

**Physicochemical Properties of Functionalized 1,3-
Dialkylimidazolium Ionic Liquids Based on Bis(fluorosulfonyl)imide
Anion**

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1. Synthesis procedure of the ether-functionalized 1,3 –dialkylimidazolium ILs

1.1 1-methoxyethyl-3-methylimidazolium bis(fluorosulfonyl)imide (IM2o1-1-FSI)

1-methylimidazole (6.0 g, 0.073 mol) and 2-bromoethyl methyl ether (12.2 g, 0.087 mol) were reacted in a 250 mL flask at 60 °C under argon atmosphere for 48 h with acetonitrile (10 mL) as the solvent. The product was washed with diethyl ether (100 mL × 3). Then the crude bromide was washed by active carbon with ethanol (100 mL) as the solvent for 24 h. After removing active carbon and ethanol by filtration and rotary evaporation respectively, the bromide was dissolved in deionized water with same molar amount lithium bis(fluorosulfonyl)imide (LiFSI) and stirred for 4 h at ambient temperature. Dichloromethane was used to extract the IL from the mixture and then the solvent was washed with deionized water for 3 times until no halide residual could be detected by AgNO₃ solution. The dichloromethane was removed by rotary evaporation. The IL was dried under high vacuum for 24 h at 100 °C. Colorless liquid (yield: 86 %). ¹H NMR (400 MHz, (CD₃)₂CO): δ (ppm) 9.03-8.98 (s, 1H), 7.76-7.72 (s, 1H), 7.72-7.69 (s, 1H), 4.57-4.52 (t, 2H), 4.11 4.07 (s, 3H), 3.85-3.80 (t, 2H), 3.39-3.34(s, 3H).

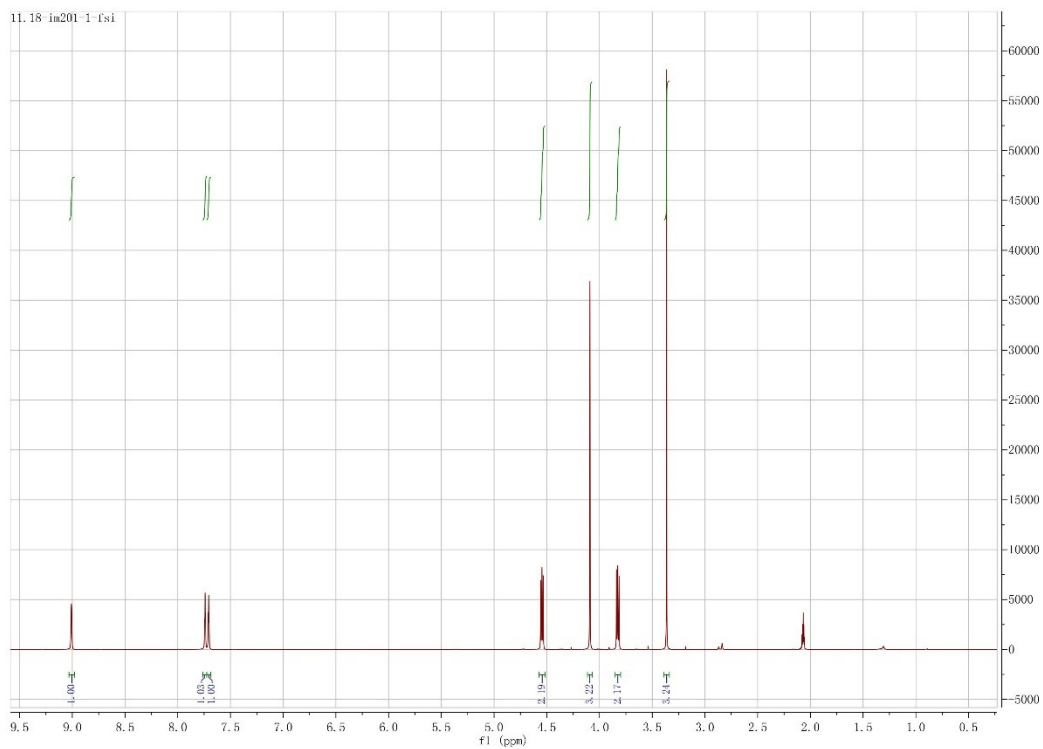


Fig. S1 ¹H NMR spectrum of IM2o1-1-FSI.

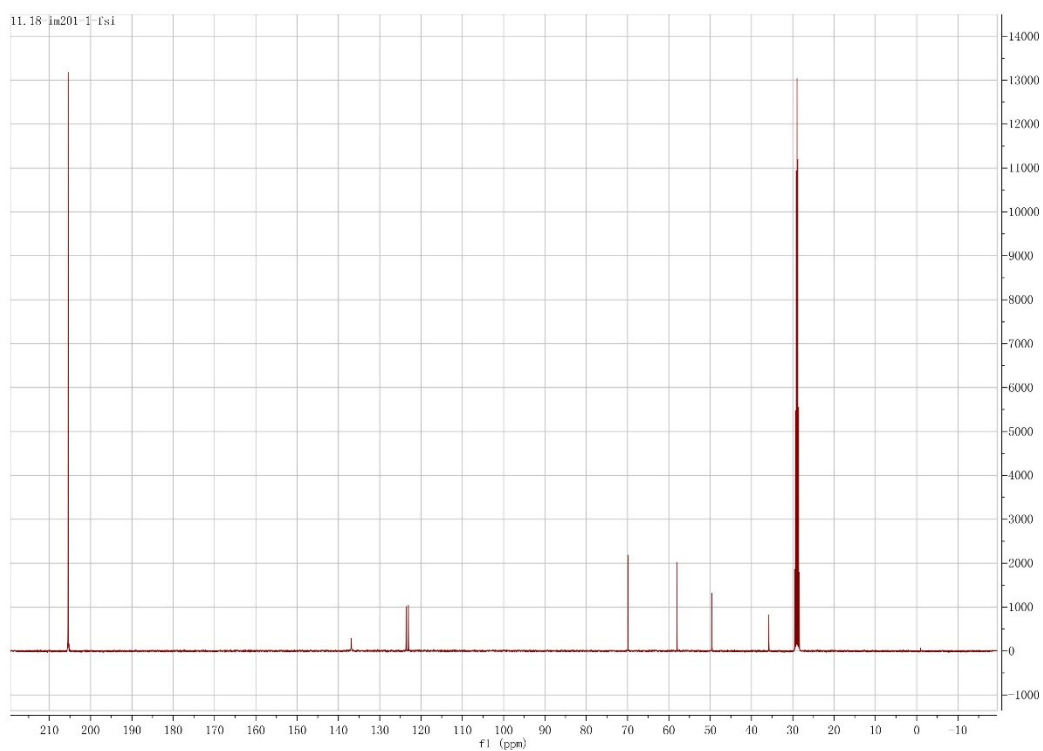


Fig. S2 ¹³C NMR spectrum of IM2o1-1-FSI.

1.2. 1-methoxyethyl-3-ethylimidazolium bis(fluorosulfonyl)imide (IM2o1-2-FSI)

1-ethylimidazole (6.0 g, 0.062 mol) and 2-bromoethyl methyl ether (10.4 g, 0.075 mol) were reacted in a 250 mL flask at 60 °C under argon atmosphere for 48 h with acetonitrile (10 mL) as the solvent. The following steps were similar with IM2o1-1-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Light yellow liquid (yield: 81 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.16-8.97 (s, 1H), 7.83-7.77 (s, 1H), 7.77-7.73 (s, 1H), 4.58-4.51 (t, 2H), 4.48 4.40 (q, 2H), 3.88-3.79 (t, 2H), 3.39-3.33(s, 3H), 1.63-1.55(t, 3H).



