Supporting Information

Extraction of Phenols from Water with Functionalized Ionic Liquids

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I. Synthesis of ILs

1. $[C_4C_7im]PF_6$

1-Bromoheptane (0.2 mol) was added dropwise to N-butylimidazole (0.2 mol) under 50 °C over 20 min and then the mixture was kept at 70 °C for 10 h under stirring; the resultant sticky product ($[C_4C_7im]Br$) was dissolved with 30 mL of water, followed by the addition of 0.2 mol of KPF_6. After stirring for 1 h, two phases formed where the bottom phase was $[C_4C_7im]PF_6$; after decanting the top phase, 10 mL of water was added to wash the IL phase; this was repeated several times until Br^- free, as indicated by the $AgNO_3$ test of the water washings. After vacuum drying 24 h at 75 °C, $[C_4C_7im]PF_6$ was obtained as a light yellow liquid (90% yield).

2. $[C_4C_7im]BF_4$

This synthesis followed the same procedure as for $[C_4C_7im]PF_6$ described above, although $NaBF_4$ was used instead of KPF_6; $[C_4C_7im]BF_4$ was a light yellow liquid and the yield was 79%.

3. $[C_4C_7im]NTf_2$

As for the preparation of $[C_4C_7im]PF_6$ except $LiNTf_2$ was employed to afford $[C_4C_7im]NTf_2$ as a light yellow liquid (92% yield).

4. [C_4C_6OHim]PF_6

N-Butylimidazole (0.2mol) was mixed with 6-chloro-1-hexanol (0.2mol); this mixture was stirred at 70 °C for 10 h, the resulting sticky product ([C_4C_6OHim]Cl) was dissolved with 30 mL of water, followed by the addition of 0.2 mol of KPF_6. After stirring for 1 h, two phases formed where the bottom phase was [C_4C_6OHim]PF_6; after decanting the top phase, 10 mL of water was added to wash the IL phase; this was repeated several times until Cl^- free, as indicated by the $AgNO_3$ test of the water washings. After vacuum drying 24 h at 75 °C, [C_4C_6OHim]PF_6 was obtained as a light yellow liquid (70% yield).

5. [C_4C_6OHim]BF_4

Briefly, 0.2 mol of [C_4C_6OHim]Cl (following the same synthesis procedure described above), was dissolved with 30 mL of water, and then 0.4 mol of $NaBF_4$ was added; the mixture was stirred for 2 h and two phases formed. The upper phase was [C_4C_6OHim]BF_4, after phase separation with a separatory funnel (100 mL), [C_4C_6OHim]BF_4 was dissolved with 20 mL of dichloromethane and washed with aliquots of water until Cl^- free, as indicated by the $AgNO_3$ test of the water washings. After vacuum drying 24 h at 75 °C, [C_4C_6OHim]BF_4 was obtained as a light yellow liquid (15% yield).

6. [C_4C_6OHim]NTf_2

As for the preparation of [C_4C_6OHim]PF_6 except $LiNTf_2$ was employed to afford [C_4C_6OHim]NTf_2 as a light yellow liquid (85% yield).

7. [C_4C_8OHim]PF_6

As for the preparation of [C_4C_6OHim]PF_6 except 8-chloro-1-octanol was employed to afford [C_4C_8OHim]PF_6 as a light yellow liquid (82% yield).

8. [C_4C_8OHim]BF_4

As for the preparation of [C_4C_8OHim]PF_6 except $NaBF_4$ was employed to afford [C_4C_8OHim] BF_4 as a light yellow liquid (61% yield).

9. $[C_4C_8OHim]NTf_2$

As for the preparation of $[C_4C_8OHim]PF_6$ except $LiNTf_2$ was employed to afford $[C_4C_8OHim]NTf_2$ as a light yellow liquid (86% yield).

10. $[C_4C_9im]PF_6$

As for the preparation of $[C_4C_6OHim]PF_6$ except 1-chlorononane was used to react with equal molar amount (0.2 mol) of N-butylimidazole to afford $[C_4C_9im]PF_6$ as a colorless liquid (91% yield).

11. $[C_4C_9im]BF_4$

As for the preparation of $[C_4C_9im]PF_6$ except $NaBF_4$ was employed to afford $[C_4C_9im]BF_4$ as a colorless liquid (83% yield).

12. $[C_4C_9im]NTf_2$

As for the preparation of $[C_4C_9im]PF_6$ except $LiNTf_2$ was employed to afford $[C_4C_9im]NTf_2$ as a colorless liquid (95% yield).

13. $[C_4C_{12}im]PF_6$

As for the preparation of $[C_4C_9im]PF_6$ except 1-chlorododecane was employed to afford $[C_4C_{12}im]PF_6$ as a colorless liquid (92% yield).

14. $[C_4C_{12}im]BF_4$

As for the preparation of $[C_4C_{12}im]PF_6$ except $NaBF_4$ was employed to afford $[C_4C_{12}im]BF_4$ as a colorless liquid (90% yield).

15. $[C_4C_{12}im]NTf_2$

As for the preparation of $[C_4C_{12}im]PF_6$ except $LiNTf_2$ was employed to afford $[C_4C_{12}im]NTf_2$ as a colorless liquid (96% yield).

16. $[C_4C_{11}OHim]PF_6$

Briefly, 0.2 mol of 11-bromo-1-undecanol was dissolved with 40 mL of acetonitrile, and then 0.2 mol of

N-butylimidazole was added; this mixture was stirred at 70 °C for 12 h. After removing acetonitrile under reduced pressure evaporation, the resulting product ([$C_4C_{11}OHim$]Br) was dissolved with 30 mL of water, followed by the addition of 0.2 mol of KPF_6; After stirring for 1 h, two phases formed where the bottom phase was [$C_4C_{11}OHim$]PF_6; after decanting the top phase, 10 mL of water was added to wash the IL phase; this was repeated several times until Br^- free, as indicated by the $AgNO_3$ test of the water washings. After vacuum drying 24 h at 75 °C, [$C_4C_{11}OHim$]PF_6 was obtained as a light yellow liquid (91% yield).

17. [$C_4C_{11}OHim$]BF_4

As for the preparation of [$C_4C_{11}OHim$]PF_6 except $NaBF_4$ was employed to afford [$C_4C_{11}OHim$]BF_4 as a light yellow liquid (89% yield).

18. [$C_4C_{11}OHim$]NTf_2

As for the preparation of [$C_4C_{11}OHim$]PF_6 except $LiNTf_2$ was employed to afford [$C_4C_{11}OHim$] NTf_2 as a light yellow liquid (92% yield).

19. [C_4Beim]PF_6

Briefly, 0.2 mol of N-benzylimidazole was dissolved with 40 mL of acetonitrile, and then 0.2 mol of 1-bromobutane was added; this mixture was stirred at 70 °C for 12 h. After removing acetonitrile under reduced pressure evaporation, the resulting product ([C_4Beim]Br) was dissolved with 30 mL of water, followed by the addition of 0.2 mol of KPF_6. After stirring for 1 h at 60 °C, two phases formed where the bottom phase was [C_4Beim]PF_6; after decanting the top phase, 10 mL of hot water (60 °C) was added to wash the IL phase; this was repeated several times until Br^- free, as indicated by the $AgNO_3$ test of the water washings. After vacuum drying 24 h at 75 °C, [C_4Beim]PF_6 was obtained as a light yellow solid (melting point: 48 – 50 ^{o}C, 85 % yield).

20. [C_4Beim]BF_4

As for the preparation of [C_4Beim]PF_6 except $NaBF_4$ was employed and the ion exchange of [C_4Beim]Br and $NaBF_4$ and the IL phase washing process were conducted at room temperature; [C_4Beim]BF_4 was a light yellow liquid (62% yield).

21. [C_4Beim]NTf_2

As for the preparation of [C_4Beim]BF_4 except $LiNTf_2$ was employed to afford [C_4Beim]NTf_2 as a light yellow liquid (87% yield).

II. Characterization of the Synthesized ILs.

All the synthesized ILs were characterized with NMR spectra (Bruker, AV-400, Karlsruhe, Germany) and elemental analysis (FLASH 2000 analyzer, Thermo Fisher Scientific, Belmont, MA, USA), the identification of signals of solvent residue and trace water in solvent was referred to the Fulmer's work (Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg. K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176.).

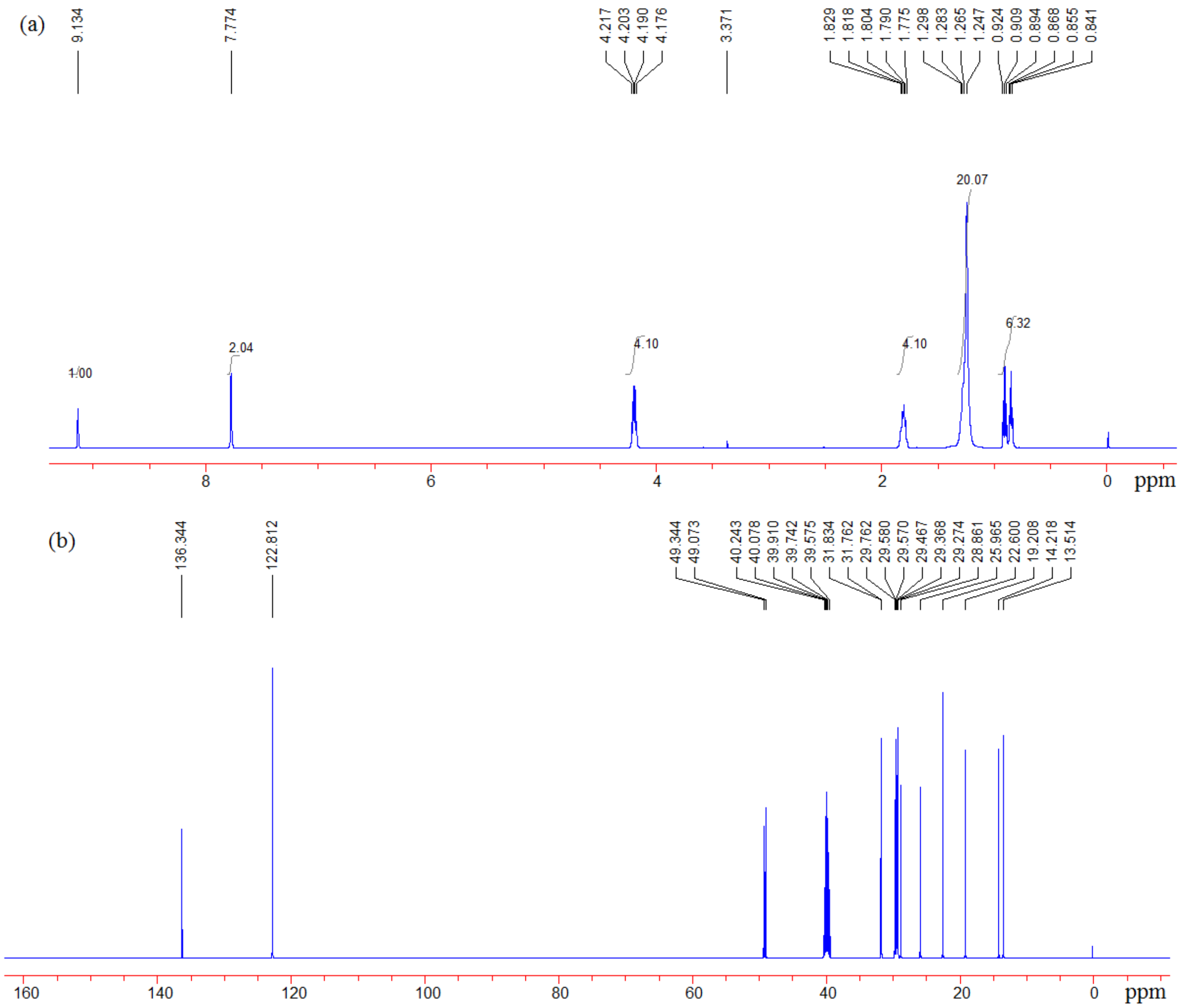


Fig. S1 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{12}im]PF_6$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.841-0.924 (6H, m), 1.247-1.298 (20H, m), 1.775-1.829 (4H, m), 3.371(signal of trace water in solvent), 4.176-4.217 (4H, m), 7.774 (2H, s), 9.134 (1H, s);

^{13}CNMR: 13.514, 14.218, 19.208, 22.600, 25.965, 28.861, 29.274, 29.368, 29.467, 29.570, 29.580, 29.762, 31.762, 31.834, 49.073, 49.344, 122.812, 136.344.

Elemental analysis (%, calc.): C 52.2 (52.1), H 8.4 (8.5), N 6.4 (6.4).

