Supplementary Information of

New Lanthanide(III) Coordination Polymers: Synthesis, Structural Features, and Catalytic Activity in CO_2 Fixation

Cong Xu[a], Yan Liu[a], Li Wang[a], Jingxin Ma[b], Lizi Yang[a], Fu-xin Pan[a], Alexander M. Kirillov[c] and Weisheng Liu[a,*]

a. Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China
b. College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, P.R. China
c. Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisbon, Portugal.

Content

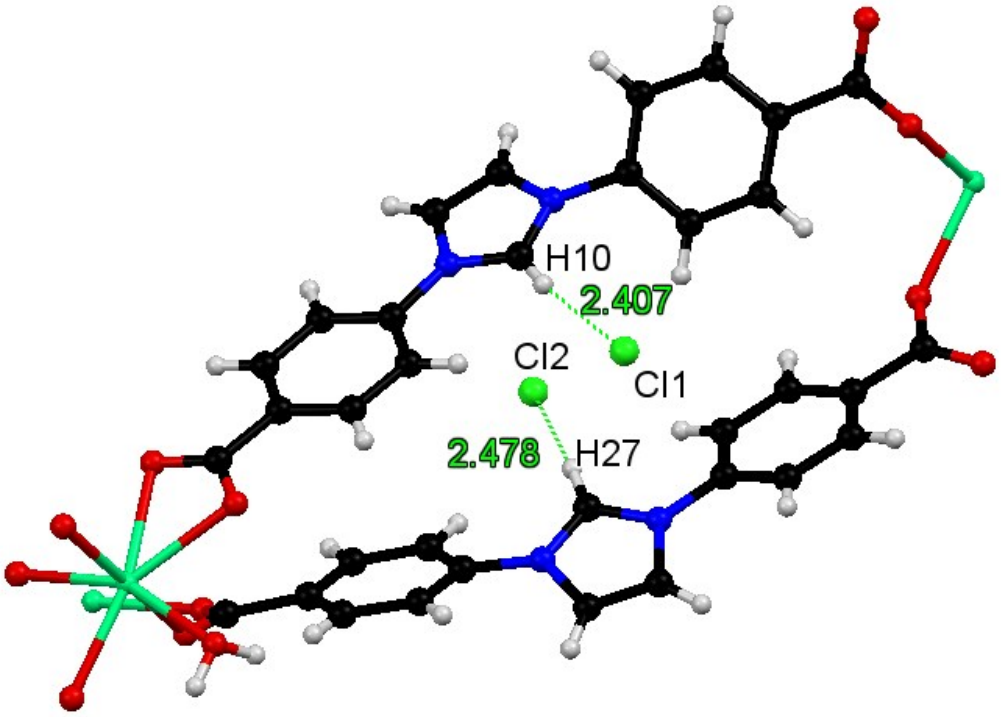


Figure S1. Weak interactions in compound **1**.

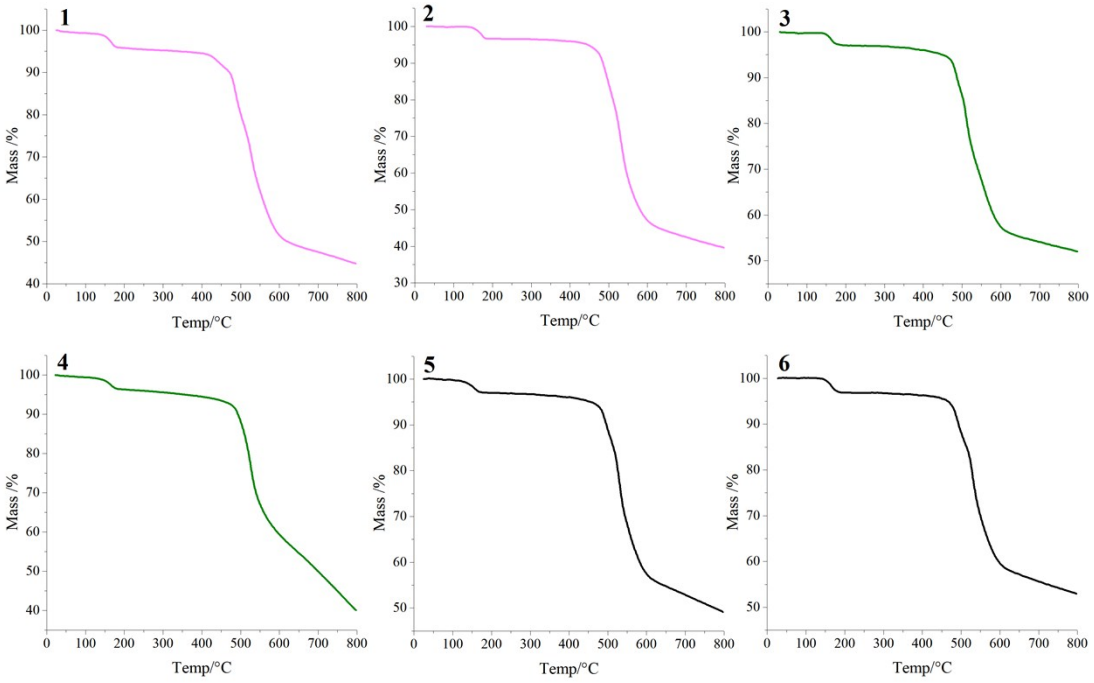


Figure S2. Thermogravimetric (TGA) analysis of **1-6.**

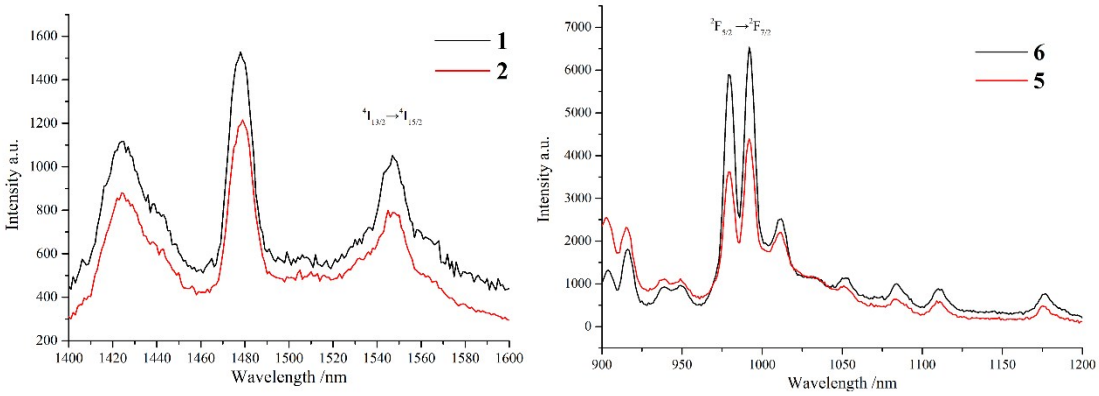


Figure S3. Solid-state emission spectra of **1/2** (under the excitation at 310 nm) and **5/6** (under the excitation at 332 nm).

