Electronic Supplementary Information (ESI)

A general in-situ approach to functionalize metal–organic frameworks with tertiary aliphatic amino groups

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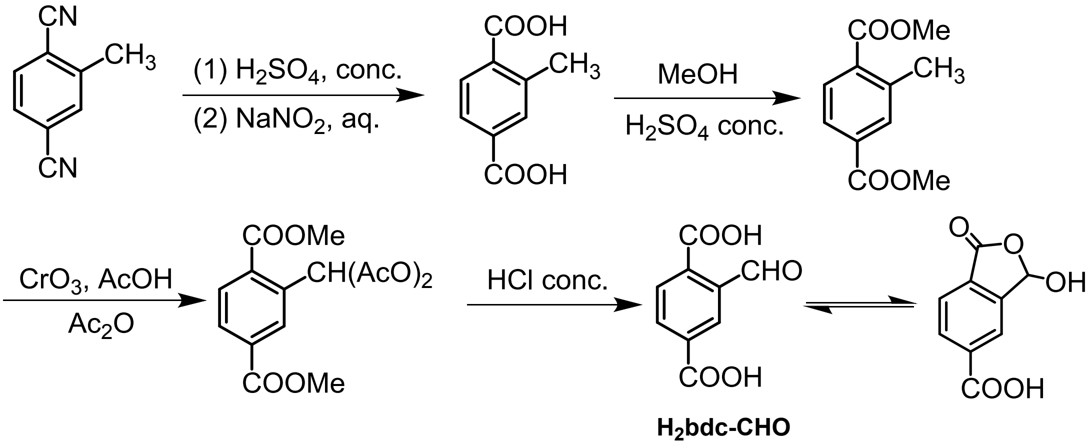
1. Physical Measurements

Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku Ultima IV X-ray Diffractometer with Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 5 °/min, with accelerating voltage and current of 35 kV and 25 mA, respectively. Proton nuclear magnetic resonance spectra (^{1}H NMR) were performed on a Bruker Ascend 400 (400 MHz) spectrometer. Gas Chromatography (GC) was conducted using a Shimadzu GC-2014 instrument equipped with an FID detector. Fourier Transform Infrared Spectra (FT-IR) were recorded on a Nicolet NEXUS 670 and subtracted the background of pure KBr. Nitrogen adsorption and desorption isotherm measurements (BET) were performed on a Micromeritics, ASAP2020 at 77K. Energy Dispersive Spectrometer (EDS) were recorded on a Hitachi S4800 field emission scanning electron microscope.

2. Synthesis of organic ligands

Starting materials and solvents were purchased from commercial suppliers and used without further purification. H_2bpdc-CHO (2-formylbiphenyl-4,4′-dicarboxylic acid) was synthesized according to the procedures reported in the literature with some modification.[1]

Synthesis of H_2bdc-CHO (Scheme S1)



Scheme S1 Synthesis of H_2bdc-CHO

(i) synthesis of 2-methylterephthalic acid

A solution of 2-methylterephthalonitrile (4.6 g, 32.4 mmol) in sulfuric acid (80 mL, conc.) was stirred for 24 h at 90 ℃ in an oil bath. After cooling to room temperature, the solution was placed in an ice bath while deionized water (60 mL) was added. After the solution was cooled to 0 ℃, an aqueous solution of $NaNO_2$ (6.62 g, 3.2 mol/L) was added dropwise with vigorously stirring. A large amount of white solid precipitated out and reddish brown NO_2 was generated in this procedure. After NO_2 ceased to release, the reaction solution was stirred for 24 h at 110 ℃ in an oil bath. After cooling to 25 ℃, deionized water (120 mL) was added. The solids were collected by filtration and washed with deionized water. The resulting white solid was dried in air for 12 h at 50 ℃. Yield 5.36 g (92 %). δ_H (400 MHz; DMSO-d_6): 2.56 (s, 3 H), 7.81~7.89 (m, 3 H).

(ii) Synthesis of dimethyl 2-methylterephthalate

2-methyl terephthalic acid (5.36 g, 29.8 mmol) was dissolved in MeOH (55 mL) sulfuric acid (3 mL, conc.) was added, the solution was refluxed for 18 h at 95 ℃. After cooled to 25 ℃, deionized water (220 mL) was added and lots of white solids precipitated out from the solution. The solids were collected by filtration, and the filter cake was washed with abundant deionized water and dried for 12 h at 40 ℃ in an oven, give rise to a white solid 5.89 g (95 %). δ_H (400 MHz; DMSO-d_6): 2.55 (s, 3 H), 3.87 (s, 3 H), 3.89 (s, 3 H),7.83~7.90 (m, 3 H).

(iii) Synthesis of dimethyl 2-(diacetoxymethyl)terephthalate

Dimethyl 2-methylterephthalate (5.89 g, 28.3 mmol) was dissolved in dissolved in a mixture of AcOH (73 mL) and Ac_2O (74 mL). The solution was placed in an ice bath, and H_2SO_4 (12 mL, conc.) was added slowly under stirring. After cooling to 0~5 ℃, CrO_3 (8.49 g, 84.9 mmol) was added in very small portions. The mixture was continuously stirred. The reaction was monitored by TLC. When TLC showed the appearance of a byproduct, the reaction was quenched by pouring the reaction solution into crushed ice. When the ice was completely melted, the mixture was extracted with ethyl acetate (100 mL×3), and the combined organic phase was ordinally washed with saturated Na_2CO_3 aqueous and brine for several times until a clear solution was obtained. The organic phase was dried with anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate (10/1~3/1)). Yield 3.64 g (40 %). δ_H (400 MHz; DMSO-d_6): 2.13 (s, 6 H), 3.36 (s, 1 H), 3.88 (s, 3 H), 3.91 (s, 3 H), 8.04~8.18 (m, 3 H).

(iv) Synthesis of 2-formylterephthalic acid

Dimethyl 2-(diacetoxymethyl)terephthalate was added to a HCl solution (90 mL, 4 mol/L). The mixture was heated at 100 ℃ until complete conversion (determined by TLC). The solid was precipitated by cooled the mixture in an ice bath for 10 min, collected by filtration and washed with deionized water, dried at 40 ℃ in air oven. Yield 2.02 g (92 %). δ_H (400 MHz; DMSO-d_6): 6.74 (s, 1 H), 7.93~8.19 (m, 3 H), 8.30 (s, 1 H).

