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

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(1) Synthesis of Compound (S)-6: 1-methyl-2-imidazolecarboxaldehyde (550 mg, 5 mmol) was reacted with (S)-leucinol (585 mg, 5 mmol) according to the procedure described for the preparation of (S)-5 to give product (S)-6 (761 mg, 72%) as a colorless oil. $[\alpha]_D^{20} = -7.0^\circ$ (c = 0.55, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 6.91 (d, $J = 1.5$ Hz, 1H), 6.82 (d, $J = 1.5$ Hz, 1H), 3.86 (AB, $\Delta\nu = 41.7$ Hz and $J_{AB} = 15.0$ Hz, 2H), 3.62 (s, 3H), 3.61 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.32 (dd, $J = 11.1$ and 6.2 Hz, 1H), 3.33-2.82 (br, 2H), 2.80-2.71 (m, 1H), 1.77-1.62 (m, 1H), 1.42-1.31 (m, 1H), 1.29-1.18 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.9, 126.5, 121.0, 63.0, 56.9, 42.6, 41.0, 32.4, 24.6, 22.7, 22.5; IR (neat) $\nu = 3319, 2954, 1467, 1052\text{ cm}^{-1}$; HRMS (ESI) m/z (%) Calcd for $\text{C}_{11}\text{H}_{22}\text{N}_3\text{O}$ (MH^+): 212.1757, Found: 212.1755.

(2) Synthesis of Compound (R)-6: 1-methyl-2-imidazolecarboxaldehyde (1.32 g, 12 mmol) was reacted with (R)-leucinol (1.40 g, 12 mmol) according to the procedure described for the preparation of (S)-5 to give product (R)-6 (1.90 g, 75%) as a colorless oil. $[\alpha]_D^{20} = 7.2^\circ$ (c = 1.26, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 6.92 (d, $J = 1.5$ Hz, 1H), 6.83 (d, $J = 1.5$ Hz, 1H), 3.88 (AB, $\Delta\nu = 40.8$ Hz and $J_{AB} = 14.7$ Hz, 2H), 3.63 (s, 3H), 3.63 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.33 (dd, $J = 11.1$ and 6.2 Hz, 1H), 3.33-2.82 (br, 2H), 2.82-2.72 (m, 1H), 1.78-1.63 (m, 1H), 1.43-1.32 (m, 1H), 1.30-1.19 (m, 1H), 0.92 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.8, 126.4, 121.0, 62.9, 56.8, 42.4, 40.9, 32.4, 24.6, 22.7, 22.5.

(3) Synthesis of Compound (S)-7: 1-methyl-2-imidazolecarboxaldehyde (1.1 g, 10 mmol) was reacted with (S)-tert-leucinol (1.17 g, 10 mmol) according to the

procedure described for the preparation of **(S)-5** to give product **(S)-7** (1.96 g, 90%) as a colorless oil. $[\alpha]_D^{20} = -33.0^\circ$ ($c = 1.29$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 6.93 (d, $J = 1.2$ Hz, 1H), 6.83 (d, $J = 1.2$ Hz, 1H), 3.96 (AB, $\Delta\nu = 62.4$ Hz and $J_{AB} = 15.6$ Hz, 2H), 3.79 (dd, $J = 11.1$ and 3.6 Hz, 1H), 3.59 (s, 3H), 3.46 (dd, $J = 11.1$ and 7.8 Hz, 1H), 2.41 (dd, $J = 7.8$ and 3.4 Hz, 1H), 0.93 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.2, 125.8, 120.8, 67.5, 61.2, 45.4, 34.3, 32.1, 26.7; IR (neat) $\nu = 3338, 2951, 1477, 1284, 1045\text{ cm}^{-1}$; HRMS (ESI) m/z (%) Calcd for $\text{C}_{11}\text{H}_{22}\text{N}_3\text{O}$ (MH^+): 212.1757, Found: 212.1767.

