Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Thermally-Promoted Post-synthetic Pummerer Chemistry in a Sulfoxide-functionalized Metal-Organic Framework

Macguire R. Bryant,[a] and Christopher Richardson*[a]

[a] School of Chemistry, University of Wollongong, Wollongong NSW 2522, Australia

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1. PXRD Data

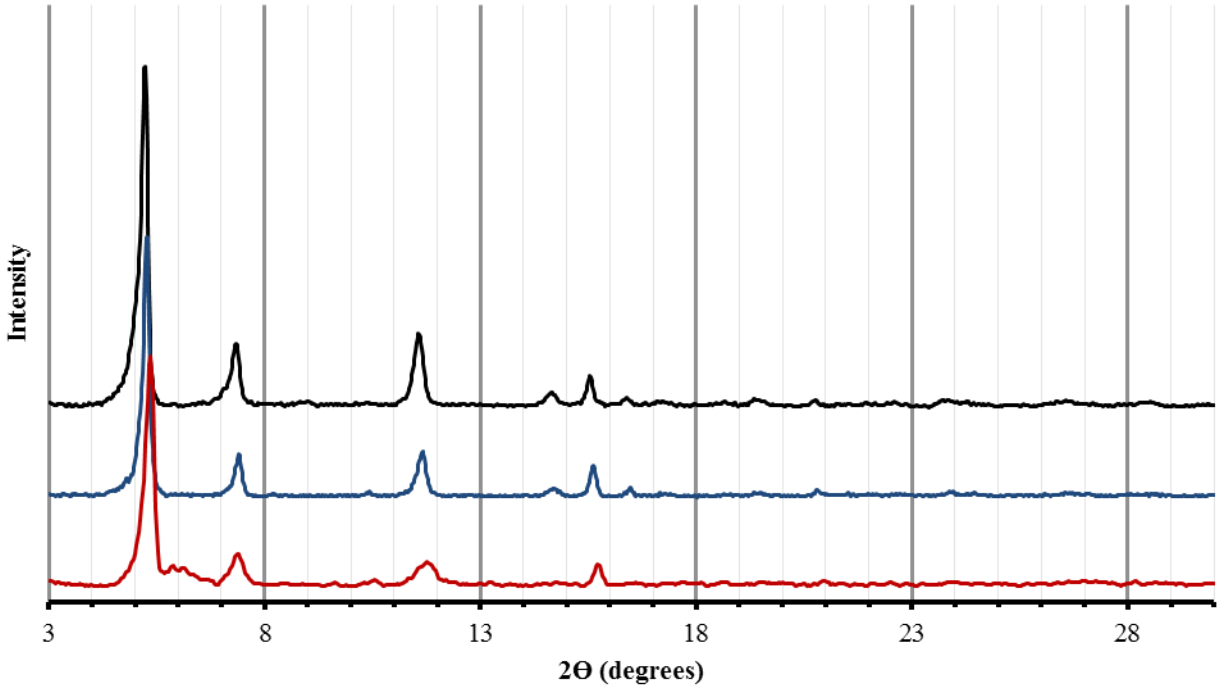


Figure S 1: An enlarged image of the PXRD patterns shown in the manuscript of 1 (red), 2 (blue) and of the sulfone sample[1] (black).

2. Disproportionation reaction of H_2L^1 to H_2L^2 and H_2L^3 during synthesis

The presence of sulfone can be explained by considering the diagram below (Fig S 2). During synthesis two sulfoxide ligands come together and undergo a disproportionation reaction.[2-5] The sulfide that is produced is then oxidized regenerating sulfoxide. Direct oxidation of sulfides to sulfoxides is easier to achieve than direct oxidation of sulfoxides to sulfones.[3, 5]

