Executive Summary

of the thesis entitled

"SYNTHESIS AND STUDY OF HETEROHEICENES"

to be submitted

as a partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Bhalodi Esha Hasmukhbhai

under the supervision of

Prof. Ashutosh V. Bedekar

Professor

Department of Chemistry

Faculty of Science

The Maharaja Sayajirao University of BarodaVadodara 390 002, Gujarat (INDIA)

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AIM OF THE THESIS

The major objectives of this research work include: synthesis of heterohelicene framework which is thermally stable at room temperature, functionalization of these molecules and resolution or separation of helical isomers in order to study their properties such that their applications in the field of asymmetric catalysis and organic electronics can be explored.

RESEARCH METHODOLOGY and KEY FINDINGS

The actual research work is mainly described into three chapters. (Chapter 1 being Introduction)

Chapter - 1

Introduction

1.1 Introduction to Helical Structure

Helical structures are very common in nature and are observed in diverse natural formations ranging from macroscopic (sea shells, horns, seed pods, weather patterns, etc.) to microscopic level (DNA double helix).

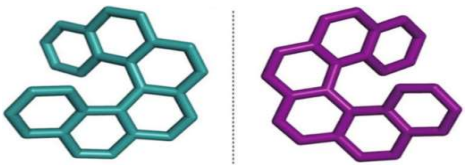



Design and development of helical structures in various fields of chemistry has surfaced as an ever demanding area of science with a scope of building some new molecules and understanding its properties and applications.

Helicenes are part of an intriguing class of polycyclic aromatic compounds formed from ortho-fused benzene (carbohelicene) or other aromatic rings (heterohelicene) that adopt a helical topology to avoid overlapping of the terminal rings resulting in helically chiral structures.

1.2 General properties of helicenes

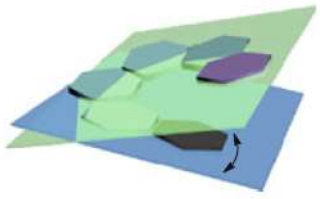
- Helicity: The steric hindrance of the terminal rings forces the helicene to wind in opposite directions. This renders them chiral even though they have no asymmetric carbons or other elements of chirality. On the basis of CIP rule, right-handed helix is designated as plus and denoted as *P* whereas left-handed helix is designated as minus and denoted as *M*.
- Helicenes show a greater distortion from planarity and the two terms used to explain the extent of distortion are torsional angle and interplanar angle.
- They are good π-donors and can form charge-transfer complexes with many π-acceptors.
- They exhibit very large specific rotation.
- Their specific backbone which combines electron delocalization and non-planarity of the π-electron network makes them very stable towards acids, bases and high temperature.



(*M*)-[6]helicene **(*P*)-[6]helicene**

Interplanar angle or the dihedral angle is the angle between the two terminal rings.
Torsional angle is the dihedral angle of four adjacent inner carbon atoms a, b, c, and d.

Torsional angle



Interplanar angle

1.3 Applications of helicenes

The distinguishing feature of helical molecules is the combination of π-conjugated system and helicity. Hence the applications of helical molecules can be classified on the basis of these two properties. For racemic helicenes, π-conjugated system is responsible

for some interesting applications in the field of material science, in liquid crystals, etc. In case of optically pure helicenes, applications are based on its helical chirality in the chiral recognition study, in asymmetric synthesis and also in the field of biological sciences.

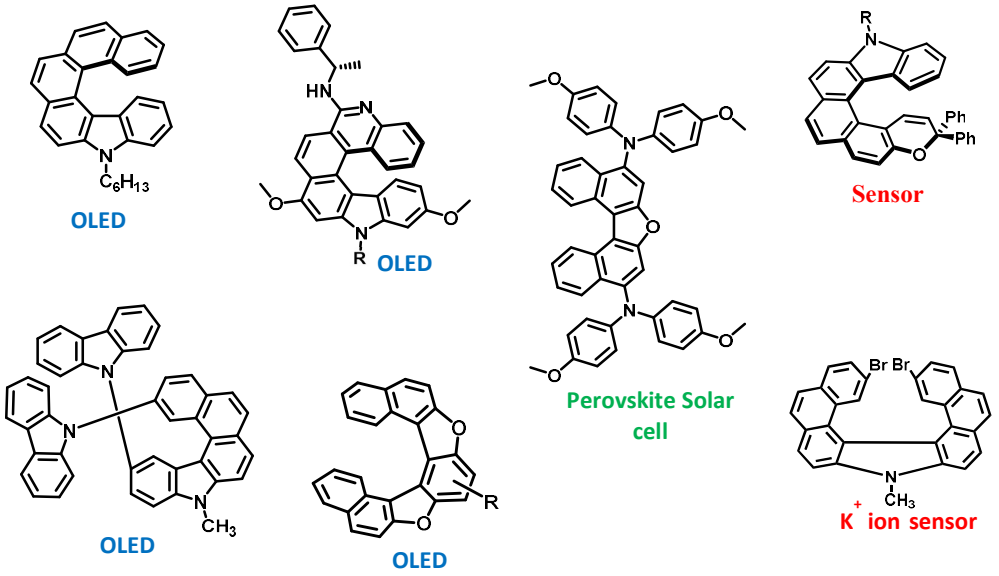


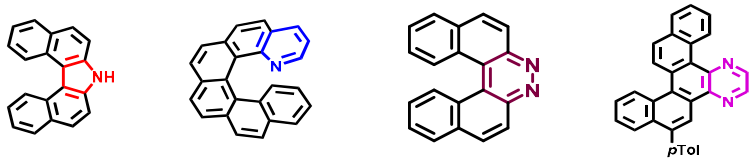
Figure 1.1: Reported helicenes with interesting applications

Chapter - 2

Synthesis and study of aza[n]helicene based chiral amines

2.1 Azahelicene

Azahelicene belong to the subgroup of heterohelicenes. They are composed of ortho fused benzene, pyrrole, pyridine, pyridazine, pyrazine or other *N*-heterocyclic rings to form helical framework.



