

## Supporting Information

# **(Chlorosulfonyl)(trifluoromethanesulfonyl)imide — A** **Versatile Building Block for Battery Electrolytes**

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## List of contents

1. Materials and Characterizations.....	3
2. Experimental Details.....	5
2.1 Synthesis of zwitterion compounds .....	5
2.2 Chemical reactions between H[CITFSI] and tertiary amines .....	6
3 Supplementary Schemes, Tables and Figures.....	7
References .....	23

## 1. Materials and Characterizations

**Materials.** Acetonitrile (MeCN, Sinopharm Chemical Reagent Co., Ltd), dichloromethane (Sinopharm Chemical Reagent Co., Ltd), methyl tertiary butyl ether (Sinopharm Chemical Reagent Co., Ltd), dimethylethylamine (DMEA, **4a**, Shanghai Aladdin Biochemical Technology Co., Ltd.), diethylmethylamine (DEMA, **4b**, Shanghai Aladdin Biochemical Technology Co., Ltd.), triethylamine (TEA, **4c**, Shanghai Aladdin Biochemical Technology Co., Ltd.), *N,N*-diisopropylethylamine (DIPEA, **4d**, Shanghai Aladdin Biochemical Technology Co., Ltd.), pyridine (Py, **4e**, Shanghai Aladdin Biochemical Technology Co., Ltd.), 2-methylpyridine (MPy, **4f**, Shanghai Aladdin Biochemical Technology Co., Ltd.), and 2,6-dimethylpyridine (DMPy, **4g**, Shanghai Aladdin Biochemical Technology Co., Ltd.), thionyl chloride (SOCl<sub>2</sub>, Sinopharm Chemical Reagent Co., Ltd), chlorosulfonic acid (ClSO<sub>3</sub>H, Shanghai Aladdin Biochemical Technology Co., Ltd.) and trifluoromethanesulfonamide (CF<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>, Solvay). All the solvents were dried and purified using standard procedures before use.<sup>4</sup>

**Structural characterizations.** The spectra of <sup>1</sup>H- (399.65 MHz), <sup>19</sup>F- (376.05 MHz), and <sup>13</sup>C- (101.00 MHz) nuclear magnetic resonance (NMR) were recorded on a Bruker AV400 spectrometer using acetone-*d*<sub>6</sub> as the deuterated solvent. Chemical shift values are reported in ppm with respect to tetramethylsilane (TMS) internal reference for <sup>1</sup>H and <sup>13</sup>C NMR and external reference trichlorofluoromethane (CCl<sub>3</sub>F) in acetone-*d*<sub>6</sub> for <sup>19</sup>F NMR. Mass spectra characterization was performed on a high-performance liquid chromatography-electrospray time-of-flight high-resolution mass spectrometer (Agilent 1100 LC/MSD, Agilent, USA). The sample (ca. 8–10 mg) was dissolved in acetonitrile or methanol (300 μL). Infrared spectral characterization was performed on a Fourier transform infrared spectroscopy (FT-IR, Bruker Equinox 55, Bruker, Germany) with the wavenumber ranging from 4000 to 400 cm<sup>-1</sup>.

**Single-crystal X-ray diffraction (XRD) characterizations.** Single-crystal XRD characterizations were performed on a single-crystal diffractometer (XtaLAB PRO MM007HF Cu, Rigaku, Japan). The analytical software (Olex2) was used to analyze the single crystal structure data of the compound,<sup>5</sup> and the open-source software Diamond was used to draw the oak ridge thermal ellipsoid plot diagram of the single crystal structure of the compound.<sup>6</sup> The crystallographic data (*i.e.*, CCDC 2218540 and 2218543) for this work could be accessed free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2; fax: +44 1223 336033.

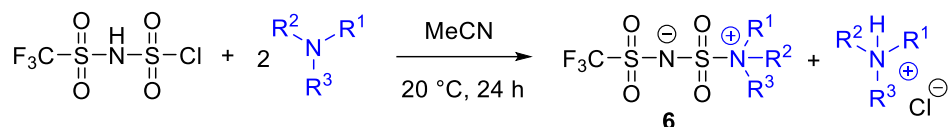
**Thermal properties.** Thermogravimetric analysis (TGA) characterizations were performed on a thermogravimetric analyzer (Diamond TG/DTA, PerkinElmer Instruments, USA). The sample (ca. 5–10 mg) was put into an aluminum pan and heated at a ratio of 10 °C min<sup>-1</sup> from 30 to 800 °C under a flow of argon. The temperature at which 5% weight lost was defined as the decomposition temperature (*T*<sub>d</sub>). Differential scanning calorimetry (DSC) characterization was acquired on a Netzsch DSC instrument (DSC 200 F3, Netzsch, Germany). Following the initial cooling scan from ambient temperature to -70 °C, two continuous cooling-heating scans from -70 to 150 °C were applied and the scan rates for both cooling and heating processes were kept at 10 °C min<sup>-1</sup>. The onset and the peak of heat capacity changes were used to define the melting point (*T*<sub>m</sub>).

**General procedure for experimental of hydrolysis.** Hydrolysis of H[CITFSI] and as-prepared zwitterion compounds (**6c** and **6e**) was carried out in 25 mL sealed glass bottle, and their experimental steps were

similar. In a typical experiment (*i.e.*, H[CITFSI]), to a stirred solution of H[CITFSI] (1.25 g, 5 mmol) in dichloromethane (15 mL), a certain amount of deionized water (H<sub>2</sub>O, 9 mg, 5 mmol) was added. The resulting mixture was left stirring under room temperature for required durations, and then subjected to NMR characterizations with co-axial NMR tubes, as described in our previous work.<sup>4</sup>

## 2. Experimental Details

### 2.1 Synthesis of zwitterion compounds



First, (chlorosulfonyl)(trifluoromethanesulfonyl)imide (H[N(SO<sub>2</sub>Cl)(SO<sub>2</sub>CF<sub>3</sub>)], H[CITFSI]) was synthesized following the procedures reported in previous work.<sup>1</sup> Typically, to a stirred flask containing a predetermined amount of CF<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (40.04 g, 0.27 mol), the solution of ClSO<sub>3</sub>H (44.25 g, 0.38 mol) and SOCl<sub>2</sub> (73.71 g, 0.62 mol) was added at room temperature. The resulting mixture was left under reflux (*ca.* 120 °C) for 48 h. The product, H[CITFSI], was readily obtained as white solid (63.06 g, 0.26 mol; yield 95%) by distillation under vacuum (110 °C/2 mmHg).

Subsequently, the zwitterion compounds (**6a**, **6b**, **6c**, and **6e**) were obtained from nucleophilic substitution reactions between H[CITFSI] and different tertiary amines. Taking compound **6c** (i.e., R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = CH<sub>2</sub>CH<sub>3</sub>) as an example, to a stirred solution of H[CITFSI] (5.20 g, 21 mmol) in acetonitrile (50 mL), TEA (4.34 g, 43 mmol) was added dropwise at room temperature, and the resulting solution was stirred for 24 h. The insoluble phase was removed by filtration, and the supernatant liquid phase was concentrated under reduced pressure. The as-obtained yellow solid was washed three times with deionized water (50 mL) and then recrystallized with dichloromethane/methyl tert-butyl ether, resulting in (triethylammoniosulfonyl)(trifluoromethanesulfonyl)imide **6c** as a white solid (3.93 g, 13 mmol, 60% yield). m.p. 62 °C; <sup>1</sup>H NMR (400 MHz; acetone-*d*<sub>6</sub>; TMS; ppm): δ<sub>H</sub> = 3.71 (q, *J*<sub>H-H</sub> = 7.3 Hz, 6H, —CH<sub>2</sub>CH<sub>3</sub>), 1.49 (t, *J*<sub>H-H</sub> = 7.4 Hz, 9H, —CH<sub>2</sub>CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; acetone-*d*<sub>6</sub>; CFCl<sub>3</sub>; ppm): δ<sub>F</sub> = -79.9 (s, —CF<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, acetone-*d*<sub>6</sub>; ppm): δ<sub>C</sub> = 205.2, 124.4, 121.2, 118.1, 114.9, 51.9, 29.5, 29.3, 29.1, 28.9, 28.7, 28.6, 28.4, 8.6; FT-IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3008 (m), 2953 (m), 1465 (s), 1377 (vs), 1349 (vs), 1346 (vs), 1216 (s), 1198 (vs), 1069 (vs), 1001 (s), 896 (m), 837 (m), 785 (s), 712 (s), 609 (s), 548 (s), 523 (vs); ESI-MS (m/z) calcd. for [C<sub>7</sub>H<sub>15</sub>F<sub>3</sub>S<sub>2</sub>O<sub>4</sub>N<sub>2</sub> + Na]<sup>+</sup>: 335.0323; found: 335.0870.

