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Easily recoverable BINOL ligand with ionic tag for asymmetric catalysis

Benoît Gadenne, Peter Hesemann and Joël J. E. Moreau*

UMR5076 CNRS/ENSCM, Hétérochimie Moléculaire et Macromoléculaire, 8, rue de l'Ecole Normale, 34296 Montpellier, France

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Abstract—A new chiral task specific ionic species containing chiral (*S*)-binaphthyl unit was synthesized and used as an auxiliary in the Ti-promoted addition of diethylzinc to benzaldehyde. The utilization of the ionic ligand containing the (*S*)-BINOL substructure led to enantioselectivities similar to those of the related non-ionic counterpart. The ionic substructure allowed an appropriate tuning of the solubility of the BINOL ligands in order to ensure reaction in a homogeneous medium and recovery of the chiral auxiliary. The reaction was performed in CH_2Cl_2 while the chiral ionic auxiliary was re-used in three catalytic cycles without a loss in activity or enantioselectivity.
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1. Introduction

Transition metal catalysis in ionic liquid (IL) media has recently attracted considerable interest and led to numerous applications in organic synthesis and organometallic catalysis.[1–6] Particular attention has been paid to enantioselective transformations in IL media.[7–15] The immobilization of the catalyst species in IL media was shown to a be suitable way for catalyst recovery and recycling. In many cases, transition metal complexes in hydrophobic ILs form catalytic solutions, which can easily be separated from the product mixture and re-used.

Tethering functional groups to ionic substructures gives rise to task-specific ionic liquids (TSILs).[16,17] These compounds combine the properties of the anchored organic groups with the solubility behavior of ionic liquids. Anchoring transition metal containing substructures led to catalytic TSILs with enhanced ionophilicity,[18] which improves catalyst re-usability.[19–25]

As part of our current interest in immobilized ionic species,[26] we recently focused on the utilization of TSIL ligands in homogeneous asymmetric catalysis using organic solvents as reaction media.[27] Readily available D-camphorsulfonamides functionalized with ionic imidazolium substructures showed high solubility in polar organic solvents and were used as chiral auxiliaries in the Ti-promoted diethylzinc addition to benzaldehyde. The ionic entity served as catalyst recovery vehicle and allowed a simple recycling of the chiral auxiliary. Herein, we report a new ionic chiral auxiliary containing (*S*)-BINOL substructures with enhanced enantioselectivity.

Chiral binaphthyls are among the most efficient auxiliaries in asymmetric catalysis.[28,29] We observed that the immobilization of catalytic binaphthyl species in hybrid silica gels[30] and reticulated polystyrene gels[31] led to limited recycling of the immobilized catalyst systems. We explored the ionic tag strategy as a means to generate highly selective and re-usable BINOL derived chiral ligands.

2. Results and discussion

2.1. Synthesis of a BINOL containing ionic liquid

The synthesis of the BINOL functionalized TSIL was realized in a multi-step synthesis starting from (*S*)-BINOL (Scheme 1).

In a first reaction sequence, we synthesized 6-bromo-1,1′-bi-2-naphthol according to a literature procedure described.[32,33] The monoesterification of 1,1′-bi-2-naphthol

* Corresponding author. Tel.: +33 4 67 14 72 11; fax: +33 4 67 14 72 12; e-mail: jmoreau@cit.enscm.fr

