Supplementary Information

for

Atmospheric-pressure synthesis of glycerol carbonate from CO_2 and glycerol catalyzed by protic ionic liquids

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1. Influence of different reaction conditions on the one-pot reaction

$$\text{Carbon balance}_{\text{SO}}\,(\%) = \frac{\text{mol}_{\text{SO, unreacted}} + \text{mol}_{\text{SG}} + \text{mol}_{\text{SC}}}{\text{mol}_{\text{SO, initial}}} \quad \text{(S1)}$$

$$\text{Carbon balance}_{\text{Gly}}\,(\%) = \frac{\text{mol}_{\text{Gly, unreacted}} + \text{mol}_{\text{GC}}}{\text{mol}_{\text{Gly, initial}}} \quad \text{(S2)}$$

Table S1. One-pot synthesis of GC from CO_2, Gly, and SO catalyzed by protic ILs.

Entry	Catalyst	Conv. (%)		Yield (%)			Products (mmol)			Carbon balance (%)	
		Gly	SO	SC[a]	SG[a]	GC[b]	SC	SG	GC	SO	Gly
1	HDBUI	92	84	39	34	86	3.0	2.6	2.2	91	94
2	HDBUBr	77	49	14	28	68	1.1	2.1	1.7	93	92
3	HDBUCl	29	18	2	11	24	0.1	0.8	0.6	95	96
4	HDBNI	92	87	48	33	84	3.6	2.5	2.1	95	93
5	HDBNBr	83	57	22	29	75	1.6	2.2	1.9	93	92
6	HDBNCl	36	21	1	11	27	0.1	0.9	0.7	92	91
7	HMTBDI	92	83	42	37	85	3.2	2.8	2.1	96	93
8	HTBDI	91	85	41	37	85	3.1	2.8	2.1	93	94
9	HDMAPI	91	87	41	35	80	3.0	2.6	2.0	89	89
10	HPyI	90	81	43	33	79	3.2	2.4	2.0	94	89
11	DBU	28	28	2	12	21	0.2	0.9	0.5	86	94
12	DBN	8	12	<1	6	8	<0.1	0.5	0.2	96	>99
13	TEA	13	20	<1	8	13	<0.1	0.6	0.4	90	>99
14	$NaOCH_3$	<1	13	<1	3	<1	<0.1	0.3	<0.1	91	>99
15	NaOH	10	16	<1	6	5	<0.1	0.4	0.1	90	95
16	KOH	<1	12	<1	4	<1	<0.1	0.3	<0.1	92	>99

Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), catalyst loading (5 mol% based on Gly), 100 °C, 4 h. [a] Based on SO. [b] Based on Gly.

Table S2. Effect of reaction time on GC synthesis by the one-pot reaction at 0.1 MPa of CO_2.

Entry	Reaction time (h)	Conv. (%)		Yield (%)			Products (mmol)			Carbon balance (%)	
		Gly	SO	SC[a]	SG[a]	GC[b]	SC	SG	GC	SO	Gly
1	1	73	42	12	24	70	0.9	1.8	1.8	94	98
2	2	89	69	36	32	83	2.7	2.4	2.1	99	94
3	4	92	84	39	34	86	3.0	2.6	2.2	91	94
4	6	91	89	46	35	88	3.6	2.6	2.2	92	98
5	8	91	97	55	36	91	4.1	2.6	2.3	94	>99
6	10	91	96	54	38	90	4.1	2.9	2.2	96	>99

Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), catalyst loading (5 mol% based on Gly), 100 °C. [a] Based on SO. [b] Based on Gly.

Table S3. Effect of reaction temperature on GC synthesis by the one-pot reaction at 0.1 MPa of CO_2.

Entry	Reaction temperature (°C)	Conv. (%)		Yield (%)			Products (mmol)			Carbon balance (%)	
		Gly	SO	SC[a]	SG[a]	GC[b]	SC	SG	GC	SO	Gly
1	60	85	61	24	33	75	1.9	2.5	1.9	96	90
2	70	90	83	46	35	87	3.5	2.7	2.2	98	97
3	80	90	92	52	34	86	3.9	2.6	2.1	94	96
4	90	90	92	49	34	88	3.7	2.6	2.2	92	98
5	100	91	97	55	36	91	4.1	2.6	2.3	94	>99
6	110	90	97	50	34	89	3.8	2.6	2.2	87	99

Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), catalyst loading (5 mol% based on Gly), 8 h. [a] Based on SO. [b] Based on Gly.

Table S4. Effect of catalyst loading on GC synthesis by the one-pot reaction at 0.1 MPa of CO_2.

Entry	Catalyst loading (%)	Conv. (%)		Yield (%)			Products (mmol)			Carbon balance (%)	
		Gly	SO	SC[a]	SG[a]	GC[b]	SC	SG	GC	SO	Gly
1	1	77	53	15	29	70	1.2	2.2	1.7	91	93
2	2.5	88	89	42	33	84	3.1	2.4	2.1	86	96
3	5	91	97	55	36	91	4.1	2.6	2.3	94	>99
4	7.5	90	97	51	38	90	3.8	2.8	2.3	92	>99

Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), 100 °C, 8 h. [a] Based on SO. [b] Based on Gly.

Table S5. Effect of SO/Gly molar ratio on GC synthesis by the one-pot reaction at 0.1 MPa of CO_2.

Entry	SO/Gly molar ratio	Conv. (%)		Yield (%)			Products (mmol)			Carbon balance (%)	
		Gly	SO	SC[a]	SG[a]	GC[b]	SC	SG	GC	SO	Gly
1	1	63	97	21	62	58	0.6	1.7	1.5	86	95
2	2	83	97	40	52	81	2.0	2.6	2	94	98
3	3	91	97	55	36	91	4.1	2.6	2.3	94	>99
4	4	95	92	55	29	95	5.6	3.0	2.4	92	>99

Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), catalyst loading (5 mol% based on Gly), 100 °C, 8 h. [a] Based on SO. [b] Based on Gly.

