

Supplementary Information

Atmosphere-Controlled Solvatomorphic Transitions of Ternary Copper(II) Coordination Compounds in Solid State

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Table S1. Mechanochemical synthetic conditions and the amounts of reactants and solvents used for the reactions with copper(II) sulfate pentahydrate.

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Table S2. Mechanochemical synthetic conditions and the amounts of reactants and solvents used for the reactions with copper(II) sulfate trihydrate and monohydrate.

Synthesis number		8	9	10	11	12	13
Reactants	$n(\text{CuSO}_4 \cdot x\text{H}_2\text{O})/\text{mmol}$	0.25	0.25	0.25	0.25	0.25	0.25
	$m(\text{CuSO}_4 \cdot x\text{H}_2\text{O})/\text{mg}$	53.8	53.6	53.2	44.3	44.3	44.4
	x	3	3	3	1	1	1
	$n(\text{Cu}(\text{OH})_2)/\text{mmol}$	0.25	0.25	0.25	0.25	0.25	0.25
	$m(\text{Cu}(\text{OH})_2)/\text{mg}$	24.3	24.6	24.5	24.9	24.9	24.2
	$n(\text{bpy})/\text{mmol}$	0.5	0.5	0.5	0.5	0.5	0.5
	$m(\text{bpy})/\text{mg}$	78.3	78.1	78.0	78.5	78.6	78.1
	$n(\text{L-ser})/\text{mmol}$	0.5	0.5	0.5	0.5	0.5	0.5
	$m(\text{L-ser})/\text{mg}$	52.6	52.7	52.7	52.6	52.0	52.6
Liquid	$\eta/\mu\text{L mg}^{-1}$	0.1	0.2	-	0.1	0.2	-
	$V(\text{CH}_3\text{OH})/\mu\text{L}$	20.9	41.8	-	20.0	40.0	-
	Product	1a-α + UP^a	1a-α + UP^a	- ^b	1a-α	1a-α	- ^c

^a unknown phase(s)

^b very small amount of new phases formed, possibly **1a- α** and unknown phases

^c no reaction

Table S3. Mechanochemical synthetic conditions and the amounts of reactants and solvents used for the reactions with anhydrous copper(II) sulfate.

Synthesis number		14	15	16	17	18	19
Reactants	<i>n</i> (CuSO ₄)/mmol	0.25	0.25	0.25	0.25	0.25	0.25
	<i>m</i> (CuSO ₄)/mg	39.6	40.1	39.0	40.2	39.9	39.9
	<i>n</i> (Cu(OH) ₂)/mmol	0.25	0.25	0.25	0.25	0.25	0.25
	<i>m</i> (Cu(OH) ₂)/mg	24.3	24.6	24.3	24.6	24.2	24.2
	<i>n</i> (bpy)/mmol	0.5	0.5	0.5	0.5	0.5	0.5
	<i>m</i> (bpy)/mg	78.0	78.1	78.4	78.1	78.0	78.3
Liquid	<i>n</i> (L-ser)/mmol	0.5	0.5	0.5	0.5	0.5	0.5
	<i>m</i> (L-ser)/mg	52.7	52.7	52.8	52.6	52.3	52.7
Liquid	$\eta/\mu\text{L mg}^{-1}$	-	0.1	0.2	0.4	0.6	1.8
	<i>V</i> (CH ₃ OH)/ μL	-	19.6	38.9	78.2	116.6	351.2
	Product	- ^a	1a-α	1a-α	1a-α + UP^b	1a-α + UP^b	1a-α^c + 1b·3CH₃OH^c

^a no reaction

^b unknown phase(s)

^c It is possible that **1a- α** does not form in reaction but only after decomposition of **1b·3CH₃OH**. PXRD experiment was conducted ex situ.

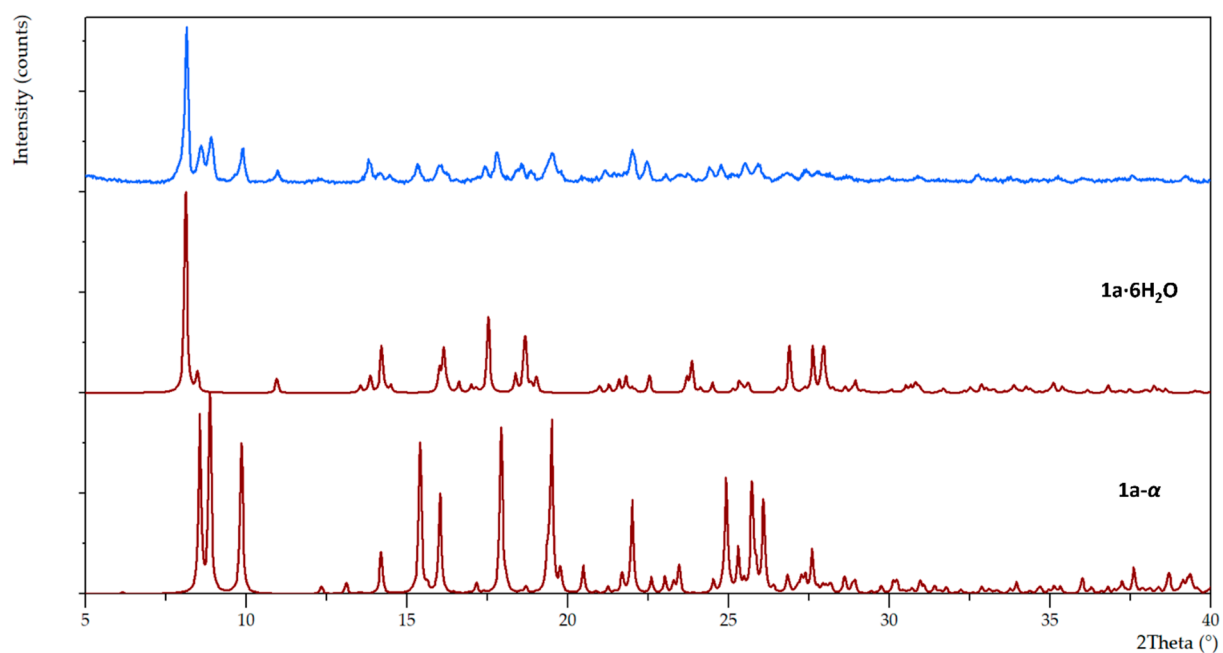


Figure S1. Experimental PXRD pattern (blue) of the products of synthesis no. 1 from Table S1 compared with calculated PXRD patterns from the crystal structures of **1a- α** and **1a·6H₂O** (red).

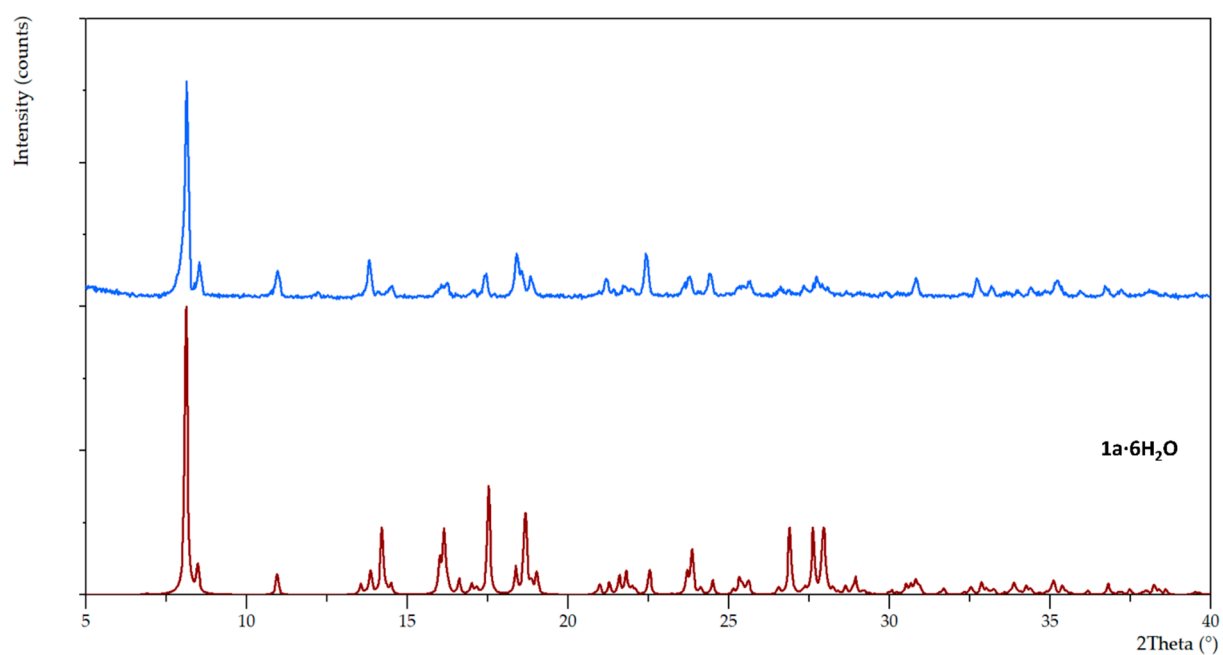


Figure S2. Experimental PXRD pattern (blue) of the products of synthesis no. 2 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a- α** (red).