3. Synthesis of MOFs

(1) Synthesis of UiO-67-CH_2NMe_2

H_2bpdc-CHO (50 mg, 0.185 mmol), $ZrCl_4$ (43 mg, 0.185 mmol), *N*,*N*-dimethylformamide (DMF, 2 mL) and glacial acetic acid (317 μL,5.5 mmol) were mixed in a 23 mL Teflon vessel. The mixture was sonicated to a clear solution and sealed in stainless steel shell, followed by incubation at 120 °C for 24 h. After cooling to room temperature, the solids were collected by filtration, washed with DMF (10mL×3), and dried in the air. Yield: 46 mg. To remove DMF, the material was immersed in methanol (MeOH, 10 mL×3), with the solvent being exchanged with fresh one every 8 h. The methanol-exchanged sample was collected by centrifugation and evacuated under dynamic vacuum at 80°C for 3 h.

The reactions at 80 and 100°C under otherwise identical conditions gave UiO-67-CHO and mixed-linker MOF, respectively.

(2) Synthesis of IRMOF-9-CH_2NMe_2

H_2bpdc-CHO (108 mg, 0.4 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (324 mg, 1.09mmol) and DMF(10 mL) were placed in a 23 mL Teflon liner. The mixture was sonicated to a clear solution and sealed in stainless steel shell, followed by incubation at 120 °C for 24 h. After cooling to room temperature, the crystals were collected by filtration and washed with DMF.

(3) Synthesis of MIL-101(Fe)-CH_2NMe_2

H_2bdc-CHO and Hcpa (194 mg, 1.0 mmol), $FeCl_3{\cdot}6H_2O$ (541 mg, 2.0mmol) and DMF (16 mL) were placed in a 23 mL Teflon liner. The mixture was sonicated for 20 min and sealed in stainless steel shell, followed by incubation at 135 °C for 48 h. After cooling to room temperature, the solids were collected by centrifugation, washed with DMF (15mL×2) and MeOH (15mL×5), and dried in an oven at 100 °C for 12 h, yielding a red brown powder, 134 mg.

(4) Synthesis of UiO-66-type MOFs

(i) **Synthesis of UiO-66-CH_2NMe_2**

H_2bdc-CHO and Hcpa (194 mg, 1 mmol), $ZrCl_4$ (233 mg, 1 mmol), DMF (7 mL) and HCOOH (755 μL, 20 mmol) were placed in a 23 mL Teflon vessel. The mixture was sonicated for 20 min and sealed in a stainless steel shell, followed by incubation in an oven preheated to 120 °C for 48 h. After cooling to room temperature, the solids were collected by centrifugation, washed with DMF (15 mL×2) and MeOH (15 mL×5), and dried in an oven at 100 °C for 12 h, giving a white powder, 207 mg. For N_2 adsorption and catalytic use, the product was washed

Et_3N/MeOH (15 mL × 3, 10% Et_3N) before washing with MeOH (15 mL × 3).

(ii) **Synthesis of UiO-66-CH_2NEt_2 and UiO-66-$CH_2N(CH_2)_5$**

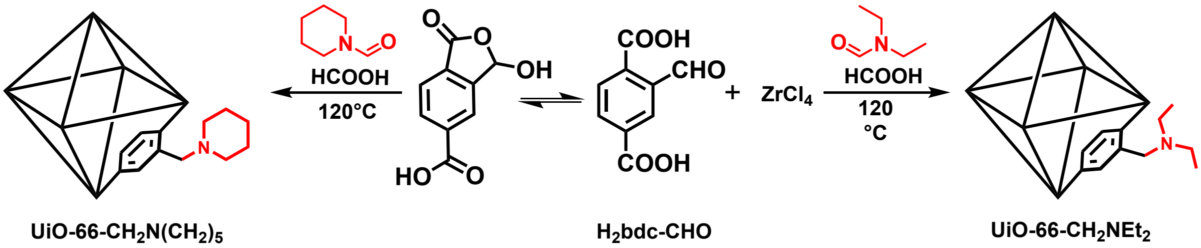
These MOFs were prepared according to the above procedure, using DEF (*N*,*N*-diethylformamide) and *N*-formylpiperidine in the place of DMF, yield: 160 mg and 183 mg respectively.

(iii) **Synthesis of UiO-66-CH_2NMe_2-14/24/60**

The mixed-linker MOFs were prepared according to the above procedure for UiO-66-CH_2NMe_2, using a mixture of H_2bdc-CHO and H_2bdc (terephthalic acid) in the molar ratios of 1:10, 1:4 and 1:1. The total amount of the ligands was fixed at 1.0 mmol. The yield was 203 mg, 180 mg and 196 mg respectively.

4. Catalytic experiment

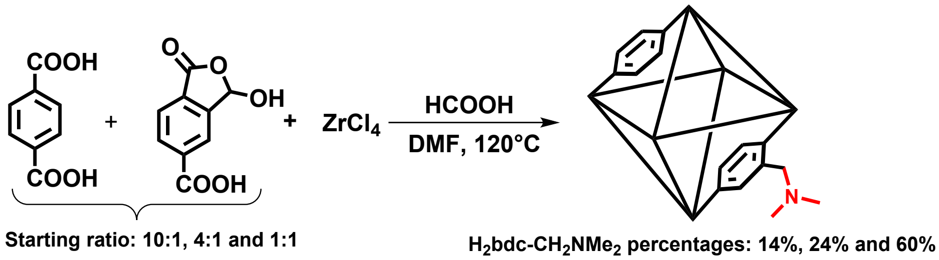
An amine-tagged UiO-66 catalyst in given amount was placed in a 50 mL two-necked round bottom flask and heated at 80 ℃ for 30 min under dynamic vacuum. After filling with nitrogen and cooling to room temperature, the solution of benzaldehyde (255 μL, 2.5 mmol) and 1,2,4-trichlorobenzene (315 μL, 5.0 mmol) in toluene (3 mL) was added. Then a solution of malononitrile (330 mg, 5.0 mmol) in toluene (2 mL) was added to start the reaction. The conversions at different time intervals were calculated from GC using 1,2,4-trichlorobenzene as the internal standard.



Scheme S2 Synthesis of UiO-66-CH$_2$N(Et)$_2$ and UiO-66-CH$_2$N(CH$_2$)$_5$.

$$6\,ZrCl_4 + 6\,H_2BDC + 8\,H_2O = Zr_6O_4(OH)_4(BDC)_6 + 24\,HCl$$

Scheme S3 Synthesized equation of UiO-66



Scheme S4 Synthesis of UiO-66-CH$_2$NMe$_2$ with mixture ligand.