(4) Synthesis of Compound (S)-8: 1-methyl-2-imidazolecarboxaldehyde (550 mg, 5 mmol) was reacted with (S)-(-)-2-amino-3-phenyl-1-propanol (755 mg, 5 mmol) according to the procedure described for the preparation of **(S)-5** to give product **(S)-8** (1.14 g, 92%) as a colorless oil. $[\alpha]_D^{20} = -27.0^\circ$ ($c = 0.8$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.17 (m, 5H), 6.90 (d, $J = 1.2$ Hz, 1H), 6.78 (d, $J = 1.2$ Hz, 1H), 3.81 (AB, $\Delta\nu = 51.9$ Hz and $J_{AB} = 11.7$ Hz, 2H), 3.63 (dd, $J = 11.4$ and 3.6 Hz, 1H), 3.46 (s, 3H), 3.60-3.00 (br, 2H), 3.41 (dd, $J = 11.4$ and 6.0 Hz, 1H), 3.01-2.92 (m, 1H), 2.76 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 146.6, 139.1, 129.1, 128.2, 126.5, 126.0, 121.1, 62.5, 60.5, 43.1, 38.4, 32.2; IR (neat) $\nu = 3317, 2921, 1496, 1454, 1043\text{ cm}^{-1}$; HRMS (ESI) m/z (%) Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}$ (MH^+): 246.1601, Found: 246.1608.

(5) Synthesis of Compound (S)-10: Imidazole **(S)-6** (470 mg, 2.2 mmol) react with bromobutane (310 mg, 2.2 mmol) according to the procedure described for the preparation of **(S)-9** to give product **(S)-10** (598 mg, 77%) as a viscous oil. ^1H NMR

(300 MHz, CDCl₃) δ 7.59 (d, J = 1.6 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 4.39 (t, J = 7.2 Hz, 2H), 4.31 (AB, $\Delta\nu$ = 137.1 Hz and J_{AB} = 15.0 Hz, 2H), 4.12 (s, 3H), 3.90-3.50 (br, 2H), 3.82 (dd, J = 12.0 and 3.0 Hz, 1 H), 3.45 (dd, J = 12.0 and 6.0 Hz, 1H), 1.90-1.62 (m, 3H), 1.48-1.12 (m, 4H), 0.97 (t, J = 7.5 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H). This compound was used for the next step directly without further characterization.

(6) Synthesis of Compound (R)-10: Imidazole (R)-6 (1.16 g, 5.5 mmol) react with bromobutane (0.754 g, 5.5 mmol) according to the procedure described for the preparation of (S)-9 to give product (R)-10 (1.54 g, 80%) as a viscous oil. ¹H NMR (300 MHz, D₂O) δ 7.28 (d, J = 1.8 Hz, 1H), 7.22 (d, J = 1.8 Hz, 1H), 4.02 (t, J = 7.5 Hz, 2H), 3.97 (s, 2H), 3.51 (dd, J = 11.7 and 3.9 Hz, 1 H), 3.32 (dd, J = 11.4 and 6.3 Hz, 1H), 2.64-2.54 (m, 1H), 1.70-1.58 (m, 2H), 1.52-1.38 (m, 1H), 1.23-1.07 (m, 4H), 0.80-0.65 (m, 9H). This compound was used for the next step directly without further characterization.

(7) Synthesis of Compound (S)-11: Imidazole (S)-7 (710 mg, 3.36 mmol) reacted with bromobutane (460 mg, 3.36 mmol) according to the procedure described for the preparation of (S)-9 to give (S)-11 (1.04 g, 90%) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.41 (m, 1H), 7.31-7.26 (m, 1H), 4.50-4.30 (br, 1H), 4.41 (t, J = 7.2 Hz, 2H), 4.35 (AB, $\Delta\nu$ = 213.6 Hz and J_{AB} = 14.4 Hz, 2H), 4.13 (s, 3H), 3.91 (dd, J = 12.3 and 3.3 Hz, 1 H), 3.68 (t, J = 12.0 Hz, 1H), 2.29 (dd, J = 9.0 and 3.6 Hz, 1H), 2.00-1.70 (br, 1H), 1.92-1.78 (m, 2H), 1.48-1.34 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H), 0.90 (s, 9H). This compound was used for the next step directly without further

characterization.

