Electronic supporting information

Comparison between mechanochemical and solution synthesis of Zn and Cu complexes containing pyridine and p-halogen substituted benzoates

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Content:

FT-IR ATR spectra

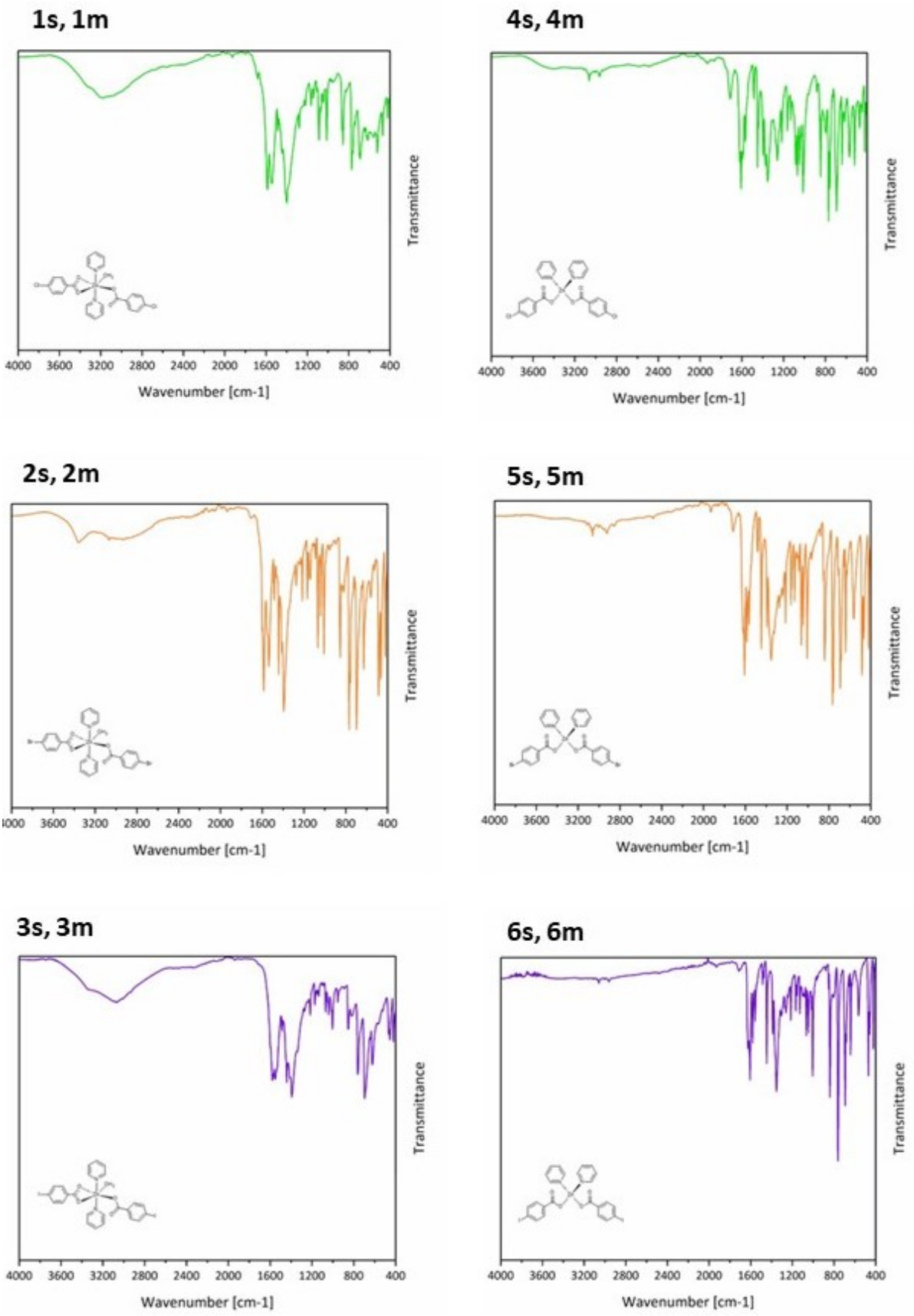


Figure S1. FTIR spectra of complexes

