

Supporting Information

High Efficient 3d / 4d-4f Coordination Polymer Catalyst for Carbon Dioxide Fixation into Cyclic Carbonates

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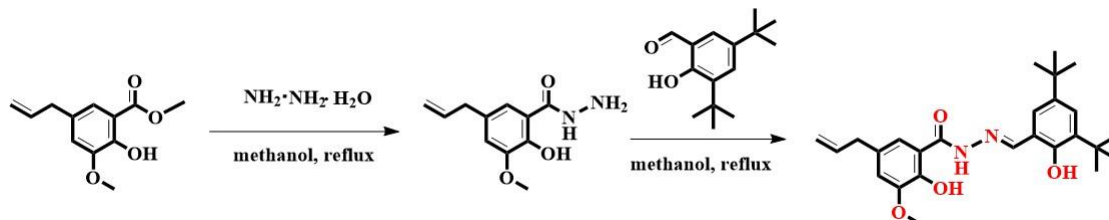
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1. Experimental section

1.1 Synthesis of ligand H₃L

All reagents were used as purchased without further purification. 5-allyl-2-hydroxy-3-methoxy benzohydrazide was prepared according to the literature method ¹.



Scheme. S1. Synthesis of ligand H₃L

The synthesis of ligand H₃L: 5-allyl-2-hydroxy-3-methoxy benzohydrazide (2.22 g, 10 mmol) was added to a solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) in 30 mL methanol. The mixture was stirred at reflux for 6 h at 60°C and then cool to room temperature. The product was separated by filtration and further washing with ethanol to afford H₃L as a pale yellow green solid (3.6 g, Yield: 82%). ¹H NMR (400 MHz, DMSO-d₆): δ 8.75 (s, 8H), 8.62 (s, 8H), 7.57 – 7.47 (m, 10H), 6.69 (d, J = 6.7 Hz, 2H), 6.22 (s, 3H), 5.00 – 4.86 (m, 2H), 4.04 (ddt, J = 16.8, 10.1, 6.7 Hz, 1H), 3.02 (d, J = 2.3 Hz, 1H), 2.80 (d, J = 2.4 Hz, 1H), 2.71 (d, J = 2.3 Hz, 1H), 1.43 (s, 1H), -1.33 (s, 1H), -2.06 (s, 1H), -2.14 (s, 1H). IR (KBr, cm^{-1}): 3435 (s), 2960 (s), 1590 (s), 1460 (s), 1369 (s), 1265 (s), 1245 (s), 1210 (s), 1175 (s), 1302 (s), 1067 (w), 995 (w), 920 (m), 875(m), 780(m). ESI-MS m/z [(M+H)⁺]: 439.27.

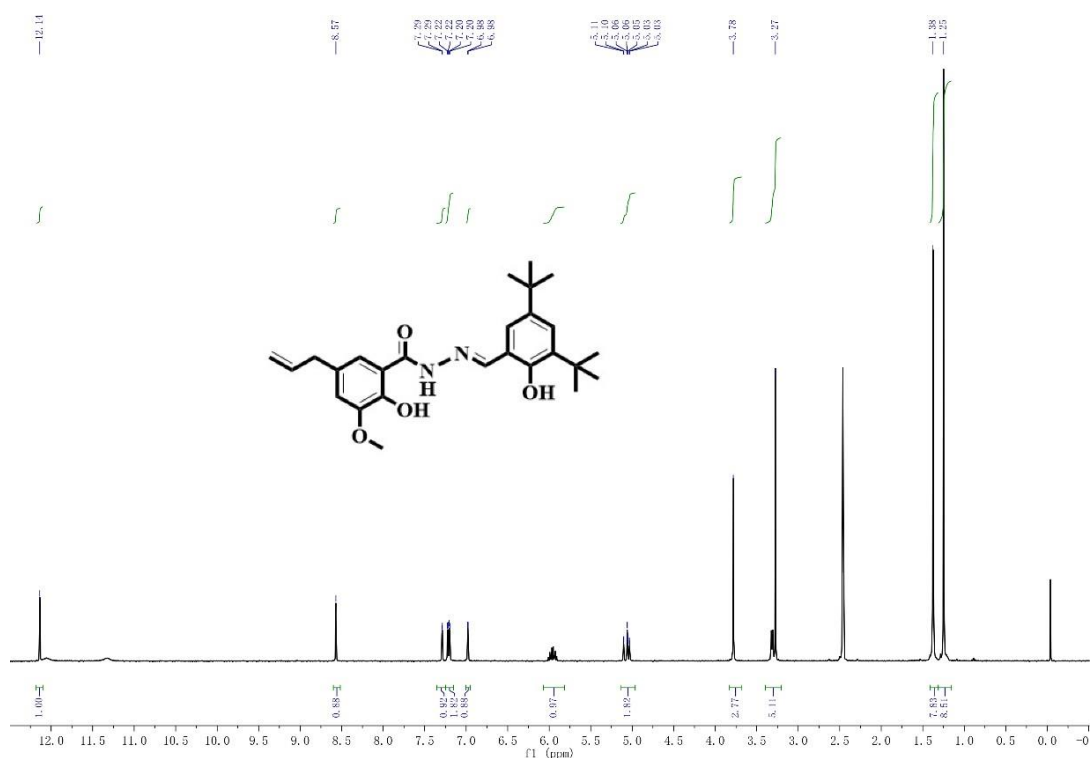


Fig. S1. ¹H-NMR (400 MHz, DMSO-d₆) spectra of the H₃L

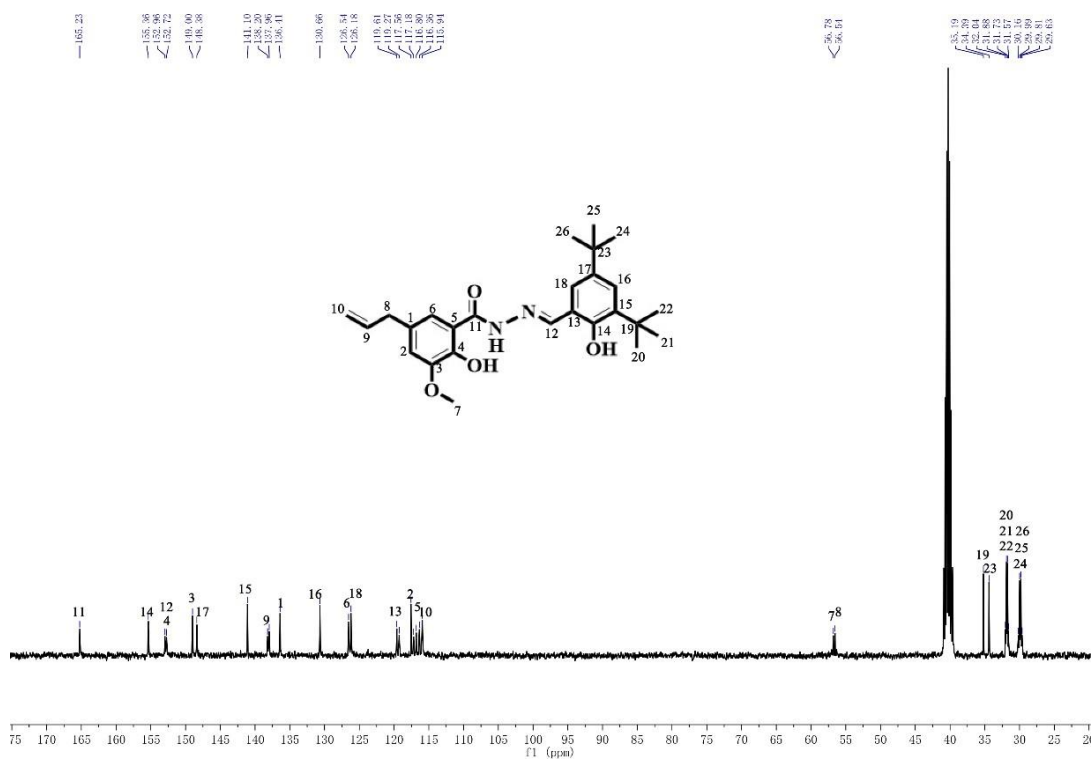


Fig. S2. ¹³C-NMR (100 MHz, DMSO-d₆) spectra of the H₃L

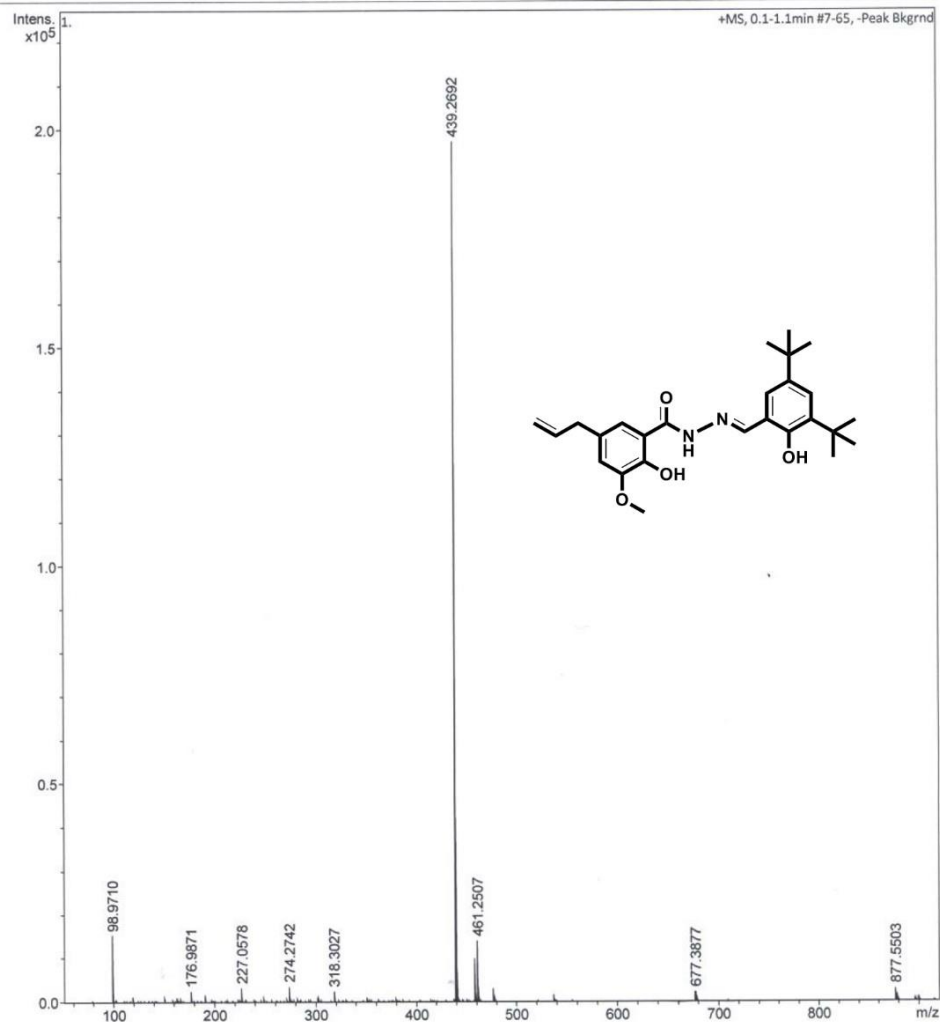
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Operator LZU
Instrument micrOTOF



