Electronic Supplementary Material (ESI) for CrystEngComm.

Fecht's acid revisited: a spirocyclic dicarboxylate for non-aromatic MOFs

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Supporting Information

1. Additional Figures

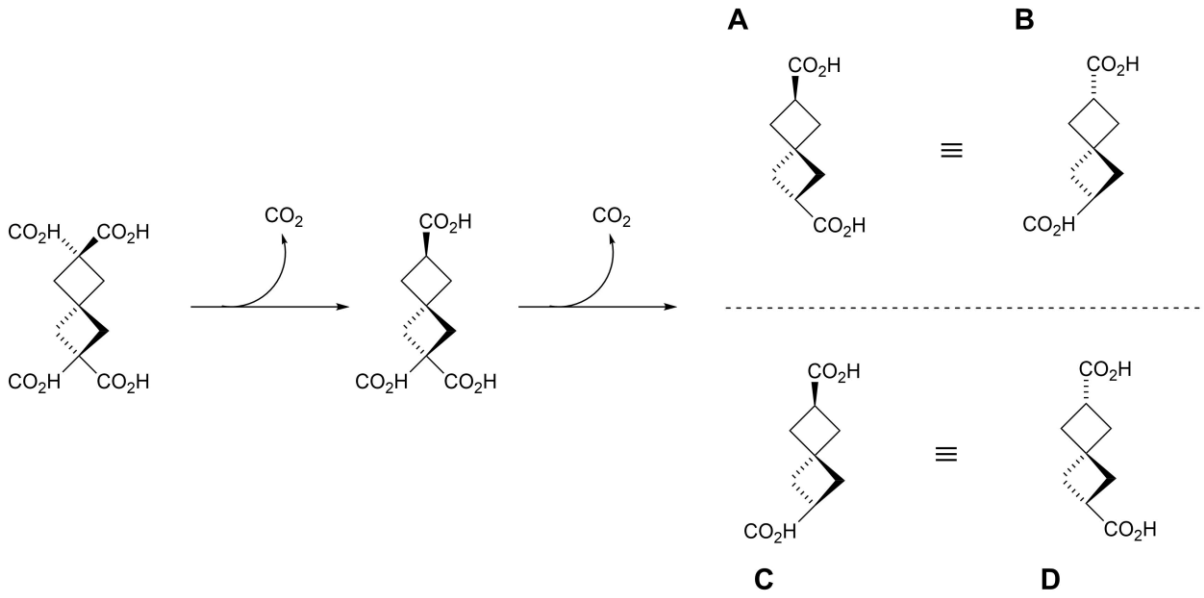

Figure S1 Description of the double decarboxylation step in the synthesis of **H_2SHDC** which gives only two enantiomers, shown here as the four possible combinations of decarboxylations from the tetracarboxylate. A/B and C/D are identical, related by rotation. A/D and B/C are enantiomers, visualised by reflection in the plane of the page, and A/C and B/D are enantiomers by reflection perpendicular to the page.

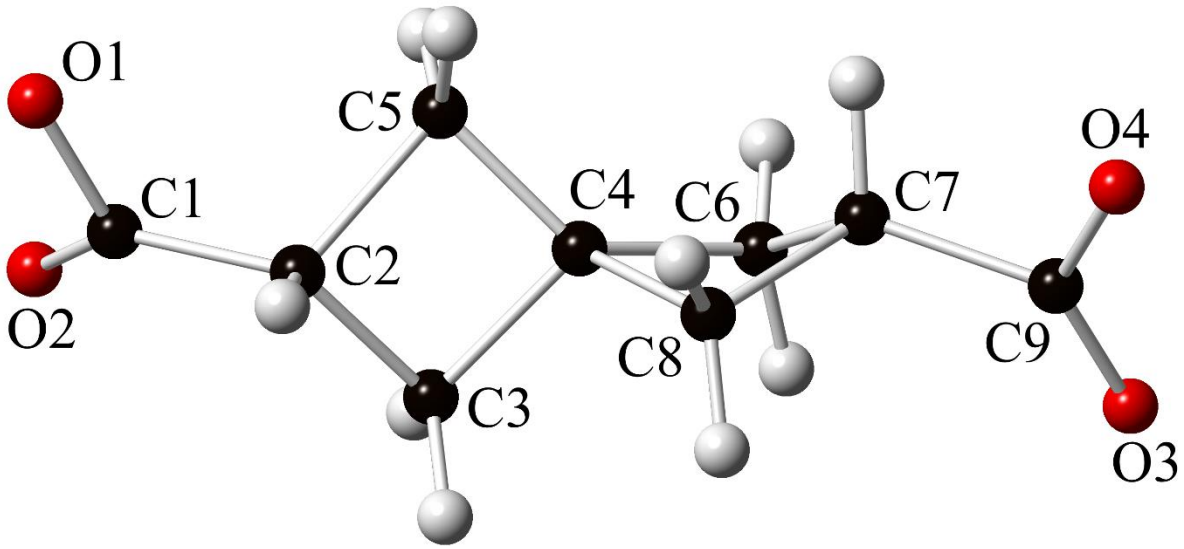

Figure S2. Representative structure of **SHDC** with calculated hydrogen atom positions shown

