Supporting Information

Efficient Transformation of Atmospheric CO_2 to Carbonates by Bifunctional Ionic Liquids under Mild Conditions

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Xiangping Zhang[a,c]*

Supporting information

1. Experimental section

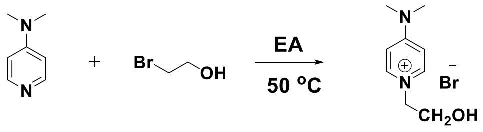
1.1 General information

Carbon dioxide and nitrogen were supplied by Beijing Analytical Instrument Factory with a purity of 99.99% and 99.999% separately. Simulated flue gas was made by controlling the gas flow rate (CO_2:N_2=3:17) using gas flowmeter. 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU 99%), 4-dimethylaminopyridine (99%), bromoethane (98%), bromoacetic acid (98%), 2-bromoethanol (95%), 1,3-dibromo-2-propanol (95%), 4-bromophbenol (98%), 1-butyl-3-methylimidazolium bromide (97%) and all of the epoxides unless otherwise specified were bought from Aladdin Reagent Co. Glycidyl phenyl ether was bought from TCI Shanghai. Lithium Bis(trifluoromethanesulphonyl)imide and ethylacetate were bought from Sinopharm Chemical Reagent Co., Ltd, and were used without further purification. All calculations were carried out with B3LYP-D3/6-31+G** level implemented in Gaussian 09 package.

1.2 Synthesis of catalysts

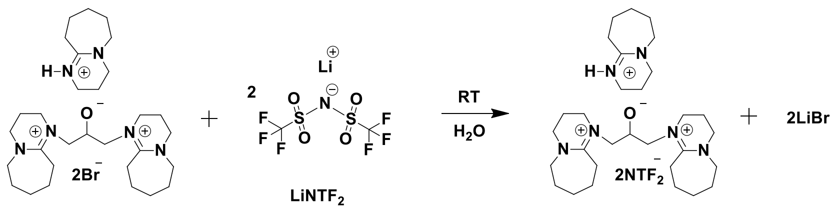
Scheme S1 One step synthesis of catalysts in this study.

All of the DBU-based catalysts with bromide were synthesized by using one-step method. **1b** was chosen as a model to show the process. In a typical reaction, bromoacetic acid (20.00 mmol) was dissolved in ethyl acetate. Then DBU (40.00 mmol) was dropped into the flask. The mixture was stirred for an hour at room temperature. After the reaction, the top phase was immediately poured out and the residue liquid was washed three times with ethyl acetate in separatory funnel and dried at 50^{o}C for 24 h under vacuum. Finally, a viscous liquid was obtained.



Scheme S2 One step synthesis of catalyst **1e**.

4-dimethylaminopyridine (DMAP) based ILs (**1e**) were synthesized according to the literature[59]. In a typical reaction, DMAP (50.00 mmol) and 2-bromoethanol (60.00 mmol) were dissolved in ethyl acetate and added into a 250 mL three-necked flask. The mixture was stirred for 12 h at 50 ^oC. When it is cool down, the top phase was poured out and the solid was washed three times with ethyl acetate and dried at 50^{o}C in a vacuum oven for one day.



Scheme S3 Synthesis of catalyst **1f** in this study.

DBU-based catalysts **1g** with NTF_2 was synthesized by using ion-exchange method. In a typical reaction, **1f** (4.00 mmol) was added into a 250 mL flask and dissolved in water. Then Bis(trifluoromethanesulphonyl)imide (10.00 mmol) was poured into the flask. The mixture was stirred for 24 h at room temperature. After the reaction, the top phase was poured out and the residue was washed three times with water in separatory funnel. Then the product was dried at 50^{o}C for 24 h under vacuum.

1.3 Characterization of the catalysts

The morphology was observed through a scanning electron microscope (JEOL JSM 6700F). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 spectrophotometer with anhydrous KBr as standard (Thermo Electron Co.). NMR spectra were recorded on a Bruker AVANCE III HD 600 spectrometer with DMSO-d_6 as solvent.

1.4 Procedure of the cycloaddition reaction of CO_2 with propylene oxide

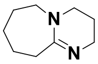
The coupling reaction of carbon dioxide and epoxide was carried out in a 20 mL Schlenk tube with a magnetic stirrer and an automatic temperature control system in a fume hood. In a typical reaction, 0.5ml of epichlorohydrin and appropriate amounts of catalyst were charged into the reactor at room temperature. Then, a balloon of CO_2 was connected to the schlenk tube, control the temperature within the desired range afterwards. After the reaction, the remaining CO_2 was vented out slowly. The yield of the products was characterized by HNMR spectroscopy of the crude reaction mixture by using $CDCl_3$ as solvents.

1.5 Recycle experiment

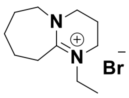
After the reaction, 10 ml water was poured in to the schlenk tube to wash the product. The mixture was stirred for 1 h at room temperature. The product was separated from the mixture by filtration and washed one more time with water. Afterwards, the product was dried at 80 ^{o}C for 24 h under vacuum. The yield of the product was calculated by weight. The liquid phase was first separated with **2f** in a separatory funnel. Then water was removed by vacuum distillation. The obtained catalysts were washed three times by ethyl acetate and dried at 50^{o}C for 24 h under vacuum, and ready for the recycling experiment.

2. Experimental characterization data

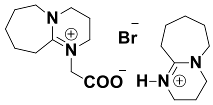
Characterization of the catalysts

DBU: 

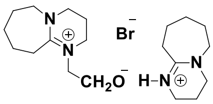
Liquid:^{1}H NMR (600 MHz, DMSO): 3.14 (dd, *J* = 10.8, 3.7 Hz, 4H), 3.09 – 3.04 (m, 2H), 2.27 – 2.21 (m, 2H), 1.64 (dq, *J* = 8.1, 5.9 Hz, 2H), 1.57 (ddd, *J* = 11.0, 5.6, 2.0 Hz, 2H), 1.54 – 1.45 (m, 4H). ^{13}CNMR (151 MHz, DMSO): 159.50, 51.75, 47.44, 43.45, 36.33, 29.02, 28.06, 25.74, 22.31.

1a: 

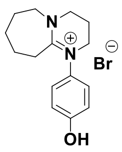
Solid powder:^{11}H NMR (600 MHz, DMSO): δ 3.68 – 3.62 (m, 2H), 3.57 (q, *J* = 7.2 Hz, 2H), 3.48 (dt, *J* = 17.0, 5.8 Hz, 4H), 2.92 – 2.86 (m, 2H), 2.04 – 1.90 (m, 2H), 1.74 – 1.67 (m, 2H), 1.67 – 1.58 (m, 4H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, DMSO):165.67, 53.86, 48.41, 48.08, 45.87, 27.69, 27.00, 25.46, 22.65, 19.61, 13.58.

1b: 

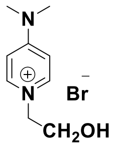
Viscous solid: ^{1}H NMR (600 MHz, DMSO): δ 9.69 (s, 1H), 3.55 (dd, *J* = 19.5, 15.0 Hz, 4H), 3.49 (t, *J* = 5.8 Hz, 4H), 3.30 (d, *J* = 31.3 Hz, 2H), 3.25 (t, *J* = 5.7 Hz, 4H), 2.80 – 2.57 (m, 4H), 2.02 – 1.85 (m, 4H), 1.72 – 1.65 (m, 4H), 1.65 – 1.57 (m, 8H). ^{13}C NMR (151 MHz, DMSO): 165.37, 53.36, 47.87, 37.52, 31.59, 28.19, 25.89, 23.28, 18.84.

