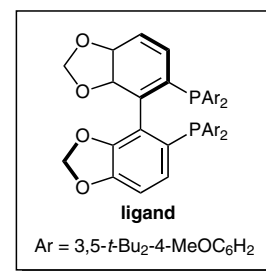
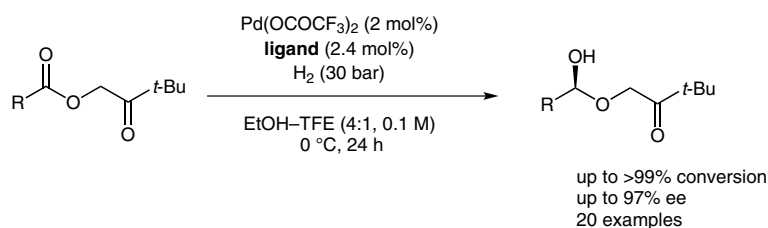


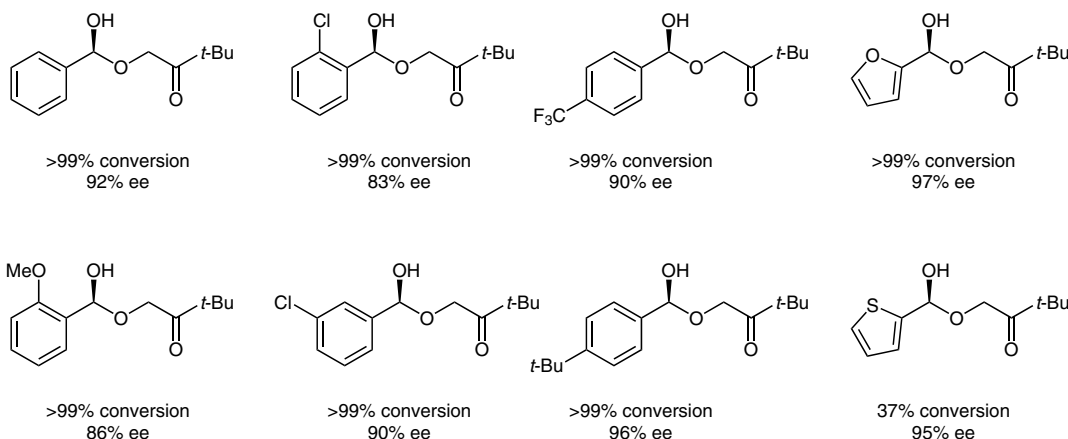
J. CHEN, D. LIU, N. BUTT, C. LI, D. FAN, Y. LIU, W. ZHANG* (SHANGHAI JIAO TONG UNIVERSITY, P. R. OF CHINA)

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

Enantioselective Palladium-Catalyzed Allylic Dearomatization



Selected examples:



Significance: Chiral α -acyloxy-1-arylethanols are an important class of useful structural motifs (R. S. Bhondwea 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. Fiecchi, 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.

SYNFACTS Contributors: Mark Lautens, Zafar Qureshi
Synfacts 2014, 10(1), 0064 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340444; **Reg-No.:** L15413SF