Bruker Compass DataAnalysis 4.1

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Fig. S3. Mass spectrum of the H₃L

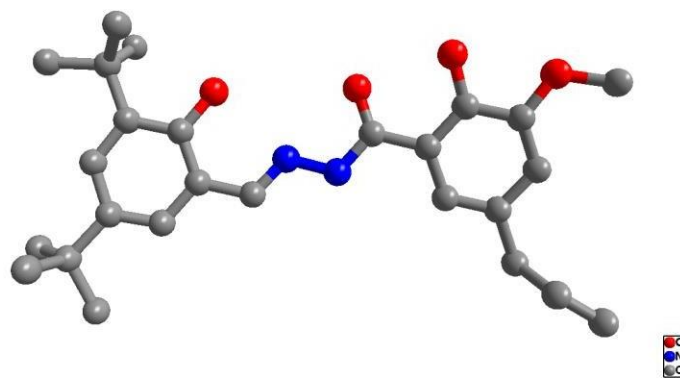


Fig. S4. Single crystal structure of H₃L

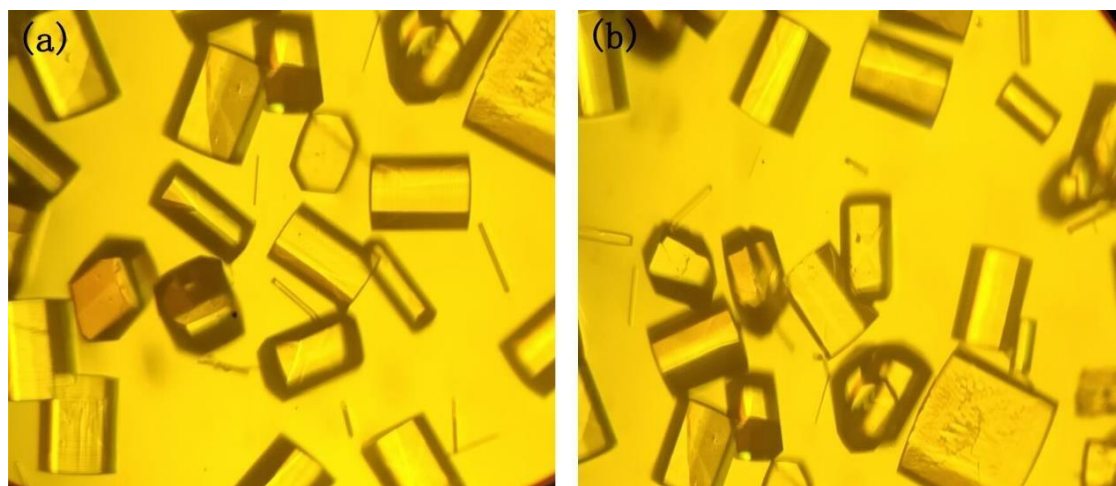


Fig. S5. Photographs of as-synthesized crystals of complex 1 (a) and complex2 (b)

Crystallography

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

	H ₃ L	Complex 1	Complex 2
Empirical Formula	C ₂₆ H ₃₄ N ₂ O ₄	C ₁₁₇ H ₁₆₀ Zn ₂ Dy ₂ N ₉ O ₂₈	C ₁₁₃ H ₁₅₀ Cd ₂ Dy ₂ N ₉ O ₂₅
Formula weight	438.55	2596.27	1765.73
Temp (K)	100K	100 K	100 K
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	P 2 ₁ /c	P 2 ₁ /c
a (Å)	23.436 (2),	19.7435(11)	19.5629(9)
b (Å)	8.3954 (7),	30.6695(7)	30.9876(7)
c (Å)	25.163 (2)	27.5210(15)	27.6893(14)
(deg)	90	90	90
(deg)	90	120.528(3)	121.014(3)
(deg)	90	90	90
V(Å ³)	4951.1 (8)	14354.6(12)	14385.8(11)
Z	8	4	4
D _{calc} (Mg/m ³)	1.177	1.201	1.194
(mm ⁻¹)	0.08	6.372	1.380
F(000)	1888	5364	5279
Reflections collected	15891	18199	16532
No. of parameters	306	1463	1443
R _{int}	0.070	0.079	0.066
R ₁ [I > 2σ(I)]	0.078	0.080	0.0717
wR ₂ [I > 2σ(I)]	0.1999	0.247	0.1858

Goodness-of-fit on F ²	1.04	1.02	1.03
CCDC number	1829444	1815465	1815466

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

Complex1			
Dy1—O1	2.218 (4)	Dy2—O16 ⁱⁱⁱ	2.194 (5)
Dy1—O2	2.405 (4)	Dy2—O25	2.430 (5)
Dy1—O7 ⁱ	2.354 (5)	Dy2—O26	2.427 (5)
Dy1—O8 ⁱ	2.188 (5)	Dy2—N5	2.509 (5)
Dy1—O21	2.407 (6)	Dy2—N7 ⁱⁱⁱ	2.530 (6)
Dy1—O22	2.401 (6)	Zn2—O11	1.972 (5)
Dy1—N1	2.530 (5)	Zn2—O12	2.301 (8)
Dy1—N3 ⁱ	2.529 (6)	Zn2—O13	2.380 (7)
Zn1—O3	2.008 (5)	Zn2—O14	1.969 (6)
Zn1—O4	2.325 (5)	Zn2—O19	1.979 (8)
Zn1—O5	2.448 (6)	Zn2—O24	2.123 (9)
Zn1—O6	1.971 (5)	O15—Dy2 ^{iv}	2.375 (4)
Zn1—O17	1.991 (6)	O16—Dy2 ^{iv}	2.194 (5)
Zn1—O23	2.100 (6)	N7—Dy2 ^{iv}	2.530 (6)
O7—Dy1 ⁱⁱ	2.354 (5)	O8—Dy1 ⁱⁱ	2.188 (5)
N3—Dy1 ⁱⁱ	2.529 (6)		
O1—Dy1—O2	134.38 (17)	O9—Dy2—O15 ⁱⁱⁱ	80.36 (16)
O1—Dy1—O7 ⁱ	80.02 (18)	O9—Dy2—O25	152.09 (16)
O1—Dy1—O21	91.5 (2)	O9—Dy2—O26	87.95 (19)
O1—Dy1—O22	151.7 (2)	O9—Dy2—N5	70.25 (17)
O1—Dy1—N1	69.91 (17)	O9—Dy2—N7 ⁱⁱⁱ	82.24 (17)
O1—Dy1—N3 ⁱ	85.65 (17)	O10—Dy2—O25	70.77 (16)
O2—Dy1—O21	73.3 (2)	O10—Dy2—O26	75.09 (19)
O2—Dy1—N1	64.66 (17)	O10—Dy2—N5	64.56 (17)
O2—Dy1—N3 ⁱ	134.49 (17)	O10—Dy2—N7 ⁱⁱⁱ	137.01 (17)
O7 ⁱ —Dy1—O2	131.31 (17)	O15 ⁱⁱⁱ —Dy2—O10	131.36 (17)
O7 ⁱ —Dy1—O21	72.57 (19)	O15 ⁱⁱⁱ —Dy2—O25	72.14 (16)
O7 ⁱ —Dy1—O22	72.2 (2)	O15 ⁱⁱⁱ —Dy2—O26	73.85 (18)
O7 ⁱ —Dy1—N1	134.64 (18)	O15 ⁱⁱⁱ —Dy2—N5	136.43 (18)
O7 ⁱ —Dy1—N3 ⁱ	64.33 (19)	O15 ⁱⁱⁱ —Dy2—N7 ⁱⁱⁱ	64.23 (18)
O8 ⁱ —Dy1—O1	99.22 (18)	O16 ⁱⁱⁱ —Dy2—O9	99.74 (17)
O8 ⁱ —Dy1—O2	81.20 (17)	O16 ⁱⁱⁱ —Dy2—O10	80.63 (17)
O8 ⁱ —Dy1—O7 ⁱ	134.04 (17)	O16 ⁱⁱⁱ —Dy2—O15 ⁱⁱⁱ	133.69 (17)
O8 ⁱ —Dy1—O21	152.54 (19)	O16 ⁱⁱⁱ —Dy2—O25	95.90 (17)
O8 ⁱ —Dy1—O22	96.4 (3)	O16 ⁱⁱⁱ —Dy2—O26	152.14 (18)
O8 ⁱ —Dy1—N1	84.97 (17)	O16 ⁱⁱⁱ —Dy2—N5	83.75 (19)
O8 ⁱ —Dy1—N3 ⁱ	69.78 (18)	O16 ⁱⁱⁱ —Dy2—N7 ⁱⁱⁱ	69.88 (17)
O21—Dy1—N1	75.1 (2)	O25—Dy2—N5	134.79 (17)

O21—Dy1—N3 ⁱ	136.7 (2)	O25—Dy2—N7 ⁱⁱⁱ	81.66 (17)
O22—Dy1—O2	71.4 (2)	O26—Dy2—O25	88.9 (2)
O22—Dy1—O21	85.3 (3)	O26—Dy2—N5	73.7 (2)
O22—Dy1—N1	135.3 (2)	O26—Dy2—N7 ⁱⁱⁱ	137.95 (18)
O22—Dy1—N3 ⁱ	77.7 (2)	N5—Dy2—N7 ⁱⁱⁱ	137.90 (19)
N3 ⁱ —Dy1—N1	141.59 (19)	O11—Zn2—O12	74.7 (2)
O3—Zn1—O4	72.74 (19)	O11—Zn2—O13	86.1 (3)
O3—Zn1—O5	83.0 (2)	O11—Zn2—O19	98.2 (3)
O3—Zn1—O23	93.0 (2)	O11—Zn2—O24	89.5 (3)
O4—Zn1—O5	83.2 (2)	O12—Zn2—O13	80.9 (3)
O6—Zn1—O3	149.5 (2)	O14—Zn2—O11	157.0 (3)
O6—Zn1—O4	87.6 (2)	O14—Zn2—O12	93.4 (3)
O6—Zn1—O5	71.5 (2)	O14—Zn2—O13	72.5 (2)
O6—Zn1—O17	108.1 (2)	O14—Zn2—O19	103.9 (3)
O6—Zn1—O23	99.3 (3)	O14—Zn2—O24	97.0 (3)
O17—Zn1—O3	98.2 (3)	O19—Zn2—O12	105.3 (4)
O17—Zn1—O4	99.4 (2)	O19—Zn2—O13	173.2 (3)
O17—Zn1—O5	177.3 (2)	O19—Zn2—O24	88.6 (4)
O17—Zn1—O23	95.9 (2)	O24—Zn2—O12	160.2 (3)
O23—Zn1—O4	160.3 (2)	O24—Zn2—O13	86.2 (3)
O23—Zn1—O5	81.6 (2)		

Symmetry codes: (i) $-x-1, y+1/2, -z-3/2$; (ii) $-x-1, y-1/2, -z-3/2$; (iii) $-x, y-1/2, -z-3/2$; (iv) $-x, y+1/2, -z-3/2$.

