Supplementary Information (SI) for CrystEngComm.

Two novel tetranuclear Yb(III)-based compounds for highly efficient conversion of CO_2 to cyclic carbonates

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1. Experimental section

1.1 Materials and methods

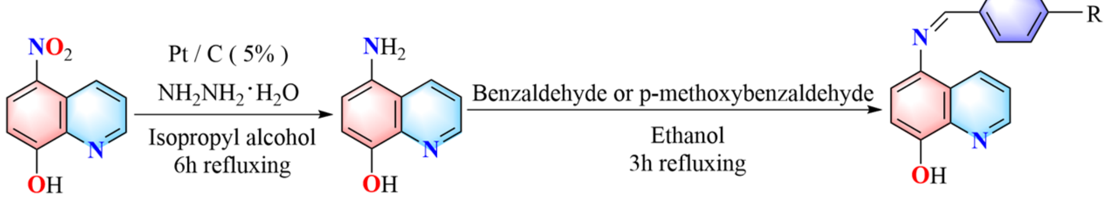
5-amino-8-hydroxylquinoline, benzaldehyde, 4-Methoxybenzaldehyde, and Ytterbium nitrate hexahydrate ($Yb(NO_3)_3 \cdot 6H_2O$) were provided by the Energy Chemical Co. Ltd. Methanol, formic acid, acetonitrile, dichloromethane, and dibenzoyl methane were obtained by the Beijing Chemical Reagent Company. The two Schiff base ligands (HL1 and HL2) were prepared by a previously published method [1]. $Yb(dbm)_3 \cdot 2H_2O$ was also prepared using the methods described in reference [2].

1.2 Instruments

UV test (UV-VIS) using UV-2450 UV-visible spectrophotometer, scanning range of 200-800 nm; American EA1112 element analyzer was used for element molecules. Thermal analysis (TG-DTA) adopts Du Pont 1090B thermal analyzer with temperature rise rate of 10℃/min. The PXRD data were obtained by the Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.54056 A) at a speed of 10 min^{-1} and a range of 2θ = 5-50°.

1.3 Preparations of the ligand

Synthesis of ligand (HL). 5-amino-8-hydroxylquinoline (20 mmol) and [1,1'-biphenyl]-4-carbaldehyde (20 mmol,3.644g) were added to 50 ml of methanol and five drops of formic acid were added as catalyst (Scheme S1). The resulting product was then heated and refluxed at 70 ° C for six hours, filtered and washed three times with a small amount of methanol, and dried in vacuum at 70 ° C for three hours. Finally, the green solid of Schiff base ligand 5-(4-phenyl-benzylidene)-8-hydroxyquinoline (HL) (yield 2.1 g, 80.2 %) was obtained. Elemental analysis (%) Calcd for HL: $C_{22}H_{17}O_1N_2$ (F w = 325): C, 81.23; H, 5.23; N, 8.62. Found: C, 81.20; H, 5.21 3; N, 8.59.



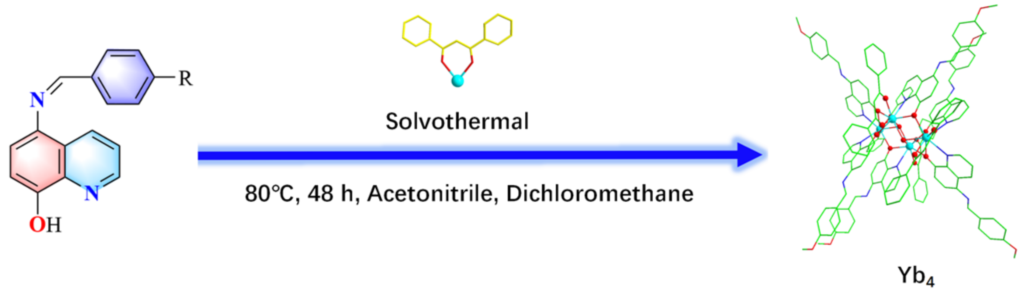
Scheme S1. The synthesis of HL1 (-R = $-OCH_3$) and HL2 (-R = -H).

1.4 Preparations of compounds 1 and 2

The two Yb_4 compounds (**1** and **2**) have been synthesized according to the following methods (Scheme S2). $Yb(dbm)_3 \cdot 2H_2O$ (0.025 mmol) (**1**) was dissolved in a mixture of 6 mL acetonitrile and 5 mL dichloromethane, and then the prepared Schiff base ligands (HL1 or HL2) (0.025 mmol) were added to the above mixed solution. The mixed solution was oscillated under ultrasound for about half an hour and then transferred to a vial, where it was reacted at 80 ° C for 48 hours to produce light yellow strip crystals.

