Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Highly active and robust [DBUH]Br@PILCOOH catalyst for CO_2 Cycloaddition: One-pot fabrication via ionic liquid immobilization on poly(ionic liquid)s

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S1: Synthesis of catalyst ILCOOH and [DBUH]Br [1].

3-Bromopropionic acid (2.0 g, 0.013 mol) was dissolved in anhydrous acetonitrile (2 mL) in a 10 mL Schlenk tube. DMAEMA (2.0 mL, 0.011 mol) was then added to the solution. The reaction mixture was stirred at 60 °C for 24 hours. After cooling to r.t., methyl tert-butyl ether (20 mL) was introduced, resulting in the precipitaion of a significant amount of solid. The solid was collected by centrifugation and washed three times with ethyl acetate. The desired product ILCOOH was obtained as white powder (3.0 g, 90% yield) after vacuum drying at room temperature. The ^{1}H NMR spectrum is shown in **Fig. S1** and the data are listed here. ^{1}H NMR (600 MHz, DMSO-d_6): δ 12.80 (s, 1H), 6.08 (s, 2H), 5.75 (t, J = 1.8 Hz, 2H), 4.54 - 4.50 (m, 4H), 3.80 - 3.75 (m, 4H), 3.68 - 3.62 (m, 4H), 3.15 (s, 10H), 2.90 - 2.83 (m, 4H), 1.90 (s, 5H).

Fig. S1. ^{1}H NMR(600 MHz, DMSO) spectra of the product from ILCOOH .

S2: Synthesis of IL [DBUH]Br [2].

NH_4Br (0.685 g, 7 mmol) was dissolved in anhydrous methanol (10 mL) and DBU (1.05 mL, 7 mmol) was then added. The mixture was stirred overnight at 60 °C under reflux. Upon completion of the reaction, the solvent was removed by rotary evaporation. The concentrated solution was dissolved in dichloromethane (6 mL) and added to ethyl acetate (14 mL), resulting in the formation of a significant amount of precipitate. The precipitate was collected by centrifugation and washed three times with methyl tert-butyl ether (20 mL each time). Finally, [DBUH]Br was obtained as white powder (2.8 g, 87% yield) after vacuum drying at room temperature (**Fig. S2.**). ^1H NMR (600 MHz, DMSO-d_6) δ 3.59 - 3.54 (m, 1H), 3.49 (t, J = 5.9 Hz, 1H), 3.25 (t, J = 5.8 Hz, 1H), 2.70 - 2.66 (m, 1H), 1.92 (p, J = 5.8 Hz, 1H), 1.67 (q, J = 5.8 Hz, 1H), 1.62 (tt, J = 10.6, 5.6 Hz, 2H).

Fig. S2. ^1H NMR(600 MHz, DMSO) spectra of the product from [DBUH]Br.

S3. GC-MS spectra of the reaction mixture for the preparation of the cyclic carbonates.

Fig. S3. GC-MS detection of the reaction mixturer of CO_2 - ECH cycloaddition catalyzed by [DBUH]Br@PILCOOH.

S4. XPS spectra of the catalysts.

Fig. S4. XPS spectra of [DBUH]Br@PIL and [DBUH]Br.

Fig. S5. XPS spectra of [DBUH]Br@PIL-1/0.6/1.

S5. Optimization of the reaction parameters

Using the as-prepared [DBUH]Br@PILCOOH catalyst, the effects of catalyst dosage, reaction temperature, reaction time and CO_2 pressure on the catalytic activity were examined (**Fig. S6**). As illustrated in **Fig. S6a**, increasing the amount of [DBUH]Br@PILCOOH led to a higher CPC yield. The yield reached 97.8% with 30 mg of catalyst, and no significant improvement was observed with further increase in catalyst dosage. In terms of temperature, the product yields were low at room temperature (33.8%) but increased significantly to 97.8% as the temperature rose to 80 ^{o}C (Fig.e S6b). Considering the mildness of the conditions and energy consumption associated with higher temperature, 80 ^{o}C was chosen as the optimal temperature. As shown in Fig. S6c, the CPC yield rapidly increased to 74.8% within 4 hours at 80 ^{o}C, then gradually reached 97.8% over the next 20 hours, with no notable yield increase for extended reaction times. Regarding the reaction pressure, when CO_2 pressure rose from 0.1 to 1.5 MPa, the yield increased from 74.8% to 99% in 4 hours (Fig. S6d).

