Acceptorless Dehydrogenative Cross-coupling Reactions Enabled by Photoredox/Hydrogen-Atom Transfer Cooperative Catalysis

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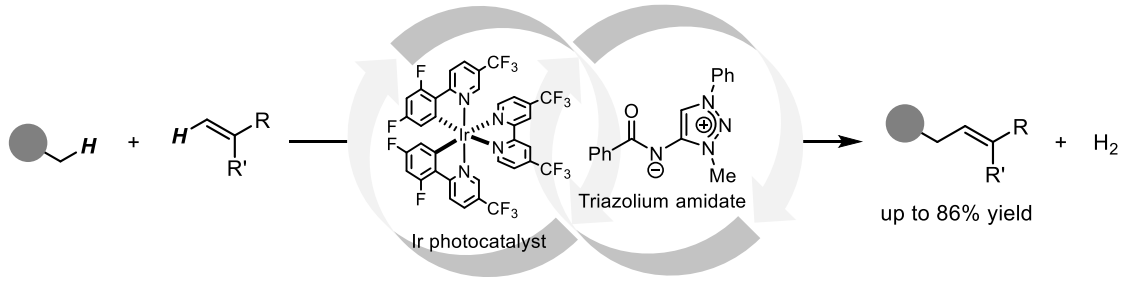
Development of efficient and sustainable transformations is of central importance in the field of synthetic chemistry. Acceptorless dehydrogenative cross-coupling (ADC) between two different C–H bonds represents one of the most powerful methodologies to address this issue. Compared to conventional oxidative dehydrogenative coupling, ADC proceeds without any external oxidants, releasing molecular hydrogen as a sole byproduct. However, harsh reaction conditions are generally required, owing to the thermodynamically unfavorable nature of hydrogen evolution. Recently, electro- and photochemistry have made notable contributions to this field by taking advantage of facile dehydrogenation via cathodic proton reduction or the merger of transition-metal hydrogen evolution catalysis with photoredox catalysis.[1] Despite these significant advances, the catalyses available for ADC reactions are still very limited; hence, the potential of this mode of transformations is yet to be fully explored.[2]

Here, we have discovered an unconventional cooperative catalytic platform for the development of ADC reactions. The combined use of iridium-based photosensitizer and zwitterionic triazolium amidate[3] enabled the C–H/C–H cross-coupling between various heteroatom-containing C−H donors and terminal alkenes without the need for any oxidants, hydrogen evolution catalysts, or electrodes. A key to establishing this catalysis is the susceptibility of the conjugate acid of the triazolium amidate, amide triazolium, toward single-electron reduction to complete the catalytic cycle.



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