Supporting Information

Efficient Dimerization of Perfluoroolefin with Strong Nucleophilic Ionic Liquids Catalysts by Adjusting the Interaction of Anion and Cation

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Characterizations of IL

FT-IR, NMR and ESI-MS, as shown in Figure S1-S11, were carried out to identify the structures of the prepared ILs. The results of the chosen catalyst, [$C_n$mmim][SCN], [C_4Py][SCN] and [$N_{4,4,4,4}$][SCN] are mainly displayed here.

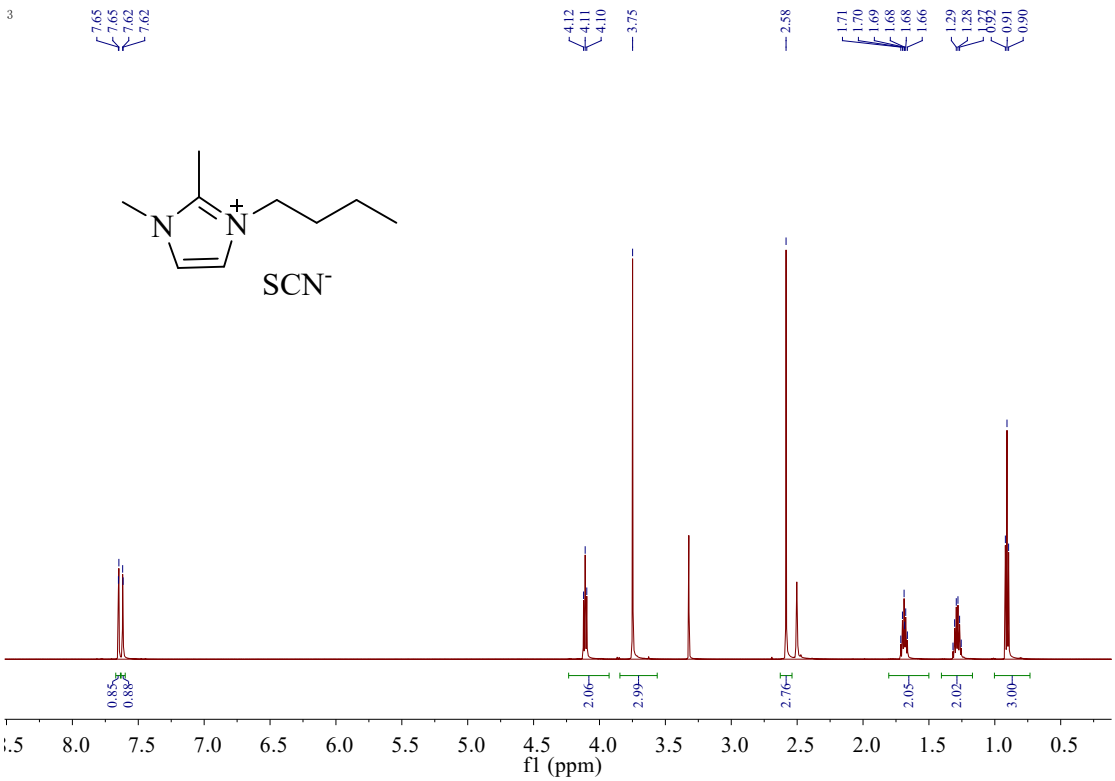

Fig. S1 The ^{1}H NMR spectrum of [C_4mmim][SCN] (DMSO)

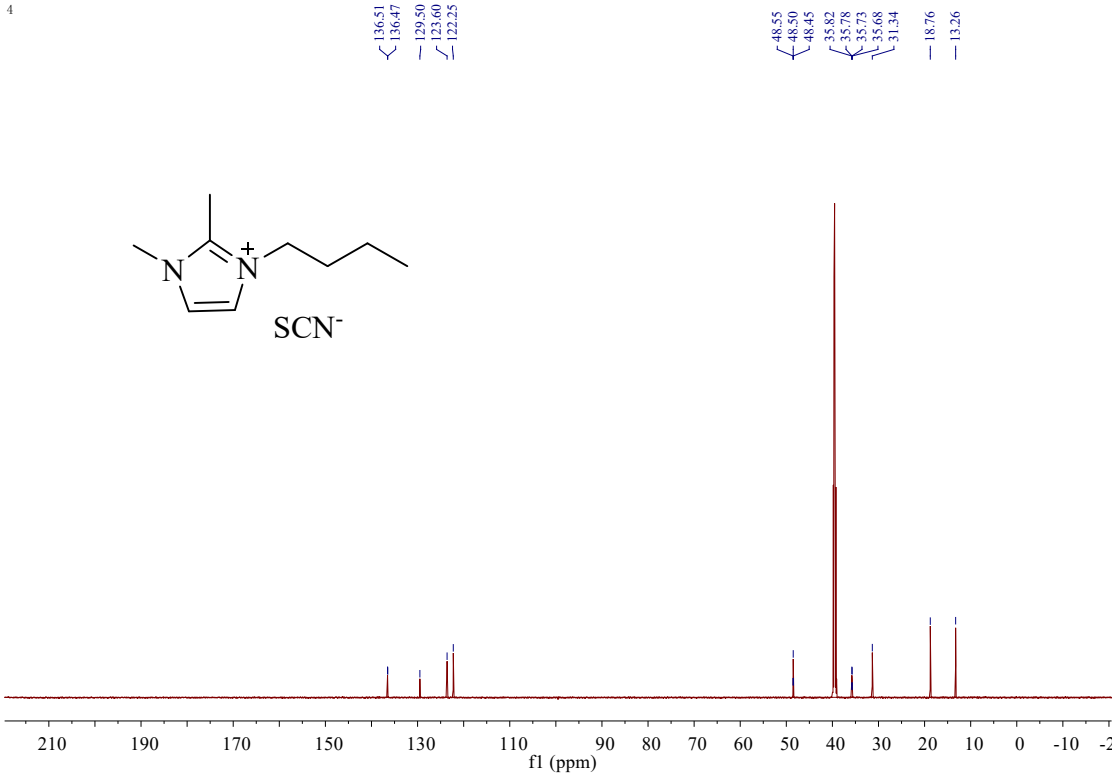

Fig. S2 The ^{13}C NMR spectrum of [C_4mmim][SCN] (DMSO)

[C_4mmim][SCN]: ^{1}H NMR (600 MHz, DMSO) δ 7.65 (d, J = 2.1 Hz, 1H), 7.62 (d, J = 2.0 Hz, 1H), 4.11 (t, J = 7.3 Hz, 2H), 3.75 (s, 3H), 2.58 (s, 3H), 1.76 – 1.59 (m,

2H), 1.35 – 1.19 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). 13C NMR (151 MHz, DMSO) δ 137.00, 136.96, 129.99, 124.09, 122.74, 49.04, 48.99, 48.95, 36.27, 36.22, 31.83, 19.25, 13.75.

