



SYNTHESIS, CHARACTERIZATION AND SPECTROPHOTOMETRIC STUDY OF [5] AZA-HELICENE DERIVATIVES

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Abstract

Literature search indicated that the preparation of helical carbazole has been reported by Shin group but the synthetic route is entirely different and only one such derivative has been reported. It was therefore decided to attempt this route for the synthesis of pentacyclic carbazole-based helicenes. It was realized that these molecules were unlikely to yield sufficiently crowded helicenes for possible separation and chiral application. It was therefore decided to restrict the studies to synthesis of carbazole based pentahelicene derivatives and their luminescence properties. In this paper the successful preparation and characterization of aza [5] helicene using palladium mediated double N-arylation reaction of BINOL Triflate and Aniline derivatives has been presented.

Keywords: Carbazole-based Helicenes, Pentahelicenes, BINOL-TRIFLATE, Double N-arylation, Aza[5] Helicene

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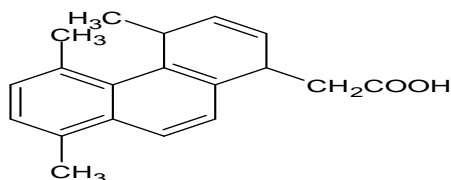
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1. Introduction

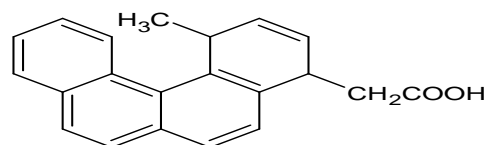
The term helical is derived from the word helix, which comes from the Greek word for spiral. Helicity is ubiquitous in nature and pervades every sphere of day-to-day life. Historically, helical structures have elicited tremendous interest as aesthetic marvels. In 1947, Newmanns and Hussey succeeded in resolving 4,5,8-



[1]
Figure 1

Helicenes are the polycyclic aromatic compounds that, due to an overlapping of their terminal aromatic ring, possess a helical conformation. As a result of the helical conformation they form a pair of conformational enantiomers, which upon resolution exhibit extremely large specific rotation of the order of 1000° to 100000° . The magnitude of helicene's specific rotation is known to increase nonlinearly with an increase in the number of fused aromatic rings within the helicene structure. When the ring number of helicene is more than six, the inter-conversion between the helicities requires high temperature because of steric crowding. Furthermore, helicenes are known to racemize thermally and half-life for racemization is known to increase with increasing helicene size. Of all the nature's structures, there is arguably none more beautiful or widely scrutinized than the helix. A helix is a geometric motif, which is found in nature as well as in artificial structures. Helicity can be observed in the spiral arms of galaxies or in microscopic structures such as right or left-handed quartz as well as in human art and architecture. In chemistry or biochemistry helicity is present in various systems. Amylase is a macromolecule with a helical structure that contains about six glucose units per helical turn. Deoxy-ribonucleic acid (DNA) exists as double helix in which the two strands are connected by hydrogen bonds between

trimethylphenanthrene-1-acetic acid (1) and correctly established its optical rotation to non-planarity enforced by the crowding of the 4,5-methyl substituents. The molecule had low optical stability and racemized in a matter of minutes. However, much more stable molecule (2) of this type were subsequently synthesized and resolved.

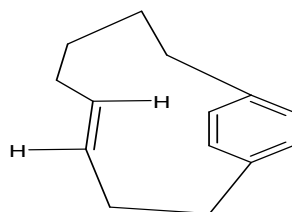


[2]
Figure 2

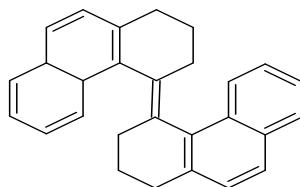
complementary bases. It stores and transmits our genetic makeup and therefore is essential for life. Peptides can adopt α -helical structure or form larger helical arrays as, for example, found in the collagen triple helices. Various polypeptide systems exist in helical forms. Protein α -keratin too exists as α -helix

Within the realm of organic chemistry there are also many examples of helical molecules, some of which are illustrated in figure 3-13 (Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 8, Figure 9, Figure 10, figure 11-12, figure 13).

