Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Simultaneous crystal transformation 2D to 3D and doped metal transitions on zeolitic imidazole framework-67 under free-solvent

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1. Experiment

Synthesis ZIF-67

A three-dimensional structure (ZIF-67) was synthesized following the previous report, while modified condition to enhance the yield, decrease the chemical usage.[1] A typical synthesis of ZIF-67(3D), the 10 mmol of metal source ($Co(NO_3)_2 \bullet 6H_2O$) and 80 mmol of ligand source (2-methylimidazole, 2-MIM) were separately dissolved in 100 mL of deionized water. The triethylamine (5 mL) as a deprotonating agent was added in an aqueous 2-MIM before mixing with an aqueous metals under vigorous stirring. The mixture was vigorously stirring at room temperature for 24 h, and then the precipitated solid was separated using a centrifuge (9500 rpm, 5 min). The solid products were washed by deionized water three times or until the obtained solution after centrifugal was clear. The solid products were dried at 100°C under vacuum overnight before further use or analysis.

Catalytic reduction of methylene blue (MB)

An aqueous solution of methylene blue (1mL, 2mM) was added in aqueous solution of borohydride solution (0.5mL, 0.4M). The extra water (6.3mL) was poured in previous solution under vigorous stirring of magnetic bar. The initial solution (t_0) was measured via UV-vis spectroscopic (UV-shimasu) before added 10 mg of synthesized catalysts in to the above solution. The progress reaction was measured at various time points (t_x) to monitor the reaction. For each sampling solution, the solution in 80 uL from mixture solution was diluted with 500uL water (DI) and filtrated through the membrane filter (2um) before measurement the spectrum via UV-vis.

Catalytic reaction of CO_2 cycloadditional

The synthesized catalysts (50 mg) and substrates (9.2 mmol) were charged in a high-pressure glass tube (15 mL) with a magnetic stir bar. The reactor's atmosphere was exchanged with CO_2 (99.9% purities) before pressurizing to 1.5 bar of CO_2. The reactor was immersed in a pre-heated oil bath at 60°C under stirring conditions (400 rpm) for 24h. The reactor was cooled to room temperature and $CDCl_3$ (1 mL) were added. The reaction mixture was analyzed via ^1H NMR using $CDCl_3$ as a solvent.

2. Material characterization

2.1. Powder X-Ray diffraction

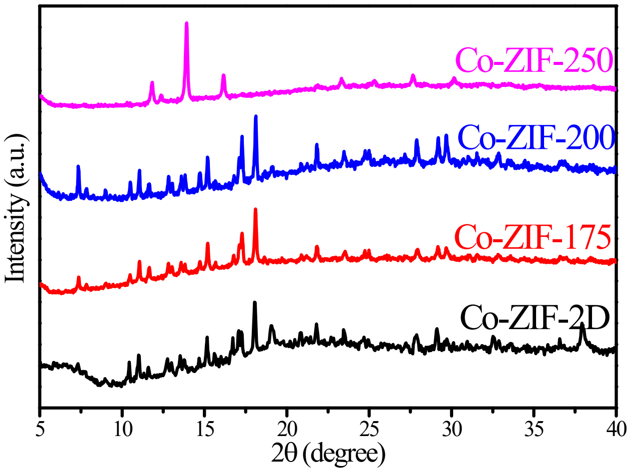


Figure S1. XRD patterns in different temperature treatment of PTT method for 1h under flowing Ar (50 cm^3/min)

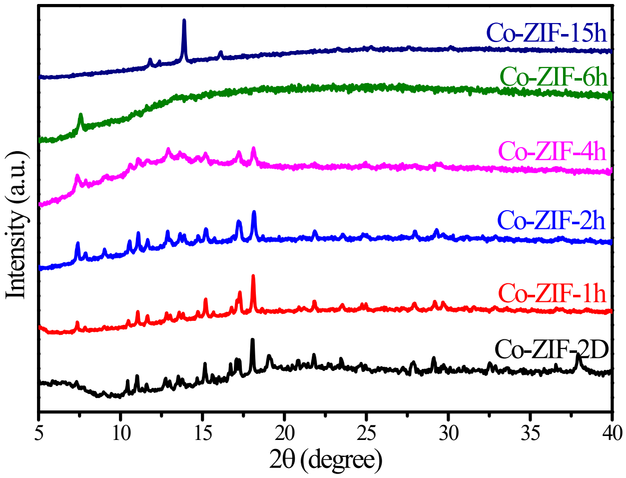


Figure S2. XRD patterns of different treated time of PTT method at 200°C under flowing Ar (50 cm^3/min)

