

Supporting Information

Metal Embedded Porous Carbon for Efficient CO₂ Cycloaddition under Mild Conditions

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1. Material synthesis

1.1. Zeolitic imidazole frameworks (ZIFs) synthesis

All chemical reagents for synthesis of materials and substrates were purchased from Aladdin Chemical and used as received. The solvents were directly used after purchase from Sinopharm Chemical. The ZIFs (template materials) were synthesized at room temperature. A typical synthesis, the metal sources (Zn(NO₃)₂•6H₂O and/or Co(NO₃)₂•6H₂O) and ligand source (2-methylimidazole, Hmim) were separately dissolved in 100 mL deionized water). The mole ratio Metal:Ligand:Water is 1:8:1100 and was constant for all synthesized ZIFs. The triethylamine (5mL) as deprotonating agent was added in an aqueous Hmim before mixing with an aqueous metal solution under vigorous stirring. The details of metal, ligand source, and solvent (water) are provided in Table S1. The homogeneous solutions of metal and ligand were mixed under vigorous

stirring at room temperature for 24 h. The solid precipitate was separated using a centrifuge (9500 rpm, 5 min) and washed with deionized water for four times or until the obtained solution after centrifugal was clear. The solid products were dried at 90°C under vacuum for overnight before further used in next step.

Table S1. The mole and mass/volume of reagent were obtained to synthesis ZIF-8, ZIF-67 and dual metal Zn/Co-ZIF.

Sample	Metal source		Ligand	TEA	water
	Zn(NO ₃) ₂ ·6H ₂ O	Co(NO ₃) ₂ ·6H ₂ O	2-MIM		
ZIF-8	10 mmol, 2.97g	-	80 mmol, 6.5g	5 mL	200 ml
ZIF-67	-	10 mmol, 2.91g	80 mmol, 6.5g	5 mL	200 ml
ZnCo-ZIF	10 mmol, 1.48 g	0.5 mmol, 1.45g	80 mmol, 6.5g	5 mL	200 ml

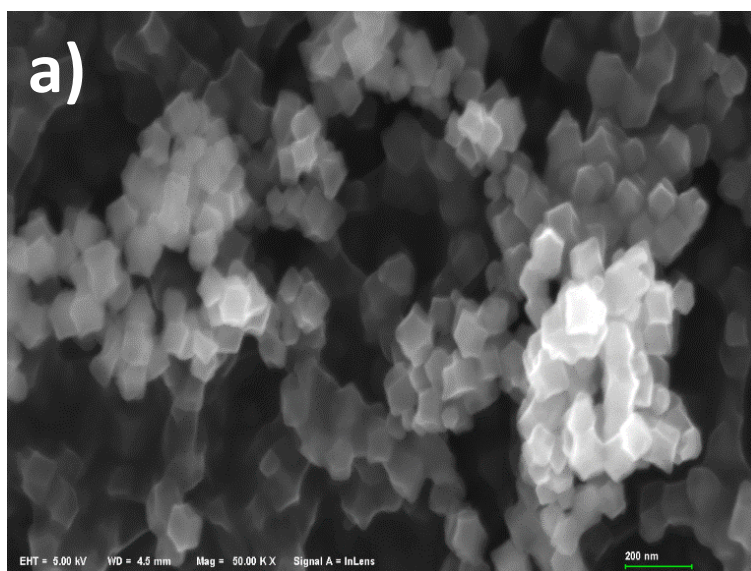
1.2. Porous carbonaceous material synthesis

An alumina ceramic boat (30x60x15 mm) containing the template material (250-300 mg of ZIFs) is transferred into a quartz tube (OD 60 mm, 1000 mm), which is installed in the muffle furnace (TL 1200, Nanjing Bo Yun Tong Instrument Technology Co. Ltd.). The system is purged with a 5%H₂/Ar flow having a rate of 50 cm³·min⁻¹ (mass flow controller, S48-32HMT, Nanjing Bo Yun Tong Instrument Technology Co. Ltd.) for 20 min before ramping the temperature. The pyrolysis process was controlled using a temperature program with a heating rate of 10°C·min⁻¹. The final temperature was kept for 1h up to 4h before cooling to room temperature. During the pyrolysis, a continuous flow (50 cm³·min⁻¹) of 5%H₂/Ar was applied. The pyrolyzed materials were stored for further use in a desiccator to avoid moisture adsorption. The pyrolyzed materials revealed a weight loss of about 50-60% based on the weight of the template material.



Figure S1. The muffle furnace: TL 1200, Nanjing Bo Yun Tong Instrument Technology Co. Ltd.

2. Characterization



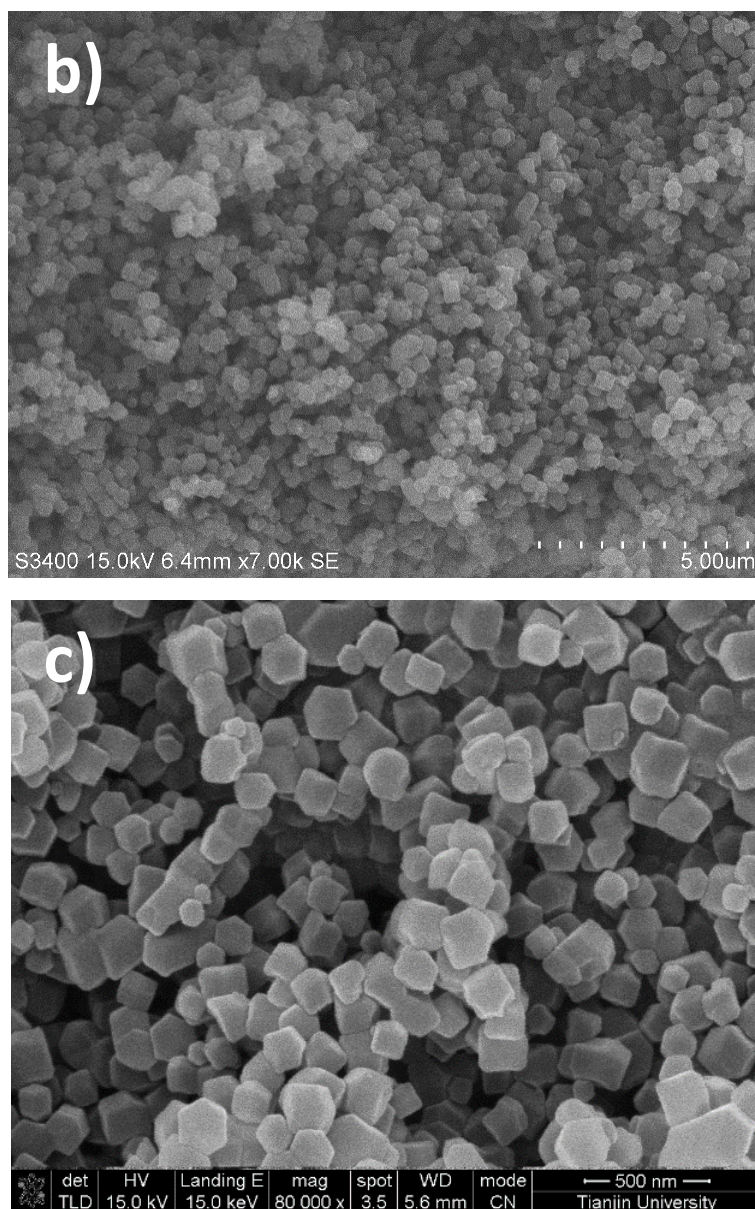


Figure S2. Crystal morphologies of as synthesized ZIF-8 (a), ZIF-67 (b), and bimetal ZnCo-ZIF(c) using SEM.

