Supplementary Information

High temperature expulsion of thermolabile groups for pore-space expansion in metal-organic frameworks

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1. Ligand Syntheses

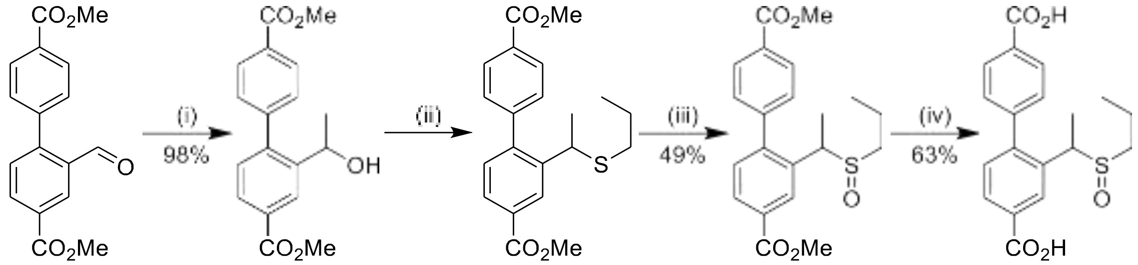
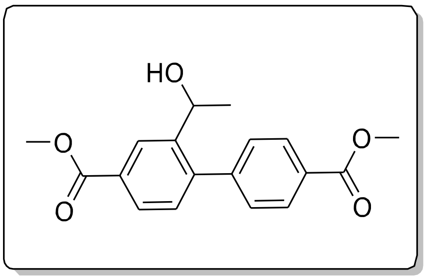


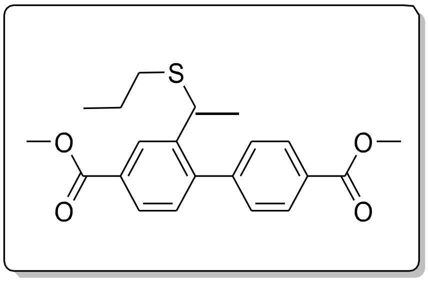
Figure S 1 Synthetic pathway to H_2bpdcPSO with yields; (i) MeMgBr, THF, 0 °C; (ii) Propane thiol, ZnI_2, DCE, reflux; (iii) mCPBA, CH_2Cl_2, 0 °C; (iv) 1M NaOH, MeOH/THF, rt.

Dimethyl 2-(1-hydroxyethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate



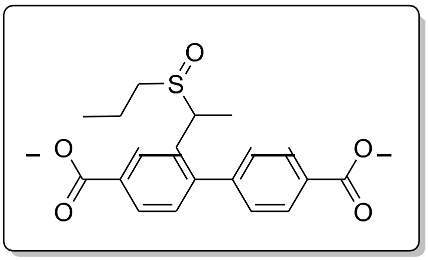
A 3.0 M solution of methylmagnesium bromide in diethyl ether (2.23 mL, 6.69 mmol) was added dropwise *via* syringe to dimethyl 2-formyl-[1,1'-biphenyl]-4,4'-dicarboxylate (1.90 g, 6.37 mmol) dissolved in anhydrous THF (13 cm^3) at ice bath temperature. After an hour at ice bath temperature the reaction was quenched with acidified water (5 mL of 1.0 M HCl in 20 mL of water) with stirring. The mixture was rotary evaporated to a residue, taken up in EtOAc (50 mL), washed with H_2O (3 × 50 mL) and saturated NaCl solution (50 mL), dried over Na_2SO_4 and rotary evaporated under reduced pressure to produce a yellow oil that solidified on standing. Yield = 1.94 g (98%). δ_H (400 MHz, $CDCl_3$) 8.38 (1 H, d, *J* 1.7), 8.11 (2 H, d, *J* 8.5), 7.99 (1 H, dd, *J* 8.0, 1.8), 7.39 (2 H, d, *J* 8.5), 7.27 (1 H, d, *J* 8.4), 5.00–4.91 (1 H, m), 3.95 (6 H, s), 1.81 (1 H, s), 1.41 (3 H, d, *J* 6.4). δ (101 MHz, CDCl3) 167.51, 167.47, 145.42, 144.37, 144.08, 130.93, 130.54, 130.27, 130.11, 129.77, 128.94, 127.80, 66.87, 52.93, 52.90, 25.67.

Dimethyl 2-(1-(propylthio)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate



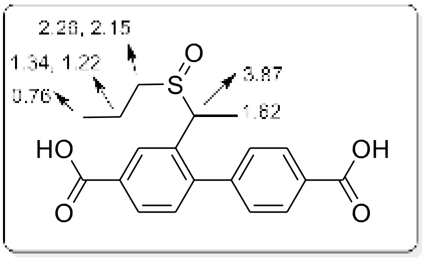
Anhydrous zinc(II) iodide (275.2 mg, 0.086 mmol) was added to dimethyl 2-(1-hydroxyethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (541.3 mg, 1.72 mmol) dissolved in anhydrous DCE (18 cm^3) and stirred vigorously. Propane thiol (160 µL, 1.72 mmol) was added to the pink suspension after 20 minutes and the mixture refluxed with stirring under anhydrous conditions for 24 hours The cooled solution was quenched with distilled H_2O and transferred to a separatory funnel. The aqueous layer was run off and the organic solution washed with saturated NaCl solution, dried over Na_2SO_4, and rotary evaporated under reduced pressure to yield a yellow oil. Yield = 595.8 mg (93%). This product was used without purification in the next step.

Dimethyl 2-(1-(propylsulfinyl)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (Me_2bpdc-PSO)



mCPBA (33.3 mg, 0.193 mmol), dissolved in CH_2Cl_2 (1.5 cm^3), was added dropwise over one hour to a stirred solution of dimethyl 2-(1-(propylthio)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (73.4 mg, 0.197 mmol) in CH_2Cl_2 (1.5 cm^3) chilled in an ice bath. After two hours the organic solution was diluted with CH_2Cl_2 (20 cm^3), transferred to a separatory funnel and washed with saturated $NaHCO_3$ solution (2×), H_2O, and then rotary evaporated under reduced pressure to produce a yellow oil. The oil was purified *via* silica gel column chromatography (R_f = 0.32, 1:1 EtOAc:CH_2Cl_2). Yield = 37.6 mg (49%) with an approximate 2.7:1 ratio of diastereomers. No further separation was attempted. ^{1}H NMR δ_H (400 MHz; $CDCl_3$). 8.27 (1 H, d, *J* 1.6, Minor), 8.14 (2 H, d, *J* 8.4, Major), 8.13 (2 H, d, *J* 8.6, Minor), 8.08 (1 H, d, *J* 1.6, Major), 8.06 (1 H, dd, *J* 8.0, 1.6, Minor), 8.04 (1 H, dd, *J* 8.0, 1.7, Major), 7.43 (2 H, d, *J* 7.6, Minor), 7.40 (1 H, d, *J* 7.9, Major), 7.38 (2 H, d, *J* 7.9, Minor), 7.34 (2 H, d, *J* 8.4, Major), 4.03-3.93 (~9.5 H, m, Major + Minor (4×–CH_3 & 2×–CH)), 2.12 (2 H, m (pseudo triplet), Major + Minor –CH_2), 1.79 (3 H, d, *J* 7.1, Major), 1.70 (3 H, d, *J* 7.2, Minor), 1.60-1.40 (2 H, m, Major + Minor –$C\underline{H_2}$), 0.93 (3 H, t, *J* 7.4, Minor), 0.85 (3 H, t, *J* 7.4, Major). ^{13}C NMR δ_C (101 MHz; $CDCl_3$) A full list of signals is provided here without attempt to assign to major or minor diastereomers. Please note the provision of this spectrum. 167.29, 167.16, 167.11, 166.86, 146.87, 146.28, 145.13, 144.72, 136.15, 134.68, 131.29, 131.24, 130.95, 130.80, 130.69, 130.51, 130.42, 130.22, 130.06, 129.81, 129.65, 129.49, 78.02, 77.70, 77.38, 58.32, 55.52, 53.10, 53.04, 53.01, 52.98, 52.16, 51.84, 17.25, 16.98, 16.94, 16.78, 14.04, 13.84.

