

Supporting information for

Synthesis of 9,9-Bis(4-hydroxyphenyl) fluorene Catalyzed by Bifunctional Ionic Liquid

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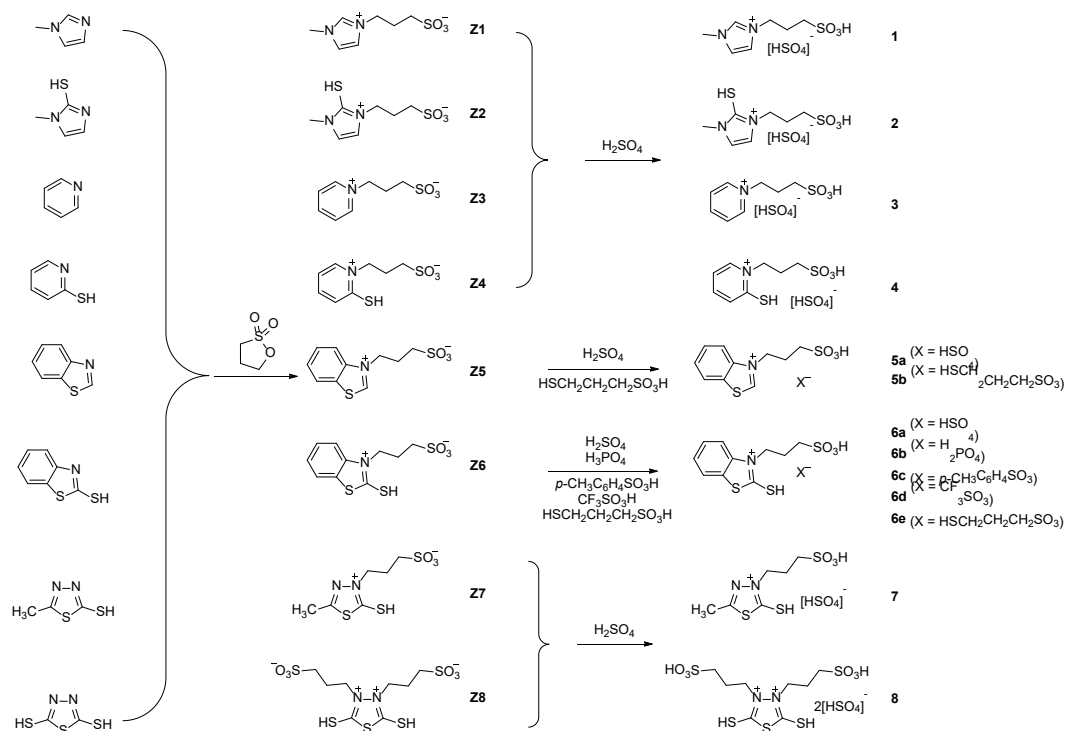
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1. Functionalized ILs preparation

The ILs based on 1-methylimidazole, 2-mercapto-1-methylimidazole, pyridine, 2-mercaptopyridine, benzothiazole, 2-mercaptobenzothiazole, 2-mercapto-5-methyl-1,3,4-thiadiazole and 2,5-dimercapto-1,3,4-thiadiazole were synthesized by two-step method.



Scheme S1 The synthetic of functionalized ionic liquids

In the two-step synthesis of ionic liquid, the yields of each step and the total reaction are as follows:

Table S1 The yield of zwitterions and ionic liquids

ILs	The yield of zwitterions(%)	The yield of ILs (%)	Total yield(%)
1	91.5	97.8	89.5
2	85.6	98.9	84.7
3	78.2	97.7	76.4
4	89.9	98.9	88.9
5a	73.3	91.3	66.9
5b		98.1	71.9
6a	82.1	97.2	79.8
6b		98.1	80.5
6c		98.5	80.9
6d		92.2	75.7
6e	65.8	96.4	79.1
7		98.3	64.7
8	60.5	97.9	59.2

2. ^1H and ^{13}C NMR spectra

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance II 400 MHz with TMS as an internal standard.

