

Supporting Information for

## **Pd(0)@UiO-68-AP: chelating-directed bifunctional heterogeneous catalyst for stepwise organic transformations**

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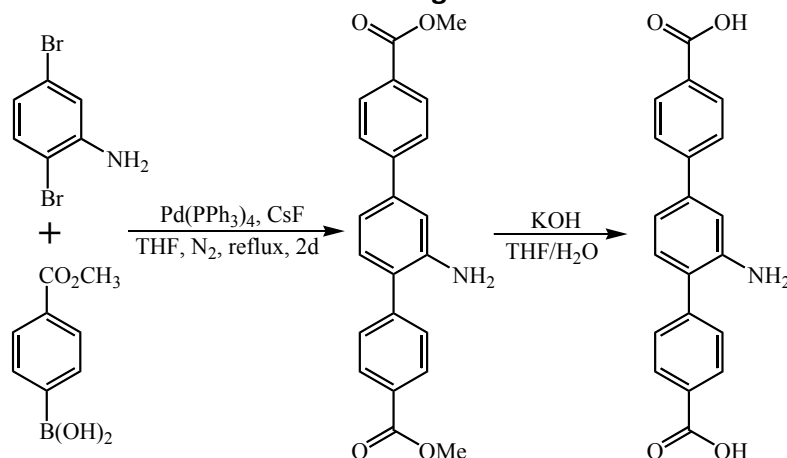
### **Section 7. Reference**

### **Section 1. Materials and instrumentation**

All of the starting materials were purchased from J & K Chemical Technology, unless otherwise noted, and used without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm<sup>-1</sup> range using a Perkin-Elmer 1600 FTIR spectrometer. <sup>1</sup>H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in  $\delta$  relative to TMS. The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope. The X-ray diffraction (XRD) experiments were obtained on a D8 ADVANCE X-ray powder diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Thermo gravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. ICP-LC was performed on an IRIS InterpidII XSP and NU Atto M. HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. GC analysis was performed on a 7890B gas chromatograph (Agilent Technologies, CA, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The GC capillary column (DB-WAX, 30 m length  $\times$  0.53 mm; HP-5, 30 m length  $\times$  0.32 mm) was

purchased from the Agilent Technologies. XPS spectra were obtained from THI5300 (PE). ICP measurement was performed on an IRIS Interpid (II) XSP and NU AttoM.

## Section 2. Synthesis and characterization of ligand



### The 1<sup>st</sup> step

A mixture of 2,5-Dibromoaniline (10 mmol, 2.51 g), 4-methoxyl carbonylphenylboronic acid (30 mmol, 5.4 g), CsF (47.5 mmol, 7.22 g), tetrakis(triphenylphosphine) palladium (3.3 mmol, 3.8 g) and anhydrous tetrahydrofuran (150 mL) were refluxed for 2 days under nitrogen atmosphere. After cooling to room temperature, the solvent was evaporated to dryness. The residue was washed with water, and purified on column (silica gel, CH<sub>2</sub>Cl<sub>2</sub> : ethylacetate = 40 : 1) to give the esterified ligand as yellow solid (2.3 g, yield: 63.9%). IR (KBr pellet cm<sup>-1</sup>): 3457 (m), 3374 (m), 2946 (m), 1706 (s), 1606 (s), 1434 (s), 1280 (m), 1106 (w), 767 (s), 704 (s). <sup>1</sup>HNMR(300 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS, ppm): 8.05-8.02 (d, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.78-7.75 (d, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.64-7.62 (d, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.17-7.16 (d, 1H, -C<sub>6</sub>H<sub>3</sub>-), 7.15 (s, 1H, -C<sub>6</sub>H<sub>3</sub>-), 7.03-7.00 (d, 1H, -C<sub>6</sub>H<sub>3</sub>-), 5.10 (s, 2H, -NH<sub>2</sub>), 3.88 (s, 6H, -CH<sub>3</sub>). Elemental analysis(%) calcd : C 73.12, H 5.30, N 3.88; Found: C 73.54, H 5.70, N 3.36.

### The 2<sup>st</sup> step

The esterified ligand (1.66 mmol, 0.60 g) was stirred in THF (20 mL), to which an aqueous solution of KOH (3.0 g, 53.6 mmol) (50 mL) was added. This mixture was heated at 50°C for 12 h. After removal of THF in vacuum, water was added inside. The mixture was heated until the solid was fully dissolved, then the solution was acidified with diluted HCl until no precipitate formed (pH<2). The green yellow powder was collected by filtration, washed with water and dried in air (0.45 g, yield: 81.4%). IR (KBr pellet cm<sup>-1</sup>): 2887 (s), 1683 (s), 1603 (m), 1518 (s), 1387 (m), 1287 (m), 1235 (s), 1181 (m), 1112 (w), 769 (s). <sup>1</sup>HNMR (300 MHz, DMSO-*d*<sub>6</sub>, 25 °C, TMS, ppm): 8.05-8.03 (d, 4H, -C<sub>6</sub>H<sub>4</sub>-), 7.78-7.75 (d, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.66-7.64 (d, 2H, -C<sub>6</sub>H<sub>4</sub>-), 7.44-7.42 (d, 1H, -C<sub>6</sub>H<sub>3</sub>-), 7.35 (s, 1H, -C<sub>6</sub>H<sub>3</sub>-), 7.33-7.30 (d, 1H, -C<sub>6</sub>H<sub>3</sub>-),

4.47 (s, 2H, -NH<sub>2</sub>). Elemental analysis(%) calcd: C 72.06, H 4.54, N 4.20; Found: C 71.75, H 4.67, N 4.36.

