研究论文

单面桥联手性金属卟啉的合成、构象分析及不对称催化氧化性能

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摘要 合成并表征了新型单面桥连手性卟啉(1a)及其铁配合物(1b),利用分子力学方法和¹H NMR对手性卟啉的 空间构象及手性空腔特征进行了分析. 将化合物1b用于苯乙烯衍生物的催化环氧化反应, 结果表明, 轴向配体的存 上本文推荐给朋友 在使化合物1b获得了较高的对映选择性(e.e.为73%-80%), 反应产率及速率也有大幅度提高, 4-叔丁基吡啶的 效果最好. 催化体系中轴向配体控制了反应底物向化合物1b手性空腔的定向趋近, 从而有效地提高了手性催化性

关键词 手性卟啉 不对称催化 e.e.值 构象分析

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Synthesis, Conformation Analysis and Asymmetric Catalytic Oxidation Performance of Mono-faced Bridged Chiral Porphyrins

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Abstract Novel mono-faced bridged chiral porphyrins 1a and iron complex 1b were synthesized and characterized. Conformation analysis was performed by using molecular mechanics conformation search method. The theoretic viable lowest energy conformation of compound 1a greatly coincided with ¹H NMR data. Compound 1b was used as the catalyst in asymmetric styrene devivatives epoxidation. In the absence of nitrogen base ligand, the epoxides were formed on a lower e.e. (25%—28%), when axial ligand was present, compound 1b exhibited an increased epoxidation rate, yield and much higher e.e. (73%—80%). The added nitrogen base can efficiently block the oxidation reaction at the unhinded side of the porphyrin ring and directionally control the oxygen transfer and substrate approach to the chiral cavity.

Key words Chiral porphyrin; Asymmetric catalysis; e.e. value; Conformation analysis

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