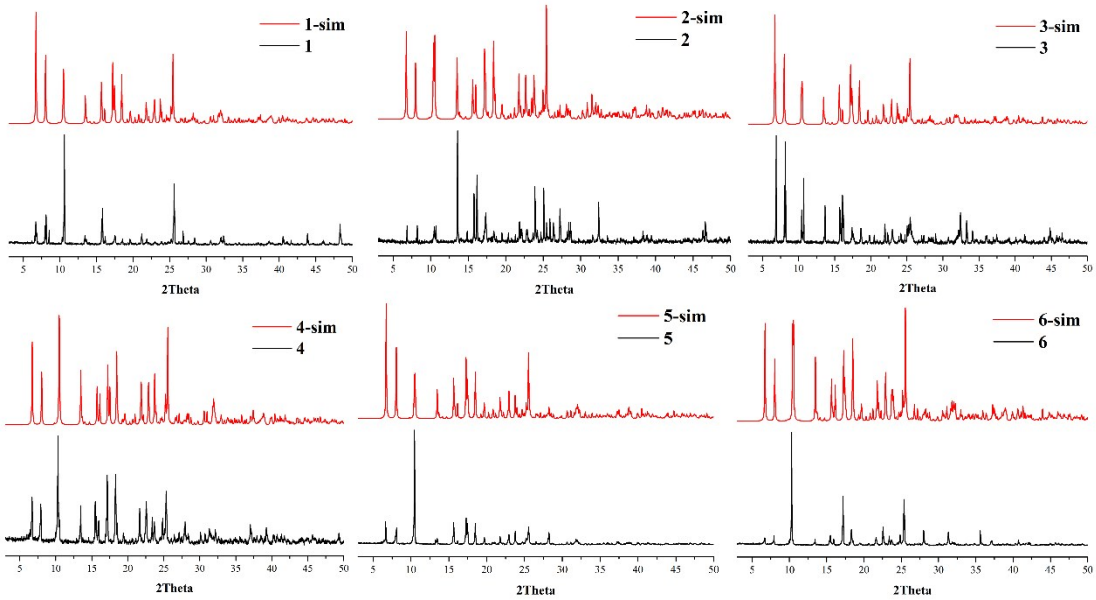


Figure S4. PXRD plots of compounds **1-6**. Experimental (black lines), calculated (red lines).

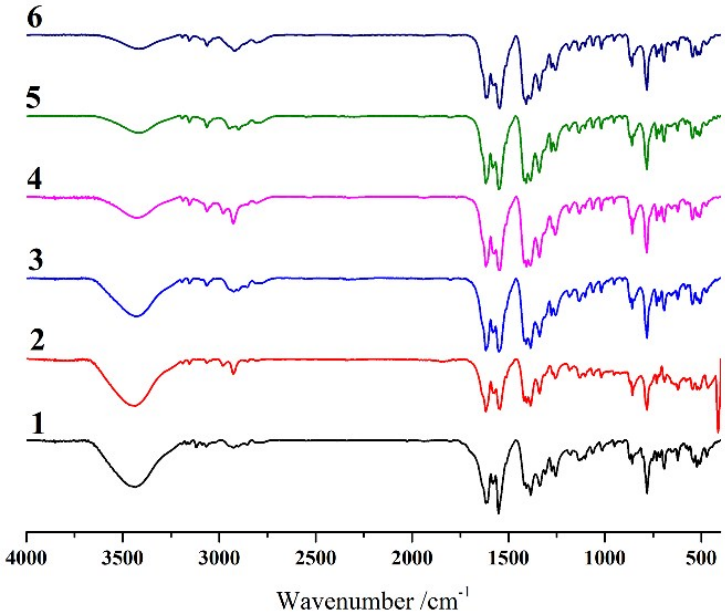


Figure S5. FT-IR spectra of compounds **1–6.**

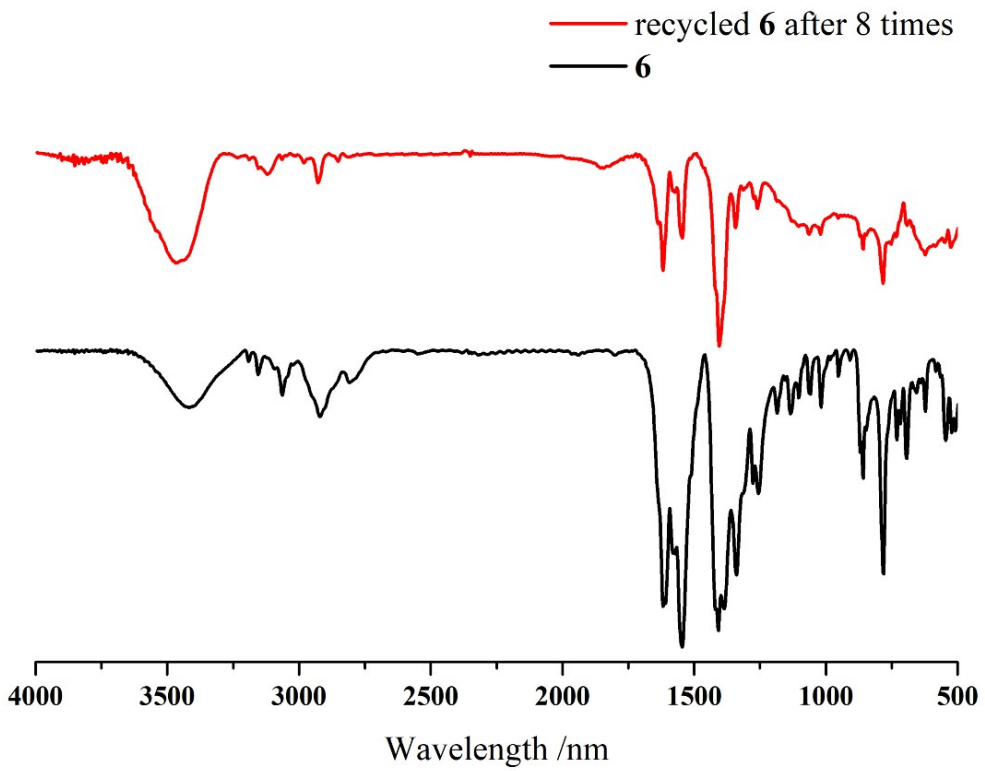
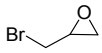
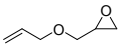
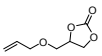
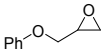
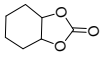
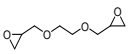
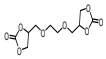


Figure S6. FT-IR spectra of **6** and **recycled 6** after 8 times.

Table S1. Epoxide substrate scope in CO_2 fixation reactions catalysed by **6**.

