dimethylacetamide (2 mL) at room temperature with constant stirring until a homogenous solution was obtained.. At 100°C, the catalyst solution was added drop wise and the mixture was heated to 140^{0}C for 48 h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (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 (95:5) as eluent to afford *cis-trans* isomers of the compound **52c**

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.20 (d, J = 1.6, 2H), 7.63–7.58 (m, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.31-7.35(m, 4H), 7.25 (d, J = 16.4 Hz, 2H), 7.12–7.08 (d, J = 16.4 Hz, 2H), 6.93–6.91 (broad d, 2H),4.32 (t, J = 7.2, 2H), 3.8 (s, 3H), 1.93–1.86 (m, 2H), 1.47–1.38 (m, 2H),0.97 (t, *J* = 7.2 Hz,3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 158.96, 141.57, 141.44, 140.63, 140.42, 138.02, 135.09, 130.77, 129.57, 129.10, 128.73, 128.69, 128.67,127.49, 127.42, 127.39, 127.06, 126.27, 126.23, 126.11, 125.76, 124.61, 124.47, 123.26, 118.69, 118.33, 114.14, 109.06, 55.36, 43.13, 31.21, 20.57, 13.92.

HRMS (ESI-TOF): m/z calcd. for $C_{33}H_{32}NO$ is 458.2488; found, 458.2478

9-butyl-3-(4-chlorostyryl)-6-(4-methylstyryl)-9*H*-carbazole (52d)



Molecular formula: $C_{33}H_{30}NCl$
Molecular weight: 475.20
Physical state: white crystalline solid
R*f*=0.5 (5:95 EtOAc/petroleum ether).
M.p = 180 ^{0}C.

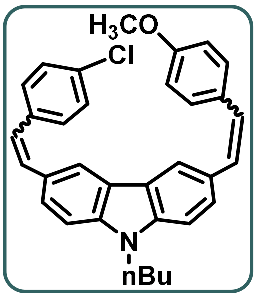
A two-necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazole-3-carbaldehyde (**51**) (1.000 g, 3.00 mmol), 4-chloro styrene (**55y**) (0.419 g, 3.00 mmol), 4-methylbenzyltriphenylphosphonium bromide (**54z**) (1.34 g, 3.00 mmol), dry potassium carbonate (1.675 g, 12.10 mmol), TBAB (0.195 g, 0.600 mmol, 20 mol %), and *N*,*N*-dimethylacetamide (10 mL) and the mixture was heated up to 100°C. A catalyst solution of palladium acetate (0.013 g, 0.06 mmol, 1 mol %) and 1,3-bis(diphenylphosphinopropane) (0.049 g, 0.121 mmol, 2 mol %) in *N*,*N*-dimethylacetamide (2 mL) at room temperature was prepared under nitrogen atmosphere with constant stirring until a homogenous solution was obtained. .At 100°C, the catalyst solution was added drop wise and the mixture was heated to 140^{0}C for 48 h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (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 (95:5) as eluent to afford *cis-trans* isomers of the compound **52d**

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.27 (d, J = 2.8, 2H), 7.70–7.66 (m, 2H), 7.54–7.48 (m, 4H), 7.41–7.29 (m, 6H), 7.22-7.18(m, 2H), 7.15–7.10 (d, J = 16.4 Hz, 2H), 4.32 (t, J = 7.2, 2H), 2.39 (s, 3H), 1.85–1.92 (m, 2H), 1.47–1.38 (m, 2H),0.97 (t, *J* = 7.2 Hz,3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 140.85, 140.18, 138.09, 137.89, 137.65, 130.65, 129.27, 128.85, 128.67, 128.53, 128.31, 127.03, 126.60, 126.17, 126.76, 125.55, 124.36, 124.15, 123.16, 122.87, 120.81, 120.43, 120.28, 118.95, 118.84, 118.61, 108.88, 108.75, 108.17, 42.96, 31.18, 21.40, 20.59, 13.93.

HRMS(ESI-TOF): m/z calcd. for $C_{33}H_{31}NCl$ is 476.2140; found, 476.2138.

9-butyl-3-(4-chlorostyryl)-6-(4-methoxystyryl)-9*H*-carbazole (52e)



Molecular formula: $C_{33}H_{30}ClNO$
Molecular weight: 491.20
Physical state: white crystalline solid
R$_f$ =0.5 (5:95 EtOAc/petroleum ether).
M.p = 192 ^{0}C.

A catalyst solution was prepared under nitrogen atmosphere using palladium acetate (0.002 g, 0.014 mmol, 1 mol %) and 1,3-bis(diphenylphosphinopropane) (0.037 g, 0.091 mmol, 2 mol %) in *N*,*N*-dimethylacetamide (5 mL) at room temperature with constant stirring until a homogenous solution was obtained. A two-necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazole-3-carbaldehyde (**51**) (1.500 g, 4.54 mmol), 4-methoxy styrene (**55z**) (0.640 g, 5.450 mmol), 4-chlorobenzyltriphenylphosphonium bromide (**54z**) (2.120 g, 5.450 mmol), dry potassium carbonate (2.510 g, 18.200 mmol), TBAB (0.290 g, 0.908 mmol, 20 mol %), and *N*,*N*-dimethylacetamide (10 mL) and the mixture was heated up to 100°C. At 100°C, the catalyst solution was added drop wise and the mixture was heated to 140^{0}C for 48 h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (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 (95:5) as eluent to afford *cis-trans* isomers of the compound **52e**.

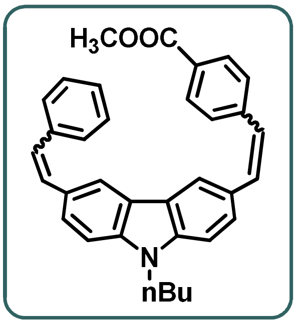
IR (KBr): υ 3423, 3016, 2947, 1863, 1596, 1489, 1388, 1349, 1306, 1250, 1179, 1116, 1038, 970, 861, 823, 750 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.26-8.24(dd, *J* = 7.2,1.2, 2H), 7.68–7.66 (d, J = 8.4 Hz, 2H), 7.53–7.49 (m, 4H), 7.40-7.35(m, 4H), 7.33-7.29 (d, J = 16.4 Hz, 1H), 7.23–7.19 (d, J = 16.0 Hz, 1H), 7.16-7.10(m, 2H), 6.97–6.94 (broad d, 2H),4.32 (t, J = 7.2, 2H), 3.87 (s, 3H), 1.93–1.86 (m, 2H), 1.47–1.38 (m, 2H),0.97 (t, *J* = 7.2 Hz,3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 158.92, 140.74, 140.43, 136.49, 132.47, 130.74, 130.20, 129.18, 128.82, 128.30, 127.44, 127.40, 127.36, 125.83, 124.74, 124.61, 124.55, 123.28, 123.20, 118.78, 118.31, 114.15, 109.11, 55.36, 43.09, 31.20, 20.56, 13.91.

HRMS(ESI-TOF): m/z calcd. for $C_{33}H_{30}NClNaO$ is 514.1902; found, 514.1908

Methyl 4-(2-(9-butyl-6-styryl-9*H*-carbazol-3-yl) vinyl) benzoate (52f)



Molecular formula: $C_{34}H_{31}NO_2$
Molecular weight: 485.61
Physical state: white crystalline solid
R$_f$ =0.5 (5:95 EtOAc/petroleum ether).
M.p = 180 ^{0}C.

A catalyst solution solution was prepared under nitrogen atmosphere using palladium acetate (0.026 g 0.12 mmol, 2 mol%) and 1,3-bis(diphenylphosphonopropane) (0.098 g, 2.4 mmol, 4%) in *N,N*-dimethylacetamide (5 mL) at room temperature with constant stirring until a homogenous solution was obtained. A two necked round bottom flask was charged with 6-bromo-9-butyl-9*H*-carbazol-3-carbaldehyde (2.0 g, 6.00 mmol), styrene (0.75 g ,7.2 mmol), 4-(methoxycarbonyl)-benzyltriphenylphosphonium bromide (3.57 g, 7.2 mmol), dry potassium carbonate (3.31 g, 24.00 mmol), TBAB (0.38 g, 0.12 mmol), and *N,N* dimethylacetamide (10 mL) and the mixture was heated up to 100^0 C . At 100^{0}C, the catalyst solution was added drop wise, and the mixture was heated up to 140^{0}C for 48 h. After the completion of the reaction, the mixture was poured into water and extracted with Ethyl Acetate (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 (95:5) as eluent to afford methyl 4-(2-(9-butyl-6-styryl-9*H*-carbazol-3-yl)vinyl)benzoate.

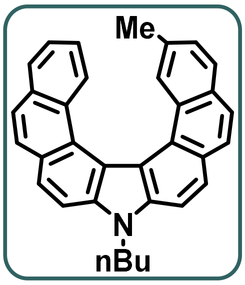
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (dd, *J* = 9.6 & 1.2, 2H), 8.06 (d, *J* = 8.4, 2H), 7.70 (d, *J* = 8.4, 2H), 7.64-7.58 (m, 4H), 7.48-7.33 (m, 4H), 7.30-7.26 (m, 3H), 7.23-7.17 (m, 2H), 4.33 (t, *J* = 7.2, 2H), 3.96 (s, 3H), 1.93-1.86 (m, 2H), 1.47-1.38 (m, 2H), 0.98 (t, *J* = 7.2, 3H).

^{13} C NMR (100 MHz, CDCl3): δ 167.0, 142.9, 140.6, 137.9, 132.20, 130.1, 129.5, 128.7. 128.4, 127.1, 126.3, 126.0, 124.8, 123.3, 119.2, 118.7, 109.1, 52.0, 43.1, 31.1, 20.5, 13.8

IR (KBr): *ν* 3024, 2928, 2869, 1713, 1594, 1484, 1208, 1104, 958, 801, 692 cm^{-1}

HRMS: m/z calcd. for [$C_{34}H_{31}NO_2$ + H] is 486.2355; found, 486.2335

2-methyl-9-butyl-9*H*-aza[7]helicene (53a)



Molecular formula: $C_{33}H_{27}N$
Molecular weight: 437.21
Physical state: yellow solid
R$_f$ =0.4 (5:95 EtOAc/petroleum ether)
M.p = >200^{0}C

A solution of 3,6-distyryl-*N*-butylcarbazole **52a** (0.200 g, 0.45 mmol), Iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the 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 reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (98:2) as eluent to obtain a pale yellow solid.

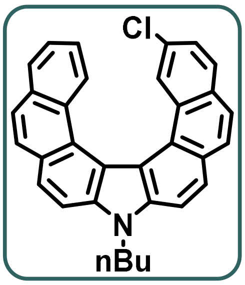
IR (KBr): υ 3427, 3042, 2952, 2927, 2867, 1725, 1660, 1588, 1522, 1495, 1450, 1339, 1283, 1218, 795, 746, 645 cm.$^{-1}$

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.8, 2H), 8.06 (d, *J* = 8.4, 2H), 7.99–7.96 (m, 3H), 7.90–7.88 (d, J = 8.4 Hz, 1H), 7.83-7.79 (m, 2H), 7.75 (d, J = 8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz,1H), 7.22-7.18 (m,2H), 7.05-7.03 (dd, *J* = 8,1.2Hz,1H), 6.28-6.24 (m, 1H), 4.79 (t, *J* = 7.2, 2H), 1.44 (s, 3H), 1.04 (t, *J* = 7.2Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ=139.23, 132.47, 131.49, 130.11, 129.91, 129.43, 128.34, 127.74, 127.43, 127.20, 126.82, 126.73, 126.61, 126.57, 126.53, 126.40, 126.14, 126.10, 125.91, 125.78, 124.03, 123.96, 122.34, 120.18, 116.75, 116.70, 109.57, 109.45, 43.44, 31.96, 20.77, 20.71, 13.98.

HRMS(ESI-TOF): m/z calcd. for $C_{33}H_{27}N$ is 437.2143; found, 437.2140.

2-chloro-9-butyl-9*H*-aza[7]helicene (**53b**)



Molecular formula: $C_{33}H_{24}NCl$
Molecular weight: 457.16
Physical state: yellow solid
R*f* =0.3 (5:95 EtOAc/petroleum ether).
M.p = 168 ^{0}C.

A solution of 3,6-distyryl-*N*-butylcarbazole **52b** (0.200 g, 0.45 mmol), Iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the 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 reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (98:2) as eluent to obtain a pale yellow solid. (0.06 g; 30%).

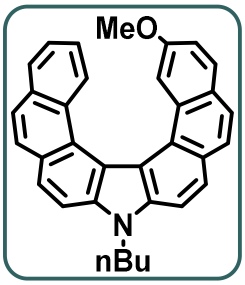
IR (KBr): υ 3010, 2956, 1682, 1599, 1500, 1220, 838, 762, 674 cm.$^{-1}$

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17-8.12 (m, 2H), 8.08 (d, *J* = 8.8 Hz, 2H), 8.03 (m, 2H), 7.89 (d, *J* = 7.6, 1H), 7.82 (d, *J* = 8.4, 1H), 7.77(d, *J* = 8.8, 1H), 7.40 - 7.38 (m, 2H), 7.25-7.24 (m, 1H), 7.15 (dd, *J* = 8.4 & 2.0, 1H) 6.32-6.27(m, 1H), 4.33(t, *J* = 7.2 Hz, 2H), 1.93-1.85 (m, 2H), 1.47-1.39 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ= 139.38, 139.28, 132.06, 130.96, 129.57, 129.53, 129.51, 128.90, 127.74, 127.55, 127.43, 127.13, 126.90, 126.88, 126.83, 126.81, 126.65, 126.40, 126.06, 125.95, 125.83, 124.56, 123.54, 122.35, 116.62, 116.25, 110.26, 109.61, 43.48, 31.95, 20.70, 13.96.

HRMS (ESI-TOF): m/z calcd. for $C_{33}H_{25}NCl$ is 458.1672; found, 458.1670.

2-methoxy-9-butyl-9*H*-aza[7]helicene (**53c**)



Molecular formula: $C_{33}H_{27}NO$
Molecular weight: 453.21
Physical state: yellow solid
R$_f$ =0.2 (5:95 EtOAc/petroleum ether).
M.p = 182 ^{0}C.

A solution of 3,6-distyryl-*N*-butylcarbazole **52c** (0.200 g, 0.45 mmol), Iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the 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 reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (98:2) as eluent to obtain a pale-yellow solid. (0.06 g; 30%).

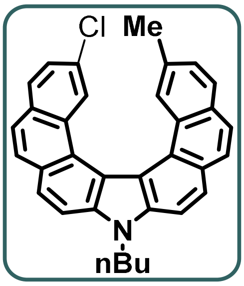
IR (KBr): υ 3430, 3040, 2956, 2929, 2870, 1728, 1665, 1592, 1525, 1498, 1454, 1343, 1286, 1223, 798, 749, 647 cm.$^{-1}$

^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.07(d, J = 8.8 Hz, 2H), 8.03(m, 2H), 7.54-7.47(m, 3H),7.41-7.29(m,5H), 7.22-7.11(m,4H), 4.33(t, J = 7.2 Hz, 2H), 2.39(s,3H), 1.93-1.85 (m, 2H), 1.47-1.39 (m, 2H), 0.97(t, J = 7.2 Hz, 3H).

^{13}C NMR 158.92, 140.74, 140.43, 136.49, 132.47, 130.74, 130.20, 129.18, 128.82, 128.30, 127.44, 127.40, 127.36, 125.83, 124.74, 124.61, 124.55, 123.28, 123.20, 118.78, 118.31, 114.15, 109.11, 55.36, 43.09, 31.20, 20.56, 13.91.

HRMS (ESI-TOF): m/z calcd. for $C_{33}H_{27}NO$ is 476.1986; found, 476.1985 $[M+Na]^+$

2-chloro-16-methyl-9-butyl-9*H*-aza[7]helicene (**53d**)



Molecular formula: $C_{33}H_{26}NCl$
Molecular weight: 471.17
Physical state: yellow solid
R$_f$ =0.4 (5:95 EtOAc/petroleum ether)
M.p = >200^{0}C

A solution of 3,6-distyryl-*N*-butylcarbazole **52d** (0.200 g, 0.45 mmol), Iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the 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 reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (98:2) as eluent to obtain a pale yellow solid. (0.06 g; 30%).

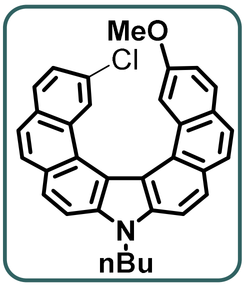
IR (KBr): υ 3430, 3036, 2948, 2924, 2854, 1730, 1650, 1595, 1532, 1495, 1450, 1342, 1285, 1222, 792, 741, 640 cm.$^{-1}$

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.02 (dd, *J* = 8.4 & 1.2 , 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.8, 1H), 7.85(d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.74(d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 2.4), 7.16 (dd, *J* = 8.4 & 1.2 Hz, 1H), 7.12-7.08 (m, 2H), 4.80(t, *J* = 7.2 Hz, 2H), 2.11-2.09(m,2H), 1.59-1.55(m, 2H), 1.53(s,3H), 1.04(t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.30, 139.19, 132.17, 130.68, 130.22, 129.75, 129.44, 128.66, 127.60, 127.43, 127.38, 127.23, 127.14, 126.97, 126.89, 126.74, 126.67, 126.41, 126.19, 125.96, 125.75, 124.32, 123.23, 116.59, 116.26, 110.23, 109.46, 43.49, 31.99, 20.80, 20.70, 13.96

HRMS (ESI-TOF): m/z calcd. for $C_{33}H_{26}NClNa$ is 494.1641; found, 494.1646

2-chloro-16-methoxy-9-butyl-9*H*-aza[7]helicene (53e).



