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Asymmetric Transfer Hydrogenation of Ketone Catalyzed by Novel Ru(II)-Chiral Sulfonamide Complex

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Abstract: Two new chiral Ru(II)-sulfonamide complex have been used to catalyze the enantioselective transfer hydrogenation of prochiral ketones and the secondary alcohols are obtained with good to excellent optical yields.

Keywords: Sulfonamide, transfer hydrogenation.

Asymmetric catalytic transfer hydrogenation, due to its practical method for the stereoselective synthesis of chiral alcohols, attracts much attention and has been extensively studied. The most well known ligands is chiral 1,2-diamine with C2-symmetry[1]. But the tridentate nitrogen ligand having quinoline group has relatively been neglected. We have investigated sulfonamide derivatives in the use of enantioselective transfer hydrogenation of ketone[2]. In this paper, we report two new chiral Ru (II)-sulfonamide catalysts prepared *in situ* from chiral sulfonamide and $[RuCl_2(\eta^6\text{-cumene})]_2$ for the asymmetric transfer hydrogenation of ketone.

The two chiral sulfonamide (1R,2R) N-quinoline-8-sulphonyl-1,2-diphenylethy-lenediamine **L1** and (1R,2R) N-quinoline-8-sulphonyl-1,2-cyclohexanediamine **L2** were synthesized as **Scheme 1**. Their structures were confirmed by elemental analysis, MS and ^{1}HNMR.

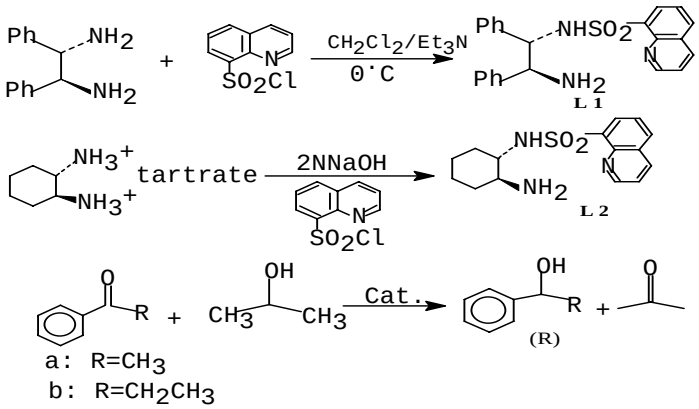
The ligand **L1** was prepared from the reaction of chiral (1R,2R)-1,2-diphenylethylenediamine with 8-quinoline sulfonyl chloride at 0°C for 24 h. In the case of **L2**, we adopted Jaume 3 method, starting from tartrate salt of (1R,2R)-1,2-cyclohexane diamine, firstly the tartrate salt was added to 2 mol/L NaOH solution to generate the free chiral diamine, then dichloromethane was added, the solution was cooled in ice bath, afterward the CH_2Cl_2 solution of quinoline-8-sulphonyl chloride was added, the mixture was stirred overnight at r.t. , the solvent was removed and **2** was obtained in high yield.

The catalytic transfer hydrogenation of ketones with the *in situ* formed from Ru (II)- sulfonamide catalysts **1** and **2** has been investigated. Isopropanol was used as hydrogen donor.

In a typical procedure under argon atmosphere, the mixture of $[RuCl_2(\eta^6\text{-cumene})]_2$ (0.02 mmol), **L1** or **L2** (0.04 mmol), KOH (0.05 mmol) and ketone (0.8

mmol) in 4 mL isopropanol was stirred at 35°C for 6 days. After reaction the yield (82~96%) of optical active alcohol was measured by GC,enantiomeric excess was determined by capillary GC analysis of the product using a CP-Cyclodex-236 mm (0.25 mm × 25 mm) chiral column.

Scheme 1



In the presence of 5 mol% or 10 mol% **1**, the transfer hydrogenation of acetophenone afforded R-phenylethanol in 83.8% and 92.1% e.e. In the use of 10 mol% of **1** ,propiophenone gave R-1-phenyl-1-propanol in 60.4% e.e. In the presence of 5 mol% 2, acetophenone or propiophenone gave corresponding alcohols in 57.6% e.e and 47.5% e.e respectively.

In summary, both **1** and **2** are good catalysts for enantioselective transfer hydrogenation of ketones. Further studies on the asymmetric transfer hydrogenation of ketones catalyzed by **1** and **2** are in progress.

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References and Notes

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