Electronic Supplementary Material (ESI) for Dalton Transactions.

Influence of solvent on the synthesis of Zn^{II}-5-methoxy isophthalate MOFs

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Supporting Information

S1. Powder X-ray Diffraction

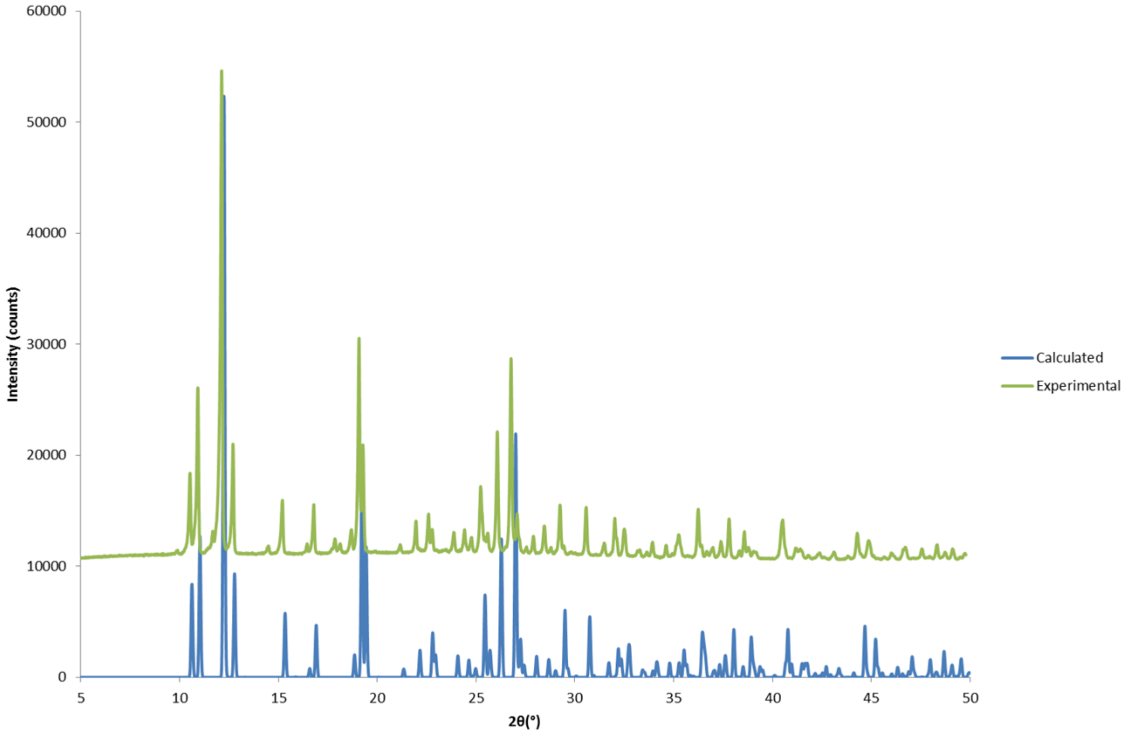


Figure S1.1: Comparison of calculated and experimental powder diffraction patterns of Compound **1** $Zn_2(HMeOip)(MeOip)(OAc)$.

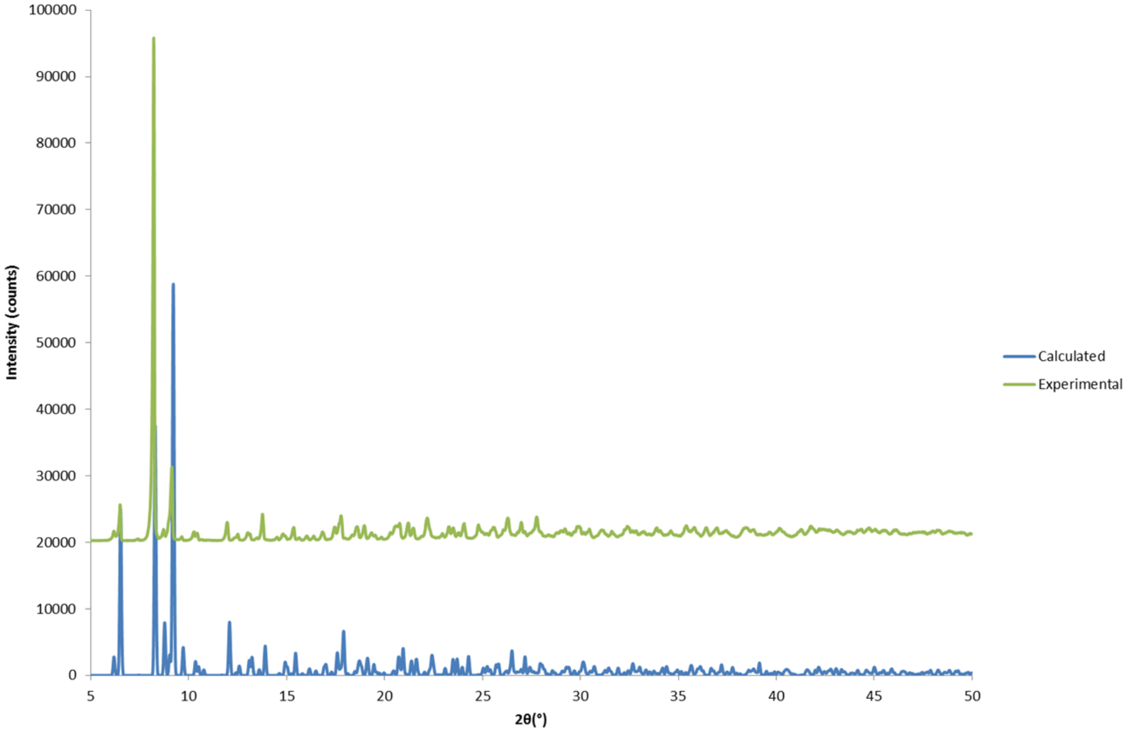


Figure S1.2: Comparison of calculated and experimental powder diffraction patterns of Compound **2** $Zn_6(MeOip)_{4.5}(HMeOip)(OH)_2(H_2O)_2 \cdot 5.5H_2O$.

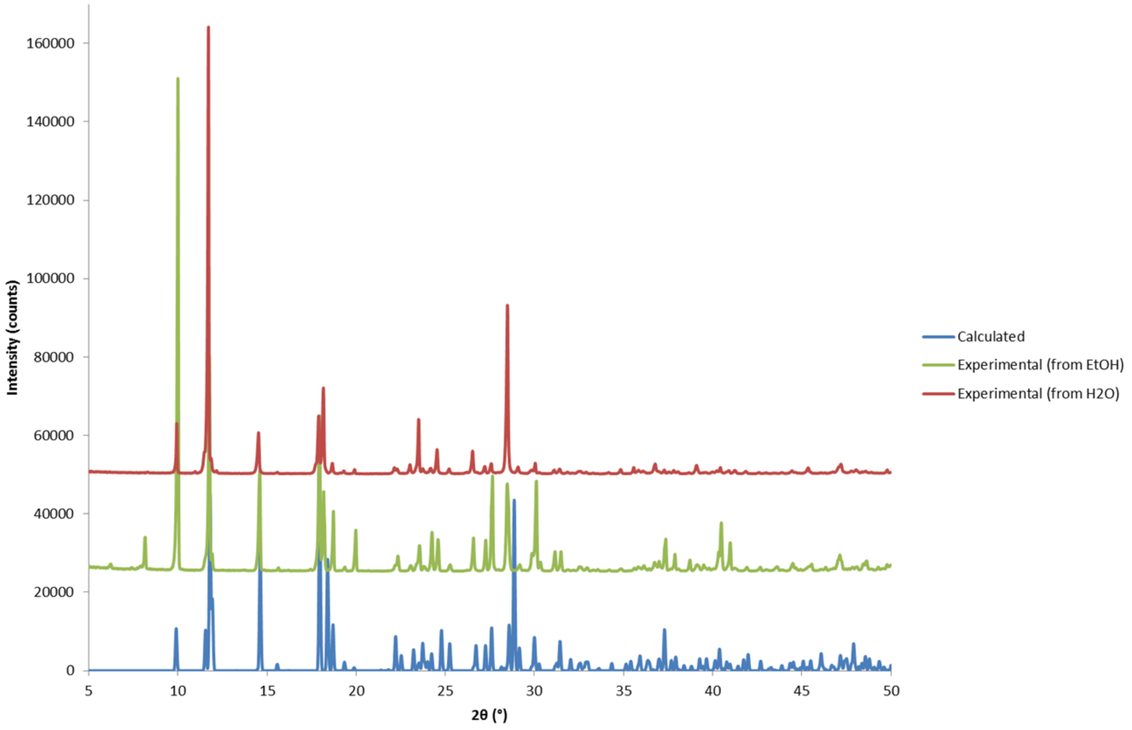


Figure S1.3: Comparison of calculated and experimental powder diffraction patterns of Compound **3** $Zn(MeOip)(H_2O)_2\ H_2O$.

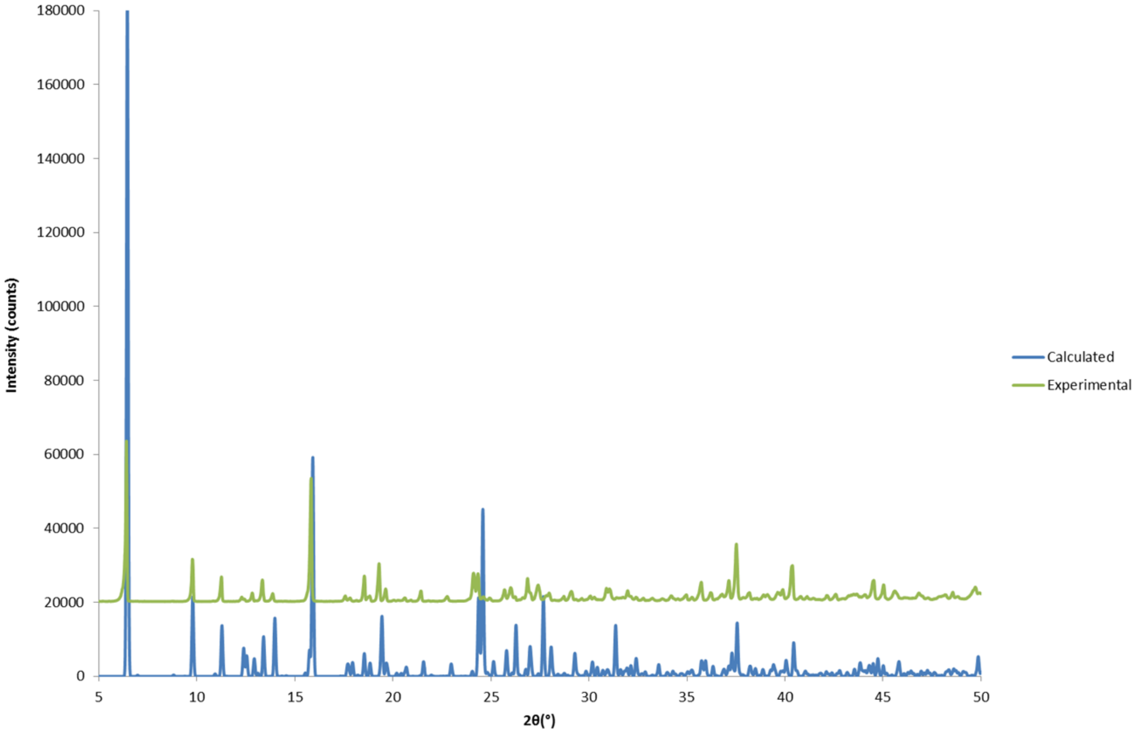


Figure S1.4: Comparison of calculated and experimental powder diffraction patterns of Compound **4** $Zn_5(MeOip)_4(OH)_2(H_2O)_4{\cdot}H_2O$.

S2. Thermogravimetric Analyses

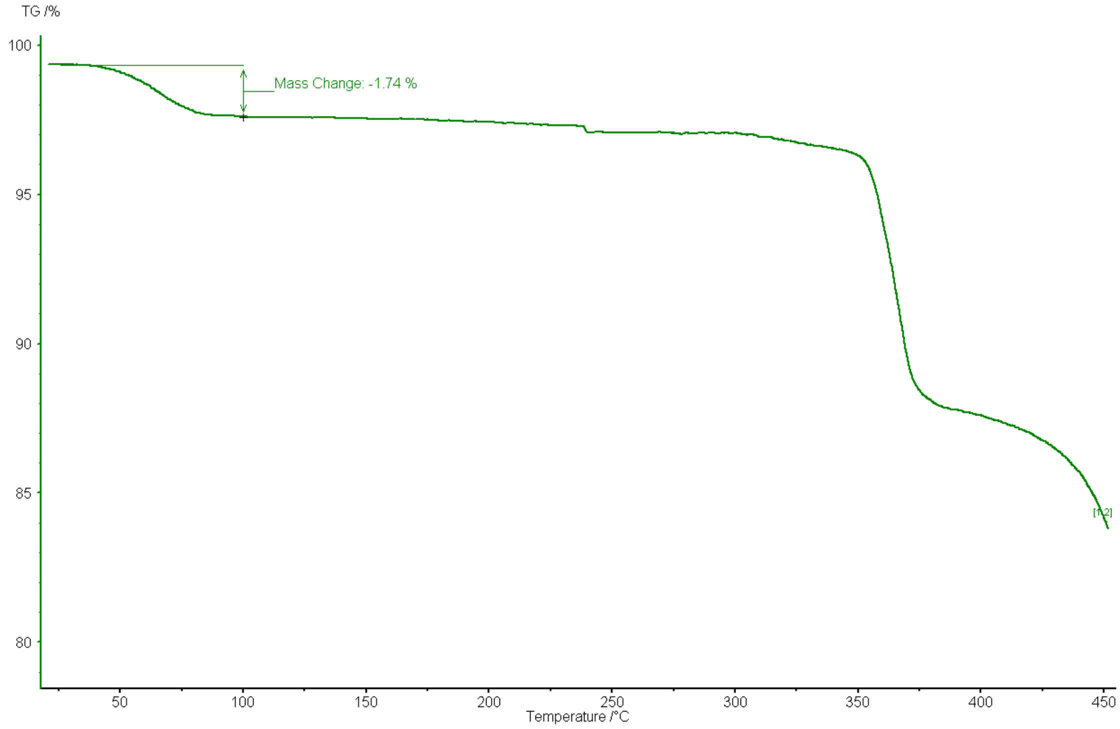


Figure S2.1: Thermogravimetric analysis trace for Compound **1** $Zn_2(HMeOip)(MeOip)(OAc)$. The mass loss occurring over the 25 to 100°C range (1.74%) is presumed to be loss of surface water.