2. ^{13}C NMR, ^{1}H NMR and FT-IR spectra during the one-pot reaction

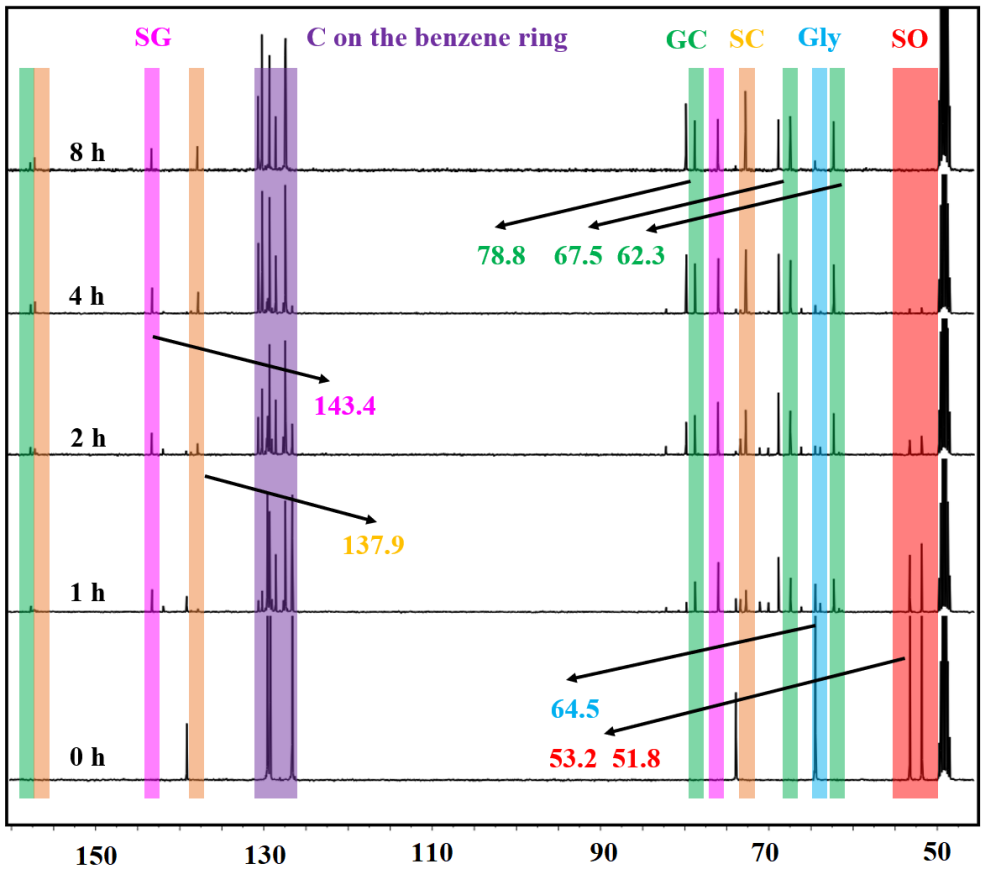


Fig. S1 ^{13}C NMR spectra of reaction mixture during the one-pot reaction (100 MHz CD_4O).

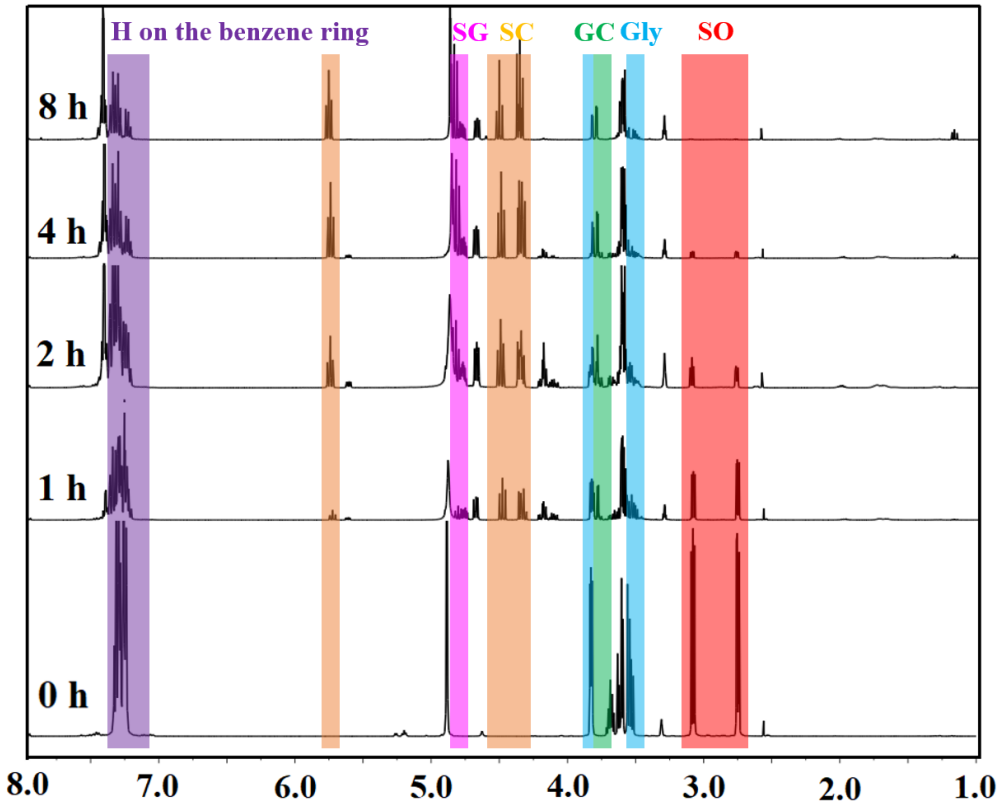


Fig. S2 ^{1}H NMR spectra of the reaction mixture during the one-pot reaction (400 MHz CD_4O).

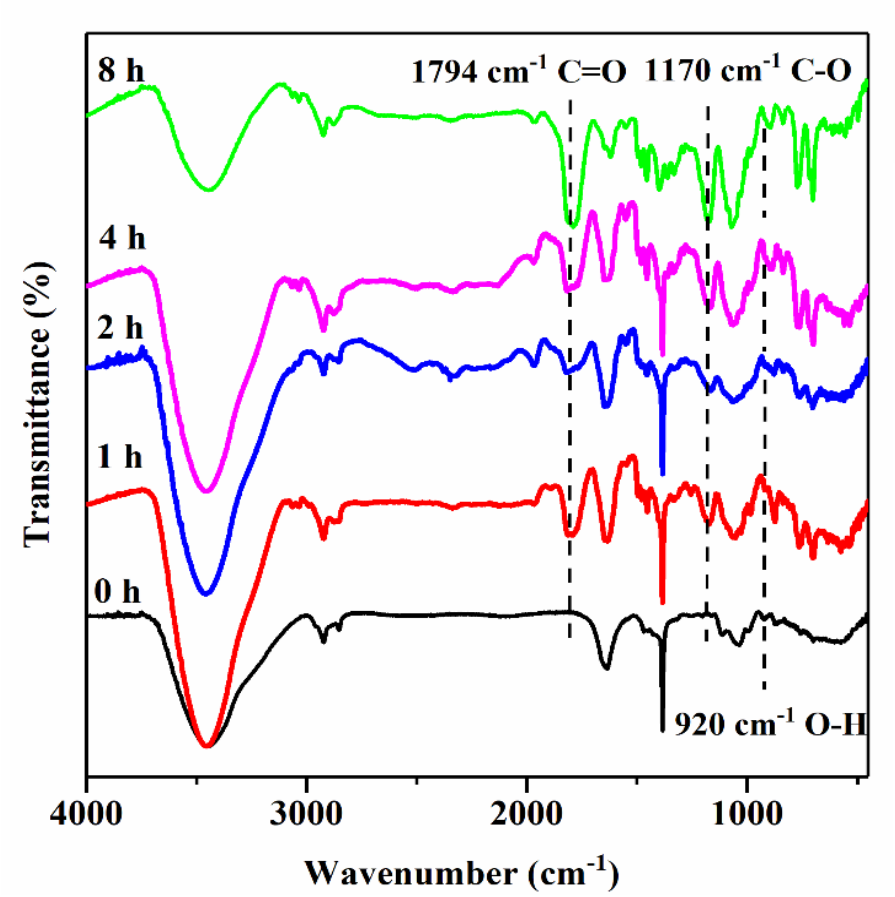


Fig. S3 FT-IR of the reaction mixture during the one-pot reaction.