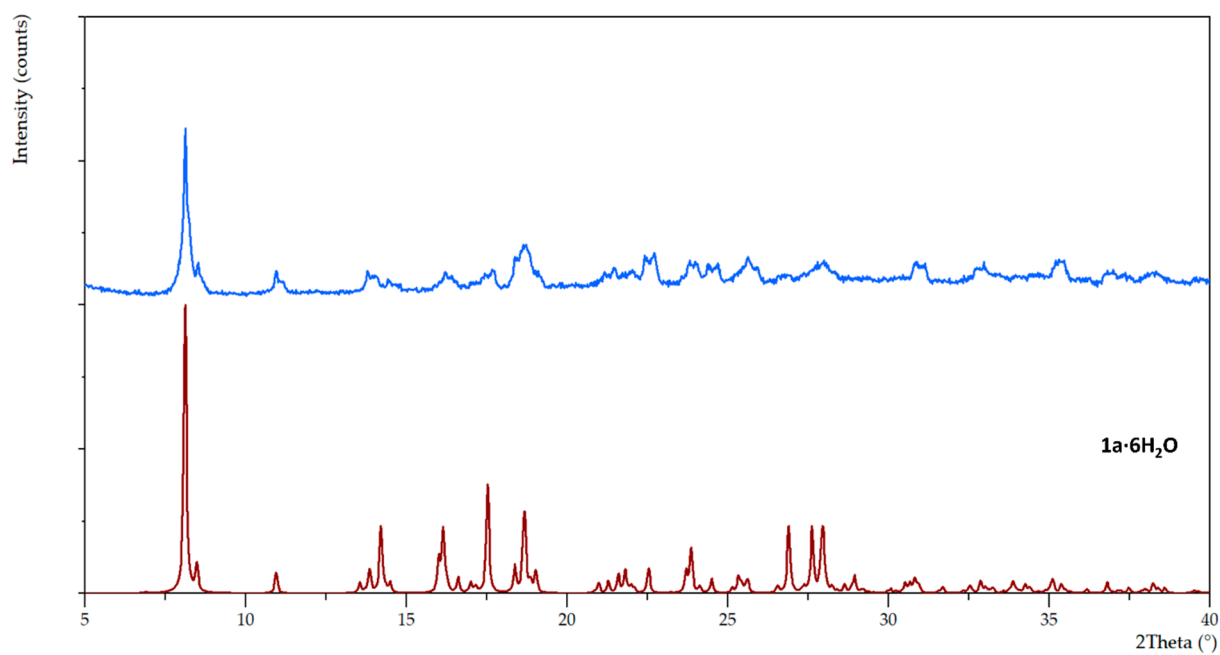


Figure S3. Experimental PXRD pattern (blue) of the products of synthesis no. 3 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a- α** (red).

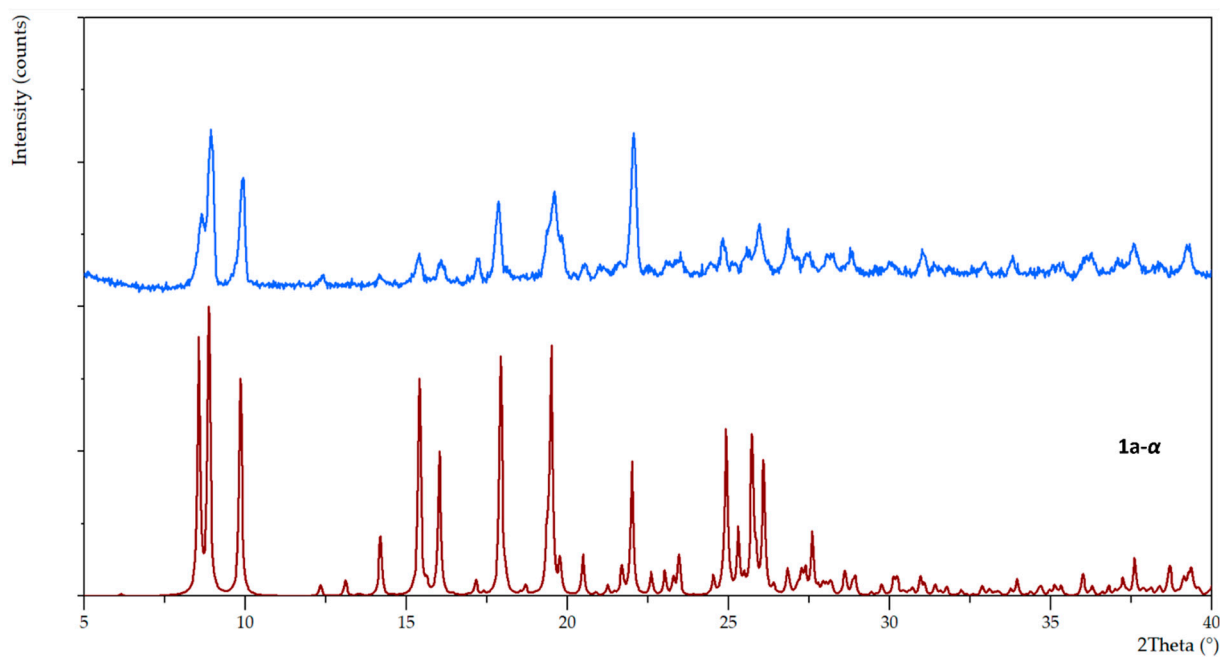


Figure S4. Experimental PXRD pattern (blue) of the products of synthesis no. 4 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a- α** (red).

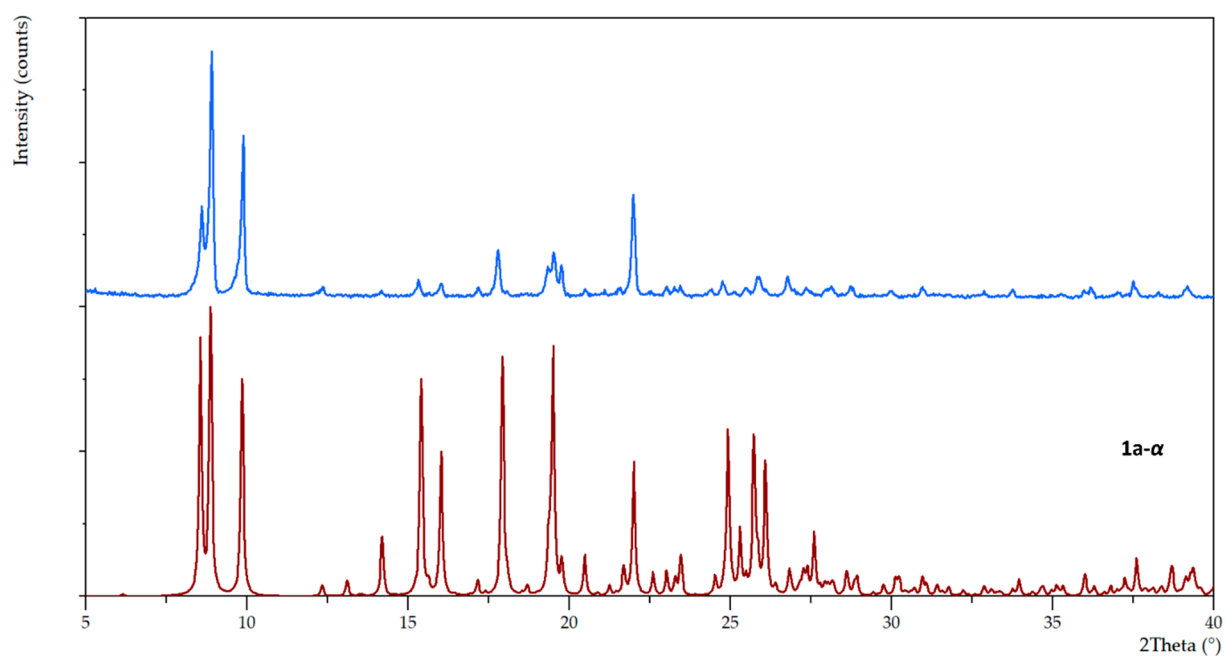


Figure S5. Experimental PXRD pattern (blue) of the products of synthesis no. 5 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a- α** (red).

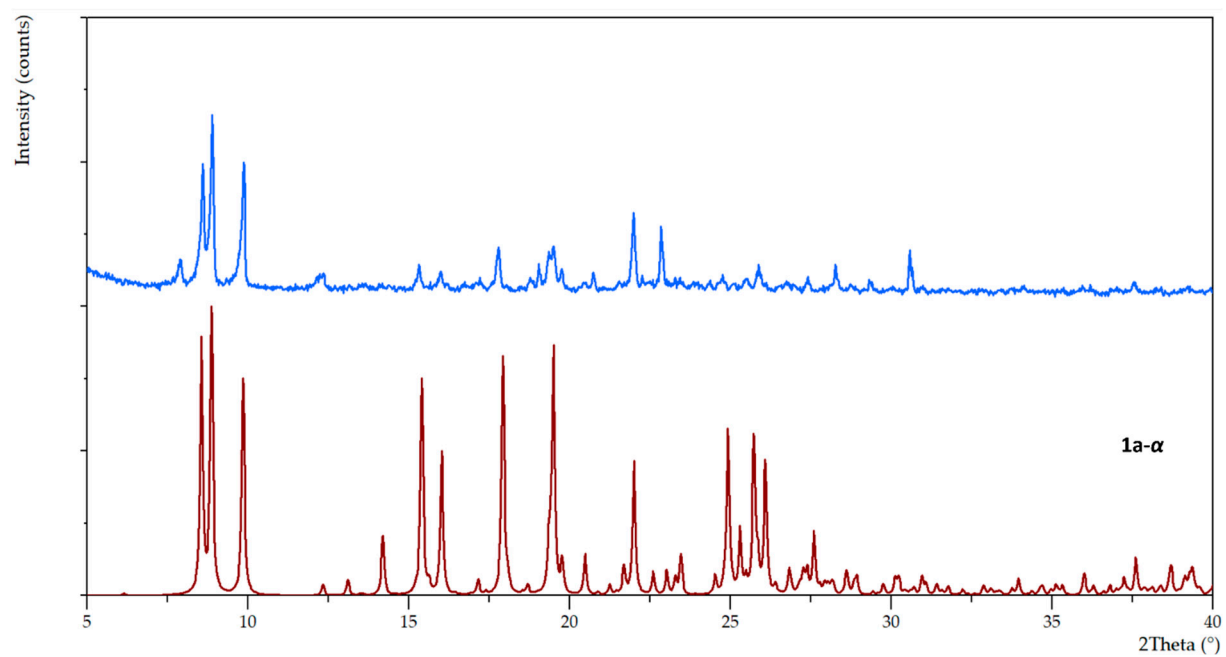


Figure S6. Experimental PXRD pattern (blue) of the products of synthesis no. 6 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a- α** (red).

