

## Electronic Supplementary Information

### A new site-isolated acid-base bifunctional metal-organic framework for one-pot tandem reaction

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### Chemicals

Chromium(III) nitrate nonahydrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 99%), chromium(VI) oxide ( $\text{CrO}_3$ , 99%), 1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ , 98%), hydrofluoric acid (HF, 47% aq.), hydrochloric acid (HCl, 37% aq.) and tin(II) chloride dehydrate ( $\text{SnCl}_2$ , 98%) were purchased from Aldrich. Ethanol (>99.5%), methanol (>99.5%), and ammonium fluoride ( $\text{NH}_4\text{F}$ , >99.9%) were supplied from Samchun chemicals in Korea. 2-Amino-1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC-NH}_2$ , 99%), monosodium 2-sulfoterephthalate ( $\text{H}_2\text{BDC-SO}_3\text{Na}$ , 98%), and 2-nitrobenzene-1,4-dicarboxylic acid ( $\text{H}_2\text{BDC-NO}_2$ , 98%) was purchased from TCI (Japan). Sulfonic acid- and primary amine-bound polymer resins (K2621, VP OC 1065) were supplied by Lanxess (Germany).

### Catalyst preparation

Synthesis of MIL-101: In a typical experiment,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.6 g, 4mmol),  $\text{H}_2\text{B}$

DC (0.64 g, 4mmol), HF (0.02 g, 1mmol) and H<sub>2</sub>O (19.2 mL) were mixed under stirring. The substrate mixture was transferred to a Teflon-lined steel autoclave and heated at 493 K for 8 h in a convection oven. After the hydrothermal reaction, the mixture was maintained at 423 K for 1 h, and cooled naturally to room temperature. The green solid product was filtered through 100 µm sieves to remove the crystalline BDC and then through 25 µm filter paper to separate the MIL-101 product. The separated MIL-101 product was washed three times with deionized water, and purified further by following steps; (i) soaked in H<sub>2</sub>O at 343 K for 12 h, (ii) hot ethanol washing at 353 K for 24 h, (iii) an aqueous 0.03 M NH<sub>4</sub>F solution washing at 333 K for 12 h, and (iv) hot H<sub>2</sub>O at 333 K for 12 h. The purified sample was dried in a vacuum at 423 K for 12 h after filtration [12].

Synthesis of MIL-101-NH<sub>2</sub>: Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1.25 g, 3.13 mmol) and H<sub>2</sub>BDC-NH<sub>2</sub> (0.58 g, 3.15 mmol) were added to H<sub>2</sub>O (17.5 mL) and stirred for 3 h at room temperature. The reaction solution was heated at 403 K for 24 h in a convection oven. After the synthesis, the obtained dark-green MIL-101-NH<sub>2</sub> crystals were filtered and washed three times with H<sub>2</sub>O and once with ethanol. Finally, residual solvent was removed at 343 K for 12h under vacuum condition [13].

Synthesis of MIL-101-SO<sub>3</sub>H: CrO<sub>3</sub> (0.50 g, 5 mmol), H<sub>2</sub>BDC-SO<sub>3</sub>Na(1.34 g, 5 mmol), and 12 M HCl (0.36 g, 10 mmol) were dissolved in H<sub>2</sub>O (20 mL), then transferred to a Teflon-lined steel autoclave. This acidic solution was heated at 453 K for 6 days under hydrothermal condition. After the reaction, the resulting greenish solid was filtered and washed with H<sub>2</sub>O and methanol. The sample was dried at 353K for 12 min in a vacuum oven [10].

Synthesis of MIL-101-NO<sub>2</sub>-SO<sub>3</sub>H: CrO<sub>3</sub> (0.5 g, 5 mmol), H<sub>2</sub>BDC-SO<sub>3</sub>Na(0.67 g, 2.5 mmol), H<sub>2</sub>BDC-NO<sub>2</sub>(0.53 g, 2.5 mmol), and 12 M hydrochloric acid (0.72 g, 20 mmol) were added in H<sub>2</sub>O (25 mL), and stirred at 323 K until dissolved. The highly acidic solution was quickly transferred to a Teflon-lined steel autoclave and then heated at 453 K for 6 days in a convection oven. After cooling to room temperature, the dark green-colored product was washed several times with H<sub>2</sub>O, methanol, ethanol, and dried at 343 K for 6 h under vacuum condition.

