

A reagentless thermal post-synthetic rearrangement of an allyloxy-tagged metal-organic framework

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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. 4-Bromo-3-hydroxy benzoic acid was prepared via the method of Buehler *et al.*¹

¹H NMR and ¹³C 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 ¹H and 75.5 MHz for ¹³C. ¹H NMR spectra were referenced to the residual protio peaks at 7.26 ppm (CDCl₃) and 2.50 ppm (*d*₆-DMSO). ¹³C NMR spectra were referenced to the solvent peaks at 77.0 ppm (CDCl₃) and 39.6 ppm (*d*₆-DMSO).

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" SiO₂ substrates and measured using a 2θ angle range of 3-30 with a step size of 0.02° at 1° per minute. Single crystal X-ray analysis was carried out on a Nonius Kappa CCD diffractometer using Mo-K_α radiation.

TGA-DTA traces 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 5 or 10 °C per min under nitrogen flow (20 cm³min⁻¹) were used. Data analysis was performed on Ta60 version 2.20 software system.

IR spectra were obtained using a Shimadzu IRAffinity-1 FTIR, fitted with a MIRacle 10 single reflection ATR accessory. Data collection was performed on Shimadzu IRsolution version 1.50. Each background and sample reading was given 20 scans.

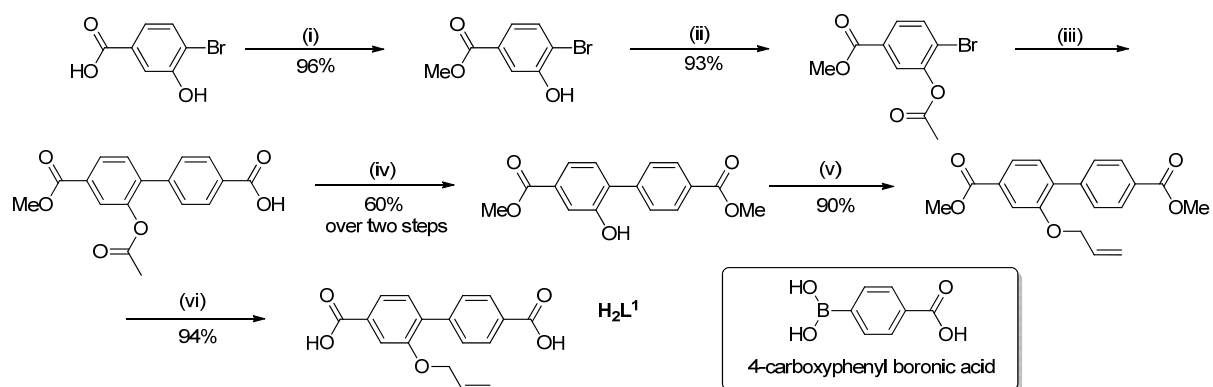
High – Resolution ESI spectra were obtained using a Waters Xevo Quadrupole time-of-flight mass spectrometer at the University of Wollongong or on a Bruker MicroTOF spectrometer at the University of Bath.

For ¹H NMR analysis MOF samples (~10 mg) were digested by adding 35% DCl in D₂O (3 μL) and DMSO (500 μL) and sonicating until a homogeneous solution was obtained.

Elemental microanalysis was performed by the Microanalytical Unit at the Australian National University using a Carlo Erba 1106 automatic analyser or by Alan Carver at the University of Bath using a CE-440 Elemental Analyser.

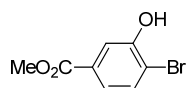
¹ Buehler, C. A.; Harris, J. O.; Shacklett, C.; Block, B. P., The action of formaldehyde on m-hydroxybenzoic acid. II. *Journal of the American Chemical Society* **1946**, *68* (4), 574-577.