1c: 

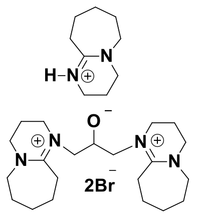
Solid: ^{1}H NMR (600 MHz, DMSO): δ 9.67 (s, 1H), 3.60 – 3.54 (m, 4H), 3.50 (t, *J* = 5.8 Hz, 4H), 3.33 (s, 2H), 3.26 (t, *J* = 5.7 Hz, 4H), 2.78 – 2.62 (m, 4H), 1.96 – 1.87 (m, 4H), 1.72 – 1.65 (m, 4H), 1.65 – 1.57 (m, 8H). ^{13}C NMR (151 MHz, DMSO): 165.35, 53.63, 48.18, 37.48, 31.52, 27.89, 25.66, 23.29, 19.13.

1d: 

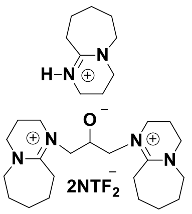
Solid: ^{1}H NMR (600 MHz, DMSO): δ 12.04 (s, 1H), 7.30 – 6.89 (m, 2H), 6.61 – 6.45 (m, 2H), 3.34 (dd, J = 11.4, 6.9 Hz, 2H), 3.31 (t, *J* = 5.9 Hz, 4H)., 3.16 (t, J = 5.6 Hz, 2H), 1.83 – 1.75 (m, 2H), 1.65 – 1.57 (m, 2H), 1.57 – 1.49 (m, 4H). ^{13}C NMR (151 MHz, DMSO): δ 163.52, 162.08, 131.48, 118.69, 105.41, 52.63, 47.65, 32.87, 28.56, 26.77, 24.33, 20.22.

1e: 

Solid: ^{1}H NMR (600 MHz, DMSO) δ 8.26 – 8.23 (m, 2H), 7.06 – 7.03 (m, 2H), 5.10 (t, J = 5.1 Hz, 1H), 4.28 – 4.17 (m, 2H), 3.79 – 3.65 (m, 2H), 3.19 (s, 6H). ^{13}C NMR (151 MHz, DMSO) δ 156.44 (s), 142.97 (s), 107.81 (s), 60.55 (s), 59.49 (s).

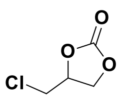
1f: 

Solid: ^{1}H NMR (600 MHz, DMSO): δ 9.61 (s, 1H), 3.64 – 3.53 (m, 6H), 3.49 (t, *J* = 5.8 Hz, 6H), 3.30 (s, 4H), 3.26 (t, *J* = 5.7 Hz, 6H), 2.75 – 2.65 (m, 6H), 2.09 (s, 1H), 1.96 – 1.86 (m, 6H), 1.73 – 1.65 (m, 6H), 1.65 – 1.54 (m, 12H). ^{13}C NMR (151 MHz, DMSO): 165.39, 53.38, 47.89, 37.53, 31.60, 28.19, 25.89, 23.29, 18.85.

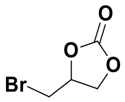
1g: 

Liquid: ^{1}H NMR (600 MHz, DMSO): δ 9.61 (s, 1H), 3.64 – 3.53 (m, 6H), 3.49 (t, *J* = 5.8 Hz, 6H), 3.30 (s, 4H), 3.26 (t, *J* = 5.7 Hz, 6H), 2.75 – 2.65 (m, 6H), 2.09 (s, 1H), 1.96 – 1.86 (m, 6H), 1.73 – 1.65 (m, 6H), 1.65 – 1.54 (m, 12H). ^{13}C NMR (151 MHz, DMSO): 165.39, 53.38, 47.89, 37.53, 31.60, 28.19, 25.89, 23.29, 18.85.

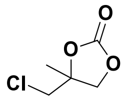
Spectra of product ^{1}H NMR and ^{13}C NMR of Products

4-chloromethyl-1, 3-dioxolan-2-one: 

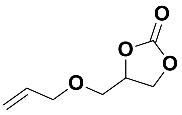
^{1}H NMR (($CDCl_3$, TMS, 400 MHz): 3.84 (d, J = 6.0 Hz, 2H), 4.05 (t, J = 8.4 Hz, 1H), 4.60 (t, J = 8.0 Hz, 1H), 5.07–5.10 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 44.15, 70.46, 73.51, 154.94.

3a: 

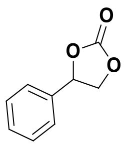
^{1}H NMR (($CDCl_3$, TMS, 400 MHz): 3.84 (d, J = 6.0 Hz, 2H), 4.05 (t, J = 8.4 Hz, 1H), 4.60 (t, J = 8.0 Hz, 1H), 5.07–5.10 (m, 1H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 44.15, 70.46, 73.51, 154.95.

3b: 

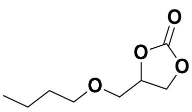
^{1}H NMR (($CDCl_3$, TMS, 400 MHz): 1.63 (s, 3H), 3.67 (d, J = 11.57 Hz, 1H), 3.75 (d, J = 12.1 Hz, 1H), 4.21 (d, J = 8.8 Hz, 1H), 4.53 (d, J = 8.8 Hz, 1H). ^{13}C NMR (CDCl3, TMS, 100 MHz): 44.15, 70.46, 73.51, 154.95.

3c: 

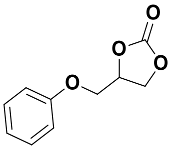
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 3.63 (dd, J = 4.0, 11.2 Hz, 1H), 3.70 (dd, J = 4.0, 11.2 Hz, 1H), 4.02–4.11 (m, 2H), 4.41 (dd, J = 6.4, 8.0 Hz, 1H), 4.51 (dd, J = 8.4, 8.4 Hz, 1H), 4.79–4.85 (m, 1H), 5.22–5.32 (m, 2H), 5.83–5.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 65.9, 68.6, 72.0, 75.0, 117.1, 133.5, 154.8.

3d: 

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.34 (t, 1H, J = 8.4 Hz); 4.80 (t, 1H, J = 8.4 Hz); 5.68 (t, 1H, J = 8.0 Hz); 7.35–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 71.10, 77.92, 125.81, 129.12, 129.63, 135.70, 154.81

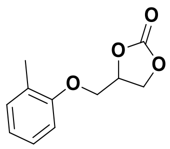
3e: 

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 0.88 (t, J = 7.5 Hz, 1H), 1.32 (dq, J = 14.8, 7.4 Hz, 2H), 1.42 – 1.56 (m, 2H), 3.46 (t, J = 6.5 Hz, 2H), 3.56 (dd, J = 11.5, 4.2 Hz, 1H), 3.63 (dd, J = 11.5, 2.7 Hz, 1H), 4.25 (dd, J = 8.3, 5.9 Hz, 1H) 4.52 (t, 3J = 8.4 Hz, 1H), 4.91 (dddd, *J* = 8.6, 6.0, 4.1, 2.8 Hz, 1H), ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 13.55, 18.63, 31.06, 66.00, 69.52, 70.54, 75.48, 154.88.



