

Supporting Information

Ionic liquid [DBUH][BO₂]: excellent catalyst for chemical fixation of CO₂ at mild conditions

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1. General

CO₂ was supplied by Tianjin Feilin Gases Co., Ltd. with a purity of 99.99%. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (98%) and 2-amino-5-bromobenzonitrile (99%) were purchased by J&K Scientific Ltd. 2-Amino-5-chlorobenzonitrile (98%) and 2-aminobenzonitrile (98%) were obtained from 3A chemicals Ltd. Boric acid (99%), metaboric acid (99%) and glacial acetic acid (99%) were purchased by Shanghai Aladdin Bio-Chem Technology Co., Ltd. Epichlorohydrin (99%), butylene oxide (98%) and 3-bromo-1,2-epoxypropane (97%) were purchased by Tokyo Chemical Inorganic Co., Ltd. 1,2-Epoxy-3-phenoxy-propane (99%) was purchased by InnoChem Co., Ltd. N,N-dimethylformamide (AR), dimethyl sulfoxide (AR), tert-butyl methyl ether (AR), ethanol (AR) and diethyl ether (AR) were purchased by Shanghai Macklin Biochemical Co., Ltd. Dimethyl sulfoxide-d₆ (99.9%) was supplied by Cambridge Isotope Laboratories, Inc. The chemicals above were used without further purification.

The ILs 1-butyl-3-methylimidazolium nitrate ([Bmim][NO₃]), 1-butyl-3-methylimidazolium dicyanamide ([Bmim][N(CN)₂]) and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) were supplied by Lanzhou Yulu Fine Chemical Co., LTD. The ILs were used without further purification.

Standard column chromatography was performed on 20-40 μm silica gel using flash column chromatography. NMR spectra were recorded on a Bruker Fourier 400 MHz NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C).

2. Experimental Results

2.1 The procedure for the synthesis of [DBUH][BO₂]

The IL [DBUH][BO₂] were synthesized by neutralization. In the experiment, methanol (10 mL), DBU (10 mmol, 1.5224 g) and HBO₂ (10 mmol, 0.4382 g) were loaded into a 50 mL flask in a water bath of 30 °C and the neutralization reaction was allowed to proceed for 24 h. Then, the solvent was removed by rotary evaporation under vacuum at 70 °C, and finally the IL was obtained.

2.2 Figures S1 - S3

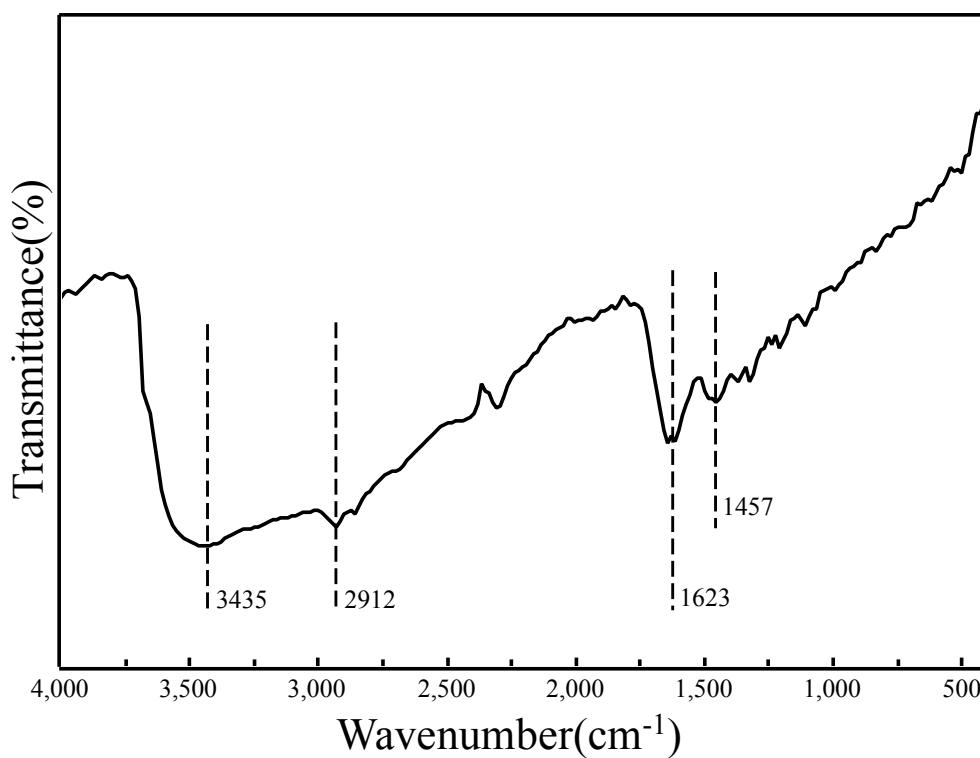


Figure S1 The FT-IR spectroscopy of IL [DBUH][BO₂]

