Electronic Supplementary Information

Two pillared-layer metal-organic frameworks based on pinwheel trinuclear carboxylate-clusters of Zn(II) and Co(II): synthesis, crystal structures, magnetic study, and Lewis acid catalysis

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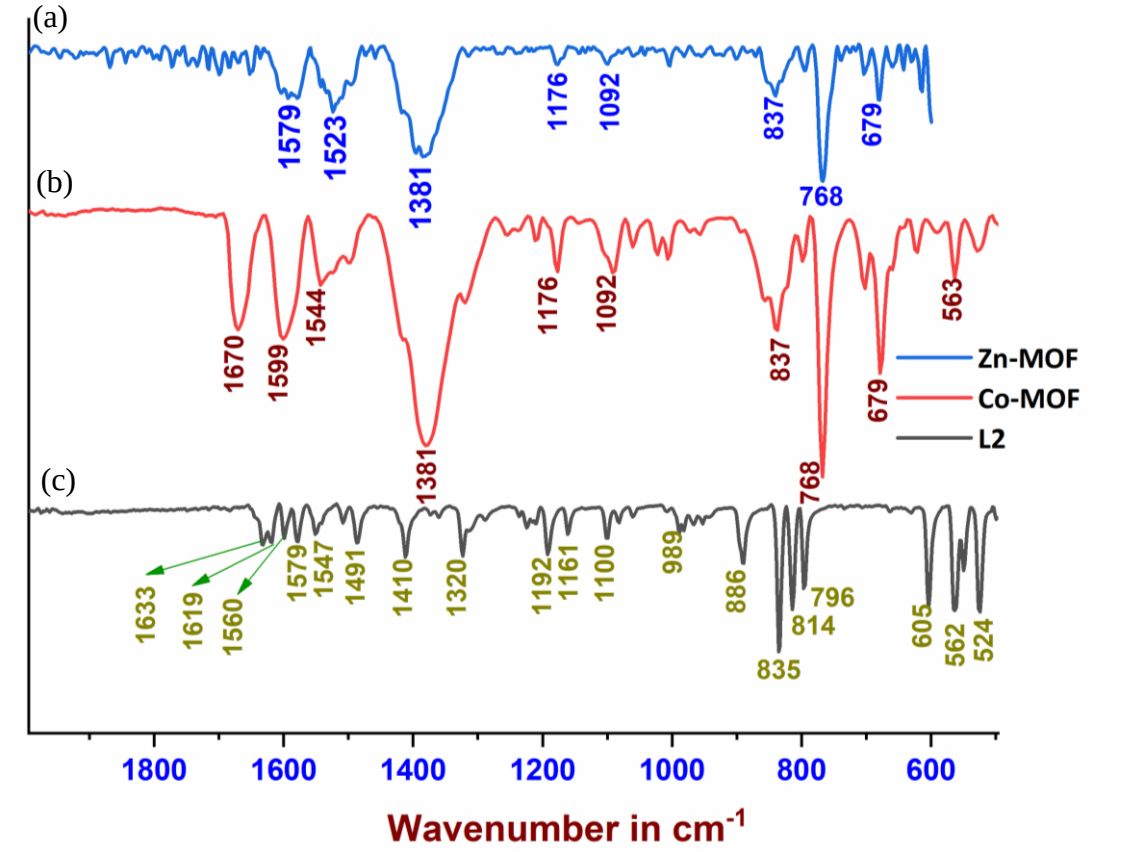


Fig. S1 FTIR spectra of (a) **Zn-MOF**, (b) **Co-MOF** and (c) **L2**.

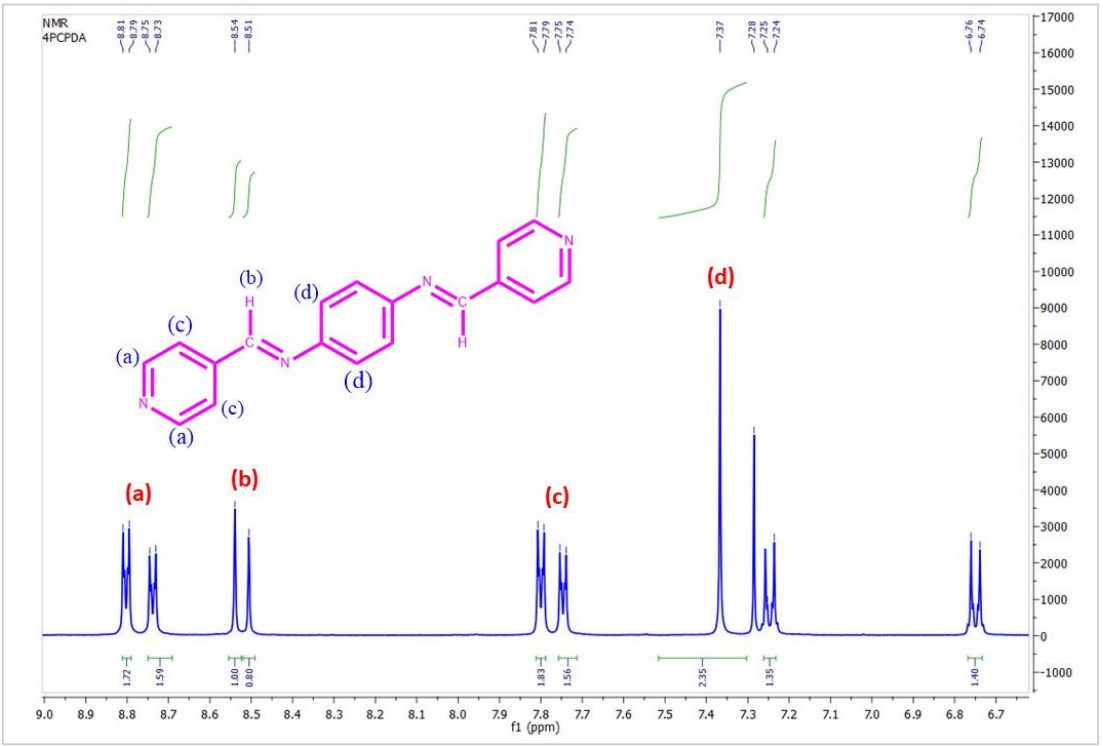


Fig. S2 ^{1}H NMR spectrum of **L2**.

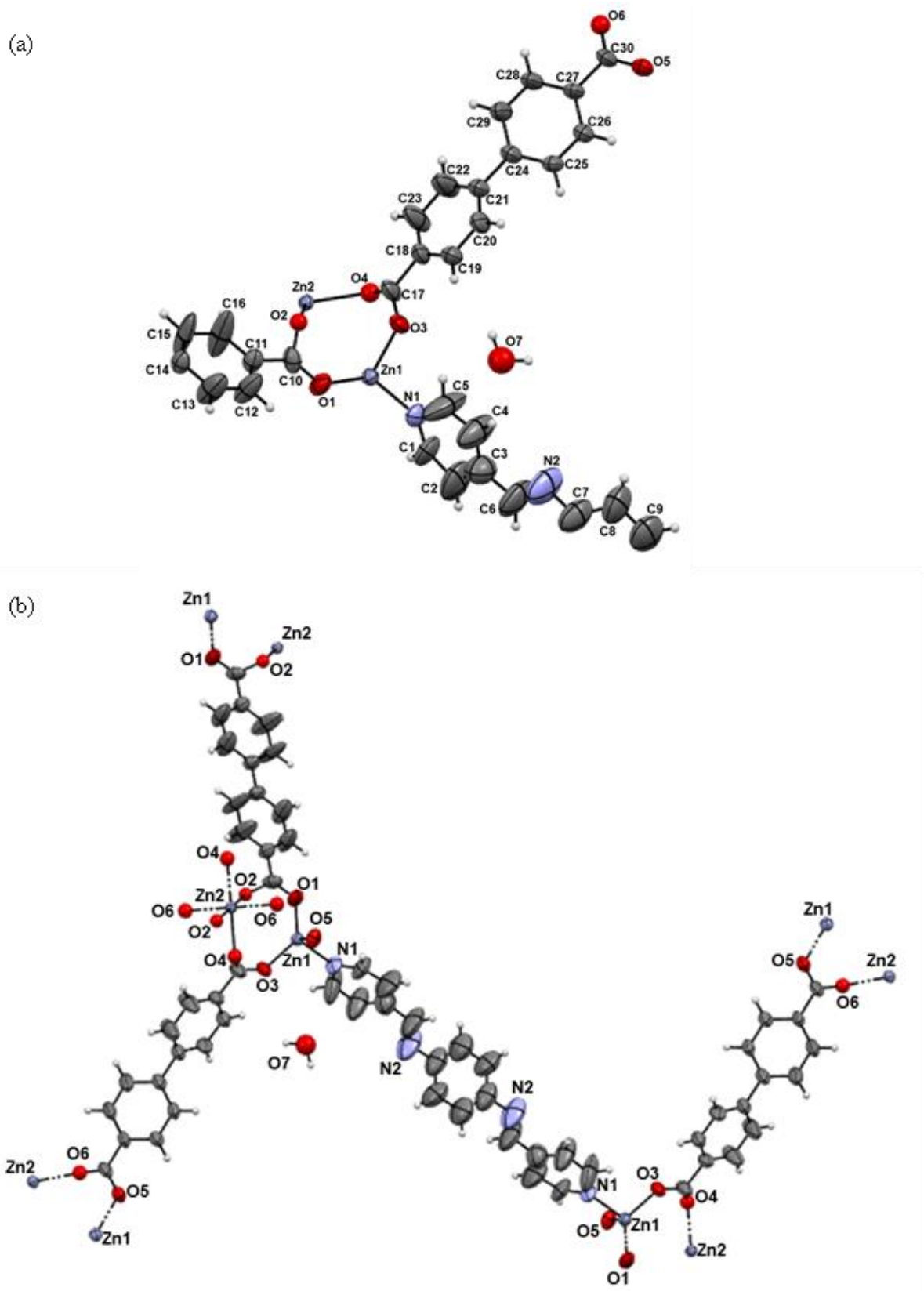


Fig. S3 ORTEP of **Zn-MOF** to show the atom numbering scheme(a) Asymmetric unit and (b) Extended network; thermal ellipsoids shown at 50% probability.