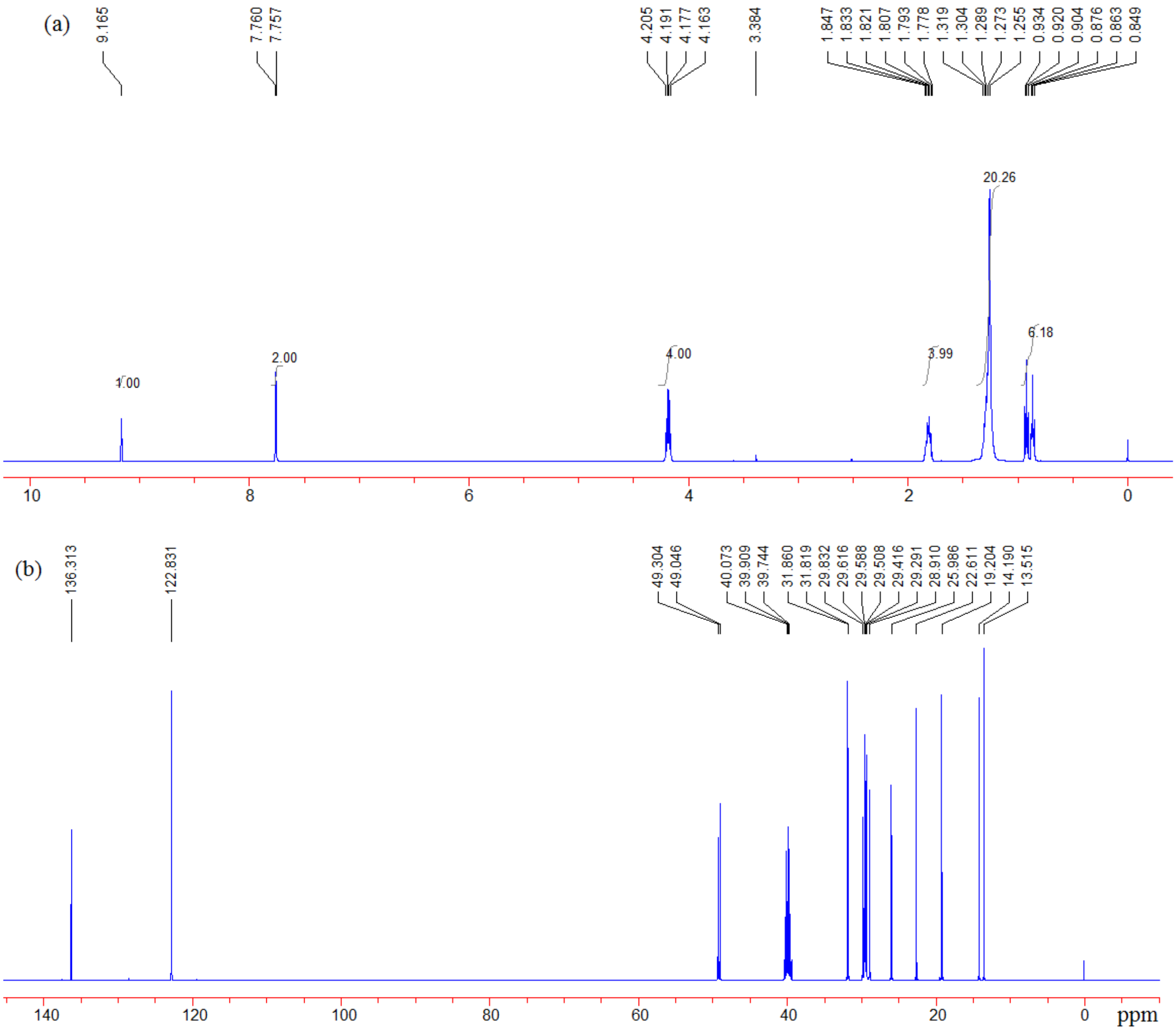


Fig. S2 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{12}im]BF_4$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.849-0.934 (6H, m), 1.255-1.319 (20H, m), 1.778-1.847 (4H, m), 3.384 (signal of trace water in solvent), 4.163-4.205 (4H, m), 7.757-7.760 (2H, d), 9.165 (1H, s);

^{13}CNMR: 13.515, 14.190, 19.204, 22.611, 25.986, 28.910, 29.291, 29.416, 29.508, 29.588, 29.616, 29.832, 31.819, 31.860, 49.046, 49.304, 122.831, 136.313.

Elemental analysis (%, calc.): C 60.2 (60.0), H 9.8 (9.8), N 7.3 (7.4).

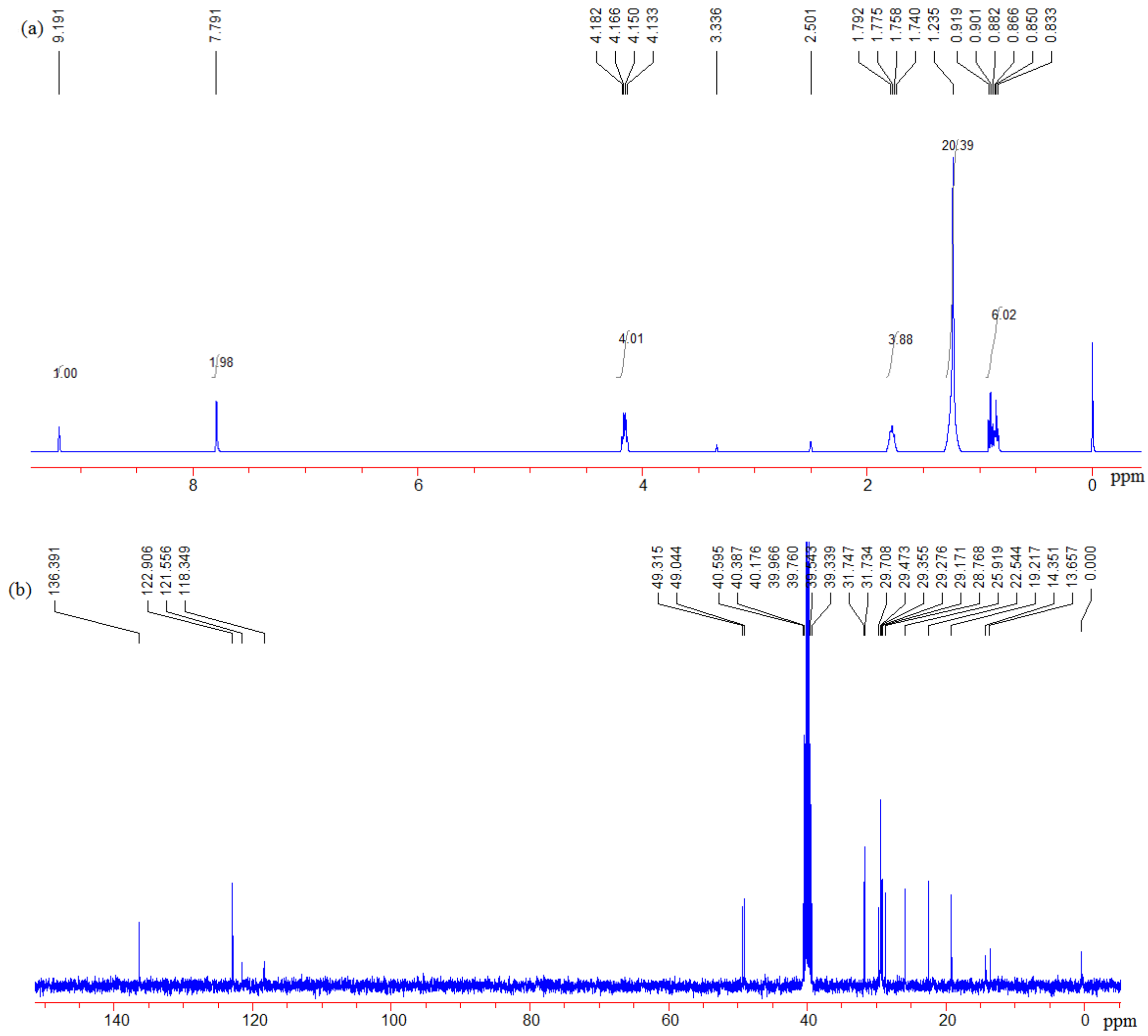


Fig. S3 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{12}im]NTf_2$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.833-0.919 (6H, m), 1.235 (20H, s), 1.740-1.792 (4H, m), 2.501 (solvent residual signal), 3.336 (signal of trace water in solvent), 4.133-4.182 (4H, m), 7.791 (2H, s), 9.191 (1H, s);

^{13}CNMR: 13.657, 14.351, 19.217, 22.544, 25.919, 28.768, 29.171, 29.276, 29.355, 29.473, 29.708, 31.734, 31.747, 49.044, 49.315, 118.349, 121.556, 122.906, 136.391.

Elemental analysis (%, calc.): C 44.5 (44.0), H 6.4 (6.5), N 7.2 (7.3), S 11.4 (11.2).

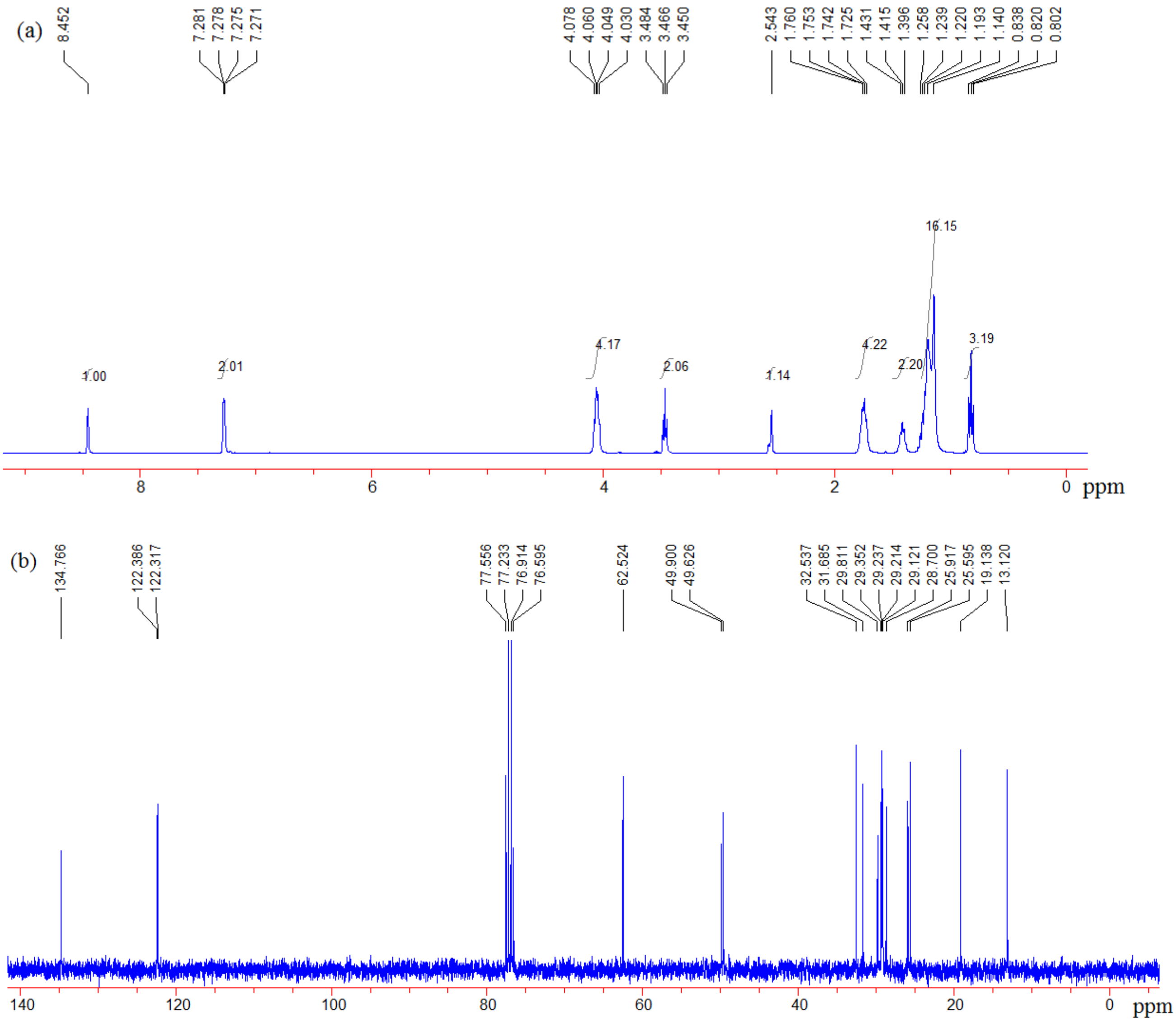


Fig. S4 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{11}OHim]BF_4$; solvent: $CDCl_3$.

^{1}HNMR: 0.802-0.838 (3H, t), 1.140-1.258 (16H, m), 1.396-1.431 (2H, t), 1.725-1.760 (4H, m), 2.543 (1H, s), 3.450-3.484 (2H, t), 4.030-4.078 (4H, m), 7.271-7.281 (2H, m), 8.452 (1H, s);

^{13}CNMR: 13.120, 19.138, 25.595, 25.917, 28.700, 29.121, 29.214, 29.237, 29.352, 29.811, 31.685, 32.537, 49.626, 49.900, 62.524, 122.317, 122.386, 134.766.

Elemental analysis (%, calc.): C 56.0 (56.6), H 9.3 (9.2), N 7.4 (7.3).

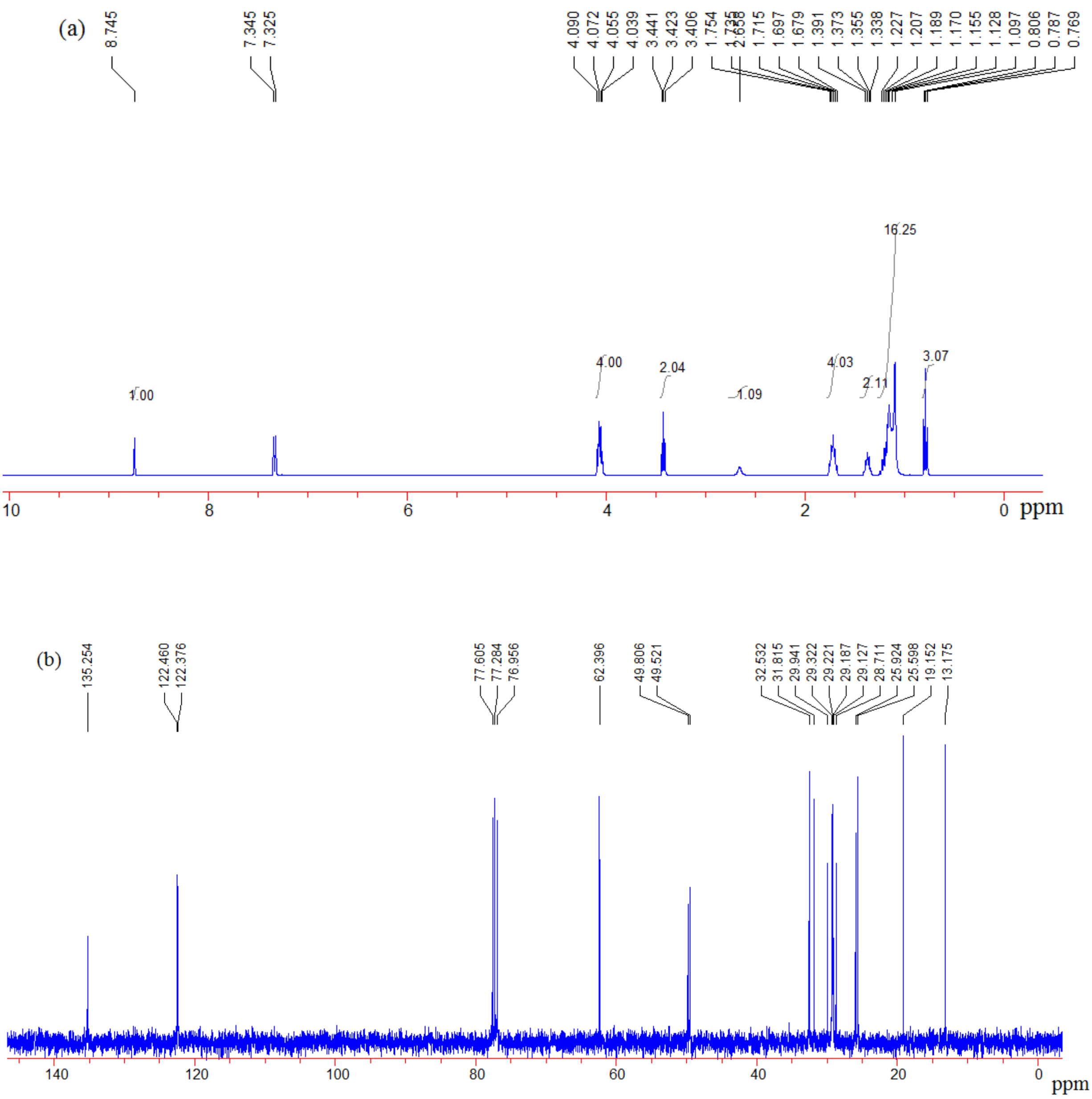
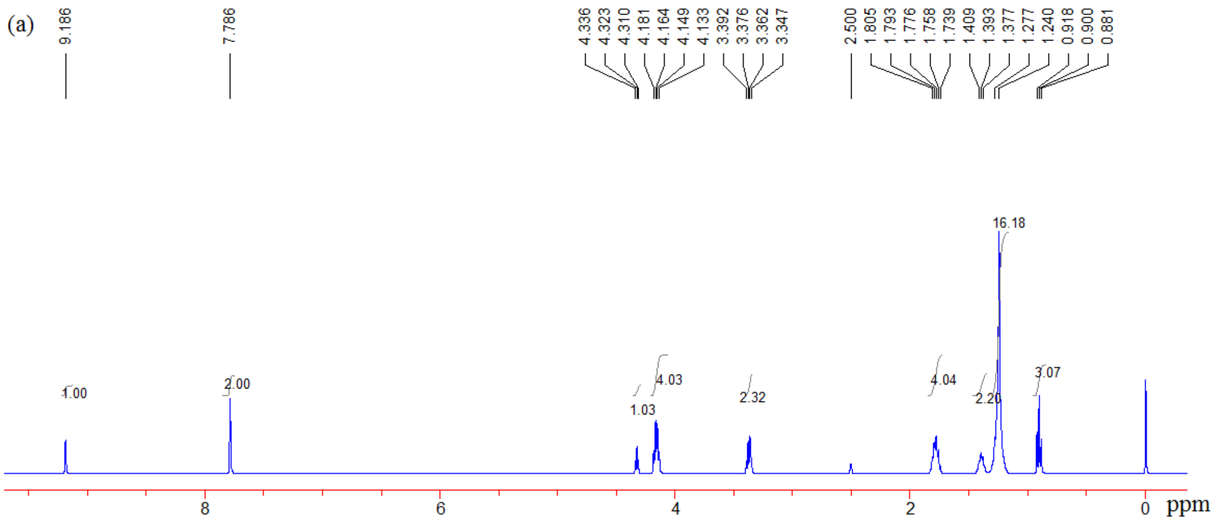


