An executive summary of Ph.D. thesis

on

Synthesis and Study of Carbazole Derived Helicenes

Submitted to

The Maharaja Sayajirao University of Baroda

For the degree of

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

Submitted by

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February 2020

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Aim of the thesis: The aza helicenes belongs 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. 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 so we took up this challenge to synthesize aza helicenes and study their properties.

The focus of the work reported in this thesis is to synthesize carbazole derived new aza helicenes and to study their properties in both racemic and chirally pure forms. Largely the thesis (**Chapter 2 and Chapter 3**) is organized on the basis of number of nitrogen atoms present in the helical backbone. **Chapter 2** deals with the synthesis and study of mono-aza helicenes while **Chapter 3** deals with bis-aza helicenes. We also presents our efforts towards the study of spontaneous resolution of cyano aza[7]helicenes. The contents of the thesis are divided in 4 chapters.

Chapter 2 is subdivided in two parts **Part-I** deals with the synthesis and study of carbazole derived symmetrical aza[7]helicenes and their larger analogue; aza[9]helicene. Photocyclization was chosen as the method for preparation. A striking difference was observed in the photocyclization towards aza[7]helicene and aza[9]helicene; sterically less demanding aza[7]helicene resulted in smooth reaction giving only the desired angular-angular cyclization product. While, in the case of aza[9]helicene, along with the expected angular-angular cyclization, three other products involving linear mode of cyclization were isolated and fully characterized by ^{1}H-NMR and single crystal analysis. Another important observation was, the helical compound aza[9]helicene was predominantly formed at lower concentration (of precursor olefin) while the other isomers were obtained when the photocyclization was performed at higher concentration. The photo physical properties of all the products were studied. **Part-II** of Chapter 2 deals with the functionalization of aza helicenes. Here we synthesized various cyano group containing [5], [6] and [7] helicene. We could demonstrate the importance of cyano group on regioselectivity of the photocyclization. We carried out functional group transformation of -CN in to carboxylic acid and *N*,*N*,-dimethyl amine. Various electrophilic aromatic substitutions were also performed on cyano aza[6]helicene. Three different ligands derived from aza[6]helicene were synthesized and attempts on their resolution are discussed.

Chapter 3 is also subdivided in two parts. **Part-I** deals with the synthesis and study of bi-aza[5] and bi-aza[6] helicenes using photocyclization. The new helical compounds were characterized and their photophysical properties were studied; also the effect of solvents on their photophysical properties was presented. In **Part-II** of chapter 3 we mainly focused on the preparation of challenging bis-carbazole based target molecules. In the course of this study we found an interesting reaction of converting mono formyl carbazole directly in to dihydroxy bis-carbazole using H_2O_2 in presence of acid catalyst. We presented various successful and unsuccessful attempts while targeting the desired final products.

Chapter 4 deals with the synthesis and study of crystallization behavior of five derivatives of cyano-containing 9-alkyl-9*H*-aza[7]helicenes. Only one of the derivatives, 5,13-dicyano-9-butyl-9*H*-aza[7]helicenes, showed the phenomenon of spontaneous resolution, which was attributed to the conglomerate formation of the same helical isomer via CN···H−Ar interaction. The helical molecules with same chiral description were aligned to form a necklace-like chain of secondary superhelix architecture of the same chirality. A correlation between the position of the cyano group and spontaneous resolution phenomena has been discussed.

Brief research methodology and chapter wise key findings

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[3] and catalysis, as molecular motor,[4] in biology[5] etc. A number of approaches have been developed for the synthesis of these screw shape molecules due to efforts required to overcome the inherent steric factors or steric crowding.[6] Therefore, the synthesis of new helical molecules remains an exciting challenge and a rewarding endeavor.

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.

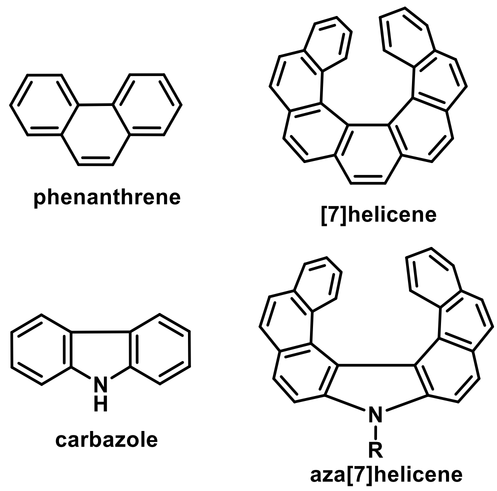
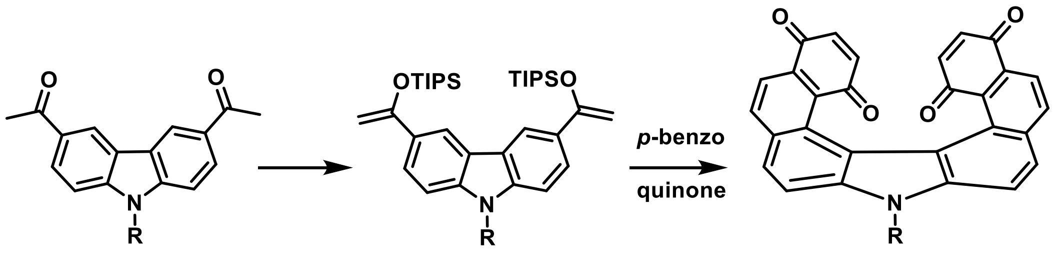


Figure 1. Few helicene systems.

Katz *et al.* synthesized the first carbazole derived helicene. He used Diels-Alder strategy for synthesis of aza[7]helicene bisquinones by employing 3,6-diacetyl carbazole derived diene with *p*-benzoquinone as dienophile[8] (**Scheme 1**).



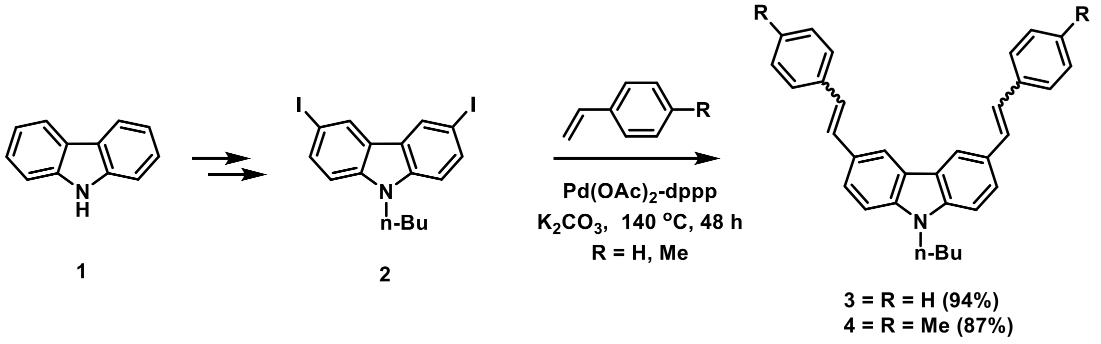
Scheme 1. Katz synthesis of aza[7]helicene bisquinone using carbazole as starting material.

