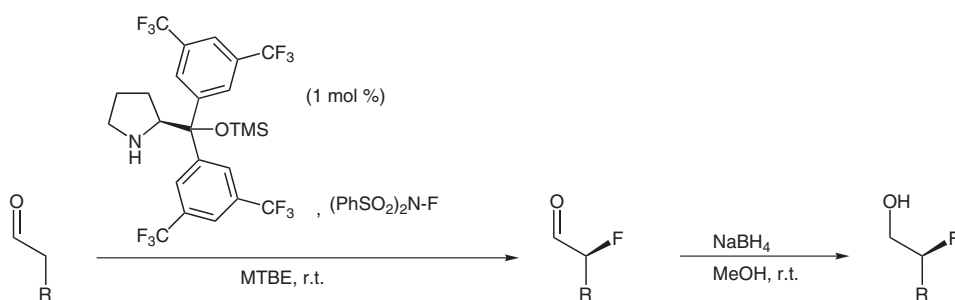


M. MARIGO, D. FIELENBACH, A. BRAUNTON, A. KJÆRSGAARD, K. A. JØRGENSEN*
(AARHUS UNIVERSITY, DENMARK)
Enantioselective Formation of Stereogenic Carbon-Fluorine Centers by a Simple Catalytic Method
Angew. Chem. Int. Ed. **2005**, *44*, 3703-3706.

Enantioselective Fluorination With a Simple Organic Catalyst



Significance: Fluorinated molecules are very important in medicinal, agricultural and materials science. This report is the first asymmetric fluorination of aldehydes with a simple catalyst obtaining extremely high ee's. The use of methyl *tert*-butyl ether as a solvent proved to be critical to reduce difluorination. The use of *N*-fluorodibenzene-sulfonimide (NFSI), which is a commercially available, stable and easy to handle fluoride source, is an excellent complement to the already simple catalyst system. The optically active α -fluorinated aldehydes were directly reduced to the corresponding α -fluorinated alcohols since the α -fluorinated aldehydes are unstable and more volatile than starting materials.

Comment : The authors have shown this proline-derived catalyst to be efficient for fluorination under ideal conditions (low catalyst loading, room temperature) for a variety of substrates. The catalyst is believed to operate through fluorination of the enamine intermediate. The proposed reason for the high yields of mono-fluorinated compounds with high ee's is rationalized through shielding of the α -proton by the bulky aryl groups, prohibiting racemization. For the same catalyst and asymmetric epoxidation see: *J. Am. Chem. Soc.* **2005**, *127*, 6964-6965.

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Key Words

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N-fluorodibenzene-
sulfonimide