Supporting Information

New copper aryl phosphonates with auxiliary nitrogen ligands

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TABLE AND FIGURE CAPTIONS

Table S1. Selected bond distances (Å) and angles (°) for **1** - **5**.

1

Cu(1)-O(4)	1.9053(15)	Cu(1)-O(1)	2.3596(15)	S(1)-C(13)	1.7750(19)
Cu(1)-O(6)	1.9136(14)	S(1)-O(3)	1.4356(17)	P(1)-O(4)	1.4867(15)
Cu(1)-N(1)	2.0113(16)	S(1)-O(2)	1.4491(17)	P(1)-O(6)	1.4939(14)
Cu(1)-N(2)	2.0146(16)	S(1)-O(1)	1.4653(15)	P(1)-O(5)	1.5510(18)

O(4)-Cu(1)-O(6)	94.41(6)	N(1)-Cu(1)-O(1)	88.93(6)	O(4)-P(1)-O(6)	116.27(10)
O(4)-Cu(1)-N(1)	91.69(7)	N(2)-Cu(1)-O(1)	90.41(6)	O(4)-P(1)-O(5)	110.94(12)
O(6)-Cu(1)-N(1)	161.49(7)	O(3)-S(1)-O(2)	114.80(11)	O(6)-P(1)-O(5)	111.49(11)
O(4)-Cu(1)-N(2)	173.31(7)	O(3)-S(1)-O(1)	113.21(10)	O(4)-P(1)-C(16)	105.88(9)
O(6)-Cu(1)-N(2)	92.07(7)	O(2)-S(1)-O(1)	109.83(10)	O(6)-P(1)-C(16)	107.65(9)
N(1)-Cu(1)-N(2)	81.63(7)	O(3)-S(1)-C(13)	107.36(10)	O(5)-P(1)-C(16)	103.62(9)
O(4)-Cu(1)-O(1)	89.10(7)	O(2)-S(1)-C(13)	105.31(9)		
O(6)-Cu(1)-O(1)	108.61(7)	O(1)-S(1)-C(13)	105.56(9)		

2

Cu(1)-O(2)	1.9107(19)	Cu(1)-O(4)	2.215(2)	O(5)-C(18)	1.271(3)
Cu(1)-O(5)	1.9616(18)	P(1)-O(2)	1.5043(19)	O(5)-Cu(1)	1.9616(18)
Cu(1)-N(2)	2.031(2)	P(1)-O(3)	1.508(2)	O(6)-C(18)	1.244(3)
Cu(1)-N(1)	2.045(2)	P(1)-O(1)	1.5653(18)		

O(2)-Cu(1)-O(5)	96.02(8)	O(2)-Cu(1)-O(4)	90.56(9)	O(3)-P(1)-O(1)	111.93(11)
O(2)-Cu(1)-N(2)	167.50(9)	O(5)-Cu(1)-O(4)	102.93(8)	O(2)-P(1)-C(12)	110.72(12)
O(5)-Cu(1)-N(2)	93.59(9)	N(2)-Cu(1)-O(4)	95.06(9)	O(3)-P(1)-C(12)	108.46(12)
O(2)-Cu(1)-N(1)	88.30(9)	N(1)-Cu(1)-O(4)	89.26(8)	O(1)-P(1)-C(12)	102.62(11)
O(5)-Cu(1)-N(1)	166.98(9)	O(2)-P(1)-O(3)	111.29(11)	P(1)-O(2)-Cu(1)	144.48(13)
N(2)-Cu(1)-N(1)	80.64(9)	O(2)-P(1)-O(1)	111.45(12)	C(18)-O(5)-Cu(1)	110.47(17)

O(6)-C(18)-O(5) 123.0(2) O(6)-C(18)-C(19) 119.7(2)

3

Cu(1)- O(4) 1.9367(13) P(1)- O(3) 1.5042(15) P(2)- O(6) 1.5782(16)

Cu(1)- O(1) 1.9799(13) P(1)- O(1) 1.5290(14) P(3)- O(7) 1.5060(18)

Cu(1)- N(1) 1.9985(17) P(1)- O(2) 1.5526(15) P(3)- O(8) 1.5217(17)

Cu(1)- N2 2.0241(16) P(2)- O(5) 1.5009(17) P(3)- O(9) 1.5675(18)

Cu(1)- O(1) 2.2569(14) P(2)- O(4) 1.5092(15)

O(4) -Cu(1)- O(1) 91.55(6) O3 -P(1)- O2 110.16(9) O(7) -P(3)- O(8) 116.98(10)

O(4) -Cu(1)- N(1) 91.23(7) O(1) -P(1)- O2 108.87(8) O(7) -P(3)- O9 109.83(9)

O(1) -Cu(1)- N(1) 176.85(6) O3 -P(1)- C1 107.10(8) O(8) -P(3)- O(9) 107.11(11)

O(4) -Cu(1)- N(2) 165.03(7) O(1) -P(1)- C1 108.93(8) O(7) -P(3)- C3 109.34(10)

O(1) -Cu(1)- N(2) 95.14(6) O2 -P(1)- C1 107.61(8) O(8) -P(3)- C3 106.64(9)

N(1) -Cu(1)- N(2) 81.81(7) O(5) -P(2)- O(4) 117.04(9) O(9) -P(3)- C3 106.41(10)

O(4) -Cu(1)- O(1) 97.11(6) O(5) -P(2)- O(6) 110.81(9) P(1) -O(1)- Cu(1) 128.44(8)

O(1) -Cu(1)- O(1) 82.09(5) O(4) -P(2)- O(6) 107.14(9) P(1) -O(1)- Cu(1) 133.27(8)

N(1) -Cu(1)- O(1) 99.03(6) O(5) -P(2)- C2 109.69(9) Cu(1) -O(1)- Cu(1) 97.91(5)

N(2) -Cu(1)- O(1) 97.07(6) O(4) -P(2)- C2 105.53(9)

O3 -P(1)- O(1) 113.96(8) O(6) -P(2)- C2 105.96(9)

4

Cu(1)-O(3)	1.9260(12)	Cu(1)-O(5)	2.2589(13)	P(2)-O(4)	1.4968(12)
Cu(1)-O(1)	1.9334(12)	P(1)-O(1)	1.5039(13)	P(2)-O(5)	1.5125(12)
Cu(1)-N(1)	1.9939(14)	P(1)-O(2)	1.5593(13)	P(2)-O(6)	1.5694(13)
Cu(1)-N(2)	2.0216(15)	P(1)-C(1)	1.7987(15)	P(2)-C(4)	1.8142(16)