(8) Synthesis of Compound (S)-12: Imidazole (S)-8 (928 mg, 3.8 mmol) reacted with bromobutane (521 mg, 3.8 mmol) according to the procedure described for the preparation of (S)-9 to give (S)-12 (1.09 g, 75%) as a viscous oil. ¹H NMR (300 MHz, CDCl₃) δ 7.38 (d, *J* = 1.5 Hz, 1H), 7.27-7.17 (m, 6H), 4.50 (d, *J* = 15.0 Hz, 1H), 4.22-4.02 (m, 2H), 3.96-3.82 (m, 5H), 3.80-3.40 (br, 2H), 3.58 (dd, *J* = 11.7 and 6.3 Hz, 1H), 3.05-2.94 (m, 1H), 2.78 (dd, *J* = 13.8 and 5.4 Hz, 1H), 6.4 (dd, *J* = 13.8 and 9.0 Hz, 1H), 1.71-1.59 (m, 2H), 1.34-1.20 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). This compound was used for the next step directly without further characterization.

(9) Synthesis of (S)-14a: imidazolium bromide (S)-10 (315 mg, 0.91 mmol) reacted with potassium tetrafluoroborate (126 mg, 1 mmol) according to the procedure described for the preparation of (S)-13a to give (S)-14a (290 mg, 91%) as a colorless oil. $[\alpha]_D^{20} = -7.5^\circ$ (*c* = 1.51, EtOH); ¹H NMR (300 MHz, CDCl₃) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 4.51 (d, *J* = 14.7 Hz, 1H), 4.38 (t, *J* = 7.5 Hz, 2H), 4.11 (s, 3H), 4.07 (d, *J* = 7.2 Hz, 1H), 3.81 (dd *J* = 11.7 and 3.0 Hz, 1 H), 3.45 (dd, *J* = 11.7 and 6.3 Hz, 1H), 2.83-2.71 (m, 1H), 1.89-1.61 (m, 3H), 1.46-1.13 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 144.5, 123.2, 121.1, 63.2, 57.5, 48.5, 40.8, 39.5, 36.3, 32.0, 24.5, 22.8, 22.3, 19.4, 13.4; IR (neat) ν = 3395, 2955, 2870, 1638, 1466, 1047 cm⁻¹; HRMS (ESI +) *m/z* (%) Calcd for [C₁₅H₃₀N₃O]⁺: 268.2389, Found: 263.2381.

(10) Synthesis of (R)-14a: imidazolium bromide (R)-10 (348 mg, 1.0 mmol) reacted with potassium tetrafluoroborate (151 mg, 1.2 mmol) according to the procedure

described for the preparation of **(S)-13a** to give **(R)-14a** (324 mg, 91%) as a white solid. $[\alpha]_D^{20} = 7.6^\circ$ ($c = 0.62$, EtOH); ^1H NMR (300 MHz, DMSO- d_6) δ 7.70 (d, $J = 2.1$ Hz, 1H), 7.66 (d, $J = 2.1$ Hz, 1H), 4.63 (t, $J = 4.8$ Hz, 1H), 4.24-3.94 (m, 4H), 3.83 (s, 3H), 3.48-3.24 (m, 2H), 2.58-2.46 (br, 1H), 2.36-2.22 (br, 1H), 1.80-1.58 (m, 3H), 1.36-1.20 (m, 2H), 6.14 (t, $J = 7.2$ Hz, 2H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.83 (d, $J = 6.9$ Hz, 3H), 0.78 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, MeOD- d_4) δ 146.5, 124.2, 122.6, 65.2, 58.4, 42.2, 40.1, 36.0, 33.3, 25.9, 23.5, 22.9, 20.7, 14.0.