3. Recycling and thermal stability of HDBUI

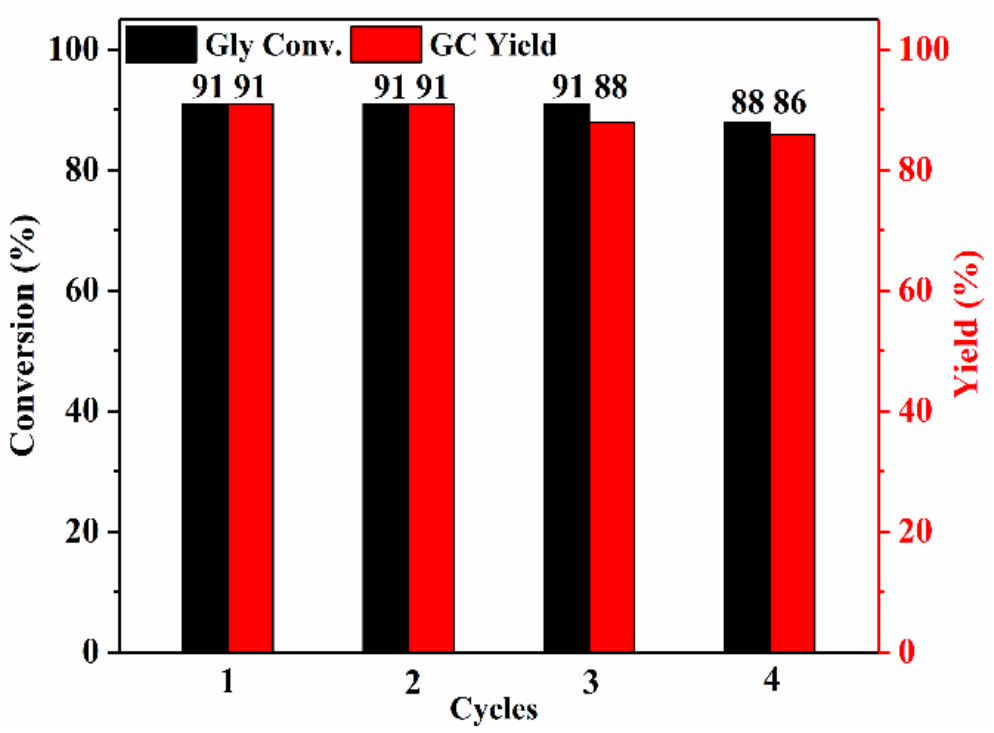


Fig. S4 Catalyst recycling for the one-pot reaction. Conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), catalyst loading (10 mol% based on Gly), 100 °C, 4 h.

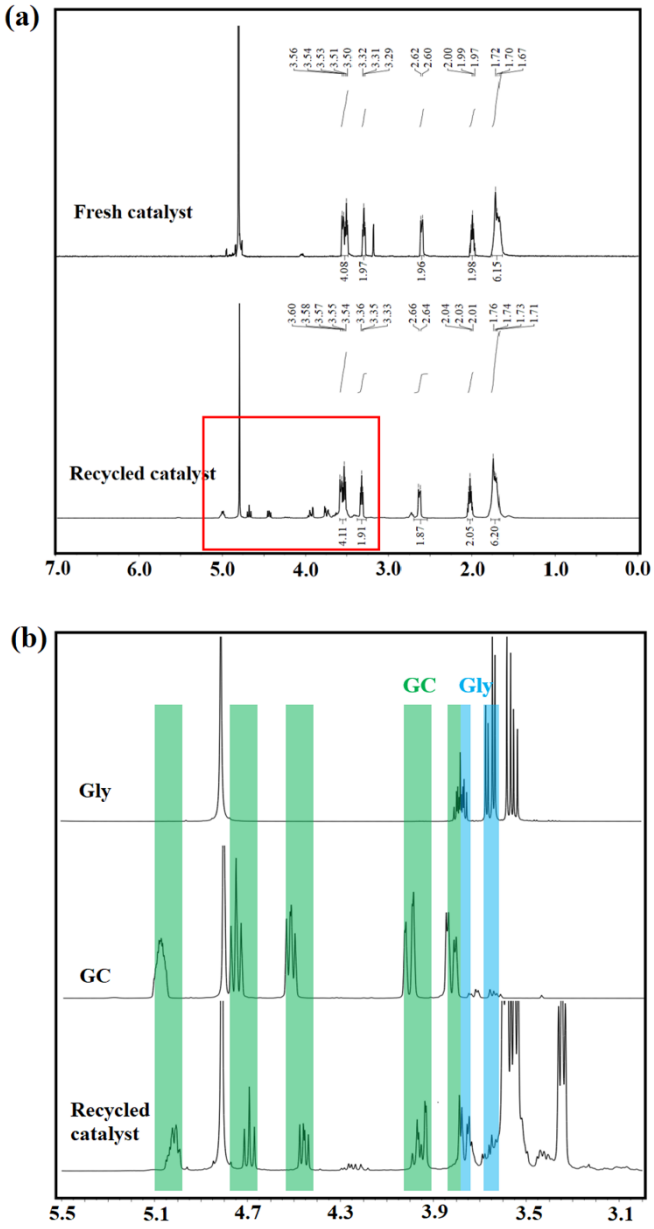


Fig. S5 ^{1}H NMR spectra of (a) the catalyst before and after the cycle, (b) Gly, GC and the catalyst after the cycle (400 MHz, D_2O).

^{1}H NMR spectra of recycled catalyst demonstrated no significant variation of HDBUI (**Fig. S5a**). A small amount of impurities in the recovered catalyst is Gly and GC that are difficult to be completely separated (**Fig. S5b**).

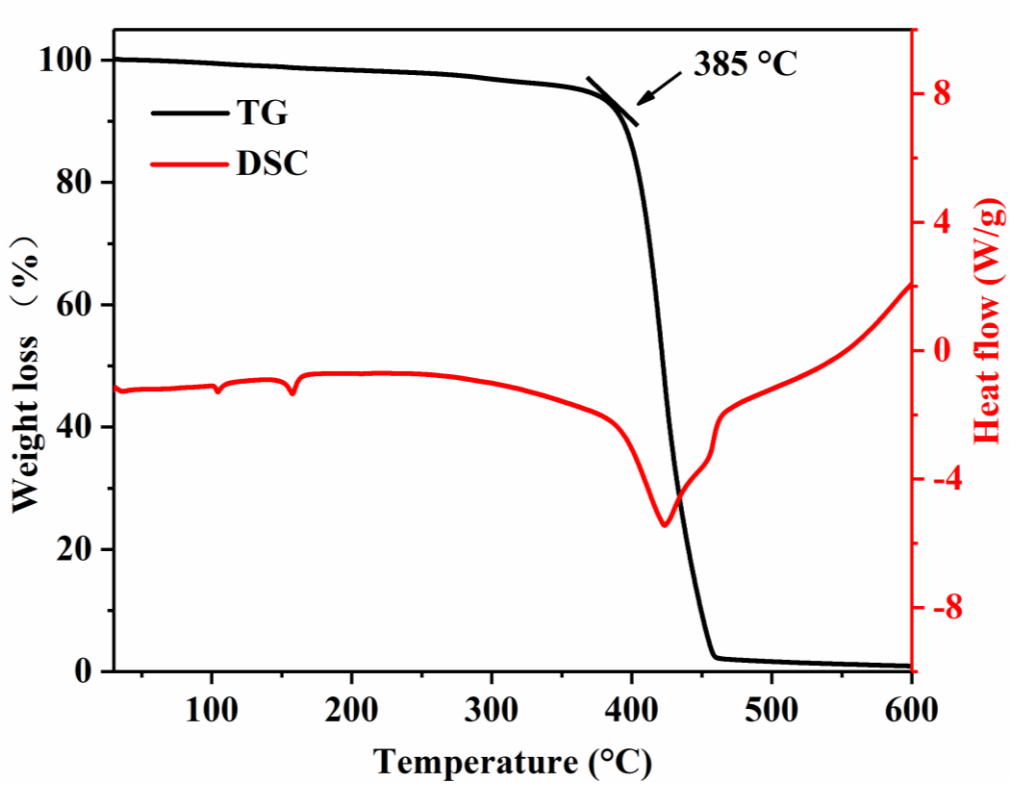
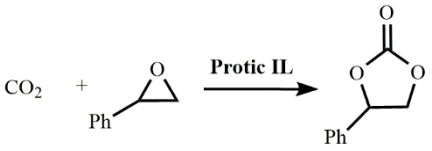


Fig. S6 The TG and DSC curves of HDBUI.