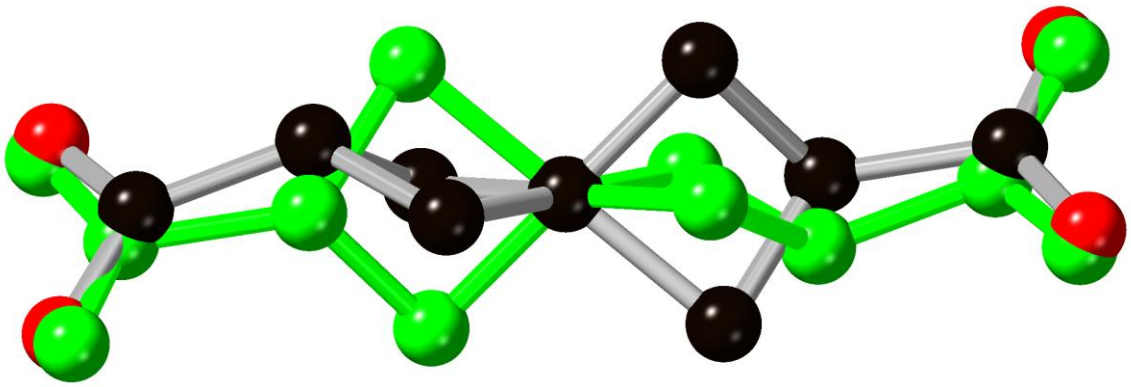

Figure S3 Typical disorder mode observed for **SHDC** molecules in complexes **1** and **2**. In this example the spiro carbon atom position is precisely shared between two orientations of the molecule (coloured separately), but for the examples in complex **1** this atom is also split across the symmetry element. Hydrogen atoms are omitted for clarity.

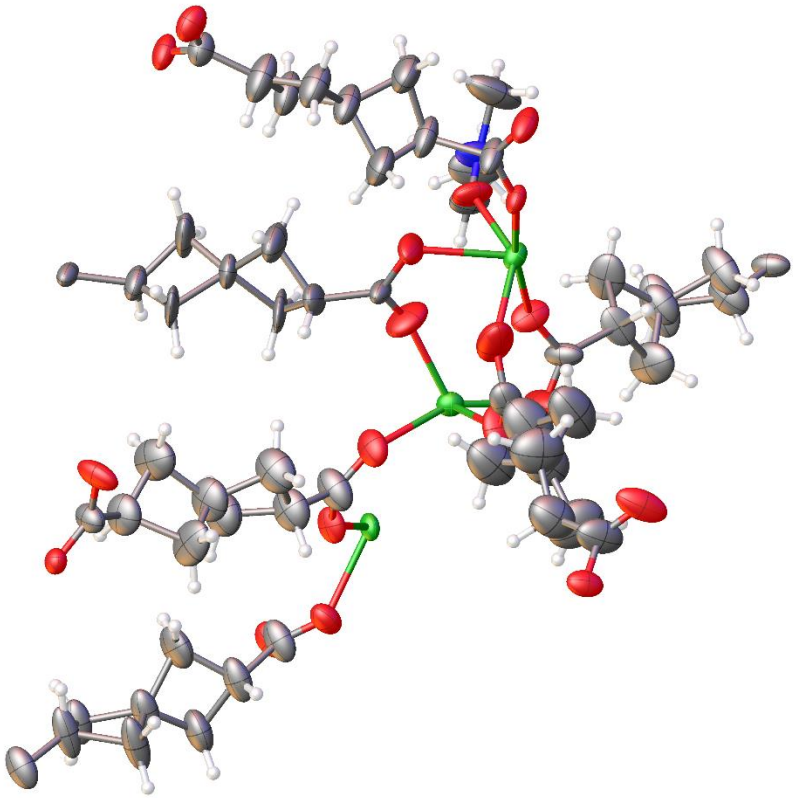

Figure S4 The asymmetric unit of complex **1**, ADPs are rendered at the 50% probability level**.** Note that the carbon backbones of the three SHDC residues missing terminal carboxylates from the asymmetric unit are modelled at 50% occupancy and split across inversion centres; the carboxylate (COO) atoms are generated by symmetry.

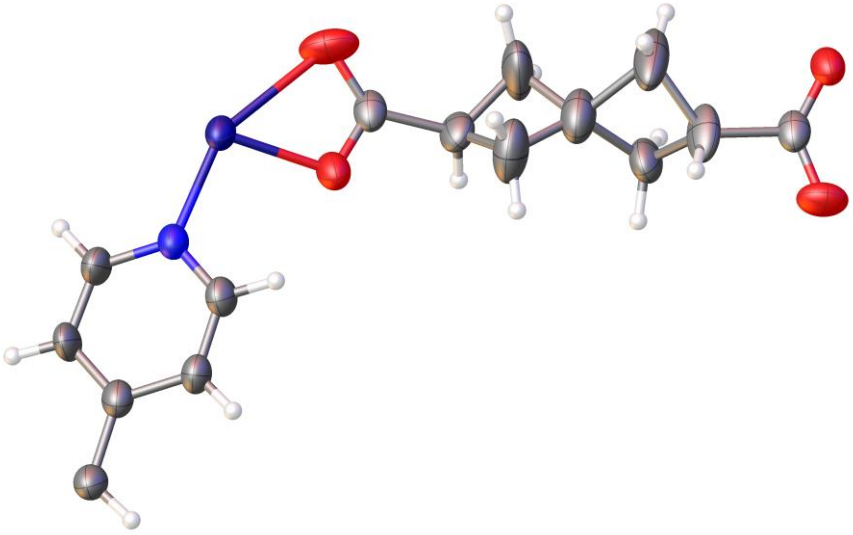

Figure S5 The asymmetric unit of complex **2**, with ADPs rendered at the 50% probability level. Note that the spiro carbon atom occupies an inversion centre and all remaining atoms of the **SHDC** molecule are modelled at half occupancy, with the second overlapping (Fig. S2) orientation generated by symmetry.

