Supporting Information

Self-assembly of tetranuclear 3d-4f helicates as highly efficient catalysts for CO_2 cycloaddition reactions under mild conditions

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Contents

1. Characterization data of H_2L and catalysts

Materials and Methods. Chemicals were purchased from commercial sources and used without further purification. The infrared spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer using KBr pellets in the 400-4000 cm^{-1} region. ^{1}H and ^{13}C NMR spectra were recorded using a JNM-ECS 400M spectrometer using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard. The C, H, and N microanalyses were performed by using a Vario EL cube elemental analyzer. TGA/NETZSCH STA449C instrument for thermogravimetric analysis experiments was carried out under nitrogen atmosphere, the test temperature is from 35 °C to 800 °C with the heating rate of 10 °C min^{-1}. Single-crystal X-ray diffraction data were collected on a Bruker FRAMBO diffractometer (Mo radiation, λ = 0.71073 Å) at 293 K. Data reduction was accomplished by the Bruker SAINT program. Empirical absorption corrections were carried out on the SADABS program. All the structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 of the SHELXL 2018 through Olex 2 program. All the non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were generated geometrically. The specific data of X-ray crystallography and experiment for the crystal are listed in table S1-S4. For details, see the cif date in the supporting part. The CCDC reference numbers of complexes **1**-**3** are 1942931-1942933.

2. Structure of ligand and the classical N2O2 pocket.

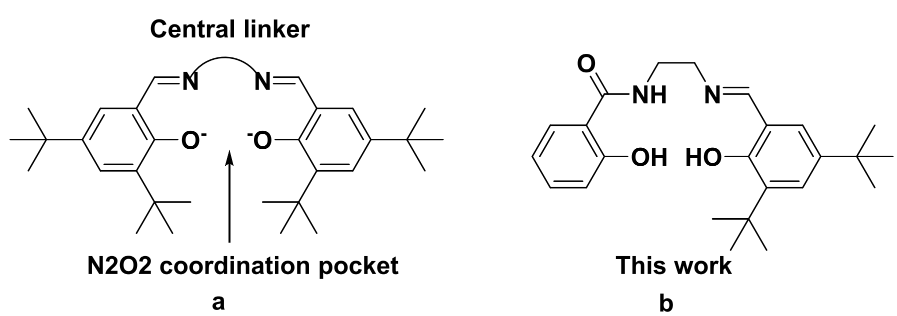


Figure S1. (a) General structure of a symmetrical salen ligand. (b) Amide-functionalized asymmetrical salen ligand in this work.

3. Mass Spectra and NMR spectra of the H_2L

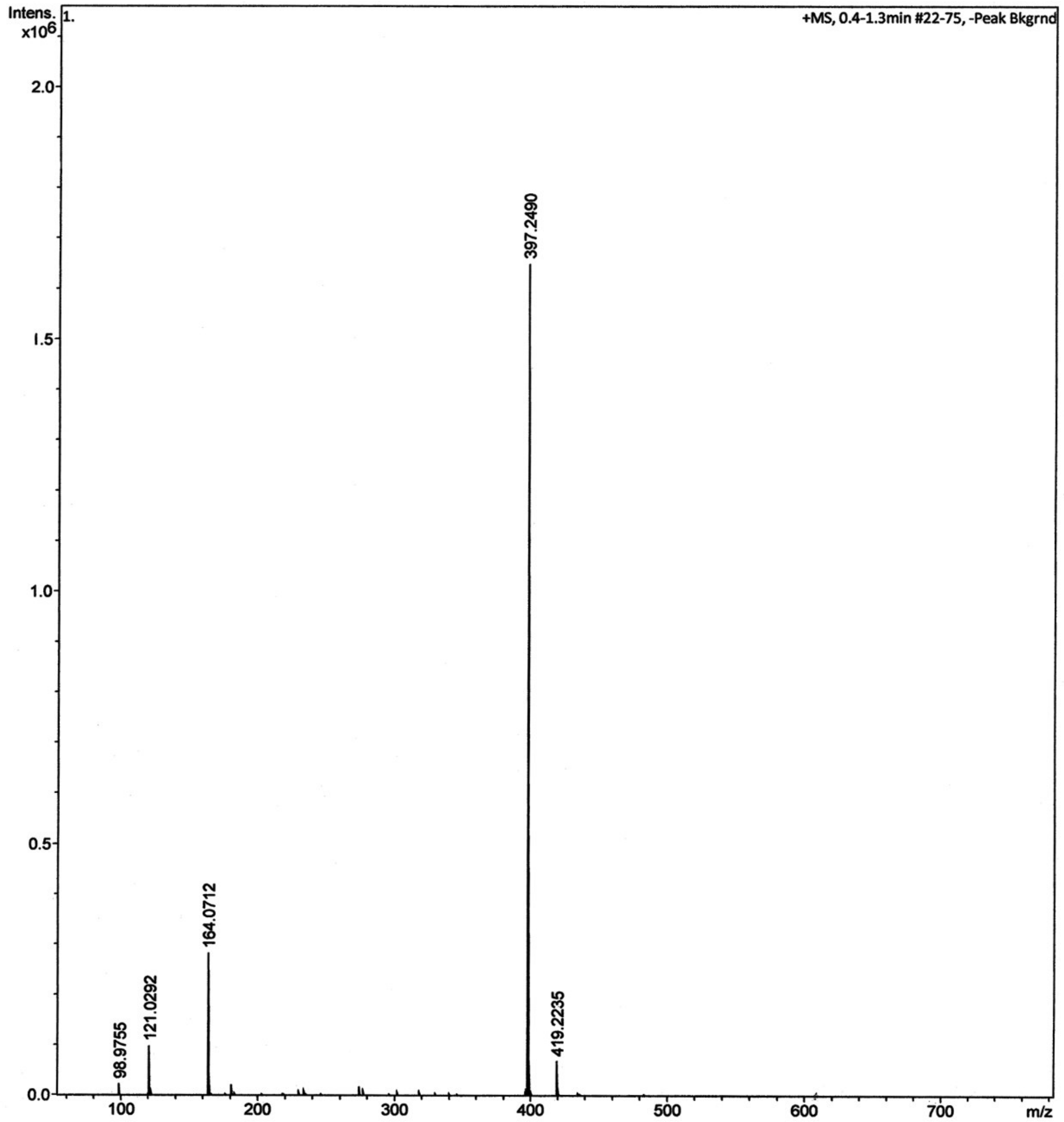


Figure S2. Mass Spectrum of H_2**L**.

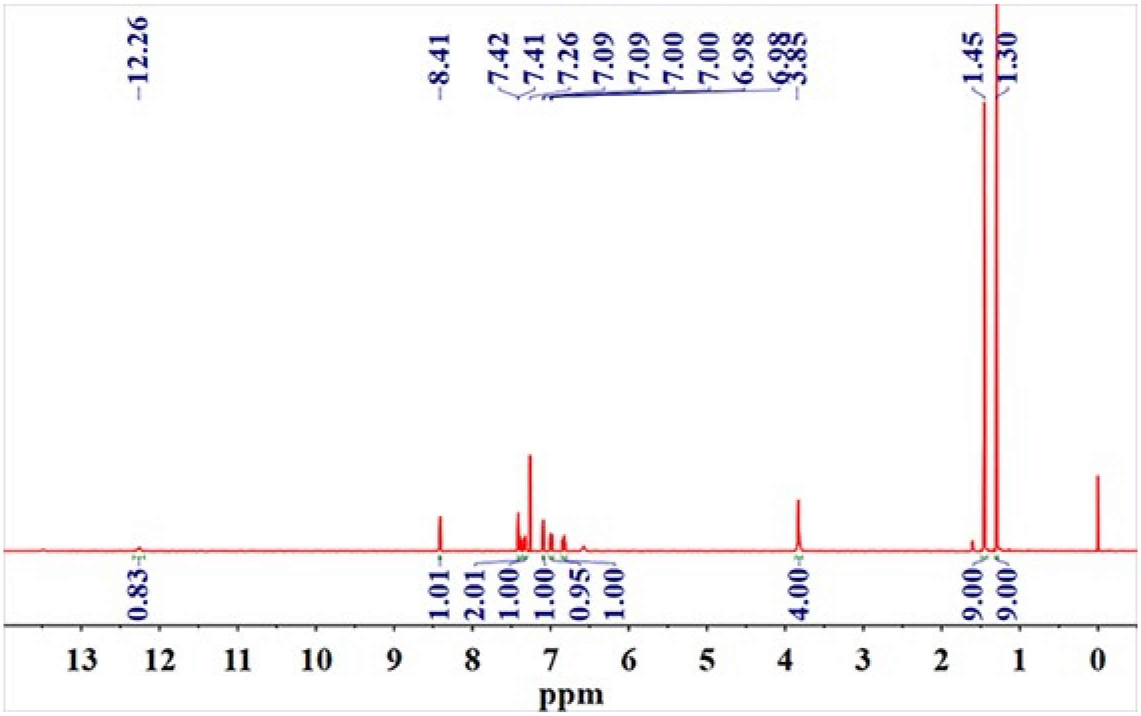


Figure S3. ^{1}H NMR Spectrum of H_2**L**.

