Supporting Information

Synthesis and Catalytic Activities of a Zn(II) Based Metallomacrocycle and a Metal-Organic Framework towards One-pot Deacetalization–Knoevenagel Tandem Reactions under Different Strategies: A Comparative Study

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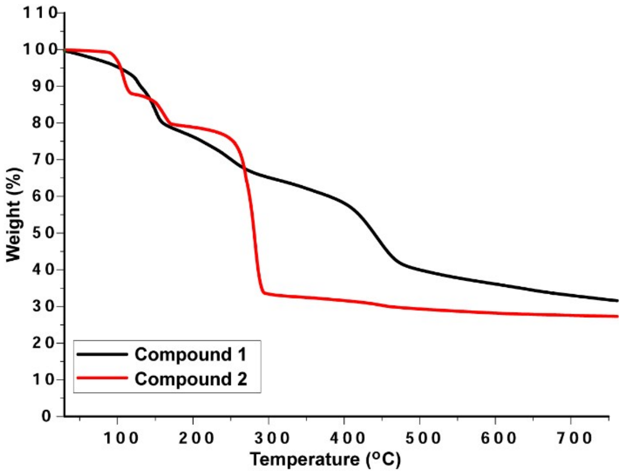


Figure S1 Thermogravimetric curves of compounds **1** and **2**.

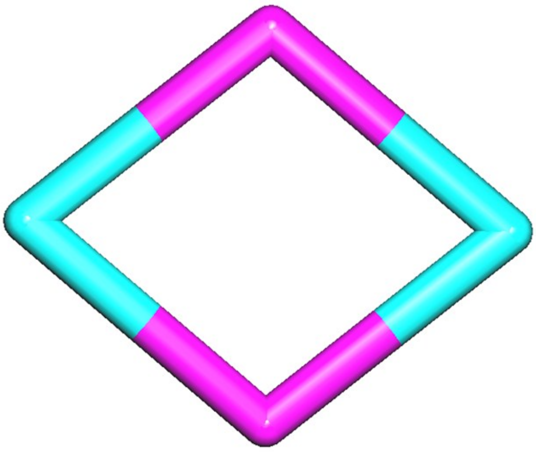


Figure S2 Topological representation of compound **1** (the metal nodes are represented in pink and the linker L^{2-} in cyan color).

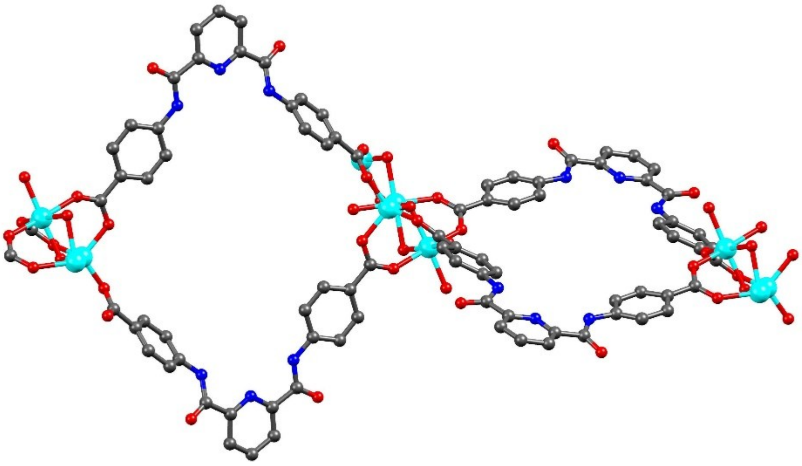
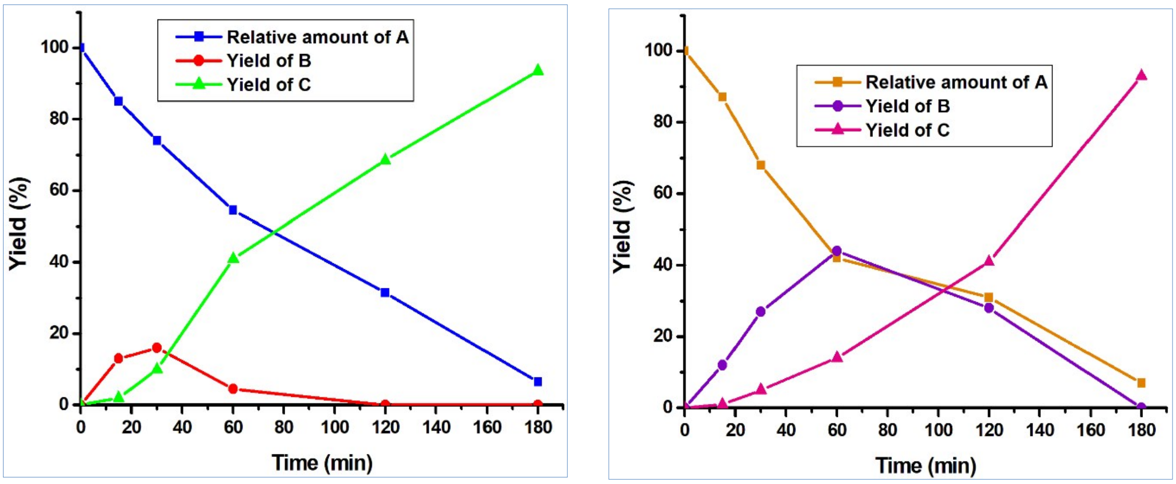


