Supporting Information

Ambient chemical fixation of CO_2 by using highly efficient heterometallic helicates catalyst system

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Note added after first publication: These Supplementary Information files replace those originally published on 21st December 2017, in which an incorrect crystal structure data file was presented for CCDC 1506319.

Contents

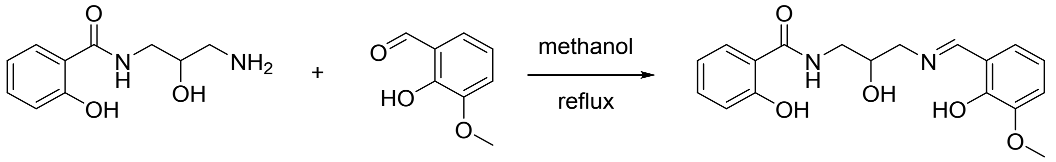
1. Experimental section

Materials and Methods. Chemicals were purchased from commercial sources and used without further purification. The infrared spectra were recorded on a Bruker VERTEX 70 FTIR spectrometer using KBr pellets in the 400-4000cm^{-1}region. X-ray powder diffraction data were collected on PANalytical X'Pert Pro Diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (λ=1.5406Å). Thermogravimetric analysis experiments were performed using a TGA/NETZSCH STA449C instrument heated from 30~800 °C (heating rate of 10 °C/min, nitrogen stream). UV/Vis absorption spectra were determined on an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. Solid-state and solution excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The absolute emission quantum yields of the compounds were measured at room temperature using a calibrated integrating sphere as a sample chamber, and specpure $BaSO_4$ was used as a reflecting standard. Crystal data were collected on a Bruker FRAMBO diffractometer (Mo Kα radiation, λ = 0.71073 Å) at 293 K. Data reduction was accomplished by the Bruker SAINT program. Multi-scan absorption corrections were applied by using the program SADABS. Structures were solved by direct methods and refined by a full matrix least-squares technique based on F2 using the SHELXL 97 program. All of the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. For details, see cif data in Supporting Information. X-ray crystallographic data for all complexes see cif files (CCDC number: 1506319 and 1506320)

Preparation

All reagents were used as purchased without further purification. 2-hydroxy-3-methoxybenzaldehyde was prepared according to the literature method[1].

Scheme S1. Synthesis of ligand H_3L



The synthesis of ligand **H_3L**: 2-hydroxy-3-methoxybenzaldehyde (0.76 g, 5 mmol) was added to a solution of N-(3-amino-2-hydroxypropyl)-2-hydroxybenzamide (1.05 g, 5 mmol) in 50 mL methanol. The mixture was stirred at reflux for 5 h and then cool to room temperature. The crude product was separated by filtration and further recrystallized with ethanol to afford **H_3L** as a yellow solid (1.51 g, Yield: 85%). ^1H NMR (400 MHz, DMSO-d6): δ 12.29 (s, 1H), 8.72 (d, *J* = 5.2 Hz, 1H), 8.47 (s, 1H), 7.86 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.37 (td, *J* = 8.0, 0.4 Hz, 1H), 7.00 (s, 1H), 6.98 (s,1H), 6.92–6.84 (m, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 5.2 Hz, 1H), 4.02–3.90 (m, 1H), 3.78 (s, 3H), 3.73 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.56 (q, *J* = 6.4 Hz, 1H), 3.52–3.50 (m, 1H), 3.40–3.29 (m, 1H), 3.16 (s, 2H) ppm. ^{13}C NMR (400 MHz, DMSO-d6): δ 169.43, 167.47, 160.25, 153.37, 148.92, 133.97, 128.66, 123.96, 119.04, 118.99, 117.80, 117.76, 116.35, 115.80, 69.17, 62.38, 56.57, 43.97 ppm. IR (KBr, υ, cm^{-1}): 3412 (s), 1644 (s), 1597 (s), 1523 (s), 1497 (s), 1447 (s), 1380 (s), 1340 (s), 1302 (s), 1254 (s), 1233 (s), 1207 (m), 1172 (m), 1114 (w), 893 (w), 846 (w), 750 (s). ESI-MS *m/z* $[(M+H)^+]$: 345.14.

The general synthetic procedure of complex **1-2:** 27 μL (0.2 mmol) triethylamine was added to a 15 ml acetonitrile solution of 0.1 mmol H_3L. Then 0.1 mmol $Zn(NO_3)_2{\cdot}H_2O$ was added and stirred for 15 min to obtain a suspension. To this solution 0.075 mmol $Ln(NO_3)_3{\cdot}6H_2O$ ($Ln=Tb^{3+}$, Dy^{3+}) in 5 mL of methanol was added and obtained a clear solution. The mixture was stirred 1 h and filtered for crystallization at room temperature. After about two weeks colorless single crystals suitable for crystal analysis were obtained. The abundant complexes powder for catalytic reaction were collected with the same method only differing with rather small amount of solvent stirring overnight to obtained white solid and by filtration, washed with acetonitrile, and dried in the air, 56%, 70 % yield. Further, the products were characterized by IR, PXRD and TGA.

$Zn_4Tb_3C_{72}H_{79}N_{18}O_{53}$: Elemental analysis (%) found (calcd): C 31.03 (31.08), H 2.83 (2.86), N 9. 09 (9.06). IR (KBr, υ, cm^{-1}): 3428 (s), 1618(s), 1589 (s), 1555 (s), 1470(s), 1383(s), 1297 (s), 1249 (s), 1221 (s), 1168 (m), 1112 (m), 1077 (w), 853 (w), 815 (w), 743 (s).

$Zn_4Dy_3C_{72}H_{79}N_{18}O_{53}$: Elemental analysis (%) found (calcd): C 30.93 (30.96), H 2.81 (2.85), N 9.04 (9.03). IR (KBr, υ, cm^{-1}): 3421 (s), 1621 (s), 1591 (s), 1553 (s), 1470(s), 1387(s), 1298 (s), 1249 (s), 1226 (s), 1171 (m), 1118 (m), 1077 (w), 853 (w), 817 (w), 743 (s).

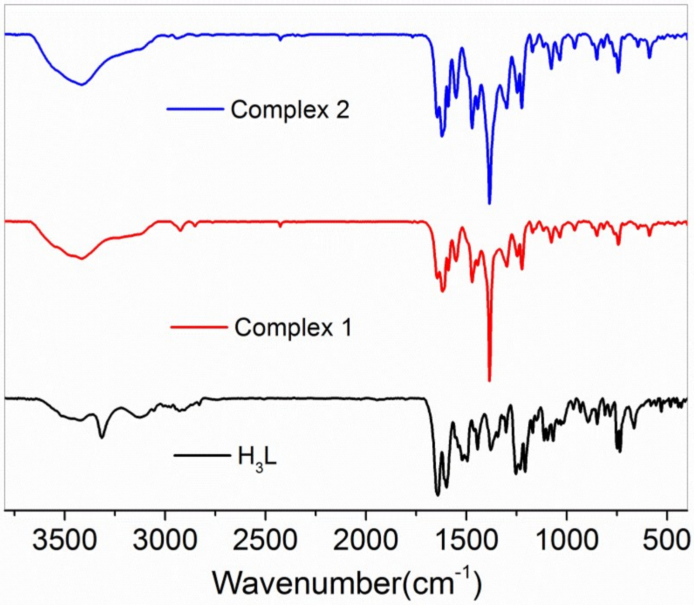


Figure S1. IR of H_3L, complex **1** and **2**

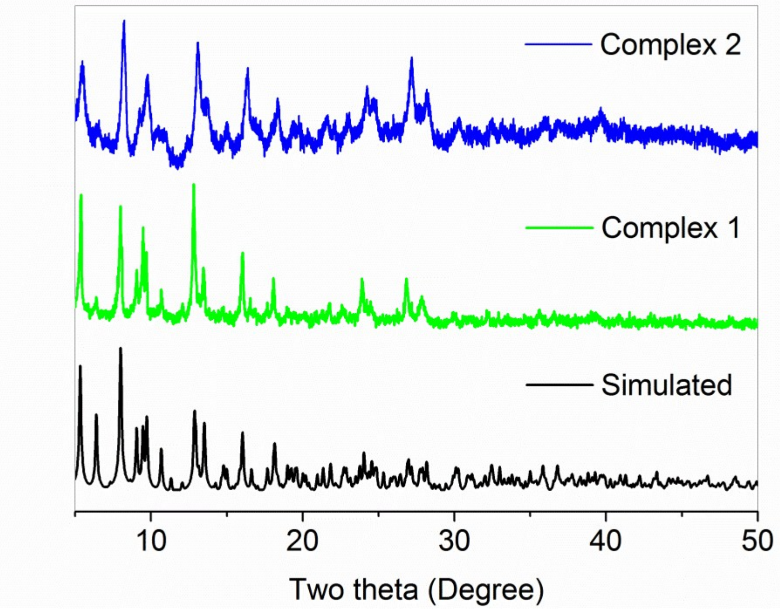


Figure S2. Comparing the simulated PXRD with experimental patterns of complexes **1**-**2**.