Table S1 Crystal data and structure refinement for Zn-MOF-CH_2NMe_2

Empirical formula	$C_{51}H_{48}N_3O_{15}Zn_4$
Formula weight	1260.49
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C*2/m
a	22.3686(14) Å
b	25.4298(15) Å
c	17.1469(13) Å
β	101.016(2) deg.
Volume	9573.9(11) $Å^3$
Z	4
Absorption coefficient	1.030 mm^{-1}
Calculated density	0.874 Mg/m^3
F(000)	2584
Theta range for data collection	2.401 to 24.361 deg.
Limiting indices	-27<=h<=26, -31<=k<=31, -21<=l<=20
Reflections collected	60285
Reflections unique	9564
Completeness	99.1 %
R(int)	0.1636
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9498 / 241 / 472
Goodness-of-fit on F^2	1.011
Final R indices [$I>2\sigma(I)$]	R1 = 0.0827, wR2 = 0.2083
R indices (all data)	R1 = 0.1737, wR2 = 0.2655
Largest diff. peak and hole	0.802 and -0.417 $eÅ^{-3}$

Table S2 Knoevenagel condensation reaction catalyzed by the UiO-66-type MOFs[a]

catalyst	Amount of Catalyst (mol%)		Time	Conv.(%)[b]	TOF(h^{-1}/amine)
	Zr	Amine			
UiO-66-CH_2-NMe_2-14	10	1.4	10 / 30 min	81/98	348/140
UiO-66-CH_2-NMe_2-14	5	0.70	10 / 30 min	62/91	533/260
UiO-66	5	-	2 h	9	-
-	-	-	3 h	3	-
UiO-66+Et_3N	5	0.70	30 min	56	160

[a] Conditions: benzaldehyde (255 μL, 2.5 mmol), malononitrile (330 mg, 5.0 mmol), catalyst (71 mg, 0.25 mmol or 36 mg 0.13 mmol), toluene (3 mL), r.t. [b] GC Conversion was determined by using 1,2,4-trichlorobenzen (315 μL, 5.0 mmol) as the internal standard.

Table S3 Comparison of the performance of different *N*-containing MOFs for Knoevenagel condensation reactions of benzaldehyde and malononitrile.

Entry	Catalysts	Mol%^{a}	Solvent	Temp	Time	Yeild	TOF(h^{-1})	Ref.
1	$[Cd(4\text{-}btapa)_2(NO_3)_2]\cdot 6H_2O\cdot 2DMF$ 4-btapa=1,3,5-Benzene Tricarboxylic Acid Tris[N-(4-pyridyl)amide]	4^a	benzene	r.t.	12 h	98%	2	[2]
2	$Zn_2(tpt)_2(2\text{-}atp)I_2$ tpt = tris (4-pyridyl) triazine, 2-atp = 2-aminoterephthalate	0.5^a	EtOH	60 ℃	2 h	99%	99	[3]
3	ZIF-8	5^a	Toluene	r.t.	3 h	99%	6.7(3 h)	[4]
4	ZIF-9	5^a	Toluene	r.t.	4	96%	4.8(4 h)	[5]
5	$[Gd_2(tnbd)_3(DMF)_4]\cdot 4DMF\cdot 3H_2O$ tnbd = 2,6,2',6'-tetranitro-biphenyl-4,4'-dicarboxylic acid	6^b	C_6H_6	r.t.	20 min	96%	48	[6]
6	Al-MIL-101-NH_2	7.4^b	Toluene	80 ℃	30 min	61%	16	[7]
	Fe-MIL-101-NH_2	6.7^b				78%	23	
7	DETA-MIL-101	-	Toluene	r.t.	30 min	40%	108	[8]
					1 h	71%		
					2 h	98%		
8	UiO-66-NH_2	9^b	DMF	40 ℃	40 min	98%	17	[9]
9	TMU-5	2^b	H_2O	r.t.	30 min	100%	100(30min)	[10]
10	$[Zn(L)(H_2O)_2]_n\cdot n(NMF)$ L = 5-acetamidoisophthalate	3^a	THF	40 ℃	1.5	98%	22	[11]
11	UiO-66-NH-RNH_2	1^b	Toluene	r.t.		99%	50 (2 h)	[12]
	Cr-MIL-101-NH-RNH_2	1^b	Toluene	r.t.		33%	396(5min)	
						88%	264(20min)	
12	Au@Cu(II)-MOF	3^a	Toluene	r.t.	7 h	99%	5	[13]
13	$[Ni_3(TBIB)_2(BTC)_2(H_2O)_6]\cdot 5C_2H_5OH\cdot 9H_2O$ TBIB = 1,3,5-tri(1H-benzo[d]imidazol-1-yl)benzene	3.2^b	DCM	60 ℃	2 h	100%	16	[14]
14	CAU-1-NH_2	19^b	EtOH	40 ℃	7 h	98%	0.73	[15]
15	NH_2(50%)-MIL-53	25^b	DMF	80 ℃	5 h	99%	0.79	[16]
16	STU-1	3^a	THF	45 ℃	4 h	94%	8	[17]
17	[Zn(Py2TTz)(2-NH2BDC)]·(DMF)n 2,5-Bis(4-pyridyl)thiazolo[5,4-d]thiazole	2^a	Solvent Free	60 ℃	6 h	99.9%	8.3	[18]
18	Nanoplate TMU-33	13^b	H_2O	r.t.	5 min	100%	93	[19]
19	[Zn2(1κN,2κO-μ-L)2(κO^4-μ4-BTC)]n·3n(DMF)·2n(H2O)	1^a	THF	r.t.	30 min	28%	56	[20]
					1 h	65%	65	
					1.5 h	80%	53.3	
20	UiO-66-CH_2NMe_2-14	0.7^b	Toluene	r.t.	5 min	20%	349(5min)	This work
					10 min	62%	533(10min)	This work
					20 min	81%	348(20min)	This work
					30 min	91%	260(30min)	This work

[a] The mole percentage of the catalysts were calculated based on the metal.
[b] The mole percentage of the catalysts were calculated based on the nitrogen.

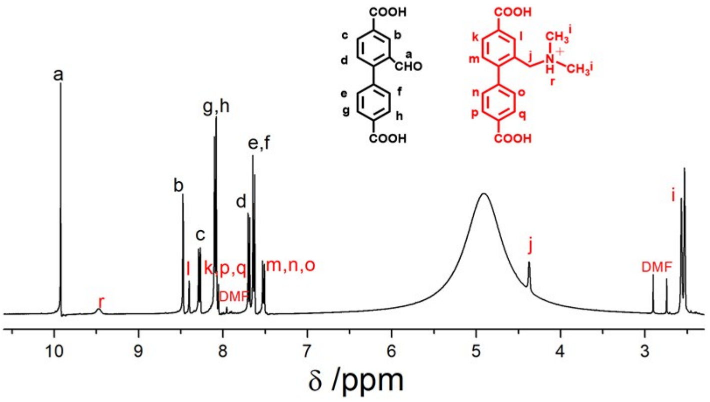


Fig S1 ^{1}H NMR of the UiO-67-type material synthesized at 100℃. The material was digested in HF (aq.)/d_6-DMSO for ^{1}H NMR measurement.