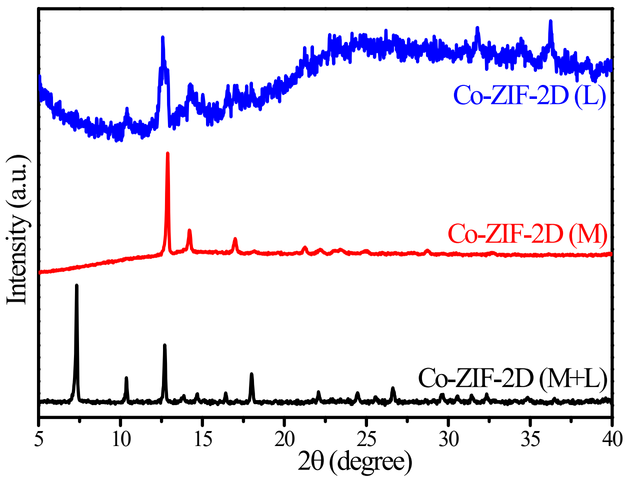


Figure S3. XRD patterns of post-thermal treatment (PTT) on Co-ZIF-2D with only added cobalt acetylacetonat (M, 0.5mmol), Co-ZIF-2D(M) or only adding 2-methylimidazole (L, 2mmol), Co-ZIF-2D(L)under thermal treatment at 200C under flowing Ar (50 cm^3/min) comparable to Co-ZIF-2D(M+L) or Co-ZIF-3D which added both of cobalt acetylacetonat (0.5 mmol) and 2-methylimidazole (2 mmol).

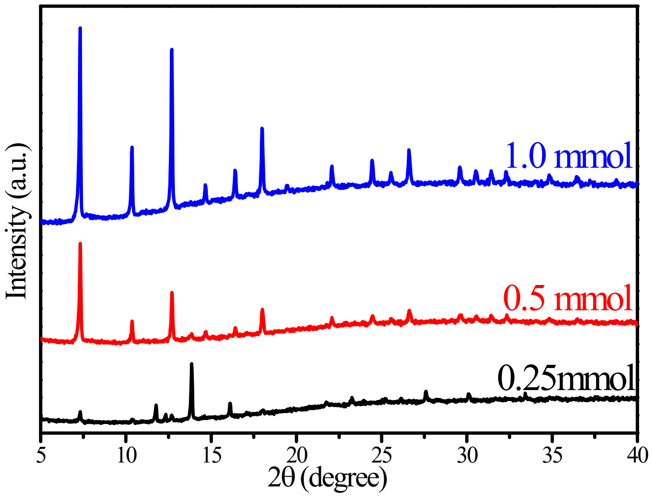


Figure S4. The diffraction patterns of Co-ZIF-3D with different amount of additive cobalt acetylacetonate with constant 2-methylimidazole (2mmol) and pristine Co-ZIF-2D (100 mg) following the proceed the PTT method at 200°C for 1h under flowing Ar (50 cm^3/min).

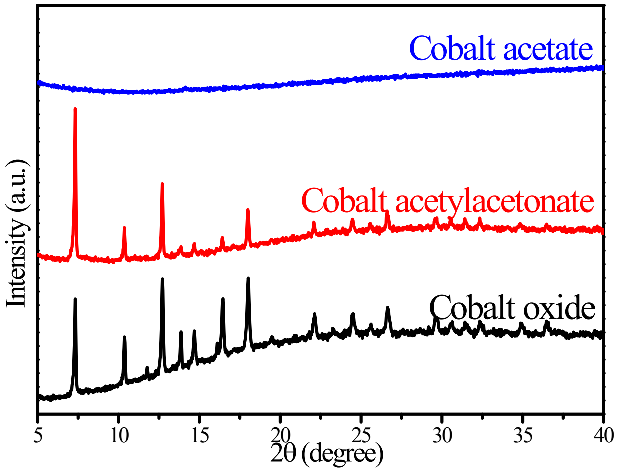


Figure S5. The diffraction patterns of Co-ZIF-3D with different sources of additive cobalt with constant 2-methylimidazole (2mmol) and pristine Co-ZIF-2D (100 mg) following the proceed PTT method at 200°C for 1h under flowing Ar (50 cm^3/min).