$[Yb_4(\mu_3\text{-}O)_2(dbm)_4(L1)_6]\cdot 2CH_2Cl_2\cdot 6CH_3CN$ (1). Yield: 53 % (based on $Yb(dbm)_3 \cdot 2H_2O$). Elemental analysis (%) calcd for $C_{176}H_{144}Cl_4N_{18}O_{22}Yb_4$ (F_w = 3697.04): C, 57.13; H, 3.90; N, 6.82. Found: C, 57.09; H, 3.87; N, 6.86. IR (KBr, cm^{-1}; Fig. S1): 3630(w), 3040(w), 2865(w), 2570(w), 2330(w), 2160(w), 2050(w), 1600(m), 1560(w), 1500(m), 1460(m), 1380(s), 1320(s), 1261(w), 1170(w), 1100(m), 1060(w), 1010(w), 964(w), 921(w), 876(w), 842(m), 779(s), 715(s), 629(s), 526(m).

$[Yb_4(\mu_3\text{-}O)_2(dbm)_4(L2)_6]$ (2). Yield: 49 % (based on $Yb(dbm)_3 \cdot 2H_2O$). Elemental analysis (%) calcd for $C_{156}H_{110}N_{12}O_{16}Yb_4$ (F_w = 3100.72): C, 60.37; H, 3.55; N, 5.42. Found: C, 60.44; H, 3.49; N, 5.46. IR (KBr, cm^{-1}; Fig. S1): 3633(w), 2960(w), 2908(w), 2853(w), 2785(w), 2451(w), 2284(w), 2118(w), 1886(w), 1681(w), 1590(s), 1508(m), 1459(w), 1400(s), 1315(m), 1254(s), 1184(w), 1081(m), 1007(m), 912(m), 825(m), 771(m), 728(w), 614(m), 525(m), 438(w).



Scheme S2. The synthesis of two Yb_4 compounds.

Table S1 Crystallographic data and structures refinements for **1** and **2**.

	1	**2**
Formula	$C_{176}H_{144}Cl_4N_{18}O_{22}Yb_4$	$C_{156}H_{110}N_{12}O_{16}Yb_4$
Mr (g mol^{-1})	3697.04	3100.72
T (K)	150.00	150.00
cryst syst	monoclinic	triclinic
Space group	$P2_1/n$	P-1
a (Å)	21.4927(3)	14.8563(9)
b (Å)	15.5992(2)	15.2810(8)
c (Å)	25.5168(4)	16.5287(12)
α (°)	90	76.367(2)
β (°)	95.3090(10)	85.738(2)
γ (°)	90	66.875(2)
V (Å^3)	8518.3(2)	3352.9(4)
Z	2	1
cryst size (mm^3)	0.2 × 0.15 × 0.1	0.2 × 0.15 × 0.1
D_c (g cm^{-3})	1.441	1.536
μ (mm^{-1})	5.040	2.834
limiting indices	$-25 \leq h \leq 26$, $-19 \leq k \leq 14$, $-31 \leq l \leq 28$	$-18 \leq h \leq 18$, $-19 \leq k \leq 19$, $-20 \leq l \leq 20$
reflns collected	69197	183131
unique	17460	13817
Params	1015	783
R_{int}	0.0477	0.1026
GOF on F^2	1.065	1.060
R_1, wR_2 [$I > 2\sigma(I)$]	0.0718, 0.2059	0.0529, 0.1306
R_1, wR_2 (all data)	0.0784, 0.2127	0.0735, 0.1460

Table S2 The SHAPE 2.0 soft analysis of the Yb(III) ions in compound **1**.

Cluster **1**	SAPR-8	BTPR-8	JBTPR-8	TDD-8	JSD-8
Yb1	0.981	1.633	2.132	2.432	4.617
Cluster **1**	SAPR-8	TDD-8	BTPR-8	JBTPR-8	JSD-8
Yb2	0.889	2.049	2.227	2.937	4.816

SAPR-8 = Square antiprism; **BTPR-8** = Biaugmented trigonal prism; **JBTPR-8** = Biaugmented trigonal prism J50; **TDD-8=** Triangular dodecahedron; **JSD-8** = Snub disphenoid J84.

Table S3 The ICP results of compound **1** after recycling the cycloaddition of epoxides with CO_2 (filter liquor).

Compound **1**	Yb(III)
1 after catalytic recycling (filter liquor)	0.4 %

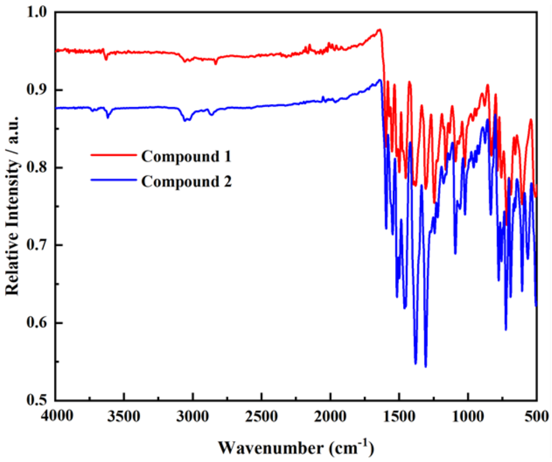


Fig. S1 The IR spectra of **1** and **2**.