Following a similar procedure described for **6c** except replacing TEA with DMEA, the (dimethylethylammoniosulfonyl)(trifluoromethanesulfonyl)imide **6a** was obtained as a white solid (3.51 g, 16 mmol, 78% yield). m.p. 56 °C; <sup>1</sup>H NMR (400 MHz; acetone-*d*<sub>6</sub>; TMS; ppm): δ<sub>H</sub> = 3.74 (q, *J*<sub>H-H</sub> = 7.3 Hz, 2H, —CH<sub>2</sub>CH<sub>3</sub>), 3.30 (s, 6H, —CH<sub>3</sub>), 1.61–1.50 (m, 3H, —CH<sub>2</sub>CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; acetone-*d*<sub>6</sub>; CFCl<sub>3</sub>; ppm): δ<sub>F</sub> = -79.8 (s, —CF<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, acetone-*d*<sub>6</sub>; ppm): δ<sub>C</sub> = 56.1, 56.1, 56.1, 44.8, 44.7, 44.7, 8.2; FT-IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3056 (w), 3001 (w), 1620 (m), 1479 (s), 1379 (vs), 1201 (vs), 1070 (vs), 1006 (s), 975 (s), 910 (s), 783 (s), 746 (s), 621 (vs), 563 (s), 522 (s); ESI-MS (m/z) calcd. for [C<sub>5</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> + Na]<sup>+</sup>: 307.0010; found: 307.0525.

Following a similar procedure described for **6c** except replacing TEA with DEMA, the (diethylmethylammoniosulfonyl)(trifluoromethanesulfonyl)imide **6b** was obtained as a white solid (4.13 g, 14 mmol, 66% yield). m.p. 57 °C; <sup>1</sup>H NMR (400 MHz; acetone-*d*<sub>6</sub>; TMS; ppm): δ<sub>H</sub> = 3.73 (ddt, *J*<sub>H-H</sub> = 32.2, 13.8, 7.2 Hz, 4H, —CH<sub>2</sub>CH<sub>3</sub>), 3.25 (s, 3H, —CH<sub>3</sub>), 1.50 (tt, *J*<sub>H-H</sub> = 7.3, 1.8 Hz, 6H, —CH<sub>2</sub>CH<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; acetone-*d*<sub>6</sub>; CFCl<sub>3</sub>; ppm): δ<sub>F</sub> = -79.8 (s, —CF<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, acetone-*d*<sub>6</sub>; ppm): δ<sub>C</sub> = 121.2, 118.1, 53.2, 53.2, 53.2, 43.5, 43.4, 43.4, 8.6; FT-IR (KBr, ν<sub>max</sub>, cm<sup>-1</sup>): 3012 (m), 1635 (w), 1467 (s), 1361 (vs), 1195 (vs), 1085 (vs), 1002 (s), 962 (s), 877 (m), 779 (s), 715 (s), 617 (vs), 563 (vs), 518 (vs); ESI-MS (m/z) calcd. for

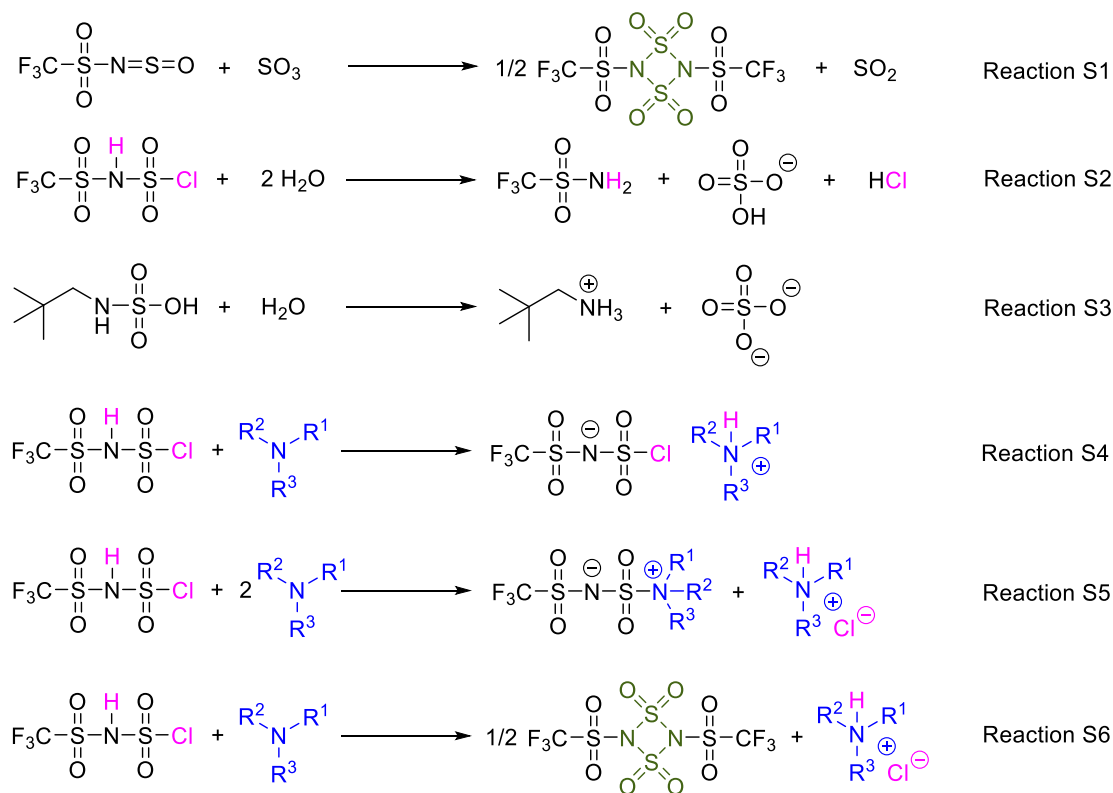
$[\text{C}_6\text{H}_{13}\text{F}_3\text{N}_2\text{O}_4\text{S}_2 + \text{Na}]^+$ : 321.0161; found: 321.0684.

Following a similar procedure described for **6c** except replacing TEA with Py, the (pyridinosulfonyl)(trifluoromethanesulfonyl)imide **6e** was obtained as a white solid (2.43 g, 8.4 mmol, 42% yield). m.p. 117 °C; **<sup>1</sup>H NMR** (400 MHz; acetone-*d*<sub>6</sub>; TMS; ppm):  $\delta_{\text{H}} = 9.45$  (d,  $J_{\text{H-H}} = 6.1$  Hz, 2H, —NCHCHCH—), 8.95 (t,  $J_{\text{H-H}} = 8.1$  Hz, 1H, —NCHCHCH—), 8.43 (t,  $J_{\text{H-H}} = 7.1$  Hz, 2H, —NCHCHCH—); **<sup>19</sup>F NMR** (376 MHz; acetone-*d*<sub>6</sub>; CFCl<sub>3</sub>; ppm):  $\delta_{\text{F}} = -79.5$  (s, —CF<sub>3</sub>); **<sup>13</sup>C NMR** (101 MHz, acetone-*d*<sub>6</sub>; ppm):  $\delta_{\text{C}} = 205.5, 149.1, 140.9, 140.4, 128.3, 127.8, 127.7$ ; **FT-IR** (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 3136 (m), 3095 (w), 1613 (s), 1466 (s), 1393 (vs), 1346 (vs), 1216 (s), 1198 (vs), 1141 (s), 1060 (vs), 1044 (s), 864 (s), 794 (s), 774 (s), 677 (s), 627 (s), 605 (s), 563 (vs), 522 (s); **ESI-MS** (m/z) calcd. for  $[\text{C}_6\text{H}_5\text{F}_3\text{N}_2\text{O}_4\text{S}_2 + \text{K}]^+$ : 328.9280; found: 328.9300.

