Supporting Information

Amino acid ionic liquids as efficient catalysts for CO_2 capture and chemical conversion with epoxides under metal/halogen/cocatalyst/solvent-free conditions

Ye Qu, Jianwen Lan, Yanglin Chen, Jianmin Sun*

†State Key Laboratory of Urban Water Resource and Environment, MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150080, China

*Corresponding author, E-mail: sunjm@hit.edu.cn

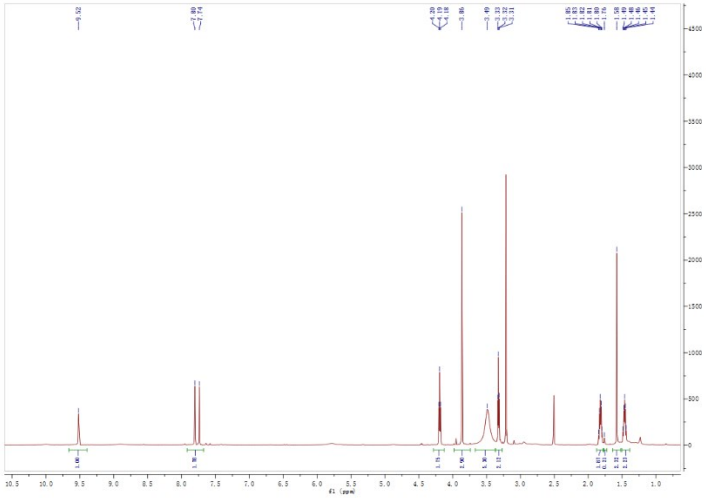


Figure S1. ^{1}H NMR spectrum of [MOBMIM][Gly]

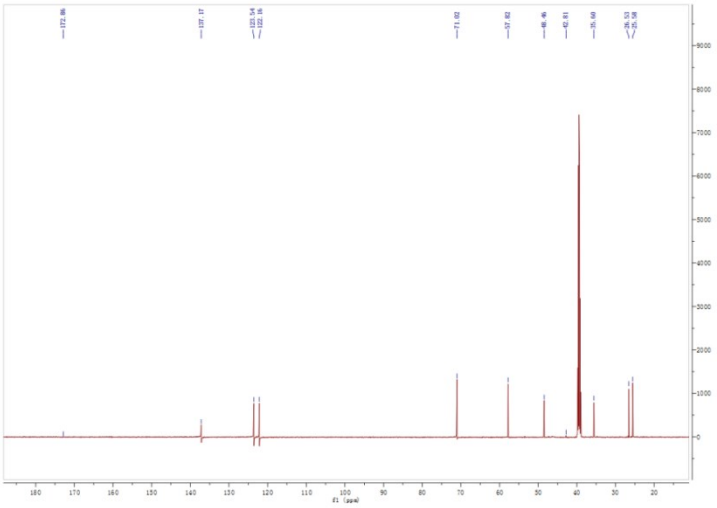


Figure S2. ^{13}C NMR spectrum of [MOBMIM][Gly]

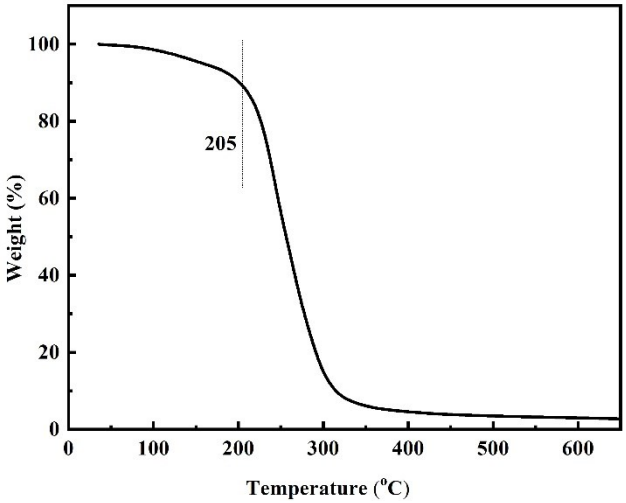


Figure S3. TGA curve for [MOBMIM][Gly]

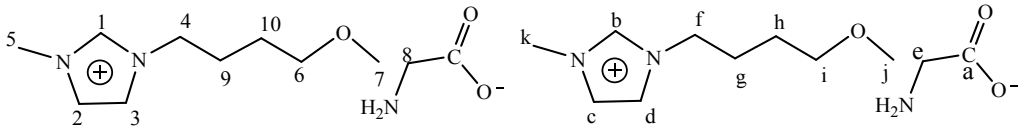


Figure S4. Assignments of NMR signals of [MOBMIM][Gly]

