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Defense: April 29, 2022

PhD Thesis title:

„Novel avenues in C-C bond-forming rearrangements, harnessing the power of cationic intermediates“

The work presented in this thesis describes the development of new synthetic methods in organic synthesis.

The first chapter contains a series of cationic rearrangements mediated by iodine(III) reagents related to the chemistry of non-classical carbocations. Initially, an oxidative 1,2-aryl shift to afford α-aryl-ß-mesyl ketones is described, including a promising precedent of an asymmetric variant.

A second subchapter is devoted to the generation of non-classical cyclopropylcarbinyl cations which are readily functionalised by a variety of nucleophiles to deliver trans-cyclopropanes.

Finally, norbornyl ketones were shown to be amenable to oxidative functionalisation featuring an interesting C-H insertion process, proven to be feasible also for the corresponding amides when a state-of-the-art umpolung approach was employed. The second chapter describes the development of a methodology connecting simple feedstock starting materials, namely amines, aldehydes and electron poor olefins to form azabicyclic scaffolds.

This strategy employs Lewis acid catalysts from the frustrated Lewis pair regime to enable the key C-C bond formation with high diastereoselectivity via an inverse hydride shuttle.

Importantly, the reaction can be performed in an asymmetric fashion and a number of derivatisations highlight the versatility of the bicyclic alkaloids frameworks.