

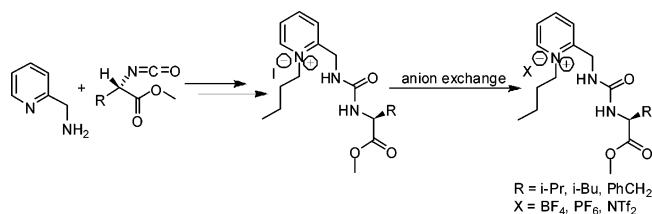
## Design and Synthesis of Pyridinium Chiral Ionic Liquids Tethered to a Urea Functionality

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Nine chiral room-temperature ionic liquids (RTILs), which contain a chiral moiety and a urea functionality bonded to a pyridinium ring, have been designed and synthesized. The synthesis of these ionic liquids is concise and practical due to the commercial availability of the starting materials. These novel RTILs were readily prepared from 2-(aminomethyl)pyridine and amino acid ester derived isocyanates. We envision that these new chiral RTILs can serve as effective reaction media as well as chiral catalysts for asymmetric reactions, which are presently being investigated in our laboratory.

There has been increased interest in recent years in using room-temperature ionic liquids (RTILs) as solvents for organic synthesis.<sup>1</sup> Owing to their unique physical properties, such as recyclability and involatility,<sup>2</sup> they are rapidly becoming the solvents of choice for a wide variety of reactions.<sup>3</sup> RTILs consist of cation and anion counterparts; cations are typically imidazolium or pyridinium species, and anions normally include halogen anions,  $\text{AlX}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ , or  $(\text{CF}_3\text{SO}_3)_2\text{N}^-$ . By modification of the structures of the cations or anions of ionic liquids, their properties can be altered to influence the outcome of reactions.

In recent years, the use of chiral RTILs as reaction media for chiral discrimination, as well as optical resolution of racemic mixtures,<sup>4</sup> has increased dramatically. Even though a limited number of chiral RTILs have been designed and synthesized in

an attempt to influence the outcome of asymmetric organic reactions,<sup>5</sup> there are only a few chiral ionic liquids that can effectively influence the outcome of asymmetric reactions.<sup>6</sup> Compared to the chiral imidazolium ionic liquids, chiral ionic liquids that contain the pyridinium cation moiety have been exploited far less. A major problem encountered in the use of imidazolium derived ionic liquids as solvents is that side products often result due to the acidic nature of the C2 hydrogen of the imidazolium ring.<sup>7</sup> Only recently have there been reports of the synthesis and utilization of pyridinium derived ionic liquids as solvents for reactions; Figure 1 shows examples of chiral pyridinium ionic liquids that have been synthesized, but only a limited number to date have resulted in influencing asymmetric reactions.<sup>8</sup> As a result, chiral RTILs that contain the pyridinium moiety are promising candidates for further investigation in the development of asymmetric catalysis.

It is known that urea derivatives have been used as efficient Lewis-acidic catalysts for organic transformations due to effective H-bonds that are formed with the amide hydrogens. Due to the acidic hydrogens in urea compounds that contain electron-withdrawing substituents, stable cocrystals with a variety of proton acceptors, including carbonyl compounds, are readily formed. For example, Cannon et al. have demonstrated that catalytic amounts of bis(aryl) ureas can be used to accelerate the Baylis–Hillman reaction,<sup>9</sup> Berkessel and co-workers have demonstrated that dynamic kinetic resolution of azlactones by urea-based organocatalysts with high enantioselectivity is possible,<sup>10</sup> and Jacobsen has utilized urea derivatives as catalysts for a variety of reaction.<sup>11</sup> Surprisingly, there have been no