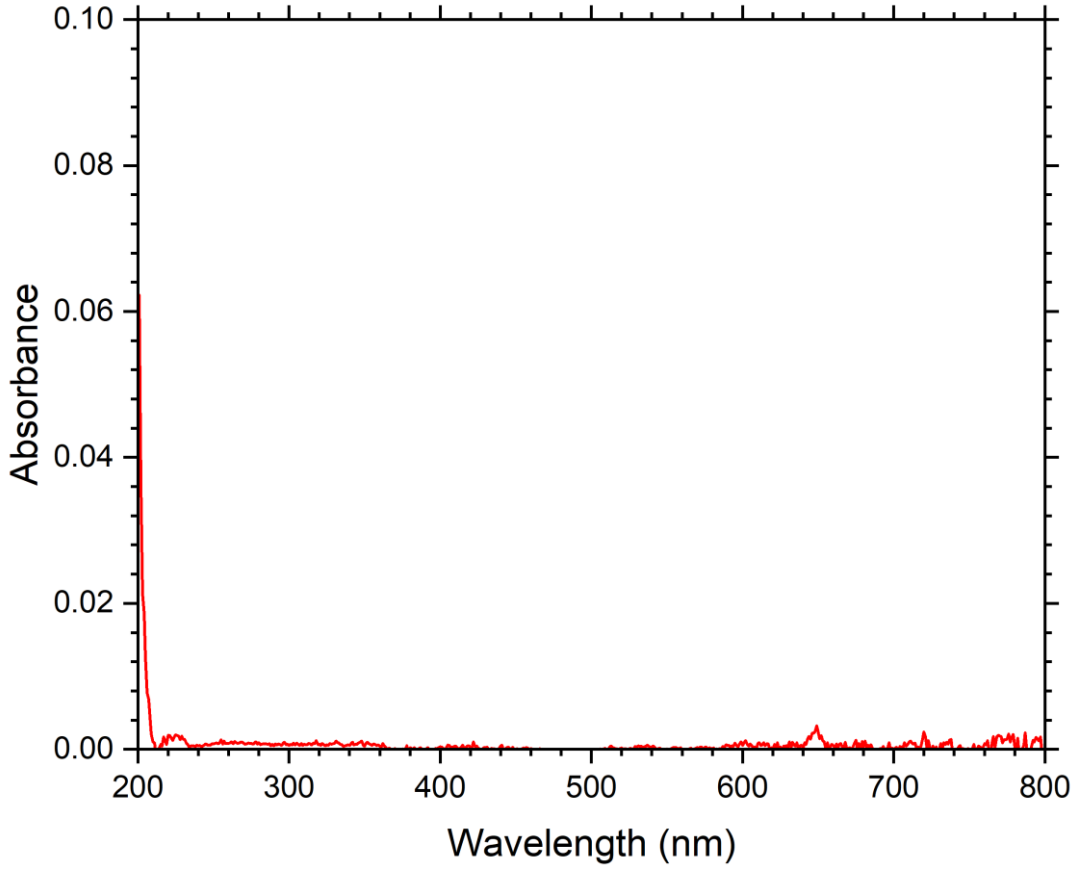

Figure S6 UV-Visible absorption spectrum of a 40 μM solution of **H_2SHDC** in methanol showing only baseline noise above 235 nm.

2. Crystallographic Data Tables

Table S1. Crystallographic Tables for Complex 1 and Complex 2

Compound Reference	**1**	**2**
Empirical formula	$C_{88}H_{104}N_2O_{38}Yb_6$	$C_{21}H_{20}N_2O_4Zn$
Formula weight	2835.97	429.76
Temperature/K	150	150
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	*Pnna*
a/Å	12.4079(8)	11.3429(10)
b/Å	20.8937(14)	12.4311(10)
c/Å	19.4442(12)	18.5115(14)
α/°	90	90
β/°	90.801(2)	90
γ/°	90	90
Volume/Å^3	5040.4(6)	2610.2(4)
Z	2	4
ρ_{calc}g/cm^3	1.869	1.094
μ/mm^{-1}	5.593	0.963
F(000)	2740	888
Crystal size/mm^3	0.15 × 0.14 × 0.05	0.35 × 0.31 × 0.16
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.19 to 53.074	6.556 to 53
Index ranges	$-13 \le h \le 15$, $-26 \le k \le 26$, $-24 \le l \le 22$	$-12 \le h \le 14$, $-15 \le k \le 15$, $-23 \le l \le 23$
Reflections collected	50050	15765
Independent reflections	10423 [R_{int} = 0.0868, R_{sigma} = 0.0597]	2688 [R_{int} = 0.0469, R_{sigma} = 0.0297]
Data/restraints/parameters	10423/640/703	2688/81/171
Goodness-of-fit on F^2	1.019	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0599, wR_2 = 0.1446	R_1 = 0.0501, wR_2 = 0.1293
Final R indexes [all data]	R_1 = 0.0952, wR_2 = 0.1663	R_1 = 0.0758, wR_2 = 0.1502
Largest diff. peak/hole / e Å^{-3}	3.51/-1.85	0.33/-0.36
CCDC Number	2106213	2106214

