Supporting Information

N-1 Functionalized Trialkylimidazolium Ionic Liquids with Alkoxymethyl Group: Synthesis, Characterization, and Application as Electrolytes for Lithium Battery

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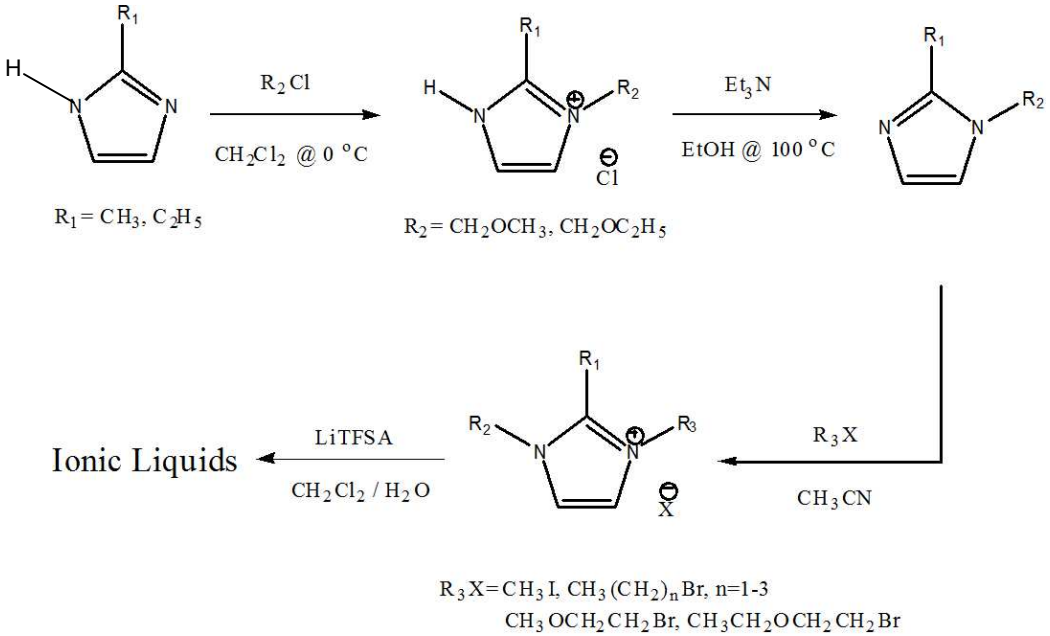
1. Synthetic procedure of N-1 functionalized trialkylimidazolium ionic liquids with alkoxymethyl group

The synthesis procedure of these trialkylimidazolium ionic liquids was illustrated in Scheme S1.



Scheme S1. Synthesis of these N-1 functionalized trialkylimidazolium ionic liquids with alkoxymethyl group.

1.1. Synthesis of N-1 ether substituted imidazoles

1.1.1. 1-methoxymethyl-2-methylimidazole (IM(1O1)1)

2-methyl-imidazole (16.4 g, 0.2 mol) was dissolved in dichloromethane (100 ml), and chloromethyl methyl ether (17.7 g, 220 mmol) was added dropwise to the solution at 0 ^{o}C. Then the pale yellow solution stirred vigorously at room temperature for 4 h. The dichloromethane was removed by rotary evaporator, and highly viscous raw product was dissolved with 20 ml ethanol and transferred to a 100 ml autoclave. Triethylamine (20.2 g, 200 mmol) was added in the autoclave and reacted at 100 ^{o}C for 24 h. The solid salt formed was filtered off, and the residue was distilled under reduced pressure using a 15 cm vigreux-columne. The product was collected at

130-132 ^{o}C (boiling point) when the pressure was about 10 Pa. 1-methoxymethyl-2-methylimidazole (Yield 15 g (60 %) as colourless liquid), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.92 (s, 2H), 5.16 (s, 2H), 3.27 (s, 3H), 2.44 (s, 3H).

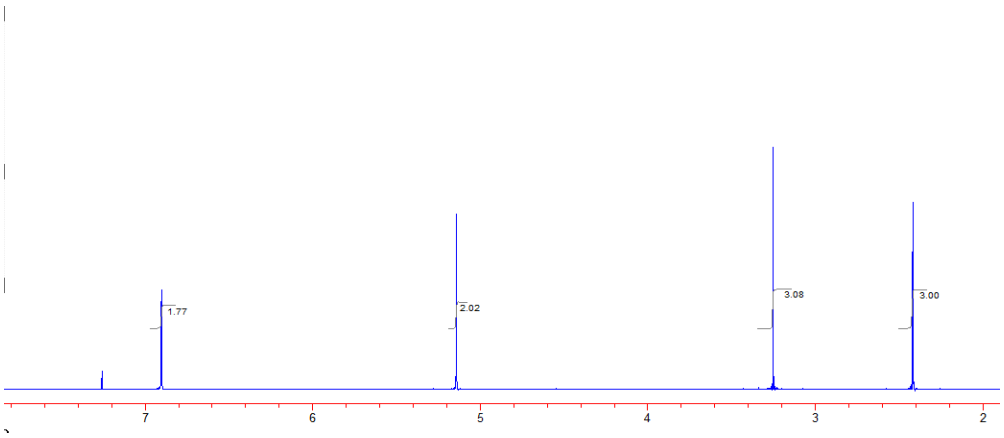


Fig. S1 ^{1}H NMR spectrum of 1-methoxymethyl-2-methylimidazole.

1.1.2. 1-methoxymethyl-2-ethylimidazole (IM(1O1)2)

Chloromethyl methyl ether (17.7 g, 220 mmol) was added dropwise to a stirring solution of 2-ethylimidazole (19.2 g, 0.2 mol) in dichloromethane (100 ml) cooled in an ice-water bath. The following procedures were similar to IM(1O1)1. The product was collected at 140-142 ^{o}C (boiling point) when the pressure was about 10 Pa. 1-methoxymethyl-2-ethylimidazole (Yield 18 g (65 %) as colourless liquid), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.94-6.93 (d, 1H), 6.91-6.90 (d, 1H), 5.15 (s, 2H), 3.26 (s, 3H), 2.77-2.70 (m, 2H), 1.35-1.31 (t, 3H).

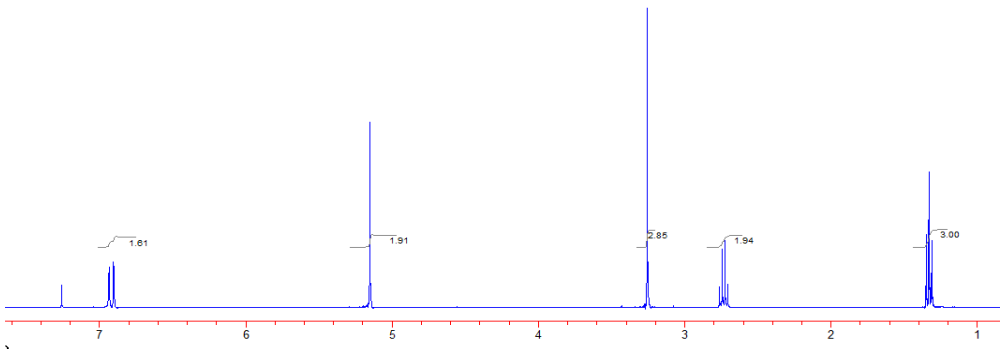


Fig. S2 ^{1}H NMR spectrum of 1-methoxymethyl-2-ethylimidazole.

1.1.3. 1-ethoxymethyl-2-methylimidazole (IM(1O2)1)

Chloromethyl ethyl ether (20.8 g, 220 mmol) was added dropwise to a stirring solution of 2-methylimidazole (16.4 g, 0.2 mol) in dichloromethane (100 ml) cooled in an ice-water bath. The following procedures were similar to IM(1O1)1. The product was collected at 146-147 ^{o}C (boiling point) when the pressure was about 10 Pa. 1-ethoxymethyl-2-methylimidazole (Yield 20 g (70 %) as colourless liquid), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.90 (s, 2H), 5.20 (s, 2H), 3.46-3.40 (m, 2H), 2.43 (s, 3H), 1.19-1.14 (t, 3H).

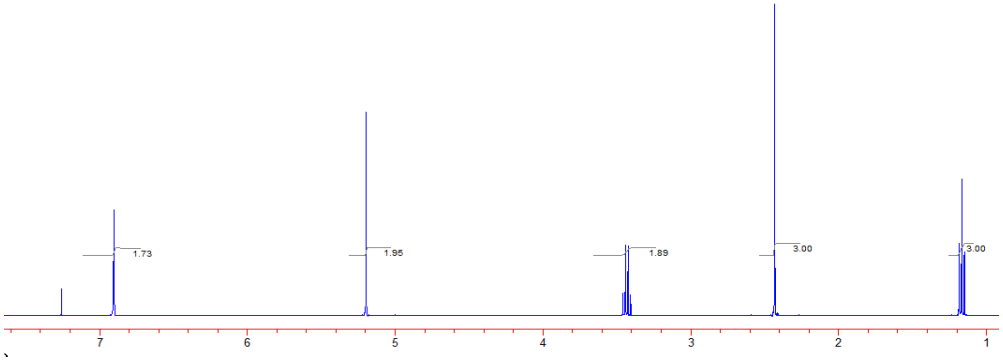


Fig. S3 ^{1}H NMR spectrum of 1-ethoxymethyl-2-methylimidazole.

1.1.4. 1-ethoxymethyl-2-ethylimidazole (IM(1O2)2)

Chloromethyl ethyl ether (20.8 g, 220 mmol) was added dropwise to a stirring solution of 2-ethylimidazole (19.2 g, 0.2 mol) in dichloromethane (100 ml) cooled in an ice-water bath. The following procedures were similar to IM(1O1)1. The product was collected at 152-154 ^{o}C (boiling point) when the pressure was about 10 Pa. 1-ethoxymethyl-2-ethylimidazole (Yield 22 g (70 %) as colourless liquid), ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.95-6.93 (d, 1H), 6.92-6.90 (d, 1H), 5.21 (s, 2H), 3.47-3.41 (m, 2H), 2.79-2.72 (m, 2H), 1.37-1.32 (t, 3H), 1.19-1.15 (t, 3H).

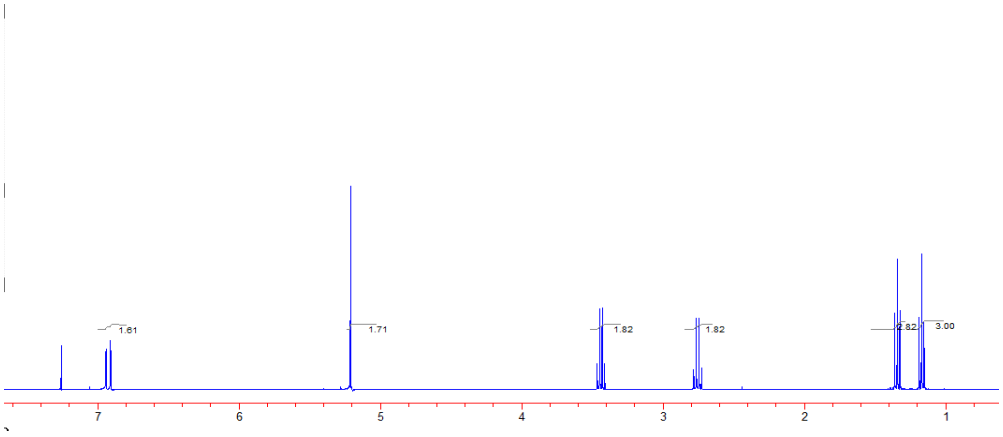


Fig. S4 ^{1}H NMR spectrum of 1-ethoxymethyl-2-ethylimidazole.

1. 2. Preparation of N-1 functionalized trialkylimidazolium ionic liquids with alkoxymethyl group

1.2.1. 1-methoxymethyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)11-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with Iodomethane (6.3 g, 44 mmol) at room temperature for 24 hours in a 250 mL flask with acetonitrile (10 mL) as solvent. The produced iodide was acquired after washing with ether. The iodide and LiTFSA was dissolved in deionized water and mixed for 2 hours at ambient temperature. The crude IL was dissolved with dichloromethane, and washed with deionized water until no residual halide anions in the deionized water used to rinse the IL could be detected by $AgNO_3$. The dichloromethane was removed by rotating evaporation. The product was dried under high vacuum for more than 24 hours at 105 ^{o}C. Yield 12.0 g (74 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (d, 1H), 7.22 (d, 1H), 5.39 (s, 2H), 3.84 (s, 3H), 3.41 (s, 3H), 2.67 (s, 3H); ^{13}C NMR: δ (ppm) 145.28, 124.58-115.04, 122.44, 121.22, 79.45, 57.09, 35.04, 9.33. HRMS (ESI): m/z calcd for [IM(1O1)11^{+}]: 141.1028; found: 141.1031; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9151.

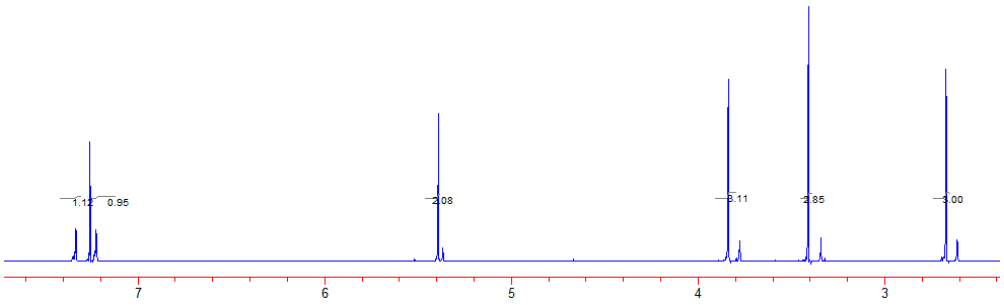


Fig. S5 ^{1}H NMR spectrum of IM(1O1)11-TFSA.

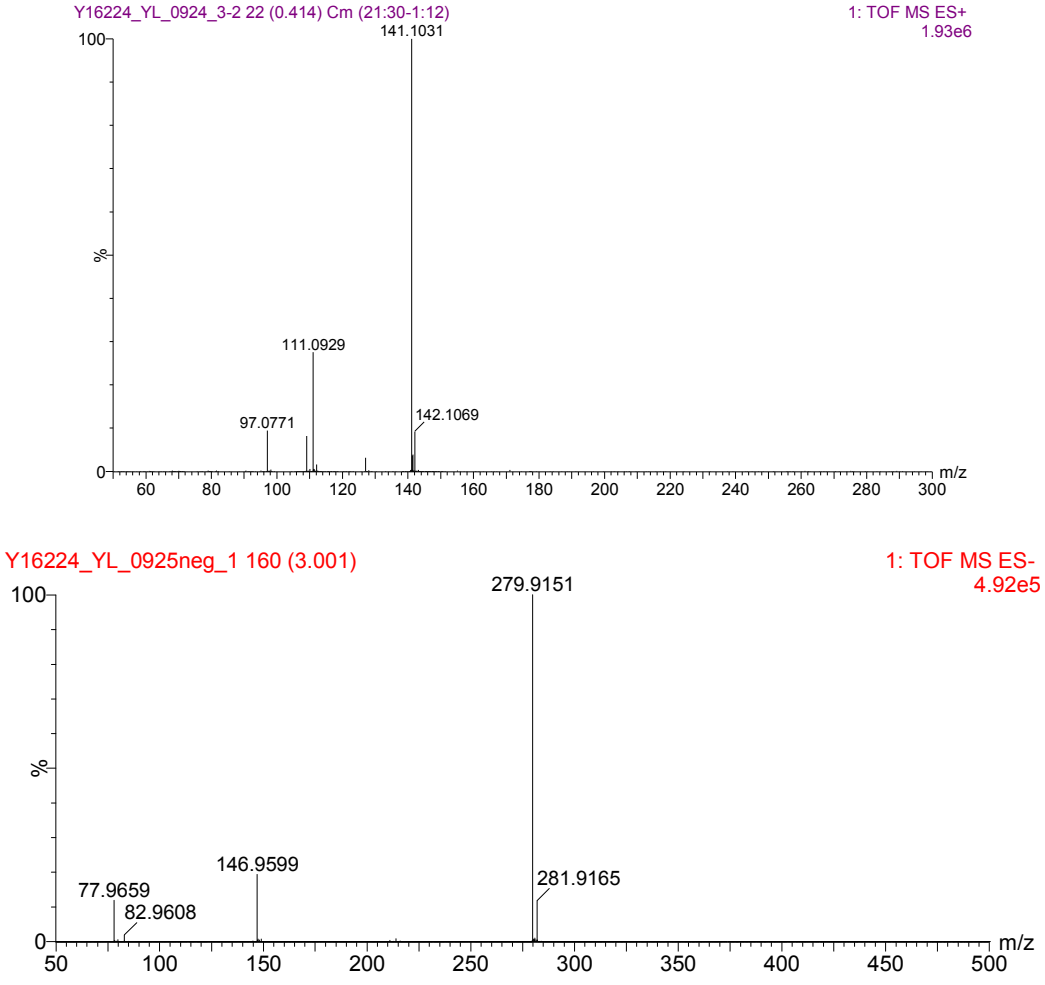


Fig. S6 HRMS spectrum of IM(1O1)11-TFSA.

1.2.2. 1-methoxymethyl-2-methyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)12-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with bromoethane (8.7 g, 80 mmol) at 30 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The produced bromide was acquired after washing with ether. The bromide was dissolved in 100 ml ethanol and decolorized by active carbon, and colorless bromide could be obtained after filtered the active carbon and removed ethanol by rotary evaporation. The bromide and LiTFSA was dissolved in deionized water and mixed for 24 hours at ambient temperature. The crude IL was dissolved with dichloromethane, and washed with deionized water until no residual halide anions in the deionized water used to rinse the IL could be detected by $AgNO_3$. The dichloromethane was removed by rotating evaporation. The product was dried under high vacuum for more than 24 hours at 105 ^{o}C. Yield 13.1 g (78 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, 1H), 7.27 (d, 1H), 5.40 (s, 2H), 3.85 (s, 3H), 3.41 (s, 3H), 3.08-3.01 (m, 2H), 1.33-1.29 (t, 3H); ^{13}C NMR: δ (ppm) 144.49, 124.65-115.07, 121.79, 120.56, 79.61, 57.25, 43.83, 14.43, 9.40. HRMS (ESI): m/z calcd for [IM(1O1)12^{+}]: 156.1263; found: 156.1241; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9168.

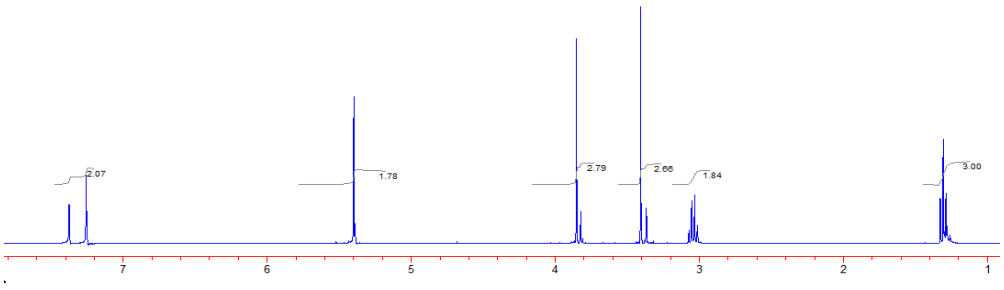


Fig. S7 ^{1}H NMR spectrum of IM(1O1)12-TFSA.

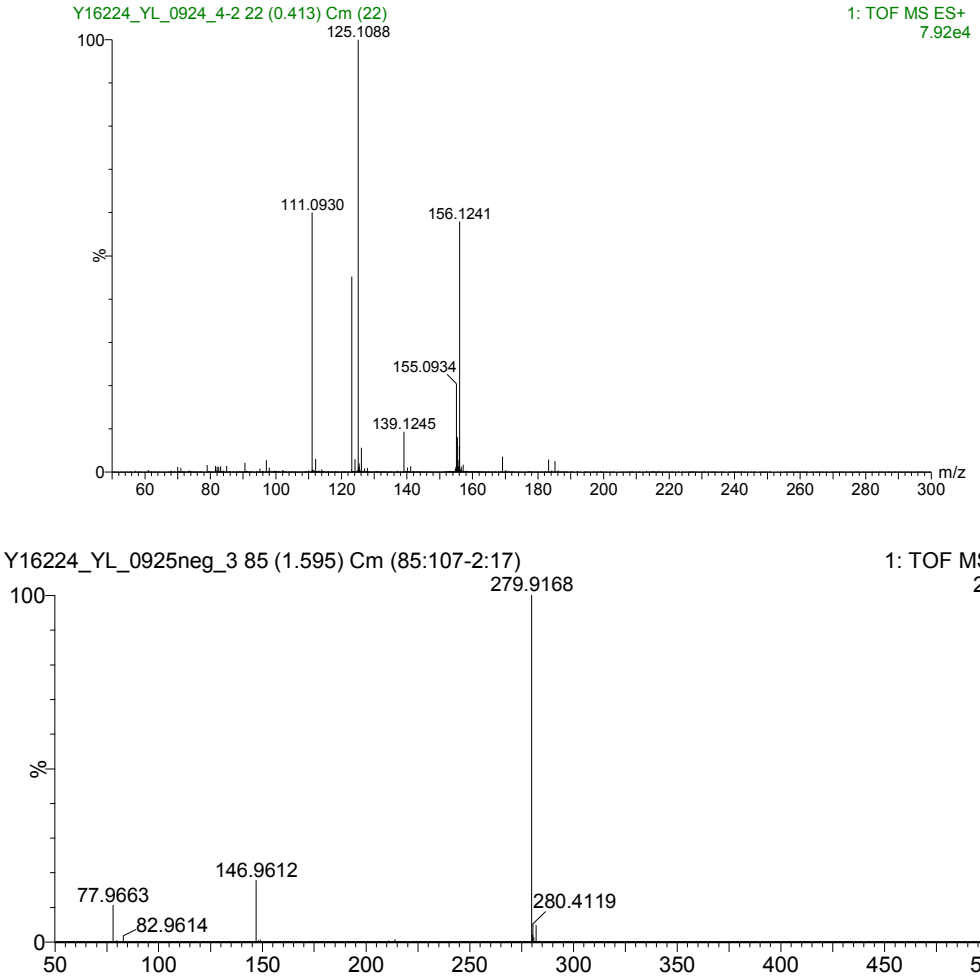


Fig. S8 HRMS spectrum of IM(1O1)12-TFSA.

1.2.3. 1-methoxymethyl-2-methyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)13-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with bromopropane (9.8 g, 80 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were similar with IM(1O1)12-TFSA. Yield 13.8 g (80 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39-7.38 (d, 1H), 7.25 (d, 3H), 5.40 (s, 2H), 4.08-4.04 (t, 2H), 3.39 (s, 3H), 2.66 (s, 3H), 1.90-1.83 (m, 2H), 1.00-0.96 (t, 3H); ^{13}C NMR: δ (ppm) 144.68, 124.65-115.07, 121.53, 121.17, 79.38, 56.95, 49.97, 22.70, 10.23, 9.31. HRMS (ESI): m/z calcd for [IM(1O1)13^{+}]: 170.1419;

found: 170.1408; m/z calcd for [TFSA$^-$]: 279.9173; found: 279.9151.

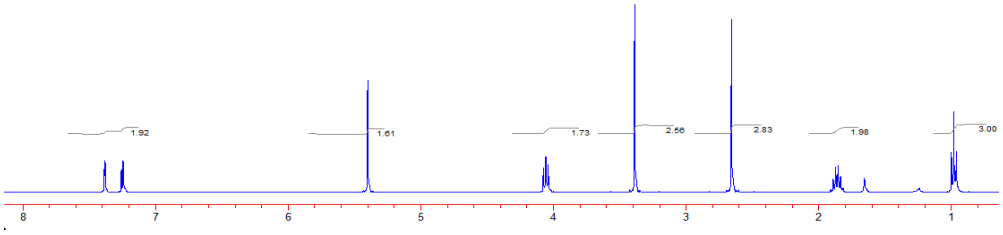


Fig. S9 ^{1}H NMR spectrum of IM(1O1)13-TFSA.

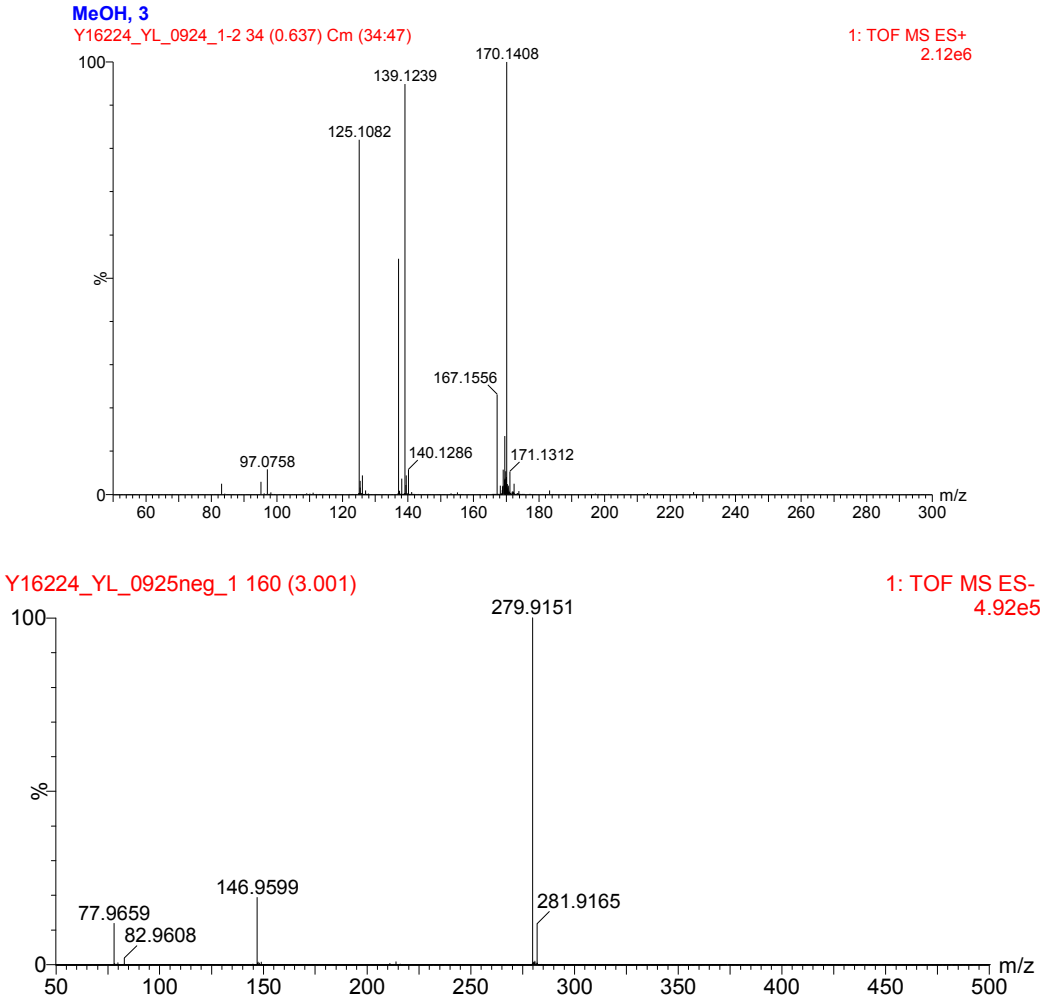


Fig. S10 HRMS spectrum of IM(1O1)13-TFSA.

