Electronic Supplementary Information

Metal-organic Frameworks constructed with acid-base mixed ligands carboxylic acids and N-containing chalcone and their catalytic performance for Knoevenagel condensation

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Table S1. Crystal data and structure refinements for MOFs **1**−**3**

MOFs	**1**	**2**	**3**
Empirical formula	$C_{45}H_{36}CdN_6O_8$	$C_{50}H_{47}CdN_7O_9$	$C_{50}H_{47}CoN_7O_9$
Formula weight	901.20	1002.34	948.87
Temperature (K)	300	300.15	300.15
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.7214(9)	9.6539(4)	9.6124(3)
b (Å)	15.1141(14)	14.9335(6)	14.9026(5)
c (Å)	17.2898(19)	17.6393(7)	17.2025(6)
α (°)	114.157(10)	81.467(3)	82.802(3)
β (°)	95.733(9)	82.719(3)	81.793(3)
γ (°)	94.009(9)	89.187(3)	87.487(3)
V (Å^3)	2053.6(4)	2494.54(18)	2418.92(15)
Z	2	2	2
Dc (g/cm^3)	1.338	1.334	1.303
μ (mm^{-1})	4.703	4.007	3.297
F (000)	838	1032.0	990.0
Radiation	Cu-$K\alpha$ (λ = 1.54184)	Cu-$K\alpha$ (λ = 1.54184)	Cu-$K\alpha$ (λ = 1.54184)
Reflections collected	11681	14420	36110
Independent reflections	7754	9410	9814
R_{int}	0.0818	0.0427	0.1540
Data/restraints/parameters	7755/269/590	9410/589/876	9814/467/876
GOF on F^2	0.984	1.088	0.997
R_1/wR_2 [$I > 2\sigma(I)$]	0.0673/0.1514	0.0524/0.1412	0.0731/0.1725
R_1/wR_2 [all data]	0.1078/0.1830	0.0595/0.1485	0.1375/0.2154

$^aR_1 = \Sigma \, ||F_o|-|F_c|| / \Sigma \, |F_o|$. $^bwR_2 = (\Sigma \, [w(F_o^2 - F_c^2)^2] / \Sigma \, [w(F_o^2)^2])^{1/2}$

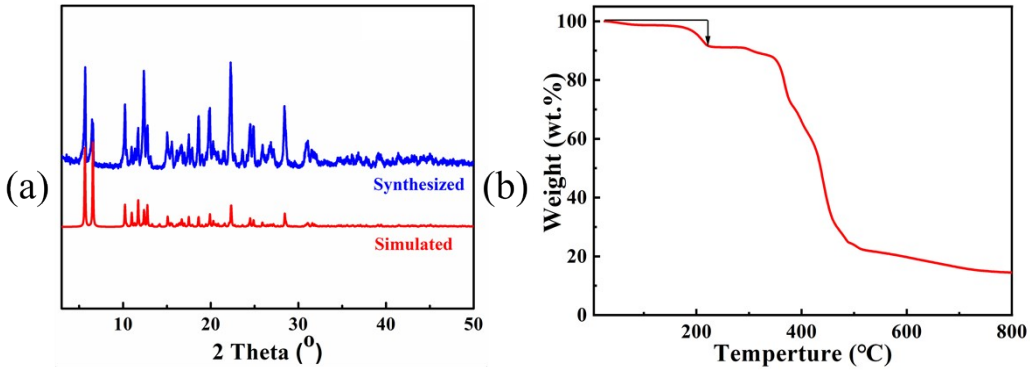


Fig. S1 PXRD pattern and TGA curve of **1**.

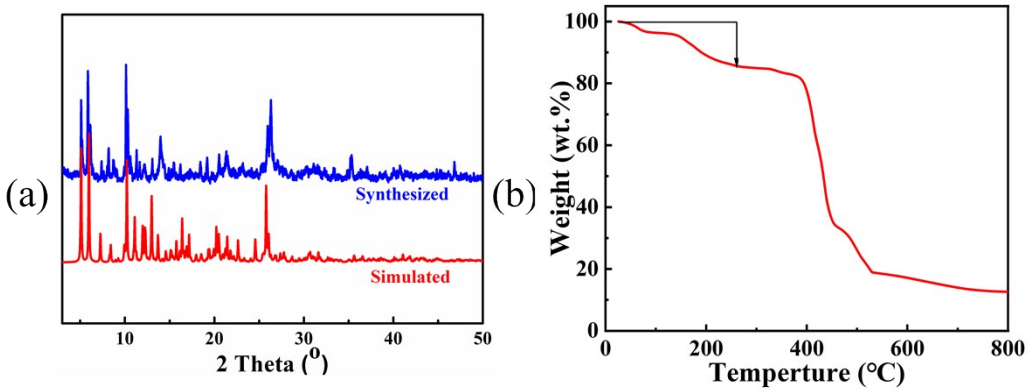


Fig. S2 PXRD pattern and TGA curve of **2**.

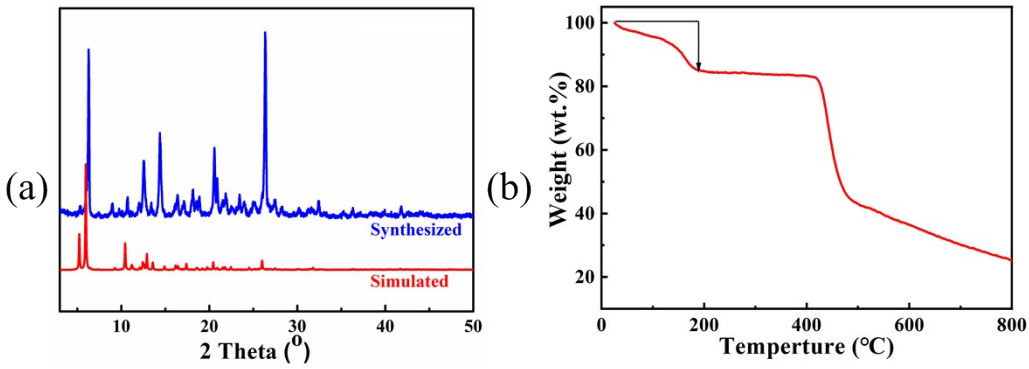


Fig. S3 PXRD pattern and TGA curve of **3**.