O(3)-Cu(1)-O(1)	93.74(5)	O(3)-Cu(1)-O(5)	99.05(6)	O(3)-P(1)-O(2)	110.50(8)
O(3)-Cu(1)-N(1)	90.85(6)	O(1)-Cu(1)-O(5)	93.31(5)	O(1)-P(1)-C(1)	106.12(7)
O(1)-Cu(1)-N(1)	171.79(5)	N(1)-Cu(1)-O(5)	92.69(6)	O(4)-P(2)-O(5)	115.60(7)
O(3)-Cu(1)-N(2)	164.22(6)	N(2)-Cu(1)-O(5)	94.53(5)	O(4)-P(2)-O(6)	111.15(7)
O(1)-Cu(1)-N(2)	93.46(5)	O(1)-P(1)-O(3)	116.36(7)	O(5)-P(2)-O(6)	109.89(7)
N(1)-Cu(1)-N(2)	80.47(6)	O(1)-P(1)-O(2)	111.20(7)		

5

Cu(1)-N(3)	2.0485(19)	P(1)-O(2)	1.4924(17)	P(2)-O(4)	1.5003(17)
Cu(1)-N(2)	2.054(2)	P(1)-O(3)	1.5244(17)	P(2)-O(6)	1.5090(17)
Cu(1)-N(1)	2.055(2)	P(1)-O(1)	1.5484(17)	P(2)-O(5)	1.5622(17)
Cu(1)-N(4)	2.071(2)	P(1)-C(25)	1.799(2)		

N(3)-Cu(1)-N(2)	147.36(9)	O(2)-P(1)-O(3)	115.54(10)	O(4)-P(2)-O(6)	115.61(10)
N(3)-Cu(1)-N(1)	118.01(8)	O(2)-P(1)-O(1)	112.64(10)	O(4)-P(2)-O(5)	111.78(10)
N(2)-Cu(1)-N(1)	81.18(8)	O(3)-P(1)-O(1)	105.12(10)	O(6)-P(2)-O(5)	106.16(10)
N(3)-Cu(1)-N(4)	80.95(8)	O(2)-P(1)-C(25)	107.70(10)	O(4)-P(2)-C(28)	109.02(9)
N(2)-Cu(1)-N(4)	104.32(8)	O(3)-P(1)-C(25)	108.33(10)	O(6)-P(2)-C(28)	109.02(10)
N(1)-Cu(1)-N(4)	135.32(9)	O(1)-P(1)-C(25)	107.15(10)	O(5)-P(2)-C(28)	104.63(10)

Table S2. Distances (Å) and angles (°) of hydrogen bonds.

compound	D-H···A	D-H	H···A	D···A	D-H···A
1	O7-H14···O1	0.899(2)	1.919(2)	2.786(2)	161.5(1)
	O7-H15···O2	0.899(2)	1.863(2)	2.736(2)	163.2(1)
	O5-H13···O7	0.913(2)	1.662(2)	2.564(2)	169.0(1)
2	O1-H1···O3	0.820(2)	1.760(2)	2.571(2)	170.3(1)
	O4-H4··· O3	0.700(2)	2.061(2)	2.758(2)	179.1(1)
	O4-H4···O6	0.694(2)	2.056(2)	2.750(2)	178.7(1)
3	O2-H17···O5	0.9249(1)	1.5988(1)	2.5184(2)	172.358(8)
	O6-H16···O7	0.8506(1)	1.7886(1)	2.6257(2)	167.558(8)
	O9-H15···O7	0.798(1)	1.8064(1)	2.5931(1)	168.464(9)
4	O2-H02···O5	0.907(2)	1.620(2)	2.526(2)	176.2(1)
	O6-H06···O4	0.891(1)	1.714(1)	2.604(2)	176.5(1)
5	O1-H22···O4	1.005(1)	1.527(1)	2.527(1)	172.5(1)
	O5-H21···O2	0.858(1)	1.764(1)	2.600(1)	164.3(1)
	O3-H23···O6	0.820(1)	1.639(1)	2.435(1)	162.8(2)

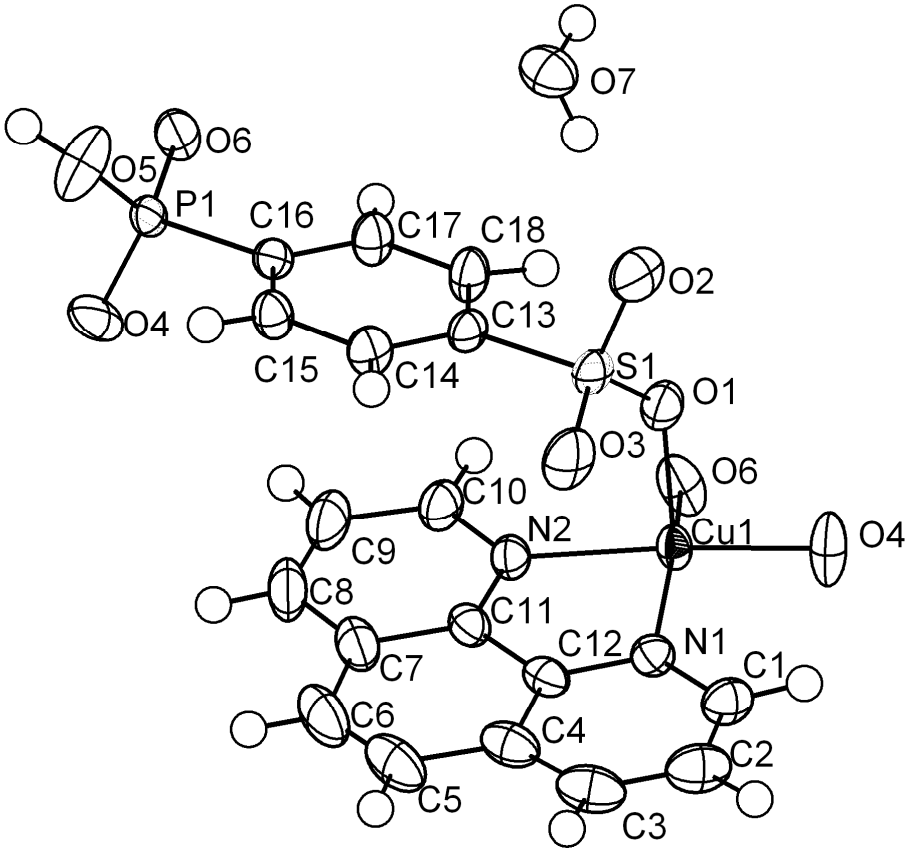

Figure S1 ORTEP drawing of **1**.

