

Synthesis and crystal structures of Zn(II) and Co(II) coordination compounds with ortho substituted pyridine ligands: Two structure types and polymorphism in the region of their coexistence.

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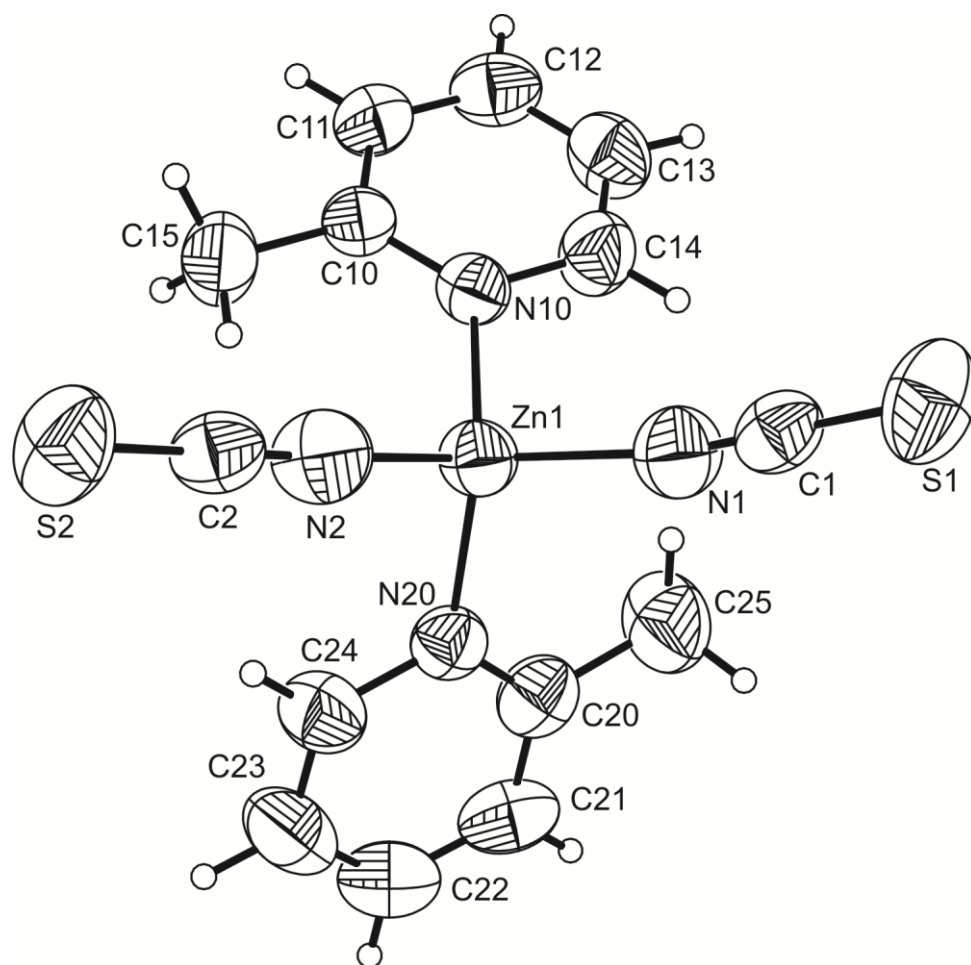


Figure S1. Crystal structure of Zn(NCS)₂(2-methylpyridine)₂ (**1-Zn**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