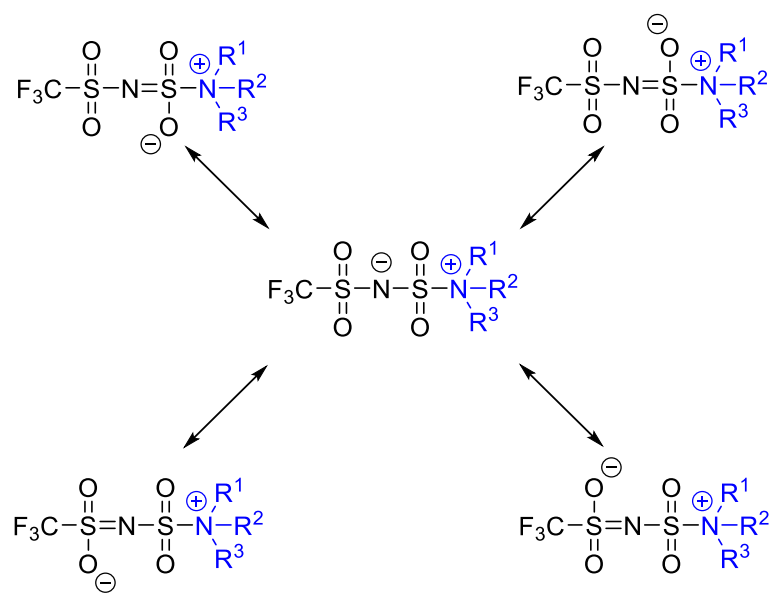
## 2.2 Chemical reactions between H[CITFSI] and tertiary amines

The experimental procedures of H[CITFSI] with equal or twice amounts of tertiary amines (including DMEA, DEMA, TEA, DIPEA, Py, MPy, and DMPy) were carried out using an air-tight glass tube. In a typical example, H[CITFSI] (0.25 g, 1 mmol), acetonitrile (3 mL) and TEA (0.11 g, 1 mmol) were mixed under room temperature and left stirring under a given temperature (e.g., 20 or 80 °C) for 24 h. The reaction products were characterized by NMR characterizations with co-axial NMR tubes, as described in our previous work.<sup>4</sup>

### 3 Supplementary Schemes, Tables, and Figures



**Scheme S1.** Summary of the reactions discussed in this work.



**Scheme S2.** Negative delocalization of the sulfonimide-type zwitterion compounds.



**Table S1.** Experimental results of the reaction of H[CITFSI] with equivalent amount of tertiary amines.

Entry	Base	Temperature / °C	NMR yield / %			
			5 <sup>a</sup>	6 <sup>a</sup>	7 <sup>a</sup>	8 <sup>a</sup>
S1	<b>4a</b>	20	87	4	0	9
S2	<b>4b</b>	20	90	5	0	5
S3	<b>4c</b>	20	88	0	0	12
S4	<b>4d</b>	20	93	0	0	7
S5	<b>4e</b>	20	79	0	0	21
S6	<b>4f</b>	20	88	0	1	11
S7	<b>4g</b>	20	84	0	0	16
S8	<b>4a</b>	80	65	0	0	35
S9	<b>4b</b>	80	79	0	0	21
S10	<b>4c</b>	80	88	0	0	12
S11	<b>4d</b>	80	4	0	11	85
S12	<b>4e</b>	80	80	0	0	20
S13	<b>4f</b>	80	82	0	3	15
S14	<b>4g</b>	80	90	0	0	10

<sup>a</sup>5, 6, 7, and 8 represent neutralization products, nucleophilic substitution products, elimination products, and trifluoromethanesulfonamide (CF<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>), respectively.

**Table S2.** Assignments of the NMR spectral peaks for the species reported in this work.

Compounds	Abbreviation	Assignments	$\delta$ ( $^1\text{H}$ NMR) / ppm) / ( $J_{\text{H-H}}$ / Hz)	$\delta$ ( $^{19}\text{F}$ NMR) / ppm) / ( $J_{\text{F-F}}$ / Hz)	Ref.
$\text{CF}_3\text{SO}_2\text{N}^{(-)}\text{SO}_2\text{N}^{(+)}(\text{CH}_3)_2(\text{CH}_2\text{CH}_3)$	<b>6a</b>	$-\underline{\text{C}}\text{H}_2\text{CH}_3$	3.74 (q, 7.3)		This work
		$-\underline{\text{C}}\text{H}_3$	3.30 (s)		
		$-\text{CH}_2\underline{\text{C}}\text{H}_3$	1.55 (m)		
		$-\underline{\text{C}}\text{F}_3$		-79.8 (s)	
$\text{CF}_3\text{SO}_2\text{N}^{(-)}\text{SO}_2\text{N}^{(+)}(\text{CH}_3)(\text{CH}_2\text{CH}_3)_2$	<b>6b</b>	$-\underline{\text{C}}\text{H}_2\text{CH}_3$	3.73 (ddt, 32.2, 13.8, 7.2)		This work
		$-\text{CH}_2\underline{\text{C}}\text{H}_3$	1.50 (tt, 7.3, 1.8)		
		$-\underline{\text{C}}\text{H}_3$	3.25 (s)		
		$-\underline{\text{C}}\text{F}_3$		-79.8 (s)	
$\text{CF}_3\text{SO}_2\text{N}^{(-)}\text{SO}_2\text{N}^{(+)}(\text{CH}_2\text{CH}_3)_3$	<b>6c</b>	$-\underline{\text{C}}\text{H}_2\text{CH}_3$	3.71 (q, 7.3)		This work
		$-\text{CH}_2\underline{\text{C}}\text{H}_3$	1.49 (t, 7.4)		
		$-\underline{\text{C}}\text{F}_3$		-79.9 (s)	
$\text{CF}_3\text{SO}_2\text{N}^{(-)}\text{SO}_2\text{N}^{(+)}\text{C}_5\text{H}_5$	<b>6e</b>	$-\text{N}\underline{\text{C}}\text{HCHCH}-$	9.45 (d, 6.1)		This work
		$-\text{NCHCH}\underline{\text{C}}\text{H}-$	8.95 (t, 8.1)		
		$-\text{NCH}\underline{\text{C}}\text{HCH}-$	8.43 (t, 7.1)		
		$-\underline{\text{C}}\text{F}_3$		-79.5 (s)	
$(\text{CF}_3\text{SO}_2\text{N}=\text{SO}_2)_2$	<b>7</b>	$-\underline{\text{C}}\text{F}_3$		-79.5 (s)	This work and ref. 2
				-77.7 (s)	
				-73.6 (s)	
$\text{CF}_3\text{SO}_2\text{NH}_2$	<b>8</b>	$-\underline{\text{N}}\text{H}_2$	8.02 (s)		This work and ref. 4
			8.07 (s)		
		$-\underline{\text{C}}\text{F}_3$		-80.7 (s)	
				-81.2 (s)	This work and ref. 4

**Table S3.** Crystal data and structure refinement for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (**6c**).

Identification code	C <sub>7</sub> H <sub>15</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
Empirical formula	C <sub>7</sub> H <sub>15</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	312.33
Temperature/K	100.00 (10)
Crystal system	monoclinic
Space group	P21/n
a / Å	10.71570 (10)
b / Å	9.79090 (10)
c / Å	12.25870 (10)
α / °	90
β / °	97.9860 (10)
γ / °	90
Volume / Å <sup>3</sup>	1273.67 (2)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.629
μ / mm <sup>-1</sup>	4.282
F(000)	648
Crystal size / mm <sup>3</sup>	0.28*0.22*0.18
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection / °	10.282 to 147.908
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 12, -15 ≤ l ≤ 14
Reflections collected	28042
Independent reflections	2572 [R <sub>int</sub> = 0.0359, R <sub>sigma</sub> = 0.0121]
Data/restraints/parameters	2572/0/167
Goodness-of-fit on F <sup>2</sup>	1.071
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0250, wR <sub>2</sub> = 0.0662
Final R indexes [all data]	R <sub>1</sub> = 0.0251, wR <sub>2</sub> = 0.0663
Largest diff. peak/hole / e Å <sup>-3</sup>	0.39/-0.36

**Table S4.** Bond length data for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (**6c**).

Atom	Atom	Length / Å	Atom	Atom	Length / Å
S2	O2	1.4287	F2	C1	1.3341
S2	O1	1.4285	F1	C1	1.3205
S2	N1	1.5839	N2	C4	1.5284
S2	C1	1.8323	N2	C7	1.5268
S1	O4	1.4266	N2	C2	1.5276
S1	O3	1.4251	C4	C5	1.5168
S1	N2	1.8668	C7	C6	1.5147
S1	N1	1.5710	C2	C3	1.5166
F3	C1	1.3294			

**Table S5.** Bond angle data for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> (**6c**).

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
O2	S2	N1	116.38	C7	N2	C4	112.12
O2	S2	C1	104.99	C7	N2	C2	109.18
O1	S2	O2	118.70	C2	N2	S1	110.84
O1	S2	N1	107.91	C2	N2	C4	108.84
O1	S2	C1	104.09	S1	N1	S2	125.34
N1	S2	C1	102.71	C5	C4	N2	114.95
O4	S1	N2	103.89	C6	C7	N2	115.24
O4	S1	N1	116.77	F3	C1	S2	111.19
O3	S1	O4	119.07	F3	C1	F2	108.08
O3	S1	N2	102.75	F2	C1	S2	109.29
O3	S1	N1	109.43	F1	C1	S2	111.03
N1	S1	N2	102.19	F1	C1	F3	108.72
C4	N2	S1	107.22	F1	C1	F2	108.45
C7	N2	S1	108.64	C3	C2	N2	116.51

**Table S6.** Crystal data and structure refinement for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>C<sub>5</sub>H<sub>5</sub> (**6e**).