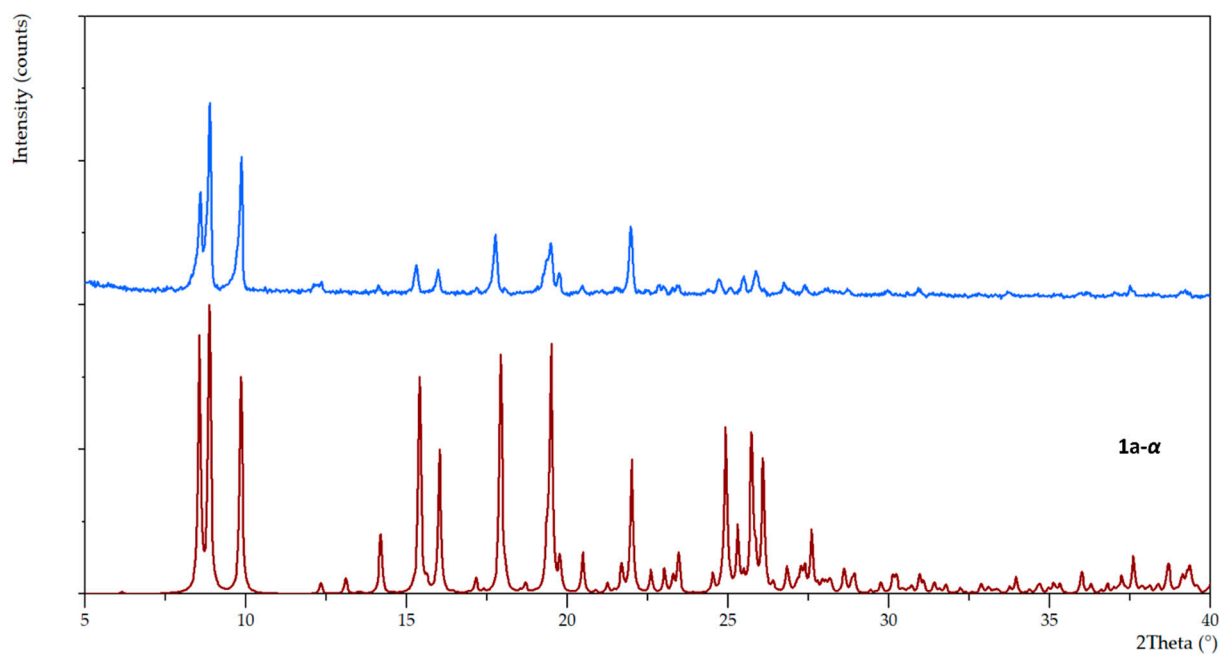


Figure S7. Experimental PXRD pattern (blue) of the products of synthesis no. 7 from Table S1 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

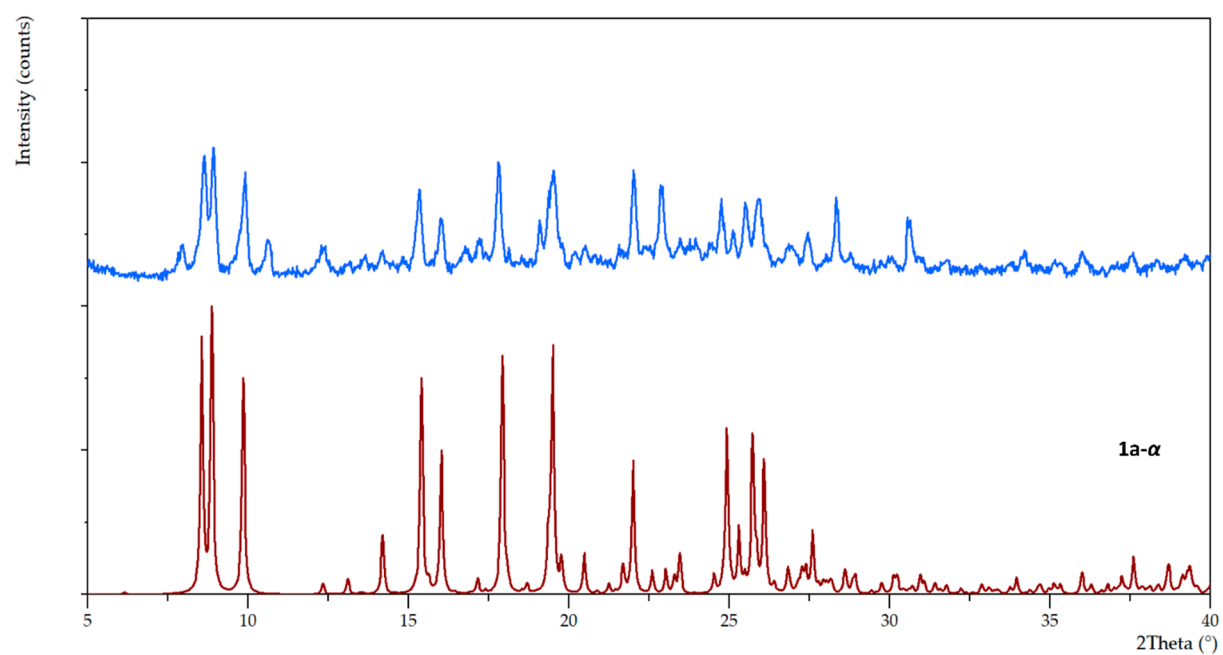


Figure S8. Experimental PXRD pattern (blue) of the products of synthesis no. 8 from Table S2 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

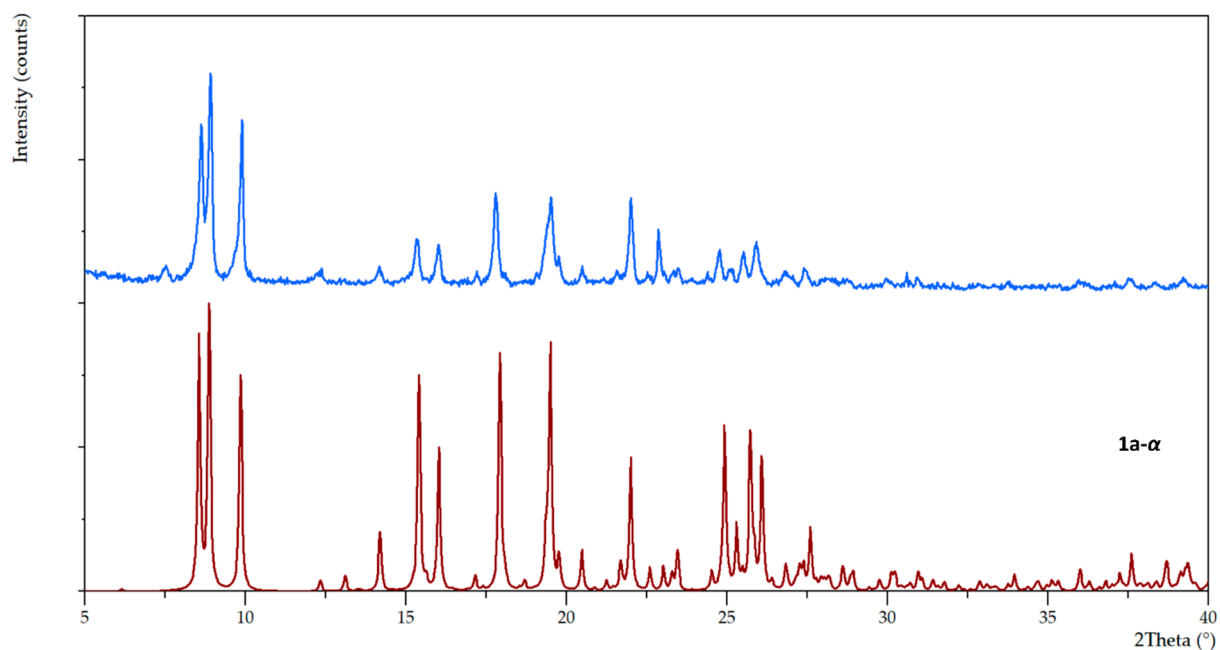


Figure S9. Experimental PXRD pattern (blue) of the products of synthesis no. 9 from Table S2 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

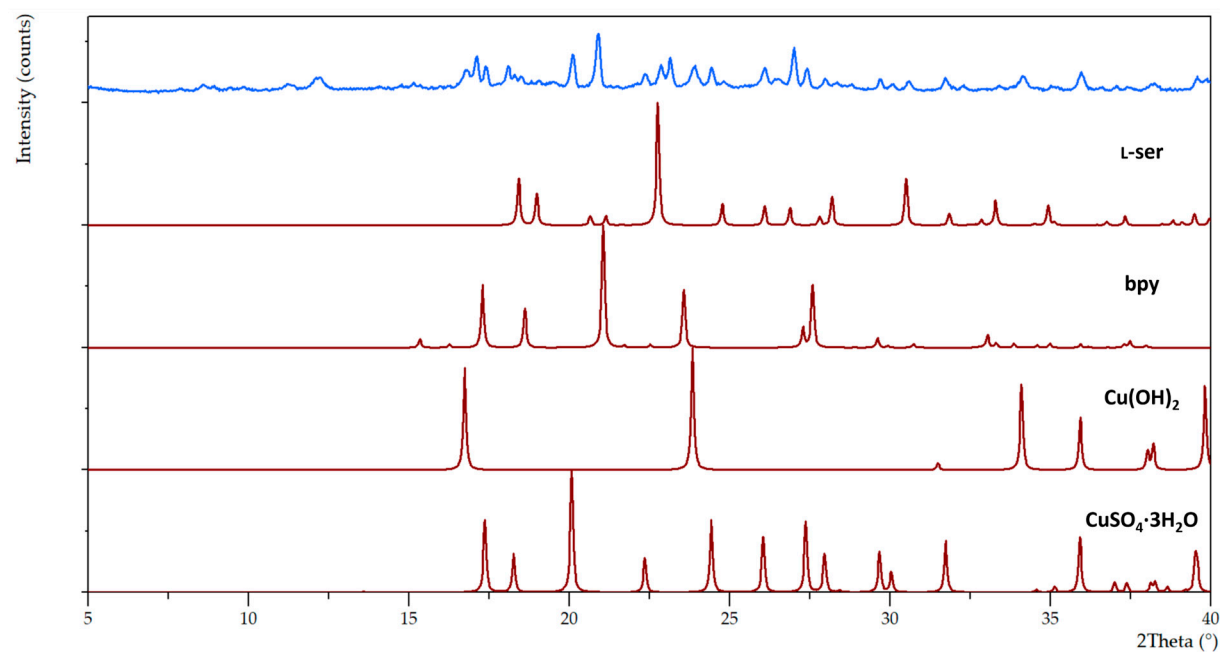


Figure S10. Experimental PXRD pattern (blue) of the products of synthesis no. 10 from Table S2 compared with calculated PXRD patterns from the crystal structures of reactants (red).