2.1 ^1H and ^{13}C NMR spectra of zwitterionic precursors

2.1.1 ^1H and ^{13}C NMR spectra of Z1

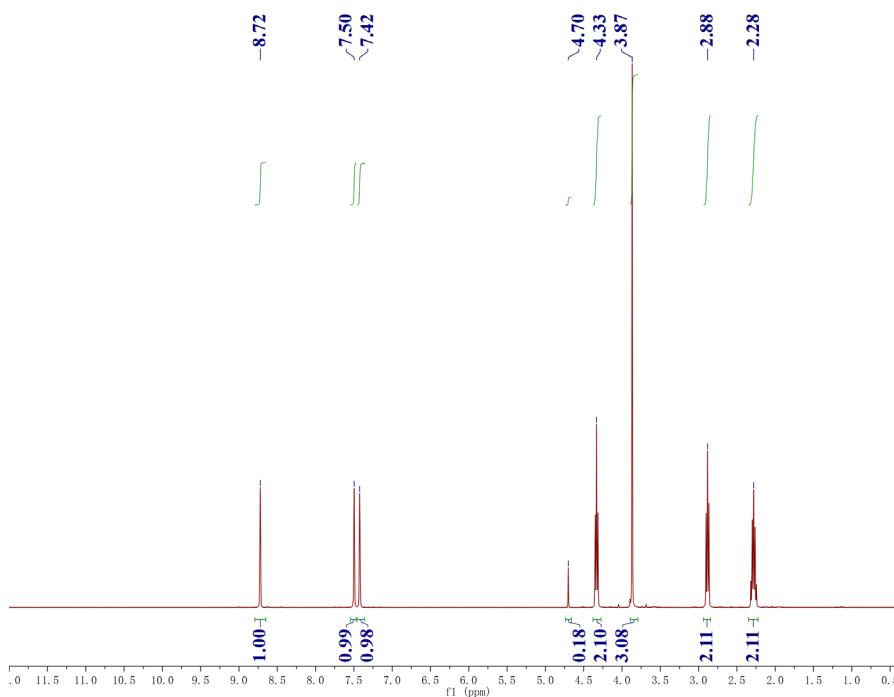


Figure S1 ^1H NMR for Z1

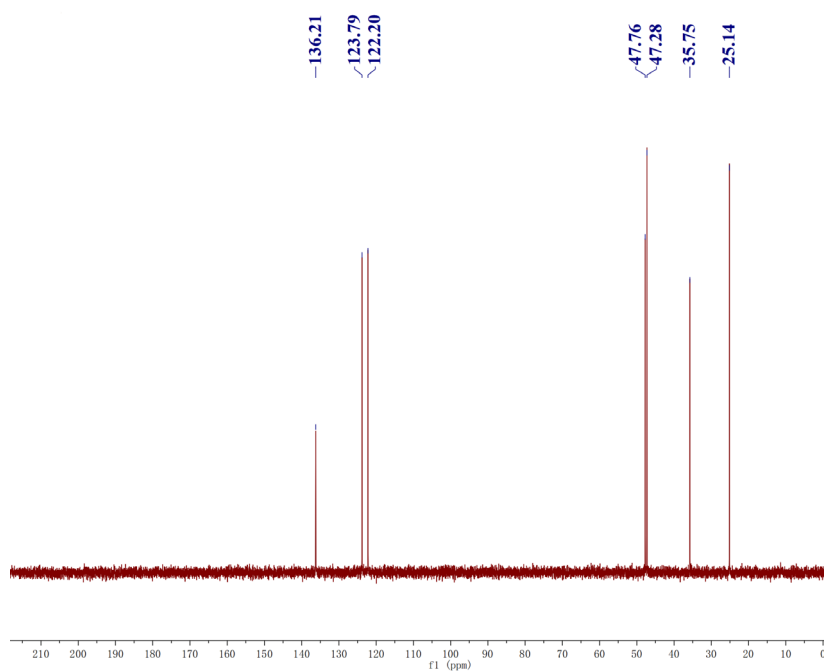


Figure S2 ^{13}C NMR for Z1

2.1.2 ^1H and ^{13}C NMR spectra of Z2

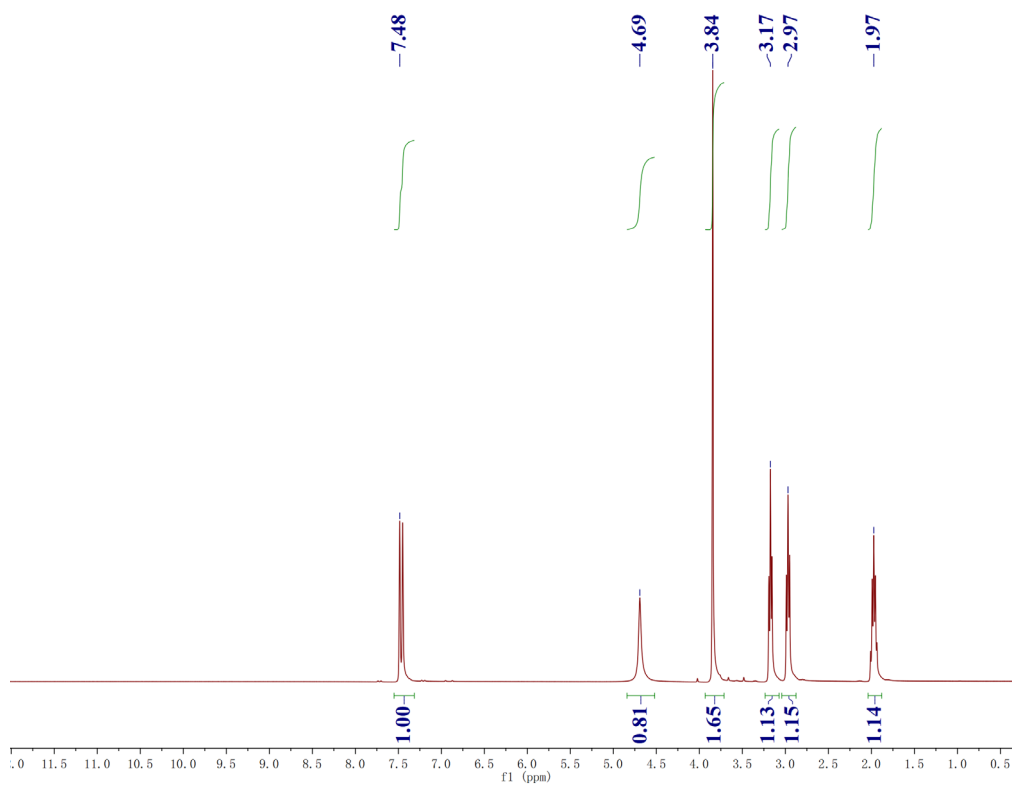


Figure S3 ^1H NMR for Z2

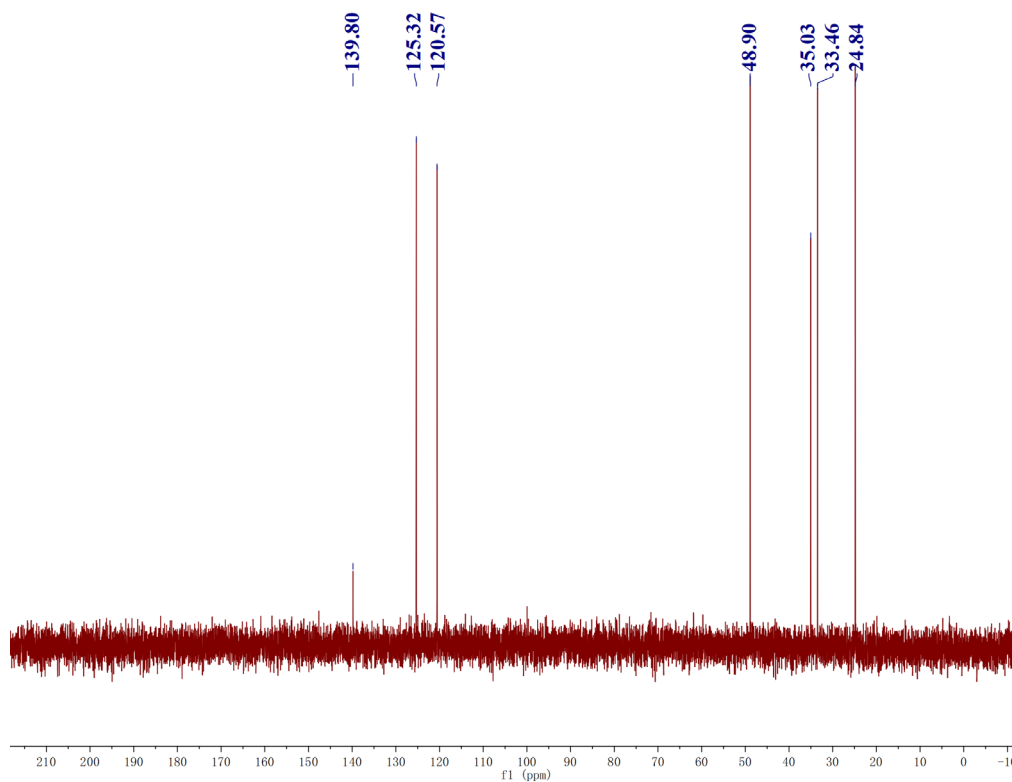


Figure S4 ^{13}C NMR for Z2

2.1.3 ^1H and ^{13}C NMR spectra of Z3