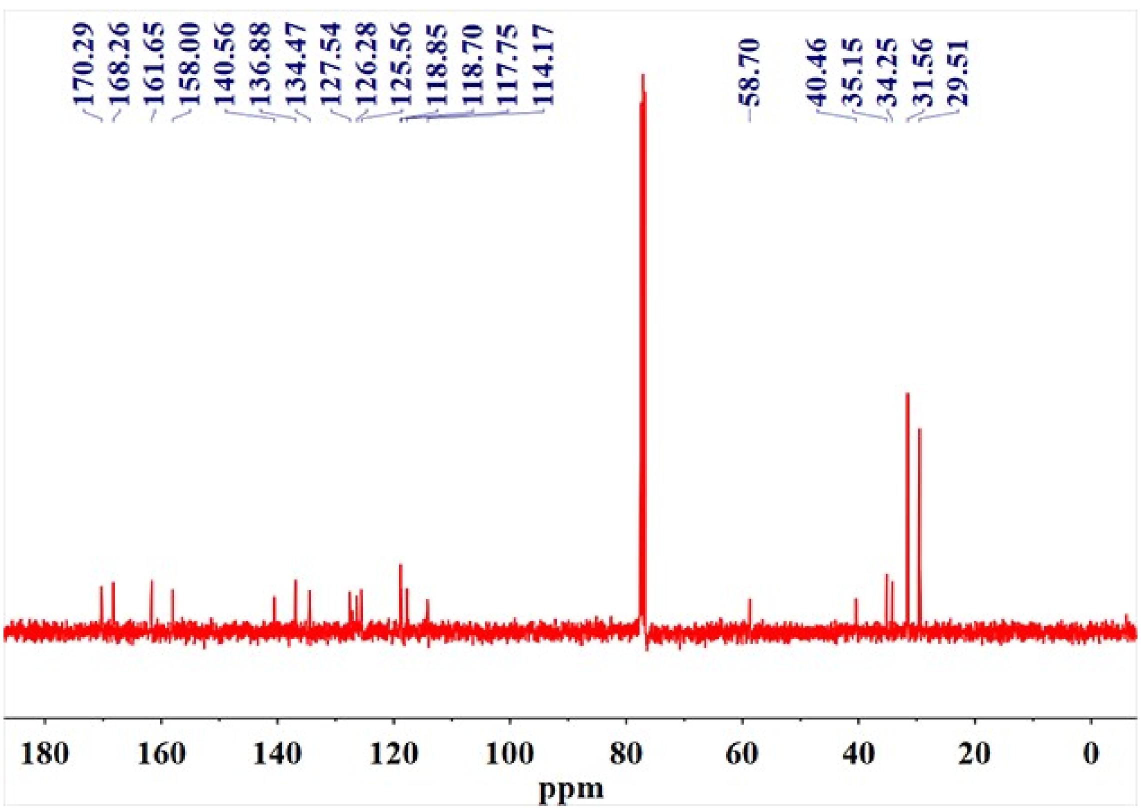


Figure S4. ^{13}C NMR Spectrum of H_2**L.**

4. IR Spectra of ligands and helicates

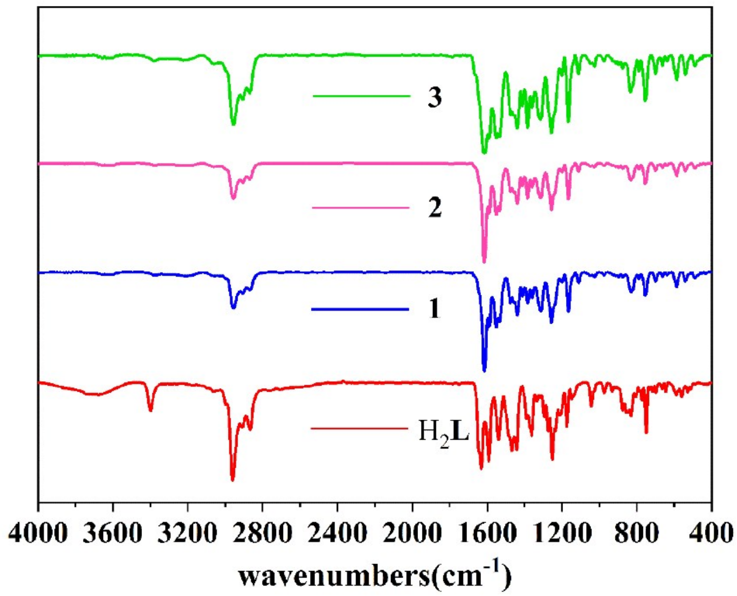


Figure S5. IR of H_2**L** and complex **1**-**3.**

5. TGA curves of complexes

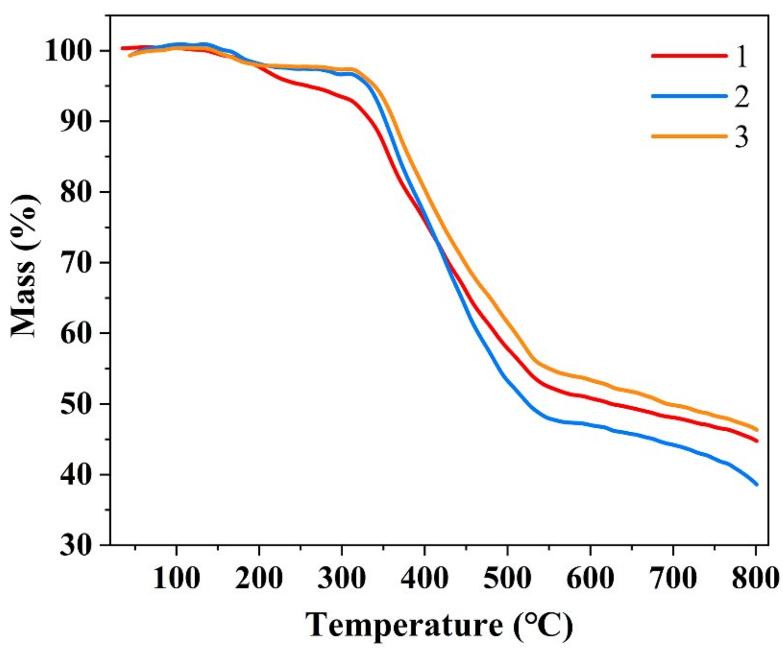


Figure S6. TGA curves of complexes **1**-**3**.

6. Single-Crystal X-ray diffraction analysis

Table S1. Crystal data and structure refinement parameters for complexes **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{98}H_{123}DyN_{10}O_{15}Zn_3$	$C_{98}H_{123}GdN_{10}O_{15}Zn_3$	$C_{98}H_{123}ErN_{10}O_{15}Zn_3$
Formula weight	2039.76	2034.52	2044.51
T/K	291.73(10)	173.00(10)	295.42(10)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	15.2010(6)	15.1548(12)	15.2301(4)
b/Å	19.7221(4)	19.2532(17)	19.7361(5)
c/Å	19.7307(5)	19.4848(13)	19.7667(6)
α /°	70.729(2)	72.372(7)	70.414(2)
β/ °	87.962(3)	85.842(6)	87.940(2)
γ/°	85.124(2)	89.624(7)	85.250(2)
V/Å^3	5563.4(3)	5403.3(8)	5578.3(3)
Z	2	2	2
D_{calc}/Mg m^{-3}	1.218	1.282	1.236
F(000)	2114.0	2162.0	2154.0
ϑ range for data collection	6.546 to 50.02°	6.6 to 52.044°	6.586 to 50.02°
Data/restraints/parameters	19482/144/1211	21257/80/1204	19441/78/1218
Goodness-of-fit on F^2	0.850	1.043	1.032
Final R indices [I>2sigma (I)]^a	R_1=0.0637,	R_1=0.0649,	R_1=0.0550,
R indices (all data)^b	R_1=0.1007,	R_1=0.1137,	R_1=0.0838,
Largest diff. peak/hole/e. Å^{-3}	1.31/-1.01	1.74/-0.91	1.19/-0.93

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^b wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) for complexes **1-3**

		Zn_3DyL_4 (1)			
Dy1—Zn2	3.3230 (8)	Dy1—O1	2.382 (4)	Zn1—O4	1.969 (4)
Dy1—Zn1	3.3305 (8)	Dy1—O4	2.396 (4)	Zn1—N2	1.991 (6)
Dy1—O11	2.289 (5)	Zn2—O6	1.911 (4)	Zn3—O9	2.038 (4)
Dy1—O10	2.406 (4)	Zn2—O10	1.956 (4)	Zn3—O44	2.090 (7)
Dy1—O7	2.370 (4)	Zn2—O1	1.966 (4)	Zn3—N6	2.085 (6)
Dy1—O2	2.291 (4)	Zn2—N4	1.993 (5)	Zn3—O12	2.049 (4)
Dy1—O5	2.291 (4)	Zn1—O3	1.910 (4)	Zn3—N8	2.076 (6)
Dy1—O8	2.282 (4)	Zn1—O7	1.971 (4)		
O11—Dy1—O10	72.06 (14)	O7—Dy1—O10	136.23 (15)	O5—Dy1—O10	73.76 (15)
O11—Dy1—O7	77.53 (15)	O7—Dy1—O1	131.63 (14)	O5—Dy1—O7	140.39 (14)
O11—Dy1—O2	147.74 (15)	O7—Dy1—O4	69.86 (14)	O5—Dy1—O2	96.42 (17)
O11—Dy1—O5	94.72 (17)	O2—Dy1—O10	140.20 (15)	O5—Dy1—O1	76.64 (15)
O11—Dy1—O1	141.81 (14)	O2—Dy1—O7	74.61 (16)	O5—Dy1—O4	70.54 (14)
O11—Dy1—O4	80.01 (16)	O2—Dy1—O1	70.40 (14)	O8—Dy1—O7	72.42 (14)
O2—Dy1—O4	75.40 (15)	O1—Dy1—O10	69.80 (14)	O8—Dy1—O2	98.53 (16)
O8—Dy1—O11	88.17 (16)	O1—Dy1—O4	128.80 (15)	O8—Dy1—O5	146.87 (15)
O8—Dy1—O10	75.83 (14)	O4—Dy1—O10	132.03 (14)	O8—Dy1—O1	80.82 (15)
O8—Dy1—O4	142.06 (15)	O6—Zn2—O1	119.10 (17)	O9—Zn3—N6	86.4 (2)
O3—Zn1—O4	117.71 (18)	O6—Zn2—N4	97.0 (2)	O9—Zn3—O12	171.2 (2)
O3—Zn1—N2	96.3 (2)	O1—Zn2—N4	118.8 (2)	O9—Zn3—N8	89.8 (2)
O7—Zn1—N2	117.2 (2)	O10—Zn2—O1	88.62 (18)	N6—Zn3—O44	117.9 (3)
O4—Zn1—O7	87.65 (17)	O10—Zn2—N4	120.9 (2)	O12—Zn3—O44	91.9 (2)
O4—Zn1—N2	123.5 (2)	N8—Zn3—N6	137.5 (3)	O12—Zn3—N6	91.4 (2)
O3—Zn1—O7	116.4 (2)	N8—Zn3—O44	104.6 (3)	O12—Zn3—N8	86.0 (2)

Table S3. Selected bond lengths (Å) for complex **2**

Zn_3GdL_4 (**2**)					
Zn1—O6	1.905 (3)	Zn2—O3	1.907 (4)	Zn3—O12	2.031 (4)
Zn1—O7	1.951 (4)	Zn2—O10	1.978 (3)	Zn3—N8	2.078 (5)
Zn1—O1	1.967 (3)	Zn2—O4	1.969 (3)	Zn3—O13	2.104 (5)
Zn1—N4	1.989 (4)	Zn2—N2	1.988 (4)	Zn3—O9	2.047 (4)
Zn3—N6	2.073 (5)	Gd1—O8	2.314 (4)	Gd1—O11	2.314 (3)
Gd1—O1	2.399 (4)	Gd1—O7	2.419 (3)	Gd1—O4	2.402 (3)
Gd1—O5	2.312 (3)	Gd1—O10	2.376 (3)	Gd1—O2	2.310 (3)
O8—Gd1—O7	71.76 (12)	O10—Gd1—O7	136.30 (11)	O2—Gd1—O10	74.62 (12)
O8—Gd1—O10	77.92 (12)	O10—Gd1—O1	131.85 (12)	O2—Gd1—O1	70.13 (12)
O8—Gd1—O1	141.43 (11)	O10—Gd1—O4	69.93 (12)	O2—Gd1—O5	96.80 (13)
O8—Gd1—O11	88.60 (13)	O2—Gd1—O8	148.39 (13)	O2—Gd1—O11	97.37 (13)
O8—Gd1—O4	80.30 (12)	O2—Gd1—O7	139.83 (13)	O11—Gd1—O7	76.64 (11)
O2—Gd1—O4	75.82 (12)	O5—Gd1—O10	140.00 (12)	O11—Gd1—O10	71.83 (12)
O1—Gd1—O7	69.70 (11)	O5—Gd1—O1	76.76 (12)	O11—Gd1—O1	81.21 (12)
O1—Gd1—O4	128.47 (12)	O5—Gd1—O11	147.87 (12)	O11—Gd1—O4	141.60 (12)
O5—Gd1—O8	94.20 (13)	O5—Gd1—O4	70.10 (12)	O4—Gd1—O7	132.06 (11)
O5—Gd1—O7	73.94 (12)	O6—Zn1—N4	97.04 (16)	O6—Zn1—O7	114.17 (15)
O7—Zn1—N4	120.94 (17)	O7—Zn1—O1	89.26 (14)	O6—Zn1—O1	118.77 (15)
O1—Zn1—N4	118.56 (16)	O3—Zn2—O10	115.62 (15)		

Table S4. Selected bond lengths (Å) for complex **3**

Zn_3ErL_4 (3)					
Zn3—O12	2.050 (4)	Zn2—O6	1.907 (4)	Zn1—O3	1.910 (5)
Zn3—O9	2.047 (4)	Zn2—O10	1.954 (4)	Zn1—N2	1.991 (5)
Zn3—O15	2.081 (4)	Zn2—O1	1.959 (4)	Zn1—O7	1.965 (4)
Zn3—N7	2.084 (5)	Zn2—N4	2.005 (5)	Zn1—O4	1.957 (4)
Zn3—N6	2.066 (5)	O5—Er1	2.290 (4)	O2—Er1	2.290 (4)
O8—Er1	2.264 (4)	O10—Er1	2.380 (4)	O1—Er1	2.355 (4)
O4—Er1	2.369 (4)	Er1—O11	2.266 (4)	O7—Er1	2.333 (4)
O3—Zn1—N2	96.4 (2)	O6—Zn2—O10	115.03 (17)	O12—Zn3—O15	92.38 (19)
O3—Zn1—O7	116.72 (18)	O6—Zn2—O1	119.25 (18)	O12—Zn3—N6	92.3 (2)
O3—Zn1—O4	117.12 (19)	O6—Zn2—N4	97.0 (2)	O9—Zn3—O12	170.85 (16)
O7—Zn1—N2	116.6 (2)	O10—Zn2—O1	88.36 (17)	O9—Zn3—O15	96.08 (18)
O4—Zn1—N2	124.9 (2)	O10—Zn2—N4	118.5 (2)	O9—Zn3—N6	86.51 (19)
O4—Zn1—O7	86.96 (17)	O1—Zn2—N4	120.6 (2)	N6—Zn3—O15	120.1 (2)
O8—Er1—O5	145.55 (15)	O5—Er1—O7	141.20 (15)	O7—Er1—O1	131.06 (15)
O8—Er1—O10	75.10 (14)	O5—Er1—O4	71.17 (15)	O7—Er1—O4	70.03 (15)
O8—Er1—O2	100.78 (15)	O2—Er1—O10	141.03 (15)	O4—Er1—O10	131.31 (14)
O8—Er1—O1	81.25 (15)	O2—Er1—O1	70.74 (15)	O11—Er1—O5	95.04 (15)
O8—Er1—O7	72.91 (14)	O2—Er1—O7	74.21 (16)	O11—Er1—O10	72.78 (14)
O8—Er1—O4	142.46 (15)	O2—Er1—O4	74.78 (15)	O11—Er1—O2	146.17 (15)
O8—Er1—O11	87.93 (14)	O1—Er1—O10	70.34 (14)	O11—Er1—O1	143.09 (14)
O5—Er1—O10	73.11 (14)	O1—Er1—O4	128.88 (14)	O11—Er1—O7	77.40 (14)
O5—Er1—O2	95.65 (16)	O7—Er1—O10	136.54 (13)	O11—Er1—O4	78.53 (14)
O5—Er1—O1	75.91 (16)				