1.2.4. 1-methoxymethyl-2-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)14-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with 1-bromobutane (11.0 g, 80 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (10 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 14.7 g (82 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, 1H), 7.24 (d, 1H), 5.41 (s, 2H), 4.11-4.07 (t, 2H), 3.40 (s, 3H), 2.67 (s, 3H), 1.85-1.76 (m, 2H), 1.44-1.34 (m, 2H), 1.00-0.95 (t, 3H); ^{13}C NMR: δ (ppm) 144.62, 124.65-115.04, 121.60, 121.18, 79.45, 57.09, 48.47, 31.32, 19.38, 13.16, 9.43. HRMS (ESI): m/z calcd for [IM(1O1)14^{+}]: 184.1576; found: 184.1548; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9171.

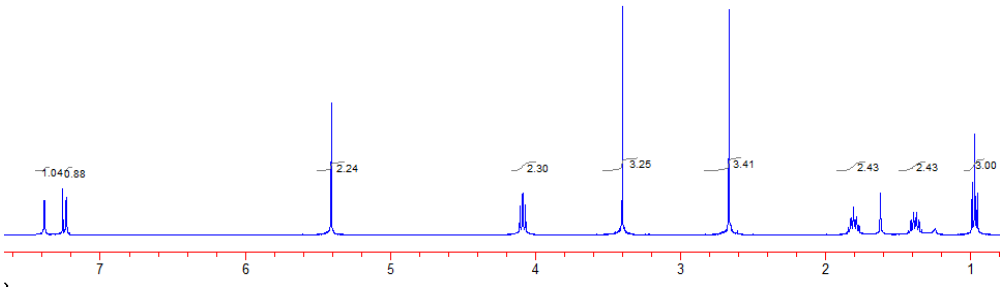


Fig. S11 ^{1}H NMR spectrum of IM(1O1)14-TFSA.

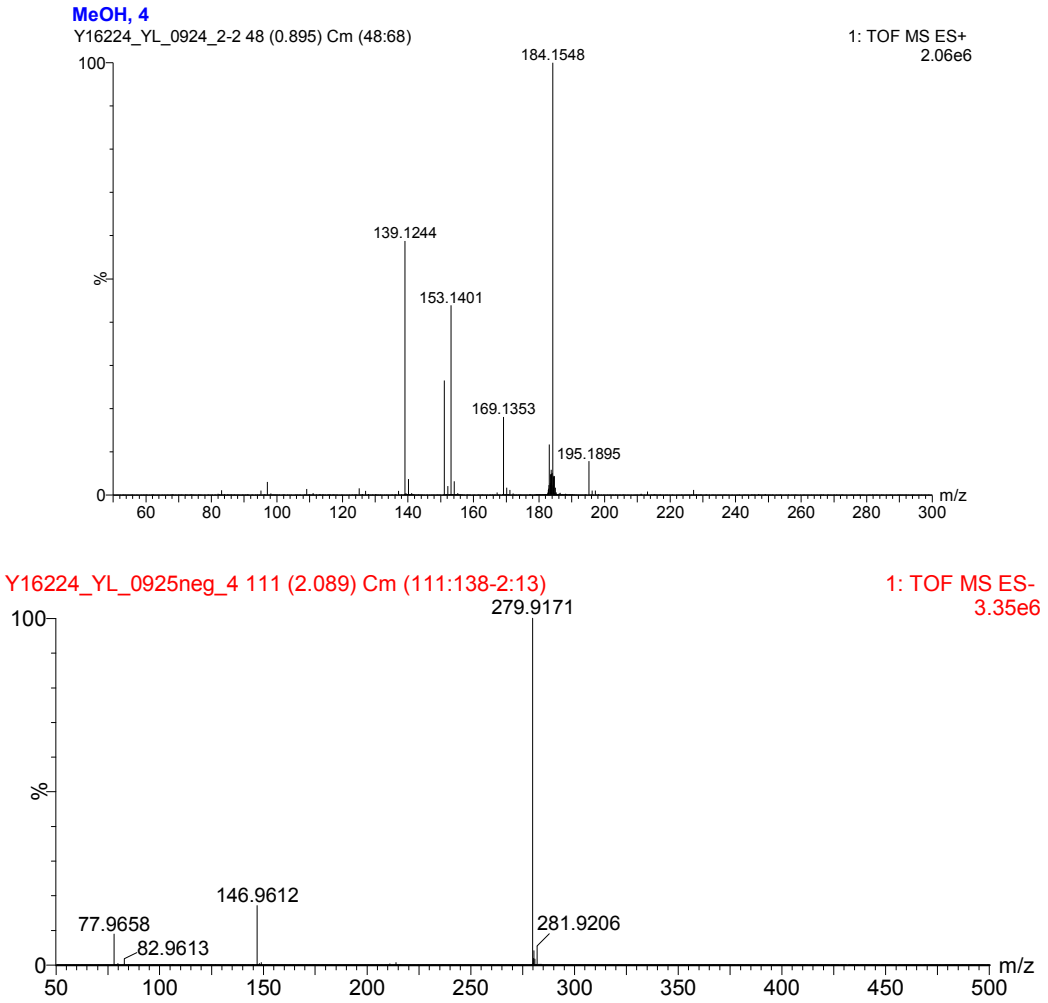


Fig. S12 HRMS spectrum of IM(1O1)14-TFSA.

1.2.5. 1-methoxymethyl-2-methyl-3-(2-methoxyethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)1(2o1)-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with 2-methoxyethyl bromide (7.0 g, 48 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 15.3 g (85 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 1H), 7.34 (d, 1H), 5.40 (s, 2H), 4.29-4.27 (t, 2H), 3.71-3.69 (t, 2H), 3.40 (s, 3H), 3.31 (s, 3H), 2.67 (s, 3H); ^{13}C NMR: δ (ppm) 145.71, 124.67-115.06, 121.70, 121.43, 79.48, 70.09, 58.79, 57.10, 48.64, 9.73. HRMS (ESI): m/z calcd for [IM(1O1)1(2o1)$^{+}$]: 186.1368;

found: 186.1339; m/z calcd for [TFSA$^-$]: 279.9173; found: 279.9166.

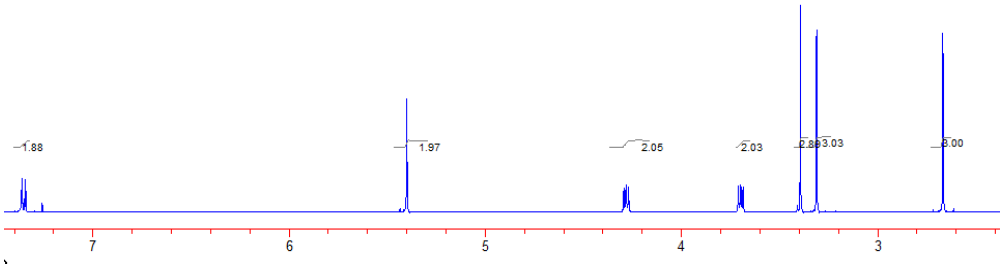
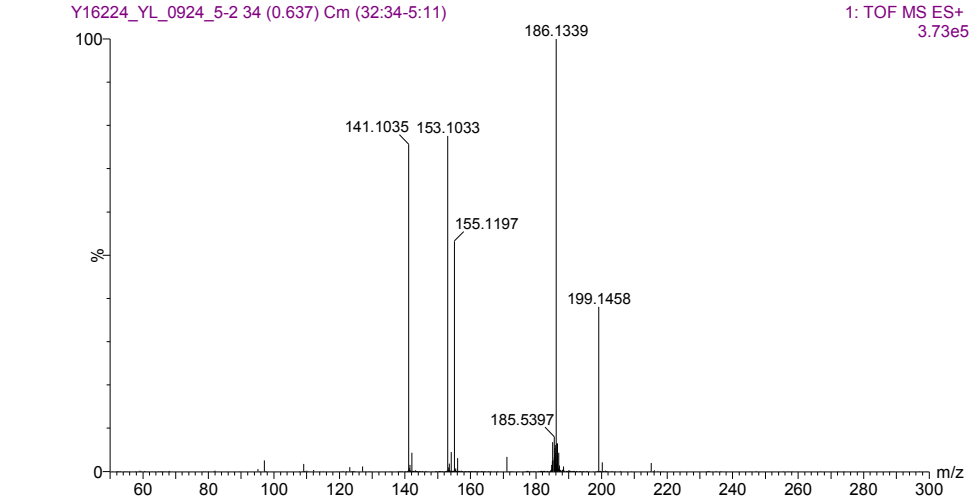


Fig. S13 ^{1}H NMR spectrum of IM(1O1)1(2o1)-TFSA.



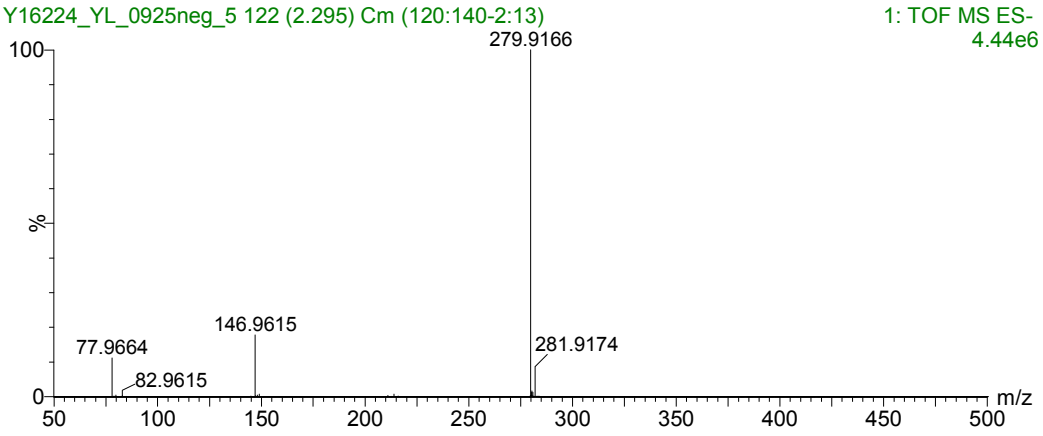


Fig. S14 HRMS spectrum of IM(1O1)1(2o1)-TFSA.

1.2.6. *1-methoxymethyl-2-methyl-3-(2-ethoxyethyl)-imidazolium*

bis(trifluoromethanesulfonyl)imide (IM(1O1)1(2o2)-TFSA)

IM(1O1)1 (5.0 g, 40 mmol) reacted with 2-ethoxyethyl bromide (7.4 g, 48 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM1(1O2)2-TFSA. Yield 16.0 g (91 %) as colorless liquid (water content, 30 ± 1 ppm); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 1H), 7.34 (d, 1H), 5.40 (s, 2H), 4.29-4.26 (t, 2H), 3.74-3.71 (t, 2H), 3.47-3.42 (m, 2H), 3.38 (s, 3H), 2.67 (s, 3H), 1.13-1.09 (t, 3H); ^{13}C NMR: δ (ppm) 145.79, 124.63-115.09, 121.62, 121.51, 79.47, 68.04, 66.66, 57.10, 48.61, 14.68, 9.79. HRMS (ESI): m/z calcd for [IM(1O1)1(2o2)$^{+}$]: 200.1525; found:200.1500; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9162.

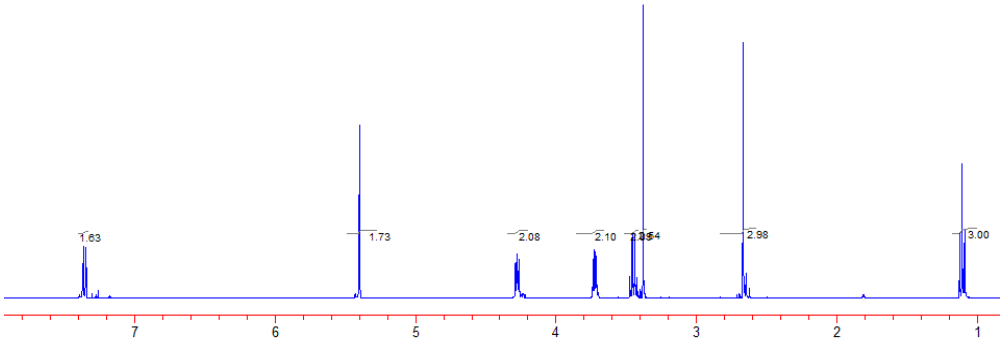


Fig. S15 ^{1}H NMR spectrum of IM(1O1)1(2o2)-TFSA.

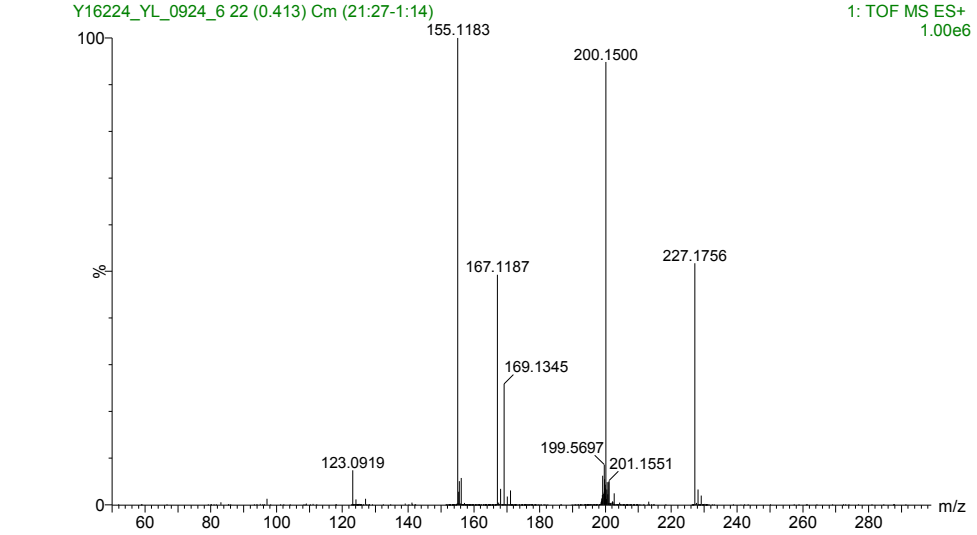


Fig. S16 HRMS spectrum of IM(1O1)1(2o2)-TFSA.

1.2.7. 1-methoxymethyl-2-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)21-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with Iodomethane (6.0 g, 43 mmol) at room temperature for 24 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)11-TFSA. Yield 12.2 g (81 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (s, 2H), 4.74 (s, 2H), 3.90 (s, 3H), 3.57-3.53 (t, 2H), 1.68-1.58 (m, 2H), 0.95-0.91 (t, 3H); ^{13}C NMR: δ (ppm) 149.11, 124.66-115.08, 122.67, 121.43, 79.39, 57.07, 34.88, 17.09, 10.94. HRMS (ESI): m/z calcd for [IM(1O1)21^{+}]: 156.1263; found:156.1245; m/z calcd

for [TFSA$^-$]: 279.9173; found: 279.9159.

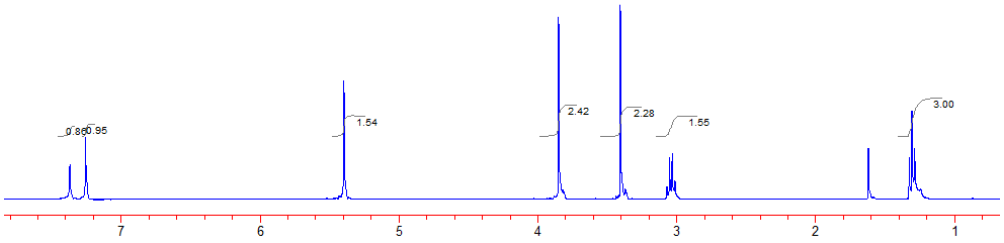


Fig. S17 ^{1}H NMR spectrum of IM(1O1)21-TFSA.

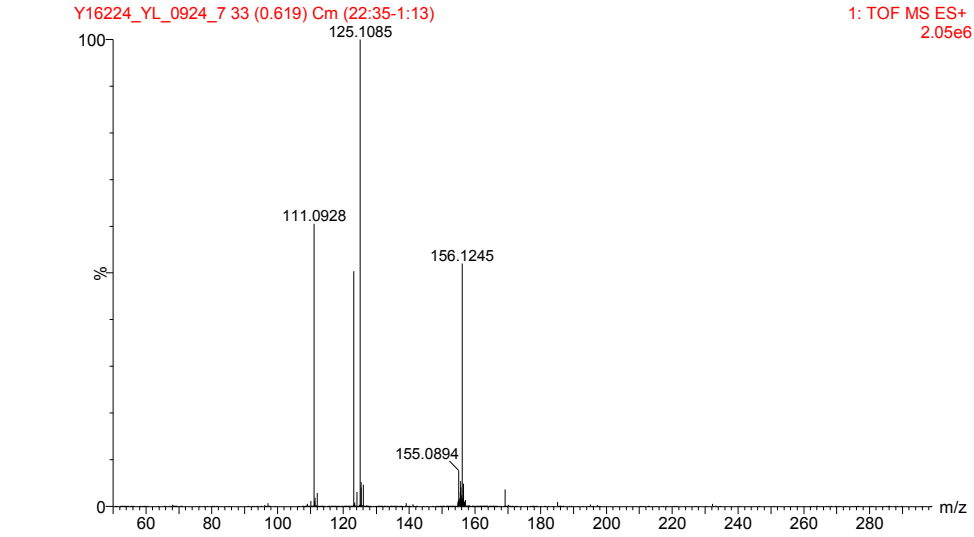


Fig. S18 HRMS spectrum of IM(1O1)21-TFSA.

1.2.8. 1-methoxymethyl-2,3-diethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)22-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with bromoethane (7.8 g, 72 mmol) 30 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 12.8 g (82 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, 1H), 7.31 (d, 1H), 5.40 (s, 2H), 4.20-4.14 (m, 2H), 3.40 (s, 3H), 3.08-3.01 (m, 2H), 1.55-1.50 (t, 3H), 1.33-1.29 (t, 3H); ^{13}C NMR: δ (ppm) 148.47, 124.64-115.06, 121.88, 120.51, 79.27, 56.96, 43.41, 16.94, 14.77, 11.53. HRMS (ESI): m/z calcd for [IM(1O1)22^{+}]: 170.1419; found:170.1402; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9169.

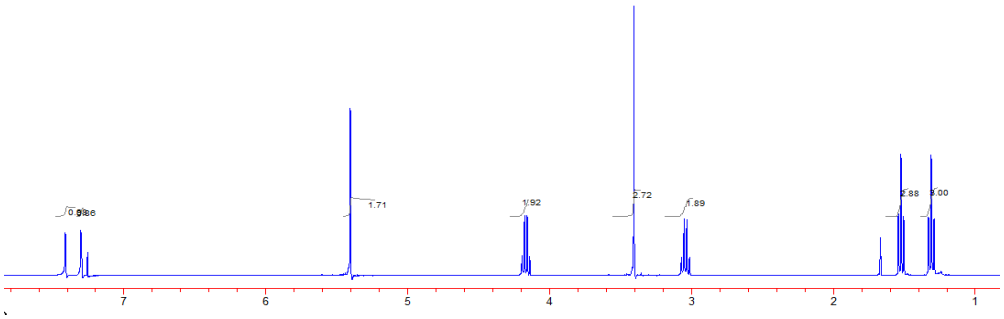


Fig. S19 ^{1}H NMR spectrum of IM(1O1)22-TFSA.

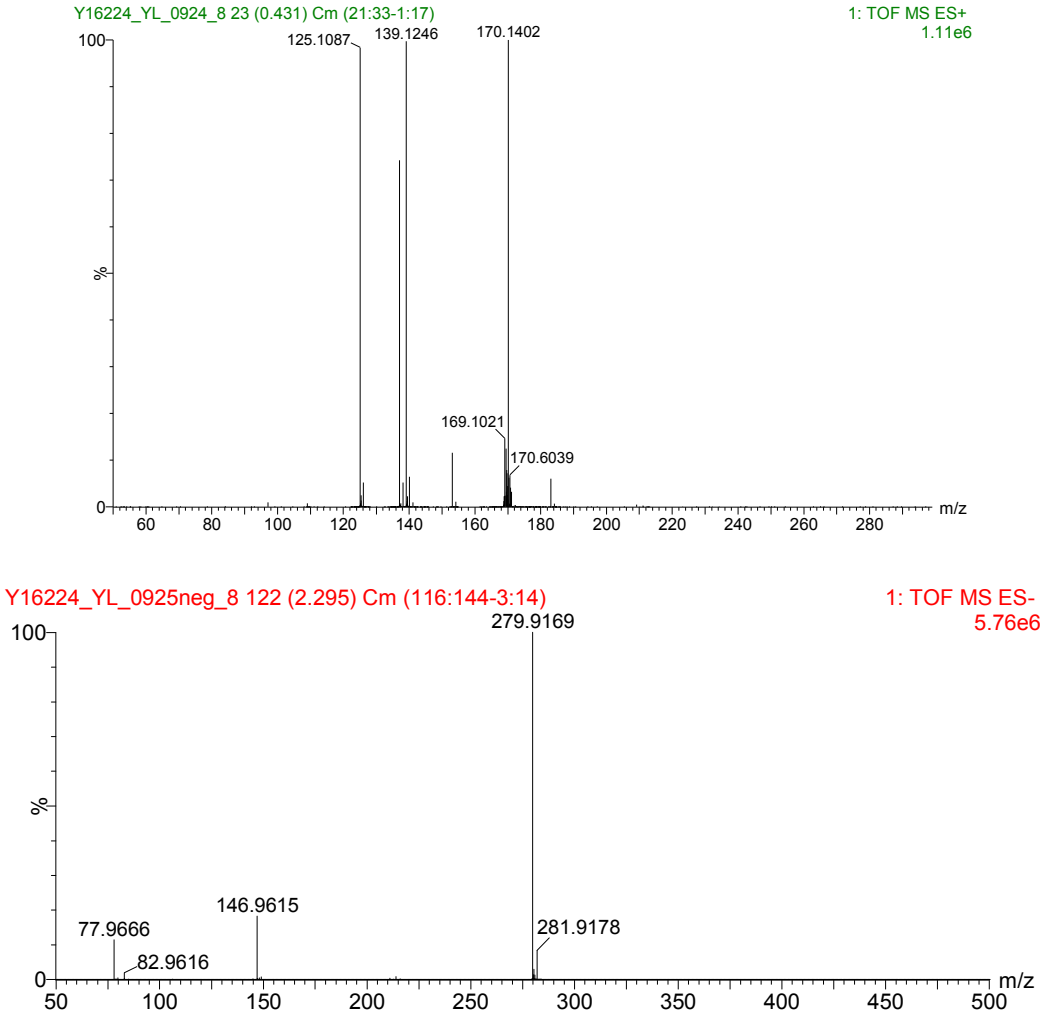


Fig. S20 HRMS spectrum of IM(1O1)22-TFSA.

1.2.9. 1-methoxymethyl-2-ethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)23-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with 1-bromopropane (8.9 g, 72 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 12.7 g (79 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.43 (d, 1H), 7.28 (d, 1H), 5.43 (s, 2H), 4.09-4.04 (t, 2H), 3.42(s, 3H), 3.08-3.02 (m, 2H), 1.95-1.86 (m, 2H), 1.34-1.31 (t, 3H), 1.04-1.00 (t, 3H); ^{13}C NMR: δ (ppm) 148.72, 124.63-115.02, 121.92, 121.13, 79.40, 57.11, 49.75, 23.17, 17.04, 11.71, 10.38. HRMS (ESI): m/z calcd for

[IM(1O1)23^{+}]: 184.1576; found:184.1553; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9167.

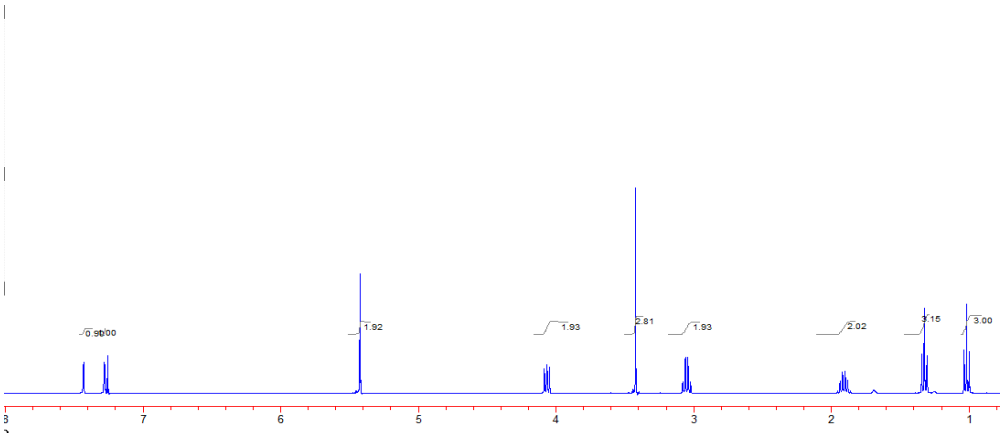


Fig. S21 ^{1}H NMR spectrum of IM(1O1)23-TFSA.