2-(1-(Propylsulfinyl)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2bpdc-PSO)



1.0 M NaOH (190 µL, 0.19 mmol) was added dropwise to dimethyl 2-(1-(propylsulfinyl)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate (33.8 mg, 0.087 mmol) dissolved in a mixture of MeOH (1.5 cm^3) and THF (0.5 cm^3). The solution was stirred for 18 hours at room temperature before dilution with distilled H_2O (2 cm^3) and acidification with 1.0 M HCl. A white precipitate was collected by vacuum filtration, washed with of H_2O (3×), and air died in the fume hood for 18 hours. Yield = 19.7 mg (63%). This gives ~6:1 ratio of diastereomers; only signals for the major diastereomer are reported here: ^{1}H NMR δ_H (400 MHz; *d*$_6$-DMSO) 13.16 (2 H, s(br)), 8.06 (2 H, d, *J* 8.1), 7.96 (2 H, m), 7.47 (3 H, m), 3.87 (1 H, q, *J* 6.9), 2.26 (1 H, m 1×-CH), 2.11 (1 H, m 1×-CH), 1.62 (3 H, d, *J* 6.9), 1.34 (1 H, m 1×-CH), 1.22 (1 H, m, 1×-CH), 0.76 (1 H, t, *J* 7.4). ^{13}C NMR δ_C (101 MHz; $CDCl_3$) 167.04, 166.80, 145.13, 143.62, 135.95, 130.89, 130.70, 130.39, 129.70, 129.53, 128.67, 128.42, 55.55, 50.41, 15.56, 14.05, 12.93.

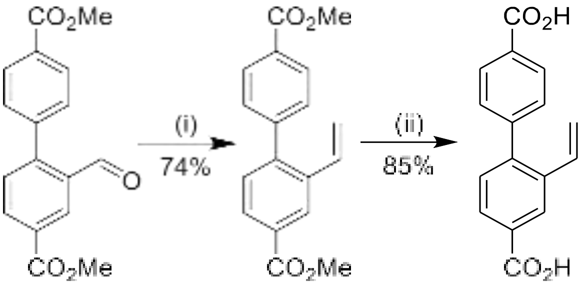
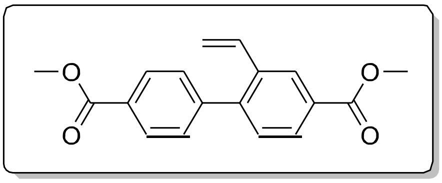


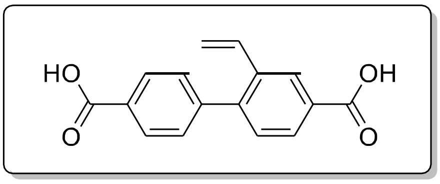
Figure S 2 Synthetic pathway to H_2bpdc-CH=CH_2 with yields; (i) Ph_3PMeBr, ^nBuLi, THF, 0 °C; (ii) NaOH, THF/MeOH.

Dimethyl 2-vinyl-[1,1'-biphenyl]-4,4'-dicarboxylate (Me_2bpdc-CH=CH_2)



Anhydrous, N_2 sparged THF (2.5 cm^3) was admitted *via* syringe through a Subaseal to a dry flask charged with methyltriphenylphosphonium bromide (108.0 mg, 0.302 mmol) and a stir bar under N_2. After chilling to ice bath temperature, 2.5 M n-butyl lithium in diethyl ether (120 µL, 0.302 mmol) was added dropwise via syringe, and the mixture left to stir for 10 minutes. A solution of dimethyl 2-formyl-[1,1'-biphenyl]-4,4'-dicarboxylate (60.0 mg, 0.201 mmol) in anhydrous, N_2 sparged THF (2.0 cm^3) was then added dropwise and the cooling bath was removed. The reaction was quenched with H_2O after stirring for 16 hours at room temperature. The product was obtained as an oil following extraction of the aqueous solution with diethyl ether (2×), washing the combined organic extracts with H_2O (3×), saturated NaCl solution, drying over Na_2SO_4, decantation and rotary evaporation. The product was purified by silica gel column chromatography (R_f 0.83, CH_2Cl_2). Yield = 44.1 mg (74%). ^{1}H NMR δ_H (400 MHz; $CDCl_3$) 8.33 (1 H, d, *J* 1.6), 8.11 (2 H, d, *J* 8.5), 8.00 (1 H, dd, *J* 8.0, 1.7), 7.44 (2 H, d, *J* 8.5), 7.37 (1 H, d, *J* 8.0), 6.65 (1 H, dd, *J* 17.5, 11.0), 5.83 (1 H, d, *J* 17.4), 5.30 (1 H, d, *J* 11.0), 3.97 (3 H, s), 3.96 (3 H, s). ^{13}C NMR δ_C (101 MHz; $CDCl_3$) 167.51, 145.25, 144.57, 136.77, 135.31, 130.72, 130.53, 130.32, 130.16, 130.07, 129.23, 128.06, 117.35, 52.94, 52.90.

2-Vinyl-[1,1'-biphenyl]-4,4'-dicarboxylic acid (H_2bpdc-CH=CH_2)



1.0 M NaOH aqueous solution was added dropwise with stirring to dimethyl 2-vinyl-[1,1'-biphenyl]-4,4'-dicarboxylate (30.5 mg, 0.103 mmol) dissolved in a mixture of 3:1 MeOH:THF (4 cm^3), and the mixture was stirred for 18 hours at room temperature. MeOH and THF were removed by rotary evaporation under reduced pressure and 1.0 M HCl was added until no more precipitation was observed. The white precipitate was collected by vacuum filtration, washed with H_2O (3×) and dried in the fume hood for 18 hours. Yield = 23.4 mg (85%). ^{1}H NMR δ_H (400 MHz; d_6-DMSO) 13.10 (2 H, s), 8.23 (1 H, d, *J* 1.6), 8.04 (2 H, d, *J* 8.3), 7.93 (1 H, dd, *J* 8.0, 1.7), 7.48 (2 H, d, *J* 8.3), 7.45 (1 H, d, *J* 8.0), 6.62 (1 H, dd, *J* 17.5, 11.0), 5.85 (1 H, d, *J* 17.4), 5.34 (1 H, d, *J* 11.7). ^{13}C NMR δ_C (101 MHz; d_6-DMSO) 167.09, 167.03, 143.70, 143.27, 135.38, 134.29, 130.69, 130.40, 130.14, 129.66, 129.43, 128.66, 126.79, 117.20.

