

## Supporting Information

### **Polyaromatic Carboxylate Ligands Based Zn(II) Coordination Polymers for Ultrasound-assisted One-pot Tandem Deacetalization – Knoevenagel Reactions**

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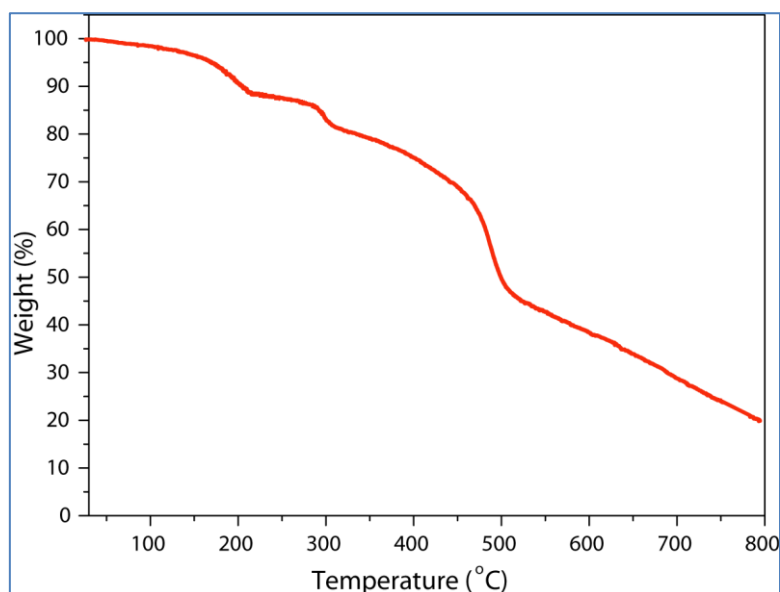


Figure S1 Thermogravimetric analysis curve for CP 1.

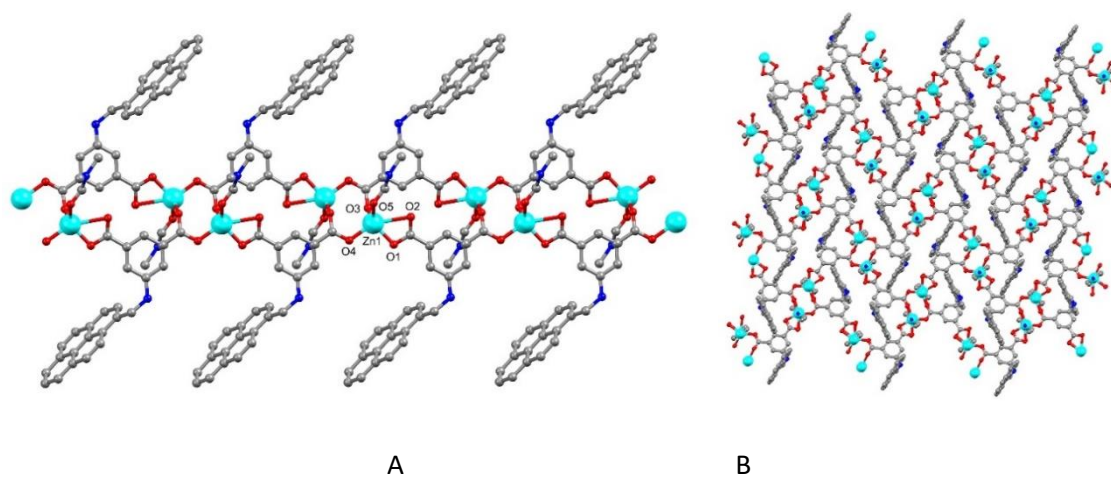


Figure S2 One-dimensional structure of CP 2 (A) and three-dimensional structure of CP 3 (B).