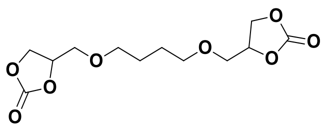
3f:

^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 4.15 (dd, 3J = 4.4 Hz, 2J = 10.8 Hz, 1H), 4.24 [dd, 3J = 3.6 Hz, 2J = 10.8 Hz, 1H), 4.55 (dd, 3J = 8.4 Hz, 2J = 6 Hz, 1H), 4.62 (t, 3J = 8.4 Hz, 1H), 5.03 (m, 1H), 6.91 [d, 3J = 8.0 Hz, 2H), 7.08 (s, 1H), 7.31 (t, 3J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65



3g:

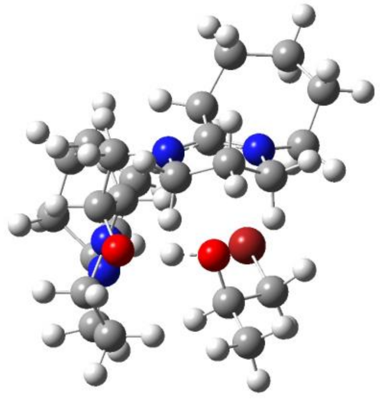
^{1}H NMR (CDCl3, TMS, 400 MHz): 2.13 (s, 3H), 4.18 (dd, J = 11.2, 3.5 Hz, 1H), 4.27 (dd, J = 11.2, 2.4 Hz, 1H), 4.47 (dd, 3J = 8.4 Hz, 5.2Hz, 1H), 4.64 (t, 3J = 8.5 Hz, 1H), 5.17 (m, 1H), 6.88 (td, J = 7.4, 0.8 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 7.14-7.17 (m, 2H). ^{13}C NMR (CDCl3, TMS, 100 MHz): 15.49, 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65



3h:

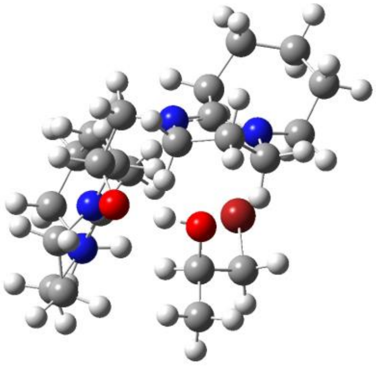
^{1}H NMR ($CDCl_3$, TMS, 400 MHz): 1.52 – 1.55 (m, 2H), 3.46 (t, J = 5.9 Hz, 2H), 3.55 (dd, J = 11.5, 4.2 Hz, 1H), 3.63 (dd, J = 11.5, 2.7 Hz, 1H), 4.25 (dd, J = 8.2 5.9 Hz, 1H) 4.52 (t, 3J = 8.4 Hz, 1H), 4.91 (dddd, *J* = 8.6, 5.9, 4.2, 2.8 Hz, 1H), ^{13}C NMR ($CDCl_3$, TMS, 100 MHz): 25.60, 66.09, 69.51, 70.55, 75.50, 154.93.

3. The Cartesian coordinates



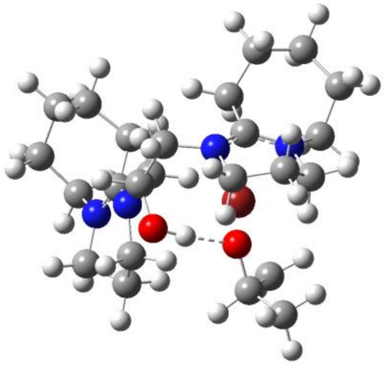
C	0.952	-1.92	-2.215
O	1.694	-1.65	0.033
H	1.892	-1.489	-2.564
H	0.537	-2.59	-2.967
Br	-0.325	-0.374	-2.158
C	1.111	-2.564	-0.845
H	0.112	-2.861	-0.485
C	1.975	-3.829	-0.992
H	1.511	-4.577	-1.645
H	2.961	-3.574	-1.394
H	2.113	-4.271	-0.002
C	-2.67	1.472	-0.126
C	-2.846	0.021	0.256
H	-1.61	1.711	-0.135
H	-3.012	1.604	-1.157
N	-3.96	-0.601	-0.16
C	-4.126	-2.067	-0.096
H	-4.496	-2.396	-1.074
H	-4.888	-2.305	0.654
C	-2.804	-2.736	0.239
H	-2.972	-3.786	0.494
H	-2.13	-2.701	-0.624
C	-2.161	-2.003	1.409
H	-2.82	-2.023	2.287
H	-1.186	-2.403	1.696
N	-1.948	-0.587	1.029
C	-0.703	0.118	1.426
H	-0.989	1.123	1.742
H	-0.064	0.168	0.544
C	0.122	-0.535	2.565
C	1.259	0.479	2.962
H	0.887	1.498	3.104

H	1.654	0.15	3.924
N	2.414	0.464	2.031
C	3.446	-0.538	2.394
H	3.631	-0.424	3.465
H	3.025	-1.531	2.227
C	4.724	-0.307	1.606
H	5.417	-1.134	1.784
H	5.216	0.615	1.937
C	4.395	-0.216	0.126
H	5.273	0.094	-0.447
H	4.019	-1.171	-0.255
N	3.351	0.8	-0.088
C	2.442	1.087	0.847
C	1.505	2.243	0.565
H	0.854	1.978	-0.275
H	0.858	2.39	1.424
C	2.239	3.575	0.266
H	3.111	3.669	0.925
H	1.558	4.389	0.537
C	2.654	3.754	-1.201
H	3.067	4.76	-1.335
H	1.753	3.703	-1.827
C	3.666	2.718	-1.703
H	4.637	2.86	-1.212
H	3.83	2.865	-2.776
C	3.207	1.273	-1.483
H	2.171	1.126	-1.803
H	3.814	0.593	-2.084
C	-5.141	0.162	-0.622
H	-5.907	-0.588	-0.826
H	-4.925	0.653	-1.58
C	-5.677	1.167	0.413
H	-6.728	1.359	0.167
H	-5.67	0.687	1.4
C	-4.938	2.513	0.461
H	-5.036	3	-0.519
H	-5.44	3.169	1.181
C	-3.448	2.422	0.815
H	-3.321	2.089	1.854
H	-3.002	3.42	0.748
H	-0.529	-0.564	3.467
O	0.621	-1.763	2.248
H	1.24	-1.74	1.013



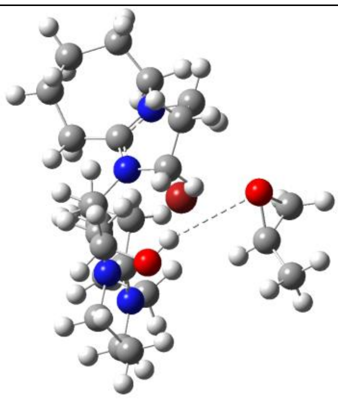
C	0.288	-0.747	-2.915
O	1.26	-1.587	-0.901
H	1.292	-0.619	-3.32
H	-0.433	-0.911	-3.715
Br	-0.206	1.038	-2.155
C	0.244	-1.817	-1.837
H	-0.741	-1.751	-1.347
C	0.365	-3.202	-2.491
H	-0.457	-3.403	-3.188
H	1.314	-3.291	-3.031
H	0.352	-3.962	-1.705
C	-2.491	1.556	0.387
C	-2.819	0.081	0.378
H	-1.421	1.686	0.51
H	-2.735	1.984	-0.588
N	-4.004	-0.288	-0.136
C	-4.445	-1.695	-0.203
H	-4.942	-1.837	-1.168
H	-5.192	-1.865	0.583
C	-3.267	-2.64	-0.053
H	-3.627	-3.66	0.104
H	-2.663	-2.641	-0.966
C	-2.407	-2.209	1.124
H	-2.963	-2.292	2.067
H	-1.49	-2.801	1.179
N	-1.993	-0.793	0.954
C	-0.664	-0.351	1.47
H	-0.832	0.456	2.191
H	-0.092	0.02	0.617
C	0.165	-1.481	2.137
C	1.46	-0.86	2.775
H	1.272	0.081	3.298
H	1.817	-1.569	3.522

