Supporting Information for

Microporous 2D indium metal-organic frameworks for selective CO_2 capture and their application in the catalytic CO_2-cycloaddition of epoxides

Yuan-Han Li,[a] Sue-Lein Wang,[*a,b] Yu-Chia Su,[c] Bao-Tsan Ko[*b,c] Chen-Yen Tsai[b] and Chia-Her Lin[*b,d]

[a]Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan
[b]Department of Chemistry, Chung-Yuan Christian University, Chungli 32023, Taiwan
[c]Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
[d]R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli 32023, Taiwan.

Corresponding Author
*Tel: (+886) 3-5715131. E-mail: slwang@mx.nthu.edu.tw (S.-L. Wang)
*Tel: (+886) 4-22840411-715. E-mail: btko@dragon.nchu.edu.tw (B.-T. Ko)
*Tel: (+886) 3-2653315. E-mail: chiaher@cycu.edu.tw (C.-H. Lin)

Table S1. Crystallographic Data.

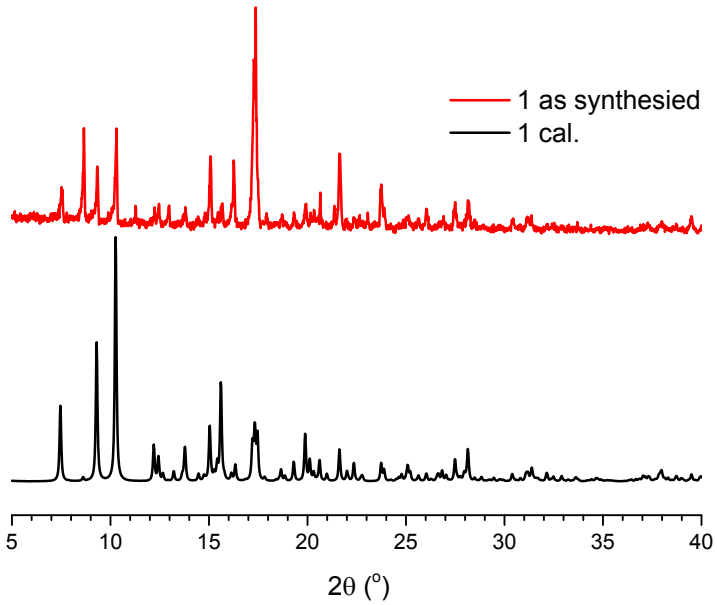
	1	**2**	**3**	**4**
formula	$C_{28}H_{16}InO_{12}S_2$	$C_{105}H_{108}In_4O_{44}N_4S_4$	$C_{11}H_{6.50}In_{0.50}N_{0.50}O_5S_{0.50}$	$C_{70}H_{40}Cl_2In_3O_{20}$
fw	723.37	362.36	299.1	1614.38
space group	*P*-1	*Ccca*	*Ccca*	$P2_12_12$
a, Å	7.2978(4)	14.5653(3)	15.0622(4)	29.6876(5)
b, Å	12.1206(7)	21.0484(5)	20.9202(5)	33.7481(5)
c, Å	20.9806(11)	23.9140(9)	23.4817(7)	9.4487(5)
α,°	78.626(3)	90	90	90
β,°	85.181(3)	90	90	90
γ,°	84.564(3)	90	90	90
volume, Å^3	1807.12(17)	7331.5(3)	7399.2(4)	9466.7(2)
Z	2	2	16	4
D_{cacl}, g cm^{-3}	1.329	1.060	1.074	1.134
μ, mm^{-1}	0.821	0.736	0.732	6.755
T, °C	296(2)	295(2)	296(2)	296(2)
λ, Å	0.71073	0.71073	0.71073	1.54178
reflections collected	27446	31859	32917	63217
independent reflections	8698	4517	4598	16415
R(int)	0.0896	0.1087	0.0913	0.0414
Goodness-of-fit on F^2	0.902	0.807	0.886	1.086
$R_1[I>2\sigma(I)]$	0.0280	0.0876	0.0501	0.0656
$wR_2[I>2\sigma(I)]$	0.0654	0.2662	0.1407	0.2044
R_1[all data]	0.0353	0.1408	0.1121	0.0737
wR_2[all data]	0.0679	0.2852	0.1449	0.2162
CCDC No.	1823435	1823434	1823437	1823436

Table S2. Selected bond lengths (Å).

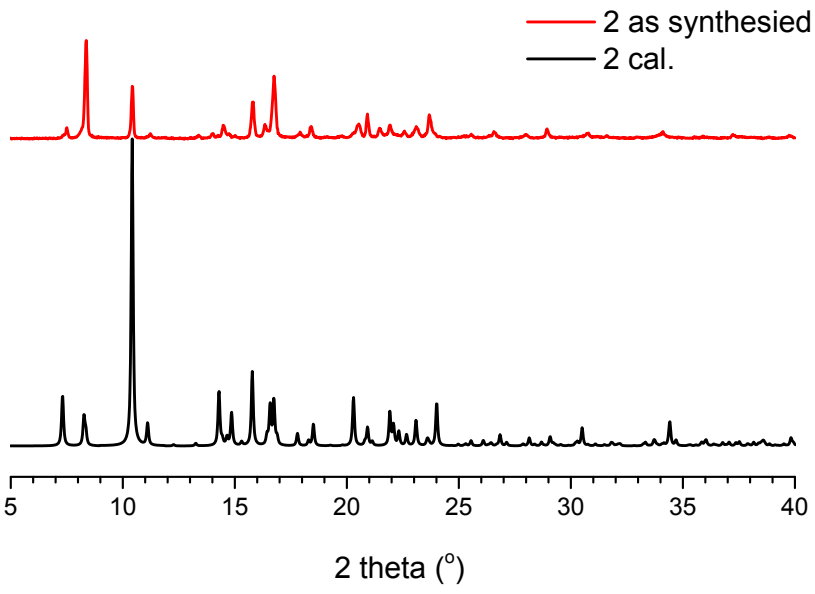
		1	
In(1)-O(1)	2.351(3)	In(1)-O(2)	2.169(3)
In(1)-O(3)	2.207(3)	In(1)-O(4)	2.422(3)
In(1)-O(5)	2.286(3)	In(1)-O(6)	2.257(3)
In(1)-O(7)#1	2.415(4)	In(1)-O(8)#1	2.222(4)
		2	
In(1)-O(1)	2.305(3)	In(1)-O(1)#1	2.305(3)
In(1)-O(2)	2.257(3)	In(1)-O(2)#1	2.257(3)
In(1)-O(4)	2.300(3)	In(1)-O(4)#1	2.300(3)
In(1)-O(5)	2.237(3)	In(1)-O(5)#1	2.236(3)
		3	
In(1)-O(1)	2.306(6)	In(1)-O(4)	2.312(5)
In(1)-O(1)#1	2.306(6)	In(1)-O(4)#1	2.312(5)
In(1)-O(2)	2.270(6)	In(1)-O(5)	2.235(5)
In(1)-O(2)#1	2.270(5)	In(1)-O(5)#1	2.235(5)
		4	
In(1)-O(15)	2.154(9)	In(1)-O(17)	2.230(7)
In(1)-O(19)	2.239(9)	In(1)-O(4)	2.246(8)
In(1)-O(3)	2.247(8)	In(1)-O(18)	2.318(7)
In(1)-O(20)	2.358(11)	In(1)-O(16)	2.539(12)
In(2)-O(8)	2.147(8)	In(2)-O(12)	2.155(7)
In(2)-O(9)	2.168(6)	In(2)-O(10)	2.322(8)
In(2)-O(11)	2.430(9)	In(2)-O(7)	2.564(9)
In(2)-Cl(1)	2.385(3)	In(3)-O(5)	2.162(8)
In(3)-O(14)	2.169(7)	In(3)-O(1)	2.234(7)
In(3)-O(2)	2.244(6)	In(3)-O(13)	2.457(9)
In(3)-O(6)	2.491(9)	In(3)-Cl(2)	2.386(3)

