Supporting Information

Novel Benzenesulfonamide Based-Ionic Liquids for Energy-efficient CO_2 Capture and Conversion

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1. Preparation of [$P_{6\,6\,6\,14}$] [p-MBSA]

An ethanol solution of [$P_{6\,6\,6\,14}$][OH] was prepared according to the following procedure. The Amberlite ®IRA402 Cl resin was immersed in a sodium hydroxide solution (concentration of 0.03 mol/L) for a duration of 3 days. Thereafter, the resin was filtered out, and then washed several times with deionsied water until the filtrate was neutral, obtaining the hydroxide anion exchange resin. Then, at least three equivalents (based on the mass of [$P_{6\,6\,6\,14}$] [Cl]) resin was loaded onto the column. Subsequently, the ethanol solution containing [$P_{6\,6\,6\,14}$] [Cl] (15.58g, 30 mmol, 25 mL EtOH) was pass through the column, and the flow rate was controlled about less than 5 drops per min. After anion exchange had been performed twice, the fresh hydroxide anion exchange resin was replaced and the anion was exchanged again for a third time. The obtained [$P_{6\,6\,6\,14}$] [OH] was determined the absence of remaining chloride ion by standard acidification and treatment with the silver nitrate. The concentration of [$P_{6\,6\,6\,14}$] [OH] was determined by ^{1}H NMR. Then, an equivalent amount of *p*-toluenesulfonamide was introduced into the prepared solution and stirred at room temperature for 24 h. Subsequently, evaporated the solvent in vacuum and the obtained product was then dried under vacuum (-0.01 MPa) at 60 °C for 24 h to remove any possible traces of water, a colorless and viscous liquid was obtained.

2. Characterization data of BSA-ILs

(1) [$P_{6\,6\,6\,14}$][*p*-MBSA]：^{1}H NMR (300MHz，DMSO-d_6): δ 7.61 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 2.32 (s, 3H), 2.26 - 2.11 (m, 7H), 1.59 - 1.15 (m, 50H), 0.87 (q, J = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.02, 139.27, 128.90, 125.71, 31.78, 30.89, 30.53, 30.33, 30.13, 29.50, 29.45, 29.20, 29.12, 28.57, 22.58, 22.30, 21.28, 21.04, 20.98, 18.23, 17.61, 14.43, 14.35. ESI-MS(m/z): calcd for $C_{32}H_{68}P[M+H]^{+}$: 483.87; found: 483.51. ESI-MS(m/z): calcd for $C_7H_8NO_2S[M-H]^{-}$: 170.21; found: 170.03.

(2) [$P_{4\,4\,4\,4}$][*p*-MBSA]：^{1}H NMR (300 MHz, DMSO-d_6): δ 7.53 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.9 Hz, 2H), 2.28 (s, 3H), 2.26 - 2.10 (m, 8H), 1.40 (dd, J = 13.1, 5.7 Hz, 16H), 0.92 (t, J = 7.0 Hz, 12H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.97, 137.00, 128.24, 125.42, 23.94, 23.73, 23.21, 23.15, 21.19, 18.12, 17.49, 13.75. HR-MS(m/z):

calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.2543. HR-MS(m/z): calcd for $C_7H_8NO_2S[M-H]^-$: 170.21; found: 170.0275.

(3) $[P_{4\,4\,4\,4}][BSA]$：^1H NMR (400 MHz, DMSO-d_6): δ 7.72 (dd, J = 7.4, 2.2 Hz, 2H), 7.41 - 7.32 (m, 3H), 2.29 - 2.12 (m, 6H), 1.52 - 1.32 (m, 12H), 0.91 (t, J = 7.0 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.74, 127.81, 127.73, 125.33, 23.91, 23.76, 23.27, 23.23, 18.09, 17.62, 13.73. ESI-MS(m/z): calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.26. ESI-MS(m/z): calcd for $C_6H_6NO_2S[M-H]^-$: 156.18; found: 156.01.

(4) $[P_{4\,4\,4\,4}][p\text{-MOBSA}]$：$^1H$ NMR (300 MHz, DMSO-d_6): δ 7.61 - 7.53 (m, 2H), 6.85 - 6.77 (m, 2H), 3.74 (s, 3H), 2.29 - 2.10 (m, 8H), 1.55 - 1.31 (m, 16H), 0.92 (d, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.01, 142.71, 127.33, 113.40, 55.71, 23.92, 23.77, 23.12, 17.99, 17.52, 13.76. HR-MS(m/z): calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.2537. HR-MS(m/z): calcd for $C_7H_8NO_3S[M-H]^-$: 186.21; found: 186.0235.

(5) $[P_{4\,4\,4\,4}][p\text{-CBSA}]$：$^1H$ NMR (400 MHz, DMSO-d_6): δ 7.64 (d, J = 8.4 Hz, 2H), 7.34 - 7.29 (m, 2H), 2.26 - 2.12 (m, 8H), 1.42 (tq, J = 15.4, 8.9, 8.3 Hz, 17H), 0.91 (t, J = 7.0 Hz, 13H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 152.72, 132.27, 127.78, 127.35, 23.91, 23.76, 23.11, 18.03, 17.56, 13.74. HR-MS(m/z): calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.2537. HR-MS(m/z): calcd for $C_6H_5ClNO_2S[M-H]^-$: 190.62; found: 189.9733.

(6) $[P_{4\,4\,4\,4}][o\text{-NBSA}]$：$^1H$ NMR (400 MHz, DMSO-d_6): δ 7.92 (dd, J = 7.4, 2.2 Hz, 1H), 7.64 - 7.57 (m, 2H), 7.53 - 7.48 (m, 1H), 2.26 - 2.13 (m, 8H), 1.43 (ddq, J = 27.5, 14.0, 6.6, 6.1 Hz, 16H), 0.91 (t, J = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.76, 143.41, 131.80, 130.03, 128.76, 123.34, 23.92, 23.76, 23.13, 18.00, 17.53, 13.75. ESI-MS(m/z): calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.26. ESI-MS(m/z): calcd for $C_6H_5N_2O_4S[M-H]^-$: 201.18; found: 201.00.

(7) $[P_{4\,4\,4\,4}][p\text{-ABSA}]$：$^1H$ NMR (300 MHz, DMSO-d_6): δ 7.35 - 7.26 (m, 2H), 6.45 - 6.36 (m, 2H), 5.08 (s, 2H), 2.28 - 2.09 (m, 8H), 1.44 (tp, J = 14.1, 7.0 Hz, 16H), 0.92 (t, J = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.59, 141.74, 126.60, 112.56, 23.91, 23.76, 23.18, 23.13, 18.04, 17.56, 13.76. HR-MS(m/z): calcd for $C_{16}H_{36}P[M+H]^+$: 259.44; found: 259.2557. HR-MS(m/z): calcd for $C_6H_7N_2O_2S[M-H]^-$:

171.19; found: 171.0231.

(8) [$N_{4\,4\,4\,4}$][*p*-MBSA]：^{1}H NMR (300 MHz, DMSO-d_6): δ 7.52 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H), 1.55 (dd, J = 16.0, 8.5 Hz, 8H), 1.31 (h, J = 7.2 Hz, 8H), 0.92 (d, J = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.91, 128.26, 125.42, 23.52, 21.20, 19.68, 13.98. HR-MS(m/z): calcd for $C_{16}H_{36}N[M+H]^+$: 242.47; found: 242.2849. HR-MS(m/z): calcd for $C_7H_8NO_2S[M-H]^-$: 170.21; found: 170.0282.

(9) [$N_{1\,1\,1}C_2OH$][*p*-MBSA]：^{1}H NMR (400 MHz, DMSO-d_6): δ 7.54 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 7.9 Hz, 2H), 3.86 - 3.80 (m, 2H), 3.44 - 3.38 (m, 2H), 3.11 (s, 9H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.91, 137.64, 128.52, 125.42, 67.54, 55.28, 53.56, 53.49, 40.44, 21.22. HR-MS(m/z): calcd for $C_5H_{14}NO[M+H]^+$: 104.17; found: 104.1067. HR-MS(m/z): calcd for $C_7H_8NO_2S[M-H]^-$: 170.21; found: 170.0280.

3. Table S1

p*K*a of substituted BSA molecules

Entry	Molecule	p*K*a / H_2O / 20 ℃
1	*p*-MBSA	10.21
2	*p*-MOBSA	10.28
3	*o*-NBSA	9.24 [a]
4	*p*-CBSA	9.79
5	BSA	10.07
6	*p*-ABSA	10.51

[a] Data from ACS Scifinder, calculated using Advanced Chemistry Development (ACD/Labs) Software (© 1994-2026 ACD/Labs).

4. NMR spectroscopy for BSA-ILs

Figure S1A ^{1}H NMR for [$P_{6\,6\,6\,14}$][*p*-MBSA].

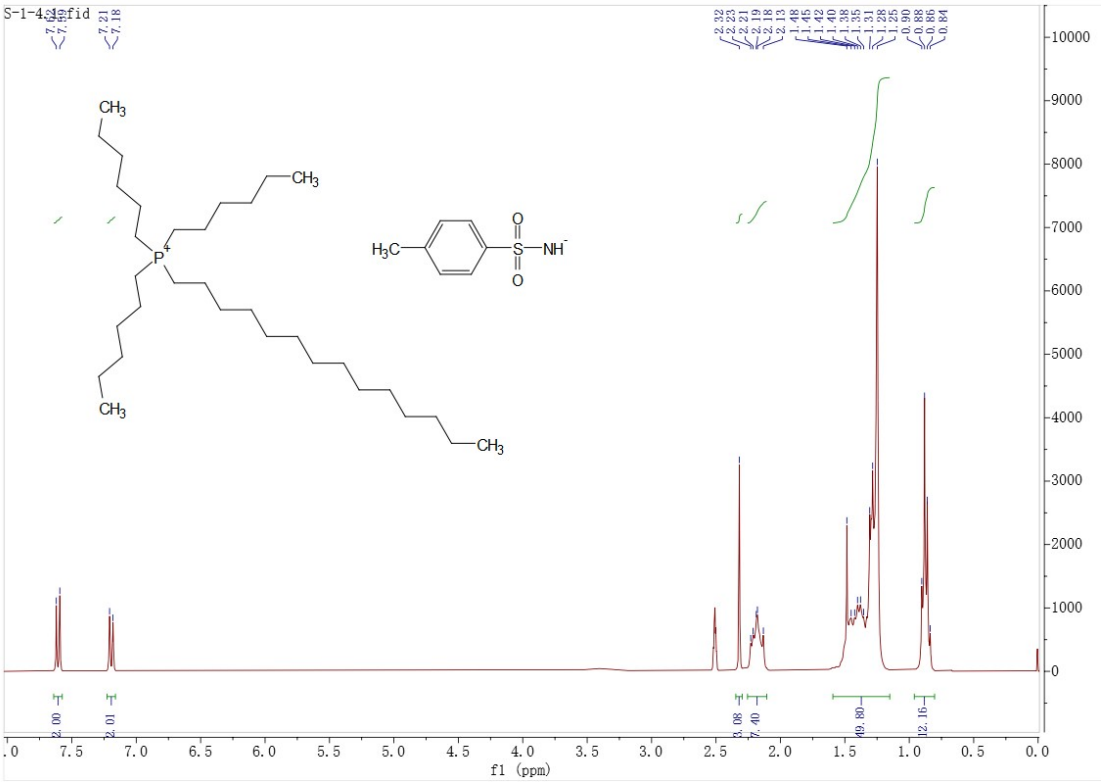


Figure S1B ^{13}C NMR for [$P_{6\,6\,6\,14}$][*p*-MBSA].

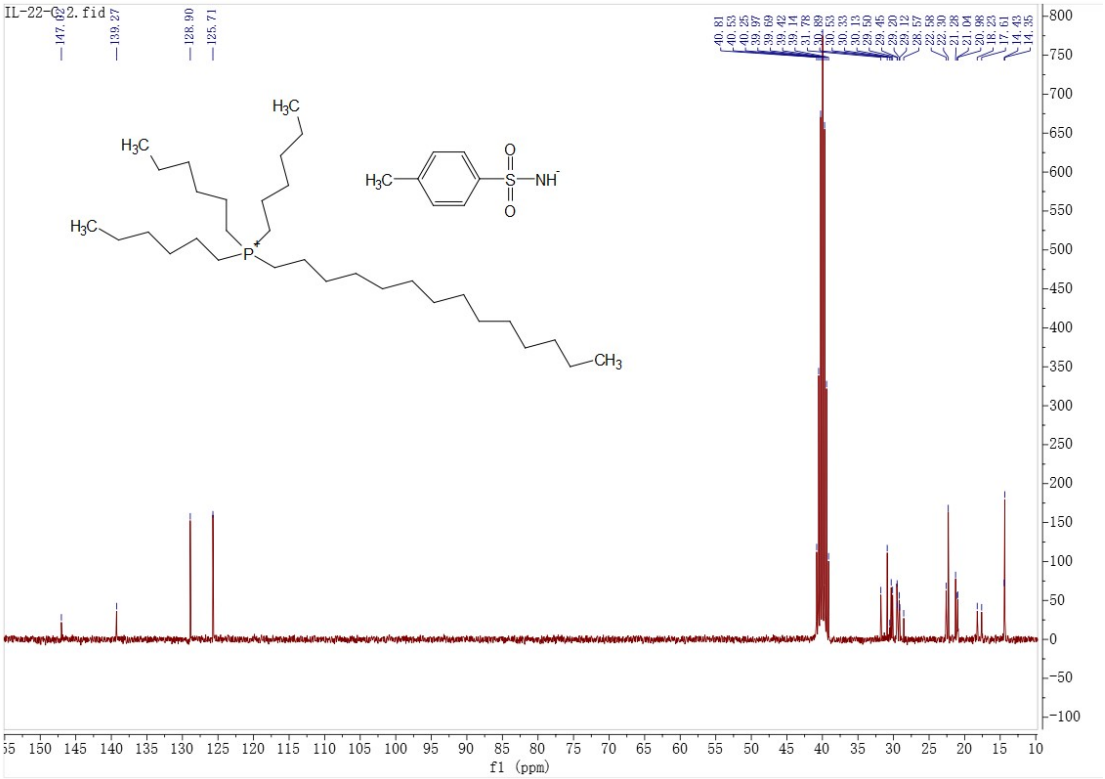


Figure S2A ^{1}H NMR for $[P_{4\,4\,4\,4}][BSA]$.

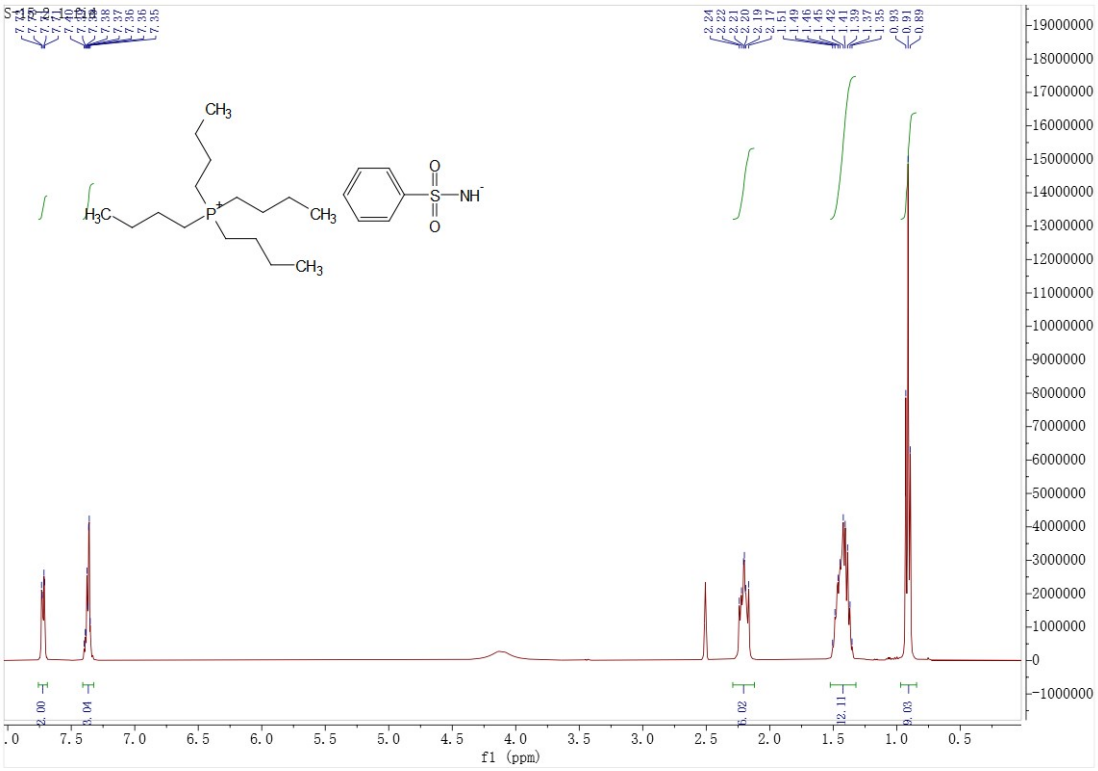


Figure S2B ^{13}C NMR for $[P_{4\,4\,4\,4}][BSA]$.