(11) Synthesis of (S)-15a: imidazolium bromide **(S)-11** (348 mg, 1.0 mmol) reacted with potassium tetrafluoroborate (151 mg, 1.2 mmol) according to the procedure described for the preparation of **(S)-13a** to give **(S)-15a** (336 mg, 95%) as a white solid. $[\alpha]_D^{20} = -7.8^\circ$ ($c = 0.89$, EtOH); ^1H NMR (300 MHz, DMSO- d_6) δ 7.71 (d, $J = 1.5$ Hz, 1H), 7.67 (d, $J = 1.8$ Hz, 1H), 4.60 (t, $J = 4.8$ Hz, 1H), 4.30-4.12 (m, 3H), 4.02 (dd, $J = 15.0$ and 6.6 Hz, 1H), 3.85 (s, 3H), 3.76-3.67 (m, 1H), 3.4-3.24 (m, 1H), 2.30-2.16 (m, 1H), 2.12-2.02 (m, 1H), 1.80-1.68 (m, 2H), 1.36-1.22 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.81 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.6, 123.0, 120.9, 68.8, 61.5, 48.4, 42.4, 36.1, 33.9, 31.9, 26.7, 19.2, 13.2; IR (neat) $\nu = 3376, 3069, 2956, 1536, 1465, 1041, 796\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}]^+$: 268.2389, Found: 263.2380.

(12) Synthesis of (S)-16a: imidazolium bromide **(S)-12** (360 mg, 0.94 mmol) reacted with potassium tetrafluoroborate (151 mg, 1.2 mmol) according to the procedure described for the preparation of **(S)-13a** to give **(S)-16a** (351 mg, 95%) as a colorless oil. $[\alpha]_D^{20} = -18.2^\circ$ ($c = 0.78$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.42 (d, $J = 1.5$

Hz, 1H), 7.30-7.13 (m, 6H), 4.50 (d, $J = 14.7$ Hz, 1H), 4.24-4.03 (m, 3H), 3.97 (d, $J = 15.0$ Hz, 1H), 3.92-3.80 (m, 1H), 3.87 (s, 3H), 3.76-3.45 (m, 2H), 3.14-2.97 (br, 1H), 2.87-2.60 (m, 2H), 1.72-1.58 (m, 2H), 1.34-1.18 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.0, 139.4, 129.1, 128.1, 125.9, 123.1, 121.0, 63.3, 61.7, 48.2, 40.1, 38.3, 36.0, 31.8, 19.3, 13.4; IR (neat) $\nu = 3416, 2933, 2874, 1631, 1535, 1030\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{18}\text{H}_{28}\text{N}_3\text{O}]^+$: 302.2232, Found: 302.2221.

(13) Synthesis of (S)-14b: imidazolium bromide **(S)-10** (263 mg, 0.76 mmol) reacted with potassium hexafluorophosphate (168 mg, 0.91 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(S)-14b** (275 mg, 87%) as a colorless oil. $[\alpha]_{\text{D}}^{20} = -6.0^\circ$ ($c = 0.73$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 2.1$ Hz, 1H), 7.21 (d, $J = 2.1$ Hz, 1H), 4.22-4.10 (m, 4H), 3.88 (s, 3H), 3.73 (dd, $J = 11.4$ and 3.6 Hz, 1H), 3.42 (dd, $J = 11.4$ and 6.6 Hz, 1H), 2.79-2.73 (m, 1H), 2.40-1.90 (br, 2H), 1.86-1.58 (m, 3H), 1.44-1.13 (m, 4H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, $\text{MeOD}-d_4$) δ 146.4, 124.1, 122.4, 66.2, 63.1, 40.9, 35.7, 33.2, 30.4, 20.6, 19.4, 18.8, 13.8; IR (neat) $\nu = 3600, 3362, 2959, 2873, 1536, 1468, 1049, 842\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}]^+$: 268.2389, Found: 268.2384; HRMS (ESI -) m/z (%) Calcd for $[\text{PF}_6]^-$: 144.9642, Found: 144.9648.

(14) Synthesis of (R)-14b: imidazolium bromide **(R)-10** (256 mg, 0.74 mmol) reacted with potassium hexafluorophosphate (147 mg, 0.80 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(R)-14b** (291 mg, 95%) as

a colorless oil. $[\alpha]_{\text{D}}^{20} = 6.2^{\circ}$ ($c = 0.77$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.24 (d, $J = 2.1$ Hz, 1H), 7.21 (d, $J = 2.1$ Hz, 1H), 4.25-4.05 (m, 4H), 3.90 (s, 3H), 3.75 (dd, $J = 11.4$ and 3.6 Hz, 1 H), 3.43 (dd, $J = 11.4$ and 6.6 Hz, 1H), 2.79-2.69 (m, 1H), 2.30-1.88 (br, 2H), 1.88-1.60 (m, 3H), 1.46-1.15 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 3H), 0.91 (d, $J = 6.6$ Hz, 3H), 0.88 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.5, 123.1, 121.1, 64.4, 57.3, 48.4, 40.7, 38.9, 35.3, 32.0, 24.8, 22.8, 22.6, 19.5, 13.4.