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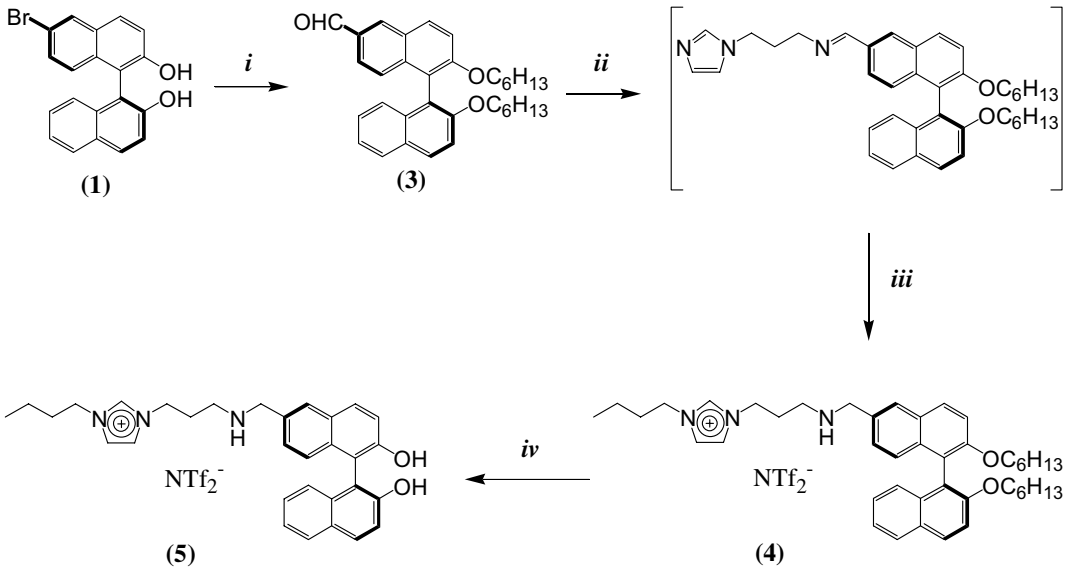


Scheme 1. Synthesis of the (*S*)-BINOL containing ionic compound **5**. Reactions and conditions: (i) (a) *n*-$C_6H_{13}Br$, K_2CO_3, acetone; (b) *n*-BuLi, Et_2O, then DMF/H^+; (ii) 3-(aminopropyl)-imidazole, CH_2Cl_2; (iii) (a) *n*-C_4H_9Br; (b) $NaBH_4$, MeOH; (c) Li NTf_2, H_2O; (iv) BBr_3, CH_2Cl_2, −78 °C.

was achieved using pivaloyl chloride leading to the formation of (*S*)-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl in excellent selectivity. Monobromination, occurring exclusively on the non-esterified naphthyl groups, followed by the saponification of the pivaloyl ester afforded 6-monobromo-1,1′-bi-2-naphthol **1**.

In a second reaction sequence, we synthesized the chiral monofunctional binaphthyl building block. Protection of the hydroxyl groups of **1** by etherification using *n*-bromohexane under basic reaction conditions yielded (*S*)-6-bromo-2,2′-dihexyloxy-1,1′-binaphthyl **2**. 2,2′-Bis(hexyloxy)binaphthyls are convenient binaphthyl derived intermediates due to their solubility and their conformational stability. The monofunctionalized key intermediate (*S*)-2,2′-dihexyloxy-1,1′-binaphthyl-6-carbaldehyde **3** was prepared via bromine–lithium exchange followed by formylation using DMF and acidic work-up. Both steps afforded the products in yields >90%.

In the third part of the synthetic procedure, we realized the coupling of the chiral binaphthyl building block with an ionic imidazolium substructure. The reaction of carbaldehyde **3** with *N*-3-aminopropylimidazole firstly led to the formation of the corresponding imine functionalized with a terminal imidazole group, which was then alkylated using 1-bromobutane. The resulting ionic imine was reduced with sodium borohydride. Finally, anion metathesis was achieved with *N*-lithiotrifluoromethanesulfonimide leading to the highly viscous and water immiscible product **4**. It is noteworthy that the intermediate products in this reaction sequence were directly processed without further purification or characterization. The overall yield for the preparation of the hydrophobic TSIL **4** starting from carbaldehyde **3** was about 67%. This method for the anchoring of imidazolium substructures involving the formation of an imine–alkylation–reduction–anion metathesis should be of general interest for the synthesis of TSILs from aldehydes.