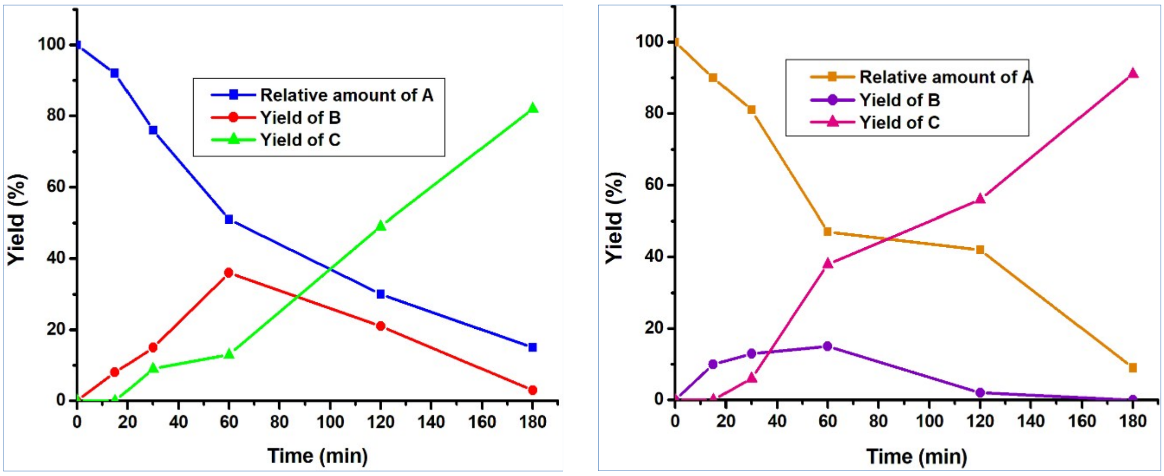
Figure S3 Interlink between two metallomacrocylic units of framework **2**.



A

B

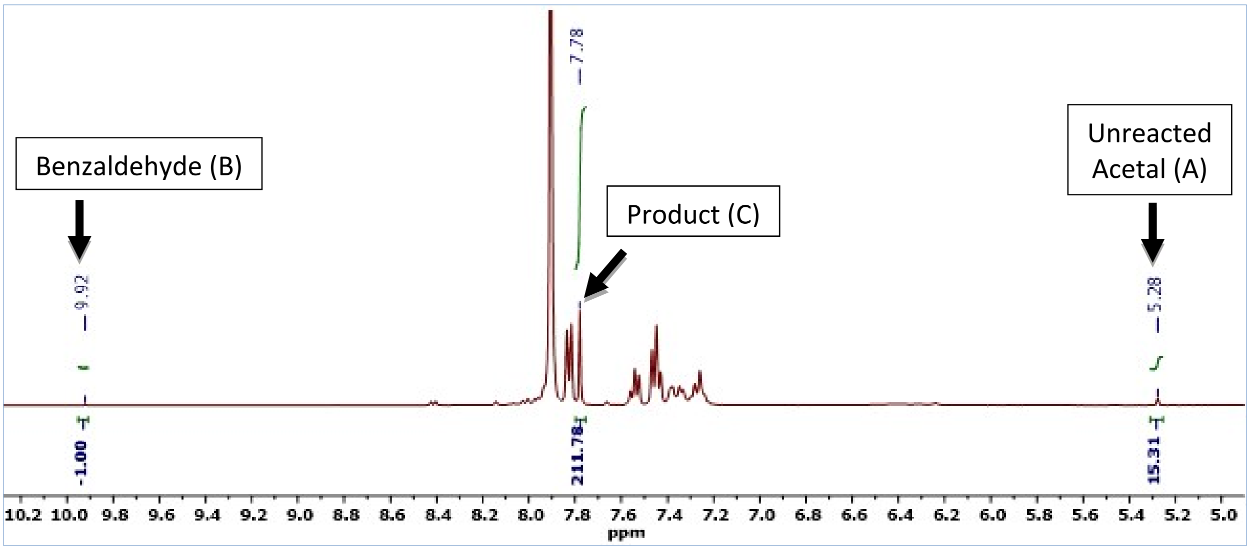
Figure S4 Plot of yield vs. time for the one-pot tandem deacetalization-Knoevenagel condensation reactions catalysed by compound **1** (A) [blue line: yield of unreacted benzaldehyde dimethyl acetal (**A**); red line: yield of intermediate benzaldehyde (**B**); green line: yield of 2-benzylidenemalononitrile (**C**)] and framework **2** (B) [dark yellow line: yield of unreacted benzaldehyde dimethyl acetal (**A**); purple line: yield of intermediate benzaldehyde (**B**); pink line: yield of 2-benzylidenemalononitrile (**C**)] under normal heating condition.



