Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Radii-dependent self-assembly polynuclear lanthanide complexes as catalysts for CO_2 transformation into cyclic carbonates

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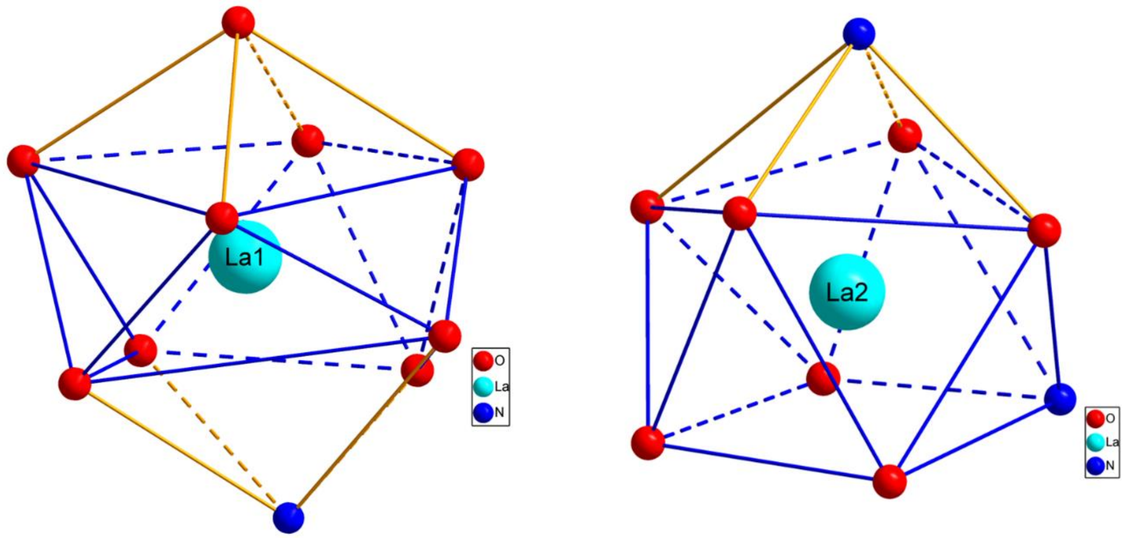

Figure S1. Coordination polyhedron of La1 and La2 in complex **1**.

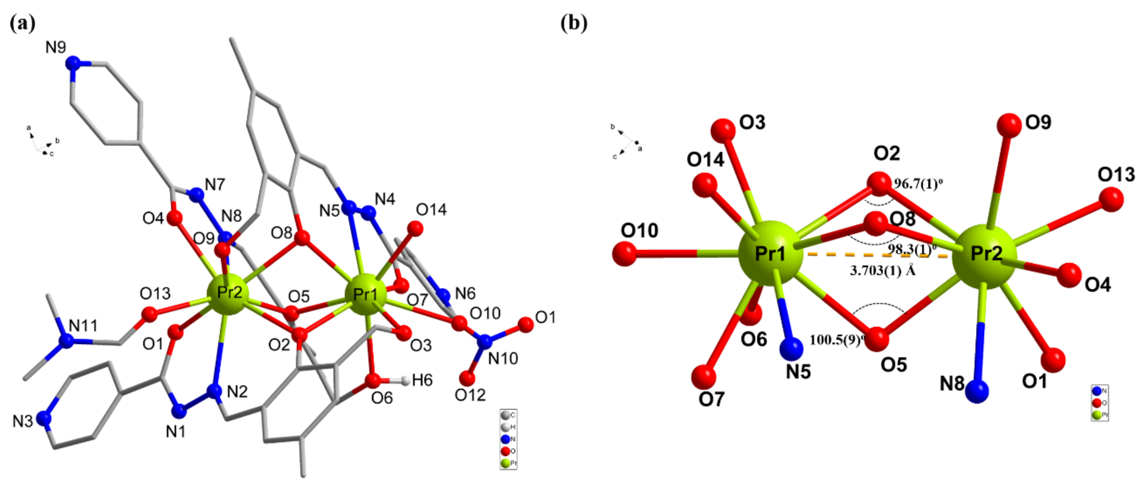

Figure S2. **(a)** Molecular structure of complex **2**. All hydrogen atoms (except for benzyl alcoholic oxygen atom of singly deprotonated H_2L^- anion) have been omitted for clarity; **(b)** Dinuclear Pr_2O_3 core structure of Pr(III) ions in complex **2**.

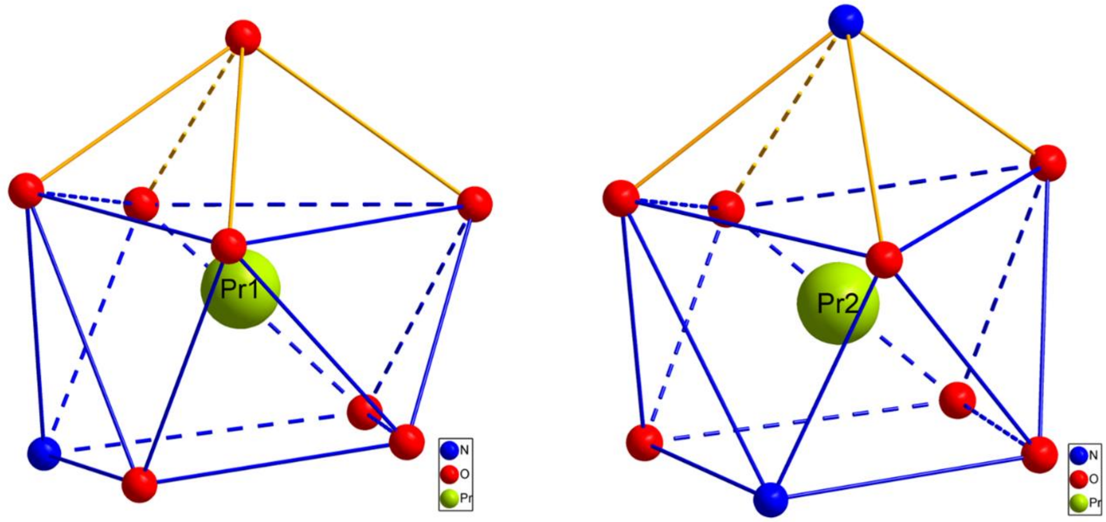

Figure S3. Coordination polyhedron of Pr1 and Pr2 in complex **2**.

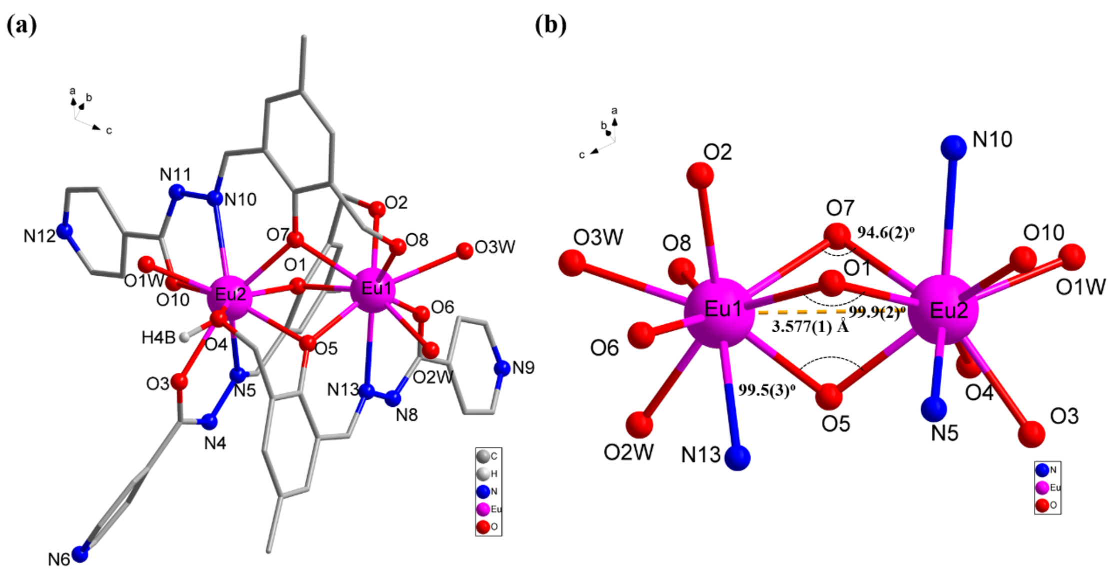

Figure S4. **(a)** Molecular structure of complex **3**. All hydrogen atoms (except for benzyl alcoholic oxygen atom of singly deprotonated H_2L^- anion) have been omitted for clarity; **(b)** Dinuclear Eu_2O_3 core structure of Eu(III) ions in complex **3**.

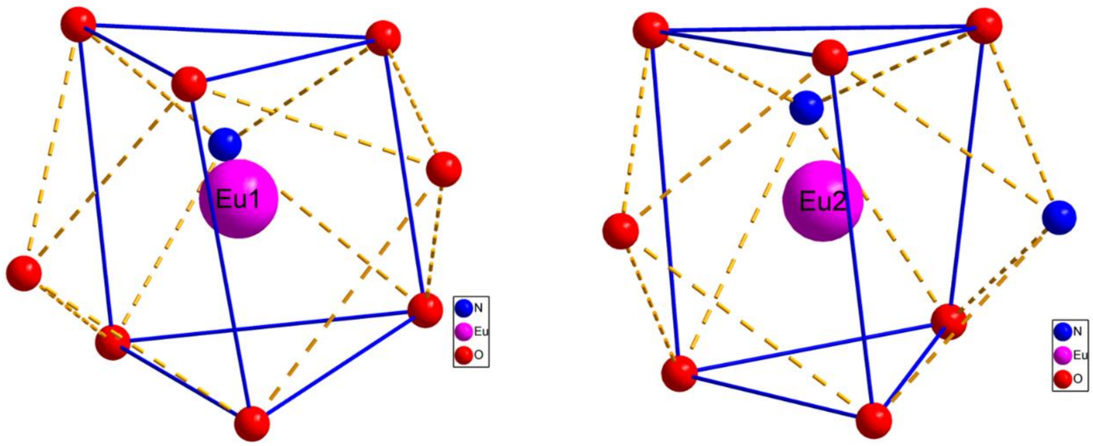

Figure S5. Coordination polyhedron of Eu1 and Eu2 in complex **3**.

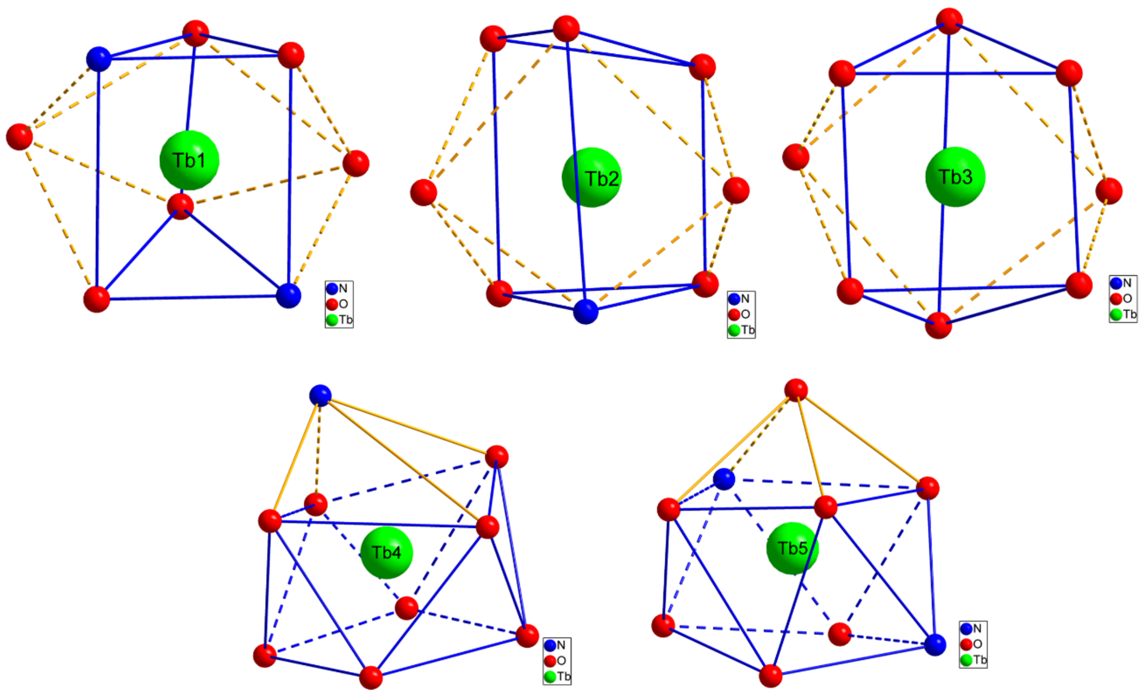

Figure S6. Coordination polyhedron of Tb1, Tb2, Tb3, Tb4, Tb5 in complex **4**.

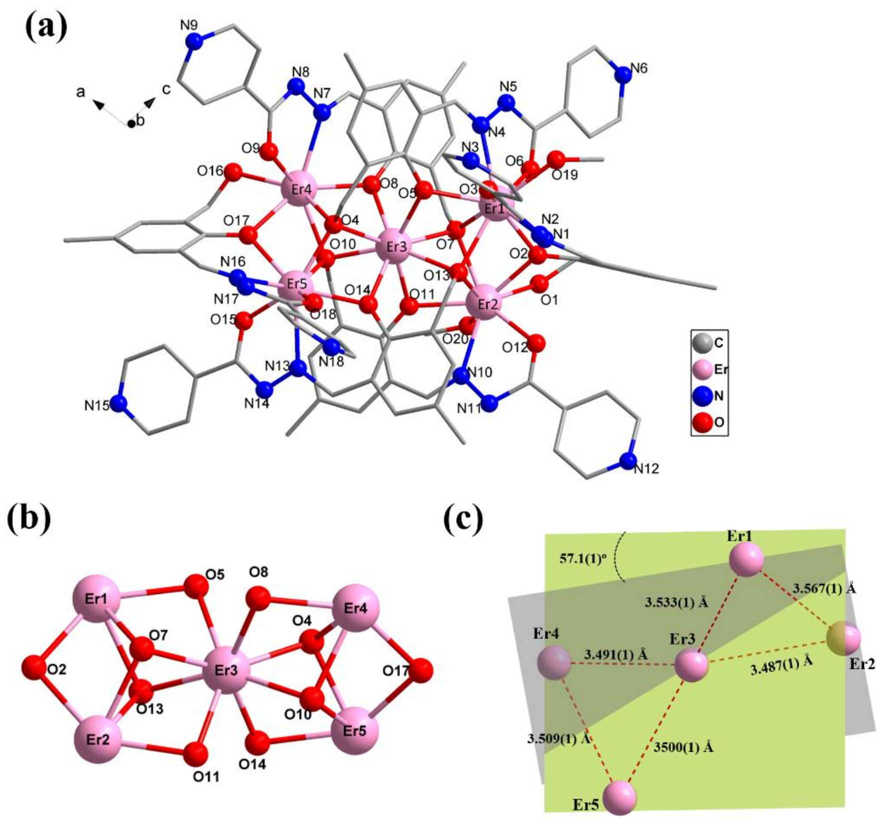

Figure S7. **(a)** Molecular structure of complex **5**. All hydrogen atoms have been omitted for clarity; **(b)** $[Er_5(\mu_3\text{-}O)_4(\mu_2\text{-}O)^6]^{5+}$core of complex **5**; **(c)** $[Er_5(\mu_3\text{-}O)_4(\mu_2\text{-}O)_6]^{5+}$core showing the dihedral angle between the two triangular motifs along with the distance between the Er^{3+} ions.

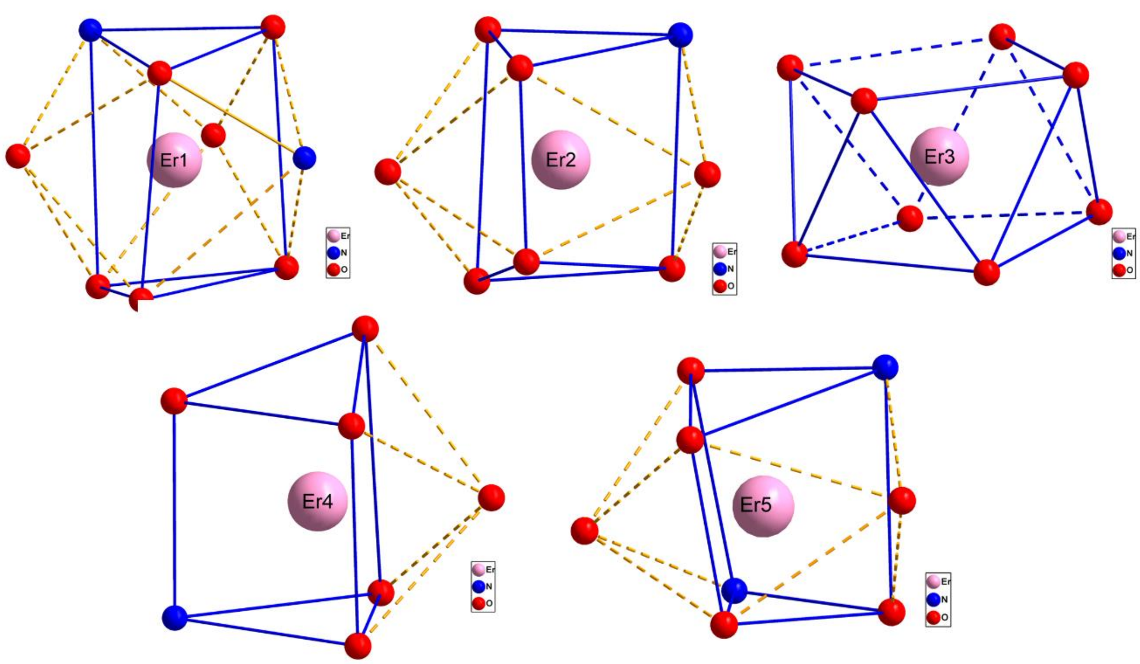

Figure S8. Coordination polyhedron of Er1, Er2, Er3, Er4, Er5 in complex **5**.

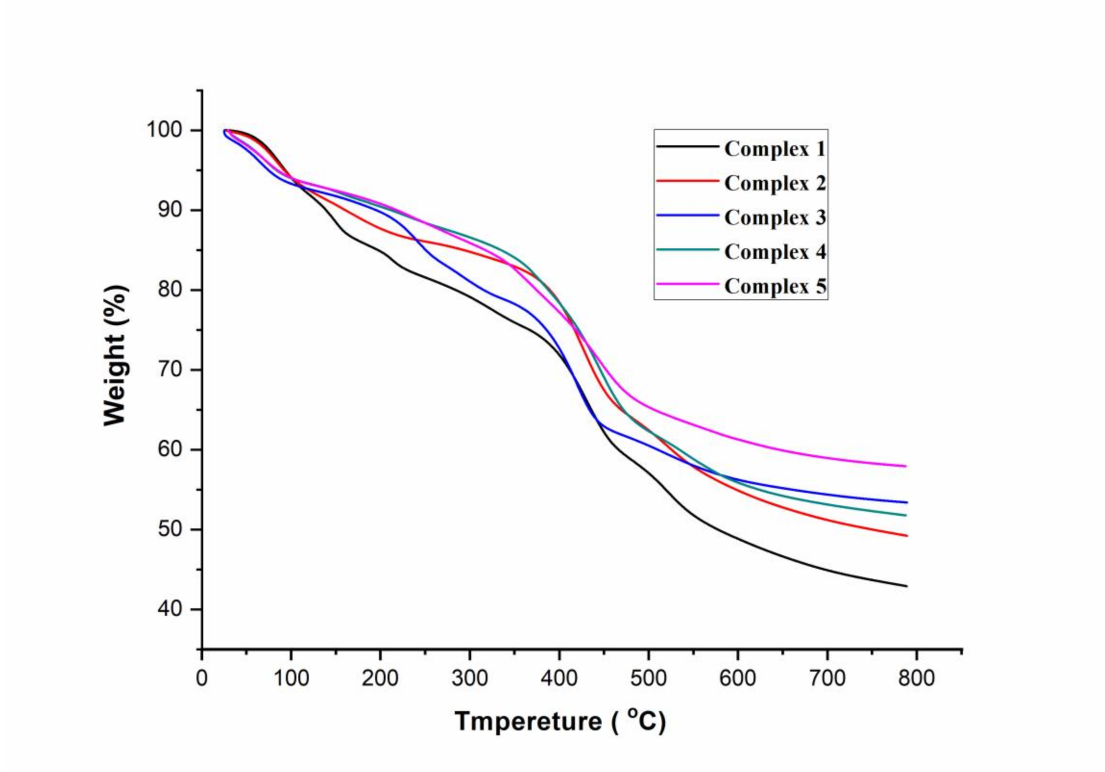

Figure S9. TGA curves of complexes **1-5**.

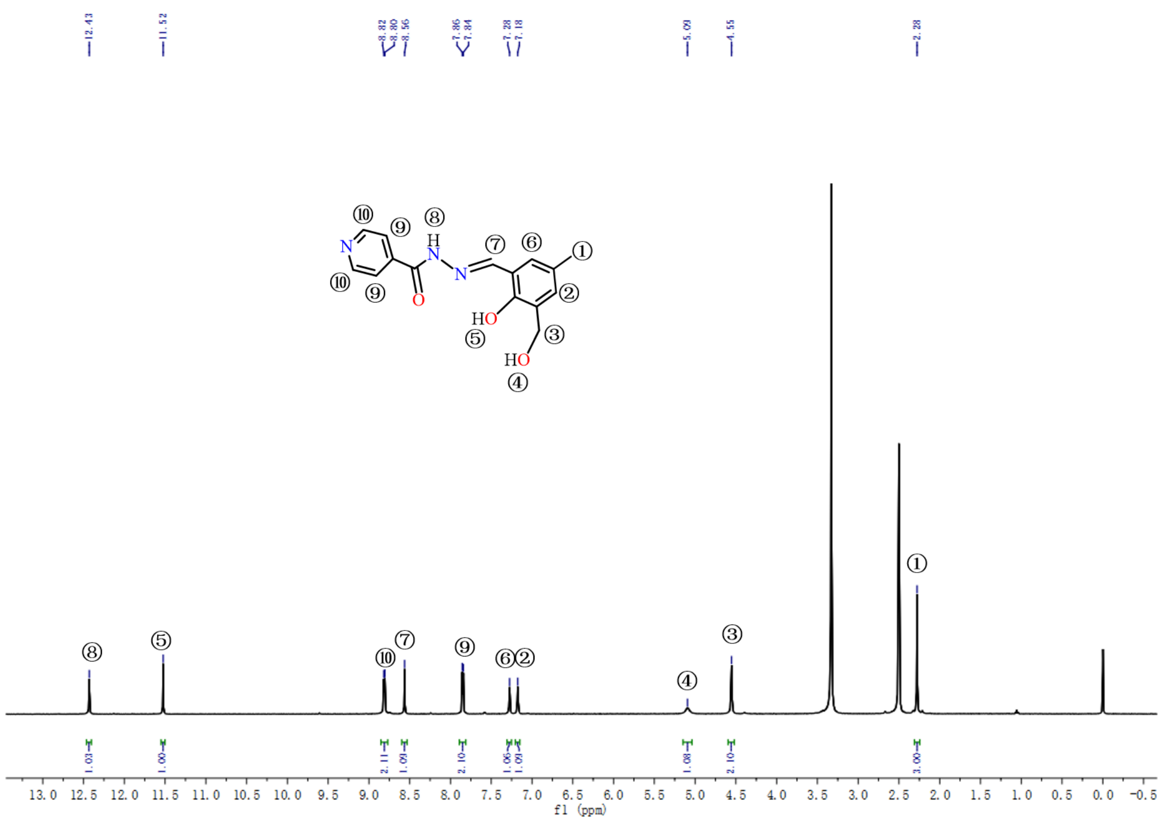

Figure S10. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) spectrum of the H_3L.

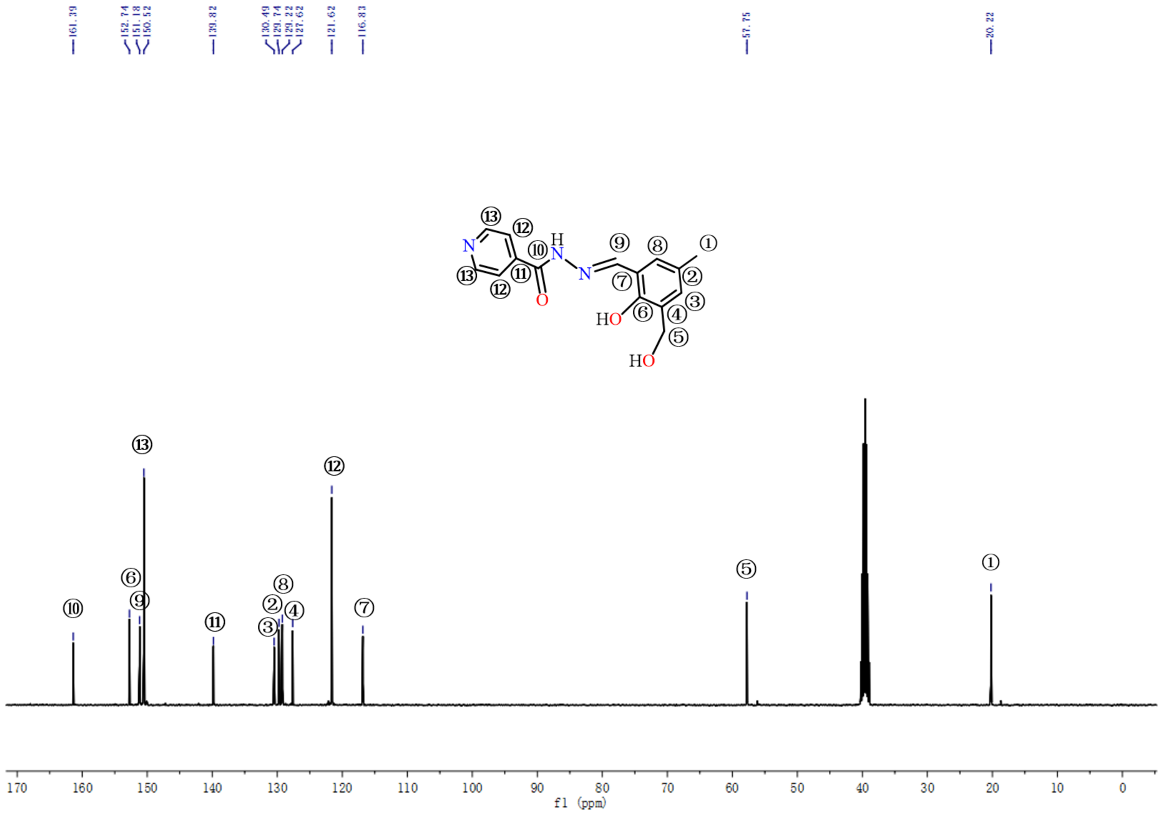

Figure S11. ^{13}C NMR (100 MHz, DMSO-d_6, 25 ºC) spectrum of the H_3L.