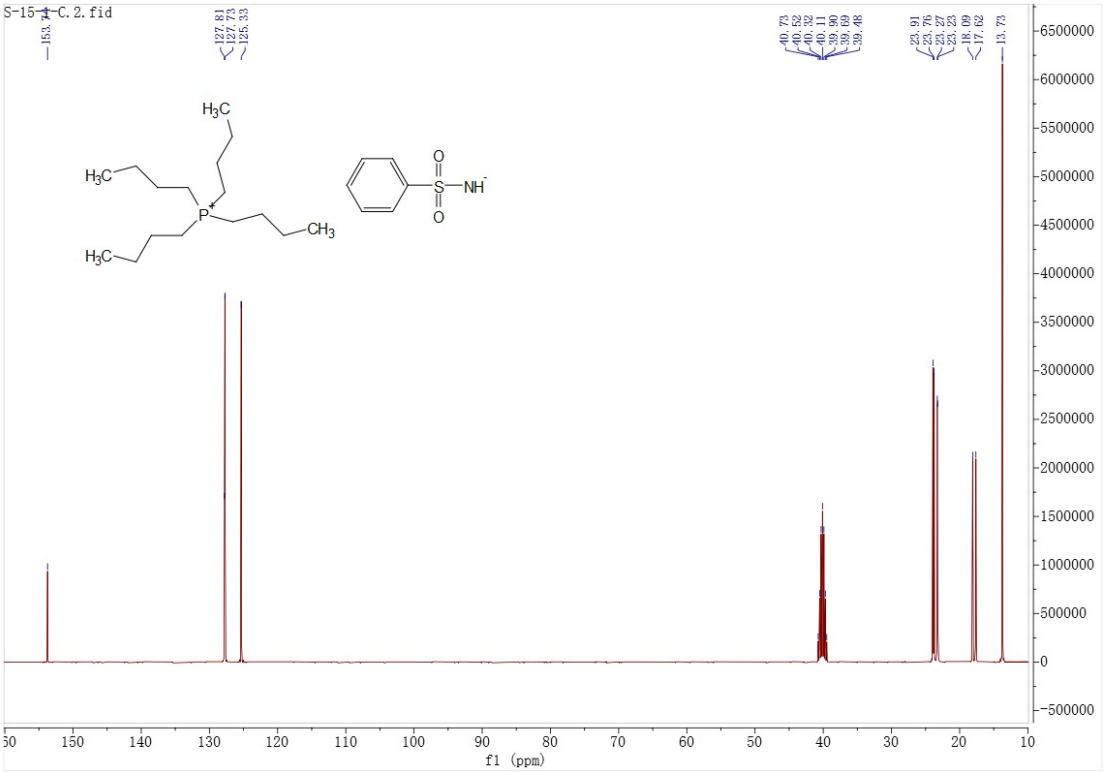


Figure S3A ^{1}H NMR for [$P_{4\,4\,4\,4}$][*p*-MOBSA].

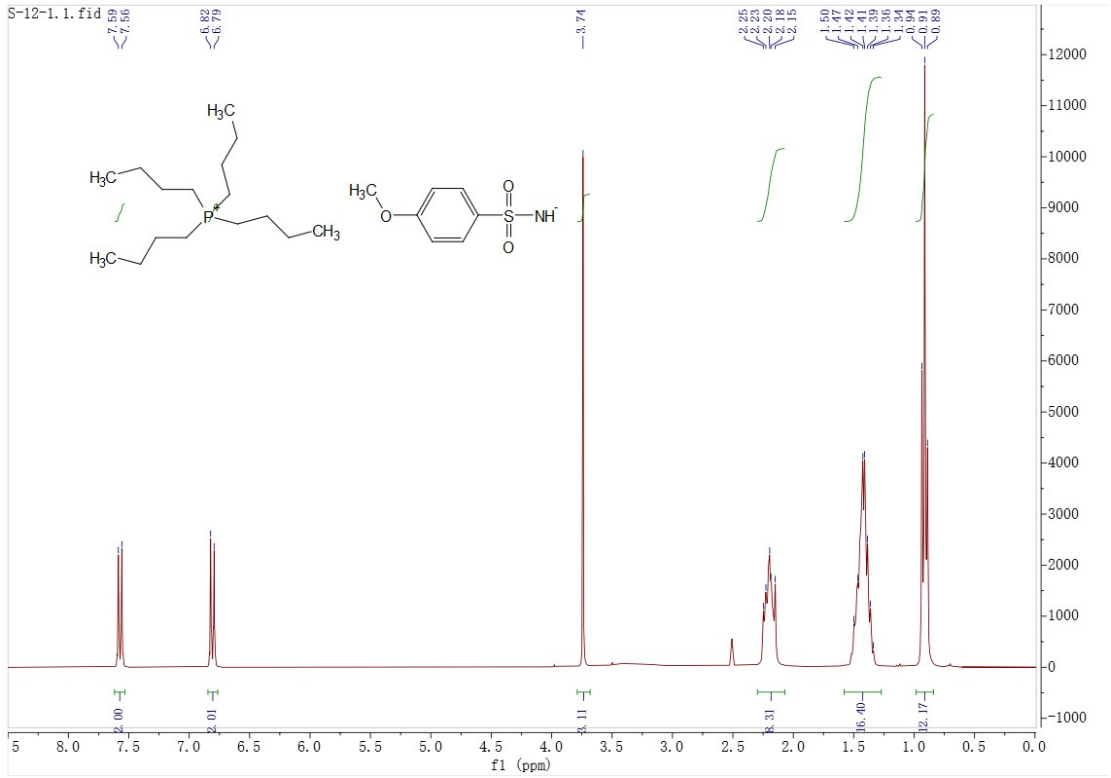


Figure S3B ^{13}C NMR for [$P_{4\,4\,4\,4}$][*p*-MOBSA].

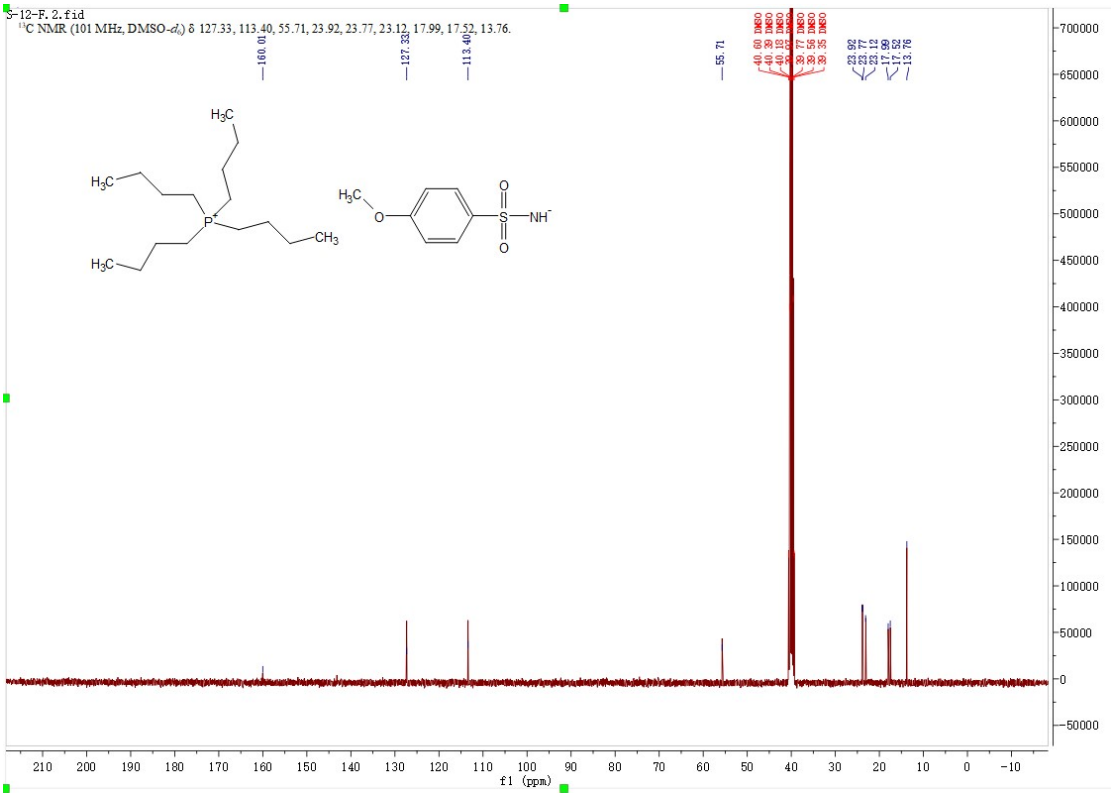


Figure S4A ^{1}H NMR for [$P_{4\,4\,4\,4}$][*p*-ABSA].

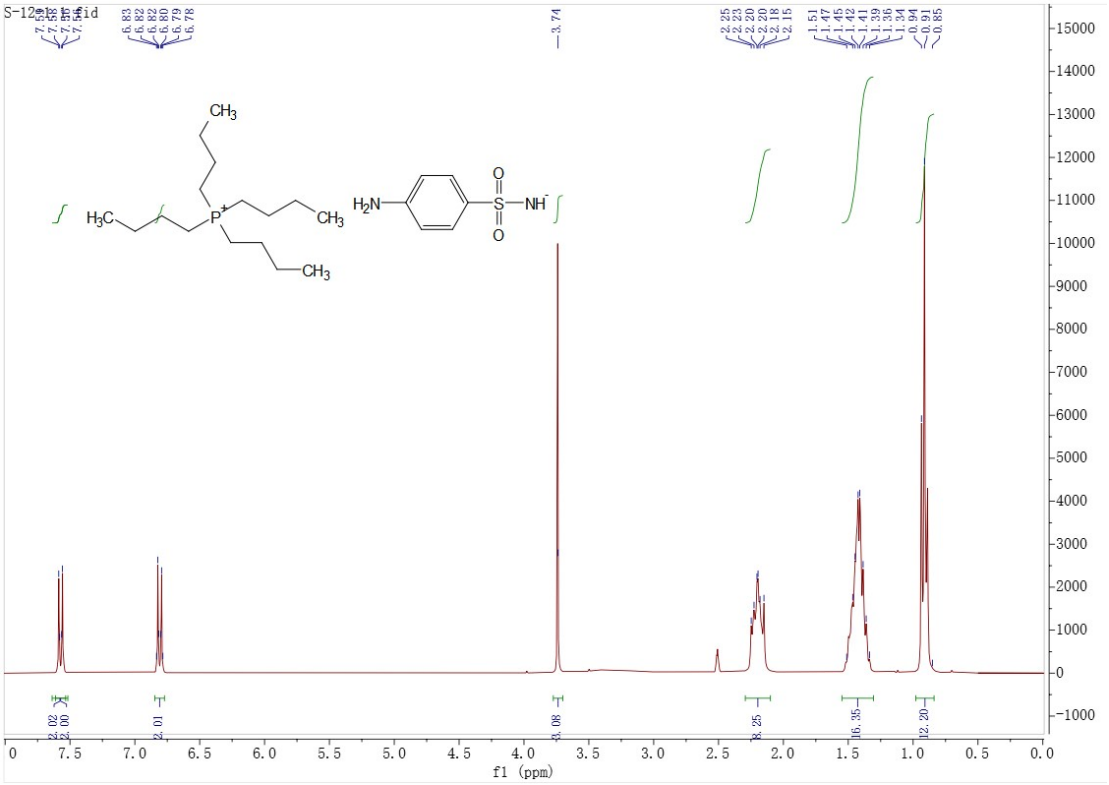


Figure S4B ^{13}C NMR for [$P_{4\,4\,4\,4}$][*p*-ABSA].

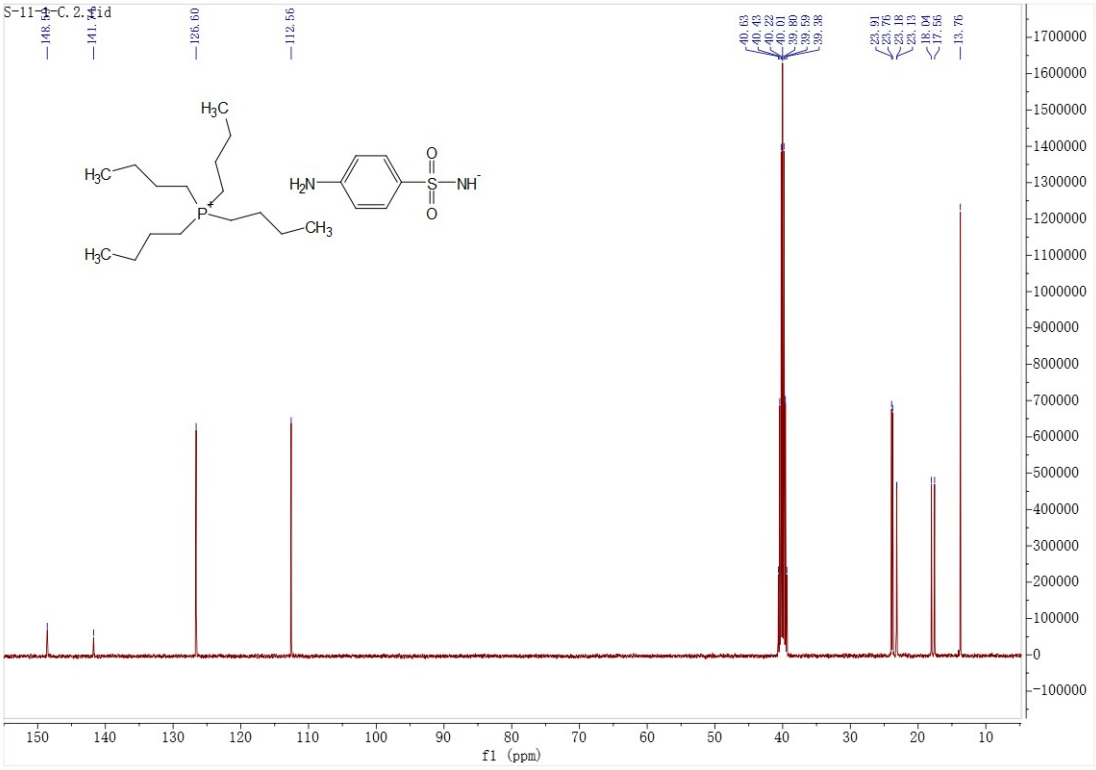


Figure S5A ^{1}H NMR for [$P_{4\,4\,4\,4}$][*p*-MBSA].

