ABSTRACT

The purpose of the doctoral thesis was comparison of two synthesis methods leading to arylated compounds, based on the Heck methodology. The Heck reaction has been extensively and precisely studied since the 1970s, as evidenced by the ever-growing number of publications in this field. In addition to this popular method leading to arylated olefins, the Heck-type reaction using phenylboronic acid as an aryl donor can be considered. This oxidative variant of the Heck reaction is less studied than the Heck arylation, and therefore it was interesting to check which method is more effective for the selected group of olefins. In addition, the reaction conditions were optimized, taking into account the principles of "Green chemistry" and using simple catalysts.

As a result, optimal conditions for the coupling of allyl alcohol with iodobenzene and its derivatives were developed. The elaborated procedure allowed to obtain high yield of saturated arylated aldehydes (>70%) and their halogen derivatives. Moreover, effective Heck coupling of cinnamyl alcohol and linalool was performed. It has been shown that arylation of cinnamyl alcohol according to the Heck type procedure led mainly to 2,3-diphenyl-2-propen-1-ol (75% yield) in addition to the saturated diaryl aldehydes observed in the Heck reaction.

In the further studies, the Heck procedure and the Heck type procedure for eugenol and estragole were developed. For estragole, the rate of both reactions was similar, whereas for eugenol, the Heck reaction was faster than the oxidative Heck coupling. In both reactions, new catalysts with phosphine ligands heterogenized in MOF materials, Pd-1@Ni-MOF and Pd-2@Ni-MOF, were used. Using Pd-2@Ni-MOF, the Heck reactions of estragol and iodobenzene were repeated five times with good results (57-68% PhI conversion). Both catalysts were used in the Heck type arylation of eugenol and similar product yields were obtained. ICP and SEM analyses performed for both materials Pd@Ni-MOFs before and after the reaction showed that the palladium-phosphine complex was leached from the MOF materials during the reaction.

In the last part of the study derivative an estragole, 4-allyl-1,2-dimethoxybenzene and trans-anethole were successfully used coupled with iodobenzene. The oxidative Heck coupling was also carried out and similar product yields were obtained in both methods. In addition, 4-allyl-1,2-dimethoxybenzene reacted faster than trans-anethole (trans-1-methoxy-4-(1-propenyl) benzene) under the Heck oxidative reaction conditions. In addition, the Heck type reaction for trans-anethole proceeded with different selectivity towards formation of the α-arylation product.