The properties and chemical behaviour of azahelicenes are practically unknown apart

from their basicity and few other studies. They can form complexes with transition metal, can assist in the formation of large supramolecular assemblies complexes and they are basic enough to act as enantioselective catalyst. The promising applications of azahelicenes in various branches of chemistry might be investigated and thus there is scope for further research in this field.

For the synthesis of aza[*n*]helicenes, carbazole was chosen as our structural motif. As it is: cheap building block, three inbuilt rings, easy and regioselective functionalization, access to gram scale starting material.

Chapter - 2A

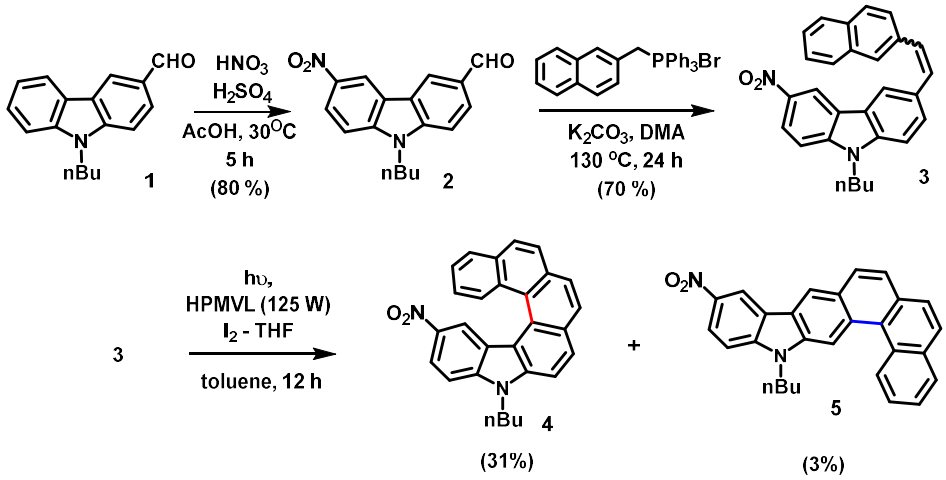
Synthesis and resolution of unsymmetrical 2-aminoaza[6]helicene

The synthesis and studies of amino-substituted azahelicenes are relatively less explored as seen in the available literature. The presence of primary amino group on aromatic rings of helical system can be useful to introduce various functional groups for suitable modifications as well as it can be helpful in searching applications as observed in the literature. The amino group is also adequate to form salts with chiral acids to prepare diastereomers or to conveniently attach chiral modifiers to make diastereomeric derivatives for easy separation of isomers. In this chapter we shall discuss the preparation of 2-amino-5-aza[6]helicene via reduction of its corresponding nitro derivative and elaborate on our efforts to isolate it in optically pure form.

Result and Discussion

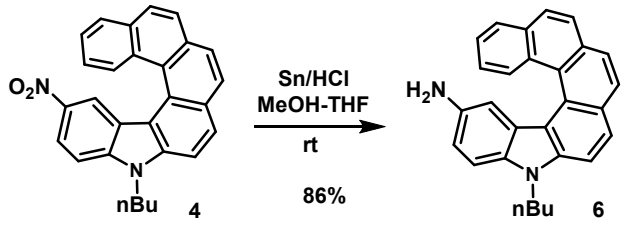
2A.1 Synthesis of 2-amino-5-aza[6]helicene

The synthesis of **4** was started from the nitration of readily available 3-formyl-*N*-butyl carbazole **1**, followed by its Wittig reaction with the triphenylphosphonium salt derived from 2-bromomethyl naphthalene. The stilbenoid **3** was then subjected to standard conditions of photochemical cyclodehydrogenation under the irradiation of 125 W HPMVL. This reaction resulted into the formation of the desired angularly cyclized isomer **4** as the major product, while the linear one **5** was also obtained in minor amount (85.5:14.5 as seen on ^{1}H NMR). (**Scheme-2A.1**)



Scheme 2A.1: Synthesis of 2-nitro aza[6]helicene

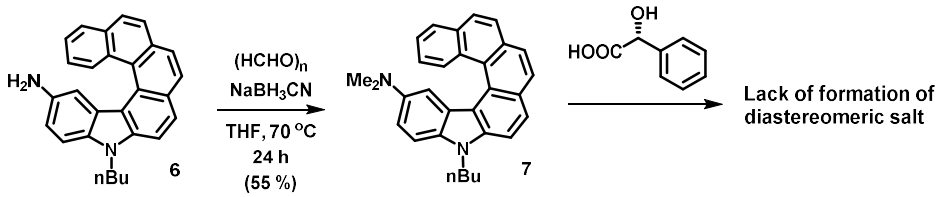
The compound **4** was also characterized by single crystal X-ray analysis. The nitro helicene **4** was then reduced to the target molecule **6**. Various conditions of reduction were carried out, where the best results were obtained using Sn-HCl method. (**Scheme-2A.2**)



Scheme 2A.2: Reduction of 2-nitro-5-aza[6]helicene

2A.2 Resolution of 2-amino-5-aza[6]helicene

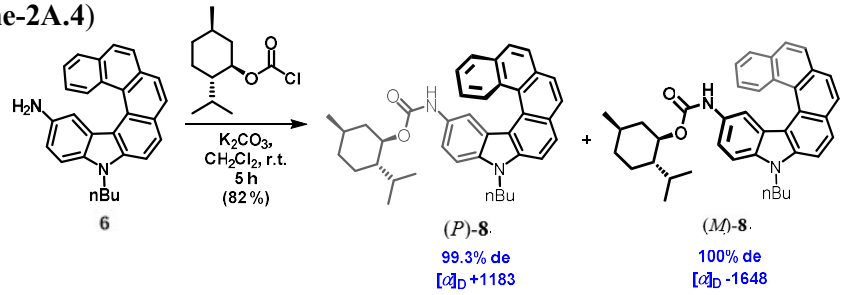
After synthesis, our next target was its resolution. In our first attempt we converted the primary amine **6** to its *N*,*N*-dimethylamino derivative **7** which was then subjected to co-crystallization with chial acids in different solvents. Here, either amorphous solid fell out or oily mass was obtained. Analysis of this material indicated lack of enrichment of one of the isomers. (**Scheme-2A.3**)



