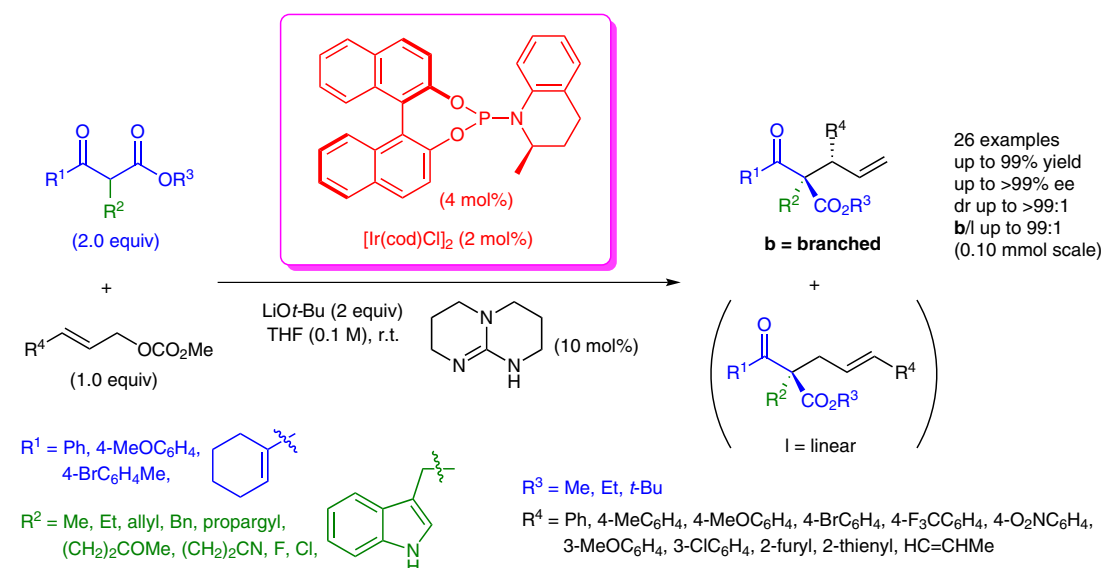


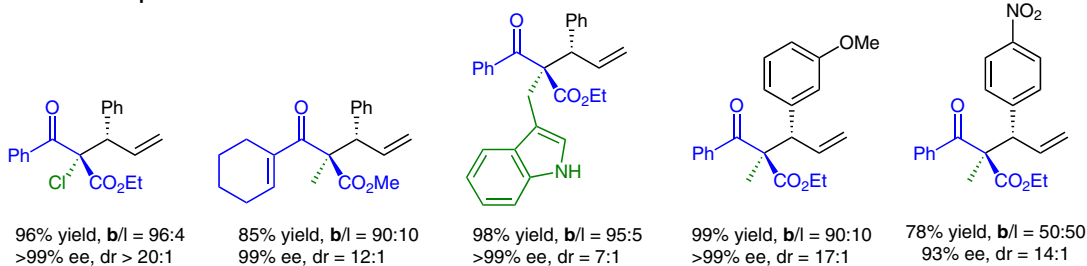
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Enantio-, Diastereo-, and Regioselective Iridium-Catalyzed Asymmetric Allylic Alkylation of Acyclic β -Ketoesters
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Asymmetric Allylic Alkylation of Acyclic β -Keto Esters Catalyzed by Iridium



Selected examples:



Significance: The asymmetric allylic alkylation belongs to one of the fundamental C–C bond-formation reactions and a variety of nucleophiles are successfully employed. However, the formation of an all-carbon quaternary stereocenter is still a challenging case. Herein, the authors report an efficient allylic alkylation of acyclic β -keto esters catalyzed by an Ir–*N*-aryl-phosphoramidite catalyst. The products bearing vicinal quaternary and tertiary stereocenters are obtained in high yield, regio-, diastereo-, and almost perfect enantioselectivity.

Comment: The substrate scope of the iridium-catalyzed diastereoselective allylic alkylation covers aryl, heteroaryl and alkenyl substituents on the allyl carbonate electrophile. Interestingly, the regioselective outcome of the reaction (branched vs. linear) is influenced by the substituent's ability to donate or withdraw electron density. In the case of 4-MeOAr, the branched product is formed almost exclusively. Variations on the β -keto ester moiety are also conducted and a variety of functional groups are tolerated at the α position (R^2), including alkyl, allyl, propargyl, and heteroaryl groups.

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asymmetric allylic
alkylation

β -keto esters

all-carbon
stereocenters

N-aryl
phosphoramidites

iridium