2. NMR Spectra

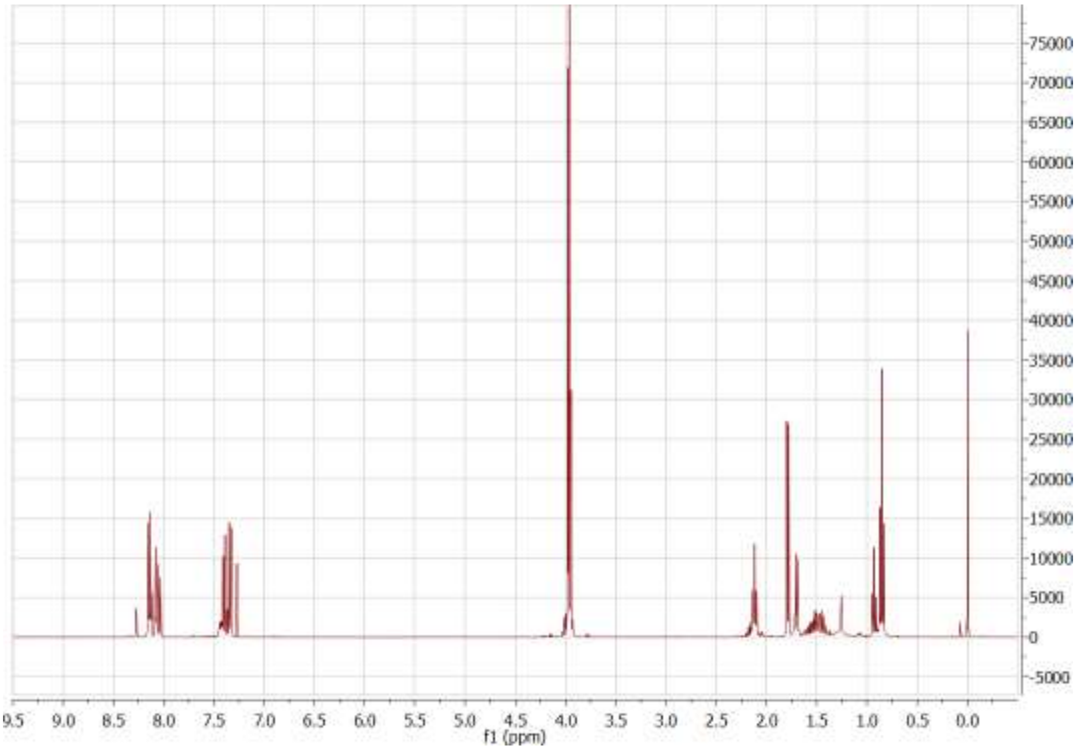


Figure S 3 ^{1}H NMR spectrum of the diastereomeric mixture of dimethyl 2-(1-(propylsulfinyl)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylate, Me$_2$bpdcPSO, in CDCl$_3$.

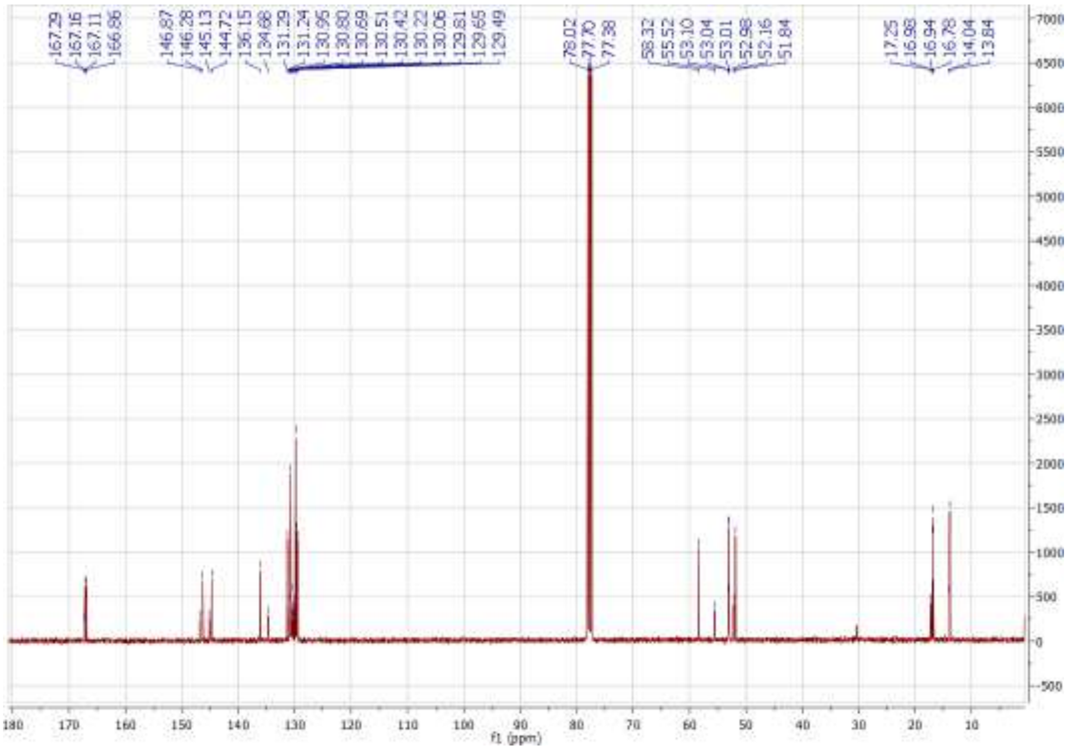


Figure S 4 ^{13}C NMR spectrum of the diastereomeric mixture of Me$_2$bpdcPSO in CDCl$_3$.