N	2.57	-0.719	1.804
C	3.39	-1.95	1.679
H	3.626	-2.273	2.697
H	2.764	-2.718	1.219
C	4.664	-1.682	0.897
H	5.165	-2.63	0.683
H	5.354	-1.065	1.484
C	4.311	-0.972	-0.398
H	5.215	-0.659	-0.927
H	3.706	-1.609	-1.052
N	3.529	0.239	-0.101
C	2.695	0.295	0.94
C	1.973	1.601	1.184
H	1.326	1.813	0.327
H	1.32	1.495	2.044
C	2.938	2.79	1.437
H	3.774	2.451	2.061
H	2.392	3.532	2.03
C	3.459	3.469	0.164
H	4.061	4.34	0.445
H	2.6	3.855	-0.402
C	4.282	2.556	-0.754
H	5.23	2.281	-0.276
H	4.536	3.105	-1.668
C	3.536	1.279	-1.154
H	2.507	1.495	-1.454
H	4.015	0.816	-2.019
C	-5.041	0.707	-0.502
H	-5.854	0.129	-0.945
H	-4.663	1.364	-1.293
C	-5.577	1.518	0.688
H	-6.561	1.909	0.407
H	-5.741	0.835	1.532
C	-4.684	2.693	1.11
H	-4.632	3.409	0.278
H	-5.159	3.224	1.943
C	-3.255	2.305	1.508
H	-3.262	1.693	2.419
H	-2.695	3.214	1.749
H	-0.418	-1.825	3.021
O	0.459	-2.497	1.275
H	0.953	-2.008	0.016



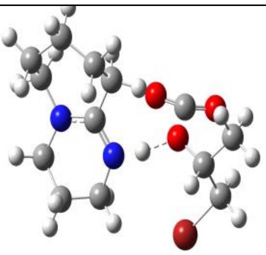
C	1.094	-2.525	-1.953
O	1.585	-1.971	0.011
H	1.859	-1.991	-2.504
H	0.162	-2.715	-2.467
Br	-0.353	-0.191	-2.101
C	1.481	-3.18	-0.694
H	0.67	-3.828	-0.311
C	2.771	-3.998	-0.749
H	2.646	-4.925	-1.321
H	3.582	-3.415	-1.198
H	3.059	-4.261	0.276
C	-2.76	1.548	-0.061
C	-2.898	0.069	0.207
H	-1.706	1.81	-0.077
H	-3.096	1.723	-1.087
N	-4.037	-0.524	-0.171
C	-4.199	-1.978	-0.012
H	-4.951	-2.311	-0.729
H	-4.566	-2.202	0.999
C	-2.855	-2.638	-0.274
H	-2.93	-3.722	-0.155
H	-2.546	-2.421	-1.302
C	-1.826	-2.092	0.7
H	-1.906	-2.543	1.69
H	-0.821	-2.274	0.324
N	-1.935	-0.615	0.839
C	-0.697	0.066	1.262
H	-0.953	1.097	1.492
H	-0.02	0.035	0.405
C	0.027	-0.482	2.501
C	1.202	0.485	2.847
H	0.849	1.511	2.972
H	1.605	0.168	3.81
N	2.328	0.421	1.889
C	3.355	-0.594	2.232

H	3.54	-0.509	3.305
H	2.95	-1.586	2.026
C	4.627	-0.351	1.44
H	5.329	-1.171	1.615
H	5.111	0.579	1.762
C	4.274	-0.273	-0.034
H	5.141	0.021	-0.631
H	3.88	-1.228	-0.394
N	3.232	0.745	-0.243
C	2.35	1.057	0.703
C	1.445	2.243	0.441
H	0.794	2.011	-0.41
H	0.797	2.392	1.299
C	2.225	3.559	0.19
H	3.083	3.613	0.873
H	1.56	4.385	0.466
C	2.68	3.765	-1.261
H	3.137	4.756	-1.353
H	1.792	3.77	-1.908
C	3.659	2.703	-1.775
H	4.623	2.784	-1.257
H	3.856	2.882	-2.838
C	3.126	1.276	-1.625
H	2.087	1.183	-1.957
H	3.706	0.587	-2.242
C	-5.204	0.251	-0.653
H	-5.956	-0.492	-0.92
H	-4.942	0.777	-1.578
C	-5.789	1.218	0.391
H	-6.825	1.427	0.097
H	-5.837	0.702	1.358
C	-5.044	2.553	0.526
H	-5.102	3.085	-0.434
H	-5.564	3.181	1.258
C	-3.566	2.429	0.921
H	-3.472	2.03	1.939
H	-3.118	3.429	0.934
H	-0.652	-0.454	3.365
O	0.492	-1.798	2.374
H	0.913	-1.912	1.463



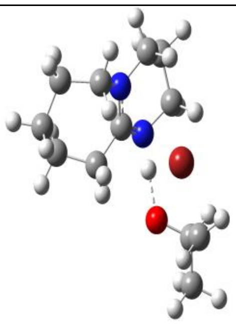
C	-1.973	3.332	-2.223
O	-2.722	3.031	-1.02
H	-2.483	4.001	-2.915
H	-1.459	2.476	-2.658
Br	-0.018	0.365	-1.128
C	-1.532	3.849	-0.921
H	-0.701	3.327	-0.444
C	-1.739	5.282	-0.505
H	-0.851	5.878	-0.744
H	-2.6	5.716	-1.022
H	-1.913	5.349	0.574
C	2.608	-1.678	-0.24
C	2.787	-0.275	0.293
H	1.789	-2.157	0.286
H	2.303	-1.628	-1.287
N	3.605	0.547	-0.362
C	3.807	1.968	0
H	3.62	2.561	-0.9
H	4.862	2.091	0.272
C	2.888	2.403	1.129
H	3.271	3.32	1.585
H	1.882	2.595	0.754
C	2.816	1.276	2.151
H	3.811	1.04	2.552
H	2.171	1.543	2.983
N	2.283	0.067	1.495
C	1.081	-0.593	2.038
H	1.357	-1.311	2.821
H	0.617	-1.118	1.213
C	0.02	0.39	2.595
C	-1.361	-0.315	2.783
H	-1.235	-1.322	3.185
H	-1.918	0.248	3.534
N	-2.21	-0.323	1.578
C	-2.966	0.937	1.348

H	-3.208	1.354	2.327
H	-2.326	1.641	0.817
C	-4.212	0.668	0.528
H	-4.699	1.618	0.297
H	-4.918	0.034	1.078
C	-3.779	-0.001	-0.761
H	-4.641	-0.347	-1.337
H	-3.186	0.691	-1.369
N	-2.944	-1.181	-0.469
C	-2.212	-1.284	0.639
C	-1.438	-2.567	0.831
H	-0.686	-2.609	0.034
H	-0.892	-2.53	1.768
C	-2.311	-3.847	0.826
H	-3.248	-3.652	1.363
H	-1.777	-4.61	1.403
C	-2.603	-4.406	-0.573
H	-3.149	-5.35	-0.475
H	-1.646	-4.65	-1.055
C	-3.384	-3.452	-1.483
H	-4.408	-3.319	-1.111
H	-3.467	-3.897	-2.481
C	-2.727	-2.077	-1.629
H	-1.652	-2.147	-1.821
H	-3.149	-1.548	-2.485
C	4.31	0.13	-1.598
H	4.748	1.041	-2.006
H	3.571	-0.216	-2.328
C	5.416	-0.908	-1.364
H	6.094	-0.868	-2.224
H	6.004	-0.604	-0.488
C	4.908	-2.345	-1.2
H	4.442	-2.664	-2.142
H	5.761	-3.013	-1.035
C	3.891	-2.533	-0.067
H	4.353	-2.317	0.905
H	3.587	-3.584	-0.038
H	0.32	0.713	3.6
O	-0.09	1.554	1.816
H	-0.13	1.281	0.862



