

Secondary amine-functionalised metal-organic frameworks: direct syntheses versus tandem post-synthetic modifications

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1. General experimental details

Powder X-ray diffraction (PXRD) data was collected at 298 K on a Bruker axis D8 Advance diffractometer with copper K_{α} radiation of wavelength $\lambda = 1.5406 \text{ \AA}$. A beam slit of 1 mm, a detector slit of 0.2 mm and an anti-scattering slit of 1 mm were used. Samples were lightly ground in a small amount of solvent and packed into capillary tubes for analysis.

Single crystal X-ray diffraction analyses were carried out at 250 K using synchrotron radiation of wavelength 0.6889 \AA , using beamline I19 at the Diamond Light Source. The optimal data collection strategy with crystals from this family was found to be to use large crystals in conjunction with extensive beam attenuation (3.75 mm aluminium) and a speedy data collection. This minimised the influence of the (extensive) diffuse scattering during integration of the intensities and, more importantly, provided the best means of ensuring that the data collections completed without degradation of the samples by the X-ray beam.

PSM reaction product crystals were generally of a poor diffraction quality even using a synchrotron source. Generally the MOF crystals were stored in toluene before being selected for the measurement and quickly mounted in Fomblin[®] oil, at 250 K. There was evidence for a phase change, below 220 K, that disastrously impacted upon the quality of the diffraction patterns. Structure solution and refinement were implemented using SHELXS-97 and SHELXL-97, respectively.^{S1}

¹H NMR spectra were carried out on digested samples of the MOFs and were recorded at 298 K on a Bruker Avance 300 MHz Ultrashield NMR spectrometer. ¹H NMR spectra were referenced to the residual *protio* peaks at $\delta 7.26 \text{ ppm}$ (CDCl_3) and $\delta 2.50 \text{ ppm}$ for $\text{DMSO-}d_6$. ¹³C NMR spectra were referenced to the residual solvent peaks at $\delta 77.2 \text{ ppm}$ for CDCl_3 and $\delta 39.5 \text{ ppm}$ for $\text{DMSO-}d_6$ and carried out at 75 MHz. ¹¹B NMR spectra were carried out at 160 MHz and referenced to $\text{BF}_3 \cdot \text{OEt}_2$ at $\delta 0.0 \text{ ppm}$.

Digestions of the zinc MOFs were carried out using approximately 5 mg of crystalline sample in 0.4 mL of DMSO and 0.2 mL of a stock solution comprising 0.1 mL of 35 % $\text{DCI/D}_2\text{O}$ in 3 mL DMSO. The resultant mixture was sonicated for three hours or until the solid had completely dissolved. Digestions of the chromium MOFs were carried out using approximately 1 mg of crystalline sample suspended in 0.4 mL D_2O . To this was added 0.2 mL of a stock solution comprising 0.1 mL $\text{NaOD/D}_2\text{O}$ (30% wt) in 3 mL D_2O . When a resultant spectrum showed peaks that were wide and overlapping, the sample was further diluted with D_2O and the spectrum re-recorded.

Mass spectra were carried out on digested MOF solutions, diluted in EtOH, using a Bruker microTOF electrospray ionization time-of-flight (ESI-TOF) instrument. FT-IR analyses were implemented on solid, ground, dried samples using a PerkinElmer Spectrum 100 spectrometer containing an ATR accessory. Spectra of **2a-g** were carried in the presence of toluene.

Thermogravimetric analyses were obtained using a PerkinElmer TGA 4000 analyser over a temperature range of 40°C to 600°C at a rate of $5^\circ\text{C}/\text{min}$ under a flow of N_2 gas (20 mL/min). The samples of **2a-g** were dried under a N_2 flow (293 K), evaporating toluene until the mass became constant, before taking any measurements.

The N_2 sorption isotherms of N_2 were recorded at 77 K employing a BELSORP Mini-II (BEL Japan) instrument. The standard range $0.05 < P/P_0 < 0.3$ was used in calculations of BET surface area, with the proviso that this range was linear, and with a positive y-intercept.

Activation conditions for **2a-g** and **5a-g** involved using toluene and a flow of N₂ to reduce exposure to atmospheric humidity before activating at 150°C for 3 h, under vacuum (~0.1 bar) on the instrument. Samples of **4a-d** were activated at 150°C for 4 h, under vacuum.

Atomic absorption spectra was recorded by Mr Alan Carver on a Perkin Elmer 3100 spectrometer using aqueous solutions of digested MOFs. Microanalysis was carried out on dried samples by Mr Alan Carver, using an Exeter Analytical Inc. CE-440 elemental analyser.

2. PSM procedures for reactions on IRMOF-3

2.1 Reaction of IRMOF-3 with MeCHO and NaCNBH₃ (**2a**)

IRMOF-3 was synthesised according to a modified preparation by Cohen *et al*^{S2} washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH₂ eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. This was cooled in an ice bath to 5°C. Ethanal (51 µL, 0.92 mmol, 4 eq.) and then NaCNBH₃ (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min, to allow for effervescence, the mixture was sealed and heated to 50°C for 48 h, without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3 × 5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. The IR spectrum of [Zn₄O(bdc-NH₂)_{0.78}(bdc-NHEt)_{2.22}]·7C₆H₅Me, **2a** is shown in Figure S1, and the ¹H NMR spectrum of the acid digested MOF is shown in Figure S2.

$m/z = 208.0646$ (predicted [C₁₀H₁₀NO₄]⁻, [M - H]⁻ = 208.0615).

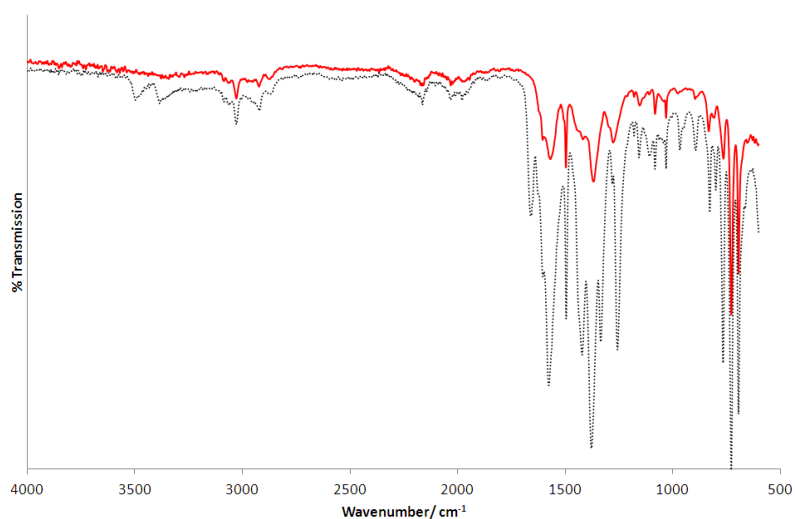


Figure S1. FT-IR spectrum of **2a** (red) and IRMOF-3 (black).

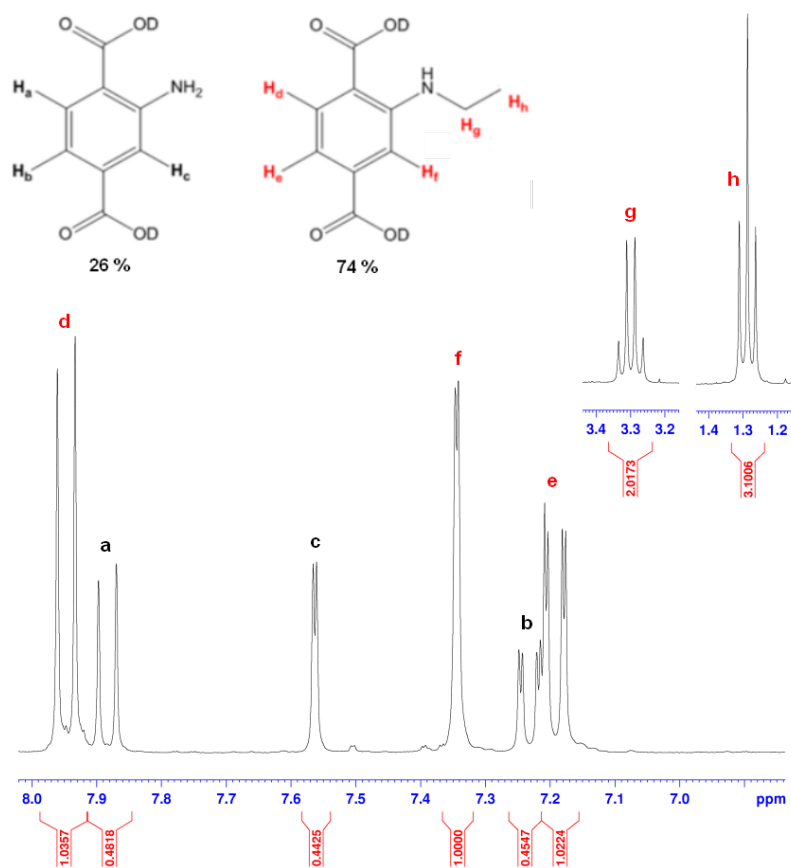


Figure S2. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **2a**.

2.2 Reaction of IRMOF-3 with EtCHO and NaCNBH_3 (**2b**)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH_2 eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. Propanal (67 μL , 0.92 mmol, 4 eq.) and then NaCNBH_3 (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 48 h, without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3×5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. The IR spectrum of $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{0.93}(\text{bdc-NHPr})_{2.07}] \cdot 5.5\text{C}_6\text{H}_5\text{Me}$, **2b** is shown in Figure S3, and the ^1H NMR spectrum of the acid digested MOF is shown in Figure S4.

$m/z = 222.0784$ (predicted $[\text{C}_{11}\text{H}_{12}\text{NO}_4]^-$, $[\text{M} - \text{H}]^- = 222.0766$).

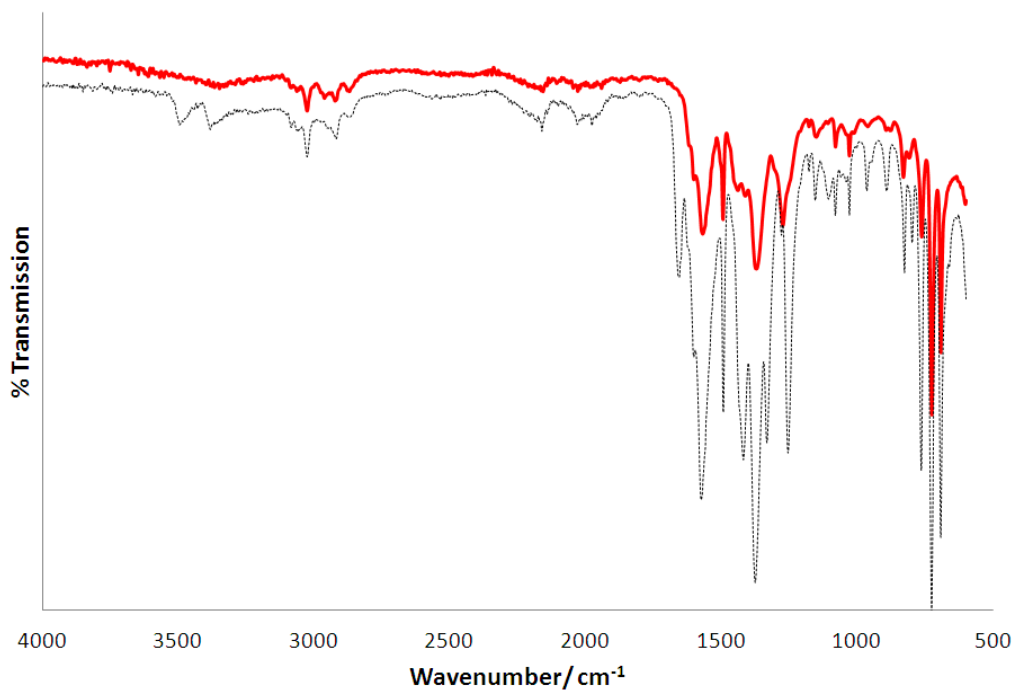


Figure S3. FT-IR spectrum of **2b** (red) and IRMOF-3 (black).

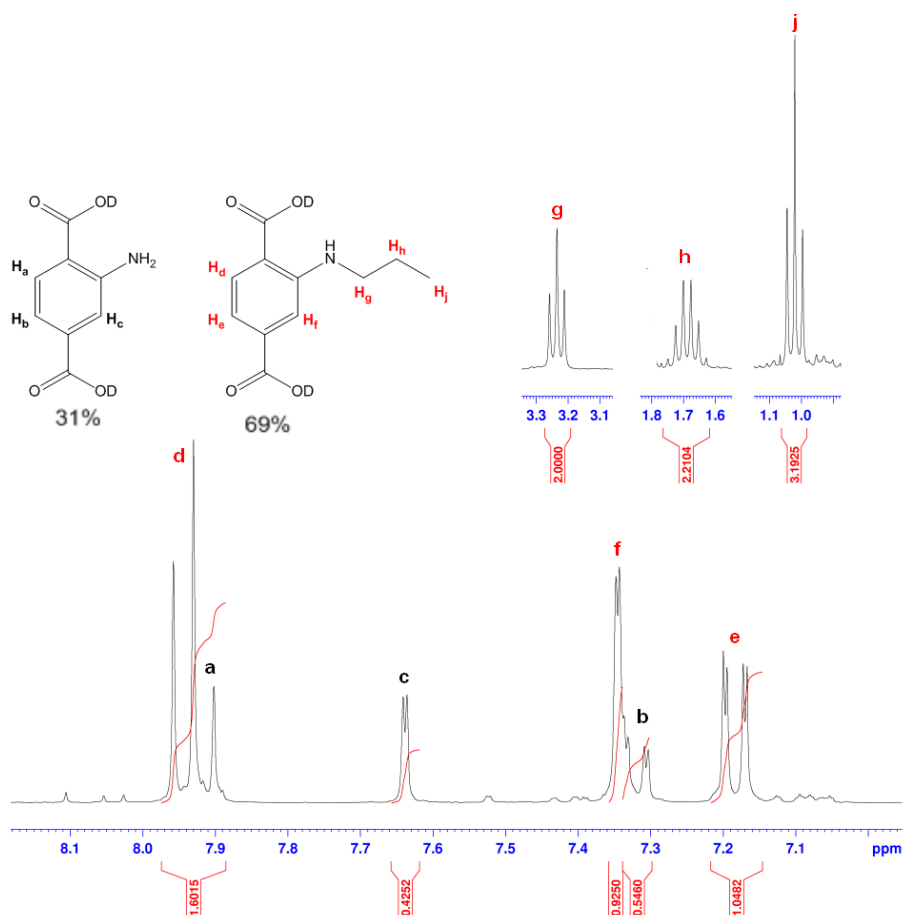


Figure S4. Aromatic and aliphatic (insert) regions of the 1H NMR spectrum of digested **2b**.

2.3 Reaction of IRMOF-3 with PrCHO and NaCNBH₃ (**2c**)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH₂ eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. Butanal (81 μ L, 0.92 mmol, 4 eq.) and then NaCNBH₃ (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 48 h without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3 \times 5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. The IR spectrum of [Zn₄O(bdc-NH₂)_{1.05}(bdc-NHBu)_{1.95}] \cdot 5.5C₆H₅Me, **2c** is shown in Figure S5, and the ¹H NMR spectrum of the acid digested MOF is shown in Figure S6.

$m/z = 236.0934$ (predicted [C₁₂H₁₄NO₄]⁻, [M - H]⁻ = 236.0923).

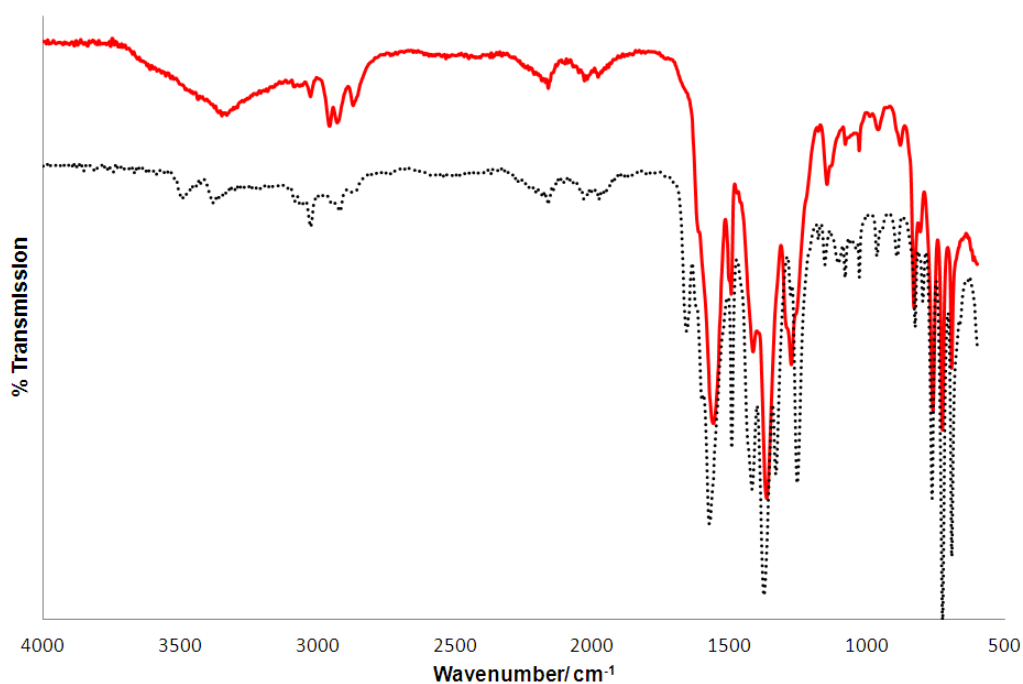


Figure S5. FT-IR spectrum of **2c** (red) and IRMOF-3(black).

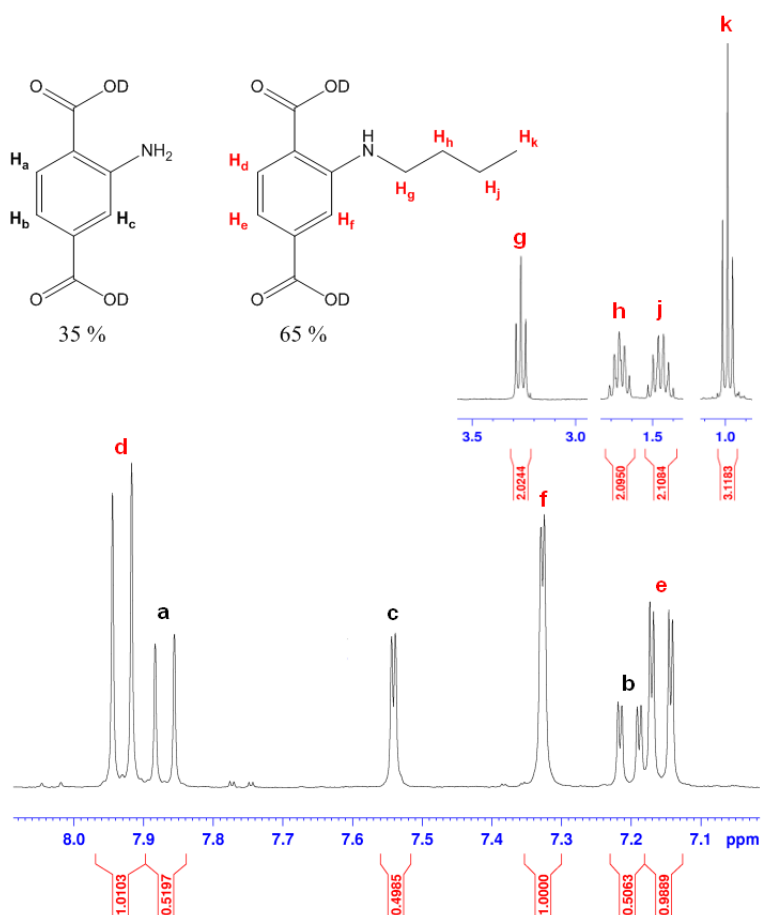


Figure S6. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **2c**.

2.4 Reaction of IRMOF-3 with $\text{C}_7\text{H}_{15}\text{CHO}$ and NaCNBH_3 (**2d**)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH_2eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. Octanal (144 μL , 0.92 mmol, 4 eq.) and then NaCNBH_3 (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 48 h without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3×5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. The IR spectrum of $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{1.59}(\text{bdc-NHC}_8\text{H}_{17})_{1.41}] \cdot 4\text{C}_6\text{H}_5\text{Me}$, **2d** is shown in Figure S7, and the ^1H NMR spectrum of the acid digested MOF is shown in Figure S8.

$m/z = 292.1558$ (predicted $[\text{C}_{16}\text{H}_{22}\text{NO}_4]^-$, $[\text{M} - \text{H}]^- = 292.1554$).

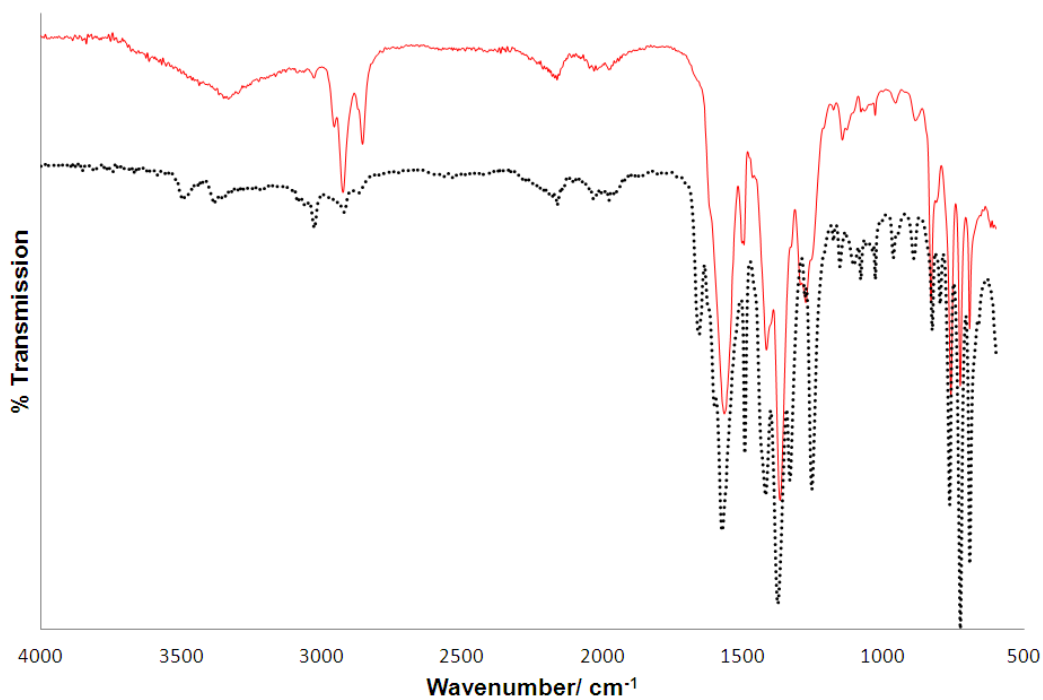


Figure S7. FT-IR spectrum of **2d** (red) and IRMOF-3 (black).

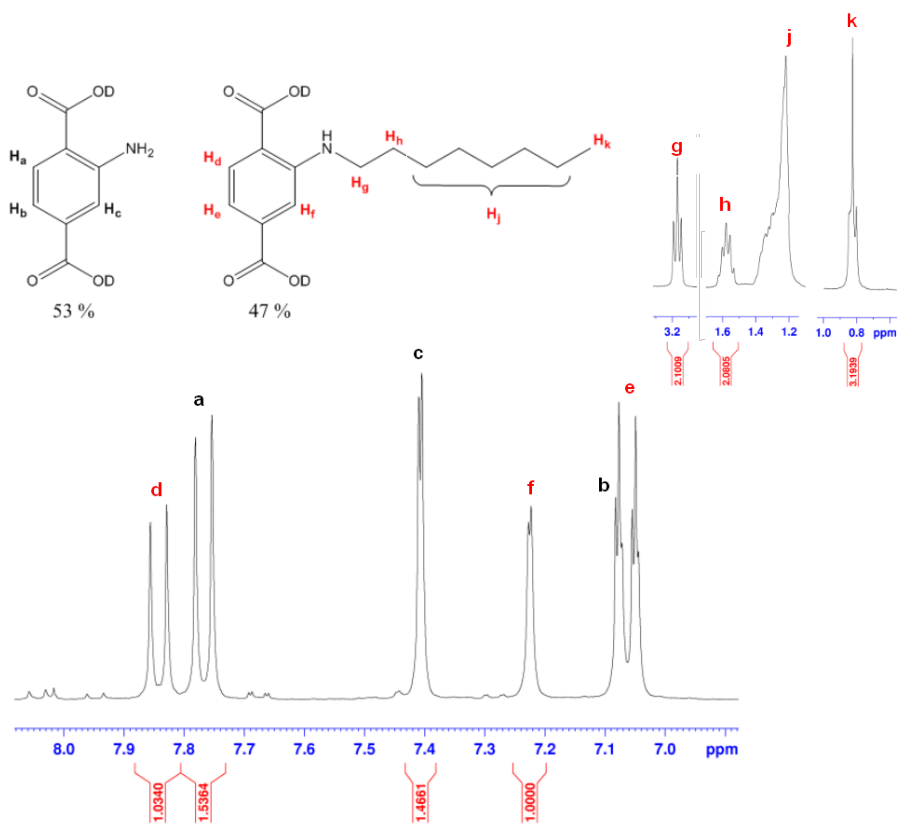


Figure S8. Aromatic and aliphatic (insert) regions of the ¹H NMR spectrum of digested **2d**.