Complex2			
Dy2—O17	2.187 (4)	Dy1—O5	2.194 (5)
Dy2—O13	2.202 (5)	Dy1—O6	2.406 (5)
Dy2—O14	2.382 (4)	Dy1—O10	2.416 (5)
Dy2—O18	2.399 (4)	Dy1—O2	2.392 (5)
Dy2—O22	2.403 (5)	Dy1—O9	2.431 (6)
Dy2—O21	2.415 (6)	Dy1—N1	2.516 (6)
Dy2—N5	2.519 (6)	Dy1—N3	2.508 (6)
Dy2—N7	2.528 (5)	Cd1A—O8	2.424 (8)
Cd2—O15	2.169 (5)	Cd1A—O7	2.092 (7)
Cd2—O20 ⁱ	2.480 (5)	Cd1A—O11	2.360 (11)
Cd2—O19 ⁱ	2.204 (4)	Cd1A—O12	2.141 (12)
Cd2—O16	2.547 (5)	Cd1A—C55	2.49 (2)
Cd2—O23	2.529 (6)	Cd1A—Cd1B	0.881 (8)
Cd2—O25	2.341 (6)	O3—Cd1B ⁱⁱⁱ	1.950 (6)
Cd2—O24	2.272 (6)	O7—Cd1B	2.396 (9)
Cd2—C110	2.748 (11)	O4—Cd1B ⁱⁱⁱ	2.047 (11)
O20—Cd2 ⁱⁱ	2.480 (5)	O12—Cd1B	2.602 (15)
O19—Cd2 ⁱⁱ	2.204 (4)	C10—Cd1B ⁱⁱⁱ	2.671 (11)
O19—C92	1.315 (8)	Cd1B—O3 ^{iv}	1.950 (6)

Dy1—O1	2.189 (5)	Cd1B—O4 ^{iv}	2.047 (11)
Cd1B—C10 ^{iv}	2.671 (11)		
O17—Dy2—O13	98.64 (17)	O1—Dy1—O6	79.88 (17)
O17—Dy2—O14	79.50 (16)	O1—Dy1—O10	97.14 (16)
O17—Dy2—O18	134.99 (16)	O1—Dy1—O2	134.75 (17)
O17—Dy2—O22	90.61 (19)	O1—Dy1—O9	151.42 (17)
O17—Dy2—O21	152.46 (19)	O1—Dy1—N1	70.14 (17)
O17—Dy2—N5	84.26 (16)	O1—Dy1—N3	83.12 (17)
O17—Dy2—N7	70.33 (17)	O5—Dy1—O6	135.41 (16)
O13—Dy2—O14	134.57 (15)	O5—Dy1—O10	151.10 (16)
O13—Dy2—O18	80.58 (17)	O5—Dy1—O2	79.80 (16)
O13—Dy2—O22	152.72 (17)	O5—Dy1—O9	91.1 (2)
O13—Dy2—O21	96.8 (2)	O5—Dy1—N1	81.19 (17)
O13—Dy2—N5	69.97 (17)	O5—Dy1—N3	70.69 (18)
O13—Dy2—N7	83.80 (17)	O6—Dy1—O10	71.75 (16)
O14—Dy2—O18	131.88 (17)	O6—Dy1—O9	74.83 (18)
O14—Dy2—O22	72.26 (16)	O6—Dy1—N1	136.12 (17)
O14—Dy2—O21	73.4 (2)	O6—Dy1—N3	64.80 (18)
O14—Dy2—N5	64.66 (17)	O10—Dy1—O9	87.5 (2)
O14—Dy2—N7	134.84 (17)	O10—Dy1—N1	80.82 (18)
O18—Dy2—O22	74.85 (18)	O10—Dy1—N3	135.82 (19)
O18—Dy2—O21	70.13 (18)	O2—Dy1—O6	132.30 (18)
O18—Dy2—N5	134.66 (16)	O2—Dy1—O10	72.12 (16)
O18—Dy2—N7	64.83 (18)	O2—Dy1—O9	73.50 (19)
O22—Dy2—O21	86.0 (3)	O2—Dy1—N1	64.81 (19)
O22—Dy2—N5	136.85 (18)	O2—Dy1—N3	135.30 (18)
O22—Dy2—N7	75.21 (18)	O9—Dy1—N1	138.3 (2)
O21—Dy2—N5	79.8 (2)	O9—Dy1—N3	74.3 (2)
O21—Dy2—N7	134.23 (19)	N3—Dy1—N1	138.0 (2)
N5—Dy2—N7	140.22 (18)	O8—Cd1A—C55	113.6 (5)
O15—Cd2—O20 ⁱ	88.73 (18)	O7—Cd1A—O8	69.9 (3)
O15—Cd2—O19 ⁱ	145.71 (19)	O7—Cd1A—O11	117.3 (4)
O15—Cd2—O16	67.03 (16)	O7—Cd1A—O12	105.1 (4)
O15—Cd2—O23	83.9 (2)	O7—Cd1A—C55	114.1 (6)
O15—Cd2—O25	101.6 (2)	O11—Cd1A—O8	86.6 (4)
O15—Cd2—O24	119.1 (2)	O11—Cd1A—C55	29.6 (4)
O15—Cd2—C110	103.3 (3)	O12—Cd1A—O8	138.5 (5)
O20 ⁱ —Cd2—O16	77.26 (17)	O12—Cd1A—O11	58.3 (4)
O20 ⁱ —Cd2—O23	75.75 (18)	O12—Cd1A—C55	28.7 (4)
O20 ⁱ —Cd2—C110	95.7 (3)	Cd1B—Cd1A—O8	109.5 (3)
O19 ⁱ —Cd2—O20 ⁱ	67.42 (16)	Cd1B—Cd1A—O7	99.2 (3)
O19 ⁱ —Cd2—O16	83.33 (17)	Cd1B—Cd1A—O11	143.5 (4)
O19 ⁱ —Cd2—O23	111.7 (2)	Cd1B—Cd1A—O12	111.9 (5)
O19 ⁱ —Cd2—O25	87.4 (2)	Cd1B—Cd1A—C55	132.2 (6)

O19 ⁱ —Cd2—O24	94.0 (2)	O25—Cd2—O23	137.4 (2)
O19 ⁱ —Cd2—C110	103.3 (3)	O25—Cd2—C110	113.2 (3)
O16—Cd2—C110	167.8 (3)	O24—Cd2—O20 ⁱ	116.0 (2)
O23—Cd2—O16	140.37 (19)	O24—Cd2—O16	164.3 (2)
O23—Cd2—C110	27.6 (3)	O24—Cd2—O23	54.7 (2)
O25—Cd2—O20 ⁱ	145.67 (19)	O24—Cd2—O25	87.5 (3)
O25—Cd2—O16	77.0 (2)	O24—Cd2—C110	27.2 (3)

Symmetry codes: (i) $-x, y-1/2, -z+3/2$; (ii) $-x, y+1/2, -z+3/2$; (iii) $-x+1, y+1/2, -z+3/2$; (iv) $-x+1, y-1/2, -z+3/2$.

2.Characterization

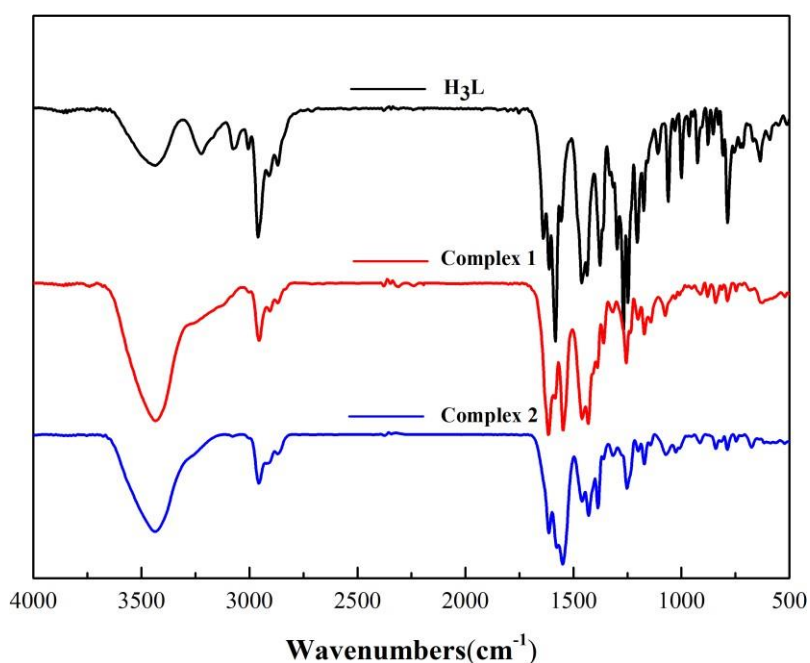


Fig. S6. FT-IR spectra of H₃L, complex 1 and 2

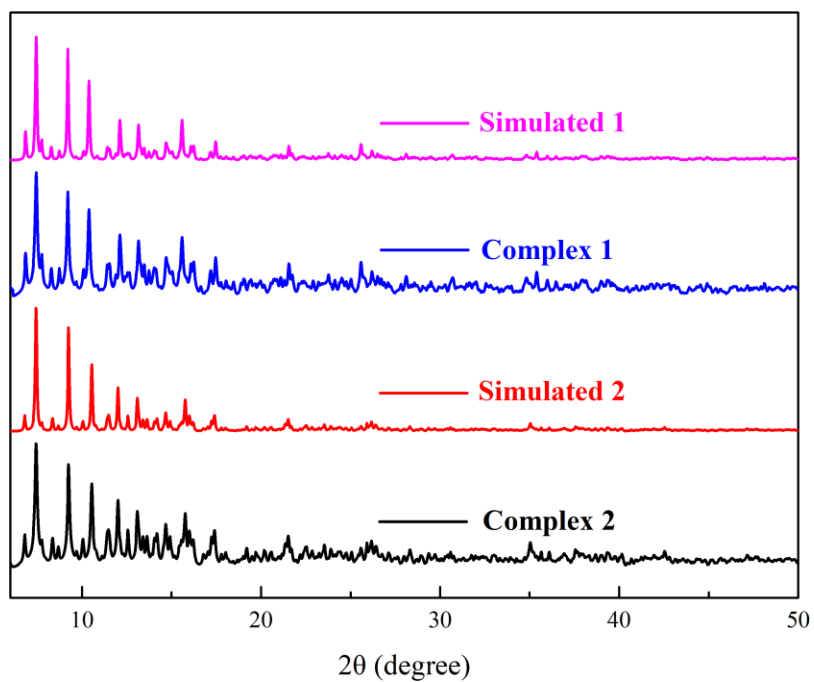


Fig. S7. Comparing the simulated PXRD with experimental patterns of complexes 1-2.

