Electronic Supplementary Information (ESI)

Cd(II) and Zn(II) coordination polymers assisted CO_2/cyclohexene oxide copolymerization with double metal cyanide catalyst

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EXPERIMENTAL

X-ray crystallography. Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The integration of diffraction data and intensity corrections for the Lorentz and polarization effects were performed by using SAINT program.[1] Semi-empirical absorption corrections were applied using SADABS program.[2] The structures were solved by direct methods with SHELXT-2014, expanded by subsequent Fourier-difference synthesis, and all the non-hydrogen atoms were refined anisotropically on F^2 using the full-matrix least-squares technique with the SHELXL-2018 crystallographic software package.[3,4] The free solvent molecules in the unit cell have been taken into account by SQUEEZE option of the PLATON program.[5] The reported refinements are of the guest-free structures obtained by the SQUEEZE routine and the results were attached to the CIF files. The details of crystal parameters, data collection and refinements for **1** - **3** are listed in Table 1, and the selected bond lengths and angles are given in Table S1.

Table S1 Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

		1	
Cd(1)-O(1)	2.5525(17)	O(2)-Cd(1)-N(2)	146.05(8)
Cd(1)-O(2)	2.2417(18)	O(2)-Cd(1)-N(3)	82.83(7)
Cd(1)-O(3)	2.5287(19)	O(3)-Cd(1)-O(1)	90.95(6)
Cd(1)-O(4)	2.2988(17)	O(4)-Cd(1)-O(1)	136.15(6)
Cd(1)-N(1)	2.3447(19)	O(4)-Cd(1)-O(3)	53.80(6)
Cd(1)-N(2)	2.3372(18)	O(4)-Cd(1)-N(1)	114.48(8)
Cd(1)-N(3)	2.407(2)	O(4)-Cd(1)-N(2)	100.69(7)
O(2)-Cd(1)-O(1)	53.88(6)	O(4)-Cd(1)-N(3)	83.45(7)
O(2)-Cd(1)-O(3)	83.46(8)	N(1)-Cd(1)-O(1)	80.56(6)
O(2)-Cd(1)-O(4)	92.83(8)	N(1)-Cd(1)-O(3)	82.59(6)
O(2)-Cd(1)-N(1)	131.87(7)	N(1)-Cd(1)-N(3)	136.30(7)
N(2)-Cd(1)-O(1)	122.94(6)	N(2)-Cd(1)-N(3)	68.18(7)
N(2)-Cd(1)-O(3)	129.43(6)	N(3)-Cd(1)-O(1)	114.77(6)
N(2)-Cd(1)-N(1)	69.40(7)	N(3)-Cd(1)-O(3)	134.12(6)
		2	
Zn(1)-O(1)#1	2.009(5)	O(3)-Zn(1)-O(1)#1	103.20(18)
Zn(1)-O(3)	1.985(5)	O(3)-Zn(1)-N(1)	101.1(2)
Zn(1)-N(1)	2.169(6)	O(3)-Zn(1)-N(2)	131.3(2)
Zn(1)-N(2)	2.081(5)	O(3)-Zn(1)-N(3)	96.5(2)
Zn(1)-N(3)	2.195(6)	N(1)-Zn(1)-N(3)	150.3(2)
O(1)#1-Zn(1)-N(1)	97.7(2)	N(2)-Zn(1)-N(1)	75.8(2)
O(1)#1-Zn(1)-N(2)	125.5(2)	N(2)-Zn(1)-N(3)	74.7(2)
O(1)#1-Zn(1)-N(3)	101.2(2)		
Symmetry code: #1 +x, -1+y, +z			
		3	
Cd(1)-O(1)	2.252(3)	O(1)-Cd(1)-N(1)	99.63(12)
Cd(1)-O(7)#1	2.398(3)	O(1)-Cd(1)-N(2)	106.57(12)
Cd(1)-O(8)#1	2.376(3)	O(1)-Cd(1)-N(3)	91.71(12)
Cd(1)-N(1)	2.367(4)	O(7)#1-Cd(1)-N(3)	103.02(13)
Cd(1)-N(2)	2.342(4)	O(8)#1-Cd(1)-O(7)#1	54.82(12)
Cd(1)-N(3)	2.407(4)	O(8)#1-Cd(1)-N(3)	79.98(13)

O(1)-Cd(1)-O(7)#1	148.45(13)	N(1)-Cd(1)-O(7)#1	88.12(12)
O(1)-Cd(1)-O(8)#1	101.89(11)	N(1)-Cd(1)-O(8)#1	135.51(13)
N(1)-Cd(1)-N(3)	137.68(14)	N(2)-Cd(1)-O(7)#1	104.79(13)
N(2)-Cd(1)-N(1)	69.41(13)	N(2)-Cd(1)-O(8)#1	137.40(12)
N(2)-Cd(1)-N(3)	68.28(13)		
Symmetry code: #1 -x, 1-y, -1/2+z			

Table S2 The member atoms of selected conjugate rings for **1** - **3** (CgI = plane number I).