Entry	Catalyst	Substrate	Product	Catalyst (mol%)	TBAB (mol%)	Yield (%)	TON	TOF (h^{-1})
1	**6**			0.025	3.00	92	3680	307
2	**6**			0.025	3.00	74	2960	247
3	**6**			0.025	3.00	42	1680	140
4	**6**			0.025	3.00	58	2320	193
5	**6**			0.025	3.00	47	1880	157
6	**6**			0.025	3.00	13	520	43
7	**6**			0.025	3.00	40	1600	133
8	**6**			0.025	3.00	34	1360	113
9	**6**			0.025	3.00	41	1640	137

General conditions: 10 mmol epoxide, 70 ℃, 12 h. TON and TOF was calculated by the formula:

$$TON = \frac{Yield.}{n_{cat}}, \quad TOF = \frac{\frac{Yield.}{n_{cat}}}{Recation\ Time}$$

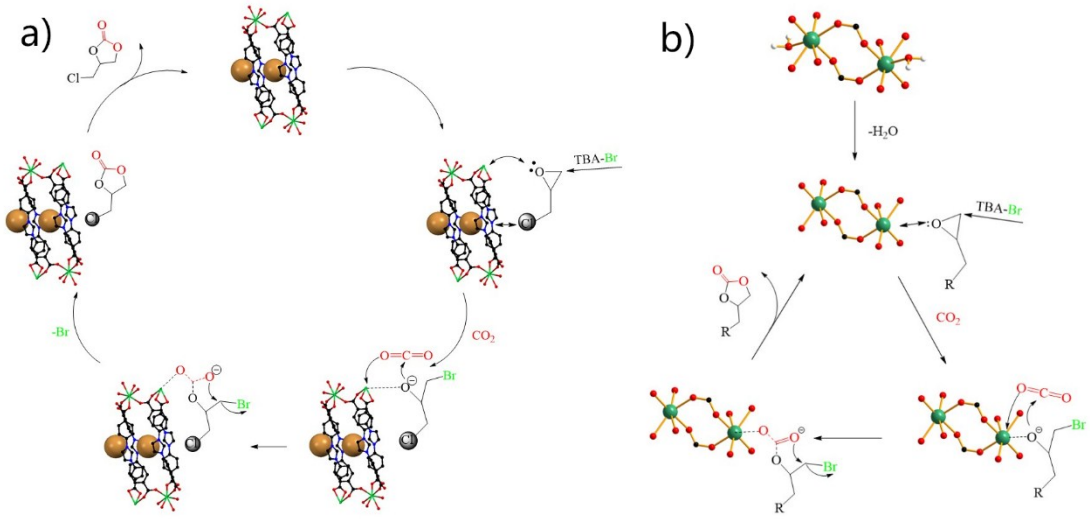
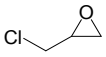
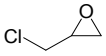
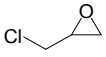
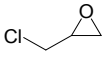
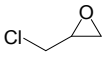
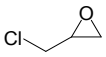
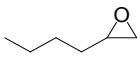
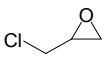


Figure S7. Two possible catalytic mechanisms. a) Hypothesized catalytic mechanism. b) Traditional catalytic mechanism.

Table S2. Comparison of cycloaddition reaction of CO_2 with epoxides catalyzed by different catalysts.

Entry	Substrate	Cat.	T (℃)	P_{CO_2}(bar	Co-catalyst ([Bu_4N]Br %)	Time (h)	Conv.[b] (%)	TOF(h^{-1})[c]	Ref.
1		**6**	70	1	3.00	12	98	326.7	This work
2		Yb-complex	90	1	0.75	12	83	69	**1**
3		Ni-TCPE	100	10	1.5	12	99	167	**2**
4		Eu-MOF	70	1	2.5	12	99	2.36	**3**
5		gea-MOF-1	120	20	0.15	6	89	99	**4**
6		Tb_4-MOF	60	1	2.50	12	99	4.125	**5**
7		**2**·THF	90	1	/	12	97	40.4	**6**
8		Complex **5**	85	1	0.6	24	96	40	**7**
9		UiO-67-NH_2	100	1	10	5	99	20	**8**
10		MMPF-18	r.t.	1	7.2	48	97	2.03	**9**
11		BIT-C	60	1	5	6	99	16.5	**10**