2 Synthesis of 2-allyloxy-biphenyl-4,4'-dicarboxylic acid, H₂L¹



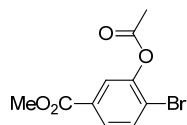
Scheme S1. (i) H₂SO₄, MeOH (ii) AcCl, triethylamine (iii) 4-carboxyphenyl boronic acid, [PdBr₂(dppf)], DMF/K₃PO₄ (iv) MeOH, H₂SO₄ (v) allyl bromide, K₂CO₃/acetone (vi) NaOH_(aq), MeOH

Methyl 4-bromo-3-hydroxybenzoate



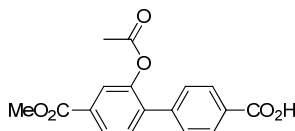
Concentrated H₂SO₄ (1 mL) was added dropwise to 4-bromo-3-hydroxy benzoic acid (2.37 g, 10.9 mmol) in MeOH (20 mL) while stirring and then the mixture was heated at reflux overnight. The solvent was removed by rotary evaporation and the syrupy residue taken up in EtOAc (50 cm³), washed with H₂O (3 × 15 cm³) and brine (15 cm³) and dried over Na₂SO₄. The solvent was removed by rotary evaporation to reveal the product as a colourless solid. Yield 2.43 g (96%). ¹H NMR δ_H (300 MHz, DMSO-*d*₆): 3.86 (3 H, s), 7.28 (1 H, dd, *J* = 8.20, 2.05 Hz), 7.56 (1 H, d, *J* = 2.05 Hz), 7.67 (1 H, d, *J* = 8.20 Hz), 10.78 (1 H, s).

Methyl 3-acetoxy-4-bromobenzoate



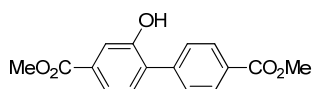
Et₃N (1.60 cm³, 11.8 mmol) was added to a stirred solution of methyl 4-bromo-3-hydroxybenzoate (2.43 g, 10.7 mmol) in dichloromethane (20 cm³) cooled to ice bath temperature. While stirring, acetyl chloride (1.3 cm³, 11.8 mmol) was added dropwise and the mixture was left to stir for 30 min. The reaction mixture filtered to remove precipitated byproduct, diluted with dichloromethane (50 cm³) and washed with 0.25 M HCl (25 cm³), H₂O (3 × 25 cm³), and brine, dried over anhydrous Na₂SO₄ and evaporated to dryness by rotary evaporation. Yield 2.66 g (93%). δ_H (300 MHz, DMSO-*d*₆): 2.38 (3 H, s), 3.91 (3 H, s), 7.77 (1 H, dd, *J* = 8.20, 1.76 Hz), 7.81 (1 H, d, *J* = 2.05 Hz), 7.89 (1 H, d, *J* = 8.49 Hz); δ_C (75.5 MHz; CDCl₃): 20.68, 52.46, 121.96, 124.78, 128.17, 130.74, 133.42, 148.25, 165.49, 168.28.

2'-Acetoxy-4'-(methoxycarbonyl)-[1,1'-biphenyl]-4-carboxylic acid



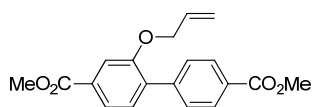
Methyl 3-acetoxy-4-bromobenzoate (2.65 g, 9.7 mmol), 4-carboxyphenyl boronic acid (1.78 g, 10.7 mmol), PdCl₂(dppf)·CH₂Cl₂ (0.103 g, 2 mol%) and K₃PO₄·H₂O (2.46 g, 10.7 mmol) were dissolved in nitrogen-purged DMF (20 cm³). The reaction mixture was stirred under an atmosphere of N₂ at 95 °C for 4 h. After cooling, the reaction mixture was diluted with H₂O (~150 cm³) and acidified with 1 M HCl to a pH of less than 2. The precipitate that formed was then collected by vacuum filtration, washed with water and placed in an oven at 80 °C to dry. Yield 1.95 g. This material was used in the next reaction with no further purification.