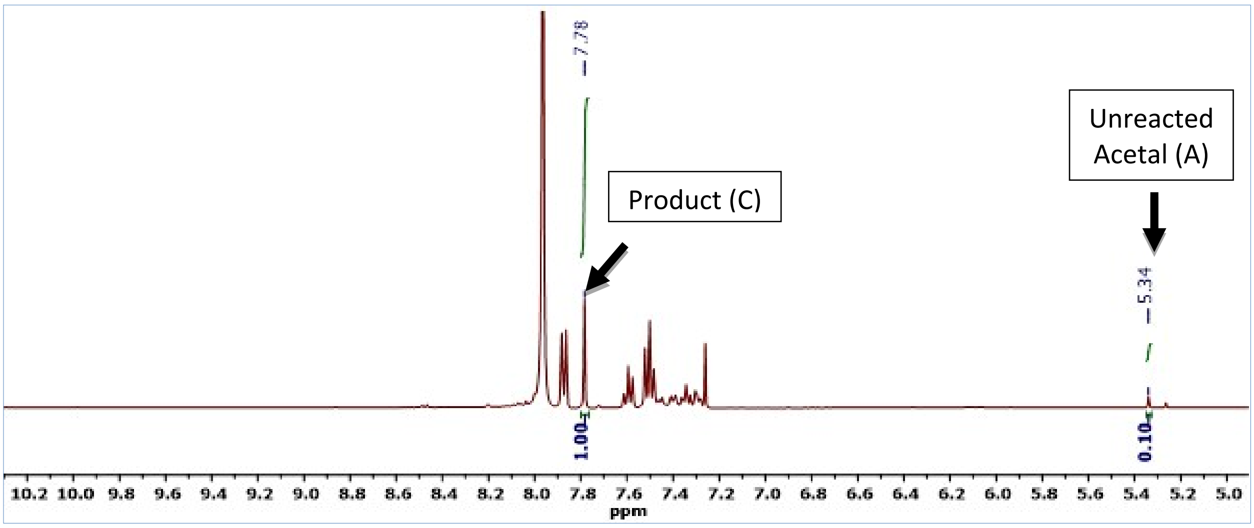
A

B

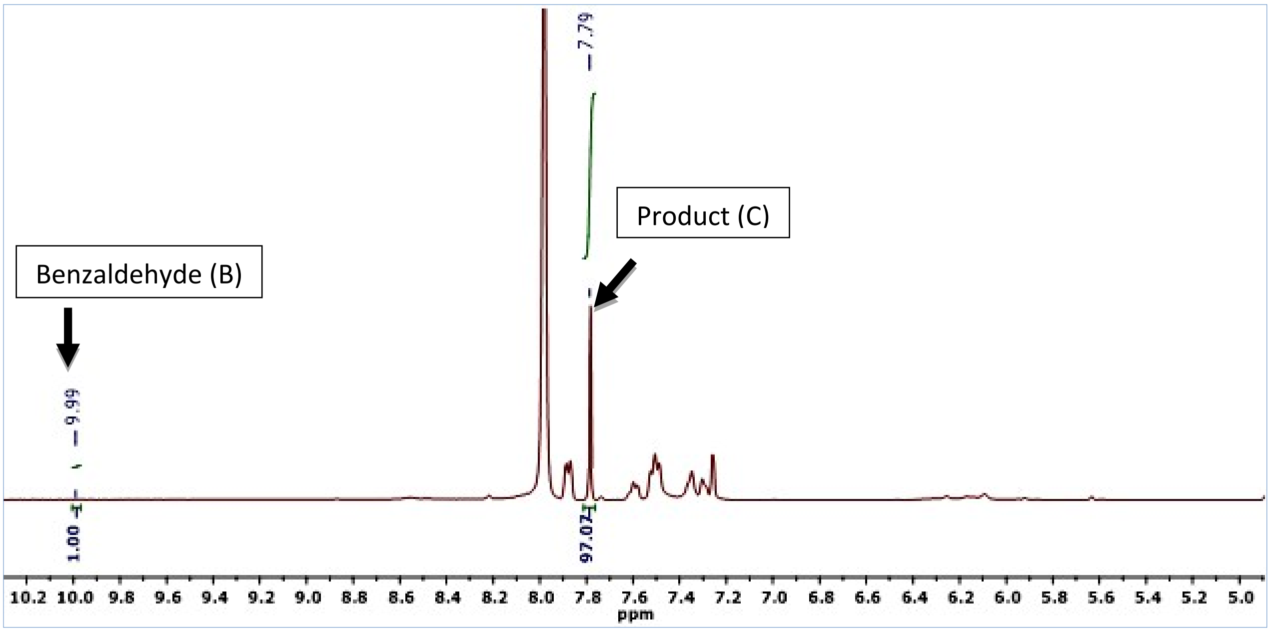
Figure S5 Plot of yield vs. time for the one-pot tandem deacetalization-Knoevenagel condensation reactions catalysed by compound **1** (A) [blue line: yield of unreacted benzaldehyde dimethyl acetal (**A**); red line: yield of intermediate benzaldehyde (**B**); green line: yield of 2-benzylidenemalononitrile (**C**)] and framework **2** (B) [dark yellow line: yield of unreacted benzaldehyde dimethyl acetal (**A**); purple line: yield of intermediate benzaldehyde (**B**); pink line: yield of 2-benzylidenemalononitrile (**C**)] under microwave irradiation condition.