Fig. S5 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{11}OHim]PF_6$; solvent: $CDCl_3$.

^{1}HNMR: 0.769-0.806 (3H, t), 1.097-1.227 (16H, m), 1.338-1.391 (2H, m), 1.679-1.754 (4H, m), 2.658 (1H, s), 3.406-3.441 (2H, t), 4.039-4.090 (4H, m), 7.325-7.345 (2H, d), 8.745 (1H, s);

^{13}CNMR: 13.175, 19.152, 25.598, 25.924, 28.711, 29.127, 29.187, 29.221, 29.322, 29.941, 31.815, 32.532, 49.521, 49.806, 62.396, 122.376, 122.460, 135.254.

Elemental analysis (%, calc.): C 49.2 (49.1), H 8.1 (8.0), N 6.5 (6.4).



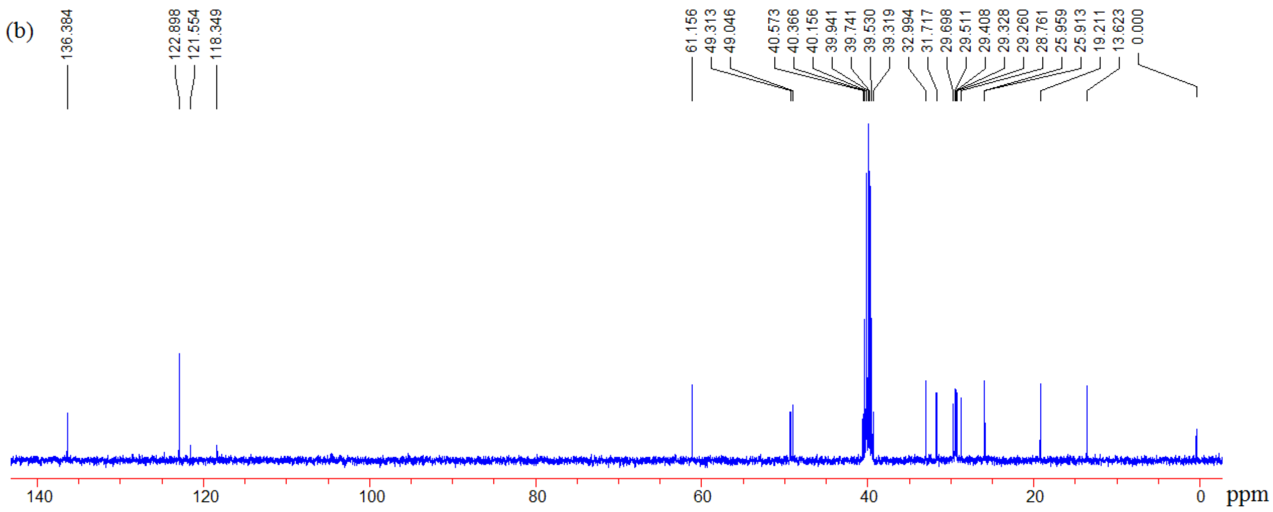


Fig. S6 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_{11}OHim]NTf_2$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.881-0.918 (3H, t), 1.240-1.277 (16H, d), 1.377-1.409 (2H, t), 1.739-1.805 (4H, m), 2.500 (solvent residual signal), 3.347-3.392 (2H, m), 4.133-4.181 (4H, m), 4.310-4.336 (1H, t), 7.786 (2H, s), 9.186 (1H, s);

^{13}CNMR: 13.623, 19.211, 25.913, 25.959, 28.761, 29.260, 29.328, 29.408, 29.511, 29.698, 31.717, 32.994, 49.046, 49.313, 61.156, 118.349, 121.554, 122.898, 136.384.

Elemental analysis (%, calc.): 42.1 (41.7), H 6.2 (6.1), N 7.2 (7.3), S 10.9 (11.1).

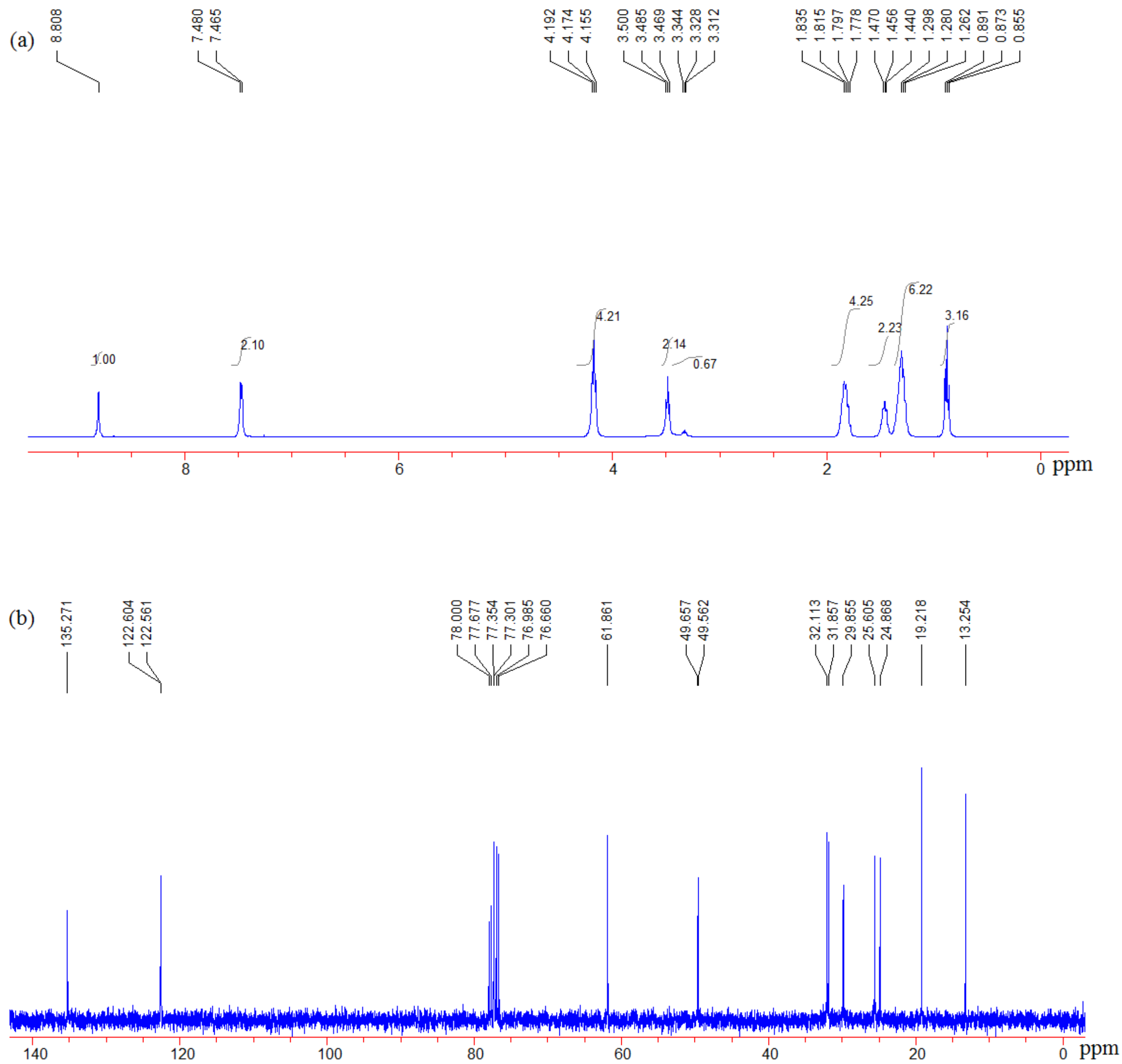


Fig. S7 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of [C_4C_6OHim]BF_4; solvent: $CDCl_3$.

^{1}HNMR: 0.855-0.891 (3H, t), 1.262-1.298 (6H, t), 1.440-1.470 (2H, t), 1.778-1.835 (4H, m), 3.312-3.344 (1H, t), 3.469-3.500 (2H, t), 4.155-4.192 (4H, t), 7.465-7.480 (2H, d), 8.808 (1H, s);

^{13}CNMR: 13.254, 19.218, 24.868, 25.605, 29.855, 31.857, 32.113, 49.562, 49.657, 61.861, 122.561, 122.604, 135.271.

Elemental analysis (%, calc.): C 50.1 (50.0), H 8.2 (8.1), N 9.1 (9.0).

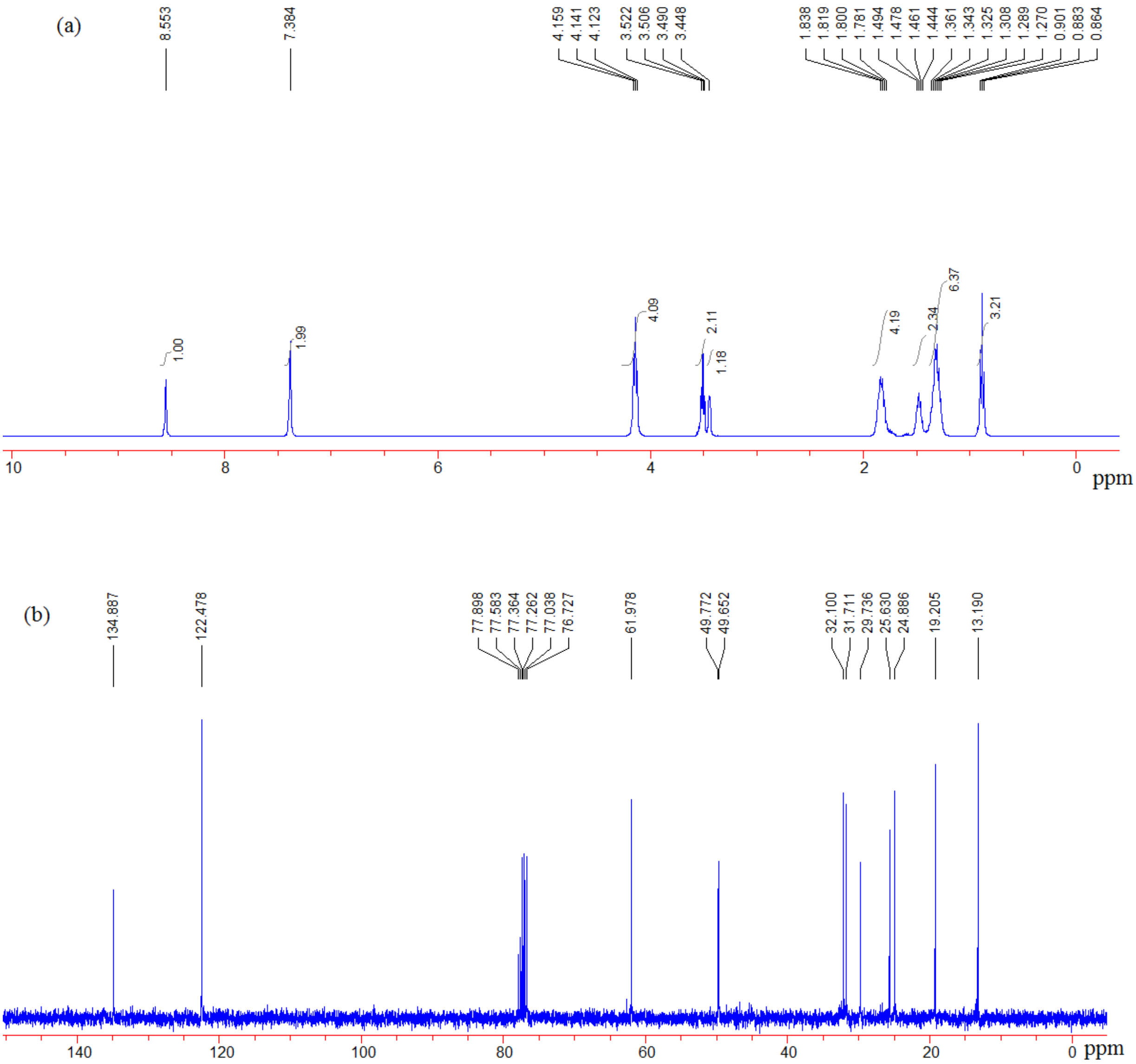


Fig. S8 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_6OHim]PF_6$; solvent: $CDCl_3$.

