

## Conversion of primary amines into secondary amines on a metal-organic framework using a tandem post-synthetic modification

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### Supplementary information

#### General experimental details

Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2-aminobenzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>), anhydrous DMF, NaBH<sub>3</sub>CN, ethanal, propanal, butanal and octanal were purchased from Sigma-Aldrich and used without further purification. Anhydrous THF was taken from an in-house solvent purification system and kept under an inert atmosphere of nitrogen. Methanol (Fisher) was laboratory reagent grade and kept over 4 Å molecular sieves. Reactions were carried out in glass 10 cm<sup>3</sup> vials (Biotage) in a Sanyo drying oven. [Zn<sub>4</sub>O(bdc-NH<sub>2</sub>)<sub>3</sub>] (IRMOF-3) was prepared following the previously reported method.<sup>S1</sup>

Powder X-ray diffraction (PXRD) was carried out on a Bruker axs D8 Advance diffractometer with a Super Speed detector, using copper K<sub>α</sub> radiation, with wavelength,  $\lambda = 1.5406 \text{ \AA}$ , at 298 K and with a beam slit set to 1 mm, detector slit set to 0.2 mm and anti-scattering slit set to 1 mm. Samples were ground in THF, then packed into 0.5 mm diameter capillary tubes. The scan speed was 1 s per step with a step size ( $2\theta$ ) of 0.02.

Samples for NMR studies were dried in an oven for 1 h at 100 °C, then digested in 0.4 cm<sup>3</sup> DMSO-*d*<sub>6</sub> and 0.2 cm<sup>3</sup> stock DCl solution (0.1 cm<sup>3</sup> 35% DCl/D<sub>2</sub>O, in 3 cm<sup>3</sup> DMSO-*d*<sub>6</sub>). Spectra were recorded at 298 K on a Bruker Advance 300 MHz Ultrashield NMR spectrometer. <sup>1</sup>H NMR spectra were referenced to the residual *protio* peaks at  $\delta$  2.50 ppm for DMSO-*d*<sub>6</sub>.

## Synthesis of 2-(ethylamino)benzene-1,4-dicarboxylic acid, H<sub>2</sub>bdc-NHEt

2-Aminobenzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>) (0.200 g, 1.104 mmol) was dissolved in *N,N'*-dimethylformamide (DMF) (10 cm<sup>3</sup>), then ethanal (0.124 cm<sup>3</sup>, 2.208 mmol) was added at 10 °C and the solution stirred at this temperature for 1 h. The solution was then cooled in an ice bath and NaBH<sub>3</sub>CN (0.139 g, 2.204 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.146 g (63 %). <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 7.79 (d, 1H, *J* = 7.8 Hz), 7.05 (s (br), 1H), 6.97 (dd, 1H, *J* = 7.8 Hz, 1.5 Hz), 3.11 (q, 2H, *J* = 7.0 Hz), 1.21 (t, 3H, *J* = 7.0 Hz). <sup>13</sup>C NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 169.9, 167.5, 150.7, 136.1, 132.3, 114.7, 113.3, 112.1, 37.05, 14.6. *m/z* (ESI) 208.0598 ([M – H]<sup>–</sup>. [C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>N]<sup>–</sup> requires 208.0610). Found C: 57.15, H: 5.41, N: 7.01 %. C<sub>10</sub>H<sub>11</sub>O<sub>4</sub>N requires C: 57.41, H: 5.30, N: 6.70 %.

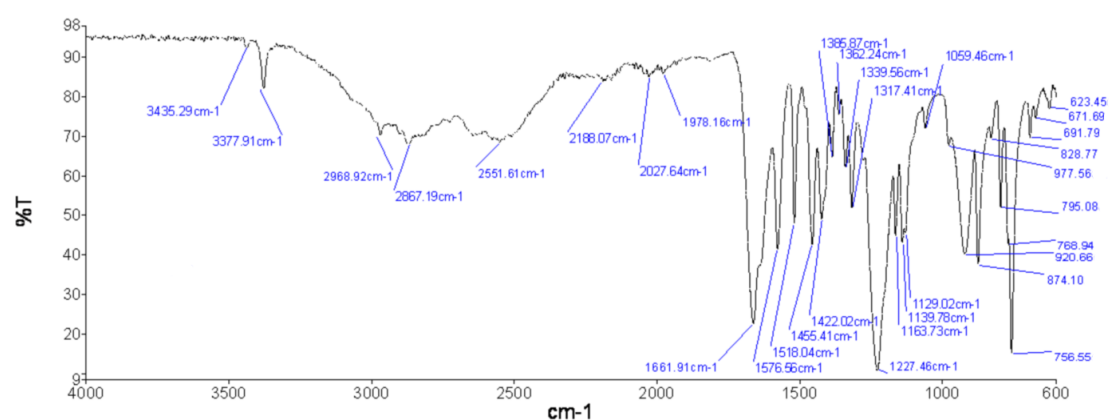


Fig. S1. Infrared spectrum for H<sub>2</sub>bdc-NHEt

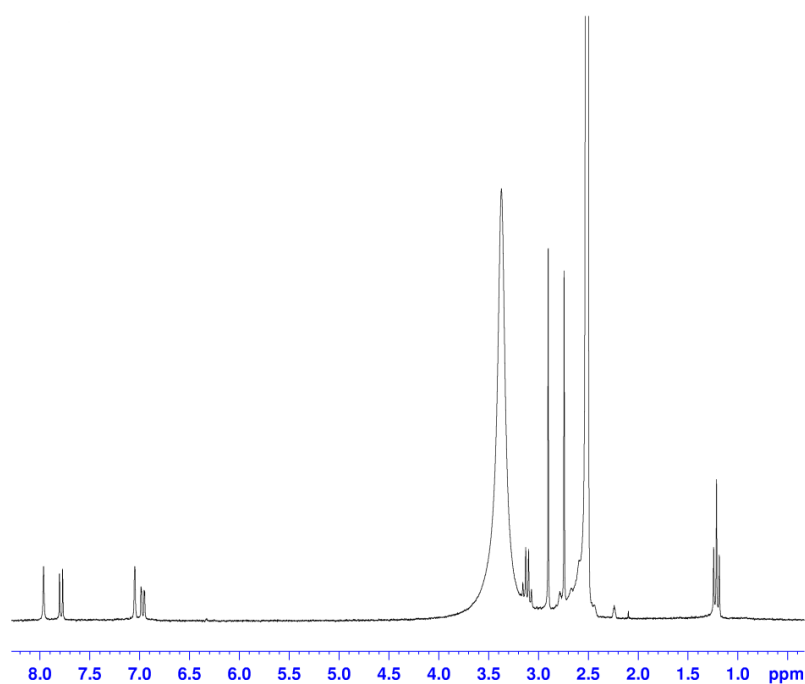


Fig. S2. <sup>1</sup>H NMR spectrum for H<sub>2</sub>bdc-NHEt in DMSO-*d*<sub>6</sub>.

## Synthesis of 2-(propylamino)benzene-1,4-dicarboxylic acid, H<sub>2</sub>bdc-NHPr

2-Aminobenzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>) (0.200 g, 1.104 mmol) was dissolved in *N,N*-dimethylformamide (DMF) (10 cm<sup>3</sup>), then propanal (0.161 cm<sup>3</sup>, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH<sub>3</sub>CN (0.139 g, 2.204 mmol) added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.227 g (92 %). <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 7.85 (d, 1H, *J* = 8.0 Hz), 7.22 (d, 1H, *J* = 1.6 Hz), 7.05 (dd, 1H, *J* = 8.0 Hz, 1.4 Hz), 3.15 (t, 2H, *J* = 7.2 Hz), 1.61 (sextet, 2H, *J* = 7.2 Hz), 0.95 (t, 3H, *J* = 7.2 Hz). <sup>13</sup>C NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 169.9, 167.5, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 44.2, 22.1, 11.8. *m/z* (ESI) 222.0807 ([M – H]<sup>−</sup>. [C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>N]<sup>−</sup> requires 222.0766). Found C: 59.00, H: 5.95, N: 6.50 %. C<sub>11</sub>H<sub>13</sub>O<sub>4</sub>N requires C: 59.45, H: 5.44, N: 6.30 %.