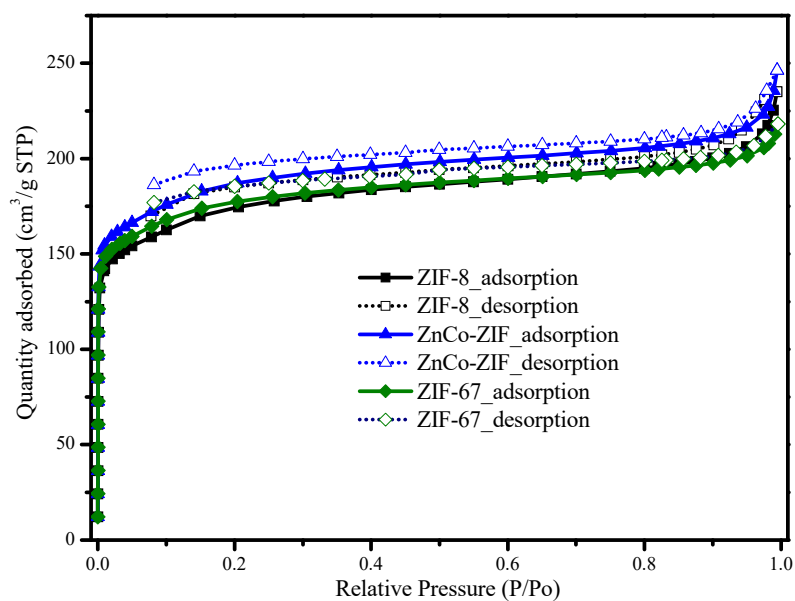


Figure S3. N₂ adsorption isotherms at 77K of template ZIF-8, ZIF-67, and bimetal ZnCo-ZIF

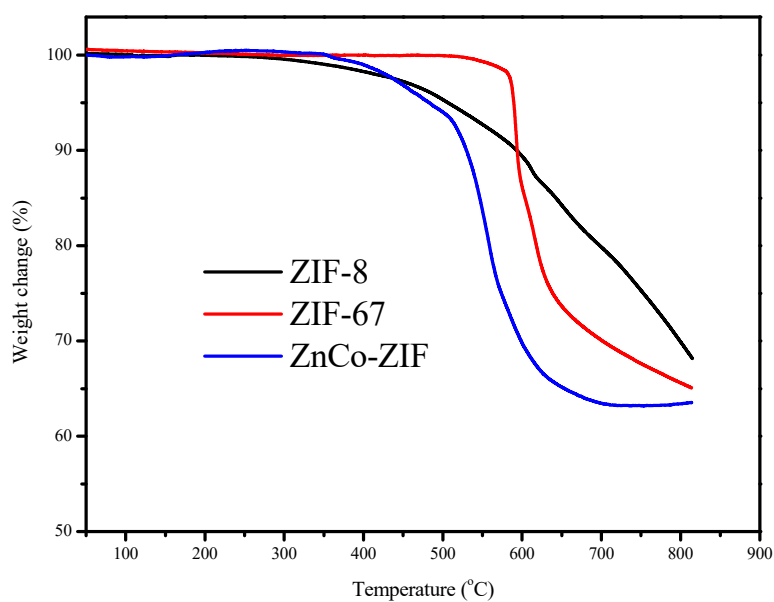


Figure S4. TGA analyses of ZIF series from room temperature up to 800°C with a heating rate of 10°C/min under Ar atmosphere (20 cc/min). All the ZIF-8 samples were activated at 200°C under vacuum for 3h before TGA analysis.

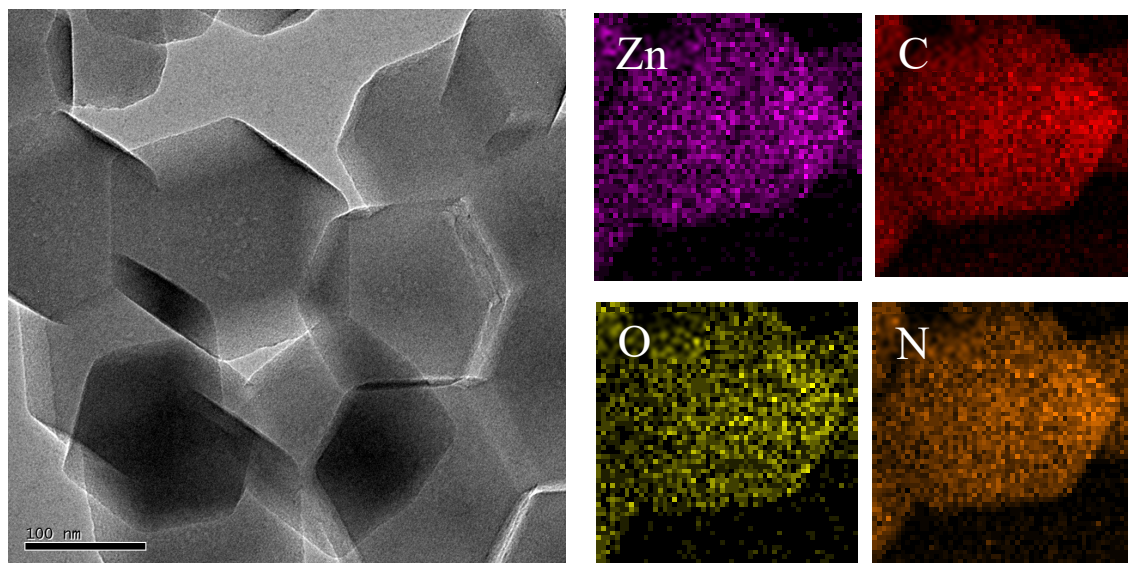


Figure S5. Transmission electron microscope (TEM) image and elemental mapping (EDX) of ZIF-8. High-resolution transmission electron microscope (HR-TEM) and energy dispersive X-ray spectroscopy (EDS) analyses were carried out using a JEOL JEM-2100F microscope operating at a high voltage of 200 kV.