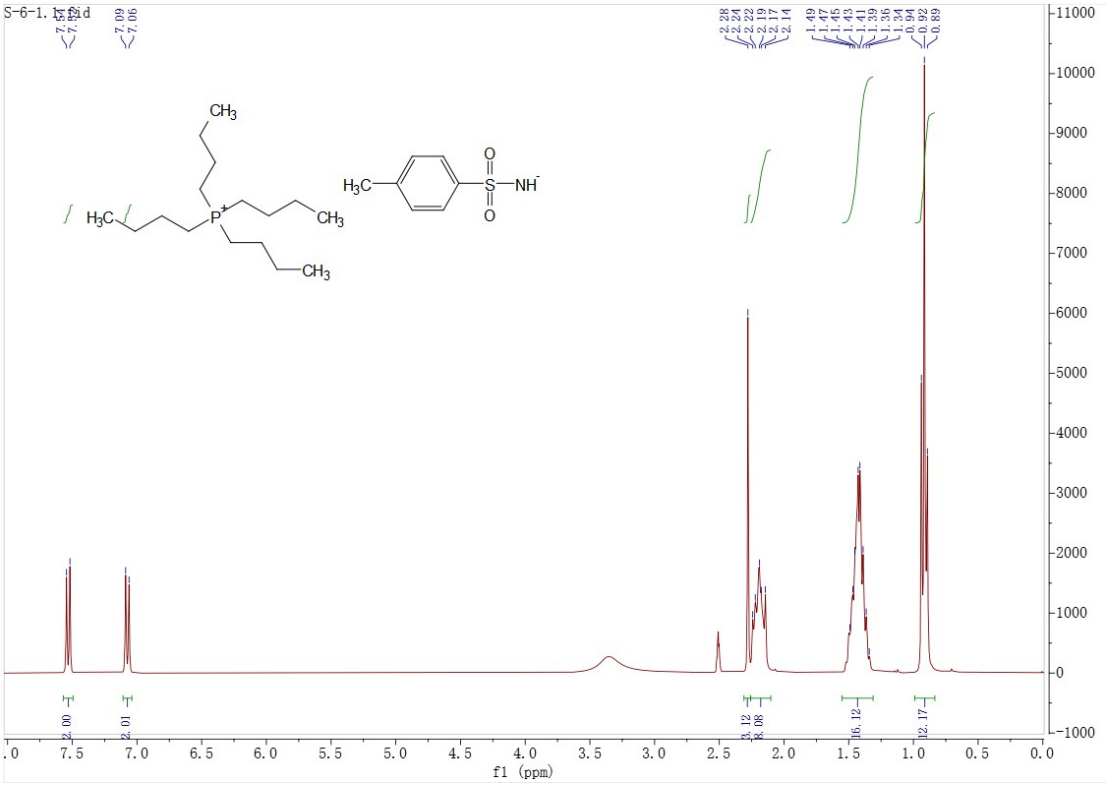


Figure S5B ^{13}C NMR for [$P_{4\,4\,4\,4}$][*p*-MBSA].

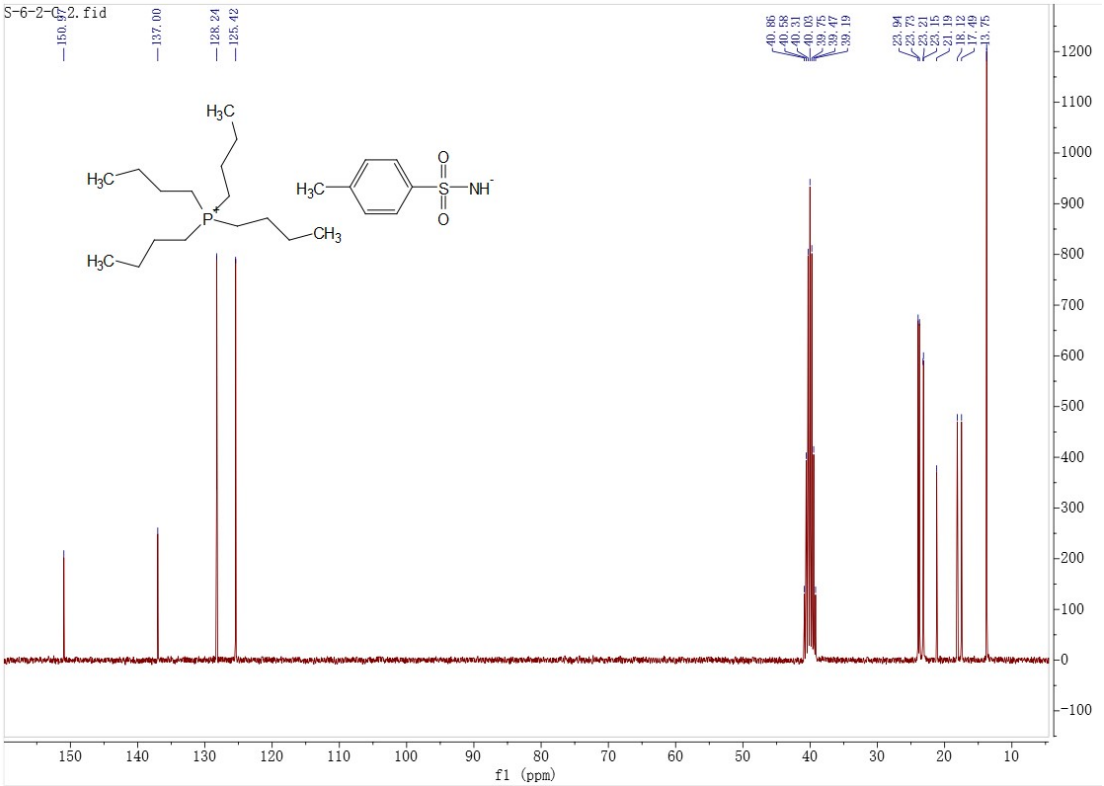


Figure S6A ^{1}H NMR for [$P_{4\,4\,4\,4}$][*p*-CBSA].

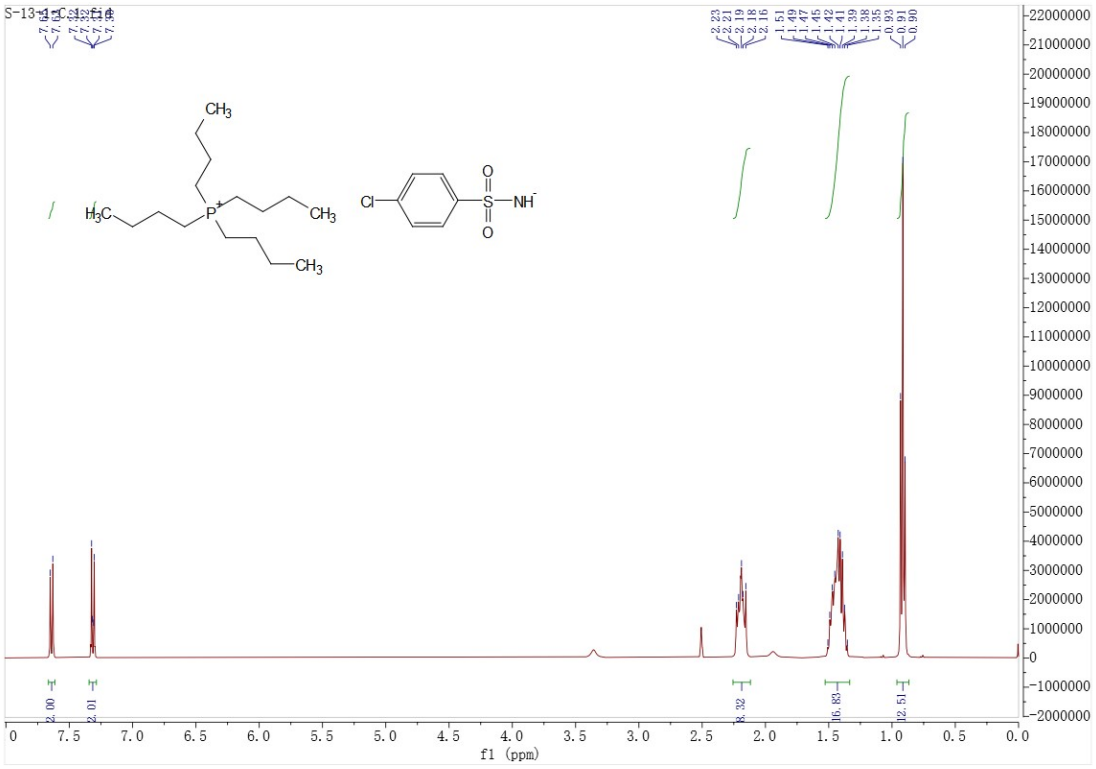


Figure S6B ^{13}C NMR for [$P_{4\,4\,4\,4}$][*p*-CBSA].

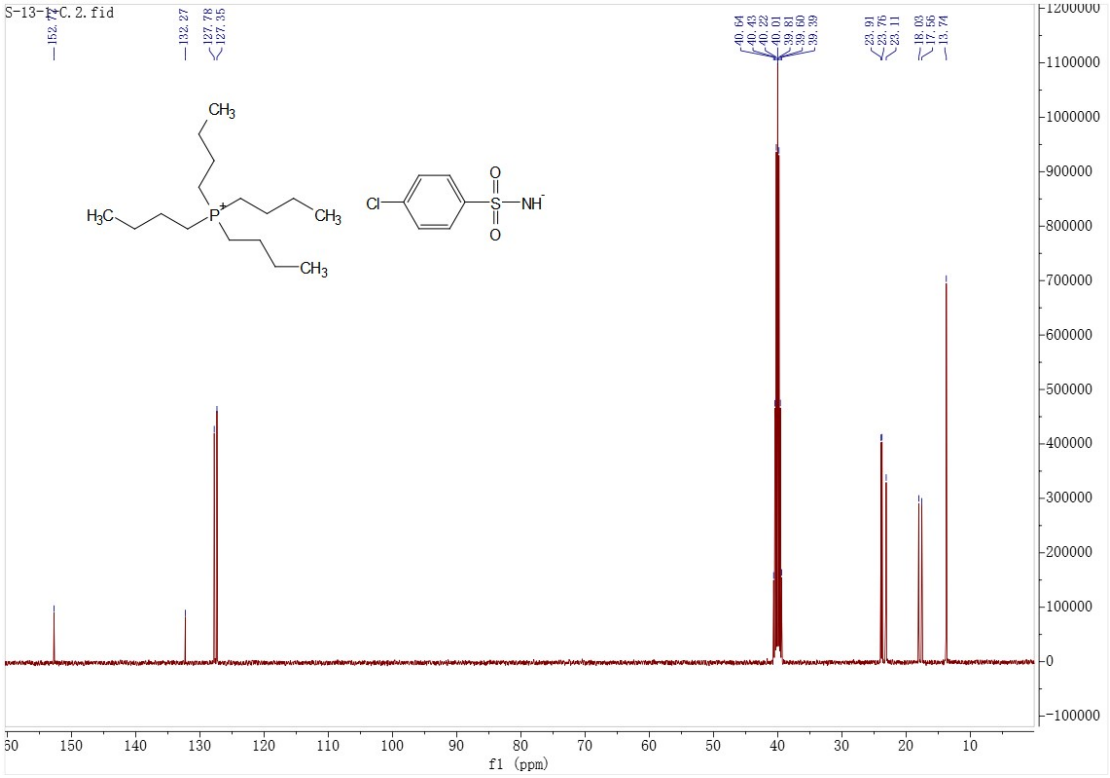


Figure S7A ^{1}H NMR for [$N_{4\,4\,4\,4}$][*p*-MBSA].

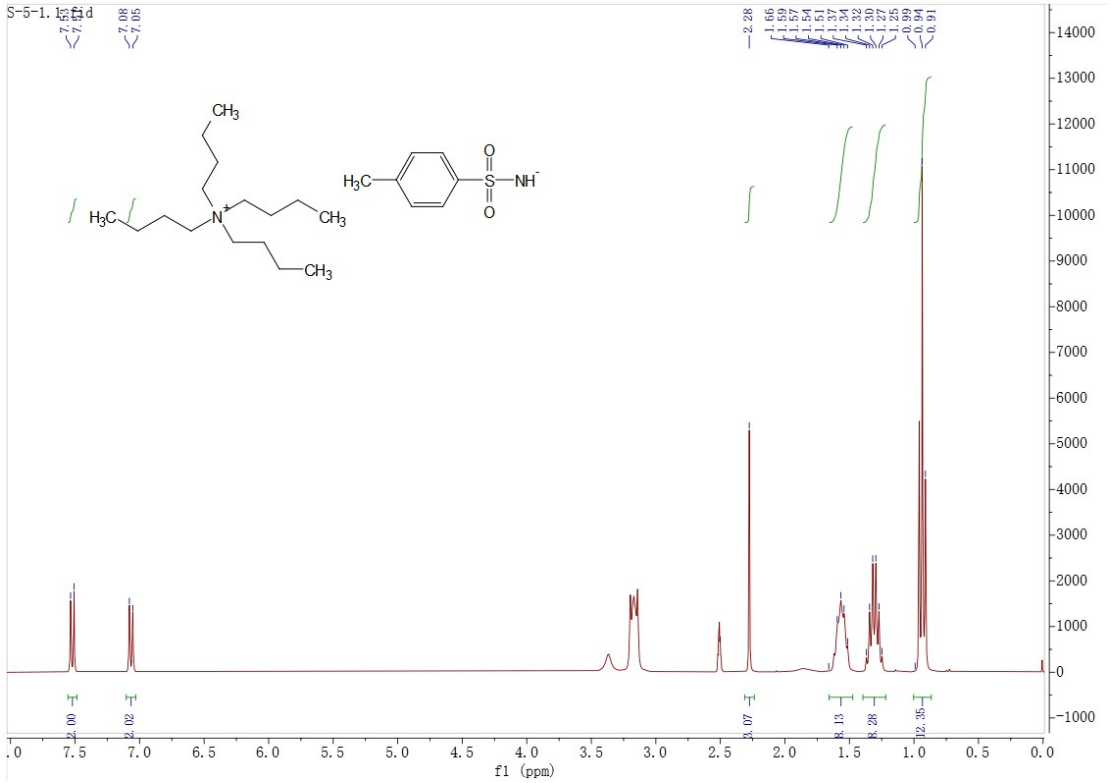


Figure S7B ^{13}C NMR for [$N_{4\,4\,4\,4}$][*p*-MBSA].

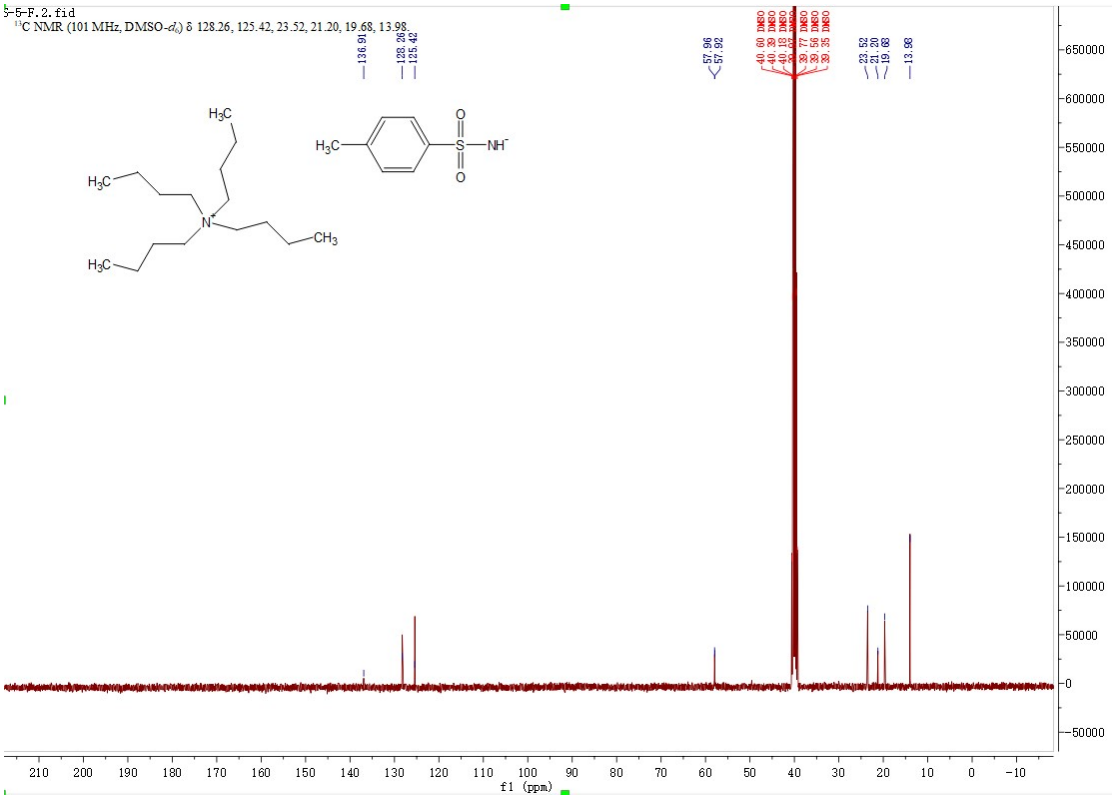


Figure S8A ^{1}H NMR for [$P_{4\,4\,4\,4}$][*o*-NBSA].