Dimethyl 2-hydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate



Conc. H₂SO₄ (1.0 cm³) was added drop wise to a stirred solution of 2'-acetoxy-4'-(methoxycarbonyl)-[1,1'-biphenyl]-4-carboxylic acid (1.95 g) in MeOH (20 cm³). This mixture was heated at reflux overnight. Some of the product precipitated during this time and was collected by vacuum filtration (1.10 g). The solvent was removed from the filtrate by rotary evaporation and the residue taken up in EtOAc (75 cm³). This organic layer was washed with H₂O (4 × 15 cm³), brine (15 cm³) and dried over anhydrous Na₂SO₄. The EtOAc was then removed by rotary evaporation to give a dark residue. This was taken up in CHCl₃ and passed through a silica gel plug eluting with CHCl₃-EtOAc (9–1, R_f ~0.50). After removal of the solvent by rotary evaporation, the white solid was triturated with a minimum amount of MeOH, separated by filtration and washed sparingly with fresh MeOH to provide an additional 0.58 g. After confirmation by TLC and ¹H NMR spectroscopy that they were the same compound, this product was combined with the original precipitate. Yield 1.68 g (60% over two steps). Found: C, 67.1; H, 4.90. C₁₆H₁₄O₅ requires C, 67.1; H, 4.93. δ_H (300 MHz; CDCl₃) 3.86 (3 H, s), 3.88 (3 H, s), 7.46 (1 H, d, *J* = 7.99 Hz), 7.50 (1 H, dd, *J* = 7.99, 1.38 Hz), 7.59 (1 H, d, *J* = 1.38 Hz), 7.75 (2 H, d, *J* = 8.56 Hz), 8.01 (2 H, d, *J* = 8.53 Hz), 10.22 (1 H, s(br)); δ_C (75.5 MHz; CDCl₃) 52.22, 52.26, 116.66, 120.34, 128.37, 128.99, 129.47, 130.37, 130.80, 131.15, 142.29, 154.65, 166.00, 166.16. *m/z* (ESI) ([M+Na]⁺ 309.0727 [C₁₆H₁₄O₅+Na]⁺ requires 309.0739).

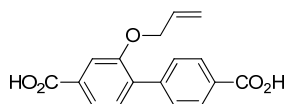
Dimethyl 2-(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylate



Allyl bromide (1.08 g, 8.4 mmol) was added to a stirred solution of dimethyl 2-hydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (0.735 g, 2.6 mmol) and anhydrous potassium carbonate (0.704 g, 5.1 mmol) in acetone (~30 cm³) and the reaction mixture was left to stir overnight. The solvent was then removed by rotary evaporation and the residue was partitioned between EtOAc (50 cm³) and H₂O (20 cm³). This solution was then washed with H₂O (3 × 20 cm³), brine and dried over

anhydrous Na₂SO₄. The solution was reduced to dryness by rotary evaporation and the product was purified by chromatography on silica gel (R_f ~0.25 (1–1, CH₂Cl₂–Pet. Ether)) and crystallised from CH₂Cl₂/MeOH. Yield 0.76 g (90%). Found: C, 69.6; H, 5.56. C₁₉H₁₈O₅ requires C, 69.9; H, 5.56. ¹H NMR δ_H (300 MHz; CDCl₃) 3.94 (6 H, s), 4.61 (2 H, dt, *J* = 4.89, 1.59 Hz), 5.23 (1 H, dq, *J* = 10.60, 2.97, 1.47 Hz), 5.33 (1 H, dq, *J* = 17.26, 3.30, 1.71 Hz), 5.98 (1 H, qt, *J* = 17.26, 10.60, 4.86 Hz), 7.41 (1 H, d, *J* = 7.90 Hz), 7.65 (3 H, m), 7.72 (1 H, dd, *J* = 7.90, 1.50 Hz), 8.09 (2 H, d, *J* = 8.56 Hz); δ_C (75.5 MHz; CDCl₃) 52.12, 52.27, 69.22, 113.50, 117.40, 122.41, 129.25, 129.54, 130.72, 130.90, 132.48, 134.41, 155.32, 166.69, 166.97.