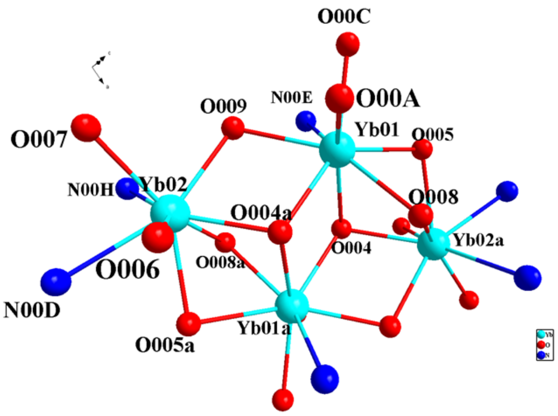


Fig. S2 The coordinate atom labels of central Yb1(III) and Yb2(III) ions in **1**.

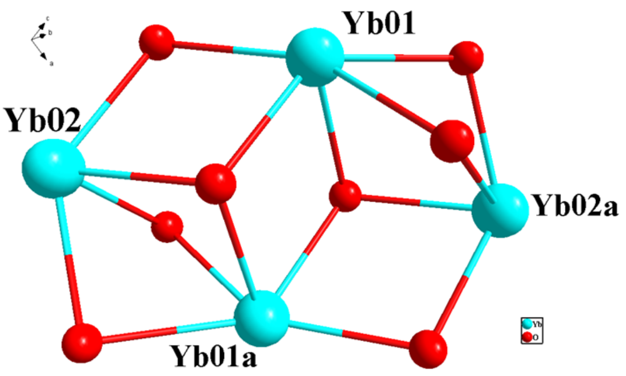


Fig. S3 The Yb_4 core bridged by six μ_2-O and two μ_3-O in **1.**

Fig. S4 PXRD patterns for **1** (a) and **2** (b).

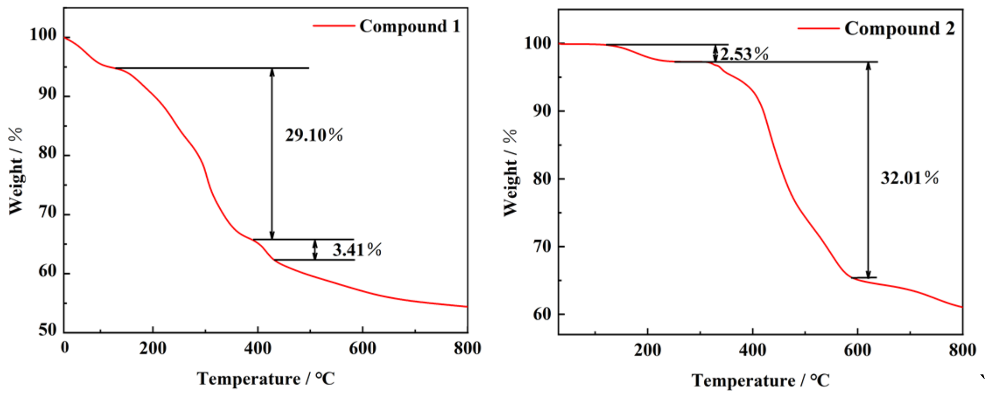


Fig. S5 The TGA curves of compounds **1** and **2**.

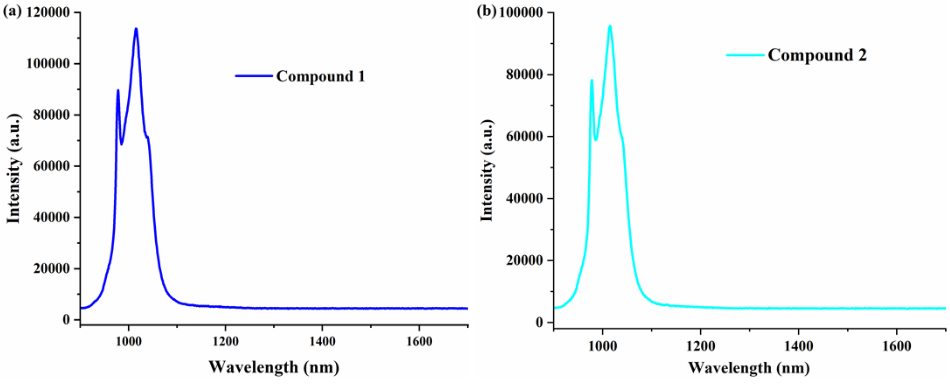


Fig. S6 The NIR luminescence for compounds **1** (a) and **2** (b) in CH_3OH at room temperature (λ_{ex} = 398 nm).

