



Synthesis of carbazole derived aza[7]helicenes



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ABSTRACT

Synthesis of four derivatives of symmetrical aza[7]helicenes is achieved by I₂-THF mediated photocyclization of corresponding bis-styryl derivatives. The cyclization furnished the desired angularly fused aza-helicene in moderate yields. The structures are established by NMR spectroscopy and single crystal X-ray analysis for the difluoro derivative. The series of synthesized aza[7]helicenes showed remarkable thermal stability as indicated by DSC analysis.

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Molecules possessing *ortho*-fused aromatic rings, acquire a unique shape in order to release the internal strain. This type of molecular arrangement acquires helical structure and shows stereoisomerism. The helical molecules have attracted much attention in recent years due to some unique properties associated with their structure.¹ The efficient delocalization of π -electrons and non-planarity of the structure in helicenes enable them to be stable to strong acids and high temperature. Applications of helical molecules cover a wide range in fields of material science,² asymmetric synthesis and catalysis,³ as molecular motor,⁴ in biology⁵ etc. A number of approaches have been developed for the synthesis of these screw shaped molecules due to efforts required to overcome the inherent steric factors or steric crowding. Therefore, the synthesis of new helical molecules remains an exciting challenge and a rewarding endeavor.

Helical or helicene like molecules possessing heteroatoms are of considerable interest due to the additional properties. Although considerable attention has been devoted to the thia-helicenes,⁶ the aza-helicenes, containing one or more nitrogen atom, have also gained interests.⁷ Most of these aza-helicenes or aza-helicene like compounds are derivatives of pyridine, but only a few analogues of pyrrole (pyrrolohelicenes) are studied. The first example, pyrrolo[5]helicene **I** (Fig. 1), was reported by Meisenheimer and Witte,⁸ way back in early 20th century, which was followed by a report on the synthesis of pyrrolo[6]helicene **II** by Fuchs and Niszel.^{9a}

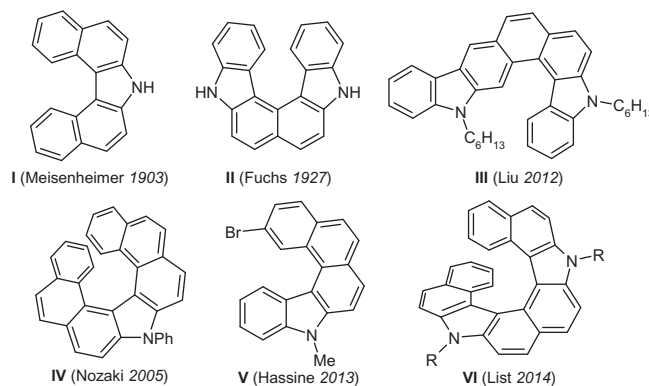


Figure 1. Known carbazole-based azahelicenes.

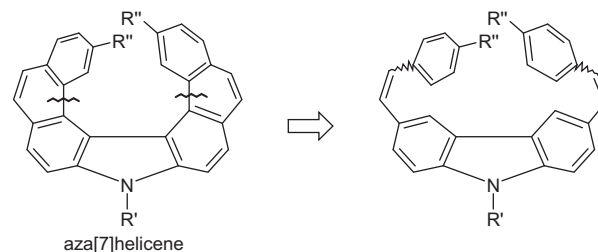


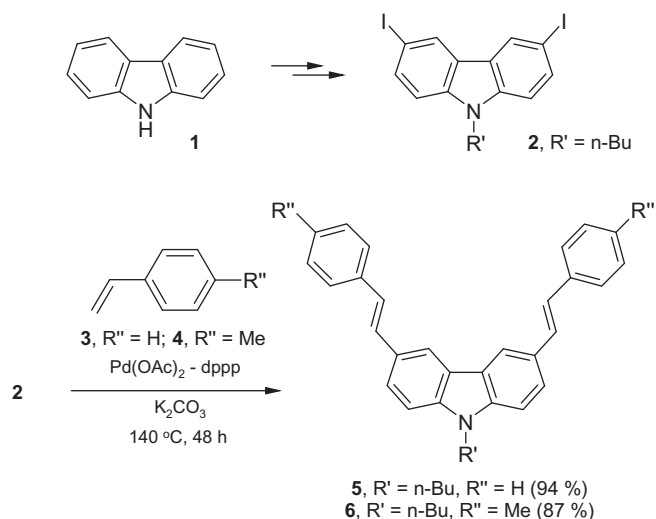
Figure 2. Retrosynthetic scheme for aza[7]helicene

Later the same type of compound was synthesized and resolved by Pischel et al.^{9b} Lately another derivative **III** was synthesized