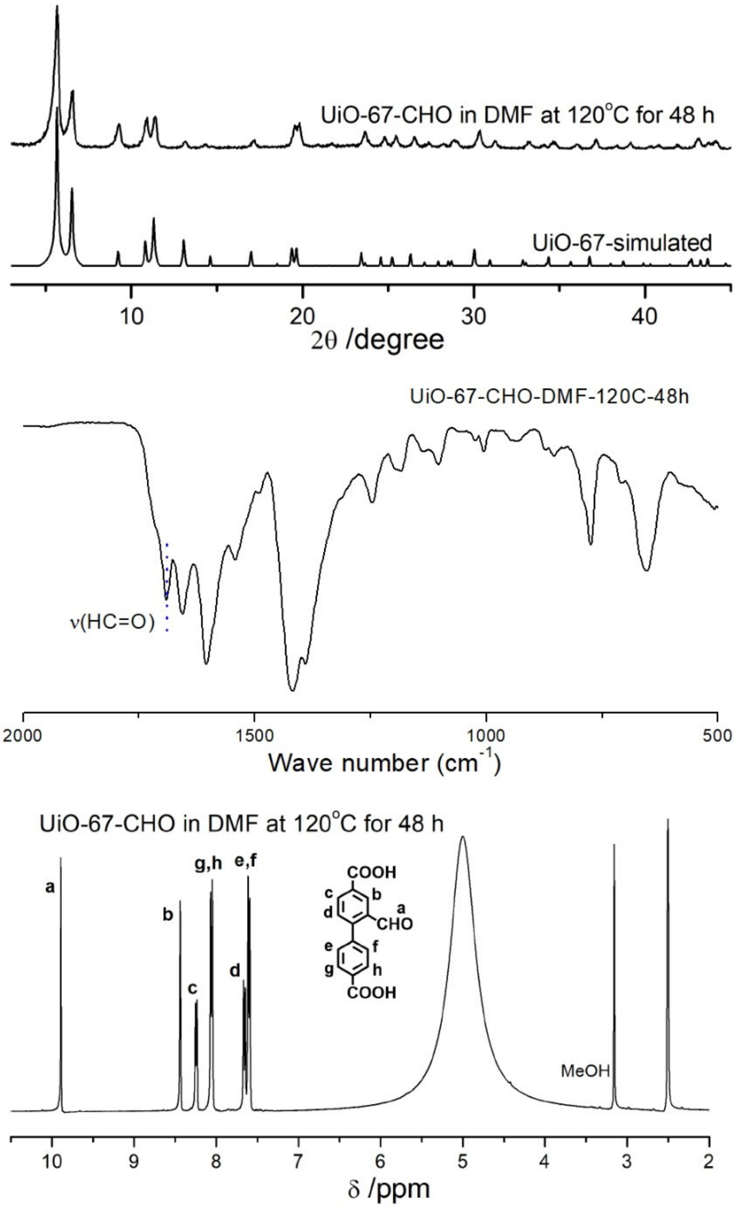


Fig S2 PXRD, IR and ^{1}H NMR of UiO-67-CHO solvothermally treated in DMF at 120 ℃ for 48 h. The material was digested in HF (aq.)/d_6-DMSO for ^{1}H NMR measurement.

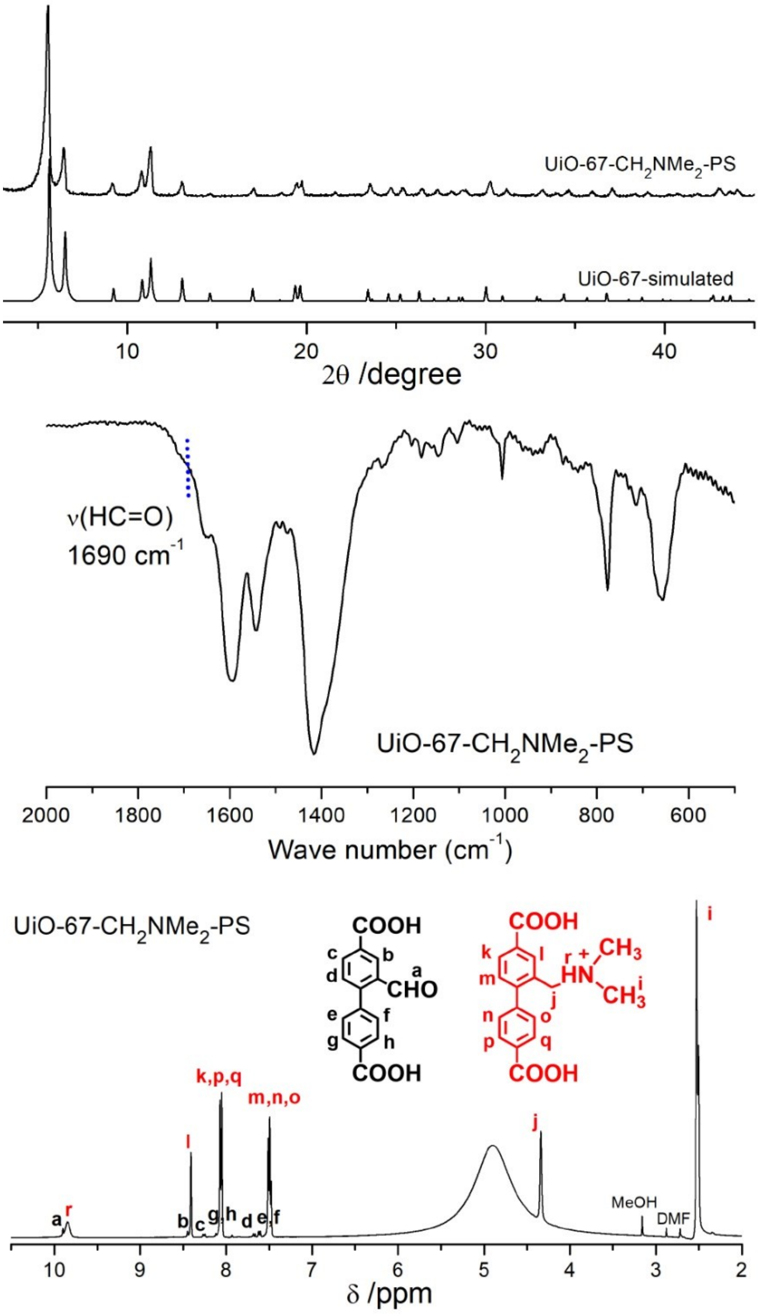


Fig S3 PXRD, IR and ^1H NMR of UiO-67-CH_2NMe_2-PS, which was obtained from postsynthetic (PS) solvothermal treatment of UiO-67-CHO with HCOOH in DMF at 120 °C for 48 h. The material was digested in HF (aq.)/*d*$_6$-DMSO for ^1H NMR measurement.