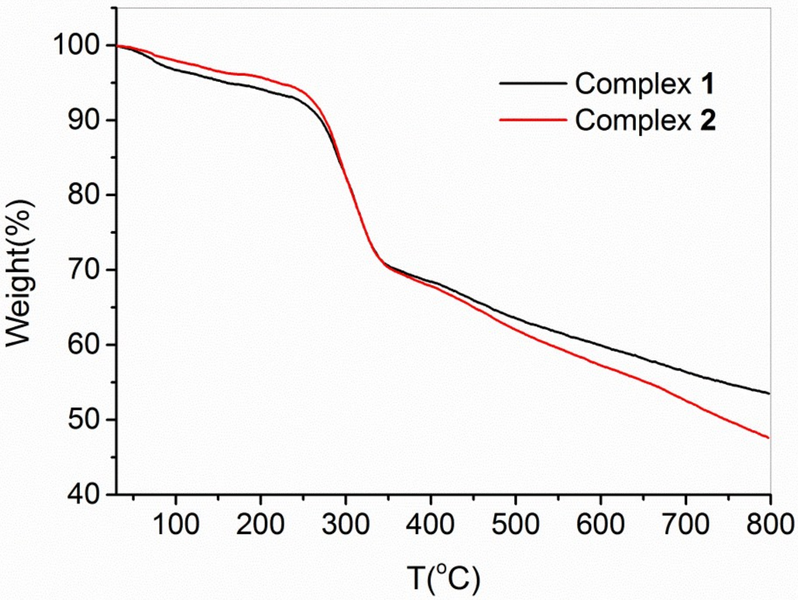


Figure S3. TGA curves of complex **1**-**2**

Crystallography

Table S1. Crystal data and structure refinement parameters for complex **1** and **2**

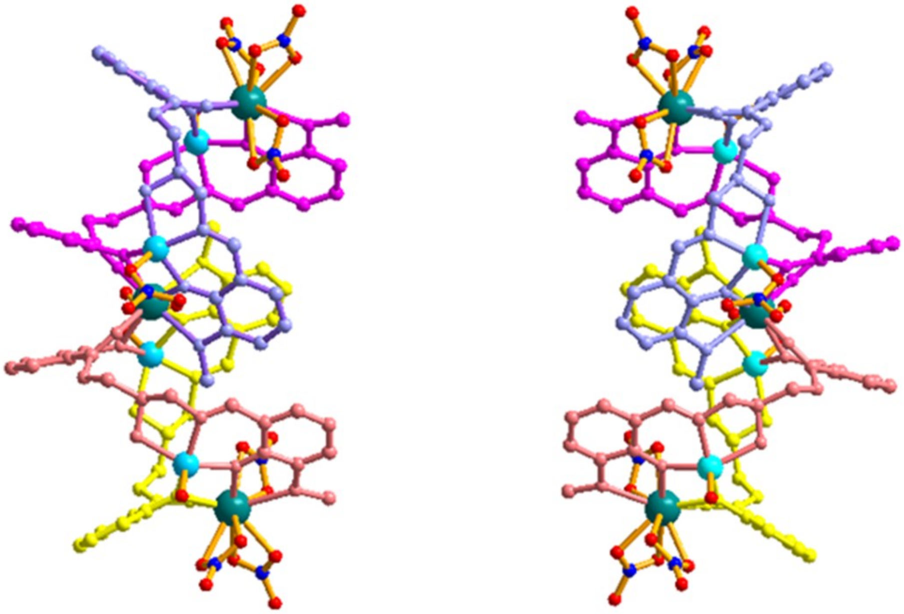
	1	**2**
Empirical formula	$Zn_4Tb_3C_{72}H_{79}N_{18}O_{53}$	$Zn_4Dy_3C_{72}H_{79}N_{18}O_{53}$
Formula weight	2782.77	2793.51
T/K	291.48(10)	297.16(10)
Crystal system	monoclinic	monoclinic
Space group	P2/c	P2/c
a/Å	16.6079(8)	16.7456(18)
b/Å	12.0821(4)	12.2808(4)
c/Å	27.6915(9)	27.4108(12)
α /°	90	90
β/ °	94.344(4)	94.542(6)
γ/°	90	90
V/Å^3	5540.6(4)	5619.3(7)
Z	2	2
D_{calc}/Mg m^{-3}	1.668	1.651
F(000)	2752.0	2758.0
θ range for data collection	3.368 to 51.188°	6.786 to 52.744°
Reflections collected/unique	21545/10260 (R_{int} =0.0465)	24643/11471 (R_{int}= 0.0988)
Data/restraints/parameters	10260/986/717	11471/461/689
Goodness-of-fit on F^2	1.028	1.031
Final R indices [I>2sigma (I)][a]	R_1=0.0822, wR_2=0.2176	R_1=0.0843, wR_2= 0.1843
R indices (all data)[b]	R_1=0.1223, wR_2=0.2456	R_1=0.1586, wR_2=0.2340
Largest diff. peak/hole/e. Å^{-3}	2.12/-1.73	2.63/-1.39

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; [b] $wR_2 = \Sigma [w(F_o^2 - F_c^2)2] / \Sigma [w(F_o^2)2]^{1/2}$

Table S2. Selected bond lengths (Å) for complexes **1** and **2**

Complex **1**					
Tb(1)—O(1)	2.343(9)	Tb(1)—O(2)	2.324(8)	Tb(1)—O(6)	2.564(9)
Tb(1)—O(7)	2.355(9)	Tb(1)—O(11)	2.440(12)	Tb(1)—O(12)	2.470 (14)
Tb(1)—O(14)	2.435(14)	Tb(1)—O(15)	2.636(15)	Tb(1)—O(17)	2.460(9)
Tb(1)—O(18)	2.495(9)	Tb(1)—N(5)	2.87(2)	Tb(1)—N(6)	2.84(2)
Tb(2)—O(4)	2.301(7)	Tb(2)—O(5’)	2.571(8)	Tb(2)—O(4’)	2.301(7)
Tb(2)—O(9)	2.279(8)	Tb(2)—O(9’)	2.279(8)	Tb(2)—O(5)	2.571(8)
Tb(2)—O(10’)	2.354(7)	Zn(1)—O(1)	2.001(8)	Tb(2)—O(10)	2.354(7)
Zn(1)—O(8)	2.138(9)	Zn(1)—O(23)	2.029(9)	Zn(1)—O(7)	2.036(9)
Zn(2)—O(3)	2.203(7)	Zn(2)—O(4)	2.009(7)	Zn(1)—N(3)	2.033(11)
Zn(2)—O(20)	1.992(9)	Zn(2)—N(2)	2.036(10)	Zn(2)—O(10)	2.013(8)
[1]-X,+Y,1/2-Z					
Complex **2**					
Dy(1)—O(1)	2.369(7)	Dy(1)—O(2)	2.292(9)	Dy(1)—O(6)	2.583(8)
Dy(1)—O(7)	2.349(8)	Dy(1)—O(11)	2.548(10)	Dy(1)—O(12)	2.479(11)
Dy(1)—O(14)	2.436(9)	Dy(1)—O(15)	2.646(10)	Dy(1)—O(17)	2.464(9)
Dy(1)—O(18)	2.469(9)	Dy(1)—N(6)	2.930(13)	Dy(1)—N(7)	2.908(13)
Dy(2)—O(4)	2.274(8)	Dy(2)—O(5’)	2.574(8)	Dy(2)—O(4’)	2.274(8)
Dy(2)—O(9)	2.287(9)	Dy(2)—O(9’)	2.287(9)	Dy(2)—O(5)	2.574(8)
Dy(2)—O(10’)	2.322(7)	Zn(1)—O(1)	1.985(7)	Dy(2)—O(10)	2.322(7)
Zn(1)—O(8)	2.162(8)	Zn(1)—O(20)	2.016(11)	Zn(1)—O(7)	2.048(7)
Zn(2)—O(3)	2.199(9)	Zn(2)—O(4)	1.997(8)	Zn(1)—N(3)	2.031(10)
Zn(2)—O(21)	2.041(9)	Zn(2)—N(2)	2.040(9)	Zn(2)—O(10)	2.047(8)
[1]-X,+Y,1/2-Z					

Supplementary Structural Figures.