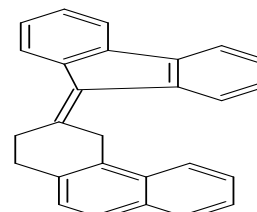
All the compounds illustrated are chiral and form pair of enantiomers, but their chirality is not due to a configuration around a chiral carbon, as with more traditional enantiomers. Rather, the illustrated compounds all form a pair of helical enantiomers, which because of confirmation they are forced into due to the presence of steric repulsions within the molecule; they are so called conformational enantiomers. Representatives of these class of chiral compounds include aryl alkene, triphenylenicenes, tetraphenylnicenes, helicenes, heterohelicenes and bihelicenes. All the molecules illustrated in figure have been synthesized, resolved, their optical rotations determined. In some cases their absolute configurations determined by X-ray crystallography.



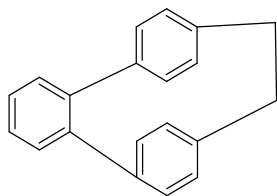
[3]
Figure 3



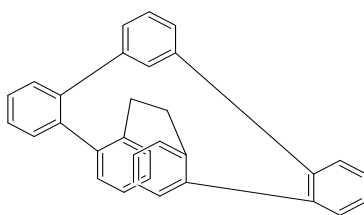
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Figure 4



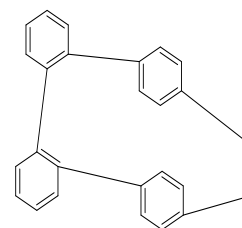
[5]
Figure 5



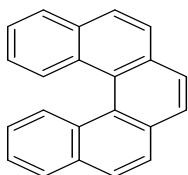
[6]
Figure 6



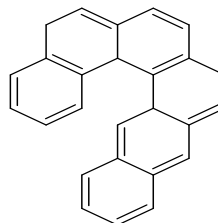
[7]
Figure 7



[8]
Figure 8

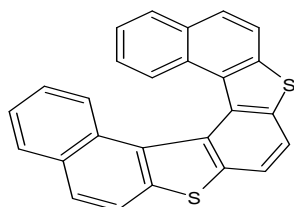


[9]

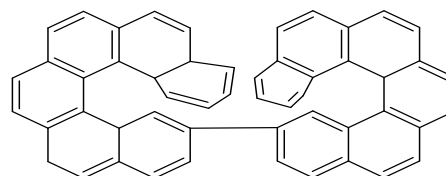


[10]

Figure 9-10

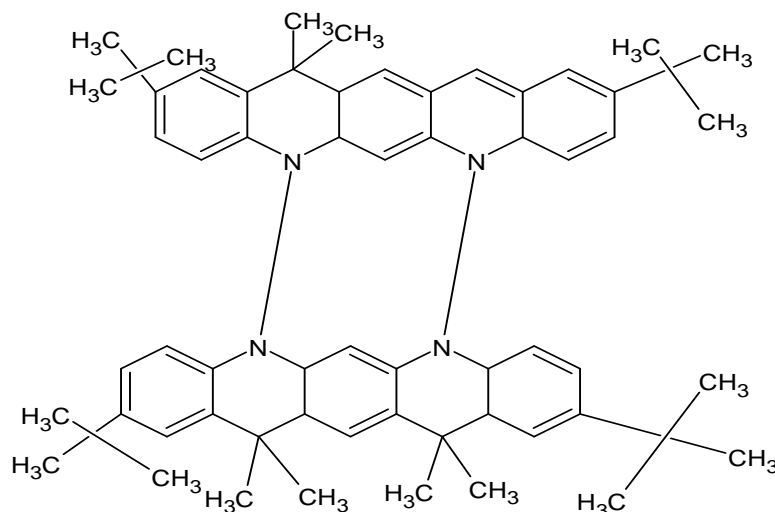


[11]



[12]

figure 11- 12



[13]
figure 13

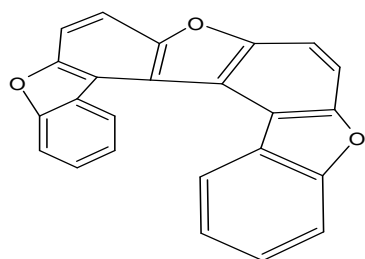
Double helicenes are also being studied extensively. An efficient synthesis of a chiral α -conjugated dihydrazone in which two [5] helicene-like fragments are annelated in their mid-sections to give a conjugated double helicene structure, has been reported. These chiral α -conjugated conjoined *Eur. Chem. Bull.* **2023**, 12(Special Issue 5), 6378 - 6387

double helical were reported to possess remarkable configurational stability, (K., Rajca, Pink, & Rajca, 2005)(Shiraishi K.,; Rajca, A.; Pink,M.; Rajca ,S.,“ π -conjugated conjoined double helicenes via a sequence of three oxidative CC- and NN-homocouplings” , *J. Am. Chem. Soc.*, 127, 9312-6380