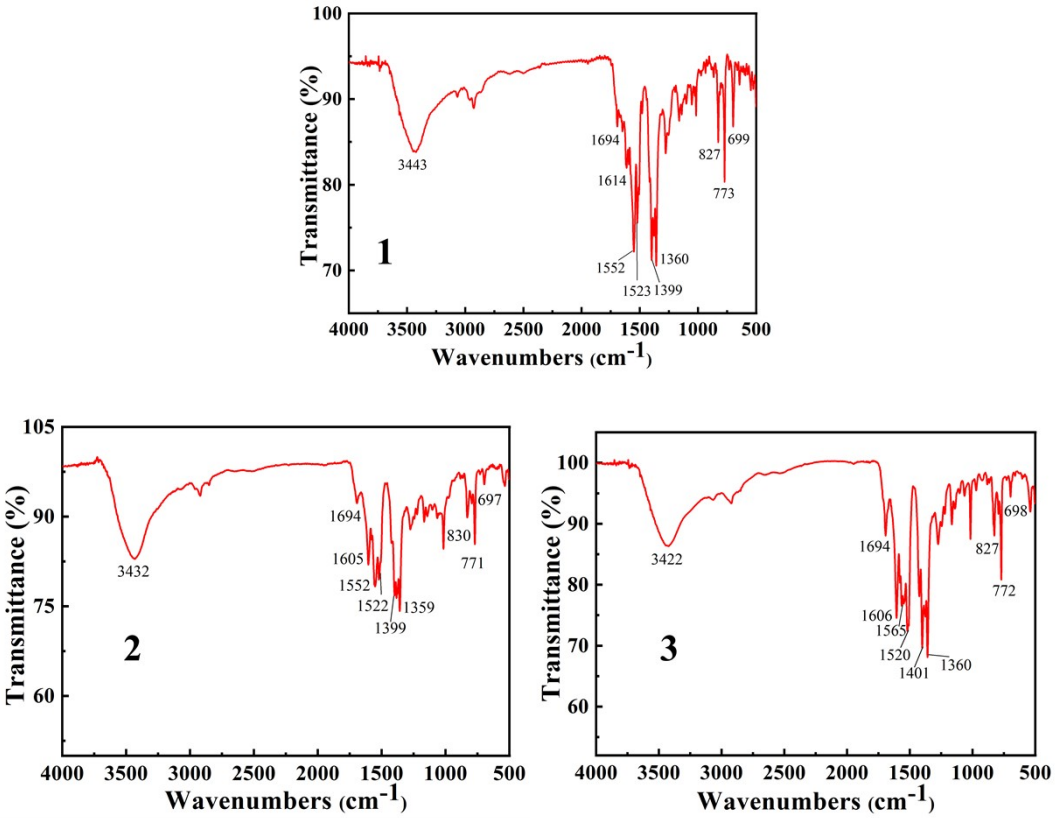


Fig. S4 IR spectra of **1**, **2**, and **3**.

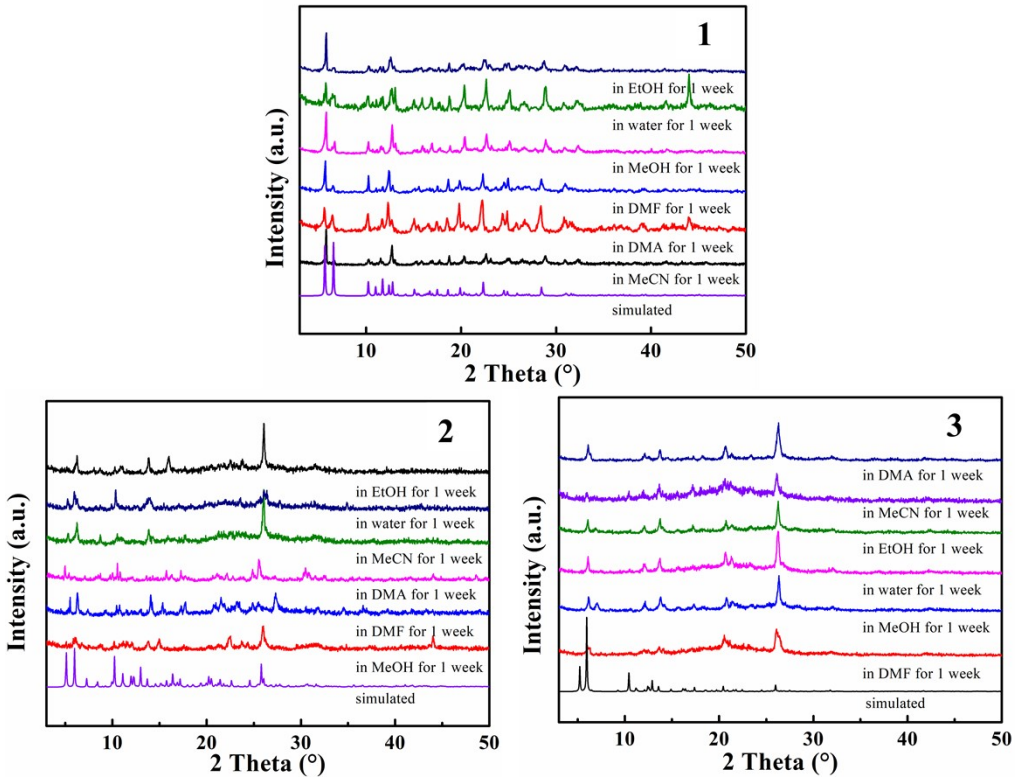


Fig. S5 PXRD patterns of **1**, **2**, and **3** soaked in different solvents.

