Diamine ligands : design, synthesis and application in asymmetric catalysis

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Presented dissertation contains results of research on synthesis of chiral diamines and aminoalcohols and their application in asymmetric catalysis.

The first objective of my thesis was to optimize the structure of spiro-indan-2,2'-pyrrolidine ligands developed in the team XII of Institute of Organic Chemistry PAS and to test their properties in nitroaldol reaction between nitromethane and aromatic, heteroaromatic and aliphatic aldehydes. As a result of the optimization of the spiro-ligand structure I obtained a ligand that offered the nitroaldol reaction products with the enantiomeric excesses up to 96%.

During analysis of spiro-ligands structure I have decided to examine properties of ligands with similar structure lacking spiro-connection. I have planned and performed the synthesis of open-chain analogues of spiro-ligands - arylmethanamine derivatives of L-Proline. I have investigated the effect of the stereogenic center at the methanamine position on the direction and value of asymmetric induction. As a result of optimization of the ligand structure I obtained the diamine derivative that gave the nitroaldol reaction products with enantiomeric excesses up to 92%.

During the study, I have noticed a correlation between asymmetric induction and copper acetate : ligand ratio for some particular ligands. I have proven that this phenomenon is caused by the equilibrium between two types of copper complexes that differ in structure, as evidenced by the X-ray structure.

To test whether 1,3-dihydrospiro[indene-2,2'-]pyrrolidine backbone can be used efficiently in organocatalysis I have obtained a number of aminoalcohols that are spiro-analogues of the Hayashi-Jorgensen catalyst. The organocatalysts I synthesized have been tested in the Michael addition of dimethyl malonate to cinnamaldehyde. The results obtained (*ee* and product yields) were slightly lower than those reported in the literature.