### Section 3. Synthesis and characterization of UiO-68-NH<sub>2</sub> and 1-2

#### Synthesis of UiO-68-NH<sub>2</sub><sup>1</sup>

A mixture of ZrCl<sub>4</sub> (0.080 mmol, 19.20 mg), H<sub>2</sub>L (0.080 mmol, 26.64 mg) and acetic acid (240 μL) in DMF (3.2 mL) was heated to 120 °C for 24 h. After cooling down to room temperature, the product was collected by centrifugation and washed with DMF (three times). In addition, the obtained yellowish powder was successively soaked in fresh DMF (80 °C, 6 h) and alcohol (60 °C, 2 days) with replacing the soaking solvent every 12 h to exchange alcohol. Finally, the product was washed with alcohol (three times) and dried at 80 °C in an oven. IR (KBr pellet cm<sup>-1</sup>): 3336 (w), 3297 (w), 1708 (w), 1599 (vs), 1544 (s), 1479 (w), 1415 (vs), 1329 (w), 1211 (w), 1191 (w), 1054 (w), 1003 (w), 872 (w), 831 (w), 779 (s), 674 (s), 557 (w), 516 (w), 458 (w). Elemental analysis (%) calcd: C 54.04, H 3.10, N 3.15; Found: C 53.78, H 3.24, N 3.33.

#### Synthesis of 1

UiO-68-NH<sub>2</sub> (0.67 mmol, 0.30 g) was dispersed into EtOH (50 mL) under ultrasound, and pyridine-2-carboxaldehyde (2.7 mmol, 0.29 g) was added. The mixture was refluxed at 70°C for 10 h. Afterwards, the precipitate was washed with abundant ethanol (three times) and dried in air. Elemental analysis (%): C 57.75, H 3.14, N 4.89 (Yield 80 %). After the 2-iminopyridine attached MOF particles were dispersed into CH<sub>3</sub>CN (50 mL), Pd(NO<sub>3</sub>)<sub>2</sub> (0.70 mmol, 0.16 g) was added, and the mixture was heated at 70°C for additional 1 h. The precipitate was collected and washed with abundant CH<sub>3</sub>CN (three times) and dried overnight in vacuum at 40°C. The ICP (based on Zr/Pd ratios, 1 : 0.68) indicated that the yield of **1** is 68 %. IR (KBr pellet cm<sup>-1</sup>): 1702(w), 1604(s), 1415(vs), 1277(w), 1186(w), 1107(w), 1014(w), 904(w), 831(w), 779(s), 740(w), 707(s), 655(s), 557(w), 464(s). Elemental analysis (%): C 44.66, H 2.42, N 6.61.

#### Synthesis of 2

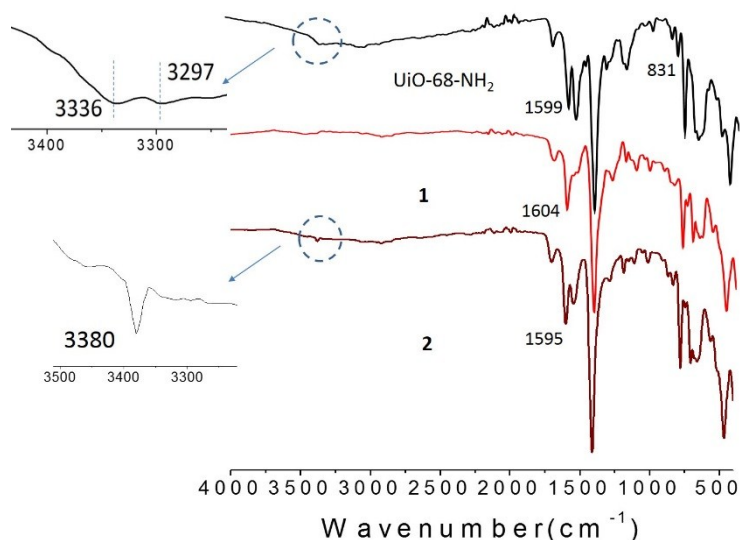
**1** (0.50 mmol, 0.30 g) was dispersed into aqueous solution (40 mL) of NaBH<sub>4</sub> (0.50 mmol, 1.9 mg) under ultrasound for 10 min., the resulting solids were collected by centrifugation, washed with water (2 times) and dried in air. IR (KBr pellet cm<sup>-1</sup>): 3380(w), 1709(w), 1595(w), 1533(s), 1407(vs), 1191(w), 1106(w), 1014(w), 831(w), 779(s), 708(w), 648(s), 451(s). Elemental analysis (%): C 43.68, H 2.61, N 6.45.

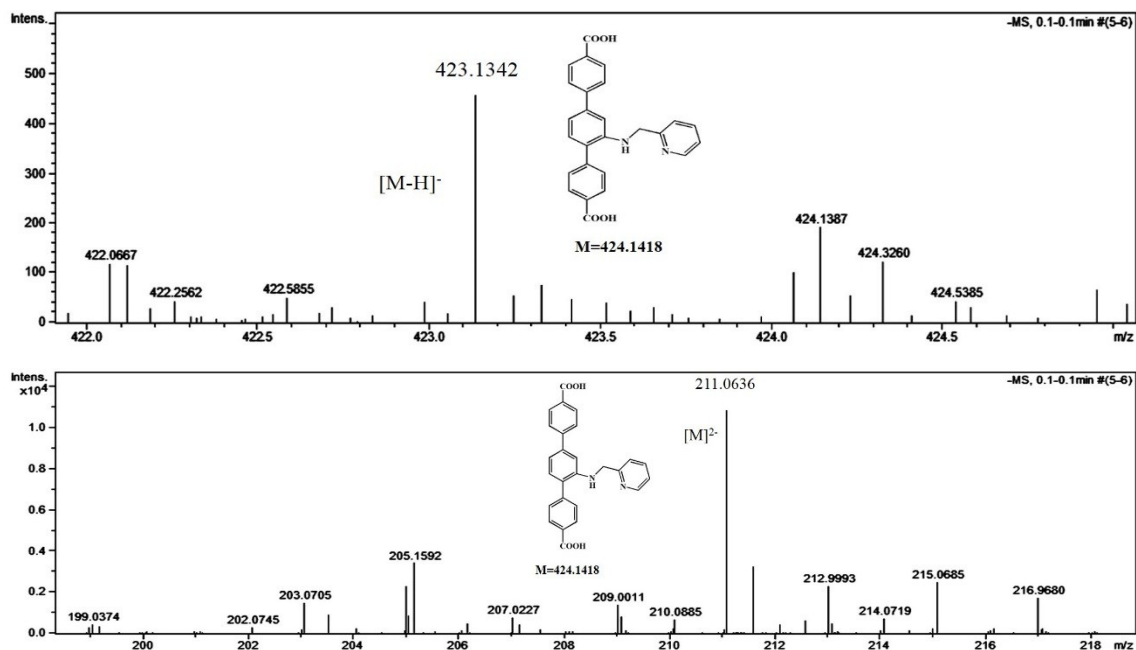
### Section 4. Reaction conditions

**Catalytic oxidation reaction:** **2** (10 mg, 1 mol %) was added to a toluene solution (2 mL) of the phenylcarbinol (1.0 mmol), and the mixture was stirred at 80°C (monitored by GC) to afford the corresponding products. The conversion and selectivity were determined by GC. **2** was recovered by centrifugation and filtration, and then directly reused in the next run under the same reaction conditions.