Powder X-Ray diffraction patterns

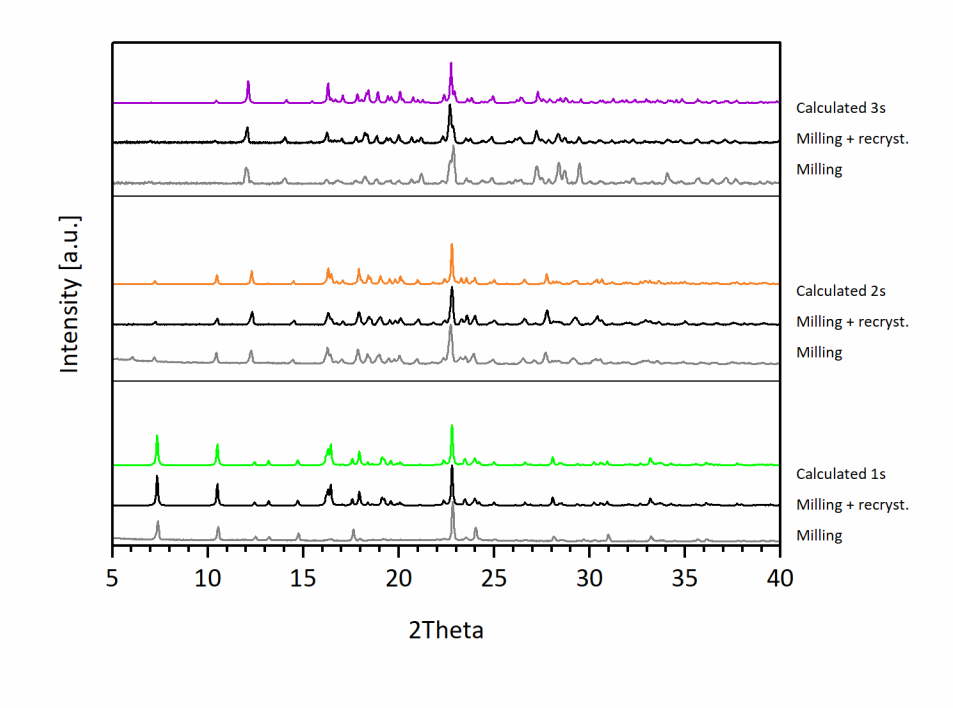


Figure S2. Comparison between experimental XRPD of **1m**, **2m** and **3m** (30Hz and 30min of milling) following a recrystallization step and those calculated from **1s**, **2s** and **3s**.

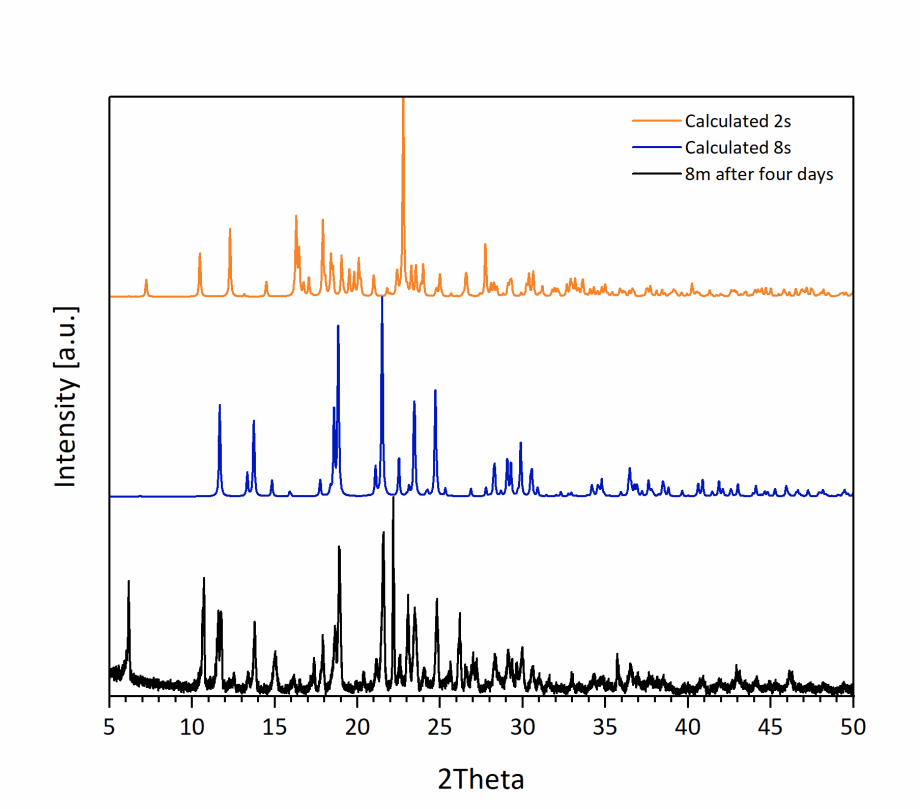
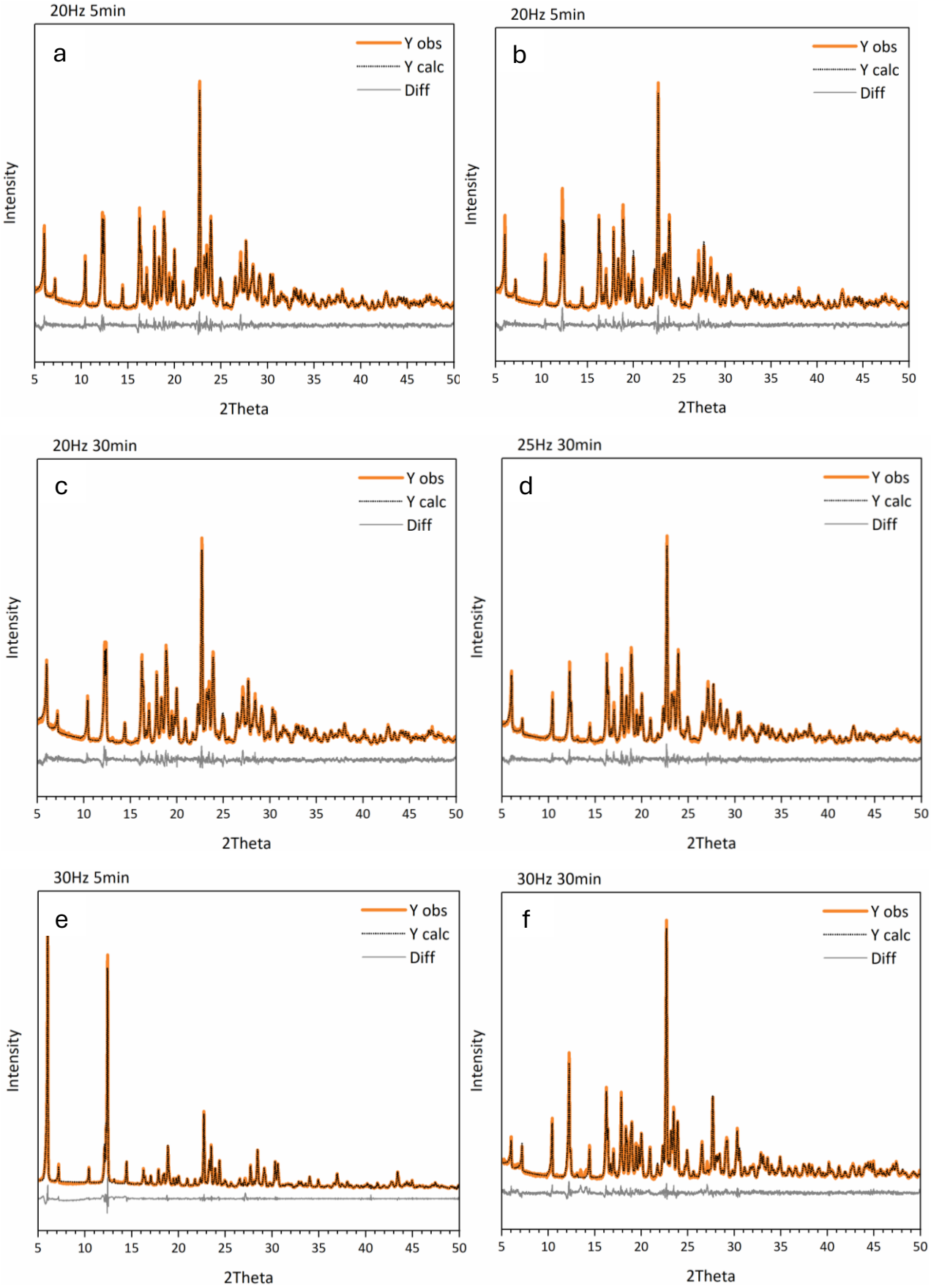


