Synopsis of thesis entitled

"Synthesis and Study of Carbazole Derived Helicenes"

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in

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By

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Title of thesis	**: Synthesis and Study of Carbazole Derived Helicenes.**
Place of work	**: Department of Chemistry, Faculty of Science, The Maharaja Sayajirao university of Baroda, Vadodara. Gujarat**

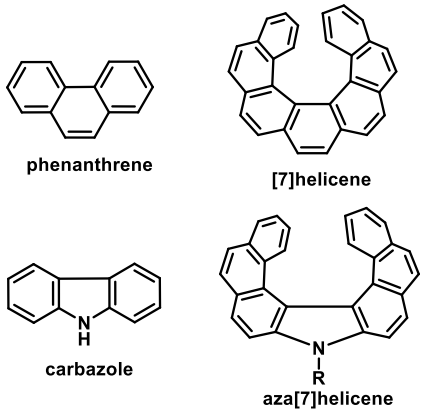
Chapter 1. Introduction

Helical molecules: Molecules possessing *ortho*-fused aromatic rings, acquire a unique shape in order to release the internal strain. This type of molecular arrangement acquire helical structure and shows stereoisomerism. The helical molecules have attracted much attention in recent years due to some unique properties associated with its structure.[1] The efficient delocalization of π-electrons and non-planarity of the structure in the helicenes enable them to be stable to strong acids and high temperature. The applications of helical molecules cover a wide range in the fields of material science,[2] asymmetric synthesis and catalysis,[3] as molecular motor,[4] in biology[5] etc. A number of approaches have been developed for the synthesis of these screw shape molecules. Their synthesis is challenging due to the efforts required to overcome the inherent steric factors or internalsteric crowding. Therefore, the synthesis of new helical molecules remains an exciting task and a rewarding endeavor.

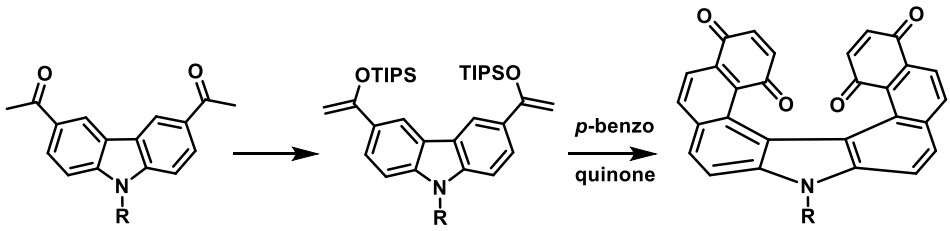
Aza helicenes: The carbahelicenes, [*n*]helicenes, are perhaps the most studied systems. The aza helicenes belong to the subgroup of heterohelicenes. In recent years, the synthesis of heterohelicenes has been studied extensively; however studies of Azahelicenes have received less attention compared to thiahelicenes and oxahelicenes.The properties and chemical behavior of nitrogen containing helicenes are practically unknown apart from their basicity and few other studies.[6] Nitrogen containing helicenes can form complexes with transition metal, can assist in formation of large supramolecular complexes and they are basic enough to act as enantioselective catalyst. The possible promising applications of nitrogen containing helicenes in various branches of chemistry and material science might be investigated and therefore there is scope for further research in this field.

Carbazole derived aza[n]helicenes: Most of the reported aza-helicenes are derivatives of pyridine and pyrrole,[7] we chooses carbazole for the synthesis of aza[*n*] helicenes because:

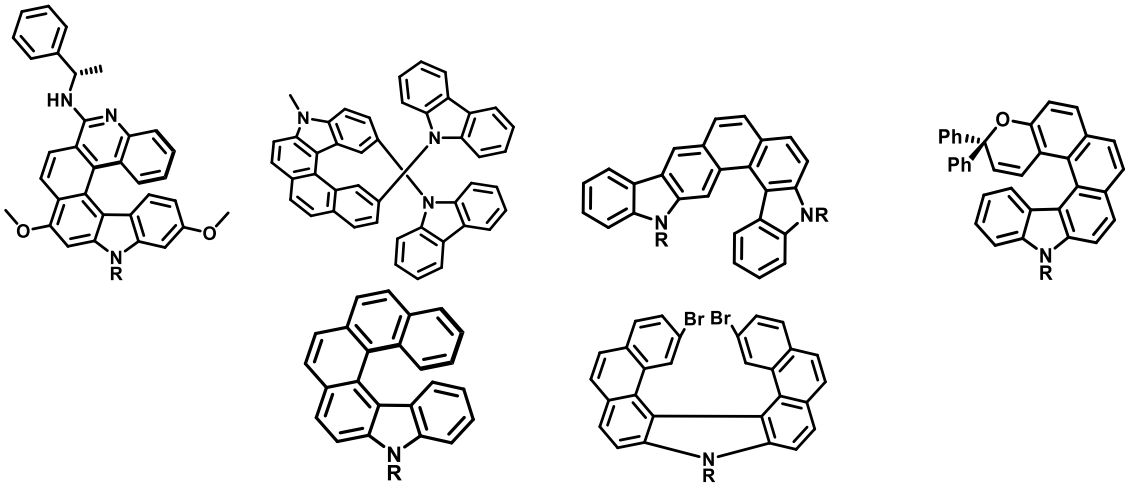
1. It has three in built rings
2. Cheap building block.
3. Easy and regioselective functionalization is possible.
4. Access to gram scale starting material.



Katz et al synthesized the first carbazole derived helicene. He used Diels Alder strategy for synthesizing Aza[7]helicene bisquinones by employing 3,6-diacetylcarbazole with *p*-benzoquinone as the diene and dienophile, respectively.[8]



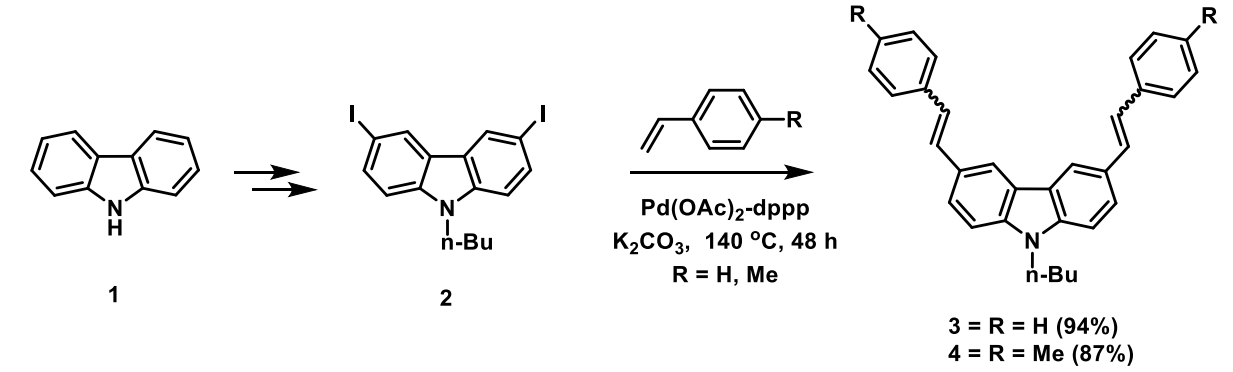
The carbazole group is a popular functional unit in conjugated systems owing to its planarity and N-H bond, which can be easily substituted for other functional groups. The good emission nature and DFT studies suggest carbazole based helical molecules to be ideal candidate for OLED devises.[9] Majority of cases the conventional photocyclization strategy was the choice for making helical molecules. Following are some examples of carbazole based helical molecules reported in the literature.