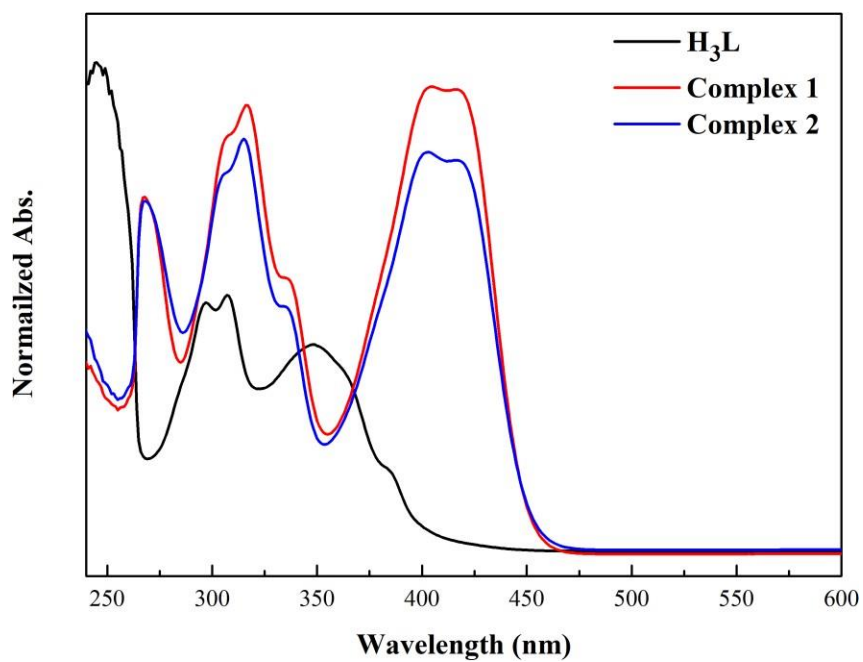


Fig. S8. UV/Vis absorption spectra of H_3L , and complexes 1-2 in DMF solution at room temperature.

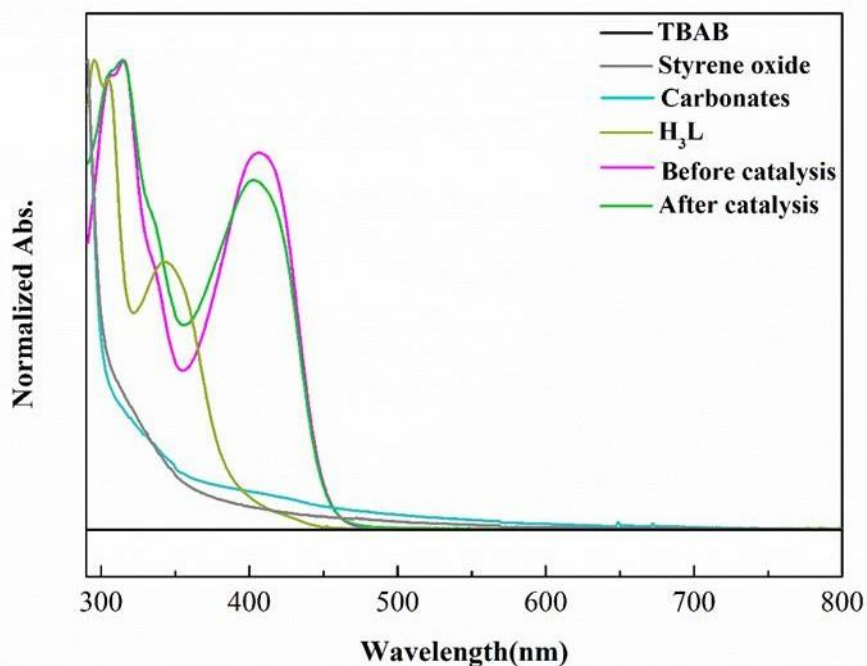


Fig. S9. UV/Vis absorption spectra of TBAB, free styrene oxide, free carbonates, H₃L, before catalysis, and after catalysis, in MeOH solution at room temperature.

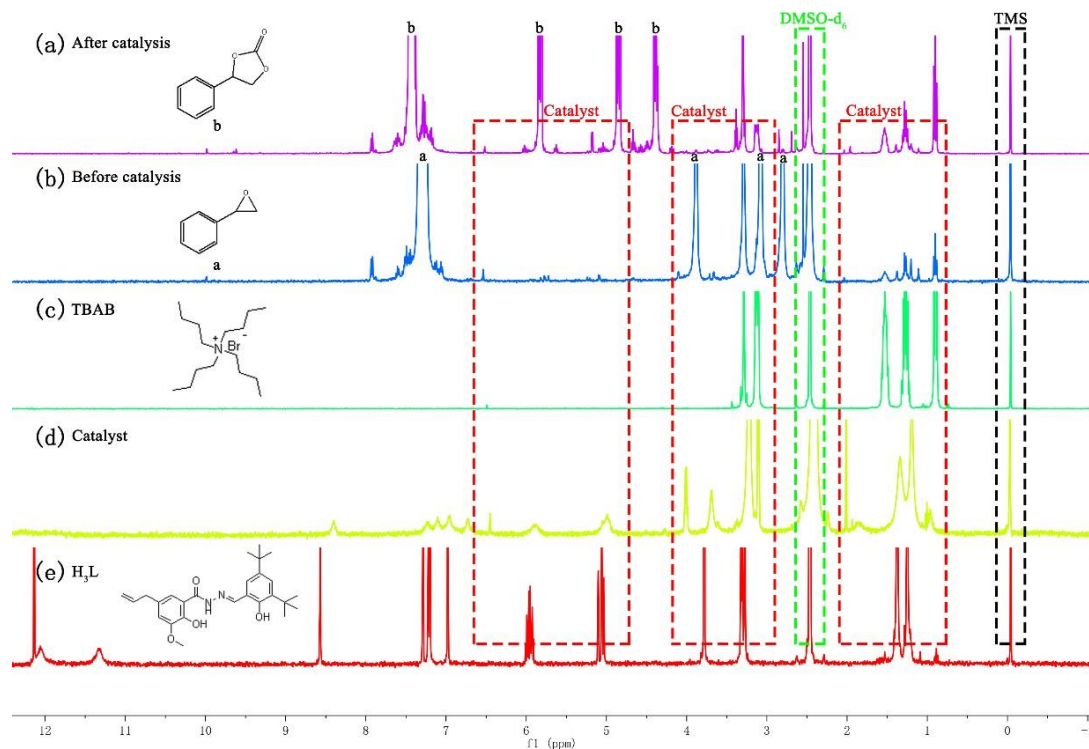


Fig. S10. ¹H-NMR spectra of after catalysis (a) before catalysis (b) TBAb (c) catalyst1 (d) and (e) H₃L dissolved in DMSO-*d*₆.

3. Supplementary Structural Figures

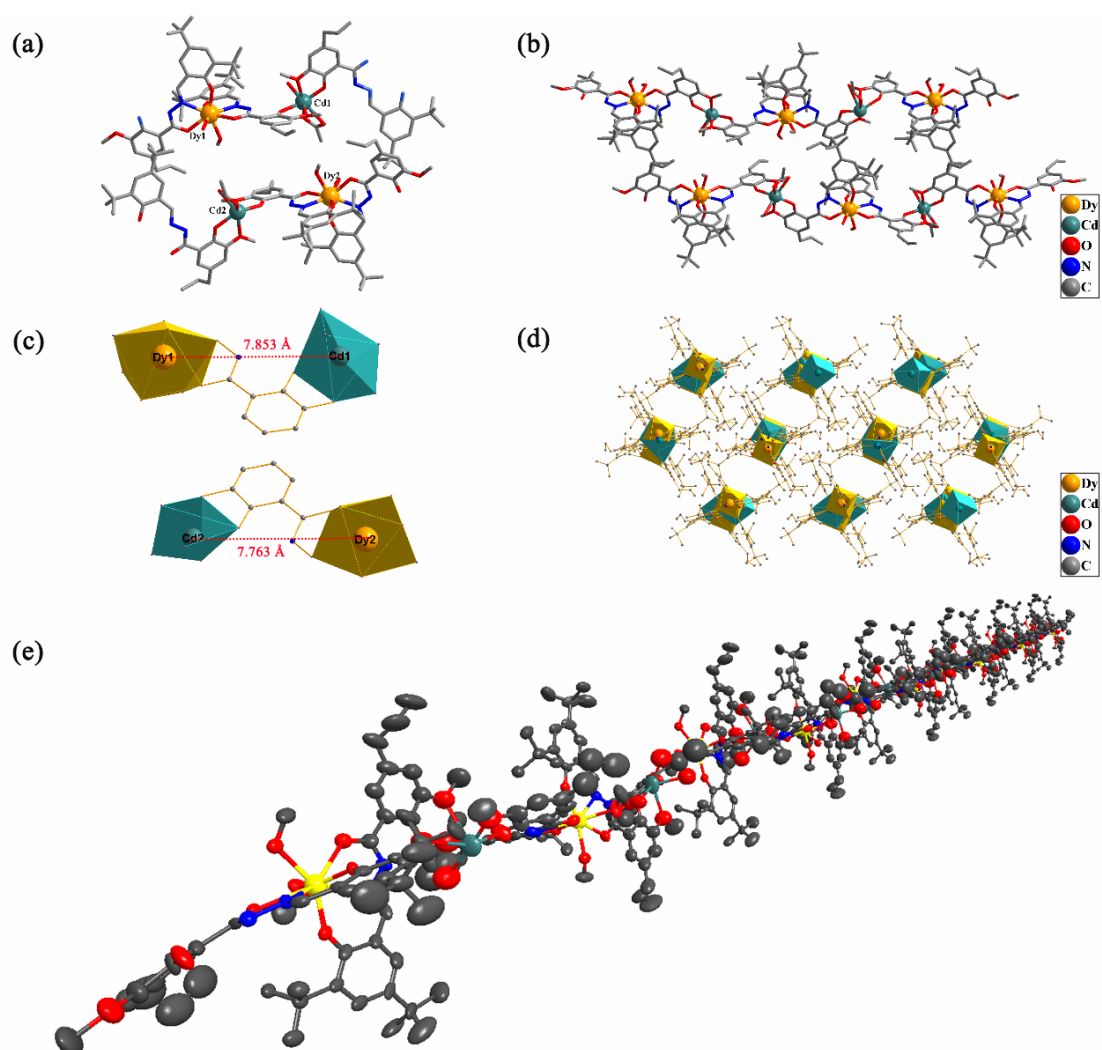


Fig. S11. Structural fragments of complex2. (a) The coordination environment of two adjacent Dy1, Dy2, and Cd1, Cd2 centers. (b) 1D double-chain structure. (c) Dy1, Dy2 and Zn1, Zn2 centers coordination polyhedra. (d) Packing diagram along the axis showing three adjacent 1D double chains. (e) Single chain thermo-ellipsoid model diagram

Table S3. Comparison of cycloaddition reaction of CO₂ with epoxides catalysed by different catalysts.

Cat.(%)	Cocat.(%)	Catalyst/Epoxide (Mole ratio)	P (MPa)	T (°C)	Time (h)	Yields (%)	TOF (h ⁻¹)	Ref.
[EMIm] ₂ [Br ₂ Zn (Et ₂ PO ₄) ₂]	—	(propylene epoxide) 1:3000	3.5	120	1	99	2362	2
[L ₁ Zn ₂] ₄	TBAI (2.5)	(propylene oxide) 1:40	1	45	68	87	—	3
Zn(OPO) ₂	TBAB (0.9)	(propyleneepoxide) 1:40000	3	120	1	46	18400	4

Ni(PPh₃)Cl₂/PPh₃/ Zn	TBAB	(propylene epoxide) 1:3570	2.5	120	1	99	3544	5
ZnBr₂	E	(propyleneepoxide) 1:1790	3	140	1	81	8670	6
Zn-CMP	TBAB (0.9)	(propyleneepoxide) 1:40000	3	120	1	29	11600	7
Mg-porphyrin	—	(1,2-Epoxyhexane) 1:33333	1.7	120	1	36	12000	8
Yb-DDPY	TBAB (0.5)	(styrene oxide) 1:400	1	60	12	52	17	9
Ionic Rare Earth Metal	—	(styrene oxide) 1:500	0.1	90	12	93	38	10
Al- aminotriphenolae	PPN-Br	(1,2-Epoxyhexane) 1:200000	1	90	2	36	36000	11
Yb-mesocate	TBAB (0.75)	(styrene oxide) 1:1000	1	120	2.5	95	380	12
Helicate-1(Zn-Tb)	TBAB (0.5)	(styrene oxide) 1:40000	1	120	1	67	26800	13
[Yb(μ-L)(μ₃- L)(H₂O)]_nBr_n	TBAB (3.0)	(Epichlorohydrin) 1:4000	0.1	70	12	98	327	14
Complex 1	TBAB (0.75)	styrene oxide) 1:40000	1	120	1	71	28400	This work
Complex 2	TBAB (0.75)	styrene oxide) 1:40000	1	120	1	60	12000	This work
Complex 1	TBAB (0.75)	styrene oxide) 1:10000	1	100	1	72	7200	This work
Complex 1	TBAB (0.75)	styrene oxide) 1:10000	1	80	1	42	4200	This work
Complex 1	TBAB (0.75)	styrene oxide) 1:10000	1	60	1	19	1900	This work

4. ¹H NMR spectra of the substrates and products.