Synthesis of MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H: The resulting MIL-101-NO<sub>2</sub>-SO<sub>3</sub>H (0.1 g) was dehydrated at 398 K for 4 h and suspended in 20 mL of ethanol. To this suspension, SnCl<sub>2</sub>·2H<sub>2</sub>O (3.26g) was added slowly and stirred for 2 h at room temperature. The mixture was heat

ed at 343 K for 6 h in an oven and the product was centrifuged and soaked in 20 mL of 12 M hydrochloric acid for 24 h. After filtration, the greenish solid was washed with H<sub>2</sub>O and ethanol, dried at 343 K, and stored in a desiccator.

### **Catalyst characterization**

X-ray powder diffraction (XRD) analysis was performed on a Rigaku diffractometer using CuK $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation at 0.5 °/min. N<sub>2</sub> adsorption and desorption isotherms were measured in a BELsorp-Max (BEL, JAPAN) at 77K. The specific surface areas and pore volume of samples were calculated by the BET (Brunauer–Emmett–Teller) method, and pore size distribution by Horvath-Kawazoe (HK) method. Prior to the adsorption, MIL-101 and MIL-101-NH<sub>2</sub> were activated at 423 K for 12 h under vacuum condition, whereas MIL-101-SO<sub>3</sub>H, MIL-101-NO<sub>2</sub>-SO<sub>3</sub>H, and MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H were activated at 398 K for 6 h in vacuum. FT-IR spectra were obtained on a VERTEX 80V FT-IR spectrometer (Bruker) at ambient conditions. The sulfur and nitrogen contents in the MOFs were measured using an elemental analysis (Flash EA1112, Thermo). Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) profiles of the MIL-101 and its functionalized forms were obtained using a homemade TPD apparatus. Before ammonia adsorption, samples were treated in a helium flow of 100 ml/min at 373 K for 2 h. The samples were subsequently exposed to pulses of ammonia (1,000 ppm with H<sub>2</sub> balance) until saturation, and then purged with helium flow at 373 K for 1 h. The temperature of the samples was increased to 673 K at a ramping rate of 5 K/min, and the desorbed ammonia was detected using a quadrupole mass unit (Agilent 5000A).

### **Catalytic activity test**

One-pot tandem conversion of benzaldehydedimethylacetal **1** to trans-1-nitro-2-phenylethylene **3** was carried out in liquid phase under atmospheric pressure. Before use, MIL-101 series catalysts were activated at 393 K for 4 h under vacuum condition. Polymer resin catalysts stored in a desiccator after washing with H<sub>2</sub>O and nitromethane were directly used without further activation. In a typical run, 1 mmol of benzaldehydedimethylacetal, 0.1 g of o-xylene (internal standard), 5 ml of nitromethane, and 0.05 g of activated catalyst were introduced

to a 25 ml three-necked round bottom flask equipped with a condenser and a thermocouple. When temperature reached to 323 K, reaction was started by stirring (800 rpm) for 6 h under  $N_2$ . After a reaction, catalyst was separated from reaction product by centrifugation. The reaction product was analyzed by HP 5890 Gas Chromatography (GC) equipped with Carbowax column with a Flame Ignition Detector (FID). The recovered catalyst was thoroughly washed with nitromethane and acetone, and reused for recycle runs.