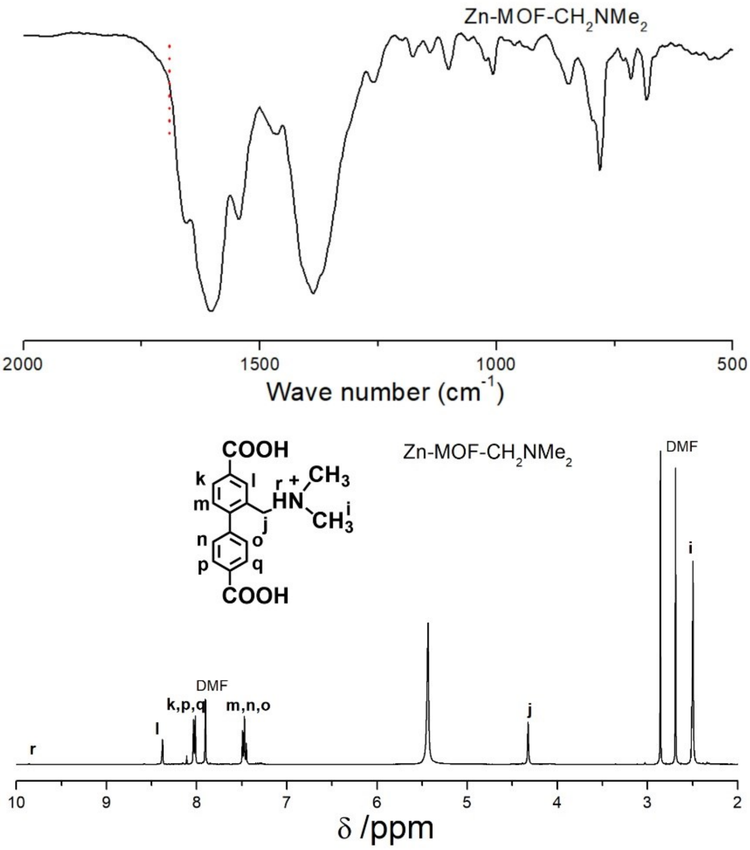


Fig S4 IR and ^{1}H NMR of Zn-MOF-CH$_2$NMe$_2$. The material was digested in HCl (aq.)/d_6-DMSO for ^{1}H NMR measurement.

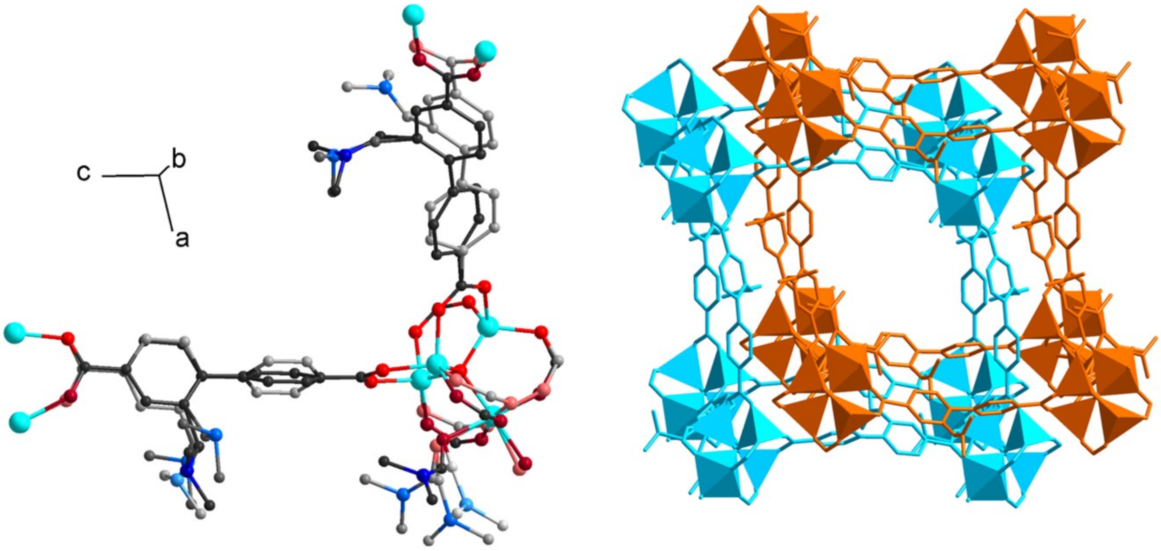


Fig S5 Asymmetric unit and doubly-interpenetrated frameworks of Zn-MOF-CH$_2$NMe$_2$.

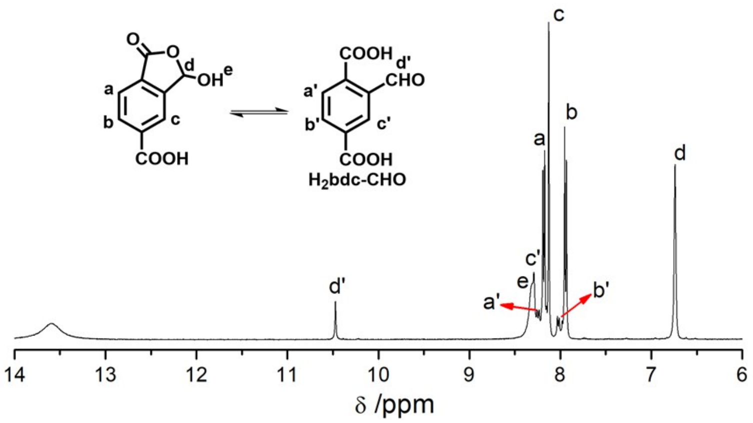


Fig S6 ^{1}H NMR (d_6-DMSO) of the as-synthesized H_2bdc-CHO ligand, which exists in equilibrium with its lactone isomer.

