

## Supporting Information

### Highly active dinuclear cobalt complexes for solvent-free cycloaddition of CO<sub>2</sub> to epoxides at ambient pressure

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## 1. General comments

CoCl<sub>2</sub>·6H<sub>2</sub>O, salicylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, 3,5-di-*tert*-butyl salicylaldehyde, tris(hydroxymethyl)aminomethane, *tertiary*-butylammonium bromide, triethylamine, and methanol were purchased from Aladdin and were used without any further purification. Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature using 500 MHz Bruker Advance III-HD at 500 MHz and 125 MHz for <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, respectively. All chemical shifts are expressed in δ units (ppm). Fourier Transform Infrared (FT-IR) spectra were measured from KBr pellets using a Thermo-Nicolet 6700 spectrometer over the 4000-400 cm<sup>-1</sup> range.

## 2. Synthesis

### 2.1 Synthesis of ligands

The Schiff base ligands were synthesized according to the reported methods<sup>1</sup> *via* amine-aldehyde condensation. To the solution of salicylaldehyde or its derivatives (10 mmol) in methanol was added tris(hydroxymethyl)aminomethane (10 mmol, 1.21 g) and the reaction mixture was refluxed overnight at room temperature. On evaporation under reduced pressure, a yellow mass of the ligand was obtained, which was then dried under vacuum at room temperature.

**Ligand H<sub>4</sub>L<sup>1</sup>:** Yield: 81 %. <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 14.52 [s, 1H, (O-H)<sub>phenolic</sub>], 8.57 [s, 1H, (N=C-H)<sub>imine</sub>], 7.41 [d, 1H, (Ar-H)], 7.28 [t, 1H, (Ar-H)], 6.79 [d, 2H, (Ar-H)], 4.73 [t, 3H, (O-H)<sub>alcoholic</sub>], 3.63 [d, 6H, (-CH<sub>2</sub>-)<sub>aliphatic</sub>] ppm. <sup>13</sup>C-NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 164.9 (Ar-C)<sub>phenolic</sub>, 163.7 (C=N)<sub>imine</sub>, 132.8 (Ar-C), 132.6 (Ar-C), 118.9 (Ar-C), 117.8 (Ar-C), 117.6 (Ar-C), 67.5 (-C(CH<sub>2</sub>)<sub>3</sub>-), 61.8 (-CH<sub>2</sub>-OH) ppm. **FT-IR Data [KBr,  $\bar{\nu}$  (cm<sup>-1</sup>):** 3600-3200 [br, (O-H)<sub>phenolic</sub>, alcoholic], 3066 [br, (C-H)<sub>sp2</sub> and (=C-H)<sub>imine</sub>], 2819 [m, (C-H)<sub>sp3</sub>], 1635, 1611 and 1539 [s, (C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1483 (m, CH<sub>2</sub> bending), 1230 [s, (C-O)<sub>phenolic</sub>], 1060 [s, (C-O)<sub>alcohol</sub>], 764 (s, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>4</sub>: C, 58.66; H, 6.71; N, 6.22%. Found: C, 58.73; H, 6.74; N, 6.17%.

**Ligand H<sub>4</sub>L<sup>2</sup>:** Yield: 89 %. <sup>1</sup>H-NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 14.27 [d, 1H, (O-H)<sub>phenolic</sub>] 8.27 [s, 1H, (N=C-H)<sub>imine</sub>], 7.16 [d, 1H, (Ar-H)], 6.12 [dd, 2.4 Hz, 1H, (Ar-H)], 6.04 [d, 1H, (Ar-H)],

4.93 [t, 3H, (O-H)<sub>alcoholic</sub>], 3.71 [s, 3H, (O-CH<sub>3</sub>)] 3.60 [s, 6H, (-CH<sub>2</sub>-)<sub>aliphatic</sub>] ppm. <sup>13</sup>C-NMR (125 MHz, DMSO- *d*<sub>6</sub>) δ 174.3 (Ar-C)<sub>phenolic</sub>, 165.3 (C=N)<sub>imine</sub>, 162.4 (Ar-C), 134.9 (Ar-C), 111.4 (Ar-C), 105.3 (Ar-C), 102.3 (Ar-C), 65.6 (-C(CH<sub>2</sub>)<sub>3</sub>-), 61.4 (-CH<sub>2</sub>-OH), 55.4 (-OCH<sub>3</sub>) ppm. **FT-IR Data [KBr,  $\bar{\nu}$  (cm<sup>-1</sup>)]:** 3500-3000 [m, br, (O-H)<sub>phenolic, alcoholic</sub>, (C-H)<sub>sp2</sub>, (N=C-H)<sub>imine</sub>], 2838 [m, (C-H)<sub>sp3</sub>], 1638, 1619 and 1525 [s, (C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1481 (s, CH<sub>2</sub> bending), 1358 (m, CH<sub>3</sub> bending), 1323 [s, (C-O)<sub>methoxy</sub>], 1227 [s, (C-O)<sub>phenolic</sub>], 1042 [s, (C-O)<sub>alcoholic</sub>], 788 (s, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>12</sub>H<sub>17</sub>NO<sub>5</sub>: C, 56.46; H, 6.71; N, 5.49%. Found: C, 56.59; H, 6.79; N, 5.51%.

**Ligand H<sub>4</sub>L<sup>3</sup>:** Yield: 90 %. <sup>1</sup>H-NMR (500 MHz, DMSO- *d*<sub>6</sub>) δ 14.04 [d, 1H, (O-H)<sub>phenolic</sub>], 8.91 [s, 1H, (N=C-H)<sub>imine</sub>], 7.95 [d, 1H, (Ar-H)], 7.68 [d, 1H, (Ar-H)], 7.60 [d, 1H, (Ar-H)], 7.41 [t, 1H, (Ar-H)], 7.16 [t, 1H, (Ar-H)], 6.64 [d, 1H, (Ar-H)], 5.13 [t, 3H, (O-H)<sub>alcoholic</sub>], 3.66 [d, 6H, (-CH<sub>2</sub>-)<sub>aliphatic</sub>] ppm. <sup>13</sup>C-NMR (125 MHz, DMSO- *d*<sub>6</sub>) δ 179.7 (Ar-C)<sub>phenolic</sub>, 156.1 (C=N)<sub>imine</sub>, 137.7 (Ar-C), 135.3 (Ar-C), 129.3 (Ar-C), 128.3 (Ar-C), 127.2 (Ar-C), 125.3 (Ar-C), 122.4 (Ar-C), 118.5 (Ar-C), 105.6 (Ar-C), 64.9 (-C(CH<sub>2</sub>)<sub>3</sub>-), 61.3 (-CH<sub>2</sub>-OH) ppm. **FT-IR Data [KBr,  $\bar{\nu}$  (cm<sup>-1</sup>)]:** 3500-3000 [m, br, (O-H)<sub>phenolic, alcoholic</sub>, (C-H)<sub>sp2</sub> and (N=C-H)<sub>imine</sub>], 2924 [m, (C-H)<sub>sp3</sub>], 1635 and 1542 [s, (C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1490 (m, CH<sub>2</sub> bending), 1171 [w, (C-O)<sub>aromatic</sub>], 1023 [s, (C-O)<sub>alcoholic</sub>], 750 (s, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>: C, 65.44; H, 6.22; N, 5.09%. Found: C, 65.48; H, 6.31; N, 5.15%.

## 2.2 Synthesis of cobalt complexes (1-3)

Cobalt-Schiff base complexes were synthesized by the dropwise addition of CoCl<sub>2</sub>·6H<sub>2</sub>O solution (1 mmol, 0.23 g in 10 mL methanol) to the solution of the ligand (1 mmol) in 10 mL methanol. The solution was then stirred for 24 hours at room temperature. The dark brown solution was filtered, and the precipitate obtained was washed with acetone and dried under vacuum at room temperature.

**Complex 1**, [Co(HL<sup>1</sup>)<sub>2</sub>]: Yield: 73%. **FT-IR Data [KBr,  $\bar{\nu}$  (cm<sup>-1</sup>)]:** 3600-3000 [m, br, (O-H)<sub>alcoholic</sub>, (C-H)<sub>sp2</sub> and (N=C-H)<sub>imine</sub>], 2866 [w, (C-H)<sub>sp3</sub>], 1633, 1595 and 1547 [s, (C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1446 (m, CH<sub>2</sub> bending), 1275 [m, (C-O)<sub>phenolic</sub>], 1031 [s, (C-O)<sub>alcoholic</sub>] 756 (s, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>22</sub>H<sub>26</sub>ClCo<sub>2</sub>N<sub>2</sub>O<sub>9</sub>: C, 42.91; H, 5.76; N, 4.55%. Found: C, 43.01; H, 5.83; N, 4.46%. **ESI-MS** (negative mode): *m/z* = 597.9931 [(Co<sub>2</sub>(H<sub>2</sub>L<sup>1</sup>)(HL<sup>1</sup>)]<sup>-</sup> (calc.

597.9969);  $m/z = 505.0993$   $[(\text{Co}(\text{H}_2\text{L}^1)_2)^-]$  (calc. 505.1027);  $m/z = 328.1166$   $[(\text{Co}(\text{H}_2\text{L}^1)(\text{C}_2\text{H}_5\text{OH})]$  (calc. 328.0595).

**Complex 2**,  $[\text{Co}(\text{HL}^2)]_2$ : Yield: 65%. **FT-IR Data [KBr,  $\bar{\nu}$  ( $\text{cm}^{-1}$ )]:** 3600-3000 [m, br, (O-H)<sub>alcoholic</sub>, (N=C-H)<sub>imine</sub>], 2857 [m, (C-H)<sub>sp3</sub>], 1630, 1601 and 1543 [s, (C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1485 (m, CH<sub>2</sub> bending), 1360 (m, CH<sub>3</sub> bending), 1288 [s, (C-O)<sub>methoxy</sub>], 1227 [s, (C-O)<sub>phenolic</sub>], 1025 [s, (C-O)<sub>alcoholic</sub>], 799 (w, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>24</sub>H<sub>30</sub>ClCo<sub>2</sub>N<sub>2</sub>O<sub>11</sub>: C, 42.65; H, 4.47; N, 4.15%. Found: C, 42.74; H, 4.58; N, 4.06%. **ESI-MS (negative mode):**  $m/z = 658.0127$   $[(\text{Co}_2(\text{H}_2\text{L}^2)(\text{HL}^2)^-]$  (calc. 658.0180);  $m/z = 565.1194$   $[(\text{Co}(\text{H}_2\text{L}^2)_2)^-]$  (calc. 565.1238);  $m/z = 346.9943$   $[(\text{Co}(\text{H}_2\text{L}^2)\text{Cl})]$  (calc. 346.9971).