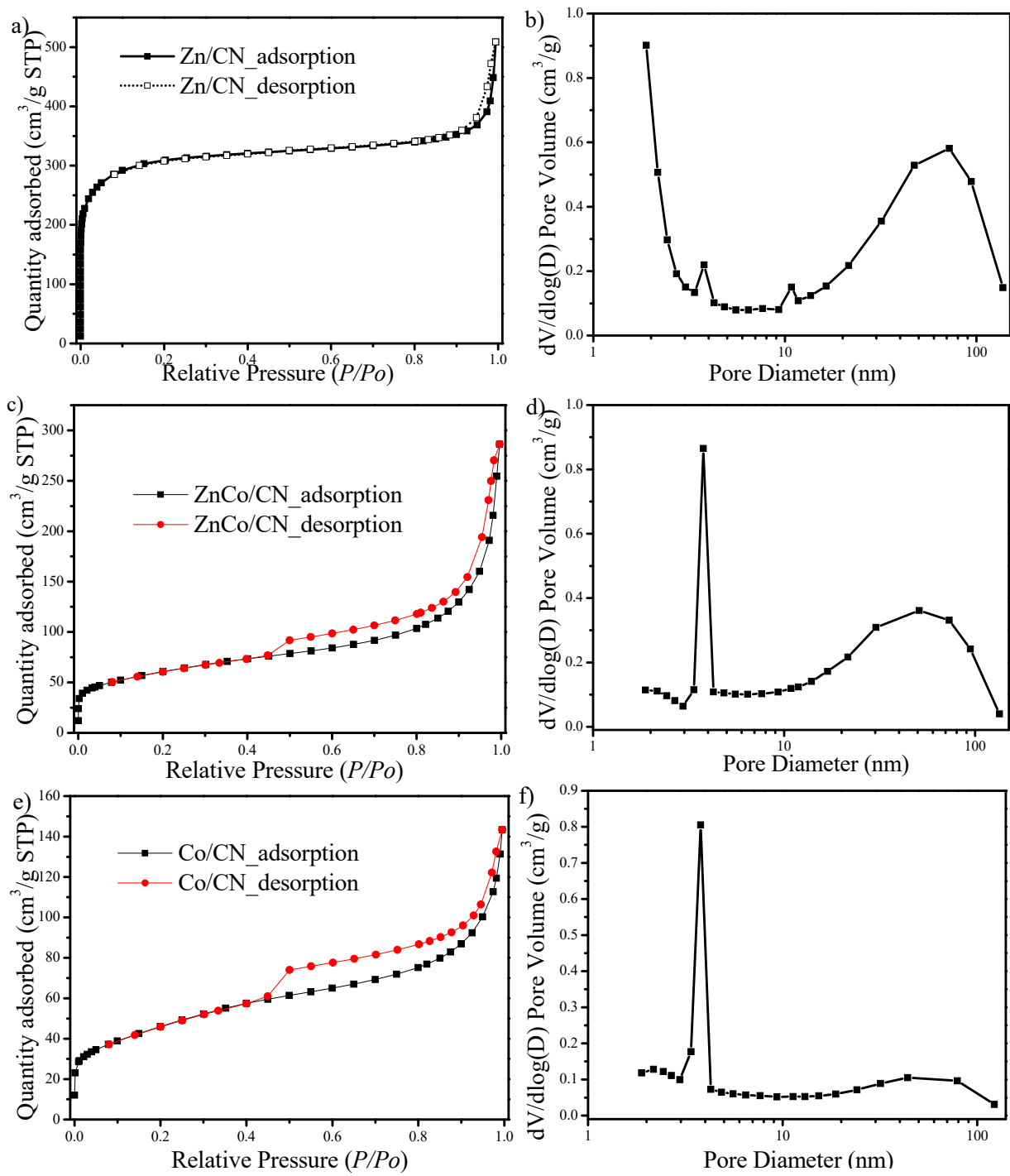


Figure S6. N₂ adsorption isotherm at 77K and pore size distribution (BJH) of Zn/CN-1000 (a, b). ZnCo/CN-1000 (c, d), and bimetal Zn/CN-1000 (e, f).

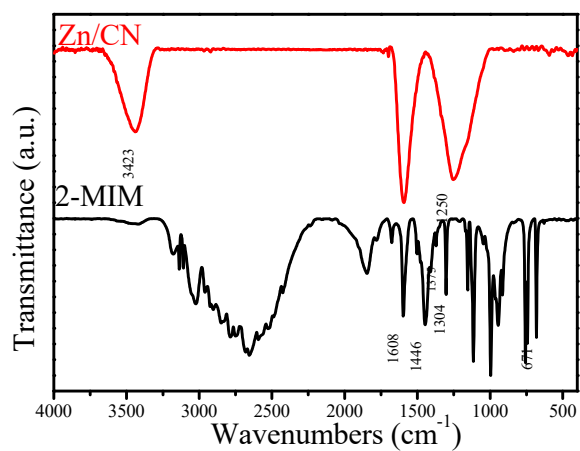


Figure S7. FTIR spectra of pyrolyzed ZIF compared with organic linker.

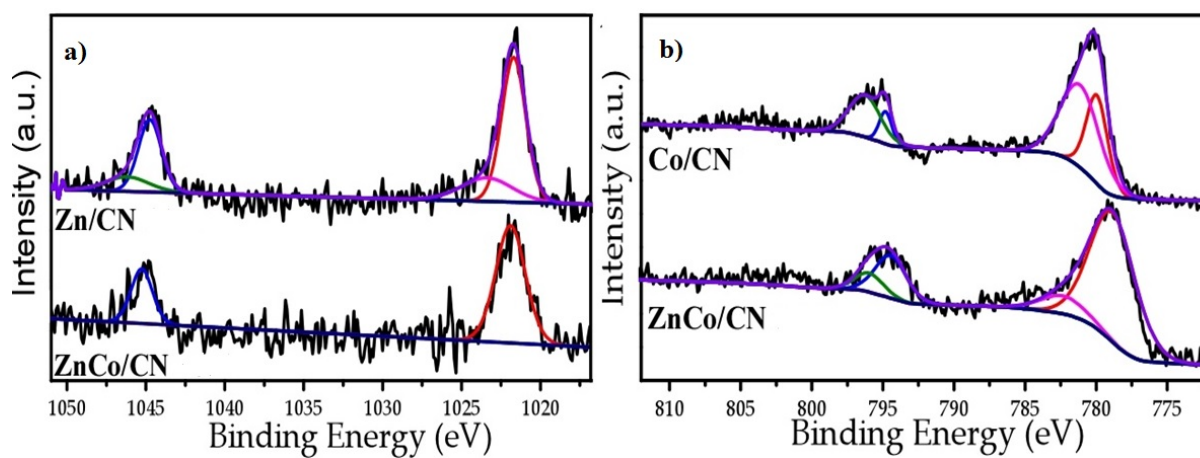


Figure S8. High-resolution XPS spectra of zinc (a) and cobalt region (b) from Zn/CN, Co/CN and ZnCo/CN

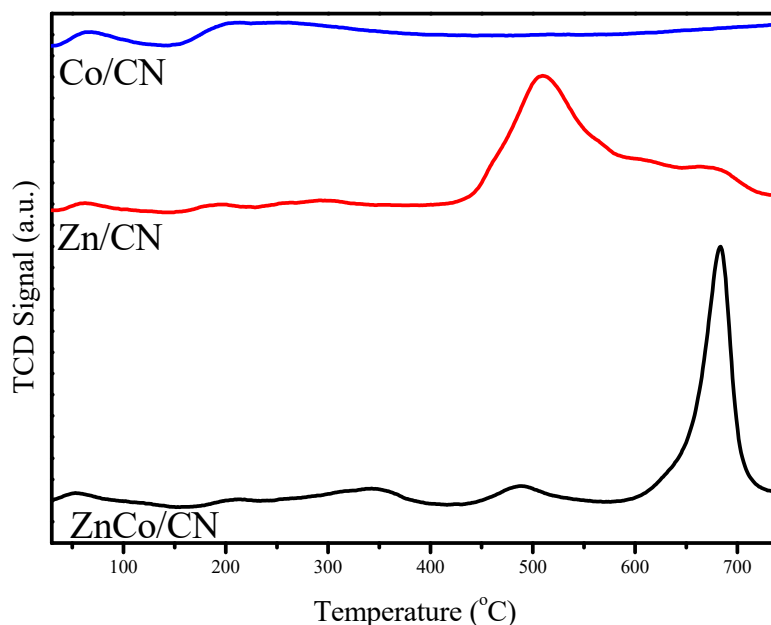


Figure S9. CO₂-TPD analysis of synthesized porous carbon: ZnCo/CN (bottom), Zn/CN(middle), and Co/CN(top).

Temperature programmed desorption (TPD) was performed for all samples using a Micromeritics Chemisorb (AutoChem II 2920) with ChemiSoft TPx software. The samples were pretreated at 150°C under carrier He gas for 3h, and then cooled to the adsorption temperature at 25 °C. NH₃ as probe gas was introduced to the sample by continuous flow. The probe gas was adsorbed to saturation at adsorption temperature of 25°C which can be observed from the stable TCD detector signal. The physically adsorbed gas on the samples was then removed by flushing the samples with He-gas till a stable TCD signal was obtained. The temperature programmed desorption was measured using a TCD detector, temperature rising to 750 °C at a rate of 10 °C/min.

