

Supporting Information

Novel Supramolecular Cobalt Complex as Efficient Catalyst for Converting CO₂ into Cyclic Carbonates under mild conditions

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1. Crystallography data

Table S1. Crystal data and structure refinement for complex **2**.

Empirical formula	$C_{18}H_{20}CoN_8O_2S_2$
Crystal system, space group	Orthorhombic, <i>Aba2</i>
Unit cell dimensions	a = 21.5377 (12) Å b = 13.9985 (7) Å c = 7.1137 (4) Å
V/Å ³	2144.7 (2)
Z, D _{calcd} /Mg·m ⁻³	4, 1.559
μ/mm ⁻¹	1.029
F (0 0 0)	1036
Theta range for data collection/deg	1.89 to 27.50
Completeness to theta=25.0°	99.9 %
Limiting indices	-27 ≤ h ≤ 27, -16 ≤ k ≤ 18, -9 ≤ l ≤ 9
Reflections collected/unique	10283/2465 [R(int) = 0.0370]
Data/restraints/parameters	2465 / 1 / 144
Goodness-of-fit on F ²	1.171
Final R indices [I>2σ(I)]	R1 = 0.0501, wR2 = 0.1236
R indices (all data)	R1 = 0.0524, wR2 = 0.1249
Largest diff. peak and hole (e/Å ⁻³)	1.441 and -0.497

Table S2. Bond lengths [Å] and angle [°] for complex **2**.

Bond	Dist.	Bond	Dist.
Co(1)-N(5)	2.059(3)	Co(1)-N(5A)	2.059(3)
Co(1)-N(1)	2.139(3)	Co(1)-N(1A)	2.139(3)

Co(1)-N(3)	2.121(6)	Co(1)-N(4A)	2.202(6)
N(5A)-Co(1)-N(4A)	86.54(10)	N(5A)-Co(1)-N(5)	173.1(2)
N(5A)-Co(1)-N(3)	93.46(10)	N(5)-Co(1)-N(3)	93.46(10)
N(5A)-Co(1)-N(1A)	91.62(12)	N(5)-Co(1)-N(1A)	89.08(12)
N(3)-Co(1)-N(1A)	84.18(8)	N(5A)-Co(1)-N(1)	89.08(12)
N(5)-Co(1)-N(1)	91.62(12)	N(3)-Co(1)-N(1)	84.18(8)
N(1A)-Co(1)-N(1)	168.37(16)	N(1)-Co(1)-N(4A)	95.82(8)
N(5)-Co(1)-N(4A)	86.54(10)	N(3)-Co(1)-N(4A)	180.000(1)
N(1A)-Co(1)-N(4A)	95.82(8)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, z; #2 x, y, z-1; #3 x, y, z+1

Table S3. Hydrogen-bond geometry (Å, °) for complex **2**.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...O1	0.88	2.12	2.794	132.58
O1—H1B...S1	0.84	2.34	3.168	168.31

2. Frontier molecular orbital analysis

All DFT calculations involved in this work were performed with B3LYP functional by using Gaussian 09W program. Effective nuclear LanL2DZ basis set was adopted for metal atoms and 6-31+G(d, p) basis set for other atoms.

Table S4. Highest Occupied Molecular Orbital (HOMO), and Lowest Unoccupied Molecular Orbital (LUMO) of complex **2**.