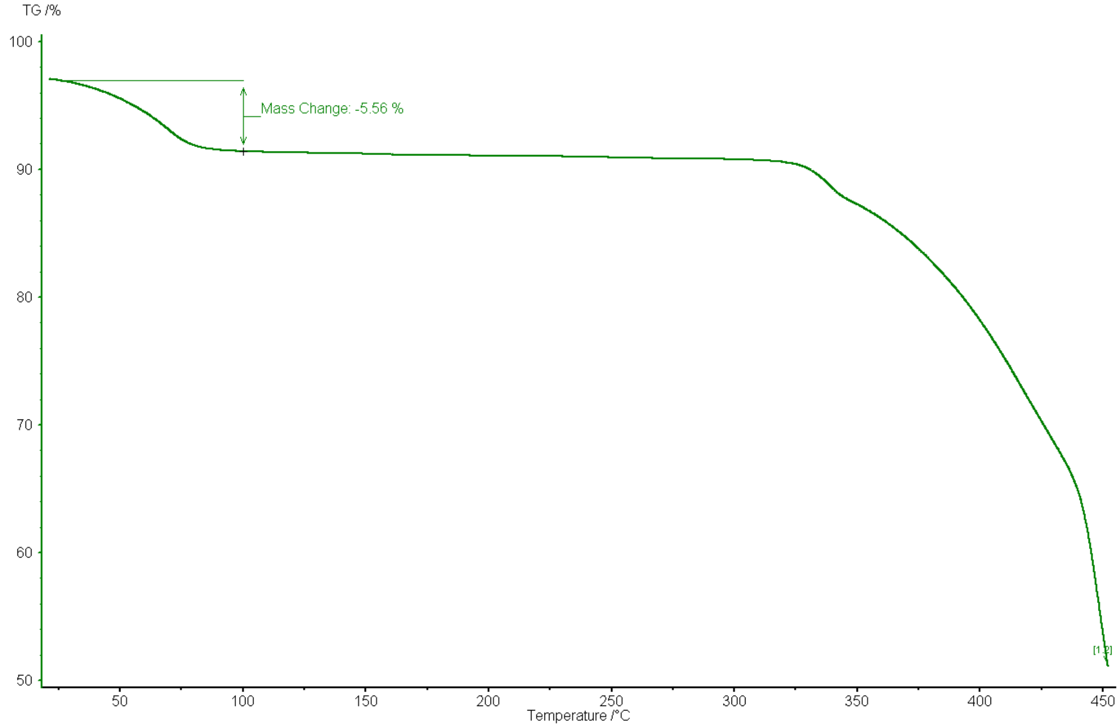


Figure S2.2: Thermogravimetric analysis trace for Compound **2** $Zn_6(MeOip)_{4.5}(HMeOip)(OH)_2(H_2O)_2 \cdot 5.5H_2O$. The mass loss that occurs between 25 and 100°C (5.56%) corresponds to the loss of both coordinated water molecules and 3.00 water molecules from within the channels (5.68%).

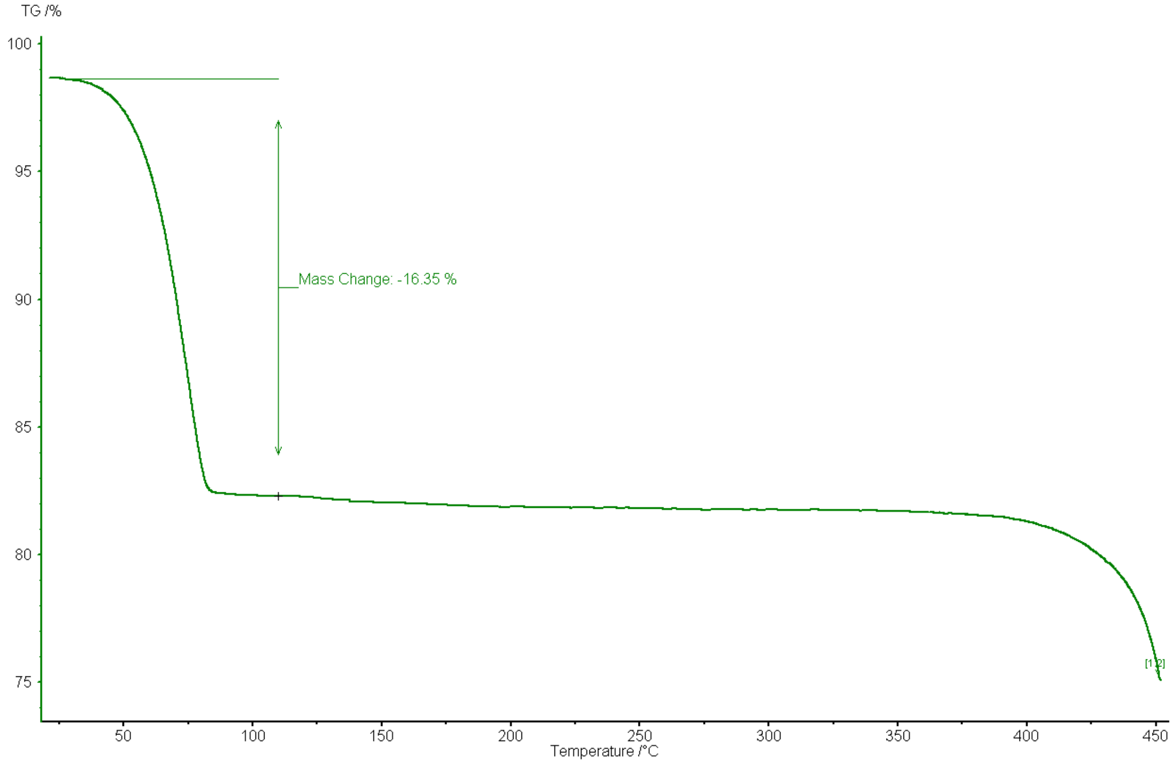


Figure S2.3: Thermogravimetric analysis trace for Compound **3** Zn(MeOip)$(H_2O)_2$ H_2O. The mass loss that occurs between 25 and 100°C (16.35%) corresponds to the loss of 2.85 water molecules (16.37%).

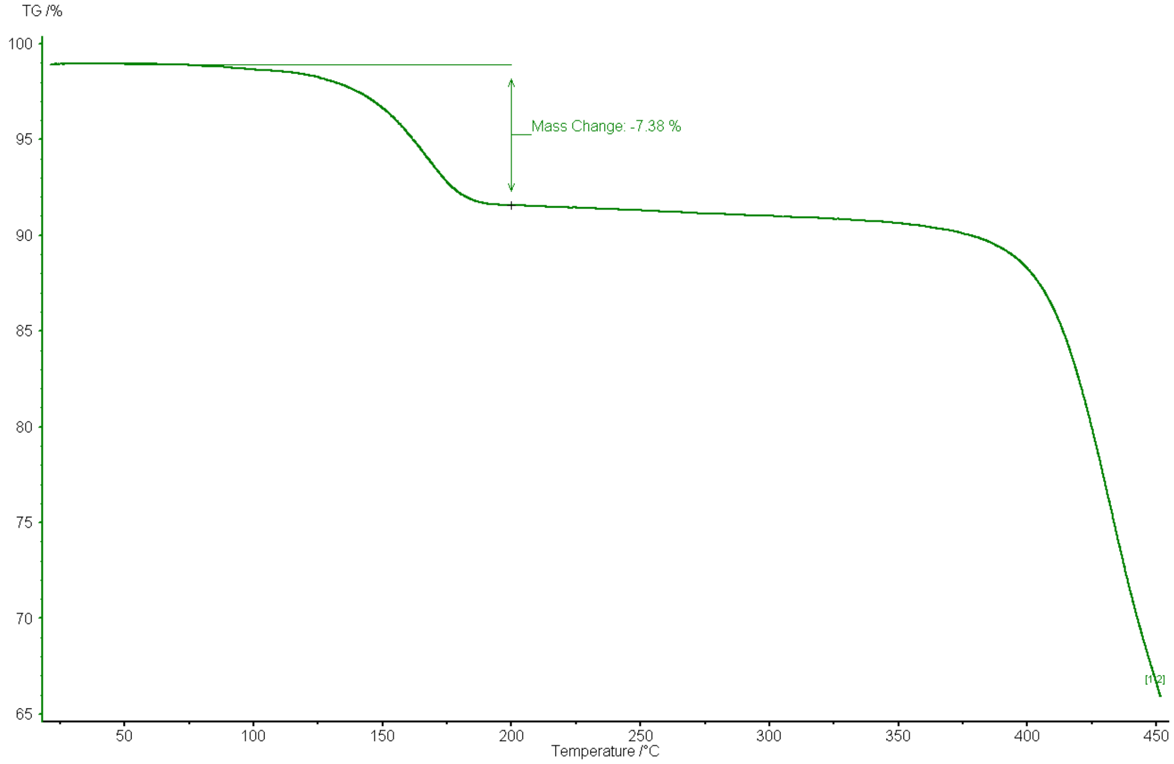


Figure S2.4: Thermogravimetric analysis trace for Compound **4** $Zn_5(MeOip)_4(OH)_2(H_2O)_4{\cdot}H_2O$. The mass loss that occurs between 25 and 200°C (7.38%) corresponds to the loss of 5.00 water molecules (7.34%).

S3. Details of Nitric Oxide Release Experiments

S3.1 Nitric Oxide Release Measurement Experimental Details

NO release measurements were performed using a Sievers NOA 280 (Compound **4**) or 280i (Compound **2**) chemiluminescence Nitric Oxide Analyser. The instrument was calibrated using air passed through a zero filter (< 1 ppb NO) and 87.6 ppm NO gas in N_2 (Air Products). The flow rate through the instrument was set to 200 mL/min with a cell pressure of approximately 5.2 Torr and an oxygen pressure of 6.0 psig. Nitrogen gas of known humidity was achieved by passing dry N_2 over a saturated aqueous solution of LiCl to give 11% relative humidity. Humid N_2 was passed over the powders at room temperature, and the resulting NO/N_2 mixture was then passed through the analyser and the NO concentration recorded at 1 second intervals. Loaded sample mass used values were weighed by difference, and so represent the mass of sample used in a given measurement. Data collection was stopped after the concentration of NO in the carrier gas dropped below 20 ppb.

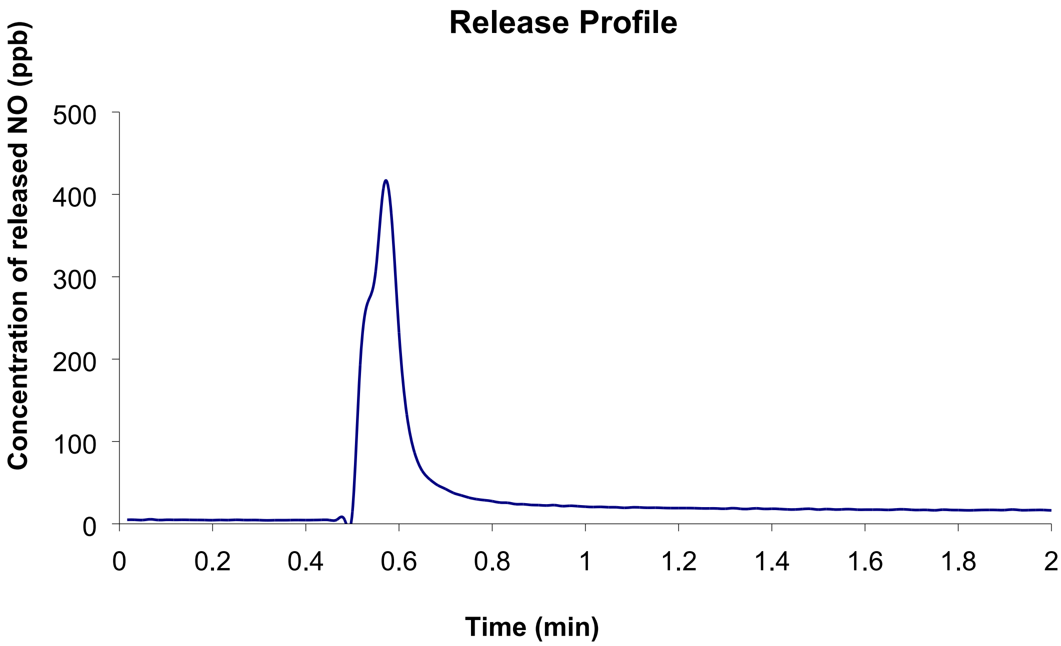
*S3.2 Summary of Nitric Oxide Release Experiments on Compound **2***

Sample number	Pre-loaded weight (mg)	Loaded weight (mg)	Peak NO release concentration (ppb)	Total amount of NO released after 120 s (nmol/g)
1	20.5	17.8	407	29.6
2	20.1	18.4	248	22.3
3	20.2	19.3	226	18.7
4	2.03	17.7	175	16.6

*S3.3 Summary of Nitric Oxide Release Experiments on Compound **4***

Sample number	Pre-loaded weight (mg)	Loaded weight (mg)	Peak NO release concentration (ppb)	Total amount of NO released after 60 s (nmol/g)
1	14.4	12.3	337	17.4
2	14.0	9.2	177.9	13.5
3	14.0	12.2	254.2	13.5
4	14.2	11.1	442	22.3
5	14.3	12.6	479.1	23.1