3. Powder X-Ray Diffraction Data

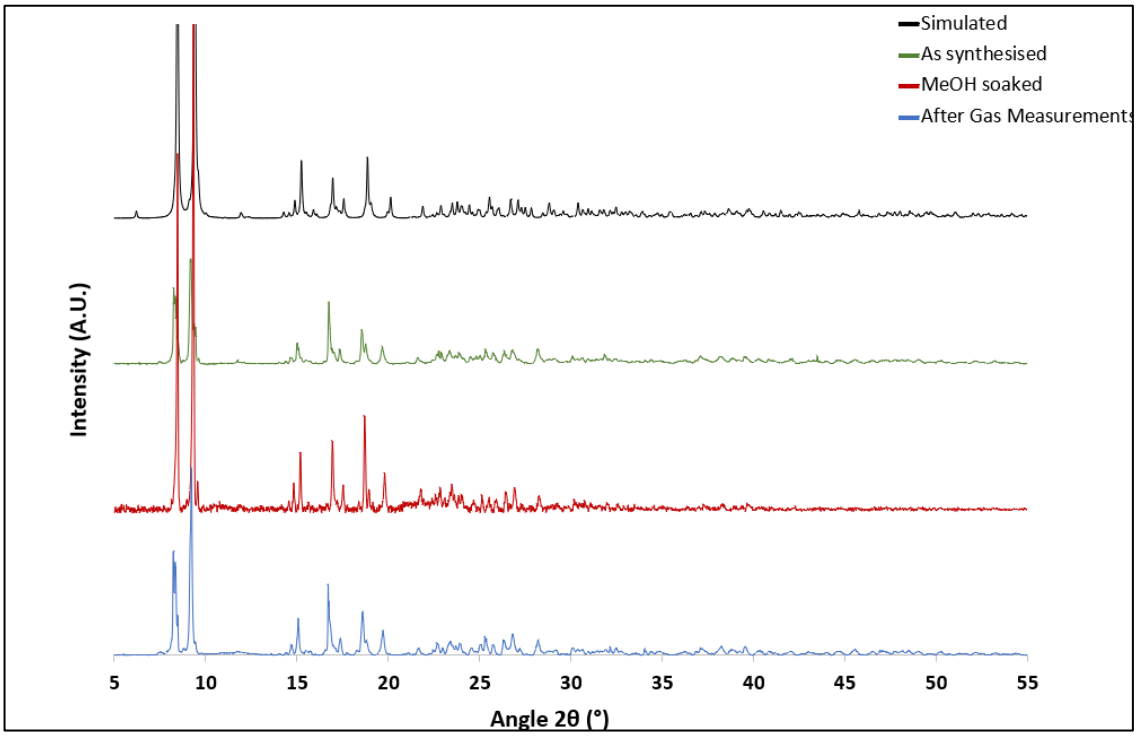

Figure S7 X-ray powder diffraction data for complex **1** showing pattern simulated from single crystal data at 150K (black), measured as synthesised (green, room temperature), measured after soaking in methanol (red, room temperature/capillary) and measured after gas adsorption measurements (blue, room temperature)

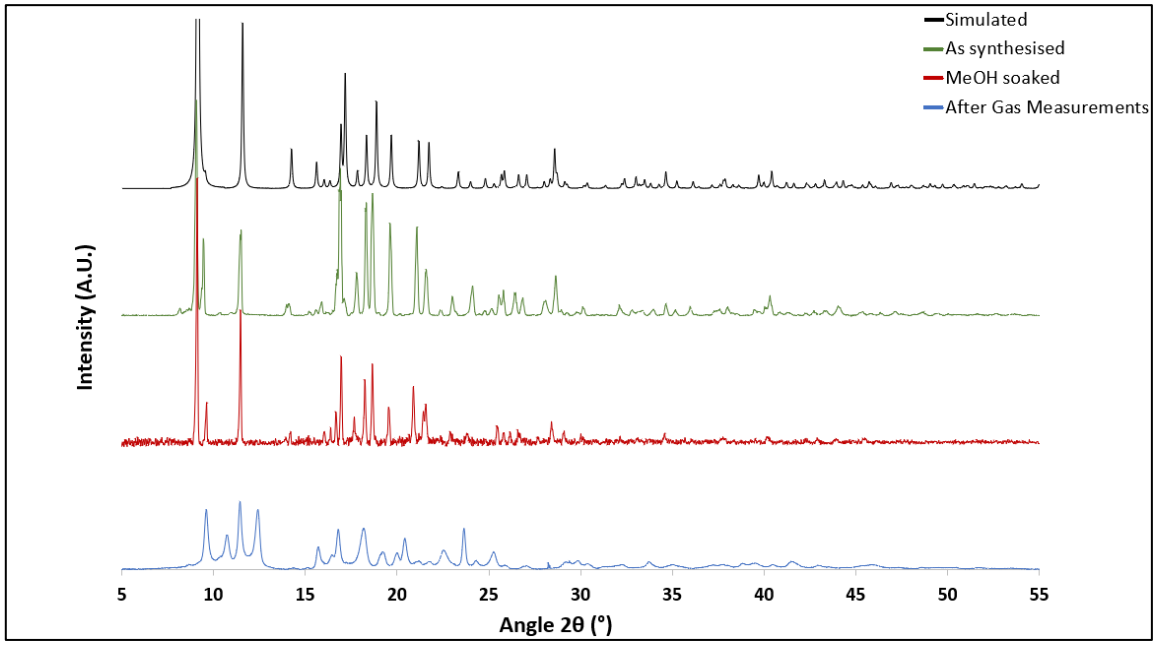

Figure S8 X-ray powder diffraction data for complex **2** showing pattern simulated from single crystal data at 150K (black), measured as synthesised (green, room temperature), measured after soaking in methanol (red, room temperature/capillary) and measured after gas adsorption measurements (blue, room temperature)