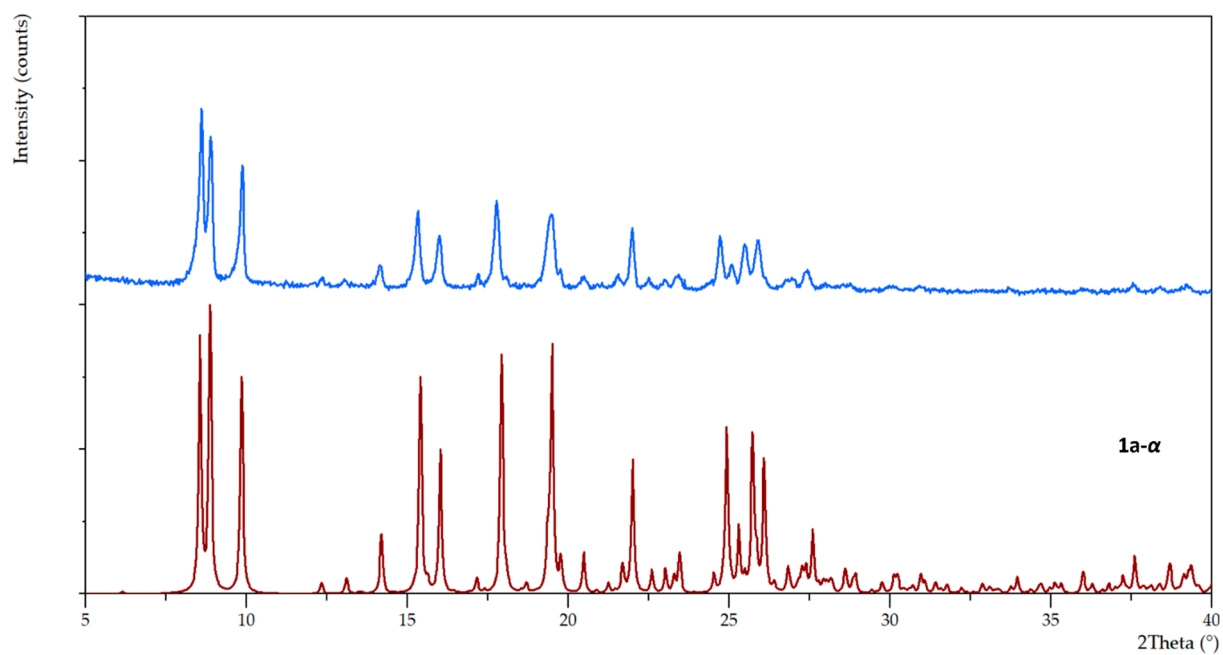


Figure S11. Experimental PXRD pattern (blue) of the products of synthesis no. 11 from Table S2 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

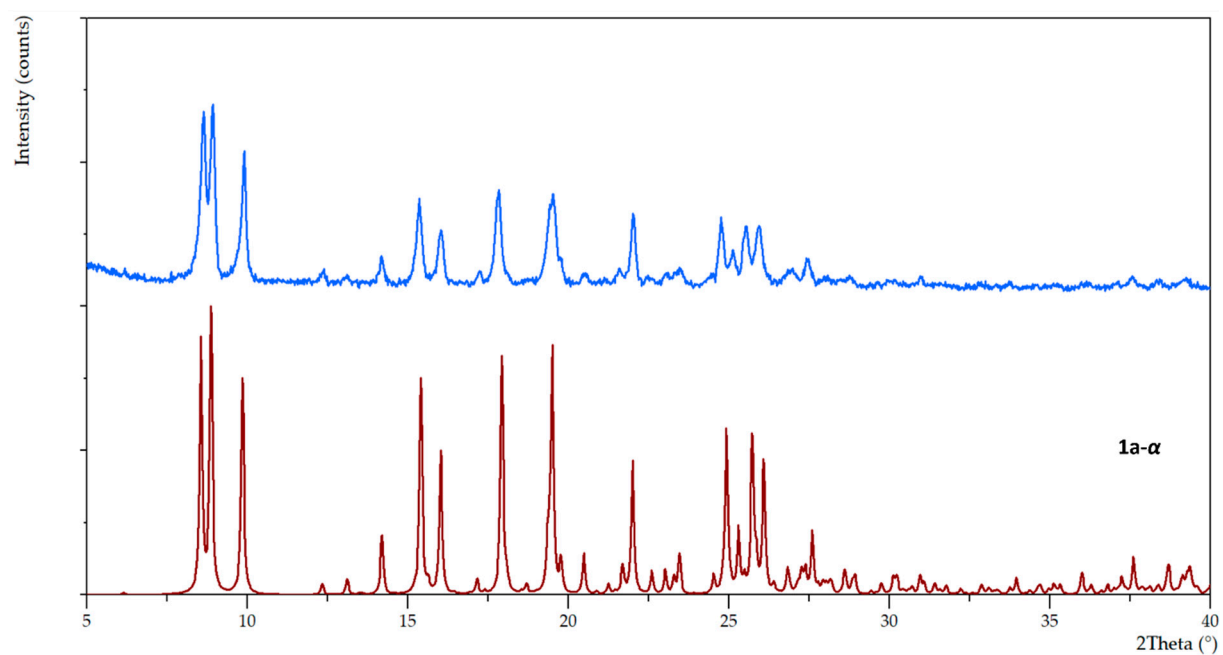


Figure S12. Experimental PXRD pattern (blue) of the products of synthesis no. 12 from Table S2 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

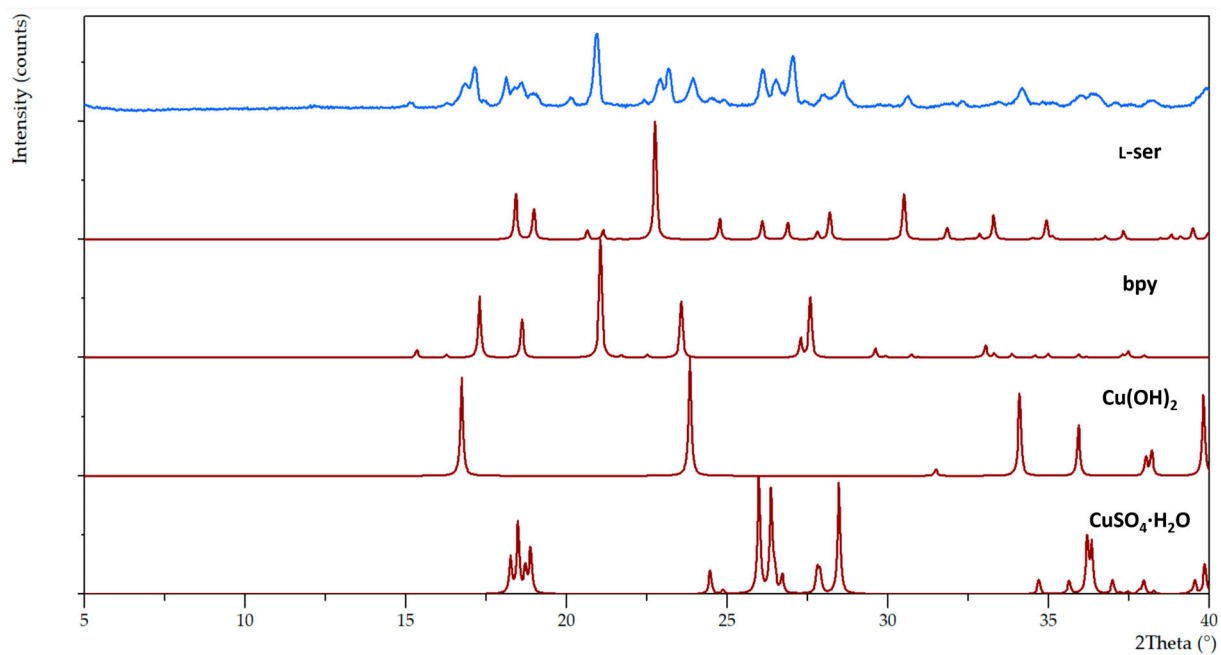


Figure S13. Experimental PXRD pattern (blue) of the products of synthesis no. 13 from Table S2 compared with calculated PXRD patterns from the crystal structures of reactants (red).