A

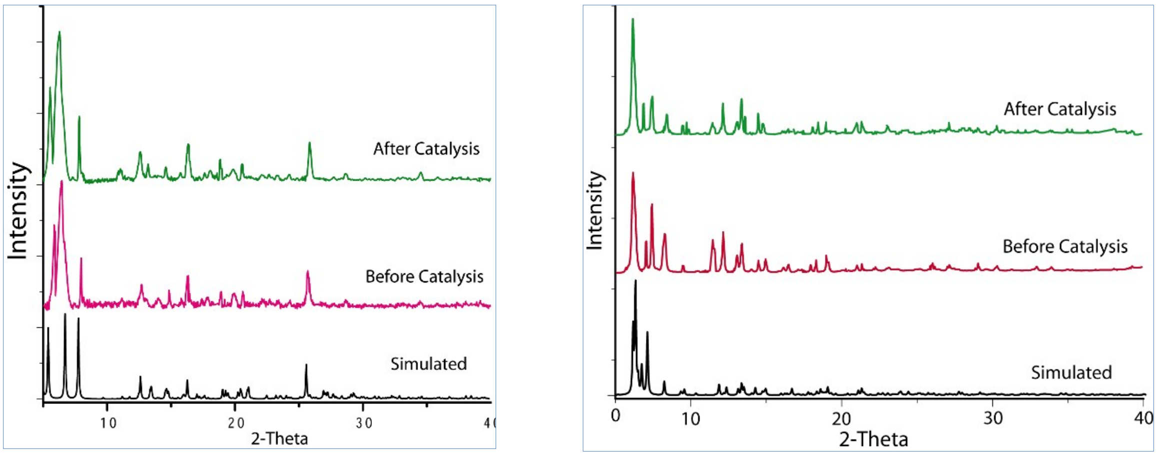


B



C

Figure S6 Example of integration in the ^{1}H-NMR spectrum for the determination of the product yield in the one-pot tandem deacetalization−Knoevenagel condensation reactions catalysed by **1** and **2** under normal heating (A) [Table 1, entry 10], microwave irradiation (B) [Table 1, entry 20] and ultrasonic method (C) [Table 1, entry 25].



A B

Figure S7 Powder XRD diffractograms of **1** (A) and **2** (B) simulated (in black), as synthesized (in red) and after the tandem reactions under ultrasonic method (in green).