Table S1. ^{1}H NMR data of [MOBMIM]Gly in DMSO (ppm)

H(1)	H(2)	H(3)	H(4)	H(5)	H(6,7)	H(8)	H(9)	H(10)
9.52	7.80	7.74	4.19	3.86	3.49	3.32	1.82	1.48
(1H s)	(2H s)	(2H s)	(2H m)	(3H s)	(5H s)	(2H m)	(2H m)	(2H m)

Table S2. ^{13}C NMR data of [MOBMIM][Gly] in DMSO (ppm)

C^a	C^b	C^c	C^d	C^e	C^f	C^g	C^h	C^i	C^j	C^k
172.86	137.17	123.54	122.16	71.02	57.82	48.46	42.81	35.60	26.53	25.58

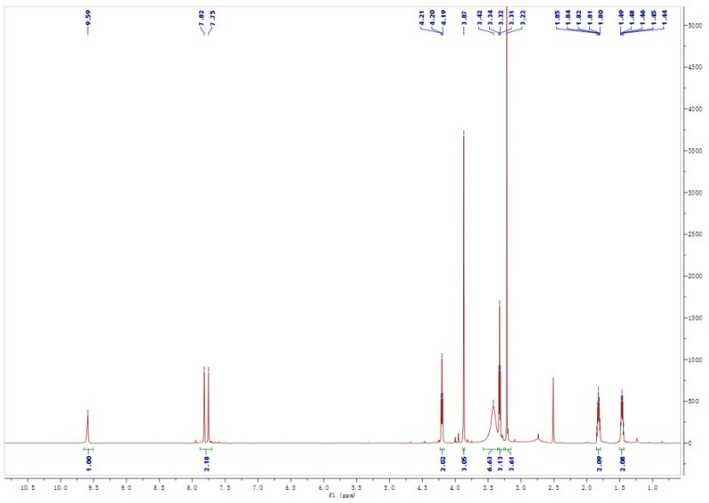


Figure S5. ^1H NMR spectrum of [MOBMIM][Lys]

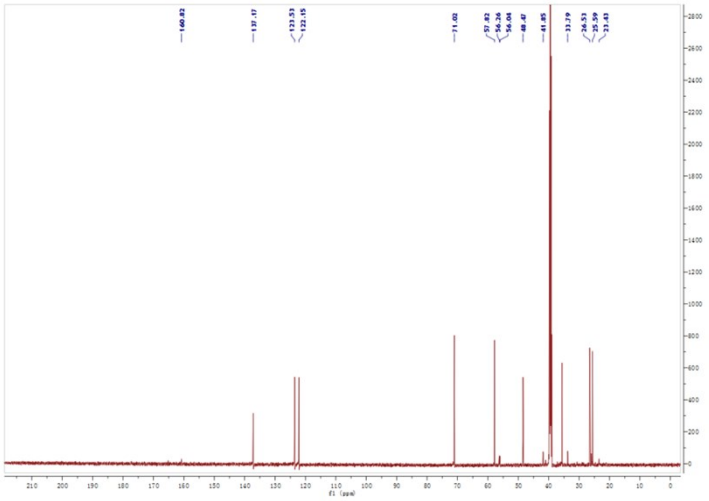


Figure S6. ^{13}C NMR spectrum of [MOBMIM][Lys]

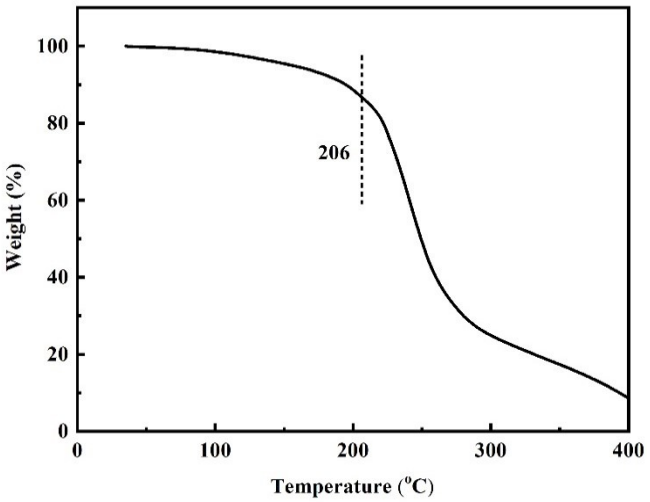


Figure S7. TGA curve for [MOBMIM][Lys]