7. Diagram of crystal structure

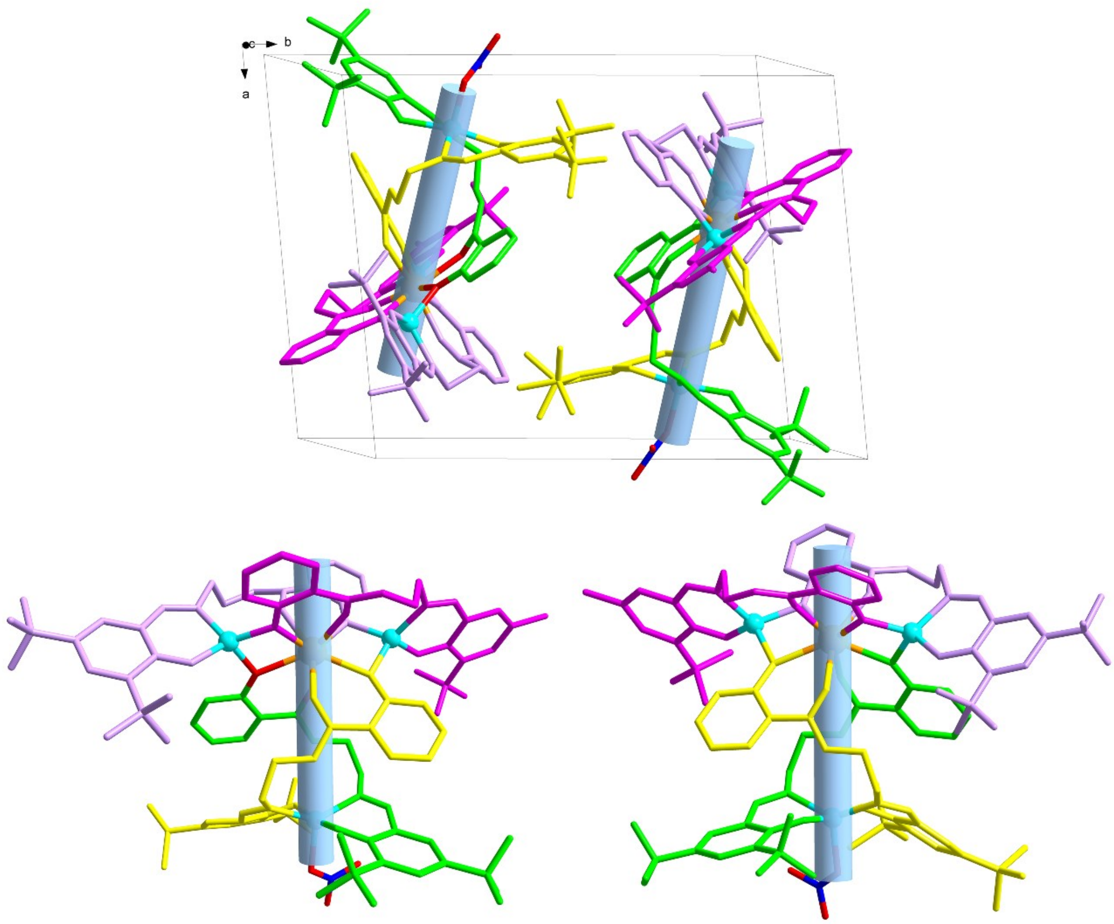


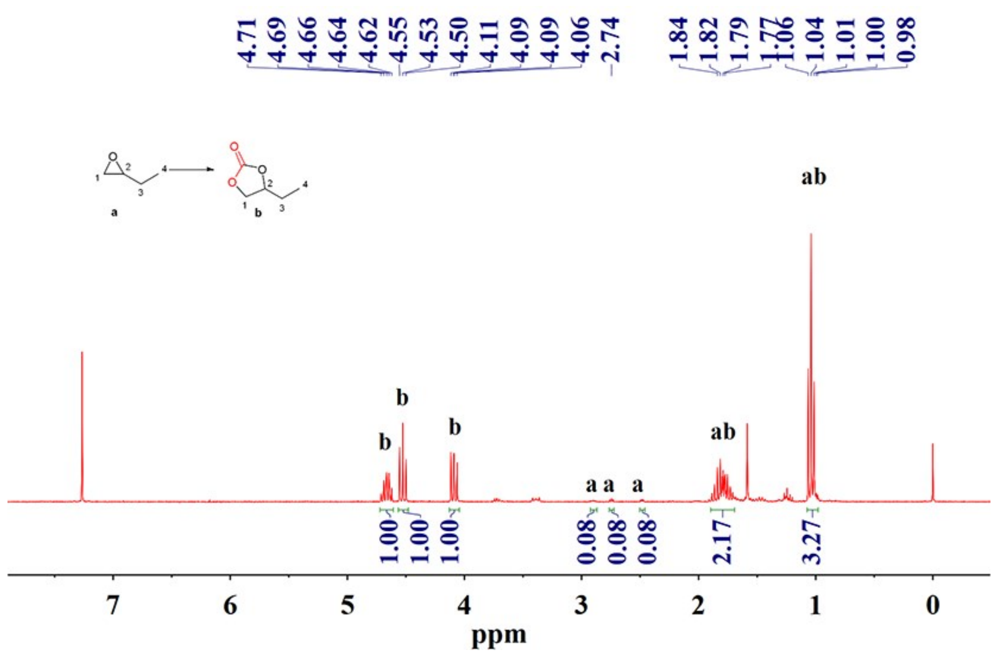
Figure S7. Wires/Sticks representation of complex **3** in crystal cell, in which two kinds of lanthanide helicates with *M* helical configuration and *P* helical configuration arranged and self-assembled alternatively. All hydrogen atoms, solvent molecules and uncoordinated anions are omitted for clarity.

8. Catalytic performance

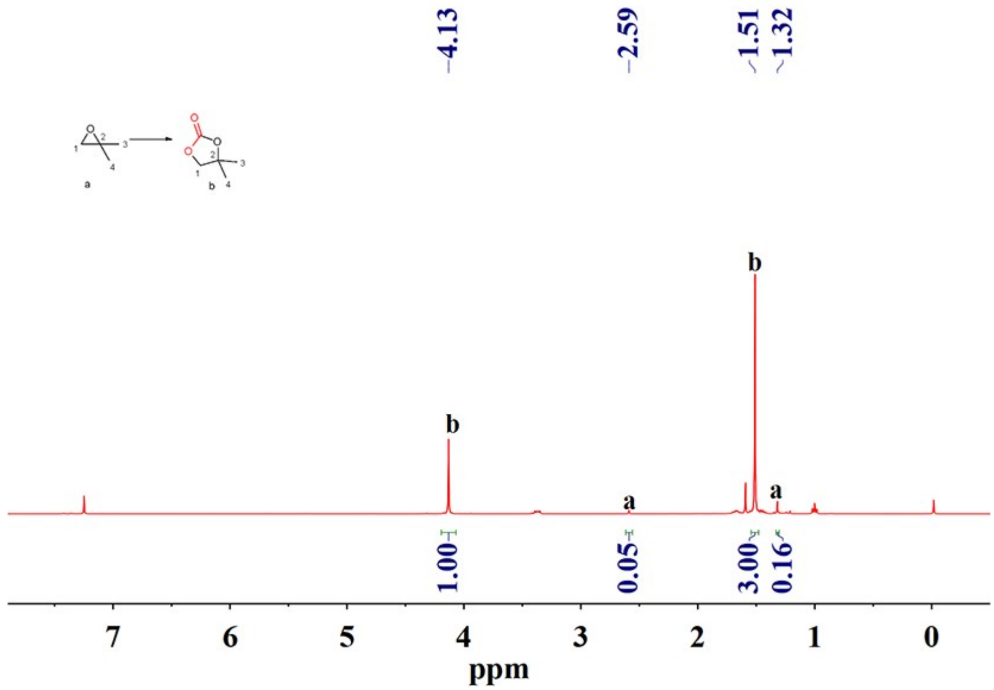
Table S5. Representative homogeneous and heterogeneous catalysts with high TOF used for the synthesis of cyclic carbonates

Cat.	Co-cat.	Epoxide (Mole ratio)	T (°C)	P (MPa)	Time (h)	Yield (%)	TOF (h^{-1})
$Zn(OPO)_2$[1]	TBAB (0.9)	(propylene epoxide) 1:40000	120	3	1	46	18400
Zn-CMP[2]	TBAB (0.9)	(propylene epoxide) 1:40000	120	3	1	29	11600
$ZnBr_2$[3]	-	(propylene epoxide) 1:1790	140	3	1	81	8670
$Ni(PPh_3)Cl_2/PPh_3/Zn$[4]	TBAB	(propylene epoxide) 1:3570	120	2.5	1	99	3544
Yb-mesocate[5]	TBAB (0.75)	(styrene oxide) 1:1000	120	1	2.5	95	380
Helicate-1(Zn-Tb)[6]	TBAB (0.5)	(styrene oxide) 1:40000	120	1	1	67	26800
3 (This work**)**	TBAB (0.8)	(styrene oxide) 1:50000	120	1	2	86	21500

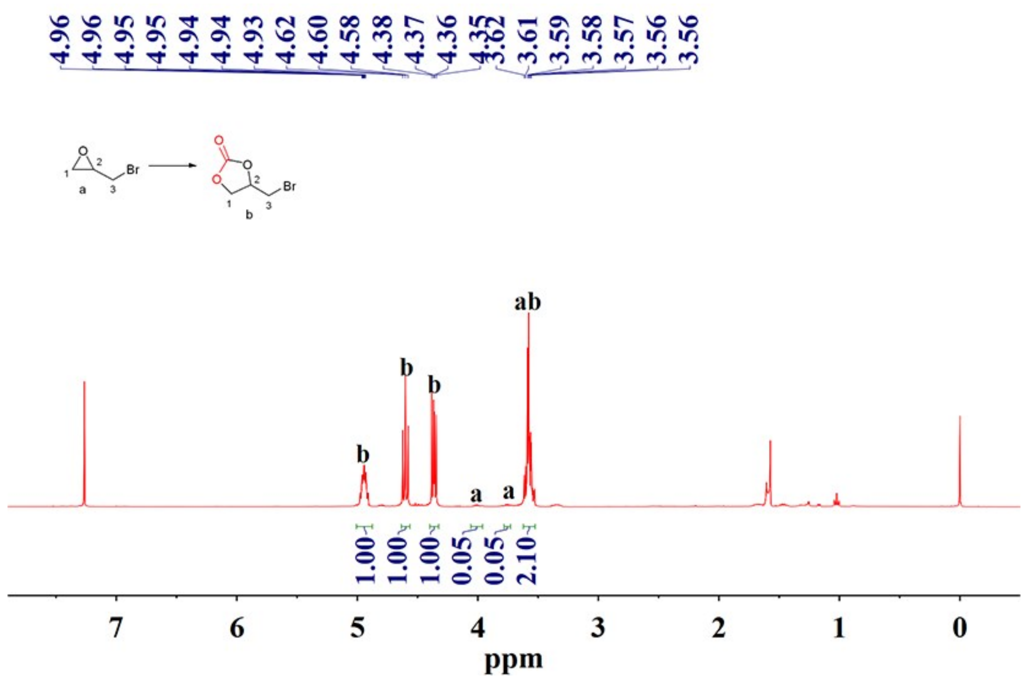
9. ^{1}H NMR spectra of substrates and products under 120 ℃[7-12]



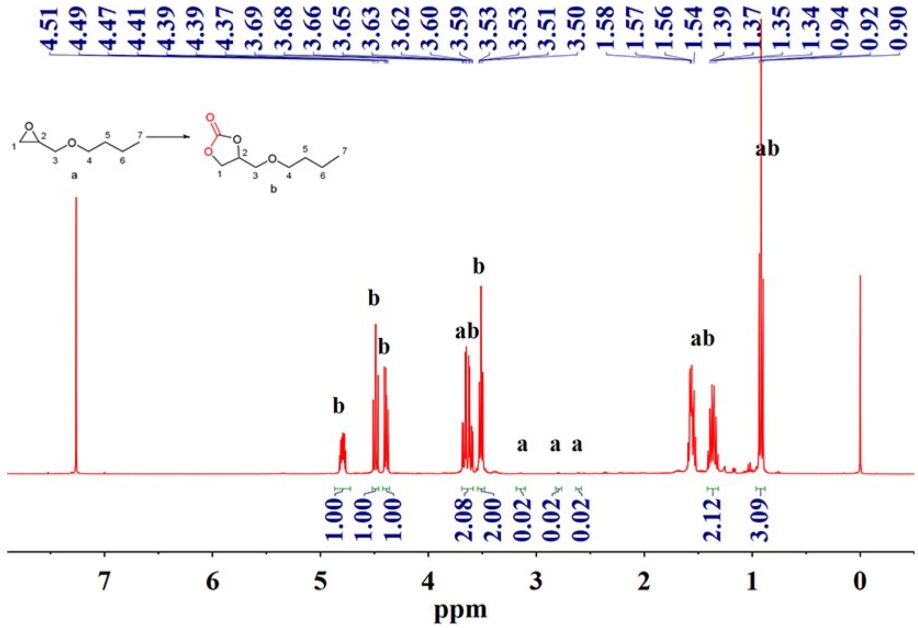
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.72 – 4.61 (m, 1H.), H^{b1} δ4.53 (t, *J* = 8.1 Hz, 1H), $H^{b1'}$ δ 4.09 (dd, *J* = 8.3, 7.0 Hz, 1H), H^{b3} δ 1.90 – 1.69 (m, 2H), H^{b4} δ 1.07 – 0.98 (m, 3H). $[(M+H)^+]$: 117.1 (calculated m/z 116.1).



