Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key Words

asymmetric catalysis
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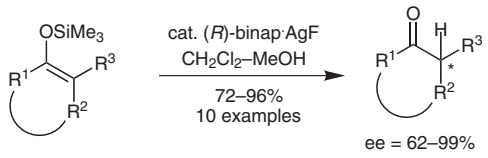

Significance: A catalytic enantioselective protonation of trimethylsilyl enol ethers using AgF·binap under very mild conditions (CH_2Cl_2–MeOH, –20 °C to 0 °C) is reported. Generally good to excellent yields and ee's were obtained. This method allows for preparation of enantiomerically enriched α-chiral ketones from racemic ketones by silyl enol ether formation followed by enantioselective protonation.

Comments: Cyclic trimethylsilyl enol ethers gave generally good yields and ee's using methanol as the proton source.

In the cases when R^3 = aryl, excellent yields and up to 99% ee's were obtained. Both 6- and 7-membered ring systems work well. However, no acyclic silyl enol ethers were reported in this communication. It was rationalized that Ag(I) acts as a Lewis acid to activate MeOH and F^- interacts with the silyl group in the protonation process. Previously, Yamamoto has reported that a chiral Lewis acid $SnCl_4$/BINOL-catalyzed enantioselective protonation of silyl enol ethers and ketene disilyl acetals using 2,6-dimethylphenol as the proton source (S. Nakamura, M. Kaneeda, K. Ishihara, H. Yamamoto *J. Am. Chem. Soc.* **2000**, *122*, 8120-8130). Nakai has reported cationic Pd(II)/BINAP systems to achieve the same reactions using H_2O as the proton source (M. Sugiura, T. Nakai *Angew. Chem. Int. Ed.* **1997**, *36*, 2366-2368).

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