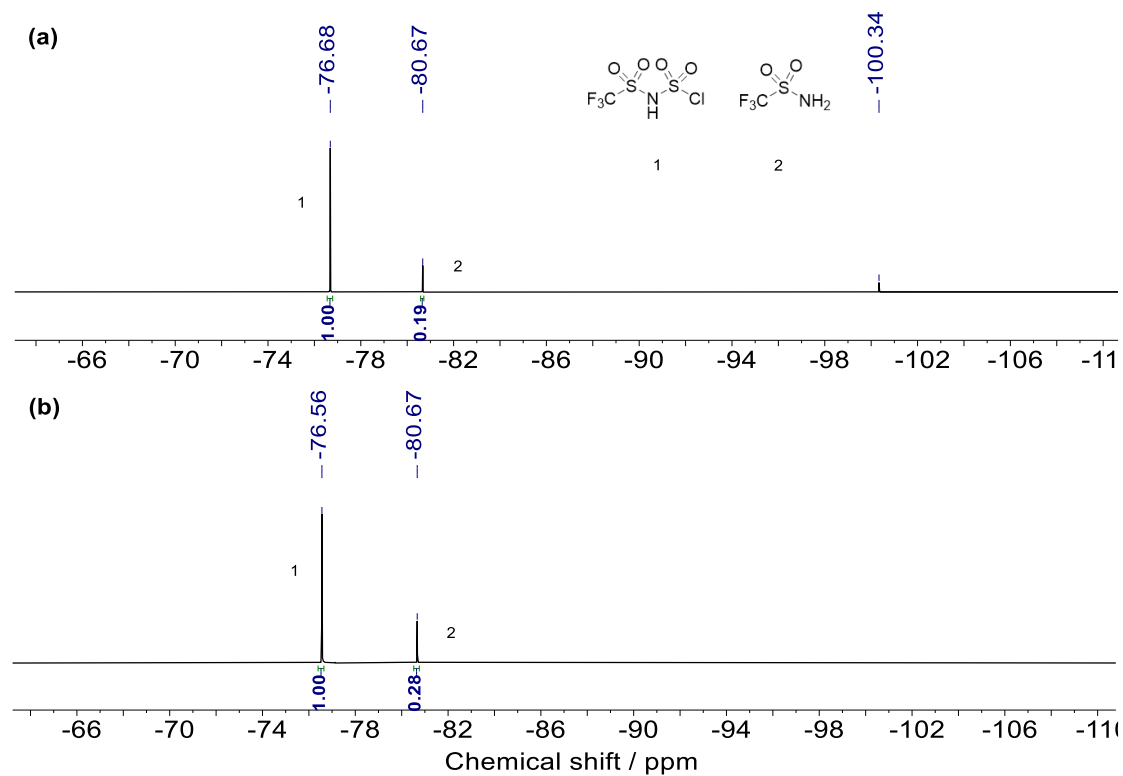
Identification code	C <sub>6</sub> H <sub>5</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
Empirical formula	C <sub>6</sub> H <sub>5</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
Formula weight	290.24
Temperature/K	100.00 (10)
Crystal system	monoclinic
Space group	Cc
a / Å	6.92930 (10)
b / Å	15.0444 (2)
c / Å	10.37300 (10)
α / °	90
β / °	106.3650 (10)
γ / °	90
Volume / Å <sup>3</sup>	1037.55 (2)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.858
μ / mm <sup>-1</sup>	5.220
F(000)	584.0
Crystal size / mm <sup>3</sup>	0.25 × 0.2 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection / °	11.764 to 147.786
Index ranges	-8 ≤ h ≤ 8, -18 ≤ k ≤ 18, -12 ≤ l ≤ 12
Reflections collected	9536
Independent reflections	2038 [R <sub>int</sub> = 0.0296, R <sub>sigma</sub> = 0.0153]
Data/restraints/parameters	2038/2/155
Goodness-of-fit on F <sup>2</sup>	1.088
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0305, wR <sub>2</sub> = 0.0789
Final R indexes [all data]	R <sub>1</sub> = 0.0305, wR <sub>2</sub> = 0.0789
Largest diff. peak/hole / e Å <sup>-3</sup>	0.47/-0.35

**Table S7.** Bond length data for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>C<sub>5</sub>H<sub>5</sub> (**6e**).

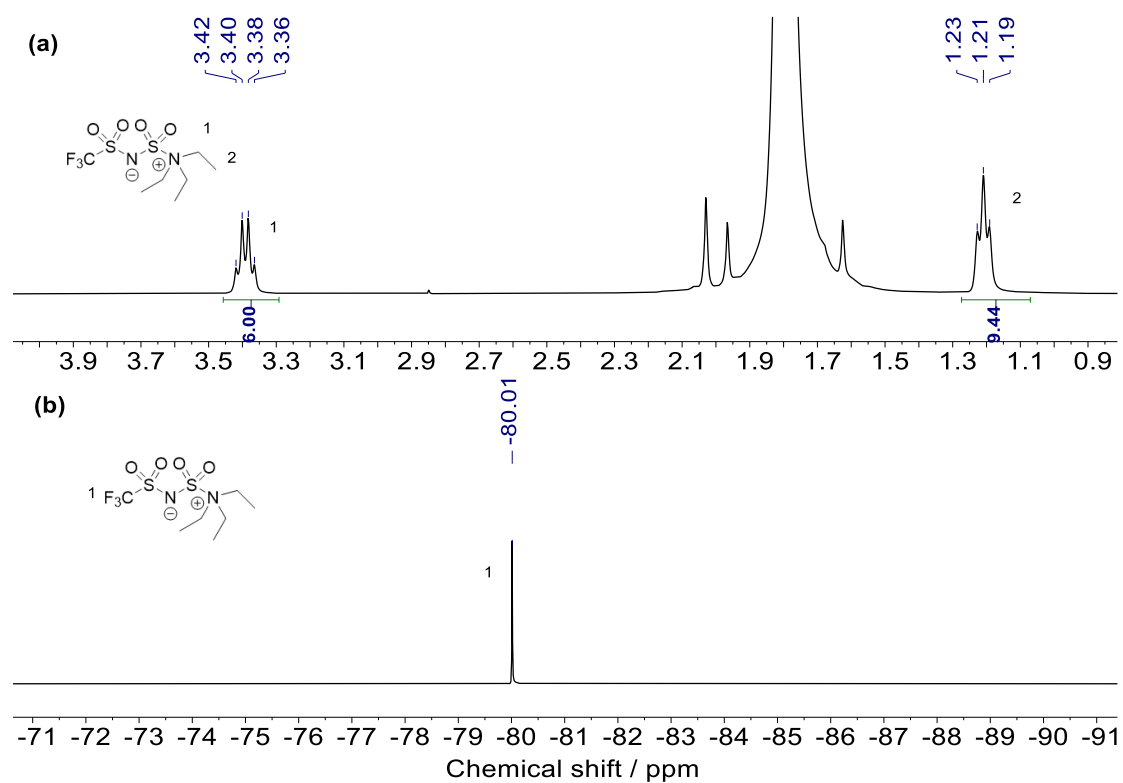
Atom	Atom	Length / Å	Atom	Atom	Length / Å
S1	O2	1.422	N1	C2	1.365
S1	O1	1.424	F3	C1	1.340
S1	N1	1.794	F1	C1	1.324
S1	N2	1.552	C6	C5	1.369
S2	O3	1.423	F2	C1	1.314
S2	O4	1.435	C2	C3	1.366
S2	N2	1.592	C5	C4	1.392
S2	C1	1.833	C4	C3	1.384
N1	C6	1.342			

**Table S8.** Bond angle data for CF<sub>3</sub>SO<sub>2</sub>N<sup>(-)</sup>SO<sub>2</sub>N<sup>(+)</sup>C<sub>5</sub>H<sub>5</sub> (**6e**).

