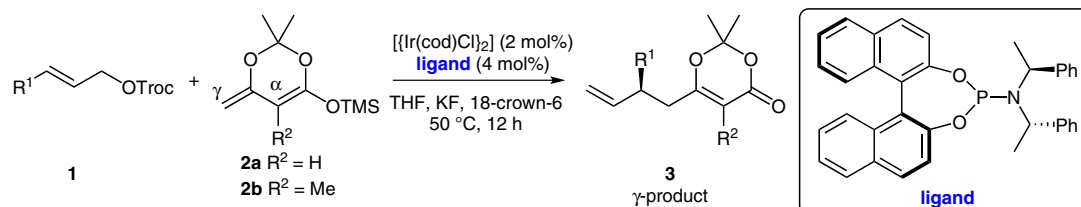
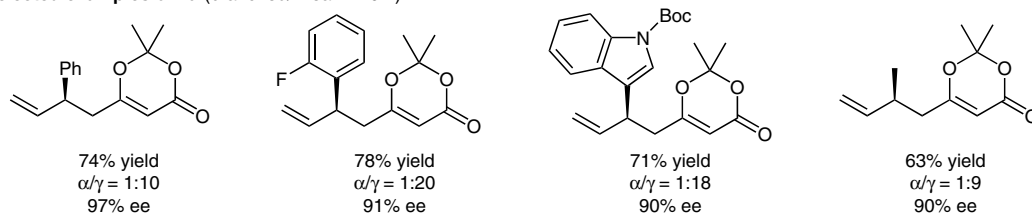


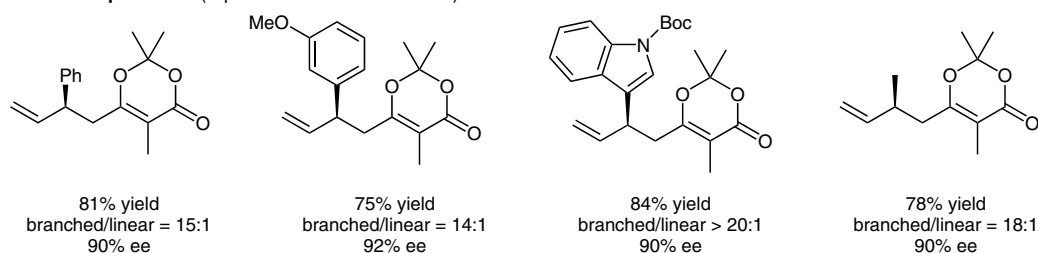
Iridium-Catalyzed Allylic Substitution of Silyl Dienolates



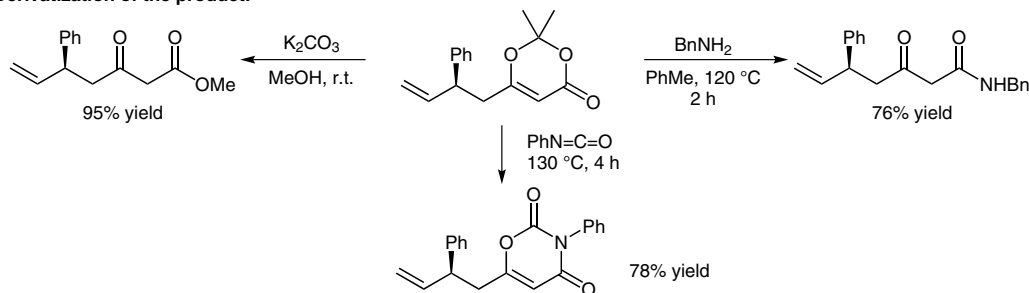
Selected examples of 2a (branched/linear > 20:1):



Selected examples of 2b (α -products were not observed):



Derivatization of the product:



Significance: The allylic substitution at the γ -position of 1,3-dicarbonyl compounds has not been studied so far. Herein, the authors present the iridium phosphoramidite catalyzed allylic substitution reaction with high regio- and enantioselectivities. Silyl dienolates act as synthetic equivalents of β -keto ester dianions.

Comment: In this reaction, the combination of a leaving group on the allylic substrates and a chiral phosphoramidite ligand plays a crucial role to obtain high regioselectivities. The dioxinone moiety in the products can be converted easily into useful structures such as teramic acids.