(M)-form

(P)-form

Figure S4. M and P enantiomers extracted from the structure of complex **1**

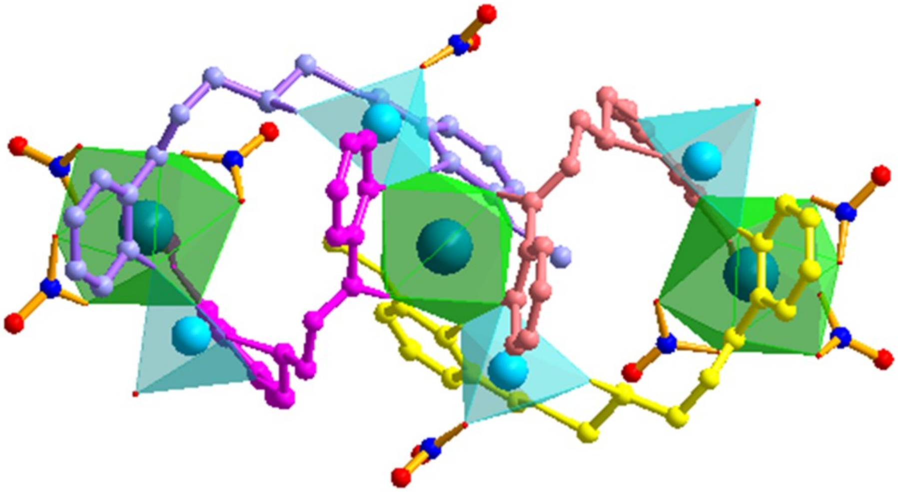


Figure S5. Coordination polyhedrons of the Tb and Zn ions in complex **1**

2. Photophysical properties

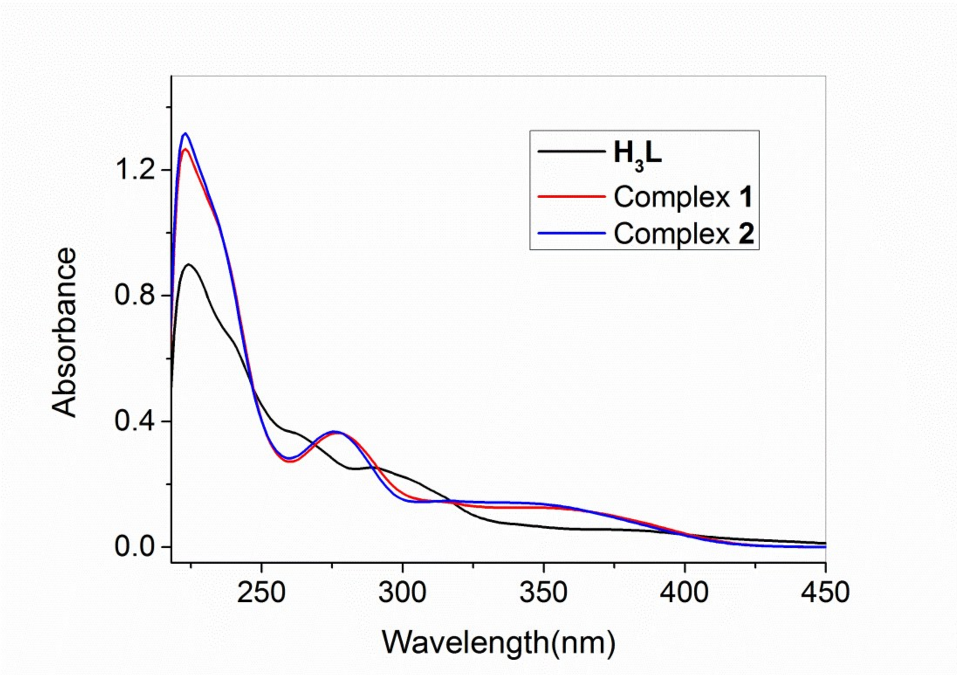


Figure S6. UV/Vis absorption spectra of $\mathbf{H_3L}$, and complexes **1-2** in MeCN solution ($1x10^{-5}$ m) at room temperature.

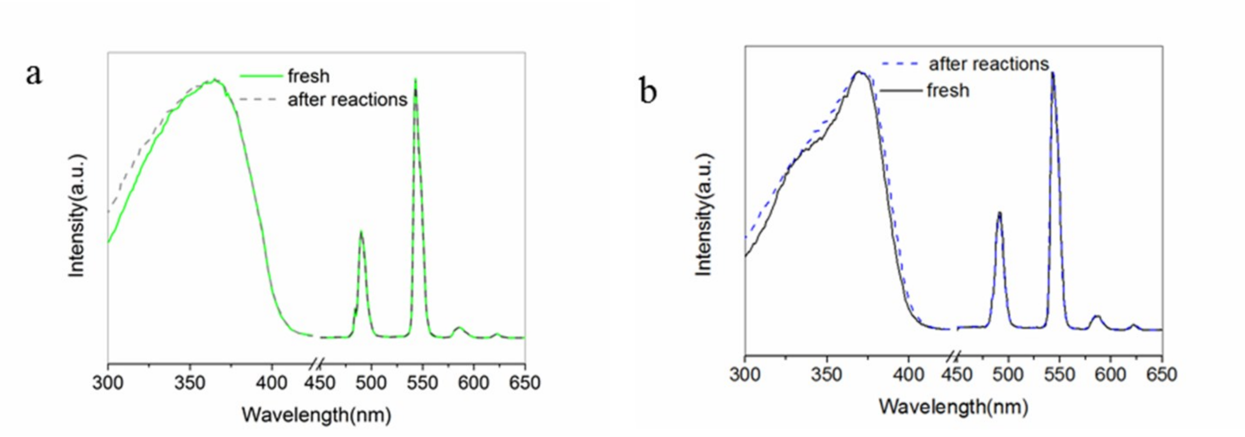


Figure S7. Normalized excitation and emission spectra of the recycled catalyst in the solid state (a) and MeCN solution (1×10^{-5} m); (b) at room temperature

Table S3. Comparison of luminescence lifetimes and quantum yields of **1** and after reactions in the solid state and MeCN solution (1×10^{-5} m) under excitation at 365 nm at room temperature.

Complex **1**	State/solvent	τ_1(us)	τ_2(us)	Φ(%)
Fresh	solid	385	898	15.06
	CH_3CN	291	702	9.10
After reactions	solid	353	831	11.16
	CH_3CN	170	571	5.98

3. Catalysis Details

General procedure for the reaction of CO_2 cycloaddition of Epoxides.

The reactions were conducted in a 50 mL autoclave reactor and three cycles of pressurisation and depressurisation of the reactor (with CO_2 at 0.4 MPa) were carried out before finally stabilizing the pressure at 1 MPa. Then the vessel was set in an oil bath and stirring at 120 ^{o}C. After 1 h, the reaction was cooled down to room temperature and a small liquot of the supernatant reaction mixture was taken to be analyzed by ^{1}H NMR to calculate the yields of the reaction. Ambient experiments were conducted in a 20 mL flask that was charged with catalyst, TBAB and epoxide at room temperature for 48 h under an atmosphere of CO_2. The residue containing recovered catalyst was through centrifugal separation, washed with CH_3CN for three times and dried in vacuum, which can be used for the recycle reaction directly.

Table S4. Overview of salen-Zn and lanthanide complexes catalysts

Cat. (%)	Co-cat. (%)	Catalyst/Epoxide (Mole ratio)	P (MPa)	T (^oC)	Time (h)	Yields (%)	TOF (h^{-1})	Ref
$(C_6H_5)_3Nd(THF)$	TBAI (0.8)	(styrene oxide) 1:500	0.1	85	24	93	19	2
Ionic Rare Earth Metal Complexes	-	(styrene oxide) 1:500	0.1	90	12	93	38	3
{[Eu(BTB)(phen)] ·4.5DMF·$2H_2O$}n	TBAB (2.5)	(styrene oxide) 1:286	0.1	80	12	68	2	4
Tb_4 MOF	TBAB (2.5)	(styrene oxide) 1:50	0.1	60	12	95	4	5
1·Gd	TBAB (2.5)	(styrene oxide) 1:133	0.1	60	12	70	1	6
3d-4f MOF	TBAB (2.5)	(styrene oxide) 1:100	0.1	70	12	77	6.5	7
Yb-mesocate	TBAB (0.75)	(styrene oxide) 1:1000	1	120	2.5	95	380	8
$[La\{N(SiHMe_2)_2\}_{2-}$ $\{k^3$-bpzcp}]	TBAB (0.05)	(propylene oxide) 1:1000	1	70	4	95	59	9
Yb-DDPY	TBAB (0.5)	(styrene oxide) 1:400	1	60	12	52	17	10
Salen-Zn[a]	TBAI (0.5)	(styrene oxide) 1:670	1	80	6	89	99	11
$[L1Zn_2]_4$	TBAI (2.5)	(propylene oxide) 1:40	1	45	68	87	-	12
Zn_3	-	(epichlorohydrin) 1:40	1	85	18	80	1.8	13
1	TBAB (0.75)	(styrene oxide) 1:4000	1	120	1	96	3840	This work
1	TBAB (0.75)	(styrene oxide) 1:4000	1	80	6	94	627	This work
1	TBAB (0.75)	(styrene oxide) 1:4000	1	60	1	15	600	This work
1	TBAB (3)	(styrene oxide) 1:800	1	40	18	85	36	This work

a. N, N-phenylene-1,2-bis-salicylideneimine (salen Zn).

Table S5. Representative homogeneous and heterogeneous catalysts with high TOF used for the synthesis of cyclic carbonates.

Cat.	Co-cat.	Catalyst/Epoxide (Mole ratio)	P (MPa)	T (°C)	Time (h)	Yields (%)	TOF (h^{-1})	Ref
-	TBAB (0.9)	(propylene epoxide) 1:40000	3	120	1	11.5	-	14
Zn-CMP	TBAB (0.9)	(propylene epoxide) 1:40000	3	120	1	29	11600	14
$Zn(OPO)_2$	TBAB (0.9)	(propylene epoxide) 1:40000	3	120	1	46	18400	11
1	TBAB (0.9)	(propylene epoxide) 1:40000	2	120	1	59	23600	This work
1	TBAB (0.9)	(styrene oxide) 1:40000	2	120	1	78	31200	This work
Zn-porphyrin	-	(1,2-Epoxyhexane) 1:33333	1.7	160	1	79	26333	15
Al-aminotriphenolate	PPN-Br	(1,2-Epoxyhexane) 1:200000	1	90	2	36	36000	16
Mg-porphyrin	-	(1,2-Epoxyhexane) 1:33333	1.7	120	1	36	12000	17
1	TBAB (0.5)	(styrene oxide) 1:40000	1	120	1	67	26800	This work
-	TBAB (0.5)	(styrene oxide) 1:40000	1	120		19	-	This work

E. hexabutylguanidinium bromide

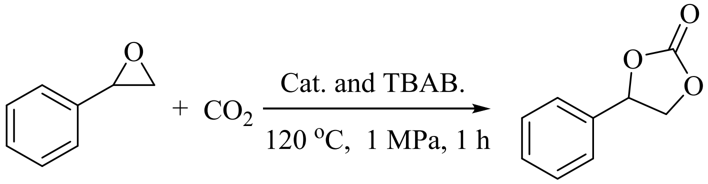


Table S6. Synthesis of cyclic carbonate via insertion of CO_2 to styrene oxide catalysed by **1** and $\mathbf{H_3L}$ under 120 °C, respectively.