(15) Synthesis of (S)-15b: imidazolium bromide **(S)-11** (348 mg, 1.0 mmol) reacted with potassium hexafluorophosphate (202 mg, 1.1 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(S)-15b** (413 mg, 100%) as a colorless oil. $[\alpha]_{\text{D}}^{20} = -6.9^{\circ}$ ($c = 0.91$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.24 (d, $J = 2.1$ Hz, 1H), 7.21 (d, $J = 2.1$ Hz, 1H), 4.25 (AB, $\Delta\nu = 87.0$ Hz and $J_{\text{AB}} = 15.0$ Hz, 2H), 4.22 (t, $J = 7.2$ Hz, 2H), 3.96 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.92 (s, 3H), 3.54 (dd, $J = 11.1$ and 8.1 Hz, 1H), 2.25 (dd, $J = 8.1$ and 3.6 Hz, 1H), 1.90-1.76 (m, 2H), 1.66-1.42 (br, 2H), 1.46-1.30 (m, 2H), 0.96 (t, $J = 7.5$ Hz, 3H), 0.89 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.6, 123.0, 121.0, 68.5, 63.0, 48.4, 41.8, 35.3, 34.2, 32.0, 26.9, 19.5, 13.4; IR (neat) $\nu = 3603, 3383, 2962, 2876, 1536, 1469, 1041, 843\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}]^+$: 268.2389, Found: 263.2383; HRMS (ESI -) m/z (%) Calcd for $[\text{PF}_6]^-$: 144.9642, Found: 144.9665.

(16) Synthesis of (S)-16b: imidazolium bromide **(S)-11** (382 mg, 1.0 mmol) reacted with potassium hexafluorophosphate (202 mg, 1.1 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(S)-16b** (421 mg, 94%) as a colorless oil. $[\alpha]_{\text{D}}^{20} = -29.4^{\circ}$ ($c = 0.52$, EtOH); ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 7.63 (d, $J =$

2.1 Hz, 1H), 7.57 (d, $J = 2.1$ Hz, 1H), 7.29-7.13 (m, 5H), 4.72 (t, $J = 5.1$ Hz, 1H), 4.14-3.92 (m, 4H), 3.67 (s, 3H), 3.46-3.28 (m, 2H), 2.80-2.50 (m, 3H), 2.44-2.30 (m, 1H), 1.70-1.56 (m, 2H), 1.29-1.14 (m, 2H), 0.86 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, MeOD- d_4) δ 145.9, 140.8, 130.3, 129.5, 127.3, 124.1, 122.3, 65.0, 62.4, 40.3, 39.3, 35.4, 33.0, 20.5, 13.8; IR (neat) $\nu = 3603, 3357, 2936, 1536, 1032, 843\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{18}\text{H}_{28}\text{N}_3\text{O}]^+$: 302.2232, Found: 302.2224; HRMS (ESI -) m/z (%) Calcd for $[\text{PF}_6]^-$: 144.9642, Found: 144.9649.

(17) Synthesis of (S)-14c: imidazolium bromide **(S)-10** (348 mg, 1.0 mmol) reacted with lithium bis(trifluoromethanesulfonyl)imide (287 mg, 1.0 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(S)-14c** (510 mg, 93%) as a colorless oil. $[\alpha]_{\text{D}}^{20} = -5.0^\circ$ ($c = 0.66$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 2.1$ Hz, 1H), 7.20 (d, $J = 2.1$ Hz, 1H), 4.26-4.08 (m, 4H), 3.92 (s, 3H), 3.74 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.42 (dd, $J = 11.1$ and 6.9 Hz, 1H), 2.77-2.67 (m, 1H), 2.40-1.90 (br, 2H), 1.88-1.75 (m, 2H), 1.75-1.58 (m, 1H), 1.46-1.12 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.5, 123.0, 121.1, 119.6 (q, $J = 319.4$ Hz), 64.5, 57.2, 48.5, 40.6, 39.1, 35.4, 31.9, 24.7, 22.7, 22.4, 19.5, 13.3; IR (neat) $\nu = 2961, 1351, 1194, 1057\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}]^+$: 268.2389, Found: 268.2385; HRMS (ESI -) m/z (%) Calcd for $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$: 279.9173, Found: 279.9177.