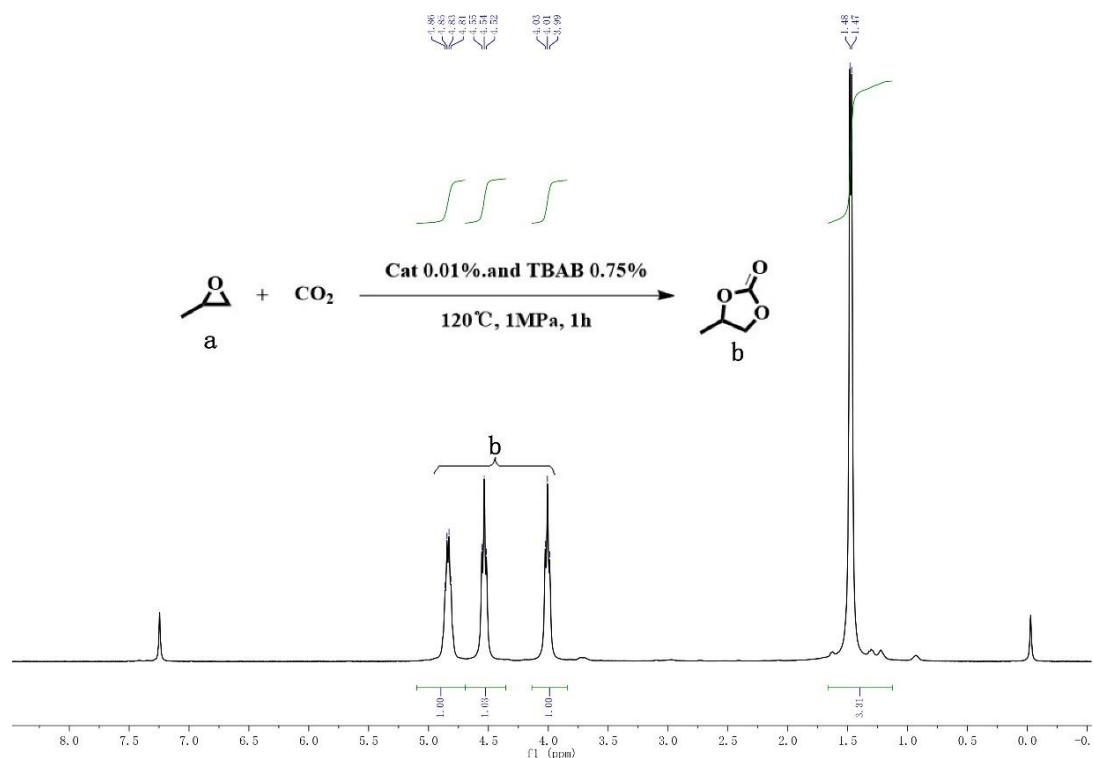


Fig. S12. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with PO catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the PO almost converts to cyclic carbonates catalyzed by **Complex 1** at 120°C for 1h.

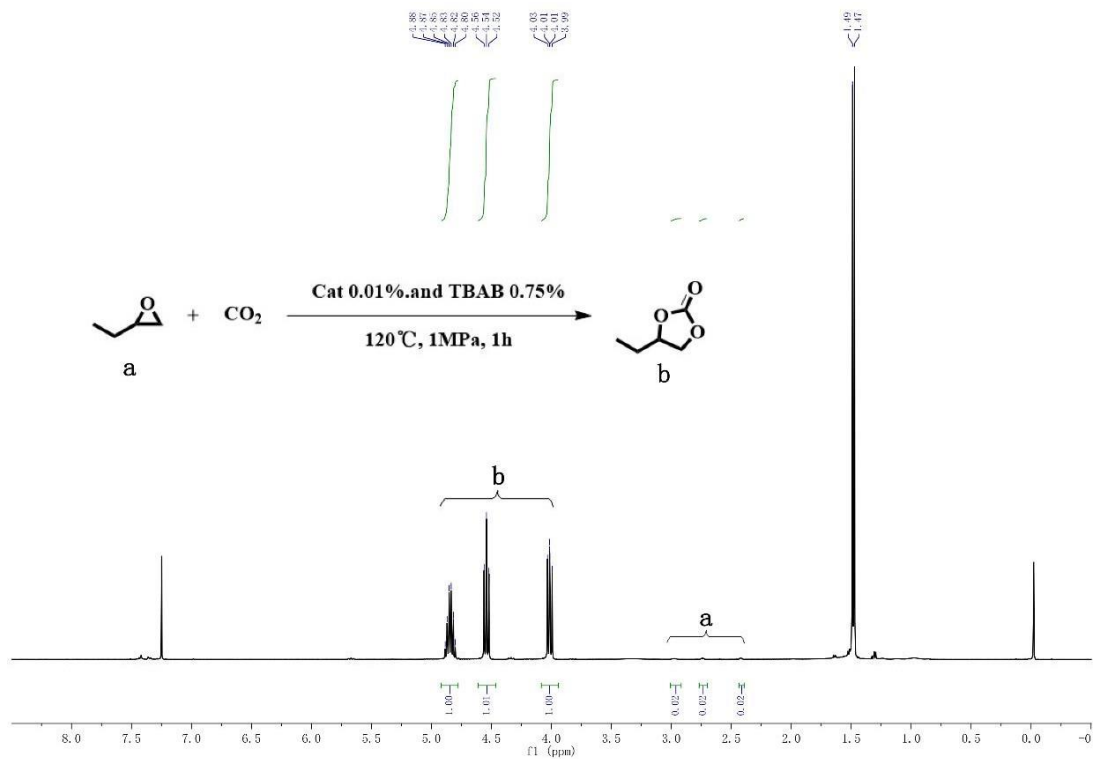


Fig. S13. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with epoxybutane catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the epoxybutane almost converts to cyclic carbonates catalyzed by **Complex 1** at 120°C for 1h.

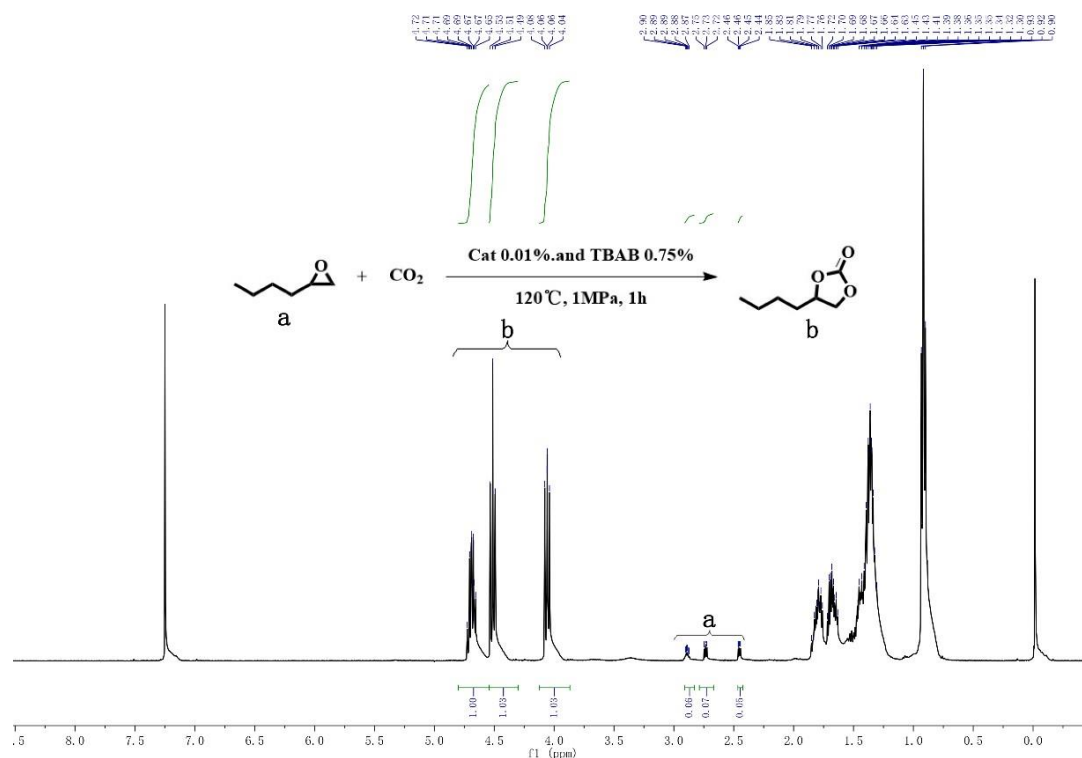


Fig. S14. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with 1,2-Epoxyhexane catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the 1,2-Epoxyhexane converts to cyclic carbonates up to 94% catalyzed by **Complex 1** at 120°C for 1h.