2.5 Reaction of IRMOF-3 with 1,2,3,6-tetrahydrobenzaldehyde and NaCNBH₃ (2e)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH₂eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. 1,2,3,6-Tetrahydrobenzaldehyde (104 μ L, 0.92 mmol, 4 eq.) and then NaCNBH₃ (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50 $^{\circ}$ C for 48 h without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3 \times 5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. Analysis found: C 42.0, H 3.44, N 4.83. Predicted activated sample: C 42.37 H 3.00 N 4.49 (43 % conversion batch). The IR spectrum of [Zn₄O(bdc-NH₂)_{1.53}(bdc-NHCH₂C₆H₉)_{1.47}] \cdot 3.5C₆H₅Me, **2e** is shown in Figure S9, and the ¹H NMR spectrum of the acid digested MOF is shown in Figure S10.

$m/z = 247.1124$ (predicted [C₁₅H₁₆O₄N]⁻, [M - H]⁻ = 274.1085).

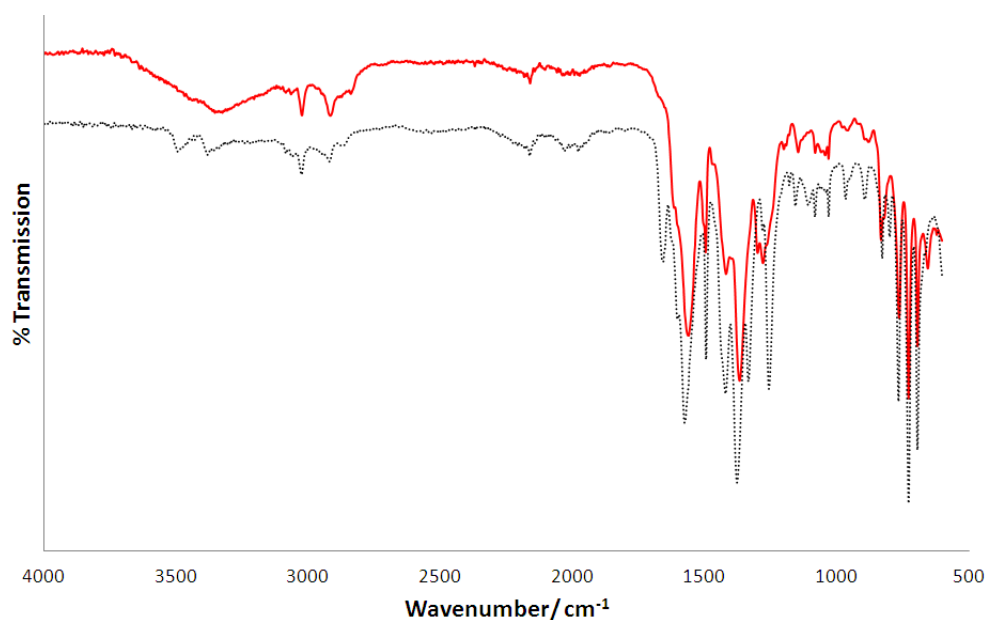


Figure S9. FT-IR spectrum of **2e** (red) and IRMOF-3 (black).

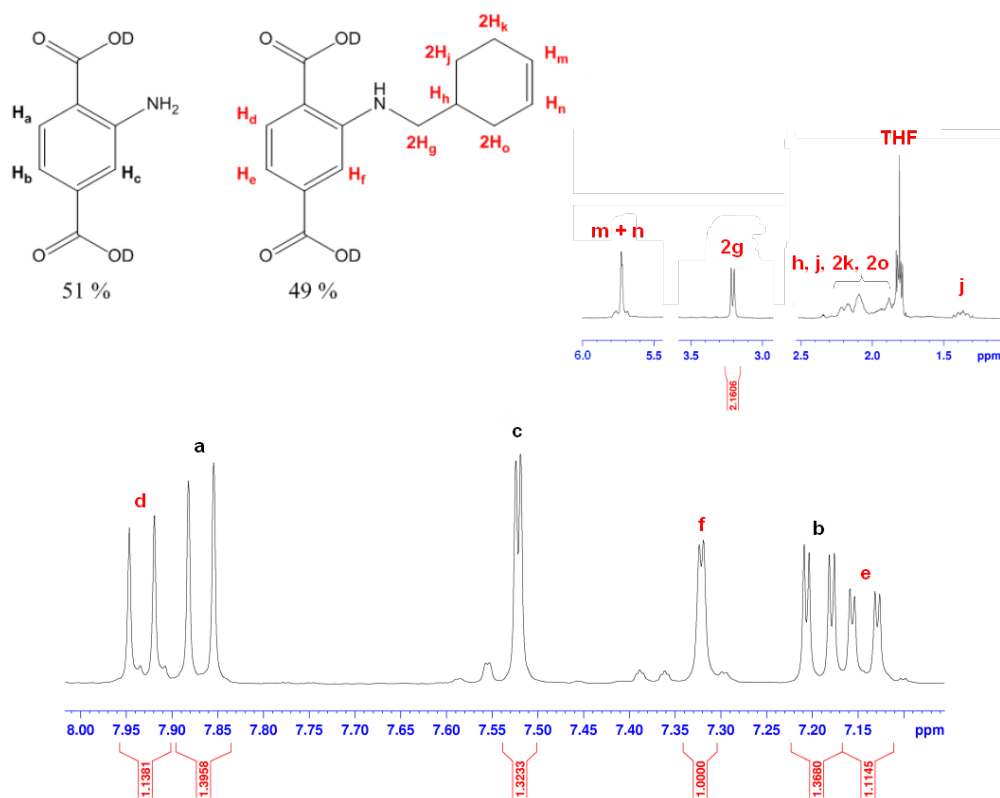


Figure S10. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **2e**.

2.6 Reaction of IRMOF-3 with ferrocenecarboxaldehyde and NaCNBH_3 (**2f**)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH_2eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. Ferrocenecarboxaldehyde (197 mg, 0.92 mmol, 4 eq.) and then NaCNBH_3 (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 48 h without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3×5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. Atomic absorption spectrometry: Fe:Zn 1:6.2 (predicted 1:6.8). The IR spectrum of $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{2.19}(\text{bdc-NHCH}_2\text{Fc})_{0.81}] \cdot 2.5\text{C}_6\text{H}_5\text{Me}$, **2f** is shown in Figure S11, and the ^1H NMR spectrum of the acid digested MOF is shown in Figure S12.

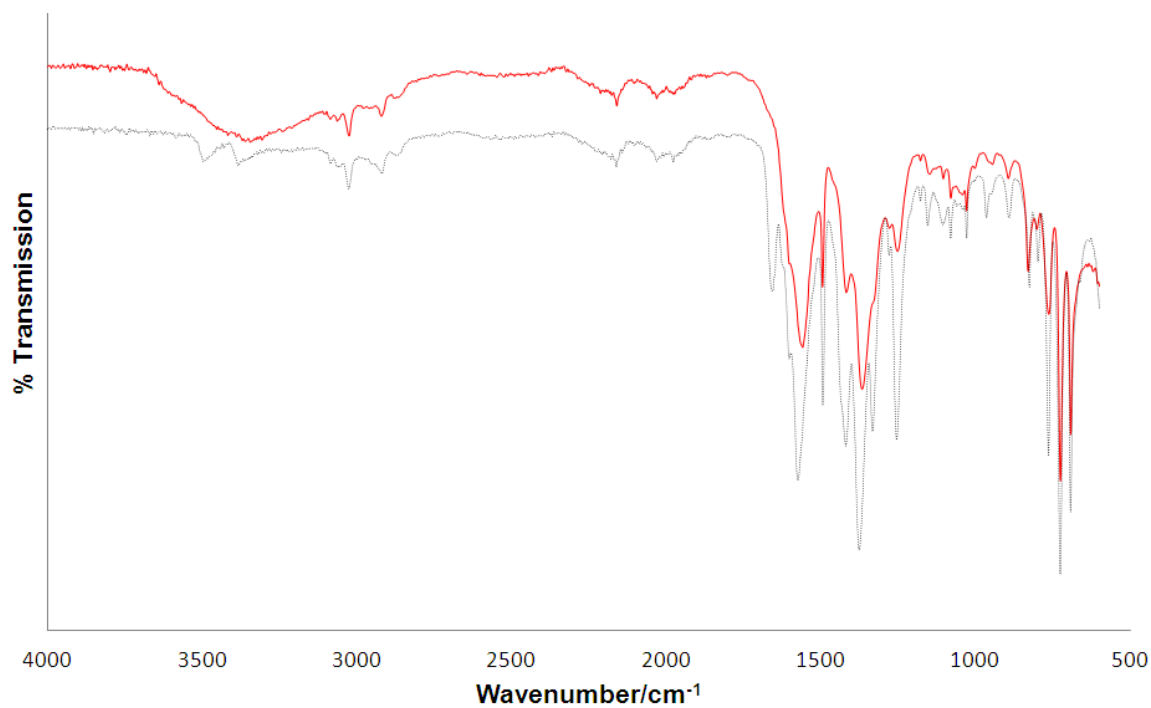


Figure S11. FT-IR spectrum of **2f** (red) and IRMOF-3 (black).

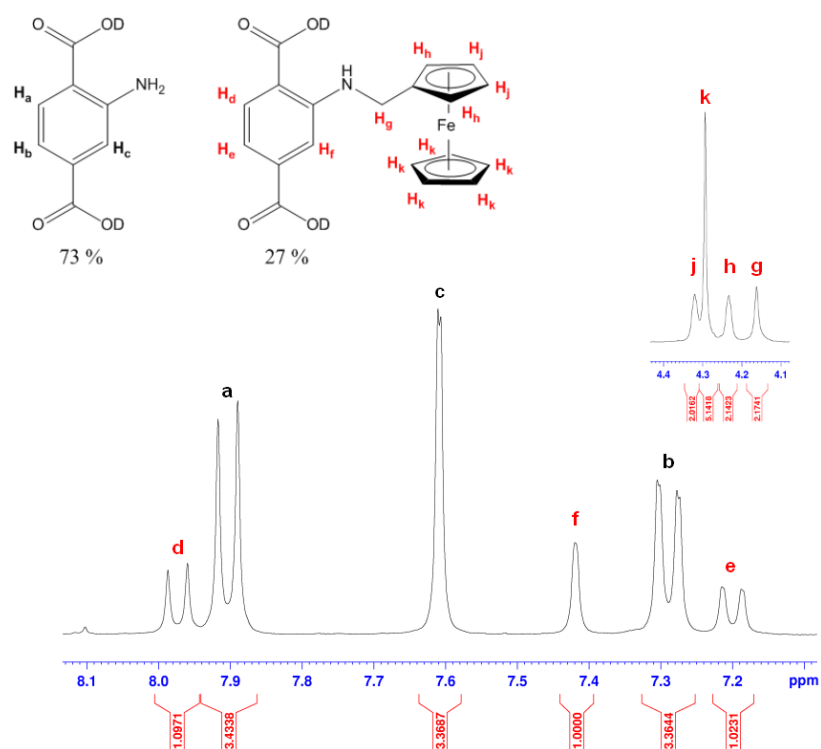


Figure S12. Aromatic and aliphatic (inset) regions of the ^1H NMR spectrum of digested **2f**.

2.7 Reaction of IRMOF-3 with 4-methylthiobenzaldehyde and NaCNBH₃ (2g)

IRMOF-3 was washed with solvent (THF) for 3 days with fresh solvent every 24 h. 100 mg IRMOF-3 (0.23 mmol NH₂eq) was added to a mixture of 5.625 mL THF:0.375 mL MeOH (15:1) in a glass vial. 4-Methylthiobenzaldehyde (122 μ L, 0.92 mmol, 4 eq.) and then NaCNBH₃ (58 mg, 0.92 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 48 h without stirring, before cooling to ambient temperature. The crystalline product was rinsed with THF:MeOH 15:1. The resulting yellow-orange crystals were washed with 3 \times 5 mL toluene over 3 days, by decantation and replacing with fresh toluene once every 24 h, and stored in fresh toluene. The IR spectrum of [Zn₄O(bdc-NH₂)_{2.25}(bdc-NHCH₂C₆H₄SMe)_{0.75}]·4C₆H₅Me, **2g** is shown in Figure S13, and the ¹H NMR spectrum of the acid digested MOF is shown in Figure S14.

$m/z = 316.0757$ (predicted [C₁₆H₁₄O₄NS]⁻, [M - H]⁻ = 316.0649).

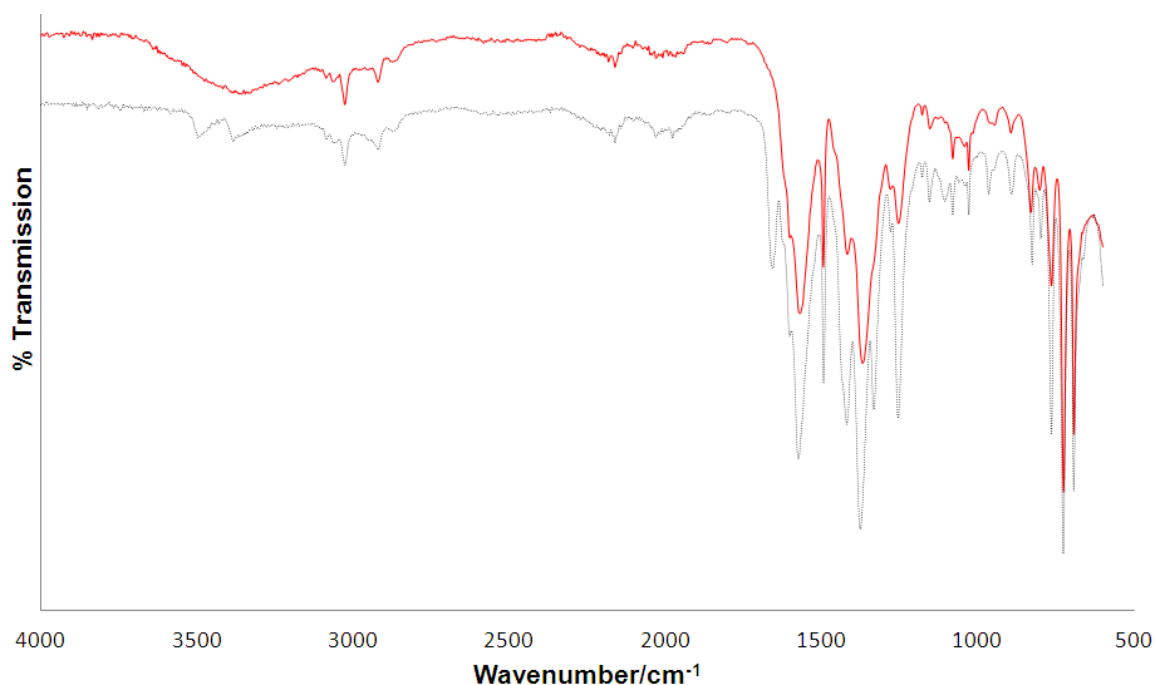


Figure S13. FT-IR spectrum of **2g** (red) and IRMOF-3 (black).

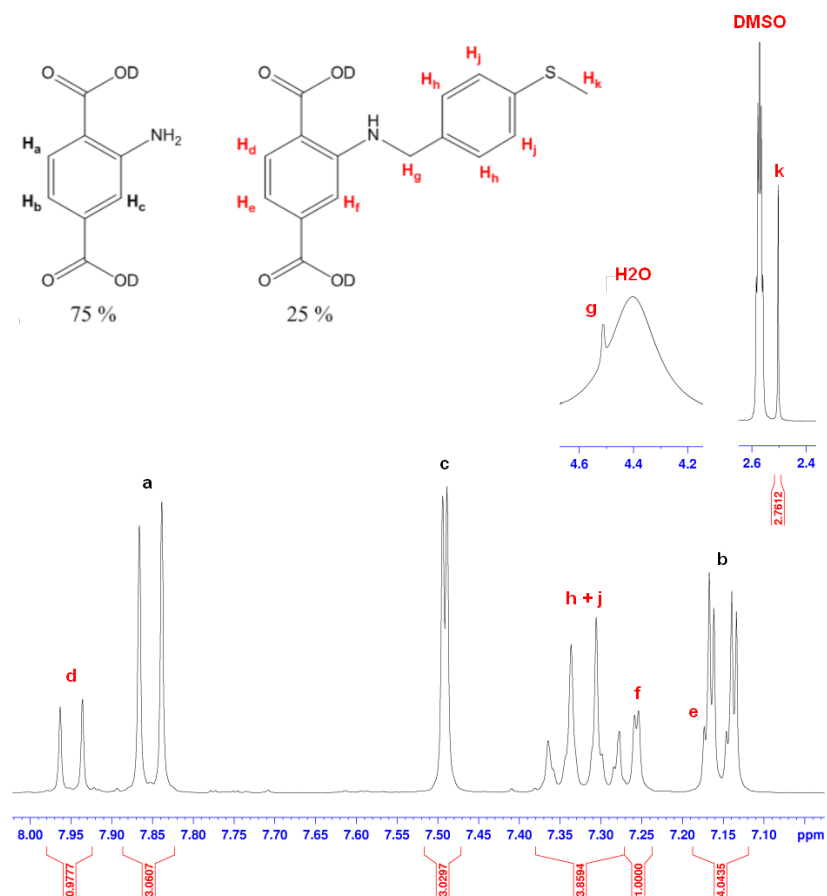


Figure S14. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **2g**.

2.8 Powder X-ray diffraction studies

Powder X-ray diffraction patterns for **2a-g** are shown in Figures S15-16, in comparison with that for IRMOF-3.

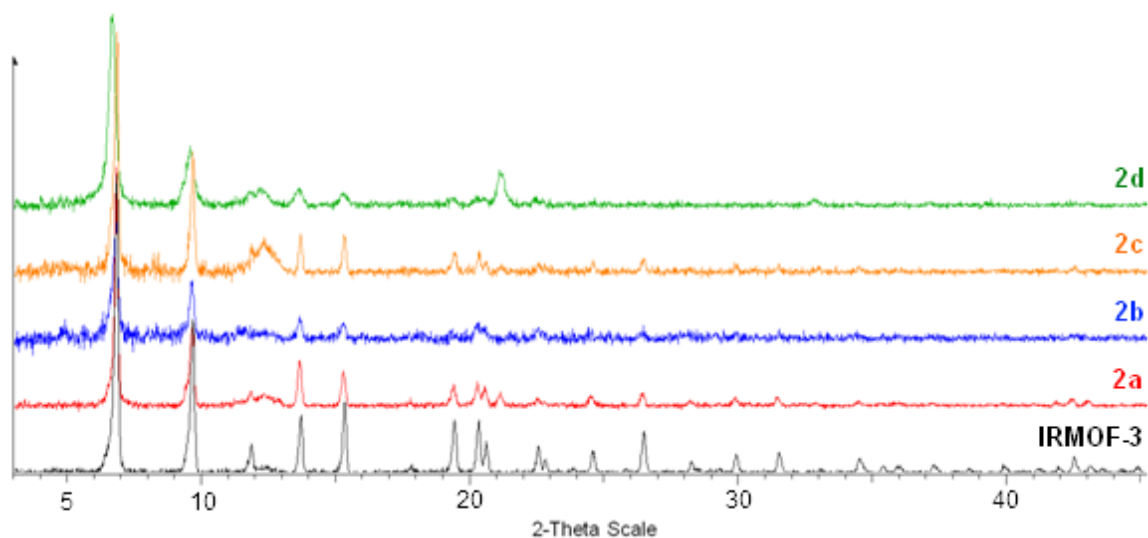


Figure S15. PXRD patterns of PSM products **2a-d** from the reaction between IRMOF-3, an aldehyde and NaCNBH_3 in $\text{THF}:\text{MeOH}$ (15:1), at 50°C alongside the PXRD pattern for IRMOF-3.

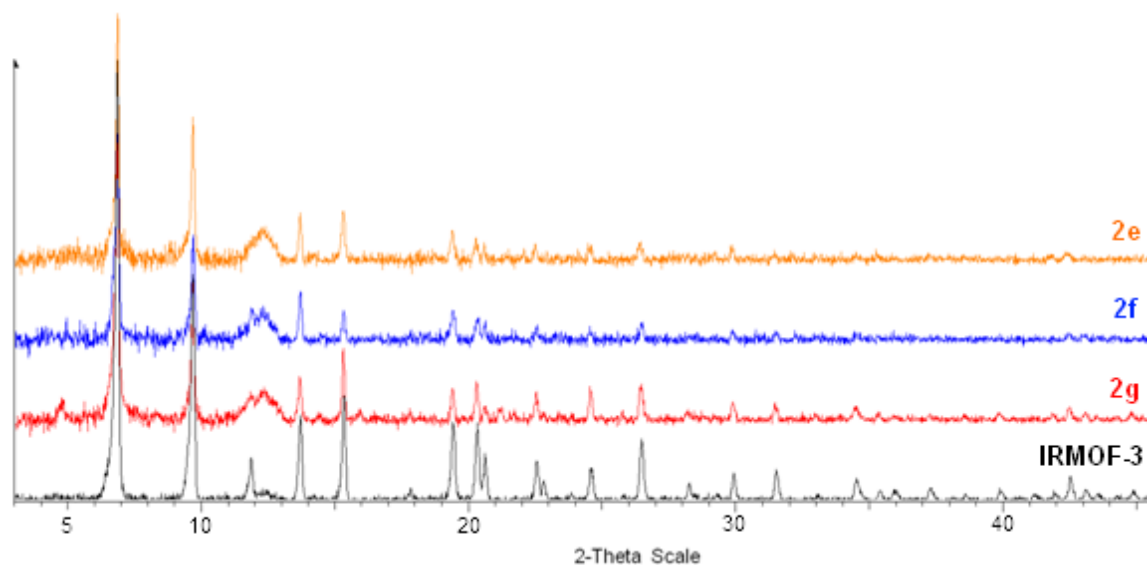


Figure S16. PXRD patterns of PSM products **2e-g** from the reaction between IRMOF-3, an aldehyde and NaCNBH_3 in THF:MeOH (15:1), at 50°C alongside the PXRD pattern for IRMOF-3.

2.9 Reaction of IRMOF-3 with 2-pyridinecarboxaldehyde and NaCNBH_3 (**2h**)

Crystals of IRMOF-3 were washed and suspended in anhydrous DMF for 3 days, replacing the solvent every 24 h. IRMOF-3 (0.100 g, 0.23 mmol eq. NH_2), 2-pyridinecarboxaldehyde (0.088 mL, 0.92 mmol) and NaCNBH_3 (0.058 g, 0.92 mmol) were added to a glass vial containing a mixture of 5 mL of DMF and 0.17 mL of MeOH. The glass vial was then sealed and placed in an oven at 50°C for 4 days. The resulting brown cubic crystals were washed by decantation with fresh anhydrous DMF three times over 3 days. The powder X-ray diffraction pattern for $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{2.34}(\text{bdc-NHCH}_2\text{C}_5\text{H}_4\text{N})_{0.66}]$, **2h** is shown in Figure S17 and the ^1H NMR spectrum of the acid digested MOF is shown in Figure S18.

$m/z = 271.0732$ (predicted $[\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4]^-$, $[\text{M} - \text{H}]^- = 271.0719$).

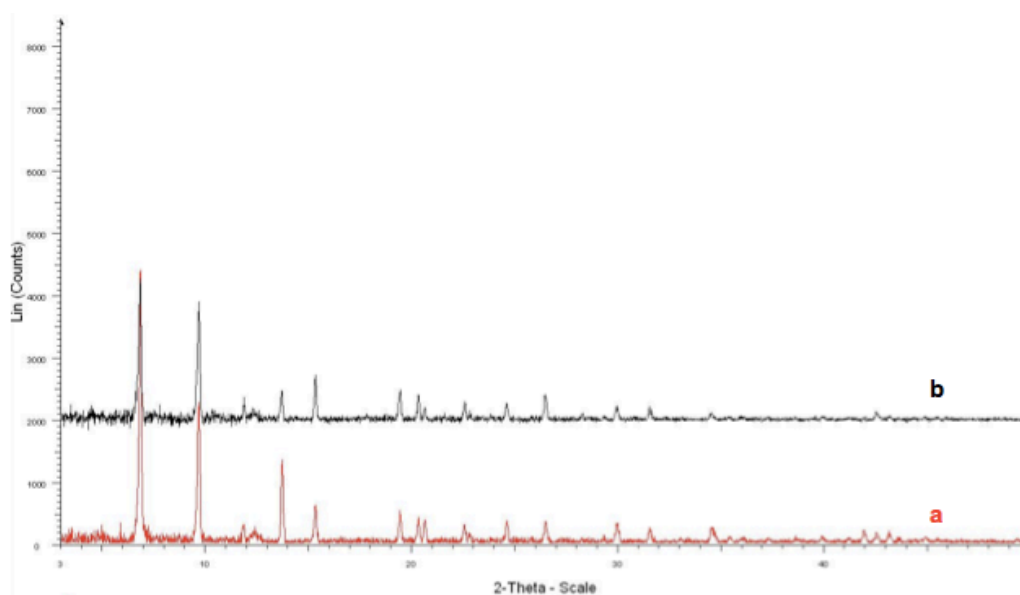


Figure S17. PXRD patterns for (a) IRMOF-3 and (b) 2h.

