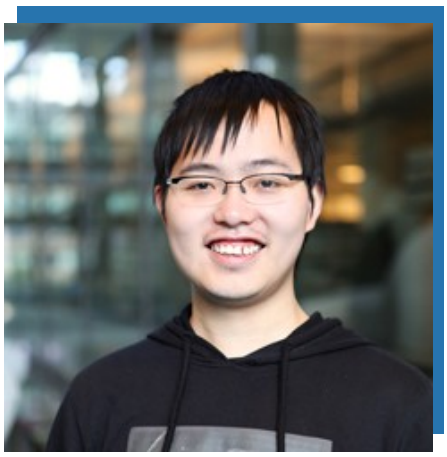
Organic Colloquium



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"Strategic Bond Construction and Cleavage Enabled by Photocatalytic Radical Transformations"

Abstract: Radical chemistry is an important class of reactions in modern organic synthesis, due to the high reactivity and versatile bond formation and cleavage events that can happen with radical intermediates. One of the current challenges in radical chemistry is to generate these reactive open-shell intermediates from accessible starting materials under mild conditions. We have developed several powerful strategies to homolytically cleave strong X–H bonds and generate the corresponding X• radical via proton-coupled electron transfer (PCET). In this talk, I will present a photocatalytic intermolecular anti-Markovnikov hydroamination reaction of sulfonamides, and a remote C–H alkylation reaction of amides, enabled by the amidyl radicals generated via PCET. Moreover, we also developed a photocatalytic condition to conduct various carbocation reactions via mesolytic cleavage of alkoxyamine compounds. Lastly, to understand the remarkable chemoselectivity and improve the quantum efficiency of a set of photocatalytic hydroamination reactions, we performed detailed mechanistic studies, using advanced spectroscopic and electroanalytical tools to unveil the origin of the chemoselectivity of this reaction, and also improved the reaction quantum yields. Based on these studies, gram-scale synthesis of several dialkylamines were performed in a flow reactor.

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