

Supporting information

## **Phenolate platform for anion exchange in ionic liquids**

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### **Tetrabutylphosphonium acetate (1)**

To a solution of tetrabutylphosphonium chloride (10 g, 33.91 mmol) in dry toluene (400 mL) was added sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol). The reaction mixture was stirred vigorously for 12 h and afterwards filtered through Celite. An aqueous solution (500 mL) of acetic acid (2.84 g, 47.47 mmol) was added to the reaction mixture and stirred for 30 minutes. The organic phase was separated and washed with 50 mL of H<sub>2</sub>O. The water was removed under vacuum to yield the product as a white solid. Yield: 9.07 g (84%). mp: 57 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.37 (m, 16H), 1.84 (s, 3H), 2.06 (m, 8H). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 12.55, 17.45 (d), 22.71 (d), 22.88, 23.22 (d), 180.71. CHN elemental analysis for C<sub>18</sub>H<sub>39</sub>O<sub>2</sub>P·2H<sub>2</sub>O: calculated (%): C 60.98, H: 12.23, found (%): C: 60.63, H: 12.40.

### **Tetrabutylphosphonium methanesulfonate (2)**

Tetrabutylphosphonium methanesulfonate was prepared by the procedure described for ionic liquid (1) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and methanesulfonic acid (2.93 g, 30.51 mmol) to give a colorless solid. Yield: (10.45 g, 87%). mp: 65 °C (lit: 59-62 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.84 (t, 12H), 1.41 (m, 16H), 2.05 (m, 8H), 2.70 (s, 3H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.53, 17.95 (d), 22.73 (d), 23.18 (d), 38.44. CHN elemental analysis for C<sub>19</sub>H<sub>41</sub>O<sub>2</sub>P·1.5H<sub>2</sub>O: calculated (%): C: 63.47, H: 12.34 found (%): C: 63.32, H: 15.54.

### **Tetrabutylphosphonium 4-methylbenzenesulfonate (3)**

Tetrabutylphosphonium 4-methylbenzenesulfonate was prepared by the procedure described for ionic liquid (1) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and 4-methylbenzenesulfonic acid (5.25 g, 30.51 mmol) to give a colorless solid. Yield: (12.70 g, 87%). mp: 57 °C (lit: 54-57 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.81 (t, 12H, 7), 1.32 (m, 16H), 2.01 (m, 8H), 2.31 (s, 3H), 7.27 (d, 2H, 8.44 Hz), 7.59 (d, 2H, 8.44 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.51, 17.28 (d), 20.48, 22.64 (d), 23.15 (d), 125.35, 129.40, 139.58, 142.32. CHN elemental analysis for C<sub>23</sub>H<sub>43</sub>O<sub>3</sub>PS·2H<sub>2</sub>O: calculated (%): C: 59.20, H: 10.15. found (%): C: 59.03, H: 10.61.

#### **Tetrabutylphosphonium isonicotinate (4)**

Tetrabutylphosphonium isonicotinate was prepared by the procedure described for ionic liquid (1) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and isonicotinic acid (4.17 g, 33.91 mmol) to give a colorless solid. Yield: (11.77 g, 91 %). mp: 215 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.40 (m, 16H), 2.06 (m, 8H), 7.87 (d, 2H, 5.2 Hz), 8.61 (d, 2H, 5.0 Hz). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 12.56, 17.41 (d), 20.45 (d), 23.20 (d), 124.21, 146.48, 148.49, 171.53. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>NO<sub>2</sub>P·3H<sub>2</sub>O: calculated (%): C: 60.66, H: 10.64, N: 3.22, found (%): C: 60.57, H: 8.81, N: 3.22.

#### **Tetrabutylphosphonium nicotinate (5)**

Tetrabutylphosphonium nicotinate was prepared by the procedure described for ionic liquid (1) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butyl phenolate (5.83 g, 33.91 mmol) and nicotinic acid (4.17 g, 33.91 mmol) to give a colorless solid. Yield: (10.86 g, 84 %). mp: 186 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.41(m, 16H), 2.05 (m, 8H), 7.98 (m, 1H), 8.75 (m, 2H), 9.05 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.59, 17.32 (d), 22.68 (d), 23.20 (d), 120.62, 125.94, 130.03, 142.19, 153.25, 169.06. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>NP·H<sub>2</sub>O: calculated (%): C: 66.13, H: 10.60, N: 3.51, found (%): C: 66.07, H: 10.48, N: 3.39.

#### **Tetrabutylphosphonium picolinate (6)**

Tetrabutylphosphonium picolinate was prepared by the procedure described for ionic liquid (1) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and picolinic acid (3.34 g, 27.12 mmol) to give a colorless solid. Yield: (10.86 g, 84 %). mp: 59 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 12H), 1.32 (m, 16H), 2.01 (m, 8H), 7.98 (m, 1H), 8.25 (d, 1H, 8.10 Hz), 8.51 (m, 1H), 8.63 (d, 1H, 5.40 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.54, 17.32 (d), 22.67 (d), 23.18 (d), 126.25, 128.30, 141.60, 146.30, 146.69, 164.36. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>NO<sub>2</sub>P·3H<sub>2</sub>O: calculated (%): C: 60.66, H: 10.64, N: 3.22, found (%): C: 60.70, H: 10.92, N: 3.27.