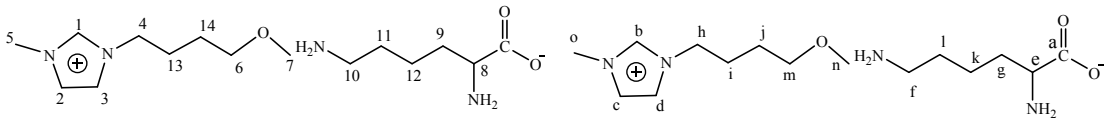


Figure S8. Assignments of NMR signals of [MOBMIM][Lys]

Table S3. ^{1}H NMR data of [MOBMIM][Lys] in DMSO (ppm)

H(1)	H(2)	H(3)	H(4)	H(5)	H(6,7,8)	H(9,10)	H(11,12)	H(13)	H(14)
9.59 (1H s)	7.82 (2H s)	7.75 (2H s)	4.20 (2H m)	3.87 (3H s)	3.42 (6H s)	3.34 (4H m)	3.22 (4H m)	1.82 (2H m)	1.48 (2H m)

Table S4. ^{13}C NMR data of [MOBMIM][Lys] in DMSO (ppm)

C^a	C^b	C^c	C^d	C^e	C^f	C^g	C^h	C^i	C^j	C^k	C^l	C^m	C^n	C^o
160.82	137.17	123.53	122.15	71.02	57.82	56.26	56.04	48.47	41.85	35.60	33.79	26.53	25.59	23.43

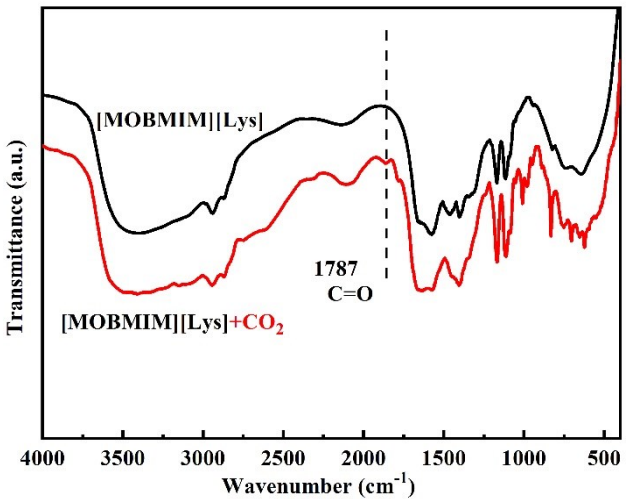


Figure S9. FT-IR spectra of the [MOBMIM][Lys] before and after adsorbing CO_2 (reaction conditions: IL 1 mmol, 50 °C, 0.5 MPa, 0.5 h)

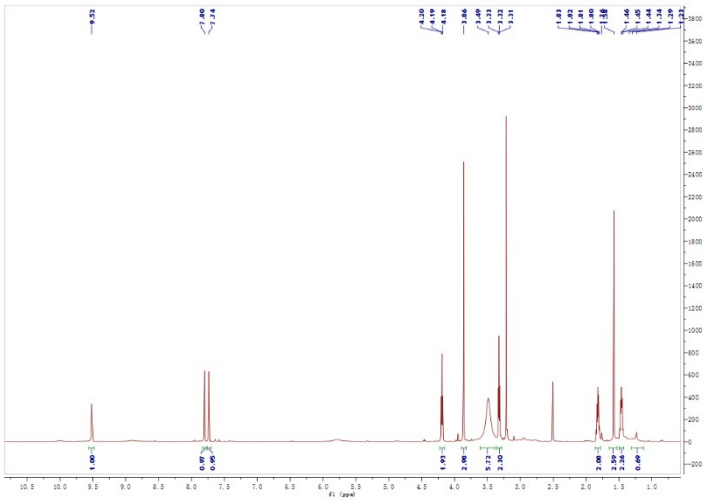


Figure S10. ^{1}H NMR spectrum of [MOBMIM][Arg]

