Supplementary Information

Dual Metal Organic Framework Postsynthetic Modification; Two Birds with One Stone

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1 General Experimental

All chemicals used were of analytical grade and purchased from either Sigma Aldrich or Ajax Finechem Pty Ltd. 2-(Propargyloxy)-[1,1-biphenyl]-4,4-dicarboxylic acid (H_2**L**^{1})[1] and 2-(allyloxy)-[1,1-biphenyl]-4,4-dicarboxylic acid (H_2**L**^{2})[2] were prepared by reported procedures.

^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury VX-300-MHz NMR spectrometer, data collection was performed using VNMR 6.1c software on a SUN Solaris 9 operating system operating at 300 MHz for ^{1}H or a Bruker Ascend NMR spectrometer operating at 400 MHz for ^{1}H. ^{1}H NMR spectra were referenced to the residual protio peaks at 2.50 ppm (d_6-DMSO). For ^{1}H NMR analysis MOF samples (~10 mg) were digested by adding 35% DCl in D_2O (3 μL) and DMSO (500 μL) and briefly sonicating to aid a homogeneous solution being obtained.

PXRD patterns were obtained using a GBC-MMA X-Ray diffractometer equipped with Visual XRD 122D version 3.04 and Traces version 6.6.10 diffraction screen processing software and accessories. Samples were mounted on 1" SiO_2 substrates and measured using a 2θ angle range of 3-30 with a step size of 0.02° at 1° per minute.

TG-DTA data were obtained using a Shimadzu DTG-60 simultaneous Thermogravimetry and Differential Thermal Analyser, fitted with a FC-60A Flow Rate controller and TA-60WS Thermal Analyser. Measuring parameters of 10 °Cmin^{-1} under nitrogen flow (20 cm^{3}min^{-1}) were used. Data analysis was performed on Ta60 version 2.20 software system. Data were also recorded using a Netzsch STA449F3 instrument with SiC furnace at 10 °Cmin^{-1} under N_2 flow at 20 cm^{3}min^{-1}.

Gas adsorption studies were carried out using a Quantachrome Autosorb MP instrument and high purity nitrogen gas (99.999%) at 77 K. Surface areas were determined using Brunauer−Emmett−Teller (BET) calculations. Samples for gas adsorption were freeze-dried for 1 hour before being heated at 120 °C under vacuum for 5 h to produce activated samples. Freeze-drying was carried out in a Christ Alpha 1−2 LDplus freeze-dryer.

Elemental microanalysis was performed by the Microanalytical Unit at the Australian National University using a Carlo Erba 1106 automatic analyser.

2 MOF Synthesis

General Procedure for Multivariate MOF synthesis

H_2**L**^{1} and H_2**L**^{2} were weighed out into nine vials according to Table S1. $Zn(NO_3)_2 \cdot 6H_2O$ (152.3 mg, 0.17 mmol) and DMF (8 cm^3) were added to each vial. The vials were capped and swirled to dissolve the solids, before being placed in an oven held at 100 °C for 23 hours. The crystals were manipulated to the bottom of each reaction flask and the solvent was replaced with fresh DMF with brief periods of heating at 100 °C (2 × 3 mL), and then exchanged for DCM over a period of a week (4 × 2 mL exchanges). Lastly, the DCM was exchanged for benzene (1 exchange) and then stored under benzene until required. Samples were freeze dried and then heated on the Quantachrome surface area analyser to 120 °C under vacuum and held at that temperature for 5 hours to produce activated samples.

Table S 1 Quantities of H_2**L**^{1} and H_2**L**^{2} used in the multivariate MOF syntheses and yields of air-dried crystals.

MOF	H_2L^1	H_2L^2	Ratio of H_2L^1:H_2L^2	Mass of air-dried crystals
WUF-44-89	5.0 mg, 0.017 mmol	45.6 mg, 0.153 mmol	1:9	26.4 mg
WUF-44-82	10.1 mg, 0.034 mmol	40.6 mg, 0.136 mmol	2:8	24.1 mg
WUF-44-75	15.1 mg, 0.051 mmol	35.5 mg, 0.119 mmol	3:7	24.7 mg
WUF44-65	20.1 mg, 0.068 mmol	30.4 mg, 0.102 mmol	4:6	24.9 mg
WUF44-56	25.2 mg, 0.085 mmol	25.4 mg, 0.085 mmol	5:5	26.0 mg
WUF44-47	30.2 mg, 0.102 mmol	20.3 mg, 0.068 mmol	6:4	24.1 mg
WUF-44-33	35.3 mg, 0.119 mmol	15.2 mg, 0.051 mmol	7:3	23.6 mg
WUF-44-22	40.3 mg, 0.136 mmol	10.1 mg, 0.034 mmol	8:2	23.2 mg
WUF-44-13	45.3 mg, 0.153 mmol	5.1 mg, 0.017 mmol	9:1	24.7 mg

Microanalytical data

WUF-44-90: Found C, 51.50; H, 3.03; N, 0.00. Calc $C_{51}H_{38.4}O_{17.5}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{0.29}(C_{17}H_{12}O_5)_{2.71}]\cdot 1.5H_2O$ | $[Zn_4O(\mathbf{L^1})_{0.29}(\mathbf{L^2})_{2.71}]\cdot 1.5H_2O$ C, 51.35; H, 3.25; N, 0.00.

WUF-44-82: Found C, 48.87; H, 2.73; N, 0.00. Calc for $C_{51}H_{44.9}O_{21}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{0.54}(C_{17}H_{12}O_5)_{2.46}]\cdot 5H_2O$ | $[Zn_4O(\mathbf{L^1})_{0.54}(\mathbf{L^2})_{2.46}]\cdot 5H_2O$ C, 48.79; H, 3.61; N, 0.00.

WUF-44-75: Found C, 51.34; H, 3.09; N, 0.00. Calc $C_{51}H_{37.5}O_{17.5}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{0.76}(C_{17}H_{12}O_5)_{2.24}]\cdot 1.5H_2O$ | $[Zn_4O(\mathbf{L^1})_{0.76}(\mathbf{L^2})_{2.24}]\cdot 1.5H_2O$ C, 51.37; H, 3.17; N, 0.00.

WUF-44-65: Found C, 51.35; H, 3.03; N, 0.00. Calc for $C_{51}H_{36.9}O_{17.5}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{1.04}(C_{17}H_{12}O_5)_{1.96}]\cdot 1.5H_2O$ | $[Zn_4O(\mathbf{L^1})_{1.04}(\mathbf{L^2})_{1.96}]\cdot 1.5H_2O$ C, 51.40; H, 3.12; N, 0.00.

WUF-44-56: Found C, 51.02; H, 3.17; N, 0.00. Calc. for $C_{51}H_{37.4}O_{18}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{1.32}(C_{17}H_{12}O_5)_{1.68}]\cdot 2H_2O$ | $[Zn_4O(\mathbf{L^1})_{1.32}(\mathbf{L^2})_{1.68}]\cdot 2H_2O$ C, 51.06; H, 3.14; N, 0.00.

WUF-44-47: Found C, 51.22; H, 3.26; N, 0.00. Calc. for $C_{51}H_{36.8}O_{18}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{1.58}(C_{17}H_{12}O_5)_{1.42}]\cdot 2H_2O$ | $[Zn_4O(\mathbf{L^1})_{1.58}(\mathbf{L^2})_{1.42}]\cdot 2H_2O$ C, 51.06; H, 3.10; N, 0.00.

WUF-44-33: Found C, 51.79; H, 3.19; N, 0.00. Calc. for $C_{51}H_{35}O_{17.5}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{1.99}(C_{17}H_{12}O_5)_{1.01}]\cdot 1.5H_2O$ | $[Zn_4O(\mathbf{L^1})_{1.99}(\mathbf{L^2})_{1.01}]\cdot 1.5H_2O$ C, 51.48; H, 2.97; N, 0.00.

WUF-44-22: Found C, 51.38; H, 3.21; N, 0.00. Calc. for $C_{51}H_{35.6}O_{18}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{2.22}(C_{17}H_{12}O_5)_{0.78}]\cdot 2H_2O$ | $[Zn_4O(\mathbf{L^1})_{2.22}(\mathbf{L^2})_{0.87}]\cdot 2H_2O$ C, 51.11; H, 2.99; N, 0.00.

WUF-44-13: Found C, 51.81; H, 3.23; N, 0.00. Calc. for $C_{51}H_{33.5}O_{17.5}Zn_4$ | $[Zn_4O(C_{17}H_{10}O_5)_{2.75}(C_{17}H_{12}O_5)_{0.25}]\cdot 1.5H_2O$ | $[Zn_4O(\mathbf{L^1})_{2.75}(\mathbf{L^2})_{0.25}]\cdot 1.5H_2O$ C, 51.55; H, 2.84; N, 0.00.

3 ^{1}H NMR Digestion Spectra

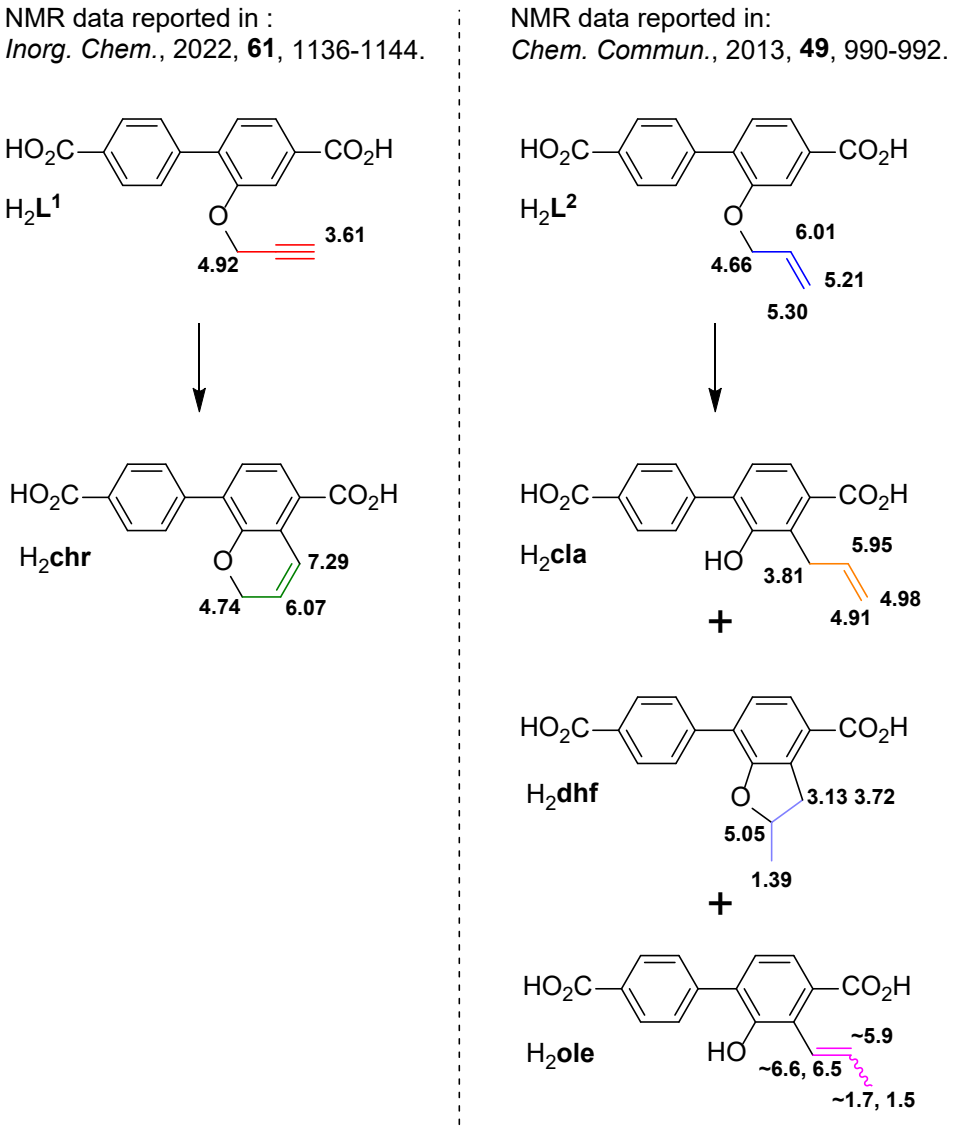


Figure S 1 ^{1}H NMR chemical shifts of the tag groups in the linkers. The groups are colour coded here and in the ^{1}H NMR spectra that follow. The propargyloxy tag group in **L^{1}** linkers give 1 major product under transformation under N_2 gas while 3 major products occur for **L^{2}**. The cyclised product and the internal alkenes are derived from the terminal alkene product. The multiple values for the internal alkene at bottom right is due to *cis*- and *trans*-isomers.

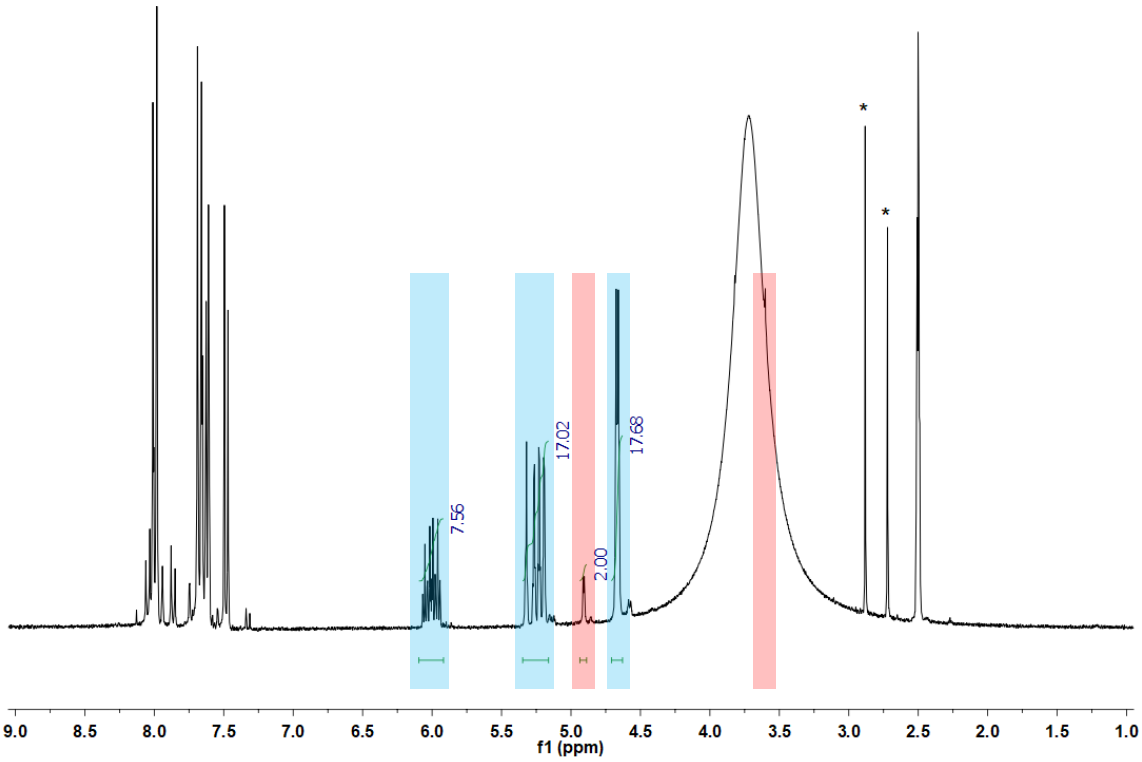


Figure S 2 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-89 ($Zn_4O(L^1)_{0.32}(L^2)_{2.68}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61 ppm) is obscured by the large signal for HOD in these air-dried crystals.

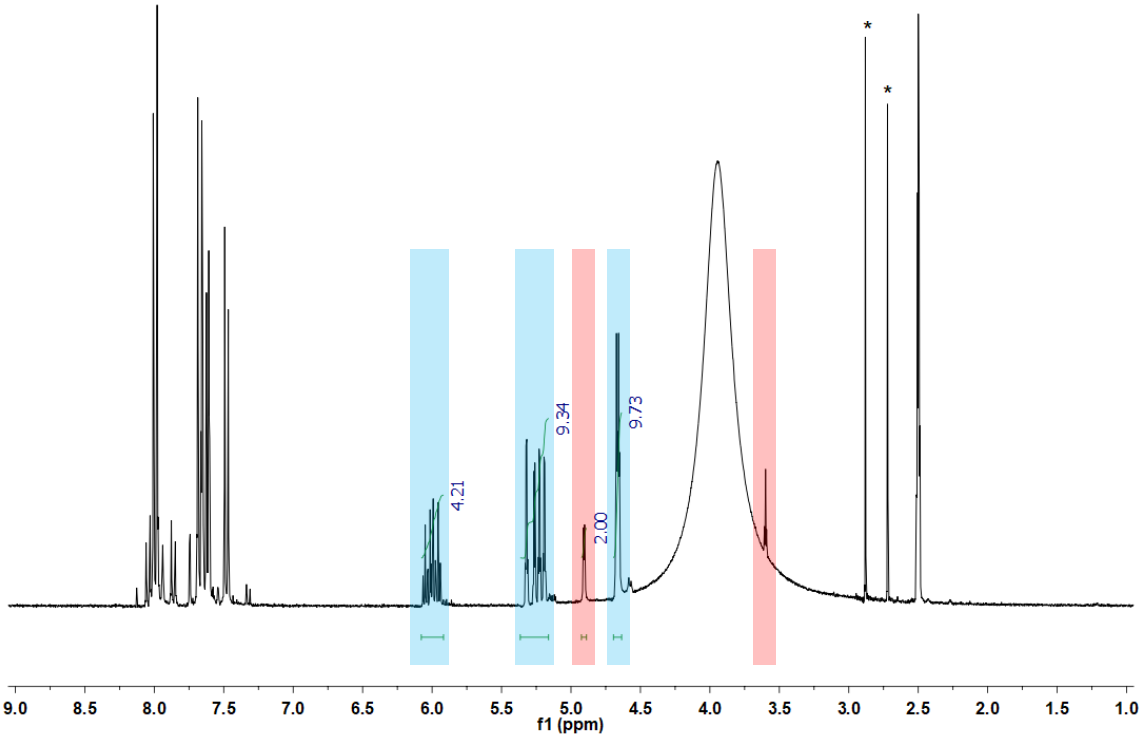


Figure S 3 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-82 ($Zn_4O(L^1)_{0.53}(L^2)_{2.47}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61 ppm) is obscured by the large signal for HOD in these air-dried crystals.