Scheme 2A.3: Diastereomeric salt formation with chiral acid

[6] Then we changed our approach, where the primary amino group was converted into the diastereomeric menthyl carbamates by attaching the chiral auxiliary (*R*)-(-)-

menthylchloroformate. The diastereomers were separated by alumina column chromatography and were analyzed by HPLC analysis and their SOR were measured. (**Scheme-2A.4**)



Scheme 2A.4: Formation of diastereomers by reaction with chiral auxiliary

The separated diastereomers were further analyzed by circular dichroism spectroscopy where they displayed opposite Cotton effect. Since the menthyl group showed no significant response in this particular UV-visible range this mirror image relationship was purely due to the helical framework of the two isomers. CD Spectra of diastereomeric carbamates (*P*)-**8** and (*M*)-**8** was recorded in (1.0 x 10^{-5} M in $CHCl_3$).

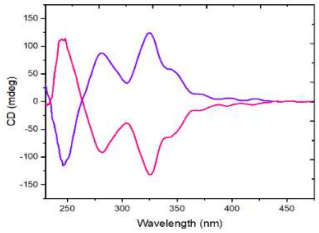
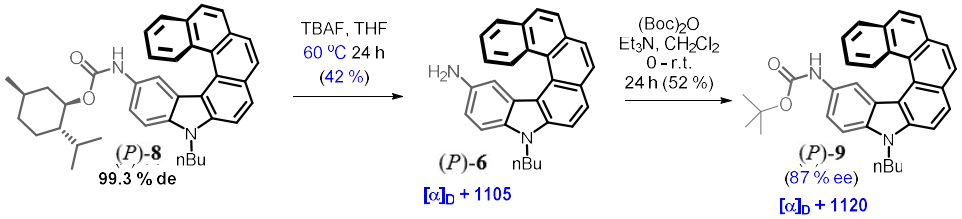


Figure 2A.1: CD Spectra of diastereomers (*P*)-**8** (pink) and (*M*)-**8** (blue)

For accessing optically pure amine, pure sample of (*P*)-**8** was subjected to standard conditions of deprotection using TBAF. The reaction was sluggish at ambient temperature but proceeded smoothly at elevated temperature. The amine sample being less stable was converted to its *N*-Boc derivative to study its optical purity. *N*-Boc derivative of the amine obtained after cleavage at lower temperature showed optical purity of 87%, while the one obtained from the amine derived at higher temperature showed only 56% ee. (**Scheme-2A.5**)



Scheme 2A.5: Deprotection of diastereomer **8**

It was observed that the isomerization of helical structure is not taking place during the introduction of Boc group, but must be during the deprotection of carbamate. Our efforts to attempt deprotection of carbamate with TBAF at lesser temperature (50-55 ^{o}C) resulted in negligible conversion. We also investigated other known methods of deprotection of carbamate, trifluoroacetic acid in dichloromethane, diethylenetriamine, and aqueous phosphoric acid (85 wt%), but did not result in the cleavage.

Chapter – 2B

Accessing optically pure dimethylaza[7]helicene via hydrogenative deprotection of chiral helical diamines

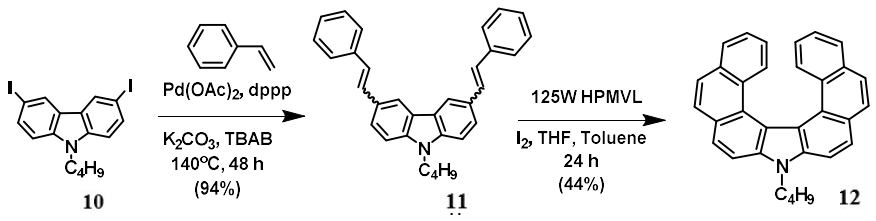
Accessing optically pure isomers of helicenes without any functional group is a daunting task, as by detaching any chiral auxiliary, optically pure helicenes are obtained with original functional group intact. In the chapter we discuss our efforts to synthesize methyl substituted helicene in enantiomerically pure form, where the operation of attachment and removal of chiral auxiliary results in overall transformation of a formyl group to an alkyl moiety.

Result and Discussion

2B.1 Synthesis of 5,13-diformyl-aza[7]helicene

Approach-1: By formylation of 9-butyl-9*H*-aza[7]helicene

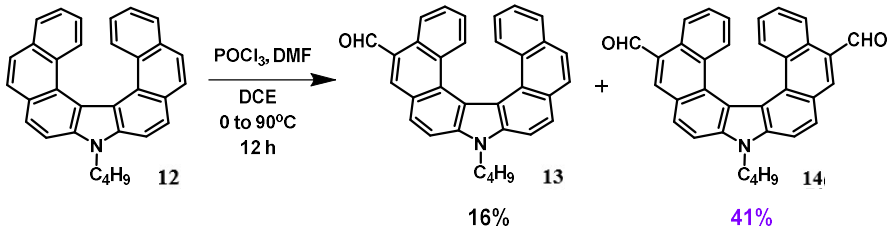
Aza[7]helicene **12** was synthesized by the photocyclization of bis-stilbene derivative **11** obatined by Heck olefination of 3,6-diiodo-*N*-butylcarbazole **10** with styrene.



Scheme 2B.1: Synthesis of 9-butyl-9*H*-aza[7]helicene

This aza[7]helicene was then subjected to Vilsmeier-Haack formylation, where the TLC

of the reaction mixture showed the presence of multiple spots. (**Scheme 2B.2**) The desired diformyl derivative **14** was isolated in very less amount.