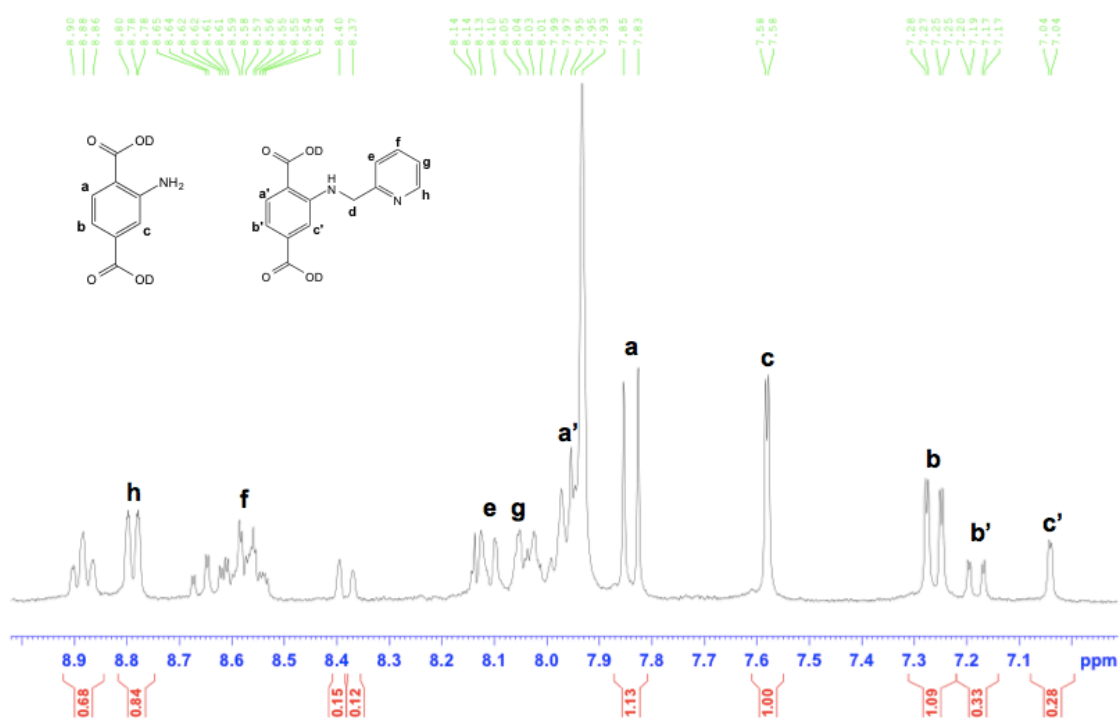


Figure S18. Aromatic region of the ^1H NMR spectrum of digested 2h.

2.10 Reaction of IRMOF-3 with 3-(methylthio)propionaldehyde and NaCNBH_3 (2i)

Crystals of IRMOF-3 were washed and suspended in anhydrous DMF for 3 days, replacing the solvent every 24 h. IRMOF-3 (0.100 g, 0.23 mmol eq. NH_2), 3-

(methylthio)propionaldehyde, (0.091 mL, 0.92 mmol) and NaCNBH₃ (0.058 g, 0.92 mmol) were added to a glass vial containing 5 mL of DMF. The vial was sealed and placed in an oven at 50°C for 3 days. After this time, the solid product was washed several times with fresh DMF, followed by soaking in anhydrous DMF for 3 days before characterisation. The powder X-ray diffraction pattern for [Zn₄O(bdc-NH₂)_{2.49}(bdc-NHCH₂CH₂CH₂SMe)_{0.51}], **2i** is shown in Figure S19 and the ¹H NMR spectrum of the acid digested MOF is shown in Figure S20.

$m/z = 268.0673$ (predicted [C₁₂H₁₄NO₄S]⁻, [M - H]⁻ = 268.0644).

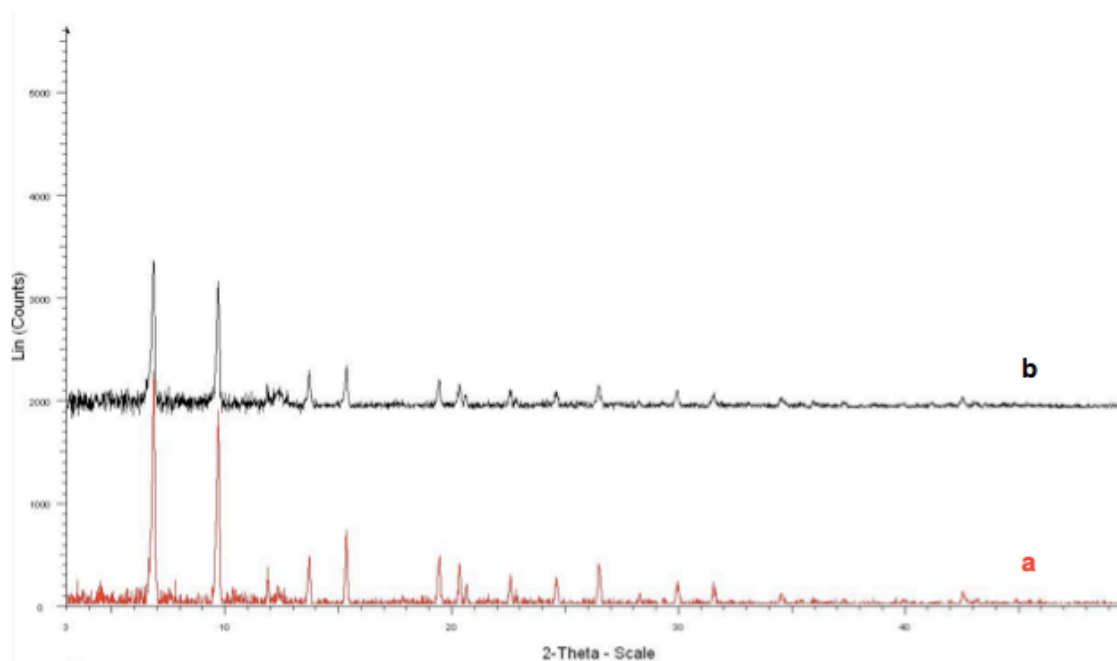


Figure S19. PXRD patterns for (a) IRMOF-3 and (b) **2i**.

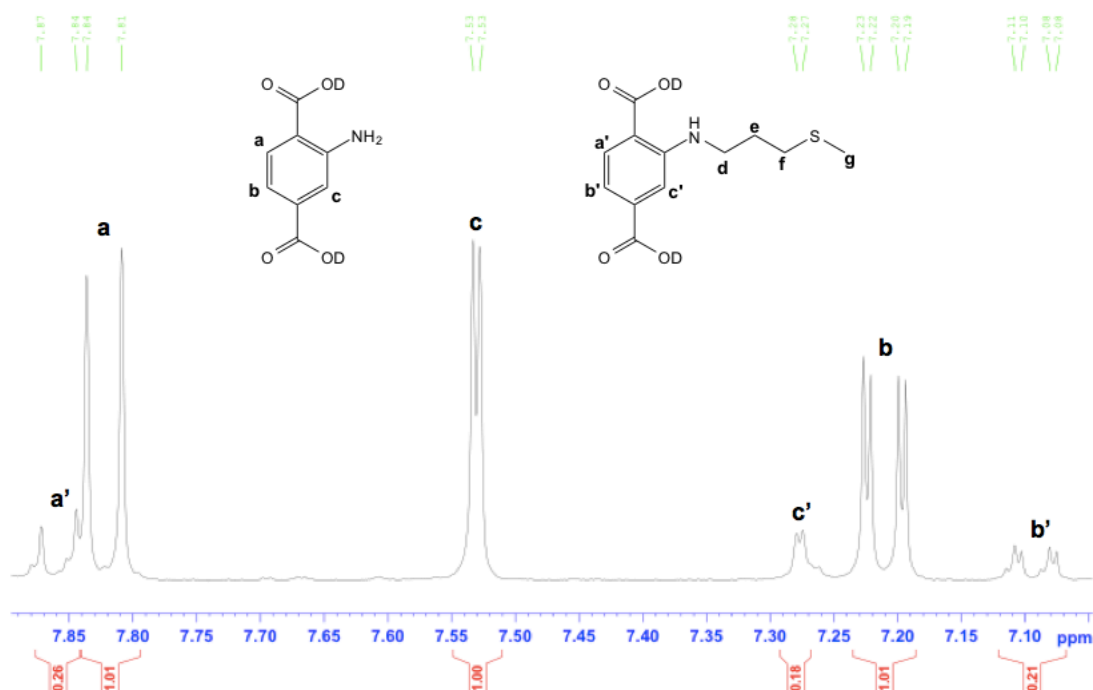


Figure S20. Aromatic region of the ^1H NMR spectrum of digested **2i**.

2.11 Reaction of IRMOF-3 with tribromoacetaldehyde and NaCNBH_3 (**2j**)

Crystals of IRMOF-3 were washed and suspended in anhydrous DMF/THF for 3 days, replacing the solvent every 24 hours. For the PSM reaction, IRMOF-3 (0.100 g, 0.23 mmol eq. NH_2), tribromoacetaldehyde (0.097 mL, 0.92 mmol) and NaCNBH_3 (0.058 g, 0.92 mmol) were added to a glass vial containing 5 mL of DMF/THF. The glass vial was then sealed to generate autogenous pressure and placed in an oven at 50°C for 3 days. The crystals were then washed by decantation with fresh anhydrous DMF/THF every 24 hours for 3 days. ^1H NMR analysis revealed that no reaction had occurred.

2.12 Reaction of IRMOF-3 with 3-(methylthio)propionaldehyde and NaCNBH_3 followed by EtCHO and NaCNBH_3 (**2k**)

Crystals of IRMOF-3 were washed and suspended in anhydrous DMF for 3 days, replacing the solvent every 24 h. IRMOF-3 (0.100 g, 0.23 mmol eq. NH_2), 3-(methylthio)propionaldehyde, (0.091 mL, 0.92 mmol) and NaCNBH_3 (0.058 g, 0.92 mmol) were added to a glass vial containing 5 mL of DMF. The vial was sealed and placed in an oven at 50°C for 3 days. After this time, the solid product was washed several times with fresh DMF, then propanal (0.031 mL, 0.44 mmol) and NaCNBH_3 (0.028 g, 0.44 mmol) were added to the vial and the mixture was left at room temperature for a further 3 days. After this time the solid was washed with DMF. The powder X-ray diffraction pattern for $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{1.94}(\text{bdc-NHCH}_2\text{CH}_2\text{CH}_2\text{SMe})_{0.47}(\text{bdc-NHPr})_{0.59}]$, **2k** is shown in Figure S21 and the ^1H NMR spectrum of the acid digested MOF is shown in Figure S22.

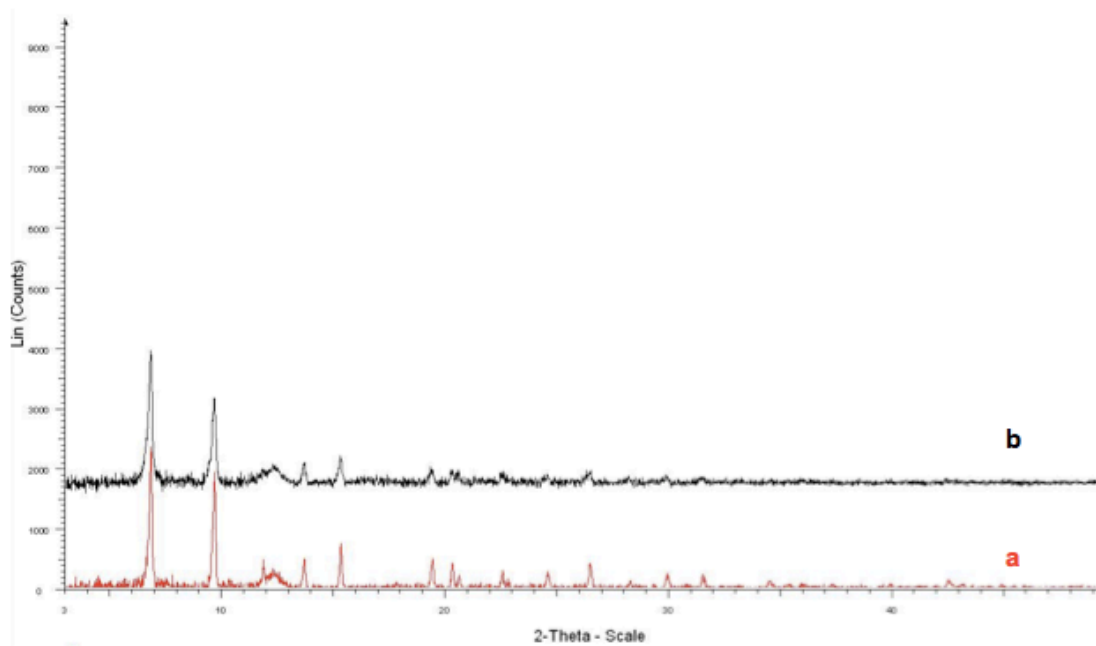


Figure S21. PXRD patterns for (a) IRMOF-3 and (b) tandem PSM product **2k**.

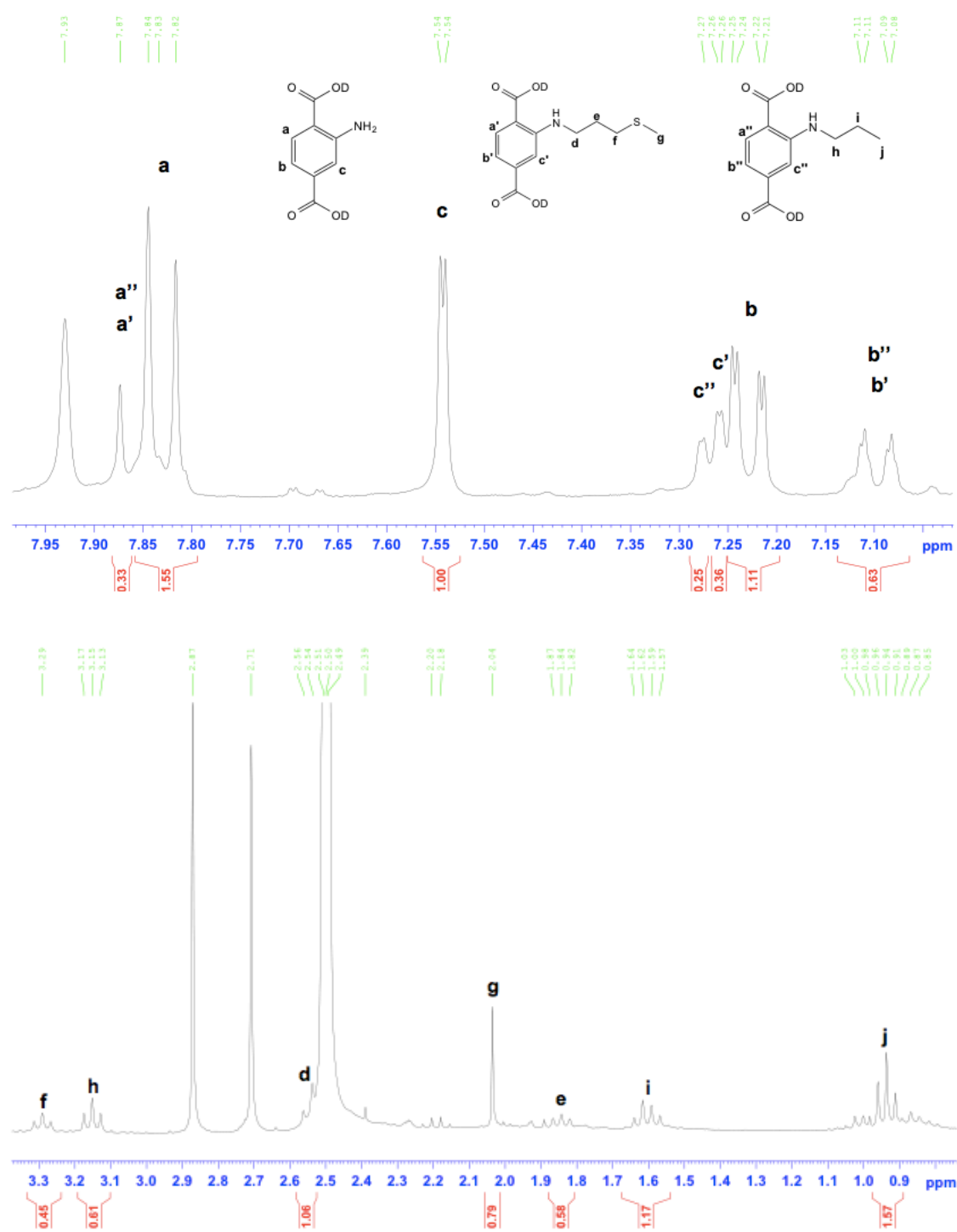


Figure S22. Aromatic and aliphatic regions of the ^1H NMR spectrum of the digested tandem PSM product **2k**.

2.13 Thermogravimetric analysis on 2a-g

Thermogravimetric analyses on **2a-g** are shown in Figures S23-24, with the powder diffraction pattern of the final decomposition product of **2a** shown in Figure S25.

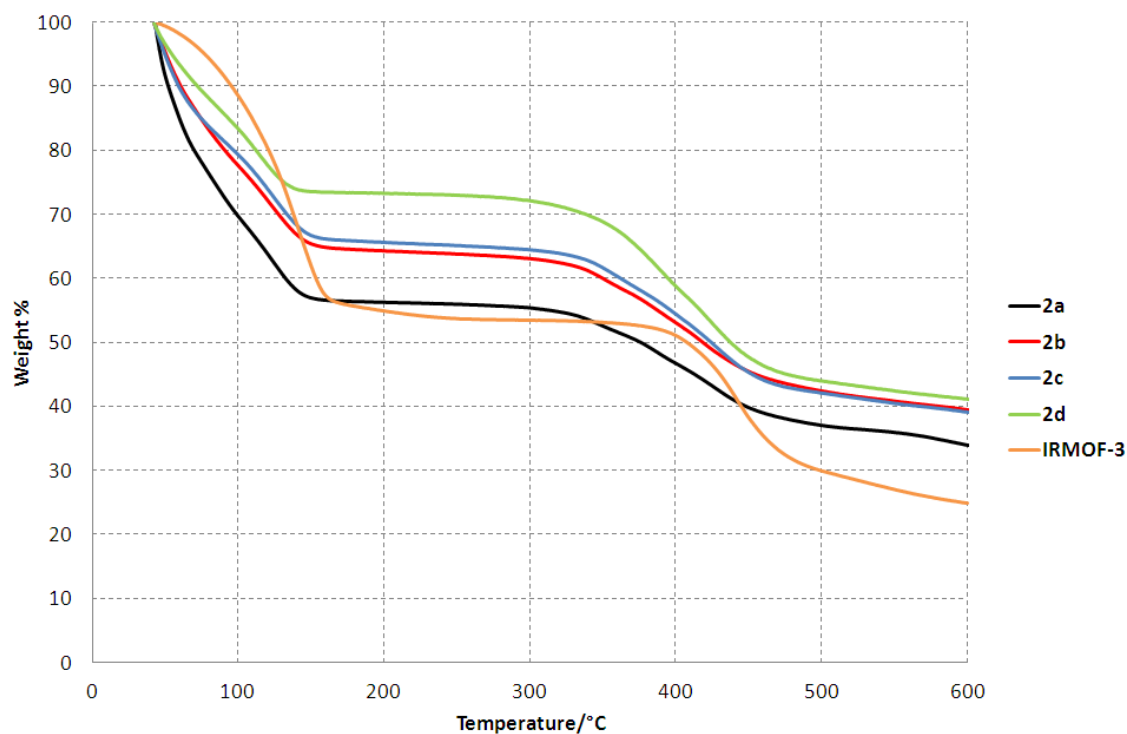


Figure S23. Thermogravimetric analyses of **2a-d** and IRMOF-3.

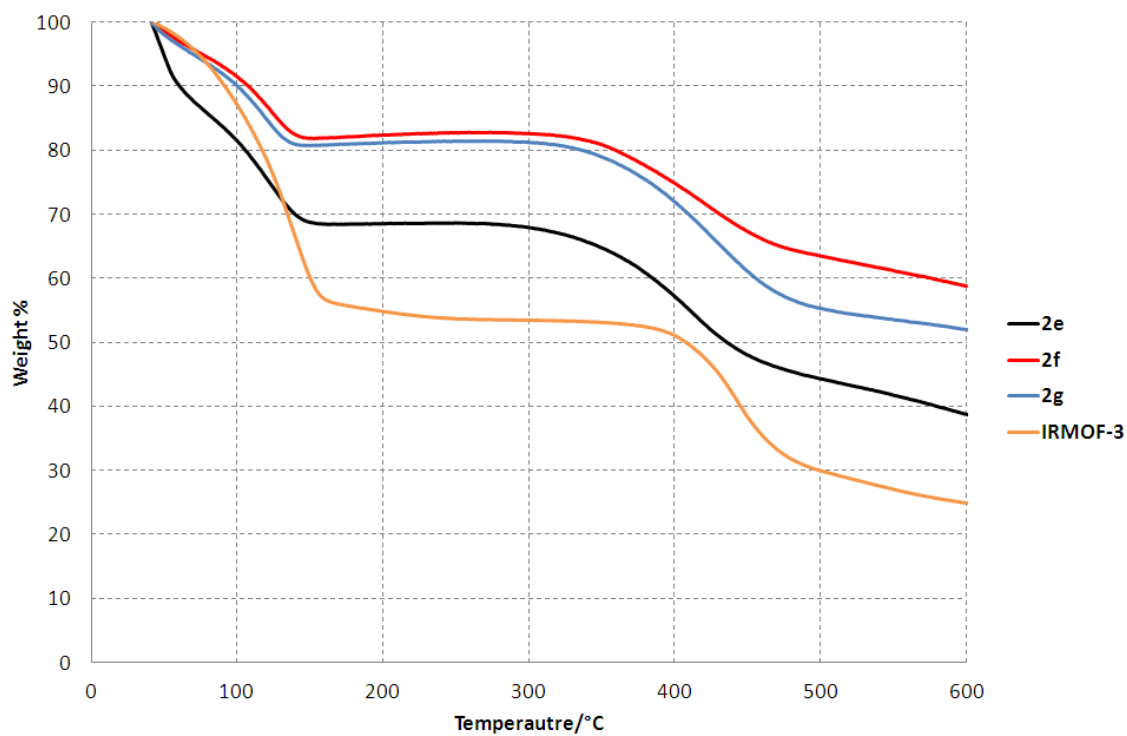


Figure S24. Thermogravimetric analyses of **2e-g** and IRMOF-3.

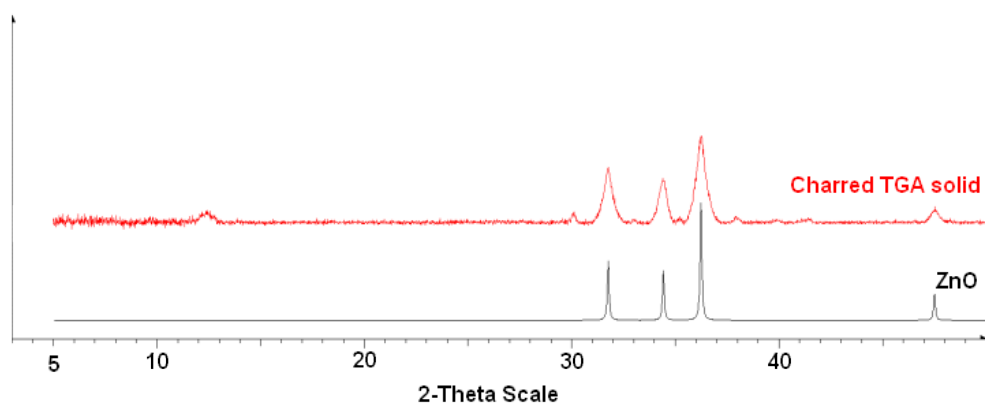


Figure S25. PXRD pattern of the residue after the thermogravimetric analysis of **2a** and the calculated pattern from the crystal structure of ZnO, zincite (black).^{S3}

2.14 Nitrogen adsorption studies on **2a-g**

BJH plots for **2a-g** are shown in Figures S26-27, showing the existence of mesopores.

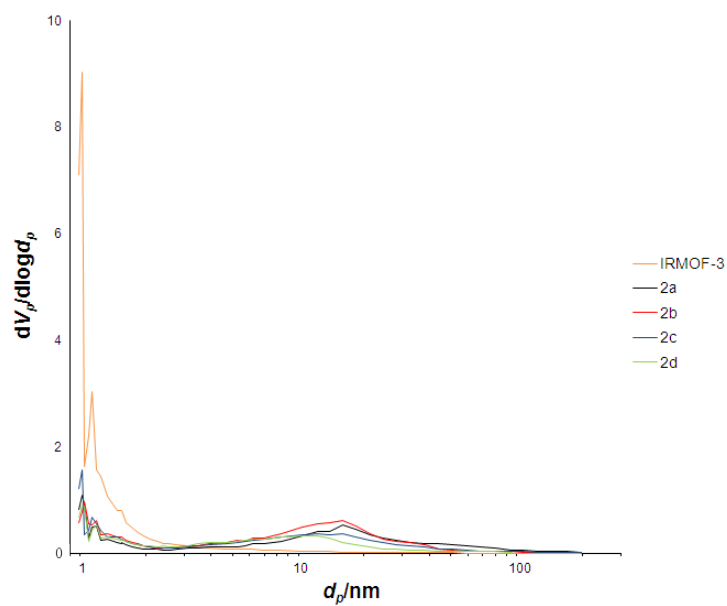


Figure S26. BJH plot of IRMOF-3 and compounds **2a-d**.