Figure S3. Comparison between experimental XRPD of **8m**, after 4 days left in open air and those calculated from **2s** and **8s,**.

Rietveld refinements



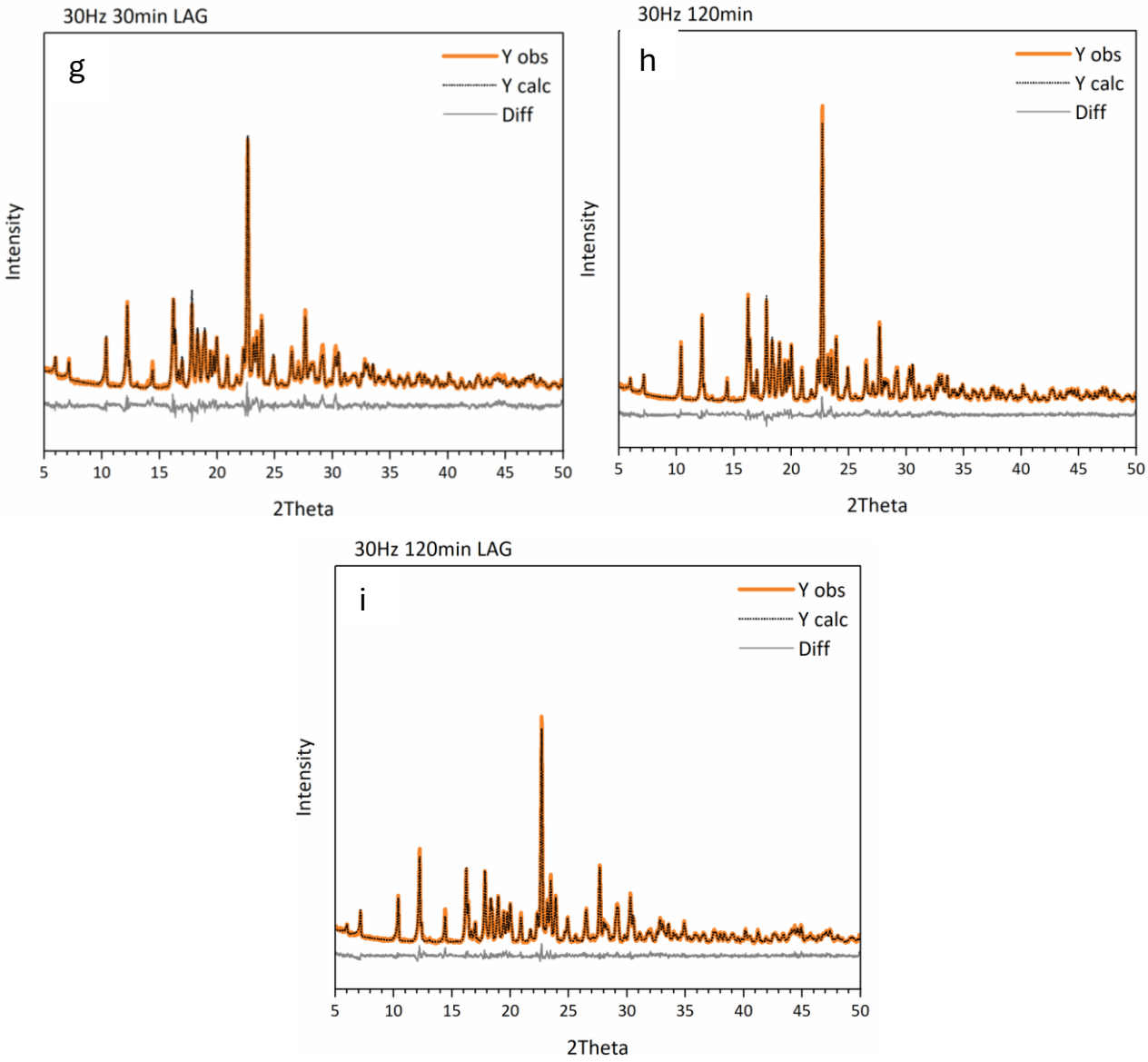


Figure S4. Rietveld refinement performed on outcome treated in mechanochemical conditions a) at 20Hz 5min, b) 25Hz 5min, c) 20Hz 30min, d) 25Hz 30min, e) 30Hz 5min, f) 30Hz 30min, g) 30Hz 30min with LAG (THF), h) 30Hz 120min, i) 30Hz 120min with LAG (THF). Experimental dare are reported in orange dots while calculated patter by Rietveld Refinement are reported in solid black line. Differential pattern Y_{cal}-Y_{obs} are reported in grey line.

Table S1. Mechanochemical reaction yields determined through quantitative phase analysis based on the weight percentage of Complex 2s relative to the total crystalline content in the reaction mixture.

			Complex 2s	4-Bromobenzoic acid	$Zn(OAc)_2 \cdot 2H_2O$	**YIELD**
