Abstract

2,2'-Bipyridines and their appropriate \(N,N'-\)-dioxides form a significant class of heteroaromatic compounds, which has found application in various fields of chemistry and predominantly in asymmetric catalysis. One of the most powerful methods for their synthesis is cocyclotrimerization of alkynes with nitriles.

A new variant of cyclotrimerization reaction – cocyclotrimerization of halodiynes with nitriles, which results in the formation of 2- and 3-halopyridines, has been developed. The reaction was studied on a wide range of substrates providing the pyridine products in good isolated yields. Formation of an unexpected product of halogen exchange reaction was observed during the course of the study and its origin was elucidated by experimental studies.

The prepared 2-halopyridines were used as starting materials for syntheses of new chiral 2,2'-bipyridine ligands. The crucial step of their synthesis turned out to be the reductive dimerization of 2-halopyridines to the corresponding 2,2'-bipyridines. Application of the formed bipyridine ligands was then tested in various metal-catalyzed asymmetric reactions, namely Mukaiyama aldol reaction, hydroxymethylation, conjugate addition, C–H activation of indole and desymmetrization of \(meso\)-epoxides, in which one of the bipyridine ligands showed extraordinary activity and robustness. The structural properties of this ligand were then studied based on the NMR analyses, DFT calculations and single crystal X-ray analyses.

New axially chiral 2,2'-bipyridine \(N,N'-\)-dioxides were synthesized \(via\) two approaches, which differed in the type of the key dimerization step. While the first approach, based on the reductive dimerization of 2-halopyridines, furnished only one atropoisomer of the target \(N,N'-\)-dioxide by an eight-step reaction sequence, the second approach, based on oxidative dimerization of pyridine-\(N\)-oxides, provided both atropoisomers in only five steps. The applicability of these novel \(N,N'-\)-dioxides as Lewis base catalysts were then examined in the enantioselective allylation of benzaldehyde and aldol reaction of trichlorosilyl ketene acetal with acetophenone.