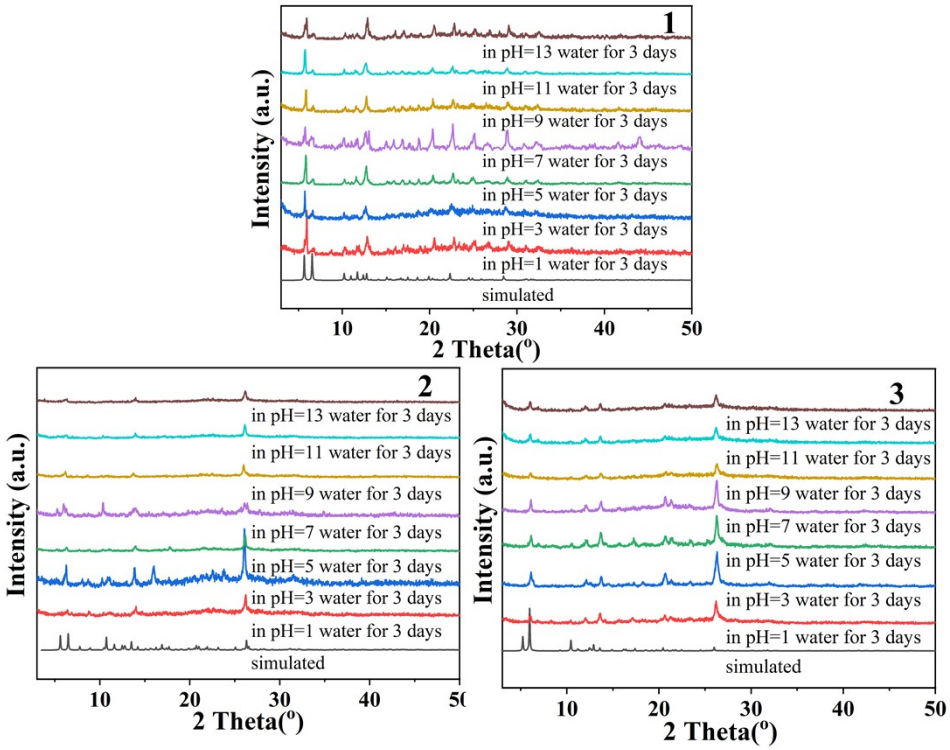


Fig. S6 PXRD patterns for water-, acid- and alkali-treated **1-3.**

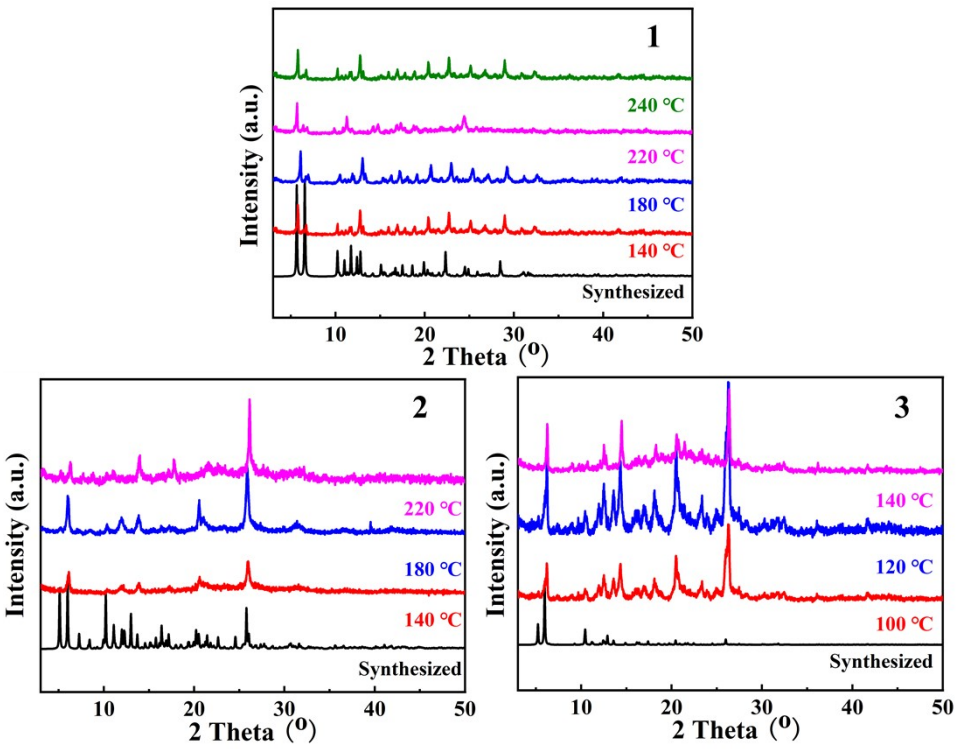


Fig. S7 Variabletemperature PXRD patterns of **1-3**.

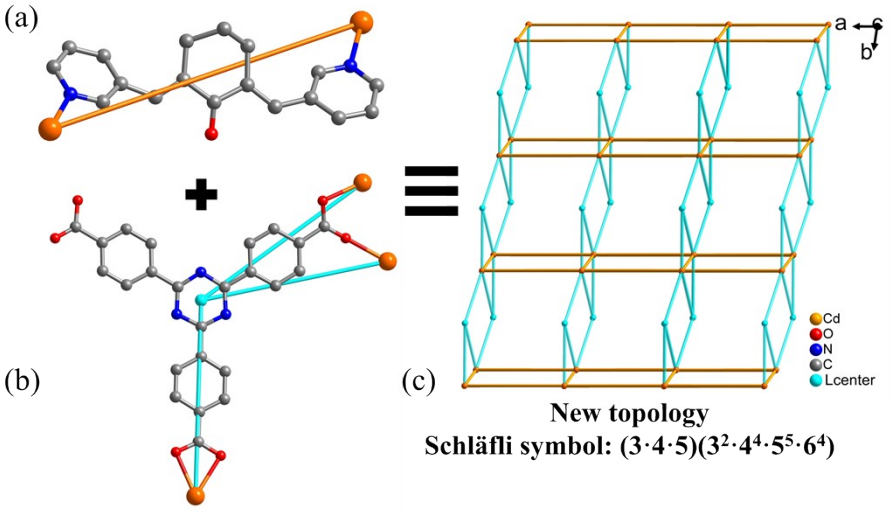


Fig. S8 Topology analysis of **1.**

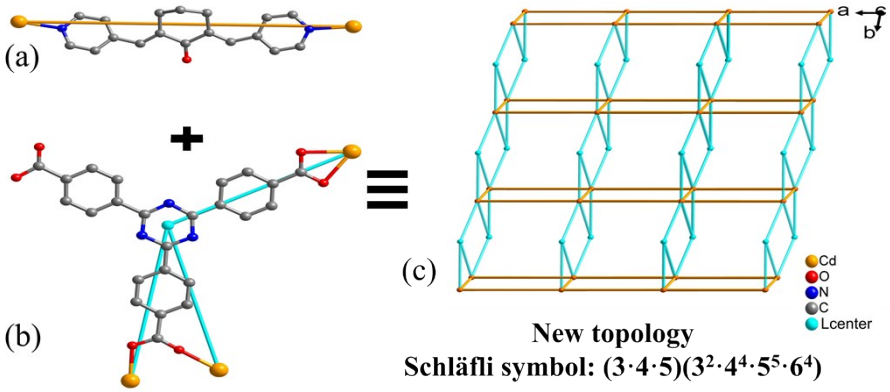


Fig. S9 Topology analysis of **2**.

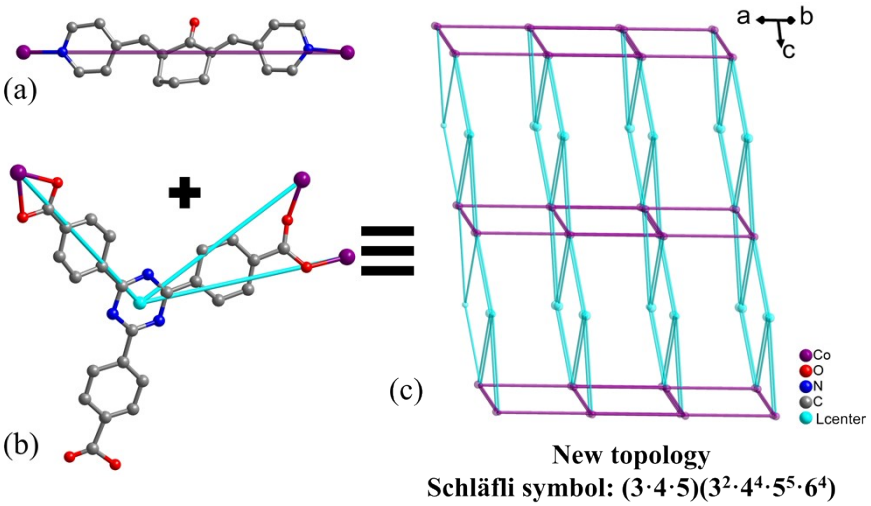


Fig. S10 Topology analysis of **3**.

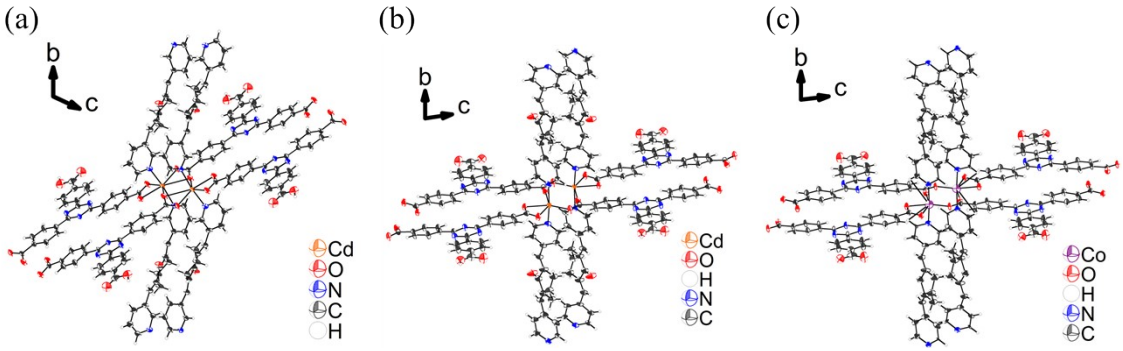


Fig. S11 The ellipsoid diagram of dinuclear metal unit in **1-3**.