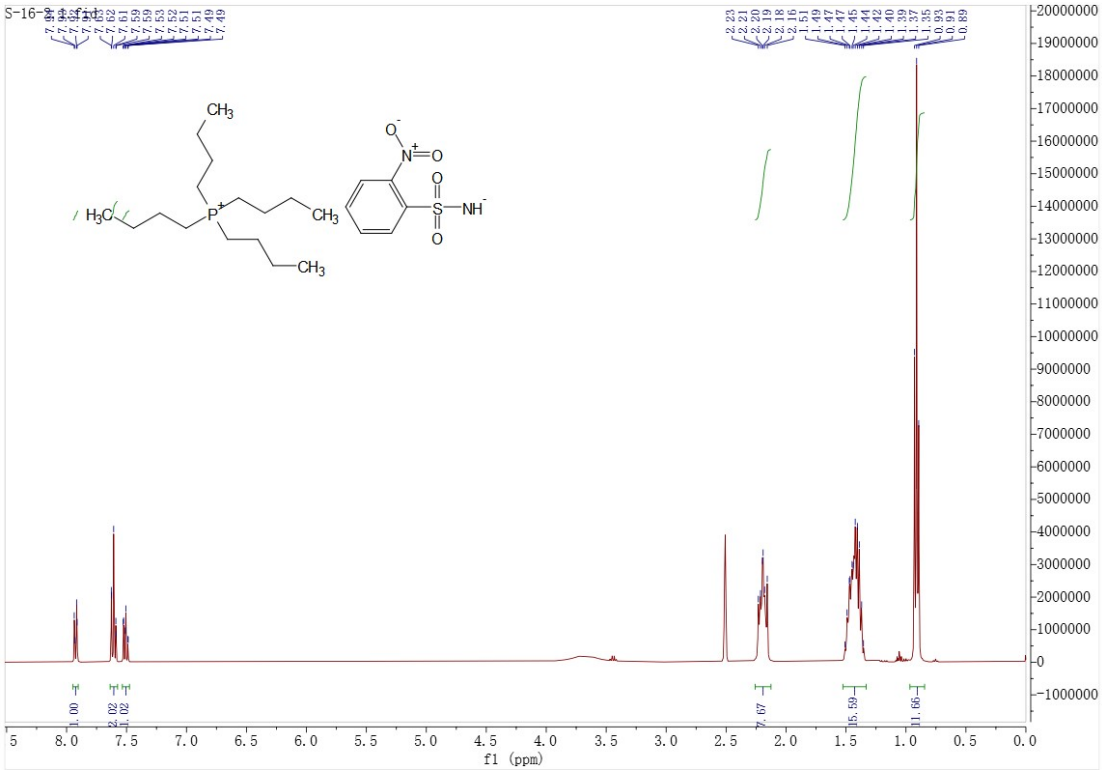


Figure S8B ^{13}C NMR for [$P_{4\,4\,4\,4}$][*o*-NBSA].

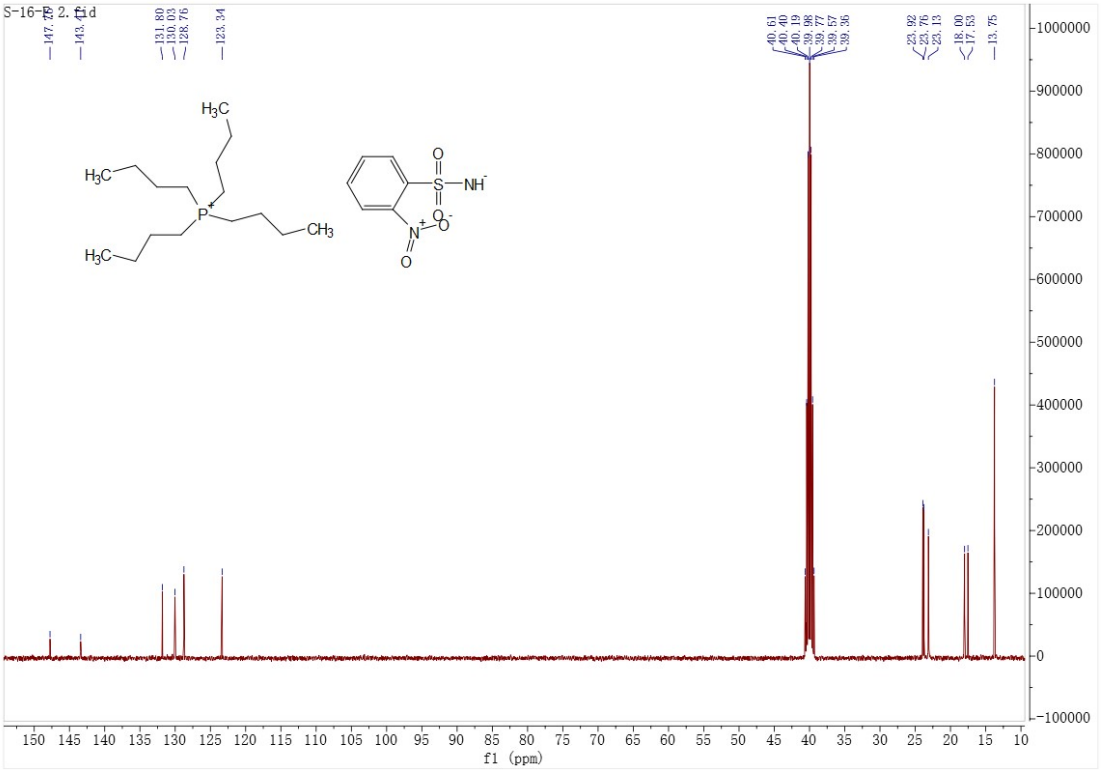


Figure S9A ^{1}H NMR for [$N_{1\,1\,1}OH_{2\,2}$][*p*-MBSA].

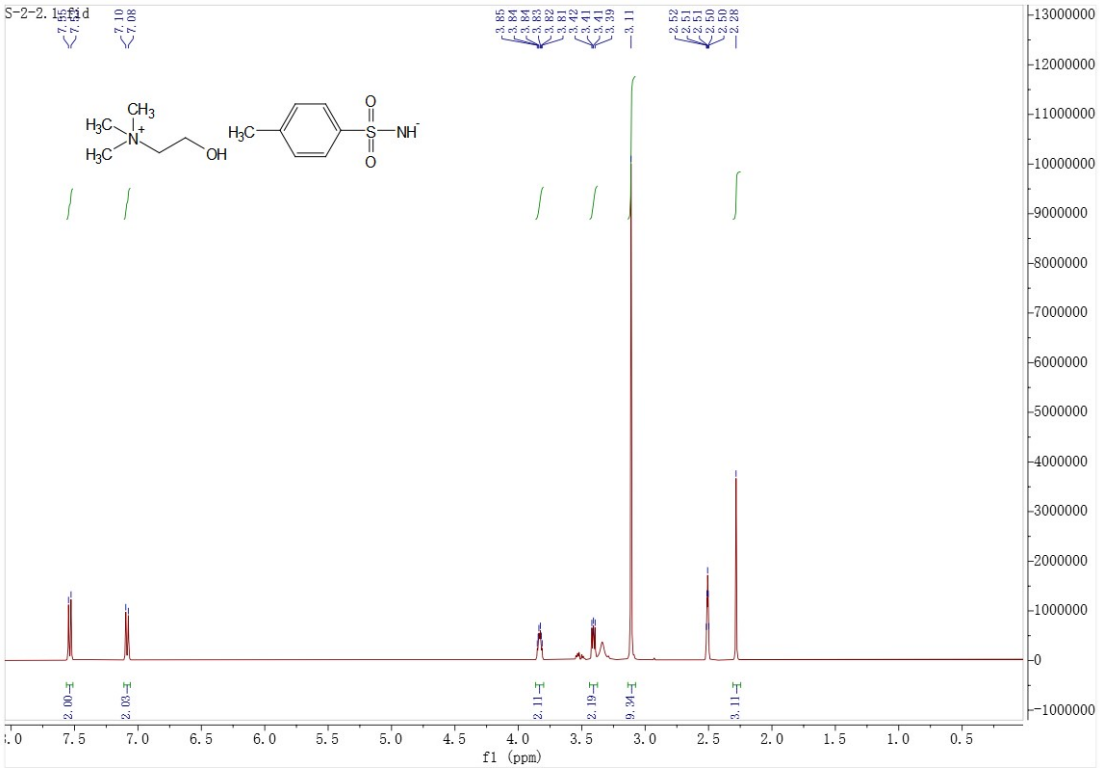
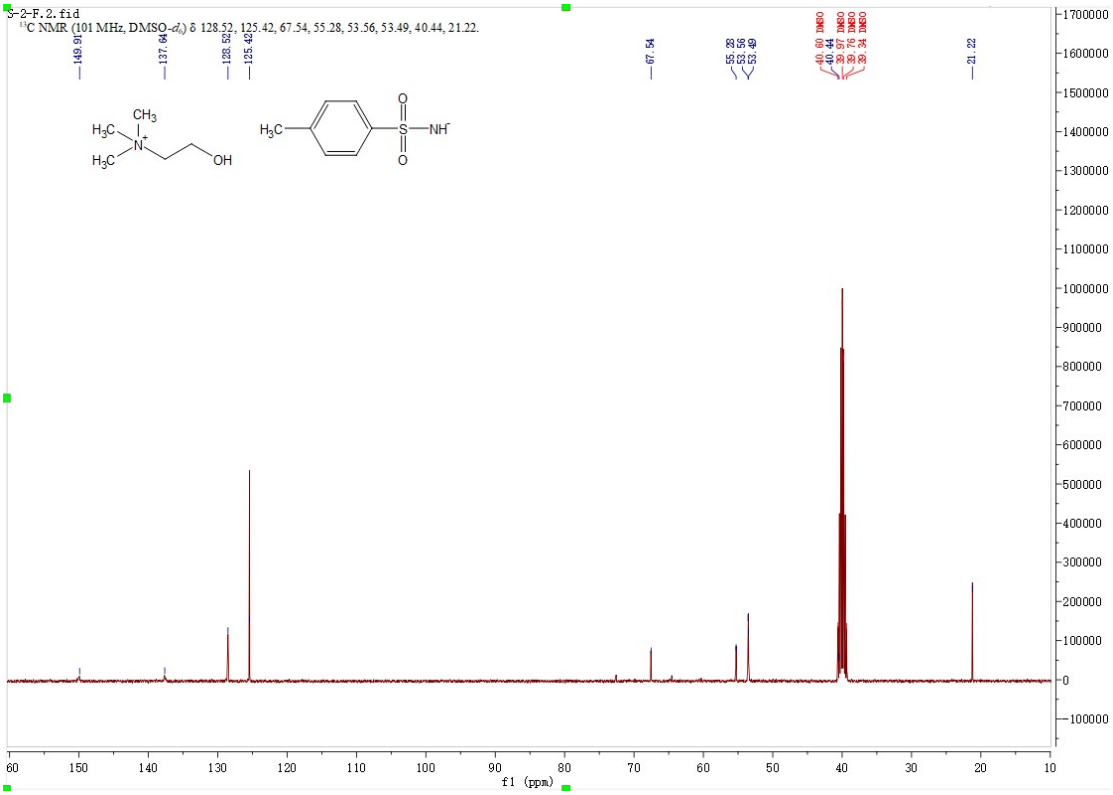


Figure S9B ^{13}C NMR for [$N_{1\,1\,1}OH_{2\,2}$][*p*-MBSA].



5. ESI-MS spectroscopy for BSA-ILs

Figure S10A: Anion MS for [$P_{6\,6\,6\,14}$][*p*-MBSA].

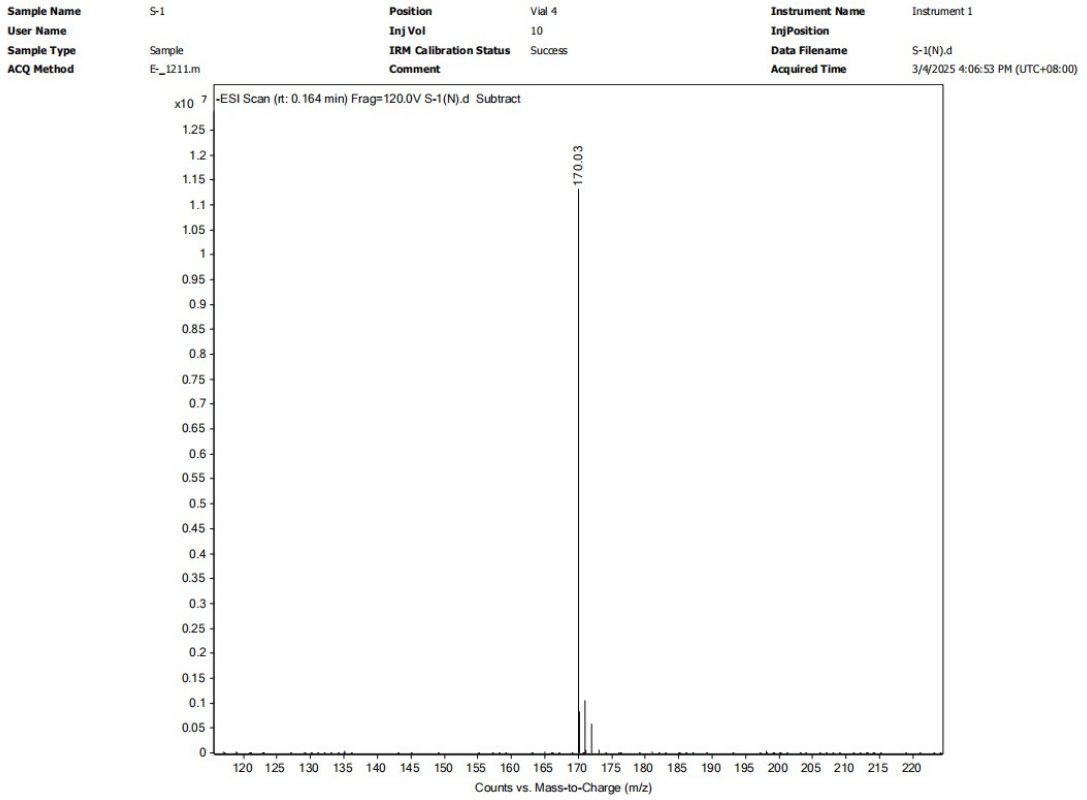


Figure S10B: Cation MS for [$P_{6\,6\,6\,14}$][*p*-MBSA].

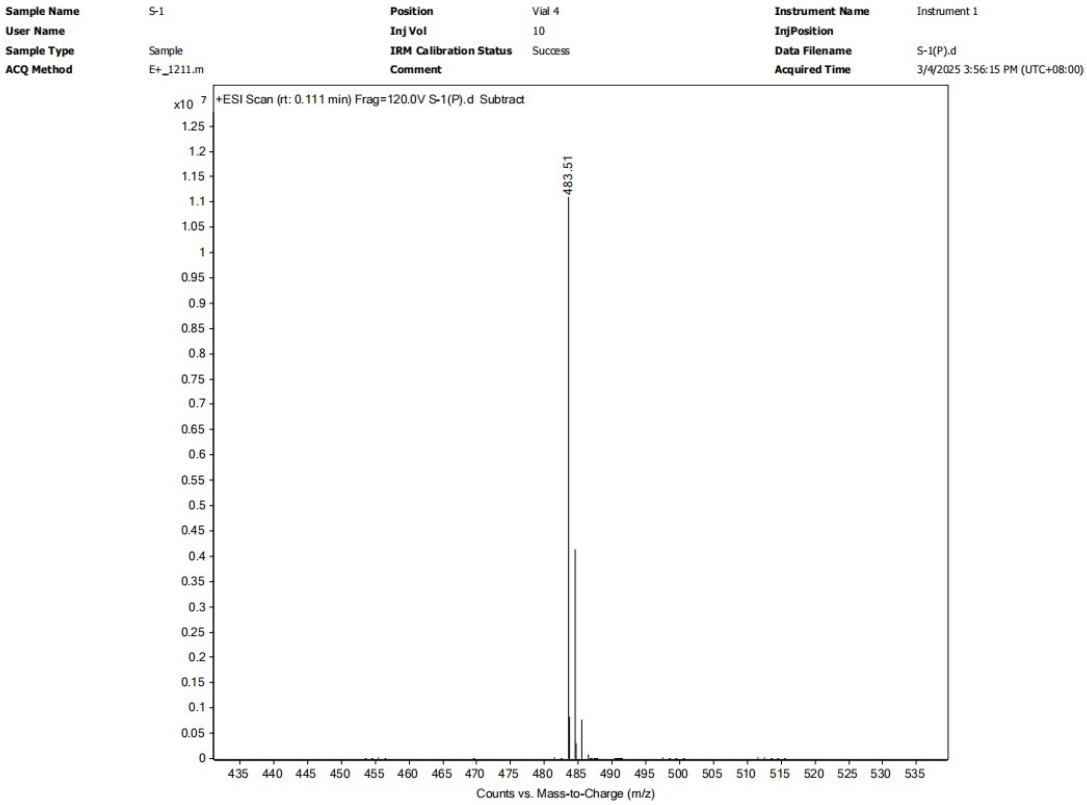


Figure S11A: Anion MS for [P_{4444}][*p*-MBSA].