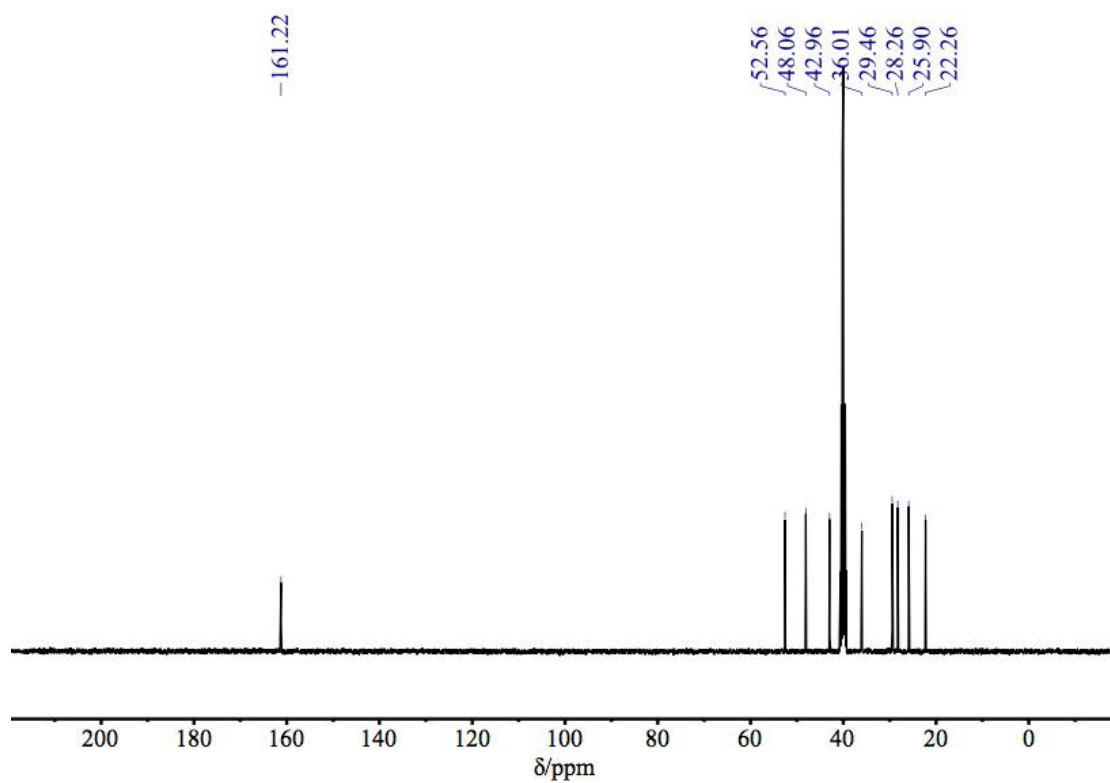
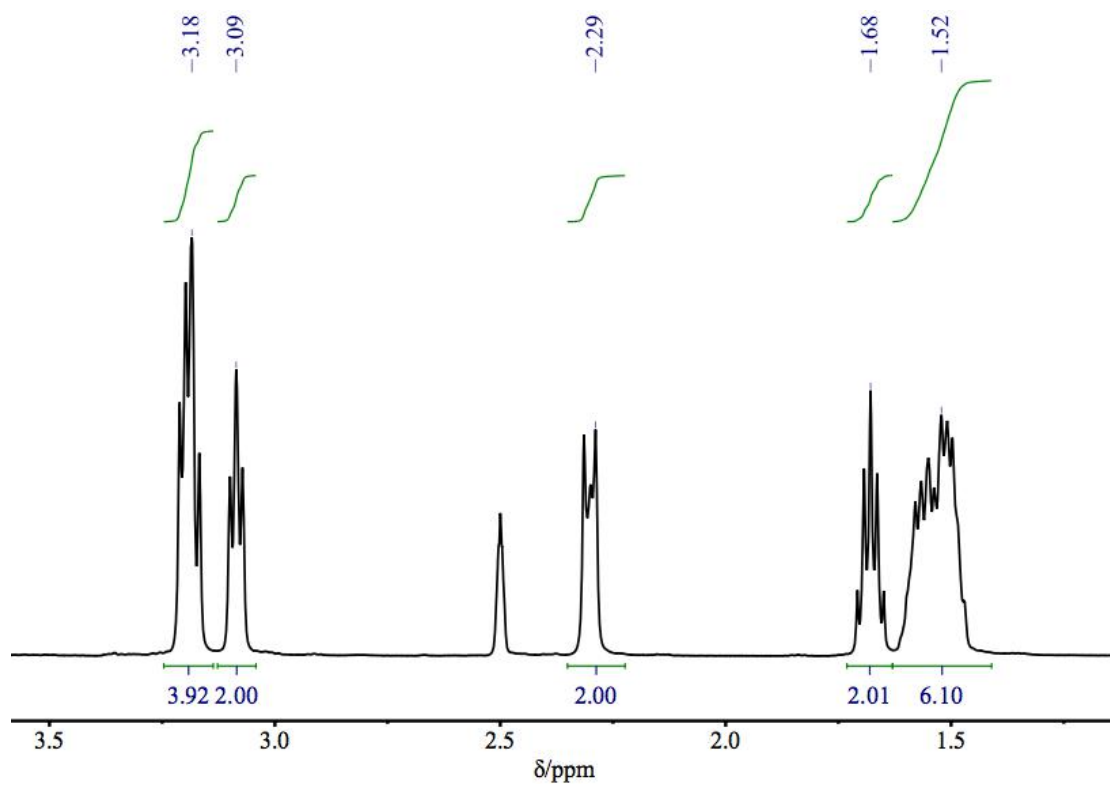