Fig. S3 ^1H NMR spectrum of Im2o1-2-FSI.

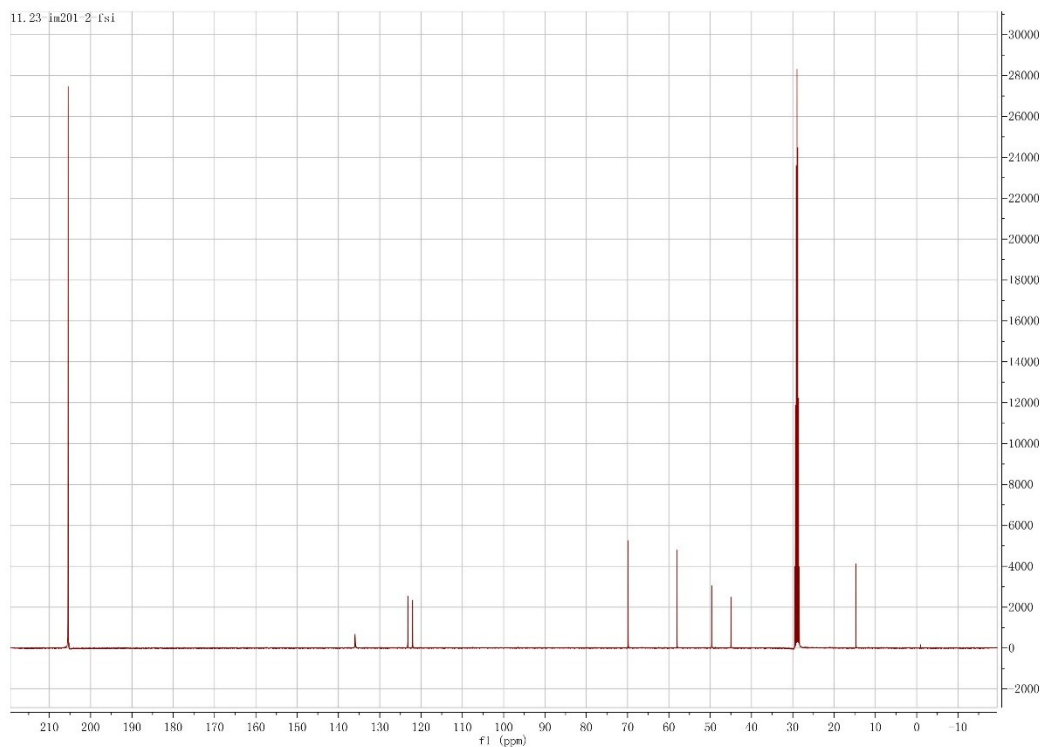


Fig. S4 ^{13}C NMR spectrum of Im2o1-2-FSI.

1.3. 1-ethoxyethyl-3-methylimidazolium bis(fluorosulfonyl)imide (IM2o2-1-FSI)

1-methylimidazole (6.0 g, 0.073 mol) and 2-bromoethyl ethyl ether (13.5 g, 0.088 mol) were reacted in a 250 mL flask at 60 °C under argon atmosphere for 48 h with acetonitrile (10 mL) as the solvent. The following steps were similar with IM2o1-1-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Colorless liquid (yield: 82 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.08-8.94 (s, 1H), 7.78-7.72 (s, 1H), 7.72-7.67 (s, 1H), 4.58-4.50 (t, 2H), 4.11 4.05 (s, 3H), 3.89-3.83 (t, 2H), 3.59-3.49(q, 2H), 1.21-1.09(t, 3H).

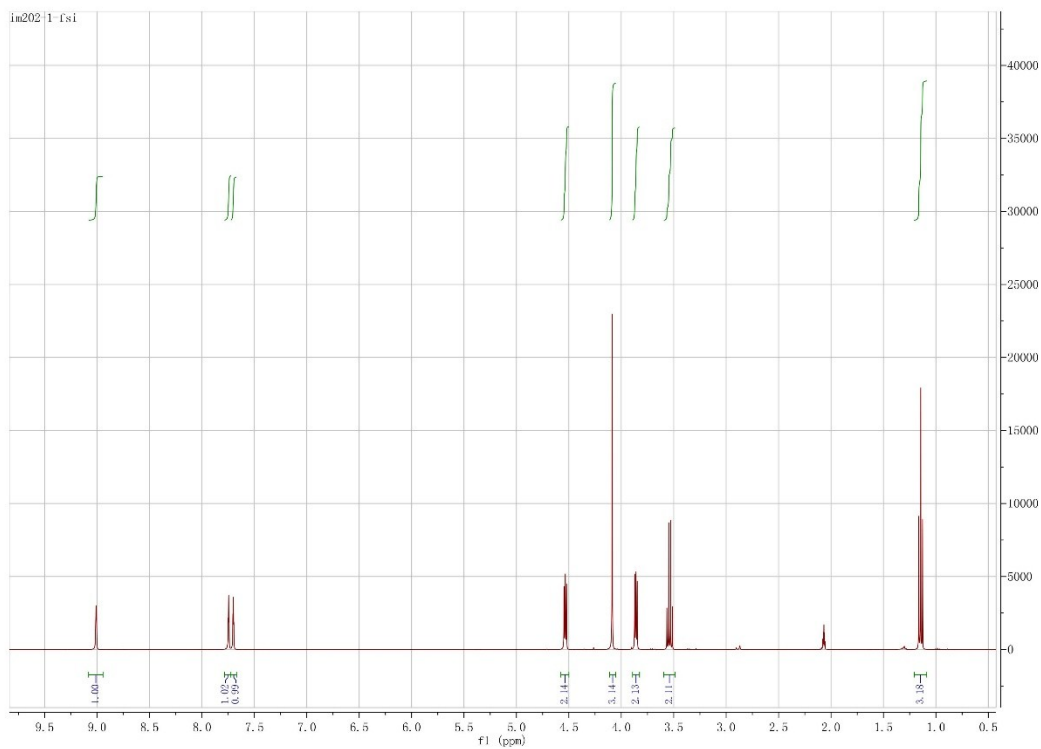


Fig. S5 ^1H NMR spectrum of Im2o2-1-FSI.