Chapter 2. Synthesis and Study of Mono Aza[*n*]helicenes.

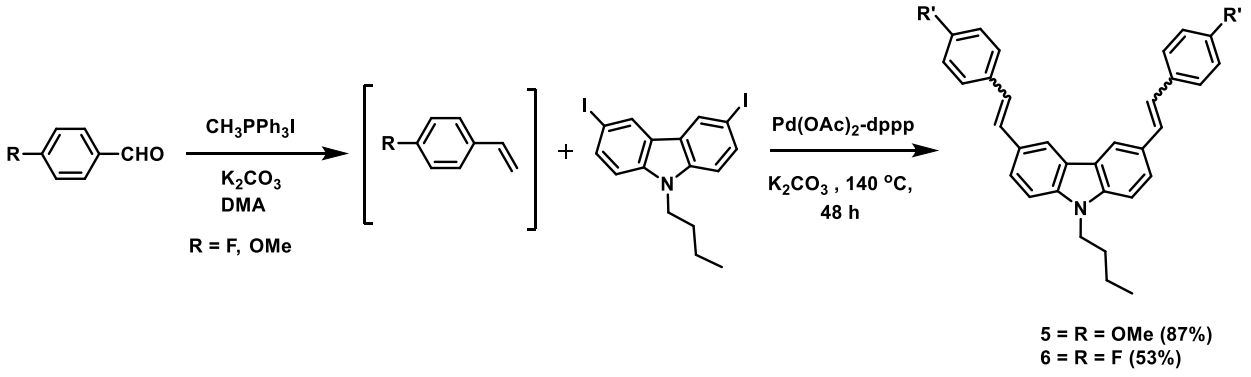
Part 1. Non Functionalized aza[n]helicenes (aza[7]helicene)

In this part we present the synthesis of a series of symmetrical aza[7]helicenes. The required starting material 3,6-diiodo-9-butyl-9*H*-carbazole **2** was prepared from carbazole **1** by known procedures.[10] To increase the solubility of resultant aza[7]helicene the n-Bu group was selected. It was then subjected to double Mizoroki–Heck reaction in the presence of palladium catalyst, dppp, K_2CO_3, and corresponding styrenes in order to obtain corresponding (E,E)-3,6-distyryl-9-butyl-9*H*-carbazole **3** and **4** in excellent yields.



Scheme 1. Synthesis of (E,E) 3,6-distyryl-9-butyl-9H-carbazoles by Mizoroki–Heck reaction.

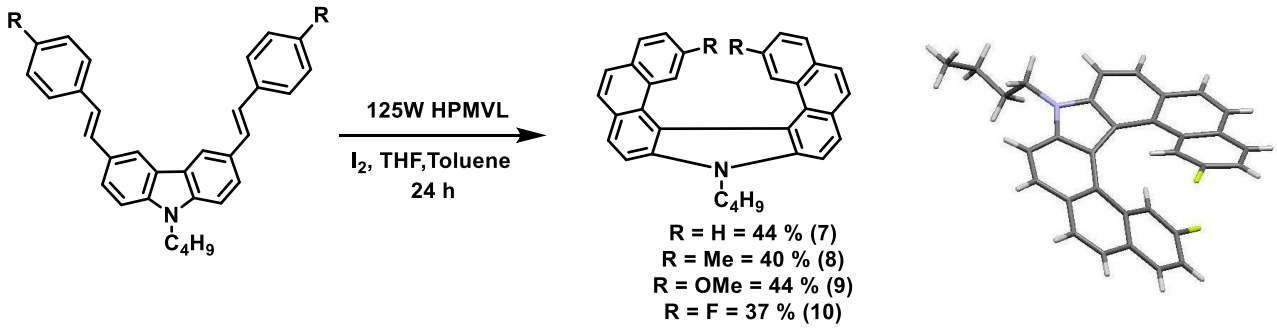
However, this option has the limitation of the availability of the required styrene derivative for the Mizoroki–Heck reaction. Some substituted styrenes are not readily available or are unstable; hence to overcome this problem we have used a protocol of making them *in situ* for a one-pot reaction.[11]



Scheme 2. Synthesis of (E,E) 3,6-distyryl-9-butyl-9H-carbazoles by one-pot Wittig–Heck reaction.

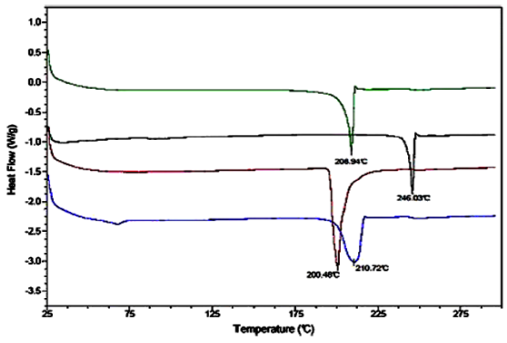
In this process an aldehyde with required substituent was subjected to the Wittig reaction with a one carbon phosphonium salt (Ph_3PCH_3I)to generate the desired styrene derivative, which was further subjected to Mizoroki–Heck condition in the same flask to give the stilbene derivative.

This process was also applied for the synthesis of two more derivatives of the present distyryl carbazoles. In the present work two derivatives from 4-methoxy benzaldehyde and 4-fluoro benzaldehyde are utilized to prepare 4-methoxy styrene and 4-fluoro styrene, respectively, which were *in situ* subjected to one-pot Mizoroki–Heck reaction with **2**. The styryl derivative of carbazole were then subjected to standard photocyclization conditions[12]to get the angularly cyclized aza[7]helicenes.



Scheme 3. Photocyclization of distyrylcarbazoles.

Studies of aza[7]helicenes: Thermal behavior of aza[7]helicenes (**7** to **10**) was investigated by means of differential scanning calorimetry (DSC) where the sample was heated at the rate of 10 ^{o}C/min from 25 to 300 ^{o}C, under the inertatmosphere of nitrogen (Fig. 1). The analysis indicated the melting point of compounds to be in the range of 200–246 ^{o}C. The glass transition temperatures (Tg) of aza[7]helicenes lie in 147–197 ^{o}C, which point toward high thermal stability of the helicalsystem.