*S3.4 Plots of Nitric Oxide release experiments on Compound **2***



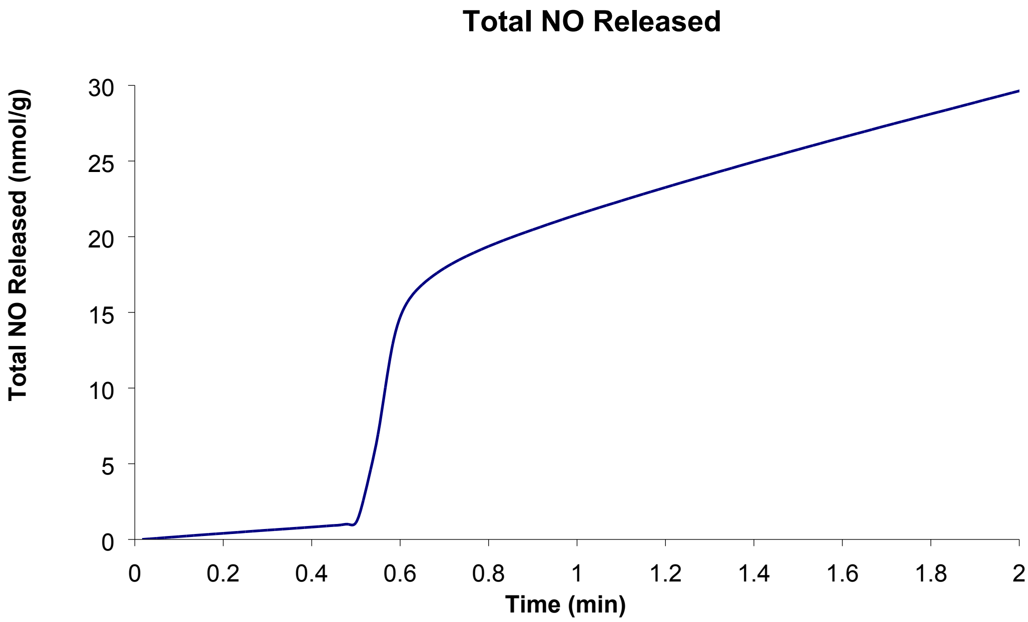


Figure S3.4.1: Plots of the nitric oxide release profile and total nitric oxide released by sample 1 of Compound **2**.

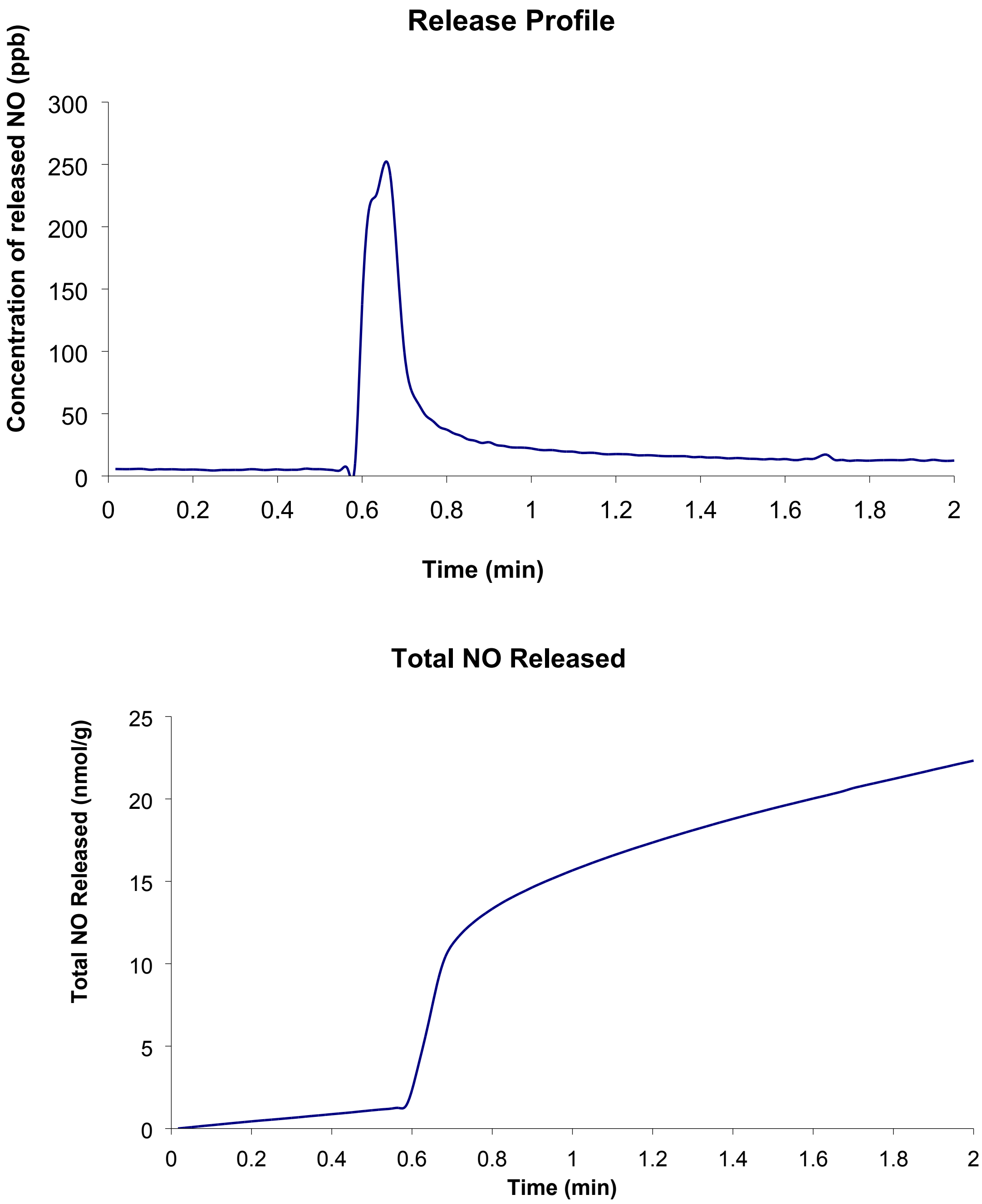


Figure S3.4.2: Plots of the nitric oxide release profile and total nitric oxide released by sample 2 of Compound **2**.

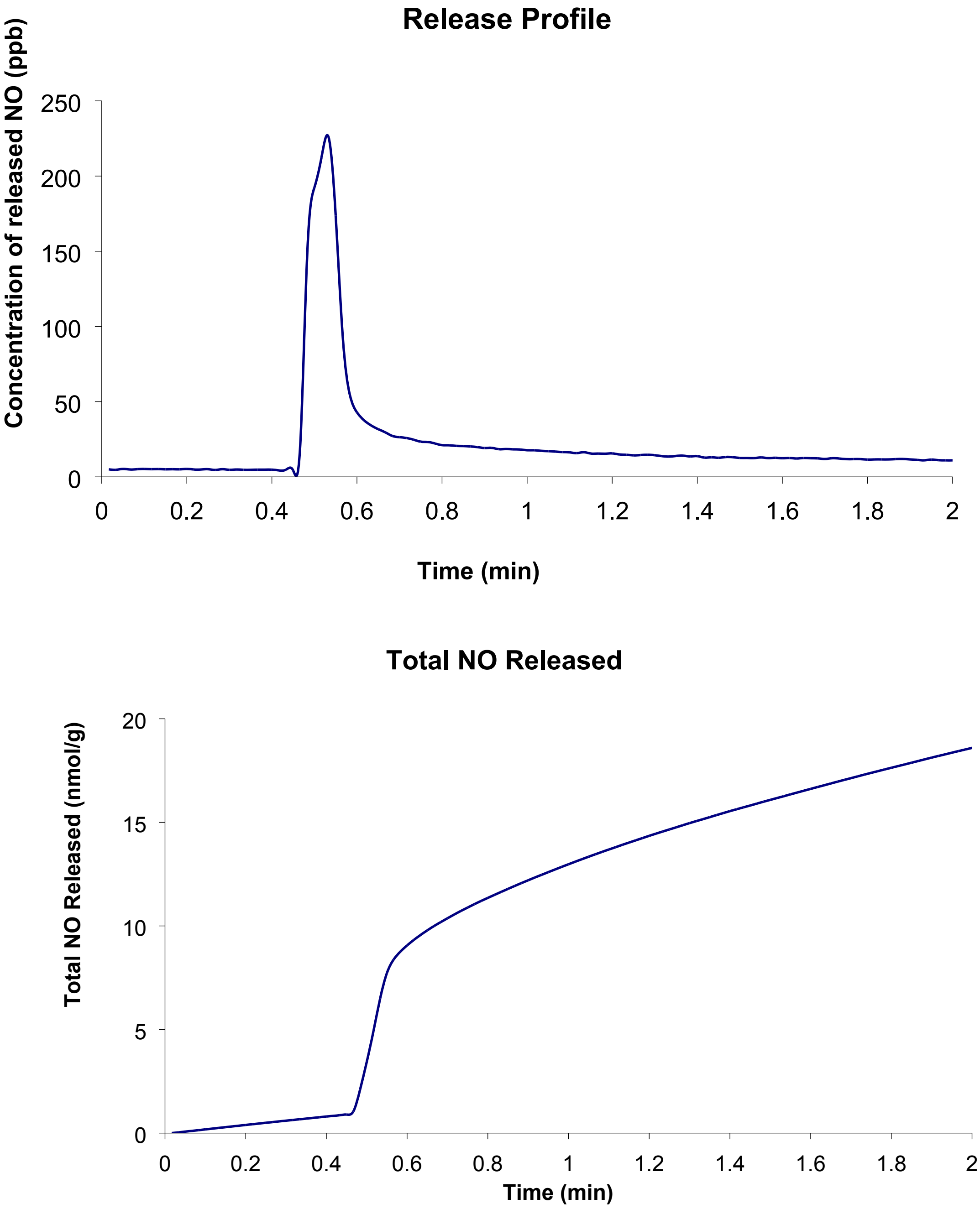
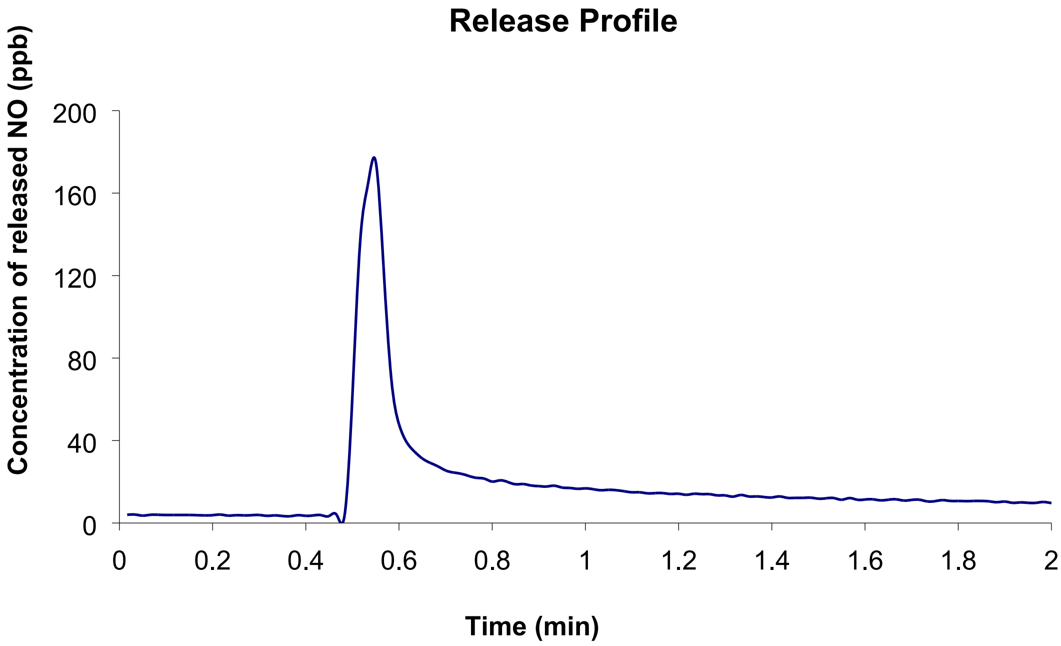


Figure S3.4.3: Plots of the nitric oxide release profile and total nitric oxide released by sample 3 of Compound **2**.



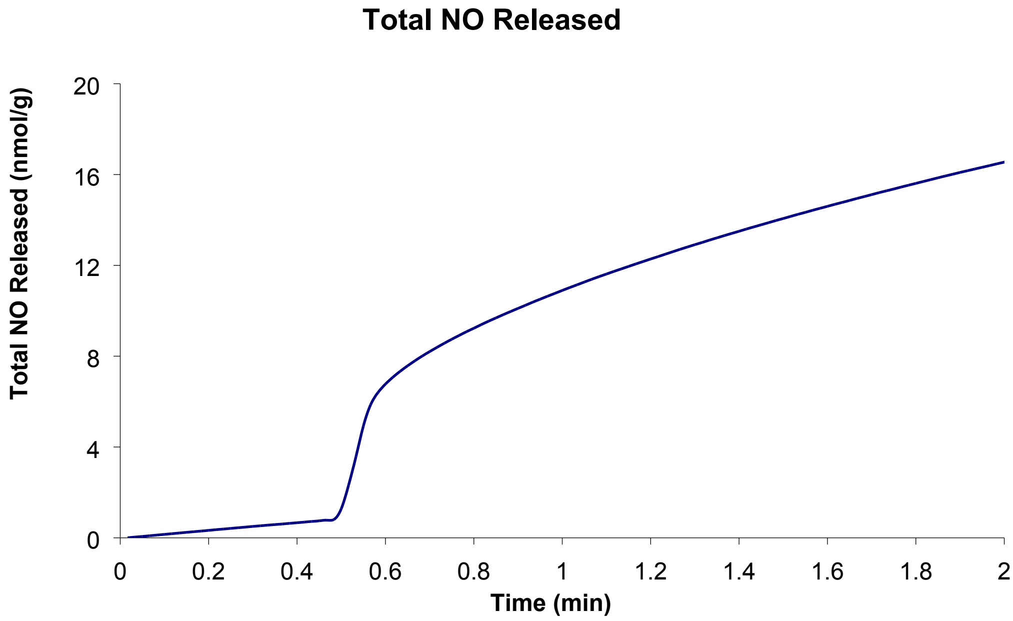


Figure S3.4.4: Plots of the nitric oxide release profile and total nitric oxide released by sample 4 of Compound **2**.