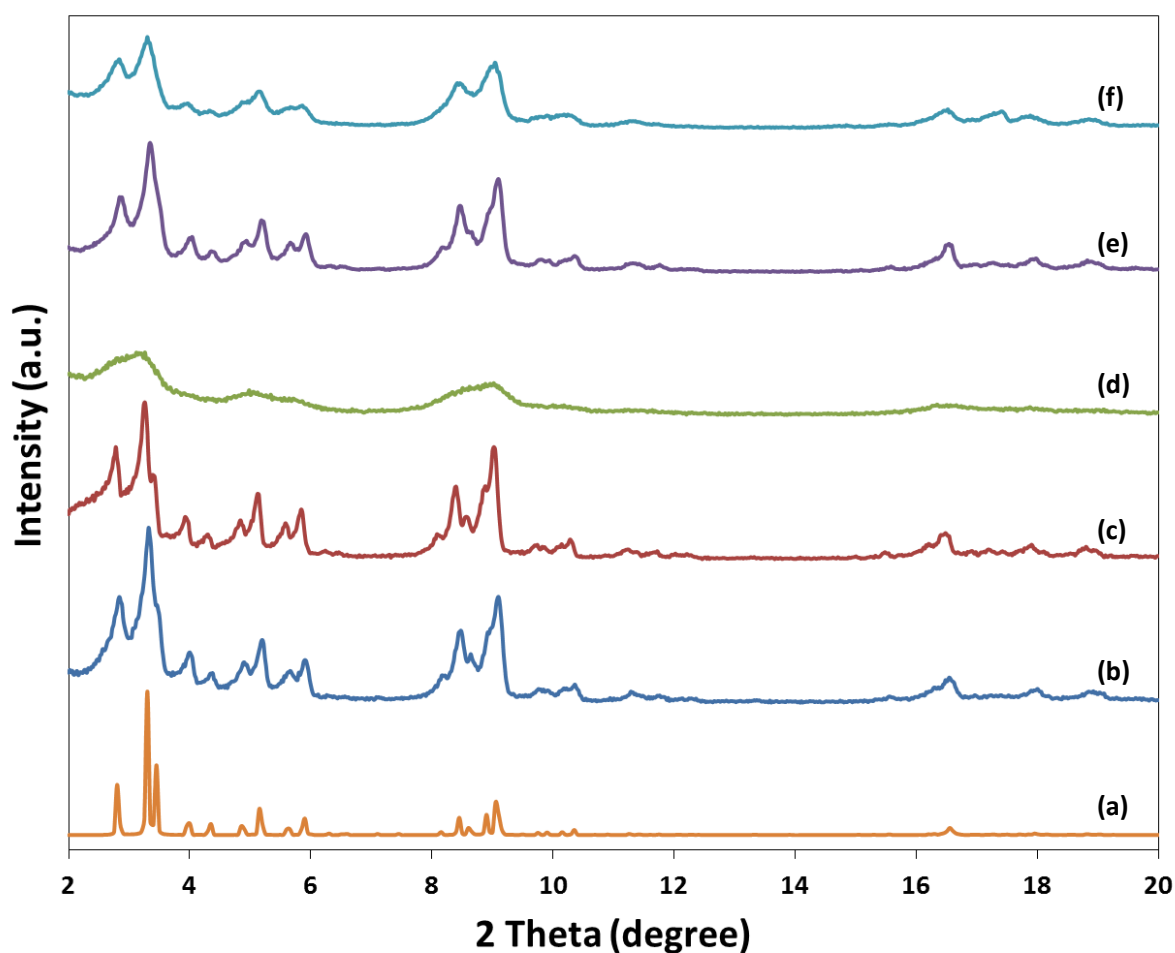


Fig. S1. XRD patterns of MIL-101 and its functionalized forms; (a) MIL-101 simulated, (b) MIL-101, (c) MIL-101-SO<sub>3</sub>H, (d) MIL-101-NH<sub>2</sub>, (e) MIL-101-NO<sub>2</sub>-SO<sub>3</sub>H, and (f) MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H.