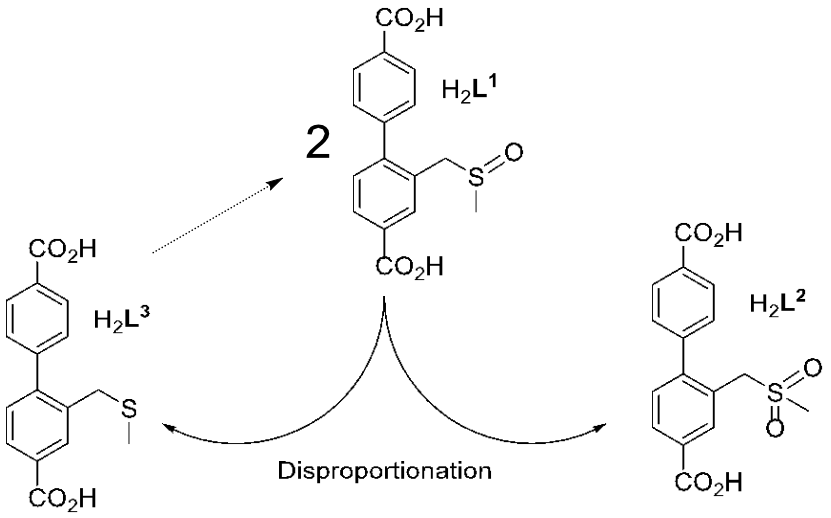


Figure S 2: Disproportionation chemistry by which H_2L^2 can be formed during solvothermal synthesis and be incorporated into the crystals of MOF **1**.

3. TG-DTA Data

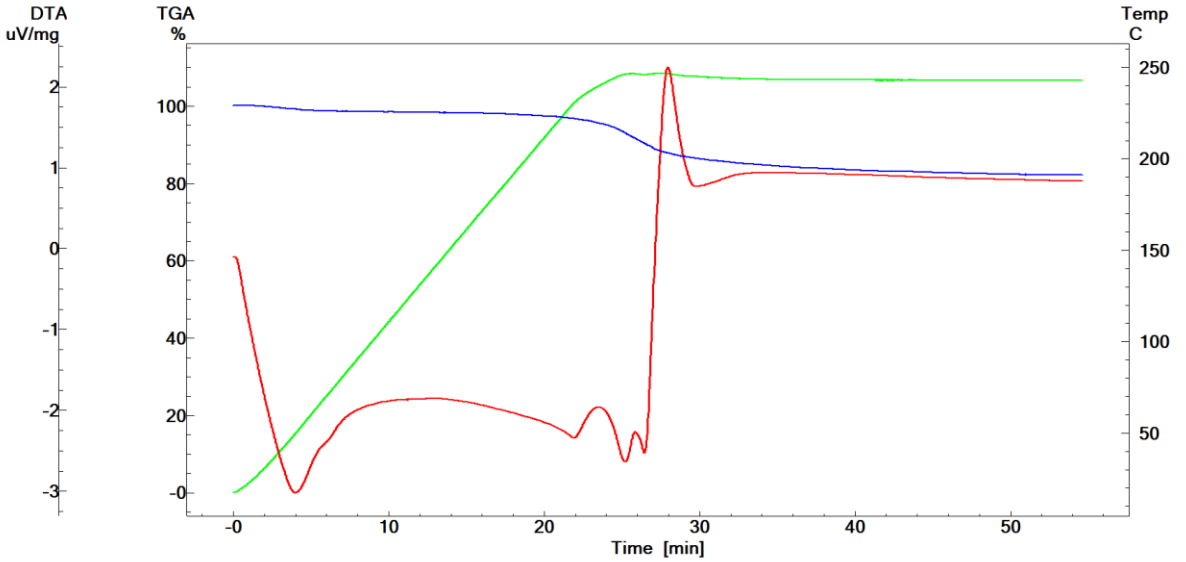


Figure S 3: TG-DTA of H_2L^1, holding at 245 °C for 30 minutes. Blue line is the TG curve; red line is DT curve; green line is temperature program.