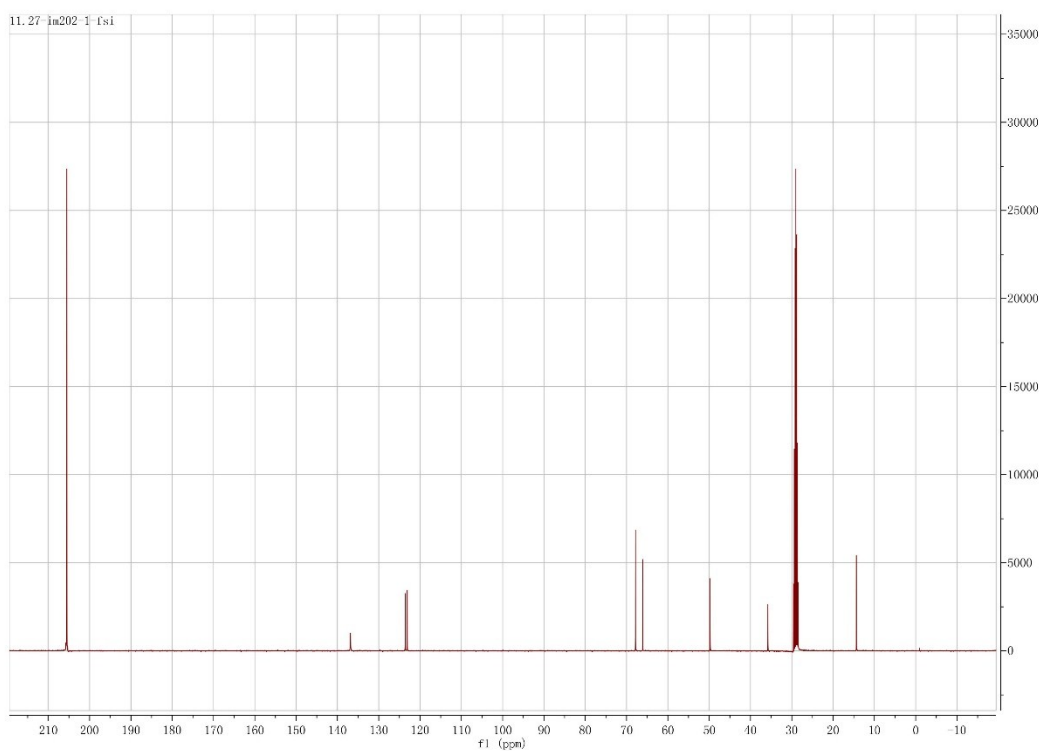


Fig. S6 ^{13}C NMR spectrum of Im2o2-1-FSI.

1.4. 1-ethoxyethyl-3-ethylimidazolium bis(fluorosulfonyl)imide (IM2o2-2-FSI)

1-ethylimidazole (6.0 g, 0.062 mol) and 2-bromoethyl ethyl ether (11.5 g, 0.075 mol) were reacted in a 250 mL flask at 60 °C under argon atmosphere for 48 h with acetonitrile (10 mL) as the solvent. The following steps were similar with IM2o1-1-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Light yellow liquid (yield: 85 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.18-8.95 (s, 1H), 7.81-7.78 (s, 1H), 7.78-7.74 (s, 1H), 4.60-4.50 (t, 2H), 4.49-4.38 (q, 2H), 3.92 3.82 (t, 2H), 3.60-3.49 (q, 2H), 1.67-1.52 (t, 3H), 1.21-1.07 (t, 3H).

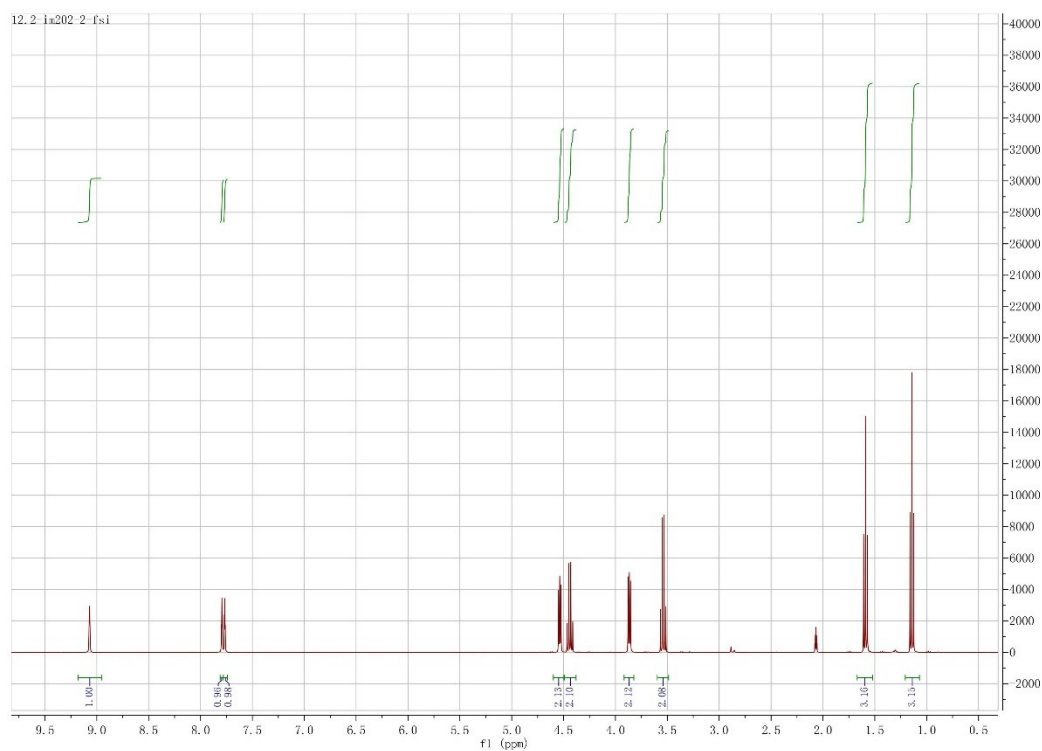


Fig. S7 ^1H NMR spectrum of Im202-2-FSI.

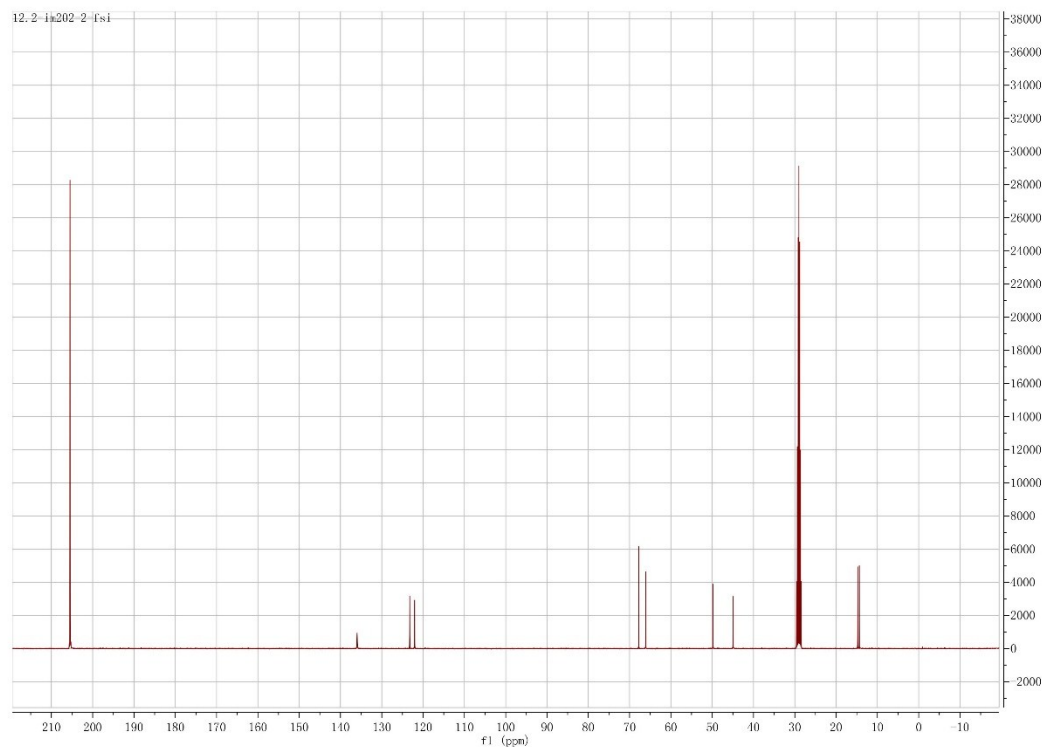


Fig. S8 ^{13}C NMR spectrum of Im202-2-FSI.

2. Synthesis procedure of the alkenyl -functionalized 1,3 -dialkylimidazolium ILS

2.1 1-vinyl-3-ethylimidazolium bis(fluorosulfonyl)imide (VEI-FSI)

The synthesis procedure of VEI-FSI had been described in the Experimental part of the paper.