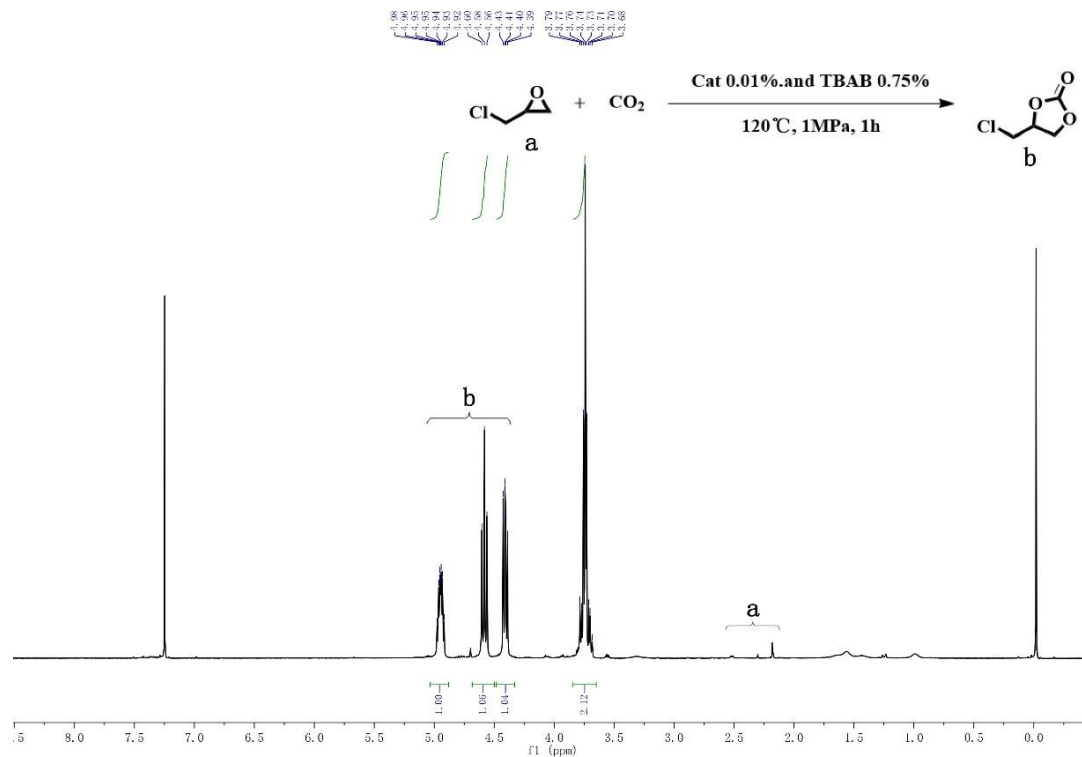


Fig. S15. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with epichlorohydrin catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the converts to cyclic carbonates almost catalyzed by **Complex 1** at 120°C for 1h.

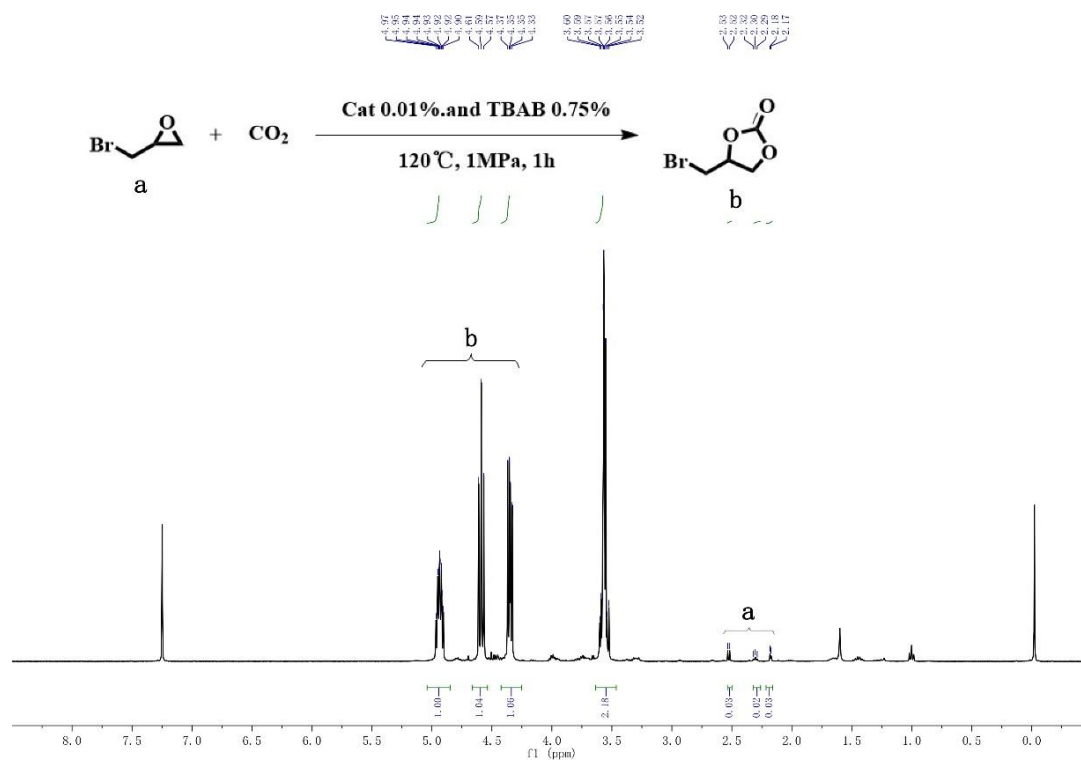


Fig. S16. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with 1-bromo-2,3-epoxypropane catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the 1-bromo-2,3-epoxypropane converts to cyclic carbonates almost catalyzed by **Complex 1** at 120°C for 1h.

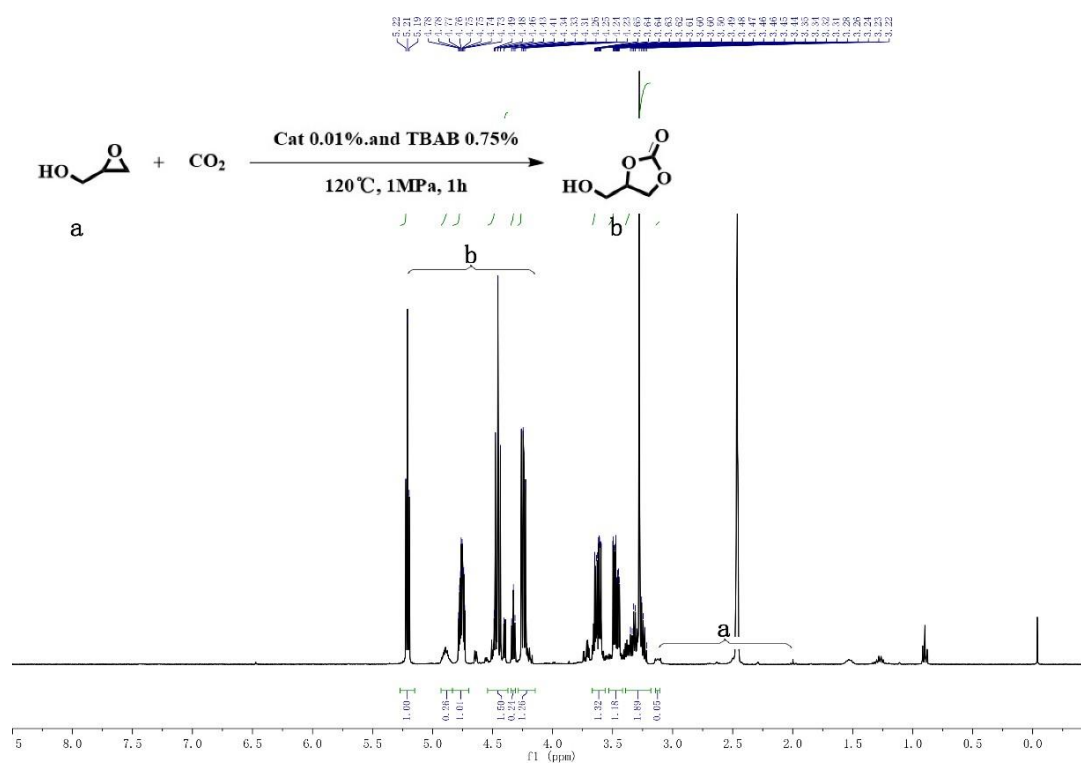


Fig. S17. ¹H-NMR (DMSO-d₆, 25°C) spectrum of the reaction substrate of cycloaddition of CO₂ with glycidol catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the glycidol converts to cyclic carbonates almost catalyzed by **Complex 1** at 120°C for 1h.

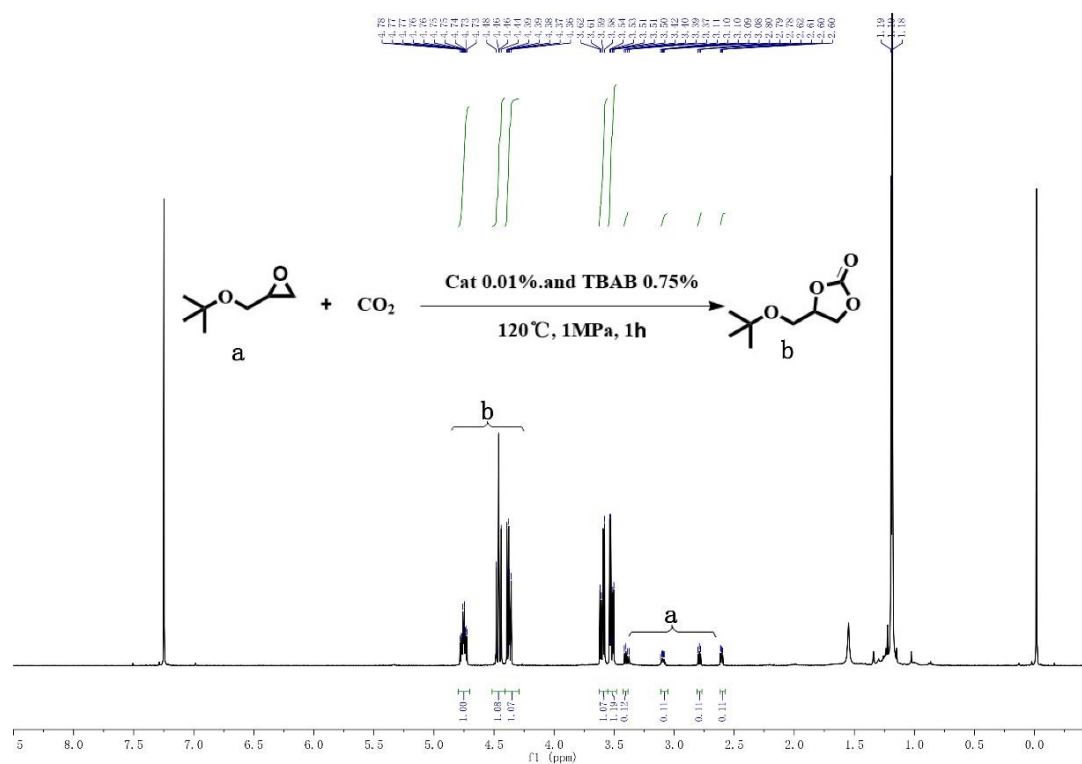


Fig. S18. $^1\text{H-NMR}$ (CDCl_3) spectrum of the reaction substrate of cycloaddition of CO_2 with t-butyl glycidyl ether catalyzed by **Complex 1**. $^1\text{H-NMR}$ analysis of the reaction substrates indicates that the t-butyl glycidyl ether converts to cyclic carbonates up to 90% catalyzed by **Complex 1** at 120°C for 1h.