**Complex 3**,  $[\text{Co}(\text{HL}^3)]_2$ : Yield: 66%. **FT-IR Data [KBr,  $\bar{\nu}$  ( $\text{cm}^{-1}$ )]:** 3600-3000 [m, br, (O-H)<sub>alcoholic</sub>, (N=C-H)<sub>imine</sub>], 2934 [m, br, (C-H)<sub>sp3</sub>], 1626 (s) and 1539 (w) [(C=C)<sub>aromatic</sub> and (C=N)<sub>imine</sub>], 1460 (m, CH<sub>2</sub> bending), 1178 [s, (C-O)<sub>aromatic</sub>], 1040 [s, (C-O)<sub>alcoholic</sub>], 742 (s, CH<sub>2</sub> bending). Anal. Calcd. for C<sub>30</sub>H<sub>30</sub>ClCo<sub>2</sub>N<sub>2</sub>O<sub>9</sub>: C, 50.33; H, 4.22; N, 3.91%. Found: C, 50.46; H, 4.31; N, 3.87 **ESI-MS (negative mode):**  $m/z = 698.0222$   $[(\text{Co}_2(\text{H}_2\text{L}^3)(\text{HL}^3)^-]$  (calc. 698.0282);  $m/z = 605.1292$   $[(\text{Co}(\text{H}_2\text{L}^3)_2)^-]$  (calc. 605.1340);  $m/z = 402.9758$   $[(\text{Co}(\text{H}_3\text{L}^3)\text{Cl}_2)]$  (calc. 402.9794);  $m/z = 366.9994$   $[(\text{Co}(\text{H}_3\text{L}^3)\text{Cl})]$  (calc. 367.0022).

### 3. General catalytic procedure

In a typical coupling reaction of epoxides and CO<sub>2</sub>, a 30 mL stainless steel autoclave with a magnetic stirrer was charged with an appropriate ratio of catalyst, cocatalyst, and substrate and connected to CO<sub>2</sub> cylinder. After purging the autoclave at gentle pressure of CO<sub>2</sub> the outlet was closed and the pressure was set to 1 bar from CO<sub>2</sub> cylinder once the temperature of the autoclave (reactor) reached to the appropriate temperature of the oil bath. After the allotted reaction time, the autoclave was cooled to room temperature. After carefully removing the excess of CO<sub>2</sub>, a small amount of the reaction mixture was taken from the autoclave for <sup>1</sup>H-NMR analysis in CDCl<sub>3</sub> to quantitatively give the conversion rate of the substrate used. The different substrates (epoxides) used in this study are: epichlorohydrin (10 mmol, 0.93 g), allyl glycidyl ether (10 mmol, 1.14 g), butyl glycidyl ether (10 mmol, 1.3 g), benzyl glycidyl ether (10 mmol, 1.6 g), glycidyl isopropyl ether (10 mmol, 1.2 g), vinyl oxirane (10 mmol, 0.70 g), styrene oxide (10 mmol, 1.2 g), propylene oxide (10 mmol, 0.58 g), 1,2-epoxyhexane (10 mmol, 1.0 g), isobutylene oxide (10 mmol, 0.7 g),

3,6-Dioxabicyclo [3,1.0] hexane (10 mmol, 0.98 g), cyclopentene oxide (10 mmol, 0.98 g), and cyclohexene oxide (10 mmol, 0.98 g).

## 4. Stability and recycling of the catalyst

The recyclability and hence stability of the catalysts were carried out using epichlorohydrin as a substrate. 1 mol% of the catalyst (0.05 mmol) and epichlorohydrin (5 mmol, 0.463g) was taken in an autoclave with a stirrer and connected to CO<sub>2</sub> cylinder. After purging with CO<sub>2</sub> for a few seconds at room temperature the pressure was set to 1 bar when the reactor temperature reach to 120 °C in an oil bath. After the given reaction time, the conversion of the substrate into the product was analyzed by <sup>1</sup>H-NMR in CDCl<sub>3</sub> and the catalyst was recovered from the reaction mixture by adding acetone, which helps in the precipitation of the catalyst, and doing centrifugation. The catalyst was washed with acetone and dried in vacuum at 60 °C before using for the next cycle. The catalyst was characterized by FT-IR after each cycle.

## 5. Optimization Table of the catalytic activity of Co-complexes

Table S1. Optimizing conditions for the cycloaddition of CO<sub>2</sub> and epichlorohydrin at 1 bar

Entry	Catalyst	Cat. : Cocat. : Substrate	T (°C)	Time (h)	Conversion (%)	TON	TOF (h <sup>-1</sup> )
1	H <sub>4</sub> L <sup>1</sup>	1: 0: 1000	120	6	6.5	65	11
2	H <sub>4</sub> L <sup>2</sup>	1: 0: 1000	120	6	9	90	15
3	H <sub>4</sub> L <sup>3</sup>	1: 0: 1000	120	6	12	120	20
4	<b>1</b>	1: 0: 1000	120	6	22	220	37
5	<b>2</b>	1: 0: 1000	120	6	25	250	42
6	<b>3</b>	1: 0: 1000	120	6	19	190	32
7	<b>2</b>	1: 0: 100	120	6	100	1000	167
8 <sup>a</sup>	-	0: 1: 1000	120	6	66	660	110
9 <sup>b</sup>	-	0: 1: 1000	120	6	61	610	102
10 <sup>a, c</sup>	<b>2</b>	1: 1: 1000	120	5	100	1000	200

<sup>a</sup> DMAP was used as cocatalyst, <sup>b</sup> TBAB was used as cocatalyst, <sup>c</sup> carried out at 10 bar pressure of CO<sub>2</sub>. TON and TOF values are calculated per mole of complex.

## 6. Comparison of the catalytic activity with reported complexes

**Table S2.** Comparison of TON and TOF values for cycloaddition of CO<sub>2</sub> to epoxides of this study with the reported literature.

Entry	Catalyst <sup>a</sup>	Cocatalyst	Temp. (°C)	P (bar)	TON	TOF (h <sup>-1</sup> )	Reference
1 <sup>b</sup>	Cobalt, (2)	TBAB	120	1	168,600	3333	This work
2 <sup>c</sup>	Cobalt	-	120	20	2,930	122	2
3 <sup>c</sup>	Cobalt	DMAP	130	20	1,986	662	3
4 <sup>c</sup>	Cobalt	TBAB	25	34	2025	169	4
5 <sup>b</sup>	Cobalt	DMAP	100	16	716	358	5
6 <sup>c</sup>	Cobalt	TPPB	120	20	888	296	6
7 <sup>b</sup>	Cobalt	DMAP	100	16	886	443	7
8 <sup>b</sup>	Cobalt	DMAP	100	16	832	416	7
9 <sup>d</sup>	Cobalt	TBAB	130	5	1756	73	8
10 <sup>d</sup>	Cobalt	TBAB	130	5	1461	61	8
11 <sup>c</sup>	Cobalt	TBAB	20	1	119	20	9
12 <sup>c</sup>	Aluminium	PPNBr	90	10	10,000	36,000	10
13 <sup>c</sup>	Aluminium	PPNCl	120	30	92,500	185,000	11
14 <sup>c</sup>	Magnesium	-	120	17	138,000	19,000	12
15 <sup>c</sup>	Magnesium	-	120	17	220,000	46,000	13
16 <sup>c</sup>	Iron	TBAB	120	20	3,480	5,200	14
17 <sup>c</sup>	Iron	-	120	10	7,900	7,900	15
18 <sup>c</sup>	Zinc	-	120	17	310,000	40,000	13
19 <sup>c</sup>	Zinc	-	120	17	240,000	2,000	16

<sup>a</sup> Only the metal centre is mentioned here instead of the whole complex. <sup>b</sup> epichlorohydrin substrate; <sup>c</sup> propylene oxide substrate; <sup>d</sup> Styrene epoxide substrate, <sup>e</sup> 1,2-epoxyhexane substrate, ( TBAB = tetrabutylammonium bromide, DMAP = 4-dimethylamino pyridine, TPPB = tetraphenyl phosphonium bromide, PPNBr = bis(triphenylphosphoranylidene)ammonium bromide, PPNCl = bis(triphenylphosphoranylidene)ammonium chloride).