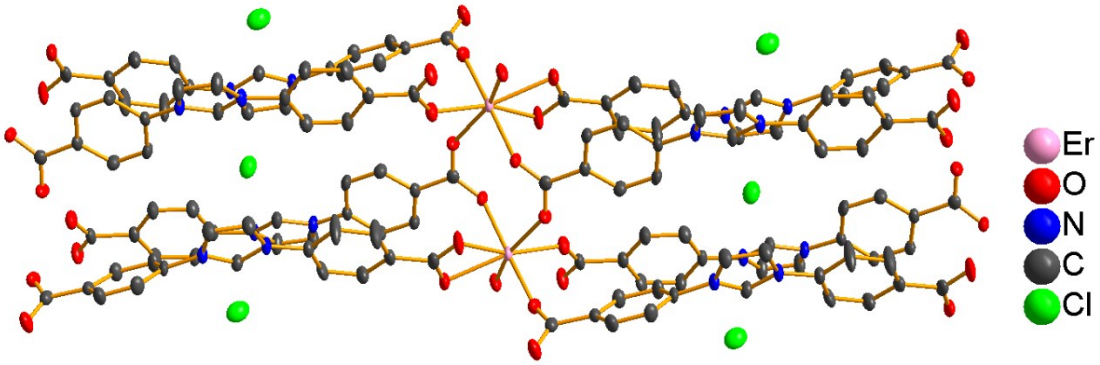
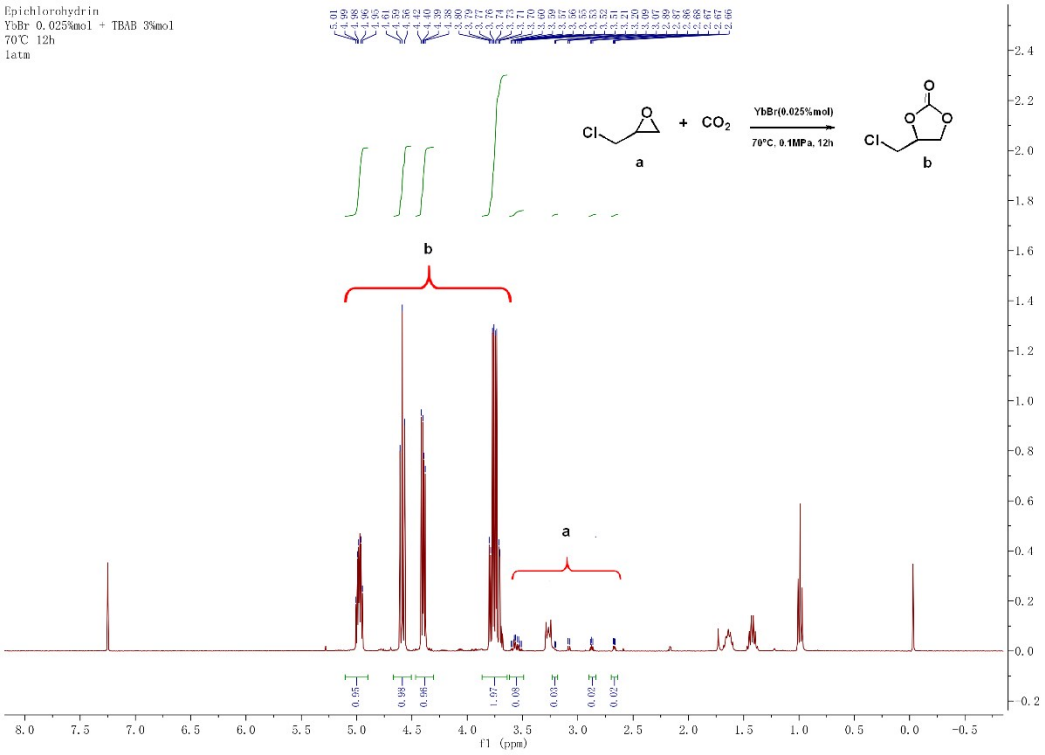
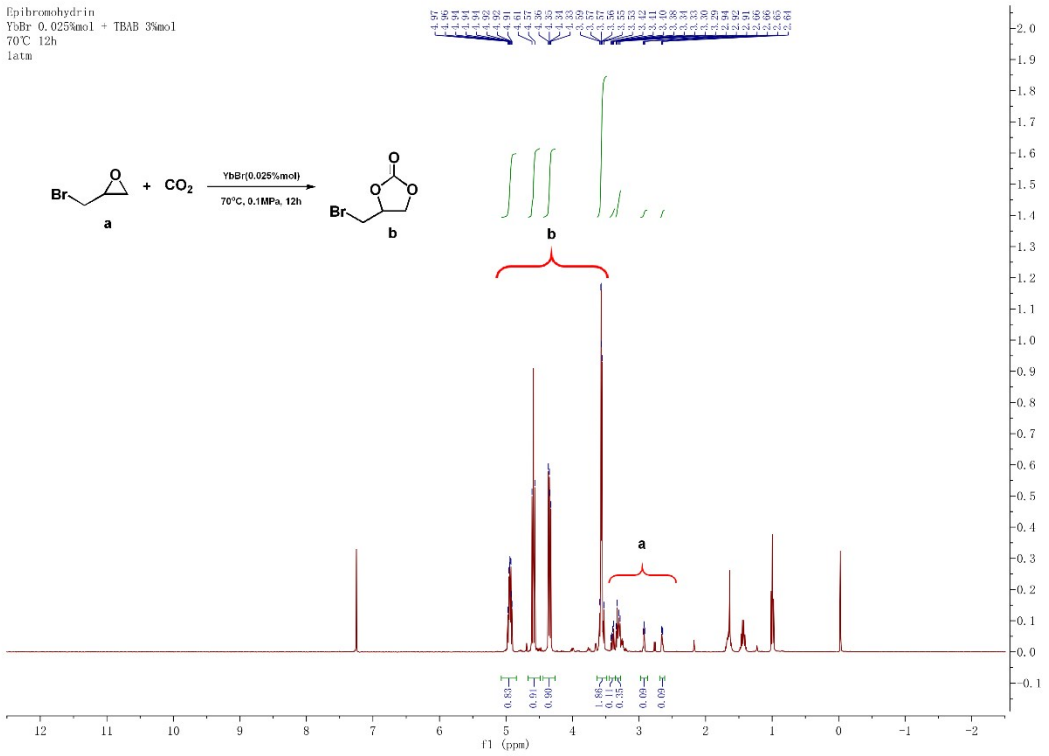
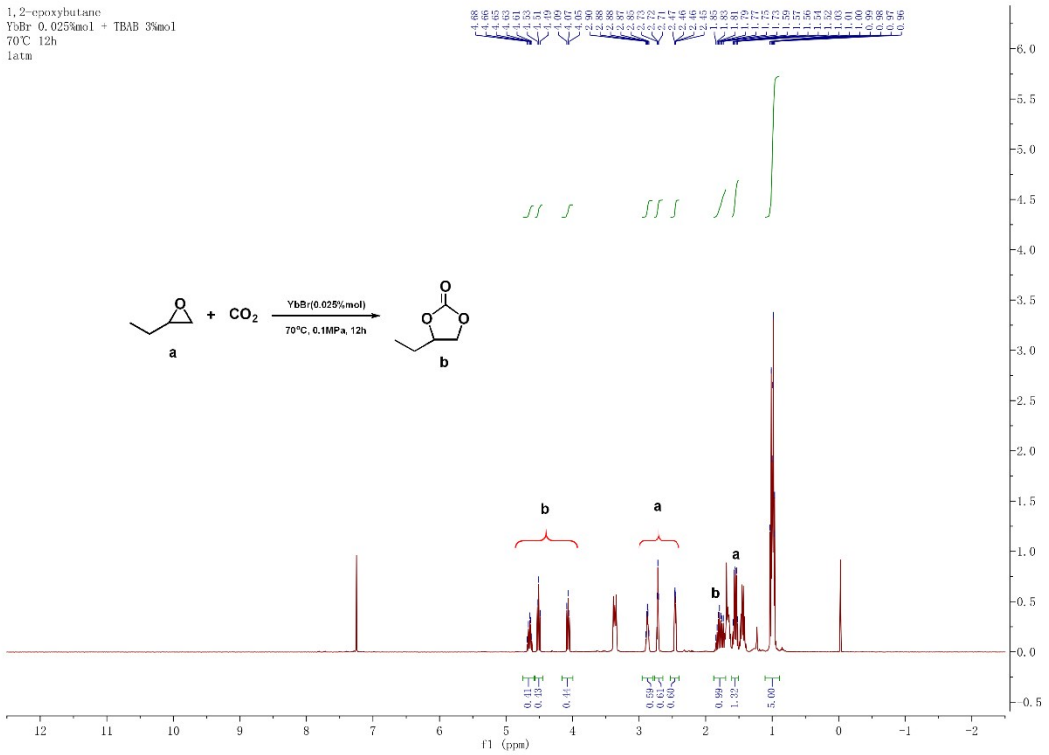


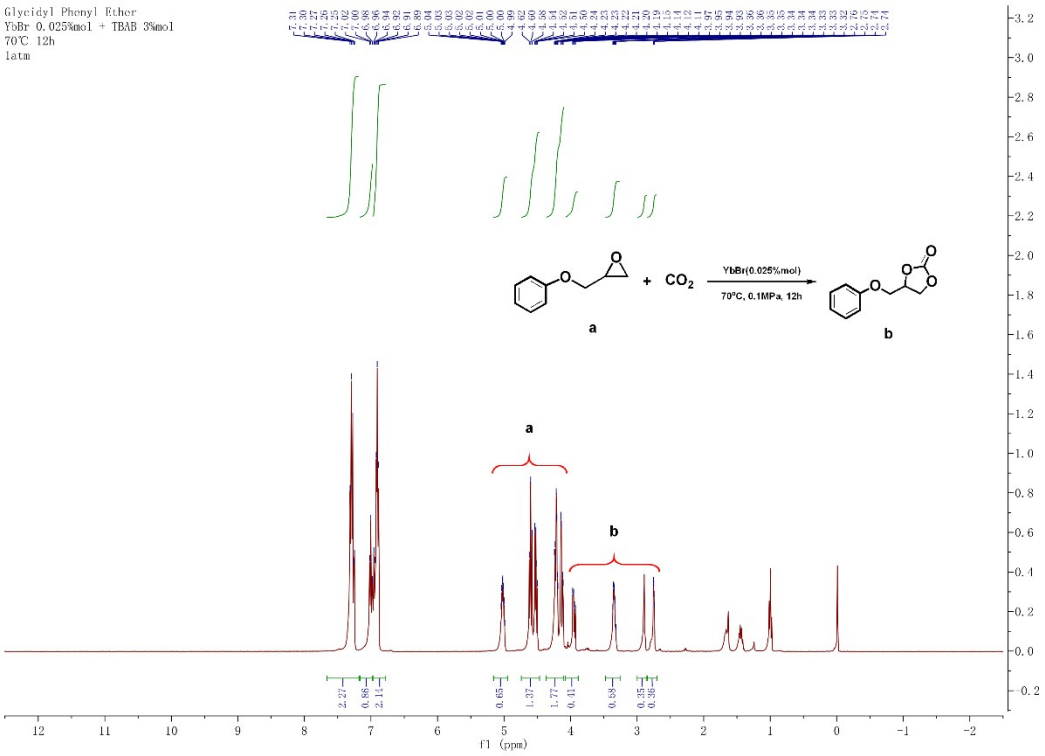
Figure S8. The ORTEP-style image of **1.**