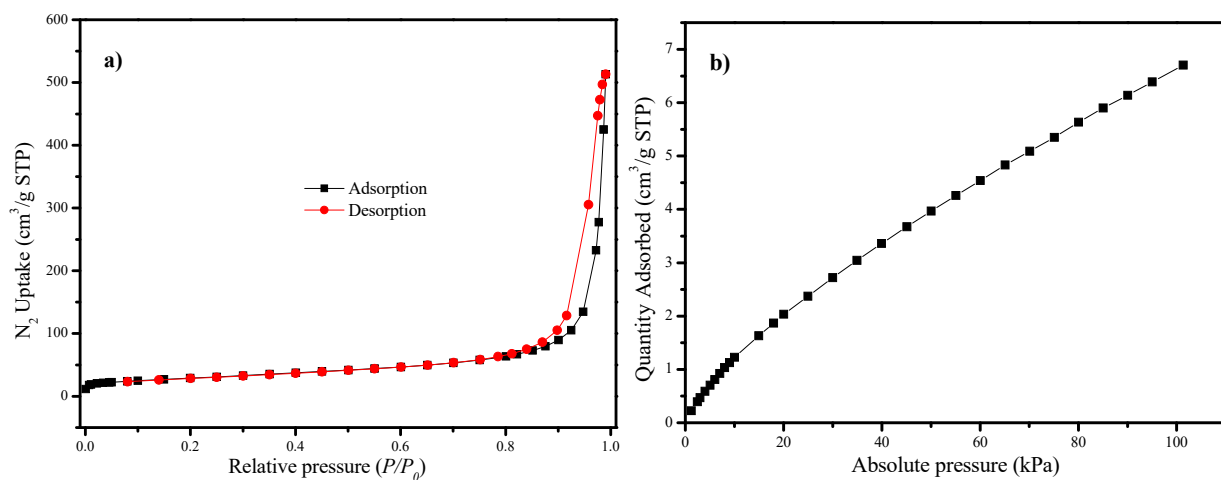


Figure S10. Nitrogen adsorption isotherm at 77K (a) and CO_2 adsorption at 273K (b) on Carbon graphite

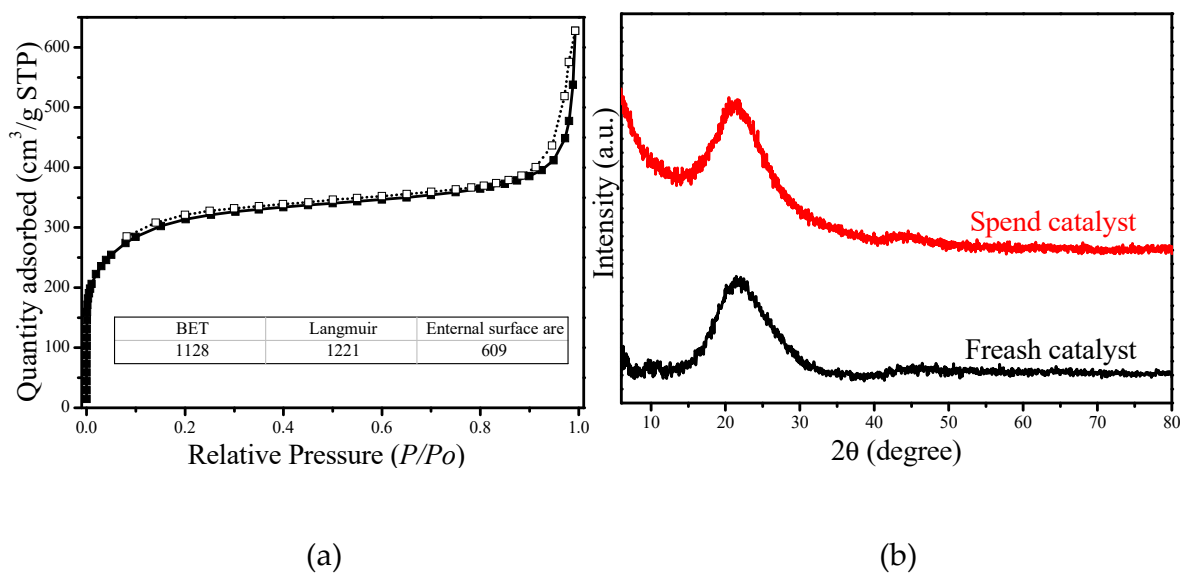


Figure S11. (a) N_2 adsorption isotherm at 77K of Zn/CN after reaction (spend catalyst). (b) XRD diffraction of fresh and spend Zn/CN

Table S2. The elemental composition of materials

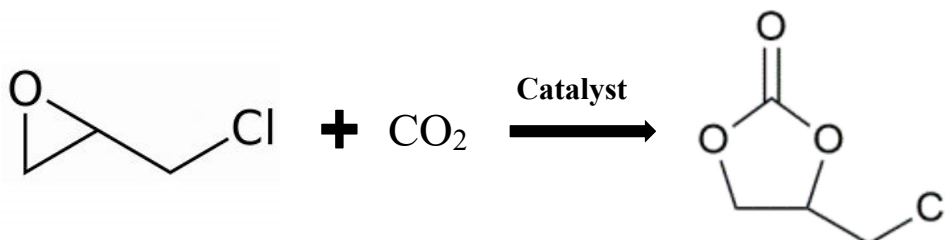
Samples	Zn % wt ¹	Co %wt ¹	N %wt ²	C %wt ²
ZnCo-ZIF	16.0	16.4	24.5	41.9
ZnCo/CN	0.05	5.85	1.9	53.7
ZIF-67	0.0	27.7	25.1	43.1
Co/CN	0.0	29	6.9	27.6
ZIF-8	27.8	0.0	24.2	43.1
Zn/CN ³	1.80	0.0	3.5	61.9

¹ ICP in wt% from Inductively coupled plasma atomic emission spectroscopy (ICP-OES, Varian VISTAMPX),

² CHN Elemental analysis (Vario EL cube),

³ holding pyrolysis at 1000°C for 1h,

3. Catalytic experiments



CO₂ addition into epichlorohydrin producing 3-chloro-1-propene carbonate.

The progression of reaction was identified from ¹H NMR in CDCl₃ 500 MHz:

Epichlorohydrin: δ 3.57-3.63 (m, 2H), **3.23 (m, 1H)**, 2.68 (m, 1H), 2.88 (m, 1H);

3-chloro-1-propene carbonate: ¹H NMR (500 MHz, CDCl₃): δ **4.90-5.02 (m, 1H)**, 4.61 (dd, *J* = 8.6 Hz, 1H), 4.45 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.68-3.78 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 154.5, 74.5, 67.0, 44.1.

The catalytic performance was calculated from reaction conversion which is measured from the peak ratio 3.23 (m, 1H) of epichlorohydrin and 4.90-5.02 (m, 1H) of 3-chloro-1-propene carbonate.