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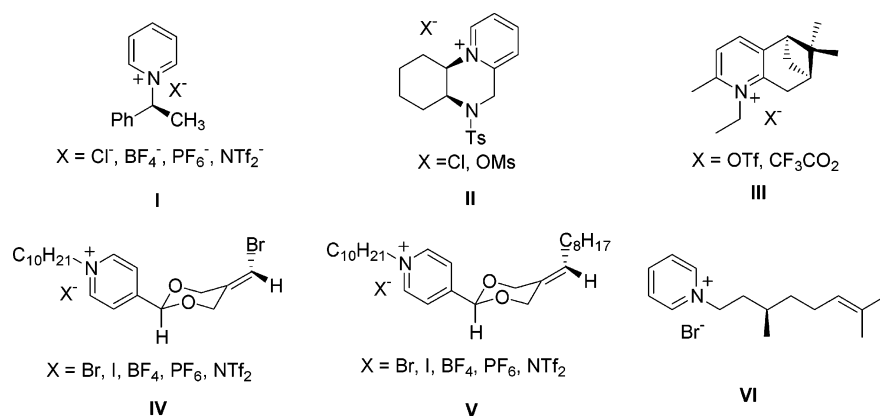
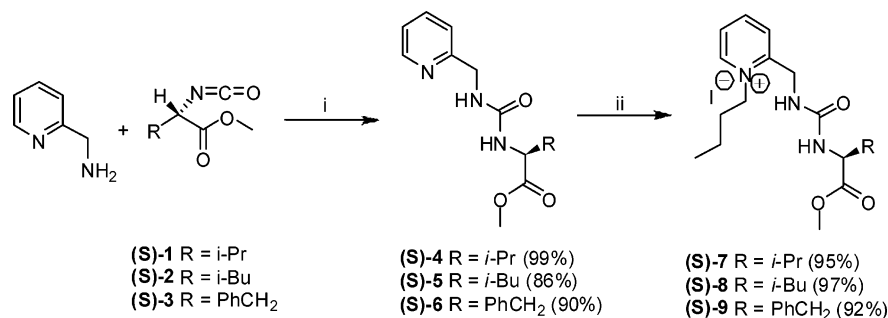


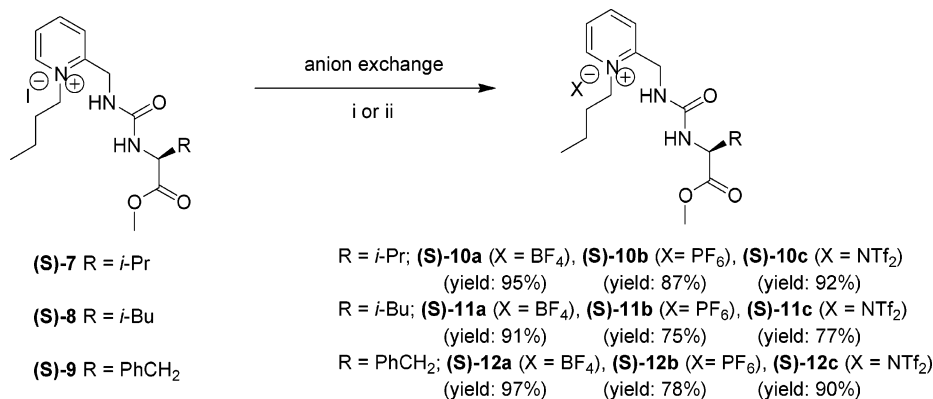
FIGURE 1. Chiral pyridinium ionic liquids.

SCHEME 1<sup>a</sup>



<sup>a</sup> Reaction conditions: (i) CH<sub>2</sub>Cl<sub>2</sub>, rt, 24 h; (ii) iodobutane, 90 °C, 20 h.

SCHEME 2<sup>a</sup>



<sup>a</sup> Reaction conditions: (i) KBF<sub>4</sub>, MeOH-H<sub>2</sub>O, rt, 2d; (ii) KPF<sub>6</sub> or Tf<sub>2</sub>NLi, H<sub>2</sub>O, rt, 1 h.

reports regarding the introduction of the urea unit into ionic liquids in an effort to influence the outcome of asymmetric reactions. In this report, we have designed a unique series of chiral RTILs that contain the pyridinium cation, a chiral moiety, and also embedded is a urea unit (Scheme 1). The present design is concise and practical due to the ready availability and low cost of the starting materials.

As shown in Scheme 1, 2-(aminomethyl)pyridine was treated with substituted (*S*)-(-)-2-isocyanato-3-methylbutyrate to yield

the desired urea with excellent yields (86–99%). The alkylation salt formation was carried out by heating pyridine urea derivatives (S)-4–(S)-6 with 1 equiv of iodobutane at 85–90 °C in neat for 24 h to form the pyridinium iodide salts (S)-7–(S)-9 in 92–97% yield.

The next step of the synthesis involves the transformation of pyridinium iodide salts to ionic liquids (S)-10a–(S)-12c by anion exchange of (S)-7–(S)-9 with different anions (BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>), Scheme 2.