1						
CgI	Ring member atoms					
Cg1	N4	N5	N6	C22	C23	
Cg2	N1	C1	C2	C3	C4	C5
Cg3	N2	C6	C7	C8	C9	C10
Cg4	N3	C11	C12	C13	C14	C15
Cg5	C16	C17	C18	C19	C20	C21
2						
CgI	Ring member atoms					
Cg1	N4	N5	N5	C30	C31	
Cg2	N1	C9	C10	C11	C12	C13
Cg3	N2	C14	C15	C16	C17	C18
Cg4	N3	C19	C20	C21	C22	C23
3						
CgI	Ring member atoms					
Cg1	N4	N5	N6	C22	C23	
Cg2	N1	C1	C2	C3	C4	C5
Cg3	N2	C6	C7	C8	C9	C10
Cg4	N3	C11	C12	C13	C14	C15
Cg5	C16	C17	C18	C19	C20	C21

Table S3 The selected Cg-Cg distances (Å) between ring centroids for **1** - **3**.

			1		
	CgI->CgJ	Distance		CgI->CgJ	Distance
1	Cg1->Cg4	3.6677 (18)	3	Cg3->Cg2	3.7984 (15)
2	Cg5->Cg3	3.6615 (16)			
			2		
	CgI->CgJ	Distance		CgI->CgJ	Distance
1	Cg4->Cg2	3.5902 (4)	3	Cg3->Cg2	3.7962 (5)
2	Cg1->Cg1	3.6726 (4)			
			3		
	CgI->CgJ	Distance		CgI->CgJ	Distance
1	Cg4->Cg5	3.5741(3)	4	Cg1->Cg2	3.8046(3)
2	Cg3->Cg3	3.5896(3)	5	Cg5->Cg2	3.9194(3)
3	Cg2->Cg2	3.5968(3)	6	Cg5->Cg4	3.5741(3)

Table S4 Hydrogen bonding data of **1** - **3**.

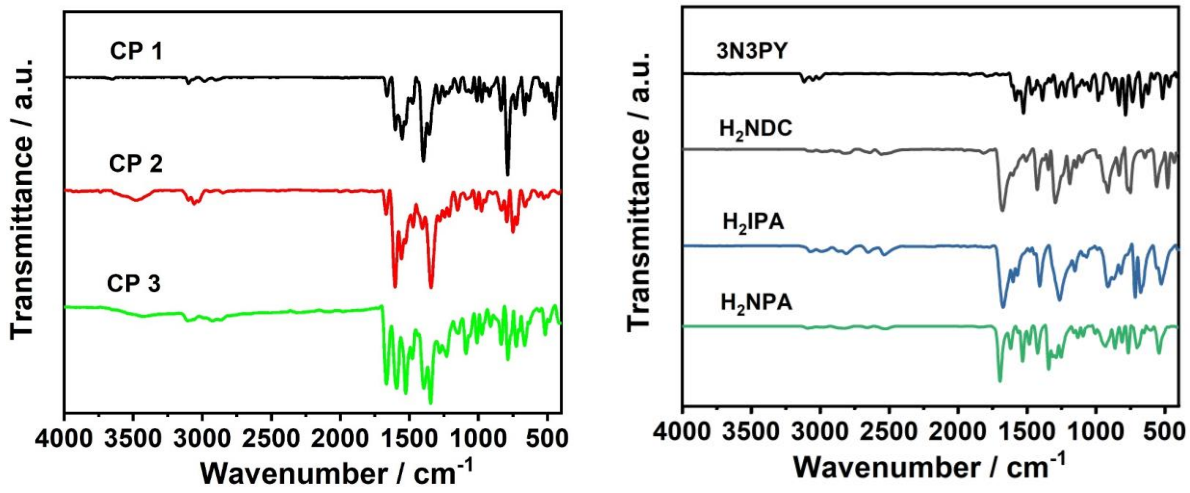
		1		
D-H···A	d(*D*-H) / Å	d(H···A) / Å	d(*D*···A) / Å	*D*-H···A / °
C(23)-H(23)---O(3) #1	0.93	2.47	3.330(4)	154
C(4)-H(4)---O(1) #2	0.93	2.53	3.448(3)	169
C(7)-H(7)---O(1) #2	0.93	2.38	3.286(3)	164
C(9)-H(9)---O(5) #3	0.93	2.26	3.163(8)	165
C(21)-H(21)---O(5) #3	0.93	2.30	3.014(7)	133
Symmetry code: #1 -1+x,3/2-y,-3/2+z; #2 x,3/2-y,-1/2+z; #3 -1+x,y,-1+z				
		2		
D-H···A	d(*D*-H) / Å	d(H···A) / Å	d(*D*···A) / Å	*D*-H···A / °
C(9)-H(9)---N(6) #1	0.95	2.44	3.3393(4)	158
C(12)-H(12)---O(4) #2	0.95	2.25	3.1769(4)	163
C(20)-H(20)---O(2) #3	0.95	2.36	3.2800(4)	162
Symmetry code: #1 x,y,-1+z; #2 2-x,-y,1-z; #3 1-x,-y,1-z				
		3		
D-H···A	d(*D*-H) / Å	d(H···A) / Å	d(*D*···A) / Å	*D*-H···A / °
C(17)-H(17)---O(1) #1	0.95	2.44	3.3557(3)	162