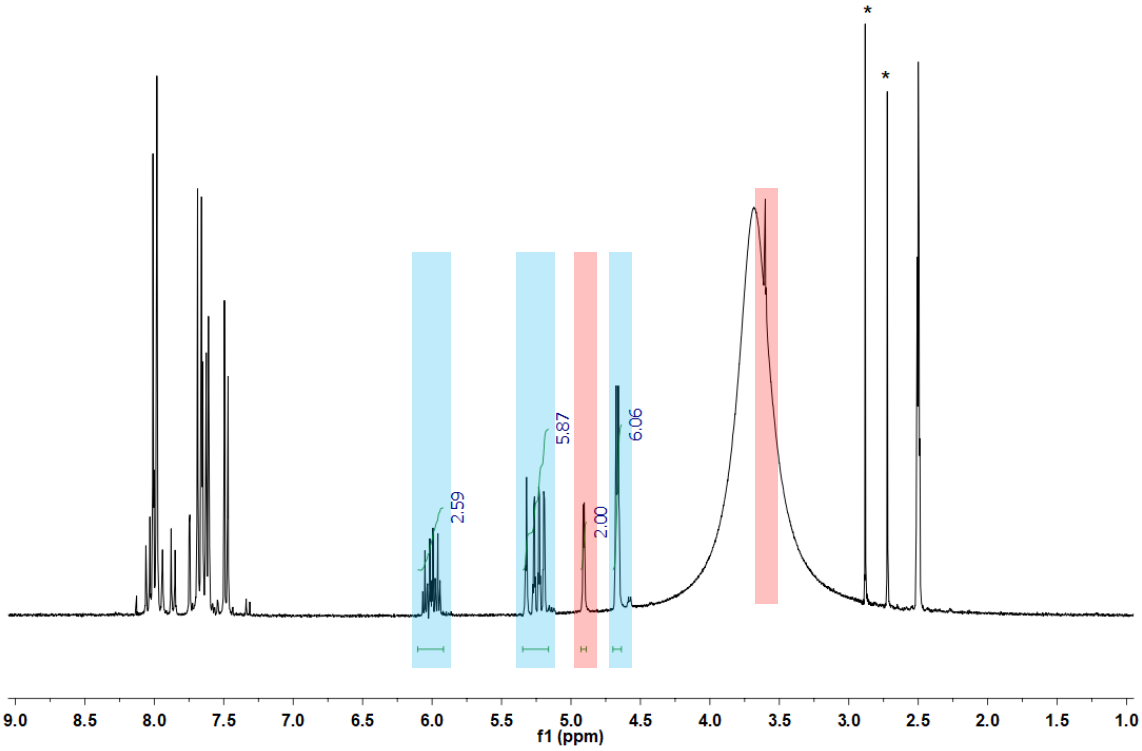


Figure S 4 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-75 ($Zn_4O(L^1)_{0.76}(L^2)_{2.24}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L^1** (δ 3.61 ppm) is obscured by the large signal for water in these air-dried crystals.

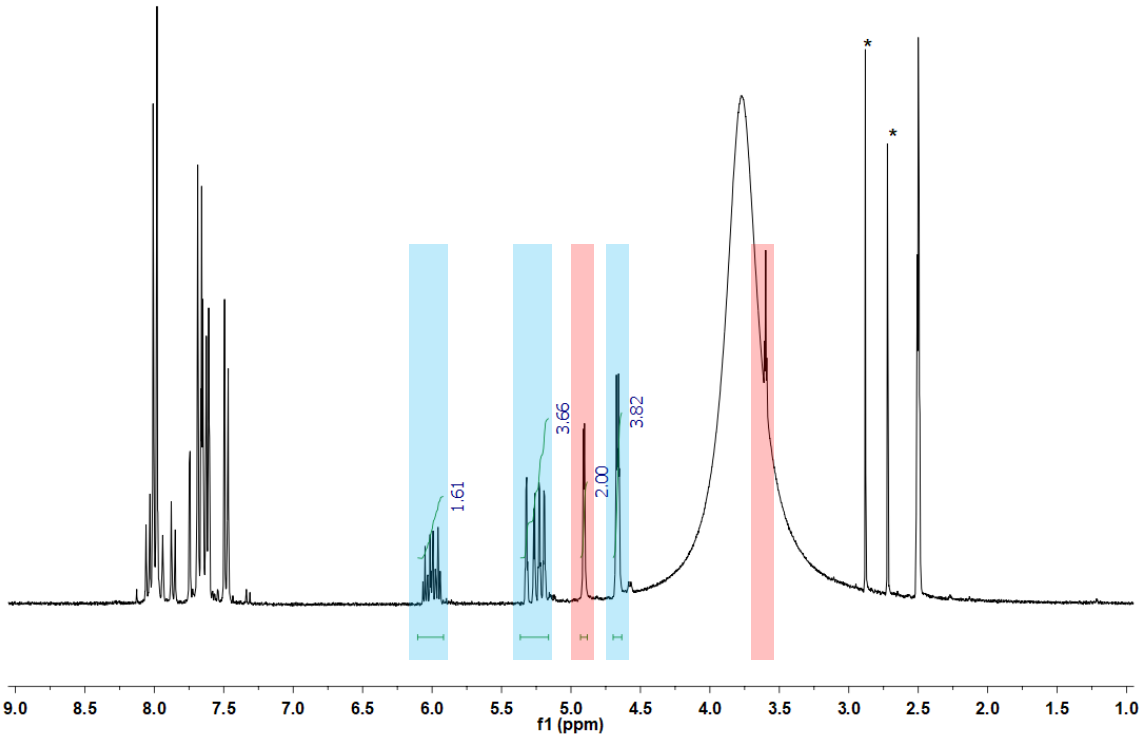


Figure S 5 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-65 ($Zn_4O(L^1)_{1.04}(L^2)_{1.96}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L^1** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

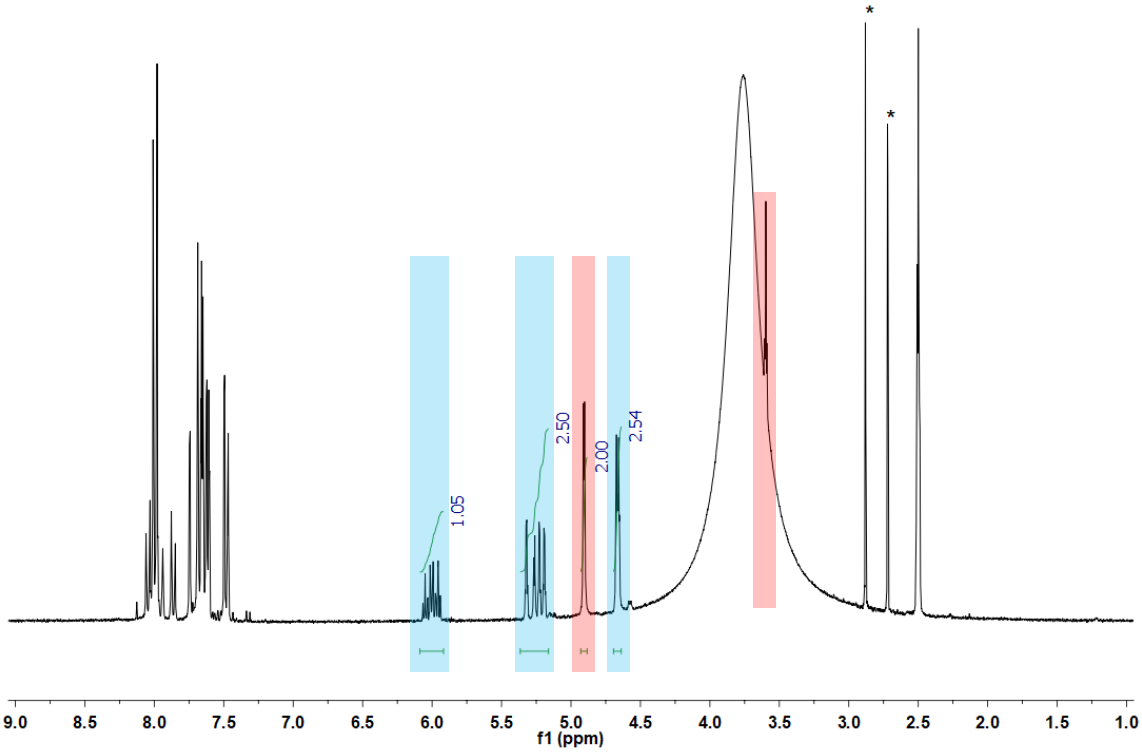


Figure S 6 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-56 ($Zn_4O(L^1)_{1.33}(L^2)_{1.67}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

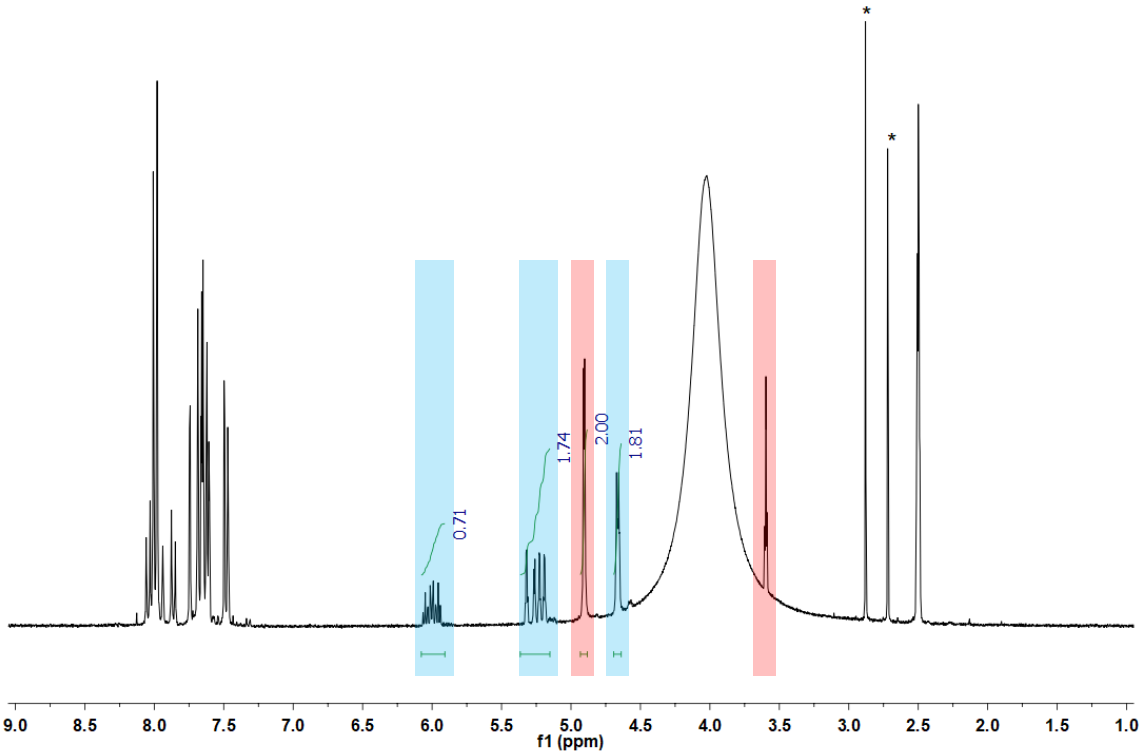


Figure S 7 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-47 ($Zn_4O(L^1)_{1.60}(L^2)_{1.40}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

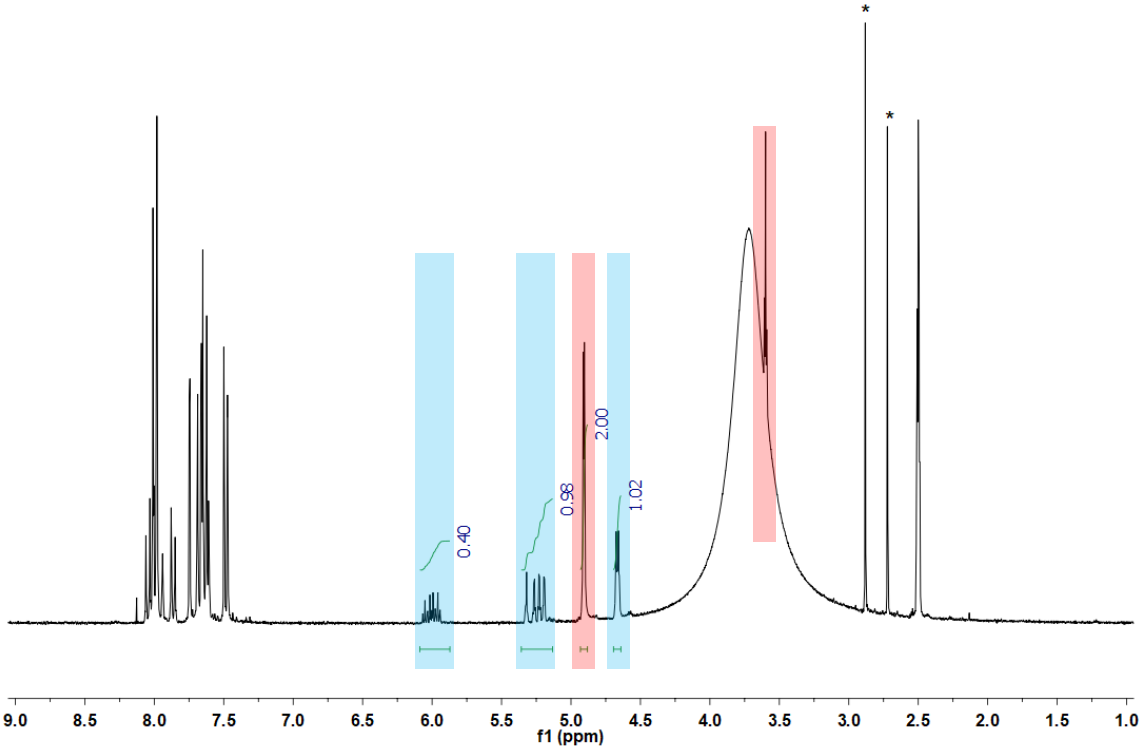


Figure S 8 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-33 ($Zn_4O(L^1)_{2.01}(L^2)_{0.99}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

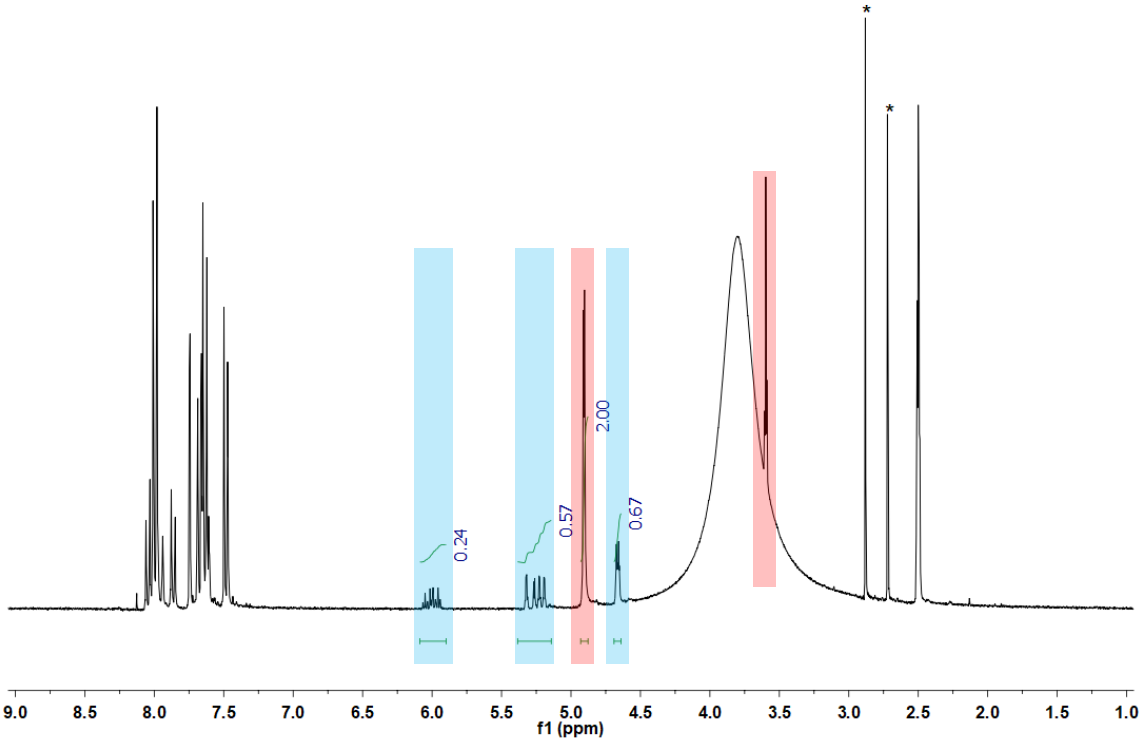


Figure S 9 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-22 ($Zn_4O(L^1)_{2.33}(L^2)_{0.67}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L¹** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

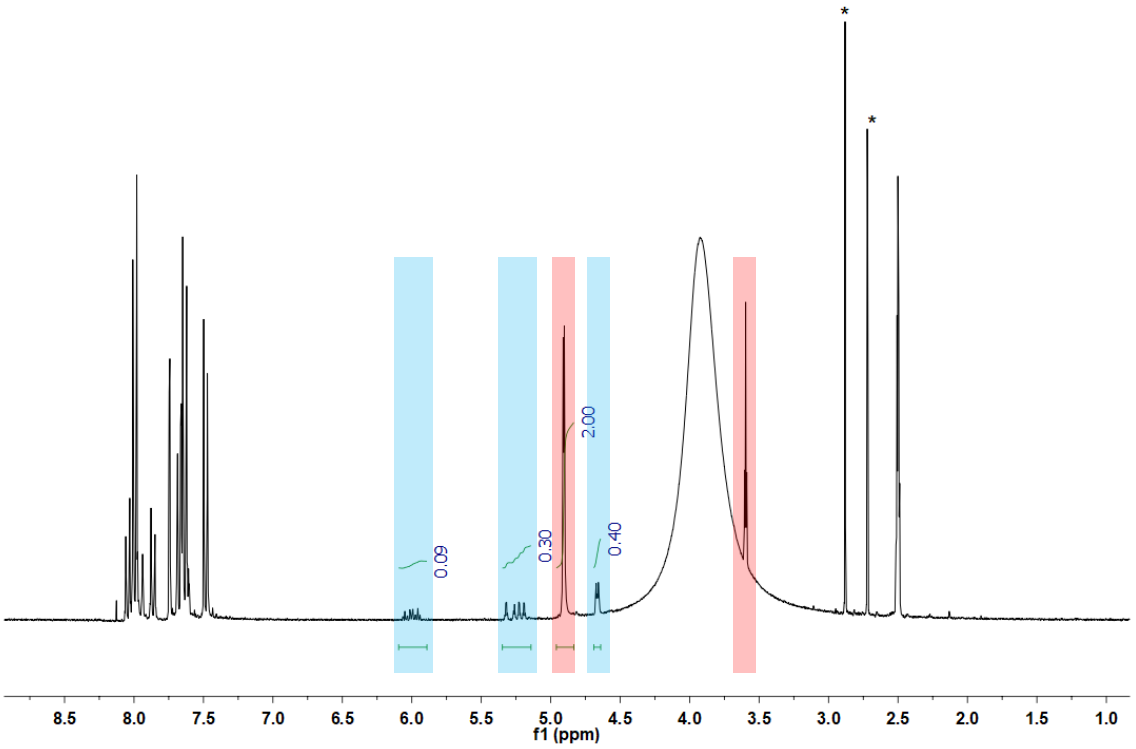


Figure S 10 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-13 ($Zn_4O(L^1)_{2.61}(L^2)_{0.39}$). Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The methyl signals for DMF are marked with an asterisk (*). The signal for the terminal alkyne of **L^1** (δ 3.61) is obscured by the large signal for water in these air-dried crystals.

