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C(sp^3)–H Methylation Enabled by Peroxide Photosensitization and Ni-Mediated Radical Coupling
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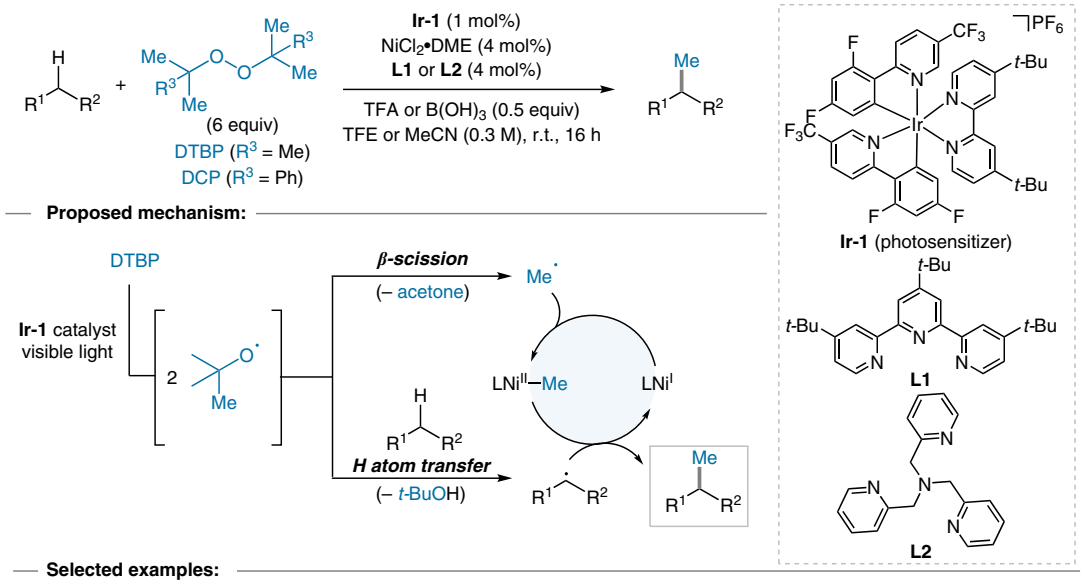
Nickel-Mediated C(sp^3)–H Methylation via Photochemical Activation of Peroxides



Significance: A novel method for late-stage C(sp^3)–H methylation is reported. An iridium photocatalyst is used for the activation of peroxide, the latter serving as both an oxidant for C–H cleavage and a source of methyl radical. The nickel catalyst is essential to enable formal recombination of two different radical species and promote C–C bond formation; in its absence, the methyl radical undergoes unproductive H atom transfers (HAT).

Comment: The authors thoroughly studied the effects of solvent, temperature, concentration, and nature of peroxide on the relative rates of HAT vs. methyl radical formation. As the rates of HAT differ from substrate to substrate, the results of these studies were used as a guide during the investigation of the reaction scope; different set of conditions were developed, enabling the methylation of various substrate classes.

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