2-Allyloxy-biphenyl-4,4'-dicarboxylic acid [**H₂L**¹]



1 M NaOH (6 mL, 6 mmol) was added to dimethyl 2-(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylate (0.75 g, 2.3 mmol) in a solvent mixture of MeOH–THF (1–1, 15 cm³) and the mixture stirred for 6 hours. The solution was reduced to dryness by rotary evaporation and the residue taken up in H₂O (20 cm³) and filtered. After dilution of the filtrate with H₂O (20 cm³) acidification with 1M HCl precipitated a white solid and this was collected by filtration, washed with H₂O (3 × 5 cm³) and oven dried (80 °C). Yield 0.65 g (94%). Found: C, 66.6; H, 4.62. C₁₇H₁₄O₅·½H₂O requires C, 66.4; H, 4.92. ¹H NMR δ_H (300 MHz; DMSO-*d*₆) 4.66 (2 H, dt, *J* = 4.42, 1.71 Hz), 5.21 (1 H, dq, *J* = 10.63, 3.39, 1.74 Hz), 5.30 (1 H, dq, *J* = 17.29, 3.42, 1.62 Hz), 6.01 (1 H, qt, *J* = 17.29, 10.63, 4.74 Hz), 7.47 (1 H, d, *J* = 7.78 Hz), 7.64 (4 H, m), 8.00 (2 H, d, *J* = 8.41 Hz); ¹³C NMR δ_C (300 MHz; DMSO-*d*₆) 68.66, 113.37, 116.94, 122.16, 129.10, 129.56, 129.76, 130.78, 131.82, 133.26, 133.29, 141.61, 154.96, 166.99, 167.17. *m/z* (ESI) 297.0746 ([M–H]⁺). [C₁₇H₁₃O₅ – H][–] requires 297.0763).

3 Additional TG–DTA data

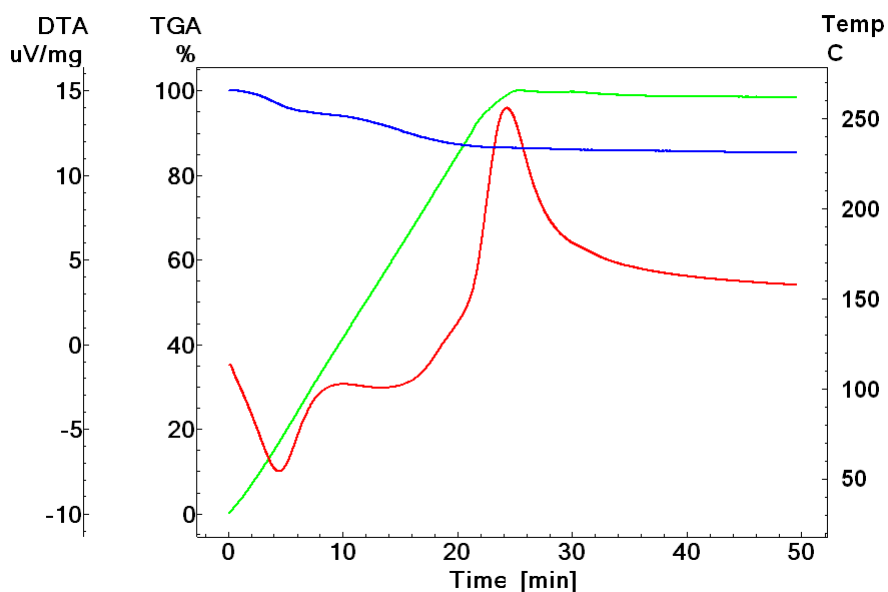


Figure S1. TG–DTA curves and temperature protocol for heating dried **1** up to 260 °C and holding for 20 minutes; blue curve represents the TGA; the red curve represents the DTA; the green line represents the heating protocol.