Molecular formula: $C_{33}H_{26}ClNO$
Molecular weight: 487.17
Physical state: yellow solid
R$_f$ =0.2 (5:95 EtOAc/petroleum ether)
M.p = >200^{0}C

A solution of 3,6-distyryl-*N*-butylcarbazole **52e** (0.200 g, 0.45 mmol), Iodine (0.253 g, 0.99 mmol), dry THF (3.26 g, 3.67 mL, 45.3 mmol), and toluene (610 mL) was irradiated using a 250W HPMV lamp (10 h monitored by TLC). After the completion of the 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 reduced pressure to obtain the crude product. The crude product was purified by column chromatography over silica gel using petroleum ether-ethyl acetate (98:2) as eluent to obtain a pale yellow solid. (0.06 g; 30%).

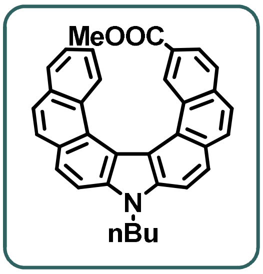
IR (KBr): υ 3445, 3030, 2900, 2870, 1725, 1670, 1591, 1523, 1500, 1447, 1334, 1284, 1218, 787, 749, 638 cm.$^{-1}$

^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.16(d, *J* = 8.8 Hz, 1H), 8.11(d, *J* = 8.4 Hz, 1H), 8.05(d, *J* = 8.4 Hz, 1H), 8.02(d, *J* = 8.8 Hz, 1H), 7.97(d, *J* = 8.8 Hz, 2H), 7.91(d, *J* = 8.8 Hz, 1H), 7.83(d, *J* = 7.6 Hz, 1H), 7.81(d, *J* = 8.4 Hz, 1H), 7.77(d, *J* = 8.4 Hz, 1H), 7.39(s, 1H), 7.20-7.17(m, 1H), 6.90-6.87(m, 1H), 6.77(d, *J* = 2 Hz, 1H), 4.80(t, *J* = 7.2 Hz, 2H), 2.47(s,3H), 2.47-2.11 (m, 2H), 1.60-1.55 (m, 2H), 1.05(t, *J* = 7.2 Hz, 3H).

^{13}C NMR:δ= 155.04, 139.16, 130.91, 130.72, 129.44, 129.03, 128.42, 127.67, 127.26, 127.11, 126.96, 126.82, 126.77, 126.28, 126.23, 125.66, 124.25, 124.22, 123.51, 117.61, 116.29, 116.05, 110.43, 109.71, 106.71, 53.48, 43.54, 32.05, 20.72, 13.98.

HRMS (ESI-TOF): m/z calcd for $C_{33}H_{26}NClO$ is 510.1593; found, 510.1595[M+Na]$^+$

Methyl-9-butyl-9*H*-aza[7]helicene2-carboxylate (53f)



Molecular formula: $C_{34}H_{27}NO_2$
Molecular weight: 481.58
Physical state: yellow solid
R*f* =0.2 (5:95 EtOAc/petroleum ether)
M.p = >215^{0}C

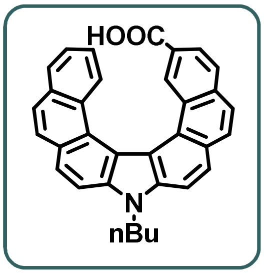
A solution of methyl 4-(2-(9-butyl-6-styryl-9*H*-carbazol-3-yl)vinyl) benzoate (0.2g,0.41mmol), iodine (0.23g,0.91mmol), dry THF (2.97g, 3.34ml , 0.41mmol), and toluene (600 ml) was irradiated using a 125W HPMV lamp (8 h monitored by TLC). After the completion of reaction, excess of iodine was removed from the mixture by treating it with a solution of sodium thiosulfate, followed by distilled water. The organic layer was concentrated under reduced pressure which gave crude product. Purification of crude product was done by performing column chromatography over silica gel using petroleum ether: ethyl acetate (95:5) as eluent to obtain methyl-9-butyl-9H-aza[7]helicene2-carboxylate.

^{1}H NMR (400 MHz, CDCl$_3$) : δ 8.19-8.15 (m, 3H), 8.12-8.01 (m, 4H), 7.98-7.89 (d, *J* = 8.4, 1H), 7.88-7.83 (m, 3H), 7.75 (d, *J* = 8.4, 1H), 7.34 (d, *J* = 8.4, 1H), 7.20-7.16 (m, 1H), 6.24-6.20 (m, 1H), 4.80 (t, *J* = 7.6, 2H), 3.43 (s, 3H), 2.13-2.09 (m, 2H), 1.63-1.54 (m, 2H), 1.05 (t, *J* = 5.2, 3H).

^{13}C NMR: δ = 167.04, 142.56, 140.98, 140.67, 137.91, 132.20, 130.07, 129.47, 128.96, 128.71. 128.28, 128.17, 127.13, 126.34, 126.26, 125.99, 124.95, 124.89, 124.82, 123.33, 119.16, 118.68, 109.19, 52.05, 43.11, 31.19, 20.55, 13.89

HRMS (ESI-TOF): m/z calcd. for [$C_{34}H_{27}NO_2$ + H] is 482.2042; found, 482.2068

9-butyl-9*H*-aza[7]helicene2-carboxylic acid (57)



Molecular formula: $C_{33}H_{25}NO_2$
Molecular weight: 467.55
Physical state: yellow solid
R*f* =0.2 (5:95 EtOAc/petroleum ether)
M.p = >215^{0}C

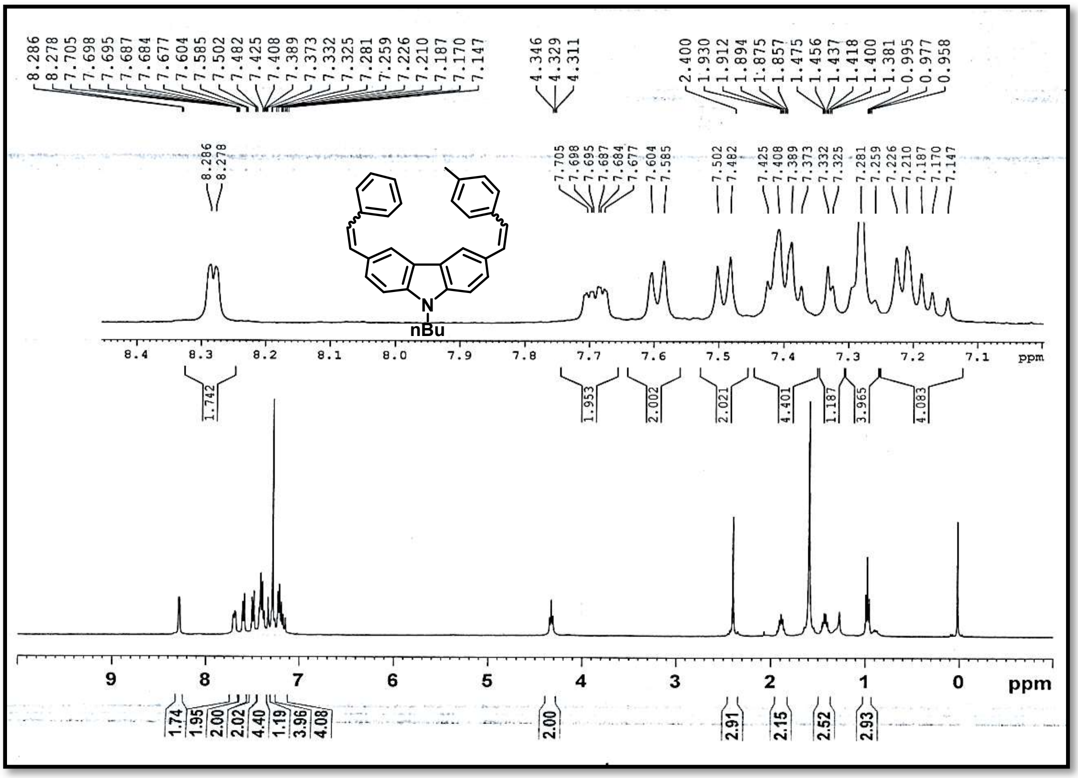
To a solution of 2 (0.1 g, 0.21 mmol) in THF (10 mL) was added aq. KOH (10 M, 1.0 mL). The mixture was heated at 80 ^{o}C for 8h. The cooled solution was poured into ice water. The solution was acidified with 1N HCl and extracted with dichloromethane (3 X 25 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated at reduced pressure to afford 1 (0.097g, 98%) as a yellow solid. Mp = 142-144 ^{o}C

^{1}H NMR (400 MHz, CDCl$_3$) : δ 8.24-8.16 (m, 3H), 8.07-8.00 (m, 3H), 7.95-7.89 (m, 3H), 7.86 (dd, *J* = 8.4 & 1.6, 1H), 7.78 (m, 2H), 7.30 (d, *J* = 8.4, 1H), 7.18 (m, 1H), 6.22 (m, 1H), 4.83 (t, *J* = 7.2, 2H), 2.13 (m, 2H), 1.63 (m, 2H), 1.06 (t, *J* = 7.2, 3H).

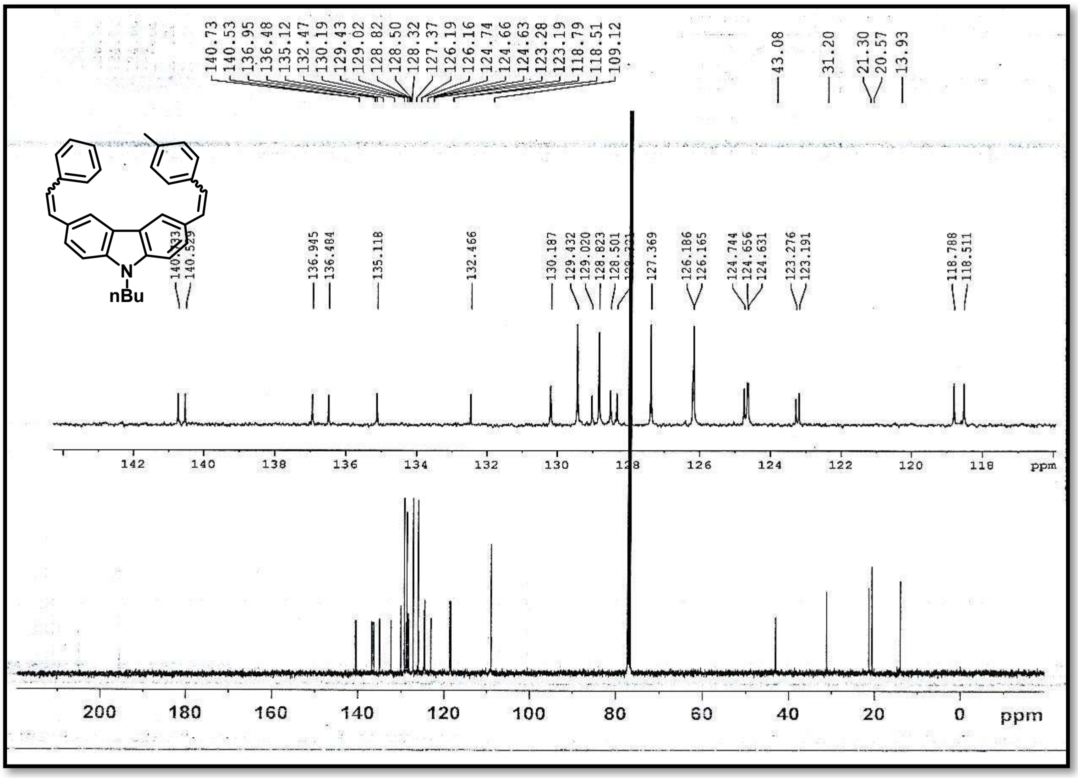
^{13}C NMR: δ = 166.98, 139.69, 139.57, 133.60, 131.99, 130.38, 129.76, 129.42, 129.38, 127.55, 127.43, 127.14, 127.05, 126.96, 126.90, 126.84, 126.70, 126.63, 126.26, 125.89, 124.95, 124.85, 123.88, 122.25, 115.93, 115.77, 111.62, 110.97, 43.12, 34.59, 34.36, 32.03, 26.75, 25.19, 20.30, 14.19

HRMS (ESI-TOF): m/z calcd. for [$C_{33}H_{25}NO_2$ + H] is 468.1885; found, 468.1804