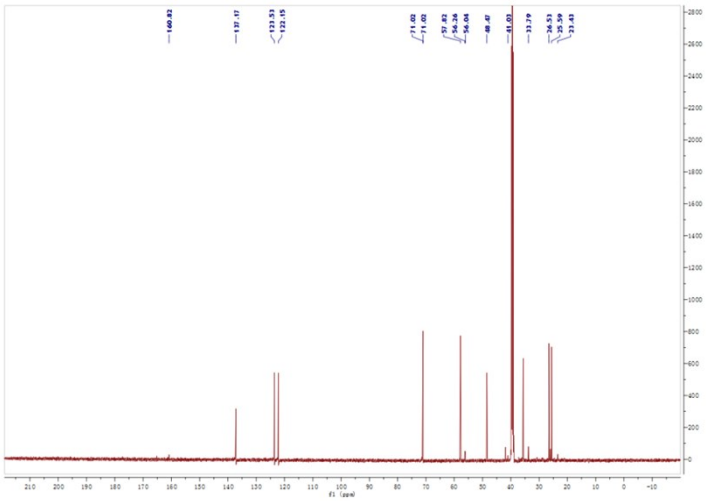


Figure S11. ^{13}C NMR spectrum of [MOBMIM][Arg]

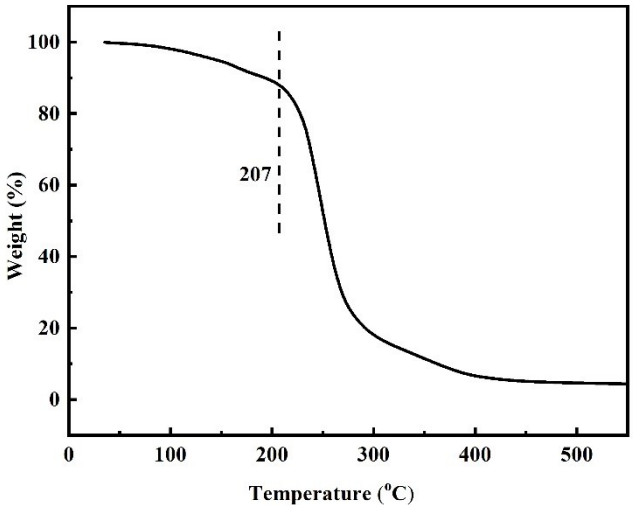


Figure S12. TGA curve for [MOBMIM][Arg]

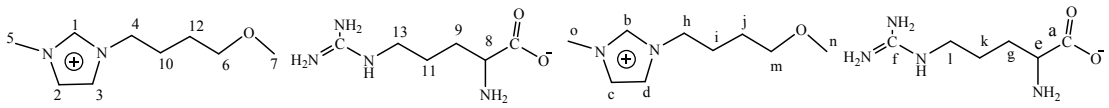


Figure S13. Assignments of NMR signals of [MOBMIM][Arg]

Table S5. ^{1}H NMR data of [MOBMIM][Arg] in DMSO (ppm)

H(1)	H(2)	H(3)	H(4)	H(5)	H(6,7,8)	H(9)	H(10)	H(11)	H(12)	H(13)
9.52 (1H s)	7.80 (2H s)	7.74 (2H s)	4.19 (2H m)	3.86 (3H s)	3.49 (6H s)	3.32 (2H m)	1.81 (2H m)	1.58 (1H s)	1.46 (2H m)	1.29 (1H m)

Table S6. ^{13}C NMR data of [MOBMIM][Arg] in DMSO (ppm)

C^a	C^b	C^c	C^d	C^e	C^f	C^g	C^h	C^i	C^j	C^k	C^l	C^m	C^n	C^o
160.82	137.17	123.53	122.15	71.02	57.82	56.26	56.04	48.47	41.85	41.03	33.79	26.53	25.59	23.43

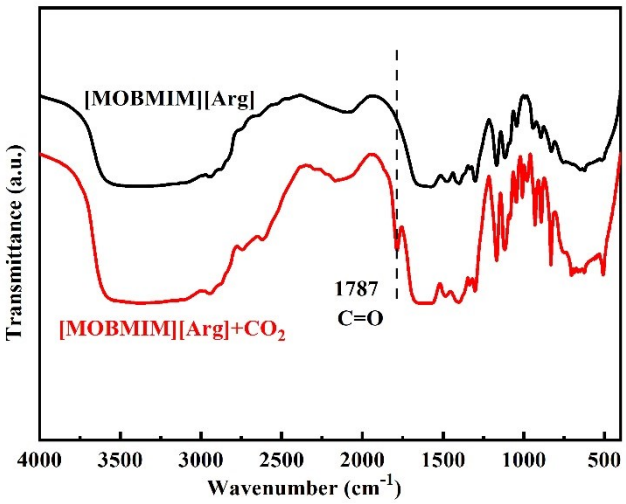


Figure S14. FT-IR spectra of the [MOBMIM][Arg] before and after adsorbing CO_2 (reaction conditions: IL 1 mmol, 50 °C, 0.5 MPa, 0.5 h)

