Category

Key words

epoxidation

alkenes

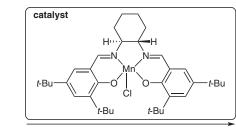
Metals in Synthesis

manganese catalysis enantioselective

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Highly Enantioselective Epoxidation Catalysts Derived from 1,2-Diaminocyclohexane *J. Am. Chem. Soc.* **1991**, *113*, 7063–7064.

The Jacobsen Epoxidation



aqueous NaOCl, $\mathrm{CH_2Cl_2}$, 4 °C, 6 h

0.25 mmol scale

R¹ R²

Reported examples:



84% yield, 92% ee 4 mol% of catalyst required



96% yield, 97% ee 3 mol% of catalyst required

67% yield, 92% ee 4 mol% of catalyst required



84% yield, 92% ee 15 mol% of catalyst required

72% yield, 98% ee 2 mol% of catalyst required

84% yield, 92% ee 10 mol% of catalyst required

Significance: Although manganese-catalyzed enantioselective epoxidation of nonactivated alkenes had been previously described by Jacobsen (*J. Am. Chem. Soc.* **1990**, *112*, 2801) and Katsuki (*Tetrahedron: Asymmetry* **1991**, *2*, 481), this report was the first general and highly enantioselective method to achieve this transformation. When compared to the Sharpless epoxidation, this method does not require allylic alcohols and works best with *cis*-alkenes.

Comment: Jacobsen found that by optimizing the size of the salen ligand, the approach of the olefin towards the metal center could be controlled. Thus, the bulky *tert*-butyl groups on the aromatic rings of the salen ligand limit the chance of competing approaches to the substrate.

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