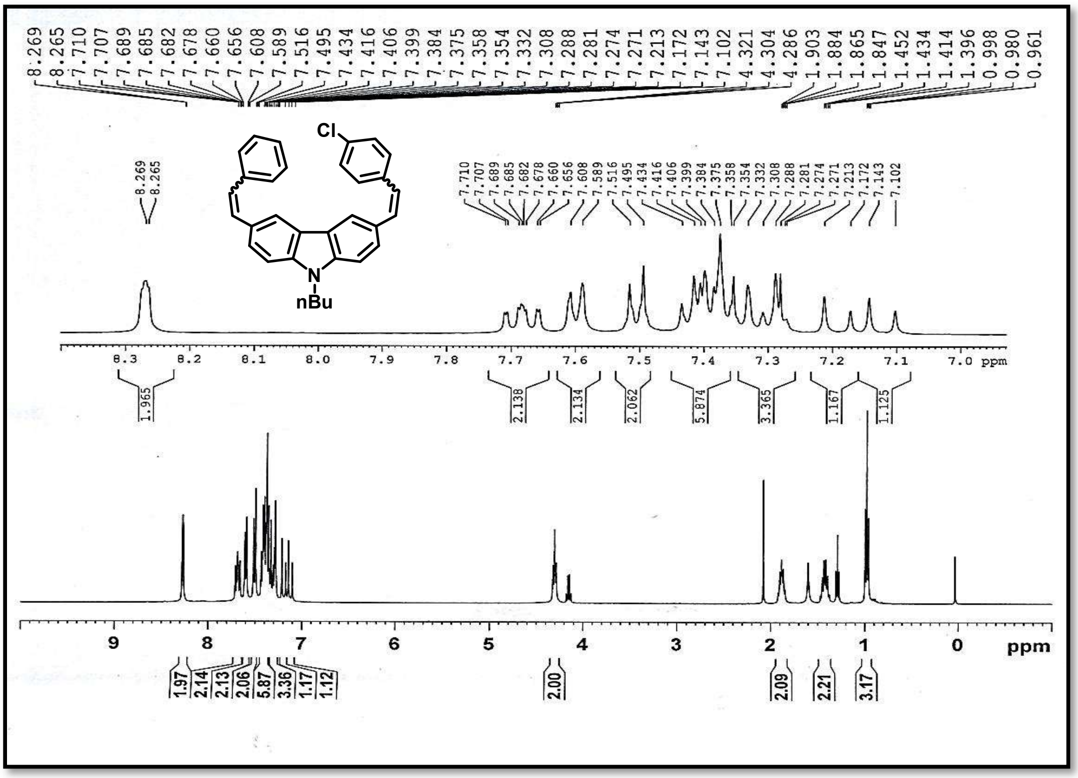
3.2.8 Spectral Data



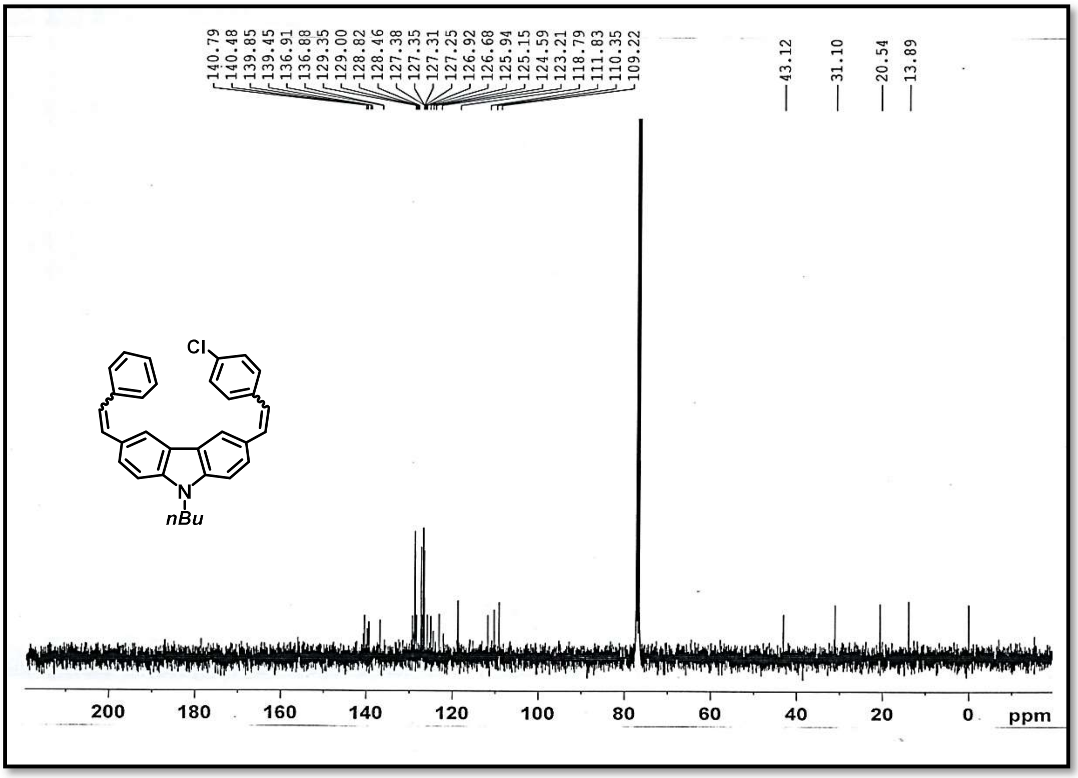
^{1}H NMR spectra of compound 52a



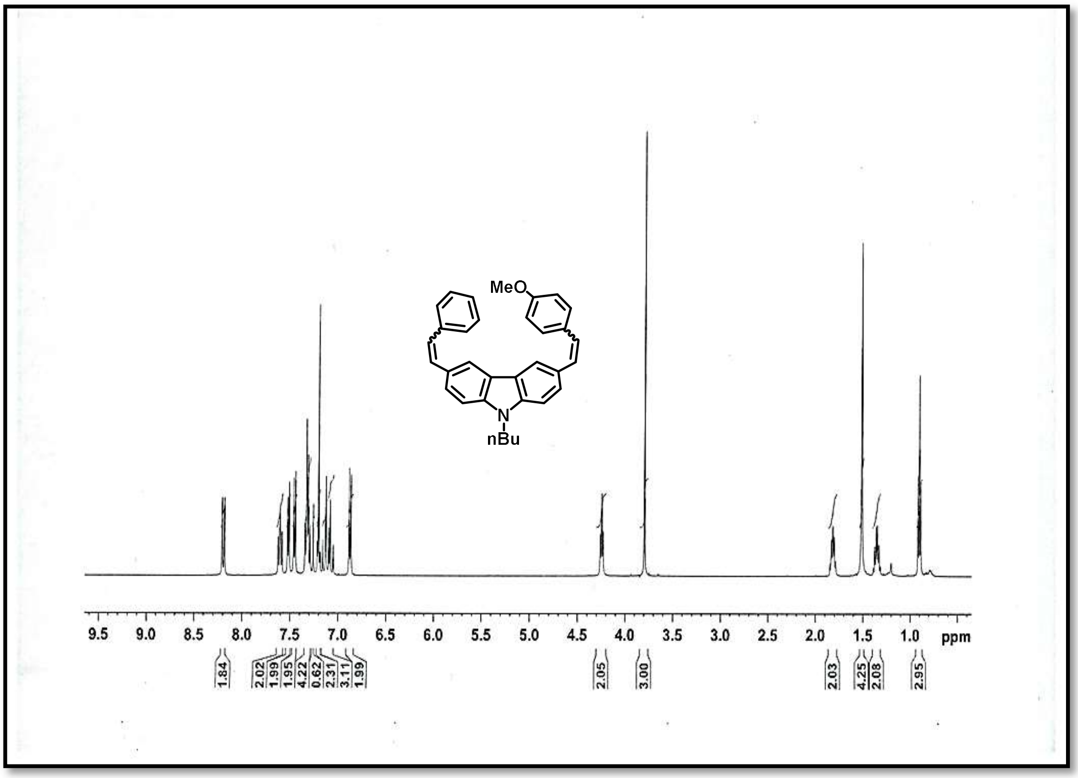
^{13}C NMR spectra of compound 52a



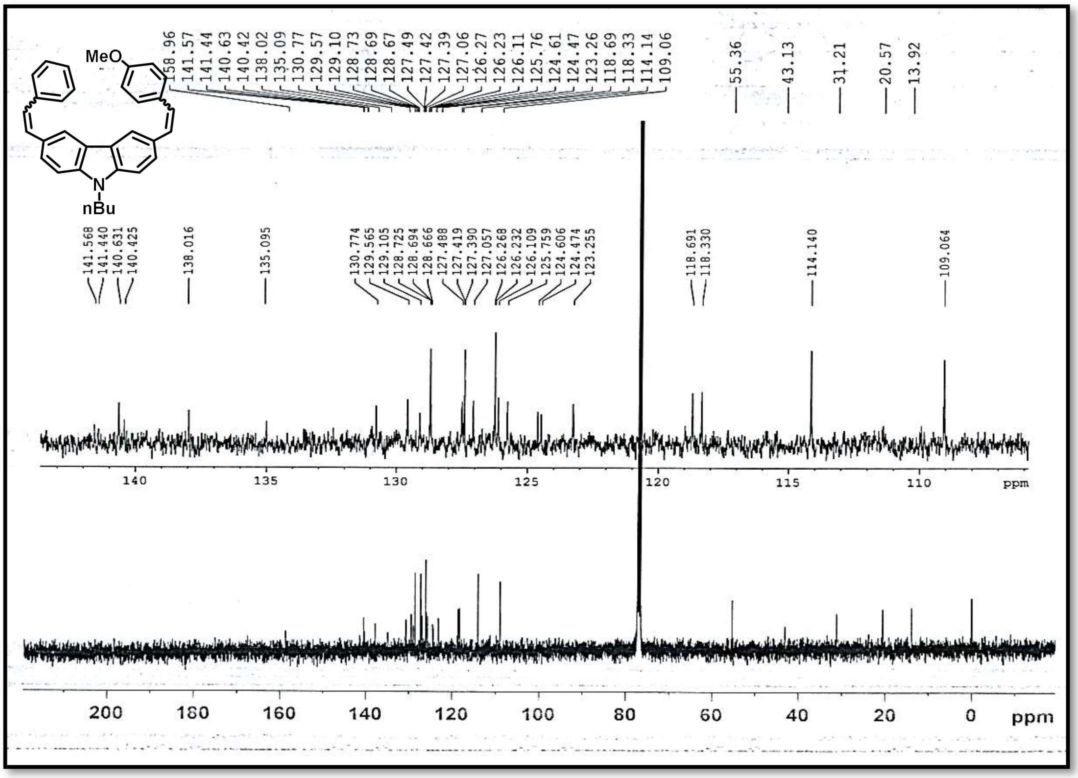
^{1}H NMR spectra of compound 52b



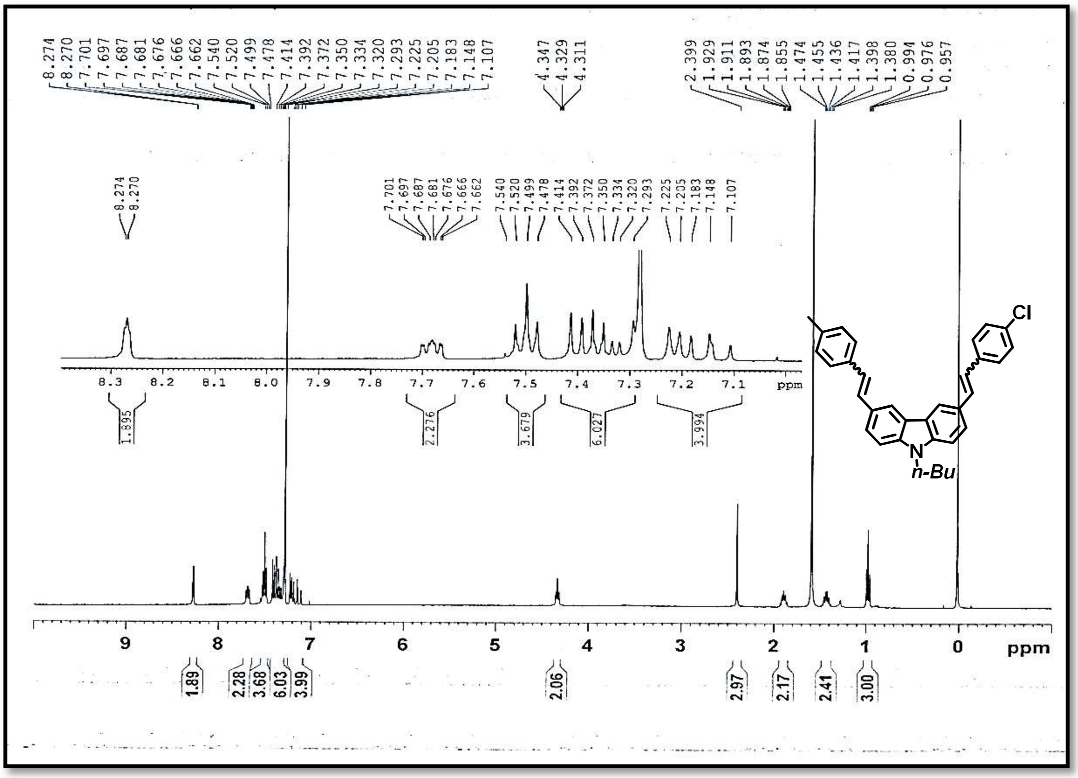
^{13}C NMR spectra of compound 52b



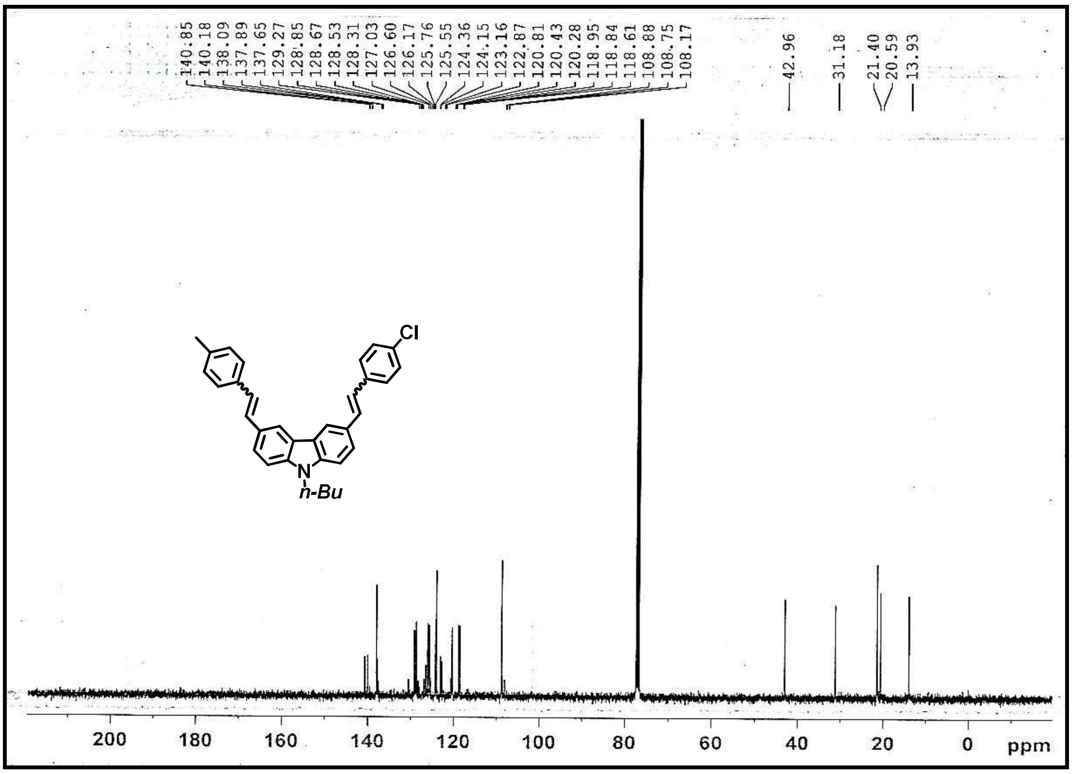
^{1}H NMR spectra of compound 52c



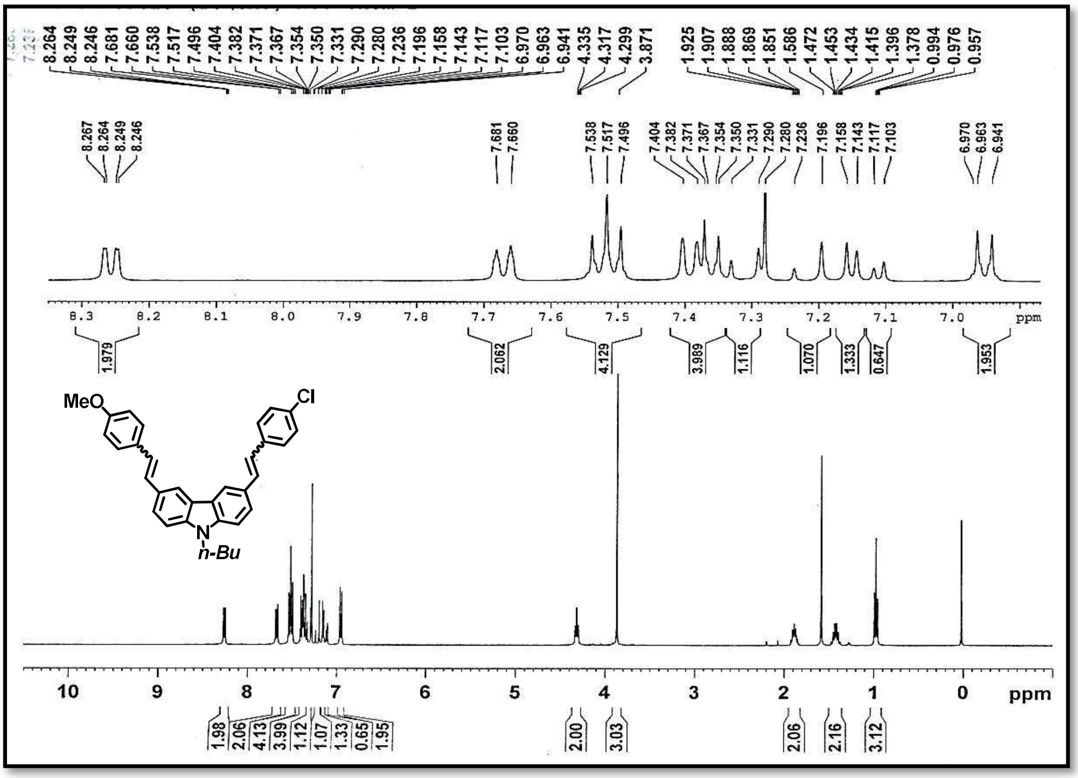
^{13}C NMR spectra of compound 52c



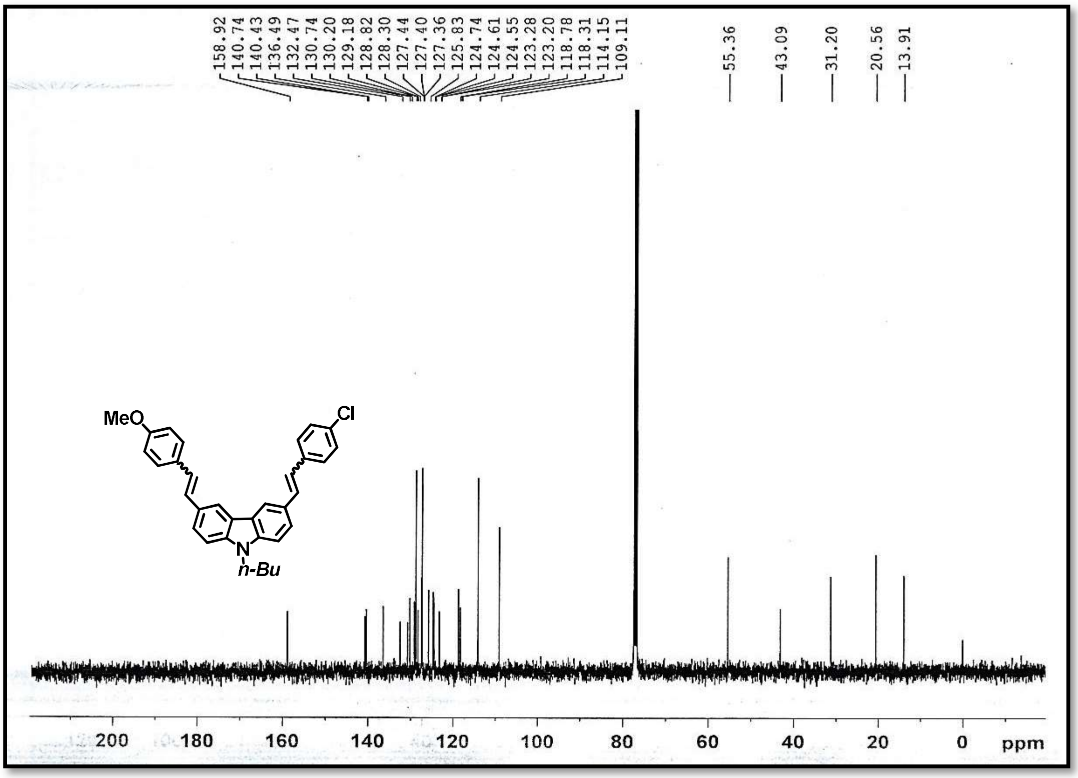
^{1}H NMR spectra of compound 52d



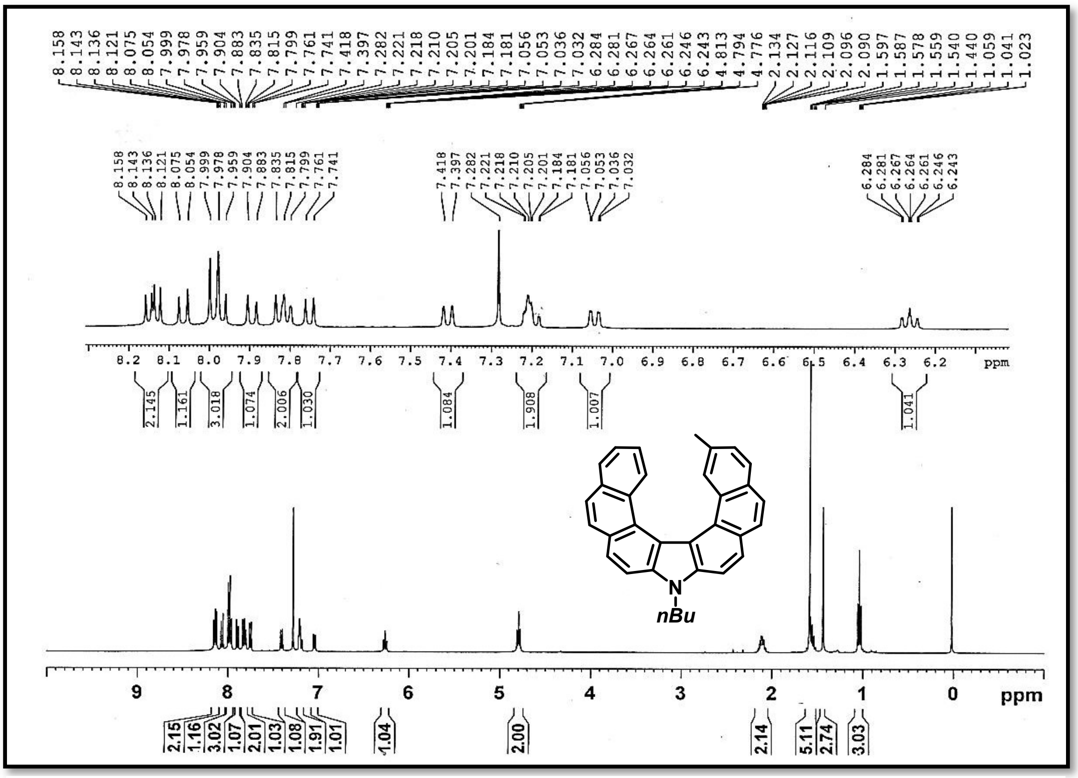
^{13}C NMR spectra of compound 52d



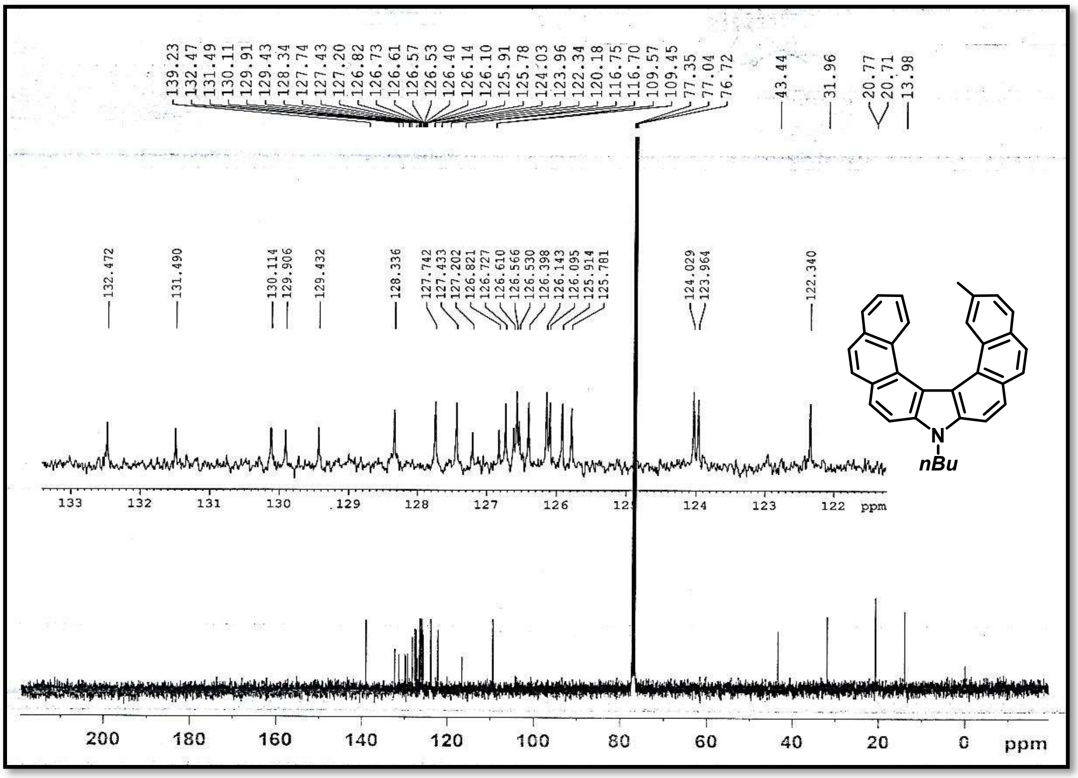