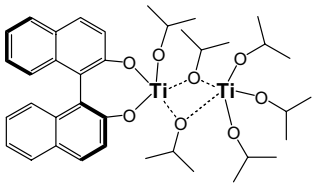
The last step concerns the generation of functionalized (*S*)-BINOL species by the deprotection of the ionic hexyloxy binaphthyl **4**. The cleavage of aryl–alkyl ethers is generally performed in strongly acidic media and requires drastic reaction conditions. The ether cleavage using boron tribromide[34] is a suitable way of generating polymer supported BINOL from the corresponding hexyloxy binaphthyls.[31] We applied this procedure for the deprotection of binaphthyl functionalized TSIL. Interestingly, this reaction occurred very selectively and afforded the BINOL-functionalized IL in high purity and quantitative yield, indicating high stability of imidazolium derived ionic liquids under strongly acidic conditions.

Although the enantiomeric excess of the BINOL entity in the TSIL **5** cannot be measured, we believe that no racemization occurred during the multi-step synthesis of this compound, as we observed configurational stability of BINOL derivatives under similar reaction conditions.[31] The BINOL functionalized TSIL **5** is a glassy product, which is insoluble in common organic solvents except for methanol, ethanol, and DMSO. However, the compound becomes soluble in dichloromethane upon addition of titanium tetraisopropoxide, allowing us to perform the test reaction under standard conditions in a homogeneous CH_2Cl_2 solution.

2.2. Utilization of the (*S*)-BINOL containing ionic liquid in asymmetric catalysis

The Ti-promoted asymmetric addition of diethylzinc to benzaldehyde is a useful model reaction for the evaluation of the catalytic properties of various chiral auxiliaries such as 1,2-cyclohexyl-bis(sulfonamides), TADDOL, or BINOL derivatives.[35,36] A BINOL-Ti^{IV} complex is a very efficient catalyst for the addition of diethylzinc to benzaldehyde. It has been established that the catalytic species in this reaction is a dinuclear

titanium complex bound to one chiral BINOL entity (Scheme 2).[37,38]



Scheme 2. Supposed structure of the catalytic (S)-BINOL-Ti^{IV}-complex.

We used this simple reaction for the evaluation of the catalytic activity of TSIL **5** and a comparison with those of molecular (*S*)-BINOL. The results are summarized in Table 1.

The utilization of molecular (*S*)-BINOL at room temperature gave (*S*)-1-phenylpropan-1-ol in quantitative yield and in 82% ee (entry 1). A selectivity of 92% was reported at 0 °C.[38] The ionic compound **5** showed similar activity and enantioselectivity in the test reaction (entry 2). This result indicates that the covalently bound imidazolium substructure in compound **5** does not affect either the composition of the formed catalytic complex nor the catalytic reaction cycle. Furthermore, this result shows that no racemization of the BINOL-backbone occurred during the synthetic procedure of the task specific salt.

The main aspect of this study concerned the re-usability of chiral ionic auxiliary **5**. After the hydrolysis of the reaction mixture (0.1 M hydrochloric acid), the reaction products were isolated by extraction using diethyl ether. Rapid filtration of the resulting heterogeneous aqueous phase and washing of the precipitate with 1 M hydrochloric acid and water afforded, after drying, the pure TSIL as a brownish powder in a nearly quantitative yield (>95%). The isolated product was re-used under similar reaction conditions in a three further reaction cycles. After each reaction cycle, characterization of the recovered TSIL by ^{1}H NMR spectroscopy confirmed the structural integrity of the chiral auxiliary.

In all reaction cycles, the recovered chiral ionic ligand showed identical catalytic properties in terms of catalytic activity and selectivity (Table 1, entries 3–5).

We showed that the recycling of catalytic species can be achieved by grafting ionic substructures to chiral auxiliaries. Conversely to supported catalyst systems, where a high proportion of the reagent mass and volume serves as support for the catalytic species, this approach minimizes mass increase and achieves the recovery of the catalyst by a rather slight structural modification. The catalytic properties can be transposed from the molecular catalyst [(*S*)-BINOL] to the ionic system. The reactions can be carried out in homogeneous solution, and the negative effects of the support (heterogeneous kinetics, accessibility of the catalytic species), often observed for polymer supported catalysts, can nearly be neglected. Thus, the use of chiral auxiliaries tagged with ionic entities combine the advantages of homogeneous catalysis (reactivity, defined structure of the catalyst) with those of heterogeneous catalysis (easy product–catalyst separation, reusability). This approach simplifies the recovery of chiral auxiliaries, and can be transposed to the recycling of other functional organic compounds.