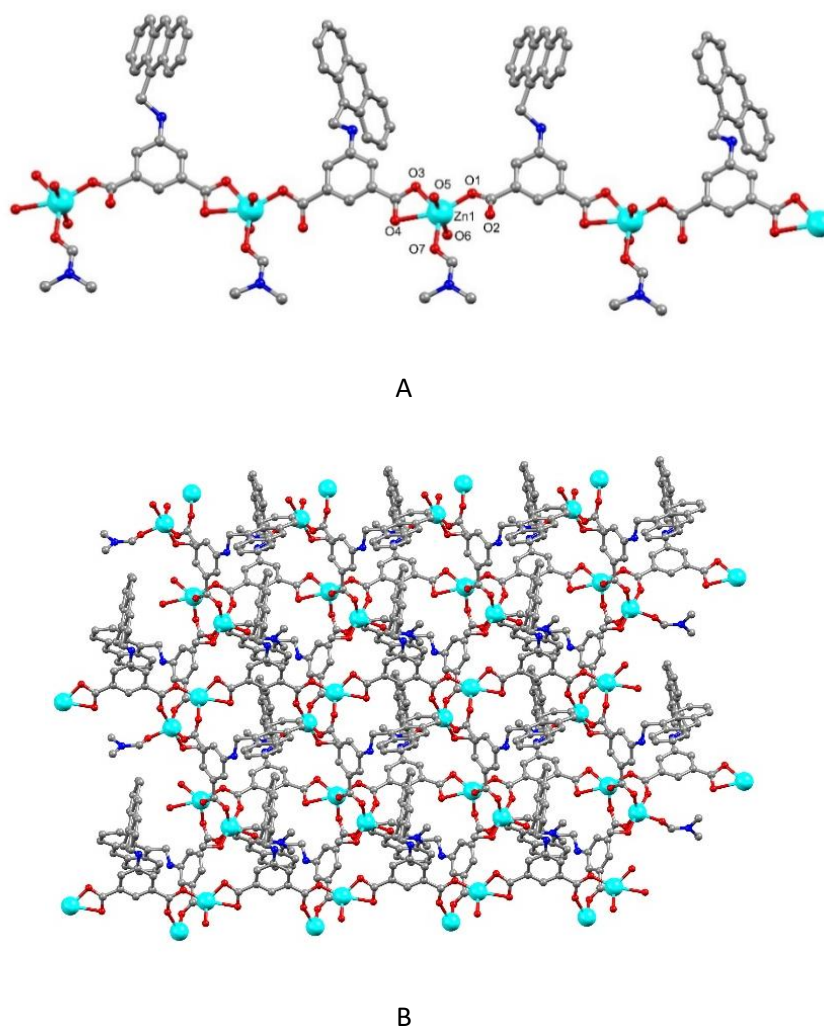


Figure S3 Crystal structures of one-dimensional CP 4 (A) and two-dimensional CP 5 (B).