^{1}H NMR spectra of compound 52e



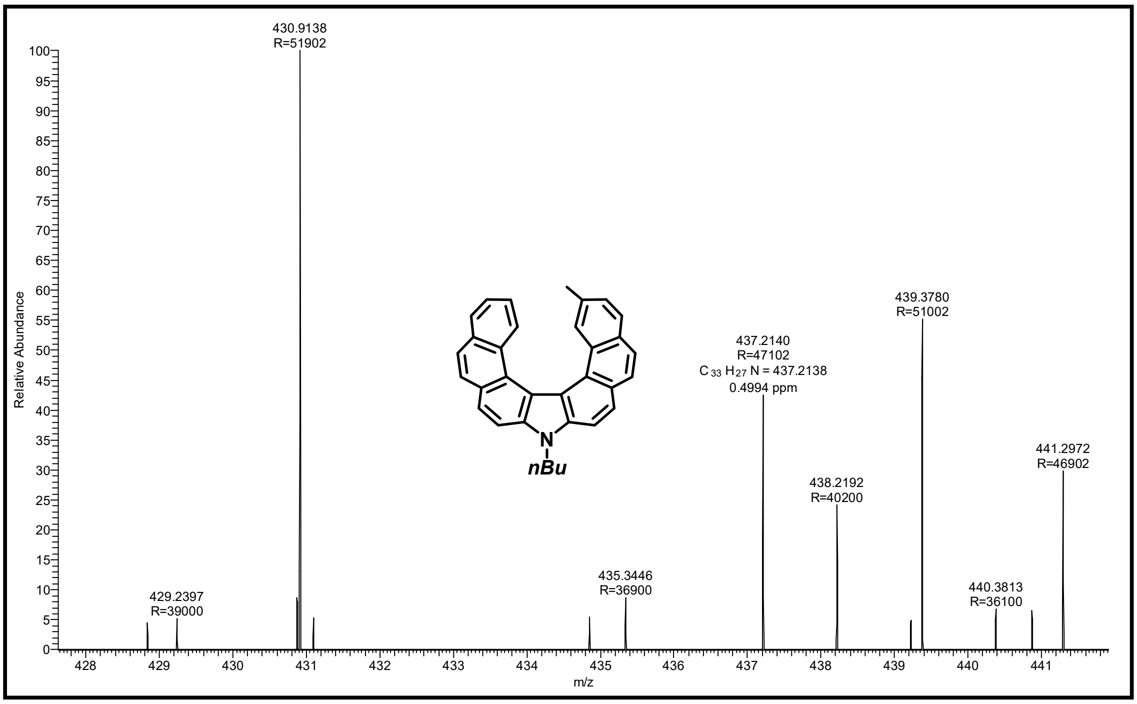
^{13}C NMR spectra of compound 52e



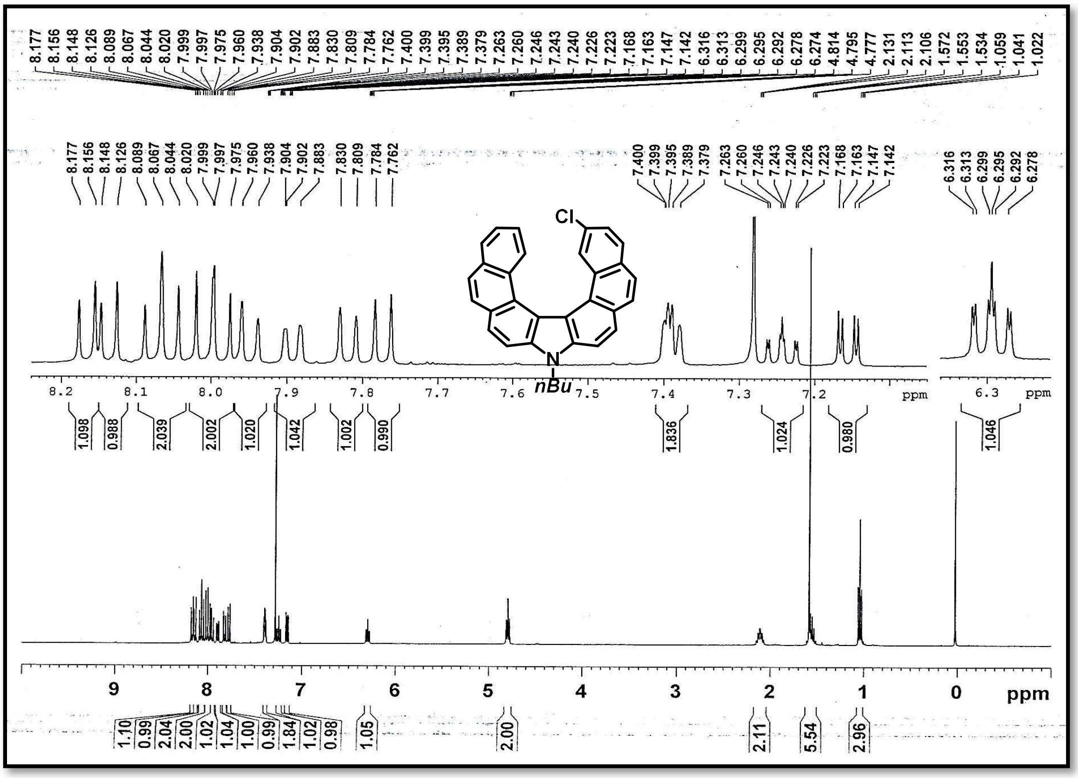
^{1}H NMR spectra of compound 53a



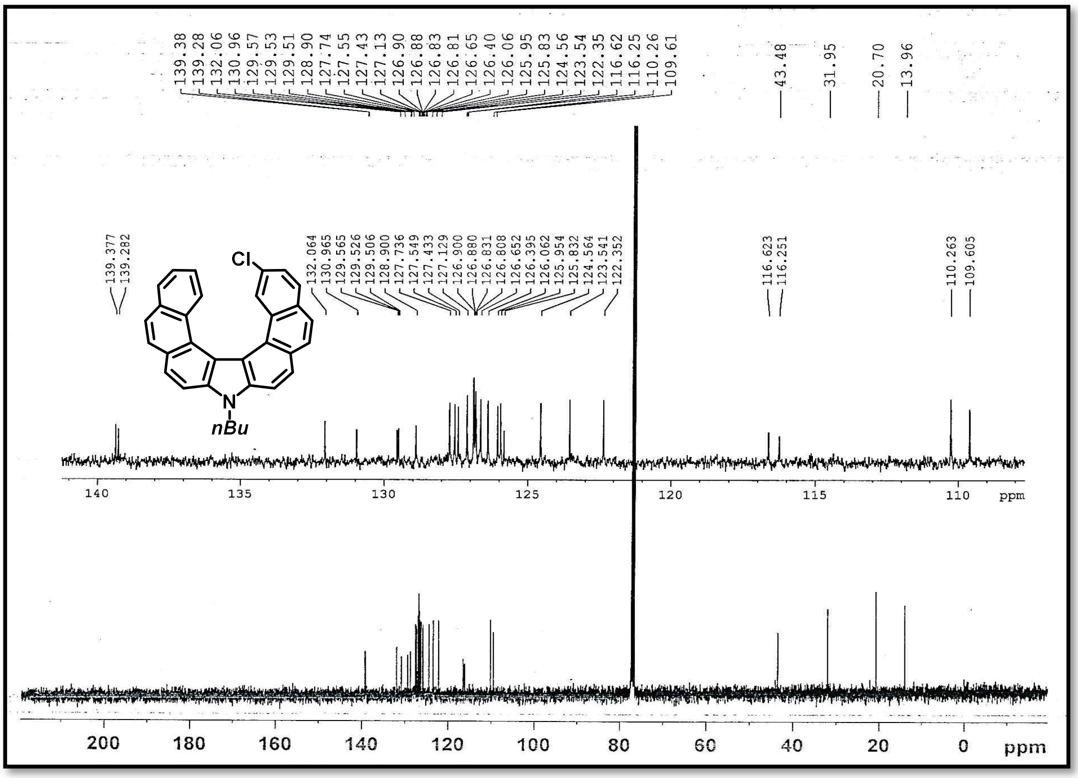
^{13}C NMR spectra of compound 53a



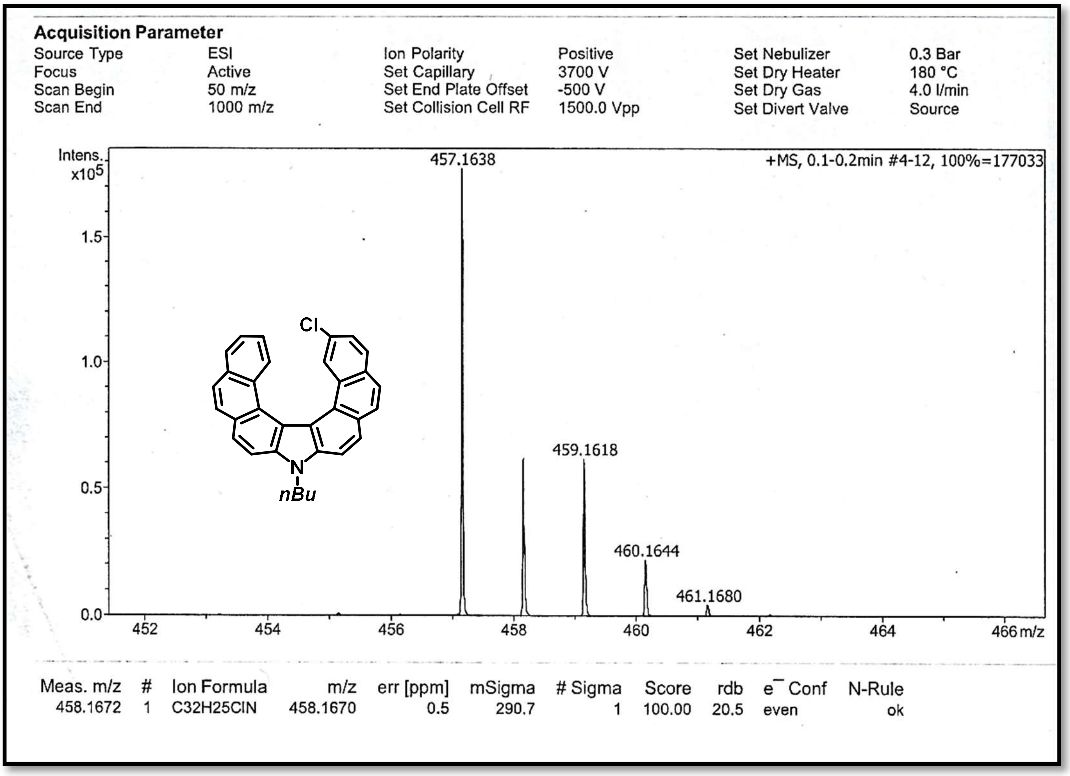
HRMS spectra of compound 53a



^{1}**H NMR spectra of compound 53b**



^{13}C NMR spectra of compound 53b

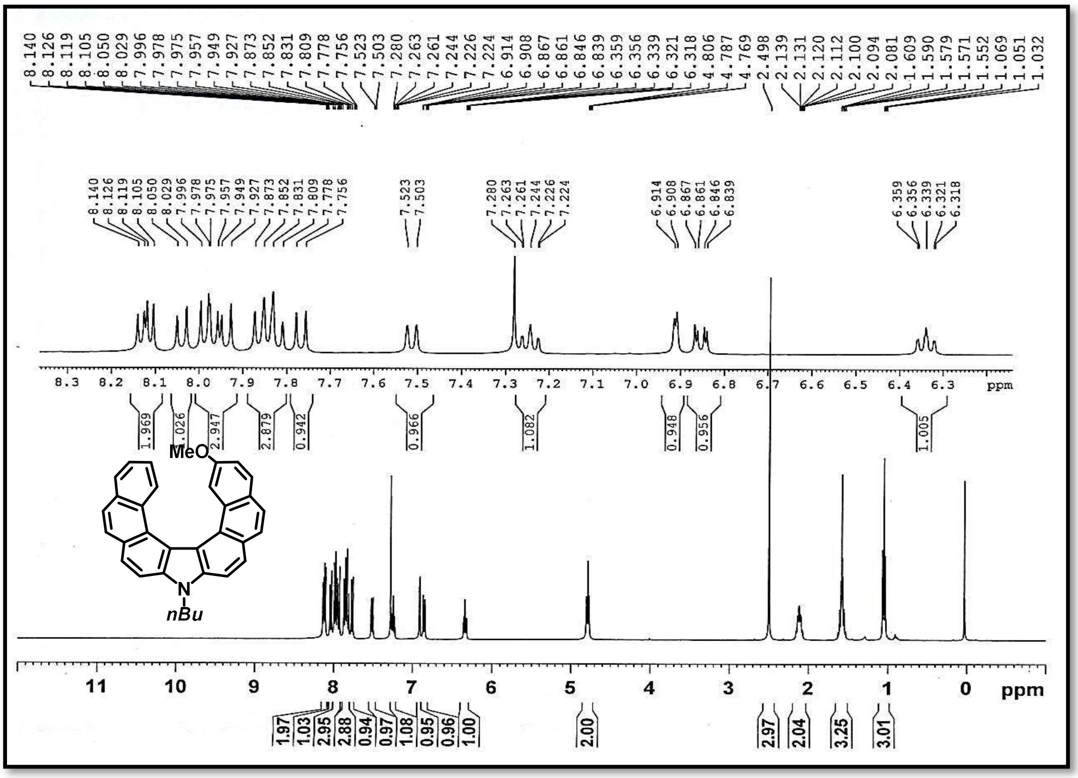


Acquisition Parameter

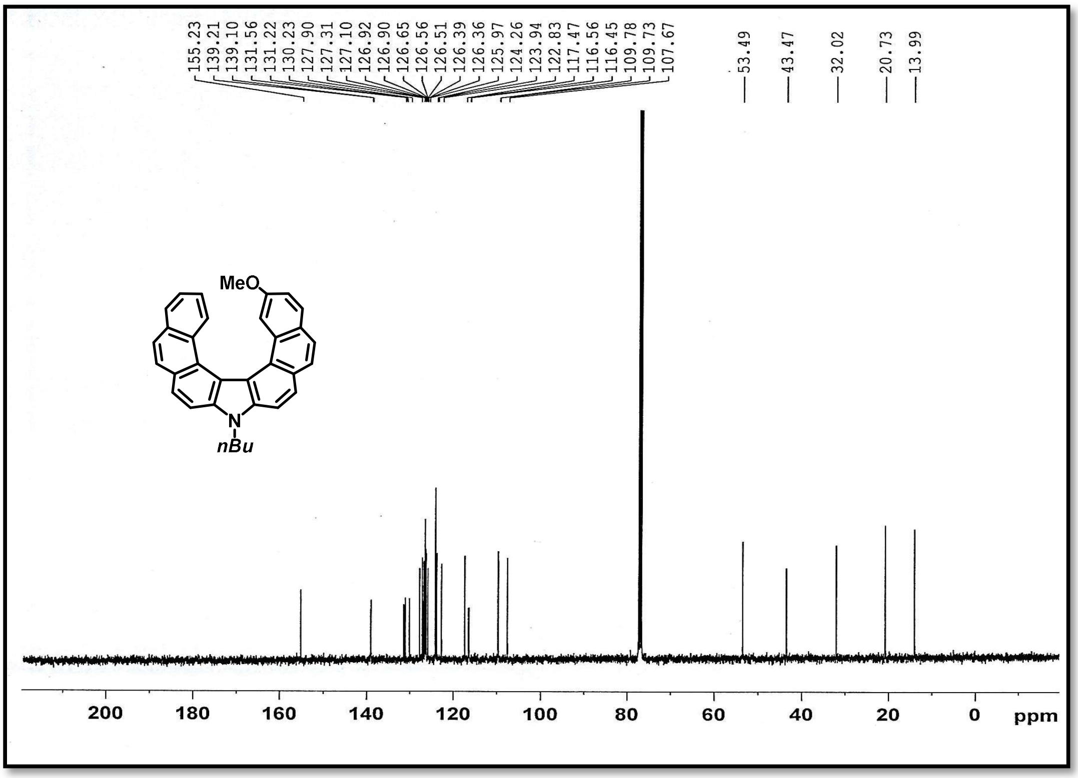
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	1500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
458.1672	1	C32H25ClN	458.1670	0.5	290.7	1	100.00	20.5	even	ok