Generic Display Report

Analysis Info

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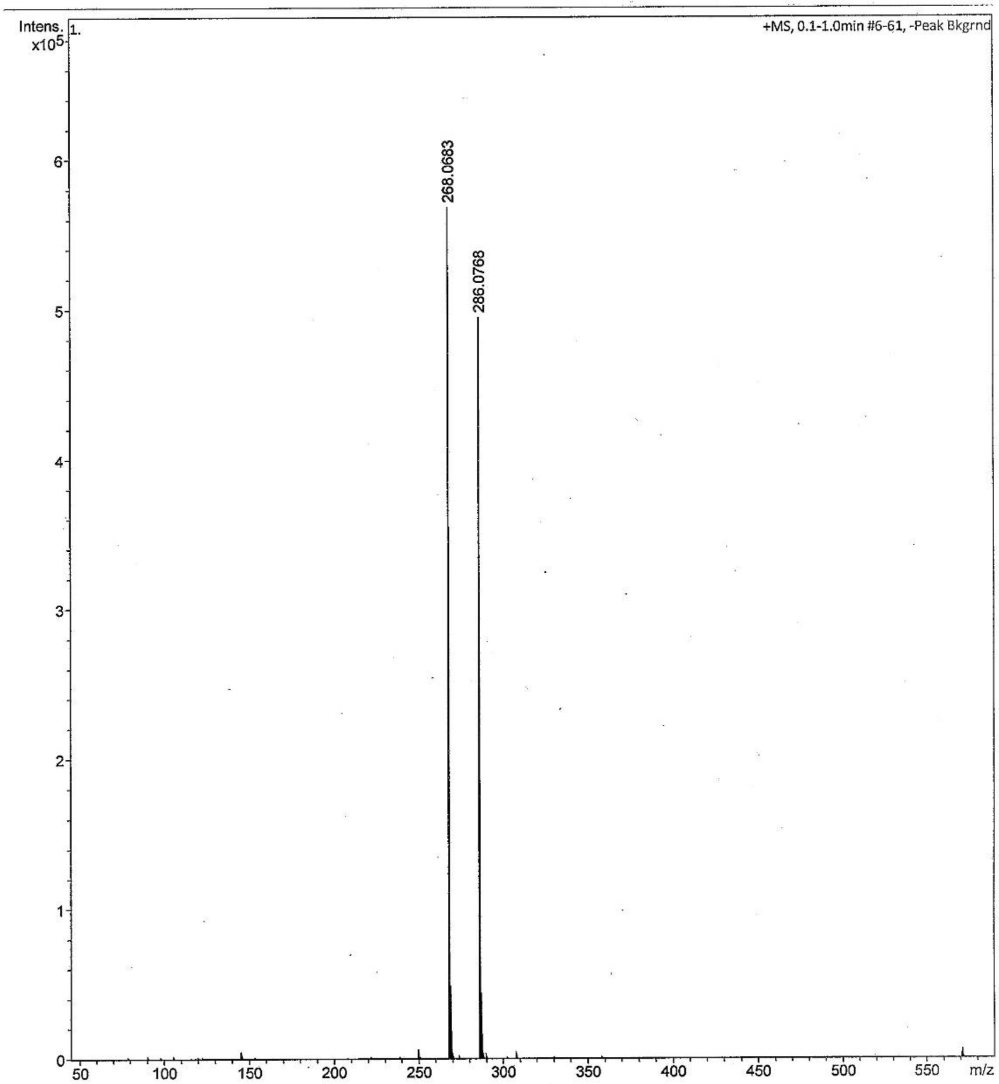

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Figure S12. Mass Spectrum of H_3L.

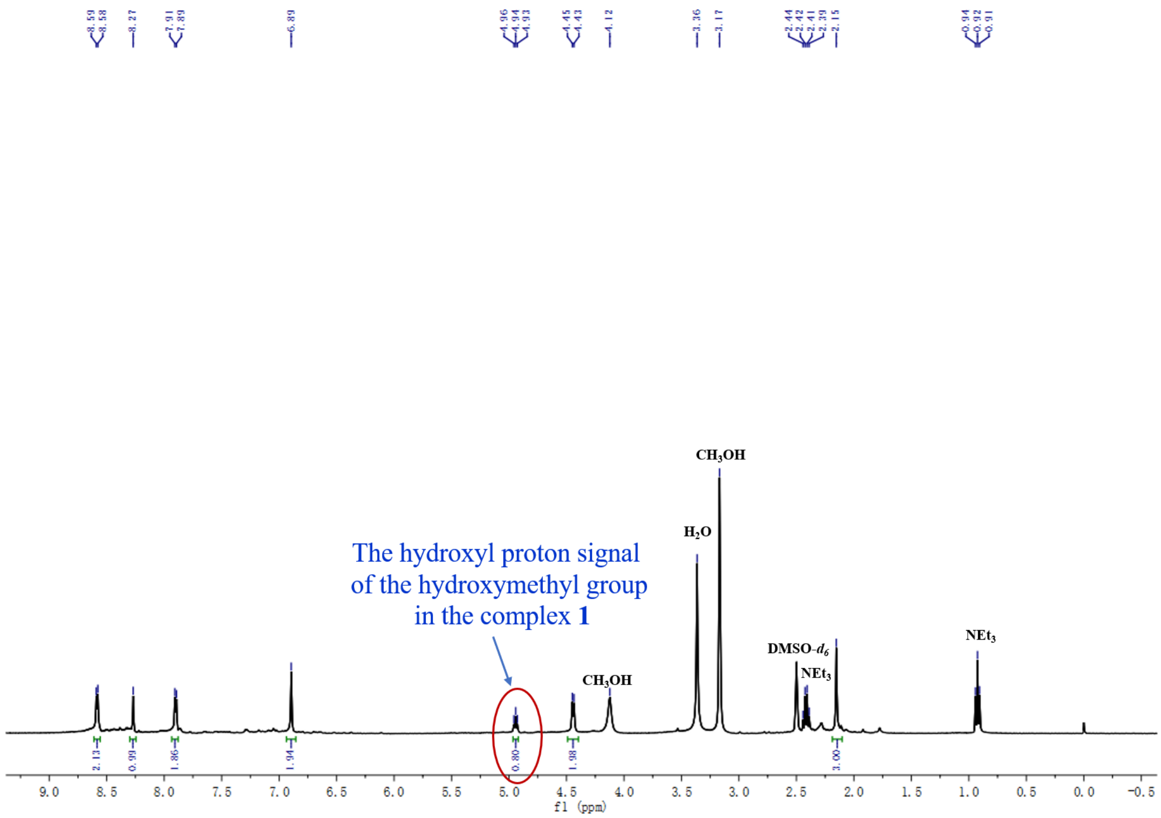

Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) spectrum of the complex **1**.

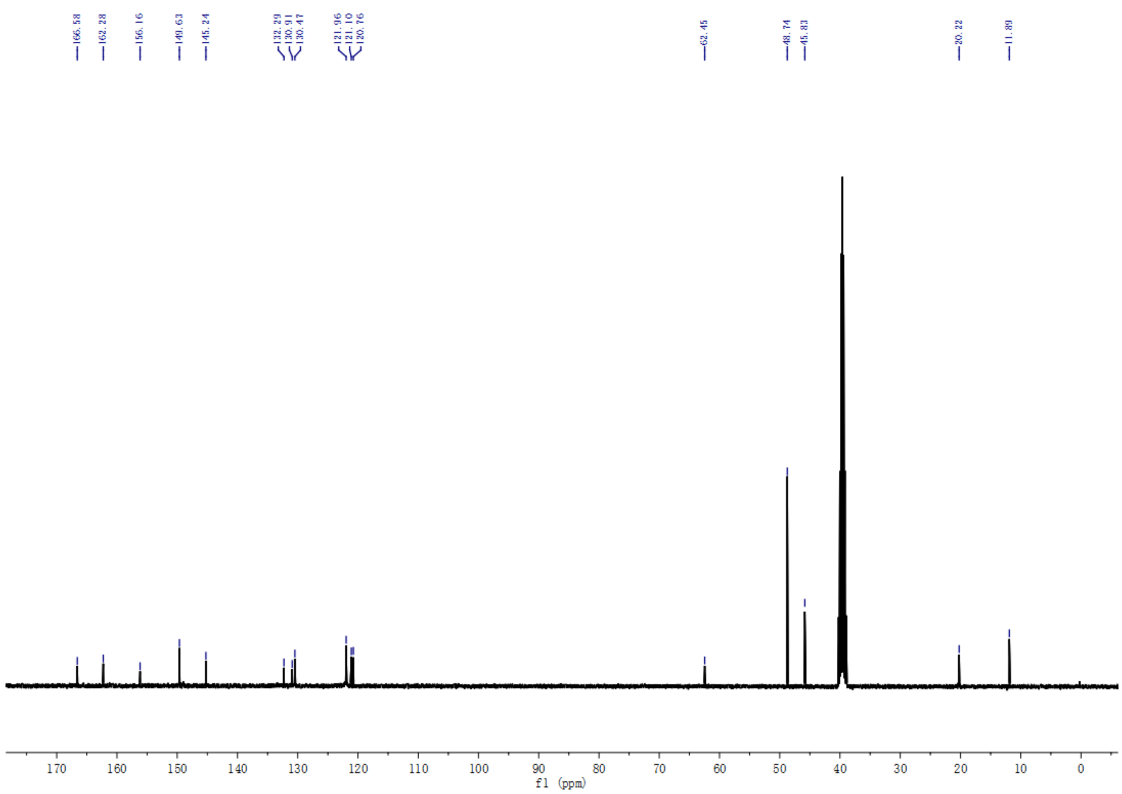

Figure S14. ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) spectrum of the complex **1**.

Table S1. Crystallographic and structure refinement data for complexes **1-5.**

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$\mathbf{C_{46}H_{46}La_2N_{10}O_{14}}$	$\mathbf{C_{48}H_{48}N_{11}O_{14}Pr_2}$	$\mathbf{C_{45}H_{46}Eu_2N_{10}O_{15}}$	$\mathbf{C_{214}H_{271}N_{43}O_{60}Tb_{10}}$	$\mathbf{C_{124}H_{131}Er_5N_{24}O_{33}}$
*F*w	1240.75	1284.79	1270.84	5994.92	3321.82
T(K)	173(2)	296.1(5)	296.1(5)	291.1(5)	291.1(5)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a (Å)	17.973(3)	17.4217(14)	17.693(16)	36.9338(14)	35.3440(16)
b (Å)	14.747(2)	14.6810(11)	16.389(5)	20.8248(13)	20.8374(14)
c (Å)	27.502(4)	27.191(2)	24.679(8)	21.7478(13)	21.3950(15)
α (deg)	90	90	90	90	90.00
β(deg)	97.637(3)	106.684(2)	107.611(5)	101.087(3)	100.671(3)
γ(deg)	90	90	90	90	90.00
V Å^3	7224.5(19)	6661.9(9)	6821(4)	16414.9(16)	15484.4(17)
Z	4	4	4	2	4
D_{calcd} g.cm^{-3}	1.141	1.281	1.238	1.213	1.425
μ (mm^{-1})	1.22	1.50	1.88	2.19	2.75
F (000)	2472	2572	2528	5972	6588
Index ranges	$-20\leq h\leq 22$ $-17\leq k\leq 18$ $-31\leq l\leq 34$	$-21\leq h\leq 22$ $-14\leq k\leq 19$ $-35\leq l\leq -34$	$-17\leq h\leq 21$ $-19\leq k\leq 19$ $-29\leq l\leq 27$	$-47\leq h\leq 40$ $-26\leq k\leq 19$ $-27\leq l\leq 28$	$-45\leq h\leq 45$ $-27\leq k\leq 25$ $-26\leq l\leq 27$
Data/restr./param	14852/20/660	15554/6/664	11709/820/652	37306/6/1796	35308/43/1841
GOF	0.96	1.08	1.08	1.03	0.95
$[I > 2\sigma(I)]$	$R_1 = 0.066$ $wR_2 = 0.148$	$R_1 = 0.041$ $wR_2 = 0.117$	$R_1 = 0.090$ $wR_2 = 0.242$	$R_1 = 0.044$ $wR_2 = 0.098$	$R_1 = 0.055$ $wR_2 = 0.130$
CCDC number	2060402	2060405	2060404	2060401	2060403

Table S2. Selected Bond Lengths (Å) and Angles (°) for complexes **1-5.**

Complex 1					
La1-O2	2.430 (5)	La1-O11	2.633 (6)	La2-O5	2.502 (5)
La1-O8	2.466 (5)	La1-O5	2.679 (5)	La2-O2	2.517 (5)
La1-O13	2.510 (5)	La1-O10	2.785 (6)	La2-O7	2.585 (6)
La1-O1	2.572 (5)	La1-N2	2.865 (6)	La2-N5	2.608 (6)
La1-O6	2.572 (5)	La1-La2	3.800 (1)	La2-O3	2.654 (5)
La1-O9	2.610 (5)	La2-O4	2.409 (6)	La2-N8	2.808 (7)
La2-O8	2.422 (5)				
O2-La1-O8	71.3(2)	O9-La1-O10	114.4 (2)	O5-La2-O14	108.8 (2)
O2-La1-O13	72.5(2)	O11-La1-O10	47.3 (2)	O2-La2-O14	132.8(2)
O8-La1-O13	142.8 (2)	O5-La1-O10	159.6 (2)	O7-La2-O14	77.8 (2)
O2-La1-O1	116.2 (2)	O2-La1-N2	62.3 (2)	O4-La2-N5	61.6 (2)
O8-La1-O1	75.0 (2)	O8-La1-N2	75.9 (2)	O8-La2-N5	82.4(2)
O13-La1-O1	129.8 (2)	O13-La1-N2	94.3 (2)	O5-La2-N5	69.7(2)
O2-La1-O6	118.3 (2)	O1-La1-N2	57.8 (2)	O2-La2-N5	136.6 (2)
O8-La1-O6	122.2 (2)	O6-La1-N2	161.7 (2)	O7-La2-N5	139.4(2)
O13-La1-O6	69.8 (2)	O9-La1-N2	121.1 (2)	O14-La2-N5	73.6 (2)
O1-La1-O6	125.5 (2)	O11-La1-N2	101.8 (2)	O4-La2-O3	137.2 (2)
O2-La1-O9	137.8 (2)	O5-La1-N2	123.1 (2)	O8-La2-O3	136.8(2)
O8-La1-O9	69.8 (2)	O10-La1-N2	60.9 (2)	O5-La2-O3	83.6 (2)
O13-La1-O9	140.2 (2)	O2-La1-La2	40.7 (1)	O2-La2-O3	69.3 (2)
O1-La1-O9	67.8 (2)	O8-La1-La2	38.6(1)	O7-La2-O3	71.7 (2)
O6-La1-O9	71.9 (2)	O13-La1-La2	105.3 (1)	O14-La2-O3	63.7 (2)
O2-La1-O11	148.4 (2)	O1-La1-La2	110.3 (1)	N5-La2-O3	118.0(2)
O8-La1-O11	134.5 (2)	O6-La1-La2	109.7 (1)	O4-La2-N8	65.3 (2)
O13-La1-O11	82.4 (2)	O9-La1-La2	97.3 (1)	O2-La2-N8	79.7 (2)
O1-La1-O11	66.6 (2)	O11-La1-La2	170.9 (2)	O7-La2-N8	58.6 (2)
O6-La1-O11	68.1 (2)	O5-La1-La2	41.0(1)	O14-La2-N8	123.3 (2)
O9-La1-O11	73.7 (2)	O10-La1-La2	140.2 (1)	N5-La2-N8	117.2 (2)

O2-La1-O5	67.3 (2)	N2-La1-La2	82.6 (1)	O3-La2-N8	123.4 (2)
O8-La1-O5	64.2 (2)	O4-La2-O8	85.8 (2)	O4-La2-La1	125.2 (1)
O13-La1-O5	94.3 (2)	O4-La2-O5	127.0 (2)	O8-La2-La1	39.4 (1)
O1-La1-O5	135.5 (2)	O8-La2-O5	67.6 (2)	O5-La2-La1	44.7 (1)
O6-La1-O5	68.81 (2)	O4-La2-O2	144.0 (2)	O2-La2-La1	39.0 (1)
O9-La1-O5	81.6(2)	O5-La2-O2	68.9 (2)	O7-La2-La1	118.5 (1)
O11-La1-O5	135.0 (2)	O4-La2-O7	84.5 (2)	O14-La2-La1	151.4 (2)
O2-La1-O10	103.3 (2)	O8-La2-O7	118.8 (2)	N5-La2-La1	99.9 (1)
O8-La1-O10	131.8 (2)	O5-La2-O7	148.5 (2)	O3-La2-La1	97.6 (1)
O13-La1-O10	65.3 (2)	O2-La2-O7	83.9 (2)	N8-La2-La1	84.7 (1)
O1-La1-O10	64.7 (2)	O4-La2-O14	77.0 (2)	O6-La1-O10	103.0 (2)
O8-La2-O14	155.0 (2)				

Complex 2

N2-Pr2	2.585 (3)	O4-Pr2	2.492 (3)	O9-Pr2	2.583 (3)
N5-Pr1	2.859 (3)	O5-Pr2	2.392 (2)	O10-Pr1	2.624 (3)
N8-Pr2	2.763 (3)	O5-Pr1	2.423 (3)	O13-Pr2	2.493 (4)
O1-Pr2	2.388 (3)	O6-Pr1	2.543 (3)	O14-Pr1	2.426 (3)
O2-Pr2	2.452 (3)	O7-Pr1	2.454 (3)	Pr1-Pr2	3.703 (1)
O2-Pr1	2.503 (3)	O8-Pr1	2.379 (3)	O3-Pr1	2.487 (3)
O8-Pr2	2.514 (3)				
O8-Pr1-O5	72.3 (1)	O14-Pr1-N5	75.4 (1)	O1-Pr2-O9	140.8 (1)
O8-Pr1-O14	78.6 (1)	O7-Pr1-N5	57.6 (1)	O5-Pr2-O9	137.2 (1)
O5-Pr1-O14	145.5 (1)	O3-Pr1-N5	149.6 (1)	O2-Pr2-O9	81.9 (1)
O8-Pr1-O7	118.9 (1)	O2-Pr1-N5	123.6 (1)	O13-Pr2-O9	67.2 (1)
O5-Pr1-O7	81.5 (1)	O6-Pr1-N5	120.6 (1)	O4-Pr2-O9	70.0(1)
O14-Pr1-O7	97.0 (1)	O10-Pr1-N5	109.3 (1)	O8-Pr2-O9	69.2 (1)
O8-Pr1-O3	108.5 (1)	O8-Pr1-Pr2	42.2 (1)	O1-Pr2-N2	63.2 (1)
O5-Pr1-O3	132.7 (1)	O5-Pr1-Pr2	39.4 (1)	O5-Pr2-N2	86.2 (1)
O14-Pr1-O3	74.2 (1)	O14-Pr1-Pr2	119.9 (1)	O2-Pr2-N2	68.6 (1)
O7-Pr1-O3	129.1 (1)	O7-Pr1-Pr2	117.6 (1)	O13-Pr2-N2	68.5 (1)
O8-Pr1-O2	66.8(1)	O3-Pr1-Pr2	109.5(1)	O4-Pr2-N2	137.2 (1)
O5-Pr1-O2	67.7 (1)	O2-Pr1-Pr2	41.06 (6)	O8-Pr2-N2	133.4 (7)

O14-Pr1-O2	117.0 (1)	O6-Pr1-Pr2	96.2 (1)	O9-Pr2-N2	112.2 (1)
O7-Pr1-O2	145.6 (1)	O10-Pr1-Pr2	163.0 (1)	O1-Pr2-N8	68.4 (1)
O3-Pr1-O2	69.8 (1)	N5-Pr1-Pr2	83.7 (1)	O5-Pr2-N8	64.1 (1)
O8-Pr1-O6	138.3 (1)	O1-Pr2-O5	82.0 (1)	O2-Pr2-N8	128.7 (1)
O5-Pr1-O6	69.4 (1)	O1-Pr2-O2	124.6 (1)	O13-Pr2-N8	120.8 (1)
O14-Pr1-O6	142.8 (1)	O5-Pr2-O2	69.0 (1)	O4-Pr2-N8	59.4 (1)
O7-Pr1-O6	71.2 (1)	O1-Pr2-O13	75.8 (1)	O8-Pr2-N8	79.8 (1)
O3-Pr1-O6	86.2 (1)	O5-Pr2-O13	151.9 (1)	O9-Pr2-N8	120.4 (1)
O2-Pr1-O6	83.6 (1)	O2-Pr2-O13	110.2 (1)	N2-Pr2-N8	125.9 (1)
O8-Pr1-O10	153.8 (1)	O1-Pr2-O4	87.9 (1)	O1-Pr2-Pr1	121.5(1)
O5-Pr1-O10	131.8 (1)	O5-Pr2-O4	122.3 (1)	O5-Pr2-Pr1	40.1 (1)
O14-Pr1-O10	75.2 (1)	O2-Pr2-O4	147.5 (1)	O2-Pr2-Pr1	42.2 (1)
O7-Pr1-O10	64.4 (1)	O13-Pr2-O4	74.3 (1)	O13-Pr2-Pr1	152.0 (1)
O3-Pr1-O10	64.9 (1)	O1-Pr2-O8	144.7 (1)	O4-Pr2-Pr1	124.4 (1)
O2-Pr1-O10	127.1 (1)	O5-Pr2-O8	70.5 (1)	O8-Pr2-Pr1	39.5 (1)
O6-Pr1-O10	67.9 (1)	O2-Pr2-O8	65.6 (1)	O9-Pr2-Pr1	97.9 (1)
O8-Pr1-N5	62.6 (1)	O13-Pr2-O8	136.3 (1)	N2-Pr2-Pr1	97.7 (1)
O5-Pr1-N5	74.9 (1)	O4-Pr2-O8	88.5 (1)	N8-Pr2-Pr1	87.2 (1)

Complex 3

Eu1-O5	2.298 (6)	Eu1-O7	2.514 (7)	Eu2-O1W	2.409 (8)
Eu1-O1	2.346 (7)	Eu1-N13	2.698 (7)	Eu2-O3	2.438 (6)
Eu1-O6	2.405 (7)	Eu1-Eu2	3.577 (1)	Eu2-O4	2.481 (6)
Eu1-O2W	2.423 (8)	Eu2-O1	2.329 (6)	Eu2-N10	2.602 (9)
Eu1-O8	2.442 (7)	Eu2-O7	2.345 (6)	Eu2-N5	2.707 (8)
Eu1-O2	2.450 (7)	Eu2-O10	2.391 (7)	Eu1-O3W	2.497 (8)
Eu2-O5	2.387 (6)				
O6-Eu1-O2	72.9 (3)	O3W-Eu1-Eu2	159.8 (2)	O4-Eu2-N10	116.3 (2)
O2W-Eu1-O2	140.6 (3)	O7-Eu1-Eu2	40.8 (2)	O1-Eu2-N5	64.0 (2)
O8-Eu1-O2	96.7 (2)	O1-Eu2-O7	69.5 (2)	O7-Eu2-N5	129.6 (2)
O5-Eu1-O3W	152.7 (3)	O1-Eu2-O10	82.6 (3)	O10-Eu2-N5	66.3 (3)
O1-Eu1-O3W	134.1 (3)	O7-Eu2-O10	126.2 (3)	O5-Eu2-N5	80.9 (2)
O6-Eu1-O3W	66.8 (3)	O1-Eu2-O5	71.8 (2)	O1W-Eu2-N5	124.8 (3)

O2W-Eu1-O3W	73.4 (3)	O7-Eu2-O5	66.6 (2)	O3-Eu2-N5	60.5 (2)
O8-Eu1-O3W	67.6 (3)	O1-Eu2-O1W	146.5 (3)	O4-Eu2-N5	123.1 (2)
O2-Eu1-O3W	67.4 (3)	O7-Eu2-O1W	104.7 (3)	N10-Eu2-N5	119.7 (3)
O5-Eu1-O7	65.3 (2)	O10-Eu2-O1W	74.7 (3)	O1-Eu2-C40	81.5 (3)
O6-Eu1-O7	147.1 (3)	O5-Eu2-O1W	137.9 (3)	O7-Eu2-C40	109.6 (3)
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O8-Eu1-O7	68.5 (3)	O7-Eu2-O3	148.6 (2)	O5-Eu2-C40	152.8 (3)
O2-Eu1-O7	81.4 (2)	O10-Eu2-O3	85.2 (2)	O1W-Eu2-C40	69.2 (3)
O3W-Eu1-O7	121.3 (3)	O5-Eu2-O3	89.3 (2)	O3-Eu2-C40	101.1 (3)
O5-Eu1-N13	64.5 (2)	O1W-Eu2-O3	79.3 (3)	O4-Eu2-C40	136.5 (3)
O6-Eu1-N13	60.5 (2)	O1-Eu2-O4	139.6 (2)	N10-Eu2-C40	44.9 (3)
O2W-Eu1-N13	68.9 (3)	O7-Eu2-O4	82.0 (2)	N5-Eu2-C40	82.5 (3)
O8-Eu1-N13	137.0 (3)	O10-Eu2-O4	137.8 (3)	O1-Eu2-Eu1	40.1 (2)
O2-Eu1-N13	124.5 (2)	O5-Eu2-O4	70.7 (2)	O7-Eu2-Eu1	44.4 (2)
O3W-Eu1-N13	114.2 (3)	O1W-Eu2-O4	67.3 (3)	O10-Eu2-Eu1	122.5 (2)
O7-Eu1-N13	124.4 (2)	O3-Eu2-O4	70.7 (2)	O5-Eu2-Eu1	39.3 (2)
O5-Eu1-Eu2	41.1 (2)	O1-Eu2-N10	78.6 (3)	O1W-Eu2-Eu1	148.9 (2)
O6-Eu1-N13	60.5 (2)	O7-Eu2-N10	66.7 (3)	O3-Eu2-Eu1	124.4 (2)
O6-Eu1-Eu2	121.7 (2)	O10-Eu2-N10	63.2 (3)	O4-Eu2-Eu1	99.6 (2)
O2W-Eu1-Eu2	122.6 (2)	O5-Eu2-N10	130.9 (2)	N10-Eu2-Eu1	94.5 (2)
O8-Eu1-Eu2	104.0 (2)	O1W-Eu2-N10	69.3 (3)	N5-Eu2-Eu1	86.2 (2)
O2-Eu1-Eu2	96.6 (2)	O3-Eu2-N10	139.8 (3)	C40-Eu2-Eu1	118.2 (2)

