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Design and Synthesis of C-2 Substituted Chiral Imidazolium Ionic Liquids from Amino Acid Derivatives

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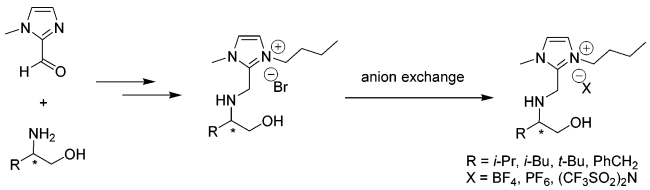

A series of novel chiral ionic liquids (CILs) has been synthesized and fully characterized. The reaction of 1-methyl-2-imidazolecarboxaldehyde and chiral amino alcohols followed by reduction is key to the design of these new CILs. This is the first time that CILs have been synthesized by introducing chiral scaffolds on the C-2 position of the imidazolium cation of ILs. The simple and straightforward procedure resulted in CILs as colorless oils at room temperature in good yields.

Room-temperature ionic liquids (RTILs) have attracted widespread interest in the chemical community due to their ability to serve as reaction media for organic synthesis.[1,2] This is mainly a result of their unique properties, such as recyclability, involatility, and incombustibility.[3] RTILs consist of anions and cations counterparts; anions normally include halogen anions, AlX_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, or $(CF_3SO_3)_2N^-$, and cations are typically imidazolium or pyridium species. One of the most important properties of RTILs is their extremely high polarity, which makes them ideal candidates to dissolve a wide variety of polar reactants and to stabilize polar reaction intermediates. In addition, by modifying the structures of these cations or anions, the properties of RTILs can be fine-tuned to meet specific solvation requirements in order to influence reaction outcomes. In recent years, the use of chiral RTILs as reaction media for asymmetric organic reactions[4] and chiral discrimination, as well as optical resolution of racemic mixtures,[5] has dramatically increased. Unfortunately, there are only a few chiral ionic liquids that are designed, synthesized, and used as solvents for asymmetric reactions.[4,6]

A thorough review of the literature reveals that known chiral RTILs [6] are derived through various modifications of cations such as ammonium,[7] pyridinium,[8] oxazolinium,[7a] and thiazolium.[9] The imidazolium-cation-derived chiral RTILs (Figure 1) have gained widespread usage due to their facile preparation, low melting points, and relatively favorable viscosity.[10] As shown in Figure 1, the best known imidazole-derived chiral RTILs that have been reported thus far contain the chiral moieties bonded to one or both of the nitrogen atoms on positions 1 and 3 of the imidazolium cation (**I**−**VI**).[11,12] Also, there are several chiral RTILs in which the chiral moiety is contained in the anion (**VII**−**IX**)[4a,13] (Figure 1).

For imidazolium-derived ionic liquids, we have previously found that there is an intimate interaction of the hydrogen on the C-2 position of the imidazolium cation of RTILs with the counteranions as compared to the other

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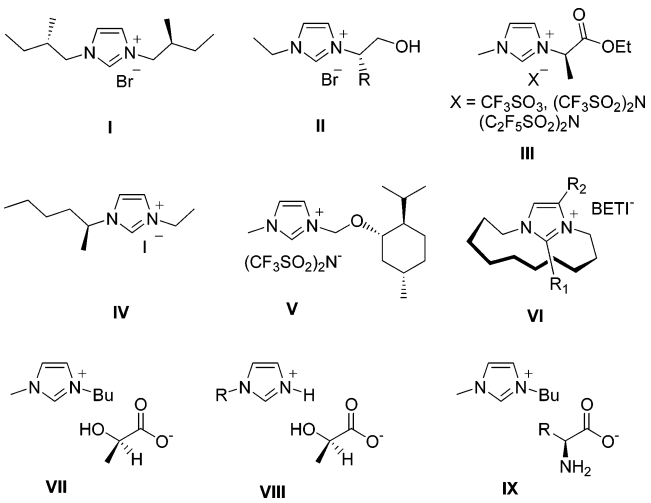


FIGURE 1. Chiral imidazolium ionic liquids.