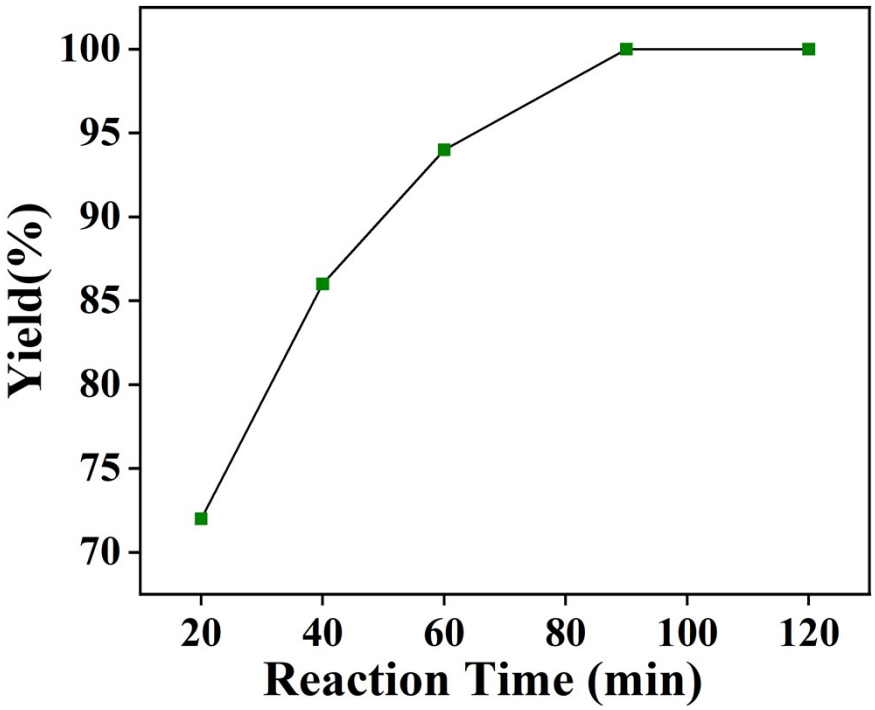


Fig. S12 Kinetics curves of Knoevenagel condensation catalyzed by **1** at 25℃

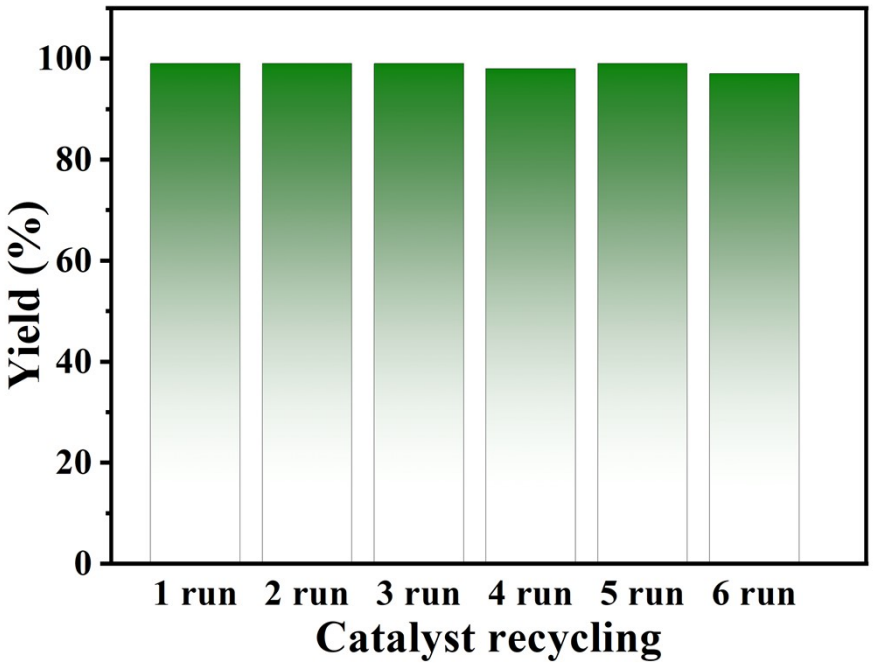


Fig. S13 Catalyst recycling experiments in the Knoevenagel condensation of benzaldehyde with propanedinitrile catalyzed by **1**.