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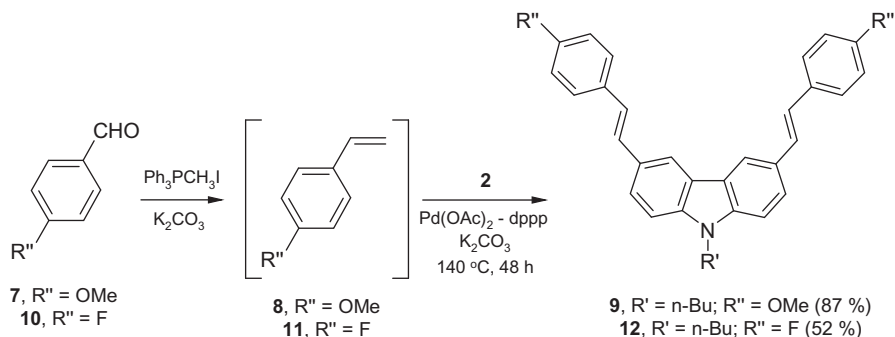
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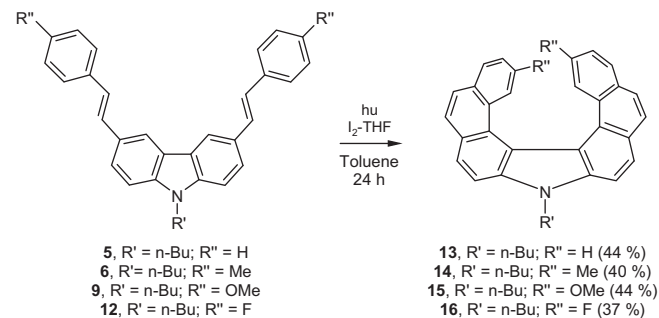
Scheme 1. Synthesis of (*E,E*) 3,6-distyryl-9-butyl-9H-carbazoles by Mizoroki–Heck reaction.

and investigated as deep-blue-emitting OLED by Liu et al.¹⁰ This particular diaza[7]helicene consists of two linear and angularly cyclized units of carbazole moiety. However, the angularly cyclized aza[7]helicene **IV** has been previously reported by Nozaki.¹¹ The synthesis was independently reported by Pd catalyzed coupling reactions. Another pyrrolo[5]helicene **V** system was recently prepared by Hassine et al.¹² which consisted of an unsymmetric unit of carbazole. Very recently List and co-workers¹³ have efficiently synthesized bis-azahelicene **VI**, along with other derivatives with an elegant use of organocatalysts for double Fischer indolization-oxidation protocol. The synthesis has also been extended to asymmetric version by using chiral phosphoric acid catalyst. Considering the large interest in the field of helical molecules these form a small group of examples of pyrrole based heterohelices and the area still remains scarcely explored.

In continuation of our work on photocyclization¹⁴ and helicene-like molecules,^{15,16} this Letter presents the synthesis of symmetrical aza[7]helicenes. The retrosynthetic plan to access these molecules indicates the possible option of oxidative double photocyclization of stilbene type analogues of carbazole (Fig. 2). The required starting material for the photoreaction can be easily prepared by Mizoroki–Heck reaction of 3,6-diiodo-9-alkyl-9H-carbazole with appropriate styrene. By choosing a suitable styrene, different functional groups can be introduced on aza[7]helicenes and can be a general preparative method. The earlier synthesis of similar aza[7]helicene was performed by different methods of cyclization.¹¹



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



Scheme 3. Photocyclization of distyryl carbazoles.

The required starting material 3,6-diiodo-9-butyl-9H-carbazole **2** was prepared from carbazole **1** by known procedures.¹⁷ To increase the solubility of resultant aza[7]helicene the *n*-Bu group was selected.¹⁸ It was then subjected to double Mizoroki–Heck reaction in the presence of palladium catalyst, dppp, K₂CO₃, and styrene **3**, in order to obtain corresponding (*E,E*)-3,6-distyryl-9-butyl-9H-carbazole **5** in excellent yields.¹⁹ A similar scheme with 4-methyl styrene **4** was followed to prepare the corresponding dimethyl derivative **6** (Scheme 1).

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 recently developed a protocol of making them in situ for a one-pot reaction.²⁰ In this process an aldehyde with required substituent was subjected to the Wittig reaction with a one carbon phosphonium salt (Ph₃PCH₃I) to generate the desired styrene derivative, which was further subjected to Mizoroki–Heck condition in the same flask to give the stilbene derivative. This new methodology is advantageous due to the availability of substituted aldehydes which can compensate for the poor accessibility of certain styrenes. This process was also applied for the synthesis of two more derivatives of the present distyryl carbazoles. In this way a method can be developed to prepare any type of (*E,E*)-3,6-distyryl-9-alkyl-9H-carbazole required for the synthesis of aza[7]helicene. In the present work two derivatives from 4-methoxy benzaldehyde **7** and 4-fluoro benzaldehyde **10** are utilized to prepare 4-methoxy styrene **8** and 4-fluoro styrene **11**, respectively, which were in situ subjected to one-pot Mizoroki–Heck reaction with **2** (Scheme 2).

The distyryl derivative of carbazole **5** obtained was subjected to photocyclization in toluene with the high pressure mercury vapor lamp. The reaction was carried out in the presence of stoichiometric amount of iodine as an oxidizing agent and THF as a scavenger of the hydrogen iodide formed.¹⁴ Careful analysis of the reaction mixture revealed consumption of the starting material and forma-

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