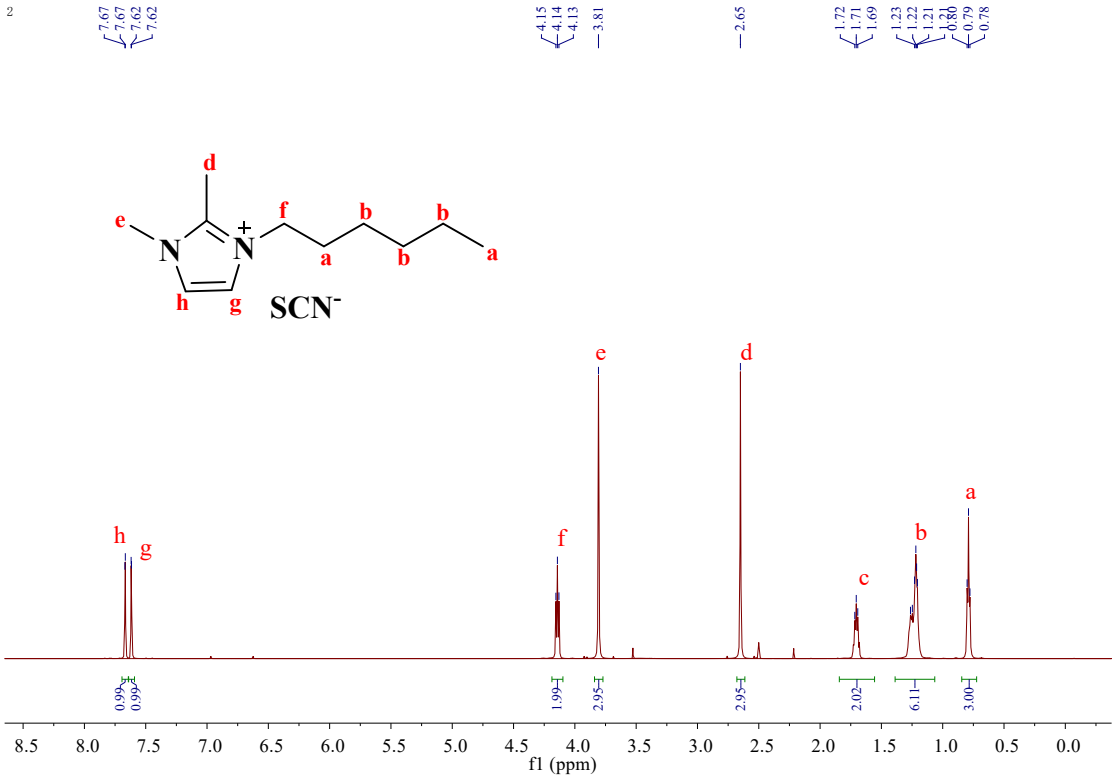

Fig. S3 The ^{1}H NMR spectrum of [C_6mmim][SCN] (DMSO)

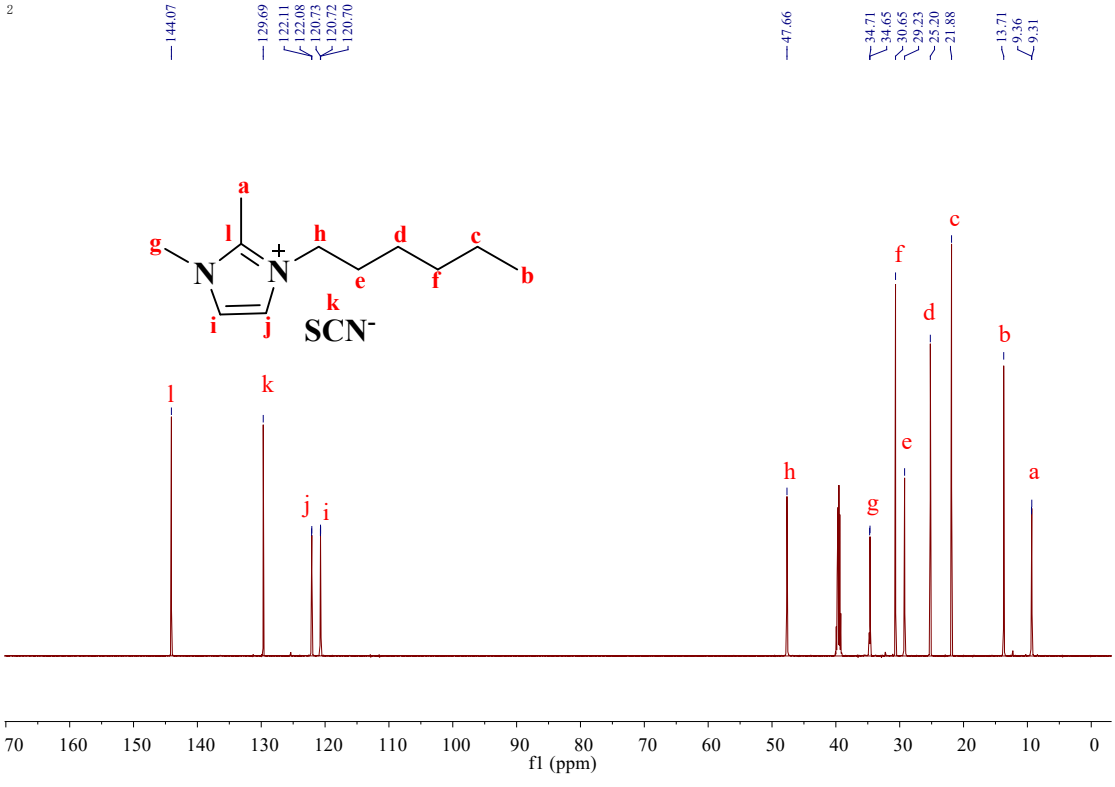

Fig. S4 The ^{13}C NMR spectrum of [C_6mmim][SCN] (DMSO)

[C_6mmim][SCN]: ^1H NMR (600 MHz, DMSO) δ 7.67 (d, J = 2.0 Hz, 1H), 7.62 (d, J = 1.9 Hz, 1H), 4.14 (t, J = 7.4 Hz, 2H), 3.81 (s, 3H), 2.65 (s, 3H), 1.84 – 1.56 (m, 2H), 1.39 – 1.06 (m, 6H), 0.79 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 144.07, 129.69, 122.11, 122.08, 120.73, 120.72, 120.70, 120.63, 47.71, 47.66, 47.60, 34.76, 34.71, 34.65, 34.60, 30.65, 29.23, 25.20, 21.88, 13.71, 9.40, 9.36, 9.31, 9.27.

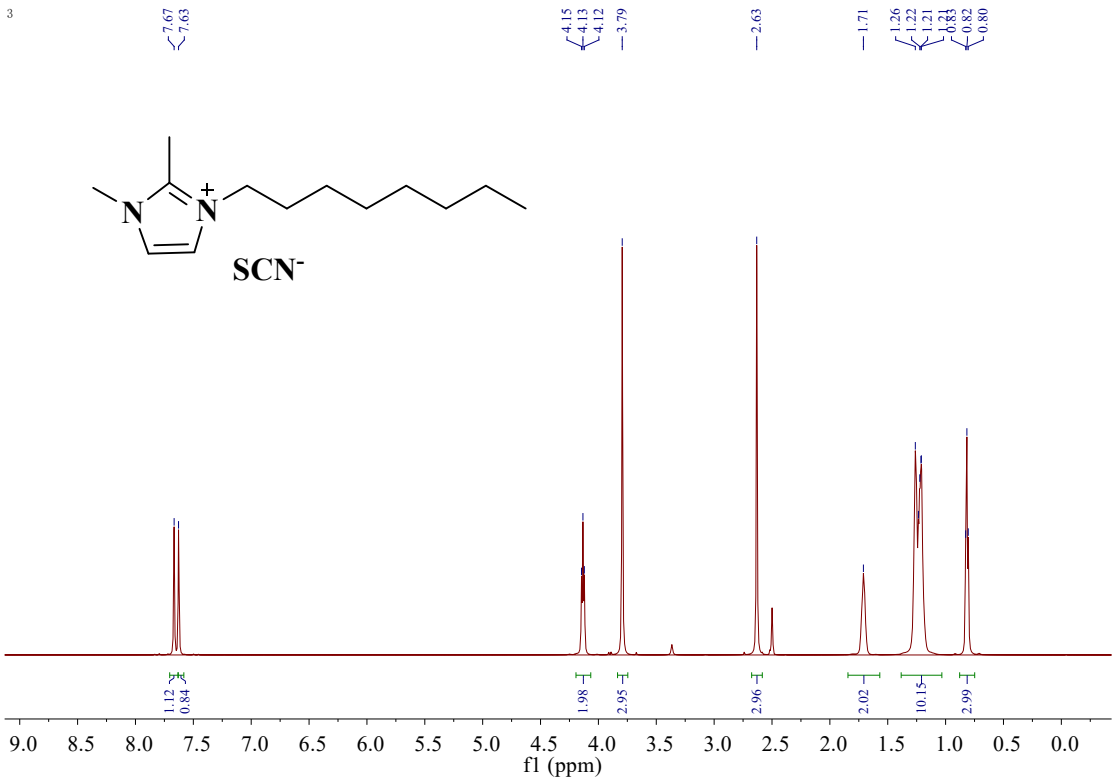

Fig. S5 The ^1H NMR spectrum of [C_8mmim][SCN] (DMSO)