The carbazole group is a popular functional unit in conjugated systems owing to its good planarity and N-H bond, which can be easily substituted for other functional groups. On the basis of DFT studies and good emission behavior, carbazole based helical molecules attract researcher as an important and effective material for OLED devises.[9] Majority of cases the conventional photocyclization strategy was the choice for making helical molecules

Chapter 2: Synthesis and Study of aza[7], aza[9] and Functionalized aza[*n*] helicenes with one nitrogen atom

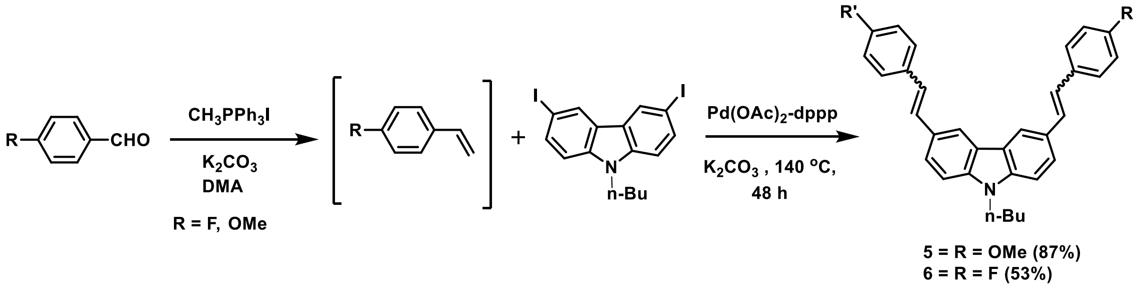
Chapter 2 Part A. Synthesis and study of aza[7]helicene

In this part we have synthesized 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 2**)



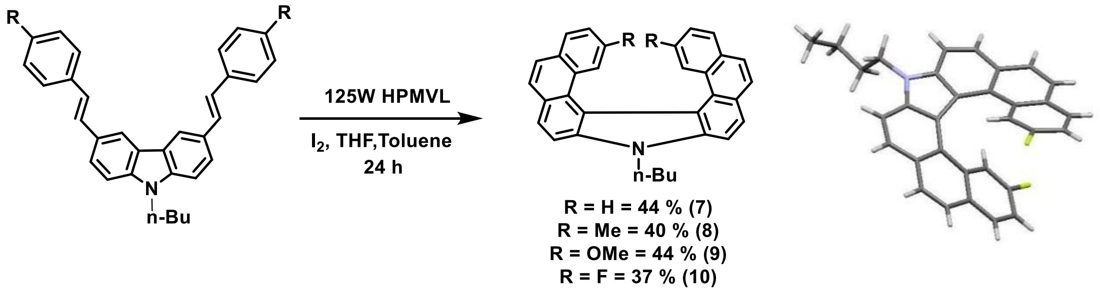
Scheme 2. Synthesis of (*E*,*E*) 3,6-distyryl-9-butyl-9*H*-carbazoles by Mizoroki–Heckreaction.

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 3. Synthesis of (*E*,*E*) 3,6-distyryl-9-butyl-9*H*-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** (**Scheme 3**). The styryl derivative of carbazole were then subjected to standard photocyclization conditions[12] to get the angularly cyclized aza[7]helicenes (**Scheme 4**)



Scheme 4. Photocyclization of distyryl carbazoles and ORTEP plot of compound **10**.

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 °C/min from 25 to 300 °C, under the inert atmosphere of nitrogen (**Figure 2**). The analysis indicated the melting point of compounds to be in the range of 200–246 °C. The glass transition temperatures (Tg) of aza[7]helicenes lie in 147–197 °C, which point toward high thermal stability of the helical system.

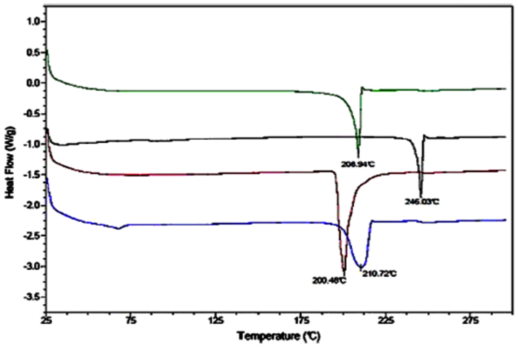


Figure 2: DSC Thermograms of aza[7]helicenes

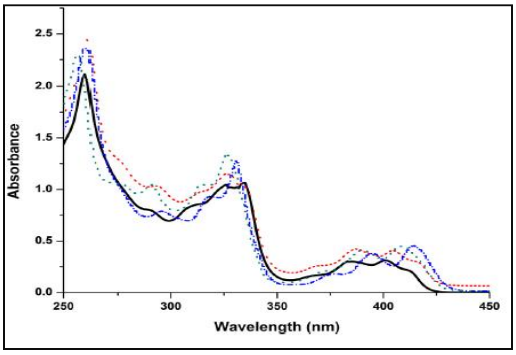
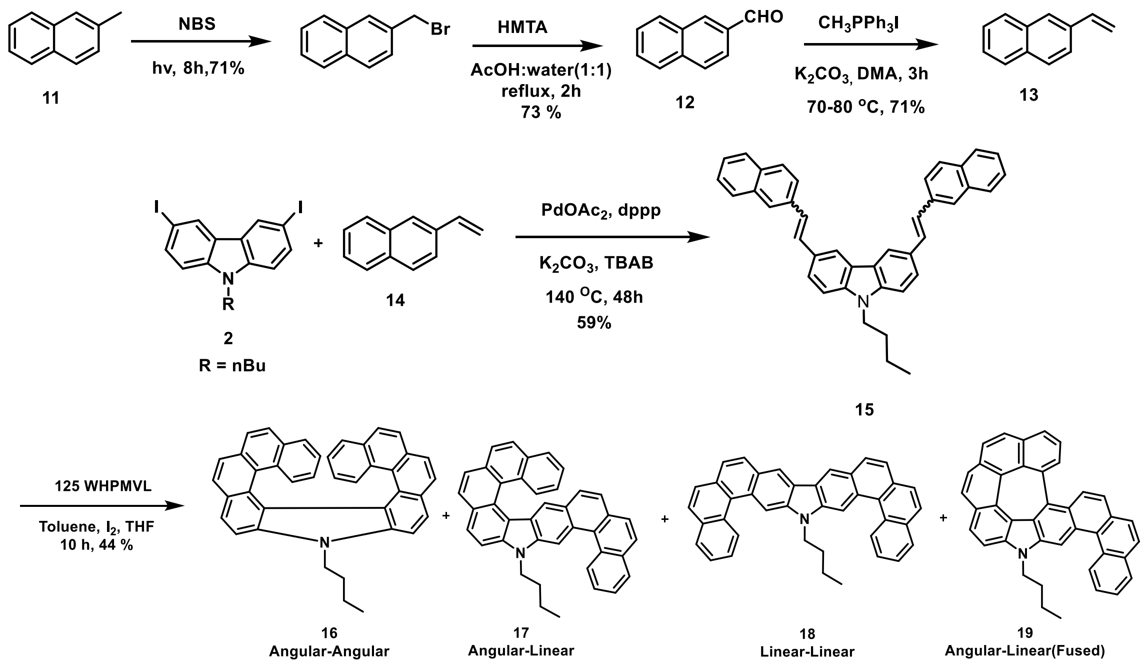