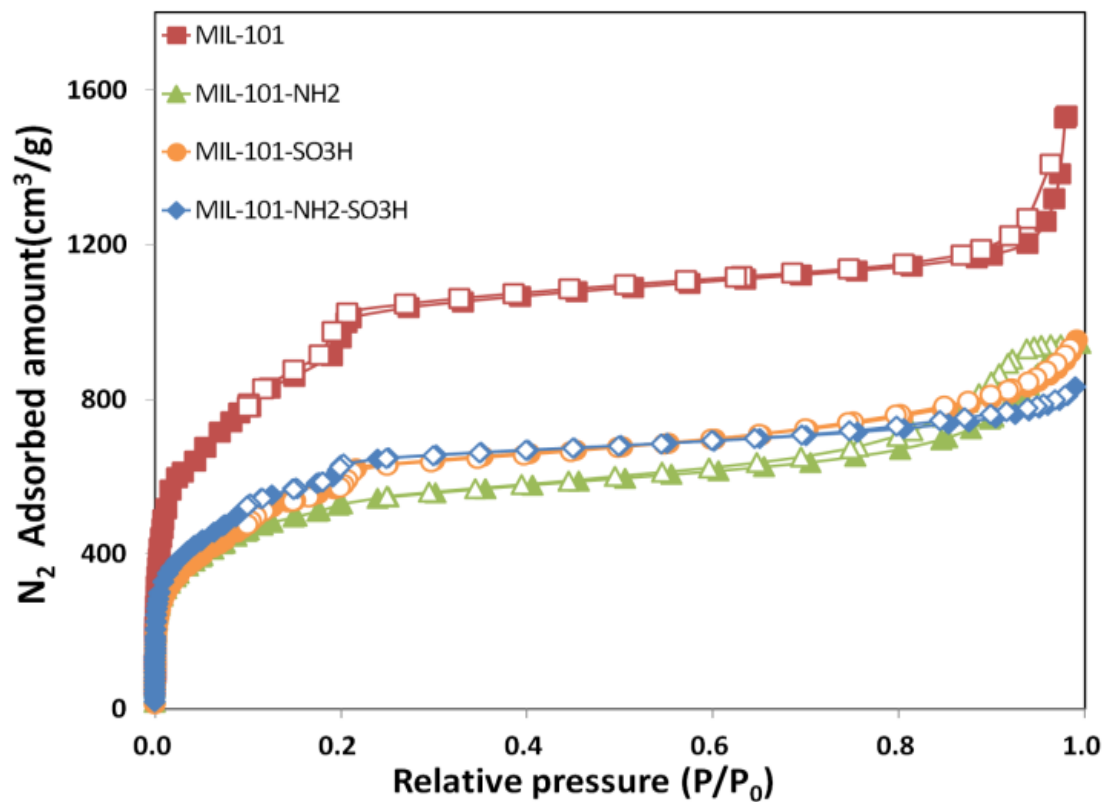
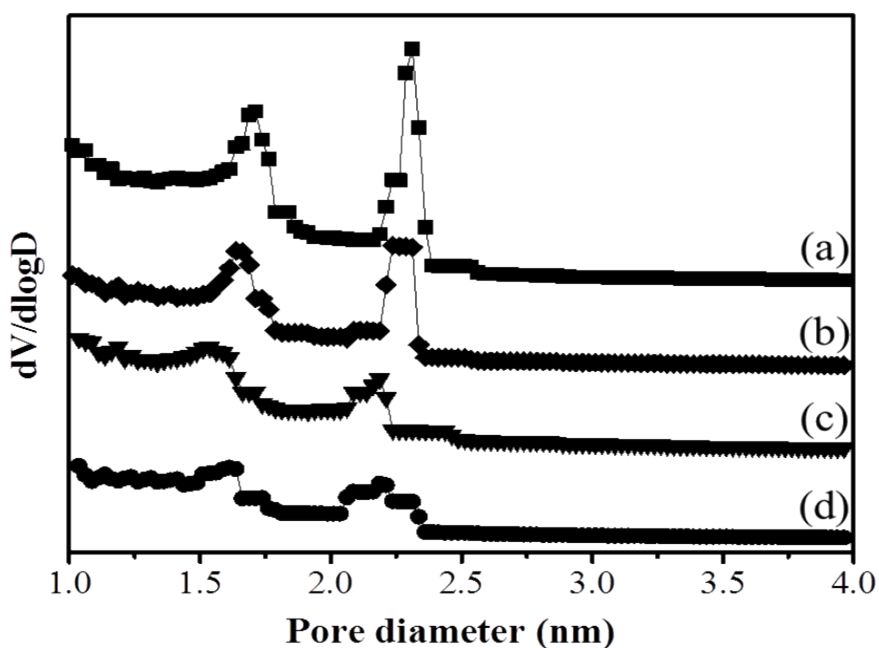


Fig. S2. N<sub>2</sub> adsorption–desorption isotherms of MIL-101 and its functionalized forms.



**Fig. S3** Pore size distribution curves calculated by Horvath-Kawazoe (HK) method of (a) MIL-101, (b) MIL101-SO<sub>3</sub>H, (c) MIL101-NH<sub>2</sub>, and (d) MIL101-NH<sub>2</sub>-SO<sub>3</sub>H.