Milling conditions	**R_{wp} [%]**	**GOF**	**Weight %**	**Weight %**	**Weight %**	**[%]**
20Hz - 5 min	6.47	1.570	67.92	23.77	8.30	**60.82**
20Hz - 30 min	6.03	1.446	72.08	20.12	7.78	**66.39**
25Hz - 5 min	6.04	1.437	68.06	26.71	5.21	**60.94**
25Hz - 30 min	6.21	1.485	70.46	23.82	5.71	**68.10**
30Hz - 5 min	7.66	1.128	73.06	21.26	5.67	**78.26**
30Hz - 30 min	7.01	1.551	89.69	7.15	3.14	**82.02**
30Hz - 120 min	6.67	1.520	93.56	4.92	1.51	**86.80**
30Hz - 5 min LAG	8.09	1.097	82.76	16.01	1.21	**80.53**
30Hz - 30 min LAG	8.65	1.823	88.56	9.29	2.14	**91.96**
30Hz - 120 min LAG	6.56	1.417	97.50	1.27	1.21	**97.28**

VT-PXRD of 2m dehydration

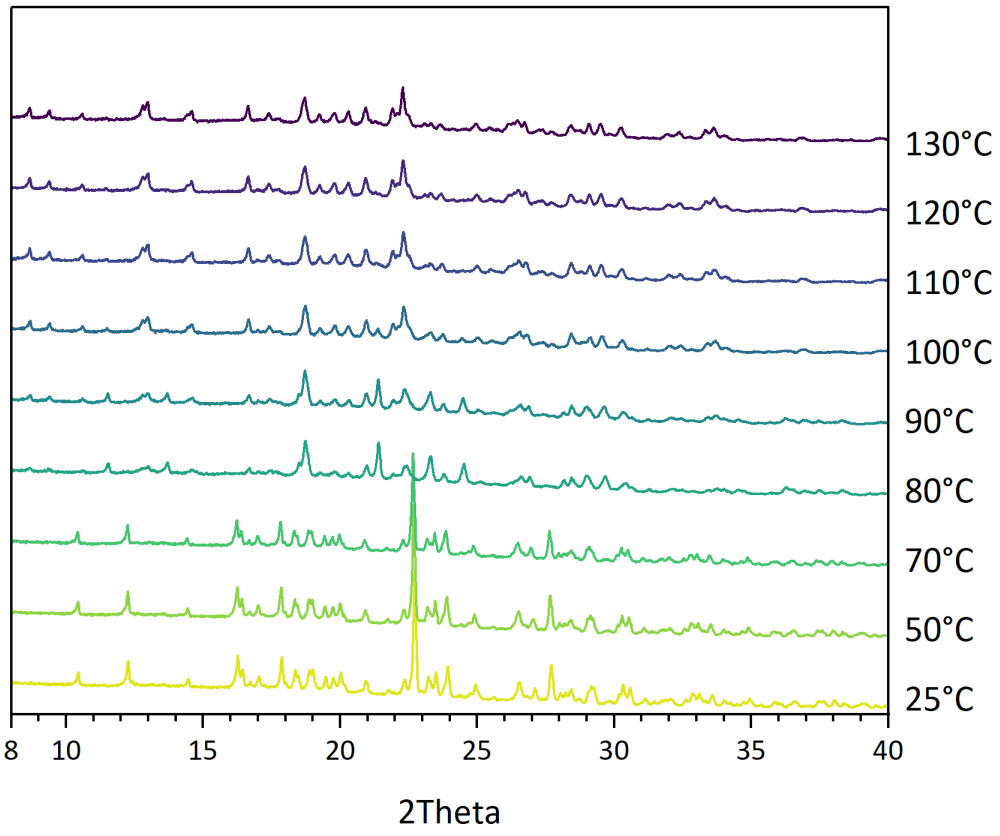


Figure S5. Variable temperature X-Ray powder diffraction analysis on complex **2m**; patterns were collected at 25°C, 50°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C.