Entry	Cat.(%)	Co-cat.(%)	T(°C)	P(bar)	Time(h)	Yield(%)	TOF(h^{-1})
1	-	TBAB(0.75)	120	10	1	25	-
2	**1**(0.025)	TBAB(0.75)	120	10	1	96	3840
3	**1**(0.025)	TBAB(0.5)	120	10	1	85	3400
4	**1**(0.025)	TBAB(0.4)	120	10	1	80	3200
5	**1**(0.025)	TBAB(0.25)	120	10	1	54	2160
6	**1**(0.0025)	TBAB(0.5)	120	10	1	67	26800
7	**1**(0.0025)	TBAB(0.9)	120	20	1	78	31200
8	$\mathbf{H_3L}$	-	120	10	1	0	-
9	$\mathbf{H_3L}$	TBAB(0.75)	120	10	1	47	470

Reaction conditions: 10 mmol epoxide, 0.0025-0.025 mol % catalyst, 0.25-0.9 mol % TBAB, 120 °C, 1 h, 10-20 atm. $\mathbf{H_3L}$ utilized was with the same amount in 0.025 mol % of **1**. Yields were determined by ^1H NMR analysis. Selectivity of cyclic carbonates were all >99%.

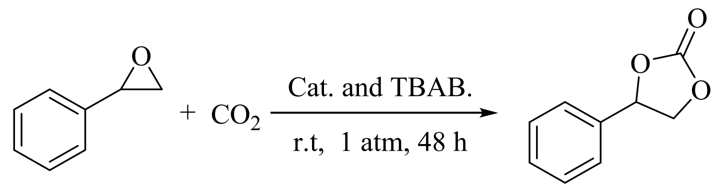


Table S7. Synthesis of cyclic carbonate via insertion of CO_2 to styrene oxide catalysed by catalyst **1** under ambient condition.

Entry	Cat.(%)	Co-cat.(%)	T(°C)	P(bar)	Time(h)	Yield(%)
1	-	TBAB(7.2)	r.t	1	48	11
2	**1**(0.125)	TBAB(7.2)	r.t	1	48	81
3	**1**(0.125)	TBAB(6)	r.t	1	48	80
4	**1**(0.125)	TBAB(4.8)	r.t	1	48	79
5	**1**(0.125)	TBAB(3.6)	r.t	1	48	76
6	**1**(0.125)	TBAB(1.8)	r.t	1	48	46

Reaction conditions: 10 mmol epoxide, 0.125 mol % catalyst, 1.8-7.2 mol % TBAB, r,t, 48 h, 1 atm; Yields were determined by ^1H NMR analysis. Selectivity of cyclic carbonates were all >99%.

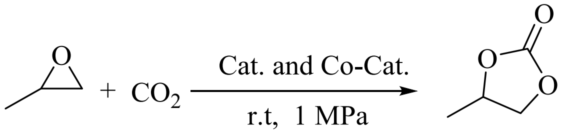


Table S8. Synthesis of cyclic carbonate via insertion of CO_2 to PO catalysed by catalyst **1**.

Entry	Cat.(%)	Co-cat.(%)	T(°C)	P(bar)	Time(h)	Yield(%)[a]
1	-	TBAB(7.2)	r.t	10	24	16
2	**1**(0.125)	TBAB(7.2)	r.t	10	24	96
3	-	TBAB(2.5)	r.t	10	24	14
4	**1**(0.125)	TBAB(2.5)	r.t	10	24	79

Reaction conditions: 10 mmol epoxide, 0.125 mol % catalyst, 2.5-7.2 mol % TBAB, r.t, 24 h, 10 atm; Yields were determined by ^{1}H NMR analysis. Selectivity of cyclic carbonates were all >99%.

Table S9. Recycling experiments of CO_2 cycloaddition of styrene oxide under the ambient conditions (styrene oxide, 10 mmol; catalyst, 12.5 μmol; TBAB, 0.72 mmol; 1atm, r.t, 48 h)

Entry	Round	Yield/%
1	1	81
2	2	80
3	3	77
4	4	76
5	5	74

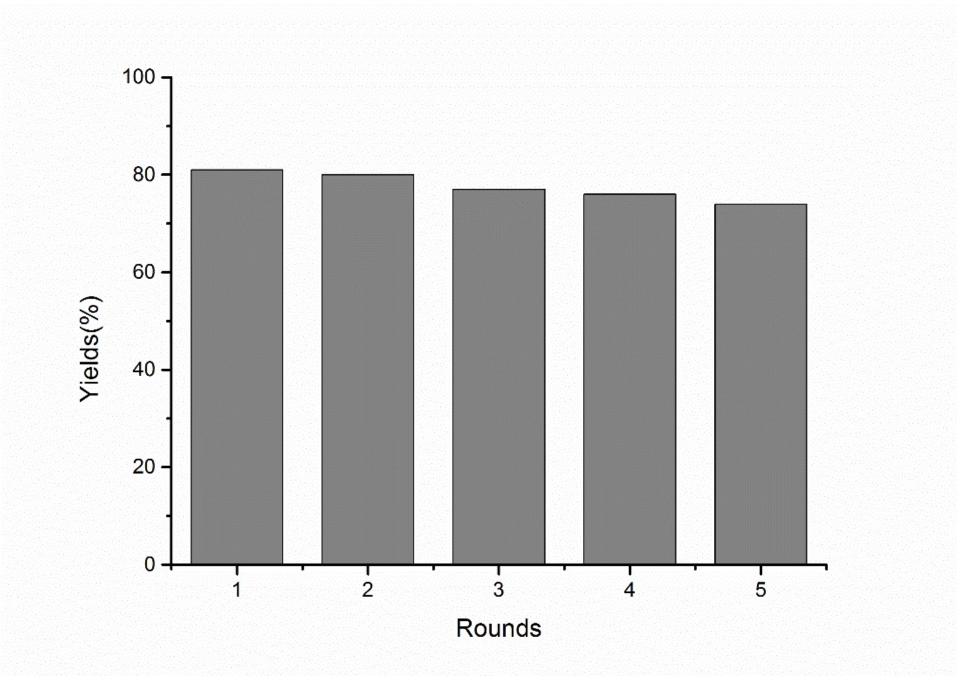


Figure S8. Recycling experiments of CO_2 cycloaddition of styrene oxide under ambient conditions

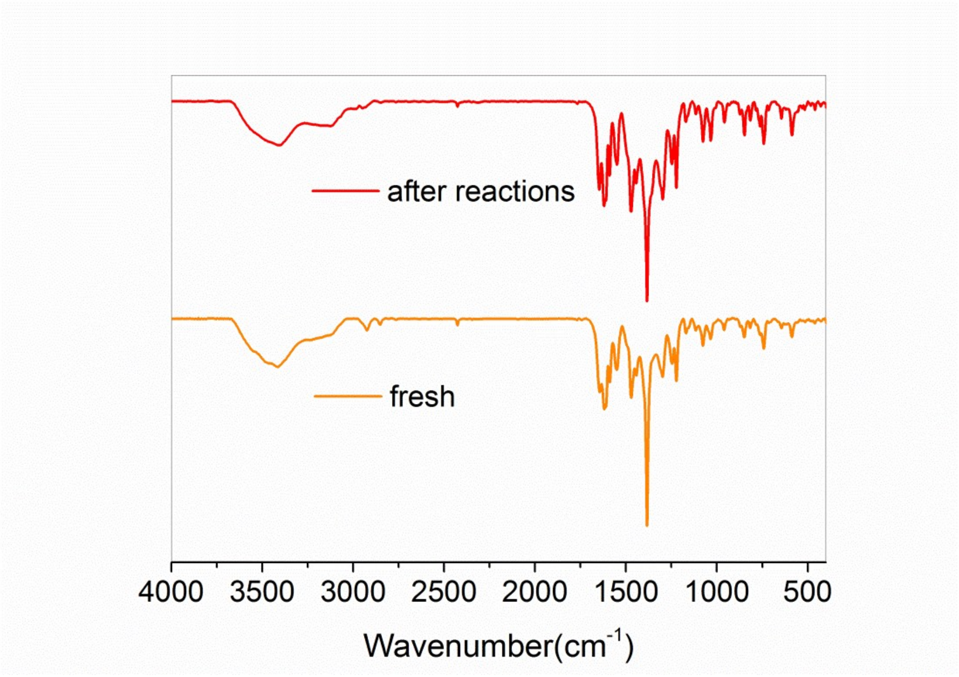


Figure S9. IR spectra of **1** and its sample after recycled reactions.