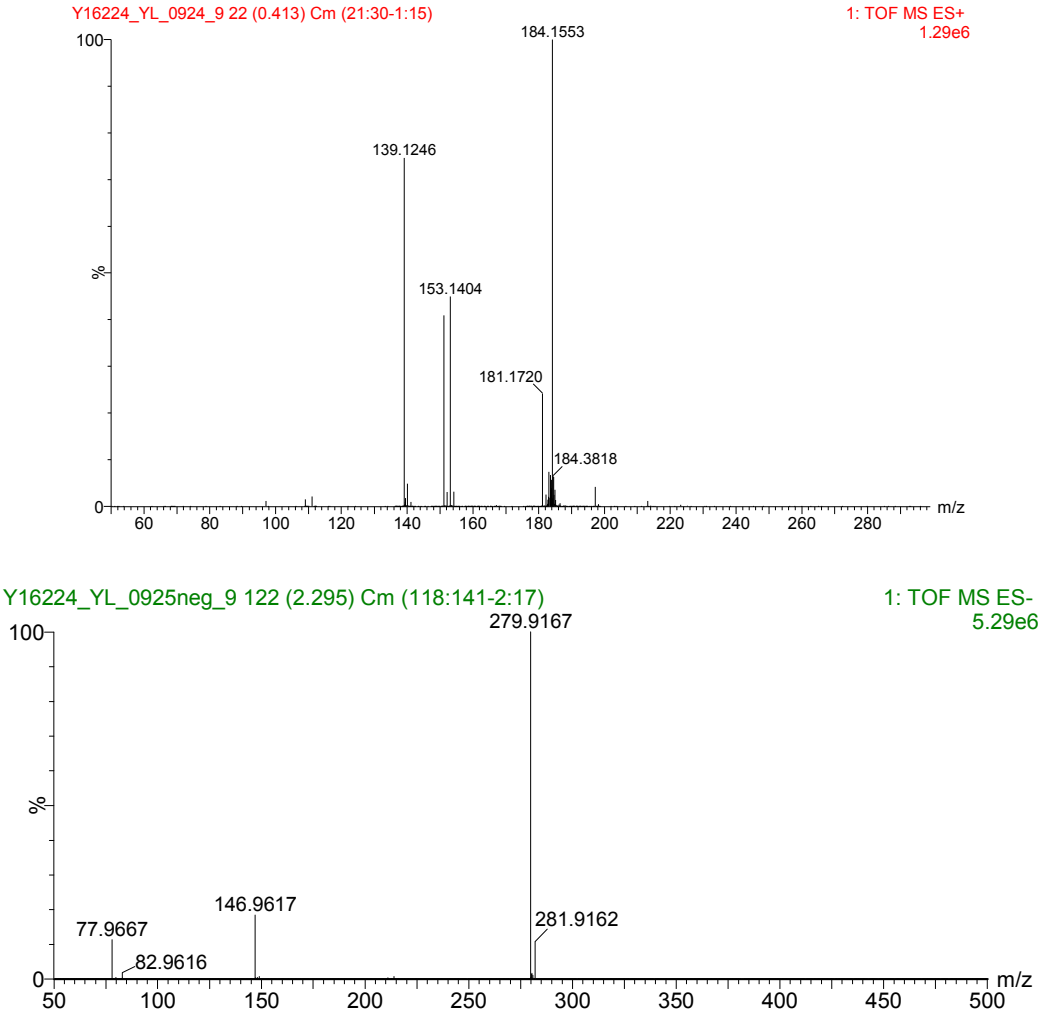


Fig. S22 HRMS spectrum of IM(1O1)23-TFSA.

1.2.10. 1-methoxymethyl-2-ethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)24-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with 1-bromobutane (10.0 g, 72 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 15.2 g (84 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (d, 1H), 7.27 (d, 1H), 5.43 (s, 2H), 4.12-4.07 (t, 2H), 3.44 (s, 3H), 3.09-3.03 (m, 2H), 1.90-1.81 (m, 2H), 1.46-1.39 (m, 2H), 1.36-1.31 (t, 3H), 1.02-0.97 (t, 3H); ^{13}C NMR: δ (ppm) 148.63, 124.61-115.01, 121.89, 121.10, 79.37, 57.07, 48.17, 31.75, 19.41, 17.04, 13.18, 11.64. HRMS (ESI): m/z calcd for [IM(1O1)24^{+}]: 198.1732; found:198.1720; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9163.

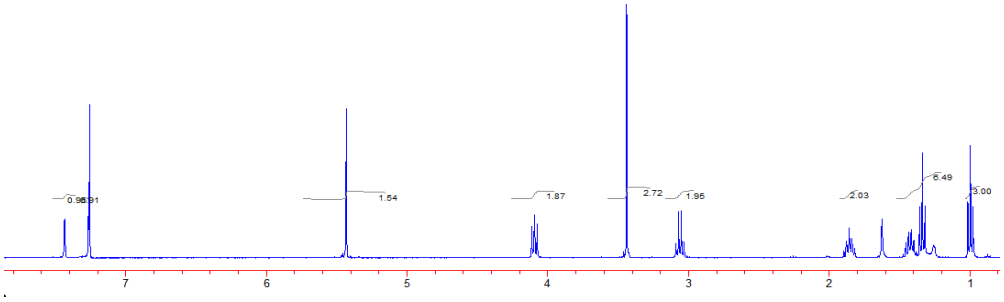


Fig. S23 ^{1}H NMR spectrum of IM(1O1)24-TFSA.

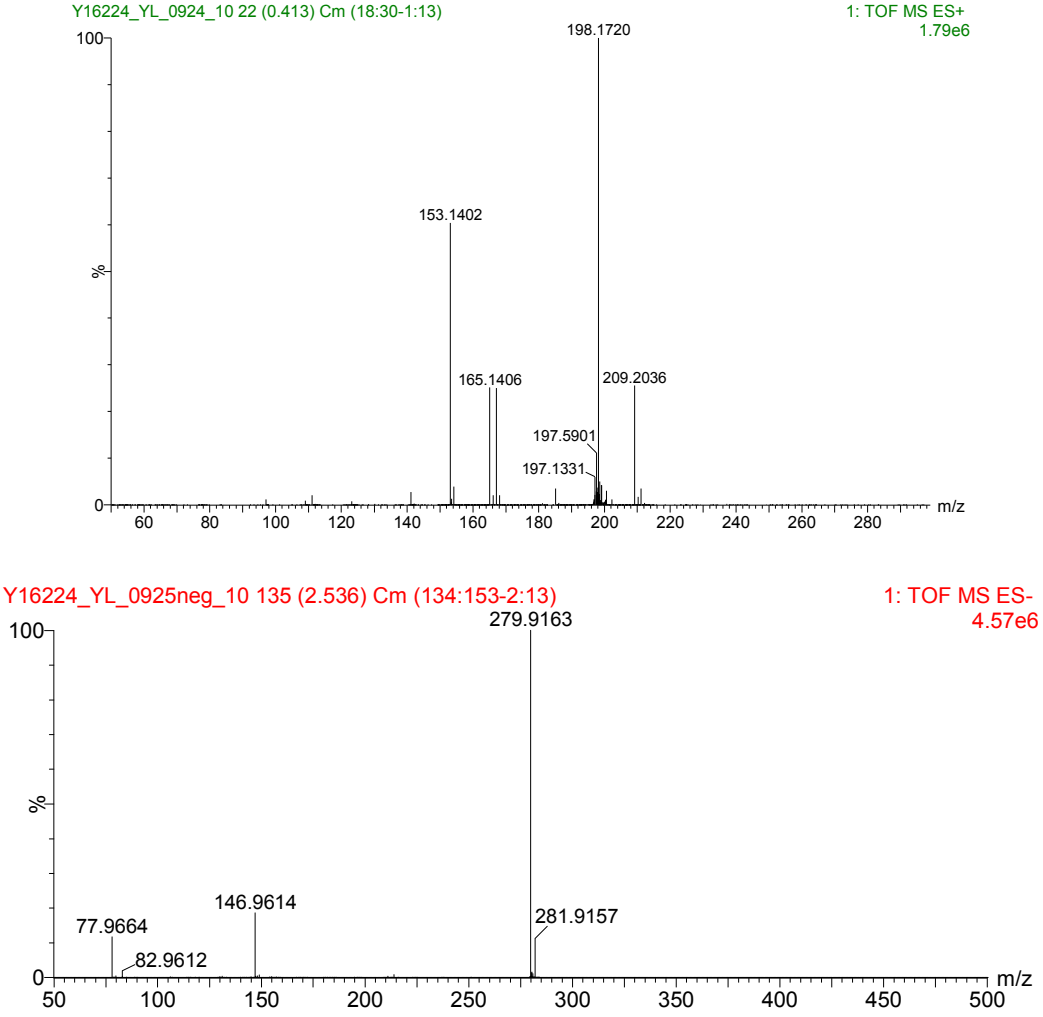


Fig. S24 HRMS spectrum of IM(1O1)24-TFSA.

1.2.11. 1-methoxymethyl-2-ethyl-3-(2-ethoxymethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)2(2o1)-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with 2-ethoxymethyl bromide (6.1 g, 43 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.4 g (80 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (d, 1H), 7.27 (d, 1H), 5.43 (s, 2H), 4.12-4.07 (t, 2H), 3.44 (s, 3H), 3.09-3.03 (m, 2H), 1.90-1.81 (m, 2H), 1.46-1.39 (m, 2H), 1.36-1.31 (t, 3H), 1.02-0.97 (t, 3H); ^{13}C NMR: δ (ppm) 148.63, 124.61-115.01, 121.89, 121.10, 79.37, 57.07, 48.17, 31.75, 19.41, 17.04, 13.18,

11.64. HRMS (ESI): m/z calcd for [IM(1O1)2(2o1)$^+$]: 200.1525; found:200.1509; m/z calcd for [TFSA$^-$]: 279.9173; found: 279.9167.

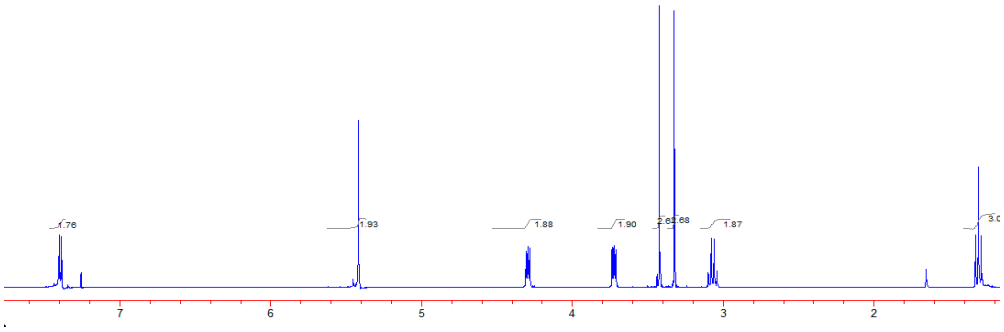
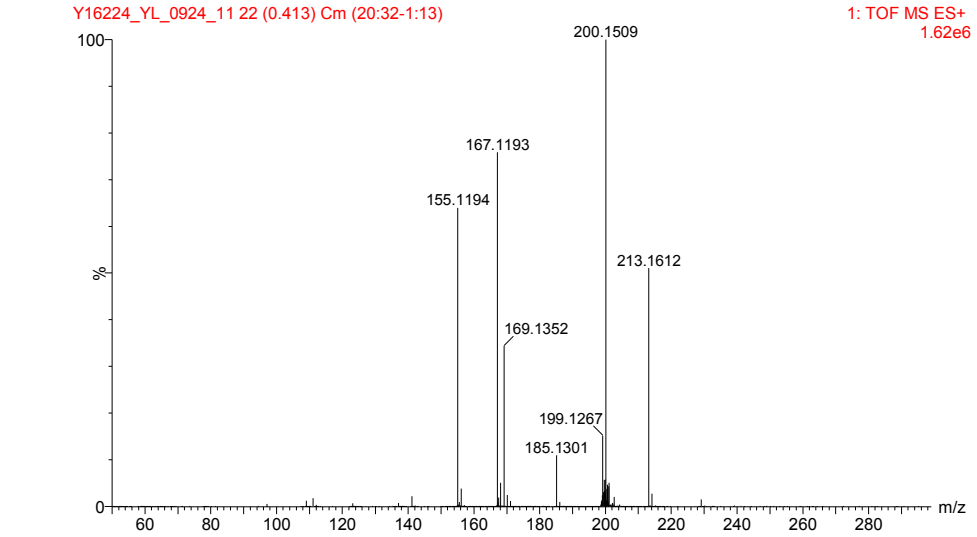


Fig. S25 ^{1}H NMR spectrum of IM(1O1)2(2o1)-TFSA.



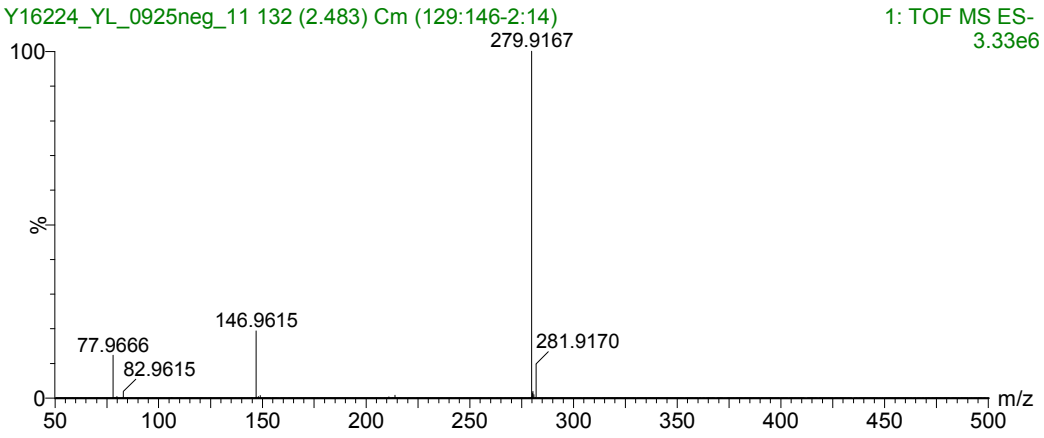


Fig. S26 HRMS spectrum of IM(1O1)2(2o1)-TFSA.

1.2.12. 1-methoxymethyl-2-ethyl-3-(2-ethoxyethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O1)2(2o2)-TFSA)

IM(1O1)2 (5.0 g, 36 mmol) reacted with 2-ethoxyethyl bromide (6.6 g, 43 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 14.1 g (82 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (m, 2H), 5.43 (s, 2H), 4.31-4.29 (t, 2H), 3.78-3.75 (t, 2H), 3.51-3.45 (m, 2H), 3.43 (s, 3H), 3.11-3.06 (m, 2H), 1.34-1.30 (t, 3H), 1.15-1.11 (t, 3H); ^{13}C NMR: δ (ppm) 149.56, 124.65-115.07, 121.78, 121.62, 79.42, 67.90, 66.77, 57.16, 48.63, 17.10, 14.69, 11.66. HRMS (ESI): m/z calcd for [IM(1O1)2(2o2)$^{+}$]: 214.1681; found:214.1662; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9158.

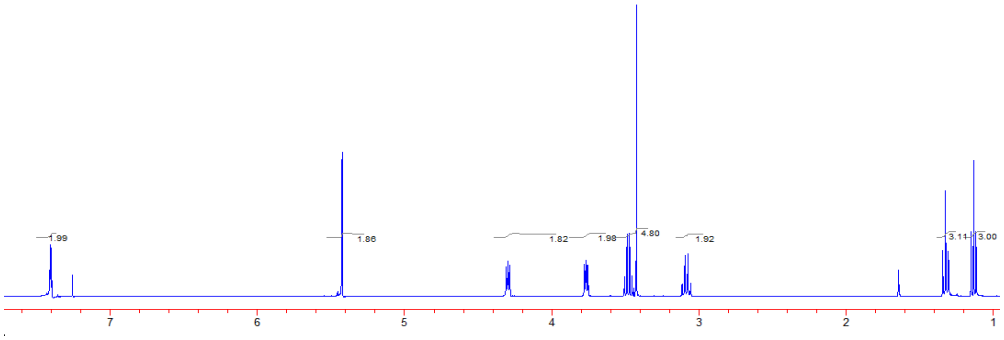


Fig. S27 ^{1}H NMR spectrum of IM(1O1)2(2o2)-TFSA.

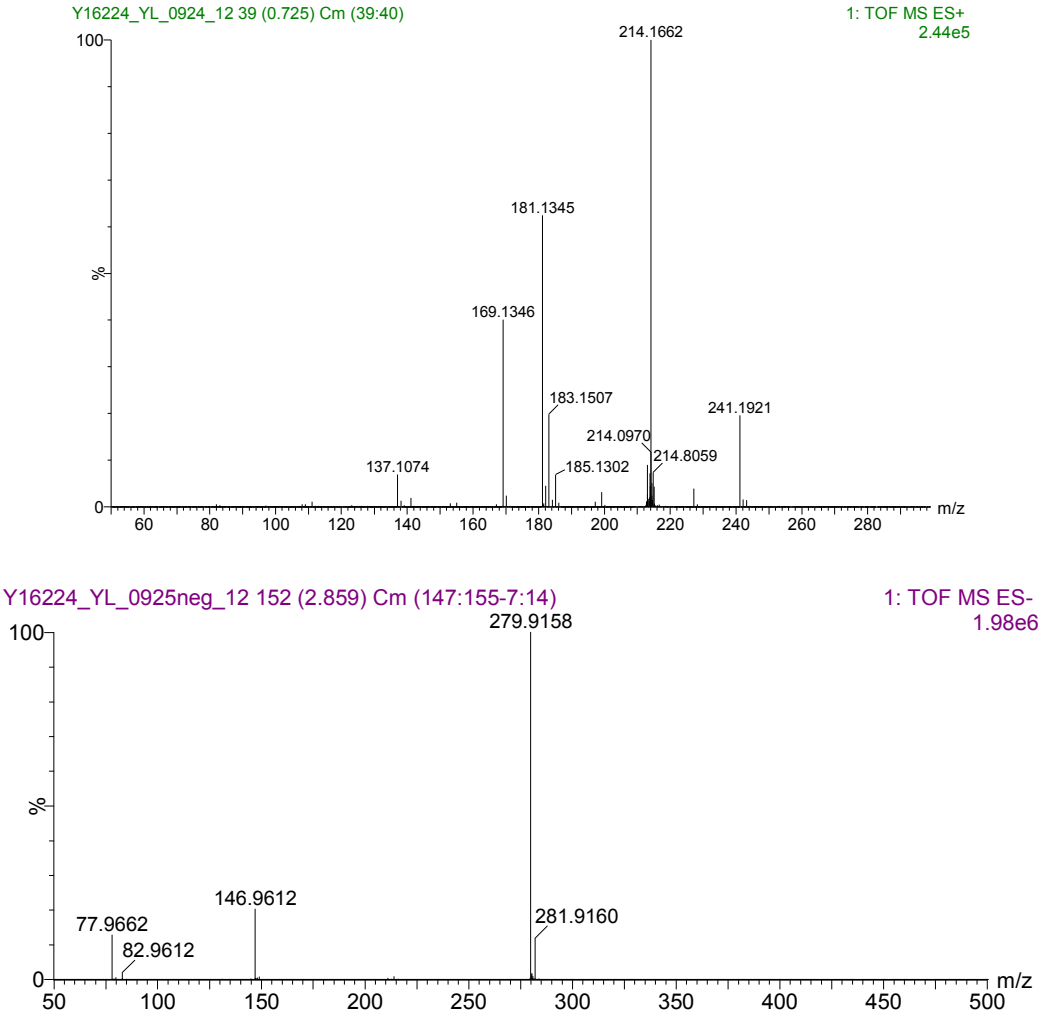


Fig. S28 HRMS spectrum of IM(1O1)2(2o2)-TFSA.

1.2.13. 1-ethoxyethyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)11-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with Iodomethane (6.0 g, 43 mmol) at room temperature for 24 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were similar with IM(1O1)11-TFSA. Yield 11.8 g (78 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32 (d, 1H), 7.22 (d, 1H), 5.42 (s, 2H), 3.82 (s, 3H), 3.60-3.54 (m, 2H), 2.66 (s, 3H), 1.29-1.19 (t, 3H); ^{13}C NMR: δ (ppm) 145.15, 124.65-115.07, 122.45, 121.16, 85.88, 78.23, 36.15, 14.51, 9.57. HRMS (ESI): m/z calcd for $[IM(1O2)11^+]$: 156.1263; found:156.1243; m/z

calcd for [TFSA$^-$]: 279.9173; found: 279.9167.

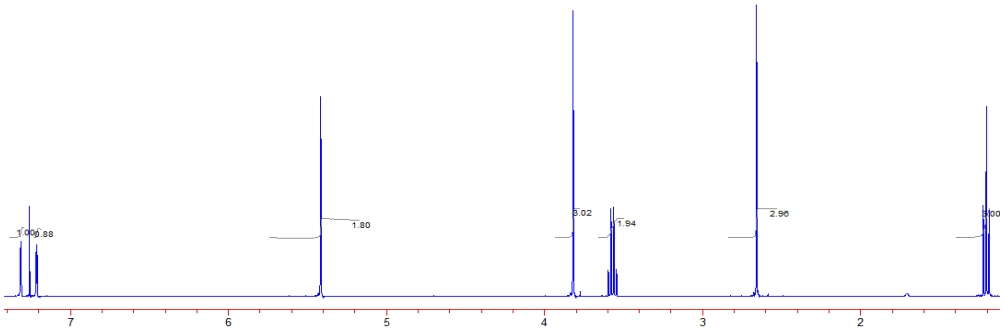


Fig. S29 ^{1}H NMR spectrum of IM(1O2)11-TFSA.

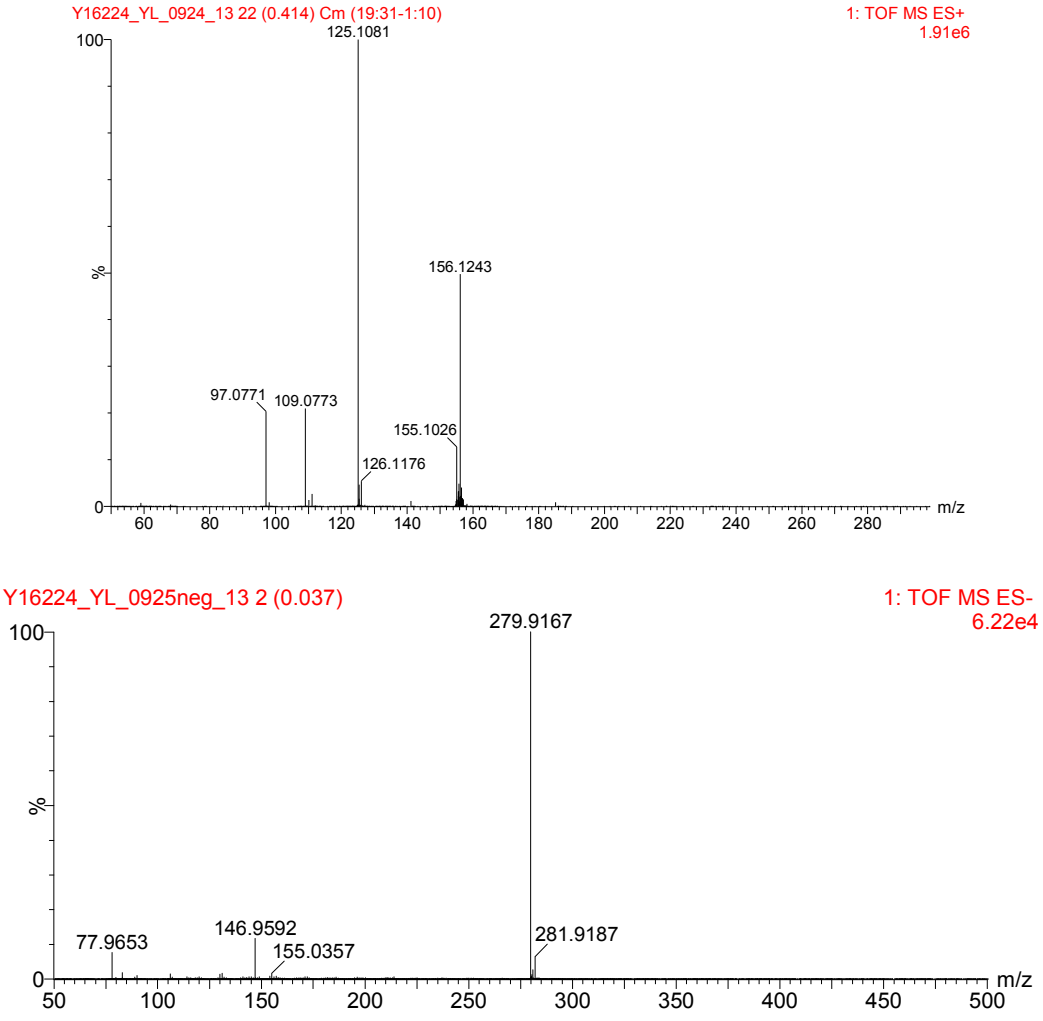


Fig. S30 HRMS spectrum of IM(1O2)11-TFSA.

1.2.14. 1-ethoxymethyl-2-methyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)12-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with bromoethane (7.8 g, 72 mmol) 30 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were similar with IM(1O1)12-TFSA. Yield 12.6 g (81 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 1H), 7.27 (d, 1H), 5.43 (s, 2H), 4.19-4.13 (m, 2H), 3.61-3.55 (m, 2H), 2.69 (s, 3H), 1.52-1.48 (t, 3H), 1.23-1.19 (t, 3H); ^{13}C NMR: δ (ppm) 144.35, 124.69-115.12, 121.63, 120.55, 78.25, 65.98, 43.89, 14.69, 14.53, 9.59. HRMS (ESI): m/z calcd for [IM(1O2)12^{+}]: 170.1419; found:170.1403; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9169.

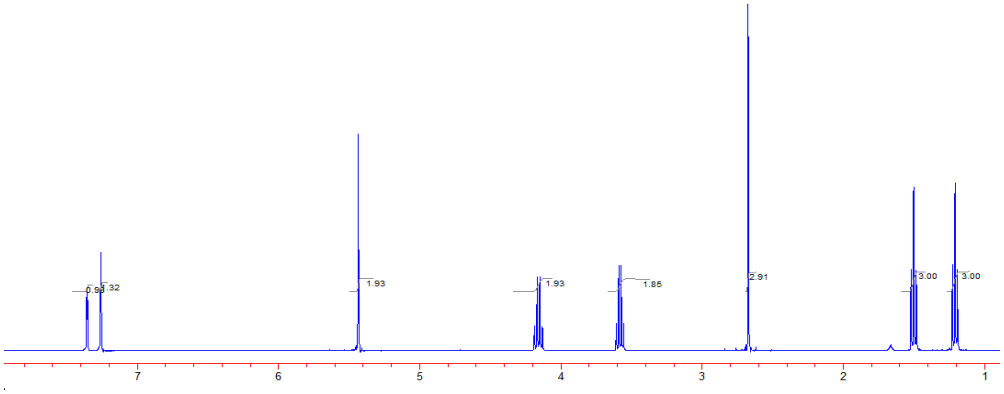


Fig. S31 ^{1}H NMR spectrum of IM(1O2)12-TFSA.