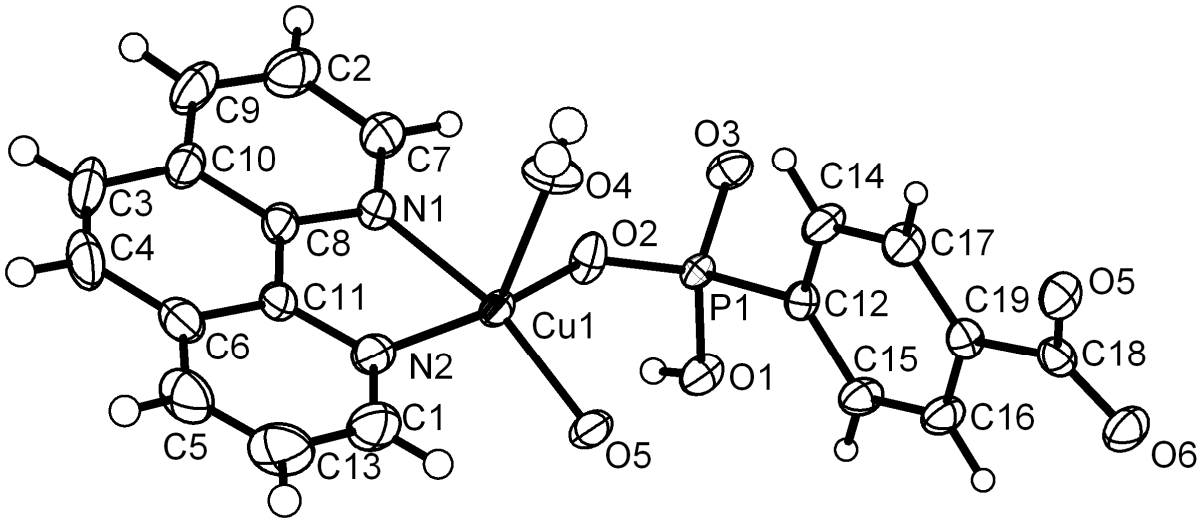

Figure S2 ORTEP drawing of **2**.

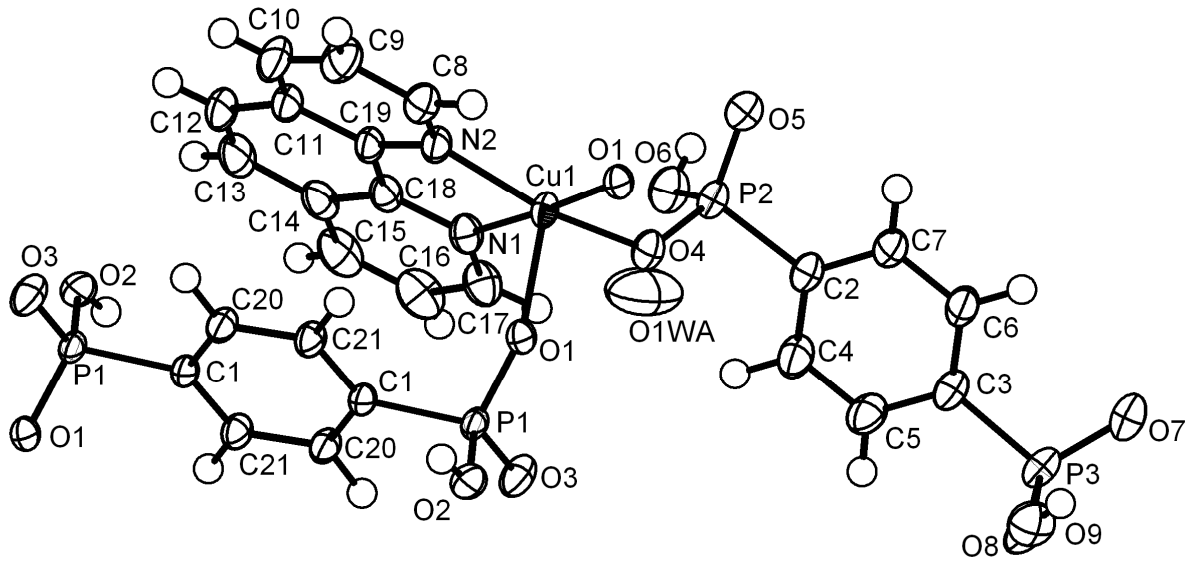

Figure S3 ORTEP drawing of **3**.

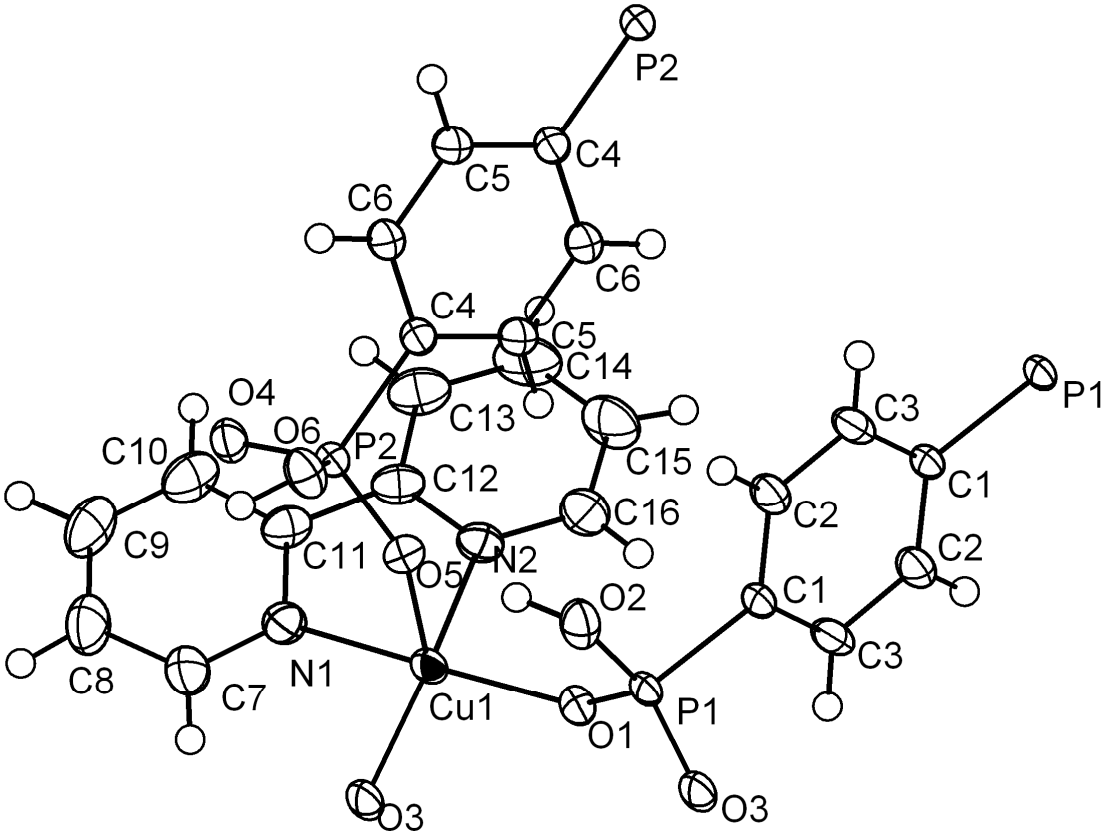

Figure S4 ORTEP drawing of **4**.