Complex 4

N3-Tb1	2.538 (4)	O3-Tb3	2.361 (3)	O16-Tb4	2.407 (3)
N6-Tb1	2.533 (4)	O7-Tb2	2.362 (3)	O17-Tb3	2.338 (3)
N9-Tb2	2.473 (4)	O8-Tb2	2.364 (3)	O17-Tb4	2.341 (3)
N12-Tb5	2.542 (4)	O8-Tb3	2.380 (3)	O18-Tb3	2.265 (3)
N15-Tb5	2.595(4)	O9-Tb3	2.399 (3)	O18-Tb1	2.329 (3)
N18-Tb4	2.583 (4)	O9-Tb5	2.434 (3)	O18-Tb2	2.424 (3)
N19-Tb4	2.953 (5)	O9-Tb4	2.474 (3)	O19-Tb4	2.531 (4)
O1-Tb1	2.334 (3)	O10-Tb5	2.462 (3)	O20-Tb4	2.536 (4)
O2-Tb1	2.365 (3)	O11-Tb3	2.346 (3)	O22-Tb5	2.528 (3)

O2-Tb3	2.411 (3)	O11-Tb5	2.388 (3)	O23-Tb2	2.497 (3)
O3-Tb3	2.361 (3)	O12-Tb2	2.348 (3)	Tb1-Tb2	3.543 (1)
O3-Tb5	2.462 (3)	O12-Tb3	2.385 (3)	Tb1-Tb3	3.579(1)
O3-Tb4	2.467 (3)	O12-Tb1	2.448 (3)	Tb2-Tb3	3.541 (1)
O4-Tb1	2.355 (3)	O13-Tb5	2.362 (4)	Tb3-Tb4	3.545 (1)
O5-Tb2	2.302 (3)	O14-Tb5	2.321 (3)	Tb3-Tb5	3.570 (1)
O5-Tb1	2.365 (3)	O14-Tb4	2.565 (3)	Tb4-Tb5	3.682 (1)
O6-Tb2	2.446 (3)	O15-Tb4	2.510 (3)		
O2-Tb1-Tb2	101.6 (1)	O3-Tb3-O2	79.9 (1)	O15-Tb4-N19	64.4 (1)
O12-Tb1-Tb2	41.4 (1)	O8-Tb3-O2	141.8 (1)	O19-Tb4-N19	24.7 (1)
N6-Tb1-Tb2	100.2 (1)	O12-Tb3-O2	73.7 (1)	O20-Tb4-N19	24.2 (1)
N3-Tb1-Tb2	148.7 (1)	O9-Tb3-O2	135.7 (1)	O14-Tb4-N19	128.0 (1)
O18-Tb1-Tb3	37.7 (1)	O18-Tb3-Tb2	42.6 (1)	N18-Tb4-N19	90.3 (2)
O1-Tb1-Tb3	129.7 (1)	O17-Tb3-Tb2	119.5 (1)	O17-Tb4-Tb3	40.8 (1)
O4-Tb1-Tb3	99.7 (1)	O11-Tb3-Tb2	92.4 (1)	O16-Tb4-Tb3	124.8 (1)
O5-Tb1-Tb3	99.4 (1)	O3-Tb3-Tb2	164.0 (1)	O3-Tb4-Tb3	41.5 (1)
O2-Tb1-Tb3	42.0 (1)	O8-Tb3-Tb2	41.3 (1)	O9-Tb4-Tb3	42.6 (1)
O12-Tb1-Tb3	41.6 (1)	O12-Tb3-Tb2	41.3 (1)	O15-Tb4-Tb3	151.1 (1)
N6-Tb1-Tb3	140.1 (1)	O9-Tb3-Tb2	121.2 (1)	O19-Tb4-Tb3	119.0 (1)
N3-Tb1-Tb3	106.9 (1)	O2-Tb3-Tb2	100.7 (1)	O20-Tb4-Tb3	95.4 (1)
Tb2-Tb1-Tb3	59.6 (1)	O18-Tb3-Tb4	120.9 (1)	O14-Tb4-Tb3	97.6 (1)
O5-Tb2-O12	78.0 (1)	O17-Tb3-Tb4	40.9 (1)	N18-Tb4-Tb3	100.9 (1)
O5-Tb2-O8	142.4 (1)	O11-Tb3-Tb4	103.9 (1)	N19-Tb4-Tb3	109.2 (1)
O12-Tb2-O8	76.9 (1)	O3-Tb3-Tb4	43.9 (1)	O17-Tb4-Tb5	99.8 (1)
O5-Tb2-O7	77.7 (1)	O8-Tb3-Tb4	119.6 (1)	O16-Tb4-Tb5	94.5 (1)
O12-Tb2-O7	82.5 (1)	O12-Tb3-Tb4	164.8 (1)	O3-Tb4-Tb5	41.6 (1)
O8-Tb2-O7	125.6 (1)	O9-Tb3-Tb4	44.1 (1)	O9-Tb4-Tb5	40.9 (1)
O5-Tb2-O18	72.7 (1)	O2-Tb3-Tb4	92.1 (1)	O15-Tb4-Tb5	104.2 (1)
O12-Tb2-O18	58.8 (1)	Tb2-Tb3-Tb4	151.2(1)	O19-Tb4-Tb5	160.1 (1)
O8-Tb2-O18	70.5 (1)	O18-Tb3-Tb5	167.7 (1)	O20-Tb4-Tb5	111.4 (1)
O7-Tb2-O18	134.9 (1)	O17-Tb3-Tb5	103.2 (1)	O14-Tb4-Tb5	38.6 (1)
O5-Tb2-O6	74.9 (1)	O11-Tb3-Tb5	41.6 (1)	N18-Tb4-Tb5	132.7 (1)

O12-Tb2-O6	148.8 (1)	O3-Tb3-Tb5	43.5 (1)	N19-Tb4-Tb5	135.5 (1)
O8-Tb2-O6	134.3 (1)	O8-Tb3-Tb5	95.0 (1)	Tb3-Tb4-Tb5	59.1 (1)
O7-Tb2-O6	76.8 (1)	O12-Tb3-Tb5	119.7 (1)	O14-Tb5-O13	128.3 (1)
O18-Tb2-O6	125.0 (1)	O9-Tb3-Tb5	42.9 (1)	O14-Tb5-O11	142.2 (1)
O5-Tb2-N9	141.3 (1)	O2-Tb3-Tb5	119.9 (1)	O13-Tb5-O11	67.9 (1)
O12-Tb2-N9	103.3 (1)	Tb2-Tb3-Tb5	128.3 (1)	O14-Tb5-O9	76.6 (1)
O8-Tb2-N9	72.2 (1)	Tb4-Tb3-Tb5	62.42 (1)	O13-Tb5-O9	140.1 (1)
O7-Tb2-N9	64.4 (1)	O18-Tb3-Tb1	39.1 (1)	O11-Tb5-O9	74.6 (1)
O18-Tb2-N9	141.5 (1)	O17-Tb3-Tb1	92.1 (1)	O14-Tb5-O10	72.8 (1)
O6-Tb2-N9	88.7 (1)	O11-Tb3-Tb1	118.6 (1)	O13-Tb5-O10	137.5 (1)
O5-Tb2-O23	115.4 (1)	O3-Tb3-Tb1	119.6 (1)	O11-Tb5-O10	121.2 (1)
O12-Tb2-O23	140.4 (1)	O8-Tb3-Tb1	100.6 (1)	O9-Tb5-O10	74.5 (1)
O8-Tb2-O23	71.0 (1)	O12-Tb3-Tb1	42.9 (1)	O14-Tb5-O3	74.1 (1)
O7-Tb2-O23	135.4 (1)	O9-Tb3-Tb1	165.2 (1)	O13-Tb5-O3	92.4 (1)
O18-Tb2-O23	88.5 (1)	O2-Tb3-Tb1	41.2 (1)	O11-Tb5-O3	71.0 (1)
O6-Tb2-O23	67.3(1)	Tb2-Tb3-Tb1	59.6 (1)	O9-Tb5-O3	62.2 (1)
N9-Tb2-O23	88.5 (1)	Tb4-Tb3-Tb1	127.1 (1)	O10-Tb5-O3	130.1 (1)
O5-Tb2-Tb3	102.0 (1)	Tb5-Tb3-Tb1	150.3 (1)	O14-Tb5-O22	93.3(1)
O12-Tb2-Tb3	42.1 (1)	O17-Tb4-O16	128.3 (1)	O13-Tb5-O22	71.6 (1)
O8-Tb2-Tb3	42.0 (1)	O17-Tb4-O3	74.1 (1)	O11-Tb5-O22	124.2 (1)
O7-Tb2-Tb3	121.2 (1)	O16-Tb4-O3	85.5 (1)	O9-Tb5-O22	145.2 (1)
O18-Tb2-Tb3	38.9 (1)	O17-Tb4-O9	73.3 (1)	O10-Tb5-O22	70.6 (1)
O6-Tb2-Tb3	161.1 (1)	O16-Tb4-O9	135.5 (1)	O3-Tb5-O22	147.2 (1)
N9-Tb2-Tb3	103.9 (1)	O3-Tb4-O9	61.7 (1)	O14-Tb5-N12	136.4(1)
O23-Tb2-Tb3	98.6 (1)	O17-Tb4-O15	143.6 (1)	O13-Tb5-N12	85.5 (1)
O5-Tb2-Tb1	41.5 (1)	O16-Tb4-O15	76.8 (1)	O11-Tb5-N12	70.2 (1)
O12-Tb2-Tb1	43.1 (1)	O3-Tb4-O15	140.3 (1)	O9-Tb5-N12	94.4 (1)
O8-Tb2-Tb1	102.4 (1)	O9-Tb4-O15	108.9 (1)	O10-Tb5-N12	63.7 (1)
O7-Tb2-Tb1	95.7 (1)	O17-Tb4-O19	80.3 (1)	O3-Tb5-N12	138.9 (1)
O18-Tb2-Tb1	40.6 (1)	O16-Tb4-O19	101.0 (1)	O22-Tb5-N12	69.9 (1)
O6-Tb2-Tb1	115.3 (1)	O3-Tb4-O19	151.4 (1)	O14-Tb5-N15	66.4 (1)
N9-Tb2-Tb1	145.3 (1)	O9-Tb4-O19	122.4 (1)	O13-Tb5-N15	62.4 (1)

O23-Tb2-Tb1	123.0 (1)	O15-Tb4-O19	67.8 (1)	O11-Tb5-N15	122.0 (1)
Tb3-Tb2-Tb1	60.8 (1)	O17-Tb4-O20	78.5 (1)	O9-Tb5-N15	134.9 (1)
O18-Tb3-O17	80.7 (1)	O16-Tb4-O20	139.6 (1)	O10-Tb5-N15	115.4 (1)
O18-Tb3-O11	133.9 (1)	O3-Tb4-O20	134.3 (1)	O3-Tb5-N15	82.9 (1)
O17-Tb3-O11	144.8 (1)	O9-Tb4-O20	75.9 (1)	O22-Tb5-N15	64.4(1)
O18-Tb3-O3	147.9 (1)	O15-Tb4-O20	67.4 (1)	N12-Tb5-N15	130.2 (1)
O17-Tb3-O3	76.1 (1)	O19-Tb4-O20	48.8 (1)	O14-Tb5-Tb3	102.0 (1)
O11-Tb3-O3	73.7 (1)	O17-Tb4-O14	138.4 (1)	O13-Tb5-Tb3	98.3 (1)
O18-Tb3-O8	73.0 (1)	O16-Tb4-O14	69.0 (1)	O11-Tb5-Tb3	40.6 (1)
O17-Tb3-O8	116.9 (1)	O3-Tb4-O14	70.0 (1)	O9-Tb5-Tb3	42.1 (1)
O11-Tb3-O8	76.4 (1)	O9-Tb4-O14	71.7 (1)	O10-Tb5-Tb3	113.9 (1)
O3-Tb3-O8	137.8 (1)	O15-Tb4-O14	70.6 (1)	O3-Tb5-Tb3	41.2 (1)
O18-Tb3-O12	60.6 (1)	O19-Tb4-O14	138.4 (1)	O22-Tb5-Tb3	164.7 (1)
O17-Tb3-O12	134.6 (1)	O20-Tb4-O14	113.3 (1)	N12-Tb5-Tb3	98.5 (1)
O11-Tb3-O12	79.0 (1)	O17-Tb4-N18	73.9 (1)	N15-Tb5-Tb3	121.8 (1)
O3-Tb3-O12	125.7 (1)	O16-Tb4-N18	60.4 (1)	O14-Tb5-Tb4	43.6 (1)
O8-Tb3-O12	75.6 (1)	O3-Tb4-N18	93.7 (1)	O13-Tb5-Tb4	132.2 (1)
O18-Tb3-O9	129.8 (1)	O9-Tb4-N18	143.4 (1)	O11-Tb5-Tb4	99.0 (1)
O17-Tb3-O9	74.6 (1)	O15-Tb4-N18	107.2 (1)	O9-Tb5-Tb4	41.7 (1)
O11-Tb3-O9	76.1 (1)	O19-Tb4-N18	66.8 (2)	O10-Tb5-Tb4	89.4 (1)
O3-Tb3-O9	64.2 (1)	O20-Tb4-N18	112.9 (2)	O3-Tb5-Tb4	41.6 (1)
O8-Tb3-O9	80.3 (1)	O14-Tb4-N18	127.9 (1)	O22-Tb5-Tb4	136.8 (1)
O12-Tb3-O9	148.6 (1)	O17-Tb4-N19	79.3 (1)	N12-Tb5-Tb4	135.0 (1)
O18-Tb3-O2	72.3 (1)	O16-Tb4-N19	121.2 (1)	N15-Tb5-Tb4	93.3 (1)
O17-Tb3-O2	72.5 (1)	O3-Tb4-N19	150.7 (1)	Tb3-Tb5-Tb4	58.5 (1)
O11-Tb3-O2	118.7 (1)	O9-Tb4-N19	99.3 (1)		

Complex 5

Er1-O3	2.298 (4)	Er2-N10	2.451 (5)	Er4-O8	2.346 (4)
Er1-O2	2.299 (4)	Er2-O1	2.453 (5)	Er4-O10	2.370 (4)
Er1-O5	2.379 (4)	Er2-O13	2.459 (4)	Er4-O4	2.383 (4)
Er1-O19	2.391 (4)	Er2-Er3	3.487 (1)	Er4-O16	2.416 (4)
Er1-O7	2.407 (4)	Er3-O14	2.311 (4)	Er4-N7	2.486 (5)

Er1-O6	2.425 (4)	Er3-O8	2.317 (4)	Er4-Er5	3.509 (1)
Er1-N1	2.430 (6)	Er3-O10	2.319 (4)	Er5-O15	2.260 (4)
Er1-O13	2.486 (4)	Er3-O5	2.321 (4)	Er5-O18	2.267 (4)
Er1-N4	2.509 (5)	Er3-O11	2.340 (4)	Er5-O14	2.318 (4)
Er1-Er3	3.533 (1)	Er3-O7	2.341 (4)	Er5-O4	2.325 (4)
Er1-Er2	3.567 (1)	Er3-O4	2.364 (4)	Er5-O17	2.357 (4)
Er2-O11	2.337 (4)	Er3-O13	2.409 (4)	Er5-O10	2.370 (4)
Er2-O2	2.339 (4)	Er3-Er4	3.491 (1)	Er5-N16	2.452 (5)
Er2-O12	2.380 (5)	Er3-Er5	3.500 (1)	Er5-N13	2.488 (5)
Er2-O20	2.397 (5)	Er4-O17	2.304 (4)	Er2-O7	2.404 (4)
Er4-O9	2.343 (4)				
O3-Er1-O2	129.3 (2)	O11-Er2-Er3	41.8 (1)	O17-Er4-O9	75.8 (2)
O3-Er1-O5	68.2 (2)	O2-Er2-Er3	99.4 (1)	O17-Er4-O8	141.8 (2)
O2-Er1-O5	139.2 (2)	O12-Er2-Er3	131.6 (1)	O9-Er4-O8	124.5 (1)
O3-Er1-O19	73.1(2)	O20-Er2-Er3	106.6 (1)	O17-Er4-O10	73.3 (1)
O2-Er1-O19	95.5 (2)	O7-Er2-Er3	42.0 (1)	O9-Er4-O10	135.3 (1)
O5-Er1-O19	125.1 (1)	N10-Er2-Er3	100.0 (1)	O8-Er4-O10	70.4 (1)
O3-Er1-O7	139.6 (2)	O1-Er2-Er3	131.6 (0)	O17-Er4-O4	75.1 (1)
O2-Er1-O7	72.4 (2)	O13-Er2-Er3	43.7 (1)	O9-Er4-O4	80.1 (1)
O5-Er1-O7	74.9 (1)	O11-Er2-Er1	101.7 (1)	O8-Er4-O4	77.3 (1)
O19-Er1-O7	145.4 (2)	O2-Er2-Er1	39.3 (1)	O10-Er4-O4	61.2 (1)
O3-Er1-O6	138.0 (1)	O12-Er2-Er1	98.4 (1)	O17-Er4-O16	73.8 (2)
O2-Er1-O6	72.7 (1)	O20-Er2-Er1	138.3 (1)	O9-Er4-O16	86.2 (2)
O5-Er1-O6	121.8 (1)	O7-Er2-Er1	42.2 (1)	O8-Er4-O16	133.1 (2)
O19-Er1-O6	69.1 (1)	N10-Er2-Er1	137.5 (1)	O10-Er4-O16	114.6 (1)
O7-Er1-O6	76.3 (1)	O1-Er2-Er1	93.1 (1)	O4-Er4-O16	148.3 (2)
O3-Er1-N1	62.1 (2)	O13-Er2-Er1	44.1 (1)	O17-Er4-N7	139.3 (2)
O2-Er1-N1	68.0 (2)	Er3-Er2-Er1	60.1 (1)	O9-Er4-N7	64.2 (2)
O5-Er1-N1	121.3 (2)	O14-Er3-O8	142.8 (1)	O8-Er4-N7	72.9 (2)
O19-Er1-N1	66.6 (2)	O14-Er3-O10	75.5 (1)	O10-Er4-N7	142.5 (2)
O7-Er1-N1	131.4 (2)	O8-Er3-O10	71.8 (1)	O4-Er4-N7	103.5 (2)
O6-Er1-N1	115.8 (2)	O14-Er3-O5	117.3(1)	O16-Er4-N7	95.9 (2)

O3-Er1-O13	87.6 (1)	O8-Er3-O5	75.7 (1)	O17-Er4-Er3	101.7 (1)
O2-Er1-O13	74.2 (1)	O10-Er3-O5	133.6 (1)	O9-Er4-Er3	118.5 (1)
O5-Er1-O13	69.9 (1)	O14-Er3-O11	74.7 (1)	O8-Er4-Er3	41.2 (1)
O19-Er1-O13	145.0 (1)	O8-Er3-O11	116.3 (1)	O10-Er4-Er3	41.3 (1)
O7-Er1-O13	64.2 (1)	O10-Er3-O11	80.8 (1)	O4-Er4-Er3	42.5 (1)
O6-Er1-O13	134.3 (1)	O5-Er3-O11	144.4 (2)	O16-Er4-Er3	153.5 (1)
N1-Er1-O13	78.6 (2)	O14-Er3-O7	135.8 (1)	N7-Er4-Er3	103.3 (1)
O3-Er1-N4	86.5 (2)	O8-Er3-O7	79.6 (1)	O17-Er4-Er5	41.8 (1)
O2-Er1-N4	136.3 (2)	O10-Er3-O7	126.5 (1)	O9-Er4-Er5	93.8 (1)
O5-Er1-N4	71.2 (2)	O5-Er3-O7	77.3 (1)	O8-Er4-Er5	100.9 (1)
O19-Er1-N4	69.0 (2)	O11-Er3-O7	72.7 (1)	O10-Er4-Er5	42.2 (1)
O7-Er1-N4	97.1 (2)	O14-Er3-O4	71.0 (1)	O4-Er4-Er5	41.2 (1)
O6-Er1-N4	63.6 (2)	O8-Er3-O4	78.2 (1)	O16-Er4-Er5	112.4 (1)
N1-Er1-N4	131.1 (2)	O10-Er3-O4	62.2 (1)	N7-Er4-Er5	143.3 (1)
O13-Er1-N4	140.1 (2)	O5-Er3-O4	79.6 (1)	Er3-Er4-Er5	60.0 (1)
O3-Er1-Er3	98.4 (1)	O11-Er3-O4	134.3 (1)	O15-Er5-O18	126.4 (2)
O2-Er1-Er3	98.9 (1)	O7-Er3-O4	151.2 (1)	O15-Er5-O14	128.7 (1)
O5-Er1-Er3	40.6 (1)	O14-Er3-O13	78.4(1)	O18-Er5-O14	71.2 (2)
O19-Er1-Er3	165.5 (1)	O8-Er3-O13	137.2 (1)	O15-Er5-O4	142.5 (1)
O7-Er1-Er3	41.2 (1)	O10-Er3-O13	150.1 (1)	O18-Er5-O4	88.1 (1)
O6-Er1-Er3	114.1 (1)	O5-Er3-O13	72.3 (2)	O14-Er5-O4	71.5 (1)
N1-Er1-Er3	120.4 (1)	O11-Er3-O13	78.3 (2)	O15-Er5-O17	71.9 (2)
O13-Er1-Er3	42.9 (1)	O7-Er3-O13	66.4 (1)	O18-Er5-O17	127.6 (2)
N4-Er1-Er3	99.3(1)	O4-Er3-O13	121.7 (1)	O14-Er5-O17	141.0 (1)
O3-Er1-Er2	128.9 (1)	O14-Er3-Er2	92.6 (1)	O4-Er5-O17	75.2 (2)
O2-Er1-Er2	40.1 (1)	O8-Er3-Er2	119.7 (1)	O15-Er5-O10	90.9 (1)
O5-Er1-Er2	99.2 (1)	O10-Er3-Er2	122.0 (1)	O18-Er5-O10	140.2 (1)
O19-Er1-Er2	135.7 (1)	O5-Er3-Er2	102.7 (1)	O14-Er5-O10	74.5 (1)
O7-Er1-Er2	42.1 (1)	O11-Er3-Er2	41.8 (1)	O4-Er5-O10	62.0 (1)
O6-Er1-Er2	91.6 (1)	O7-Er3-Er2	43.4 (1)	O17-Er5-O10	72.4 (1)
N1-Er1-Er2	89.4 (1)	O4-Er3-Er2	162.0 (1)	O15-Er5-N16	83.5 (2)
O13-Er1-Er2	43.5 (1)	O13-Er3-Er2	44.8 (1)	O18-Er5-N16	65.1 (2)

N4-Er1-Er2	138.1 (1)	O14-Er3-Er4	101.1 (1)	O14-Er5-N16	136.0 (2)
Er3-Er1-Er2	58.8 (1)	O8-Er3-Er4	41.9 (1)	O4-Er5-N16	101.9 (2)
O11-Er2-O2	140.5 (1)	O10-Er3-Er4	42.5 (1)	O17-Er5-N16	70.4 (2)
O11-Er2-O12	134.3 (1)	O5-Er3-Er4	91.7 (1)	O10-Er5-N16	142.2 (2)
O2-Er2-O12	72.4 (2)	O11-Er3-Er4	120.1 (1)	O15-Er5-N13	63.4 (2)
O11-Er2-O20	72.2 (2)	O7-Er3-Er4	120.9 (1)	O18-Er5-N13	80.4 (2)
O2-Er2-O20	128.7 (2)	O4-Er3-Er4	42.9 (1)	O14-Er5-N13	76.0 (2)
O12-Er2-O20	115.5 (2)	O13-Er3-Er4	161.0 (1)	O4-Er5-N13	147.5 (2)
O11-Er2-O7	71.6 (1)	Er2-Er3-Er4	153.0 (1)	O17-Er5-N13	135.1 (2)
O2-Er2-O7	71.8 (1)	O14-Er3-Er5	41.0 (1)	O10-Er5-N13	110.1 (2)
O12-Er2-O7	140.5 (2)	O8-Er3-Er5	101.8 (1)	N16-Er5-N13	100.6 (2)
O20-Er2-O7	99.9 (1)	O10-Er3-Er5	42.3 (1)	O15-Er5-Er3	128.8 (1)
O11-Er2-N10	71.7 (2)	O5-Er3-Er5	118.0 (1)	O18-Er5-Er3	99.0 (1)
O2-Er2-N10	136.7 (2)	O11-Er3-Er5	93.3 (1)	O14-Er5-Er3	40.8 (1)
O12-Er2-N10	65.8 (2)	O7-Er3-Er5	164.6 (1)	O4-Er5-Er3	42.1 (1)
O20-Er2-N10	81.1 (2)	O4-Er3-Er5	41.3 (1)	O17-Er5-Er3	100.3 (1)
O7-Er2-N10	141.1 (2)	O13-Er3-Er5	118.0 (1)	O10-Er5-Er3	41.2 (1)
O11-Er2-O1	130.4 (1)	Er2-Er3-Er5	127.8 (1)	N16-Er5-Er3	143.0 (1)
O2-Er2-O1	63.9 (2)	Er4-Er3-Er5	60.3 (1)	N13-Er5-Er3	109.7 (1)
O12-Er2-O1	88.6 (1)	O14-Er3-Er1	120.8 (1)	O15-Er5-Er4	100.1 (1)
O20-Er2-O1	65.7 (2)	O8-Er3-Er1	92.7 (1)	O18-Er5-Er4	127.2 (1)
O7-Er2-O1	90.5 (1)	O10-Er3-Er1	163.7 (1)	O14-Er5-Er4	100.4 (1)
N10-Er2-O1	123.8 (2)	O5-Er3-Er1	41.9 (1)	O4-Er5-Er4	42.5 (1)
O11-Er2-O13	77.4(1)	O11-Er3-Er1	102.6 (1)	O17-Er5-Er4	40.6 (1)
O2-Er2-O13	74.0 (1)	O7-Er3-Er1	42.7 (1)	O10-Er5-Er4	42.2 (1)
O12-Er2-O13	89.7 (1)	O4-Er3-Er1	120.6 (1)	N16-Er5-Er4	102.0 (1)
O20-Er2-O13	149.1 (1)	O13-Er3-Er1	44.7 (1)	N13-Er5-Er4	150. (1)
O7-Er2-O13	64.7 (1)	Er2-Er3-Er1	61.1 (1)	Er3-Er5-Er4	59.7 (1)
N10-Er2-O13	94.7 (2)	Er4-Er3-Er1	126.8 (1)	O1-Er2-O13	136.3 (1)
Er5-Er3-Er1	151.1 (1)				

Table S3. The average Ln-$O_{hydrazone}$, Ln-O_{alkoxy}, Ln–$O_{phenoxy}$, Ln–N_{imine} bond lengths (Å) and the distances of Ln-Ln (Å)in dinuclear units or pentanuclear units for complexes **1-5.**

Complex	Ln-$O_{hydrazone}$	Ln-O_{alkoxy}	Ln–$O_{phenoxy}$	Ln–N_{imine}	Ln-Ln
1	2.522 (6)	2.612 (5)	2.503 (5)	2.760 (7)	3.800 (1)
2	2.445 (3)	2.538 (3)	2.444 (3)	2.736 (3)	3.703 (1)
3	2.411 (7)	2.458 (7)	2.370 (7)	2.669 (9)	3.577 (1)
4	2.380 (3)	2.411(3)	2.374 (3)	2.544 (4)	3.577 (1)
5	2.329 (5)	2.393 (5)	2.331 (4)	2.469 (6)	3.515 (1)

Table S4. Representative homogeneous lanthanide polynuclear catalysts with high TOF used for the synthesis of cyclic carbonates.

