Supporting information

Protic ionic liquids tailored by different cationic structures for the efficient chemical fixation of diluted and waste CO_2 into cyclic carbonates

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[DBUH]Br: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 9.58 (s, 1H), 3.76-3.74 (d, 2H), 3.58-3.41 (m, 6H), 2.68-2.63 (d, 2H), 2.33-2.29 (m, 2H), 1.94-1.81 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C (ppm), 165.44, 53.53, 47.92, 39.64, 37.46, 31.57, 28.20, 25.84, 23.23, 18.84.

[AlDBU]Br: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 5.86-5.76 (m, 1H), 5.29-5.19 (m, 2H), 4.22-4.20 (d, 2H), 3.75-3.60 (m, 6H), 2.86-2.83 (d, 2H), 2.18-2.13 (m, 2H) 1.77 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C (ppm), 167.33, 130.53, 118.23, 56.06, 55.87, 49.60, 47.35, 29.23, 28.59, 26.15, 22.99, 20.34.

[DBUH]Cl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 10.45 (s, 1H), 3.92-3.90 (d, 2H), 3.81-3.69 (m, 6H), 2.82-2.77 (d, 2H), 2.47-2.44 (m, 2H), 1.83-1.72 (d, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C (ppm), 165.58, 53.50, 47.93, 39.54, 37.85, 31.71, 28.53, 25.82, 23.47, 18.86.

[MimH]Br: ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 8.74 (s, 1H), 7.51 (s, 2H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ_C (ppm) 135.87, 123.91, 119.71, 39.59, 35.58.

[TMGH]Br: ^{1}H NMR (400 MHz, D_2O): δ_H (ppm) 3.13 (s, 12H). ^{13}C NMR (101 MHz, D_2O): δ_C (ppm) 161.40, 39.10.

[AlTMG]Br: ^{1}H NMR (400 MHz, $CDCl_3$): 6.08-5.77 (m, 1H), 5.36-5.13 (m, 2H), 3.94-3.81 (m, 2H), 3.08 (d, 4H), 2.87 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C (ppm), 162.90, 161.79, 138.17, 135.89, 133.57, 129.22, 127.01, 115.07, 53.32, 41.20, 40.52, 40.28.

[4-VBTMG]Cl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 7.46 (d, 2H), 7.23 (d, 2H), 6.76-6.69 (q, 1H), 5.79 (d, 1H), 5.32 (d, 2H), 4.35 (d, 1H), 3.96 (d, 1H), 3.23 (s, 2H), 3.13 (s, 2H) 3.06 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$): δ_C (ppm), 162.90, 161.79, 138.17, 135.89, 133.52, 129.22, 127.01, 115.07, 53.32, 41.20, 40.52, 40.28.

[DABCOH]Br: ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 3.07 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6): δ_C (ppm) 44.10, 39.43.

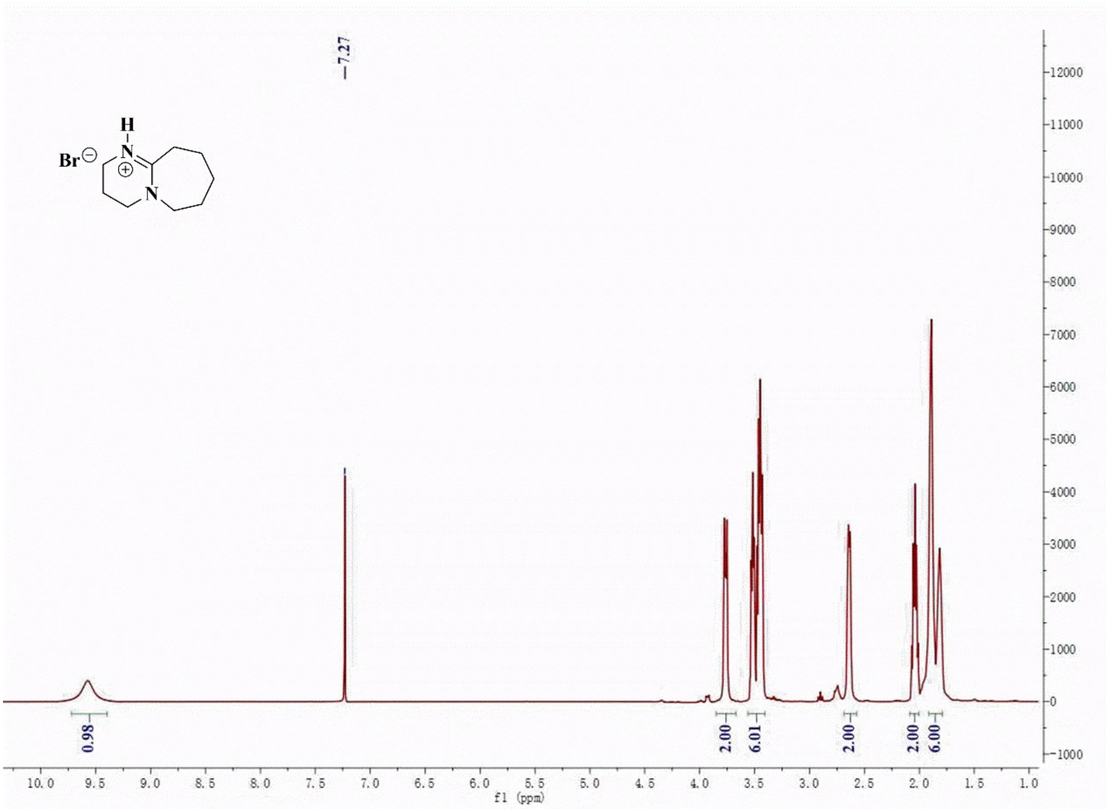

Figure S1. The ^{1}H NMR spectrum of [DBUH]Br.