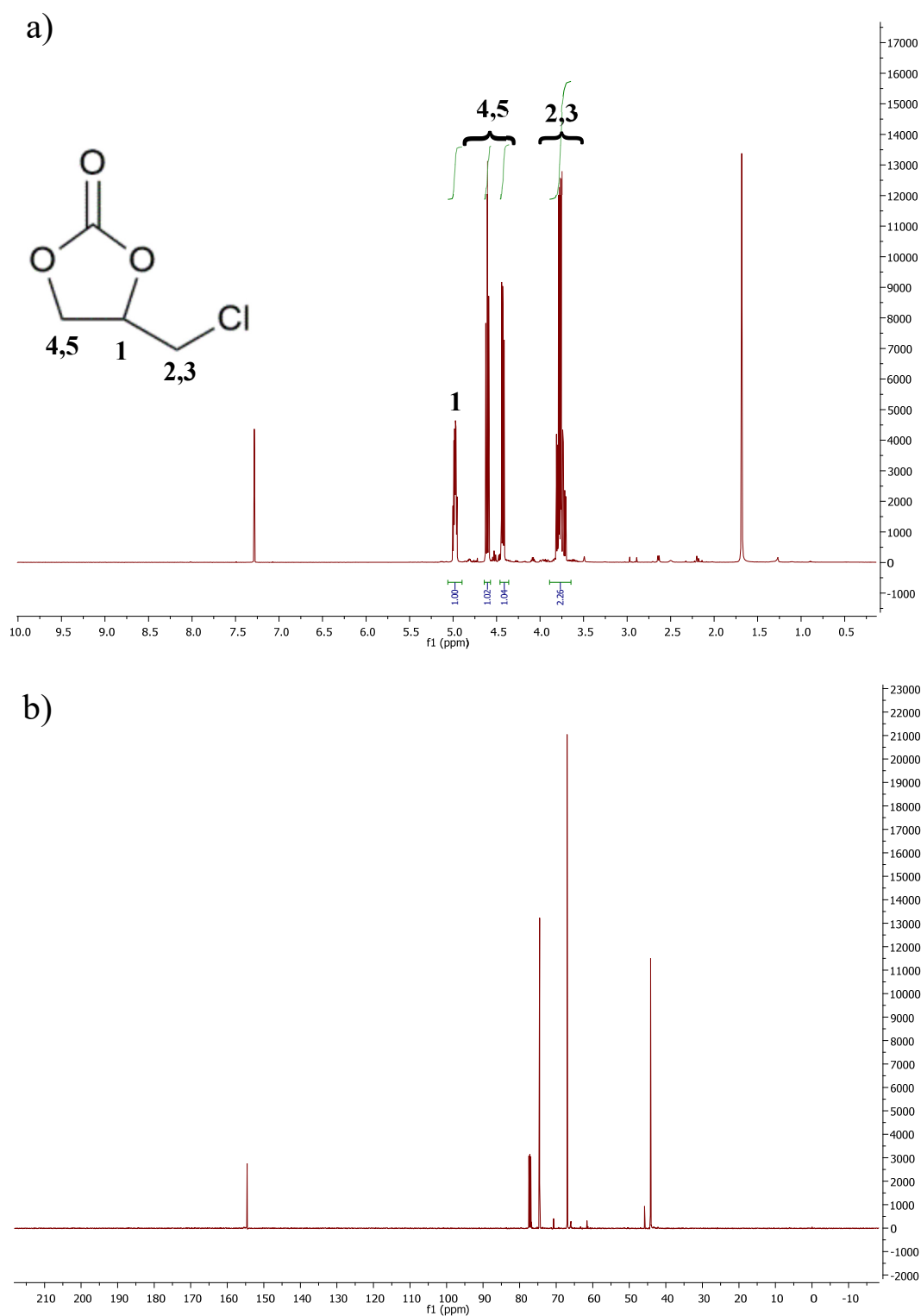


Figure S12. ^1H -NMR (a) and ^{13}C -NMR (b) spectrum in CDCl_3 of the product [3-chloro-1-propene carbonate] obtained from the conversion of epichlorohydrin with CO_2 . Reaction condition: 850 mg epichlorohydrin, 50 mg of Zn/Cn-1000, 140°C , 8 bar of CO_2 , 8h.

Table S3. Overview of catalytic performance under different reaction conditions

Entry	Catalyst	Substrate (mg)	Temperature	Time	Reactivity (% Conv.)
1	non	Epichlorohydrin (850mg)	80	24	0
2	non	Epichlorohydrin (850mg)	140	8	1
3	ZnCo-ZIF ^a	Epichlorohydrin (850mg)	80	24	58
4		Epichlorohydrin (850mg)	140	24	100
5	ZIF-8 ^a	Epichlorohydrin (850mg)	100	24	40
6		Epichlorohydrin (850mg)	140	24	100
7	ZIF-67 ^a	Epichlorohydrin (850mg)	90	24	50
8		Epichlorohydrin (850mg)	140	24	100
9	Carbon graphite oxide ^d	Epichlorohydrin (850mg)	80	24	5
10	g-C ₃ N ₄ ^d	Epichlorohydrin (850mg)	80	24	21
11	Carbonized-Co(NO ₂) ₃ ·6H ₂ O ^b	Epichlorohydrin (850mg)	80	24	0
12	Carbonized-Zn(NO ₂) ₃ ·6H ₂ O ^c	Epichlorohydrin (850mg)	80	24	0
13	Zinc oxide ^d	Epichlorohydrin (850mg)	80	24	6
14	Zinc carbonate ^d	Epichlorohydrin (850mg)	80	24	2
15	2-Methylimidazole (2-MIM) ^d	Epichlorohydrin (850mg)	80	24	90
16	Zn/CN	Epichlorohydrin (850mg)	80	24	85
17	Zn/CN	Epibromohydrin (1260mg)	80	24	80
18	Zn/CN	Propylene oxide (534mg)	80	24	80
19	Zn/CN	1,2-Epoxyhexane (921mg)	80	24	83
20	Zn/CN ^f	Glycidol (682mg)	140	8	78

21	Zn/CN ^f	Butyl Glycidyl Ether (1198mg)	140	8	70
22	Zn/CN ^f	Allyl Glycidyl Ether (1050mg)	140	8	54
23	Zn/CN ^f	Styrene Oxide (1105mg)	140	8	52
24	Zn/CN ^f	Benzyl Glycidyl Ether (1510mg)	140	8	35
25	Zn/CN ^f	Cyclopentene oxide (774mg)	140	8	23

Note: The reaction condition using substrate 9.2 mmol, Catalyst 50 mg, 1 bar of CO₂ pressure.

^{a)} Synthesized material via room temperature reported by Kui Zhou, etc.[1]

^{b)} The metal precursor to synthesized ZIFs and carbonization under 5%H₂/Ar at 1000°C for 4h.

^{c)} The metal precursor to synthesized ZIFs and carbonization under 5%H₂/Ar at 800°C for 4h.

^{d)} Using catalyst weight of 50 mg

^{e)} Reaction condition: 1.7 g of Epichlorohydrin, 50mg of catalyst (Zn/CN-1000-4h)

^{f)} Reaction under 8 bar of CO₂ pressure

Table S4. Summary catalyst performance and reaction system based on the carbon-based materials for the synthesis of cyclic carbonates with reaction condition

Catalyst	Epoxide	Co-catalyst or solvent	Reaction condition			Conv.	Yield	Ref.
			T(°C)	P(bar)	T (h)			
ZnO@NPC-Ox-700	SO	TBAB, Acetonitrile	60	1	48	98	98	[2]
	ECH	TBAB, Acetonitrile	60	1	24	94	94	
N-GMC	SO	TBAB, 2-propanol	80	10	15	-	98	[3]
C600-ZIF-9	ECH	-	80	6	6	93	90	[4]
AA-950	ECH	-	150	40	16		84.3	[5]
CNFWs-600-2	ECH	biphenyl	150	20	12	98	86	[6]
TW-900	SO	TBAB	100	8	1	99	95	
Zn-NCF-1000	ECH	-	140	8	8	99	99	[7]
Cu/NC-0.5	SO	TBAB	40	1	48	80	100	[8]
ZnNx@C-700	SO	TBAB	100	5	2	-	93	[9]
	PO		100	5	2	-	92	
	ECH		100	5	2	-	97	