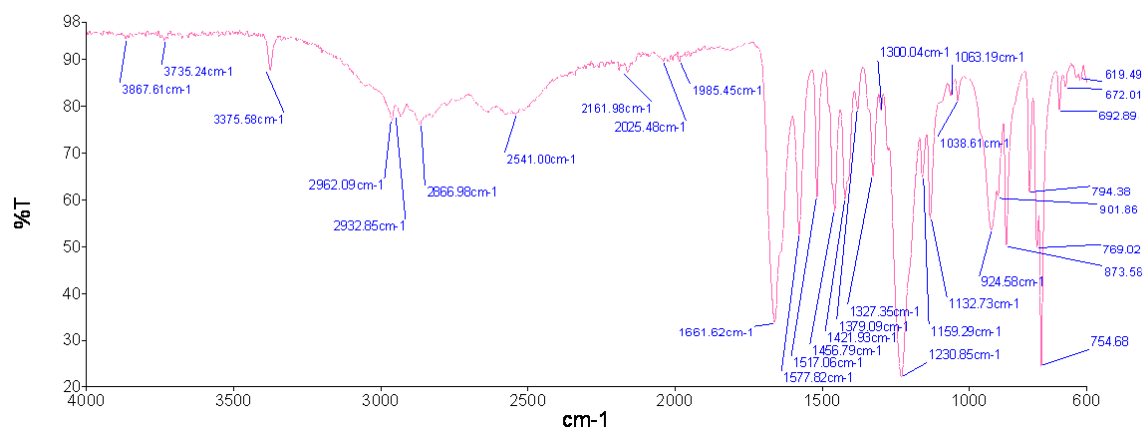


Fig. S3. Infrared spectrum for H<sub>2</sub>bdc-NHPr

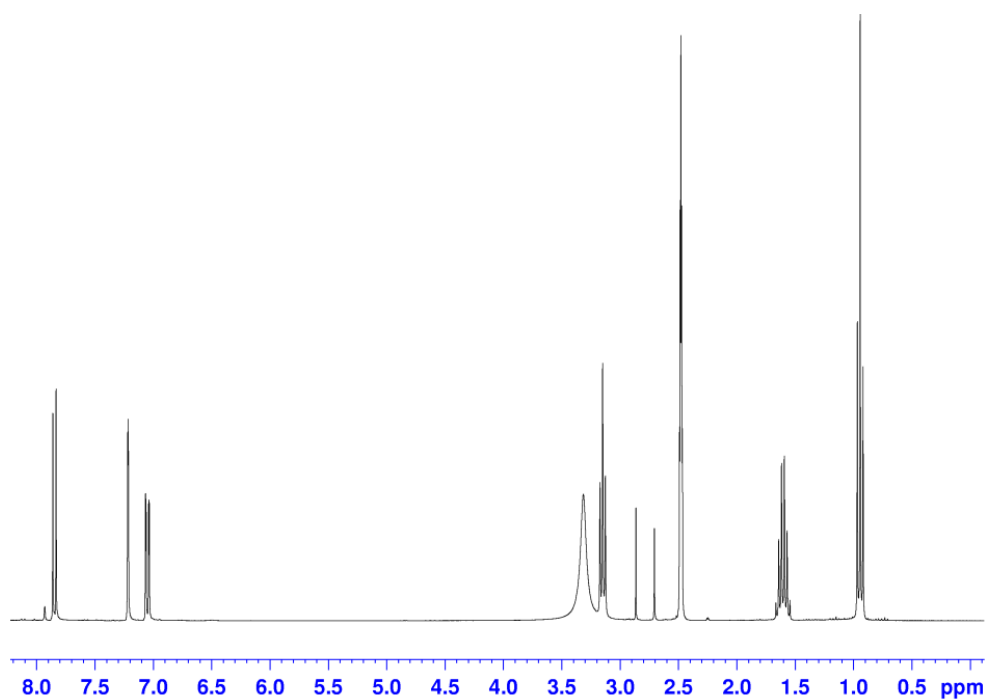


Fig. S4. <sup>1</sup>H NMR spectrum for H<sub>2</sub>bdc-NHPr in DMSO-*d*<sub>6</sub>.

## Synthesis of 2-(butylamino)benzene-1,4-dicarboxylic acid, H<sub>2</sub>bdc-NHBu

2-Aminobenzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>) (0.200 g, 1.104 mmol) was dissolved in *N,N'*-dimethylformamide (DMF) (10 cm<sup>3</sup>), then butanal (0.195 cm<sup>3</sup>, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH<sub>3</sub>CN (0.139 g, 2.204 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.117 g (45 %). <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 7.84 (d, 1H, *J* = 8.2 Hz), 7.22 (d, 1H, *J* = 1.5 Hz), 7.05 (dd, 1H, *J* = 7.8 Hz, 1.5 Hz), 3.18 (t, 2H, *J* = 7.5 Hz), 1.58 (quintet, 2H, *J* = 6.7 Hz), 1.38 (sextet, 2H, *J* = 7.5 Hz), 0.91 (t, 3H, *J* = 6.7 Hz). <sup>13</sup>C NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 169.9, 167.5, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 42.1, 30.9, 20.1, 14.0. *m/z* (ESI) 236.0948 ([M – H]<sup>–</sup>. [C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>N]<sup>–</sup> requires 236.0923). Found C: 60.80, H: 6.49, N: 6.06 %. C<sub>12</sub>H<sub>15</sub>O<sub>4</sub>N requires C: 60.75, H: 6.37, N: 5.90 %.

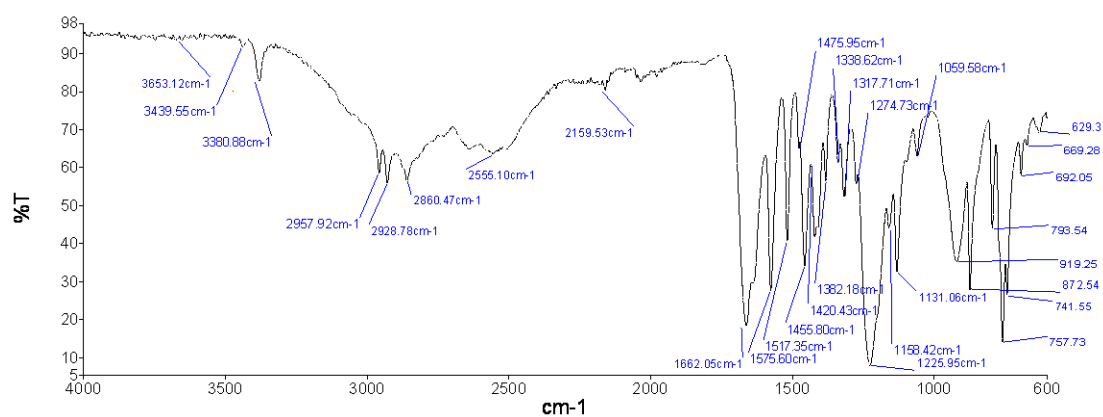


Fig. S5. Infrared spectrum for H<sub>2</sub>bdc-NHBu

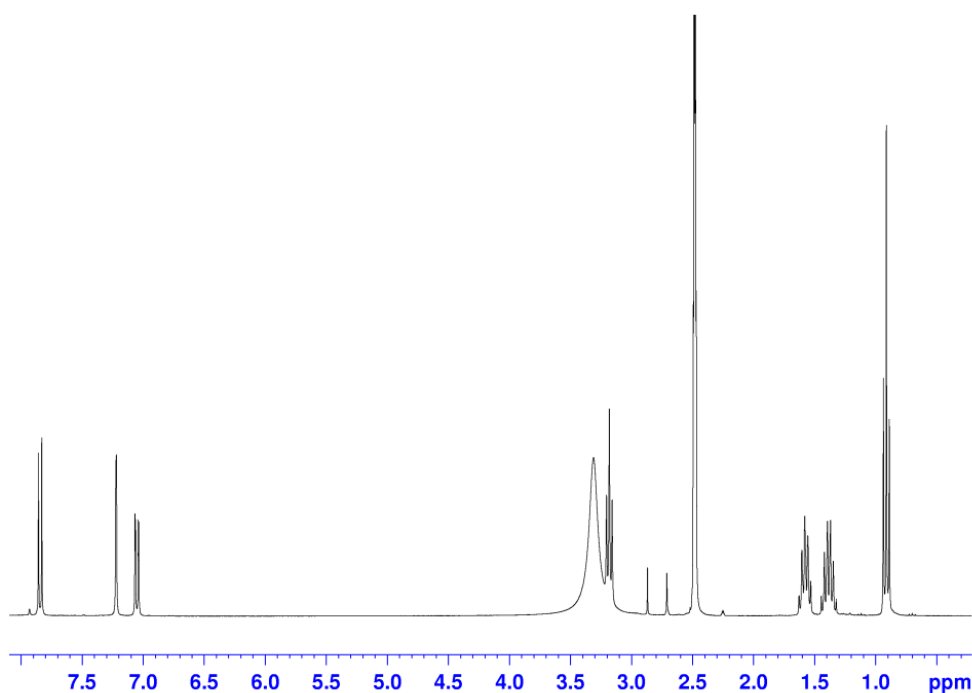


Fig. S6. <sup>1</sup>H NMR spectrum for H<sub>2</sub>bdc-NHBu in DMSO-*d*<sub>6</sub>.