Symmetry transformations used to generate equivalent atoms: for **2,** #1 -x+1/2,-y,z, #2 -x,y,-z+1/2#3 x+1/2,-y,-z+1/2; for**3**, #1 -x+1/2,-y,z #2 -x+0,-y-1/2,z #3 -x+1,-y,-z+1;for **4,** #1 x+1/2,y-1/2,-z, #2 x-1/2,y+1/2,-z, #3 -x,-y,-z.

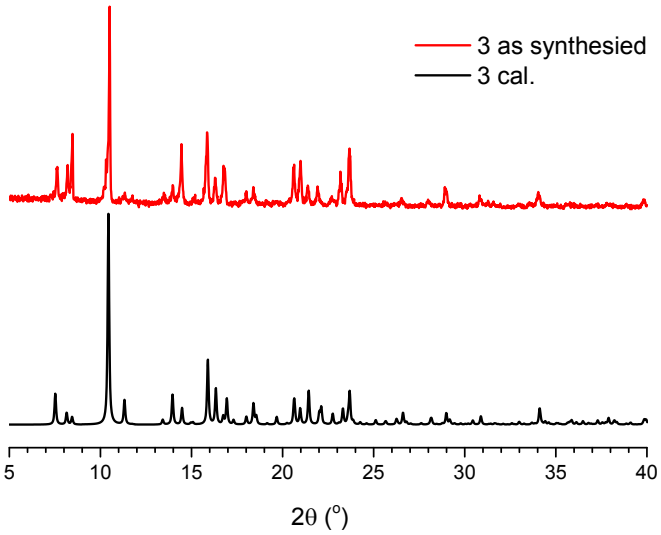
(a)


1 as synthesied
1 cal.
5
10
15
20
25
30
35
40
2θ (°)

(b)


2 as synthesied
2 cal.
5
10
15
20
25
30
35
40
2 theta (°)

(c)



(d)

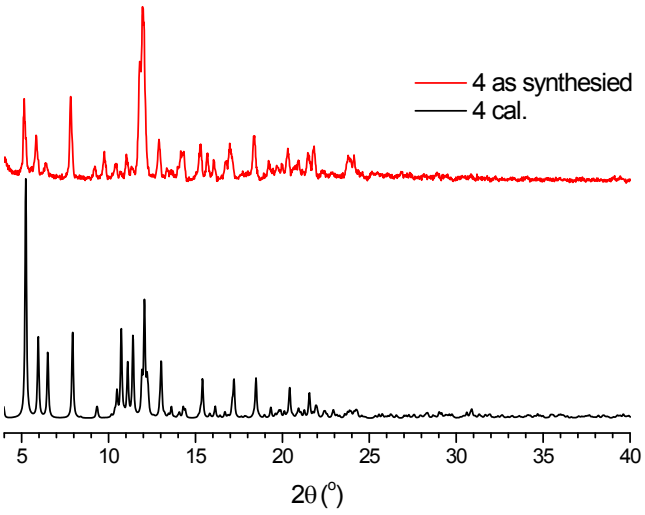


Figure S1. The PXRD patterns of compounds **1** (a), **2** (b), **3** (c), **4** (d).