Figure 3 : Absorption spectra of aza[7]helicenes

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 absorption in the region of 257–414 nm (**Figure 3**).

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 vinylnaphthalene **14**. A solution of **15** in toluene was subjected to photochemical reaction (125W HPMV lamp) in a standard immersion well reactor (**Scheme 5**)



Scheme 5. 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 of aza[7]helicene. This is probably due to the different possible modes of cyclization of the intermediate species in the stilbenoid derivative. We separated all the four regiomers carefully by column chromatography and crystallization technique. The structures confirmed by ^{1}H NMR, ^{13}C NMR and X-ray analysis (**Figure 4**)

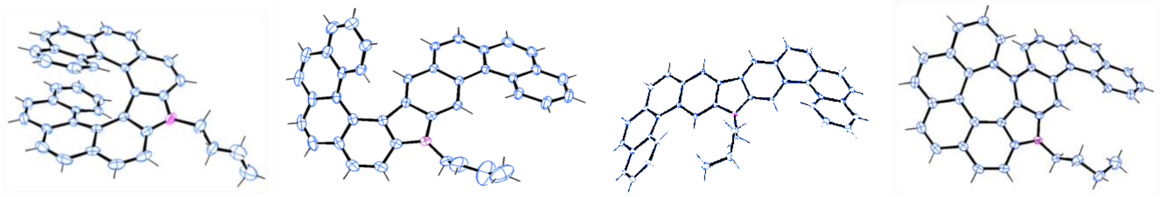


Figure 4. ORTEP Plots of regiomers **16** to **19**.

Effect of Concentration on product distribution: In the exploratory stage of our current investigation, the ^1H NMR 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 ^1H 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.

Entry	**Concentration Moles/Liter**	**16 d = 6.12 (d)**	**17 9.13 (s)**	**18 8.91 (s)**	**19 8.87 (s)**
1	150 mg in 1L ($2.86X10^{-4}$)	60.97	4.87	24.39	9.75
2	250 mg in 1L ($4.78X10^{-4}$)	38.46	14.61	22.30	24.61
3	500 mg in 1L ($9.56X10^{-4}$)	18.66	44.77	27.98	8.58
4	800 mg in 1L ($1.52X10^{-3}$)	14.32	45.27	31.80	8.59
5	1.0 g in 1L ($1.91X10^{-3}$)	ND	48	52	ND

Table 1. Effect of concentration of olefin photocyclization on the product distribution

Studies of photophysical 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 in **Table 2**. The Φ (Fluorescence quantum yield) of all regiomers were found to be low 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 ($\Phi = 0.546$)

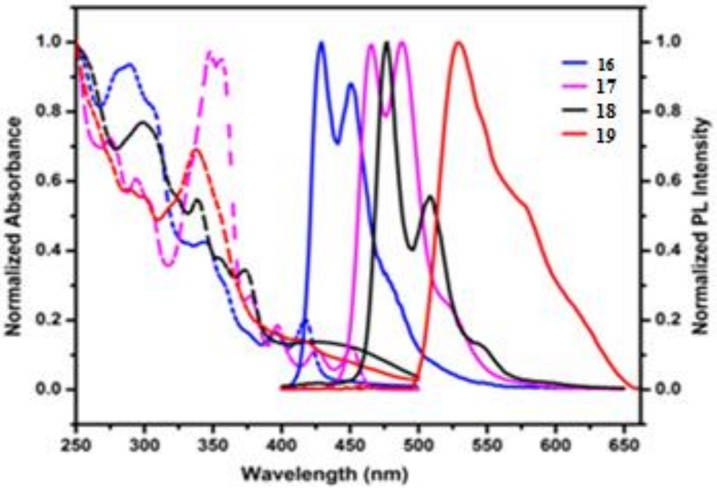


Figure 5. Absorption and emission spectra of regiomers.

Compound	λ_{abs}/nm	λ_{em}/nm (λ_{exc}/nm)	Stokes shift/nm	Φ_{FL} (λ_{exc}, nm)
16	289	429, 451 (289)	140	0.20 (313)
17	348	465, 488 (348)	117	0.19 (306)
18	299	477, 508 (299)	178	0.21 (363)
19	338	529, 578 (338)	191	0.07 (338)