^{1}HNMR: 0.864-0.901 (3H, t), 1.270-1.361 (6H, m), 1.444-1.494 (2H, m), 1.781-1.838 (4H, m), 3.448 (1H, s), 3.490-3.522 (2H, t), 4.123-4.159 (4H, t), 7.384 (2H, s), 8.553 (1H, s);

^{13}CNMR: 13.190, 19.205, 24.886, 25.630, 29.736, 31.711, 32.100, 49.652, 49.772, 61.978, 122.478, 134.887.

Elemental analysis (%, calc.): C 42.6 (42.2), H 6.7 (6.8), N 7.6 (7.6).

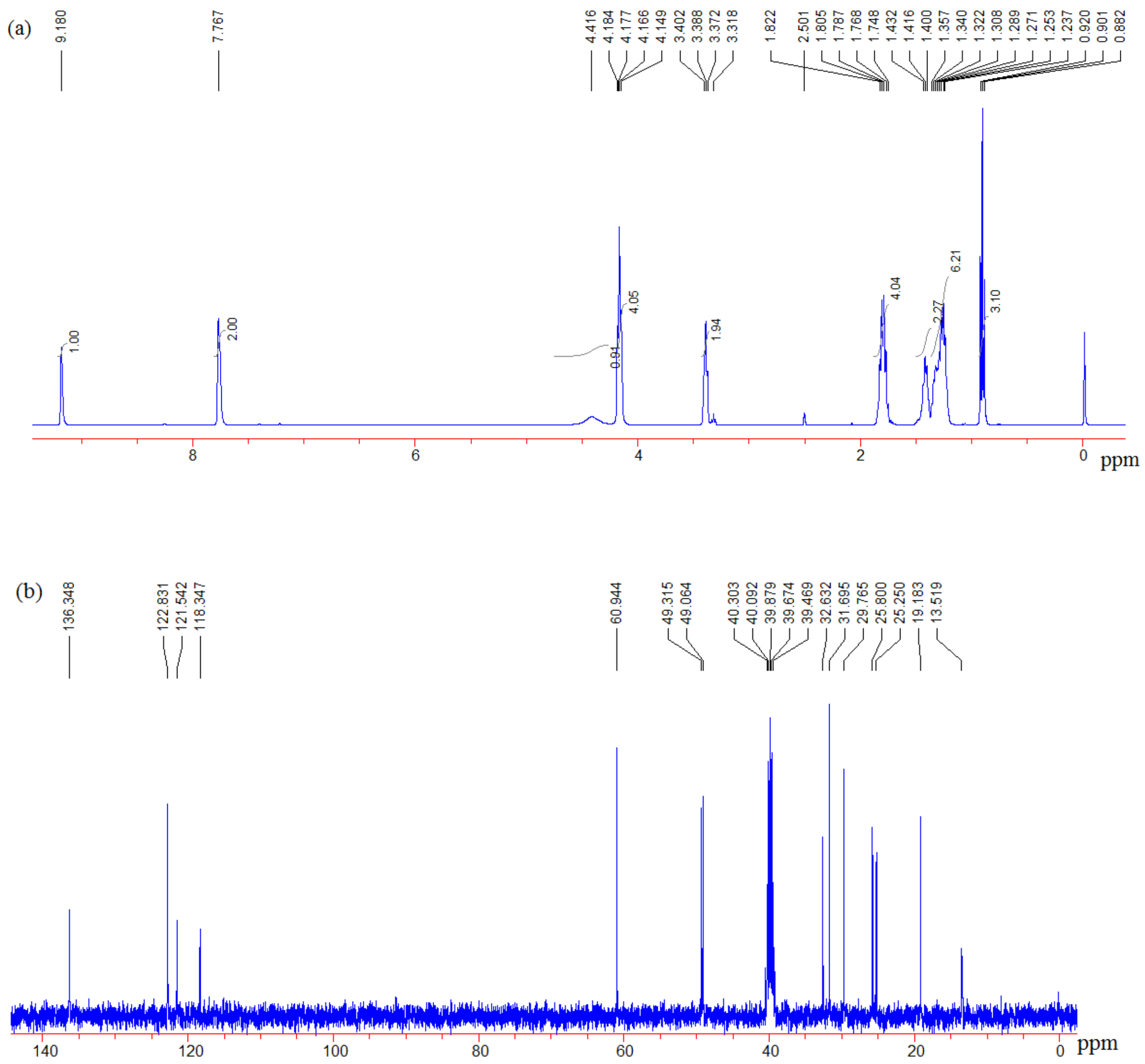


Fig. S9 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_6OHim]NTf_2$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.882-0.920 (3H, t), 1.237-1.357 (6H, m), 1.400-1.432 (2H, t), 1.748-1.822 (4H, m), 2.501 (solvent residual signal), 3.318 (signal of trace water in solvent), 3.372-3.402 (2H, t), 4.149-4.184 (4H, m), 4.416 (1H, s), 7.767 (2H, s), 9.180 (1H, s);

^{13}CNMR: 13.519, 19.183, 25.250, 25.800, 29.765, 31.695, 32.632, 49.064, 49.315, 60.944, 118.347, 121.542, 122.831, 136.348.

Elemental analysis (%, calc.): C 35.8 (35.7), H 4.9 (5.0), N 8.4 (8.3), S 12.4 (12.7).

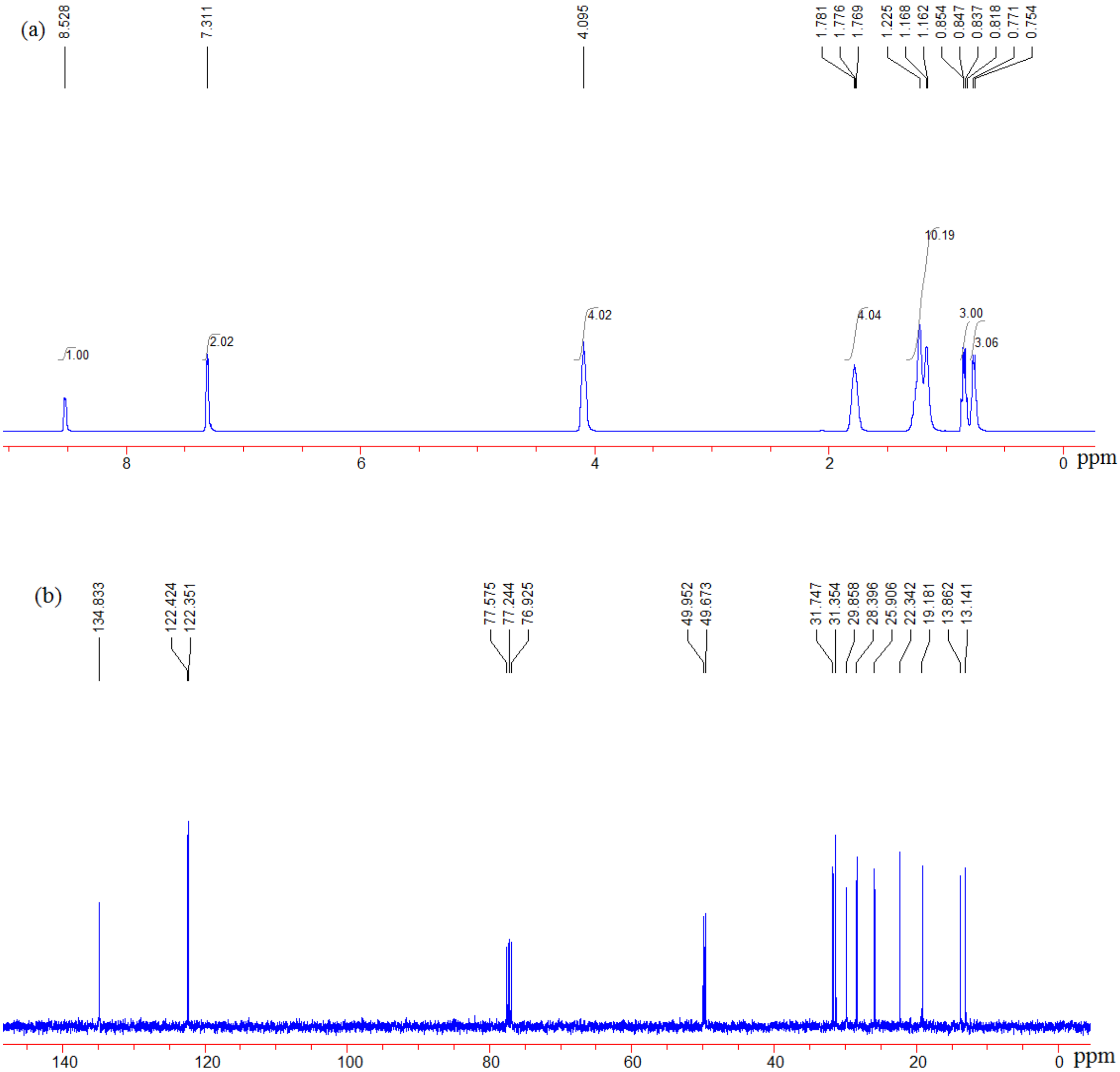


Fig. S10 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_7im]PF_6$; solvent: $CDCl_3$.

^{1}HNMR: 0.754-0.771 (3H, d), 0.818-0.854 (3H, m), 1.162-1.225 (10H, t), 1.769-1.781 (4H, t), 4.095 (4H, s), 7.311 (2H, s), 8.528 (1H, s);

^{13}CNMR: 13.141, 13.862, 19.181, 22.342, 25.906, 28.396, 29.858, 31.354, 31.747, 49.673, 49.952, 122.351, 122.424, 134.833.

Elemntal analysis (%, calc.): C 45.5 (45.7), H 7.4 (7.4), N 7.8 (7.6).

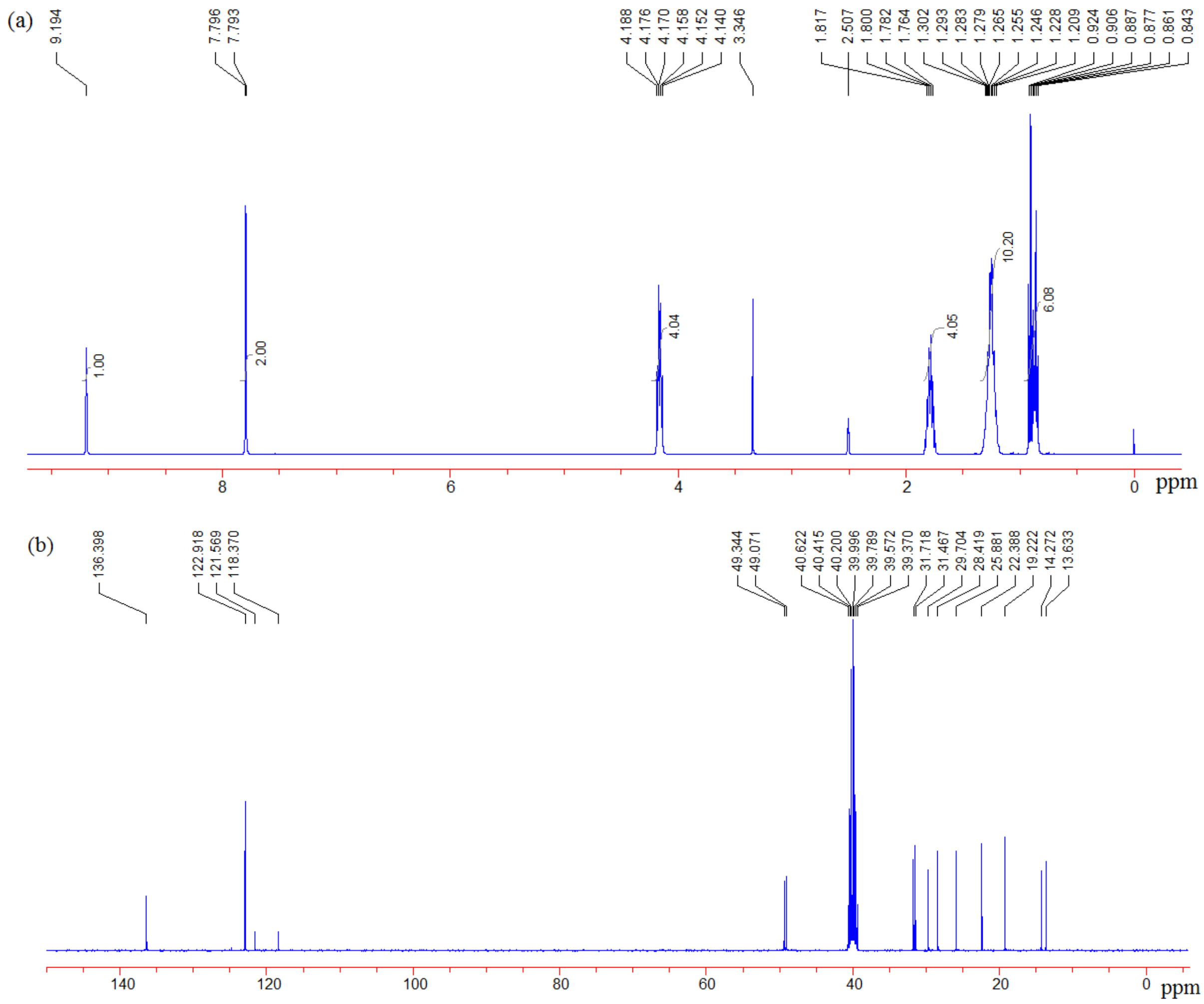


Fig. S11 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_7im]NTf_2$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.843-0.924 (6H, m), 1.209-1.302 (10H, m), 1.764-1.817 (4H, m), 2.507 (solvent residual signal), 3.346 (signal of trace water in solvent), 4.140-4.188 (4H, m), 7.793-7.796 (2H, d), 9.194 (1H, s);

^{13}CNMR: 13.633, 14.272, 19.222, 22.388, 25.881, 28.419, 29.704, 31.467, 31.718, 49.071, 49.344, 118.370, 121.569, 122.918, 136.398.

Elemental analysis: C 38.4 (38.2), H 5.5 (5.4), N 8.5 (8.3), S 12.5 (12.7).