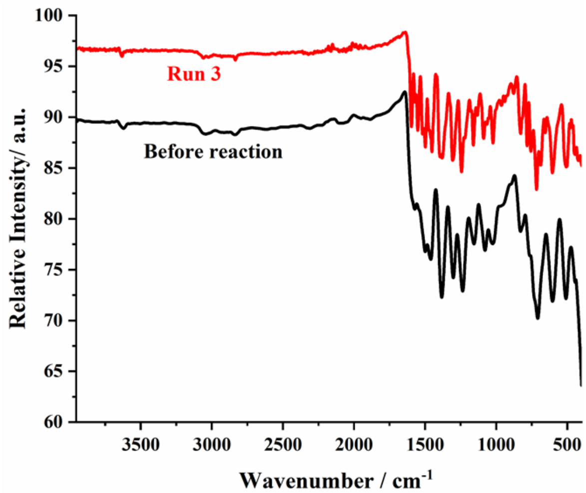


Fig. S7 The IR of catalyst **1** after three times catalytic reaction for the cycloaddition of epoxides with CO_2.

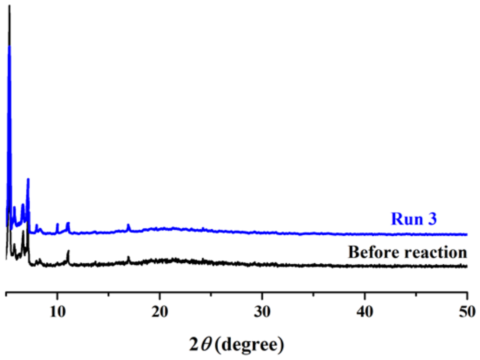


Fig. S8 The PXRD of catalyst **1** after three times catalytic reaction for the cycloaddition of epoxides with CO_2.

