Abstract

The Thesis describes our successful endeavour to develop asymmetric synthesis of functionalized 2*H*-pyran or 2,7-dihydrooxepine helicene-like compounds in an optically pure form. These helicene surrogates were fully characterized and their use in enantioselective catalysis as chiral ligands, organocatalysts or chiral modifiers was explored. A general method for the preparation of optically pure [5]- and [6]heterohelicenes by asymmetric synthesis is based on highly diastereoselective [2+2+2] cycloisomerization of centrally chiral triynes mediated/catalyzed by transition metal complexes. Stereochemical outcome of the cyclization process is controlled by 1,3-allylic-type strain. This new methodology is highly versatile providing an easy access to chiral ligands, organocatalysts or modifiers in a nonracemic form. Optically pure 2,7-dihydrooxepine [5]helicene-like phosphite ligands were explored in enantioselective allylic amination under catalysis by iridium(I) complexes to reach up to 82% *ee*. An organocatalysts represented by the optically pure 2*H*-pyran [5]helicene-like DMAP analogue was synthesized and applied to kinetic resolution of racemic sulfoximines. Finally, various functionalized derivatives of helicenes and helicene-like compounds (azahelicenes, DMAP analogues, (thio)urea derivatives) were prepared and their possible role as new chiral modifiers in asymmetric heterogeneous reduction of ethyl pyruvate to ethyl lactate was studied.