4. Reaction mechanism studies

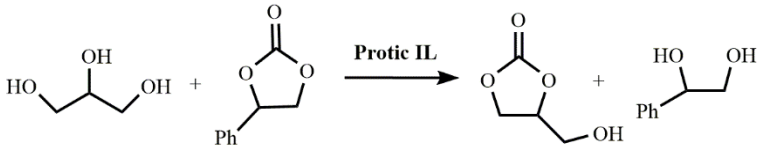
Table S6. Cycloaddition of CO_2 and SO catalyzed by protic ILs.



Entry	Catalyst	SO conv. (%)	SC yield[a] (%)	SC (mmol)	Carbon balance of SO (%)
1	HDBUI	88	88	6.8	>99
2	HDBUBr	80	80	6.0	>99
3	HDBUCl	60	53	4.0	93
4	HPyI	66	63	4.8	97

Reaction conditions: 0.1 MPa of CO_2 (balloon), SO (7.5 mmol), catalyst loading (1.67 mol%), 100 °C, 4 h. [a] Based on SO.

Table S7. Transesterification of Gly and SC catalyzed by protic ILs.



Entry	Catalyst	Conv. (%)		Yield (%)		Products (mmol)		Carbon balance (%)	
		Gly	SC	SG[a]	GC[b]	SG	GC	SC	Gly
1	HDBUI	91	35	31	87	2.4	2.2	97	96
2	HDBUBr	92	33	31	87	2.4	2.2	99	95
3	HDBUCl	92	35	34	88	2.7	2.2	>99	96
4	HPyI	3	1	1	3	<0.1	<0.1	>99	>99

Reaction conditions: Gly (2.5 mmol), SC (7.5 mmol), catalyst loading (5 mol% based on Gly), 100 °C, 4 h. [a] Based on SC. [b] Based on Gly.

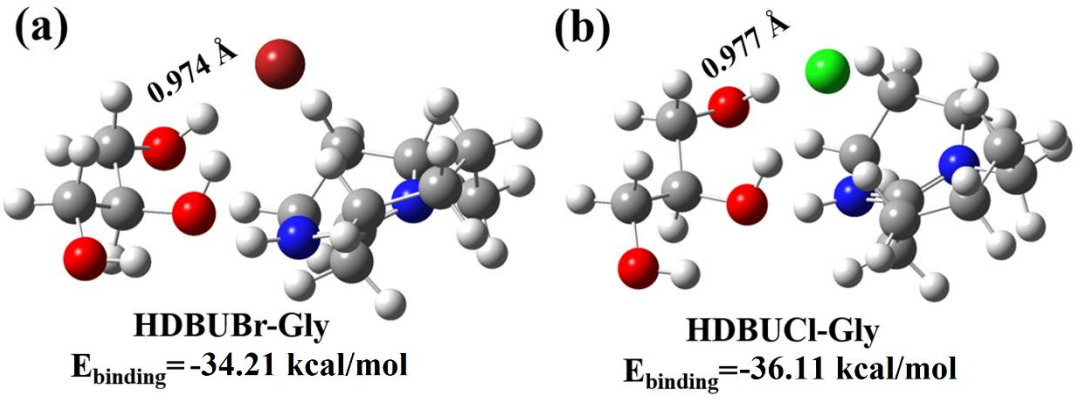


Fig. S7 The interaction between protic ILs and Gly. (a) HDBUBr-Gly, (b) HDBUCl-Gly.

Table S8. Data of optimized structures of protic IL-Gly.

Protic IL-Gly	O−H (Å)[a]	Binding energy (kcal/mol)
Gly	0.958	-
HDBUI-Gly	0.973	-32.49
HDBUBr-Gly	0.974	-34.21
HDBUCl-Gly	0.977	-36.11
HPyI-Gly	0.970	-23.85

[a] Bond length of Gly hydroxyl group activated by the protic ILs.

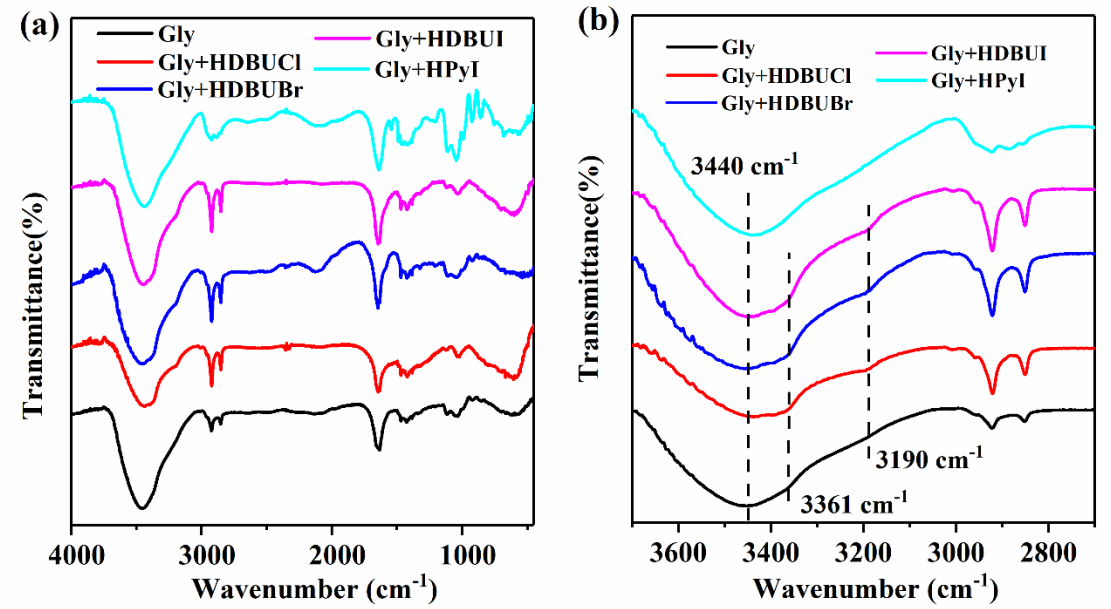


Fig. S8 FT-IR spectra of Gly, Gly + protic ILs (molar ratio 4:1). (a) 4000 cm^{-1}–450 cm^{-1}, (b) 3700 cm^{-1}–2700 cm^{-1}.

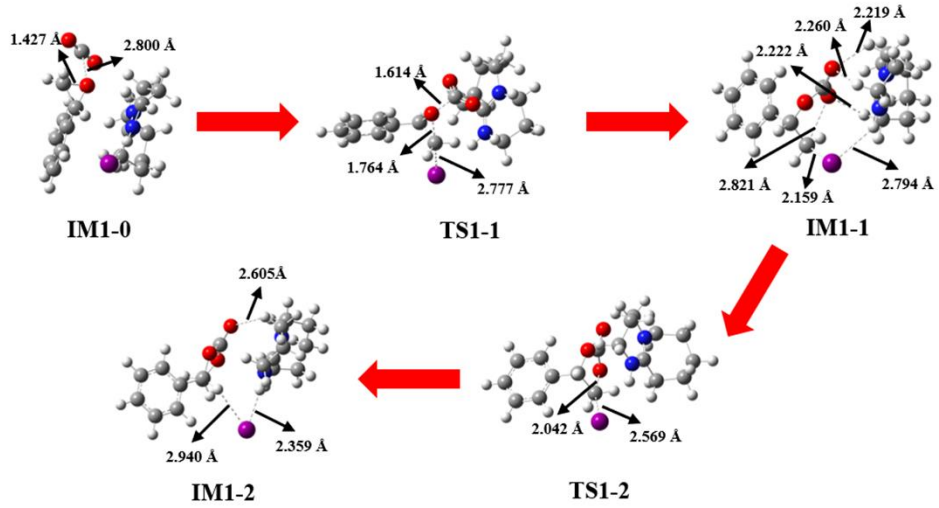


Fig. S9 The optimized geometries of transition states and intermediates involved HDBUI catalyzed cycloaddition.