(18) Synthesis of (R)-14c: imidazolium bromide **(R)-10** (348 mg, 1.0 mmol) reacted with lithium bis(trifluoromethanesulfonyl)imide (287 mg, 1.0 mmol) according to the procedure described for the preparation of **(S)-13b** to give **(R)-14c** (512 mg, 93%) as

a colorless oil. $[\alpha]_D^{20} = 5.2^\circ$ ($c = 1.22$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.22 (d, $J = 2.1$ Hz, 1H), 7.20 (d, $J = 2.1$ Hz, 1H), 4.26-4.09 (m, 4H), 3.92 (s, 3H), 3.74 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.42 (dd, $J = 11.1$ and 6.9 Hz, 1H), 2.78-2.68 (m, 1H), 2.60-2.10 (br, 2H), 1.88-1.75 (m, 2H), 1.75-1.58 (m, 1H), 1.46-1.13 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.87 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.5, 123.0, 121.1, 119.6 (q, $J = 319.4$ Hz), 64.4, 57.2, 48.5, 40.6, 39.0, 35.4, 31.9, 24.7, 22.6, 22.3, 19.4, 13.2.

(19) Synthesis of (S)-15c: imidazolium bromide (S)-11 (348 mg, 1.0 mmol) reacted with lithium bis(trifluoromethanesulfonyl)imide (287 mg, 1.0 mmol) according to the procedure described for the preparation of (S)-13b to give (S)-15c (537 mg, 98%) as a colorless oil. $[\alpha]_D^{20} = -5.5^\circ$ ($c = 1.03$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.24 (d, $J = 2.1$ Hz, 1H), 7.22 (d, $J = 2.1$ Hz, 1H), 4.27 (AB, $\Delta\nu = 78.3$ Hz and $J_{\text{AB}} = 14.7$ Hz, 2H), 4.23 (t, $J = 7.5$ Hz, 2H), 3.97 (dd, $J = 11.1$ and 3.6 Hz, 1 H), 3.94 (s, 3H), 3.53 (dd, $J = 11.1$ and 8.1 Hz, 1H), 2.70-2.30 (br, 1H), 2.24 (dd, $J = 8.1$ and 3.3 Hz, 1H), 1.90-1.76 (m, 2H), 1.68-1.44 (br, 1H), 1.46-1.31 (m, 2H), 0.96 (t, $J = 7.5$ Hz, 3H), 0.89 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.6, 122.9, 121.0, 119.6 (q, $J = 319.4$ Hz), 68.4, 63.0, 48.4, 41.9, 35.4, 34.1, 31.9, 26.7, 19.4, 13.2; IR (neat) $\nu = 3552, 2964, 1536, 1351, 1196, 1137, 1057\text{ cm}^{-1}$; ; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}]^+$: 268.2389, Found: 268.2381; HRMS (ESI -) m/z (%) Calcd for $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$: 279.9173, Found: 279.9211.

(20) Synthesis of (S)-16c: imidazolium bromide (S)-12 (200 mg, 0.52 mmol) reacted with lithium bis(trifluoromethanesulfonyl)imide (160 mg, 0.55 mmol) according to