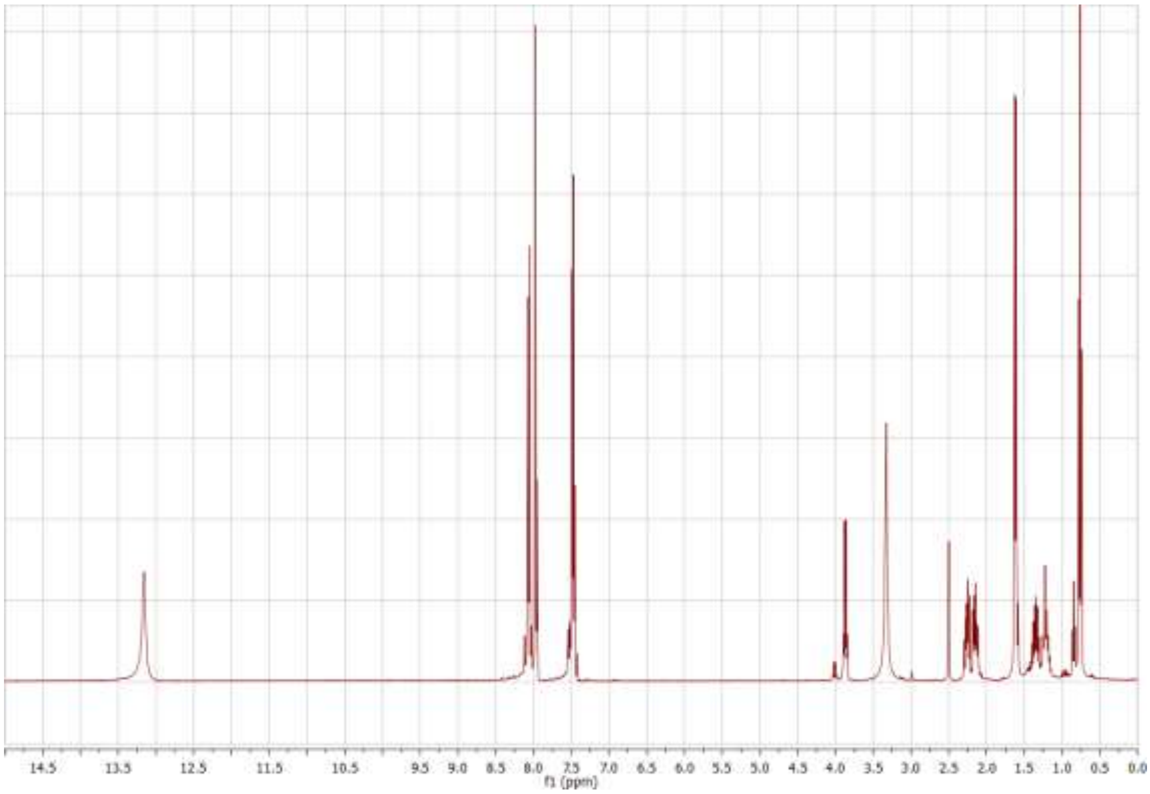


Figure S 5 ^{1}H NMR spectrum of the diastereomeric mixture of 2-(1-(propylsulfinyl)ethyl)-[1,1'-biphenyl]-4,4'-dicarboxylic acid, H$_2$bpdcPSO, in d_6-DMSO.

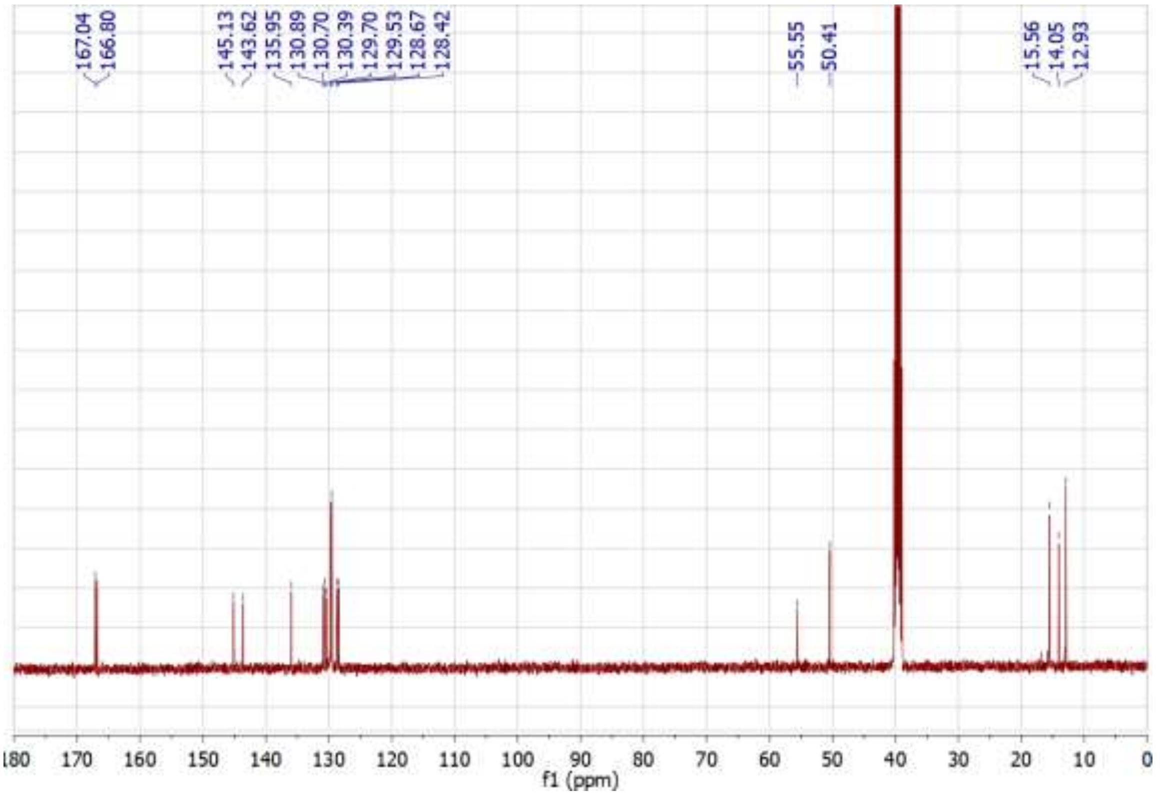


Figure S 6 ^{13}C NMR spectrum of the diastereomeric mixture of H$_2$bpdcPSO in d_6-DMSO.

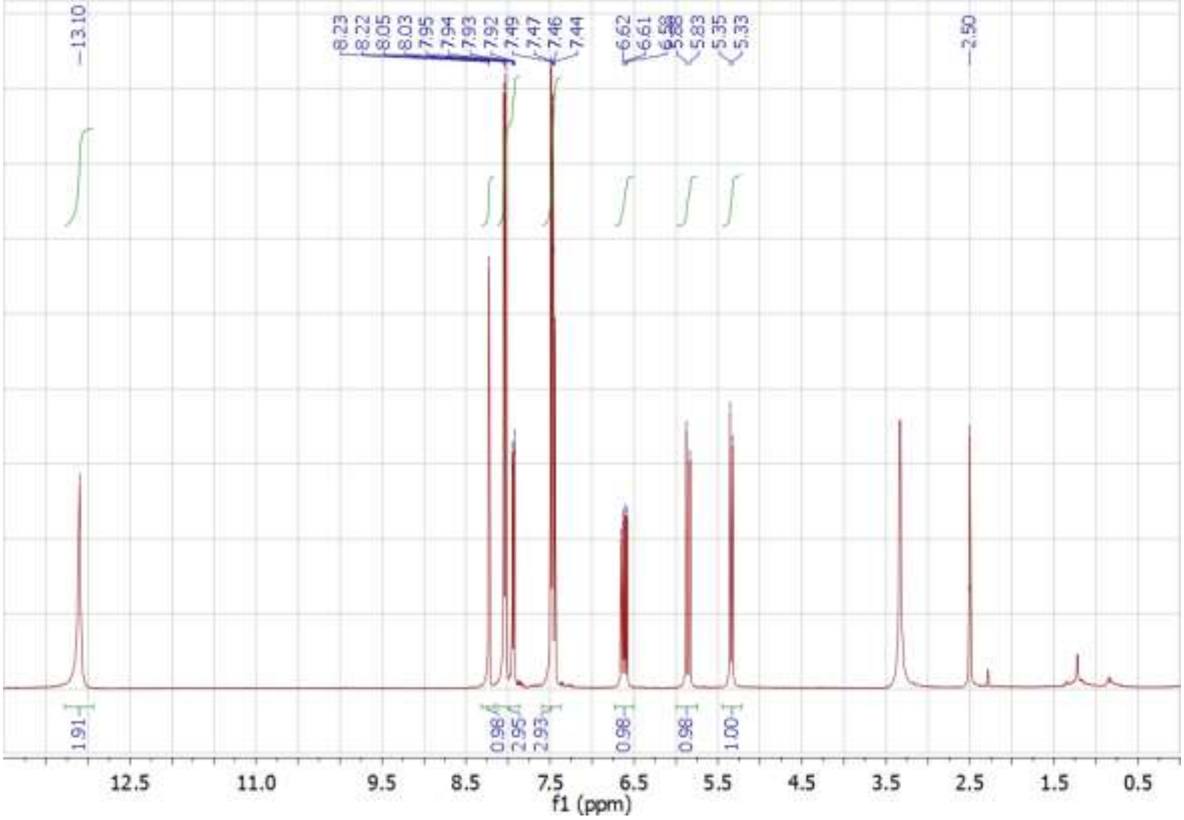


Figure S 7: ^{1}H NMR spectrum of 2-vinyl-[1, 1'-biphenyl]-4,4'-dicarboxylic acid, H_2bpdc-CH=CH$_2$, in *d_6*-DMSO.