Table S 2 MOF formulas derived from ^{1}H NMR data of the digestions of air-dried crystals.

Propargyl integration	Allyl integration	MOF Formula	WUF Code
2	17.02	$Zn_4O(\mathbf{L^1})_{0.32}(\mathbf{L^2})_{2.68}$	WUF-44-89
2	9.34	$Zn_4O(\mathbf{L^1})_{0.53}(\mathbf{L^2})_{2.47}$	WUF-44-82
2	5.87	$Zn_4O(\mathbf{L^1})_{0.76}(\mathbf{L^2})_{2.24}$	WUF-44-75
2	3.66	$Zn_4O(\mathbf{L^1})_{1.06}(\mathbf{L^2})_{1.94}$	WUF-44-65
2	2.50	$Zn_4O(\mathbf{L^1})_{1.33}(\mathbf{L^2})_{1.67}$	WUF-44-56
2	1.74	$Zn_4O(\mathbf{L^1})_{1.60}(\mathbf{L^2})_{1.40}$	WUF-44-47
2	0.98	$Zn_4O(\mathbf{L^1})_{2.01}(\mathbf{L^2})_{0.99}$	WUF-44-33
2	0.57	$Zn_4O(\mathbf{L^1})_{2.33}(\mathbf{L^2})_{0.67}$	WUF-44-22
2	0.30	$Zn_4O(\mathbf{L^1})_{2.61}(\mathbf{L^2})_{0.39}$	WUF-44-13

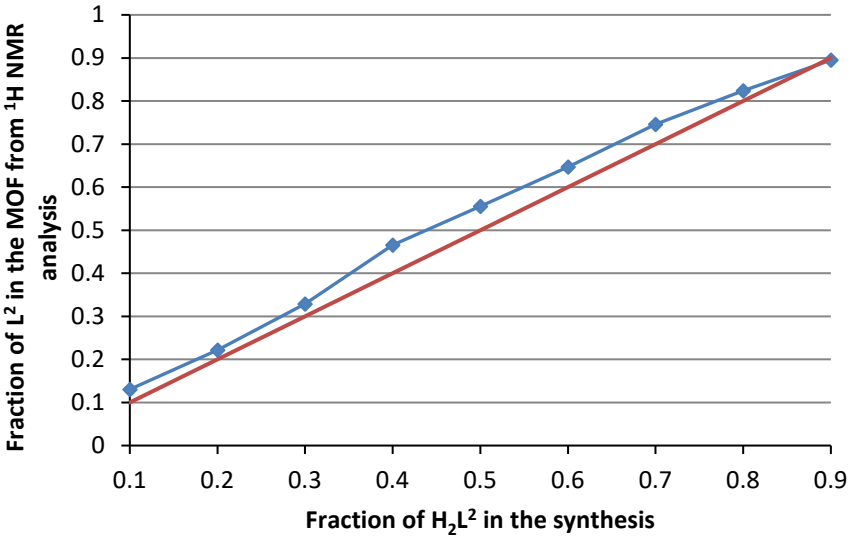


Figure S 11 A plot of **L²** incorporation in the MOFs. The red line is provided to guide the eye for what would be expected if the incorporation matched the synthesis fraction.

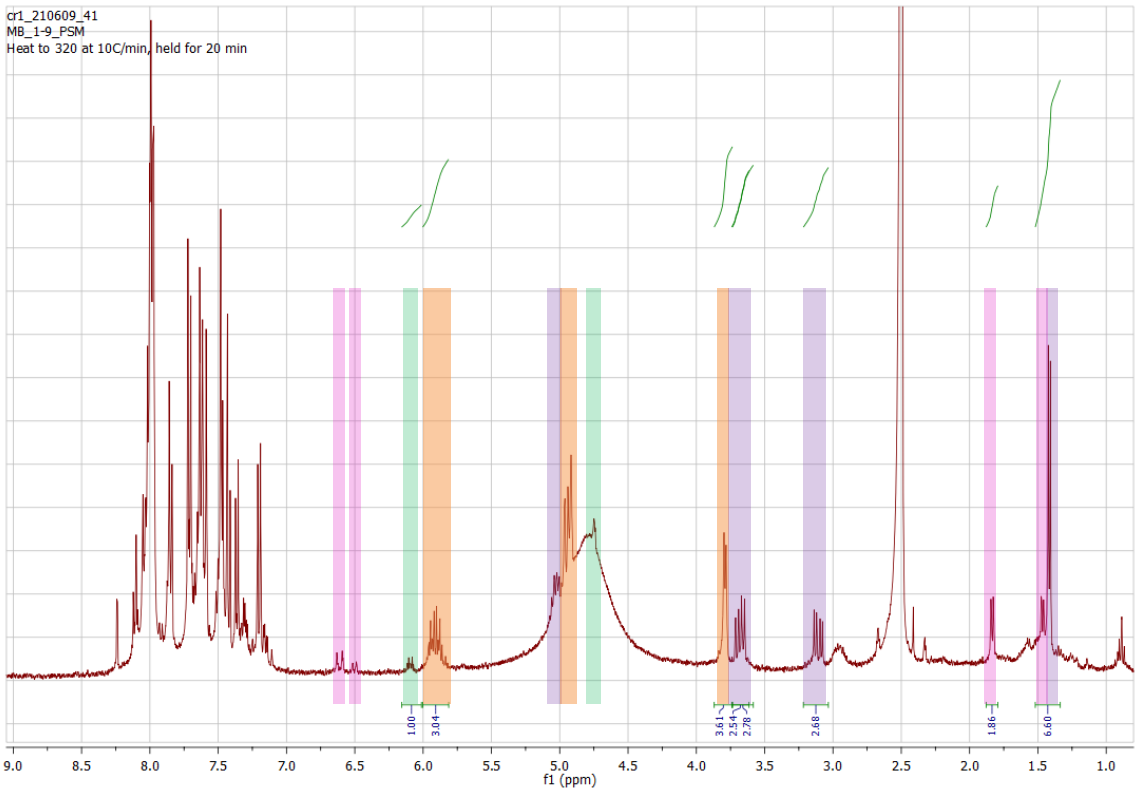


Figure S 12 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution (reference δ 2.50 ppm) of WUF-44-90PSM. The large broad signal centred around 4.75 ppm is the HOD signal. There are no signals for **L¹** (4.92 -CH_2; 3.61-C<u>H</u>) and **L²** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

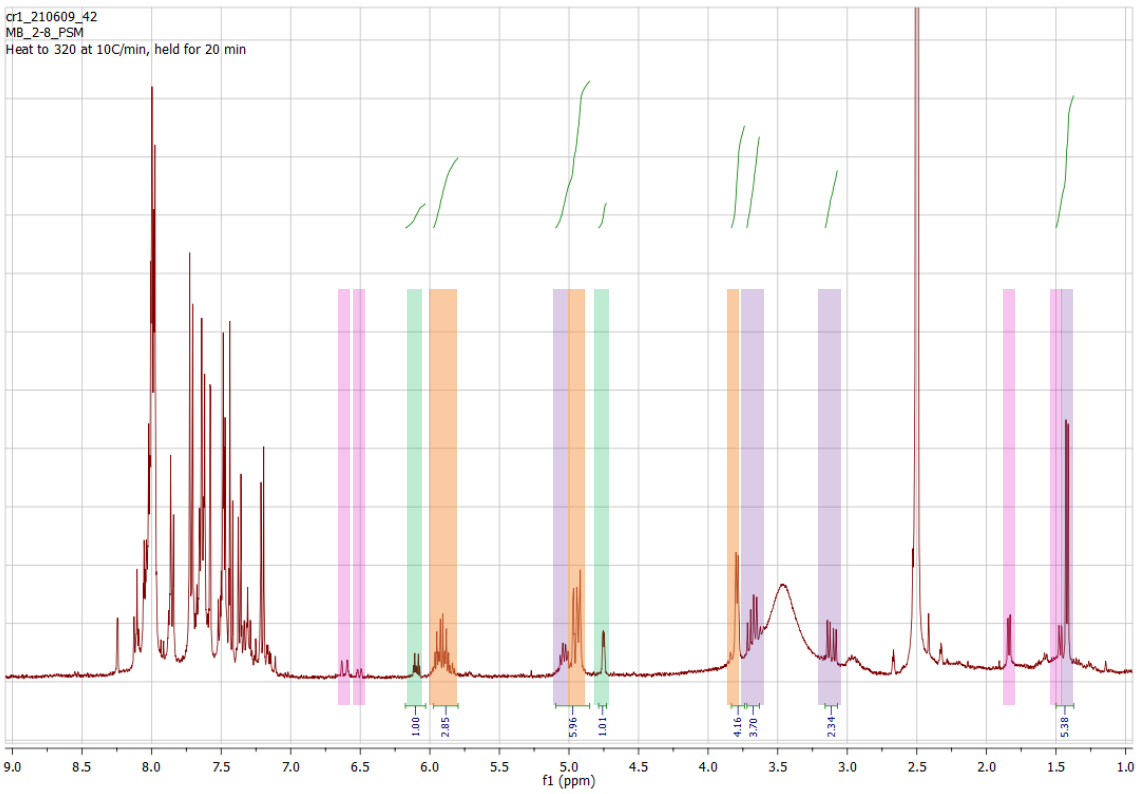


Figure S 13 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution (reference δ 2.50 ppm) of WUF-44-82PSM. The large broad signal centred around 3.5 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

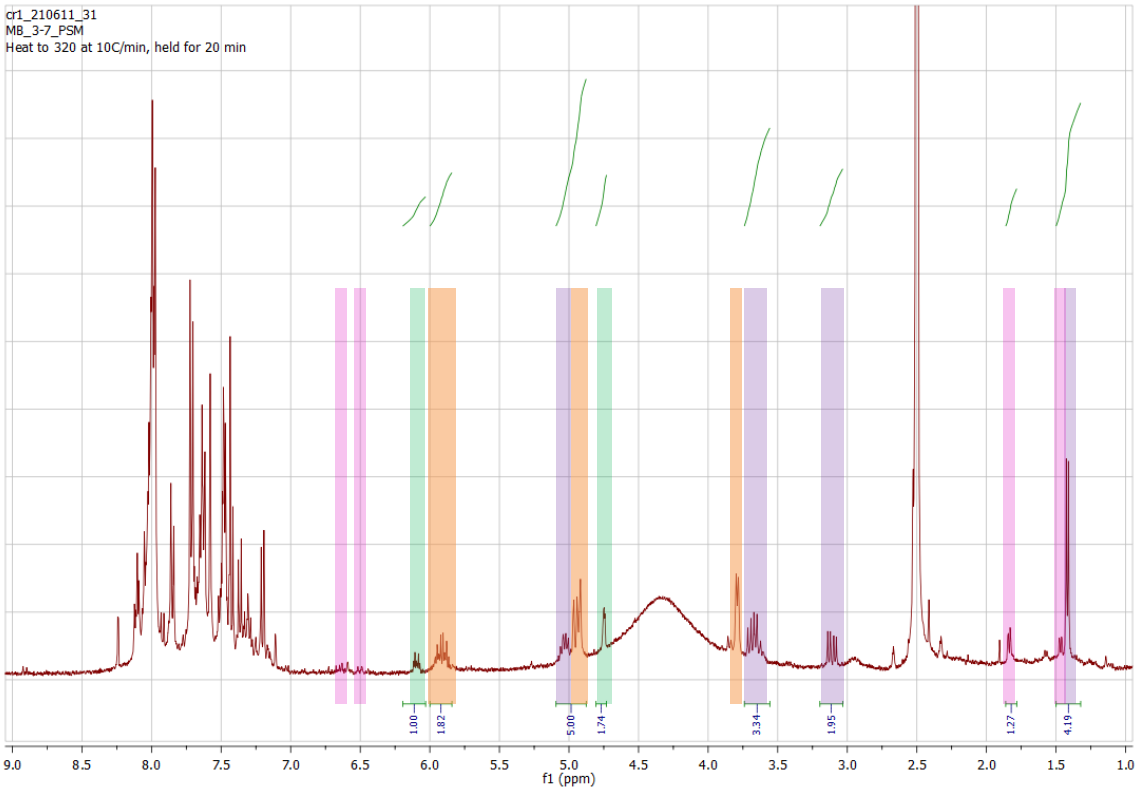


Figure S 14 ^{1}H NMR spectrum in DCl and DMSO-d_6 (reference δ 2.50 ppm) solution of WUF-44-75PSM. The large broad signal centred around 4.25 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

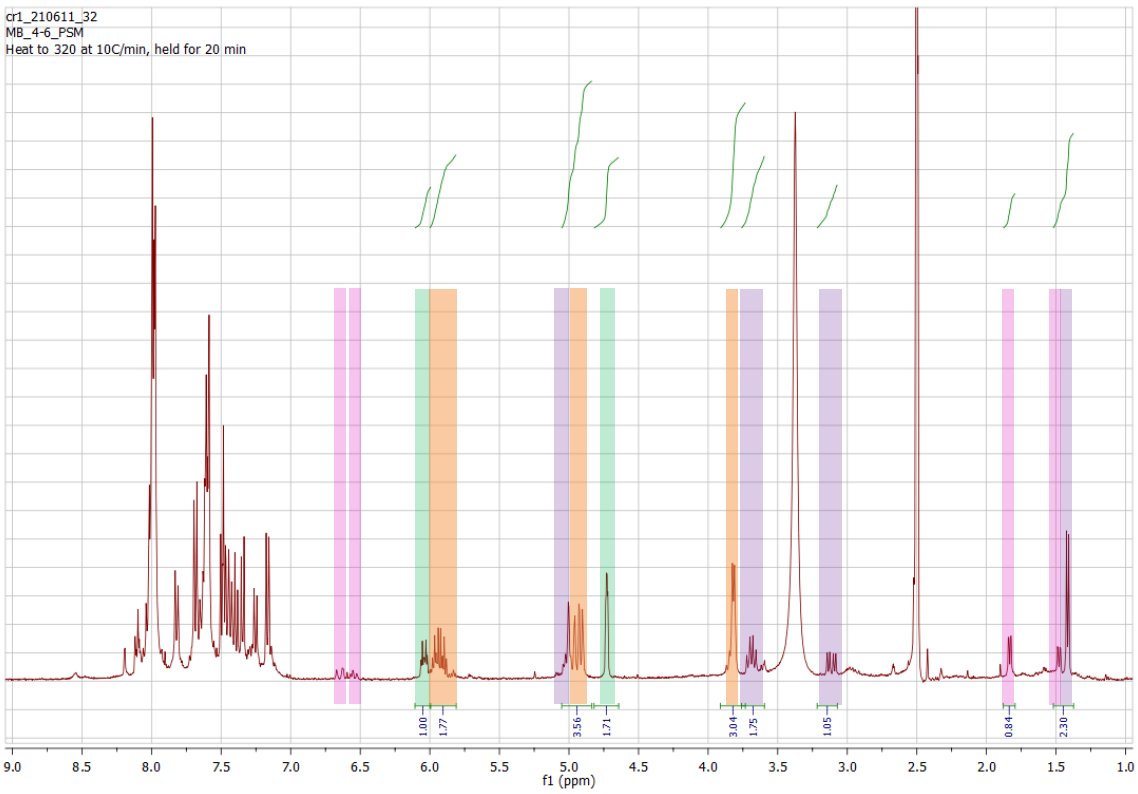


Figure S 15 ^{1}H NMR spectrum in DCl and DMSO-d_6 (reference δ 2.50 ppm) solution of WUF-44-65PSM. Spectrum referenced to δ 2.50 ppm for DMSO-d_6. The large signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

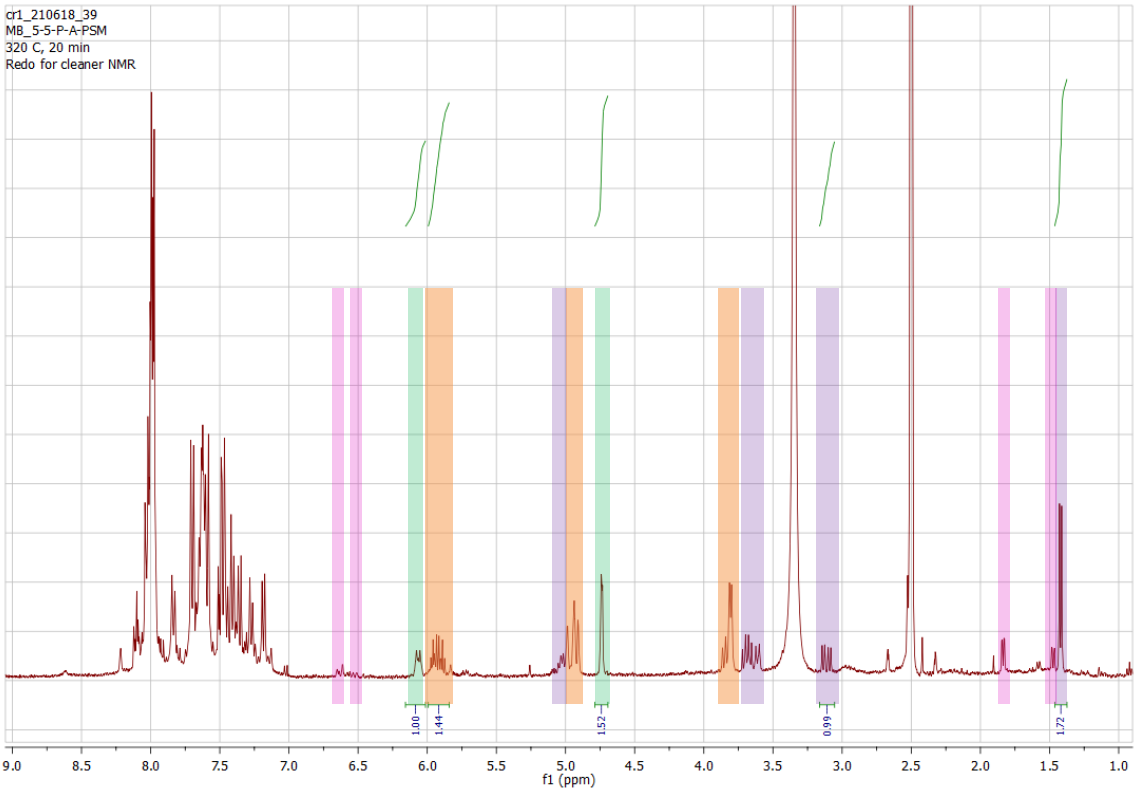


Figure S 16 ^{1}H NMR spectrum in DCl and DMSO-d_6 (reference δ 2.50 ppm) solution of WUF-44-56PSM. The large signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