ZIF-8/CN-foam	ECH	-	80	10	24		93	[10]
Zn/Co-ZIF-H ₂ Ar-1000	ECH	-	140	8	8		93	[11]
	PO	-	140	8	8		95	
Zn-N-HOPCPs (light irradiation)	PO	TBAB	-	1	10		95	[12]
Zn-Asp-300	PO	TBAB	80	10	2	-	97	[13]
	ECH		80	10	2	99.9	96.6	
	EBr		80	10	2	-	96.7	
HPC-800	EBr	TBAB	-	1	10	-	94	[14]
Co@N0.07C	SO	TBAB	60	1	4	99	92	[15]
	ECH		60	1	12	>84	84	
	Glycido l		150	15	15	99		
JA500	ECH	-	150	15	15	99	93	[16]
	Glycido l		150	15	15	99	94	
M-500	ECH	-	150	15	15	99		[16]
	PO		150	15	24	84	99	
ZnCl ₂ /Al ₂ O ₃	ECH	TBAI	60	6	6	-	87	[17]
	SO		60	4	6	-	100	
ZNC-800	PO	TBAB	15-85	1	10	-	80 ^b	[18]
Zn ₄ @POSS-1 ^a	SO	TBAI	100	1	4	96	-	[19]
Zn(salen) ^a	SO	TBAB	50	50	24	98	>99	[20]
Zn/CN-1000	ECH	-	90	1	24	98	91	This work
	PO		80	1	24	80	80	

Abbreviation: SO = Styrene oxide, ECH = epichlorohydrin, PO = propylene oxide, EBr = Epibromohydrin, TBAB = tetrabutylammonium bromide,

^a Metal complex used as a homogeneous catalyst

^b Photothermally-driven CO₂ cycloaddition

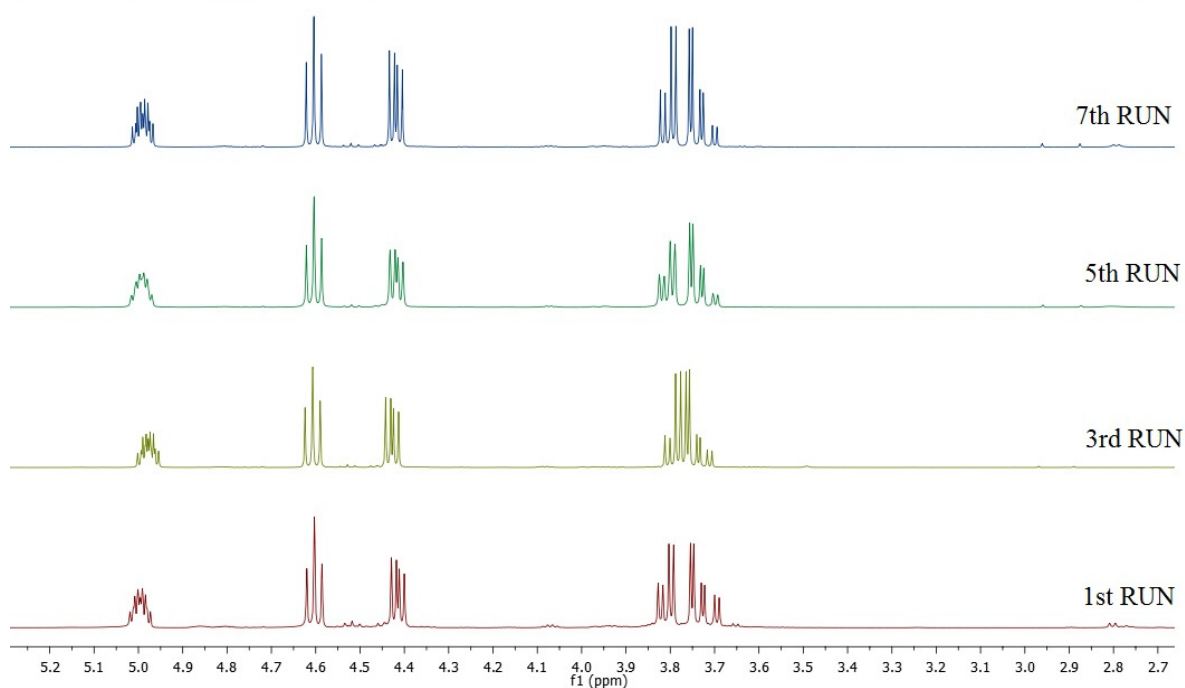


Figure S13. The NMR of the recycling experiment using Zn/CN-1000 (reaction conditions: epichlorohydrin 850 mg (9.2 mmol), Catalyst 50 mg, 90°C, 1.5 bar of CO₂ pressure for 24h).

Recycle experiment, the catalyst was separated from solution via centrifugal (9500 rpm, 15 min) and washed with methanol 4 times before drying at 100°C under vacuum overnight. The weight of catalyst was measurement before each cycle to keep the ratio constant between catalyst and substrate.

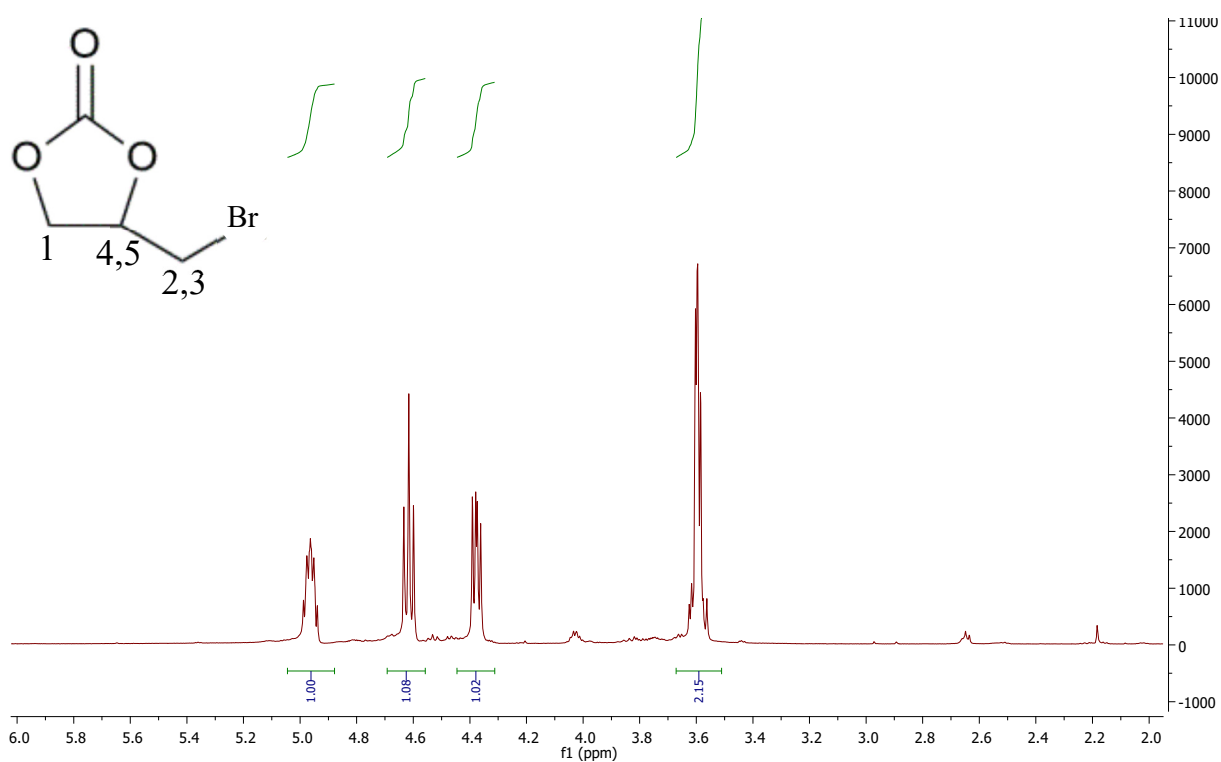


Figure S14. ^1H NMR spectrum in CDCl_3 of the product [4-(bromomethyl)-1,3-dioxolan-2-one] obtained from the conversion of epibromohydrin using Zn/CN-1000 (50 mg), CO_2 pressure 1.5 bar, 80°C for 24h.