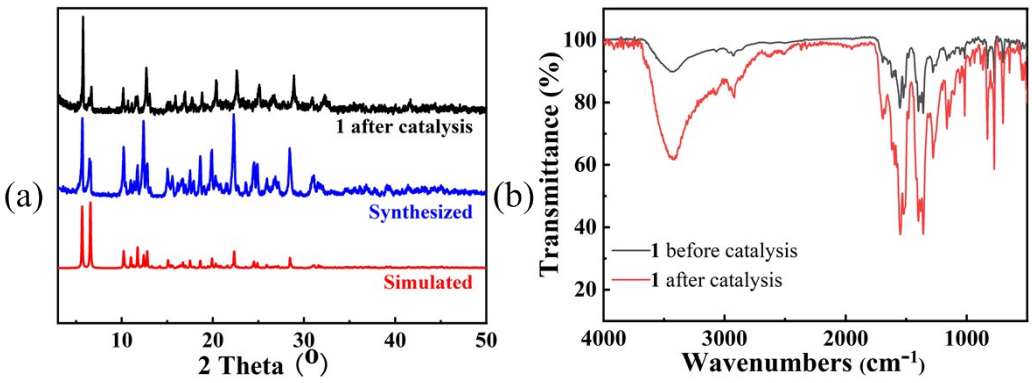
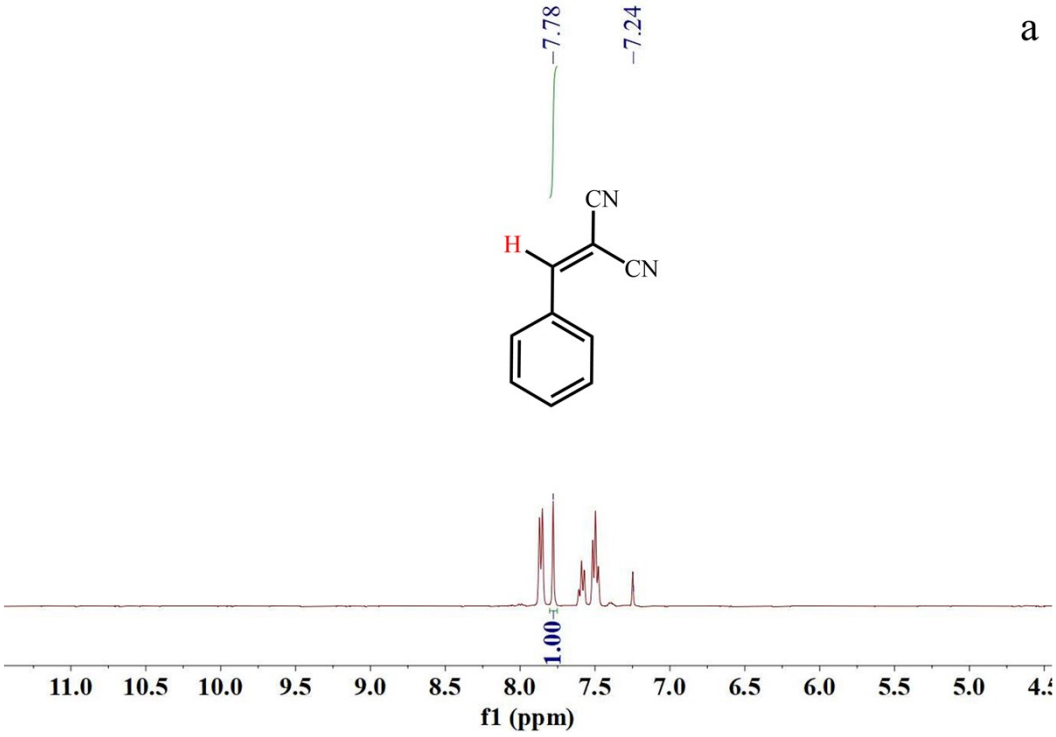
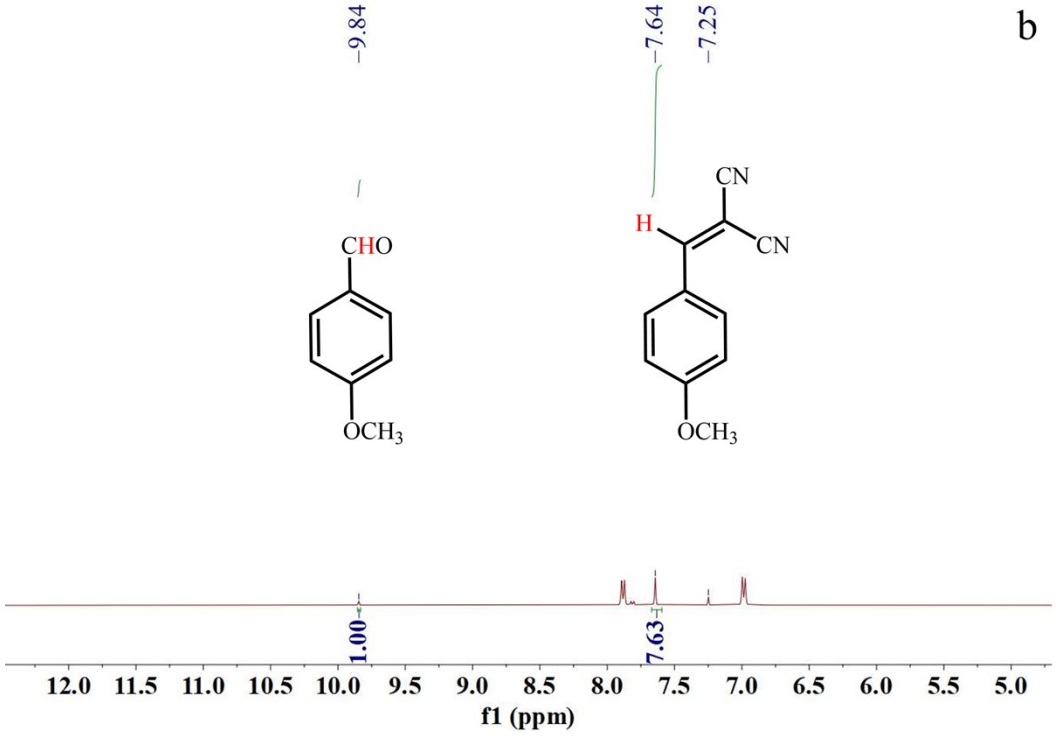
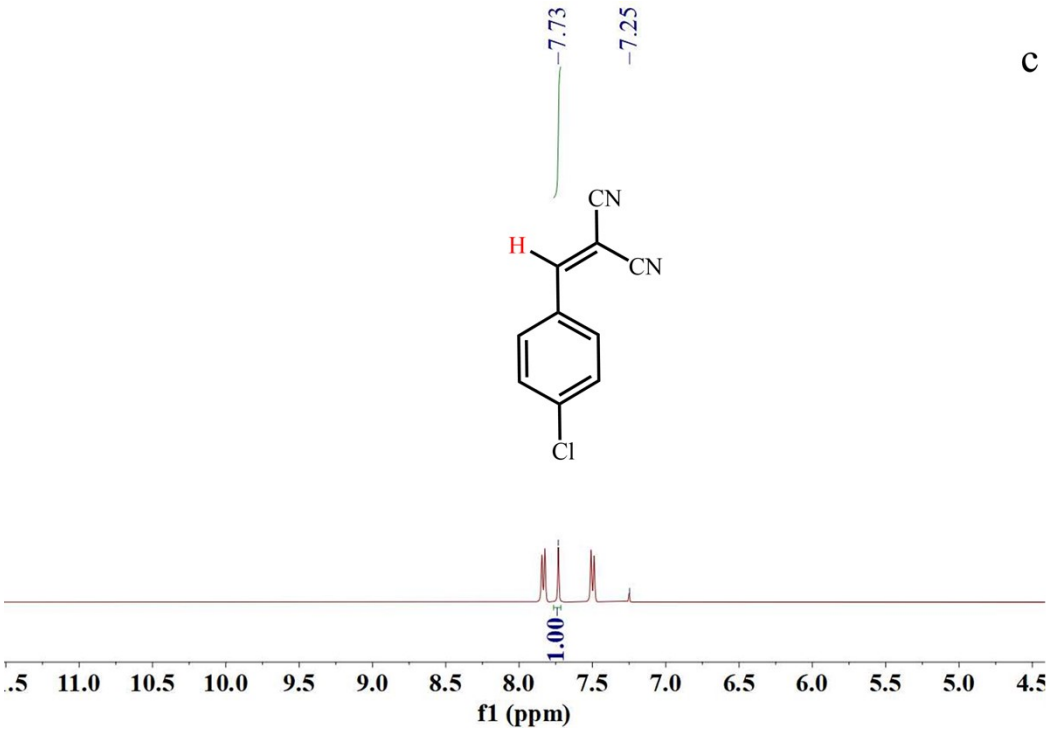