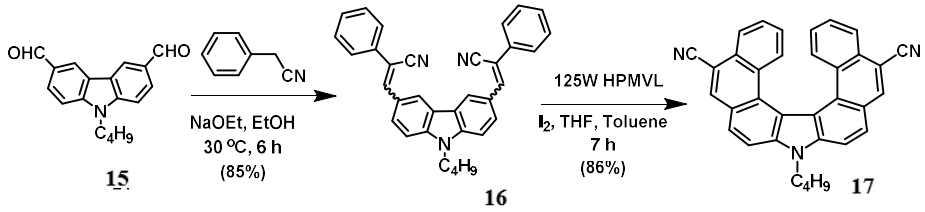


Scheme 2B.2: Vilsmeier-Haack formylation of 9-butyl-9*H*-aza[7]helicene

Drawbacks of this approach: Low yielding photocyclization reaction, long duration of photocyclization reaction, low yield of **14**. Thus we changed our approach towards the synthesis of helicene **14**.

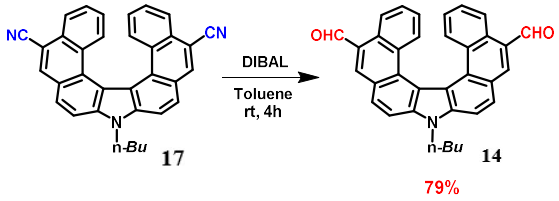
Approach-2: By reduction of 5,13-dicyano-9-butyl-9*H*-aza[7]helicene

5,13-dicyano-9-butyl-9*H*-aza[7]helicene **17** was synthesized by the photocyclization of bis- olefin **16** which was synthesized by the Knovaenegel condensation of 3,5-diformyl-*N*-butylcarbazole **15** with benzyl cyanide. (**Scheme 2B.3**)



Scheme 2B.3: Synthesis of 5,13-dicyano-9-butyl-9*H*-aza[7]helicene

The dicyanohelicene **17** was subjected to reduction using DIBAL which is a selective reagent for the reduction of cyano group to aldehyde group. (**Scheme 2B.4**) Here, the desired diformyl helicene **14** was obtained in good yield. Compound **14** was also analyzed by single crystal X-ray analysis.

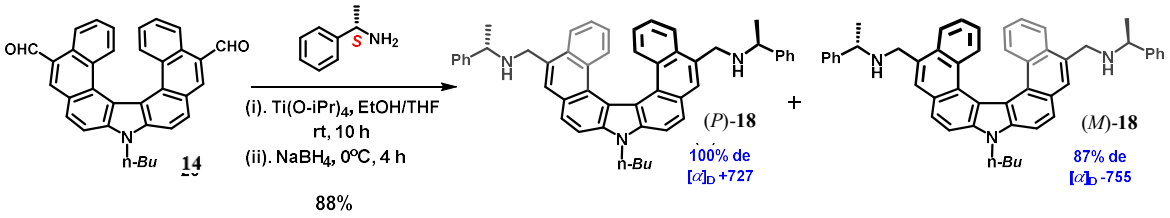


Scheme 2B.4: Reduction of 5,13-dicyano-9-butyl-9*H*-aza[7]helicene

2B.2 Synthesis of chiral helical diamines

Reductive amination of helicene **14** with titanium isopropoxide and sodium borohydride

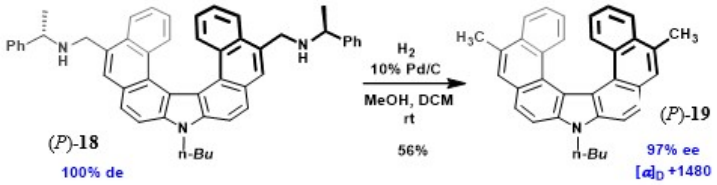
was carried out to obtain the diastereomeric mixture of helical diamines which were separated by alumina column chromatography. (**Scheme 2B.4**) The isomers were then analysed by HPLC analysis and their SOR were recorded.

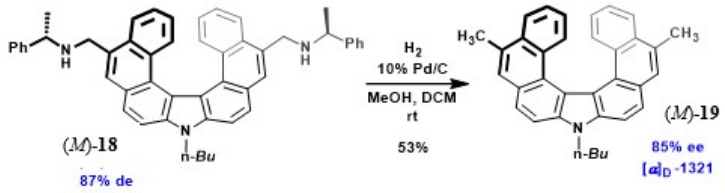


Scheme 2B.5: Synthesis of diastereomeric amine via reductive amination

2B.3 Selective hydrogenation of helical diamines

Then, we attempted hydrogenation of the separated diastereomers. The palladium-on-carbon catalyzed hydrogenative deprotection of one the *N*-benzyl group occurred selectively, leading to the formation of optically pure 5,13-dimethylaza[7]helicene **19**.





Scheme 2B.6: Hydrogenative deprotection of the diastereomeric helical diamines

The isomers (*P*)-**19** and (*M*)-**19** were also analysed by the CD spectroscopy where they displayed opposite Cotton effect.

Thus, a new method was established for the formation of optically pure helicene with methyl substituents from the corresponding diastereomeric helical diamine via selective removal of the (*S*)-(-)-α-methylbenzylamine moiety. Generally, the cleavage of chiral

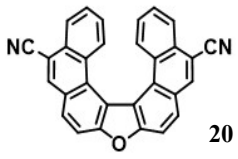
auxiliary from the helical diastereomers leaves the helicenes with the functional group intact, whereas in this method we obtained methyl substituents by cleaving the chiral attachment.

Chapter – 3

Synthesis and study of symmetrical dicyano derivative of oxa[7]helicene

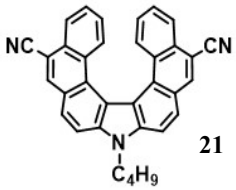
In this chapter 6,12-dicyano-9-oxa[7]helicene was synthesized in order to study the phenomenon of spontaneous resolution.

