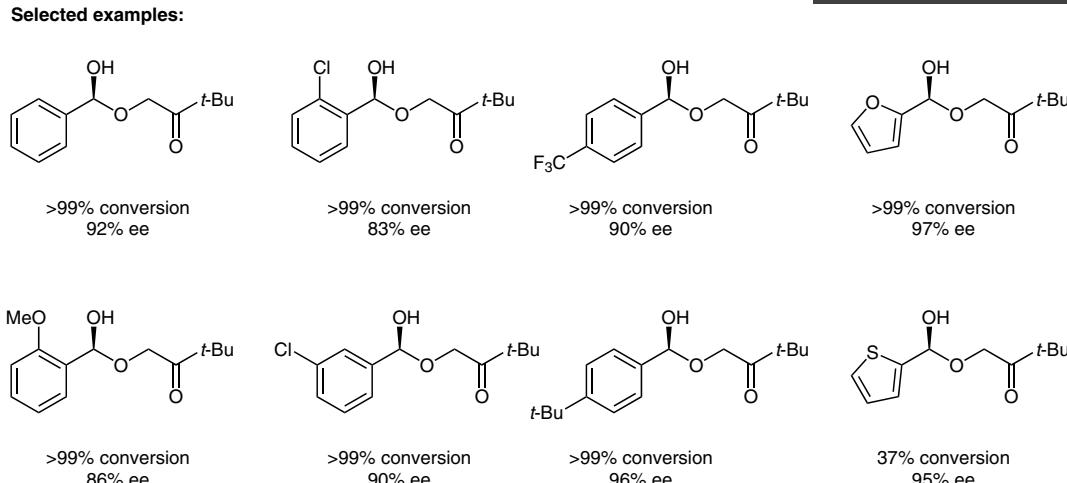
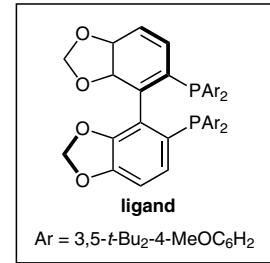
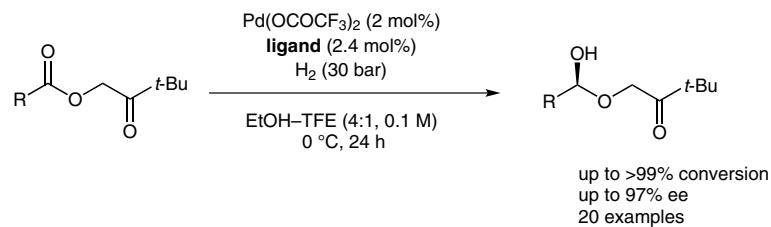


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Palladium-Catalyzed Asymmetric Hydrogenation of α -Acyloxy-1-arylethanones
Angew. Chem. Int. Ed. **2013**, *52*, 11632–11636.

Enantioselective Palladium-Catalyzed Allylic Dearomatization



Significance: Chiral α -acyloxy-1-arylethanols are an important class of useful structural motifs (R. S. Bhondwe et al. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 3656). The authors report a palladium catalyzed enantioselective reduction of α -acyloxy-1-arylethanones to access α -acyloxy-1-arylethanols in high enantioselectivities.

Comment: The first synthesis of α -acyloxy-1-arylethanols was achieved using a chiral diamine ligand and SnCl₂ (T. Mukaiyama, K. Tomimori, T. Oriyama *Chem. Lett.* **1985**, 1359). Then, the use of enzymatic methods for their synthesis with excellent enantioselectivities but moderate regioselectivity was reported (A. Manzocchi, A. Fiechii, E. Santaniello *J. Org. Chem.* **1988**, *53*, 4405; T. Ema, Y. Sugiyama, M. Fukumoto, H. Moriya, J.-N. Cui, T. Sakai, M. Utaka *J. Org. Chem.* **1988**, *63*, 4996; R. Hayakawa, M. Shimizu, T. Fujisawa *Tetrahedron Asymmetry* **1997**, *8*, 3201). With a palladium catalyst and a bisphosphine ligand, the authors were able to show excellent selectivities for a variety of substrates. In addition, catalyst loadings could be lowered to 0.2 mol% without affecting enantioselectivity.

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