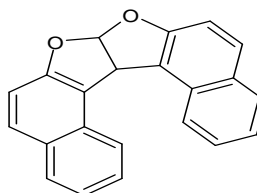
9313,2005.. The possibility of constructing helicenes with five-membered heterocycles is obvious if we compare the geometry of benzene with thiophene, furan and pyrrole. Most important in this respect are the angles between the two formal carbon-carbon double bonds which can take part in the annellation to form helicenes since the sum of these angles of all fused rings is an approximate measure for the overcrowding and therefore for the stability of the helix configuration. To get a full turn of a helix this sum has to be 360° as is relaxed in hexahelicenes but which is at least in principle possible by proper annellation of eight thiophene rings.

Helicenes are of two major types depending on the structure of the molecule, they are all benzene-helicenes and heterohelicenes. All benzene helicenes are polycyclic aromatic compounds that, due to an overlapping of their terminal aromatic rings, possess a helical conformation. Moreover, heterohelicenes are the polycyclic aromatic compounds containing one or more heteroatoms in the ring system, due to an overlapping of their

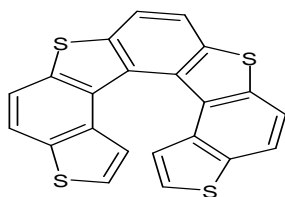
terminal aromatic rings, possess a helical conformation. Within the class of heterohelicene, there are three major subdivisions Oxahelicene, Thiahelicene and Azahelicene which corresponds to helicenes containing the heteroatoms Oxygen, Sulphur and Nitrogen respectively. The synthesis of all these is relatively difficult, usually requiring photochemical or radical reactions, which result in low yield and multiple side products. The synthesis of functionalized helicenes even more difficult and has thus inhibited the exploration of these systems as functional materials. Recently Katz and co-workers (Thomas J., 2000) (Thomas J., Katz Prof., "Syntheses of Functionalized and Aggregating Helical Conjugated Molecules", *A journal of the German Chemical Society*, 39(11).1921-1923,2000) reported a new, high yielding synthesis of functionalized carbohelicenes that does not require radical or photo-cyclization. This work represents the milestone for helicenes as a viable source for interesting functional materials. Representative examples of all three classes of heterohelicenes have been listed (figure 24, figure 35, figure 46)



OXAHELICENE
figure 24



THIAHELICENE
figure 35



AZAHELICENE
figure 46

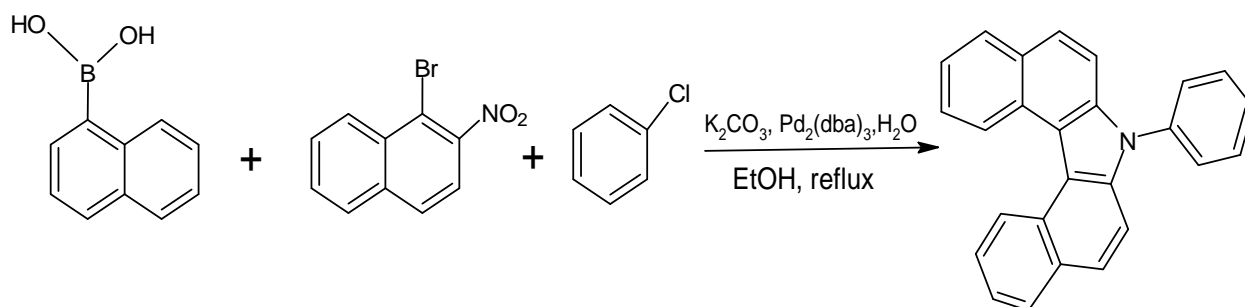
Newman, Lutz and Lednicher (Melvin S. Newman, 1955) (Melvin S. Newman, Wilson B. Lutz and Daniel Lednicher, "A new reagent for resolution by complex formation; The resolution of Phenanthro-[3,4-c] Phenanthrene", *J. Am. Chem. Soc.*, 77, 12, 3420–3421, 1955.) gave the first experimental proof of helicene in 1955. The brilliant resolution of [6] helicene was accomplished using an optically active complexing agent (TAPA) specially synthesized for this purpose. Helicenes have been resolved as ion via its D(-) dibenzoyltartrates, [6] helicene-2-carboxylic acid by column chromatography of its methyl ester, 2-bromo [6] helicene with TAPA. Heterohelicenes containing carbazole system has been partially resolved into enantiomers by column chromatography on acetylated cellulose. X-ray crystallographic data of hexahelicenes and of higher helicenes confirmed the helical nature of molecules. In hexahelicenes the interplanar angle of the terminal rings is 58.5° . Hexahelicene is resolved to the extent of 20% ee, enantiomerically pure crystals can then be obtained from the solution. While in case of [7], [8], [9] helicenes the conglomerates can be separated by repeated recrystallization after initial seeding with handpicked crystal. Among these previous examples only few demonstrated the Pd mediated synthesis of azahelicenes with pyrrole ring in spite of their potential to alter the molecular properties. The [5] aza helicene reported as an electroluminescent compound which prompted us to develop a generalized approach for the same (Shin & Hyo) (Shin; Hyo, *N.PCT Int. Appl.* 2010114264). Synthesis of aza helicenes from ortho dihydroxy atropisomers was reported separately by two research groups (Nakano, Hidehira, Takahashi, Hiyama, & Nozaki, 2005) (Nakano, K.; Hidehira, Y.; Takahashi, K.;