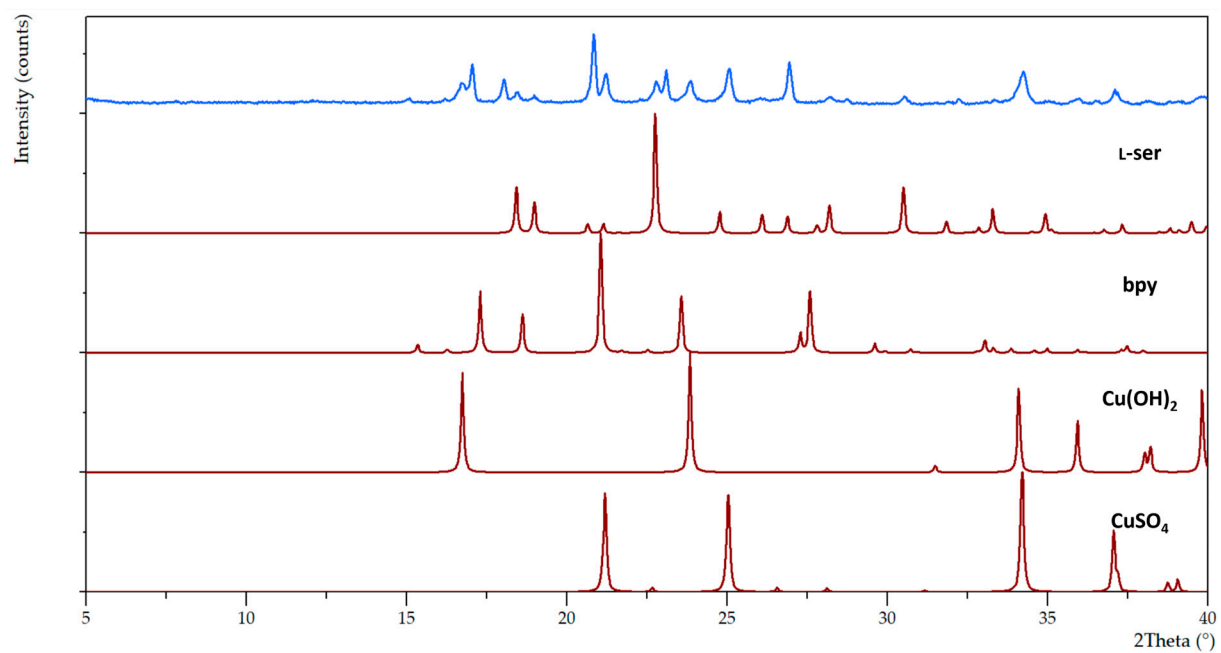


Figure S14. Experimental PXRD pattern (blue) of the products of synthesis no. 14 from Table S3 compared with calculated PXRD patterns from the crystal structures of reactants (red).

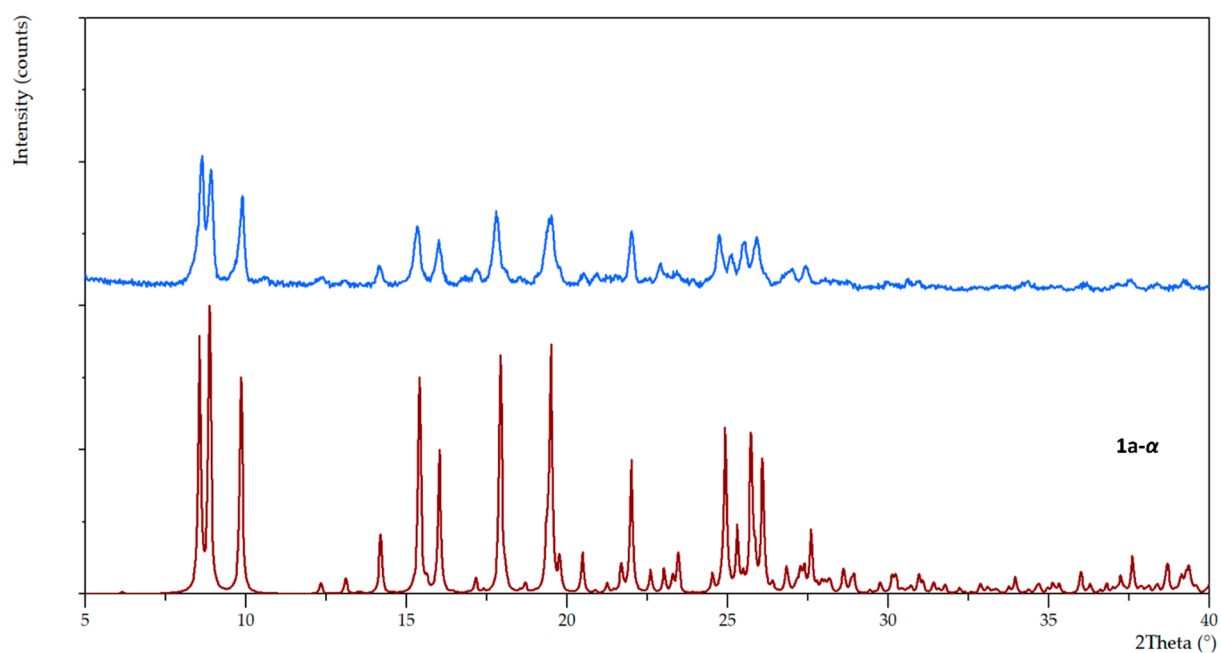


Figure S15. Experimental PXRD pattern (blue) of the products of synthesis no. 15 from Table S3 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

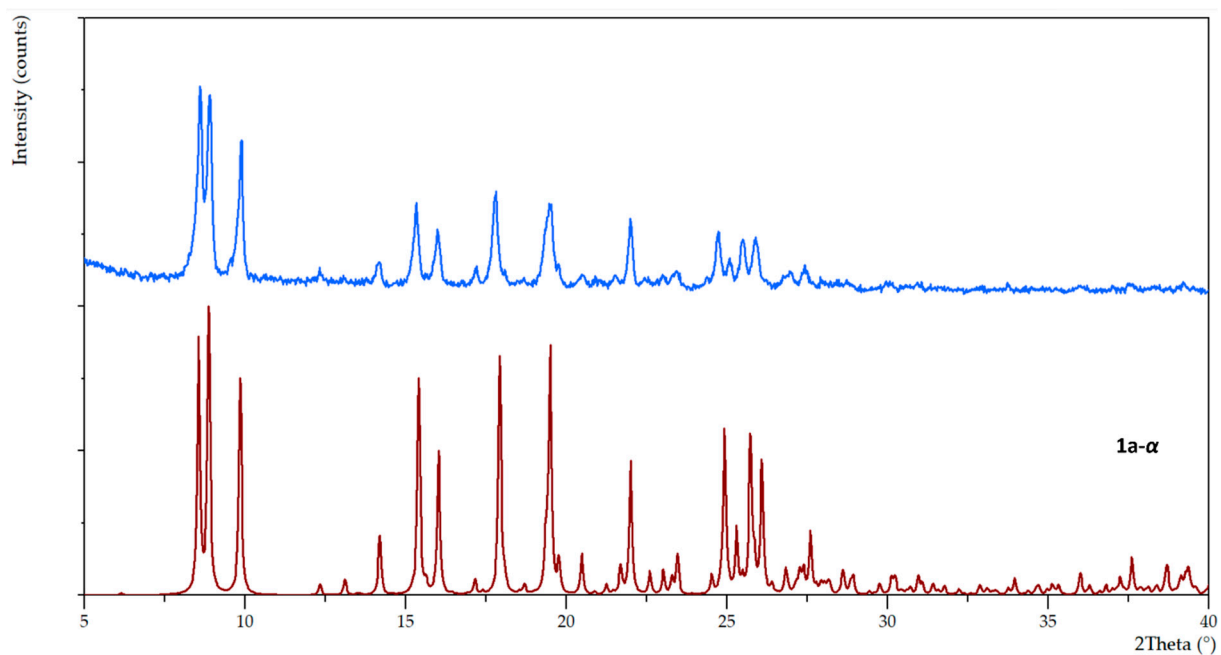


Figure S16. Experimental PXRD pattern (blue) of the products of synthesis no. 16 from Table S3 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

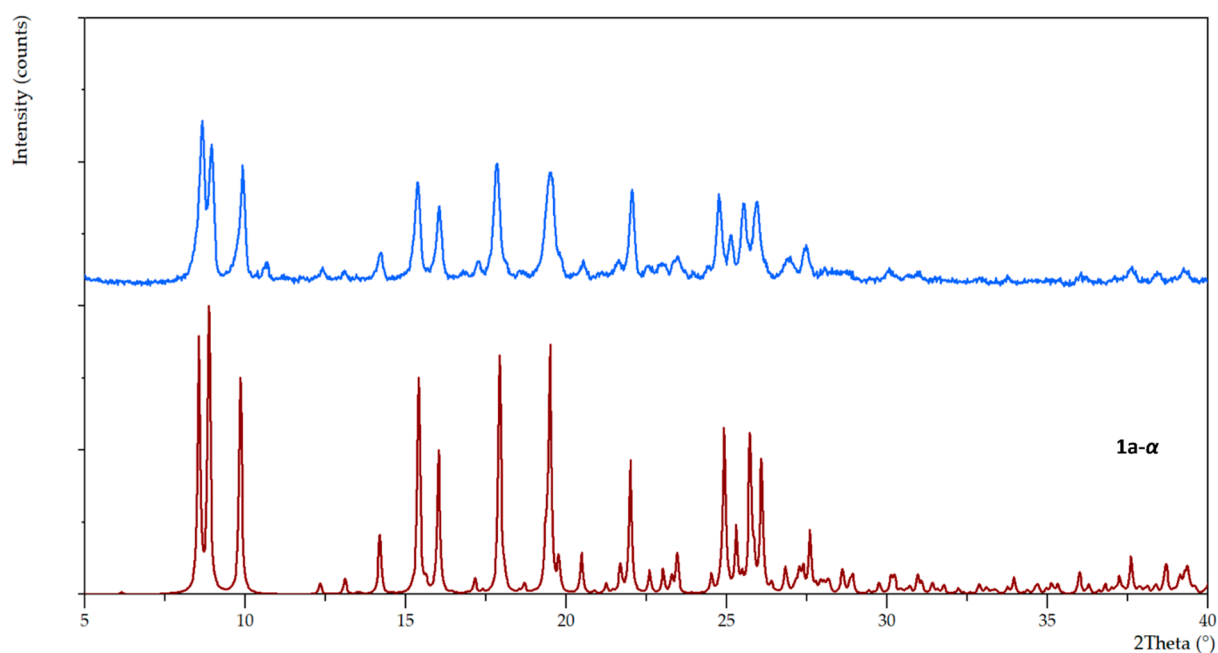


Figure S17. Experimental PXRD pattern (blue) of the products of synthesis no. 17 from Table S3 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