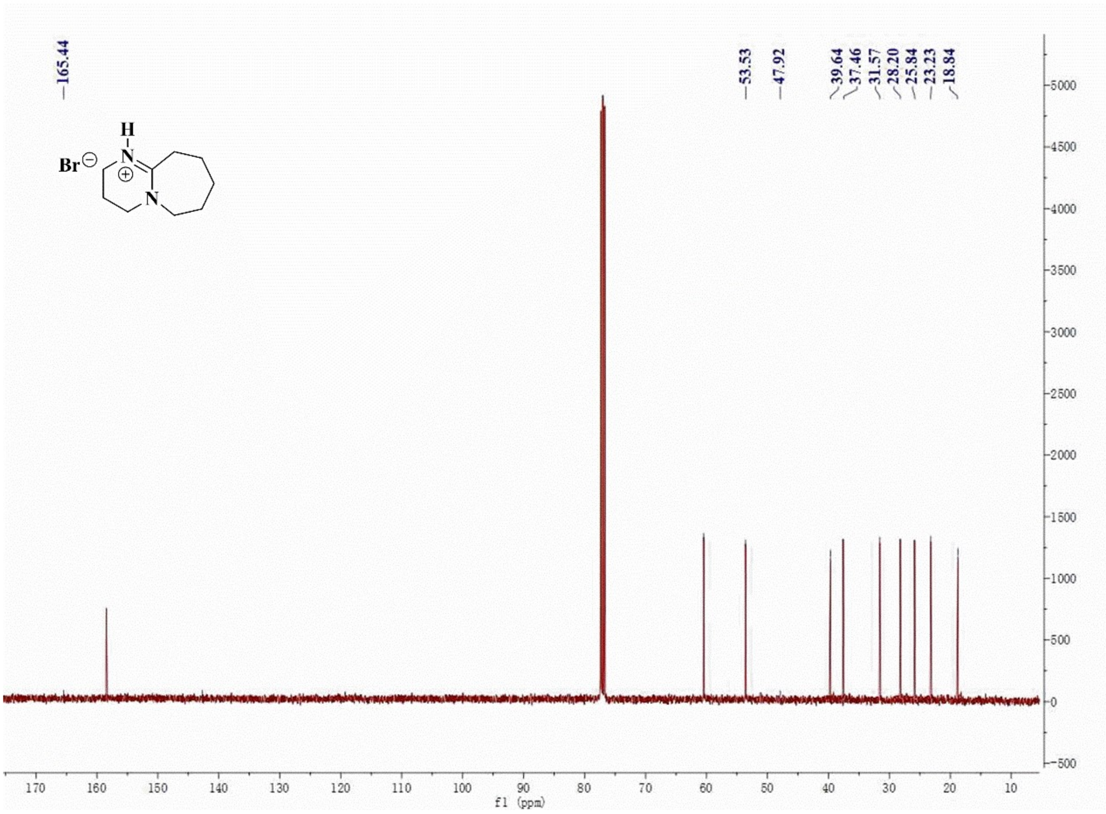

Figure S2. The ^{13}C NMR spectrum of [DBUH]Br.

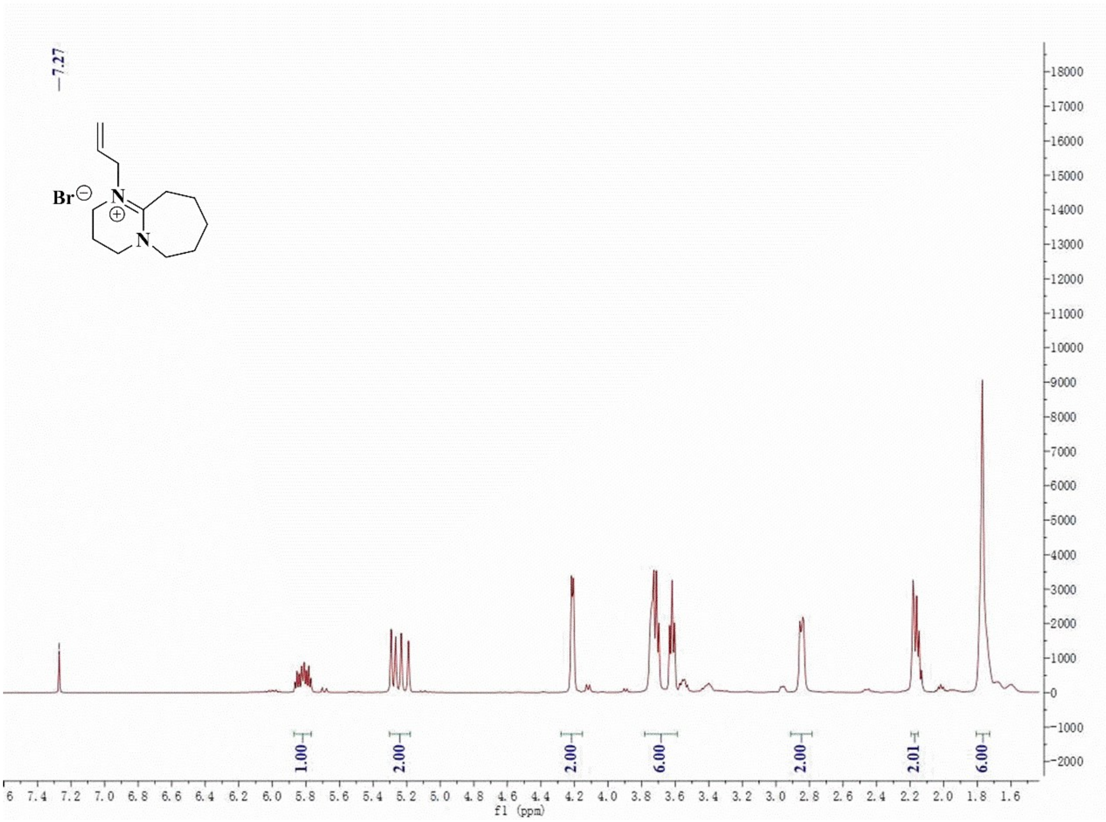

Figure S3. The ^{1}H NMR spectrum of [AlDBU]Br.

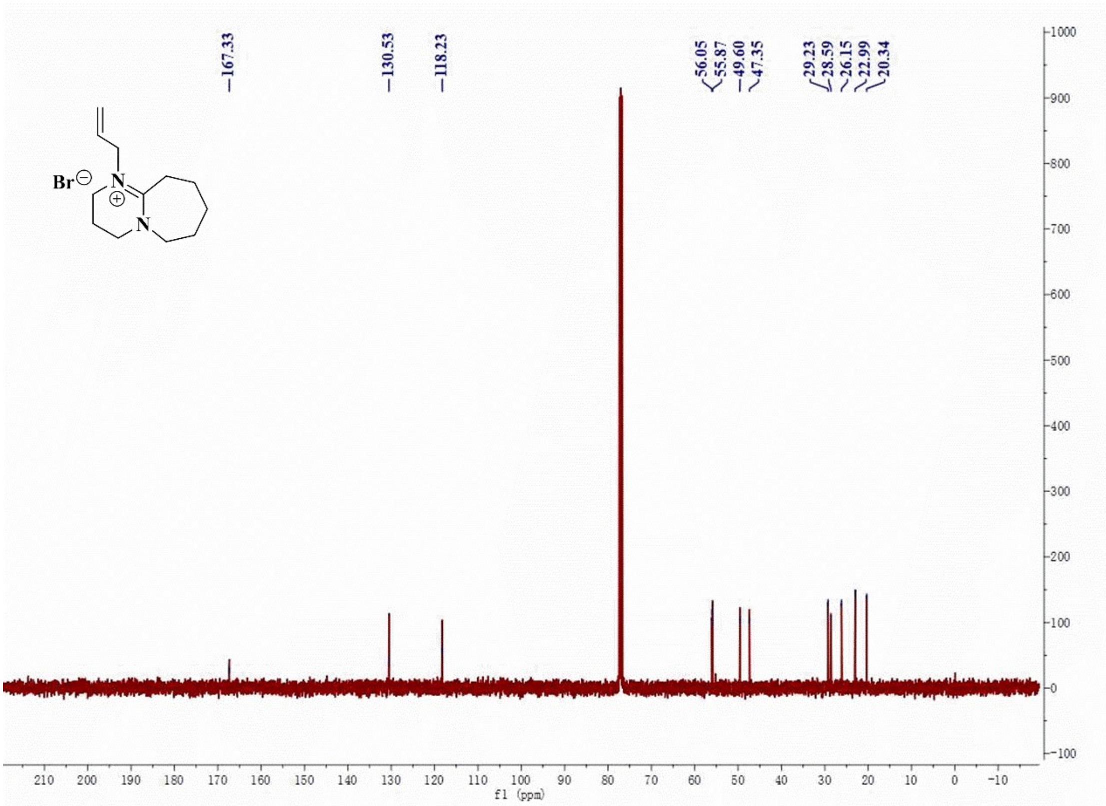

Figure S4. The ^{13}C NMR spectrum of [AlDBU]Br.