*S3.5 Plots of Nitric Oxide release experiments on Compound **4***

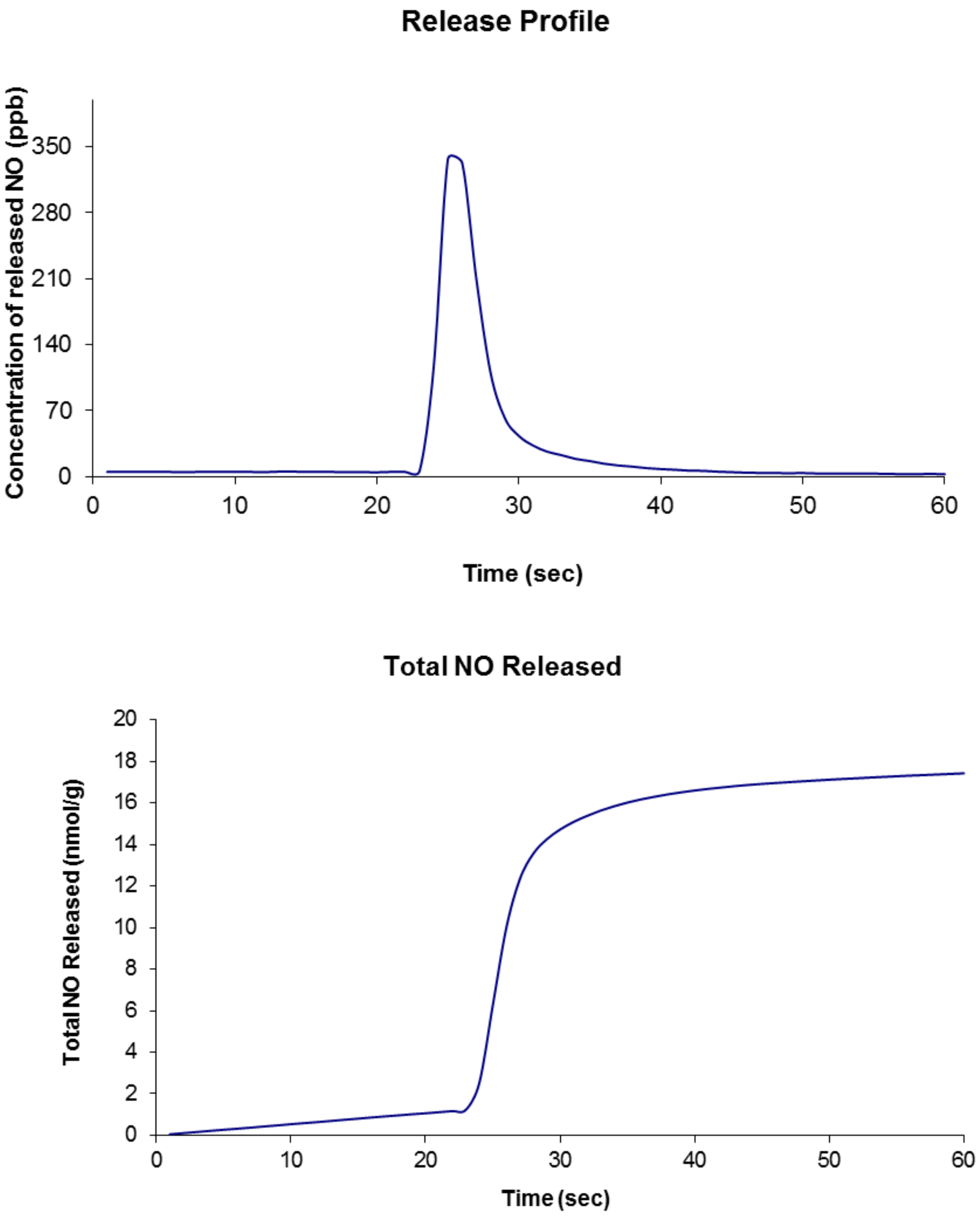


Figure S3.5.1: Plots of the nitric oxide release profile and total nitric oxide released by sample 1 of Compound **4**.

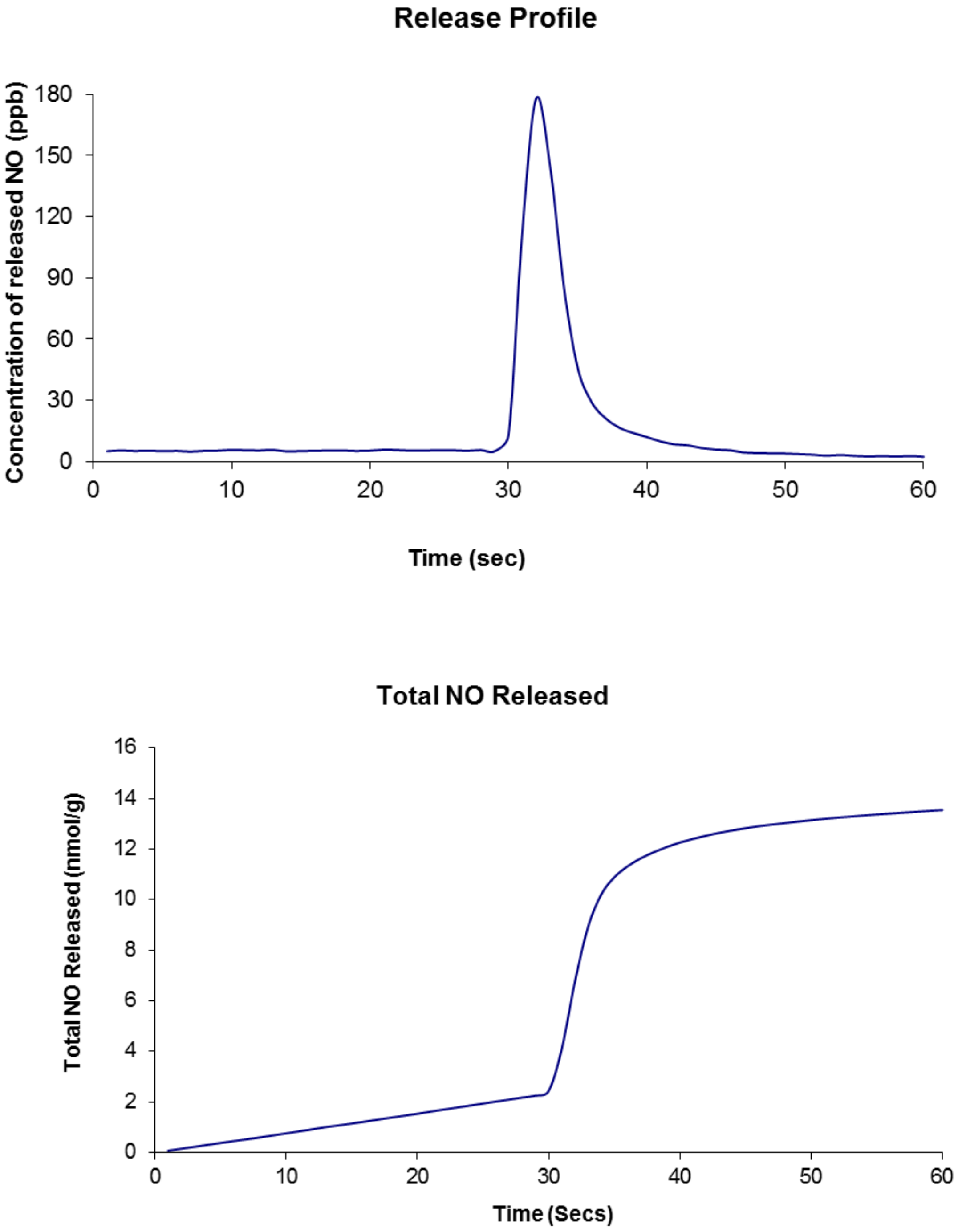
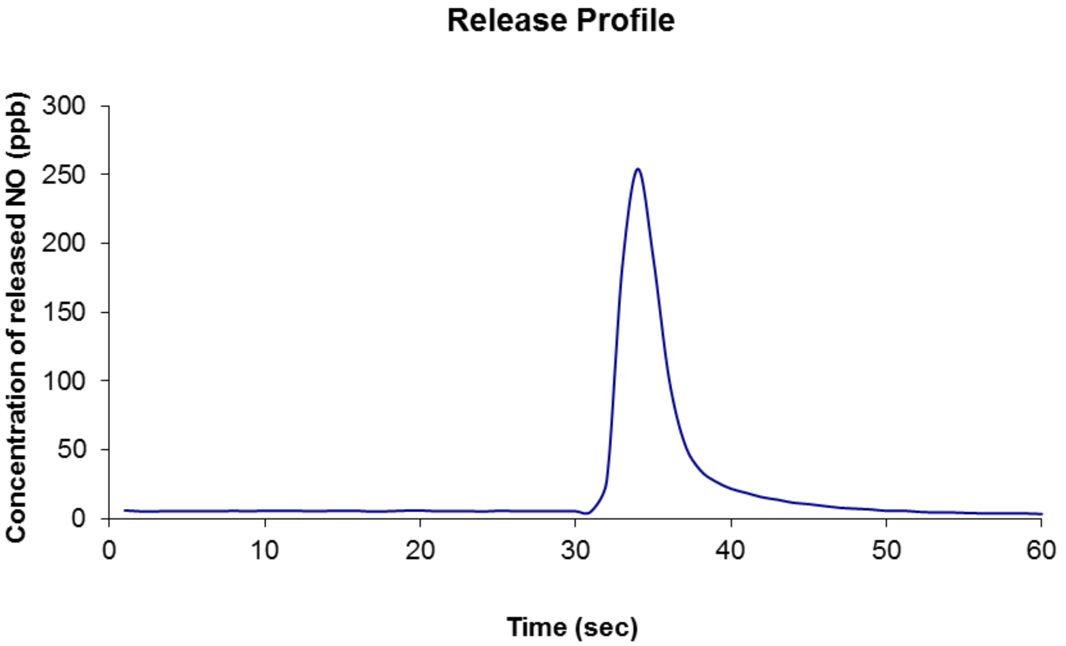


Figure S3.5.2: Plots of the nitric oxide release profile and total nitric oxide released by sample 2 of Compound **4**.



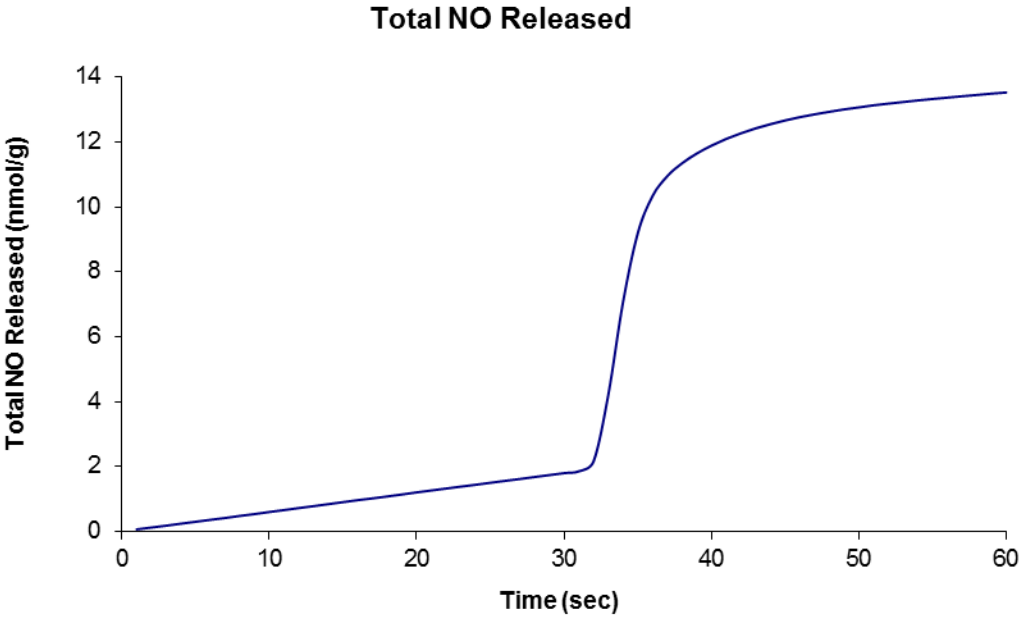


Figure S3.5.3: Plots of the nitric oxide release profile and total nitric oxide released by sample 3 of Compound **4**.