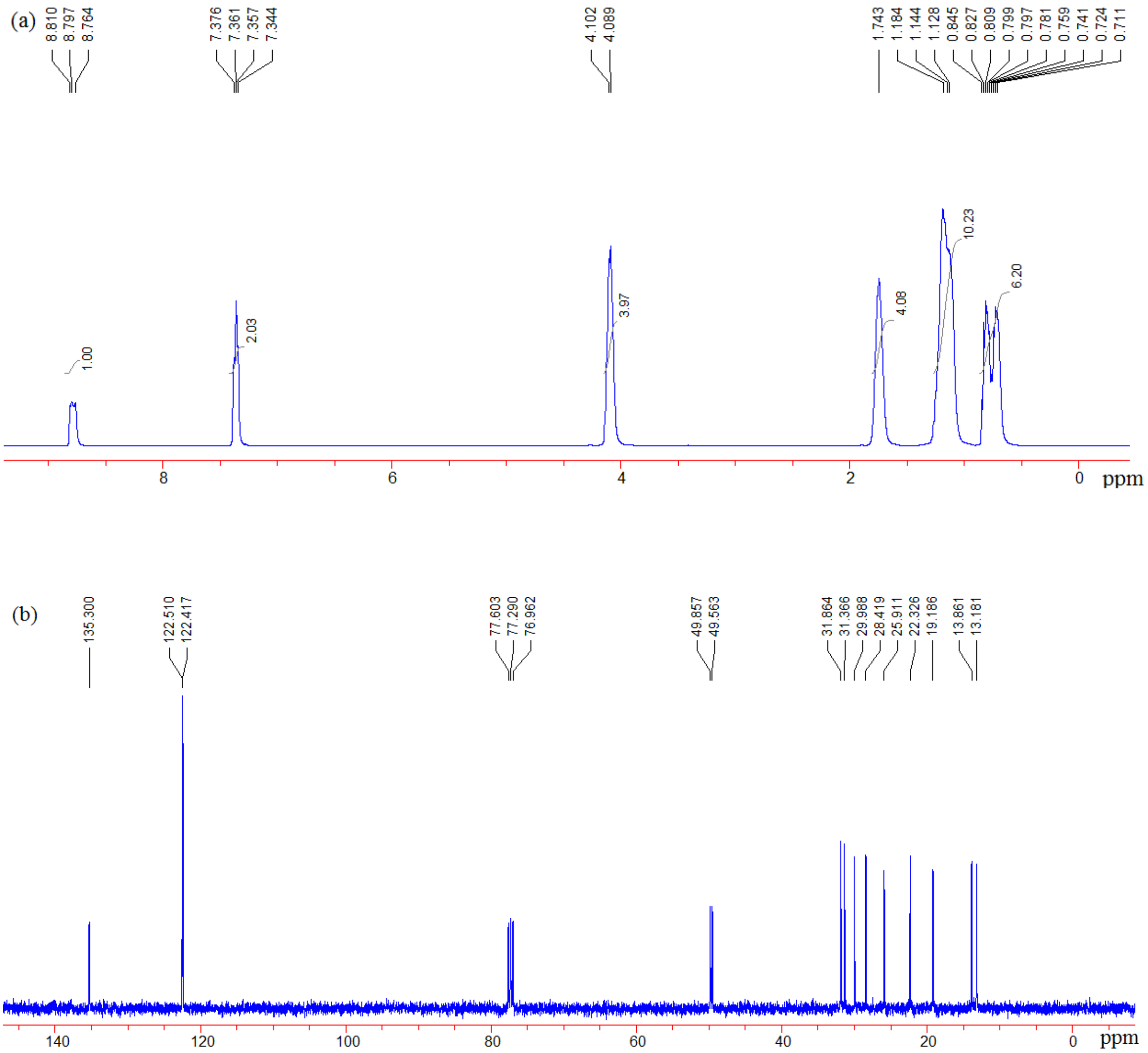


Fig. S12 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_7im]BF_4$; solvent: $CDCl_3$.

^{1}HNMR: 0.711-0.845 (6H, m), 1.128-1.184 (10H, t), 1.743 (4H, s), 4.089-4.102 (4H, d), 7.344-7.376 (2H, m), 8.764-8.810 (1H, m);

^{13}CNMR: 13.181, 13.861, 19.186, 22.326, 25.911, 28.419, 29.988, 31.366, 31.864, 49.563, 49.857, 122.417, 122.510, 135.300.

Elemenal analysis (%, calc.): C 54.1 (54.2), H 8.6 (8.8), N 9.1 (9.0).

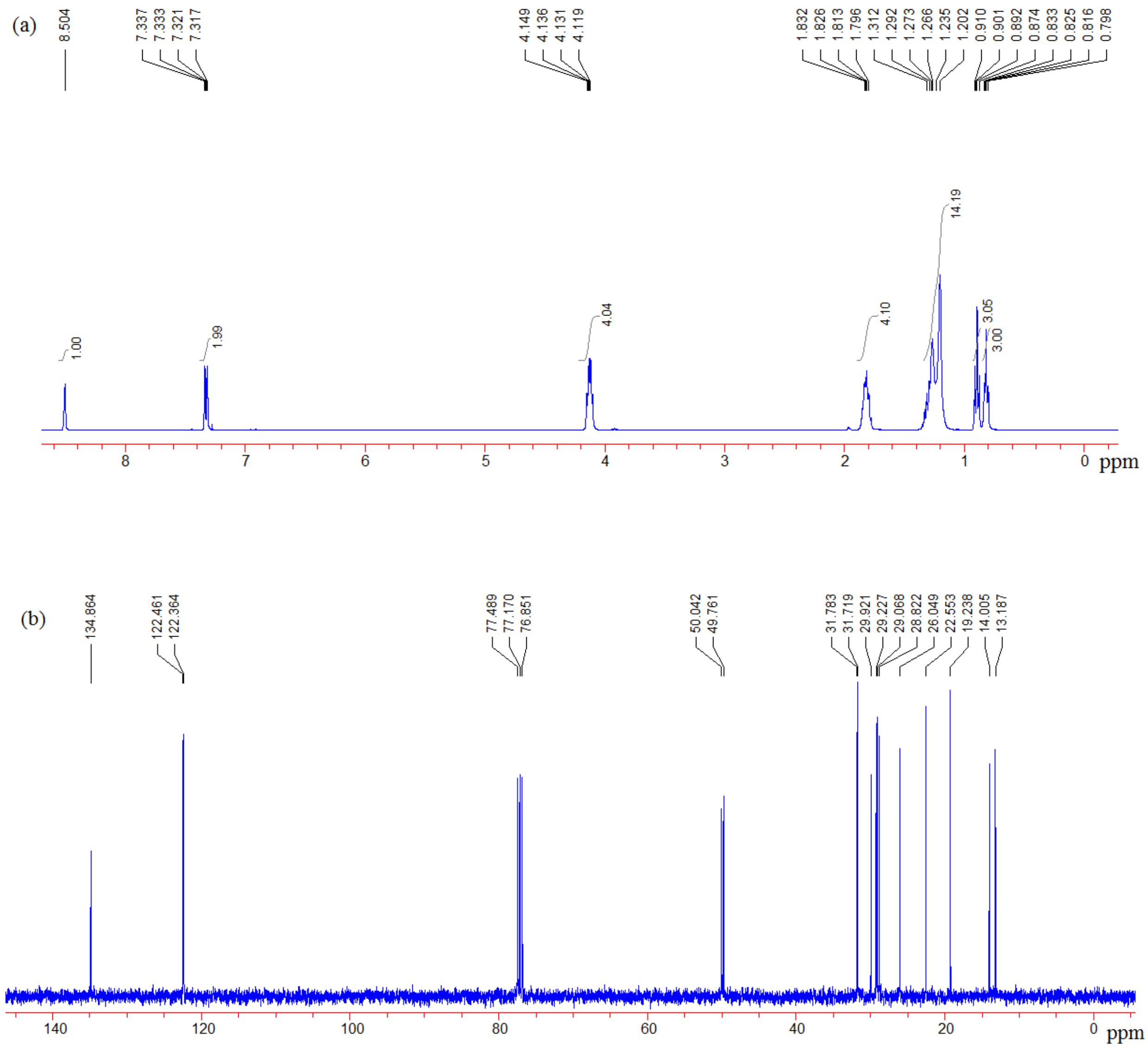
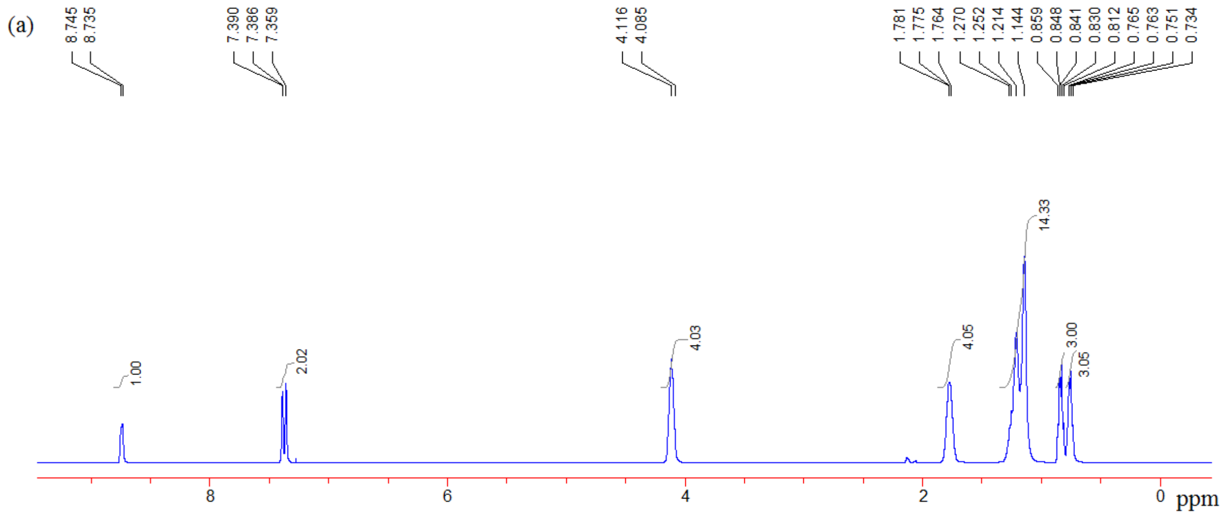


Fig. S13 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_9im]PF_6$; solvent: $CDCl_3$.

^{1}HNMR: 0.798-0.833 (3H, m), 0.874-0.910 (3H, m), 1.202-1.312 (14H, m), 1.796-1.832 (4H, m), 4.119-4.149 (4H, m), 7.317-7.337 (2H, m), 8.504 (1H, s);

^{13}CNMR: 13.187, 14.005, 19.238, 22.553, 26.049, 28.822, 29.068, 29.227, 29.921, 31.719, 31.783, 49.761, 50.042, 122.364, 122.461, 134.864.

Elemental analysis (%, calc.): C 49.0 (48.5), H 7.9 (7.9), N 7.2 (7.1).



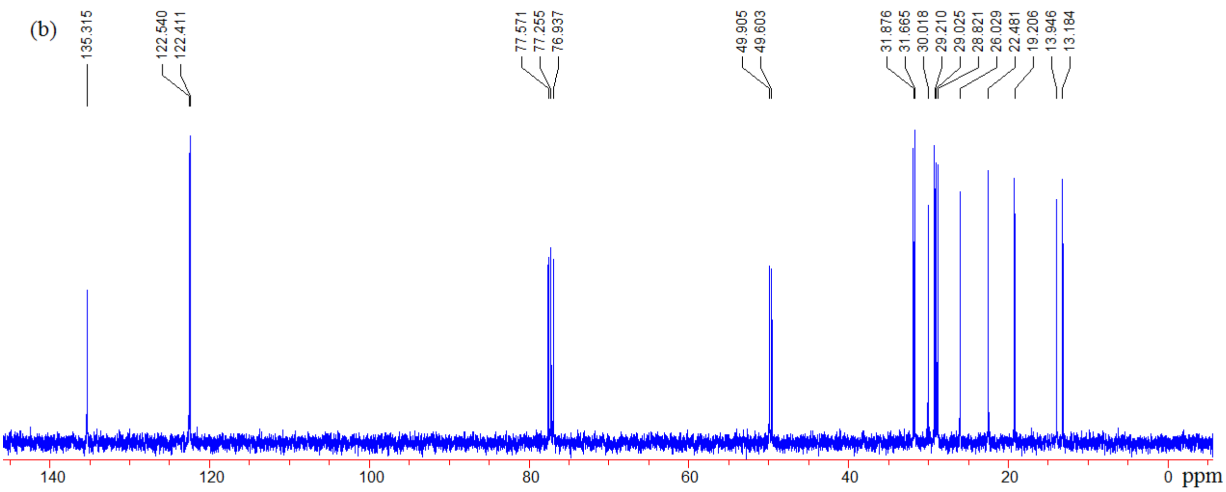


Fig. S14 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_9im]BF_4$; solvent: $CDCl_3$.

^{1}HNMR: 0.734-0.765 (3H, m), 0.812-0.859 (3H, m), 1.144-1.270 (14H, m), 1.764-1.781 (4H, t), 4.085-4.116 (4H, d), 7.359-7.390 (2H, t), 8.735-8.745 (1H, d);

^{13}CNMR: 13.184, 13.946, 19.206, 22.481, 26.029, 28.821, 29.025, 29.210, 30.018, 31.665, 31.876, 49.603, 49.905, 122.411, 122.540, 135.315.

Elemental analysis (%, calc.): C 56.8 (56.8), H 9.3 (9.2), N 8.4 (8.3).