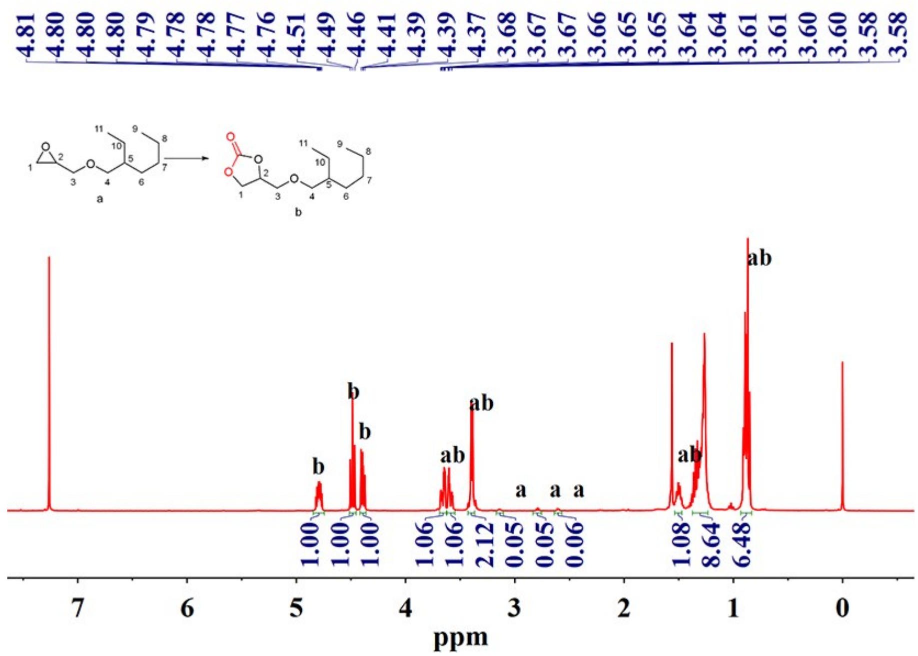
^{1}H NMR (400 MHz, $CDCl_3$): H^{b1} δ 4.13 (s, 2H), H^{b3} and H^{b4} δ 1.51 (s, 6H,). [$(M+H)^+$]: 117.0 (calculated m/z 116.1).



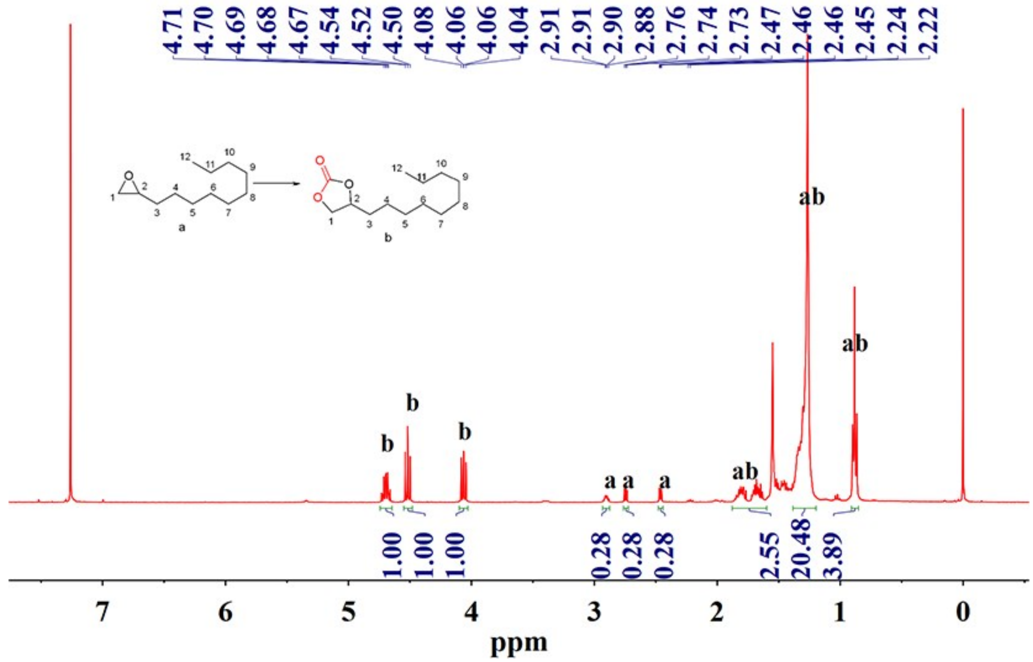
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.95 (ddt, 1H), H^{b2} δ4.60 (t, J = 8.5 Hz, 1H), H^{b1} δ 4.36 (dd, J = 8.8, 5.9 Hz, 1H), H^{b3} δ 3.80 – 3.28 (m, 2H). [$(M+H)^+$]: 180.8 (calculated m/z 179.9).



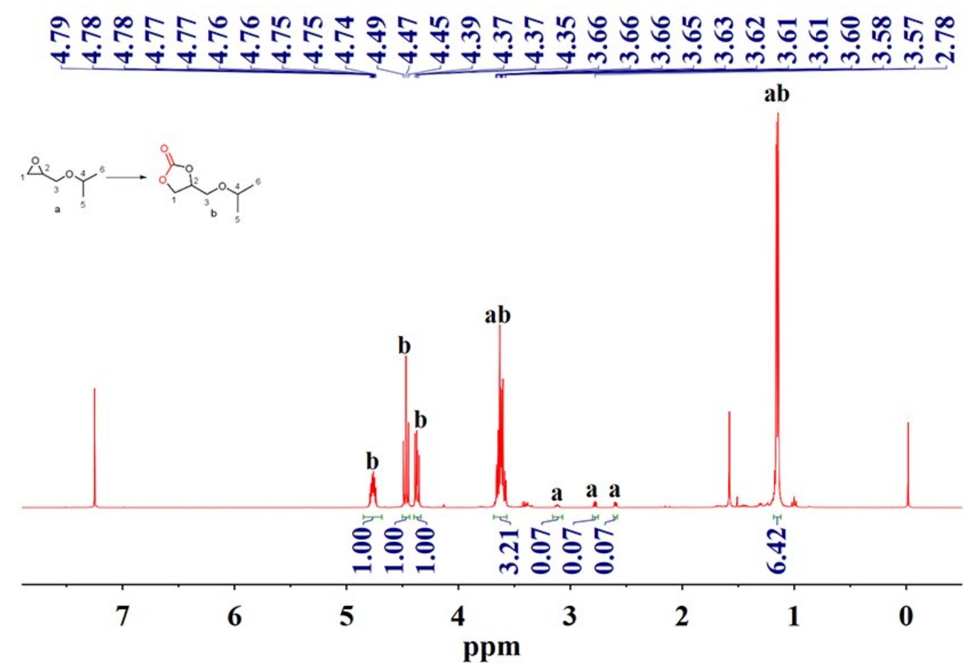
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ (ddt, *J* = 8.0, 6.0, 3.9 Hz, 1H), H^{b1} δ 4.49 (t, *J* = 8.4 Hz, 1H), H^{b1} δ 4.39 (dd, *J* = 8.3, 6.0 Hz, 1H), H^{b3} δ 3.64 (qd, *J* = 10.9, 3.9 Hz, 2H), H^{b4} 3.51 (t, 2H), H^{b3}1.44 – 1.29 (m, 2H), H^{b7} 0.92 (t, *J* = 7.4 Hz, 3H). Due to the influence of moisture in CDCl3, H^{b5} is not discussed. [$(M+H)^+$]: 175.0 (calculated m/z 174.2).



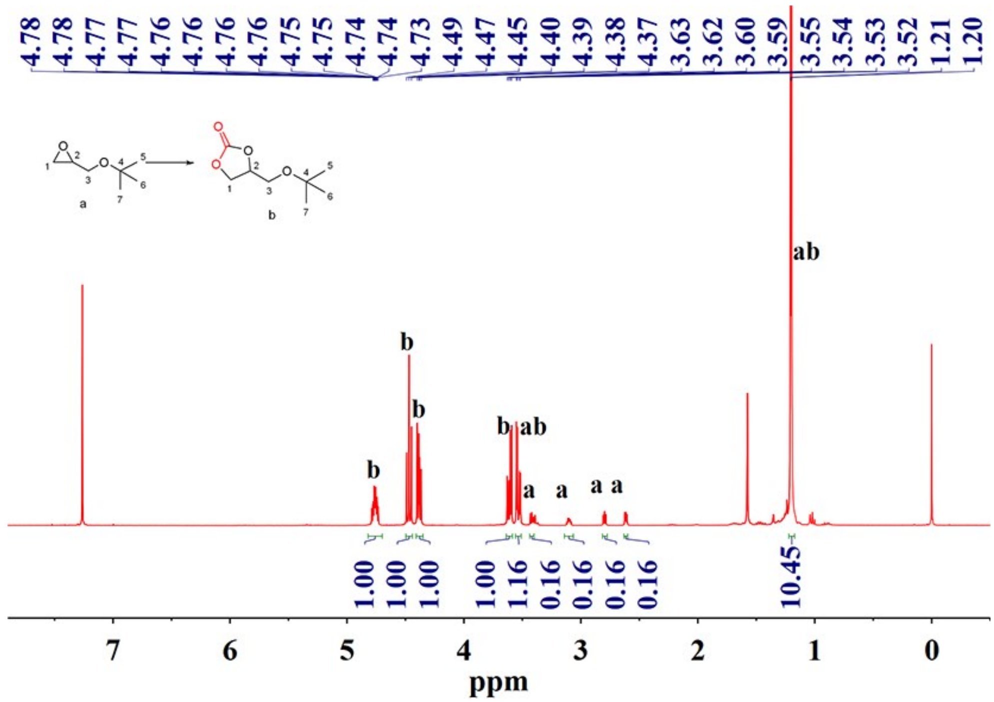
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.79 (ddt, *J* = 8.0, 6.0, 3.8 Hz, 1H), H^{b1} δ 4.49 (t, *J* = 8.3 Hz, 1H), H^{b1} δ 4.39 (dd, *J* = 8.2, 6.0 Hz, 1H), H^{b3} δ 3.62 (dddd, *J* = 26.9, 10.9, 3.7, 2.0 Hz, 2H), H^{b4} δ 3.40 (dd, 2H), 1.50 (dd, *J* = 11.8, 5.9 Hz, 1H), 1.42 – 1.19 (m, 8H), 0.88 (dt, *J* = 10.2, 7.0 Hz, 6H). [$(M+H)^+$]: 231.2 (calculated m/z 230.3).



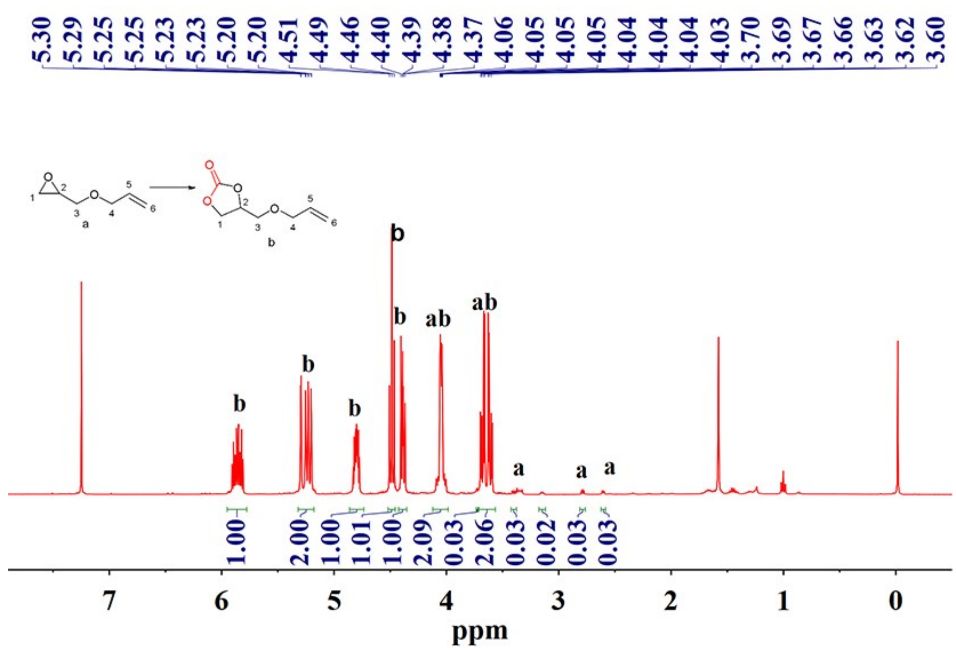
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.69 (ddt, 1H), H^{b1} δ 4.52 (t, J = 8.1 Hz, 1H), H^{b1} δ 4.06 (dd, J = 8.4, 7.3 Hz, 1H), H^{b2} δ 1.81 (ddd, J = 14.2, 10.4, 5.3 Hz, 1H), H^{b2} δ 1.68 (ddd, J = 14.2, 10.4, 5.3 Hz, 1H), 1.43 – 1.17 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H). $[(M+H)^+]$: 229.1 (calculated m/z 228.17).