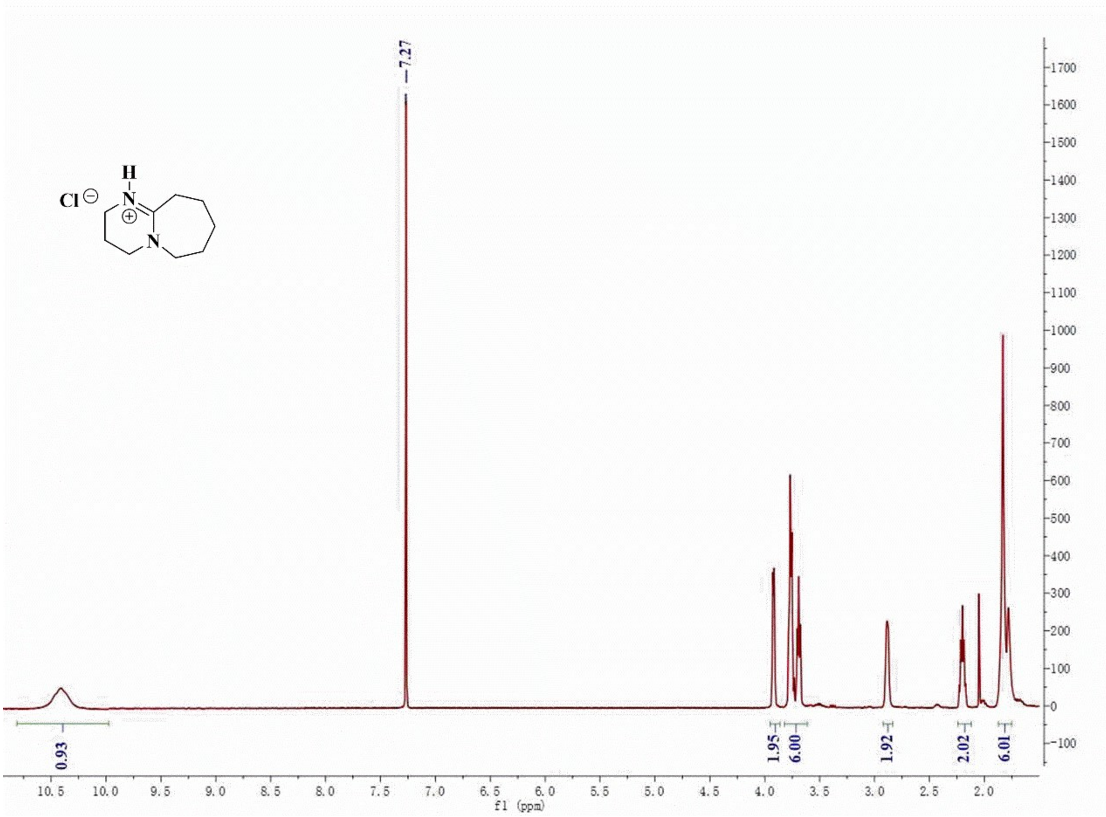

Figure S5. The ^{1}H NMR spectrum of [DBUH]Cl.

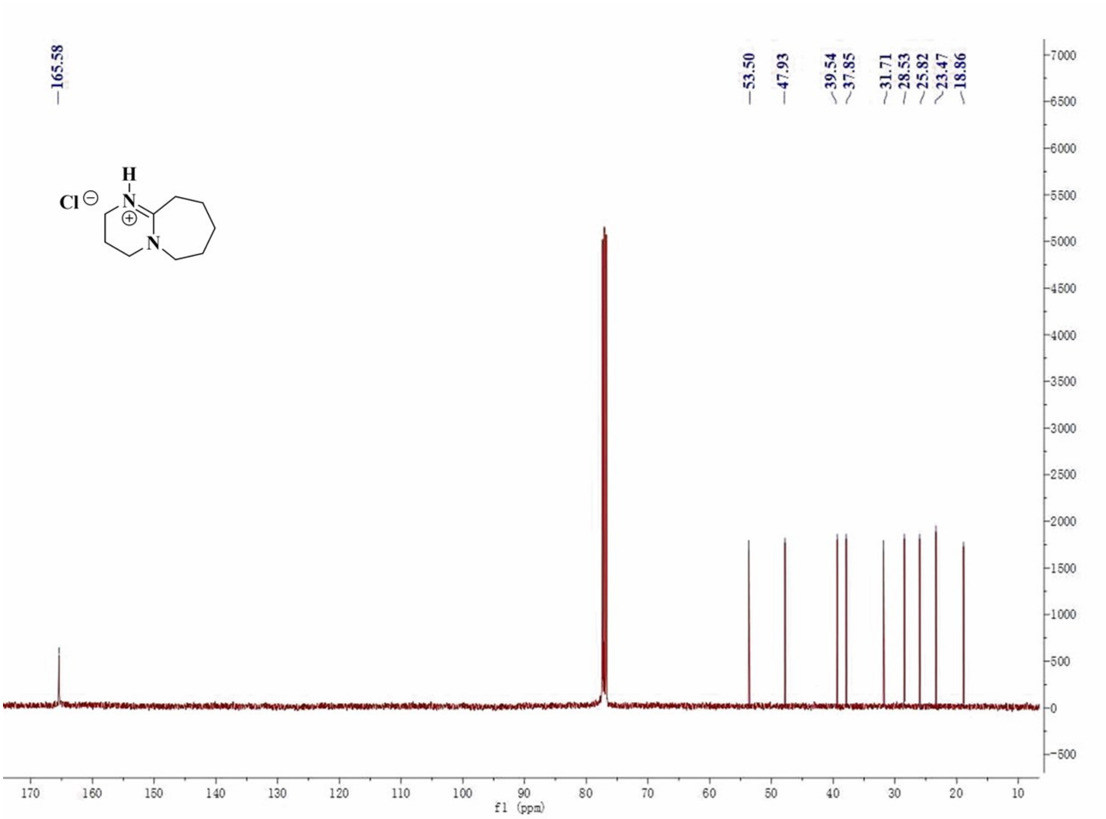

Figure S6. The ^{13}C NMR spectrum of [DBUH]Cl.