Substance	Cat. (mol %)	Co-cat. (mol %)	Epoxide (Mole ratio)	T (°C)	P (MPa)	Time (h)	Yield (%)	TOF[b] (h^{-1})	TOF[c] h^{-1} Ln^{-1}
styrene oxide	Yb complex[1] 0.1	TBAB 0.75	1:1000	120	1	2.5	95	380	190
3,3-dimethyl-1,2-butylene oxide	Ce complex[2] 0.25	TBAB 1	1:400	90	0.1	24	96	16	4
styrene oxide	La complex[3] 0.2	TBAB 0.4	1:500	100	0.1	18	93	26	13
styrene oxide	Sm complex[4] 0.01	TBAB 0.75	1:10000	120	1	1.5	97	6565	1641
styrene oxide	La complex 0.025 **This work**	TBAB 0.75	1:1000	120	0.8	2	97	1940	970
styrene oxide	Tb complex 0.01 **This work**	TBAB 0.75	1:1000	120	0.8	2	96	4800	960

Turnover frequency (TOF) [b] = (mol $_{(product\ formed)}$ per mol_{cat} per h per molecule; Turnover frequency (TOF) [c] = (mol $_{(product\ formed)}$ per mol_{cat} per h per metal)

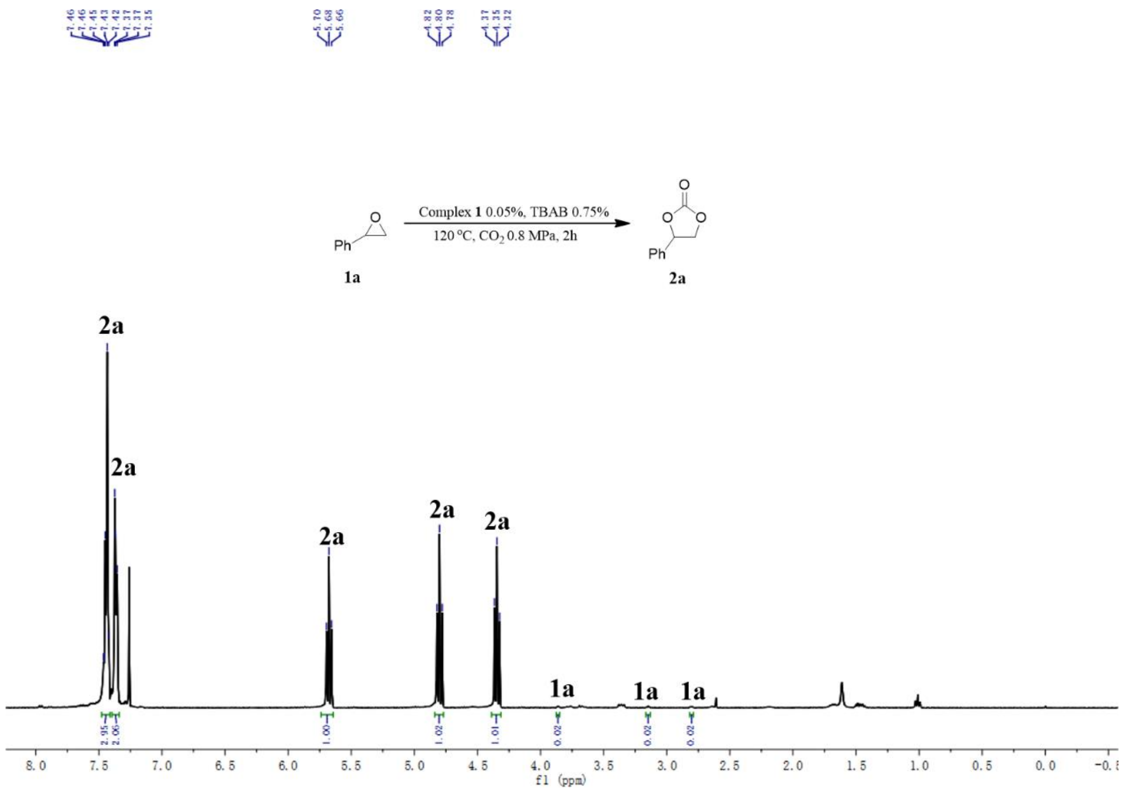

Figure S15. ^{1}H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and styrene oxide catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

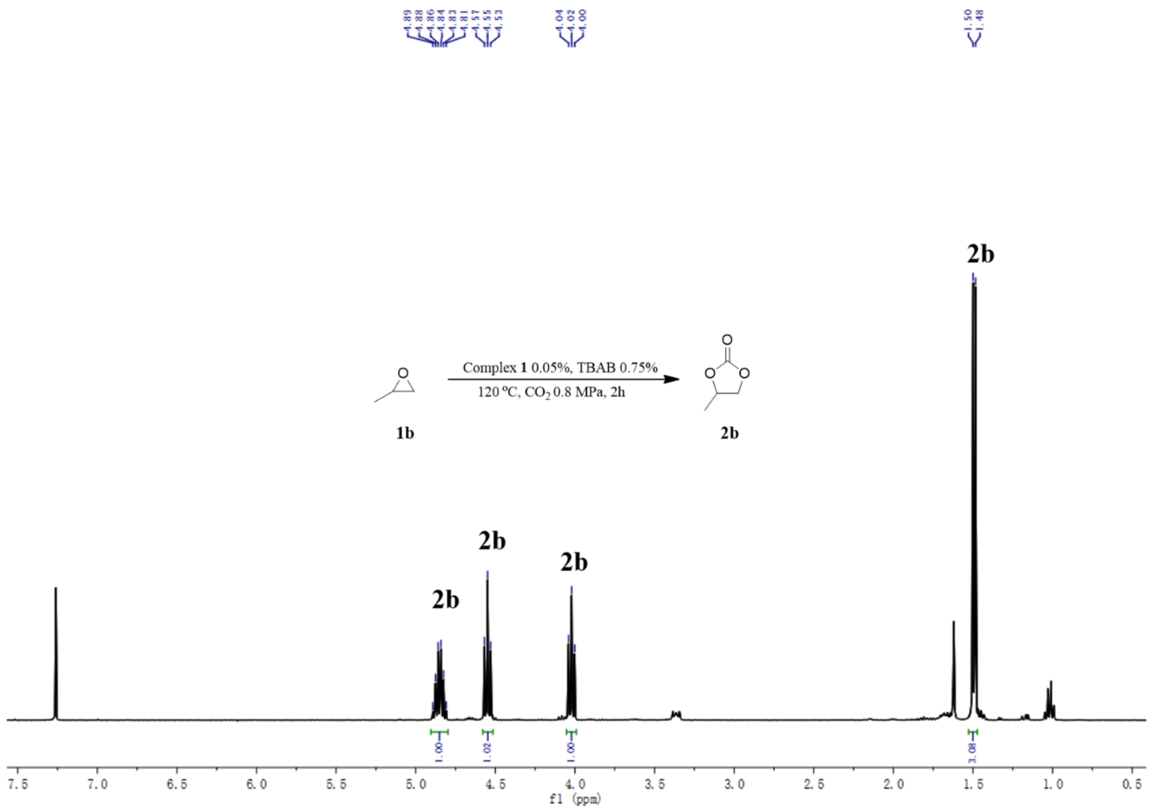

Figure S16. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and propylene oxide catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

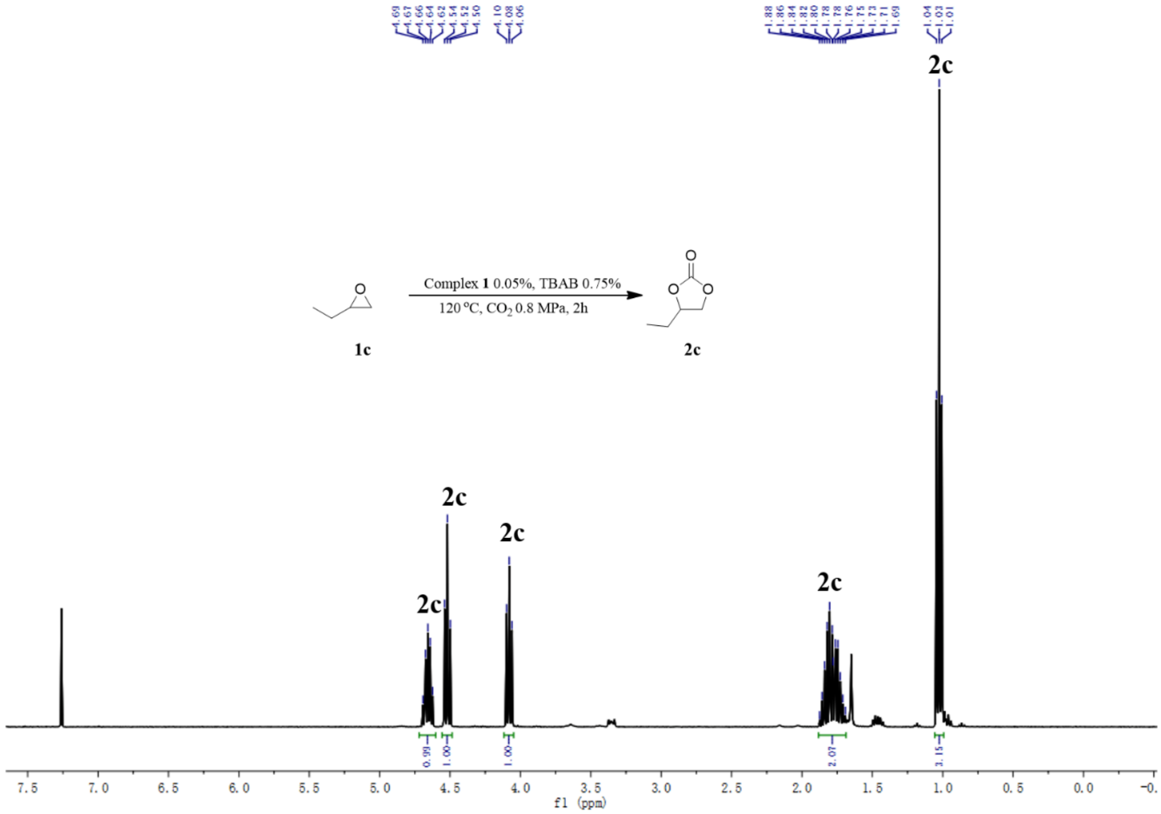

Figure S17. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and 1,2-epoxybutane catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

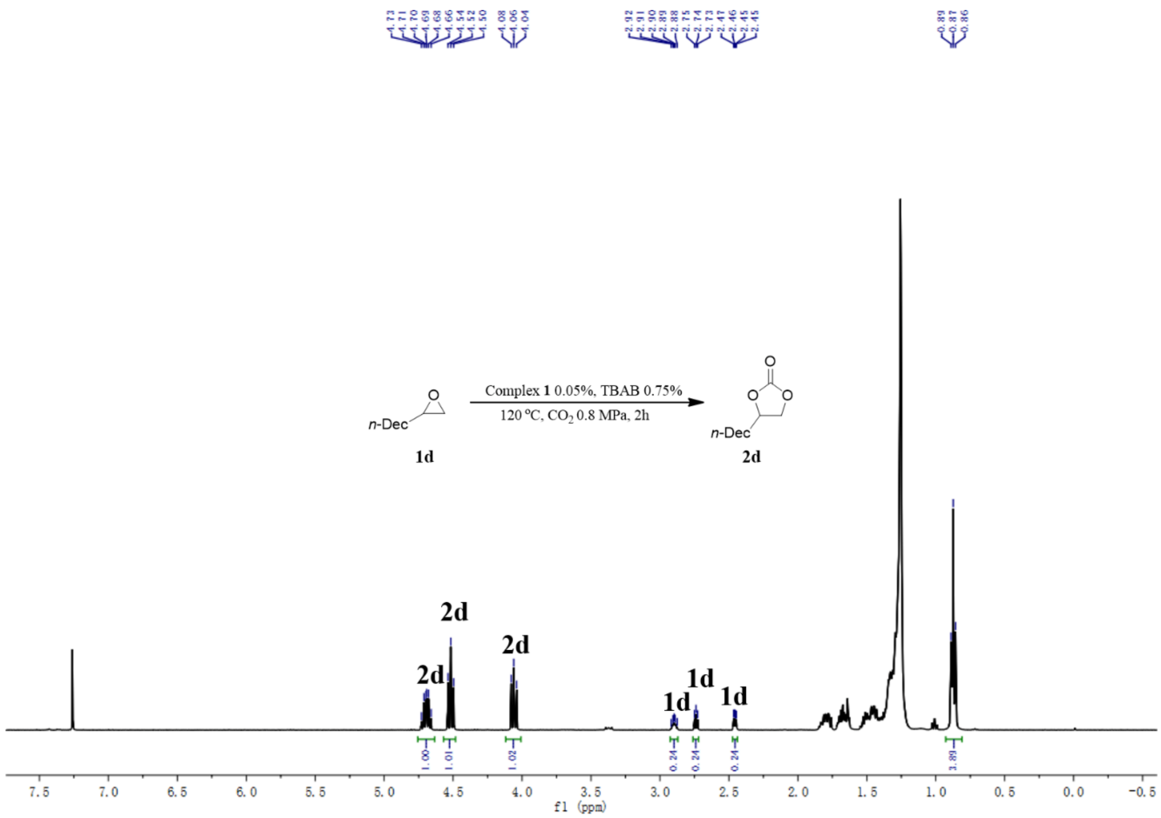

Figure S18. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and 1,2-epoxydodecane catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

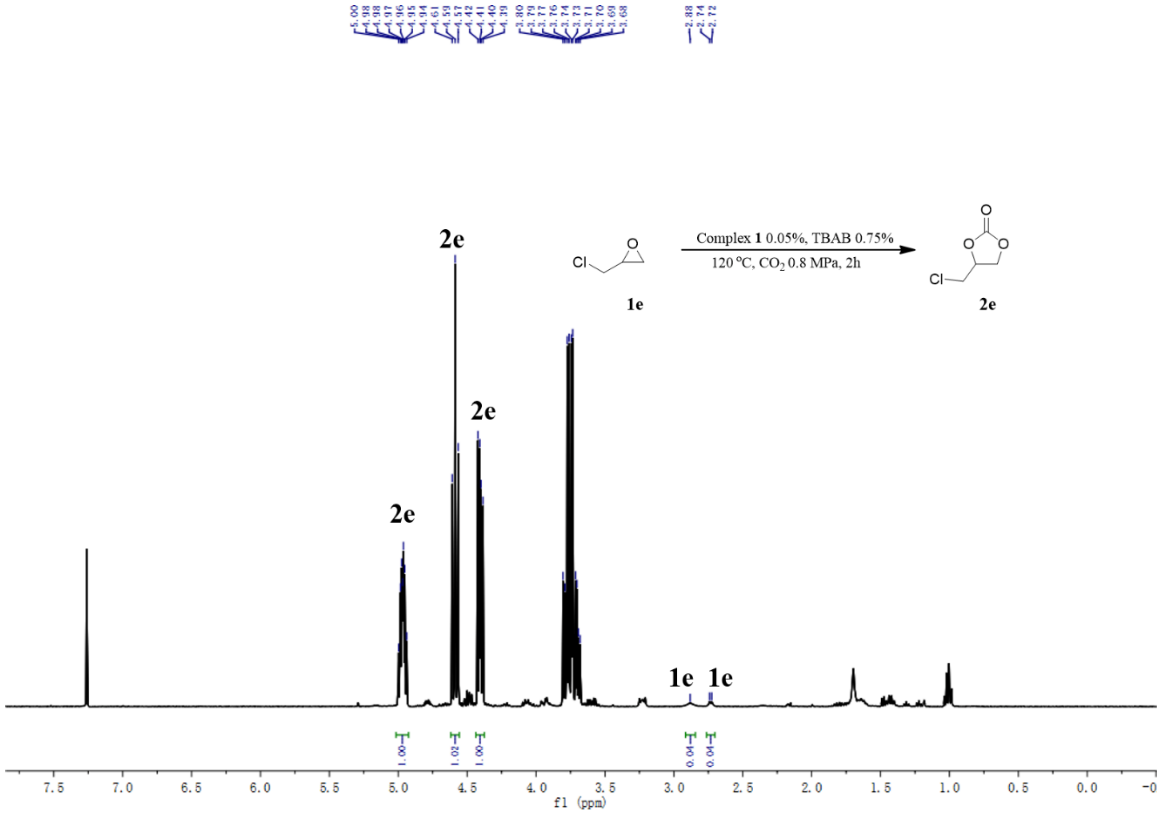

Figure S19. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and epichlorohydrin catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

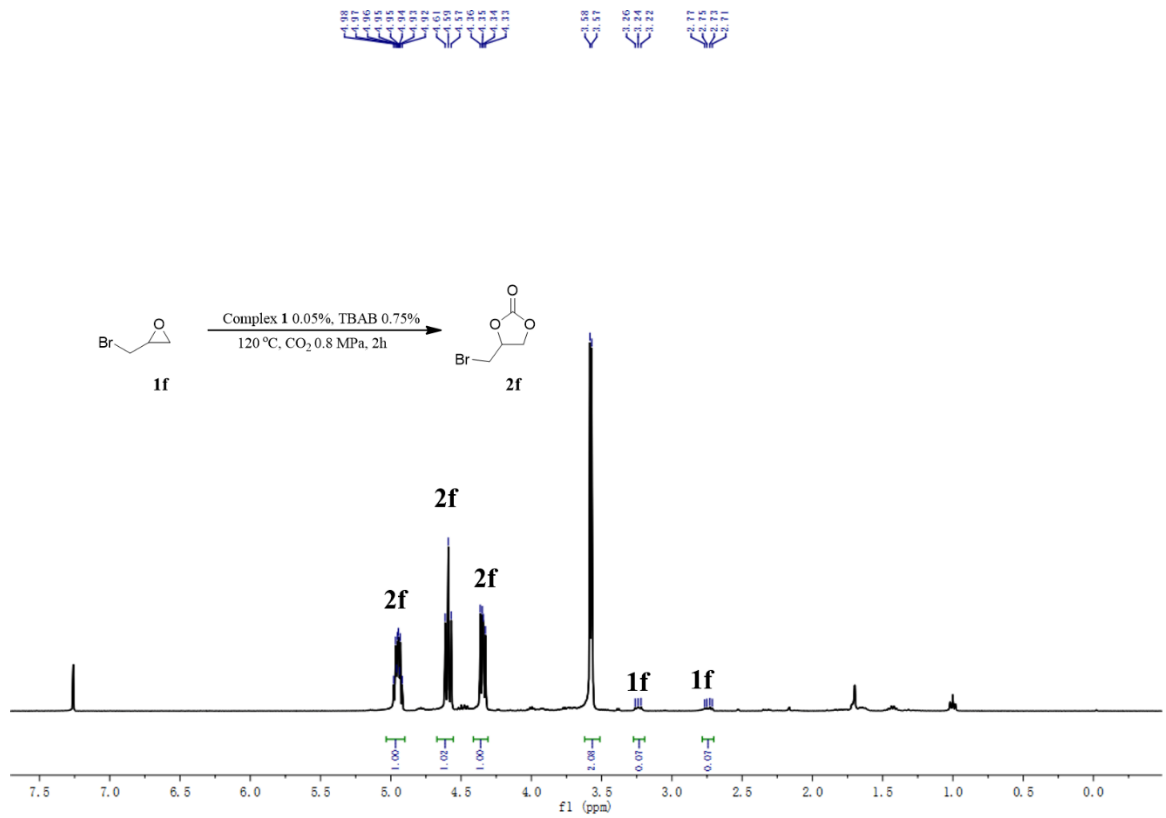

Figure S20. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and epibromohydrin catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

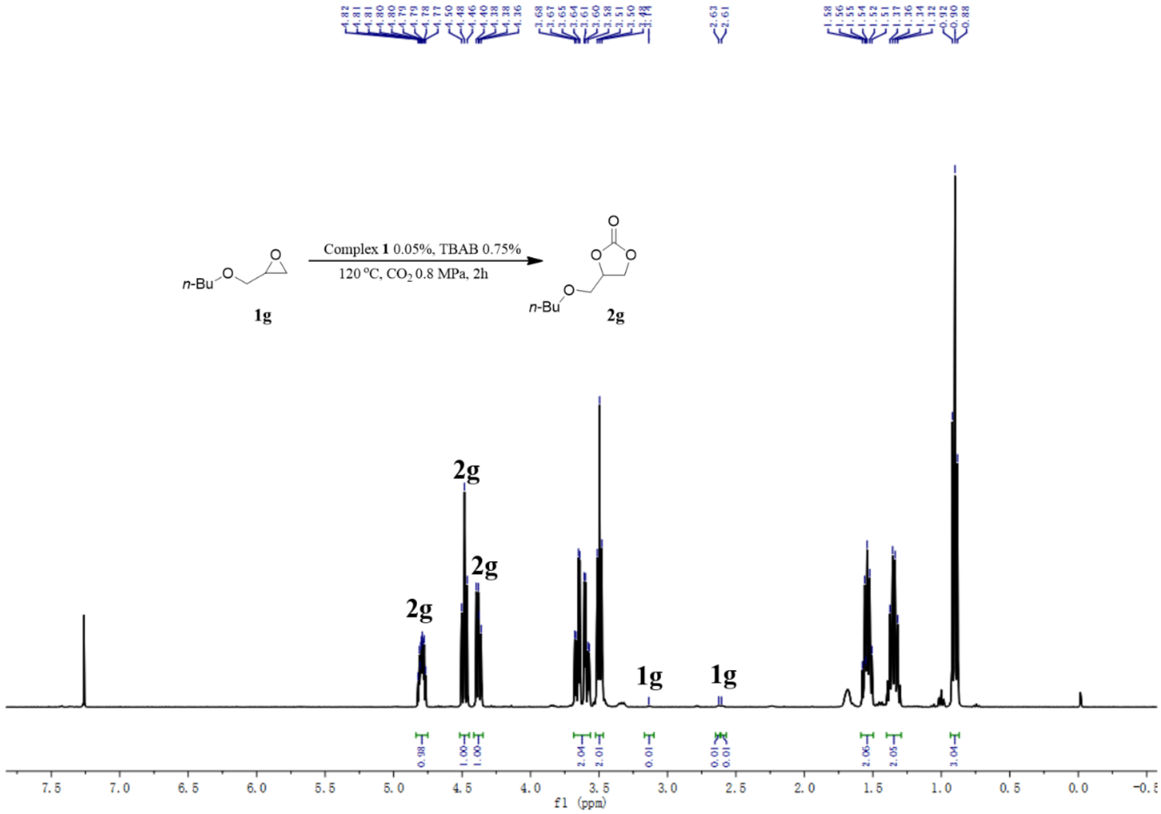

Figure S21. ^{1}H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and *n*-butyl glycidyl ether catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

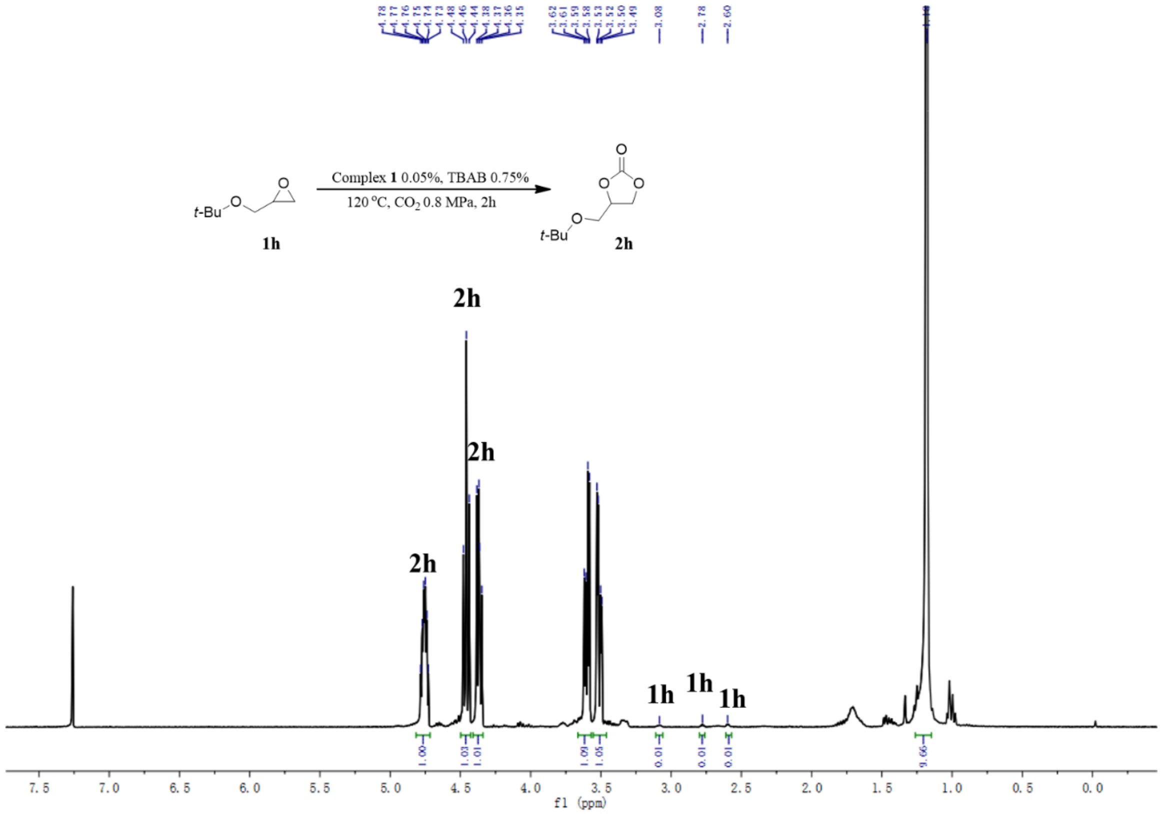

Figure S22. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and *tert*-butyl glycidyl ether catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