The separation of crystals of the enriched isomers of 5,13-dicyano-9-butyl-9*H*-aza[7]helicene **21** was achieved by our group by crystallization from 1,2-dichloroethane. In addition to **21**, several other derivatives of dicyano aza[7]helicene were investigated, but none of them resulted in spontaneous resolution. The detailed study of supramolecular interactions gave us some insight in the correlation of structure and favorable intermolecular interactions resulting in such separation. Its oxygen analogue, 5,13-dicyano-9-oxa[7]helicene **20** was also synthesized by our group. This molecule too could not result in its spontaneous resolution. The crystallization study was severely hampered by its very poor solubility in most of the common organic solvents. In this chapter we present our efforts to synthesize the isomer **22** where the cyano groups are attached at different positions.



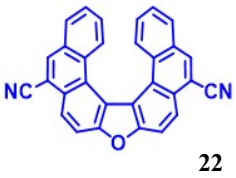
20

Eur. J. Org. Chem. **2018**
Spontaneous resolution was not observed



21

Cryst. Growth Des. **2019**
Spontaneous resolution was observed



22

Target molecule

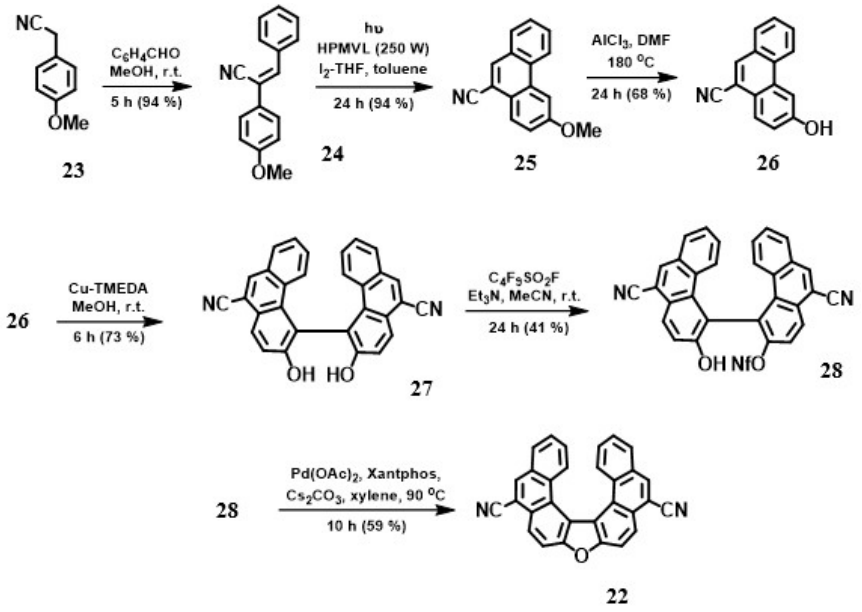
In the previous study of the spontaneous resolution of **21**, a key supramolecular interaction, H-bonding, was observed between the nitrogen of cyano group of one molecule and the C-H *ortho* hydrogen of other molecule, for spontaneous resolution between the enantiomers of the same description. This depended on the precise electronic nature of the hydrogen for successful chiral recognition between the two molecules of

some optical description. In an effort to extrapolate this hypothesis we designed molecule **22** and attempted its synthesis and crystallization study. It is assumed that by changing the location of the cyano groups with respect to the oxygen of the oxa[7]helicene framework, we can anticipate some variation in the electropositive nature of hydrogen atoms at C-5 and C-13 which may influence its physical characteristics.

Result and Discussion

3.1 Synthesis of 6,12-dicyano-9-oxa[7]helicene

The synthesis of 6,12-dicyano-9-oxa[7]helicene **22** was started from the Knovaenegel condensation of 4-methoxybenzyl cyanide and benzaldehyde. The olefin **24** obtained was further subjected to photocyclization under the irradiation of 250 W HPMVL to obtain methoxy phenanthrene derivative **25** in good yield. Several known methods of cleavage of methoxy group were employed, where BBr_3 did not show any conversion, LiBr in DMF and HBr in glacial acetic acid offered lower yields. The best results were obtained using $AlCl_3$ in DMF. Homocoupling of 3-hydroxyphenanthrene-10-carbonitrile **26** proceeded smoothly with the standard reagent of Cu-TMEDA to obtain one of the diol **27** regioselectively. It was followed by Pd catalyzed cyclization after due activation of diol **27**. This activation was achieved by converting one of the hydroxyl group to nonafluorobutanesulfonate which was further reacted with $Pd(OAc)_2$, xantphos and Cs_2CO_3 system, where the desired target molecule **22** was obtained in good yield.



Scheme 3.1: Synthesis of 6,12-dicyano-9-oxa[7]helicene

The ^{1}H NMR spectra of **22** indicated not only the formation of the desired angular-angular cyclization but the effect of change in the position of cyano group on the electronic nature of hydrogen at C-5 (& C-13). The hydrogen at C-6 / C-12 in the case of **20** appeared at δ 9.03, s while the protons attached to C-5 / C13 shifted to δ 8.86 (DMSO-d_6).

Another major difference was observed in their solubility. Compound **20** had poor solubility in most of the organic solvents, except DMSO. However, the present isomer **22** was found to be readily soluble in many organic solvents, like dichloromethane, chloroform, 1,2-dichloroethane, toluene, chlorobenzene, and poorly soluble in acetone, ethylacetate, acetonitrile, THF, diethylether and alcohols. By looking at these differences in their solubility, we focused our efforts for its crystallization to study the spontaneous resolution. Various experiments of crystallization were performed for helicene **22**: chlorinated solvents, pure and in combination resulted in the thin hair-like crystals with no enrichment of isomers, amorphous solid was observed in case of chlorobenzene and good quality crystals were obtained only in case of toluene. However, to our disappointment no enrichment of isomers was seen in HPLC analysis.

The photophysical properties of both the compounds were studied. The emission maxima were almost identical for both, difference of 12 nm was observed in their absorption maxima values, which further leads to the difference in their Stokes shift.