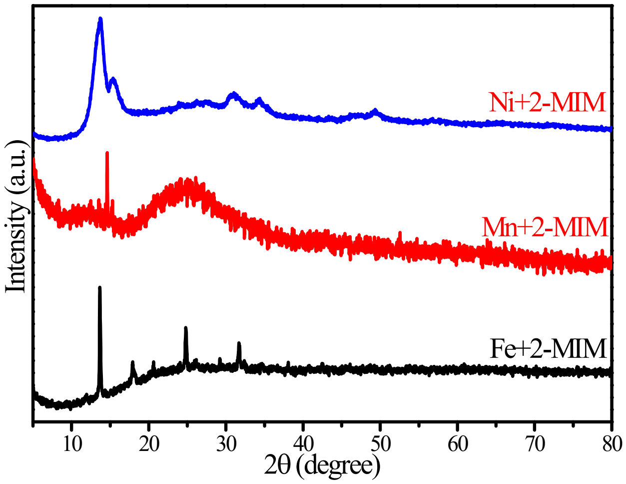


Figure S6. The diffraction patterns of thermal treatment on solid mixture metal precursor (0.5 mmol of iron acetylacetonate, or 0.5 nickel acethylacetonate, or 0.25 mmol of manganese acetylacetonate) with 2-methylimidzole (2 mmol) without Co-ZIF-2D at 200°C for 1h under flowing Ar (50 cm^3/min).

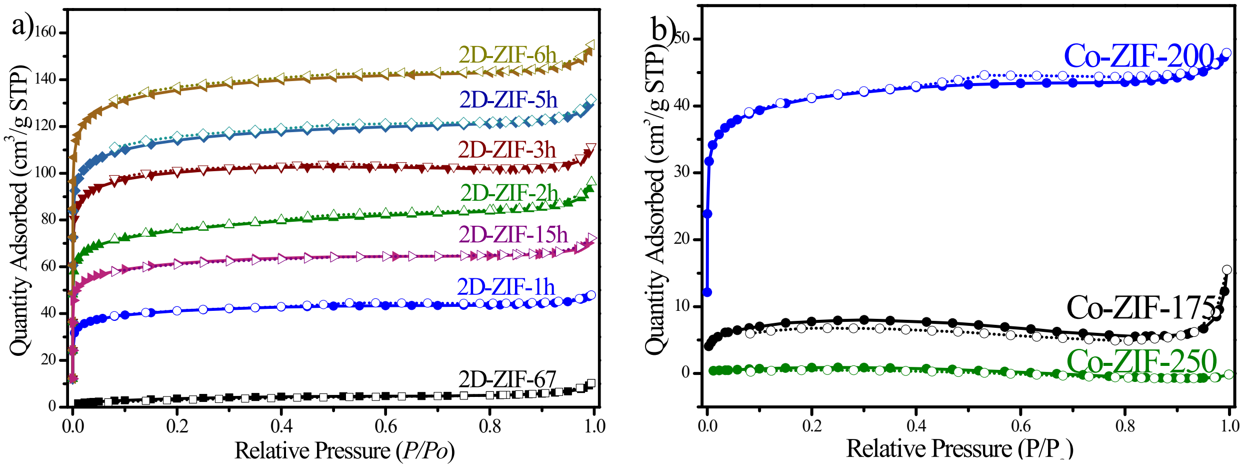


Figure S7. The isotherm of N_2 adsorption at 77K, a) different times of PTT method, and b) different temperature of PTT method.