Fig. S14 (a) PXRD patterns and (b) IR spectra of **1** after catalytic reaction





c



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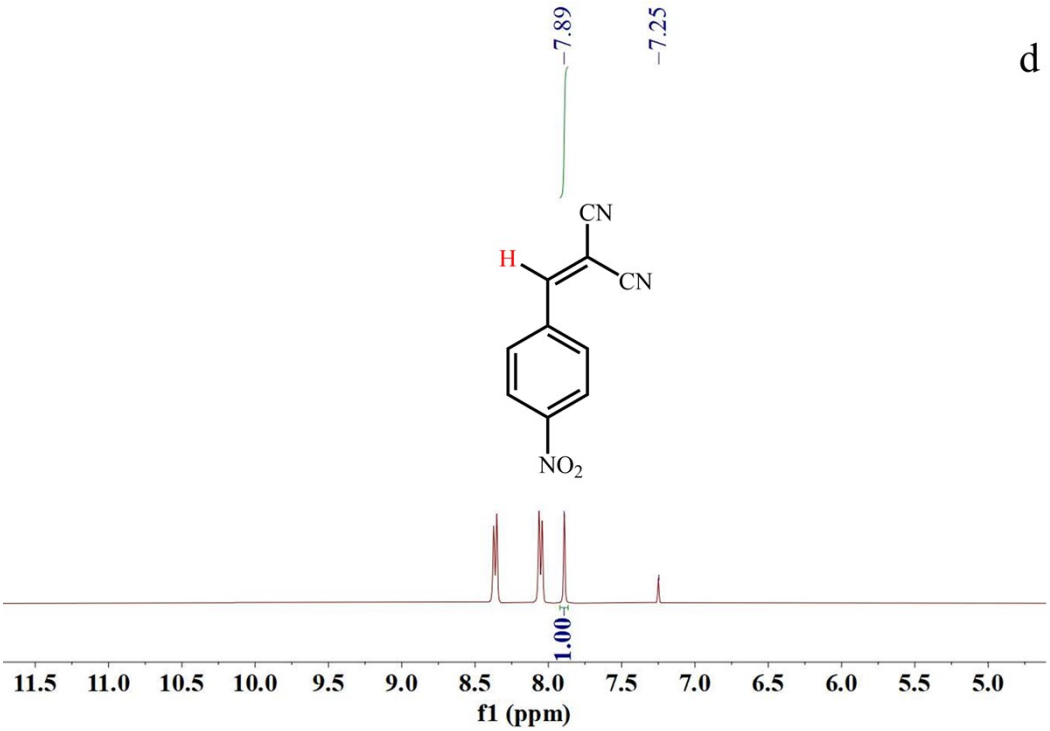
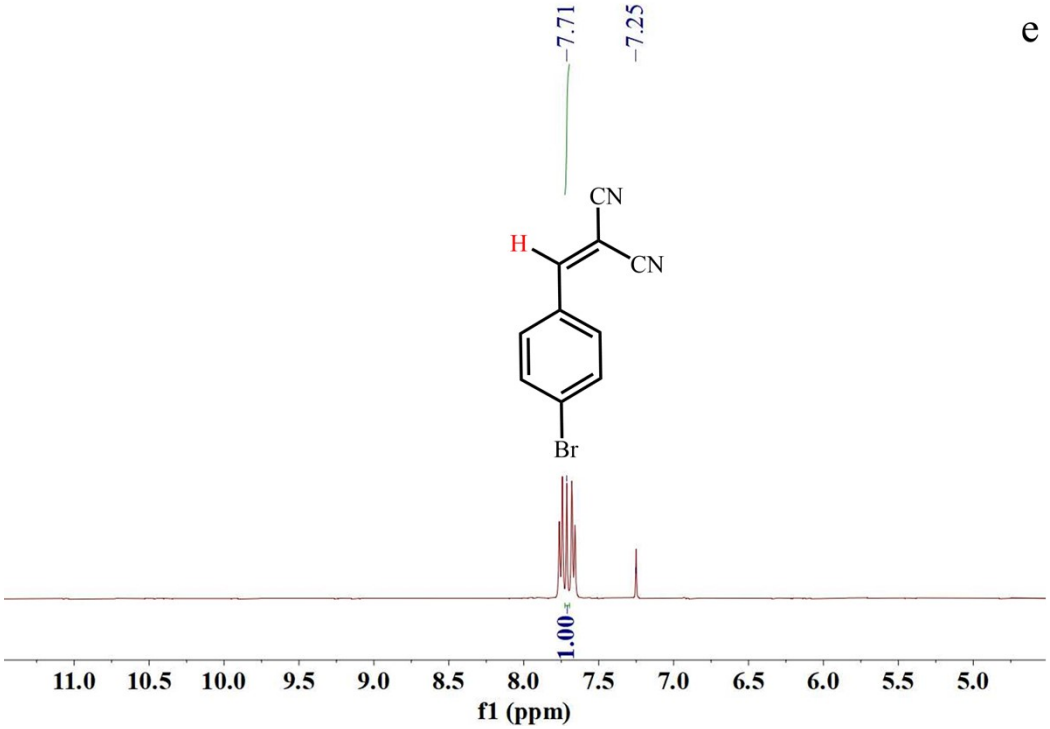
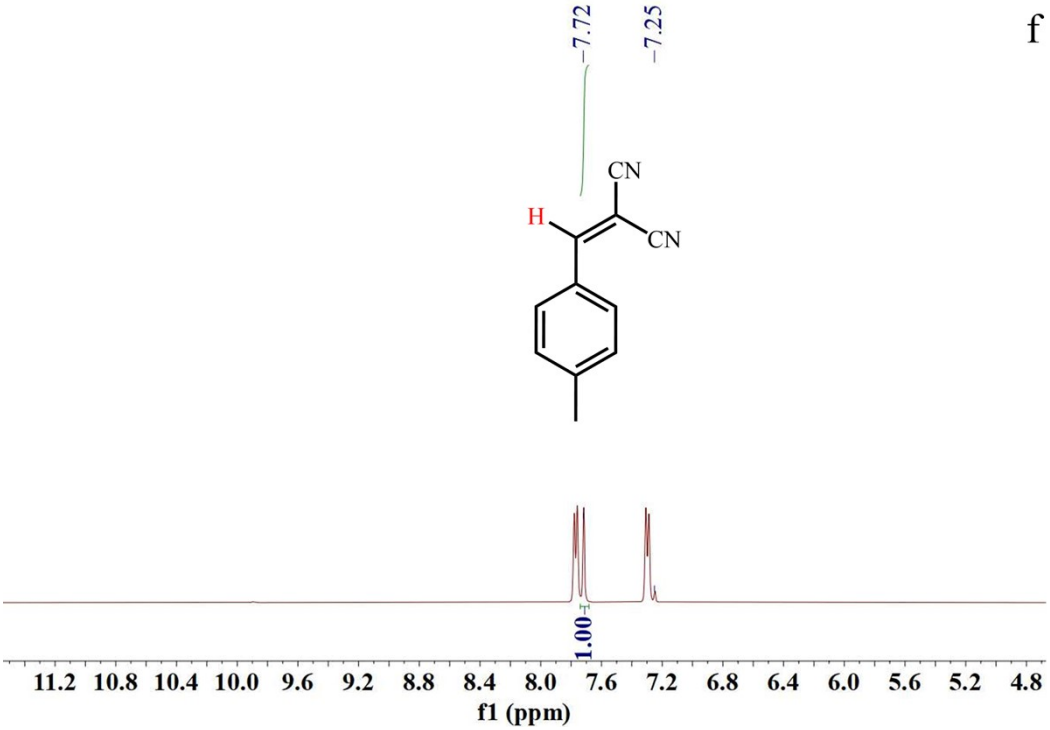
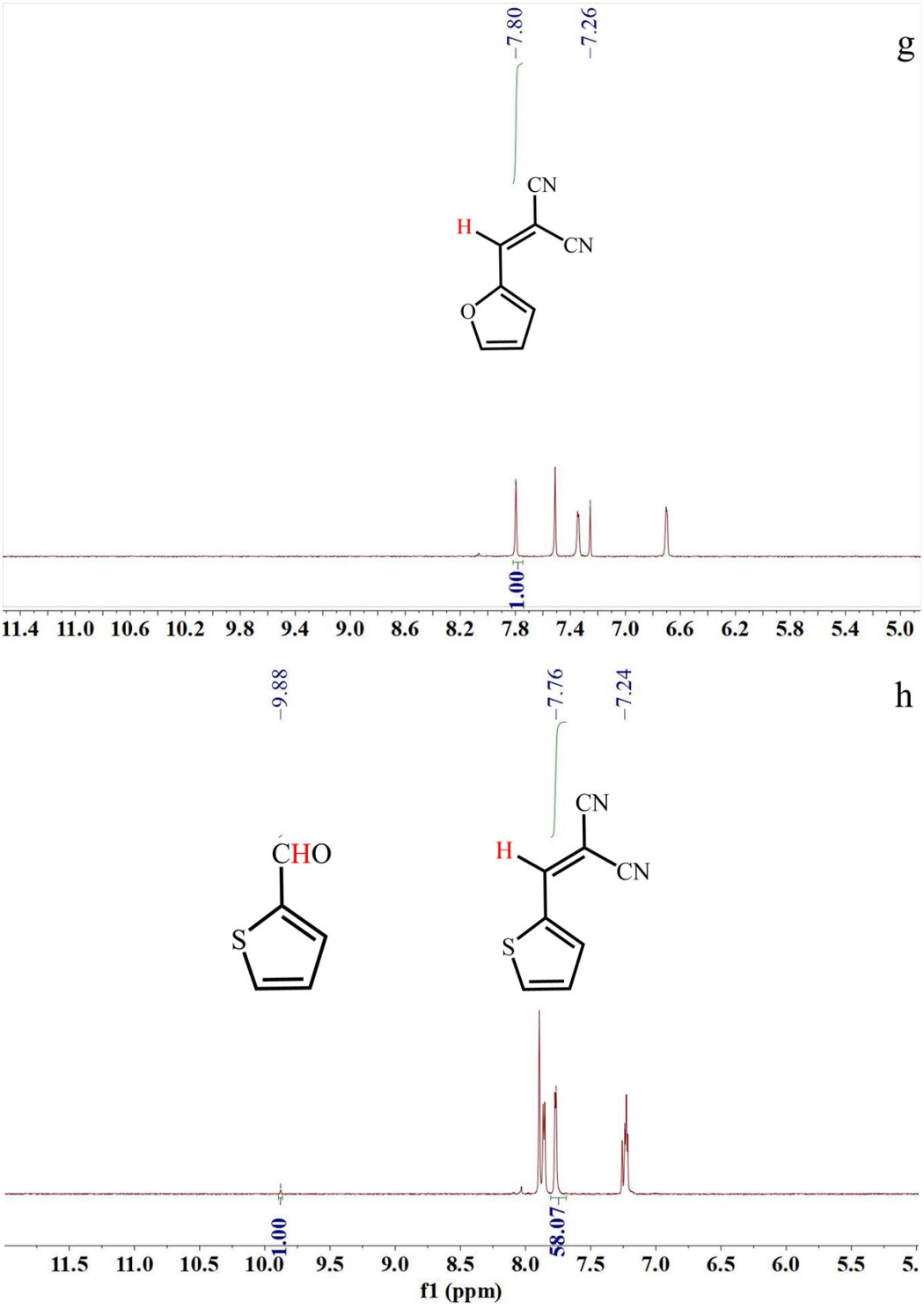
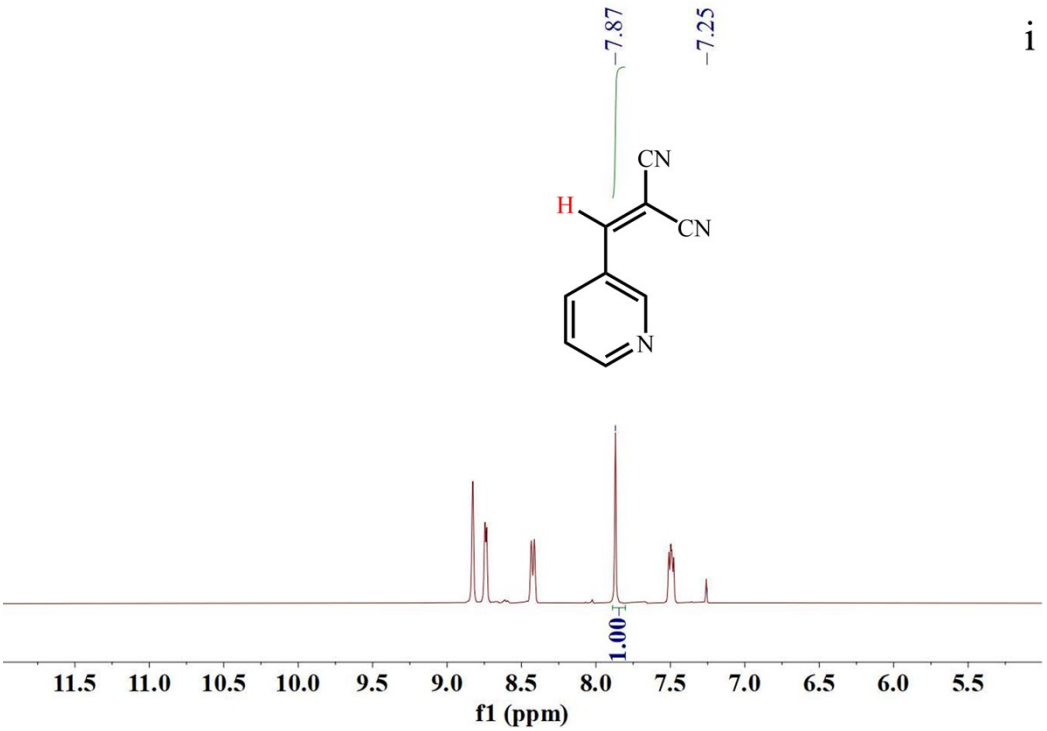