Atom	Atom	Atom	Angle / °	Atom	Atom	Atom	Angle / °
O2	S1	O1	119.93	C2	N1	S1	118.1
O2	S1	N1	102.07	N1	C6	C5	120.5
O2	S1	N2	116.02	N1	C2	C3	119.2
O1	S1	N1	102.67	S1	N2	S2	122.5
O1	S1	N2	109.09	C6	C5	C4	119.0
N2	S1	N1	104.61	C3	C4	C5	119.6
O3	S2	O4	118.88	C2	C3	C4	120.0
O3	S2	N2	110.59	F3	C1	S2	109.8
O3	S2	C1	105.4	F1	C1	S2	111.4
O4	S2	N2	115.47	F1	C1	F3	109.7
O4	S2	C1	104.3	F2	C1	S2	108.5
N2	S2	C1	99.4	F2	C1	F3	108.0
C6	N1	S1	120.2	F2	C1	F1	109.3
C6	N1	C2	121.7				



**Figure S1.**  $^{19}\text{F}$  NMR spectra of the reactions between H[CITFSI] and equivalent amount of  $\text{H}_2\text{O}$  for 4 h (a) and 24 h (b) (reaction temperature: 20 °C; solvent: acetone- $d_6$ ).



**Figure S2.**  $^1\text{H}$  NMR (a) and  $^{19}\text{F}$  NMR (b) spectra of the reaction between compound **6c** and equivalent amount of  $\text{H}_2\text{O}$  for 24 h utilizing acetonitrile as solvent (reaction temperature:  $20\text{ }^\circ\text{C}$ ; solvent: acetone- $d_6$ ).

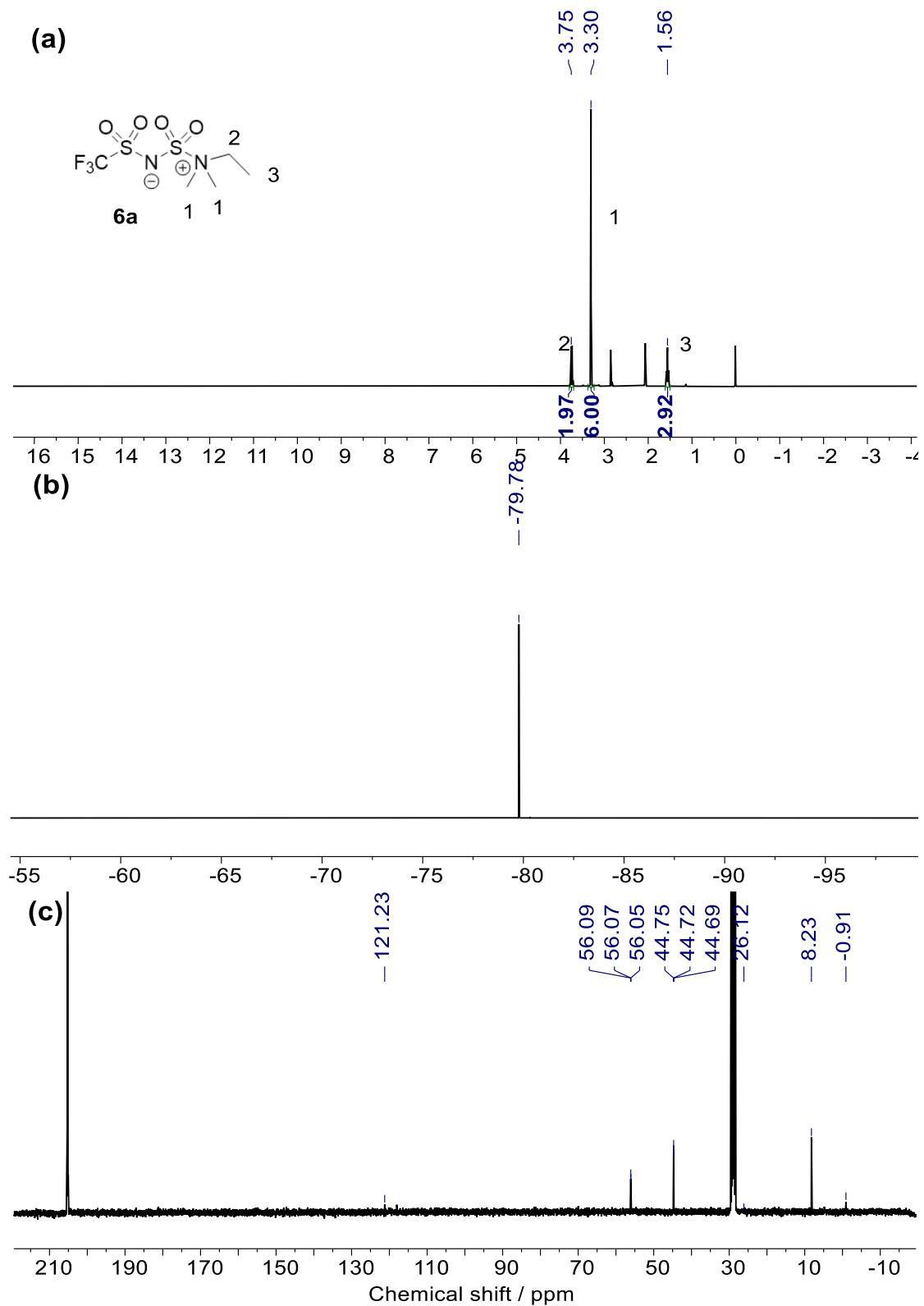
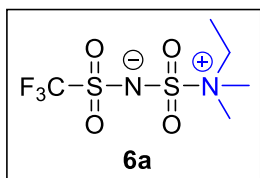


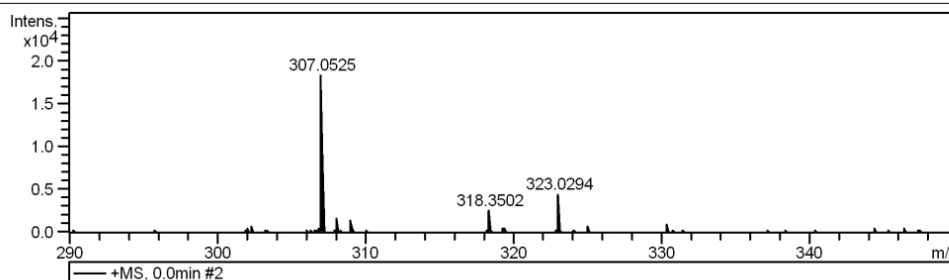
Figure S3.  $^1\text{H}$  NMR (a),  $^{19}\text{F}$  NMR (b), and  $^{13}\text{C}$  NMR (c) spectra of compound **6a** (solvent: acetone- $d_6$ ).



(Dimethylethylammoniumsulfonyl)(trifluoromethanesulfonyl)imide

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	307.0525	6976	75.4	18398	0.0440
2	308.0548	6651	6.5	1593	0.0463
3	309.0489	6233	6.0	1477	0.0496
4	318.3502	5448	10.4	2626	0.0584
5	323.0294	7290	18.1	4524	0.0443

Figure S4. Mass spectrum of compound 6a.