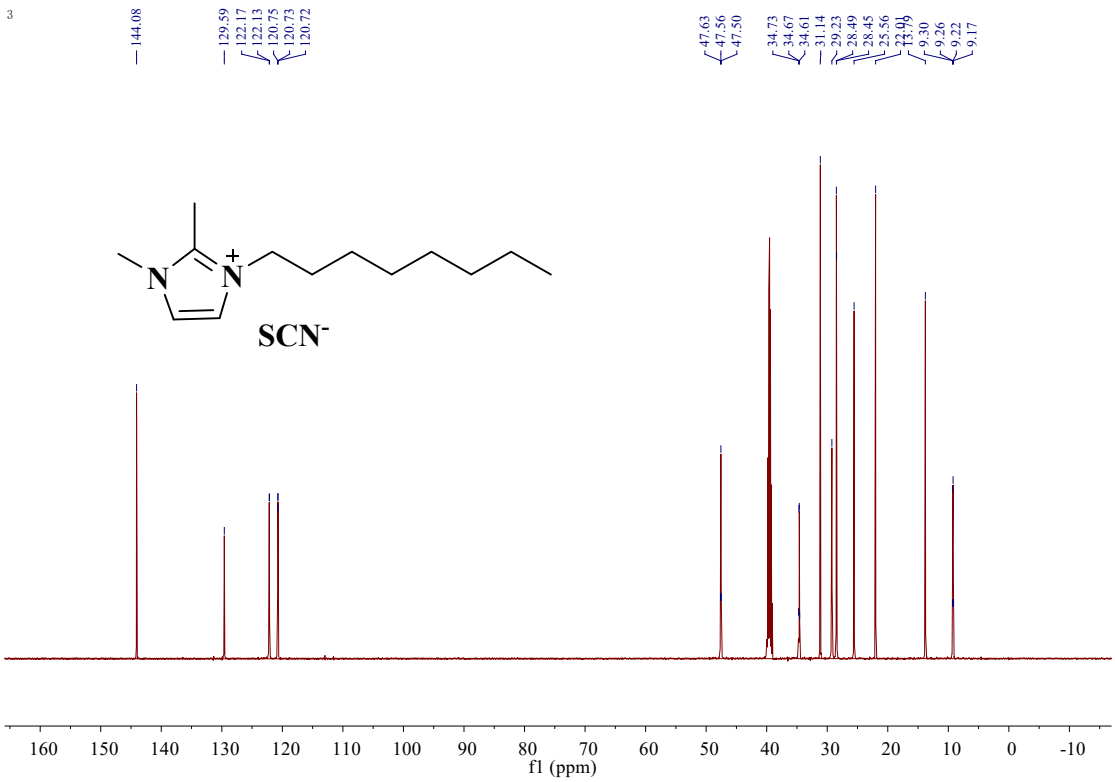

Fig. S6 The ^{13}C NMR spectrum of [C_8mmim][SCN] (DMSO)

[C_8mmim][SCN]: ^{1}H NMR (600 MHz, DMSO) δ 7.67 (s, 1H), 7.63 (s, 1H), 4.13 (t, J = 7.3 Hz, 2H), 3.79 (s, 3H), 2.63 (s, 3H), 1.71 (s, 2H), 1.38 – 1.03 (m, 10H), 0.82 (t, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 144.08, 129.59, 122.17, 122.13, 120.75, 120.73, 120.72, 47.63, 47.56, 47.50, 34.73, 34.67, 34.61, 34.56, 31.14, 29.23, 28.49, 28.45, 25.56, 22.01, 13.79, 9.30, 9.26, 9.22, 9.17.

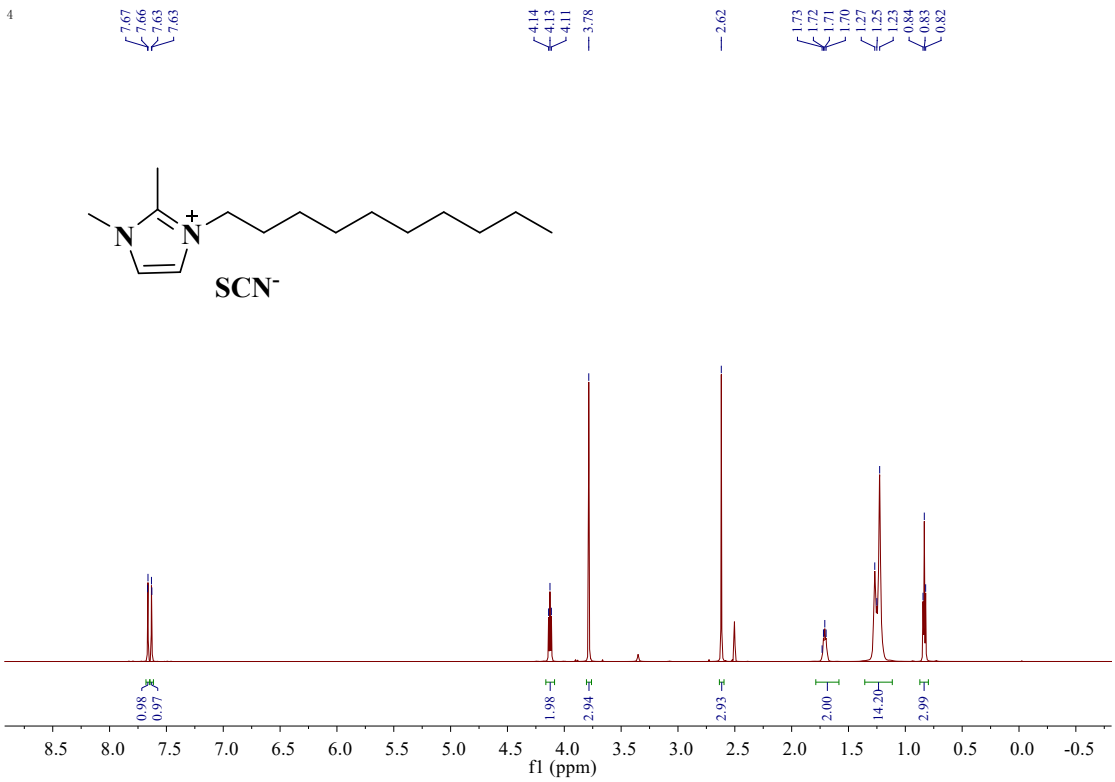

Fig. S7 The ^{1}H NMR spectrum of [C_{10}mmim][SCN] (DMSO)