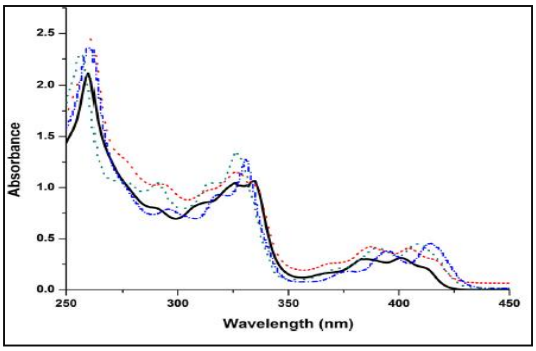
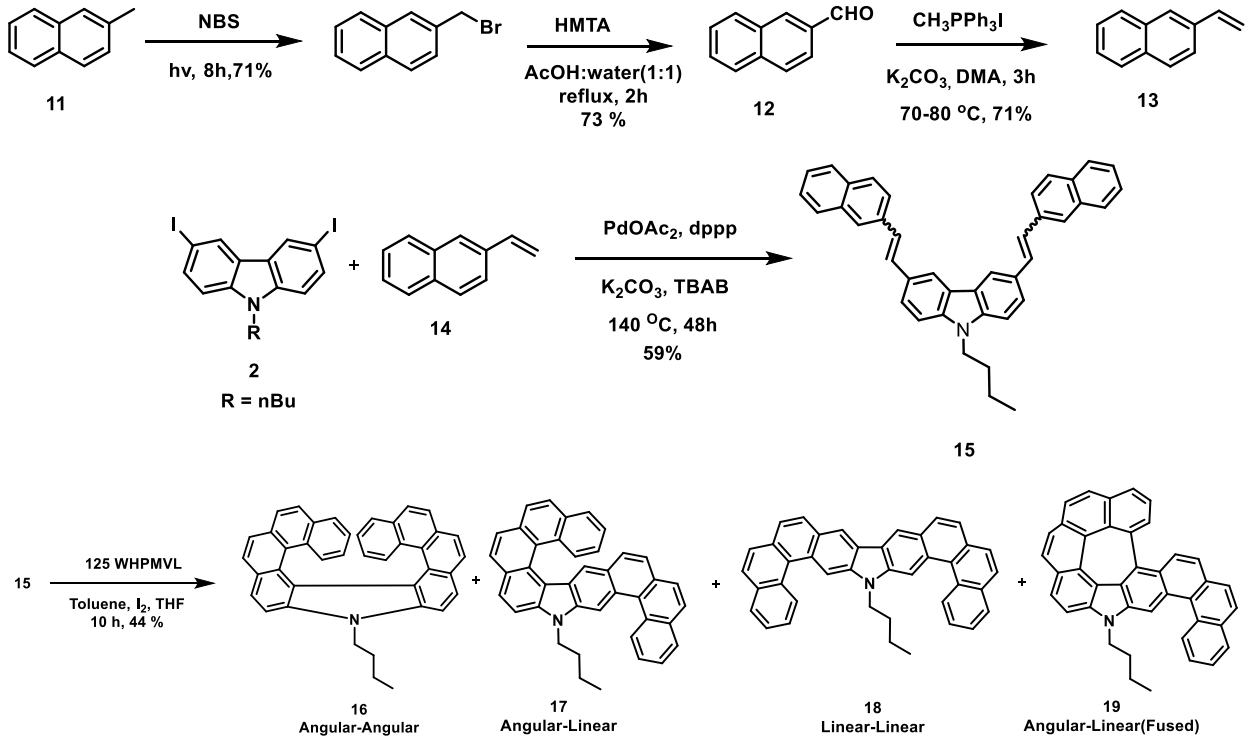


Figure1: DSC Thermograms of aza[7]helicenes Figure**2** : Absorption spectra of aza[7]helicenes

The aza[7]helicene derivatives were investigated using UV–vis absorption study, performed in methanolic solution (5.0 X10^{-5}mol). Spectra of these compounds exhibited a strong absorptionin the region of 257–414 nm.

Chapter 2 (Part 1 Synthesis and study of aza[9]helicene): After the successful synthesis of series of aza[7]helicenes, we attempted the synthesis of larger aza[9]helicene. The synthetic methodology was very much similar to that of aza[7]helicene, the 3,6-diiodo-*N*-butylcarbazole **2** was converted to bis-olefin **15** by its Mizoroki−Heck reaction with vinyl naphthalene **14**. A solution of **15** in toluene was subjected to photochemical reaction (125W HPMV lamp) in a standard immersion well reactor.



Scheme 4. Synthesis of Aza[9]helicene.

The initial analysis of the reaction mixture indicated the formation of a complex mixture of the products, contrary to the earlier observation during the synthesis of aza[7]helicene. This is probably due to the different modes of cyclization of the intermediate species in the stilbenoid derivative. We separated all the four regiomers carefully by column chromatography and repeated crystallizations. The structures confirmed by ^{1}H NMR, ^{13}C NMR and X-ray analysis.

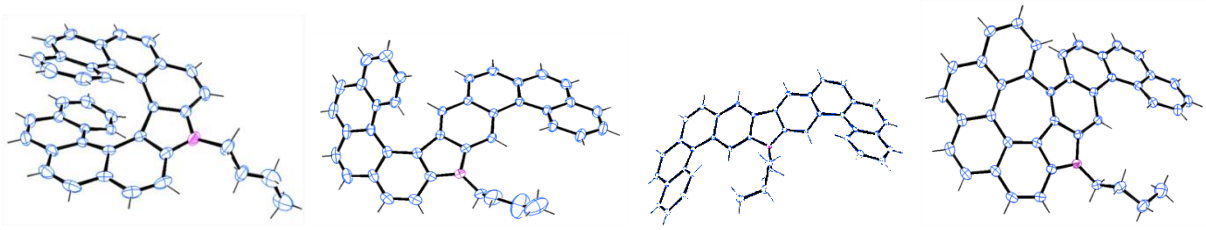


Figure 3. ORTEP Plots of regiomers.

Effect of Concentration on Product Distribution: In the exploratory stage of our current investigation, the ^{1}HNMR analysis of the crude reaction mixture indicated that the distribution of four observed products was concentration dependent, prompting us to investigate this further. The ratios of characteristics ^{1}H NMR signals were used for measuring the yields of respected regiomers. It was established from the above study that the desired angular-angular isomer **16**formed predominantly at higher dilution (lower concentration) while the other regiomer formed at higher concentration. The observed ratio can be attributed to the population of excited state intermediates, their stabilities, and their relative rates for the electrocyclization reactions.

Studies of photo physical properties: The absorption and emission spectra of all of the compounds were recorded in dilute solutions of dichloromethane at room temperature. The emission spectra of compounds show bathochromic shifts from moving to the helical structure to the linear structure. The fluorescence quantum yields of four isomers were recorded in dilute dichloromethane solution (10^{-6} M) at room temperature; data are summarized. The Φ (Fluorescence quantum yield) of all regiomers were found to below to moderate (0.07−0.21). Fluorescence quantum yields were determined using a solution of quinine sulfate in H_2SO_4 (0.5 M) as a reference standard (ΦFL = 0.546).