Light yellow liquid (Yield: 85 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.34-9.21 (s, 1H),

8.20-7.99 (s, 1H), 7.96-7.77 (s, 1H), 7.42-7.29 (q, 1H), 6.04-5.95 (m, 1H), 5.60-5.39 (m, 1H),

4.60-4.33 (q, 2H), 1.71-1.50 (t, 3H).

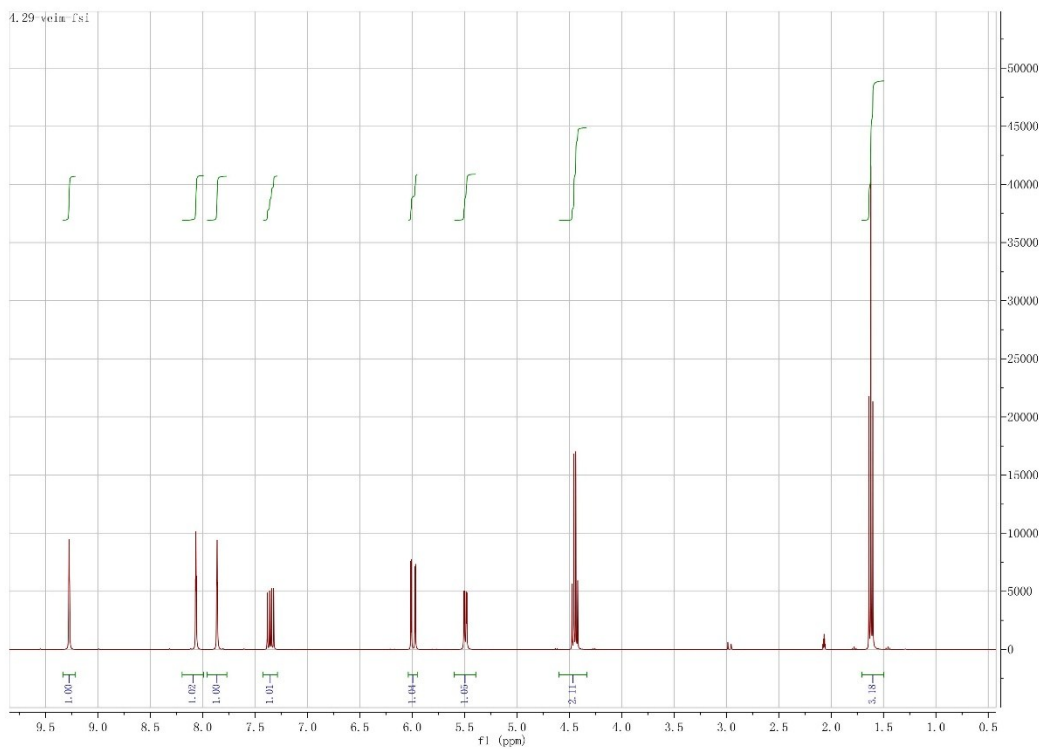


Fig. S9 ^1H NMR spectrum of VEI-FSI

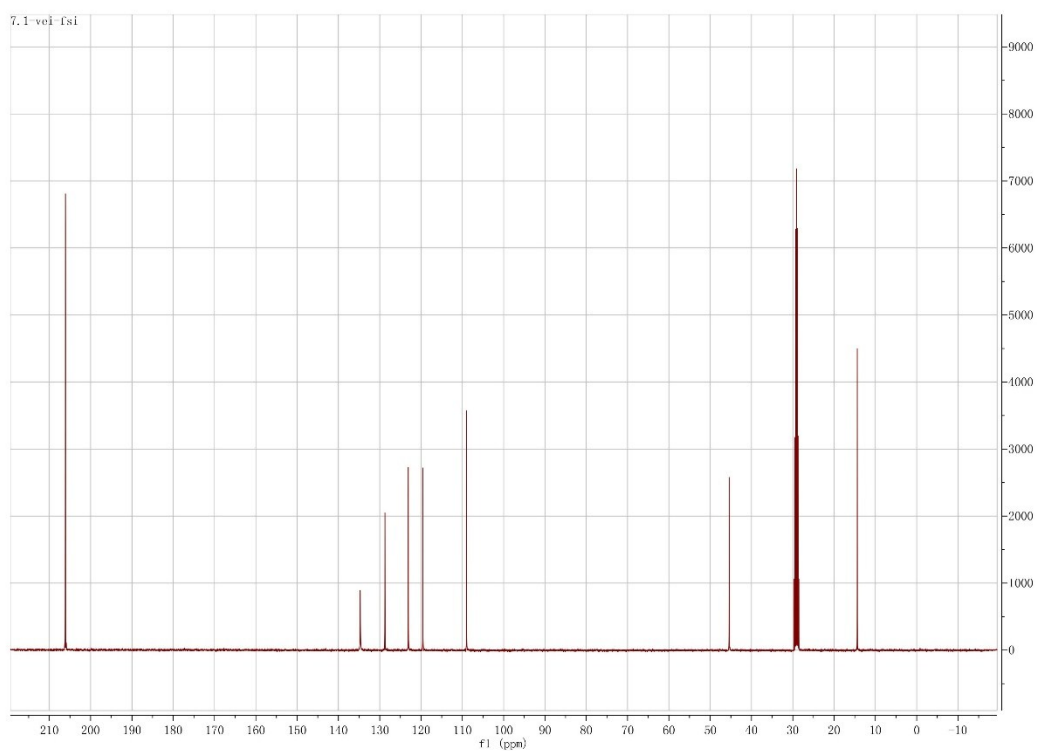


Fig. S10 ^{13}C NMR spectrum of VEI-FSI

2.2 1-allyl-3-methylimidazolium bis(fluorosulfonyl)imide (AMI-FSI)

1-methylimidazole (5 g, 0.061 mol) was dissolved in 10 mL acetonitrile in a 250 mL flask. Then allyl bromide (8.9 g, 0.073 mol) was added dropwise to the solution at 0 °C. The reaction time is 24 h. The following steps were similar with the synthesis of VEI-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Light yellow liquid (Yield: 85%). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.19-8.76 (s, 1H), 7.74-7.72 (s, 1H), 7.72-7.69 (s, 1H), 6.37-5.94 (m, 1H), 5.57-5.33 (m, 2H), 5.11-4.89 (d, 2H), 4.12-4.04 (s, 3H).