Hiyama T.; Nozaki K., *Angew. chem. Int. Ed.*, 44, 7136) (Kelgtermans, Dobrz, & W., 2012) (Kelgtermans, H.; Dobrz, L.; Dehaen W., *Organic letters*, 6, 1500, 2012). The method involved palladium catalyzed reaction of triflates of atropisomers with aniline in presence of phosphine ligand. The fully conjugated helical structures offer several possibilities due to smaller energy gap between HOMO-LUMO as well as proximity induced charge transfer processes for a suitably substituted helicenes, the natural claw like structure can be suitable for a molecular recognition and if sufficiently non-planar then they can be ideal candidates for several types of chiral processes. The ortho fused helical molecules can have many potential applications such as: Asymmetric catalysis ((a) Takenaka, Sarangthem, & Captain, 2008) ((b) Chen & Takenaka, 2009) (a) Takenaka, N.; Sarangthem, R.S.; Captain, B. *Angew. Chem. Int. Ed.*, 47, 9708, 2008; (b) Chen, J.S.; Takenaka, N. *Chem. Eur. J.* 15, 7268, 2009, Dye materials ((a) Ooyama, et al., 2010) (Y., Ishii, Kagawa, Imae, & Harima, 2007) (a) Ooyama, Y.; Ito, G.; Fukuoka, H.; Nagano, T.; Kagawa, Y.; Imae, I.; Komaguchi, K.; Harima, Y.; *Tetrahedron*, 66, 7268, 2010.; (b) Ooyama Y.; Ishii, A.; Kagawa, Y.; Imae, I.; Harima, Y., *New. J. Chem.*, 31, 2076, 2007., Self-assembly (Murguly, McDonald, & Branda, 2000) (Murguly, E.; McDonald, R.; Branda, N.R. *Org. Lett.*, 2, 3169, 2000.), Molecular recognition (Ibon, Fernando, Jose, & Detlef, 2010) (Ibon, A.; Fernando, B.; Jose, E.; Detlef, S. *Tetrahedron: Asymmetry*, 21, 962, 2010) and biological applications (Passeri, et al., 2009) (Passeri, R.; Aloisi, G.G.; Elisei, F.; Latterini, L.; Caronna, T.; Fontana, F.; Sora, I.N., *Photochem. photobiol. Sci.* 8, 1574, 2009).