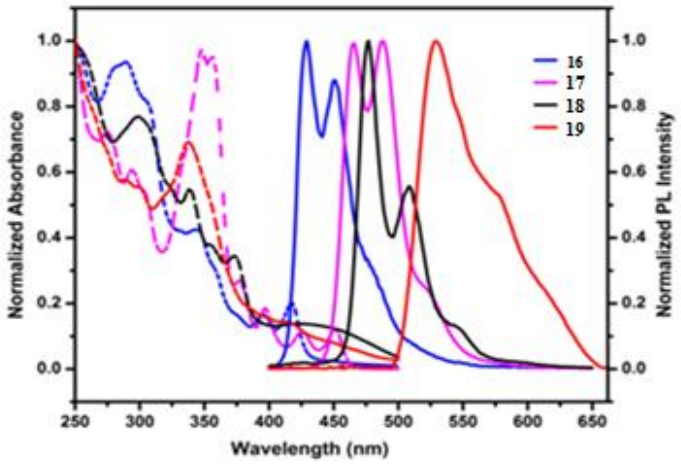
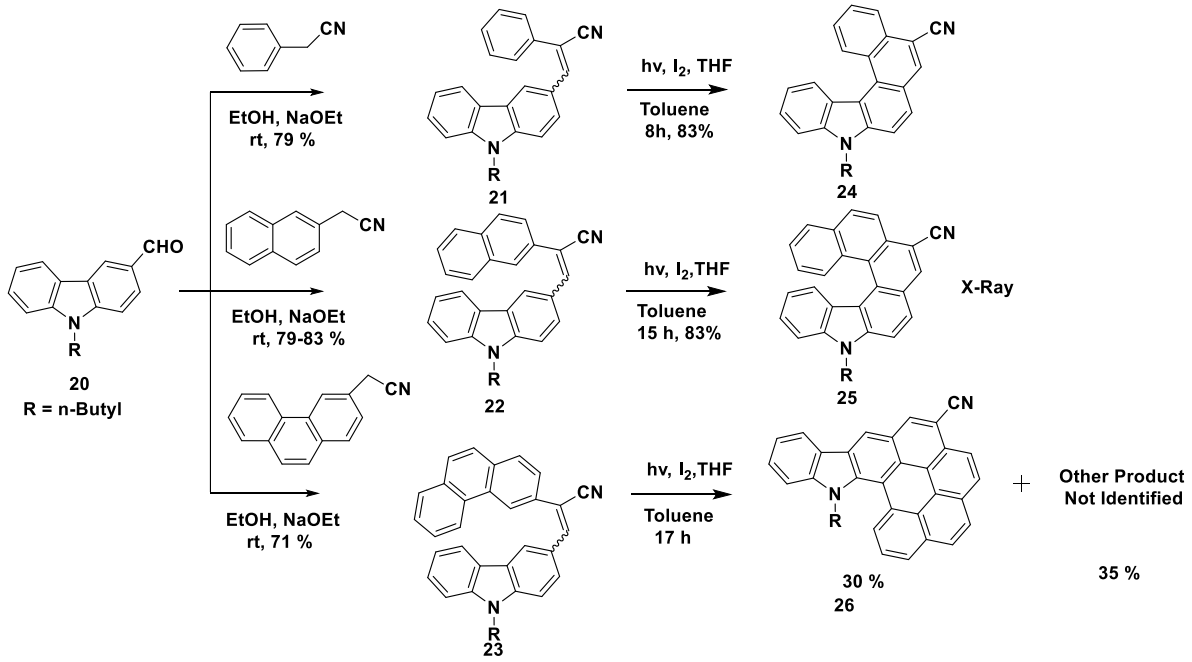


Figure 4. Absorption and emission spectra of regiomers

Chapter 2. Part 2.Synthesis and Study of Functionalized Aza[*n*]helicenes.

In the second part of the work we have synthesized cyano derivatives of aza helicenes. We have chosen to incorporate cyano group in helical framework due to its versatility and ease in conversion to many other functional groups.

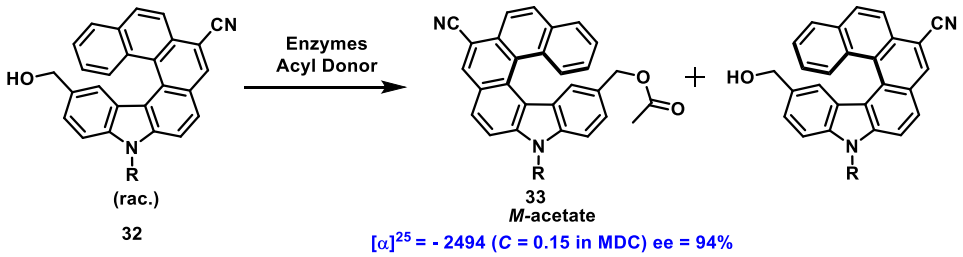
The 3-formyl *N*-butyl carbazole **20** was prepared from *N*-butyl carbazole by Vilsmeier-Haack reaction using phosphorous oxychloride and dimethyl formamide in excellent yield. The aldehyde was then treated with respective cyano derivatives and sodium ethoxide to effortlessly furnish required cyanostilbenes **21**, **22** and **23**respectively. Their photocyclization under the standard condition gave the desired angular products **24**, **25** and **26** respectively. Their structures were confirmed by ^{1}H-NMR analysis and X-ray analysis (compound **25**). We attempted to resolve these compounds on chiral HPLC column; [5]helicene **24** shows a single peak suggesting low barrier of racemisation while [6]helicene **25** show two well separated suggesting rigidity in helical framework and possibility for the separation of two isomers.