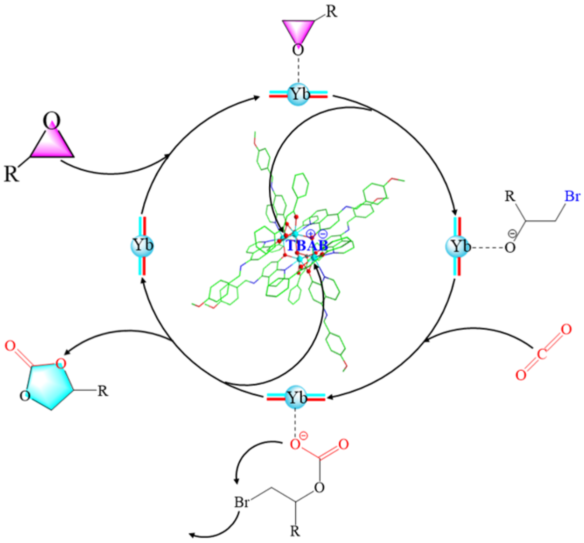
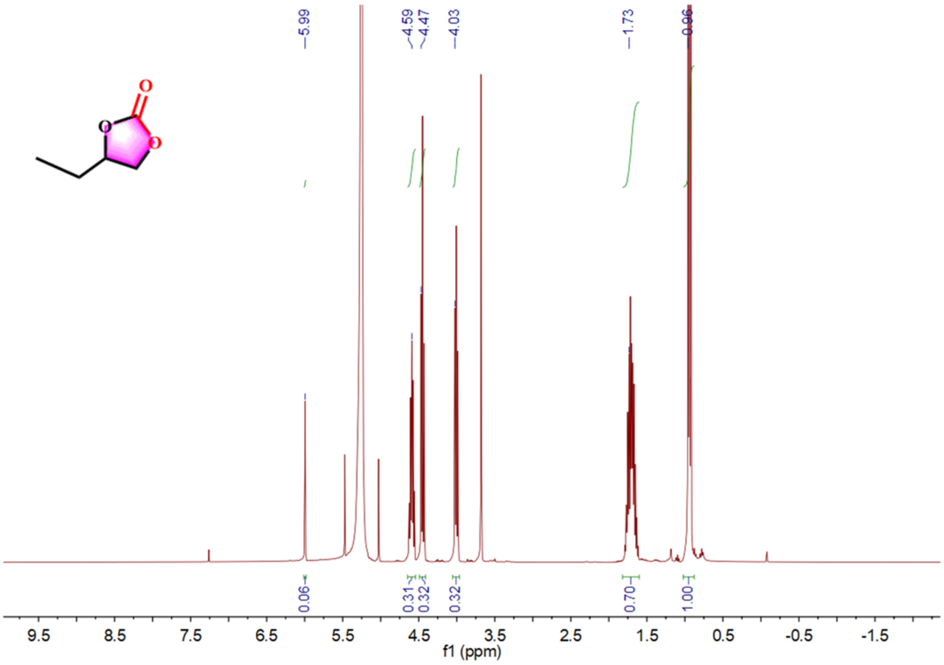
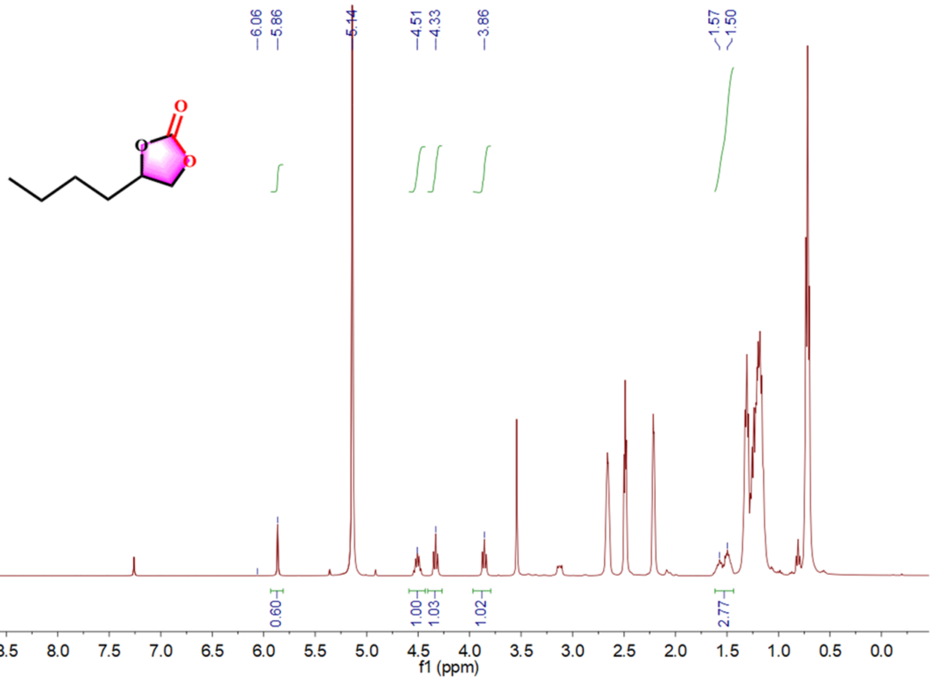
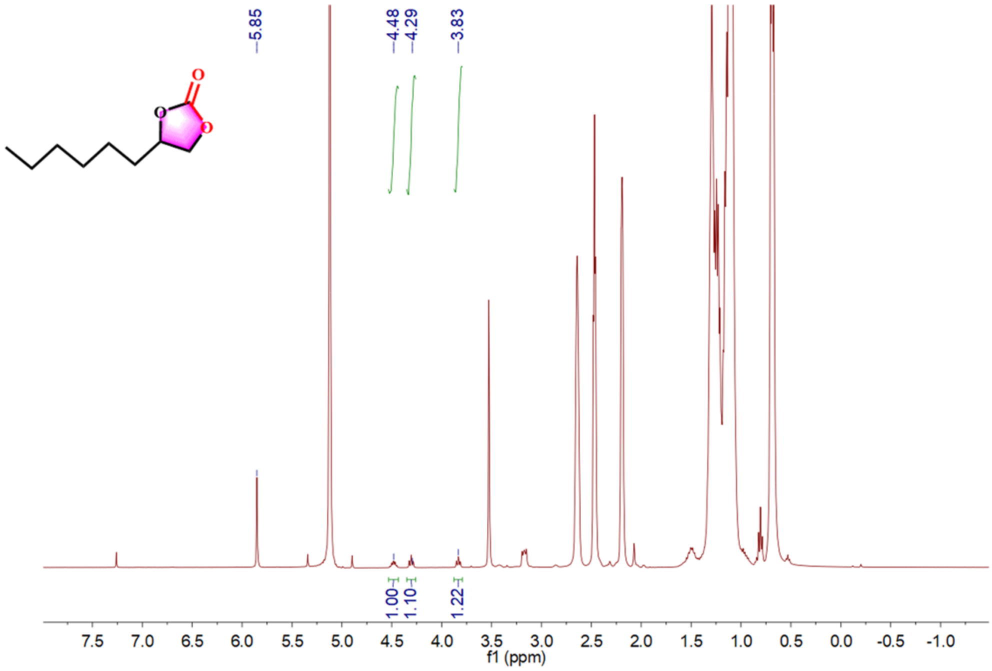


Fig. S9. Tentative reaction mechanism catalyzed by the Yb_4 clusters **1** and **2**.