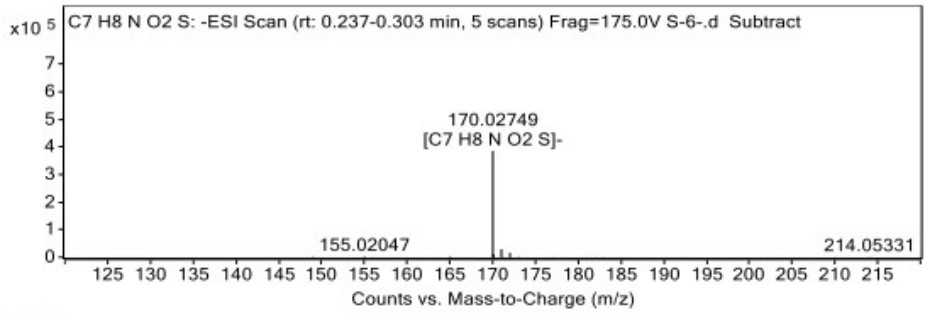
Qualitative Analysis Report

Data Filename	S-6-.d	**Sample Name**	S-6
Sample Type	Sample	**Position**	Vial 72
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/22/2024 11:03:21 AM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group Info.			
Stream Name	LC 1	**Acquisition Time (Local)**	7/22/2024 11:03:21 AM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
170.02749	1	384989.91	C7 H8 N O2 S	M-
379.25858	1	43021.89		
409.26895	1	70463.7		
504.28676	1	51352.33		
599.30479	1	43223.52		

Formula Calculator Element Limits

Element	Min	Max
C	5	9
H	6	10
O	1	3
N	0	2
S	0	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C7 H8 N O2 S	TRUE	170.02697	170.02757	3.54	C7 H8 N O2 S	170.02812

--- End Of Report ---

Figure S11B: Cation MS for [P_{4444}][*p*-MBSA].

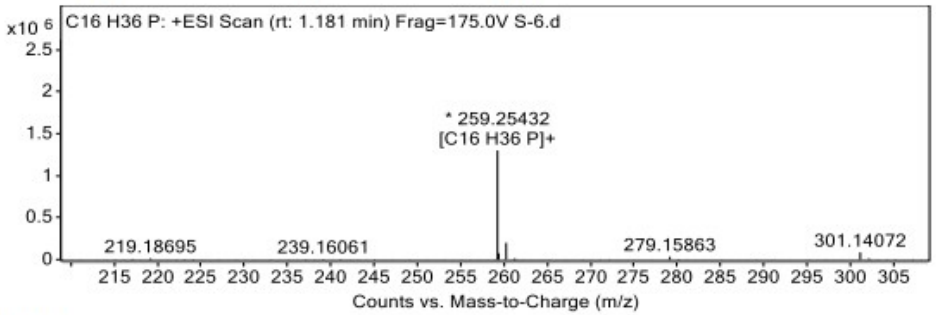
Qualitative Analysis Report

Data Filename	S-6.d	**Sample Name**	S-6
Sample Type	Sample	**Position**	Vial 72
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/22/2024 11:00:33 AM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group Info.			
Stream Name	LC 1	**Acquisition Time (Local)**	7/22/2024 11:00:33 AM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
149.02332	1	39689.12		
259.25432	1	1301121.63	C16 H36 P	M+
259.40749	2	74689.47		
260.25798	1	200382.91	C16 H36 P	M+
301.14072	1	85832.21		

Formula Calculator Element Limits

Element	Min	Max
C	6	26
H	26	46
P	1	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C16 H36 P	TRUE	259.2549	259.25546	2.16	C16 H36 P	259.25491

--- End Of Report ---

Figure S12A: Cation MS for [$P_{4\,4\,4\,4}$][*p*-MOBSA].

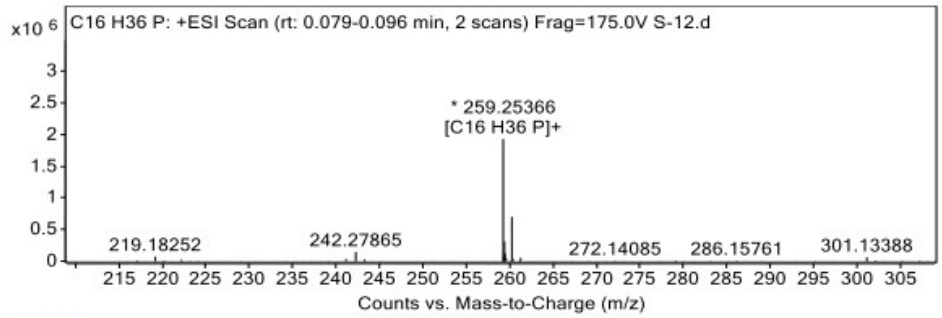
Qualitative Analysis Report

Data Filename	S-12.d	**Sample Name**	S-12
Sample Type	Sample	**Position**	Vial 74
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/21/2024 3:55:20 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 3:55:20 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
242.27865	1	144102.09		
259.25366		1929231.75	C16 H36 P	M+
259.40194	1	311552.91		
259.44196	2	126089.5		
260.2522	1	699542		

Formula Calculator Element Limits

Element	Min	Max
C	6	26
H	26	46
P	1	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C16 H36 P	TRUE	259.25421	259.25546	4.83	C16 H36 P	259.25491

--- End Of Report ---

Figure S12B: Anion MS for [P_{4444}][*p*-MOBSA].

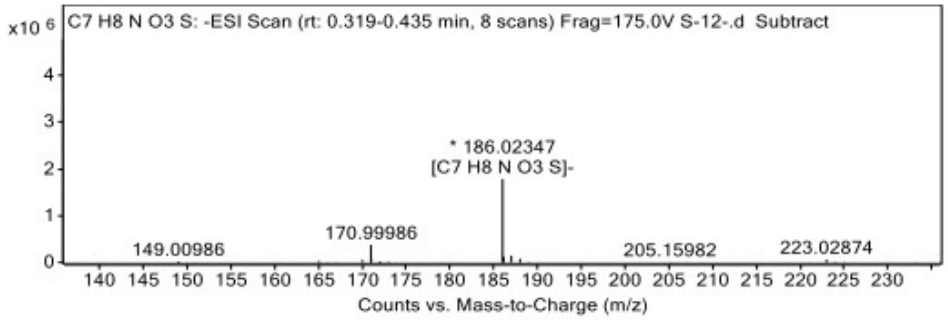
Qualitative Analysis Report

Data Filename	S-12-.d	**Sample Name**	S-12
Sample Type	Sample	**Position**	Vial 74
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/21/2024 5:45:49 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 5:45:49 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
107.03745	1	272316.06		
170.99986	1	376046.59		
186.02347	1	1785103.38	C7 H8 N O3 S	M-
187.02633	1	144745.45	C7 H8 N O3 S	M-
631.29989	1	129946.1		

Formula Calculator Element Limits

Element	Min	Max
C	5	9
H	6	10
N	0	2
O	2	4
S	1	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	Calculated Mz
C7 H8 N O3 S	TRUE	186.02292	186.02249	-2.32	C7 H8 N O3 S	186.02304

--- End Of Report ---

Figure S13A: Anion MS for [P_{4444}][BSA].

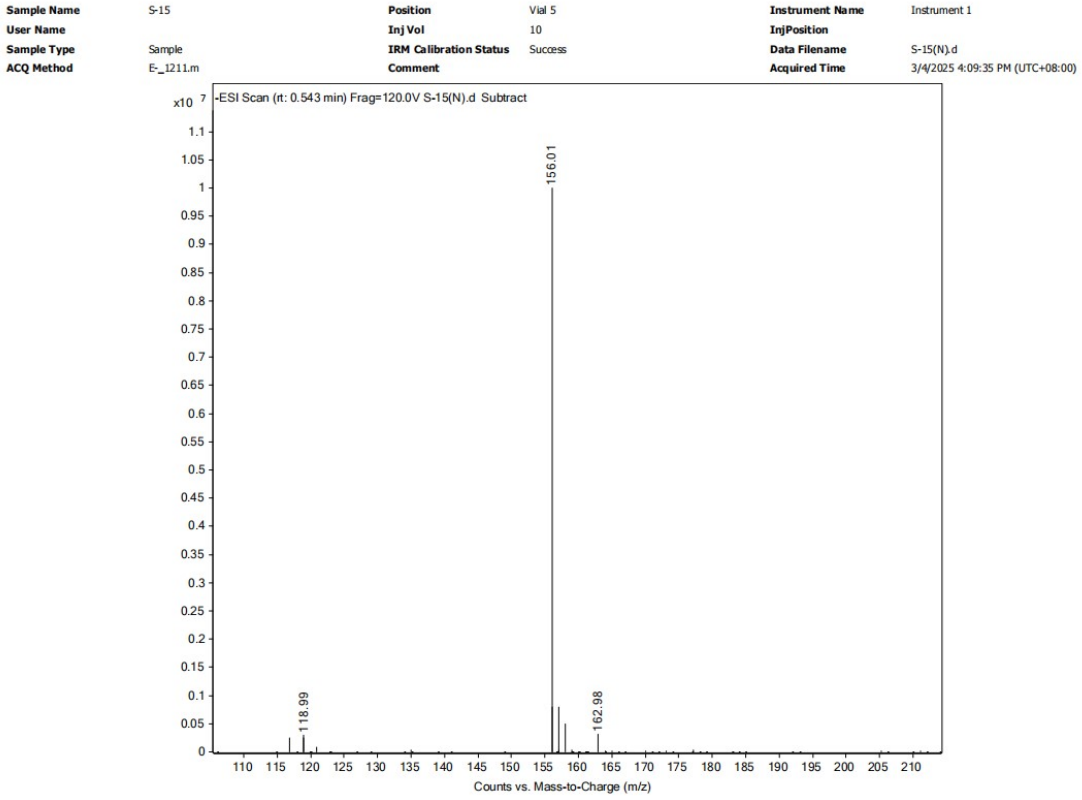


Figure S13B: Cation MS for [P_{4444}][BSA].

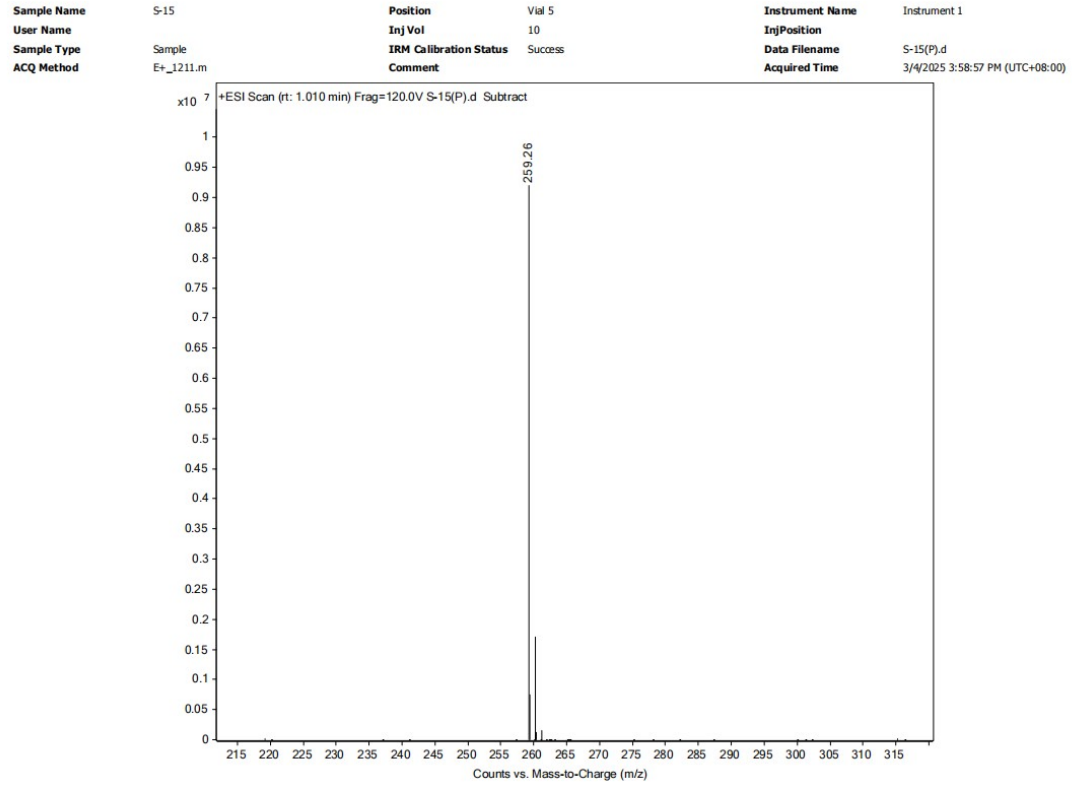


Figure S14A: Anion MS for [P_{4444}][*p*-CBSA].

Qualitative Analysis Report

Data Filename	S-13-.d	**Sample Name**	S-13
Sample Type	Sample	**Position**	Vial 75
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/21/2024 5:48:38 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 5:48:38 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

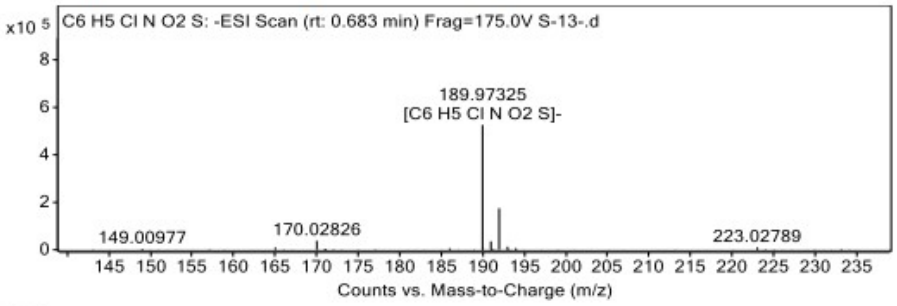


Figure S14B: Cation MS for [P_{4444}][*p*-CBSA].

Qualitative Analysis Report

Data Filename	S-13.d	**Sample Name**	S-13
Sample Type	Sample	**Position**	Vial 75
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/21/2024 3:58:09 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 3:58:09 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

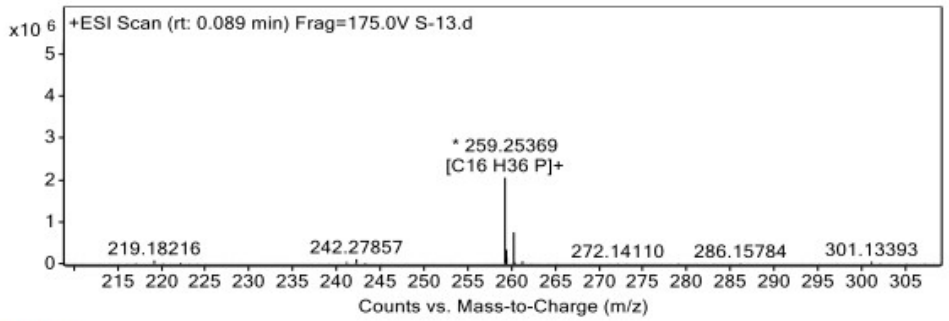


Figure S15A: Anion MS for [P_{4444}][*p*-ABSA].

Qualitative Analysis Report

Data Filename	S-11-.d	**Sample Name**	S-11
Sample Type	Sample	**Position**	Vial 73
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/22/2024 11:21:45 AM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/22/2024 11:21:45 AM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

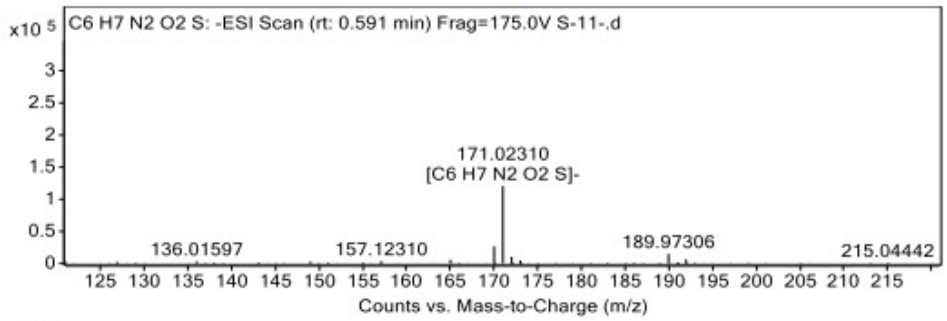


Figure S15B: Cation MS for [P_{4444}][*p*-ABSA].