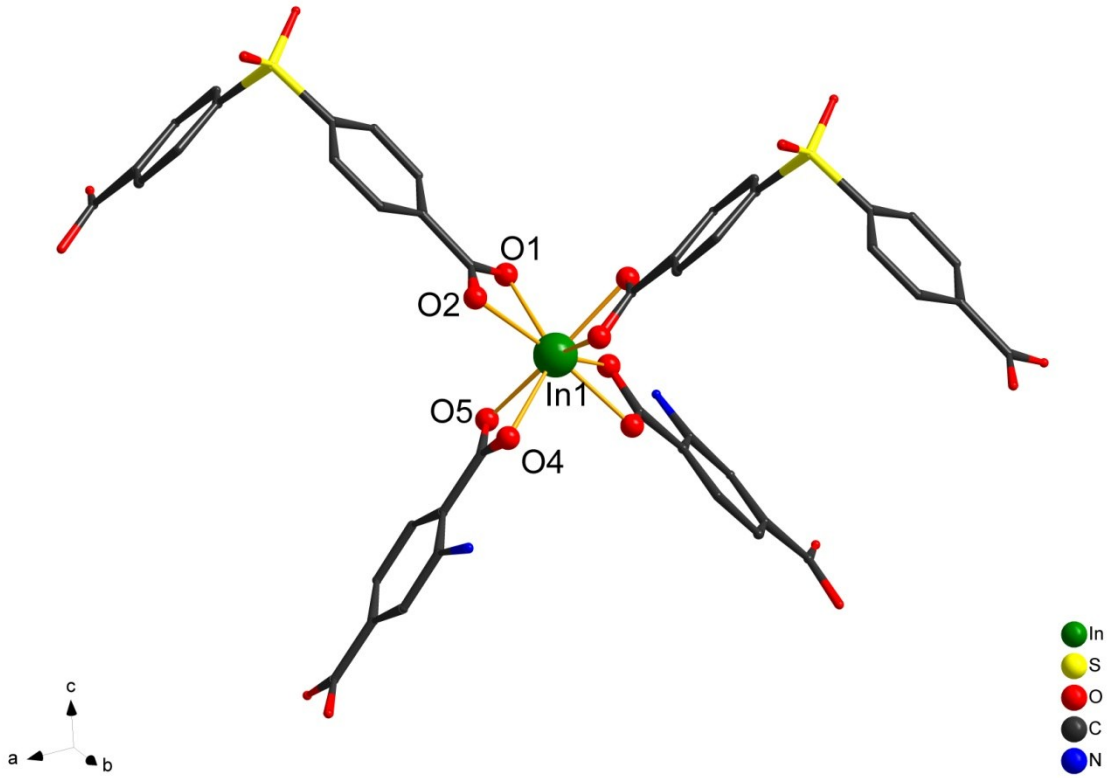


Figure S2. (a) The coordination environment around Incenters in **3**

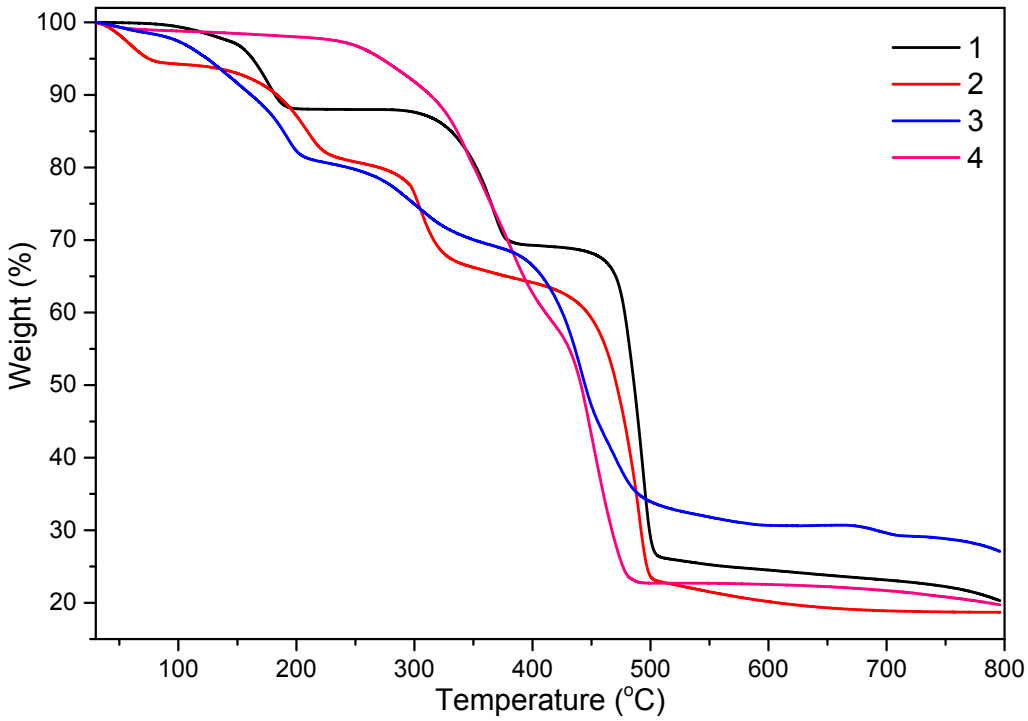
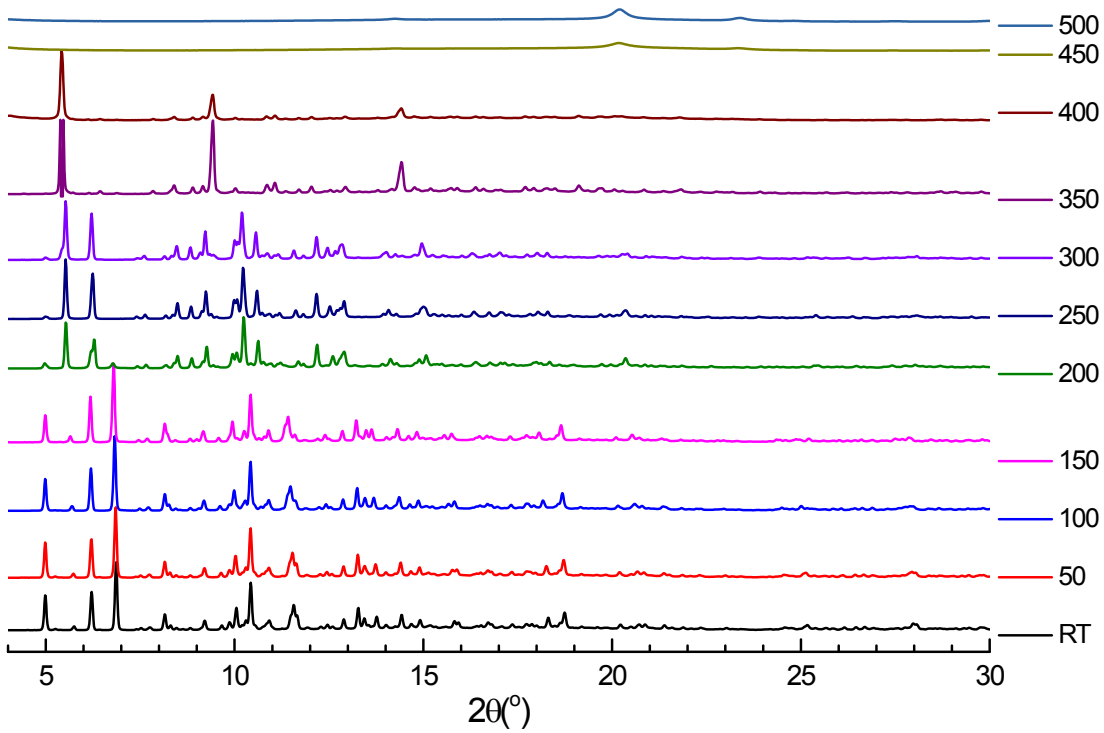
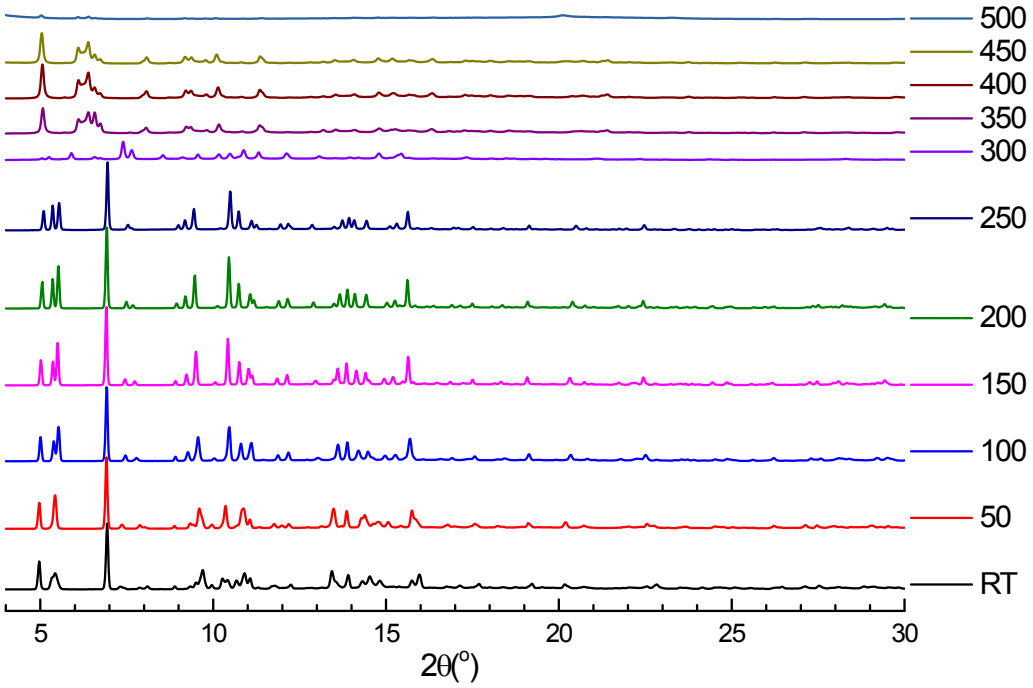


Figure S3. TGA curves of compound **1** (black), **2** (red), **3** (blue), and **4** (pink).