### **Tetrabutylphosphonium 6-carboxypicolinate (7)**

Tetrabutylphosphonium 6-carboxypicolinate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and pyridine-2,6-dicarboxylic acid (5.10 g, 30.51 mmol) to give a colorless solid. Yield: (11.68 g, 81 %). mp: 205 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.81 (t, 12H), 1.32 (m, 16H), 2.02 (m, 8H), 8.33 (m, 3H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.53, 17.32 (d), 22.67 (d), 23.18 (d), 128.20, 143.23, 146.37, 165.75. CHN elemental analysis for C<sub>23</sub>H<sub>40</sub>NO<sub>4</sub>P·2H<sub>2</sub>O: calculated (%): C: 59.85, H: 9.61, N:3.03. found (%): C: 59.79, H: 10.32, N:2.58.

### **Tetrabutylphosphonium nitrate (8)**

Tetrabutylphosphonium nitrate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and nitric acid (65 % solution, 3.29 mL, 2.14 g, 33.91 mmol) to give a colorless solid. Yield: (9.81 g, 90 %). mp: 70 °C (lit: 70-73 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 12H), 1.32 (m, 16H), 2.01 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.51, 17.30 (d), 22.66 (d), 23.18 (d). CHN elemental analysis for C<sub>16</sub>H<sub>36</sub>NO<sub>3</sub>P·2H<sub>2</sub>O: calculated (%): C: 56.61, H: 11.28, N: 4.13, found (%): C: 56.87, H: 11.61, N: 4.11.

### **Tetrabutylphosphonium hydrogen sulfate (9)**

Tetrabutylphosphonium hydrogen sulfate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and sulfuric acid (95 % solution, 3.49 mL, 3.32 g, 33.91 mmol) to give a colorless solid. Yield: (10.75 g, 90 %). mp: 124 °C (lit: 122 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 12H), 1.32 (m, 16H), 2.01 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.51, 17.28 (d), 22.64 (d), 23.15(d). CHN elemental analysis for C<sub>16</sub>H<sub>37</sub>O<sub>4</sub>P3·5H<sub>2</sub>O: calculated (%): C: 45.80, H: 10.57 found (%): C: 45.84, H: 10.08.

### **Tetrabutylphosphonium dihydrogen phosphate (10)**

Tetrabutylphosphonium dihydrogen phosphate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butyl phenolate (5.83 g, 33.91 mmol) and phosphoric acid (85 % solution, 3.90 mL, 3.32 g, 33.91 mmol) to give a colorless solid. Yield: (10.27 g, 85 %). mp: 149 °C (lit: 148-151 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.79 (t, 12H), 1.31 (m, 16H), 2.00 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.51, 17.29 (d), 22.65 (d), 23.39 (d). CHN elemental analysis for C<sub>16</sub>H<sub>38</sub>O<sub>4</sub>P<sub>2</sub>·2H<sub>2</sub>O: calculated (%): C: 48.97, H: 10.79 found (%): C: 49.11, H: 11.08.

### **Tetrabutylphosphonium formate (11)**

Tetrabutylphosphonium formate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate (5.83 g, 33.91 mmol) and formic acid (7.80 g, 169.55 mmol) to give a colorless solid. Yield: (8.46 g, 82 %). mp: 41 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.35 (m, 16H), 2.04 (m, 8H), 8.17 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.54, 17.32 (d), 22.67 (d), 23.39(d), 166.07. CHN elemental analysis for C<sub>17</sub>H<sub>37</sub>O<sub>2</sub>P·3H<sub>2</sub>O: calculated (%): C: 56.96, H: 12.09 found (%): C: 57.13, H: 12.30.

### **Tetrabutylphosphonium trifluoroacetate (12)**

Tetrabutylphosphonium trifluoroacetate was prepared by the procedure described for ionic liquid (**1**) from tetrabutylphosphonium chloride (10 g, 33.91 mmol), sodium 4-*tert*-butylphenolate 5.83 g, 33.91 mmol) and trifluoroacetic acid (3.86 g, 33.91 mmol) to give a colorless liquid. Yield: (10.23 g, 81 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.35 (m, 16H), 2.04 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.51, 17.29 (d), 22.65 (d), 23.16 (d), 114.27 (q), 162.44 (q). CHN elemental analysis for C<sub>18</sub>H<sub>36</sub>F<sub>3</sub>O<sub>2</sub>P·H<sub>2</sub>O calculated (%): C: 55.37, H: 9.81 found (%): C: 56.00, H: 10.08.

### **Tetrabutylammonium acetate (13)**

To a solution of tetrabutylammonium bromide (10 g, 31.02 mmol) in dry toluene (400 mL) was added sodium 4-*tert*-butyl phenolate (5.34 g, 31.02 mmol). The reaction mixture was stirred vigorously for 12 h and afterwards filtered through Celite. An aqueous solution (500 mL) of acetic acid (2.84 g, 47.47 mmol) was added to the reaction mixture and stirred for half an hours. The organic phase was separated and washed with 50 mL of H<sub>2</sub>O. The solvent was removed under vacuum to yield the product as a white solid. Yield: 8.41 g (90 %). mp: 90 °C (lit: 95-98 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.85 (t, 12H), 1.25 (m, 8H), 1.55 (m, 8H), 2.01 (s, 3H), 3.09 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.82, 19.13, 20.98, 23.13, 58.08, 177.62. CHN elemental analysis for C<sub>18</sub>H<sub>39</sub>O<sub>2</sub>N·H<sub>2</sub>O: calculated (%): C: 67.66, H:12.93, N:4.38 found (%): C: 67.61, H: 12.89, N:4.41.