4 Additional Powder X-ray Diffraction data

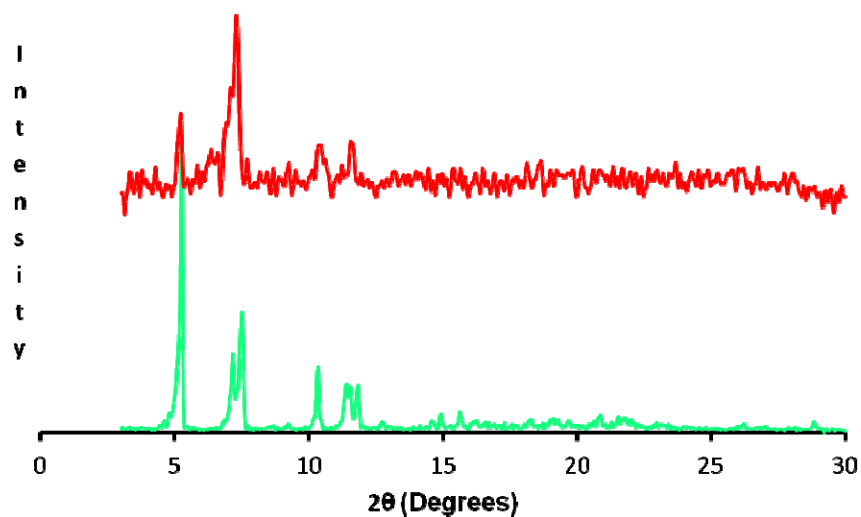


Figure S2 PXRD patterns for **1** (bottom) and **3** (top). The pattern for **3** has been increased in intensity by a factor of three for clarity.

5 Single Crystal X-ray Crystallography

Table S1. Crystal data and structure refinement for **1**.

Identification code	k08adb06
Empirical formula	C ₅₇ H ₅₀ N ₂ O ₁₈ Zn ₄
Formula weight	1312.47
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/m
Unit cell dimensions	a = 26.0930(15) Å alpha = 90.00 b = 21.5800(15) Å beta = 92.593(4)° c = 17.2380(19) Å gamma = 90.00
Volume	9696.6(14) Å ³
Z	4
Density (calculated)	0.899 Mg/m ³
Absorption coefficient	1.021 mm ⁻¹
F(000)	2680
Crystal size	0.25 x 0.225 x 0.10 mm
Theta range for data collection	3.65 to 23.25°
Index ranges	-28 ≤ h ≤ 28; 0 ≤ k ≤ 23; 0 ≤ l ≤ 19
Reflections collected	6941
Independent reflections	6941 [R(int) = 0.0000]
Reflections observed (>2σ)	3005
Data Completeness	0.967
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.763 and 0.646
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6941 / 53 / 349
Goodness-of-fit on F ²	0.912
Final R indices [I > 2σ(I)]	R1 = 0.0963 wR2 = 0.2619
R indices (all data)	R1 = 0.1662 wR2 = 0.2908
Largest diff. peak and hole	0.643 and -0.518 eÅ ⁻³

Notes:

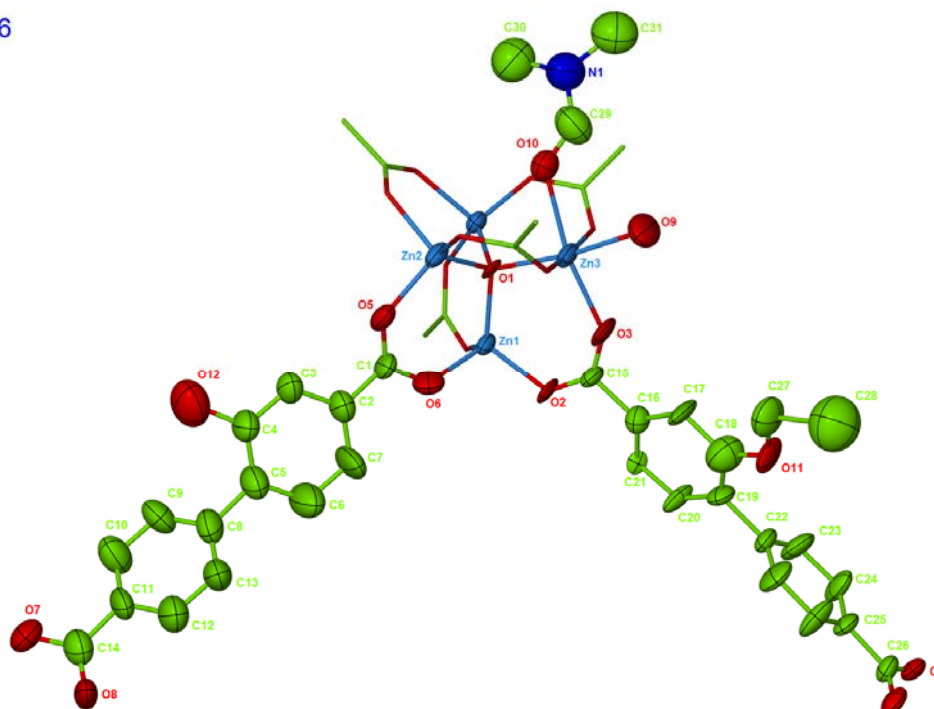
The asymmetric unit in this structure comprises one full occupancy zinc atom (Zn2), two half occupancy zinc atoms (Zn1, Zn3), one half-occupancy oxygen centre (O1), one complete L¹ ligand moiety (based on C1), and another half of a L¹ ligand (atoms O2, O3, C15, C19, C22, C25 and C26 in the latter exhibit half-occupancy), a DMF ligand with half-occupancy (based on O10), and an additional half-occupancy oxygen atom (O9).