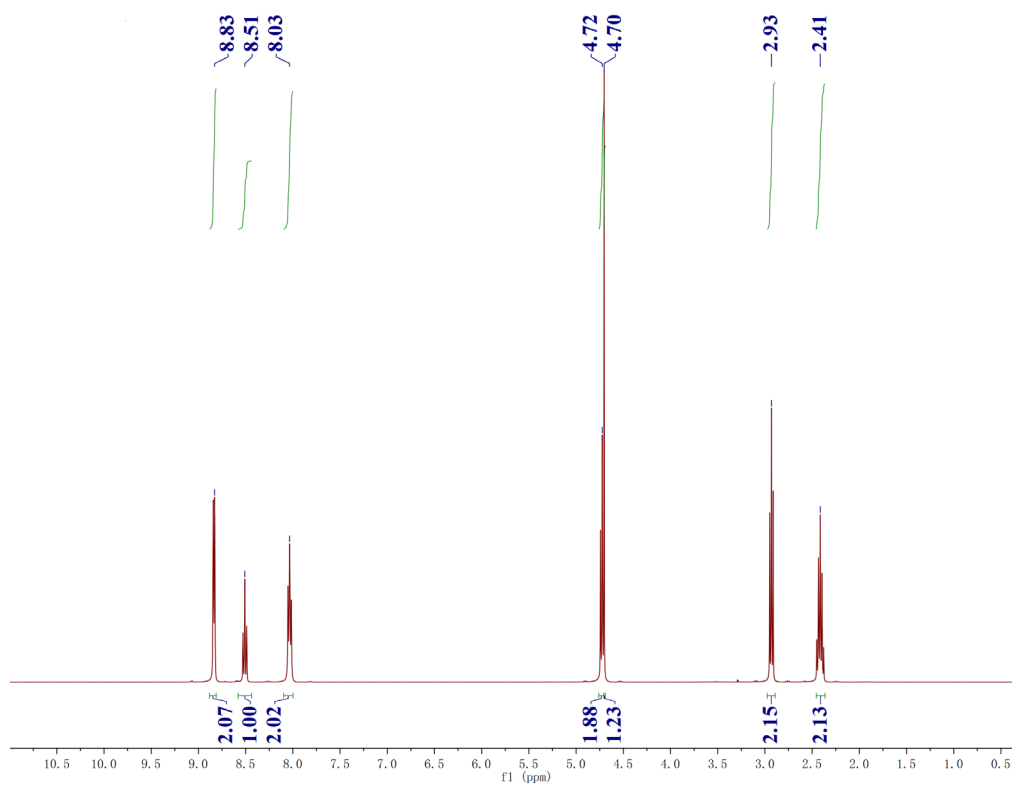


Figure S5 ^1H NMR for Z3

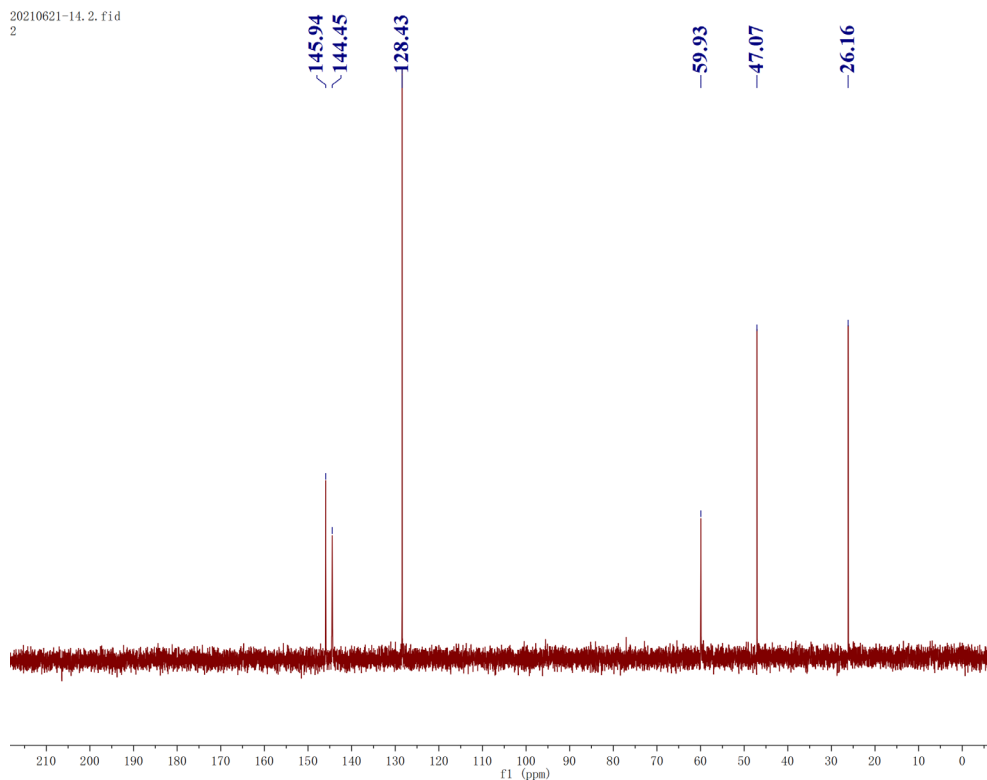


Figure S6 ^{13}C NMR for Z3

2.1.4 ^1H and ^{13}C NMR spectra of Z4

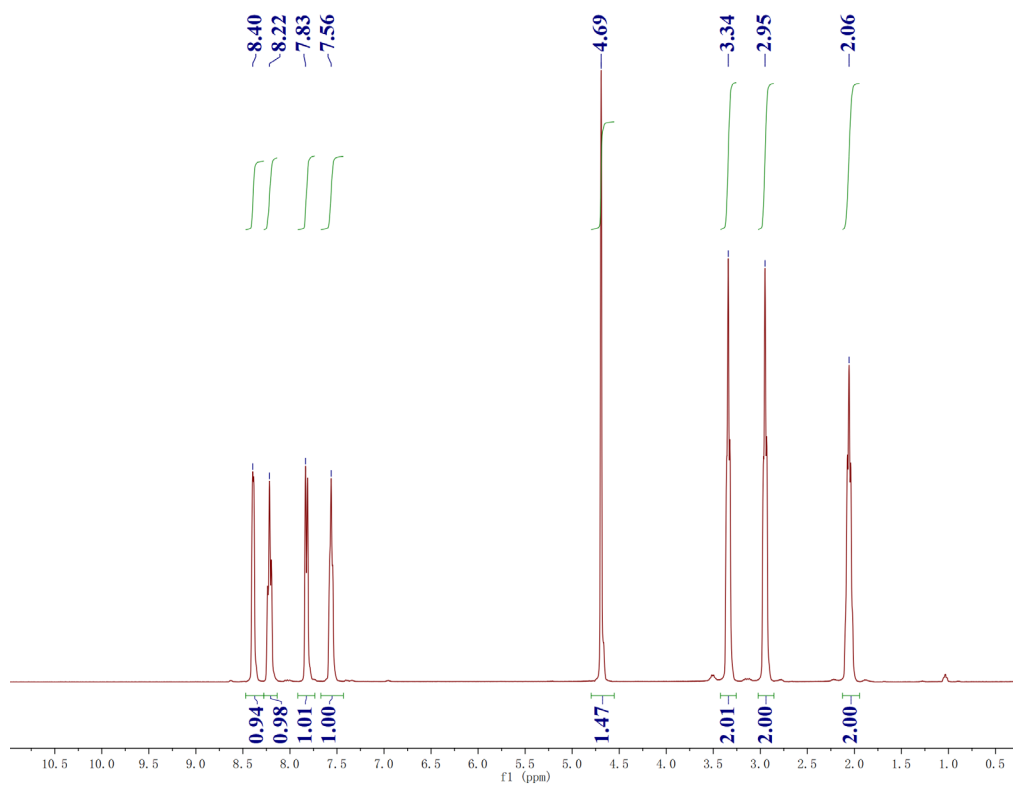


Figure S7 ^1H NMR for Z4

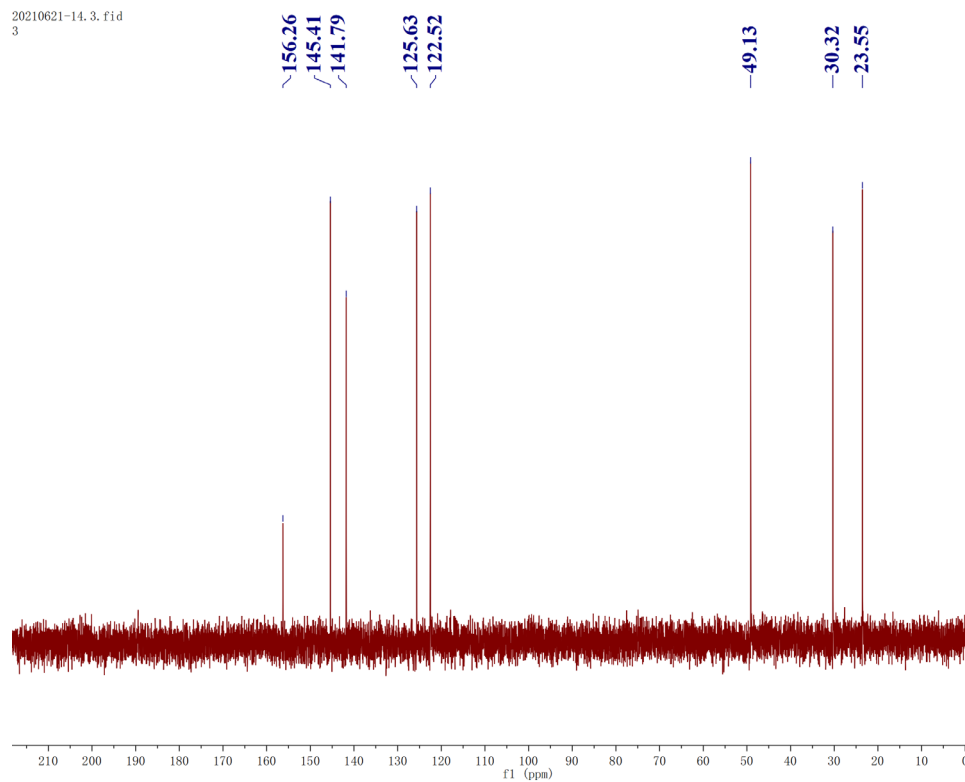


Figure S8 ^{13}C NMR for Z4

2.1.5 ^1H and ^{13}C NMR spectra of Z5

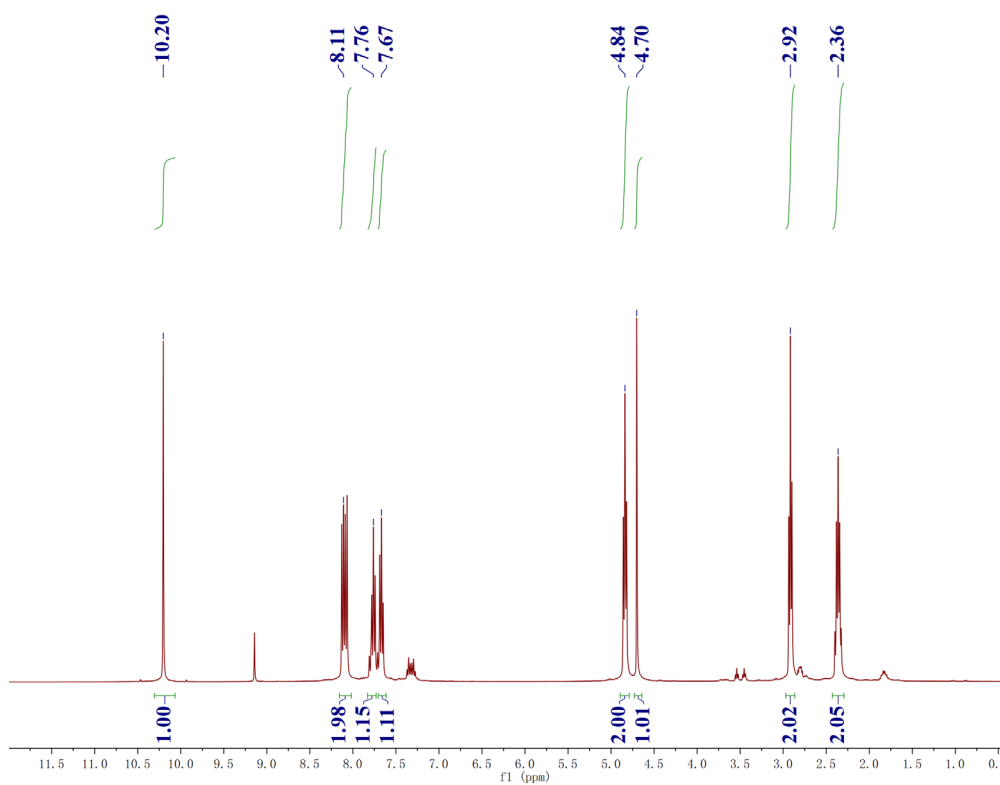


Figure S9 ^1H NMR for Z5