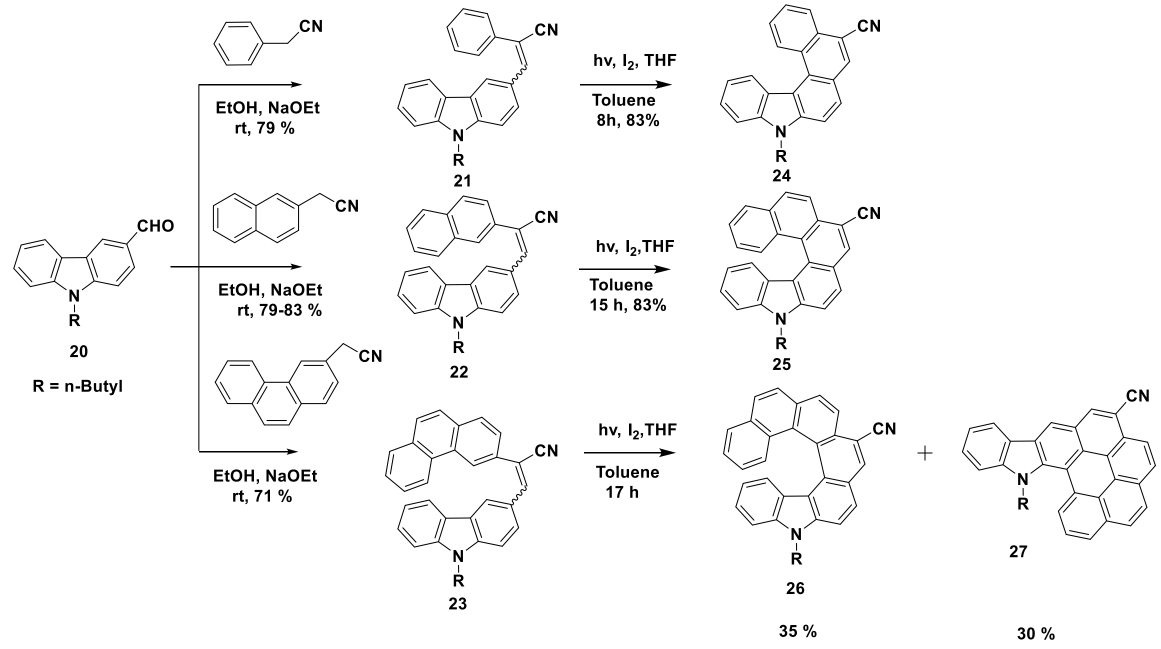
Table 2. Photophysical properties of regiomers.

Chapter 2 Part B. 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 group.

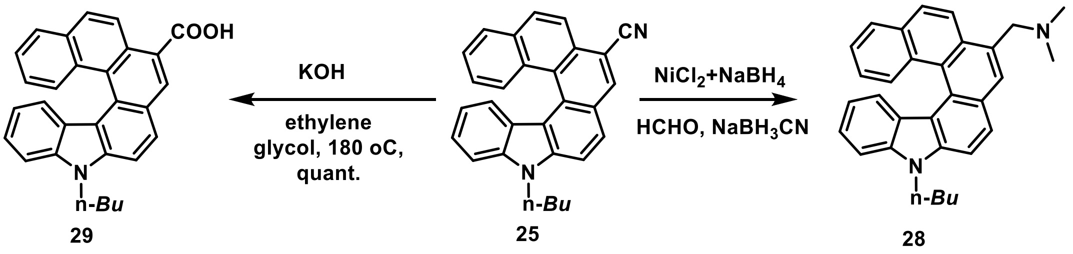
The 3-formyl *N*-butyl carbazole **20** was prepared from *N*-butyl carbazole by Vilsmeier-Haack reaction using phosphorous oxychloride and dimethyl formamide in excellent yield. The aldehyde was then treated with respective cyano derivatives and sodium ethoxide to effortlessly furnish required cyanostilbenes **21**, **22** and **23** respectively. Their photocyclization under the standard condition gave the desired angular products **24**, **25**, and **26** respectively (**Scheme 6**). 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;

aza[5]helicene **24** shows a single peak suggesting low barrier of racemisation while aza[6]helicene **25** show two well separated peak at retention times 20.9 and 22.6 suggesting rigidity in helical framework and possibility for the separation of two isomers.



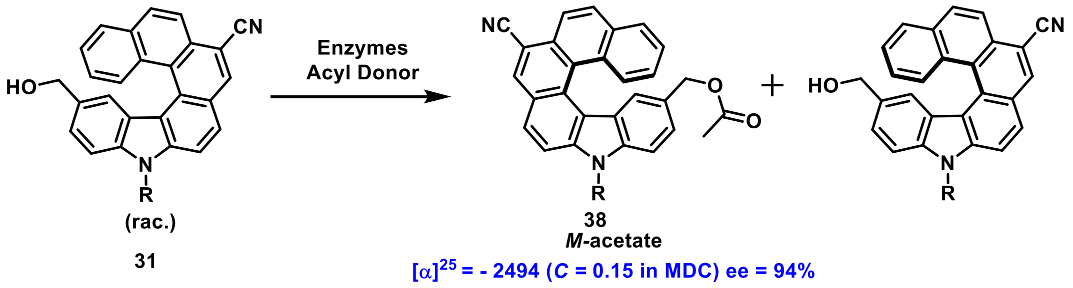
Scheme 6. Synthesis of functionalized aza[*n*] helicenes.

Post Functionalization and functional group manipulations: We successfully converted the cyano group of **25** in to *N*,*N*-Dimethyl derivative **28** using nickle chloride ($NiCl_2$) 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 **29** (**Scheme 7**)