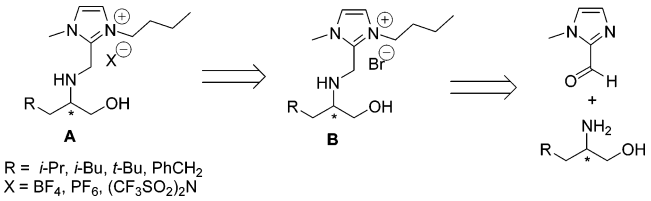


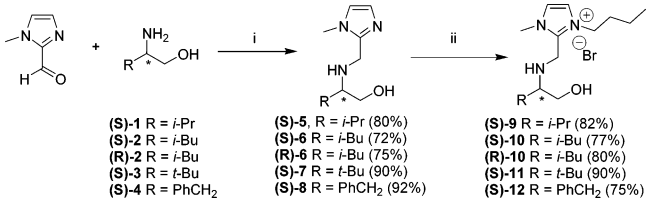
FIGURE 2. Retrosynthetic analysis of CILs.

imidazolium hydrogens.[14] This results from the fact that this hydrogen is relatively acidic.[15] Consequently, when they are used as solvents under basic conditions, the deprotonation of this hydrogen can occur to give undesired side products. For example, Aggarwal and coworkers have recently encountered this problem during the study of the Baylis–Hillman reaction when the ionic liquid butylmethylimidazolium chloride is used as a solvent.[16] To solve this serious problem, the introduction of a nonprotic substitutent into the C-2 position of the imidazolium moiety will result in more inert ionic liquids for reactions that can be carried out under basic conditions or in the presence of anionic intermediates. As a result, unwanted side reactions can be avoided or minimized when reactions are carried out in such chiral RTILs. Surprisingly, there have been no reports regarding the synthesis of RTILs with chiral auxiliaries bonded to the C-2 positions of the imidazolium ring.

In this report we have designed a series of C-2 substituted imidazolium chiral RTILs **A** (Figure 2). The present design is concise and practical because of the ready availability and low cost of the starting materials, as well the feasible synthesis of the final RTILs under mild conditions to avoid possible racemization of enantiomerically pure reactants.

The retrosynthetic design of these RTILs is shown in Figure 2. It was envisioned that synthesis of a variety of C-2 substituted chiral imidazolium ionic liquids **A** could be derived from its precursor imidazolium bromide salts

SCHEME 1[a]



[a] Reaction conditions: (i) (a) MeOH, 4 Å MS, 70 °C, 24 h, (b) $NaBH_4$, rt; (ii) bromobutane, toluene, 85–90 °C, 24 h.

B via anion exchange. Precursor **B** can be prepared by the reaction of bromobutane and the corresponding imidazole derivatives, which were synthesized via condensation with 1-methyl-2-imidazolecarboxaldehyde and a chiral amino alcohol.

As shown in Scheme 1, the condensation of 1-methyl-2-imidazolecarboxaldehyde and (*S*)-(+)-2-amino-3-methyl-1-butanol **(S)-1** in MeOH was accomplished to give the corresponding Schiff base precursor, which was reduced with $NaBH_4$ to give the desired imidazole derivative **(S)-5** in 80% yield. The condensation of 1-methyl-2-imidazolecarboxaldehyde with (*S*)-leucinol and (*R*)-leucinol resulted in the corresponding imidazole derivatives **(S)-6** and **(R)-6** in 72% and 75% yield, respectively. Similarly, the more stericly substituted imidazole derivatives **(S)-7** and **(S)-8** were obtained in 90% and 92% yields starting from (*S*)-*tert*-leucinol and (*S*)-3-phenyl-2-amino-propanol. The alkylation salt formation was carried out by heating imidazoles **(S)-5**–**(S)-8** with 1 equiv of bromobutane at 85–90 °C in toluene for 24 h to form the imidazolium bromide salts **(S)-9**–**(S)-12** in 75%–90% yield (Scheme 1).

