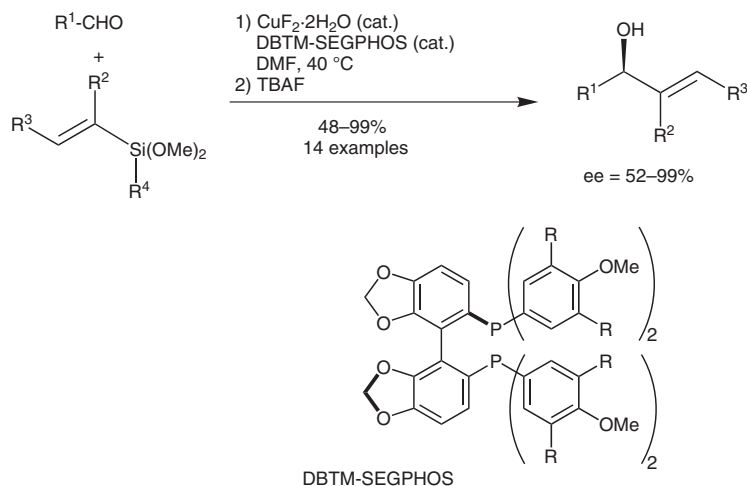


## CuF<sub>2</sub>-Catalyzed Enantioselective Synthesis of Allylic Alcohols and Diarylmethanols



**Significance:** Fast, effective and reliable methods for obtaining chiral allylic alcohols generally employ enantioselective resolution or alkenylzinc addition to aldehydes. These methods either waste half of the available reagent, or use pyrophoric, potentially dangerous reagents. Herein is presented a catalytic enantioselective method to synthesize chiral allylic alcohols and diarylmethanols from addition of air-stable vinyl- or phenylsiloxanes to aldehydes. Various aromatic, heteroaromatic, and easily enolizable aliphatic aldehydes can be coupled with simple and highly substituted vinylsiloxanes with excellent enantioselectivity.

**Comment:** The CuF<sub>2</sub>-(DBTM-SEGPHOS) catalyst is proposed to transmetallate the vinylsiloxane moiety to generate a fluorosiloxane and a chiral vinylcopper species. This species shows opposite reactivity to traditional organocopper reagents, displaying complete 1,2-selectivity in one of the examples. Ligand acceleration was observed, and suggested to be due to steric rather than electronic factors (for examples see: A. F. Littke, L. Schwarz, G. C. Fu *J. Am. Chem. Soc.* **2002**, *124*, 6343-6348; E. R. Strieter, D. G. Blackmond, S. L. Buchwald *J. Am. Chem. Soc.* **2003**, *125*, 13978-13980; S. Yamasaki, M. Kanai, M. Shibasaki *J. Am. Chem. Soc.* **2001**, *123*, 1256-1257). Finally, easily accessible 1,1'-disubstituted vinylsiloxanes were used with modest selectivity, whereas the alkenylzinc analogue is not readily accessible.