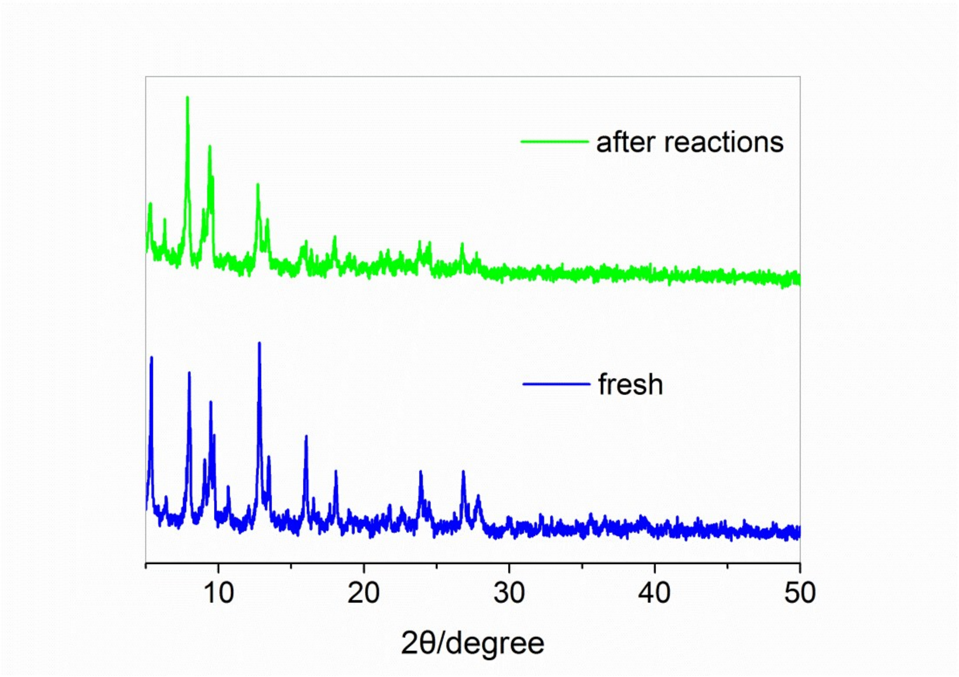


Figure S10. PXRD patterns of **1** and the recycled catalyst after reactions

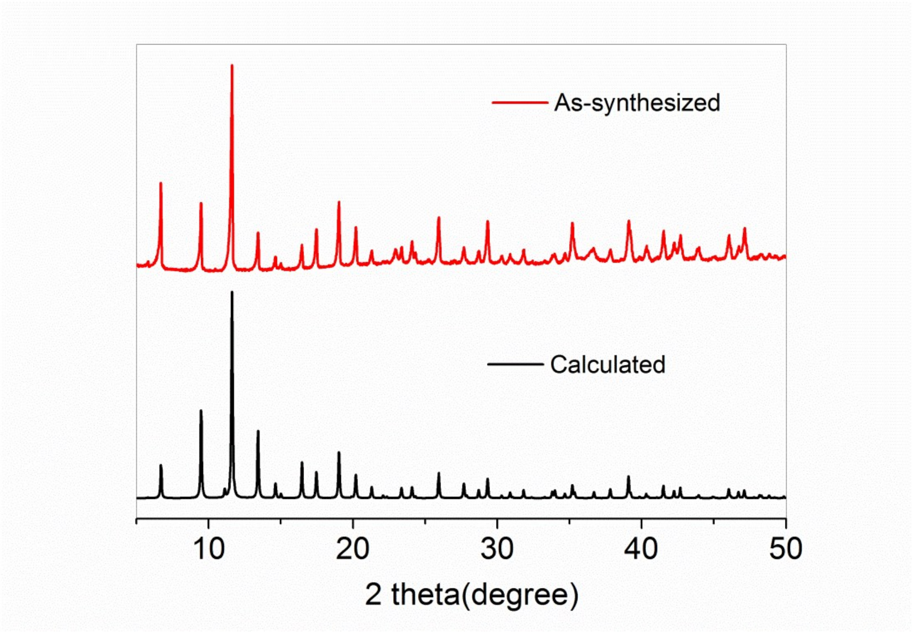


Figure S11. Comparing the simulated PXRD with experimental patterns of HKUST-1.

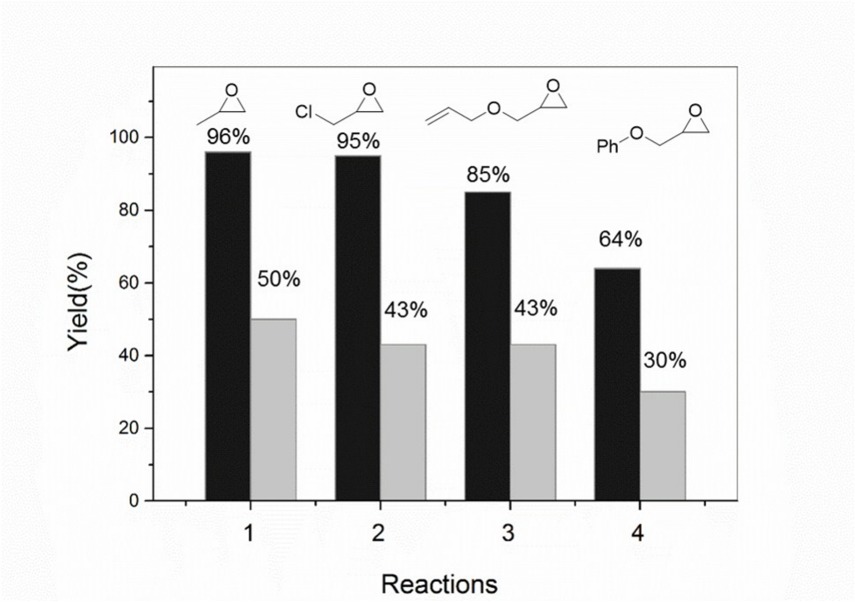


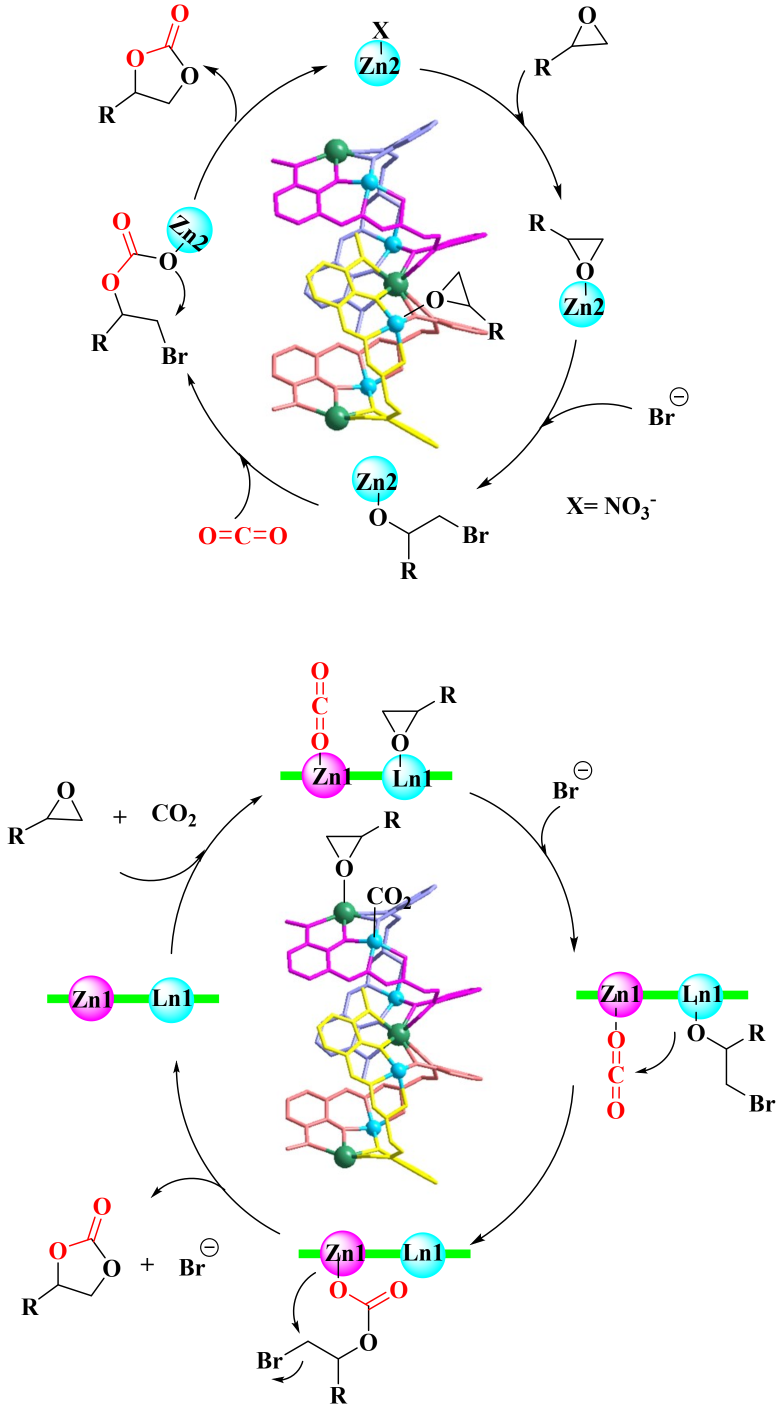
Figure S12. The yields of various cyclic carbonates catalyzed by **1** (black) and HKUST-1 (grey) after 48 h reactions under ambient condition, respectively.

Table S10. Overview of the MOFs catalysts for the conversion of CO_2 to cyclic carbonates under similar conditions