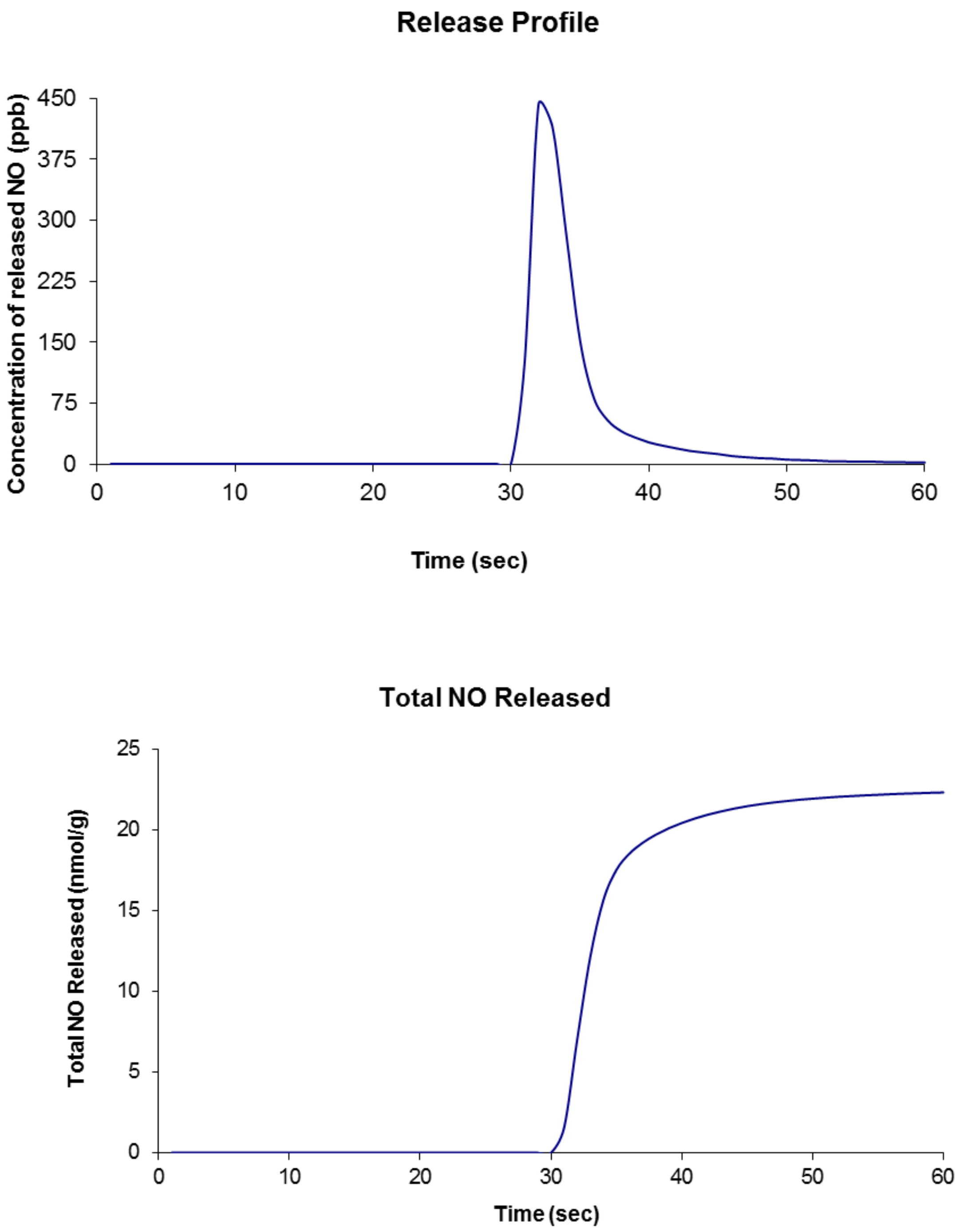
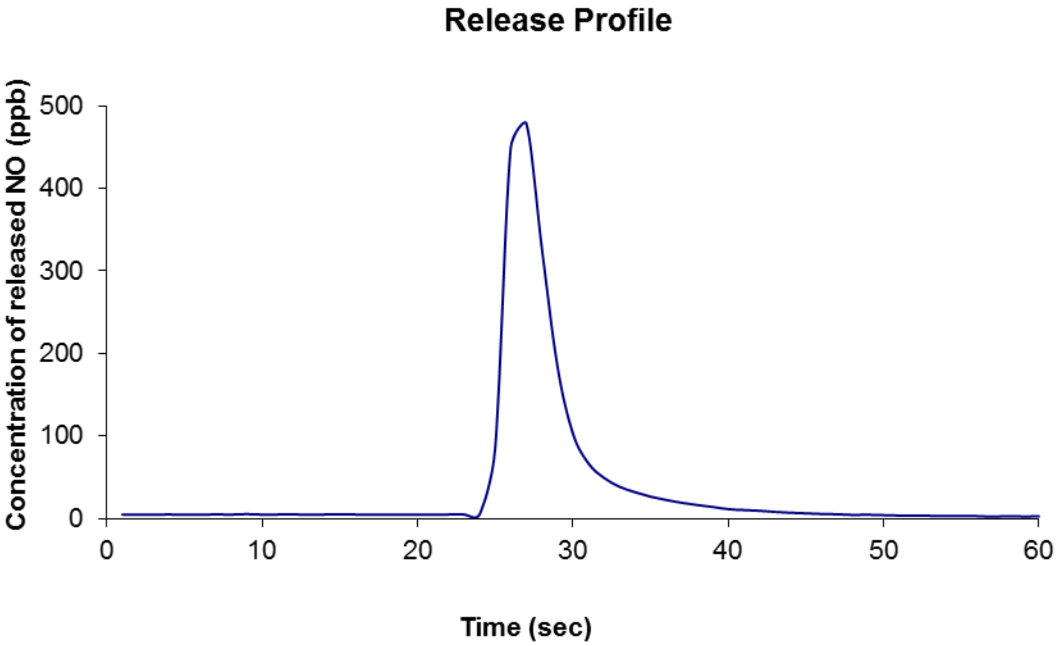


Figure S3.5.4: Plots of the nitric oxide release profile and total nitric oxide released by sample 4 of Compound **4**.



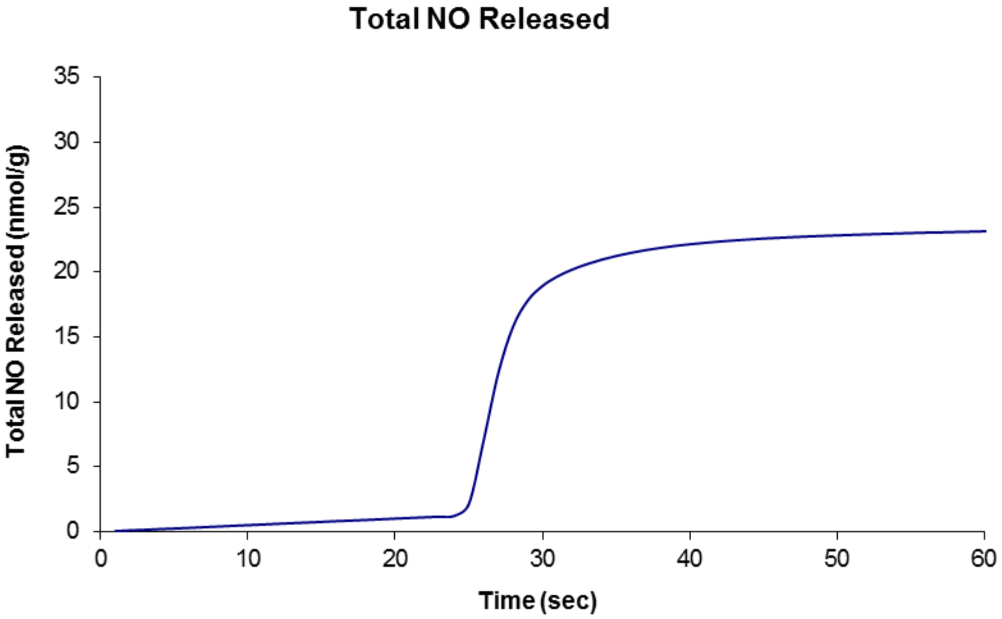


Figure S3.5.5: Plots of the nitric oxide release profile and total nitric oxide released by sample 5 of Compound **4**.

S4. Additional Crystallographic Information on Compound 2

Elongated anisotropic thermal displacement parameters were observed for four of the six 5-methoxy isophthalate ligands, which lead to each of the ligands being partially modelled over two sites with complementary site occupancy factors. Ligands involving C10-C18 and C19-C27 displayed rotational disorder of aromatic ring hinged at the carboxylate linkages and three of the six aromatic carbon atoms, as well as both non-hydrogen atoms of the methoxy group, were modelled over two sites. Ligands involving C1-C9 showed similar disorder of the methoxy groups, which have been modelled over two sites less than 1 Å apart. Disorder of the methoxy group of the C46-C51 ligand occurs over two pairs of symmetry-related sites. A small amount of rotational disorder of the O18-C32-O19 is observed, and O18 has been modelled over two sites of complementary occupancy. Attempts were made to model O19 over two sites, however these attempts were unsuccessful.

Large peaks of electron density located in the channels of the 3D framework were assigned as the oxygen atoms of partial occupancy water molecules. The isotropic thermal displacement parameters of these oxygen atoms were fixed at 0.08 and their site occupation factors were allowed to refine. The group of water molecules O109-O112-O100-O107-O113 are located within a short distance of each other and the sum of the groups O100-O109-O112 and O100-O107-O113 were each greater than 1. Each atom was given a unique site occupation factor and the sums of those within each group were constrained to sum to 1 whilst letting the isotropic thermal displacement parameter refine. The central O100 refined well, but the four peripheral oxygen atoms had large thermal displacement parameters so these were fixed at 0.08 and the refinement repeated. The site occupation factors of the oxygen atoms nearest O100 (O112 and O107) refined to similar values of approximately 0.32, so these atoms were given a common site occupation factor. Likewise O113 and O109 refined to give similar site occupancy factors of approximately 0.27, so these were given a common site occupation factor and allowed to refine. The sum of the three site occupancy factors was constrained to sum to 1 (actual value 1.03).

Refinement of Compound **2** shows a peak of electron density (Q1) of 1.60 e/Å^3 located approximately 1.3 Å from O19, making a Zn-O-Q1 angle of approximately 116°. Initial attempts were made to model this peak as a partial occupancy carbon atom, which refined to site occupancy of 0.35. This partial methylation of the carboxylate group did not make chemical sense, so the peak was assigned as a carboxylic hydrogen atom and fixed at a distance of 0.90 Å from O19.

The C-C bond distance between C31 and C32 refined to just over 1.6 Å, so this bond length was constrained to 1.5 Å

S5. Selected bond lengths and angles for Compounds 1 – 4

*S5.1 Selected bond lenths and angles for Compound **1***

Table S5.1.1: Bond lengths [Å] and angles [°] forCompound **1**.

O(1)-Zn(1)	1.934(2)	O(1A)-Zn(1)-O(3)^{IV}	125.66(7)
O(1A)-Zn(1)	1.923(2)	O(1A)-Zn(1)-O(1)	102.27(7)
O(3)-Zn(1)^{II}	1.9319(19)	O(3)^{IV}-Zn(1)-O(1)	111.56(8)
O(4)-Zn(1)^{III}	1.9506(18)	O(1A)-Zn(1)-O(4)^{III}	109.82(8)
Zn(1)-O(3)^{IV}	1.9319(19)	O(3)^{IV}-Zn(1)-O(4)^{III}	104.73(9)
Zn(1)-O(4)^{III}	1.9506(18)	O(1)-Zn(1)-O(4)^{III}	100.01(9)

Symmetry transformations used to generate equivalent atoms:
I: -x+1/2, y, -z+1/2 **II:** x+1/2, -y, z+1/2 **III:** -x+1, -y, -z+1
IV: x-1/2, -y, z-1/2

Table S5.1.2: Hydrogen bonds for Compound **1** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(2)...O(2)^{V}	0.84	1.61	2.435(3)	165.8
C(2A)-H(2A3)···O(4)^{VI}	0.98	2.90	3.565(4)	125.9
C(2A)-H(2A1)···O(4)^{VII}	0.98	3.04	3.565(4)	114.8
C(2A)-H(2A3)···O(3)^{VI}	0.98	3.15	3.601(4)	109.5
C(2A)-H(2A2)···O(3)^{VII}	0.98	2.89	3.601(4)	130.5

Symmetry transformations used to generate equivalent atoms:
I: -x+1/2, y, -z+1/2 **II:** x+1/2, -y, z+1/2 **III:** -x+1, -y, -z+1
IV: x-1/2, -y, z-1/2 **V:** -x+3/2, y, -z+1/2 **VI:** x-1/2, -y+1, z-1/2
VII: -x+1,-y+1,-z+1

*S5.2 Selected bond lenths and angles for Compound **2***

Table S5.2.1: Bond lengths [Å] and angles [°] for Compound **2**.