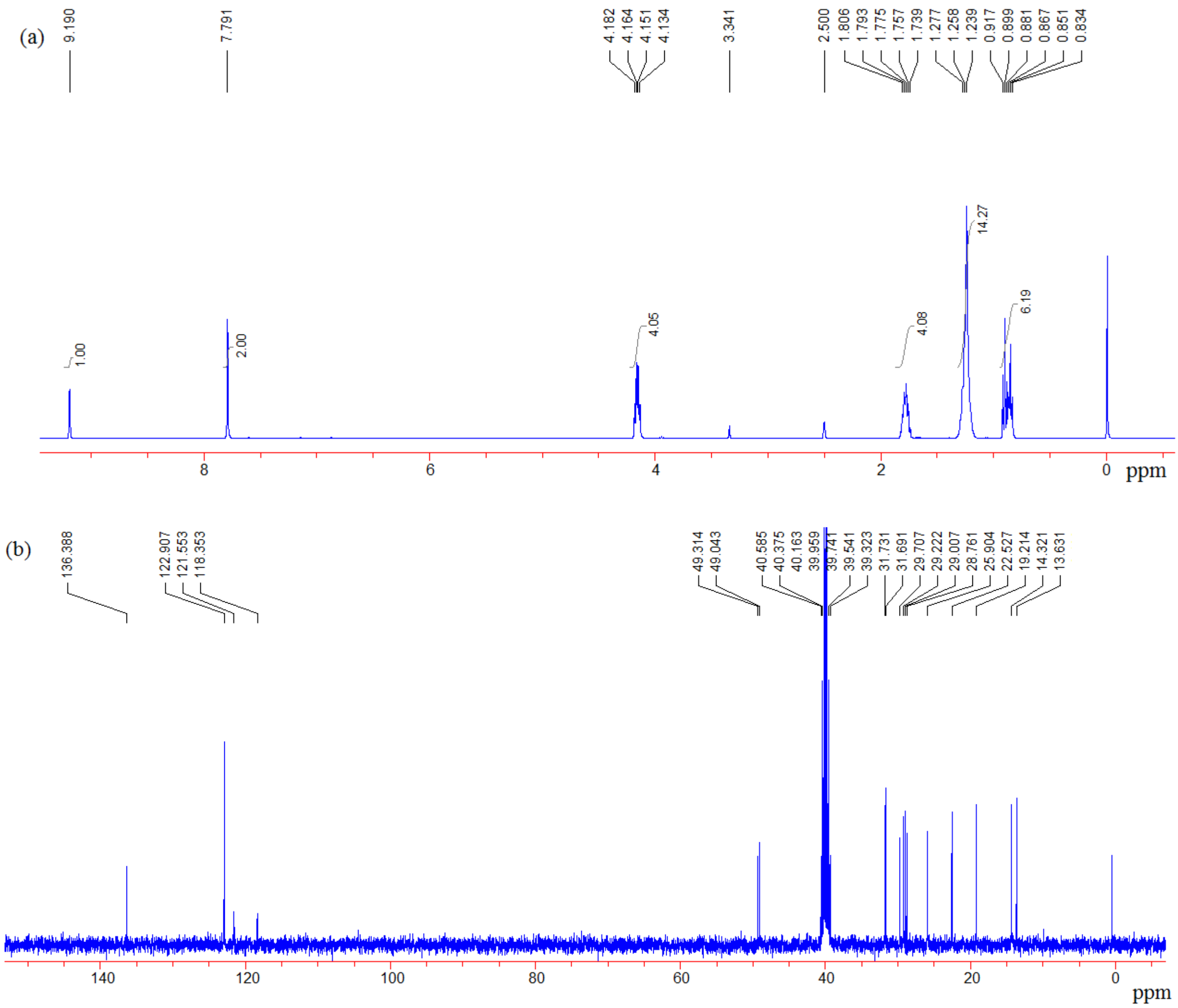


Fig. S15 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_9im]NTf_2$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.834-0.917 (6H, m), 1.239-1.277 (14H, t), 1.739-1.806 (4H, m), 2.500 (solvent residual signal), 3.341 (singal of trace water in solvent), 4.134-4.182 (4H, m), 7.791 (2H, d), 9.190 (1H, s);

^{13}CNMR: 13.631, 14.321, 19.214, 22.527, 25.904, 28.761, 29.007, 29.222, 29.707, 31.691, 31.731, 49.043, 49.314, 118.353, 121.553, 122.907, 136.388.

Elemental analysis (%, calc.): C 40.6 (40.7), H 5.9 (5.9), N 7.8 (7.9), S 11.8 (12.1).

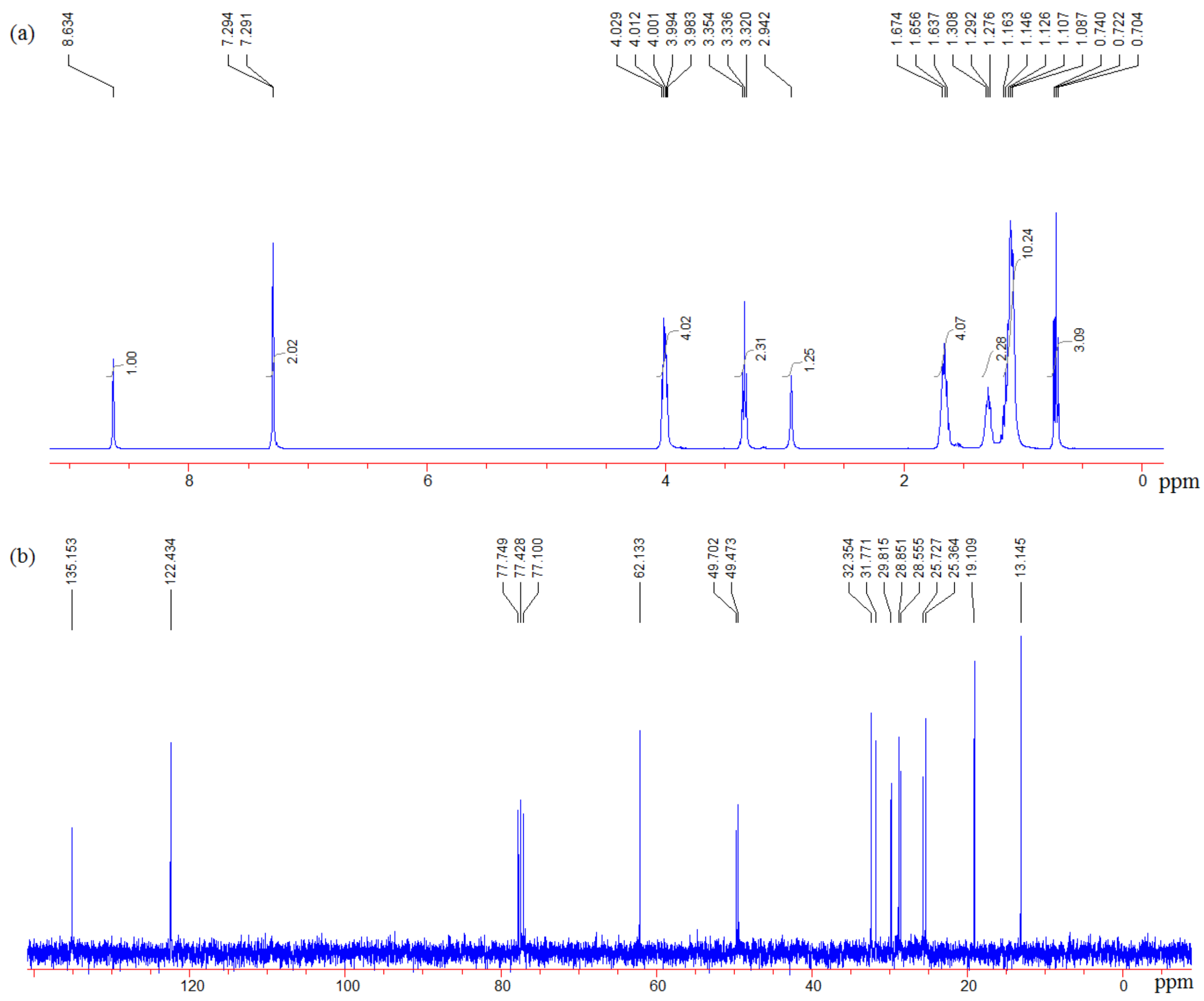


Fig. S16 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4C_8OHim]BF_4$; solvent: $CDCl_3$.

^{1}HNMR: 0.704-0.740 (3H, t), 1.087-1.146 (10H, m), 1.276-1.308 (2H, t), 1.637-1.674 (4H, t), 2.942 (1H, s), 3.320-3.354 (2H, t), 3.983-4.029 (4H, m), 7.292-7.294 (2H, d), 8.634 (1H, s);

^{13}CNMR: 13.145, 19.109, 25.364, 25.727, 28.555, 28.851, 29.815, 31.771, 32.354, 49.473, 49.702, 62.133, 122.434, 135.153.

Elemental analysis (%, calc.): C 53.1 (53.0), H 8.7 (8.6), N 8.1 (8.2).

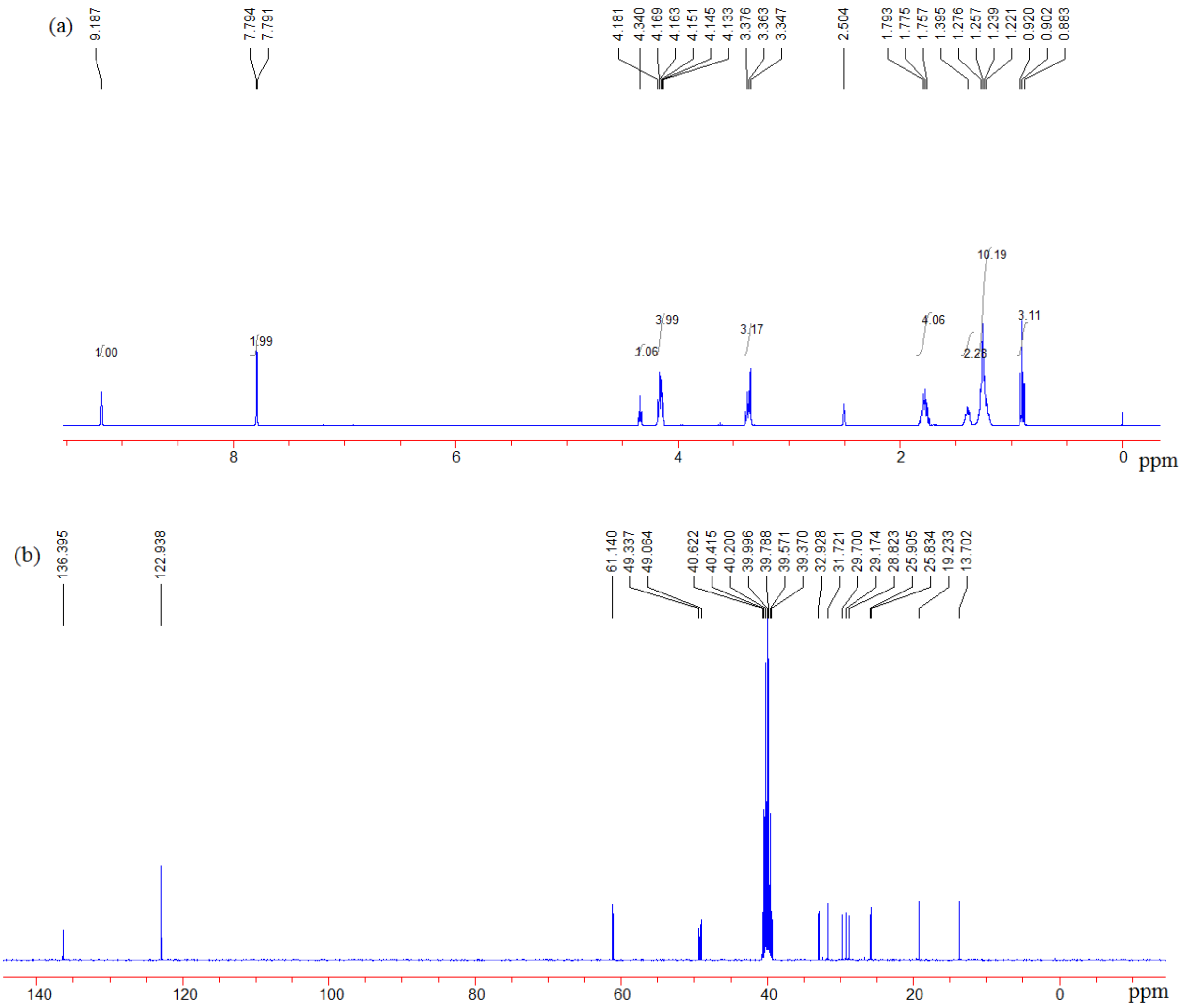


Fig. S17 ¹HNMR (a) and ¹³CNMR (b) spectra of $[C_4C_8OHim]PF_6$; solvent: $(CD_3)_2SO$.

¹HNMR: 0.883-0.920 (3H, t), 1.221-1.276 (10H, m), 1.395 (2H, s), 1.757-1.793 (4H, t), 2.504 (solvent residual signal), 3.347-3.376 (2H, t, containing the signal of trace water in solvent), 4.133-4.181 (4H, m), 4.340 (1H, s), 7.791-7.794 (2H, d), 9.187 (1H, s);

¹³CNMR: 13.702, 19.233, 25.834, 25.905, 28.823, 29.174, 29.700, 31.721, 32.928, 49.064, 49.337, 61.140, 122.938, 136.395.

Elemental analysis (%, calc.): C 45.4 (45.2), H 7.4 (7.3), N 6.9 (7.0).

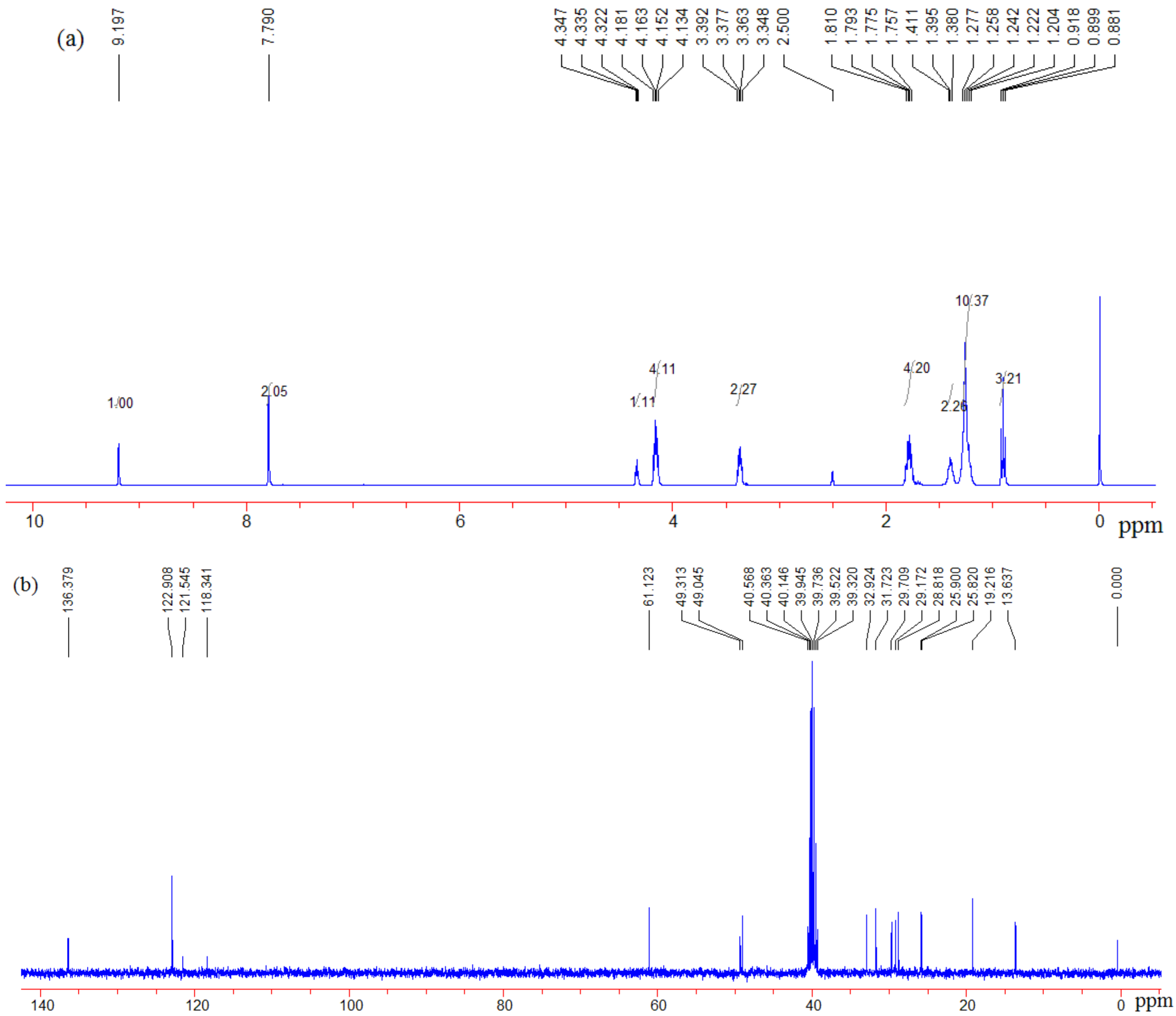


Fig. S18 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of [C_4C_8OHim]NTf_2; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.881-0.918 (3H, t), 1.204-1.277 (10H, m), 1.380-1.411 (2H, t), 1.757-1.810 (4H, m), 2.500 (solvent residual signal), 3.348-3.392 (2H, m), 4.134-4.181 (4H, m), 4.322-4.347 (1H, t), 7.790 (2H, s), 9.197 (1H, s);

^{13}CNMR: 13.637, 19.216, 25.820, 25.900, 28.818, 29.172, 29.709, 31.723, 32.924, 49.045, 49.313, 61.123, 118.341, 121.545, 122.908, 136.379.