Chiral pyridinium tetrafluoroborates (S)-10a–(S)-12a were prepared by the treatment of their precursors, pyridinium iodide (S)-7–(S)-9, with potassium tetrafluoroborate in methanol and water at room temperature for 2 days in 91–97% yields after purification. Chiral pyridinium hexafluorophosphates (S)-10b–

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TABLE 1. Physical Properties of Chiral Ionic Liquids

chiral ILs	solubility <sup>a</sup>	immiscibility <sup>a</sup>	viscosity (10 <sup>3</sup> cP) <sup>b</sup>	Mp (°C) <sup>c</sup>	T <sub>d</sub> (°C) <sup>d</sup>
(S)-10a	A, C	B	81.5		171
(S)-10b	A, D	B		140–141	169
(S)-10c	A	B, C	66.2		233
(S)-11a	A, C	B		42–44	176
(S)-11b	A, D	B		82–84	173
(S)-11c	A	B, C	14.6		236
(S)-12a	A, C	B		48–50	151
(S)-12b	A, D	B		50–52	161
(S)-12c	A	B, C	103.2		226

<sup>a</sup> Solubility and immiscibility: (A) CHCl<sub>3</sub>, AcOEt, MeOH, EtOH, DMF, DMSO; (B) Et<sub>2</sub>O, hexane; (C) H<sub>2</sub>O; (D) partially miscible in H<sub>2</sub>O. <sup>b</sup> At 25 °C. <sup>c</sup> Melting point. <sup>d</sup> Thermal degradation.

(S)-12b were also readily obtained by anion exchange of pyridinium iodide (S)-7–(S)-9 with potassium hexafluorophosphate in H<sub>2</sub>O at room temperature for 1 h in 75–87% yields. Similarly, pyridinium bis(trifluoromethanesulfonyl)imides (S)-10c–(S)-12c were obtained in 92–98% yields (Scheme 2).

Shown in Table 1 are the physical properties for the chiral pyridinium ionic liquids (S)-10a–(S)-12c. They were found to be very soluble in common solvents, such as alcohols, CHCl<sub>3</sub>, ethyl acetate, DMF, and DMSO, but were immiscible with ether and hexane. Chiral pyridinium tetrafluoroborates (S)-10a, (S)-11a, and (S)-12a are soluble in H<sub>2</sub>O, while the anion hexafluorophosphate compounds (S)-10b, (S)-11b, and (S)-12b were only partially miscible in H<sub>2</sub>O. The bis(trifluoromethanesulfonyl)imides (S)-10c, (S)-11c, and (S)-12c were immiscible in H<sub>2</sub>O. For the chiral pyridinium ILs studied, (S)-10a, (S)-10c, (S)-11c, and (S)-12c were highly viscous liquids as shown in Table 1. A key observation from the presented data in Table 1 is that ILs that contain the NTf<sub>2</sub><sup>-</sup> anion exist as viscous liquids.

The thermal stabilities of the chiral pyridinium ILs were determined using thermogravimetric analysis (TGA), and the results are shown in Table 1. The thermal stabilities of the ILs (S)-10a–(S)-12c range from 151 to 236 °C, with the tetrafluoroborates, (S)-10a, (S)-11a, and (S)-12a, being the least stable (degradation 151–171 °C). The hexafluorophosphate ILs, (S)-10b, (S)-11b, and (S)-12b, exhibit a higher degree of stability (degradation temperature range 161–173 °C), but the most stable ILs are (S)-10c, (S)-11c, and (S)-12c, which contain the NTf<sub>2</sub><sup>-</sup> anion; they exhibit a degradation temperature range of 226–236 °C.

In summary, we have designed and synthesized nine chiral room-temperature pyridinium ionic liquids, which contain a chiral moiety tethered to a urea unit. These novel RTILs can readily be prepared from 2-(aminomethyl)pyridine and amino acid ester derived isocyanates. The synthesis is concise and practical due to the commercial availability of the starting materials and convenient reaction conditions of their synthesis. Compared to ILs that contains the BF<sub>4</sub> and PF<sub>6</sub> anions, ILs with the NTf<sub>2</sub><sup>-</sup> anion are very stable and exist as highly viscous liquids. We envision that these new chiral RTILs will serve as effective solvents, as well as chiral catalysts for a variety of asymmetric reactions, which are currently being investigated in our laboratories.