## 7. NMR Spectra of Ligands

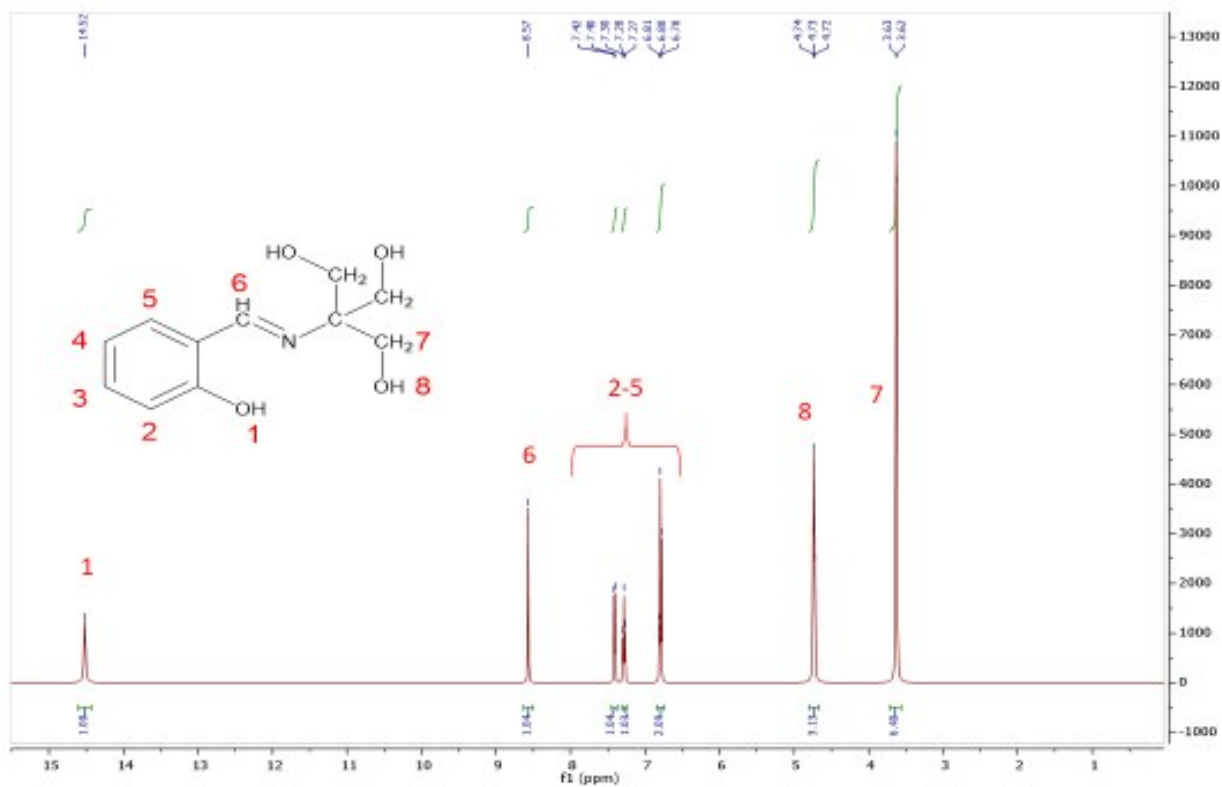


Fig. S1:  $^1H$ -NMR Spectrum of Ligand,  $H_4L^1$

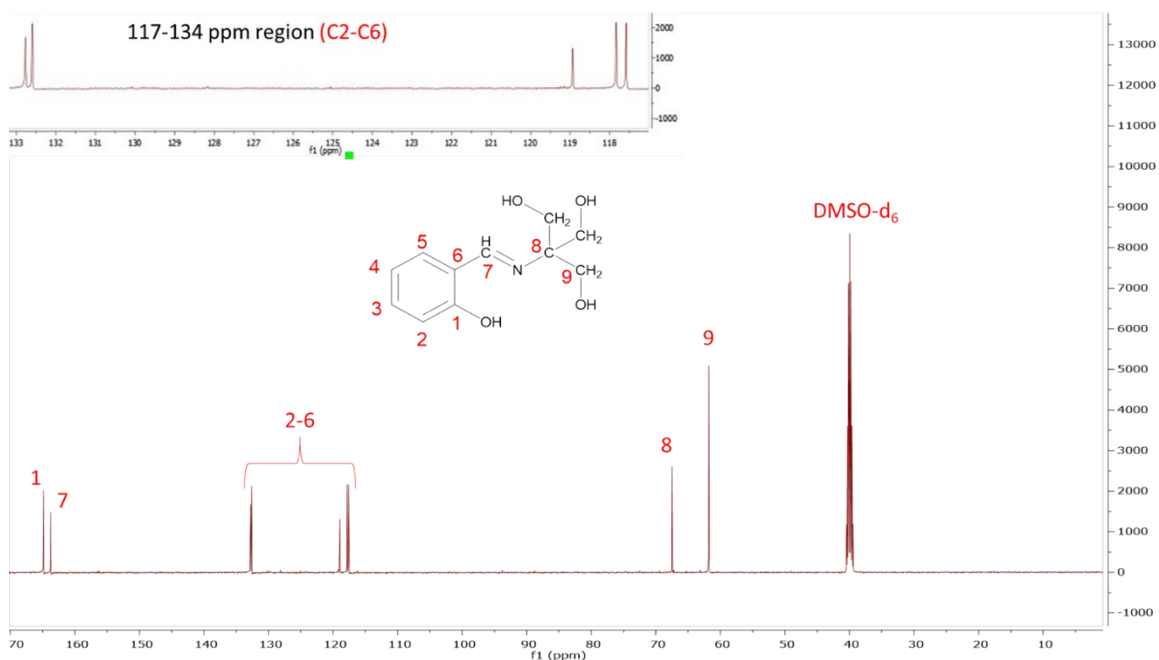


Fig. S2:  $^{13}C$ -NMR Spectrum of Ligand,  $H_4L^1$



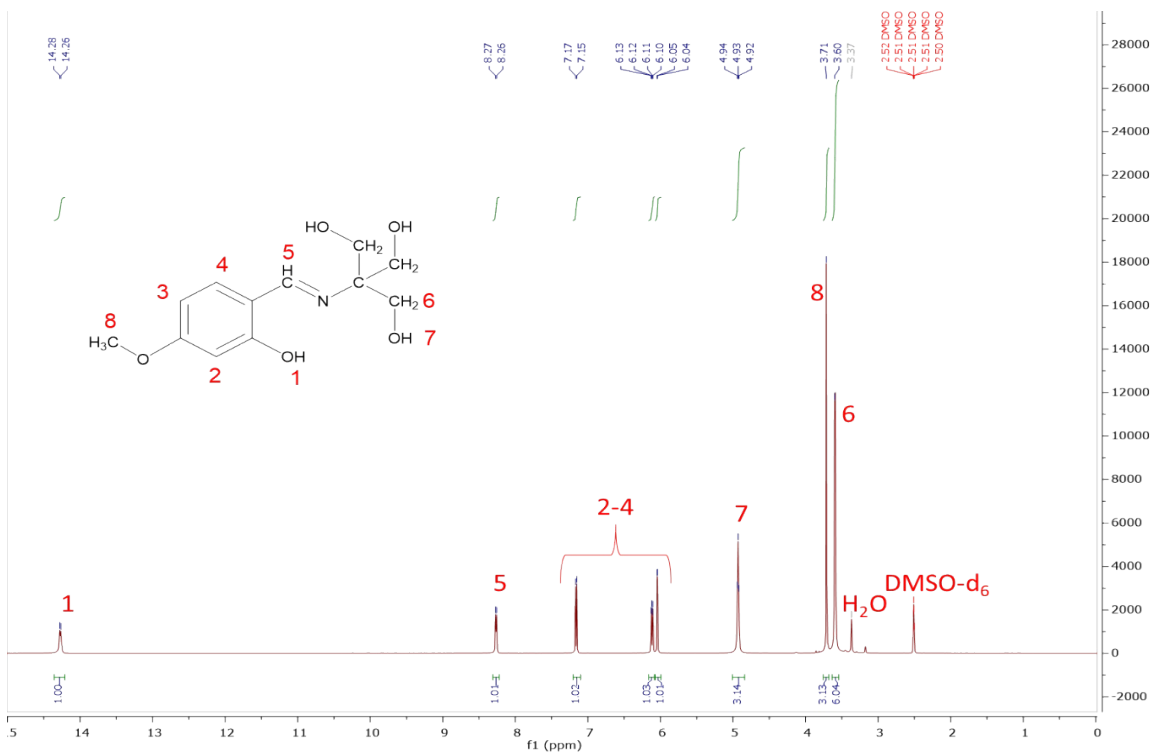


Fig. S3:  $^1H$ -NMR Spectrum of Ligand,  $H_4L^2$

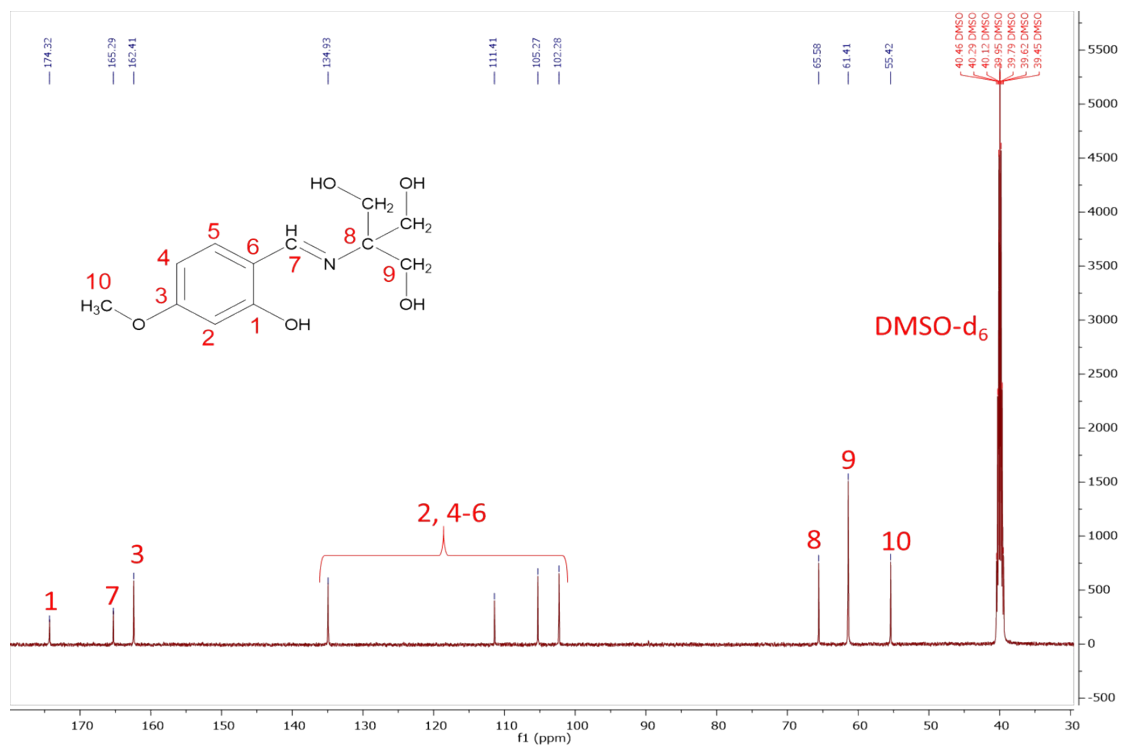


Fig. S4:  $^{13}C$ -NMR Spectrum of Ligand,  $H_4L^2$

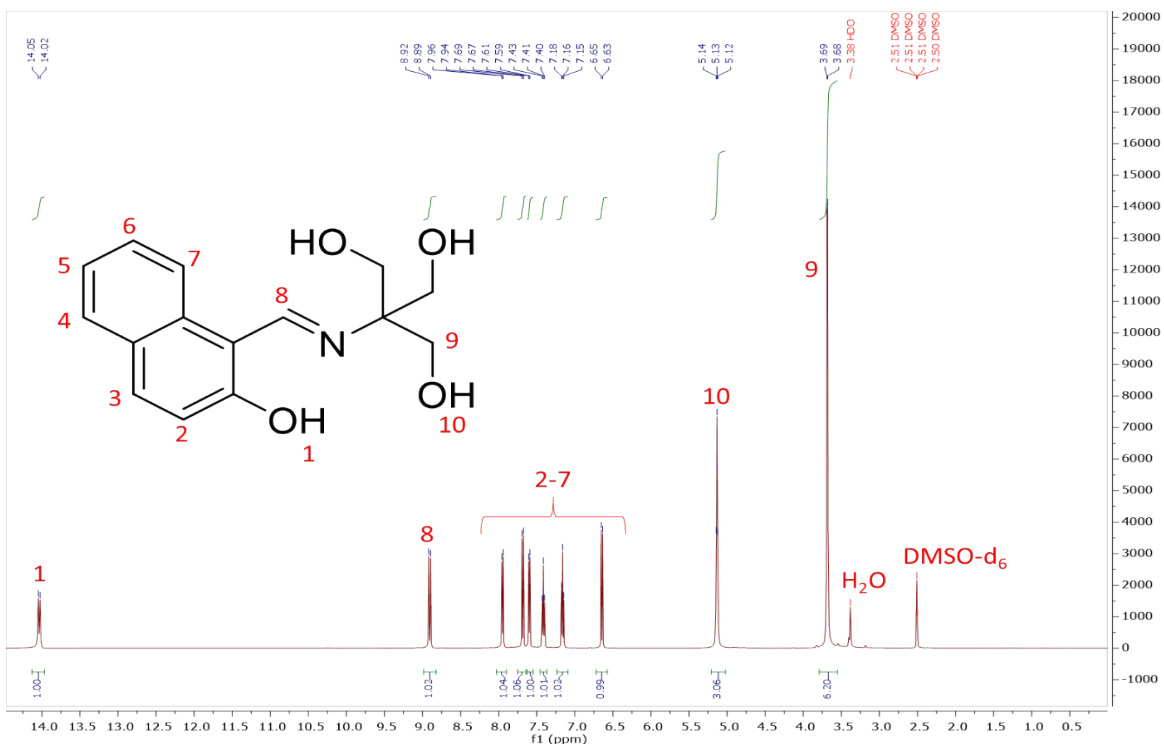


Fig. S5:  $^1H$ -NMR Spectrum of Ligand,  $H_4L^3$

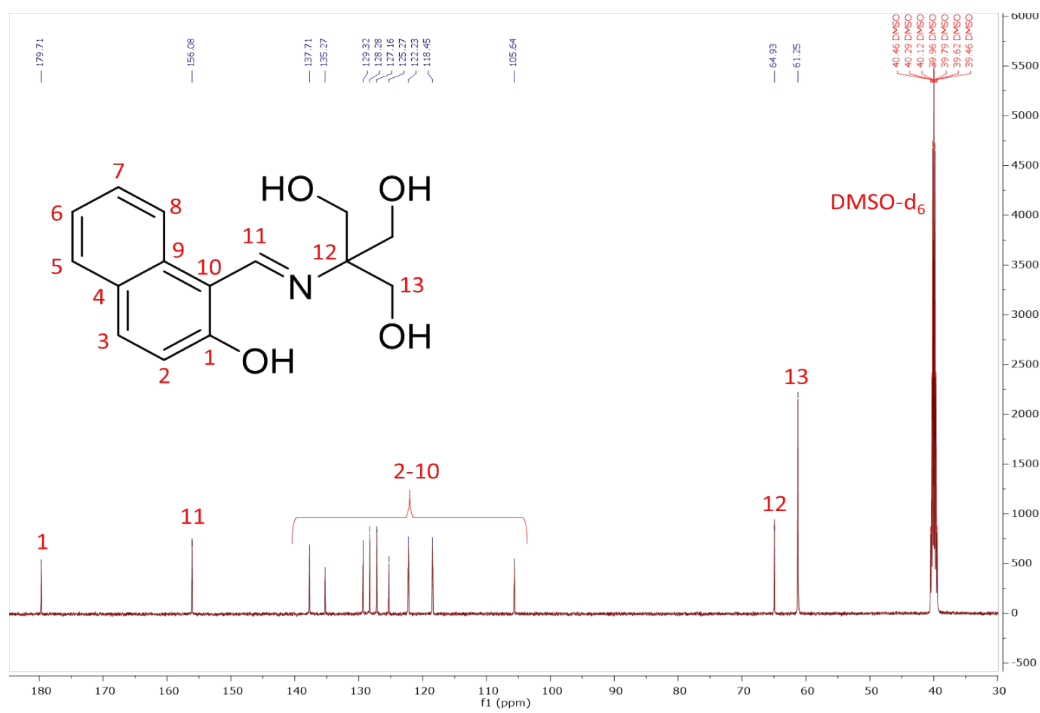
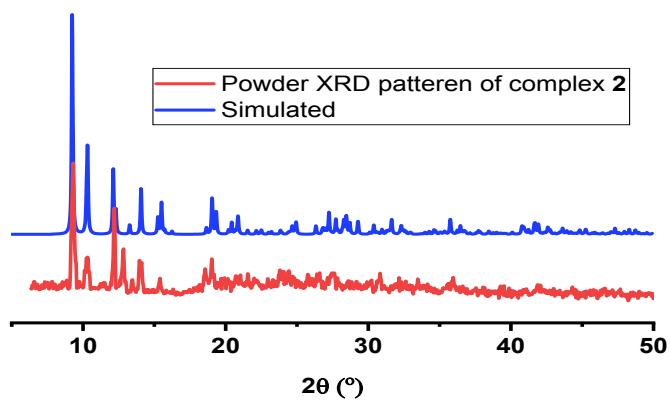


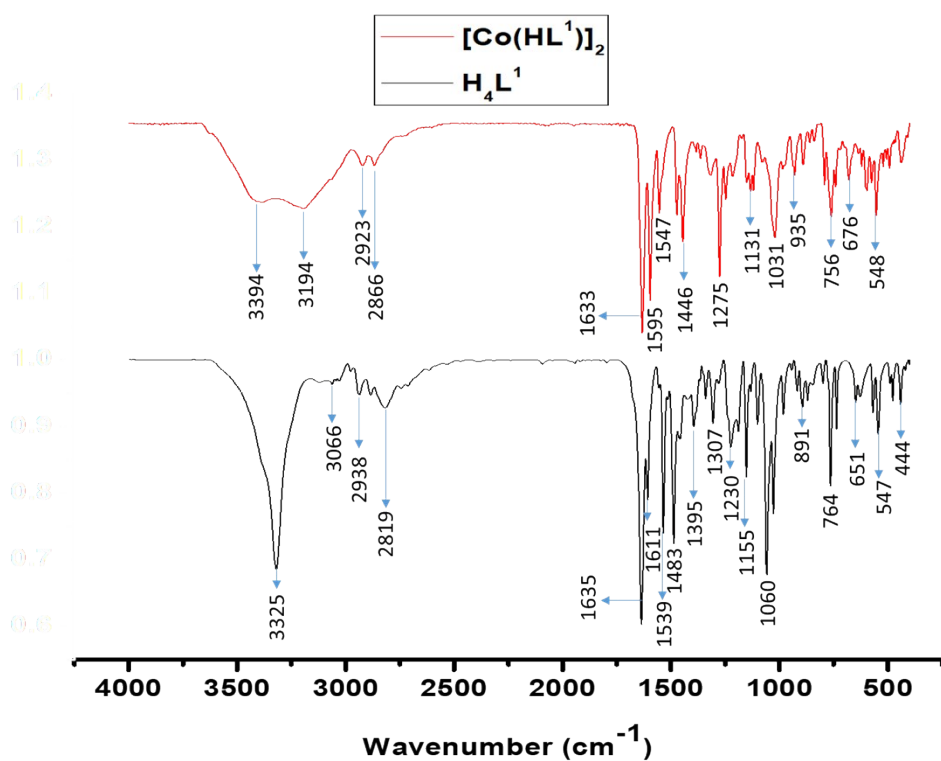