C(18)-H(18)---O(7) #2	0.95	2.54	3.3430(3)	142
C(20)-H(20) ···O(5) #3	0.95	2.45	3.3664(3)	163
C(22)-H(22) ···O(7) #2	0.95	2.48	3.3703(3)	156
C(29)-H(29) ···O(2) #4	0.95	2.12	3.0632(2)	174
C(36)-H(36) ···O(8) #5	0.95	2.48	3.2531(2)	138

Symmetry codes: #1 1-y,1-x,1/2-z; #2 3/2-x,1/2+y,1/4-z; #3 3/2-y,-1/2+x,1/4+z; #4 1/2+y,1/2-x,-1/4+z; #5 1/2-y,-1/2+x,1/4+z

Table S5 Comparison with other reported systems in CO_2/CHO reaction.

Catalyst	T (℃)	P_{CO2} (MPa)	F(CO_2) (%)	Time (h)	Reference
DMC/CP **1**	80	1	65	12	**This work**
Zn-Co DMC-Cl	80	0.96	53	4	6
DMC-EEA	115	4.35	86	3	7
Fe Cat. PPNCl	90	4.5	78	3	8
Zn-Ni DMC	110	5	45	20	9
DMC/Salen-Co(III)/PPNCl	60	13.79	98.7	Flushing method	10



(a) (b)

Fig. S1 FTIR spectra of CPs **1** – **3** (a) and ligands (b).

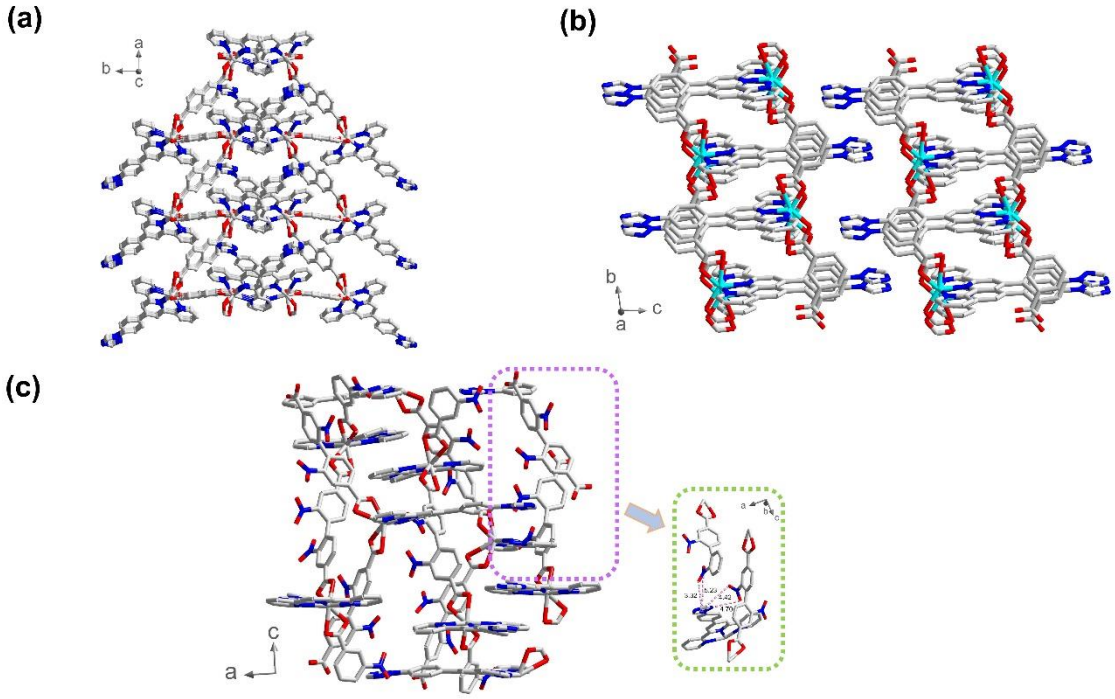


Fig. S2 3D supramolecular structures of **1** (a), **2** (b) and **3** (c).