4. Thermogravimetric Analysis

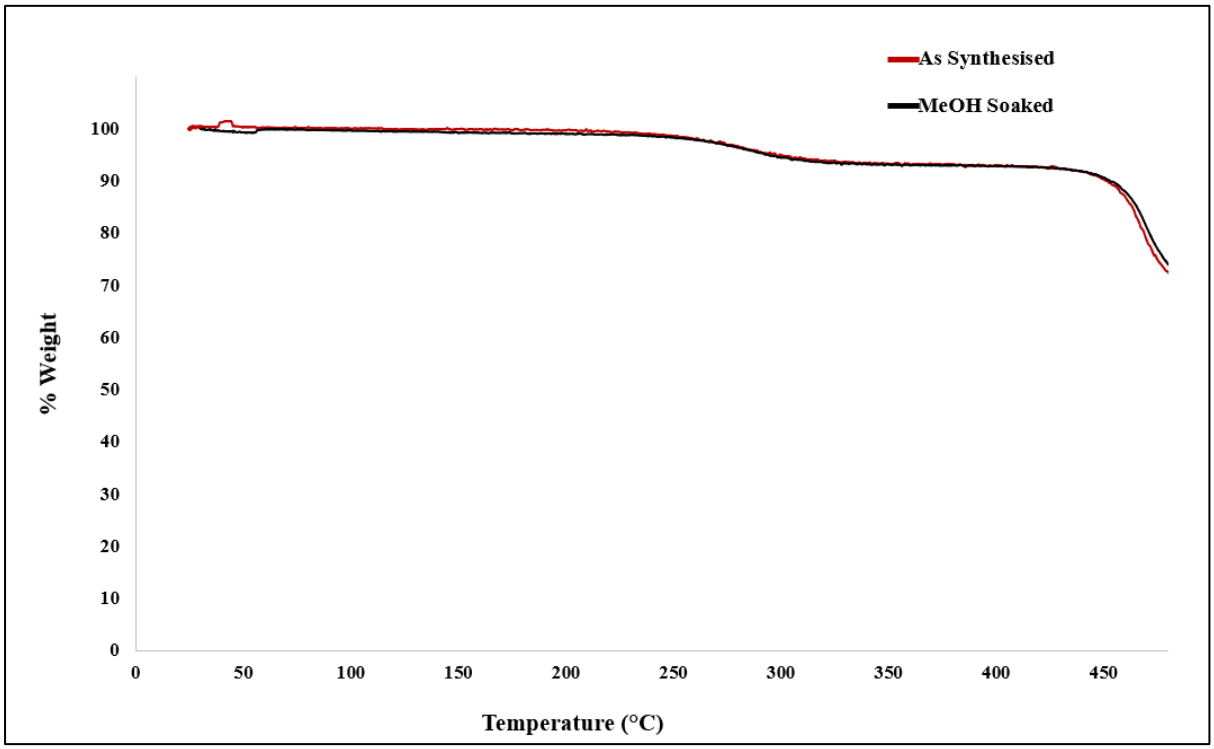

Figure S9 Thermogravimetric analysis plots for complex **1**, as synthesised (red) and after soaking in MeOH (black)

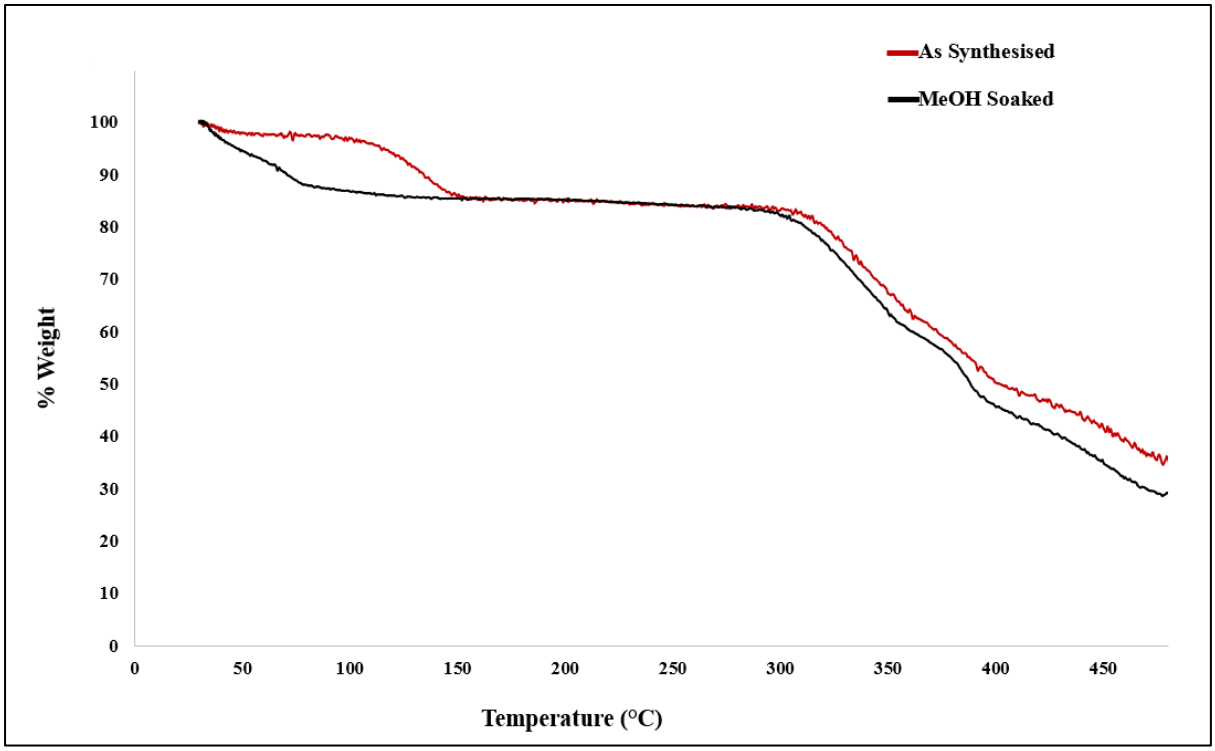

Figure S10 Thermogravimetric Analysis for complex **2**, as synthesised (red) and after soaking in MeOH (black)

5. Gas Adsorption Data

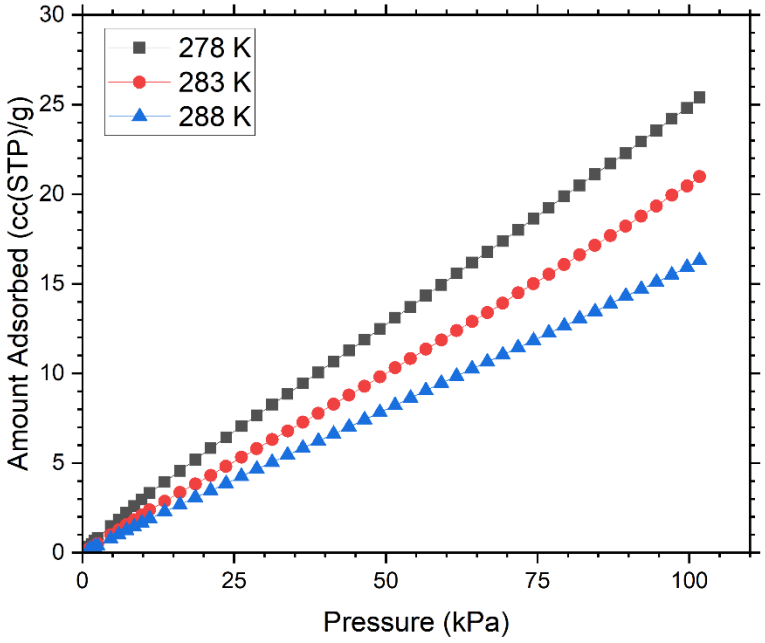

Figure S11 CO_2 adsorption isotherms for compound **1** at 278, 283 and 288 K.