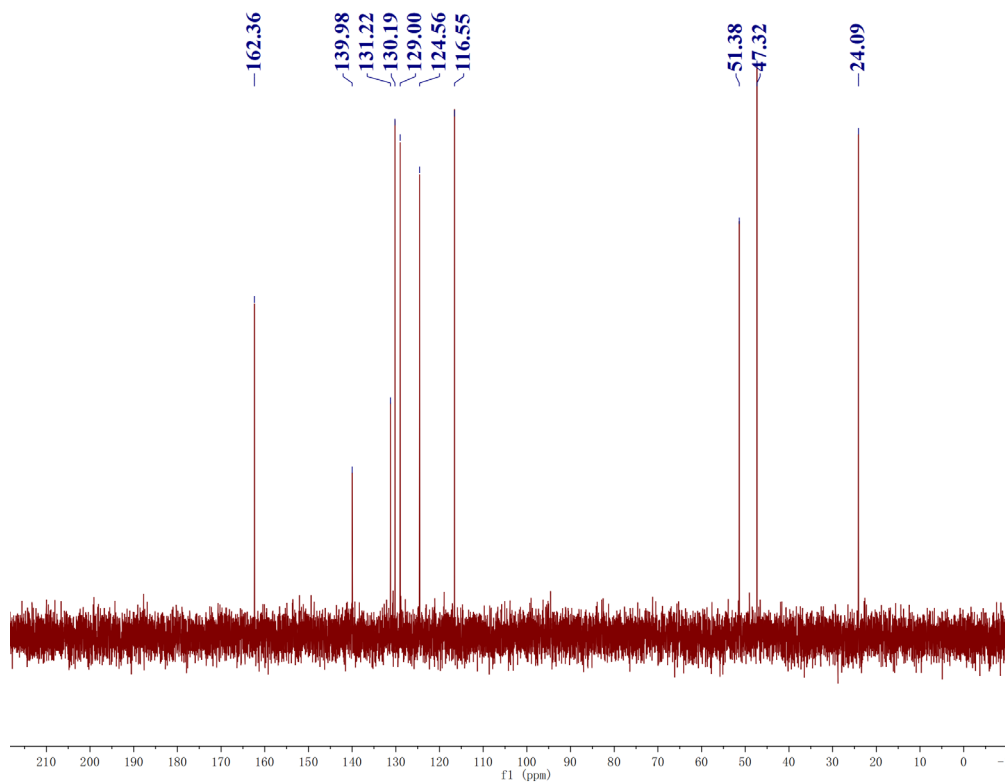


Figure S10 ^{13}C NMR for Z5

2.1.6 ^1H and ^{13}C NMR spectra of Z6

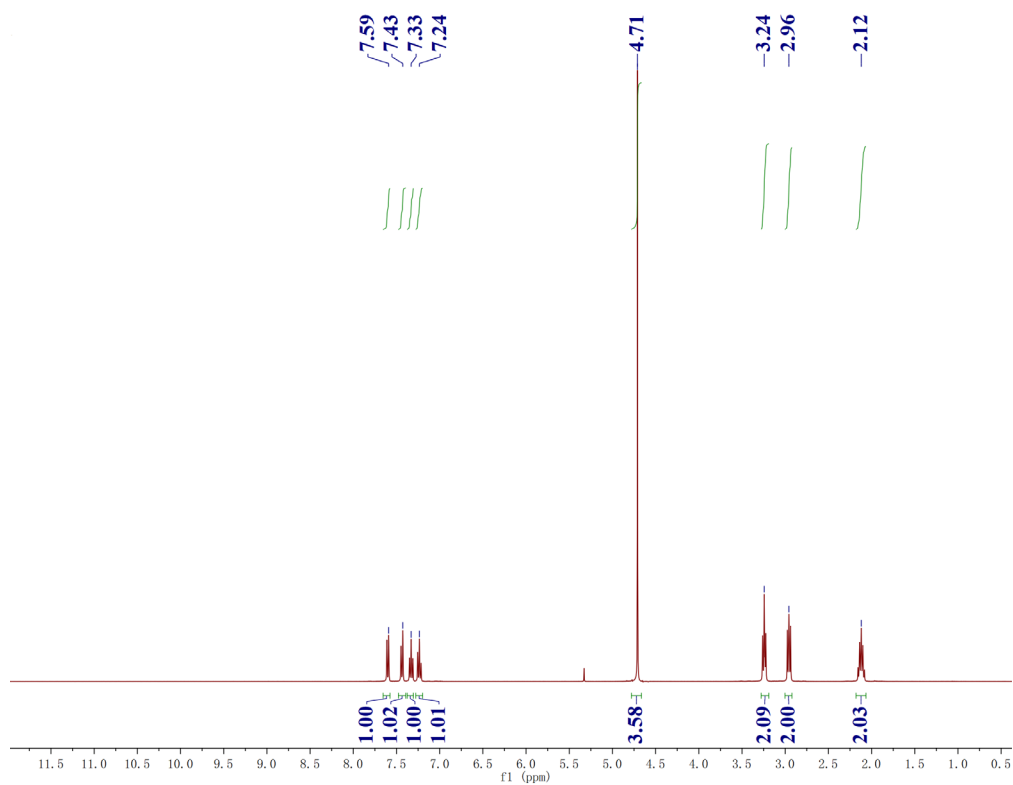


Figure S11 ^1H NMR for Z6

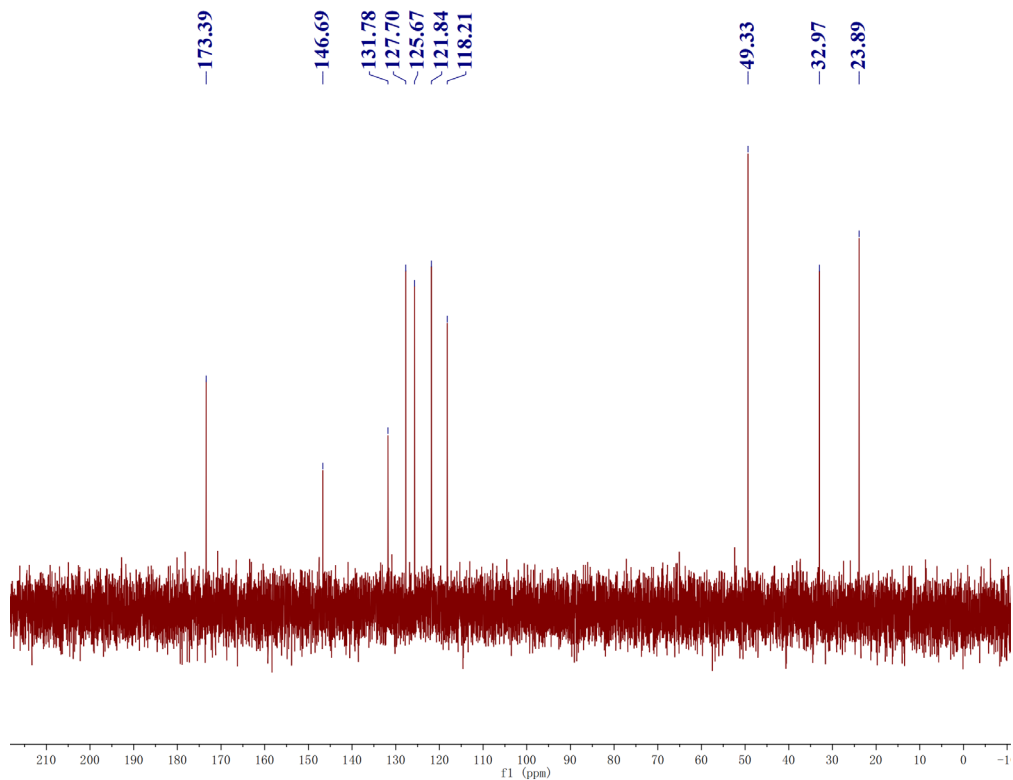


Figure S12 ^{13}C NMR for Z6

2.1.7 ^1H and ^{13}C NMR spectra of Z7

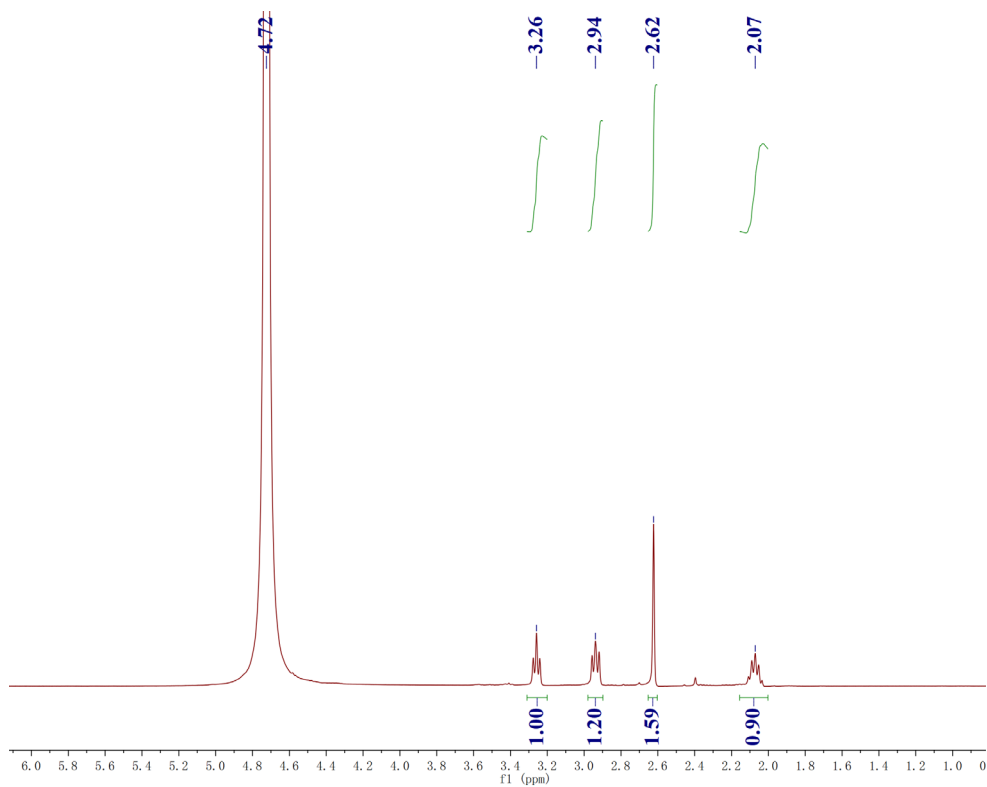


Figure S13 ^1H NMR for Z7

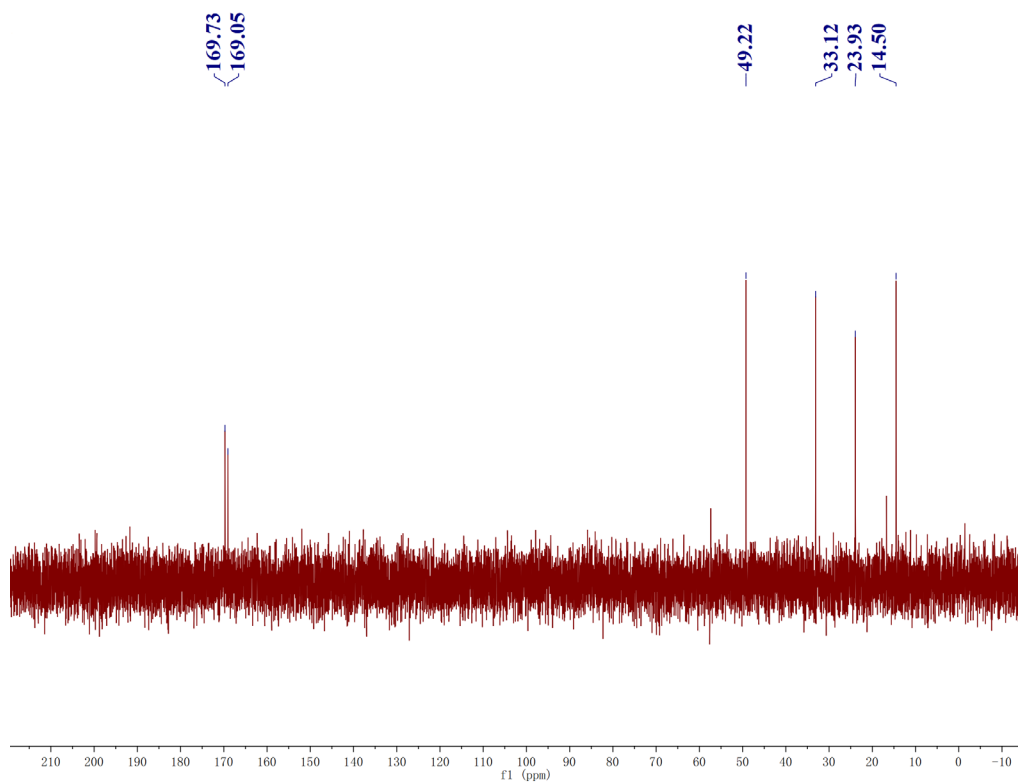


Figure S14 ^{13}C NMR for Z7

2.1.8 ^1H and ^{13}C NMR spectra of Z8