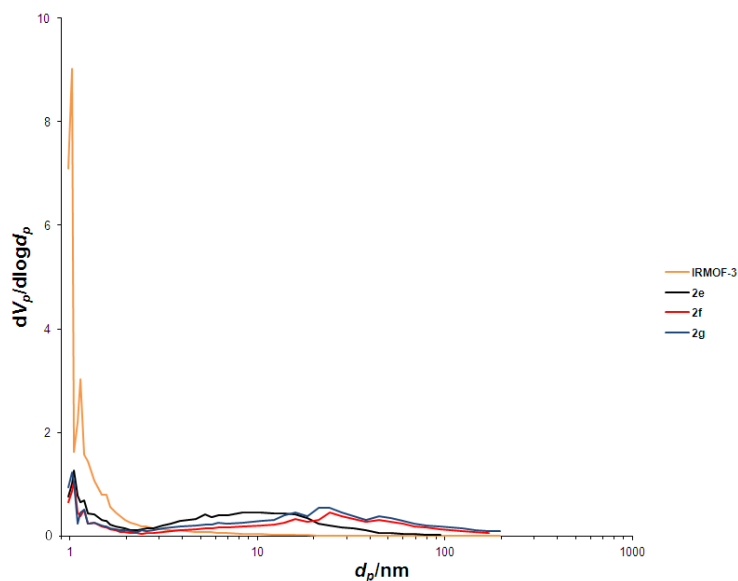


Figure S27. BJH plot of IRMOF-3 and compounds **2e-g**.

3. Experimental: tandem PSM reaction of MIL-101(Cr)-NHCH₂R

The general PSM procedure requires MeOH exchanged MIL-101(Cr)-NH₂ which was synthesised according to a previously reported preparation.^{S4}

3.1 Reaction of MIL-101(Cr)-NH₂ with MeCHO and NaCNBH₃ (**4a**)

MIL-101(Cr)-NH₂·7EtOH was washed with solvent (MeOH) for 3 days with fresh solvent every 24 h. 75 mg MIL-101(Cr)-NH₂ (0.295 mmol NH₂ eq) was added to 5 mL MeOH in a glass vial. This was cooled in an ice bath to less than 5°C. Ethanal (66 µL, 1.18 mmol, 4 eq.) and then NaCNBH₃ (74 mg, 1.18 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 72 h without stirring, before cooling to ambient temperature. The product was separated by centrifugation and rinsed with MeOH. The resulting green micro-crystals were then washed in EtOH once per day for three days and dried under a flow of N₂. The ¹H NMR spectrum of digested [Cr₃O(OH)(OH₂)₂(bdc-NH₂)_{1.47}(bdc-NHEt)_{1.53}]·3EtOH, **4a** is shown in Figure S28.

$m/z = 208.0618$ (predicted [C₁₀H₁₀NO₄]⁻, [M - H]⁻ = 208.0615).

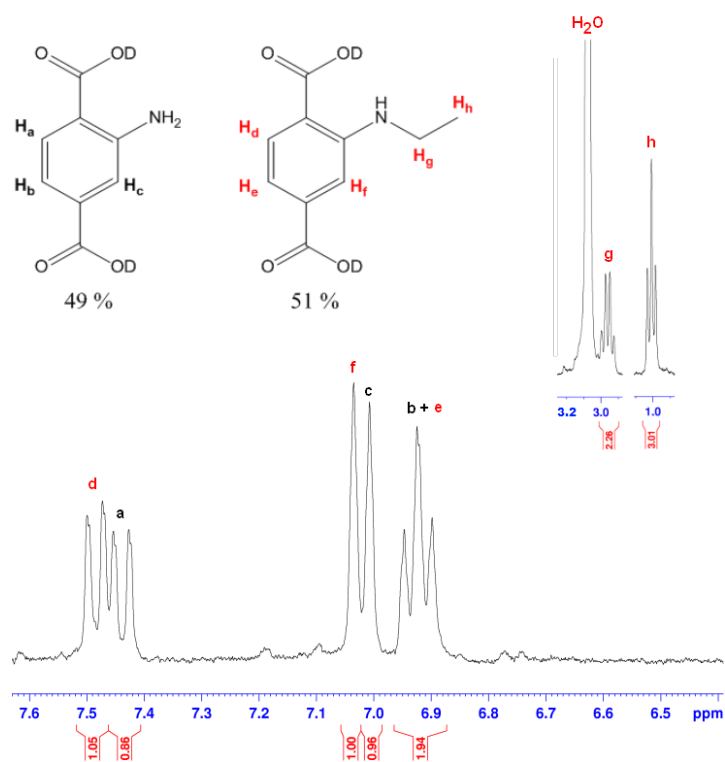


Figure S28. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **4a**.

3.2 Reaction of MIL-101(Cr)-NH₂ with EtCHO and NaCNBH₃ (**4b**)

MIL-101(Cr)-NH₂·7EtOH was washed with solvent (MeOH) for 3 days with fresh solvent every 24 h. 75 mg MIL-101(Cr)-NH₂ (0.295 mmol NH₂ eq) was added to 5 mL MeOH in a glass vial. Propanal (86 μL , 1.18 mmol, 4 eq.) and then NaCNBH₃ (74 mg, 1.18 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 72 h without stirring, before being removed from the oven and cooled to ambient temperature. The product was separated by centrifugation and rinsed with MeOH. The resulting green micro-crystals were then washed in EtOH once per day for three days and dried under a flow of N₂. The ^1H NMR spectrum of digested [Cr₃O(OH)(OH₂)₂(bdc-NH₂)_{1.53}(bdc-NHPr)_{1.47}]·1.5EtOH, **4b** is shown in Figure S29.

$m/z = 222.0768$ (predicted [C₁₁H₁₂NO₄]⁻, [M - H]⁻ = 222.0766).

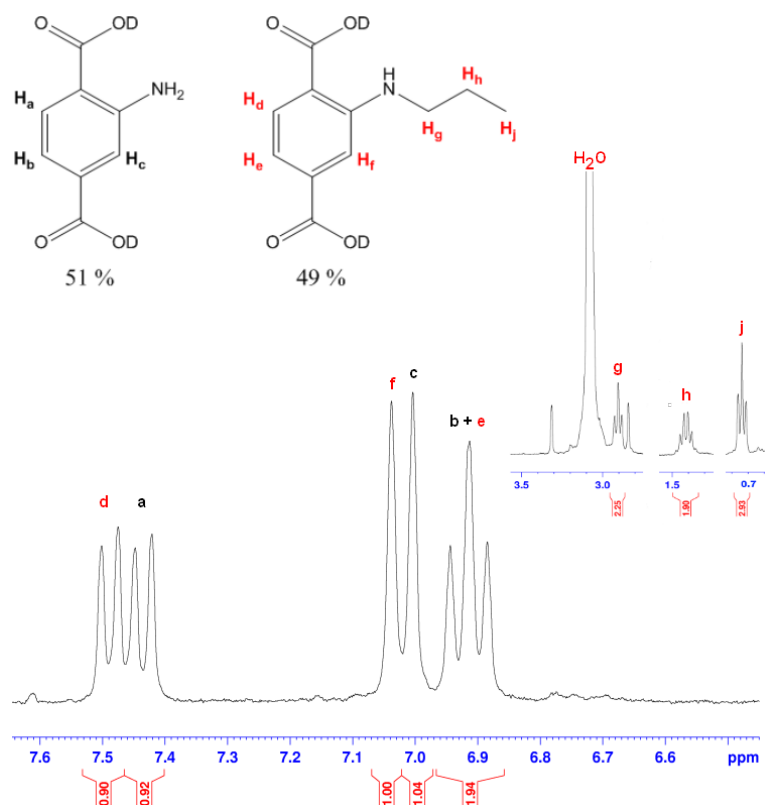


Figure S29. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **4b**.

3.3 Reaction of MIL-101(Cr)-NH₂ with PrCHO and NaCNBH₃ (**4c**)

MIL-101(Cr)-NH₂·7EtOH was washed with solvent (MeOH) for 3 days with fresh solvent every 24 h. 75 mg MIL-101(Cr)-NH₂ (0.295 mmol NH₂ eq) was added to 5 mL MeOH in a glass vial. Butanal (104 μL , 1.18 mmol, 4 eq.) and then NaCNBH₃ (74 mg, 1.18 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50°C for 72 h without stirring, before cooling to ambient temperature. The product was separated by centrifugation and rinsed with MeOH. The resulting green micro-crystals were then washed in EtOH once per day for three days and dried under a flow of N₂. The ^1H NMR spectrum of digested [Cr₃O(OH)(OH₂)₂(bdc-NH₂)_{1.65}(bdc-NHBU)_{1.35}]·3EtOH, **4c** is shown in Figure S30.

$m/z = 236.0916$ (predicted [C₁₂H₁₄NO₄]⁻, [M - H]⁻ = 236.0923).

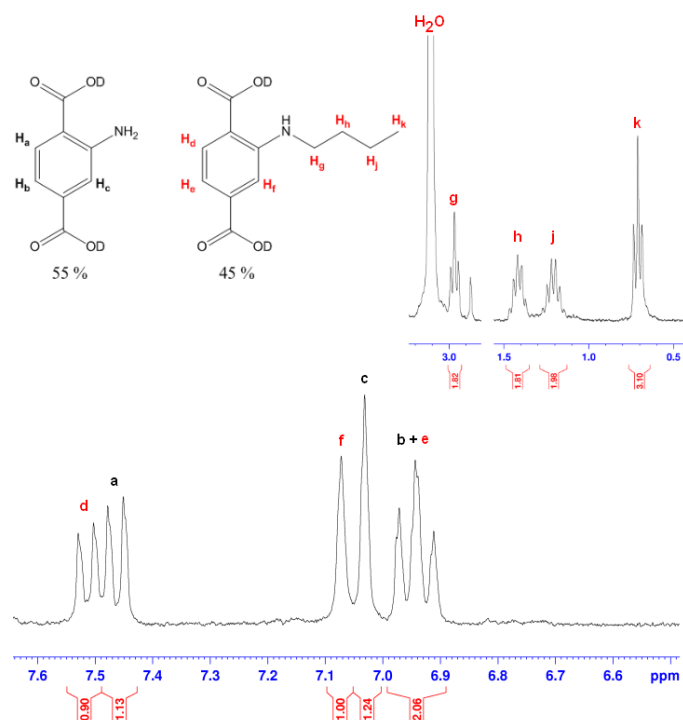


Figure S30. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **4c**.

3.4 Reaction of MIL-101(Cr)-NH₂ with C₇H₁₅CHO and NaCNBH₃ (**4d**)

MIL-101(Cr)-NH₂·7EtOH was washed with solvent (MeOH) for 3 days with fresh solvent every 24 h. 75 mg MIL-101(Cr)-NH₂ (0.295 mmol NH₂ eq) was added to 5 mL MeOH in a glass vial. Octanal (184 μL , 1.18 mmol, 4 eq.) and then NaCNBH₃ (74 mg, 1.18 mmol, 4 eq.) were added to this mixture. After 30 min effervescence the mixture was sealed and heated to 50 $^\circ\text{C}$ for 48 h without stirring, before cooling to ambient temperature. The product was separated by centrifugation and rinsed with MeOH. The resulting green micro-crystals were then washed in EtOH once per day for three days and dried under a flow of N₂. The ^1H NMR spectrum of digested [Cr₃O(OH)(OH)₂(bdc-NH₂)_{1.95}(bdc-NHC₈H₁₇)_{1.05}] \cdot 2EtOH, **4d** is shown in Figure S31.

$m/z = 292.1549$ (predicted [C₁₆H₂₂NO₄]⁻, [M - H]⁻ = 292.1554).

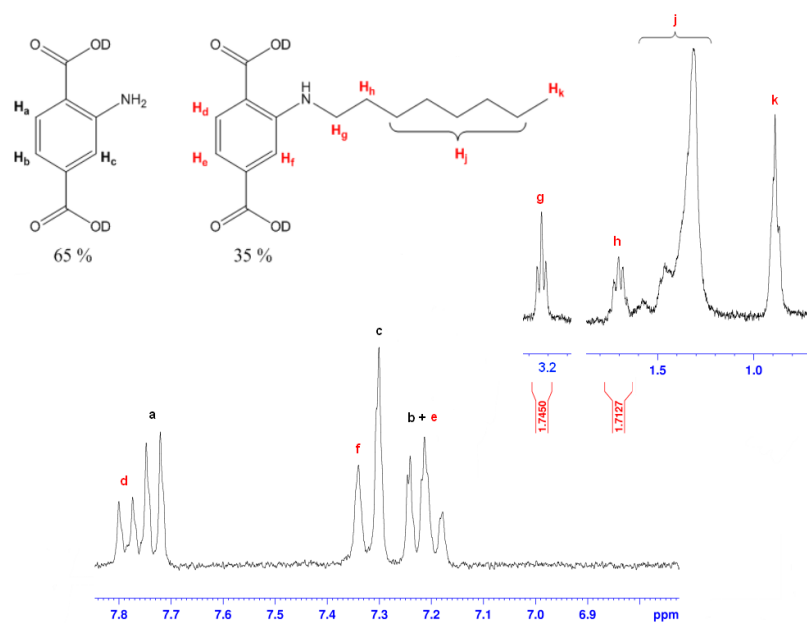


Figure S31. Aromatic and aliphatic (insert) regions of the ^1H NMR spectrum of digested **4d**.

3.5 Further characterisation of **4a-d**

The PXRD patterns for **4a-d** are shown in Figure S32, revealing the decrease in crystallinity with increasing chain length following post-synthetic modification. IR spectra for **4a-d** are shown in Figure S33, and nitrogen adsorption/desorption data are shown in Figure S34.

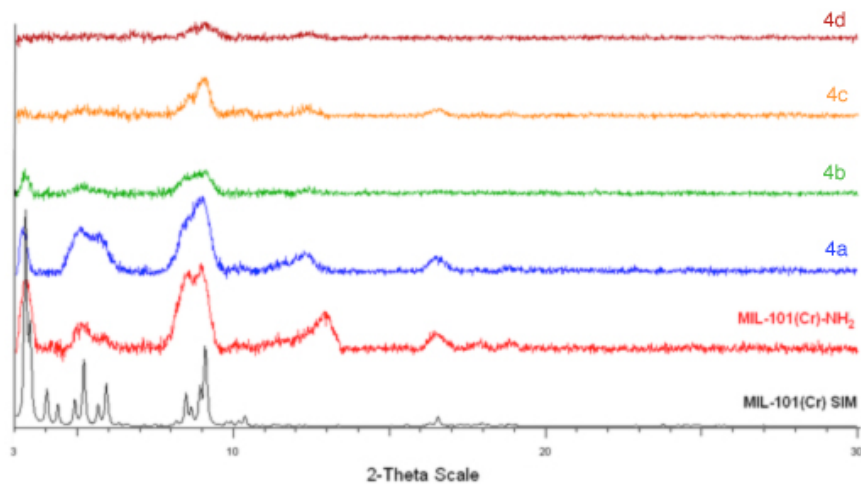


Figure S32. PXRD diffraction patterns for **4a-d** and MIL-101(Cr)- NH_2 as made (red) and simulated from the structure of MIL-101(Cr) (black).^{S5}

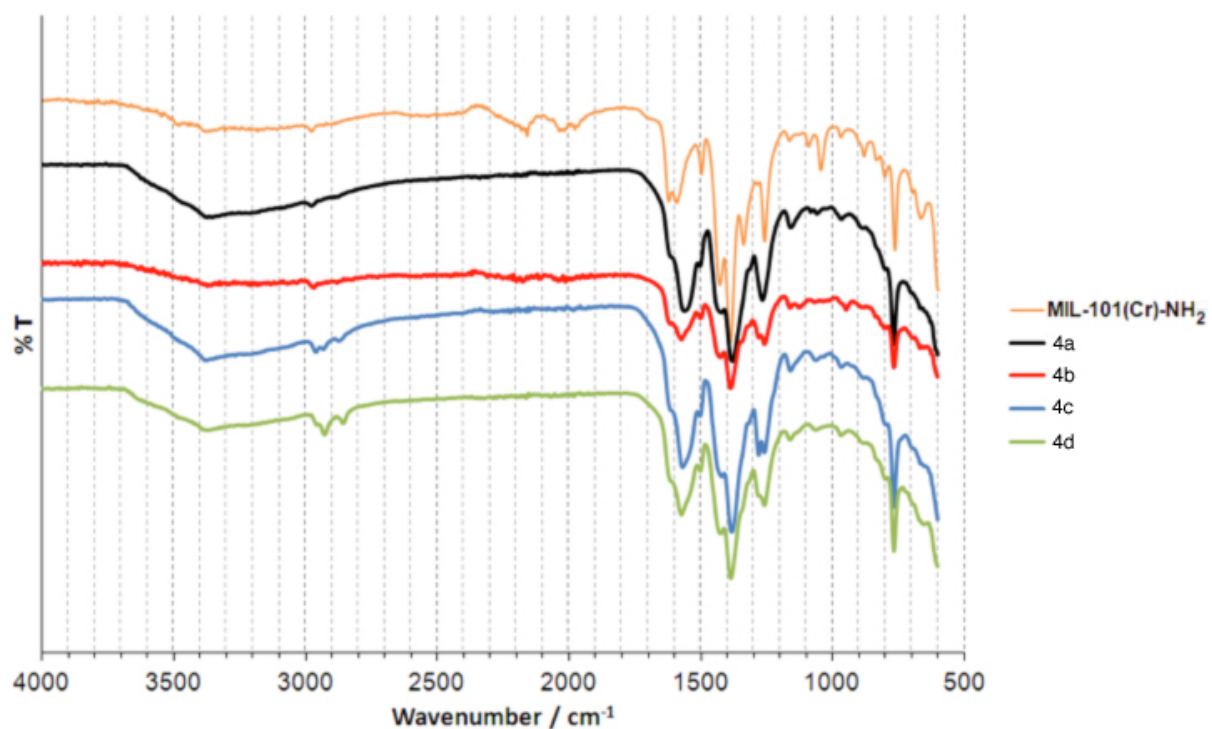


Figure S33. FT-IR spectra of compounds 4a-d.

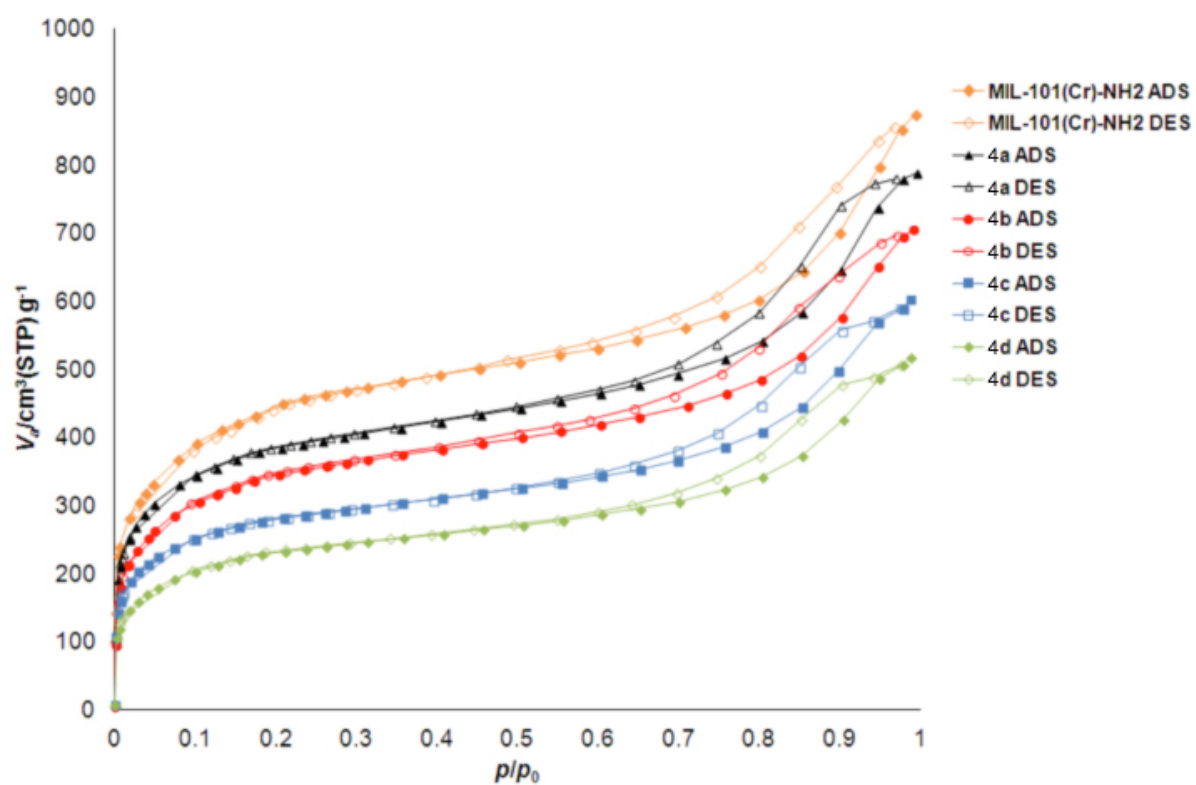


Figure S34. N₂ adsorption (filled points) and desorption (open points) isotherms of 4a-d at 77 K.

4. Dicarboxylic acid syntheses

4.1 2-(Ethylamino)benzene-1,4-dicarboxylic acid, H₂bdc-NHEt, H₂L¹

2-Aminobenzene-1,4-dicarboxylic acid (H₂bdc-NH₂) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then ethanal (0.124 mL, 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 NaCNBH₃ (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%). ¹H NMR (300 MHz, DMSO-*d*₆) δ/ppm: 7.79 (d, 1H, *J* = 7.8 Hz), 7.05 (s (br), 1H), 6.97 (dd, 1H, *J* = 7.8, 1.5 Hz), 3.11 (q, 2H, *J* = 7.0 Hz), 1.21 (t, 3H, *J* = 7.0 Hz). ¹³C NMR (75 MHz, DMSO-*d*₆) 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][–]). [C₁₀H₁₀O₄N][–] requires 208.0610). Found C: 57.15, H: 5.41, N: 7.01 %. C₁₀H₁₁O₄N requires C: 57.41, H: 5.30, N: 6.70 %. The IR spectrum for H₂L¹ is shown in Figure S35 and the ¹H NMR spectrum is shown in Figure S36.

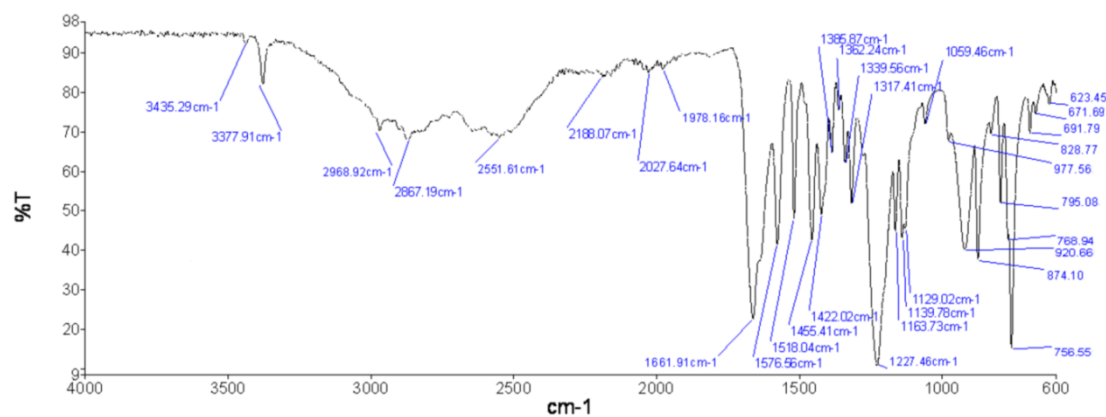


Figure S35. FT-IR spectrum of H₂bdc-NHEt, H₂L¹.

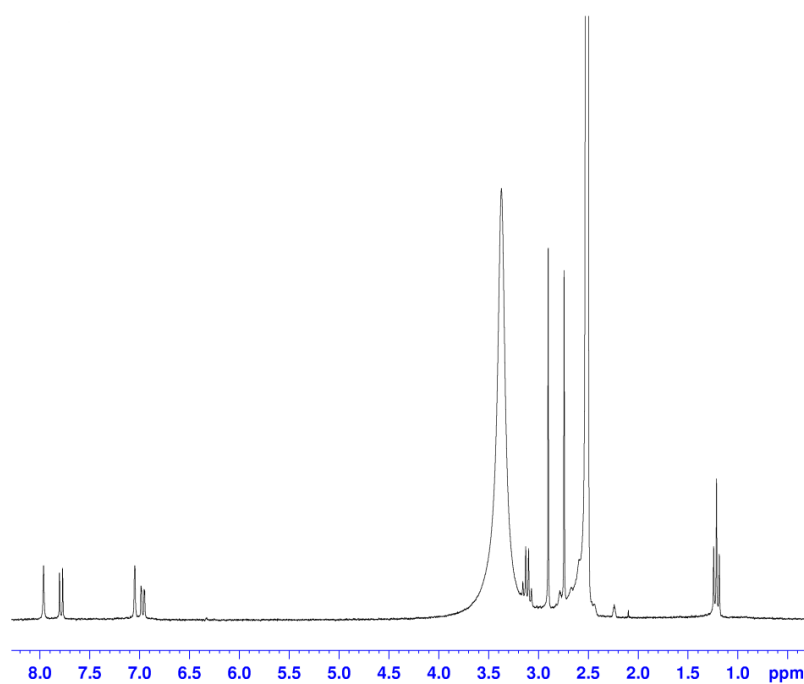


Figure S36. ¹H NMR spectrum of H₂bdc-NHEt, H₂L¹, in DMSO-*d*₆.

4.2 2-(Propylamino)benzene-1,4-dicarboxylic acid, H₂bdc-NHPr, H₂L²

2-Aminobenzene-1,4-dicarboxylic acid (H₂bdc-NH₂) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then propanal (0.161 mL, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaCNBH₃ (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%). ¹H NMR (300 MHz, DMSO-*d*₆) 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). ¹³C NMR (75 MHz, DMSO-*d*₆) 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]⁻. [C₁₁H₁₂O₄N]⁻ requires 222.0766). Found C: 59.00, H: 5.95, N: 6.50 %. C₁₁H₁₃O₄N requires C: 59.45, H: 5.44, N: 6.30 %. The IR spectrum for H₂L² is shown in Figure S37 and the ¹H NMR spectrum is shown in Figure S38.