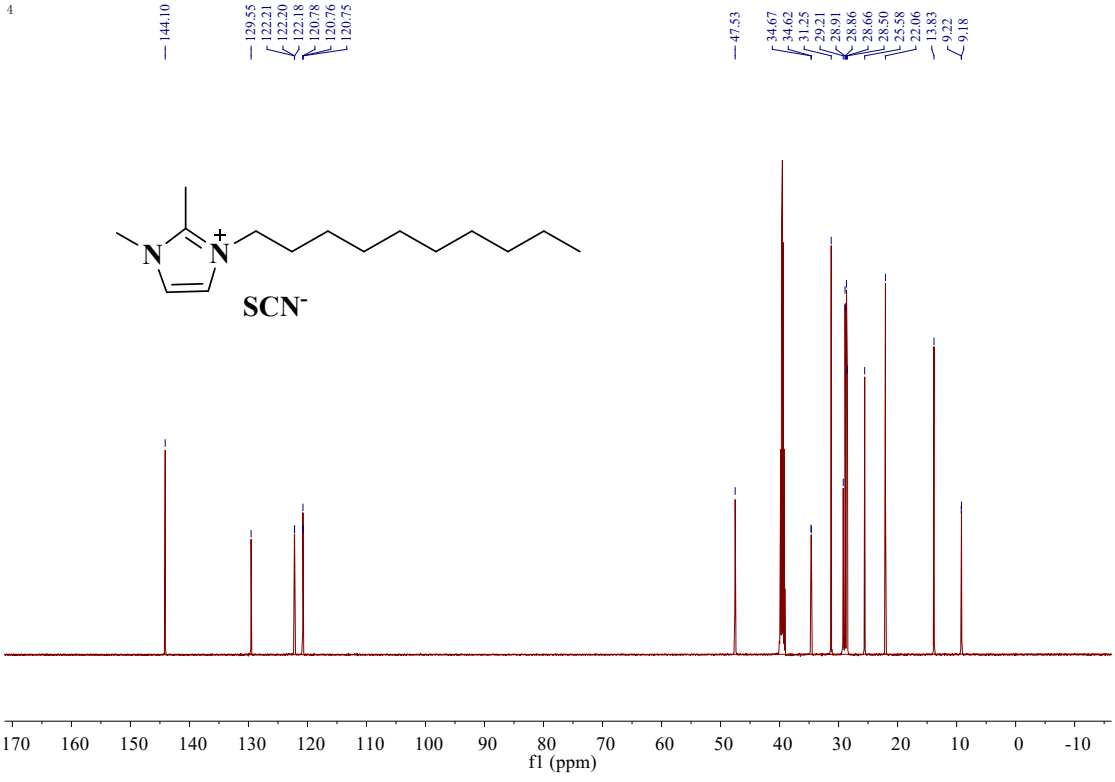

Fig. S8 The ^{13}C NMR spectrum of [C_{10}mmim][SCN] (DMSO)

[C_{10}mmim][SCN]: 1H NMR (600 MHz, DMSO) δ 7.66 (d, J = 2.1 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 4.13 (t, J = 7.4 Hz, 2H), 3.78 (s, 3H), 2.62 (s, 3H), 1.71

(dd, J = 14.0, 7.0 Hz, 2H), 1.36 – 1.11 (m, 14H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 144.10, 129.55, 122.21, 122.20, 122.18, 120.78, 120.76, 120.75, 47.53, 34.67, 34.62, 31.25, 29.21, 28.91, 28.86, 28.66, 28.50, 25.58, 22.06, 13.83, 9.22, 9.18.

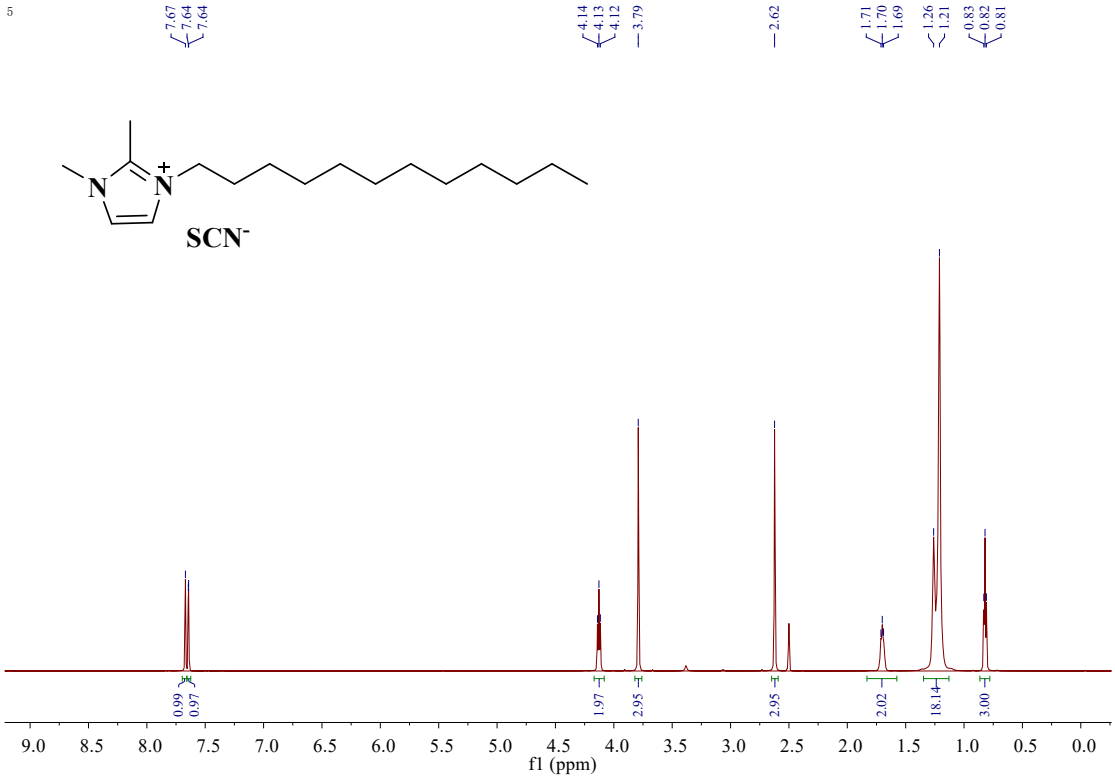

Fig. S9 The 1H NMR spectrum of [C_{12}mmim][SCN] (DMSO)

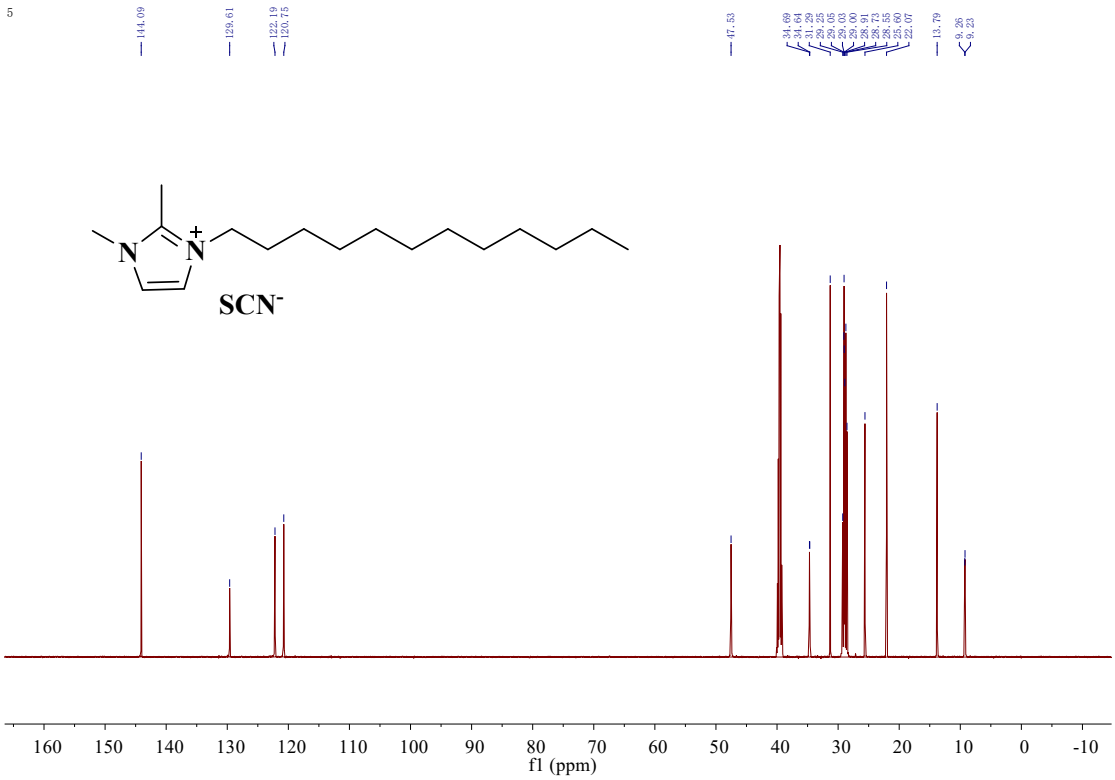

Fig. S10 The ^{13}C NMR spectrum of [C_{12}mmim][SCN] (DMSO)