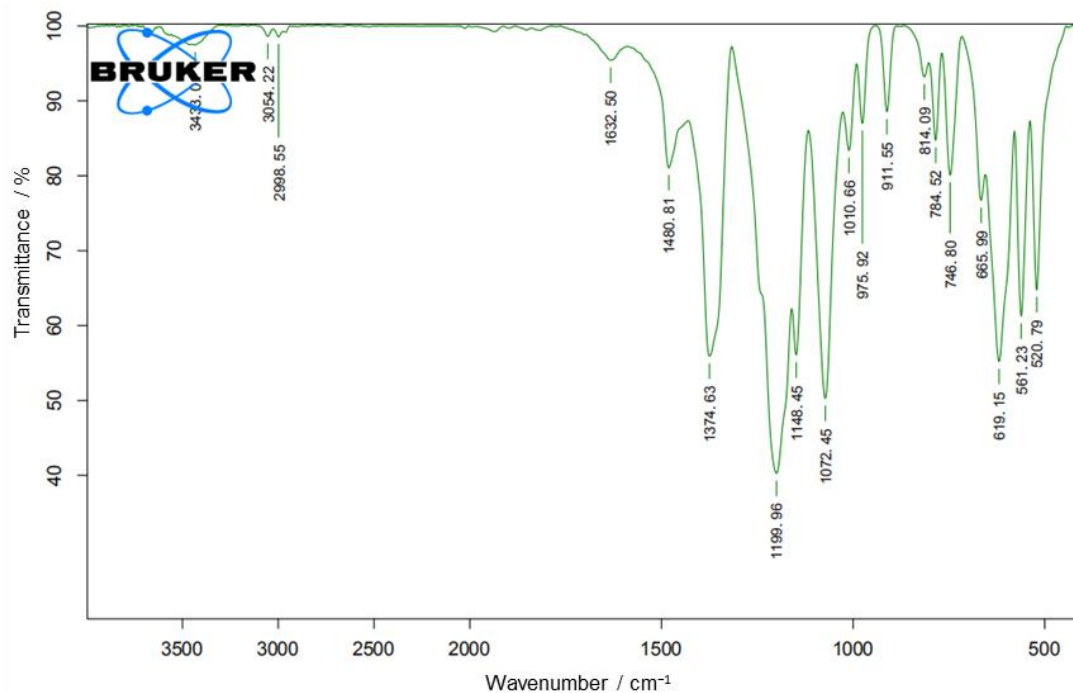
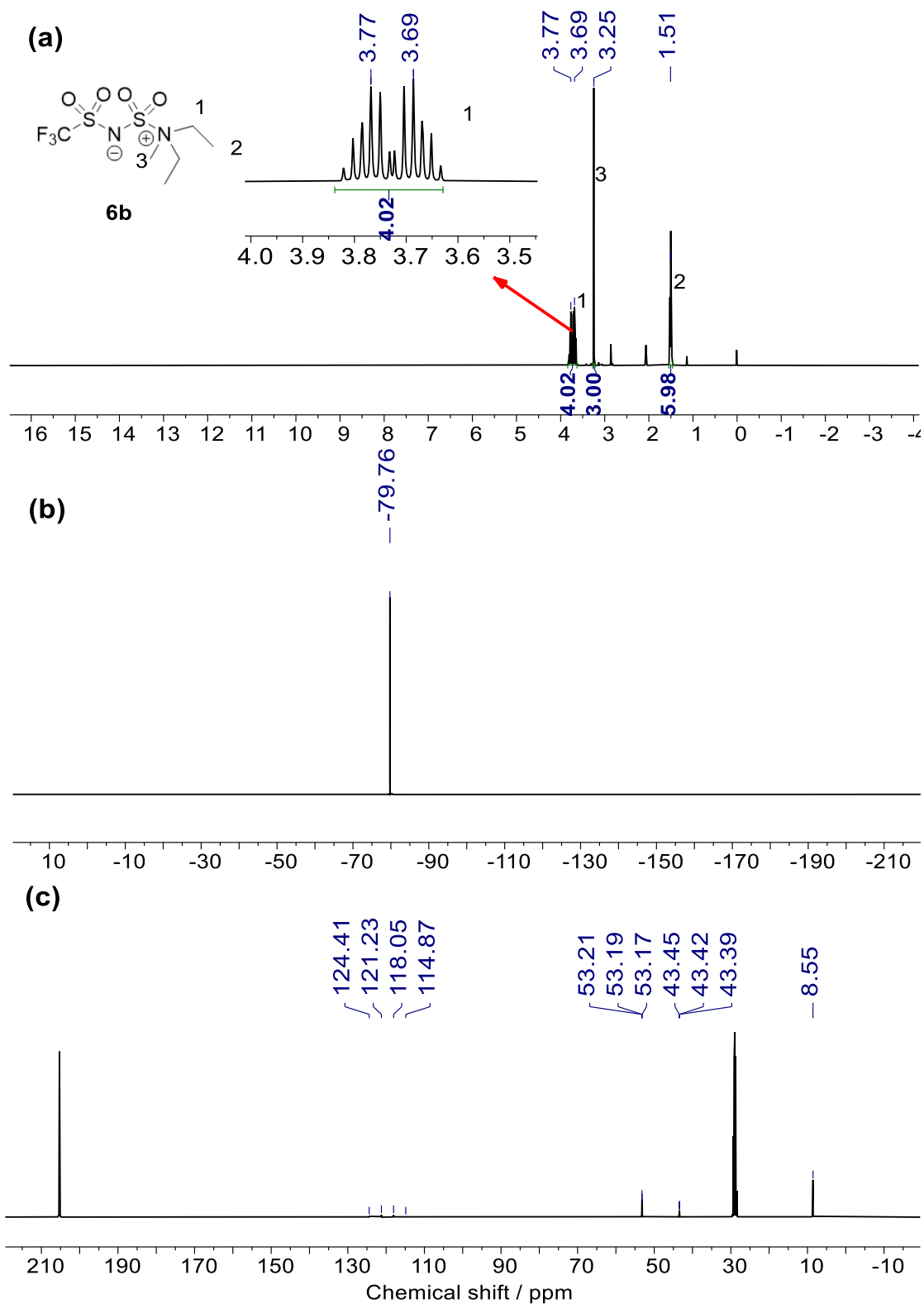
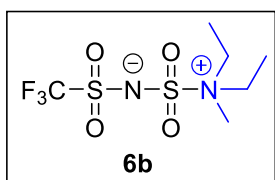


Figure S5. FT-IR spectrum of compound 6a.





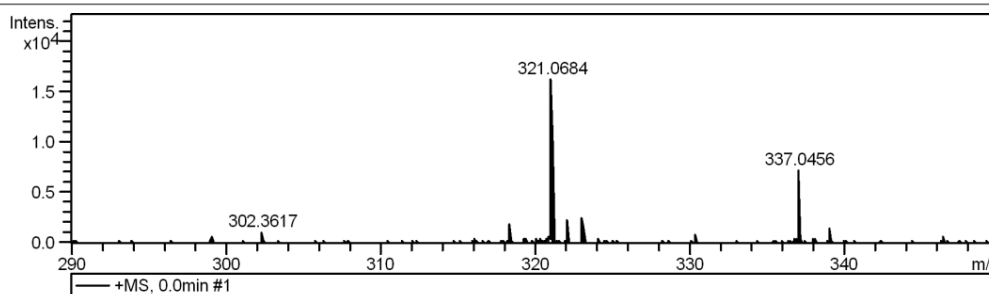
**Figure S6.**  $^1\text{H}$  NMR (a),  $^{19}\text{F}$  NMR (b), and  $^{13}\text{C}$  NMR (c) spectra of compound **6b** (solvent: acetone- $d_6$ ).



(Diethylmethylammoniumsulfonyl)(trifluoromethanesulfonyl)imide

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	302.3617	15619	3.1	1200	0.0194
2	318.3445	4986	4.7	1916	0.0638
3	321.0684	5788	40.1	16304	0.0555
4	322.0720	10841	5.8	2356	0.0297
5	323.0714	7939	6.2	2492	0.0407
6	337.0456	8335	19.1	7280	0.0404
7	339.0414	11458	4.1	1540	0.0296

Figure S7. Mass spectrum of compound 6b.