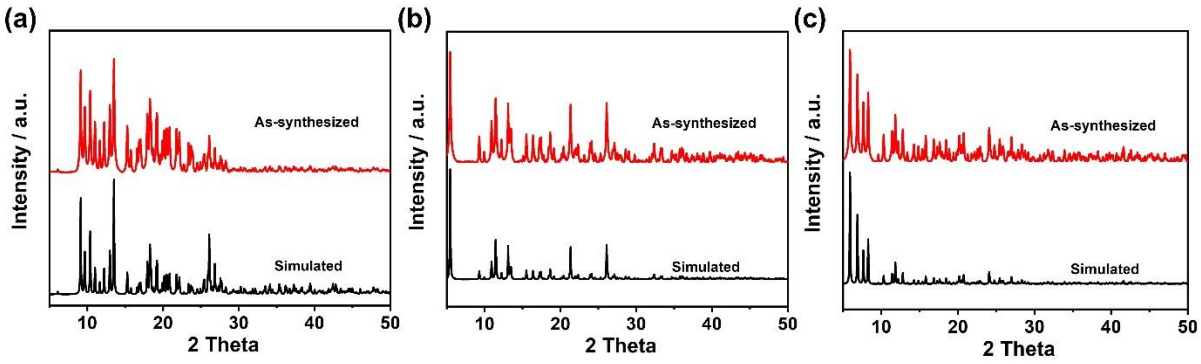


Fig. S3 PXRD patterns of **1** (a), **2** (b) and **3** (c).

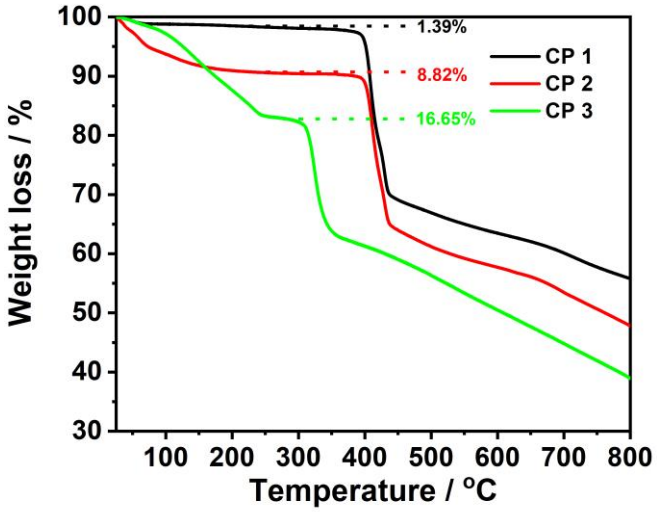


Fig. S4 TG data of CPs **1 - 3**.