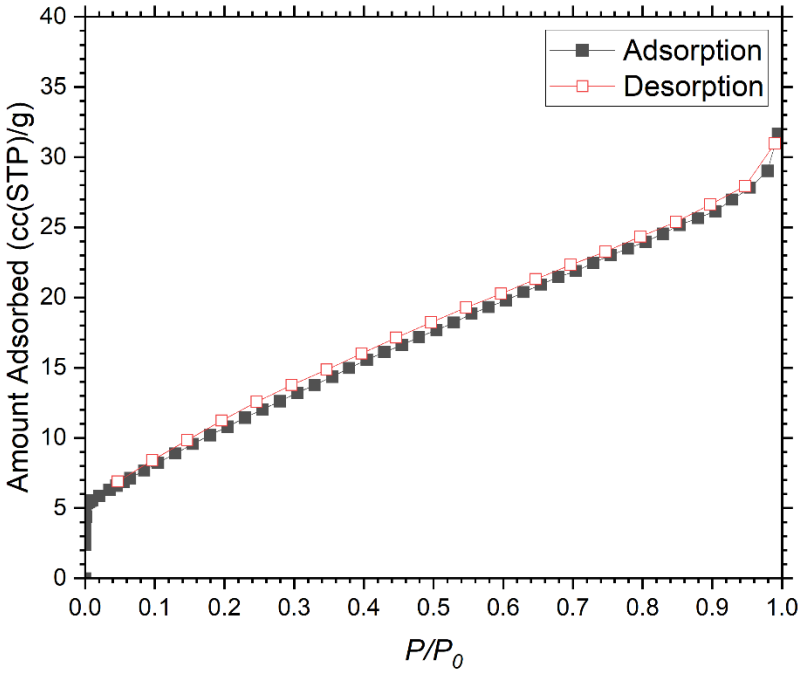

Figure S12 N_2 adsorption (black, filled) and desorption (red, hollow) isotherms for compound **1** at 77 K.

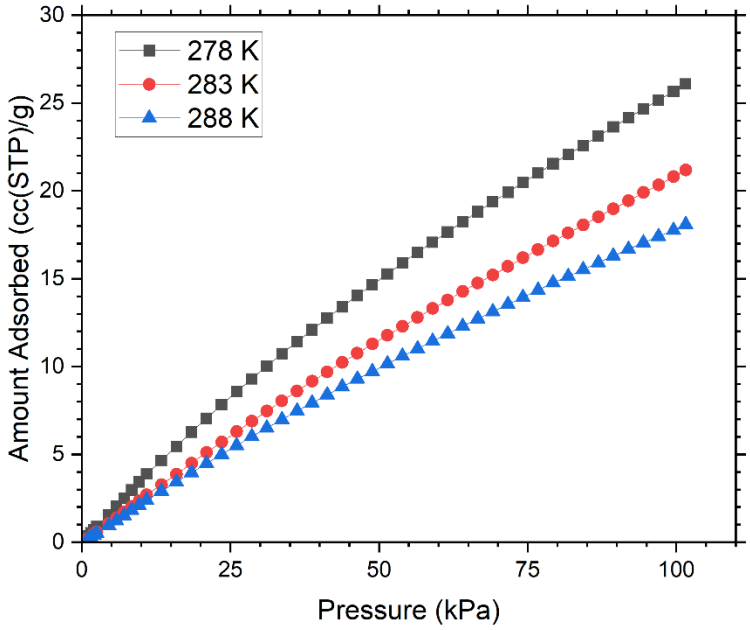

Figure S13 CO_2 adsorption isotherms for compound **2** at 278, 283 and 288 K.

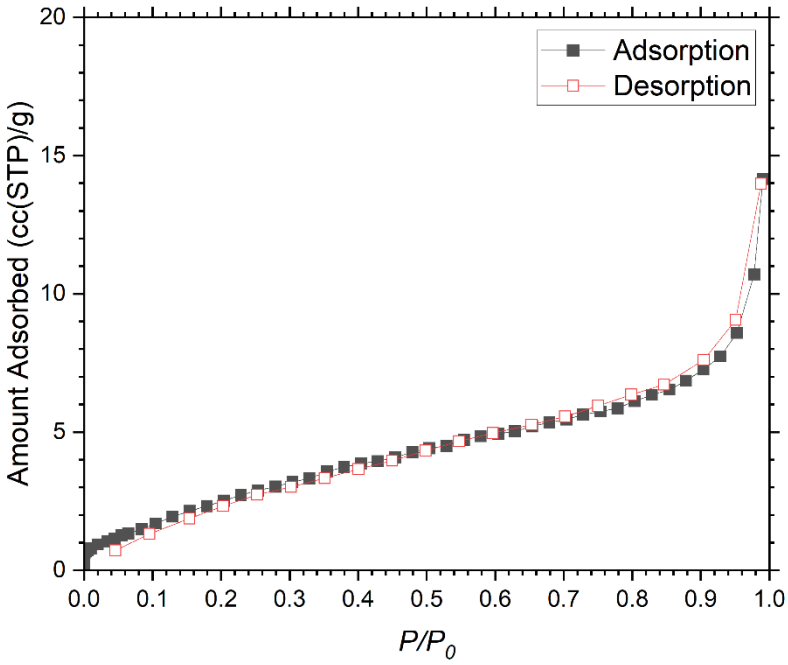

Figure S14 N_2 adsorption (black, filled) and desorption (red, hollow) isotherms for compound **2** at 77 K.