2. Experimental

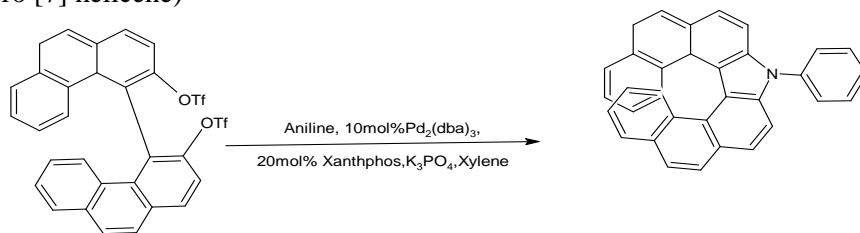
2.1. Some of the reported methods for Pd mediated Azahelicene synthesis are as follow :

1) Synthesis of novel electroluminescent compounds (Shin & Hyo) (Scheme 1: Synthesis of novel electroluminescent compounds)



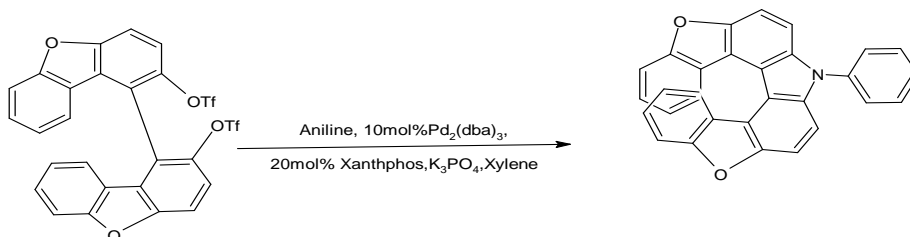
Scheme 1: Synthesis of novel electroluminescent compounds

2) Synthesis of Hetero [7] helicene (Nakano, Hidehira, Takahashi, Hiyama, & Nozaki, 2005)(Scheme 2: Synthesis of Hetero [7] helicene)



Scheme 2: Synthesis of Hetero [7] helicene

3) Synthesis of dioxo-aza [7] helicene (Kelgtermans, Dobrz, & W., 2012)(Scheme 3: Synthesis of dioxo-aza [7] helicene)



Scheme 3: Synthesis of dioxo-aza [7] helicene

2.2. Synthesis of BINOL

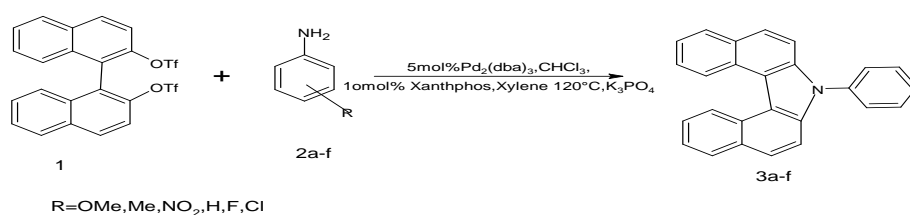
β -naphthol (5g, 34.72mmol) and water (210ml) was taken in a two necked R.B (500ml) attached with reflux condenser. The reaction mixture was then heated till the oily suspension formed. In that, Ferric chloride (6.195g, in 20ml water) was added and further heated for 10 minutes. The hot reaction mixture was then filtered, washed with boiling water recrystallized from toluene. The obtained product was then dried and weighed. The yield was found to be 55% (5.46g) and melting point was 216°C.

2.3. Synthesis of BINOL TRIFLATE

BINOL (1g, 3.49mmol) was taken in single neck R.B (100ml). To that dry DCM (30ml) and pyridine (0.62ml) was added. The reaction mixture was surrounded by ice-salt mixture to attain 0°C temperature. After some time when the reaction mixture was attained a temperature 0°C, Triflic anhydride (1.546ml) was added drop wise and reaction mixture allowed to stir for one day. The reaction mixture was then extracted using ethyl acetate (50ml) and washed the organic layer by 1M HCl (15ml) thrice, then the organic layer was dried

by passing through the sodium sulphate. The crude product obtained by concentrating the organic layer and purified using column chromatography, petroleum ether was an eluent. The yield obtained was 1.72g .90%.

2.3. General procedure for synthesis of [5] Aza-helicene derivatives (Scheme 4: Synthesis of Aza [5] Helicene Derivatives) BINOL triflate (0.5g, 0.9083mmol), K_3PO_4 (0.289g), $Pd_2(dba)_3$ (47mg, 5mol%), Xantphos (52.55mg, 10mol%) and Xylene (20ml) was taken into two necked dry R.B flask (100ml) attached with air condenser and nitrogen inlet. In the reaction mixture added respective aniline derivatives (1.5eq), allowed to stir at 120°C for 5 days. After that the reaction mixture was cooled down to ambient temperature and was then diluted with ethyl acetate (50ml). The resulting mixture was washed with 1M aqueous HCl (15ml X 2), dried over anhydrous Na_2SO_4 , concentrated under reduced pressure. The resulting crude residue was purified by silica gel column chromatography with hexane as an eluent. The scheme for the synthesis was as follow:



Scheme: Synthesis of Aza [5] Helicene Derivatives

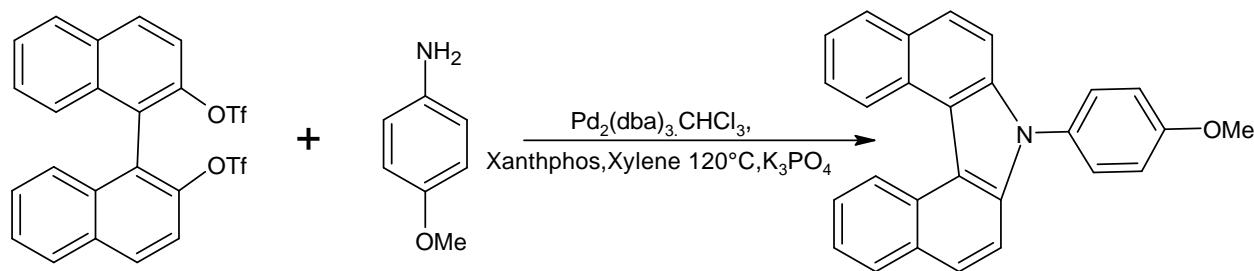
Scheme 4: Synthesis of Aza [5] Helicene Derivatives

3. Result and Discussion

3.1. Optimization of catalyst loading

The optimization of the catalyst loading $\text{Pd}_2(\text{dba})_3$ CHCl_3 and Xanthphos ligand has shown in **table 1**

(Table 1: For catalyst and ligand loading) for the reaction of Binol triflate and p-Anisidine (Scheme 5: Catalyst and Ligand loading)



Scheme 5: Catalyst and Ligand loading

Table 1: For catalyst and ligand loading

Sr. No.	Catalyst loading $\text{Pd}_2(\text{dba})_3$ CHCl_3	Ligand loading Xanthphos	Time	Yield(%)
1	2.5mol%	5mol%	7 days	30
2	5mol%	10mol%	5 days	40
3	10mol%	20mol%	3 days	25

3.2. NMR and Electronic spectra of 3a-f

Chemical shifts in NMR are a good indicators of comparative electron densities at a different positions in the molecule. Based on the ortho-fused nature of the molecule and the proximity of the terminal rings it was expected that the inner protons present at C-1 and C-13 should experience additional deshielding, hence were expected to exhibit downfield signals. Indeed when the ^1H -NMR was examined for the compound 3a, the

following signals were obtained. ^1H NMR(DMSO) δ 9.045 (d, $J=7.5\text{Hz}$, 2H), 8.043(d, $J=6.9\text{Hz}$, 2H), 7.95 (d, $J=8.4\text{Hz}$, 2H), 7.81-7.032 (m, 6H), 6.85 (d, $J=7.2\text{Hz}$, 2H), 6.56 (d, 2H); It can be seen that the most deshielded signal was obtained at δ 9.045 can be attributed due to the protons C-1&C-13. This also indicates the proximity between the terminal rings. (Figure 17: Numbering system of Aza Helicene)

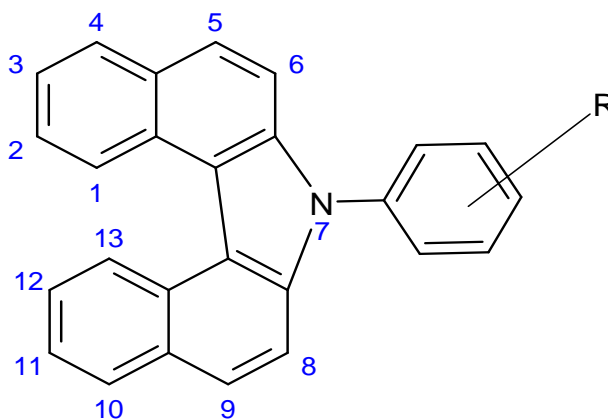


Figure 17: Numbering system of Aza Helicene

3.2.1.Characterization data for (3a): yield (0.135g, 40%); mp=150°C; ^1H NMR(DMSO) δ 9.045 (d, $J=7.5\text{Hz}$, 2H), 8.043 (d, $J=6.9\text{Hz}$, 2H), 7.95 (d, $J=8.4\text{Hz}$, 2H), 7.81-7.032 (m, 6H), 6.85 (d, $J=7.2\text{Hz}$, 2H), 6.56 (d, 2H); IR (KBr) 3054, 2922, 1601, 1500, 1421, 1246, 1071, 814, 740 cm^{-1} , λ_{max} 443nm.