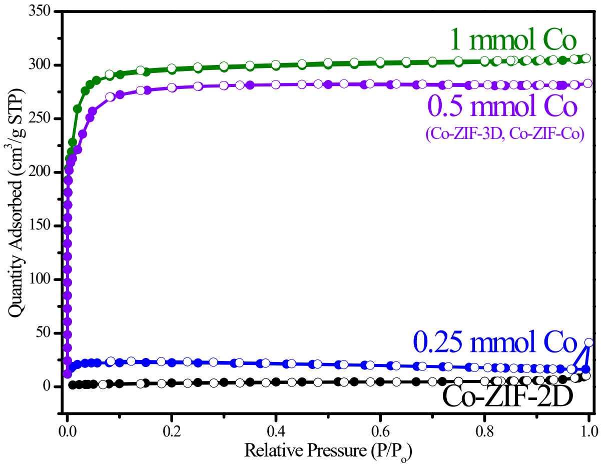


Figure S8. The isotherm of N_2 adsorption at 77K in different additional additive precursor (Cobalt acetylacetonate) with constant 2 mmol of 2-methylimidazole and 100 mg of Co-ZIF-2D following the process PTT method at 200°C for 1 h under flowing argon (50 cm^3/min)

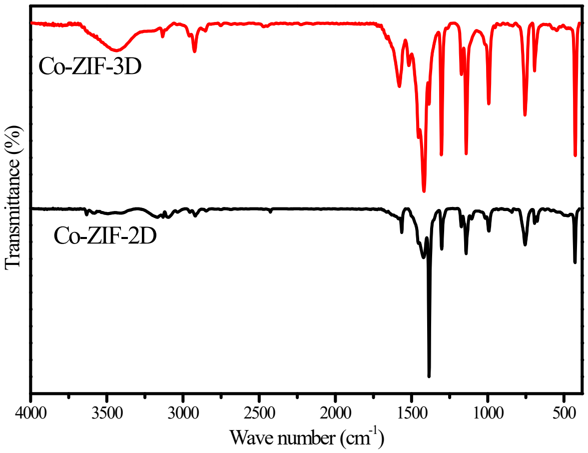
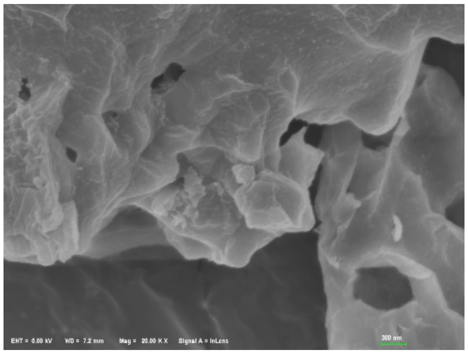
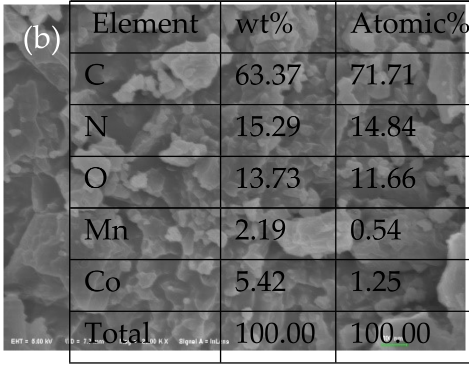


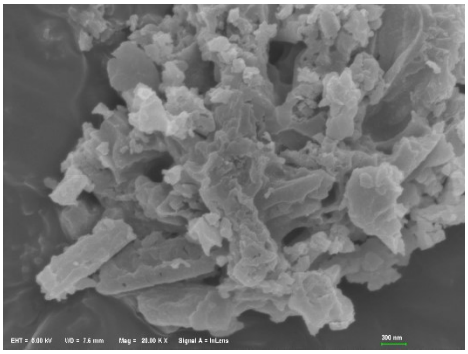
Figure S9. The FT-IR spectrum of Co-ZIF-2D and Co-ZIF-3D