Fig. S6:  $^{13}C$ -NMR Spectrum of Ligand,  $H_4L^3$

## 8. Powder XRD of complex 2



**Fig. S7** Diffractograms of the Co-complex (**2**), simulated standard pattern of CCDC 1027789<sup>1b</sup> (Blue) and that of the as-synthesized compound in this study (Red).

## 9. FTIR spectra of ligands and complexes



**Fig. S8:** FT-IR Spectrum of Ligand ( $\text{H}_4\text{L}^1$ ) and Co-complex,  $[\text{Co}(\text{HL}^1)]_2$

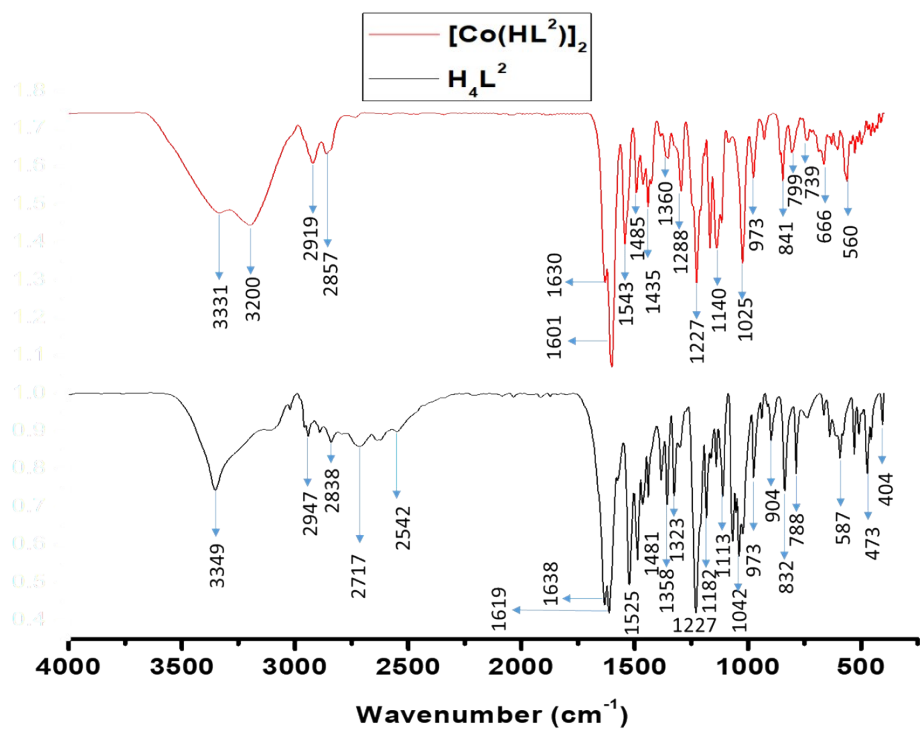


Fig. S9: FT-IR Spectrum of Ligand ( $H_4L^2$ ) and Co-complex,  $[Co(HL^2)_2]_2$

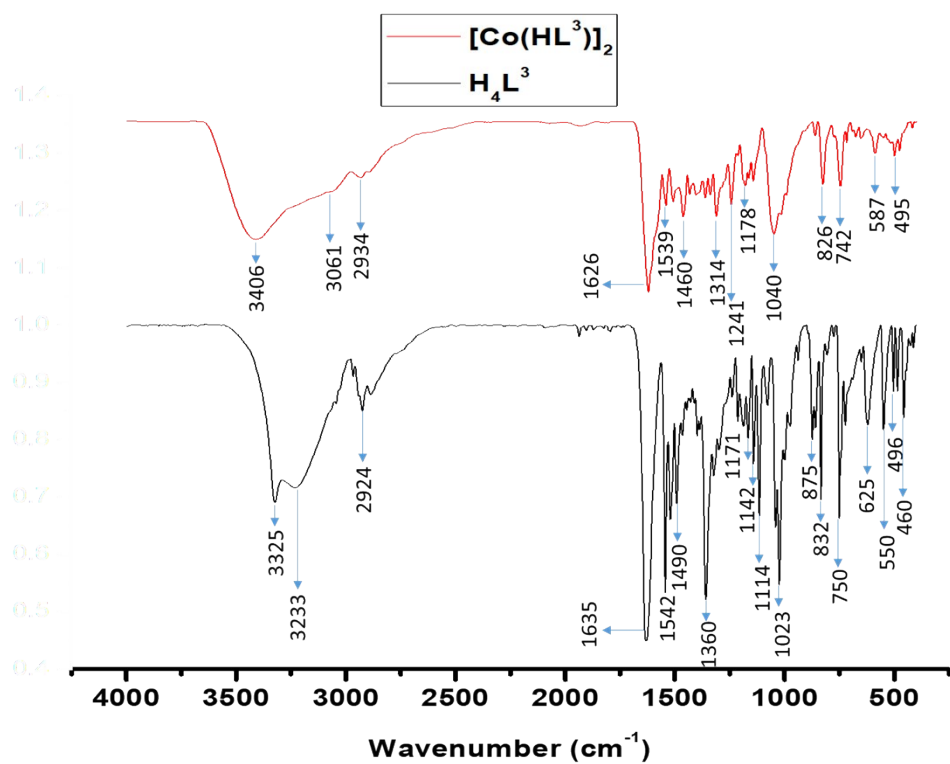


Fig. S10: FT-IR Spectrum of Ligand ( $H_4L^3$ ) and Co-complex,  $[Co(HL^3)_2]_2$