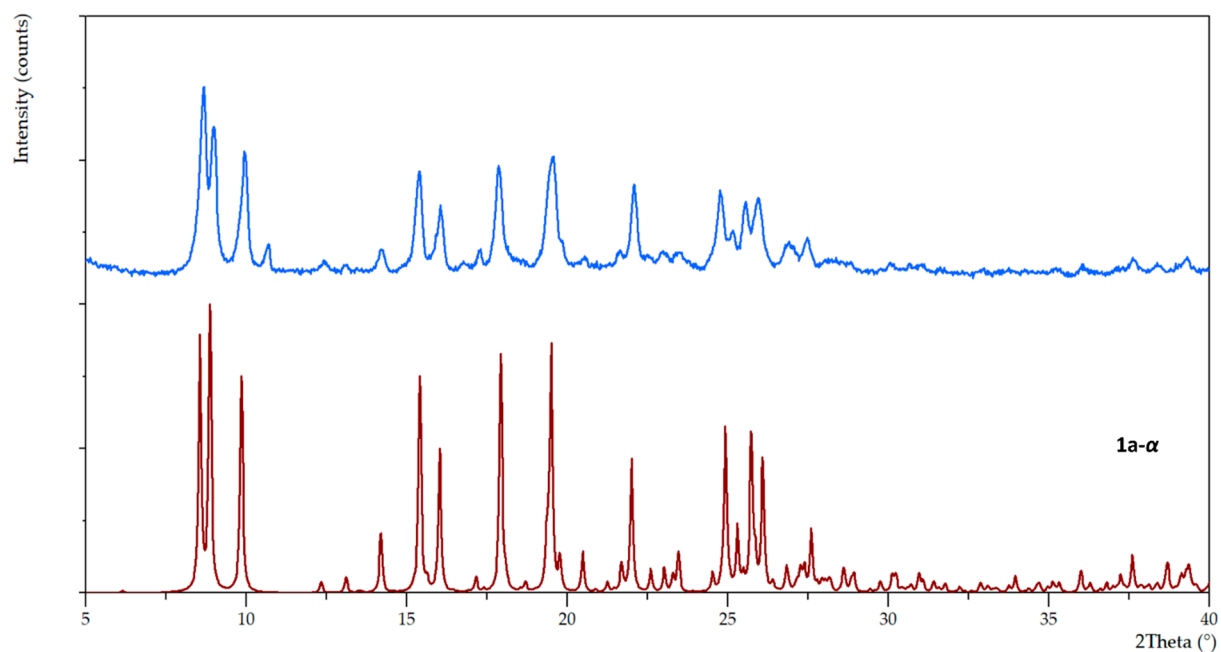


Figure S18. Experimental PXRD pattern (blue) of the products of synthesis no. 18 from Table S3 compared with calculated PXRD patterns from the crystal structure of **1a-α** (red).

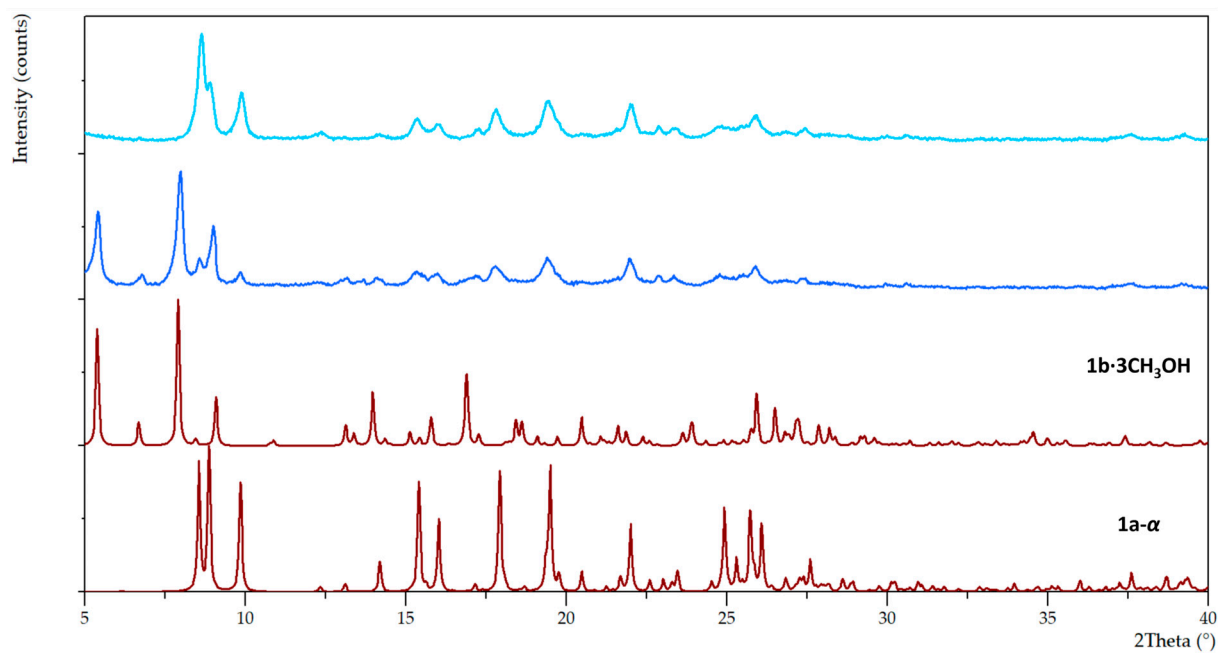


Figure S19. Experimental PXRD pattern of the products of synthesis no. 19 from Table S3 measured immediately upon opening the jar (blue) and after 2 min of standing in the air (light blue) compared with calculated PXRD patterns from the crystal structures of **1a- α** and **1b·3CH₃OH** (red).

2. Transformations $1\mathbf{a}\cdot 6\mathbf{H}_2\mathbf{O} \rightleftharpoons 1\mathbf{a}\cdot \alpha$

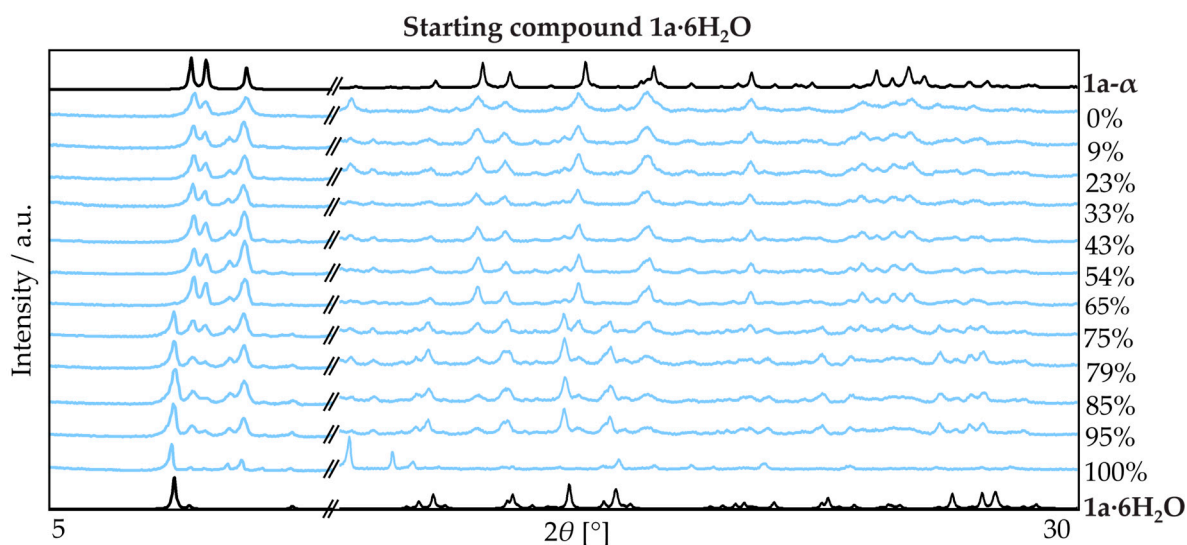


Figure S20. Experimental PXRD patterns of $1\mathbf{a}\cdot 6\mathbf{H}_2\mathbf{O}$ after aging 4 weeks (blue) in a humidity- and temperature-controlled chamber compared with calculated PXRD patterns from the crystal structures of $1\mathbf{a}\cdot \alpha$ and $1\mathbf{a}\cdot 6\mathbf{H}_2\mathbf{O}$ (black).

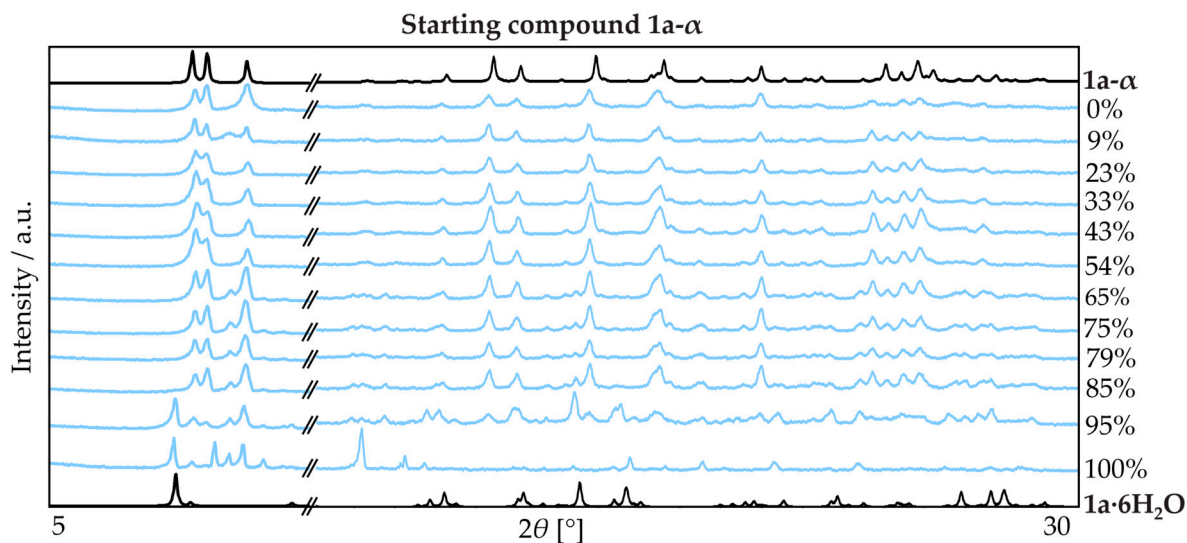


Figure S21. Experimental PXRD patterns of $1\mathbf{a}\cdot \alpha$ after aging 4 weeks (blue) in a humidity- and temperature-controlled chamber compared with calculated PXRD patterns from the crystal structures of $1\mathbf{a}\cdot \alpha$ and $1\mathbf{a}\cdot 6\mathbf{H}_2\mathbf{O}$ (black).