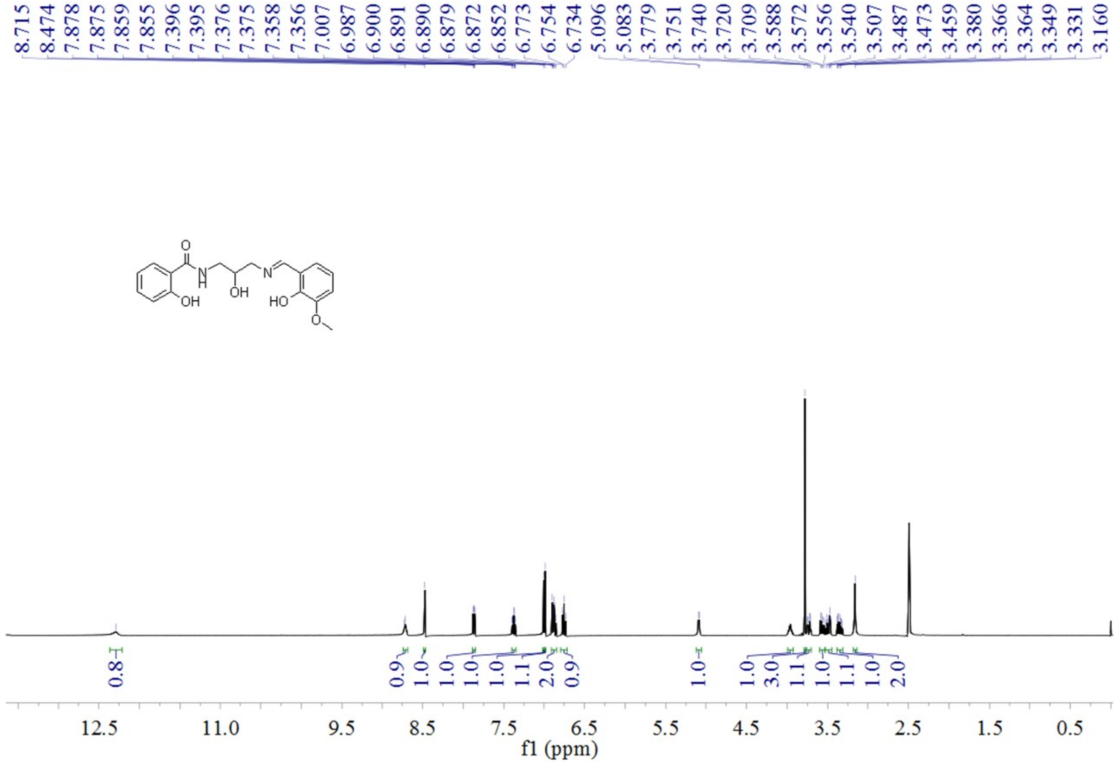
MOF (loading[a])	Co-cat. (%)	Epoxide	T (K)	p (bar)	Reaction time (h)	Yield (%)	Reusability	Substrate scope (diffusion limitation)	Ref
$(Zn_4O)_2(Zn_2)1.5(CPD)_6$ (0.016mol % of metal)	Bu_4NBr (3.7)	PO	r.t	12	60	99	good	diffusion limitation	18
Hf-NU-1000 (4.0mol %, -OH)	Bu_4NBr (10)	SO	r.t	1	56	100	good	not studied	19
USTC-253-TFA (1mol % of metal)	Bu_4NBr (6.5)	PO	298	1	72	81	good	not studied	20
MIL-53 (1mol % MOF)	Bu_4NBr (6.5)	PO	298	1	72	54	not studied	not studied	20
MOF-253 (1mol % MOF)	Bu_4NBr (6.5)	PO	298	1	72	82	not studied	not studied	20
MIL-101 (1mol % MOF)	Bu_4NBr (6.5)	PO	298	1	72	31	not studied	not studied	20
UiO-66 (1mol % MOF)	Bu_4NBr (6.5)	PO	298	1	72	55	not studied	not studied	20
ZnGlu (1.6mol % MOF)	Bu_4NBr (1.6)	PO	r.t	10	24	65	very low	not studied	21
$Zn_3(PTB)_2$	Bu_4NBr (7 .2)	PO	r.t	1	48	92	not studied	limited diffusion of larger epoxide molecules	22
MMPF-9 (0.125mol % MOF)	Bu_4NBr (7.2)	PO	r.t	1	48	87	only 1 recycling	diffusion limitation	23
MMPF-18 (0.25mol % metal)	Bu_4NBr (10)	PO	r.t.	1	48	97	low	diffusion limitation	24
MMCF-2 (0.125mol % MOF)	Bu_4NBr (7.2)	PO	r.t.	1	48	95	not studied	not studied	25
HKUST-1 (0.125mol % MOF)	Bu_4NBr (7.2)	PO	r.t.	1	48	49	not studied	not studied	25
MOF-505 (0.125mol % MOF)	Bu_4NBr (7.2)	PO	r.t.	1	48	48	not studied	not studied	25
$[Cu_4$(tetraisophtalic acid)]n (0.8mol % Cu)	Bu_4NBr (10)	PO	r.t.	1	48	96	good	low activity with bulkier substrates	26
Co-CMP (0.125mol % Co)	Bu_4NBr (7.2)	PO	r.t	1	48	81	good	not studied	27
1	Bu_4NBr	PO	r.t.	1	48	96	good	wide scope	This

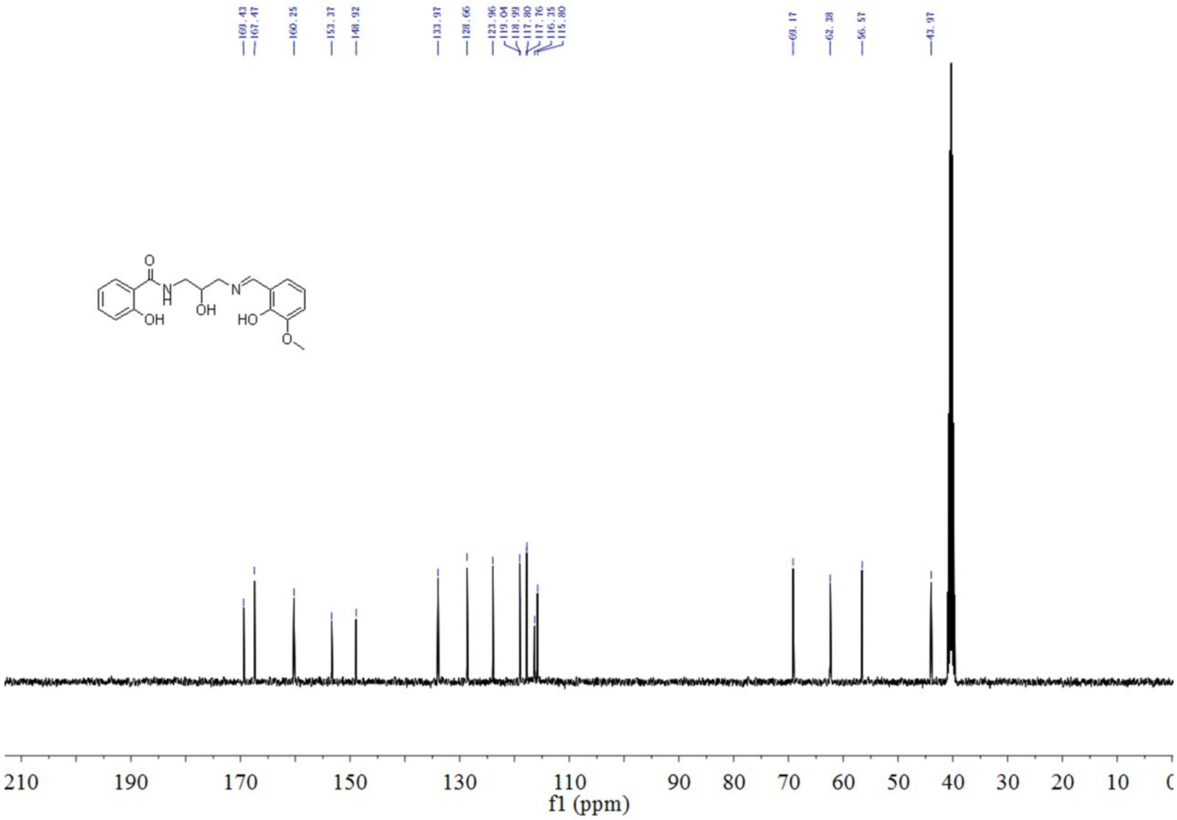
(0.125mol % complex)	(7.2)	SO	81	work

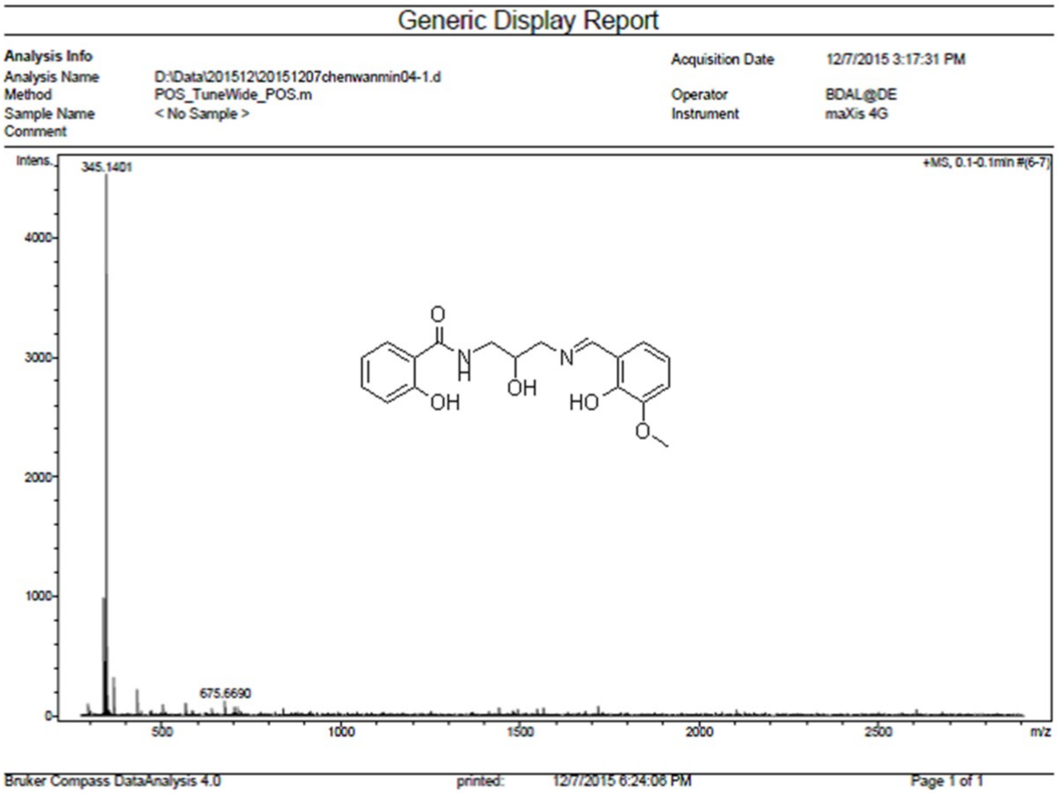
Figure S17. The proposed mechanisms for the cycloaddition reaction catalyzed by the helicates.



