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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 17 (2006) 2028–2033

Synthesis and properties of novel chiral-amine-functionalized ionic liquids

Shu-Ping Luo, Dan-Qian Xu, Hua-Dong Yue, Li-Ping Wang, Wen-Long Yang and Zhen-Yuan Xu*

State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China

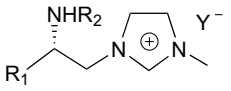
Received 8 June 2006; accepted 18 July 2006

Abstract—A novel class of chiral-amine-functionalized ionic liquids (CAFILs) has been synthesized efficiently from natural amino acids, and their structures have been determined by spectroscopic analysis and low temperature X-ray diffraction analysis. The CAFILs have been characterized by physical properties such as melting point, glass transition temperature, thermal degradation and specific rotation. NMR measurements indicate that the CAFILs may be promising alternatives in the field of chiral discrimination.

1. Introduction

Ionic liquids (ILs) have attracted considerable attention as environmentally friendly media for electrochemistry, chemical engineering, materials science and especially for organic synthesis over the past decade.[1] Recently, there have been extensive studies of so-called task-specific ILs with controllable physical and chemical properties.[2] Among these functionalized ILs, the chiral ionic liquids (CILs) are of increasing importance due to their promising applications for asymmetric synthesis, stereoselective polymerization, chiral chromatography, NMR chiral discrimination and liquid crystals. Seddon et al. reported the first example of CILs with the chirality being brought by a lactate anion in 1999.[3] Ever since then, more novel CILs with central, axial and planar chirality have been successively developed.[4,5] However, CILs are still at a very much preliminary stage of development in view of their history and applied scope.[6]

Since 2000, Chiral amines have been increasingly developed as effective organocatalysts for direct asymmetric carbon–carbon and carbon–heteroatom bond-forming reactions involving enamine- and imine-catalysis, such as Aldol, Mannich, Michael, α-amination, α-aminoxylation and α-hydroxyamination reactions of carbonyl compounds.[7,8] Therefore, we designed a novel class of CILs with a chiral amine base component being assembled to the imidazolium-type ILs (Fig. 1). We envisioned that the incorporation of this chiral amine function should impart a particularly effective asymmetric-induction pattern to the ILs and, the resulting CILs could be more efficient than conventional chiral solvents for the transfer of chirality in asymmetric synthesis. On the other hand, these novel CILs can also be regarded as ionic-liquid-supported[9] chiral amines and, due to ILs' peculiar properties, the resulting chiral amines should hopefully play a significant role in asymmetric organocatalysis in view of activity, enantioselectivity and stability of the catalysts. Herein, we report



1-3

1a-3a: R_1= Me, R_2= H, Y= Br, BF_4 or PF_6
1b-3b: R_1= *i*-Pr, R_2= H, Y= Br, BF_4 or PF_6
1c-3c: R_1= *i*-Bu, R_2= H, Y=Br, BF_4 or PF_6
1d-3d: R_1= 2-Bu, R_2= H, Y=Br, BF_4 or PF_6
1e-3e: R_1, R_2= -$(CH_2)_3$-, Y=Br, BF_4 or PF_6

Figure 1. Chiral-amine-functionalized ionic liquids (CAFILs).

* Corresponding author. Tel./fax: +86 571 88320066; e-mail: greenchem@zjut.edu.cn

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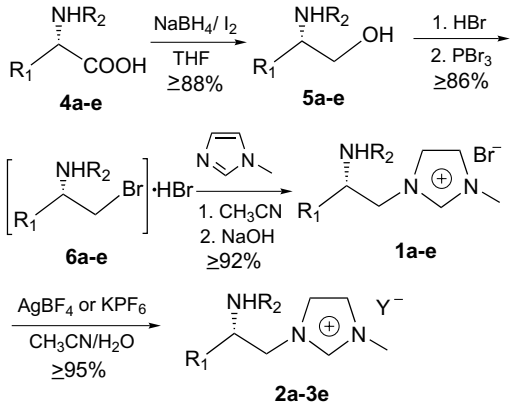
doi:10.1016/j.tetasy.2006.07.018

the synthesis and properties of our novel chiral-amine-functionalized ionic liquids (CAFILs).

2. Results and discussion

Synthesis of the novel CAFILs **1**–**3** commenced from natural amino acids **4** [(*S*)-alanine, (*S*)-valine, (*S*)-leucine, (*S*)-isoleucine and (*S*)-proline] with fairly good overall yields (66–71% yield). The key precursors **6** were synthesized by reduction of the amino acid with $NaBH_4/I_2$ followed by a neutralization step and bromination with PBr_3 successively. CAFILs **1**–**3** were thus obtained after N-alkylation of **6** to *N*-methylimidazole in refluxing MeCN followed by neutralization with NaOH to give **1a**–**e**, which underwent anion metathesis using $AgBF_4$ or KPF_6 in $MeCN/H_2O$ at room temperature to afford **2a**–**e** or **3a**–**e** (Scheme 1). It is certain that the route is concise and effective.[6d]



4a: R_1= Me, R_2= H; (*S*)-alanine
4b: R_1= *i*-Pr, R_2= H; (*S*)-valine
4c: R_1= *i*-Bu, R_2= H; (*S*)-leucine
4d: R_1= 2-Bu, R_2= H; (*S*)-isoleucine
4e: R_1, R_2= -$(CH_2)_3$-; (*S*)-proline

Scheme 1. Synthesis of CAFILs **1**–**3**.