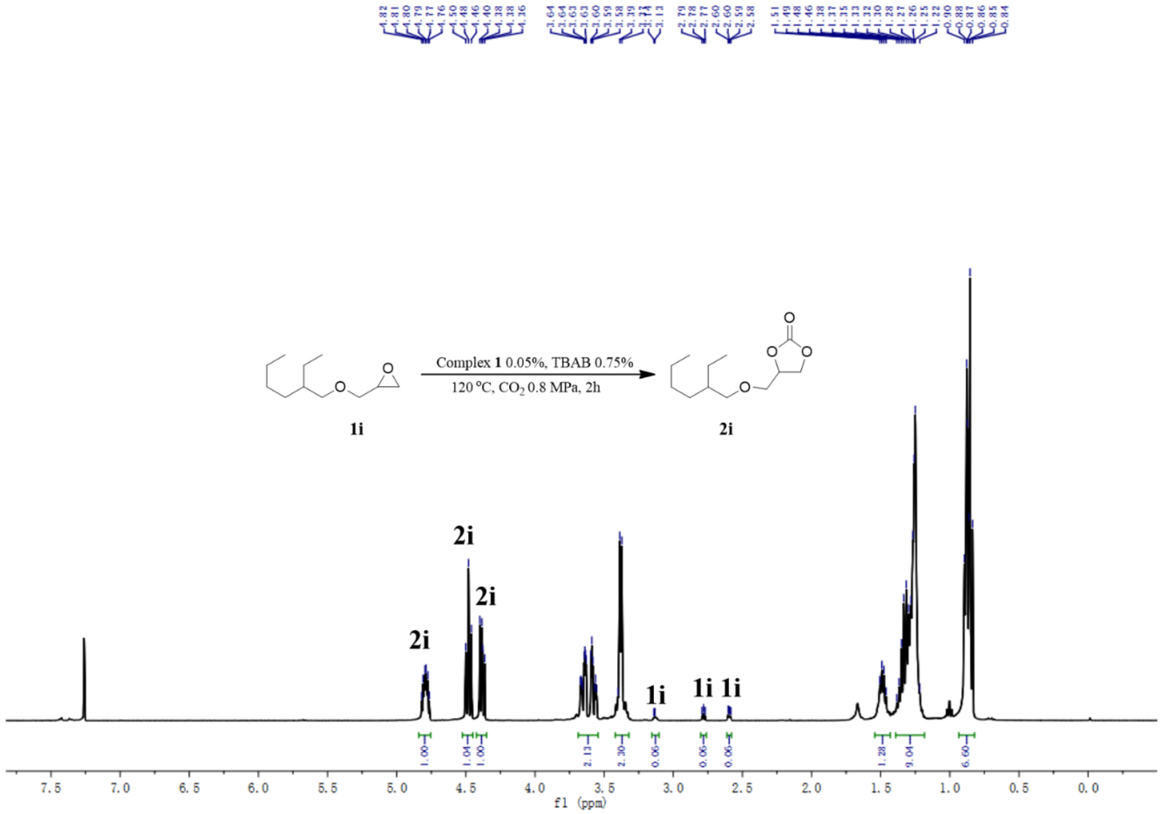

Figure S23. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and 2-ethylhexyl glycidyl ether catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

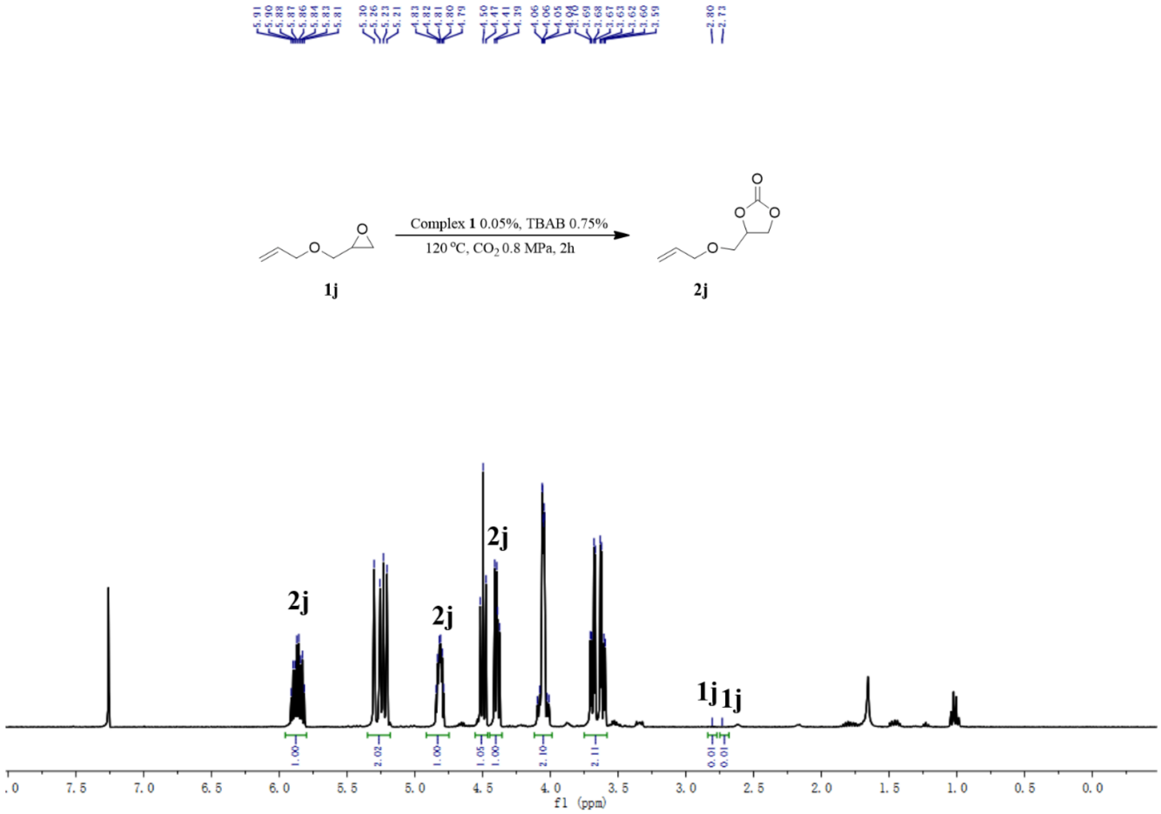

Figure S24. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and allyl glycidyl ether catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

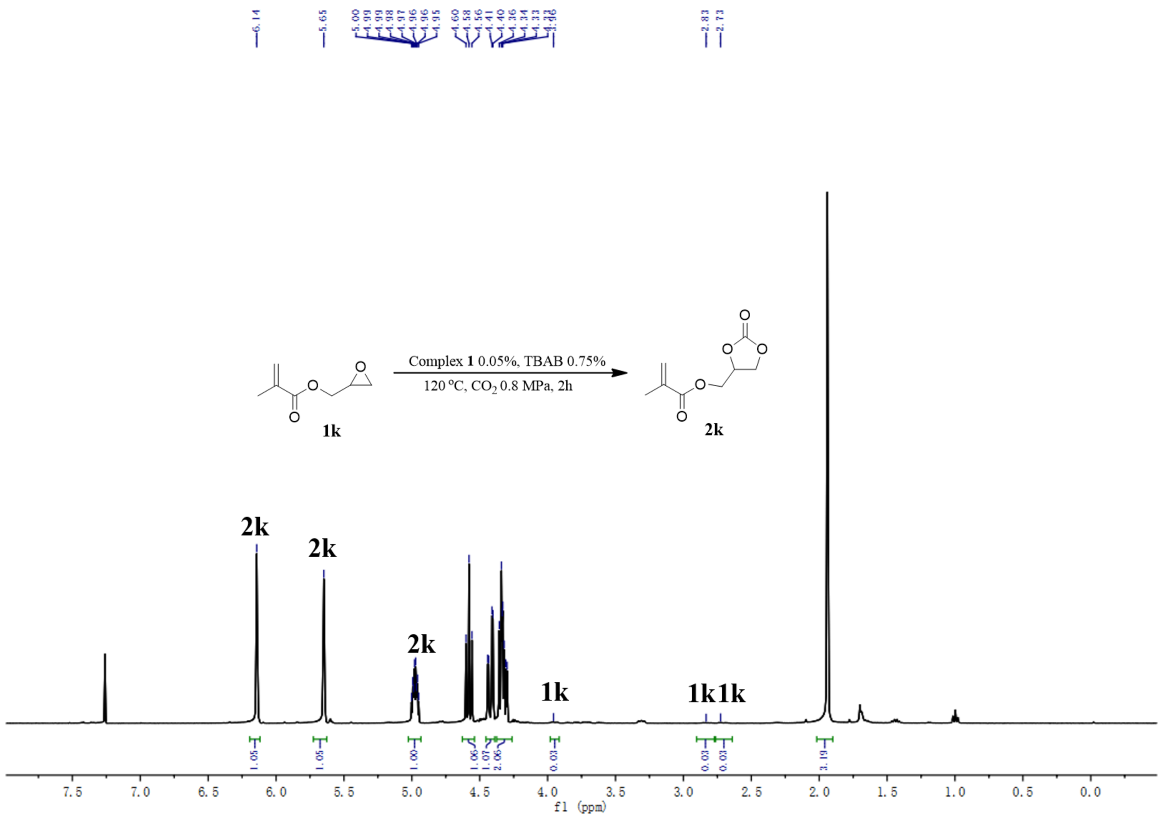

Figure S25. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and glycidyl methacrylate catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

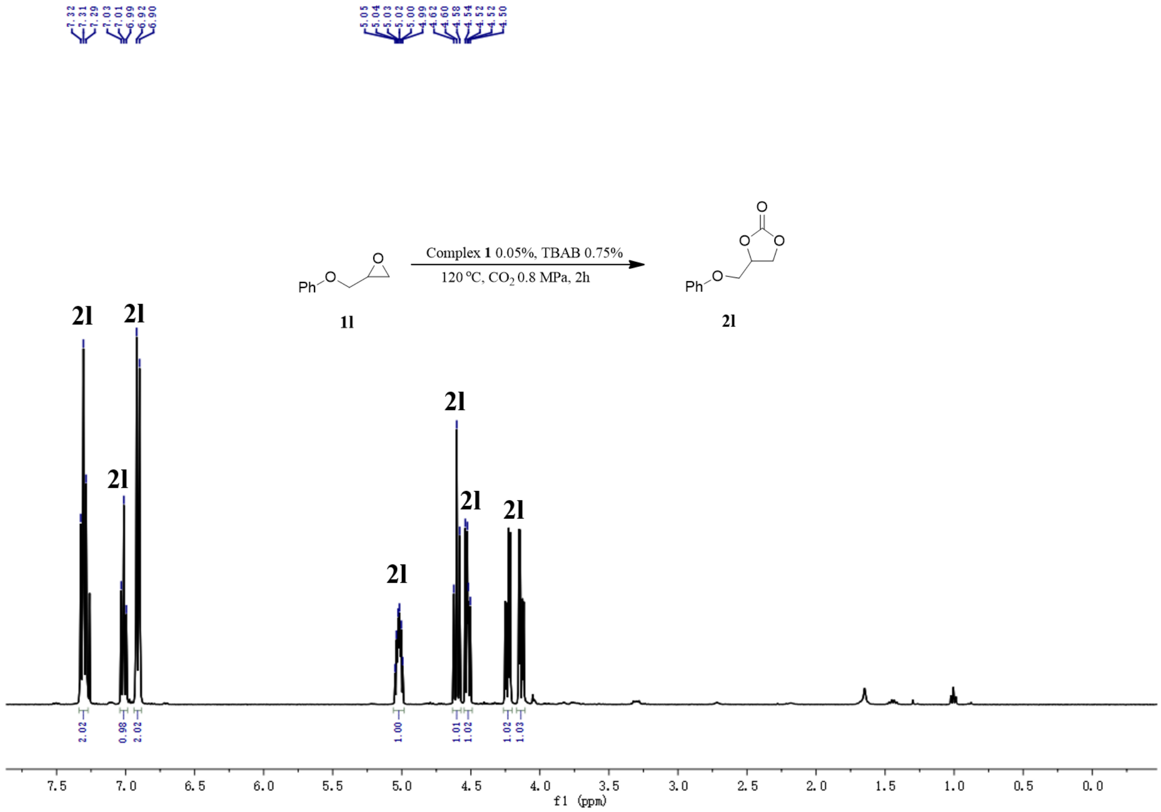

Figure S26. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and glycidyl phenyl ether catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

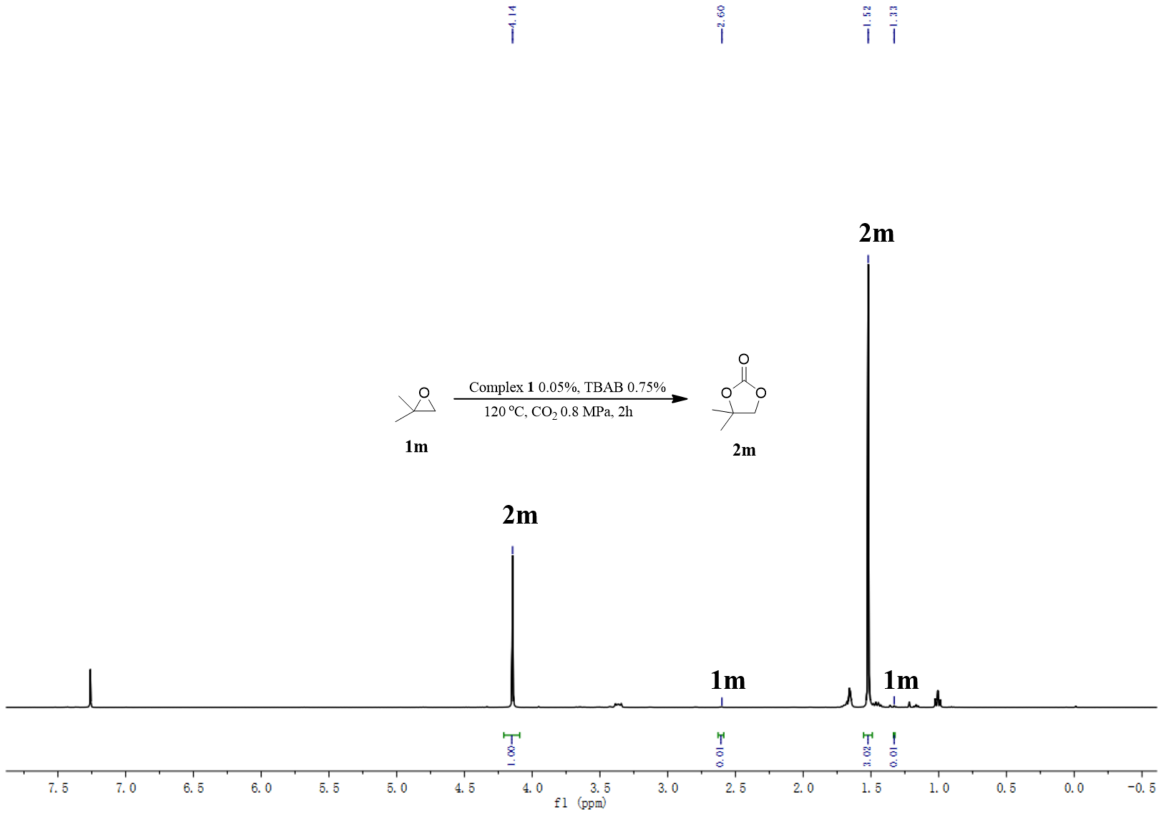

Figure S27. ^{1}H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and isobutylene oxide catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

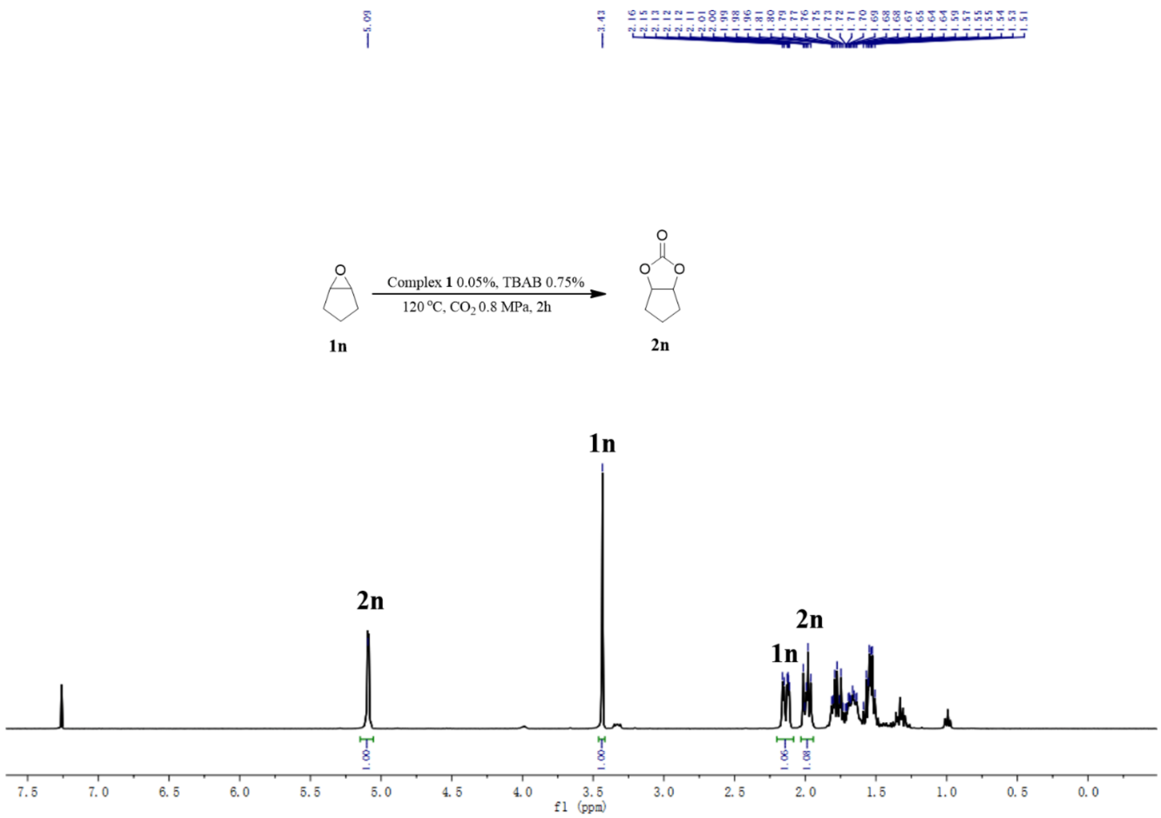

Figure S28. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and cyclopentene oxide catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

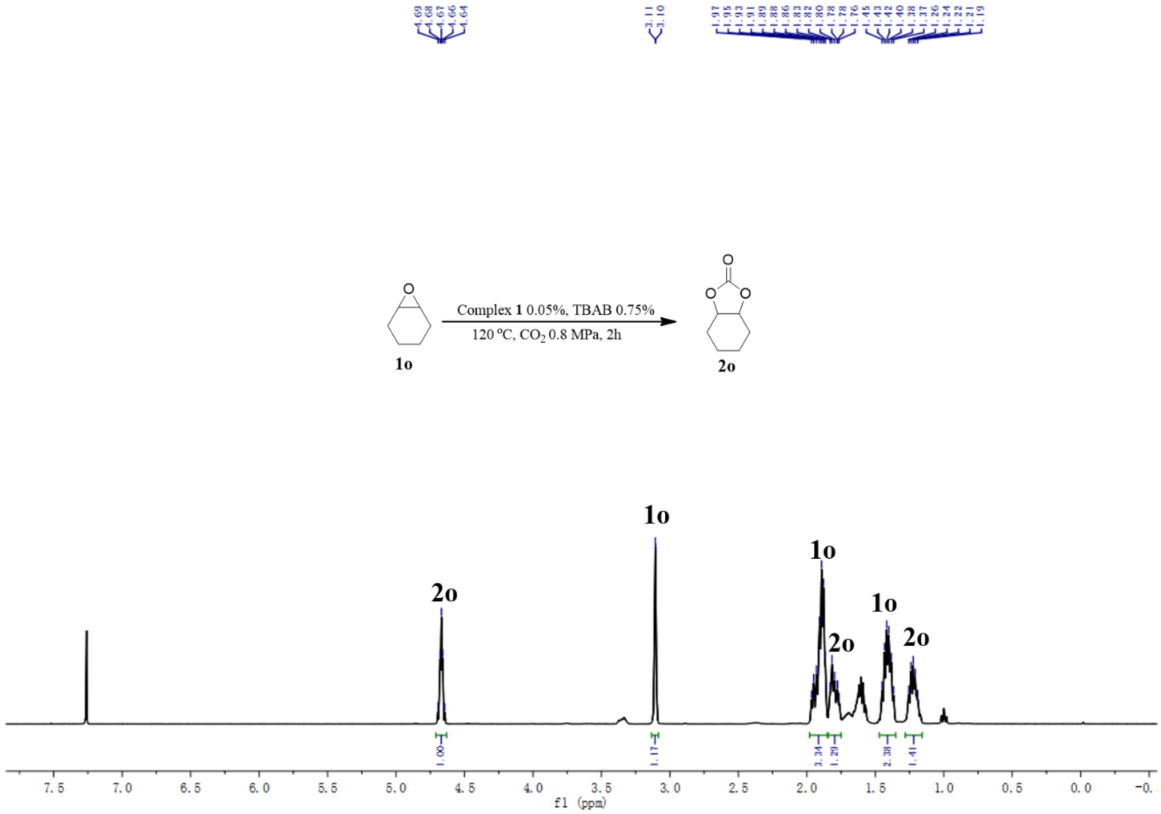

Figure S29. [1]H NMR ($CDCl_3$) spectrum for the cycloaddition reaction of CO_2 and cyclohexene oxide catalyzed by complex **1** using 10 mmol of the substrate, 0.05 mol% of catalyst (per metal), 0.75 mol % of TBAB and 8 bar CO_2 at 120 °C for 2 h under solvent-free condition.

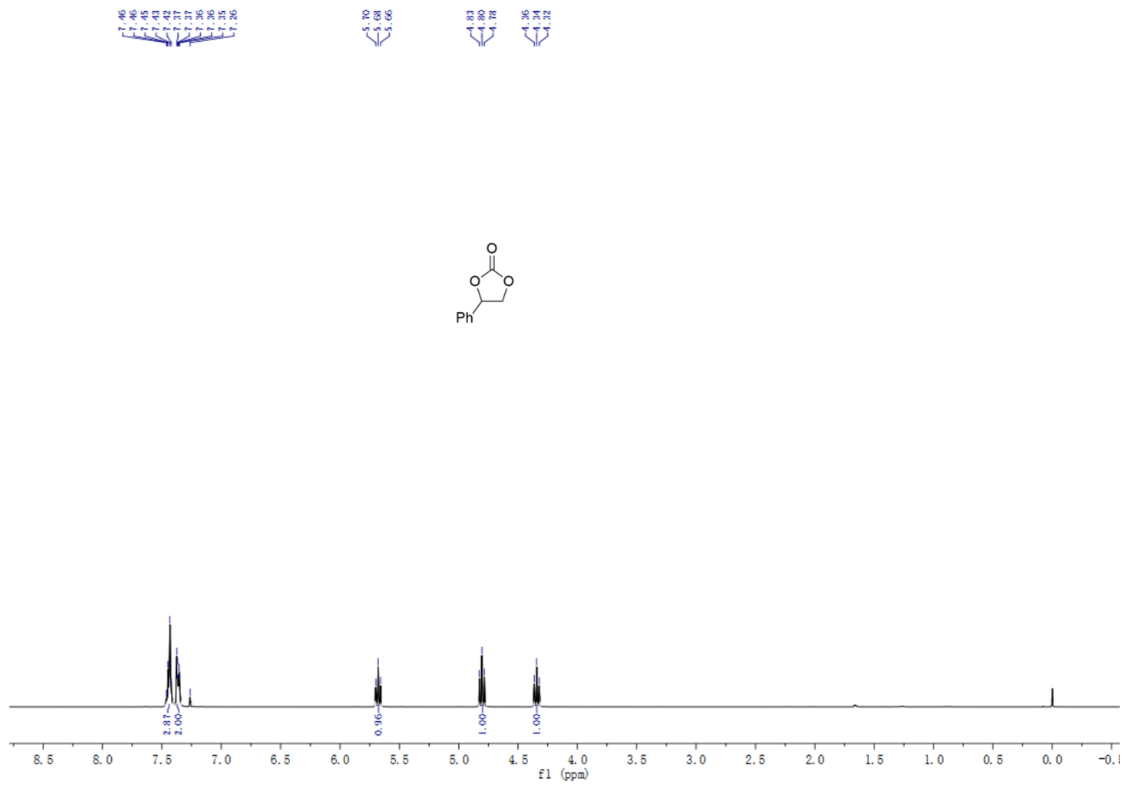

Figure S30. [1]H NMR ($CDCl_3$) spectrum for (2a).

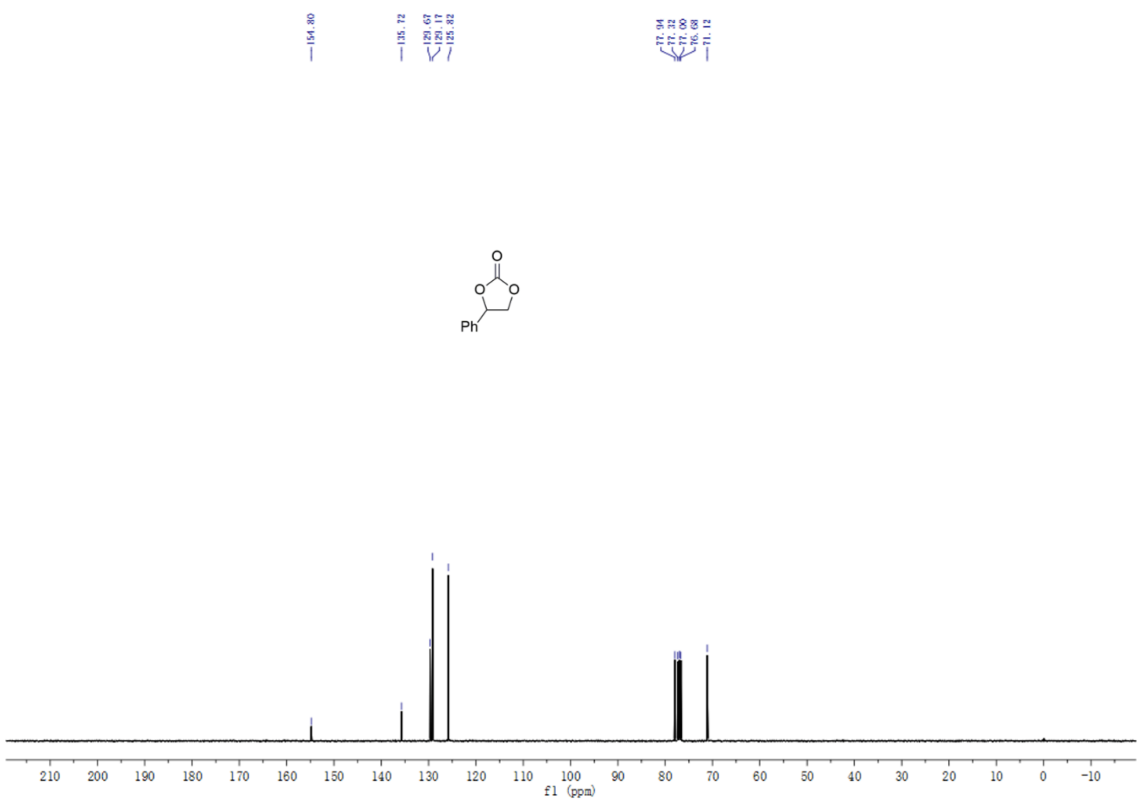

Figure S31. [13]C NMR ($CDCl_3$) spectrum for (2a).