#### **Tetrabutylammonium methanesulfonate (14)**

Tetrabutylammonium methanesulfonate was prepared by the procedure described for ionic liquid (13) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and methanesulfonic acid (2.68 g, 27.91 mmol) to give a colorless solid. Yield: (8.46 g, 82 %). mp: 78 °C (lit.: 78-80 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.81 (t, 12H), 1.22 (m, 8H), 1.52 (m, 8H), 2.69 (s, 3H), 3.06 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.82, 19.12, 23.12, 38.43, 58.07. CHN elemental analysis for C<sub>17</sub>H<sub>39</sub>NO<sub>3</sub>S·3H<sub>2</sub>O: calculated (%): C: 52.14, H: 11.58, N: 3.58, found (%): C: 51.71, H: 11.26, N: 3.20.

#### **Tetrabutylammonium 4-methylbenzenesulfonate (15)**

Tetrabutylammonium 4-methylbenzenesulfonate was prepared by the procedure described for ionic liquid (13) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and 4-methylbenzenesulfonic acid (4.80 g, 27.90 mmol) to give a colorless solid. Yield: (11.29 g, 88 %). mp: 75 °C (lit: 70-72 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.22 (m, 8H), 1.52 (m, 8H), 2.31(s, 3H), 3.05(m, 8H), 7.27(d, 2H, 8.1 Hz), 7.61(d, 2H, 8.1 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ= 12.84, 19.11, 20.49, 23.09, 58.01, 125.37, 129.41, 139.63, 142.30. CHN elemental analysis for C<sub>23</sub>H<sub>43</sub>O<sub>3</sub>N·H<sub>2</sub>O: calculated (%):C:63.99, H:10.51, N:3.24. found (%): C: 64.05, H: 10.59, N: 3.31.

### **Tetrabutylammonium isonicotinate (16)**

Tetrabutylammonium isonicotinate was prepared by the procedure described for ionic liquid (13) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and isonicotinic acid (3.81g, 31.02 mmol) to give a colorless solid. Yield: (9.72 g, 86 %). mp: 240 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.19 (m, 8H), 1.52 (m, 8H), 3.04 (m, 8H), 8.10 (d, 2H, 6.33 Hz), 8.69 (d, 2H, 6.33 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.83, 19.13, 23.13, 58.08, 125.66, 142.71, 152.87, 169.72. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>N<sub>2</sub>·H<sub>2</sub>O: calculated (%): C: 69.07, H:11.07, N: 7.32, found (%): C: 69.02, H: 11.10, N:7.37.

### **Tetrabutylammonium nicotinate (17)**

Tetrabutylammonium nicotinate was prepared by the procedure described for ionic liquid (13) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and nicotinic acid (4.20 g, 34.12 mmol) to give a colorless solid. Yield: (9.95 g, 88 %). mp: 163 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.23 (m, 8H), 1.54 (m, 8H), 3.08 (m, 8H), 7.86 (t, 1H, 6.53 Hz), 8.66 (m, 2H), 8.97 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.80, 19.13, 23.11, 58.14, 126.33, 135.04, 143.65, 144.30, 144.32, 169.26. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O: calculated (%): C: 69.07, H:11.07, N:7.32 found (%): C: 69.13, H: 11.05, N:7.40.

### **Tetrabutylammonium picolinate (18)**

Tetrabutylammonium picolinate was prepared by the procedure described for ionic liquid (13) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and picolinic acid (3.05 g, 24.81 mmol) to give a colorless solid. Yield: (10.06 g, 89 %). mp: 62 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.22 (m, 8H), 1.49 (m, 8H), 3.07 (m, 8H), 8.26 (m, 1H), 8.29 (d, 1H, 7.8 Hz), 8.50 (m, 1H), 8.63 (d, 1H, 5.4 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.84, 19.14, 23.14, 58.09, 126.28, 128.34, 141.53, 146.23, 146.79, 164.27. CHN elemental analysis for C<sub>22</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O: C: 65.96, H: 11.07, N: 6.99, found (%): C: 66.18, H: 10.98, N: 6.83.

### **Tetrabutylammonium 6-carboxypicolinate (19)**

Tetrabutylammonium 6-carboxypicolinate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and pyridine-2,6-dicarboxylic acid (4.14 g, 24.81 mmol) to give a colorless solid (10.26 g, 81 %). mp: 219 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.22 (m, 8H), 1.49 (m, 8H), 3.07 (m, 8H), 8.26 (m, 1H), 8.29 (d, 1H, 7.8 Hz), 8.50 (m, 1H), 8.63 (d, 1H, 5.4 Hz). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.84, 19.14, 23.14, 58.09, 126.28, 128.34, 141.53, 146.23, 146.79, 164.27. CHN elemental analysis for C<sub>23</sub>H<sub>40</sub>O<sub>4</sub>N<sub>2</sub>·H<sub>2</sub>O: calculated (%): C: 64.76, H: 9.92, N: 6.57 found (%): C: 64.85, H: 9.79, N: 6.53.

### **Tetrabutylammonium nitrate (20)**

Tetrabutylammonium nitrate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and nitric acid (65 % solution, 3 mL, 1.95 g, 31.02 mmol) to give a colorless solid. Yield: (8.5 g, 90 %). mp: 114 °C (lit: 116-118 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.83 (t, 12H), 1.23 (m, 8H), 1.53 (m, 8H), 3.08 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.80, 19.12, 23.12, 58.07. CHN elemental analysis for C<sub>16</sub>H<sub>36</sub>N<sub>2</sub>O<sub>3</sub>·2H<sub>2</sub>O: calculated (%): C: 56.44, H: 11.84, N: 8.23. found (%): C: 56.42, H: 11.44, 8.33.