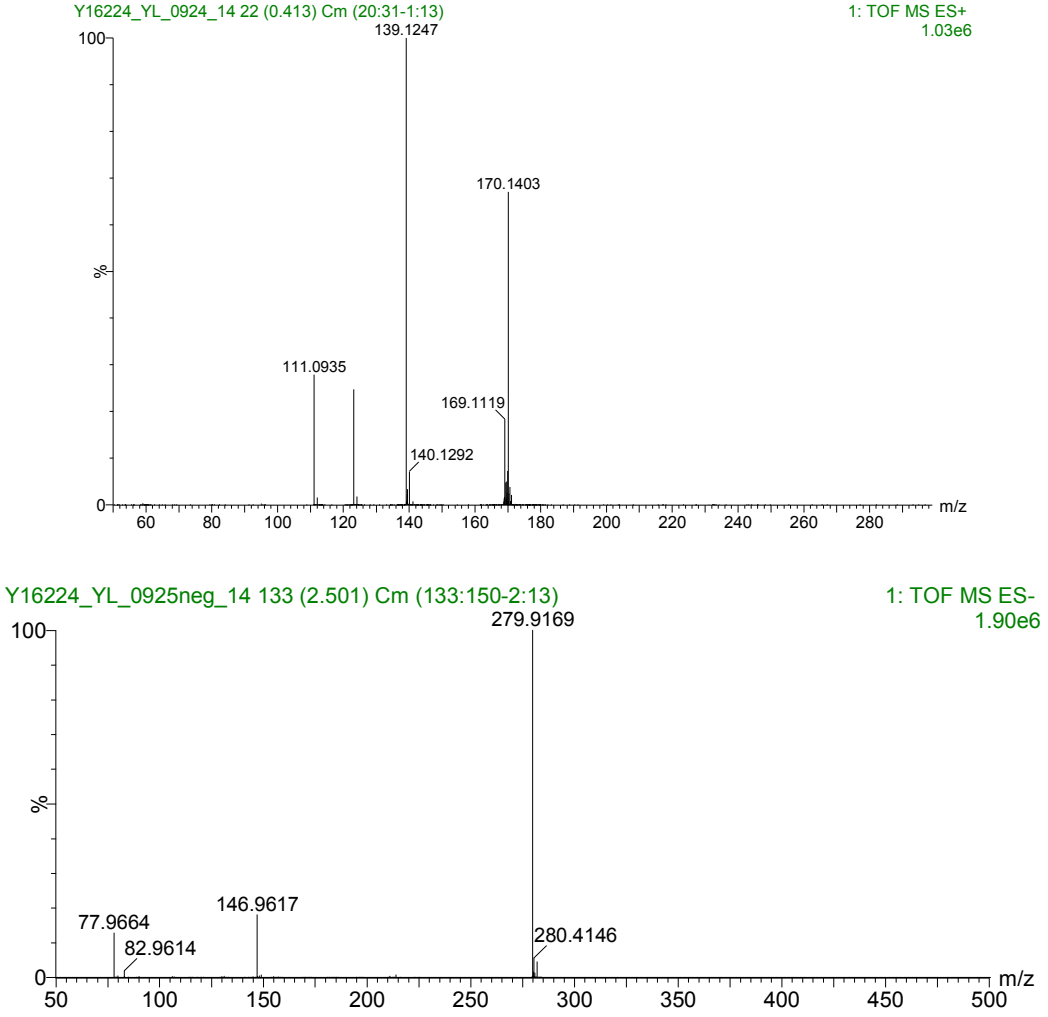


Fig. S32 HRMS spectrum of IM(1O2)12-TFSA.

1.2.15. 1-ethoxymethyl-2-methyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)13-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with 1-bromopropane (8.9 g, 72 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.4 g (83 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (d, 1H), 7.24 (d, 1H), 5.45 (s, 2H), 4.09-4.04(t, 2H), 3.62-3.56 (m, 2H), 2.68 (s, 3H), 1.93-1.82 (m, 2H), 1.24-1.19 (t, 3H), 1.02-0.97 (t, 3H); ^{13}C NMR: δ (ppm) 144.53, 124.64-115.08, 121.49, 121.19, 78.19, 66.83, 50.06, 22.83, 14.48, 10.43, 9.54. HRMS (ESI): m/z calcd for

[IM(1O2)13^{+}]: 184.1576; found:184.1554; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9166.

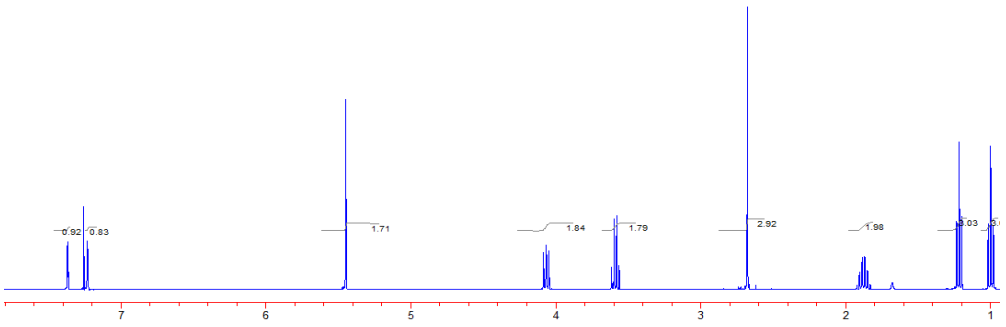


Fig. S33 ^{1}H NMR spectrum of IM(1O2)13-TFSA.

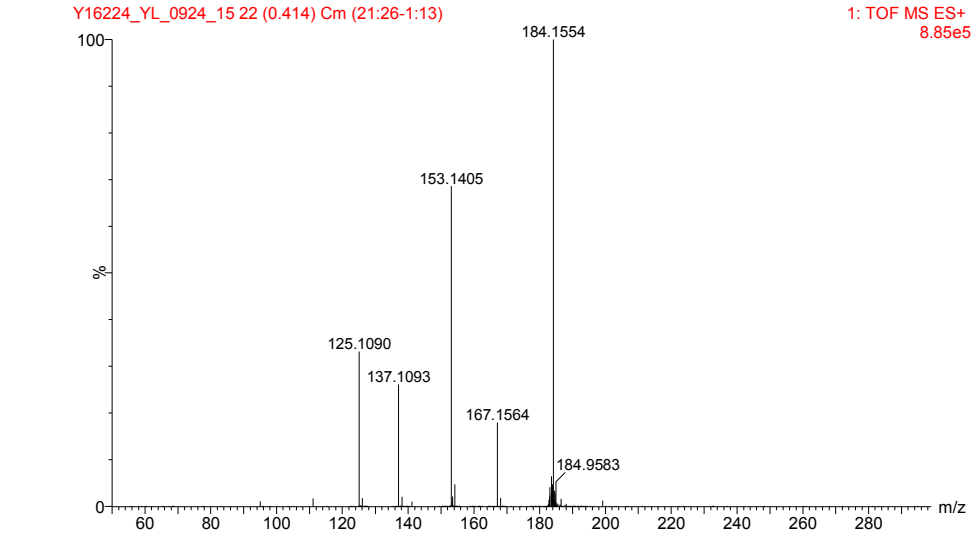


Fig. S34 HRMS spectrum of IM(1O2)13-TFSA.

1.2.16. 1-ethoxymethyl-2-methyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)14-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with 1-bromobutane (10.0 g, 72 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.3 g (80 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, 1H), 7.23 (d, 1H), 5.45 (s, 2H), 4.12-4.06 (t, 2H), 3.62-3.56 (m, 2H), 2.68 (s, 3H), 1.85-1.77 (m, 2H), 1.45-1.34 (m, 2H), 1.24-1.19 (t, 3H), 1.00-0.95 (t, 3H); ^{13}C NMR: δ (ppm) 144.47, 124.65-115.07, 121.47, 121.15, 78.18, 65.80, 48.47, 31.38, 19.41, 14.46, 13.21, 9.52. HRMS (ESI): m/z calcd for [IM(1O2)14^{+}]: 198.1732; found:198.1715; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9170.

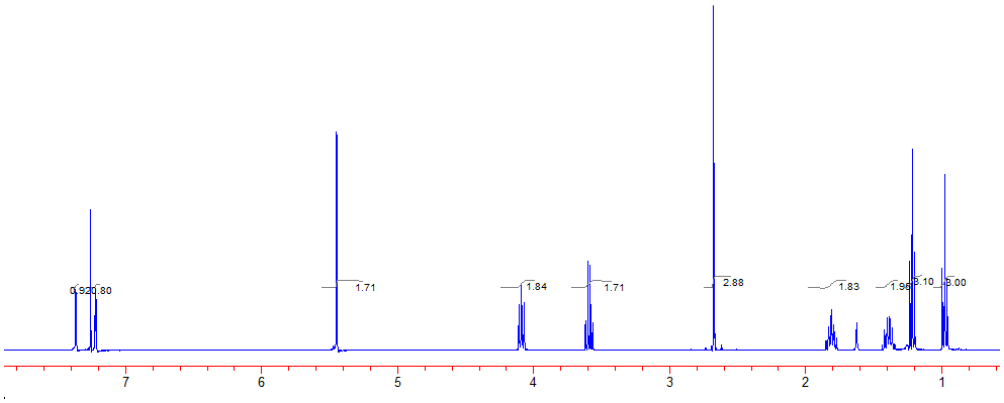


Fig. S35 ^{1}H NMR spectrum of IM(1O2)14-TFSA.

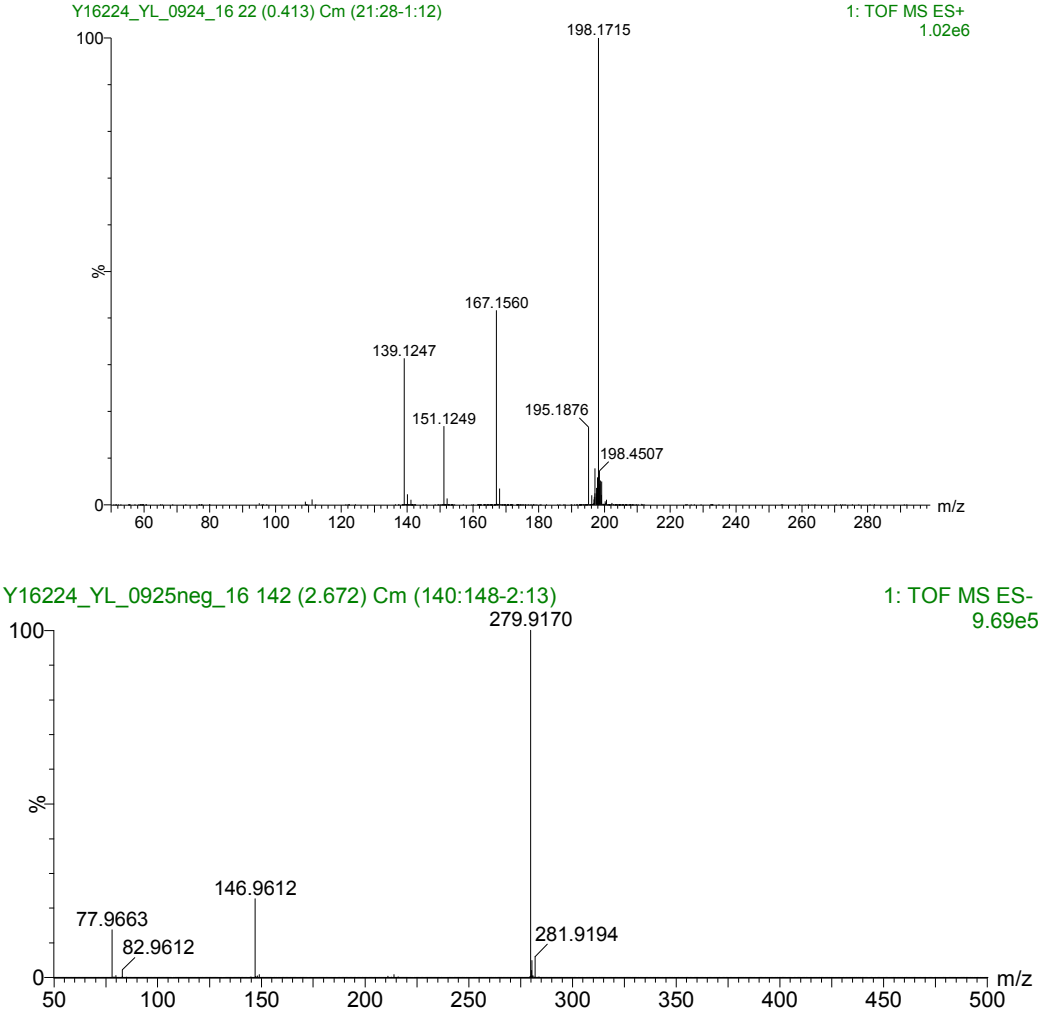


Fig. S36 HRMS spectrum of IM(1O2)14-TFSA.

1.2.17. 1-ethoxymethyl-2-methyl-3-(2-methoxyethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)1(2o1)-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with 2-ethoxymethyl bromide (6.1 g, 43 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.8 g (82 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.35 (d, 1H), 7.34 (d, 1H), 5.43 (s, 2H), 4.29-4.25 (t, 2H), 3.70-3.67 (t, 2H), 3.60-3.54 (m, 2H), 3.30 (s, 3H), 2.66 (s, 3H), 1.22-1.17 (t, 3H); ^{13}C NMR: δ (ppm) 145.57, 124.68-115.10, 121.65, 121.41, 78.25, 70.18, 65.89, 58.88, 48.68, 14.55, 9.89. HRMS (ESI): m/z

calcd for [IM(1O2)1(2o1)$^{+}$]: 200.1525; found:200.1499; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9177.

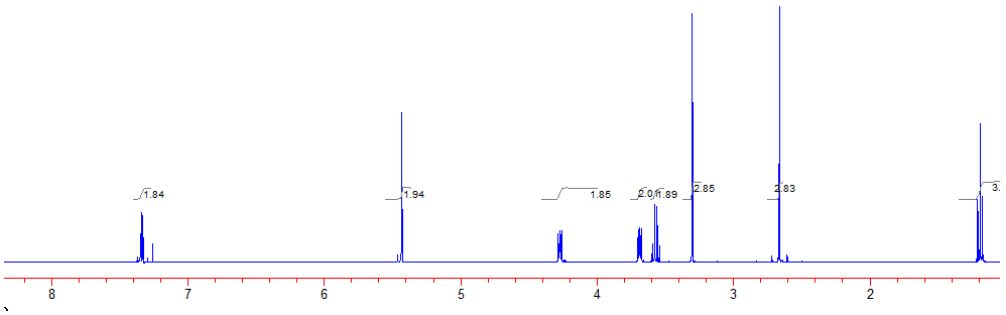
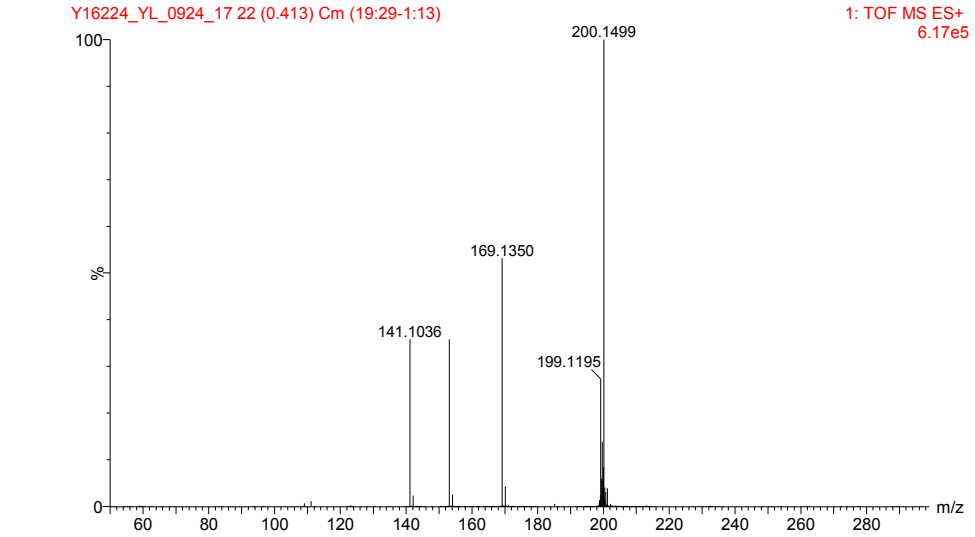


Fig. S37 ^{1}H NMR spectrum of IM(1O2)1(2o1)-TFSA.



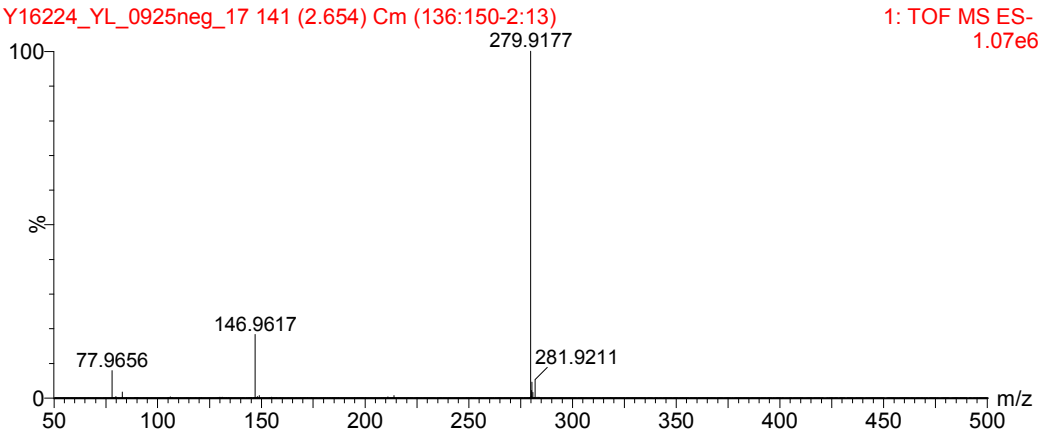


Fig. S38 HRMS spectrum of IM(1O2)1(2o1)-TFSA.

1.2.18. 1-ethoxymethyl-2-methyl-3-(2-ethoxyethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)1(2o2)-TFSA)

IM(1O2)1 (5.0 g, 36 mmol) reacted with 2-ethoxyethyl bromide (6.6 g, 43 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 14.4 g (83 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37-7.35 (m, 2H), 5.45 (s, 2H), 4.32-4.27 (t, 2H), 3.77-3.71 (m, 2H), 3.62-3.56 (m, 2H), 3.50-3.44 (m, 2H), 2.70 (s, 3H), 1.24-1.20 (t, 3H), 1.16-1.11 (t, 3H); ^{13}C NMR: δ (ppm) 145.66, 124.68-115.11, 121.64, 121.46, 78.28, 68.14, 66.80, 65.87, 48.89, 14.87, 14.57, 10.02. HRMS (ESI): m/z calcd for [IM(1O2)1(2o2)$^{+}$]: 214.1681; found:214.1677; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9165.

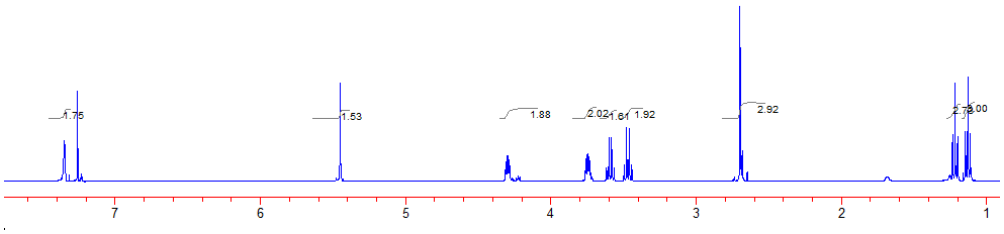


Fig. S39 ^{1}H NMR spectrum of IM(1O2)1(2o2)-TFSA.

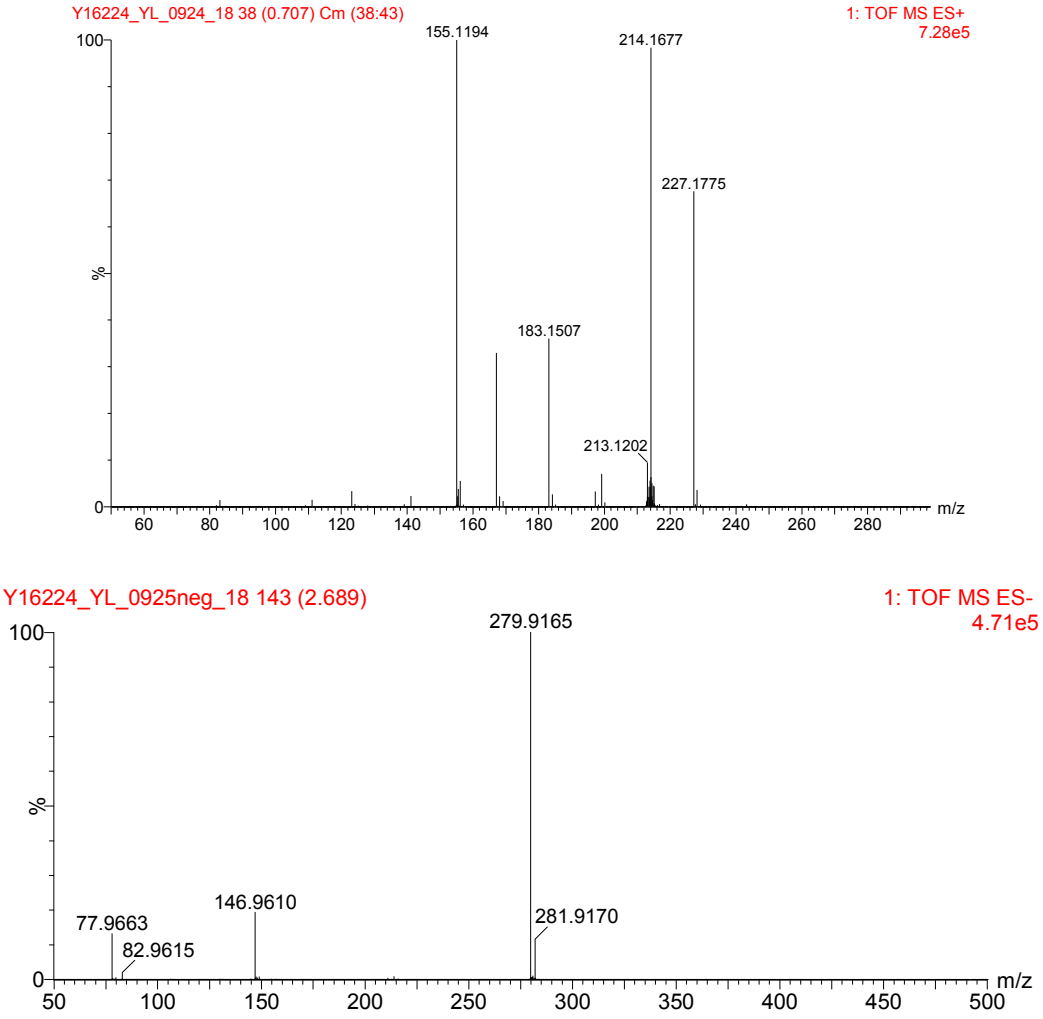


Fig. S40 HRMS spectrum of IM(1O2)1(2o2)-TFSA.

1.2.19. 1-ethoxymethyl-2-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)21-TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with Iodomethane (5.9 g, 42 mmol) at room temperature for 24 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were similar with IM(1O1)11-TFSA. Yield 12.1 g (80 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 1H), 7.25 (d, 1H), 5.43 (s, 2H), 3.84 (s, 3H), 3.60-3.54 (m, 2H), 3.07-3.00 (m, 2H), 1.33-1.28 (t, 3H), 1.22-1.17 (t, 3H); ^{13}C NMR: δ (ppm) 148.90, 124.63-115.05, 122.57, 121.33, 78.06, 65.73, 34.86, 17.11, 14.45, 10.98. HRMS (ESI): m/z calcd for

[IM(1O2)21^{+}]: 170.1419; found:170.1405; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9164.

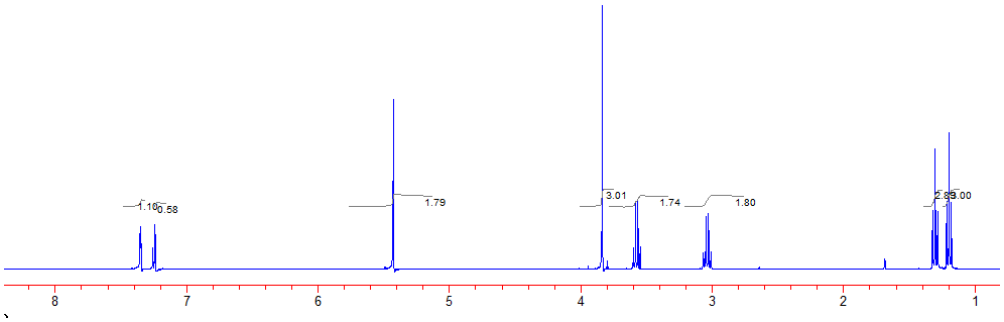
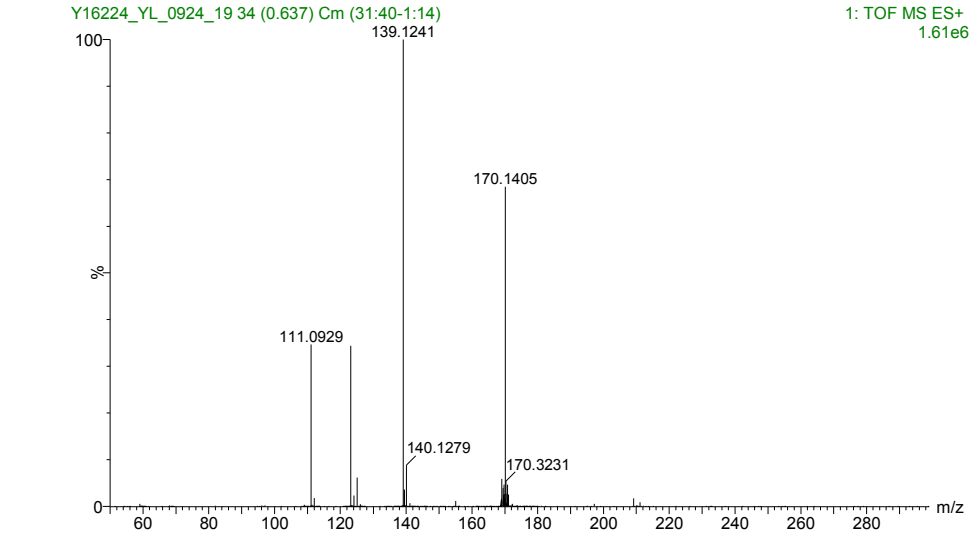


Fig. S41 ^{1}H NMR spectrum of IM(1O2)21-TFSA.



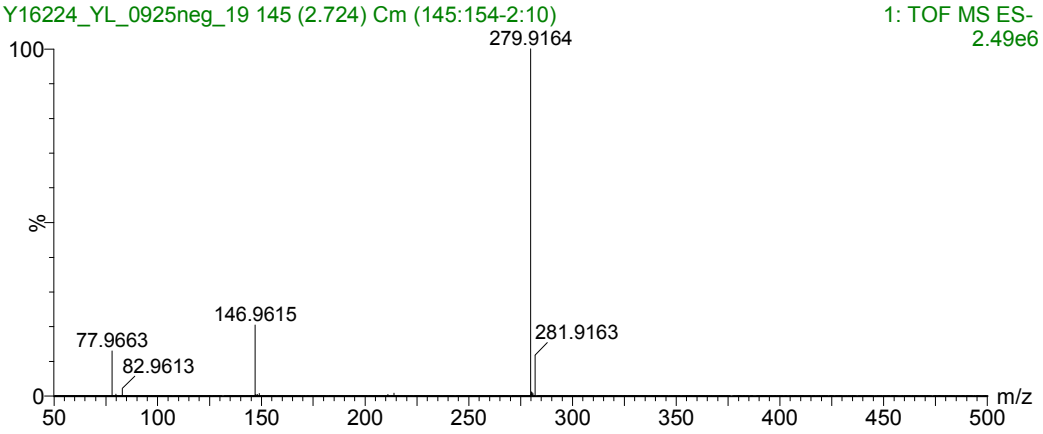


Fig. S42 HRMS spectrum of IM(1O2)21-TFSA.