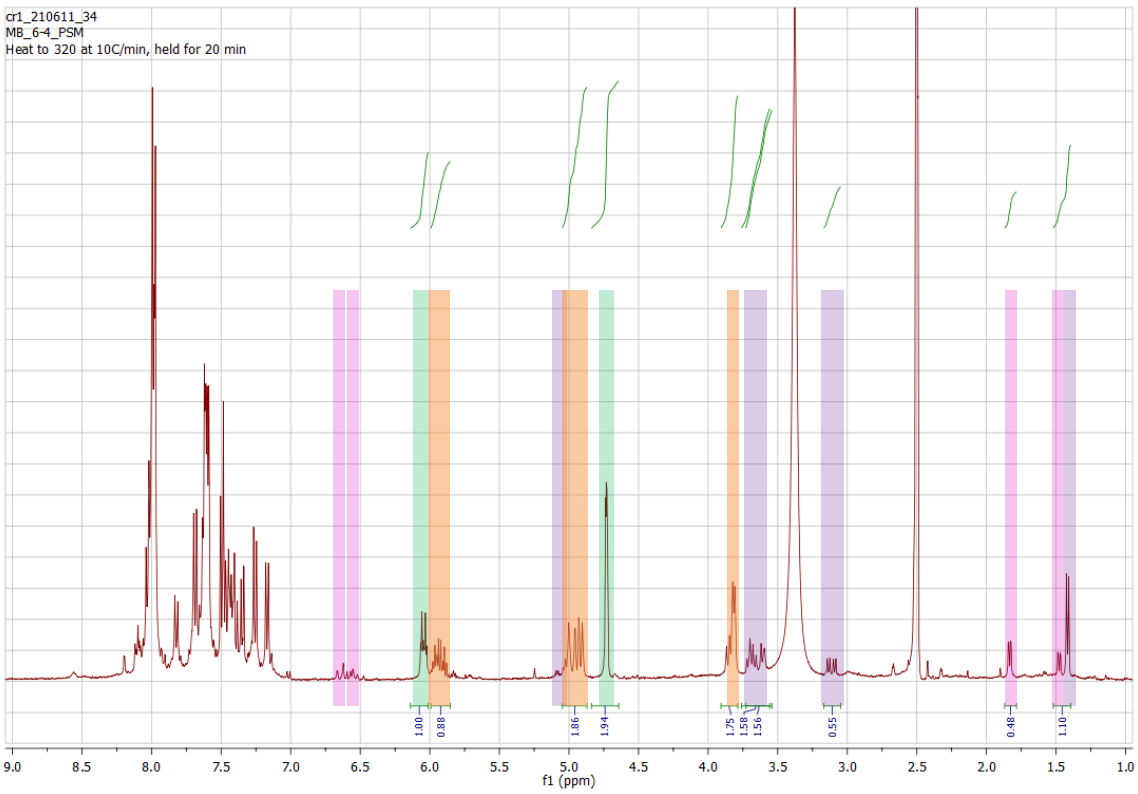


Figure S 17 ^{1}H NMR spectrum in DCl and DMSO-d_6 (reference δ 2.50 ppm) solution of WUF-44-47PSM. The large broad signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C<u>H</u>) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion.

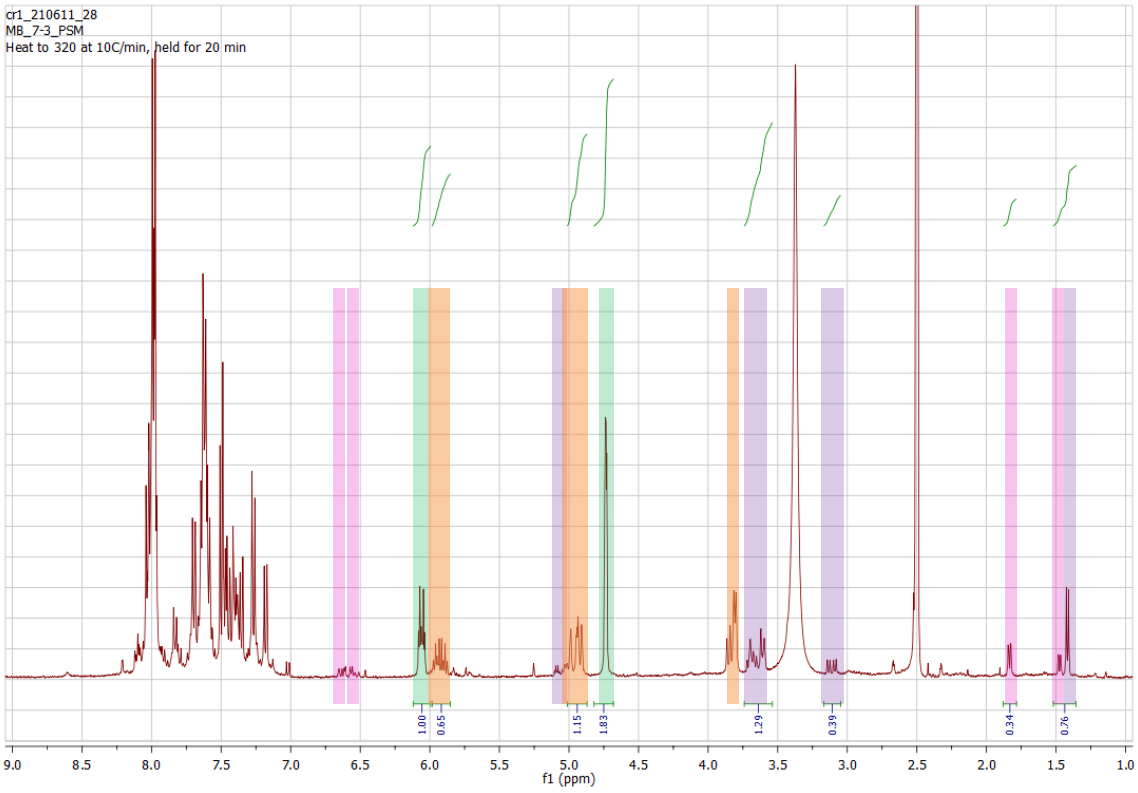


Figure S 18 ^{1}H NMR spectrum in DCl and DMSO-d_6 solution of WUF-44-34PSM. The large broad signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C<u>H</u>) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

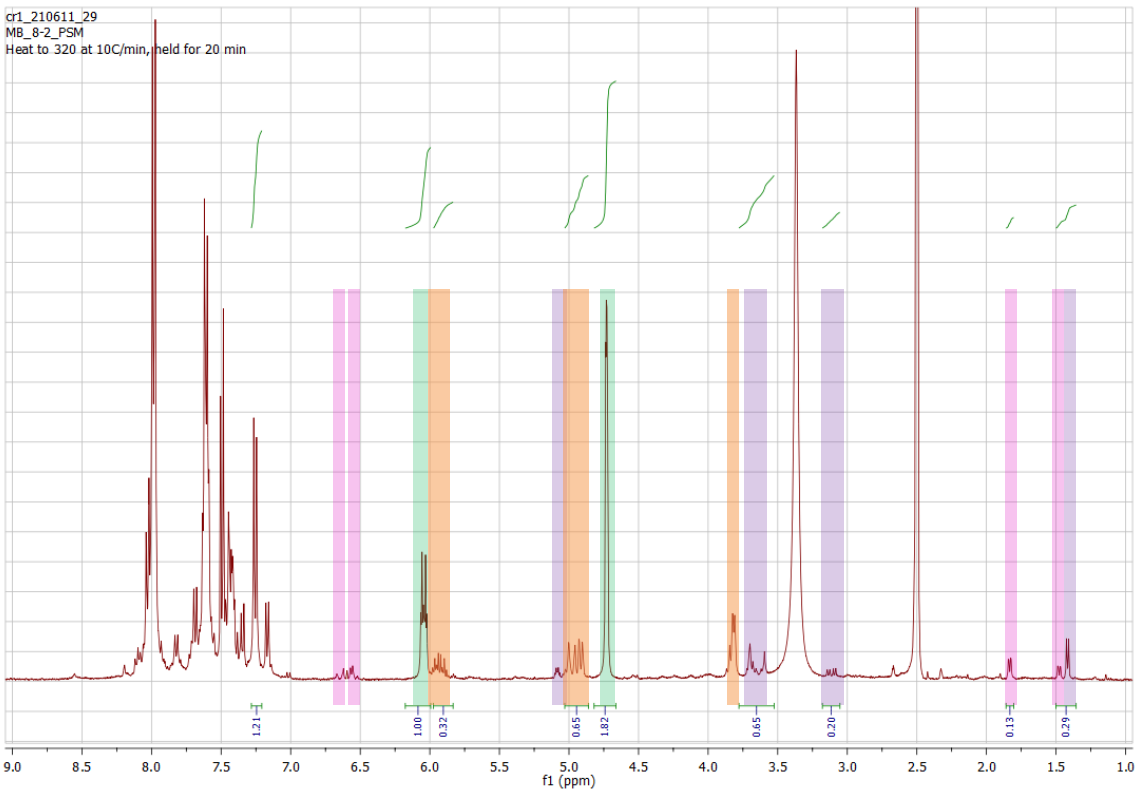


Figure S 19 ^{1}H NMR spectrum in DCl and DMSO-d_6 (reference δ 2.50 ppm) solution of WUF-44-26PSM. The large broad signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have been driven to completion. The colour codes for products are given in Figure S1.

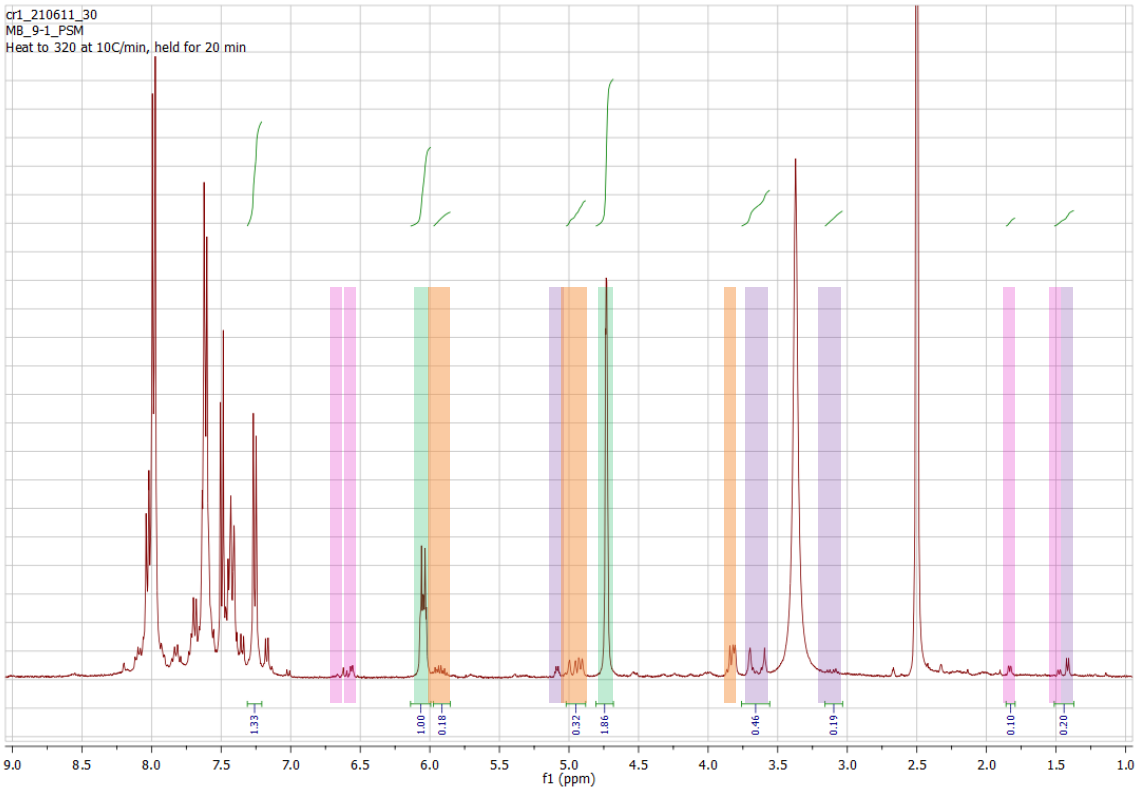


Figure S 20 ^{1}H NMR spectrum in DCl and DMSO-d_6 (δ 2.50 ppm) solution of WUF-44-8PSM. The large broad signal centred around 3.3 ppm is the HOD signal. There are no signals for **L^{1}** (4.92 -CH_2; 3.61-C$\underline{H}$) and **L^{2}** (4.66 -CH_2; 6.01-CH; 5.21/5.30 =CH_2) linkers meaning the reactions have gone to completion. The colour codes for products are given in Figure S1.

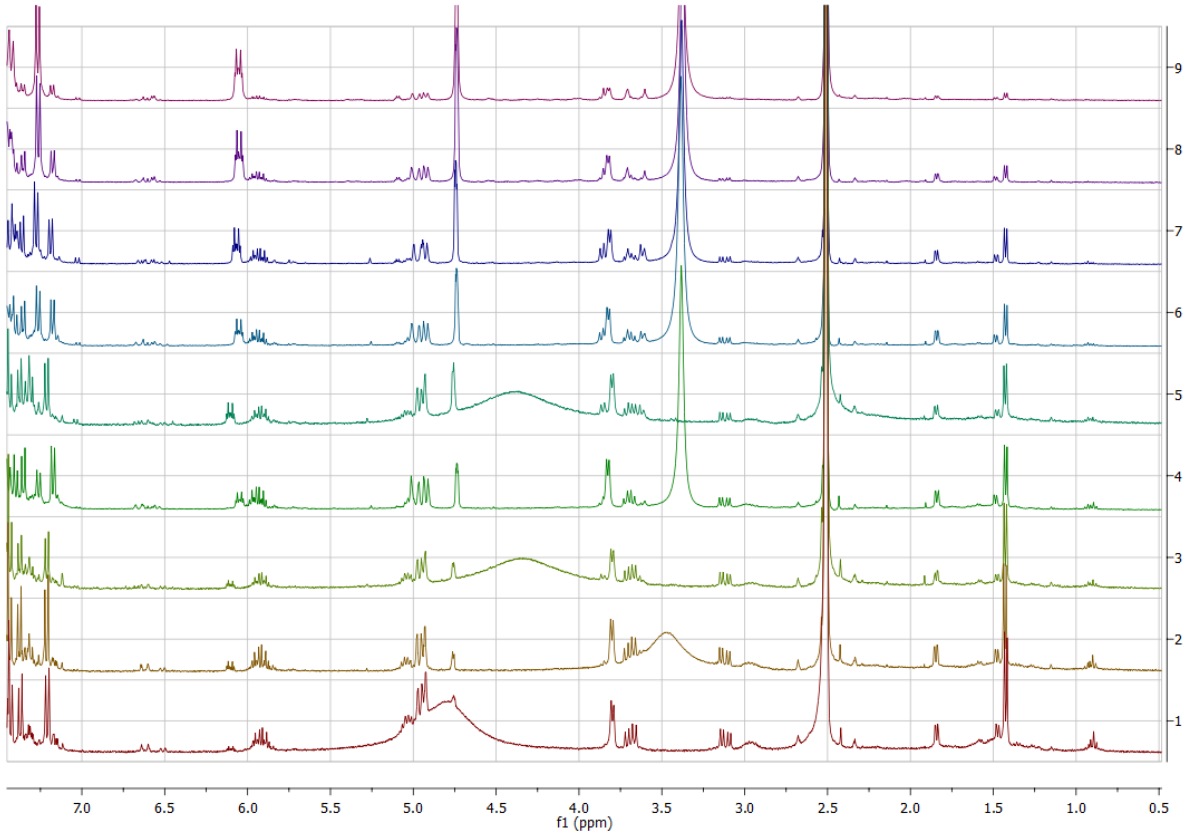
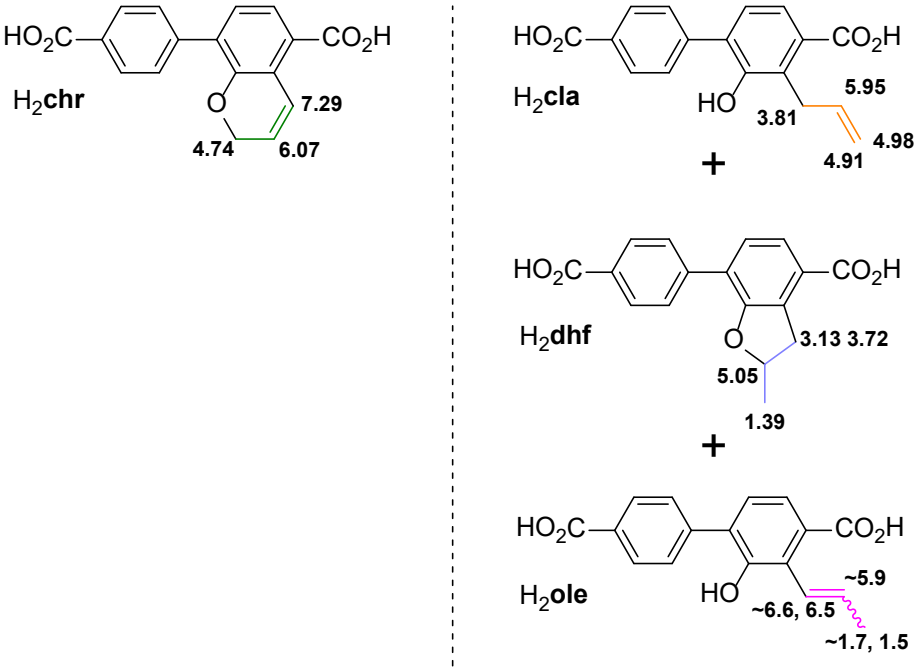


Figure S 21 Stacked spectra from Figures S12-S20 in the range 7.5-0.5 ppm showing the decrease of products arising from reactions of **L²** linkers and the increase in product arising from reaction of **L¹** linkers in the dual modified samples. The labels at right are as follows: **1** WUF-44-89PSM; **2** WUF-44-82PSM; **3** WUF-44-75PSM; **4** WUF-44-65PSM; **5** WUF-44-56PSM; **6** WUF-44-47PSM; **7** WUF-44-33PSM; **8** WUF-44-22PSM; **9** WUF-44-13PSM. Spectra are referenced to δ 2.50 ppm for DMSO-d_6.