### **Tetrabutylammonium hydrogen sulfate (21)**

Tetrabutylammonium hydrogen sulfate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and sulfuric acid (95 % solution, 2.88 mL, 3.03 g, 31.02 mmol) to give a colorless solid. Yield: (9.37 g, 89 %). mp: 168 °C (lit: 169-171°C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 12H), 1.21 (m, 8H), 1.50 (m, 8H), 3.05 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.80, 19.11, 23.11, 58.06. CHN elemental analysis for C<sub>16</sub>H<sub>37</sub>O<sub>4</sub>N·H<sub>2</sub>O: calculated (%): C: 53.75, H: 10.99, N: 3.92. found (%): C: 53.67, H: 10.79, N: 4.03.

### **Tetrabutylammonium dihydrogen phosphate (22)**



Tetrabutylammonium dihydrogen phosphate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and phosphoric acid (85 % solution, 3.03 g, 3.57 mL) to give a colorless solid. Yield (9.05 g, 86 %). mp: 154 °C (lit: 151-154 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.81 (t, 12H), 1.23 (m, 8H), 1.53 (m, 8H), 3.08 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.80, 19.12, 23.12, 58.06. CHN elemental analysis for C<sub>16</sub>H<sub>38</sub>NO<sub>4</sub>P·2H<sub>2</sub>O: calculated (%): C: 51.18, H: 11.27, N: 3.73. found (%): C: 51.31, H: 11.25, N: 3.67.

### **Tetrabutylammonium formate (23)**

Tetrabutylammonium formate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and formic acid (7.13 g, 155.10 mmol) to give a colorless solid. Yield: (7.40 g, 83 %). mp: 69 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.68 (t, 12H), 1.07 (m, 8H), 1.36 (m, 8H), 2.91 (m, 8H), 8.07 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.81, 19.12, 23.11, 58.13, 169.07. CHN elemental analysis for C<sub>17</sub>H<sub>37</sub>NO<sub>2</sub>P·2H<sub>2</sub>O: calculated (%): C: 63.11, H: 12.77, N: 4.33, found (%): C: 63.05, H: 13.06, N: 4.24.

### **Tetrabutylammonium trifluoroacetate (24)**

Tetrabutylammonium trifluoroacetate was prepared by the procedure described for ionic liquid (**13**) from tetrabutylammonium bromide (10 g, 31.02 mmol), sodium 4-*tert*-butylphenolate (5.34 g, 31.02 mmol) and trifluoroacetic acid (3.53 g, 31.02 mmol) to give a colorless solid. Yield: (9.37 g, 85 %). mp: 74 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.89 (t, 12H), 1.29 (m, 8H), 1.62 (m, 8H), 3.14 (m, 8H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.80, 19.12, 23.12, 58.06, 117.81 (q), 178.20 (q). CHN elemental analysis for C<sub>18</sub>H<sub>36</sub>F<sub>3</sub>NO<sub>3</sub>·2H<sub>2</sub>O: calculated (%): C: 53.05, H: 9.89, N: 3.44, found (%): C: 53.34, H: 9.28, N: 3.61.

### **1-Butyl-3-methylimidazolium acetate (25)**

To a solution of 1-butyl-3-methylimidazolium chloride (10g, 57.25 mmol) in dry 2-butanone (500 mL) was added sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol). The reaction

mixture was stirred vigorously for 12 h and afterwards filtered through Celite. An aqueous solution (500 mL) of acetic acid (5.15 g, 85.87 mmol) was added to the reaction mixture and stirred for half an hours. The organic phase was separated and washed with 50 mL of H<sub>2</sub>O. The water was removed under vacuum to yield the product as a colorless liquid. Yield: 9.08 g (80 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 3H; 7.37 Hz), 1.21 (m, 2H), 1.75 (m, 2H), 1.93 (s, 3H), 3.79 (s, 3H), 4.09 (m, 2H), 7.32 (m, 2H), 8.61 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.59, 18.70, 23.09, 31.21, 35.56, 49.21, 122.17, 123.43, 135.79, 180.75. CHN elemental analysis for C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O: calculated (%): C: 51.26, H: 9.46, N: 11.96, found (%): C: 51.20, H: 9.51, N: 12.03.

### **1-Butyl-3-methylimidazolium methanesulfonate (26)**

1-Butyl-3-methylimidazolium methanesulfonate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) and methanesulfonic acid (4.95g, 51.25 mmol) to give a colorless solid. Yield: (11.40 g, 85 %). mp: 76 °C (lit: 74 °). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.81 (t, 3H; 7.35 Hz), 1.17 (m, 2H), 1.71 (m, 2H), 2.70 (s, 3H), 3.78 (s, 3H), 4.06 (m, 2H), 7.31 (m, 2H), 8.59 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.62, 18.70, 31.22, 35.59, 38.48, 49.22, 122.18, 123.44, 135.79. CHN elemental analysis for C<sub>9</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>S·H<sub>2</sub>O: calculated (%): C: 42.84, H: 7.99, N: 11.10 found (%): C: 42.81, H: 9.77, N: 11.22.

### **1-Butyl-3-methylimidazolium 4-methylbenzenesulfonate (27)**

1-Butyl-3-methylimidazolium 4-methylbenzenesulfonate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) and 4-methylbenzenesulfonic acid (8.87 g, 51.52 mmol) to give a colorless solid. Yield: (14.57 g, 82 %). mp: 67 °C (lit: 67 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.87 (t, 3H; 7.36 Hz), 1.21 (m, 2H), 1.69 (m, 2H), 2.35 (s, 3H), 3.82 (s, 3H), 4.08 (m, 2H), 7.34 (m, 4H), 7.63 (d, 2H), 8.7 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.54, 18.67, 20.43, 31.18, 35.52, 49.20, 122.13, 123.38, 125.30, 129.39, 135.74, 139.40, 142.41. CHN elemental analysis for C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>·S·H<sub>2</sub>O: calculated (%): C: 54.86, H: 7.37, N: 8.53, found (%): C: 54.95, H: 7.21, N: 8.63.