## Experimental Section

### (1) General Procedure for the Synthesis of Compound (S)-4.

To a solution of 2-(aminomethyl)pyridine (865 mg, 8 mmol) in dry dichloromethane (10 mL) was slowly added methyl (S)-(-)-2-isocyanato-3-methylbutyrate (1.21 g, 8 mmol) in dry dichloromethane (8 mL) at 0 °C under N<sub>2</sub> protection. After the reaction

mixture was stirred at room temperature for 24 h, dichloromethane was removed, and the residue was purified by flash column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>:MeOH = 7:1) to give product (S)-4 (2.05 g, 99%) as a yellowish solid: mp 71–73 °C; [α]<sub>D</sub><sup>20</sup> = -1.93° (c = 1.71, EtOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.54–8.48 (m, 1H), 7.67–7.58 (m, 1H), 7.32–7.28 (m, 1H), 7.15 (t, J = 6.4 Hz, 1H), 6.24–6.04 (br, 1H), 5.86–5.64 (br, 1H), 4.49 (dd, J = 5.6 and 3.2 Hz, 2H), 4.44 (dd, J = 8.8 and 4.8 Hz, 1H), 3.72 (s, 3H), 2.19–2.06 (m, 1H), 0.95 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.0, 158.4, 158.3, 148.7, 136.8, 122.1, 122.0, 58.1, 51.8, 45.6, 31.1, 19.0, 17.7; IR (neat) ν = 3748, 2964, 1738, 1652, 1542 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>: C, 58.85; H, 7.22; N, 15.84. Found: C, 58.72; H, 7.24; N, 15.81.

(2) General Procedure for the Synthesis of Compound (S)-7. Pyridine (S)-4 (373 mg, 1.44 mmol) and 1-iodobutane (278 mg, 1.51 mmol) were stirred at 90 °C for 20 h. The reaction mixture was then cooled to room temperature. The mixture was extracted with ether, and the residue was dried to give the pyridinium iodide product (606 mg, 95%): <sup>1</sup>H NMR (400 MHz, MeOD-*d*<sub>4</sub>) δ 8.99 (d, J = 8.0 Hz, 1H), 8.54 (t, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.98 (t, J = 7.2 Hz, 1H), 4.90–4.75 (m, 2H), 4.67 (t, J = 8.0 Hz, 2H), 4.18 (d, J = 5.2 Hz, 1H), 3.71 (s, 3H), 2.20–2.10 (m, 1H), 2.10–1.95 (m, 2H), 1.60–1.45 (m, 2H), 1.03 (t, J = 7.2 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, MeOD-*d*<sub>4</sub>) δ 174.5, 160.2, 157.9, 146.8, 146.7, 128.4, 127.5, 59.9, 58.8, 52.5, 42.0, 36.6, 31.8, 20.6, 19.6, 18.2, 13.9; IR (neat) ν = 2962, 1716, 1627, 1433 cm<sup>-1</sup>. The product was used for the next step directly without further characterization.

(3) General Procedure for the Synthesis of (S)-10a. A solution of pyridinium iodide (S)-7 (638 mg, 1.44 mmol) in MeOH–H<sub>2</sub>O (2 mL, 5:1) containing potassium tetrafluoroborate (362 mg, 1.58 mmol) was stirred at rt (room temperature) for 2 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)-10a (552 mg, 95%) as a yellow liquid: [α]<sub>D</sub><sup>20</sup> = -9.28° (c = 2.93, EtOH); <sup>1</sup>H NMR (400 MHz, MeOD-*d*<sub>4</sub>) δ 8.74 (dd, J = 6.4 and 1.2 Hz, 1H), 8.31 (td, J = 8.0 and 1.6 Hz, 1H), 7.84 (dd, J = 8.0 and 0.8 Hz, 1H), 7.77–7.67 (m, 1H), 4.67–4.52 (m, 2H), 4.43 (t, J = 8.0 Hz, 2H), 3.96 (d, J = 5.2 Hz, 1H), 3.48 (s, 3H), 1.99–1.88 (m, 1H), 1.81–1.68 (m, 2H), 1.35–1.20 (m, 2H), 0.83 (t, J = 7.2 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, MeOD-*d*<sub>4</sub>) 174.5, 160.2, 158.0, 146.8, 146.7, 128.4, 127.4, 59.9, 58.8, 52.5, 42.0, 36.6, 31.8, 20.7, 19.6, 18.2, 13.9; IR (neat) ν = 3748, 2961, 1735, 1683, 1542 cm<sup>-1</sup>; HRMS (ESI+) m/z (%) calcd for [C<sub>17</sub>H<sub>28</sub>N<sub>3</sub>O<sub>3</sub>]<sup>+</sup> 322.2131, found 322.2130.