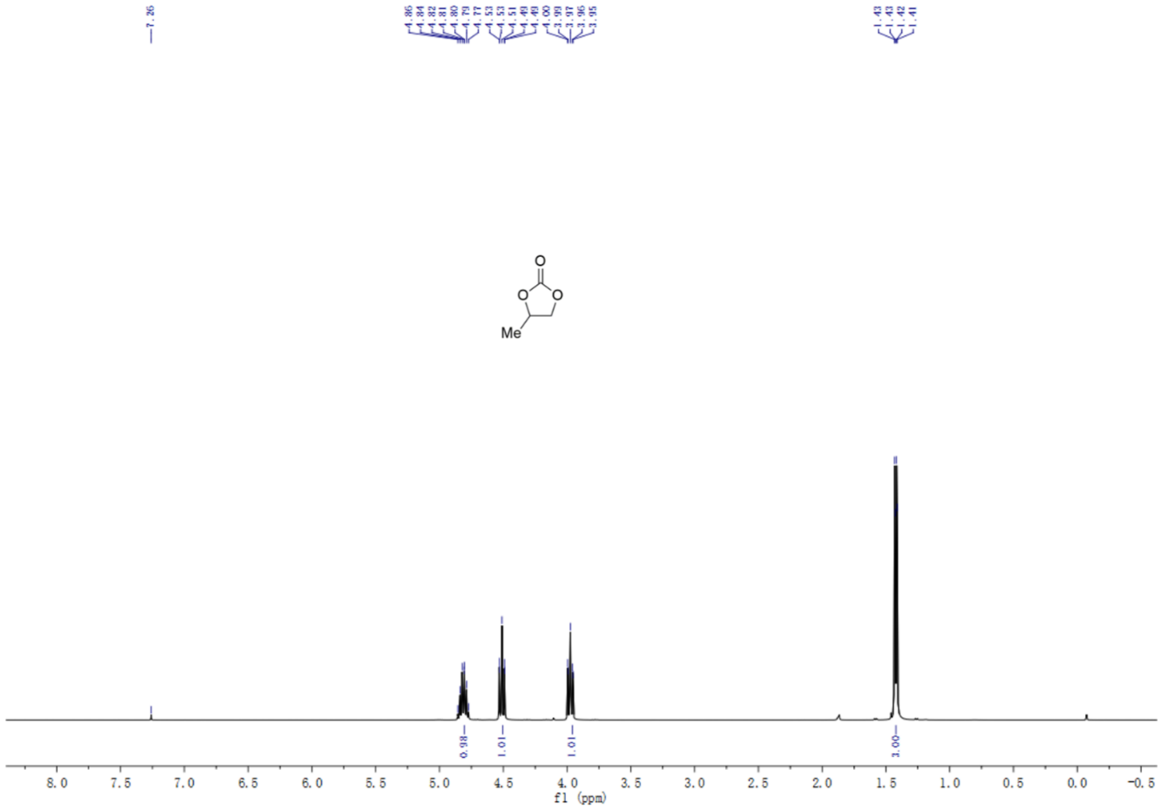

Figure S32. ^{1}H NMR ($CDCl_3$) spectrum for (2b).

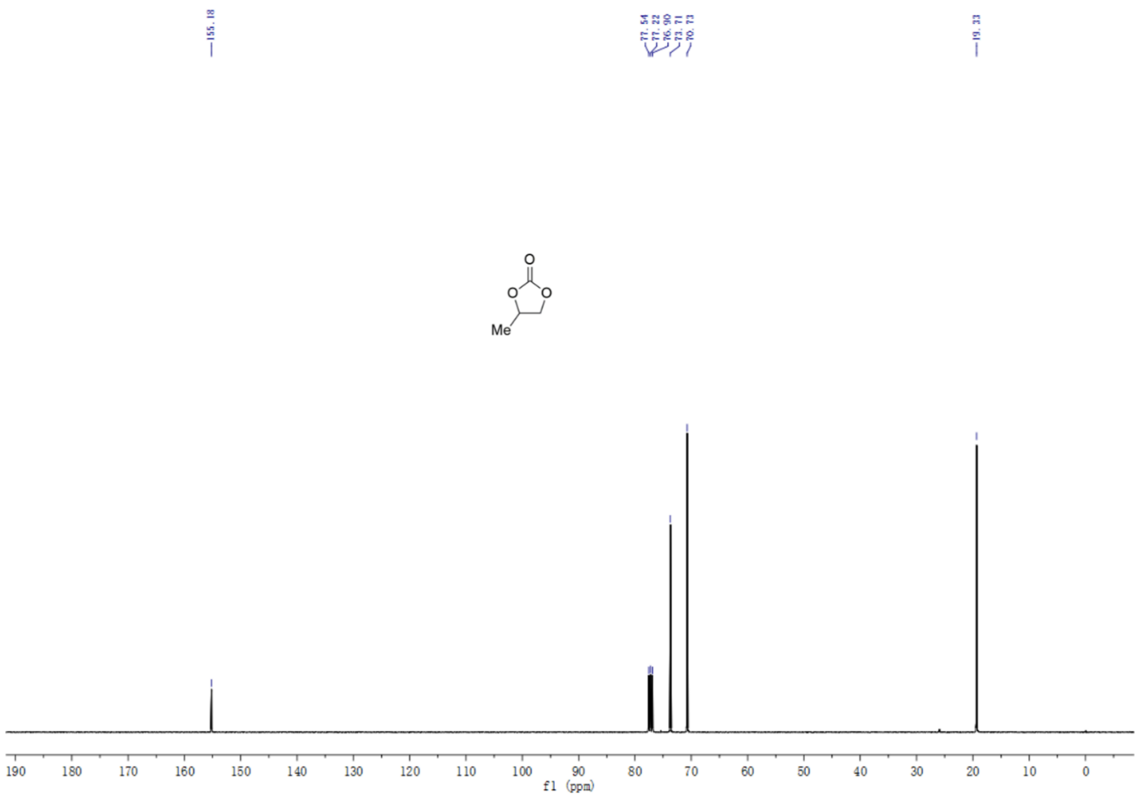

Figure S33. ^{13}C NMR ($CDCl_3$) spectrum for (2b).

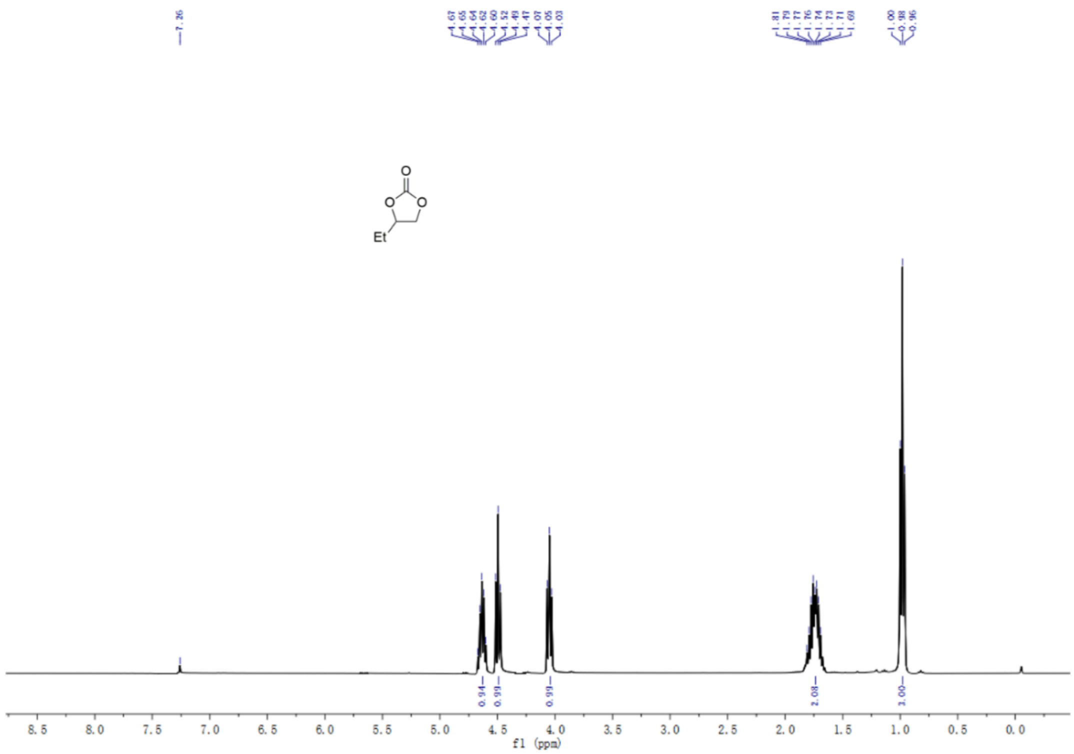

Figure S34. ^{1}H NMR ($CDCl_3$) spectrum for (2c).

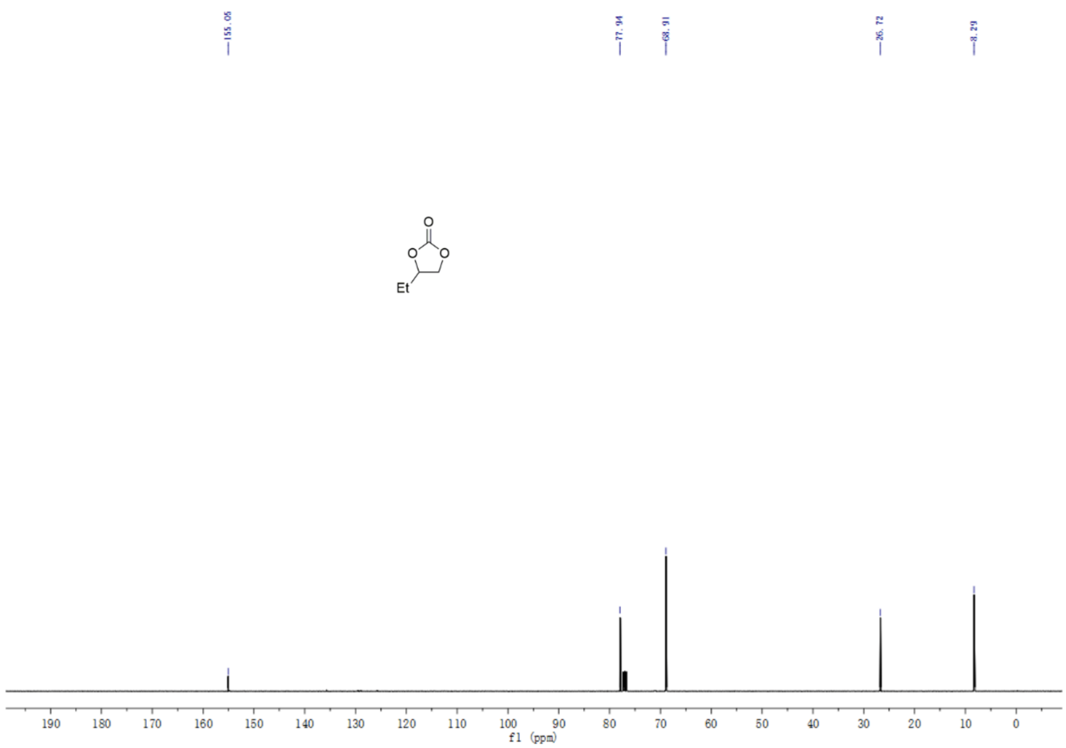

Figure S35. ^{13}C NMR ($CDCl_3$) spectrum for (2c).

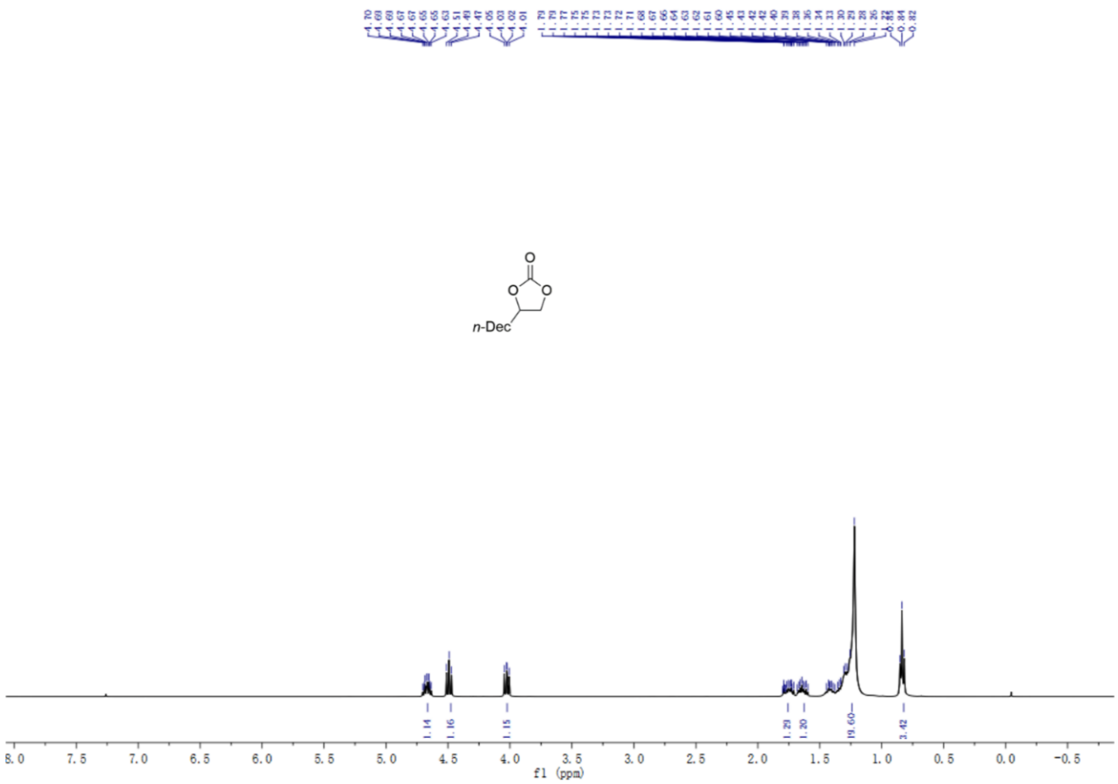

Figure S36. ^{1}H NMR ($CDCl_3$) spectrum for (2d).

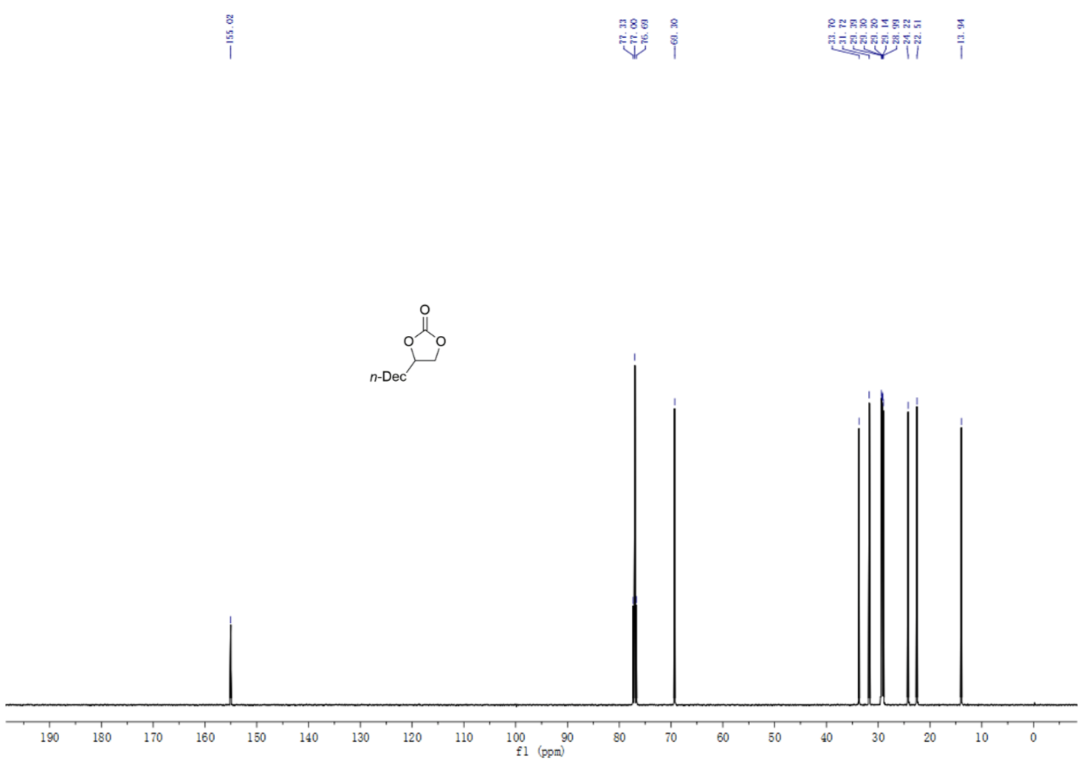

Figure S37. ^{13}C NMR ($CDCl_3$) spectrum for (2d).

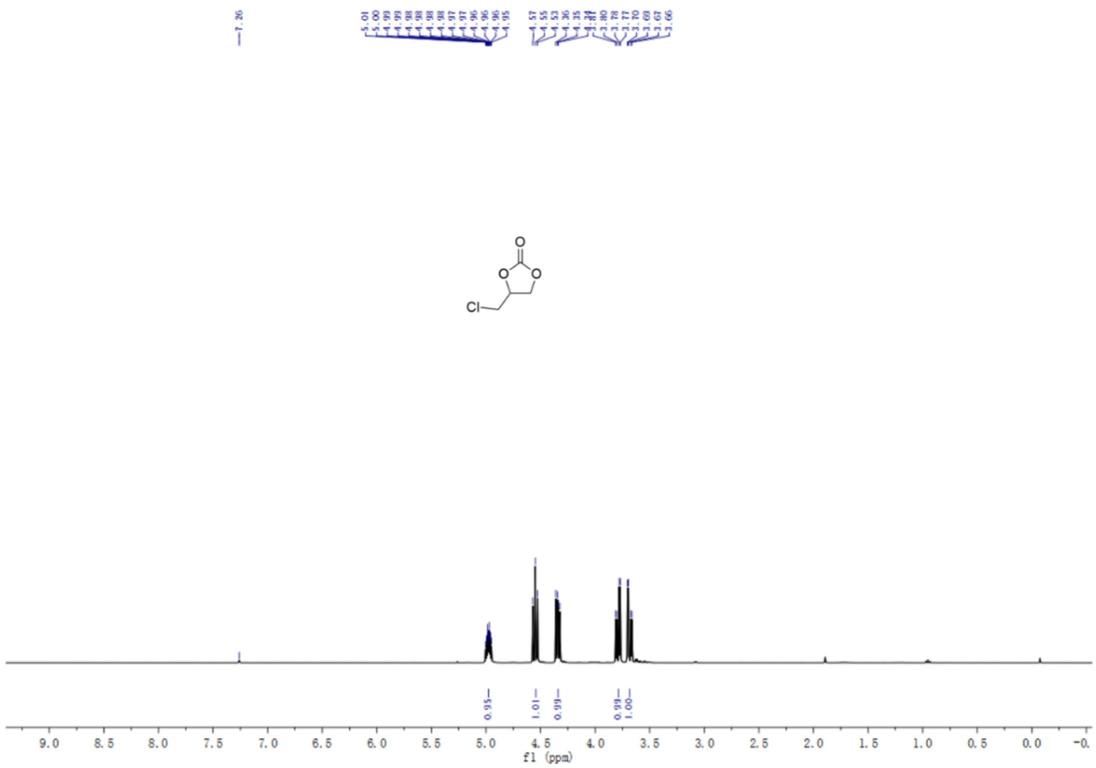

Figure S38. ^{1}H NMR ($CDCl_3$) spectrum for (2e).

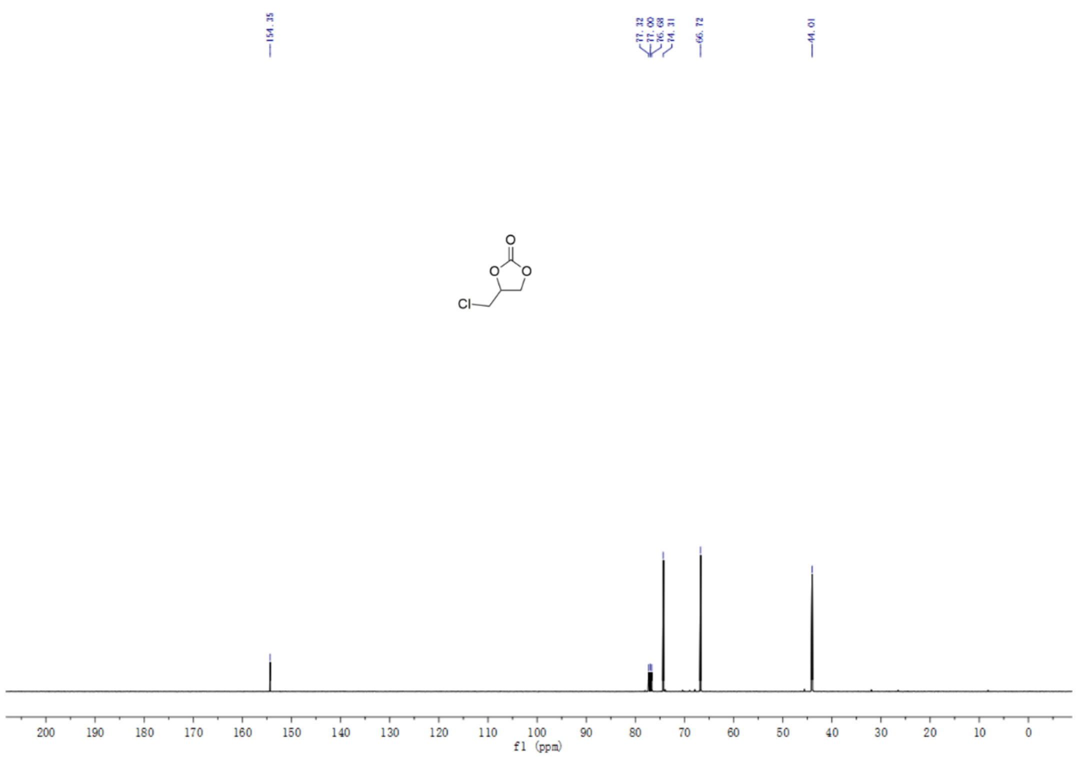

Figure S39. ^{13}C NMR ($CDCl_3$) spectrum for (2e).

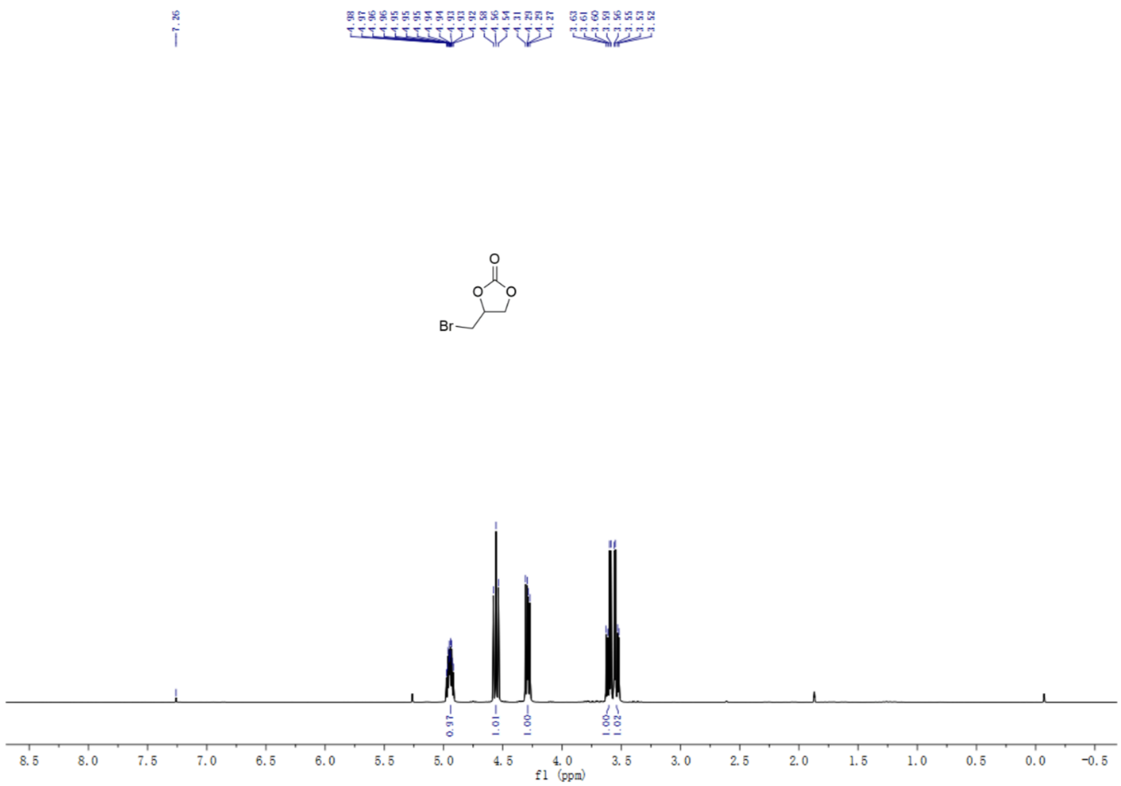

Figure S40. ^{1}H NMR ($CDCl_3$) spectrum for (2f).

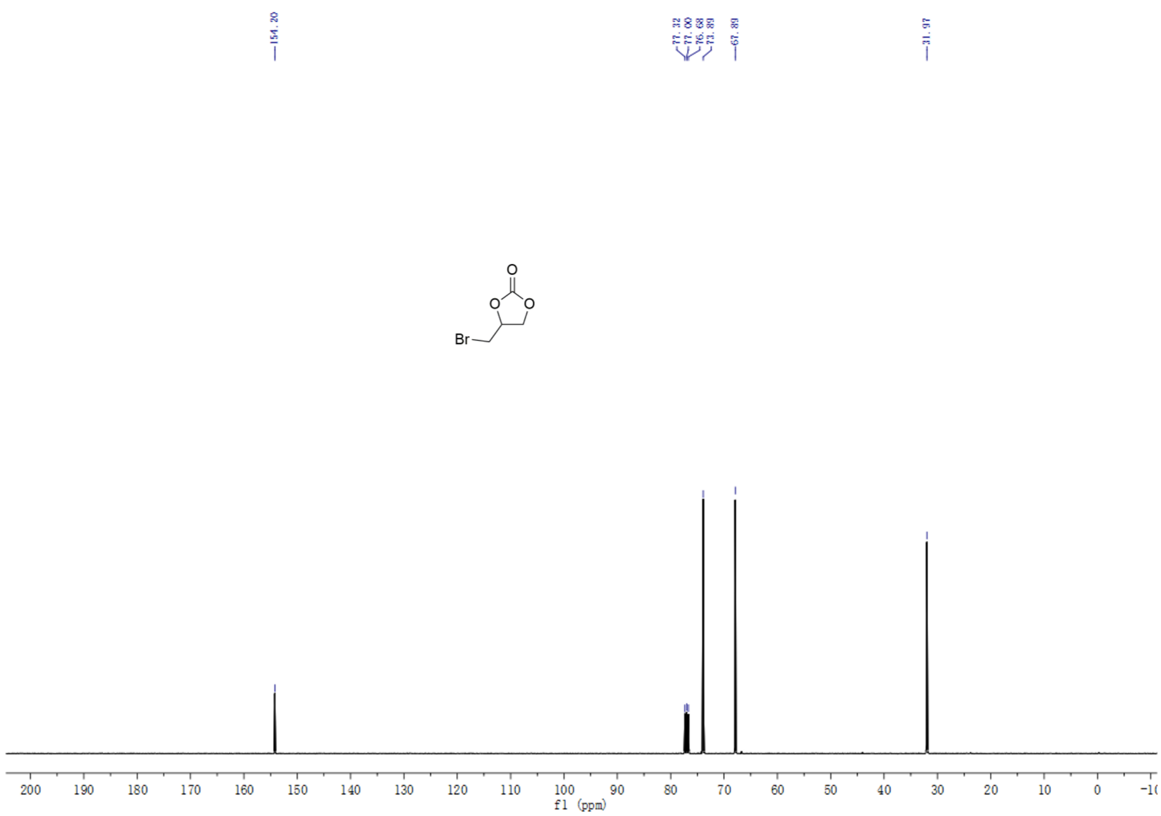

Figure S41. ^{13}C NMR ($CDCl_3$) spectrum for (2f).