### 1-Butyl-3-methylimidazolium isonicotinate (28)

1-Butyl-3-methylimidazolium isonicotinate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and isonicotinic acid (7.04 g, 57.25 mmol) to give a colorless solid. Yield: (12.41 g, 83 %). mp: 269 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 3H; 7.35 Hz), 1.16 (m, 2H), 1.72 (m, 2H), 3.77(s, 3H), 4.06 (t, 2H, 7.13 Hz), 7.30 (m, 2H), 7.79 (d, 2H, 6.35 Hz), 8.58 (m, 3H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.52, 18.65, 31.16, 35.50, 49.17, 122.11, 123.37, 123.89, 135.70, 146.86, 147.77, 171.89. CHN elemental analysis for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>P·H<sub>2</sub>O: calculated (%): C: 60.20, H: 7.58, N: 15.04, found (%): C: 60.23, H: 7.61, N: 15.10.

### 1-Butyl-3-methylimidazolium nicotinate (29)

1-Butyl-3-methylimidazolium nicotinate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and nicotinic acid (7.04 g, 57.25 mmol) to give a colorless solid. Yield: (12.86 g, 86 %). mp: 195 °C. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.87 (t, 3H; 7.32 Hz), 1.28 (m, 2H), 1.81 (m, 2H), 4.06 (s, 3H), 4.25 (t, 2H, 7.15 Hz), 7.20 (m, 3H), 8.32 (m, 2H), 8.62 (m, 1H), 9.19 (s, 1H), <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.54, 18.67, 31.19, 35.53, 49.21, 122.14, 123.40, 134.89, 135.77, 143.86, 144.58, 169.36. CHN elemental analysis for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>·H<sub>2</sub>O: calculated (%): C: 60.20, H: 7.58, N: 15.04, found (%): C: 60.13, H: 7.39, N: 15.01.

### 1-Butyl-3-methylimidazolium picolinate (30)

1-Butyl-3-methylimidazolium picolinate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and picolinic acid (5.63 g, 45.73 mmol) to give a colorless liquid. Yield: (11.96 g, 80 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.87 (t, 3H; 7.32 Hz), 1.17 (m, 2H), 1.71 (m, 2H), 3.78 (s, 3H), 4.06 (t, 2H, 7.15 Hz), 7.32 (m, 2H), 7.91 (t, 1H, 6.62 Hz), 8.19 (d, 1H, 7.78 Hz), 8.42 (m, 1H), 8.63 (m, 2H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.56,

18.68, 31.20, 35.55, 49.22, 122.15, 123.41, 125.88, 127.93, 135.79, 142.46, 145.52, 147.18, 165.56. CHN elemental analysis for  $C_{14}H_{19}N_3O_2 \cdot 2H_2O$ : calculated (%): C: 56.55, H: 7.80, N: 14.13, found (%): C: 56.52, H: 7.73, N: 14.19.

### **1-Butyl-3-methylimidazolium nitrate (31)**

1-Butyl-3-methylimidazolium nitrate was prepared by the procedure described for ionic liquid (**25**) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and nitric acid (65 % solution, 5.55 mL, 3.60 g, 57.25 mmol) to give a pale yellow liquid. Yield: (9.56 g, 83 %).  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 0.79 (t, 3H; 7.39 Hz), 1.23 (m, 2H), 1.72 (m, 2H), 3.78 (s, 3H), 4.09 (t, 2H, 7.13 Hz), 7.36 (m, 2H), 8.75 (s, 1H).  $^{13}C$  NMR (75 MHz,  $D_2O$ ):  $\delta$  = 12.54, 18.68, 31.20, 35.52, 49.21, 122.12, 123.38, 135.77. CHN elemental analysis for  $C_8H_{15}N_3O_3 \cdot H_2O$ : calculated (%): C: 43.83, H: 7.82, N: 19.17, found (%): C: 43.50, H: 7.80, N: 19.31.

### **1-Butyl-3-methylimidazolium hydrogen sulfate (32)**

1-Butyl-3-methylimidazolium hydrogen sulfate was prepared by the procedure described for ionic liquid (**25**) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and sulfuric acid (95 % solution, 5.90 mL, 5.60 g, 57.25 mmol) to give a colorless solid. Yield: (10.82 g, 80 %). mp: 30 °C (lit: 29-32 °C).  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 0.78 (t, 3H; 7.39 Hz), 1.18 (m, 2H), 1.70 (m, 2H), 3.77 (s, 3H), 4.05 (t, 2H, 7.13 Hz), 7.30 (m, 2H), 8.59 (s, 1H).  $^{13}C$  NMR (75 MHz,  $D_2O$ ):  $\delta$  = 12.55, 18.66, 31.18, 35.54, 49.19, 122.13, 123.39, 135.76. CHN elemental analysis for  $C_8H_{16}N_2O_4S \cdot 2H_2O$ : Calculated (%): C: 35.28, H: 7.40, N: 10.29, found (%): C: 35.29, H: 7.51, N: 10.30.