Elemental analysis (%, calc.): C 38.7 (38.3), H 5.4 (5.5), N 7.7 (7.9), S 11.8 (12.0).

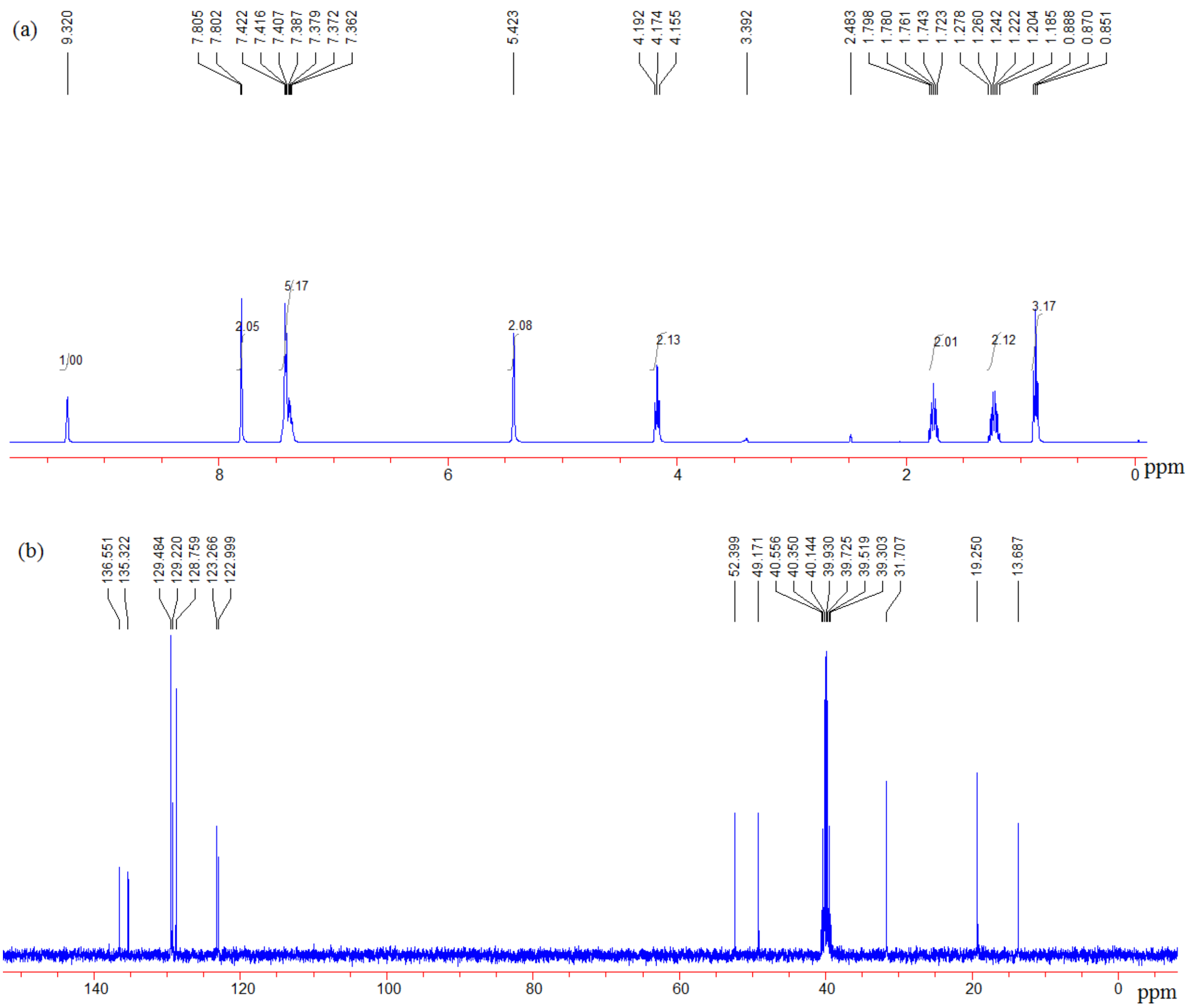


Fig. S19 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of [C_4Beim]BF_4; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.851-0.888 (3H, t), 1.185-1.278 (2H, m), 1.723-1.798 (2H, m), 2.483 (solvent residual signal), 3.392 (signal of trace water in solvent), 4.155-4.192 (2H, t), 5.423 (2H, s), 7.362-7.422 (5H, m), 7.802-7.805 (2H, d), 9.320 (1H, s);

^{13}CNMR: 13.687, 19.250, 31.707, 49.171, 52.399, 122.999, 123.266, 128.759, 129.220, 129.484, 135.322, 136.551.

Elemental analysis (%, calc.): C 55.6 (55.7), H 6.4 (6.3), N 9.2 (9.3).

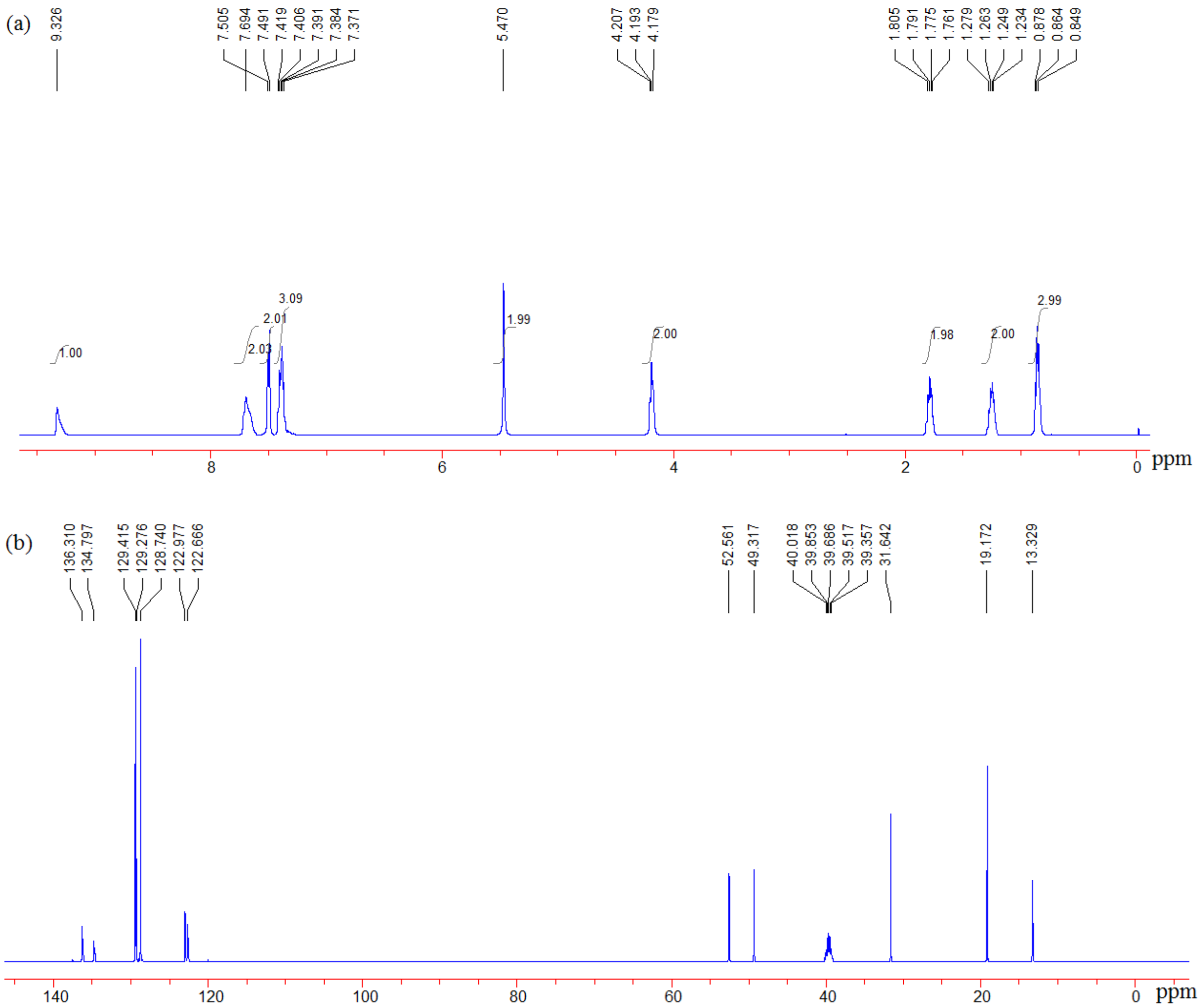


Fig. S20 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4Beim]PF_6$; solvent: $(CD_3)_2SO$.

^{1}HNMR: 0.849-0.878 (3H, t), 1.234-1.279 (2H, m), 1.761-1.805 (2H, m), 4.179-4.207 (2H, t), 5.470 (2H, s), 7.371-7.419 (3H, m), 7.491-7.505 (2H, d), 7.694 (1H, s), 9.326 (1H, s);

^{13}CNMR: 13.329, 19.172, 31.642, 49.317, 52.561, 122.666, 122.977, 128.740, 129.276, 129.415, 134.797, 136.310.

Elemental analysis (%, calc.): C 47.0 (46.7), H 5.4 (5.3), N 7.9 (7.8).

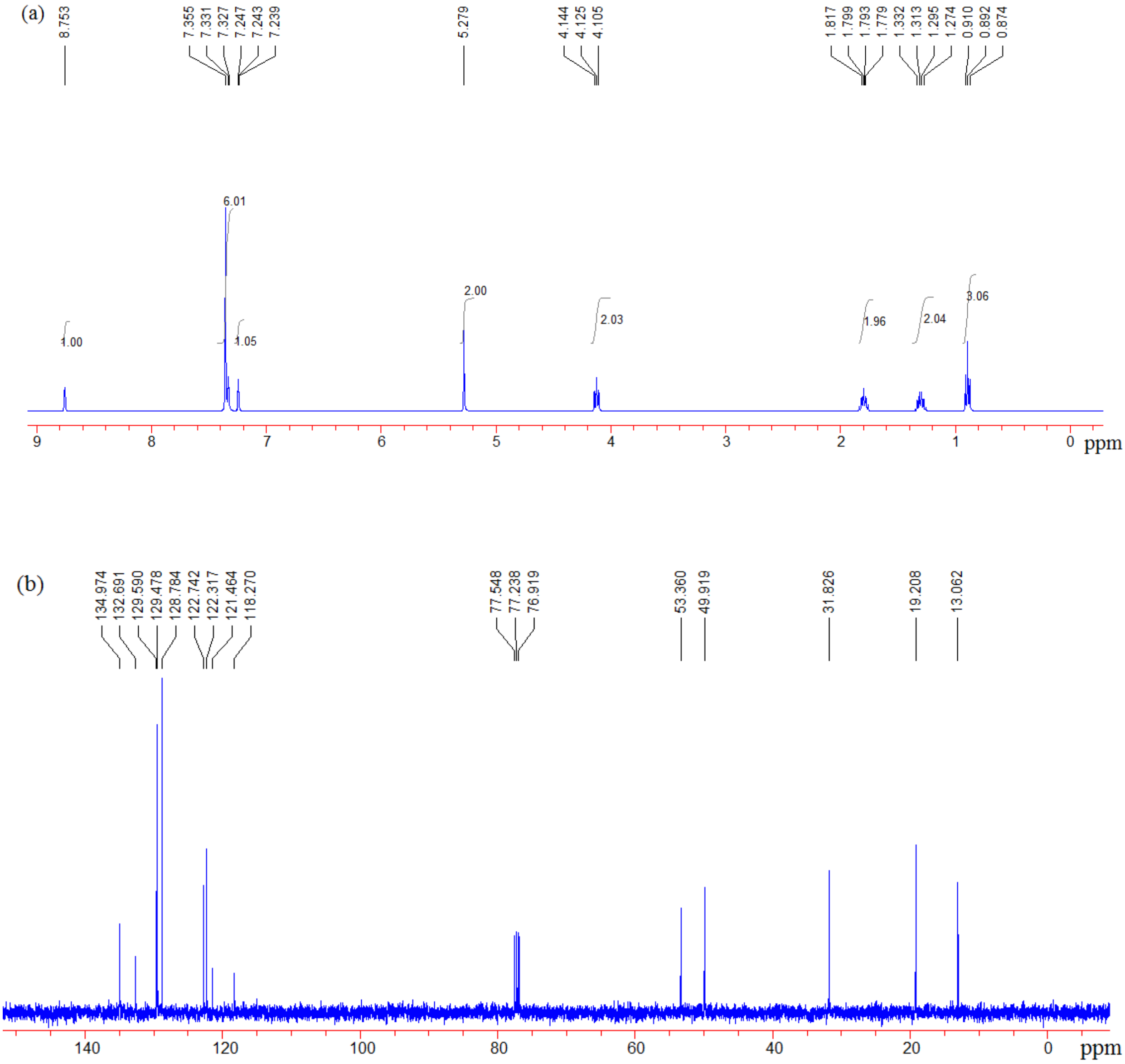


Fig. S21 ^{1}HNMR (a) and ^{13}CNMR (b) spectra of $[C_4Beim]NTf_2$; solvent: $CDCl_3$.