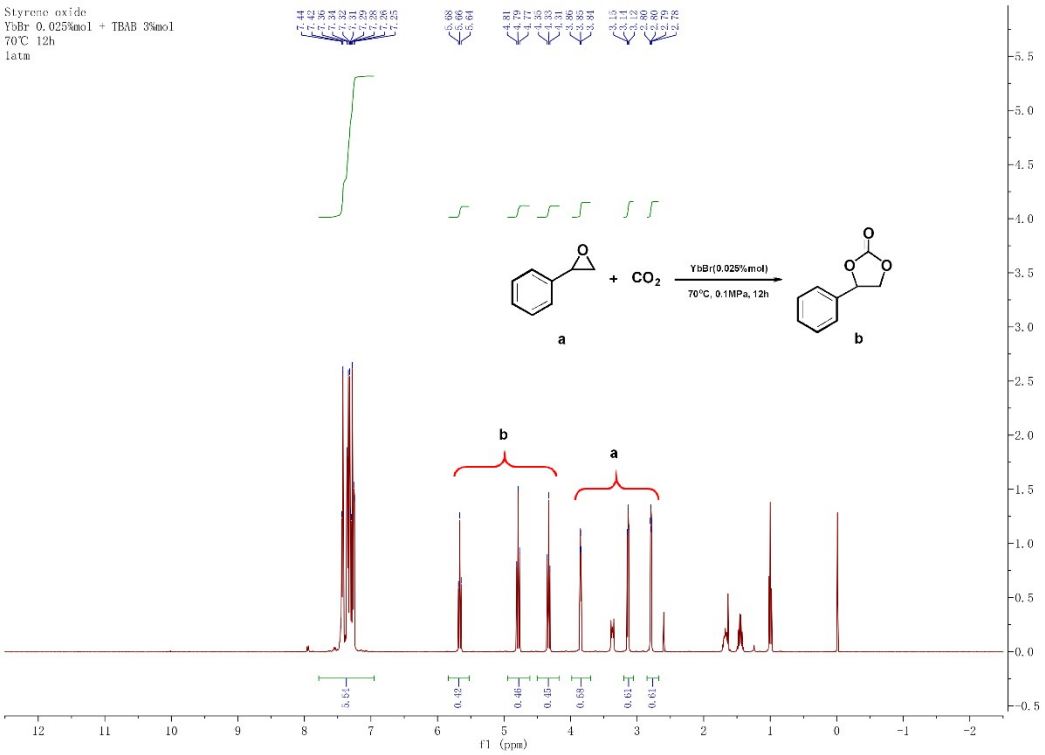
11. ^{1}H NMR spectra of the substrates and products.

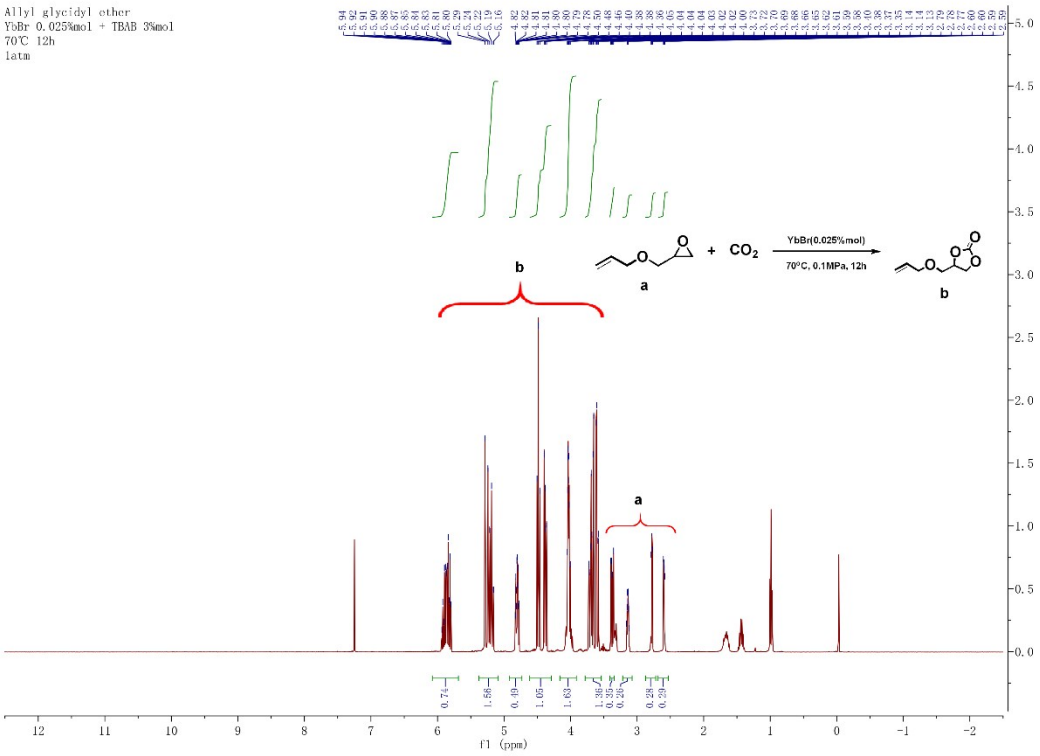


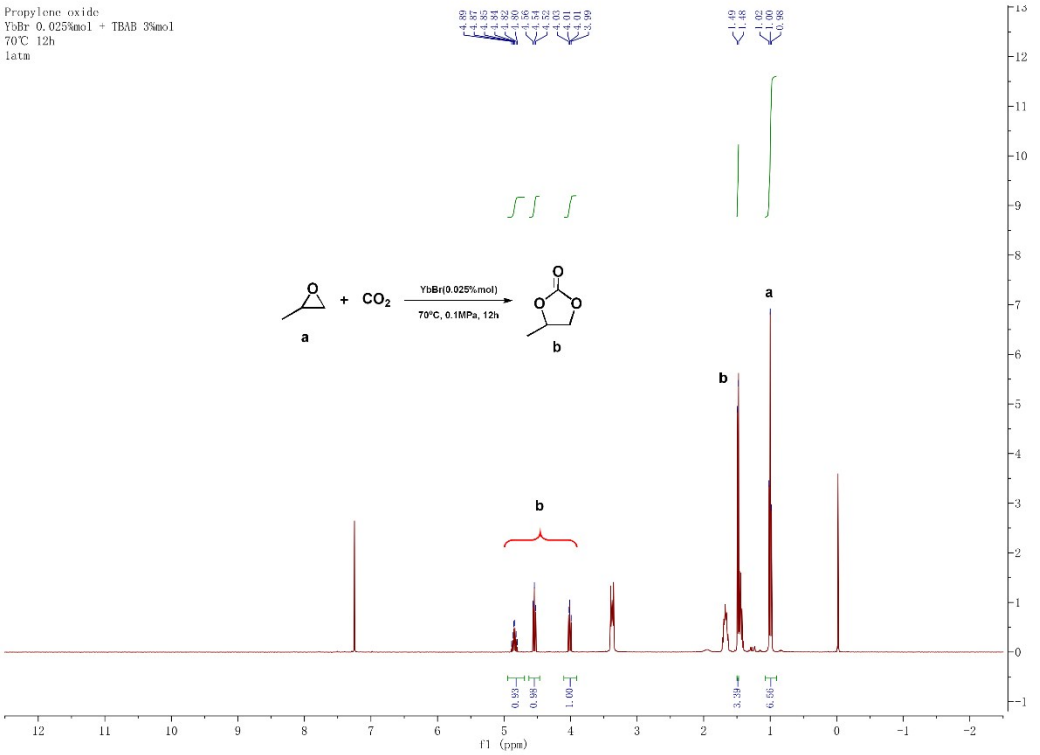

Epibromohydrin
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
Br
a
+ CO2
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
O
O
O
Br
b
b
a
f1 (ppm)