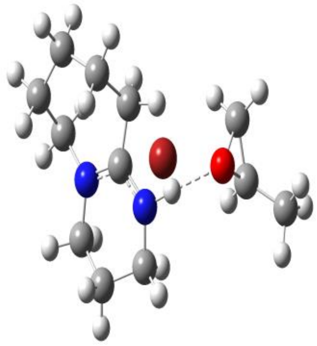
C	3.545	-0.519	-0.445
O	1.191	-1.16	-0.206
H	3.837	-0.925	0.52
H	4.386	-0.526	-1.14
Br	3.17	1.405	-0.11
C	2.324	-1.237	-1.026
H	2.086	-0.749	-1.989
C	2.708	-2.7	-1.305
H	3.557	-2.778	-1.994
H	2.959	-3.204	-0.367
H	1.849	-3.211	-1.751
C	-1.766	0.138	-0.004
N	-2.805	0.919	0.362
C	-2.665	2.383	0.427
C	-1.557	2.863	-0.505
C	-0.29	2.052	-0.257
N	-0.592	0.626	-0.328
H	-3.624	2.826	0.14
H	-1.876	2.734	-1.547
H	0.479	2.269	-0.999
C	-1.957	-1.356	-0.097
H	-2.216	-1.743	0.894
H	-0.983	-1.781	-0.341
C	-3.01	-1.777	-1.146
H	-2.798	-2.815	-1.427
H	-2.877	-1.179	-2.057
C	-4.466	-1.693	-0.665
H	-5.129	-2.08	-1.448
H	-4.586	-2.361	0.2
C	-4.933	-0.288	-0.263
H	-4.938	0.38	-1.135
H	-5.967	-0.346	0.098
C	-4.079	0.354	0.84
H	-4.623	1.183	1.298
H	-3.883	-0.368	1.642
H	0.141	2.276	0.727
H	-1.373	3.929	-0.343
H	-2.457	2.679	1.465

H	0.259	-0.105	-0.36
C	1.274	-1.511	1.69
O	2.328	-2.029	1.908
O	0.21	-1.103	2.055



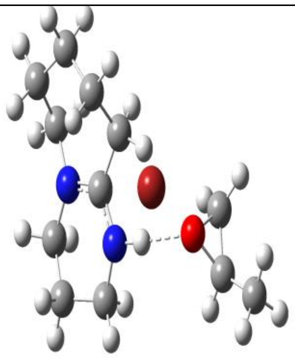
C	3.24	0.181	-0.796
O	2.239	1.163	0.769
H	3.121	0.978	-1.519
H	3.314	-0.831	-1.168
Br	0.811	-0.942	-1.666
C	3.491	0.567	0.6
H	3.634	-0.322	1.242
C	4.658	1.533	0.815
H	5.629	1.055	0.633
H	4.551	2.4	0.155
H	4.625	1.886	1.851
C	-0.853	0.207	0.65
N	-1.888	-0.603	0.373
C	-1.834	-2.02	0.768
C	-1.034	-2.2	2.055
C	0.319	-1.517	1.9
N	0.131	-0.139	1.461
H	-2.862	-2.37	0.904
H	-1.581	-1.76	2.898
H	0.87	-1.5	2.846
C	-0.82	1.604	0.084
H	-0.724	1.512	-1.004
H	0.106	2.066	0.426
C	-2.033	2.483	0.454
H	-1.727	3.53	0.349
H	-2.286	2.341	1.513
C	-3.268	2.245	-0.425
H	-4.055	2.959	-0.15
H	-2.998	2.468	-1.467

C	-3.837	0.822	-0.363
H	-4.24	0.617	0.638
H	-4.677	0.746	-1.065
C	-2.828	-0.278	-0.717
H	-3.363	-1.204	-0.935
H	-2.254	-0.031	-1.619
H	0.928	-2.035	1.147
H	-0.905	-3.267	2.259
H	-1.374	-2.584	-0.054
H	1.045	0.417	1.293



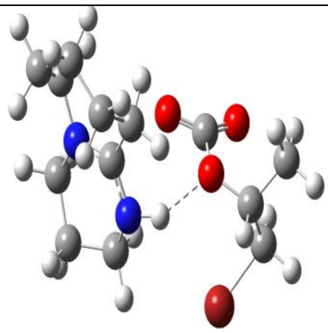
C	2.856	1.765	-0.274
O	2.57	1.247	1.056
H	3.447	2.68	-0.268
H	2.022	1.711	-0.971
Br	0.646	-0.807	-1.805
C	3.463	0.506	0.166
H	2.997	-0.396	-0.233
C	4.894	0.404	0.617
H	5.527	0.1	-0.225
H	5.254	1.364	1.001
H	4.999	-0.347	1.407
C	-0.806	0.133	0.668
N	-1.832	-0.678	0.392
C	-1.698	-2.127	0.634
C	-0.816	-2.412	1.846
C	0.497	-1.651	1.707
N	0.204	-0.244	1.45
H	-2.703	-2.531	0.787
H	-1.33	-2.109	2.766
H	1.098	-1.713	2.619
C	-0.835	1.576	0.24
H	-0.764	1.584	-0.853

H	0.082	2.038	0.612
C	-2.059	2.383	0.723
H	-1.785	3.443	0.699
H	-2.274	2.141	1.772
C	-3.312	2.18	-0.139
H	-4.107	2.847	0.215
H	-3.078	2.492	-1.167
C	-3.841	0.741	-0.174
H	-4.212	0.448	0.818
H	-4.698	0.697	-0.857
C	-2.818	-0.301	-0.642
H	-3.336	-1.225	-0.906
H	-2.274	0.015	-1.541
H	1.079	-2.035	0.859
H	-0.624	-3.488	1.906
H	-1.263	-2.565	-0.275
H	1.017	0.383	1.428



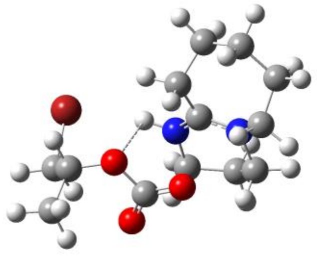
C	2.978	1.272	-0.344
O	2.488	1.472	1.02
H	3.304	2.198	-0.82
H	2.379	0.584	-0.944
Br	0.511	-1.114	-1.707
C	3.741	0.77	0.807
H	3.666	-0.302	1.006
C	4.973	1.458	1.34
H	5.871	1.015	0.888
H	4.949	2.519	1.096
H	5.042	1.345	2.427
C	-0.838	0.237	0.651
N	-1.906	-0.547	0.481
C	-1.845	-1.96	0.9
C	-0.97	-2.141	2.137