Catalytic optimization

Carrying out the tandem deacetalization-Knoevenagel condensation reactions under conventional heating in various solvents (DMF, CH_3CN, THF, MeOH and DMSO), shows that DMF (93.5% yield for **1** after 3h) is more adequate (entry 6, Table S1) and THF is the less suitable solvent (produced 46% of benzylidene malononitrile, entry 3, Table S1) for such a reaction. The use of MeOH leads to a moderate yield (79%) of the final product (entry 1, Table S1), being followed by EtOH (64%) and CH_3CN (68%). In DMSO the product yield (88%) is higher than in MeOH, but lower than in DMF. We have also observed similar solvent trends upon optimizing the reaction under microwave and ultrasonic irradiations. Thus, DMF turns out to be the best solvent (84-99.5% yield benzylidene malononitrile were obtained) for the tandem deacetalization-Knoevenagel condensation reactions under different reaction methods.

To test the effect of temperature we have carried out the reaction at the temperatures of 30 ^{o}C, 50 ^{o}C, 80 ^{o}C and 100 ^{o}C. At 30 ^{o}C, we have obtained 34% [under conventional heating (HT), entry 7, Table S1], 51% [under microwave irradiation (MW), entry 6, Table S2] and 62% [under ultrasonic irradiation (US), entry 6, Table S3] of benzylidene malononitrile after 3 h of reaction time using **1** as catalyst. However, increasing the reaction temperature to 80 ^{o}C results into a 93.5% (for HT), 84% (for MW) and 99.5% (for US) yield of benzylidene malononitrile (entry 6, Table S1; entry 1, Table S2; entry 2, Table S3, respectively). Further increasing the temperature to 100 ˚C has a negative effect on the yield in every process (entry 9, Table S1; entry 8, Table S2; and entry 8, Table S3).

In order to estimate the optimum catalyst amount, we have used 0.5, 1.0, 2.0 and 5.0 mol% of catalyst under the abovementioned experimental conditions. For 0.5 mol% of catalyst **1** at 80˚C in DMF, we obtain 87% of 2-benzylidenemalononitrile under conventional heating (entry 10, Table S1), whereas under MW and US conditions, 75% (entry 9, Table S2) and 91% (entry 9, Table S3) yields were obtained, respectively. Increasing the catalyst amount to 1 mol% resulted in a further yield increase until 93.5% (for HT), 84% (for MW) and 99.5% (for US). However, a further rise in the catalyst amount to 2 or 5 mol % did not improve the product yield further, demonstrating that 1 mol% of catalyst loading is the best fit for the reaction.

We have also performed blank tests without any metal catalyst, and only 19-29% of 2-benzylidenemalononitrile was formed in DMF at 80 °C after 3 h, under HT, MW and US methods (entry 12, Table S1; entry 12, Table S2; entry 12, Table S3). On the other hand, using the H_2L pro-ligand as catalyst leads to the conversions of 20-32% (entry 15 in Tables S1, S2 and S3). The product yield increases slightly (24-41%) using the metal salt $Zn(NO_3)_2.6H_2O$ or a mixture of $Zn(NO_3)_2.6H_2O$ and H_2L (entries 13 and 14, respectively, Tables S1, S2 and S3).

Table S1: Optimization of the one-pot deacetalization−Knoevenagel condensation reactions between benzaldehyde dimethyl acetal and malononitrile with **1** as the catalyst performed under conventional heating conditions[a]

Entry	Catalyst	Time (min)	Amount of Catalyst (mol%)	*T* (˚C)	Solvent	Yield of benzylidene malononitrile (%)[b]
Different Solvents						
1	**1**	180	1	80	MeOH	79
2	**1**	180	1	80	EtOH	64
3	**1**	180	1	80	THF	46
4	**1**	180	1	80	CH_3CN	68
5	**1**	180	1	80	DMSO	88
6	**1**	180	1	80	DMF	93.5
Different Temperatures						
7	**1**	180	1	30	DMF	34
8	**1**	180	1	50	DMF	70
9	**1**	180	1	100	DMF	91
Catalyst Amount						
10	**1**	180	0.5	80	DMF	87
11	**1**	180	2	80	DMF	93
	1	180	5	80	DMF	92
12	Blank	180	-	80	DMF	25
13	$Zn(NO_3)_2.6H_2O$	180	1	80	DMF	35
14	$Zn(NO_3)_2.6H_2O$ + H_2L	180	1	80	DMF	26

15	H_2L	180	1	80	DMF	28

[a] <u>Reaction conditions under **conventional heating**</u>: 1 mol% of catalyst **1** or **2**, DMF (0.5 mL), benzaldehyde dimethyl acetal (152 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol), 80^{o}C. [b]Calculated by ^{1}H NMR analysis.

