Iridium-Catalyzed Allylic Substitution of Silyl Dienolates

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.

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

- 74% yield α/γ = 1:10 97% ee
- 78% yield α/γ = 1:20 91% ee
- 71% yield α/γ = 1:18 90% ee
- 63% yield α/γ = 1:9 90% ee

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

- 81% yield branched/linear = 15:1 90% ee
- 75% yield branched/linear = 14:1 92% ee
- 84% yield branched/linear > 20:1 90% ee
- 78% yield branched/linear = 18:1 90% ee

Derivatization of the product:

- 95% yield
- 90% yield
- 76% yield 78% yield 90% ee
- 81% yield 75% yield 84% yield 78% yield 90% ee

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