## Synthesis of 2-(octylamino)benzene-1,4-dicarboxylic acid, H<sub>2</sub>bdc-NHC<sub>8</sub>H<sub>17</sub>

2-Aminobenzene-1,4-dicarboxylic acid (H<sub>2</sub>bdc-NH<sub>2</sub>) (0.200 g, 1.104 mmol) was dissolved in *N,N'*-dimethylformamide (DMF) (10 cm<sup>3</sup>), then octanal (0.345 cm<sup>3</sup>, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaBH<sub>3</sub>CN (0.139 g, 2.204 mmol) added. The resulting reaction mixture was stirred at room temperature for 24 h. The mixture was acidified with 1 M HCl, and water was added until a yellow solid precipitated. Yield: 0.313 g (97 %). <sup>1</sup>H NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 7.84 (d, 1H, *J* = 8.2 Hz), 7.21 (d, 1H, *J* = 1.4 Hz), 7.05 (dd, 1H, *J* = 8.2 Hz, 1.4 Hz), 3.17 (t, 2H, *J* = 7.0 Hz), 1.58 (quintet, 2H, *J* = 6.3 Hz), 1.40-1.15 (m, 10H), 0.83 (t, 3H, *J* = 6.9 Hz). <sup>13</sup>C NMR (300MHz, DMSO-*d*<sub>6</sub>) δ/ppm: 169.9, 167.6, 150.9, 136.1, 132.3, 114.6, 113.3, 112.1, 42.4, 31.5, 29.01, 28.98, 28.8, 26.8, 22.4, 14.3. *m/z* (ESI) 292.1574 ([M – H]<sup>–</sup>. [C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>N]<sup>–</sup> requires 292.1549). Found C: 66.20, H: 8.75, N: 4.26 %. C<sub>16</sub>H<sub>23</sub>O<sub>4</sub>N requires C: 65.51, H: 7.90, N: 4.77 %.

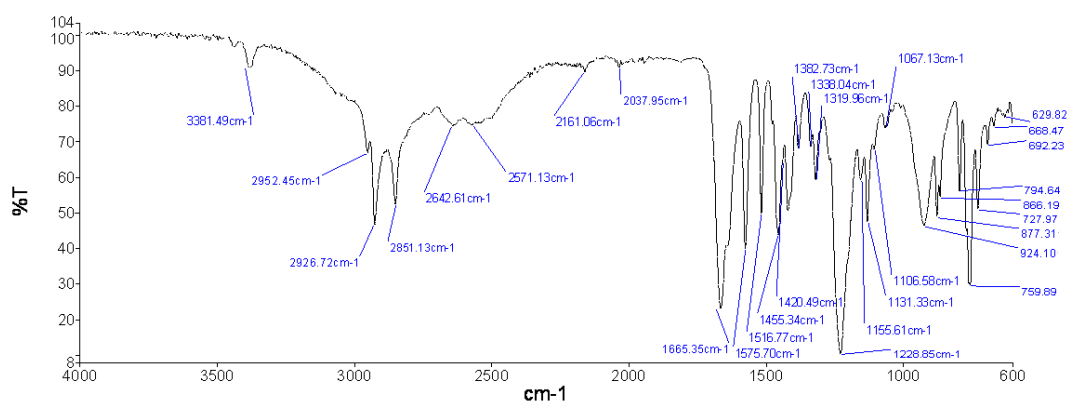


Fig. S7. Infrared spectrum for H<sub>2</sub>bdc-NHC<sub>8</sub>H<sub>17</sub>.

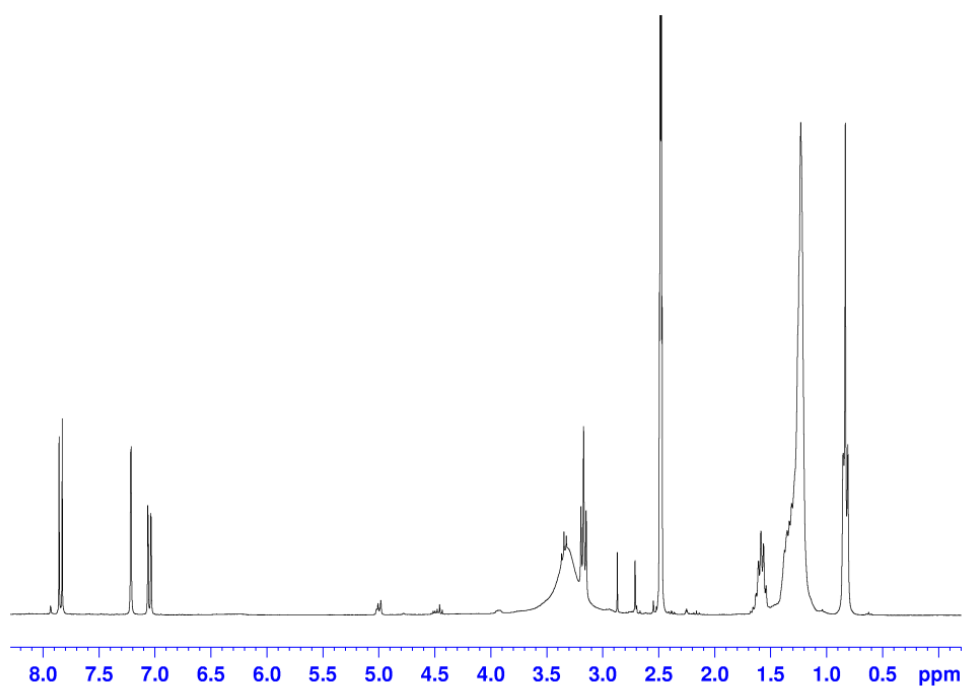
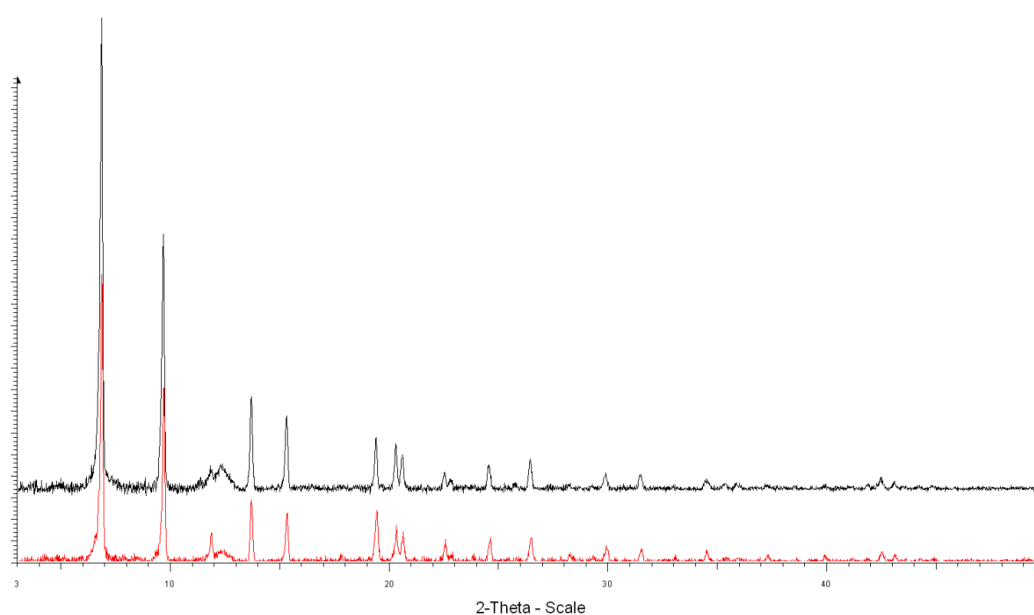


Fig. S8. <sup>1</sup>H NMR spectrum for H<sub>2</sub>bdc-NHC<sub>8</sub>H<sub>17</sub> in DMSO-*d*<sub>6</sub>.