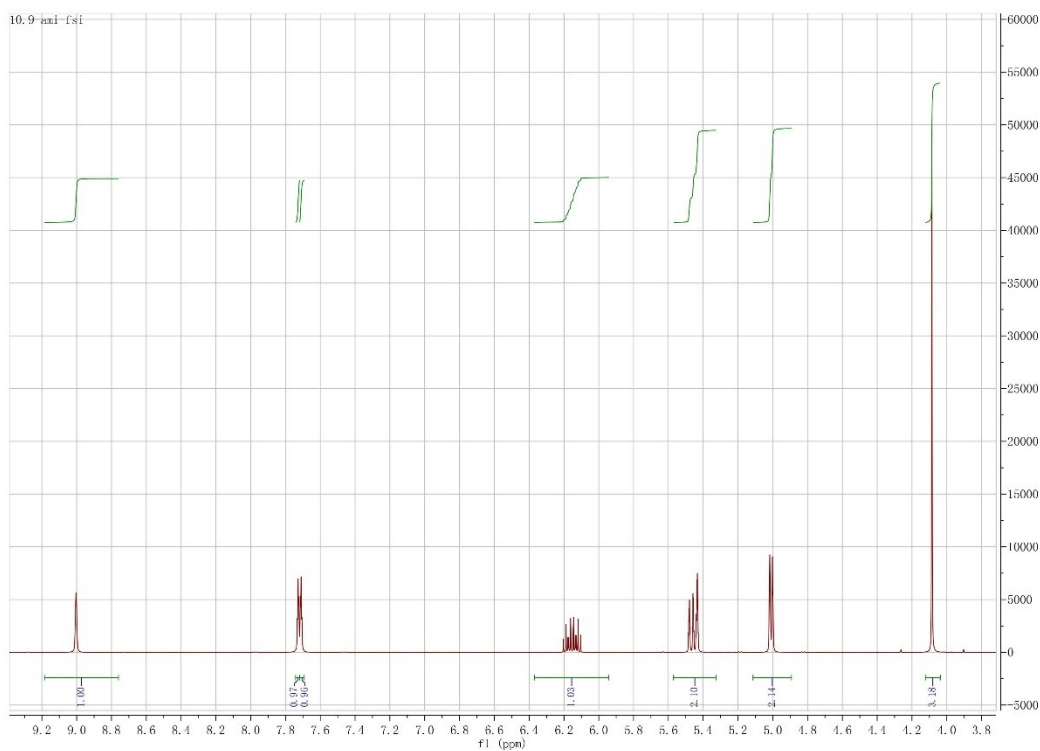


Fig. S11 ^1H NMR spectrum of AMI-FSI

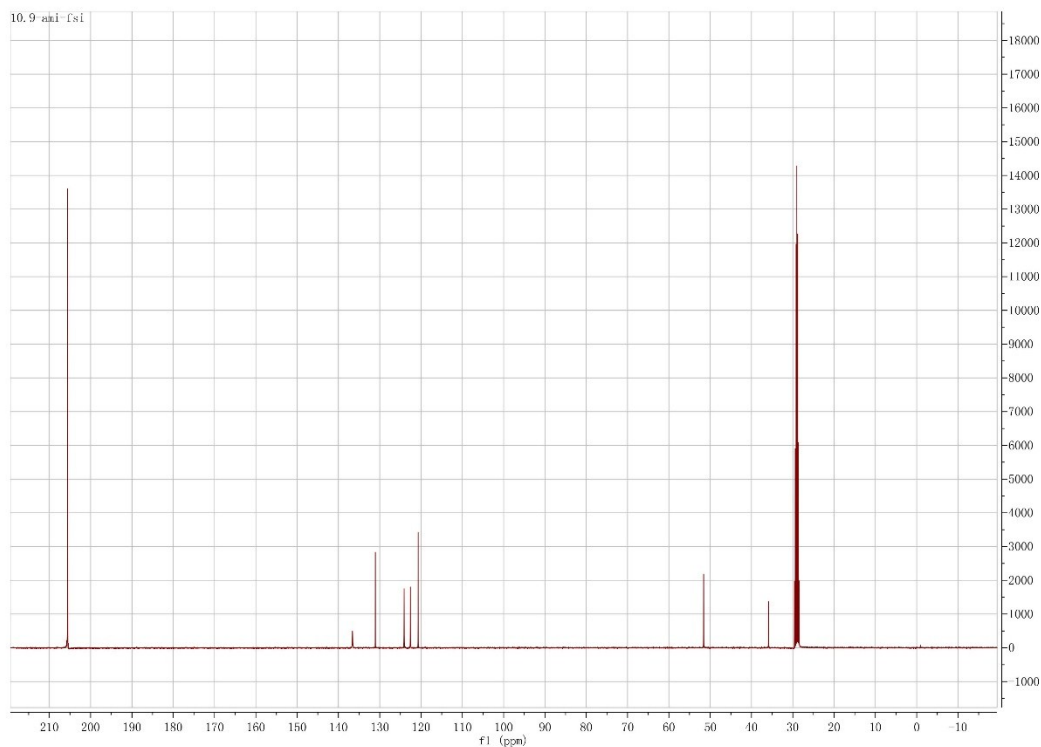


Fig. S12 ^{13}C NMR spectrum of AMI-FSI

2.3 *1-allyl-3-ethylimidazolium bis(fluorosulfonyl)imide (AEI-FSI)*

1-allylimidazole (5.0 g, 0.046 mol) and bromoethane (15.1 g, 0.138 mol) were reacted in a 250 mL flask at 30 °C for 48 h with acetonitrile (10 mL) as the solvent. The following steps were similar with the synthesis of VEI-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Yellow liquid (Yield: 88 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.20-8.96 (s, 1H), 7.99-7.80 (s, 1H), 7.79-7.70 (s, 1H), 6.33-5.98 (m, 1H), 5.51-5.42 (t, 2H), 5.06-4.97 (d, 2H), 4.50-4.39 (q, 2H), 1.68-1.51 (t, 3H).