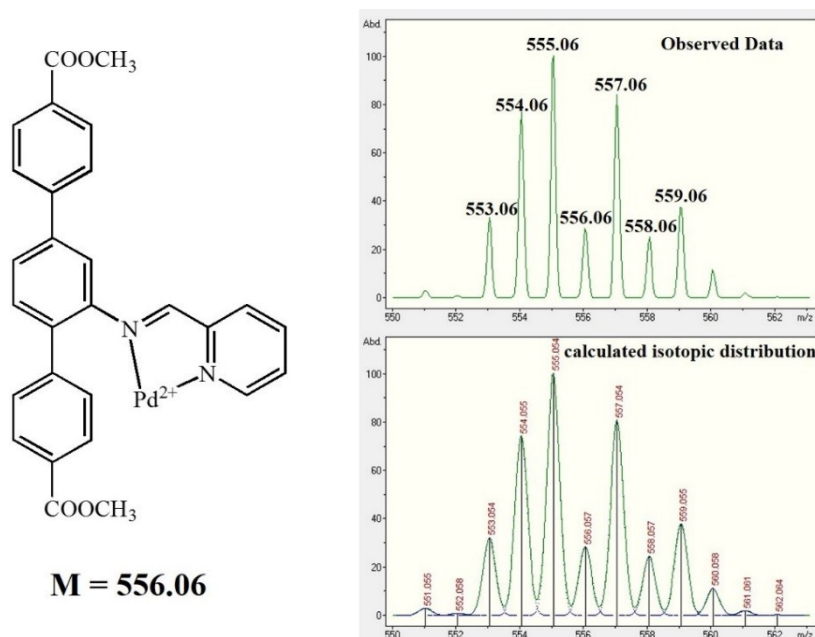
**Knoevenagel condensation reaction:** **2** (10 mg, 1 mol %) was added to a methanol solution (2 mL) of the benzaldehyde (1.0 mmol), and the mixture was stirred at room temperature (monitored by GC) to afford the corresponding products. The conversions and products were determined by GC. **2** was recovered by centrifugation and filtration, and then directly reused in the next run under the same reaction conditions.

**Oxidation-condensation catalysis:** **2** (10 mg, 1 mol %) was added to a toluene solution (2 mL) of phenylcarbinol (1.0 mmol), and the mixture was stirred at 80°C for 30 h. After cooling down to room temperature, methanol solution (2 mL) of malononitrile (1.2 mmol) was added and the mixture was stirred at room temperature for additional 8 h. The conversion and selectivity were determined by GC.

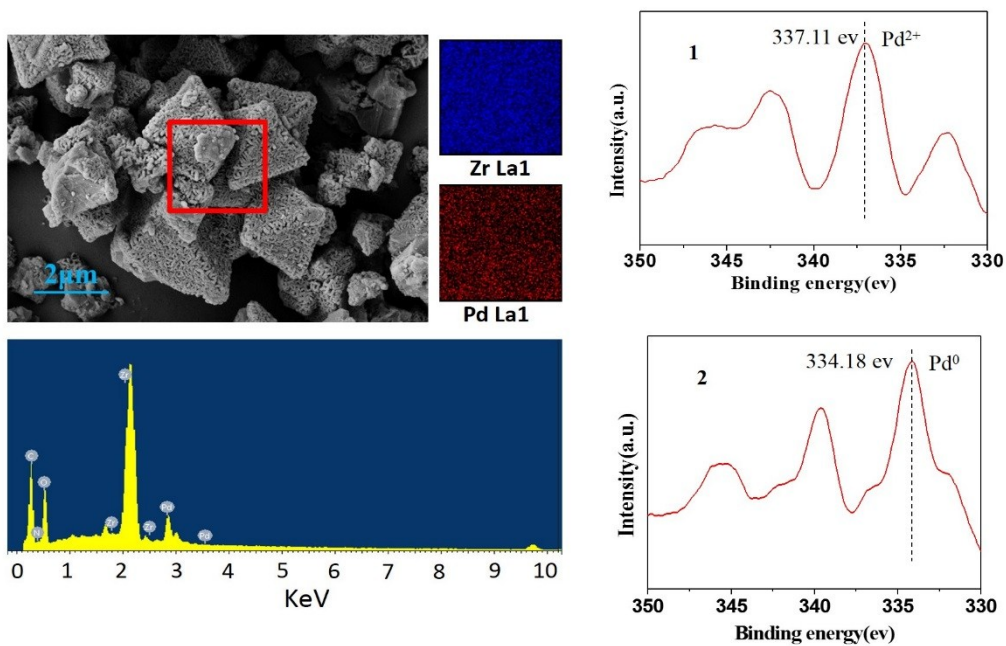




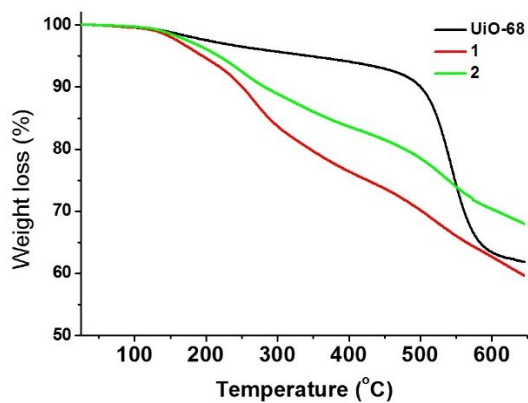
**Fig. S1** Top: IR spectra of UiO-68-NH<sub>2</sub>, **1** and **2**. Bottom: the MS spectra confirmed the formation of the corresponding secondary amino moiety along with the Pd(II) reduction.