All aforementioned half-occupancy atoms, with the exception of the DMF moiety bearing O10 are located on a mirror plane intrinsic to the space-group symmetry. The complete DMF fragment (O10) straddles this mirror plane and as such, the occupancy observed for atoms thereof is a result of disorder. Atoms C16, C17, C20 and C21 are present at half-occupancy also, as a result of similar symmetry-related disorder. Of particular note is that three atoms of the pendant allyloxy group attached to C18 (and necessarily with 50% occupancy) were readily located. U(eq) values increase as the chain extends from the ligand backbone (in the order O11, C27, C28), and the last carbon of this arm could not be located due to the progressive smearing of the electron density observed as the distance from the ligand backbone increases.

Atom O12 is the first atom of the allyloxy functionality on the complete ligand present in the motif. Unfortunately, due to rotational disorder of the phenyl groups about the long axis of this ligand backbone, the electron density beyond O12 is smeared to an extent whereby a credible disorder model could not be constructed.

Data quality and the considerable disorder present also precluded resolution of additional connectivity to O9, but it is a reasonable assumption based on our experience with other similar structures that this atom belongs to another DMF ligand at half occupancy.

k08adb06



Diffraction data for this sample was no exception to the well documented issues inherent to crystallography on porous MOF samples. Mosaicity was high, there was evidence of diffuse scattering and a rapid decline of reflection intensities were noted above the 15-16° Bragg angle region (the presented model arises from data with a max resolution of 0.9 Å). The impact of these factors is immediately obvious in the ESD values associated with the unit cell parameters, which are quoted herein as output from the integration software. Comparative ESD values on crystals of molecular compounds, using the same diffractometer and software, are routinely observed to be smaller by one order of magnitude.

Notwithstanding these limitations, this model affords clear and significant structural information. The gross MOF framework is unambiguous, and the SBU core is well defined. The ligand backbones are well resolved and despite the disorder present, there is credible crystallographic evidence for the pendant groups. We note that in many other MOF structures, pendant groups are not found at all.

ADP restraints applied in the refinement of this structure are confined to the disordered regions. While we are aware that many of the ellipsoid shapes could be ‘improved’ by adding additional ADP restraints to the carbon atoms, it is a deliberate choice not to include them. This is because, in the first instance, we make no detailed claims about the bond distances, angles or torsions present in this structure. In addition, the ellipsoid shapes give a visual indication for the presence of the disorder mentioned above.

In an effort to address the residual electron density within the structure, the SQUEEZE algorithm was employed. This suggested the presence of a 'void' channel parallel to the *c*-axis with a 'centre of gravity' proximate to the origin in the unit cell. The formulation of the model presented is $C_{48}H_{30}NO_{17}Zn_4$ (twice the asymmetric unit contents). The formulation based on O9 contributing to a DMF ligand and inclusion of unresolved atoms from the ligand pendant groups is $C_{57}H_{50}N_2O_{18}Zn_4$. The difference between these two formulae is $C_{11}H_{20}NO$ – with an electron count of 101 (i.e. 404 electrons per unit cell). SQUEEZE calculates the total electron count in the unit cell voids to be 851. This suggests that there may be some diffuse solvent present also. However, we have not included any in the formulation, as the data quality is not of sufficient calibre to make any credible assertions.