Figure S2 The ^1H and ^{13}C NMR spectroscopy of IL [DBUH][BO₂]

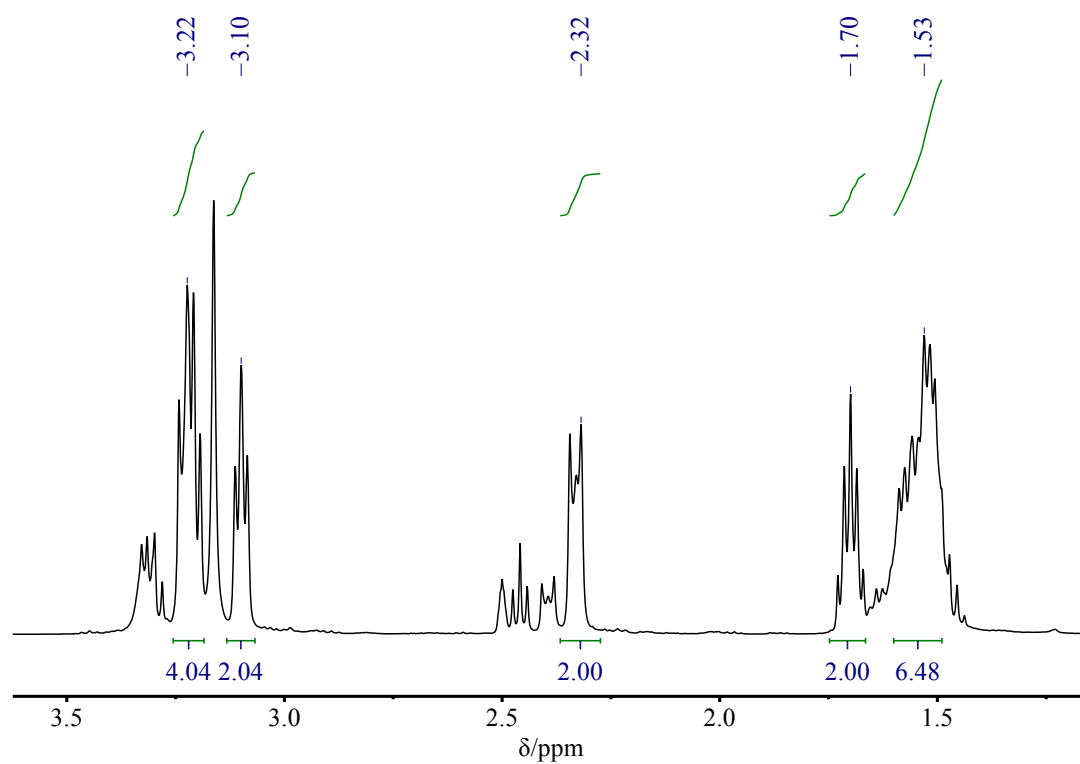


Figure S3 The ^1H spectroscopy of IL [DBUH][BO₂] after used five times.

