

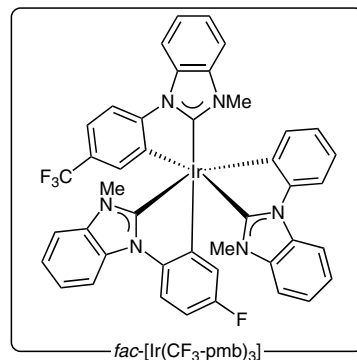
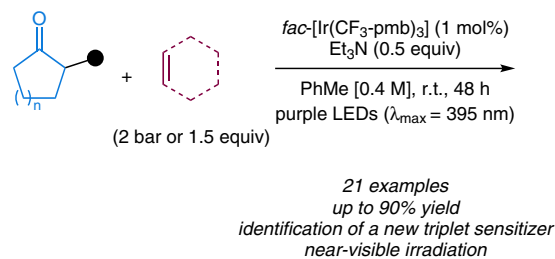
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Dynamic Kinetic Sensitization of  $\beta$ -Dicarbonyl Compounds – Access to Medium-Sized Rings via a De Mayo-Type Ring Expansion

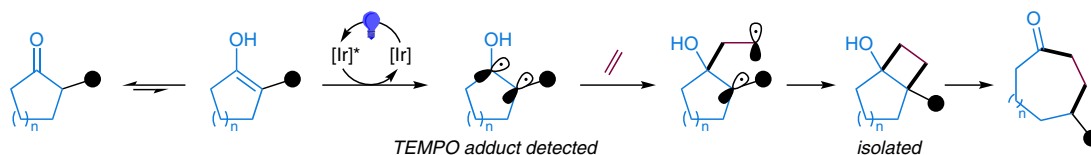
Expansion

Angew. Chem. Int. Ed. 2021, DOI: 10.1002/anie.202112695.

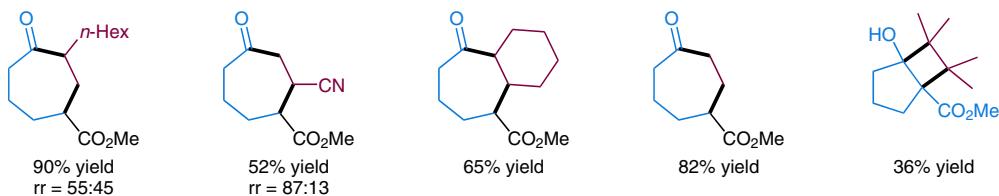
## Iridium-Catalyzed Photosensitization of $\beta$ -Dicarbonyls to Access Medium-Sized Rings



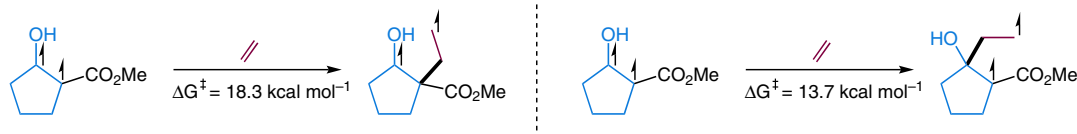
– Proposed mechanism:



– 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<sub>3</sub>-pmb)<sub>3</sub>], 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  $\alpha$ -hydroxy radical adds preferentially to the alkene to begin the stepwise cycloaddition.

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