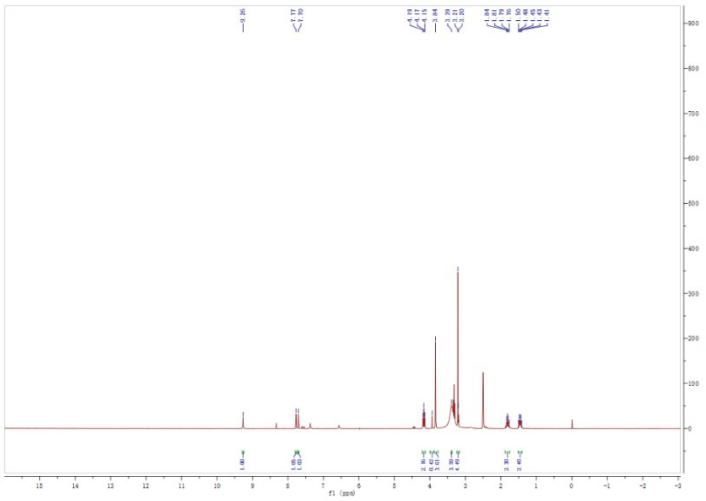


Figure S15. ^{1}H NMR spectrum of [MOBMIM][His]

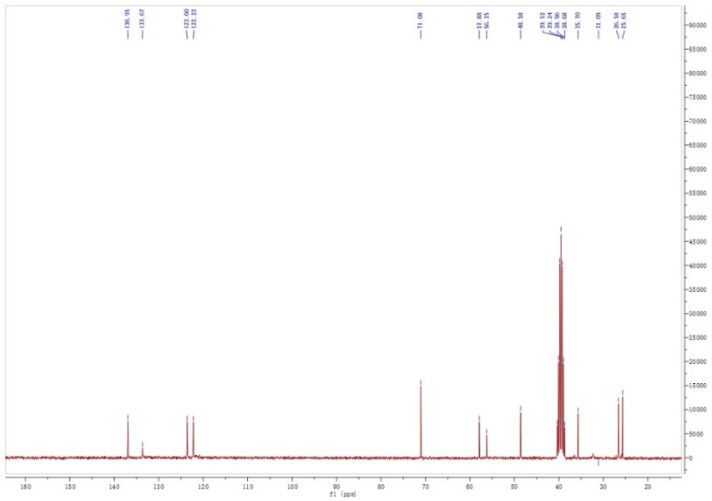


Figure S16. ^{13}C NMR spectrum of [MOBMIM][His]

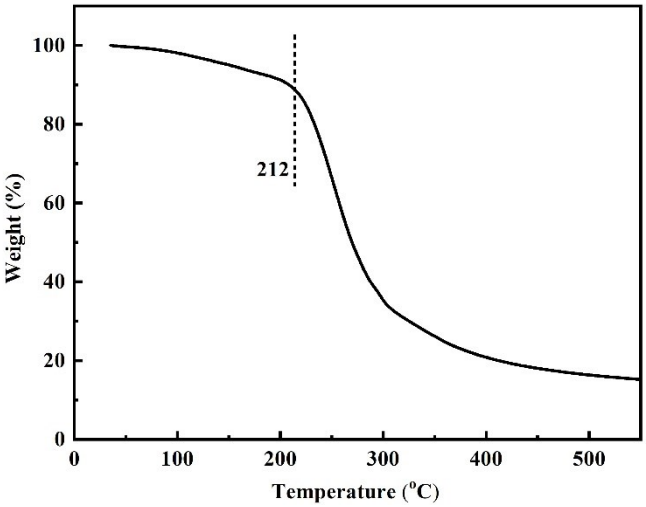


Figure S17. TGA curve for [MOBMIM][His]