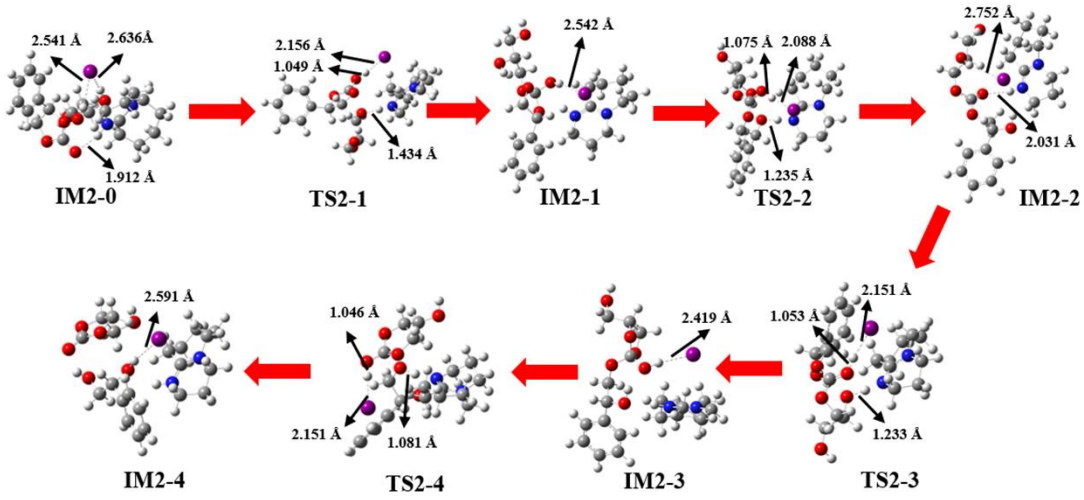


Fig. S10 The optimized geometries of transition states and intermediates involved HDBUI catalyzed transesterification.

5. Water tolerance

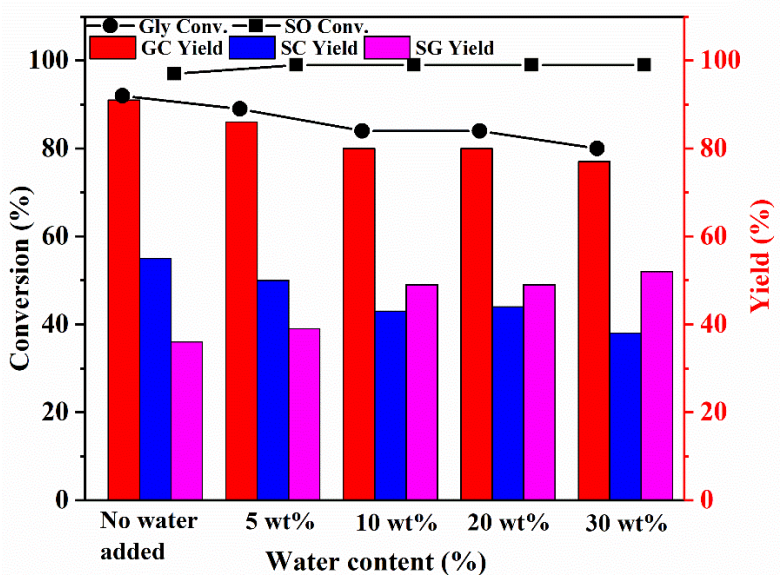


Fig. S11 Effect of water content in Gly. Reaction conditions: 0.1 MPa of CO_2 (balloon), Gly (2.5 mmol), SO (7.5 mmol), catalyst loading (5 mol% based on Gly), 100 °C, 4 h, water content based on Gly.

Table S9. Expansion of reaction conditions for one-pot synthesis of GC catalyzed by HDBUI.

Entry	Water added (wt%)[a]	Pressure (MPa)	Temperature (°C)	Time (h)	GC Yield (%)[b]	Products (mmol)			Carbon balance (%)	
						SC	SG	GC	SO	Gly
1	5	0.1 (CO_2)	100	8	86	3.7	2.9	2.2	90	97
2	10	0.1 (CO_2)	100	8	80	3.2	3.7	2.0	92	96
3	20	0.1 (CO_2)	100	8	80	3.4	3.7	2.0	94	95
4	30	0.1 (CO_2)	100	8	77	2.9	4.0	2.0	92	97
5	0	2.0[c] (15% CO_2/85% N_2)	100	8	81	3.0	2.2	2.1	86	94
6	0	2.0[c] (15% CO_2/3% O_2/82% N_2	100	8	80	2.9	2.0	2.0	77	91
7	0	0.1[d] (50% CO_2/50% CH_4)	100	8	71	0.9	2.0	1.8	80	88
8	0	0.1 (CO_2)	45	24	75	1.3	1.9	1.9	95	96
9	0	0.1 (CO_2)	45	48	94	4.2	2.4	2.3	95	99

Reaction conditions: Gly (2.5 mmol), SO (7.5 mmol), HDBUI loading (5 mol% based on Gly). [a] Water content based on Gly. [b] Based on Gly. [c] Simulated flue gas. [d] Simulated biogas.

6. ^{1}H NMR spectra of protic ILs

1,8-Diazabicyclo[5.4.0]undec-7-enenium iodide (HDBUI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.56-3.50 (m, 4H), 3.31 (t, *J* = 5.8 Hz, 2H), 2.62–2.60 (m, 2H), 2.00–1.97 (m, 2H), 1.72–1.67 (m, 6H).

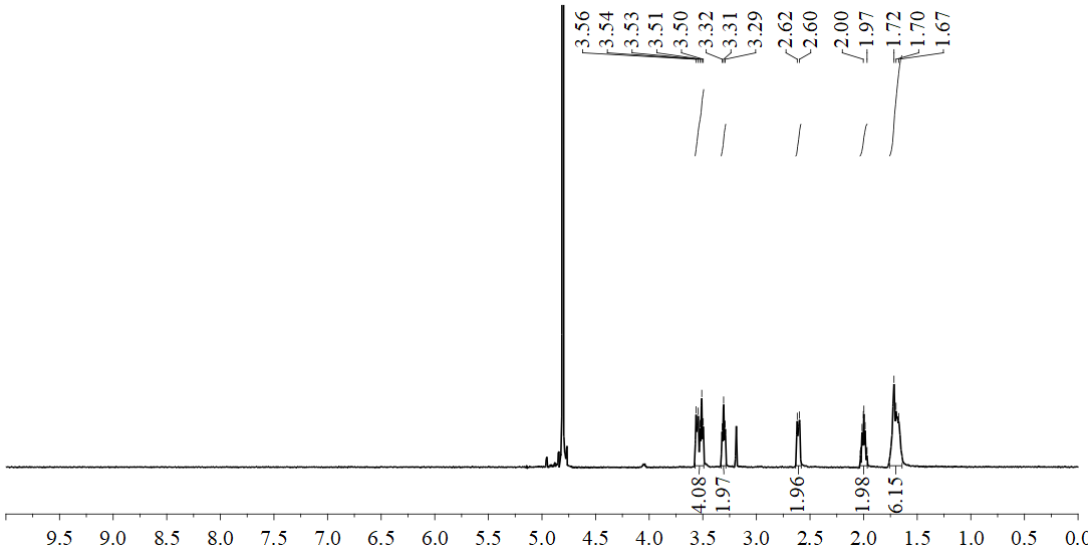


Fig. S12 ^{1}HNMR spectrum of HDBUI.