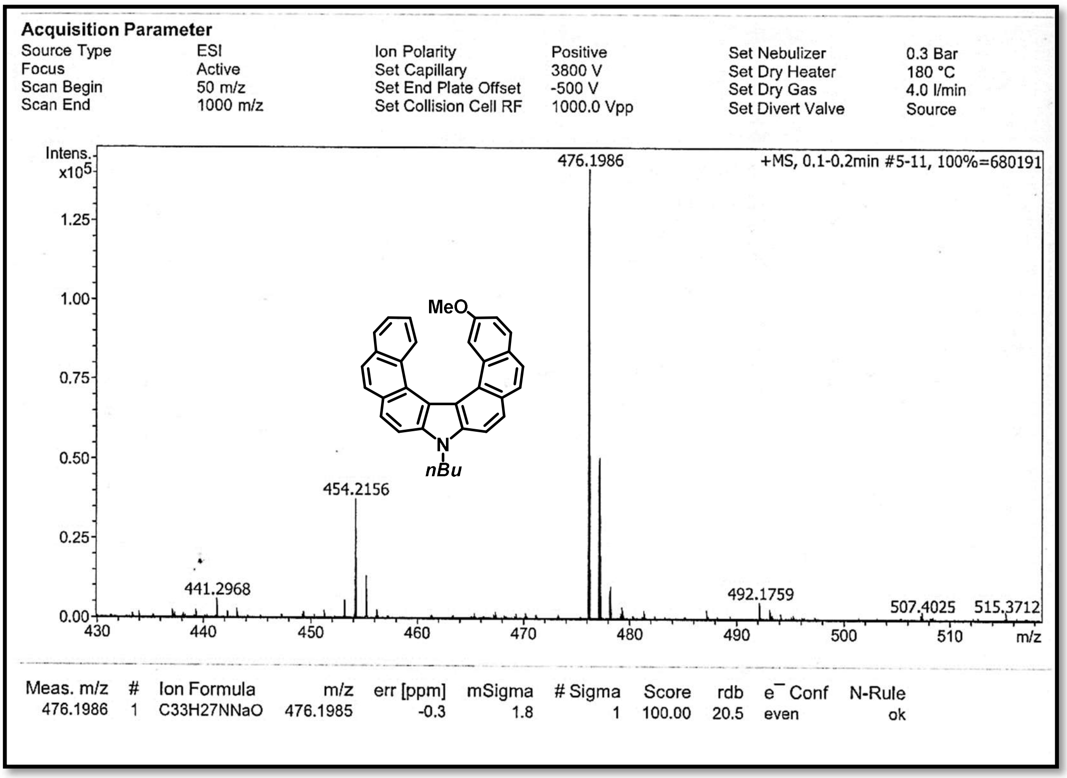
HRMS spectra of compound 53b



^{1}H NMR spectra of compound 53c



^{13}C NMR spectra of compound 53c

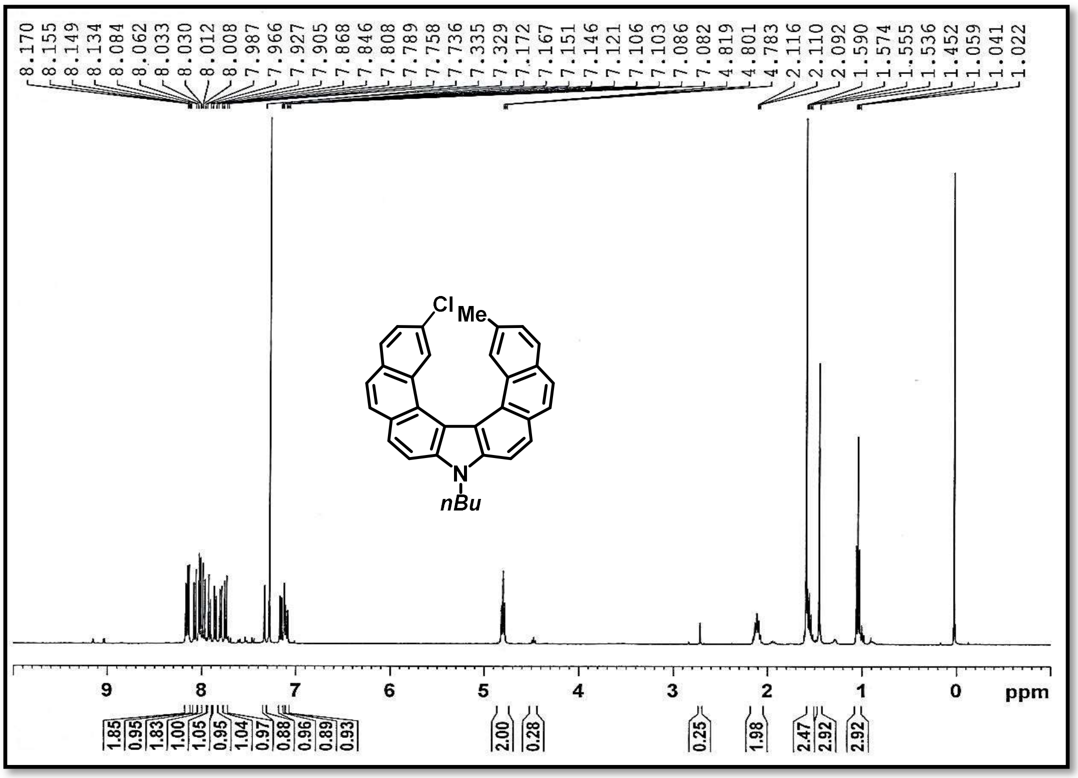


Acquisition Parameter

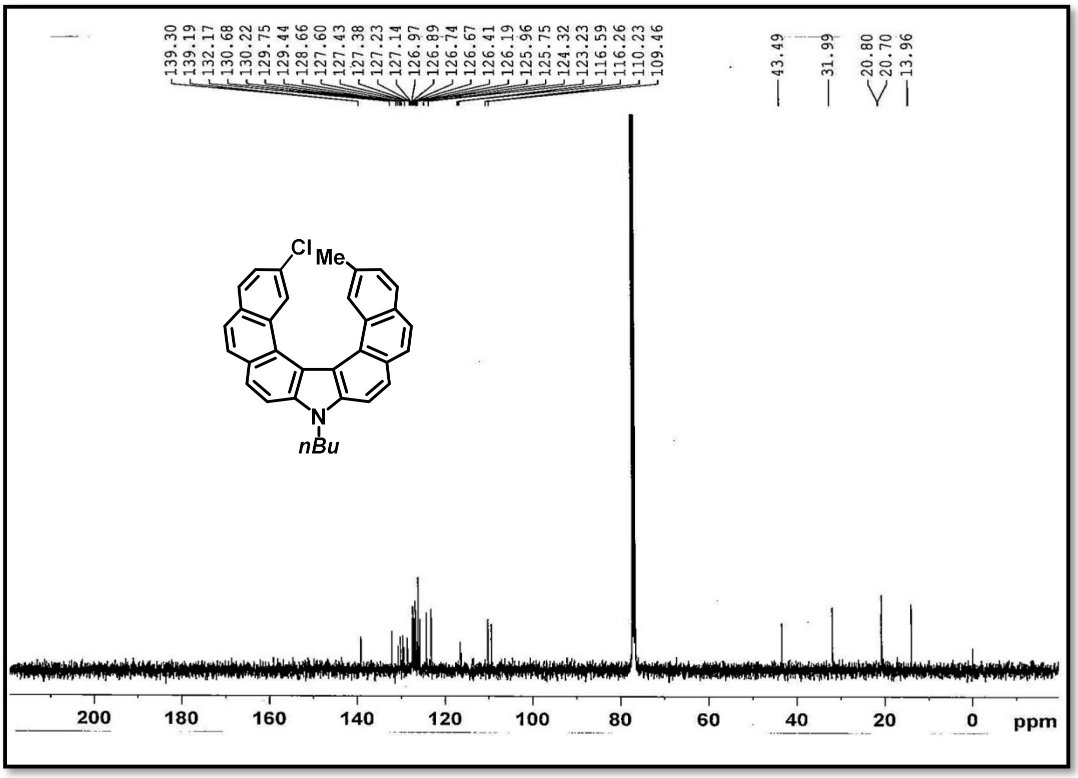
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3800 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
476.1986	1	$C_{33}H_{27}NNaO$	476.1985	-0.3	1.8	1	100.00	20.5	even	ok

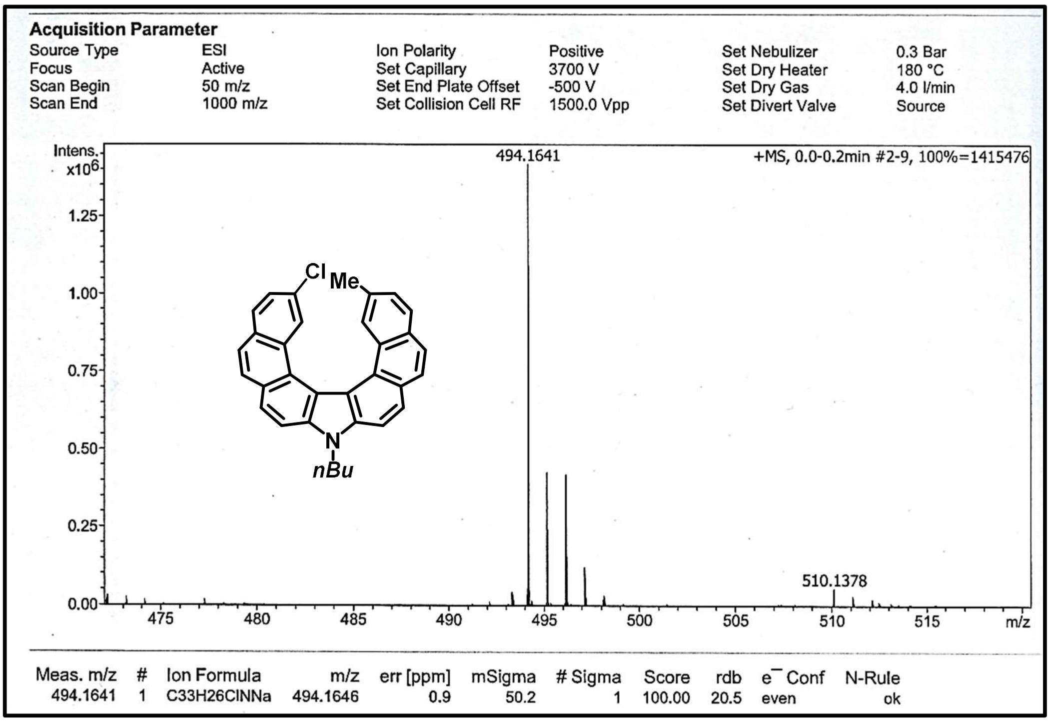
HRMS spectra of compound 53c



^{1}H NMR spectra of compound 53d



^{13}C NMR spectra of compound 53d

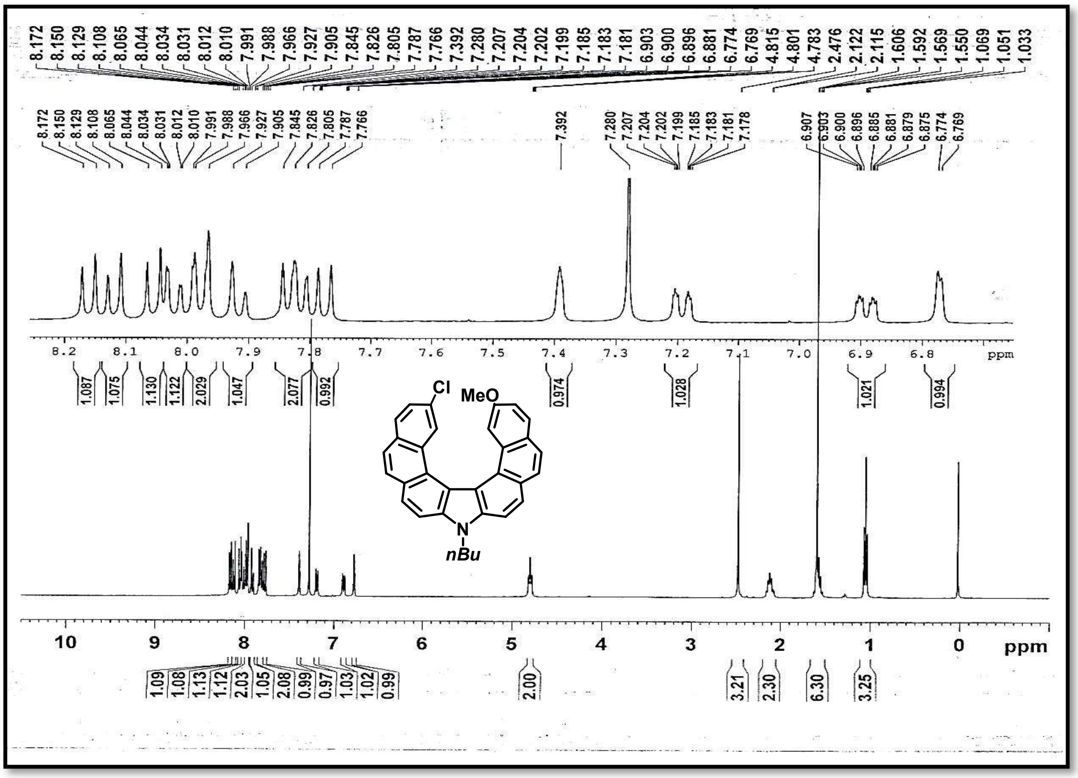


Acquisition Parameter

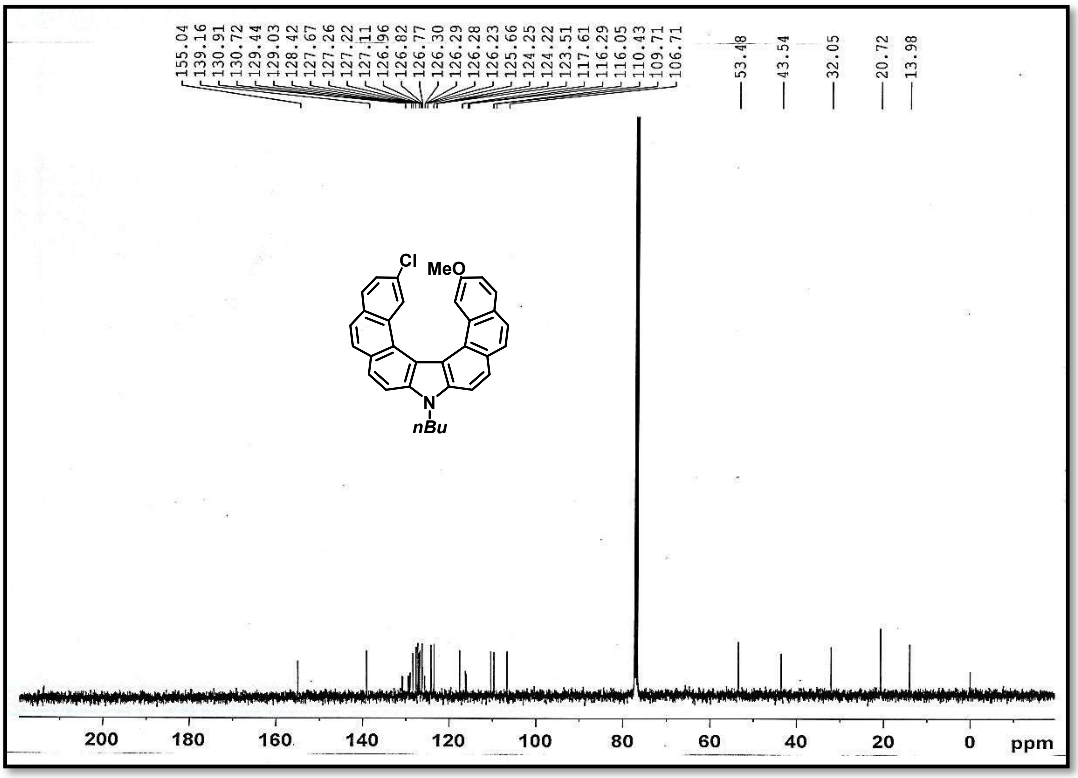
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	1500.0 Vpp	Set Divert Valve	Source

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
494.1641	1	C33H26ClNNa	494.1646	0.9	50.2	1	100.00	20.5	even	ok