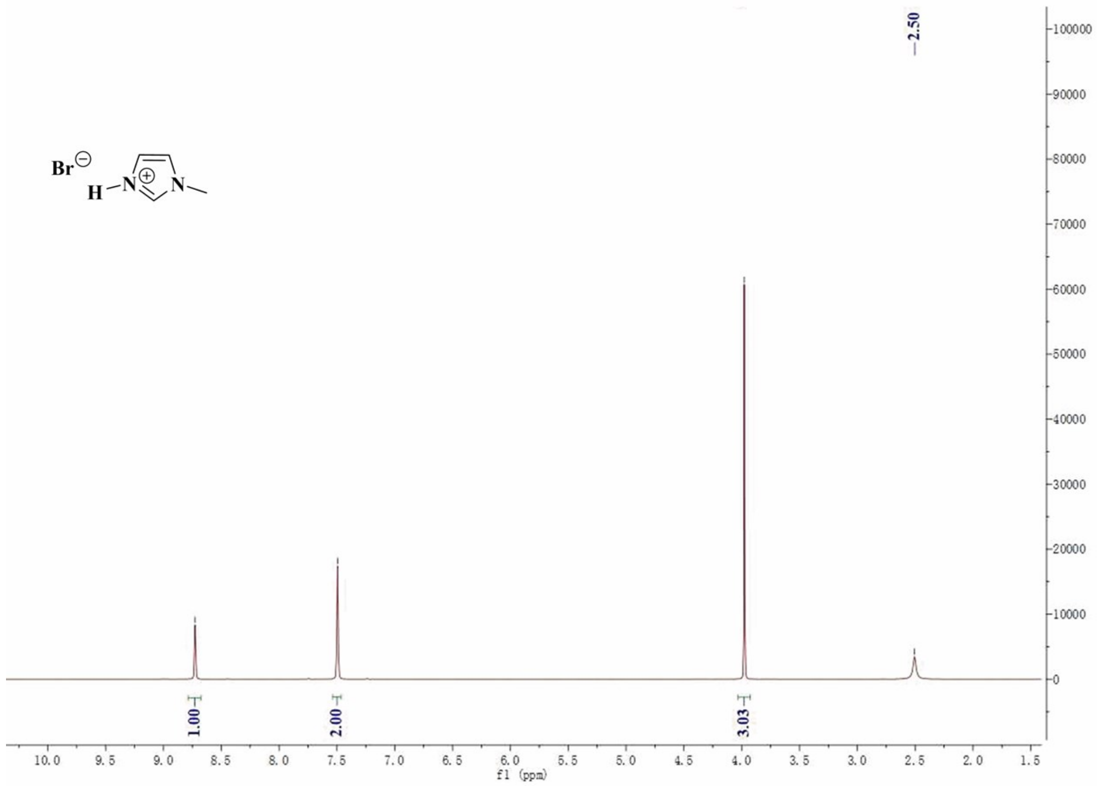

Figure S7. The ^{1}H NMR spectrum of [MimH]Br.

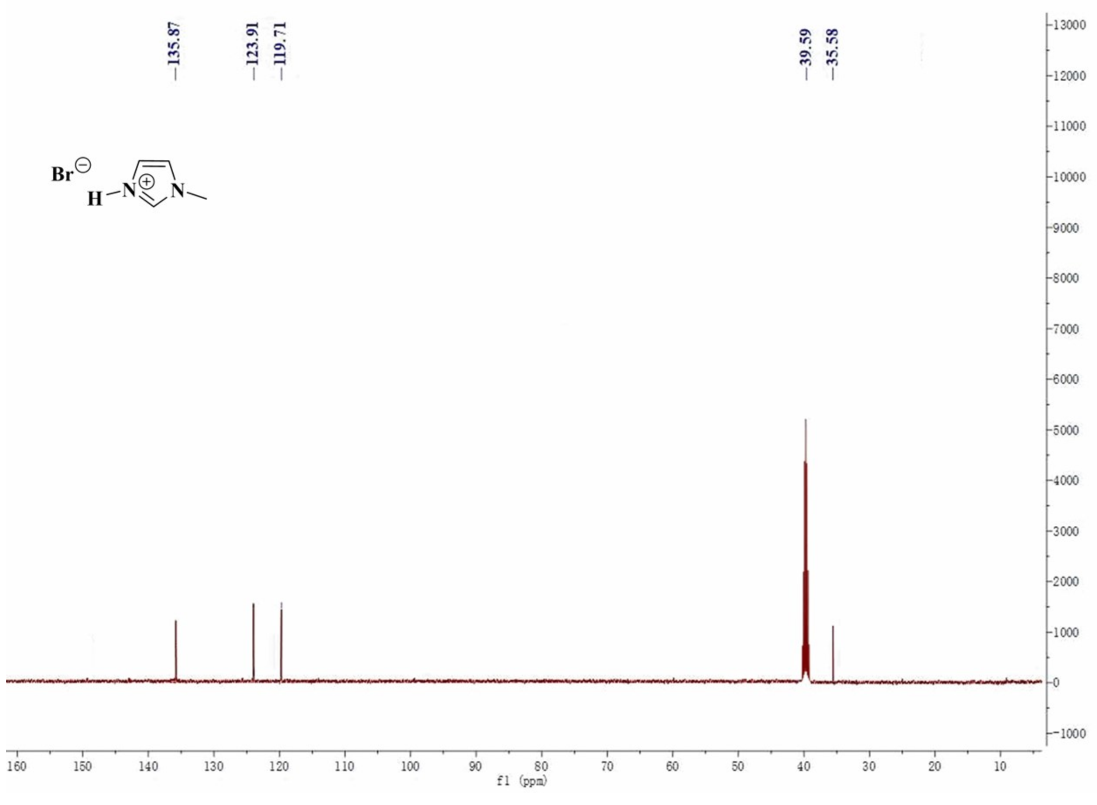

Figure S8. The ^{13}C NMR spectrum of [[MimH]Br.

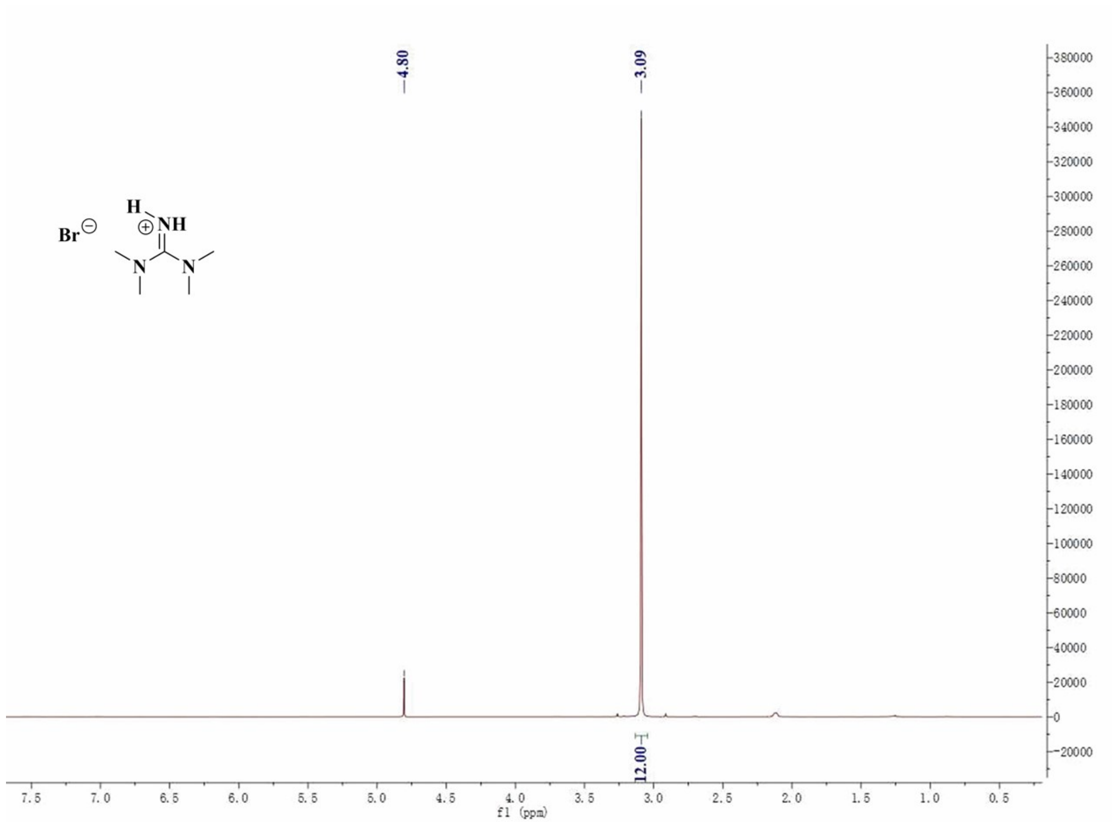

Figure S9. The ^{1}H NMR spectrum of [TMGH]Br.