i



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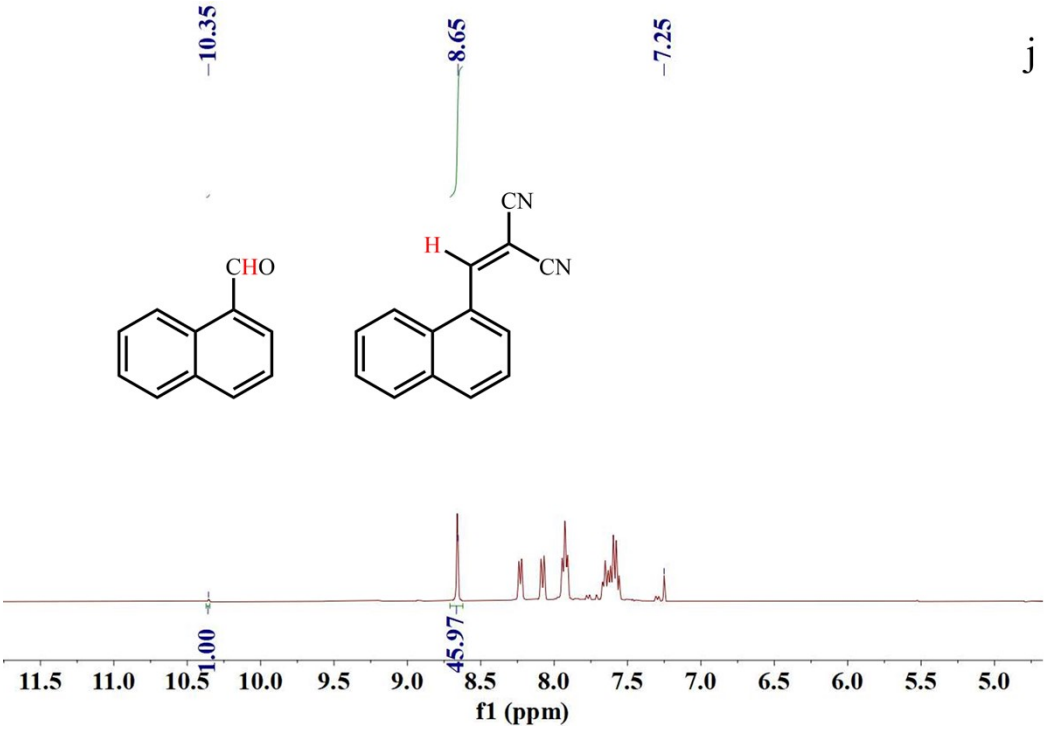

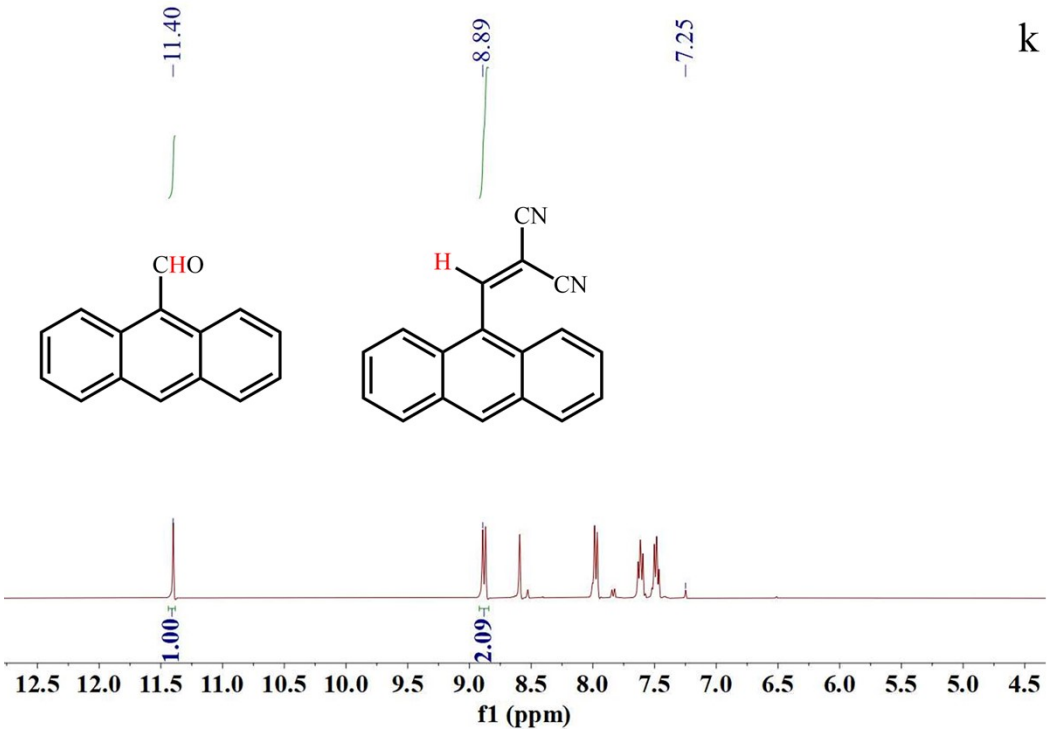

Fig. S15 Examples for integration of ^{1}H NMR spectra for the determination of Knoevenagel condensation products.