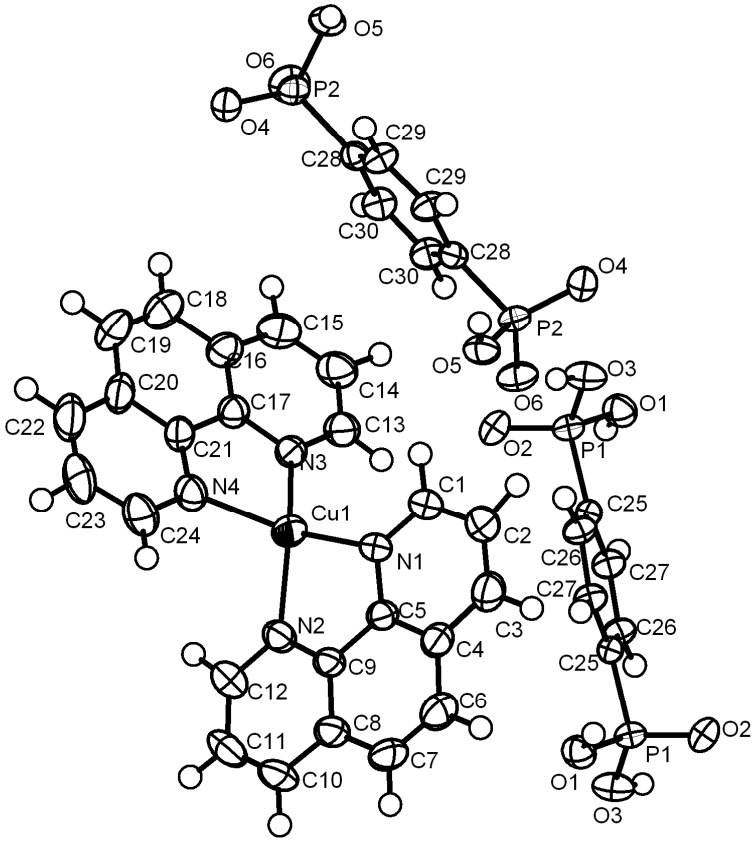

Figure S5 ORTEP drawing of **5**.

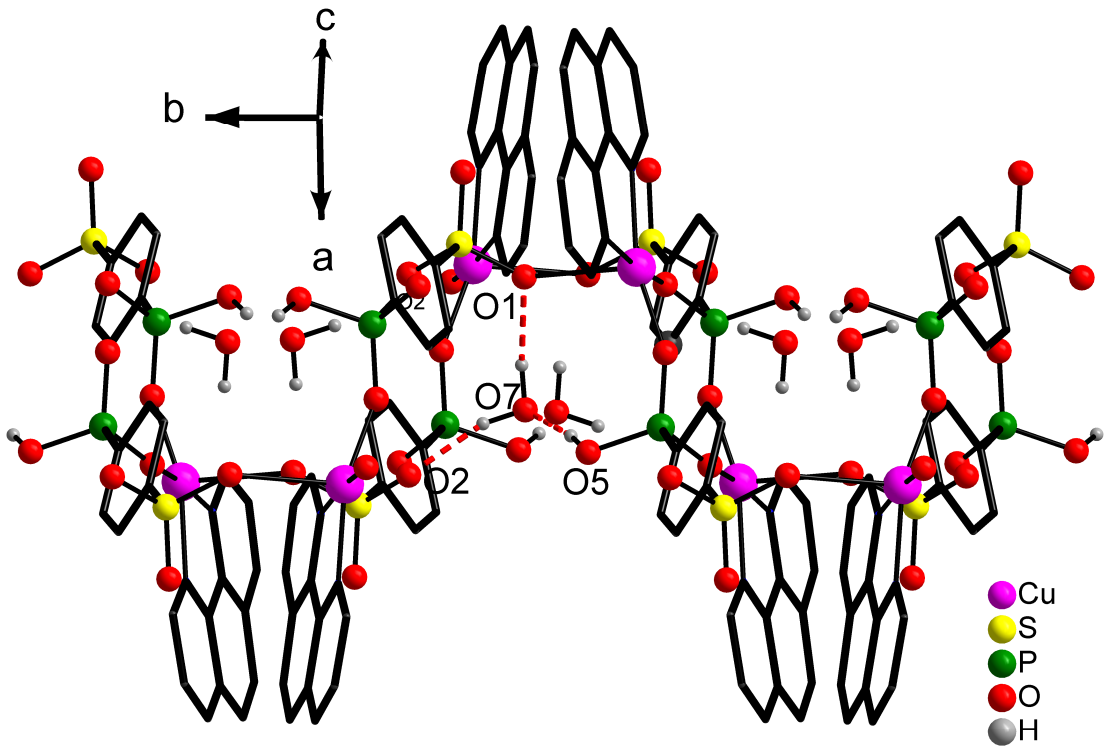

Figure S6 Fragment of the layer of **1** viewed along the ac diagonal. The hydrogen bonds are indicated by dashed lines.