The pore size distribution curves of the MIL-101 and its functionalized forms were shown above exhibiting two different monodisperse pore sizes [13]. While the average pore sizes of MIL-101 were 1.71 and 2.31 nm, those of its functionalized forms show smaller values in MIL101-SO<sub>3</sub>H with 1.63 and 2.23nm, MIL-101-NH<sub>2</sub> with 1.58 and 2.15 nm, and MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H with 1.60 and 2.20 nm (and also the pore size distribution became slightly broader) due to the presence of -NH<sub>2</sub> and -SO<sub>3</sub>H groups blocking the pores in the MIL-101.

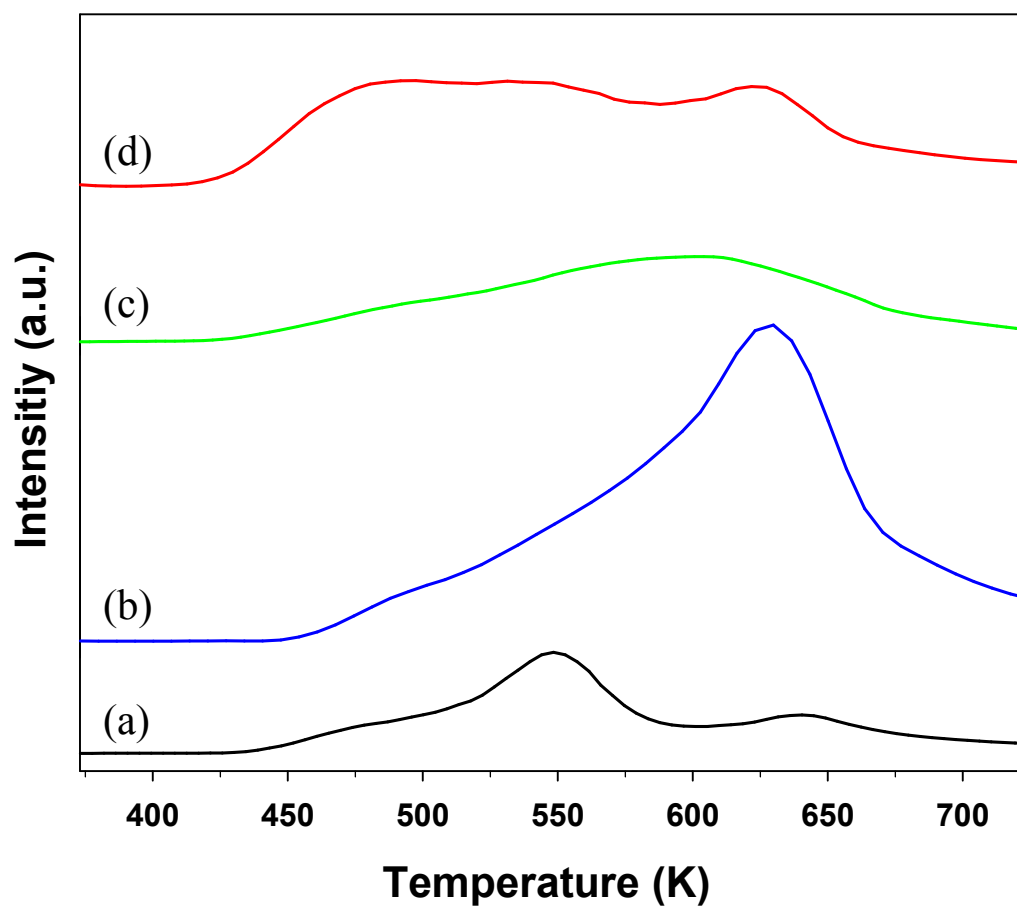


Fig. S4. NH<sub>3</sub>-TPD profiles of MIL-101 and its functionalized structures; (a) MIL-101, (b) MIL-101-SO<sub>3</sub>H, (c) MIL-101-NH<sub>2</sub>, and (d) MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H.