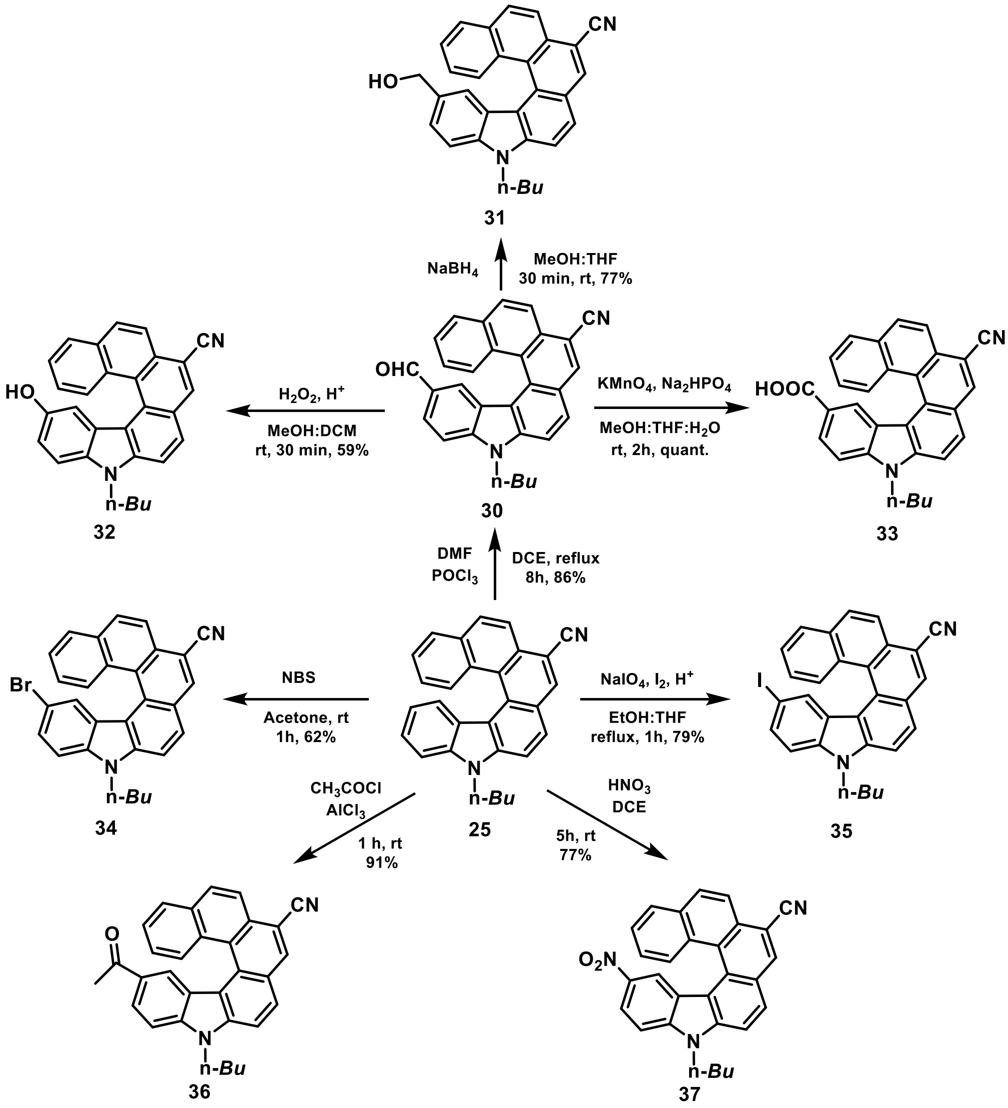


Scheme 7. Transformation of –CN of compound 25.

The compound **31** 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 enzyme and vinyl acetate as acyl donor. By the enzymatic resolution and single crystallization enantiopure acetate **38** up to 94 % ee was obtained (**Scheme 8**)



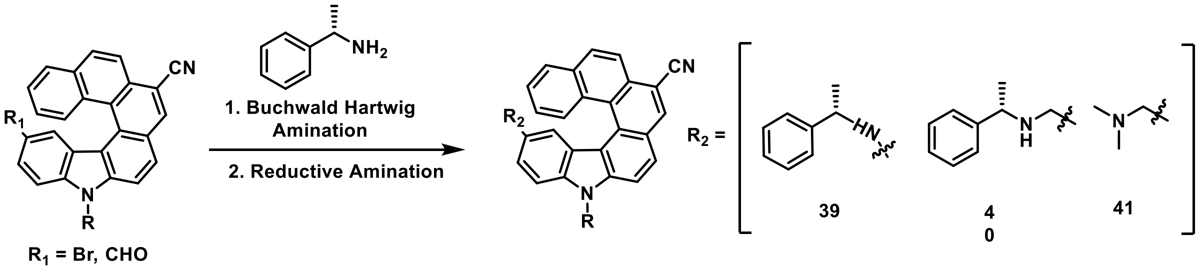
Scheme 8. Enzymatic resolution of compound **32**



Scheme 9. Post Functionalization and Functional group manipulations of compound **25**.

The electrophilic aromatic substitution reactions such as halogenations, nitration, acetylation and formylation have been easily performed on cyano aza[6]helicene **25** (**Scheme 9**).

Ligand Synthesis: We have synthesized helical based ligands **39**, **40** and **41** (**Scheme 10**). We successfully resolved ligand **39** by column chromatography and currently trying to resolve other ligands. We will test these ligands as chiral solvating agent and study their binding with biological materials.



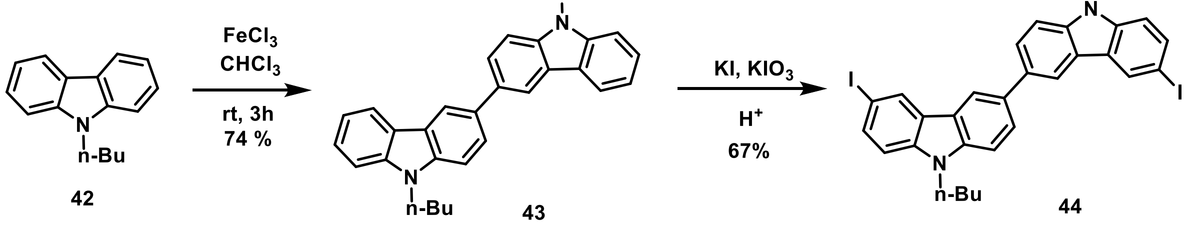
Scheme 10. Synthesis of Ligands.

Chapter 3. Synthesis and Study of aza[*n*]helicenes with more than one nitrogen atom

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]

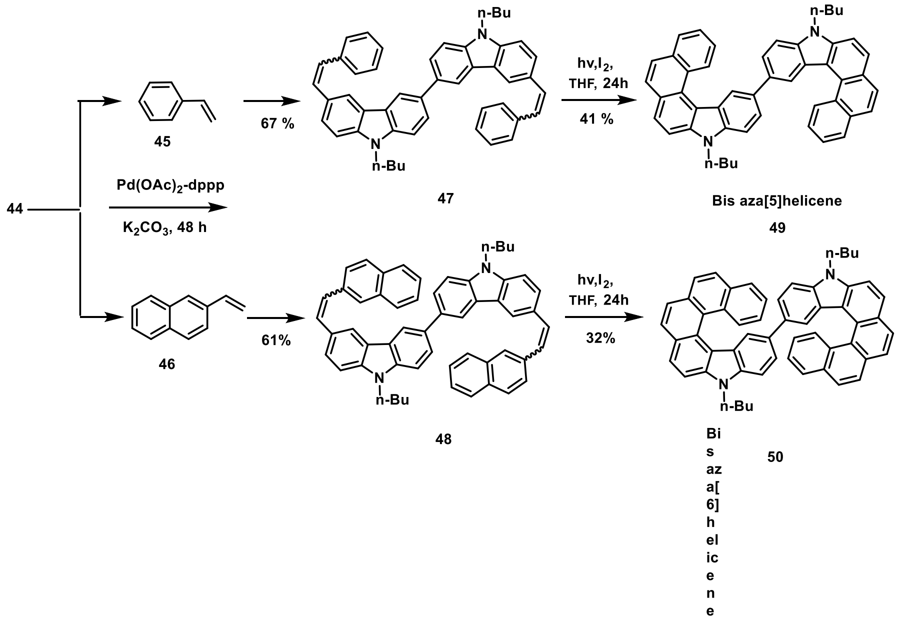
Chapter 3 Part A Synthesis and study of bi-aza helicenes.