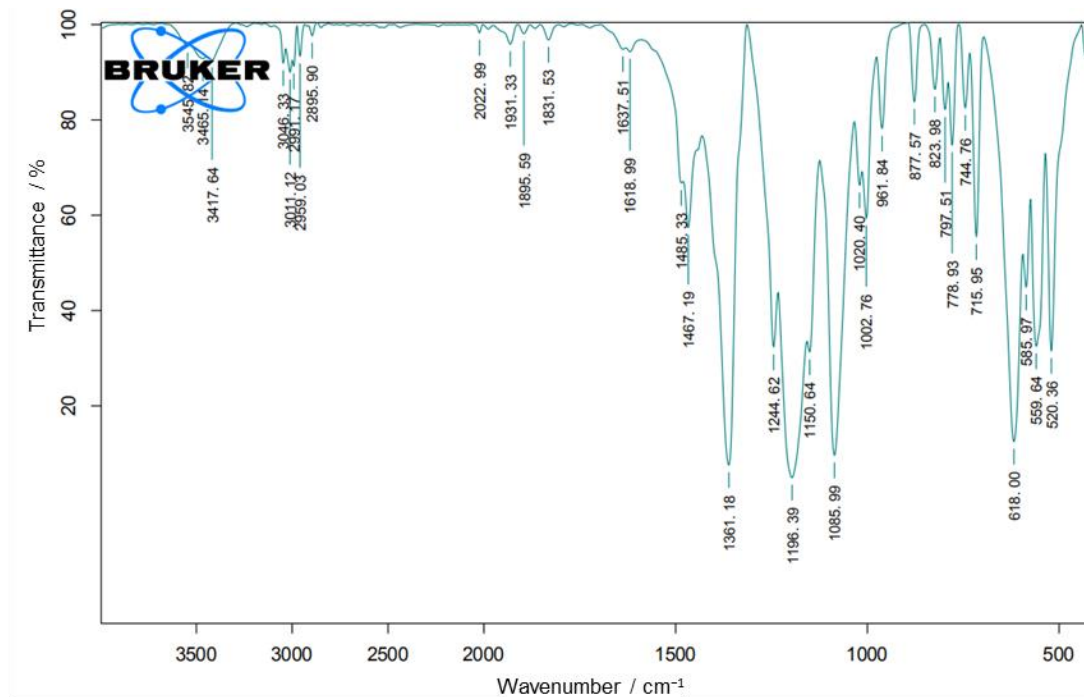
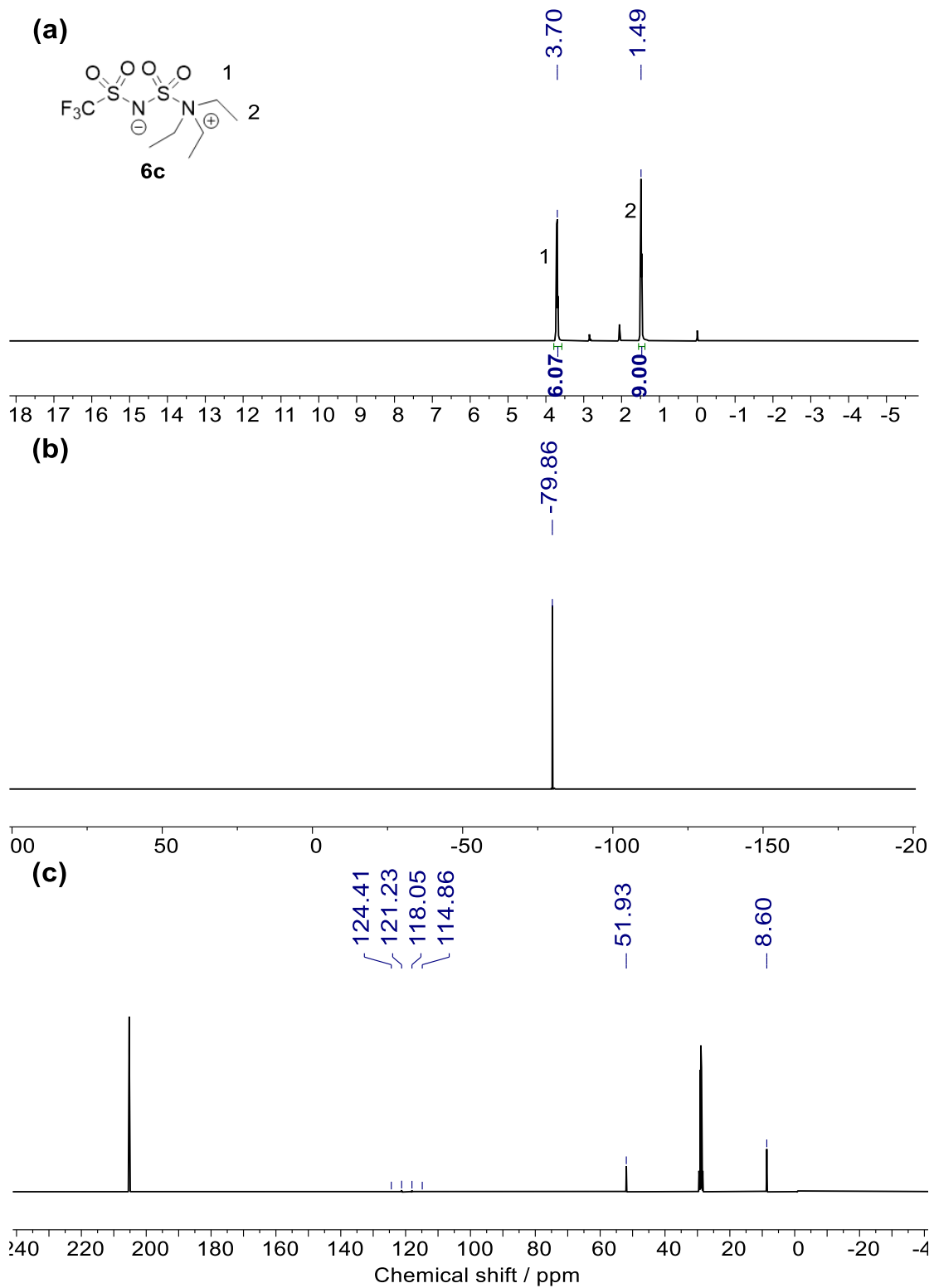
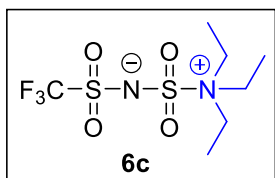


Figure S8. FT-IR spectrum of compound 6b.



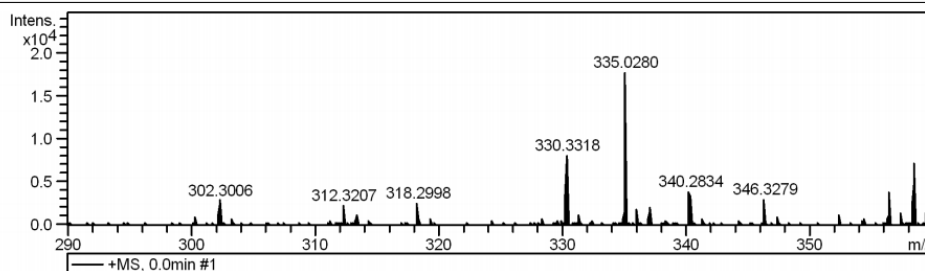
**Figure S9.**  $^1\text{H}$  NMR (a),  $^{19}\text{F}$  NMR (b), and  $^{13}\text{C}$  NMR (c) spectra of compound **6c** (solvent: acetone- $d_6$ ).



(Triethylammoniumsulfonyl)(trifluoromethanesulfonyl)imide

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	302.3006	7473	8.0	2908	0.0405
2	312.3207	6146	6.2	2356	0.0508
3	313.3275	5567	1.5	556	0.0563
4	318.2998	7157	6.8	2628	0.0445
5	330.3318	9599	20.2	8144	0.0344
6	331.3354	6540	3.2	1288	0.0507
7	335.0280	8946	43.5	17788	0.0374
8	336.0306	6623	4.8	1952	0.0507
9	337.0296	9262	5.1	2104	0.0364
10	340.2834	8392	9.5	3944	0.0405
11	346.3279	11438	7.2	3048	0.0303
12	352.3241	15602	2.9	1236	0.0226
13	356.3505	8968	8.9	3880	0.0397
14	357.3474	21862	3.4	1508	0.0163
15	358.3635	9466	16.5	7280	0.0379
16	359.3716	5980	3.4	1492	0.0601
17	360.3242	19314	2.6	1132	0.0187
18	362.3222	12666	4.9	2176	0.0286

Figure S10. Mass spectrum of compound 6c.

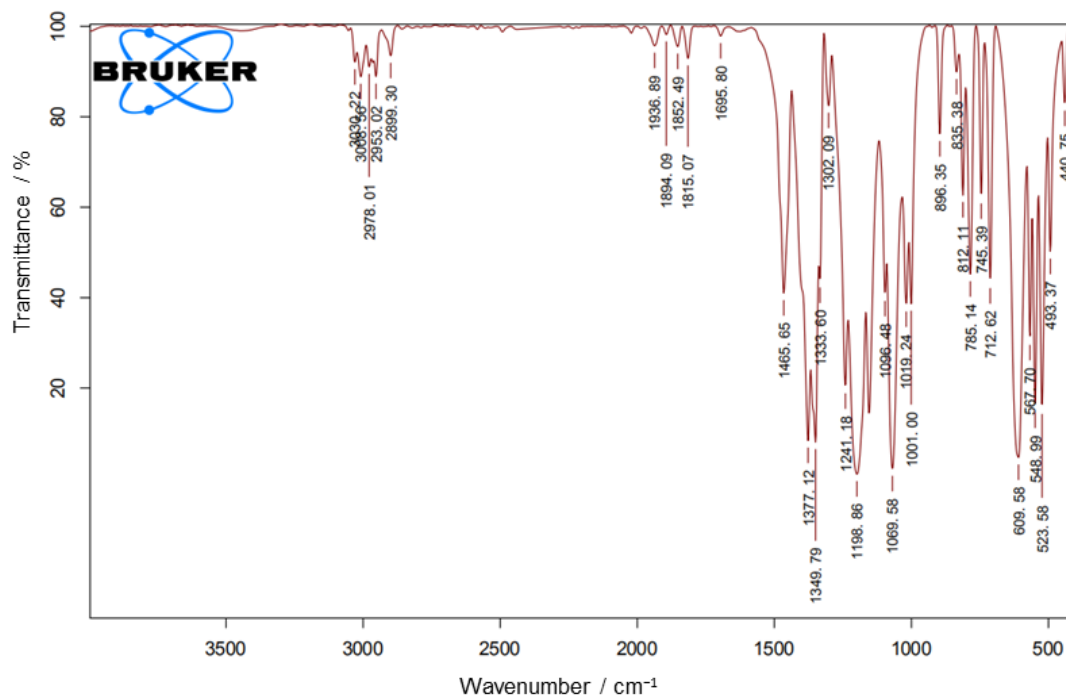


Figure S11. FT-IR spectrum of compound 6c.