^{1}H-NMR Spectrum for cyclic carbonates



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4.29
3.83
1.00
1.10
1.22
O
O
O
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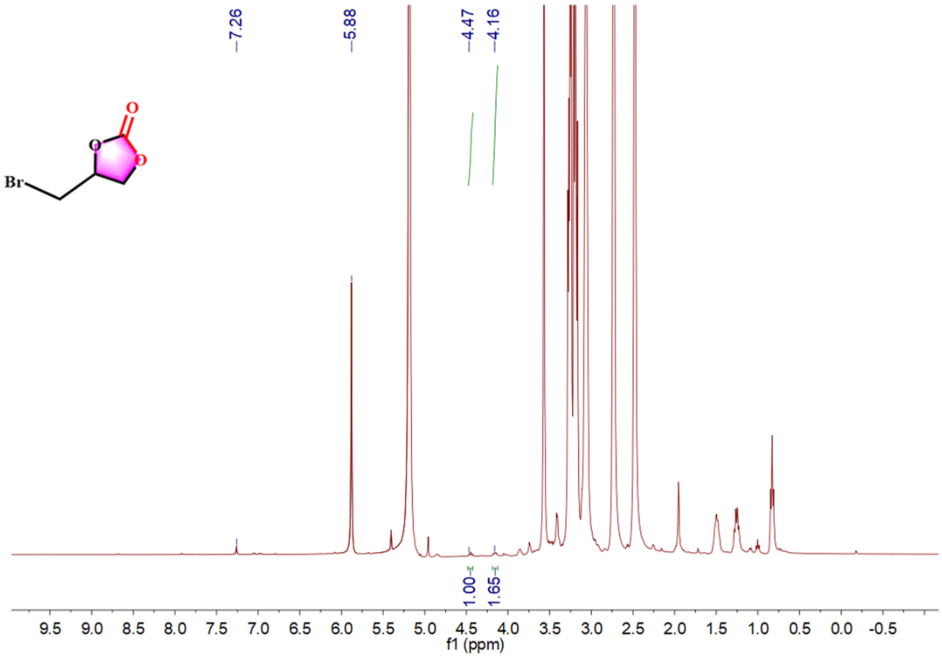
f1 (ppm)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O
O
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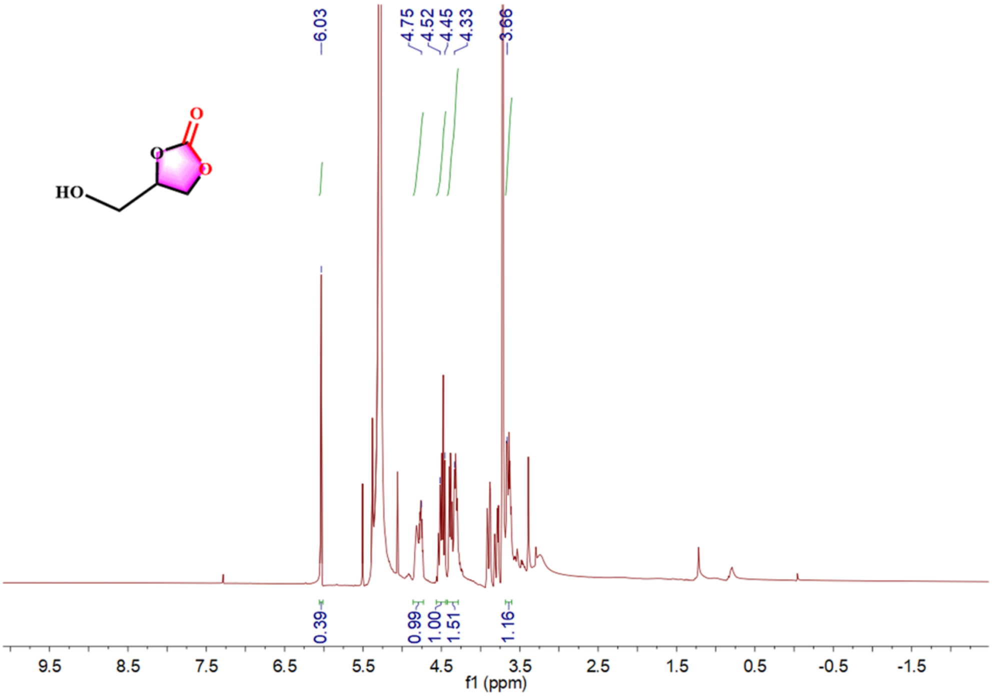
f1 (ppm)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9.5
8.5
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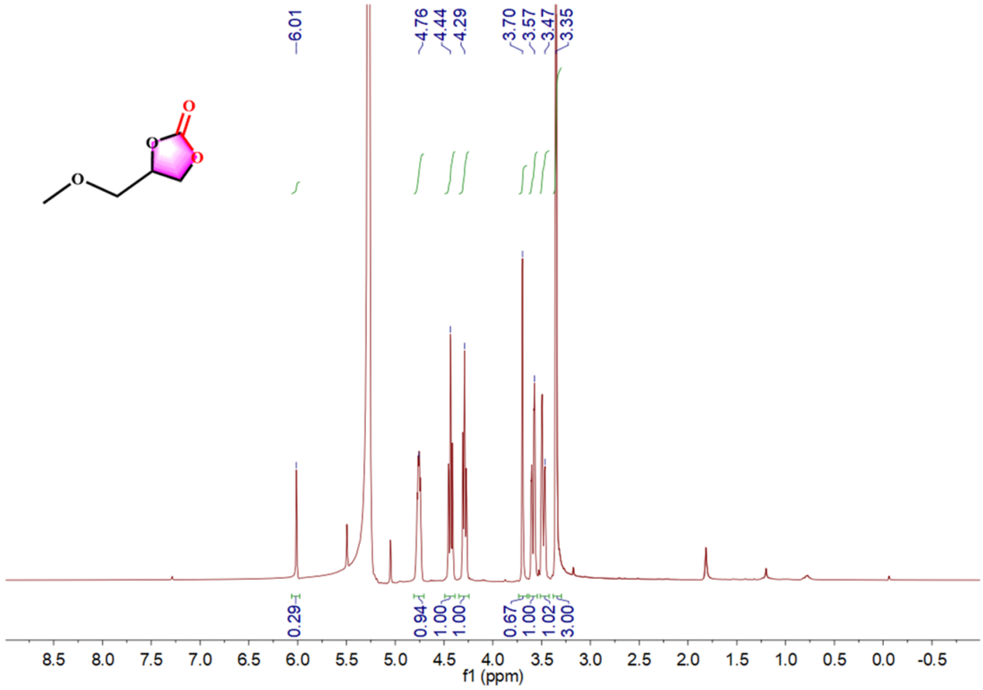