Table S2: Optimization of the one-pot deacetalization–Knoevenagel condensation reactions between benzaldehyde dimethyl acetal and malononitrile with **1** as the catalyst performed under microwave irradiation[a]

Entry	Catalyst	Time (min)	Amount of Catalyst (mol%)	*T* (˚C)	Solvent	Yield of benzylidene malononitrile (%)[b]
Different Solvents						
1	**1**	180	1	80	DMF	84
2	**1**	180	1	80	MeOH	63
3	**1**	180	1	80	THF	39
4	**1**	180	1	80	CH_3CN	44
5	**1**	180	1	80	DMSO	80
Different Temperatures						
6	**1**	180	1	30	DMF	51
7	**1**	180	1	50	DMF	67
8	**1**	180	1	100	DMF	78
Catalyst Amount						
9	**1**	180	0.5	80	DMF	75
10	**1**	180	2	80	DMF	81
11	**1**	180	5	80	DMF	82
12	Blank	180	-	80	DMF	19
13	$Zn(NO_3)_2.6H_2O$	180	1	80	DMF	25
14	$Zn(NO_3)_2.6H_2O$ + H_2L	180	1	80	DMF	24
15	H_2L	180	1	80	DMF	20

[a]<u>Reaction conditions under **microwave irradiation**</u>: 1 mol% of catalyst **1** or **2**, DMF (0.5 mL), benzaldehyde dimethyl acetal (152 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol), MW (initial power (25 W), 80 ^{o}C (15 W). [b]Calculated by ^{1}H NMR analysis.

Table S3: Optimization of the one-pot deacetalization–Knoevenagel condensation reactions between benzaldehyde dimethyl acetal and malononitrile with **1** as the catalyst performed under ultrasonic irradiation[a]

Entry	Catalyst	Time (min)	Amount of Catalyst (mol%)	*T* (˚C)	Solvent	Yield of benzylidene malononitrile (%)[b]
Different Solvents						
1	**1**	180	1	80	MeOH	77
2	**1**	180	1	80	DMF	99.5
3	**1**	180	1	80	THF	58
4	**1**	180	1	80	CH_3CN	65
5	**1**	180	1	80	DMSO	90
Different Temperatures						
6	**1**	180	1	30	DMF	62
7	**1**	180	1	50	DMF	77
8	**1**	180	1	100	DMF	98
Catalyst Amount						
9	**1**	180	0.5	80	DMF	91

10	**1**	180	2	80	DMF	98
11	**1**	180	5	80	DMF	99
12	Blank	180	-	80	DMF	29
13	$Zn(NO_3)_2.6H_2O$	180	1	80	DMF	32
14	$Zn(NO_3)_2.6H_2O$ + H_2L	180	1	80	DMF	41
15	H_2L	180	1	80	DMF	32

[a] Reaction conditions under **ultrasonic irradiation**: 1 mol% of catalyst **1** or **2**, DMF (0.5 mL), benzaldehyde dimethyl acetal (152 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol), US (80 ^{o}C, 50/60 Hz). [b]Calculated by ^{1}H NMR analysis.

Table S4: A comparison of catalytic activity of various MOFs in the one-pot deacetalization-Knoevenagel condensation reactions

Entry	Catalyst	Solvent/Temp/Time/catalyst amount	Reaction condition	Yield (%)	Reference
1	**1**	DMF/80^{o}C/2h/1 mol%	Ultrasonic	99	This work
2	**2**	DMF/80^{o}C/2h/1 mol%	Ultrasonic	98	This work
3	**1**	DMF/80^{o}C/3h/1 mol%	Heating	93.5	This work
4	**2**	DMF/80^{o}C/3h/1 mol%	Heating	93	This work
5	$[Zn_4(TBCB).(H_2O)_6]_n.5n(DMAc)$	1,4-Dioxane/90^{o}C/4h/6 mol%	Heating	99	42
6	$[Zn_2(L')(H_2O)_4]_n.4n(H_2O)$	DMF/75^{o}C/3h/1 mol%	Heating	99	43
7	$[Cd_3(HL')_2(DMF)_4\}_n.4n(DMF)$	DMF/75^{o}C/3h/1 mol%	Heating	57	43
8	$[Cd_3(SIPA)_2(ABPY)_3(DMF)_2]_n.(BPDB).(DMF)_2$	DMF/80^{o}C/5h/0.5 mol%	Heating	95	38
9	Cu-PCN-124	DMSO/50^{o}C/12h/0.5 mol%	Heating	99	40
10	MIL-101(Al)-NH_2	1,4-Dioxane/90^{o}C/3h/3 mol%	Heating	94	41
11	Cu-HNUST-8	DMSO/50^{o}C/48h/0.5 mol%	Heating	99	37

