

## ABSTRACT

This thesis is aimed to describe several aspects and stages in the development of palladium catalytic systems through several case studies connected to functionalization of terminal acetylenes.

Initially, the development of new ligand precursors is addressed through the synthesis of novel N-heterocyclic carbene (NHC) precursors, namely 1,3,4-triaryl-1*H*-1,2,3-triazolium salts. They were prepared by selective arylation of click triazoles with diaryliodonium salts in the presence of copper salts. The neat reaction protocol, which was also developed in a ‘one-pot’ fashion, allowed for the preparation of unsymmetrically substituted triazolium salts among which the examples containing pyridine substituent were particularly interesting. They were employed in the preparation of Pd<sup>II</sup>, Ru<sup>II</sup> and Ir<sup>III</sup> complexes. Additionally, Ru-NHC and Ir-NHC thus formed showed increased catalytic performance in transfer hydrogenation of benzophenone as compared to previously reported complexes with alkyl substituted Py-*tz*NHC ligands.

Mechanism of copper-free Sonogashira reaction, an important cross-coupling process employing terminal acetylenes, was elucidated through a thorough experimental-computational study. It was demonstrated through an extensive 1D and 2D NMR study of reaction mixtures combined with reaction kinetics as well as density functional theory (DFT) calculations that the reaction operates through an interplay of two Pd catalytic cycles connected in the transmetalation step. The new mechanistic understanding of the catalytic process, that was previously overlooked, should inspire the development of new and improved catalytic systems for the preparation of internal acetylenes.

The synthesis of highly substituted 1,3-enynes was investigated employing aryl halides and acetylenes. During the study, silyl-substituted geminal dimers of acetylenes were successfully coupled with aryl halides under the conditions for Heck coupling for the preparation of 1,2,4-trisubstituted analogues of 1,3-enynes.

Finally, the DFT mechanistic study of an effective hydroamination reaction of acetylenes catalysed by Pd-*i*PEPSSI (internal pyridine-enhanced precatalyst preparation, stabilization, and initiation) catalyst offered insight into the active role of pyridine substituent in pyridine substituted triazolium ligands (Py-*tz*NHCs). Noteworthy, pyridine substituent can act as an internal base and enable proton shuttling in this new type of catalysis.

**Keywords:** palladium, triazolium salts, carbenes, catalysis, reaction mechanisms