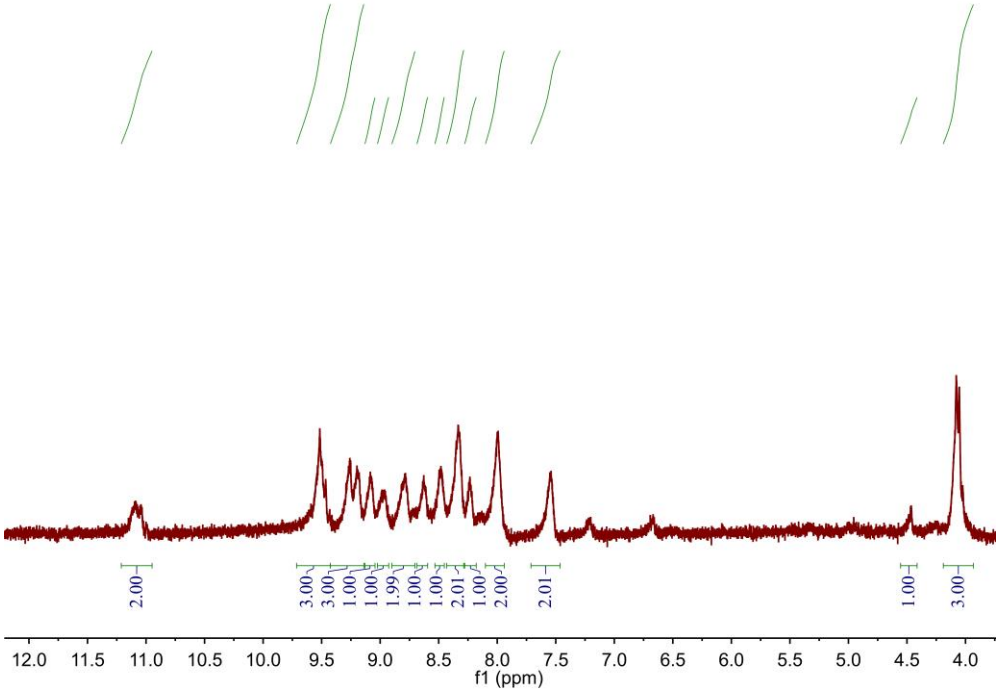


Fig. S5 ^{1}H-NMR (DMSO-d$_6$, 500M) spectrum of CP **1**Me.

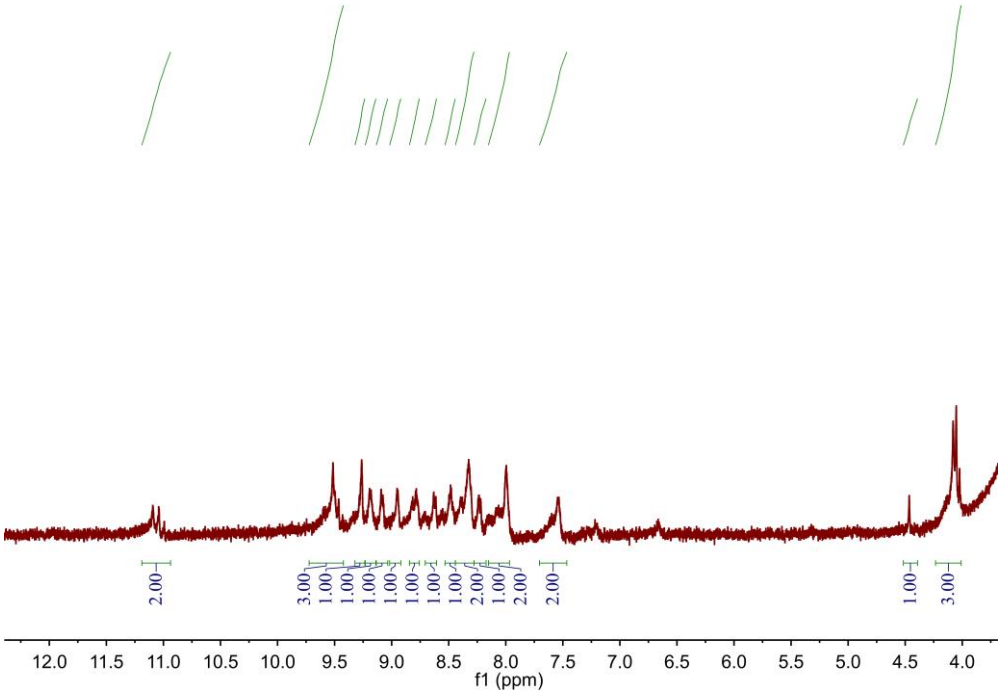


Fig. S6 ^{1}H-NMR (DMSO-d$_6$, 500M) spectrum of CP **2**Me.