6 ^1H NMR Digestion spectra

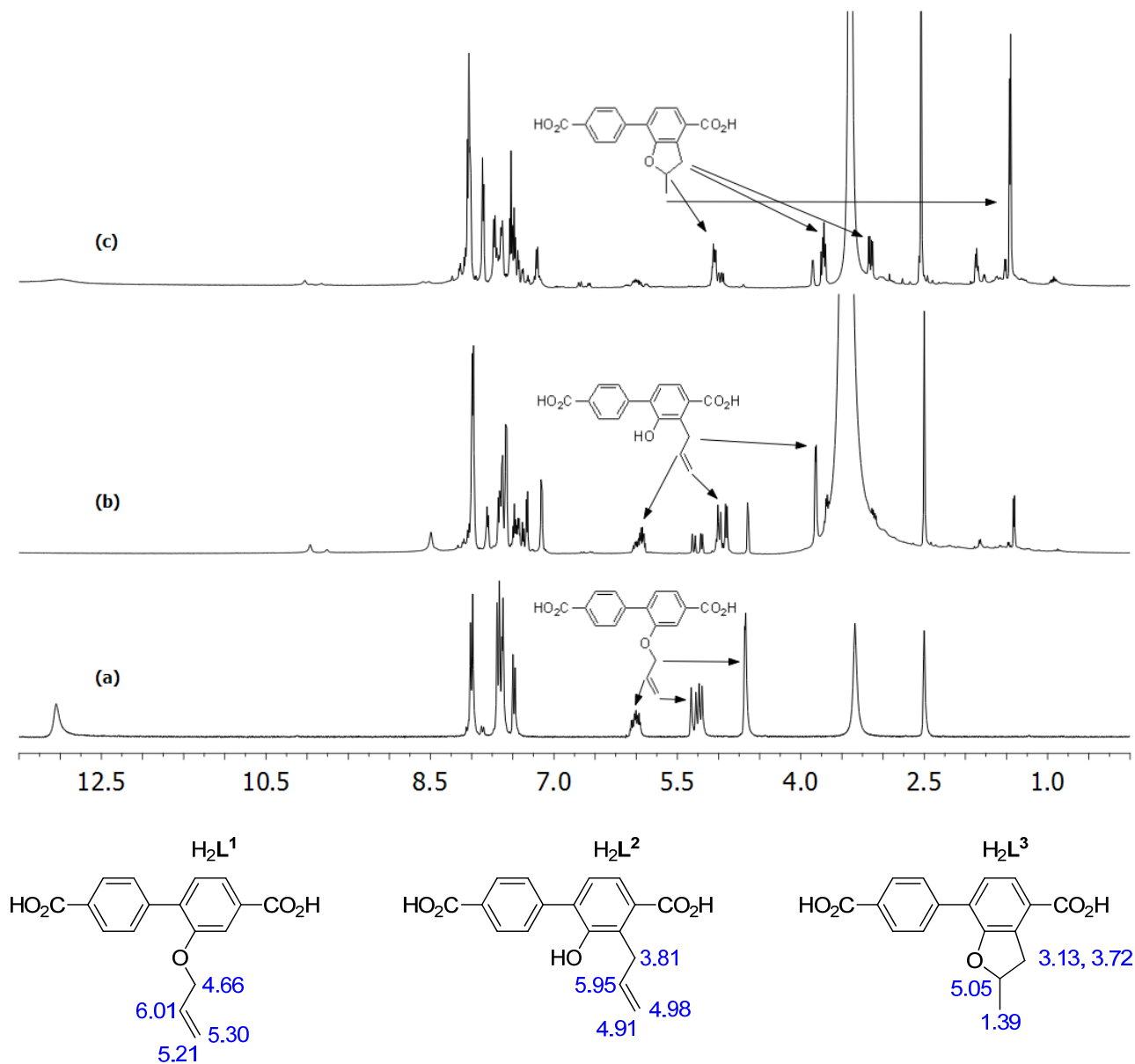


Figure S3 ^1H NMR spectra in d_6 -DMSO solutions of (a) H_2L^1 ; (b) $[\text{Zn}_4\text{O}(\text{L}^1)_{0.33}(\text{L}^2)_{2.47}(\text{L}^3)_{0.17}] \mathbf{2}$; and (c) $[\text{Zn}_4\text{O}(\text{L}^2)_{0.45}(\text{L}^3)_{2.55}] \mathbf{3}$. The signals of the allyl and furan ring protons are indicated with arrows on the spectra and denoted on the structures above.