Iridium-Catalyzed Photosensitization of β-Dicarbonyls to Access Medium-Sized Rings

Significance: The authors report the synthesis of medium-sized rings via a De Mayo-type ring expansion. The use of fac-[Ir(CF₃-pmb)₃], a tris-cyclometalated complex bearing three N-heterocyclic carbene ligands, as the photosensitizer is crucial for the reaction’s success.

Comment: The reaction tolerates mono, 1,1-, and 1,2-disubstituted olefins as coupling partners. Heavily substituted olefins could not undergo the necessary retro-aldol reaction. Density functional theory suggests that the more nucleophilic α-hydroxy radical adds preferentially to the alkene to begin the stepwise cycloaddition.