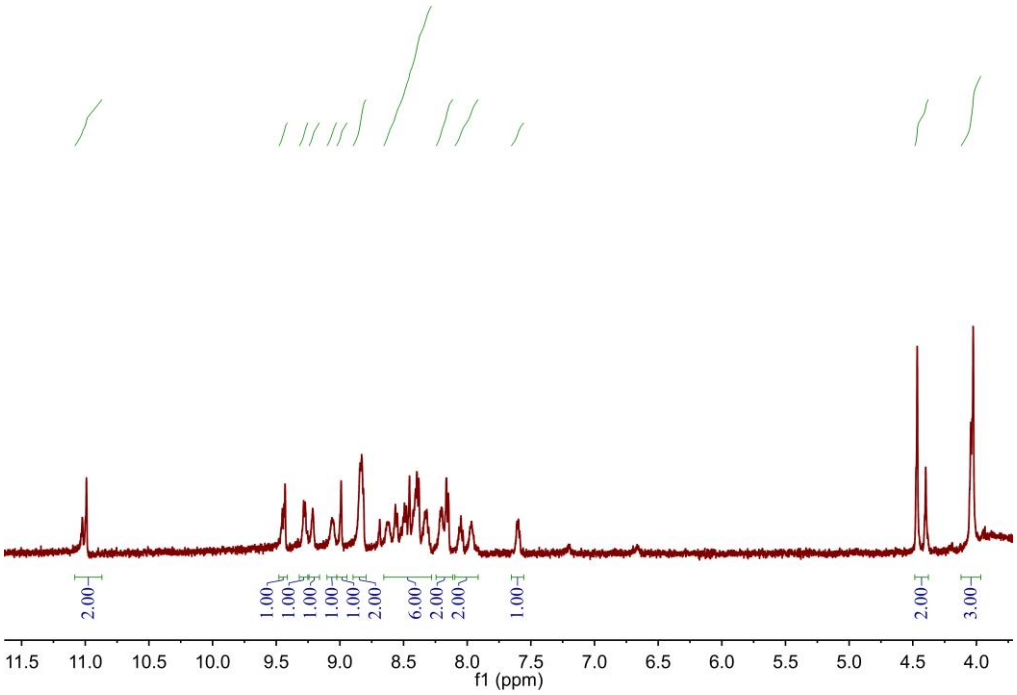


Fig. S7 ^{1}H-NMR (DMSO-d_6, 500M) spectrum of CP **3**Me.

The proportion of carbonate in the obtained polymer is recorded as $F(CO_2)$ value, and the calculated method is shown in equ. S1

$$F(CO_2) = \frac{A(4.32\text{-}4.80)}{A(4.32\text{-}4.80) + A(3.26\text{-}3.75)} \times 100\% \qquad (S1)$$

A indicates the integrated area of ^{1}H NMR signals. In addition, the formula to calculate the conversion rate of CHO (C_{CHO}) is as following:

$$C_{CHO} = \left[1 - \frac{A3.14}{A(4.32\text{-}4.80) + A(3.26\text{-}3.75) + A3.14}\right] \times 100\% \qquad (S2)$$

Besides, $P_{\text{-OC(O)O-}}$ is recorded as the proportion of carbonate in the total crude product and it is calculated as equ. S3

$$P_{\text{-OC(O)O-}} = F(CO_2) \times C_{CHO} \qquad (S3)$$

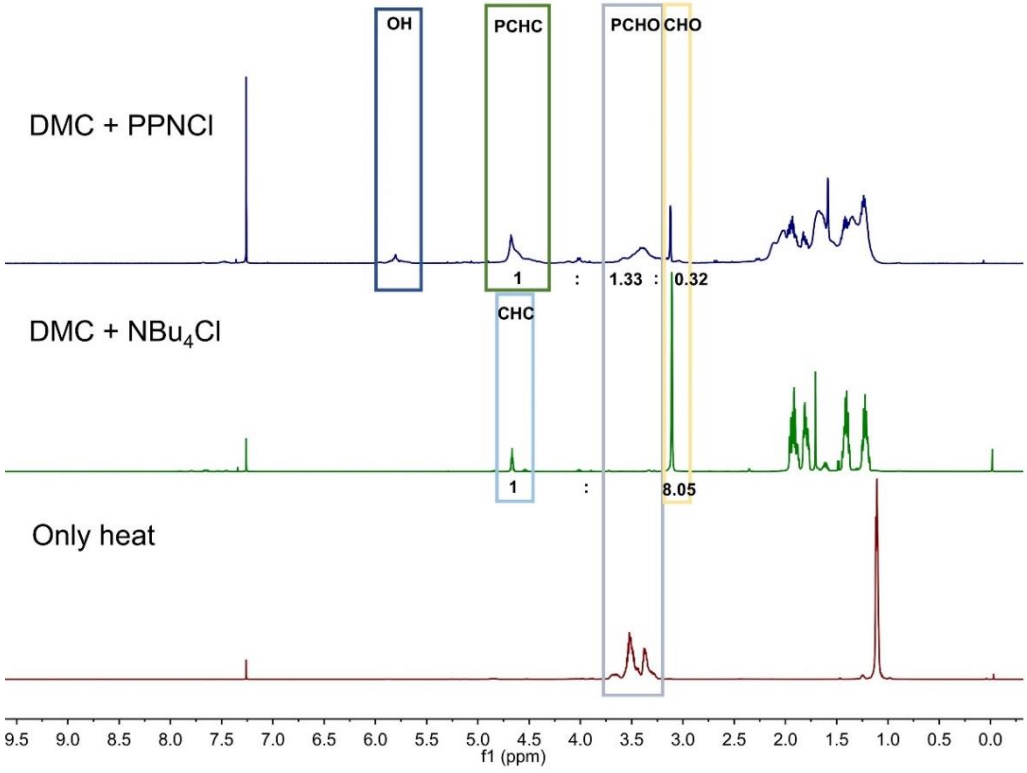


Fig. S8 ^{1}H NMR spectra ($CDCl_3$, 500M) of product at different conditions.