## 10. Mass spectra of dinuclear cobalt complexes

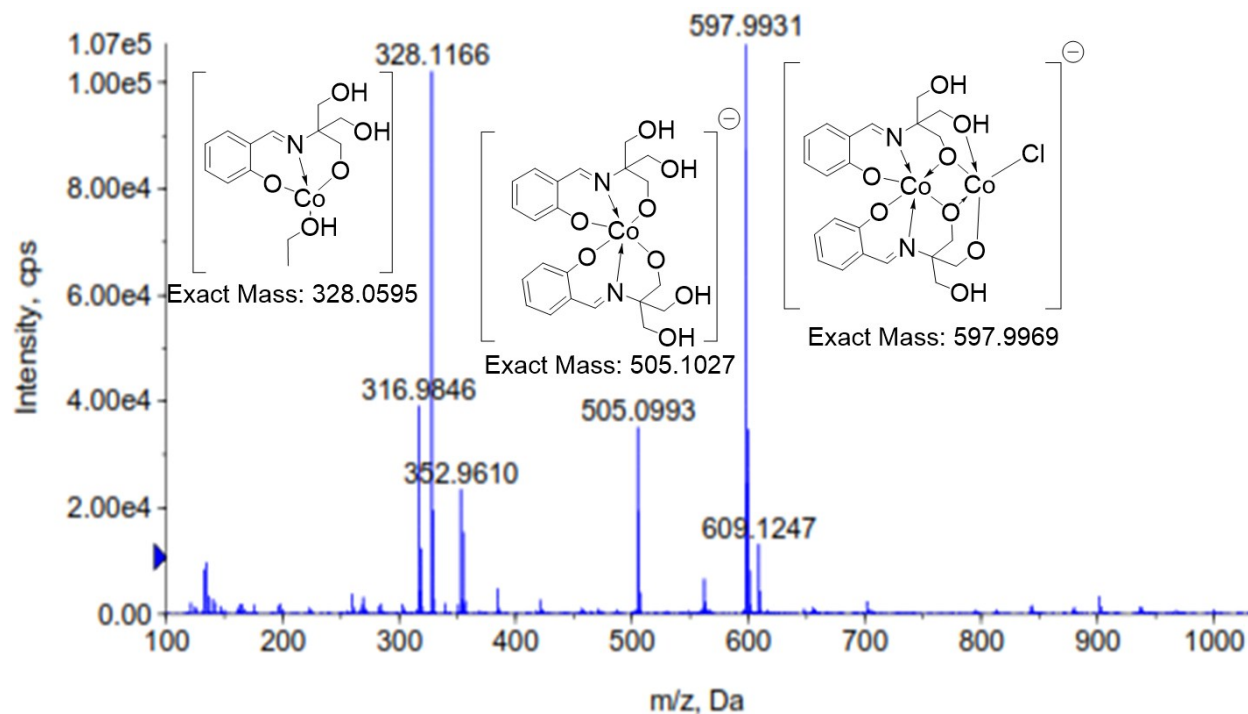


Fig. S11: Mass Spectrum complex 1,  $[\text{Co}(\text{H}_2\text{L}^1)]_2$

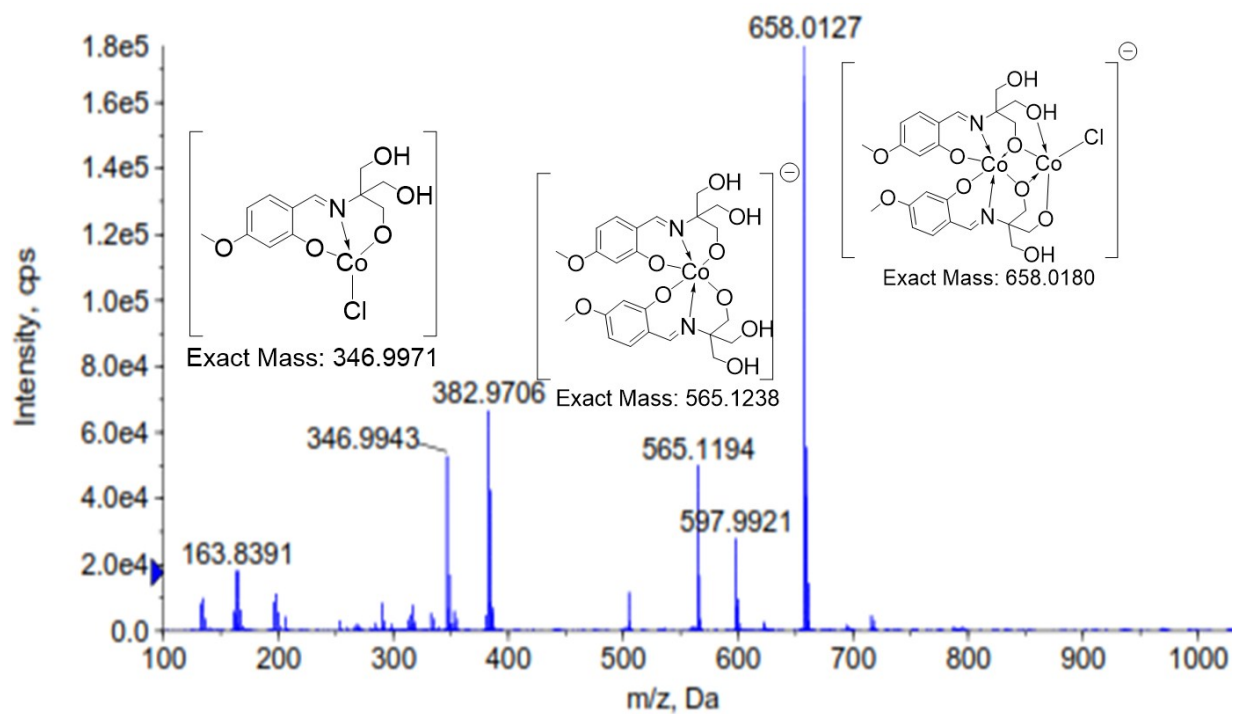


Fig. S12: Mass Spectrum complex 2,  $[\text{Co}(\text{H}_2\text{L}^2)]_2$

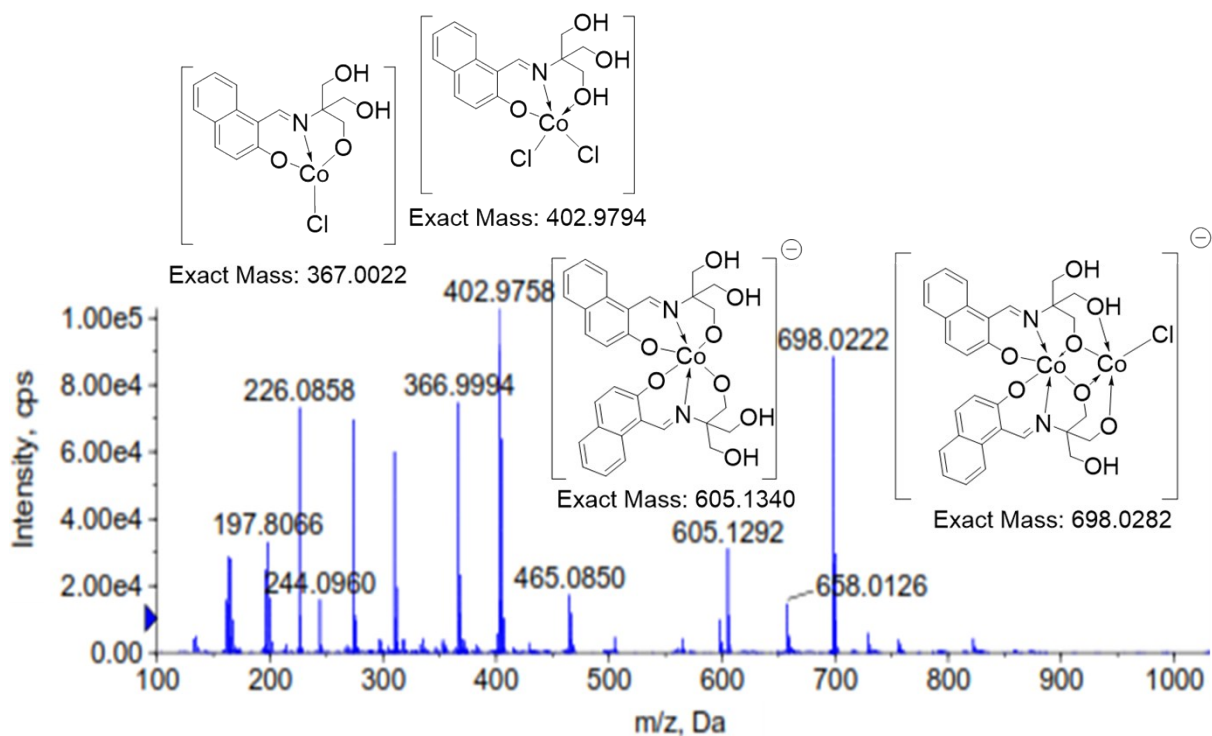


Fig. S13: Mass Spectrum complex 3,  $[\text{Co}(\text{H}_2\text{L}^3)]_2$