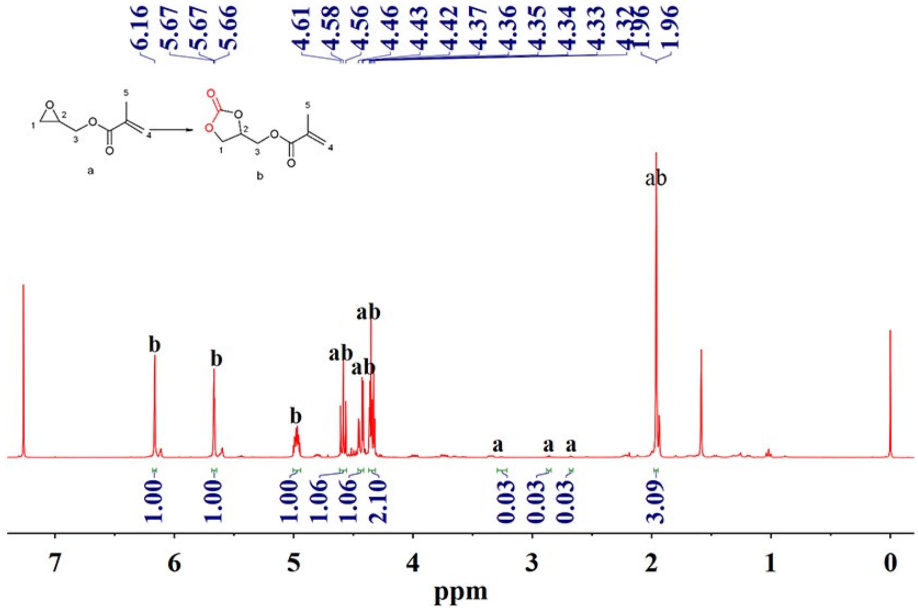
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.76 (ddt, J = 8.2, 6.0, 4.1 Hz, 1H), H^{b1} δ 4.47 (t, J = 8.3 Hz, 1H), H^{b1} δ 4.37 (dd, J = 8.3, 6.0 Hz, 1H), H^{b3} and H^{b4} δ 3.77 – 3.50 (m, 3H), 1.15 (d, J = 1.6 Hz, 6H). $[(M+H)^+]$: 162.0 (calculated m/z 161.1).



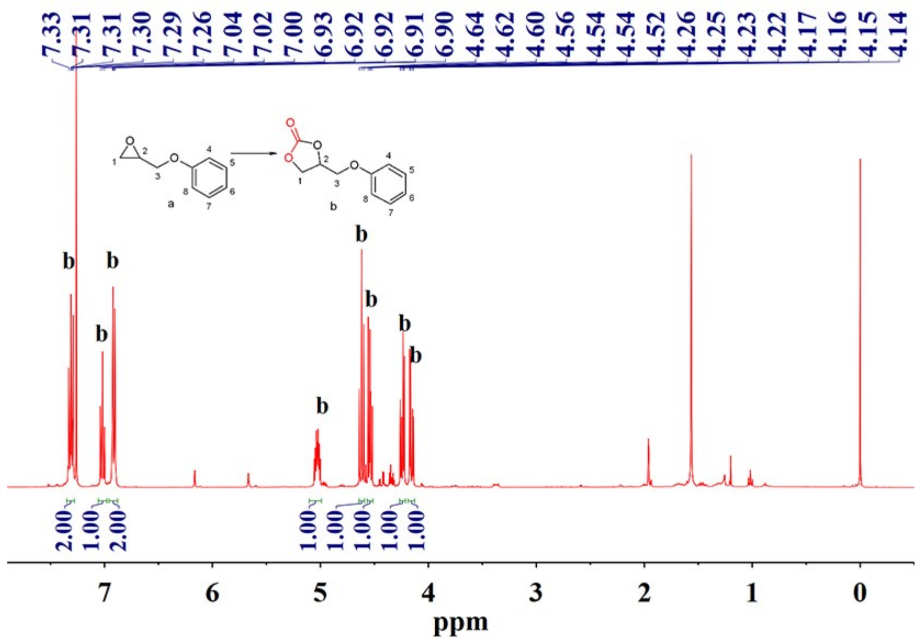
^{1}H NMR (400 MHz, $CDCl_3$): H^{b2} δ 4.76 (ddt, J = 8.3, 5.7, 4.7, 3.7 Hz, 1H), 4.47 (t, J = 8.3 Hz, 1H), 4.38 (dd, J = 8.3, 5.7 Hz, 1H), 3.57 (ddd, J = 13.8, 10.3, 4.2 Hz, 2H), 1.20 (s, 9H). [$(M+H)^+$]: 175.0 (calculated m/z 174.1).



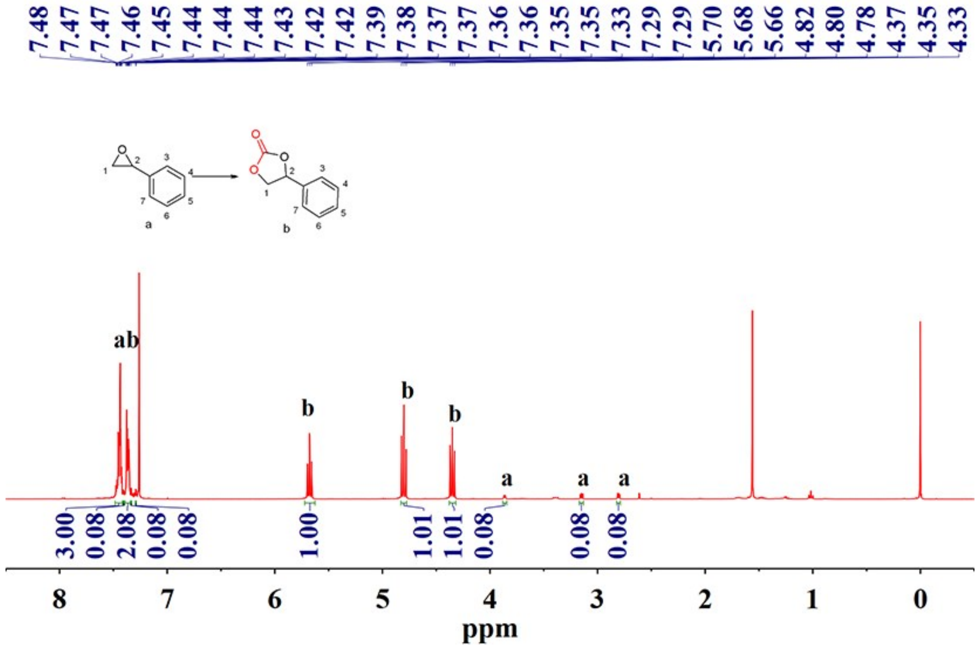
^{1}H NMR (400 MHz, $CDCl_3$): H^{b5} δ 5.97 – 5.77 (m, 1H), H^{b6} δ 5.38 – 5.15 (m, 2H), H^{b2} δ (ddt, J = 8.4, 6.0, 3.9 Hz, 1H), H^{b1} δ 4.49 (t, J = 8.4 Hz, 1H), H^{b1} δ 4.39 (dd, J = 8.4, 6.0 Hz, 1H), H^{b4} δ 4.09 – 3.96 (m, 2H), H^{b3} δ 3.64 (ddd, J = 26.7, 11.0, 3.9 Hz, 2H). [$(M+H)^+$]: 158.9 (calculated m/z 158.1)..



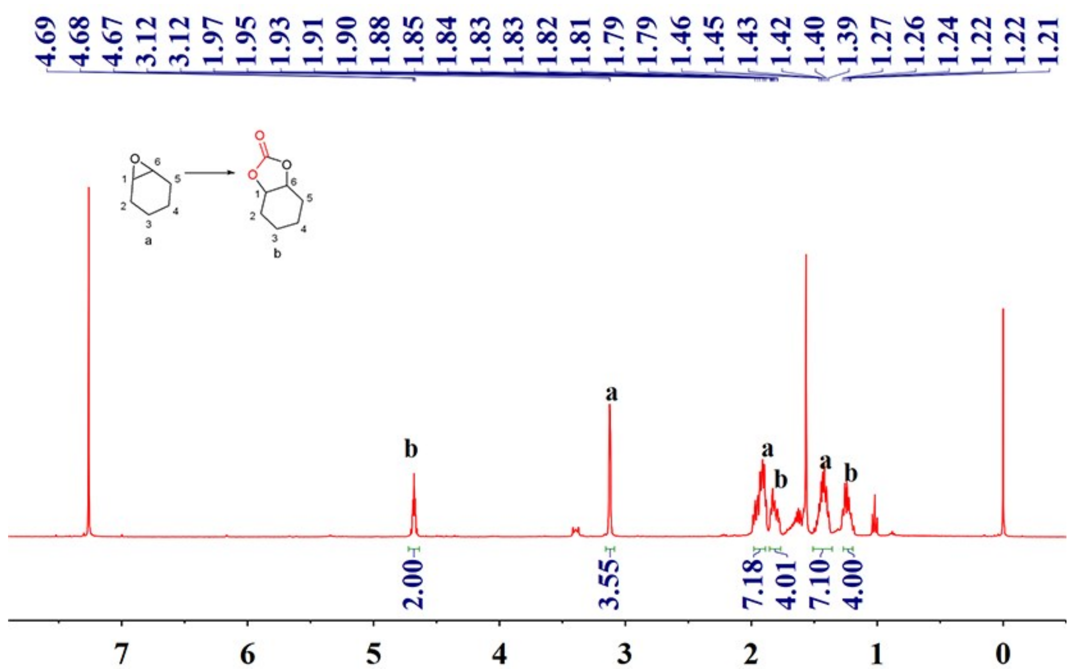
^{1}H NMR (400 MHz, $CDCl_3$): H^{b4} δ 6.16 (s, 1H), H^{b4} δ 5.68 – 5.64 (m, 1H), H^{b2} δ 4.98 (ddt, *J* = 8.0, 6.0, 3.9 Hz, 1H), H^{b1} δ 4.58 (t, *J* = 8.0 Hz, 1H), H^{b1} δ 4.36 (dd, *J* = 6.3, 2.4 Hz, 1H), H^{b3} δ 4.09 (dd, *J* = 8.0, 6.0 Hz, 1H), H^{b3} δ 4.33 (t, *J* = 4.8 Hz, 1H), H^{b5} δ 1.96 (d, *J* = 1.0 Hz, 3H). [$(M+H)^+$]: 186.9 (calculated m/z 186.1).