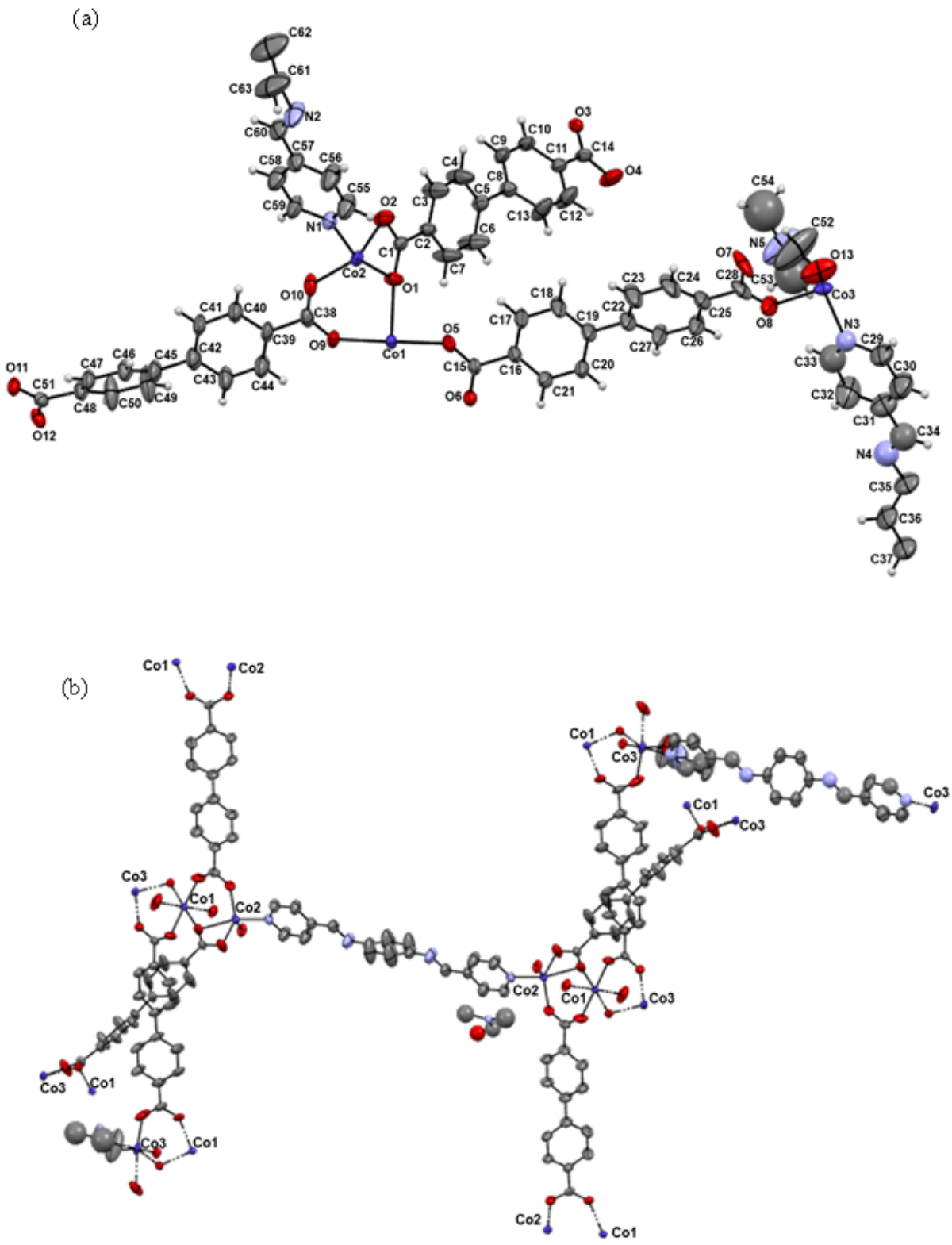


Fig. S4 ORTEP of **Co-MOF** to show the atom numbering scheme: (a) Asymmetric unit (Solvated DMF is removed for clarity) (b) Extended network (Metal centres are labelled); thermal ellipsoids shown at 50% probability.

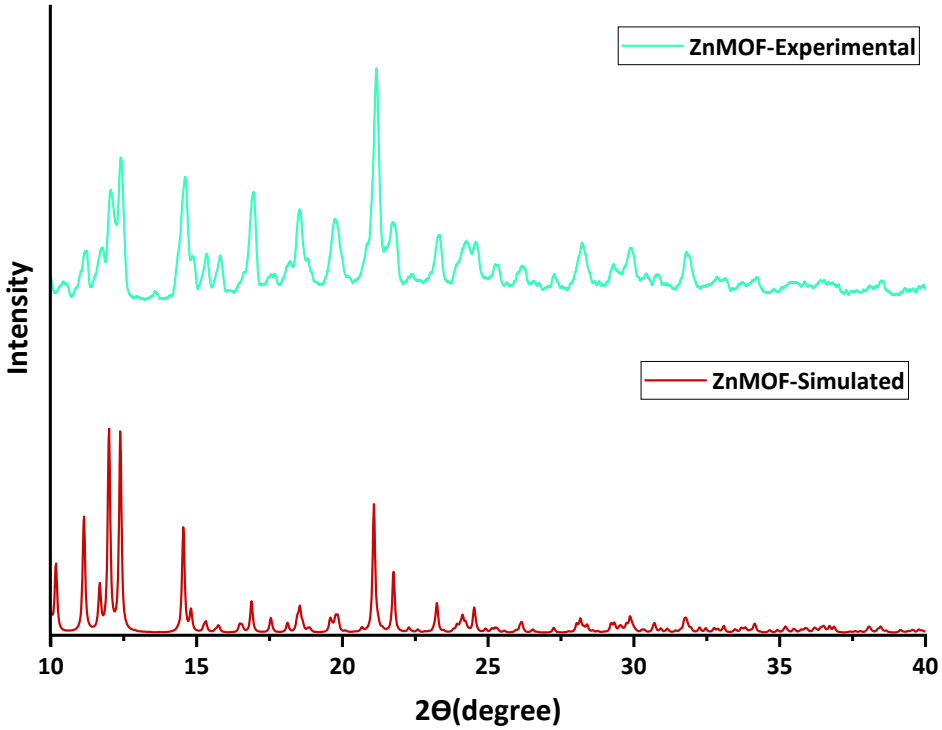


Fig. S5 Experimental and simulated PXRD patterns of **Zn-MOF**.

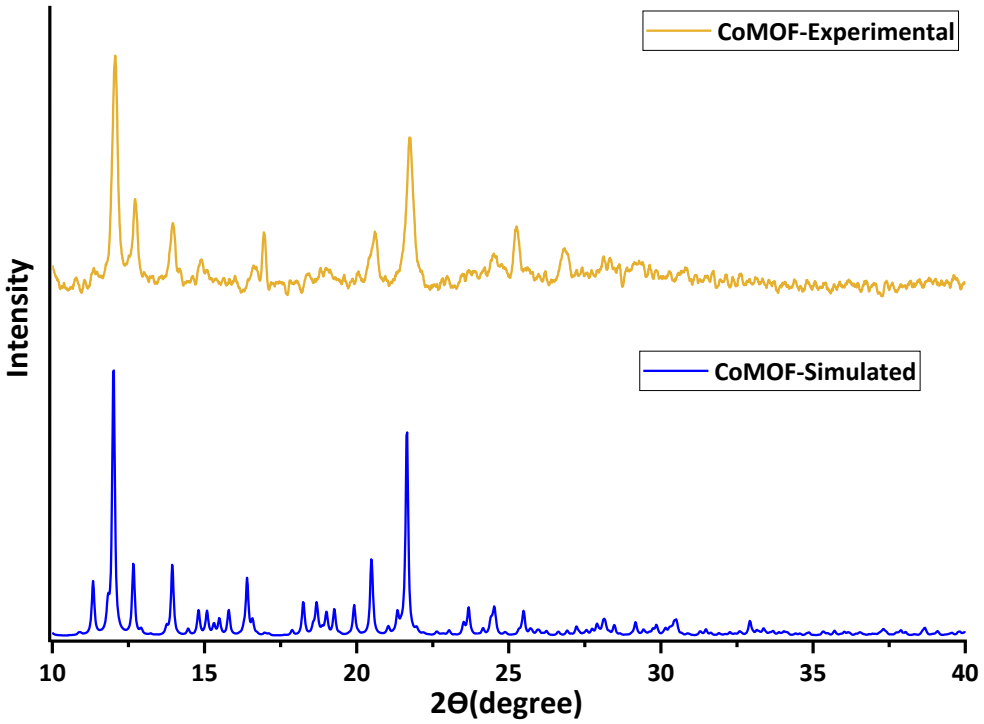


Fig. S6 Experimental and simulated PXRD patterns of **Co-MOF**.

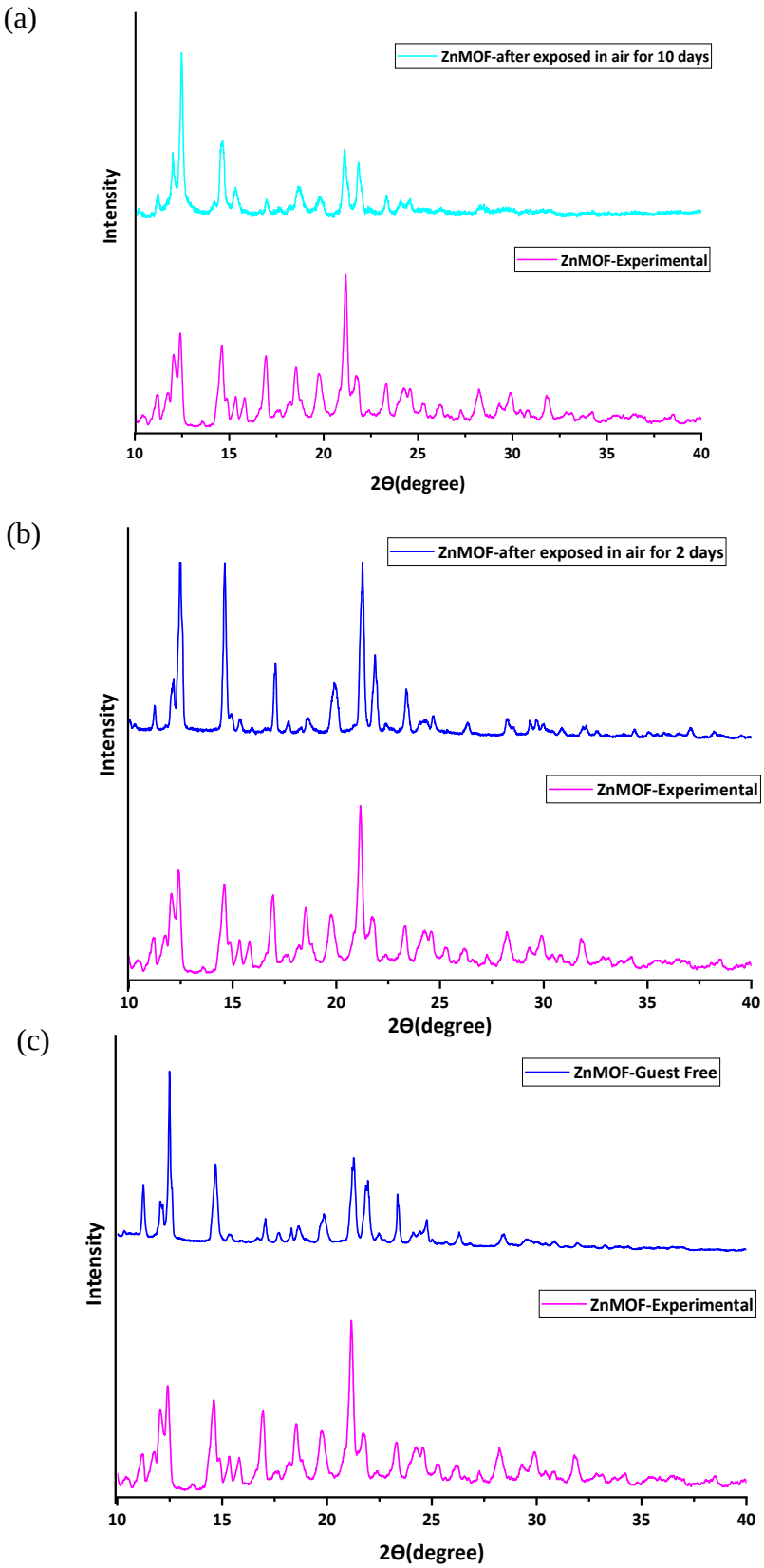
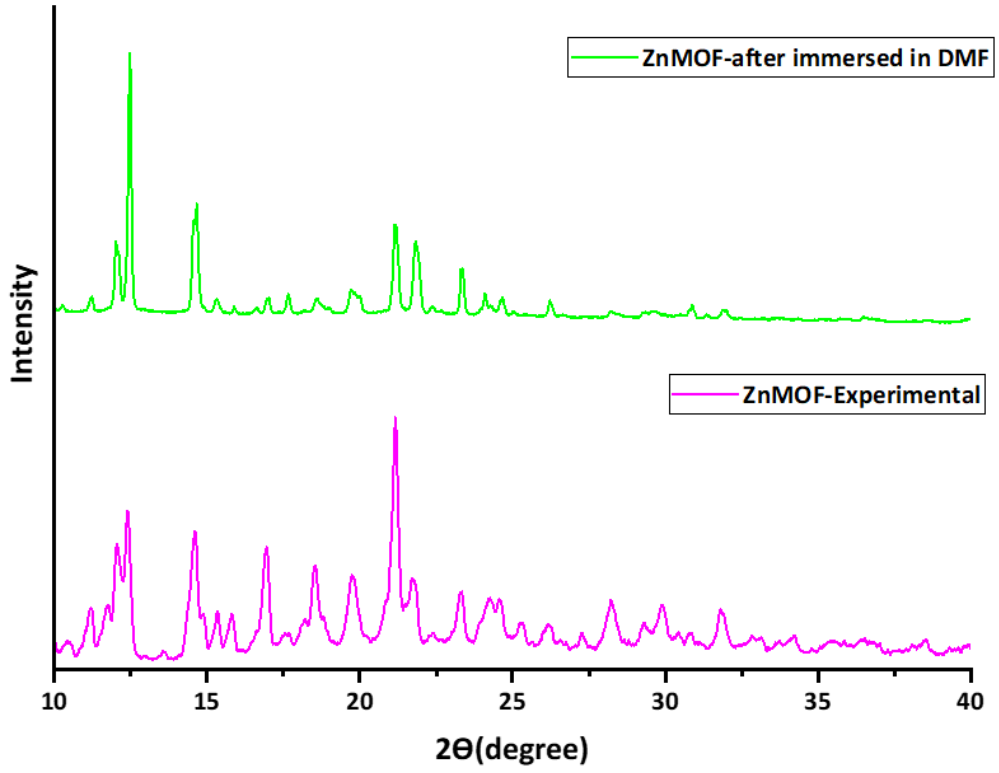