O(1)-Zn(6)^{III}	2.011(6)	Zn(4)-O(27)^{X}	2.072(6)
O(1H)-Zn(2)	1.976(5)	Zn(4)-O(7)^{V}	2.086(6)
O(1H)-Zn(3)^{IV}	2.032(5)	Zn(4)-O(1H)^{V}	2.093(5)
O(1H)-Zn(4)^{IV}	2.093(5)	Zn(4)-O(22)^{X}	2.435(6)
O(2)-Zn(1)	2.004(7)	Zn(6)-O(1)^{IX}	2.011(6)
O(1W)-Zn(1)	2.117(7)	Zn(6)-O(12)^{VII}	2.041(6)
O(2H)-Zn(5)	1.950(6)	Zn(6)-O(2H)^{XI}	2.083(5)
O(2H)-Zn(1)^{V}	2.061(6)	Zn(6)-O(22)^{XI}	2.116(6)
O(2H)-Zn(6)^{VI}	2.083(5)		
O(3)-Zn(3)^{IV}	2.221(7)	Zn(2)-O(1H)-Zn(3)^{IV}	115.5(3)
O(2W)-Zn(1)	2.106(8)	Zn(2)-O(1H)-Zn(4)^{IV}	117.2(3)
O(4)-Zn(2)	1.940(6)	Zn(3)^{IV}-O(1H)-Zn(4)^{IV}	101.9(2)
O(6)-Zn(2)	1.987(6)	Zn(5)-O(2H)-Zn(1)^{V}	112.6(3)
O(7)-Zn(4)^{IV}	2.086(6)	Zn(5)-O(2H)-Zn(6)^{VI}	114.2(3)
O(8)-Zn(3)^{V}	2.052(6)	Zn(1)^{V}-O(2H)-Zn(6)^{VI}	107.4(2)
O(9)-Zn(4)^{V}	2.018(6)	Zn(6)^{VI}-O(22)-Zn(4)^{VIII}	103.1(2)
O(11)-Zn(2)	1.964(6)	O(23)^{III}-Zn(1)-O(2)	101.5(3)
O(12)-Zn(6)^{VII}	2.041(6)	O(23)^{III}-Zn(1)-O(2H)^{IV}	95.3(2)
O(13)-Zn(3)	1.942(6)	O(2)-Zn(1)-O(2H)^{IV}	93.4(3)
O(16)-Zn(3)	1.994(6)	O(23)^{III}-Zn(1)-O(2W)	89.6(3)
O(17)-Zn(4)	2.020(5)	O(2)-Zn(1)-O(2W)	166.7(3)
O(18A)-Zn(1)^{V}	2.16(2)	O(2H)^{IV}-Zn(1)-O(2W)	92.8(3)
O(18B)-Zn(1)^{V}	2.276(16)	O(23)^{III}-Zn(1)-O(1W)	93.6(3)
O(19)-Zn(5)	1.912(8)	O(2)-Zn(1)-O(1W)	84.0(3)
O(19)-H(19)	0.94(2)	O(2H)^{IV}-Zn(1)-O(1W)	171.0(3)
O(21)-Zn(5)	1.957(7)	O(2W)-Zn(1)-O(1W)	88.0(3)
O(22)-Zn(6)^{VI}	2.116(6)	O(23)^{III}-Zn(1)-O(18A)^{IV}	173.4(7)
O(22)-Zn(4)^{VIII}	2.435(6)	O(2)-Zn(1)-O(18A)^{IV}	76.2(8)
O(23)-Zn(1)^{IX}	2.001(6)	O(2H)^{IV}-Zn(1)-O(18A)^{IV}	91.0(7)
O(24)-Zn(6)	1.993(6)	O(2W)-Zn(1)-O(18A)^{IV}	92.0(8)
O(26)-Zn(5)	1.955(6)	O(1W)-Zn(1)-O(18A)^{IV}	80.1(7)
O(27)-Zn(4)^{VIII}	2.072(6)	O(23)^{III}-Zn(1)-O(18B)^{IV}	164.2(5)
Zn(1)-O(23)^{III}	2.001(6)	O(2)-Zn(1)-O(18B)^{IV}	93.0(5)
Zn(1)-O(2H)^{IV}	2.061(6)	O(2H)^{IV}-Zn(1)-O(18B)^{IV}	89.8(4)
Zn(1)-O(18A)^{IV}	2.16(2)	O(2W)-Zn(1)-O(18B)^{IV}	75.3(5)
Zn(1)-O(18B)^{IV}	2.276(16)	O(1W)-Zn(1)-O(18B)^{IV}	81.7(5)
Zn(3)-O(1H)^{V}	2.032(6)	O(18A)^{IV}-Zn(1)-O(18B)^{IV}	16.8(7)
Zn(3)-O(8)^{IV}	2.052(6)	O(4)-Zn(2)-O(11)	96.9(3)
Zn(3)-O(3)^{V}	2.221(7)	O(4)-Zn(2)-O(1H)	115.9(3)
Zn(4)-O(9)^{IV}	2.018(6)	O(11)-Zn(2)-O(1H)	127.3(3)

O(4)-Zn(2)-O(6)	105.7(3)
O(11)-Zn(2)-O(6)	103.5(3)
O(1H)-Zn(2)-O(6)	105.5(2)
O(13)-Zn(3)-O(16)	138.0(3)
O(13)-Zn(3)-O(1H)^{V}	109.9(3)
O(16)-Zn(3)-O(1H)^{V}	107.5(2)
O(13)-Zn(3)-O(8)^{IV}	99.4(3)
O(16)-Zn(3)-O(8)^{IV}	95.5(3)
O(1H)^{V}-Zn(3)-O(8)^{IV}	95.4(2)
O(13)-Zn(3)-O(3)^{V}	84.6(3)
O(16)-Zn(3)-O(3)^{V}	79.8(3)
O(1H)^{V}-Zn(3)-O(3)^{V}	85.5(2)
O(8)^{IV}-Zn(3)-O(3)^{V}	175.2(2)
O(9)^{IV}-Zn(4)-O(17)	107.2(2)
O(9)^{IV}-Zn(4)-O(27)^{X}	88.2(2)
O(17)-Zn(4)-O(27)^{X}	95.3(2)
O(9)^{IV}-Zn(4)-O(7)^{V}	160.5(2)
O(17)-Zn(4)-O(7)^{V}	91.3(2)
O(27)^{X}-Zn(4)-O(7)^{V}	84.2(2)
O(9)^{IV}-Zn(4)-O(1H)^{V}	94.1(2)
O(17)-Zn(4)-O(1H)^{V}	95.5(2)
O(27)^{X}-Zn(4)-O(1H)^{V}	167.7(2)
O(7)^{V}-Zn(4)-O(1H)^{V}	89.9(2)
O(9)^{IV}-Zn(4)-O(22)^{X}	82.1(2)
O(17)-Zn(4)-O(22)^{X}	169.1(2)
O(27)^{X}-Zn(4)-O(22)^{X}	90.6(2)
O(7)^{V}-Zn(4)-O(22)^{X}	80.1(2)
O(1H)^{V}-Zn(4)-O(22)^{X}	77.84(19)
O(19)-Zn(5)-O(2H)	121.7(4)
O(19)-Zn(5)-O(26)	103.1(3)
O(2H)-Zn(5)-O(26)	113.1(3)
O(19)-Zn(5)-O(21)	102.6(4)
O(2H)-Zn(5)-O(21)	110.1(2)
O(26)-Zn(5)-O(21)	104.4(3)
O(24)-Zn(6)-O(1)^{IX}	107.1(3)
O(24)-Zn(6)-O(12)^{VII}	87.0(3)
O(1)^{IX}-Zn(6)-O(12)^{VII}	96.4(2)
O(24)-Zn(6)-O(2H)^{XI}	95.7(2)
O(1)^{IX}-Zn(6)-O(2H)^{XI}	95.1(2)
O(12)^{VII}-Zn(6)-O(2H)^{XI}	166.9(2)
O(24)-Zn(6)-O(22)^{XI}	155.2(2)
O(1)^{IX}-Zn(6)-O(22)^{XI}	96.6(2)
O(12)^{VII}-Zn(6)-O(22)^{XI}	83.1(2)
O(2H)^{XI}-Zn(6)-O(22)^{XI}	89.3(2)

Symmetry transformations used to generate equivalent atoms:

1: -x+1, y, -z+1/2 **II:** -x, y, -z+3/2 **III:** x+3/2, -y+1/2, -z+1
IV: x+1/2, -y+1/2, -z+1 **V:** x-1/2, -y+1/2, -z+1 **VI:** x+1, y, z
VII: -x, -y+1, -z+1 **VIII:** -x+1/2, y+1/2, z **IX:** x-3/2, -y+1/2, -z+1
X: -x+1/2, y-1/2, z **XI:** x-1, y, z

*S5.3 Selected bond lenths and angles for Compound **3***

Table S5.3.1: Bond lengths [Å] and angles [°] for Compound **3**.

O(1)-Zn(1)	1.973(3)	O(4)^{III}-Zn(1)-O(3)^{I}	130.30(11)
O(1W)-Zn(1)	2.061(3)	O(4)^{III}-Zn(1)-O(1)	125.19(12)
O(3)-Zn(1)^{I}	1.963(3)	O(3)I-Zn(1)-O(1)	103.50(12)
O(2W)-Zn(1)	2.273(3)	O(4)^{III}-Zn(1)-O(1W)	95.01(13)
O(4)-Zn(1)^{II}	1.963(3)	O(3)^{I}-Zn(1)-O(1W)	92.14(13)
Zn(1)-O(4)^{III}	1.963(3)	O(1)-Zn(1)-O(1W)	92.26(13)
Zn(1)-O(3)I	1.963(3)	O(4)^{III}-Zn(1)-O(2W)	85.94(11)
		O(3)^{I}-Zn(1)-O(2W)	88.51(12)
		O(1)-Zn(1)-O(2W)	85.83(11)
		O(1W)-Zn(1)-O(2W)	178.07(13)

Symmetry transformations used to generate equivalent atoms:

I: -x, -y+1, -z+1 **II:** x, y, z+1 **III:** x,y,z-1

Table S5.3.2: Hydrogen bonds for Compound **3** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1W)-H(1W)···O(3W)	0.897(10)	1.831(11)	2.728(4)	179(4)
O(1W)-H(2W)···O(2)^{IV}	0.898(10)	1.850(19)	2.703(4)	158(4)
O(2W)-H(3W)···O(3W)^{V}	0.901(10)	1.938(15)	2.797(4)	159(3)
O(2W)-H(4W)···O(5)^{VI}	0.895(10)	1.924(13)	2.804(4)	167(4)
O(3W)-H(6W)···O(2)^{VII}	0.901(10)	1.907(18)	2.761(4)	158(4)

Symmetry transformations used to generate equivalent atoms:

I: -x, -y+1, -z+1 **II:** x, y, z+1 **III:** x, y, z-1 **IV:** -x, -y, -z

V: x+1, y, z **VI:** x, y+1, z **VII:** x-1, y, z

*S5.4 Selected bond lenths and angles for Compound **4***

Table S5.4.1: Bond lengths [Å] and angles [°] for Compound **4**.

O(1)-Zn(5)	2.629(4)	Zn(5)-O(2H)-Zn(6)	114.54(15)
O(1H)-Zn(2)	1.979(3)	Zn(5)-O(2H)-Zn(4)	108.86(14)
O(1H)-Zn(3)	2.013(3)	Zn(6)-O(2H)-Zn(4)	114.06(14)
O(1H)-Zn(1)	2.096(3)	O(1H)-Zn(1)-O(1H)^{V}	180.00(12)
O(1W)-Zn(2)	2.004(3)	O(1H)-Zn(1)-O(8)^{VI}	89.23(12)
O(2)-Zn(5)	1.931(3)	O(1H)^{V}-Zn(1)-O(8)^{VI}	90.77(12)
O(2H)-Zn(5)	1.984(3)	O(1H)-Zn(1)-O(8)^{II}	90.77(12)
O(2H)-Zn(6)	2.119(3)	O(1H)^{V}-Zn(1)-O(8)^{II}	89.23(12)
O(2H)-Zn(4)	2.119(3)	O(8)^{VI}-Zn(1)-O(8)^{II}	180.0
O(2W)-Zn(3)	1.978(4)	O(1H)-Zn(1)-O(3)^{V}	90.88(13)
O(3)-Zn(1)	2.127(3)	O(1H)^{V}-Zn(1)-O(3)^{V}	89.12(13)
O(3W)-Zn(6)	2.029(3)	O(8)^{VI}-Zn(1)-O(3)^{V}	89.26(13)
O(4)-Zn(3)	1.960(3)	O(8)^{II}-Zn(1)-O(3)^{V}	90.74(13)
O(4W)-Zn(5)	2.013(4)	O(1H)-Zn(1)-O(3)	89.12(13)
O(6)-Zn(6)	2.439(3)	O(1H)^{V}-Zn(1)-O(3)	90.88(13)
O(7)-Zn(6)	2.000(3)	O(8)^{VI}-Zn(1)-O(3)	90.74(13)
O(8)-Zn(1)^{I}	2.120(3)	O(8)^{II}-Zn(1)-O(3)	89.26(13)
O(9)-Zn(2)^{I}	1.981(3)	O(3)^{V}-Zn(1)-O(3)	180.0(3)
O(11)-Zn(4)	2.071(3)	O(14)^{IV}-Zn(2)-O(1H)	112.18(14)
O(12)-Zn(6)	1.995(3)	O(14)^{IV}-Zn(2)-O(9)^{II}	105.43(14)
O(14)-Zn(2)^{III}	1.930(3)	O(1H)-Zn(2)-O(9)^{II}	104.42(14)
O(16)-Zn(6)	2.213(3)	O(14)^{IV}-Zn(2)-O(1W)	125.87(14)
O(17)-Zn(3)	1.920(3)	O(1H)-Zn(2)-O(1W)	103.94(14)
O(18)-Zn(4)	2.130(3)	O(9)^{II}-Zn(2)-O(1W)	102.83(14)
O(19)-Zn(5)	1.979(3)	O(14)^{IV}-Zn(2)-O(13)^{IV}	56.29(13)
Zn(1)-O(1H)^{V}	2.096(3)	O(1H)-Zn(2)-O(13)^{IV}	95.52(13)
Zn(1)-O(8)^{VI}	2.120(3)	O(9)^{II}-Zn(2)-O(13)^{IV}	157.48(13)
Zn(1)-O(8)^{II}	2.120(3)	O(1W)-Zn(2)-O(13)^{IV}	82.00(12)
Zn(1)-O(3)^{V}	2.127(3)	C(23)^{IV}-Zn(2)-O(13)^{IV}	27.90(13)
Zn(2)-O(14)^{IV}	1.930(3)	O(17)-Zn(3)-O(4)	109.79(15)
Zn(2)-O(9)^{II}	1.981(3)	O(17)-Zn(3)-O(2W)	118.49(14)
Zn(2)-O(13)^{IV}	2.587(3)	O(4)-Zn(3)-O(2W)	109.86(15)
Zn(4)-O(11)^{VII}	2.071(3)	O(17)-Zn(3)-O(1H)	118.83(14)
Zn(4)-O(2H)^{VII}	2.119(3)	O(4)-Zn(3)-O(1H)	101.46(14)
Zn(4)-O(18)^{VII}	2.130(3)	O(2W)-Zn(3)-O(1H)	96.63(14)
		O(11)^{VII}-Zn(4)-O(11)	180.00(12)
Zn(2)-O(1H)-Zn(3)	117.00(16)	O(11)^{VII}-Zn(4)-O(2H)	89.28(12)
Zn(2)-O(1H)-Zn(1)	109.99(14)	O(11)-Zn(4)-O(2H)	90.72(12)
Zn(3)-O(1H)-Zn(1)	111.62(15)	O(11)^{VII}-Zn(4)-O(2H)^{VII}	90.72(12)