Qualitative Analysis Report

Data Filename	S-11.d	**Sample Name**	S-11
Sample Type	Sample	**Position**	Vial 73
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/22/2024 11:33:00 AM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/22/2024 11:33:00 AM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI

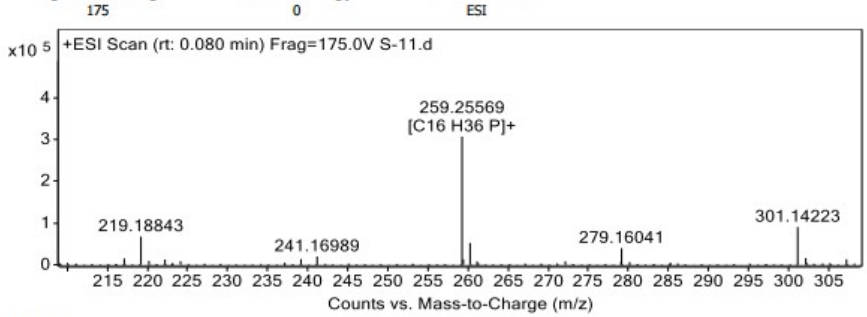


Figure S16A: Anion MS for [P_{4444}][*o*-NBSA].

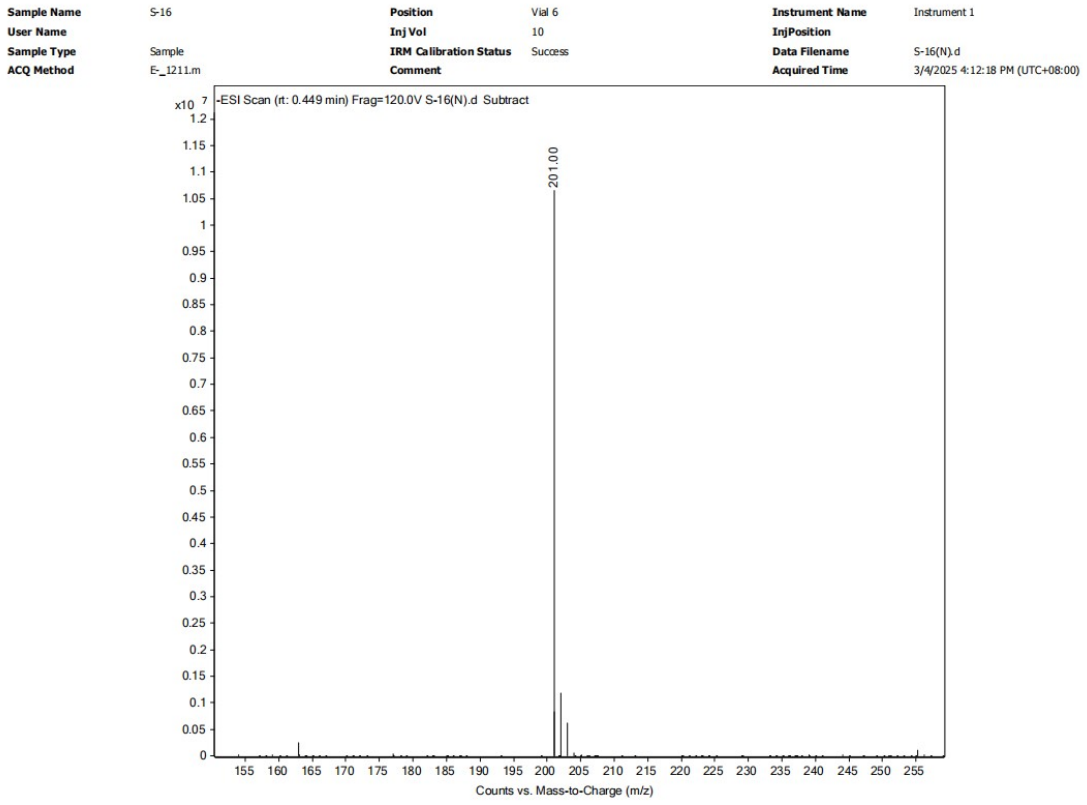


Figure S16B: Cation MS for [P_{4444}][*o*-NBSA].

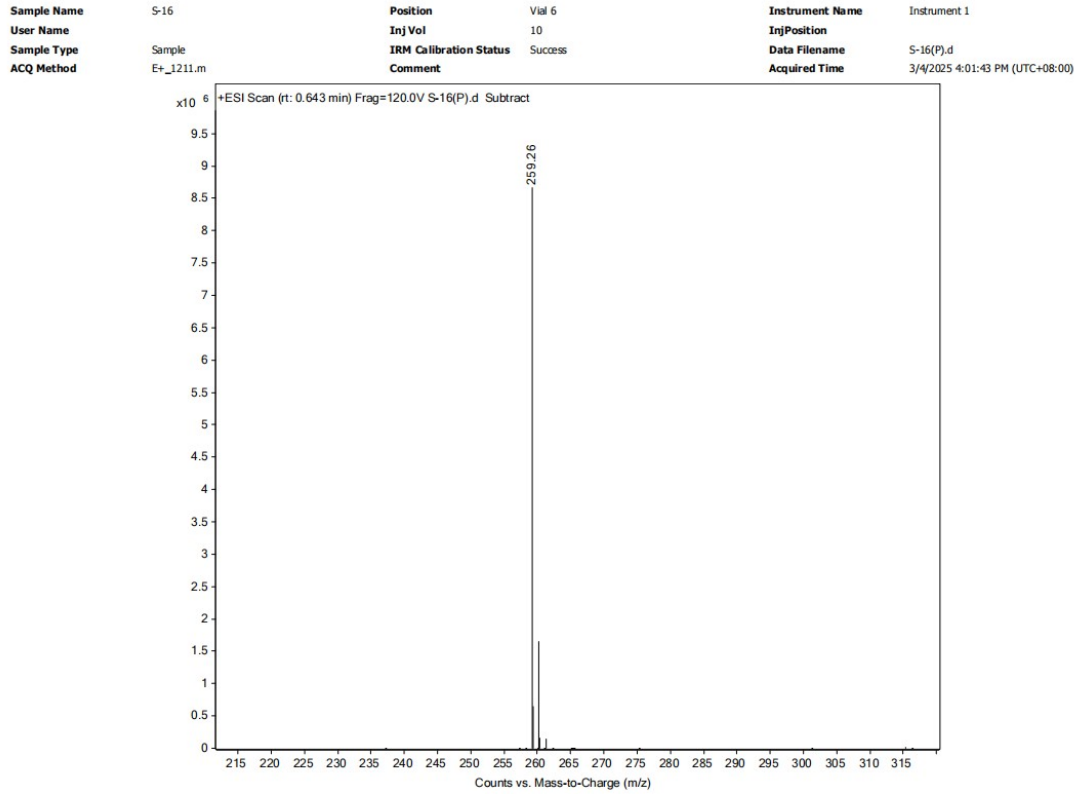


Figure S17A: Cation MS for [N_{4444}][*p*-MBSA].

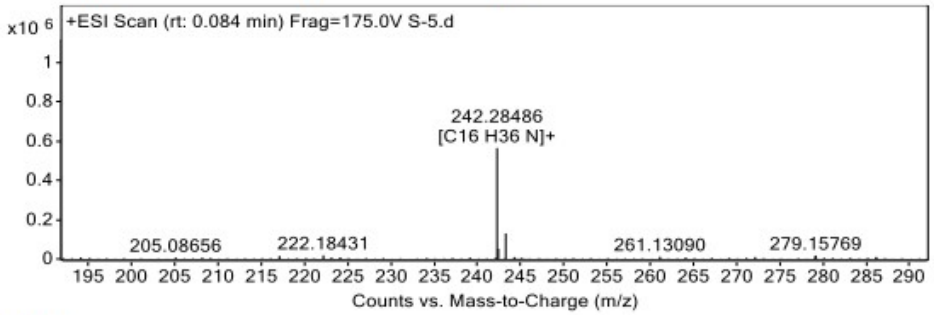
Qualitative Analysis Report

Data Filename	S-5.d	**Sample Name**	S-5
Sample Type	Sample	**Position**	Vial 71
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/21/2024 3:46:50 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group Info.			
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 3:46:50 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
130.1592	1	66542.29		
242.28486	1	565513	C16 H36 N	M+
242.43182	2	52084.15		
243.28707	1	130511.56	C16 H36 N	M+
301.14013	1	116144.56		

Formula Calculator Element Limits

Element	Min	Max
C	6	26
H	26	46
N	0	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C16 H36 N	TRUE	242.28521	242.28478	-1.79	C16 H36 N	242.28423

--- End Of Report ---

Figure S17B: Anion MS for [$N_{4\,4\,4\,4}$][*p*-MBSA].

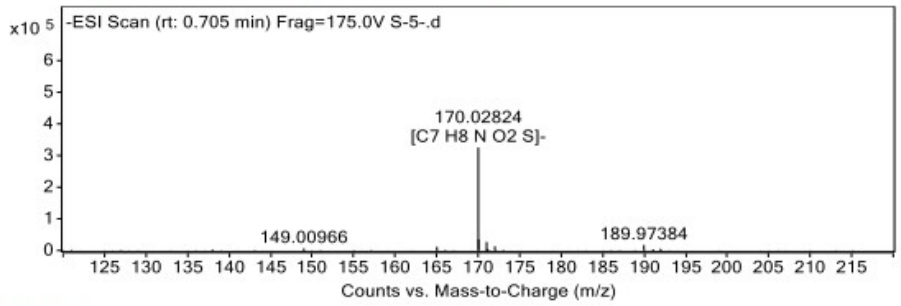
Qualitative Analysis Report

Data Filename	S-5-.d	**Sample Name**	S-5
Sample Type	Sample	**Position**	Vial 71
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/21/2024 5:37:18 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group Info.			
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 5:37:18 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
68.99625		64039.38		
170.02824	1	326483.31	C7 H8 N O2 S	M-
170.0685		35100.68		
392.30121	1	98982.31		
487.32067	1	82637.14		

Formula Calculator Element Limits

Element	Min	Max
C	5	9
H	6	10
N	0	2
O	1	3
S	1	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C7 H8 N O2 S	TRUE	170.02774	170.02757	-0.98	C7 H8 N O2 S	170.02812

--- End Of Report ---

Figure S18A: Cation MS for [$N_{1\,1\,1}C_2OH$] [*p*-MBSA].

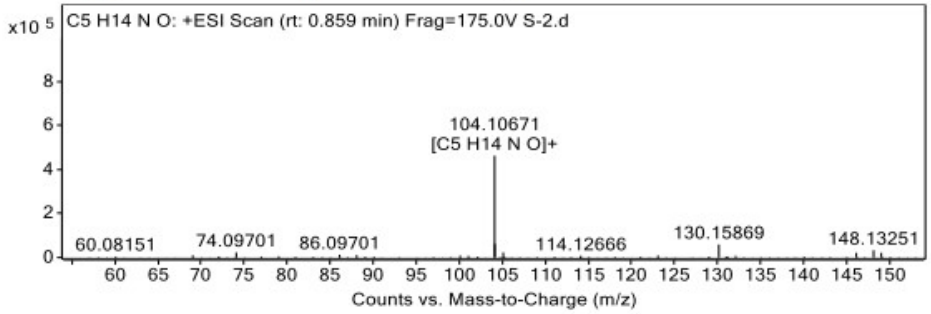
Qualitative Analysis Report

Data Filename	S-2.d	**Sample Name**	S-2
Sample Type	Sample	**Position**	Vial 69
Instrument Name	Instrument 1	**User Name**	
Acq Method	E+.m	**Acquired Time**	7/21/2024 3:41:12 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group Info.			
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 3:41:12 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
104.10671	1	463126.78	C5 H14 N O	M+
104.1286		62307.75		
130.15869	1	59163.77		
148.13251	1	32875.5		
301.13887	1	99087.33		

Formula Calculator Element Limits

Element	Min	Max
C	2	8
H	4	24
N	0	2
O	0	2

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C5 H14 N O	TRUE	104.10727	104.10754	2.62	C5 H14 N O	104.10699

--- End Of Report ---

Figure S18B: Anion MS for [$N_{1\,1\,1}C_2OH$] [*p*-MBSA].

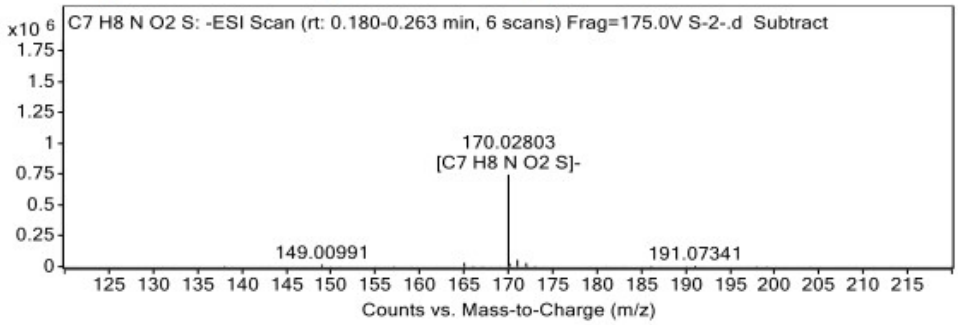
Qualitative Analysis Report

Data Filename	S-2-.d	**Sample Name**	S-2
Sample Type	Sample	**Position**	Vial 69
Instrument Name	Instrument 1	**User Name**	
Acq Method	E-.m	**Acquired Time**	7/21/2024 5:31:38 PM (UTC+08:00)
IRM Calibration Status	Success	**DA Method**	1.m
Comment			

Sample Group		**Info.**	
Stream Name	LC 1	**Acquisition Time (Local)**	7/21/2024 5:31:38 PM (UTC+08:00)
Acquisition SW Version	6200 series TOF/6500 series Q-TOF 10.1 (48.0)	**TOF Driver Version**	10.01.00
TOF Firmware Version	17.811	**Tune Mass Range Max.**	3200

Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
175	0	ESI



Peak List

m/z	z	Abund	Formula	Ion
170.02803	1	745039.25	C7 H8 N O2 S	M-
171.03118	1	56029.41	C7 H8 N O2 S	M-
223.02851	1	61838.25		
255.23272	1	138577.88		
283.26385	1	82473.28		

Formula Calculator Element Limits

Element	Min	Max
C	5	9
H	6	10
N	0	2
O	1	3
S	1	1

Formula Calculator Results

Formula	Best	Mass	Tgt Mass	Diff (ppm)	Ion Species	CalculatedMz
C7 H8 N O2 S	TRUE	170.02751	170.02757	0.36	C7 H8 N O2 S	170.02812

--- End Of Report ---

6. NMR spectroscopy for cyclic carbonates

Figure S19: ^{1}H NMR spectra of **4-(chloromethyl)-1,3-dioxolan-2-one**.

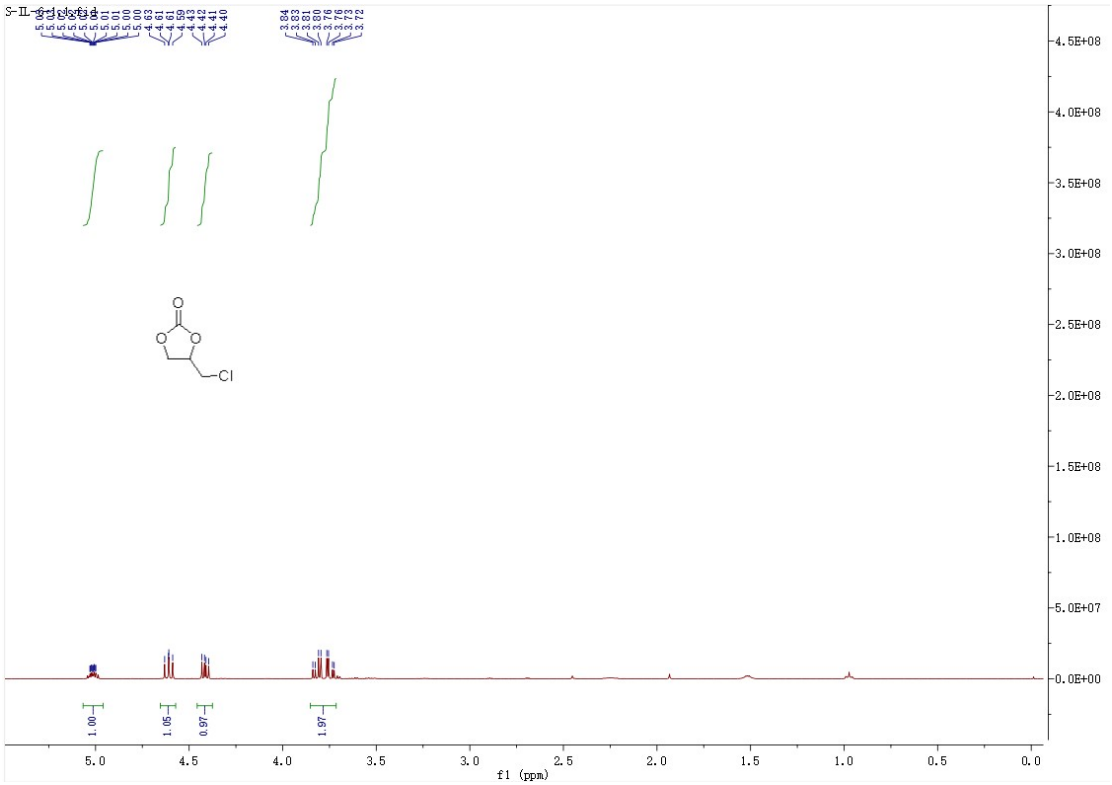


Figure S20: ^{1}H NMR spectra of **4-(bromomethyl)-1,3-dioxolan-2-one**.