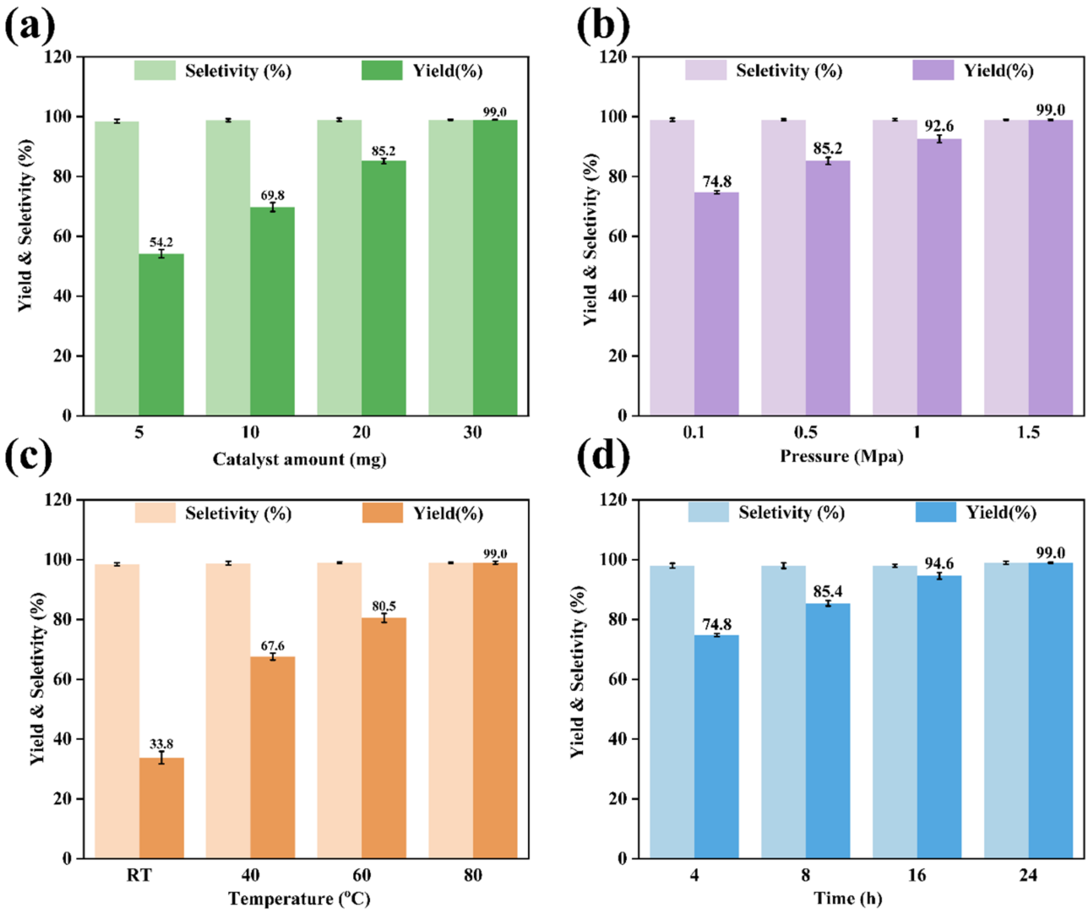
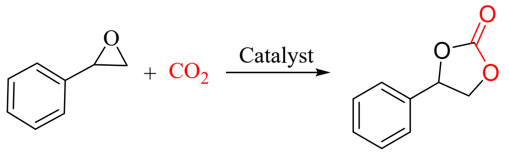


Fig. S6. Effect of reaction conditions on the catalytic activity. (a) The effect of catalyst dosage. ECH (5 mmol), CO_2 (1 atm, balloon), 24 h; (b) The effect of temperature. ECH (5 mmol), [DBUH]Br@PILCOOH (30 mg), CO_2 (1 atm, balloon), 24 h; (c) The effect of time. ECH (5 mmol), [DBUH]Br@PILCOOH (30 mg), CO_2 (1 atm, balloon), 80 ^{o}C; (d) The effect of pressure. ECH (5 mmol), [DBUH]Br@PILCOOH (30 mg), 80 ^{o}C, 4 h.

S6. Comparison of this work with the literature reports

Table S1. A comparison of the as-prepared catalyst with various reported catalytic systems concerning the CO_2 cycloadditin with styreneoxide.



Entry	Catalyst system	Temperature (°C)	Time (h)	Pressure (MPa)	Yield (%)	Ref.
1	POM3-IM (Ethanol)	120	12	1	89	[3]
2	$ZnBr_2$/polymer(A2+A6) (DMF)	25	120	0.1	93	[4]
3	MIL-101-IMBr-6 (Dichloromethane)	80	4	0.8	47	[5]
4	UIO-67-IL (TBAB)	90	3	0.1	98	[6]
5	POM@ImTD-COF (TBAB)	80	24	0.1	97	[7]
6	IL@P-BC (TBAB)	100	5	3	89	[8]
7	PIL-DVB-IV	110	6	2	89	[9]
8	MPOP-4A-IL	120	16	1	86	[10]
9	I-HMON-L-C-2.5	80	10	0.5	94	[11]
10	Pym-EtBr@Zn-MOF-NH_2	90	6	0.6	95	[12]
11	MA-PDA IL@COF	70	14	0.1	92	[13]
12	HPMBr0.5	80	36	0.1	94.7	[14]
13	HIP-His-1	120	12	1.25	93	[15]
14	[DBUH]Br@PILCOOH	80	24	0.1	98	This work

S7. Hot filtration experiment.