The next step in the synthesis involves the transformation of imidazolium bromide salts to ionic liquids **(S)-13a**–**(S)-16c** by anion exchange of **(S)-9**–**(S)-12** with different anions (BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$). Chiral imidazolium tetrafluoroborates **(S)-13a**–**(S)-16a** were prepared by the treatment of their precursors, imidazolium bromide **(S)-9**–**(S)-12,** with potassium tetrafluoroborate in the mixture solvent of methanol and water at room temperature for 3 days in 91–95% yields after purification. Chiral imidazolium hexafluorophosphates **(S)-13b**–**(S)-16b** were also readily obtained by anion exchange of imidazolium bromide **(S)-9**–**(S)-12** with potassium hexafluorophosphate in H_2O at room temperature for 1 h in 86–100% yields. Similarly, imidazolium bis(trifluoromethylsulfonyl)imides were obtained in 92–98% yields (Scheme 2).

In summary, 15 novel chiral room-temperature ionic liquids have been designed and synthesized. These RTILs were assembled by incorporating chiral side chains on the C-2 positions of the imidazolium cation rings through condensation reactions involving 1-methyl-2-imidazolecarboxaldehyde and chiral amino alcohol followed by reduction. The synthesis is concise and practical as a result of the commercial availability of the starting materials and convenient reaction conditions. The new ionic liquids avoid the shortcomings of their traditional counterparts that can participate in deprotonation side reactions on their C-2 positions. Applications of these new chiral RTILs as green media for asymmetric synthesis and catalysis will be investigated in our laboratories.

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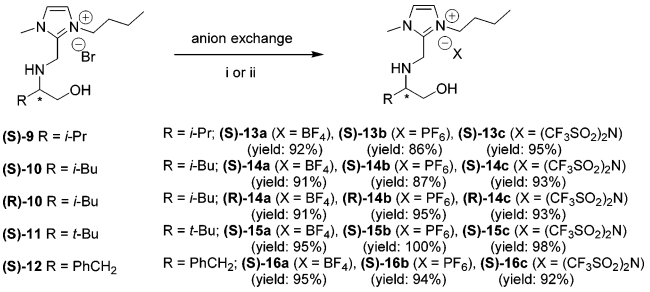
SCHEME 2[a]



(S)-9 R = *i*-Pr

(S)-10 R = *i*-Bu

(R)-10 R = *i*-Bu

(S)-11 R = *t*-Bu

(S)-12 R = $PhCH_2$

R = *i*-Pr; **(S)-13a** (X = BF_4), **(S)-13b** (X = PF_6), **(S)-13c** (X = $(CF_3SO_2)_2N$) (yield: 92%) (yield: 86%) (yield: 95%)

R = *i*-Bu; **(S)-14a** (X = BF_4), **(S)-14b** (X = PF_6), **(S)-14c** (X = $(CF_3SO_2)_2N$) (yield: 91%) (yield: 87%) (yield: 93%)

R = *i*-Bu; **(R)-14a** (X = BF_4), **(R)-14b** (X = PF_6), **(R)-14c** (X = $(CF_3SO_2)_2N$) (yield: 91%) (yield: 95%) (yield: 93%)

R = *t*-Bu; **(S)-15a** (X = BF_4), **(S)-15b** (X = PF_6), **(S)-15c** (X = $(CF_3SO_2)_2N$) (yield: 95%) (yield: 100%) (yield: 98%)

R = $PhCH_2$; **(S)-16a** (X = BF_4), **(S)-16b** (X = PF_6), **(S)-16c** (X = $(CF_3SO_2)_2N$) (yield: 95%) (yield: 94%) (yield: 92%)

[a] Reaction conditions: (i) KBF_4, MeOH−H_2O, rt, 3 d; (ii) KPF_6 or $(CF_3SO_2)_2NLi$, H_2O, rt, 1 h.