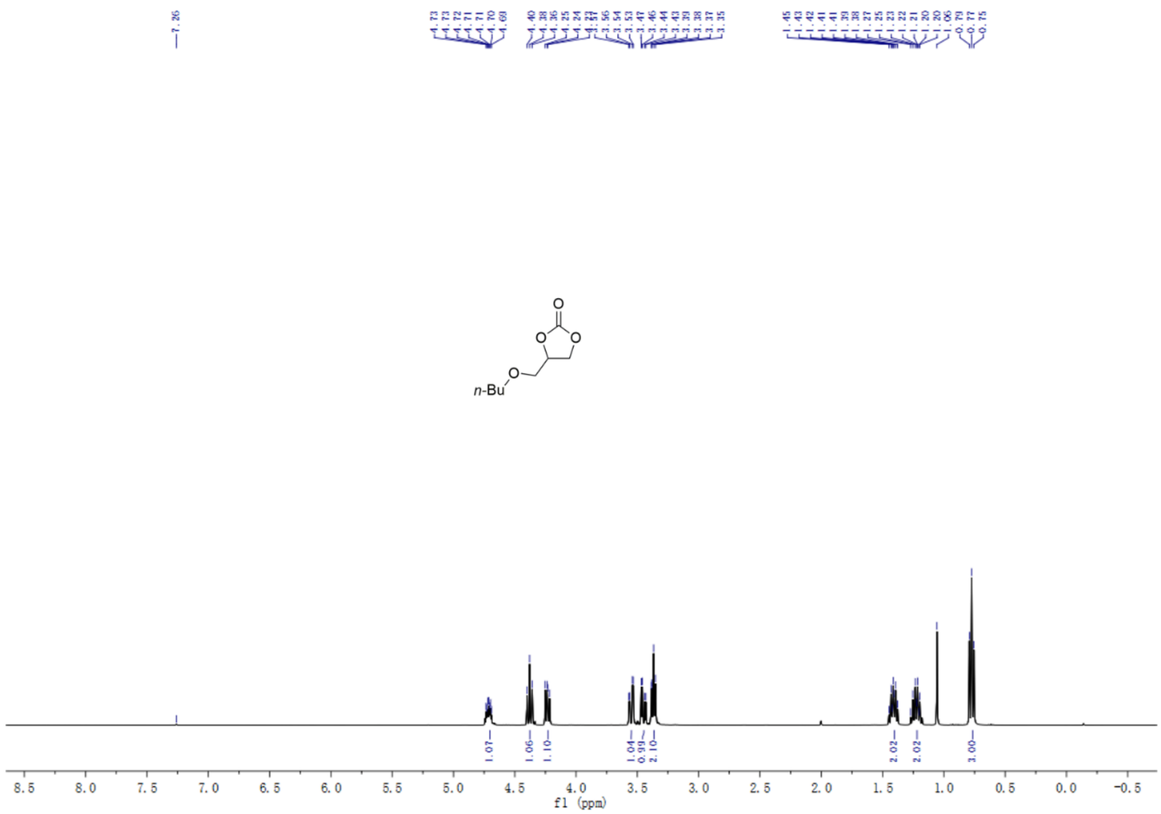

Figure S42. ^{1}H NMR ($CDCl_3$) spectrum for (2g).

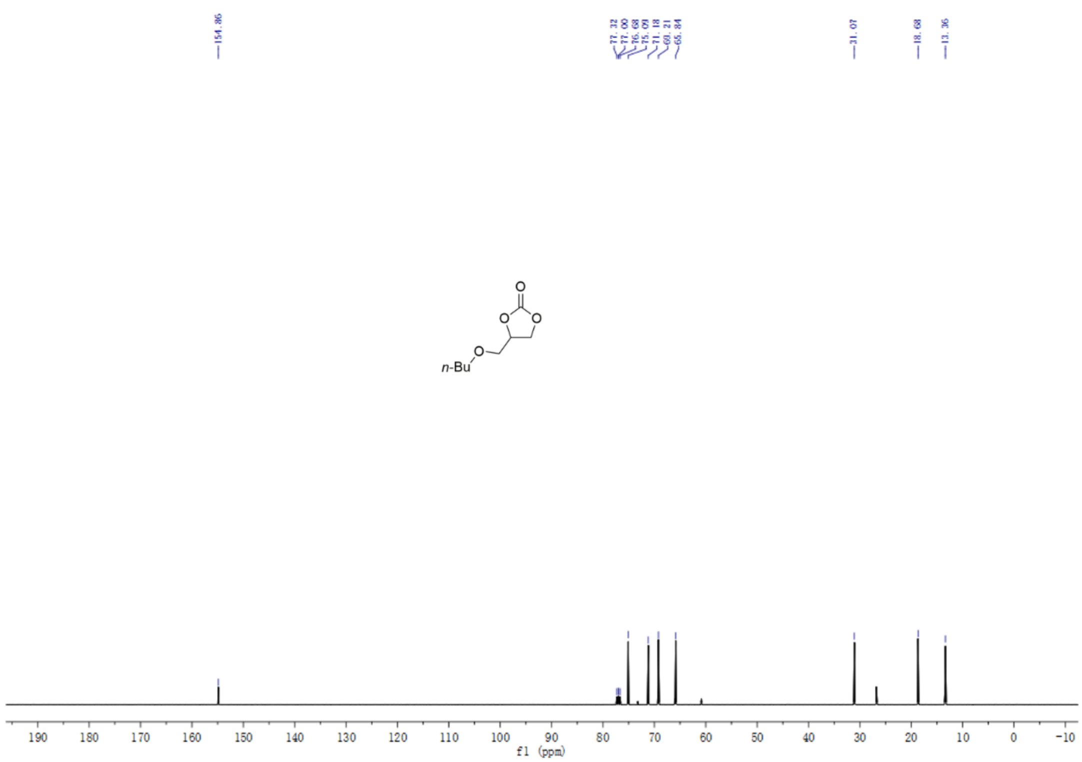

Figure S43. ^{13}C NMR ($CDCl_3$) spectrum for (2g).

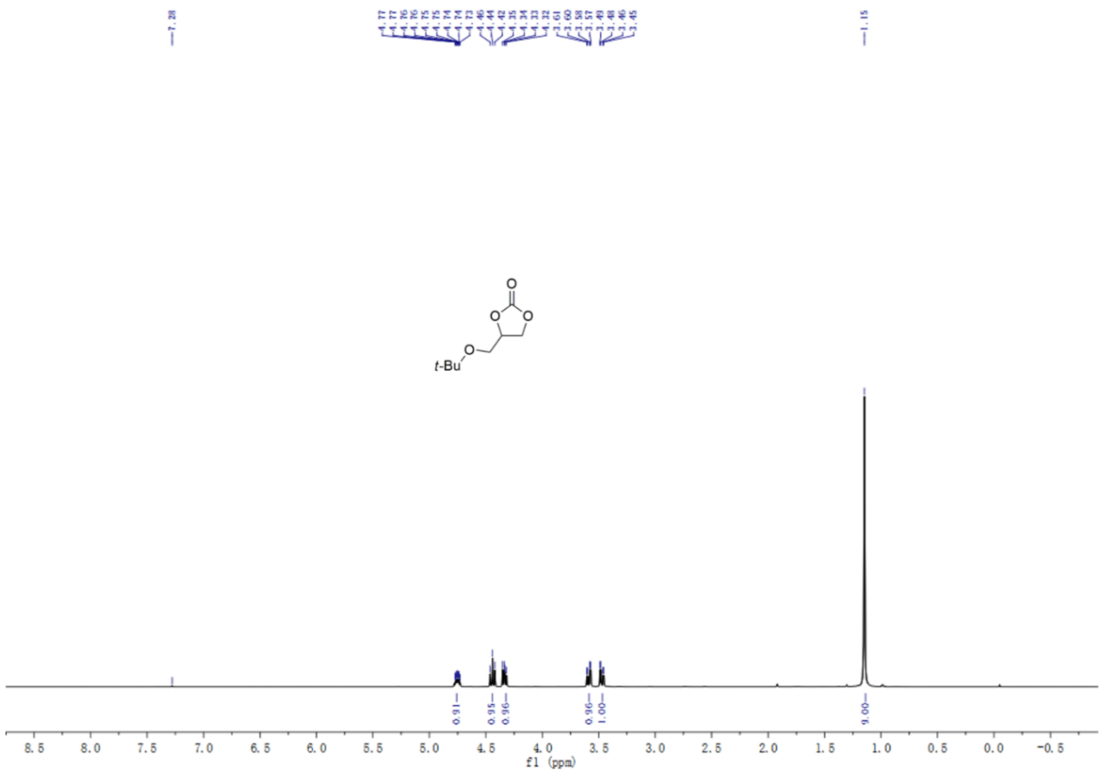

Figure S44. ^{1}H NMR ($CDCl_3$) spectrum for (2h).

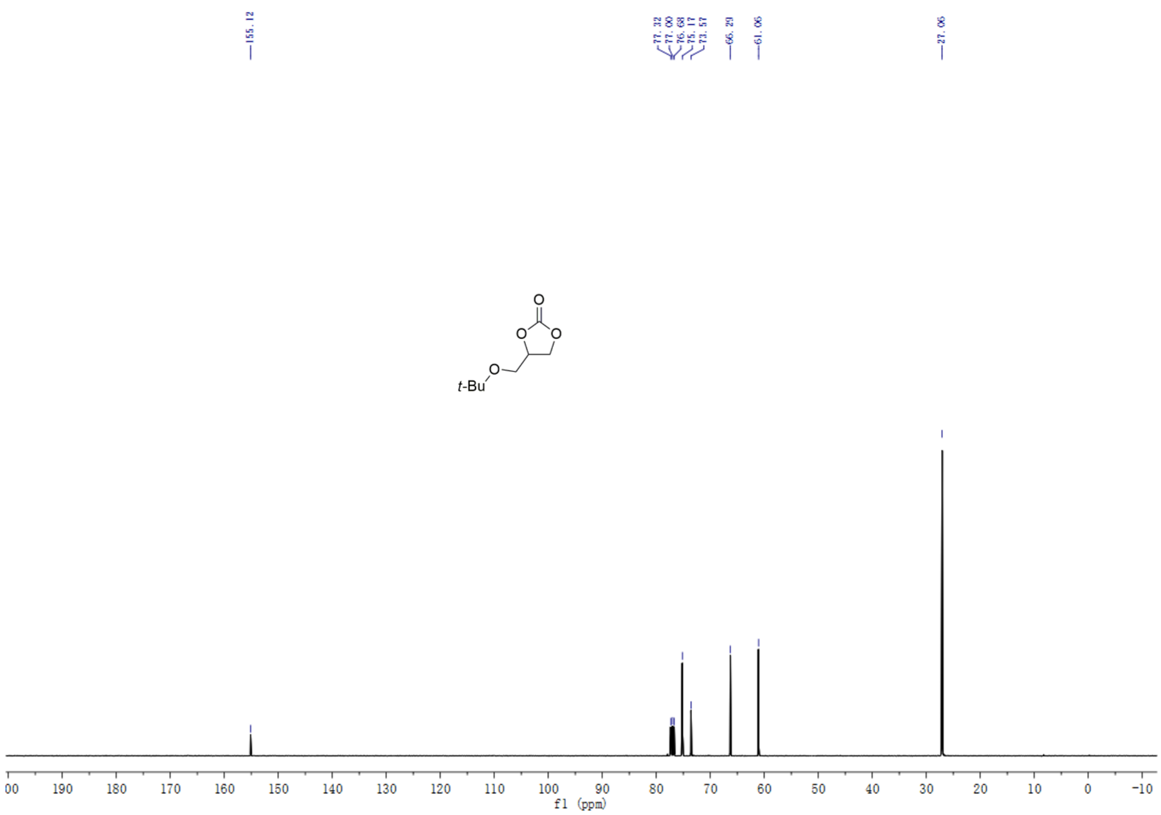

Figure S45. ^{13}C NMR ($CDCl_3$) spectrum for (2h).

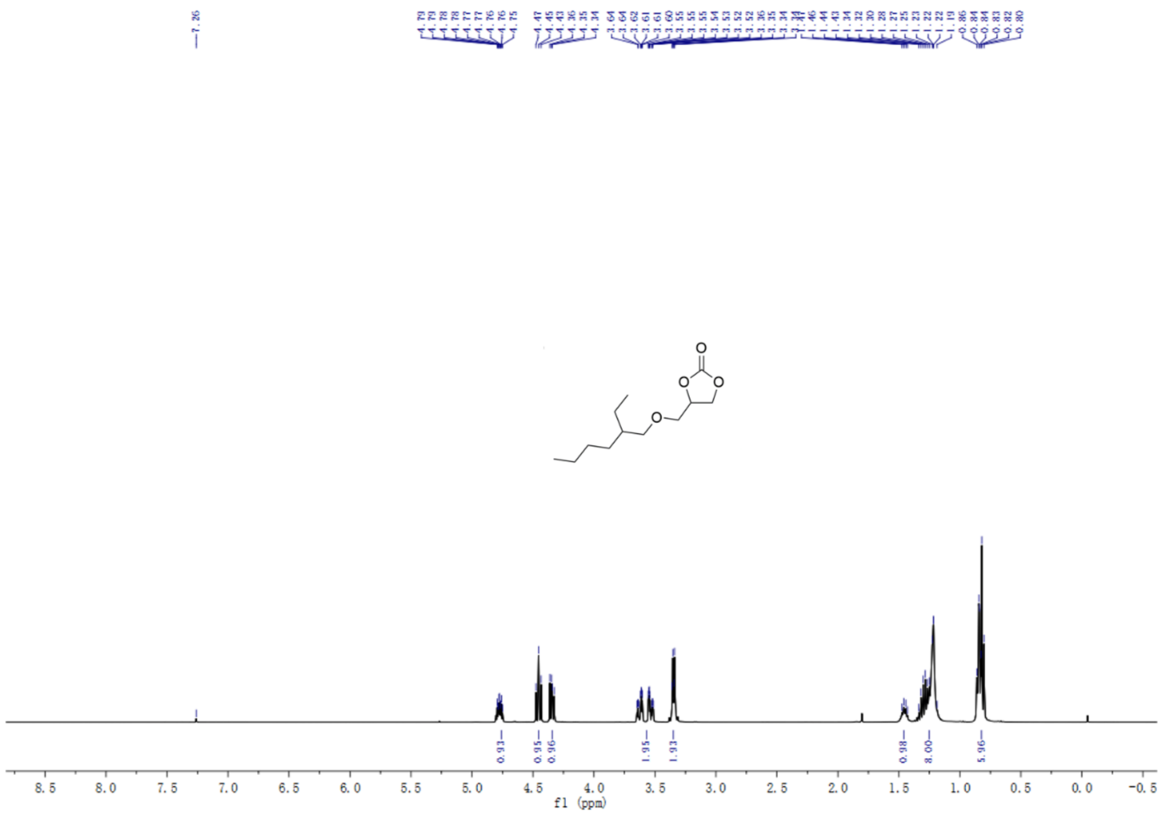

Figure S46. ^{1}H NMR ($CDCl_3$) spectrum for (2i).

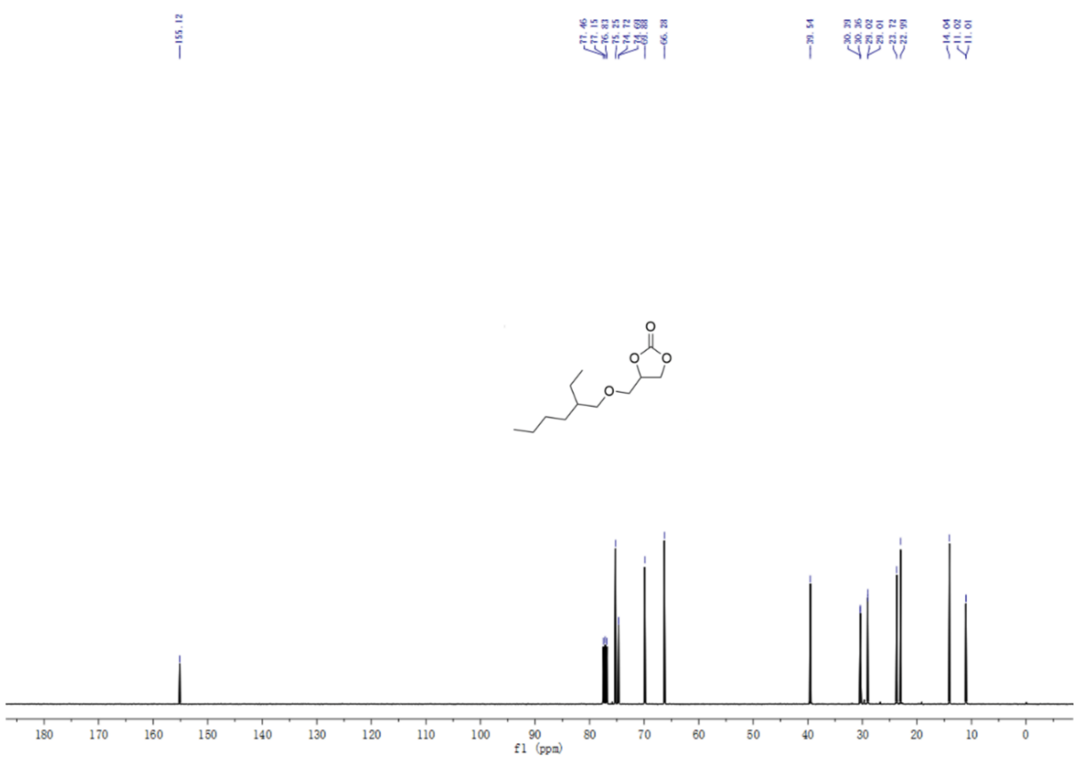

Figure S47. ^{13}C NMR ($CDCl_3$) spectrum for (2i).

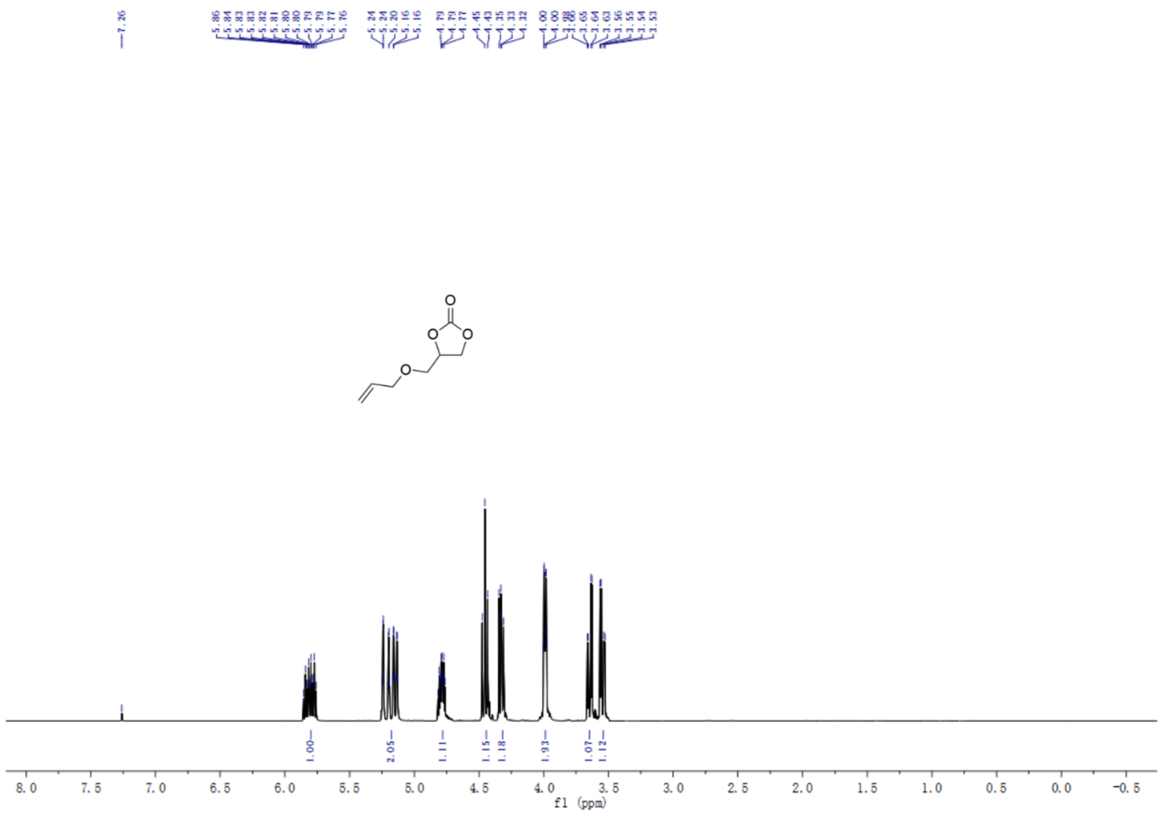

Figure S48. ^{1}H NMR ($CDCl_3$) spectrum for (2j).

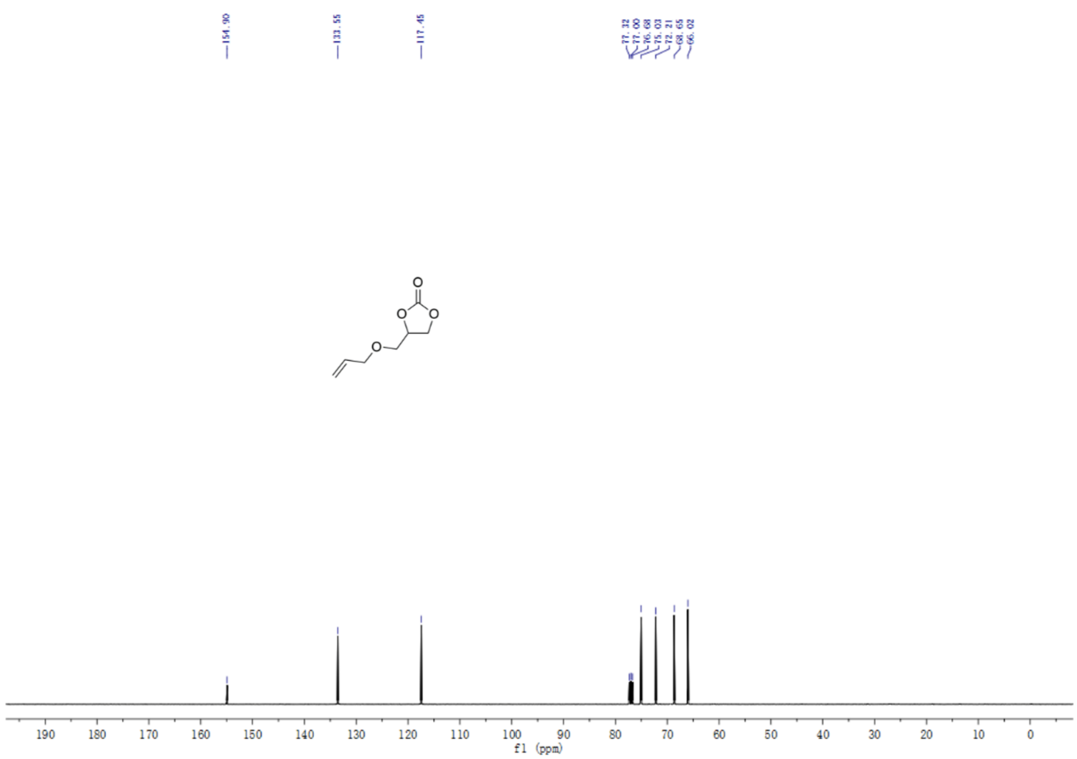

Figure S49. ^{13}C NMR ($CDCl_3$) spectrum for (2j).

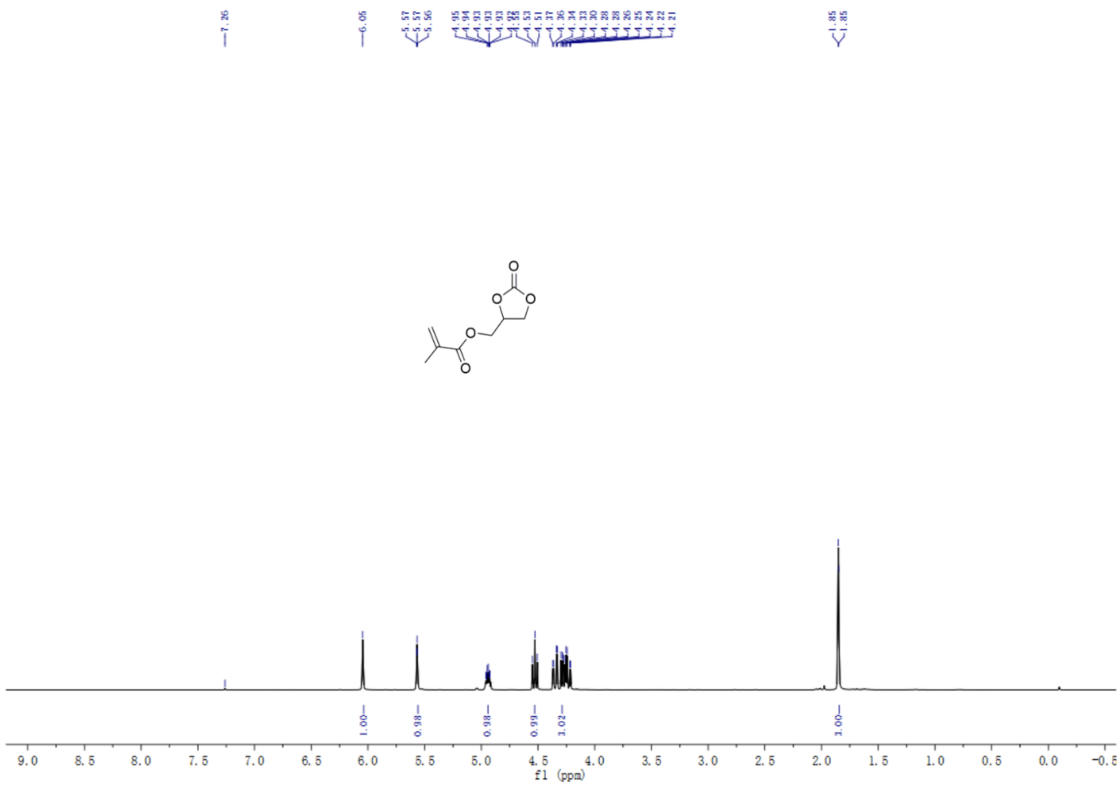

Figure S50. [1]H NMR ($CDCl_3$) spectrum for (2k).