## 11. NMR spectra of carbon dioxide fixation reactions

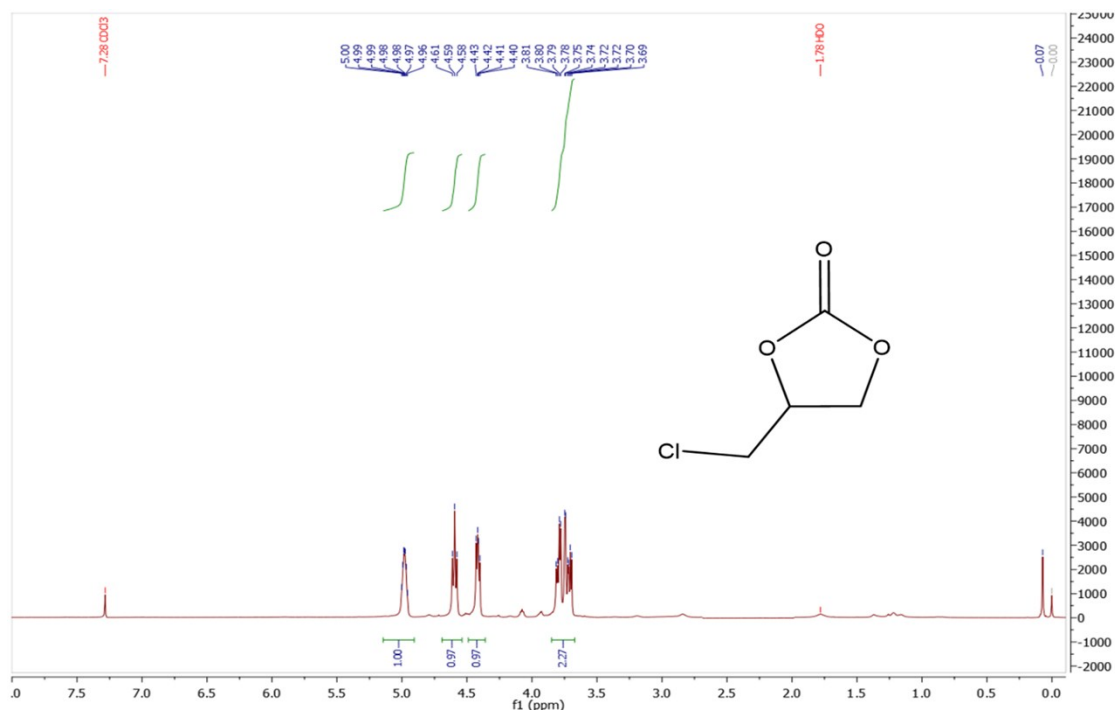
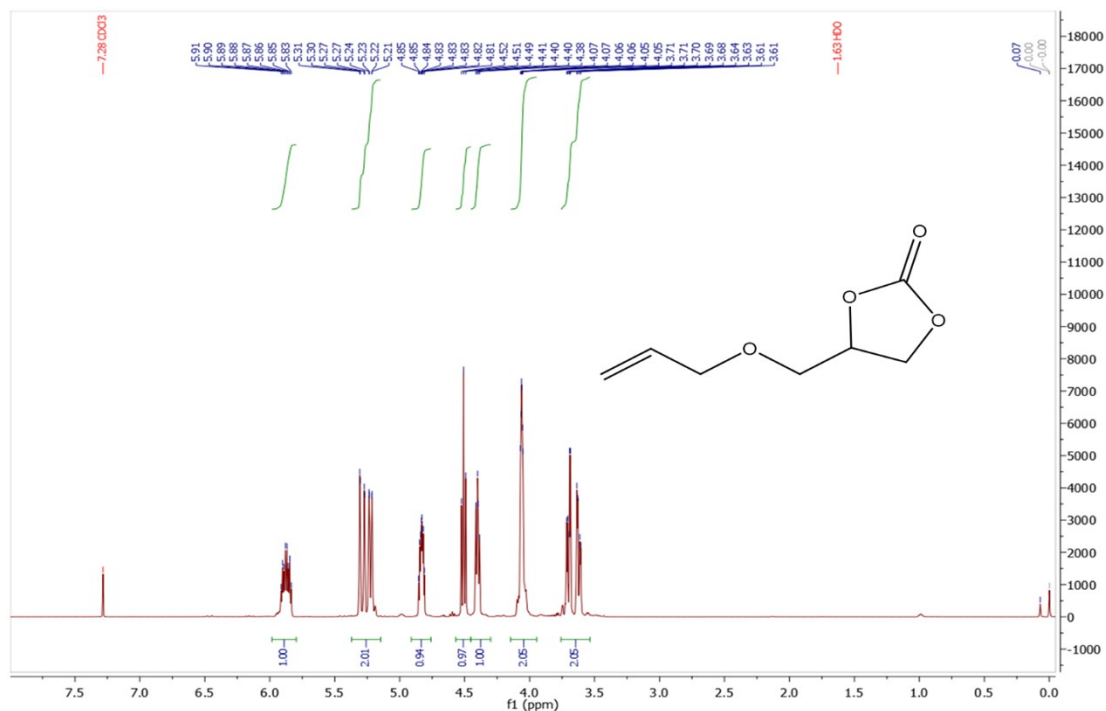
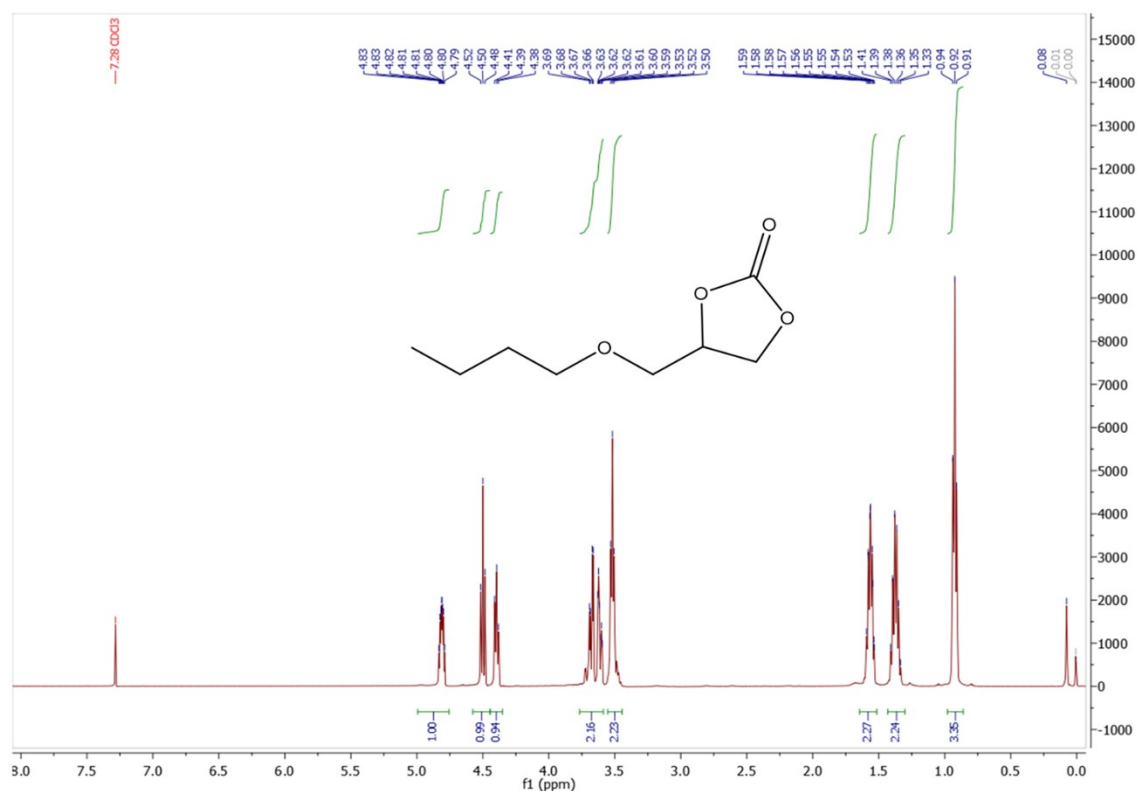


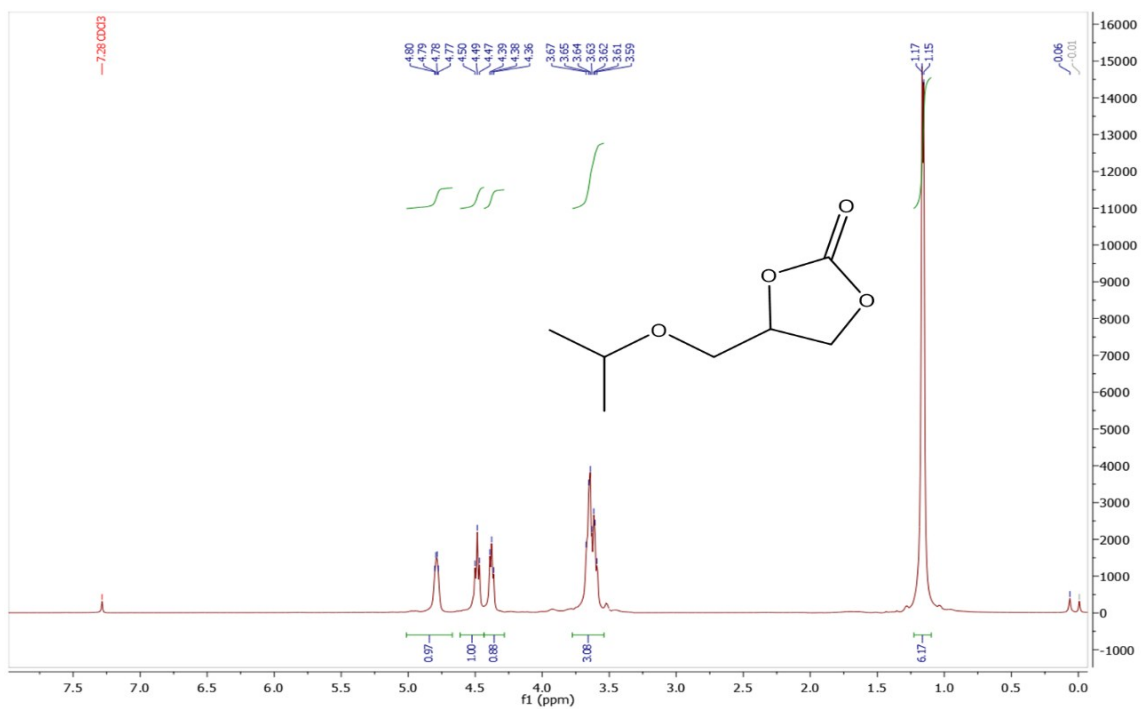
Fig. S14:  $^1\text{H}$ -NMR spectrum in  $\text{CDCl}_3$  of the crude product [4-(chloromethyl)-1,3-dioxolan-2-one] obtained from the conversion of epichlorohydrin using complex 2 as a catalyst.



