

Synthesis of new chiral task-specific ionic liquid based on 1,2-aminoalcohol derived from L-proline.

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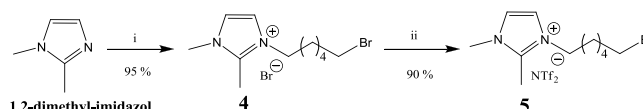
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Abstract

In this work we describe the synthesis of a chiral 1,2-aminoalcohol with attached imidazolium tags as a potential catalyst for asymmetric addition of organozinc reagents to aldehydes performed in ionic liquids (ILs).

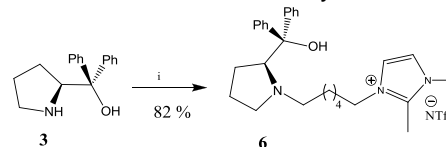
The imidazolium derivative ionic liquid **5** was obtained according to figure 2 with high yields.⁵



(i) 1,6-dibromohexane, acetonitrile, 70 °C, 15h; (ii) LiN(NTf₂)₂, H₂O

Figura 2. Synthesis of IL **5**.

The figure 3 shows the alkylation of aminoalcohol **3** using the IL **5** as alkylating agent providing the chiral IL **6** with a six carbon link in 82% yield.



(i) **5**, acetonitrile, 70 °C, 3 days.

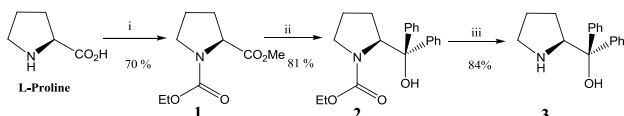
Figura 3. Synthesis of chiral ionic ligand **6**.

Introduction

The addition of dialkylzincs to aldehydes is a well established synthetic reaction, which provides a means for the preparation of secondary alcohols in high enantioselectivities.¹ Ligands which have been reported for this application include homochiral 1,2-, 1,3- and 1,4-aminoalcohols among others.¹ In recent times, as sustainability issues have gained importance, the interest in homogeneous ligands immobilized on a variety of supports (polymers, inorganic solids, hybrid materials, and nanoparticles),² which present additional advantages of simple separation, recovery and reuse of the catalyst. In this context, ionic liquids (ILs) are receiving growing attention as a means to immobilize catalysts, facilitating product isolation and also offering an opportunity to reuse the catalyst.³ Inspired by these findings, we describe the preparation of a novel task-specific chiral ionic ligand, based on a classical 1,2-aminoalcohol, with an attached imidazolium salt. Such chiral IL presents great potential to perform as catalyst in the asymmetric addition of alkylzinc reagents to aldehydes in heterogeneous media (ILs).

Results and discussion

The synthesis of classical chiral 1,2-aminoalcohol **3** from L-proline, is described below (figure 1).⁴



(i) K₂CO₃, Ethyl chloroformate, CH₃OH, r.t. 15h; (ii) PhMgBr, THF, 0°C, 2h; (iii) 1. KOH, CH₃OH, Toluene, reflux, 1h; 2. H₂O, reflux, 1h;

Figura 1. Synthesis of chiral aminoalcohol **3**.

Conclusions

In this work we synthesized a new chiral ionic ligand, 1,2-aminoalcohol, which presents great potential for evaluation as chiral catalyst in the asymmetric addition of alkylzinc to aldehydes in heterogeneous conditions provided by ILs.

Acknowledgments

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