Table S 3 Approximate MOF formulas derived from ^{1}H NMR data of the digestions of modified samples crystals.#

MOF Formula	WUF Code
$Zn_4O(chr)_{0.39}(cla)_{1.16}(dhf)_{0.92}(ole)_{0.54}$	WUF-44-89PSM
$Zn_4O(chr)_{0.41}(cla)_{1.24}(dhf)_{0.71}(ole)_{0.64}$	WUF-44-82PSM
$Zn_4O(chr)_{0.79}(cla)_{1.13}(dhf)_{0.63}(ole)_{0.44}$	WUF-44-75PSM
$Zn_4O(chr)_{0.91}(cla)_{1.15}(dhf)_{0.46}(ole)_{0.48}$	WUF-44-65PSM
$Zn_4O(chr)_{1.02}(cla)_{1.07}(dhf)_{0.52}(ole)_{0.40}$	WUF-44-56PSM
$Zn_4O(chr)_{1.23}(cla)_{1.15}(dhf)_{0.31}(ole)_{0.31}$	WUF-44-47PSM
$Zn_4O(chr)_{1.58}(cla)_{0.91}(dhf)_{0.25}(ole)_{0.26}$	WUF-44-33PSM
$Zn_4O(chr)_{2.06}(cla)_{0.66}(dhf)_{0.12}(ole)_{0.17}$	WUF-44-22PSM
$Zn_4O(chr)_{2.39}(cla)_{0.38}(dhf)_{0.08}(ole)_{0.14}$	WUF-44-13PSM

#We provide this data at the request of the referee and wish to note the inherent inaccuracy in integrations of the low-intensity signals and that caution should be exercised in the proportions estimated for some of these products. We emphasise that the reactions have gone to completion by the absence of the signals for the starting $\mathbf{L^1}$ and $\mathbf{L^2}$ linkers. The **ole** components are reported as the total of the *cis*- and *trans*-isomers.



4 Powder X-ray Diffraction Patterns

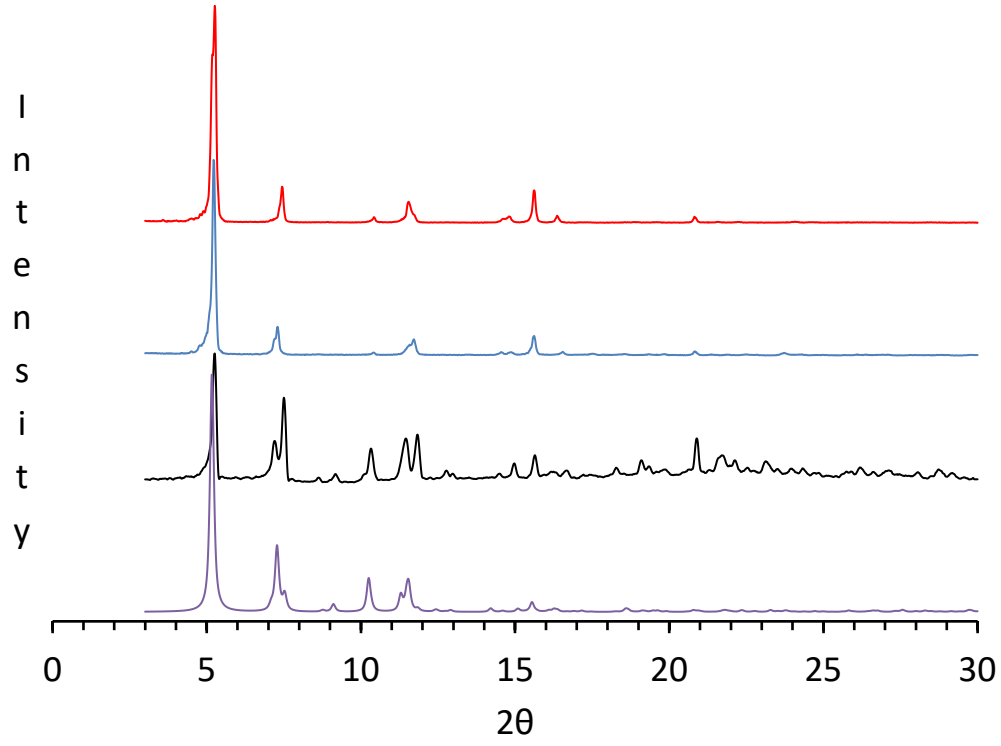


Figure S 22 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-89 and WUF-44-89PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

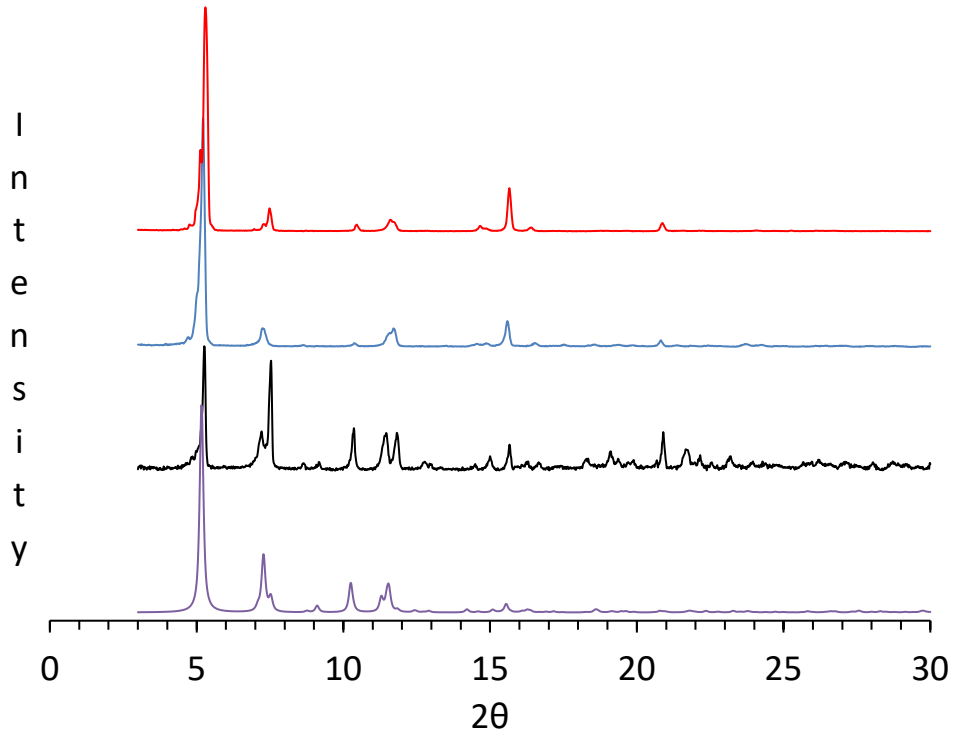


Figure S 23 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-82 and WUF-44-82PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

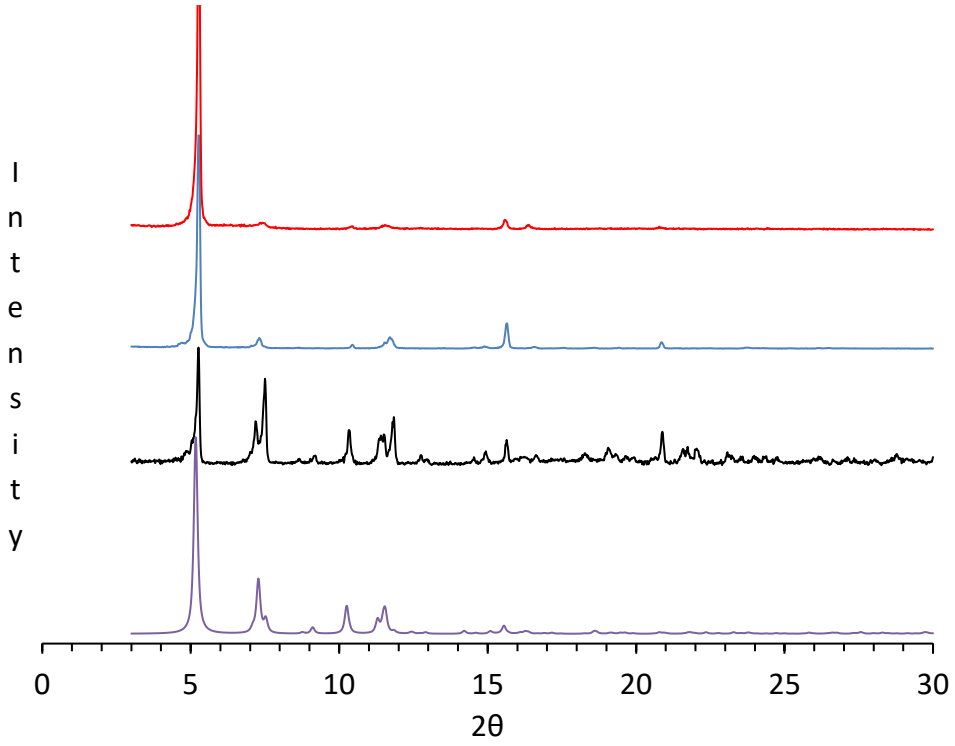


Figure S 24 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-75 and WUF-44-75PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

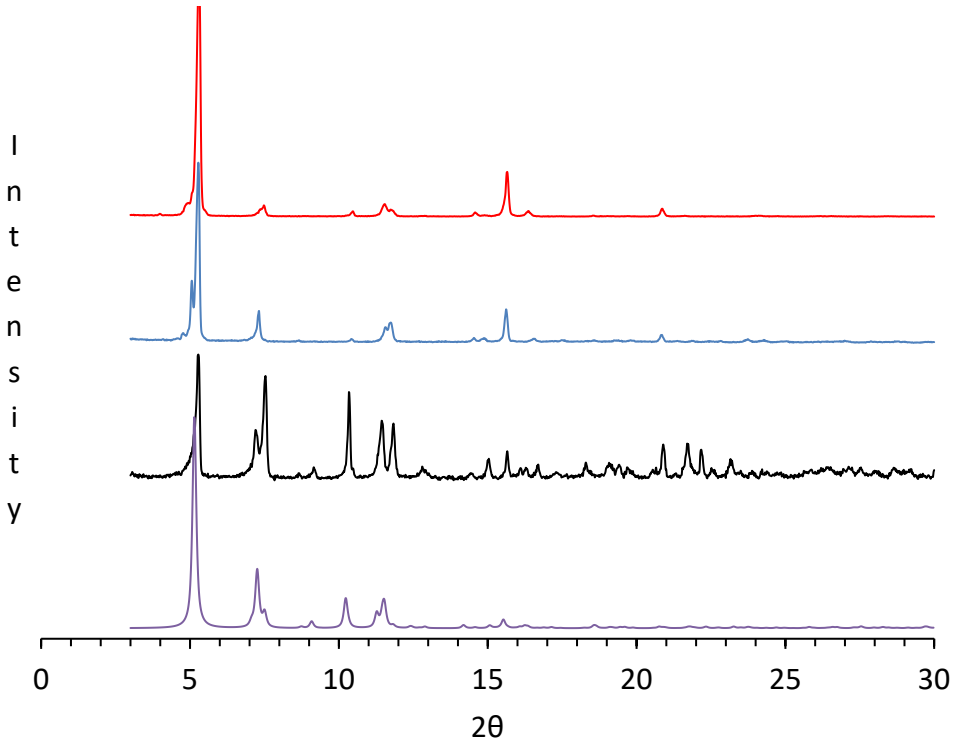


Figure S 25 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-65 and WUF-44-65PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

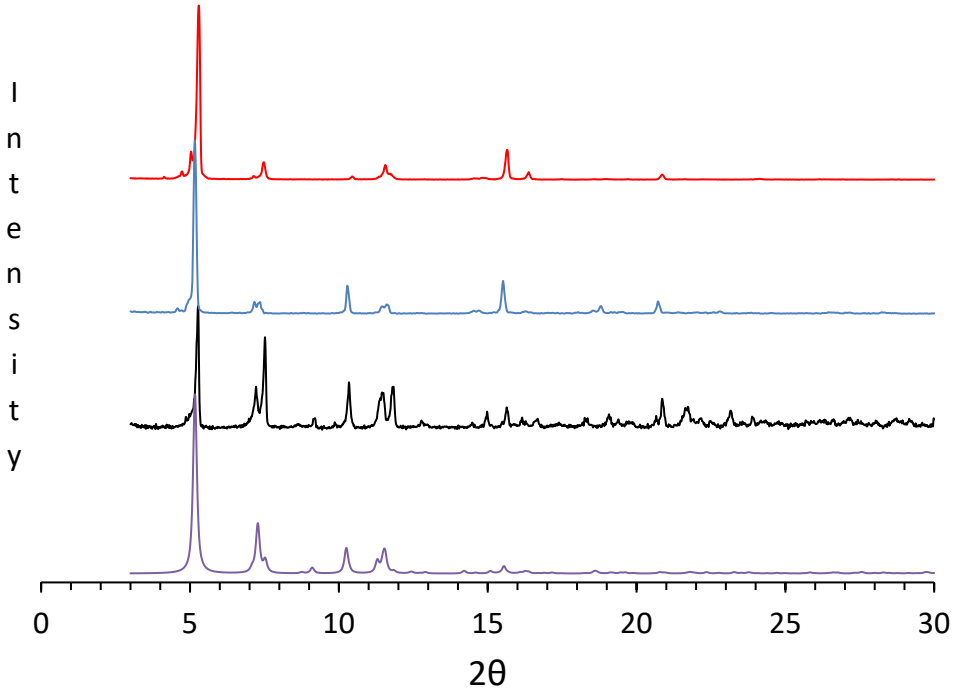


Figure S 26 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-56 and WUF-44-56PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

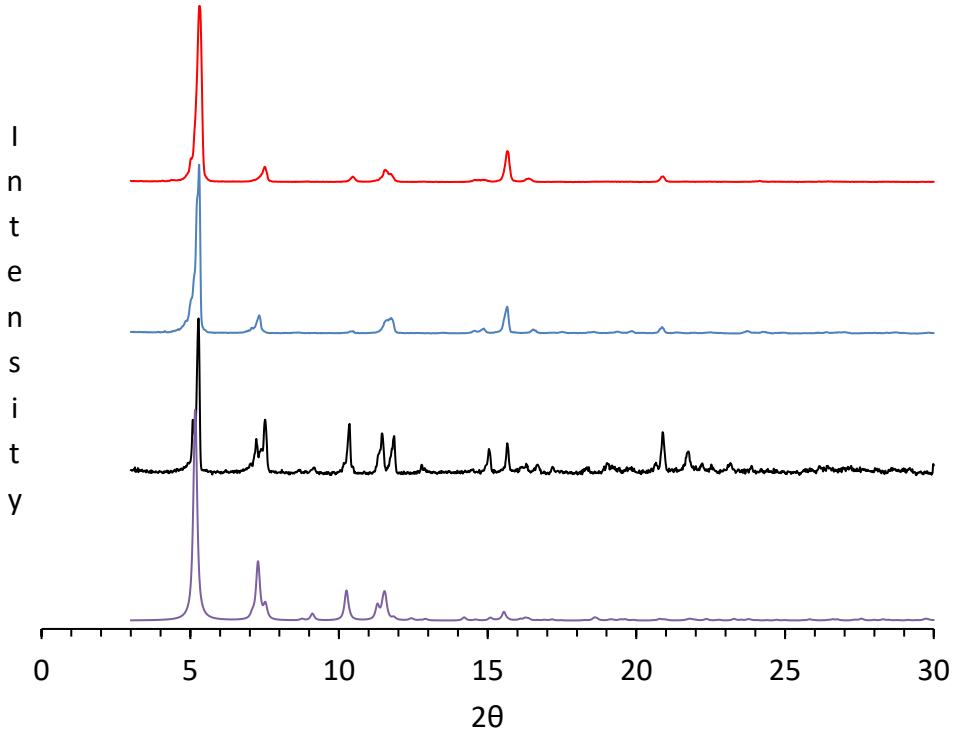


Figure S 27 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-47 and WUF-44-47PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

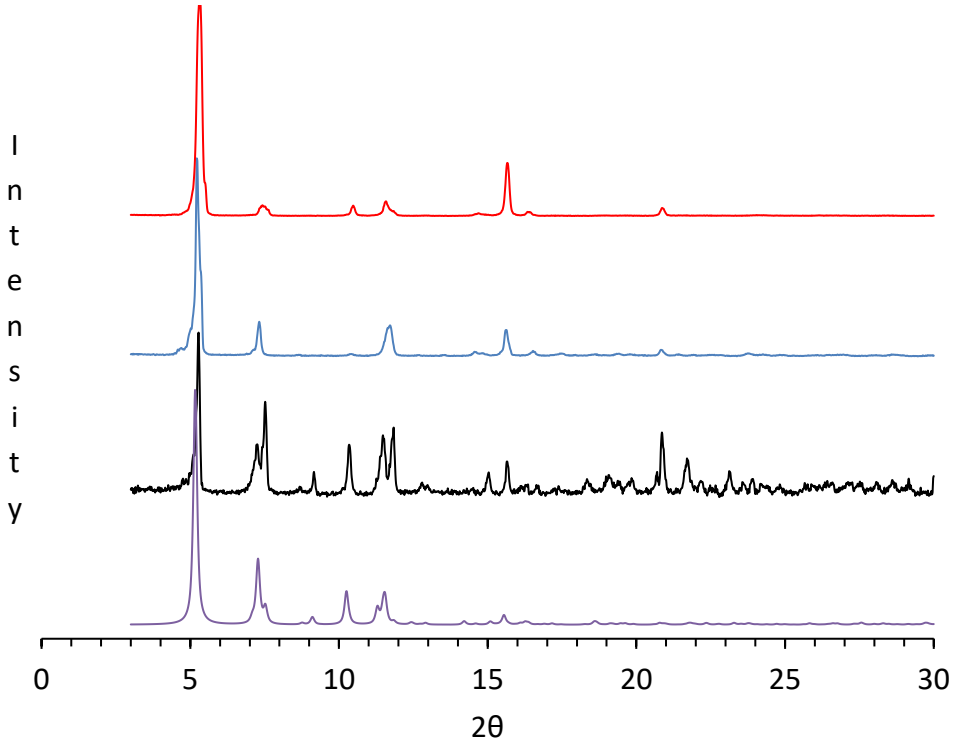


Figure S 28 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-33 and WUF-44-33PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

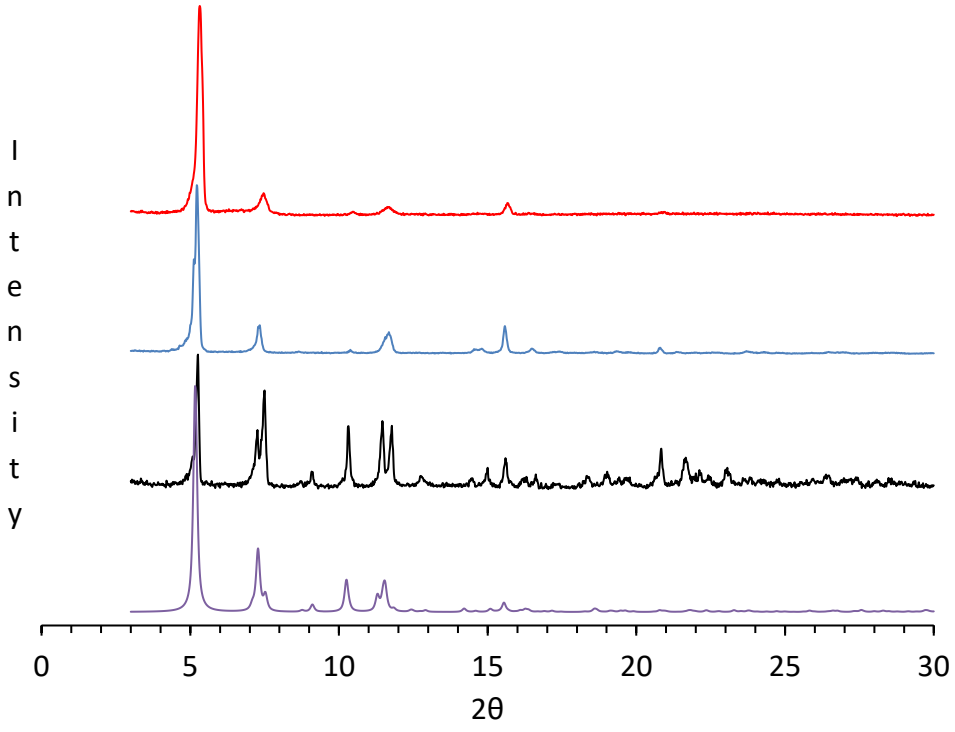


Figure S 29 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-22 and WUF-44-22PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

