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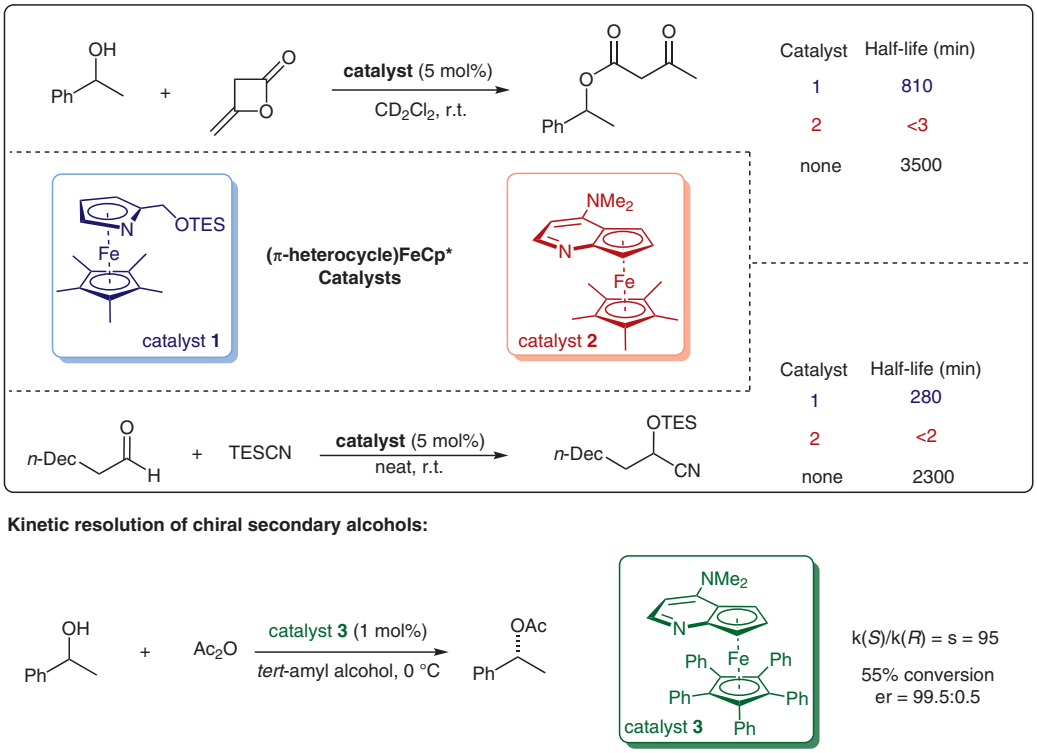
Chiral π-Complexes of Heterocycles with Transition Metals: A Versatile New Family of Nucleophilic Catalysts

J. Org. Chem. **1996**, *61*, 7230–7231.

Organometallic Organocatalysts



Kinetic resolution of chiral secondary alcohols:

Significance: In 1996, Ruble and Fu developed a series of novel ferrocenium-based planar chiral complexes that incorporated nucleophilic nitrogen heterocycles. These compounds were found to be effective catalysts in alcohol acylations and an aldehyde cyanosilylation. Kinetic resolution of chiral secondary alcohols was later investigated with an optimized catalyst (*J. Org. Chem.* **1998**, 63, 2794), and it was found to proceed with very high enantioselectivity.

Comment: Planar chirality was first described in 1941 and used in metallocatalysis, but applications subsequently extended to organocatalysis in a planar chiral flavine-based oxidation (S. Shinkai, T. Yamaguchi, O. Manabe, F. Toda *J. Chem. Soc., Chem. Commun.* **1988**, 1399) that gave only moderate enantioselectivity and showed poor generality. Fu's later work represents an optimal combination in which good facial selectivity is possible together with catalytic activity. Besides kinetic resolution, these catalysts have been applied in other fundamental reactions such as C-acylation (*Angew. Chem. Int. Ed.* **2003**, *42*, 3921) or Staudinger reactions (*J. Am. Chem. Soc.* **2000**, *122*, 7831).

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