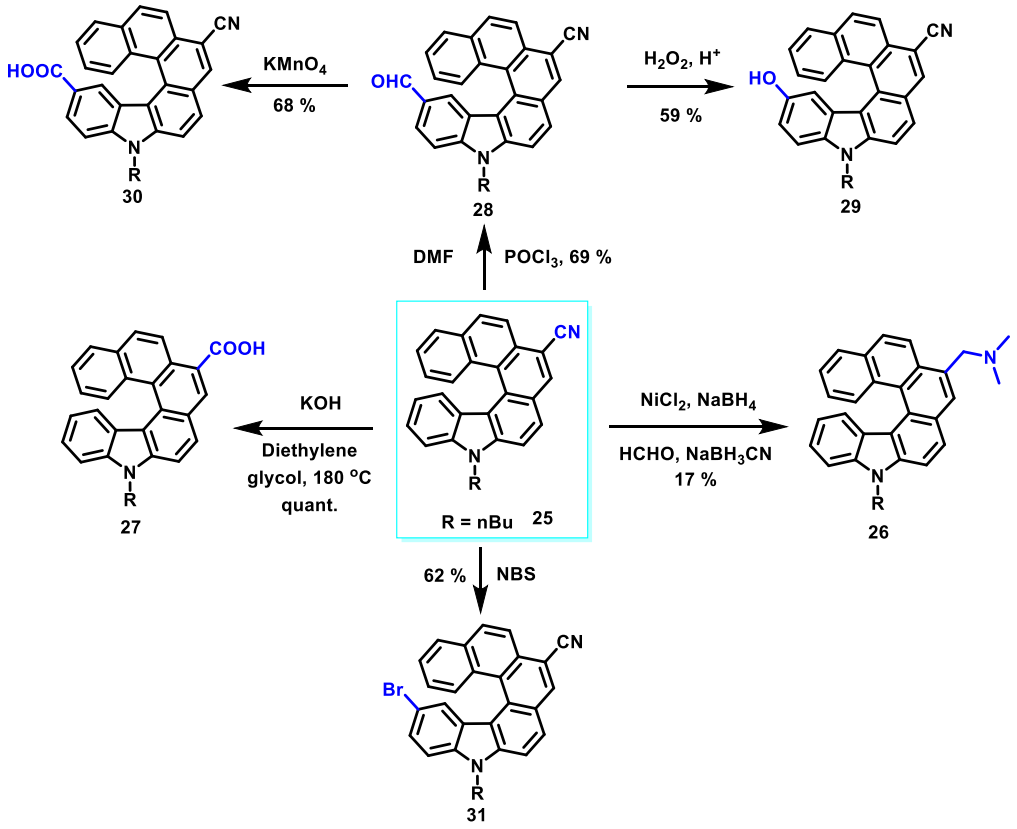
Scheme 5. Synthesis of Functionalized Aza[*n*] helicenes.

Post Functionalization and functional group manipulations: We successfully converted the cyano helicenes in to *N*, *N*, Dimethyl derivative **26** using nickel chloride and sodium borohydride as reducing agent followed by reductive amination using formaldehyde solution. Cyano group was also hydrolyzed in alkaline conditions to its carboxylic acid derivative **27**. The electrophilic aromatic substitution reactions such as halogenations, nitration and formylation have been easily performed on cyano aza[6]helicene. The formyl derivative of aza[6]helicene **28** was reduced to its alcohol derivative **32**, the aldehyde derivative was also successfully oxidized to its hydroxyl **29** and acid derivatives. Resolution of some of the compounds is currently under progress.

The compound **32** was subjected to enzymatic resolution, using different enzymes (Novozyme, Lipase and Amano PS) and acyl donors (isopropenylacetate and vinyl acetate). The best condition was found to be the combination of Novozyme and vinyl acetate as acyl donor. By the enzymatic resolution and single crystallization enantiopure acetate up to 94 % ee was obtained.

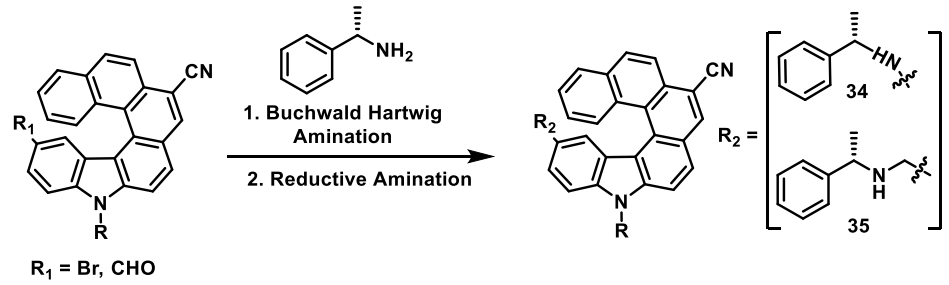


Scheme 6. Enzymatic resolution of compound **32**



Scheme 7. Post Functionalization and Functional group manipulations of compound25.

Ligand Synthesis: We have synthesized helical based ligands **34** and **35;** we are currently trying to resolve them. We will try to test these amines as agents to study applications as chiral bases, in molecular recognition or study their binding properties with certain biological materials.



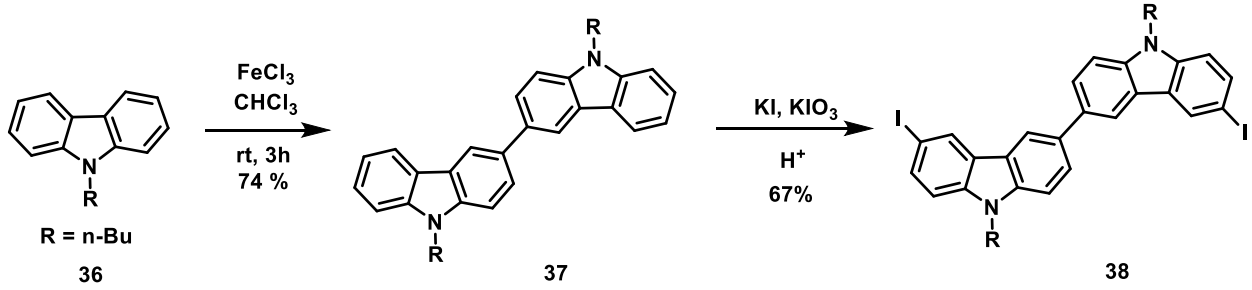
Scheme 8. Synthesis of Ligands.

Chapter 3. Synthesis and Study of Bis Aza[*n*]helicenes

Bis-helicene molecules involve two distinct helicene moieties connected by a single bond.Bis helicene possesses helical as well as axial chirality. Bis-helicenes are very effective ligands for asymmetric synthesis.[13]

Chapter 3 Part 1 Synthesis and Study of Bi-helicenes.

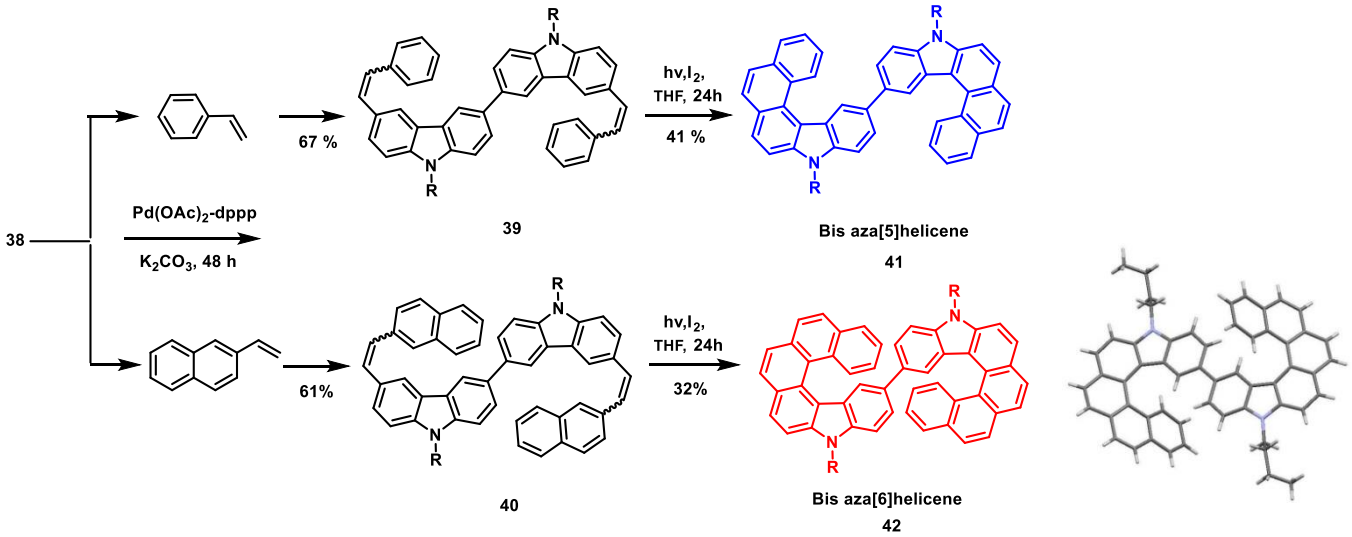
The synthesis of aza[*n*]helicene unit can be achieved by oxidative photocyclization of suitable styryl derivative of alkyl carbazole moiety. Accordingly *N*-butyl carbazole**36**, prepared by alkylation of carbazole **1**, was subjected to the dimerization reaction with ferric chloride to obtain **37** in good yield. The bi-carbazole **37** was subjected to slightly modified conditions of regioselective di iodination to afford the required precursor **38** in satisfactory yield and purity.