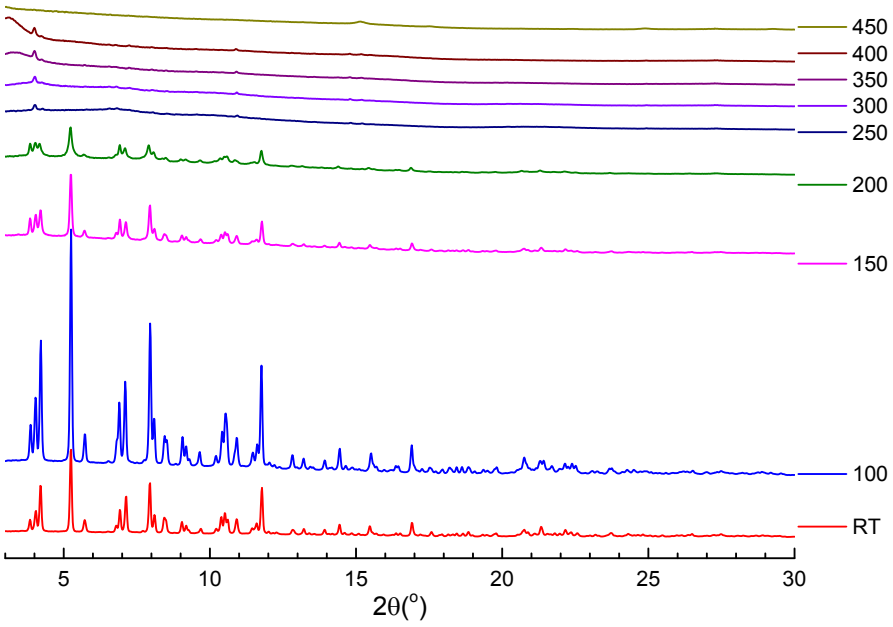
(a)


500
450
400
350
300
250
200
150
100
50
RT
5
10
15
20
25
30
2θ(°)

(b)


500
450
400
350
300
250
200
150
100
50
RT
5
10
15
20
25
30
2θ(°)

(c)



(d)

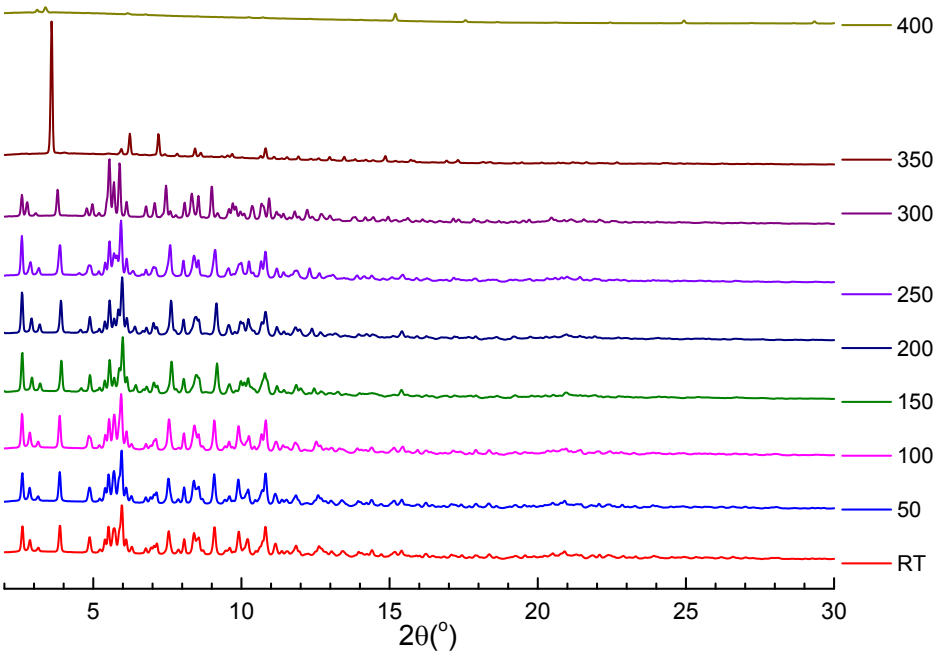


Figure S4. The varied temperature PXRD patterns of **1** (a), **2**(b), **3** (c), and **4** (d).

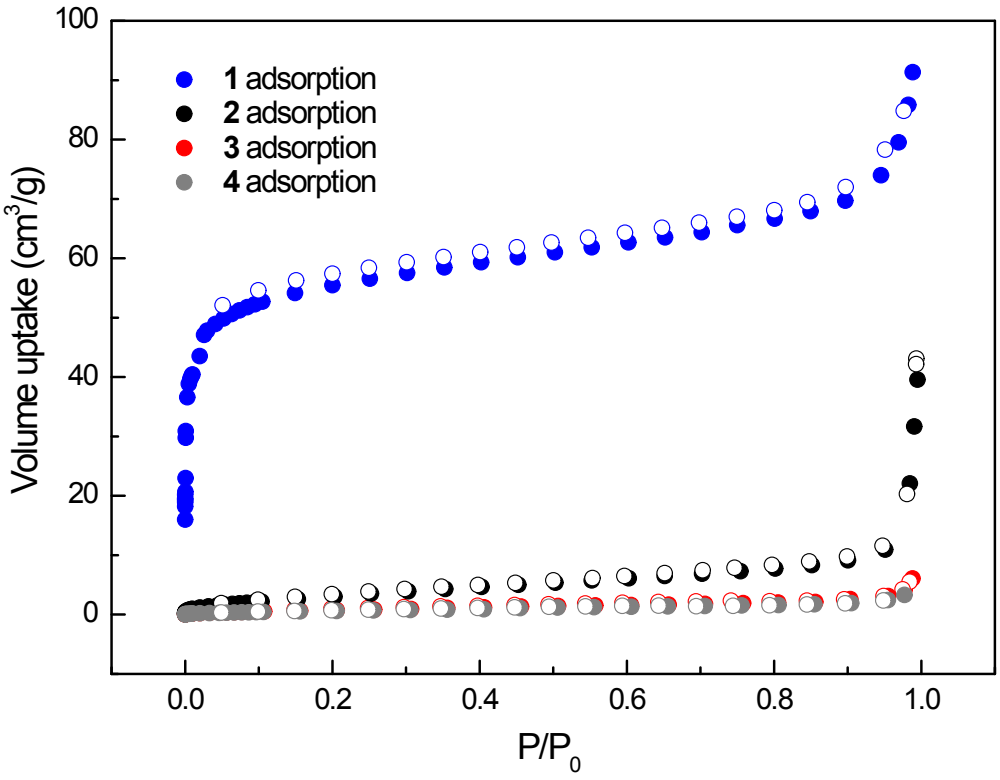
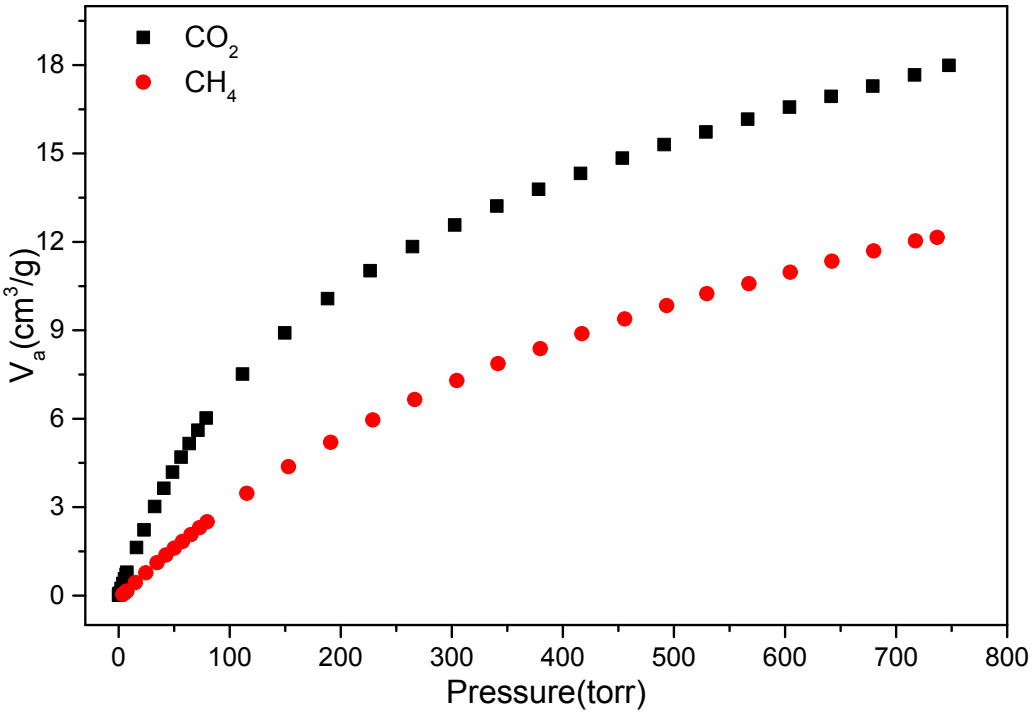