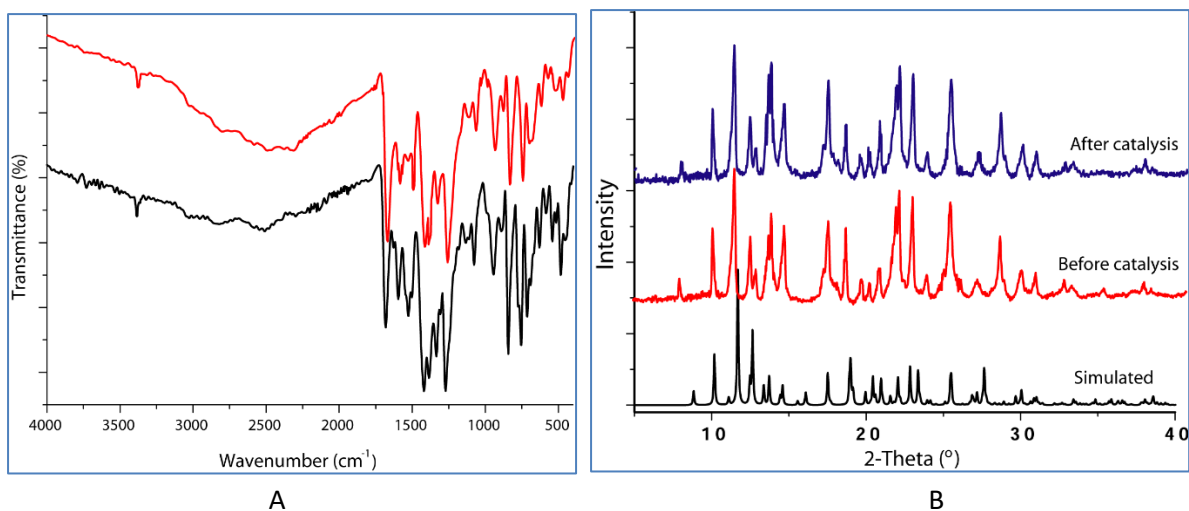


Figure S4 FT-IR spectra (A) and PXRD diffractograms (B) of catalyst CP **1** before and after the 4<sup>th</sup> recycling in tandem deacetalization–knoevenagel reactions.

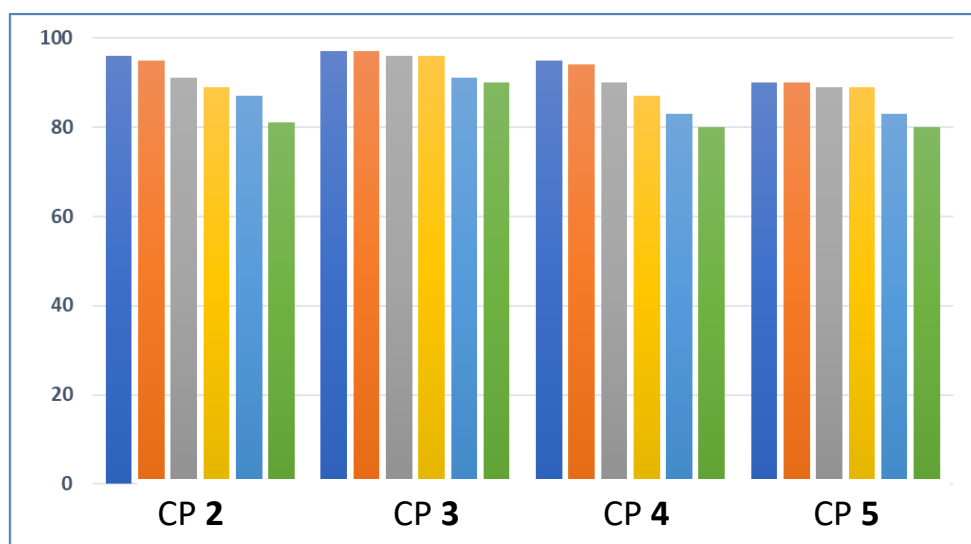
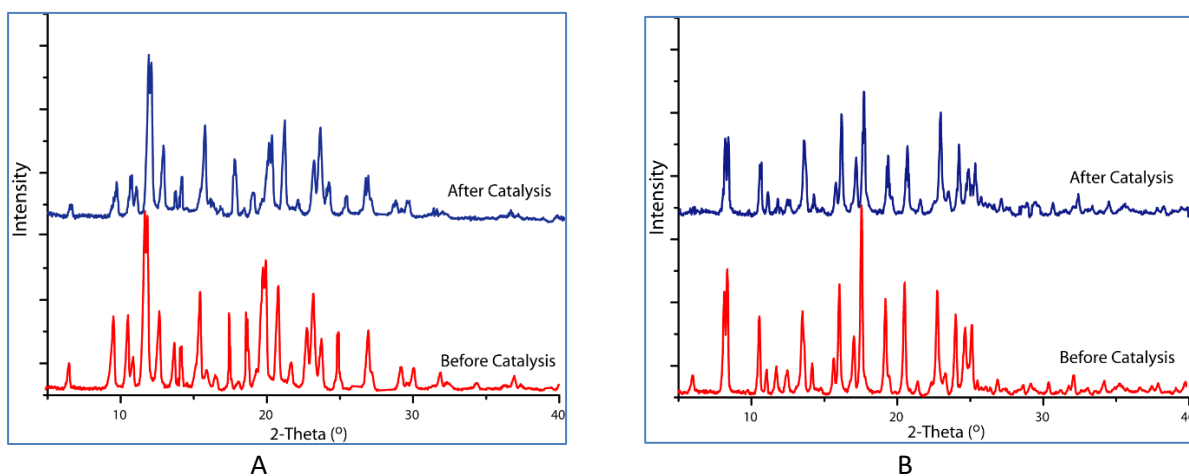


Figure S5 Yield of 2-benzylidenemalononitrile (**D**) upon catalyst recycling for the deacetalization–Knoevenagel reactions catalyzed by CPs **2-5**.