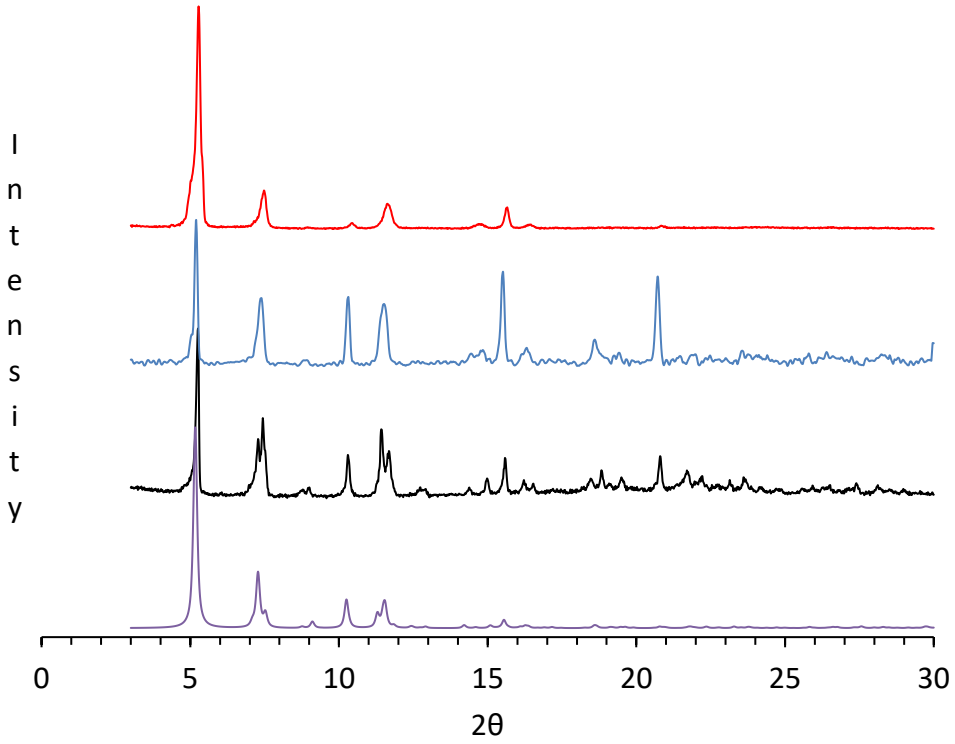


Figure S 30 Experimental PXRD patterns for 'as synthesised' (black) and activated (blue) WUF-44-13 and WUF-44-13PSM (red) alongside the calculated pattern of a parent 'as synthesised' MOF WUF-35 ($Zn_4O(\mathbf{L^1})_3$) (purple) for reference.

5 TG–DTA Data

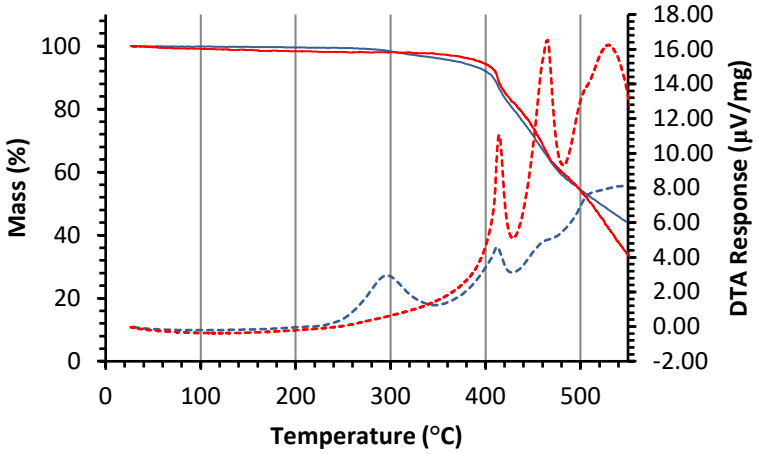


Figure S 31 TG—DTA for heating activated WUF-44-89 (blue) and WUF-44-89PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

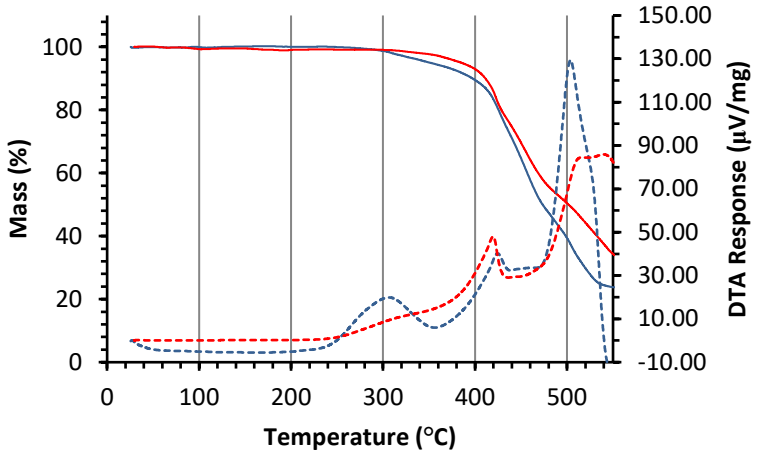


Figure S 32 TG—DTA for heating activated WUF-44-82 (blue) and WUF-44-82PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

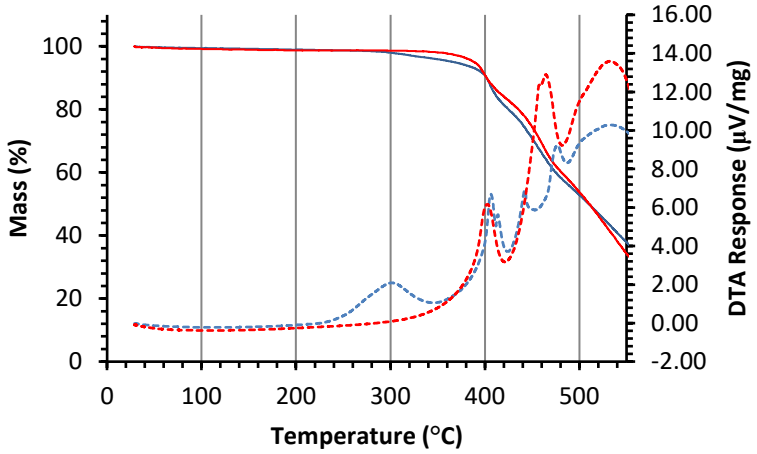


Figure S 33 TG—DTA for heating activated WUF-44-75 (blue) and WUF-44-75PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

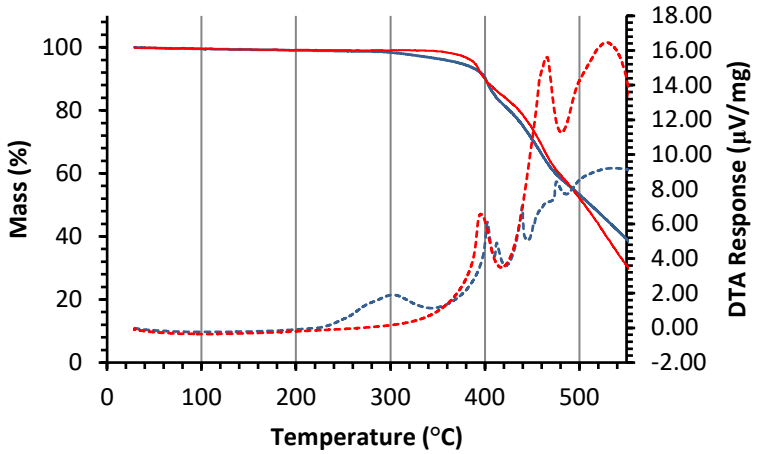


Figure S 34 TG—DTA for heating activated WUF-44-65 (blue) and WUF-44-65PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

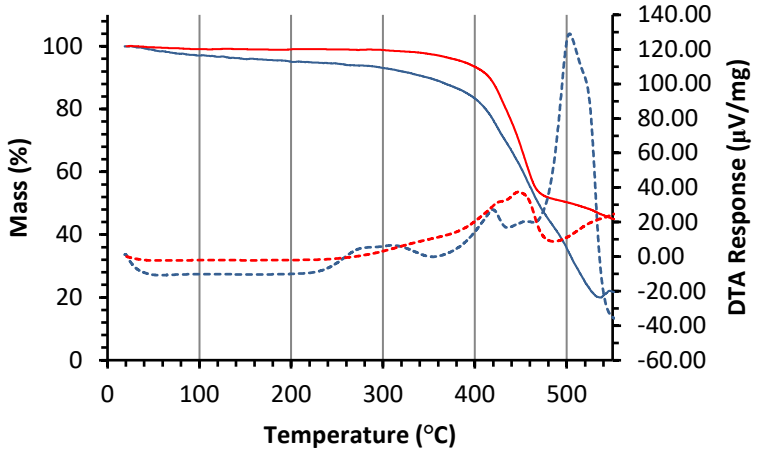


Figure S 35 TG—DTA for heating activated WUF-44-56 (blue) and WUF-44-56PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

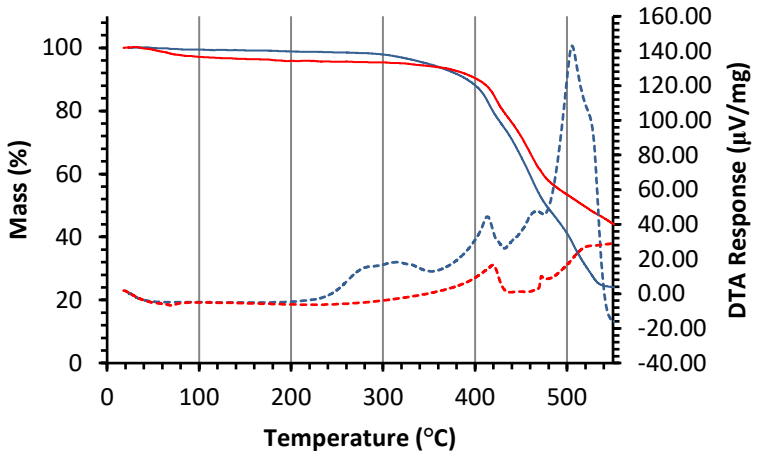


Figure S 36 TG—DTA for heating activated WUF-44-47 (blue) and WUF-44-47PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

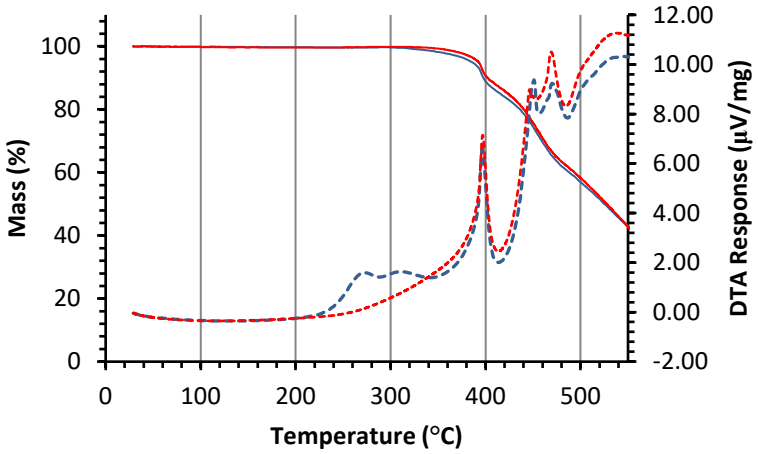


Figure S 37 TG—DTA for heating activated WUF-44-33 (blue) and WUF-44-33PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

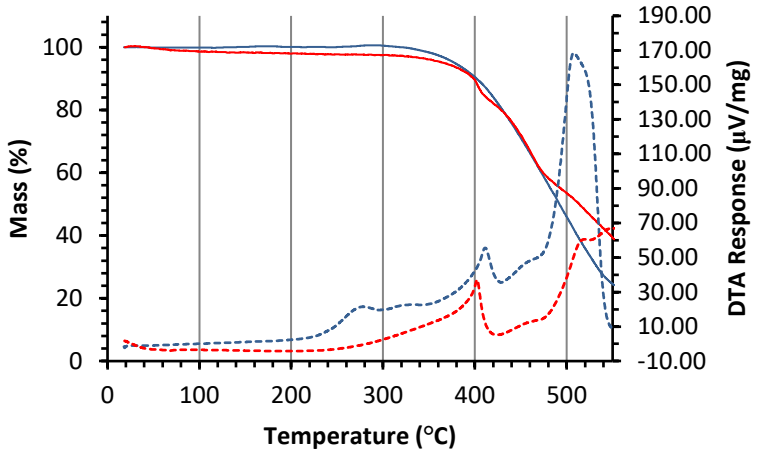


Figure S 38 TG—DTA for heating activated WUF-44-22 (blue) and WUF-44-22PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

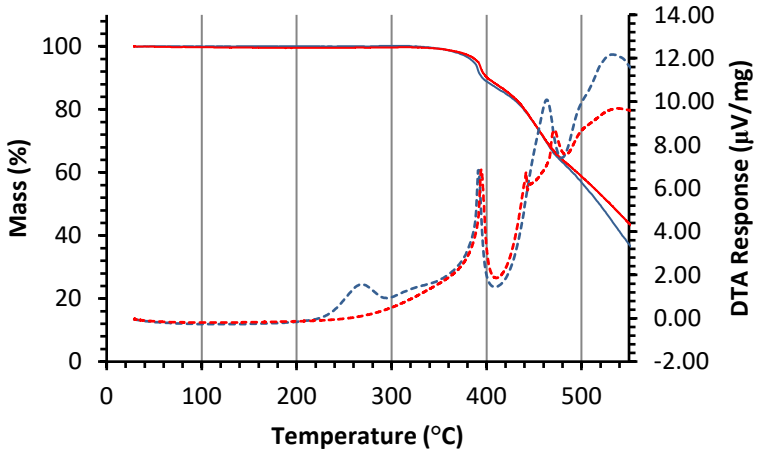


Figure S 39 TG—DTA for heating activated WUF-44-13 (blue) and WUF-44-13PSM (red) up to 550 °C; TG curves (solid lines); DTA curves (dashed lines).

6 Gas Adsorption Isotherms and BET Data

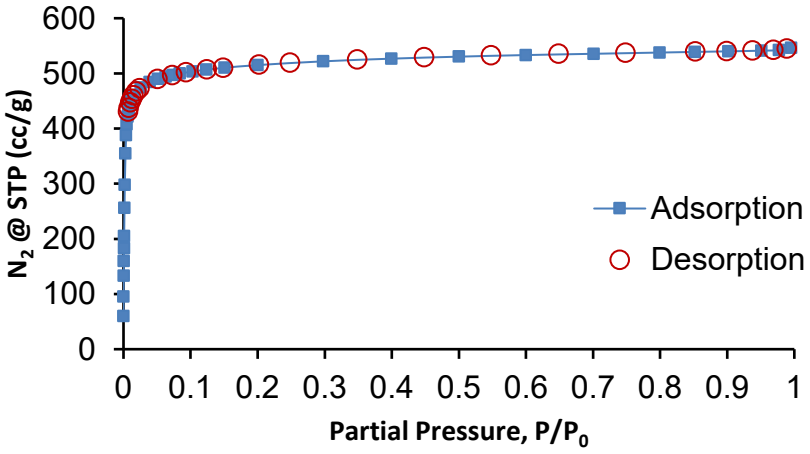


Figure S 40 Isotherm of $Zn_4O(L^2)_3$. We re-recorded this data for the current study. It was reported by us previously.[2]

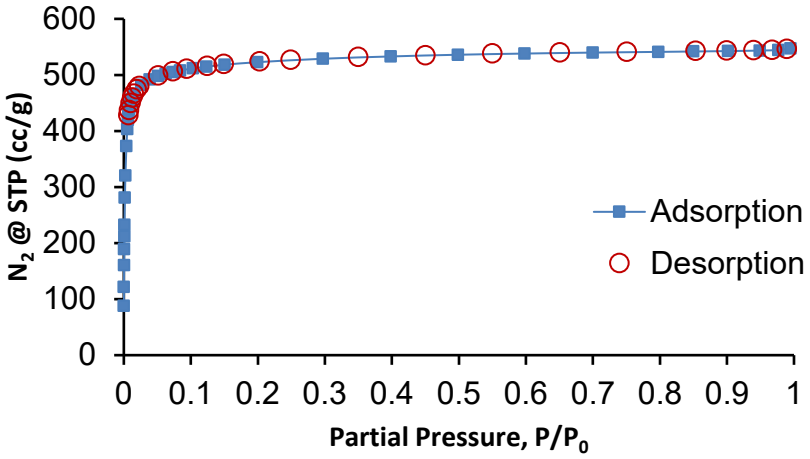


Figure S 41 Isotherm of $Zn_4O(L^2)_3$ heated to 320 °C for 20 minutes.