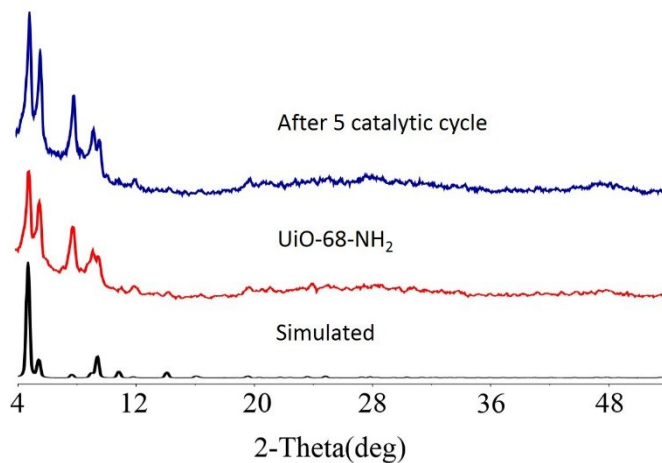
**Fig. S2** MS spectra of the metalated product of the esterified 2-iminopyridyl group-attached ligand with Pd(NO<sub>3</sub>)<sub>2</sub>.



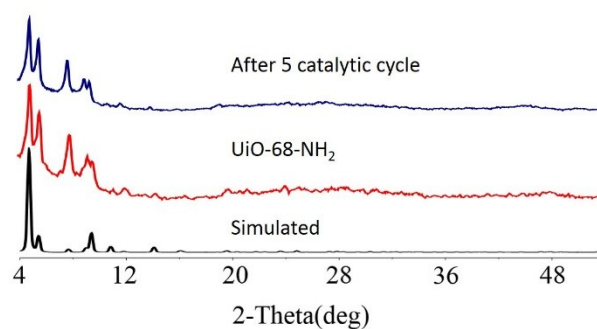
**Fig. S3** Left top: SEM image of **2** and elemental maps of Zr and Pd. Left bottom: EDS patterns of **2**. Right: XPS spectra of **1** and **2**.<sup>2</sup>



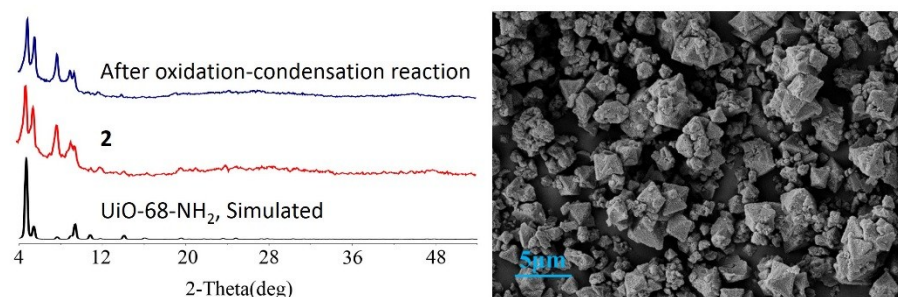
**Fig. S4** TGA traces of UiO-68-NH<sub>2</sub> and **1-2**.



**Fig. S5** XRPD patterns of simulated<sup>1</sup> and measured UiO-68-NH<sub>2</sub>, and **2** after 5 catalytic oxidation cycles.



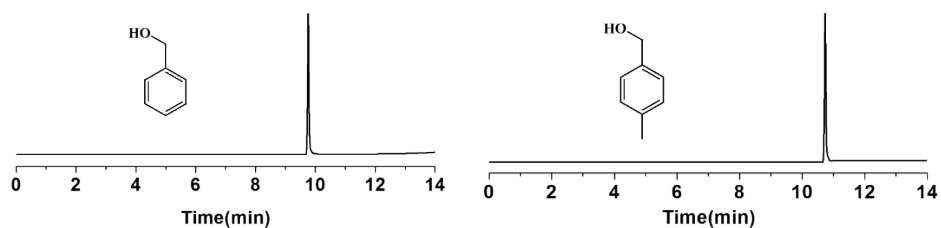
**Fig. S6** XRPD patterns of simulated<sup>1</sup> and measured UiO-68-NH<sub>2</sub>, and **2** after 5 catalytic Knoevenagel condensation cycles.