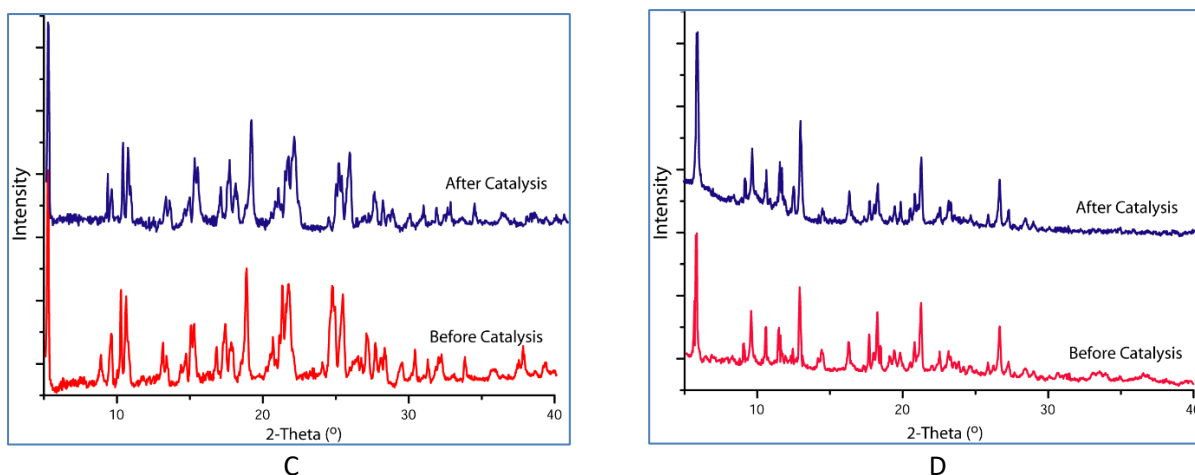


Figure S6 PXRD diffractograms of catalyst CP 2 (A), CP 3 (B), CP 4 (C) and CP 5 (D) before and after the recycling in tandem deacetalization–knoevenagel reactions.