All CAFILs were characterized by spectroscopic analysis of ^1H NMR, ^{13}C NMR, IR and MS. Furthermore, low temperature X-ray diffraction analysis of a single crystal of **1c**'s hydrobromide salt[10] unambiguously confirmed the proposed chemical structure and (*S*)-configuration (Fig. 2).

Some representative properties of CAFILs are summarized in Table 1. DSC measurements exhibited that these novel CAFILs had a melting point (T_m) or glass transition temperature (T_g) ranging from −49 to 145 °C. CAFILs bearing BF_4^- anion had T_m/T_g values lower than those of other CAFILs, whereas CAFILs bearing Br^- anion had higher values. TG determinations revealed that all CAFILs had good thermal stabilities up to at least 210 °C. In addition, all CAFILs showed a trend of being more miscible in polar solvents and much more immiscible in non-polar solvents than the related non-functionalized imdazolium-type ILs.

As a preliminary study on the chiral discrimination ability of the novel CAFILs, a mixture of 10 mg of racemic Mosher's acid with 40 mg of **2b** in 0.5 mL water-saturated CD_2Cl_2 was probed by ^{19}F NMR spectroscopy. The effect of **2b** caused a downfield shift (5.910 ppm) of the signal corresponding to the CF_3 group of the racemic acid, and the split of the signal ($J = 34.998$ Hz) clearly illustrated the existence of a strong diastereomeric interaction between **2b** and Mosher's acid (Fig. 3).

3. Conclusions

A novel class of chiral-amine-functionalized ionic liquids have been designed and readily prepared in enantiopure form from natural amino acids. Most of them show low melting point or glass transition temperature, which makes them potential alternatives for new chiral solvents. An NMR chiral discrimination study indicates that these novel CAFILs can provide a highly efficient chiral environment. Their applications in enantioselective syntheses are under investigation and will be reported in due course.

4. Experimental

4.1. General

All starting chemicals (include amino acids, $NaBH_4$, I_2, PBr_3 and 1-methylimidazol) were commercial products (Aldrich or J&K chemical) of analytical grade. Organic solvents were dried and purified before use by the usual methods. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker ARX 400. Chemical shifts of ^1H and ^{13}C were given in δ relative to tetramethylsilane (TMS). Chemical shifts of ^{19}F were given in δ relative to trifluoroacetic acid. The coupling constants J were given in hertz. IR spectra were obtained on a Bruker EQUINOX 55. Electrospray ionization (ESI) mass experiments were performed on a Finnigan LCQ Advantage. ESI-HRMS spectra were obtained on a Bruker APEX III FTICR mass spectrometer. Glass transition temperatures (T_g) and melting points (T_m) were recorded on a Thermal Analysis DSC Q100 differential scanning calorimeter with heating rate at 10 °C/min after initially cooling samples to −70 to −100 °C under nitrogen. Decomposition temperatures (T_{dec}) were determined with a PerkinElmer Diamond thermogravimetric/differential thermal analyzer module (TG/DTA) with heating rate of 10 °C/min under nitrogen. Special rotation values of the CAFILs in EtOH ($c = 2$) were obtained with a Rudolph Autompol IV polarimeter.

4.2. Experimental procedures

4.2.1. General procedure for the synthesis of compounds 5. To a solution of $NaBH_4$ (19.27 g, 0.5 mol) and (*S*)-amino acids **4** (0.2 mol) in dry THF was dropped I_2 (88.80 g, 0.35 mol)/THF solution at room temperature for 5 h. The reaction mixture was stirred at reflux for another 20 h and then cooled to room temperature. After the mixture was treated with MeOH (40 mL), the solvents were removed and, to the remaining residue was added