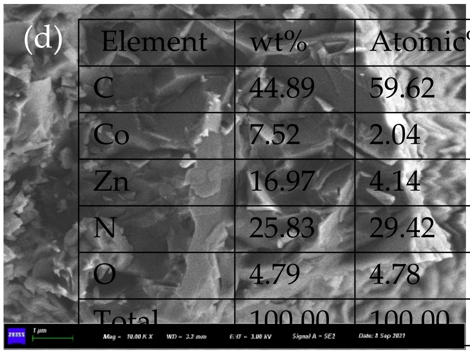
Element	wt%	Atomic%
C	52.39	60.39
N	31.75	31.38
O	7.13	6.17
Co	4.62	1.09
Ni	4.11	0.97
Total	100.00	100.00



Element	wt%	Atomic%
C	63.37	71.71
N	15.29	14.84
O	13.73	11.66
Mn	2.19	0.54
Co	5.42	1.25
Total	100.00	100.00



Element	wt%	Atomic%
C	63.05	72.18
N	13.53	13.28
O	14.43	12.40
Fe	2.78	0.68
Co	6.21	1.45
Total	100.00	100.00



Element	wt%	Atomic%
C	44.89	59.62
Co	7.52	2.04
Zn	16.97	4.14
N	25.83	29.42
O	4.79	4.78
Total	100.00	100.00

Figure S10. The crystal morphology and elemental composition via SEM-EDS analysis of Co-ZIF-Ni (a), Co-ZIF-Mn (b), Co-ZIF-Fe (c), and Zo-ZIF-Zn (d)