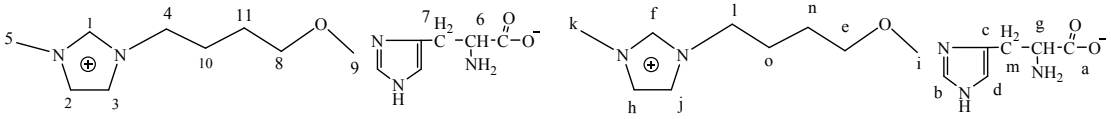


Figure S18. Assignments of NMR signals of [MOBMIM][His]

Table S7. ^{1}H NMR data of [MOBMIM][His] in DMSO (ppm)

H(1)	H(2)	H(3)	H(4)	H(5)	H(6,7,8)	H(9)	H(10)	H(11)
9.26 (1H s)	7.77 (2H s)	7.70 (2H s)	4.17 (2H m)	3.84 (3H s)	3.39 (3H s)	3. 20 (5H m)	1.79 (2H m)	1.45 (2H m)

Table S8. ^{13}C NMR data of [MOBMIM][His] in DMSO (ppm)

C^a	C^b	C^c	C^d	C^e	C^f	C^g	C^h	C^i	C^j	C^k	C^l	C^m	C^n	C^o
136.95	133.67	123.60	122.22	71.08	57.88	56.25	48.58	39.80	39.24	38.68	35.70	31.09	26.58	25.65

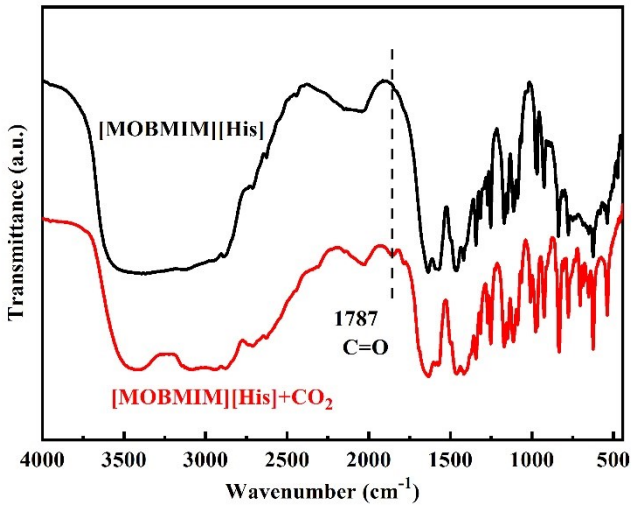


Figure S19. FT-IR spectra of the [MOBMIM][His] before and after adsorbing CO_2 (reaction conditions: IL 1 mmol, 50 °C, 0.5 MPa, 0.5 h)

The yields and selectivity were both calculated according to the external standard method. Take PC as an example, the peak area of PC standard solution in ethyl acetate with different concentrations was determined by gas chromatography. The obtained peak area was linearly fitted to PC concentration and a standard curve of peak area versus PC concentration was obtained in **Figure S20**. After each reaction, the product PC was extracted with ethyl acetate to a quantitative volume (20 mL), then the peak area of the PC product solution was measured by gas chromatography. Finally, PC yield was calculated through the standard curve of peak area versus PC concentration.

As for the selectivity, a standard curve of peak area versus PO concentration was obtained by the same method in **Figure S21**. The unreacted PO could be calculated from the peak area according to the standard curve of peak area versus PO concentration. Selectivity was equal to yield divided by conversion.

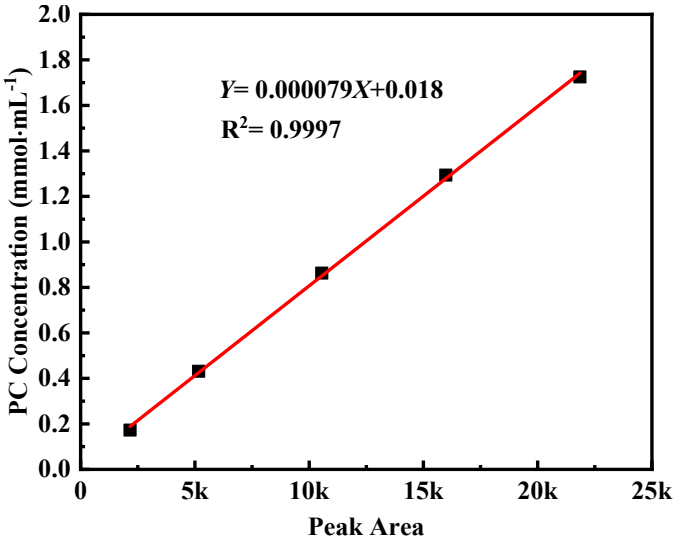


Figure S20. Standard curve of peak area *vs* PC concentration.