[C_{12}mmim][SCN]: ^{1}H NMR (600 MHz, DMSO) δ 7.67 (s, 1H), 7.64 (d, J = 1.4 Hz, 1H), 4.13 (t, J = 7.4 Hz, 2H), 3.79 (s, 3H), 2.62 (s, 3H), 1.83 – 1.58 (m, 2H), 1.24 (d, J = 29.9 Hz, 18H), 0.82 (t, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 144.09, 129.61, 122.19, 120.75, 47.53, 34.69, 34.64, 31.29, 29.25, 29.05, 29.03, 29.00, 28.91, 28.73, 28.55, 25.60, 22.07, 13.79, 9.26, 9.23.

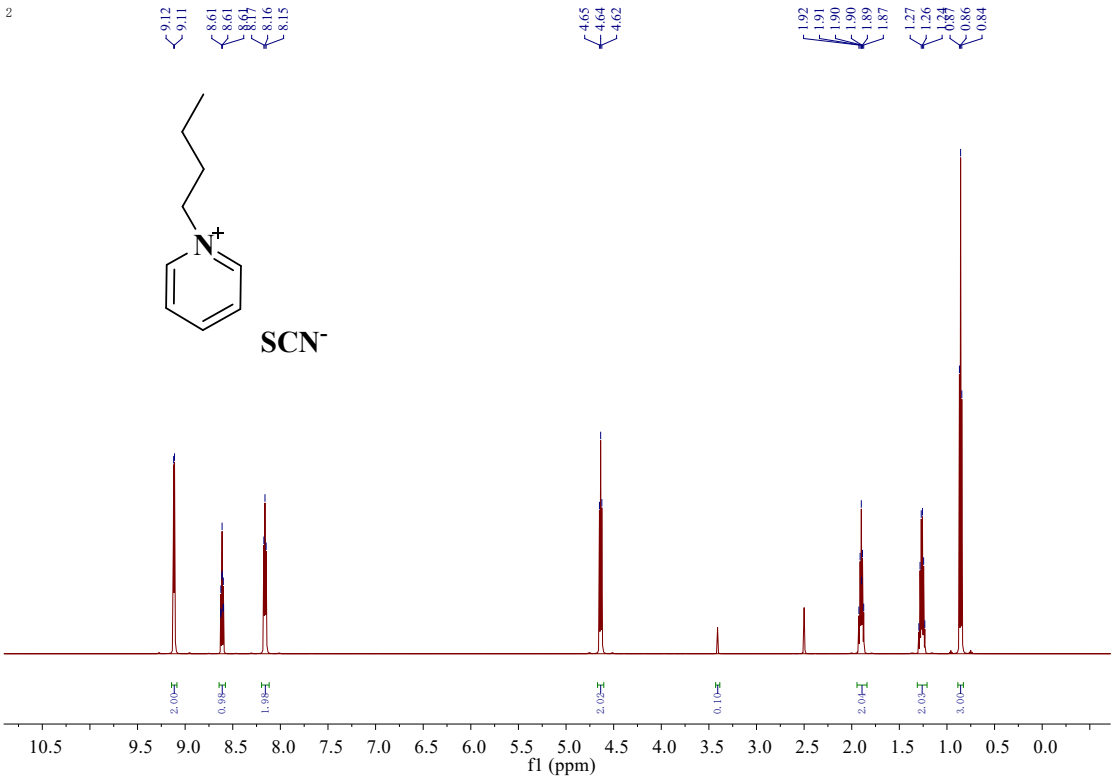

Fig. S11 The ^{1}H NMR spectrum of [C_4Py][SCN] (DMSO)

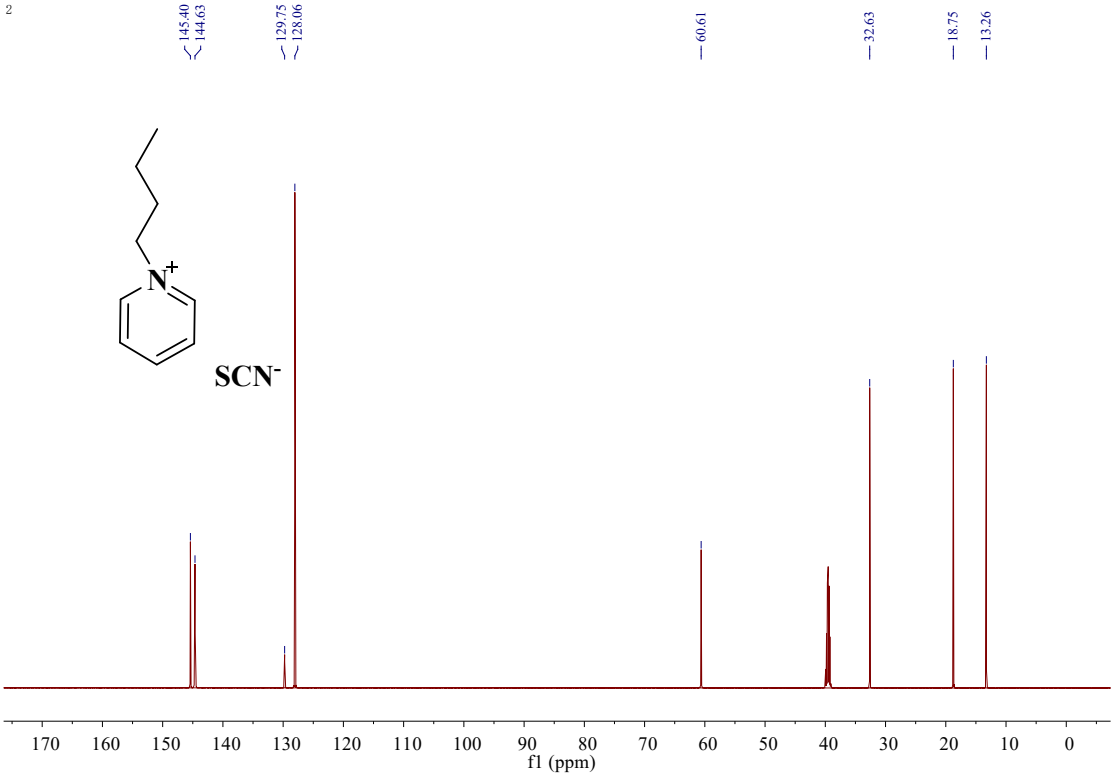

Fig. S12 The ^{13}C NMR spectrum of [C_4Py][SCN] (DMSO)

[C_4Py][SCN]:^{1}H NMR (600 MHz, DMSO) δ 9.12 (d, J = 5.5 Hz, 2H), 8.61 (tt, J = 7.8, 1.2 Hz, 1H), 8.20 – 8.12 (m, 2H), 4.67 – 4.60 (m, 2H), 3.41 (s, 1H),

1.94 – 1.84 (m, 2H), 1.31 – 1.21 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO) δ 145.40, 144.63, 129.75, 128.06, 60.61, 32.63, 18.75, 13.26.