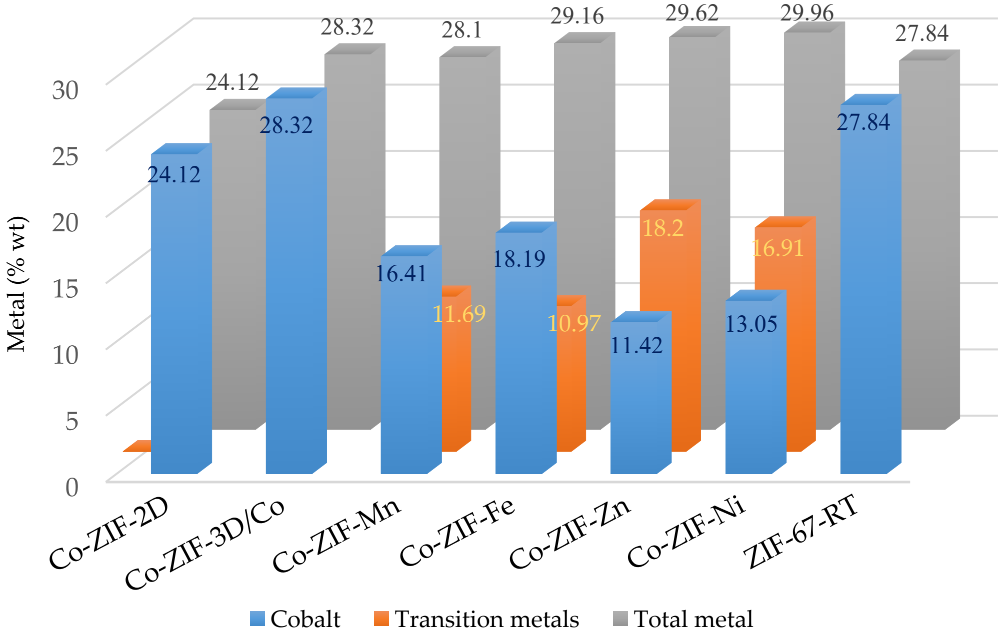


Figure S11. The metal element on synthesized materials via ICP analysis

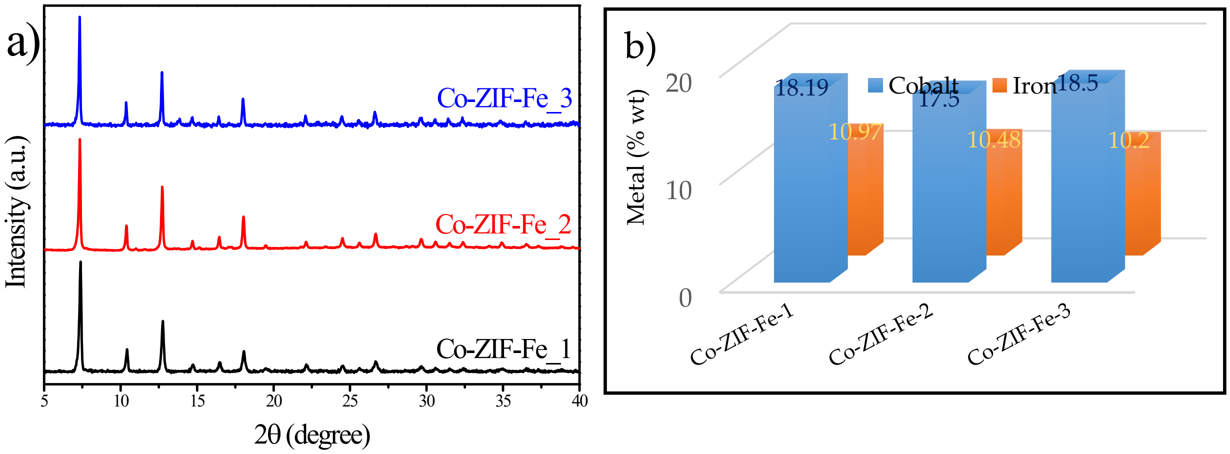


Figure S12. The repeatability studied on Co-ZIF-Fe; (a) Diffraction pattern of XRD analysis, and (b) the metal content via ICP.

3. Material application

3.1. Reduction of methylene blue (MB) to leucomethylene blue (LMB)

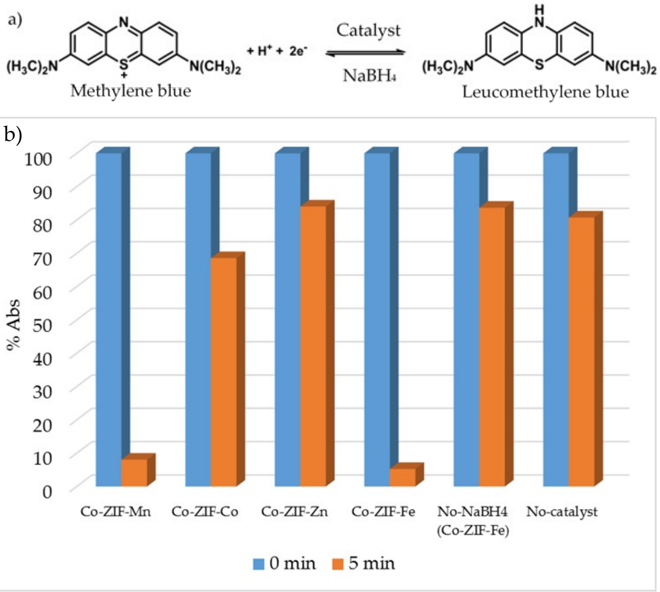
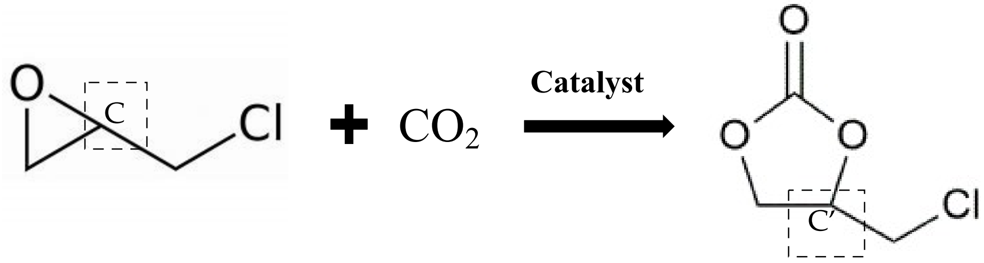


Figure. S13 a) Scheme reduction of methylene blue (MB) to leucomethylene blue (LMB), b) tracking reactivity at 5 min reaction with the initial absorbance (t= 0 min) by integrate area peak at 664 nm of UV-vis spectroscopy.

