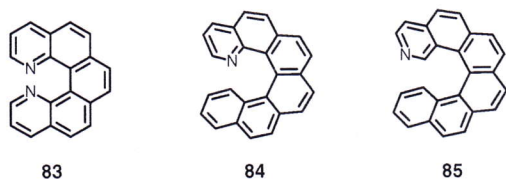


1 Abstract

A novel and modular approach to azahelicenes has been developed. Using [2+2+2] cyclotrimerisation of appropriate triyne as a key step, azahelicenes **83**, **84** and **85** have been prepared (Scheme 1).



Scheme 1.

Aza[6]helicenes **84** and **85** have shown to be sufficiently configurationally stable and have been resolved into individual enantiomers by the diastereoisomeric salt crystallisation and chiral HPLC. This allowed to determine exact values of racemisation barriers for both aza[6]helicenes **84** and **85**. In general, both hexacyclic derivatives **84** and **85** are stable enough to be used in asymmetric transformations or chiral sensing. The ability of aza[6]helicenes **84** and **85** to serve as chiral ligands for transition metals has been proven by the preparation and X-ray analysis of corresponding silver complexes. Interesting chiral self-recognition properties of aza[6]helicenes **84** in gas phase have been described using mass spectrometry techniques. In order to complement information about azahelicenes basicities, gas phase proton affinities of derivatives **84** and **85** and solution phase dissociation constants of azahelicenes **83**, **84** and **85** have been determined. Eventually, the first utilization of azahelicene in asymmetric catalysis has been demonstrated by the successful use of optically pure aza[6]helicene (*M*)-(-)-**85** in the asymmetric kinetic resolution of racemic 1-phenylethanol.