TBCB= 2,2’,6,6’-tetrakis[3,5-bis-3,5-benzenedicarboxylate]benzidine; L’= 5,5'-{(pyridine-2,6-dicarbonyl)bis(azanediyl)}diisophthalate; SIPA= 5-sulfoisopthalate; ABPY= 4,4’-azopyridine; BPDB= 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene; DMAc= N,N-dimethylacetamide; DMF= N,N’-dimethyl formamide; Cu-PCN-124= 3D Cu(II)- 5,5’-((pyridine-3,5-dicarbonyl)bis (azanediyl))diisophthalate framework; MIL-101(Al)-NH_2= 3D Al-2-amino terephthalate MOF; Cu-HNUST-8= 3D Cu(II)- 4',4'''-{(pyridine-3,5-dicarbonyl)bis(azanediyl))bis(([1,1'-biphenyl]-3,5 dicarboxylate} framework.

Table S5: Crystal data and structure refinement details for compounds 1-2

Identification name	**1**	**2**
Formulae	$C_{60}H_{84}N_{12}O_{26}Zn_2$	$C_{108}H_{126}N_{20}O_{42}Zn_5$
Mol. wt.	1520.13	2703.13
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Temperature /K	296	296
Wavelength /Å	0.71073	0.71073
a /Å	7.0336(6)	15.6267(16)
b /Å	16.5823(15)	15.6542(15)
c /Å	18.4251(15)	19.1920(17)
α/°	81.687(3)	111.050(3)

β/°	89.129(2)	99.873(3)
γ/°	85.846(3)	106.170(4)
V/ Å^3	2120.8(3)	4010.5(7)
Z	1	1
Density/Mgm^{-3}	1.190	1.119
Abs. Coeff. /mm^{-1}	0.639	0.807
F(000)	796	1400
Refl. collected	30461	23444
Refl. unique	7766	12255
Max. 2θ/°	25.499	23.999
Ranges (h, k, l)	-8<= h <=8 -19 <= k <=20 -22<= l <= 22	-17<= h <=17 -17<= k <=17 -21<= l <= 21
Complete to 2θ (%)	99.0	97.4
Refl. with I > 2σ(I)	6642	9355
Data/Restraints/Parameters	7766/28/495	12255/30/790
Goof (F^2)	1.056	1.124
R1 [I > 2s(I)]	0.0799	0.0888
wR2 [I > 2s(I)]	0.2076	0.1024
R1 [all data]	0.0908	0.2612
wR2 [all data]	0.2149	0.2751

Table S6: Hydrogen bond geometry (Å, °) in compounds 1-2

Compound	D-H···A	D···H (Å)	H···A (Å)	D···A (Å)	<D−H···A(°)
1	O12-H12B···O2	0.92	2.14	3.009(6)	157
	O12-H12A···O8	0.92	2.14	3.044(6)	169
	N1-H1N···O9	0.96	1.94	2.888(6)	169
	N3-H3N···O9	0.86	2.17	2.993(6)	161
	O11-H11B···O6	0.90	2.06	2.835(6)	145
	O11-H11A···O10	0.90	1.78	2.666(6)	166
	O10-H10B···O6	0.90	1.96	2.789(6)	152
	O10-H10A···O7	0.90	1.86	2.730(6)	162
	O13-H13A···O2	0.91	2.15	2.995(6)	154
	O13-H13B···O11	0.90	2.50	2.960(6)	115
	C20-H20···O9	0.93	2.57	3.272(6)	133
	C4-H4···O9	0.93	2.55	3.214(6)	129
	C25-H25···O3	0.93	2.38	3.307(7)	175
2	N6-H6N···N5	0.86	2.28	2.707(7)	111
	N6-H6N···O21	0.86	2.46	3.217(7)	147
	N3-H3N···O17	0.86	2.11	2.910(7)	155
	N4-H4N···O21	0.86	2.22	3.040(7)	160
	N1-H1N···N2	0.86	2.25	2.666(7)	110
	N1-H1N···O17	0.86	2.23	2.974(7)	145
	O13-H13A···O16	0.88	1.91	2.795(6)	178
	O15-H15A···O9	0.91	1.94	2.844(6)	177