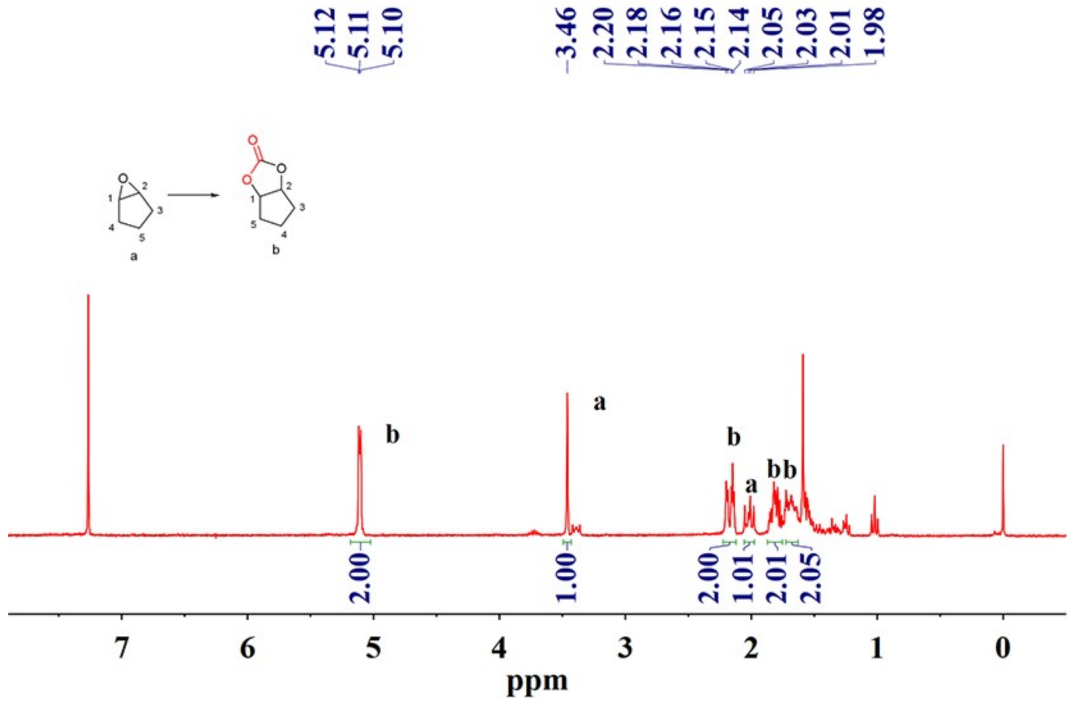
^{1}H NMR (400 MHz, $CDCl_3$): H^{b5} and H^{b7} δ 7.42 – 7.28 (m, 2H), H^{b6} δ7.10 – 6.99 (m, 1H), H^{b3} and H^{b8} δ 6.91 (dt, *J* = 9.2, 2.2 Hz, 1H), H^{b2} δ 5.02 (ddt, *J* = 8.4, 6.0, 4 Hz, 1H), H^{b1} δ 4.62 (t, *J* = 8.4 Hz, 1H), H^{b1} δ 4.54 (dd, *J* = 8.4, 6.0 Hz, 1H), H^{b3} δ 4.24 (dd, *J* = 10.5, 4.0 Hz, 1H), H^{b3} δ 4.16 (dd, *J* = 10.6, 3.6 Hz, 1H). [$(M+H)^+$]: 194.9 (calculated m/z 194.1).



^{1}H NMR (400 MHz, $CDCl_3$): H^{b3}, H^{b5} and H^{b7} δ 7.50 – 7.40 (m, 3H), H^{b4} and H^{b6} δ 7.40 – 7.32 (m, 2H), H^{b2} δ 5.68 (t, J = 8.4 Hz, 1H), H^{b1} δ 4.80 (t, J = 8.4 Hz, 1H), H^{b1} δ 4.36 (t, J = 8.4 Hz, 1H). [$(M+H)^+$]: 164.9 (calculated m/z 164.0).

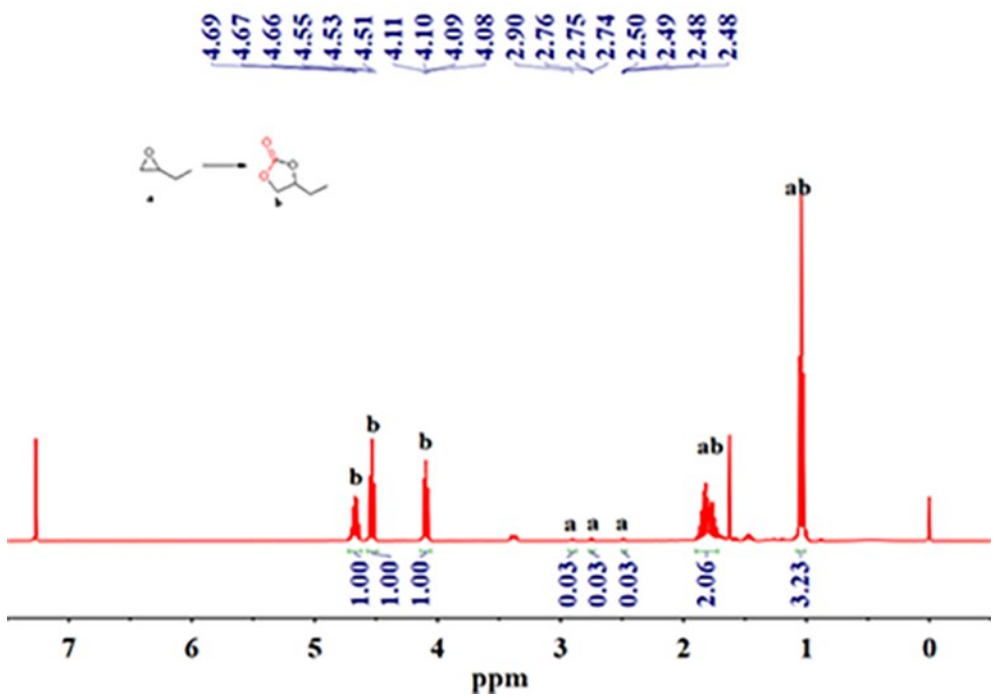


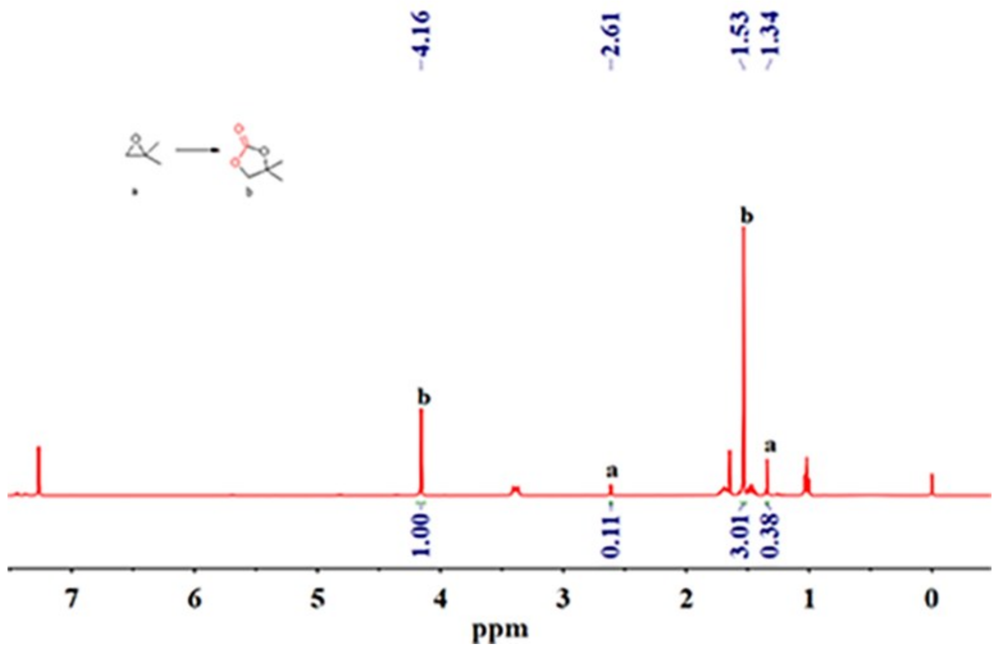
^{1}H NMR (400 MHz, $CDCl_3$): H^{b1} and H^{b6} δ 4.75 – 4.60 (m, 2H), H^{b3} and H^{b4} δ 1.93 (ddd, J = 19.6, 13.2, 6.3 Hz, 4H), H^{b2} and H^{b5} δ 1.50 – 1.37 (m, 4H). [$(M+H)^+$]: 143.0 (calculated m/z 142.1).



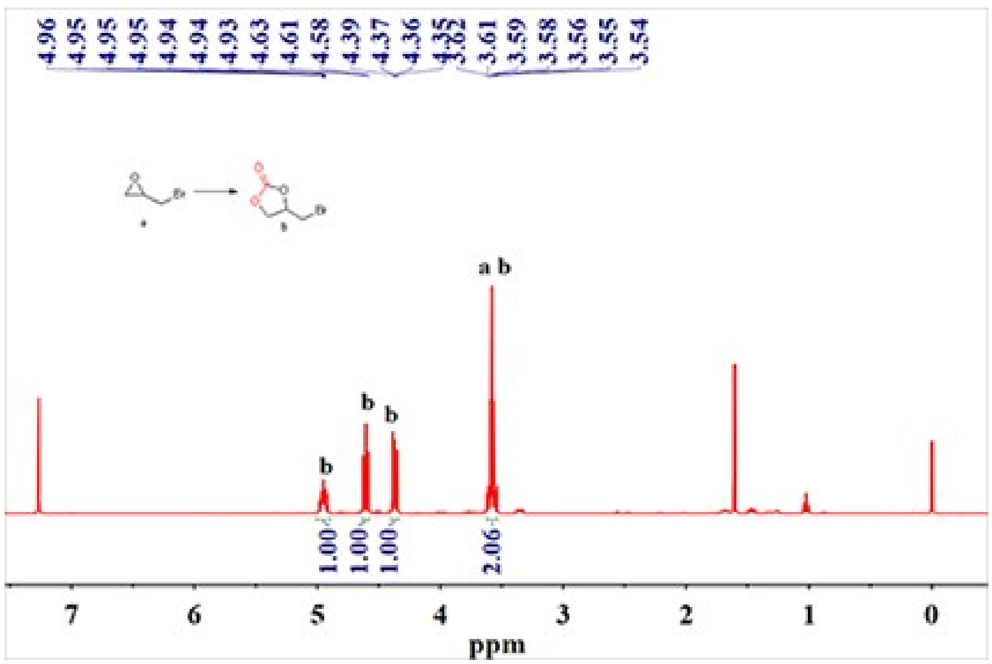
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.14 – 5.08 (m, 2H), 2.25 – 2.11 (m, 2H), 1.87 – 1.74 (m, 2H), 1.74 – 1.62 (m, 2H)。 Due to the influence of moisture in CDCl3, H^{b5} is not discussed. [$(M+H)^+$]: 129.0 (calculated m/z 128.1).

10. ^{1}H NMR spectra of substrates and products under 80 ℃[7-12]