Experimental Section

General Procedure for the Synthesis of Compound (S)-5. To a solution of 1-methyl-2-imidazolecarboxaldehyde (1.32 g, 12 mmol) in methanol (30 mL) was added (*S*)-(+)-2-amino-3-methyl-1-butanol (1.24 g, 12 mmol) and 4 Å molecular sieves (2.4 g). The reaction mixture was stirred under reflux for 24 h with exclusion of moisture and then cooled to room temperature. To the resulting solution of Schiff base was added $NaBH_4$ (0.46 g, 12 mmol), and the mixture was stirred for 2 h at room temperature. The reduction was quenched by slow and dropwise addition of concentrated HCl (0.6 mL) to the mixture and subsequent neutralization with solid Na_2CO_3 (2.0 g, 19 mmol). Then, the solid in the mixture was filtered out, the filtrate was evaporated to dryness, and the resultant product was further purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 7:1) to give product **(S)-5** (1.87 g, 80%) as a colorless oil. $[\alpha]^{20}_D = -8.9$ (*c* 0.79, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (d, J = 1.5 Hz, 1H), 6.82 (d, J = 1.5 Hz, 1H), 3.89 (AB, $\Delta\nu$ = 42.0 Hz and J_{AB} = 15.0 Hz, 2H), 3.67 (dd, J = 11.1 and 3.9 Hz, 1 H), 3.63 (s, 3H), 3.50−2.80 (br, 2H), 3.44 (dd, J = 11.1 and 7.2 Hz, 1H), 2.52−2.42 (m, 1H), 1.86−1.72 (m, 1H), 0.97 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 126.3, 121.0, 64.5, 61.0, 43.5, 32.4, 29.3, 19.1, 18.6; IR (neat) υ = 3328, 2957, 2872, 1659, 1502, 1467, 1043 cm^{-1}; HRMS (ESI) *m/z* (%) calcd for $C_{10}H_{20}N_3O$ (MH^+) 198.1601, found 198.1599.

General Procedure for the Synthesis of Compound (S)-9. A solution of imidazole **(S)-5** (860 mg, 4.36 mmol) and bromobutane (603 mg, 4.36 mmol) in toluene (2 mL) was stirred at 85−90 °C for 24 h. The reaction mixture was then cooled to room temperature, the toluene was removed, and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 7:1 to 5:1) to give product **(S)-9** (1.2 g, 82%) as a viscous oil. ^{1}H NMR (300 MHz, D_2O) δ 7.27 (d, J = 2.1 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 4.04 (t, J = 7.2 Hz, 2H), 3.99 (s, 2H), 3.72 (s, 3H), 3.55 (dd, J = 11.7 and 4.5 Hz, 1 H), 3.36 (dd, J = 14.4 and 6.9 Hz, 1H), 2.35−2.26 (m, 1H), 1.75−1.58 (m, 3H), 1.24−1.08 (m, 2H), 0.80−0.68 (m, 9H). This compound was used for the next step directly without further characterization.

General Procedure for the Synthesis of (S)-13a. A solution of imidazolium bromide **(S)-9** (334 mg, 1.0 mmol) in MeOH/H_2O (2 mL, 5:1) containing potassium tetrafluoroborate (152 mg, 1.2 mmol) was stirred at room temperature for 3 days. The reaction mixture was then filtered over Celite and concentrated to dryness. The residue was dissolved in dichloromethane and filtered again to give **(S)-13a** (314 mg, 92%) as a viscous oil. $[\alpha]^{20}_D = -2.4$ (*c* 0.70, EtOH); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.72 (d, J = 1.8 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 4.63−4.54 (m, 1H), 4.24−3.94 (m, 4H), 3.84 (s, 3H), 3.53−3.43 (m, 1H), 3.43−3.24 (br, 2H), 2.30−2.20 (m, 1H), 1.80−1.64 (m, 3H), 1.36−1.20 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H), 0.81 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 146.6, 124.2, 122.5, 66.3, 63.2, 41.2, 36.0, 33.3, 30.6, 20.7, 19.5, 19.0, 13.9; IR (neat) υ = 3298, 2956, 1647, 1533, 1470, 1099, 1048 cm^{-1}; HRMS (ESI +) *m/z* (%) calcd for $[C_{14}H_{28}N_3O]^+$ 254.2232, found 254.2230; HRMS (ESI −) *m/z* (%) calcd for $[BF_4]^-$ 87.0029, found 87.0037.