HOMO/eV	-0.13232
LUMO/eV	-0.14893

$\Delta E/eV$

0.01661

3. NMR spectra of carbon dioxide fixation reactions

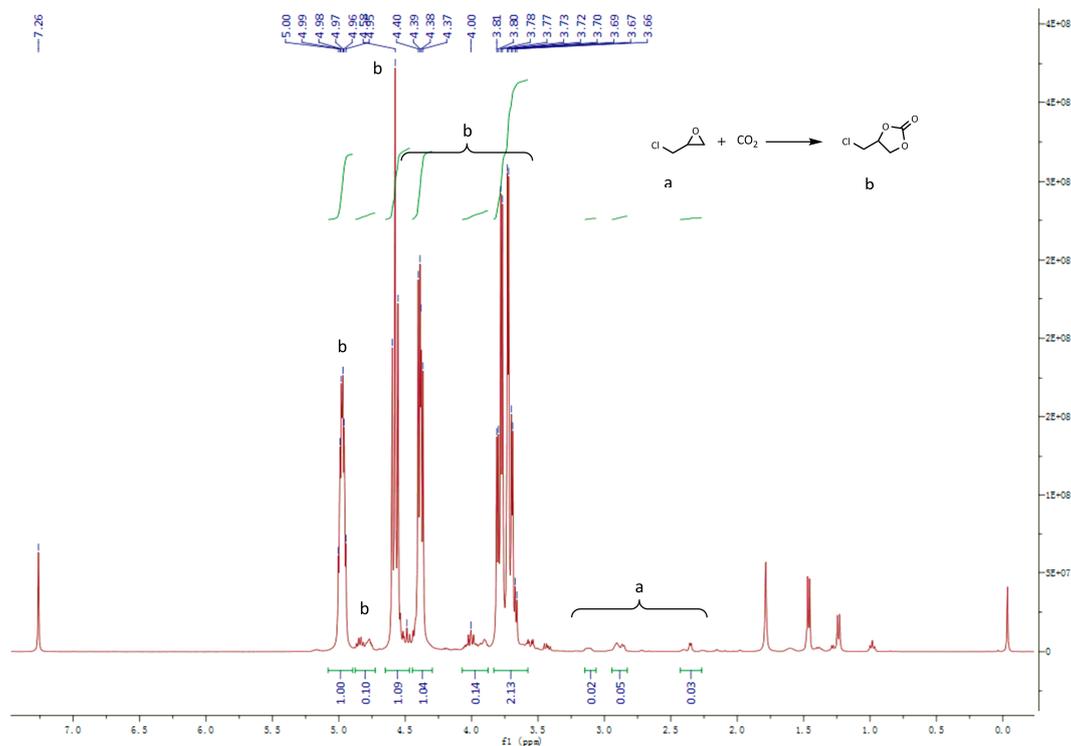
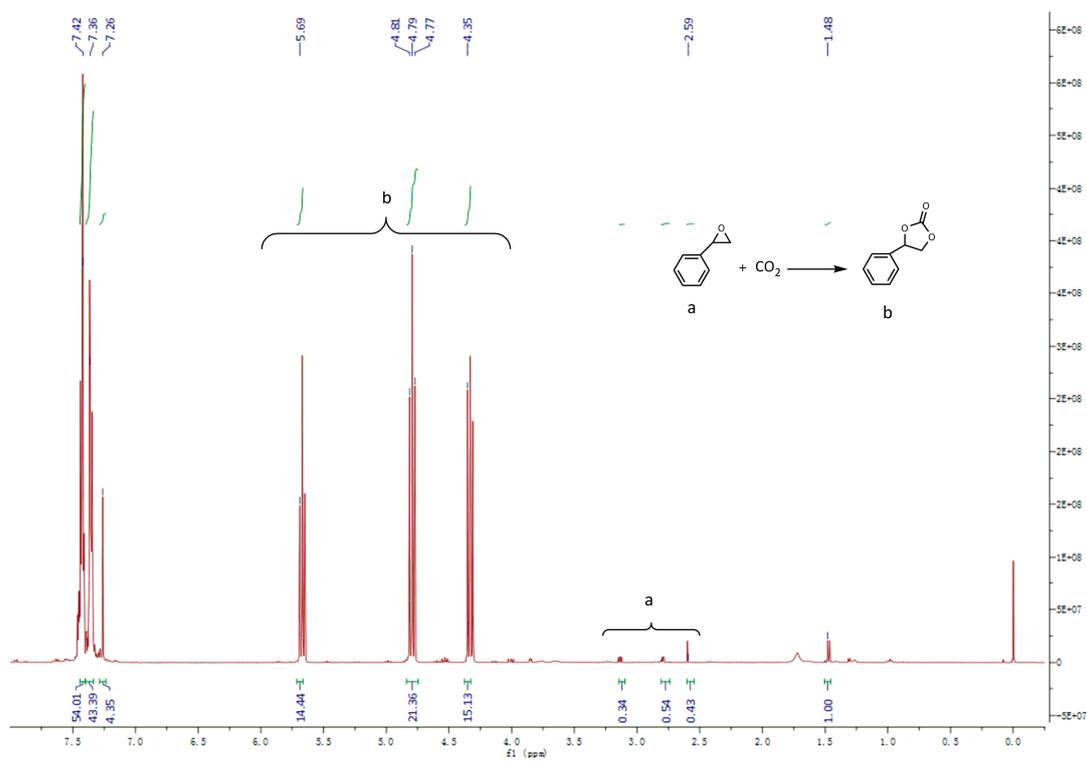
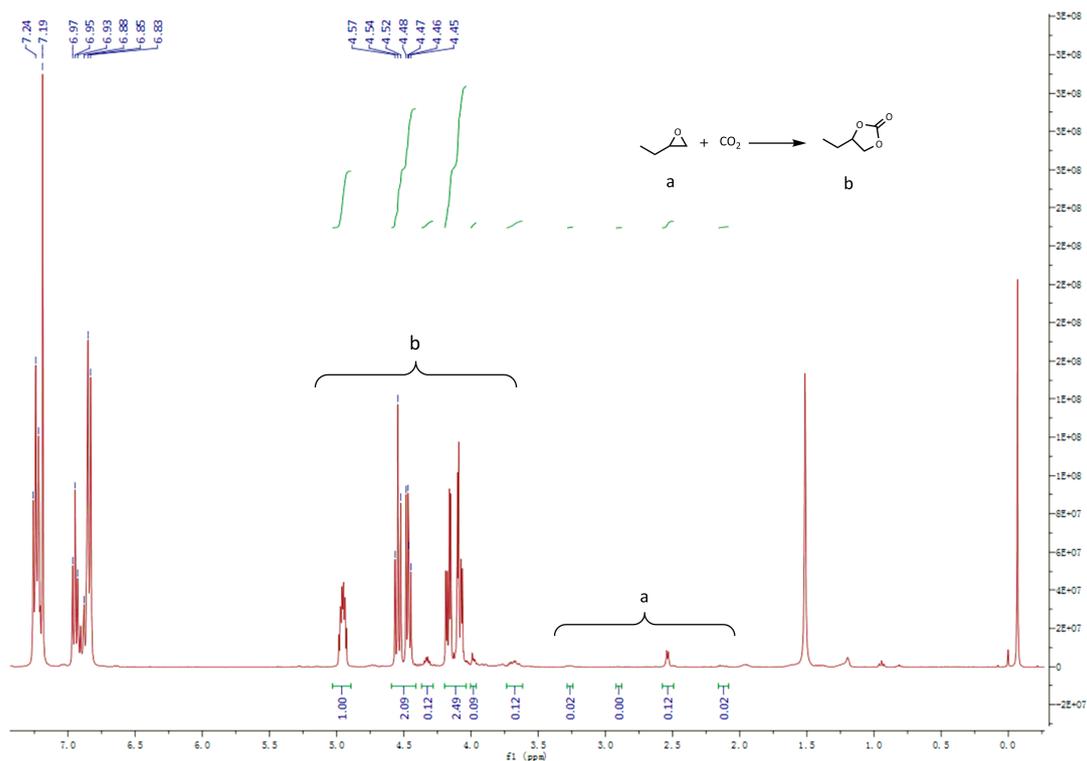