Thermogravimetric analysis

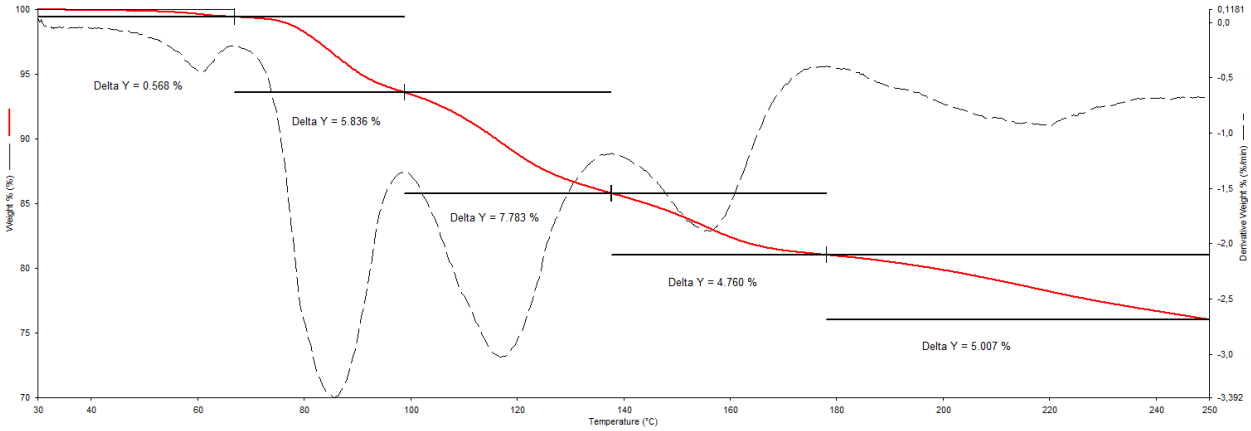


Figure S6. TGA of **2m**, starting from 30° to 250° at 5°/min, with the calculated weight losses percentages

Crystal Structure solved by Single Crystal X-Ray Diffraction

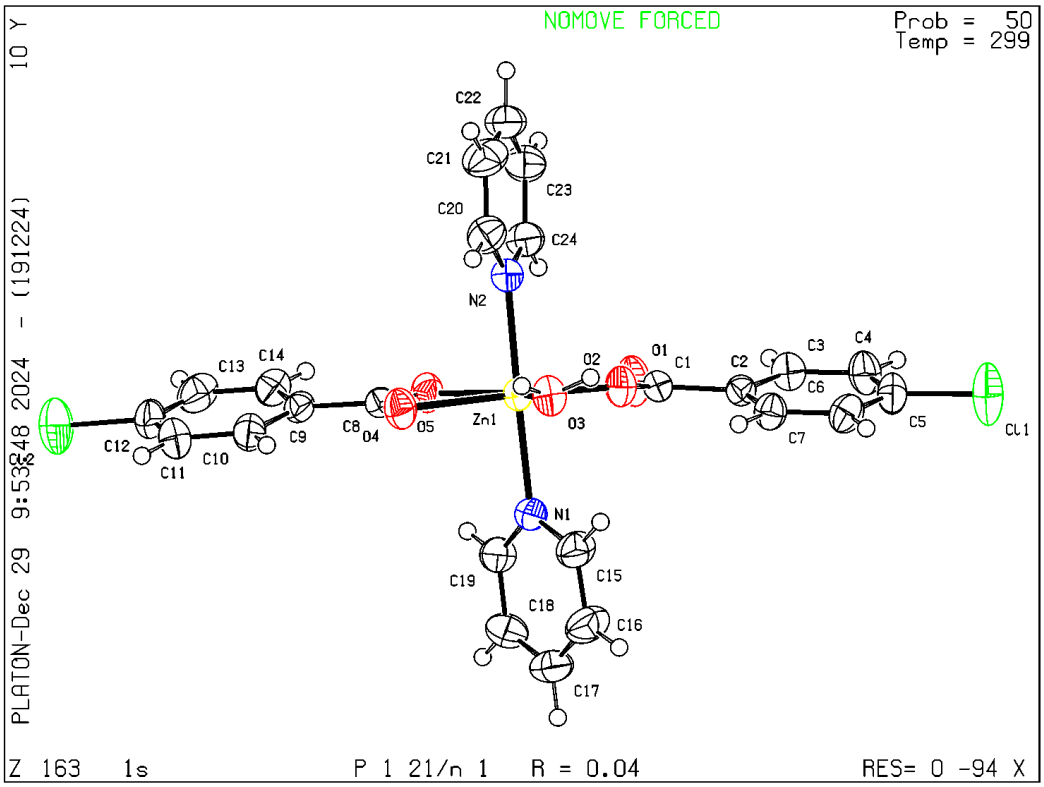


Figure S7. Ortep drawing of **1s**. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Color code: red=O, blue=N, gray=C, white=H.

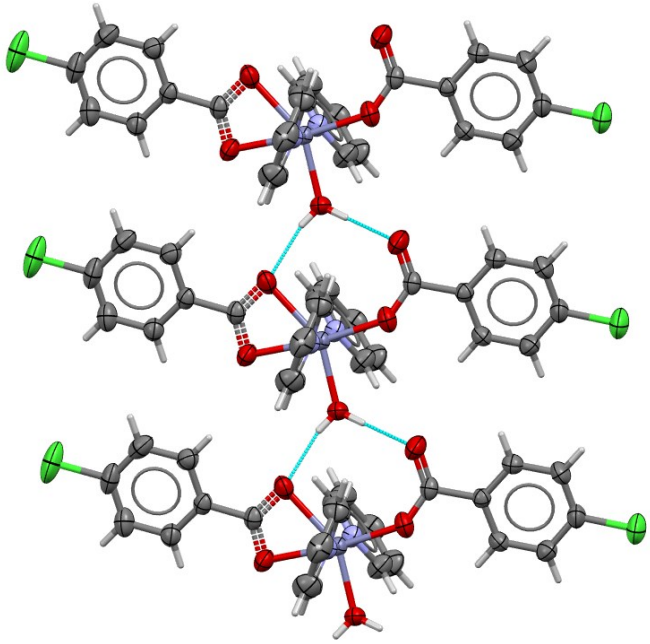


Figure S8. Interchain H-bond contacts in **1s** are reported in dotted cyan lines, running along crystallographic b-axis.