### **1-Butyl-3-methylimidazolium dihydrogen phosphate (33)**

1-Butyl-3-methylimidazolium dihydrogen phosphate was prepared by the procedure described for ionic liquid (**25**) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) and phosphoric acid (85 % solution, 6.59 mL,

5.60 g, 57.25 mmol) to give a colorless solid. Yield: (11.49 g, 85 %). mp: 165 °C (lit: 167 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.80 (t, 3H; 7.39 Hz), 1.21 (m, 2H), 1.73 (m, 2H), 3.97 (s, 3H), 4.12 (t, 2H, 7.13 Hz), 7.33 (m, 2H), 8.7 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.53, 18.66, 31.19, 35.52, 49.20, 122.12, 123.38, 135.76. CHN elemental analysis for C<sub>8</sub>H<sub>17</sub>N<sub>2</sub>O<sub>4</sub>P·2H<sub>2</sub>O: calculated (%): C: 35.29, H: 7.78, N: 10.29, found (%): C: 35.33, H: 7.91, N: 10.40.

### 1-Butyl-3-methylimidazolium formate (34)

1-Butyl-3-methylimidazolium formate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butyl phenolate (9.85 g, 57.25 mmol) and formic acid (13.17 g, 286.25 mmol) to give a colorless liquid. Yield: (11.49 g, 85 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.82 (t, 3H; 7.30 Hz), 1.28 (m, 2H), 1.74 (m, 2H), 3.78 (s, 3H), 4.09 (t, 2H, 7.15 Hz), 7.32 (m, 2H), 8.71 (m, 1H), 9.60 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.58, 18.70, 31.22, 35.58, 49.23, 122.17, 123.42, 123.89, 135.79, 167.33 CHN elemental analysis for C<sub>9</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O: calculated (%): C: 49.08, H: 9.15, N: 12.72 found (%): C: 48.95, H: 9.20, N: 12.89.

### 1-Butyl-3-methylimidazolium trifluoroacetate (35)

1-Butyl-3-methylimidazolium trifluoroacetate was prepared by the procedure described for ionic liquid (25) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) and trifluoroacetic acid (6.52 g, 57.25 mmol) to give a colorless liquid. Yield: (11.23 g, 86 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.75 (t, 3H; 7.35 Hz), 1.16 (m, 2H), 1.68 (m, 2H), 3.75 (s, 3H), 4.03 (t, 2H, 7.17 Hz), 7.28 (m, 3H), 8.57 (m, 2H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.55, 18.68, 31.19, 35.56, 49.22, 118.08(q), 122.15, 123.40, 135.75, 162.18 CHN elemental analysis for C<sub>10</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>·H<sub>2</sub>O: calculated (%): C: 44.44, H: 6.34, N: 10.37, found (%): C: 44.62, H: 6.29, N: 10.24.

### 1-Butyl-3-methylimidazolium trifluoromethanesulfonate (36)

1-Butyl-3-methylimidazolium trifluoromethanesulfonate was prepared by the procedure described for ionic liquid (**25**) from 1-butyl-3-methylimidazolium chloride (10 g, 57.25 mmol) sodium 4-*tert*-butylphenolate (9.85 g, 57.25 mmol) and trifluoromethanesulfonic acid (8.59 g, 57.25 mmol) to give a colorless liquid. Yield: (13.20 g, 80 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.78 (t, 3H; 7.35 Hz), 1.19 (m, 2H), 1.71 (m, 2H), 3.77 (s, 3H), 4.05 (t, 2H, 7.17 Hz), 7.35 (m, 3H), 8.57 (m, 2H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.56, 18.70, 31.21, 35.54, 49.24, 117.53(q), 122.17, 123.43, 135.74. CHN elemental analysis for C<sub>9</sub>H<sub>15</sub>F<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S·2H<sub>2</sub>O: calculated (%): C: 33.33, H: 5.90, N: 8.64, found (%): C: 33.32, H: 5.79, N: 8.71.

### 1-Butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (**37**)

To a solution of 1-butyl-1-methylpyrrolidinium bromide (10 g, 45.01 mmol) in dry DCM (500 mL), sodium 4-*tert*-butylphenolate (7.75 g, 45.01 mmol) was added and stirred for 12 hours. The reaction mixture was filtered through Celite to remove the precipitated sodium bromide. The solvent was removed under vacuum. 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate was obtained as a white solid. Yield (12.85 g, 98 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.82 (t, 3H, 7.32 Hz), 1.25 (m, 11H), 1.62 (m, 2H), 2.54 (m, 4H), 2.92 (s, 3H), 3.55 (m, 2H), 3.68 (m, 4H), 6.87 (d, 2H), 7.13 (d, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 13.64, 19.63, 21.52, 25.80, 29.15, 31.71, 33.84, 49.51, 64.11, 64.39, 115.51, 126.04, 140.85, 156.20. CHN elemental analysis for C<sub>19</sub>H<sub>33</sub>NO: Calculated (%) C: 78.29, H: 11.41, N: 4.81, found (%) C: 78.18, H: 11.53, N: 4.80

### 1-Butyl-1-methylpyrrolidinium acetate (**38**)

To a solution of 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) in toluene (250 mL), an aqueous solution (500 mL) of acetic acid (3.08 g, 51.45 mmol) was added and stirred for 30 minutes. The organic layer was separated and washed with water (50 mL). The combined aqueous layer was concentrated under vacuum to give 1-butyl-1-methylpyrrolidinium acetate as a colorless solid. Yield (5.66 g, 82 %). mp: 78 °C (lit: 81 °C). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): δ = 0.88 (t, 3H, 7.32 Hz), 1.25 (m, 2H), 1.62 (m, 2H), 1.98 (s, 3H), 2.10 (m, 4H), 2.94 (s, 3H), 3.19 (m, 2H), 3.40 (m, 4H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O): δ = 12.86, 19.27, 20.75, 21.33, 25.12, 48.05, 64.11, 64.30, 177.08. CHN elemental analysis for

$C_{11}H_{23}NO_2 \cdot 2H_2O$ : calculated (%): C: 55.67, H: 11.47, N: 5.90 found (%): C: 45.59, H: 11.37, N: 5.83.