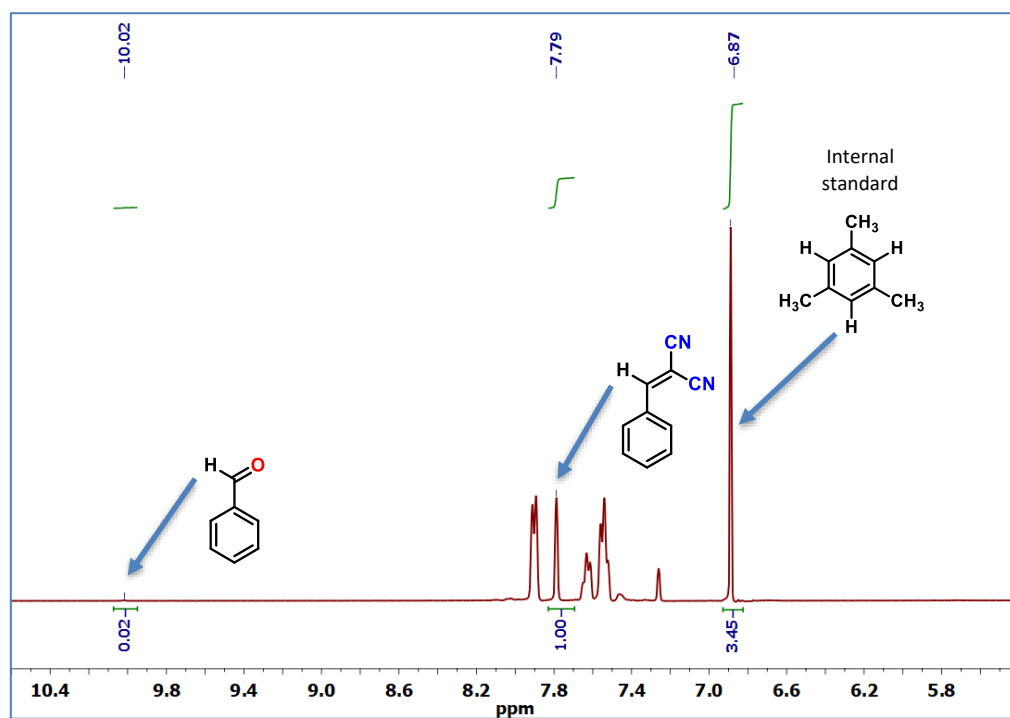


Figure S7  $^1\text{H}$ -NMR spectra of ultrasonic assisted one-pot tandem deacetalization–Knoevenagel reactions of benzaldehyde dimethyl acetal with catalyst CP 1 in  $\text{CDCl}_3$  (entry 1, Table 1) (The protons that are considered in the integrations are indicated in black colour).

#### Reaction yield calculation details from NMR:

In order to calculate the % of yield from  $^1\text{H}$ -NMR spectroscopy, at first, the molar amount of product (P) was calculated from the molar amount of internal standard (IS) and the molar ratio, where the following formula have been utilized to carry out the calculations.

Molar ratio of P:IS,  $r_{P/IS} = (\text{integral}_P/N_P)/(\text{integral}_{IS}/N_{IS})$  where  $N$  = number of nuclei present for the corresponding peaks.

Molar amount of P,  $n_P = n_{IS} \times r_{P/IS}$

NMR yield (in %) =  $(n_P \times 100)/(\text{maximum mmols of P})$

**For CP 1:**

$r_{P/IS} = (1.00/1)/(3.45/3) = 0.87$  [ $N_P = 1$  proton from P at 7.79 ppm;  $N_{IS} = 3$  protons from IS at 6.87 ppm]

Molar amount of internal standard (IS),  $n_{IS} : 1.14$  mmol

Molar amount of product (P),  $n_P = n_{IS} \times r_{P/IS} = 1.14 \times 0.87 = 0.991$  mmol

NMR yield (in %) =  $(n_P \times 100)/(\text{maximum mmols of product}) = (0.991 \times 100)/1.0 = 99.1\%$

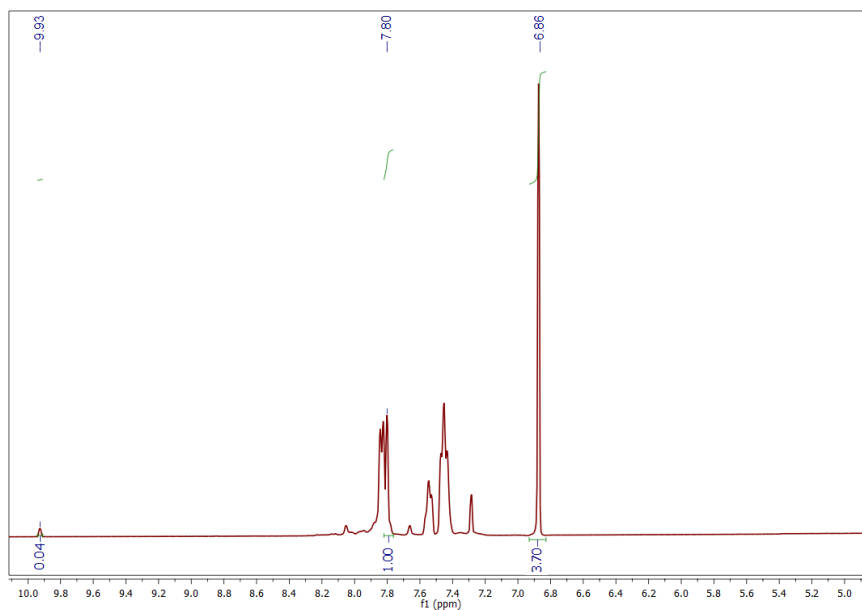


Figure S8  $^1\text{H}$ -NMR spectra of ultrasonic assisted one-pot tandem deacetalization–Knoevenagel reactions of benzaldehyde dimethyl acetal with catalyst CP 2 in  $\text{CDCl}_3$  (entry 2, Table 1).