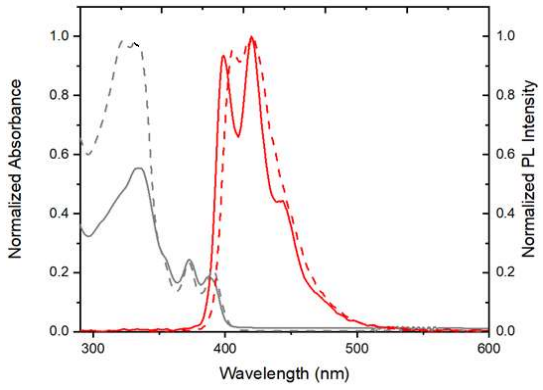
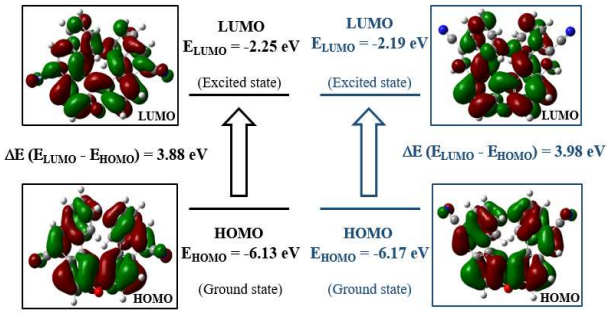


Figure 3.1: UV-Vis (10^{-5} M) and Fluorescence (1.5 X 10^{-6} M) spectra of **20** (dash line) and **22** (solid line), in DMSO

Compound	λ_{abs} (nm)	λ_{ems} (nm)	Stokes shift (nm)
20	323, 334, 372, 391	421	98
22	335, 373, 388	399, 420	85

For helicenes, the frontier molecular orbital (FMOs) distributions and energy gap (HOMO-LUMO gap) are closely associated to electronic and optical properties. Thus the energy of their HOMO and LUMO orbitals were calculated using B3LYP/631-G level of theory.



22 **20**

Compound	Band gap calculated from UV-Vis absorption edge	Theoritical Band gap
22 (Present work)	3.13 eV	3.88 eV
20	3.03 eV	3.98 eV

Thermal properties of the helicene **22** were studied by TGA and DSC analysis. The helicene **22** possessed a high thermal-decomposition temperature (T_d) of 328 °C. It is to be noted that a high T_d value is an asset to OLED applications. DSC scans were performed, where the sample was heated at the rate of 10 °C/min from 40 to 280 °C under N_2 atmosphere. During this heating process, an endothermic peak was not observed which indicates that the melting point of compound **22** is greater than 280 °C. The thermal analysis data indicated high thermal stability of compound **22**.

Chapter – 4

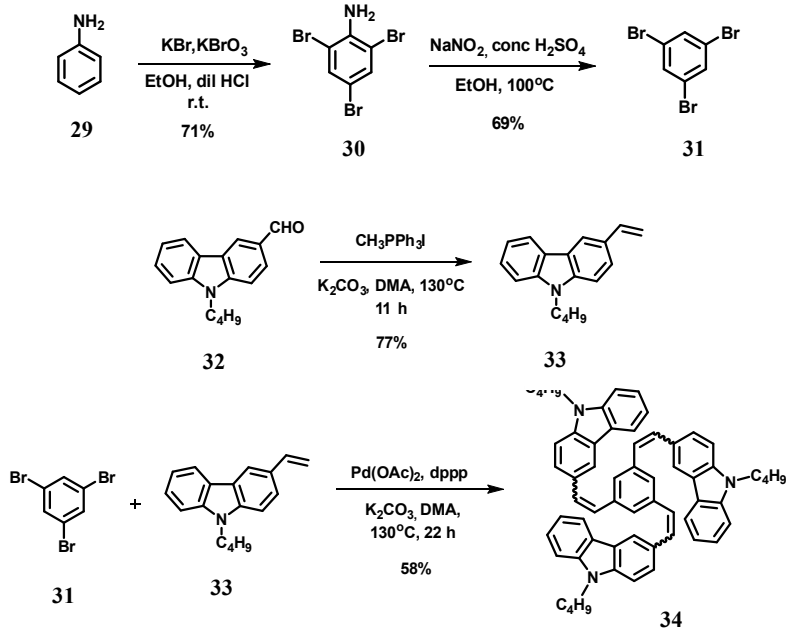
Attempts to synthesize propeller-shaped triple helicenes

The symmetric triple helicenes have become a topic of interest in the field of research as they possess unique characteristic properties along with the structural beauty and have been synthesized by employing different synthetic procedures in the literature. The

potential applications of triple helicenes inspired us to undertake the synthesis of few triple helicenes. There are very few reports in the literature where oxidative photocyclization is used for the synthesis of such molecules. In this chapter we present our efforts towards the synthesis of triple helicenes.

Result and Discussion

Our first attempt was to synthesize triple aza[6]helicene. In order to synthesize the target molecule, tris-olefin derivative 40 was synthesized by the heck reaction between 1,3,5-tribromobenzene and 3-vinyl-*N*-butylcarbazole.