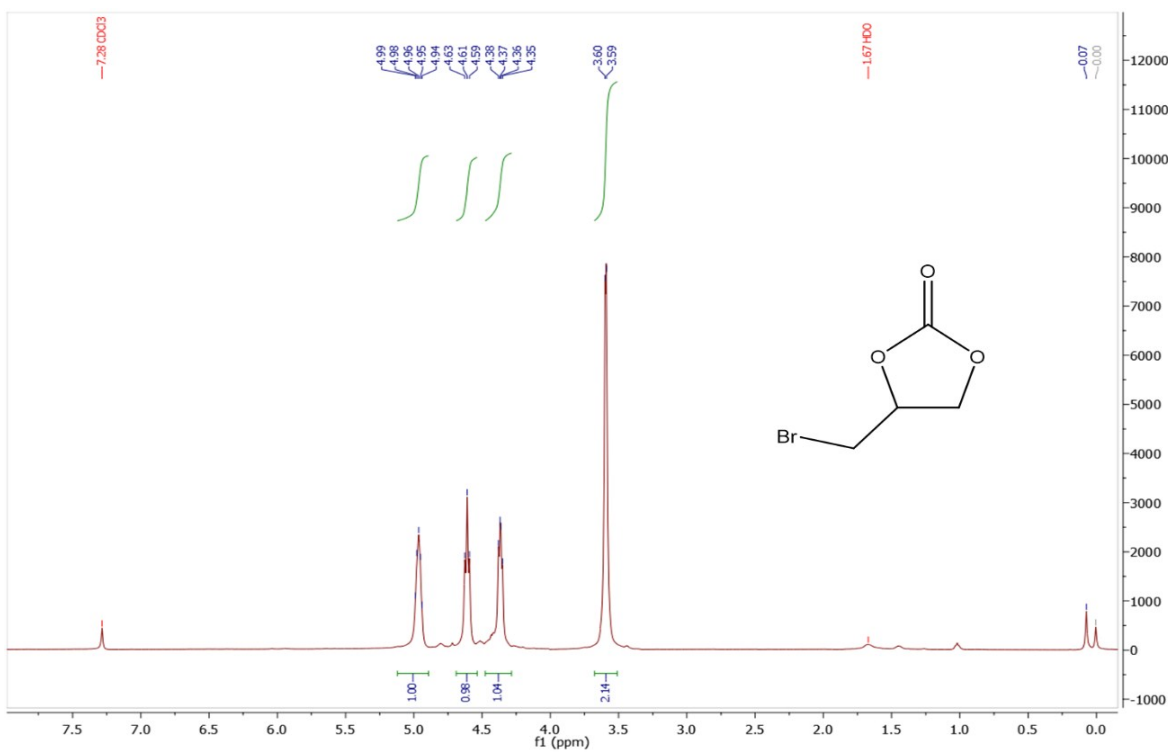
**Fig. S15:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-((allyloxy)methyl)-1,3-dioxolan-2-one] obtained from the conversion of allyl glycidyl ether using complex **2** as a catalyst.



**Fig. S16:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-(butoxymethyl)-1,3-dioxolan-2-one] obtained from the conversion of butyl glycidyl ether using complex **2** as a catalyst.

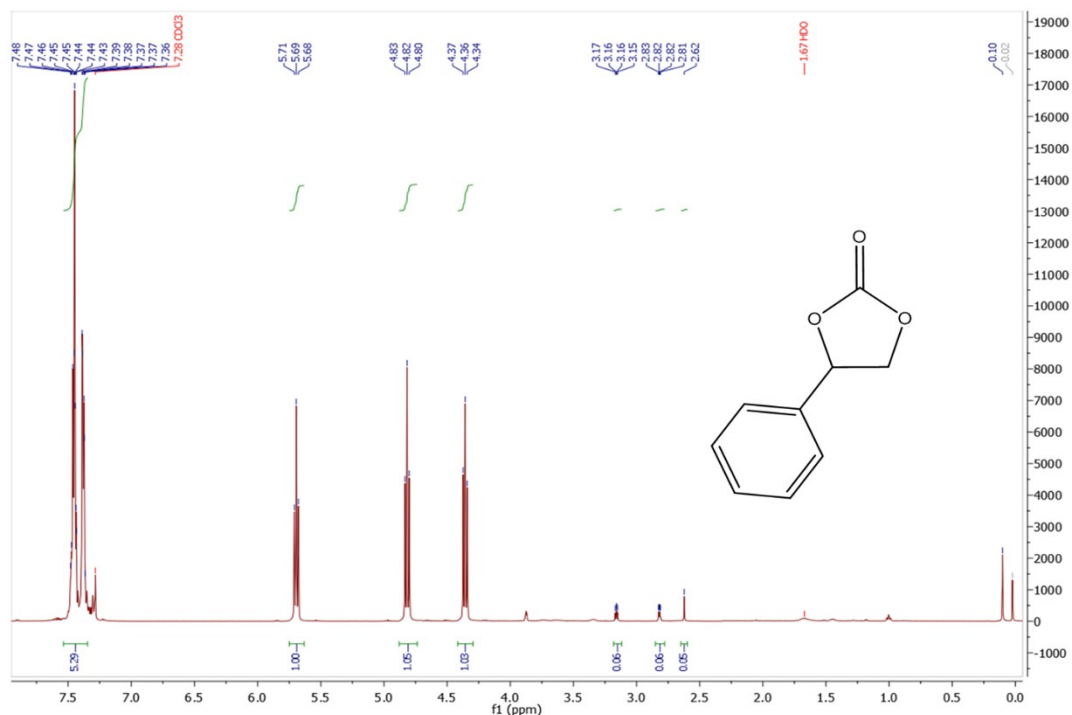


**Fig. S17:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-(isopropoxymethyl)-1,3-dioxolan-2-one] obtained from the conversion of glycidyl isopropyl ether using complex **2** as a catalyst.

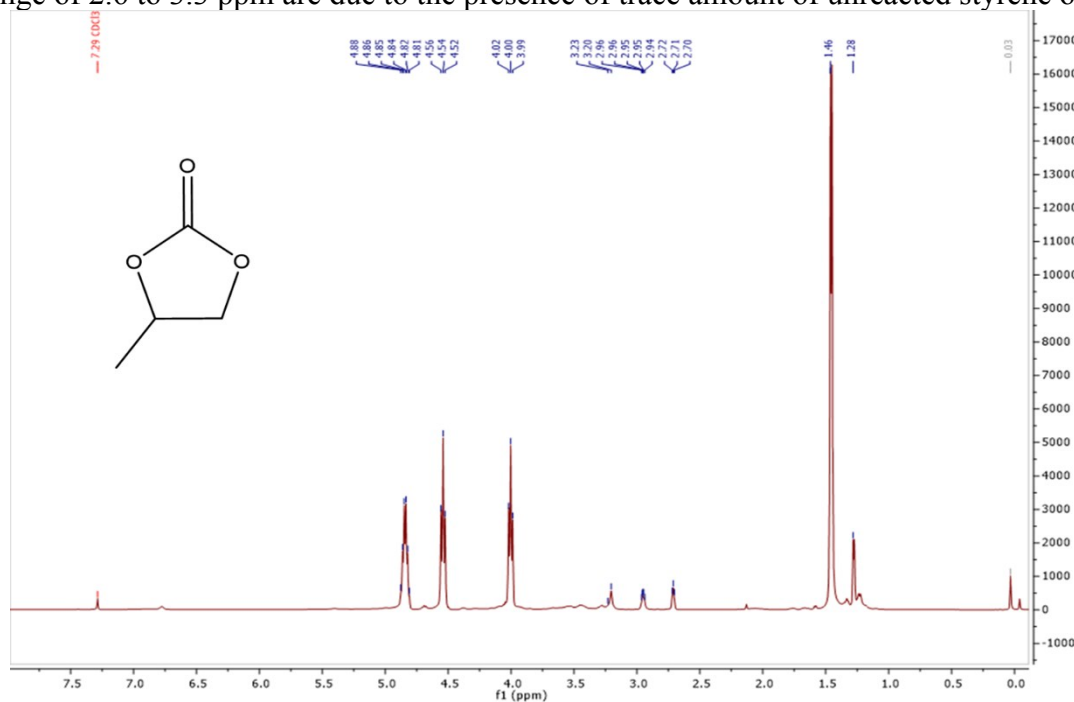


**Fig. S18:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the product [4-(bromomethyl)-1,3-dioxolan-2-one] obtained from the conversion of epibromohydrin using complex **2** as a catalyst.