f1 (ppm)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1.00
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1.00
1.02
3.00
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8.0
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6.5
6.0
5.5
5.0
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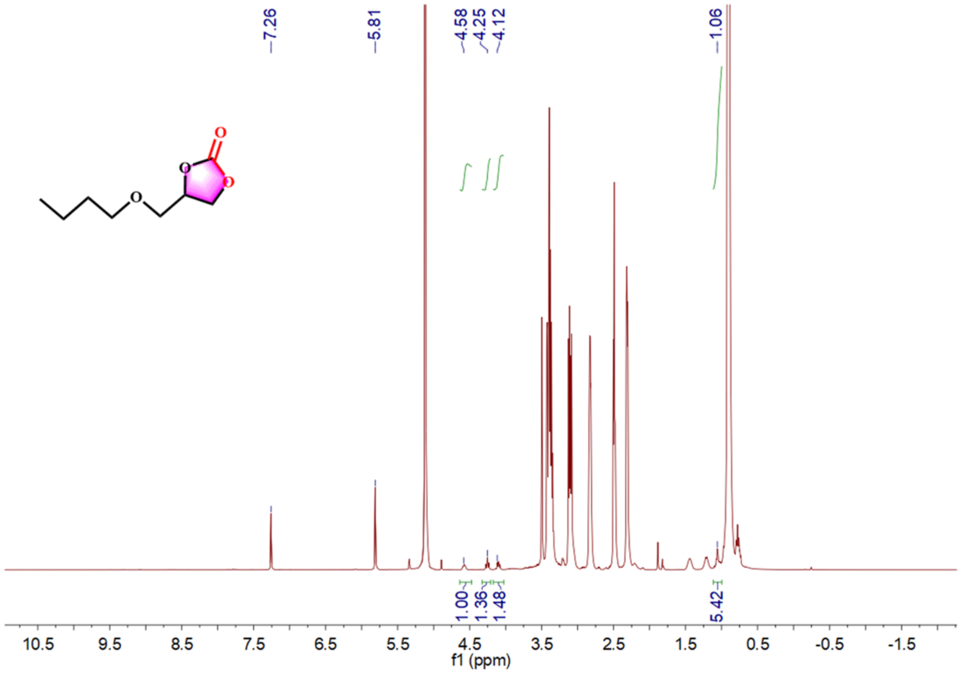
f1 (ppm)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4.12
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O