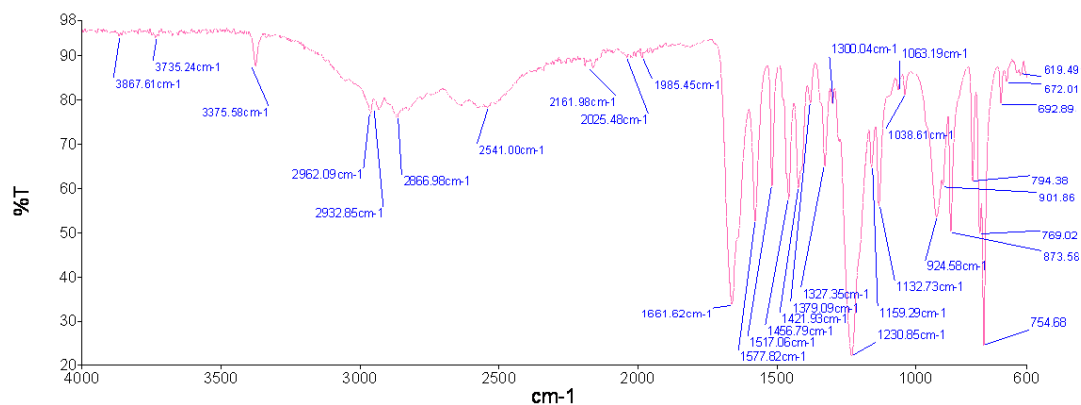


Figure S37. FT-IR spectrum of H₂bdc-NHPr, H₂L².

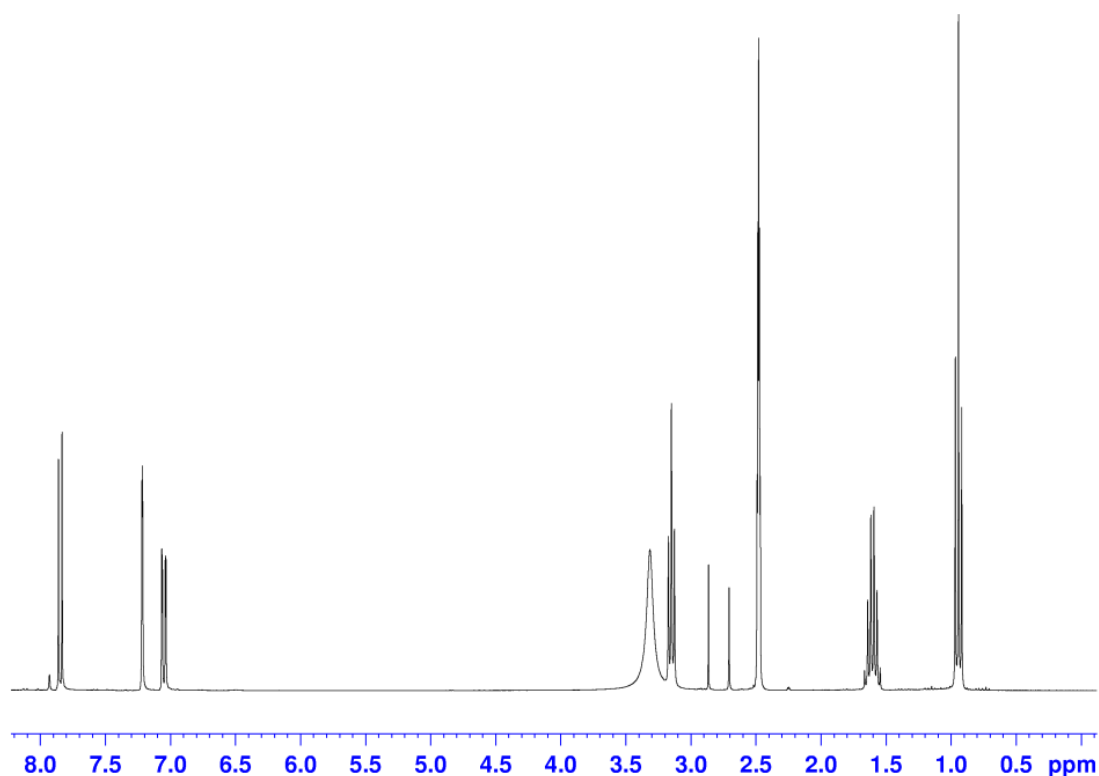


Figure S38. ^1H NMR spectrum of $\text{H}_2\text{bdc-NHPr}$, H_2L^2 , in $\text{DMSO-}d_6$.

4.3 2-(Butylamino)benzene-1,4-dicarboxylic acid, $\text{H}_2\text{bdc-NHBu}$, H_2L^3

2-Aminobenzene-1,4-dicarboxylic acid ($\text{H}_2\text{bdc-NH}_2$) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then butanal (0.195 mL, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and NaCNBH_3 (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 %). ^1H NMR (300 MHz, $\text{DMSO-}d_6$) 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). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) 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 ($[\text{M} - \text{H}]^-$. $[\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}]^-$ requires 236.0923). Found C: 60.80, H: 6.49, N: 6.06 %. $\text{C}_{12}\text{H}_{15}\text{O}_4\text{N}$ requires C: 60.75, H: 6.37, N: 5.90 %. The IR spectrum for H_2L^3 is shown in Figure S39 and the ^1H NMR spectrum is shown in Figure S40.

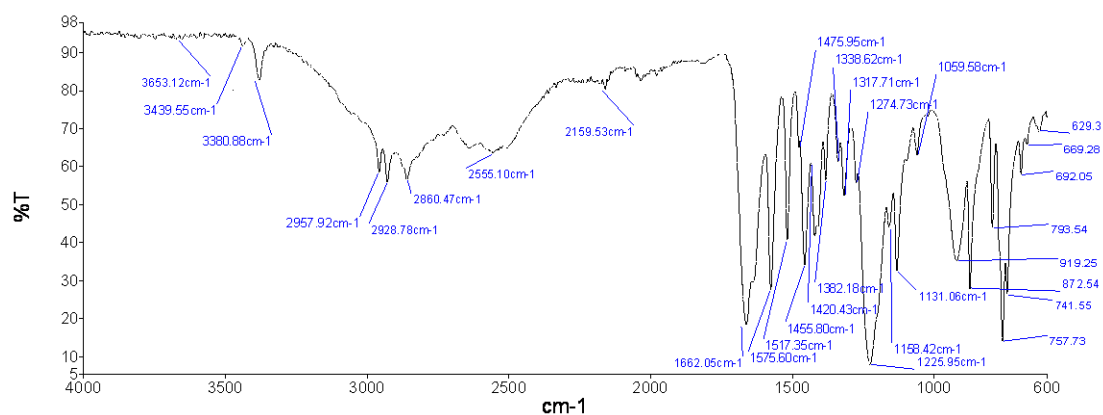


Figure S39. FT-IR spectrum of $H_2bdc-NHBu, H_2L^3$.

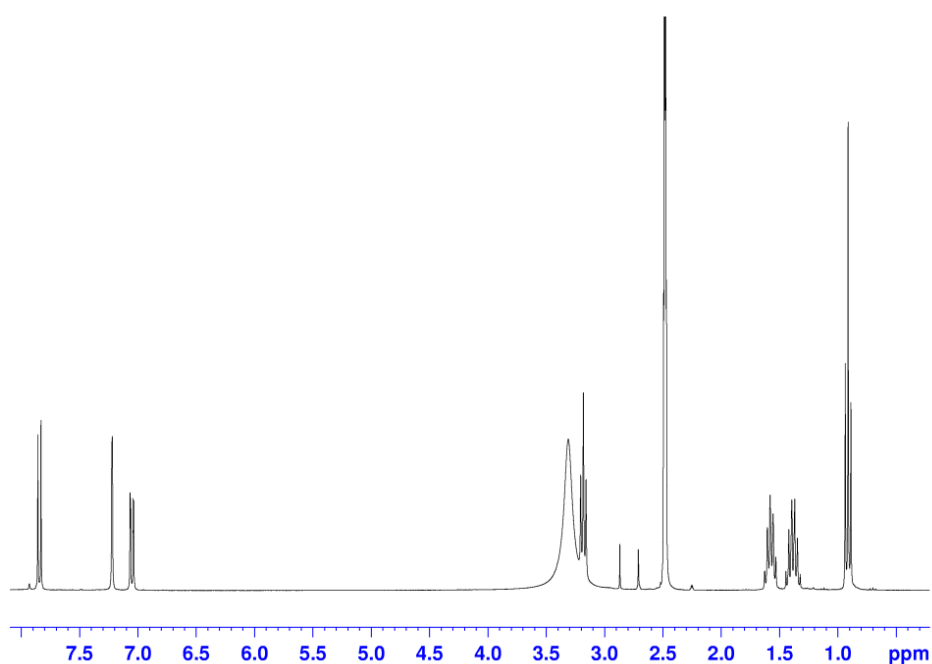


Figure S40. 1H NMR spectrum of $H_2bdc-NHBu, H_2L^3$, in $DMSO-d_6$.

4.4 2-(Octylamino)benzene-1,4-dicarboxylic acid, $H_2bdc-NHC_8H_{17}, H_2L^4$

2-Aminobenzene-1,4-dicarboxylic acid ($H_2bdc-NH_2$) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then octanal (0.345 mL, 2.208 mmol) was added and the solution stirred for 1 h. The solution was then cooled in an ice bath and $NaCNBH_3$ (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%). 1H NMR (300 MHz, $DMSO-d_6$) 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). ^{13}C NMR (75 MHz, $DMSO-d_6$) 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 ($[M - H]^-$. $[C_{16}H_{22}O_4N]^-$ requires 292.1549). Found C: 66.20, H:

8.75, N: 4.26 %. $C_{16}H_{23}O_4N$ requires C: 65.51, H: 7.90, N: 4.77 %. (matches with 0.3 eq octanal and 0.1 eq H_2O added). The IR spectrum for H_2L^4 is shown in Figure S41 and the 1H NMR spectrum is shown in Figure S42.

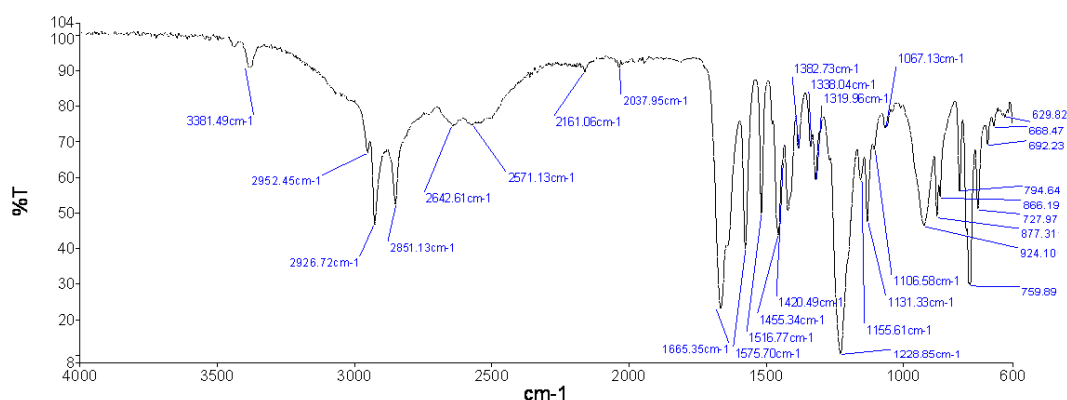


Figure S41. FT-IR spectrum of $H_2bdc-NHC_8H_{17}$, H_2L^4 .

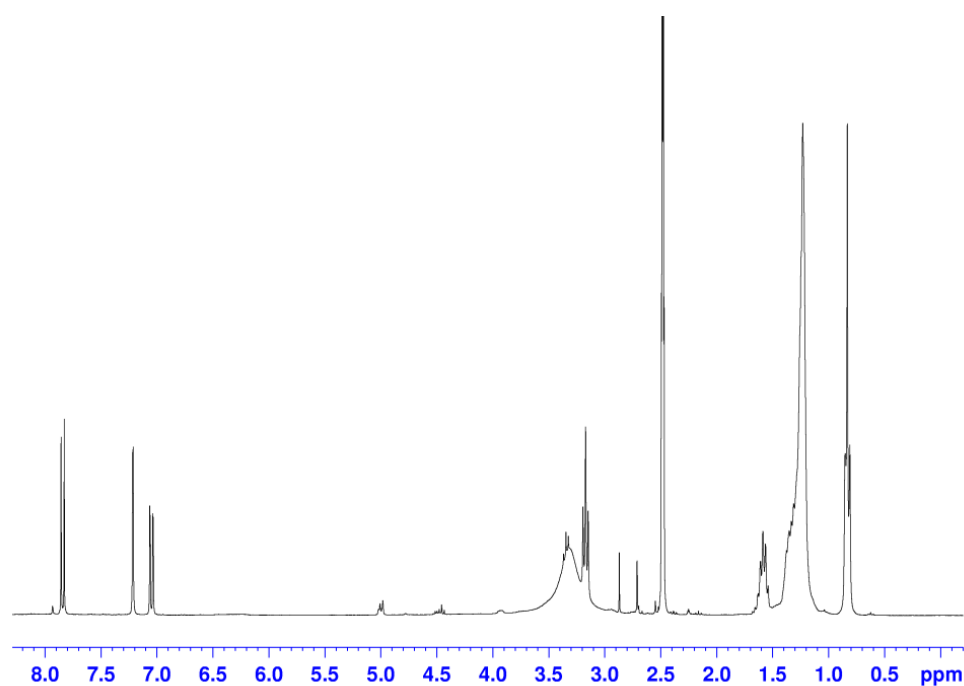


Figure S42. 1H NMR spectrum of $H_2bdc-NHC_8H_{17}$, H_2L^4 , in $DMSO-d_6$.

4.5 2-((Cyclohex-3-en-1-ylmethyl)amino)terephthalic acid, $H_2bdc-NHC_7H_{11}$, H_2L^5

2-Aminobenzene-1,4-dicarboxylic acid ($H_2bdc-NH_2$) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then 1,2,3,6-tetrahydrobenzaldehyde (0.251 mL, 2.208 mmol) was added and the solution stirred at room temperature for 1 h. The solution was then cooled in an ice bath and $NaCNBH_3$ (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 which was filtered, washed with 3×5 mL H_2O and dried in an oven at $80^\circ C$ for 1 h. The compound was recrystallised from DMF/ H_2O . Yield: 0.296 g (97 %). 1H NMR (300 MHz, $DMSO-d_6$) δ /ppm: 7.93 (d, 1H, $J = 8.2$ Hz), 7.31 (d, 1H, $J = 1.4$ Hz), 7.13 (dd, 1H, $J = 8.2, 1.5$ Hz), 5.72 (m, 2H), 3.21 (d, 2H, $J = 6.4$ Hz) 2.14 (m, 3H) 1.88

(m, 3H) 1.37 (m, 1H). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ/ppm : 170.0, 167.5, 151.1, 136.1, 132.4, 127.3, 126.1, 114.7, 113.3, 112.2, 48.0, 33.1, 29.4, 26.5, 24.6. m/z (ESI) 274.1079 ($[\text{M} - \text{H}]^-$. $[\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}]^-$ requires 274.1085). Found C: 65.70, H: 6.66, N: 5.25 %. $\text{C}_{15}\text{H}_{17}\text{O}_4\text{N}$ requires C: 65.44, H: 6.22, N: 5.09 %. The IR spectrum for H_2L^5 is shown in Figure S43 and the ^1H NMR spectrum is shown in Figure S44.

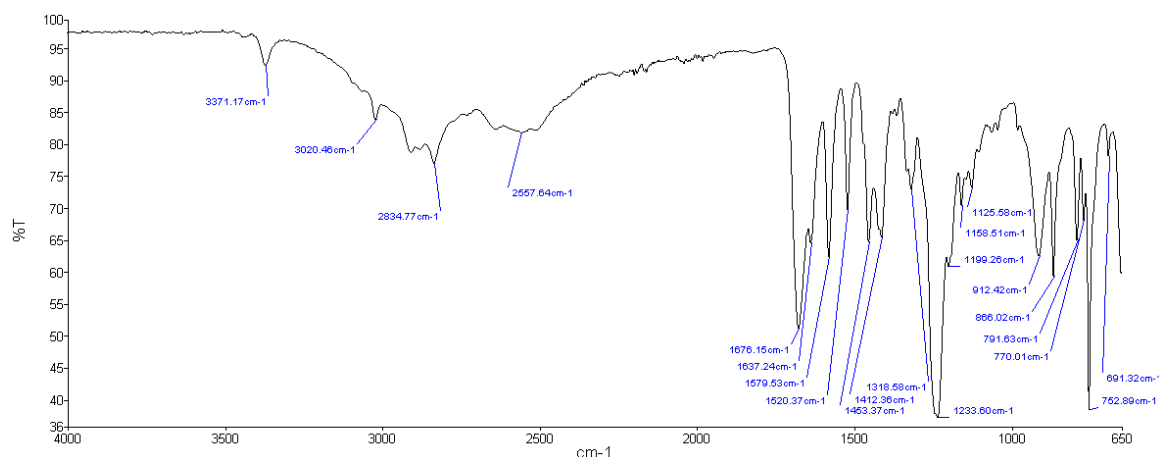


Figure S43. FT-IR spectrum of $\text{H}_2\text{bdc-NHC}_7\text{H}_{11}$, H_2L^5

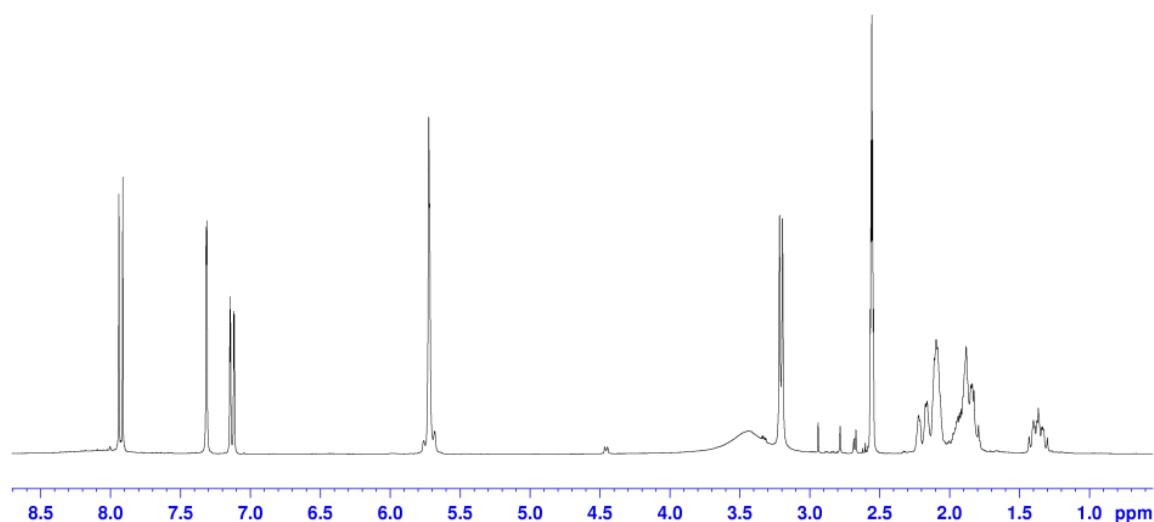


Figure S44. ^1H NMR spectrum for $\text{H}_2\text{bdc-NHC}_7\text{H}_{11}$, H_2L^5 , in $\text{DMSO-}d_6$.

4.6 2-((Ferrocenylmethyl)amino)terephthalic acid, $\text{H}_2\text{bdc-NHCH}_2\text{Fc}$, H_2L^6

2-Aminobenzene-1,4-dicarboxylic acid ($\text{H}_2\text{bdc-NH}_2$) (0.200 g, 1.104 mmol) was dissolved in DMF (10 mL), then ferrocenecarboxaldehyde (0.473 g, 2.208 mmol) was added and the solution stirred at room temperature for 1 h under N_2 . The solution was then cooled in an ice bath and NaCNBH_3 (0.139 g, 2.204 mmol) was added. The resulting reaction mixture was stirred at room temperature for 24 h. Water was added until a yellow/brown solid precipitated which was filtered, washed with 3×5 mL H_2O and dried in an oven at 80°C for 1 h. The compound was recrystallised from DMF/ H_2O . Yield: 0.323 g (77%). ^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ/ppm : 7.88 (d (br), 1H), 7.31 (s (br), 1H), 7.08 (d (br), 1H), 4.25 (br, 2H), 4.23

(br, 5H) 4.16 (br, 2H), 4.07 (br, 2H). ^{13}C NMR (75 MHz, DMSO- d_6) δ /ppm: 170.0, 167.5, 136.2, 132.4, 114.9, 113.4, 112.4, 85.9, 83.7, 69.6, 69.2, 68.9, 68.7, 67.9, 67.7, 67.2, 41.7, 15.0. m/z (ESI) 378.0432 ($[\text{M} - \text{H}]^-$. $[\text{C}_{19}\text{H}_{16}\text{O}_4\text{NFe}]^-$ requires 378.0434). Found C: 61.10, H: 4.88, N: 3.06 %. $\text{C}_{19}\text{H}_{17}\text{O}_4\text{NFe}$ requires C: 60.18, H: 4.52, N: 3.69 %. The IR spectrum for H_2L^6 is shown in Figure S45 and the ^1H NMR spectrum is shown in Figure S46.

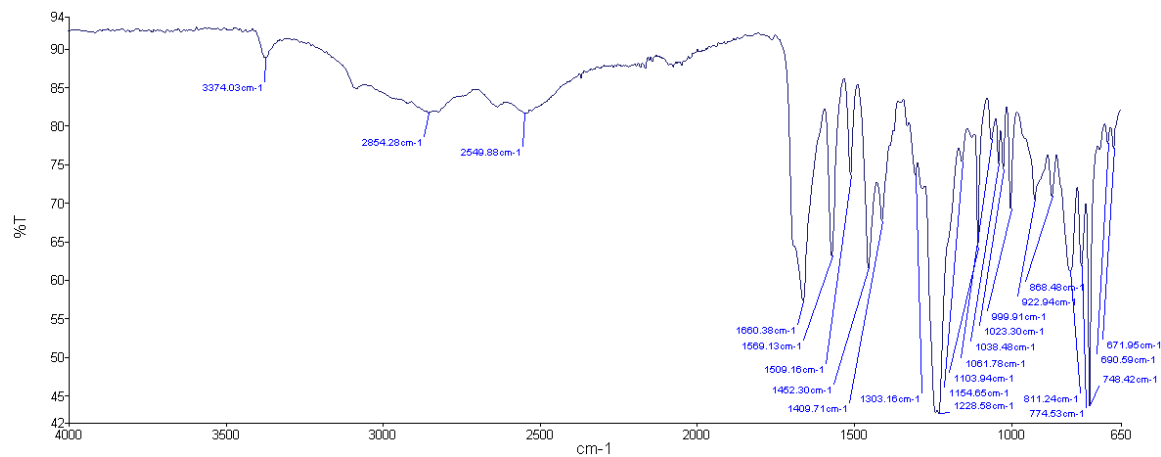


Figure S45. FT-IR spectrum of $\text{H}_2\text{bdc-NHCH}_2\text{Fc}$, H_2L^6 .

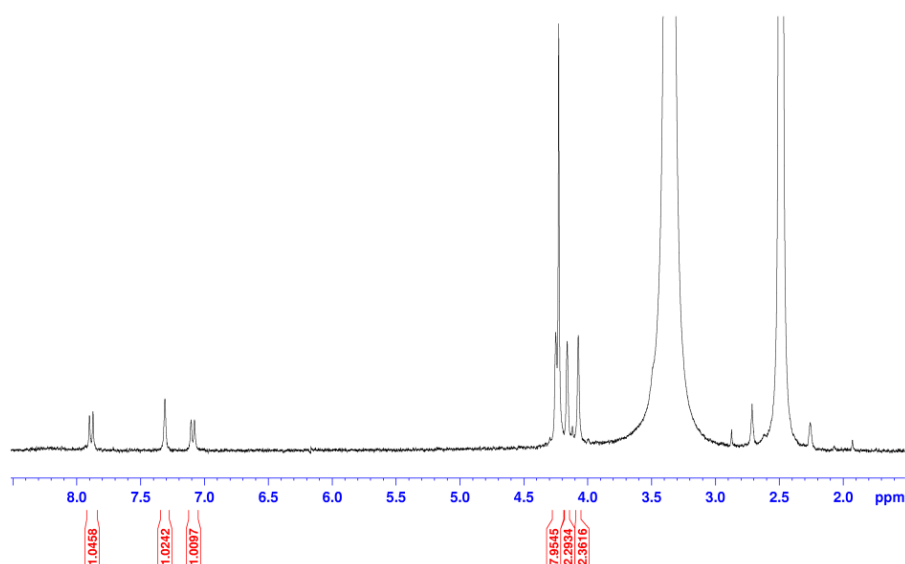


Figure S46. ^1H NMR spectrum of $\text{H}_2\text{bdc-NHCH}_2\text{Fc}$, H_2L^6 , in DMSO- d_6 .