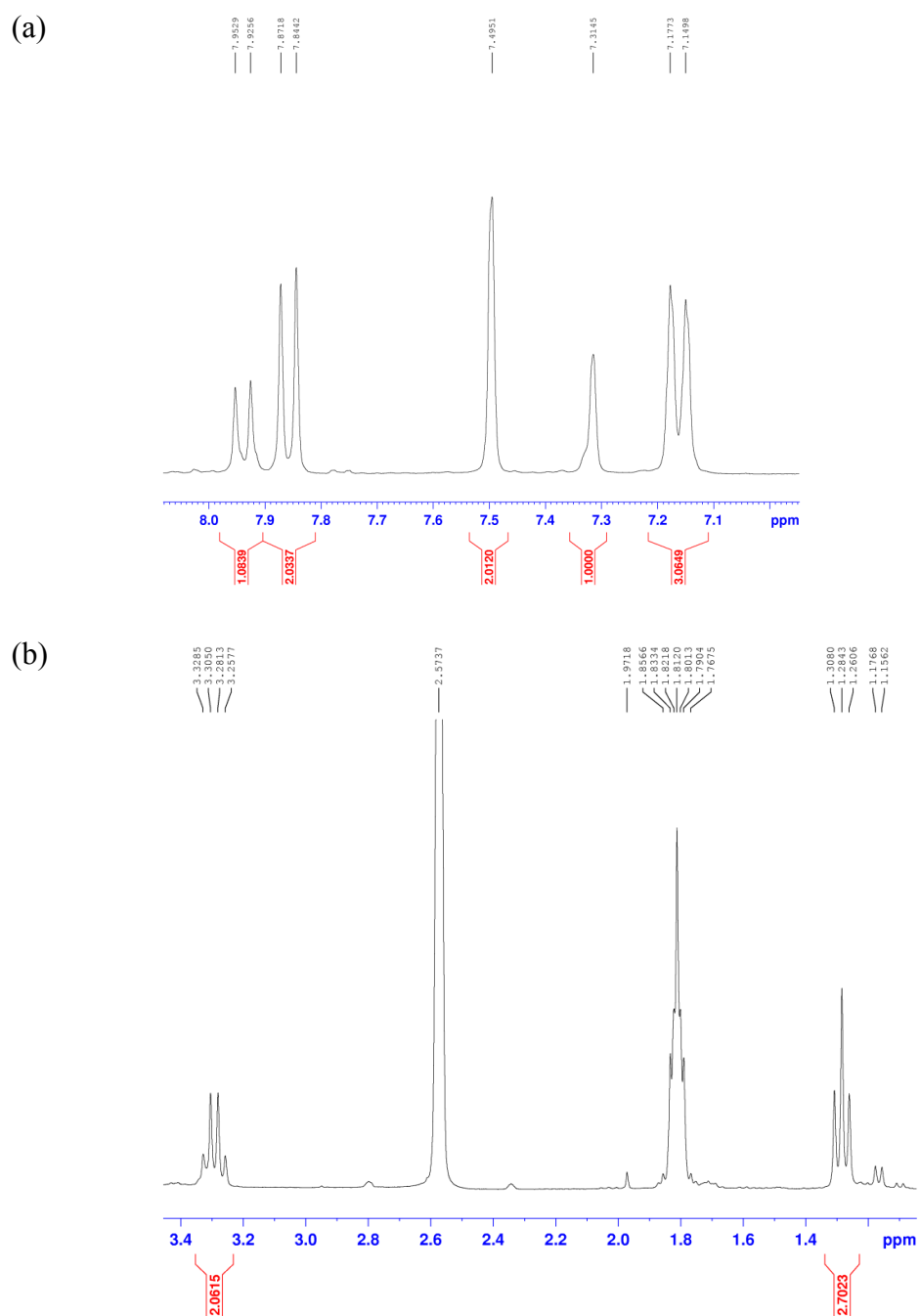
### General procedure for post-synthetic modification reactions

Crystals of IRMOF-3 (0.100 g, 0.23 mmol eq.  $\text{NH}_2$ ) were soaked in anhydrous THF for 3 days, replacing with fresh anhydrous THF every 24 h. 4 equivalents of the aldehyde (0.92 mmol) were added and the reaction mixture was left for 24 h at 293 K. 4 equivalents of  $\text{NaBH}_3\text{CN}$  (0.058 g, 0.92 mmol) were then added to the reaction mixture, which was left for a further 48 h. The product was then washed by decantation, with fresh anhydrous THF every 24 h for 3 days. The resulting solid was stored under anhydrous THF until needed for analysis.

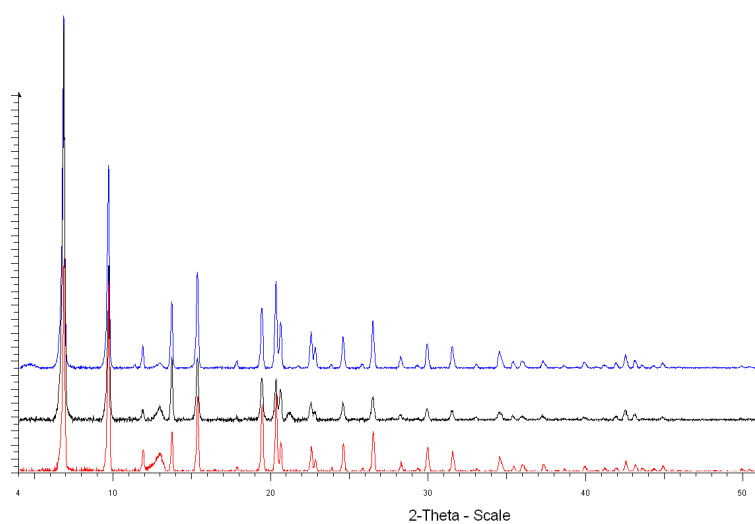
Reactions in THF-MeOH (15:1) were carried out in a similar way, differing only in the solvent used. These reactions were carried out at 293 K and 323 K.



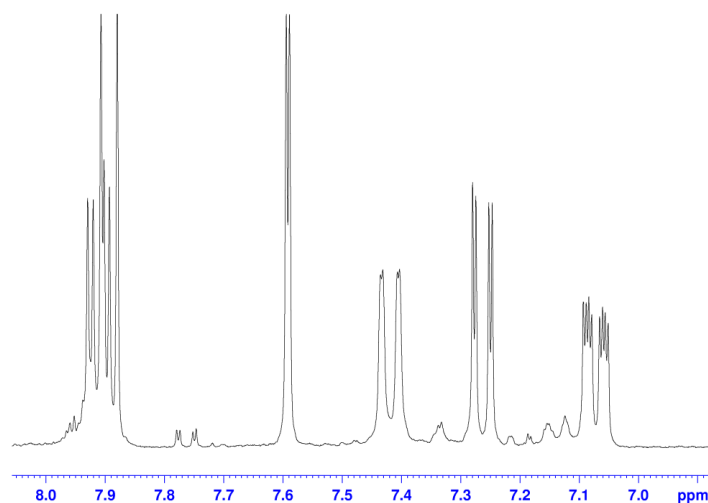
**Fig. S9.** Powder X-ray diffraction patterns for IRMOF-3 (red) and the product from the reaction between IRMOF-3, MeCHO and  $\text{NaBH}_3\text{CN}$  in THF (in black).



**Fig. S10.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3, MeCHO and  $\text{NaBH}_3\text{CN}$  in THF, showing (a) the aromatic region, (b) the aliphatic region.

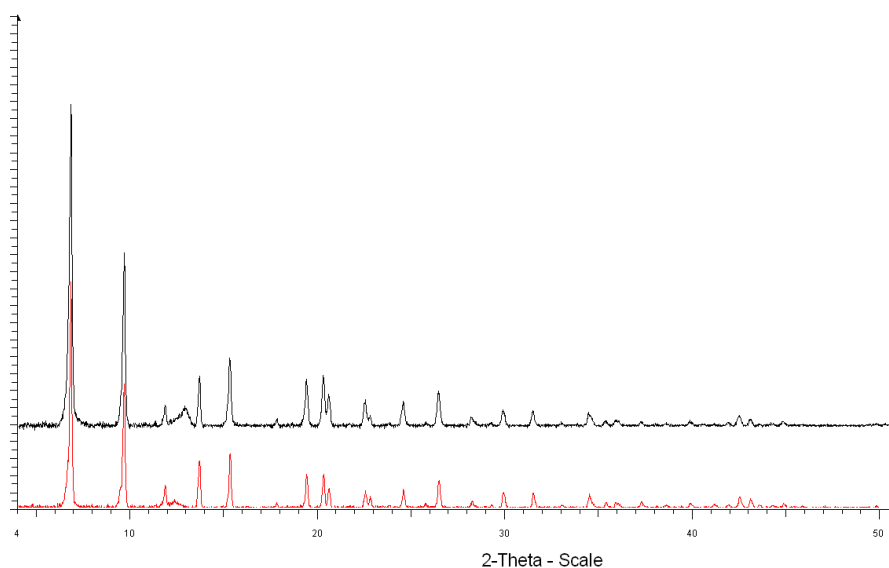


**Fig. S11.** Powder X-ray diffraction pattern for the product from the reaction between IRMOF-3, EtCHO and NaBH<sub>3</sub>CN in THF, after 1 day (red), 3 days (black) and 6 days (blue).

