Rhodium(I)-Catalyzed [(3+2)+1] and [(3+2)+2] Carbocyclization Reactions of Alkylidenecyclopropanes (ACPs) with Carbon Monoxide and Allenes

The stereoselective construction of carbon-carbon bonds represents a fundamentally important process in organic synthesis. Among these reactions, cycloadditions are widely recognized as an extremely powerful tool for the rapid construction of carbocyclic and heterocyclic compounds, displaying the ability to provide products with multiple stereogenic centres, in a highly stereoselective manner. Nevertheless, cycloaddition reactions are usually limited by the requirement for polarized functionality in the substrate due to the low reactivity of unactivated $\pi$-components: simple alkynes, alkenes and dienes. In contrast, transition metal catalysts are able to combine unactivated alkynes and olefins, leading to the formation of multiple bonds and stereogenic complexity. The most striking asset of this class of reactions is the ability to selectively and methodically tune the stereoelectronic properties of the ligands to modulate reactivity and selectivity, which results in an array of highly chemo-, regio-, stereo- and enantioselective processes.

This seminar will focus on the development of highly selective strategies for the formation of cis-fused [5,6] and [5,7] bicyclic systems via rhodium-catalyzed intermolecular [(3+2)+1] and [(3+2)+2] carbocyclizations utilizing alkenylidenecyclpropane (ACPs) in conjunction with carbon monoxide and allenes. Moreover, the extended scope of these transformations will be described in the context of synthetic applications.