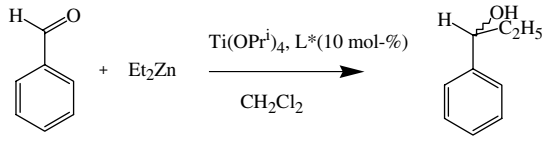
3. Conclusion

We have synthesized a new chiral task-specific ionic compound containing binaphthyl substructures. An (*S*)-BINOL containing imidazolium salt was successfully used as a chiral auxiliary in the asymmetric addition of diethylzinc to benzaldehyde and showed similar catalytic properties as the non-ionic counterpart. The ionic substructures allows convenient recovery of the ionic compound after the reaction and can be considered as a ligand recovery vehicle. The easy-to-handle (*S*)-BINOL functionalized imidazolium salt was re-used for three reaction cycles.

4. Experimental section

General remarks: The reactions were performed under a nitrogen or argon atmosphere using Schlenk tube

Table 1. Additions of diethylzinc to benzaldehyde catalyzed by various (*R*)-BINOL/Ti(IV) complexes[a]



Entry	L*	Conversion[b] (%)	Ee[c] (%)	Configuration[c]
1	(*S*)-BINOL	>99	82	*S*
2	Ionic compound **5**	>99	82	*S*
3	Ionic compound **5**; 2nd run	>99	81	*S*
4	Ionic compound **5**; 3rd run	>99	81	*S*
5	Ionic compound **5**; 4th run	>99	82	*S*

[a] General reaction conditions: benzaldehyde:(*S*)-BINOL:Ti(O-*i*Pr)$_4$:Et_2Zn = 1.0:0.1:0.7:3 (molar ratio), reaction time 20 h.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Determined by HPLC using a Daicel Chiralcel OD column.

techniques when necessary. ^{1}H and ^{13}C NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers. $CDCl_3$ and DMSO-d_6 were used as NMR solvents. Chemical shifts are reported as δ-values in ppm relative to TMS. IR-spectra were recorded with a Perkin–Elmer SPECTRUM 1000 FT-IR spectrometer. Mass spectra were measured on a JEOL MS-DX 300 mass spectrometer. Optical rotations were measured on a Perkin–Elmer polarimeter 241. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS' at Vernaison (France). Enantiomeric excess of 1-phenylpropanol were determined by chiral HPLC using a Waters 515 HPLC pump with a Waters 2487 UV-detector and a Daicel Chiralcel OD column. All reagents were obtained from commercial sources and used without purification. In experiments requiring dry solvents, THF, toluene, and diethyl ether were distilled over sodium-benzophenone, DMF was distilled over CaH_2, dichloromethane was distilled over P_2O_5, and alcohols were distilled over Mg. The preparation of (*S*)-6-bromo-2,2′-dihydroxy-1,1′-binaphthyl **1** was carried out according to the literature.[32,33]