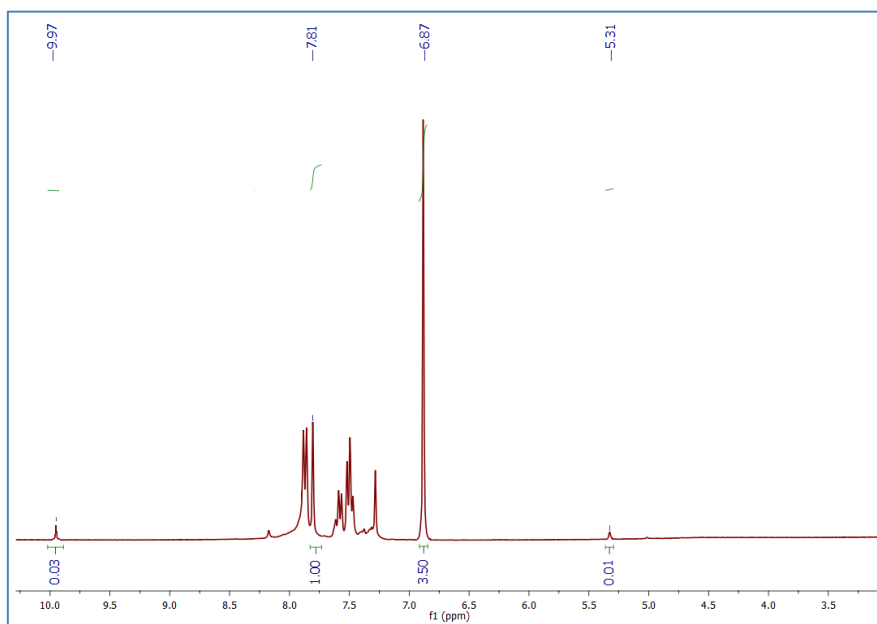


Figure S9  $^1\text{H}$ -NMR spectra of ultrasonic assisted one-pot tandem deacetalization–Knoevenagel reactions of benzaldehyde dimethyl acetal with catalyst CP **3** in  $\text{CDCl}_3$  (entry 3, Table 1).