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 **42**, prepared by alkylation of carbazole **1**, was subjected to the dimerization reaction with ferric chloride to obtain **43** in good yield. The bi-carbazole **43** was subjected to slightly modified conditions of regioselective di-iodination to afford the required precursor **44** in satisfactory yield and purity (**Scheme 11**)



Scheme 11. Synthesis of 3-iodo-6-(3-iodo-9-butyl-9H-carbazol-6-yl)-9-butyl-9Hcarbazole.

The di-iodo carbazole **44** was subjected to palladium catalyzed Mizoroki Heck reaction with styrene **45** and 2-vinylnaphthalene **46** under the suitable conditions. Corresponding bis-styryl derivative **47** and **48** were obtained with styrene and 2-vinylnaphthalene in good yields, and then they were subjected to standard photocyclization conditions (**Scheme 12**). The product of the expected angular cyclization was isolated to moderate yields from the complex reaction mixture. The styryl derivative of bi-carbazole **47** furnished the angular-angular bi-aza[5]helicene **49**, while the vinyl naphthyl derivative **48** furnished similarly cyclized bi-aza[6]helicene **50**. 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 **50** was further established by its single crystal X-ray diffraction analysis (**Figure 6**)



Scheme 12. Synthesis of bis-aza[5]helicene and bis-aza[6]helicene.

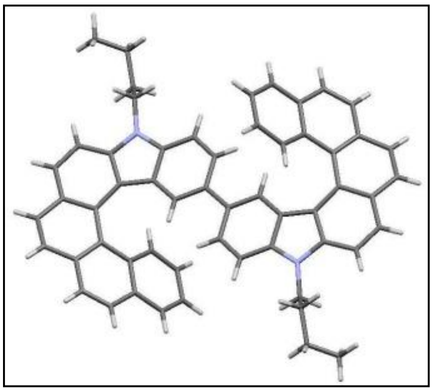


Figure 6. ORTEP plot of compound **50**.

Photo-physical properties: The UV-Vis spectra of bi-aza[5]helicene **49** and bi-aza[6]helicene **50**, in dichloromethane exhibit absorption bands in the range of 262 to 337 nm (**Figure 7**). The compounds showed blue emission in the range of 437 to 458 nm (**Figure 8)**. The compound **50** showed small red shift (21 nm) compared to 7, probably due to increase in π-conjugation. Optical measurements of compound **50** were measured in different solvents. There is no significant Solvatochromism observed.

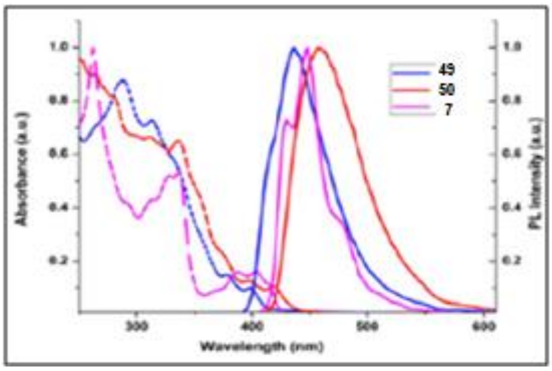


Figure 7. Absorption and emission spectra

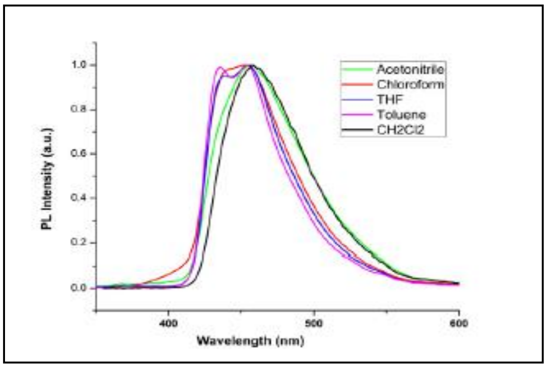
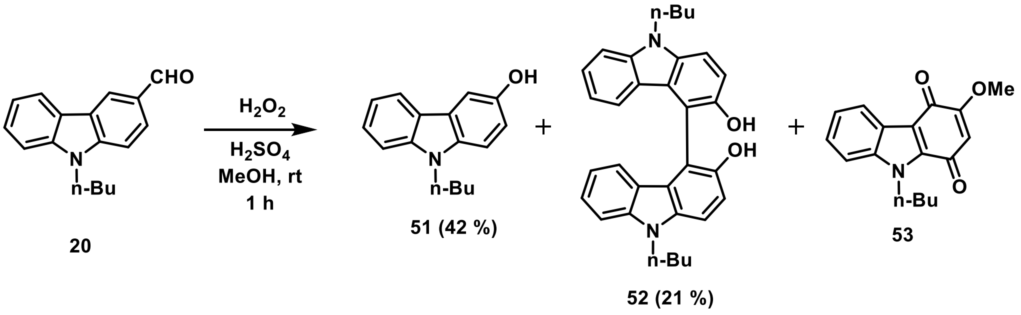


Figure 8. Solvatochromism study of compound **50**

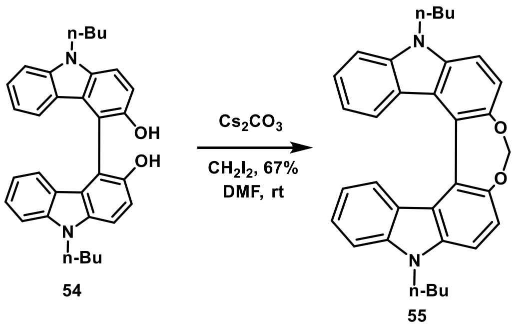
Chapter 3 Part B Synthesis and Study of bis-carbazole helicenes.

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 attempted to synthesize some bis carbazole derivative. Synthetic scheme comprises the acid catalyzed Dakin condensation of 3 formyl *N*- butyl carbazole **20** using hydrogen peroxide as an oxidant to obtain the 3-hydroxyl *N*-butyl carbazole **51**, in this course of transformation with the desired compound **51** we also got one unexpected polar product which was characterized to be coupling product **52**. Optimization to understand its formation and to improve the yield is currently under progress.