^{1}HNMR: 0.874-0.910 (3H, t), 1.274-1.332 (2H, m), 1.779-1.817 (2H, m), 4.105-4.144 (2H, t), 5.279 (2H, s), 7.239-7.247 (1H, t), 7.327-7.355 (6H, t), 8.753 (1H, s);

^{13}CNMR: 13.062, 19.208, 31.826, 49.919, 53.360, 118.270, 121.464, 122.317, 122.742, 128.784, 129.478, 129.590, 132.691, 134.974.

Elemental analysis (%, calc.): C. 39.0 (38.8), H 3.9 (3.9), N 8.6 (8.5), S 12.7 (12.9).

Table S1. Extraction Efficiencies (*E*, %) of the ILs (average value, *n* = 3).

pH	2.0	3.0	5.0	6.0	7.0	9.0	10	12
				$[C_8mim]PF_6$				
resorcinol	13.4	13.2	13.0	13.5	13.0	13.0	12.9	8.26
phenol	65.0	64.9	66.4	64.7	66.6	65.2	65.1	18.9
guaiacol	74.1	76.0	75.0	75.2	75.9	75.4	74.4	42.2
p-nitrophenol	80.0	82.7	82.3	80.0	78.9	25.6	17.0	10.7
o-cresol	82.9	85.5	83.4	84.8	83.8	83.3	84.5	46.9
				$[C_8mim]BF_4$				
resorcinol	68.8	69.0	69.4	68.8	69.5	70.9	70.7	33.7
phenol	84.0	86.1	84.7	86.0	84.7	84.8	86.0	41.2
guaiacol	87.4	88.1	88.5	87.1	85.5	88.8	87.7	44.9
p-nitrophenol	94.2	95.5	94.3	95.6	92.8	85.2	84.3	84.5
o-cresol	93.1	94.9	93.1	94.4	92.7	95.0	95.1	79.5
				$[C_4C_7im]PF_6$				
resorcinol	13.1	13.1	13.2	12.9	12.9	13.4	13.5	7.86
phenol	65.3	67.2	65.8	65.0	67.1	65.1	66.4	20.7
guaiacol	76.2	76.7	75.5	75.9	78.0	78.6	77.2	41.1
p-nitrophenol	81.4	82.0	81.1	80.9	79.3	53.9	38.1	32.6
o-cresol	84.4	85.8	85.1	84.2	86.1	86.7	85.9	48.7
				$[C_4C_7im]BF_4$				
resorcinol	71.2	72.9	71.6	72.3	69.9	72.2	73.1	32.1
phenol	86.7	89.4	87.1	87.4	87.9	89.3	88.6	45.4
guaiacol	85.3	86.8	86.6	86.4	87.3	88.8	87.9	46.2
p-nitrophenol	95.6	94.9	96.2	96.5	95.7	88.4	86.8	86.2
o-cresol	94.0	95.9	94.7	94.9	95.8	96.0	95.6	82.1
				$[C_4C_6OHim]PF_6$				
resorcinol	57.8	57.0	56.2	57.7	58.9	58.5	57.5	26.9
phenol	81.7	80.4	79.5	80.0	79.3	81.2	81.8	39.2
guaiacol	84.3	86.2	85.1	84.5	84.8	84.8	83.8	43.5
p-nitrophenol	89.9	90.3	89.9	89.8	88.7	59.8	51.4	39.7
o-cresol	89.3	92.0	89.8	88.9	88.7	92.2	92.6	64.2
				$[C_4C_9im]PF_6$				
resorcinol	12.7	12.8	12.8	13.1	13.0	13.3	13.2	5.90
phenol	63.5	63.3	63.7	63.8	63.2	63.6	64.0	20.5
guaiacol	74.0	73.9	75.9	74.4	74.8	75.6	75.2	37.8
p-nitrophenol	81.0	80.1	80.5	81.9	81.9	48.0	39.0	28.2
o-cresol	84.1	83.1	84.1	84.0	84.8	85.8	86.4	47.9
				$[C_4C_9im]BF_4$				
resorcinol	71.6	71.4	71.5	71.8	71.9	72.0	71.1	31.8
phenol	87.6	87.4	87.9	87.9	87.8	89.0	88.2	45.4
guaiacol	86.8	86.4	86.7	86.7	86.5	87.7	86.9	50.9
p-nitrophenol	96.8	96.7	96.7	96.7	96.4	86.8	87.7	86.8
o-cresol	95.4	93.2	95.7	95.0	95.5	96.0	95.9	84.7

Table S1. Continued.

pH	2.0	3.0	5.0	6.0	7.0	9.0	10	12
				$[C_4C_8OHim]PF_6$				
resorcinol	57.2	57.8	58.8	56.6	57.9	56.7	56.1	28.3
phenol	79.5	80.5	79.8	80.4	81.0	83.3	82.7	41.2
guaiacol	83.9	83.9	84.0	84.3	85.3	86.8	85.8	40.3
p-nitrophenol	93.4	93.3	93.2	93.1	91.8	57.6	55.0	43.6
o-cresol	90.5	90.6	90.6	91.0	91.6	92.1	93.4	62.9
				$[C_4C_8OHim]BF_4$				
resorcinol	59.3	59.2	59.6	61.3	61.8	61.5	61.8	28.5
phenol	70.1	69.1	69.6	71.2	71.5	71.2	71.7	35.7
guaiacol	68.8	68.9	68.8	70.2	71.3	70.7	70.6	37.1
p-nitrophenol	89.3	89.4	88.8	87.9	87.8	56.4	57.8	56.2
o-cresol	85.6	84.5	84.1	84.4	85.6	83.2	84.7	53.8
				$[C_4C_{12}im]PF_6$				
resorcinol	12.9	12.8	13.0	13.1	13.0	13.1	12.8	6.89
phenol	63.8	64.5	63.5	65.2	66.1	66.2	65.9	24.3
guaiacol	74.3	74.2	74.3	73.0	75.4	74.9	75.0	43.7
p-nitrophenol	82.7	80.8	82.5	83.2	82.5	52.7	44.2	34.6
o-cresol	83.3	83.7	83.3	83.1	85.2	86.1	85.4	51.1
				$[C_4C_{12}im]BF_4$				
resorcinol	68.9	69.0	68.5	70.3	69.1	69.2	68.8	29.3
phenol	85.0	83.9	83.2	84.3	86.2	84.9	85.4	47.0
guaiacol	83.7	83.4	83.7	84.1	84.7	84.3	84.3	49.4
p-nitrophenol	93.9	94.2	93.9	95.3	96.2	89.0	84.8	83.1
o-cresol	93.5	93.7	92.7	93.7	94.1	94.7	92.2	81.2
				$[C_4C_{11}OHim]PF_6$				
resorcinol	55.8	55.5	56.3	56.0	57.2	55.4	55.3	27.7
phenol	79.6	79.2	79.0	79.0	80.0	79.6	78.8	42.6
guaiacol	83.3	83.1	82.9	82.7	83.7	83.3	83.1	43.9
p-nitrophenol	94.4	94.4	94.3	94.2	94.9	56.9	55.1	45.3
o-cresol	91.0	91.2	90.8	90.7	91.2	91.3	91.1	65.5
				$[C_4C_{11}OHim]BF_4$				
resorcinol	80.2	80.4	80.0	79.9	80.6	79.0	77.7	36.7
phenol	86.5	86.3	86.5	86.5	87.0	86.9	86.4	48.0
guaiacol	85.6	85.5	85.3	85.4	86.0	86.1	85.7	49.9
p-nitrophenol	96.7	96.8	96.7	96.7	96.8	87.2	85.3	85.5
o-cresol	93.9	93.9	94.0	93.9	94.1	94.3	94.2	85.0
				$[C_4Beim]BF_4$				
resorcinol	55.7	55.4	54.4	53.5	54.4	54.6	54.7	21.8
phenol	72.9	72.8	71.7	72.3	74.9	74.0	74.9	42.1
guaiacol	80.6	80.6	79.7	80.1	79.9	78.3	78.1	46.4
p-nitrophenol	89.8	89.9	89.6	89.4	87.9	68.9	71.4	70.5
o-cresol	87.3	87.3	86.8	85.5	86.6	87.4	87.6	72.9

Table S1. Continued.

pH	2.0	3.0	5.0	6.0	7.0	9.0	10	12
				$[C_8mim]NTf_2$				
resorcinol	11.8	11.6	12.0	11.9	12.2	11.7	12.4	5.6
phenol	67.4	66.4	66.4	66.8	67.6	66.0	64.7	4.3
guaiacol	80.2	79.4	79.4	80.0	80.4	79.5	69.6	6.6
p-nitrophenol	80.5	79.8	80.1	78.6	77.2	4.1	4.0	4.0
o-cresol	85.7	85.1	85.2	85.4	86.1	85.8	81.4	11.5
				$[C_4C_7im]NTf_2$				
resorcinol	10.1	10.6	11.2	11.4	11.1	10.3	10.0	4.9
phenol	63.9	63.9	64.5	63.9	64.0	63.8	62.6	3.5
guaiacol	77.9	77.8	78.3	77.7	78.4	77.6	76.0	2.4
p-nitrophenol	77.9	77.7	77.7	76.2	75.6	6.0	0.3	4.6
o-cresol	85.0	84.7	85.1	84.8	85.3	85.3	82.0	9.0
				$[C_4C_9im]$ NTf_2				
resorcinol	11.3	11.0	11.8	11.5	11.2	10.8	11.6	2.4
phenol	62.5	62.4	62.9	63.4	64.2	64.1	62.3	10.8
guaiacol	75.1	75.1	76.2	76.2	77.0	76.7	74.6	7.8
p-nitrophenol	73.6	75.2	77.2	77.7	76.0	22.6	10.0	5.9
o-cresol	82.1	83.2	84.1	84.2	85.2	86.4	86.7	13.6
				$[C_4C_{12}im]NTf_2$				
resorcinol	9.2	9.0	8.9	9.1	8.7	8.8	9.0	2.3
phenol	60.0	59.8	58.5	60.2	59.6	59.9	48.3	4.0
guaiacol	75.2	74.8	73.8	74.8	74.1	73.8	69.8	3.6
p-nitrophenol	73.3	72.7	73.8	75.5	74.6	48.0	13.2	11.2
o-cresol	83.1	82.7	82.6	82.6	82.6	83.6	81.4	9.5
				$[C_4C_6OHim]NTf_2$				
resorcinol	48.3	47.5	49.6	50.3	50.5	50.3	48.4	10.3
phenol	78.3	77.9	78.6	78.9	80.5	81.0	79.3	4.2
guaiacol	84.4	83.8	84.1	84.3	85.5	86.1	83.9	7.3
p-nitrophenol	89.6	89.2	88.8	88.2	86.8	25.7	10.5	10.0
o-cresol	90.5	90.2	90.5	90.6	91.7	92.5	92.1	31.9
				$[C_4C_8OHim]NTf_2$				
resorcinol	51.3	50.2	49.3	50.4	49.8	50.1	35.0	4.0
phenol	80.0	81.2	81.2	82.4	81.8	82.4	79.3	3.8
guaiacol	84.2	85.0	84.9	85.9	85.2	85.6	82.1	2.3
p-nitrophenol	92.1	92.8	92.4	92.6	88.0	32.5	11.0	5.6
o-cresol	91.3	91.7	91.7	92.3	92.0	92.6	91.7	13.9
				$[C_4C_{11}OHim]NTf_2$				
resorcinol	45.1	44.8	44.3	45.2	45.4	46.1	44.1	9.2
phenol	79.4	78.4	78.7	78.3	79.1	73.8	73.6	2.4
guaiacol	84.0	83.1	83.2	82.8	83.4	78.9	78.6	3.2
p-nitrophenol	92.4	92.0	92.1	91.6	87.9	29.5	28.0	17.0
o-cresol	91.5	90.8	90.9	90.8	91.2	89.5	90.0	17.8

Table S1. Continued.

pH	2.0	3.0	5.0	6.0	7.0	9.0	10	12
				$[C_4Beim]NTf_2$				
resorcinol	31.0	30.8	30.7	29.8	31.5	32.4	31.4	5.6
phenol	74.7	74.9	75.1	75.7	75.0	74.3	76.0	9.7
guaiacol	80.0	81.5	82.4	82.8	81.9	83.2	82.6	13.7
p-nitrophenol	89.2	89.7	90.7	90.9	88.2	28.7	2.8	2.0
o-cresol	88.4	87.4	88.5	89.0	89.4	87.8	89.9	41.2

Table S2. Extraction Efficiencies (*E*, %) of ILs after the Compensation of Their Soluble Losses in Water at pH 7.0 and V_w:V_{IL} = 10:1 (average values, *n* = 3).

	resorcinol	phenol	guaiacol	*p*-nitrophenol	*o*-cresol
$[C_8mim]PF_6$	12.9	63.0	74.1	80.3	83.3
$[C_8mim]BF_4$	73.9	85.1	86.1	95.4	93.1
$[C_4C_6OHim]PF_6$	58.1	80.3	85.4	90.3	89.6
$[C_4C_7im]PF_6$	13.1	63.5	73.5	79.2	82.8
$[C_4C_7im]BF_4$	73.4	86.9	85.6	96.7	94.6
$[C_4C_8OHim]PF_6$	58.8	80.7	85.1	89.1	91.2
$[C_4C_8OHim]BF_4$	75.9	83.7	81.5	93.6	91.4
$[C_4C_9im]PF_6$	13.2	65.9	75.4	82.4	85.0
$[C_4C_9im]BF_4$	72.9	86.5	86.5	94.8	95.0
$[C_4C_{11}OHim]PF_6$	55.3	79.7	82.0	93.5	90.2
$[C_4C_{11}OHim]BF_4$	79.5	85.8	85.4	96.2	93.7
$[C_4C_{12}im]PF_6$	12.8	64.1	73.8	82.6	83.2
$[C_4C_{12}im]BF_4$	69.3	85.7	84.5	93.2	94.9
$[C_4Beim]BF_4$	68.3	79.8	81.1	92.2	90.0
$[C_8mim]NTf_2$	12.1	67.7	81.0	77.0	86.4
$[C_4C_7im]NTf_2$	11.2	61.2	77.6	75.8	82.3
$[C_4C_6OHim]NTf_2$	50.1	80.7	85.1	86.1	91.4
$[C_4C_8OHim]NTF_2$	52.0	81.6	85.6	86.3	92.2
$[C_4C_9im]NTf_2$	11.0	61.2	77.6	76.9	82.3
$[C_4C_{11}OHim]NTf_2$	48.6	80.1	84.7	87.5	91.8
$[C_4C_{12}im]NTf_2$	8.9	59.8	74.5	75.1	78.2
$[C_4Beim]NTf_2$	33.0	76.4	83.5	90.3	89.2