3.2.2. Characterization data for (3c): yield (0.161g, 45%); mp=158°C; ^1H NMR(CDCl_3) δ 9.19 (d, $J=7.8\text{Hz}$, 2H), 8.09(d, $J=6.8\text{Hz}$), 7.769 (d,

$J=6.3$ Hz), 7.623-6.51 (m, 7H); IR (KBr) 3054, 2922, 1600, 1500, 1224, 1071, 813, 716 cm^{-1} , λ_{max} 443nm.

3.2.3.Characterization data for (3d): yield (0.123g, 38%); mp = 146°C; ^1H NMR(CDCl_3) δ 9.19 (d, $J=8.4\text{Hz}$), 8.10 (d, $J=7.8$ Hz, 2H), 7.99 (d, $J=9\text{Hz}$, 2H), 7.87 (d, $J=8.7\text{Hz}$, 2H), 7.79-7.08 (m, 4H), 6.93 (d, $J=9.3\text{Hz}$, 2H), 6.6 (m, 2H), 2.3 (s, 3H); IR (KBr) 3054, 285, 1600, 1500, 1421, 1246, 1071, 941, 740 cm^{-1} , λ_{max} 443nm.

3.2.4.Characterization data for (3e): yield (0.123g ,38%); mp=160⁰C; ¹H NMR (CDCl₃) δ 9.2 (s, 2ArH), 8.17 (d, J=9.6 Hz, 2H), 8.03 (d,J=7.8Hz,2H),7.65-6.64(m,10H); IR (KBr) 3053, 2923, 1603, 1505, 1455, 1418 , 1329, 1249, 1205, 1136,933,759 cm⁻¹, λ_{max} 444nm.

3.2.5.Characterization data for (3f): yield (0.093g ,30%); mp=138⁰C; ¹H NMR (CDCl₃) δ 9.19 (d,J=9Hz,2H), 8.10 (d, J=7.8Hz, 2H), 7.99 (d, J=9Hz, 2H) ,7.87 (d, J=9Hz,2H), 7.79-7.08 (m, 4H), 6.93 (d, J=9Hz,2H), 6.66 (m,3H); IR (KBr) 3053, 2918, 1600, 1499, 1421, 1246, 1071, 813, 717 cm⁻¹, λ_{max} 443nm.

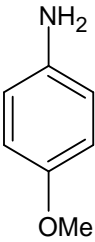
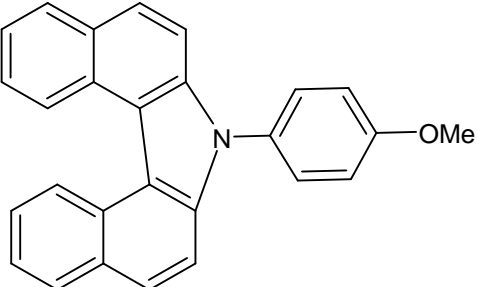
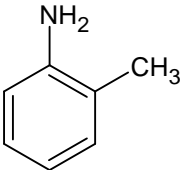
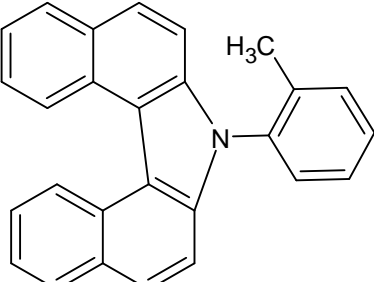
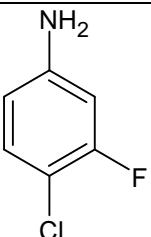
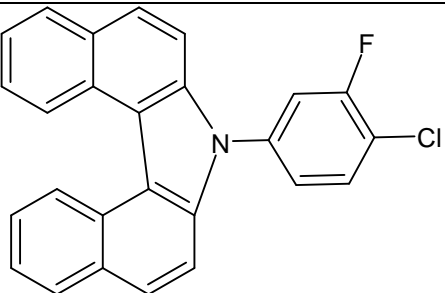
The Pd catalyzed coupling reaction for synthesis of [5] Aza helicene for various aniline derivatives is shown in **Table 2** (Table 2: The Pd catalyzed coupling reaction for synthesis of [5] Aza helicene for various aniline derivatives). The UV spectrum exhibited λ_{max} at 443nm. The λ_{max} for carbazole is merely 335nm. The higher value of λ_{max} for the compound also indicates a HOMO with enhanced energy. This could also result in higher reactivities

compared to carbazole and a possibility of use of this in certain types of photonic materials.