Enthalpy of Adsorption Calculations

The isosteric heat of adsorption for CO_2 in complexes **1** and **2** was estimated using a least-squares fitting routine of a virial thermal adsorption equation modelling ln(P) as a function of gas loading.[S1] The model takes the form $\ln(P) = \{\ln(N) + (a_0 + a_1N + a_2N^2\ldots)/T + b\}$, where N represents the surface excess adsorption (mmol) at temperature T and a_0, a_1 and a_2 are coefficients determined through least-squares fitting. The original parameter set of 5 parameters was sequentially reduced to maximise the data:parameter ratio. The enthalpy of adsorption is then given by the relation $Q(N) = -R(a_0 + a_1N + a_2N^2\ldots)$. Optimised coefficients and parameters are given below.

Compound	**1**	**2**
Temperatures (K)	278, 283, 288	278, 283, 288
a_0	-4325.95	-3847.37
a_1	29.90523	57.80537
B	19.9345	18.04117
R^2	0.9980	0.9974
Datapoints fitted	138	138

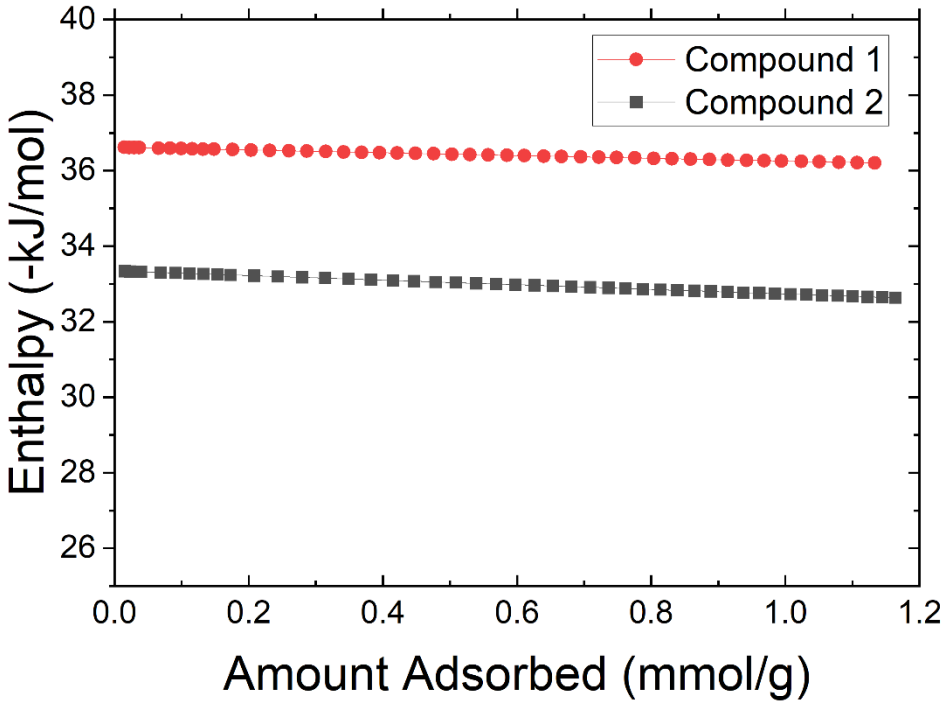

Figure S15 Estimated CO_2 adsorption enthalpy as a function of gas loading for compounds **1** and **2**.

