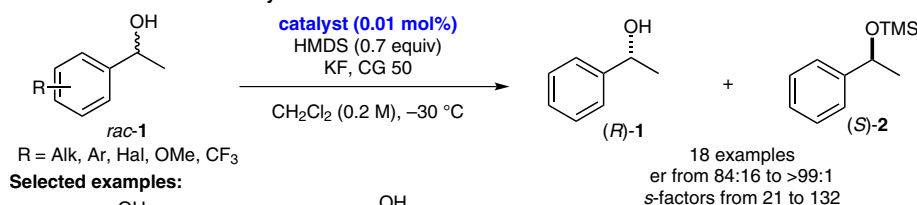
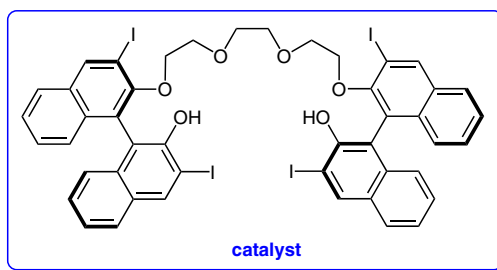
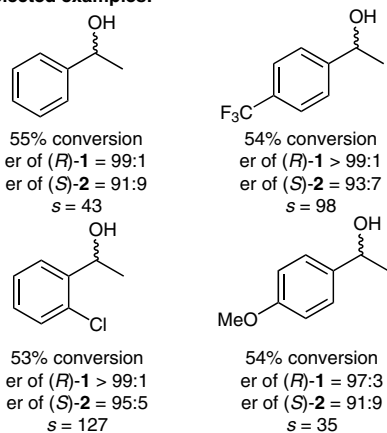


Highly Efficient and Enantioselective Silylation of Alcohols

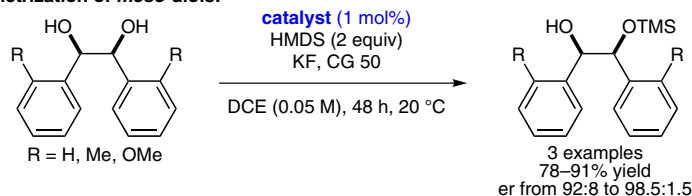
(a) Kinetic resolution of secondary alcohols:



Selected examples:



(b) Desymmetrization of meso-diols:



Significance: The Song group reports an asymmetric silylation of secondary alcohols catalyzed by a BINOL-derived polyether. By using HMDS as the silylating reagent, the authors were able to apply their developed catalytic system to kinetic resolution of secondary alcohols at a catalyst loading of 1 ppm. The system was also applied to the desymmetrization of meso-diols. Silylation of the catalyst is the predominant deactivation pathway. However, desilylation of this species is faster than that of the desired silylated products, thereby permitting regeneration of the catalytically active species through desilylation and subsequent protonation.

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Comment: Only a handful of reported organocatalytic reactions having high turnover numbers (TONs) are known (for a recent report with a TON >10⁵, see: *Angew. Chem. Int. Ed.* **2014**, 53, 8765). Song and co-workers contribute impressively to this field by presenting a catalytic system with TONs of up to 10⁶. For the first catalytic asymmetric silylation of alcohols with HMDS, see: *Synlett* **2015**, 26, 1093.

Category

Organo- and Biocatalysis

Key words

silylation

part-per-million catalysis

kinetic resolution

desymmetrization

alcohols

Synfact
of the month