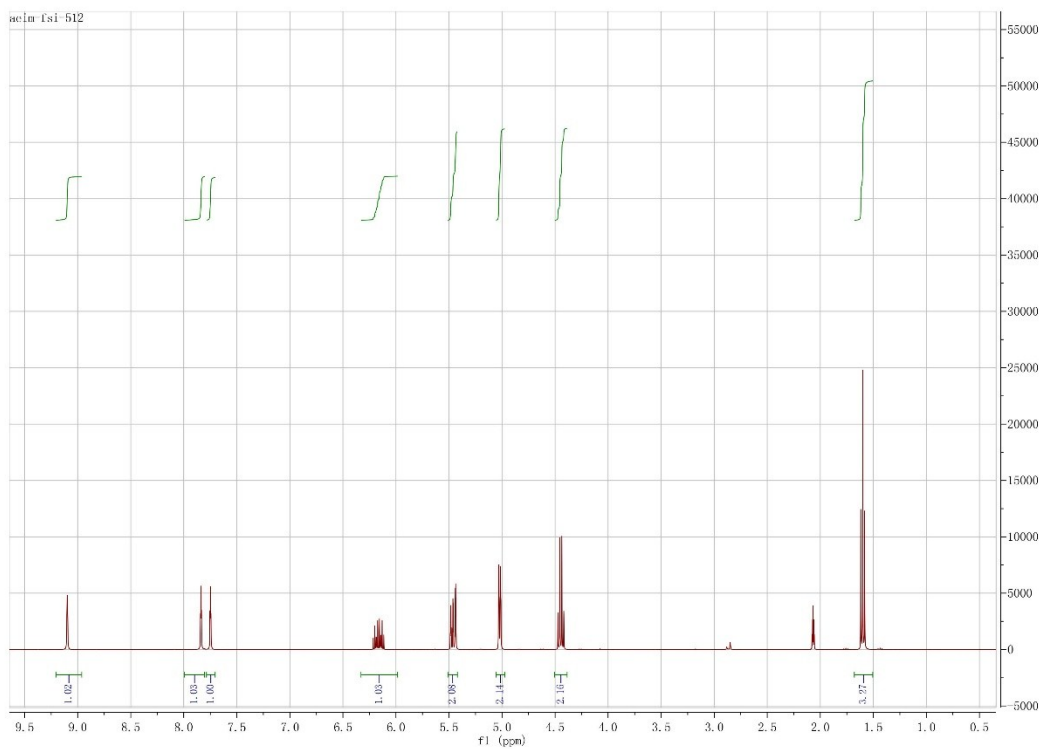


Fig. S13 ^1H NMR spectrum of AEI-FSI

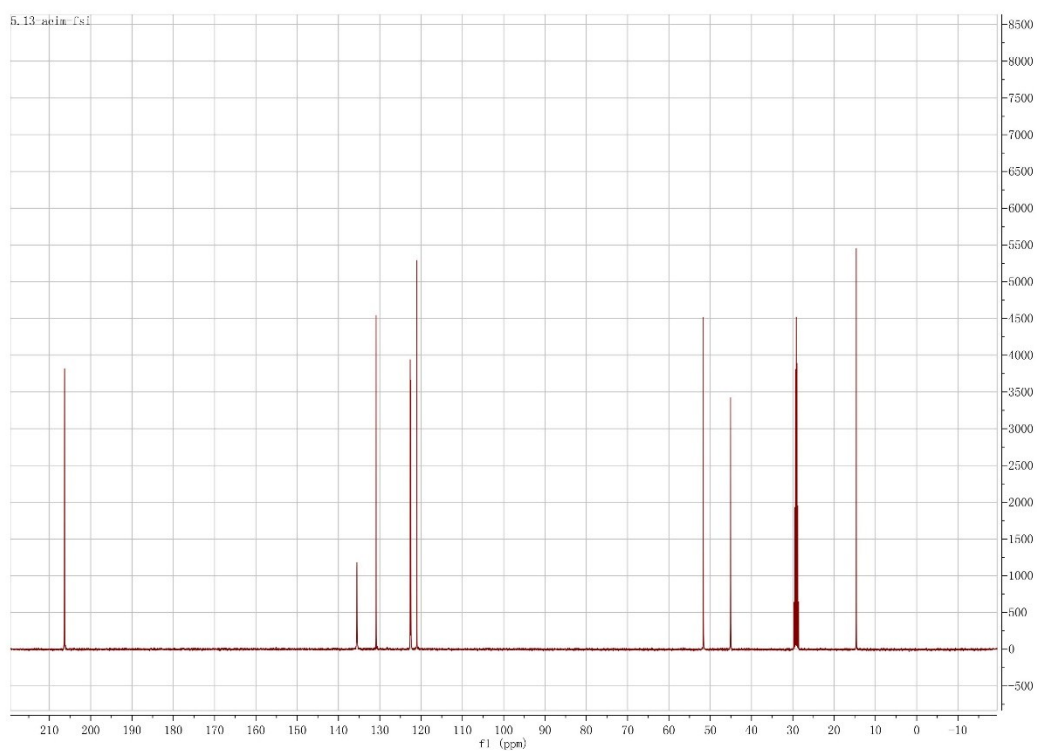


Fig. S14 ^{13}C NMR spectrum of AEI-FSI

2.4 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (VEI-TFSI)

Synthesis and purification of VEI-Br were identical to the first step of synthesis of VEI-FSI. Then the bromide was dissolved in deionized water with same molar amount lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and stirred for 4h at ambient temperature. Dichloromethane was used to extract the IL from the mixture and then the solvent was washed with deionized water for 3 times until no halide residual could be detected by AgNO₃ solution. The dichloromethane was removed by rotary evaporation. The IL was dried under high vacuum for 48 h at 110 °C. Light yellow liquid (Yield: 82 %). ¹H NMR (400 MHz, (CD₃)₂CO): δ (ppm): 9.57-9.16 (s, 1H), 8.24-8.05 (s, 1H), 8.05-7.84 (s, 1H), 7.52-7.27 (q, 1H), 6.09-5.93 (m, 1H), 5.60-5.43 (m, 1H), 4.56-4.41 (q, 2H), 1.69-1.58 (t, 3H).

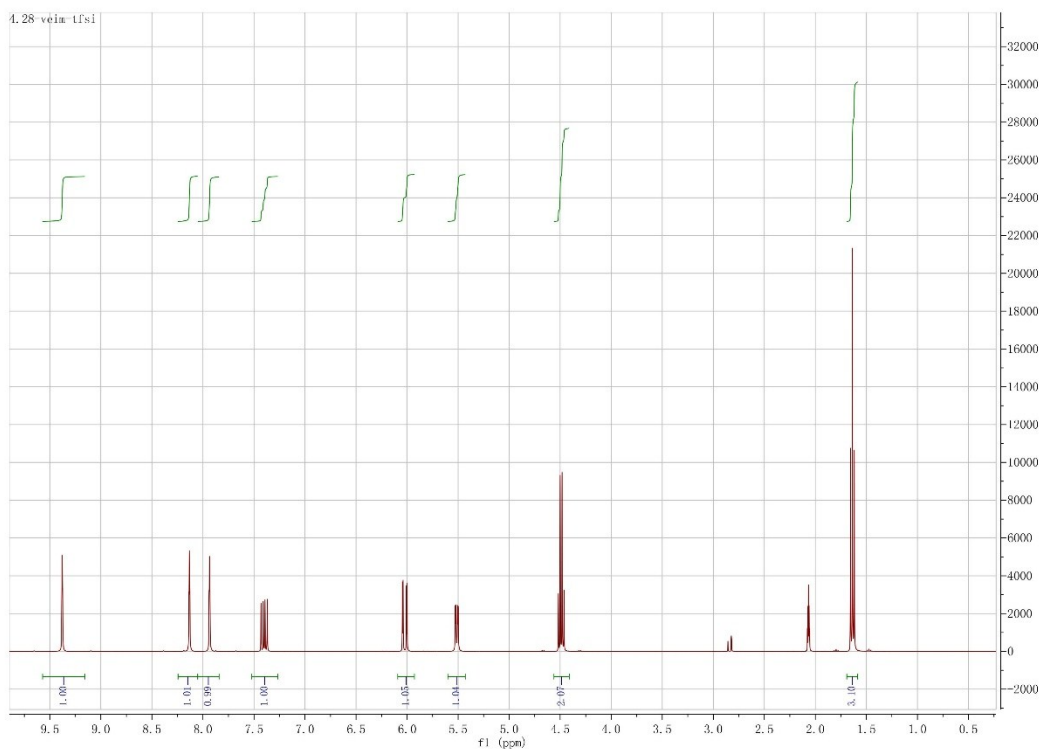


Fig. S15 ¹H NMR spectrum of VEI-TFSI

2.5 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (AMI-TFSI)

Synthesis and purification of AMI-Br were identical to the first step of synthesis of AMI-FSI.

Then the following steps were similar with VEI-TFSI. The IL was dried under high vacuum for 48 h at 110 °C. Light yellow liquid (Yield: 78 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.23-8.93 (s, 1H), 7.79-7.76 (s, 1H), 7.76-7.73 (s, 1H), 6.31-6.05 (m, 1H), 5.55-5.36 (m, 2H), 5.12-4.96 (d, 2H), 4.20-4.01 (s, 3H).