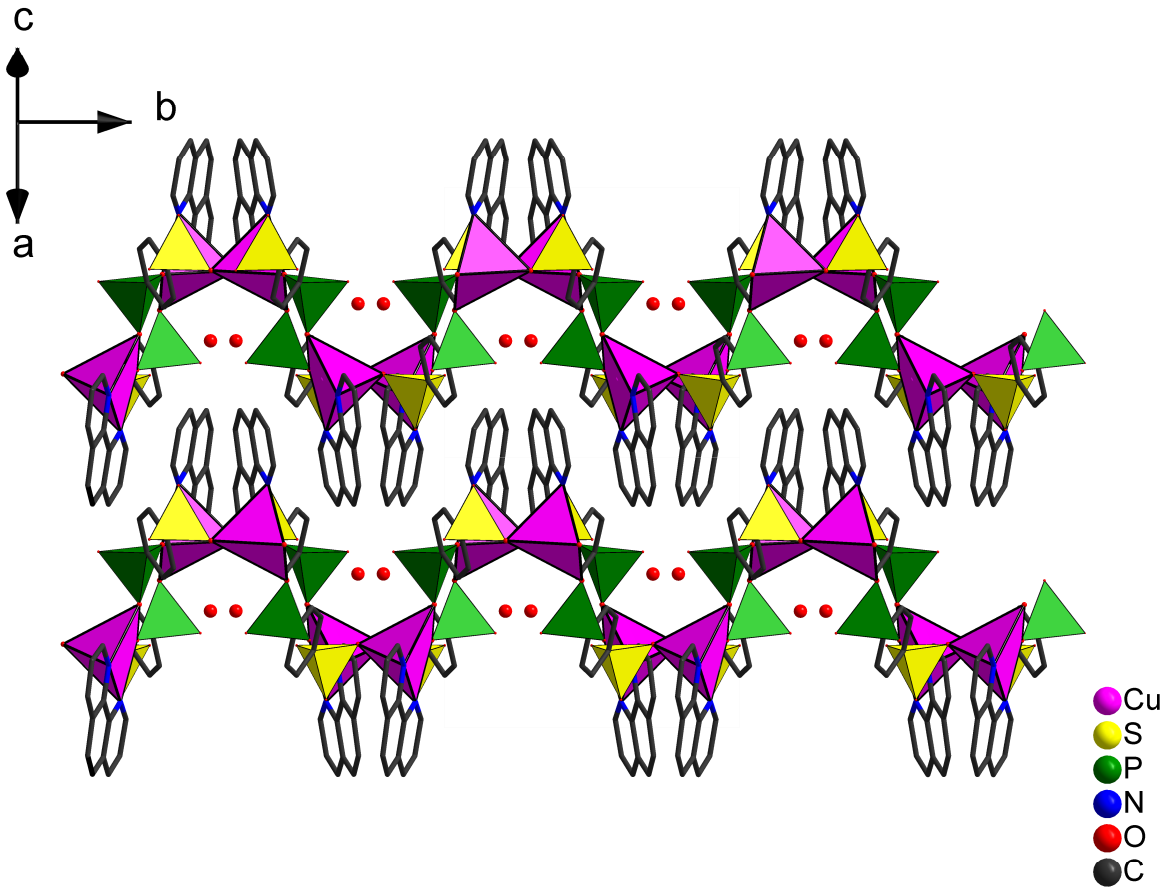

Figure S7 Stacking of the layers in **1**.

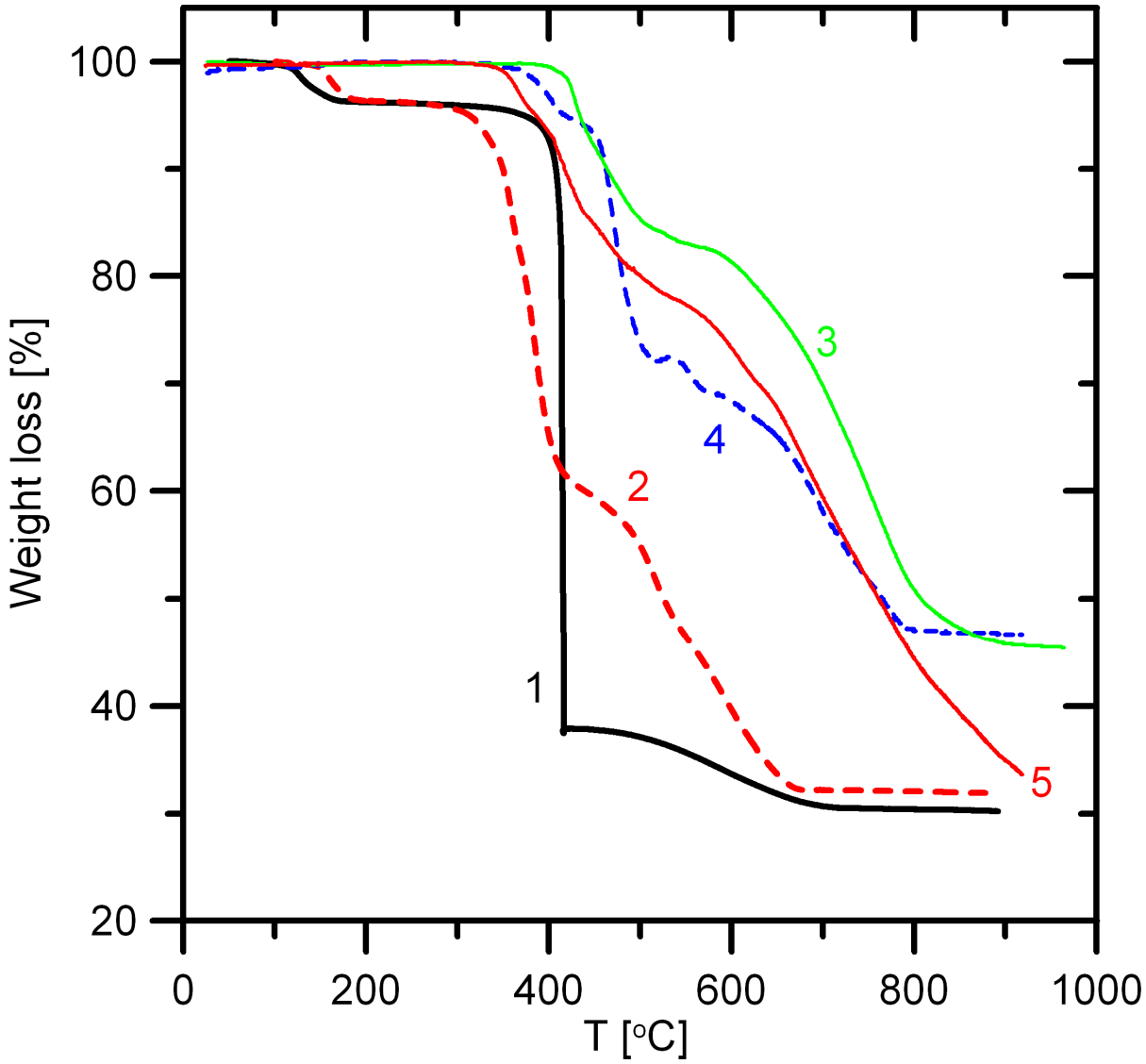

Figure S8 Thermogravimetric curves of compounds **1**-**5**.

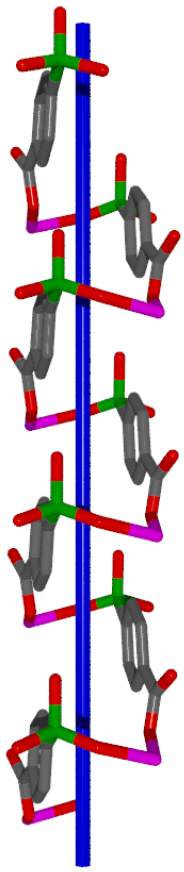

Figure S9 Formation of the helical chain in compound 2. The phen molecules are omitted for clarity.