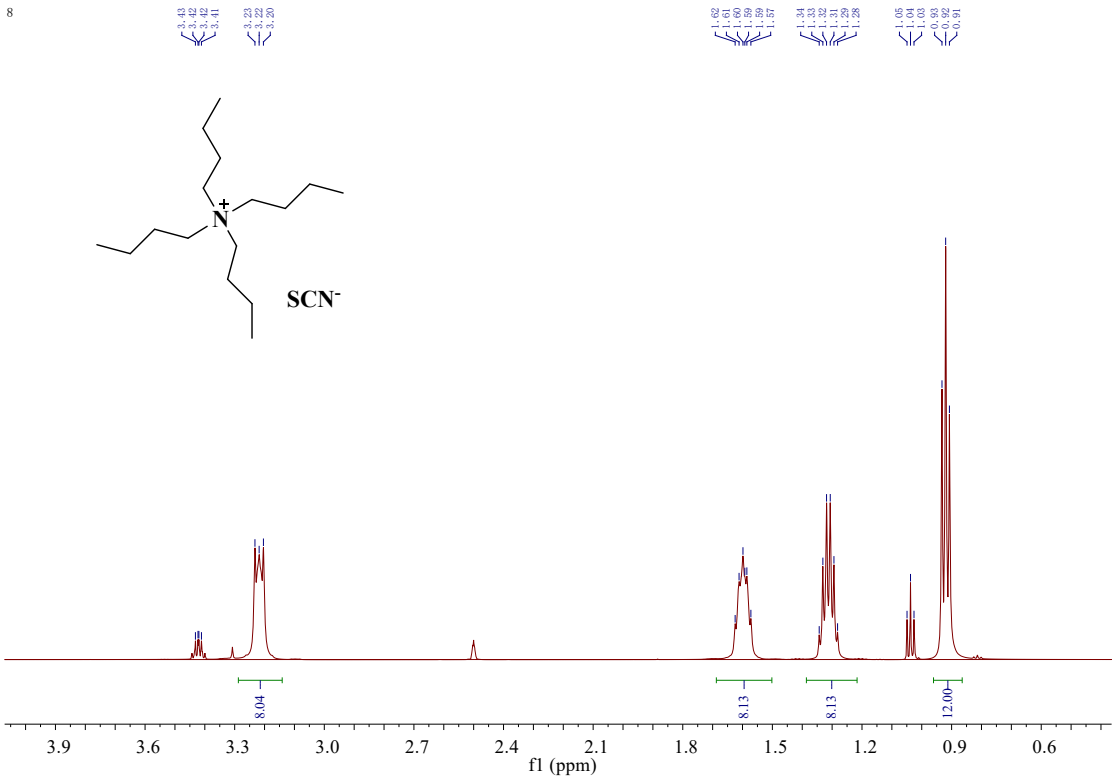

Fig. S13 The ^{1}H NMR spectrum of [$N_{4,4,4,4}$][SCN] (DMSO)

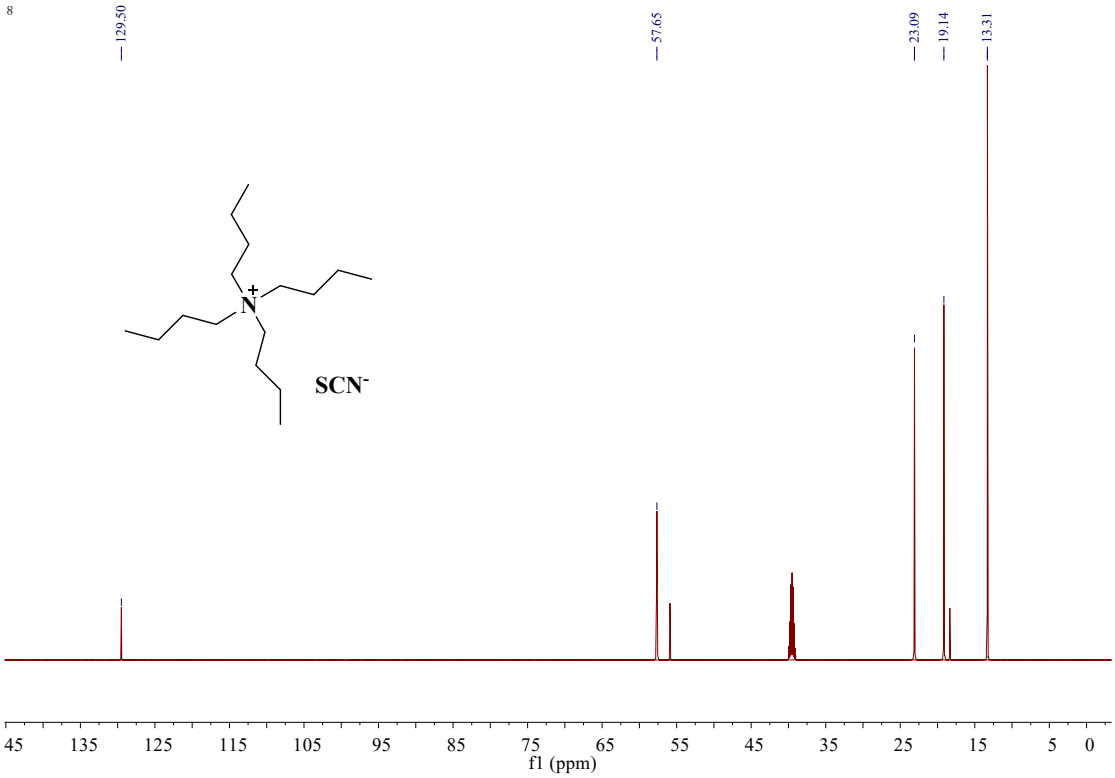

Fig. S14 The ^{13}C NMR spectrum of $[N_{4,4,4,4}][SCN]$ (DMSO)

$[N_{4,4,4,4}][SCN]$: ^{1}H NMR (600 MHz, DMSO) δ 4.35 (t, J = 5.1 Hz, 1H), 3.29 – 3.14 (m, 8H), 1.60 (dt, J = 12.2, 8.0 Hz, 8H), 1.39 – 1.22 (m, 8H), 0.92 (t, J = 7.5 Hz, 12H). ^{13}C NMR (151 MHz, DMSO) δ 130.43, 58.05, 56.40, 23.49 (d, J = 15.8 Hz), 19.83 – 18.97, 18.53, 13.88 – 12.97 (m). ^{13}C NMR (151 MHz, DMSO) δ 129.50, 57.65, 23.09, 19.14, 13.31.