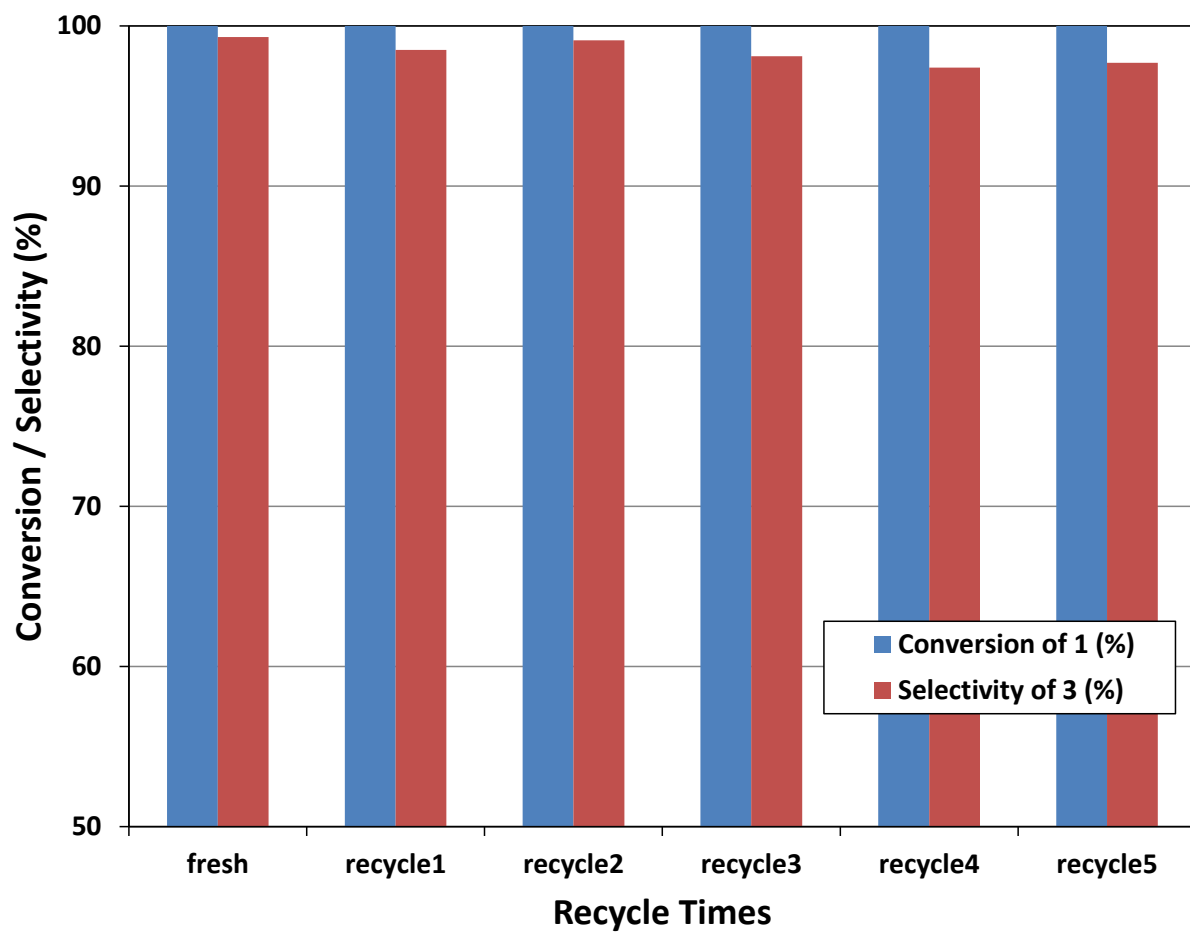


Fig. S5. Recycle test of MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H for one-pot tandem reaction.



Table S1. Elemental analysis of MIL-101 and its functionalized forms

Catalyst	Sulfonic acid (mmol/g)	Primary amine (mmol/g)
MIL-101	-	-
MIL-101-SO <sub>3</sub> H	2.22	-
MIL-101-NH <sub>2</sub>	-	2.56
MIL-101-NH <sub>2</sub> -SO <sub>3</sub> H	0.68	1.26

Table S2. Catalytic performance of resin catalysts for one-pot tandem reaction <sup>a</sup>

