The development of efficient catalytic reactions relies on the detailed understanding of and the ability to discern different mechanistic pathways and outcomes. This seminar will outline our mechanism-driven approach to designing new catalytic carbofunctionalization reactions of alkenes and alkynes. This class of transformations is extremely powerful due to the simultaneous formation of two new bonds across a \( \pi \)-system, allowing access to complex molecules from ubiquitous starting materials. Throughout the talk, I will highlight the factors influencing reactivity, regioselectivity and stereoselectivity in these types of addition reactions.

In the first part of the seminar, I will describe our work in the area of palladium-catalyzed carbohalogenation reactions of alkynes. Two mechanistically divergent pathways, involving either a Pd\(^0\)/Pd\(^{II}\) or a Pd\(^{II}\)/Pd\(^{IV}\) redox cycle, enable access to a wide range of tetrasubstituted vinyl halide products. A key finding in our investigations is that reactivity and stereoselectivity are innately tied to the steric bulk of both the substrate and the catalyst. Combined experimental and computational studies provide support for a palladium-mediated isomerization pathway, thus demonstrating that specific substrate/catalyst combinations can override the inherent cis-selectivity in carbopalladation processes.

The second part of the seminar will discuss the use of chiral ion pairing to control enantioselective addition reactions to alkynes. Chiral phosphoric acids have emerged as a diverse class of bifunctional organocatalysts that can operative via Brønsted acid and/or ion-pairing catalysis. Similar to enzymes, these catalysts offer a platform to control stereoselectivity through multiple binding motifs, including hydrogen-bonding, ion-pairing and aromatic interactions. Our work in this area involves the development of a biomimetic asymmetric zwitterionic aza-Claisen rearrangement that provides access to synthetically versatile chiral vinylogous carbamates.