4.7 2-((4-(Methylthio)benzyl)amino)terephthalic acid, $\text{H}_2\text{bdc-NHCH}_2\text{C}_6\text{H}_4\text{SMe}$, H_2L^7

2-Aminobenzene-1,4-dicarboxylic acid ($\text{H}_2\text{bdc-NH}_2$) (0.200 g, 1.104 mmol) was dissolved in N,N' -dimethylformamide (DMF) (10 mL), then 4-methylthiobenzaldehyde (0.294 mL, 2.208 mmol) was added and the solution stirred at room temperature for 1 h. The solution was then cooled in an ice bath and NaCNBH_3 (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 which was filtered, washed with 3×5 mL H_2O and dried in an oven at 80°C for 1 h. The compound was recrystallised from DMF/ H_2O . Yield: 0.174 g (50%). ^1H NMR (300 MHz, DMSO- d_6) δ /ppm: 7.87 (d, 1H, $J = 8.2$ Hz), 7.25 (m, 4H), 7.17 (d, 1H, $J = 1.4$ Hz), 7.07 (dd, 1H, $J = 8.2, 1.5$ Hz), 4.44 (s(br) 2H),

2.43 (s, 3H). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ/ppm : 169.8, 167.4, 150.6, 136.9, 136.0 (2C), 132.3, 128.0 (2C), 126.5 (2C), 115.2, 113.9, 112.7, 45.7, 15.0. m/z (ESI) 316.0644 ($[\text{M} - \text{H}]^-$. $[\text{C}_{16}\text{H}_{14}\text{O}_4\text{NS}]^-$ requires 316.0649). Found C: 60.10, H: 4.76, N: 4.50 %. $\text{C}_{16}\text{H}_{15}\text{O}_4\text{NS}$ requires C: 60.55, H: 4.76, N: 4.41 %. The IR spectrum for H_2L^7 is shown in Figure S47 and the ^1H NMR spectrum is shown in Figure S48.

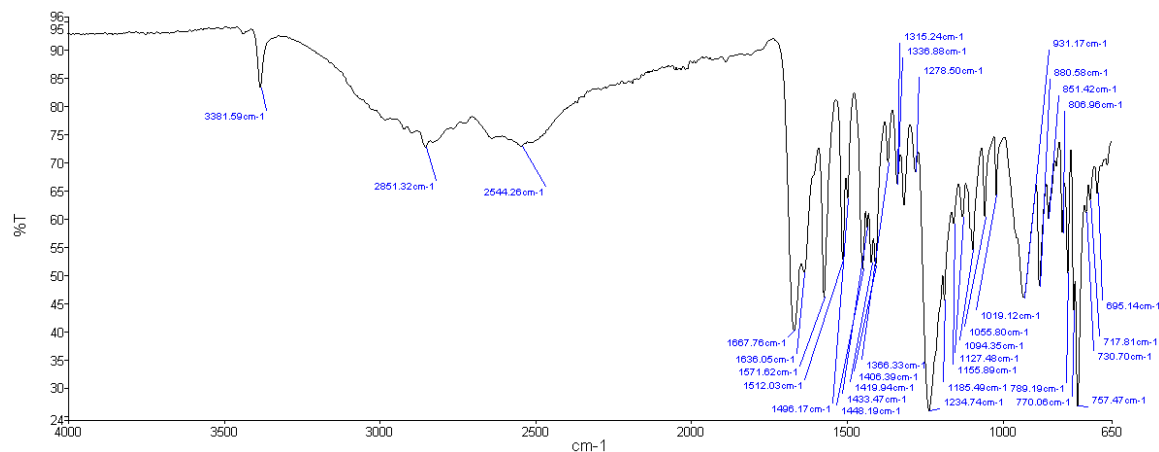


Figure S47. FT-IR spectrum of $\text{H}_2\text{bdc-NHCH}_2\text{C}_6\text{H}_4\text{SMe}$, H_2L^7 .

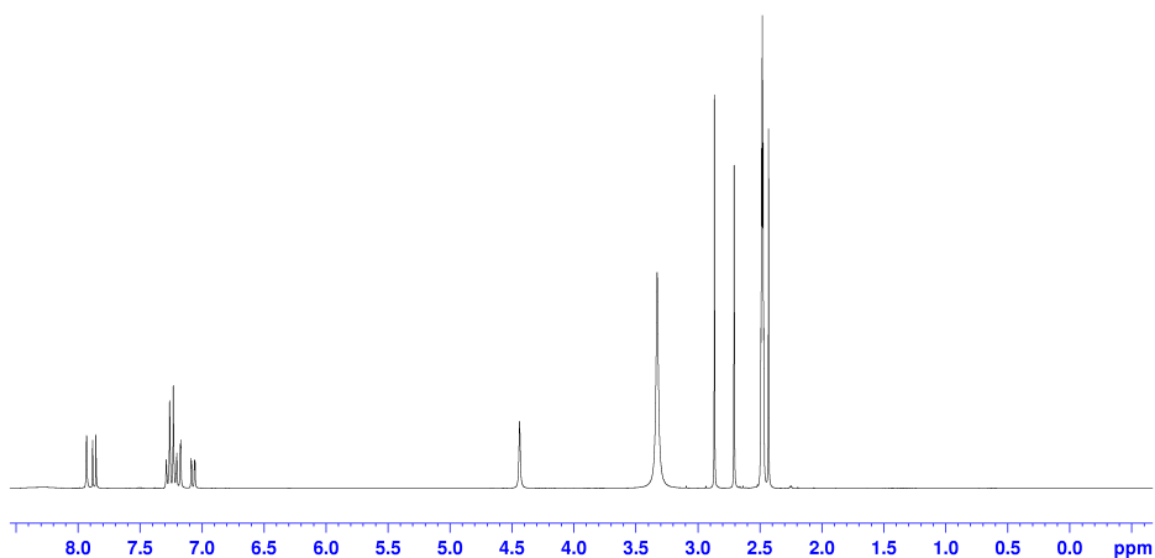


Figure S48. ^1H NMR spectrum of $\text{H}_2\text{bdc-NHCH}_2\text{C}_6\text{H}_4\text{SMe}$, H_2L^7 , in $\text{DMSO-}d_6$.

4.8 Synthesis of $\text{H}_2\text{bdc-NHCH}_2\text{C}_5\text{H}_4\text{N}$

$\text{H}_2\text{bdc-NH}_2$ (0.200 g, 1.104 mmol) was dissolved in 10 mL DMF in a glass vial. 2-pyridinecarboxaldehyde (0.211 mL, 2.208 mmol) and NaCNBH_3 (0.139 g, 2.204 mmol) were then added to the mixture. The reactants were left to react at room temperature for 24 h while stirring. 1M HCl and deionised water were added until a yellow solid precipitated. The ^1NMR spectrum of $\text{H}_2\text{bdc-NHCH}_2\text{C}_5\text{H}_4\text{N}$ is shown in Figure S49, the negative ion ESI mass spectrum is shown in Figure S50, and the ^{11}B NMR spectrum is shown in Figure S51.

$m/z = 271.0736$ (predicted $[\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_4]^-$, $[\text{M} - \text{H}]^- = 271.0719$), 310.1021 (predicted $[\text{C}_{15}\text{H}_{13}\text{BN}_3\text{O}_4]^-$, $[\text{M} - \text{H} + \text{BH}_2\text{CN}]^-$).

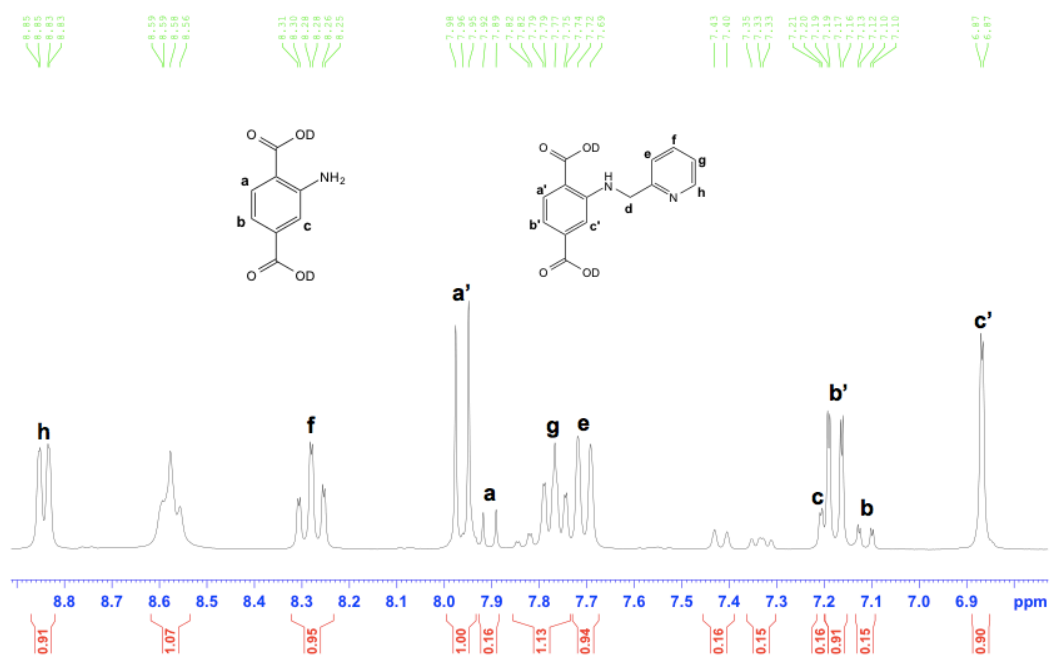


Figure S49. ¹H NMR spectrum of H₂bdc-NHCH₂C₅H₄N in DMSO-*d*₆.

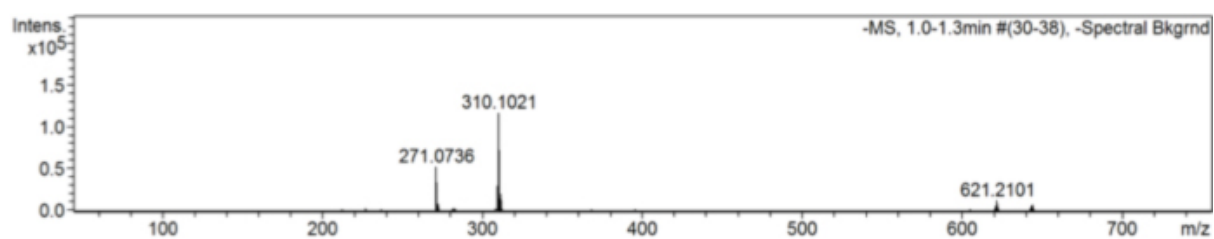


Figure S50. ESI mass spectrum of H₂bdc-NHCH₂C₅H₄N in DMSO-*d*₆.

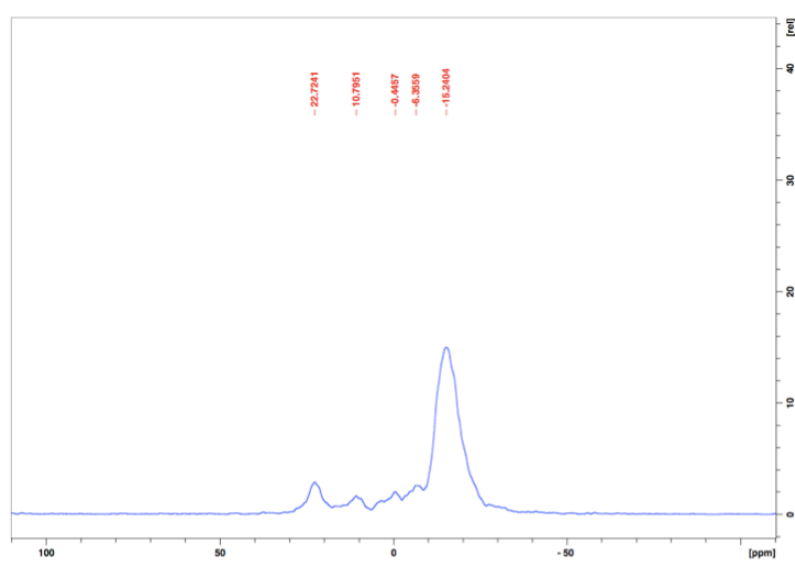


Figure S51. ¹¹B NMR spectrum of H₂bdc-NHCH₂C₅H₄N in DMSO-*d*₆.

4.9 Synthesis of H₂bdc-NHCH₂CH₂CH₂SMe, H₂L⁸

H₂BDC-NH₂ (0.200 g, 1.104 mmol) was dissolved in 10 mL MeOH in a glass vial. 3-(methylthio)propionaldehyde (0.219 mL, 2.208 mmol) and NaCNBH₃ (0.139 g, 2.204 mmol) were then added to the mixture. The reactants were left to react at room temperature for 24 hours under stirring. 1M HCl and deionised water were added until a yellow solid precipitated. The ¹H NMR spectrum of H₂L⁸ is shown in Figure S52.

$m/z = 268.0648$ (predicted [C₁₂H₁₄NO₄S]⁻, [M - H]⁻ = 268.0644).

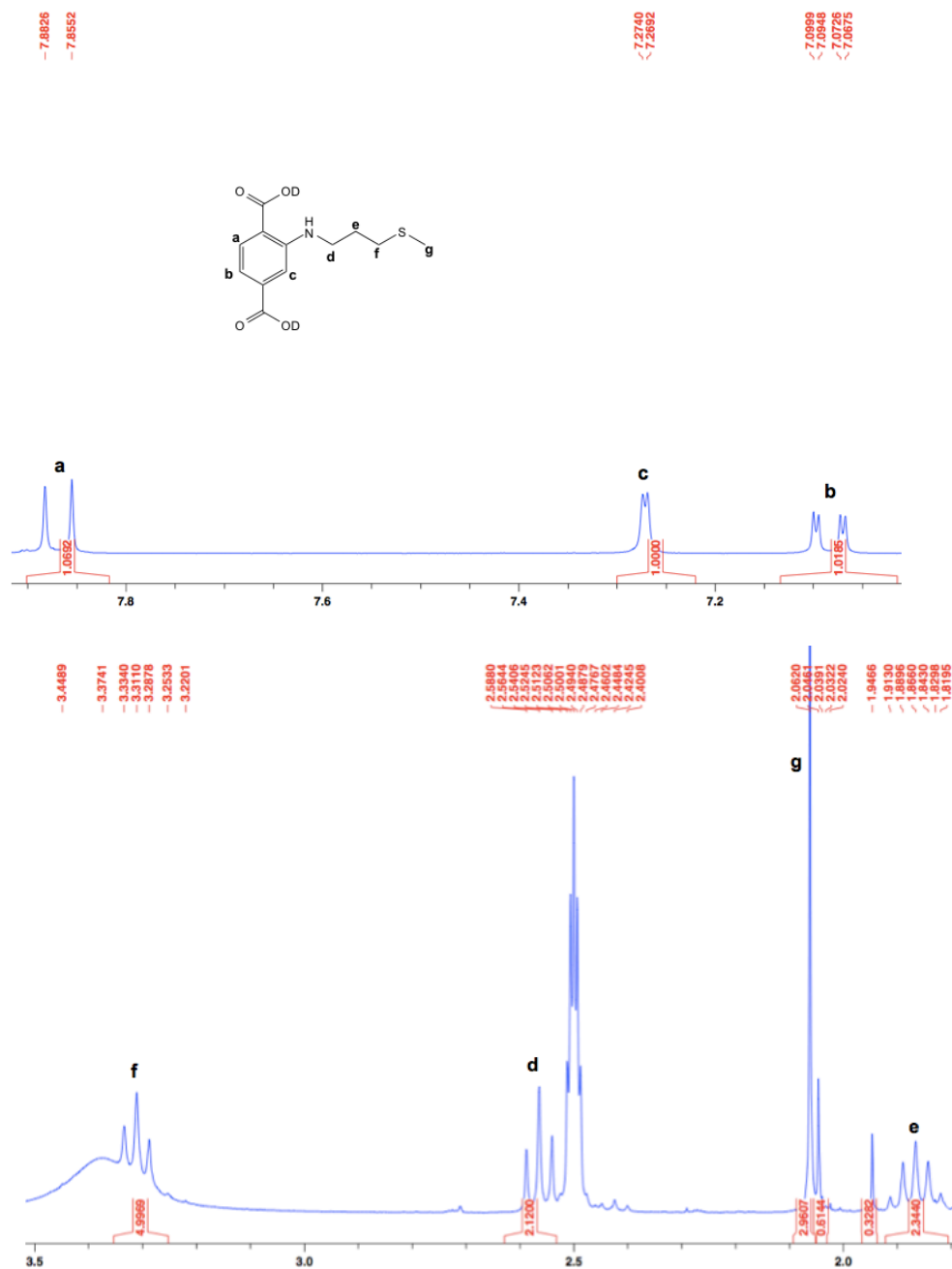


Figure S52. Aromatic and aliphatic regions of the ¹H NMR spectrum of H₂L⁸ in DMSO-*d*₆.

4.10 Synthesis of H₂bdc-NHCH₂CHBr₂

H₂bdc-NH₂ (0.200 g, 1.104 mmol) was dissolved in a mixture of 10 mL DMF and 2.63 mL MeOH in a glass vial. Tribromoacetaldehyde (0.233 mL, 2.208 mmol) and NaCNBH₃ (0.139 g, 2.204 mmol) were then added to the mixture. The reactants were left to react at room temperature for 3 days under stirring. 1M HCl and deionised water were added until a yellow solid precipitated. ¹H NMR analysis (Figure S53) revealed the product to be a 6:1 mixture of H₂bdc-NHCH₂CHBr₂ and H₂bdc. The negative ion ESI mass spectrum (Figure S54) confirms the product contains only two bromine atoms.

$m/z = 365.8816$ (predicted [C₁₀H₈Br₂NO₄]⁻, [M - H]⁻ = 365.8800).

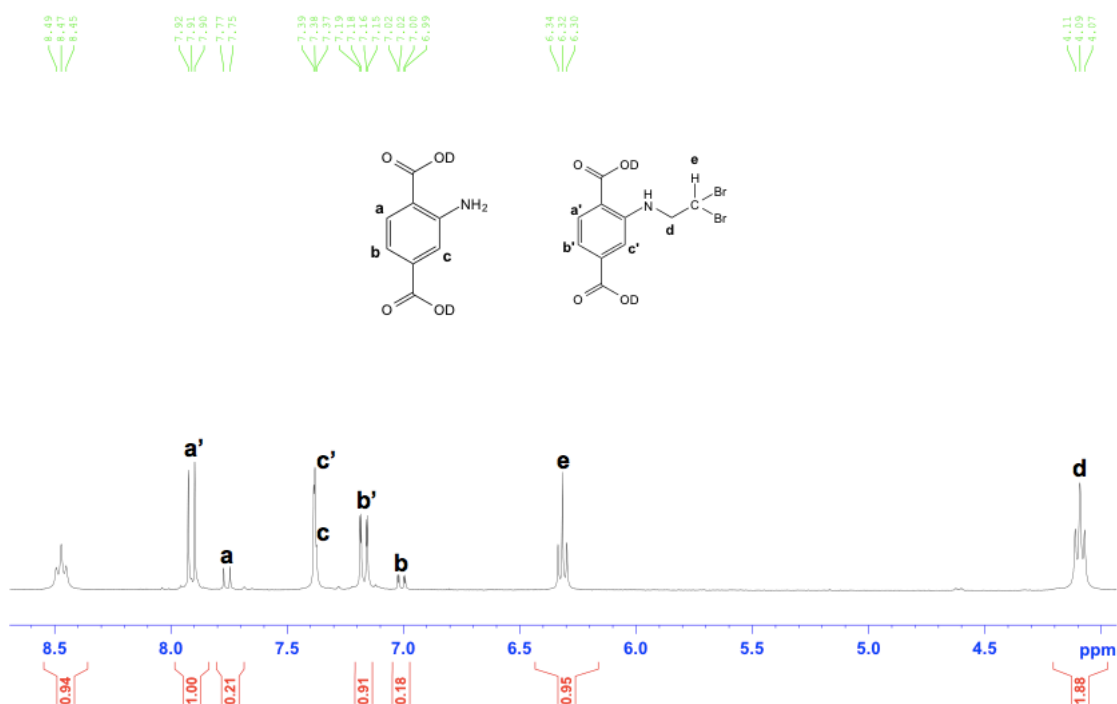


Figure S53. ¹H NMR spectrum of H₂bdc-NHCH₂CHBr₂ in DMSO-*d*₆.

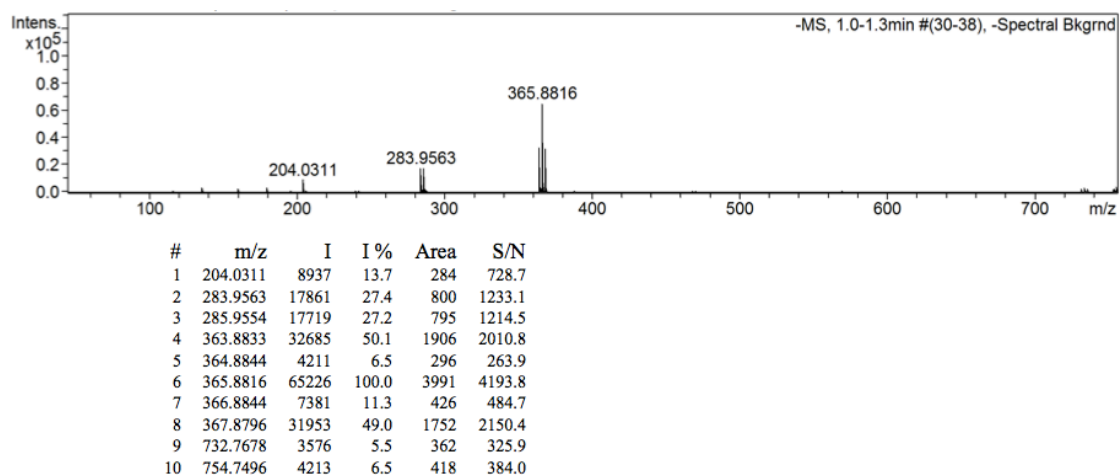


Figure S54. ESI mass spectrum of H₂bdc-NHCH₂CHBr₂.

5. Direct syntheses of functionalised zinc MOFs

5.1 $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{0.12}(\text{bdc-NHEt})_{2.88}] \cdot 7\text{C}_6\text{H}_5\text{Me}$, **5a**

H_2L^1 (46.2 mg, 0.224 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200 mg, 0.672 mmol, 3 eq.). After the mixture was stirred for 30 min, the stirrer was removed, and the vessel sealed and placed in an oven at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield 28.8 mg. The IR spectrum for **5a** is shown in Figure S55 and the ^1H NMR spectrum of the digested MOF is shown in Figure S56.

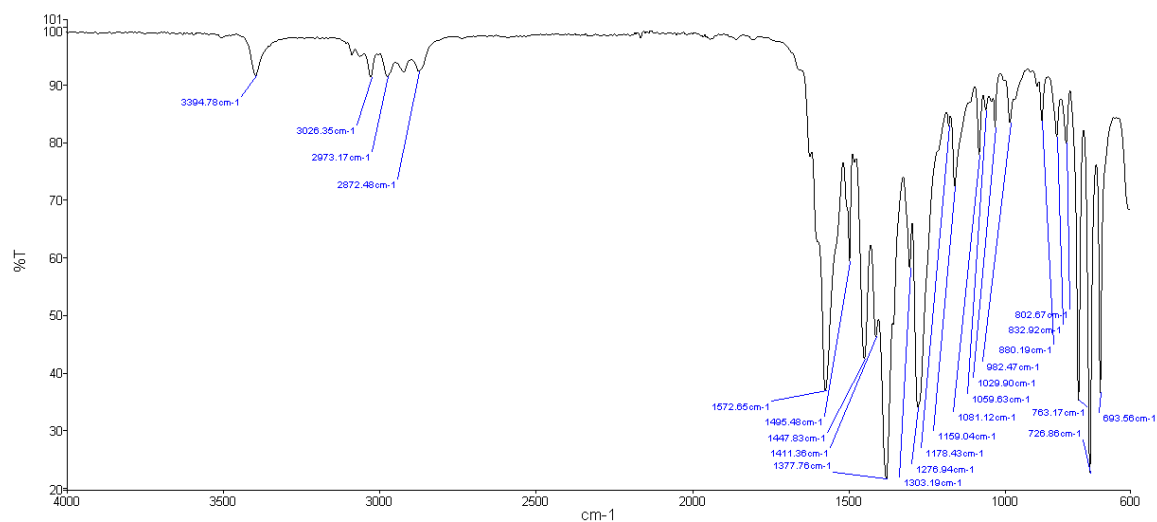


Figure S55. FT-IR spectrum of **5a**.

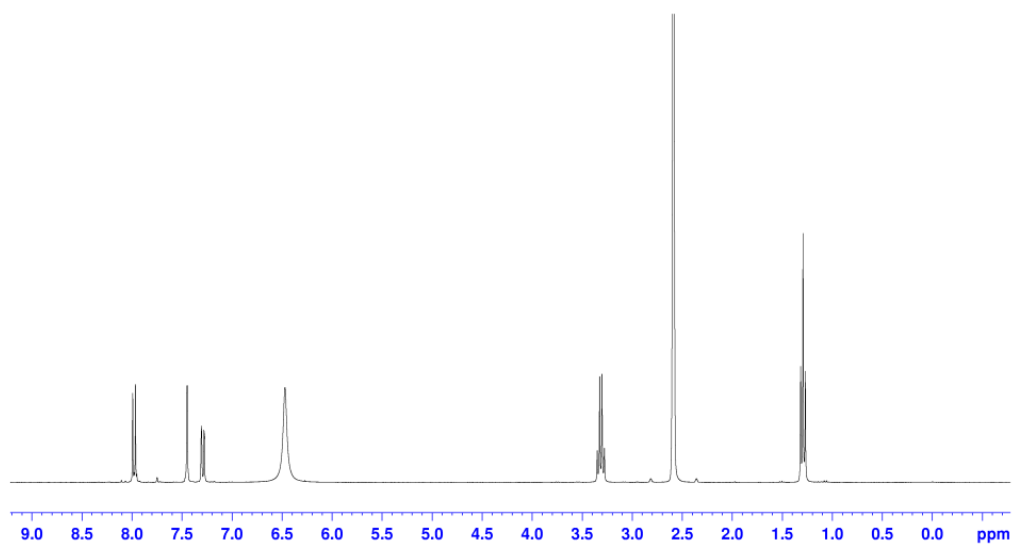


Figure S56. ^1H NMR spectrum of digested **5a**.