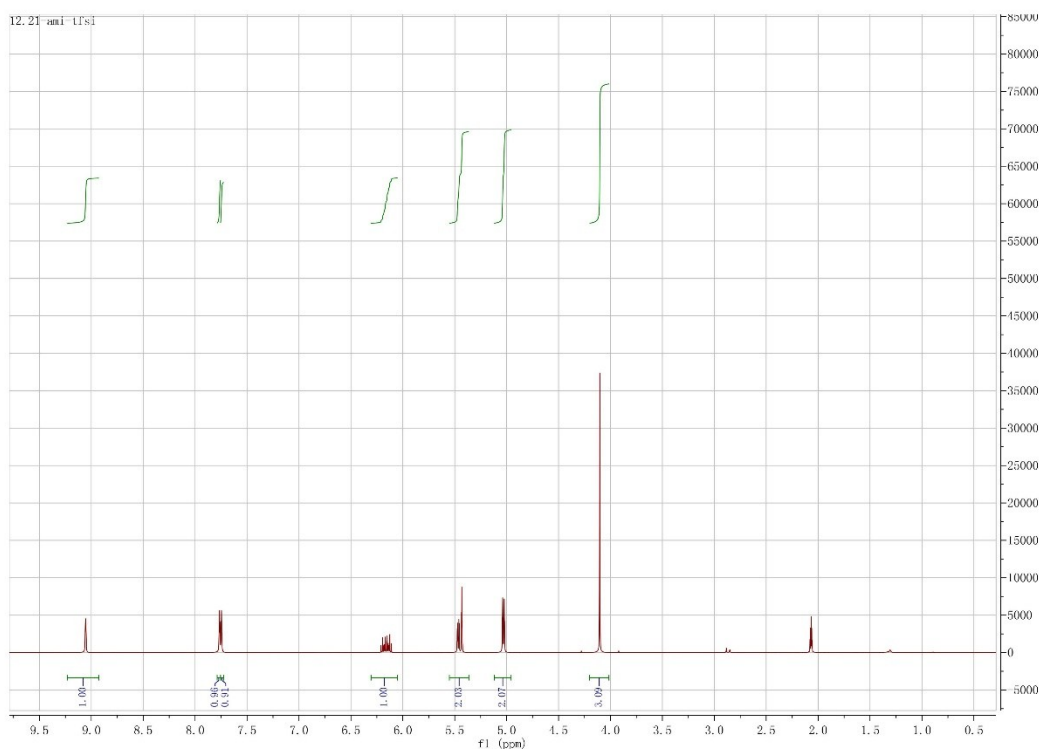


Fig. S16 ^1H NMR spectrum of AMI-TFSI

2.6 1-allyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)imide (AEI-TFSI)

Synthesis and purification of AEI-Br were identical to the first step of synthesis of AEI-FSI. Then the following steps were similar with VEI-TFSI. The IL was dried under high vacuum for 48 h at 110 °C. Yellow liquid (Yield: 90 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.23-8.95 (s, 1H), 7.98-7.81 (s, 1H), 7.80-7.57 (s, 1H), 6.38-5.96 (m, 1H), 5.69-5.26 (t, 2H), 5.08-4.97 (d, 2H), 4.52-4.37 (q, 2H), 1.66-1.50 (t, 3H).

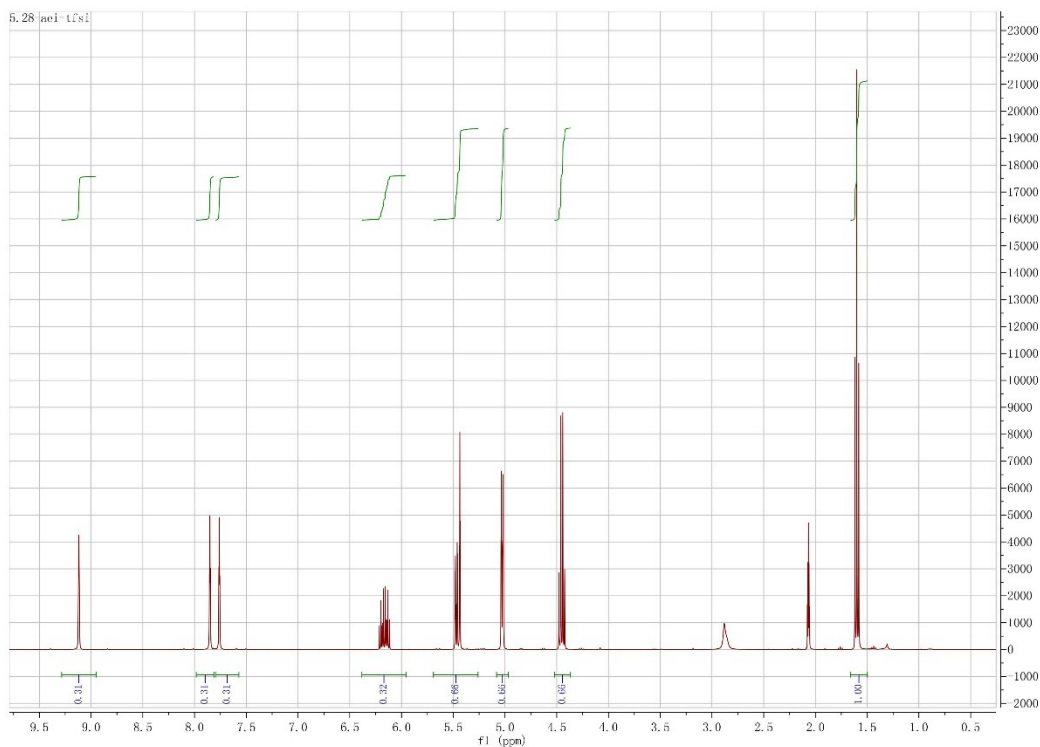


Fig. S17 ^1H NMR spectrum of AEI-TFSI

3. Synthesis procedure of 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMI-FSI)

1-methylimidazole (5.0 g, 0.061 mol) and bromoethane (19.9 g, 0.182 mol) were reacted in a 250 mL flask at 30 °C for 48 h with acetonitrile (10 mL) as the solvent. The following steps were similar with the synthesis of VEI-FSI. The IL was dried under high vacuum for 24 h at 100 °C. Colorless liquid (Yield: 88 %). ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): δ (ppm) 9.10-8.86 (s, 1H), 7.80-7.72 (s, 1H), 7.71-7.64 (s, 1H), 4.46-4.35 (m, 2H), 4.11-4.00 (s, 3H), 1.63-1.53 (t, 3H).