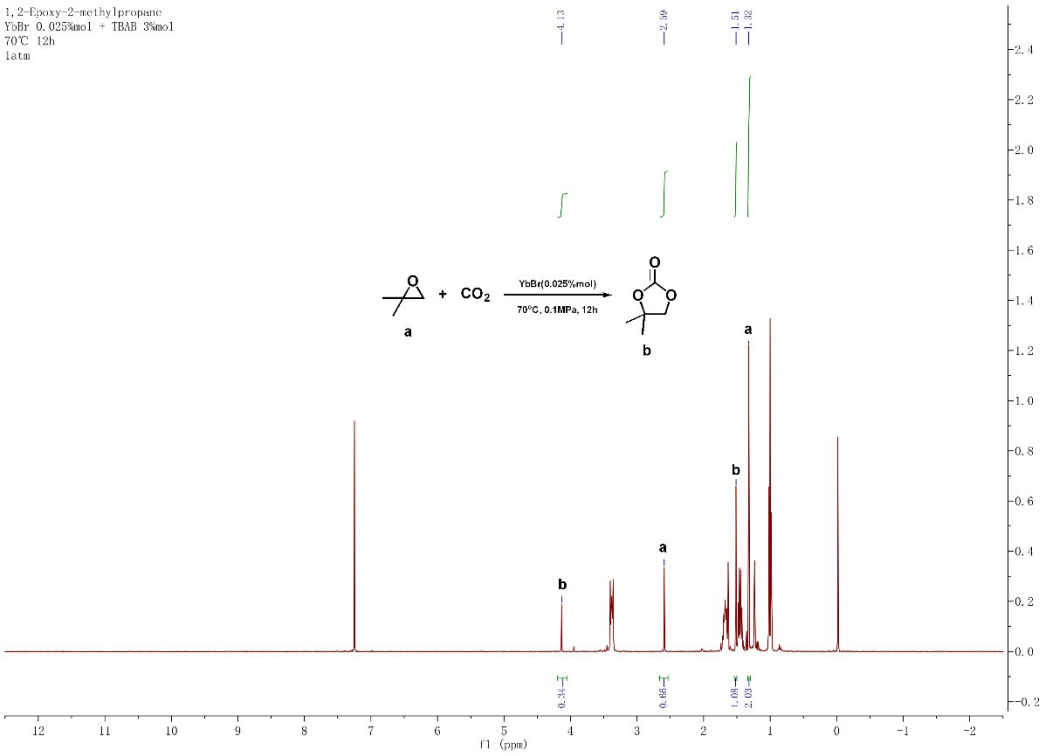

1,2-epoxybutane
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
a
+ CO2
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
O
O
O
b
b
a
a
b
f1 (ppm)


Glycidyl Phenyl Ether
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
a
b
f1 (ppm)


Styrene oxide
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
a
b
f1 (ppm)


Allyl glycidyl ether
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
+ CO2
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
a
b
f1 (ppm)


Propylene oxide
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
+ CO2
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
a
b
f1 (ppm)


1,2-Epoxy-2-methylpropane
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
4.13
2.59
1.51
1.32
+ CO2
YbBr(0.025%mol)
70°C, 0.1MPa, 12h
a
b
0.34
0.66
1.08
2.03
f1 (ppm)

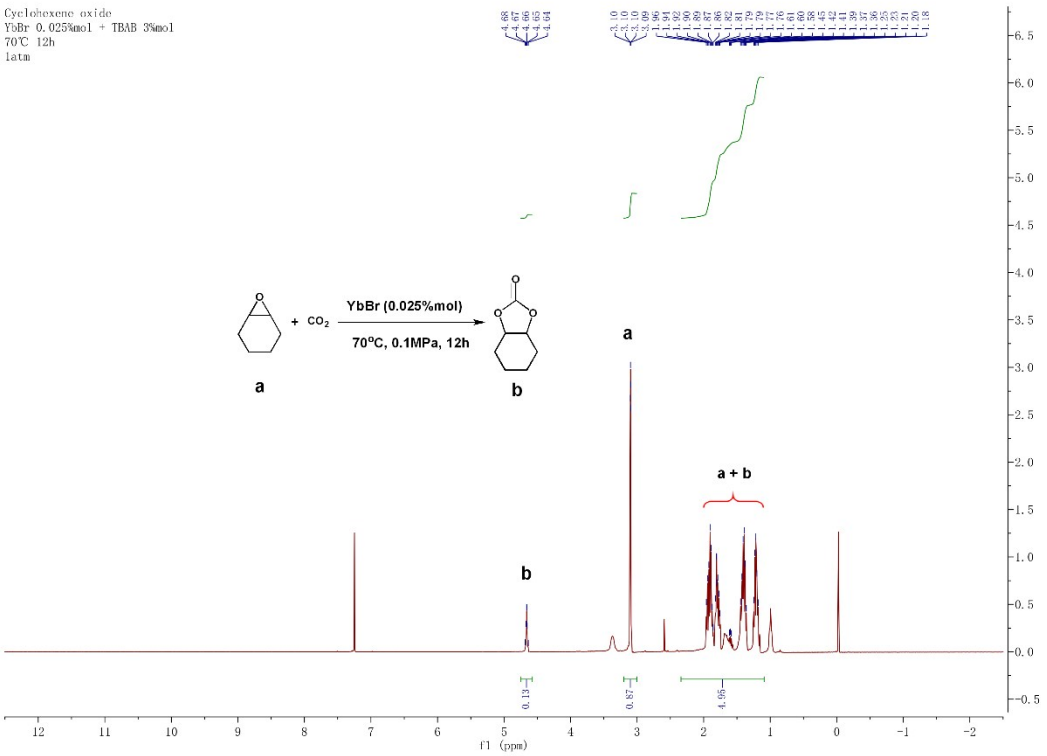

Cyclohexene oxide
YbBr 0.025%mol + TBAB 3%mol
70℃ 12h
1atm
+ CO2
YbBr (0.025%mol)
70°C, 0.1MPa, 12h
a
b
a + b
0.13
0.87
4.05
f1 (ppm)