6. NMR Spectra

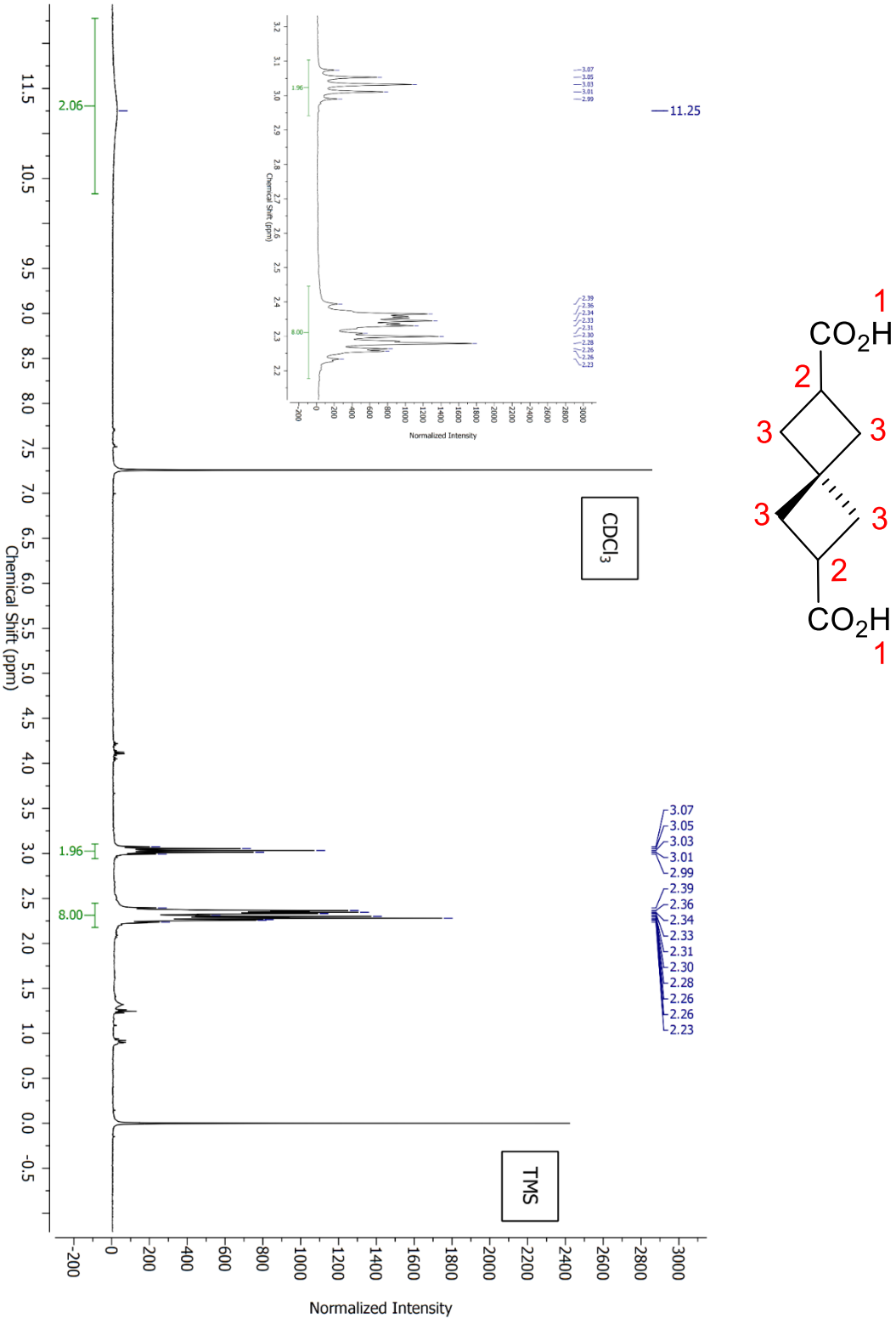

Figure S16. ^{1}H NMR spectrum for H_2SHDC with proton numbering scheme

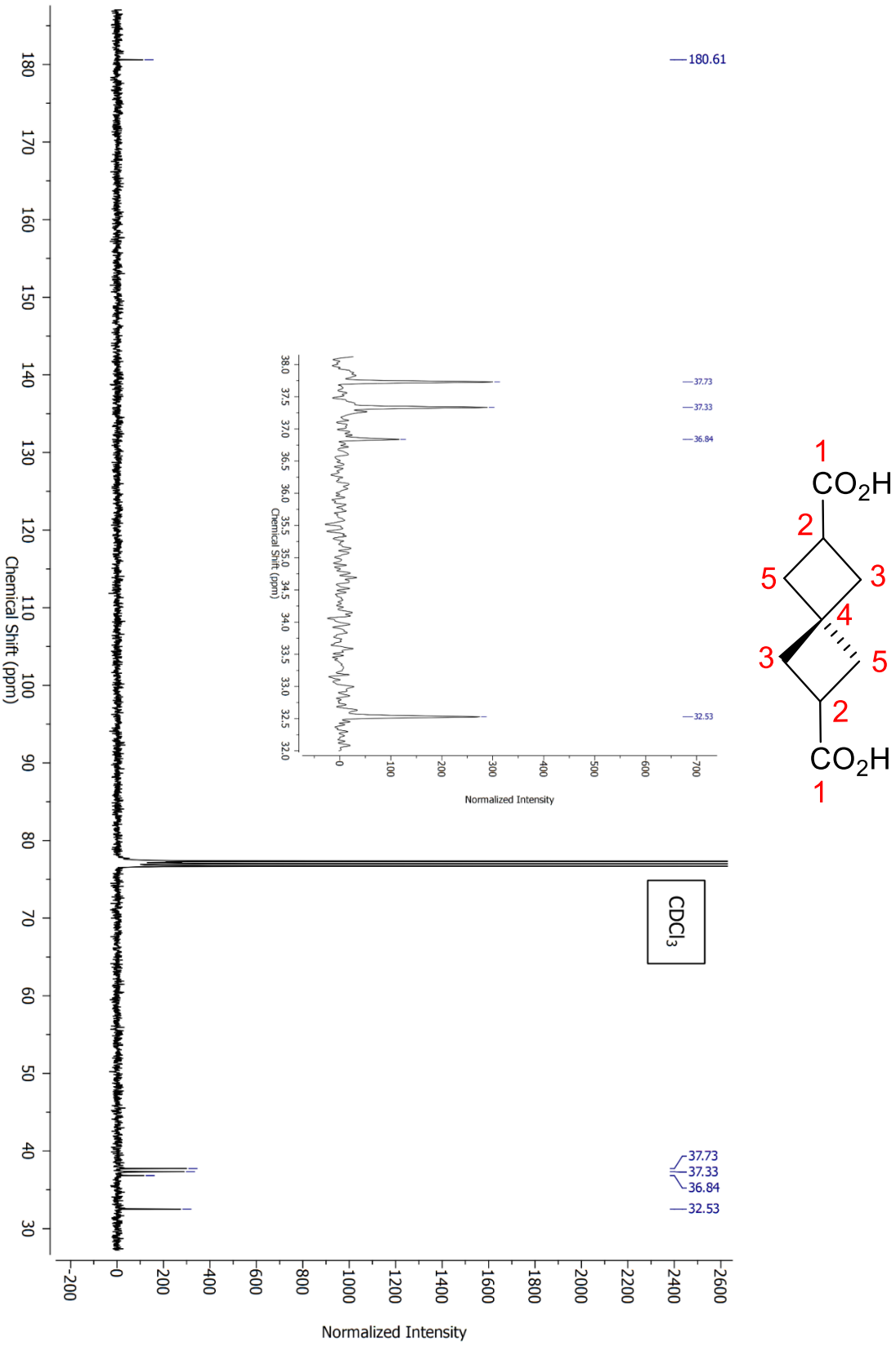

Figure S17 ^{13}C NMR Spectrum for H_2SHDC with carbon numbering scheme

7. References

S1. L. Czepirski and J. Jagiello, *Chem. Eng. Sci.* 1989, **44**, 797-801; S. Tedds, A. Walton, D. P. Broom and D. Book, *Faraday Discuss.* 2011, **151**, 75-94