1.2.20. 1-ethoxymethyl-2,3-diethylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)22-TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with 1-bromoethane (7.6 g, 70 mmol) at 30 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.1 g (84 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, 1H), 7.31 (d, 1H), 5.46 (s, 2H), 4.21-4.15 (m, 2H), 3.64-3.58 (m, 2H), 3.10-3.03 (m, 2H), 1.57-1.52 (t, 3H), 1.36-1.31 (t, 3H), 1.25-1.20 (t, 3H); ^{13}C NMR: δ (ppm) 148.41, 124.68-115.11, 121.93, 120.52, 78.10, 65.87, 43.51, 17.11, 14.99, 14.57, 11.76. HRMS (ESI): m/z calcd for [IM(1O2)22^{+}]: 184.1576; found:184.1553; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9173.

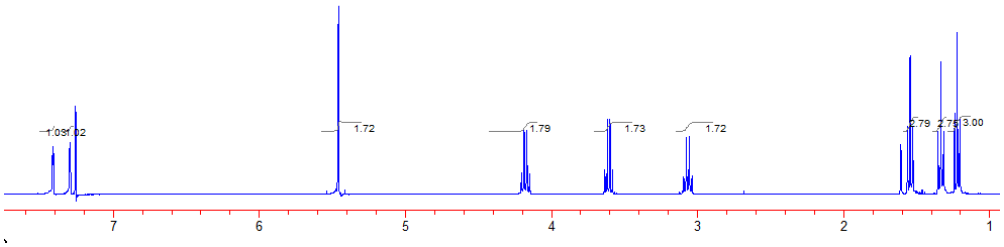


Fig. S43 ^{1}H NMR spectrum of IM(1O2)22-TFSA.

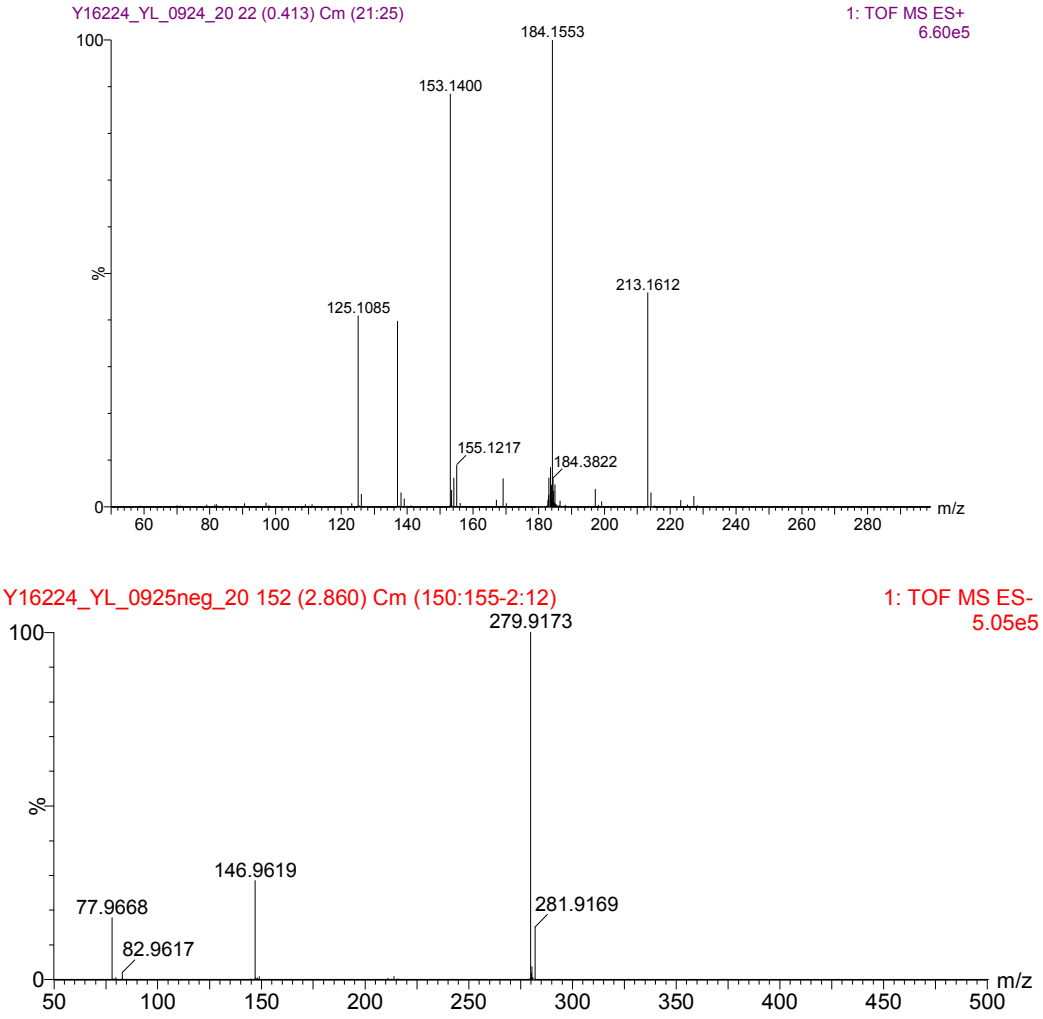


Fig. S44 HRMS spectrum of IM(1O2)22-TFSA.

1.2.21. 1-ethoxymethyl-2-ethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)23-TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with 1-boromopropane (8.6 g, 70 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.2 g (82 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, 1H), 7.28 (d, 1H), 5.46 (s, 2H), 4.08-4.04 (t, 2H), 3.64-3.57 (m, 2H), 3.09-3.03 (m, 2H), 1.94-1.88 (m, 2H), 1.36-1.31 (t, 3H), 1.24-1.20 (t, 3H), 1.04-1.00 (t, 3H); ^{13}C NMR: δ (ppm) 148.60, 124.70-115.12, 121.89, 121.08, 78.16, 65.93, 49.81, 23.27, 17.15, 14.60, 11.86, 10.54.

HRMS (ESI): m/z calcd for [IM(1O2)23^{+}]: 198.1732; found:198.1715; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9160.

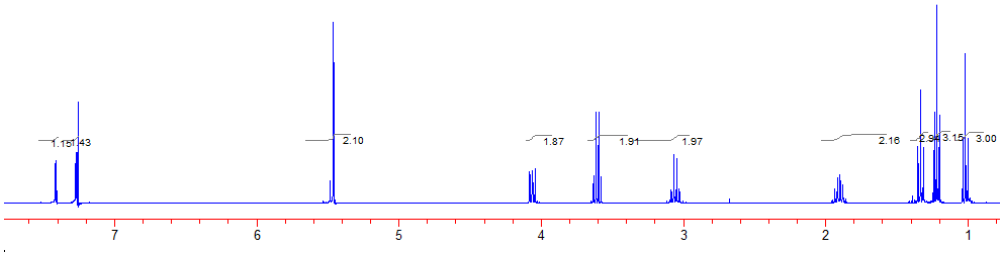
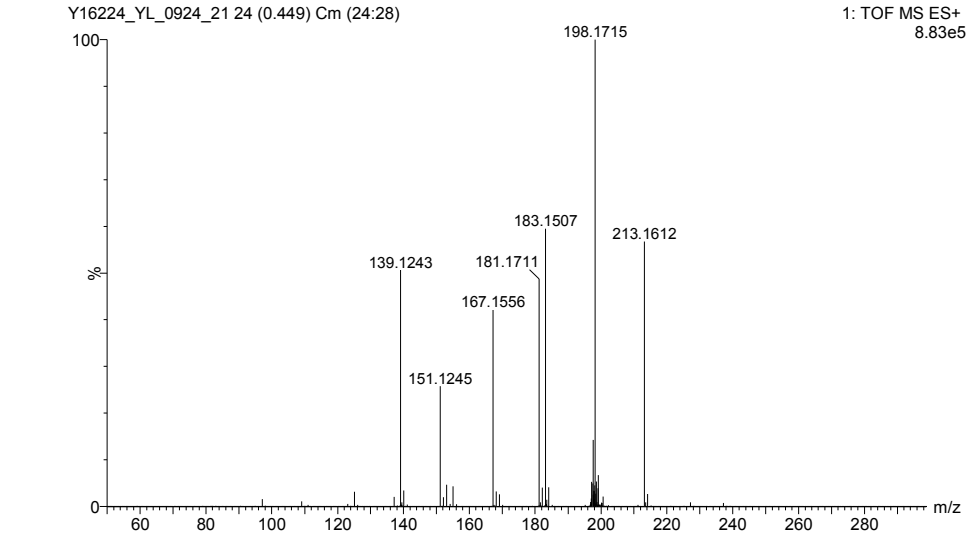


Fig. S45 ^{1}H NMR spectrum of IM(1O2)23-TFSA.



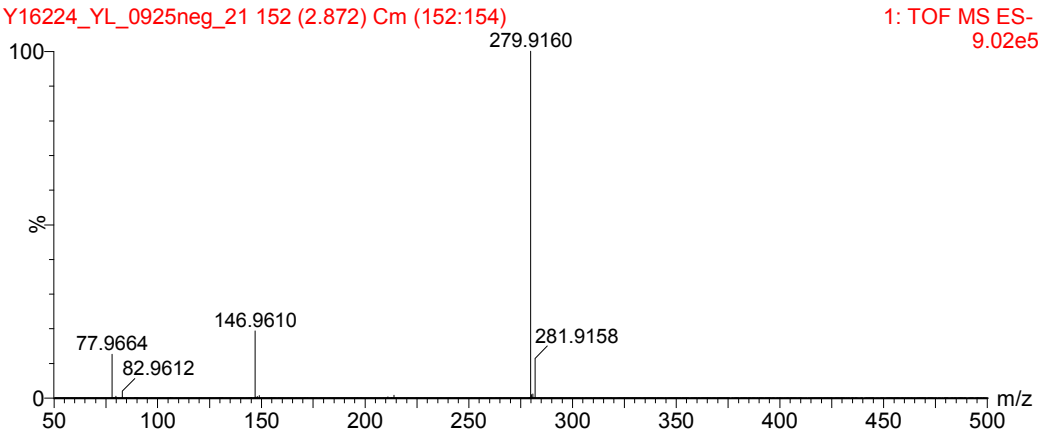


Fig. S46 HRMS spectrum of IM(1O2)23-TFSA.

1.2.22. 1-ethoxymethyl-2-ethyl-3-butylimidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)24-TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with 1-bromobutane (9.6 g, 70 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.1 g (79 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (d, 1H), 7.27 (d, 1H), 5.46 (s, 2H), 4.11-4.06 (t, 2H), 3.64-3.57 (m, 2H), 3.09-3.01 (m, 2H), 1.88-1.80 (m, 2H), 1.45-1.36 (m, 2H), 1.36-1.30 (t, 3H), 1.24-1.19 (t, 3H), 1.01-0.96 (t, 3H); ^{13}C NMR: δ (ppm) 148.53, 124.71-115.14, 121.93, 121.09, 78.20, 65.98, 48.28, 31.90, 19.58, 17.20, 14.64, 13.39, 11.89. HRMS (ESI): m/z calcd for [IM(1O2)24^{+}]: 212.1889; found:212.1882; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9167.

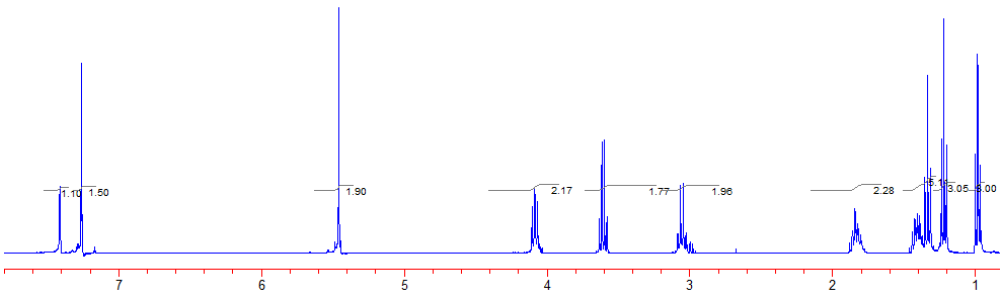


Fig. S47 ^{1}H NMR spectrum of IM(1O2)24-TFSA.

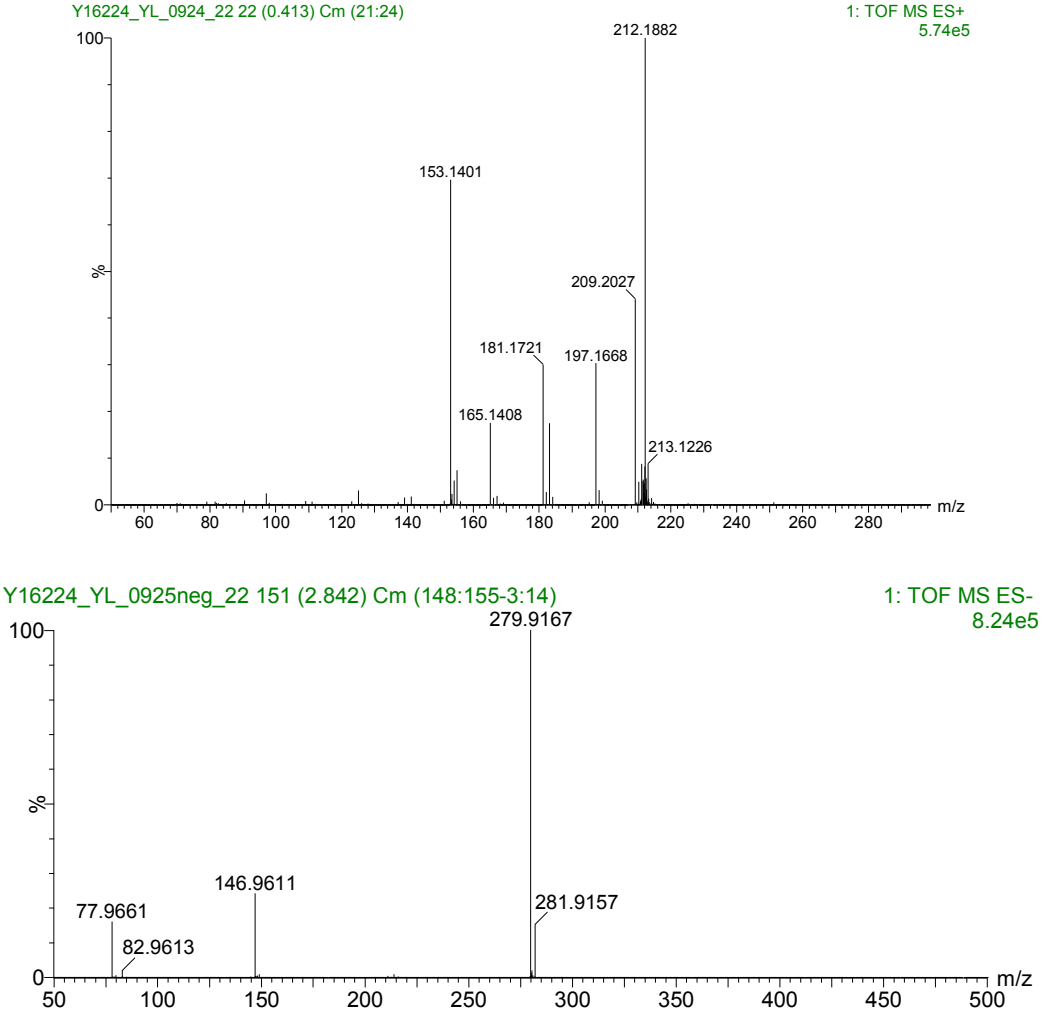


Fig. S48 HRMS spectrum of IM(1O2)24-TFSA.

1.2.23. 1-ethoxymethyl-2-ethyl-3-(2-ethoxymethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)2(2o1)-TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with 2-ethoxymethyl bromide (5.9 g, 42 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (5 mL) as solvent. The other procedures were identical with IM(1O1)12-TFSA. Yield 13.9 g (83 %) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41-7.37 (m, 2H), 5.45 (s, 2H), 4.31-4.26 (m, 2H), 3.73-3.71 (t, 2H), 3.62-3.58 (m, 2H), 3.32 (s, 3H), 3.10-3.05 (m, 2H), 1.33-1.30 (t, 2H), 1.23-1.20 (t, 3H); ^{13}C NMR: δ (ppm) 149.42, 124.71-115.11, 121.68, 121.60, 78.15, 69.98, 66.93, 58.88, 48.47, 17.16, 14.59, 11.72.

HRMS (ESI): m/z calcd for [IM(1O2)2(2o1)$^{+}$]: 214.1681; found:214.1683; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9165.

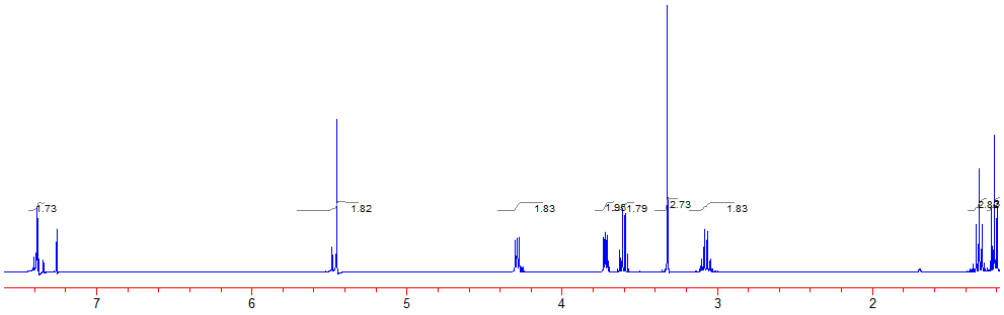
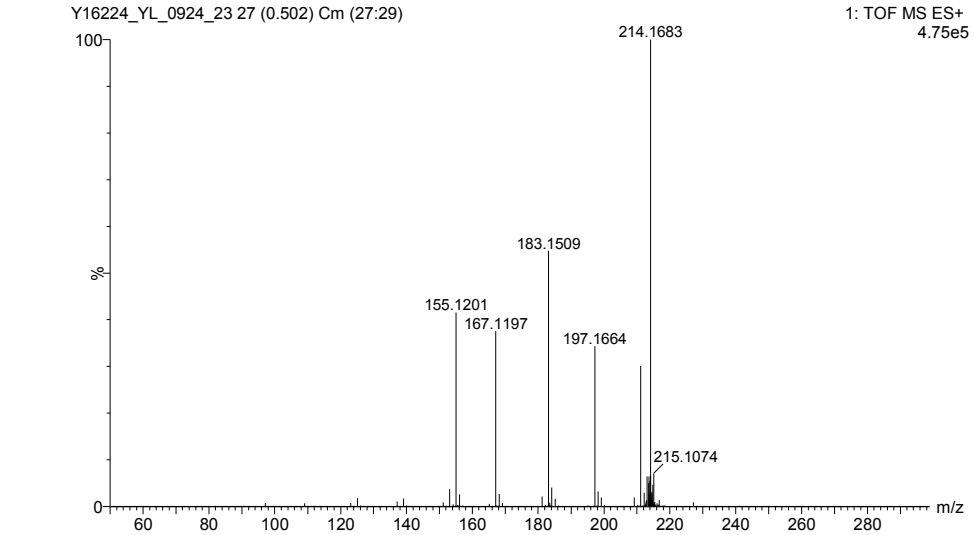


Fig. S49 ^{1}H NMR spectrum of IM(1O2)2(2o1)-TFSA.



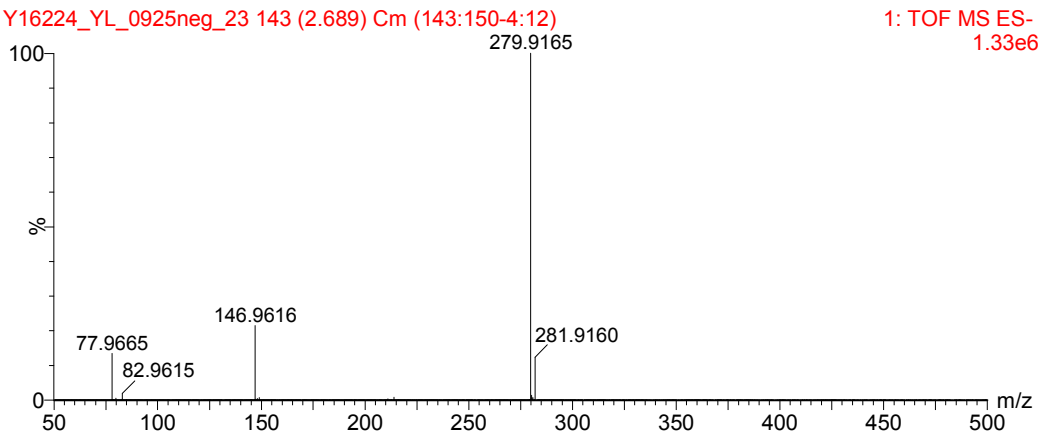


Fig. S50 HRMS spectrum of IM(1O2)2(2o1)-TFSA.

1.2.24. 1-ethoxymethyl-2-ethyl-3-(2-ethoxyethyl)-imidazolium bis(trifluoromethanesulfonyl)imide (IM(1O2)2(2o2)TFSA)

IM(1O2)2 (5.4 g, 35 mmol) reacted with 2-ethoxyethyl bromide (6.4 g, 42 mmol) at 60 ^{o}C for 48 hours in a 250 mL flask with acetonitrile (10 mL) as solvent. The other procedures were identical with IM1(1O2)2TFSA. Yield 16.6 g (92 %) as colorless liquid (water content, 33 ± 1 ppm) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ (ppm) 7.39 (s, 2H), 5.46 (s, 2H), 4.31-4.28 (t, 2H), 3.77-3.75 (t, 2H), 3.63-3.58 (m, 2H), 3.51-3.44 (m, 2H), 3.12-3.06(m, 2H), 3.32 (s, 3H), 3.10-3.05 (m, 2H), 1.33-1.30 (t, 2H), 1.23-1.20 (t, 3H), 1.15-1.20 (t, 3H); ^{13}C NMR: δ (ppm) 149.43, 124.73-115.16, 121.68, 121.53, 78.11, 67.94, 66.75, 65.82, 48.59, 17.11, 14.70, 14.54, 11.69. HRMS (ESI): m/z calcd for [IM(1O2)2(2o2)$^{+}$]: 228.1838; found:228.1812; m/z calcd for [TFSA^{-}]: 279.9173; found: 279.9165.

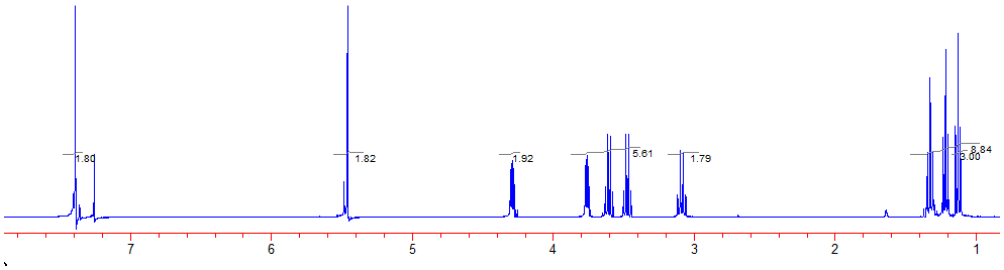


Fig. S51 ^{1}H NMR spectrum of IM(1O2)2(2o2)-TFSA.

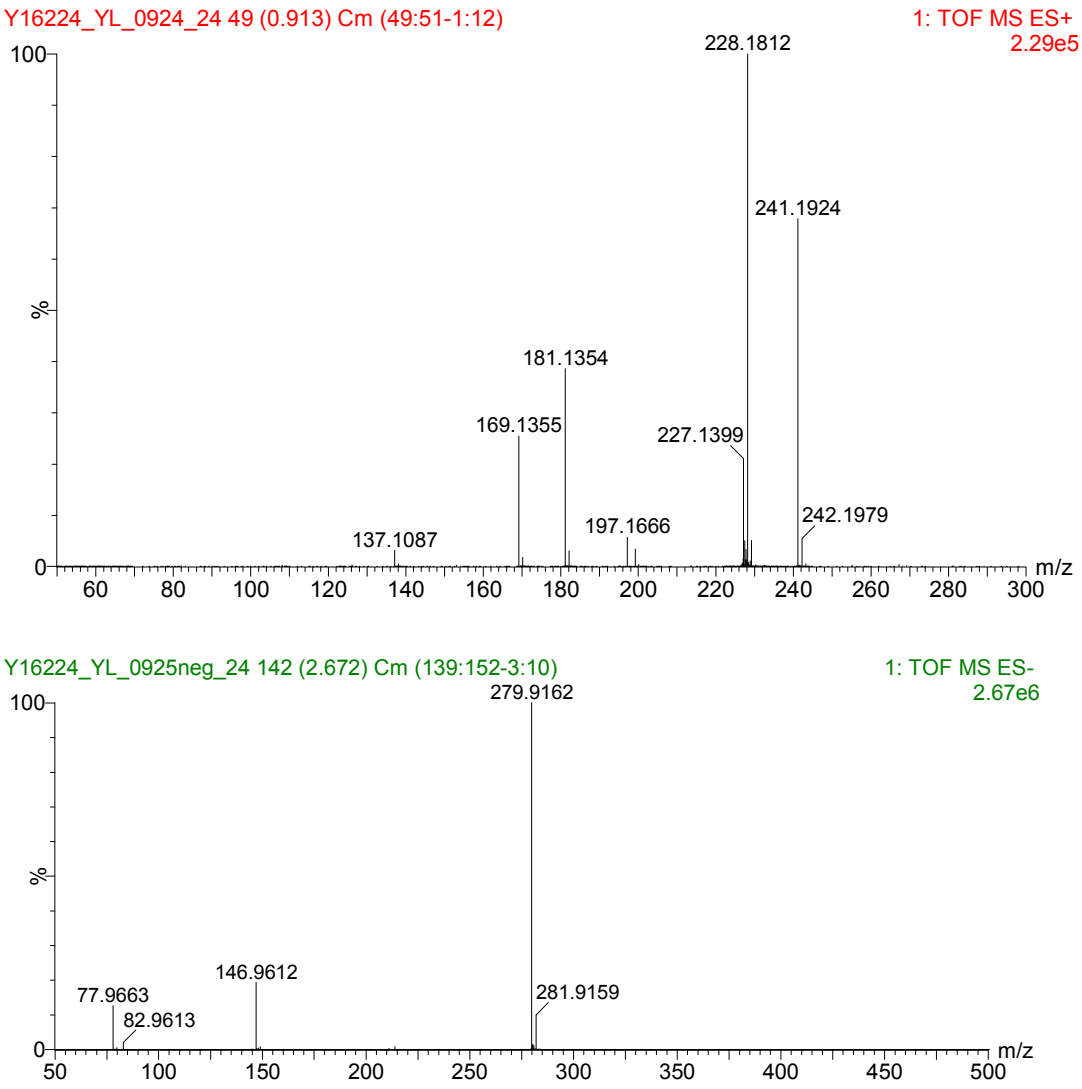


Fig. S52 HRMS spectrum of IM(1O2)2(2o2)-TFSA.