4.1. (*S*)-6-Bromo-2,2′-dihexyloxy-1,1′-binaphthyl 2

To a solution of (*S*)-6-bromo-2,2′-dihydroxy-1,1′-binaphthyl (2.19 g, 6 mmol) dissolved in 50 mL of acetone were added 7.5 g (54 mmol) of potassium carbonate and 3.4 mL (4.0 g, 24 mmol) of 1-bromohexane. The resulting heterogeneous mixture was heated under reflux for 24 h. After cooling to room temperature, the solvent was evaporated, and the crude mixture dissolved in diethyl ether (100 mL) and water (200 mL). The ether phase was separated and the aqueous layer extracted with diethyl ether (2×50 mL). The combined ether phase was dried and filtered. Evaporation of the solvent afforded the product as a viscous oil, which was purified by column chromatography (silica gel, cyclohexane/ethyl acetate 90/10). Yield: 2.99 g/5.6 mmol, 93%. ^{1}H NMR ($CDCl_3$): δ 0.70–0.77 (2t, 6H), 0.85–1.07 (m, 12H), 1.34–1.44 (m, 4H), 3.85–4.01 (m, 4H), 7.02 (d, 1H, $J = 8.9$ Hz), 7.09 (d, 1H, $J = 8.9$ Hz), 7.18–7.34 (m, 3H), 7.38 (d, 1H, $J = 4.9$ Hz), 7.42 (d, 1H, $J = 4.9$ Hz), 7.82 (d, 1H, $J = 9.0$ Hz), 7.85 (d, 1H, $J = 8.5$ Hz), 7.93 (d, 1H, $J = 9.0$ Hz), 7.99 (d, 1H, $J = 2.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 14.44, 14.47, 22.96, 23.02, 25.80, 25.89, 29.82, 29.88, 31.81, 31.85, 70.07, 70.12, 116.01, 117.17, 117,69, 120.34, 121.44, 123.95, 125.72, 126.69, 127.97, 128.39, 128.64, 129.73, 129.78, 129.82, 130.20, 130.80, 133.28, 134.61, 155.01, 155.36; ν (KBr)/cm^{-1} 3058, 2930, 2870, 1622, 1586, 1495, 1466, 1326, 1270, 1243, 1090, 1068, 803; HRMS [FAB+] calcd for $C_{32}H_{37}BrO_2$ $(M)^+$ 532.1977, found: 532.1929; $[\alpha]_D^{25} = -67.1$ (*c* 1.46, CH_2Cl_2).

4.2. (*S*)-2,2′-Dihexyloxy-1,1′-binaphthyl-6-carbaldehyde 3

In a Schlenk tube under an inert atmosphere, 1.51 g (2.8 mmol) of (*S*)-6-bromo-2,2′-dihexyloxy-1,1′-binaphthyl were solubilized in diethyl ether (30 mL). To this solution cooled to −80 °C were added dropwise 6.0 mL of butyl lithium (1.6 M in hexanes). The yellow reaction mixture was allowed to warm to −10 °C with stirring for 2 h. The solution was then cooled to −80 °C and 3 mL of DMF were added dropwise at this temperature. After stirring for 30 min at −80 °C, the reaction mixture was stirred for a further 2 h at room temperature. The resulting suspension was poured in 200 mL of crunched ice/100 mL hydrochloric acid (2 M) and stirred for 30 min. The reaction product was extracted with 3×50 mL of diethyl ether. Drying over magnesium sulfate and evaporation of the solvents under reduced pressure yielded in a highly viscous oil. Column chromatography of the crude product (silica gel, pentane/Et_2O 90/10) afforded the pure title compound. Yield: 1.29 g, 2.7 mmol, 94%. ^{1}H NMR ($CDCl_3$): δ 0.68–0.76 (2t, 6H), 0.86–1.12 (m, 12H), 1.32–1.49 (m, 4H), 3.85–4.08 (m, 4H), 7.09 (d, 1H, $J = 8.0$ Hz), 7.17–7.35 (m, 3H), 7.41 (d, 1H, $J = 9.0$ Hz), 7.49 (d, 1H, $J = 9.0$ Hz), 7.66 (dd, 1H, $^{1}J = 8.8$ Hz, $^{2}J = 1.7$ Hz), 7.89 (d, 1H, $J = 8.0$ Hz), 7.95 (d, 1H, $J = 8.9$ Hz), 8.10 (d, 1H, $J = 8.7$ Hz), 8.35 (d, 1H, $J = 1.4$ Hz), 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.33 (2C), 22.85, 22.88, 25.67, 25.76, 29.58, 29.74, 31.69 (2C), 69.70, 69.95, 115.83, 116.30, 119.89, 121.33, 123.43, 123.91, 125.46, 126.69, 126.98, 128.39, 128.44, 129.65, 129.62, 131.46, 132.51, 134.39, 135.35, 138.08, 154.91, 157.77, 192.51; ν (KBr)/cm^{-1} 3057, 2930, 2858, 1694, 1621, 1593, 1464, 1346, 1274, 1235, 1162, 1148, 1089, 1047, 806; HRMS [FAB+] calcd for $C_{33}H_{38}O_3$ $(M)^+$ 482.2821, found: 482.2825; $[\alpha]_D^{25} = -54.9$ (*c* 2.06, CH_2Cl_2).