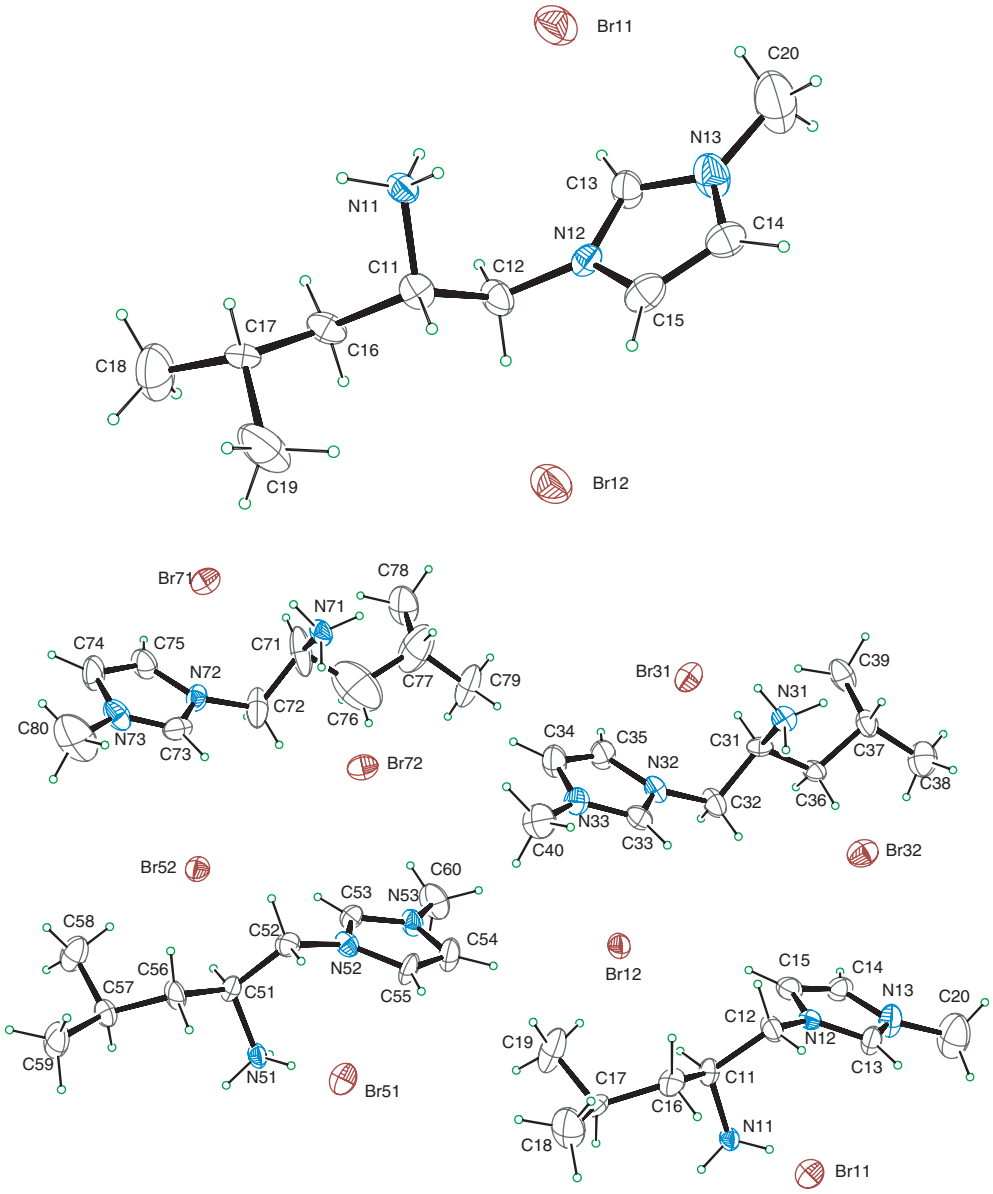


Figure 2. X-ray crystal structure of **1c**'s hydrobromide salt.

20% NaOH aqueous solution (150 mL) and stirred under reflux for 3 h. The resulting mixture was extracted three times by ethyl acetate. The combined extracts were evaporated, and the obtained crude product further purified by distillation under high vacuum to give **5a**–**e** as colourless oils (over 88% yields).

4.2.2. General procedure for the synthesis of compounds 6. A mixture of (*S*)-amino alcohols **5** (0.15 mol) dissolved in 20% HBr aqueous solution (130 mL) was concentrated to dryness under reduced pressure. Owing to complete removal of water, the residue was dissolved in hot EtOH (40 mL) and the solvent was evaporated in vacuum to give amino alcohol hydrobromides. The obtained hydrobromide salts were then mixed with PBr_3 (25.44 g, 0.093 mol) and refluxed for 10 min. After cooling, an excess of PBr_3 was then removed by washing the mixture with Et_2O several times and the residue was recrystallized from *i*-PrOH to afford **6a**–**e** (over 86% yields).

4.2.3. General procedure for the synthesis of CAFILs 1–3. A solution of *N*-methylimidazole (0.11 mol) and compound **6** (0.1 mol) in CH_3CN was stirred at 80 °C for 8 h. After completion, the solvent was removed by distillation, and the residue neutralized by NaOH and recrystallized in EtOH to afford the CAFILs **1a**–**e** (over 92% yields). A mixture of **1** (0.09 mol), $AgBF_4$ (or KPF_6) (0.09 mol) and 150 mL of CH_3CN/H_2O (1:1) was stirred at room temperature for 2 h (or 20 h). Solvents of the mixture were evaporated under vacuum. The residue was then dissolved in EtOH to allow the inorganic salts to be precipitated and filtered off. After evaporating the solvent, the desired CAFILs **2a**–**e** (over 97% yields) and **3a**–**e** (over 95% yields) were obtained.

Table 1. Properties of CAFILs **1**–**3**

Entry	CAFILs	T_m or T_g (°C)[a]	T_{dec} (°C)[b]	$[\alpha]_D^{20}$[c]
1	**1a**	131[e]	226	12.6
2	**2a**	−46[d]	261	13.9
3	**3a**	6[e]	218	7.2
4	**1b**	145[e]	270	10.3
5	**2b**	−49[d]	281	6.9
6	**3b**	38[d]	287	4.6
7	**1c**	134[e]	267	6.0
8	**2c**	−47[d]	291	7.1
9	**3c**	69[e]	287	5.4
10	**1d**	135[e]	268	11.7
11	**2d**	−35[d]	285	10.1
12	**3d**	73[e]	281	3.9
13	**1e**	141[e]	257	6.5
14	**2e**	−45[d]	291	4.5
15	**3e**	67[d]	274	2.7

[a] The data were determined by DSC.
[b] The data were determined by TG.
[c] Solution in EtOH and $c = 2$.
[d] Glass transition temperature (T_g).
[e] Melting point (T_m).