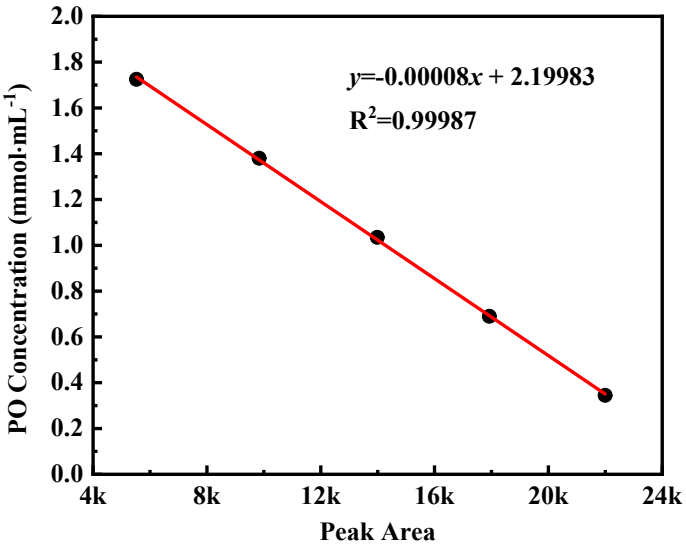
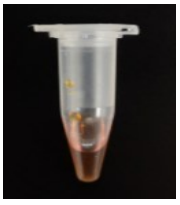
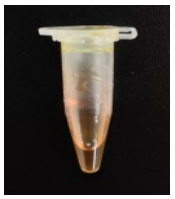
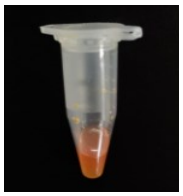
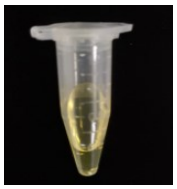
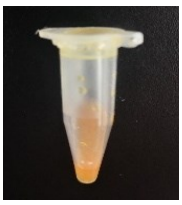


Figure S21. Standard curve of peak area *vs* PO concentration.

Table S9. Demonstration of the state for different amino acid ionic liquids

Entry	IL	State 1[a]		State 2[b]	
1	[MOBMIM]Lys	Liquid		Gel	
2	[MOBMIM]His	Liquid		Liquid	
3	[MOBMIM]Arg	Liquid		Gel	
4	[MOBMIM]Gly	Liquid		Liquid	
5	[c][MOBMIM]Arg	Liquid		Gel	
6	[d][MOBMIM]Arg	Liquid		Liquid	
7	[e][MOBMIM]Arg	Liquid		Liquid	

[a] State of the ionic liquid before adsorbing CO_2; [b] State of the ionic liquid after adsorbing CO_2; [c] 2 wt% water was adding to [MOBMIM]Arg; [d] 8 wt% water was adding to [MOBMIM]Arg; [e] 20 wt% water was adding to [MOBMIM]Arg.

Evidences of the efficient extraction of ionic liquids by ethyl acetate solvent was **in Figure S22a**. The [MOBMIM][Gly] AAIL is insoluble in ethyl acetate while both PO and PC are soluble in ethyl acetate. After the completion of catalytic reaction, by the exaction of [MOBMIM][Gly] AAILs with ethyl acetate, the AAIL catalyst was separated and recycled for the next run due to its insoluble in ethyl acetate while PO and PC soluble in ethyl acetate. For the recycling experiment, the AAIL catalyst was washed three times with ethyl acetate, then it was dried at 60 ºC under vacuum for another run.

In the case of the system of [MOBMIM][Gly] and H_2O in ethyl acetate (**Figure S22b**), it also presents two liquid phases: [MOBMIM][Gly] and H_2O in one phase, ethyl acetate phase, suggesting the easy separation of [MOBMIM][Gly] catalyst after extraction by ethyl acetate.