3.3.Fluorescence studies

To begin with UV spectrum of all substrate of concentration (1X10⁻⁵ M) was recorded and an absorbance maximum was found out. This provided the wavelength of excitation for recording the fluorescence readings. Next the fluorescence spectrum of concentration (1X10⁻⁵ M) were recorded using Perkin Elmer LS 55 fluorescence spectrum and an emission maximum was found out. The observed stokes shift was calculated and shown in the **Table 3** (Table 3: Stoke's shift). These compounds have a natural groove and hence there is a possibility of these compounds exhibiting molecular recognition with some guest molecules. A popular mode of following molecular recognition is through fluorescence activity. It is worthwhile to note that carbazoles are largely fluorescence inactive. The compounds when studied were found to exhibit fluorescence with a moderate stoke shift.

Table 2: The Pd catalyzed coupling reaction for synthesis of [5] Aza helicene for various aniline derivatives

Sr.No.	Substarte (2a-f)	Aza-helicenes (3a-f)	Yield
a)			40
b)			Nil
c)			45

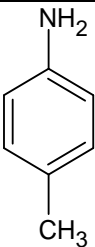
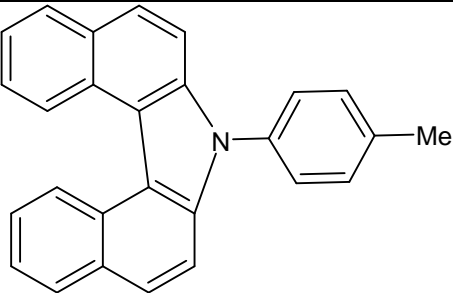
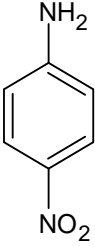
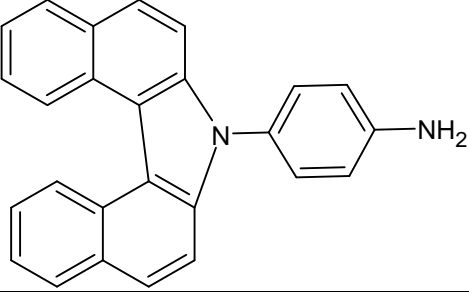
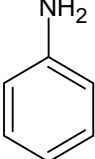
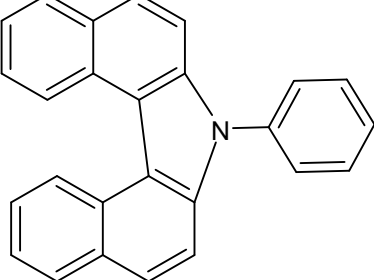
d)			38
e)			35
f)			30

Table 3: Stoke's shift

Substrate	λ_{ex} (nm)	λ_{em} (nm)	Stoke's shift (nm)
3a	415	449	34
3c	415	449	34
3d	415	449	34
3e	415	449	34
3f	415	449	34

4. Conclusion

The generalized palladium catalyzed double N-arylation approach has been developed for the first time for synthesis of [5] Aza helicene derivatives and these were successful for meta and para substituted derivatives of aniline but not for ortho substitute derivative. Chemical shifts in $^1\text{H NMR}$ indicates the change in chemical shifts of carbazole due to proximity of the terminal rings shows downfield signals for inner protons at C-1 and C-13 and shielded signals for the protons at C-6 and C-8. Spectral studies shown the higher value of λ_{max} values around 443nm indicates a HOMO with enhanced energy. This could also results in higher reactivities compared to the carbazole and a possibility of use of this in certain types of photonic materials The synthesized molecules were found to exhibits fluorescence with a moderate Stoke's shift and because of natural groove they can be useful for the molecular recognition with some guest molecules (J.B.Patil et al, 2016)J.B. Patil et al,

“Synthesis and fluorescence studies of benzothiazole and 4,5-diarylimidazole substituted 2H-1- benzo/naphtho pyran-2-one”, *Indian Journal of Chemistry*,55(b), 387-396, 2016.)

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