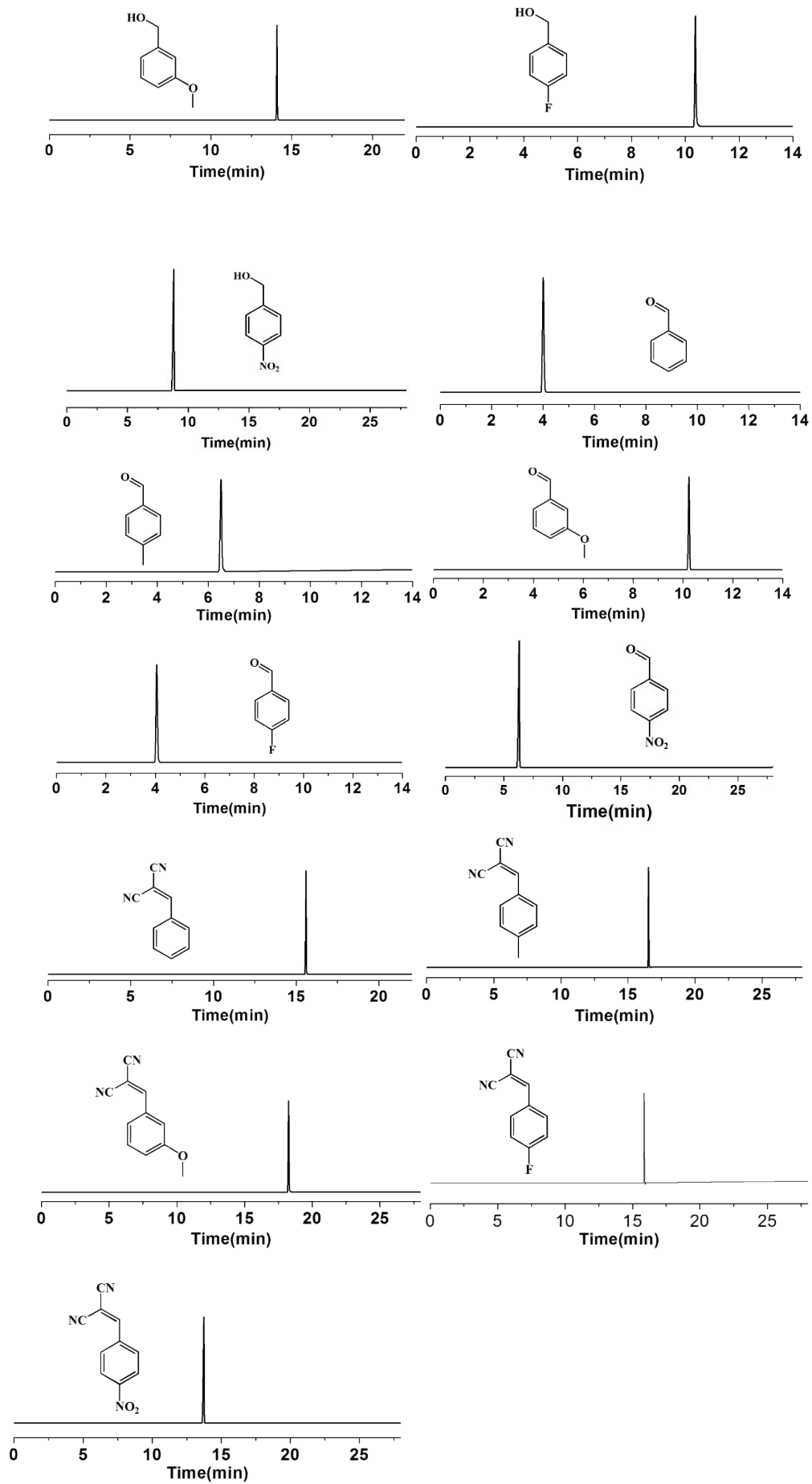


**Fig. S7** Left: Simulated (UiO-68-NH<sub>2</sub>) and measured XRPD patterns of **2** before and after catalysis. Right: SEM image of **2** after catalysis. The morphology of the microcrystals of **2** is well maintained after the two step reaction.

## Section 5. GC analyses

1. Standard sample of 4-nitrobenzyl alcohol, 4-nitrobenzaldehyde, and 2-(4-nitrobenzylidene)malononitrile were performed on HP-5 column, and the rest was performed on DB-WAX column.