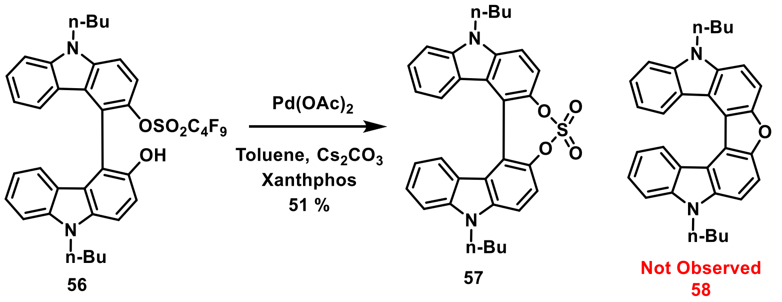
Scheme 13. Synthesis of BICOL (**52**).

Using compound **52** we synthesized a helicene like compounds and successfully inserted methylene bridge to get compound **55** (**Scheme 14**)



Scheme 14. Synthesis of bis carbazole based helicene-like molecule **55**..

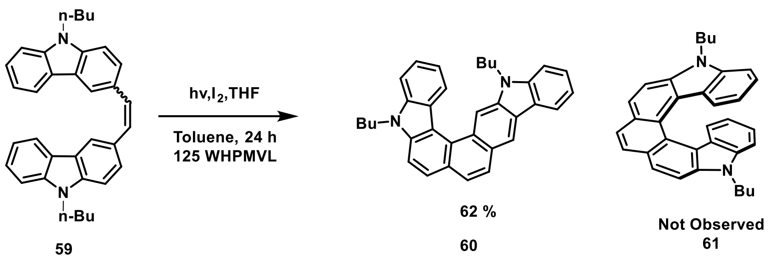
We also attempted to insert furan ring between two carbazole molecules using Buchwald Hartwig (C-O bond forming) protocol but instead of getting the desired product **58** we obtained a substitution product **57**.



Scheme 15. Attempted synthesis of compound **58**.

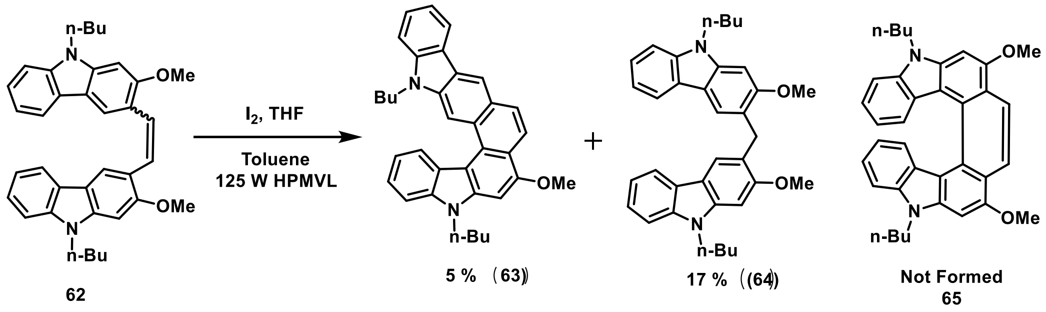
We attempted to incorporate pyrrole ring between two carbazole moieties. Attempts were also made to incorporate a benzene ring between two carbazole moieties. Photocyclization was the strategy for the choice. Various approaches are discussed below.

Approach 1



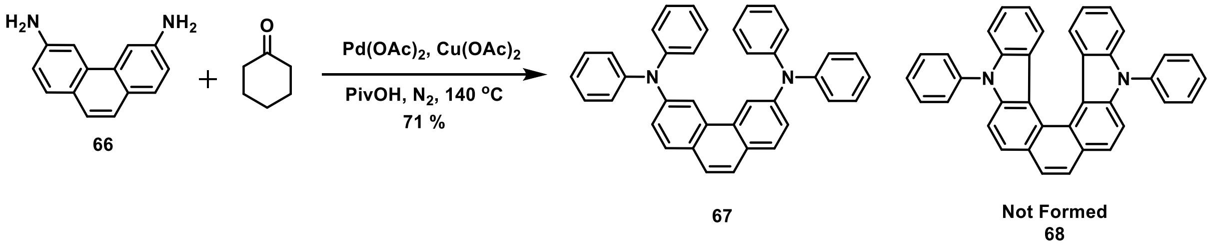
Scheme 16. Attempted synthesis of compound **61**.

Approach 2



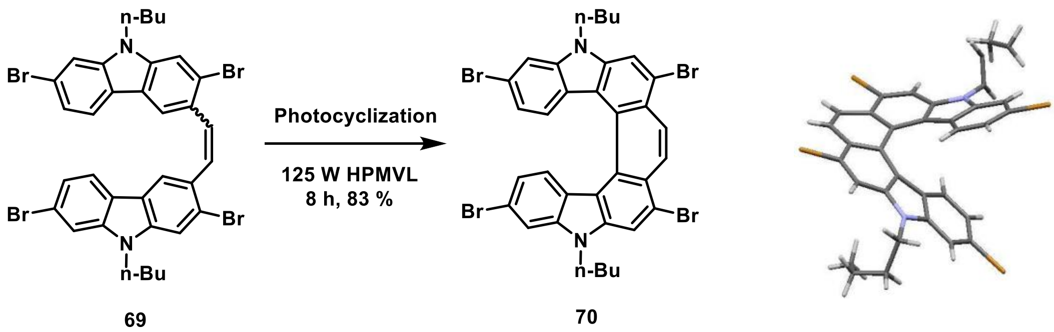
Scheme 17. Attempted synthesis of compound **65**.

Approach 3



Scheme 18. Attempted synthesis of compound **66**.

Approach 4



Scheme 19. Successful approach for synthesis of symmetrical bi-aza[7]helicene.

Study of the photophysical properties of these bis-carbazole based helicene-like and helical molecules are currently under progress.