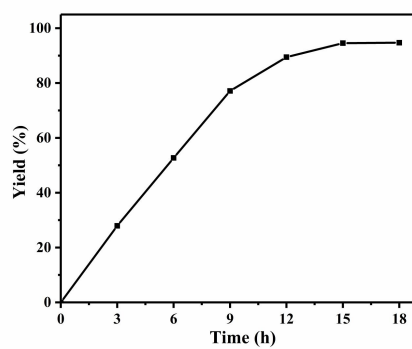


Figure S4 The effect of reaction time on the yield of **2a** with 25% [DBUH][BO₂]. Reaction conditions: **1a** (2 mmol, 0.1850 g), CO₂ (0.1 MPa), 30 °C.

Table S1 The catalytic performance of halogen-free ILs for the reaction of epichlorohydrin and CO₂.

| IL | Reaction Temperature (°C) | Reaction Time (h) | CO ₂ Pressure (MPa) | IL/catalyst molar ratio (%) | Yield (%) | Recyclability |
|-----------------------------------------------------|---------------------------|-------------------|--------------------------------|-----------------------------|-----------|-------------------------|
| [P4444][2-OP] ^[1] | room temp. | 20 | 0.1 | 10 | 90 | --- ^a |
| [DBUH] ₃ NbO ₅ ^[2] | 130 | 5 | 3 | 3 | 90 | Recycle for eight times |
| [DBUH][BO ₂] (this work) | room temp. | 6 | 0.1 | 75 | 95 | Recycle for five times |

a: ---means the work did not test the recyclability.

Reference:

[1] G. F. Yuan, Y. F. Zhao, Y. Y. Wu, , R. P. Li, , Y. Chen, D. M. Xu, Z. M. Liu, *Science China Chemistry*, **2017**, 60, 958 – 963.

[2] A. J. Chen, C. Chen, Y. H. Xiu, X. R. Liu, J. Z. Chen, L. Guo, R. Zhang, Z. S. Hou, *Green Chem.*, **2015**, 17, 1842-1852.

2.3 Typical procedure for the synthesis of cyclic carbonates

As an example, the procedure using **1a** as the substrate was described, and those for other substrates were similar. **1a** (2 mmol, 0.1850 g), [DBUH][BO₂] (1.5 mmol, 0.2941 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO₂ into the reactor. Then the pressure of CO₂ was kept at 0.1 MPa using a balloon with CO₂. The reactor was placed in a constant temperature water bath and the reaction mixture was stirred for desired time. After the reaction, the reactor was placed in ice water for 20 minutes and the reaction mixture was passed through a plug of silica gel. The crude mixture was purified by silica gel column chromatography (EtOAc:petroleumether = 1:15) to obtain the desired cyclic carbonate **2a**.

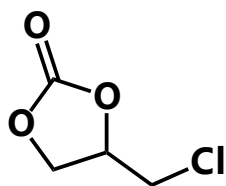
The procedures for reuse of the IL: **1a** (2 mmol, 0.1850 g) and [DBUH][BO₂] (1.5 mmol, 0.2941 g) were loaded into a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. The air in the

reactor was removed by blowing CO₂ into the reactor. Then the pressure of CO₂ was kept at 0.1 MPa using a balloon with CO₂. The reactor was placed in a water bath of 30 °C and the reaction mixture was stirred for 6 h. After the reaction, the product was extracted by diethyl ether (2 mL*3) and the yield was determined by ¹H NMR using DMF as an internal standard, especially, the extraction experiments were conducted under CO₂ atmosphere and 0 °C. The IL separated was used directly for the next run after dried under vacuum at 60 °C for 24 h.

2.4 Typical procedure for the synthesis of quinazoline-2,4(1H,3H)-diones

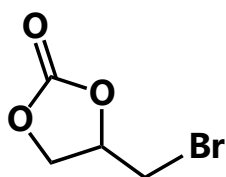
As an example, the procedure using 2-aminobenzonitrile as the substrate was described, and those for other substrates were similar. In a typical experiment, 2-aminobenzonitrile (2 mmol, 0.2643 g), Toluene (1 mL) and [DBUH][BO₂] (1.5 mmol, 0.2941 g) were loaded into a 22 mL stainlesssteel batch reactor equipped with a magnetic stirrer. The air in the reactor was removed by blowing CO₂ through the reactor. Then the pressure of CO₂ was kept at 0.1 MPa using a balloon with CO₂. The reactor was placed in a 30 °C oil bath in desired time. After reaction, 25 mL water was added into the reactor, and the mixture was centrifuged to precipitate the product. Then the product was washed with tert-butyl methyl ether (3 × 15 mL) and ethanol (3 × 15 mL). Then dried at 95 °C for 3 h to obtain the target product.