3.2. CO_2 cycloadditional in to epoxide to synthesis cyclic carbonate



Scheme S1. CO_2 addition into epichlorohydrin producing 3-chloro-1-propene carbonate. The progression of reaction was identified from ^{1}H NMR in $CDCl_3$ 500 MHz:

The conversion was calculated by measuring the integration ratio of peak c to c', see scheme 1.

$$\% \text{ Conversion} = \frac{C'}{C + C'} \times 100 \; ; \; C = \mathbf{3.23\ (m,\ 1H)},\ C' = \mathbf{4.90\text{-}5.02\ (m,\ 1H)}$$

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: ^{1}H NMR (500 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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.

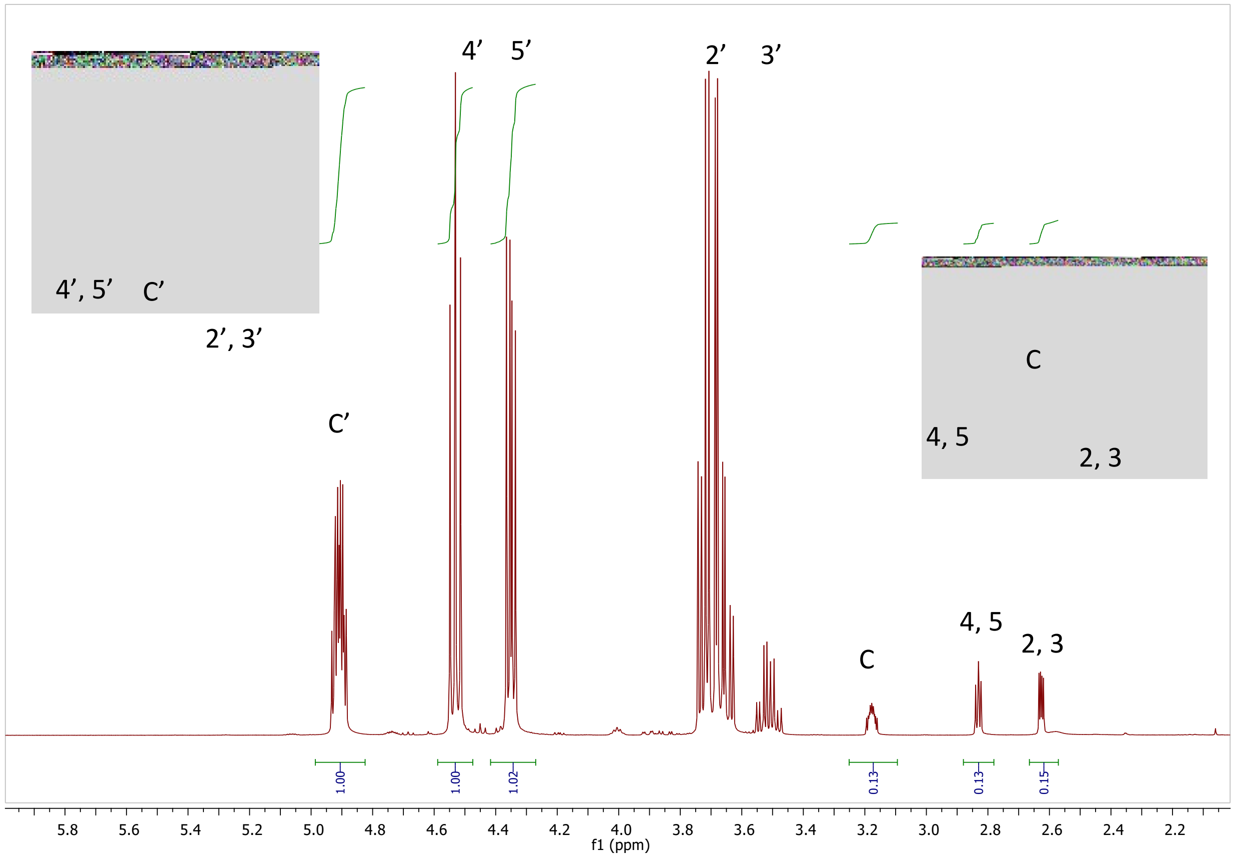


Figure S14. ^{1}H-NMR spectrum in $CDCl_3$ of the product [4-(chloromethyl)-1,3-dioxolan-2-one] obtained from the conversion of epichlorohydrin using Co-ZIF-Fe as a catalyst.