Fig. S7 Experimental PXRD patterns of **Zn-MOF** (a) after exposing to air for 10 days, (b) after exposing to air for 2 days and (c) without guest molecules compared to that of as-synthesized **Zn-MOF**.

(a)



(b)

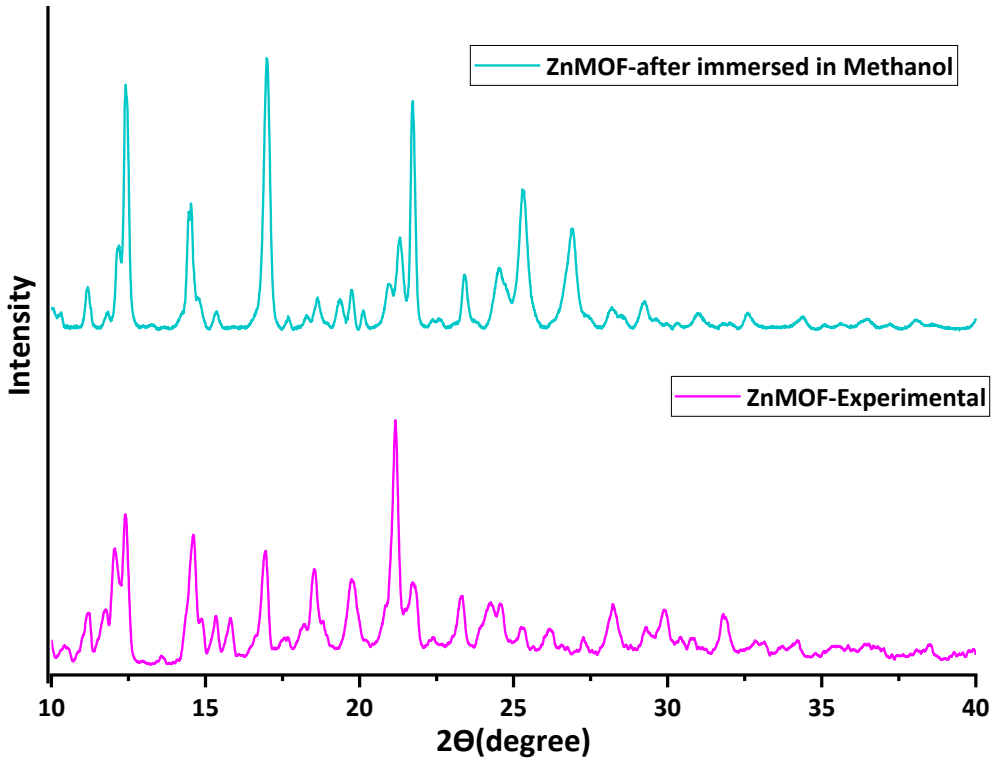


Fig. S8 Experimental PXRD patterns of **Zn-MOF** (a) after immersing in DMF and (b) after immersing in MeOH compared to that of **Zn-MOF**.

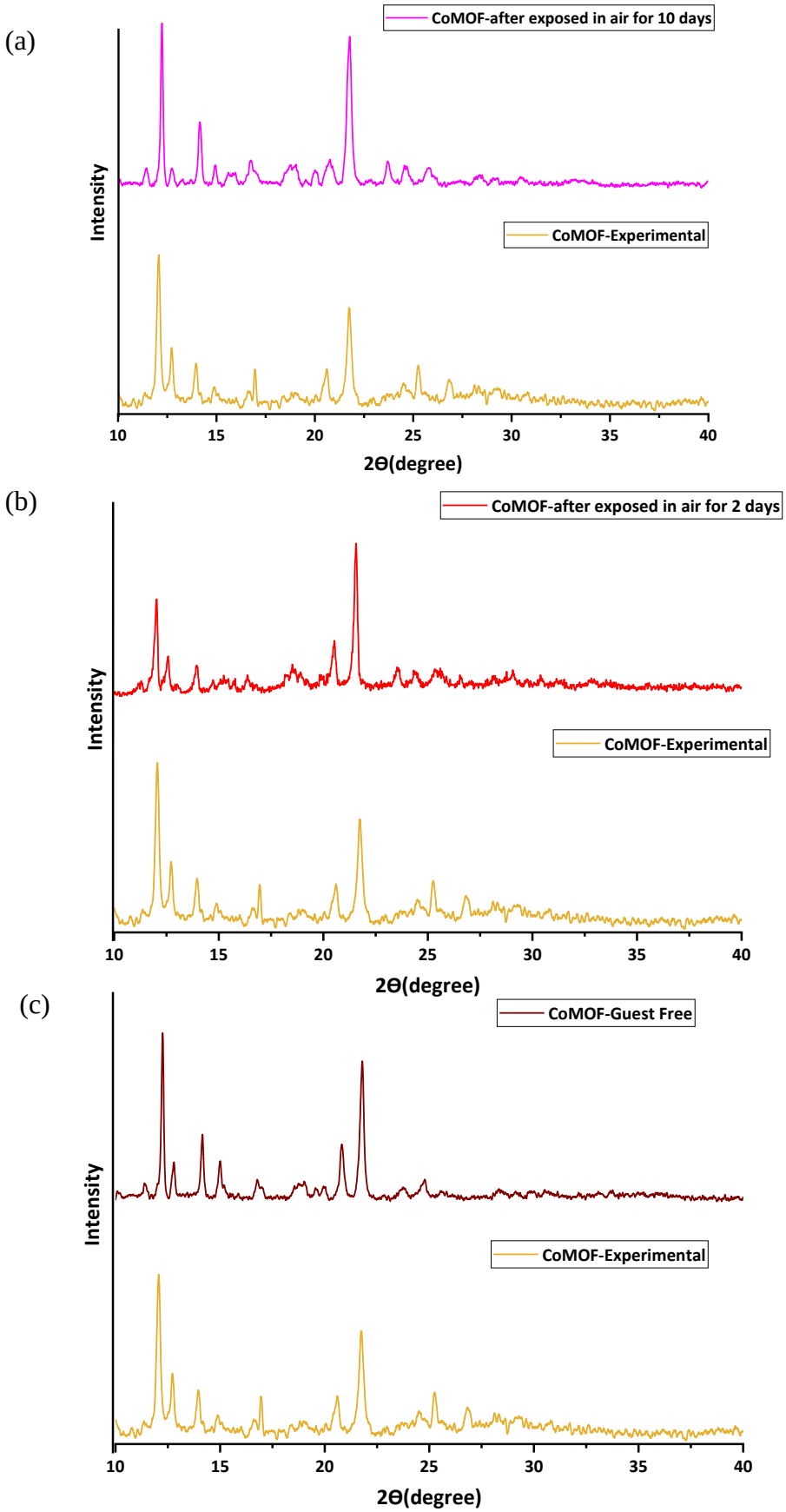
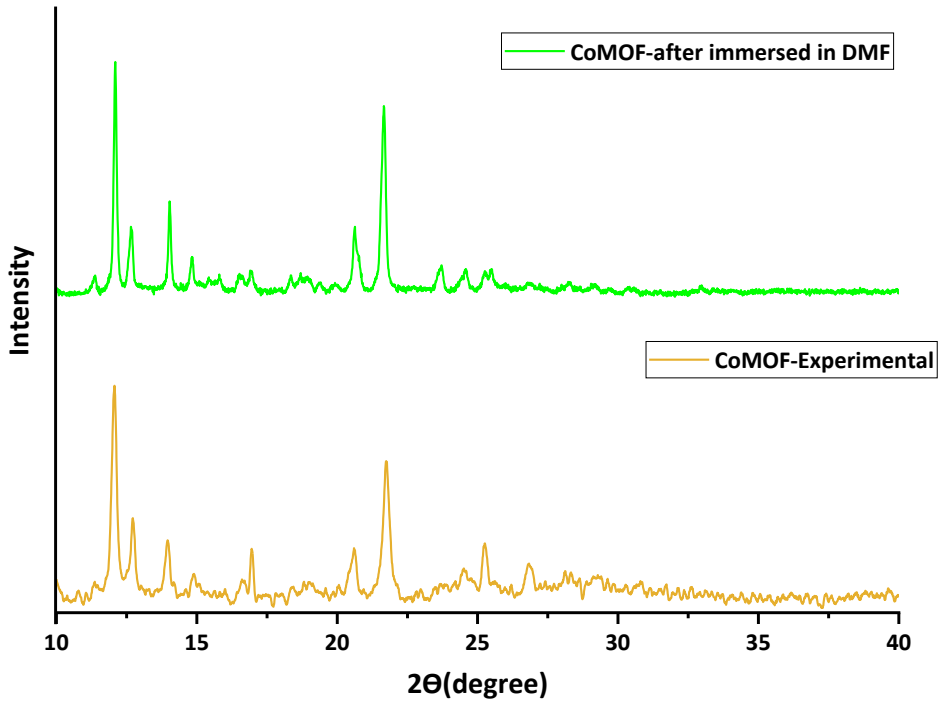


Fig. S9 Experimental PXRD patterns of **Co-MOF** (a) after exposing to air for 10 days, (b) after exposing to air for 2 days and (c) without guest molecules compared to that of as-synthesized **Co-MOF**.