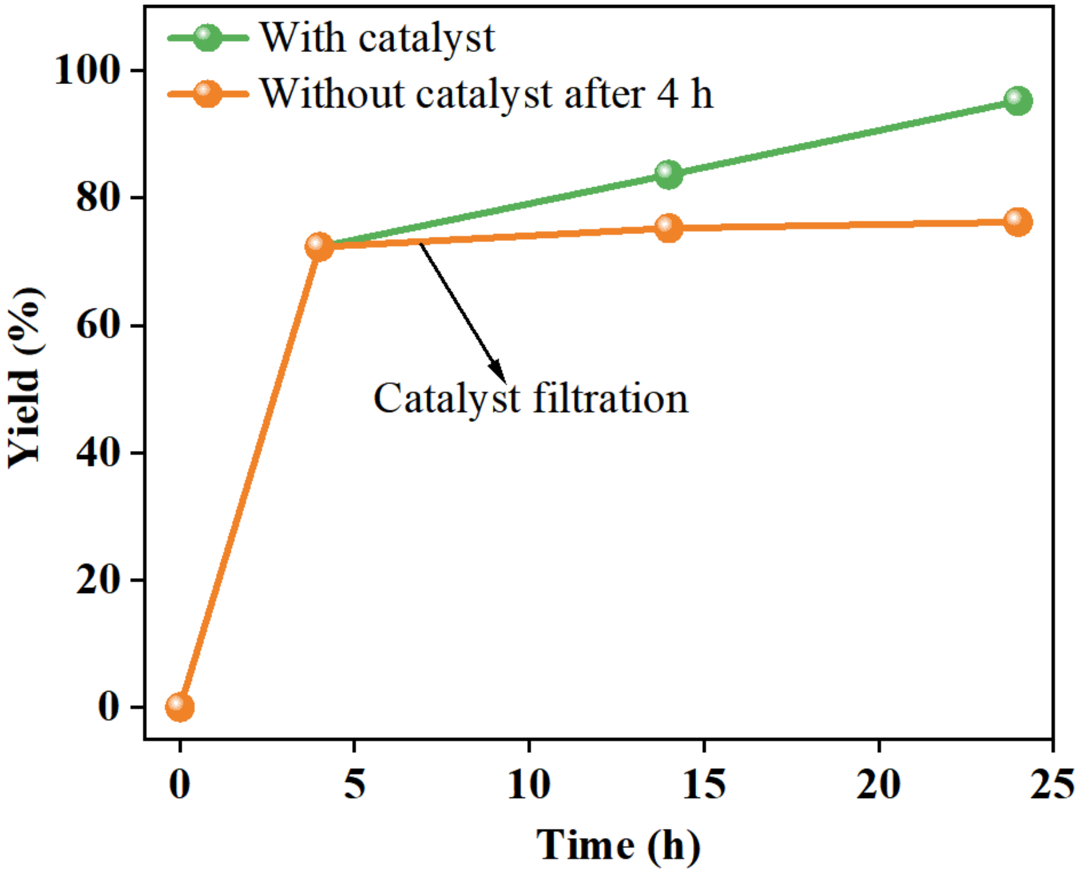
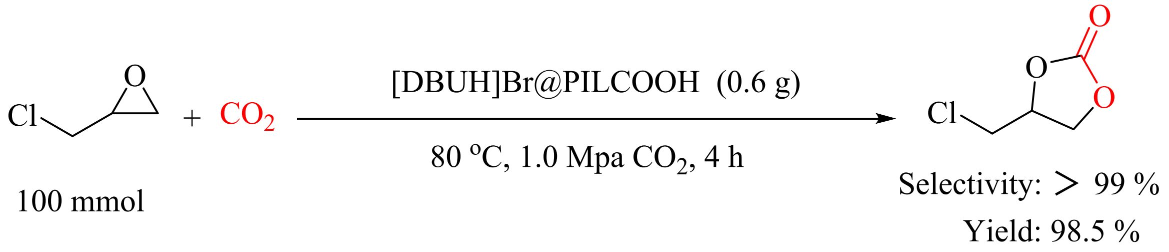


Fig. S7. Reaction conditions: ECH 20 mmol, [DBUH]Br@PILCOOH 120 mg, 80 °C, CO_2 (1 atm, balloon), 0 ~ 24 h.

S8. The scale-up synthesis of CPC.



Scheme S1. Scale-up synthesis of CPC.

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