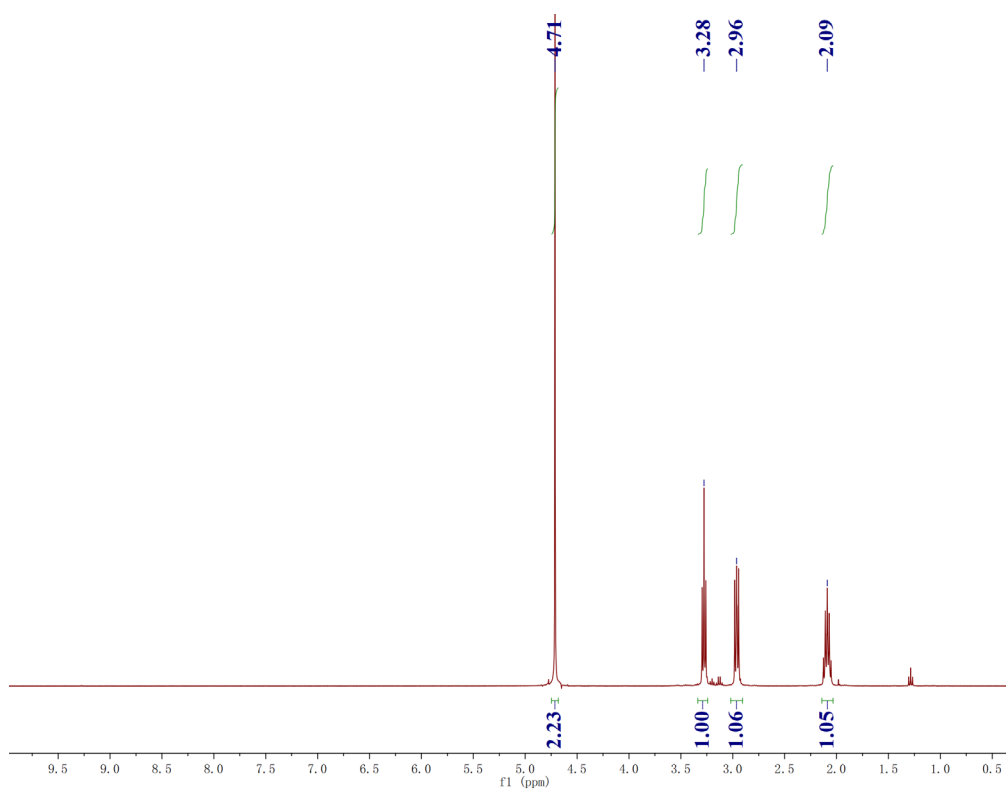


Figure S15 ^1H NMR for Z8

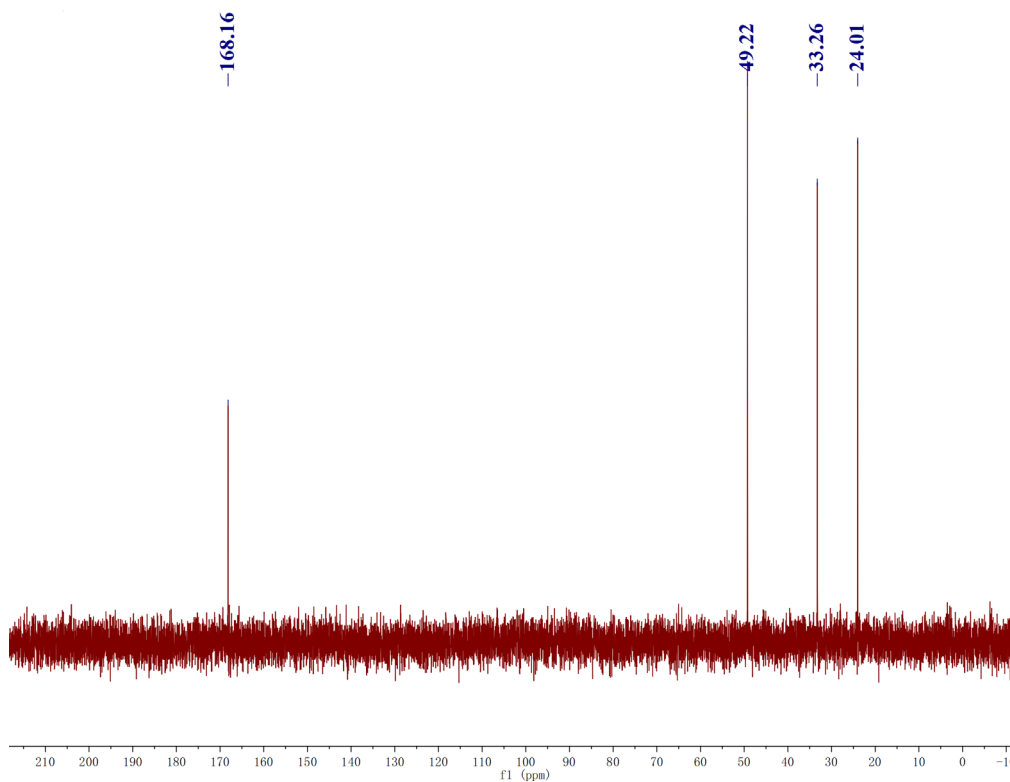


Figure S16 ^{13}C NMR for Z8

2.2 ¹H and ¹³C NMR spectra of ILs

Spectra of **(1)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 8.30 (s, 1H), 7.10 (s, 1H), 7.04 (s, 1H), 3.94 (t, 2H), 3.48 (s, 3H), 2.51 (t, 2H), 1.89 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 135.82, 123.54, 121.88, 47.45, 47.02, 35.50, 24.80.