(a)



(b)

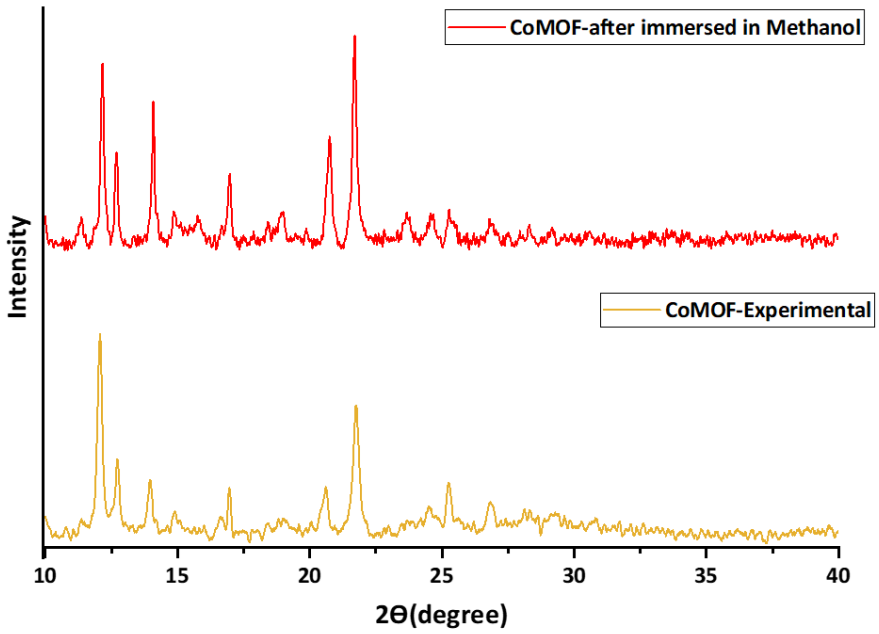


Fig. S10 Experimental PXRD patterns of **Co-MOF** (a) after immersing in DMF and (b) after immersing in MeOH compared to that of **Co-MOF**.

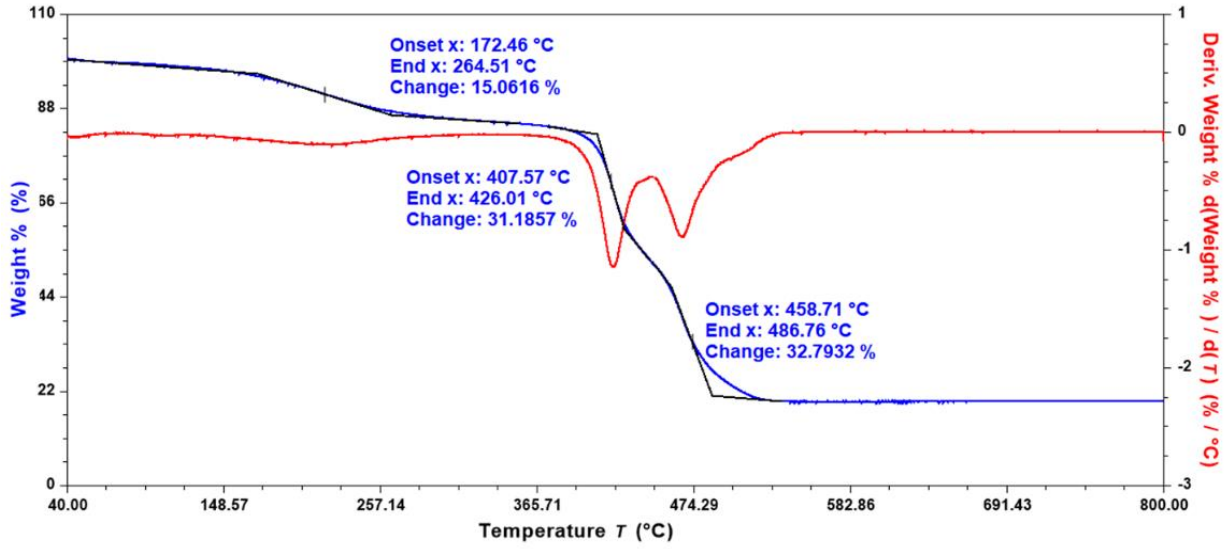


Fig. S11 TGA and DTA of **Zn-MOF**.

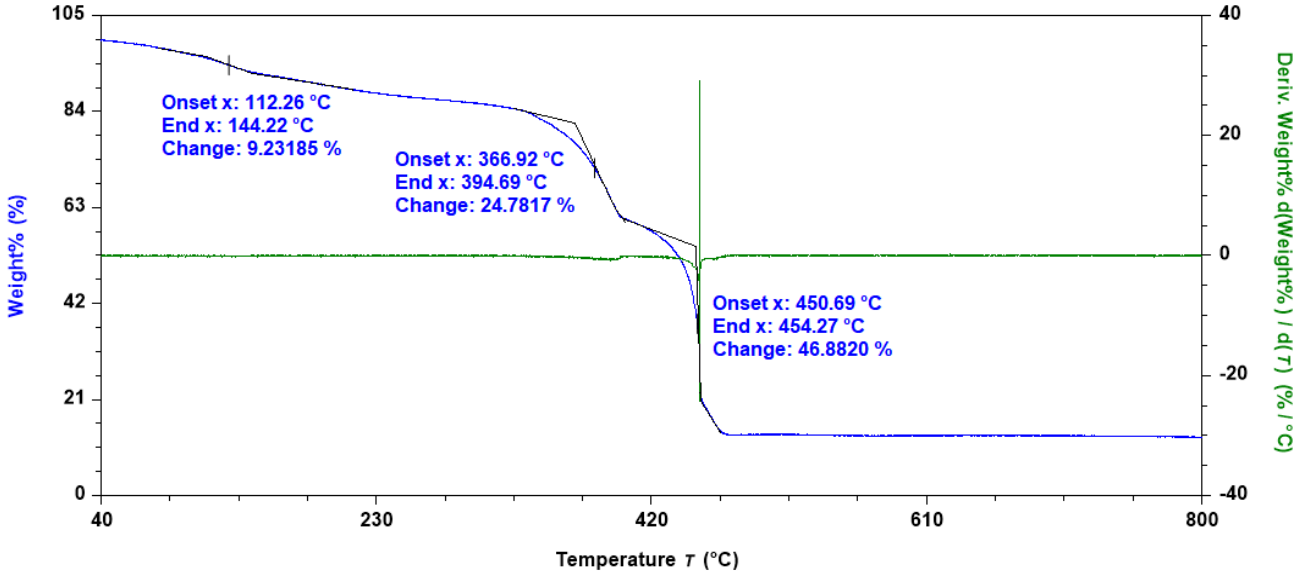
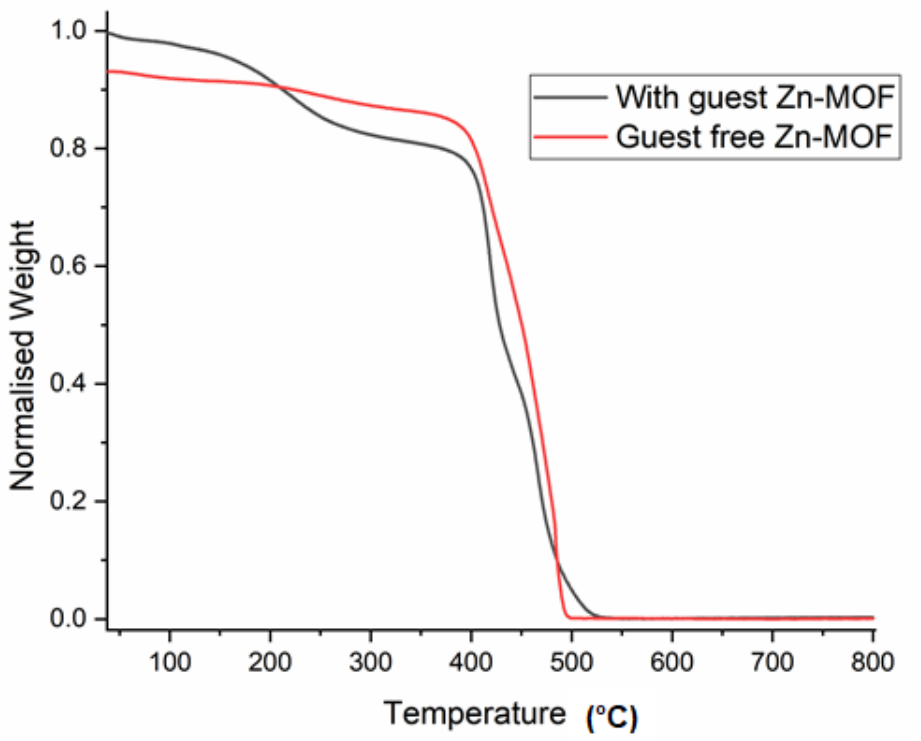


Fig. S12. TGA and DTA of **Co-MOF**.