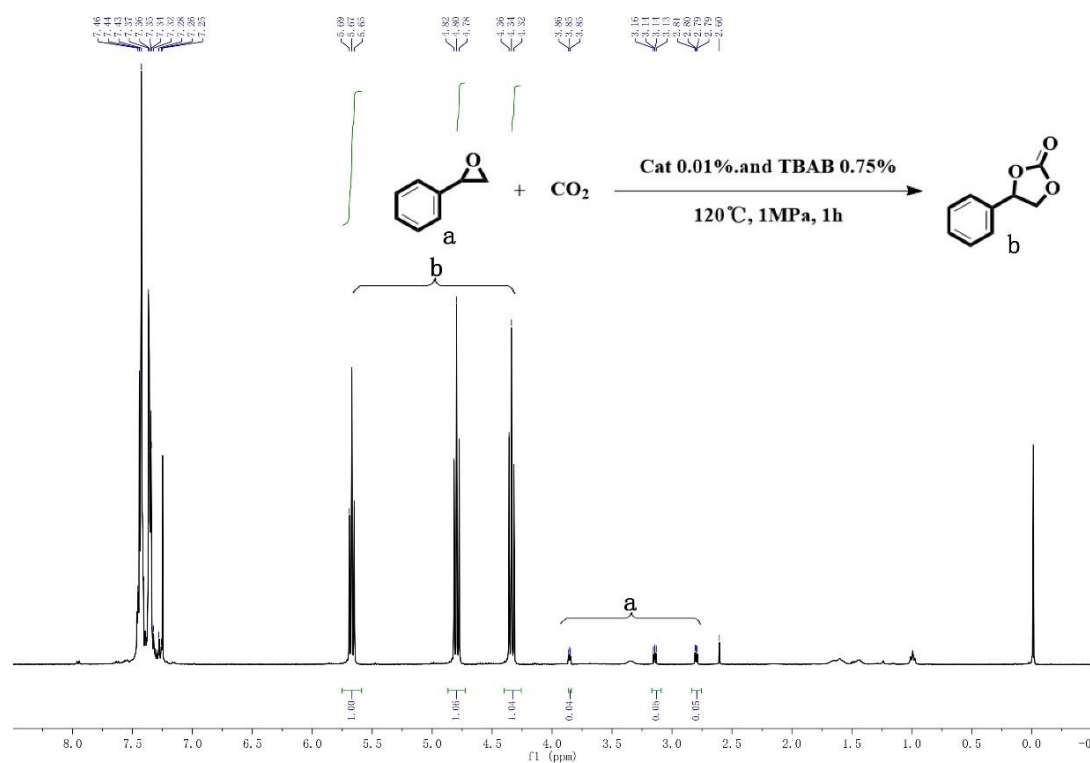


Fig. S19. $^1\text{H-NMR}$ (CDCl_3) spectrum of the reaction substrate of cycloaddition of CO_2 with styrene oxide catalyzed by **Complex 1**. $^1\text{H-NMR}$ analysis of the reaction substrates indicates that the styrene oxide to cyclic carbonates up to 95% catalyzed by **Complex 1** at 120°C for 1h.

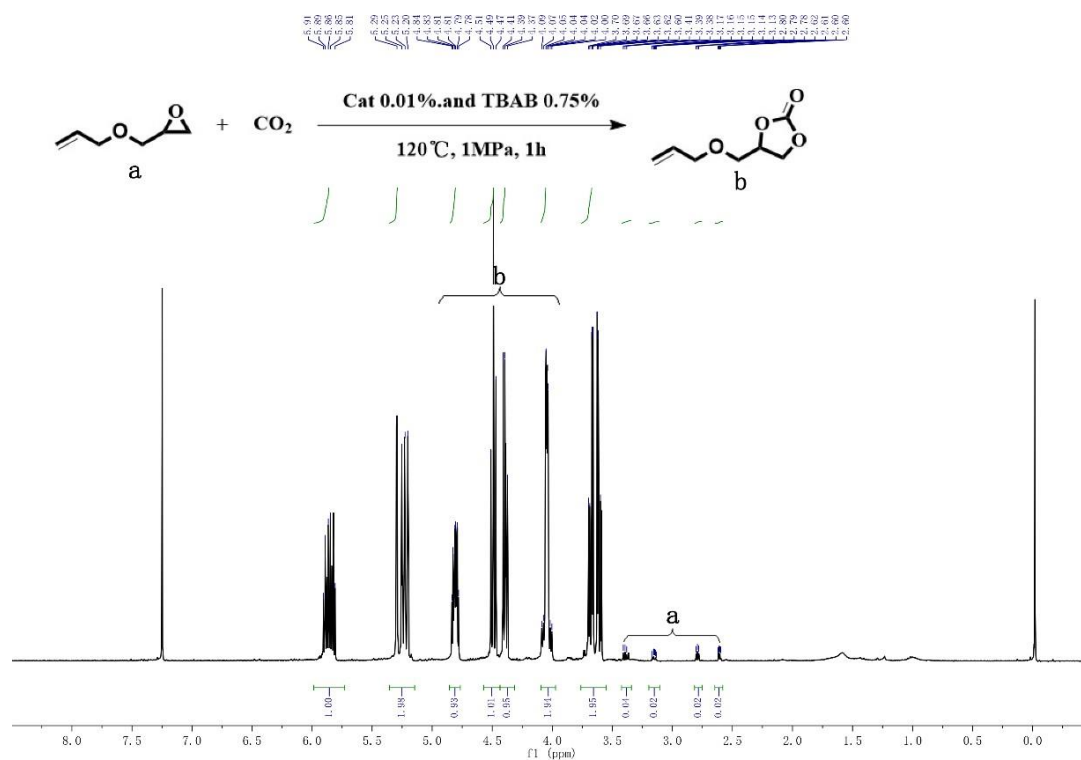


Fig. S20. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with allyl glycidyl ether catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the allyl glycidyl ether to cyclic carbonates almost catalyzed by **Complex 1** at 120°C for 1h.

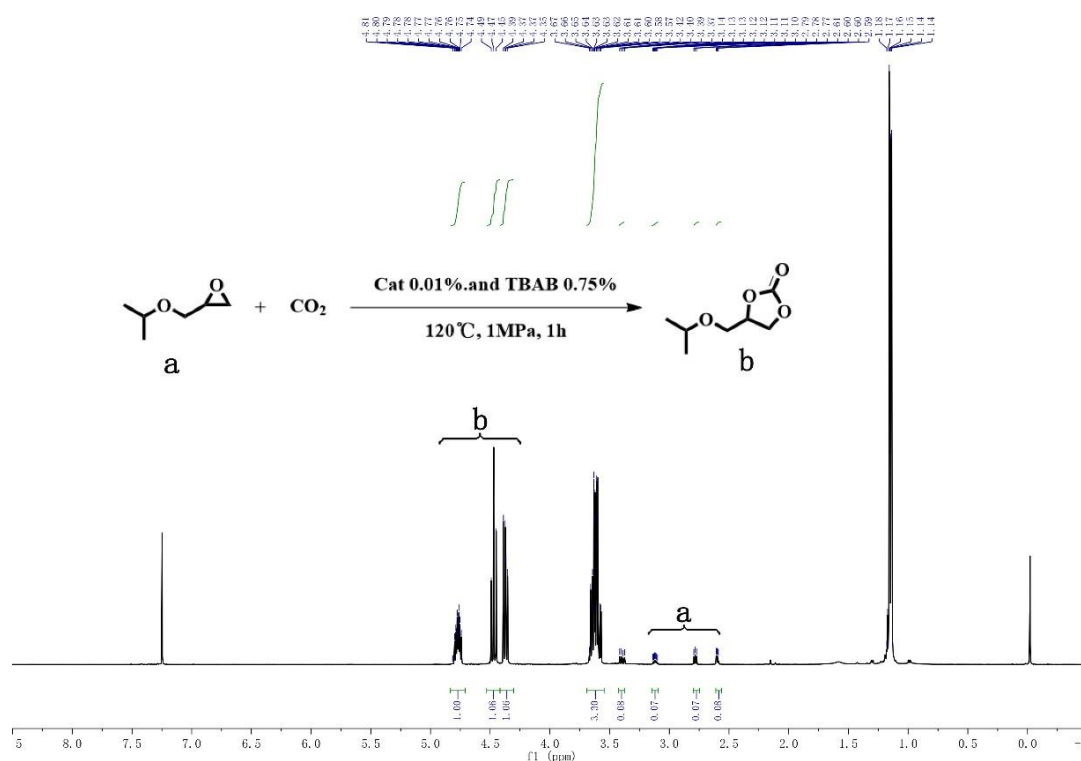


Fig. S21 ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with isopropyl glycidyl ether catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the isopropyl glycidyl ether to cyclic carbonates up to 95% catalyzed by **Complex 1** at 120°C for 1h.

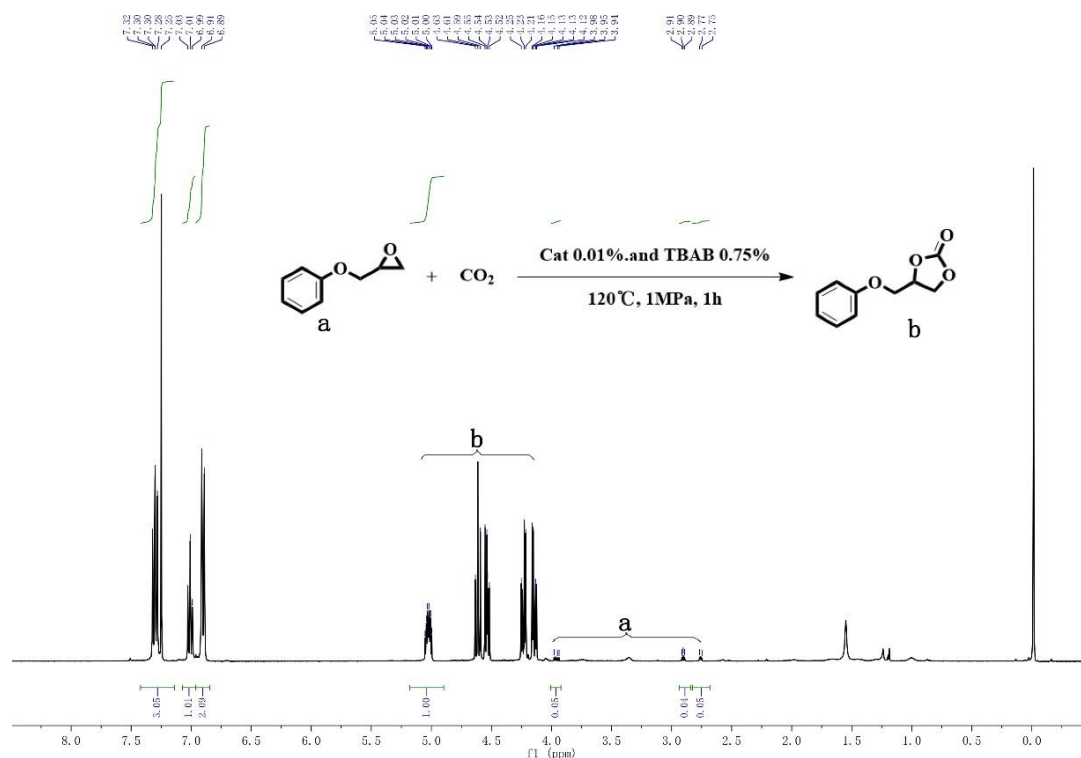


Fig. S22. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with glycidyl phenyl ether catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the glycidyl phenyl ether to cyclic carbonates up to 95% catalyzed by **Complex 1** at 120°C for 1h.