the procedure described for the preparation of **(S)-13b** to give **(S)-16c** (278 mg, 92%) as a colorless oil. $[\alpha]_D^{20} = -15.9^\circ$ ($c = 0.75$, EtOH); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.14 (m, 5H), 7.11 (d, $J = 2.1$ Hz, 1H), 7.09 (d, $J = 2.1$ Hz, 1H), 4.15-3.87 (m, 4H), 3.75 (dd, $J = 11.1$ and 3.9 Hz, 1H), 3.67 (s, 3H), 3.47-3.47 (m, 1H), 2.95-2.85 (m, 1H), 2.78 (dd, $J = 13.8$ and 8.1 Hz, 1 H), 2.58 (dd, $J = 13.8$ and 9.0 Hz, 1H) 1.72-1.58 (m, 2H), 1.35-1.20 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 144.0, 138.8, 129.0, 128.4, 126.3, 122.9, 120.9, 119.6 (q, $J = 319.4$ Hz), 64.5, 61.0, 48.2, 39.6, 38.1, 35.1, 31.7, 19.3, 13.2; IR (neat) $\nu = 3551, 2937, 1536, 1352, 1197, 1137, 1057\text{ cm}^{-1}$; HRMS (ESI +) m/z (%) Calcd for $[\text{C}_{18}\text{H}_{28}\text{N}_3\text{O}]^+$: 302.2232, Found: 302.2225; HRMS (ESI -) m/z (%) Calcd for $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$: 279.9173, Found: 279.9177.

N-2-16-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4893.1 Hz
16 repetitions
OBSERVE H1, 300.0712675 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-16

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

N-2-25-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712690 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-25

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

N-1-96

STANDARD 1H OBSERVE

Archive directory: /export/home/vmr1/vmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0712681 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 34 sec

N-2-2

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4993.1 Hz
16 repetitions
OBSERVE H1, 300.0712690 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-2

Archive directory: /export/home/vnari/vnarsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-~~4~~-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4893.1 Hz

16 repetitions

OBSERVE H1, 300.0712722 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 58 sec

N-1-83

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

N-2-18-D20

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: D2O

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.384 sec
Width 4893.1 Hz
16 repetitions
OBSERVE H1, 300.0720470 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-26-D20

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul
Solvent: D2O
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0720470 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-5

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
Mercury-300B5 "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712728 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-13-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712710 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-23-DMSO-d

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: DMSO
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.594 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0727012 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-23

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-27-DMSO

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: DMSO
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
6 repetitions
OBSERVE H1, 300.0727012 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 34 sec

N-2-27

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

(R)-14a

N-2-14-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.934 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712672 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-14

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

N-2-10-DMSO-d

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4803.1 Hz

32 repetitions

OBSERVE H1, 300.0727012 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 48 sec

N-2-10

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-17-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature

Mercury-300SB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4803.1 Hz

8 repetitions

OBSERVE H1, 300.0712675 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 34 sec

N-2-17

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

(S)-16a

N-2-22-DMSO-d

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: DMSO

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.934 sec

Width 4803.1 Hz

16 repetitions

OBSERVE H1, 300.0727012 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 58 sec

N-2-~~22~~

Archive directory: /export/home/vnarl/vnarsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-3-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712698 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-3

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-29-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature:

Mercury-300BB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4893.1 Hz

16 repetitions

OBSERVE H1, 300.0712698 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 58 sec

N-2-29
CDCl₃

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

(R)-14b

N-2-11-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDC13

Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712734 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-11
CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-15-DMSO-d

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pul

Solvent: DMSO

Ambient temperature

Mercury-300BB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4003.1 Hz

32 repetitions

OBSERVE H1, 300.0727012 MHz

DATA PROCESSING

FT size 32768

Total time 1 min, 48 sec

(S)-16b

N-2-15

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

(S)-16b

N-2-21-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

Solvent: CDC13

Ambient temperature

Mercury-300SB "Resonant"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.994 sec

Width 4803.1 Hz

18 repetitions

OBSERVE H1, 300.0712725 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 58 sec

N-2-21

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-2-28-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712731 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-28

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-1-97-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: CDC13
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.394 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712698 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-1-97

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

(S)-14c

N-2-8-CDC13

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: CDC13
Ambient temperature
Mercury-300SB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.934 sec
Width 4803.1 Hz
16 repetitions
OBSERVE H1, 300.0712716 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-2-8

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

N-1-100

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Resonant"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.994 sec
Width 4803.1 Hz
18 repetitions
OBSERVE H1, 300.0712742 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 58 sec

N-1-100

Archive directory: /export/home/vmr1/vnmrSYS/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul

(S)-16c