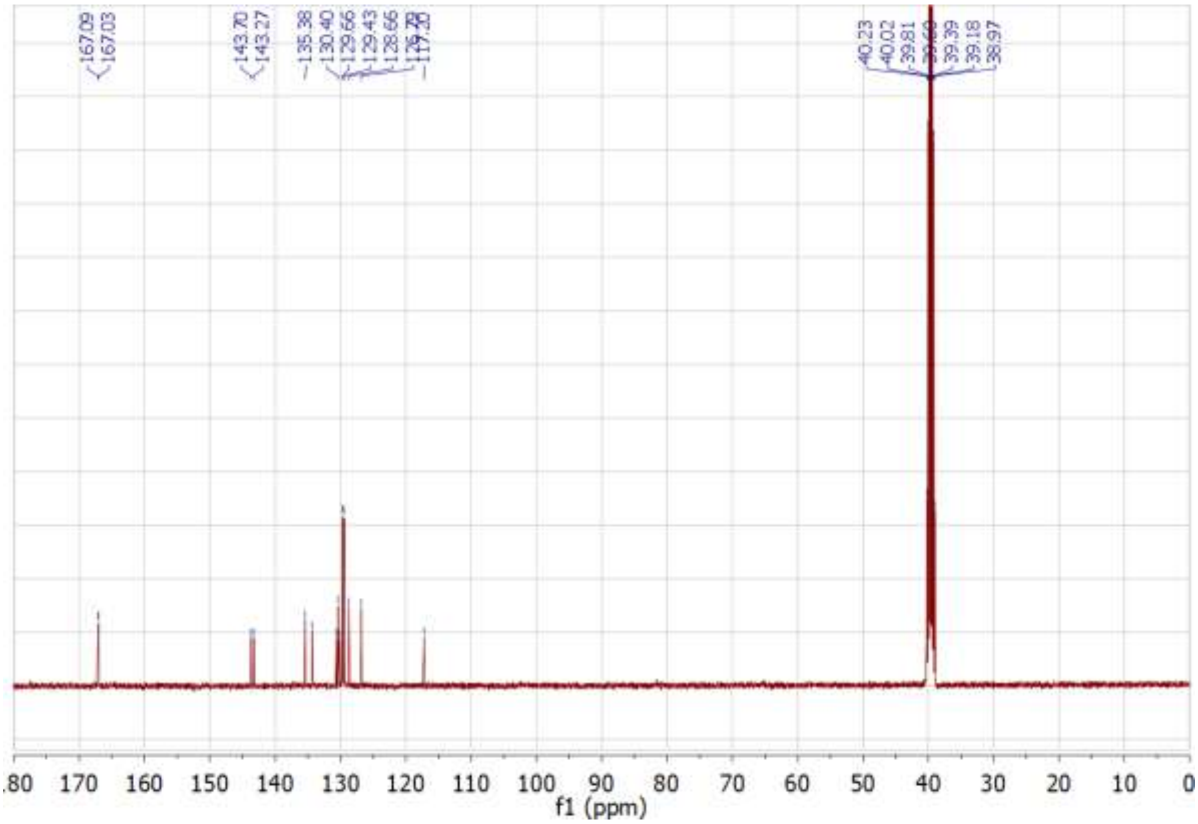


Figure S 8 ^{13}C NMR spectrum of H_2bpdc-CH=CH$_2$ in *d_6*-DMSO.

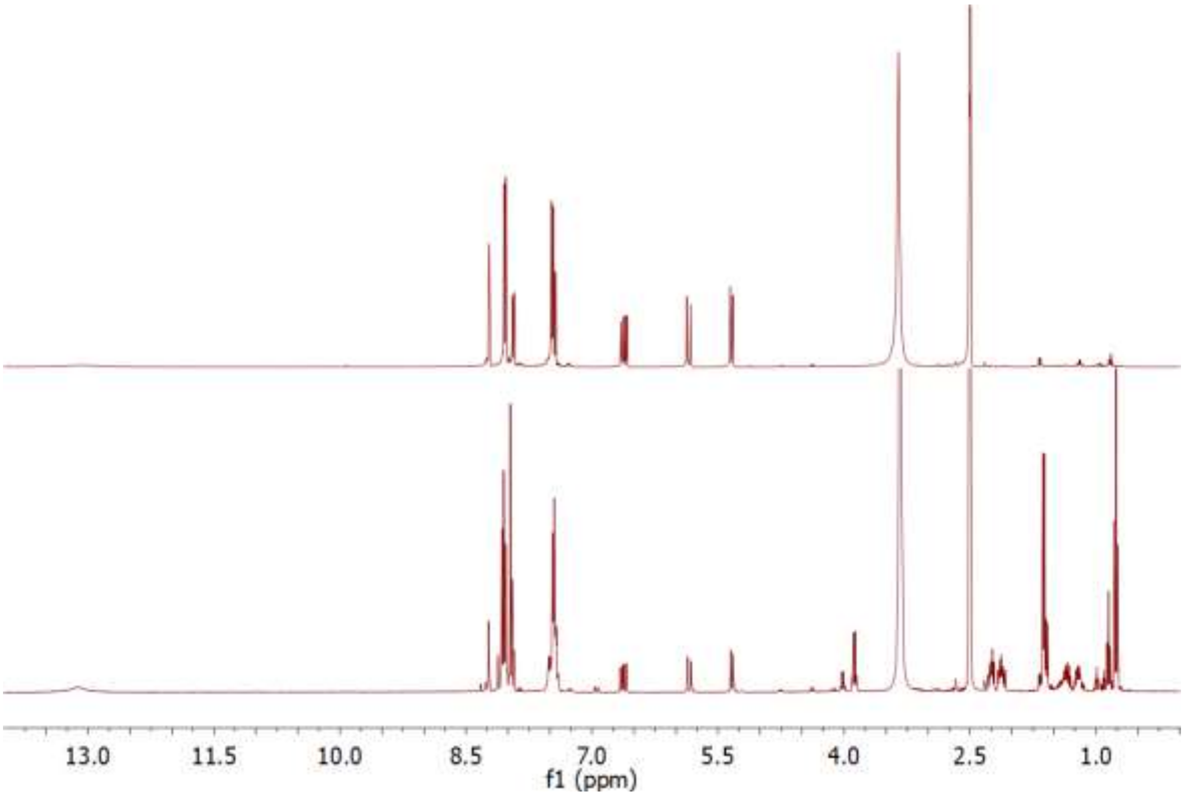


Figure S 9 ^{1}H NMR spectra recorded in DCl/d_6-DMSO of digested WUF-18 (lower spectrum) and digested WUF-19PSM (upper spectrum).