3. NMR data of products



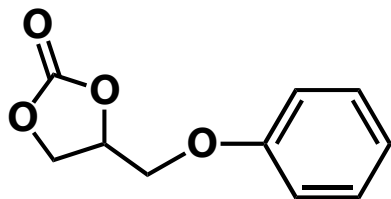
4-Chloromethyl-[1,3]dioxolan-2-one

¹H NMR (400 MHz, DMSO) δ 5.16 – 5.06 (m, 1H), 4.58 (t, *J* = 8.6 Hz, 1H), 4.26 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.96 (ddd, *J* = 16.6, 12.3, 3.8 Hz, 2H). ¹³C NMR (101 MHz, DMSO) δ 154.95, 75.42, 67.35, 45.79.



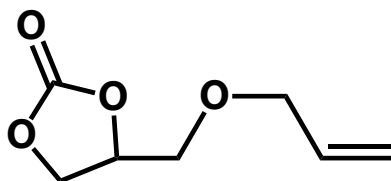
4-Bromomethyl-[1,3]dioxolan-2-one

^1H NMR (400 MHz, DMSO) δ 5.14 – 4.99 (m, 1H), 4.57 (t, J = 8.6 Hz, 1H), 4.22 (dd, J = 8.7, 5.6 Hz, 1H), 3.84 (ddd, J = 15.2, 11.6, 4.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 154.82, 74.99, 68.43, 34.88.



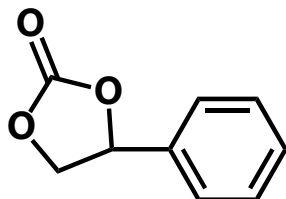
4-Phenoxymethyl-[1,3]dioxolan-2-one

^1H NMR (400 MHz, DMSO) δ 7.29 (dd, 2H), 7.02 - 6.93 (m, 3H), 5.23 – 5.02 (m, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.27 (m, 2H), 4.22 (dd, J = 8.7, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 158.91, 155.36, 130.09, 121.54, 114.79, 72.32, 70.87, 62.51.



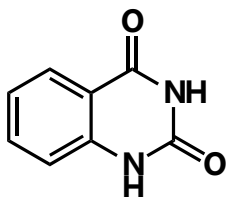
4-((Allyloxy)methyl)-[1,3]dioxolan-2-one

^1H NMR (400 MHz, DMSO- d_6) δ 5.81 (s, 1H), 5.24 (d, 1H), 5.10 (d, 1H), 4.49 (s, 1H), 4.24 (s, 1H), 3.92 (s, 2H), 3.81 (s, 1H), 3.51 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 155.72, 133.98 117.45 76.53 72.33 72.08 61.81.



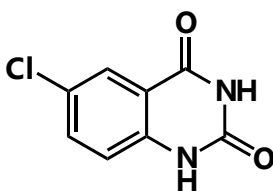
4-phenyl-1,3-dioxolan-2-one

^1H NMR (400 MHz, DMSO- d_6) δ 7.40 (dd, 2H), 7.34 - 7.14 (m, 3H), 5.51 (s, 1H), 4.60 (m, 1H), 4.38 (d, J = 8.7, 1H). ^{13}C NMR (101 MHz, DMSO) δ 154.32 133.89 129.33 127.84 127.65 94.56 66.21.



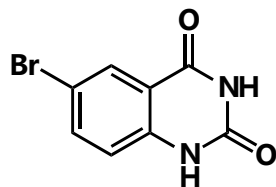
2,4(1H,3H)-Quinazolidione

^1H NMR (300 MHz, DMSO) δ 11.21 (s, 2H), 7.88 (dd, J = 8.1, 1.4 Hz, 1H), 7.76 – 7.54 (m, 1H), 7.38 – 7.07 (m, 2H). ^{13}C NMR (75 MHz, DMSO) δ 163.30, 150.78, 141.34, 135.41, 127.40, 122.77, 15.80, 114.80.



6-Chloroquinazoline-2,4(1H,3H)-dione

^1H NMR (400 MHz, DMSO) δ 11.30 (s, 2H), 7.79 (s, 1H), 7.66 (d, $J = 8.6$ Hz, 1H), 7.17 (d, $J = 8.7$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 162.47, 150.83, 140.72, 135.17, 126.49, 126.35, 118.24, 116.31.



6-Bromoquinazoline-2,4(1H,3H)-dione

^1H NMR (400 MHz, DMSO) δ 11.35 (d, $J = 66.8$ Hz, 2H), 7.93 (d, $J = 2.3$ Hz, 1H), 7.78 (dd, $J = 8.7$, 2.3 Hz, 1H), 7.12 (d, $J = 8.7$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 162.21, 150.50, 140.56, 137.97, 129.41, 118.26, 116.72, 114.31.