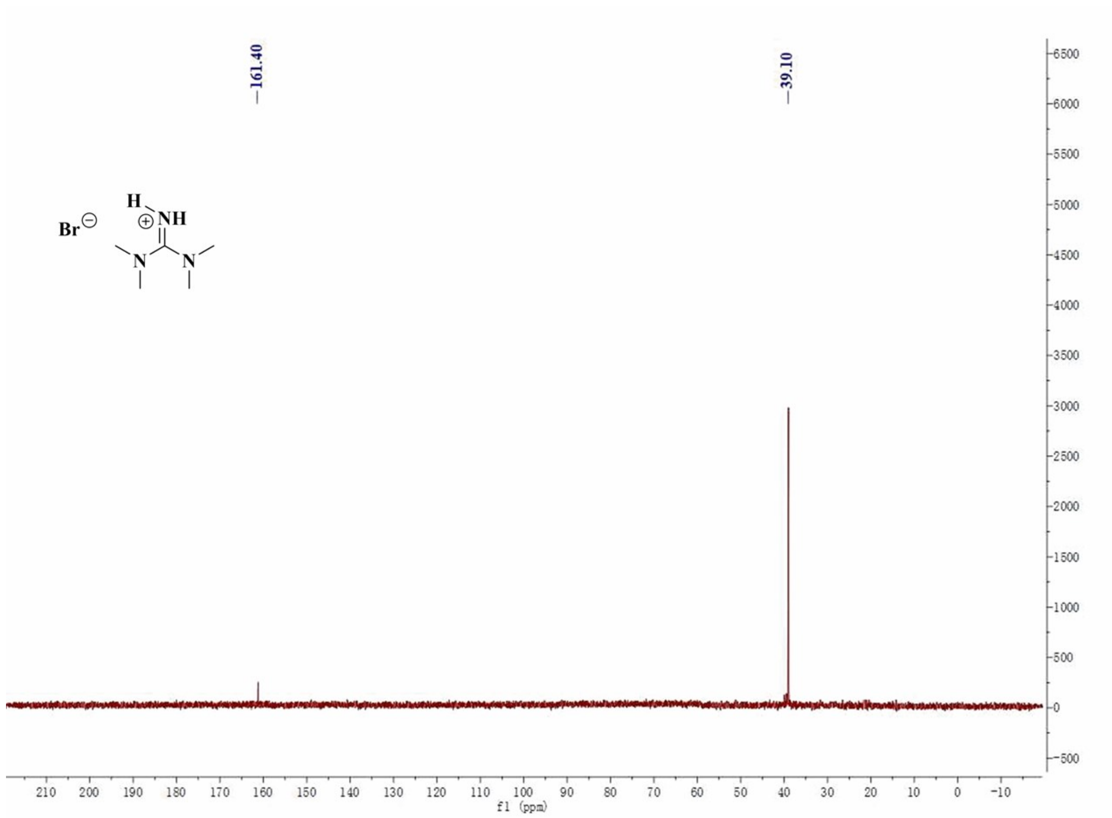

Figure S10. The ^{13}C NMR spectrum of [[TMGH]Br.

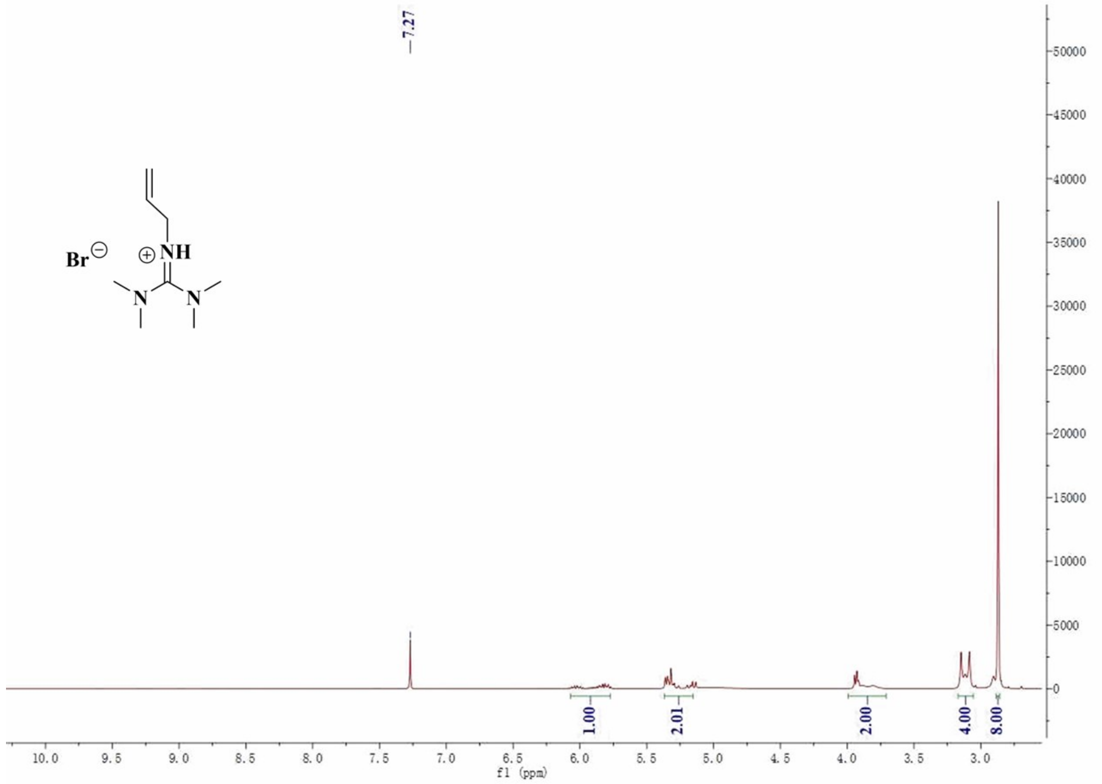

Figure S11. The ^{1}H NMR spectrum of[AlTMG]Br.

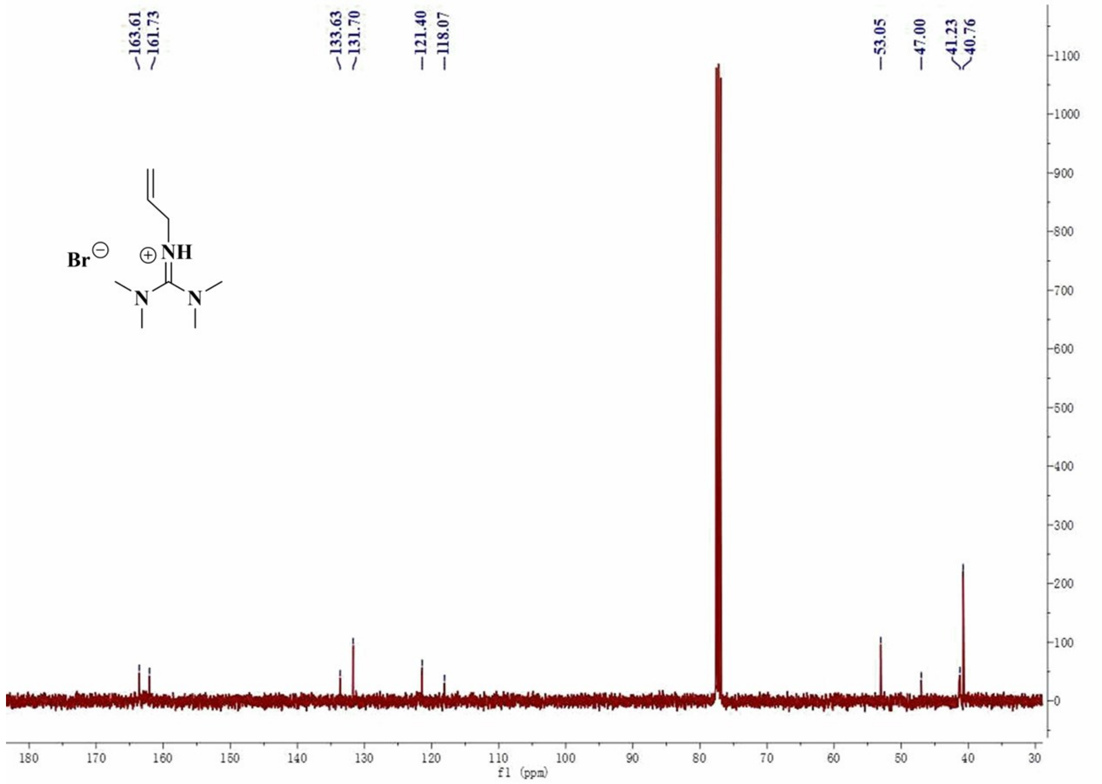

Figure S12. The ^{13}C NMR spectrum of [AlTMG]Br.

