

Catalytic Carbonyl-Olefin Metathesis – New Catalysts and Reaction Pathways

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The olefin-olefin metathesis reaction is a revolutionary industrial process that utilizes precious metal complexes to enable direct carbon-carbon bond formation from simple olefin starting materials. The carbonyl-olefin metathesis reaction similarly enables the construction of carbon-carbon bonds and has the potential to have an analogous impact on synthetic strategy. However, currently available synthetic procedures are significantly less advanced. Our research laboratory has developed a Lewis acid-catalyzed **carbonyl-olefin metathesis** that represents a new reactivity mode between carbonyl and olefin functionalities. Our design principle fundamentally differs from stoichiometric carbonyl-olefin metathesis protocols proceeding via intermediate oxametallacycles. It is instead based on the *in situ* formation of oxetanes as reactive intermediates via an asynchronous, concerted [2+2]-cycloaddition of a carbonyl and an olefin upon activation with FeCl₃ as Lewis acid catalyst. This distinct reactive intermediate no longer limits the process to precious metals, enables catalytic turnover, and prevents the formation of stoichiometric waste. We have since been able to demonstrate the generality of our approach to enable ring-opening, ring-closing, cross, and transannular carbonyl-olefin metathesis and advance our catalyst design to broaden the current scope of these transformations.

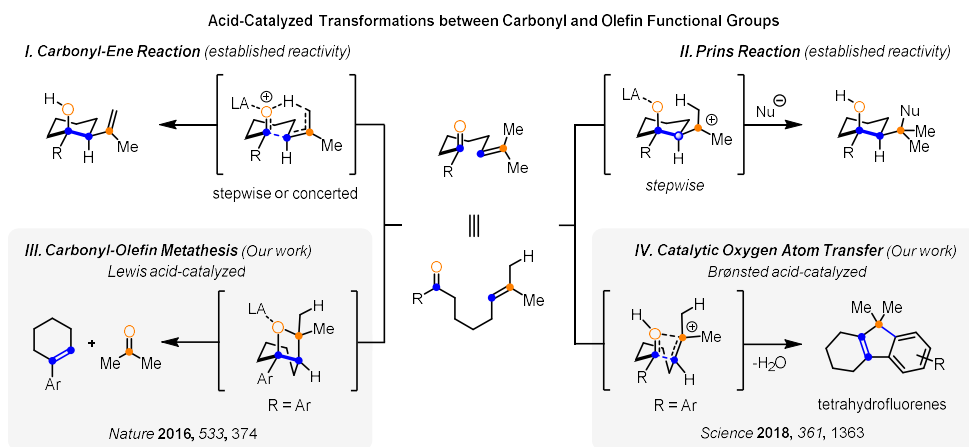


Figure. Established reactivity between carbonyl and olefin functionalities and new reactivity developed in our research program.

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