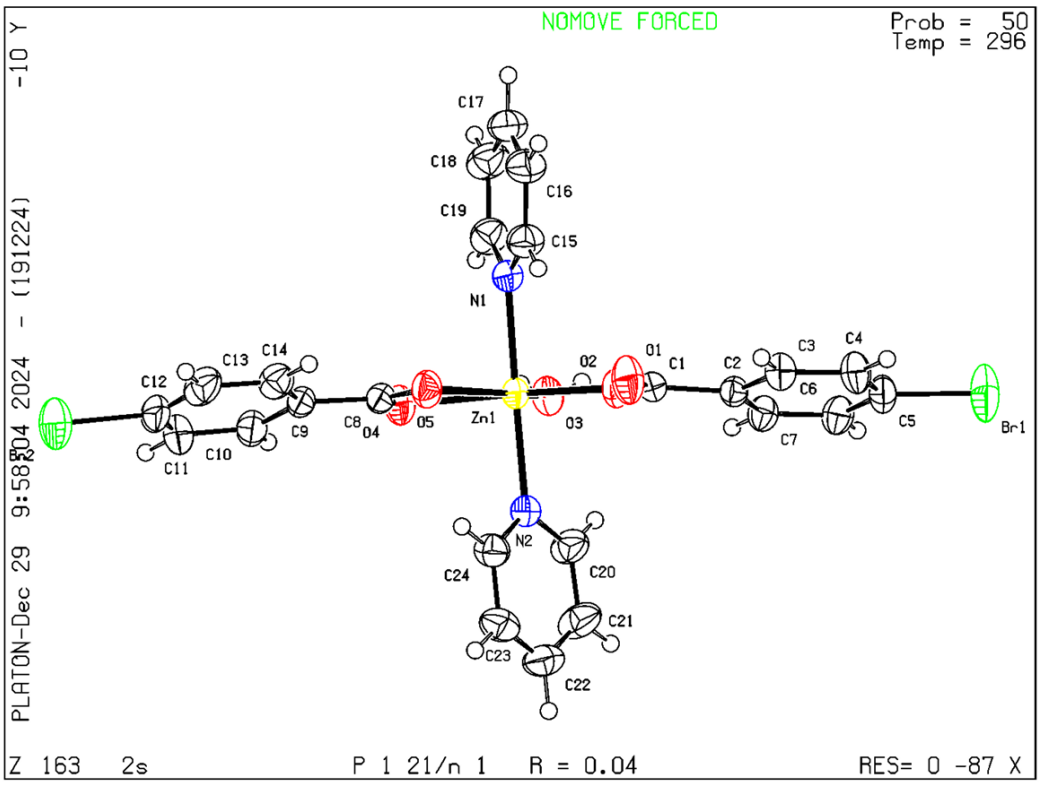


Figure S9. Ortep drawing of **2s** as obtained from the PLATON Check-cif routine. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Color code: red=O, blue=N, white=C-H.

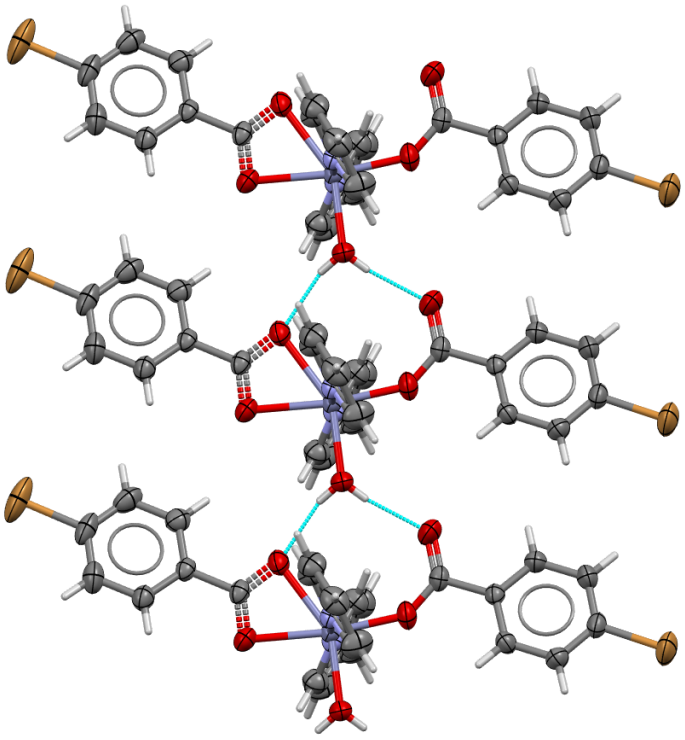


Figure S10. Interchain H-bond contacts in **2s** are reported in dotted cyan lines, running along crystallographic b-axis.