3. Thermogravimetric analysis and infrared spectroscopy

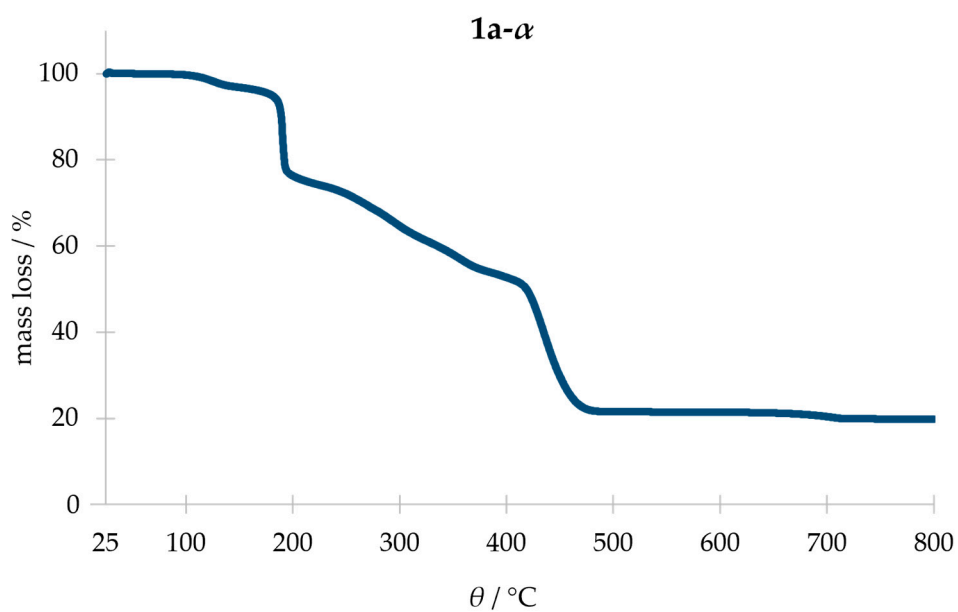


Figure S22. TGA curve of **1a- α** .

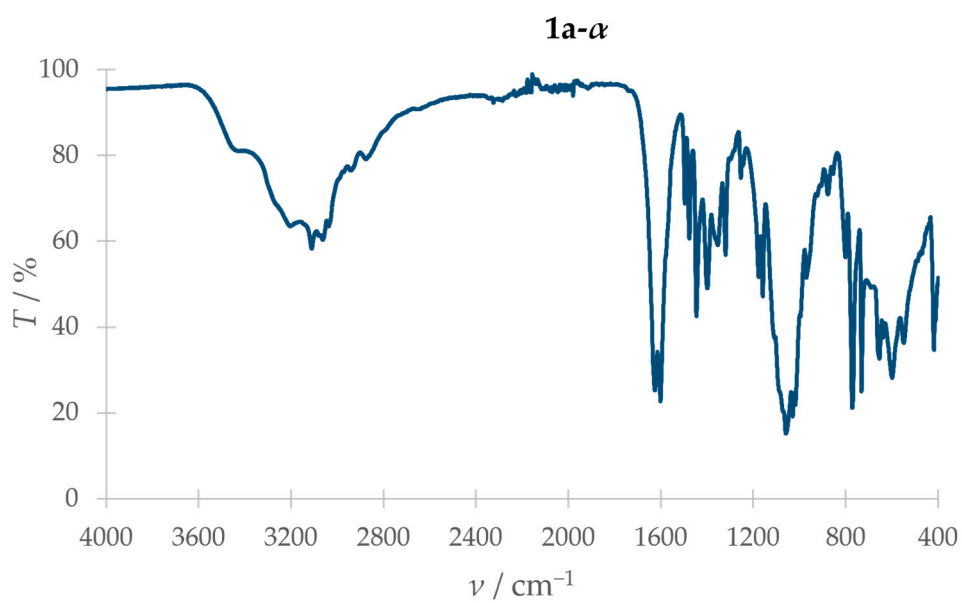


Figure S23. IR(ATR) spectrum of **1a- α** .

4. Crystal structures

Table S4. Crystallographic data for compounds **1a- α** , **1a- β** , **1a-6H₂O**, and **1b-3CH₃OH**.

	1a-α	1a-β	1a-6H₂O	1b-3CH₃OH
Formula	C ₂₆ H ₃₂ Cu ₂ N ₆ O ₁₂ S	C ₂₆ H ₃₂ Cu ₂ N ₆ O ₁₂ S	C ₂₆ H ₄₄ Cu ₂ N ₆ O ₁₈ S	C ₃₁ H ₄₈ Cu ₂ N ₆ O ₁₅ S
Formula weight	779.71	779.71	887.81	903.89
[g mol ⁻¹]				
λ [Å]	sync, 0.70000	1.54184	sync, 0.70000	sync, 0.70000
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	7.1389(1)	10.0790(3)	6.7125(1)	6.8675(1)
<i>b</i> [Å]	20.7625(4)	20.9260(5)	20.8435(2)	20.9159(2)
<i>c</i> [Å]	20.0048(4))	14.5656(3)	13.1341(1)	26.4444(3)
α [°]	90	90	90	90
β [°]	95.348(2)	107.209(3)	103.455(1)	90
γ [°]	90	90	90	90
<i>V</i> [Å ³]	2952.23(9)	2934.55(14)	1787.18(4)	3798.47(8)
<i>Z</i>	4	4	2	4
<i>T</i> [K]	100	100	100	100
ρ [g cm ⁻³]	1.754	1.765	1.650	1.581
μ [mm ⁻¹]	1.455	3.129	1.221	1.203
θ range [°]	2.0, 25.9	3.2, 68.2	1.6, 30.0	1.8, 30.0
Obs. reflections	10731	10378	9957	11324
(<i>I</i> > 2 σ (<i>I</i>))				
Number of parameters	881	876	526	514
<i>R</i> ₁ (observed reflections) ¹	0.0673	0.0620	0.0335	0.0496
<i>wR</i> ₂ (all data) ²	0.1637	0.1561	0.0937	0.1349
<i>S</i> ³	1.06	1.06	1.04	1.04
min/max residual electron density [Å ⁻³]	-0.72, 1.25	-0.77, 0.91	-0.55, 0.82	-0.63, 0.87
CCDC no.	2393622	2393624	2393621	2393623

Table S5. Distances ([Å]) within the polyhedra of copper coordination spheres in the crystal structures of **1a- α** , **1a- β** , **1a·6H₂O**, and **1b·3CH₃OH**.

Bond lengths [Å]				
	1a-α	1a-β	1a·6H₂O	1b·3CH₃OH
Cu1-O11	1.936(9)	1.949(6)	1.932(3)	1.932(3)
Cu1-O13	2.249(8)	2.298(6)	2.252(3)	-
Cu1-O1M	-	-	-	2.234(3)
Cu1-N1	1.989(10)	1.986(8)	1.994(2)	2.005(3)
Cu1-N11	1.982(9)	1.988(7)	2.005(2)	2.004(3)
Cu1-N110	1.994(10)	2.004(7)	1.992(2)	2.004(3)
Cu2-O21	1.940(8)	1.947(6)	1.945(2)	1.923(3)
Cu2-O23	2.205(8)	2.302(6)	2.253(3)	-
Cu2-O2M	-	-	-	2.347(4)
Cu2-N2	2.011(10)	1.992(7)	1.994(2)	1.974(3)
Cu2-N21	2.002(8)	1.980(7)	1.999(3)	1.993(4)
Cu2-N210	2.012(10)	2.005(7)	1.993(3)	1.993(3)
Cu3-O31	1.951(8)	1.941(6)	-	-
Cu3-O33	2.225(8)	2.221(7)	-	-
Cu3-N3	1.995(9)	1.991(8)	-	-
Cu3-N31	2.000(10)	1.999(7)	-	-
Cu3-N310	2.009(10)	2.021(8)	-	-
Cu4-O41	1.943(8)	1.955(7)	-	-
Cu4-O43	2.216(9)	2.228(6)	-	-
Cu4-N4	2.002(10)	2.002(8)	-	-
Cu4-N41	2.009(10)	2.008(8)	-	-
Cu4-N410	2.010(10)	2.039(8)	-	-

Table S6. Selected hydrogen bonds in **1a- α** , **1a- β** , **1a·6H₂O**, and **1b·3CH₃OH**.

Compound	D–H···A	<i>d</i> (D–H···A) / Å	\angle (D–H···A) / °
1a-α	O13–H13A···O31	2.952(13)	133(12)
	O23–H23B···O41	3.131(11)	145(9)
	O1G–H1G···O24S	2.56(2)	131
	O4G2–H4G2···O11S	2.730(16)	164
	N4–H4B···O3G	3.133(12)	152
1a-β	O13–H13A···O12S	2.711(9)	159(9)
	O23–H23A···O41 ¹	3.069(9)	153(11)
	O23–H23B···O21S	3.102(10)	125(9)
	O33–H33A···O11S	2.654(11)	166(13)
	O43–H43A···O24S	2.674(10)	173(9)
	O1G–H1G1···O21S	2.828(15)	172
	O2G–H2G···O11S	2.584(11)	126
	O3G–H3G···O23S	2.650(10)	153
	N1–H1B···O4G	3.403(11)	168
	N2–H2A···O3G	2.931(10)	176
	N3–H3B···O2G	3.229(10)	156
1a·6H₂O	O1W–H1WB···O12	2.665(4)	171(4)
	O13–H13A···O3W	2.697(4)	174(3)
	O23–H23A···O1W	2.771(3)	172(3) ¹
	O23–H23B···O13S ²	2.729(3)	171(4)
	O2W–H2WA···O11S	2.882(4)	165(6)
	O1G–H1G···O11S	2.844(4)	155
	O2G–H2G···O14S ²	2.736(4)	164
	N1–H1C···O2G	3.201(4)	157
1b·3CH₃OH	O1M–H1M···O12 ³	2.634(4)	171(5)
	O2M–H2M···O2S ²	2.614(5)	171(6)
	O3M–H3M···O1S	2.759(6)	157(9)
	O1G–H1G···O4S	2.799(4)	169
	O2G–H2G···O3S ⁴	2.712(4)	168
	N1–H1B···O2G	3.037(4)	160