Scheme 9. Synthesis of 3-iodo-6-(3-iodo-9-butyl-9H-carbazol-6-yl)-9-butyl-9Hcarbazole.

The diiodocarbazole **38** was subjected to palladium catalyzed Mizoroki Heck reaction with styrene and 2-vinylnaphthalene under the suitable conditions. Corresponding bis-styryl derivative **39** and **40** were obtained with styrene and 2-vinylnaphthalene in good yields mostly as the *E*-isomers, and then they were subjected to standard photocyclization conditions. The product of the expected angular cyclization was isolated to moderate yields from the complex reaction mixture. The styryl derivative of bi-carbazole **5** furnished the angular-angular bi-aza[5]helicene **41**, while the vinyl naphthyl derivative **6** furnished similarly cyclized bi-aza[6]helicene **42**. Both

the title compounds were purified by careful column chromatography over silica gel and the structure of the products were established by usual spectral analysis. The structure of the title compound bi-aza[6]helicene **42** was further established by its single crystal X-ray diffraction analysis.



Scheme 10. Synthesis of bisaza[5]helicene and bis aza[6]helicene.

Photo-physical properties: The UV-vis spectra of bi-aza[5]helicene **41** and bi-aza[6]helicene **42**, in dichloromethane exhibit absorption bands in the range of 262 to 337 nm. The compounds showed blue emission in the range of 437 to 458 nm. The compound **42** showed small red shift (21 nm) compared to **7**, probably due to increase in π-conjugation. Optical measurements of compound **42** were measured in different solvents. There is no significant Solvatochromism observed.

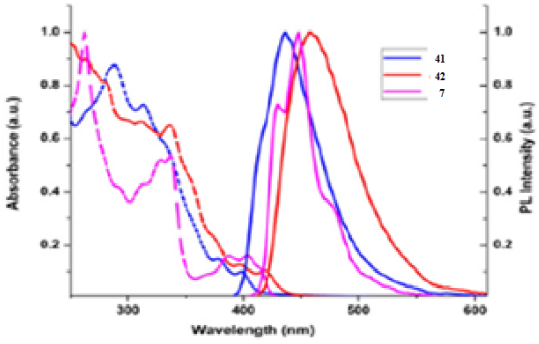


Figure 5. Absorption and emission spectra

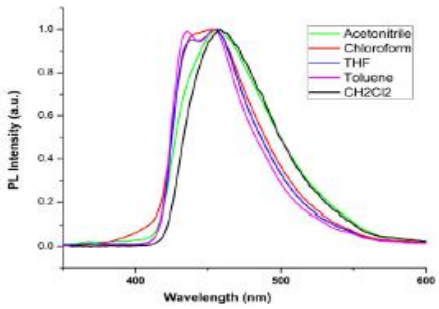
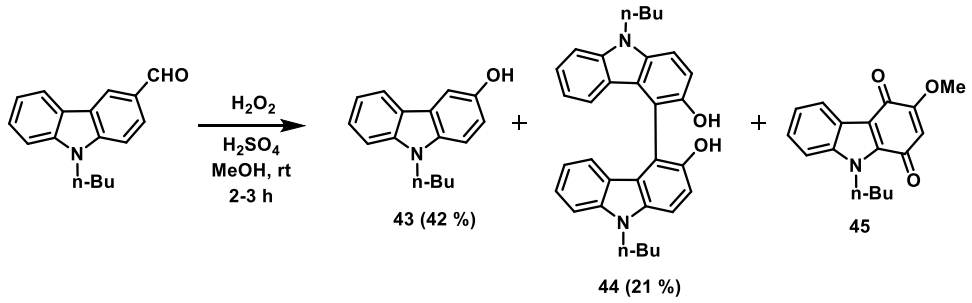


Figure 6. Solvatochromism study of compound **42**

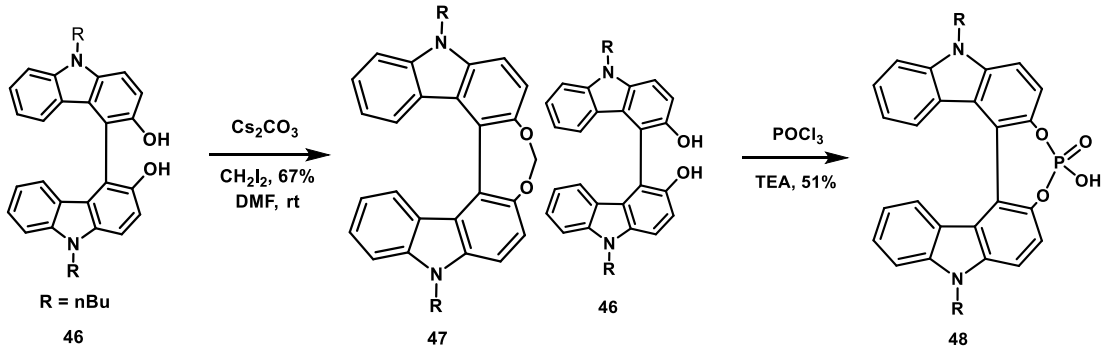
Chapter 3 Part 2 Synthesis and Study of Bis-carbazole helicenes.

Carbazole-based molecules have captured considerable interest as catalysts, bioactive compounds, sensors and electron conductors. However, just a few helicenes containing the bis(carbazole) moiety are known.[14] In this chapter we shall present our finding during the attempted synthesis of bis carbazole derivative. Synthetic scheme comprises the acid catalyzed Dakin condensation of 3 formyl *N*- butyl carbazole using hydrogen peroxide as an oxidant to obtain the 3-hydroxyl *N*-butyl carbazole **43**, in the course of this transformation with the desired compound **43** we also got one unexpected polar product which was characterized to be **44**. Optimization to understand its formation and to improve the yield of **44** is currently under progress.