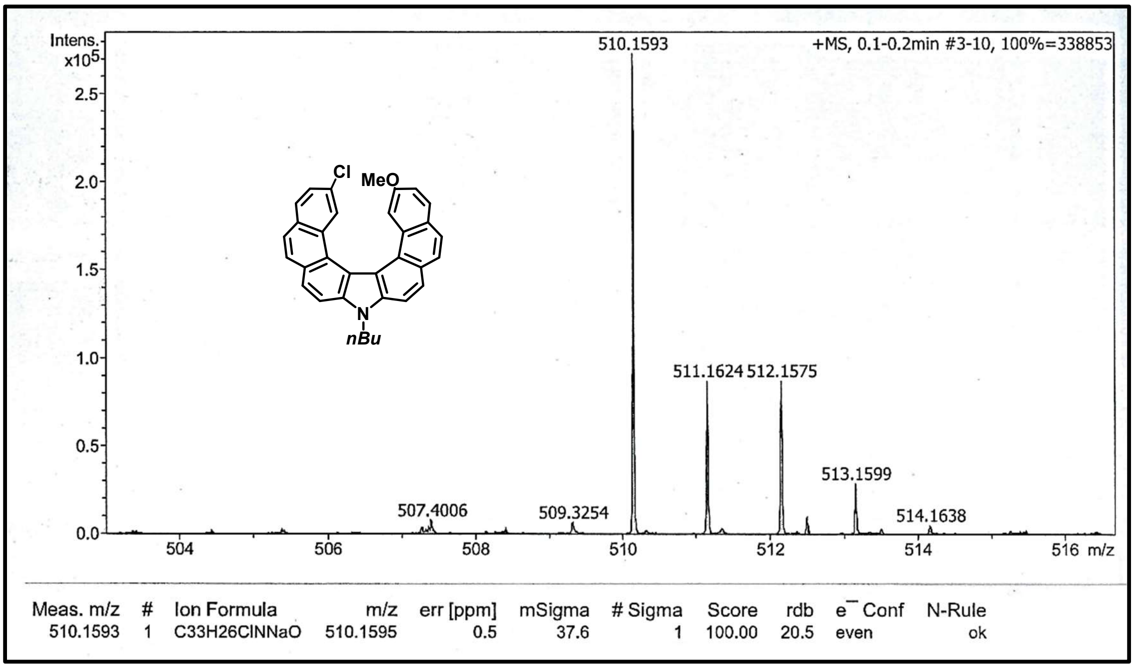
HRMS spectra of compound 53d



^{1}H NMR spectra of compound 53e

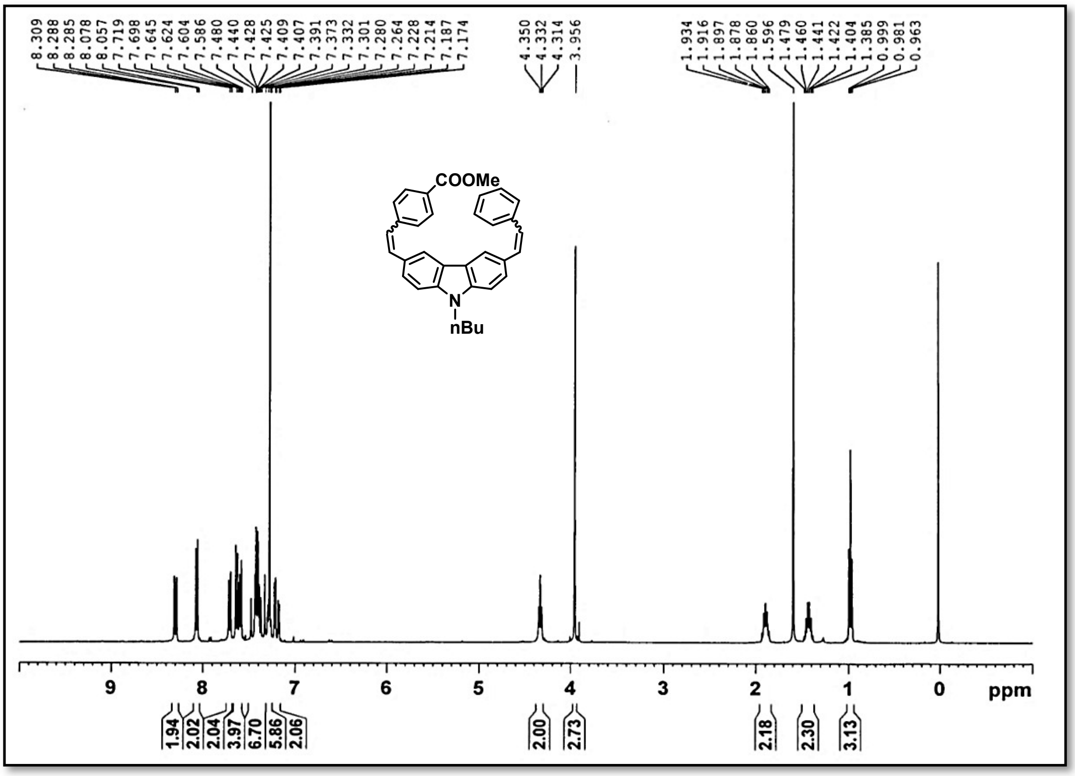


^{13}C NMR spectra of compound 53e

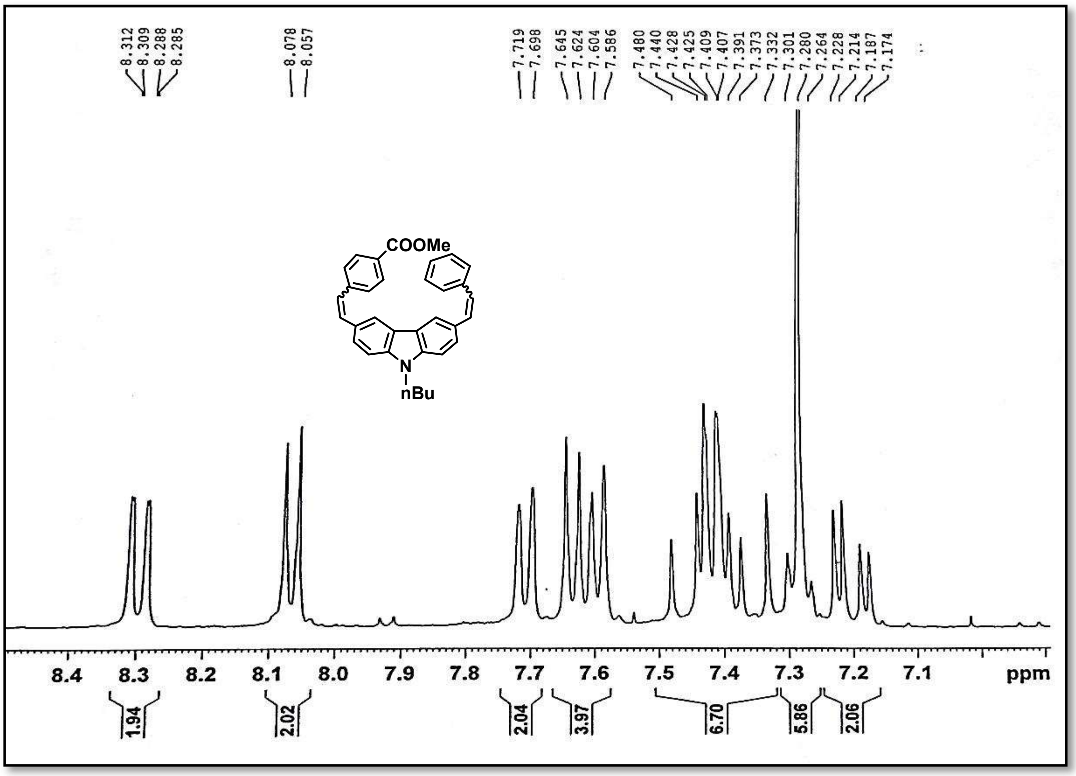


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
510.1593	1	C33H26ClNNaO	510.1595	0.5	37.6	1	100.00	20.5	even	ok

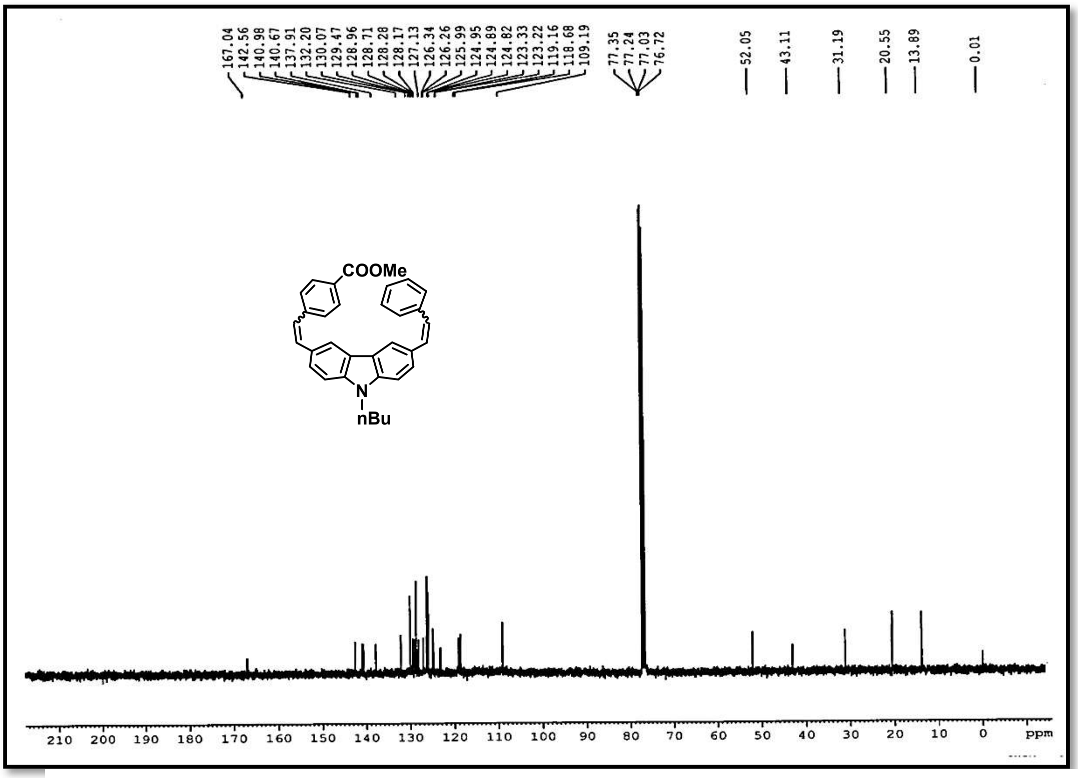
HRMS spectra of compound 53e



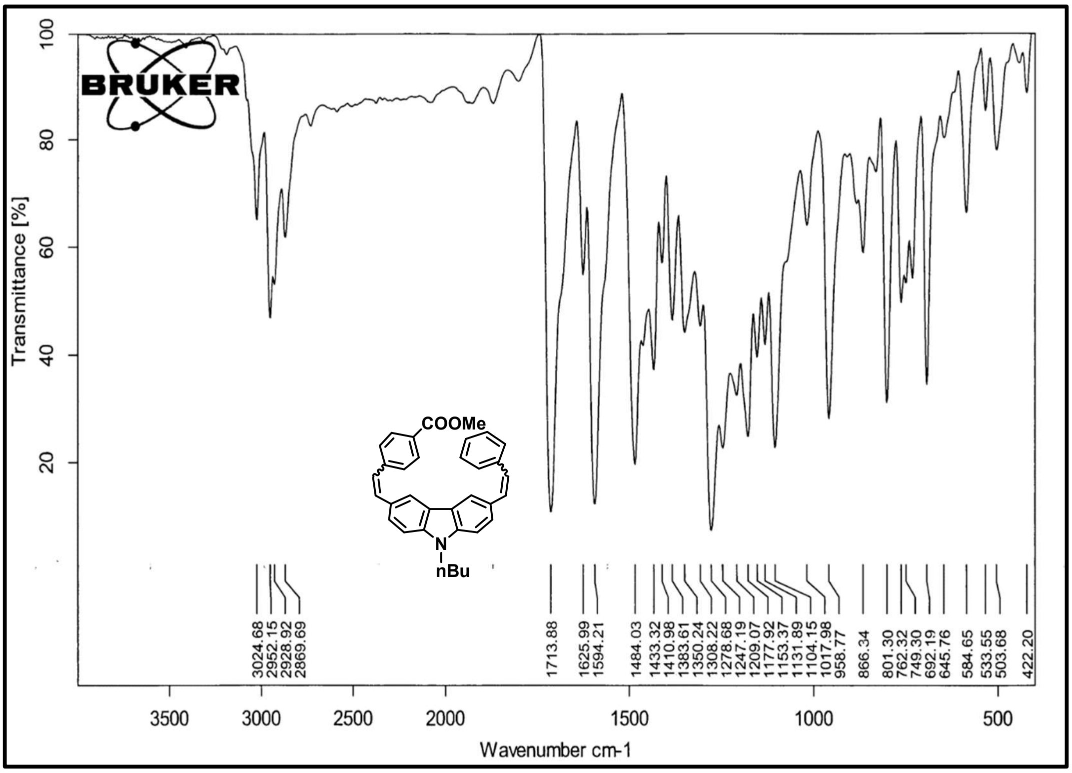
^{1}H NMR spectra of compound 52f



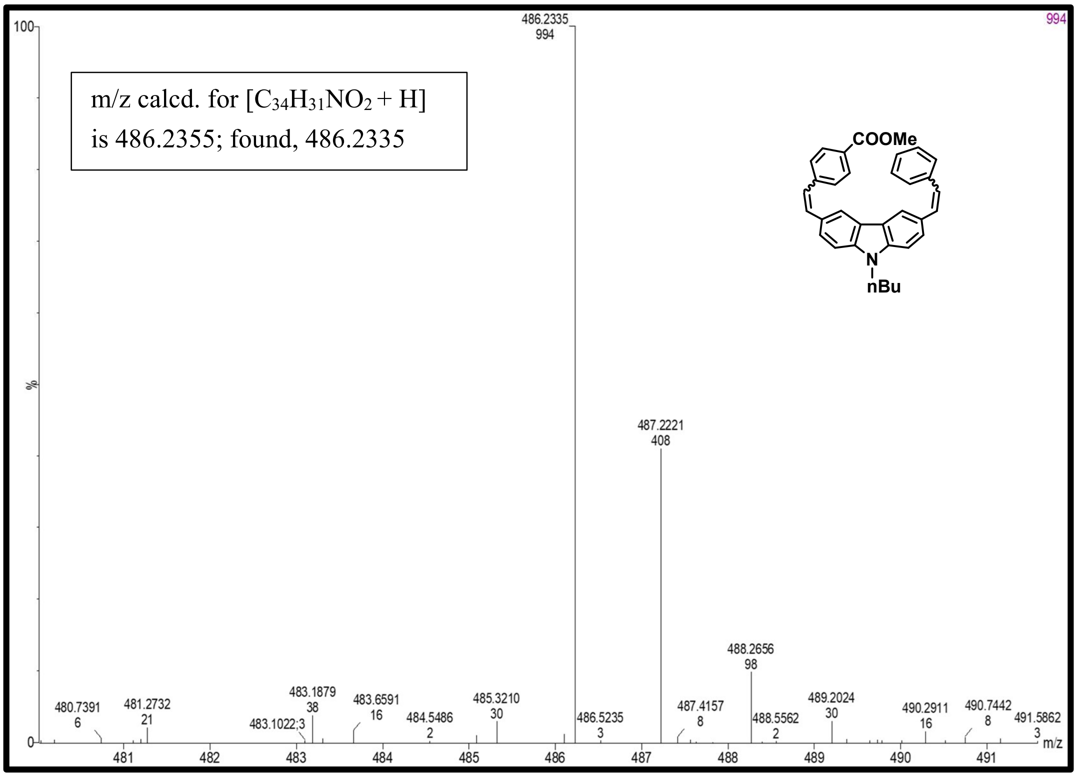
Enlarged aromatic region of ^{1}H NMR spectra of compound 52f