¹–1+x,y,–1+z; ²–x,–1/2+y,–z; ³1+x,y,z; ⁴1–x,1/2+y,1/2–z

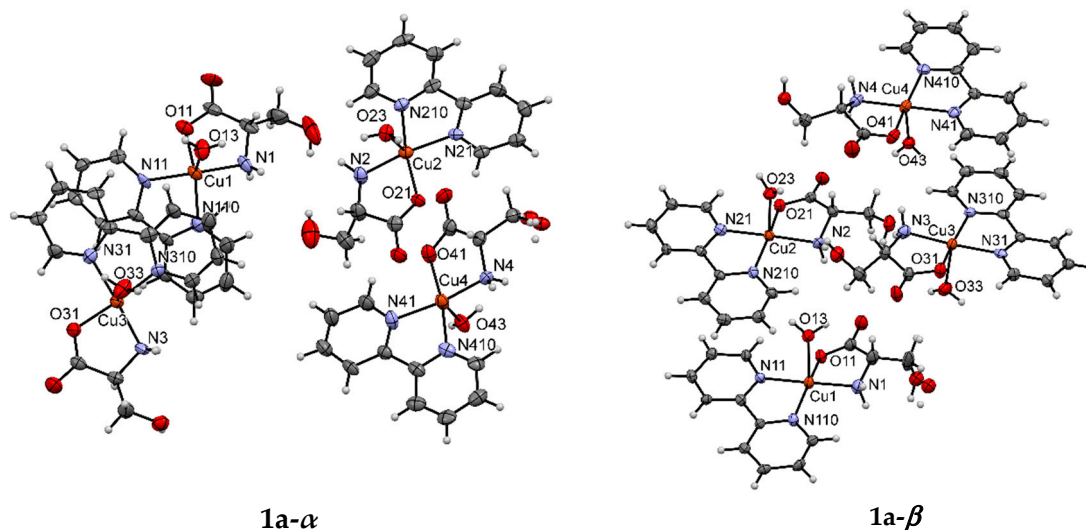


Figure S24. ORTEP plot of the asymmetric unit of **1a- α** and **1a- β** , with the atom labelling scheme in the copper coordination sphere. Crystallization water molecules and sulfate anion were omitted for clarity. Displacement ellipsoids were calculated at the 50% probability level.

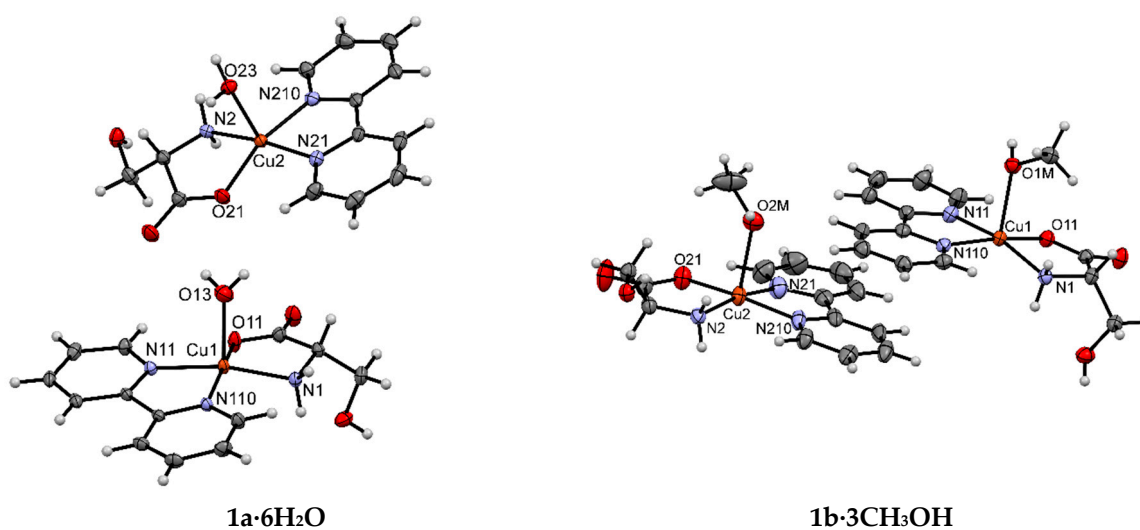


Figure S25. ORTEP plot of the asymmetric unit of **1a·6H₂O** and **1b·3CH₃OH** with the atom labelling scheme in the copper coordination sphere. Crystallization water/methanol molecules and sulfate anion were omitted for clarity. Displacement ellipsoids were calculated at the 50% probability level.

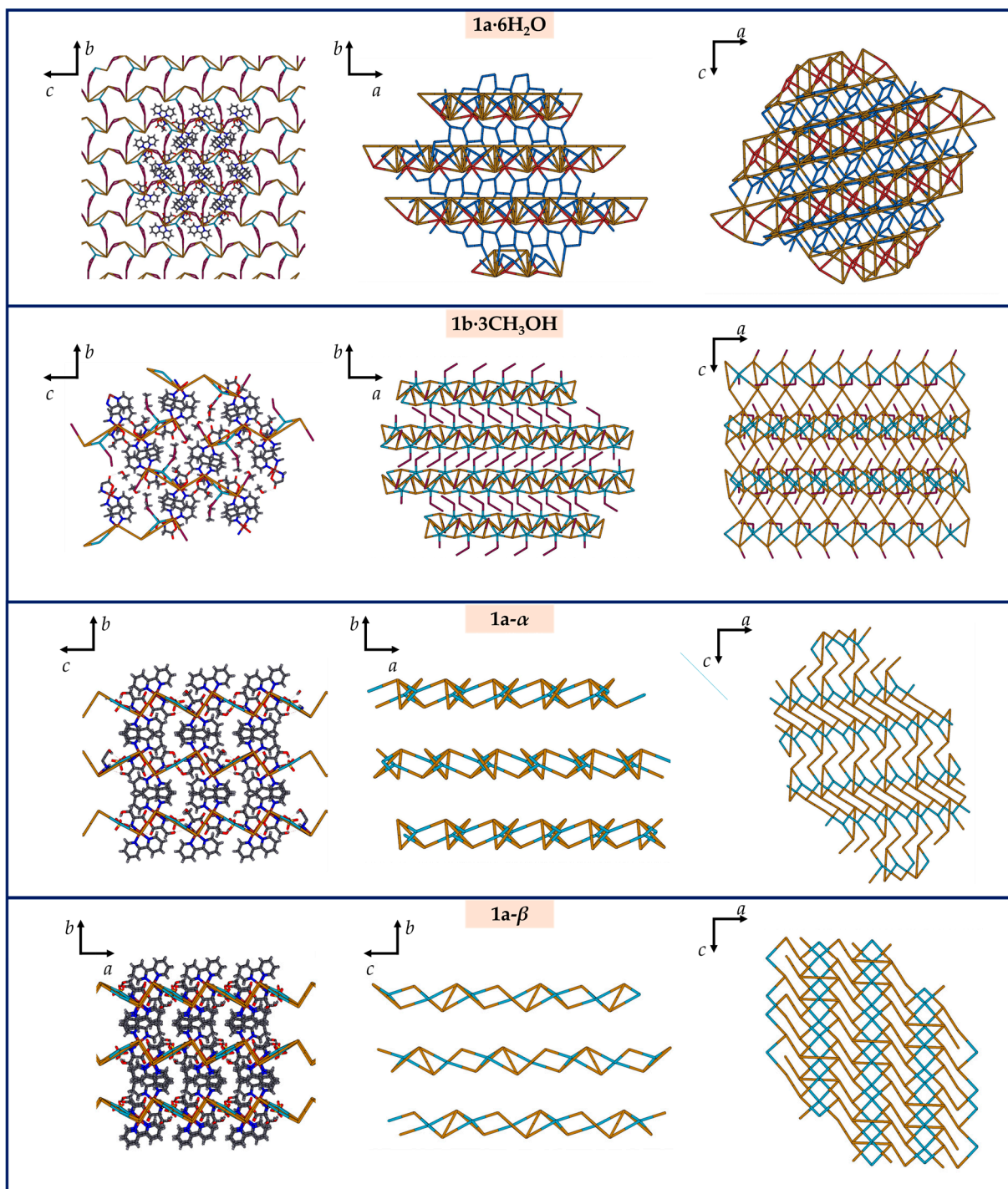


Figure S26. Simplified hydrogen bond frameworks. Brown lines represent hydrogen bonds formed by complex cations $[\text{Cu}(\text{L-ser})(\text{L})(\text{bpy})]^+$ ($\text{L} = \text{H}_2\text{O}$ or CH_3OH); light blue lines, hydrogen bonds formed by sulfate ions; dark blue lines, hydrogen bonds formed by crystallization water molecules in **1a·6H₂O**; and purple lines, hydrogen bonds formed by crystallization methanol molecules in **1b·3CH₃OH**. Atoms are shown in the pictures on the left, while the pictures in the middle and on the right, they are omitted for clarity.

5. Proliferation assays

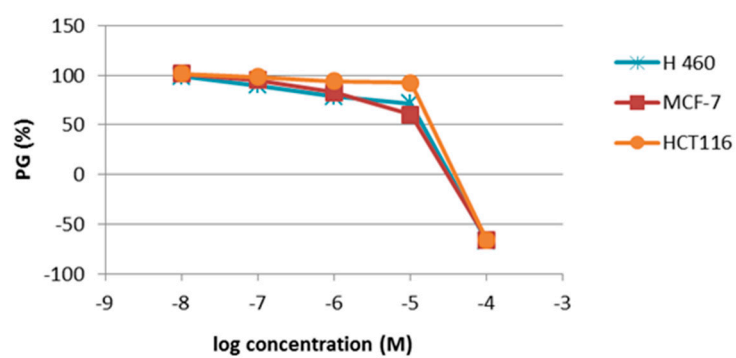


Figure S27. Concentration–response profiles for **1a-α** tested in vitro on HCT116, MCF-7, and H 460 cell lines.