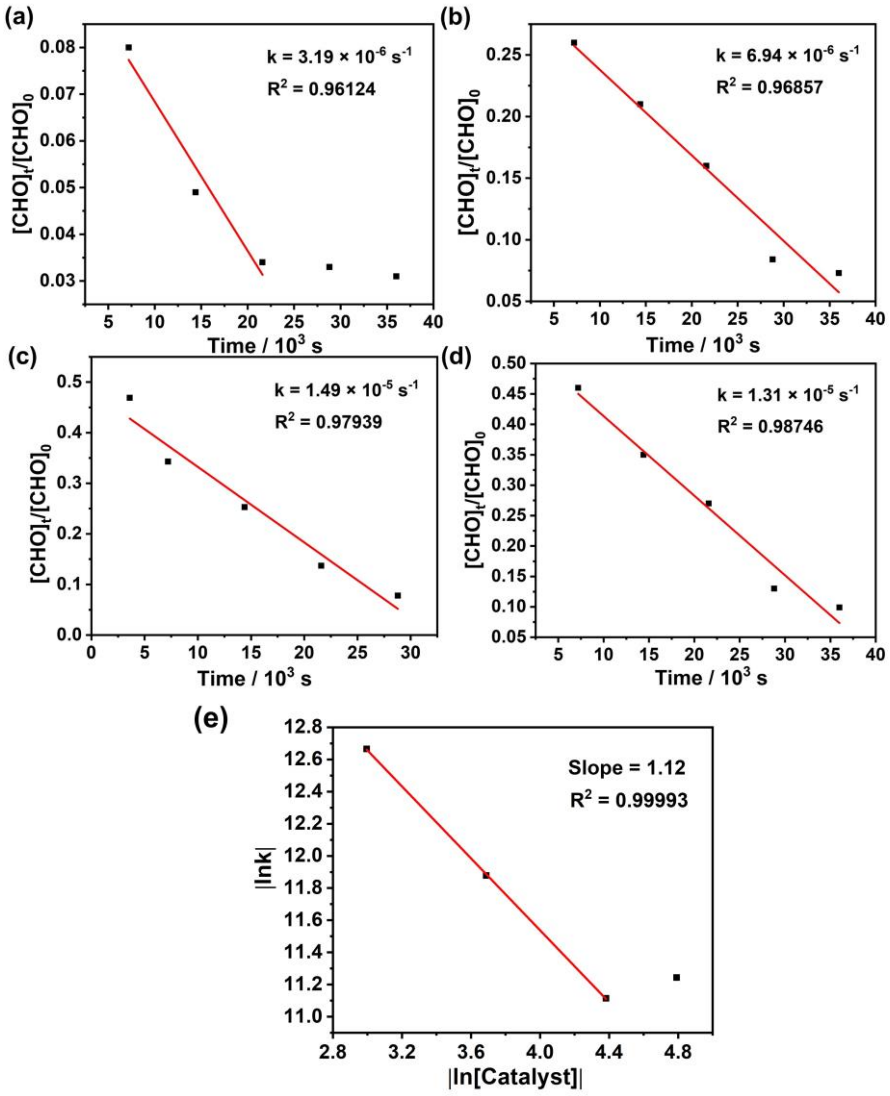


Fig. S9 Kinetic data for plot of $[CHO]_t/[CHO]_0$ versus time with catalyst 50 mM (a), 25 mM (b), 12.5 mM (c) and 8.3 mM (d). (e) Semilogarithmic plot of ln[k] vs ln[catalyst].