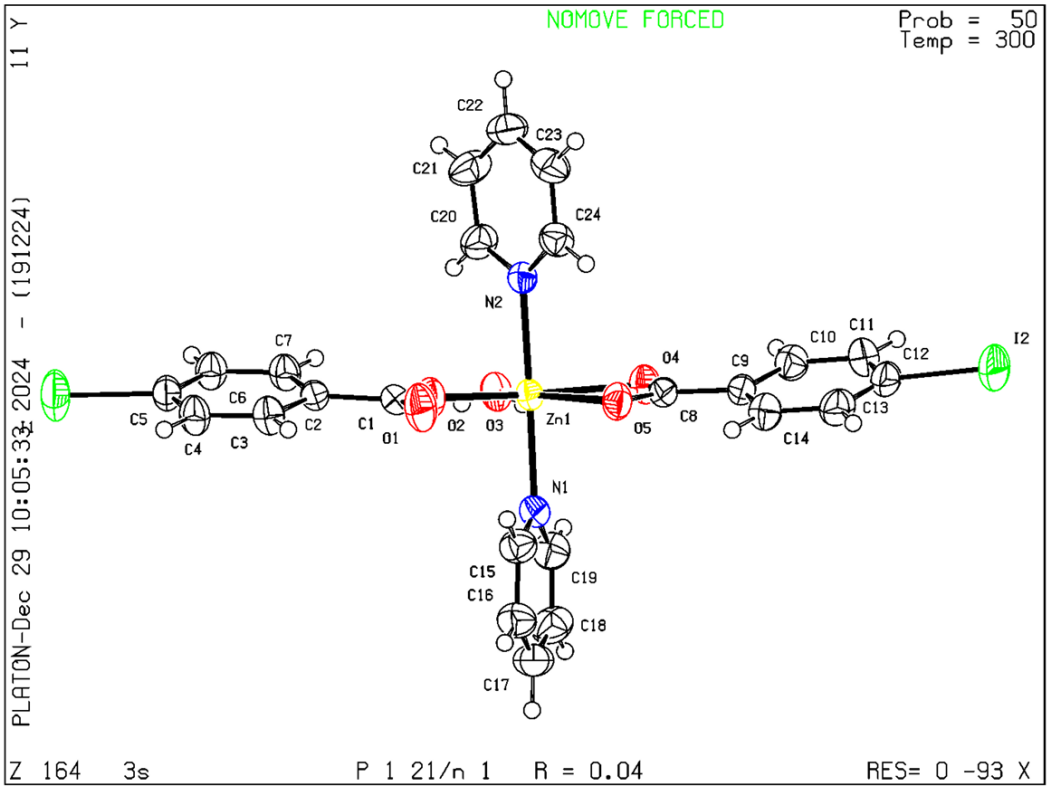


Figure S11. Ortep drawing of **3s** as obtained from the PLATON Check-cif routine. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Color code: red=O, blue=N, white=C-H.

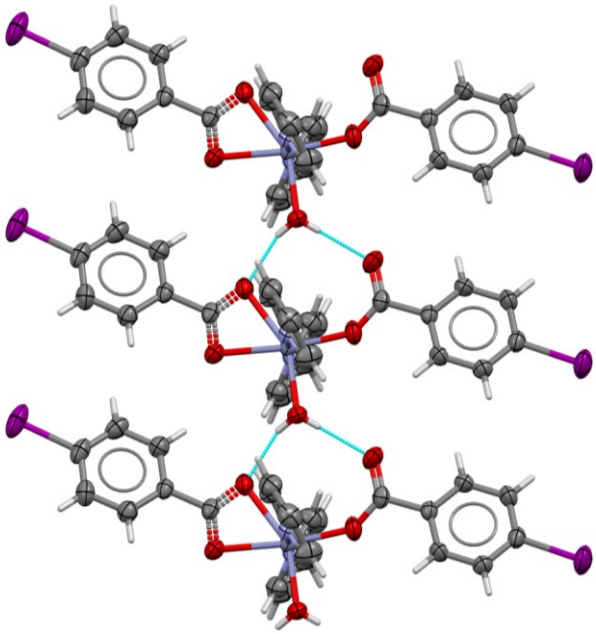


Figure S12. Interchain H-bond contacts in **3s** are reported in dotted cyan lines, running along crystallographic b-axis.