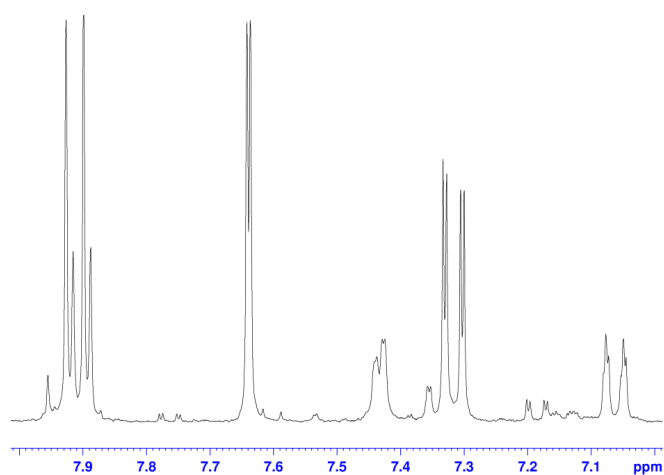


**Fig. S12.** <sup>1</sup>H NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH<sub>3</sub>CN in THF, showing the aromatic region.

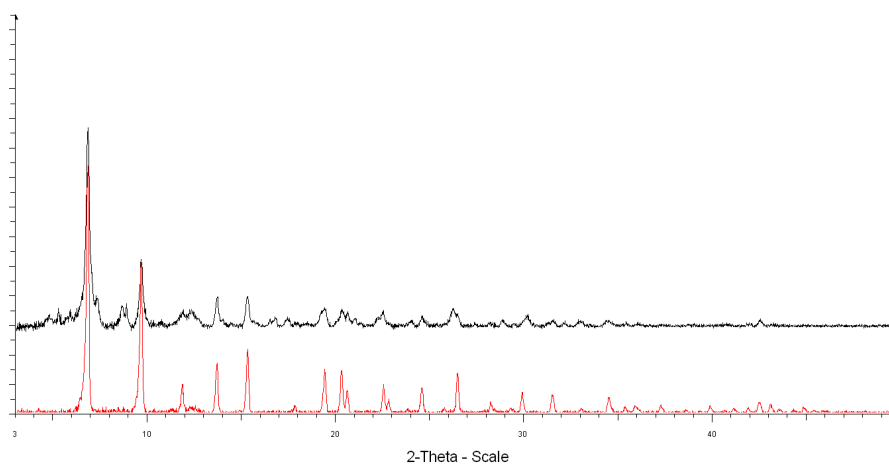




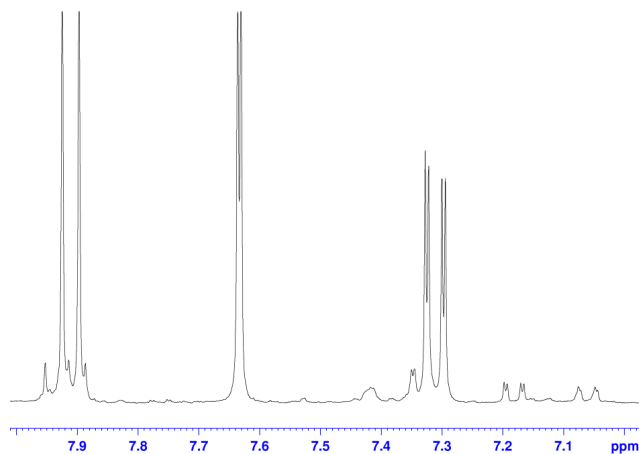
**Fig. S13.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3, PrCHO and NaBH<sub>3</sub>CN in THF (black).



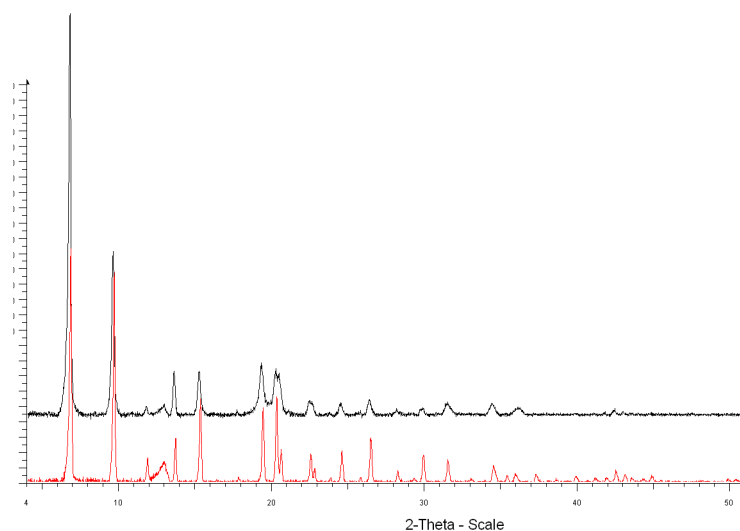
**Fig. S14.** <sup>1</sup>H NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and NaBH<sub>3</sub>CN in THF, showing the aromatic region.



**Fig. S15.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3,  $C_7H_{15}CHO$  and  $NaBH_3CN$  in THF (black).

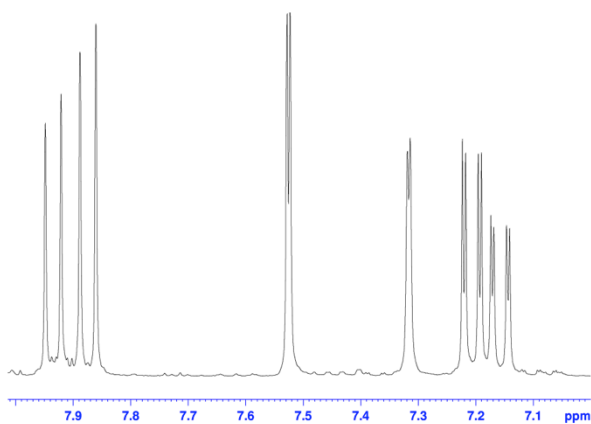


**Fig. S16.**  $^1H$  NMR spectrum for the digested product from the reaction between IRMOF-3,  $C_7H_{15}CHO$  and  $NaBH_3CN$  in THF, showing the aromatic region.

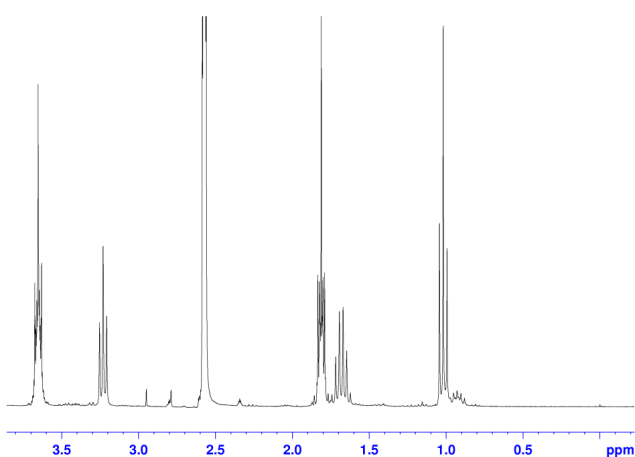


**Fig. S17.** Powder X-ray diffraction pattern for IRMOF-3 (red) and the product from the reaction between IRMOF-3, EtCHO and NaBH<sub>3</sub>CN in THF-MeOH (15:1) (black).