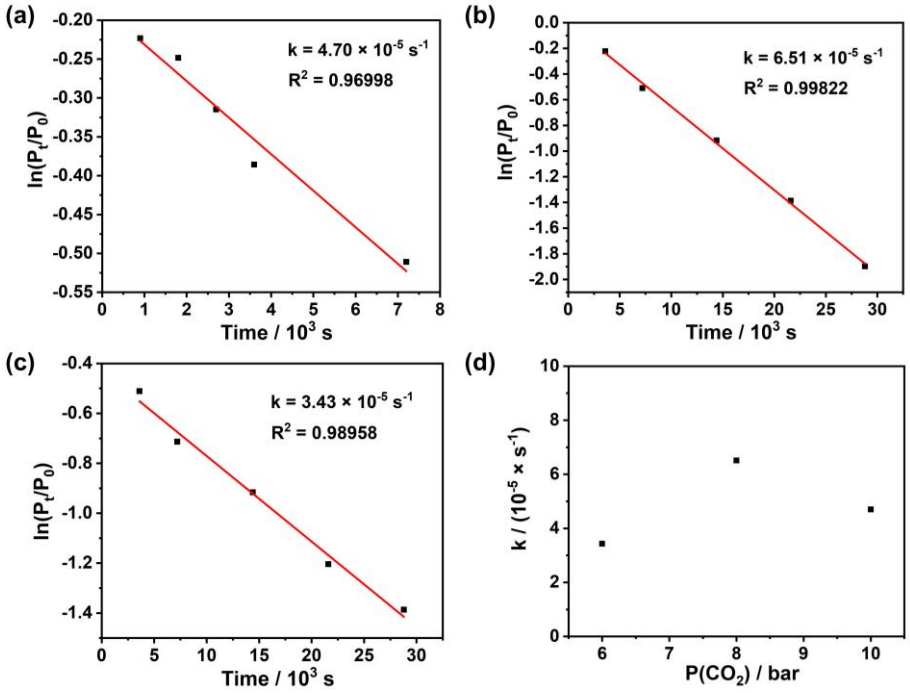


Fig. S10 Kinetic data for semilogarithmic plot of $\ln(P_t/P_0)$ versus time in CO_2 pressure of 10 (a), 8 (b), 6 (c) bar. (d) Plot of k vs $P(CO_2)$ from 6 to 10 bar.

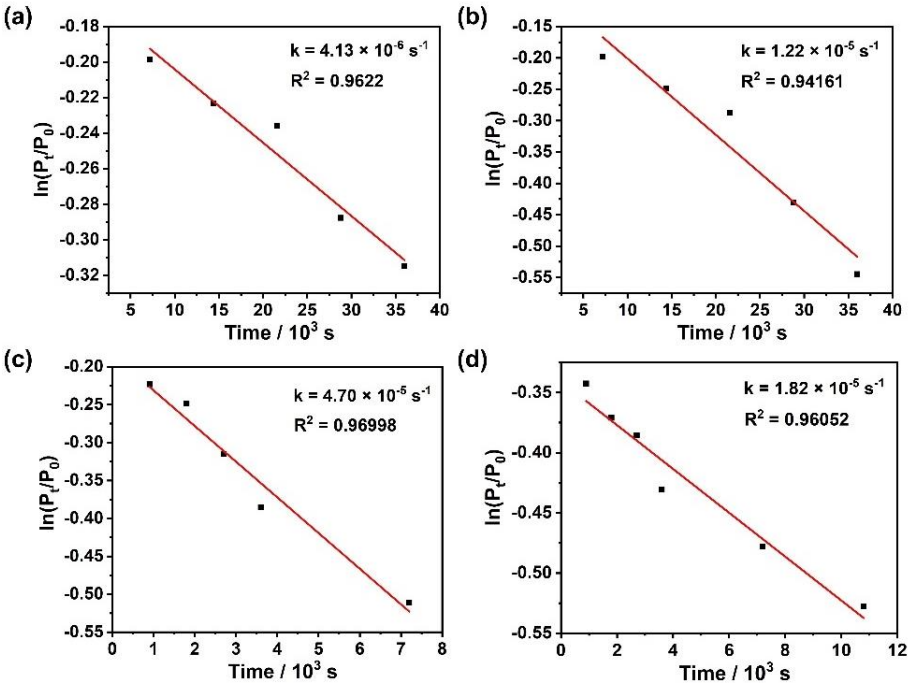


Fig. S11 Kinetic data for semilogarithmic plot of $\ln(P_t/P_0)$ versus time in 313 K (a), 333 K (b), 353 K (c) and 373 K (d).

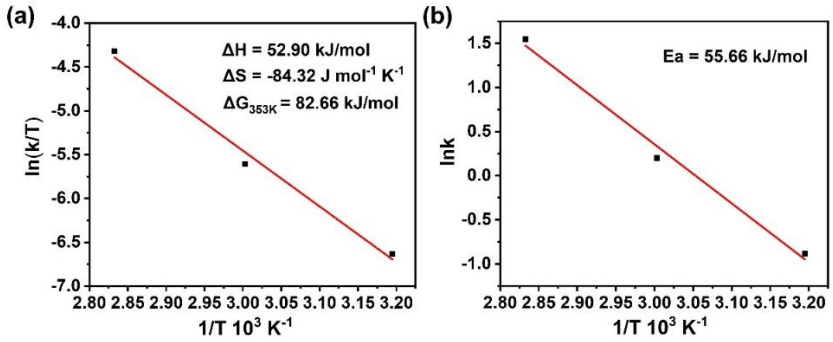


Fig. S12 (a) Eyring plot, ln(k/T) versus 1/T, for CP **2** over the temperature range 313-353 K, 18.75 mM catalyst, neat CHO (0.5 mL), under 10 bar CO_2. (b) Arrhenius analysis, plot of lnk vs 1/T for the CO_2/CHO reaction using CP **2**.

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