Table S1

VTF equation parameters of viscosity for the ILs.

ILs	η_o (cP)	B (K)	T_o (K)	R^2
IM(1O1)11-TFSA	0.217 (±15 %)	625.8 (±5 %)	194.8 (±1 %)	0.99993
IM(1O1)12-TFSA	-	-	-	-
IM(1O1)13-TFSA	0.081 (±3 %)	847.0 (±2 %)	179.6 (±1 %)	0.99999
IM(1O1)14-TFSA	0.061 (±11%)	951.5 (±3 %)	170.3 (±1 %)	0.99998
IM(1O1)1(2o1)-TFSA	0.124 (±9 %)	785.6 (±4 %)	184.8 (±1 %)	0.99998
IM(1O1)1(2o2)-TFSA	0.136 (±6 %)	736.1 (±2 %)	181.5 (±1 %)	0.99999
IM(1O1)21-TFSA	0.165 (±7 %)	698.3 (±3 %)	189.8 (±1 %)	0.99999
IM(1O1)22-TFSA	0.094 (±10 %)	834.3 (±3 %)	176.2 (±1 %)	0.99998
IM(1O1)23-TFSA	0.087 (±6 %)	813.6 (±3 %)	179.1 (±1 %)	0.99999
IM(1O1)24-TFSA	0.135 (±14 %)	752.8 (±5 %)	186.4 (±1 %)	0.99996
IM(1O1)2(2o1)-TFSA	0.126 (±1 %)	740.2 (±3 %)	187.6 (±1 %)	0.99998
IM(1O1)2(2o2)-TFSA	0.131 (±8 %)	724.6 (±3 %)	187.5 (±1 %)	0.99999
IM(1O2)11-TFSA	0.131 (±5 %)	737.3 (±2 %)	184.7 (±1 %)	1
IM(1O2)12-TFSA	-	-	-	-
IM(1O2)13-TFSA	0.111 (±10 %)	764.3 (±3 %)	183.9 (±1 %)	0.99998
IM(1O2)14-TFSA	0.071 (±3 %)	887.3 (±1 %)	174.8 (±1 %)	1
IM(1O2)1(2o1)-TFSA	-	-	-	-
IM(1O2)1(2o2)-TFSA	0.105 (±7 %)	790.8 (±2 %)	180.8 (±1 %)	0.99999
IM(1O2)21-TFSA	0.095 (±5 %)	820.0 (±1 %)	178.9 (±1 %)	1
IM(1O2)22-TFSA	0.135 (±8 %)	726.6 (±3 %)	184.2 (±1 %)	0.99999
IM(1O2)23-TFSA	0.046 (±24 %)	1004.3 (±7 %)	167.3 (±3 %)	0.99993
IM(1O2)24-TFSA	0.084 (±16 %)	855.6 (±5 %)	176.9 (±2%)	0.99996
IM(1O2)2(2o1)-TFSA	0.134 (±16 %)	715.0 (±6 %)	188.2 (±2%)	0.99994
IM(1O2)2(2o2)-TFSA	0.176 (±11 %)	657.0 (±6 %)	191.5 (±2%)	0.99993

The percentage standard errors for η_o, B and T_o have been included, and R^2 is the VTF fitting parameter.

Table S2

VTF equation parameters of conductivity for the ILs

ILs	σ_0 (cP)	B (K)	T_o (K)	R^2
IM(1O1)11-TFSA	251.3 (±3%)	431.2 (±1%)	206.3 (±1%)	0.99999
IM(1O1)12-TFSA	-	-	-	-
IM(1O1)13-TFSA	197.4 (±15%)	398.2 (±8%)	213.7 (±2%)	0.99976
IM(1O1)14-TFSA	376.1 (±3%)	588.7 (±1%)	192.3 (±1%)	1
IM(1O1)1(2o1)-TFSA	310.7 (±4%)	543.3 (±2%)	204.0 (±1%)	0.99999
IM(1O1)1(2o2)-TFSA	275.6 (±4%)	526.4 (±2%)	202.8 (±1%)	0.99999
IM(1O1)21-TFSA	285.3 (±4%)	495.2 (±2%)	201.4 (±1%)	0.99999
IM(1O1)22-TFSA	262.0 (±3%)	479.5 (±1%)	201.0 (±1%)	0.99999
IM(1O1)23-TFSA	296.0 (±5%)	521.1 (±2%)	199.8 (±1%)	0.99998
IM(1O1)24-TFSA	344.3 (±5%)	583.5 (±2%)	193.5 (±1%)	0.99999
IM(1O1)2(2o1)-TFSA	285.5 (±4%)	518.3 (±2%)	200.0 (±1%)	0.99999
IM(1O1)2(2o2)-TFSA	255.8 (±4%)	517.4 (±2%)	199.8 (±1%)	0.99999
IM(1O2)11-TFSA	224.1 (±5%)	423.0 (±3%)	206.2 (±1%)	0.99998
IM(1O2)12-TFSA	-			
IM(1O2)13-TFSA	272.1 (±4%)	500.0 (±2%)	199.0 (±1%)	0.99999
IM(1O2)14-TFSA	340.5 (±3%)	586.0 (±1%)	191.7 (±1%)	1
IM(1O2)1(2o1)-TFSA	-	-	-	-
IM(1O2)1(2o2)-TFSA	268.2 (±4%)	531.9 (±2%)	195.3 (±1%)	0.99999
IM(1O2)21-TFSA	280.6 (±3%)	505.5 (±2%)	198.9 (±1%)	0.99999
IM(1O2)22-TFSA	253.0 (±3%)	485.5 (±2%)	198.5 (±1%)	0.99999
IM(1O2)23-TFSA	306.5 (±3%)	546.3 (±2%)	196.3 (±1%)	0.99999
IM(1O2)24-TFSA	310.4 (±8%)	572.6 (±4%)	194.6 (±1%)	0.99997
IM(1O2)2(2o1)-TFSA	277.0 (±6%)	524.6 (±3%)	198.4 (±1%)	0.99998
IM(1O2)2(2o2)-TFSA	286.8 (±9%)	555.8 (±5%)	194.6 (±1%)	0.99995

The percentage standard errors for σ_o, B and T_o have been included, and R^2 is the VTF fitting parameter.

Table S3

Cathodic and anodic limiting potentials (Versus Ag) and electrochemical windows of various ILs determined at 25 ^{o}C.

ILs	Cathodic limiting potential	Anodic limiting potential	Electrochemical window
	E vs (Ag)/V	E vs (Ag)/V	/V
IM(1O1)11-TFSA	-2.1	+2.2	4.3
IM(1O1)12-TFSA	-	-	-
IM(1O1)13-TFSA	-2.1	+2.2	4.3
IM(1O1)14-TFSA	-2.1	+2.3	4.4
IM(1O1)1(2o1)-TFSA	-2.0	+2.2	4.2
IM(1O1)1(2o2)-TFSA	-2.1	+2.2	4.3
IM(1O1)21-TFSA	-2.1	+2.3	4.4
IM(1O1)22-TFSA	-2.0	+2.3	4.3
IM(1O1)23-TFSA	-2.1	+2.2	4.3
IM(1O1)24-TFSA	-2.1	+2.3	4.4
IM(1O1)2(2o1)-TFSA	-2.0	+2.2	4.2
IM(1O1)2(2o2)-TFSA	-2.1	+2.2	4.3
IM(1O2)11-TFSA	-2.0	+2.4	4.4
IM(1O2)12-TFSA	-	-	-
IM(1O2)13-TFSA	-2.1	+2.3	4.4
IM(1O2)14-TFSA	-2.1	+2.4	4.5
IM(1O2)1(2o1)-TFSA	-	-	-
IM(1O2)1(2o2)-TFSA	-2.0	+2.2	4.2
IM(1O2)21-TFSA	-2.0	+2.4	4.4
IM(1O2)22-TFSA	-2.0	+2.3	4.3
IM(1O2)23-TFSA	-2.0	+2.3	4.3
IM(1O2)24-TFSA	-2.1	+2.4	4.5
IM(1O2)2(2o1)-TFSA	-2.1	+2.2	4.3
IM(1O2)2(2o2)-TFSA	-2.1	+2.3	4.4

Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire; scan rate: 10 mV s^{-1}.

Table S4

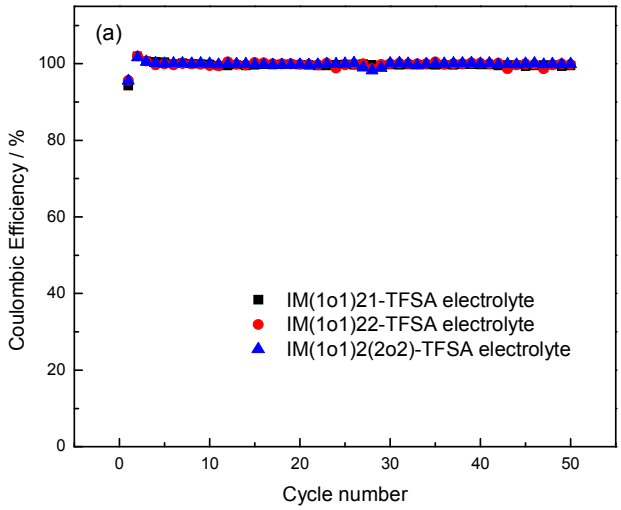
Melting enthalpy and entropy of ILs.

Ionic liquids	ΔH_m [a] /J g^{-1}	ΔS_m [b] / J mol^{-1} K^{-1}
IM(1O1)11-TFSA	67.3	96.1
IM(1O1)12-TFSA	52.3	73.6
IM(1O1)13-TFSA	58.8	90.0
IM(1O1)21-TFSA	52.2	79.3
IM(1O1)22-TFSA	50.8	78.0
IM(1O1)23-TFSA	74.4	118.0
IM(1O2)12-TFSA	81.3	117.7
IM(1O2)1(2O1)-TFSA	58.8	91.4
IM(1O2)23-TFSA	55.3	89.8
IM(1O2)2(2O1)-TFSA	54.5	93.3

[a] ΔH_m is melting enthalpy at T_m [K]. [b] $\Delta S_m = \Delta H_m / T_m$

Fig. S53

The cycle number dependences of coulombic efficiency of Li/$LiFePO_4$ cells using the IL electrolytes at 25 ^{o}C, charge-discharge current rate is 0.1 C.



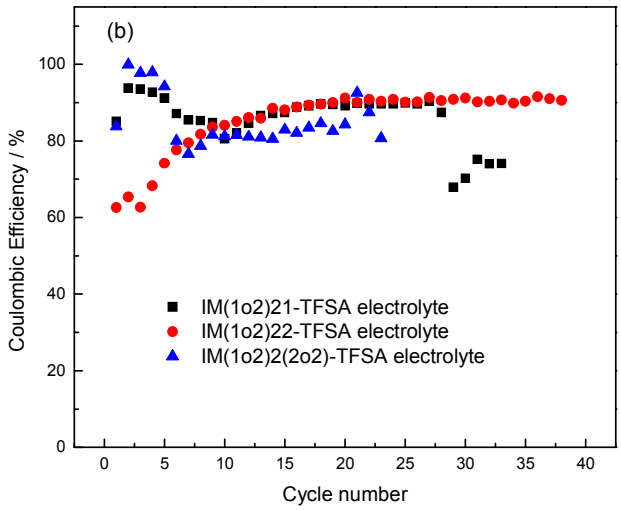


Fig. S54

Cyclic voltammograms of these IL electrolytes at 25 ^{o}C (-3.3 V to -0.3 V versus Ag). (a) IM(1O1)21-TFSA electrolyte, (b) IM(1O1)22-TFSA electrolyte and (c) IM(1O1)2(2o2)-TFSA electrolyte; (d) IM(1O2)21-TFSA electrolyte, (e) IM(1O2)22-TFSA electrolyte and (f) IM(1O2)2(2o2)-TFSA electrolyte. Working electrode, Ni; counter electrode, Pt; reference electrode, Ag; scan rate, 10 mV s^{-1}.

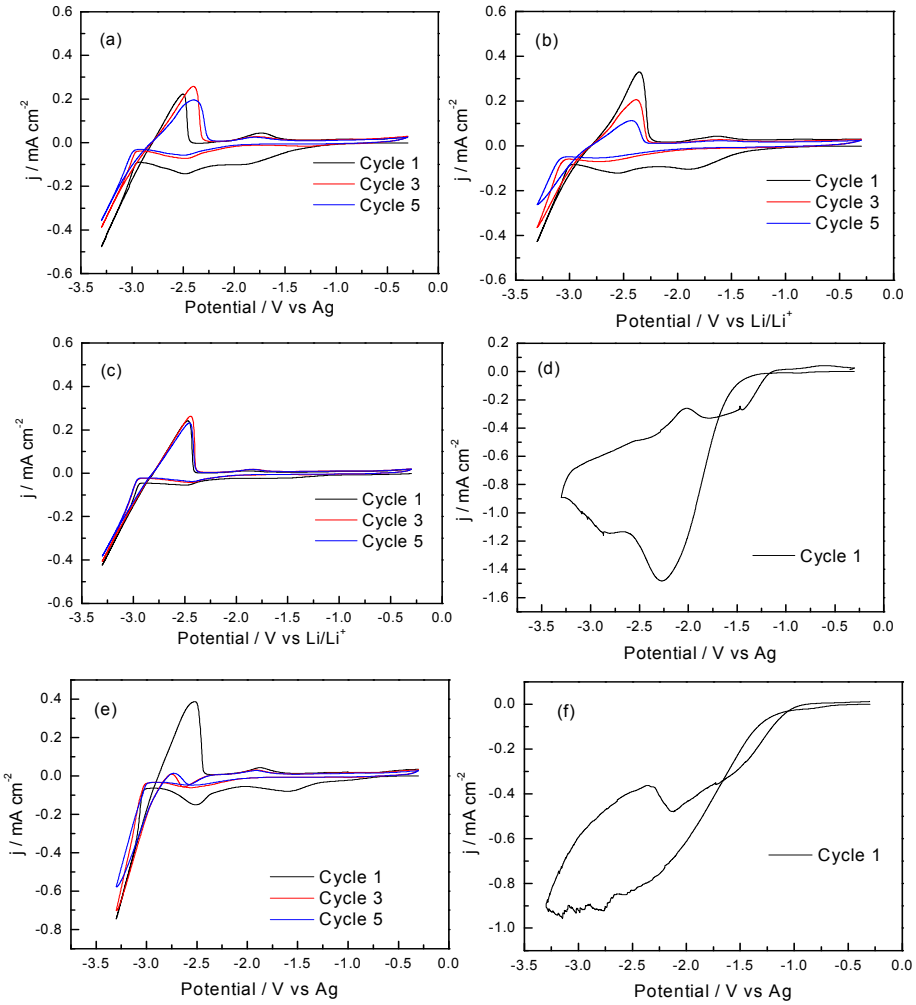


Fig. S55 DSC curves of IM(1O1)11-TFSA.

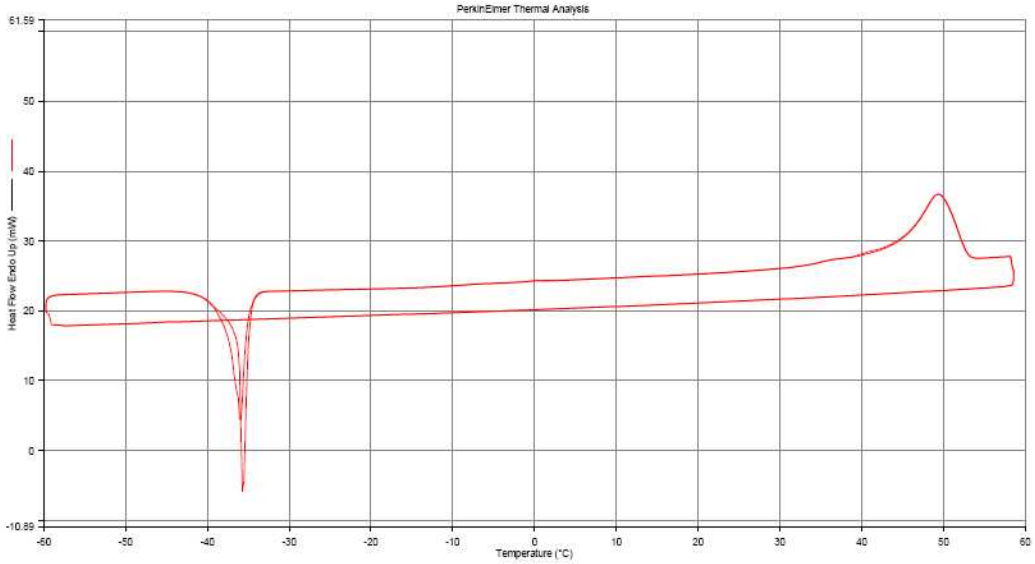


Fig. S56 DSC curves of IM(1O1)12-TFSA.

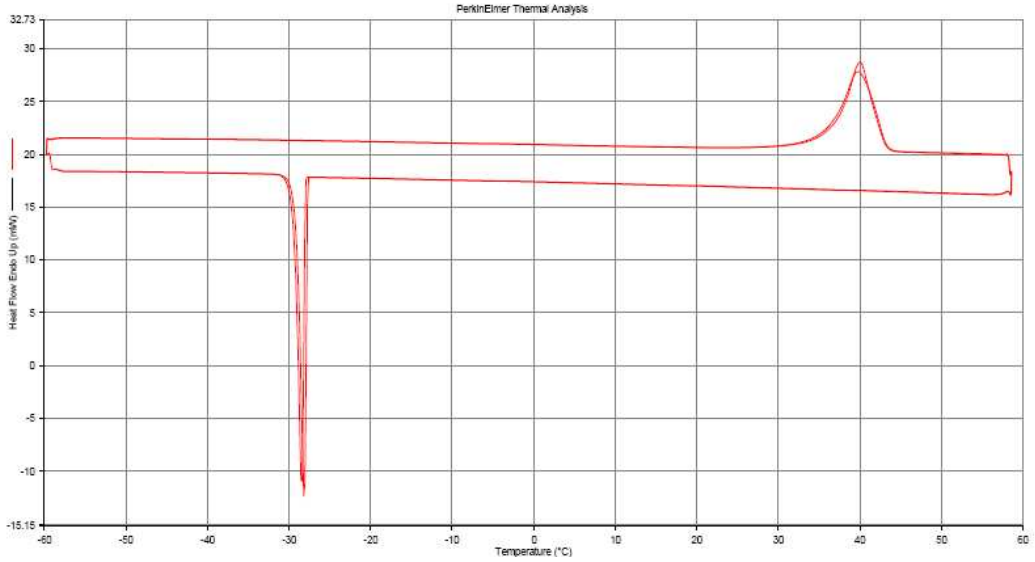


Fig. S57 DSC curves of IM(1O1)13-TFSA.

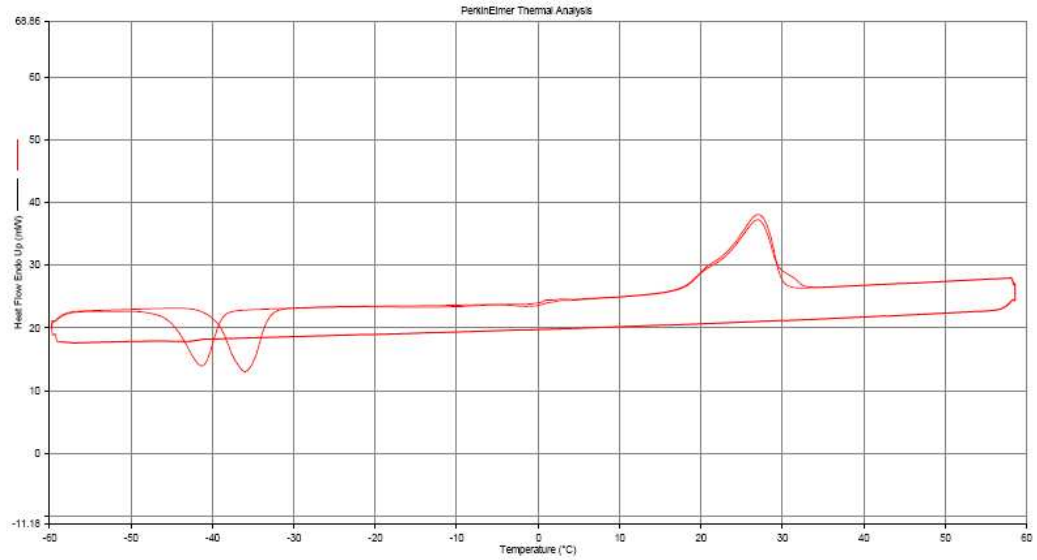


Fig. S58 DSC curves of IM(1O1)21-TFSA.

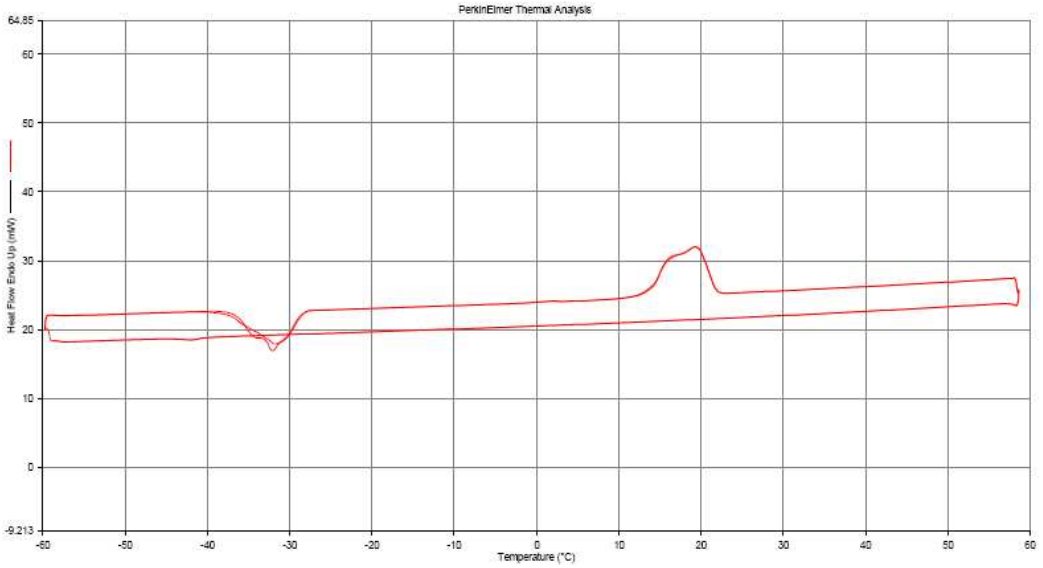


Fig. S59 DSC curves of IM(1O1)22-TFSA.

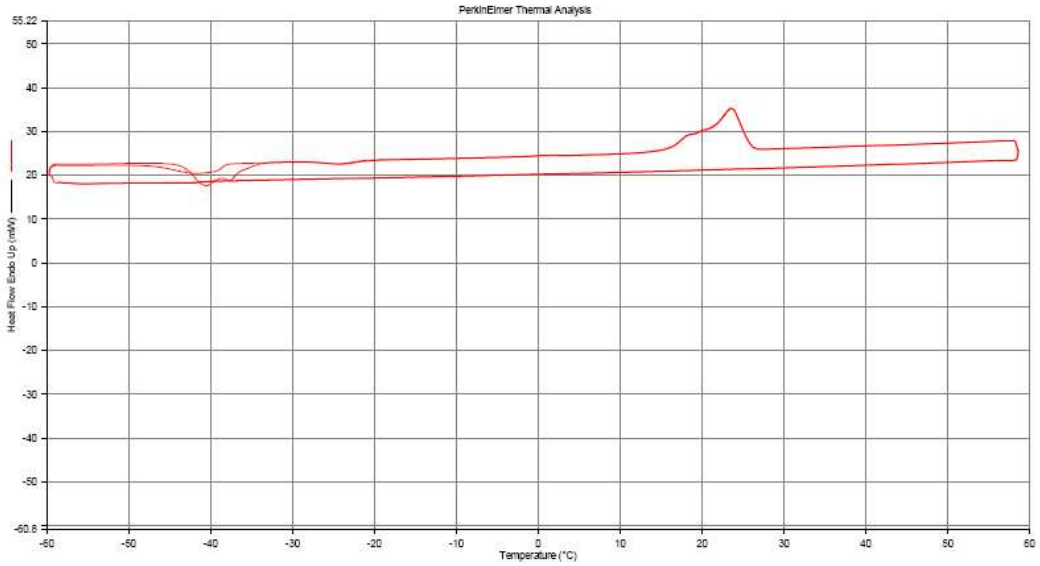


Fig. S60 DSC curves of IM(1O1)23-TFSA.

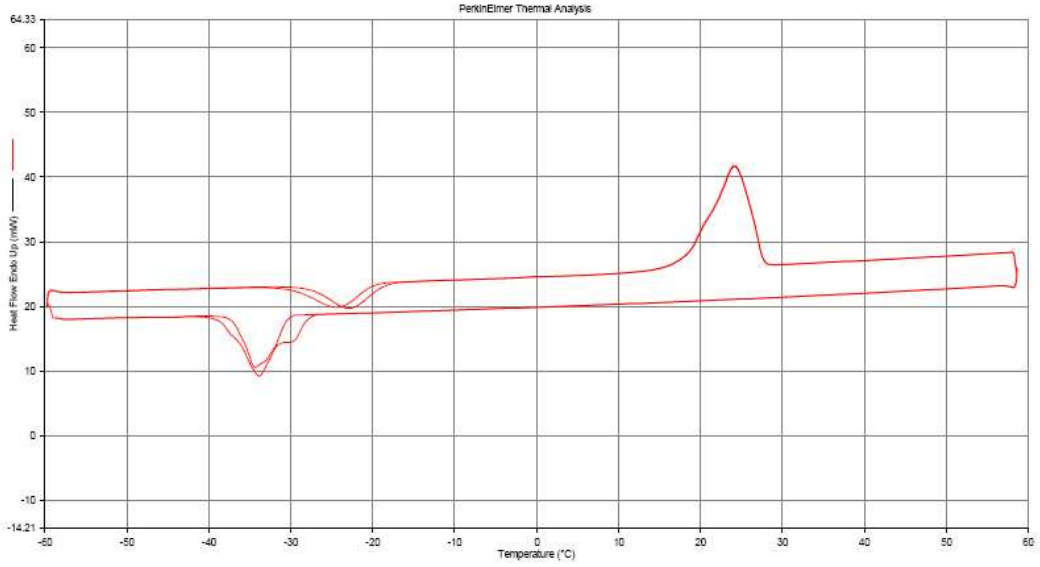


Fig. S61 DSC curves of IM(1O2)12-TFSA.