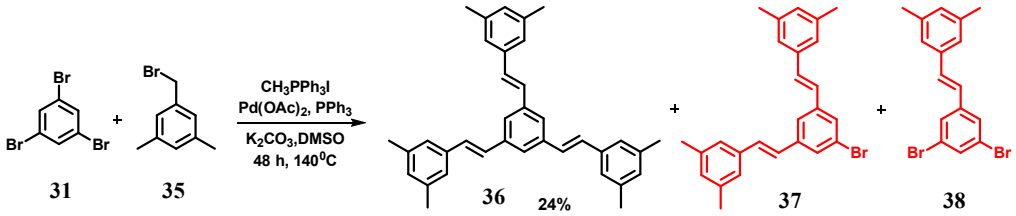


Scheme 4.1: Synthesis of tris-olefin **34**

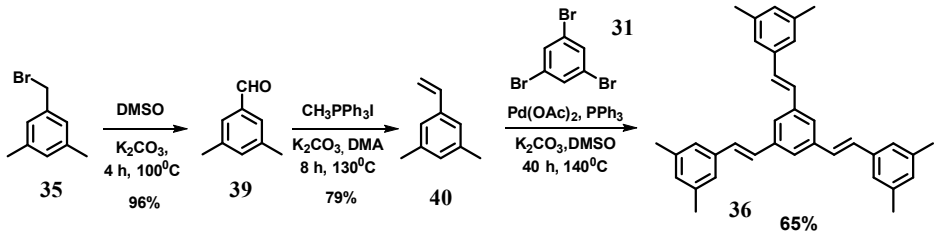
The formation of the olefin **34** was confirmed by its ^{1}H NMR. Only one set of signals in the aliphatic region indicated that the Heck reaction has occurred on all the three possible sites. The presence of a doublet with coupling constant of 16.4 Hz further confirmed its formation. This olefin was then subjected to standard conditions of photocyclization. Reaction was carried out under the presence of 125 W as well as 250 W HPMVL using different concentrations of the starting material, but in none of these cases the desired product was formed. A black sticky mass was obtained, the analysis of which showed the disappearance of the olefinic protons but the other distinct protons to be involved in the photocyclization were still present, although we were unable to predict the exact structure of this molecule. We believe that these difficulties in the photocyclization reaction might

have occurred because of the presence of three bulky carbazole groups on the benzene ring.

Thus, triple 1,3-dimethyl[4]helicene was chosen as our next target molecule, which is comparatively a smaller molecule with lesser steric strain. Smaller helicenes like [4]helicene without any substitution, does not intrinsically adapt the helical topology due to lack of overlap of the terminal rings. They have flat structures. Introducing a methyl substituent in the fjord region sufficiently raises the barrier of racemization by a considerable extent. In order to reach to our target molecule, we first synthesized the tris-olefin **42**. Initially, a one pot oxidation-Wittig-Heck reaction was carried out, where the desired olefin was obtained in lower yield along with the other side products. Then, the stepwise reactions were performed where the 3,5-dimethylstyrene was isolated, purified and then subjected to Heck olefination reaction to obtain the tris-olefin in good yield.

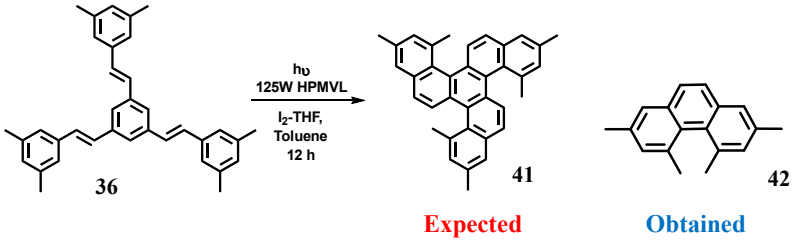


Scheme 4.2: One-pot synthesis of tris-olefin **36**



Scheme 4.3: Stepwise synthesis of tris-olefin **36**

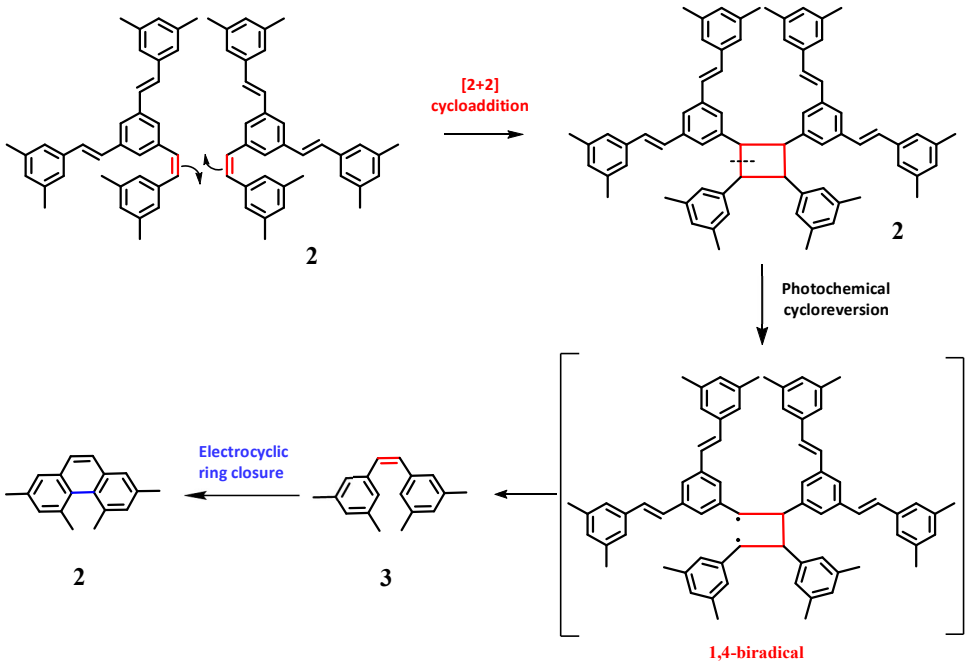
The formation of this olefin 42 was confirmed by its 1H NMR which was same as that in the literature. This olefin was subjected to photocyclization under the irradiation of 125 W HPMVL. The reaction resulted into the formation of 2,4,5,7-tetramethylphenanthrene 49 instead of our expected product.



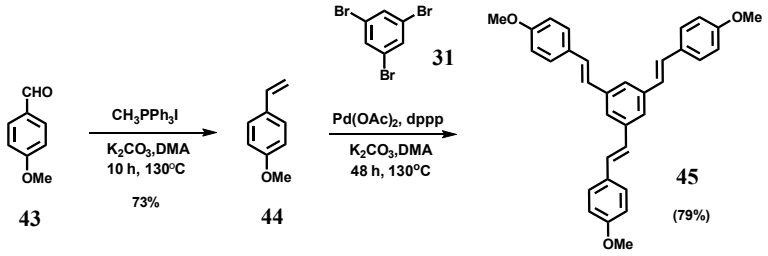
Scheme 4.3: Attempted photocyclization of **36**

The formation of **42** was confirmed by single crystal X-ray analysis. The possible mechanism for the formation of this unusual product was proposed.