(a)



(b)

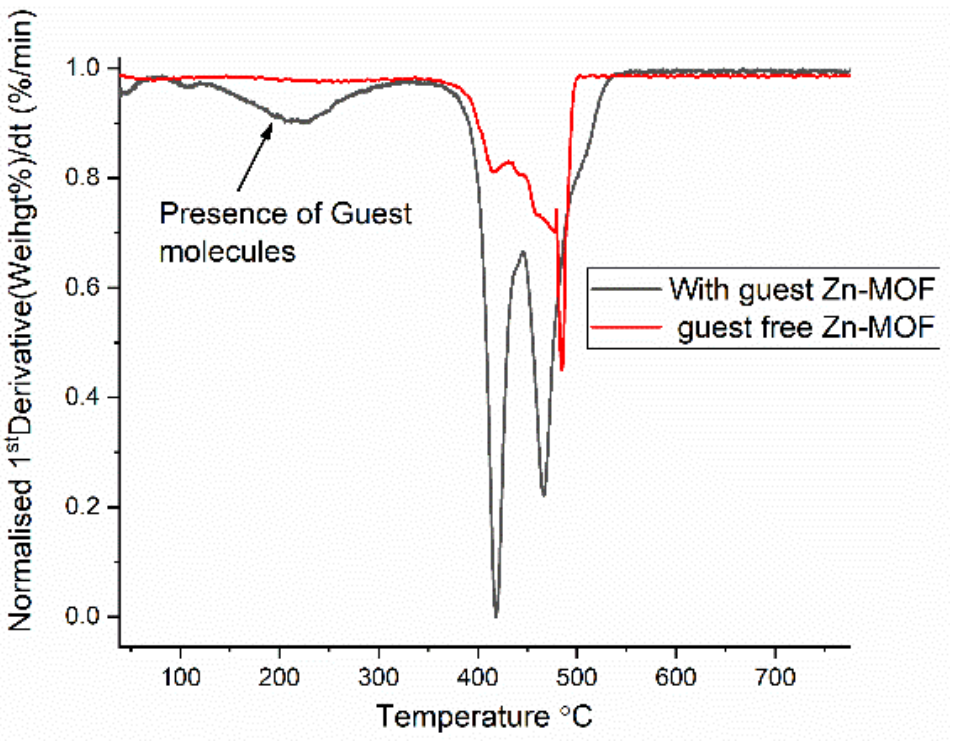
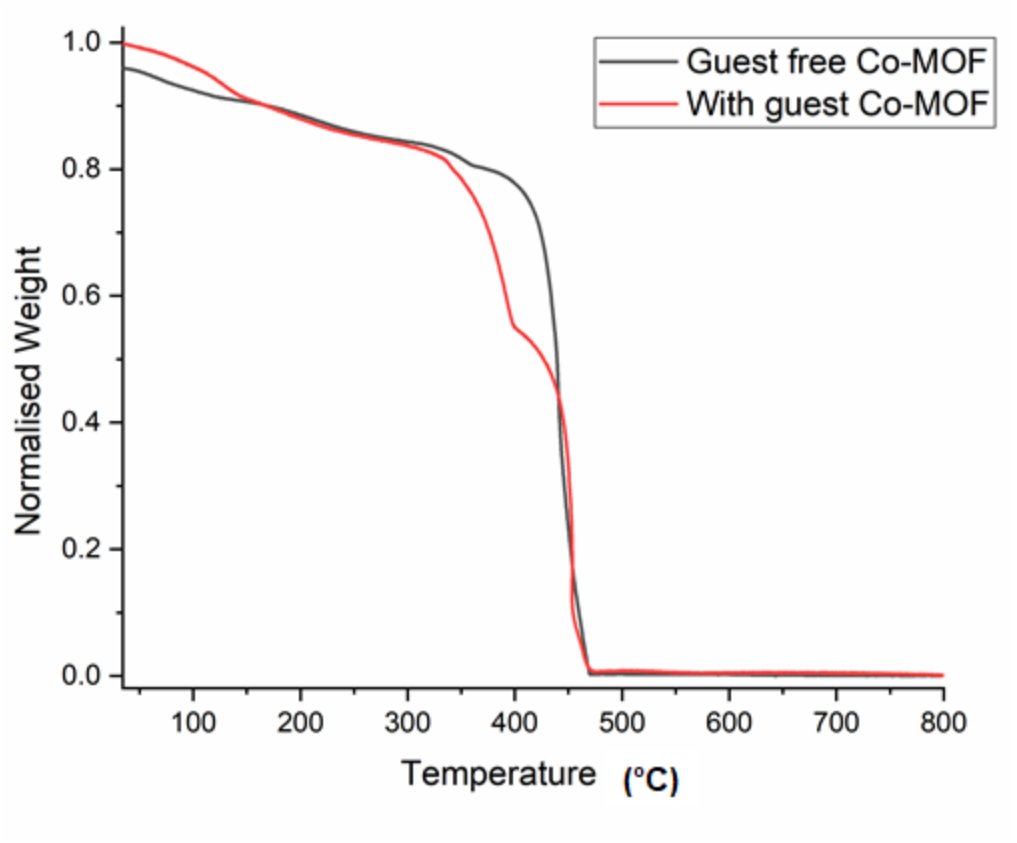


Fig. S13 Overlay of (a) TGA and (b) DTA plots of **Zn-MOF** and **Zn-MOF** after removing guest molecules.

(a)



(b)

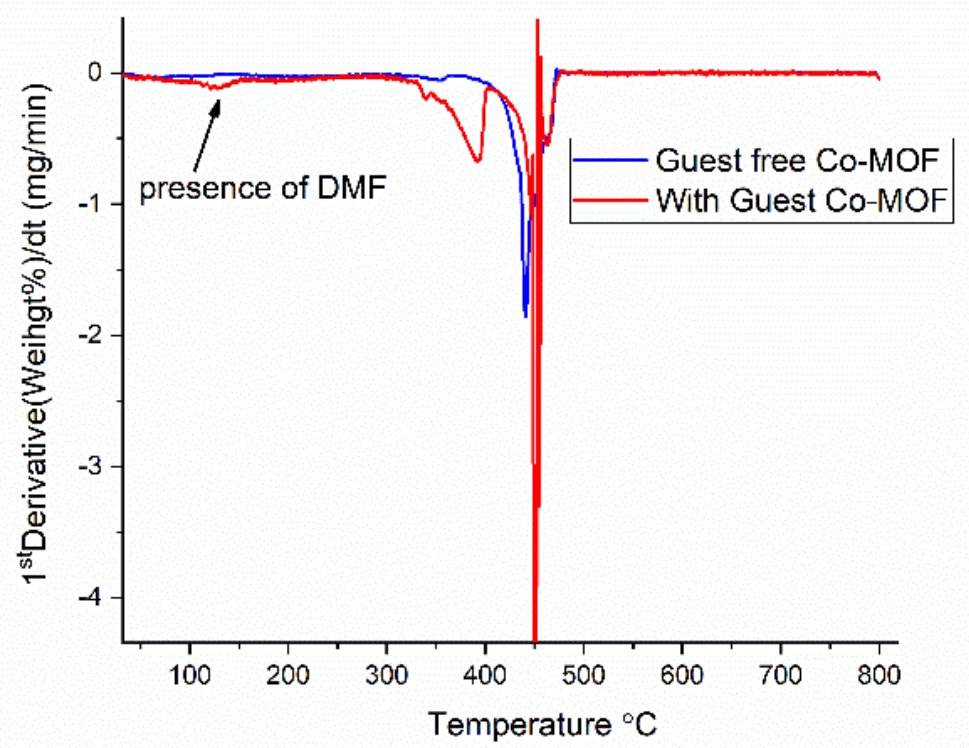


Fig. S14 Overlay of (a) TGA and (b) DTA plots of **Co-MOF** and **Co-MOF** after removing guest molecules.

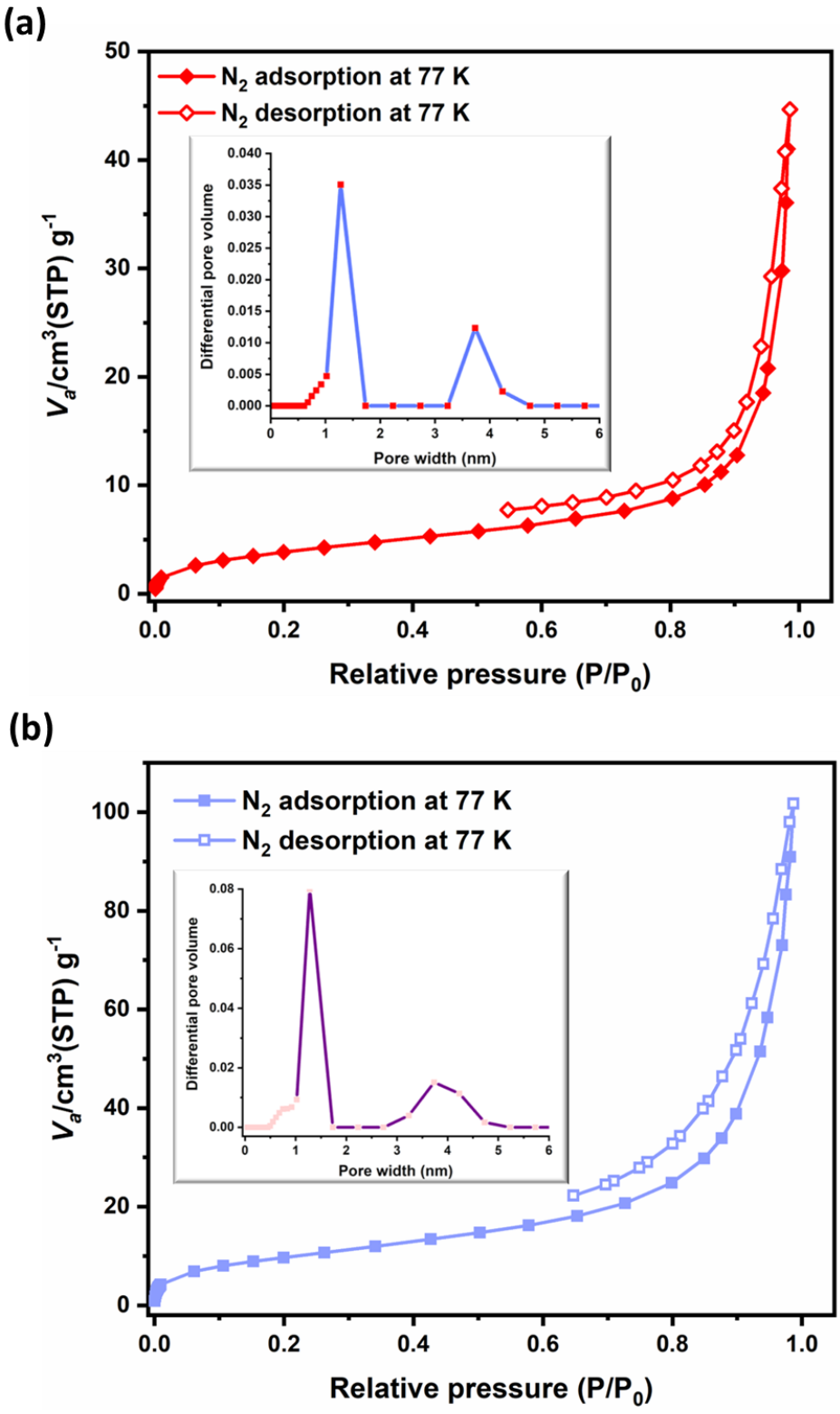


Fig. S15 N_2 adsorption-desorption isotherms (Type II) at 77 K and 1 bar: (a) **Zn-MOF** and (b) **Co-MOF**; the insets in (a) and (b) are pore size distribution of **Zn-MOF** and **Co-MOF**, respectively.