4.3. (*S*)-3-Butyl-1-{3-[(2,2′-dihexyloxy-[1,1′]binaphthalenyl-6-ylmethyl)-amino]propyl}-3*H*-imidazol-1-ium bis-(trifluoromethanesulfonyl)imide 4

Step 1, formation of the imine. (*S*)-2,2′-Dihexyloxy-1,1′-binaphthyl-6-carbaldehyde **3** (1.74 g, 3.6 mmol) was dissolved in 20 mL of ethanol and *N*-(3-aminopropyl)imidazole (0.45 g, 3.6 mmol) added. The homogeneous solution was stirred at room temperature for 30 min and then heated to reflux for 2 h. After cooling to room temperature, the volatiles were pumped off, yielding the imine as a viscous product.

Step 2, alkylation. The imine was dissolved in 10 mL of 1-bromobutane, and the mixture heated to reflux for 10 h. After this time, the heterogeneous reaction mixture was cooled to room temperature and the excess of the alkyl halide eliminated firstly by evaporation in vacuum and then by washing with pentane (3×20 mL).

Step 3, reduction. The resulting alkylated compound was dissolved in 20 mL of methanol. The resulting solution was cooled to 0 °C and sodium borohydride (180 mg, 4.8 mmol) was slowly added with vigorous stirring. The resulting suspension was stirred for 3 h. The methanol was evaporated and the crude product dissolved in water (100 mL). The aqueous solution was washed with diethyl ether (2×50 mL).

Step 4, anion metathesis. A solution of *N*-lithiotrifluoromethanesulfonimide (1.15 g, 4 mmol) in water (30 mL) was added to the aqueous solution of the functional imidazolium bromide. The hydrophobic ionic

liquid precipitated immediately. Compound **4** was isolated by extraction with dichloromethane, drying, and evaporation of the solvent. Yield: 2.25 g (2.42 mmol). ^{1}H NMR ($CDCl_3$): δ 0.69–0.77 (2t, 6H), 0.88–1.08 (m, 15H), 1.17–1.48 (m, 6H), 1.60–1.77 (m, 2H), 1.98 (q, 2H, J = 6.3 Hz), 2.61 (t, 2H, J = 6.2 Hz), 3.83 (s, 2H), 3.87–4.02 (m, 7H), 4.27 (t, 2H, J = 6.6 Hz), 6.89 (t, 1H, J = 1.9 Hz), 6.95 (t, 1H, J = 1.9 Hz), 7.06–7.34 (m, 5H), 7.41 (d, 2H, J = 9.0 Hz), 7.70 (s, 1H), 7.84–7.95 (m, 3H), 8.71 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.22, 13.87, 13.89, 19.34, 22.41, 22.46, 25.26, 25.30, 29.31, 29.36, 31.28, 31.33, 31.81, 44.15, 47.49, 49.90, 53.30, 69.66, 69.80, 77.20, 115.81, 116.15, 120.32, 120.27 (q, CF_3, J = 321 Hz), 120.50, 121.49, 122.68, 122.96, 123.42, 125.21, 125.94, 126.02, 126.90, 127.79, 127.93, 128.96, 129.02, 129.22, 129.30, 133.66, 134.10, 135.73, 154.49, 154.85; ν (KBr)/cm^{-1} 3147, 2933, 2871, 1593, 1466, 1352, 1194, 1136, 1058; HRMS [FAB+] calcd for $C_{43}H_{58}N_3O_3$ (cation) 648.4529, found: 648.4541; $[\alpha]_D^{25} = -35.5$ (c 1.04, CH_2Cl_2).