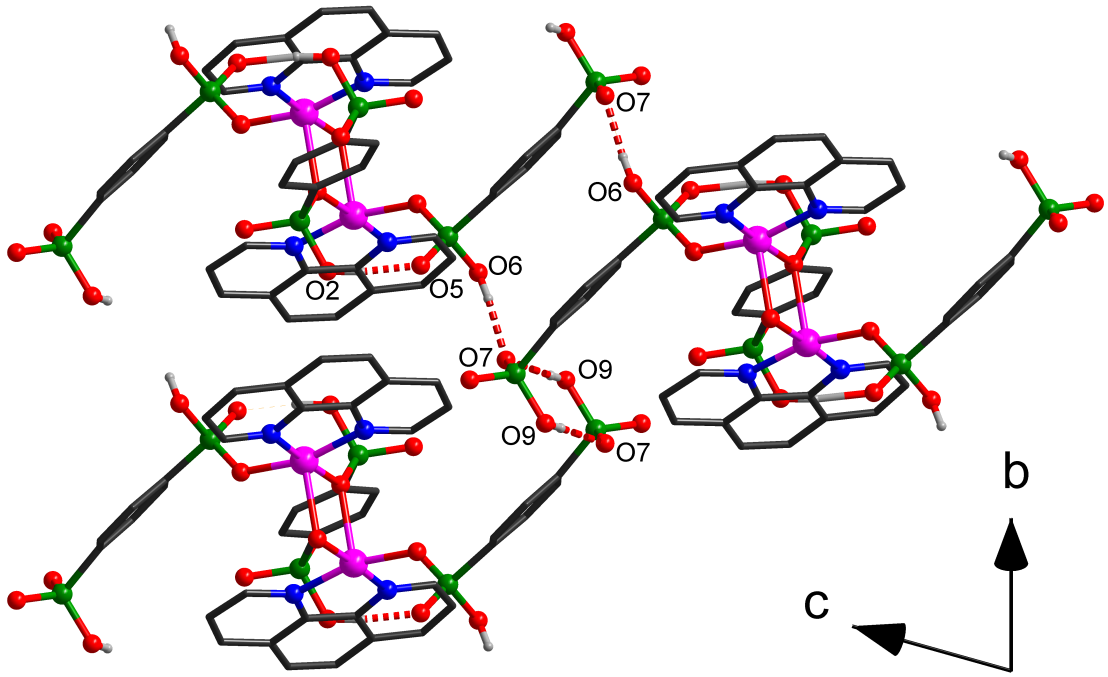

Figure S10 System of hydrogen bonds in the fragment of **3**.

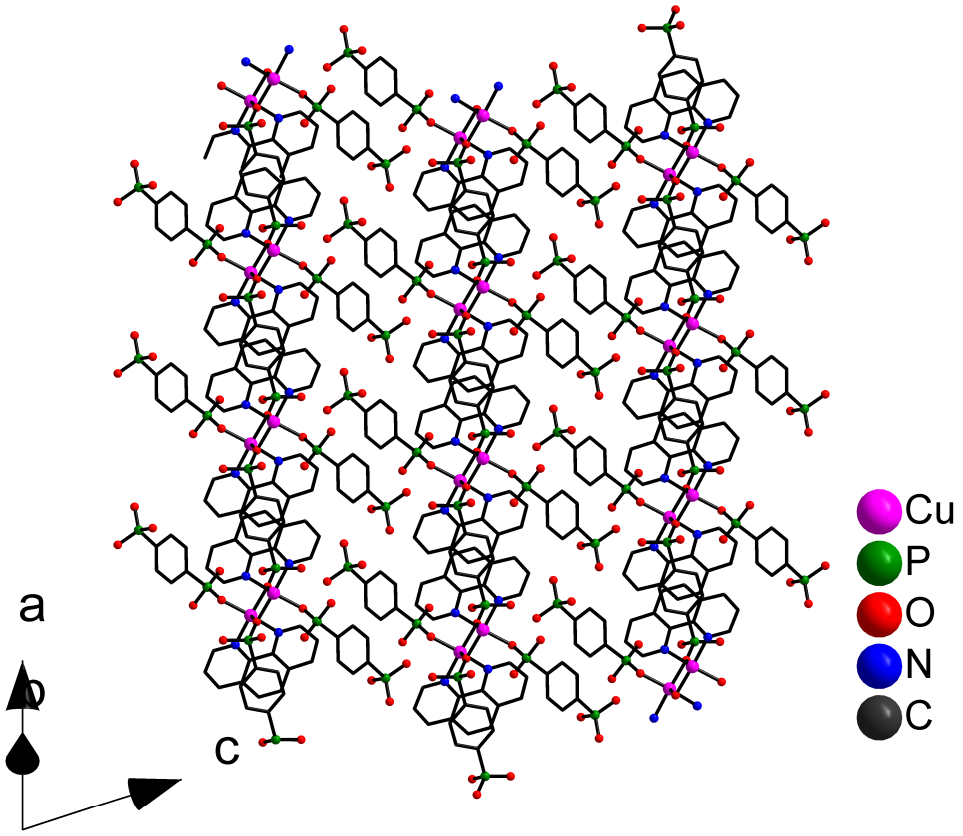

Figure S11 Chain stacking in the structure of **3**.

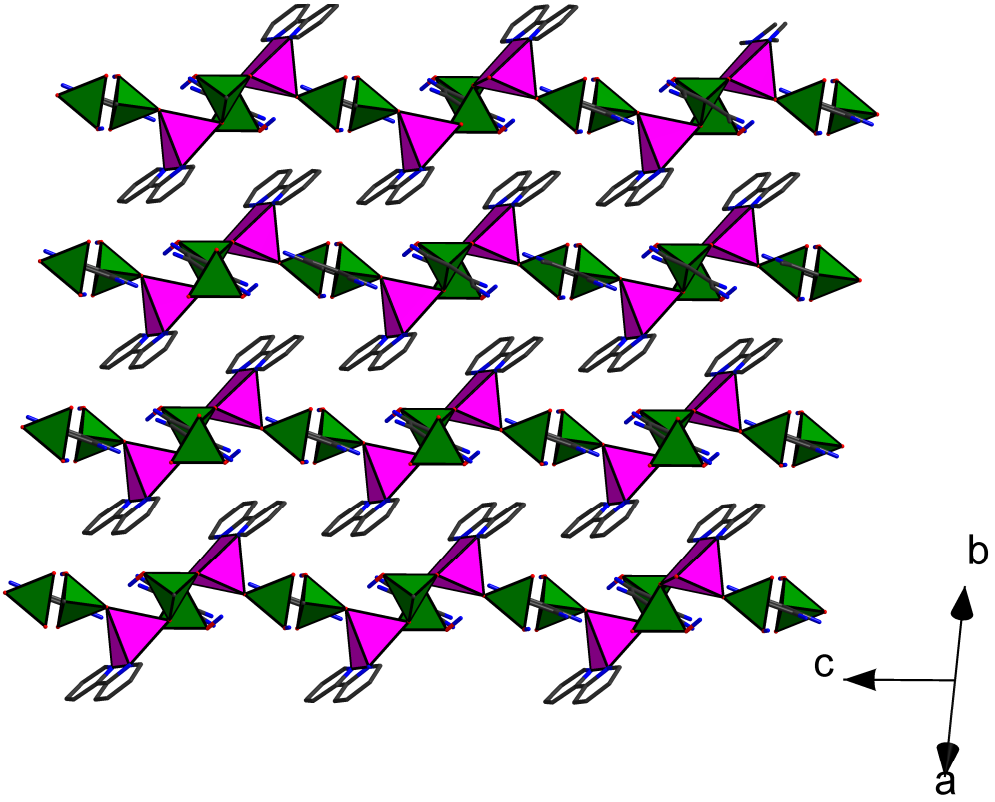

Figure S12 Stacking of the layers in **4** viewed along the *ab* diagonal.