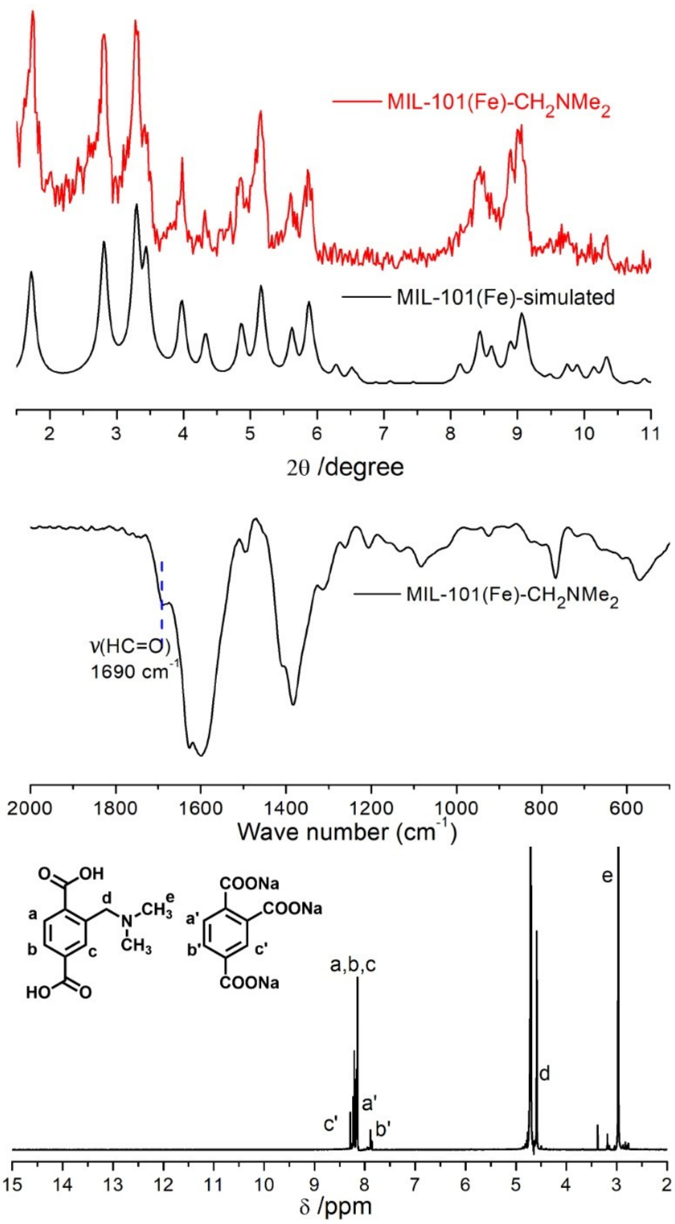


Fig S7 PXRD, IR and ^{1}H NMR of MIL-101(Fe)-CH_2NMe_2. ^{1}H NMR was recorded for the solution obtained by filtering the precipitate of the digested solution in NaOD/D_2O.

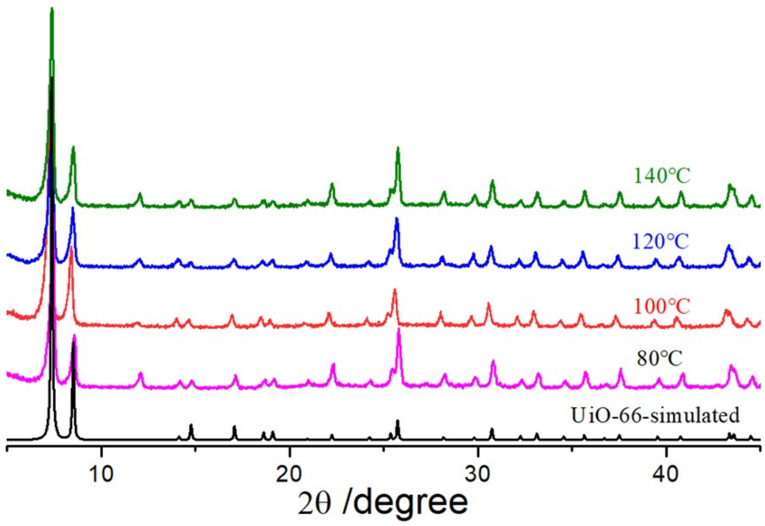


Fig S8 PXRD of UiO-66- CH_2NMe_2 synthesized at different temperature.

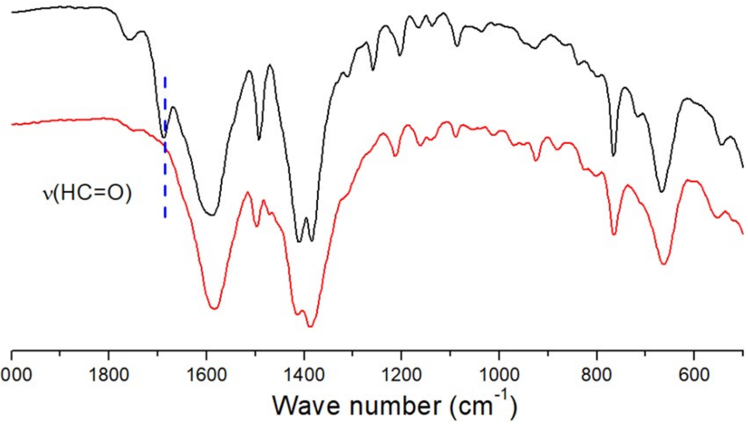


Fig S9 IR of UiO-66-CH_2NMe_2 synthesized at 80 ℃ (black) and 100 ℃ (red).

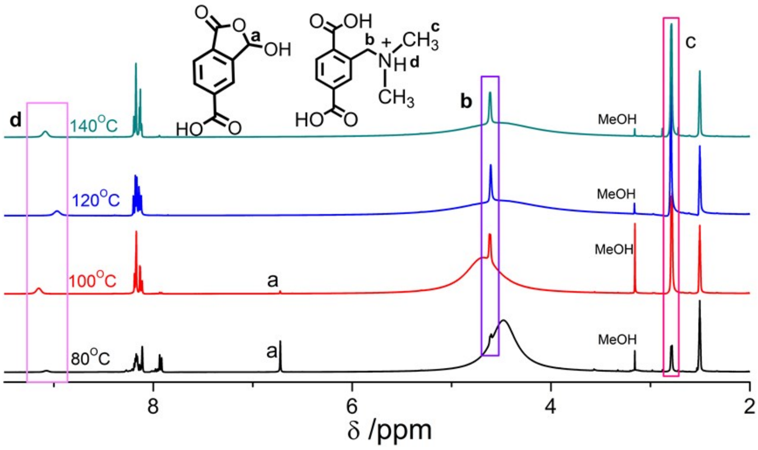


Fig S10 ^{1}H NMR of UiO-66-CH_2NMe_2 synthesized at different temperatures and digested in HF (aq.)/d_6-DMSO.