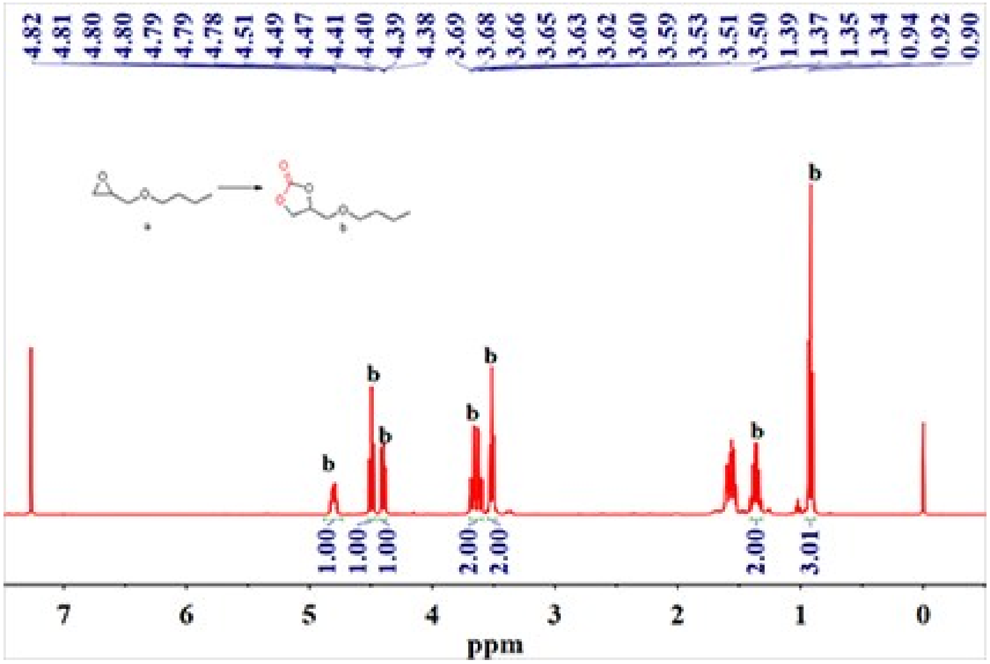


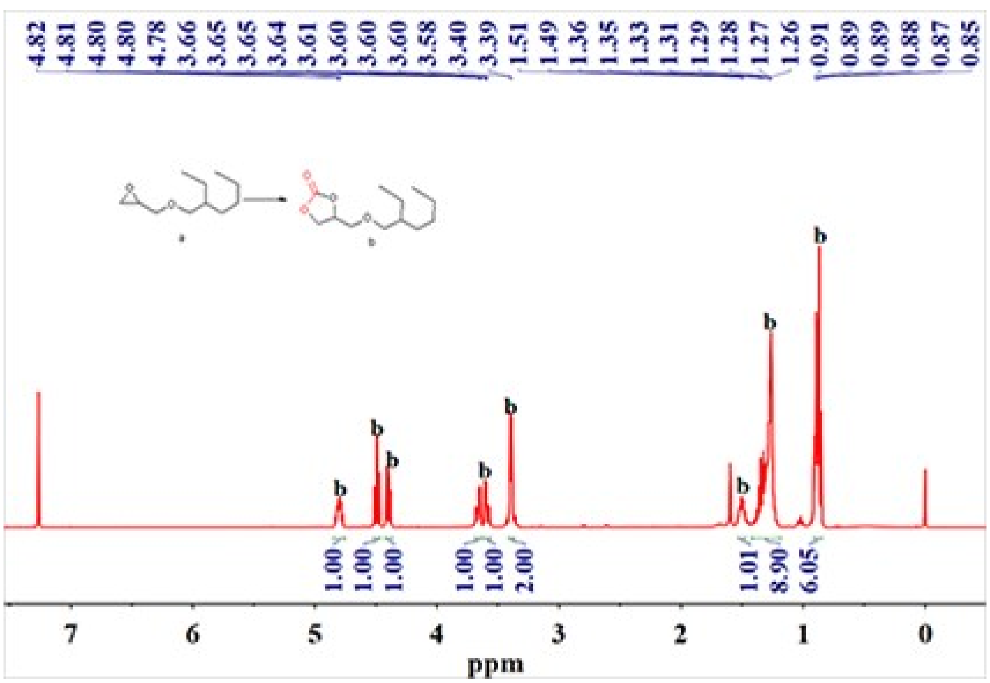


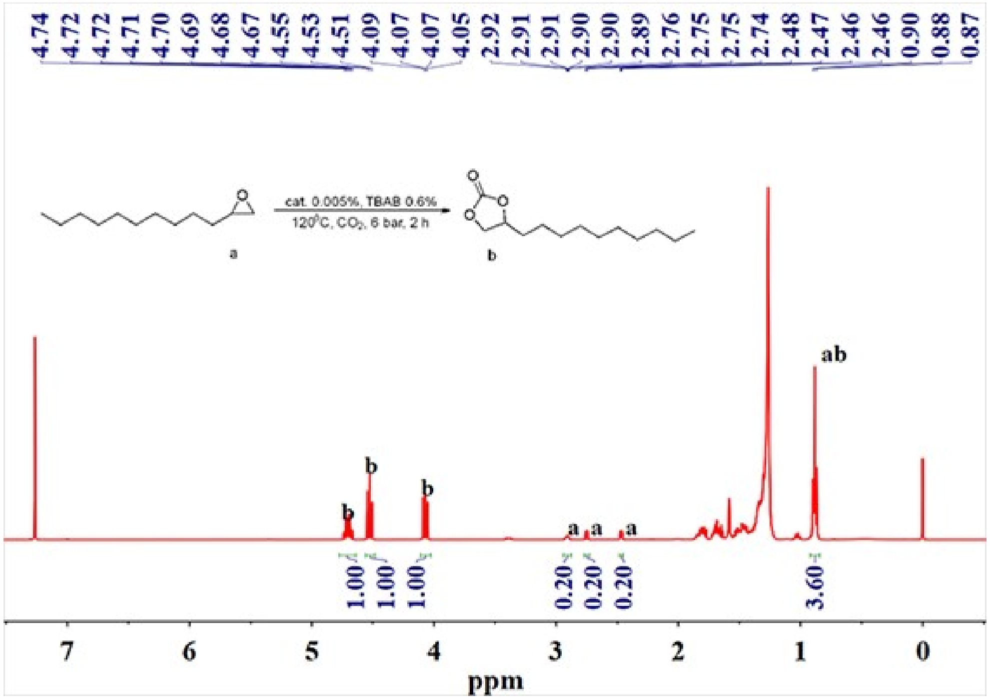
4.16
2.61
1.53
1.34
a
b
b
b
a
a
1.00
0.11
3.01
0.38
7
6
5
4
3
2
1
0
ppm

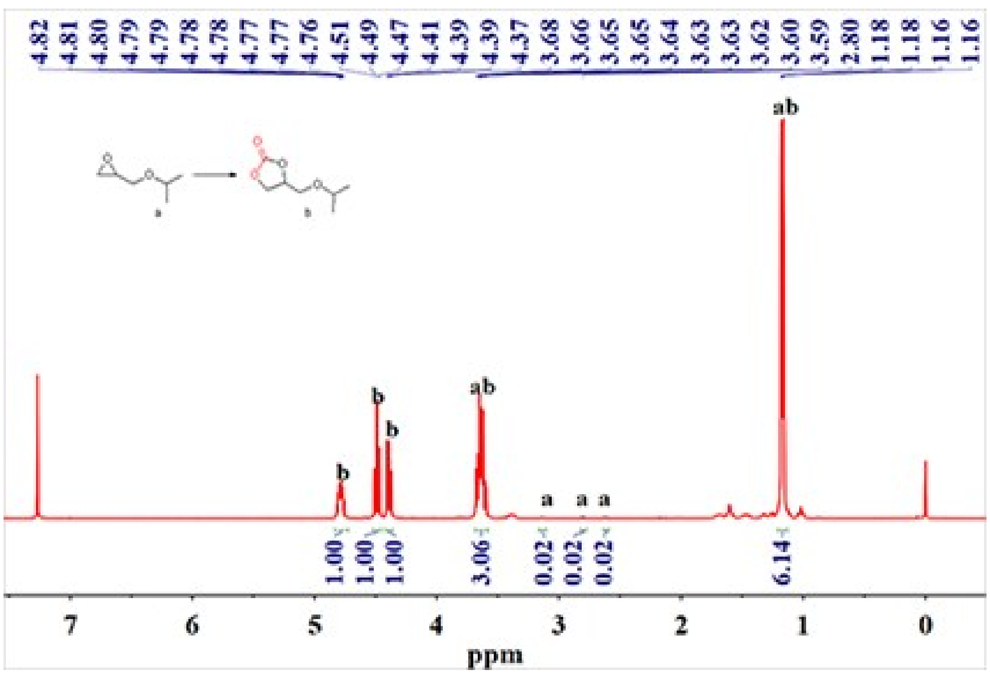


4.96
4.95
4.95
4.95
4.94
4.94
4.93
4.63
4.61
4.58
4.39
4.37
4.36
4.35
3.62
3.61
3.59
3.58
3.56
3.55
3.54
a
b
a b
b
b
b
1.00
1.00
1.00
2.06
7
6
5
4
3
2
1
0
ppm


4.82 4.81 4.80 4.80 4.79 4.79 4.78 4.51 4.49 4.47 4.41 4.40 4.39 4.38 3.69 3.68 3.66 3.65 3.63 3.62 3.60 3.59 3.53 3.51 3.50 1.39 1.37 1.35 1.34 0.94 0.92 0.90
a
b
1.00 1.00 1.00 2.00 2.00 2.00 3.01
7 6 5 4 3 2 1 0
ppm


4.82 4.81 4.80 4.80 4.78 3.66 3.65 3.65 3.64 3.61 3.60 3.60 3.60 3.58 3.40 3.39 1.51 1.49 1.36 1.35 1.33 1.31 1.29 1.28 1.27 1.26 0.91 0.89 0.89 0.88 0.87 0.85
a
b
1.00 1.00 1.00 1.00 1.00 2.00 1.01 8.90 6.05
7 6 5 4 3 2 1 0
ppm


4.74 4.72 4.72 4.71 4.70 4.69 4.68 4.67 4.55 4.53 4.51 4.09 4.07 4.07 4.05 2.92 2.91 2.91 2.90 2.90 2.89 2.76 2.75 2.75 2.74 2.48 2.47 2.46 2.46 0.90 0.88 0.87
cat. 0.005%, TBAB 0.6%
120°C, CO_2, 6 bar, 2 h
a
b
ab
1.00 1.00 1.00 0.20 0.20 0.20 3.60
7 6 5 4 3 2 1 0
ppm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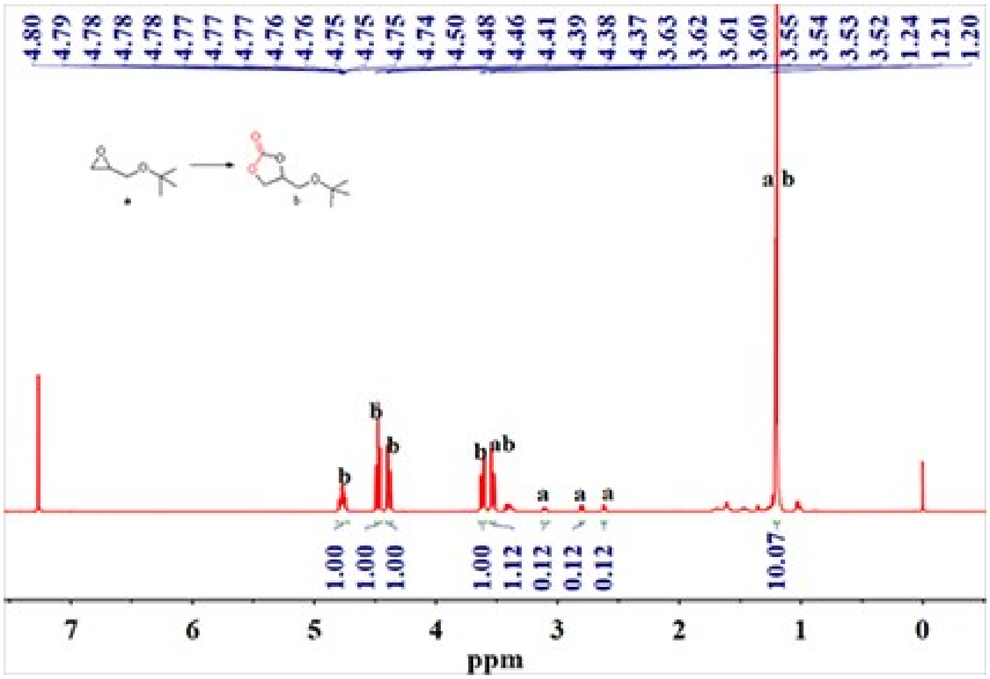
a
b
ab
1.00 1.00 1.00 3.06 0.02 0.02 0.02 6.14
7 6 5 4 3 2 1 0
ppm