Spectra of **(2)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 7.13 (d, 1H), 7.09 (d, 1H), 3.48 (s, 3H), 2.81 (t, 2H), 2.62 (t, 2H), 1.60 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 139.42, 125.03, 120.30, 48.60, 34.76, 33.13, 24.49.

Spectra of **(3)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 8.55 (d, 2H), 8.25 (t, 1H), 7.77 (t, 2H), 4.45 (t, 2H), 2.64 (t, 2H), 2.14 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 145.79, 144.19, 128.28, 59.70, 46.90, 25.95.

Spectra of **(4)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 8.35 (d, 1H), 8.19 (t, 1H), 7.79 (d, 1H), 7.53 (t, 1H), 3.29 (t, 2H), 2.90 (t, 2H), 2.01 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 156.10, 145.53, 141.56, 125.56, 122.50, 49.05, 30.25, 23.43.

Spectra of **(5a)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 8.98 (s, 1H), 8.12 (m, 2H), 7.79 (t, 1H), 7.60 (t, 1H), 4.81 (t, 2H), 2.93 (t, 2H), 2.32 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 162.27, 139.95, 131.19, 130.15, 128.97, 124.53, 116.50, 51.32, 47.27, 24.01.

Spectra of **(5b)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 10.31 (s, 1H), 8.26 (d, 1H), 8.22 (d, 1H), 7.89 (t, 1H), 7.79 (t, 1H), 4.96 (t, 2H), 3.00 (t, 2H), 2.95 (t, 2H), 2.58 (t, 2H), 2.47 (m, 2H), 1.95 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 140.00, 131.20, 130.21, 129.04, 124.60, 116.58, 51.32, 49.45, 47.29, 28.38, 24.03, 23.58, 22.53.

Spectra of **(6a)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 6.93 (d, 1H), 6.70 (m, 2H), 6.62 (t, 1H), 2.72 (t, 2H), 2.42 (t, 2H), 1.58 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 176.35, 141.77, 129.03, 128.12, 125.93, 121.69, 115.96, 48.74, 33.24, 23.15.

Spectra of **(6b)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 7.25 (d, 1H), 7.09 (d, 1H), 7.04 (t, 1H), 6.95 (t, 1H), 2.98 (t, 2H), 2.76 (t, 2H), 1.90 (m, 2H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 174.05, 145.10, 130.77, 127.74, 125.66, 121.64, 117.43, 49.15, 32.97, 23.63.

Spectra of **(6c)**: ¹H NMR (400 MHz, D₂O, TMS) δ (ppm): 7.20 (d, 1H), 7.11 (d, 2H), 7.00 (d, 1H), 6.95 (t, 1H), 6.88 (t, 1H), 6.64 (d, 2H), 2.93 (t, 2H), 2.64 (t, 2H), 1.82 (m, 2H), 1.74 (s, 3H). ¹³C NMR (400 MHz, D₂O, TMS) δ (ppm): 176.17, 142.44,

141.60, 139.28, 129.55, 128.84, 128.29, 126.13, 124.91, 121.93, 116.39, 48.96, 48.67, 33.38, 23.37, 20.20.

Spectra of **(6d)**: ^1H NMR (400 MHz, D_2O , TMS) δ (ppm): 7.20 (d, 1H), 7.01 (d, 1H), 6.98 (t, 1H), 6.89 (t, 1H), 2.99 (t, 2H), 2.69 (t, 2H), 1.86 (m, 2H). ^{13}C NMR (400 MHz, D_2O , TMS) δ (ppm): 176.10, 142.55, 129.56, 128.21, 126.07, 121.82, 116.39, 48.97, 33.38, 28.12, 23.40.

Spectra of **(6e)**: ^1H NMR (400 MHz, D_2O , TMS) δ (ppm): 7.52 (d, 1H), 7.33 (d, 2H), 7.27 (t, 1H), 7.17 (t, 1H), 3.20 (t, 2H), 2.93 (t, 2H), 2.88 (t, 2H), 2.51 (t, 2H), 2.09 (m, 2H), 1.88 (m, 2H). ^{13}C NMR (400 MHz, D_2O , TMS) δ (ppm): 174.06, 145.90, 131.41, 127.90, 125.86, 121.94, 117.92, 49.45, 49.32, 33.13, 28.37, 23.84, 22.52.

Spectra of **(7)**: ^1H NMR (400 MHz, D_2O , TMS) δ (ppm): 3.02 (t, 2H), 2.65 (t, 2H), 2.42 (s, 3H), 1.80 (m, 2H). ^{13}C NMR (400 MHz, D_2O , TMS) δ (ppm): 170.97, 170.36, 48.96, 32.96, 23.53, 14.18.

Spectra of **(8)**: ^1H NMR (400 MHz, D_2O , TMS) δ (ppm): 2.62 (t, 4H), 2.31 (t, 4H), 1.42 (m, 4H). ^{13}C NMR (400 MHz, D_2O , TMS) δ (ppm): 168.14, 48.70, 32.83, 23.42.

3. MS spectra of ILs

IR spectra were recorded on a Q-TOF Micro.

MS: calcd for **1**, m/z 301.0 (M-H), found 301.1; calcd for **2**, m/z 303.0 (M-H), found 303.1; calcd for **3**, m/z 298.0 (M-H), found 298.0; calcd for **4**, m/z 330.0 (M-H), found 330.0; calcd for **5a**, m/z 354.0 (M-H), found 354.0; calcd for **6a**, m/z 386.0 (M-H), found 386.0; calcd for **7**, m/z 351.0 (M-H), found 351.0; calcd for **8**, m/z 490.9 (M-HSO₄-2H), found 491.0.