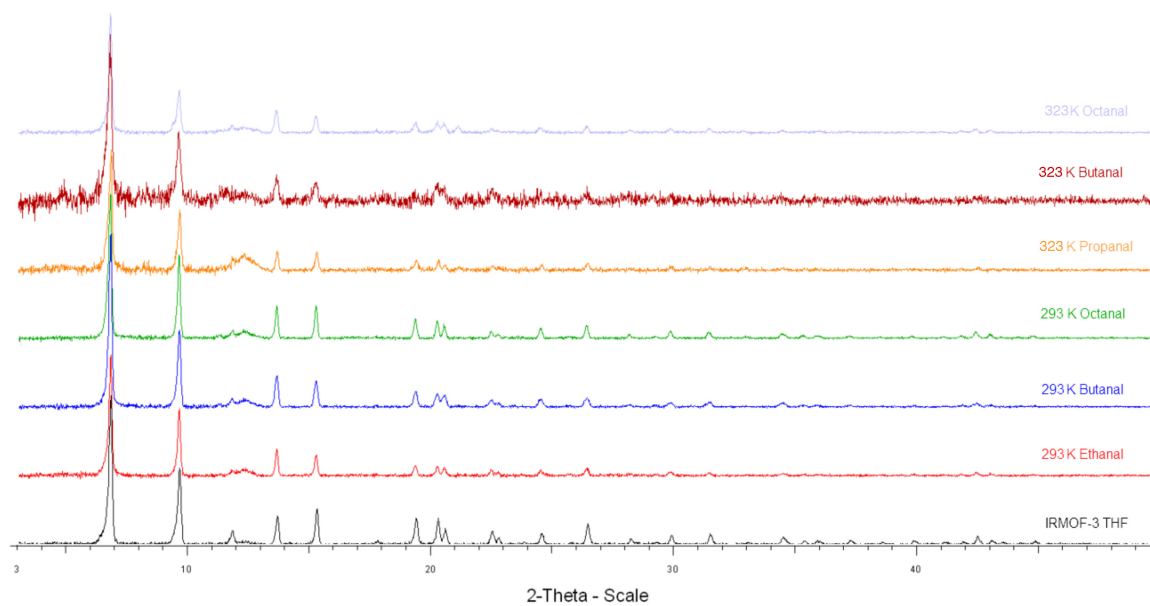
(a)



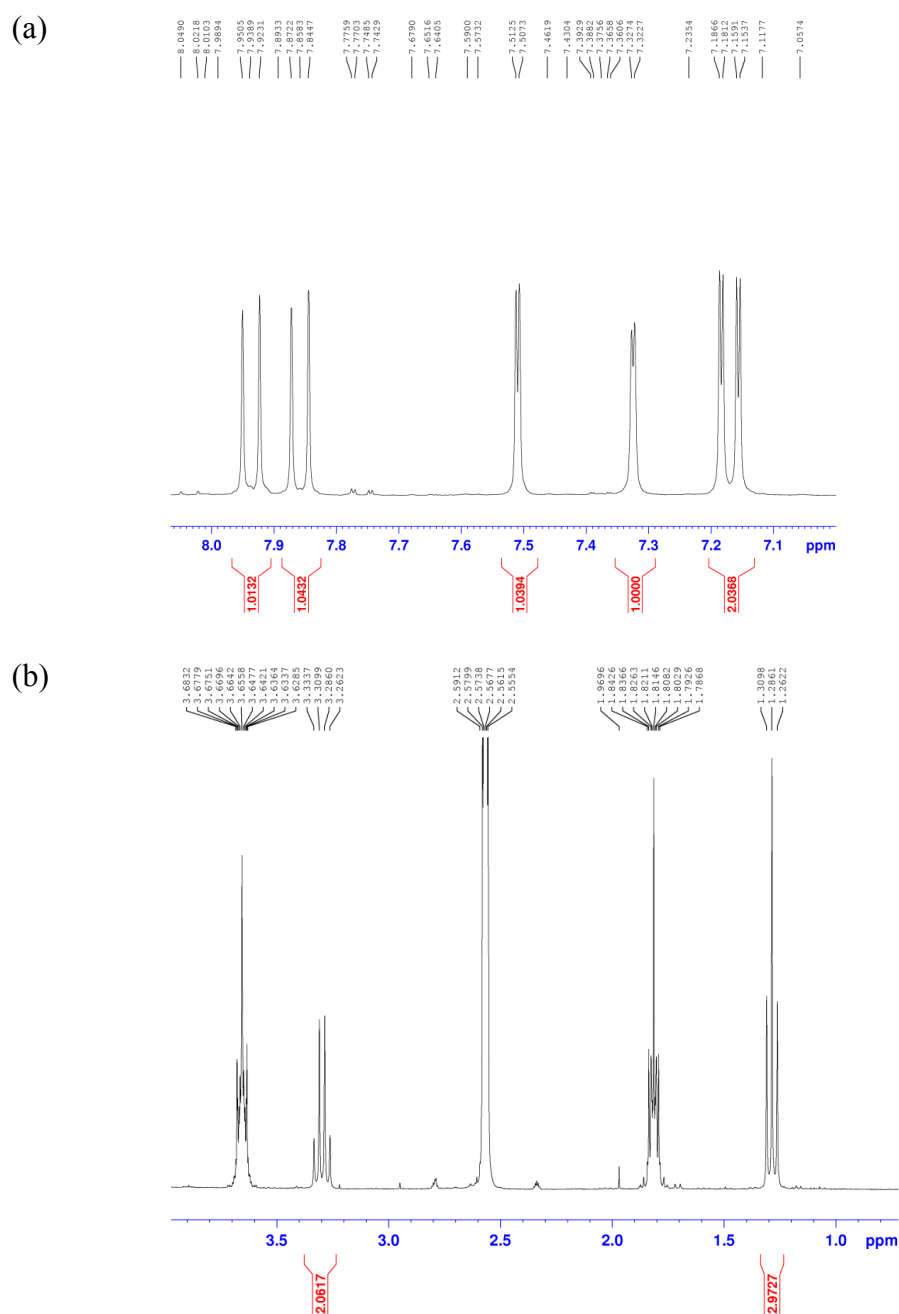
(b)



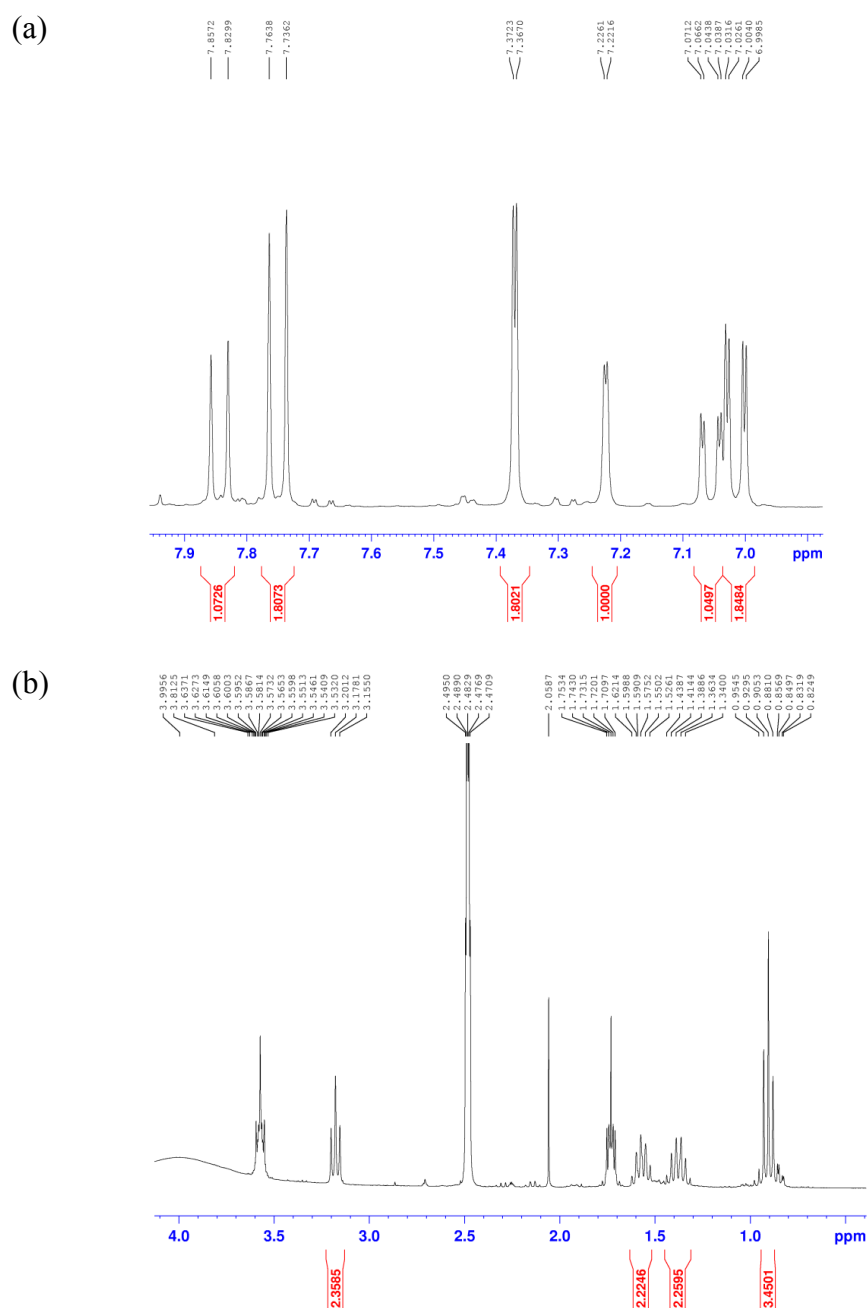
**Fig. S18.** <sup>1</sup>H NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and NaBH<sub>3</sub>CN in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.