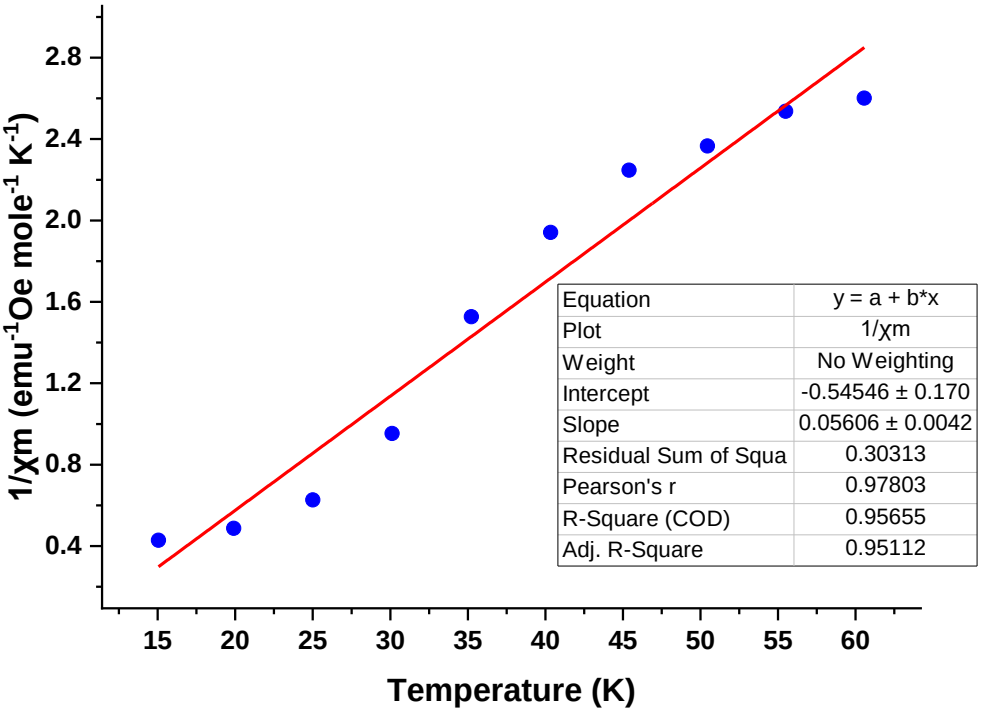


Fig. S16 $1/\chi_m$ *vs* T plot at low temperature for **Co-MOF** (Weiss constant: -5.04K).

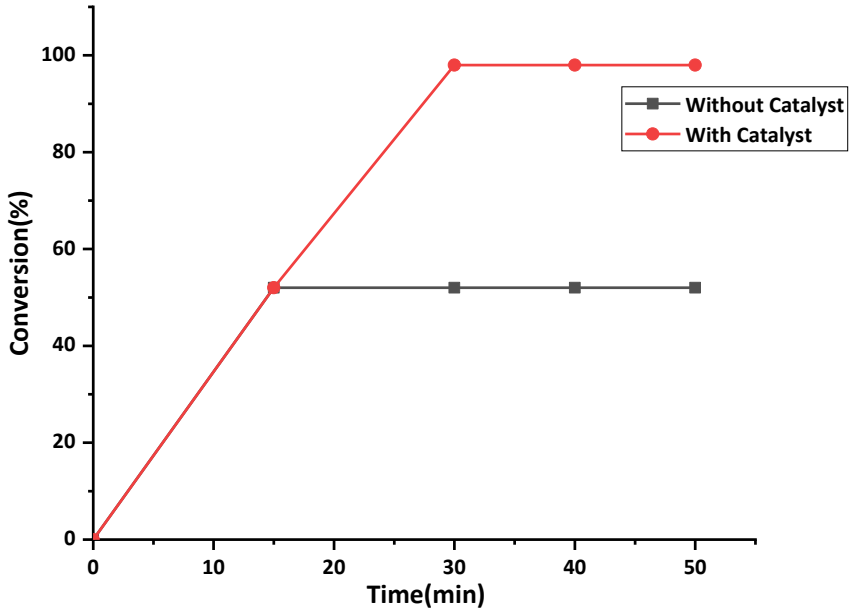


Fig. S17 Hot filtration test for the Knoevenagel condensation reaction of Malononitrile with benzaldehyde with **Zn-MOF** as catalyst and without catalyst (Reaction Condition: Substrate (0.5mmol), Malononitrile (0.65 mmol), **Zn-MOF** (catalyst) amount 5 mg (4.094×10^{-4} mmol), MeOH (0.5 mL), Temperature (78 °C)).

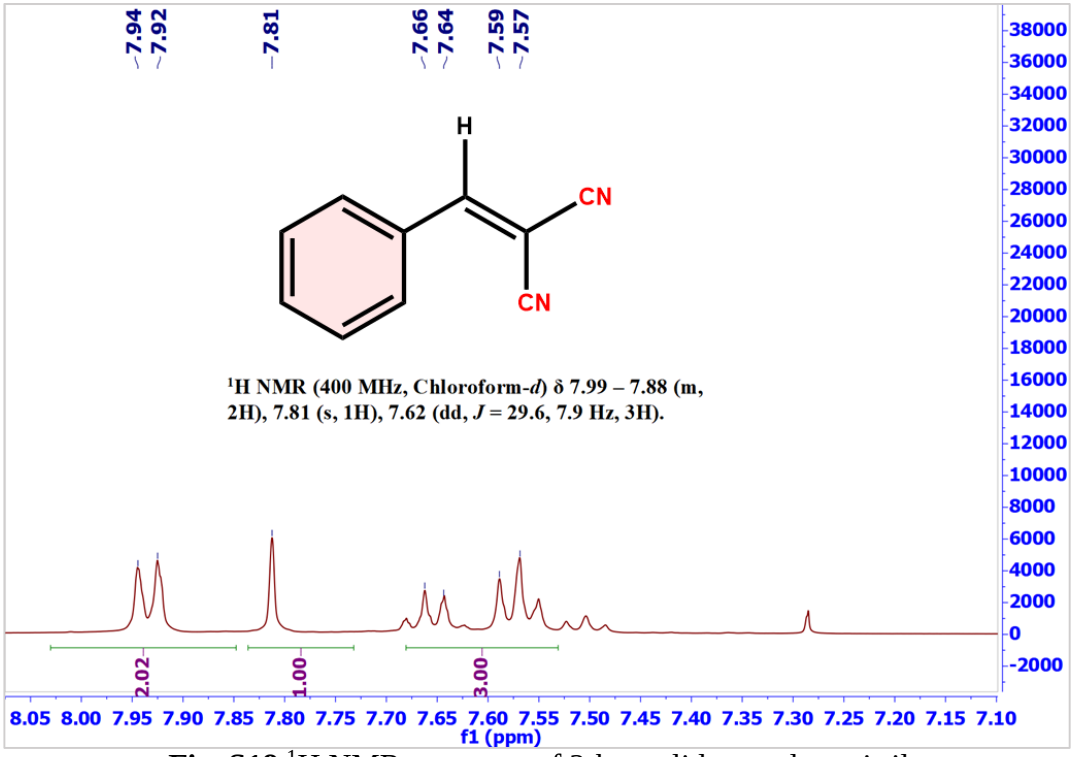


Fig. S18 [1]H NMR spectrum of 2-benzylidenemalononitrile.

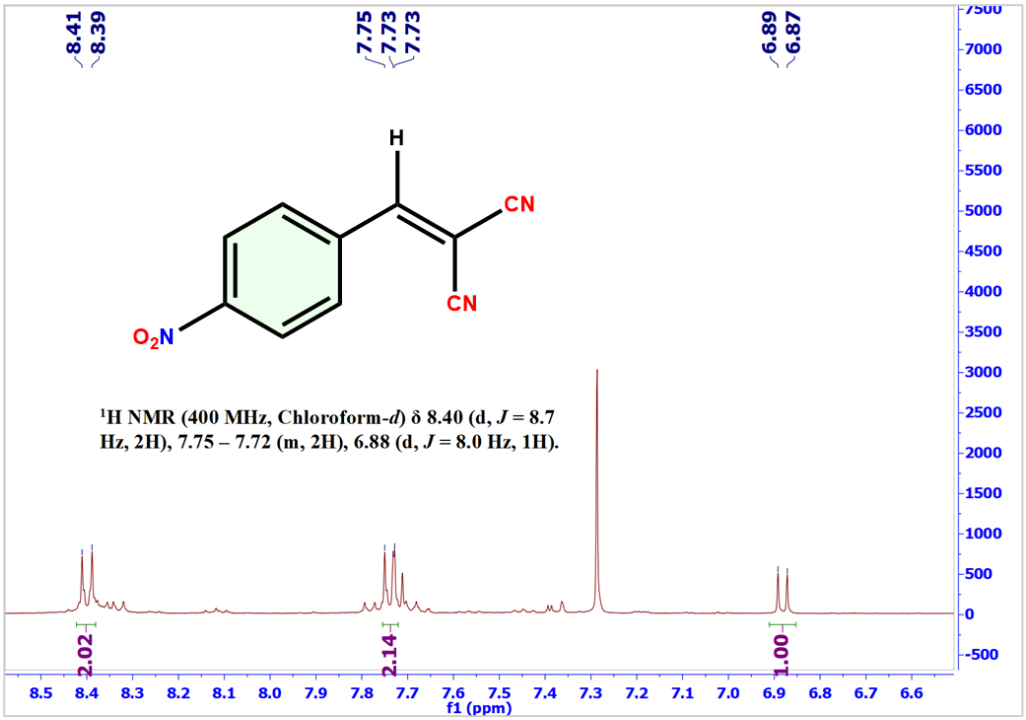


Fig. S19 [1]H NMR spectrum of 2-(4-nitrobenzylidene)malononitrile.

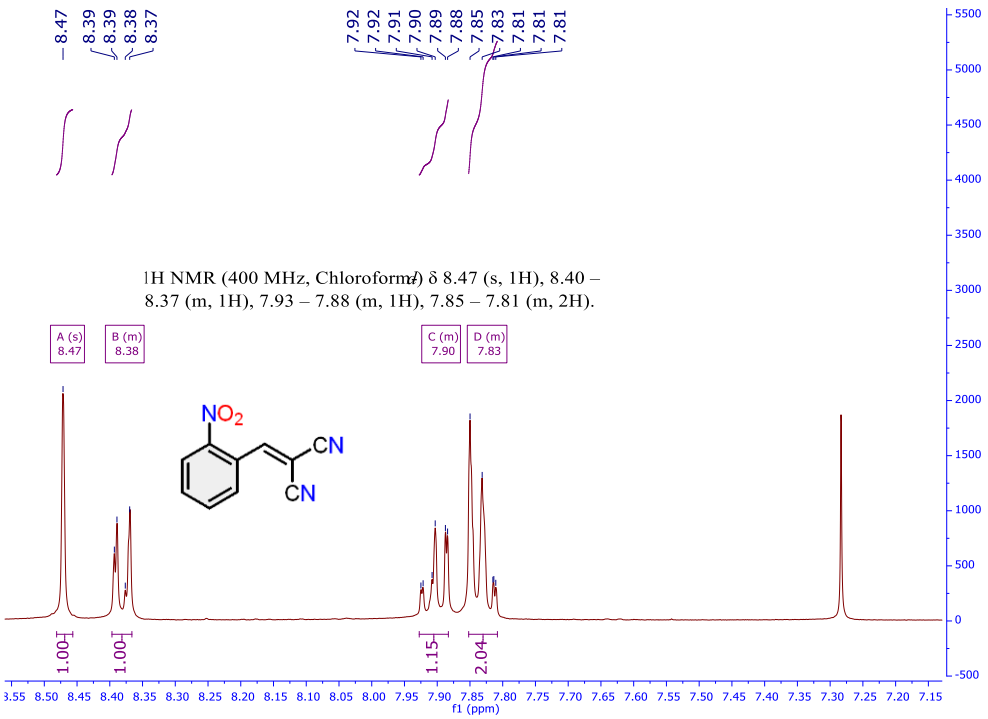


Fig. S20 ^{1}H NMR spectrum of 2-(2-nitrobenzylidene)malononitrile.