Figure S5. The N_2 adsorption-desorption isotherms of compound **1** (blue), **2** (black), **3** (red), and **4**(Gray) at 77 K (the closed and open symbol represents the adsorption and desorption respectively).

(a)



(b)

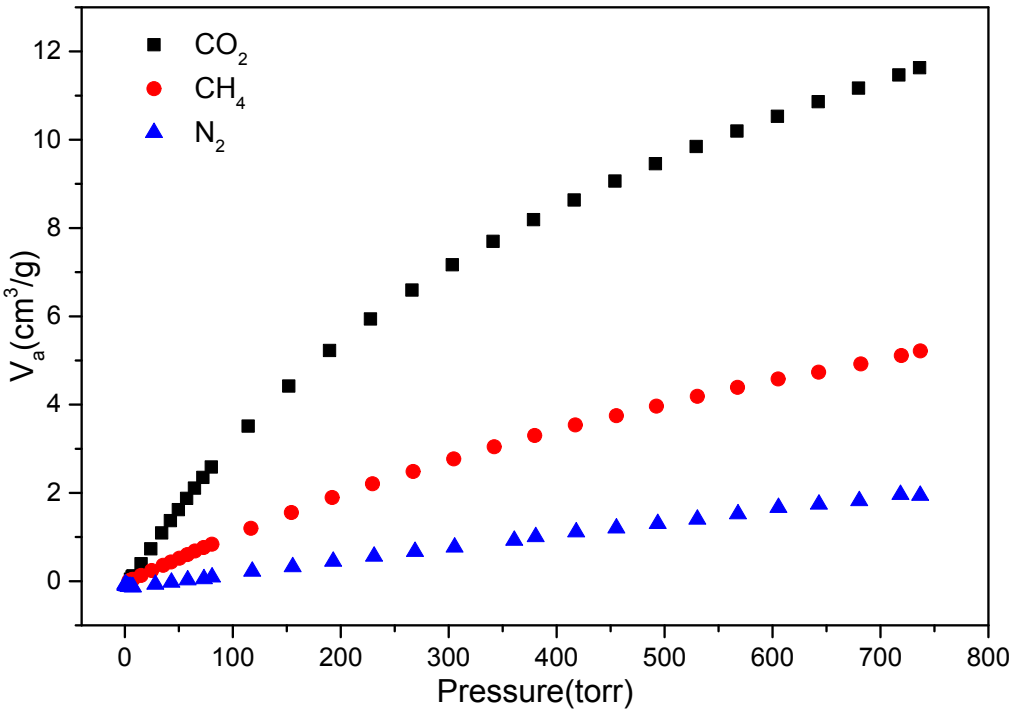
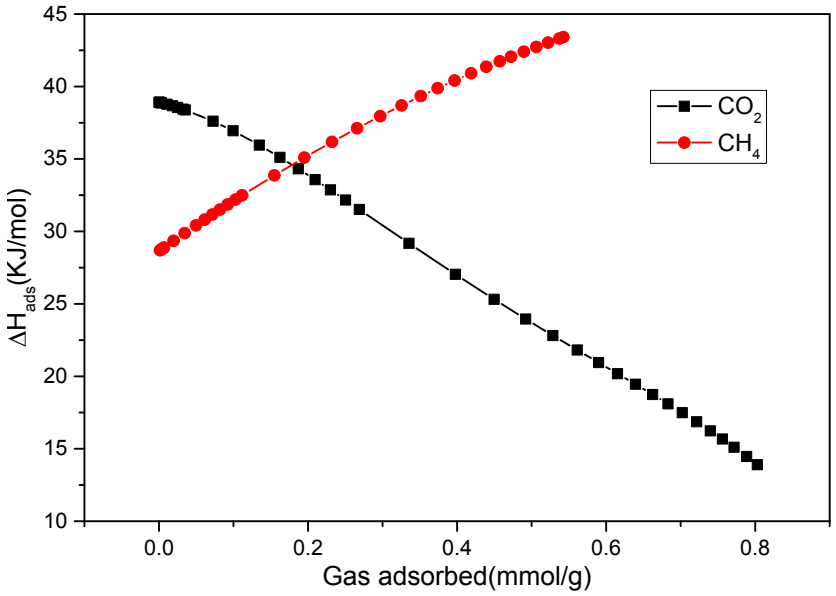


Figure S6. (a) The CO_2 and CH_4 gas adsorption isotherms of **1** recorded at 273 K. (b) The CO_2, CH_4 and N_2 gas adsorption isotherms of **1** recorded at 298 K.

(a)



(b)