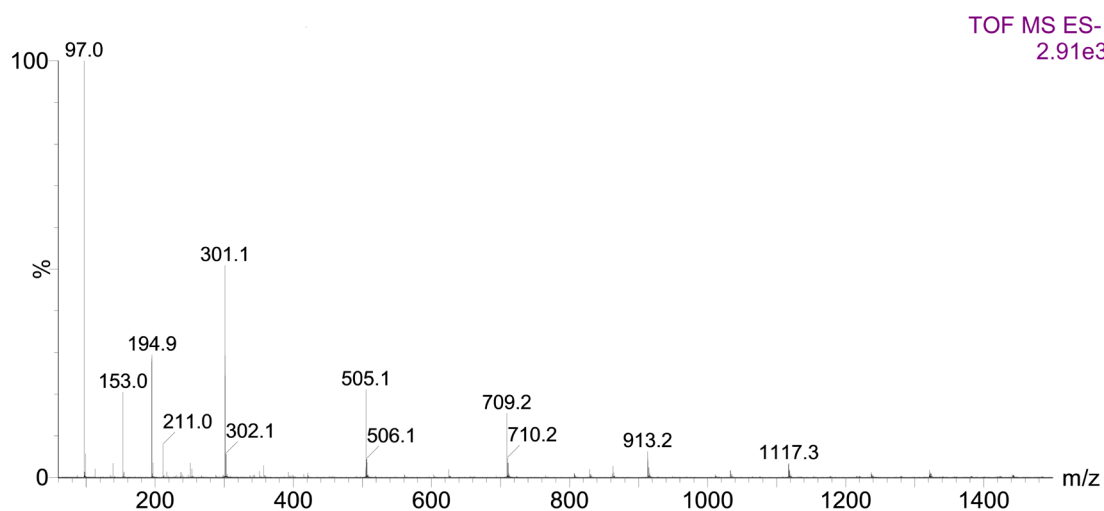


Figure S17 MS spectrum of of **1**

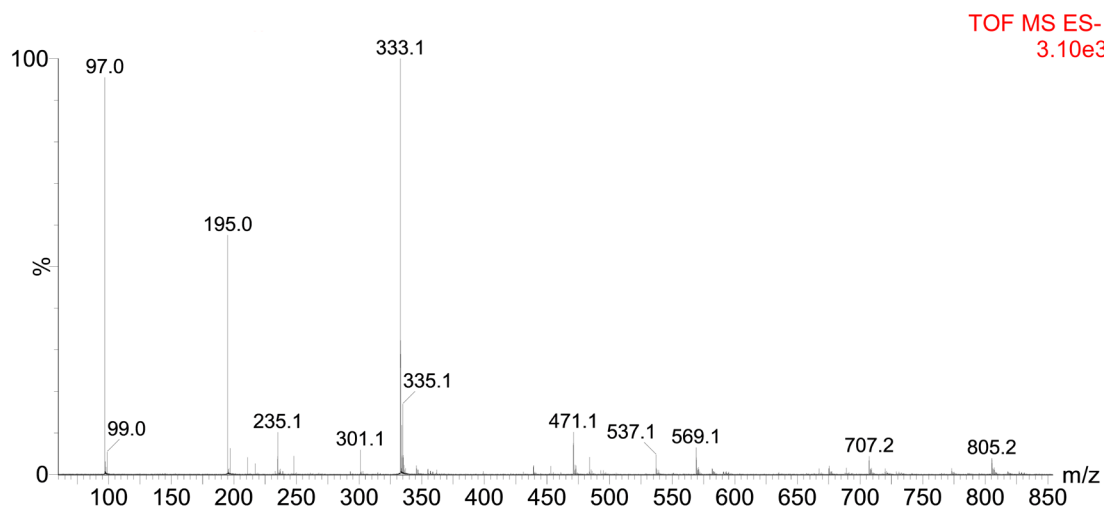


Figure S18 MS spectrum of of **2**

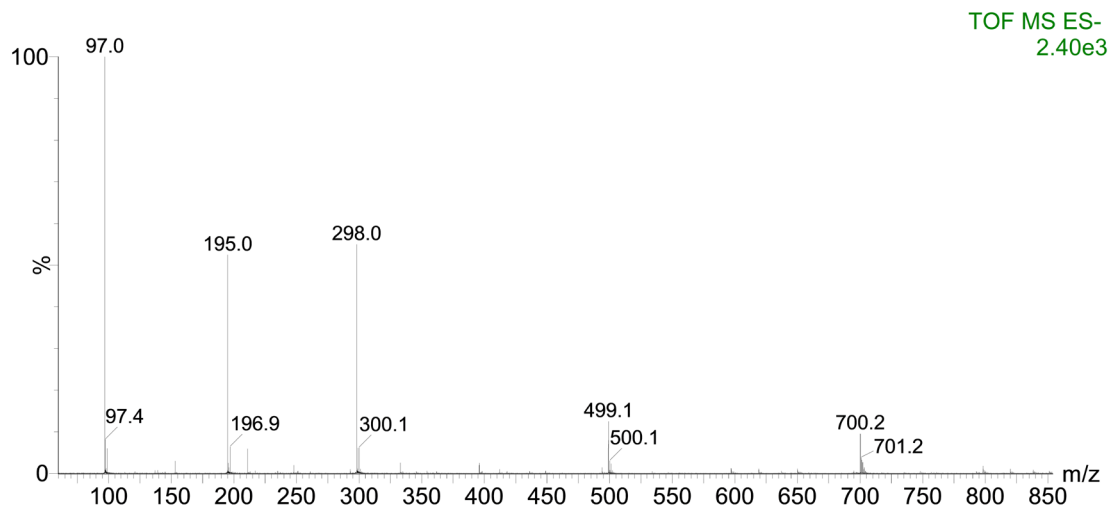


Figure S19 MS spectrum of of 3

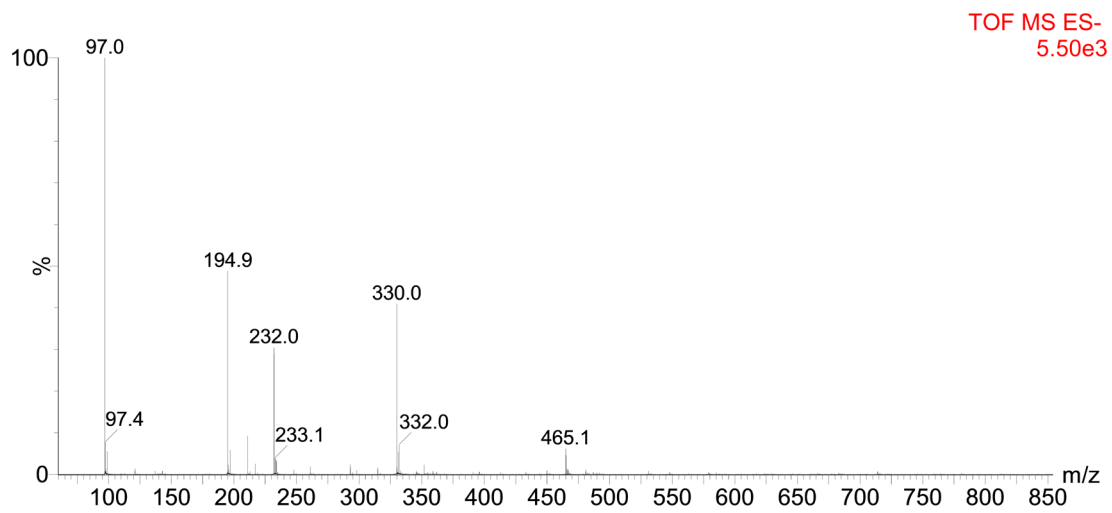


Figure S20 MS spectrum of of 4

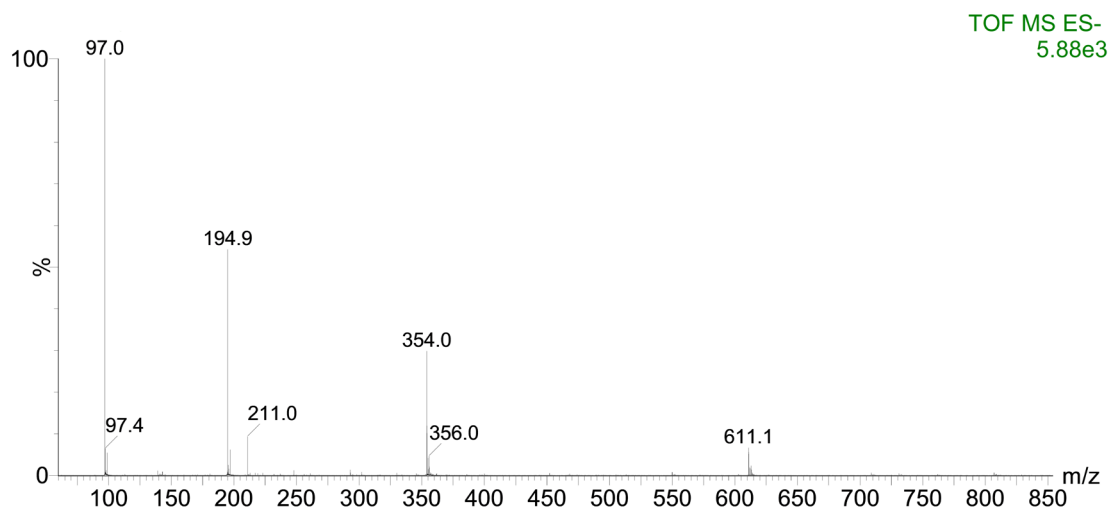


Figure S21 MS spectrum of of 5a

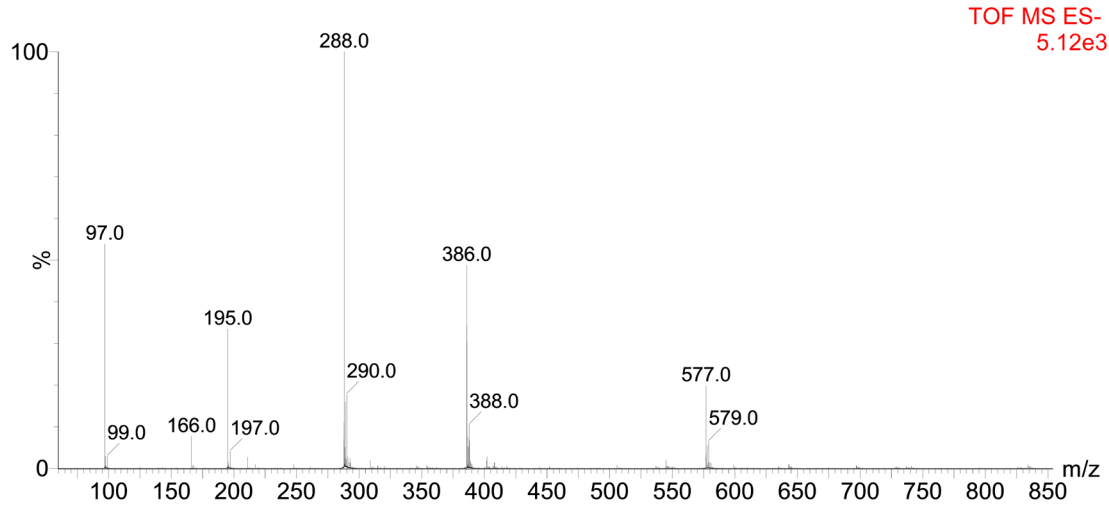


Figure S22 MS spectrum of of 6a

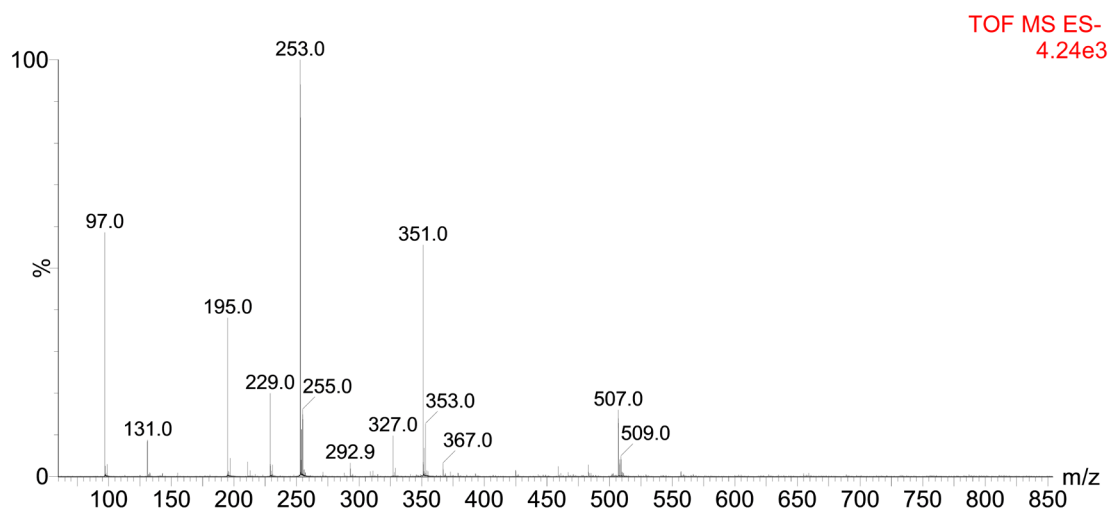


Figure S23 MS spectrum of of 7

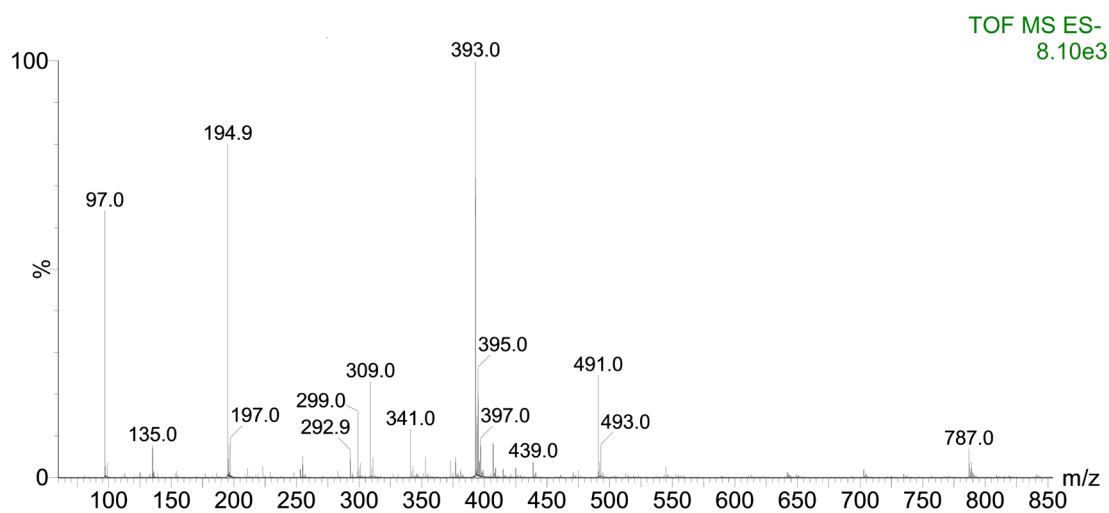


Figure S24 MS spectrum of of 8

4. Determination of -SH

The sulfhydryl content of ILs was evaluated by determination of Ellman's method using UV-vis spectrometer with 5-sulfhydryl-2-nitrobenzoic acid as indicator. Figure S25 shows the reaction principle of the Ellman's method. Figure S26 shows the maximum absorbance of unprotonated indicator in UV-vis spectra at 412 nm.

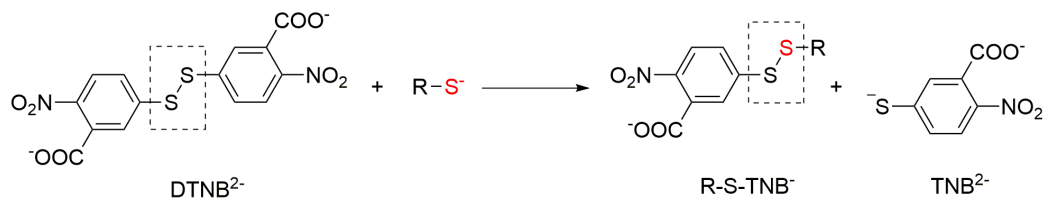


Figure S25 The maximum absorbance of indicator at 412 nm

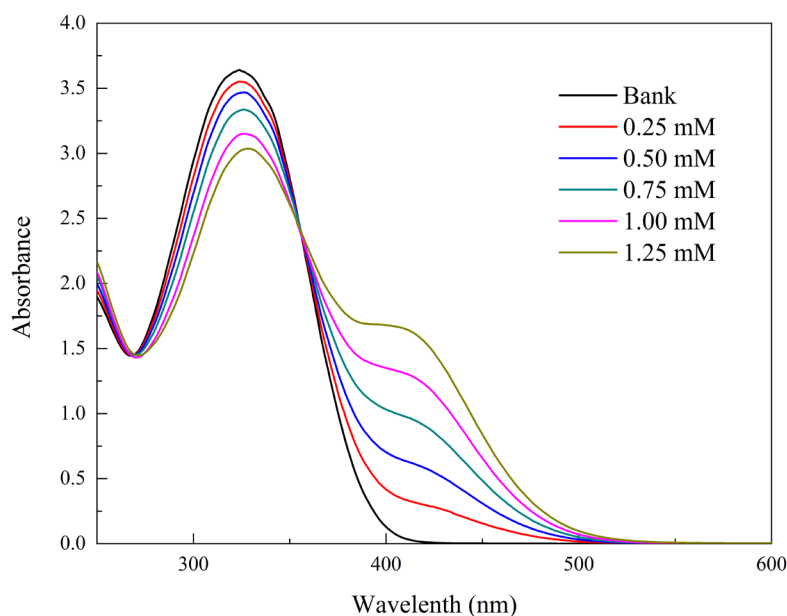


Figure S26 The maximum absorbance of indicator at 412 nm

5. Determination of conversion and selectivity