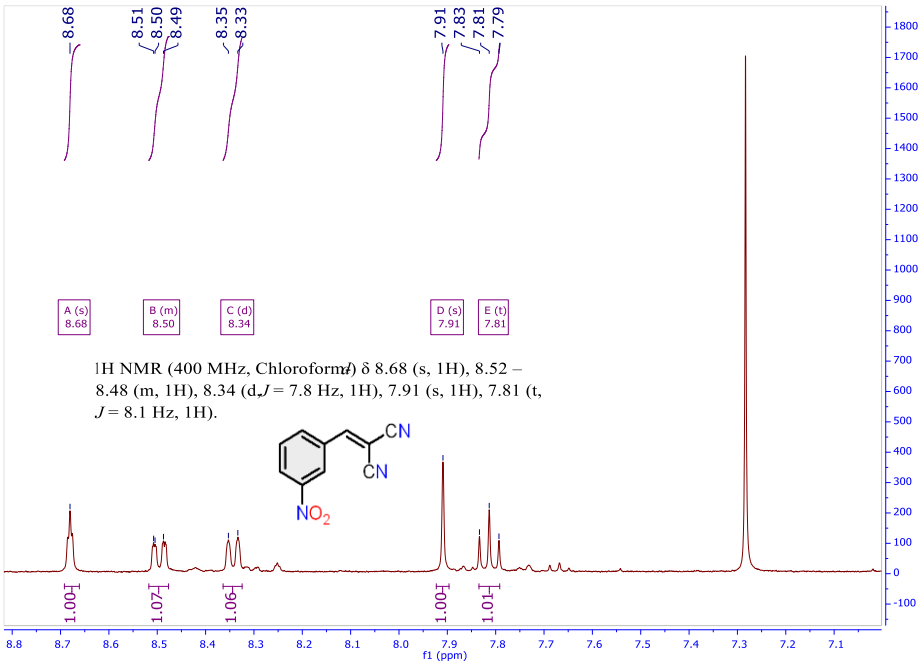


Fig. S21 ^{1}H NMR spectrum of 2-(3-nitrobenzylidene)malononitrile.

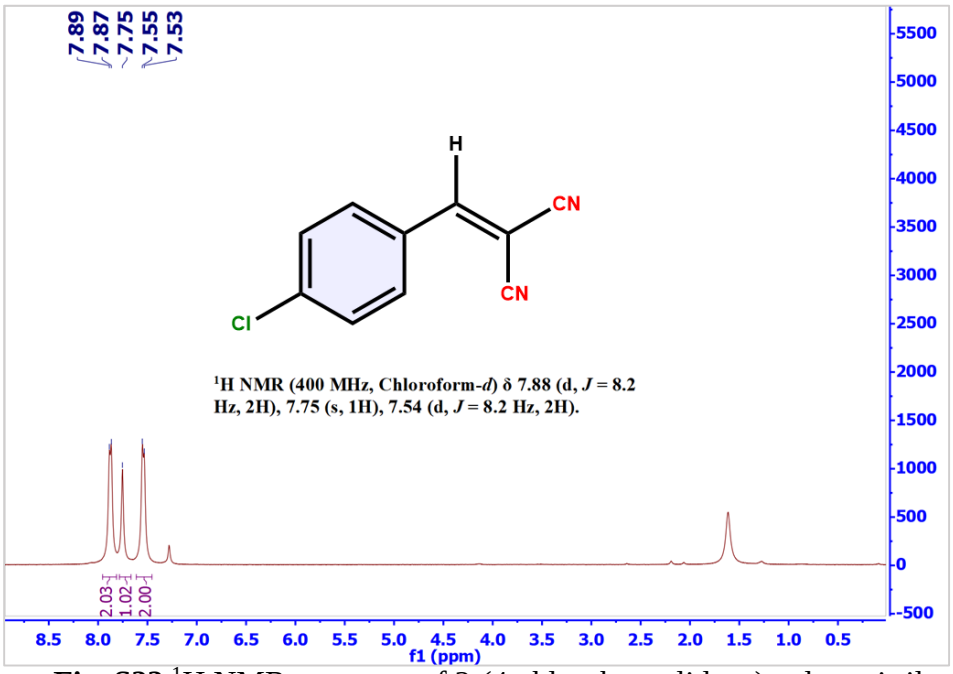


Fig. S22 ^{1}H NMR spectrum of 2-(4-chlorobenzylidene)malononitrile

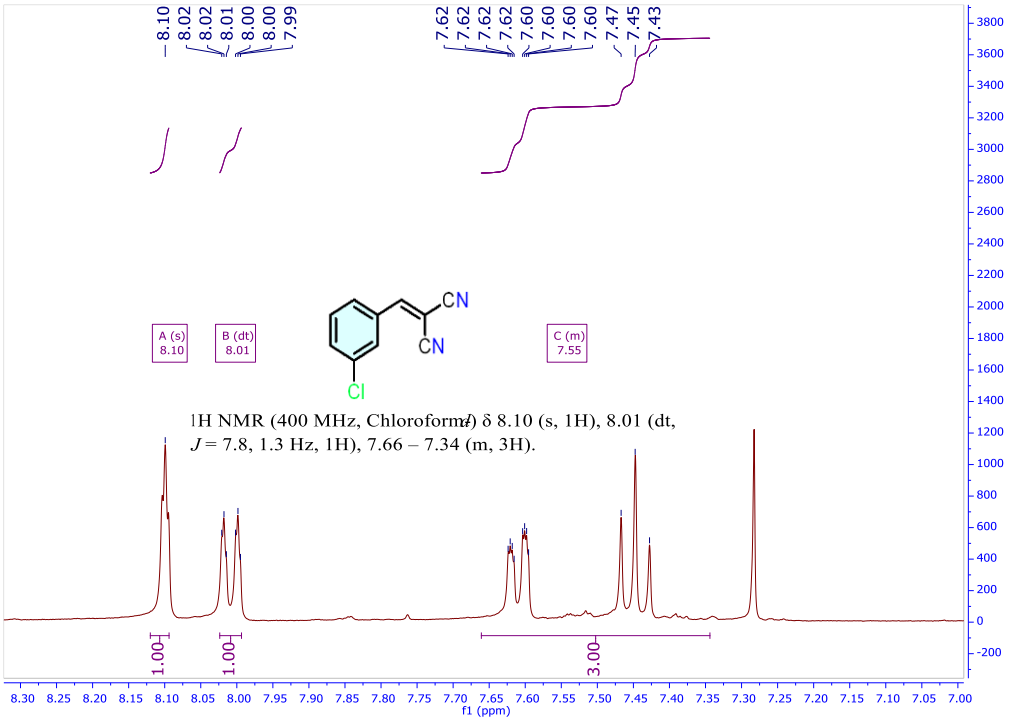


Fig. S23 ^{1}H NMR spectrum of 2-(3-chlorobenzylidene)malononitrile.

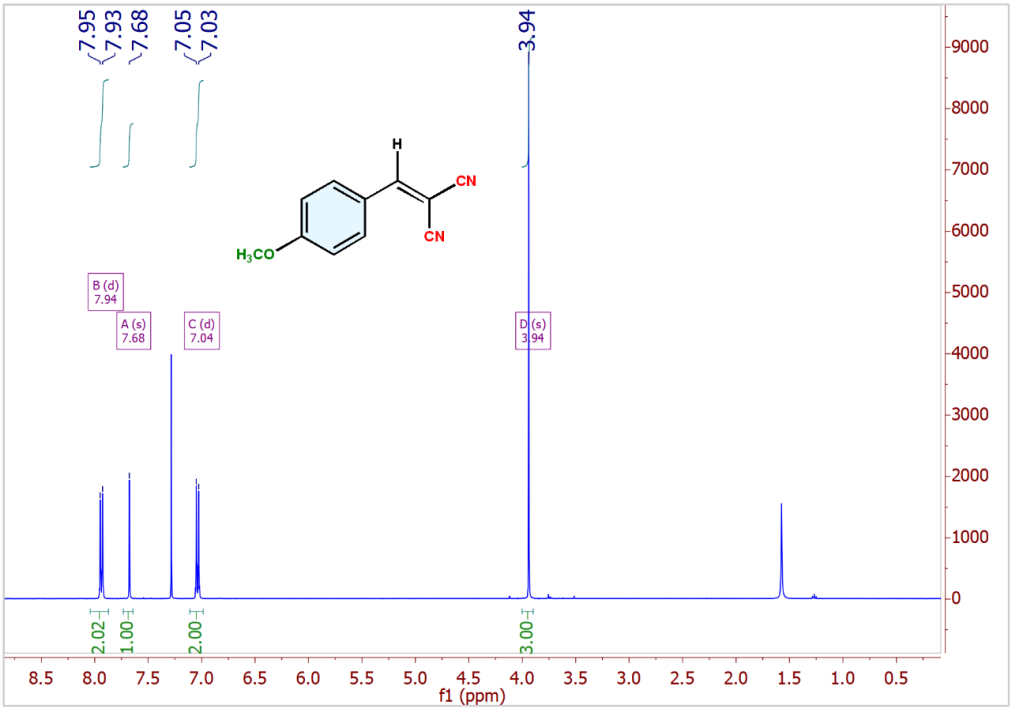


Fig. S24 ^{1}H NMR spectrum of 2-(4-methoxybenzylidene)malononitrile.

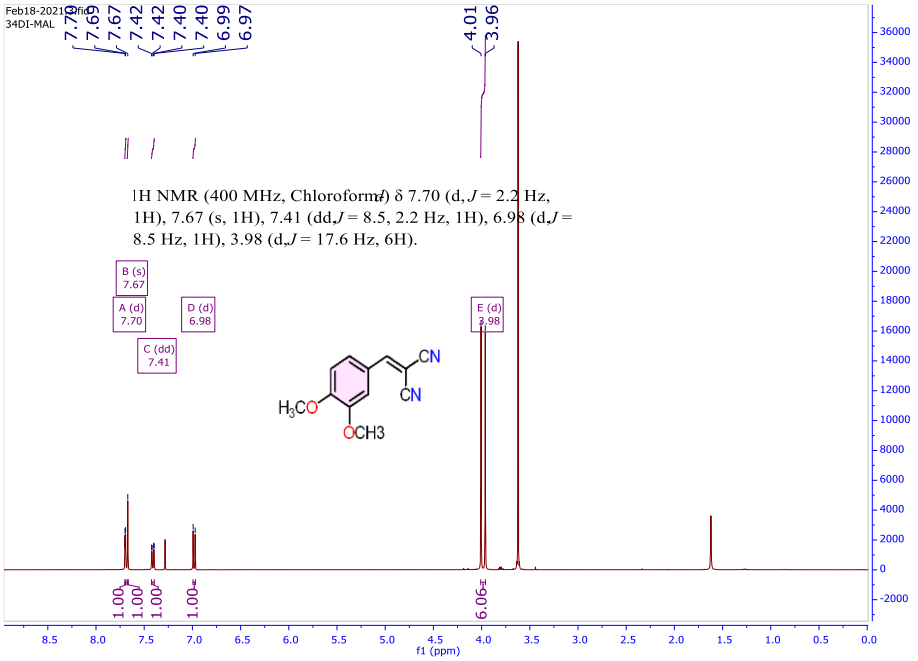


Fig. S25 ^{1}H NMR spectrum of 2-(3,4-dimethoxybenzylidene)malononitrile.