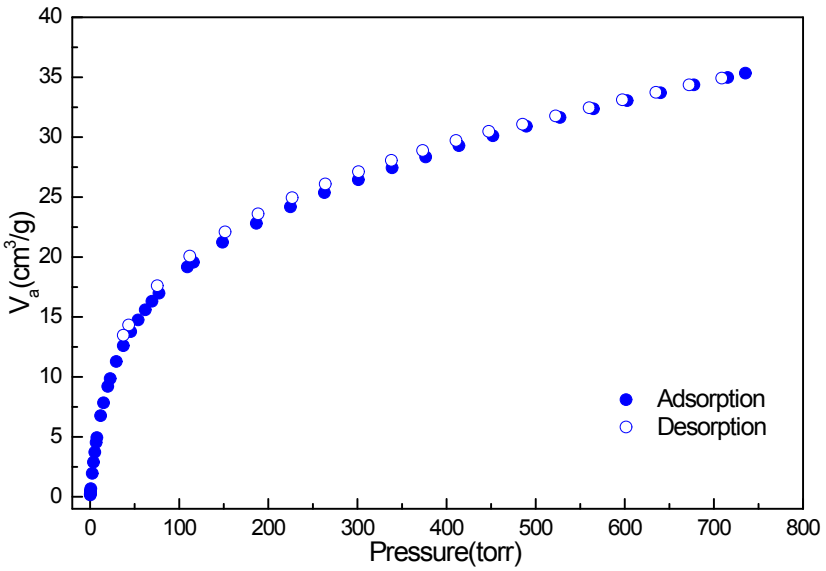
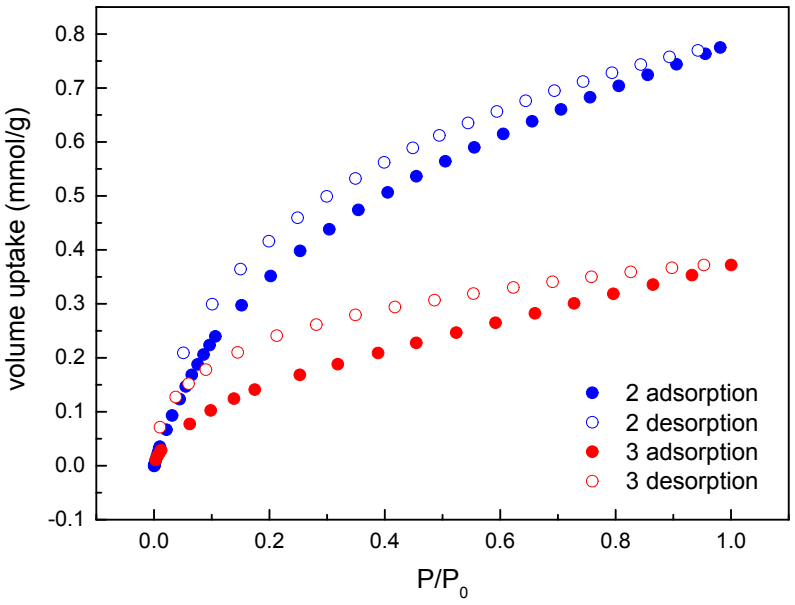


Figure S7. (a) The Q_{st} of compound **1** for CO_2 and CH_4. (b) H_2 adsorption-desorption isotherms of compound **1** at 77 K.

(a)



(b)

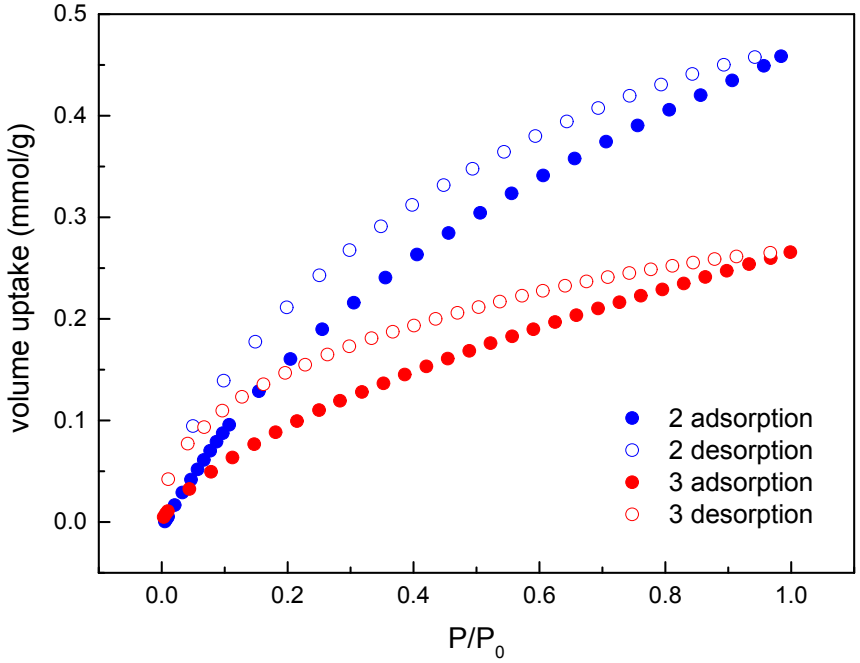


Figure S8. The CO_2 isotherm at **2** and **3** at (a) 273 K (b) 298 K.

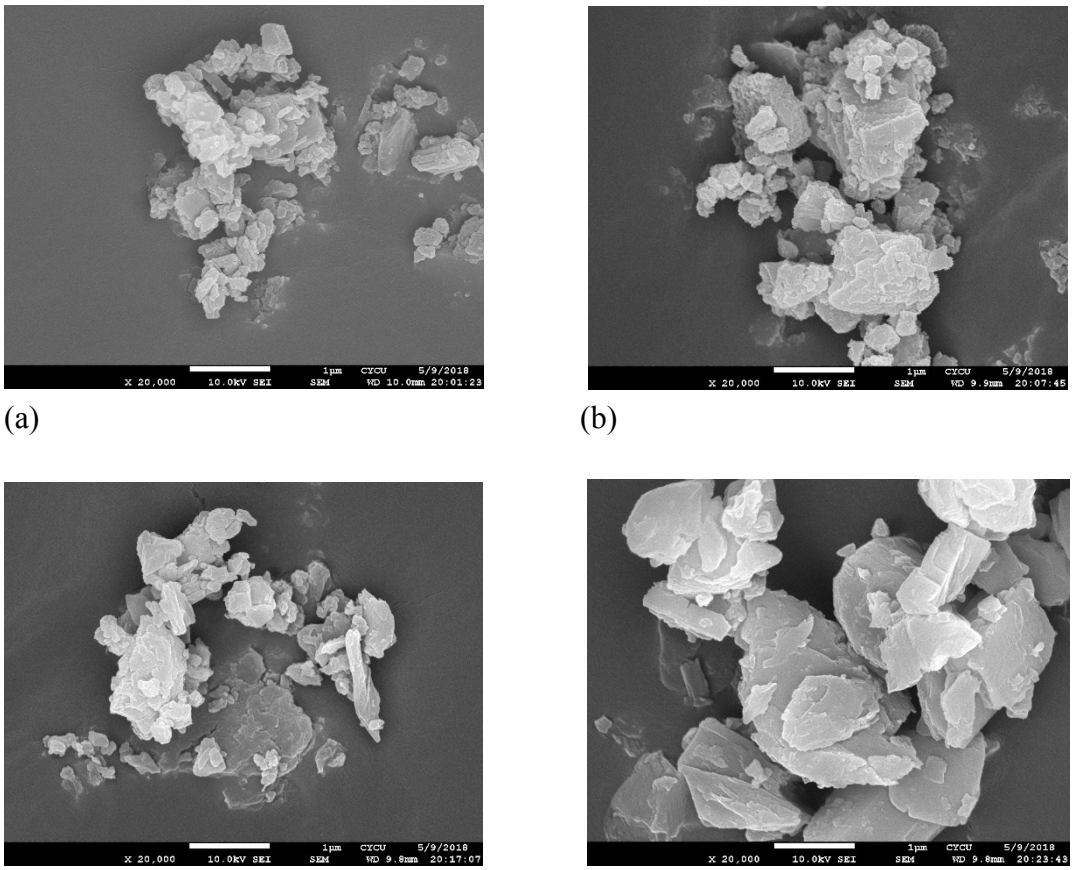


Figure S9. The SEM images for compound (a) **1**, (b) **2**, (c) **3**, and (d) **4.**

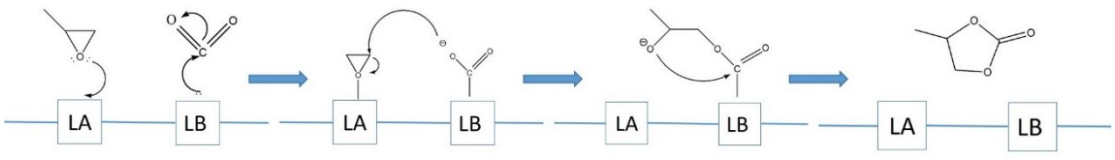


Figure S10. The proposed reaction mechanism for compound **3.**

Table S3. Coupling of propylene oxide (PO) and CO_2 to propylene carbonate (PC) catalyzed by various MOF/n-Bu_4NBr catalytic systems.