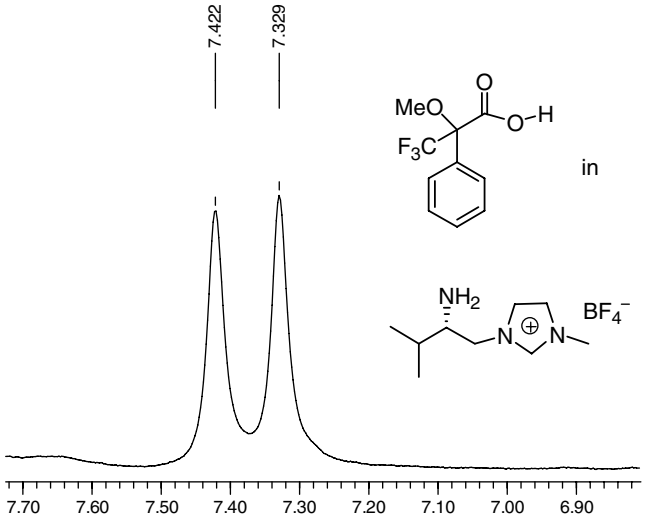


Figure 3. ^{19}F NMR of *rac*-Mosher's acid in **2b**.

4.3. Spectroscopic data

4.3.1. 1-[(*S*)-(2-Amino)propyl]-3-methylimidazolium bromide 1a. ^{1}H NMR (DMSO-d_6): δ 1.14 (3H), 3.36 (s, dr, NH_2), 3.45–3.52 (m, 1H), 3.87 (s, 3H), 4.14–4.21 (m, 1H), 4.15–4.31 (m, 1H), 7.75 (s, 1H), 7.77 (s, 1H), 9.18 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 18.480, 20.535, 35.708, 46.514, 55.766, 122.876, 123.058, 136.814. IR (film, cm^{-1}): 3428 [γ(N–H)], 3143 [γ(C–H) aromatic], 2925 and 2835 [γ(C–H) aliphatic], 1555 and 1412 [γ(C=C)]. MS: (ESI+) m/z 140 $[M-Br]^+$, (ESI−) m/z 80 $[Br]^-$. HRMS: (ESI+) m/z calcd for $[C_7H_{14}N_3]^+$ 140.1182, found 140.1178.

4.3.2. 1-[(*S*)-(2-Amino)propyl]-3-methylimidazolium tetrafluoroborate 2a. ^{1}H NMR (DMSO-d_6): δ 1.03 (d, $J = 6$ Hz, 3H), 3.22 (dd, $J = 6$, 11.6 Hz, 1H), 3.86 (s, 3H), 3.96 (dd, $J = 7.6$, 13.6 Hz, 1H), 4.15 (dd, $J = 4$, 13.6 Hz, 1H), 7.67 (s, 1H), 7.68 (s, 1H), 9.00 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 20.042, 35.701, 46.575, 55.409, 122.937, 123.255, 136.928. IR (film, cm^{-1}): 3370 [γ(N–H)], 3121 [γ(C–H) aromatic], 2971 and 2873 [γ(C–H) aliphatic], 1575 and 1460 [γ(C=C)], 1059 [γ(BF)]. MS: (ESI+) m/z 140 $[M-BF_4]^+$, (ESI−) m/z 87 $[BF_4]^-$. HRMS: (ESI+) m/z calcd for $[C_7H_{14}N_3]^+$ 140.1182, found 140.1173.

4.3.3. 1-[(*S*)-(2-Amino)propyl]-3-methylimidazolium hexafluorophosphate 3a. ^{1}H NMR (DMSO-d_6): δ 0.98 (d, $J = 6$ Hz, 3H), 3.11 (m, 1H), 3.80 (s, 3H), 3.85 (dd, $J = 5.2$, 12.8 Hz, 1H), 4.02 (dd, $J = 2.8$, 12.8 1H), 7.44 (s, 1H), 7.47 (s, 1H), 8.78 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 16.994, 35.845, 46.621, 52.133, 122.793, 123.695, 137.284. IR (film, cm^{-1}): 3394 [γ(N–H)], 3133 [γ(C–H) aromatic], 2924 and 2873 [γ(C–H) aliphatic], 1578 and 1421 [γ(C=C)], 843 [γ(PF)]. MS: (ESI+) m/z 140 $[M-PF_6]^+$, (ESI−) m/z 145 $[PF_6]^-$. HRMS: (ESI+) m/z calcd for $[C_7H_{14}N_3]^+$ 140.1182, found 140.1180.

4.3.4. 1-[(*S*)-(2-Amino)isopentyl]-3-methylimidazolium bromide 1b. ^{1}H NMR (DMSO-d_6): δ 0.92 (dd, $J = 6.4$, 14.4 Hz, 6H), 1.62–1.65 (m, 1H), 2.81 (m, 1H), 3.89 (s, 3H), 4.05 (dd, $J = 10$, 13.6 Hz, 1H), 4.28 (dd, $J = 3.6$, 13.6 Hz, 1H), 7.78 (s, 1H), 7.87 (s, 1H), 9.31 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.319, 19.170, 31.121, 35.762, 52.710, 56.304, 122.884, 123.096, 136.951. IR (film, cm^{-1}): 3395 [γ(N–H)], 3088 [γ(C–H) aromatic], 2961 and 2876 [γ(C–H) aliphatic], 1563 and 1421 [γ(C=C)]. MS: (ESI+) m/z 168 $[M-Br]^+$, (ESI−) m/z 80 $[Br]^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{18}N_3]^+$ 168.1495, found 168.1491.