O(11)-Zn(4)-O(2H)^{VII}	89.28(12)
O(2H)-Zn(4)-O(2H)^{VII}	180.00(13)
O(11)^{VII}-Zn(4)-O(18)^{VII}	88.25(13)
O(11)-Zn(4)-O(18)^{VII}	91.75(13)
O(2H)-Zn(4)-O(18)^{VII}	89.66(12)
O(2H)^{VII}-Zn(4)-O(18)^{VII}	90.34(12)
O(11)^{VII}-Zn(4)-O(18)	91.75(13)
O(11)-Zn(4)-O(18)	88.25(13)
O(2H)-Zn(4)-O(18)	90.34(12)
O(2H)^{VII}-Zn(4)-O(18)	89.66(12)
O(18)^{VII}-Zn(4)-O(18)	180.0(3)
O(2)-Zn(5)-O(19)	106.48(15)
O(2)-Zn(5)-O(2H)	127.12(15)
O(19)-Zn(5)-O(2H)	104.83(14)
O(2)-Zn(5)-O(4W)	109.91(15)
O(19)-Zn(5)-O(4W)	105.38(14)
O(2H)-Zn(5)-O(4W)	101.31(14)
O(2)-Zn(5)-O(1)	55.08(13)
O(19)-Zn(5)-O(1)	161.05(13)
O(2H)-Zn(5)-O(1)	91.57(13)
O(4W)-Zn(5)-O(1)	80.03(14)
O(12)-Zn(6)-O(7)	103.42(14)
O(12)-Zn(6)-O(3W)	107.12(14)
O(7)-Zn(6)-O(3W)	146.44(14)
O(12)-Zn(6)-O(2H)	93.78(13)
O(7)-Zn(6)-O(2H)	100.23(13)
O(3W)-Zn(6)-O(2H)	91.40(13)
O(12)-Zn(6)-O(16)	89.53(13)
O(7)-Zn(6)-O(16)	90.89(14)
O(3W)-Zn(6)-O(16)	75.91(13)
O(2H)-Zn(6)-O(16)	167.30(13)
O(12)-Zn(6)-O(6)	161.83(13)
O(7)-Zn(6)-O(6)	58.46(13)
O(3W)-Zn(6)-O(6)	90.77(12)
O(2H)-Zn(6)-O(6)	88.78(12)
O(16)-Zn(6)-O(6)	91.89(12)

Symmetry transformations used to generate equivalent atoms:
I: x, y, z+1 **II:** x, y, z-1 **III:** x+1, y, z **IV:** x-1, y, z
V: -x+1, -y, -z+1 **VI:** -x+1, -y, -z+2 **VII:** -x+2, -y, -z+2

Table S5.4.2: Hydrogen bonds for Compound **4** [Å and °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(5W)-H(5A)···O(1)	0.901(10)	1.867(19)	2.737(5)	162(4)
O(5W)-H(5B)···O(6)	0.899(10)	2.13(2)	2.964(5)	154(4)
O(2W)-H(2B)···O(3W)	0.895(10)	1.884(14)	2.771(5)	171(5)
O(2W)-H(2A)···O(8)^{VI}	0.896(10)	1.781(11)	2.676(5)	175(4)
O(1H)-H(1H)···O(5W)^{VI}	1.00	1.92	2.715(5)	134.4
O(3W)-H(3A)···O(6)^{VI}	0.899(10)	1.743(12)	2.642(5)	177(5)
O(3W)-H(3B)···O(18)^{VII}	0.90(4)	1.71(4)	2.595(5)	167(5)
O(4W)-H(4B)···O(11)^{VII}	0.899(10)	1.816(18)	2.696(5)	165(5)
O(1W)-H(1A)···O(3)^{V}	0.897(10)	1.790(19)	2.656(5)	161(5)
O(1W)-H(1B)···O(13)^{V}	0.900(10)	1.773(18)	2.645(5)	162(4)
O(4W)-H(4A)···O(1W)^{VIII}	0.901(10)	1.859(12)	2.757(5)	175(5)

Symmetry transformations used to generate equivalent atoms:
I: x, y, z+1 **II:** x, y, z-1 **III:** x+1, y, z **IV:** x-1, y, z
V: -x+1, -y, -z+1 **VI:** -x+1, -y, -z+2 **VII:** -x+2, -y, -z+2
VIII: x+1, y, z+1

S6. Powder X-ray diffraction data on repeat syntheses in water, methanol and ethanol

*S6.1 Powder diffraction patterns for repeat synthesis attempts at Compound **1***

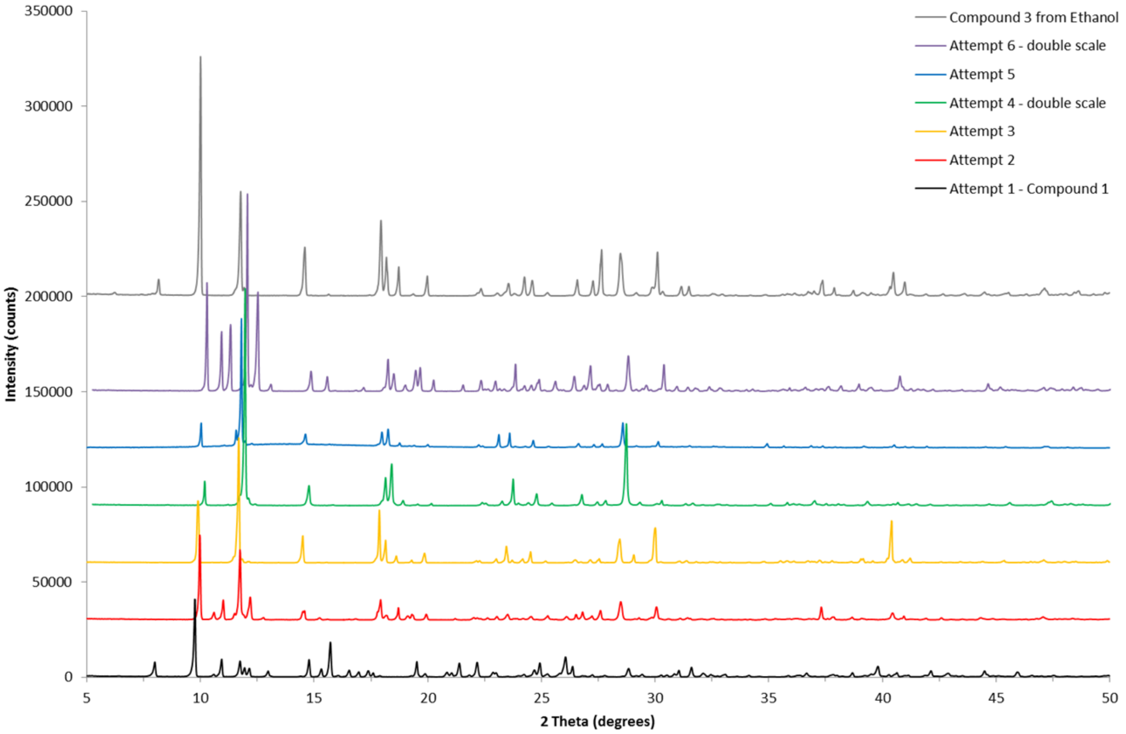


Figure S6.2.1: Comparison of PXRD patterns obtained from the products of each attempt to prepare Compound **1** from reaction of $Zn(OAc)_2 \cdot 2H_2O$ and H_2MeOip in water. For clarity, the patterns for Attempts 2 and 4 have been offset in the 2θ direction by 0.25°, and the peak intensities of Attempt 3 have been halved.

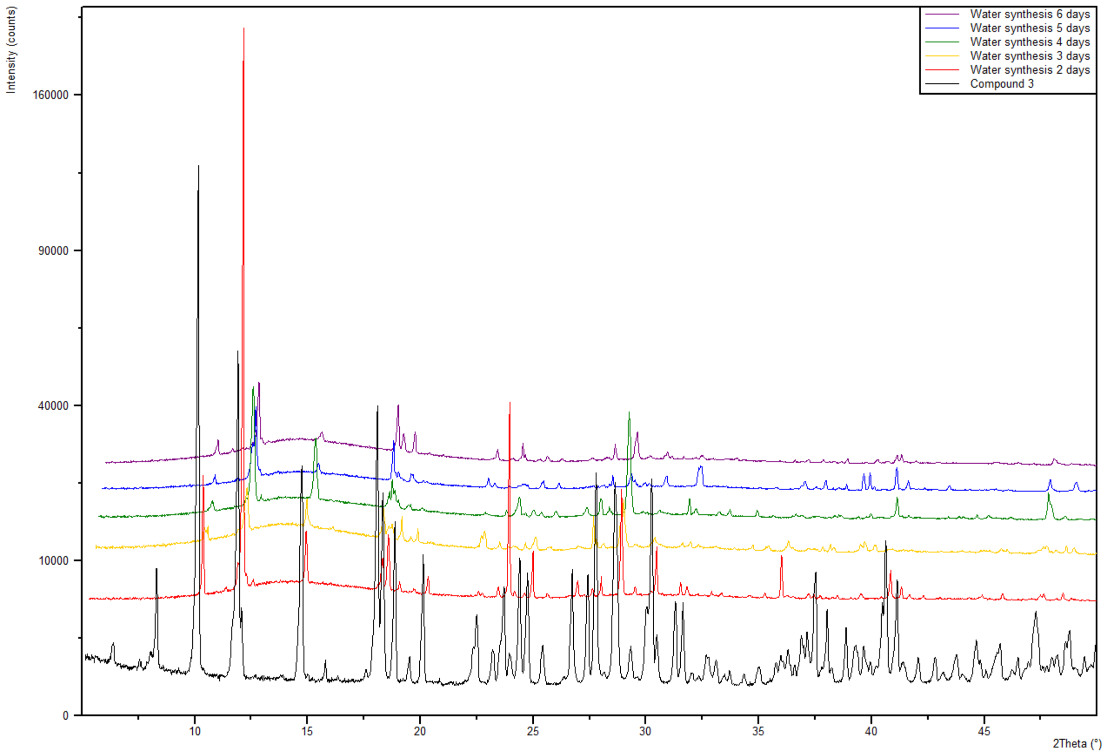


Figure S6.1.2: Comparison of the PXRD patterns of the products obtained by varying the reaction time of the aqueous synthesis of Compound **1**. The PXRD pattern of Compound 3 obtained from aqueous ethanol has been included for comparison purposes. The patterns have been offset in the 2θ direction for clarity.

*S6.2 Powder diffraction patterns for repeat synthesis attempts at Compound **2***

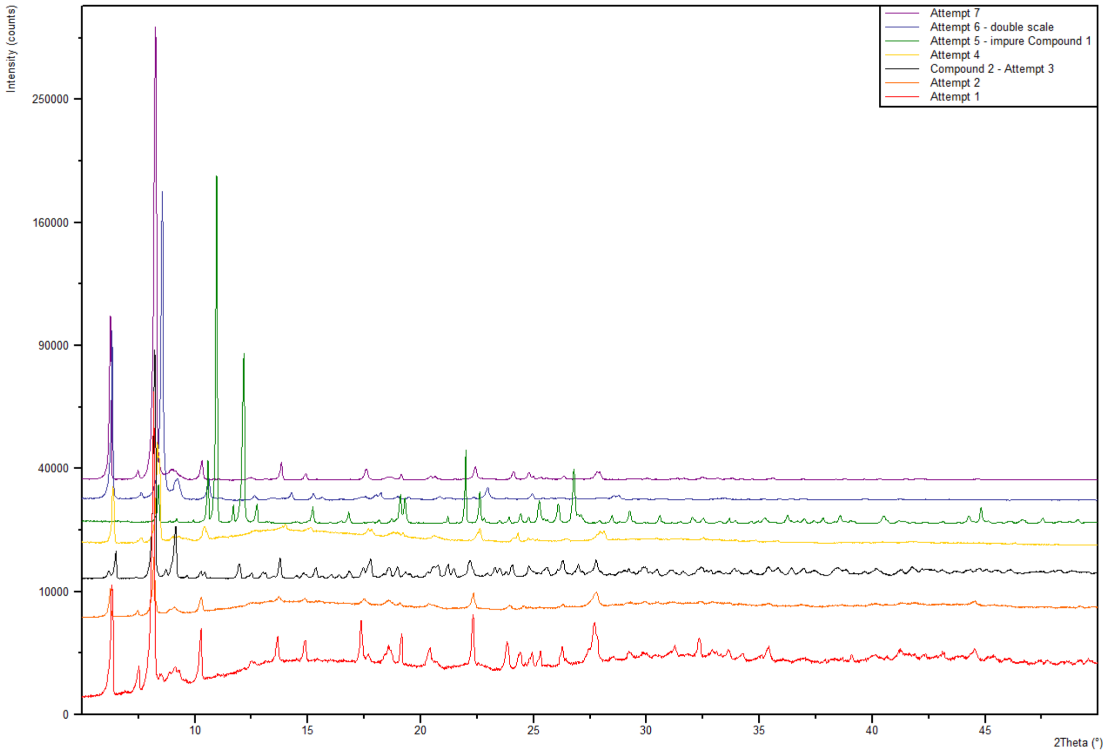


Figure S6.2.1: Comparison of PXRD patterns obtained from the products of each attempt to prepare Compound **2** from reaction of $Zn(OAc)_2 \cdot 2H_2O$ and H_2MeOip in a 2:1 methanol:water solvent system.