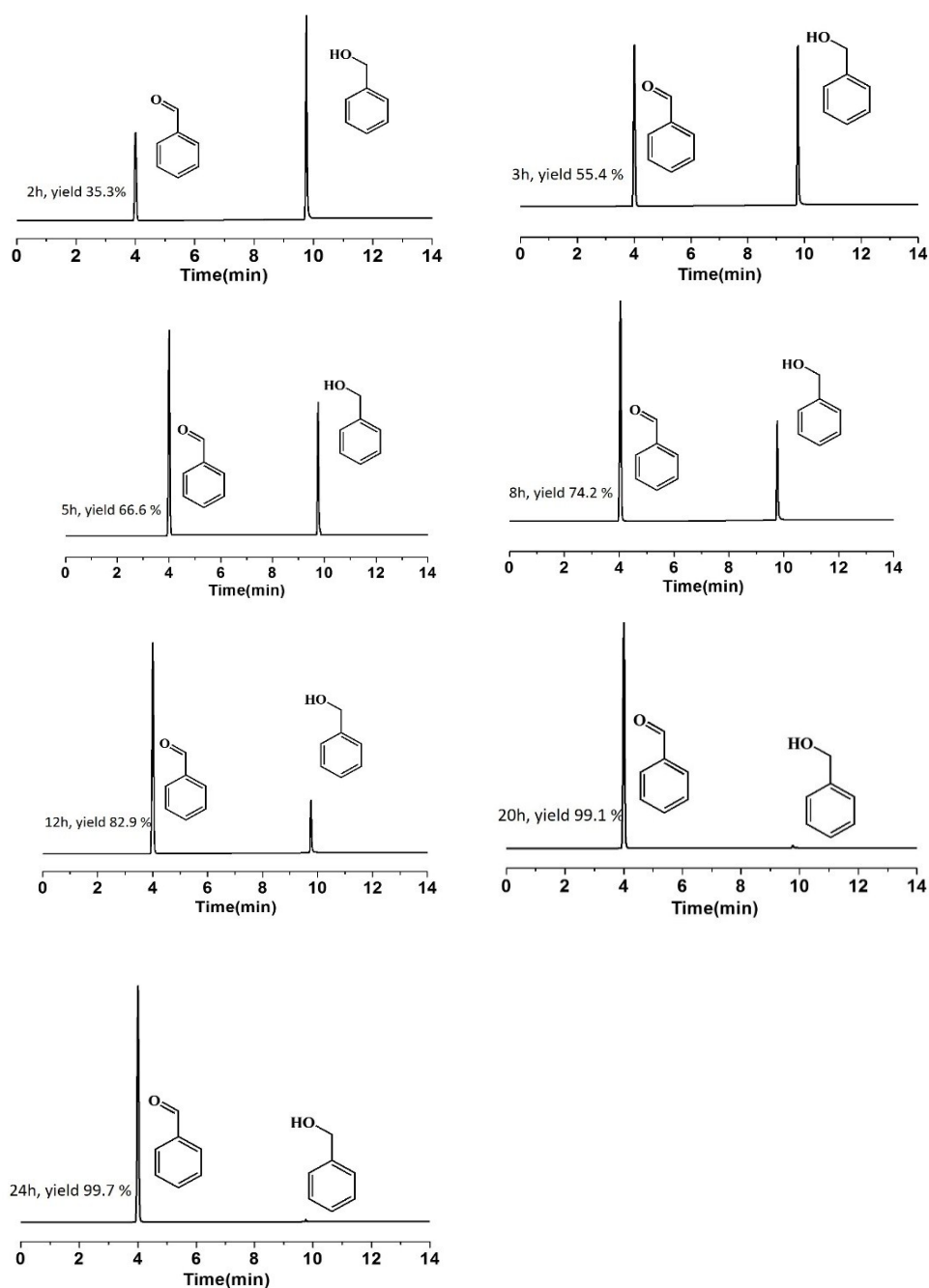






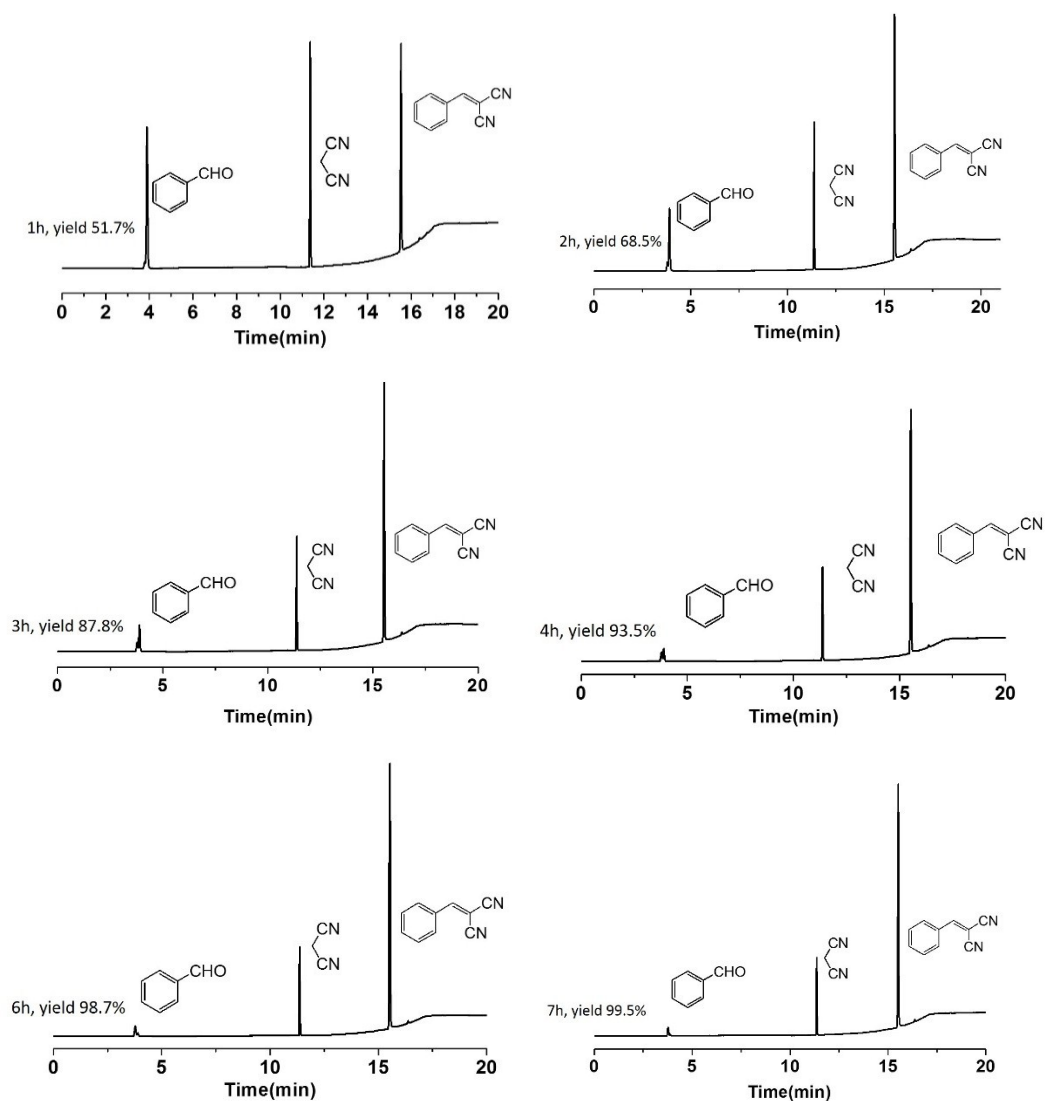
**Fig. S8** The GC spectra of all the standard samples.

2. GC monitoring of benzyl alcohol oxidation catalyzed by **2** at 80°C in toluene



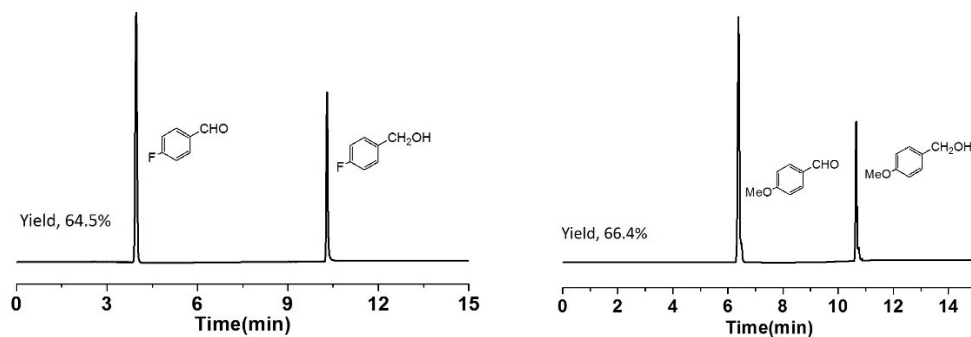
**Fig. S9** GC spectra of benzyl alcohol oxidation catalyzed by **2** at 80°C in toluene in air.