1,8-Diazabicyclo[5.4.0]undec-7-enenium bromide (HDBUBr). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.56–3.49 (m, 4H), 3.30 (t, *J* = 5.6 Hz, 2H), 2.62–2.60 (m, 2H), 2.02–1.96 (m, 2H), 1.71–1.67 (m, 6H).

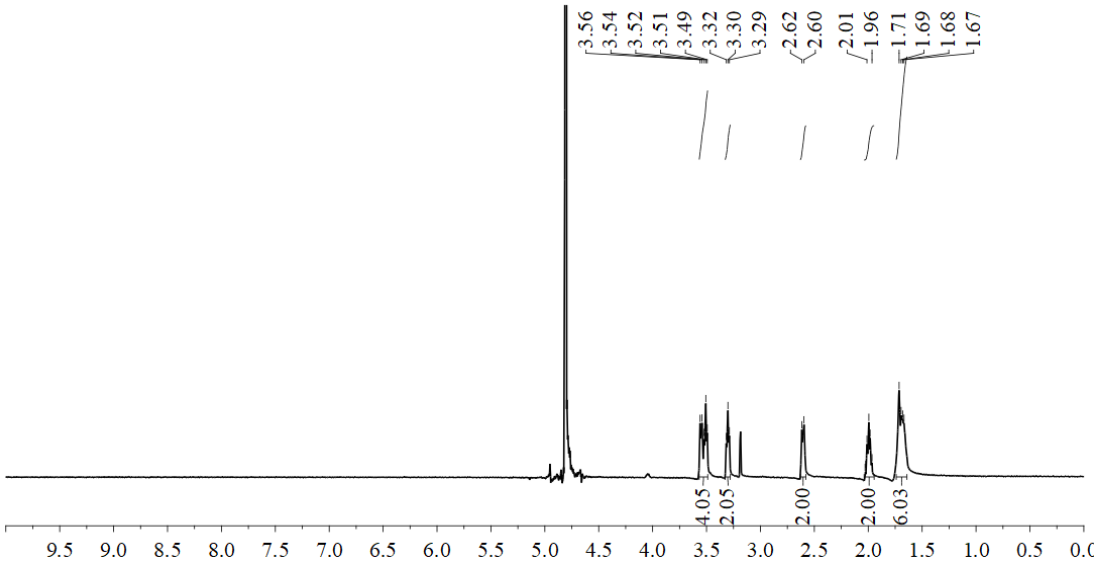


Fig. S13 ^{1}HNMR spectrum of HDBUBr.

1,8-Diazabicyclo[5.4.0]undec-7-enenium chloride (HDBUCl). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.56–3.50 (m, 4H), 3.31 (t, *J* = 4.8 Hz, 2H), 2.62–2.60 (m, 2H), 2.00–1.99 (m, 2H), 1.72–1.70 (m, 6H).

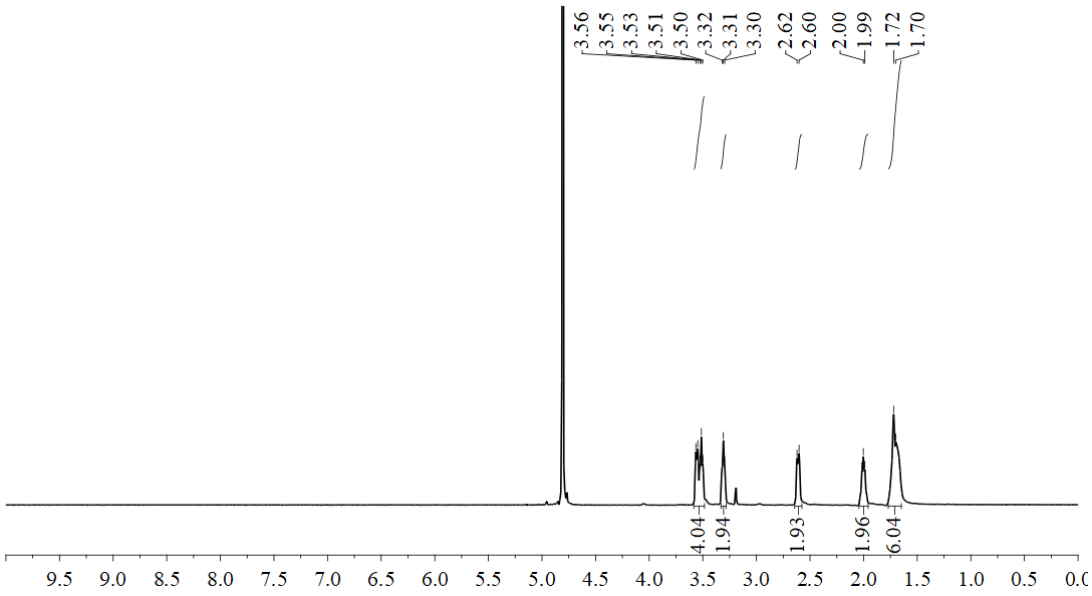


Fig. S14 ^{1}HNMR spectrum of HDBUCl.

1,5-Diazabicyclo[4.3.0]non-5-enenium iodide (HDBNI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.67 (t, *J* = 7.4 Hz, 2H), 3.43–3.35 (m, 4H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.16–2.09 (m, 2H), 2.03 –1.98 (m, 2H).

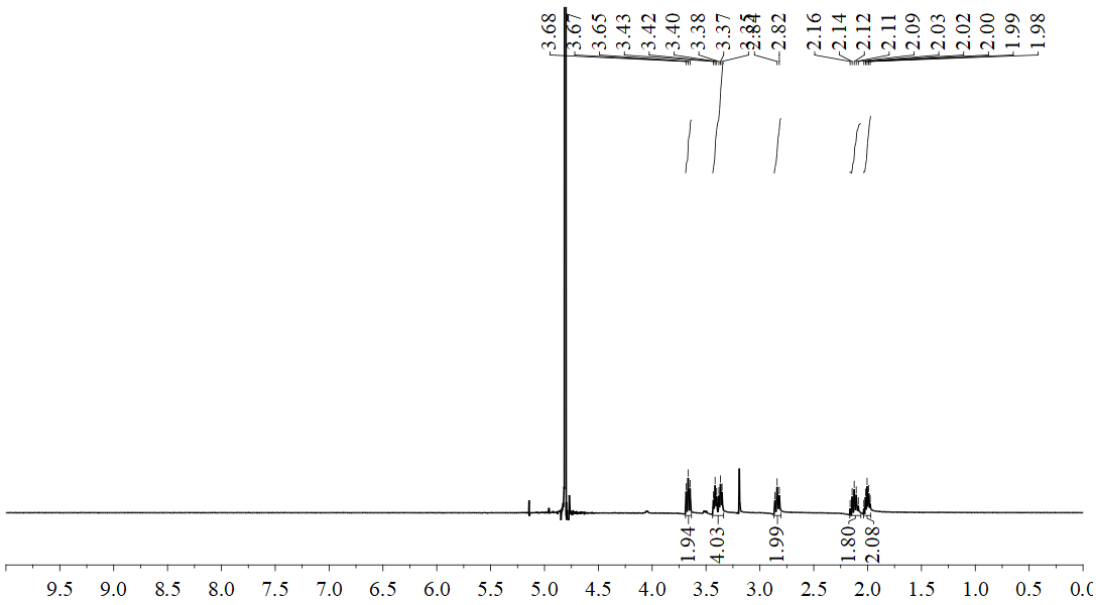


Fig. S15 ^{1}HNMR spectrum of HDBNI.