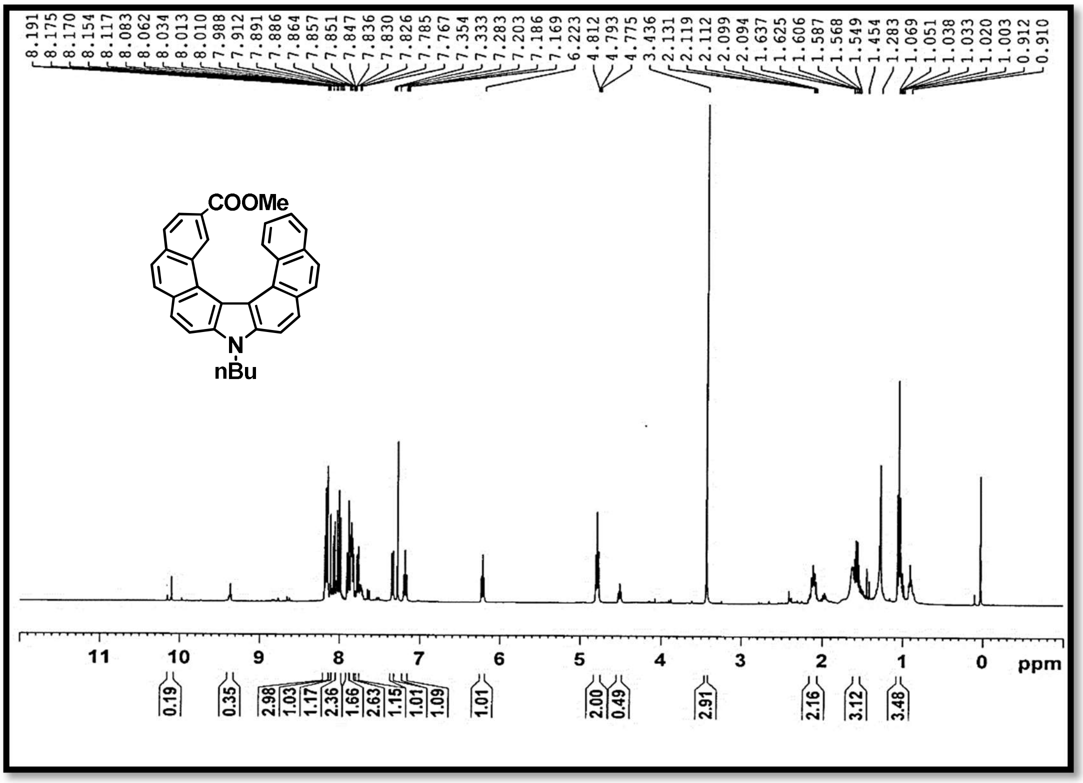
^{13}C NMR spectra of compound 52f



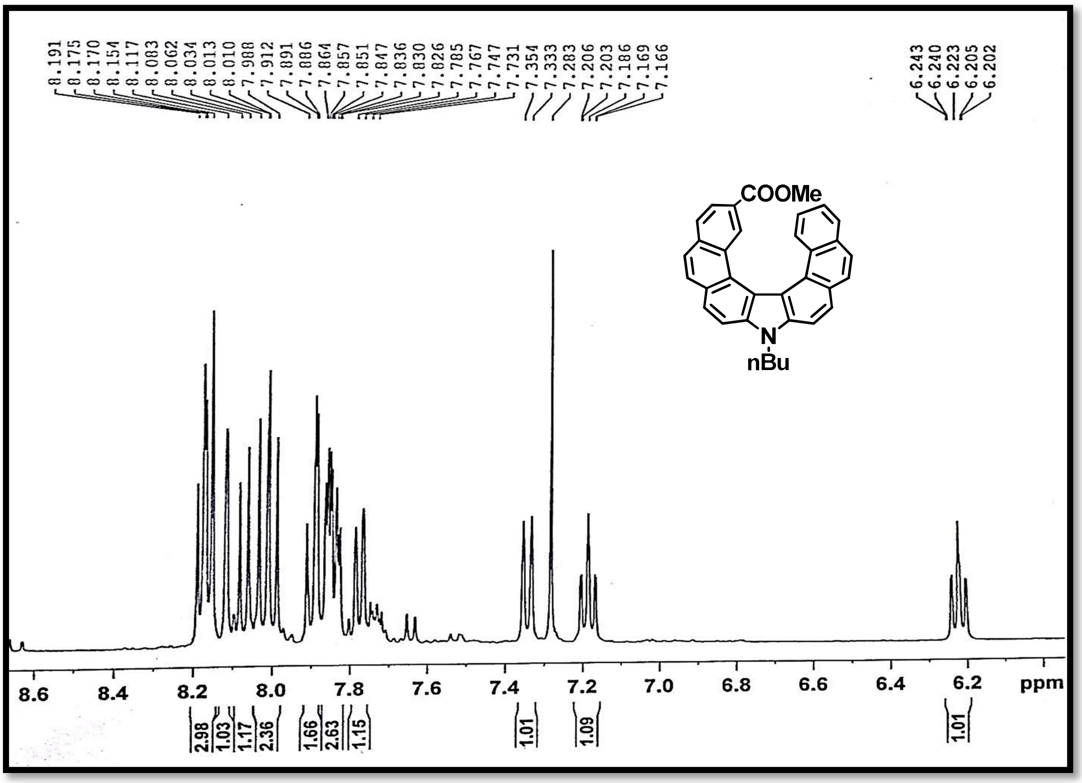
IR spectra of compound 52f


m/z calcd. for [$C_{34}H_{31}NO_2 + H$] is 486.2355; found, 486.2335

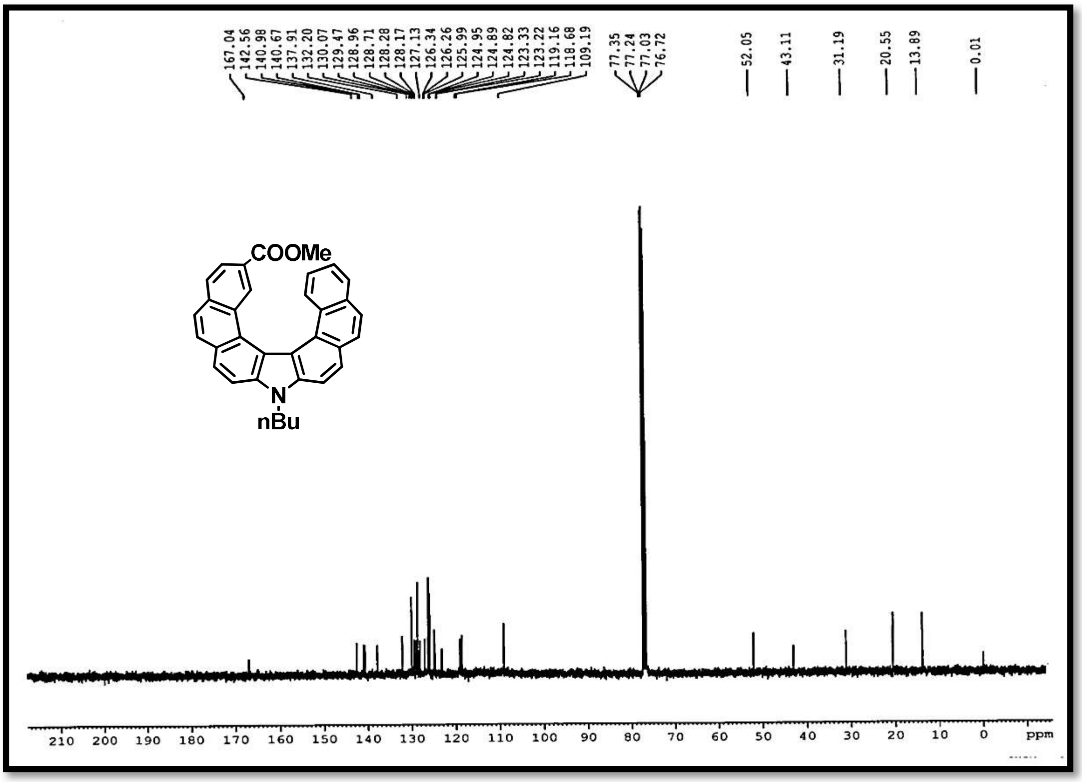
HRMS spectra of compound 52f



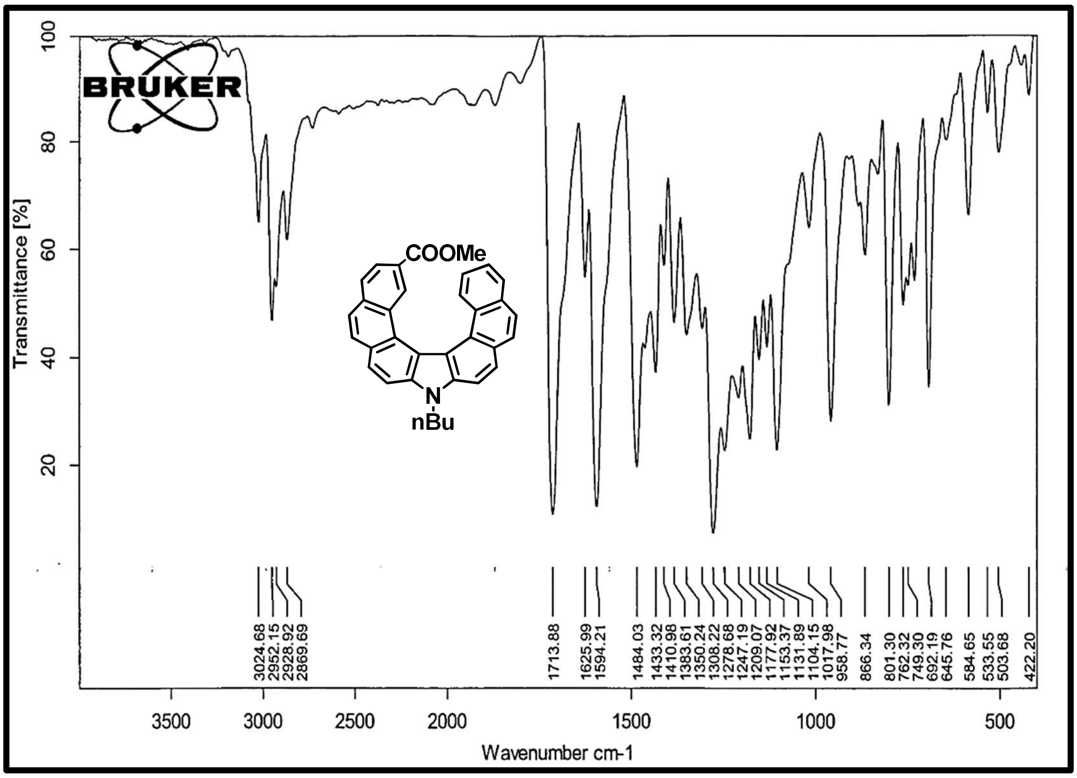
^{1}H-NMR spectra of compound 53f



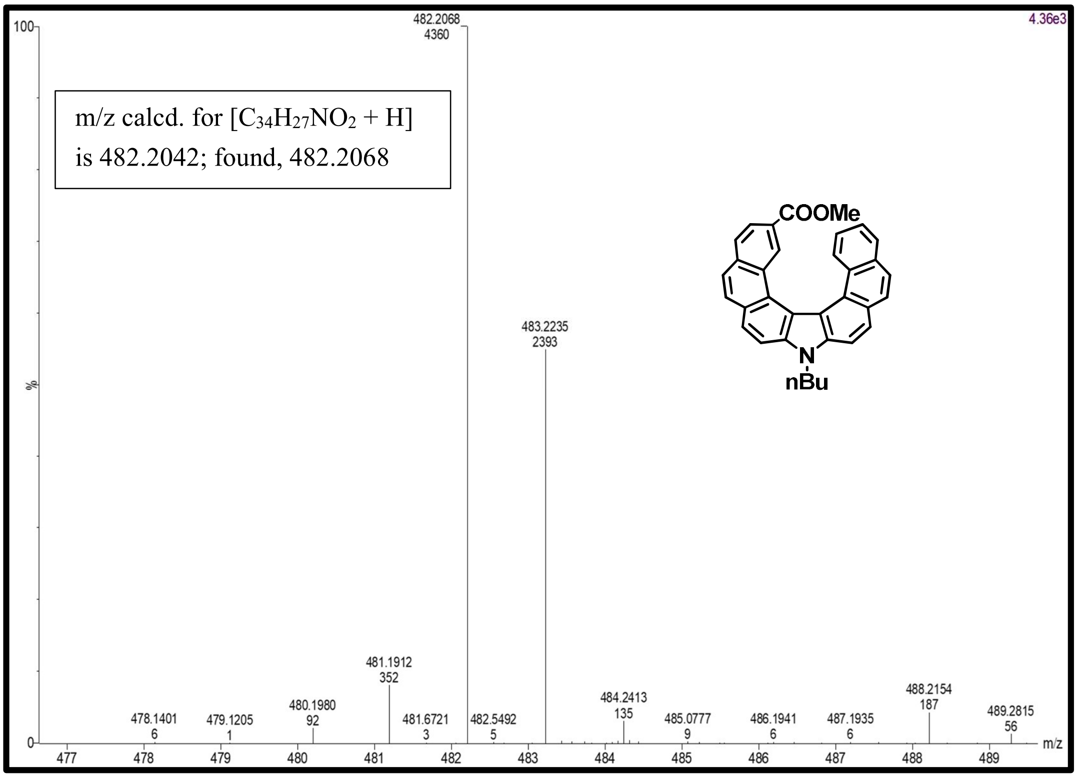
Enlarged aromatic region of ^{1}H-NMR spectra of compound 53f