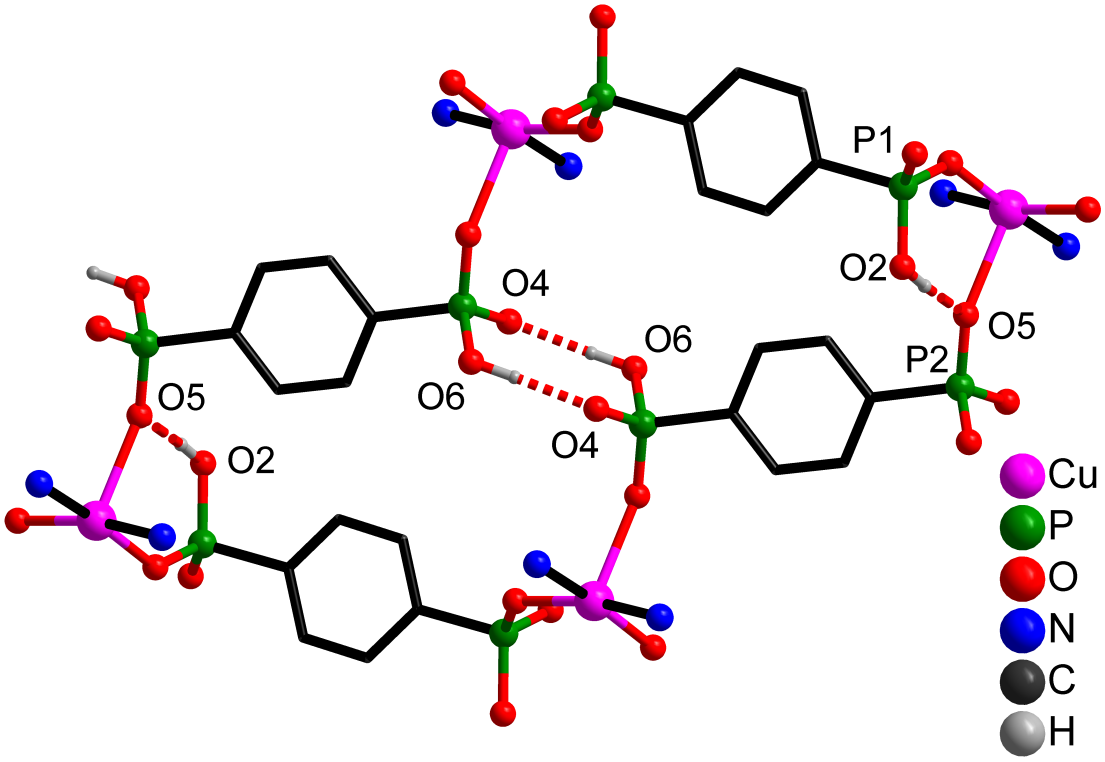

Figure S13 Hydrogen bonds in the ring fragment of **4.**

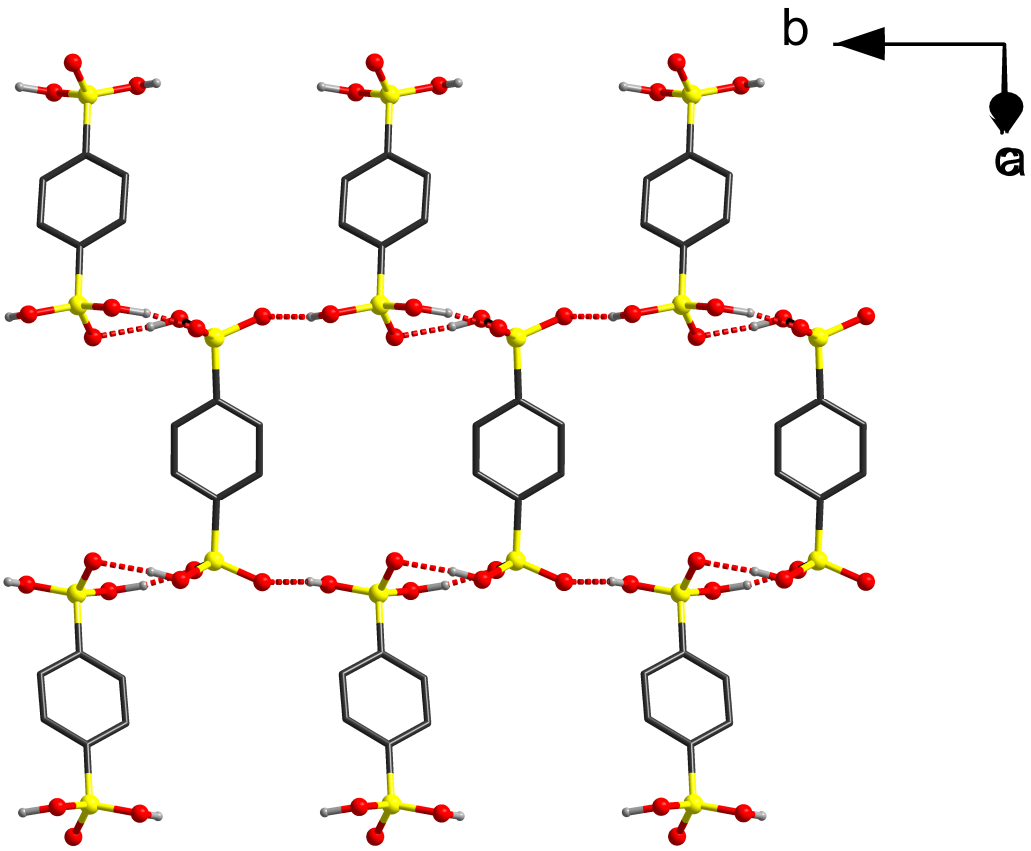

Figure S14 Hydrogen bonds in the organic fragment of **4.**