4.80
4.79
4.78
4.78
4.78
4.77
4.77
4.77
4.76
4.76
4.75
4.75
4.75
4.74
4.50
4.48
4.46
4.41
4.39
4.38
4.37
3.63
3.62
3.61
3.60
3.55
3.54
3.53
3.52
1.24
1.21
1.20
a
b
a b
b
b
b
b
ab
a
a
a
1.00
1.00
1.00
1.00
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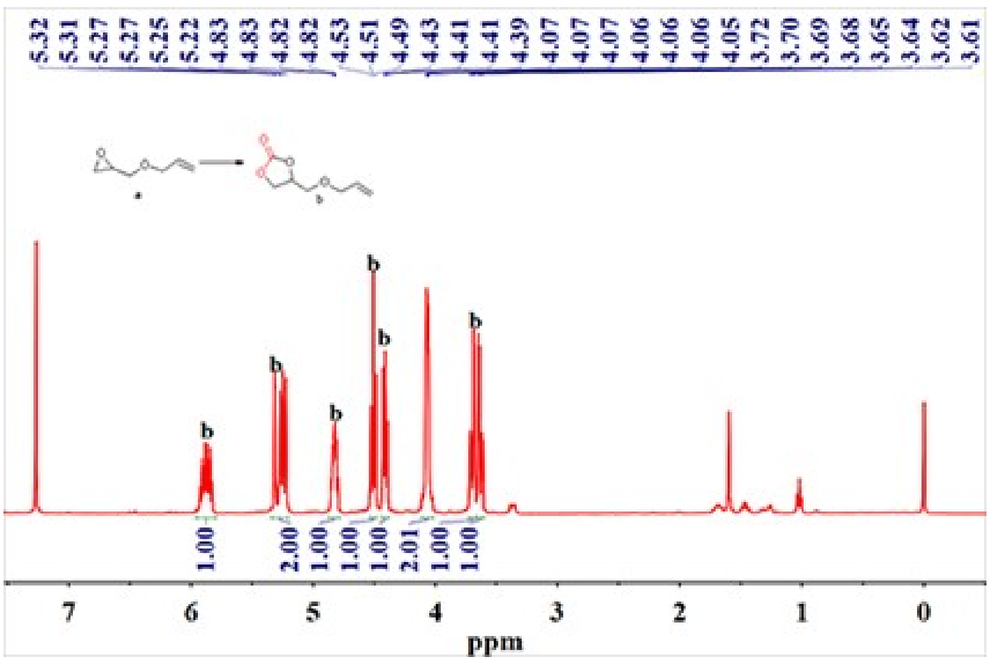
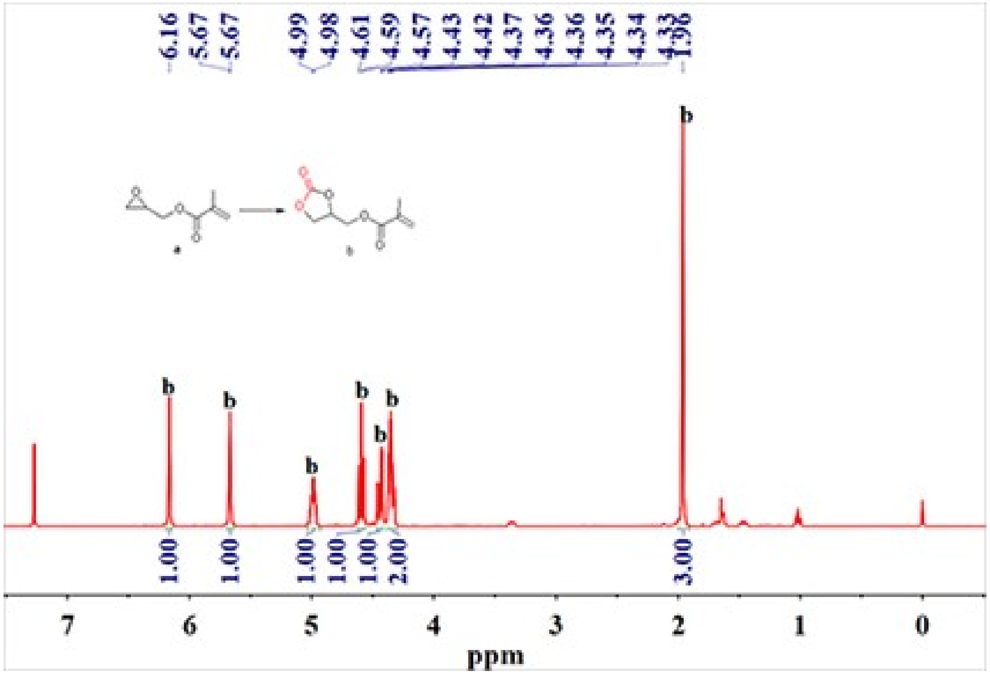
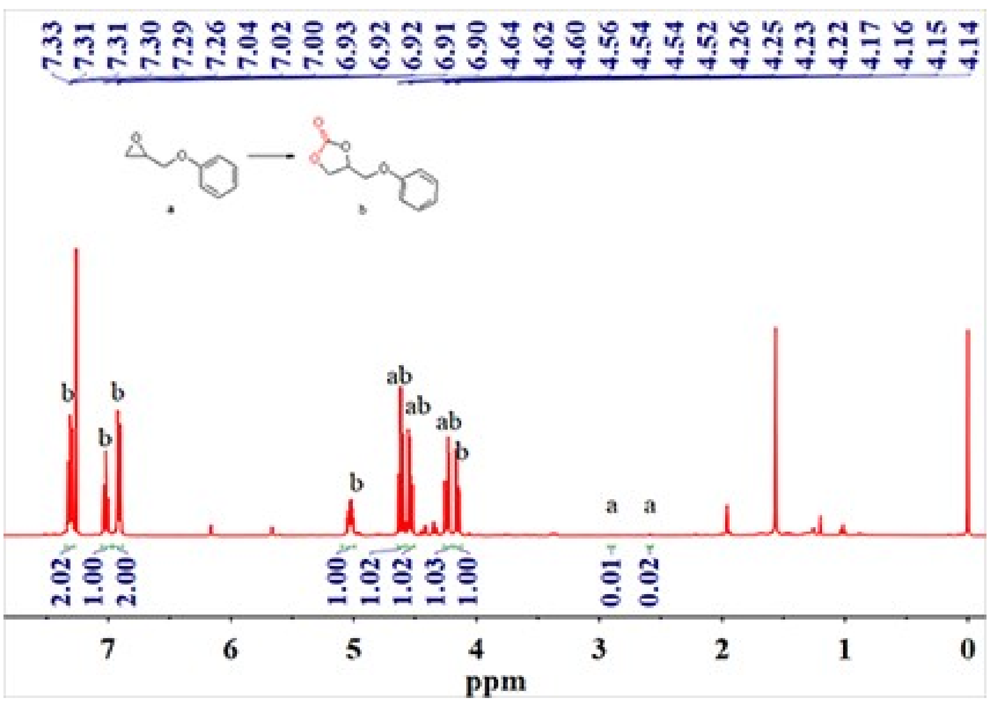
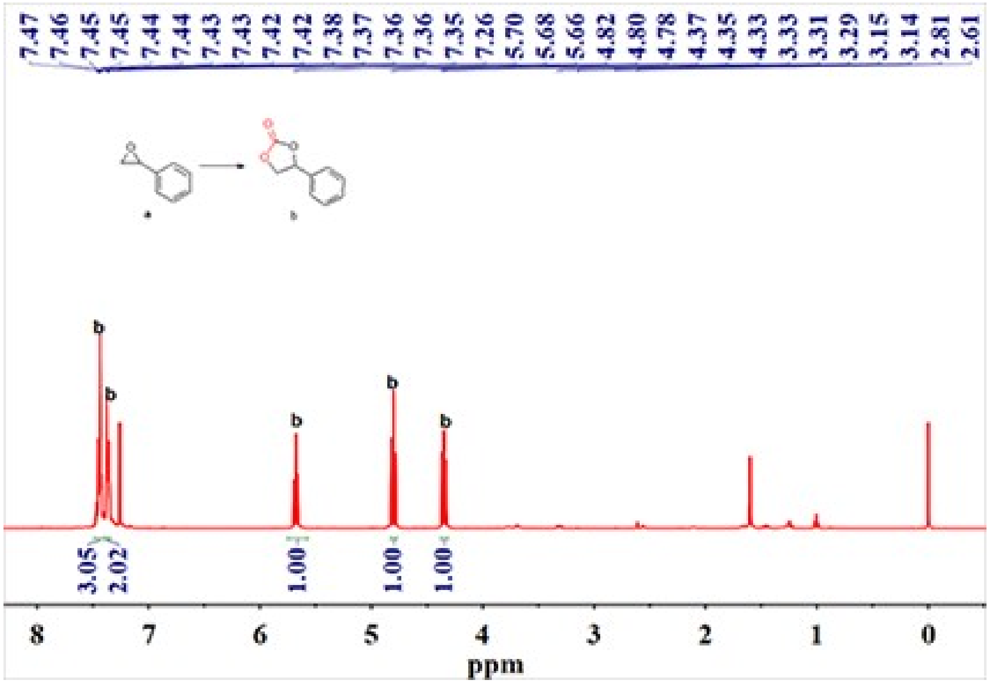
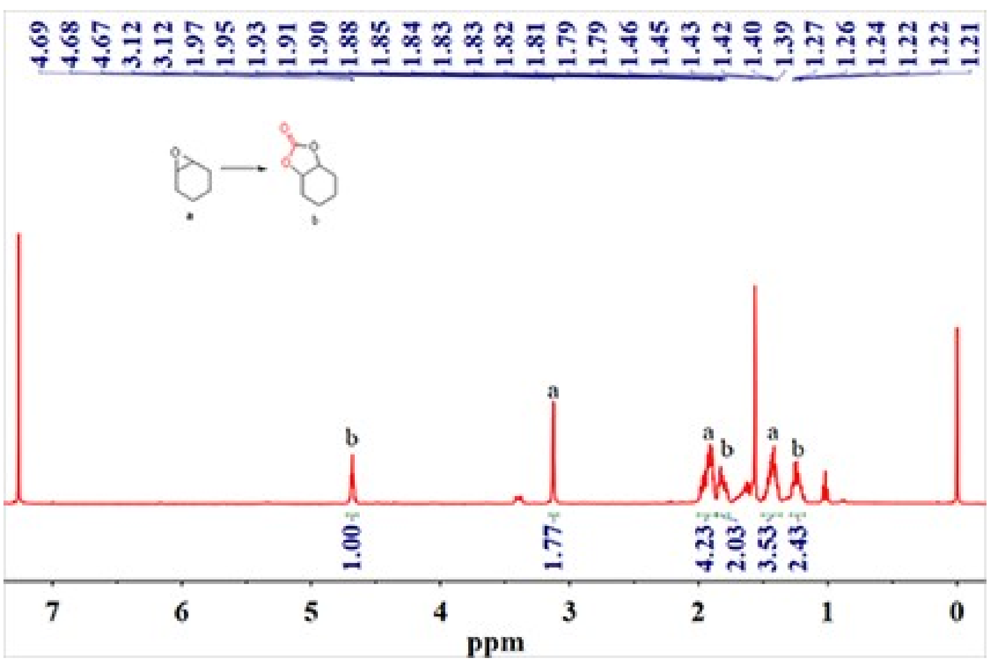
0.12
0.12
0.12
10.07
7
6
5
4
3
2
1
0
ppm

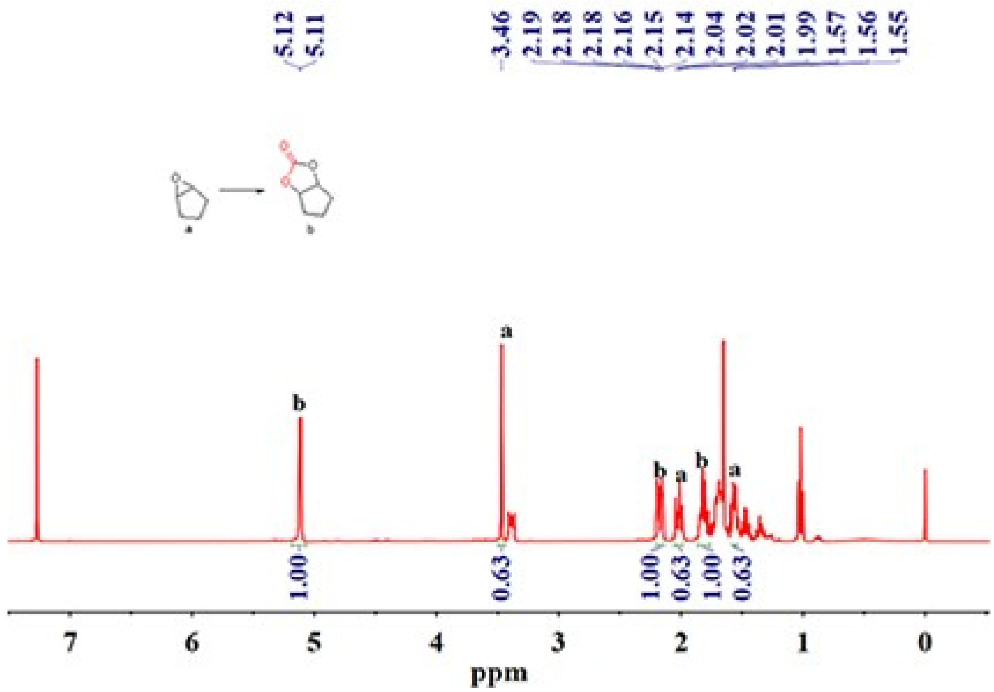

5.32
5.31
5.27
5.27
5.25
5.22
4.83
4.83
4.82
4.82
4.53
4.51
4.49
4.43
4.41
4.41
4.39
4.07
4.07
4.07
4.06
4.06
4.06
4.05
3.72
3.70
3.69
3.68
3.65
3.64
3.62
3.61
a
b
b
b
b
b
b
b
1.00
2.00
1.00
1.00
1.00
2.01
1.00
1.00
7
6
5
4
3
2
1
0
ppm


6.16
5.67
5.67
4.99
4.98
4.61
4.59
4.57
4.43
4.42
4.37
4.36
4.36
4.35
4.34
4.33
1.96
a
b
1.00
1.00
1.00
1.00
1.00
2.00
3.00
ppm


7.33
7.31
7.31
7.30
7.29
7.26
7.04
7.02
7.00
6.93
6.92
6.92
6.91
6.90
4.64
4.62
4.60
4.56
4.54
4.54
4.52
4.26
4.25
4.23
4.22
4.17
4.16
4.15
4.14
a
b
ab
2.02
1.00
2.00
1.00
1.02
1.02
1.03
1.00
0.01
0.02
ppm


7.47 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.38 7.37 7.36 7.36 7.35 7.26 5.70 5.68 5.66 4.82 4.80 4.78 4.37 4.35 4.33 3.33 3.31 3.29 3.15 3.14 2.81 2.61
b
b
b
b
b
3.05
2.02
1.00
1.00
1.00
8 7 6 5 4 3 2 1 0
ppm


4.69 4.68 4.67 3.12 3.12 1.97 1.95 1.93 1.91 1.90 1.88 1.85 1.84 1.83 1.83 1.82 1.81 1.79 1.79 1.46 1.45 1.43 1.42 1.40 1.39 1.27 1.26 1.24 1.22 1.22 1.21
b
a
a
b
a
b
1.00
1.77
4.23
2.03
3.53
2.43
7 6 5 4 3 2 1 0
ppm



11. Notes and references

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