Table S2. Comparison of the catalytic activity of various MOFs for the Knoevenagel condensation reaction

MOF	catalyst (mol%)	solvent	temperature (°C)	time (h)	yield (%)	refs
$[Zn_2(TCA)(BIB)_{2.5}](NO_3)$	0.3	C_2H_5OH	60	1	99	1
$\{[Cu_2(\mu_3\text{-pdba})_2(bipy)]\cdot 2H_2O\}_n$	2	CH_3OH	RT	1	>99	2
$Cd_2(2\text{-bpbg})(fum)_2(H_2O)_2$	1	-	27	3	100	3
Cd-CDA-MOF	0.4	C_2H_5OH	RT	12	98	4
$[Zn_{15}(mbpz)_6(Hmbpz)_6(L\text{-}NO_2)_4(HL\text{-}NO_2)(\mu_3\text{-}OH)_2]_n$	0.6	-	80	1	>99	5
NUC-58a	0.5	C_2H_5OH	65	7	98	6
$[Co_2(bptc)(H_2O)_2]\cdot 5DMA$	2	-	60	6	99	7
1	2	CH_3OH	25	1.5	100	this work
2	2	CH_3OH	25	1.5	99	this work
3	2	CH_3OH	25	1.5	96	this work

Table S3. Selected bond lengths [Å] and angles [°] for MOFs **1**–**3**.

1			
Cd1-O3^{i}	2.335(6)	Cd1-N2	2.325(6)
Cd1-O2	2.232(5)	Cd1-O5^{ii}	2.363(6)
Cd1-O4^{ii}	2.414(5)	Cd1-N1^{iii}	2.331(7)
O3^{i}-Cd1-O4^{ii}	86.65(18)	O5^{ii}-Cd1-O4^{ii}	55.05(18)
O3^{i}-Cd1-O5^{ii}	141.70(18)	N1^{iii}-Cd1-O3^{i}	83.2(2)
N2-Cd1-N1^{iii}	168.1(2)	N1^{iii}-Cd1-O4^{ii}	88.4(2)
O2-Cd1-O3^{i}	125.3(2)	N1^{iii}-Cd1-O5^{ii}	93.7(2)
O2-Cd1-O4^{ii}	147.8(2)	N2-Cd1-O3^{i}	85.9(2)
O2-Cd1-O5^{ii}	92.9(2)	N2-Cd1-O4^{ii}	86.3(2)
O2-Cd1-N1^{iii}	91.4(2)	N2-Cd1-O5^{ii}	92.0(2)
O2-Cd1-N2	98.8(2)		

Symmetry codes: (i) *1-x, 1-y, 2-z*; (ii) *x, 1+y, 1+z*; (iii) *x, -1+y, 1+z*.

2			
Cd1-O1	2.187(3)	Cd1-O6^{ii}	2.402(3)
Cd1-O2^{i}	2.312(3)	Cd1-N2^{iii}	2.302(3)
Cd1-O5^{ii}	2.375(3)	Cd1-N1	2.332(3)
O1-Cd1-O2^{i}	121.72(13)	O5^{ii}-Cd1-O6^{ii}	55.01(11)
O1-Cd1-O5^{ii}	147.87(12)	N2^{iii}-Cd1-O2^{i}	85.43(13)
O1-Cd1-O6^{ii}	92.91(12)	N2^{iii}-Cd1-O5^{ii}	89.41(13)
O1-Cd1-N2^{iii}	97.49(14)	N2^{iii}-Cd1-O6^{ii}	97.35(14)
O1-Cd1-N1	90.74(15)	N2^{iii}-Cd1-N1	169.13(13)
O2^{i}-Cd1-O5^{ii}	90.00(12)	N1-Cd1-O5^{ii}	87.33(13)
O2^{i}-Cd1-O6^{ii}	144.72(12)	N1-Cd1-O6^{ii}	89.27(14)
O2i-Cd1-N1	84.21(13)		

Symmetry codes: (i) *-1-x, 1-y, 2-z*; (ii) *+x, +y, 1+z*; (iii) *-1+x, 1+y, +z.*

3			
Co1-O1	1.999(3)	Co1-O6^{ii}	2.261(3)
Co1-O2^{i}	2.032(3)	Co1-N2^{iii}	2.160(3)
Co1-O5^{ii}	2.122(3)	Co1-N1	2.157(3)
O1-Co1-O2^{i}	112.87(13)	O2^{i}-Co1-N1	87.26(13)
O1-Co1-O5^{ii}	154.64(14)	O5^{ii}-Co1-O6^{ii}	59.81(12)
O1-Co1-O6^{ii}	94.87(12)	O5ii-Co1-N2^{iii}	89.62(12)

O1-Co1-N2^{iii}	94.33(13)	O5^{ii}-Co1-N1	87.93(13)
O1-Co1-N1	90.30(13)	N2^{iii}-Co1-O6^{ii}	94.97(13)
O2^{i}-Co1-O5^{ii}	92.31(13)	N1-Co1-O6^{ii}	88.71(13)
O2^{i}-Co1-O6^{ii}	151.97(12)	N1-Co1-N2^{iii}	173.81(14)
O2^{i}-Co1-N2^{iii}	87.16(13)		

Symmetry codes: (i) *-1-x, 1-y, 2-z*; (ii) *+x, +y, 1+z*; (iii) *-1+x, 1+y, +z.*

Table S4. The hydrogen-bonding geometry (Å, °) of MOFs **1**-**3**.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<D-H···A
		1		
C41-H41···O1^{i}	0.931	2.645	3.329	130.78
C16-H16···O5^{ii}	0.931	2.678	3.401	135.18
C10···H10B···O1^{iii}	0.971	2.691	3.351	125.69
C5-H5···O2^{iv}	0.93	2.678	3.309	125.72
C1-H1···O4^{v}	0.931	2.702	3.28	121.09
Symmetry codes: (i) *x, 2+y, z+1*; (ii) *2-x, -y, 1-z*; (iii) *3-x, 2-y, 2-z*; (iv) *x, 1+y, z*; (v) *x, 2+y, z+1*				
		2		
C5-H5···O5^{i}	0.931	2.452	3.130	129.84
C41-H41···O9^{ii}	0.929	2.685	3.238	129.09
Symmetry codes: (i) *1+x, -1+y, z+1*; (ii) *-1-x, -y, 2-z*				
		3		
C41-H41···O2^{i}	0.929	2.713	3.615	163.94
C5-H5···O5^{ii}	0.930	2.299	2.943	125.93
Symmetry codes: (i) *-x, -y, 2-z*; (ii) *1+x, -1+y, 1+z*				

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