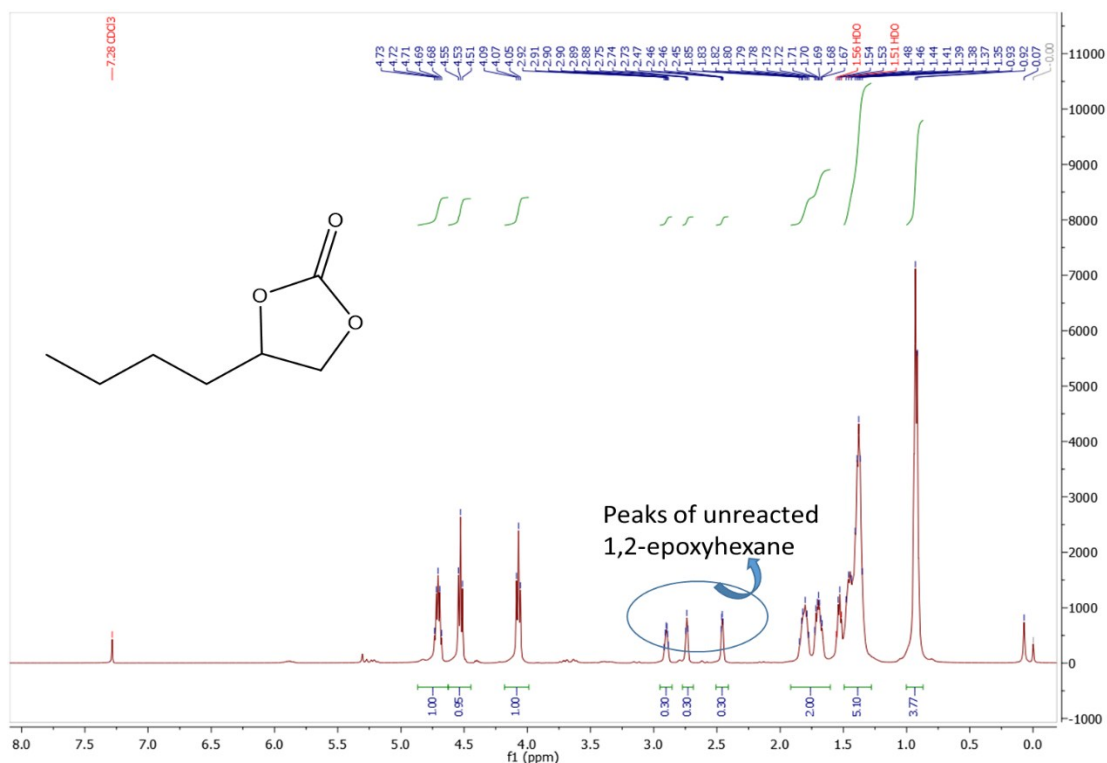




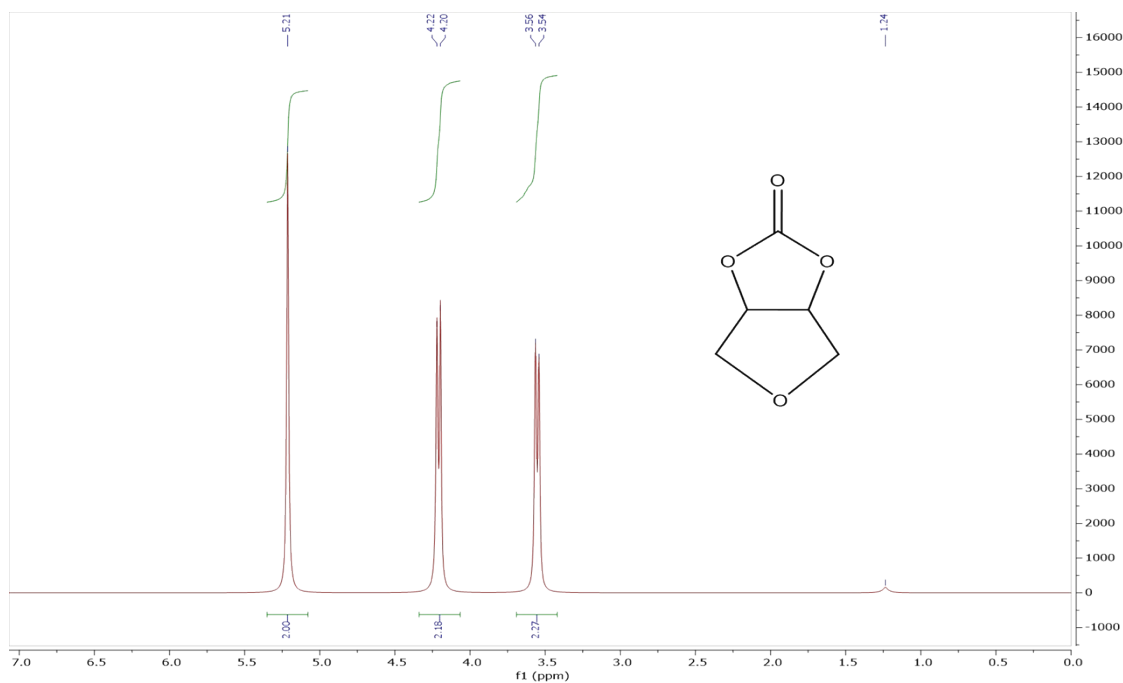
**Fig. S19:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-phenyl]-1,3-dioxolan-2-one obtained from the conversion of styrene oxide using complex **2** as a catalyst. The small peaks in the range of 2.6 to 3.3 ppm are due to the presence of trace amount of unreacted styrene oxide.



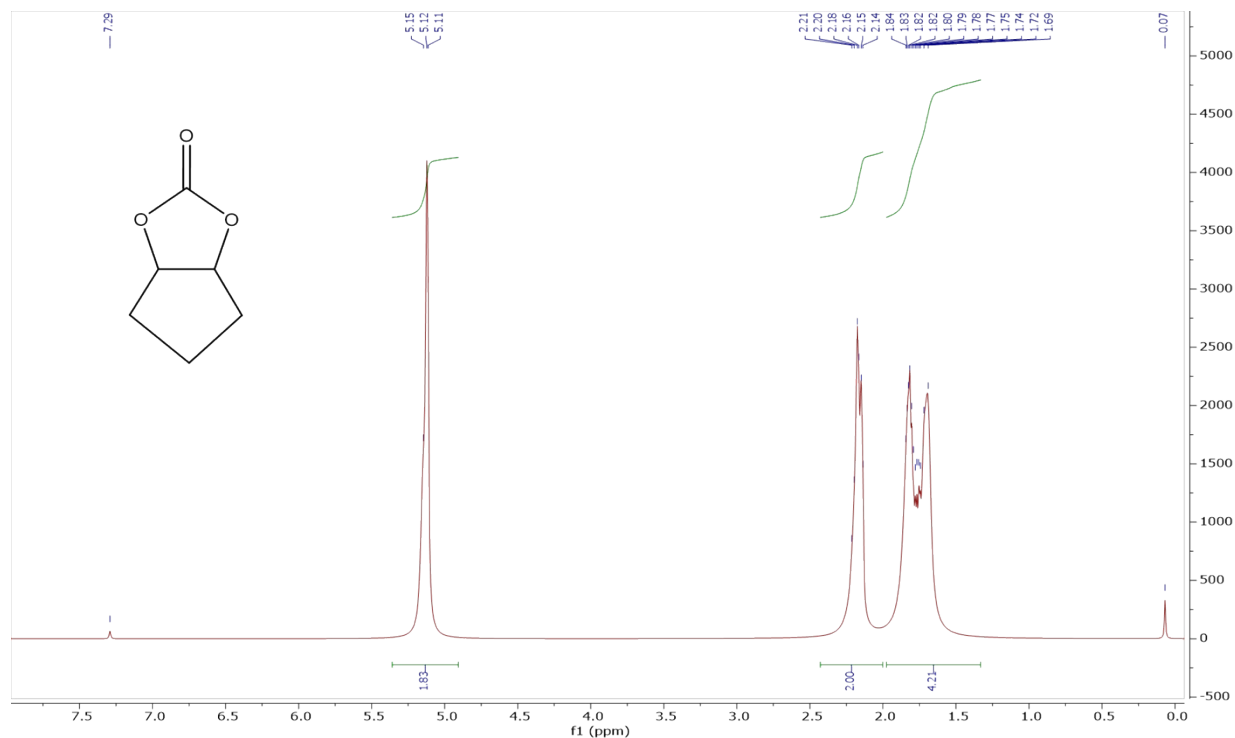
**Fig. S20:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-methyl]-1,3-dioxolan-2-one obtained from the conversion of propylene oxide using complex **2** as a catalyst. The small peaks in the range of 2.5-3.5 and at 1.28 ppm are due to the unreacted propylene oxide (substrate).



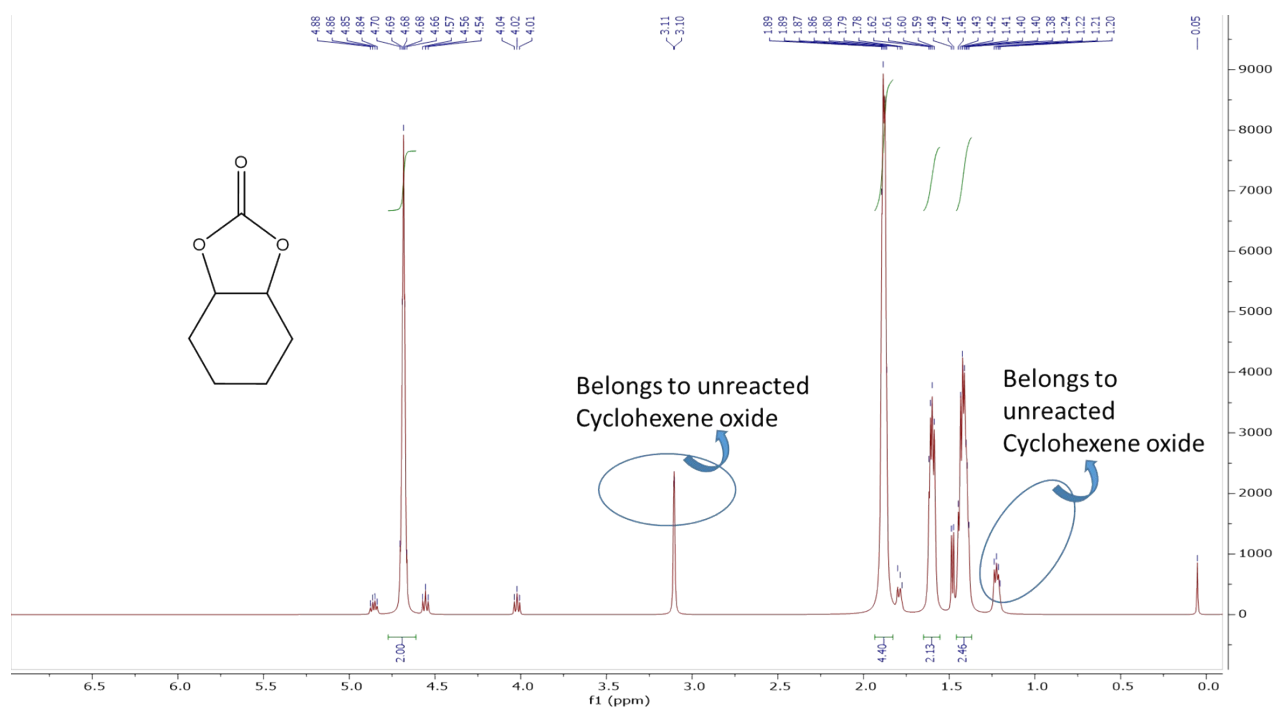
**Fig. S21:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product [4-butyl-1,3-dioxolan-2-one] obtained from the conversion of 1,2-epoxyhexane using complex **2** as a catalyst. The small peaks in the range of 2.4 to 2.8 ppm are due to the unreacted 1,2-epoxyhexane (substrate).



**Fig. S22:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product (tetrahydrofuro[3,4-d][1,3]dioxol-2-one) obtained from the conversion of 3,6-dioxabicyclo[3.1.0]hexane using complex **2** as a catalyst.



**Fig. S23:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product (tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one) obtained from the conversion of cyclopentene oxide using complex **2** as a catalyst.



**Fig. S24:**  $^1\text{H-NMR}$  spectrum in  $\text{CDCl}_3$  of the crude product (hexahydrobenzo[d][1,3]dioxol-2-one) obtained from the conversion of cyclohexene oxide using complex **2** as a catalyst.

## 12. FTIR of the recycled complex

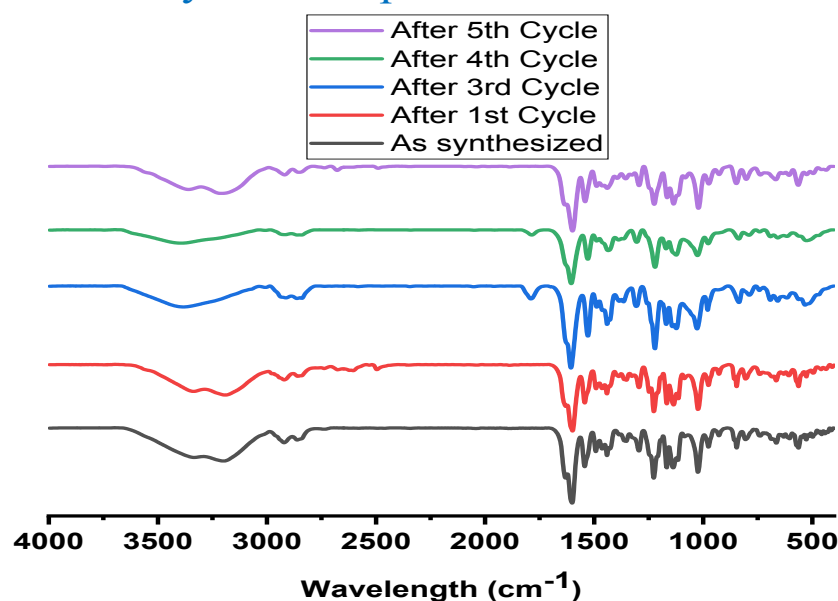


Fig. S25: FT-IR Spectra of fresh and recycled catalyst, **2**, (till five catalytic cycles).

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