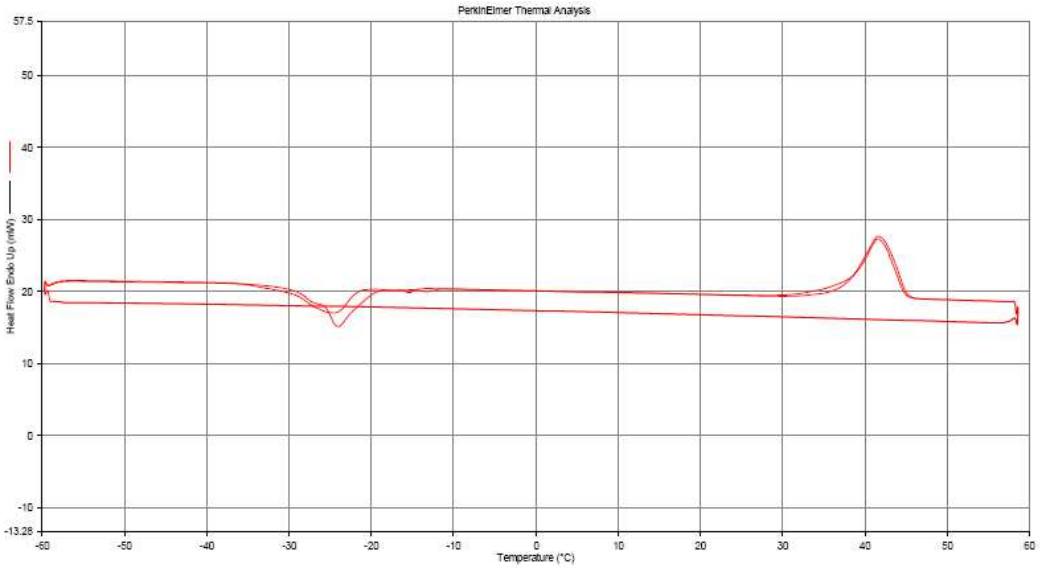


Fig. S62 DSC curves of IM(1O2)1(2O1)-TFSA.

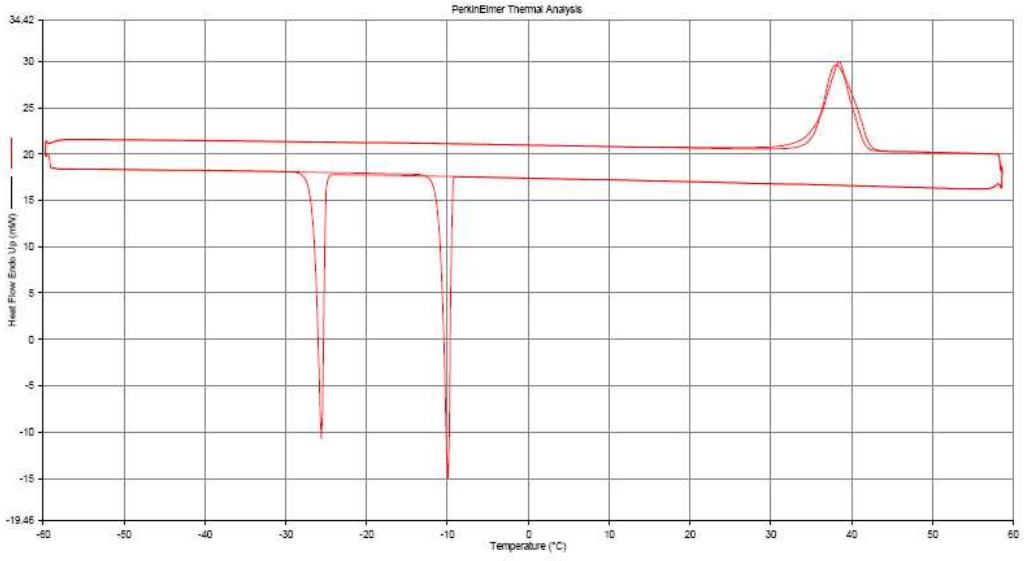


Fig. S63 DSC curves of IM(1O2)23-TFSA.

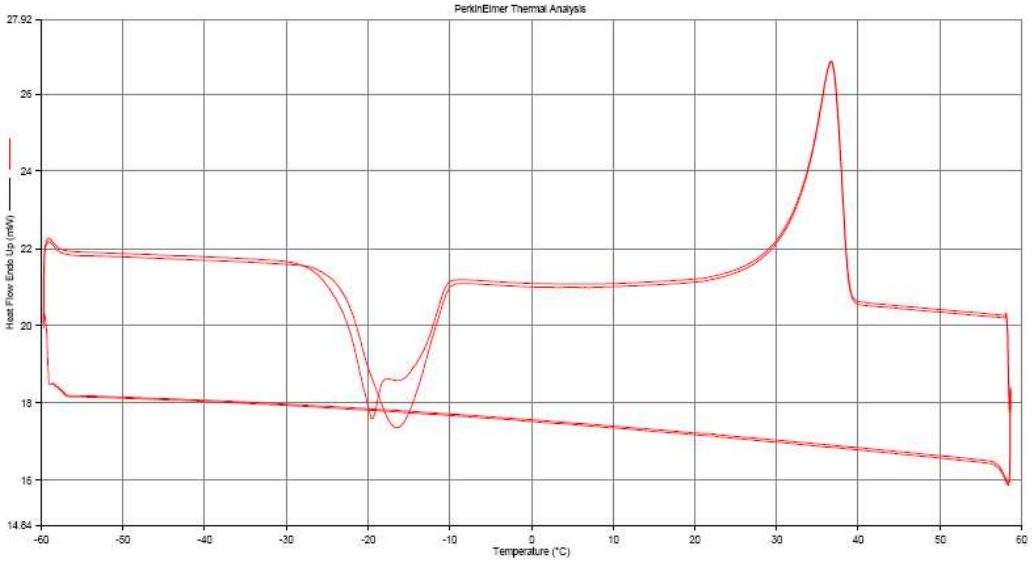


Fig. S64 DSC curves of IM(1O2)2(2O1)-TFSA.

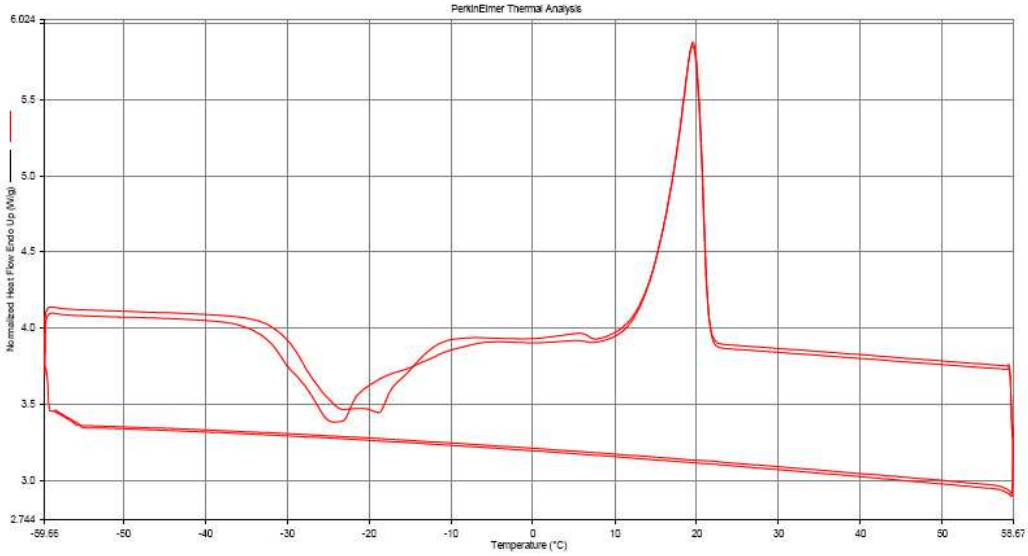


Fig. S65 DSC curves of IM(1O1)14-TFSA.(The DSC curves of the rest ILs which showed melting point lower than -60 ^{o}C was very similar with IM(1O1)14-TFSA.)

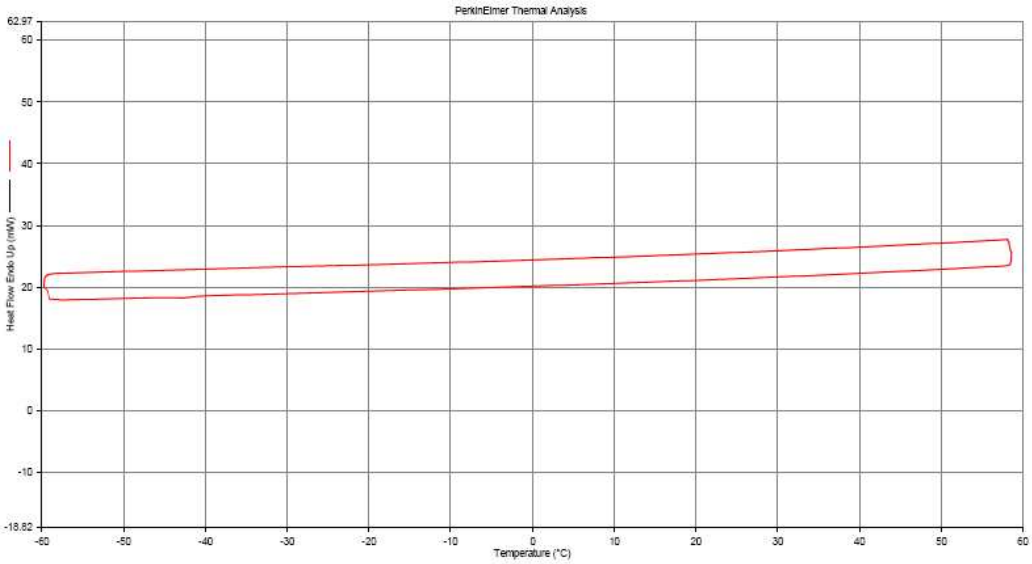


Fig. S66 TGA curve of IM(1O1)11-TFSA

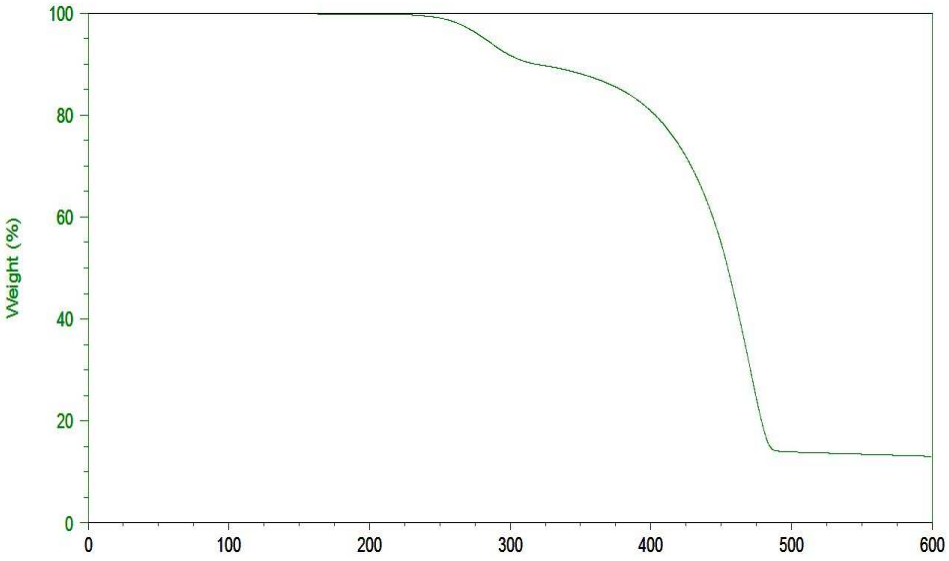


Fig. S67 TGA curve of IM(1O1)12-TFSA.

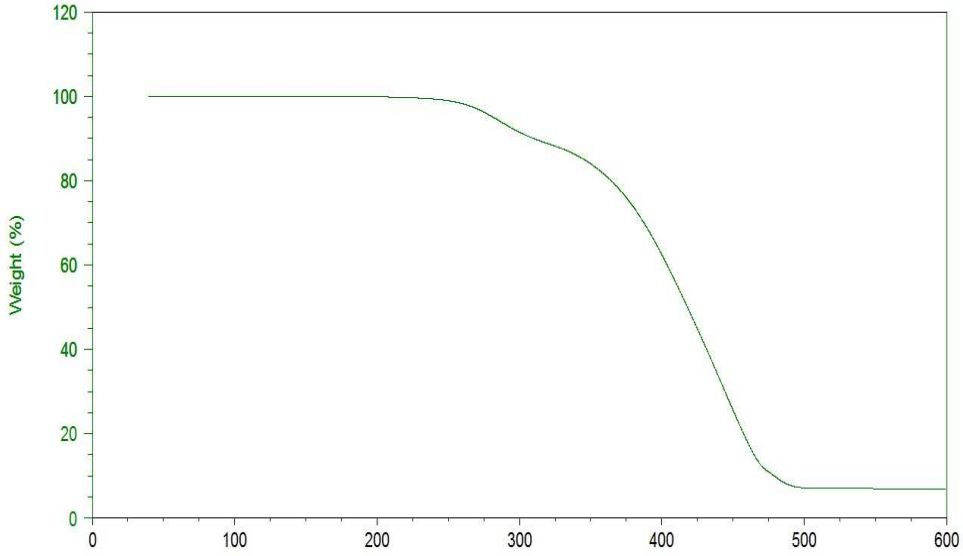


Fig. S68 TGA curve of IM(1O1)13-TFSA.

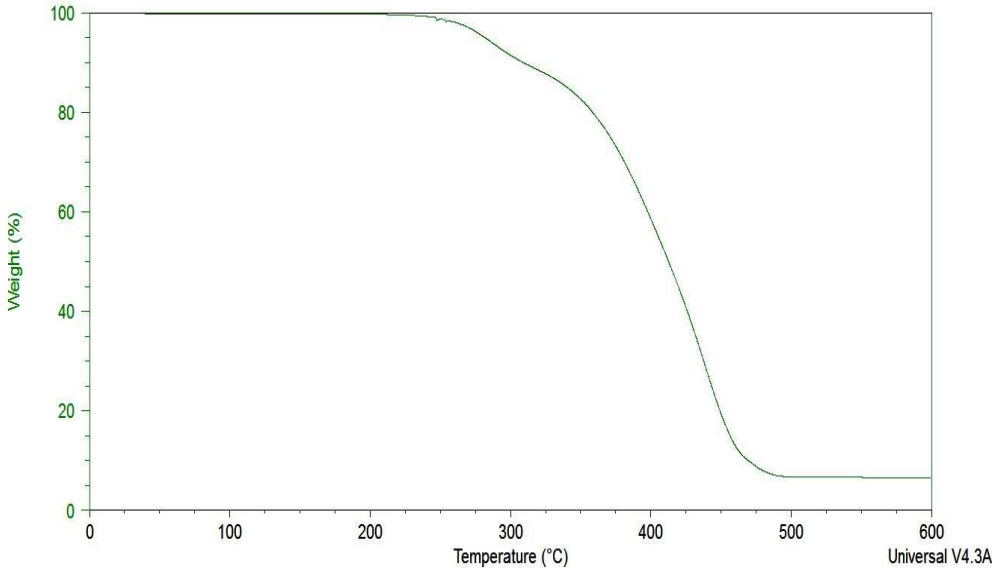


Fig. S69 TGA curve of IM(1O1)14-TFSA.

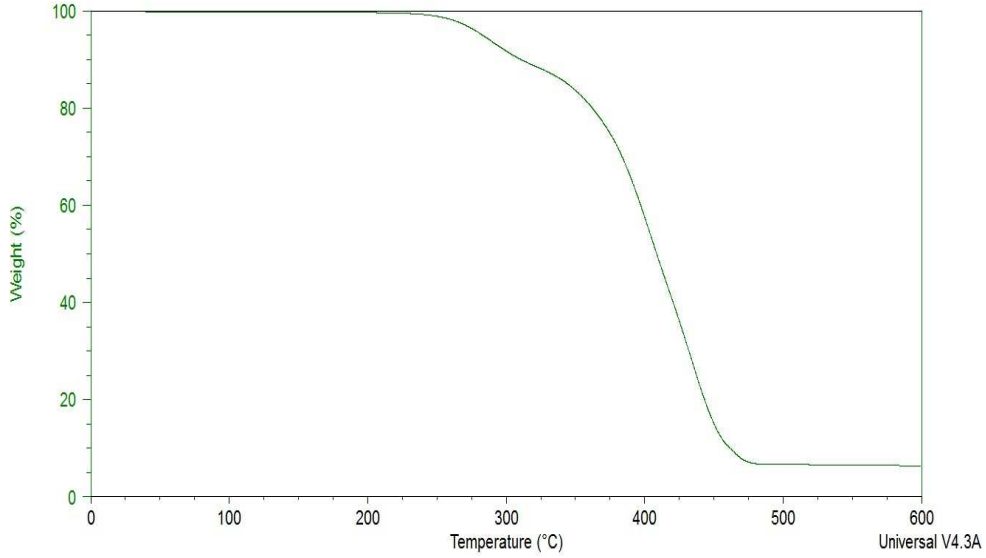


Fig. S70 TGA curve of IM(1O1)1(2O1)-TFSA.

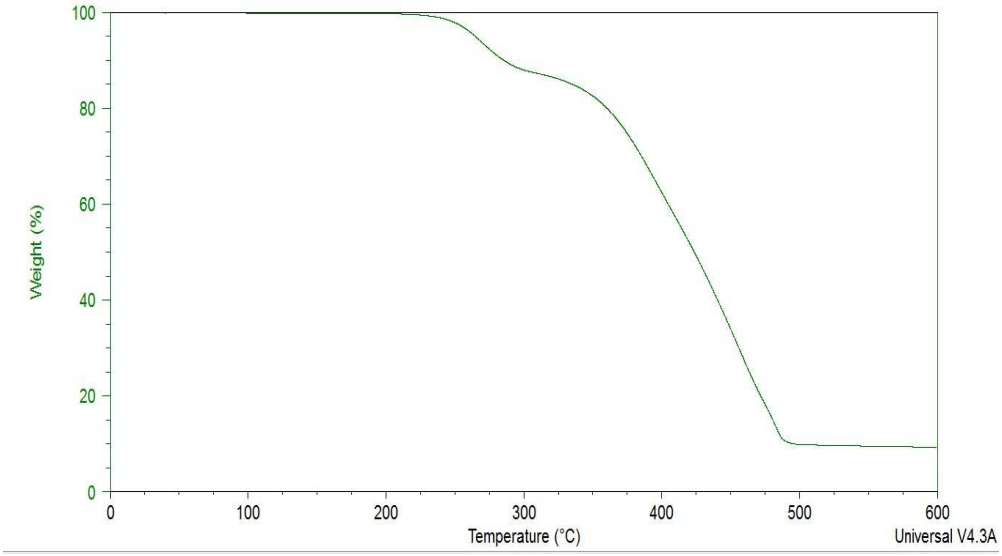


Fig. S71 TGA curve of IM(1O1)1(2O2)-TFSA.

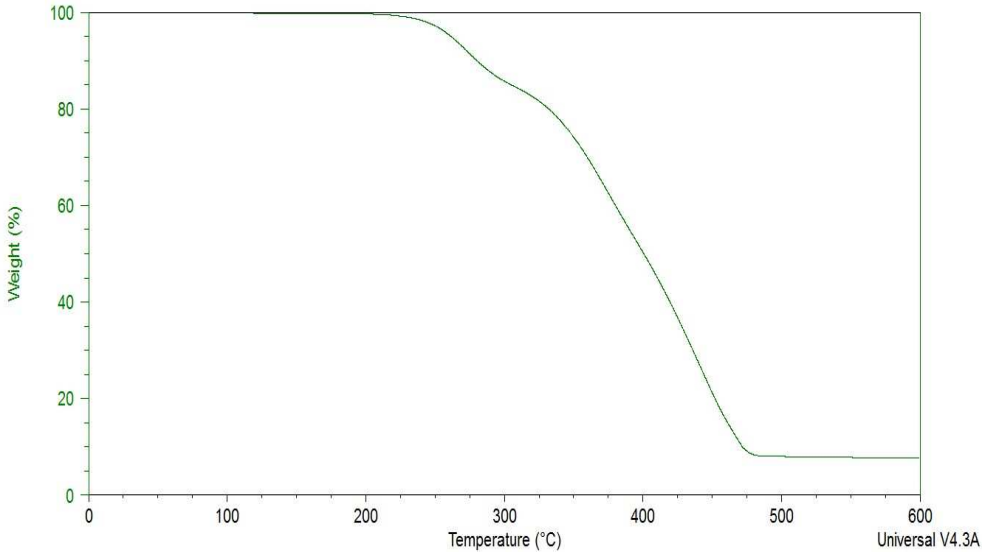


Fig. S72 TGA curve of IM(1O1)21-TFSA.

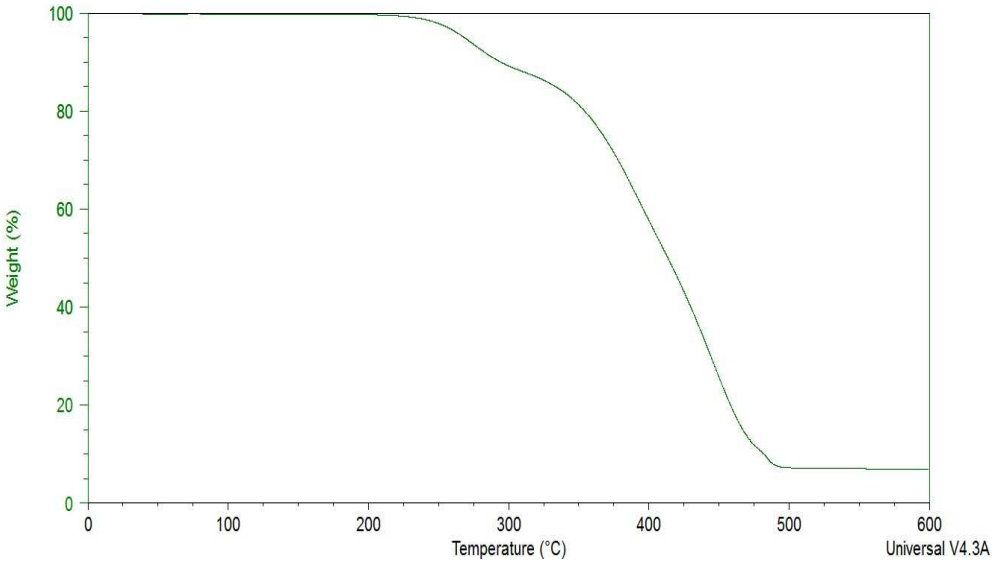


Fig. S73 TGA curve of IM(1O1)22-TFSA.

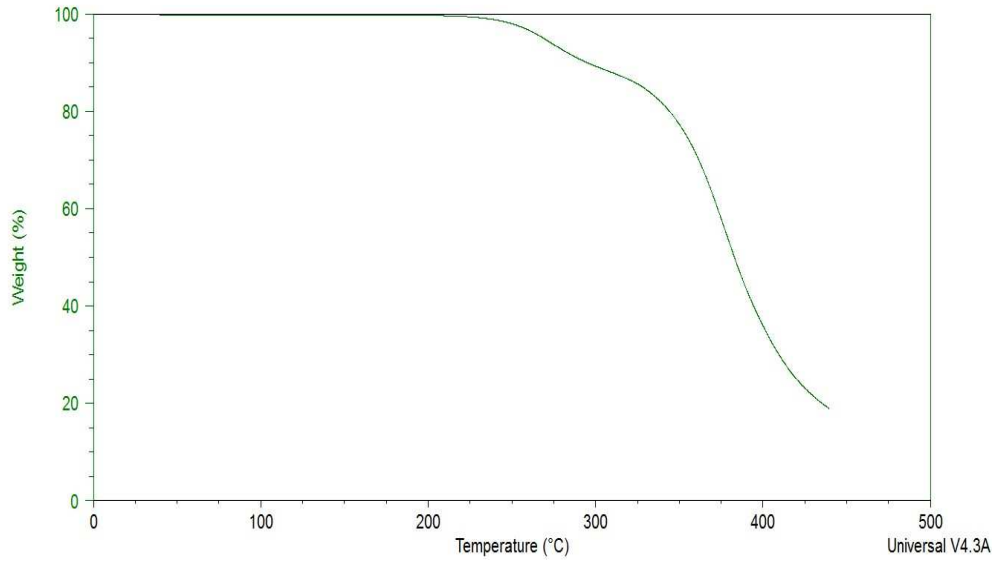


Fig. S74 TGA curve of IM(1O1)23-TFSA.

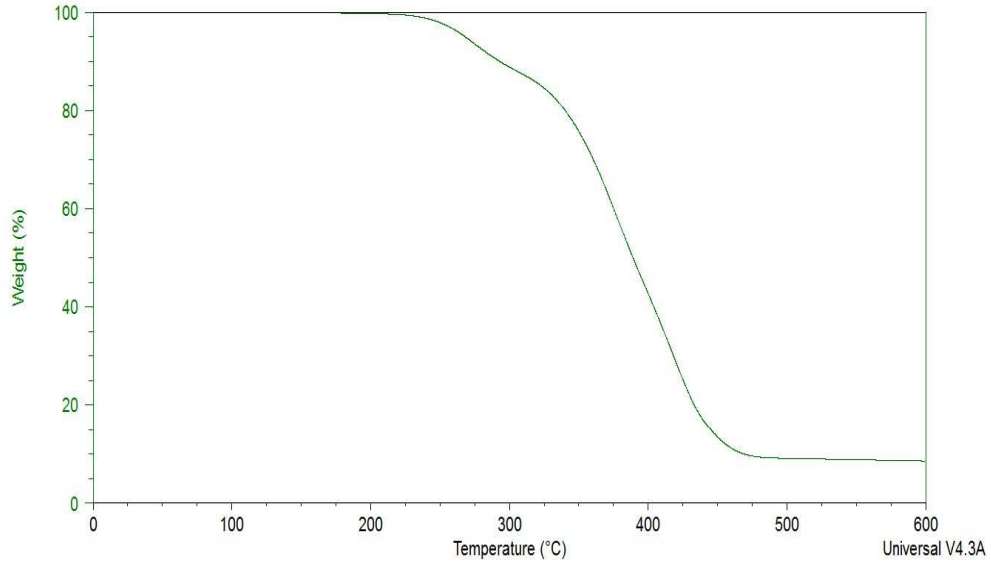


Fig. S75 TGA curve of IM(1O1)24-TFSA.