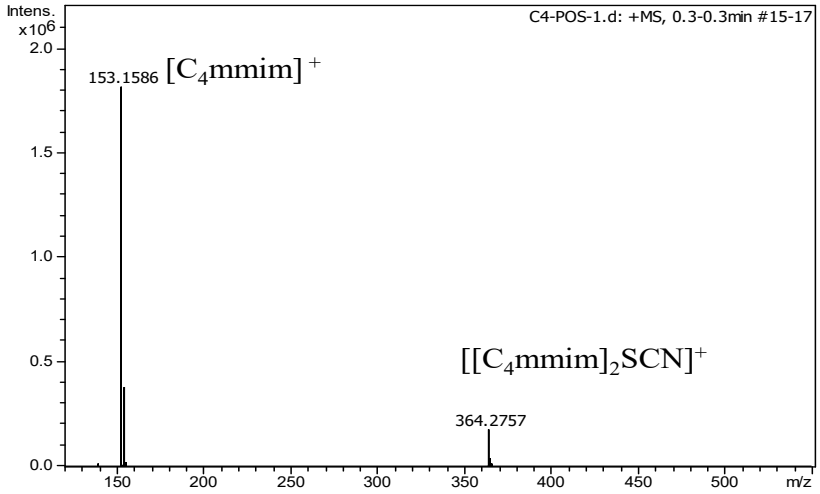

Fig. S15 The ESI-MS spectrum of $[C_4mmim][SCN]$

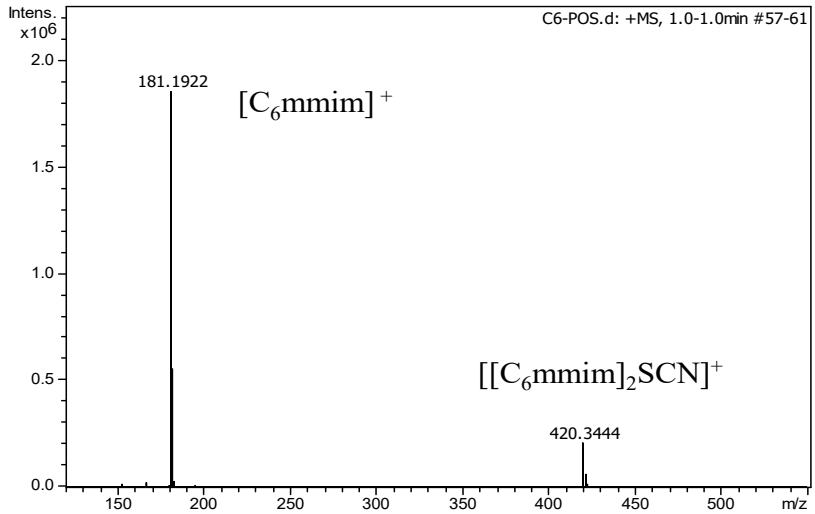

Fig. S16 The ESI-MS spectrum of $[C_6mmim][SCN]$

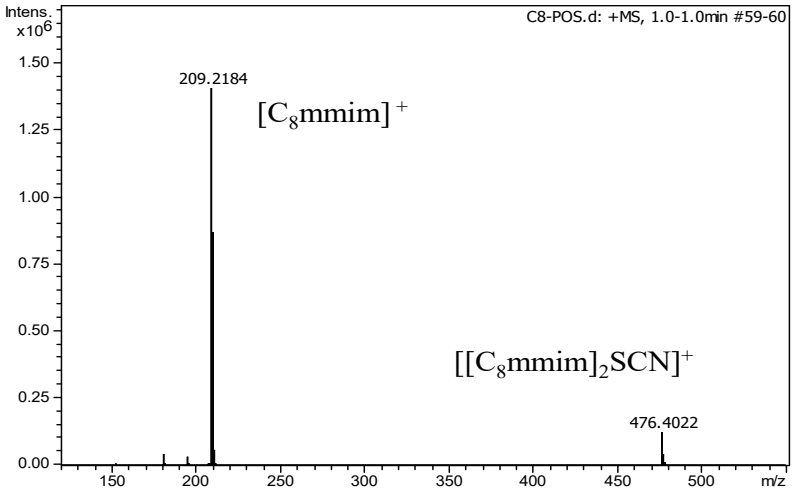

Fig. S17 The ESI-MS spectrum of $[C_8mmim][SCN]$

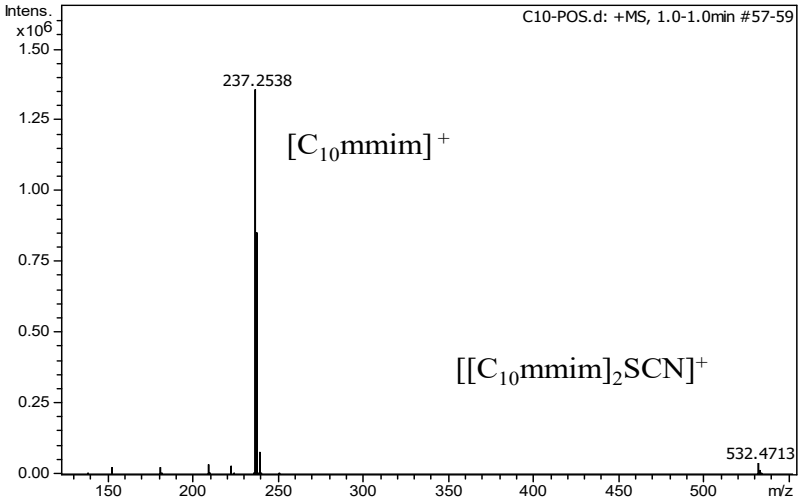

Fig. S18 The ESI-MS spectrum of $[C_{10}mmim][SCN]$

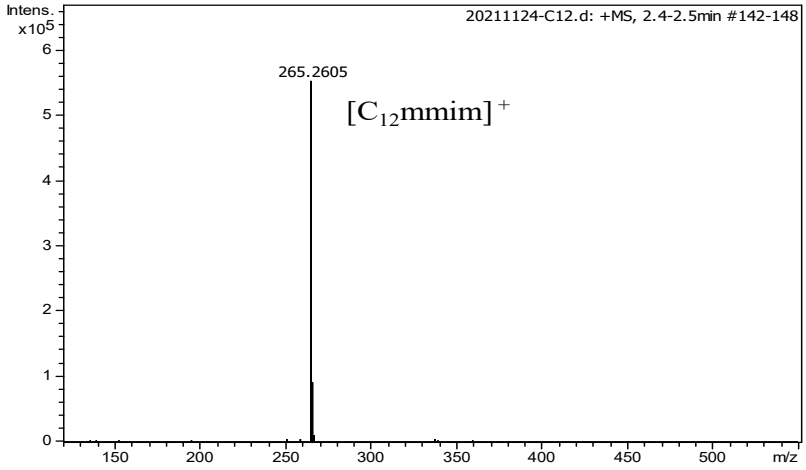

Fig. S19 The ESI-MS spectrum of [C_{12}mmim][SCN]