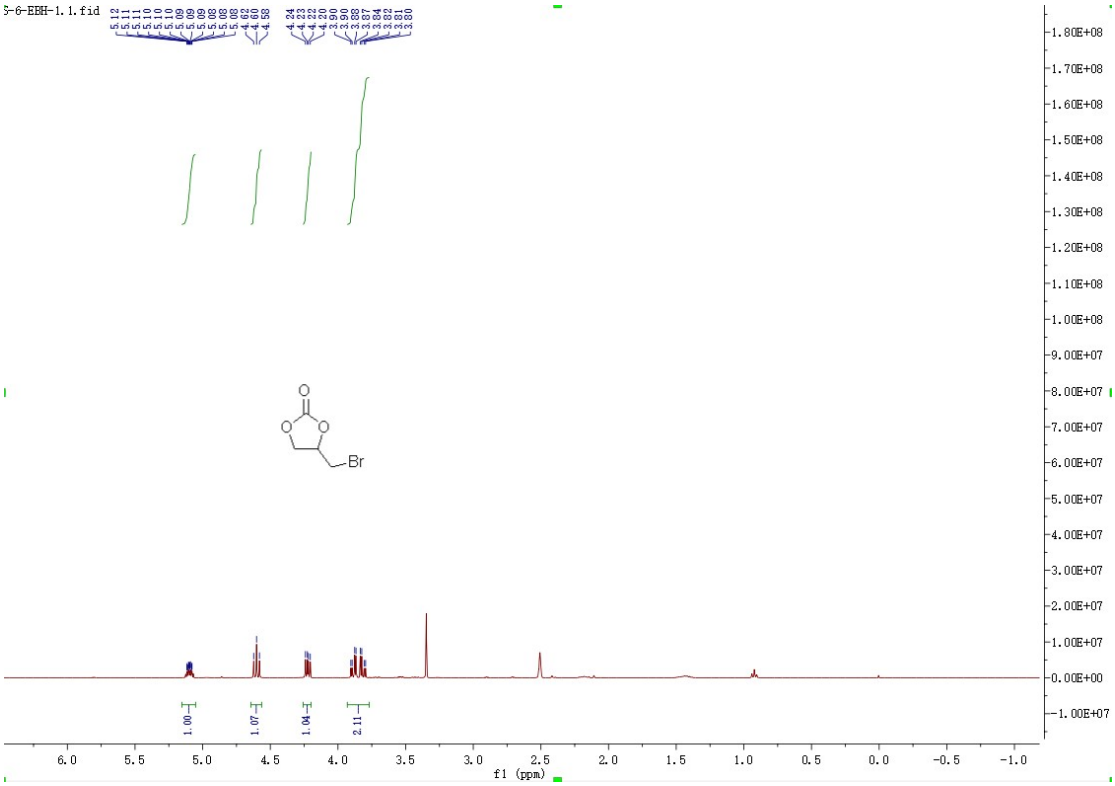


Figure S21: ^{1}H NMR spectra of **4-(phenoxymethyl)-1,3-dioxolan-2-one**.

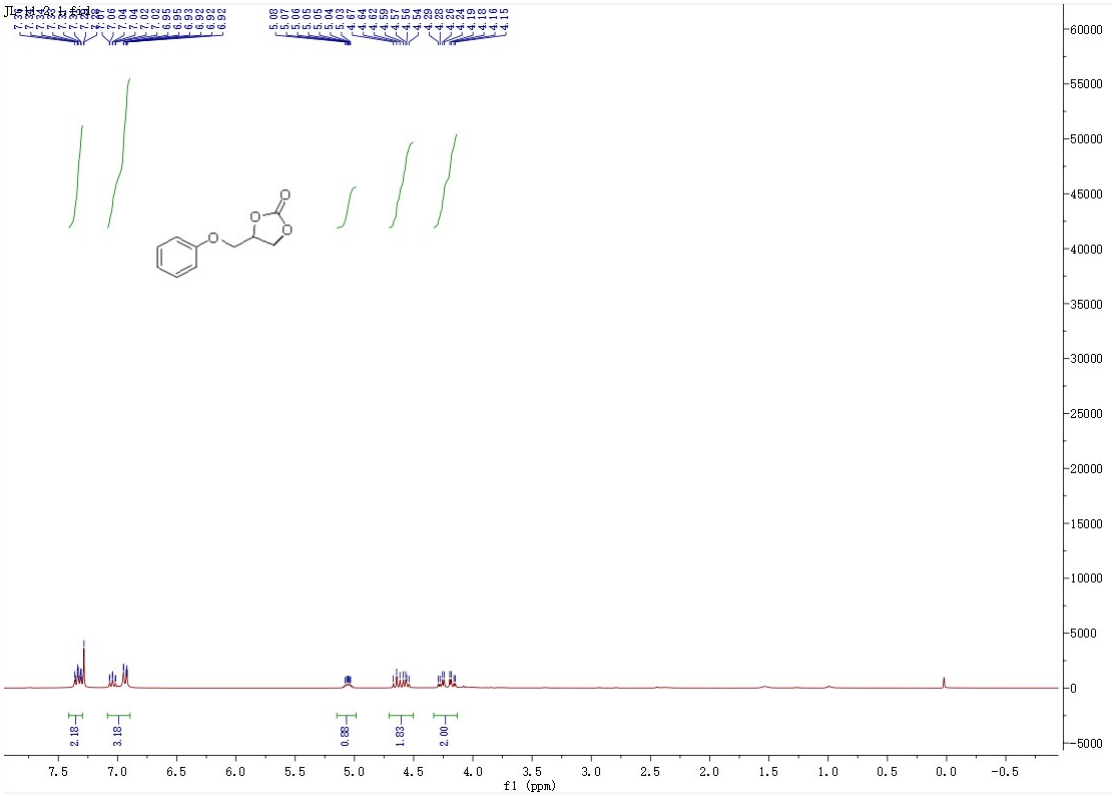


Figure S22: ^{1}H NMR spectra of **4-(benzyloxymethyl)-1,3-dioxolan-2-one**.

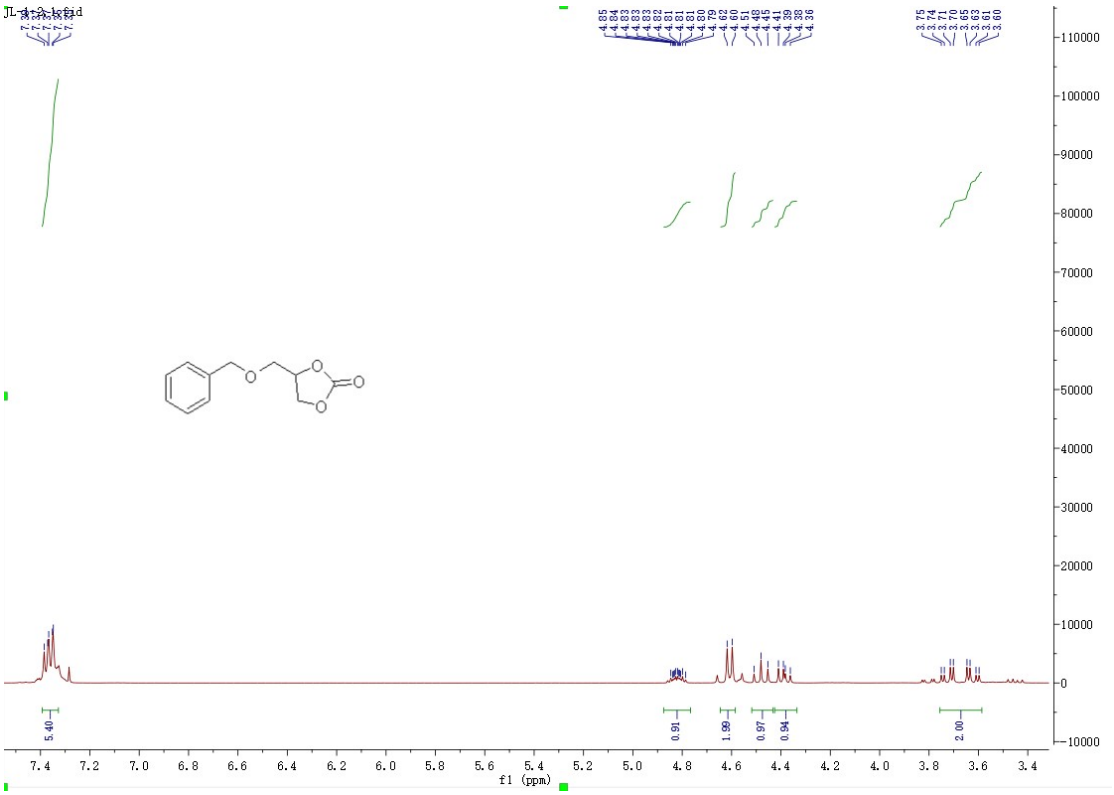
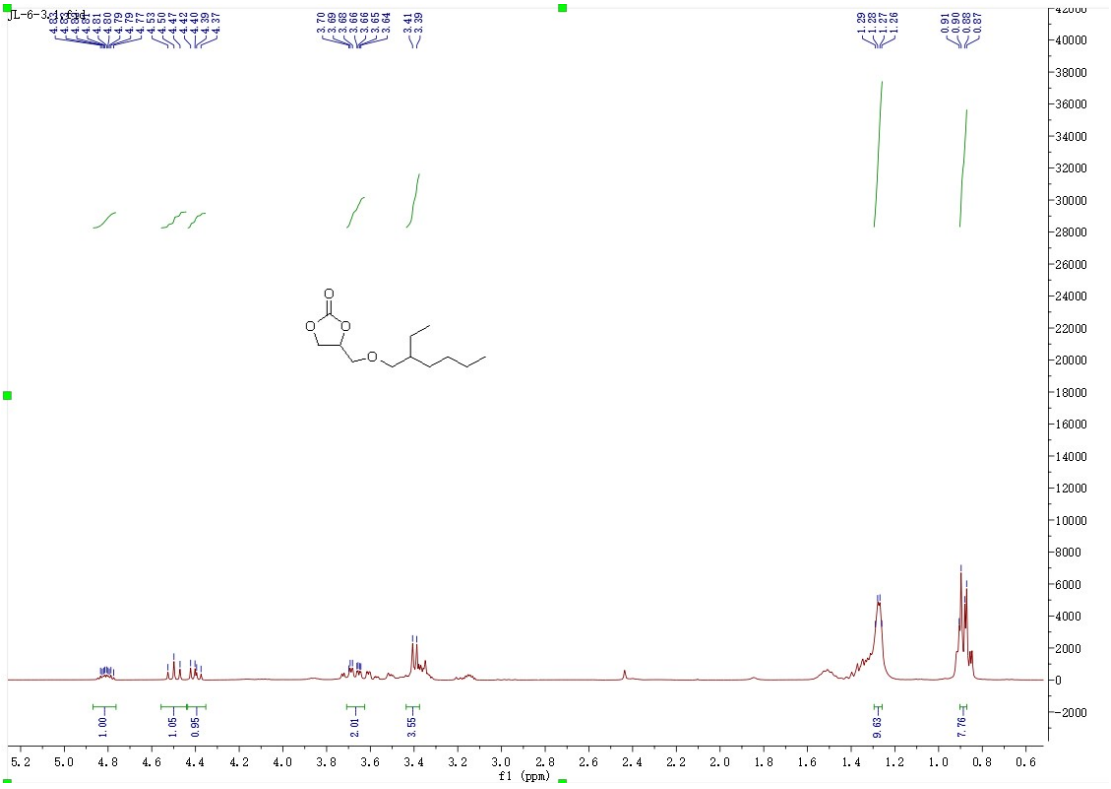
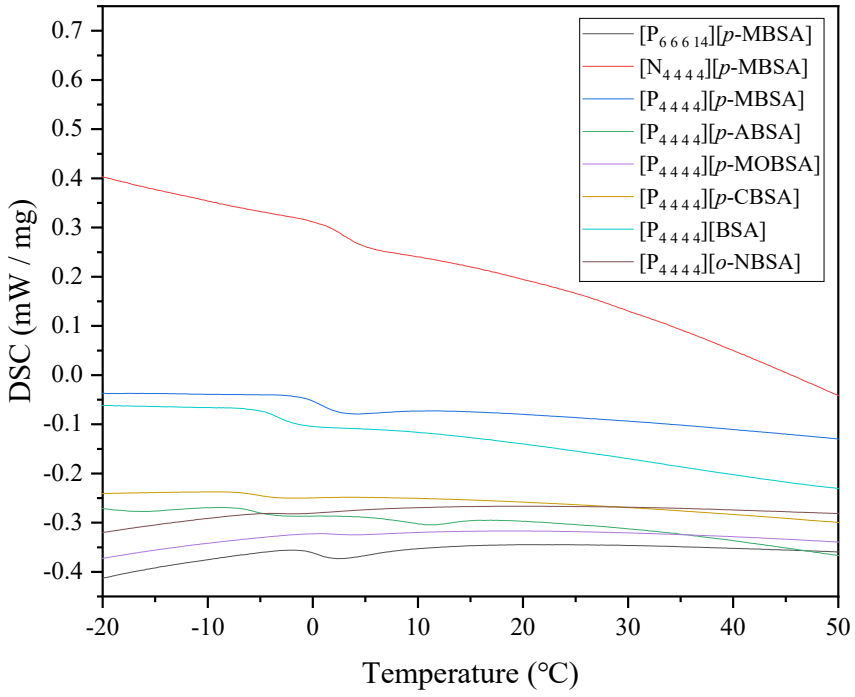


Figure S23: ^{1}H NMR spectra of **4-(octyloxymethyl)-1,3-dioxolan-2-one**.