Figure S1. $^1\text{H-NMR}$ spectrum in CDCl_3 of the crude product [4-(chloromethyl)-1,3-dioxolan-2-one] obtained from the conversion of epichlorohydrin using complex **2** as a catalyst.



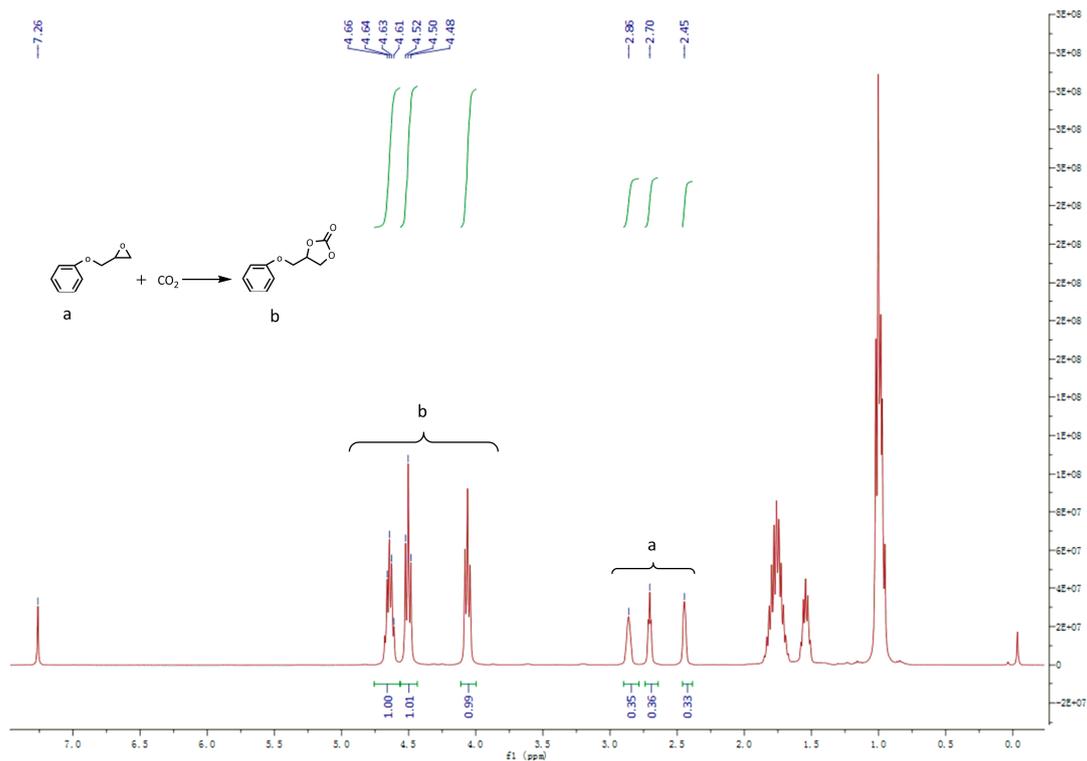


Figure S4. ¹H-NMR spectrum in CDCl₃ of the crude product [4-(phoxymethyl)-1,3-dioxolan-2-one] obtained from the conversion of 1,2-Epoxy-3-phenoxypropane using complex **2** as a catalyst.

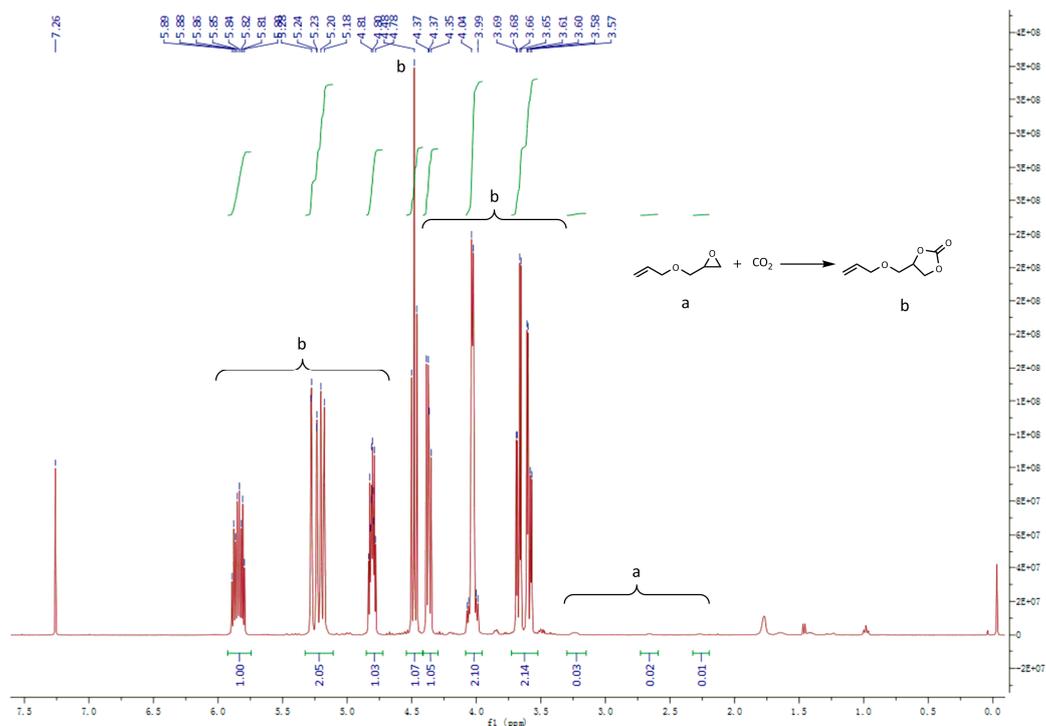


Figure S5. ¹H-NMR spectrum in CDCl₃ of the crude product [4-(allyloxymethyl)-1,3-

dioxolan-2-one] obtained from the conversion of allyl glycidyl ether using complex **2** as a catalyst.