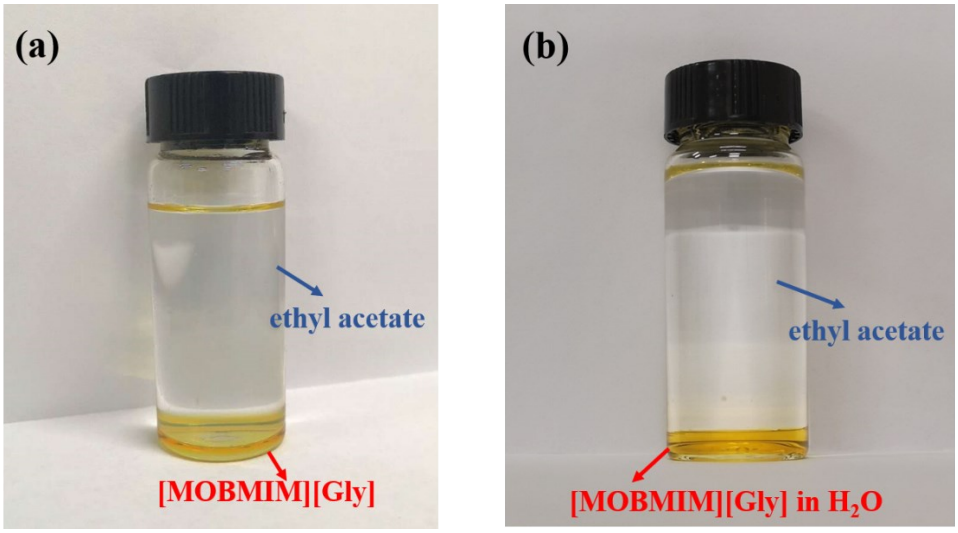


Figure S22. (a) The insoluble [MOBMIM][Gly] in ethyl acetate; (b) [MOBMIM][Gly] and H_2O in ethyl acetate.

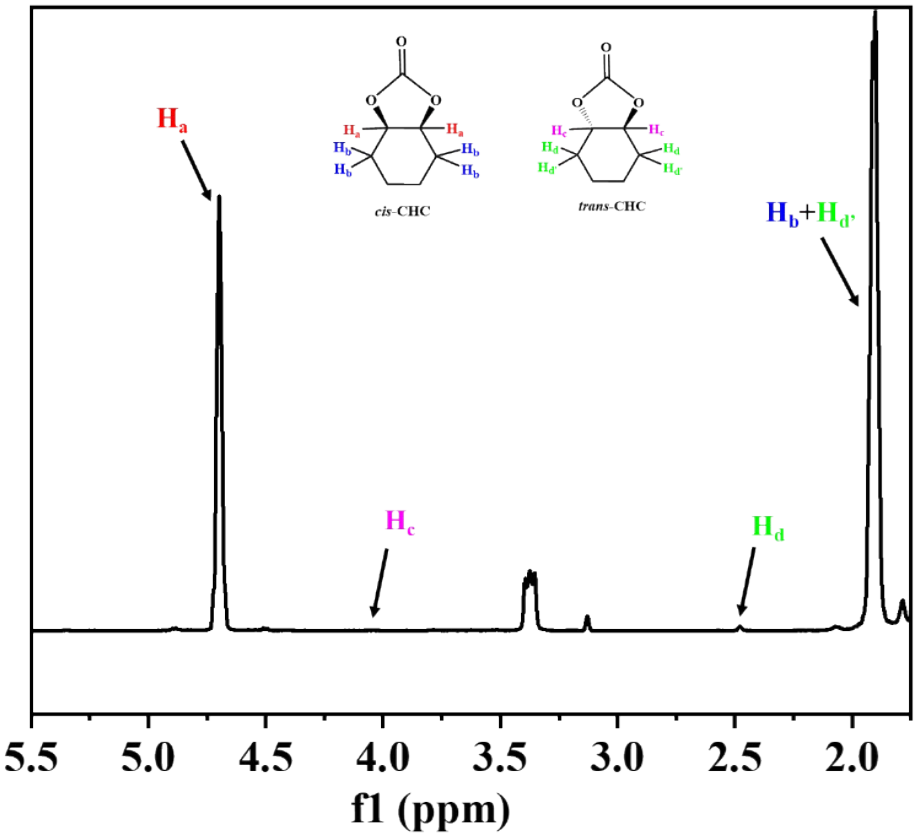


Figure S23. ^{1}H NMR spectrum of the products (cis/trans-cyclohexene carbonate, CHC) of the cycloaddition reaction between CO_2 and cyclohexene epoxide ($CDCl_3$, 400 MHz).