

## Abstract

Beside transition-metal and enzymatic catalysis plays organocatalysis an important role in asymmetric organic synthesis. In the field of organocatalysis are amines group of compounds commonly used as organocatalysts.

This thesis deals with the use of hypervalent iodine compounds in combination with amine catalysis and also with the use of Morita-Baylis-Hillman carbonates in organocatalytic allylic substitution reactions.

In the first part an organocatalytic enantioselective  $\alpha$ -selenylation reaction of saturated aldehydes using diphenyldiselenide and iodobenzene diacetate is described. Reaction is catalysed by commercially available first generation MacMillan catalyst. The products of the reaction were obtained in yields of 51-70 % and enantiomeric excess 95-99 %. Designed methodology was extended on the derivatives of  $\beta$ -ketoesters by catalysis of tertiary amines and quaternary ammonium salts. Apart from selenylation reactions we have also dealt with the possibility of formation C-C bond using hypervalent iodine compounds. Particularly, we focused on electrophilic alkylation reactions of appropriate nucleophiles using acetylene-bearing hypervalent iodine compounds. Fluorinated sulfone derivatives and enolizable heterocycles such as pyrazolone derivatives, rhodanines, oxindoles and azlactones were found as a suitable substrates, affording the corresponding alkylated products in high yields (up to 95 %), but with low enantiomeric excess (*ee* up to 62 %). Mechanistic studies revealed, that in the first step desilylation of starting material TMS-EBX occurred in presence of tertiary amine leading to reactive intermediate ethynylbenziodoxolone which subsequently reacts with appropriate nucleophile.

In the second part an organocatalytic allylic substitution reactions using Morita-Baylis-Hillman carbonates with *C*- and *N*-nucleophiles by catalysis of tertiary amines was described. In case of C-C bond formation cyclic  $\beta$ -ketoesters as a suitable *C*-nucleophiles were chosen. In optimized conditions reaction afforded good diastereoselectivity (up to 10:1) and allylated  $\beta$ -ketoesters were isolated in most cases as a pure diastereomers in the yields up to 82 % and with enantiomeric excess up to 95 %. In case of C-N bond formation silylated derivatives of Boc-hydroxycarbamates as a suitable *N*-nucleophiles were found, which by catalysis of  $\beta$ -ICD afforded allylated products in enantiomeric excess up to 90 % and in the yields up to 94 %.

Absolute configuration of new stereogenic centers was in case of  $\alpha$ -selenylation reaction determined by method based on chemical correlation with published derivatives, in case of allylated  $\beta$ -ketoesters and Boc-hydroxycarbamate derivatives was determined by X-ray analysis.