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Article

Asymmetric Transfer Hydrogenation of Ketones in Aqueous Solution Catalyzed by Rhodium(III) Complexes with C_2-Symmetric Fluorene-Ligands Containing Chiral (1*R*,2*R*)-Cyclohexane-1,2-diamine

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Dois ligantes C_2-simétricos bis(sulfonamide) contendo o fluoreno-quiral (1*R*,2*R*)-ciclohexano-1,2-diamina foram complexados com $Rh^{III}(Cp^*)$ e usados como catalizador para redução aromática de cetonas. Os alcoois secundários correspondentes foram obtidos com *ee* 87-100% e rendimento de 85-99%, sob condições de transferência de hidrogenio assimétrica (THA), usando formato de sodio aquoso como fonte de hidretos. Usando acetofenona, obteve-se *ee* de 94% e rendimento de 86-97%, com uma razão substrato/catalizador de 10.000.

Two C_2-symmetric bis(sulfonamide) ligands containing fluorene-chiral (*1R,2R*)-cyclohexane-1,2-diamine were complexed to $Rh^{III}(Cp^*)$ and used as catalyst to reduce aromatic ketones. The corresponding chiral secondary alcohols were obtained in 87-100% *ee* and 85-99% yield, under asymmetric transfer hydrogenation (ATH) conditions using aqueous sodium formate as the hydride source. With acetophenone, 94% *ee* and 86-97% yield was achieved with substrate/catalyst (S/C) ratio of 10,000.

Keywords: bis(sulfonamide) ligands, $Rh^{III}(Cp^*)$ complexes, asymmetric transfer hydrogenation

Introduction

The demand for enantiomerically pure compounds have been continuously increasing over the last three decades. This demand is due to strict government regulations that require evaluation of all the possible stereoisomers of a compound and commercialization of a chiral product only as a single enantiomer.[1] Among small chiral molecules, the chiral alcohols occupy an important place in the synthesis of pharmaceuticals,[2] cosmetic and food,[3] and agricultural chemicals.[4] Thus, the catalytic enantioselective reduction of prochiral ketones is one of the most practical ways to obtain pure chiral secondary alcohols.[5] Noyori's enantioselective reduction of prochiral ketones using molecular hydrogen and chiral Ru-BINAP-amine complex has already found a useful niche in the fine chemicals industry.[6]

However, in spite of the great advances that have been reached in the area of homogeneous asymmetric catalysis, only a limited number of catalysts have found application in the industry. This drawback is mainly due to the cost of metals, metal contamination, environmentally unfriendly solvents and disposal problems, turnover number (TON) and turnover frequency (TOF).[7] Most of the development on the homogeneous asymmetric catalysts has been made from chiral ligands, which have been synthesized based on phosphorus, amines or amino alcohols derivatives, and then coordinated to Rh^{III}, Ru^{II} or Ir^{III} metal centres.[8]

Due to the demand of environmentally friendly methods, the search for water soluble catalysts has received much attention in recent years considering its safety, economical and environmentally benign nature compared to most organic solvents.[9] Recently, a number of asymmetric transfer hydrogenation (ATH) reports have appeared, using heterogenized or water soluble metal complexes, and sodium formate as the hydride source to get enantiopure chiral alcohols from aromatic prochiral ketones.[10] Addressing this, we have reported a C_2^- symmetric bis(sulfonamide)-cyclohexane-1,2-diamine ligand [(**1**), Figure 1] complexed

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