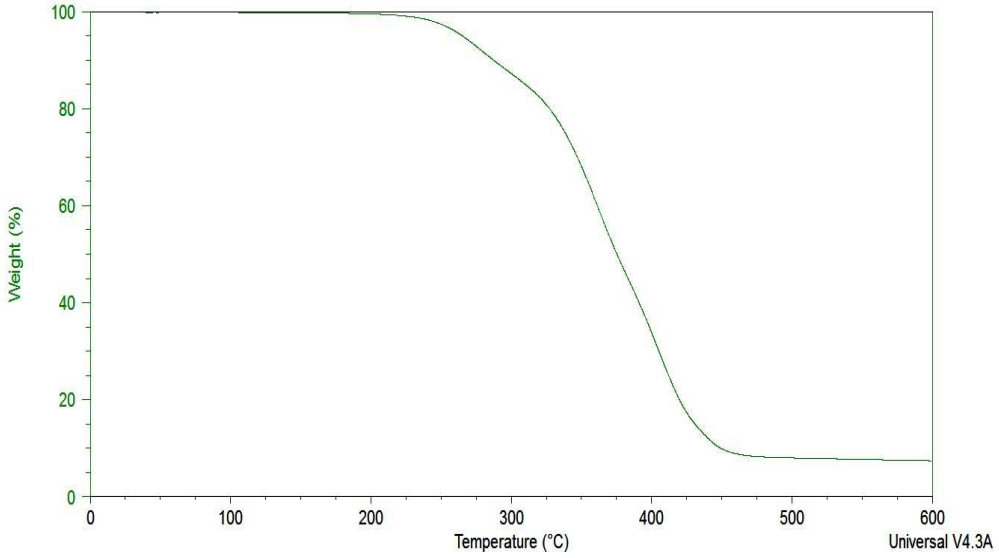


Fig. S76 TGA curve of IM(1O1)2(2O1)-TFSA.

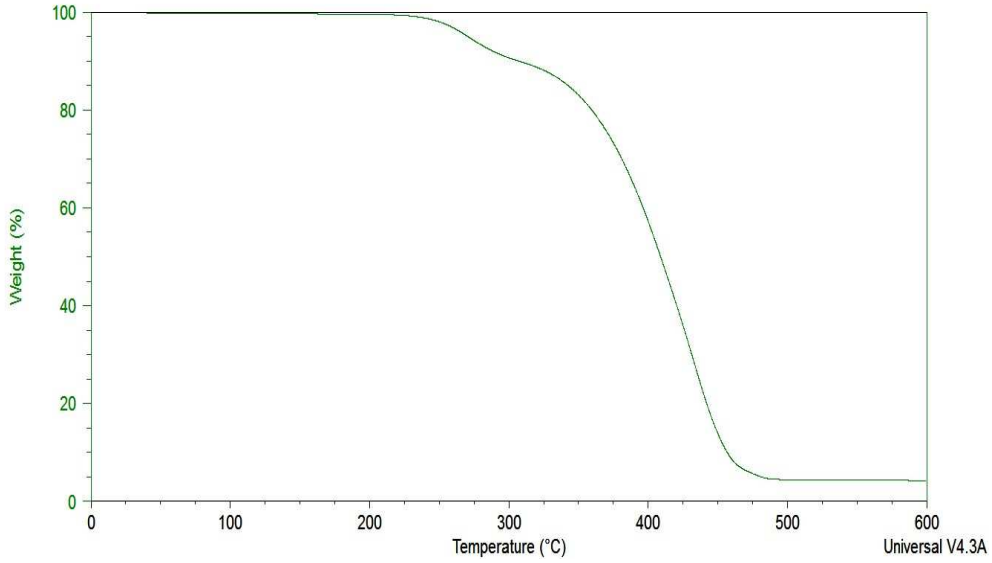


Fig. S77 TGA curve of IM(1O1)2(2O2)-TFSA.

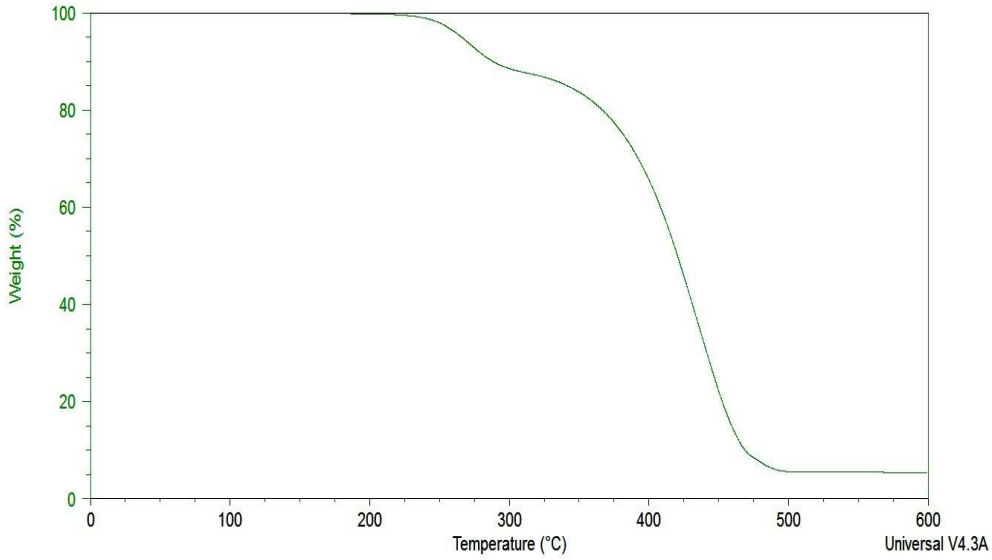


Fig. S78 TGA curve of IM(1O2)11-TFSA.

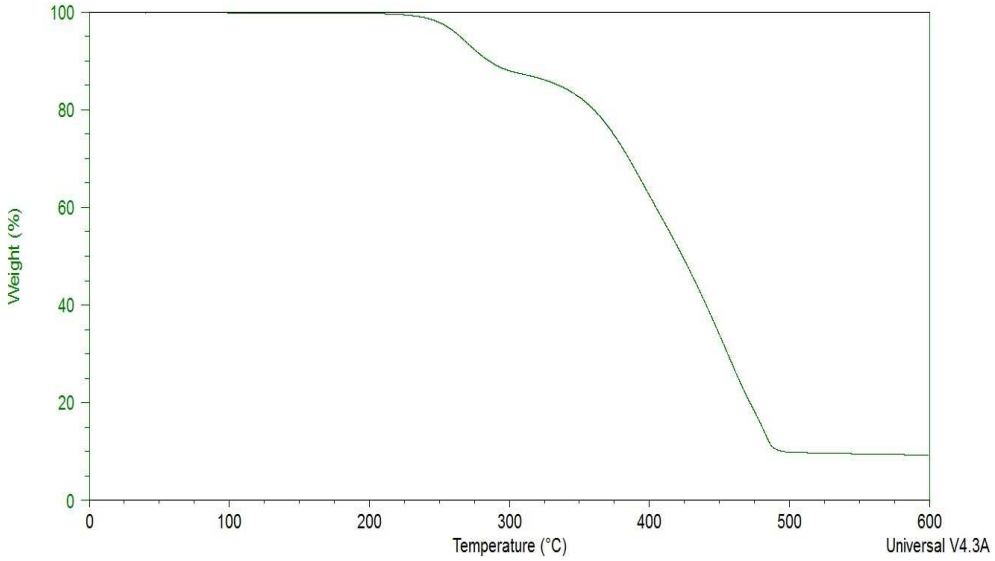


Fig. S79 TGA curve of IM(1O2)12-TFSA.

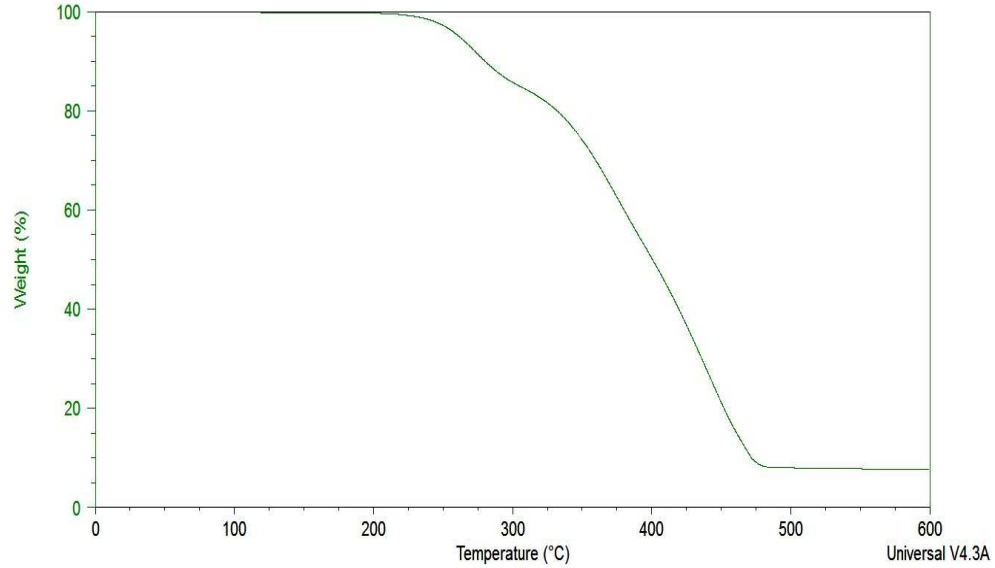


Fig. S80 TGA curve of IM(1O2)13-TFSA.

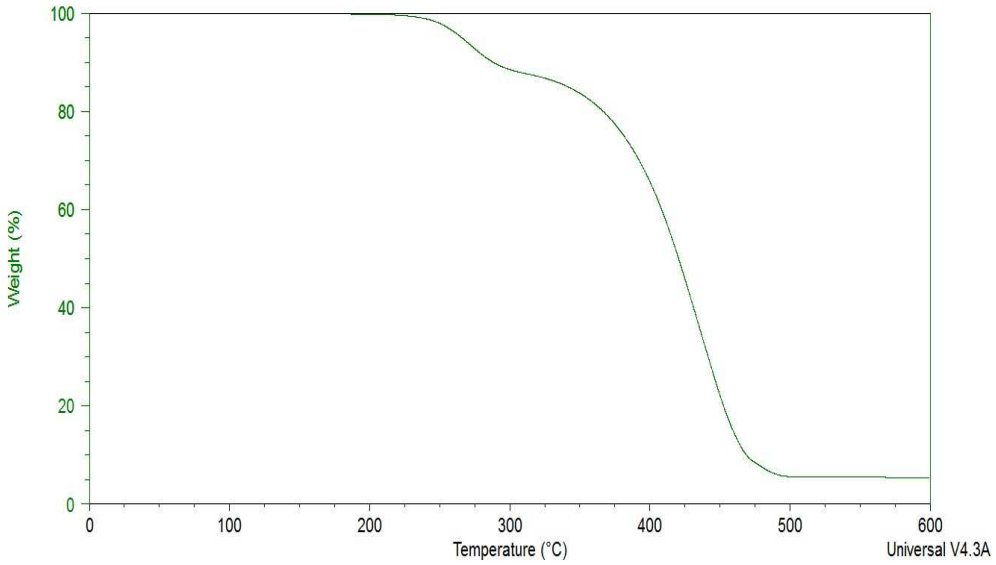


Fig. S81 TGA curve of IM(1O2)14-TFSA.

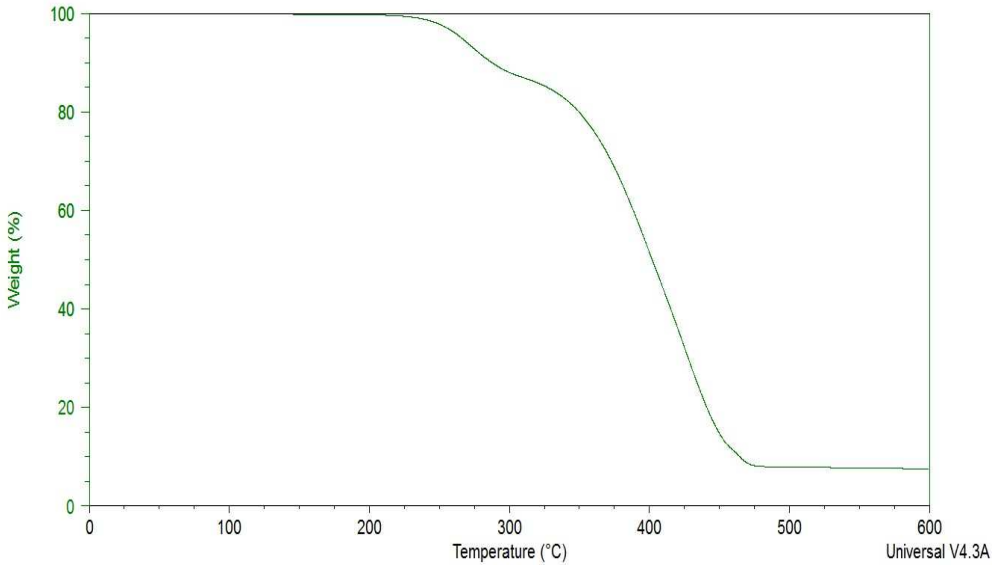


Fig. S82 TGA curve of IM(1O2)1(2O1)-TFSA.

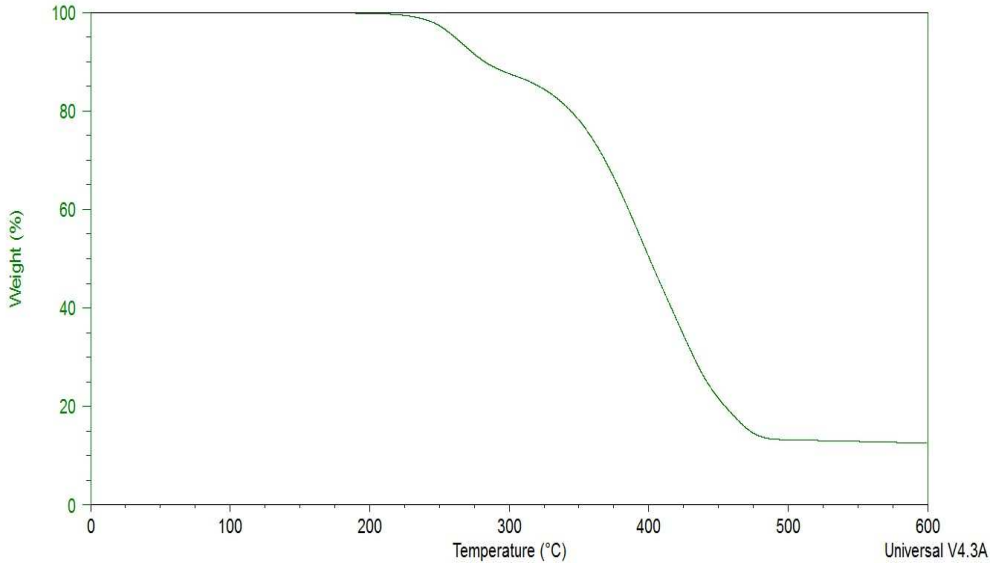


Fig. S83 TGA curve of IM(1O2)1(2O2)-TFSA.

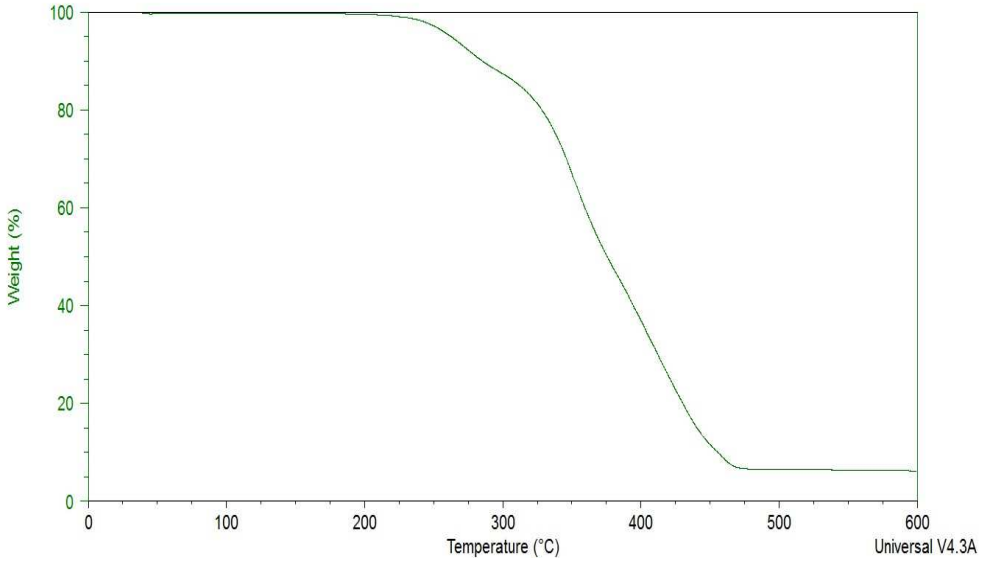


Fig. S84 TGA curve of IM(1O2)21-TFSA.

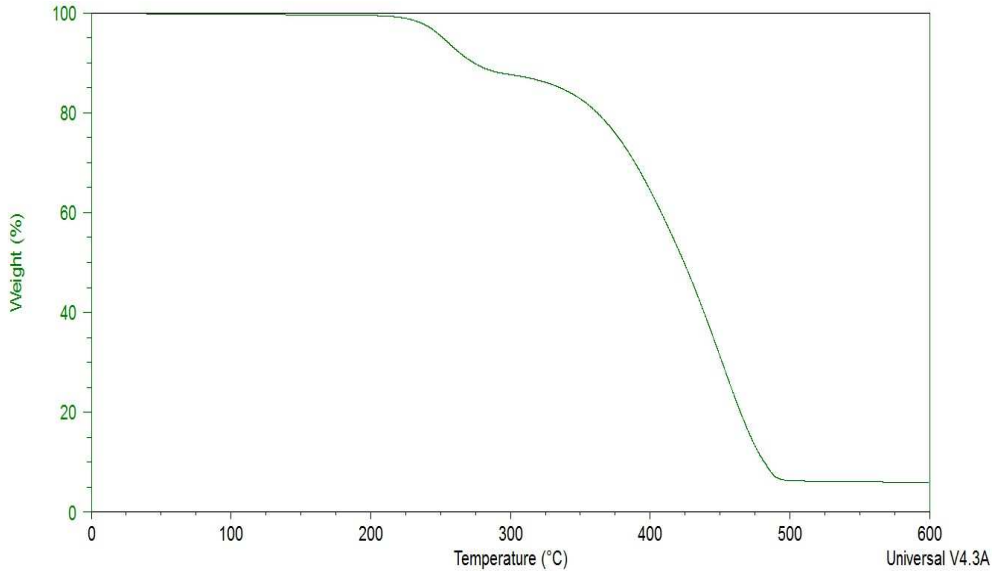


Fig. S85 TGA curve of IM(1O2)22-TFSA.

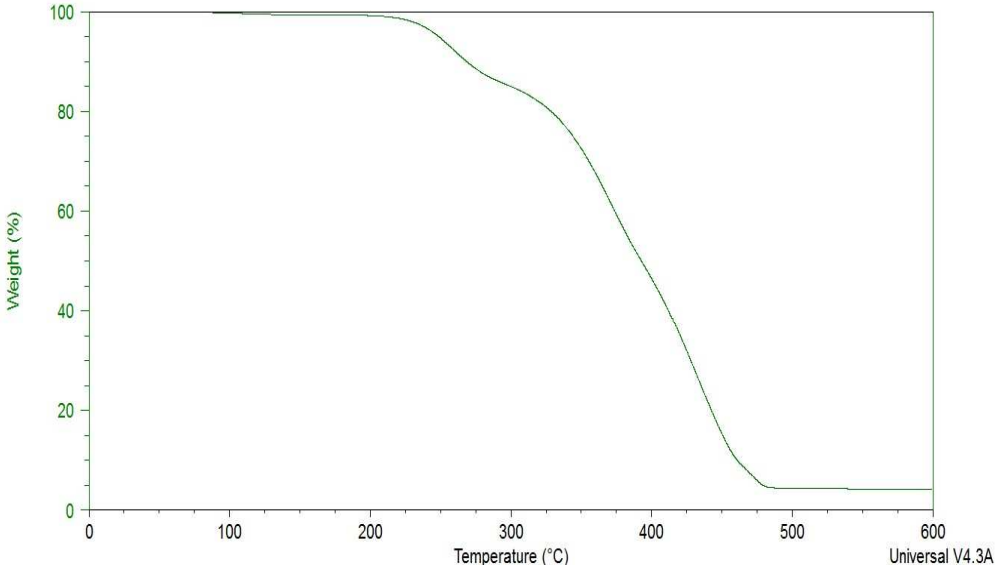


Fig. S86 TGA curve of IM(1O2)23-TFSA.

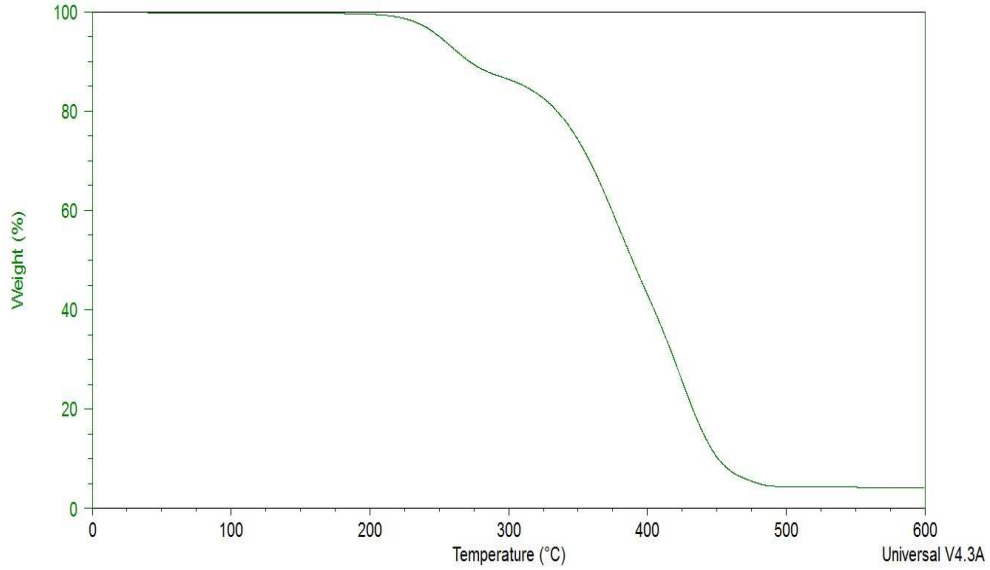


Fig. S87 TGA curve of IM(1O2)24-TFSA.

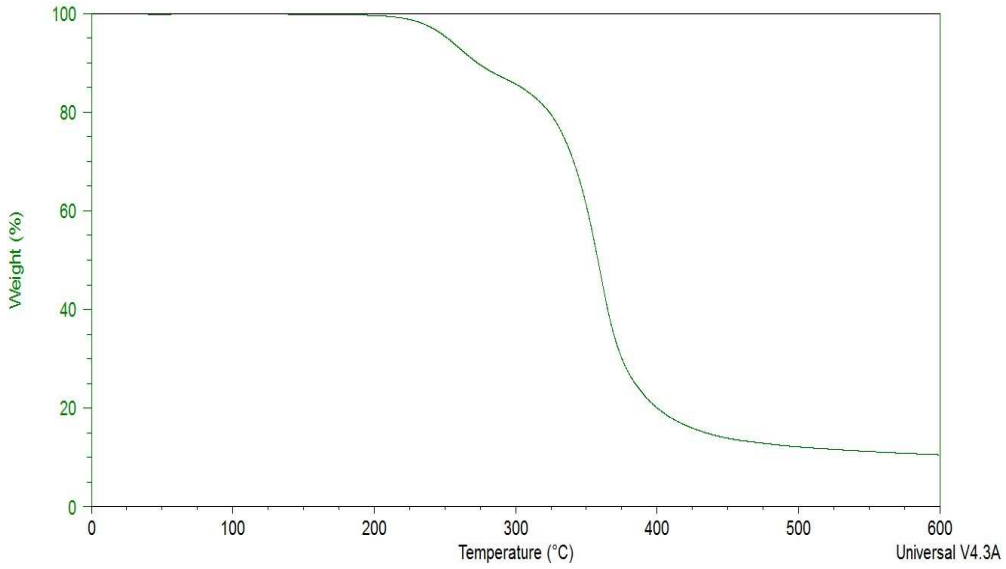


Fig. S88 TGA curve of IM(1O2)2(2O1)-TFSA.

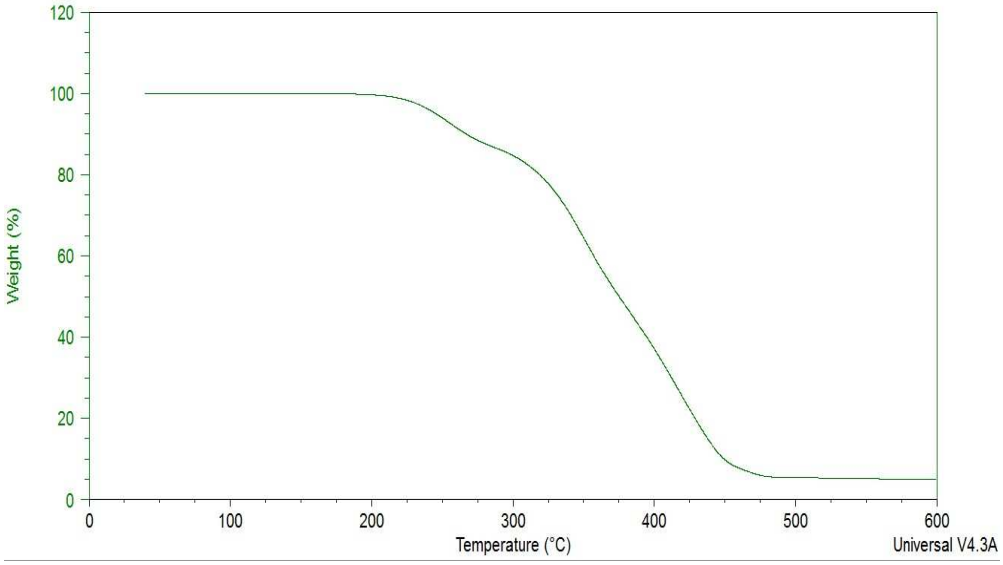


Fig. S89 TGA curve of IM(1O2)2(2O2)-TFSA.