Catalyst	Catalyst(g)	Co-catalyst (mol%)	Temperature(℃)	Pressure(MPa)	Reaction Times *T* (h)	Conversion (%)	ref.
MOF-5	2.5	2.5	60	6	4	98	37
In+Dpa+1,10 phen	0.35	0.35	60	1.2	6	92	38
In+Dpa+1,10 phen	0.35	0.35	50	1.2	6	66	38
HKUST-1	0.2	10	25	0.1	48	49	39
MOF1	0.2	10	25	0.1	48	96	39
Cr-MIL-101	1.2	0.62	25	0.8	34	82	40
CHB	1.6	1.6	120	1.2	6	62	41
PCN-224	-	-	100	2	4	42	42
Hf-Nu-1000	4	1/10	25	0.1	56	100	43
MMCF-2	0.13	7.2	25	0.1	48	95.4	44
MMPF-9	0.13	7.2	25	0.1	48	87.4	45
Zn-Glu	0.47	0.94	80	1.2	6	99	46
Ni-saldpen-MOF	0.7	2	80	2	4	86	47
MIL-47	0.1	2.5	50	2	24	95	48
MOF-205	0.6	0.6	25	1.2	24	89	49
1	0.1	1	80	2	24	85	+
2	0.1	1	80	2	24	89	+
3	0.1	1	80	2	24	92	+
4	0.1	1	80	2	24	98	+

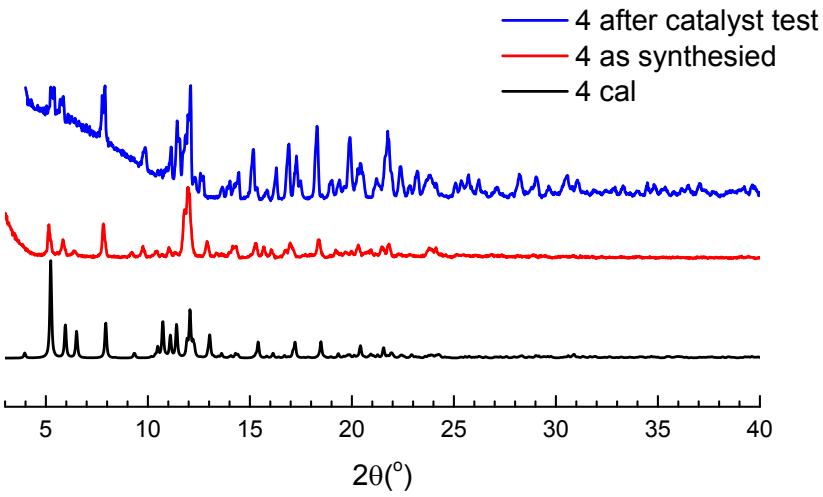


Figure S11. The PXRD after CO_2 cycloaddition of compound **4.**

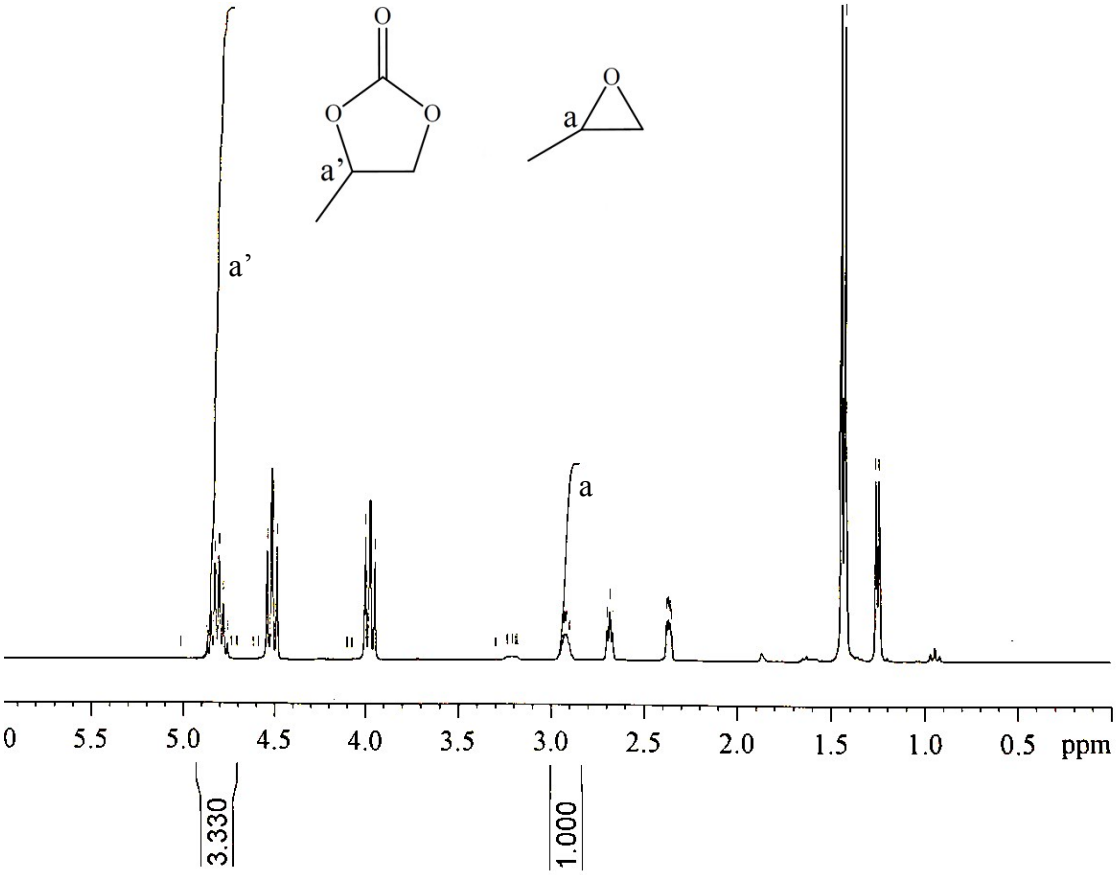


Figure S12. The ^{1}H NMR spectrum for PO to PC.

Figure S13. The ^{1}H NMR spectrum for entry 1.