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:

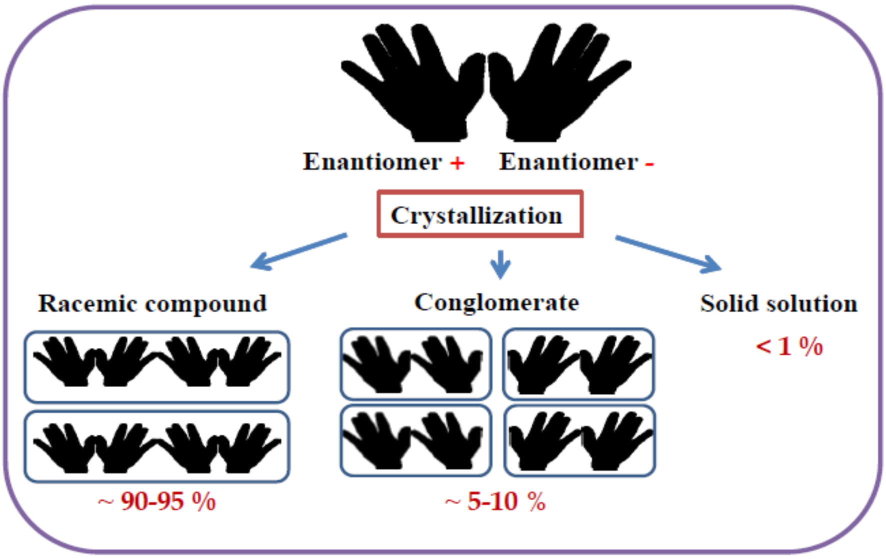
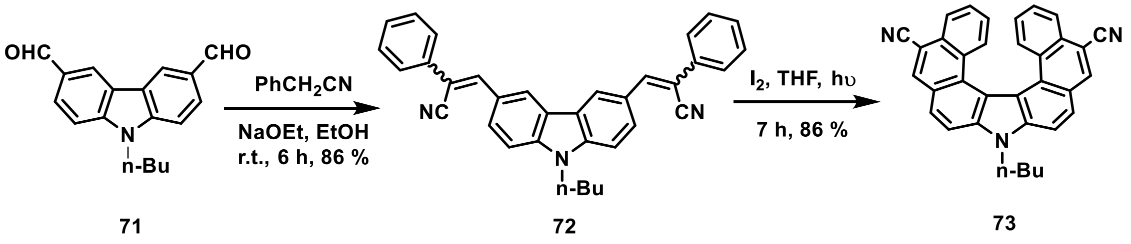


Figure 9. Crystal packing in chiral compounds.

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 **73** was achieved from 2,9-diformyl carbazole **71**, via its bis-styryl type derivative **72** prepared by Knovenagel condensation with benzyl cyanide. Conversion of **72** to the target aza[7]helicene was easily done by photodehydrocyclization procedure involving a double, regioselective angular-angular cyclization to afford the compound **73** in good overall yield.



Scheme 20. Synthesis of Dicyano aza[7]helicene.

Investigation for Spontaneous resolution: The initial attempts to enrich the helical enantiomers of **73** by crystallization in dichloromethane, chloroform, toluene, hexane-chloroform, THF etc. resulted in to isolation of only racemic crystals.The plate like single crystals of (±)-73 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 10. Optically pure diamond shaped (left) and racemic plate shaped (right) crystals of **73**

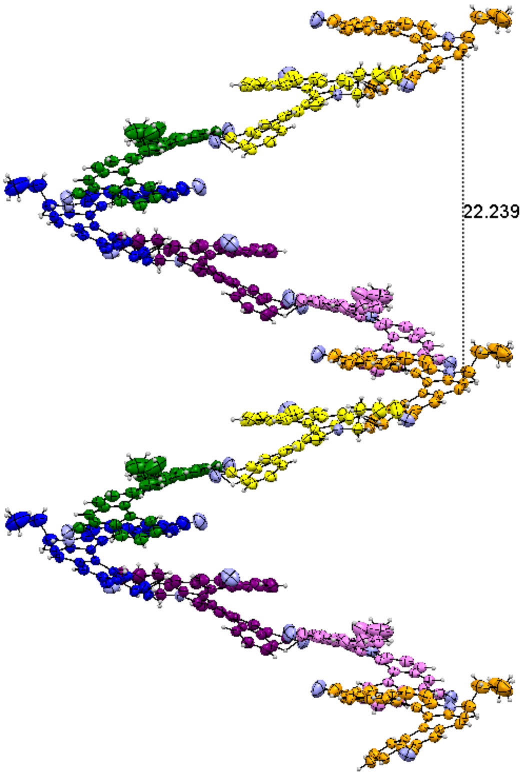
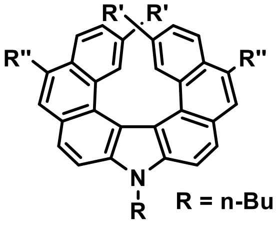
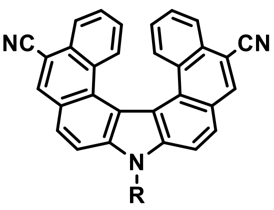


Figure 11. Side view of *P*-Super helix arrangement of the conglomerate of (*P*)-**73**. The six molecules forming one turn are given different colors.

The single crystal X-ray analysis of randomly picked diamond shaped crystal showed interesting molecular packing. Sample of (*P*)-**73** and (*M*)-**73** 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*)-**73** and (*M*)-**73** 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.



74, R' = CN, R''= H
75, R' = OMe, R'' = CN
76, R' = R'' = CN



77, 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 **74** to **77**. 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 **76**, methoxy group in **75** and phenyl group in the side chain in **77**. 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.

Conclusion:

In summary synthesis of symmetrical aza[7]helicenes have been achieved using oxidative photocyclization. Their photophysical and thermal properties were studied.

The same strategy was applied for the synthesis of larger aza[9]helicene and various regioisomers were carefully separated and their crystal structures and photophysical properties were studied.

Various CN group containing aza helicenes ([5], [6] and [7]). have been successfully synthesized. Configurationally stable aza[6]helicenes was then successfully tested for post functionalization and functional group conversion. Three different ligands have been prepared from aza[6]helicene. Two ligands were resolved and attempts to resolve third ligand is currently under process. Detailed investigations of these amino ligands as fluorescence sensors are currently under progress.

Two important observations were made during this course of study for regioselective photocyclization of carbazole based aza[*n*]helicene.

- Higher dilution not only prevent the dimerization process but also controls the formation of angularly cyclized product for larger helicenes.
- Presence of CN group near the olefinic site not only drasitically improves regioselectivity but also simplifies the purification from undesired products.

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

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

We conclude that the success of spontaneous resolution depends on the ability of molecules to form right kind of contacts among the neighbor of the same chirality. Any factor that alters this ability of a molecule either by weakening the interactions to identify its partner (similar isomer) or by making stronger interactions with the opposite isomer; decreases the chiral recognition property of a molecule. These crystallographic comparisons suggest that the presence of dipole−dipole interactions are essential but not enough for making the right contacts with the neighboring molecule of the same handedness, which is required for spontaneous resolution. We believe these findings will contribute to the general understanding of the relatively uncommon phenomena of spontaneous resolution by conglomerate formation and can lead to more success in this aspect of crystal engineering and supramolecular interactions in solids.

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