

Summary

The aim of this work was to explore the scope and limitations of [2+2+2] co-cyclotrimerization of cyanodiyne in the preparation of conformationally stable and optionally optically pure azahelicenes, helically chiral bipyridines and helicenes laterally extended by a pyridine unit.

As a key reaction for the construction of a helical skeleton, crucial [2+2+2] (co-)cyclotrimerization mediated by various transition metal complexes was chosen for the preparation of racemic azahelicenes. Oligoynes as key intermediates were prepared by a sequence of Sonogashira and Suzuki-Miyaura coupling. For optically pure azahelicenes and bispyridohelicenes, a sequence of Sonogashira and Suzuki-Miyaura coupling and Mitsunobu reaction was used. Importantly, the Mitsunobu reaction was used for its extraordinary ability to transfer chirality from the starting chiral alcohol to the early helicene precursor without configurational scrambling. It is worth noting that optical purity of the key oligoynes have crucial role in the chirality transfer to final azahelicenes or bispyridohelicenes. An *in situ* generated Ni(0) catalyst was used for bispyridohelicenes with a connection in the 2,2'-position, which enabled both [2+2+2] cyclotrimerization and Ullmann-type coupling.

The conformationally stable racemic aza[6]- and aza[7]helicenes **320** and **319** were resolved into the individual enantiomers by chiral HPLC. Barriers of their thermal racemization were determined. Optical rotations and CD spectra were measured for all optically pure azahelicenes and bispyridohelicenes. In particular, bispyridohelicene (-)-(M,R),(M,R)-**325** exhibited (chiro)optical switch properties when titrated with trifluoroacetic acid or Cu(MeCN)₄PF₆. Selected experimental results were further supported by DFT calculations. A notable effect of chiral discrimination was observed in the titration of (-)-(M,R),(M,R)-**325** with the enantiomers of camphorsulfonic acid.