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Dynamic Kinetic Sensitization of β -Dicarbonyl Compounds – Access to Medium-Sized Rings via a De Mayo-Type Ring Expansion

Expansion

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

— Proposed mechanism: —

— Highlighted examples: —

— Regioselectivity of stepwise cycloaddition: —

Significance: The authors report the synthesis of medium-sized rings via a De Mayo-type ring expansion. The use of $fac-[Ir(CF_3-pmb)_3]$, 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.

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