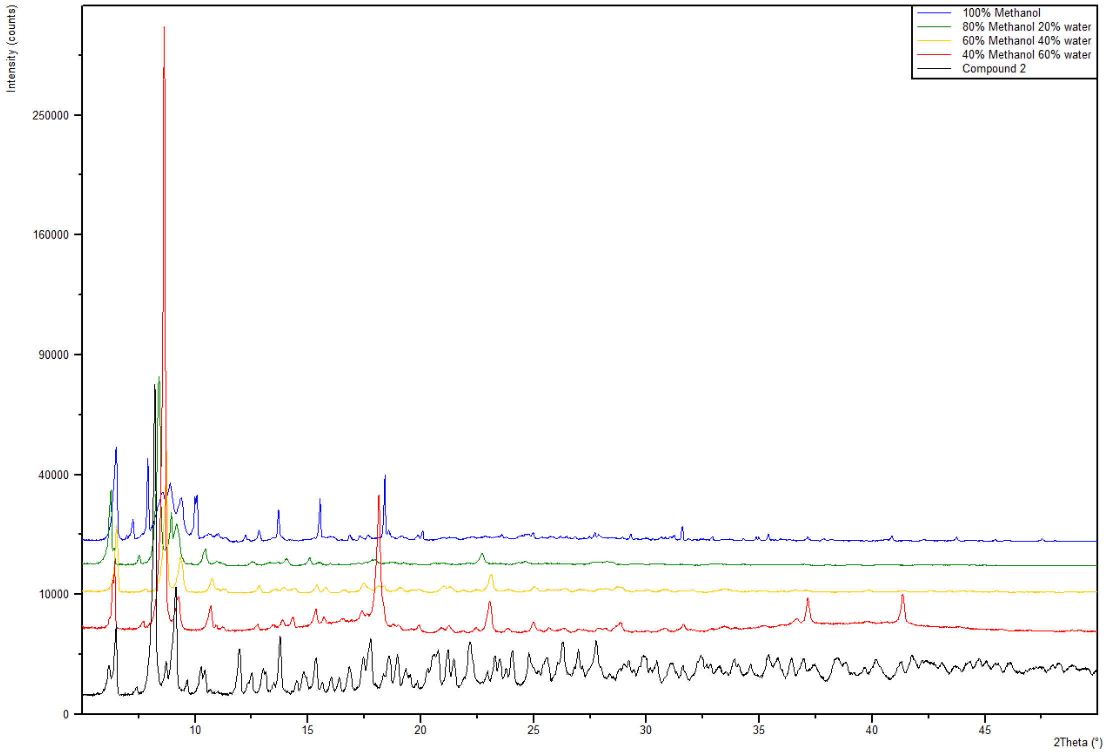


Figure S6.2.2: Comparison of the PXRD patterns of the products obtained by varying the ratio of methanol:water in the synthesis of Compound **2**. Peaks at 18°, 37° and 42° of the 40% Methanol 60% water pattern (red) are due to a teflon insert.

*S6.3 Powder diffraction patterns for repeat synthesis attempts at Compound **3***

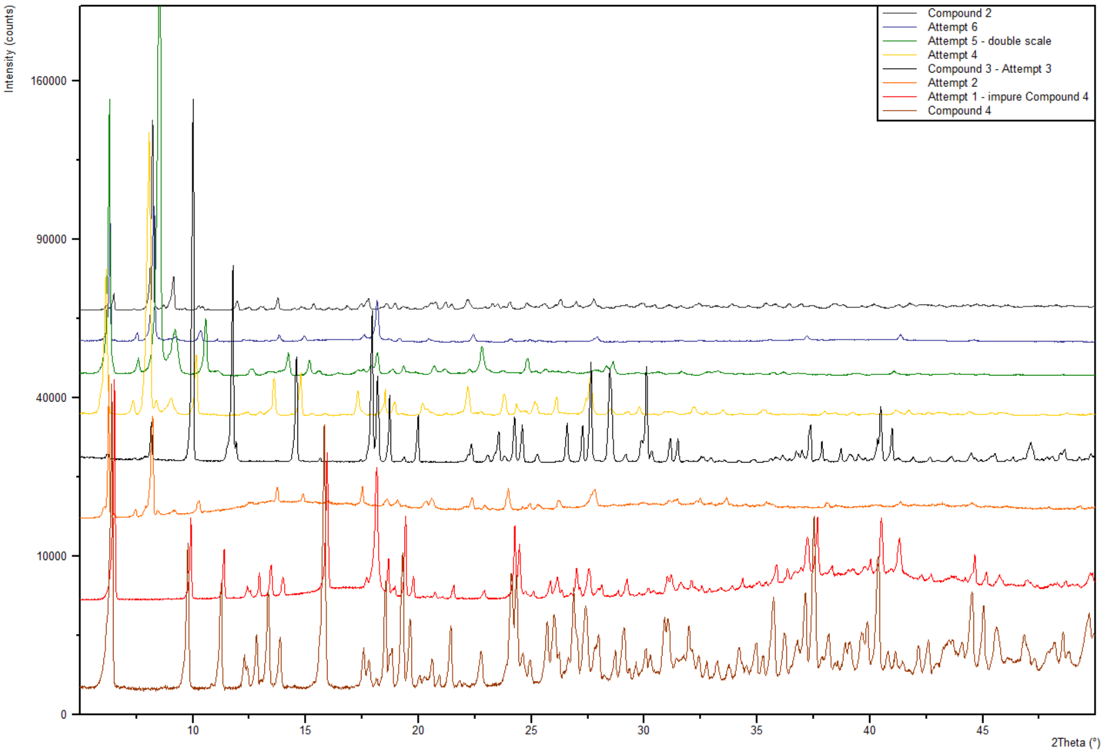


Figure S6.3.1: Comparison of PXRD patterns obtained from the products of each attempt to prepare Compound **3** from reaction of $Zn(OAc)_2{\cdot}2H_2O$ and H_2MeOip in a 2:1 ethanol:water solvent system. PXRD patterns for Compounds **2** and **4** have been included for comparison purposes.

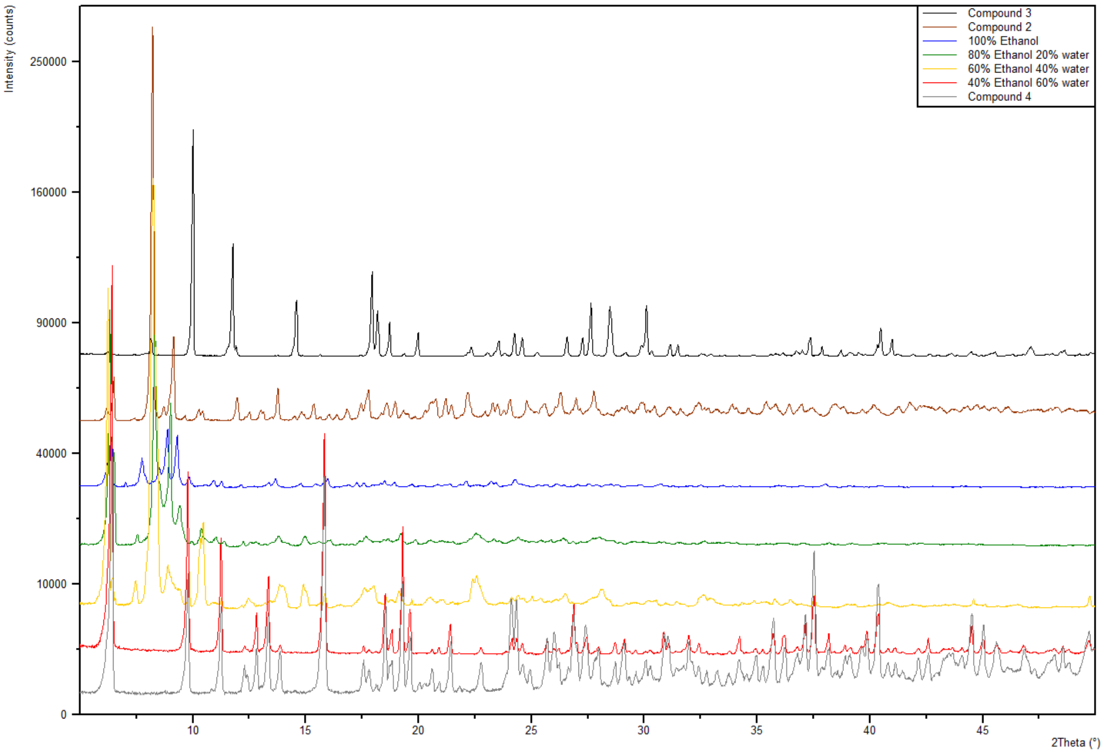


Figure S6.3.2: Comparison of the PXRD patterns of the products obtained by varying the ratio of ethanol:water in the synthesis of Compound **3**. PXRD patterns for Compounds **2** and **4** have been included for comparison purposes.

S7. Powder diffraction data on Compounds 2 and 4 before and after NO loading

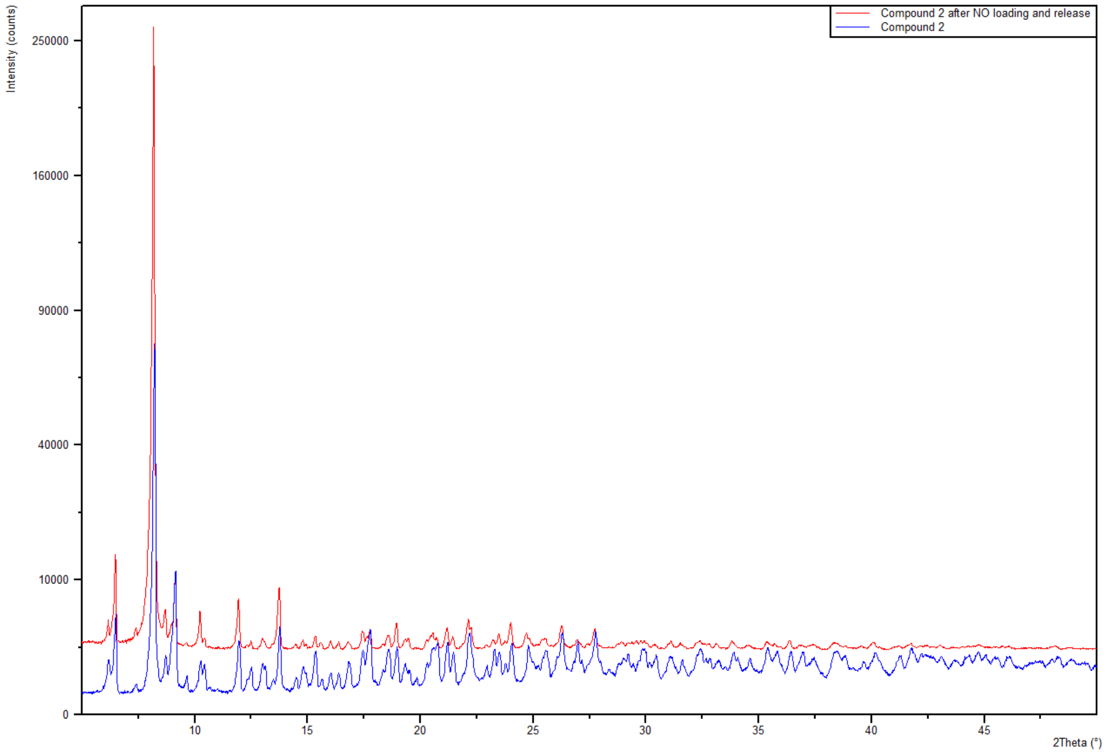


Figure S7.1: Comparison of the PXRD patterns of Compound **2** before (blue) and after (red) nitric oxide loading and release experiments.

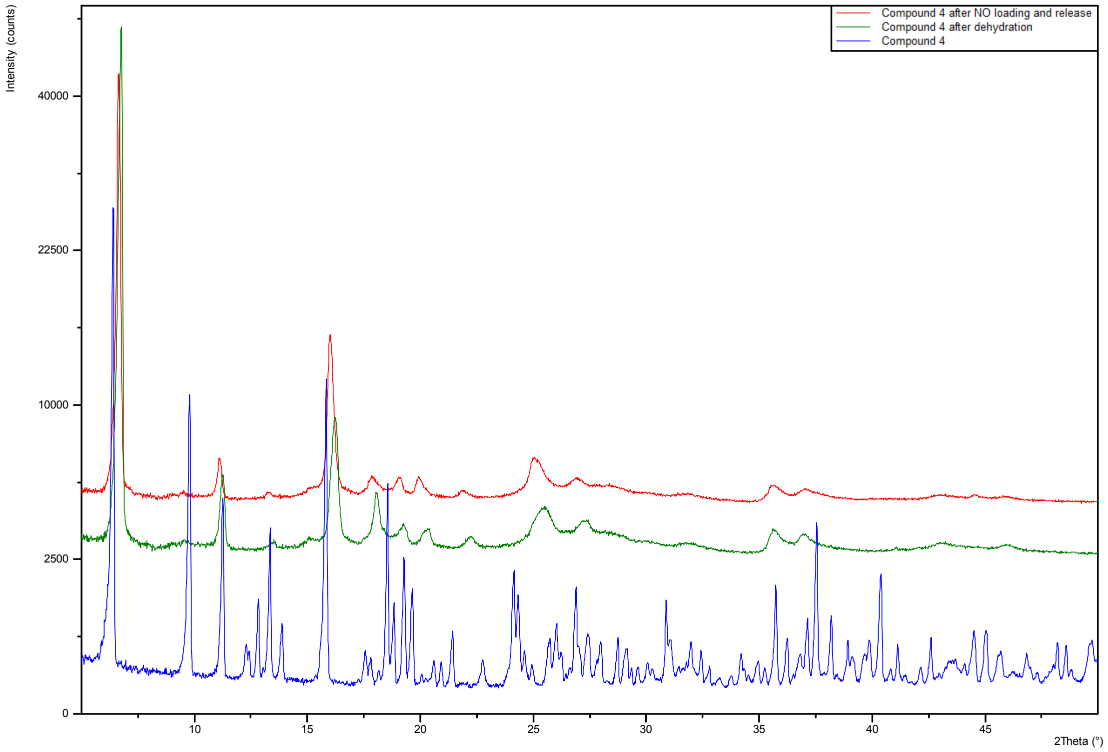


Figure S7.1: Comparison of the PXRD patterns of Compound **4** before (blue) and after dehydration (green) and nitric oxide loading and release (red) experiments.