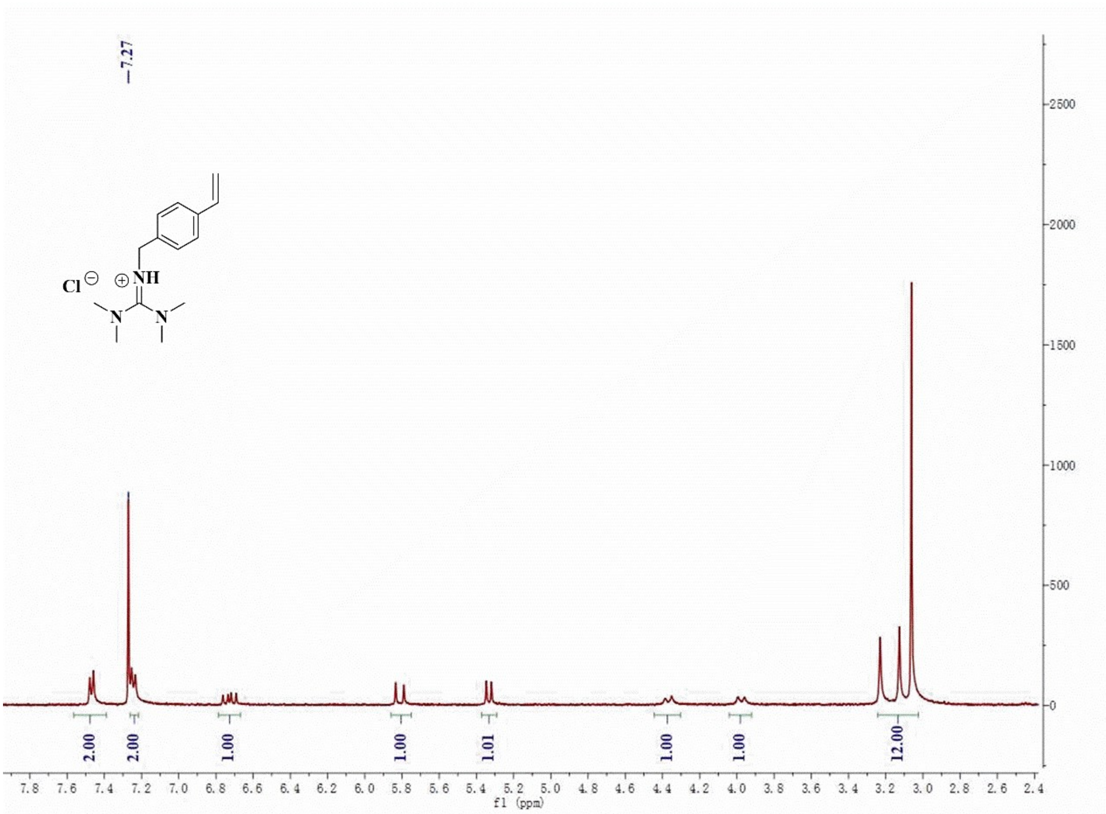

Figure S13. The ^{1}H NMR spectrum of [VBTMG]Cl.

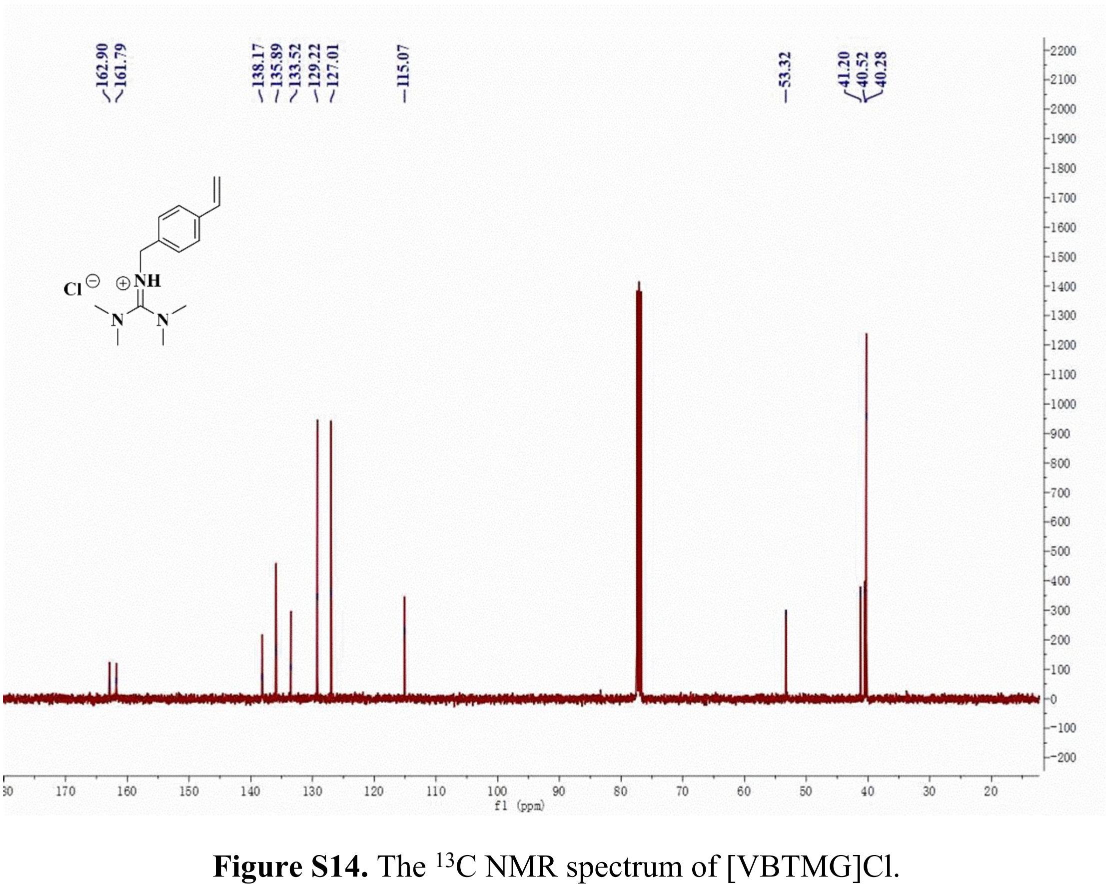

Figure S14. The ^{13}C NMR spectrum of [VBTMG]Cl.