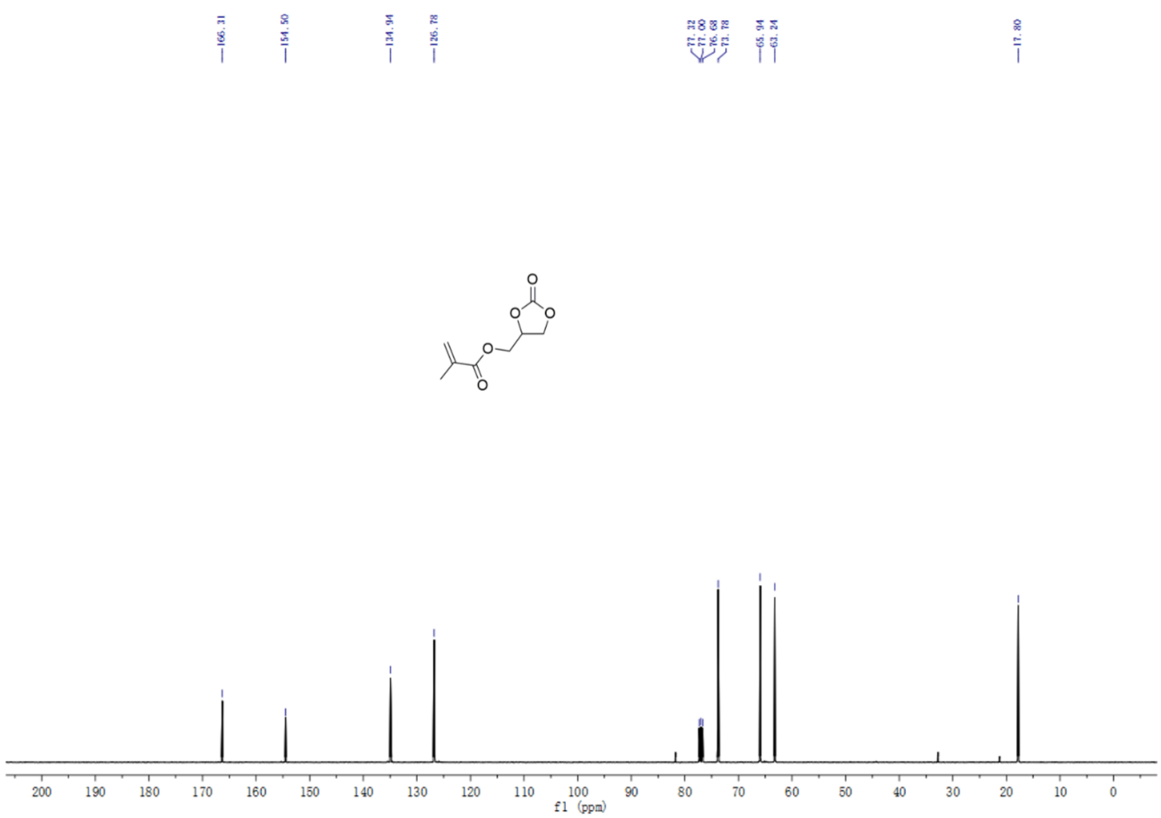

Figure S51. [13]C NMR ($CDCl_3$) spectrum for 2k

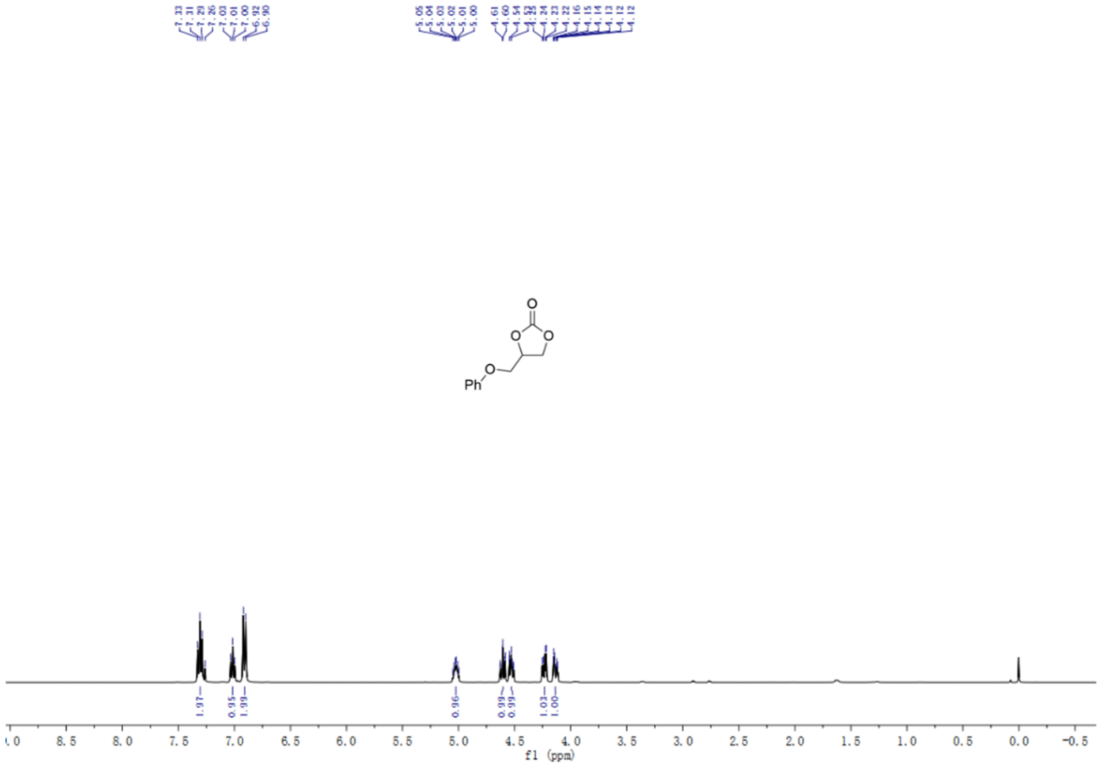

Figure S52. ^{1}H NMR ($CDCl_3$) spectrum for (2l).

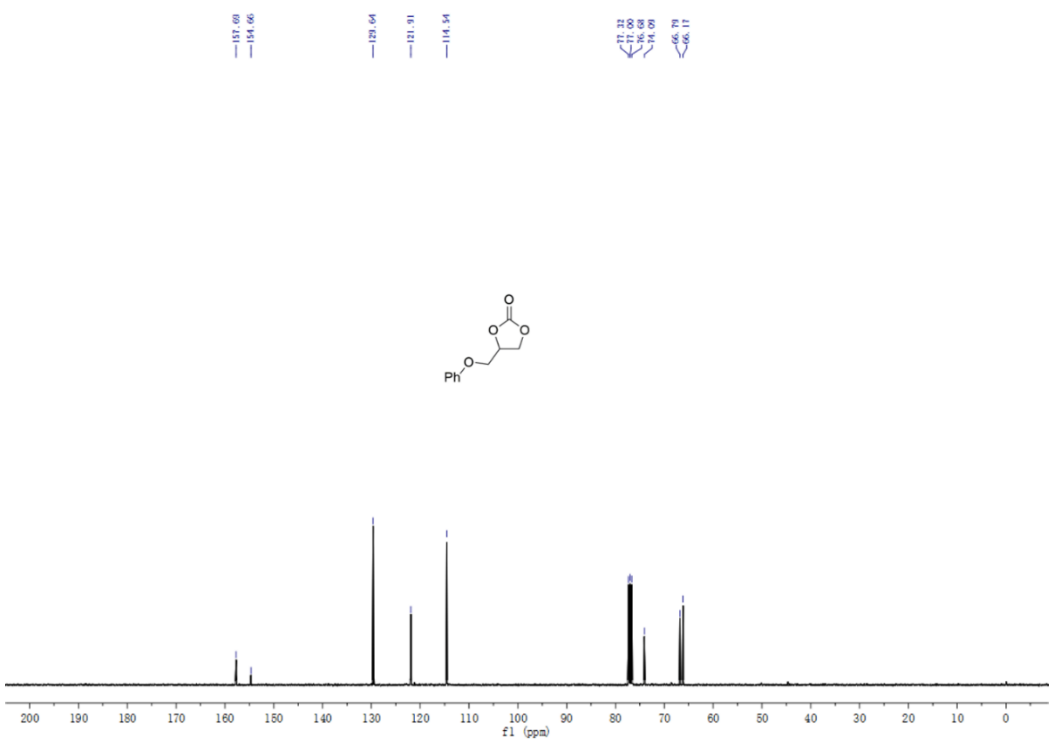

Figure S53. ^{13}C NMR ($CDCl_3$) spectrum for (2l).

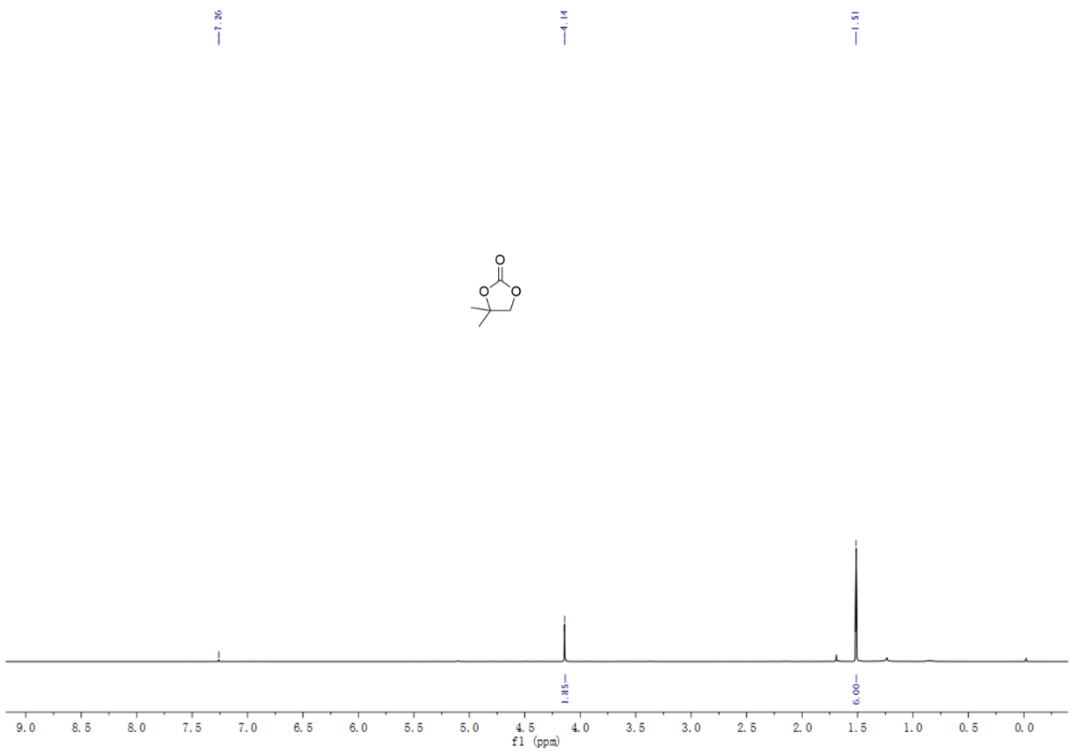

Figure S54. ^{1}H NMR ($CDCl_3$) spectrum for (2m).

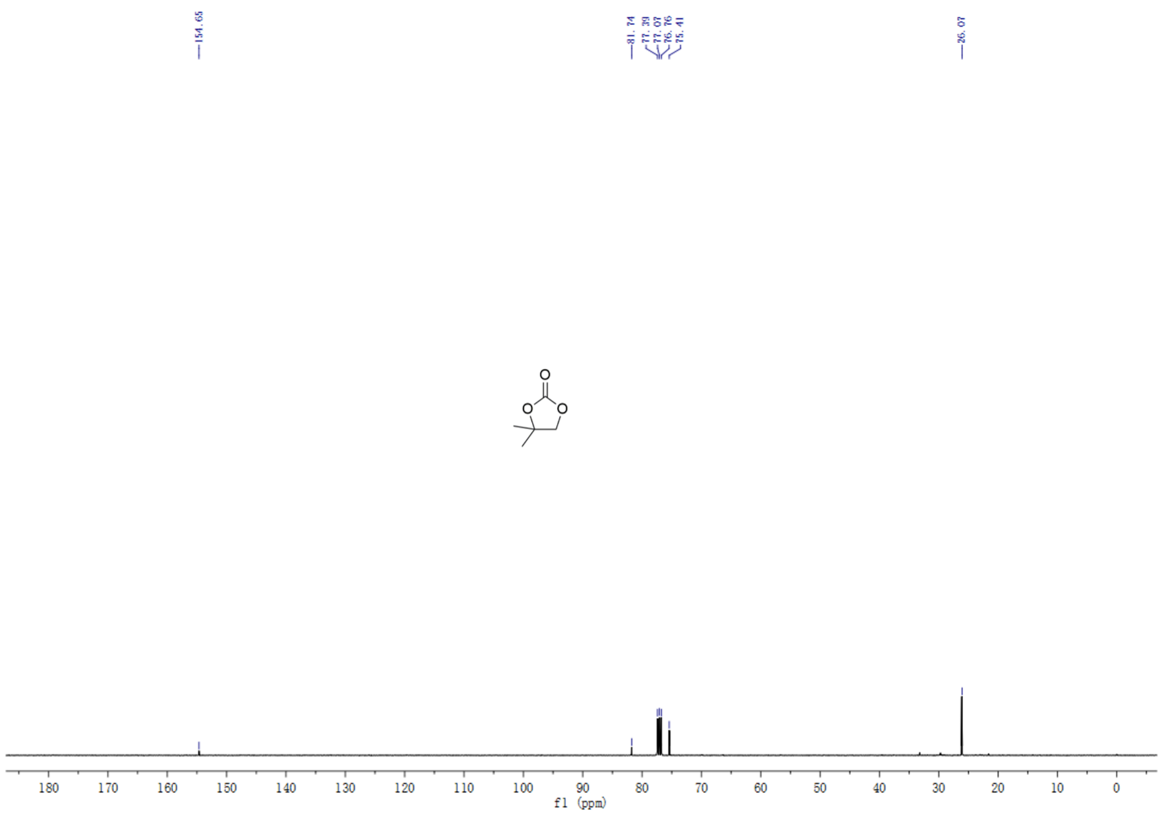

Figure S55. ^{13}C NMR ($CDCl_3$) spectrum for (2m).

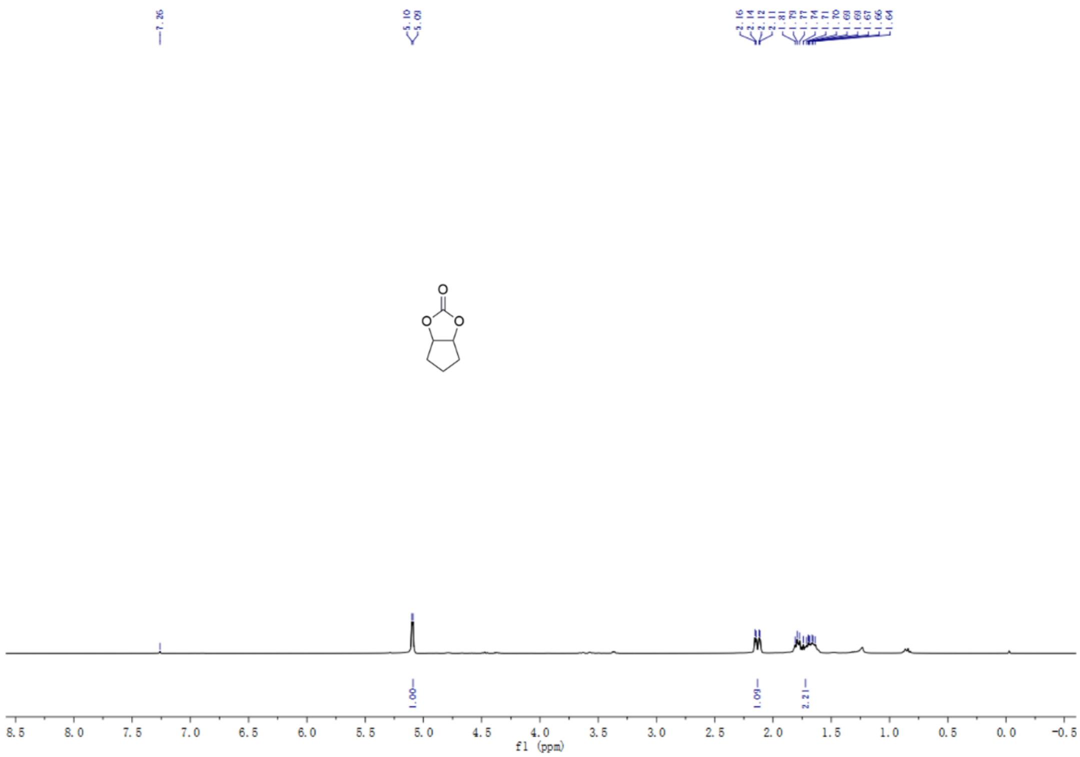

Figure S56. ^{1}H NMR ($CDCl_3$) spectrum for (2n).

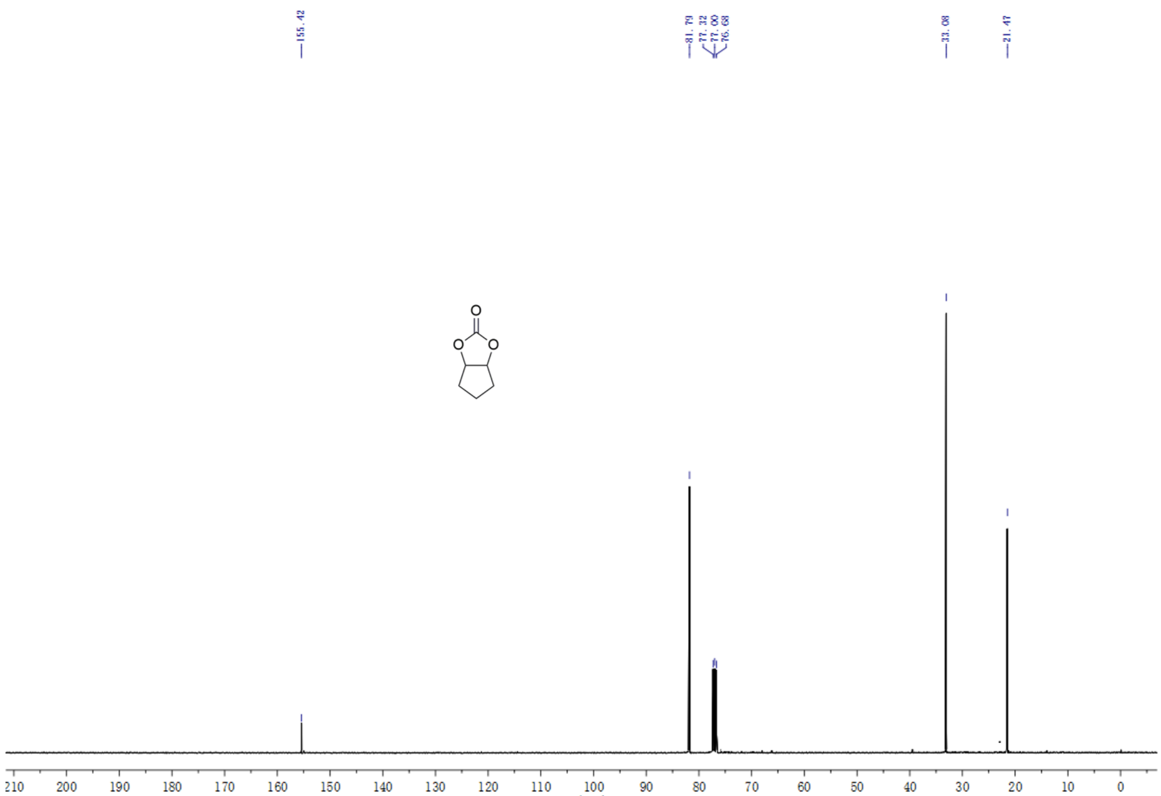

Figure S57. ^{13}C NMR ($CDCl_3$) spectrum for (2n).

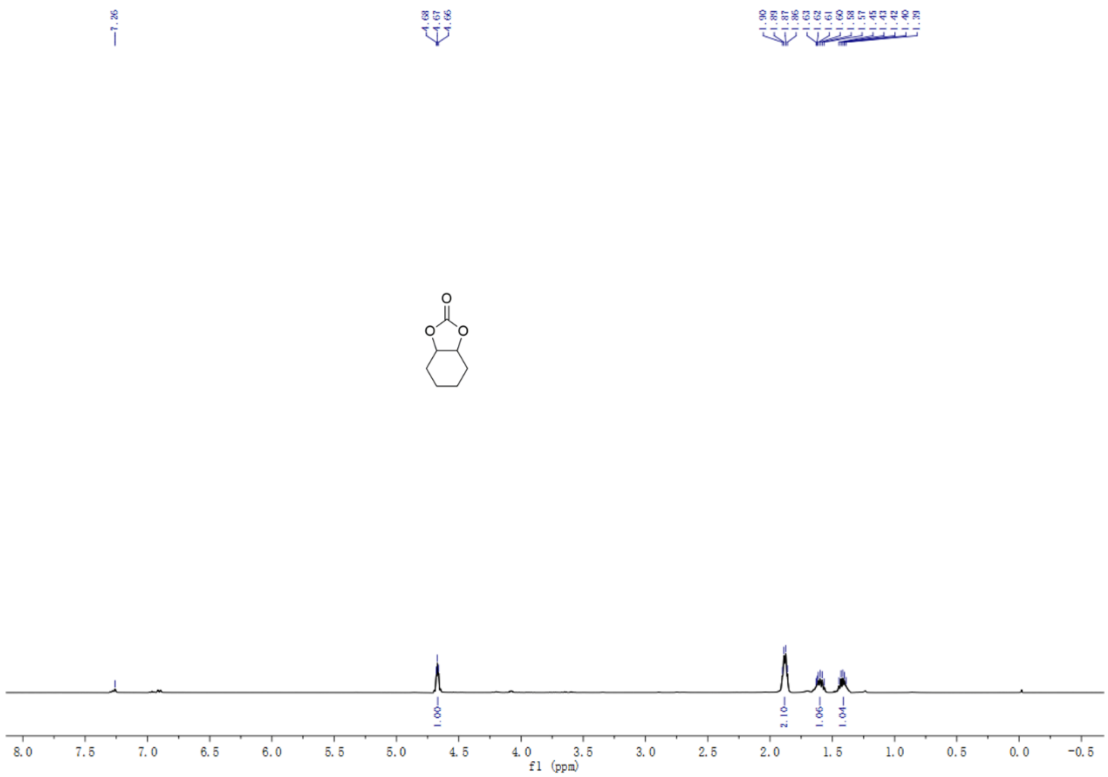

Figure S58. ^{1}H NMR ($CDCl_3$) spectrum for (2o).

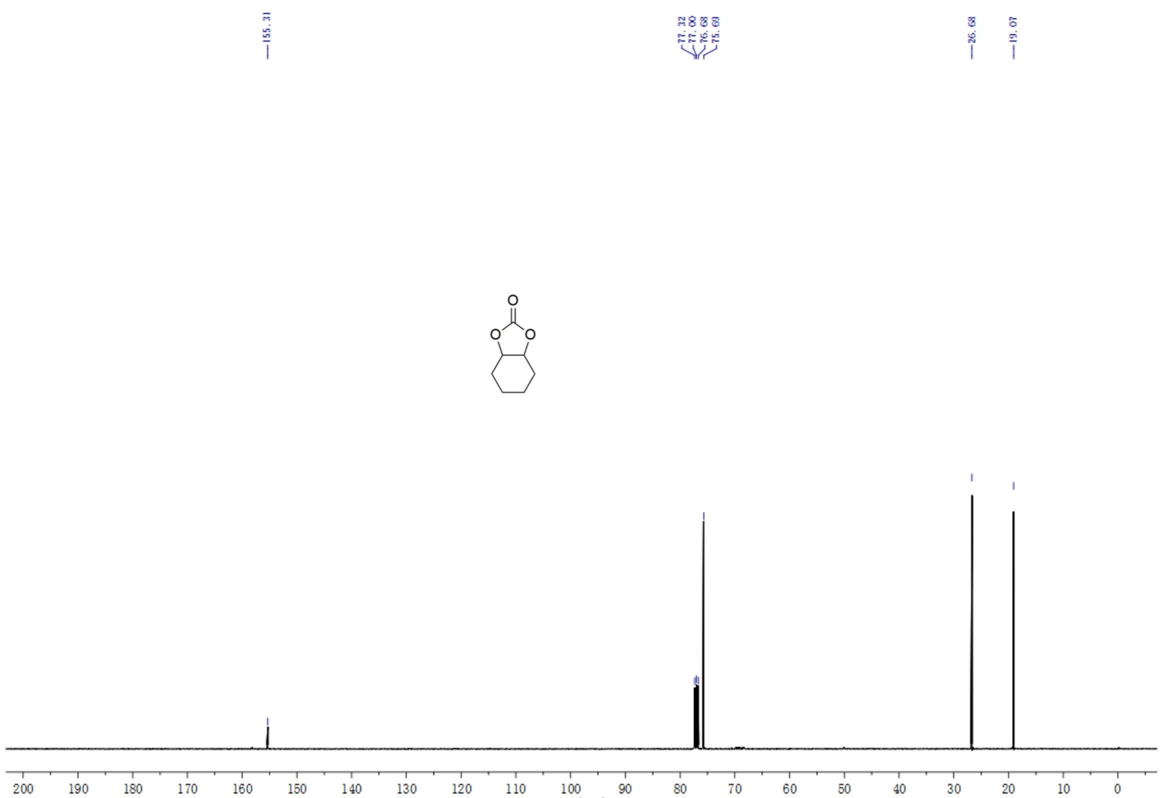

Figure S59. ^{13}C NMR ($CDCl_3$) spectrum for (2o).

Notes and references

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