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Catalytic Asymmetric C–C Cross-Couplings Enabled by Photoexcitation
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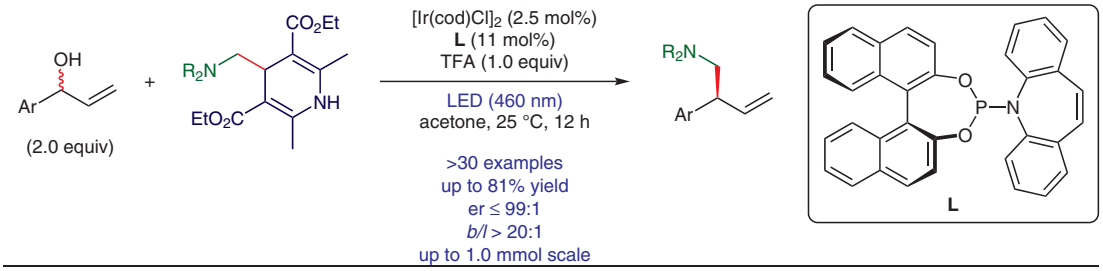
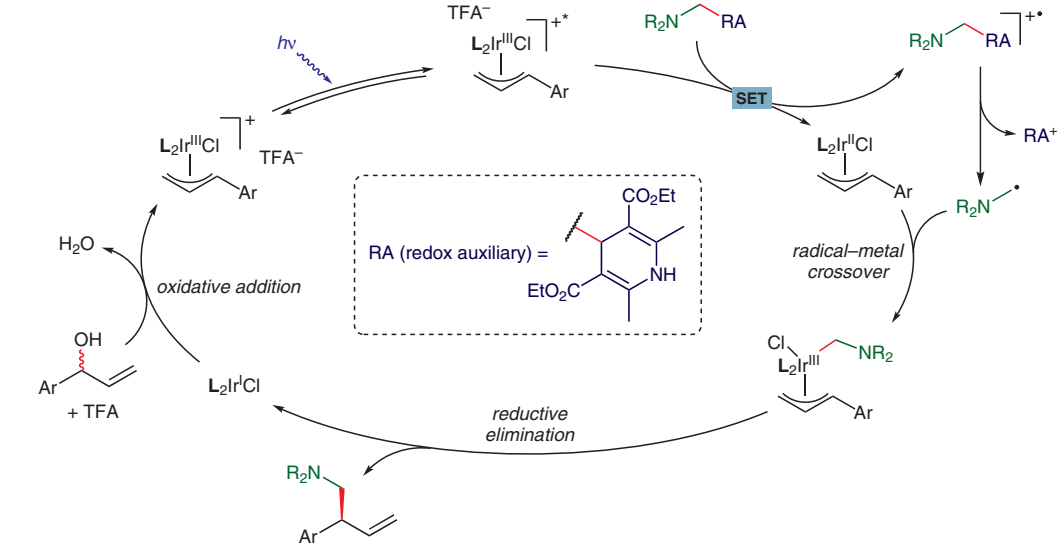
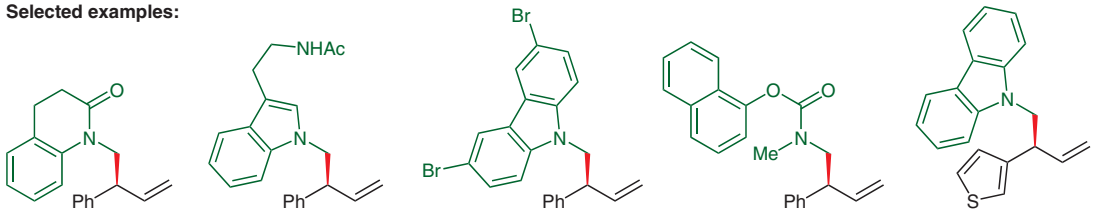
Photochemical Asymmetric Iridium-Catalyzed C(sp^3)–C(sp^3) Cross-Coupling



Proposed mechanism:



Selected examples:



Significance: The Melchiorre group reports an enantioselective C(sp^3)–C(sp^3) cross-coupling of α-vinylbenzyl alcohols with radical precursors under visible-light irradiation. In contrast to the well-established ionic reactivity of allyl-iridium(III) catalysts, photoexcitation allowed for the activation of a coupling partner via a single-electron transfer manifold.

Comment: No external photocatalyst was required as the reaction relies on the photoexcitation of the chiral organometallic intermediate. In addition to Hantzsch ester derivatives, α-amino trimethylsilanes and tetrafluoroborates could be employed as radical precursors, typically with lower efficacy.

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Category
Metals in Synthesis

Key words
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Synfact of the Month

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