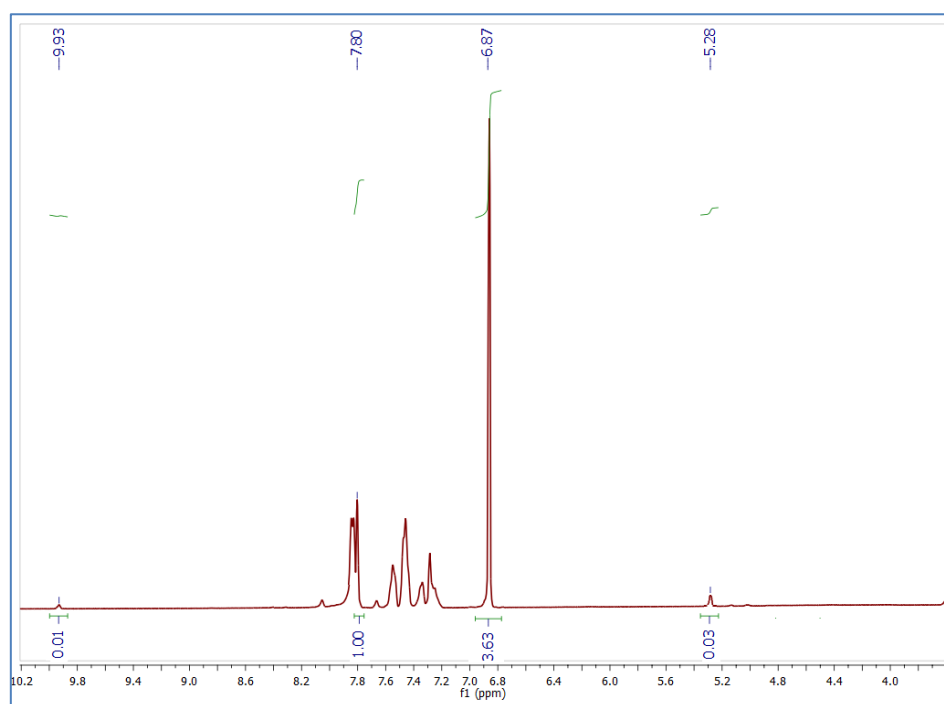


Figure S10  $^1\text{H}$ -NMR spectra of ultrasonic assisted one-pot tandem deacetalization–Knoevenagel reactions of benzaldehyde dimethyl acetal with catalyst CP **4** in  $\text{CDCl}_3$  (entry 4, Table 1).

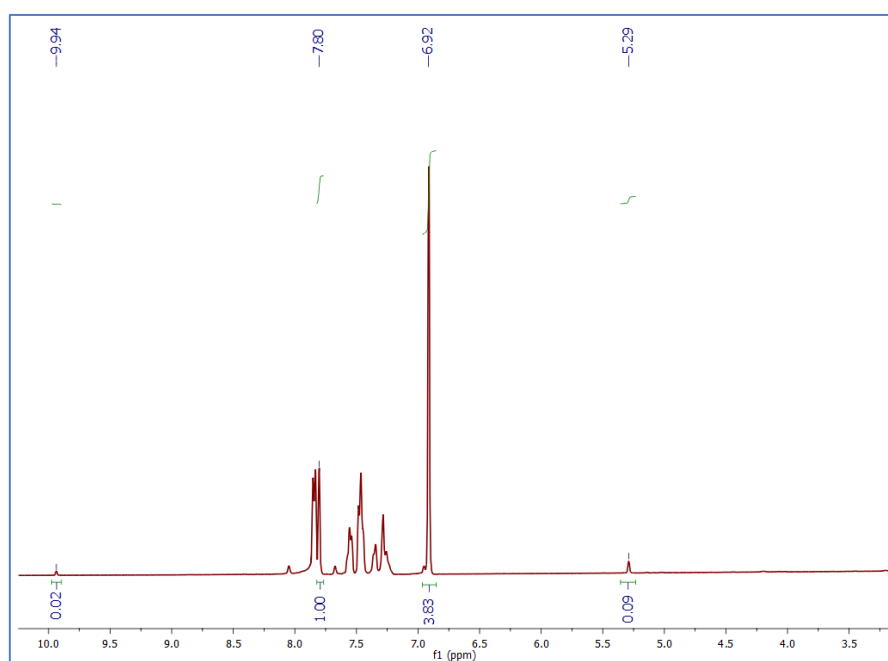


Figure S11  $^1\text{H}$ -NMR spectra of ultrasonic assisted one-pot tandem deacetalization–Knoevenagel reactions of benzaldehyde dimethyl acetal with catalyst CP **5** in  $\text{CDCl}_3$  (entry 5, Table 1).

## Crystal structure determination

X-ray quality single crystals of the CP **1** was immersed in cryo-oil, mounted in a nylon loop and measured at room temperature. Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-K $\alpha$  ( $\lambda$  0.71069) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART [29] software and refined using Bruker SAINT [29] on all the observed reflections. Absorption corrections were applied using SADABS [30]. Structures were solved by direct methods by using the SIR 97 program and refined with SHELXL-2014/6 [31]. Calculations were performed using the WinGX System-Version 2014.1 [32]. The hydrogen atoms attached to carbon and nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation;  $U_{iso}(H)$  were defined as 1.2 $U_{eq}$  of the parent atoms for phenyl and 1.5 $U_{eq}$  of the parent atoms for the methyl groups and nitrogen atoms. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed. Crystallographic data are summarized in Table S1 (Supplementary Information file), selected bond distances and angles are presented in Table S2. CCDC 2146914 and 2120925-2120928 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table S1: Crystal data and structure refinement details for CP <b>1</b>	
Identification name	<b>1</b>
Formula	C <sub>27</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> Zn
M.W. / g·mol <sup>-1</sup>	517.82
Crystal System	Triclinic
Space Group	P-1
Temperature / K	296
Wavelength / Å	0.71073
a / Å	8.8111(7)
b / Å	10.1122(8)
c / Å	13.2829(10)
$\alpha$ / °	88.952(3)
$\beta$ / °	85.025(2)
$\gamma$ / °	81.586(3)

