Enantioselective reduction and carbon–carbon bond forming reactions promoted by zinc complexes

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Asymmetric catalysis using chiral metal complexes is one of the most important method for the stereoselective formation of carbon–carbon and carbon–heteroatom bonds. The major advantage of the metal catalysis is its universality, which makes this method widely used to afford a diverse range of optically pure complex organic compounds. To date, application of the precious-metal complexes, in particular palladium, rhodium or ruthenium metals, was one of the most common approach used in asymmetric synthesis. Although these catalysts are efficient, high prices, adverse impacts on living organisms and the natural environment indicate the need for development of cheaper and less toxic solutions.

In recent years, there has been growing interest in employment of environmentally friendly and readily available zinc complexes in asymmetric catalysis, which provides the starting point for this doctoral dissertation. As a main aim of my research, I have chosen the development of efficient zinc-based catalysts in enantioselective hydrosilylation reactions, focusing on reductive aldol reaction of ketones and reduction of cyclic imines.

In the first part of the work, I showed that the catalytic systems based on zinc acetate with the readily available diamine and bis(serinamide) ligands could effectively catalyze the reductive aldol reaction of aryl ketones with acrylates, allowing the synthesis of useful β-hydroxy esters in a highly stereoselective manner. The developed methodology confirmed that *in situ* generated the zinc hydride complex successfully promote the reaction of afforded optically pure tertiary alcohols in both high yields and enantioselectivities. The described studies simultaneously represents the first example of zinc-catalyzed reductive aldol reaction without the use of high-priced and toxic platinum group-metals.

In the second part of the research, I focused on the development of enantioselective method of hydrosilylation of five-membered cyclic imines catalyzed by zinc complexes. The use of *in situ* generated zinc–ProPhenol catalyst led to obtain the desired aryl-pyrrolidine derivatives with excellent optical purities up to 99% *ee*. The versatile utility of presented methodology was demonstrated in the synthesis of selected valuable precursors for drugs and biologically active compounds, obtaining the outstanding results by using the mild reaction conditions.