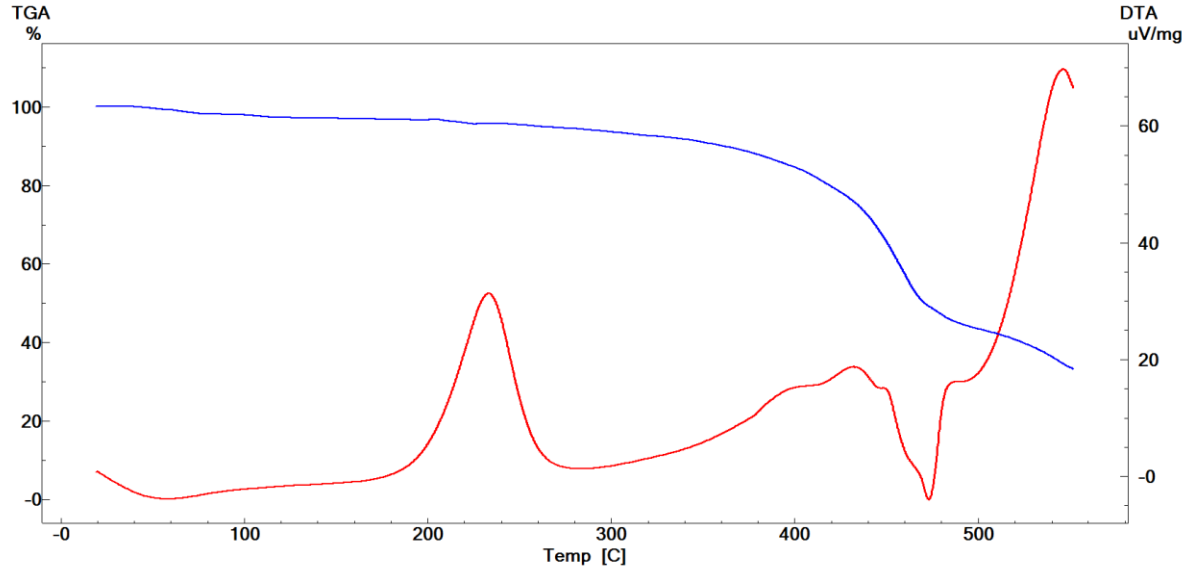


Figure S 4: An enlarged image of the TG-DTA of **1** shown in the manuscript, with weight loss calculations by TA-60 software. Blue line is the TG curve; red line is DT curve.

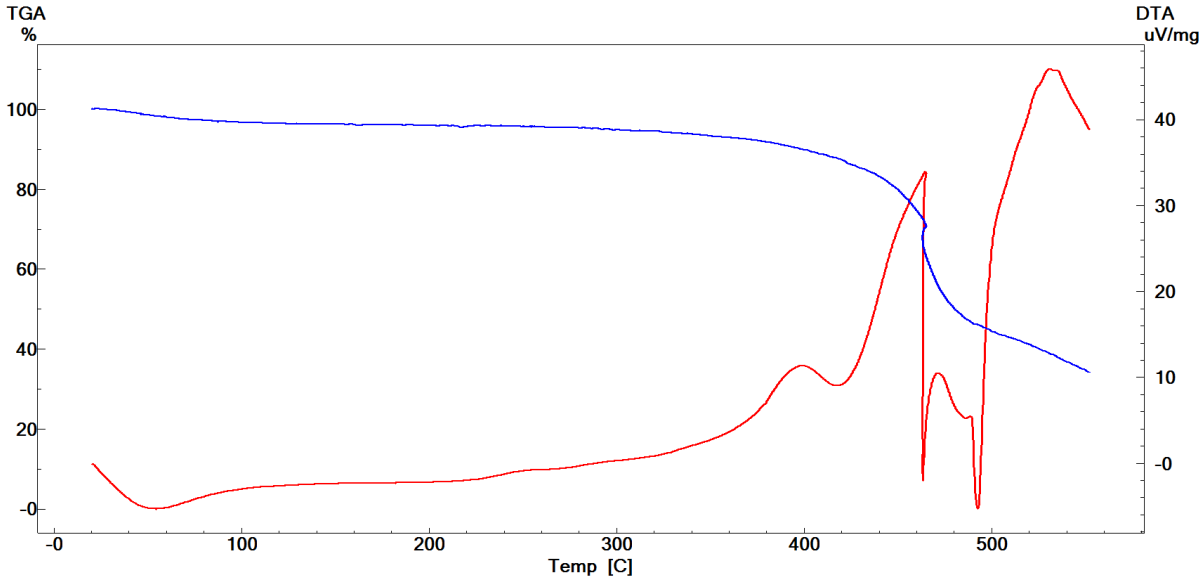


Figure S 5: TG-DTA of **2**. Blue line is the TG curve; red line is DT curve.