4. Characterization data and NMR Spectra.







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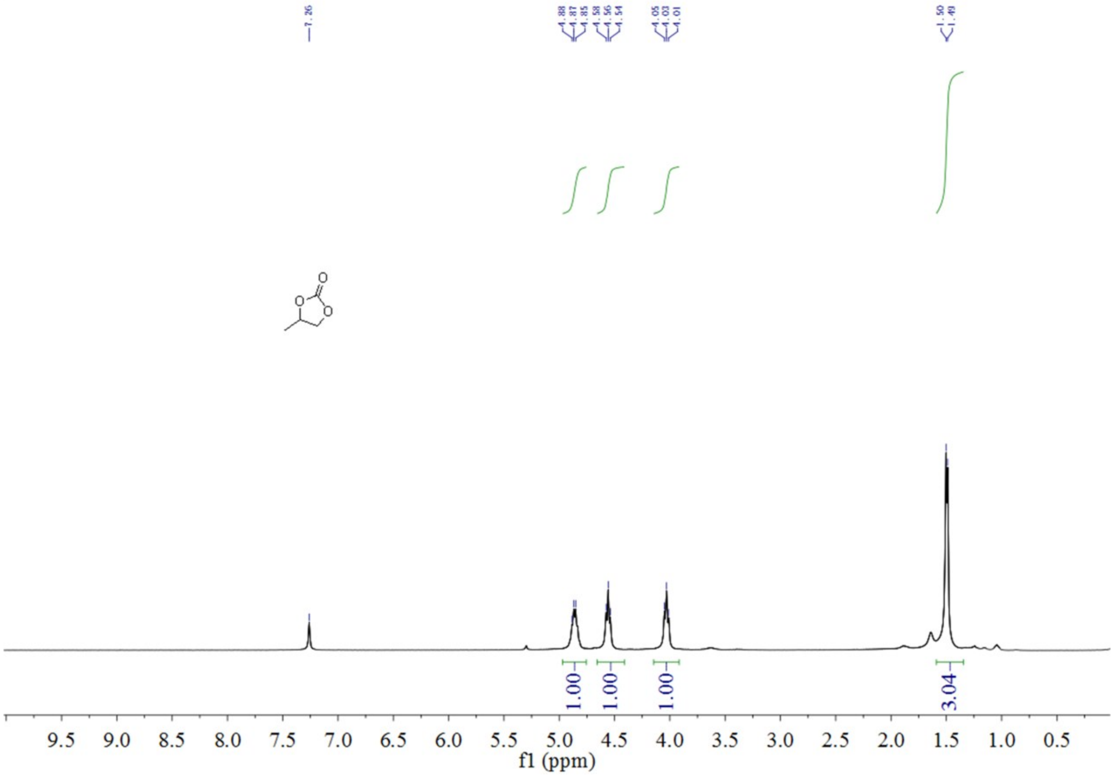

