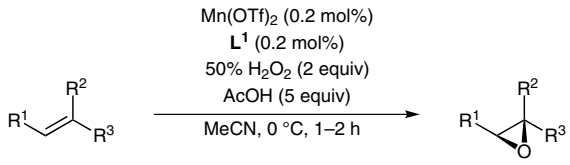
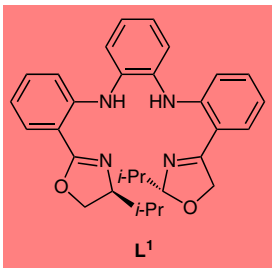
W. DAI, J. LI, G. LI, H. YANG, L. WANG, S. GAO* (DALIAN INSTITUTE OF CHEMICAL PHYSICS, DALIAN NATIONAL LABORATORY FOR CLEAN ENERGY AND UNIVERSITY OF CHINESE ACADEMY OF SCIENCES, BEIJING, P. R. OF CHINA)

Asymmetric Epoxidation of Alkenes Catalyzed by a Porphyrin-Inspired Manganese Complex
Org. Lett. **2013**, *15*, 4138–4141.

Manganese-Catalyzed Enantioselective Alkene Epoxidation

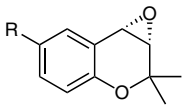
Overall transformation:



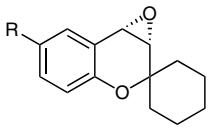


L1

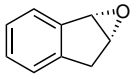
Selected examples:



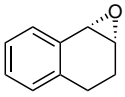
R = CN	95% yield, 95% ee
Cl	93% yield, 96% ee
Br	90% yield, 96% ee
NO_2	93% yield, 94% ee
CO_2Me	95% yield, 96% ee
Ph	98% yield, 94% ee
CH_2OH	96% yield, >99% ee



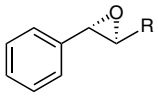
R = CN	98% yield, 90% ee
Br	91% yield, 94% ee
NO_2	92% yield, 92% ee
CO_2Me	97% yield, 90% ee
Ph	99% yield, 96% ee
NHAc	99% yield, 98% ee



93% yield, 84% ee

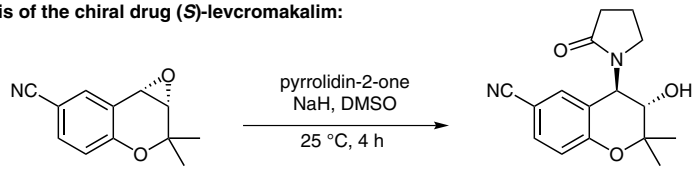


99% yield, 96% ee



R = Ph	95% yield, 92% ee
R = H	98% yield, 47% ee

Gram-scale synthesis of the chiral drug (*S*)-levcromakalim:



Significance: Epoxides are an important class of molecules and serve frequently as intermediates in complex molecule synthesis. Many highly effective protocols have been developed for the generation of enantioenriched epoxides by way of transition-metal and organocatalysis. However, not all classes of substrates proceed smoothly with high levels of enantioselectivity under the published methods, and therefore the development of new and robust epoxidation methods is of great interest.

Comment: Gao and co-workers report the use of Jacobsen-type manganese-catalyzed epoxidation of chromenes, indenes, styrenes, and dihydronapthalenes using a porphyrin-inspired tetradentate ligand. Products are obtained in excellent yields and enantioselectivities using a low catalyst loading (0.2 mol%).This environmentally friendly method makes use of two equivalents of H_2O_2 as the terminal oxidant. The authors were able to extend their methodology to the synthesis of the chiral drug (*S*)-levcromakalim.

SYNFACTS Contributors: Mark Lautens, David A. Petrone
Synfacts 2014, 10(1), 0069 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340446; **Reg-No.:** L15613SF

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

epoxidation

manganese

hydrogen peroxide