Table S 1 Solvothermal conditions applied to Me_2bpdc-PSO, and proportion of Me_2bpdc-CH=CH_2 in the product as determined by ^{1}H NMR spectroscopic analysis

Me_2bpdcPSO (mmol)	***$Zn(NO_3)_2\cdot 6H_2O$ (mmol)***	***Temp. (°C)***	***Solvent Composition***	***Solvent Volume (cm^3)***	***Conversion to Me_2bpdc-CH=CH_2***
0.039	0.116	100	DMF	1.5	64%
0.030	0.090	80	DMF : EtOH 3:1	1.2	18%
0.027	0.036	80	DMF : EtOH 3:1	1.2	22%
0.039	0.052	75	DMF : EtOH 3:1	1.8	10%

3. Single Crystal X-ray Diffraction

Table S 2 Crystal data and structure refinement for MB5071b (WUF-19)

Identification code	MB5071b
Empirical formula	$C_{48}H_{31}O_{13.5}Zn_4$
Formula weight	1085.21
Temperature/K	292
Crystal system	monoclinic
Space group	C2/m
a/Å	24.47(2)
b/Å	24.029(17)
c/Å	17.149(12)
α/°	90
β/°	90.869(18)
γ/°	90
Volume/Å^3	10082(13)
Z	4
ρ_{calc}g/cm^3	0.715
μ/mm^{-1}	1.333
F(000)	2188.0
Crystal size/mm^3	0.25 × 0.25 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	11.458 to 72.696
Index ranges	$-18 \leq h \leq 17$, $-16 \leq k \leq 16$, $-13 \leq l \leq 11$
Reflections collected	11545
Independent reflections	2365 [R_{int} = 0.1675, R_{sigma} = 0.1437]
Data/restraints/parameters	2365/473/266
Goodness-of-fit on F^2	2.771
Final R indexes [I>=2σ (I)]	R_1 = 0.1810, wR_2 = 0.4599
Final R indexes [all data]	R_1 = 0.2370, wR_2 = 0.4986
Largest diff. peak/hole / e Å^{-3}	0.94/-1.43

Diffraction data were collected at room temperature using a Cu rotating anode source and a curved image plate detector. The data quality for this structure was moderate a reflected by the diffraction and refinement statistics. However, it should be borne in mind the porous nature of the sample with large voids in the structure along the c-axis, which is filled with disordered solvent. The SQUEEZE routine in Platon was not applied. Also, the atoms of the vinyl substituents were implanted in chemically sensible positions and held fixed during refinement to complete the crystallographic model. Consequently, the goodness-of-fit value is high (2.77). The structural model is consistent with many other members of the IRMOF-9 family and it affords an unambiguous assignment of the framework, with the SBU and ligand backbones defined well.

Fig. S10 shows the asymmetric unit of WUF-19. It contains one full Zn atom (Zn4), two half Zn atoms (Zn2, Zn3), a half oxido atom (O1), one full ligand (C10-C23, O38-O41), affixed with a vinyl tag group (C60-C61), and a second ligand, based on C24-C35, O24, O36-O37, that straddles a mirror plane (Fig. S11). The atoms of this ligand not lying across the plane are O24, C26-C27 and the affixed vinyl tag group (C70-C71), the latter of which was assigned half-occupancy due to symmetry-related disorder brought about by the mirror plane. A rigid body restraint was placed over all non-hydrogen atoms and restraints to regularise the geometry and ADPs of C11-C16 and C17-C22 were applied. The vinyl tag groups were positionally fixed in representative positions and refined isotropically.

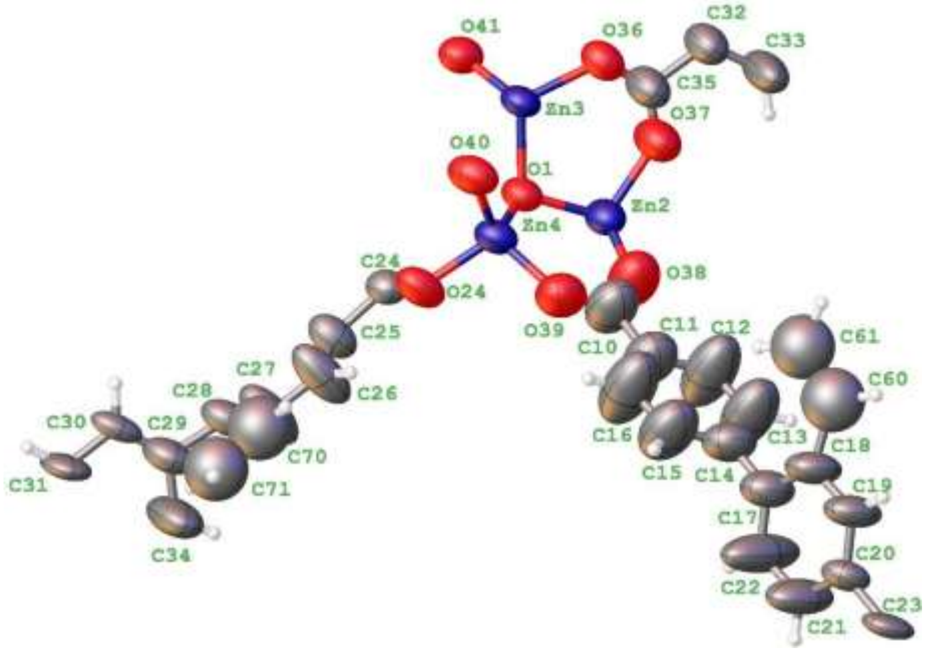


Figure S 10 A plot of the asymmetric unit of WUF-19 with thermal ellipsoids at 50%. The solvate water molecule is omitted.

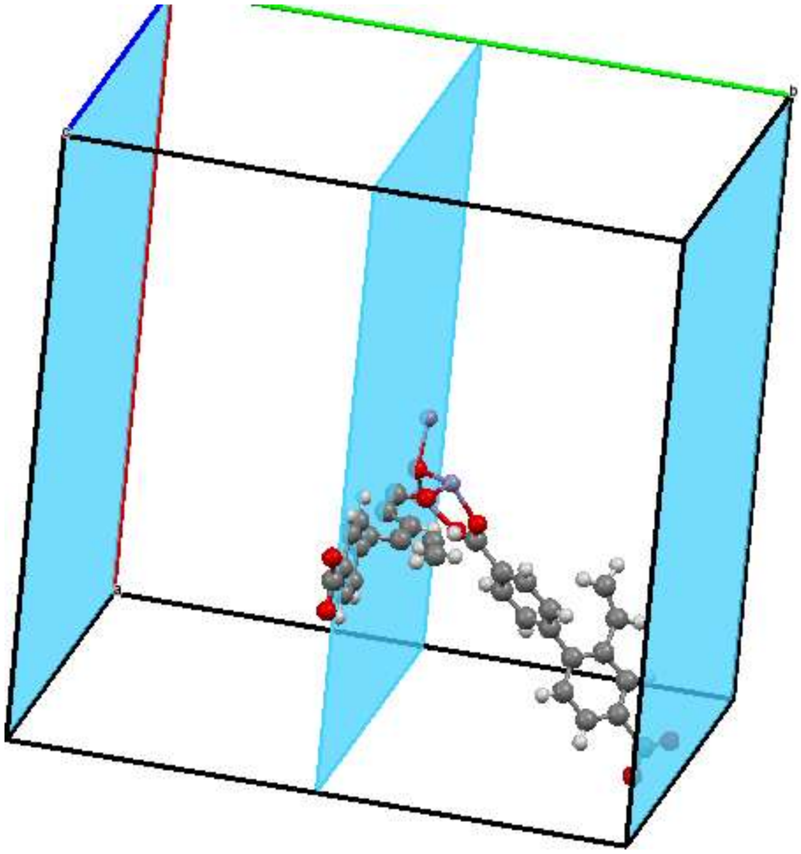


Figure S 11 A view showing the atoms of the asymmetric unit laying on a mirror plane in the unit cell of WUF-19.