Table S3. Crystal Data for Compounds **1–6.**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{34}H_{24}N_4O_9Er{\cdot}Cl$	$C_{34}H_{24}N_4O_9Er{\cdot}Br$	$C_{34}H_{24}N_4O_9Tm{\cdot}Cl$	$C_{34}H_{24}N_4O_9Tm{\cdot}Br$	$C_{34}H_{24}N_4O_9Yb{\cdot}Cl$	$C_{34}H_{24}N_4O_9Yb{\cdot}Br$
Formula mass	835.28	879.74	836.95	881.41	841.06	885.52
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1	P-1
a/Å	10.3230(5)	10.343(7)	10.3347(10)	10.3230(5)	10.2917(5)	10.226(2)
b/Å	11.8090(5)	11.870(7)	11.8348(8)	11.8090(5)	11.7702(5)	11.739(2)
c/Å	14.0890(7)	13.995(9)	14.1006(11)	14.0890(7)	14.0907(8)	13.935(3)
α/(°)	82.680(4)	81.813(6)	82.848(6)	82.680(4)	82.913(4)	82.307(4)
β/(°)	68.826(4)	69.256(6)	68.734(8)	68.826(4)	68.858(5)	69.899(3)
γ/(°)	68.581(4)	68.742(6)	68.687(8)	68.581(4)	68.718(4)	69.528(4)
V/Å^3	1490.93(12)	1497.3(17)	1497.2(2)	1490.93(12)	1483.38(12)	1471.5(5)
T/K	291	293	295	291	292	273
Z	2	2	2	2	2	2
μ/mm^{-1}	2.97	4.21	3.12	4.38	3.31	4.60
D_{calcd}/g cm^{-3}	1.861	1.951	1.856	1.963	1.883	1.999
F(000)	826	862	828	864	830	866
Measured reflections	11865	11050	12274	12611	10725	9325
Independent reflections	5867	5217	5879	5865	5208	5879
R_1 a [I > 2σ(I)]	0.030	0.030	0.029	0.037	0.027	0.028
wR_2 b [I > 2σ(I)]	0.058	0.062	0.059	0.070	0.052	0.065
GOF on F^2	1.05	1.06	1.04	1.01	1.04	1.01
CCDC Number	1051522	1051521	1051524	1051523	1051526	1051525

Table S4. The selected bond length (Å) and bond angle (deg) data for compound **1-6**.

Compound **1**				Compound **2**			
Er1—O4^{i}	2.216(3)	O4^{i}—Er1—O5	174.59(9)	Er1—O2	2.292 (3)	O2—Er1—O7^{i}	144.96 (12)
Er1—O5	2.240(2)	O4^{i}—Er1—O9	96.54(10)	Er1—O7^{i}	2.353 (3)	O2—Er1—O8^{i}	160.38 (12)
Er1—O9	2.301(3)	O4^{i}—Er1—O8^{i}	90.56(10)	Er1—O5	2.207 (3)	O2—Er1—O9	74.38 (11)
Er1—O8^{i}	2.298(3)	O4^{i}—Er1—O6^{ii}	86.1(1)	Er1—O8^{i}	2.439 (3)	O2—Er1—C34^{i}	169.42 (12)
Er1—O6^{ii}	2.268(3)	O4^{i}—Er1—O1	93.82(10)	Er1—O9	2.296 (3)	O7^{i}—Er1—O8^{i}	54.19 (12)
Er1—O1	2.448(3)	O4^{i}—Er1—O2	92.32(10)	Er1—C34^{i}	2.734 (5)	O7^{i}—Er1—C34^{i}	27.32 (13)
Er1—O2	2.369(3)	O4^{i}—Er1—C1	96.99(11)	Er1—O3^{i}	2.236 (3)	O5—Er1—O2	89.68 (11)
		O5—Er1—O9	88.81(9)	Er1—O4^{ii}	2.267 (3)	O5—Er1—O7^{i}	92.85 (11)
		O5—Er1—O8^{i}	91.62 (10)			O5—Er1—O8^{i}	93.85 (12)
		O5—Er1—O6^{ii}	89.41 (9)			O5—Er1—O9	95.13 (12)
		O5—Er1—O1	82.47 (10)			O5—Er1—C34^{i}	97.36 (12)
		O5—Er1—O2	88.73 (9)			O5—Er1—O3^{i}	175.28 (11)
		O5—Er1—C1	81.52 (10)			O5—Er1—O4^{ii}	87.15 (12)
		O9—Er1—O1	124.12 (10)			O8^{i}—Er1—C34^{i}	27.31 (13)
		O9—Er1—O2	70.29 (10)			O9—Er1—O7^{i}	70.58 (12)
		O9—Er1—C1	96.96 (12)			O9—Er1—O8^{i}	124.36 (11)
		O8^{i}—Er1—O9	74.74 (9)			O9—Er1—C34^{i}	97.05 (14)
		O8^{i}—Er1—O1	159.83 (10)			O3^{i}—Er1—O2	92.65 (11)
		O8^{i}—Er1—O2	145.02 (10)			O3^{i}—Er1—O7^{i}	87.60 (11)
		O8^{i}—Er1—C1	169.43 (10)			O3^{i}—Er1—O8^{i}	82.60 (11)
		O6^{ii}—Er1—O9	154.47 (10)			O3^{i}—Er1—O9	89.45 (12)
		O6^{ii}—Er1—O8^{i}	79.86 (9)			O3^{i}—Er1—C34^{i}	80.91 (12)
		O6^{ii}—Er1—O1	80.81 (10)			O3^{i}—Er1—O4^{ii}	89.17 (12)
		O6^{ii}—Er1—O2	135.12 (10)			O4^{ii}—Er1—O2	80.76 (11)
		O6^{ii}—Er1—C1	107.95 (12)			O4^{ii}—Er1—O7^{i}	134.26 (12)
		O1—Er1—C1	27.18 (10)			O4^{ii}—Er1—O8^{i}	80.15 (12)
		O2—Er1—O1	54.5 (1)			O4^{ii}—Er1—O9	155.01 (11)
		O2—Er1—C1	27.74 (11)			O4^{ii}—Er1—C34^{i}	107.36 (14)
Symmetry codes: (i) x−1, y+1, z+1; (ii) −x−1, −y+2, −z+2; (iii) x+1, y−1, z−1.				Symmetry codes: (i) *x*, *y*+1, *z*−1; (ii) −*x*+2, −*y*, −*z*+1; (iii) *x*, *y*−1, *z*+1.			