C	0.38	-1.471	1.904
N	0.156	-0.094	1.473
H	-2.868	-2.29	1.104
H	-1.459	-1.701	3.013
H	0.981	-1.45	2.818
C	-0.784	1.61	0.035
H	-0.714	1.464	-1.048
H	0.159	2.064	0.344
C	-1.955	2.546	0.397
H	-1.621	3.575	0.222
H	-2.177	2.47	1.469
C	-3.225	2.298	-0.428
H	-3.979	3.052	-0.17
H	-2.984	2.45	-1.489
C	-3.836	0.901	-0.261
H	-4.208	0.768	0.763
H	-4.703	0.814	-0.927
C	-2.88	-0.252	-0.59
H	-3.454	-1.171	-0.728
H	-2.328	-0.09	-1.524
H	0.937	-1.987	1.109
H	-0.833	-3.21	2.327
H	-1.441	-2.529	0.052
H	0.985	0.507	1.419



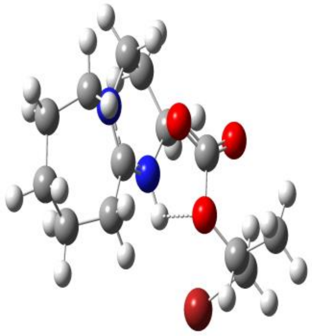
C	3.411	-0.595	-0.077
O	1.031	-1.238	-0.087
H	3.504	-0.657	1.002
H	4.366	-0.777	-0.571
Br	2.977	1.303	-0.475
C	2.33	-1.53	-0.607
H	2.224	-1.349	-1.687
C	2.74	-2.994	-0.397
H	3.66	-3.222	-0.952

H	2.891	-3.198	0.668
H	1.939	-3.645	-0.771
C	-1.853	0.092	-0.253
N	-2.81	0.663	0.476
C	-2.645	2.024	1.025
C	-1.711	2.858	0.154
C	-0.433	2.071	-0.11
N	-0.787	0.772	-0.678
H	-3.638	2.485	1.076
H	-2.202	3.101	-0.795
H	0.215	2.583	-0.823
C	-2.025	-1.319	-0.75
H	-2.055	-1.976	0.124
H	-1.112	-1.584	-1.281
C	-3.262	-1.521	-1.651
H	-3.083	-2.414	-2.261
H	-3.354	-0.681	-2.352
C	-4.574	-1.717	-0.876
H	-5.385	-1.932	-1.584
H	-4.472	-2.609	-0.24
C	-4.983	-0.531	0.005
H	-5.221	0.344	-0.615
H	-5.9	-0.792	0.55
C	-3.923	-0.128	1.037
H	-4.375	0.5	1.806
H	-3.512	-1.002	1.551
H	0.136	1.906	0.812
H	-1.482	3.798	0.664
H	-2.253	1.935	2.048
H	0.015	0.154	-0.848
C	0.792	-1.246	1.388
O	1.737	-1.606	2.089
O	-0.37	-0.87	1.634



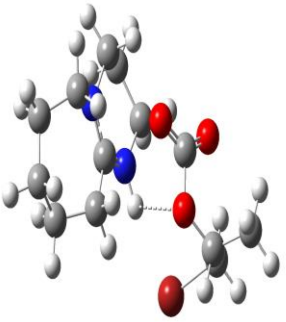
C	-3.053	-0.558	0.05

O	-0.933	-1.391	1.022
H	-2.758	-0.862	-0.952
H	-4.135	-0.574	0.175
Br	-2.586	1.381	0.189
C	-2.356	-1.389	1.122
H	-2.546	-0.919	2.097
C	-2.939	-2.813	1.14
H	-4.021	-2.786	1.325
H	-2.743	-3.325	0.195
H	-2.462	-3.37	1.956
C	1.479	0.572	-0.3
N	2.637	0.038	-0.687
C	2.737	-0.561	-2.035
C	1.902	0.21	-3.053
C	0.469	0.33	-2.55
N	0.499	0.817	-1.169
H	3.792	-0.552	-2.322
H	2.331	1.208	-3.214
H	-0.109	1.044	-3.143
C	1.217	0.939	1.135
H	1.122	-0.01	1.674
H	0.229	1.397	1.178
C	2.252	1.872	1.79
H	1.77	2.331	2.661
H	2.497	2.694	1.104
C	3.534	1.17	2.252
H	4.168	1.89	2.784
H	3.264	0.39	2.978
C	4.342	0.53	1.117
H	4.713	1.305	0.43
H	5.226	0.036	1.543
C	3.573	-0.523	0.312
H	4.282	-1.124	-0.26
H	3.013	-1.215	0.95
H	-0.042	-0.641	-2.554
H	1.92	-0.32	-4.01
H	2.39	-1.599	-1.946
H	-0.378	1.134	-0.774
C	-0.29	-1.968	-0.133
O	-1	-2.198	-1.127
O	0.937	-2.088	0.044



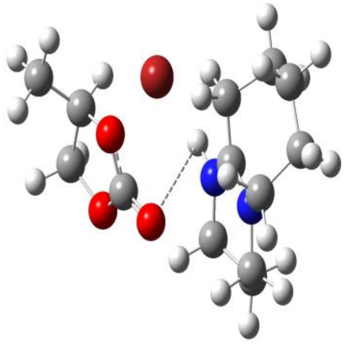
C	3.24	-0.141	0.005
O	1.318	-0.279	-1.554
H	2.933	-1.032	0.547
H	4.319	0.007	0.046
Br	2.503	1.406	1.043
C	2.734	-0.149	-1.433
H	2.937	0.834	-1.874
C	3.49	-1.215	-2.239
H	4.562	-0.988	-2.275
H	3.341	-2.205	-1.803
H	3.102	-1.219	-3.261
C	-1.438	0.173	0.478
N	-2.532	-0.568	0.302
C	-2.598	-1.909	0.921
C	-1.909	-1.931	2.282
C	-0.488	-1.399	2.139
N	-0.537	-0.13	1.407
H	-3.654	-2.172	1.024
H	-2.473	-1.319	2.996
H	-0.03	-1.206	3.113
C	-1.175	1.405	-0.343
H	-0.948	1.047	-1.355
H	-0.247	1.848	0.022
C	-2.293	2.466	-0.347
H	-1.841	3.413	-0.663
H	-2.658	2.624	0.677
C	-3.464	2.144	-1.281
H	-4.163	2.99	-1.289
H	-3.079	2.047	-2.305
C	-4.226	0.865	-0.918
H	-4.708	0.974	0.063
H	-5.029	0.712	-1.649
C	-3.364	-0.402	-0.911
H	-4.013	-1.279	-0.939
H	-2.706	-0.468	-1.784
H	0.144	-2.092	1.571

H	-1.889	-2.957	2.66
H	-2.114	-2.603	0.223
H	0.317	0.422	1.396
C	0.658	-1.473	-1.098
O	1.315	-2.259	-0.383
O	-0.535	-1.501	-1.456