4. Powder X-ray Diffraction

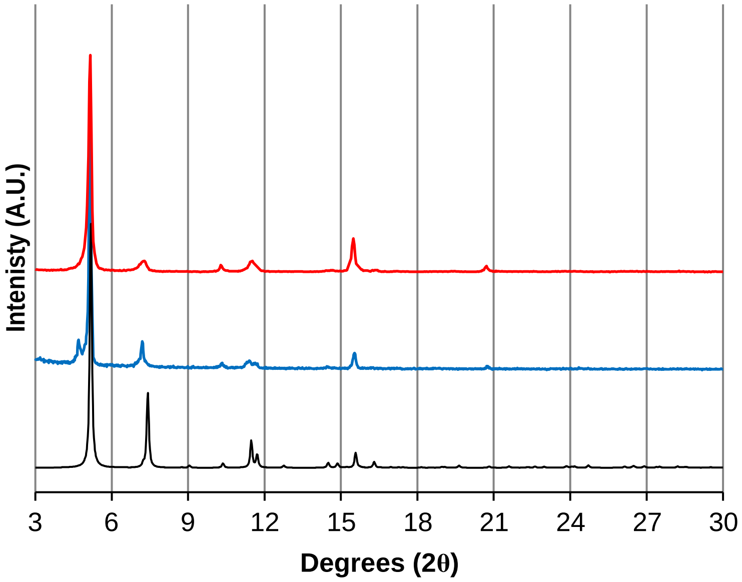


Figure S 12 PXRD patterns for activated WUF-19PSM (red), activated WUF-18 (blue) and the calculated pattern for WUF-19 from the single crystal structure analysis.

5. TG-DSC Data

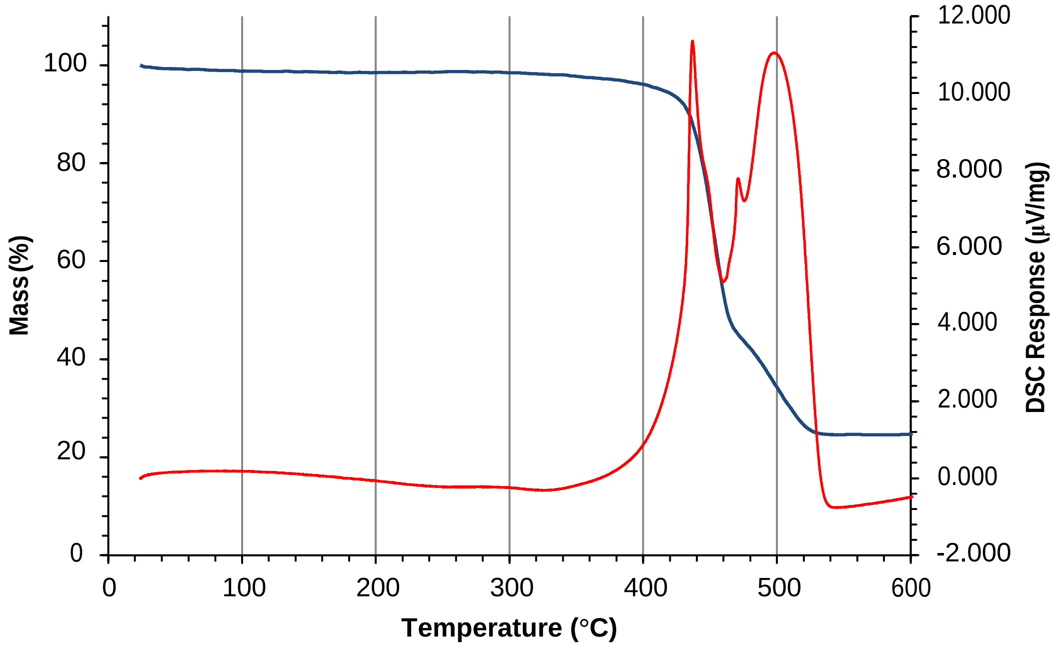


Figure S13: TG (blue line) and DSC (red line) responses for activated $Zn_4O(bpdc\text{-}CH{=}CH_2)_3$ (WUF-19) under a combined flow of N_2 (20 cm^3/min) and compressed air (20 cm^3/min).

6. N_2 Isotherms & BET Surface Area Calculations

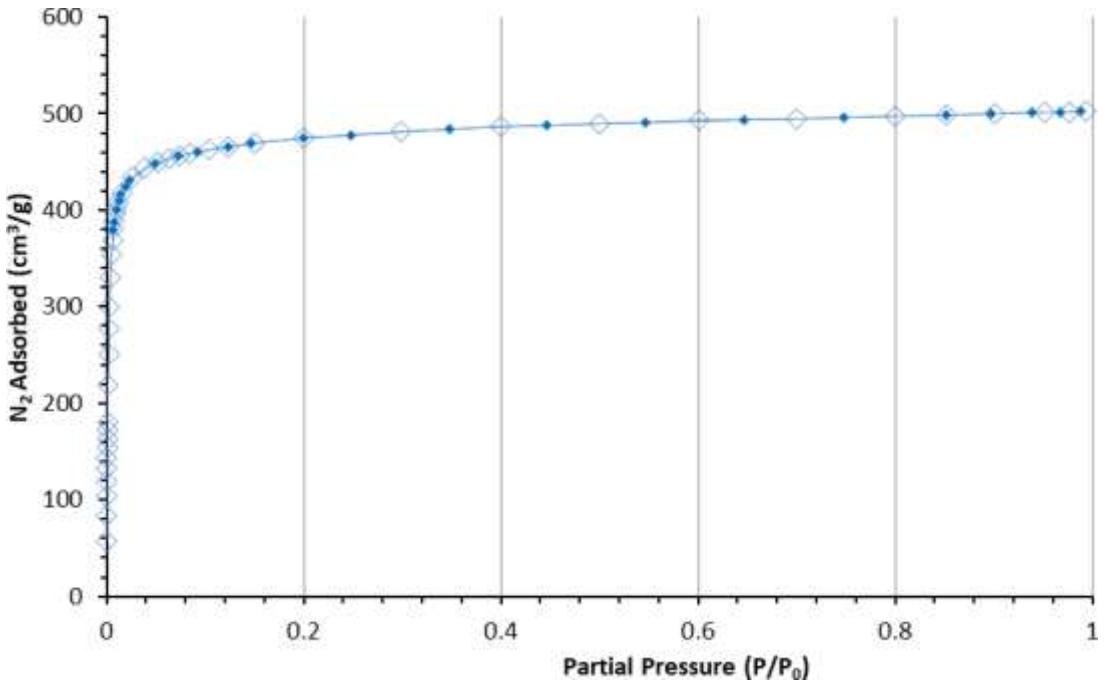


Figure S 14 N_2 adsorption-desorption isotherm at 77 K for WUF-18. Open symbols represent adsorption and closed symbols represent desorption.