4.3.5. 1-[(*S*)-(2-Amino)isopentyl]-3-methylimidazolium tetrafluoroborate 2b. ^{1}H NMR (DMSO-d_6): δ 0.89 (d, $J = 6.8$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 1.60 (m, 1H), 2.74 (m, 1H), 3.85 (s, 3H), 3.90 (dd, $J = 4.0$, 9.6 Hz, 1H), 4.20 (dd, $J = 4.0$, 9.6 Hz, 1H), 7.66 (t, $J = 1.6$ Hz, 1H), 7.71 (t, $J = 1.6$ Hz, 1H), 9.03 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.145, 19.147, 31.318, 35.663, 53.180, 56.297, 122.876, 123.127, 136.890. IR (film, cm^{-1}): 3390 [γ(N–H)], 3162 [γ(C–H) aromatic], 2966 and 2879 [γ(C–H) aliphatic], 1574 and 1433 [γ(C=C)], 1060 [γ(BF)]. MS: (ESI+) m/z 168 $[M-BF_4]^+$, (ESI−) m/z 87 $[BF_4]^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{18}N_3]^+$ 168.1495, found 168.1501.

4.3.6. 1-[(*S*)-(2-Amino)isopentyl]-3-methylimidazolium hexafluorophosphate 3b. ^{1}H NMR (DMSO-d_6): δ 0.94 (dd, $J = 5.6$, 12 Hz, 6H), 1.68–1.72 (m, 1H), 2.91–294 (m, 1H), 3.89 (s, 3H), 4.06–4.12 (m, 1H), 4.29–4.32 (m, 1H), 7.76 (s, 1H), 7.86 (s, 1H), 9.28 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.418, 19.041, 30.916, 35.875, 52.262, 56.297, 122.907, 123.202, 137.042. IR (film, cm^{-1}): 3457 [γ(N–H)], 3169 [γ(C–H) aromatic], 2921 and 2886 [γ(C–H) aliphatic], 1576 and 1437 [γ(C=C)], 838 [γ(PF)]. MS: (ESI+) m/z 168 $[M-PF_6]^+$, (ESI−) m/z 145 $[PF_6]^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{18}N_3]^+$ 168.1495, found 168.1492.

4.3.7. 1-[(*S*)-(2-Amino)isohexyl]-3-methylimidazolium bromide 1c. ^{1}H NMR ($CDCl_3$): δ 1.00 (dd, $J = 6.4$, 12.8 Hz, 6H), 1.75–1.79 (m, 1H), 2.92–2.94 (m, 1H), 4.08 (s, 3H), 4.26 (dd, $J = 10$, 12.8 Hz, 1H), 4.39 (d,

$J = 12.8$ Hz, 1H), 7.45 (s, 1H), 7.59 (s, 1H), 10.07 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.517, 18.495, 29.976, 35.853, 50.624, 55.902, 122.876, 123.483, 137.193. IR (film, cm^{-1}): 3434 [γ(N–H)], 3133 [γ(C–H) aromatic], 2944 and 2873 [γ(C–H) aliphatic], 1581 and 1459 [γ(C=C)]. MS: (ESI+) m/z 182 [M−Br]$^+$, (ESI−) m/z 80 [Br]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1652, found 182.1649.

4.3.8. 1-[(*S*)-(2-Amino)isohexyl]-3-methylimidazolium tetrafluoroborate 2c. ^{1}H NMR (DMSO-d_6): δ 0.98 (dd, $J = 7.2$, 8.8 Hz, 6H), 1.06 (m, 2H), 1.85 (m, 1H), 3.25 (m, 1H), 3.87 (s, 3H), 4.20 (dd, $J = 10$, 14 Hz, 1H), 4.37 (dd, $J = 2.8$, 14 Hz, 1H), 7.73 (s, 1H), 7.77 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.441, 18.229, 29.642, 35.822, 50.139, 55.667, 122.846, 123.627, 137.231. IR (film, cm^{-1}): 3409 [γ(N–H)], 3089 [γ(C–H) aromatic], 2963 and 2876 [γ(C–H) aliphatic], 1565 and 1463 [γ(C=C)], 1057 [γ(BF)]. MS: (ESI+) m/z 182 [M−BF$_4$]$^+$, (ESI−) m/z 87 [BF$_4$]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1652, found 182.1663.

4.3.9. 1-[(*S*)-(2-Amino)isohexyl]-3-methylimidazolium hexafluorophosphate 3c. ^{1}H NMR (DMSO-d_6): δ 0.87 (dd, $J = 4$, 6.8 Hz, 6H), 1.00 (m, 2H), 1.56–1.61 (m, 1H), 2.70–2.75 (m, 1H), 3.82 (s, 3H), 3.86–3.93 (m, 1H), 4.16–4.20 (m, 1H), 7.58 (s, 1H), 7.65 (s, 1H), 9.02 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 17.441, 19.359, 31.598, 35.981, 53.461, 56.600, 123.104, 123.392, 137.133. IR (film, cm^{-1}): 3422 [γ(N–H)], 3170 [γ(C–H) aromatic], 2968 and 2880 [γ(C–H) aliphatic], 1574 and 1431 [γ(C=C)], 837 [γ(PF)]. MS: (ESI+) m/z 182 [M−PF$_6$]$^+$, (ESI−) m/z 145 [PF$_6$]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1652, found 182.1656.

