

Chiral Diphosphine Ligands Based on Camphor: Synthesis, Structural Futures and Catalytic Applications

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Since the first revolutionary discovery and industrial application of chiral diphosphines in the late 1970's by Knowles, a large number of chiral phosphine ligands have been developed in order to effect high enantioselectivity in catalytic asymmetric reactions. Despite the fact that many different structural motives have been applied in the synthesis of diphosphine ligands, there is still a challenge in developing easy to handle, tunable, highly efficient ligands *and* providing them in industrial relevant scale. The use of readily available naturally occurring chiral, nonracemic starting materials is obviously the most effective way to access ligands in large scale.

Herein is described an efficient synthesis of new class of chiral diphosphines having a cycloolefinic unit (A) with central chirality and an (hetero)aryl moiety (B) in the backbone leading to additional atropisomerism. The new ligand system combines the features of central chirality derived from a natural product with axial chirality like in the prior mentioned biaryl type ligands. In addition to this the two disubstituted phosphorous groups (C) are introduced sequentially leading to a huge variety of tuneable ligands.

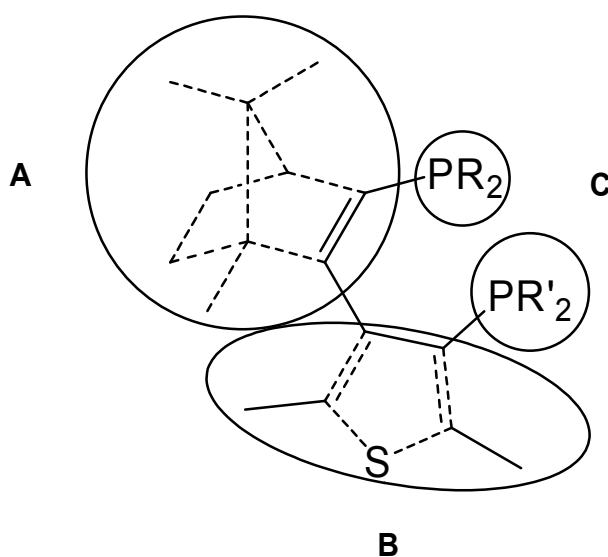


Figure 1. Tunable parts of new ligands

The structural futures of new atropisomeric system were studied with quantum chemical methods. Both atropisomers were isolated and fully characterized by X-ray and NMR analysis.

The developed ligands catalyze the asymmetric hydrogenation of different substrates in acceptable to very high enantioselectivities. Particularly, in hydrogenation of α -amidocinnamates (benchmarking substrates), more challenging simple α -enamides, (Z)- and (E)- β -dehydroaminoacids very high to excellent optical inductions are obtained. This results show that the new ligands are able to form a suitable asymmetric environment around the metal resulting in high asymmetric induction