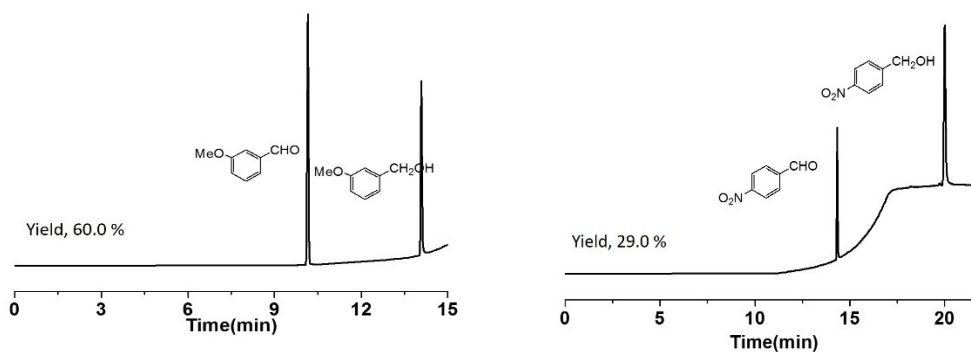
3. GC monitoring of Knoevenagel reaction of benzaldehyde catalyzed by **2** at room temperature in MeOH



**Fig. S10** GC monitoring of Knoevenagel reaction of benzaldehyde catalyzed by **2** at room temperature in MeOH.

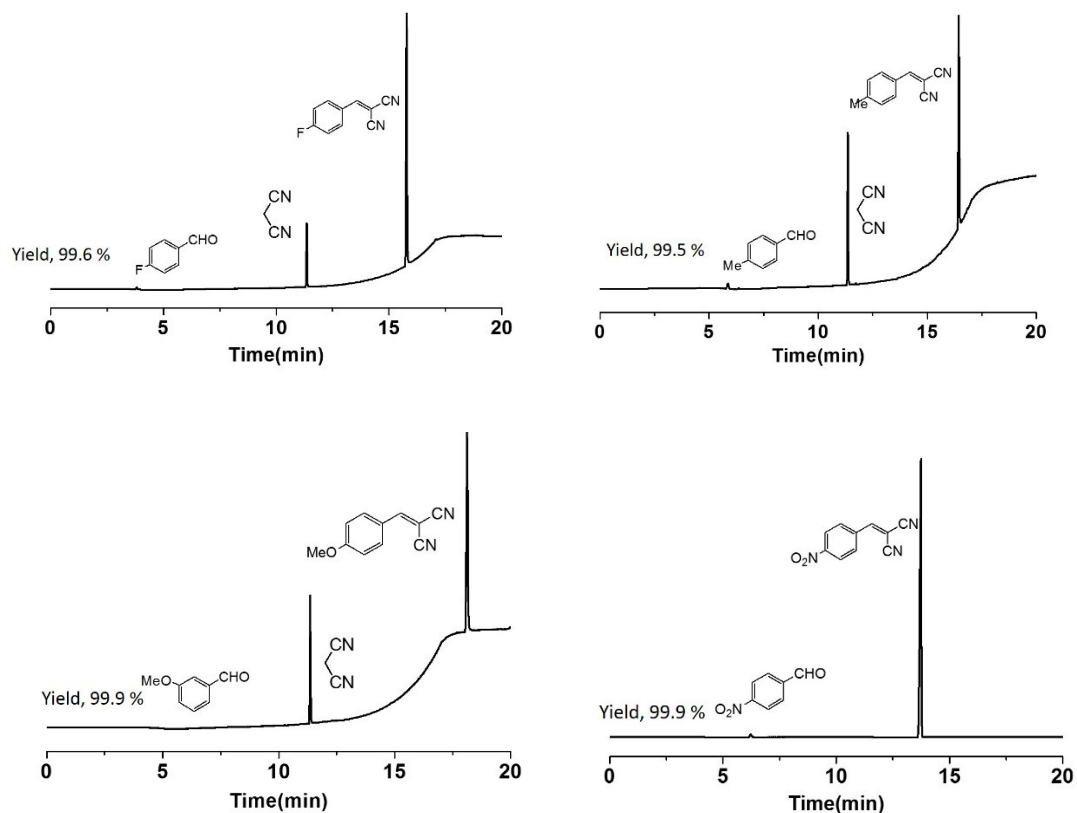
4. GC spectra of substituted benzyl alcohol oxidation catalyzed by **2** at 80°C in toluene





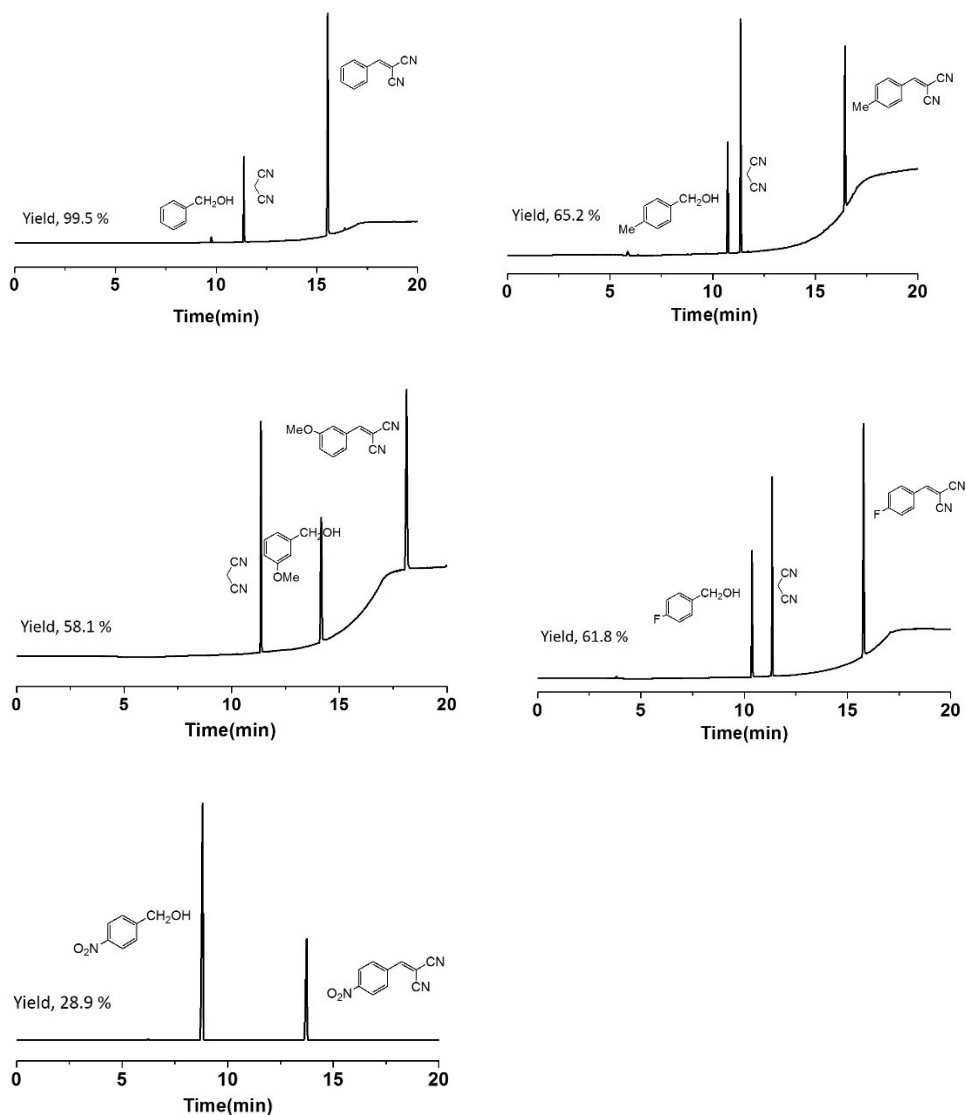
**Fig. S11** GC spectra of the substituted benzyl alcohols oxidation catalyzed by **2** at 80°C in toluene in air.