1,5-Diazabicyclo[4.3.0]non-5-enenium bromide (HDBNBr). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.67 (t, *J* = 7.4 Hz, 2H), 3.40–3.38 (m, 4H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.14–2.08 (m, 2H), 2.03 –1.97 (m, 2H).

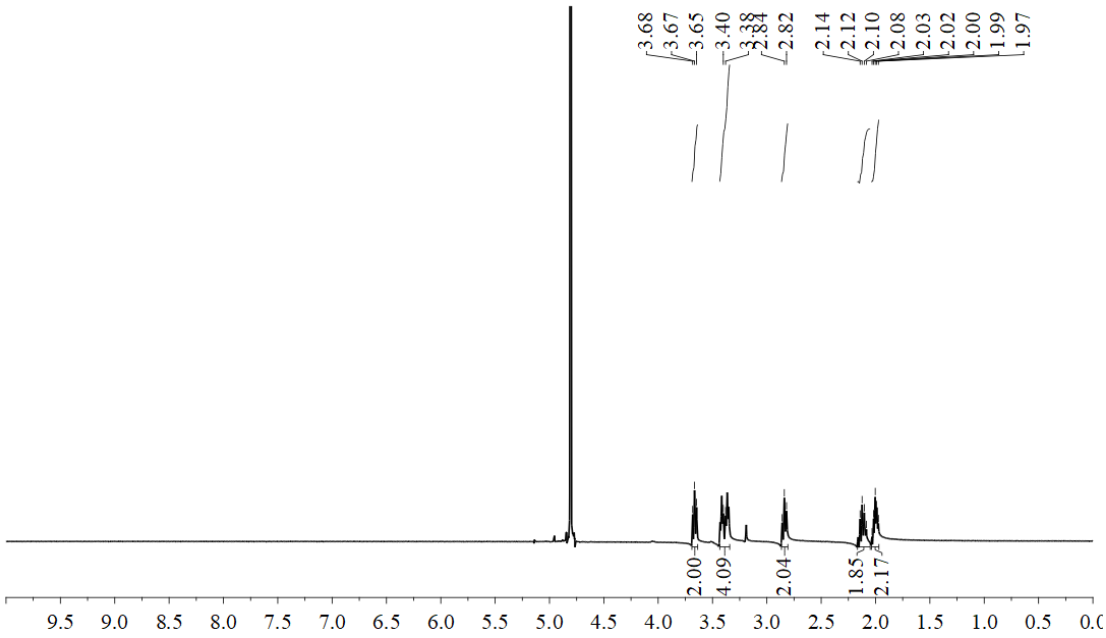


Fig. S16 ^{1}HNMR spectrum of HDBNBr.

1,5-Diazabicyclo[4.3.0]non-5-enenium chloride (HDBNCl). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.67 (t, *J* = 7.2 Hz, 2H), 3.41–3.36 (m, 4H), 2.84 (t, *J* = 8.0 Hz, 2H), 2.16–2.09 (m, 2H), 2.02–1.99 (m, 2H).

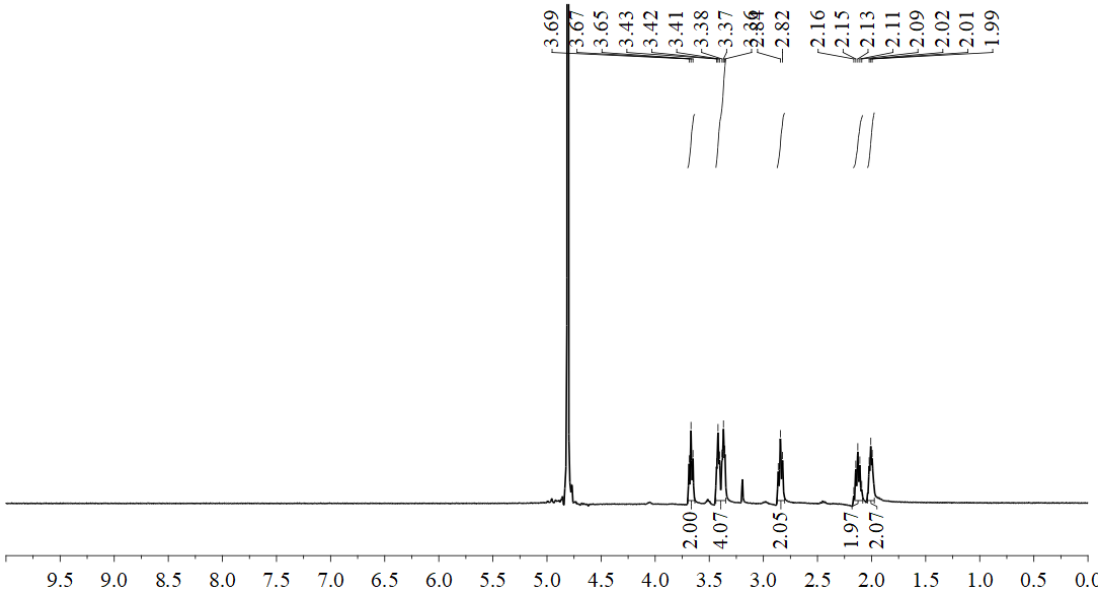


Fig. S17 ^{1}HNMR spectrum of HDBNCl.

7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enenium iodide (HMTBDI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.36–3.28 (m, 8H), 2.93 (m, 3H), 2.03–1.97 (m, 2H), 1.97–1.92 (m, 2H).

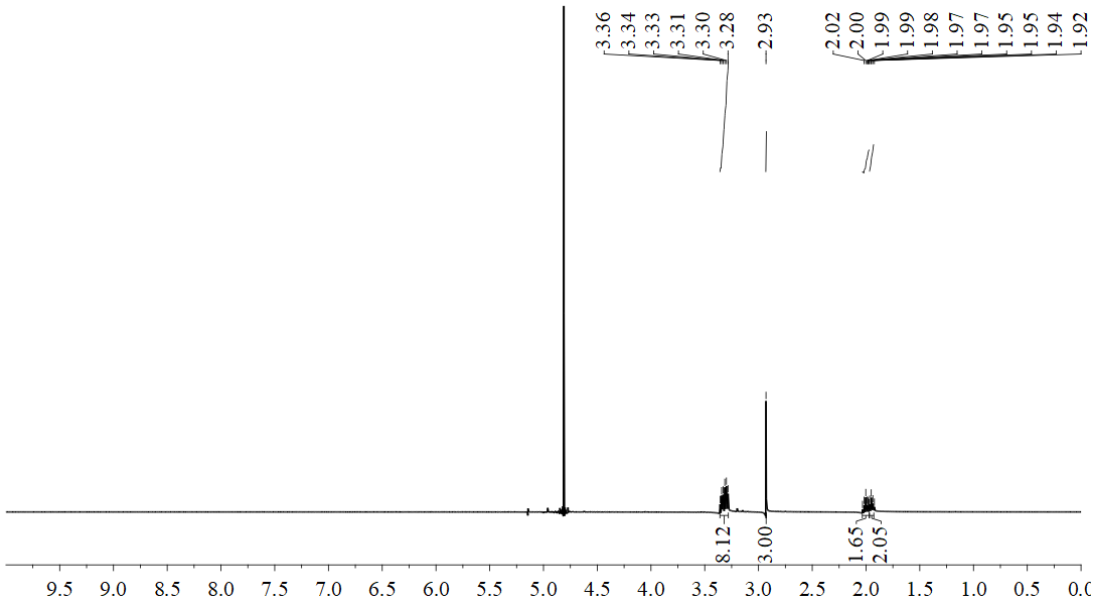


Fig. S18 ^{1}HNMR spectrum of HMTBDI.