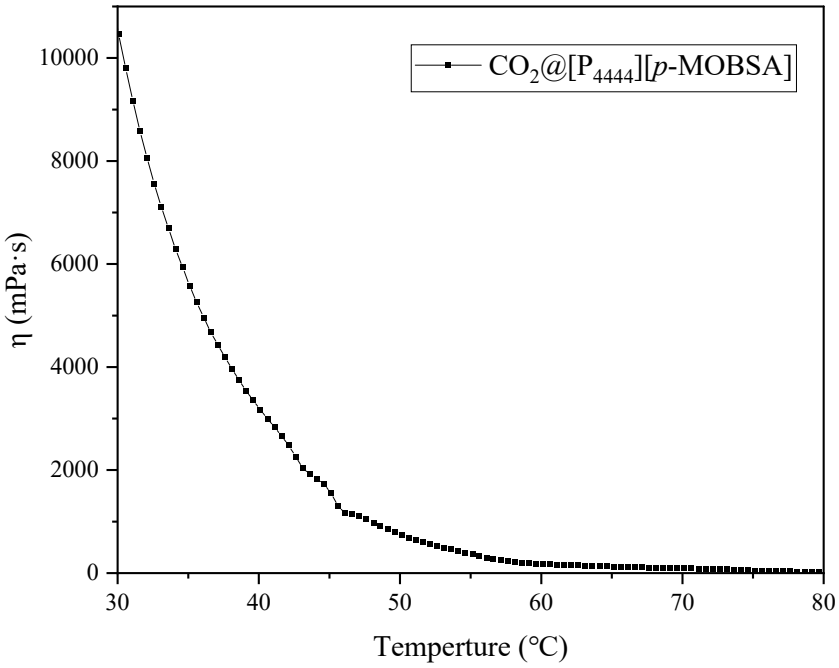
7. DSC of BSA-ILs

Figure S24



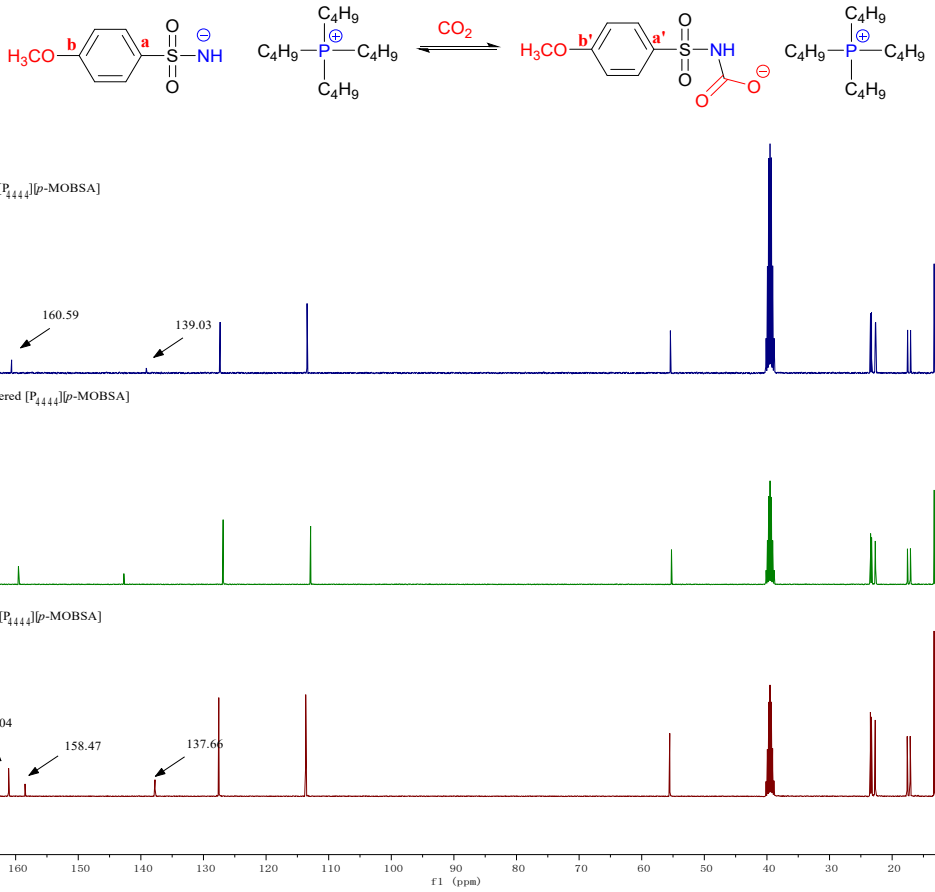
8. Viscosities of the CO_2@[P_{4444}][p-MOBSA]

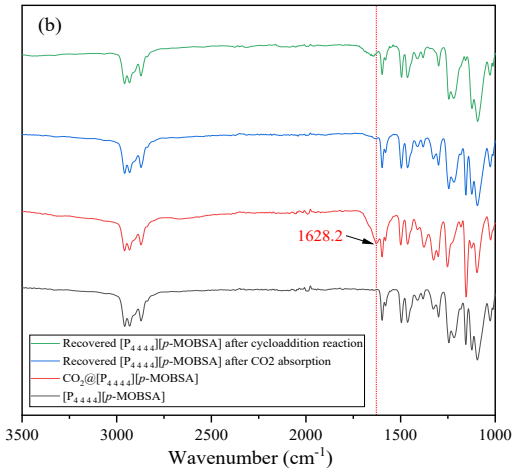
Figure S25 Viscosities of the CO_2@[P_{4444}][*p*-MOBSA]

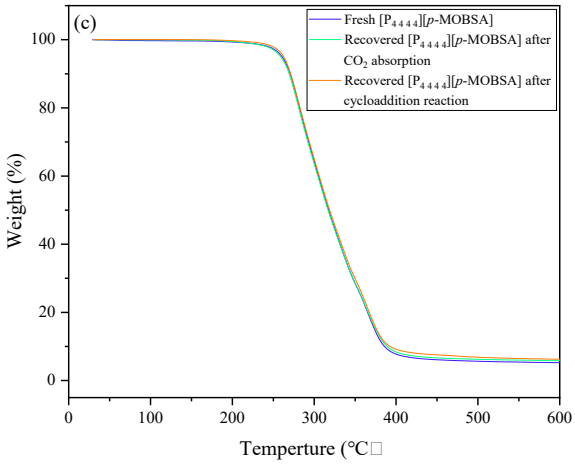


9. Mechanism of CO_2 absorption

Figure S26 (a) Stacked partial ^{13}C NMR spectra (400 MHz, DMSO-*d6*) of fresh (top), recovered [$P_{4\,4\,4\,4}$] [*p*-MOBSA] (middle) and after CO_2 absorption (bottom); (b) Stacked partial FT-IR spectra of fresh (black), after CO_2 absorption (red), recovered after CO_2 absorption (blue) and recovered after cycloaddition reaction of [$P_{4\,4\,4\,4}$] [*p*-MOBSA] (green). (c) Thermal stability of fresh (blue), recovered after CO_2 absorption (light green) and recovered after cycloaddition reaction of [$P_{4\,4\,4\,4}$] [*p*-MOBSA].







10. Recyclability of CO_2 conversion and calculation of E-factor

Figure S27 ^1H NMR of all cycles.

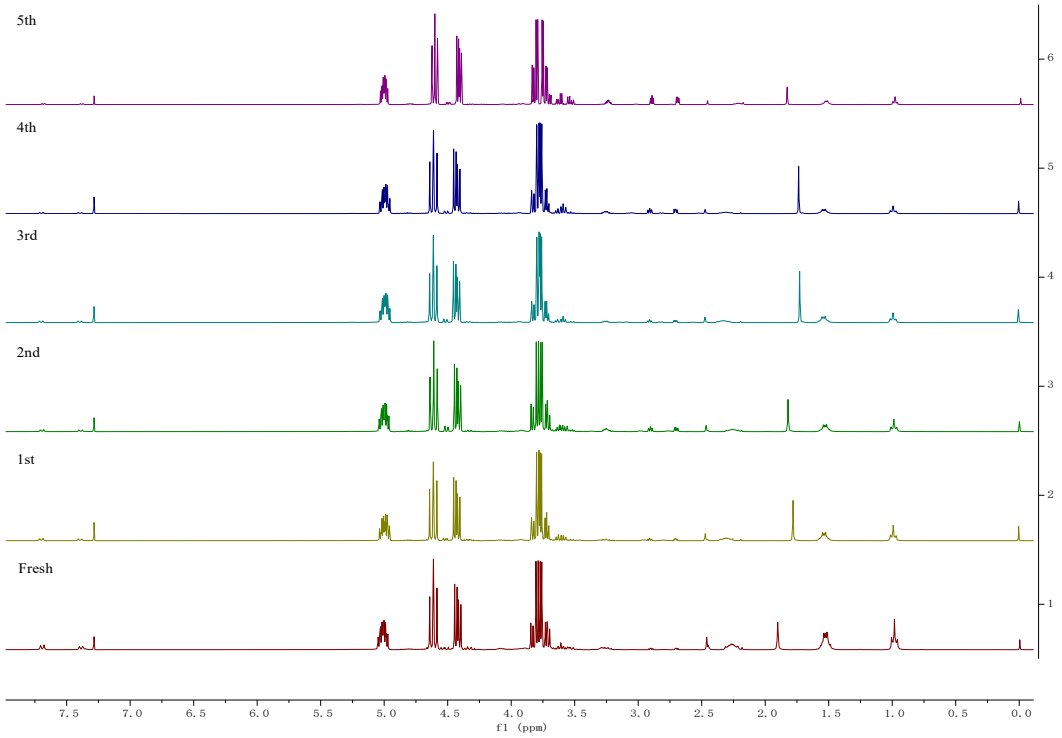


Figure S28 ^{1}H NMR of the 5th cycles.

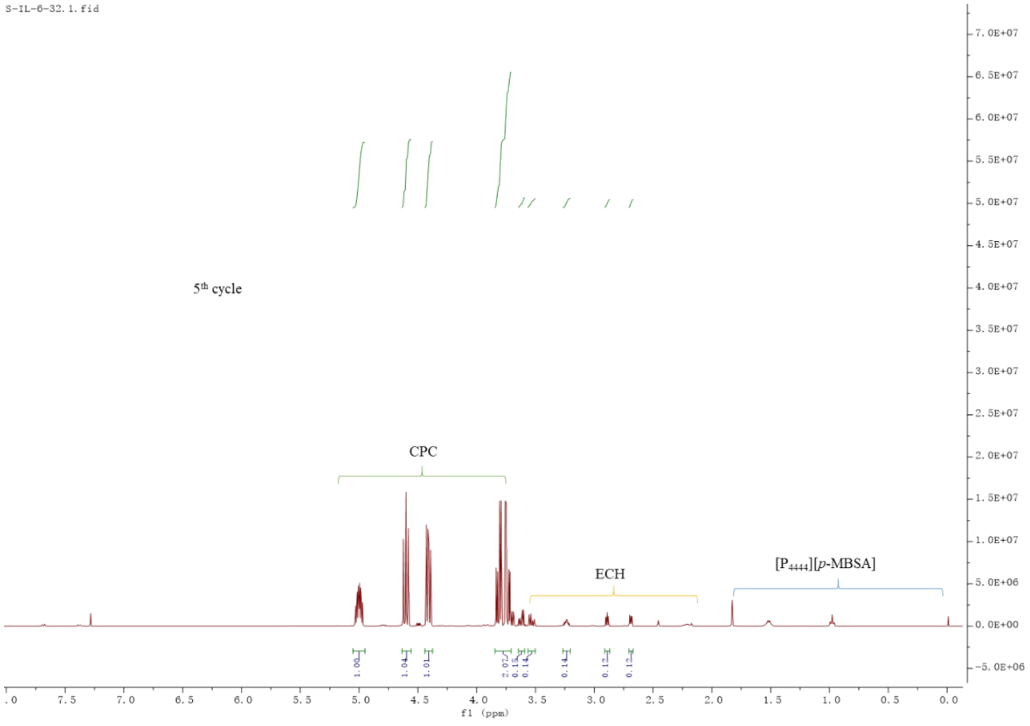


Table S2

Materials requirements and ECH residue for the cycloaddition reaction [a].

Material	Amount/mmol	Cycle [b]	ECH residue /% [c]
ECH	10	fresh	2.14
ECH	10	1	3.46

ECH	10	2	6.51
ECH	10	3	3.82
ECH	10	4	7.10
ECH	10	5	10.71
$[P_{4444}][p$-MBSA]	0.2		

[a] Reaction conditions: Epichlorohydrin (10 mmol), [$P_{4\,4\,4\,4}$] [*p*-MBSA] (0.2 mmol, 85.93 mg), 3 h, atmospheric CO_2 pressure, solvent-free conditions; [b] After the first catalytic cycle, add another 10 mmol ECH to the reaction mixture directly without separation; [c] Residue was confirmed by ^{1}H NMR.

E-factor = mass of ECH residue + mass of BSA-IL/ total mass of cyclic carbonate = 60 mmol*10.71%*92 g/mol + 0.08593 g / 60 mmol*(1-10.71%)*136 g/mol = 0.11

Table S3

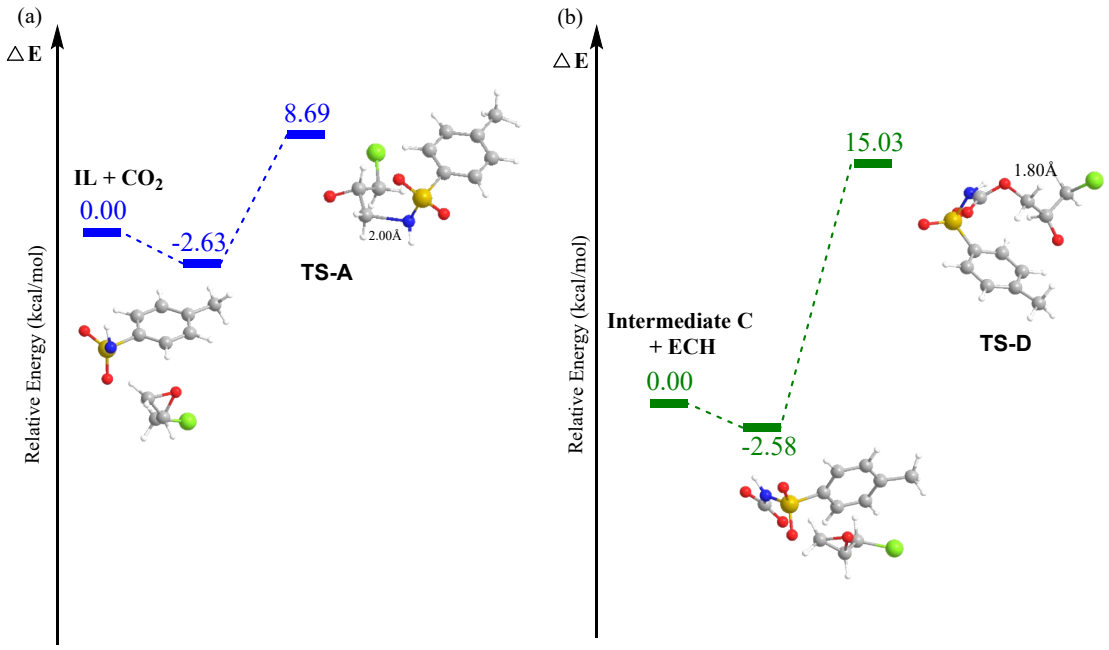
Large scale ECH conversion and CO_2 capture [a].

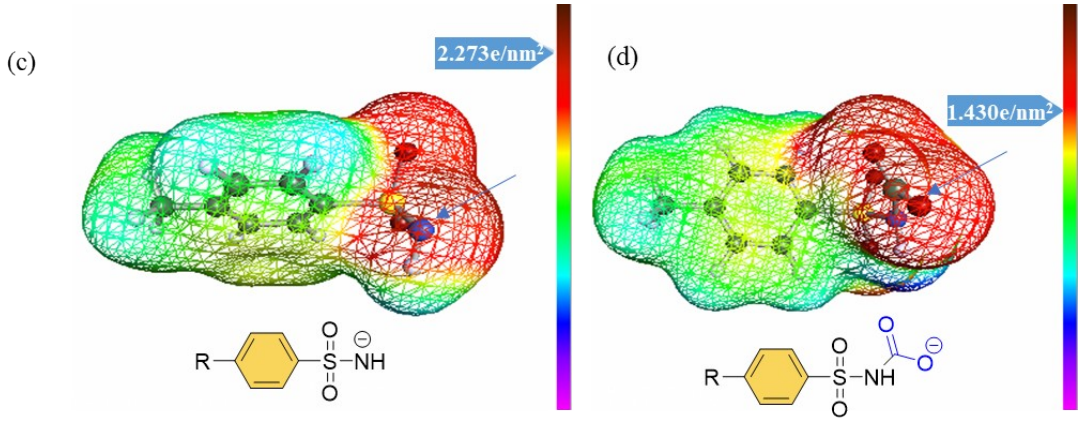
Amount/mmol	Cycle	Conversion /%	CO_2 capture mol/mol BSA-IL
60	fresh	95.2	/
			1.38

[a] Reaction conditions: Epichlorohydrin (60 mmol), [$P_{4\,4\,4\,4}$][*p*-MOBSA] (1.5 mmol, 668.5mg), atmospheric CO_2 pressure.

11. DFT calculations:

Figure S29 Calculated relative free energy diagrams for ECH-opening step initiated by [*p*-MBSA] anion (a) and [*p*-MBSA-CO_2] anion (b); Surface charge density of [*p*-MBSA] anion (c) and [*p*-MBSA-CO_2] anion (d).





12. Diagram for CO_2 absorption-desorption-conversion:

Figure S30 (1) CO_2 gas cylinder, (2) N_2 gas cylinder, (3) pressure relief valve, (4) pressure gauge, (5) gas flow meter, (6) gas drying and buffering device, (7) CO_2 capture and conversion apparatus, (8) thermostatic heating and stirring device, (9) residual gas absorption bottle (off-gas was absorbed by NaOH solution).