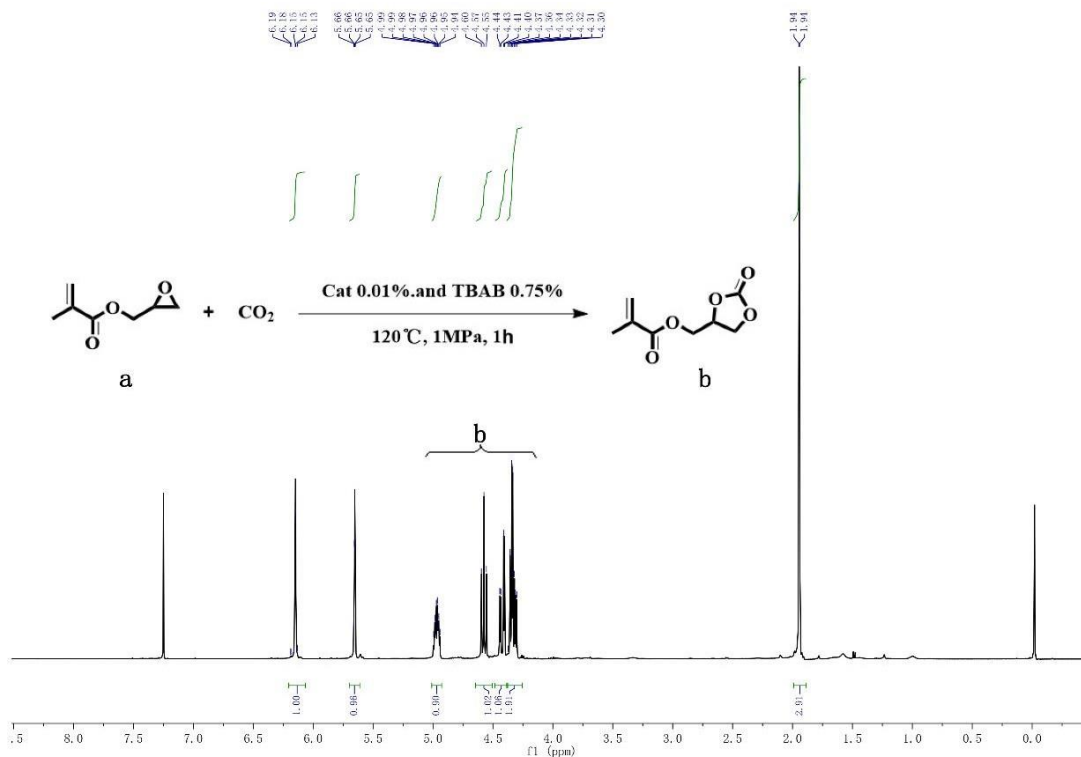


Fig. S23. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with glycidyl methacrylate catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the glycidyl methacrylate to cyclic carbonates almost catalyzed by **Complex 1** at 120°C for 1h.

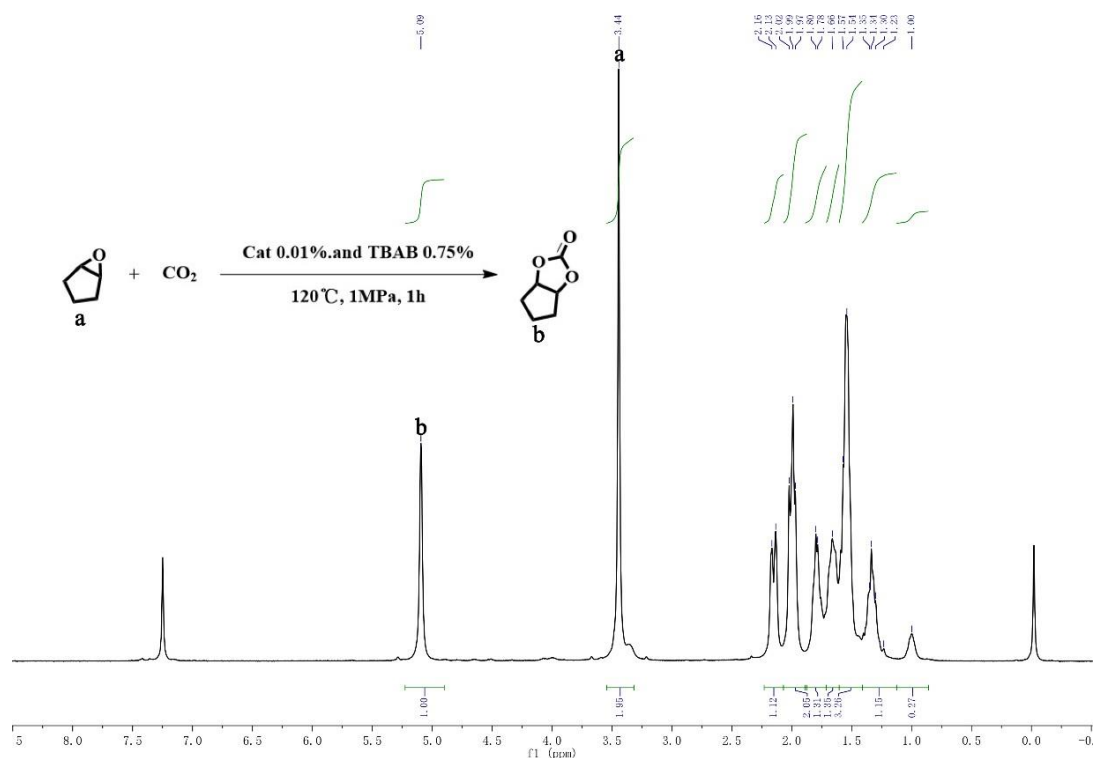


Fig. S24. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with cyclopentene oxide catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the cyclopentene oxide to cyclic carbonates up to 35% catalyzed by **Complex 1** at 120°C for 1h.

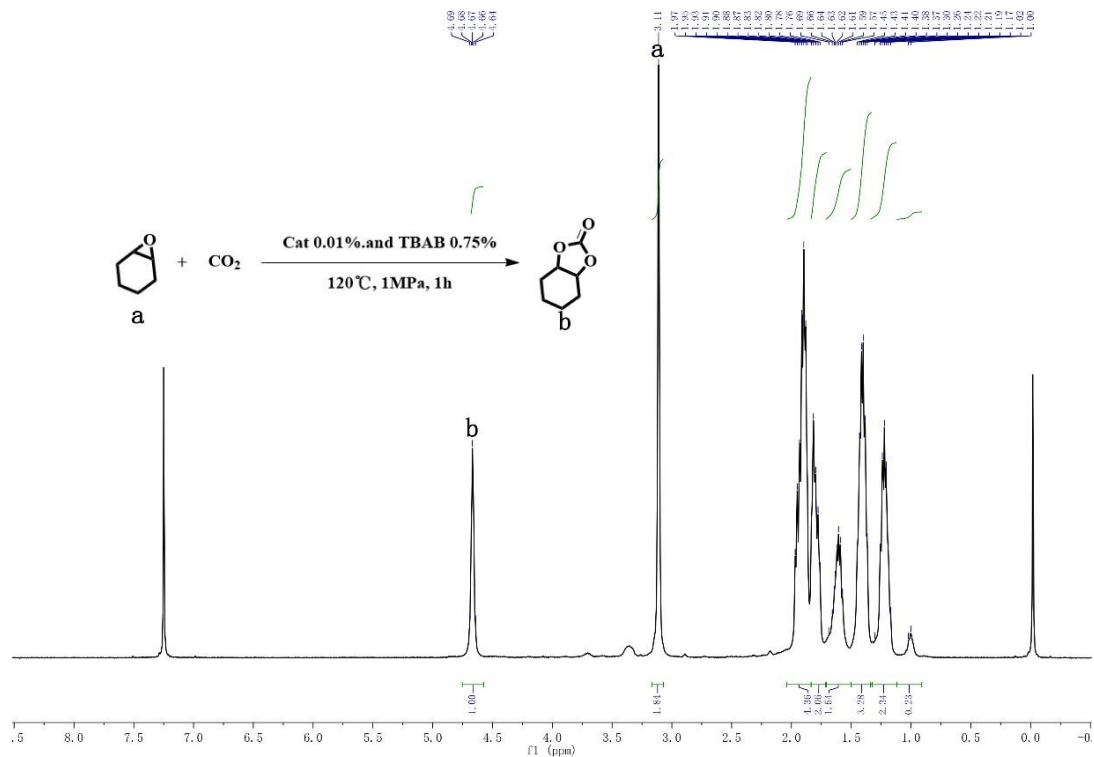


Fig. S25. ¹H-NMR (CDCl₃) spectrum of the reaction substrate of cycloaddition of CO₂ with cyclohexene oxide catalyzed by **Complex 1**. ¹H-NMR analysis of the reaction substrates indicates that the cyclohexene oxide to cyclic carbonates up to 35% catalyzed by **Complex 1** at 120°C for 1h.

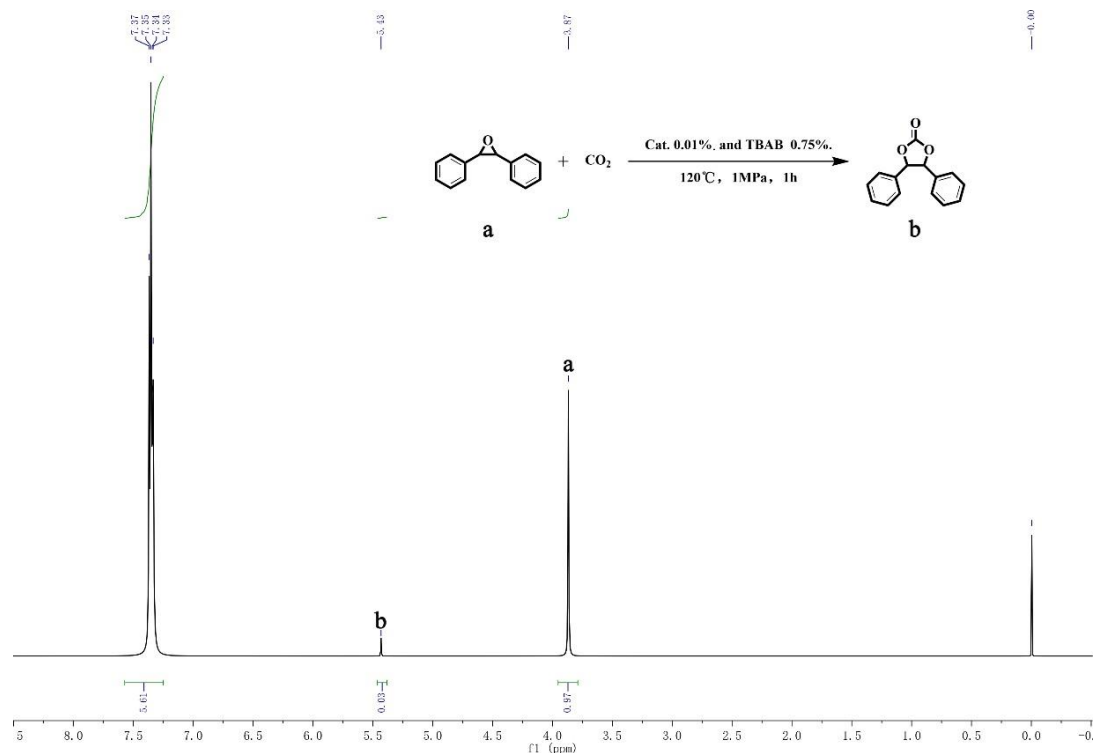


Fig. S26. $^1\text{H-NMR}$ (CDCl_3) spectrum of the reaction substrate of cycloaddition of CO_2 with stilbene oxide catalyzed by **Complex 1**. $^1\text{H-NMR}$ analysis of the reaction substrates indicates that the stilbene oxide to cyclic carbonates up to 3% catalyzed by **Complex 1** at 120°C for 1h.

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