4. NMR Spectra for H_2L^1

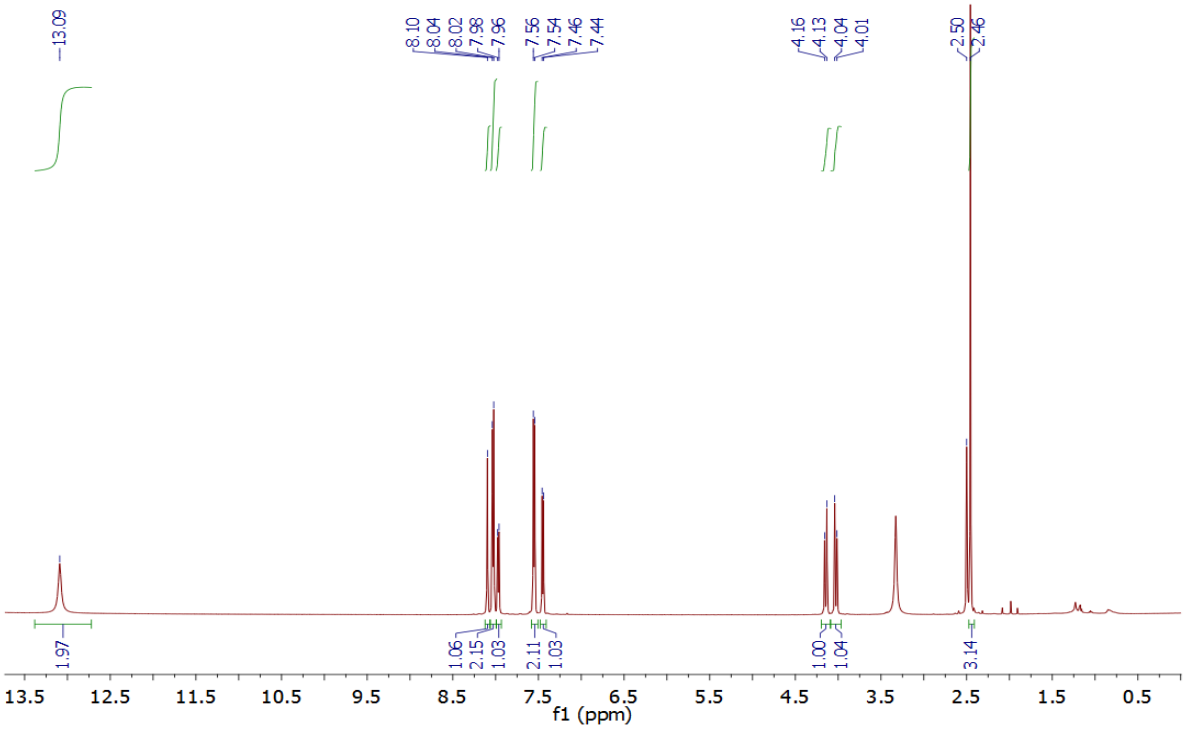


Figure S 6: ^{1}H NMR spectrum of 2-((methylsulfinyl)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylic acid, $H_2\mathbf{L^1}$; solvent: d_6-DMSO.