4.4. (*S*)-3-Butyl-1-{3-[(2,2′-dihydroxy-[1,1′]binaphthalenyl-6-ylmethyl)-amino]propyl}-3*H*-imidazol-1-ium bis-(trifluoromethanesulfonyl)imide 5

The protected ionic liquid **4** (1.89 g, 2.0 mmol) was dissolved in 20 mL of freshly distilled dichloromethane and cooled to −80 °C. At this temperature, 270 μL of boron tribromide (1.00 g, 4 mmol) was added dropwise. The mixture was allowed to reach room temperature for 2 h with stirring and quenched by pouring into crunched ice/1 M hydrochloric acid. After evaporation of the organic solvent, the precipitated product was washed several times with 1 M hydrochloric acid and water. The product was isolated as a glassy solid after dissolving in ethanol, filtration, and evaporation of the solvent in high vacuum. Yield: 1.41 g (91%). ^{1}H NMR (DMSO-d_6): δ 0.93 (t, 3H, J = 7.4 Hz), 1.31 (m, 2H), 1.78 (m, 2H), 2.30 (m, 2H), 3.11 (m, 2H), 4.07 (t, 2H, J = 7.4 Hz), 4.25 (t, 2H, J = 7.4 Hz), 4.28 (s, 2H), 6.97 (d, 1H, J = 9.0 Hz), 7.07–7.32 (m, 4H), 7.33 (d, 1H, J = 8.9 Hz), 7.39 (d, 1H, J = 9.0 Hz), 7.50 (t, 1H, J = 1.8), 7.56 (t, 1H, J = 1.8), 7.83 (d, 1H, J = 7.7 Hz), 7.87 (d, 1H, J = 8.7 Hz), 7.93 (d, 1H, J = 8.7 Hz), 8.03 (d, 1H, J = 1.3 Hz), 8.92 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 12.90, 19.50, 26.75, 31.86, 44.18, 46.77, 49.84, 51.59, 115.10, 115.85, 117.72, 118.44, 119.41, 120.29 (q, CF_3, J = 321 Hz), 122.63, 123.01, 123.23, 124.66, 125.38, 126.08, 126.53, 127.23, 128.38, 129.02, 129.39, 129.99, 130.09, 130.54, 134.68, 135.12, 136.00, 153.22, 154.30; ν (KBr)/cm^{-1} 3415, 2959, 1621, 1349, 1198, 1134, 1058; HRMS [FAB+] calcd for $C_{31}H_{34}N_3O_2$ (cation) 480.2651, found: 480.2666; $[\alpha]_D^{25} = -40.3$ (c 1.54, DMSO).

4.5. General procedure for the asymmetric addition of diethylzinc to benzaldehyde

A Schlenk tube equipped with a stirring bar was charged with ionic liquid **5** (190 mg, 0.25 mmol). After drying in vacuo, the solvent dichloromethane (10 mL) and Ti(O-*i*Pr)$_4$ (810 μL, 2.75 mmol) were added. The resulting mixture was stirred at room temperature for 1 h. Then, diethylzinc (1 M in hexane) (3.0 mL, 3.0 mmol) was added. The resulting homogeneous solution was stirred for another 15 min and benzaldehyde (228 μL, 2.5 mmol) was added. After stirring at room temperature for 18 h, the solvent was pumped off. The reaction mixture was dissolved in 1 mL of EtOH and quenched by the addition of 15 mL of 1 M hydrochloric acid. The diethyl ether extract of this mixture was dried and the conversion and ee value of the formed 1-phenylpropanol were determined by ^{1}H NMR and chiral HPLC (stationary phase: Chiralcel OD, mobile phase: hexane/isopropanol 9/1), respectively. The TSIL **5** was recovered by rapid filtration of the aqueous solution and drying.

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