	O15-H15B···O22	0.87	1.95	2.820(9)	178
	O21-H21A···O3	0.89	2.16	3.045(7)	177
	O21-H21B···O19	0.92	1.81	2.726(12)	178
	O14-H14A···O8	0.92	1.75	2.665(6)	178
	O14-H14B···O18	0.88	1.80	2.674(6)	178
	O22-H22A···O18	0.90	1.98	2.872(10)	179
	C4-H4···O3	0.93	2.34	2.925(7)	120
	C16-H16···O4	0.93	2.42	2.903(8)	112
	C12-H12···O12	0.93	2.65	3.214(7)	119
	C37-H37···O10	0.93	2.23	2.839(8)	123
	C45-H45···O1	0.93	2.59	3.194(10)	123
	C45-H45···O5	0.93	2.52	3.264(10)	138
	C48-H48C···O10	0.96	2.58	3.192(14)	122

Table S7: Selected bond distances (Å) and angles (°) for compounds 1-2	
1	Zn01-O5, 1.963(3); Zn01-O1, 1.964(3); Zn01-O13, 2.005(5); Zn01-O12, 2.014(4). <O5-Zn01-O1, 97.17(15); <O5-Zn01-O13, 115.75(17); <O1-Zn01-O13, 111.43(18); <O5-Zn01 -O12, 112.33(17); <O1-Zn01-O12, 110.74(17); <O13-Zn01-O12, 108.98(18).
2	Zn1-O13, 2.042(4); Zn1-O2, 2.083(4); Zn1-O14, 2.191(4); Zn1-Zn2, 3.1041(7); Zn2-O1, 2.054(4); Zn2-O5, 2.060(4); Zn2-O15, 2.069(4); Zn2-O11, 2.083(4); Zn2-O13, 2.097(4); Zn2-O14, 2.227(4); Zn3-O13, 1.926(4); Zn3-O7, 1.938(4); Zn3-O12, 1.963(4); Zn3-O6, 1.993(4). <O13-Zn1-O13, 180.0; <O13-Zn1-O2 89.40(15); <O13-Zn1-O2 90.60(15); <O13-Zn1-O2 90.60(15); <O13-Zn1-O2 89.40(15); <O2-Zn1-O2 180.0; <O13-Zn1-O14 86.19(15); <O13-Zn1 -O14 93.81(15); <O2-Zn1-O14 86.74(15); <O2-Zn1-O14 93.27(15); <O13-Zn1-O14 93.81(15); <O13-Zn1-O14 86.19(15); <O2-Zn1-O14 93.27(15); <O2-Zn1-O14 86.73(15); <O14 -Zn1-O14 180.00(19); <O13-Zn1-Zn2 42.09(10); <O13-Zn1-Zn2 137.91(10); <O2-Zn1-Zn2 77.72(11); <O2-Zn1-Zn2 102.28(11); <O14-Zn1-Zn2 45.84(11); <O14-Zn1-Zn2 134.16(11); <O13-Zn1 -Zn2 137.91(10); <O13-Zn-Zn2 42.09(10); <O2-Zn1-Zn2 102.28(11); <O2-Zn1-Zn2 77.72(11); <O14-Zn1-Zn2 134.16(11); <O14-Zn1-Zn2 45.84(11); <Zn2-Zn1-Zn2 180.0; <O1-Zn2-O5 96.38(16); <O1-Zn2-O15 91.25(16); <O5-Zn2-O15 91.05(18); <O1-Zn2-O11 169.49(17); <O5-Zn2-O11 93.46(17); <O15-Zn2-O11 84.89(16); <O1-Zn2-O13 89.53(15); <O5-Zn2-O13 91.32(16); <O15-Zn2-O13 177.41(16); <O11-Zn2-O13 93.92(15); <O1-Zn2-O14 87.53(15); <O5-Zn2-O14 173.86(15); <O15-Zn2-O14 93.61(17); <O11-Zn2-O14 82.97(16); <O13-Zn2-O14 83.96(15); <O1-Zn2-Zn1 78.76(11); <O5-Zn2-Zn1 131.24(12); <O15-Zn2-Zn1 137.09(13); <O11-Zn2-Zn1 97.45(12); <O13-Zn2-Zn1 40.75(10); <O14-Zn2-Zn1 44.88(10); <O13-Zn3-O7 126.33(17); <O13-Zn3-O12 113.22(16); <O7-Zn3-O12 103.15(17); <O13-Zn3-O6 104.83(16); <O7-Zn3-O6 106.51(18); <O12-Zn3-O6 99.53(18); <Zn3-O13-Zn1 129.37(18); <Zn3-O13-Zn2 104.52(17); <Zn1-O13-Zn2 97.15(15); <Zn1-O14-Zn2 89.28(14).