BET summary	$Zn_4O(L^2)_3$	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.01261e-03	437.4542	1.4774e-02
Slope	1.688	9.10737e-03	443.3428	1.6587e-02
Intercept	1.206e-03	1.00427e-02	447.2739	1.8147e-02
Correlation coefficient, r	0.999996	1.20346e-02	452.6257	2.1533e-02
C constant	1400.579	1.50070e-02	459.9681	2.6502e-02
Surface Area	2062.049 m^2/g	2.57038e-02	474.4455	4.4491e-02
		3.91115e-02	484.1217	6.7271e-02

BET summary	$Zn_4O(L^2)_3$PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.99321e-03	443.3957	1.6376e-02
Slope	1.654	9.80354e-03	448.1257	1.7677e-02
Intercept	1.426e-03	1.04610e-02	451.3749	1.8739e-02
Correlation coefficient, r	0.999992	1.20215e-02	457.0802	2.1299e-02
C constant	1161.514	1.50440e-02	465.5290	2.6251e-02
Surface Area	2103.289 m^2/g	2.63043e-02	482.2583	4.4820e-02
		3.88862e-02	491.6892	6.5839e-02

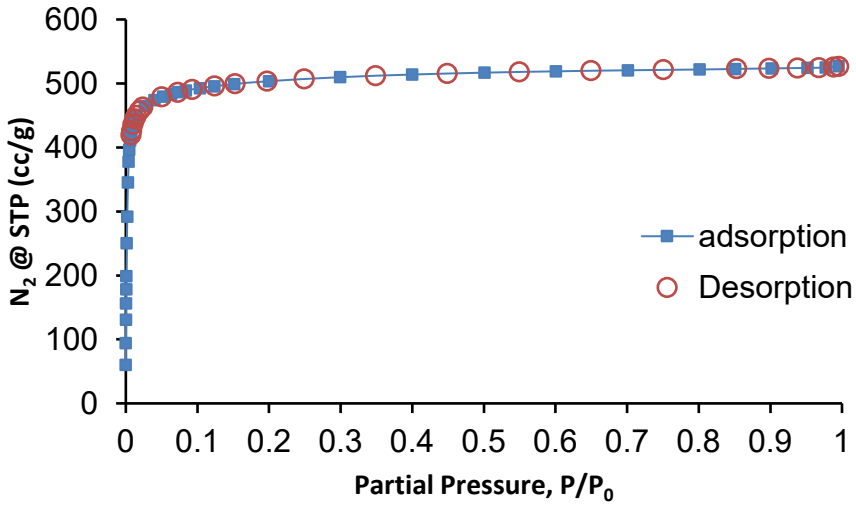


Figure S 42 Isotherm of WUF-44-89

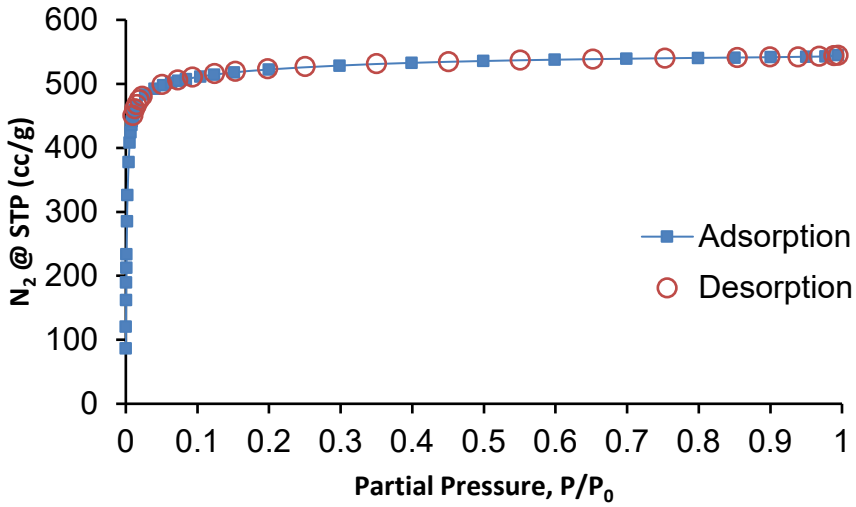


Figure S 43 Isotherm of WUF-44-89PSM.

BET summary	WUF-44-89	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.02795e-03	426.4728	426.4728
Slope	1.724	9.12510e-03	432.3239	1.7044e-02
Intercept	1.270e-03	1.00331e-02	436.1987	1.8590e-02
Correlation coefficient, r	0.999994	1.20735e-02	443.2281	2.2061e-02
C constant	1359.137	1.50762e-02	450.3068	2.7198e-02
Surface Area	2018.046 m²/g	2.66886e-02	464.9930	4.7182e-02
		4.01034e-02	474.1188	7.0505e-02

BET summary	WUF-44-89PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		9.43319e-03	446.5092	1.7065e-02
Slope	1.657	1.02311e-02	450.5847	1.8355e-02
Intercept	1.361e-03	1.08268e-02	453.1802	1.9324e-02
Correlation coefficient, r	0.999992	1.26135e-02	459.3684	2.2250e-02
C constant	1218.578	1.52747e-02	466.3038	2.6616e-02
Surface Area	2099.425 m²/g	2.73822e-02	483.2701	4.6611e-02
		4.02096e-02	492.2433	6.8096e-02

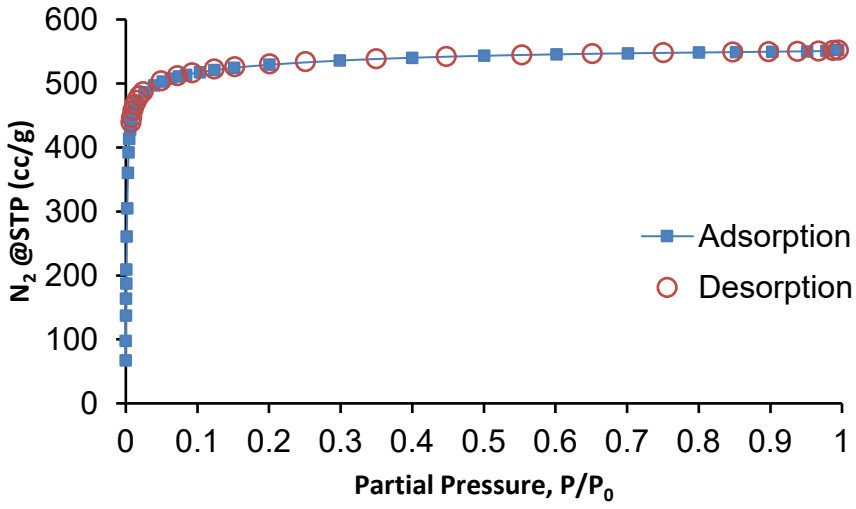


Figure S 44 Isotherm of WUF-44-82.

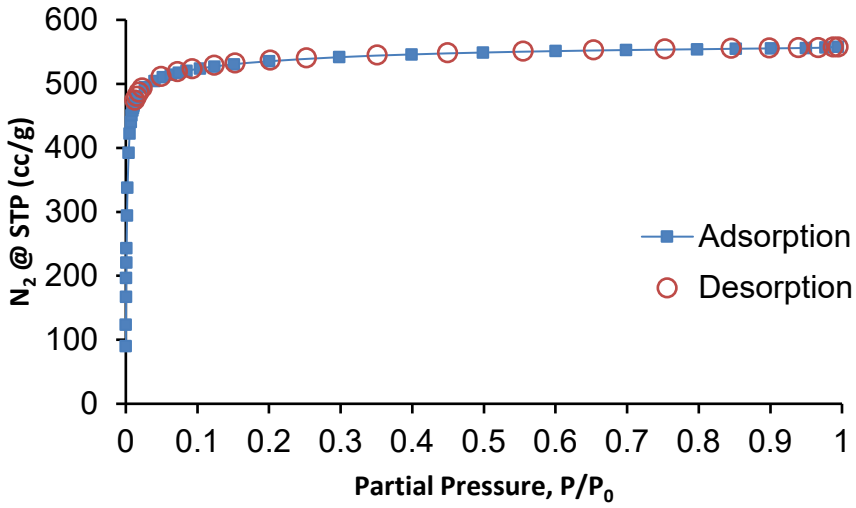


Figure S 45 Isotherm of WUF-44-82PSM.

BET summary	WUF-44-82	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.11189e-03	445.8459	1.4677e-02
Slope	1.643	9.11177e-03	451.5228	1.6295e-02
Intercept	1.290e-03	9.96736e-03	455.4914	1.7685e-02
Correlation coefficient, r	0.999995	1.21754e-02	463.8231	2.1262e-02
C constant	1274.736	1.51675e-02	471.2920	2.6146e-02
Surface Area	2118.028 m²/g	2.64232e-02	486.6893	4.4618e-02
		3.98413e-02	496.9326	6.6810e-02

BET summary	WUF-44-82PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.02152e-02	462.4973	1.7855e-02
Slope	1.619	1.08638e-02	465.4344	1.8881e-02
Intercept	1.257e-03	1.13284e-02	467.2752	1.9620e-02
Correlation coefficient, r	0.999993	1.34238e-02	473.7353	2.2981e-02
C constant	1289.144	1.60100e-02	479.9582	2.7124e-02
Surface Area	2149.065 m²/g	2.69020e-02	494.8001	4.4704e-02
		4.02114e-02	504.5221	6.6442e-02

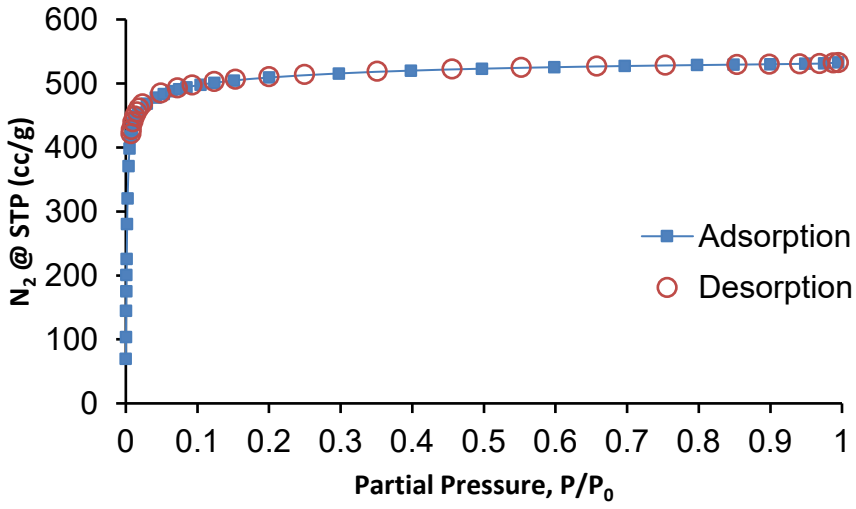


Figure S 46 Isotherm of WUF-44-75.

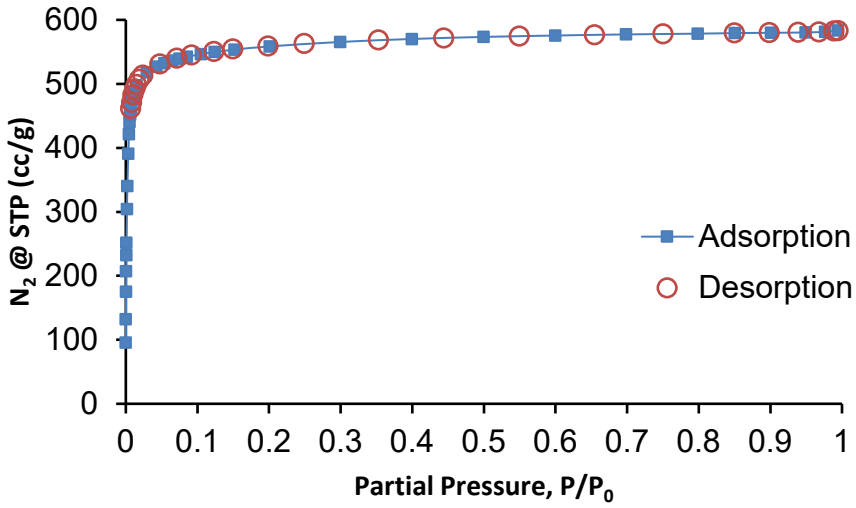


Figure S 47 Isotherm of WUF-44-75PSM.

BET summary	WUF-44-75	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.24440e-02	443.5837	2.2729e-02
Slope	1.721	1.27571e-02	444.3862	2.3266e-02
Intercept	1.266e-03	1.46283e-02	448.7678	2.6468e-02
Correlation coefficient, r	0.999994	1.74544e-02	453.9558	3.1310e-02
C constant	1361.209	2.93863e-02	468.2107	5.1738e-02
Surface Area	2021.611 m²/g	4.22211e-02	477.8506	7.3811e-02
		5.33806e-02	483.6119	9.3296e-02

BET summary	WUF-44-75PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.08445e-03	469.1373	1.3900e-02
Slope	1.555	9.03669e-03	475.8486	1.5333e-02
Intercept	1.239e-03	1.00039e-02	481.4077	1.6795e-02
Correlation coefficient, r	0.999991	1.20567e-02	488.7489	1.9978e-02
C constant	1256.610	1.50800e-02	497.6349	2.4617e-02
Surface Area	2237.398 m²/g	2.94610e-02	517.6734	4.6917e-02
		4.29608e-02	526.9727	6.8156e-02

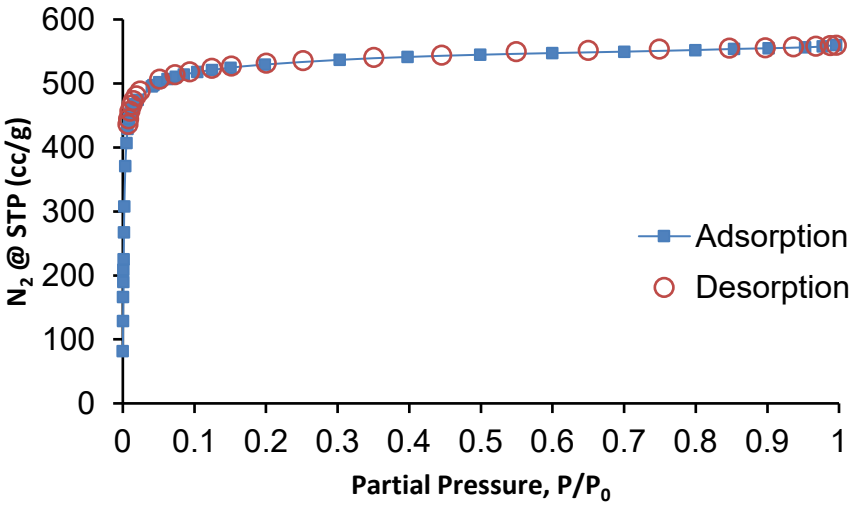


Figure S 48 Isotherm of WUF-44-65.

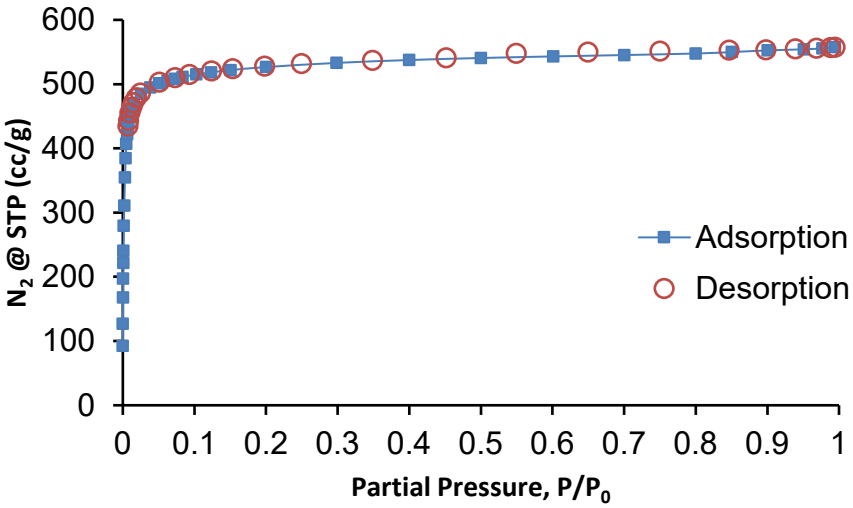


Figure S 49 Isotherm of WUF-44-65PSM.

BET summary	WUF-44-65	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.24901e-02	458.2266	2.2085e-02
Slope	1.644	1.35201e-02	461.0336	2.3785e-02
Intercept	1.585e-03	1.41958e-02	462.6371	2.4904e-02
Correlation coefficient, r	0.999998	1.64639e-02	467.3040	2.8661e-02
C constant	1038.425	2.11798e-02	474.4907	3.6487e-02
Surface Area	2116.415 m²/g	4.08573e-02	495.6612	6.8762e-02
		4.27197e-02	497.4695	7.1775e-02

BET summary	WUF-44-65PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.03316e-03	441.7625	1.4667e-02
Slope	1.643	9.11159e-03	448.7896	1.6394e-02
Intercept	1.377e-03	1.00202e-02	453.5049	1.7857e-02
Correlation coefficient, r	0.999990	1.21211e-02	461.8508	2.1256e-02
C constant	1194.693	1.49835e-02	469.6912	2.5912e-02
Surface Area	2117.539 m²/g	2.54869e-02	485.0341	4.3143e-02
		3.84401e-02	494.9045	6.4630e-02

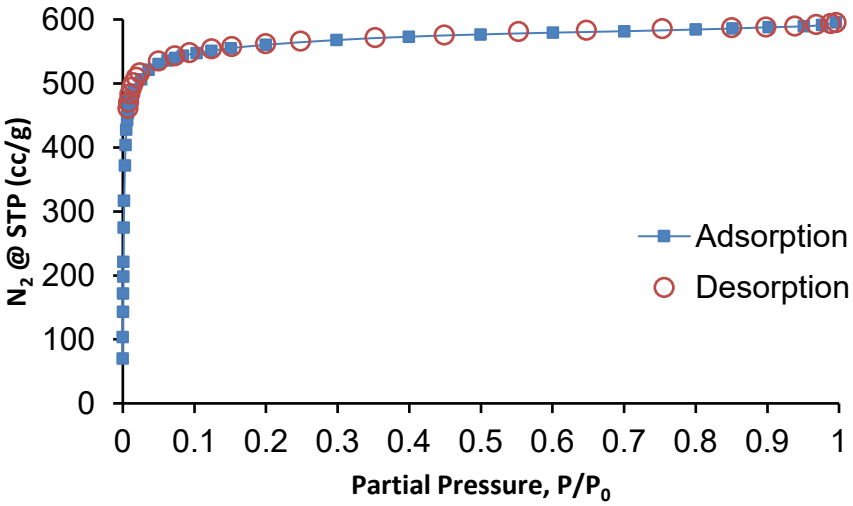


Figure S 50 Isotherm of WUF-44-56.

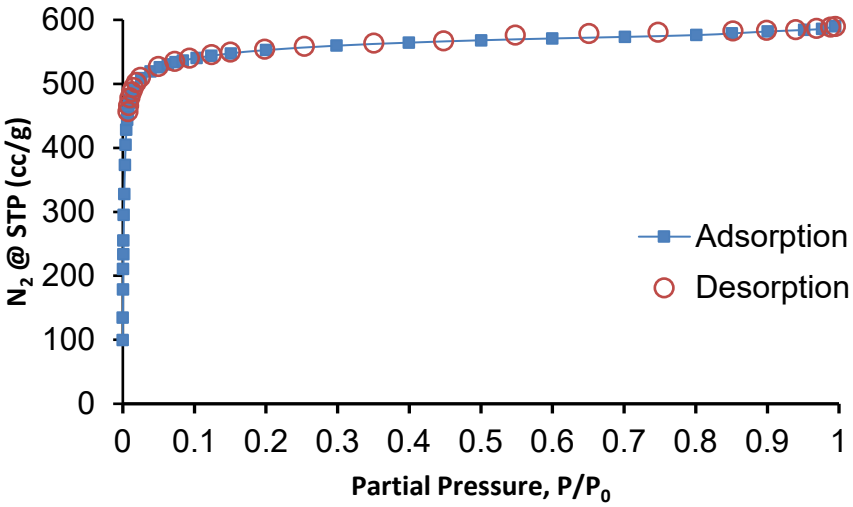


Figure S 51 Isotherm of WUF-44-56PSM.