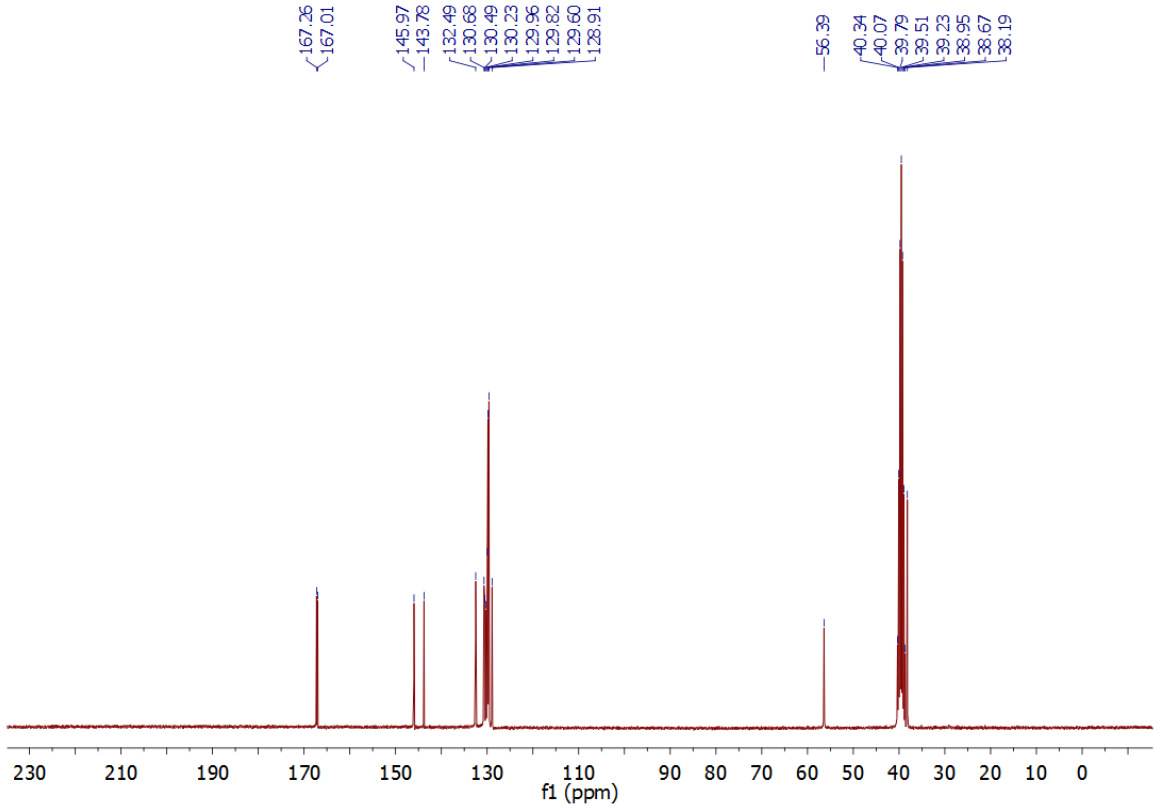


Figure S 7: ^{13}C NMR spectrum of 2-((methylsulfinyl)methyl)-[1, 1'-biphenyl]-4, 4'-dicarboxylic acid, $H_2\mathbf{L^1}$; solvent: d_6-DMSO.

5. ^{1}H NMR Spectra for Digested Samples

For H_2**L**^{1} and H_2**L**^{2}, the CH_2 protons were used for integration. For H_2**L**^{3}, the CH_3 protons were used. For H_2**L**^{4}, the aldehyde CH proton was used. Peaks used in integration are highlighted; H_2**L**^{1} (green cross), H_2**L**^{2} (red asterisk), H_2**L**^{3} (orange circle), H_2**L**^{4}(blue triangle).