5.2 $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{0.21}(\text{bdc-NHPr})_{2.79}] \cdot 6.3\text{C}_6\text{H}_5\text{Me}$, **5b**

H_2L^2 (30 mg, 0.134 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (120 mg, 0.402 mmol, 3 eq.). After the mixture was stirred for 30 min, the stirrer was removed and the vessel sealed and placed in an oven at 105°C for 48 h. The

resulting yellow-orange crystalline product, **5b**, was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield 26.8 mg. The IR spectrum for **5b** is shown in Figure S57 and the ^1H NMR spectrum of the digested MOF is shown in Figure S58.

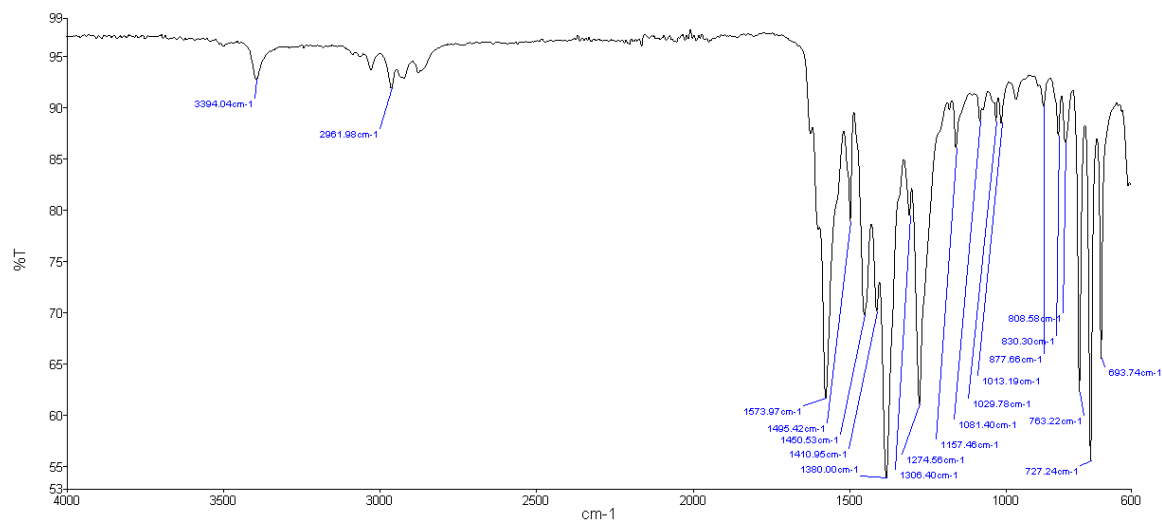


Figure S57. FT-IR spectrum of **5b**.

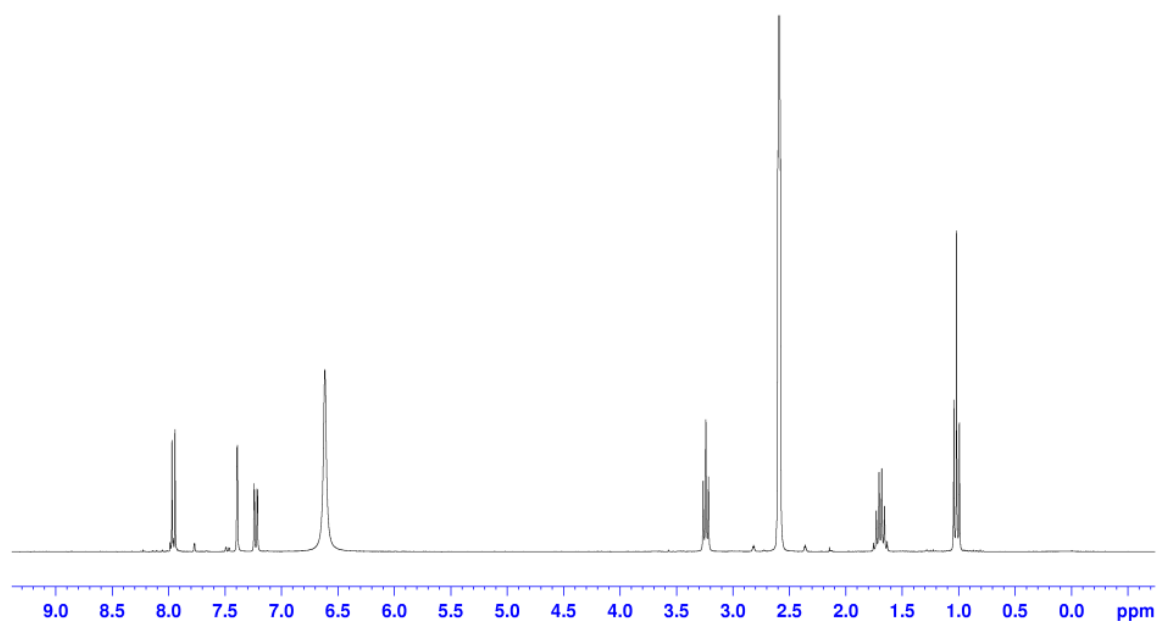


Figure S58. ^1H NMR spectrum of digested **5b**.

5.3 $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{0.24}(\text{bdc-NHBu})_{2.76}] \cdot 5.5\text{C}_6\text{H}_5\text{Me}$, **5c**

H_2L^3 (30 mg, 0.126 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (112 mg, 0.378 mmol, 3 eq.). After the mixture was stirred for 30 minutes, the stirrer was removed and the vessel sealed and placed in an oven set at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield 28.6 mg. The IR spectrum for **5c** is shown in Figure S59 and the ^1H NMR spectrum of the digested MOF is shown in Figure S60.

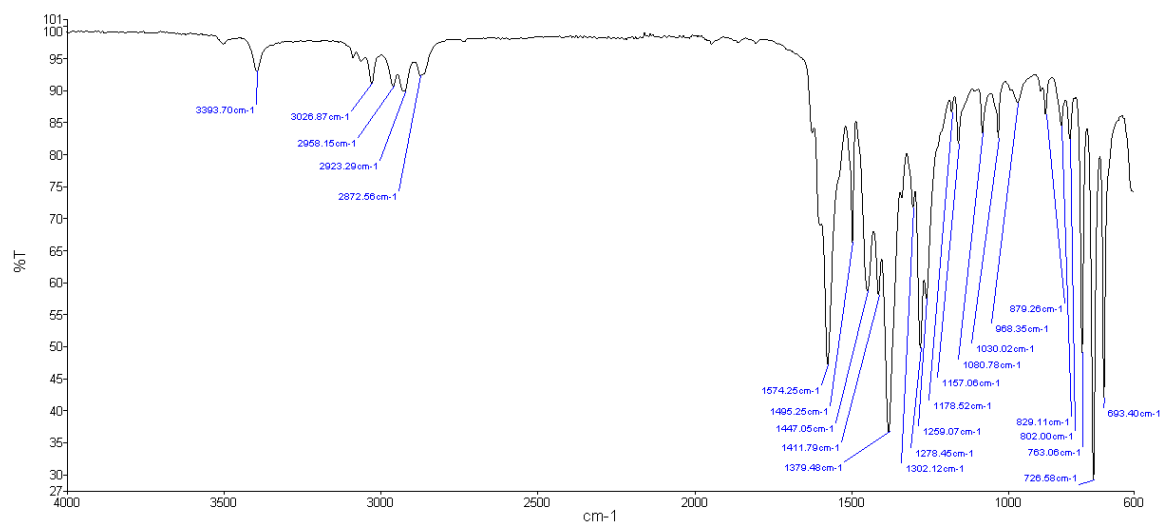


Figure S59. FT-IR spectrum of **5c**.

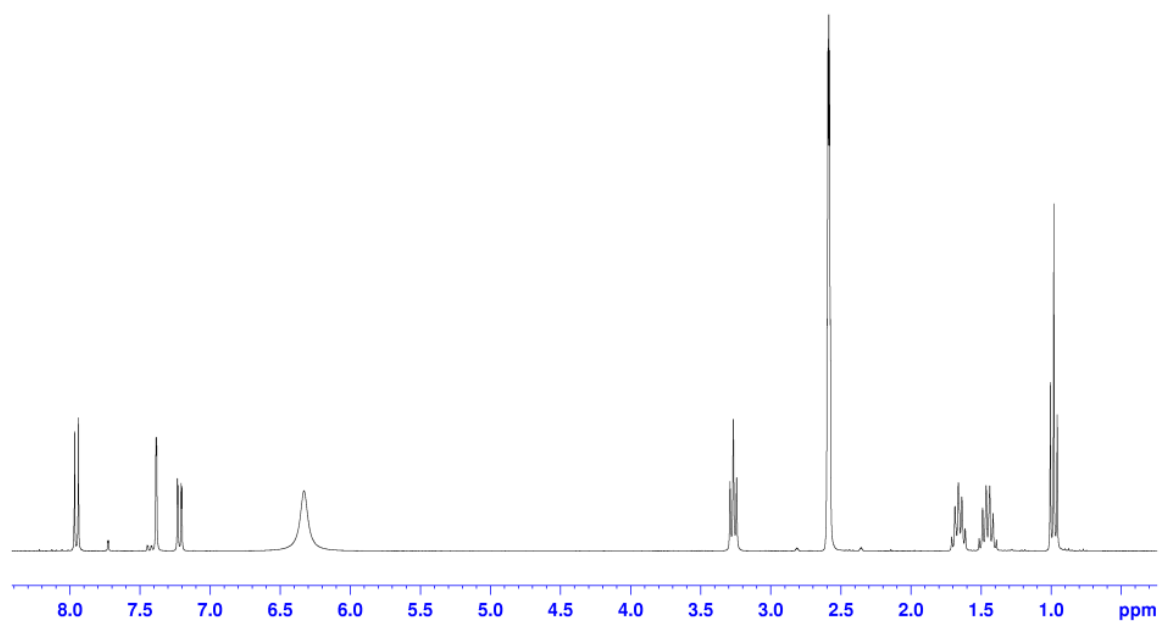


Figure S60. ¹H NMR spectrum of digested **5c**.

5.4 [Zn₄O(bdc-NH₂)_{0.21}(bdc-NHC₈H₁₇)_{2.79}]·4.5C₆H₅Me, **5d**

H₂L⁴, (30 mg, 0.102 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added Zn(NO₃)₂·6H₂O (91 mg, 0.306 mmol, 3 eq.). After the mixture was stirred for 30 min, the stirrer was removed and the vessel sealed and placed in an oven set at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield 19.4 mg. The IR spectrum for **5d** is shown in Figure S61 and the ¹H NMR spectrum of the digested MOF is shown in Figure S62.

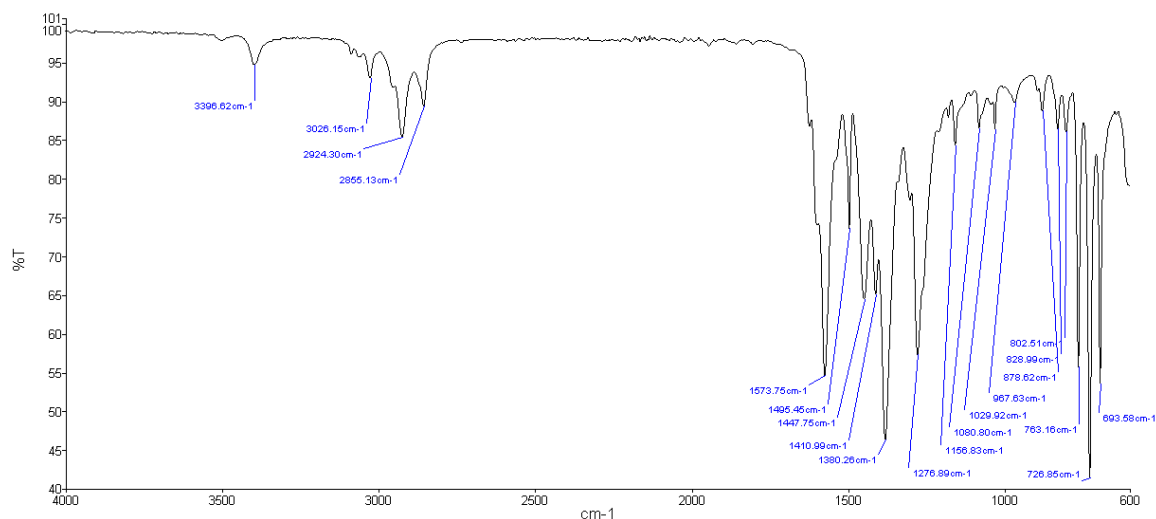


Figure S61. FT-IR spectrum of **5d**.

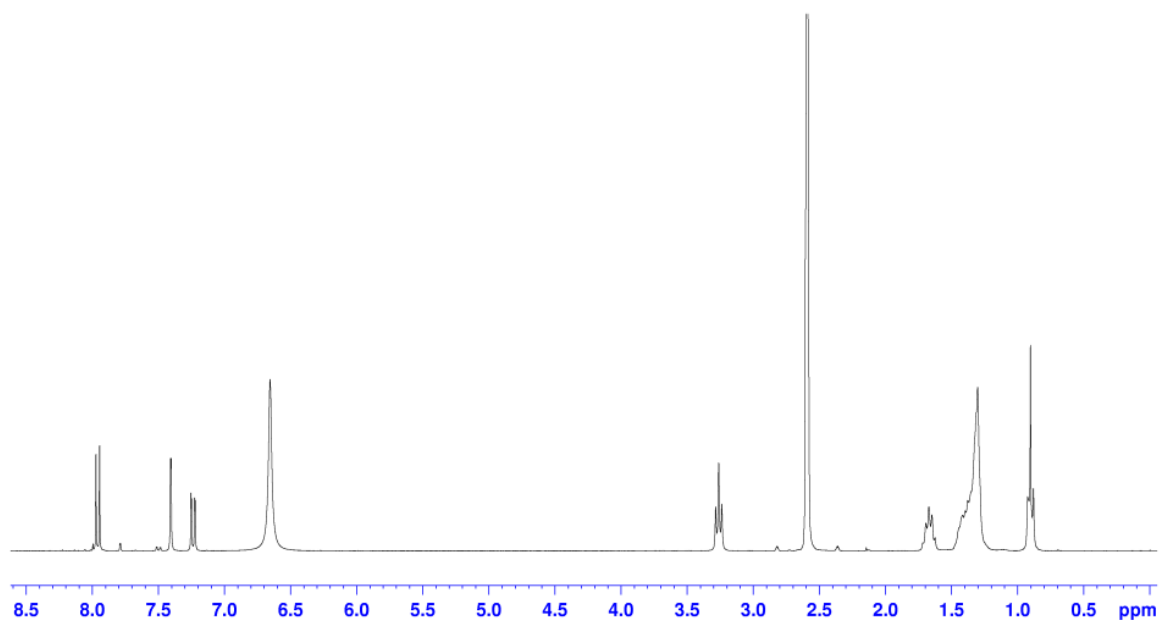


Figure S62. ¹H NMR spectrum of digested **5d**.

5.5 [Zn₄O(bdc-NH₂)_{0.4}(bdc-NHCH₂C₆H₉)_{2.6}]·4.5C₆H₅Me, **5e**

H₂L⁵ (30 mg, 0.109 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added Zn(NO₃)₂·6H₂O (97 mg, 0.327 mmol, 3 eq.). After the mixture was stirred for 30 min, the stirrer was removed and the vessel sealed and placed in an oven set at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield 19.7 mg. The IR spectrum for **5e** is shown in Figure S63 and the ¹H NMR spectrum of the digested MOF is shown in Figure S64.

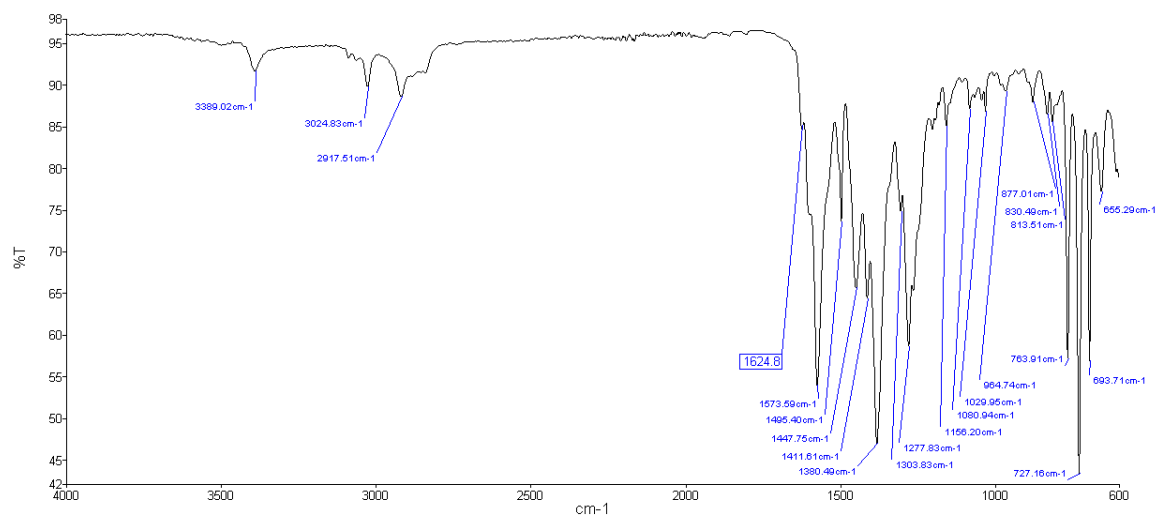


Figure S63. FT-IR spectrum of 5e.

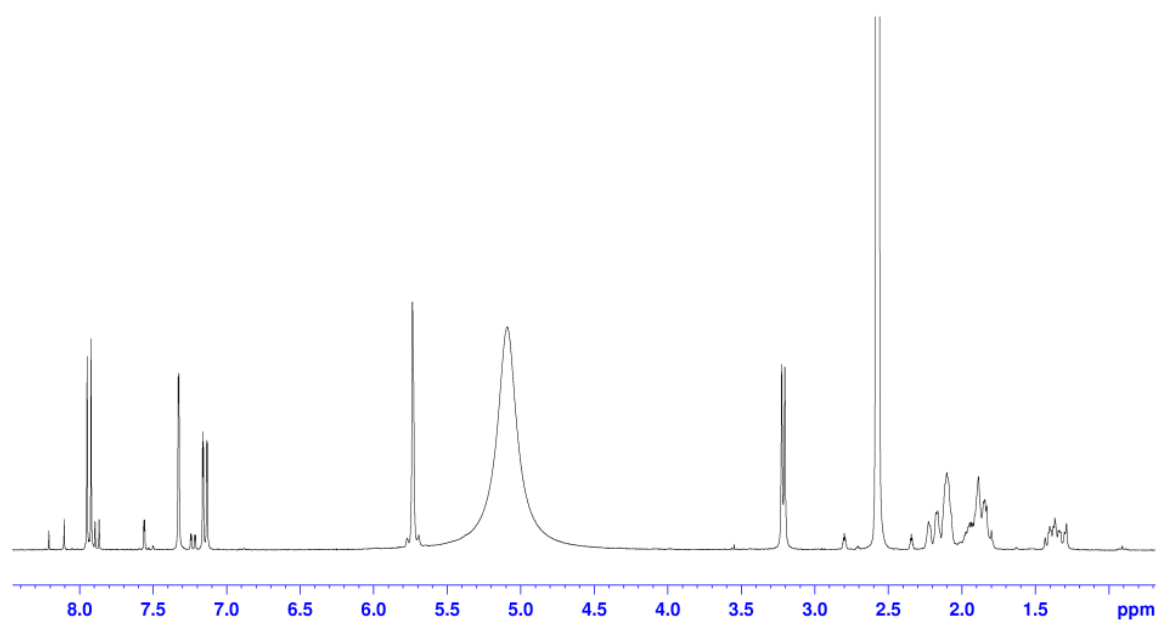


Figure S64. ¹H NMR spectrum of digested 5e.

5.6 [Zn₄O(bdc-NH₂)_{2,4}(bdc-NHCH₂Fc)_{0,6}]·6C₆H₅Me, 5f

H₂L⁶ (75 mg, 0.197 mmol, 3.5 eq.) and H₂bdc-NH₂ (10 mg, 0.056 mmol, 1 eq.) were dissolved in 5 mL DMF and to this was added Zn(NO₃)₂·6H₂O (200 mg, 0.672 mmol, 12 eq.). After the mixture was stirred for 30 min, the stirrer was removed and the vessel sealed and placed in an oven set at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Atomic absorption spectrometry gave a Fe:Zn ratio of 1:5.4 (predicted 1:7.8). Yield 14.6 mg. The IR spectrum for 5f is shown in Figure S65 and the ¹H NMR spectrum of the digested MOF is shown in Figure S66.

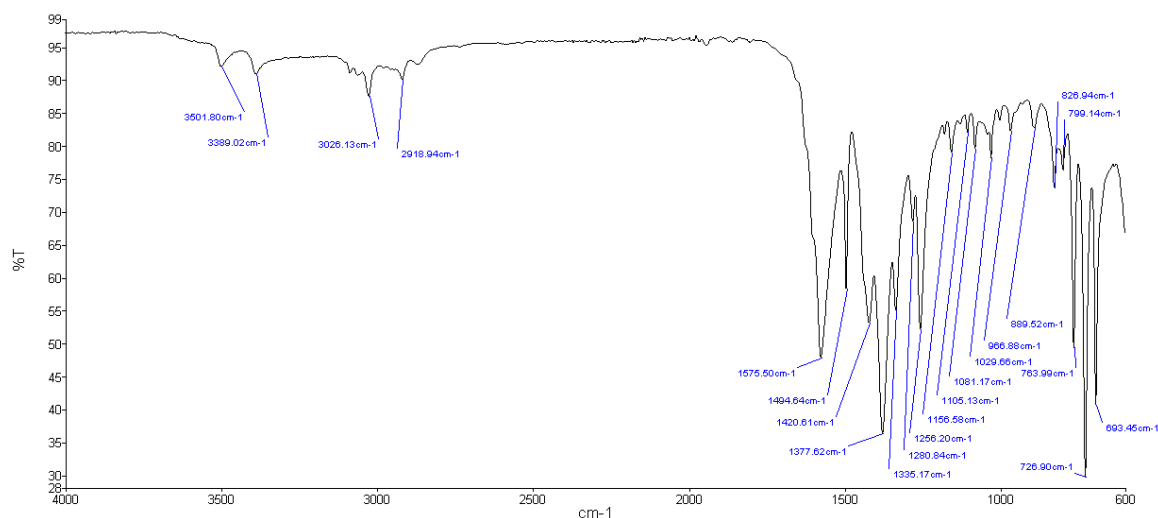


Figure S65. FT-IR spectrum of **5f**.

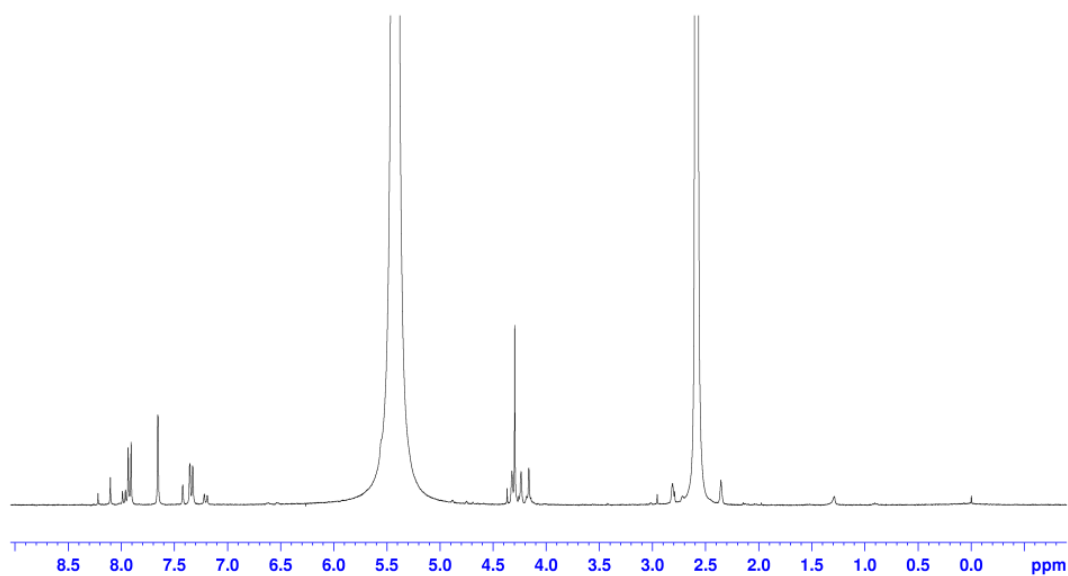


Figure S66. ^1H NMR spectrum of digested **5f**.

5.7 $[\text{Zn}_4\text{O}(\text{bdc-NH}_2)_{1.05}(\text{bdc-NHCH}_2\text{C}_6\text{H}_4\text{SMe})_{1.95}] \cdot 5.5\text{C}_6\text{H}_4\text{Me}$, **5g**

H_2L^7 (30 mg, 0.095 mmol, 1 eq.) was dissolved in 5 mL DMF and to this was added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (84.4 mg, 0.284 mmol, 3 eq.). After the mixture was stirred for 30 min, the stirrer was removed and the vessel sealed and placed in an oven set at 105°C for 48 h. The resulting yellow-orange crystalline product was washed once per day for three days with DMF and a further once per day for three days with toluene and finally stored in toluene. Yield = 24.6 mg. The IR spectrum for **5g** is shown in Figure S67 and the ^1H NMR spectrum of the digested MOF is shown in Figure S68.

