MSc Jacek Chrzanowski

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences

Sienkiewicza 112, 90-363 Łódź

„New chiral heteroorganic compounds as ligands and/or organic catalysts: preparation, structural studies and selected synthetic applications"

A search for new organocatalysts for the stereoselective formation of carbon-carbon bonds is still one of the most important and challenging tasks of contemporary organic synthesis. One of the main advantages of using organocatalysts in asymmetric synthesis is a possibility of avoiding toxic and expensive transition metal complexes.

During my research, I focused my attention on the search for new ligands and/or organocatalysts containing a stereogenic carbon, sulfur or phosphorus atom and on the demonstration of their utility in selected asymmetric carbon-carbon bond formation reactions.

The dissertation consists of three main parts. In the first one, I described the experiments leading to enantiomerically pure (*S*)-1-(2-pyridyl)ethylamine and (*S*)-1-(3-pyridyl)ethylamine *via* the separation of their diastereoisomeric salts with L-(+)-tartaric acid and the synthesis of thiourea derivatives of (*S*)-1-(2-pyridyl)ethylamine. I also showed their poor utility in some reactions of the asymmetric C-C bond formation i.e. the diethylzinc addition to benzaldehyde and the aldol reaction.

The second part of my research program was aimed for the design of *S*-chiral and/or achiral sulfinyl derivatives. I developed a novel synthetic pathway for four new catalysts. Two of them contained a stereogenic sulfinyl group and in the other two sulfinyl derivatives the stereogenic centre was located in a remote part of the molecule. These organocatalysts proved very efficient in the asymmetric diethylzinc addition to benzaldehyde, the asymmetric aldol condensation and the asymmetric Mannich reaction. This section of the dissertation is complemented by the synthesis of thiazocine-*S*-oxides, for which there was thus far no simple and efficient method of the preparation. The latter were also tested in the aldol reaction and in the Mannich reaction, in order to compare their efficacy with that of the previously obtained ligands.

The last topic of my investigations was the synthesis of *P*-chiral ligands and/or organocatalysts. In this part, I developed a useful metodology for the synthesis of new, enantiopure tertiary phosphine oxides *via* the palladium-catalyzed cross-coupling reactions of *tert*-butylphenylphosphine oxide with aryl and/or heteroaryl halides. The stereoretention of the reaction was confirmed by means of X-ray analysis. Moreover, I made an effort to achieve the stereospecific reduction of phosphorus-oxygen bond to obtain the corresponding phosphines. In the last part of the dissertation I described a new methodology for the stereospecific deprotection of phosphine borane complexes using trimethylphosphine. This innovative approach does not require any purification of air-sensitive products and enables direct preparation of transition metal complexes of phosphines.