(4) General Procedure for the Synthesis of (S)-13b. To a solution of imidazolium bromide **(S)-9** (250 mg, 0.75 mmol) in water (2 mL) was added potassium hexafluorophosphate (152 mg, 1.1 mmol), and the mixture was stirred for 1 h at room temperature. The reaction mixture was extracted with CH_2Cl_2 (15 mL), and the organic phase was washed with water (5 × 5 mL), then concentrated, and dried in a vacuum to give **(S)-13b** (257 mg, 86%) as a colorless oil. $[\alpha]^{20}_D = -2.4$ (*c* 0.37, EtOH); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.68 (d, J = 2.1 Hz, 1H), 7.63 (d, J = 2.1 Hz, 1H), 4.57 (t, J = 4.8 Hz, 1H), 4.19 (t, J = 7.5 Hz, 2H), 4.14−3.94 (m, 2H), 3.83 (s, 3H), 3.53−3.33 (m, 2H), 2.30−2.18 (br, 2H), 1.80−1.64 (m, 3H), 1.36−1.20 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H), 0.82 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, MeOD-d_4) δ 146.3, 124.1, 122.5, 65.1, 58.4, 42.0, 39.8, 35.6, 33.2, 25.9, 23.4, 22.8, 20.6, 13.9; IR (neat) υ = 3602, 3375, 2963, 1536, 1468, 1044, 843 cm^{-1}; HRMS (ESI +) *m/z* (%) calcd for $[C_{14}H_{28}N_3O]^+$ 254.2232, found 254.2226; HRMS (ESI −) *m/z* (%) calcd for $[PF_6]^-$ 144.9642, found 144.9647.

(Synthesis of (S)-13c. Imidazolium bromide **(S)-9** (250 mg, 0.75 mmol) reacted with lithium bis(trifluoromethanesulfonyl)-imide (215 mg, 0.75 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(S)-13c** (379 mg, 95%) as a colorless oil. $[\alpha]^{20}_D = -1.5$ (*c* 1.05, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 2.1 Hz, 1H), 7.21(d, J = 2.1 Hz, 1H), 4.28−4.08 (m, 4H), 3.93 (s, 3H), 3.77 (dd, J = 11.1 and 3.3 Hz, 1 H), 3.52 (dd, J = 11.1 and 7.5 Hz, 1H), 2.70−2.10 (br, 2H), 2.48−2.38 (m, 1H), 1.88−1.68 (m, 3H), 1.46−1.30 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.5, 123.0, 121.1, 119.6 (q, J = 319.4 Hz), 64.9, 62.4, 48.4, 40.1, 35.4, 31.9, 29.2, 19.4, 18.6, 18.5, 13.2; IR (neat) υ = 3556, 1536, 1352, 1196, 1058 cm^{-1}; HRMS (ESI +) *m/z* (%) calcd for $[C_{14}H_{28}N_3O]^+$ 254.2232, found 254.2224; HRMS (ESI −) *m/z* (%) calcd for $[N(SO_2CF_3)_2]^-$ 279.9173, found 279.9179.

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Supporting Information Available: Analytical data for compounds **(S)-6**−**(S)-8**, **(S)-10**−**(S)-12**, and **(S)-14a**−**(S)-16c** and ^{1}H and ^{13}C NMR spectra of those compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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