5. GC spectra of Knoevenagel reaction of substituted benzaldehydes catalyzed by **2** at room temperature in MeOH.



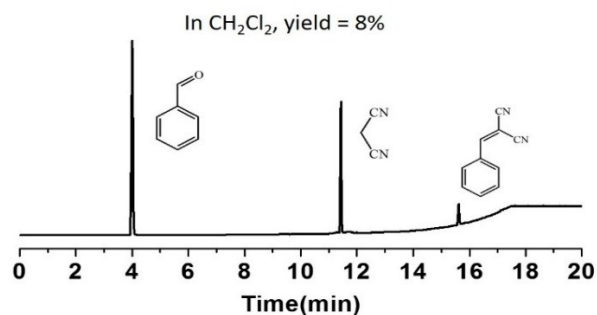
**Fig. S12** GC spectra of Knoevenagel reaction of the substituted benzaldehydes catalyzed by **2** at room temperature in MeOH.

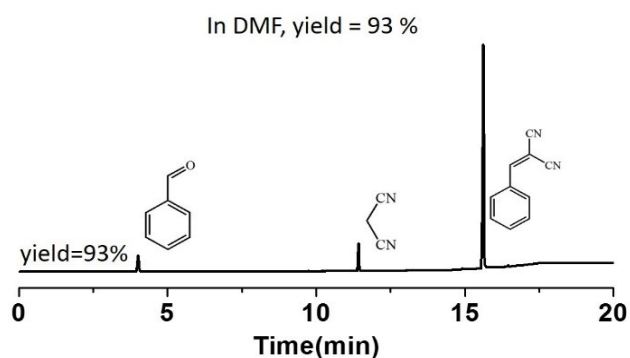
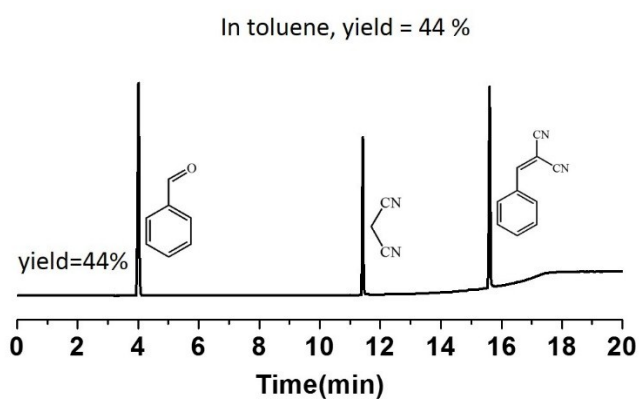
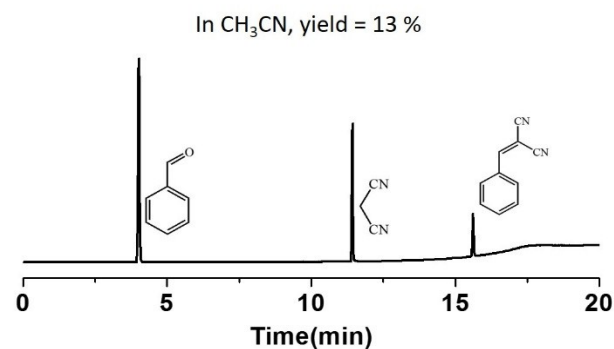
6. GC spectra of oxidation-Knoevenagel reaction of benzyl alcohol and substituted benzyl alcohols catalyzed by **2** at room temperature.



**Fig. S13** GC spectra of Knoevenagel reaction of the substituted benzaldehydes catalyzed by **2** at room temperature in MeOH.

- GC spectra of UiO-68-NH<sub>2</sub>-catalyzed Knoevenagel reaction of malononitrile with benzaldehyde in different solvent systems.





**Fig. S14** GC spectra of UiO-68-NH<sub>2</sub>-catalyzed Knoevenagel reaction of malononitrile with benzaldehyde in different solvent systems.

#### Section 6. ICP analysis for Pd-loading on UiO-68-NH<sub>2</sub> by impregnation

	Zr 339.198	Zr 257.13	Zr 272.26	Pd 340.45	Pd 324.27	Pd 229.56	Pd 344.14
mg/L	11.702	11.683	11.841	0.974	0.975	0.964	0.961

The Zr : Pd = 1 : 0.08 based on above results.

#### Section 7. Reference

1. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, *Chem. Eur. J.*, **2011**, *17*, 6643-6651.

2. (a) P. Lei, M. Hedlund, R. Lomoth, H. Rensmo, O. Johansson and L. Hammarström, *J. Am. Chem. Soc.*, **2008**, *130*, 26-27. (b) E. Karakhanov, A. Maximov, Y. Kardasheva, V. Semernina, A. Zolotukhina, A. Ivanov, G. Abbott, E. Rosenberg and V. Vinokurov, *ACS Appl. Mater. Interfaces*, **2014**, *6*, 8807-8816. (c) X, Yang, Q, Li, H. Wang, J. Huang, L. Lin, W. Wang, D. Sun, Y. Su, J. B. Opiyo, L. Hong, Y. Wang, N. He, L. Jia, *J. Nanopart. Res.*, 2010, *12*, 1589-1598.