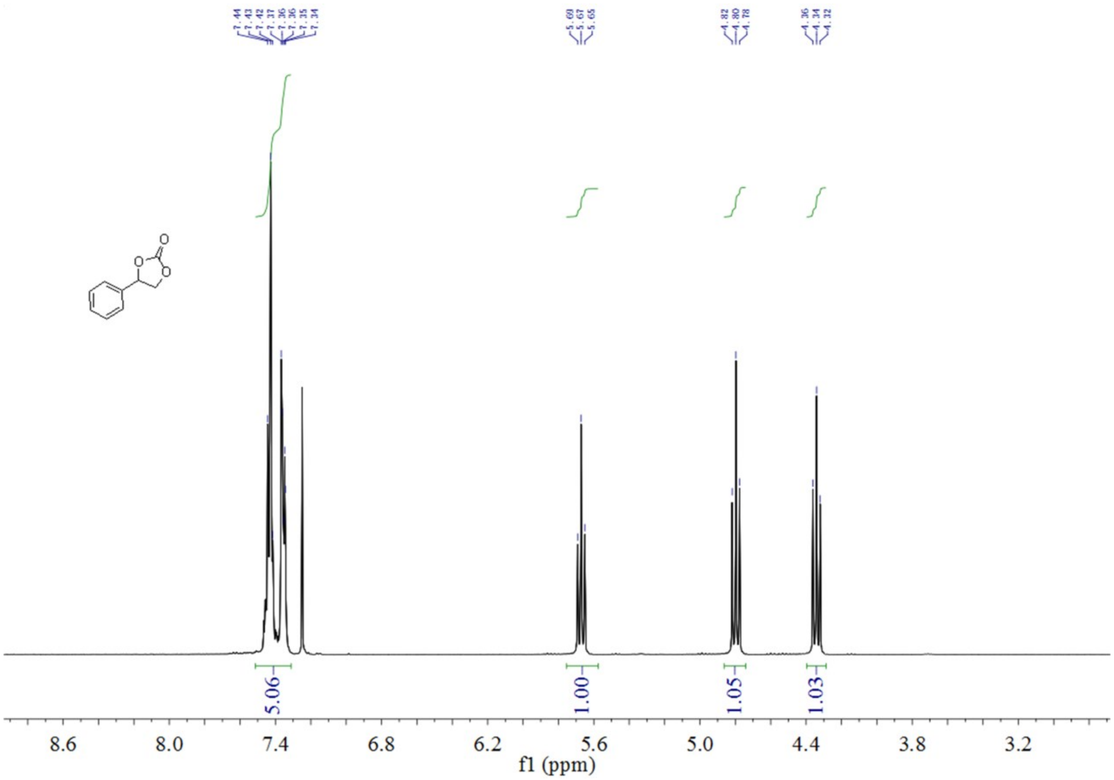
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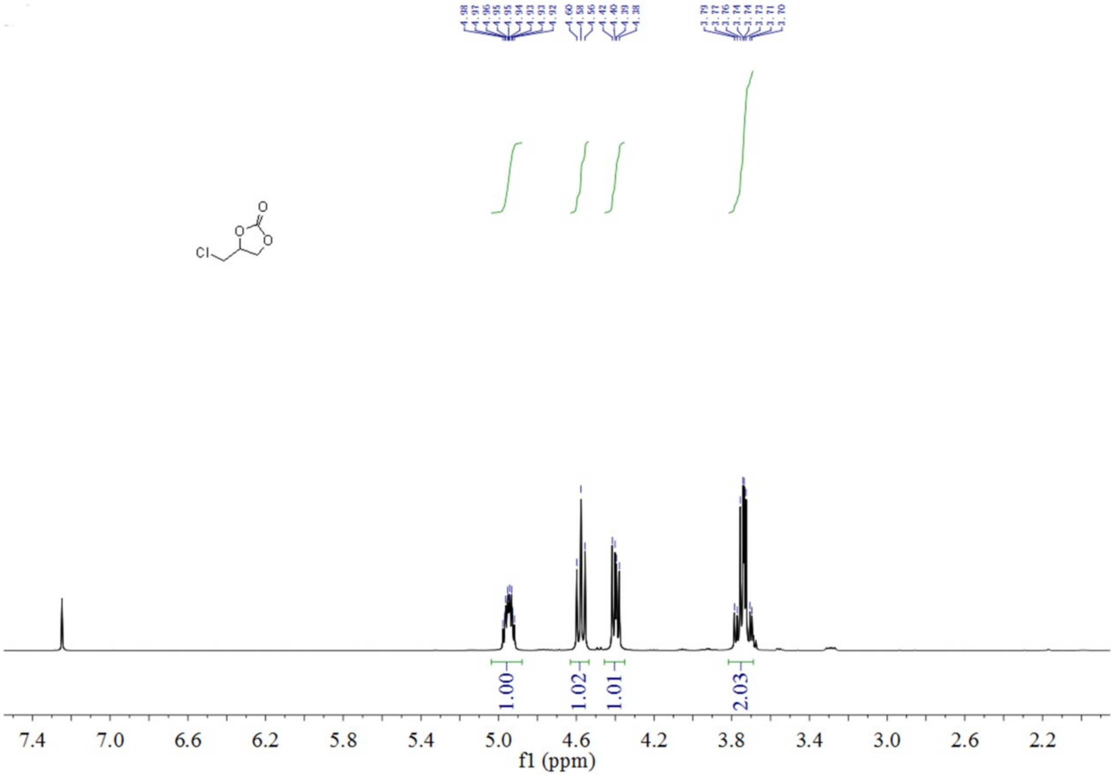
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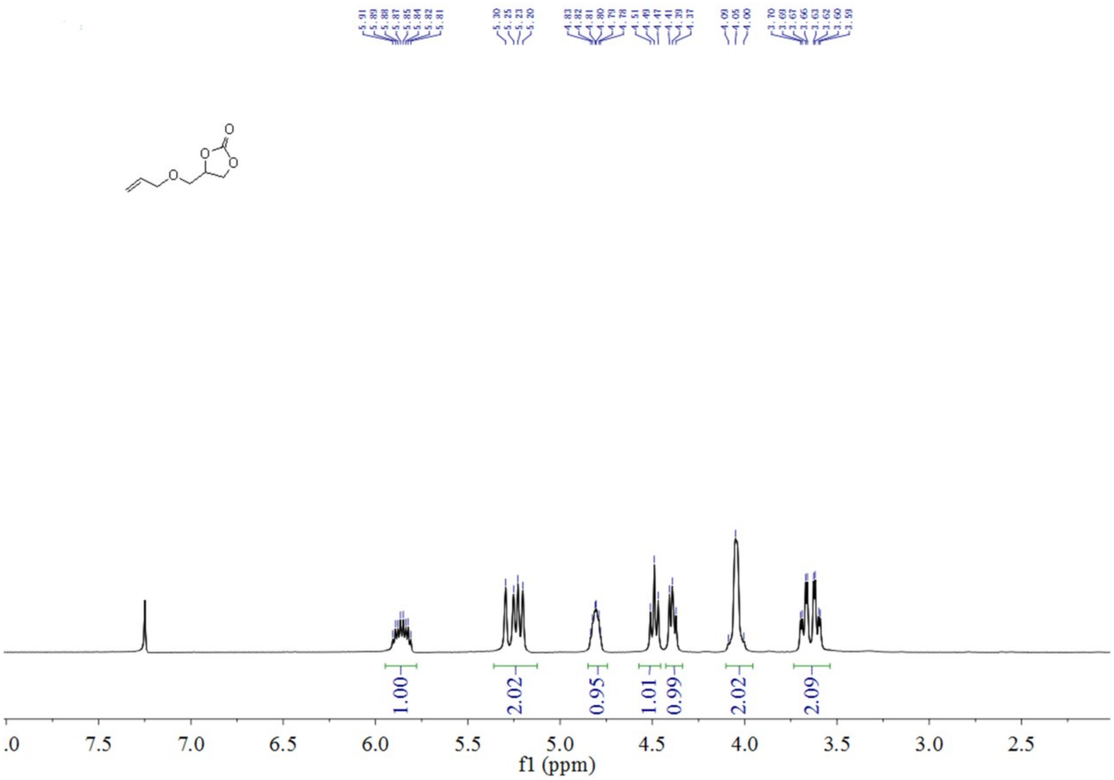
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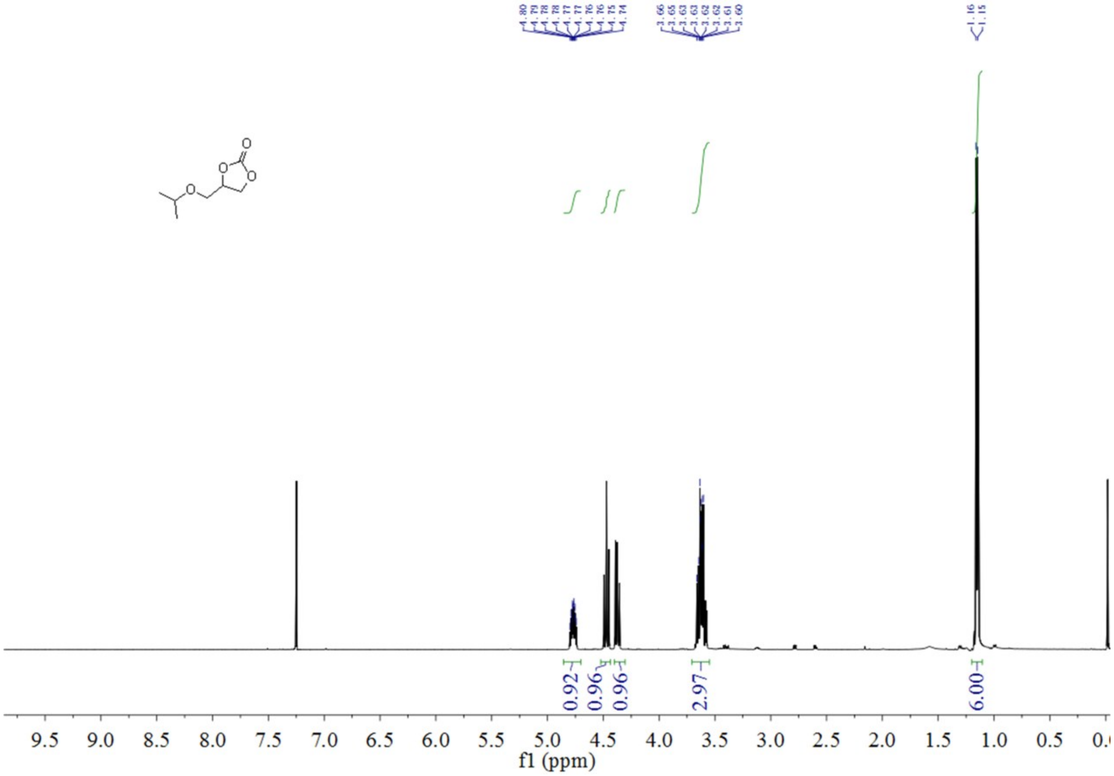
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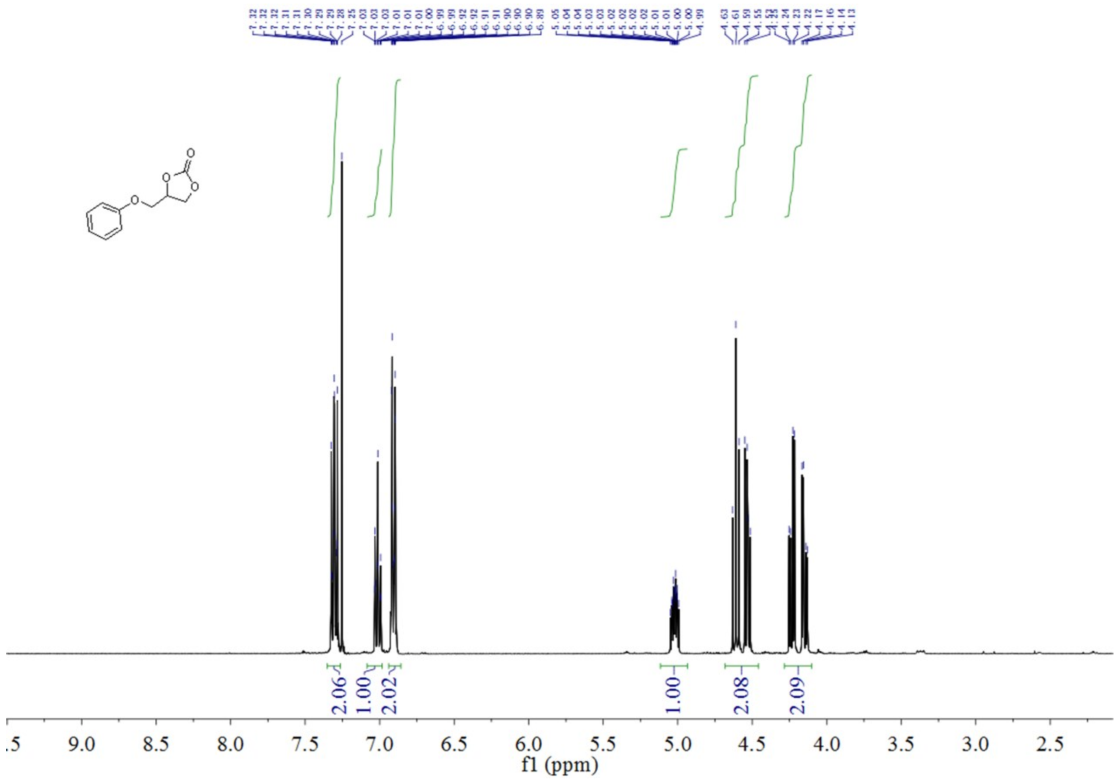
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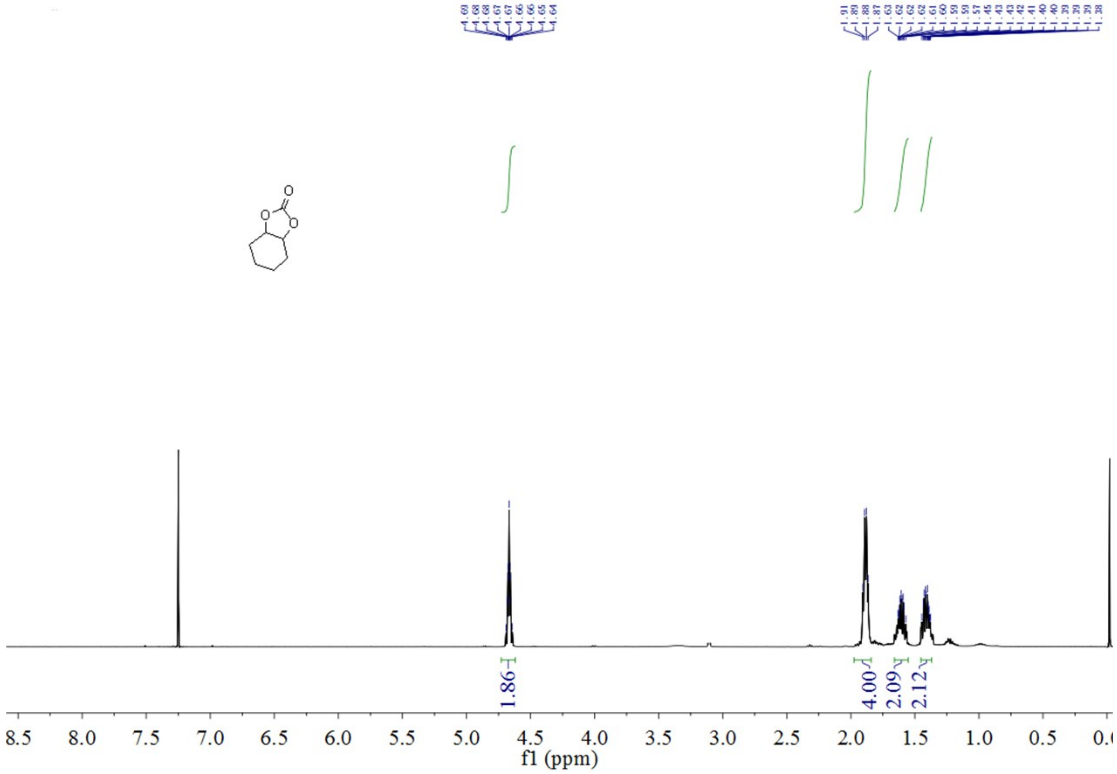
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