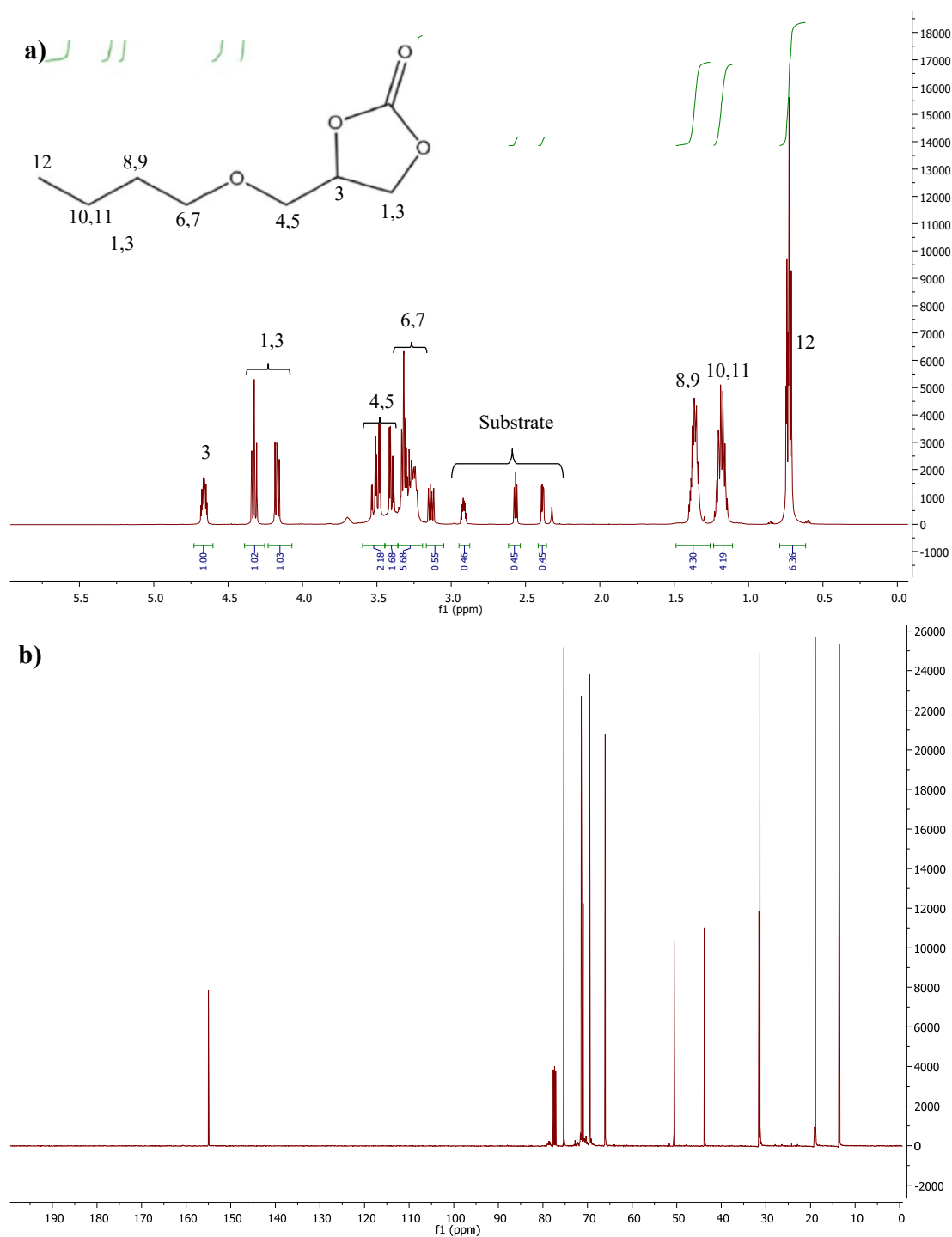


Figure S15. ^1H -NMR (a) and ^{13}C -NMR (b) spectrum in CDCl_3 of the product [4-butoxymethyl]-1,3-dioxolan-2-one] obtained from the reaction mixture of butyl glycidyl ether using Zn/CN-1000 (50 mg), CO_2 pressure 8 bar, 140°C for 24h.

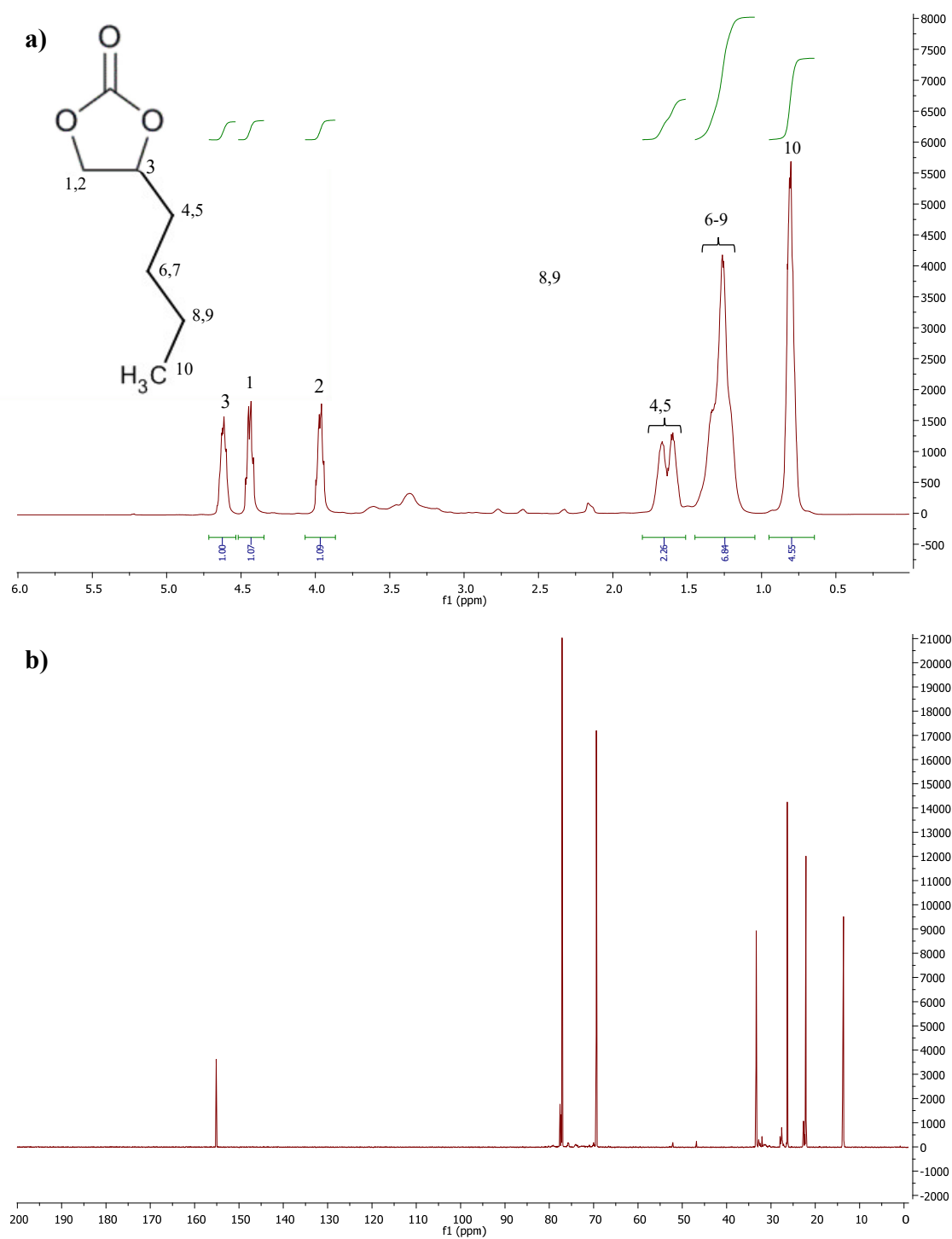


Figure S16. ^1H -NMR (a) and ^{13}C -NMR (b) spectrum in CDCl_3 of the product [4-butyl-1,3-dioxolan-2-one] obtained from the reaction mixture of 1,2-epoxyhexane using Zn/CN-1000 (50 mg), CO_2 pressure 8 bar, 140°C for 24h.