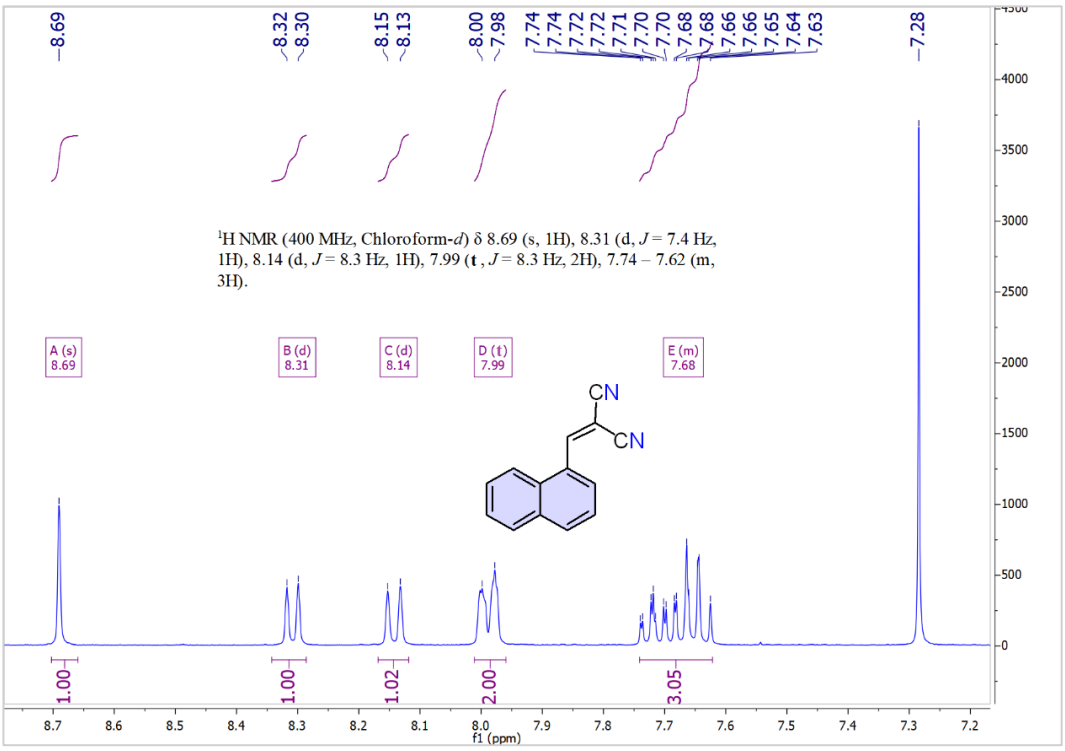


Fig. S26 ^{1}H NMR spectrum of 2-(naphthalen-1-ylmethylene)malononitrile.

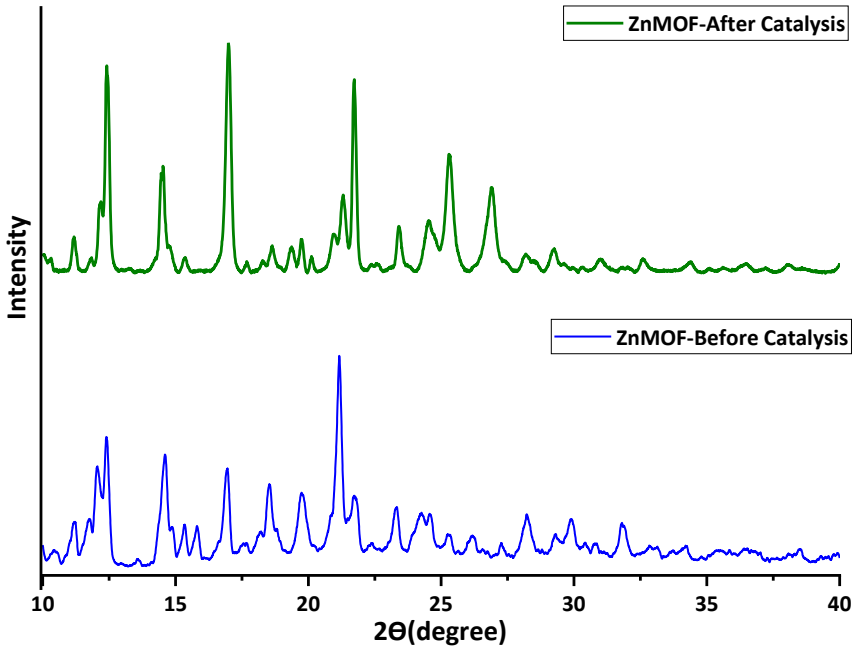


Fig. S27 PXRD patterns of **Zn-MOF** before and after catalysis.

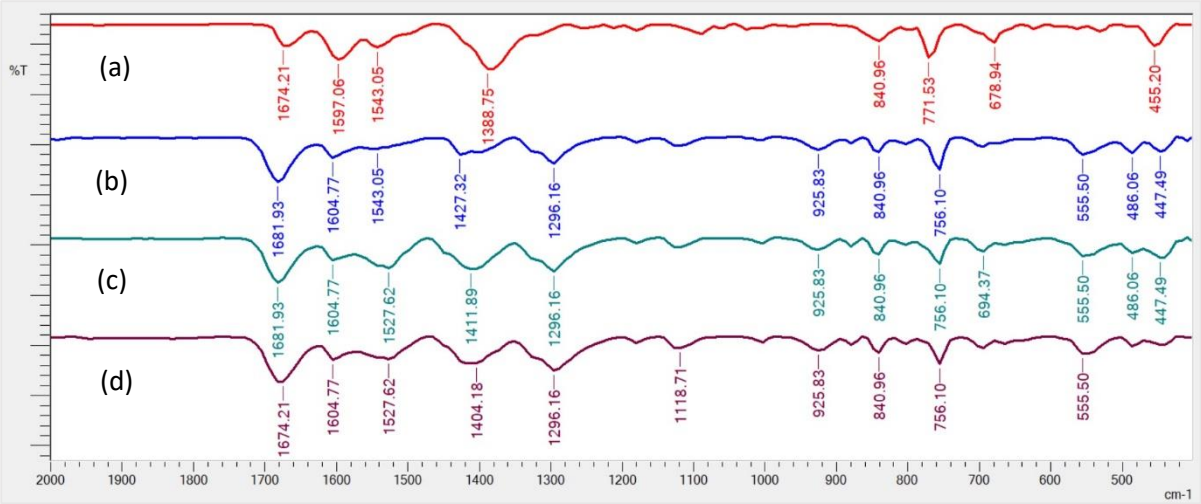


Fig. S28 Stacked FTIR spectra to compare the structural integrity of **Zn-MOF** (a) before catalysis, (b) after first cycle catalysis; (c) after second cycle catalysis; (d) after third cycle catalysis (For the reaction involving benzaldehyde with malononitrile).

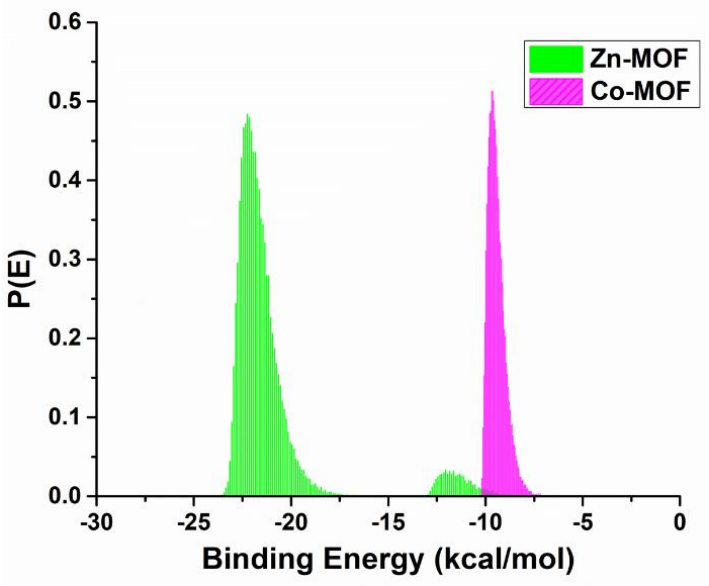


Fig. S29 Binding energy of benzaldehyde with **Zn-MOF** and **Co-MOF**.

Table S1. Selected bond distances of **Zn-MOF** involving the Zn centers (see Figure S3 for atom labels)

Atom1	Atom2	Length
Zn1	O1	1.942(7)
Zn1	O3	1.932(8)
Zn1	N1	2.046(9)
Zn1	O5	1.940(8)
Zn2	O2	2.09
Zn2	O4	2.06
Zn2	O6	2.08

Table S2. Selected bond distances of **Co-MOF** involving the Co centers (see Figure S4 for atom labels)

Atom1	Atom2	Length
Co1	O1	2.110(5)
Co1	O5	2.029(5)
Co1	O9	2.049(5)
Co1	O3	2.112(4)
Co1	O7	2.037(5)
Co1	O12	2.076(4)
Co2	O1	2.261(5)
Co2	O2	2.020(4)
Co2	O10	1.955(5)
Co2	N1	2.068(6)
Co2	O11	1.960(4)
Co3	O8	1.977(6)
Co3	O13	2.143(8)
Co3	N3	2.109(9)
Co3	O3	2.134(5)
Co3	O4	2.238(6)
Co3	O6	2.017(4)

Table S3. Optimization table for the Knoevenagel condensation reaction between Malanonitrile and Benzaldehyde

Entry	Catalyst	Catalyst Amount (mg)	Solvent	Time	Temperature	Percentage Conversion[a]
1	Catalyst free		MeOH	24 h	78 °C	27
2	**Zn-MOF**	5 mg	$CHCl_3$	6 h	65 °C	traces
3	**Zn-MOF**	5 mg	THF	4 h	50 °C	traces
4	**Zn-MOF**	5 mg	THF	4 h	65 °C	40
5	**Zn-MOF**	5 mg	Acetonitrile	6 h	80 °C	traces
6	**Zn-MOF**	5 mg	MeOH	1 h	50 °C	35
7	**Zn-MOF**	5 mg	MeOH	30 min	78 °C	98
8	**Zn-MOF**	10 mg	MeOH	30 min	78 °C	98
9	**Zn-MOF**	5 mg	Ethylacetate	1 h	70 °C	64
10	**Zn-MOF**	5 mg	DCM	2 h	35 °C	19
11	**Co-MOF**	5 mg	MeOH	45 min	78 °C	65

[a]Conversion (%) was determined from GC