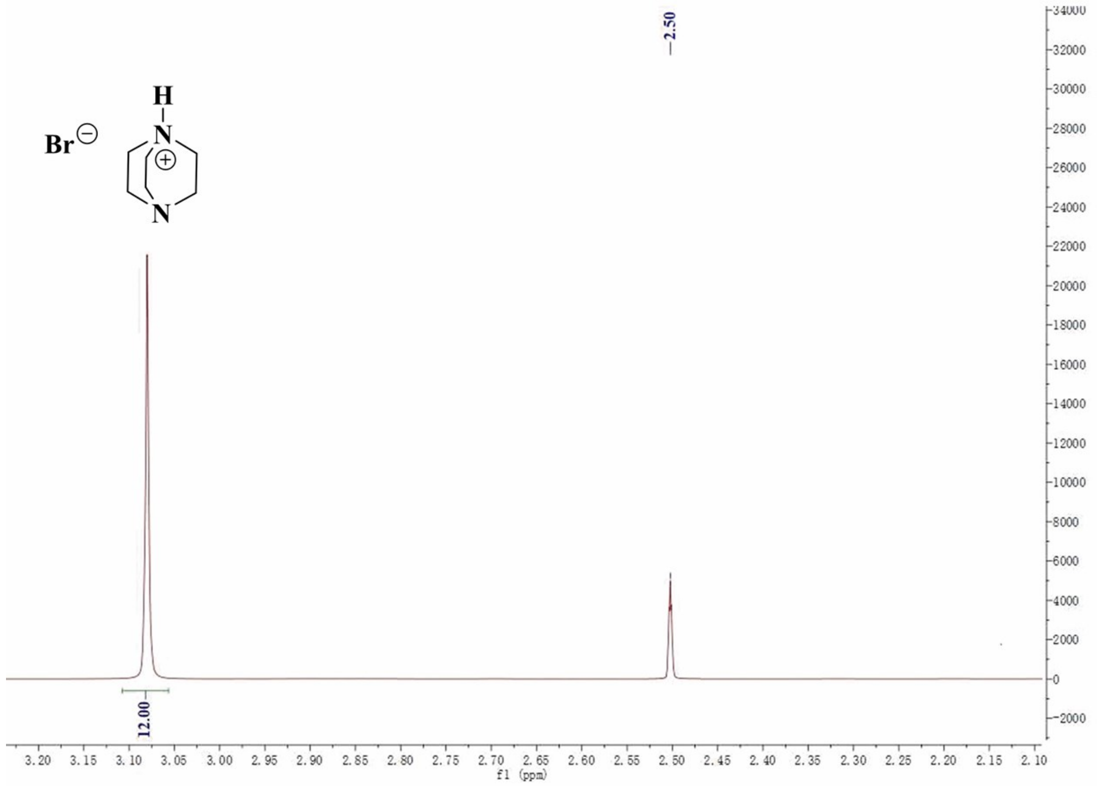

Figure S15. The ^{1}H NMR spectrum of [DABCOH]Br.

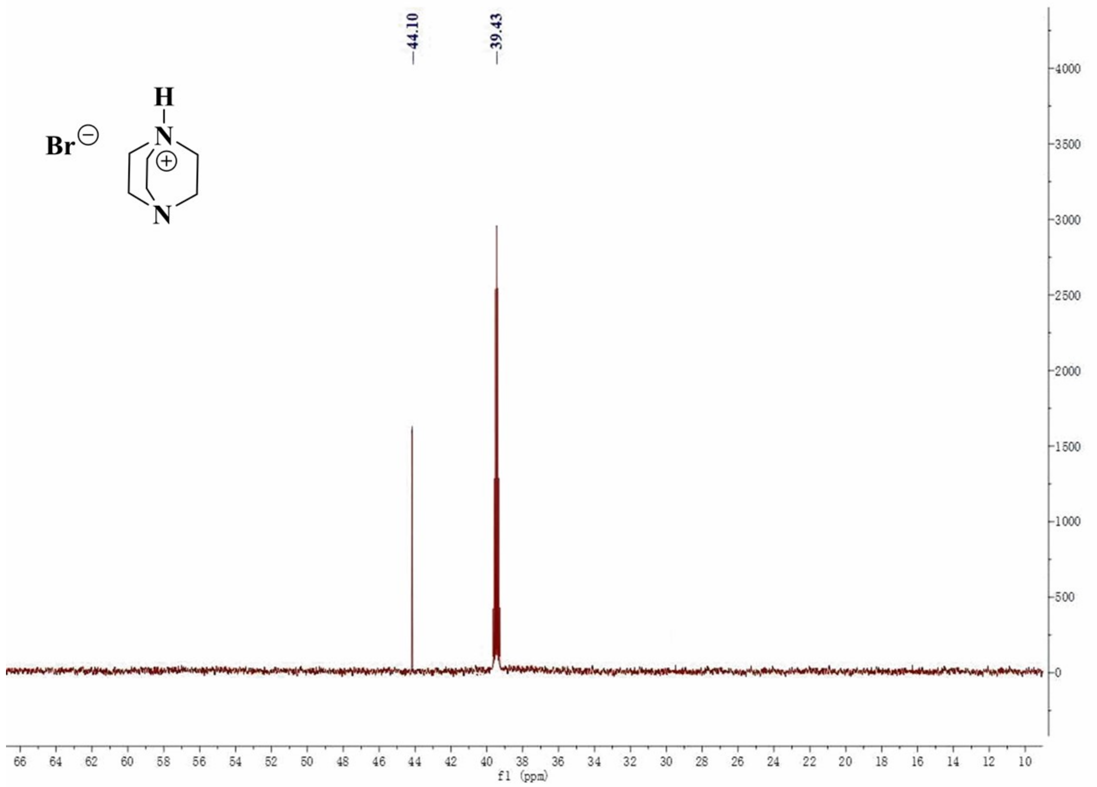

Figure S16. The ^{13}C NMR spectrum of [DABCOH]Br.

Computation details

To understand the structures and interactions of CO_2 and SO with the ILs ([DBUH]Cl, [DBUH]Br, [TMGH]Br, [DABCOH]Br, [MimH]Br, [VBTGM]Cl, [AlTGM]Br, [AlDBU]Br and tetrabutylammonium bromide TBAB) used in the present work, geometric optimizations were carried out for free CO_2, SO, all the ionic liquids and their corresponding complexes. Frequency calculations of these systems were carried out at the same theoretical level of M06/6-311+G(2d, 2p) [S1]. The binding energy of different ionic liquid-CO_2 complexes and ionic liquid-SO complexes were evaluated by the enthalpy change, $\Delta H = H_{gas,298.15\ K}$ (complex) - $H_{gas,298.15\ K}$ (IL) - $H_{gas,298.15\ K}$ (CO_2 or SO). All calculations were carried out using Gaussian [S2].