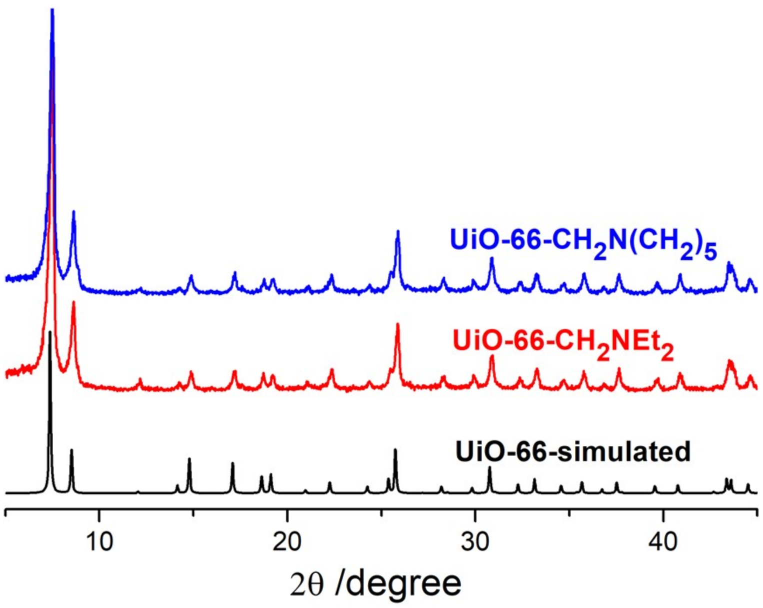


Fig S11 PXRD of UiO-66-type MOFs functionalized with different tertiary aliphatic amines.

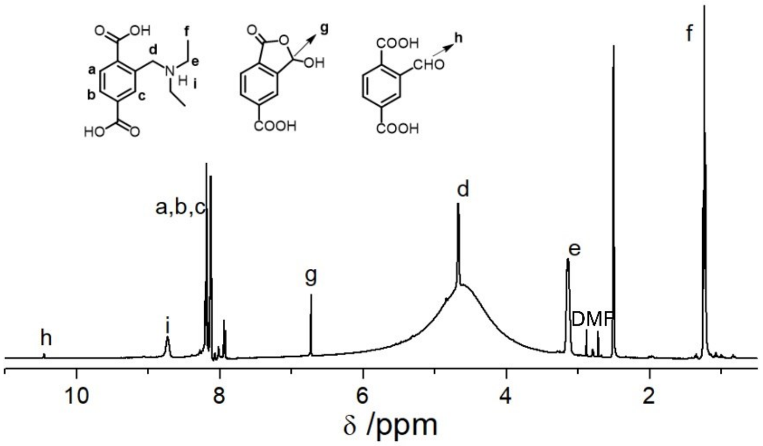


Fig S12 ^{1}H NMR of UiO-66-CH$_2$NEt$_2$ digested in HF (aq.)/d_6-DMSO.

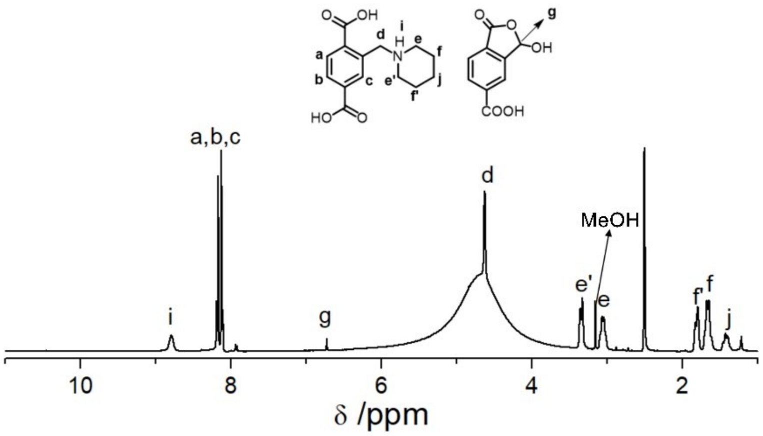


Fig. S13 ^{1}H NMR of UiO-66-CH$_2$N(CH$_2$)$_5$ digested in HF (aq.)/d_6-DMSO.

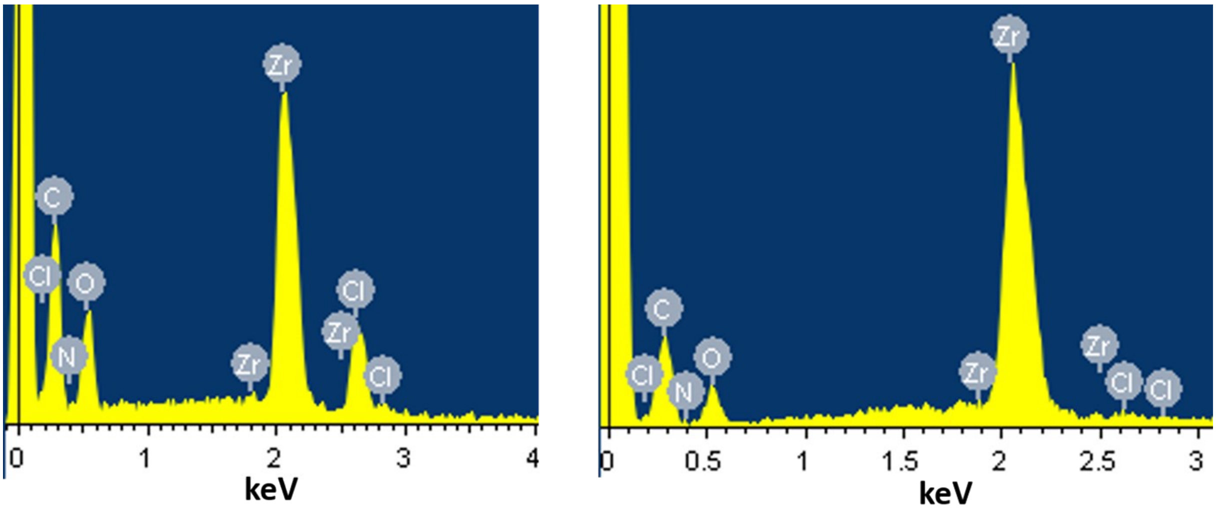


Fig. S14 EDX of UiO-66-CH_2NMe_2 before (left) and after (right) treatment with Et_3N in MeOH.

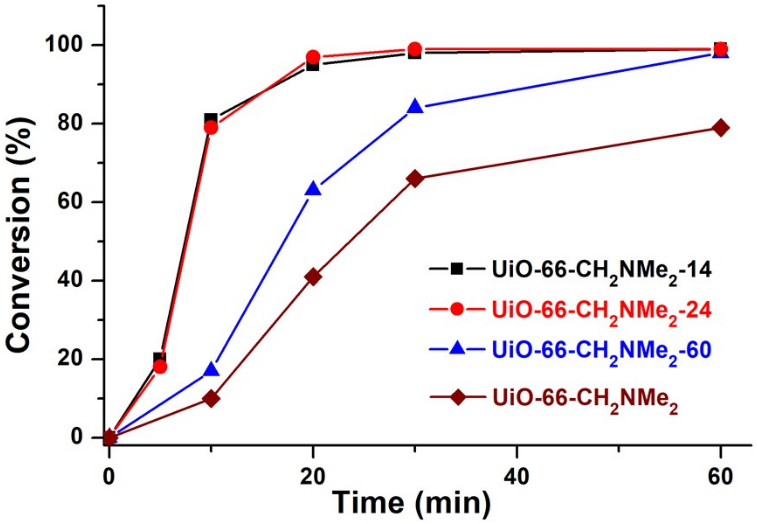


Fig.15 Kinetic curves for catalysis over different MOFs with neutral amino groups. Conditions: benzaldehyde (2.5 mmol), 1,2,4-trichlorobenzene (315 μL, 5.0 mmol), malononitrile (330 mg, 5.0 mmol) and catalyst (10 mol%, to Zr) in toluene (5 mL) under nitrogen at room temperature. The conversions were determined by GC using 1,2,4-trichlorobenzene as the internal standard.