1,5,7-Triazabicyclo[4.4.0]dec-5-enenium iodide (HTBDI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 3.33 (t, *J* = 6.0 Hz, 4H), 3.25 (t, *J* = 5.8 Hz, 4H), 2.00–1.94 (m, 4H).

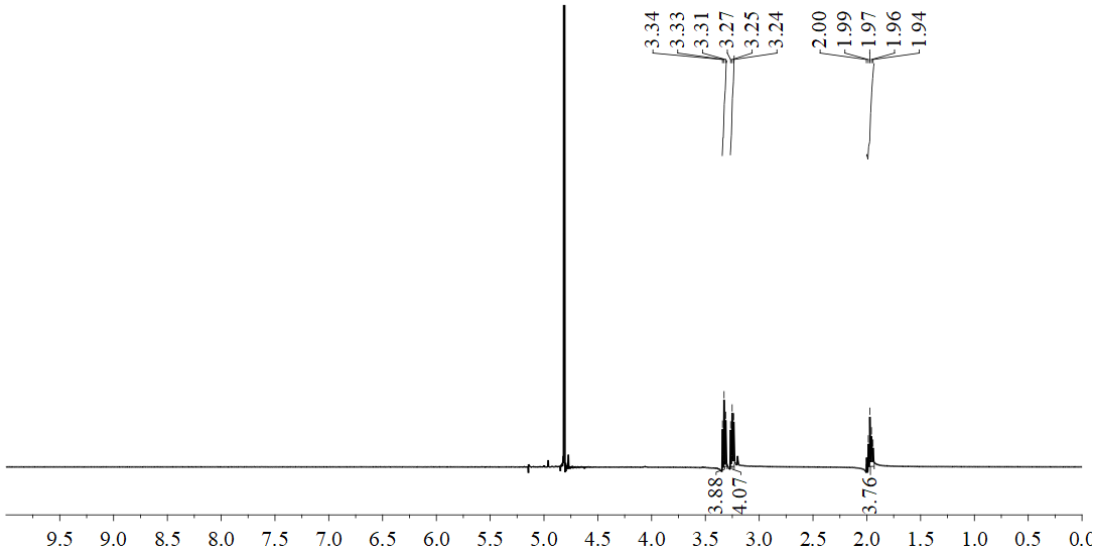


Fig. S19 ^{1}HNMR spectrum of HTBDI.

4-Dimethylaminopyridinium iodide (HDMAPI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 8.00–7.99 (m, 2H), 6.88–6.86 (m, 2H), 3.20 (m, 6H).

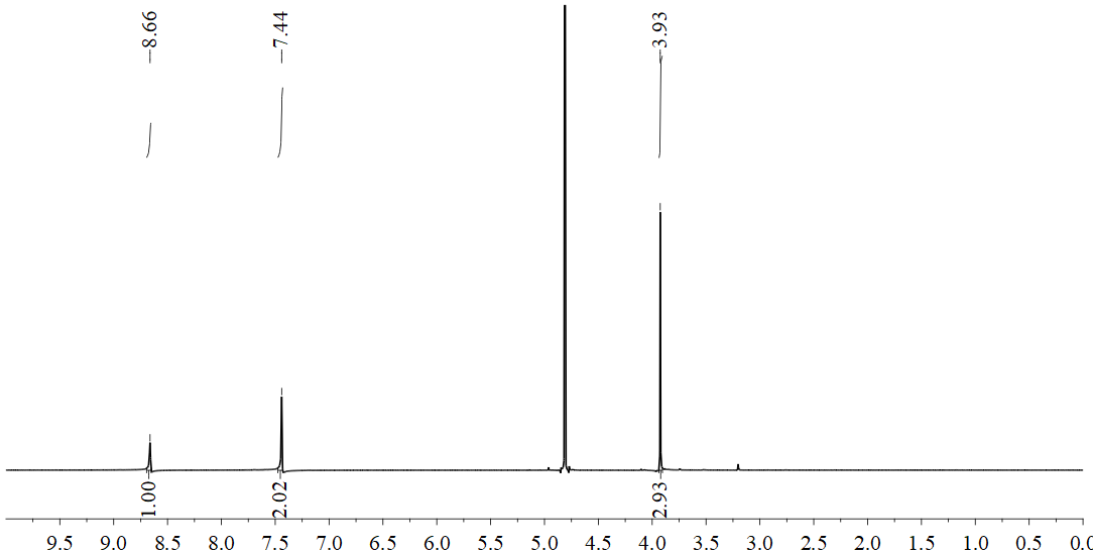


Fig. S20 ^{1}HNMR spectrum of HDMAPI.

Pyridinium iodide (HPyI). ^{1}H NMR (400 MHz, D_2O): δH (ppm) 8.81–8.79 (m, 2H), 8.66–8.62 (m, 1H), 8.09 (t, *J* = 7.0 Hz, 2H).

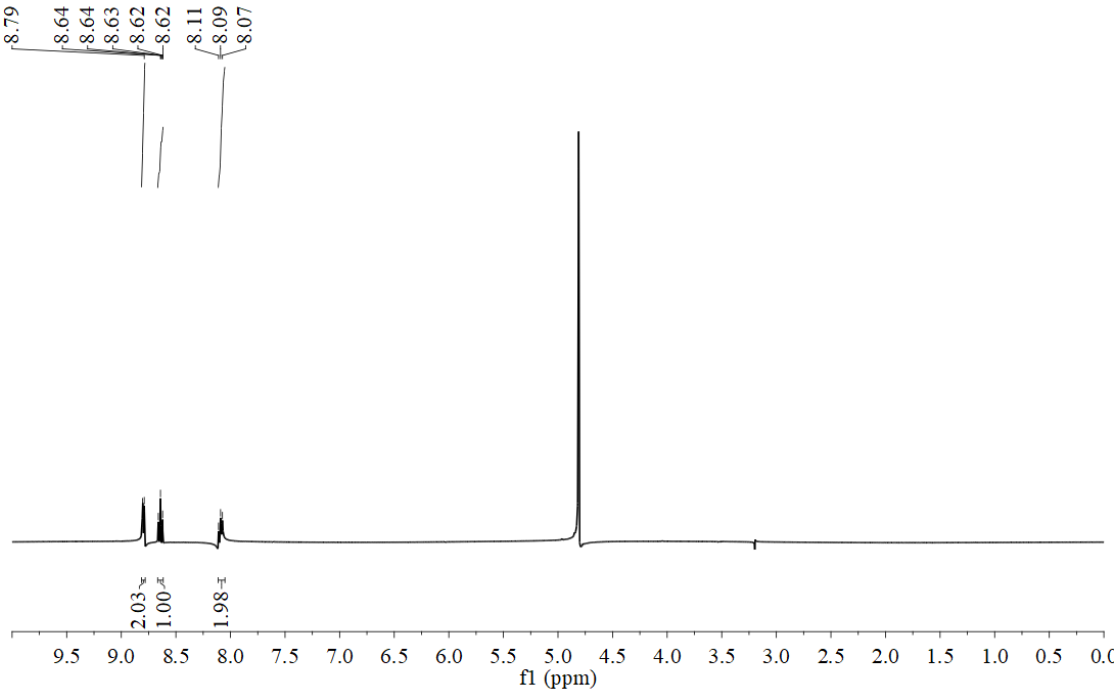


Fig. S21 ^{1}HNMR spectrum of HPyI.