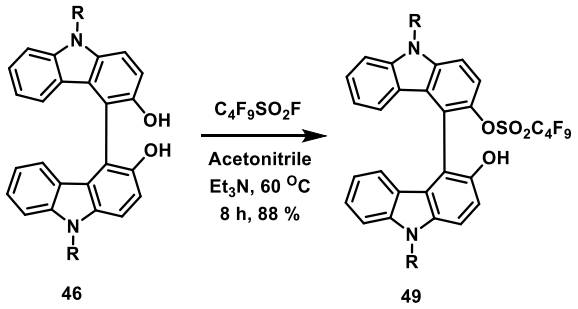
Scheme 11. Synthesis of BICOL (**44**)

Initially we synthesized some helicene like compounds and successfully inserted methylene bridge **47** and phosphorous **48** in the helical frame work.

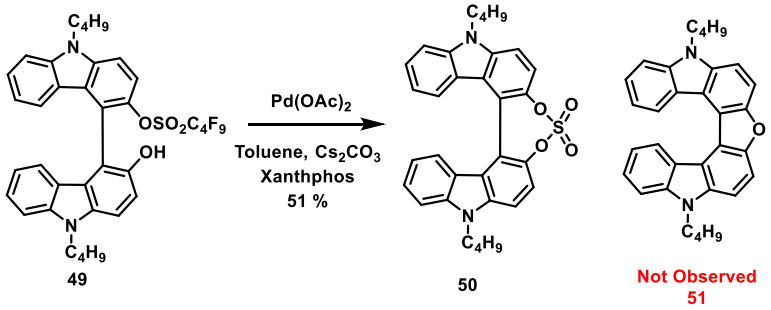


Scheme 12. Synthesis of Bis carbazole based helicene-like molecules.

We also attempted to insert furan ring between two carbazole molecules using Buchwald Hartwig (C-O bond forming) conditions but instead of getting the desired product **51** we obtained a substitution product **50**.



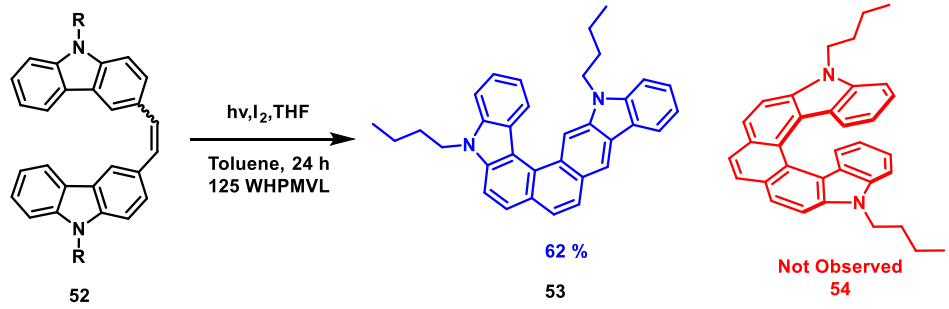
Scheme 13. Synthesis of the precursor of Buchwald Hartwig reaction.



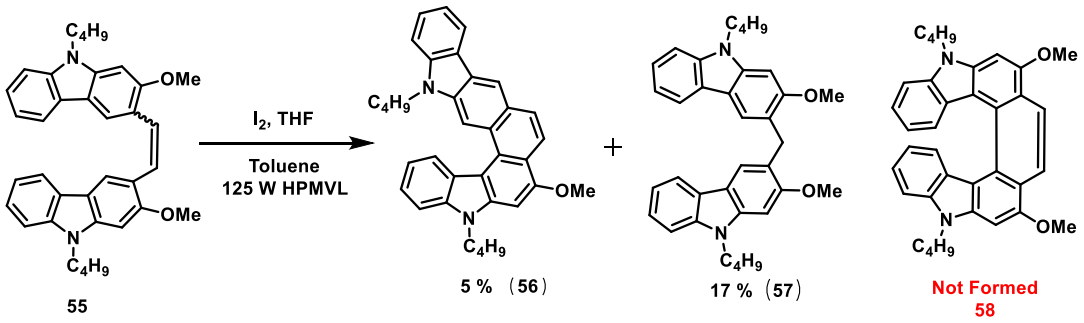
Scheme 14. Buchwald Hartwig reaction of compound **49.**

We are also trying to incorporate pyrrole ring between two carbazole moieties. Attempts were also made to incorporate a benzene ring between two carbazole moieties. Photocyclization was the strategy for the choice. Various approaches are listed below.

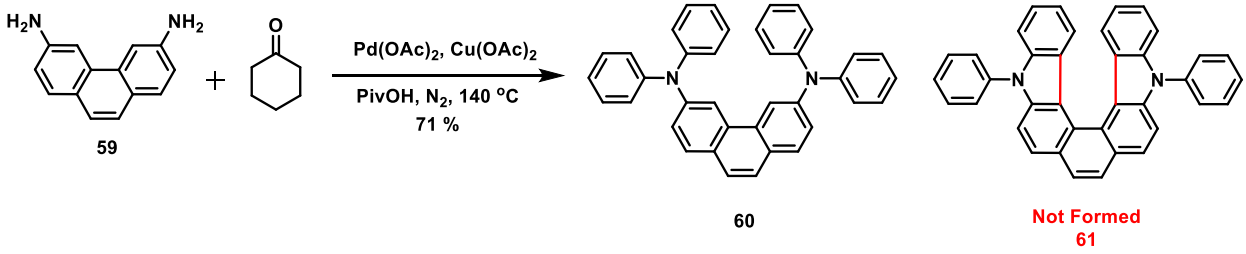
Approach 1



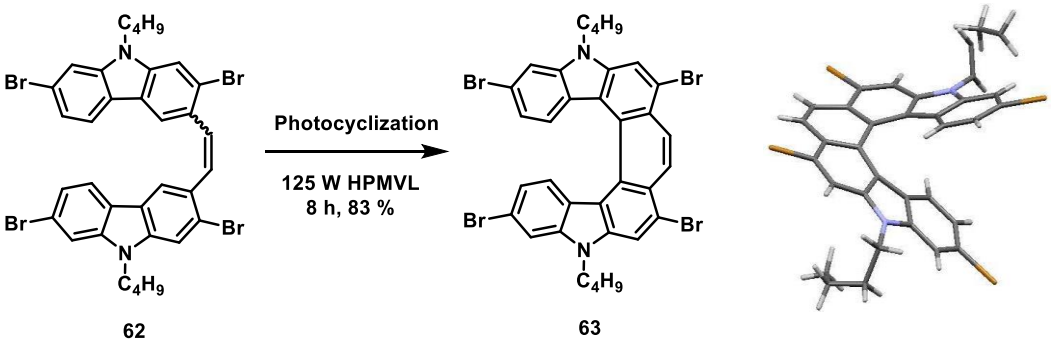
Approach 2



Approach 3



Approach 4 (Successful One !)