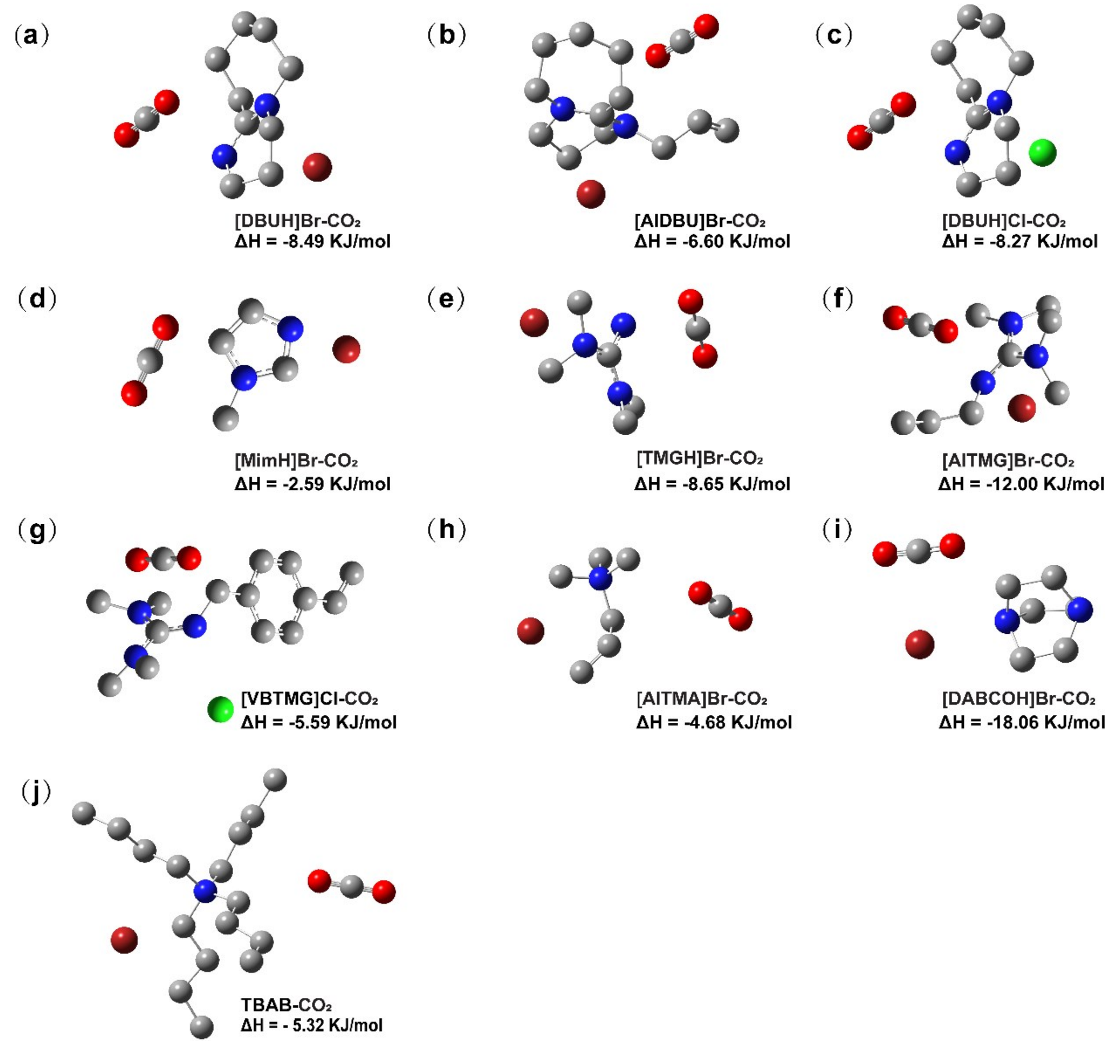

Figure S17. (a) [DBUH]Br-CO_2, (b) [AlDBU]Br-CO_2, (c) [DBUH]Cl-CO_2, (d) [MimH]Br-CO_2, (e) [TMGH]Br-CO_2, (f) [AlTMG]Br-CO_2, (g) [VBTMG]Cl-CO_2, (h) [AlTMA]Br-CO_2, (i) [DABCO]Br-CO_2, and (j) TBAB-CO_2. ΔH of interaction are also shown. C gray, O red, N blue, Br vermilion, Cl green.

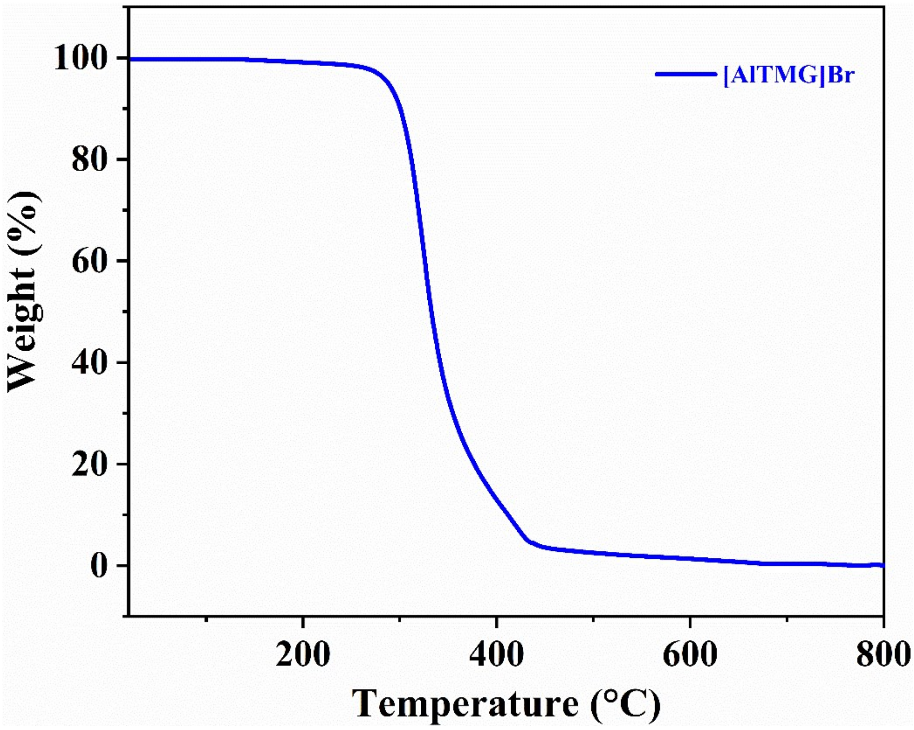

Figure S18. TGA curves of [AlTMG]Br.

Table S1. The optimization of reaction parameters for the cycloaddition of diluted CO_2 with SO using the [AlTMG]Br catalyst.[a]

Entry	Temperature (°C)	Time (h)	Yield of SC (%)	Selectivity of SC (%)
1	80	24	7	99
2	90	24	18	99
3	100	24	31	99
4	110	24	45	99
5	120	24	53	99
6	130	24	55	99
7	100	32	58	99
8	100	40	82	99
9	100	48	99	99

[a]Reaction conditions: SO (1.2 g, 10 mmol), CO_2 (1 bar, 15% CO_2/85% N_2), catalyst (1.5 mol%).

Table S2. Catalytic activity of various catalysts for cycloaddition of CO_2 with SO.

Entry	Catalyst	Additive	Reaction conditions	Yield (%)	Ref.
1	[CBDMAPy]Br	-	20 bar, 130 °C, 1 h	85	[S3]
2	BnBimBr	DEA	1 bar, 80 °C, 3 h	94	[S4]
3	DBPIL	-	1 bar, 80 °C, 6 h	87	[S5]
4	$[C_1C_4Im][HCO_3]$	SH4-Al(Cl)	10 bar, 25 °C, 24 h	88	[S6]
5	$NEt(HE)_3Br$	-	15 bar, 130 °C, 2 h	97	[S7]
6	[DMAPH]Br	-	1 bar, 120 °C, 9 h	96	[S8]
7	BMImBr	$ZnCl_2$	15 bar, 100 °C, 1 h	86	[S9]
8	Bu_4NBr	-	30 bar, 100 °C, 2 h	56	[S10]
9	$ZnBr_2$	DMF	30 bar, 150 °C, 4 h	67	[S11]
	[AlTMG]Br	-	1 bar, 100 °C, 8 h	99	
8	[AlTMG]Br	-	1 bar, 25 °C, 72 h	93	This work
	[AlTMG]Br	-	0.15 bar, 100 °C, 48 h	99	

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