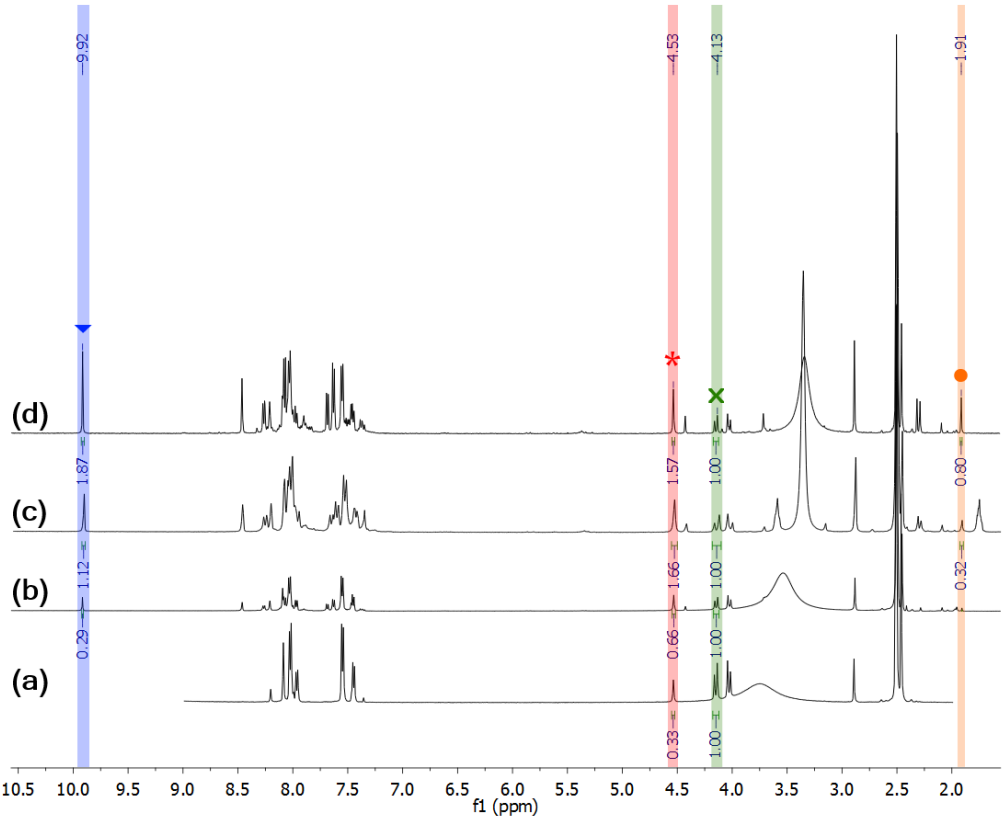
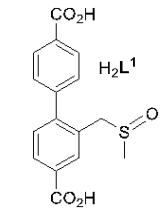
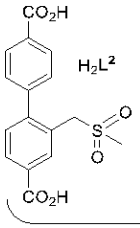
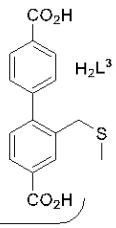


Figure S 8: ^{1}H NMR spectra of samples digested in DCl and d_6-DMSO of **1** (a), and **2** after 30 minutes (b), 180 minutes (c), and 300 minutes (d) at 240 °C.

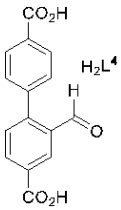


NMR data; This work





NMR data;
Chem. Commun., 2009, 4218-4220.



NMR data;
Angew. Chemie Int. Ed., 2008, **47**, 8482-8486.

6. Mass Spectrometry Data

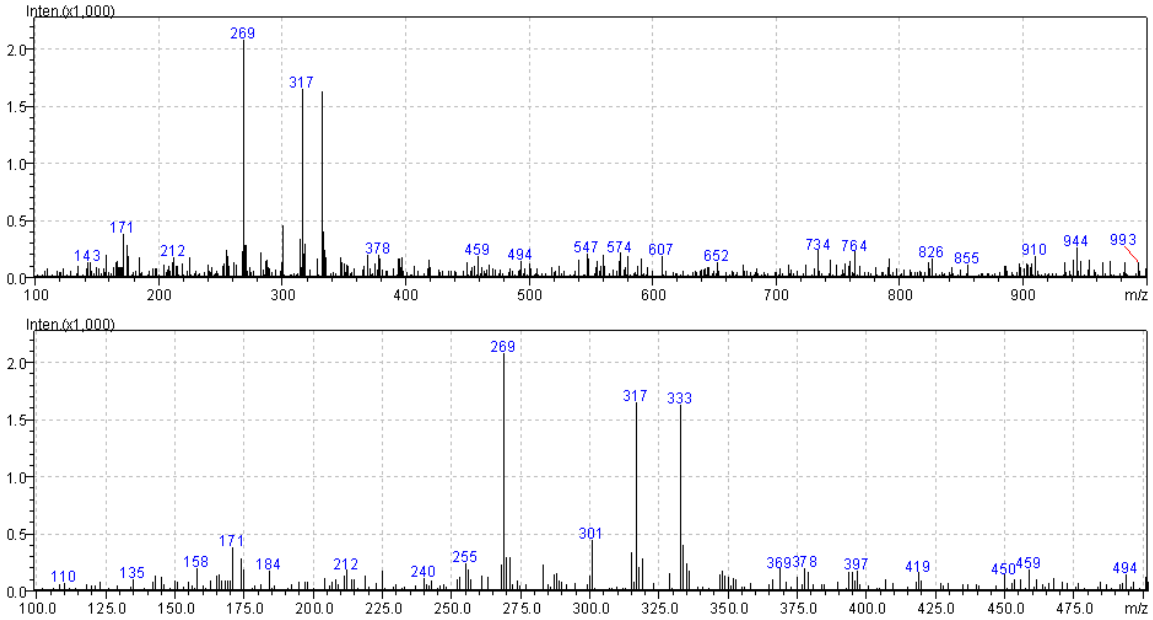
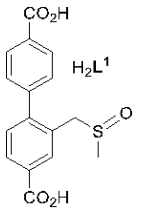
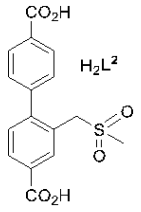