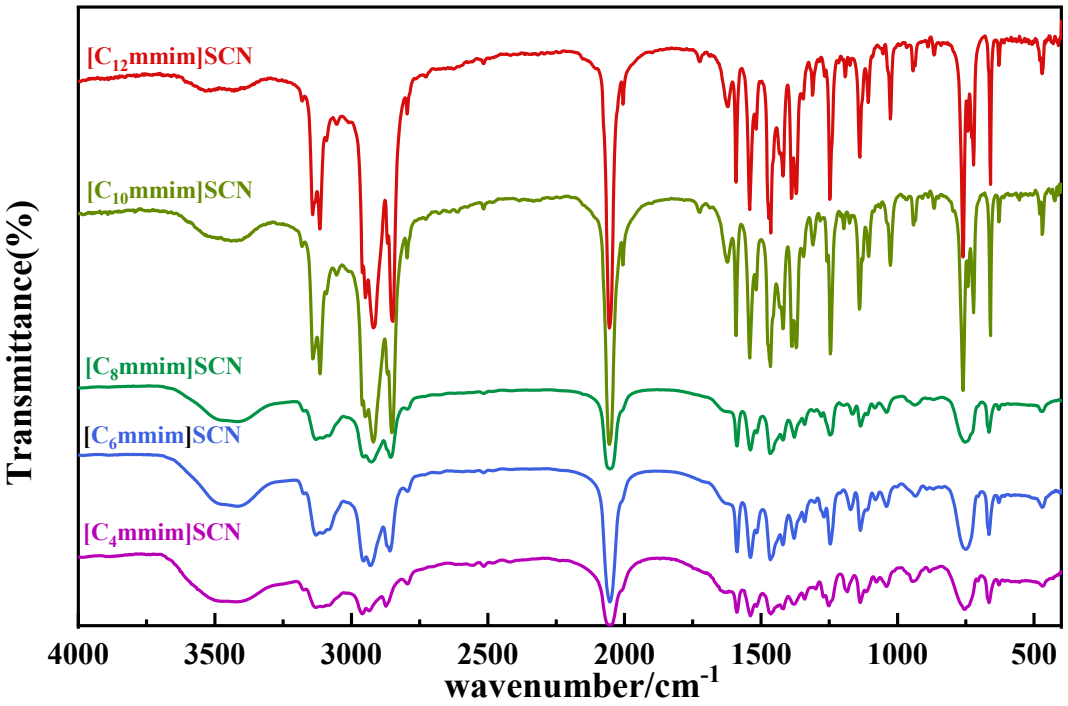

Fig. S20. FT-IR spectra of trisubstituted thiocyanate ionic liquid

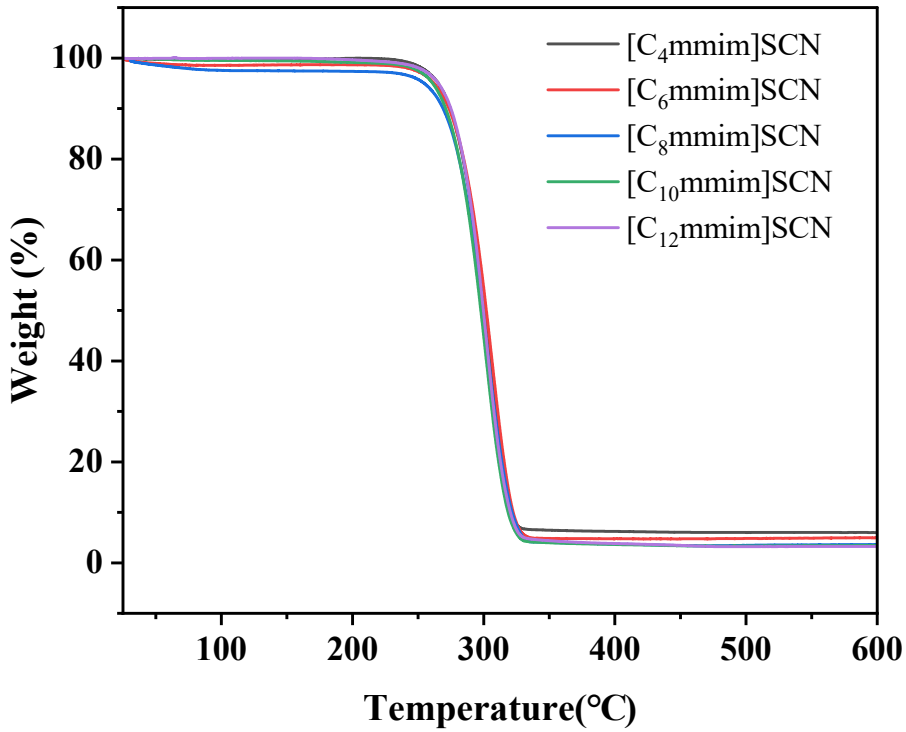

Fig. S21 TGA curves of trisubstituted thiocyanate ionic liquid

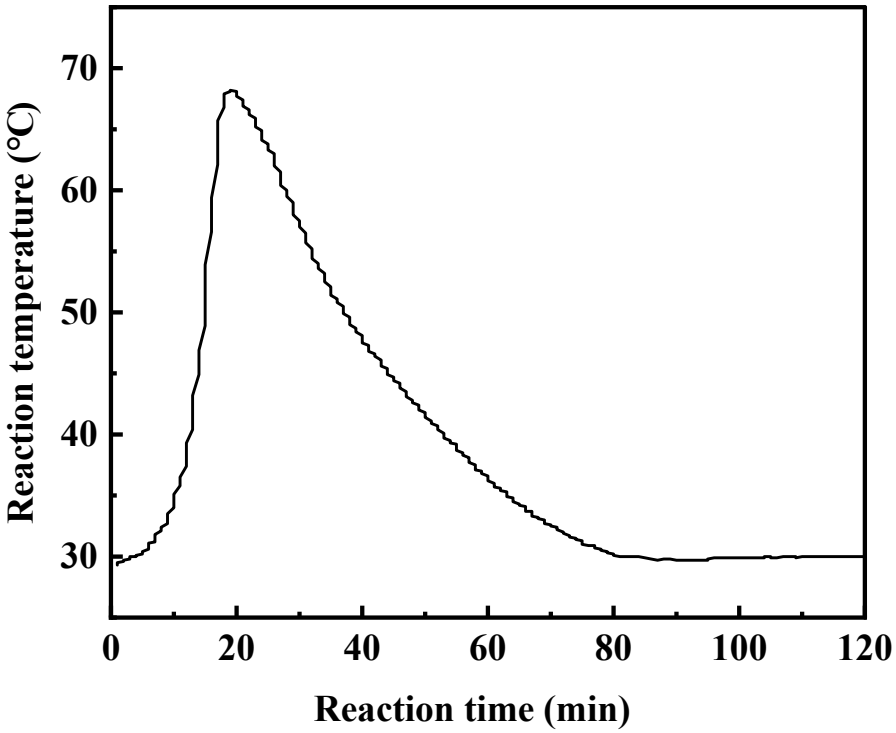

Fig. S22 Reaction temperature monitoring

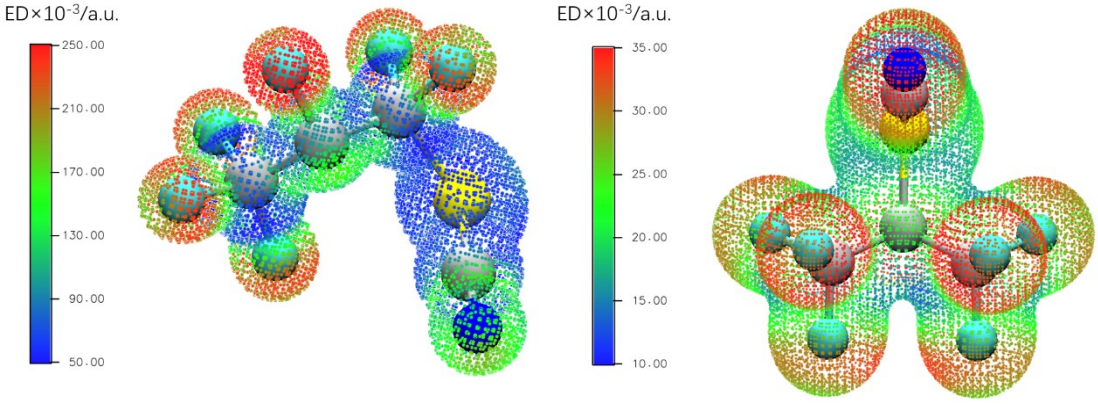

Fig. S23 The electron density distribution around the molecular surface, which is defined at the Kohn-Sham potential equaling to the negative value of first ionization energy (a.u.).

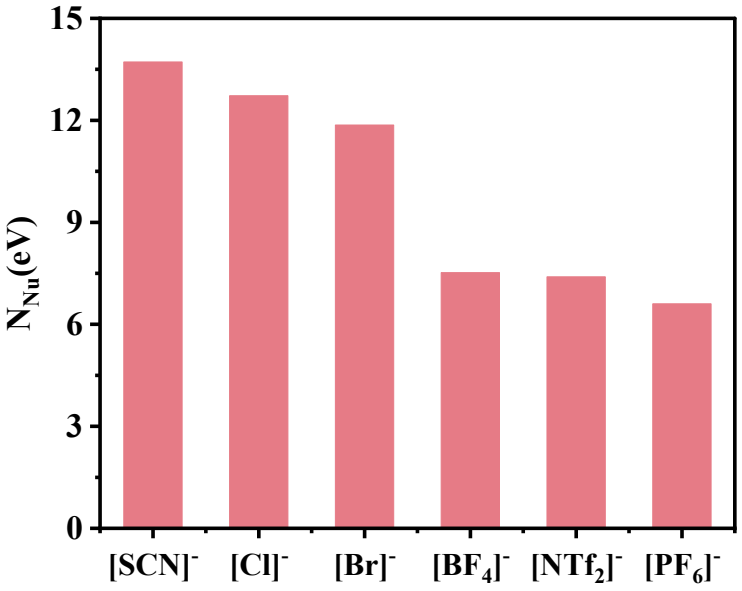

Fig. S24 Nucleophilic index of anions nucleophilic index (N_{Nu}).