### **1-Butyl-1-methylpyrrolidinium methanesulfonate (39)**

1-Butyl-1-methylpyrrolidinium methanesulfonate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and methanesulfonic acid (2.96 g, 30.87 mmol) to give a colorless solid. Yield (6.51 g, 80 %). mp: 65 °C (lit: 63 °C).  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 0.82 (t, 3H, 7.32 Hz), 1.28 (m, 2H), 1.65 (m, 2H), 2.10 (m, 4H), 2.70 (s, 3H), 2.93 (s, 3H), 3.19 (m, 2H), 3.39 (m, 4H).  $^{13}C$  NMR (75 MHz,  $D_2O$ ):  $\delta$  = 12.75, 14.80, 19.19, 21.24, 25.04, 38.40, 49.90, 64.09, 64.15 CHN elemental analysis for  $C_{10}H_{23}NO_3S \cdot H_2O$ : calculated (%): C: 47.03, H: 9.87, N: 5.48 found (%): C: 47.10, H: 8.28, N: 5.30.

### **1-Butyl-1-methylpyrrolidinium 4-methylbenzenesulfonate (40)**

1-Butyl-1-methylpyrrolidinium 4-methylbenzenesulfonate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and 4-methylbenzenesulfonic acid (5.31 g, 30.87 mmol) to give a colorless solid. Yield (8.81 g, 82 %). mp: 114 °C (lit: 115 °C).  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 0.83 (t, 2H, 7.34 Hz), 12.27 (m, 2H), 1.67 (m, 2H), 2.13 (m, 4H), 2.30 (s, 3H), 2.92 (s, 3H), 3.19 (m, 2H), 3.38 (m, 4H), 7.29 (d, 2H, 8.16 Hz), 7.61 (d, 2H, 8.16 Hz).  $^{13}C$  NMR (75 MHz,  $D_2O$ ):  $\delta$  = 15.26, 21.71, 22.96, 23.75, 27.52, 50.52, 64.05, 64.18, 127.85, 131.94, 141.95, 144.96. CHN elemental analysis for  $C_{16}H_{27}NO_3S \cdot 2H_2O$ : calculated (%): C: 54.99 H: 8.94, N: 4.01 found (%): C: 55.02, H: 8.60, N: 4.01.

### **1-Butyl-1-methylpyrrolidinium isonicotinate (41)**

1-Butyl-1-methylpyrrolidinium isonicotinate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and isonicotinic acid (4.22 g, 34.30 mmol) to give a colorless solid. Yield: (8.07 g, 89 %). mp: 227 °C.  $^1H$  NMR (300 MHz,  $D_2O$ ):  $\delta$  = 0.83 (t, 3H, 7.40 Hz), 1.27 (m, 2H), 1.68 (m,

2H), 2.11 (m, 4H), 2.93 (s, 3H), 3.20 (m, 2H), 3.39 (m, 4H), 8.16 (m, 2H), 8.73 (d, 2H, 6.33 Hz),  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.72, 19.17, 21.22, 25.02, 47.95, 64.05, 64.20, 125.82, 142.18, 163.34, 169.70. CHN elemental analysis for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ : calculated (%): C: 56.58, H: 9.50, N: 8.80. found (%): C: 56.26, H: 9.11, N: 9.01.

### **1-Butyl-1-methylpyrrolidinium nicotinate (42)**

1-Butyl-1-methylpyrrolidinium nicotinate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and nicotinic acid (4.22 g, 37.30 mmol) to give a colorless solid. Yield: (7.70 g, 85 %). mp: 174 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 0.82 (t, 3H, 7.45 Hz), 1.25 (m, 2H), 1.65 (m, 2H), 2.10 (m, 4H), 2.93 (s, 3H), 3.19 (m, 2H), 3.39 (m, 4H), 7.48 (m, 1H), 8.68 (d, 2H, 6.35), 8.99 (s, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.73, 19.18, 21.22, 25.02, 47.95, 64.05, 64.19, 126.43, 135.13, 143.33, 143.98, 144.62, 168.99. CHN elemental analysis for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$ : calculated (%): C: 63.80, H: 9.28, N: 9.92 found (%): C: 63.78, H: 9.39, N: 9.83.

### **1-Butyl-1-methylpyrrolidinium picolinate (43)**

1-Butyl-1-methylpyrrolidinium picolinate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and picolinic acid (3.37 g, 27.44 mmol) to give a colorless solid. Yield (7.52 g, 83 %). mp: 78 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 1.28 (t, 3H, 7.35 Hz), 1.29 (m, 2H), 1.30 (m, 2H), 2.11 (m, 4H), 2.94 (s, 3H), 3.23 (m, 2H), 3.40 (m, 4H), 8.04 (m, 1H), 8.33 (t, 1H), 8.67 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.77, 19.21, 21.26, 25.05, 47.97, 64.06, 64.23, 126.47, 128.54, 140.98, 146.88, 147.48, 163.58. CHN elemental analysis for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$ : calculated (%): C: 63.80, H: 9.28, 9.92, found (%): C: 63.69, H: 9.39, N: 9.87.