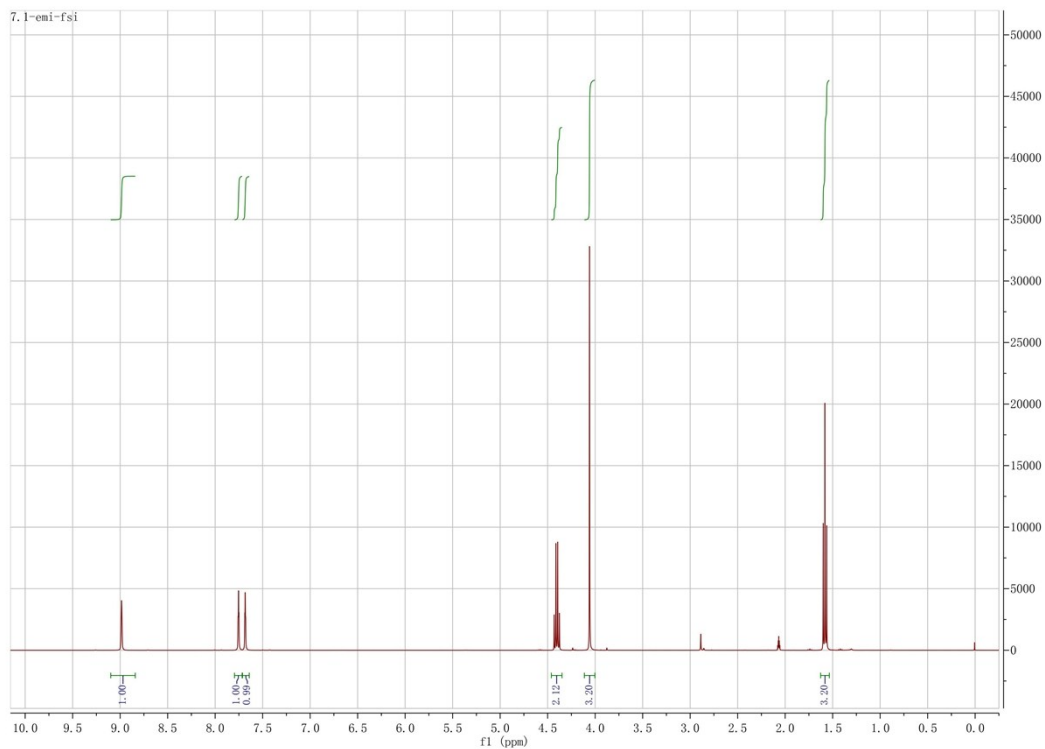


Fig. S18 ^1H NMR spectrum of EMI-FSI

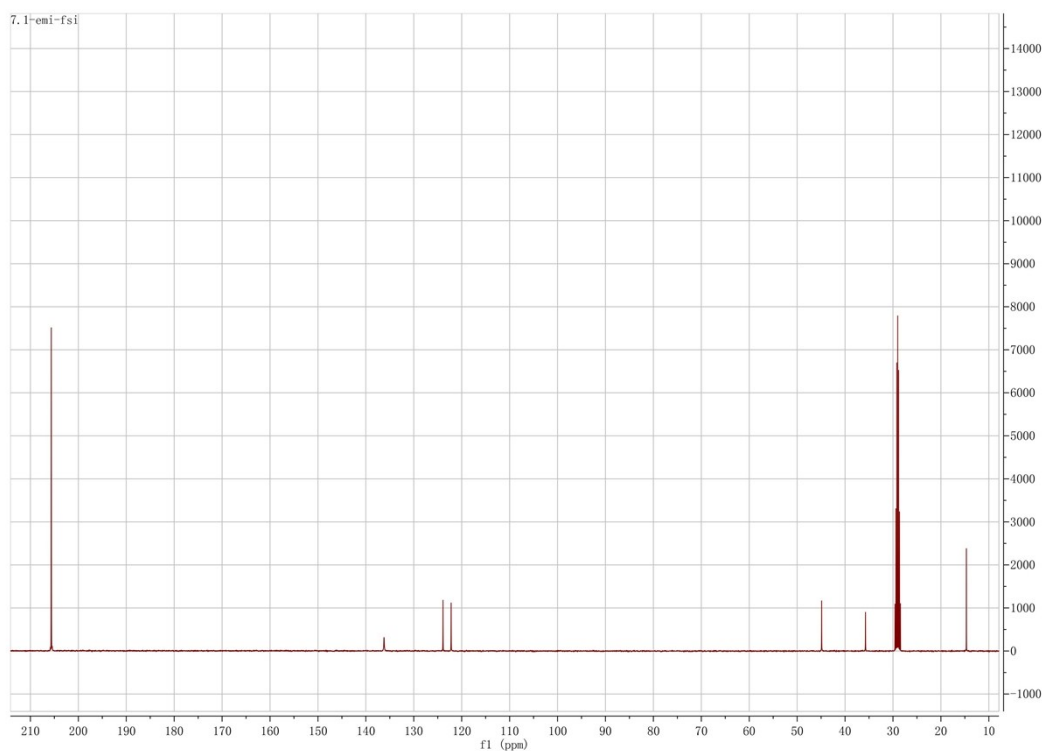


Fig. S19 ^{13}C NMR spectrum of EMI-FSI

Table S1 Adjustable parameters of VTF equation for viscosity

ILs	η_0 (mPa s)	B (K)	T_0 (K)	R^2
VEI-FSI	0.198($\pm 15\%$)	639.2($\pm 7\%$)	163.7($\pm 3\%$)	0.99989
AMI-FSI	0.108($\pm 12\%$)	815.3($\pm 5\%$)	140.9($\pm 3\%$)	0.99996
AEI-FSI	0.168($\pm 12\%$)	680.8($\pm 6\%$)	151.3($\pm 3\%$)	0.99994
Im2o1-1-FSI	0.164($\pm 8\%$)	675.0($\pm 4\%$)	167.3($\pm 2\%$)	0.99997
Im2o1-2-FSI	0.151($\pm 18\%$)	708.4($\pm 8\%$)	158.4($\pm 4\%$)	0.99988
Im2o2-1-FSI	0.215($\pm 6\%$)	594.4($\pm 3\%$)	176.3($\pm 1\%$)	0.99998
Im2o2-2-FSI	0.213($\pm 9\%$)	613.4($\pm 4\%$)	168.8($\pm 2\%$)	0.99996
EMI-FSI	0.193($\pm 14\%$)	637.9($\pm 7\%$)	157.9($\pm 4\%$)	0.99990
VEI-TFSI	0.124($\pm 5\%$)	785.9($\pm 2\%$)	165.5($\pm 1\%$)	0.99999
AMI-TFSI	0.141($\pm 7\%$)	808.3($\pm 3\%$)	148.3($\pm 1\%$)	0.99999
AEI-TFSI	0.213($\pm 11\%$)	686.6($\pm 5\%$)	157.5($\pm 3\%$)	0.99995
Im2o1-1-TFSI ^a	0.175($\pm 9\%$)	660.5($\pm 9\%$)	177.5($\pm 2\%$)	0.99997
Im2o1-2-TFSI ^a	0.167($\pm 15\%$)	663.2($\pm 15\%$)	174.7($\pm 3\%$)	0.99993
Im2o2-1-TFSI ^a	0.070($\pm 18\%$)	923.9($\pm 28\%$)	149.5($\pm 6\%$)	0.99986
Im2o2-2-TFSI ^a	0.167($\pm 28\%$)	654.1($\pm 17\%$)	173.1($\pm 3\%$)	0.99991
EMI-TFSI ^a	0.182($\pm 9\%$)	718.6($\pm 9\%$)	160.8($\pm 1\%$)	0.99991

The percentage standard errors for η_0 , B and T_0 have been included, and R^2 is the VTF fitting parameter. ^a Ref. in [36].

Table S2 Adjustable parameters of VTF equation for conductivity

ILs	σ_0 (mS cm ⁻¹)	B (K)	T_0 (K)	R^2
VEI-FSI	36.86(±6%)	38.45(±17%)	266.85(±2%)	0.99414
AMI-FSI	38.85(±7%)	42.44(±18%)	264.86(±2%)	0.99404
AEI-FSI	32.70(±4%)	31.14(±14%)	265.73(±2%)	0.99627
Im2o1-1-FSI	68.47(±12%)	129.97(±16%)	237.81(±3%)	0.99783
Im2o1-2-FSI	57.90(±11%)	107.94(±17%)	242.17(±3%)	0.99731
Im2o2-1-FSI	94.03(±10%)	194.32(±11%)	223.06(±2%)	0.99935
Im2o2-2-FSI	78.36(±11%)	170.58(±12%)	224.85(±3%)	0.99906
EMI-FSI	29.19(±2%)	16.63(±12%)	275.44(±1%)	0.99578
VEI-TFSI	92.29(±7%)	199.8(±7%)	224.66(±2%)	0.99969
AMI-TFSI	88.60(±8%)	196.8(±9%)	219.41(±2%)	0.99957
AEI-TFSI	87.62(±7%)	213.4(±7%)	210.86(±2%)	0.99976
Im2o1-1-TFSI ^a	215.9(±2%)	394.7(±1%)	195.5(±0%)	1
Im2o1-2-TFSI ^a	228.8(±5%)	419.4(±3%)	187.8(±1%)	0.99997
Im2o2-1-TFSI ^a	219.6(±7%)	425.2(±5%)	190.0(±2%)	0.99995
Im2o2-2-TFSI ^a	201.4(±2%)	409.0(±1%)	189.5(±0%)	1
EMI-TFSI ^a	191.7(±6%)	331.2(±5%)	191.3(±2%)	0.99993

The percentage standard errors for σ_0 , B and T_0 have been included, and R^2 is the VTF fitting parameter. ^a Ref. in [36].