(4) General Procedure for the Synthesis of (S)-10b. To a solution of pyridinium iodide (S)-7 (402 mg, 0.91 mmol) in water (2 mL) was added potassium hexafluorophosphate (183 mg, 1.0 mmol), and the mixture was stirred for 1 h at rt. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and the organic phase washed with water (5 × 5 mL) and then concentrated and dried in vacuum to give (S)-10b (364 mg, 87%) as a white solid: mp 140–

141 C;  $[\alpha]_{\text{D}}^{20} = -34.5^\circ$  ( $c = 1.20$ , EtOH);  $^1\text{H}$  NMR (400 MHz, MeOD- $d_4$ )  $\delta$  8.92 (dd,  $J = 32.4$  and 6.4 Hz, 1H), 8.52 (dd,  $J = 16.0$  and 8.0 Hz, 1H), 8.08–7.98 (m, 1H), 7.94 (t,  $J = 7.6$  Hz, 1H), 4.77 (t,  $J = 8.0$  Hz, 2H), 4.62 (t,  $J = 8.0$  Hz, 2H), 4.16 (dd,  $J = 18.0$  and 4.2 Hz, 1H), 3.71 (s, 3H), 2.24–2.08 (m, 1H), 2.06–1.9 (m, 2H), 1.59–1.43 (m, 2H), 1.1–0.88 (m, 9H);  $^{13}\text{C}$  NMR (100 MHz, MeOD- $d_4$ )  $\delta$  174.5, 160.2, 157.9, 146.7, 146.6, 128.2, 127.4, 59.9, 58.6, 52.5, 41.8, 33.5, 31.8, 20.6, 19.5, 18.1, 13.8; IR (neat)  $\nu = 3748, 1734, 1671, 1541, 835\text{ cm}^{-1}$ ; HRMS (ESI+)  $m/z$  (%) calcd for  $[\text{C}_{17}\text{H}_{28}\text{N}_3\text{O}_3]^+$  322.2131, found 322.2136; HRMS (ESI-)  $m/z$  (%) calcd for  $[\text{PF}_6]^-$  144.9642, found 144.9814.

**(5) Synthesis of (S)-10c.** Pyridinium iodide (**S**)-**7** (376 mg, 0.85 mmol) reacted with lithium bis(trifluoromethanesulfonyl)imide (268 mg, 0.93 mmol) according to the procedure described for the preparation of (**S**)-**10b** to give (**S**)-**10c** (466 mg, 92%) as a brown oil;  $[\alpha]_{\text{D}}^{20} = -8.5^\circ$  ( $c = 2.44$ , EtOH);  $^1\text{H}$  NMR (400 MHz, MeOD- $d_4$ )  $\delta$  8.85 (dd,  $J = 6.0$  and 0.8 Hz, 1H), 8.48 (td,  $J = 8.0$  and 1.6 Hz, 1H), 8.02 (d,  $J = 8.4$  Hz, 1H), 7.94–7.87 (m, 1H), 4.79–4.68 (m, 2H), 4.60 (t,  $J = 8.0$  Hz, 2H), 4.16 (t,  $J = 3.2$  Hz, 1H), 3.69 (s, 3H), 2.20–2.08 (m, 1H), 2.0–1.9 (m, 2H), 1.54–1.41 (m, 2H),

1.00 (t,  $J = 7.2$  Hz, 3H), 0.95 (d,  $J = 6.8$  Hz, 3H), 0.92 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, MeOD- $d_4$ )  $\delta$  174.5, 160.1, 157.9, 146.8, 146.6, 128.2, 127.4, 121.1 (q,  $J = 318.5$  Hz), 59.9, 58.7, 52.5, 41.9, 33.5, 31.8, 20.6, 19.5, 18.1, 13.8; IR (neat)  $\nu = 3748, 2965, 1735, 1650, 1558, 1189, 616\text{ cm}^{-1}$ ; HRMS (ESI+)  $m/z$  (%) calcd for  $[\text{C}_{17}\text{H}_{28}\text{N}_3\text{O}_3]^+$  322.2131, found 322.2131; HRMS (ESI-)  $m/z$  (%) calcd for  $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$  279.9173, found 279.9248.

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**Supporting Information Available:** Analytical data for compounds (**S**)-**5**–(**S**)-**6** and (**S**)-**11a**–(**S**)-**12c** and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of those compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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