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0.5
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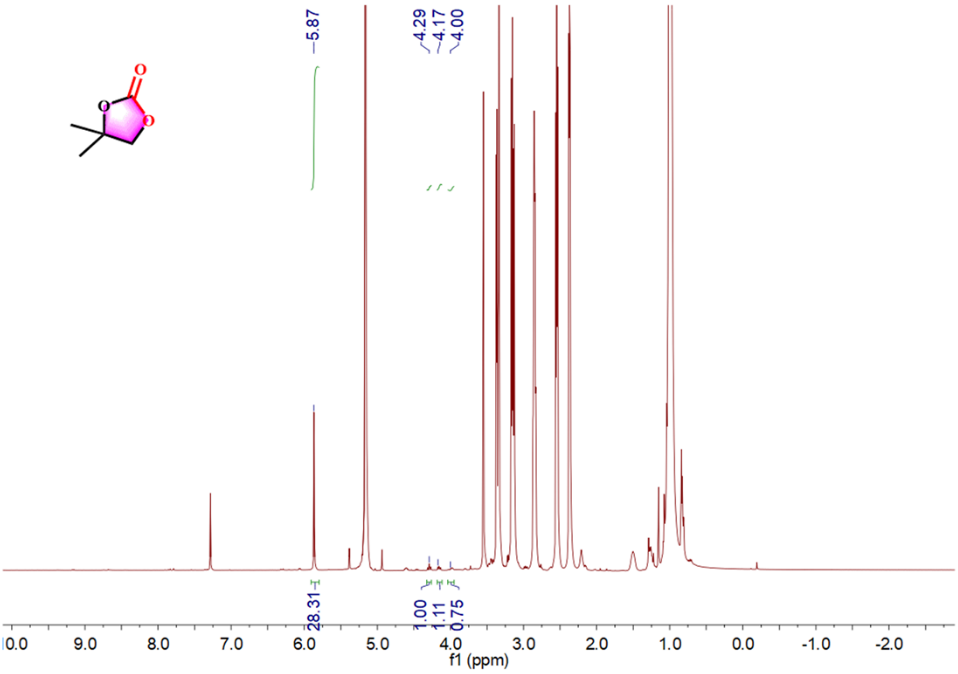
-1.5
f1 (ppm)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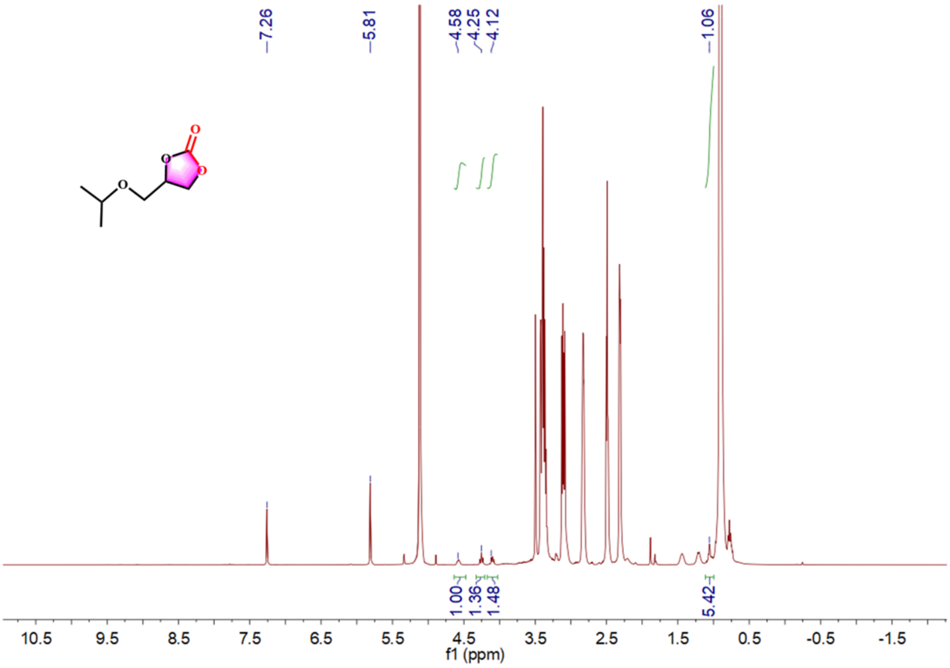
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f1 (ppm)
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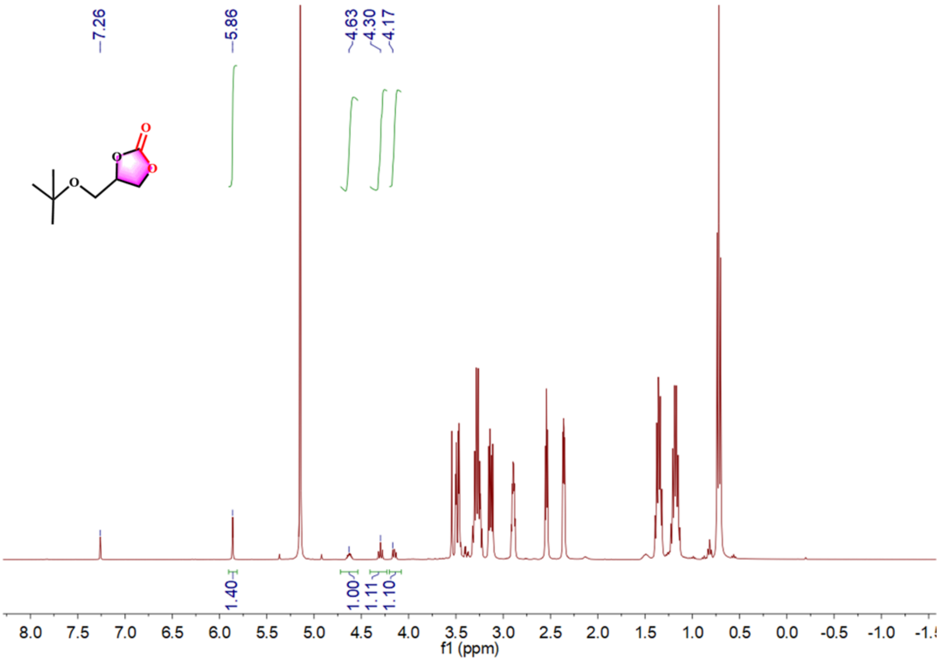
O
O
O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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.
f1 (ppm)
O
O
O
O