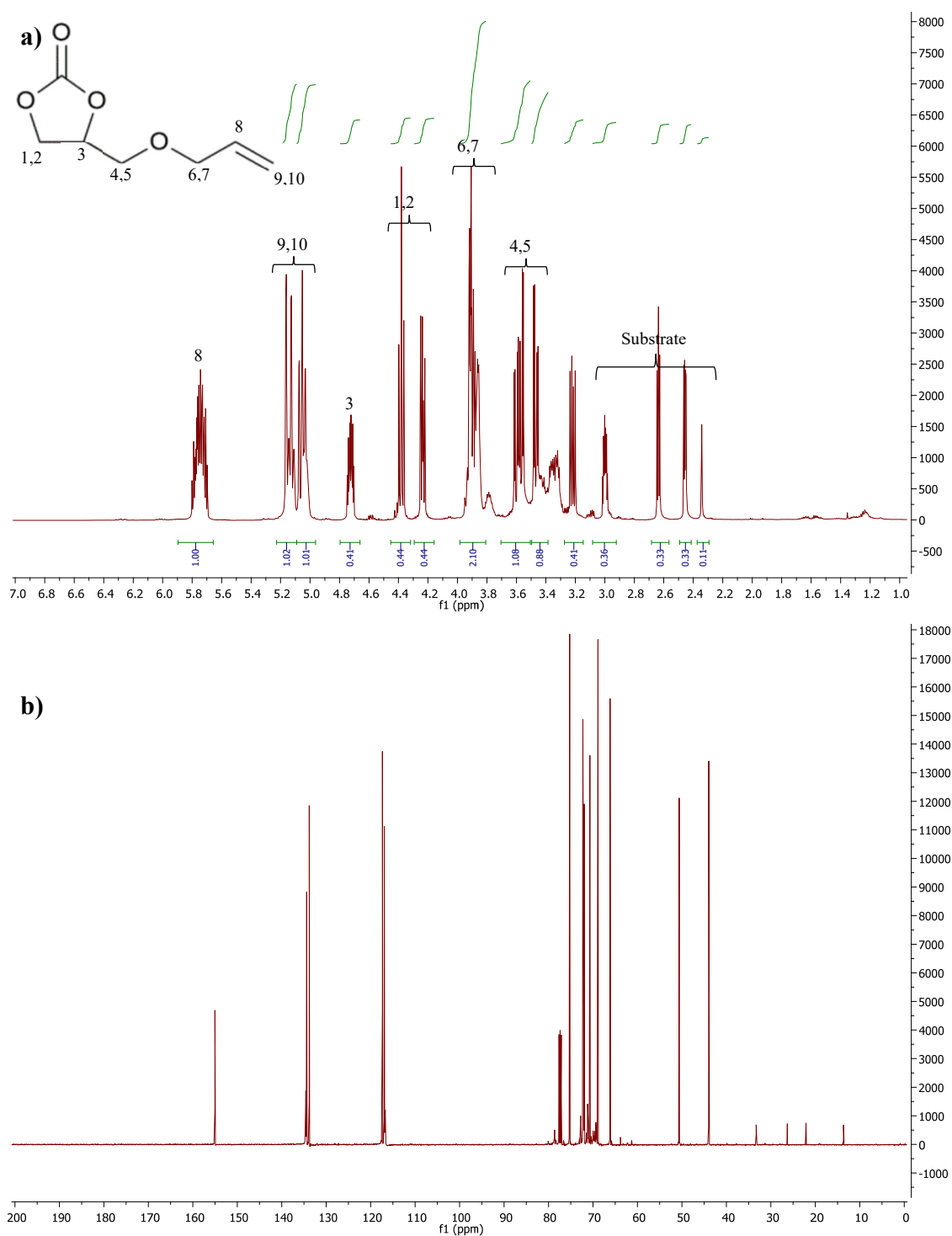


Figure S17. ^1H -NMR (a) and ^{13}C -NMR (b) spectrum in CDCl_3 of the product [Allyloxymethyl-1,3-dioxlan-2-one] obtained from the reaction mixture of allyl glycidyl ether using Zn/CN-1000 (50 mg), CO_2 pressure 8 bar, 140°C for 24h.

Boon-NMR
ZIF-8-RT-1000H2Ar-PropyleneOxide-140C8bar8h

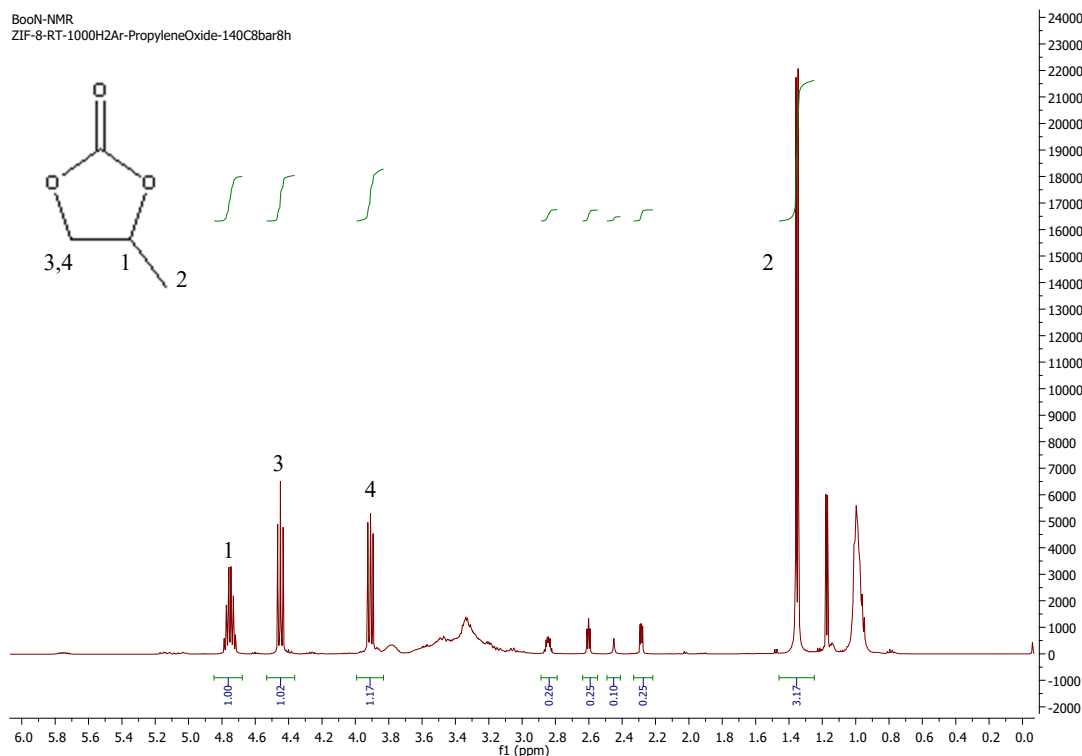


Figure S18. ^1H -NMR spectrum in CDCl_3 of the product [4-Methyl-1,3-dioxlan-2-one] obtained from the reaction mixture of propylene oxide using Zn/CN-1000 (50 mg), CO_2 pressure 1.5 bar, 80°C for 24h.

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