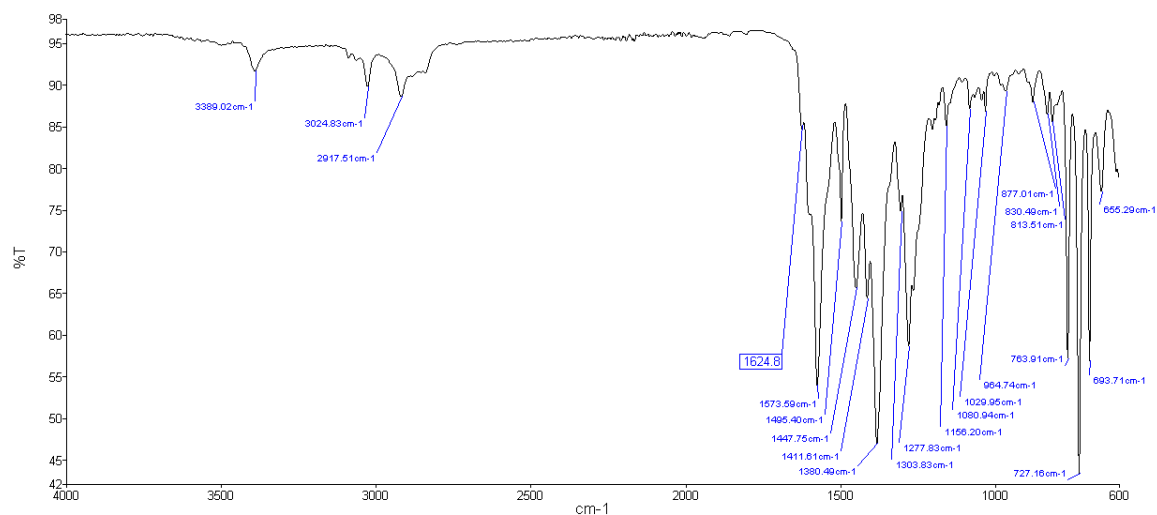


Figure S67. FT-IR spectrum of **5g**.

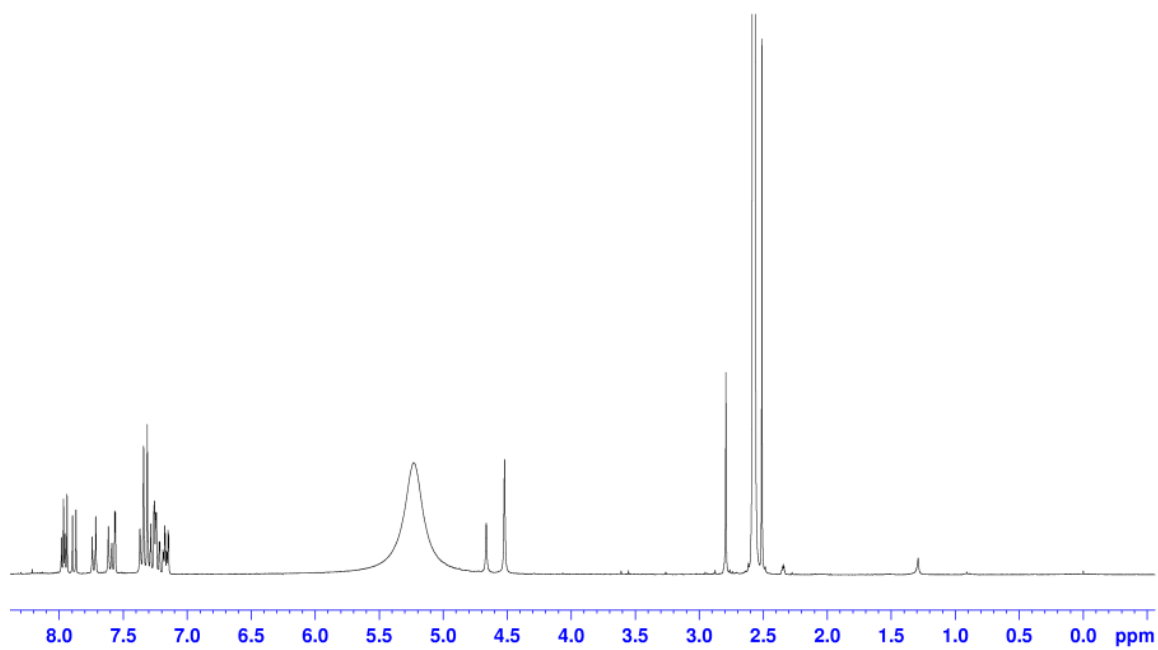


Figure S68. ¹H NMR spectrum of digested **5g**.

5.8 Powder X-ray diffraction studies on 5a-g

Powder X-ray diffraction patterns for **5a-g** are shown in Figures S69-70 in comparison with that for IRMOF-3.

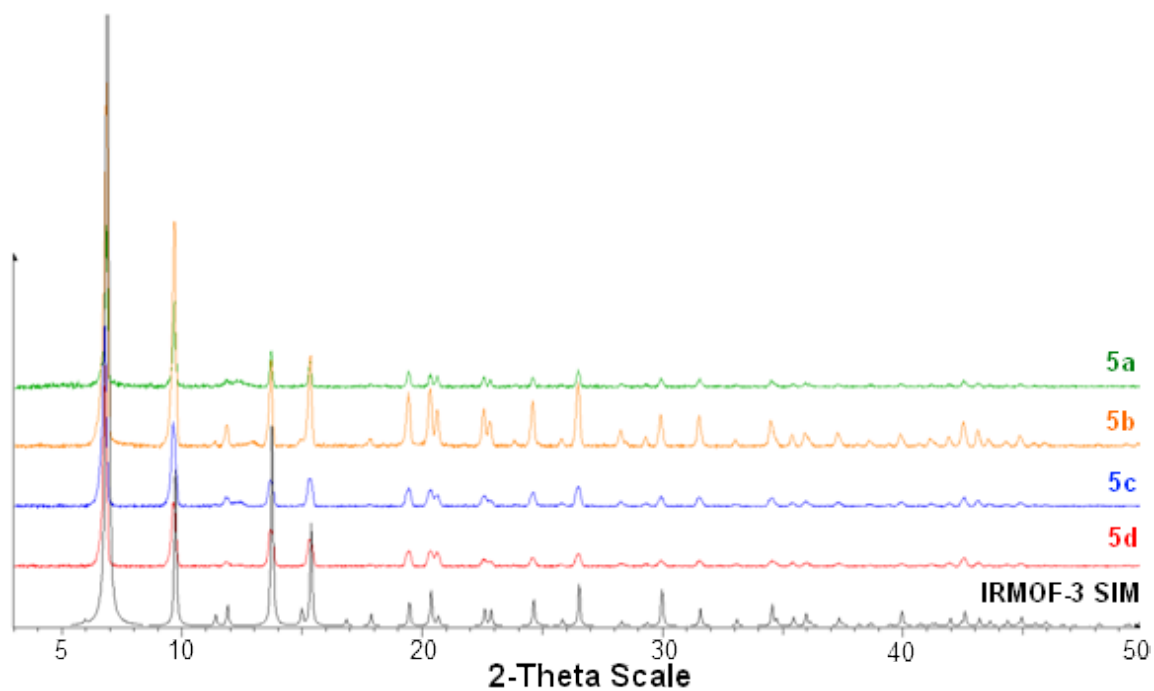


Figure S69. Powder X-ray diffraction data for **5a-d** in comparison to the simulated pattern for IRMOF-3 calculated from the single crystal data.^{S2}

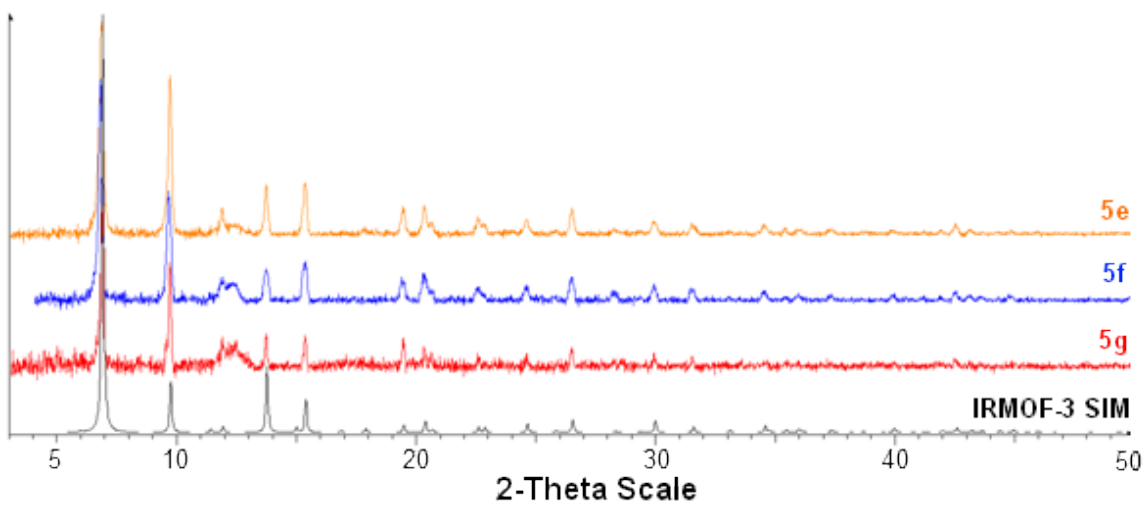


Figure S70. Powder X-ray diffraction data for **5e-g** in comparison to the simulated pattern for IRMOF-3 calculated from the single crystal data.^{S2}

5.9 Thermogravimetric analysis on 5a-g

Thermogravimetric analyses on **5a-g** are shown in Figures S71-72.

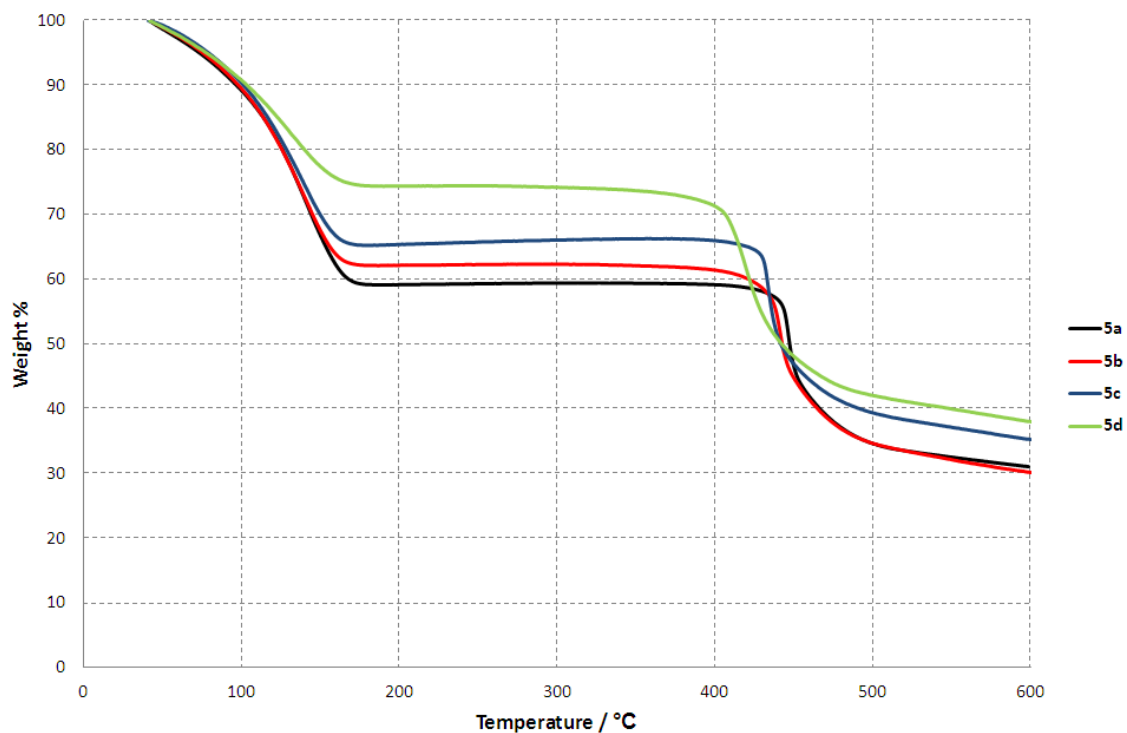


Figure S71. Thermogravimetric analyses of **5a-d**.

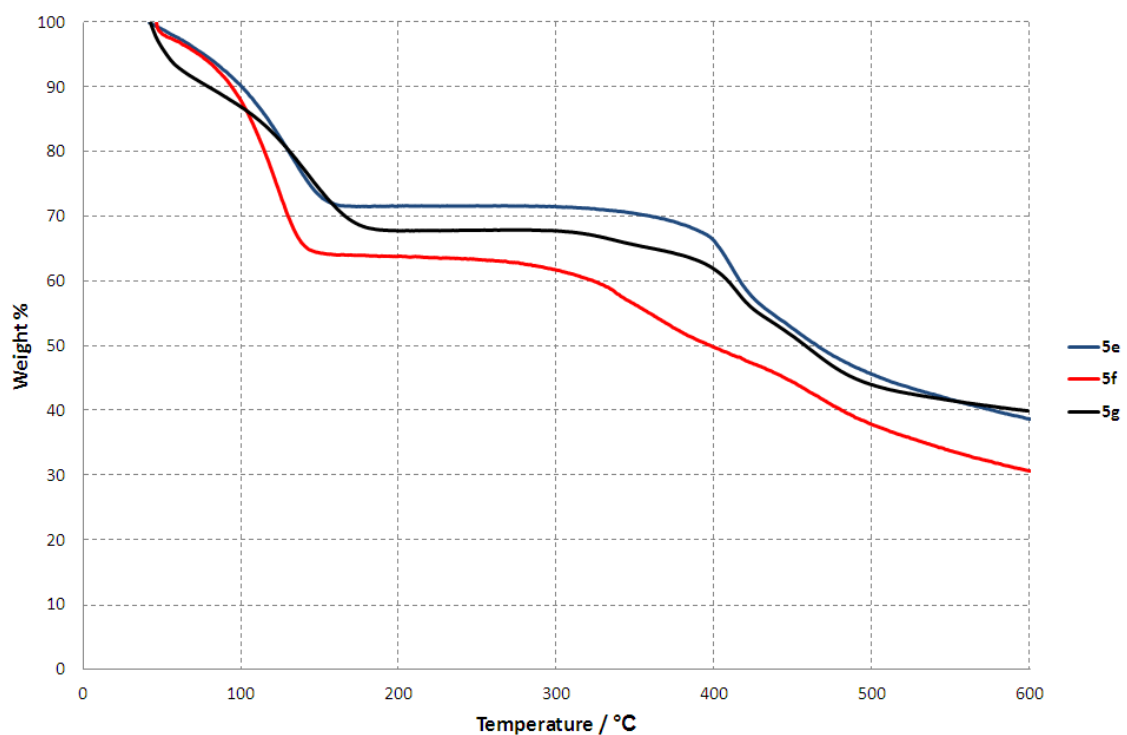


Figure S72. Thermogravimetric analyses of **5e-g**.

5.10 Nitrogen adsorption studies on 5a-g

BJH plots for **5a-g** are shown in Figures S73-74, showing the absence of mesopores, with the exception of **5g** which shows hysteresis in the isotherm (Fig. 2) and a small number of mesopores.

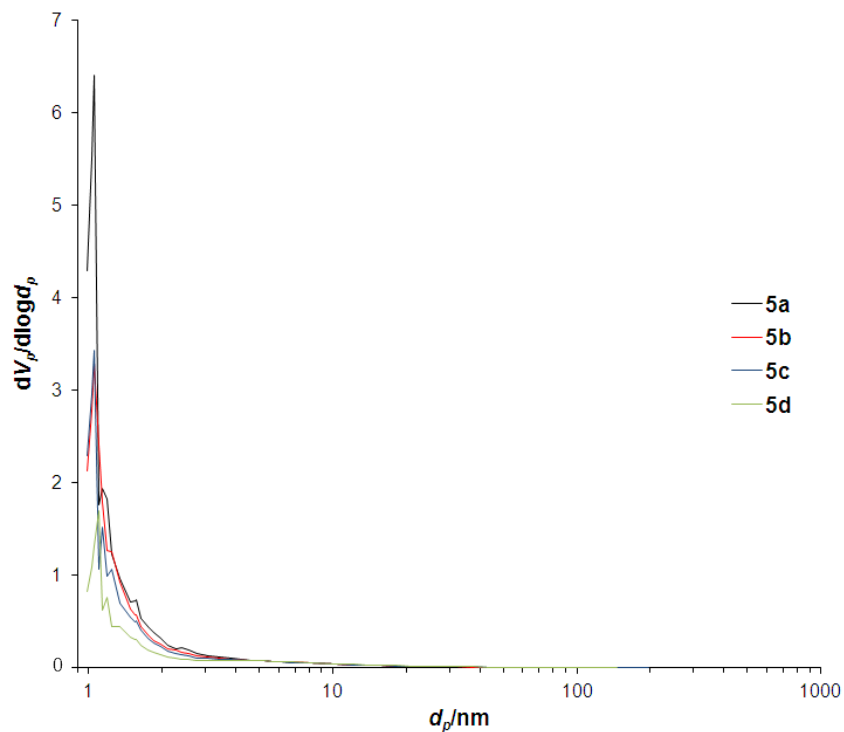


Figure S73. BJH plot for **5a-d**.

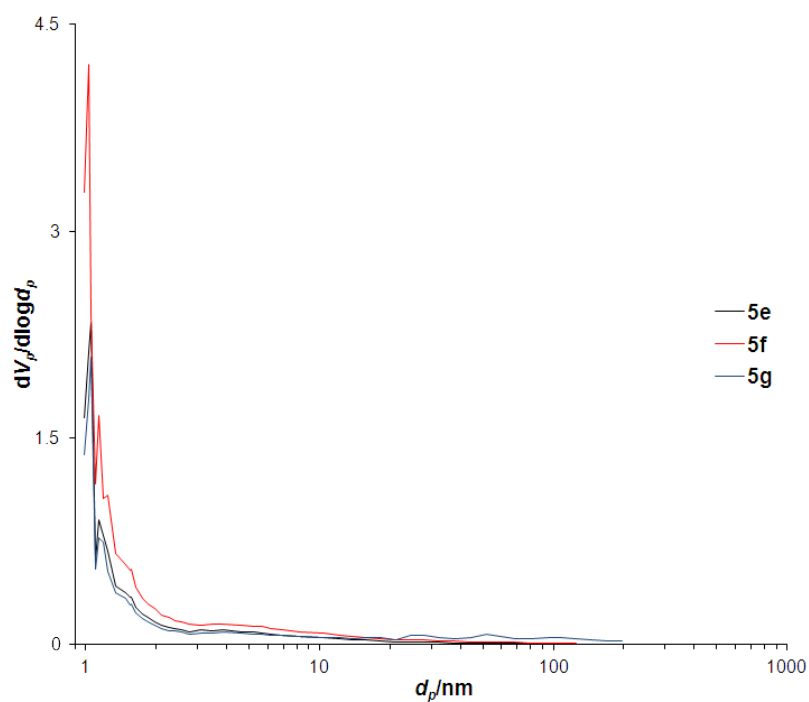


Figure S74. BJH plot for **5e-g**.

6. X-ray single crystal analyses

Details for the crystal data and structure refinement for compounds **2a**, **5a**, **5b**, **5e** and **5g** are given in Tables S1-S5 respectively.

Table S1. Crystal data and structure refinement for **2a**.

Empirical formula	C _{76.6} H _{78.2} N ₃ O ₁₃ Zn ₄
Formula weight	1510.30
Temperature/K	250(2)
Crystal system	cubic
Space group	<i>Fm</i> – <i>3m</i>
<i>a</i> /Å	25.9940(3)
<i>b</i> /Å	25.9940(3)
<i>c</i> /Å	25.9940(3)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	17563.8(5)
<i>Z</i>	8
ρ_{calc} /g cm ⁻³	1.142
μ /mm ⁻¹	1.045
<i>F</i> (000)	6262.0
Crystal size/mm ³	0.14 × 0.12 × 0.10
Radiation	Synchrotron (λ = 0.6889)
2 θ range for data collection/°	5.038 to 53.13
Index ranges	–33 ≤ <i>h</i> ≤ 33, –33 ≤ <i>k</i> ≤ 33, –33 ≤ <i>l</i> ≤ 28
Reflections collected	43780
Independent reflections	1064 [<i>R</i> _{int} = 0.0736, <i>R</i> _{sigma} = 0.0143]
Data/restraints/parameters	1064/6/31
Goodness-of-fit on <i>F</i> ²	1.048
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0550, <i>wR</i> ₂ = 0.1658
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0733, <i>wR</i> ₂ = 0.1969
Largest diff. peak/hole / e Å ⁻³	0.68/–0.43

Table S2. Crystal data and structure refinement for **5a**.

Empirical formula	C ₇₉ H ₈₃ N ₃ O ₁₃ Zn ₄
Formula weight	1543.96
Temperature/K	250(2)
Crystal system	cubic
Space group	<i>Fm</i> – <i>3m</i>
<i>a</i> /Å	25.7627(2)
<i>b</i> /Å	25.7627(2)
<i>c</i> /Å	25.7627(2)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	17099.2(5)
<i>Z</i>	8
ρ_{calc} /g cm ⁻³	1.200
μ /mm ⁻¹	1.075
<i>F</i> (000)	6416.0
Crystal size/mm ³	0.14 × 0.12 × 0.10
Radiation	Synchrotron (λ = 0.6889)
2 θ range for data collection/°	5.084 to 48.4
Index ranges	–30 ≤ <i>h</i> ≤ 25, –30 ≤ <i>k</i> ≤ 30, –30 ≤ <i>l</i> ≤ 30
Reflections collected	34745
Independent reflections	803 [<i>R</i> _{int} = 0.0273, <i>R</i> _{sigma} = 0.0063]
Data/restraints/parameters	803/6/31
Goodness-of-fit on <i>F</i> ²	1.155
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0365, <i>wR</i> ₂ = 0.1080
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0416, <i>wR</i> ₂ = 0.1175
Largest diff. peak/hole / e Å ⁻³	0.43/–0.34

Table S3. Crystal data and structure refinement for **5b**.

Empirical formula	$C_{77.1}H_{83.4}N_3O_{13}Zn_4$
Formula weight	1521.54
Temperature/K	250.15
Crystal system	cubic
Space group	$Fm\bar{3}m$
$a/\text{\AA}$	25.77025(14)
$b/\text{\AA}$	25.77025(14)
$c/\text{\AA}$	25.77025(14)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	17114.2(3)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.181
μ/mm^{-1}	1.073
$F(000)$	6328.0
Crystal size/ mm^3	$0.12 \times 0.1 \times 0.07$
Radiation	Synchrotron ($\lambda = 0.6889$)
2θ range for data collection/ $^\circ$	5.082 to 55.438
Index ranges	$-34 \leq h \leq 26, -31 \leq k \leq 34, -34 \leq l \leq 31$
Reflections collected	26286
Independent reflections	1163 [$R_{\text{int}} = 0.0450, R_{\text{sigma}} = 0.0131$]
Data/restraints/parameters	1163/12/37
Goodness-of-fit on F^2	1.172
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0382, wR_2 = 0.1323$
Final R indexes [all data]	$R_1 = 0.0421, wR_2 = 0.1370$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.70/−0.33

Table S4. Crystal data and structure refinement for **5e**.

Empirical formula	$C_{73.98}H_{77.4}N_3O_{13}Zn_4$
Formula weight	1478.02
Temperature/K	250.15
Crystal system	cubic
Space group	$Fm\bar{3}m$
$a/\text{\AA}$	25.7752(2)
$b/\text{\AA}$	25.7752(2)
$c/\text{\AA}$	25.7752(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	17124.0(4)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.147
μ/mm^{-1}	1.071
$F(000)$	6130.0
Crystal size/ mm^3	$0.12 \times 0.12 \times 0.1$
Radiation	Synchrotron ($\lambda = 0.6889$)
2θ range for data collection/ $^\circ$	7.508 to 53.132
Index ranges	$-33 \leq h \leq 33, -31 \leq k \leq 33, -33 \leq l \leq 33$
Reflections collected	42796
Independent reflections	1028 [$R_{\text{int}} = 0.0258, R_{\text{sigma}} = 0.0054$]
Data/restraints/parameters	1028/12/37
Goodness-of-fit on F^2	1.109
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0534, wR_2 = 0.1958$
Final R indexes [all data]	$R_1 = 0.0545, wR_2 = 0.1973$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.55/−0.54

Table S5. Crystal data and structure refinement for **5g**.

Empirical formula	$C_{78.1}H_{74.6}N_3O_{13}S_{1.95}Zn_4$
Formula weight	1587.20
Temperature/K	250.15
Crystal system	cubic
Space group	$Fm\bar{3}m$
$a/\text{\AA}$	25.8577(2)
$b/\text{\AA}$	25.8577(2)
$c/\text{\AA}$	25.8577(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	17289.0(4)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.220
μ/mm^{-1}	1.107
$F(000)$	6555.0
Crystal size/ mm^3	$0.12 \times 0.1 \times 0.05$
Radiation	Synchrotron ($\lambda = 0.6889$)
2θ range for data collection/ $^\circ$	3.054 to 48.402
Index ranges	$-30 \leq h \leq 29, -30 \leq k \leq 30, -30 \leq l \leq 26$
Reflections collected	34574
Independent reflections	824 [$R_{\text{int}} = 0.0745, R_{\text{sigma}} = 0.0212$]
Data/restraints/parameters	824/0/31
Goodness-of-fit on F^2	1.227
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0640, wR_2 = 0.1951$
Final R indexes [all data]	$R_1 = 0.0660, wR_2 = 0.2064$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.41/-0.49

8. References

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