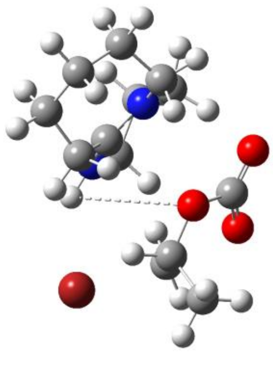
C	3.24	-0.141	0.006
O	1.319	-0.281	-1.554
H	2.933	-1.031	0.549
H	4.319	0.008	0.048
Br	2.502	1.408	1.042
C	2.735	-0.15	-1.432
H	2.938	0.832	-1.874
C	3.492	-1.218	-2.236
H	4.563	-0.991	-2.272
H	3.341	-2.207	-1.8
H	3.104	-1.222	-3.259
C	-1.438	0.172	0.477
N	-2.532	-0.568	0.301
C	-2.599	-1.909	0.919
C	-1.91	-1.931	2.281
C	-0.489	-1.399	2.139
N	-0.537	-0.131	1.406
H	-3.655	-2.173	1.021
H	-2.476	-1.319	2.994
H	-0.033	-1.206	3.114
C	-1.174	1.405	-0.344
H	-0.949	1.046	-1.356
H	-0.246	1.847	0.021
C	-2.292	2.466	-0.347
H	-1.84	3.413	-0.663
H	-2.656	2.624	0.678
C	-3.464	2.145	-1.28

H	-4.162	2.991	-1.287
H	-3.079	2.048	-2.305
C	-4.226	0.866	-0.918
H	-4.707	0.974	0.064
H	-5.029	0.714	-1.649
C	-3.364	-0.401	-0.912
H	-4.013	-1.278	-0.941
H	-2.706	-0.466	-1.786
H	0.144	-2.093	1.573
H	-1.891	-2.957	2.659
H	-2.113	-2.603	0.222
H	0.317	0.42	1.396
C	0.659	-1.474	-1.096
O	1.315	-2.258	-0.379
O	-0.534	-1.502	-1.456



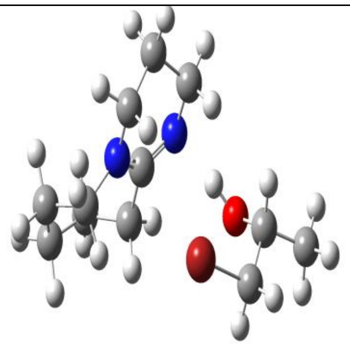
C	-3.02	1.238	0.681
O	-1.366	1.863	-0.857
H	-3.328	0.247	1.019
H	-3.741	2.008	0.973
Br	-2.148	-2.149	-0.136
C	-2.697	1.252	-0.824
H	-2.576	0.227	-1.182
C	-3.65	2.05	-1.686
H	-4.642	1.587	-1.652
H	-3.731	3.084	-1.334
H	-3.313	2.057	-2.727
C	1.342	-0.401	0.155
N	2.421	0.287	0.555
C	2.625	0.569	1.988
C	2.024	-0.532	2.859
C	0.571	-0.764	2.459
N	0.498	-0.936	1.013

H	3.703	0.643	2.16
H	2.594	-1.459	2.731
H	0.157	-1.664	2.92
C	1.046	-0.601	-1.309
H	0.786	0.378	-1.732
H	0.144	-1.216	-1.37
C	2.185	-1.255	-2.118
H	1.737	-1.683	-3.021
H	2.597	-2.098	-1.549
C	3.304	-0.292	-2.531
H	4.015	-0.82	-3.178
H	2.868	0.512	-3.142
C	4.068	0.34	-1.361
H	4.611	-0.431	-0.799
H	4.821	1.031	-1.761
C	3.184	1.129	-0.387
H	3.808	1.775	0.233
H	2.487	1.788	-0.917
H	-0.063	0.085	2.742
H	2.091	-0.241	3.912
H	2.166	1.539	2.211
H	-0.356	-1.421	0.63
C	-0.86	1.944	0.384
O	-1.754	1.556	1.314
O	0.267	2.304	0.639



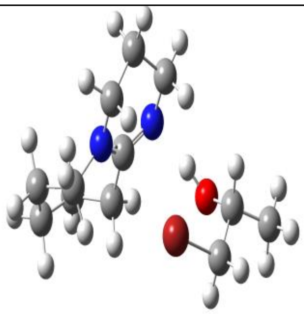
C	-2.117	-0.759	-0.318
O	-0.347	-1.724	0.969
H	-1.419	-0.338	-1.01
H	-3.072	-1.069	-0.713
Br	-2.834	1.514	0.071
C	-1.673	-1.173	1.074
H	-1.559	-0.294	1.708

C	-2.642	-2.151	1.73
H	-3.616	-1.672	1.87
H	-2.765	-3.04	1.106
H	-2.254	-2.452	2.707
C	1.063	0.811	-0.227
N	2.001	-0.063	-0.559
C	2.179	-0.504	-1.96
C	1.7	0.566	-2.938
C	0.295	1.024	-2.563
N	0.281	1.386	-1.145
H	3.245	-0.698	-2.104
H	2.382	1.424	-2.918
H	-0.014	1.901	-3.137
C	0.873	1.238	1.203
H	0.666	0.34	1.794
H	-0.023	1.861	1.248
C	2.095	1.987	1.78
H	1.748	2.576	2.635
H	2.47	2.707	1.04
C	3.226	1.06	2.248
H	4.023	1.667	2.695
H	2.839	0.417	3.05
C	3.829	0.164	1.155
H	4.335	0.775	0.395
H	4.599	-0.472	1.61
C	2.814	-0.757	0.468
H	3.311	-1.573	-0.055
H	2.135	-1.238	1.176
H	-0.434	0.225	-2.75
H	1.705	0.159	-3.953
H	1.644	-1.453	-2.078
H	-0.558	1.856	-0.793
C	-0.175	-2.499	-0.2
O	-1.203	-2.498	-0.959
O	0.931	-3.011	-0.357



C	2.905	-0.773	0.746
O	2.206	-0.742	-1.587
H	2.79	-1.857	0.713
H	3.698	-0.49	1.439
Br	1.231	-0.095	1.586
C	3.128	-0.213	-0.661
H	3.054	0.885	-0.615
C	4.536	-0.602	-1.125
H	5.31	-0.202	-0.461
H	4.631	-1.693	-1.167
H	4.698	-0.212	-2.134
C	-0.981	0.154	-0.747
N	-1.812	0.74	0.178
C	-1.685	2.172	0.464
C	-1.143	2.911	-0.755
C	0.122	2.199	-1.239
N	-0.091	0.773	-1.461
H	-2.673	2.557	0.739
H	-1.896	2.902	-1.553
H	0.484	2.641	-2.174
C	-1.108	-1.339	-0.955
H	-0.817	-1.854	-0.03
H	-0.358	-1.602	-1.702
C	-2.498	-1.825	-1.415
H	-2.37	-2.791	-1.918
H	-2.891	-1.133	-2.171
C	-3.516	-2.004	-0.28
H	-4.447	-2.416	-0.688
H	-3.126	-2.758	0.42
C	-3.836	-0.728	0.51
H	-4.344	0.002	-0.133
H	-4.532	-0.98	1.321
C	-2.602	-0.051	1.128
H	-2.926	0.643	1.909
H	-1.966	-0.796	1.624
H	0.923	2.323	-0.494

H	-0.938	3.956	-0.498
H	-1.017	2.32	1.327
H	1.381	-0.183	-1.616



C	3.54	-0.093	-0.668
O	1.411	-1.228	-0.906
H	3.922	-0.929	-0.083
H	4.351	0.41	-1.196
Br	2.882	1.226	0.663
C	2.424	-0.54	-1.61
H	2.001	0.353	-2.096
C	3.015	-1.462	-2.68
H	3.796	-0.961	-3.263
H	3.442	-2.356	-2.213
H	2.219	-1.781	-3.359
C	-1.756	0.086	-0.077
N	-2.776	0.896	0.363
C	-2.755	2.344	0.116
C	-1.689	2.707	-0.914
C	-0.401	1.955	-0.572
N	-0.627	0.514	-0.549
H	-3.748	2.648	-0.239
H	-2.022	2.41	-1.916
H	0.39	2.167	-1.296
C	-1.988	-1.411	-0.051
H	-2.129	-1.752	0.983
H	-1.064	-1.871	-0.401
C	-3.17	-1.876	-0.93
H	-3.006	-2.929	-1.186
H	-3.152	-1.322	-1.878
C	-4.554	-1.751	-0.274
H	-5.31	-2.181	-0.943
H	-4.563	-2.367	0.637
C	-4.968	-0.322	0.102

