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含有叔胺单元的手性 **Salen-Mn(III)** 复合物催化下碘甲烷加速的烯烃不对称环氧化

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收稿日期 2006-8-4 修回日期 2007-1-24 网络版发布日期 2007-5-28 接受日期

摘要 合成了一个系列含有两个叔胺取代基的手性salen-Mn(III)配合物, 并分别以吡啶氮氧化物和2,6-二甲基吡啶氮氧化物为轴向配体,

将其应用于催化非官能团化烯烃的不对称环氧化反应。以次氯酸钠为氧化剂, 在CH₂Cl₂/H₂O双相介质中, 取得了中等直至高的对映选择性和较高的产率。研究发现碘甲烷是有效的加速反应的添加剂, 推测是由于加入碘甲烷后, 催化剂上的叔胺基团转化为了季铵盐基团,

从而在CH₂Cl₂/H₂O双相介质中更有效地促进了反应的进行。催化模拟实验中对反应产物的ESI-HRMS分析表明, 添加碘甲烷后生成了一个含有两个季铵盐基团,

同时含有一分子轴向配位的吡啶氮氧化物和一个轴向配位的水分子的(salen)manganese(III)中间体。

关键词 [不对称环氧化](#), [对映体选择性](#), [非官能团化烯烃](#), [双相的](#), [相转移](#)

分类号

Methyl Iodide Accelerated Asymmetric Epoxidation of Alkenes Catalyzed by Chiral Salen-Mn(III) Complexes with Tertiary Amine Units

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Abstract A series of chiral salen-Mn(III) complexes featuring two tertiary amine units were synthesized and employed in the enantioselective epoxidation of unfunctionalized alkenes in the presence of pyridine *N*-oxide and 2,6-dimethylpyridine *N*-oxide as proximal ligands, respectively. Moderate to high enantioselectivity and acceptable yields were achieved when NaClO was used as terminal oxidant under CH₂Cl₂/H₂O biphasic media. Methyl iodide was found to be an effective additive to accelerate the epoxidation, possibly owing to the formation of quaternary ammonium units on catalysts, which may facilitate the reaction in an oil/water biphasic medium. The subsequent stimulation experiment was carried out, and the resulting ESI-HRMS analysis revealed the formation of a novel (salen)manganese(III) intermediate featuring two quaternary ammonium units, and bearing a pyridine *N*-oxide and a molecule of water simultaneously axially-coordinated backbone.

Key words [asymmetric epoxidation](#) [enantioselectivity](#) [unfunctionalized alkene](#) [biphasic](#) [phase-transfer](#)

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