DIASTEREO- AND ENANTIOPURE HELICENE 2,2'-BIPYRIDINES: A NEW TYPE OF CHIROPTICAL SWITCHES

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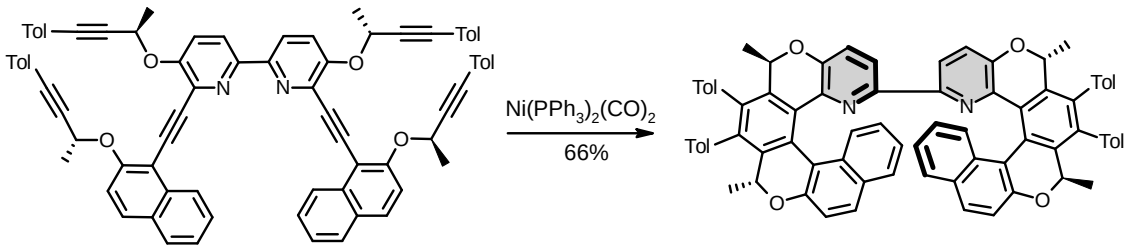
2,2'-Bipyridine along with a large family of its congeners have attained exceptional popularity across inorganic chemistry, organic chemistry and catalysis owing to their pronounced ability to form chelate complexes with transition metals in various oxidation states. However, helicene-derived 2,2'-bipyridines are so far rare in the literature and there is only a single example of their function as a chiroptical switch [1].

Herein, we developed a versatile asymmetric synthesis of the C_2 symmetric helicene 2,2'-bipyridines that relied on the double intramolecular [2+2+2] cycloisomerisation of a centrally chiral dicyanotetrayne or triyne (Scheme 1). Starting from enantiopure chiral building blocks, a multiple chirality relay took place; we reached an effective central-to-helical-to-axial chirality transfer that was controlled by various factors including the 1,3-allylic-type strain [2] leading to sterically constricted atropoisomers of the embedded 2,2'-bipyridine unit. Chiroptical properties of the helicene 2,2'-bipyridines were studied to find large responses to various solvents, acids and metal cations. The oxa[6]helicene derivative (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2** exhibits an off/on switching ability when treated by acido basic/metal cation agents. Hence, it represents a new paradigm of effective chiroptical and fluorescence switches.



(+)-(*R*,*R*),(*R*,*R*)-**1**

(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2**
>99% *ee*, >99% *de*

Scheme 1

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