H	-5.087	0.292	-0.802
H	-5.948	-0.353	0.596
C	-3.968	0.376	1.037
H	-4.447	1.234	1.52
H	-3.672	-0.302	1.847
H	-0.022	2.284	0.406
H	-1.534	3.791	-0.92
H	-2.571	2.873	1.062
H	0.651	-0.588	-0.757
C	1.673	-1.888	1.792
O	2.783	-2.242	1.682
O	0.563	-1.568	1.969

4. *Supporting Figures*

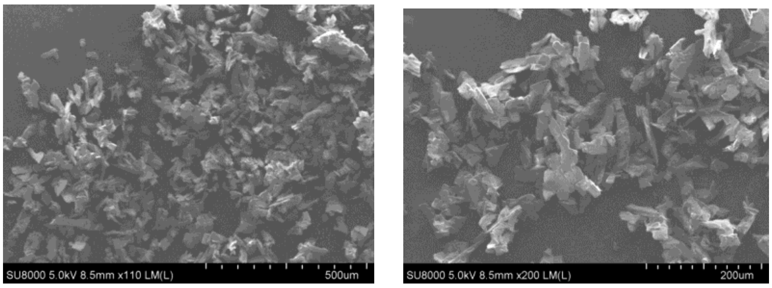


Figure S1. SEM shows the morphology of **1f.**

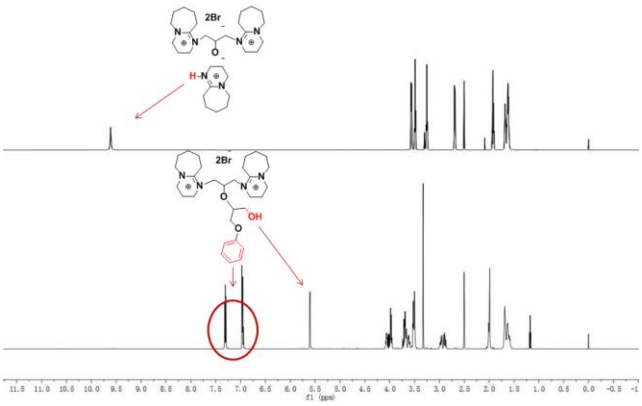
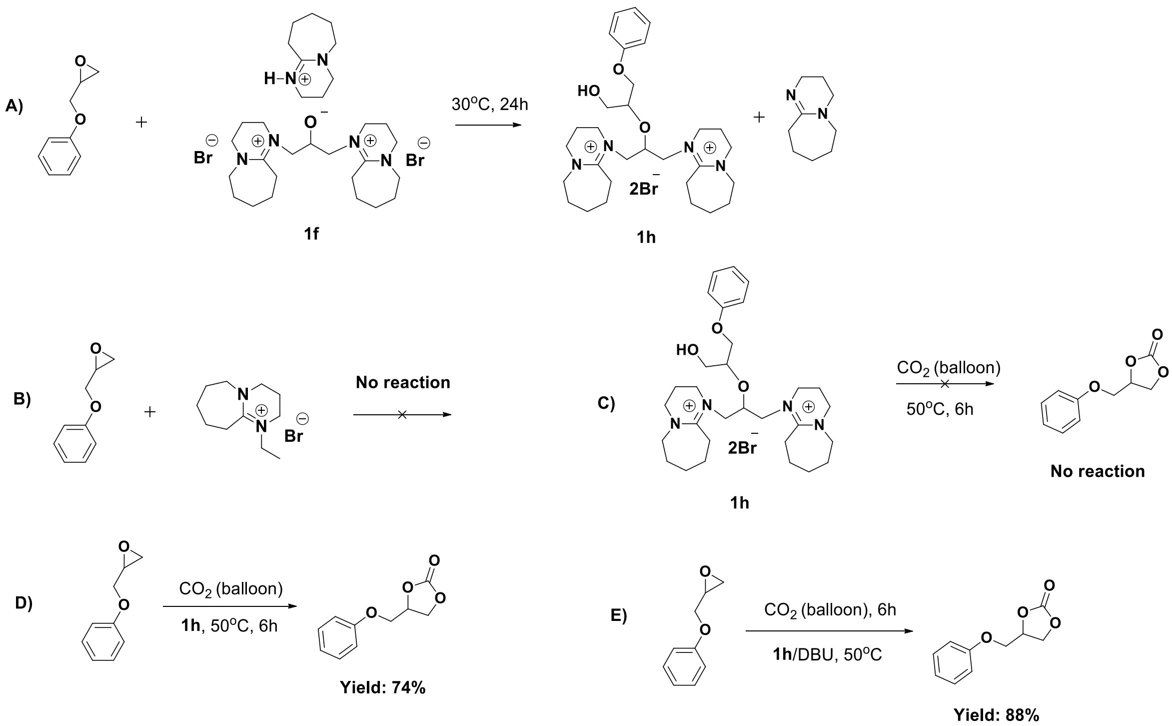


Figure S2. HNMR of **1f** and **1h**.



Scheme S4. Mechanistic studies by experiments

A series of experiments were designed to study the reason of the decreased activity (Scheme

S4). The results indicated that the DBUPILs **1f** would react with **2f** to produce **1h** with a hydroxy group (Scheme S4 A). The structure of **1h** was demonstrated by NMR and IR spectrum (Figure S1 and Figure S2). However, DBU based ILs **1a** without a protonic acid could not react with **2f** (Scheme S4 B). The above results suggested that **1f** could react with epoxide **2f** to generate **1h** and DBU, leading to the decreased activity of the catalyst system. The hydrogen proton and alkoxy anion might play key roles in the reaction of DBUILs and epoxide. In order to identify whether **1h** was a reactive intermediate of the catalytic cycle. First, **1h** was submitted to the CO_2 fixation conditions without epoxide, and no carbonate **3f** was obtained at all (Scheme S4 C). Next, we found **1h** could catalytic epoxide **2f** to afford the corresponding carbonate **3f** (Scheme S4 D), and **1h** was not changed at the end of the reaction. However, the yield of **3f** catalyzed by **1h** was only 74%. By contrast, **1f** exhibited an excellent yield of **3f** (95%, Table 2) at the same condition. The probable reason maybe that the H-bond interaction between –OH group and epoxide was weaker than hydrogen proton. Then, the catalytic activity of **1h** mixed with DBU was studied to compare with **1f** and **1h** at the same condition, because **1h** and DBU were ring-open species during the cycloaddition reaction catalyzed by **1f** (Scheme S4 A). As compared to **1h**, the **1h**/DBU system had a 88% yield of carbonate (Scheme S4 E), which was much higher than **1h** (74%). This might be caused by the absorption and activity of CO_2 by DBU. But **1h**/DBU system had a lower activity than **1f** (95%). The possible reason maybe that the hydrogen proton from **1f** could have a stronger H-bond interaction with epoxide than –OH group from **1g**, whilst alkoxy anion of **1f** played the same role with DBU.