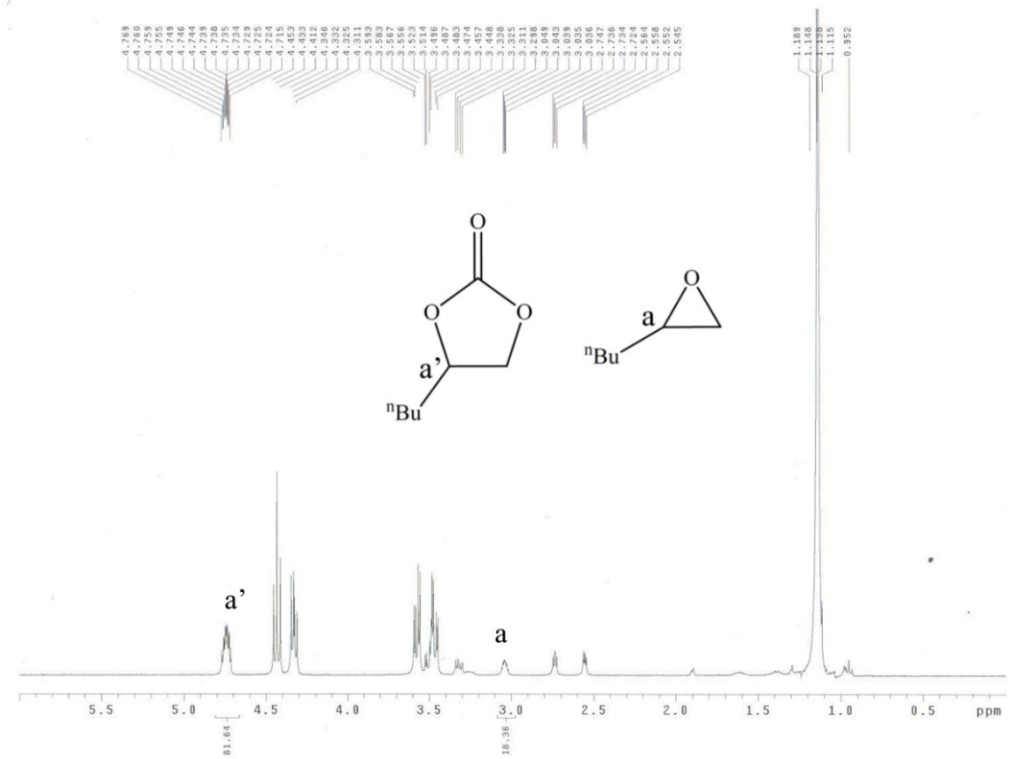


Figure S14. The ^{1}H NMR spectrum for entry 2.

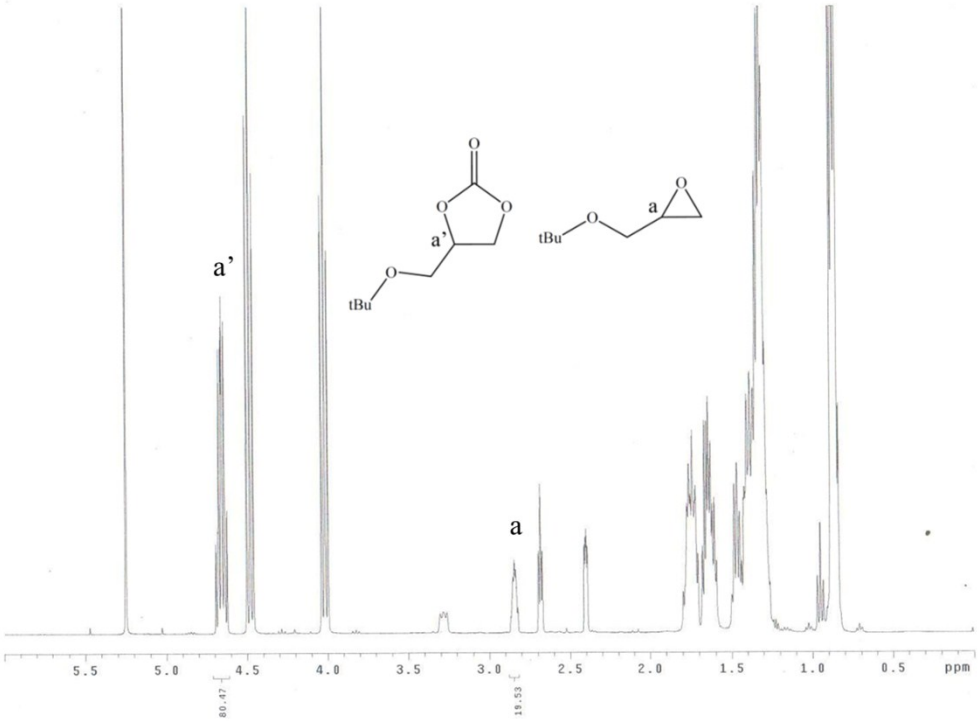


Figure S15. The ^{1}H NMR spectrum for entry 3.

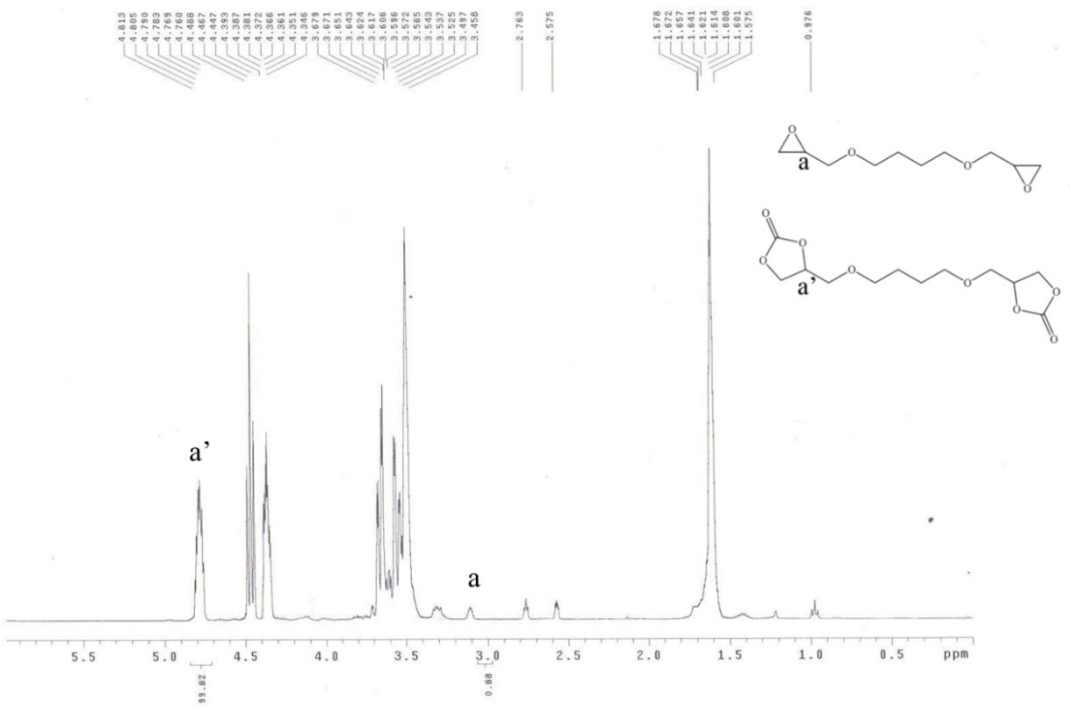


Figure S16. The ^{1}H NMR spectrum for entry 4.