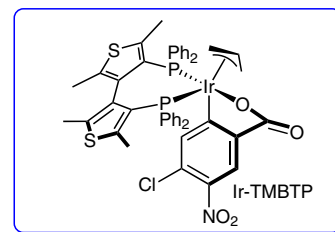
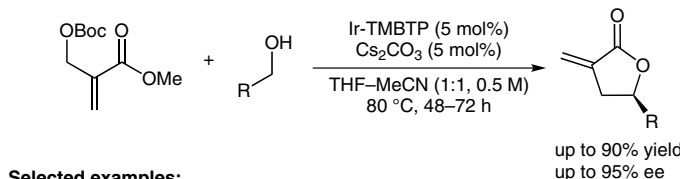
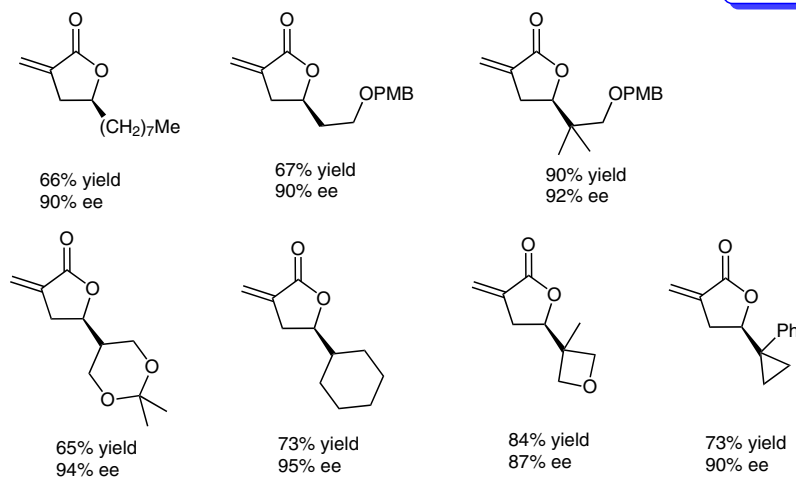


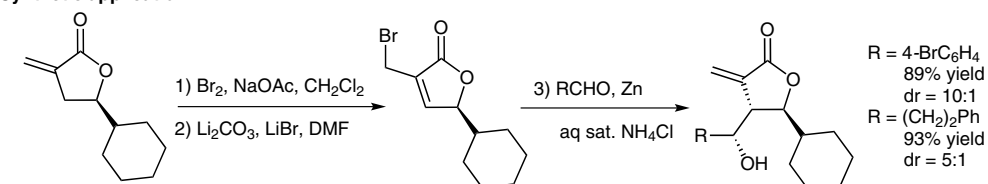
T. P. MONTGOMERY, A. HASSAN, B. Y. PARK, M. J. KRISCHE* (UNIVERSITY OF TEXAS AT AUSTIN, USA)

Enantioselective Conversion of Primary Alcohols to α -*exo*-Methylene γ -Butyrolactones via Iridium-Catalyzed C–C Bond-Forming Transfer Hydrogenation: 2-(Alkoxy carbonyl)allylation*J. Am. Chem. Soc.* **2012**, *134*, 11100–11103.Iridium-Catalyzed C–C Bond-Forming
Transfer Hydrogenation

Selected examples:



Synthetic application:



Significance: In this paper, the authors report the first example of catalytic enantioselective carbonyl 2-(alkoxycarbonyl)allylation via iridium-catalyzed transfer hydrogenative carbon–carbon bond coupling of acrylic ester to alcohols. The desired product was obtained with good yields and enantioselectivities. The synthetic application of this method was also illustrated by rapidly converting the adduct into disubstituted α -*exo*-methylene γ -butyrolactone diastereoselectively.

Comment: Previously, Krische's research on the iridium-catalyzed enantioselective carbonyl allylation was restricted to mono-substituted olefins as late transition metal–olefin π complexes become less stable with higher degrees of olefin substitution. However, the authors recently reported that the improved π -backbonding of carboxy substituents compensates the above-mentioned destabilization and therefore expanded their research to vinylogous aldol additions as well as the utilization of acrylic ester as 2-(alkoxycarbonyl)allylmetal equivalents.

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