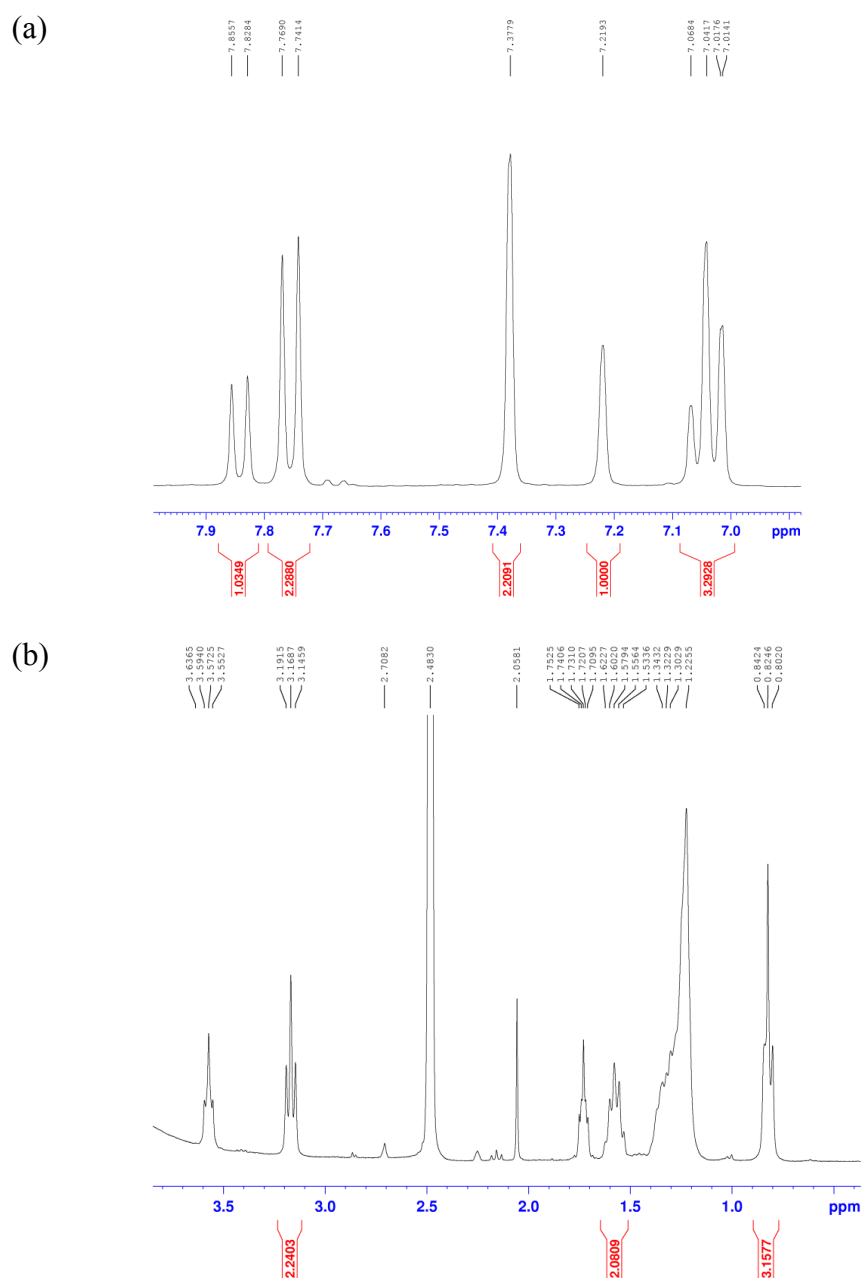
**Fig. S19.** Powder X-ray diffraction patterns for IRMOF-3 (black) and the products from the reactions between IRMOF-3, RCHO (R = Me, Et, Pr, C<sub>7</sub>H<sub>15</sub>) and NaBH<sub>3</sub>CN in THF-MeOH (15:1).



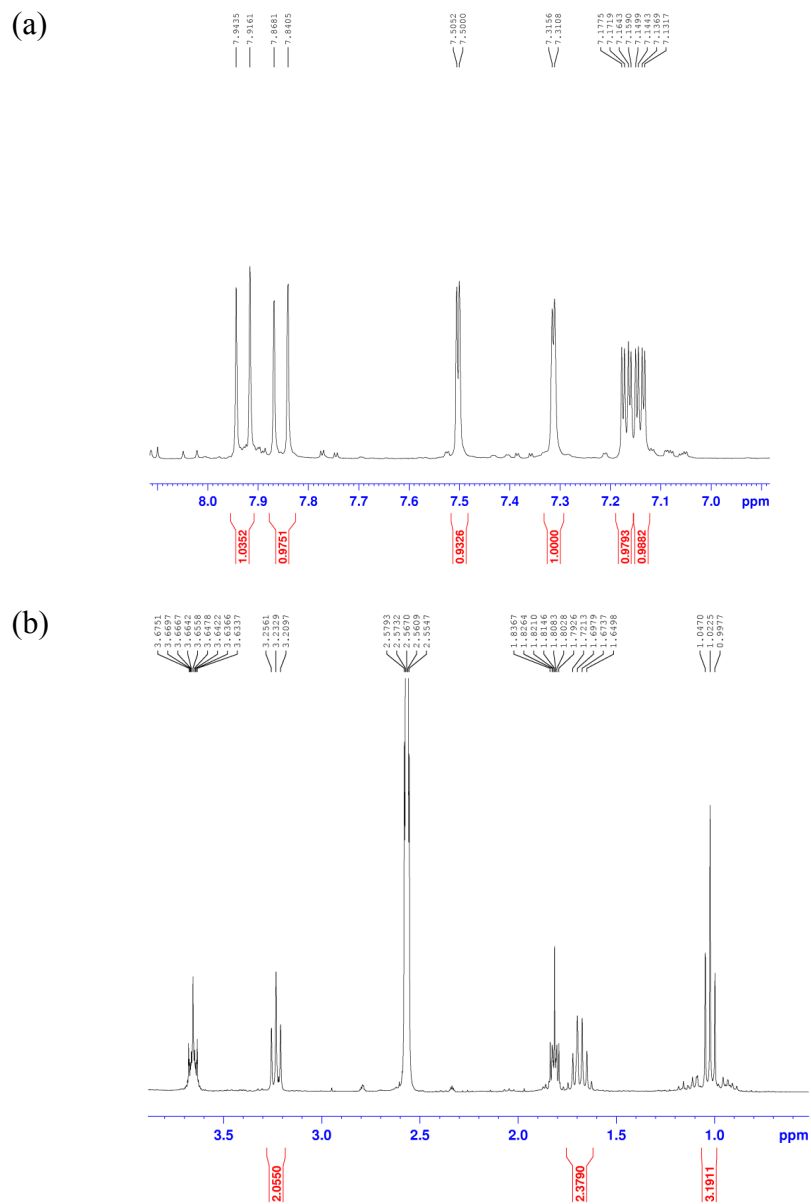
**Fig. S20.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3, MeCHO and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.