V / Å <sup>3</sup>	1166.33(16)
Z	2
Density / Mgm <sup>-3</sup>	1.474
Abs. Coeff. / mm <sup>-1</sup>	1.095
F(000)	532
Refl. collected	20109
Refl. unique	5383
Max. 2θ/°	27.644
Ranges (h, k, l)	-11<= h <=11 -12 <= k <=13 -16<= l <= 17
Complete to 2θ (%)	99.0
Refl. with I > 2σ(I)	4820
Data/Restraints/Parameters	5383/0/320
Goof (F <sup>2</sup> )	1.061
R1 [I > 2s(I)]	0.0492
wR2 [I > 2s(I)]	0.1599
R1 [all data]	0.0548
wR2 [all data]	0.1663

Table S2: Selected bond distances (Å) and angles (°) for compound 1	
1	<p>Zn1-O3 1.972(2), Zn1-O4 1.973(2), Zn1-O1 1.976(2), Zn1-O5 2.001(2).</p> <p>&lt;O3-Zn1-O4 107.50(9), &lt;O3-Zn1-O1 109.90(10), &lt;O4-Zn1-O1 99.87(10), &lt;O3-Zn1-O5 106.20(11), &lt;O4-Zn1-O5 105.26(11), &lt;O1-Zn1-O5 126.61(12).</p>

Table S3 The optimization parameters for deacetalization–Knoevenagel tandem reactions between benzaldehyde and malononitrile with CPs <b>1-5</b> as catalysts and under ultrasound irradiation. <sup>a</sup>								
Entry	Catalyst	Time (h)	Catalyst (mol%)	T (°C)	Solvent	Unreacted A (%) <sup>b</sup>	Yield of B (%) <sup>b</sup>	Yield of D (%) <sup>b</sup>
Catalyst loading								
1	<b>1</b>	2	0.5	80	DMF	0	37	63
2	<b>1</b>	2	2	80	DMF	0	0	> 99
Solvents								
3	<b>1</b>	2	1	80	CH <sub>3</sub> CN	11	79	10
4	<b>1</b>	2	1	80	EtOH	9	29	63
5	<b>1</b>	2	1	80	MeOH	7	22	71
6	<b>1</b>	2	1	80	Solvent-free	5	10	85
Temperature								



7	<b>1</b>	2	1	50	DMF	13	18	69
8	<b>1</b>	2	1	25	DMF	21	79	-
Reaction Time								
9	<b>1</b>	0.25	1	80	DMF	17	29	54
10	<b>1</b>	0.5	1	80	DMF	11	19	80
11	<b>1</b>	1	1	80	DMF	0	5	95
12	<b>1</b>	1.5	1	80	DMF	0	2	98
13	<b>1</b>	2	1	80	DMF	0	0	> 99
14	Blank	2	-	80	DMF	79	21	-
15	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2	1	80	DMF	18	82	-
16	H <sub>2</sub> L1	2	1	80	DMF	52	48	-
17	H <sub>2</sub> L2	2	1	80	DMF	55	45	-

<sup>a</sup> Typical reaction conditions: 0.5-2 mol% catalyst, solvent (0.5 mL), benzaldehyde dimethyl acetal (152 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol); 0.25-2 h, r.t., 50 or 80 °C, ultrasound irradiation (50/60 Hz for 80 °C). <sup>b</sup>Calculated by <sup>1</sup>H NMR analysis (**A** - benzaldehyde dimethyl acetal; **B** - benzaldehyde; **D** - 2-benzylidenemalononitrile).