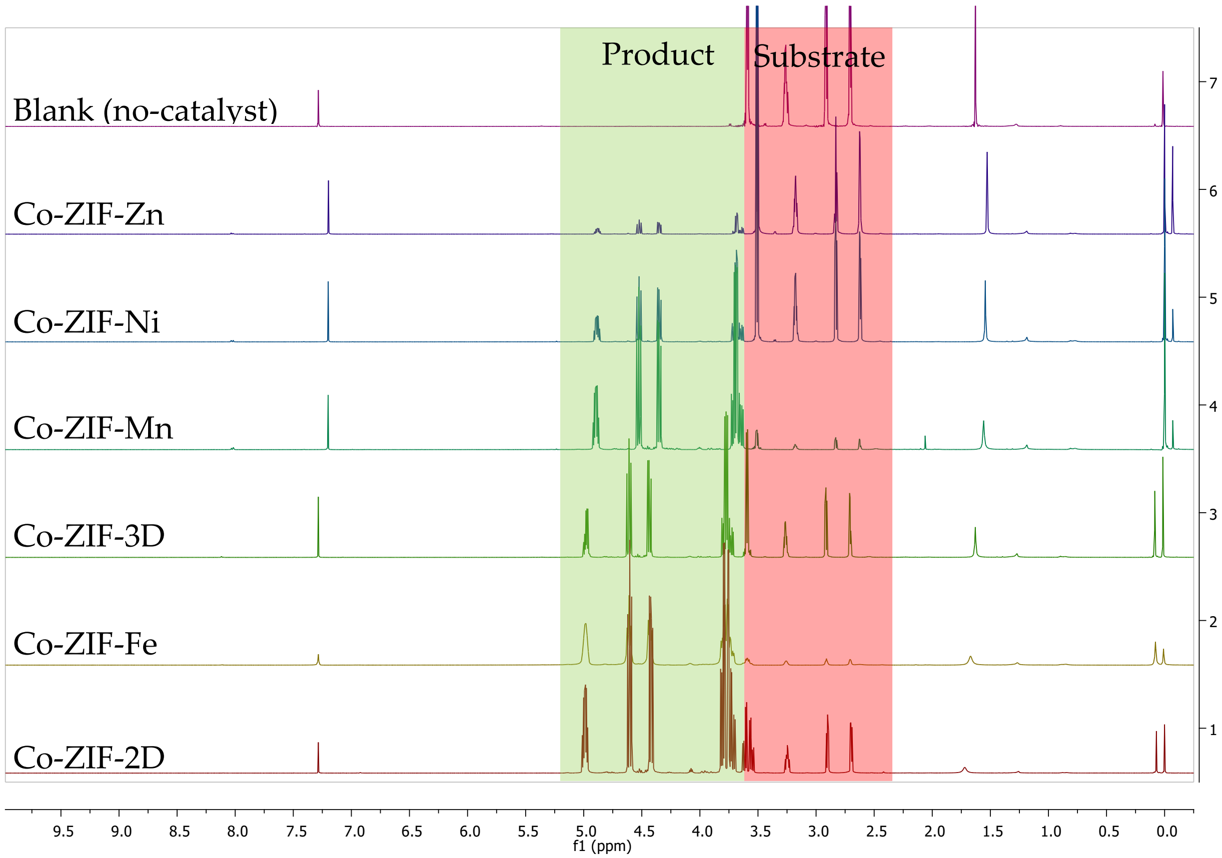


Figure S15. ^{1}H NMR spectrum of CO_2 additional into epoxide to synthesis cyclic carbonate at 60°C, 24 h, and 1 bar of CO_2 pressure using synthesized materials as a catalyst

Reference

1. I. U. Khan, M. H. D. Othman, A. F. Ismail, N. Ismail, J. Jaafar, H. Hashim, M. A. Rahman and A. Jilani, *Materials Characterization*, 2018, **136**, 407-416.