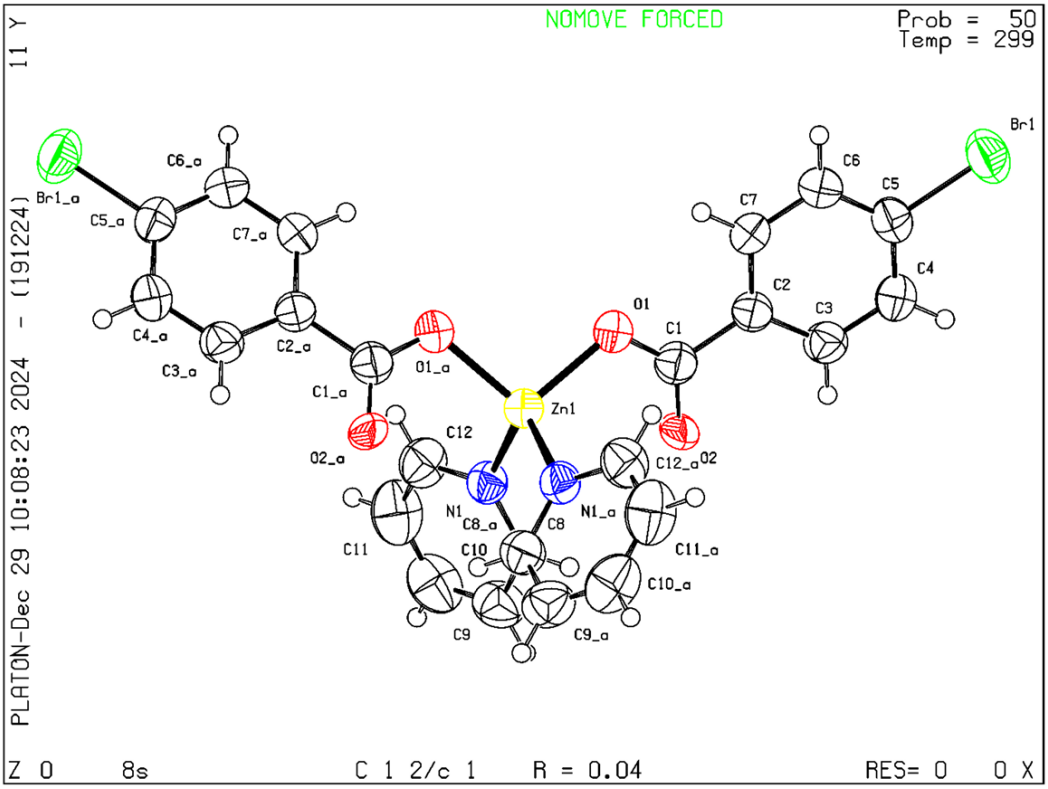


Figure S13. Ortep drawing of **8s** as obtained from the PLATON Check-cif routine. All non-hydrogen atoms are shown as ellipsoids at the 50% probability level. H atoms (isotropically refined) are reported in ball-and-stick style for the sake of clarity. Color code: red=O, blue=N, white=C-H.

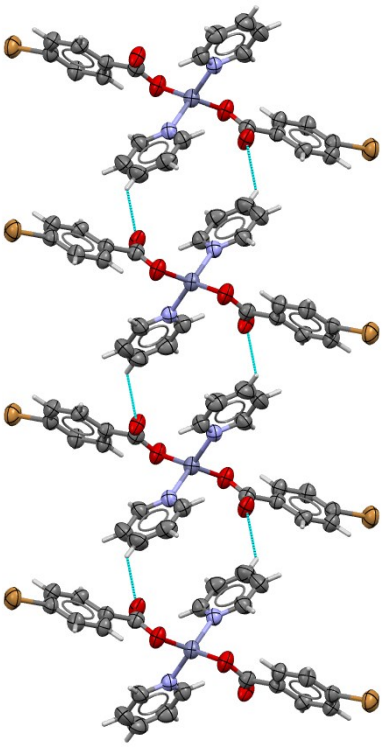


Figure S14. Interchain contacts in 8**s** are reported in dotted cyan lines, running along crystallographic c-axis

Crystallographic tables

Table S2. Crystal data and structure refinement for **1s, 2s, 3s** and **8s**.

Identification code	**1s**	**2s**	**3s**	**8s**
Empirical formula	$C_{24}H_{20}Cl_2N_2O_5Zn$	$C_{24}H_{20}Br_2N_2O_5Zn$	$C_{24}H_{20}I_2N_2O_5Zn$	$C_{24}H_{18}Br_2N_2O_4Zn$
Formula weight	552.69	641.61	735.59	623.59
Temperature/K	299.00	296.00	300.00	299.00
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	C2/c
a/Å	15.130(4)	15.382(6)	15.755(3)	25.7920(9)
b/Å	5.8821(15)	5.866(2)	5.8553(8)	6.1334(2)
c/Å	27.358(6)	27.370(9)	27.436(7)	15.1547(6)
α/°	90	90	90	90
β/°	101.212(8)	100.924(5)	100.130(7)	91.997(2)
γ/°	90	90	90	90
Volume/Å³	2388.3(10)	2424.9(15)	2491.5(8)	2395.91(15)
Z	4	4	4	4
ρ_{calc} *g/cm³*	1.537	1.757	1.961	1.729
μ *mm⁻¹*	1.291	4.347	3.502	5.613
F(000)	1128.0	1272.0	1416.0	1232.0
Crystal size/mm³	0.2 × 0.125 × 0.05	0.25 × 0.25 × 0.06	0.25 × 0.25 × 0.06	0.25 × 0.25 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.838 to 56.638	5.394 to 56.562	4.816 to 56.698	6.858 to 140.336
Index ranges	-19 ≤ h ≤ 20, -7 ≤ k ≤ 7, -36 ≤ l ≤ 34	-20 ≤ h ≤ 18, -7 ≤ k ≤ 7, -36 ≤ l ≤ 36	-20 ≤ h ≤ 21, -7 ≤ k ≤ 7, -36 ≤ l ≤ 36	-31 ≤ h ≤ 31, -7 ≤ k ≤ 7, -16 ≤ l ≤ 18
Reflections collected	71946	73004	68138	18782
Independent reflections	5915 R_{int} = 0.0954, R_{sigma} = 0.0450	5994 R_{int} = 0.0567, R_{sigma} = 0.0294	6214 R_{int} = 0.0598 R_{sigma} = 0.0329	2281 R_{int} = 0.0555 R_{sigma} = 0.0295
Data/restraints/parameters	5915/0/315	5994/0/315	6214/0/315	2281/0/150
Goodness-of-fit on F²	1.030	1.046	1.024	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.0878	R_1 = 0.0389, wR_2 = 0.0954	R_1 = 0.0372, wR_2 = 0.0791	R_1 = 0.0307, wR_2 = 0.0736
Final R indexes [all data]	R_1 = 0.0602, wR_2 = 0.0976	R_1 = 0.0477, wR_2 = 0.1002	R_1 = 0.0515, wR_2 = 0.0876	R_1 = 0.0420, wR_2 = 0.0808
Largest diff. peak/hole / e Å⁻³	0.79/-0.49	1.80/-1.54	1.31/-1.81	0.28/-0.41