**Fig. S21.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.

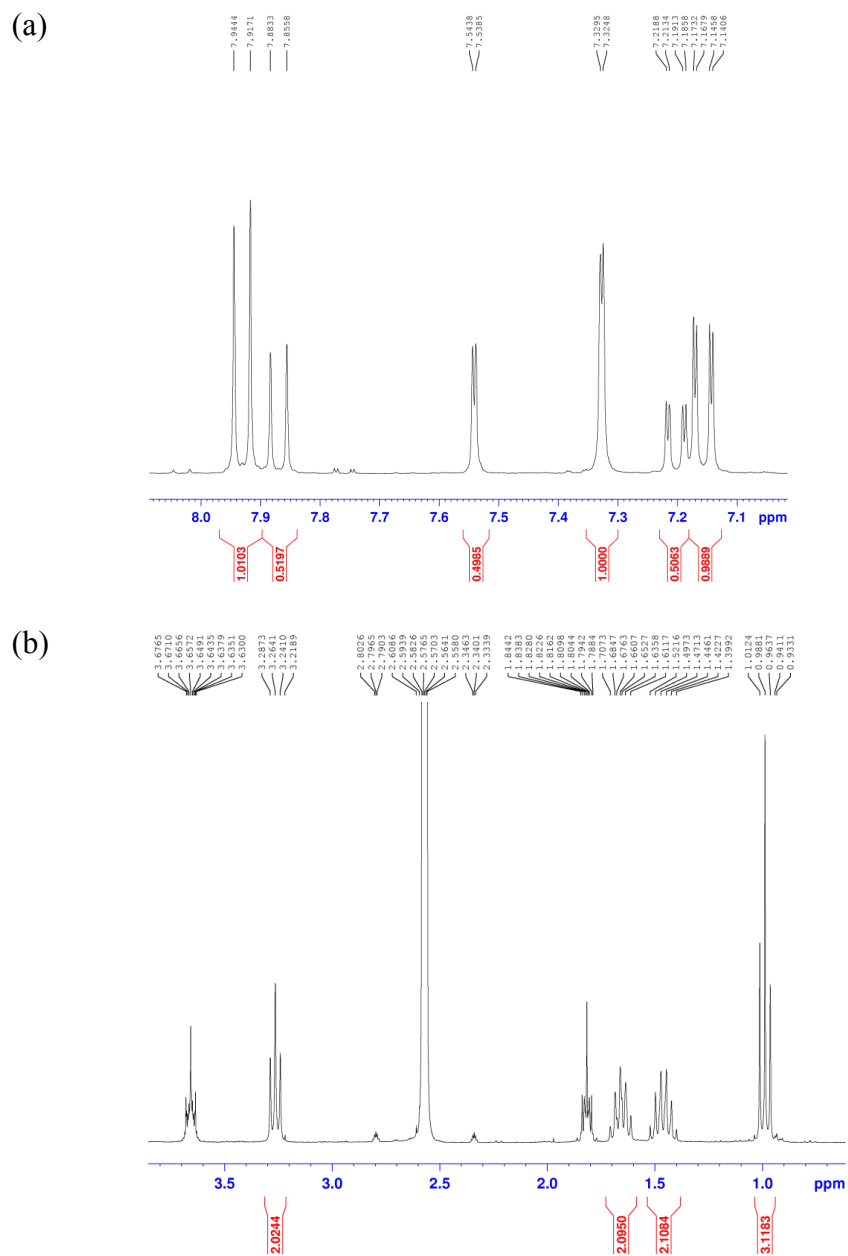


**Fig. S22.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3,  $\text{C}_7\text{H}_{15}\text{CHO}$  and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1), showing (a) the aromatic region, (b) the aliphatic region.

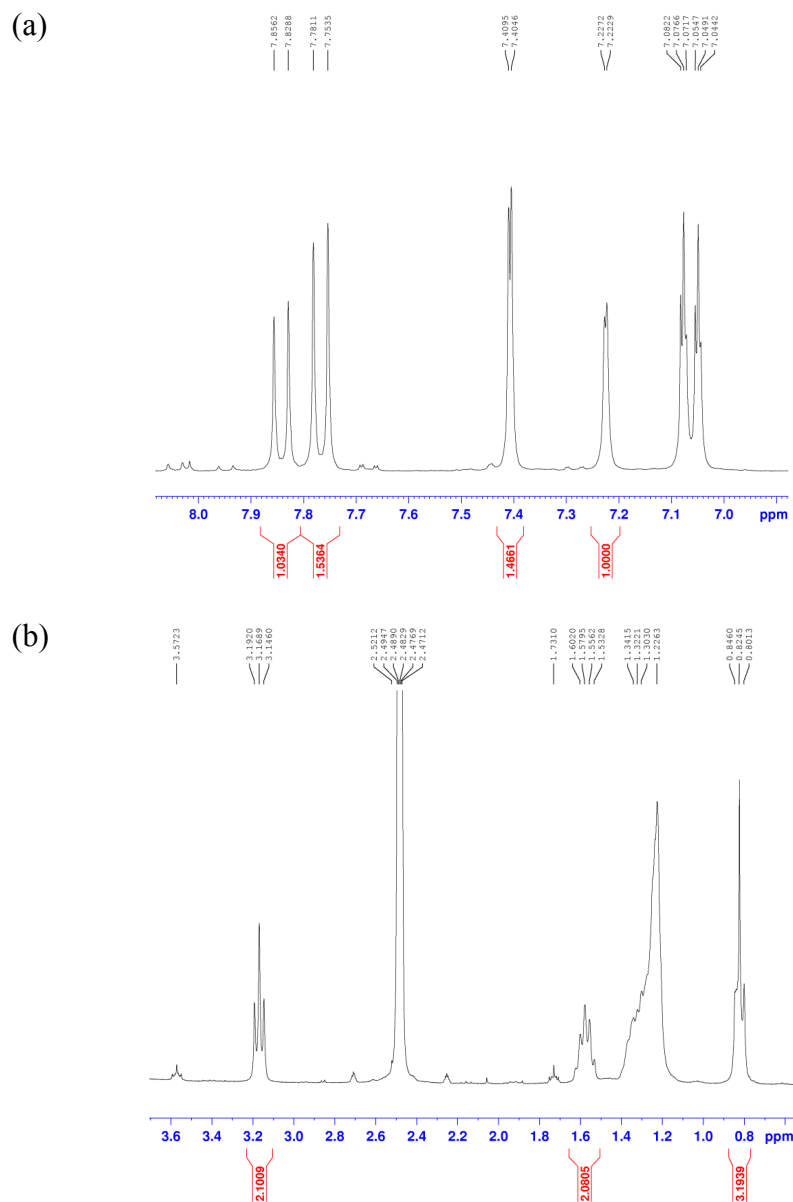


**Fig. S23.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1) at 50 °C, showing (a) the aromatic region, (b) the aliphatic region.

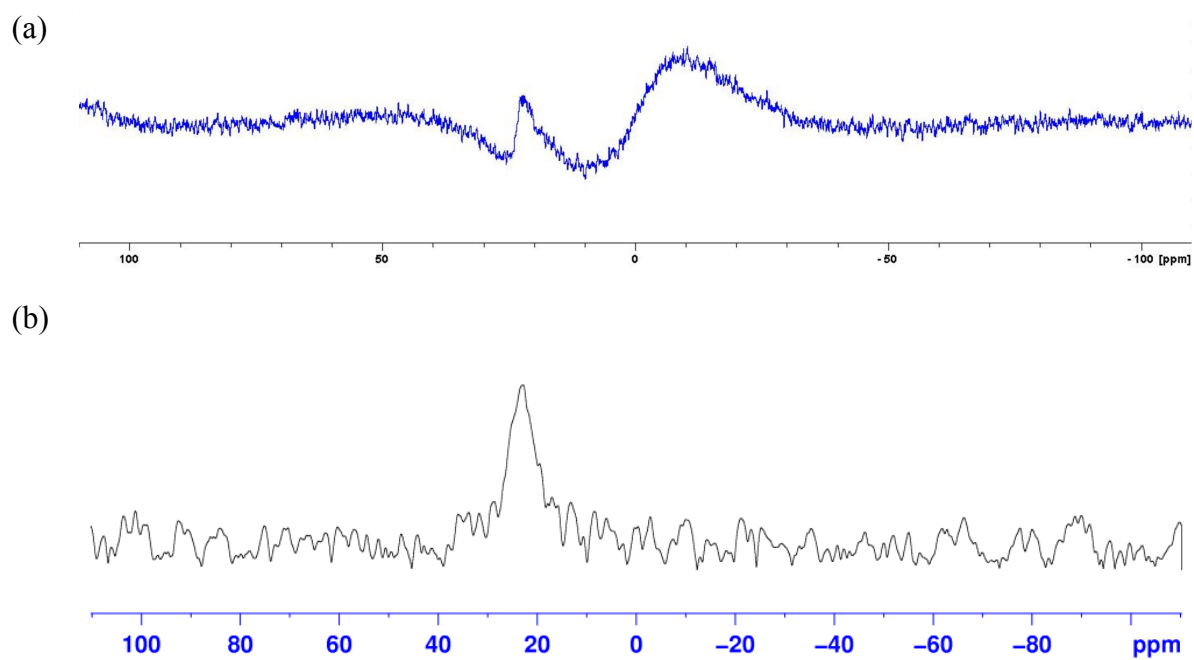




**Fig. S24.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3, PrCHO and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1) at 50 °C, showing (a) the aromatic region, (b) the aliphatic region.



**Fig. S25.**  $^1\text{H}$  NMR spectrum for the digested product from the reaction between IRMOF-3,  $\text{C}_7\text{H}_{15}\text{CHO}$  and  $\text{NaBH}_3\text{CN}$  in THF-MeOH (15:1) at  $50^\circ\text{C}$ , showing (a) the aromatic region, (b) the aliphatic region.



**Fig. S26.**  $^{11}\text{B}$  NMR spectrum for the digested product from the reaction between IRMOF-3, EtCHO and  $\text{NaBH}_3\text{CN}$  in THF, showing the presence of a boron-containing by-product. (a) original spectrum, and (b) reprocessed spectrum.

## Reference

- S1. H. Yim, E. Kang and J. Kim, *Bull. Korean Chem. Soc.* 2010, **31**, 1041.