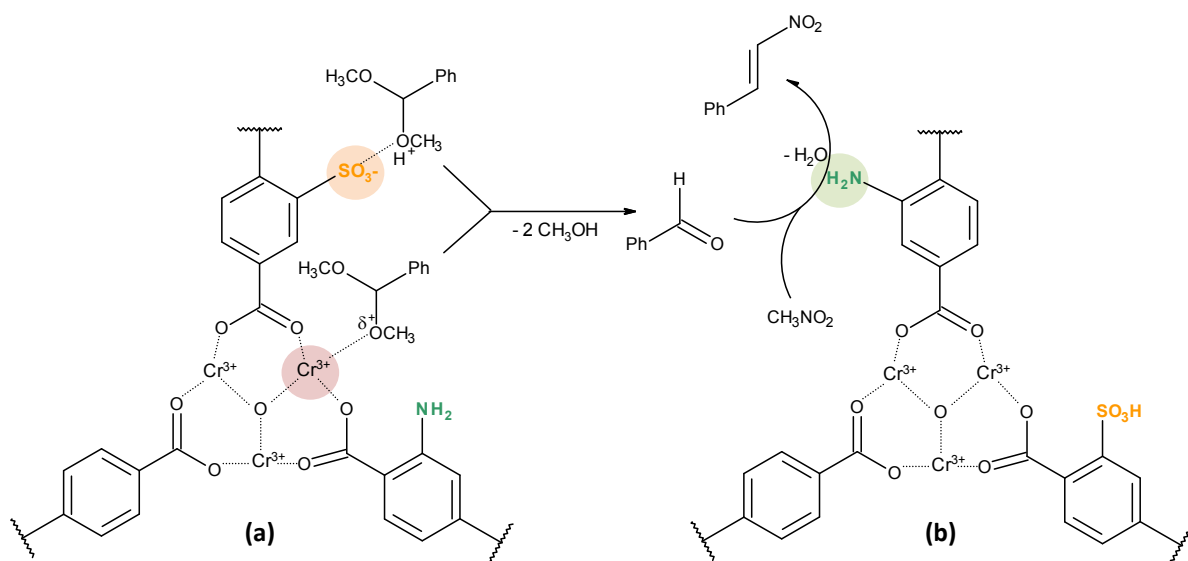
Entry	Catalyst	Conv. (%)	Selectivity (%)	
			<b>2</b>	<b>3</b>
1	SO <sub>3</sub> H-bound resin <sup>b</sup>	100	100	-
2	NH <sub>2</sub> -bound resin <sup>c</sup>	-	-	-
3	NH <sub>2</sub> -bound resin <sup>c</sup>	100 <sup>d</sup>	-	100

<sup>a</sup> Reaction conditions: catalyst (0.05 g), benzaldehydedimethylacetal (1 mmol), o-xylene (0.1 g), nitromethane (5 ml), 323 K, 6h; <sup>b</sup> commercial resin (K2621, Lanxess); <sup>c</sup> commercial resin (VP OC 1065, Lanxess); <sup>d</sup> benzaldehyde **2** was used as a reactant instead of benzaldehydedimethylacetal **1**.

Table S3. Catalytic activities of various catalysts in deacetalization-Henry reaction

Catalyst	Temp. (K)	Time (h)	Yield of <b>3</b> (%)	Reference
MIL-101-NH <sub>2</sub> -SO <sub>3</sub> H	323	6	99.3	Present work
PMO-NH <sub>2</sub> -SO <sub>3</sub> H <sup>a</sup>	363	20	97.5	[3]
HPA-NH <sub>2</sub> -SBA-15 <sup>b</sup>	323	12	97	[4]
MIL-101-NH <sub>2</sub> -SO <sub>3</sub> H <sup>c</sup>	363	24	97.0	[8]
AB-MCM-41-co <sup>d</sup>	363	7	94.5	[20]
AB-MCM-41-g <sup>e</sup>	363	1.5	98.9	[20]

<sup>a</sup> Bifunctional Periodic mesoporous organosilicas (PMOs) containing organic amines and sulfonic acid groups; <sup>b</sup> Heteropoly acid and amine-grafted SBA-15; <sup>c</sup> Solvothermal synthesis of MIL-101 and subsequent three-step post-synthetic modification of MIL-101; <sup>d</sup> Bifunctional mesoporous MCM-41 containing amine and sulfonic acid groups synthesized through co-condensation using amino-protected reagent; <sup>e</sup> Bifunctional mesoporous MCM-41 containing amine and sulfonic acid groups synthesized by the modification of SO<sub>3</sub>H-MCM-41 surfaces with organic amine group.



Scheme S1. Postulated tandem reaction pathways on the MIL-101-NH<sub>2</sub>-SO<sub>3</sub>H; (a) acid catalysis by a metal node or a sulfonic acid group at a linker, (b) base catalysis by an amine group at another linker.