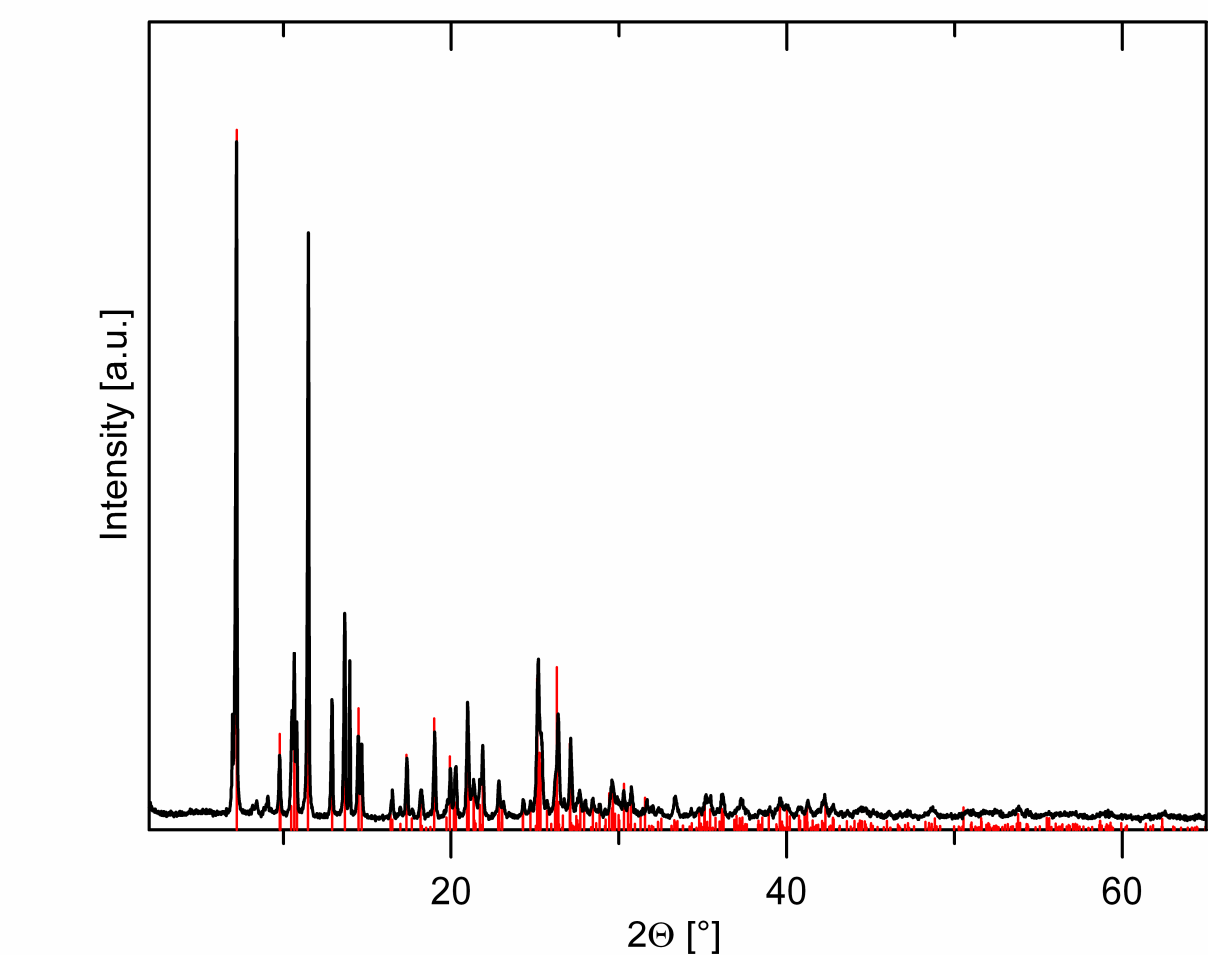

Figure S15 Powder X-ray pattern of **3**.

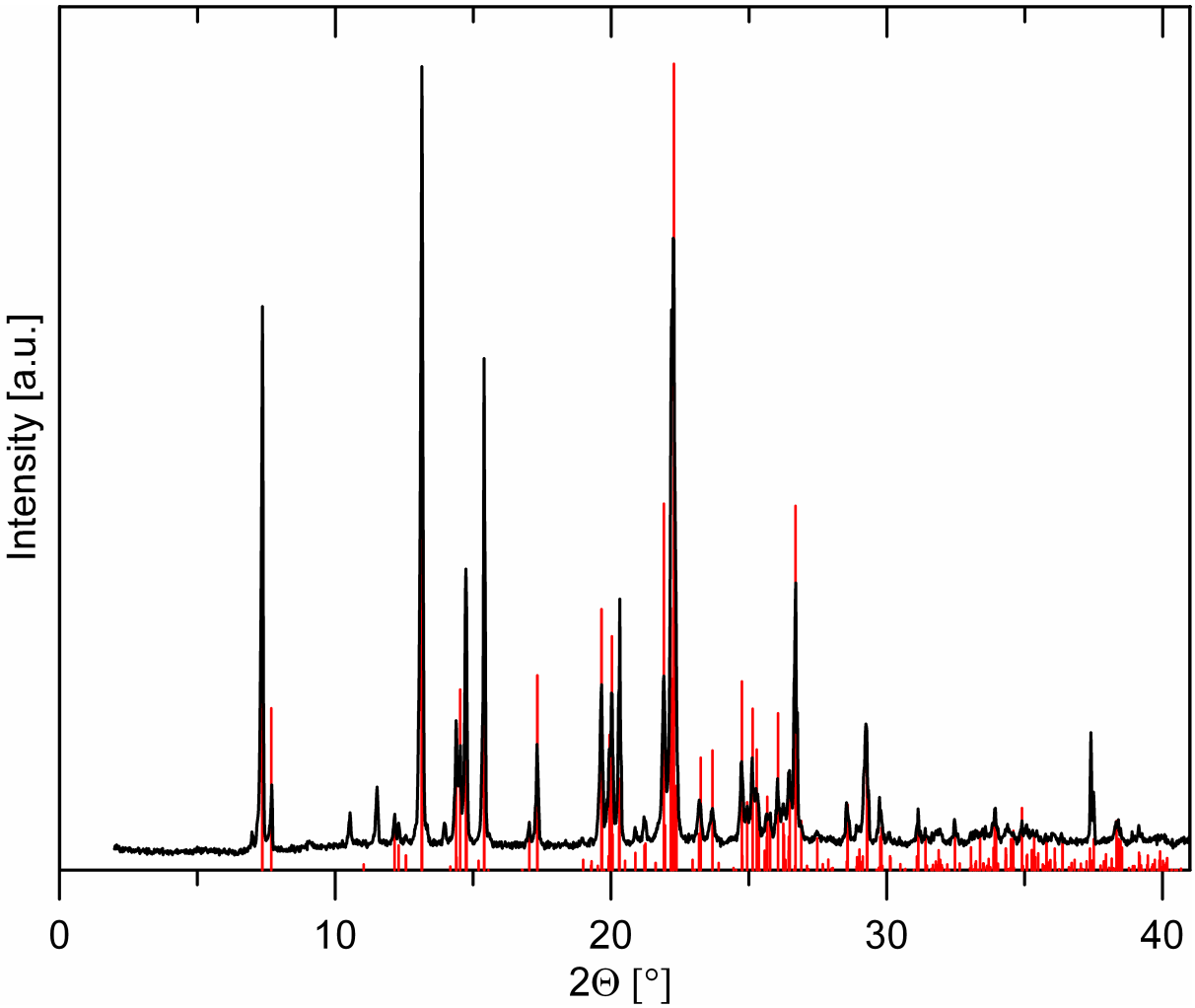

Figure S16 Powder X-ray pattern of **5**.