BET summary for WUF-18		
Slope	1.840	
Intercept	1.646e-03	
Correlation coefficient, r	0.999981	
C constant	1118.843	
Surface Area	1891.491	
Relative Pressure	**Volume @ STP**	**1 / [W((Po/P) - 1)]**
9.00051e-03	396.0433	1.8349e-02
1.00216e-02	401.8459	2.0156e-02
1.21335e-02	408.9285	2.4032e-02
1.51255e-02	417.8357	2.9409e-02
2.56209e-02	433.8173	4.8497e-02
3.94582e-02	444.0074	7.4026e-02
5.19853e-02	449.8752	9.7528e-02

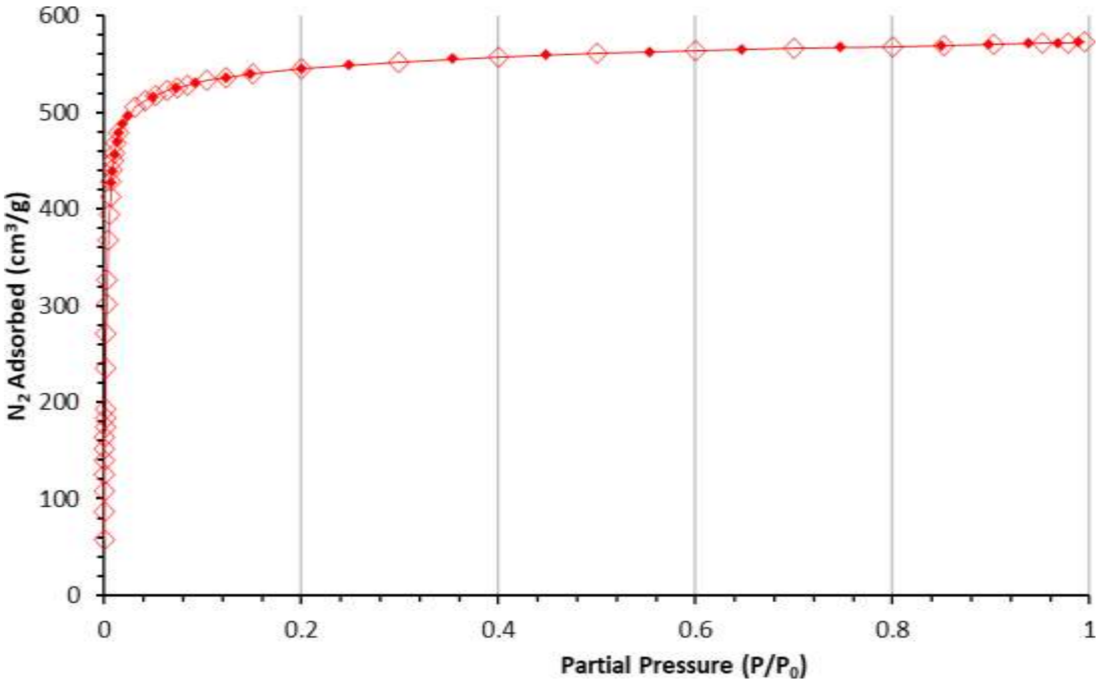


Figure S15 N_2 adsorption-desorption isotherm at 77 K for WUF-19PSM. Open symbols represent adsorption and closed symbols represent desorption.

BET summary for WUF-19PSM		
Slope	1.581	
Intercept	1.852e-03	
Correlation coefficient, r	0.999981	
C constant	854.976	
Surface Area	2199.798	
Relative Pressure	**Volume @ STP**	**1 / [W((Po/P) - 1)]**
8.05453e-03	440.7571	1.4740e-02
9.05966e-03	450.2308	1.6247e-02
1.00723e-02	457.8783	1.7780e-02
1.20548e-02	468.2912	2.0848e-02
1.49879e-02	479.3062	2.5401e-02
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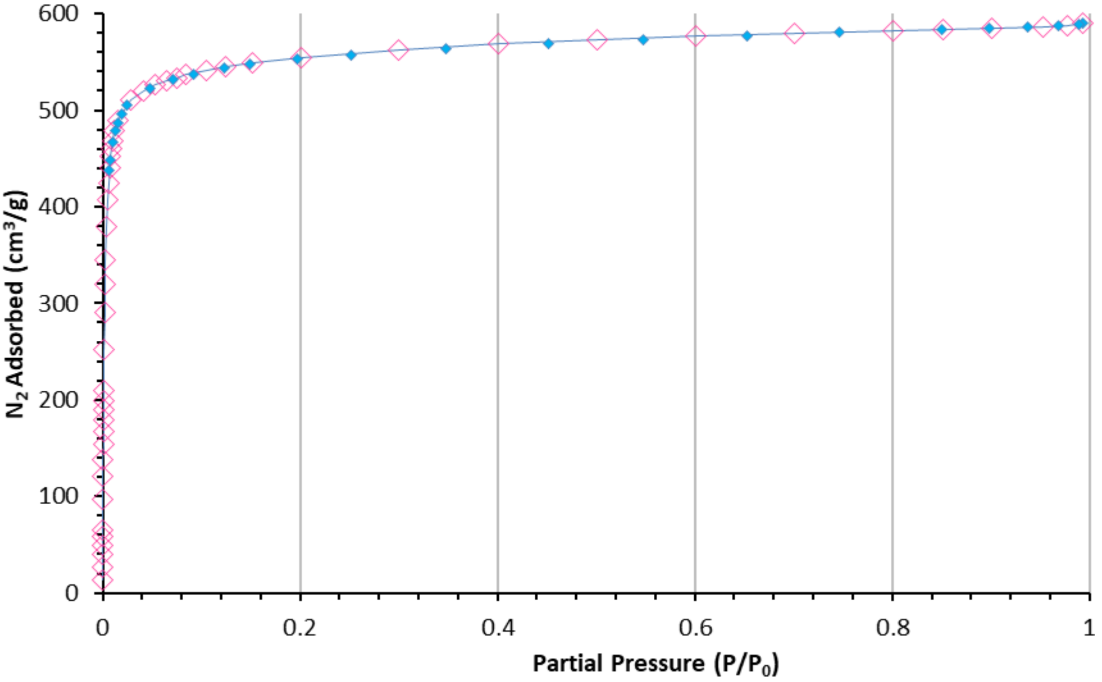

Figure S16 N_2 adsorption-desorption isotherm at 77 K for WUF-19. Open symbols represent adsorption and closed symbols represent desorption.

BET summary for WUF-19		
Slope	1.562	
Intercept	1.651e-03	
Correlation coefficient, r	0.999977	
C constant	946.691	
Surface Area	2227.731	
Relative Pressure	**Volume @ STP**	**1 / [W((Po/P) - 1)]**
8.10695e-03	452.2276	1.4461e-02
9.01753e-03	460.2863	1.5818e-02
1.00287e-02	467.6476	1.7332e-02
1.20112e-02	478.2028	2.0341e-02
1.51274e-02	489.1640	2.5123e-02
2.81077e-02	510.0338	4.5369e-02
4.19472e-02	520.5672	6.7296e-02

7. Geometric Surface Area

Geometric surface area was calculated using the RASPA software package[1] using the method described previously.[2-4] Briefly, a nitrogen probe with a diameter of 3.681 Å is rolled over the internal pore space of the framework. Symmetry-generated disordered components and the lattice water molecule of the framework were removed to generate a *P*1 model for calculation. Van der Waals diameters, derived from the DREIDING forcefield, were used for the framework atoms.[5] The Lennard-Jones parameters for the framework atoms are listed as follows:

Framework atoms	**σ (Å)**	**ε/k_B (K)**
C (MOF)	3.473	47.856
O (MOF)	3.033	48.158
H (MOF)	2.846	7.649
Zn (MOF)	4.045	27.677

8. References

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