Scheme 15. Various approaches for the synthesis of Bis aza[7]helicene.

We shall study the photophysical properties of these bis-carbazole based helicene-like and helical molecules.

Chapter 4. Spontaneous Resolution of Dicyano aza[7]helicenes

The segregation of enantiomers upon crystallization in the absence of external chiral environment is known as *spontaneous resolution.* This is based on a preference of molecules to make contacts with neighbors of the same chirality sense through supramolecular interactions.[15]

Types of packing in chiral molecules:

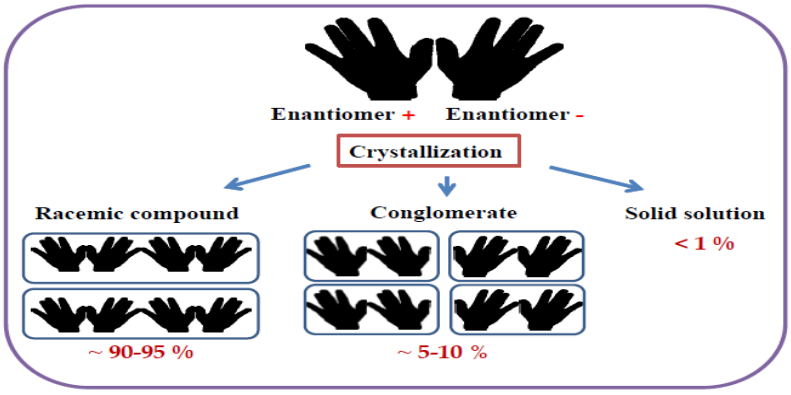
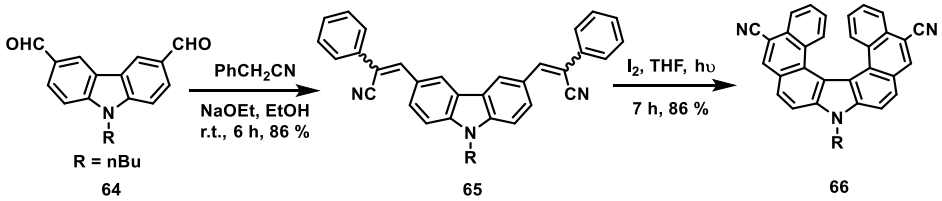


Figure 7. Crystal packing in chiral compounds.

Only the second category, the conglomerate, implies spontaneous resolution.

Synthesis of 5, 13-dicyano-9-butyl-9*H*-aza[7]helicene: Synthesis of 5,13-dicyano-9-butyl-9*H*-aza[7]helicene **66** was achieved from 2,9-diformyl carbazole **64**, via its bis-styryl type derivative **65** prepared by Knovenagel condensation with benzyl cyanide. Conversion of **65** to the target aza[7]helicene was easily done by photodehydrocyclization procedure involving a double, regioselective angular-angular cyclization to afford the compound **66** in good overall yield.



Scheme 16. Synthesis of Dicyano aza[7]helicene.

Investigation for Spontaneous resolution: The initial attempts to enrich the helical enantiomers of **66** by crystallization in dichloromethane, chloroform, toluene, hexane-chloroform, THF etc. resulted in to isolation of only racemic crystals.The plate like single crystals of (±)-**66** were obtained from dichloromethane. At the same time, crystallization from dichloroethane produced a mixture of slightly dark, yellow colored uniformly diamond shape transparent diffraction-quality crystals, along with some twined crystals .

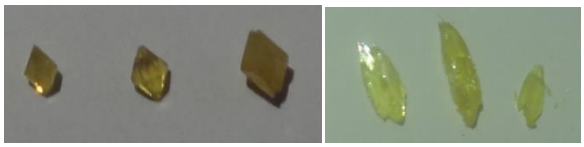


Figure 8 Optically pure diamond shaped (left) and racemic plate shaped (right) crystals of **66**

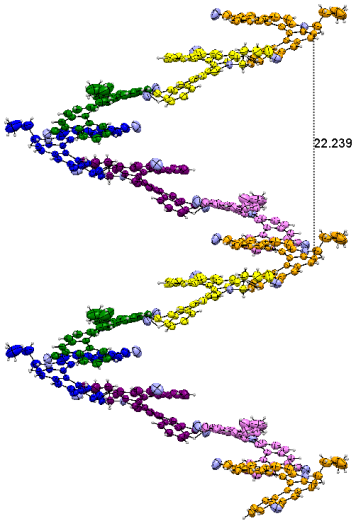
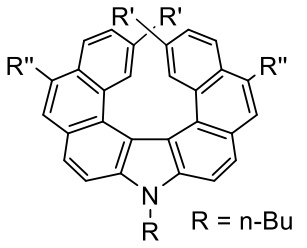
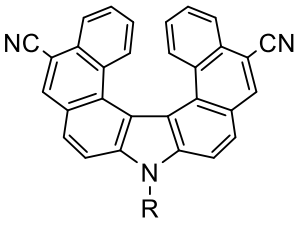


Figure 9 Side view of *P*-Super helix arrangement of the conglomerate of (*P*)-**66**. The six molecules forming one turn are given different colors.

The single crystal X-ray analysis of randomly picked diamond shaped crystal showed interesting molecular packing. Sample of (*P*)-**66** and (*M*)-**66** molecule crystallized into hexagonal crystal system with homochiral single-handed, enantiomerically-pure helicenes through self- assembly having chiral space group $P6_1$ and $P6_5$ respectively. A 6_1 axis corresponds to a right-handed helix; whereas 6_5 correspond to a left-handed helix (the two helices being enantiomorphous). Literature survey shows that, such helicene structure with a perfect hexagonal symmetry has been rarely reported.[16] Spontaneous resolution gives (*P*)-**66** and (*M*)-**66** crystals by their conglomerate formation. It could be the result of the chiral recognition during crystallization in which the helicene molecule favored the helicenes with same configuration.



67, R' = CN, R''= H
68, R' = OMe, R'' = CN
69, R' = R'' = CN



70, R = $CH_2CH_2CH_2Ph$

To establish the role of side chain of pyrrole moiety, the location of cyano group and to study the effect of other substituents on the mode of molecular recognition and spontaneous resolution, we have designed a set of derivatives **67** to **70**. Objective was to introduce functional groups which may enhance the intramolecular CH-π interactions, dipolar interactions such as the presence of additional cyano group in **69**, methoxy group in **68** and phenyl group in the side chain in **70**. These all cyano derivatives crystallizes in achiral space groups (racemic in nature), the study of their interactions reveals that this is due to stronger interactions with the opposite isomer.

We have found that the success of spontaneous resolution is very much dependent on the ability of molecules to form right kind of contacts with its neighbor with the same chirality. Any factor that alters its ability either by weakening the interactions (may be the absence of strong dipolar groups) to identify its partner (similar isomer) or by making stronger interactions with the opposite isomer decreases the recognition ability of molecule.

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