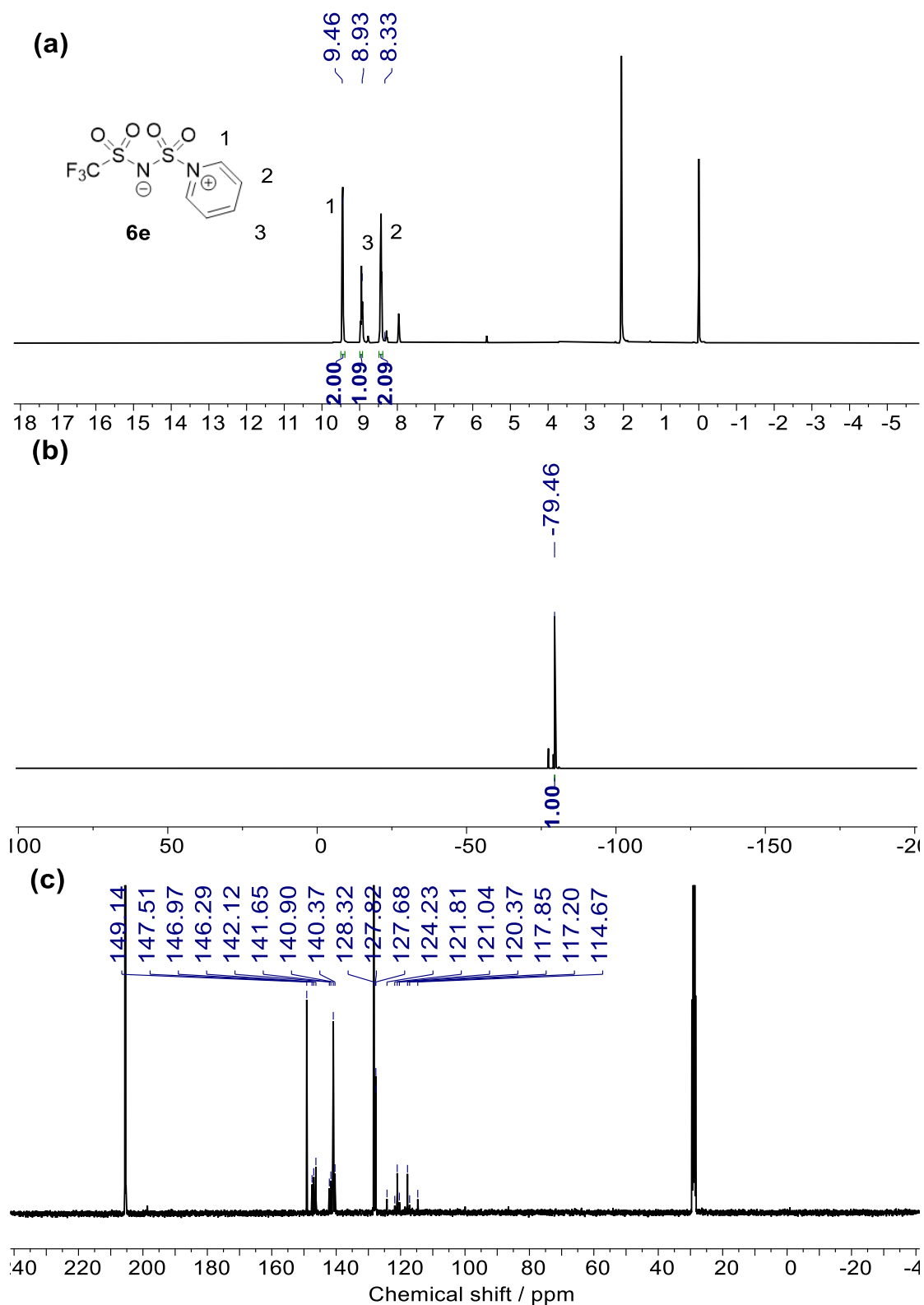
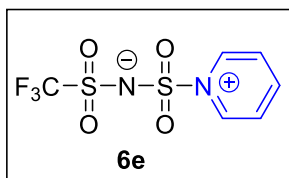


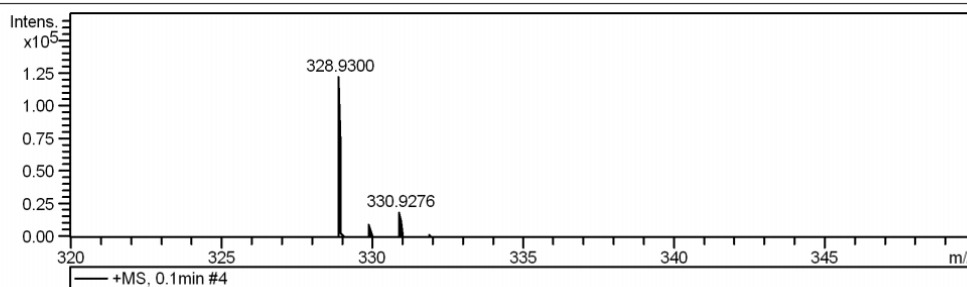
Figure S12.  $^1\text{H}$  NMR (a),  $^{19}\text{F}$  NMR (b), and  $^{13}\text{C}$  NMR (c) spectra of compound **6e** (solvent: acetone- $d_6$ ).



(Pyridiniumsulfonyl)(trifluoromethanesulfonyl)imide

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



#	m/z	Res.	S/N	I	FWHM
1	328.9300	11023	452.9	122944	0.0298
2	329.9322	9987	38.5	10393	0.0330
3	330.9276	9711	72.7	19545	0.0341

Figure S13. Mass spectrum of compound 6e.

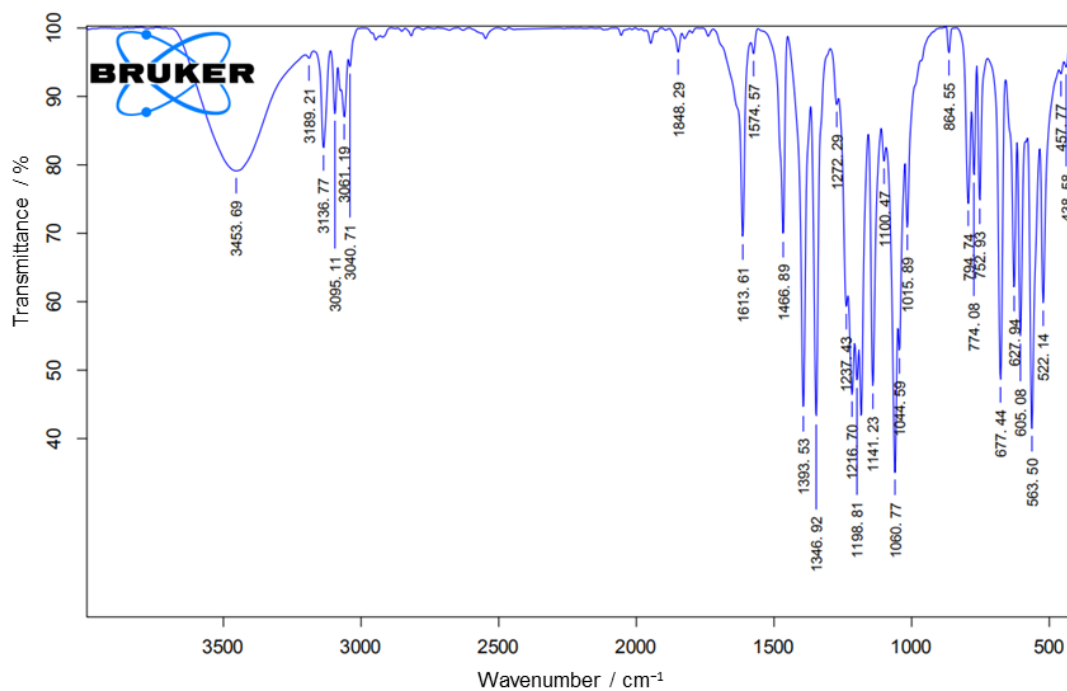


Figure S14. FT-IR spectrum of compound 6e.

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