4.3.10. 1-[(*S*)-(2-Amino)-3-methylpentyl]-3-methylimidazolium bromide 1d. ^{1}H NMR (DMSO-d_6): δ 0.90 (t, $J = 7$ Hz, 3H), 0.95 (d, $J = 6.8$ Hz, 3H), 1.15–1.22 (m, 1H), 1.48–1.62 (m, 2H), 3.18 (m, 1H), 3.37 (s, dr, NH$_2$), 3.87 (s, 3H), 4.16 (dd, $J = 10.4$, 13.2 Hz, 1H), 4.33 (d, $J = 13.2$ Hz, 1H), 7.74 (s, 1H), 7.81 (s, 1H), 9.19 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 11.549, 14.423, 24.387, 35.807, 37.240, 50.526, 54.985, 122.914, 123.415, 137.155. IR (film, cm^{-1}): 3421 [γ(N–H)], 3075 [γ(C–H) aromatic], 2963 and 2873 [γ(C–H) aliphatic], 1564 and 1389 [γ(C=C)]. MS: (ESI+) m/z 182 [M−Br]$^+$, (ESI−) m/z 80 [Br]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1645, found 182.1679.

4.3.11. 1-[(*S*)-(2-Amino)-3-methylpentyl]-3-methylimidazolium tetrafluoroborate 2d. ^{1}H NMR (DMSO-d_6): δ 0.90 (dd, $J = 6.4$, 13.2 Hz, 6H), 1.14–1.18 (m, 1H), 1.29–1.38 (m, 1H), 1.47–1.51 (m, 1H), 2.74–2.76 (m, 1H), 3.85 (s, 3H), 3.88 (dd, $J = 3.2$, 12.8 Hz, 1H), 4.19 (dd, $J = 2.4$, 12.8 Hz, 1H), 7.66 (s, 1H), 7.72 (s, 1H), 9.06 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 11.480, 14.991, 24.205, 35.648, 53.028, 55.432, 122.922, 123.043, 136.890. IR (film, cm^{-1}): 3401 [γ(N–H)], 3163 [γ(C–H) aromatic], 2967 and 2879 [γ(C–H) aliphatic], 1574 and 1429 [γ(C=C)], 1061 [γ(BF)]. MS: (ESI+) m/z 182 [M−BF$_4$]$^+$, (ESI−) m/z 87 [BF$_4$]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1645, found 182.1665.

4.3.12. 1-[(*S*)-(2-Amino)-3-methylpentyl]-3-methylimidazolium hexafluorophosphate 3d. ^{1}H NMR (DMSO-d_6): δ 0.89 (d, $J = 7.2$, 6H), 1.09–1.25 (m, 1H), 1.34–1.46 (m, 1H), 1.46–1.59 (m, 1H), 2.83 (m, 1H), 3.90 (s, 3H), 4.03 (dd, $J = 10$, 13.2 Hz, 1H), 4.27 (d, $J = 13.2$ Hz, 1H), 7.78 (s, 1H), 7.86 (s, 1H), 9.33 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 11.594, 15.060, 24.288, 35.792, 38.582, 52.566, 55.485, 122.937, 123.043, 136.973. IR (film, cm^{-1}): 3392 [γ(N–H)], 3166 [γ(C–H) aromatic], 2966 and 2879 [γ(C–H) aliphatic], 1572 and 1431 [γ(C=C)], 843 [γ(PF)]. MS: (ESI+) m/z 182 [M−PF$_6$]$^+$, (ESI−) m/z 145 [PF$_6$]$^-$. HRMS: (ESI+) m/z calcd for $[C_{10}H_{20}N_3]^+$ 182.1645, found 182.1653.

4.3.13. 1-[(*S*)-(2-Pyrrolidinyl)methyl]-3-methylimidazolium bromide 1e. ^{1}H NMR (DMSO-d_6): δ 1.69–1.74 (m, 1H), 1.90–1.94 (m, 1H), 2.00–2.01 (m, 1H), 2.10–2.14 (m, 1H), 3.16–3.21 (m, 1H), 3.26–3.31 (m, 1H), 3.90 (s, 3H), 3.99–4.03 (m, 1H), 4.62–4.67 (m, 2H), 7.80 (s, 1H), 7.91 (s, 1H), 9.29 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 23.133, 27.779, 36.390, 45.139, 49.012, 59.257, 122.854, 124.197, 137.572. IR (film, cm^{-1}): 3403 [γ(N–H)], 3133 [γ(C–H) aromatic], 2944 and 2873 [γ(C–H) aliphatic], 1566 and 1412 [γ(C=C)]. MS: (ESI+) m/z 166 [M−Br]$^+$, (ESI−) m/z 80 [Br]$^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{16}N_3]^+$ 166.1339, found 166.1338.

4.3.14. 1-[(*S*)-(2-Pyrrolidinyl)methyl]-3-methylimidazolium tetrafluoroborate 2e. ^{1}H NMR (DMSO-d_6): δ 1.70–1.77 (m, 1H), 1.88–1.95 (m, 1H), 1.97–2.05 (m, 1H), 2.08–2.15 (m, 1H), 3.17–3.23 (m, 1H), 3.29–3.30 (m, 1H), 3.90 (s, 3H), 4.00–4.04 (m, 1H), 4.56–4.67 (m, 2H), 7.79 (s, 1H), 7.87 (s, 1H), 9.23 (s, 1H), 9.25 (s, dr, NH). ^{13}C NMR (DMSO-d_6): δ 23.222, 27.885, 36.477, 45.850, 49.452, 59.340, 123.091, 124.578, 137.787. IR (film, cm^{-1}): 3406 [γ(N–H)], 3062 [γ(C–H) aromatic], 2955 and 2868 [γ(C–H) aliphatic], 1570 and 1459 [γ(C=C)], 1071 [γ(BF)]. MS: (ESI+) m/z 166 [M−BF$_4$]$^+$, (ESI−) m/z 87 [BF$_4$]$^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{16}N_3]^+$ 166.1339, found 166.1335.