BET summary	WUF-44-56	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		9.14285e-03	469.3398	1.5730e-02
Slope	1.556	9.99343e-03	473.6987	1.7050e-02
Intercept	1.522e-03	1.20866e-02	482.2964	2.0297e-02
Correlation coefficient, r	0.999988	1.52280e-02	490.6295	2.5218e-02
C constant	1023.492	2.59285e-02	506.2404	4.2071e-02
Surface Area	2236.233 m²/g	3.62767e-02	521.3861	5.7765e-02
		4.99656e-02	530.6302	7.9303e-02

BET summary	WUF-44-56PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.11664e-03	464.3036	1.4101e-02
Slope	1.567	8.99291e-03	470.2549	1.5440e-02
Intercept	1.301e-03	9.96335e-03	475.5894	1.6931e-02
Correlation coefficient, r	0.999991	1.20084e-02	484.1066	2.0088e-02
C constant	1205.395	1.52373e-02	493.3375	2.5095e-02
Surface Area	2220.369 m²/g	2.58176e-02	509.0579	4.1654e-02
		3.89743e-02	519.4898	6.2462e-02

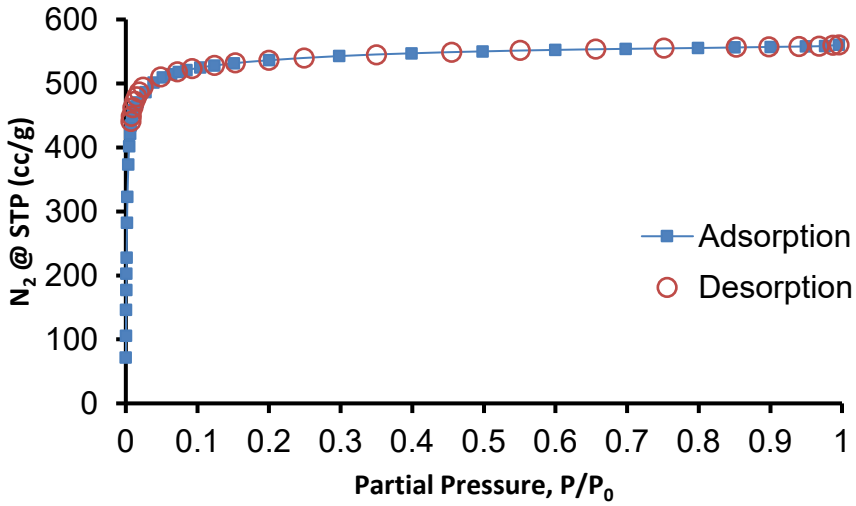


Figure S 52 Isotherm of WUF-44-47.

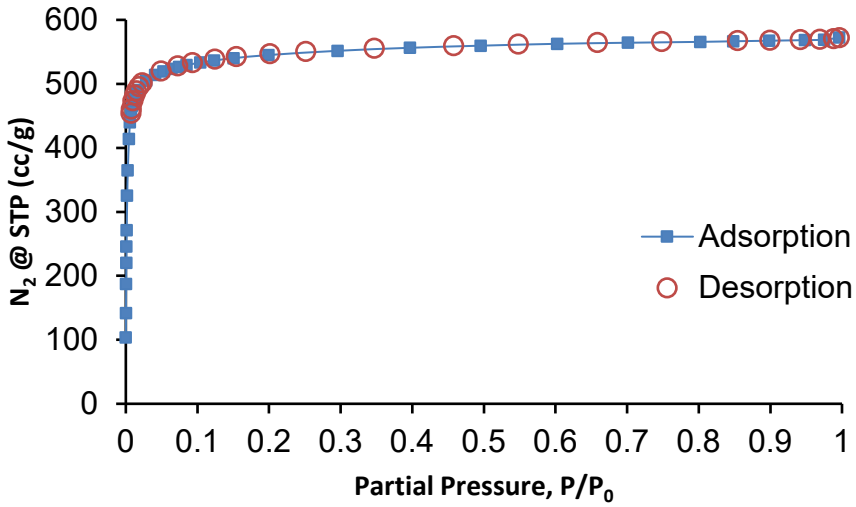


Figure S 53 Isotherm of WUF-44-47PSM.

BET summary	WUF-44-47	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.04904E-02	453.3785	1.8710E-02
Slope	1.617	1.11979E-02	456.2471	1.9860E-02
Intercept	1.802e-03	1.18131E-02	458.427	2.0864E-02
Correlation coefficient, r	0.999968	1.37660E-02	463.9469	2.4072E-02
C constant	898.759	1.65928E-02	470.3277	2.8704E-02
Surface Area	2150.676 m²/g	2.79188E-02	486.5931	4.7226E-02
		3.86611E-02	501.5225	6.4159E-02

BET summary	WUF-44-47PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.18447e-02	477.9230	2.0067e-02
Slope	1.595	1.20998e-02	478.8822	2.0464e-02
Intercept	1.130e-03	1.24007e-02	479.8479	2.0937e-02
Correlation coefficient, r	0.999994	1.41608e-02	484.6609	2.3713e-02
C constant	1412.890	1.68803e-02	490.4942	2.8008e-02
Surface Area	2181.397 m²/g	2.86067e-02	504.9726	4.6661e-02
		4.12340e-02	513.7383	6.6981e-02

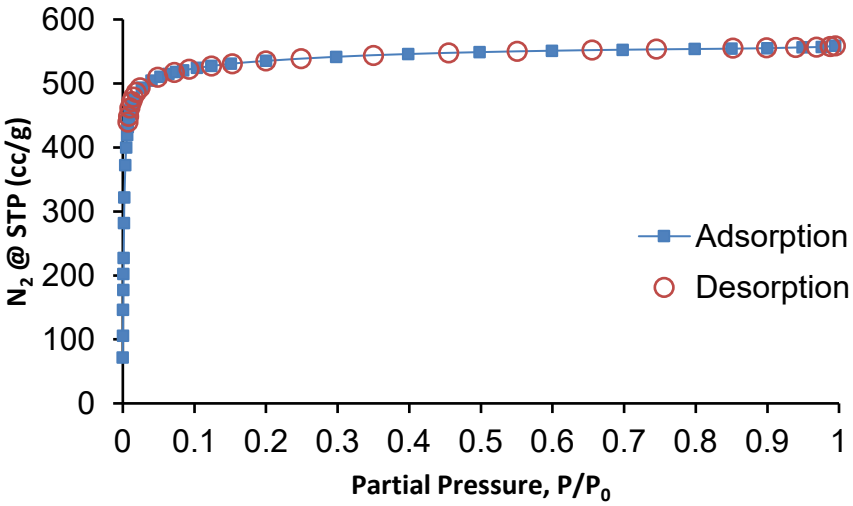


Figure S 54 Isotherm of WUF-44-33.

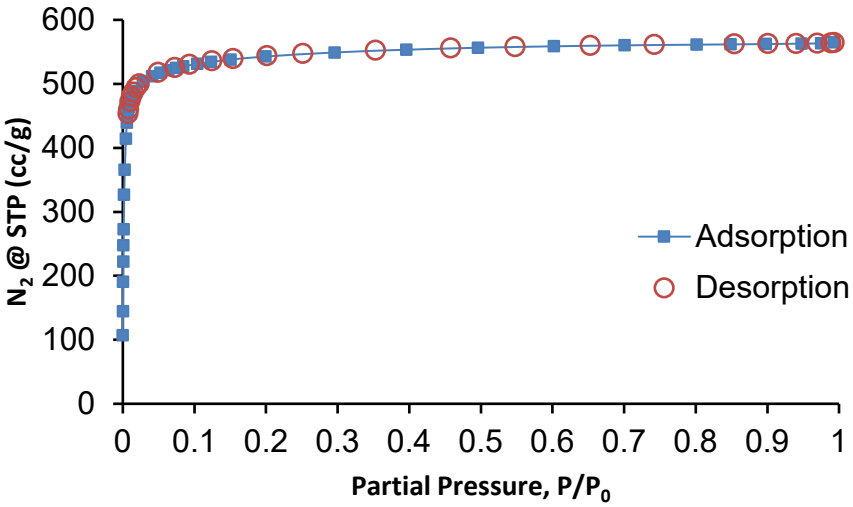


Figure S 55 Isotherm of WUF-44-33PSM.

BET summary	WUF-44-33	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		9.63901e-03	452.6748	1.7203e-02
Slope	1.610	1.03029e-02	456.9278	1.8229e-02
Intercept	1.629e-03	1.10816e-02	460.2435	1.9481e-02
Correlation coefficient, r	0.999993	1.29803e-02	467.0731	2.2528e-02
C constant	989.150	1.58025e-02	474.8742	2.7053e-02
Surface Area	2160.894 m²/g	2.67589e-02	493.5913	4.4569e-02
		4.04341e-02	504.6477	6.6809e-02

BET summary	WUF-44-33PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		1.13110e-02	475.4953	1.9251e-02
Slope	1.601	1.15654e-02	476.3544	1.9653e-02
Intercept	1.105e-03	1.19239e-02	477.5274	2.0220e-02
Correlation coefficient, r	0.999994	1.36691e-02	482.6242	2.2975e-02
C constant	1449.080	1.64836e-02	488.6542	2.7442e-02
Surface Area	2174.048 m²/g	2.80918e-02	503.1603	4.5962e-02
		4.11628e-02	512.1458	6.7068e-02

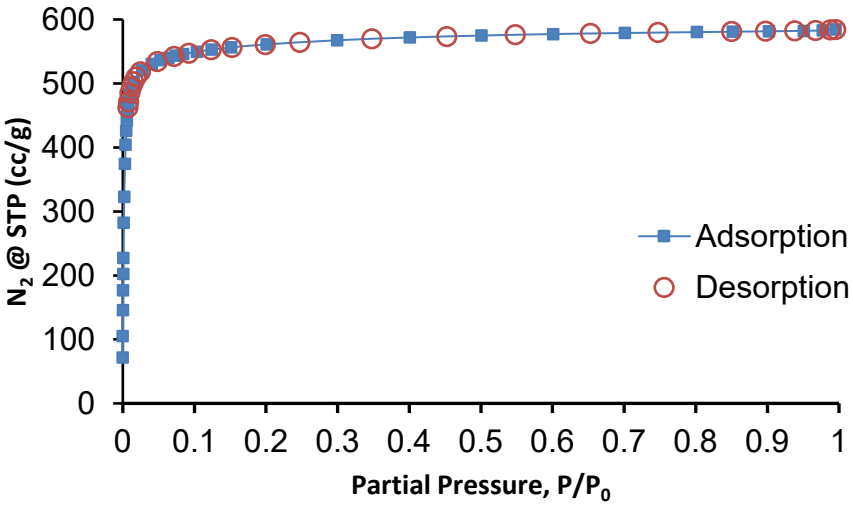


Figure S 56 Isotherm of WUF-44-22.

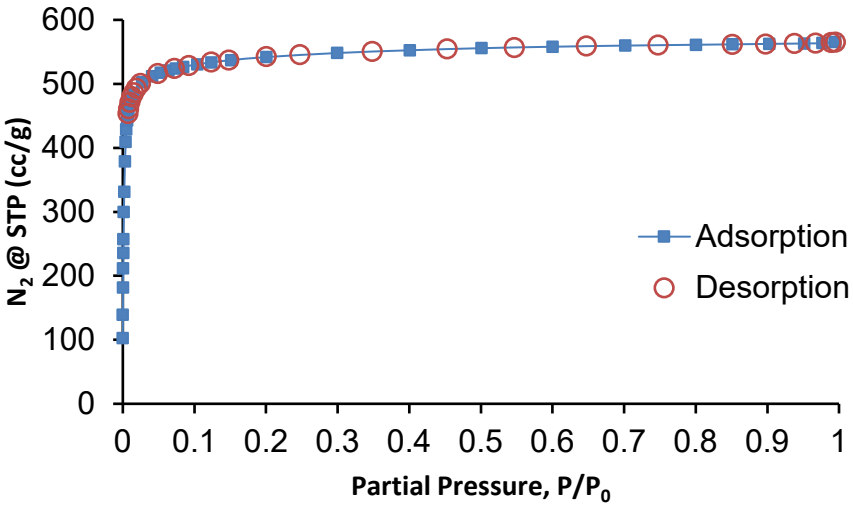


Figure S 57 Isotherm of WUF-44-22PSM.

BET summary	WUF-44-22	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.10857e-03	469.9810	1.3917e-02
Slope	1.537	9.00353e-03	477.6244	1.5220e-02
Intercept	1.328e-03	1.00193e-02	483.6480	1.6743e-02
Correlation coefficient, r	0.999983	1.20765e-02	492.7429	1.9849e-02
C constant	1158.891	1.51039e-02	502.2813	2.4429e-02
Surface Area	2263.659 m²/g	2.70788e-02	520.3263	4.2798e-02
		4.08067e-02	530.4648	6.4168e-02

BET summary	WUF-44-22PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.12115e-03	460.7094	1.4219e-02
Slope	1.600	9.05462e-03	466.2495	1.5680e-02
Intercept	1.152e-03	9.98833e-03	470.6442	1.7152e-02
Correlation coefficient, r	0.999993	1.20737e-02	478.0566	2.0454e-02
C constant	1389.884	1.50141e-02	485.5706	2.5117e-02
Surface Area	2174.491 m²/g	2.74088e-02	502.2737	4.4892e-02
		4.10757e-02	511.7205	6.6976e-02

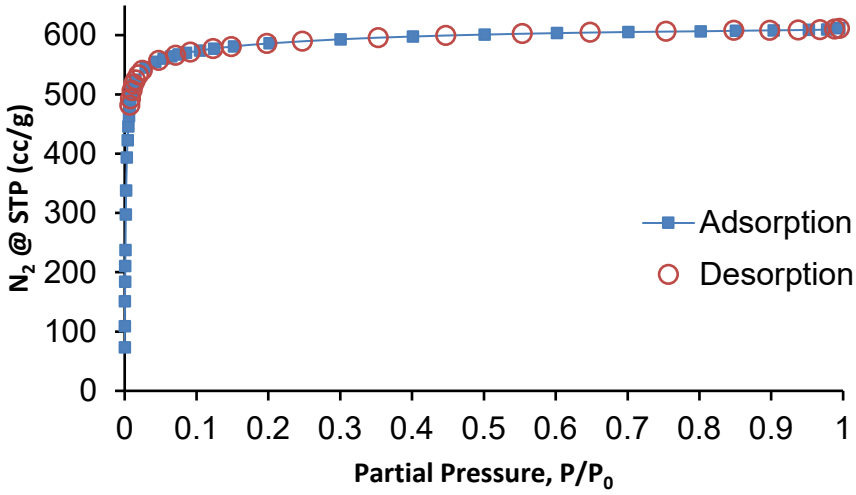


Figure S 58 Isotherm of WUF-44-13.

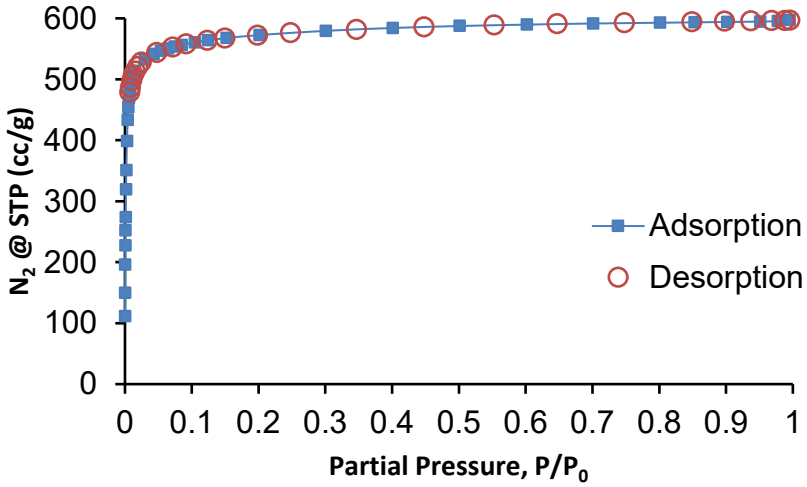


Figure S 59 Isotherm of WUF-44-13PSM.

BET summary	WUF-44-13	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.02657e-03	491.4879	1.3172e-02
Slope	1.475	9.04756e-03	499.7826	1.4617e-02
Intercept	1.214e-03	9.99161e-03	505.7598	1.5966e-02
Correlation coefficient, r	0.999983	1.21072e-02	515.5884	1.9019e-02
C constant	1215.914	1.50985e-02	524.9823	2.3364e-02
Surface Area	2359.630 m²/g	2.90352e-02	545.3957	4.3869e-02
		4.26486e-02	554.9351	6.4231e-02

BET summary	WUF-44-13PSM	Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]
		8.08400e-03	487.0586	1.3388e-02
Slope	1.517	9.07299e-03	493.0475	1.4858e-02
Intercept	1.060e-03	9.96137e-03	497.3771	1.6186e-02
Correlation coefficient, r	0.999992	1.20899e-02	505.3842	1.9375e-02
C constant	1432.060	1.51430e-02	513.4657	2.3959e-02
Surface Area	2294.591 m²/g	2.93866e-02	532.4042	4.5500e-02
		4.27379e-02	541.4736	6.5971e-02

Table S 4 Apparent BET Surface areas of the MOFs before and after dual modification.

WUF Code	BET_{SA} (m^2/g)
$Zn_4O(L^2)_3$	2062*
$Zn_4O(L^2)_3$PSM	2103
WUF-44-89	2018
WUF-44-89PSM	2099
WUF-44-82	2118
WUF-44-82PSM	2149
WUF-44-75	2021
WUF-44-75PSM	2237
WUF-44-65	2116
WUF-44-65PSM	2117
WUF-44-56	2236
WUF-44-56PSM	2220
WUF-44-47	2150
WUF-44-47PSM	2181
WUF-44-33	2160
WUF-44-33PSM	2174
WUF-44-22	2263
WUF-44-22PSM	2174
WUF-44-13	2359
WUF-44-13PSM	2294
WUF-35	2166#
WUF-35PSM	2150#

* We reported a value of 1999 m^2/g in Bryant et al.[3] We re-prepared this sample during this study.

We reported these values in Ablott et al.[1]

7 References

[1] T. A. Ablott, R. Webby, D. R. Jenkinson, A. Nikolich, L. Liu, H. Amer Hamzah, M. F. Mahon, A. D. Burrows and C. Richardson, *Inorg. Chem.*, 2022, **61**, 1136-1144.

[2] A. D. Burrows, S. O. Hunter, M. F. Mahon and C. Richardson, *Chem. Commun.*, 2013, **49**, 990-992.

[3] M. R. Bryant, T. Cunynghame, S. O. Hunter, S. G. Telfer and C. Richardson, *Inorg. Chem.*, 2021, **60**, 11711-11719.