Compound **3**				Compound **4**			
Tm1—O1	2.445 (3)	O1—Tm1—C1	27.57 (10)	Tm1—O4^{i}	2.195 (3)	O4^{i}—Tm1—O2	92.82 (13)
Tm1—O2	2.354 (3)	O2—Tm1—O1	54.51 (9)	Tm1—O2	2.360 (4)	O4^{i}—Tm1—C1	97.85 (15)
Tm1—O5	2.286 (3)	O2—Tm1—C1	27.37 (10)	Tm1—C1	2.744 (6)	O4^{i}—Tm1—O1	94.48 (14)
Tm1—O8^{i}	2.231 (2)	O5—Tm1—O1	159.50 (10)	Tm1—O1	2.426 (4)	O4^{i}—Tm1—O6^{ii}	87.87 (13)
Tm1—C1	2.734 (4)	O5—Tm1—O2	145.36 (10)	Tm1—O6^{ii}	2.244 (3)	O4^{i}—Tm1—O5	175.97 (13)
Tm1—O7^{ii}	2.255 (2)	O5—Tm1—C1	169.36 (10)	Tm1—O5	2.213 (3)	O4^{i}—Tm1—O9	94.26 (13)
Tm1—O4^{iii}	2.205 (2)	O5—Tm1—O9	75.08 (10)	Tm1—O9	2.257 (3)	O4^{i}—Tm1—O8^{i}	88.86 (14)
Tm1—O9	2.289 (2)	O8^{i}—Tm1—O1	82.48 (10)	Tm1—O8^{i}	2.293 (4)	O2—Tm1—C1	26.78 (13)
		O8^{i}—Tm1—O2	88.48 (9)			O2—Tm1—O1	53.63 (12)
		O8^{i}—Tm1—O5	91.68 (10)			O1—Tm1—C1	27.34 (13)
		O8^{i}—Tm1—C1	81.37 (10)			O6^{ii}—Tm1—O2	134.92 (13)
		O8^{i}—Tm1—O7^{ii}	89.37 (8)			O6^{ii}—Tm1—C1	108.57 (15)
		O8^{i}—Tm1—O9	89.11 (9)			O6^{ii}—Tm1—O1	81.35 (13)
		O7^{ii}—Tm1—O1	80.55 (10)			O6^{ii}—Tm1—O9	155.03 (14)
		O7^{ii}—Tm1—O2	134.89 (10)			O6^{ii}—Tm1—O8^{i}	79.41 (13)
		O7^{ii}—Tm1—O5	79.75 (10)			O5—Tm1—O2	87.51 (13)
		O7^{ii}—Tm1—C1	108.06 (11)			O5—Tm1—C1	80.66 (14)
		O7^{ii}—Tm1—O9	154.72 (10)			O5—Tm1—O1	82.48 (13)
		O4^{iii}—Tm1—O1	94.06 (10)			O5—Tm1—O6^{ii}	89.05 (12)
		O4^{iii}—Tm1—O2	92.57 (10)			O5—Tm1—O9	89.63 (12)
		O4^{iii}—Tm1—O5	90.29 (10)			O5—Tm1—O8^{i}	93.14 (13)
		O4^{iii}—Tm1—O8^{i}	174.90 (9)			O9—Tm1—O2	69.90 (13)
		O4^{iii}—Tm1—C1	97.31 (11)			O9—Tm1—C1	95.80 (15)
		O4^{iii}—Tm1—O7^{ii}	86.35 (9)			O9—Tm1—O1	123.14 (12)
		O4^{iii}—Tm1—O9	95.94 (9)			O9—Tm1—O8^{i}	75.77 (12)
		O9—Tm1—O1	124.20 (10)			O8^{i}—Tm1—O2	145.66 (12)
		O9—Tm1—O2	70.28 (10)			O8^{i}—Tm1—C1	169.66 (14)
		O9—Tm1—C1	96.64 (11)			O8^{i}—Tm1—O1	160.34 (12)
Symmetry codes: (i) x+1, y−1, z−1; (ii) −x, −y+1, −z+2; (iii) x−1, y+1, z+1.				Symmetry codes: (i) x, y−1, z+1; (ii) −x+2, −y, −z+1; (iii) x, y+1, z−1.			

Compound **5**				Compound **6**			
Tm1—O1	2.445 (3)	O1—Tm1—C1	27.57 (10)	Yb1—O5	2.268 (3)	O5—Yb1—O4^{i}	159.84 (10)
Tm1—O2	2.354 (3)	O2—Tm1—O1	54.51 (9)	Yb1—O1	2.190 (3)	O5—Yb1—O3^{i}	145.06 (10)
Tm1—O5	2.286 (3)	O2—Tm1—C1	27.37 (10)	Yb1—O4^{i}	2.421 (3)	O5—Yb1—C17^{i}	169.63 (12)
Tm1—O8^{i}	2.231 (2)	O5—Tm1—O1	159.50 (10)	Yb1—O3^{i}	2.330 (3)	O5—Yb1—H9A	58.6 (11)
Tm1—C1	2.734 (4)	O5—Tm1—O2	145.36 (10)	Yb1—C17^{i}	2.710 (4)	O1—Yb1—O5	90.05 (10)
Tm1—O7^{ii}	2.255 (2)	O5—Tm1—C1	169.36 (10)	Yb1—O9	2.254 (3)	O1—Yb1—O4^{i}	93.46 (11)
Tm1—O4^{iii}	2.205 (2)	O5—Tm1—O9	75.08 (10)	Yb1—O8^{i}	2.206 (3)	O1—Yb1—O3^{i}	92.28 (10)
Tm1—O9	2.289 (2)	O8^{i}—Tm1—O1	82.48 (10)	Yb1—O7^{ii}	2.233 (3)	O1—Yb1—C17^{i}	97.01 (11)
		O8^{i}—Tm1—O2	88.48 (9)			O1—Yb1—O9	95.47 (11)
		O8^{i}—Tm1—O5	91.68 (10)			O1—Yb1—O8^{i}	175.46 (11)
		O8^{i}—Tm1—C1	81.37 (10)			O1—Yb1—O7^{ii}	87.23 (10)
		O8^{i}—Tm1—O7^{ii}	89.37 (8)			O1—Yb1—H9A	89.6 (12)
		O8^{i}—Tm1—O9	89.11 (9)			O4^{i}—Yb1—C17^{i}	27.60 (12)
		O7^{ii}—Tm1—O1	80.55 (10)			O4^{i}—Yb1—H9A	141.2 (11)
		O7^{ii}—Tm1—O2	134.89 (10)			O3^{i}—Yb1—O4^{i}	54.67 (10)
		O7^{ii}—Tm1—O5	79.75 (10)			O3^{i}—Yb1—C17^{i}	27.56 (11)
		O7^{ii}—Tm1—C1	108.06 (11)			O3^{i}—Yb1—H9A	86.5 (11)
		O7^{ii}—Tm1—O9	154.72 (10)			C17^{i}—Yb1—H9A	113.6 (11)
		O4^{iii}—Tm1—O1	94.06 (10)			O9—Yb1—O5	74.77 (10)
		O4^{iii}—Tm1—O2	92.57 (10)			O9—Yb1—O4^{i}	124.51 (10)
		O4^{iii}—Tm1—O5	90.29 (10)			O9—Yb1—O3^{i}	70.30 (11)
		O4^{iii}—Tm1—O8^{i}	174.90 (9)			O9—Yb1—C17^{i}	96.91 (12)
		O4^{iii}—Tm1—C1	97.31 (11)			O9—Yb1—H9A	17.1 (11)
		O4^{iii}—Tm1—O7^{ii}	86.35 (9)			O8^{i}—Yb1—O5	92.31 (10)
		O4^{iii}—Tm1—O9	95.94 (9)			O8^{i}—Yb1—O4^{i}	83.01 (10)
		O9—Tm1—O1	124.20 (10)			O8^{i}—Yb1—O3^{i}	88.01 (10)
		O9—Tm1—O2	70.28 (10)			O8^{i}—Yb1—C17^{i}	81.19 (11)
		O9—Tm1—C1	96.64 (11)			O8^{i}—Yb1—O9	88.89 (11)
Symmetry codes: (i) x+1, y−1, z−1; (ii) −x, −y+1, −z+2; (iii) x−1, y+1, z+1.				Symmetry codes: (i) x, y+1, z−1; (ii) −x+1, −y, −z+2; (iii) x, y−1, z+1.			

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