4.3.15. 1-[(*S*)-(2-Pyrrolidinyl)methyl]-3-methylimidazolium hexafluorophosphate 3e. ^{1}H NMR (DMSO-d_6): δ 1.67–1.77 (m, 1H), 1.86–2.08 (m, 2H), 2.10–2.16 (m, 1H), 3.12–3.36 (m, 2H), 3.87 (s, 3H), 4.00–4.03 (m, 1H), 4.56–4.66 (m, 2H), 7.79 (s, 1H), 7.86 (s, 1H), 9.23 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 22.620, 27.306, 35.928, 44.793, 48.524, 58.776, 122.482, 123.847, 137.231. IR (film, cm^{-1}): 3406 [γ(N–H)], 3070 [γ(C–H) aromatic], 2949 and 2870 [γ(C–H) aliphatic], 1560 and 1420 [γ(C=C)], 839 [γ(PF)]. MS: (ESI+) m/z 166 [M−PF$_6$]$^+$, (ESI−) m/z 145 [PF$_6$]$^-$. HRMS: (ESI+) m/z calcd for $[C_9H_{16}N_3]^+$ 166.1339, found 166.1342.

Acknowledgements

The authors acknowledge the Ministry of Science and Technology of China for the financial support of National Basic Research Program of China (2003CB114400).