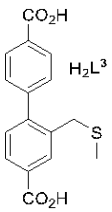
Figure S 9: Low-resolution negative-mode electrospray ionization mass spectrum of **1** heated to 240 °C for 30 mins. Top: Spectrum from 100 to 1000 m/z, Bottom: Expanded view of spectrum from 100 to 500 m/z. $[H_2\mathbf{L^1}\text{-}H]^-$ = 317 m/z, $[H_2\mathbf{L^2}\text{-}H]^-$ = 333 m/z, $[H_2\mathbf{L^3}\text{-}H]^-$ = 301 m/z, $[H_2\mathbf{L^4}\text{-}H]^-$ = 269 m/z.



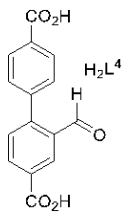
Chemical Formula: $C_{16}H_{14}O_5S$
Exact Mass: 318.1



Chemical Formula: $C_{16}H_{14}O_6S$
Exact Mass: 334.1



Chemical Formula: $C_{16}H_{14}O_4S$
Exact Mass: 302.1



Chemical Formula: $C_{15}H_{10}O_5$
Exact Mass: 270.1

7. BET Surface Area Calculations

BET summary for 1		
Slope	1.976	
Intercept	1.89e-03	
Correlation coefficient, r	0.999978	
C constant	1046.492	
Surface Area	1760.609 m²/g	
Relative Pressure	**Volume @ STP**	**1 / [W((Po/P) - 1)]**
9.00e-03	365.5448	1.99e-02
1.00e-02	371.2658	2.19e-02
1.20e-02	379.3726	2.57e-02
1.52e-02	388.2207	3.19e-02
2.66e-02	403.8505	5.42e-02
4.03e-02	413.2205	8.14e-02
5.27e-02	418.664	1.06e-01

BET summary for 2		
Slope	1.52	
Intercept	1.58e-03	
Correlation coefficient, r	0.999981	
C constant	962.461	
Surface Area	2289.411 m²/g	
Relative Pressure	**Volume @ STP**	**1 / [W((Po/P) - 1)]**
8.11e-03	465.9707	1.40e-02
9.02e-03	474.4855	1.53e-02
1.00e-02	481.8444	1.68e-02
1.20e-02	491.6319	1.98e-02
1.53e-02	503.1944	2.47e-02
2.75e-02	523.4984	4.32e-02
4.00e-02	533.5512	6.25e-02

8. References

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2. H. H. Szmant, in *Organic Sulfur Compounds*, ed. N. Kharasch, Pergamon, 1961, pp. 154-169.
3. *USA Pat.*, US2870215 A, 1959.
4. A. Wzorek, K. D. Klika, J. Drabowicz, A. Sato, J. L. Acena and V. A. Soloshonok, *Org. Biomol. Chem.*, 2014, **12**, 4738-4746.
5. L. Field and G. T. Bowman, *J. Org. Chem.*, 1981, **46**, 2771-2775.