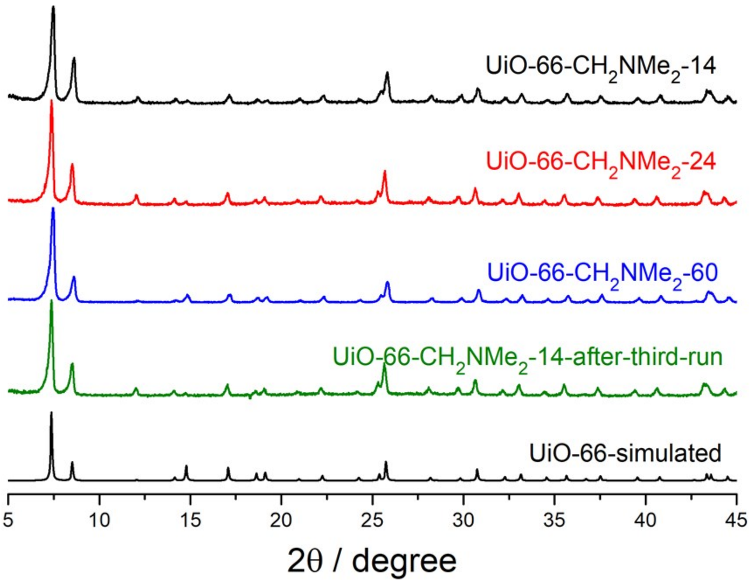


Fig. S16 PXRD of the fresh samples of UiO-66-CH_2NMe_2-14/24/60 and the used sample of UiO-66-CH_2NMe_2-14 after three catalytic runs.

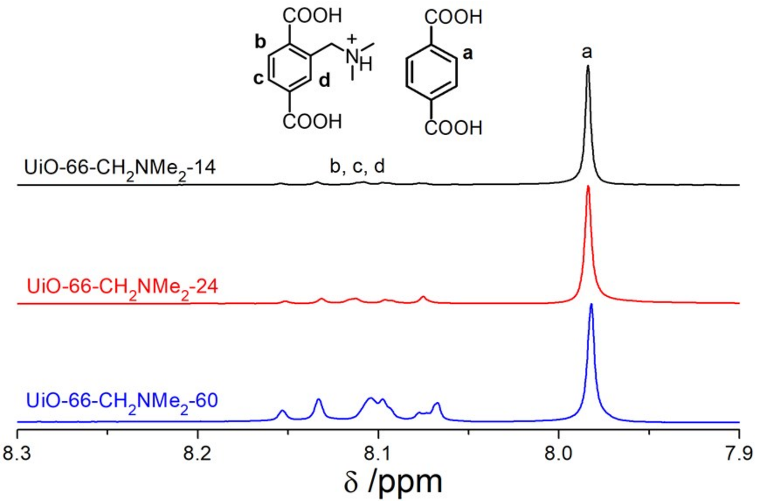


Fig. S17 ^{1}H NMR of UiO-66-CH_2NMe_2-14/24/60 digested in HF (aq.)/d_6-DMSO.

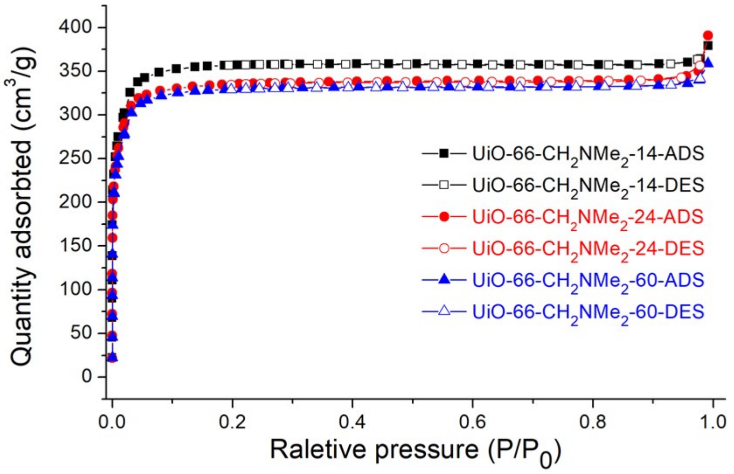


Fig. S18 N_2 adsorption/desorption isotherms of UiO-66-CH_2NMe_2-14/24/60 (with neutral amino groups) activated at 80 ℃ under dynamic vacuum.

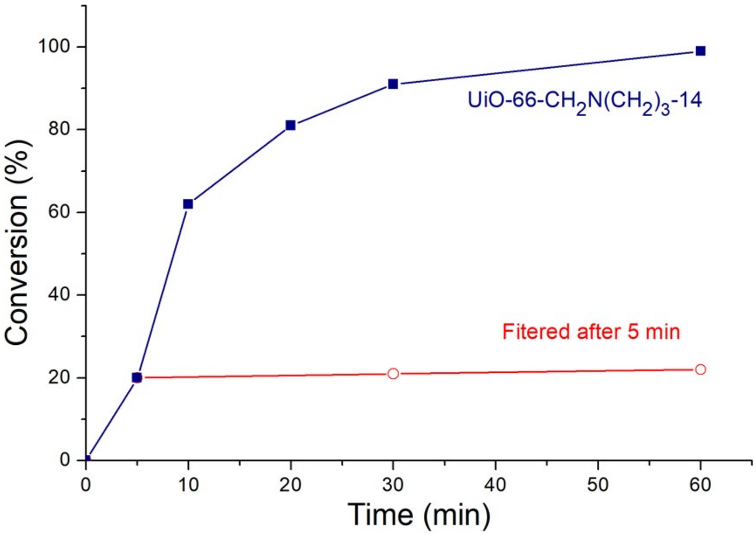


Fig. S19 Filtration test for the catalytic reaction over UiO-66-CH_2NMe_2-14 with neutral amino groups.

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