References

1. For selected reviews, see: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083; (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789; (c) Sheldon, R. *Chem. Commun.* **2001**, 2399–2409; (d) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692; (e) Rogers, R. D.; Seddon, K. R.; Volkov, S. *Green Industrial Applications of Ionic Liquids*; Kluwer Academic: Dordrecht, 2002; (f) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003; (g) Welton, T. *Coordin. Chem. Rev.* **2004**, *248*, 2459–2477; (h) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015–1060.
2. (a) Davis, J. H., Jr. *Chem. Lett.* **2004**, *33*, 1072–1077; (b) Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem. Eur. J.* **2006**, *12*, 2122–2130; (c) Liang, C.; Huang, J.-F.; Li, Z.; Luo, H.; Dai, S. *Eur. J. Org. Chem.* **2006**, 586–589; (d) Li, S.; Lin, Y.; Xie, H.; Zhang, S.; Xu, J. *Org. Lett.* **2006**, *8*, 391–394.
3. Earle, M. J.; McCormac, P. B.; Seddon, K. R. *Green Chem.* **1999**, *1*, 23–25.
4. For reviews, see: (a) Handy, S. T. *Chem. Eur. J.* **2003**, *9*, 2938–2944; (b) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292; (c) Baudequin, C.; Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *Tetrahedron: Asymmetry* **2005**, *16*, 3921–3945.
5. For recent chiral ionic liquids, see: (a) Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399; (b) Pernak, J.; Feder-Kubis, J. *Chem. Eur. J.* **2005**, *11*, 4441–4449; (c) Tao, G.-H.; He, L.; Sun, N.; Kou, Y. *Chem. Commun.* **2005**, 3562–3564; (d) Kim, E. J.; Ko, S. Y.; Dziadulewicz, E. K. *Tetrahedron Lett.* **2005**, *46*, 631–633; (e) Baudoux, J.; Judeinstein, P.; Cahard, D.; Plaquevent, J.-C. *Tetrahedron Lett.* **2005**, *46*, 1137–1140; (f) Génisson, Y.; Viguerie, N. L.; André, C.; Baltas, M.; Gorrichon, L. *Tetrahedron: Asymmetry* **2005**, *16*, 1017–1023; (g) Ni, B.; Headley, A. D.; Li, G. *J. Org. Chem.* **2005**, *70*, 10600–10602; (h) Hannig, F.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Organomet. Chem.* **2005**, *690*, 5959–5972; (i) Guillen, F.; Brégeon, D.; Plaquevent, J.-C. *Tetrahedron Lett.* **2006**, *47*, 1245–1248; (j) Tran, C. D.; Oliveira, D.; Yu, S. *Anal. Chem.* **2006**, *78*, 1349–1356; (k) Branco, L. C.; Gois, P. M. P.; Lourenco, N. M. T.; Kurteva, V. B.; Afonso, C. A. M. *Chem. Commun.* **2006**, 2371–2372.
6. For applications of chiral ionic liquids, see: (a) Kiss, L.; Kurtan, T.; Antus, S.; Brunner, H. *Arkivoc* **2003**, *5*, 69–76; (b) Pégot, B.; Vo-Thanh, G.; Gori, D.; Loupy, A. *Tetrahedron Lett.* **2004**, *45*, 6425–6428; (c) Ding, J.; Desikan, V.; Han, X.; Xiao, T. L.; Ding, R.; Jenks, W. S.; Armstrong, D. W. *Org. Lett.* **2005**, *7*, 335–337; (d) Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. *Tetrahedron Lett.* **2005**, *46*, 4657–4660; (e) Luo, S.; Mi, X.; Zhang, L.; Liu, S.; Xu, H.; Cheng, J.-P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3093–3097; (f) Ding, J.; Welton, T.; Armstrong, D. W. *Anal. Chem.* **2004**, *76*, 6819–6822; (g) Wasserscheid, P.; Bösmann, A.; Bolm, C. *Chem. Commun.* **2002**, 200–201; (h) Ishida, Y.; Miyauchi, H.; Saigo, K. *Chem. Commun.* **2002**, 2240–2241; (i) Levillain, J.; Dubant, G.; Abrunhosa, I.; Gulea, M.; Gaumont, A.-C. *Chem. Commun.* **2003**, 2914–2915; (j) Clavier, H.; Boulanger, L.; Audic, N.; Toupet, L.; Mauduit, M.; Guillemin, J.-C. *Chem. Commun.* **2004**, 1224–1225; (k) Ishida, Y.; Sasaki, D.; Miyauchi, H.; Saigo, K. *Tetrahedron Lett.* **2004**, *45*, 9455–9459; (l) Patil, M. L.; Laxman Rao, C. V.; Yonezawa, K.; Takizawa, S.; Onitsuka, K.; Sasai, H. *Org. Lett.* **2006**, *8*, 227–230.
7. For selected reviews of organocatalysis, see: (a) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138–5175; (b) List, B. *Acc. Chem. Res.* **2004**, *37*, 548–557; (c) Notz, W.; Tanaka, F.; Barbas, C. F. *Acc. Chem. Res.* **2004**, *37*, 580–591; (d) Berkessel, A.; Gröger, H. *Asymmetric Organocatalysis—From Biomimetic Concepts to Applications in Asymmetric Synthesis*; WILEY-VCH Verlag GmbH&Co. KGaA: Weinheim, 2005; (e) List, B. *Chem. Commun.* **2006**, 819–824.
8. For representative chiral amines applied as organocatalysts, see: (a) Hayashi, Y.; Yamaguchi, J.; Sumiya, T.; Shoji, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1112–1115; (b) Córdova, A.; Sundén, H.; Engqvist, M.; Ibrahem, I.; Casas, J. *J. Am. Chem. Soc.* **2004**, *126*, 8914–8915; (c) Mase, N.; Nakai, Y.; Ohara, N.; Yoda, H.; Takabe, K.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2006**, *128*, 734–735; (d) Dambruoso, P.; Massi, A.; Dondoni, A. *Org. Lett.* **2005**, *7*, 4657–4660; (e) Itagaki, N.; Kimura, M.; Sugahara, T.; Iwabuchi, Y. *Org. Lett.* **2005**, *7*, 4185–4188; (f) Tang, Z.; Yang, Z.-H.; Chen, X.-H.; Cun, L.-F.; Mi, A.-Q.; Jiang, Y.-Z.; Gong, L.-Z. *J. Am. Chem. Soc.* **2005**, *127*, 9285–9289; (g) Chen, J.-R.; Lu, H.-H.; Li, X.-Y.; Cheng, L.; Wan, J.; Xiao, W.-J. *Org. Lett.* **2005**, *7*, 4543–4545; (h) Cheong, P. H.-Y.; Zhang, H.; Thayumanavan, R.; Tanaka, F.; Houk, K. N.; Barbas, C. F., III. *Org. Lett.* **2006**, *8*, 811–814; (i) Westermann, B.; Neuhaus, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4077–4079; (j) Mitsumori, S.; Zhang, H.; Cheong, P. H.-Y.; Houk, K. N.; Tanaka, F.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2006**, *128*, 1040–1041; (k) Mossé, S.; Alexakis, A. *Org. Lett.* **2005**, *7*, 4361–4364; (l) Ishii, T.; Fujioka, S.; Sekiguchi, Y.; Kotsuki, H. *J. Am. Chem. Soc.* **2004**, *126*, 9558–9559; (m) Knudsen, K. R.; Mitchell, C. E. T.; Ley, S. V. *Chem. Commun.* **2006**, 66–68; (n) Halland, N.; Aburel, P. S.; Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1272–1277; (o) Prieto, A.; Halland, N.; Jørgensen, K. A. *Org. Lett.* **2005**, *7*, 3897–3900; (p) Wang, W.; Mei, Y.; Li, H.; Wang, J. *Org. Lett.* **2005**, *7*, 601–604; (q) Franzén, J.; Marigo, M.; Fielenbach, D.; Wabnitz, T. C.; Kjærsgaard, A.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2005**, *127*, 18296–18304; (r) Wang, W.; Wang, J.; Li, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1369–1371; (s) Huang, Y.; Walji, A. M.; Larsen, C. H.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 15051–15053; (t) Kano, T.; Ueda, M.; Takai, J.; Maruoka, K. *J. Am. Chem. Soc.* **2006**, *128*, 6046–6047; (u) Guo, H. M.; Cheng, L.; Cun, L. F.; Gong, L. Z.; Mi, A. Q.; Jiang, Y. Z. *Chem. Commun.* **2006**, 429–431.
9. (a) Miao, W.; Chan, T. H. *Org. Lett.* **2003**, *5*, 5003–5005; (b) Audic, N.; Clavier, H.; Mauduit, M.; Guillemin, J.-C. *J. Am. Chem. Soc.* **2003**, *125*, 9248–9249; (c) Qian, W.; Jin, E.; Bao, W.; Zhang, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 952–955; (d) Handy, S. T.; Okello, M. *J. Org. Chem.* **2005**, *70*, 2874–2877.
10. Crystal structure of **1c**'s hydrobromide salt: CCDC 608255.