### **1-Butyl-1-methylpyrrolidinium nitrate (44)**

1-Butyl-1-methylpyrrolidinium nitrate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and nitric acid (65 % solution, 3.32 mL, 2.15 g, 34.30 mmol) to give a colorless liquid. Yield:



(5.67 g, 81 %).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 0.82 (t, 3H, 7.45 Hz), 1.25 (m, 2H), 1.65 (m, 2H), 2.10 (m, 4H), 2.93 (s, 3H), 3.19 (m, 2H), 3.39 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.73, 19.18, 21.22, 25.02, 47.95, 64.05, 64.19, CHN elemental analysis for  $\text{C}_9\text{H}_{20}\text{N}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ : calculated (%): C: 44.98, H: 10.07, N: 11.66, found (%): C: 44.87, H: 10.21, N: 11.59.

### **1-Butyl-1-methylpyrrolidinium hydrogen sulfate (45)**

1-Butyl-1-methylpyrrolidinium hydrogen sulfate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and sulfuric acid (95 % solution, 3.53 mL, 3.36 g, 34.30 mmol) to give a colorless liquid. Yield (6.97 g, 85 %).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 0.85 (t, 3H, 7.38 Hz), 1.28 (m, 2H), 1.67 (m, 2H), 2.10 (m, 4H), 2.93 (s, 3H), 3.20 (m, 2H), 3.39 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.72, 19.17, 21.22, 25.02, 47.95, 64.05, 64.20. CHN elemental analysis for  $\text{C}_9\text{H}_{21}\text{O}_4\text{NS} \cdot 3\text{H}_2\text{O}$ : calculated (%): C: 36.85, H: 9.28, N: 4.77, found (%): C: 36.20, H: 8.27, N: 4.34.

### **1-Butyl-1-methylpyrrolidinium dihydrogen phosphate (46)**

1-Butyl-1-methylpyrrolidinium dihydrogen phosphate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and phosphoric acid (85 % solution, 3.95 mL, 3.36 g, 34.30 mmol) to give a colorless liquid. Yield (6.81 g, 83 %).  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 0.81 (t, 3H, 7.31 Hz), 1.24 (m, 2H), 1.64 (m, 2H), 2.09 (m, 4H), 2.92 (s, 3H), 3.19 (m, 2H), 3.40 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 12.77, 19.22, 21.27, 25.06, 47.96, 64.11, 64.24. CHN elemental analysis for  $\text{C}_9\text{H}_{22}\text{O}_4\text{NP} \cdot \text{H}_2\text{O}$ : calculated (%): C: 42.02, H: 9.40, N: 5.44 found (%): C: 42.12, H: 9.50, N: 5.40.

### **1-Butyl-1-methylpyrrolidinium formate (47)**

1-Butyl-1-methylpyrrolidinium formate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-*tert*-butylphenolate (10 g, 34.30 mmol) and formic acid (7.89 g, 171.5 mmol) to give a colorless liquid. Yield (5.2 g, 81 %).  $^1\text{H}$  NMR (300

MHz, D<sub>2</sub>O):  $\delta$  = 0.81 (t, 3H, 7.31 Hz), 1.24 (m, 2H), 1.64 (m, 2H), 2.09 (m, 4H), 2.92 (s, 3H), 3.19 (m, 2H), 3.40 (m, 4H), 8.21 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O):  $\delta$  = 12.77, 19.22, 21.27, 25.06, 47.96, 64.11, 64.24, 167.29. CHN elemental analysis for C<sub>10</sub>H<sub>21</sub>NO<sub>2</sub>·2H<sub>2</sub>O: calculated (%): C: 53.78, H:11.28, N:6.27, found (%): C: 53.91, H: 11;43, N:6.36.

### **1-Butyl-1-methylpyrrolidinium trifluoroacetate (48)**

1-Butyl-1-methylpyrrolidinium trifluoroacetate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-tert-butylphenolate (10 g, 34.30 mmol) and trifluoroacetic acid (3.91 g, 34.3 mmol) to give a colorless liquid. Yield (7 g, 80 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  = 0.81 (t, 3H, 7.31 Hz), 1.24 (m, 2H), 1.64 (m, 2H), 2.09 (m, 4H), 2.92 (s, 3H), 3.19 (m, 2H), 3.40 (m, 4H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O ):  $\delta$  = 12.77, 19.18, 21.24, 21.95, 25.04, 47.98, 64.11, 64.23, 117.98(q), 162.55(q). CHN elemental analysis for C<sub>11</sub>H<sub>20</sub> F<sub>3</sub>NO<sub>2</sub> ·H<sub>2</sub>O: calculated (%): C: 45.35, H: 8.30, N: 4.81. found (%): C: 45.45, H: 8.04, N: 5.49.

### **1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate (49)**

1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate was prepared by the procedure described for ionic liquid (38) from 1-butyl-1-methylpyrrolidinium 4-tert-butylphenolate (10 g, 34.30 mmol) and trifluoromethanesulfonic acid (5.14 g, 34.3 mmol) to give a colorless liquid. Yield: (8.19 g, 82 %). <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  = 0.81 (t, 3H, 7.31 Hz), 1.24 (m, 2H), 1.64 (m, 2H), 2.09 (m, 4H), 2.92 (s, 3H), 3.19 (m, 2H), 3.40 (m, 4H), 8.21 (s, 1H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O):  $\delta$  = 12.66, 19.11, 21.16,21.87, 24.97, 47.88, 64.11, 64.04, 117.47(q). CHN elemental analysis for C<sub>10</sub>H<sub>20</sub>F<sub>3</sub>NO<sub>3</sub>S·2H<sub>2</sub>O: calculated (%): C: 36.69, 7.39,N: 4.28 found (%): C: 37.01, H: 7.61, N:4.50.