Possible mechanism for the formation of **42**

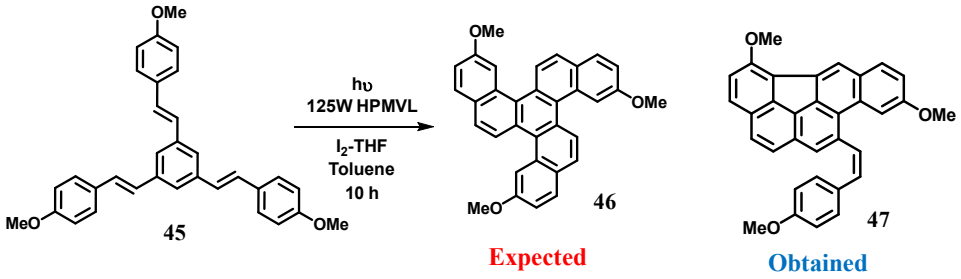


Later, another such target molecule was designed where a [4]helicene **46** was one of the desired intermediate. Here, triple olefin **45** was first synthesized. 4-methoxybenzaldehyde was subjected to Wittig reaction to form 4-methoxystyrene which was further reacted with 1,3,5-tribromobenzene in Heck olefination conditions to obtain the desired olefin **45** in good yield.



Scheme 4.4: Synthesis of tris-olefin **45**

The formation of this olefin **45** was confirmed by the ^{1}H NMR. This olefin on cyclization resulted in some unusually cyclized product **47** instead of the desired expected product **46**.



Scheme 4.5: Attempted photocyclization of **45**

The detailed analysis of this ^{1}H NMR, indicated the formation of compound **47**. Moreover, the mass analysis and the HRMS were also in favor of formation of **47**. However, we were unsuccessful in obtaining a single crystal of compound **47**, structural parameters were obtained by Computational study. Also, we were unsuccessful in predicting the mechanism for the formation of this unusual product **47**.

CONCLUSION

In **Chapter 2**, we have successfully synthesized a variety of aza[*n*]helicene based chiral amines. In **Chapter 2A** we have presented the synthesis of amino derivatives of aza[6]helicene where the basic helical skeleton was built by photochemical cyclodehydrogenation as the key step. The 2-amino-5-aza[6]helicene was converted to diastereomeric carbamate by reaction with (R)-(-)-menthyl chloroformate, which could be physically separated by column chromatography. The optically pure amines were regenerated and their chiroptical properties were measured. The diastereomeric derivatives were analyzed by CD spectroscopy, while the 2-nitro-5-aza[6]helicene and 2-*N*,*N*,-dimethylamino-5-aza[6]helicene were characterized by single crystal X-ray diffraction analysis. In **Chapter 2B** we have established a new method for the formation of optically pure helicene with methyl substituents from the corresponding diastereomeric helical diamine via selective removal of the (S)-(-)-α-methylbenzylamine moiety. Generally, the cleavage of chiral auxiliary from the helical diastereomers leaves the helicenes with the functional group intact, whereas in this method we obtained methyl substituents by cleaving the chiral attachment. The specific optical rotations were measured for the separated diastereomers and for (*P*)-(+)- and

(*M*)-(-)- isomers. The isomers of 5,13-dimethyl-aza[7]helicene were further analyzed by CD spectroscopy. The diformyl derivative of aza[7]helicene, a precursor of the helical diamine was synthesized and characterized by single crystal X-ray diffraction analysis.

In **Chapter 3** we have presented the synthesis and study of 6,12-dicyano-9-oxa[7]helicene. The helicene was synthesized by Pd catalyzed intramolecular cyclization of the activated bis-phenanthrol derivative. With the aim to study spontaneous resolution, various experiments of crystallization were performed and the crystal obtained in toluene was studied in detail by single crystal X-ray diffraction. However, our efforts to effect separation of isomers by spontaneous resolution did not meet with success. In comparison with its analogue 5,13-dicyano-9-oxa[7]helicene, we have observed changes in the overall solubility of the compound, its photophysical properties and shifting of signals in the ^{1}H NMR. The synthesized helicene also showed good thermal stability. Its geometry optimization was carried out using B3LYP/6-31G level of theory and HOMO-LUMO energy gap was also calculated.

The attempts for the synthesis of some propeller-shaped triple helicenes by oxidative photocyclization method are discussed in **Chapter 4**. Our first target was to synthesize triple aza[6]helicene, where the tris-olefin precursor was synthesized successfully, but further we failed to synthesize our target molecule. We thought that the steric strain caused by the bulky carbazole group might have hindered the usual cyclization process. So, the triple 1,3-dimethyl[4]helicene, which is comparatively a smaller moiety with lesser steric strain was chosen as our next target molecule. In the process of synthesizing this target molecule, we obtained an unexpected compound which was confirmed by single crystal X-ray analysis. The formation of this compound was explained by proposing a mechanism. Lastly, attempts to synthesize a triple helical oxazine are also discussed, where an unsually cyclized product was obtained.

PUBLICATIONS

1. Synthesis and Study of Photophysical Properties of 6,12-Dicyano-9-oxa[7]helicene.
   Esha H. Bhalodi, Vraj R. Shah, Raymond J. Butcher and Ashutosh V. Bedekar *ChemistrySelect* **2021**, *6*, 13514-13519.

2. Synthesis and resolution of 2-amino-5-aza[6]helicene.
   Esha H. Bhalodi, Krupa N. Patel and Ashutosh V. Bedekar *Tetrahedron* **2022**, *114*, 132761-132767.

3. Accessing Optically Pure 5,13-Dimethylaza[7]helicene via Selective Removal of α-Methylbenzylamine Chiral Auxiliary by Catalytic Hydrogenation Reaction.
   Esha H. Bhalodi, Raymond J. Butcher and Ashutosh V. Bedekar *Tetrahedron* **2023***, 145,* 133606-133611.

4. A serendipitous formation of 2,4,5,7-teramethyl phenanthrene, in an attempted synthesis of a symmetrical, triple 1,3-dimethyl[4]helicene.
   Esha H. Bhalodi, Ashutosh V. Bedekar *Tetrahedron Letters* **2023***, 132,* 154822-154825.