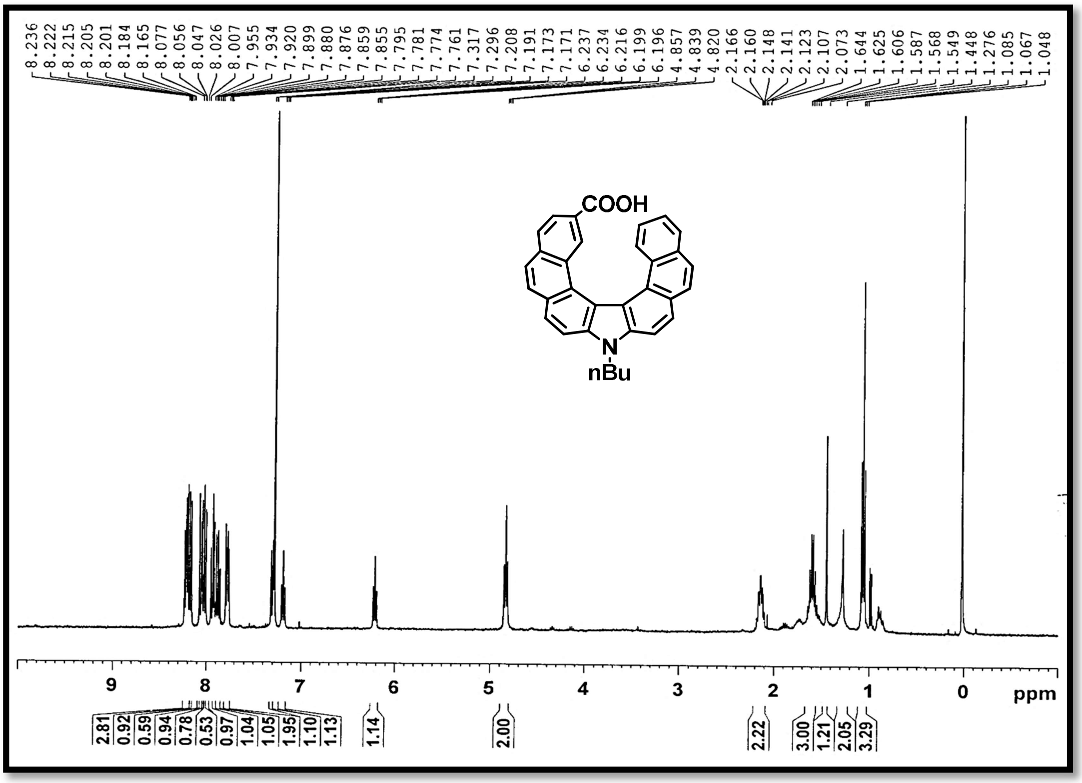
^{13}C-NMR spectra of compound 53f



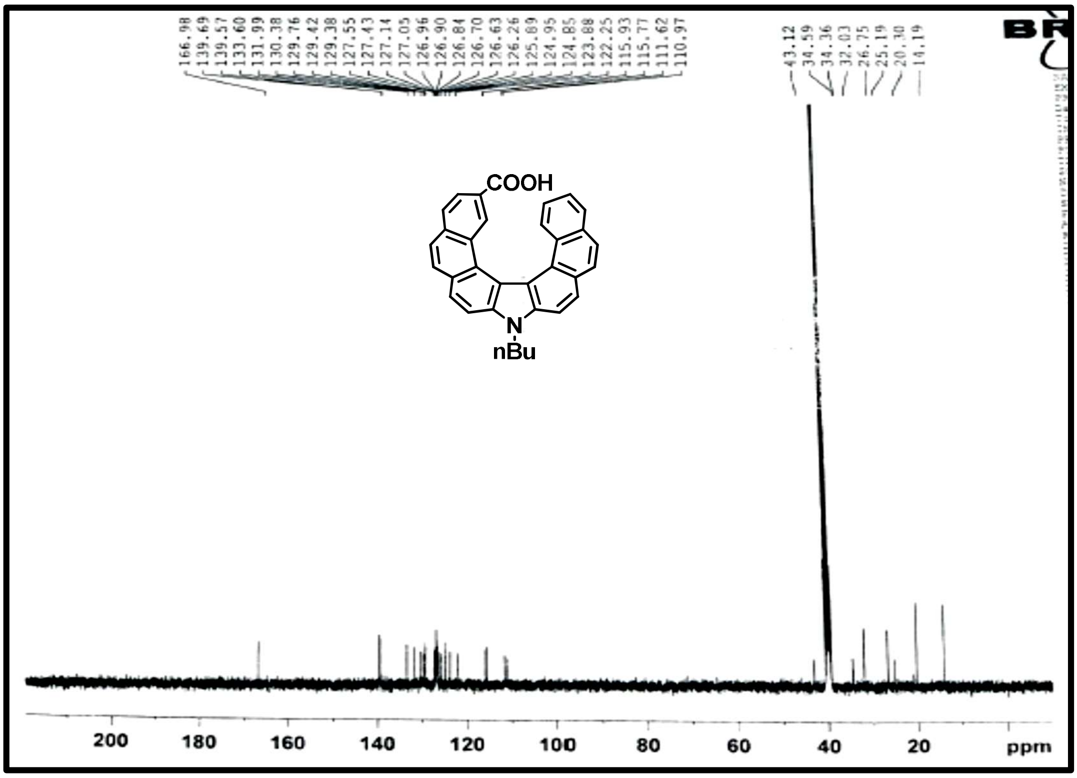
IR spectra of compound 53f



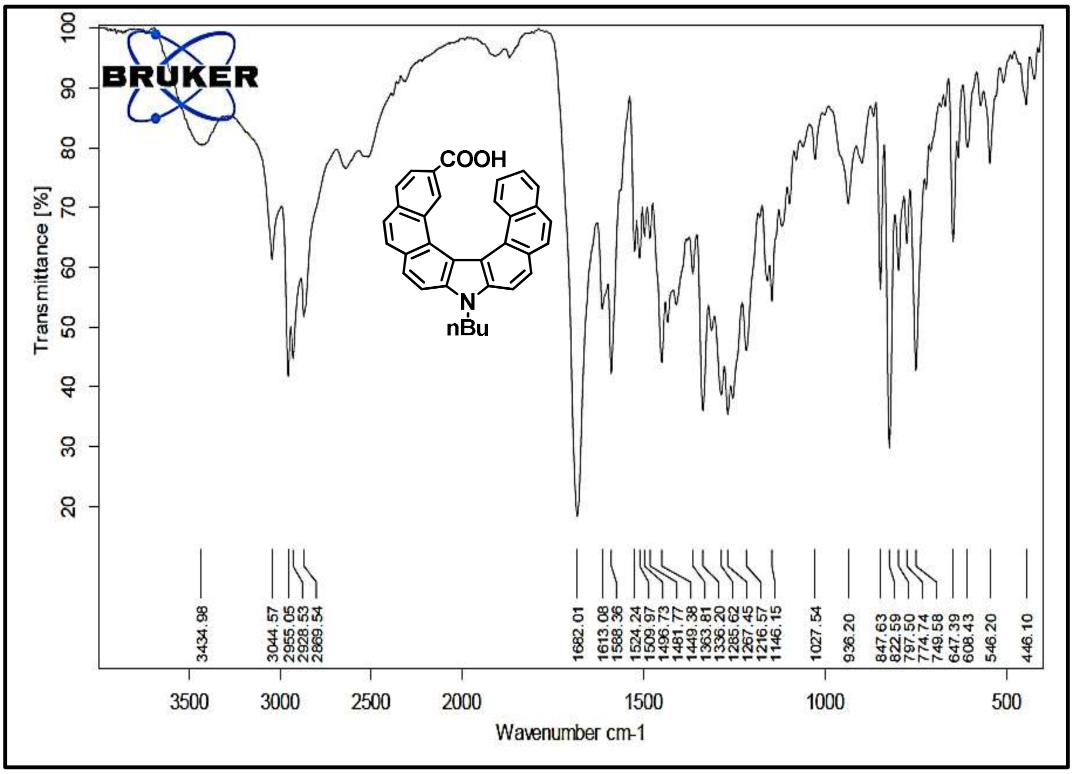
HRMS spectra of compound 53f



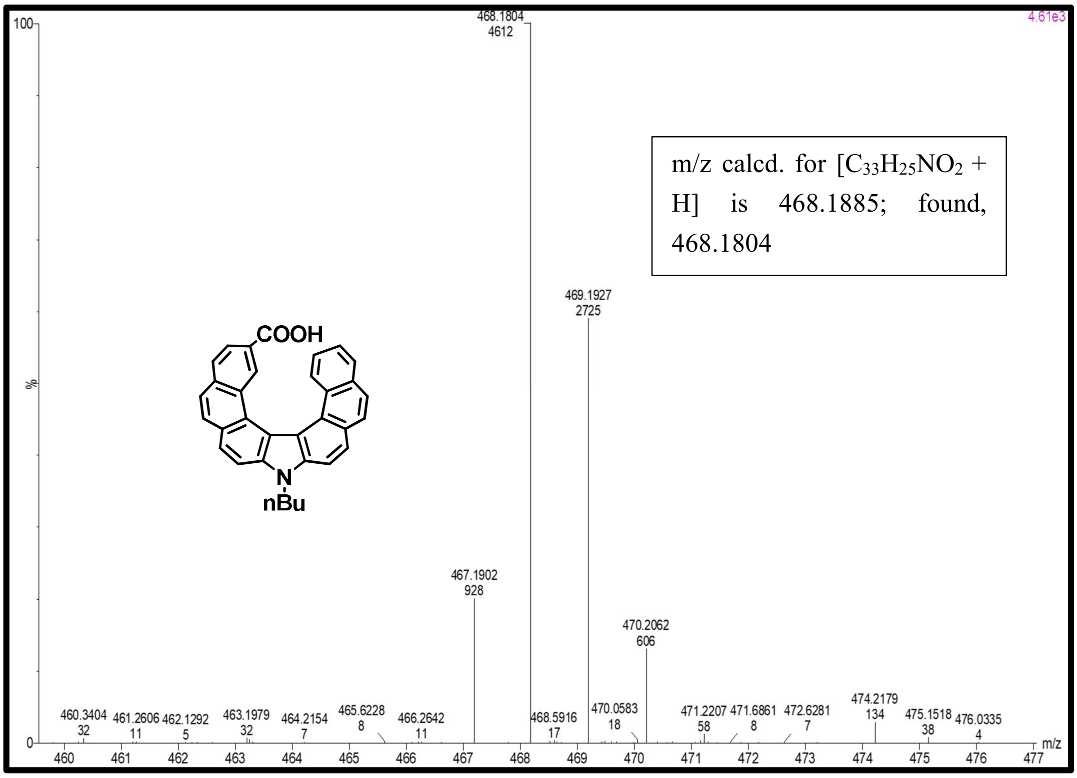
^{1}H-NMR spectra of compound 57



^{13}C-NMR spectra of compound 57

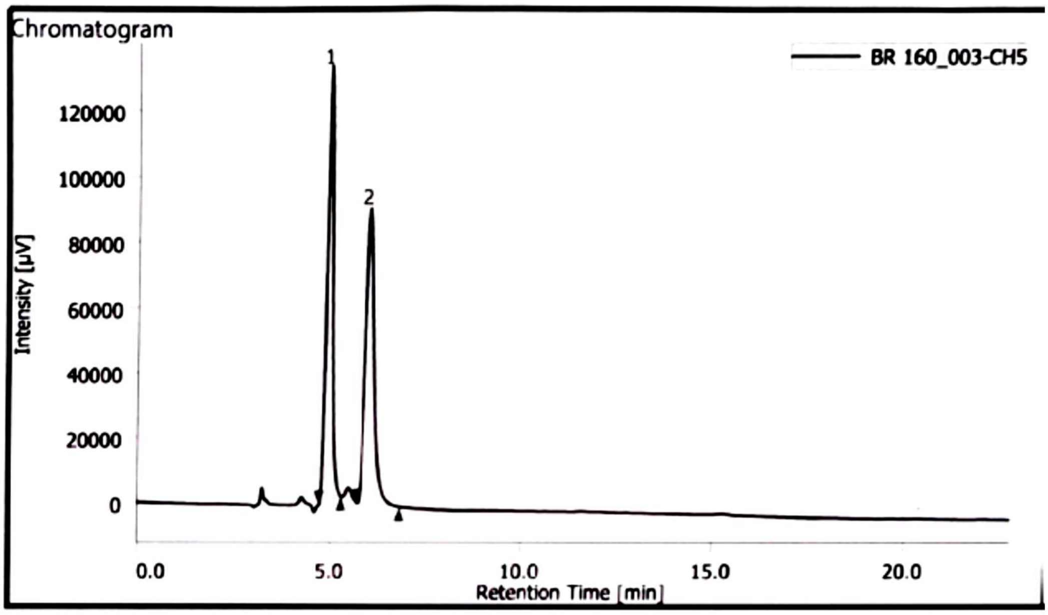


IR spectra of compound 57



m/z calcd. for [$C_{33}H_{25}NO_2$ + H] is 468.1885; found, 468.1804

HRMS spectra of compound 57



Peak Information

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	5	4.907	1430887	132945	49.624	59.582	N/A	5019	3.172	1.320	
2	Unknown	5	5.987	1452585	90186	50.376	40.418	N/A	3483	N/A	1.448	

HPLC chart of compound 57 on chiralpak-IC column with flow rate of 1 mL/min in 70:30 Hexane-Propan-2-ol, t_R = 4.9 and 5.9 min.

3.2.9 Crystallographic data

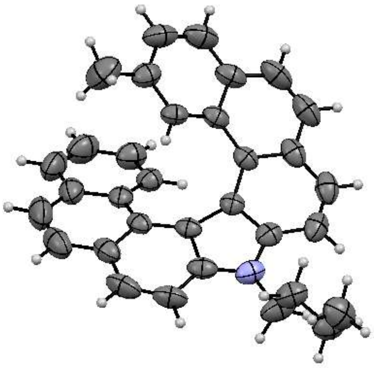


Figure 3.2.8: *ORTEP plot of compound 53a*

Table 3.2.3 : *Crystallographic data of compound 53a*

Identification Code	CCDC 1528044
Empirical Formula	$C_{33}H_{27}N$
Formula Weight	437.56
Temperature/K	293
Crystal System	Monoclinic
Space Group	C 2/C
a/Å	30.210(2)
b/Å	11.5803(5)
c/Å	13.6414(7)
α/^{0}	90
β/^{0}	97.898(6)
γ/^{0}	90
Volume/Å^3	4727.1(5)
Z	8
ρ_{calc}g/cm^3	1.230
μ/mm^{-1}	0.070
F(000)	1872
Radiation	CuKα(λ=1.5418)
h,k,lmax	41,15,18
R(reflections)	0.0677(4138)
wR2(reflections)	0.2126(5676)
Goodness of fit	1.042

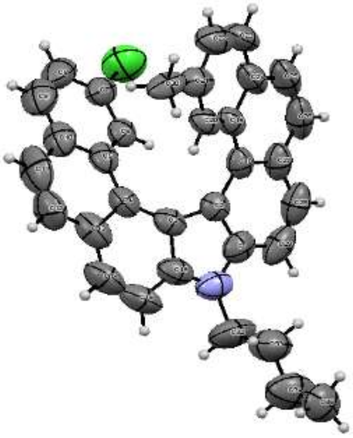


Figure 3.2.9: *ORTEP plot of compound 53d*

Empirical Formula	$C_{33}H_{26}NCl$
Formula weight	472.03
Temperature/K	293
Crystal System	monoclinic
Space group	C 2/c
a/A°	30.081(3)
b/ A°	11.4119(10)
c/ A°	14.8937(11)
α/°	90.00
β/°	100.819(8)
γ/°	90.00
Volume/A^3	5021.9(8)
Z	8
ρ_{calc} g/cm^3	1.2486
m/ mm^{-1}	0.174
F(000)	1985.8979
Radiation	MoK\a

3.2.10 Computational data

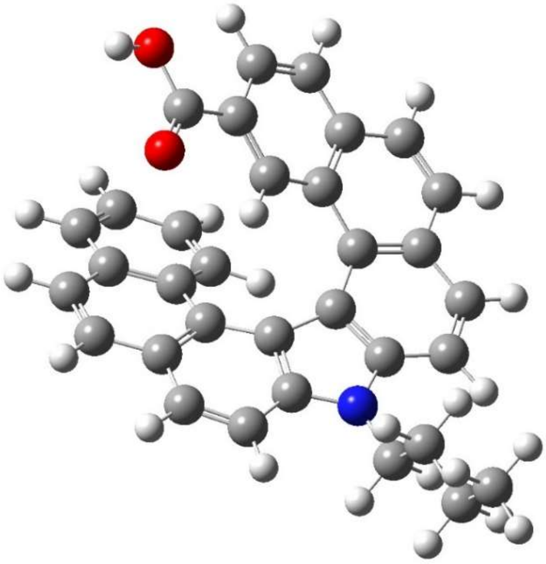


Figure 3.2.10: *Optimized geometry by B3LYP-6-31G calculation of 57*

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z
1	6	-0.16275	-1.85723	-0.355869
2	6	-0.85811	0.753571	-0.501692
3	6	1.610726	-0.76251	1.057835
4	1	0.98559	0.105875	1.20825
5	6	1.148164	-1.85082	0.283913
6	6	0.220612	1.702735	-0.610332
7	7	-3.1013	0.247211	-0.606352
8	6	-2.40721	-0.95079	-0.709552
9	6	-1.0095	-0.70843	-0.539861
10	6	-2.18281	1.276669	-0.426798
11	6	1.542268	1.423427	-1.156859
12	6	1.828462	0.258294	-1.915124
13	1	1.036745	-0.45133	-2.109807

14	6	-0.69492	-3.13322	-0.741355
15	6	1.970033	-3.02704	0.235068
16	6	-2.94657	-2.22162	-0.981861
17	1	-4.00915	-2.35877	-1.146209
18	6	-2.07223	-3.28311	-1.066605
19	1	-2.43594	-4.27053	-1.333514
20	6	-0.06468	3.058526	-0.240411
21	6	1.458772	-4.22679	-0.354087
22	1	2.099811	-5.10175	-0.39954
23	6	-2.46902	2.629813	-0.168691
24	1	-3.4893	2.979699	-0.061601
25	6	2.857017	-0.78314	1.678786
26	6	-5.20723	0.225881	0.765359
27	1	-4.95258	-0.76658	1.161426
28	1	-4.77303	0.959281	1.458475
29	6	3.705218	-1.90923	1.538591
30	1	4.680938	-1.90257	2.00699
31	6	2.581912	2.403811	-1.028535
32	6	0.159671	-4.28517	-0.769773
33	1	-0.25948	-5.21857	-1.13508
34	6	3.089266	0.025448	-2.44149
35	1	3.271749	-0.87301	-3.022237
36	6	1.003411	4.011248	-0.131693
37	1	0.760474	5.008341	0.224102
38	6	-1.40185	3.486871	-0.009065
39	1	-1.57213	4.526518	0.253037
40	6	3.255487	-3.0089	0.837779
41	1	3.874136	-3.89836	0.762864
42	6	-4.5563	0.396701	-0.620191
43	1	-4.96735	-0.336	-1.323758

44	1	-4.79025	1.385281	-1.030369
45	6	2.286376	3.683543	-0.455289
46	1	3.091286	4.403866	-0.345182
47	6	-7.39751	0.225054	2.09507
48	1	-7.19632	-0.77031	2.509771
49	1	-8.48444	0.348819	2.032491
50	1	-7.01585	0.965965	2.808192
51	6	-6.73675	0.393199	0.717582
52	1	-7.16203	-0.33931	0.01531
53	1	-6.98257	1.385994	0.312042
54	6	3.873547	2.124607	-1.543013
55	1	4.654103	2.869149	-1.413145
56	6	4.132631	0.951046	-2.229603
57	1	5.123651	0.755031	-2.626588
58	6	3.250038	0.385631	2.482097
59	8	2.559804	1.393547	2.694456
60	8	4.522899	0.273137	3.021972
61	1	4.722291	1.080858	3.541132

3.2.11 References

1. Flammang-Barbieux, M. N. J. M. R. Synthesis of heptahelicene (1) benzo [c] phenanthro [4, 3-g]phenanthrene. *Tetrahedron letters* **8**, 743–744 (1967).

2. Harrowven, D. C., Guy, I. L. & Nanson, L. Efficient Phenanthrene, Helicene, and Azahelicene Syntheses. *Angewandte Chemie* **118**, 2300–2303 (2006).

3. Guédouar, H., Aloui, F., Moussa, S., Marrot, J. & ben Hassine, B. Synthesis and characterization of new heptacyclic helicenes. *Tetrahedron Letters* **55**, 6167–6170 (2014).

4. Gingras, M. & Collet, C. Functionalized heptahelicene bidentate ligands and chiral building blocks. *Synlett* 2337–2341 (2005).

5. Garcia, M. H., Florindo, P., Piedade, M. de F. M., Maiorana, S. & Licandro, E. New organometallic Ru(II) and Fe(II) complexes with tetrathia-[7]-helicene derivative ligands. *Polyhedron* **28**, 621–629 (2009).

6. El Abed, R., Aloui, F., Genêt, J. P., ben Hassine, B. & Marinetti, A. Synthesis and resolution of 2-(diphenylphosphino)heptahelicene. *Journal of Organometallic Chemistry* **692**, 1156–1160 (2007).

7. Tanaka, K., Kimura, Y. & Murayama, K. Enantioselective Helicene Synthesis by Rhodium-Catalyzed [2+2+2] Cycloadditions. *Bulletin of the Chemical Society of Japan* **88**, (2015).

8. Murayama, K. *et al.* Enantioselective Synthesis, Crystal Structure, and Photophysical Properties of a 1,1′-Bitriphenylene-Based Sila[7]helicene. *European Journal of Organic Chemistry* **2015**, (2015).

9. Carreño, M. C., Hernández-Sánchez, R., Mahugo, J. & Urbano, A. Enantioselective Approach to Both Enantiomers of Helical Bisquinones. *The Journal of Organic Chemistry* **64**, 1387-1390 (1999).

10. Dreher, S. D.; Weix, D. J.; Katz, T. J. Easy synthesis of functionalized hetero[7]helicenes *Journal of Organic Chemistry***, 64***,* 3671-3678 (1999).

11. Shi, L.; Liu, Z.; Dong, G.; Duan, L.; Qui, Y.; Jia, J.; Guo, W.; Zhao, D.; Cui, D.; Tao, X. Synthesis, structure, properties, and application of a carbazole based…OLED. *Chemistry European Journal* **18**, 8092 (2012).

12. Moorthy, J. N., Mandal, S., Mikhopadhyay, A., Samanta, S. Helicity as a steric force: Stabilization and Helicity-dependant reversion….chromenes *Journal of. American Chemical Society.* **135**, 6872-6884 (2013)

13. Jhulki, S., Mishra, A. K., Chow, T. J., Moorthy, J. N. Helicenes as all in one organic materials for application… diamines *Chemistry European Journal,* **22**, 9375-9386 (2016).

14. Tounsi, M.; Braiek, M. B.; Barhoumi, H.; Baraket, A.; Lee, M.; Zine, N.; Maaref, A.; Errachid, A. A novel EIS field effect structures coated with…detection. *Materials Science and Engineering C*, **61**, 608-615 (2016).

15. Upadhyay, G. M., Talele, H. R., Sahoo, S. & Bedekar, A. V. Synthesis of carbazole derived aza[7]helicenes. *Tetrahedron Letters* **55**, 5394–5399 (2014).

16. Upadhyay, G. M., Talele, H. R. & Bedekar, A. V. Synthesis and Photophysical Properties of Aza[*n*]helicenes. *The Journal of Organic Chemistry* **81**, 7751-7759 (2016).

12. Liu, L., Yang, B., Katz, T. J. & Poindexter, M. K. Improved Methodology for Photocyclization Reactions *The Journal of Organic Chemistry* **56,** 3769-3775 (1991).

13. Laarhoven, W. H. & Brus, G. J. M. Polarographic data and deviations from coplanarity of helicene molecules. *Journal of the Chemical Society B: Physical Organic* 1433–1434 (1971).