As shown in Figure S27, the reaction was analyzed by High Performance Liquid Chromatography (Agilent 1100). The HPLC-system was equipped with a Supersil OSD2 C18 column (250 x 4.6 mm, 5 μ m).

The mobile phase A (methanol) and the mobile phase B (H₂O) was pumped through the column whose temp was maintained at 30°C, with a flow rate 1.0 mL/min. A:B

(60:40, v:v) gradient rises to A:B (100:0, v:v) from 0 minutes to 30 minutes. 9-Fluorenone is detected at 257 nm. BHPF, by-product B and C are detected at 275 nm.

The conversion of 9-fluorenone is calculated as follows:

$$Con. (9-fluorenone) = \frac{n(9-fluorenone)_I - n(9-fluorenone)_T}{n(9-fluorenone)_I} \times 100\%$$

where $n(9-fluorenone)_I$ and $n(9-fluorenone)_T$ are the molar of 9-fluorenone at initial and terminal reaction time. As shown in Figure S27 (b), when 9-fluorenone is converted completely, there is no peak of 9-fluorenone in HPLC spectrum.

Selectivity of product are calculated as follows:

$$Sel. (BHPF) = \frac{n(BHPF)}{n(BHPF) + n(B) + n(C)} \times 100\%$$

where $n(BHPH)$, $n(B)$ and $n(C)$ are the molar of BHPF, B and C.

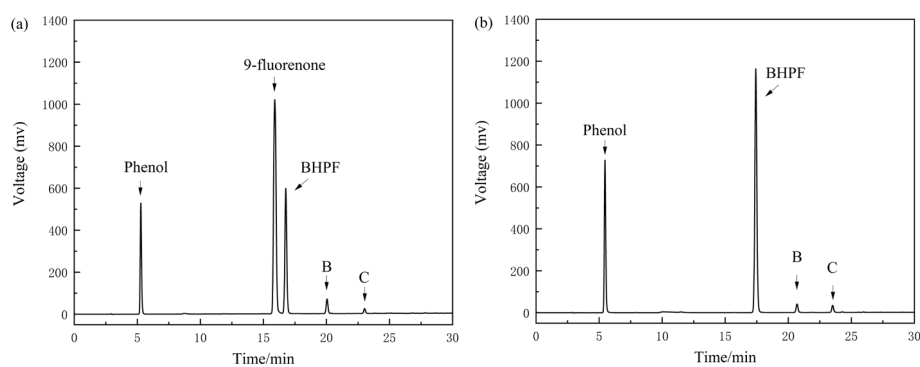


Figure S27 HPLC spectra of reaction, 257 nm. (a) 9-fluorenone is not completely converted, (b) 9-fluorenone is completely converted.