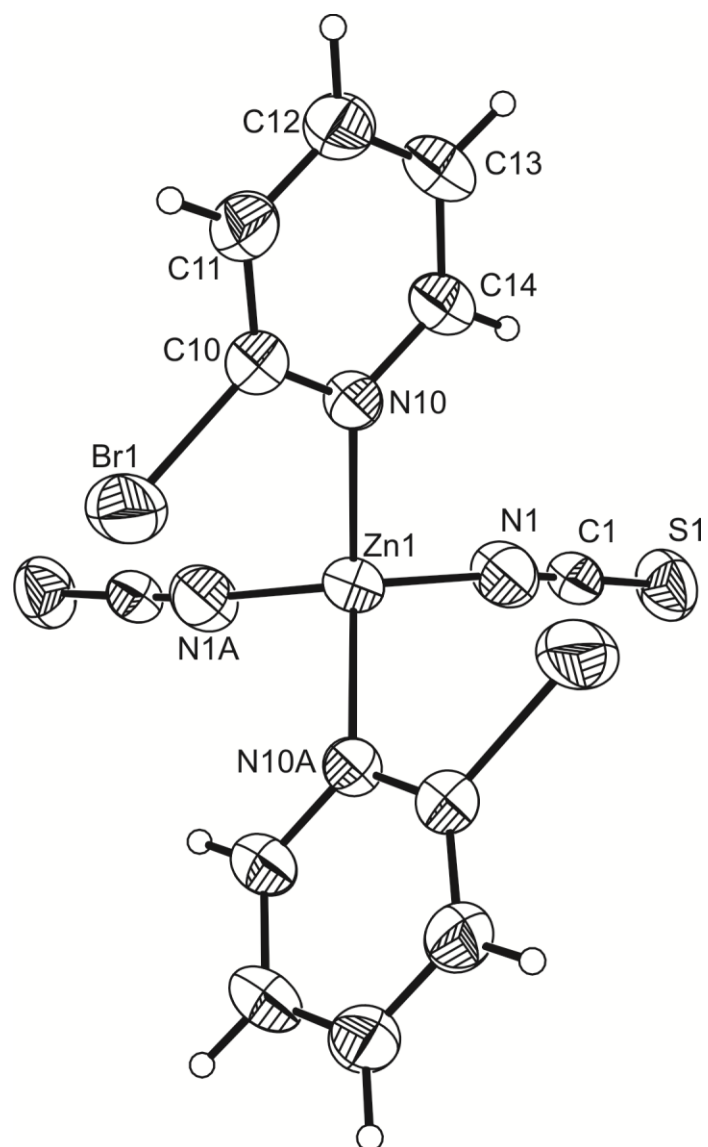


Figure S2. Crystal structure of $\text{Zn}(\text{NCS})_2(2\text{-bromopyridine})_2$ (**2-Zn**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = $-x + 1, y, -z + \frac{1}{2}$.

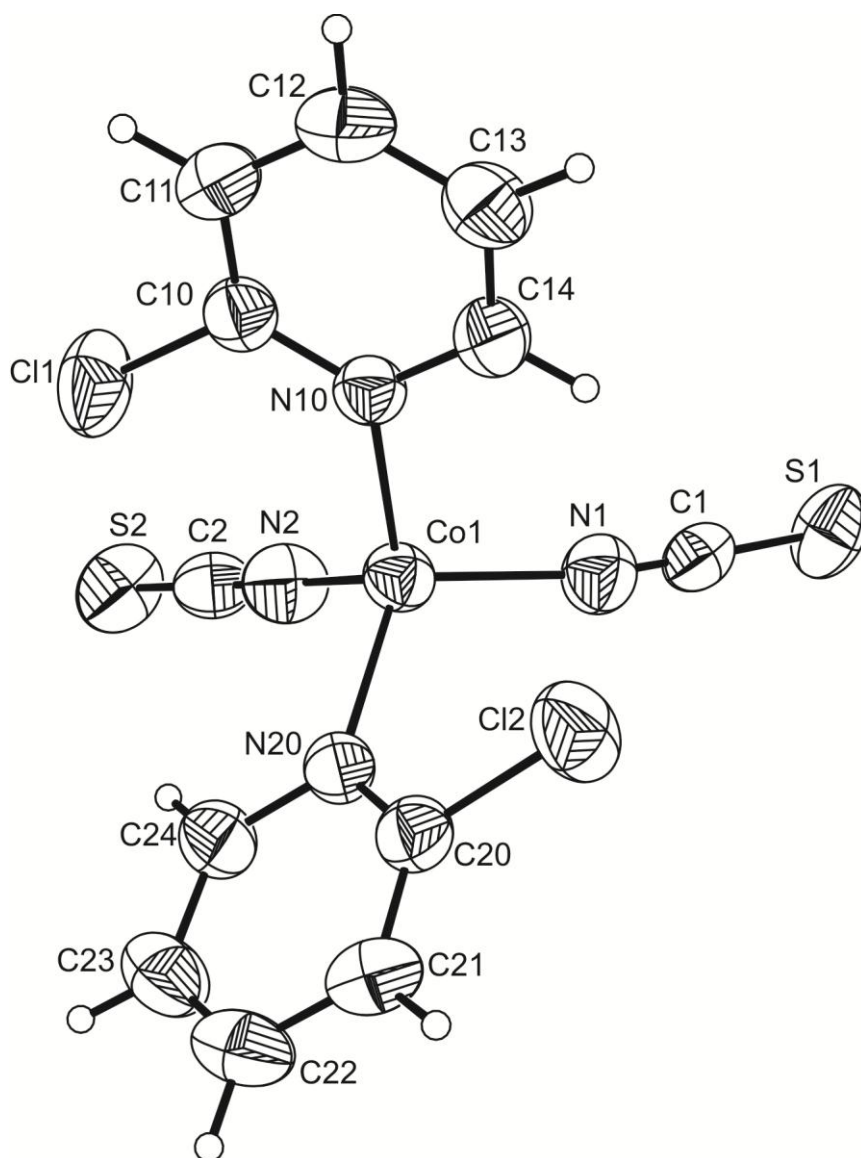


Figure S3. Crystal structure of $\text{Co}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Co α**) with view of the coordination sphere of the cobalt(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

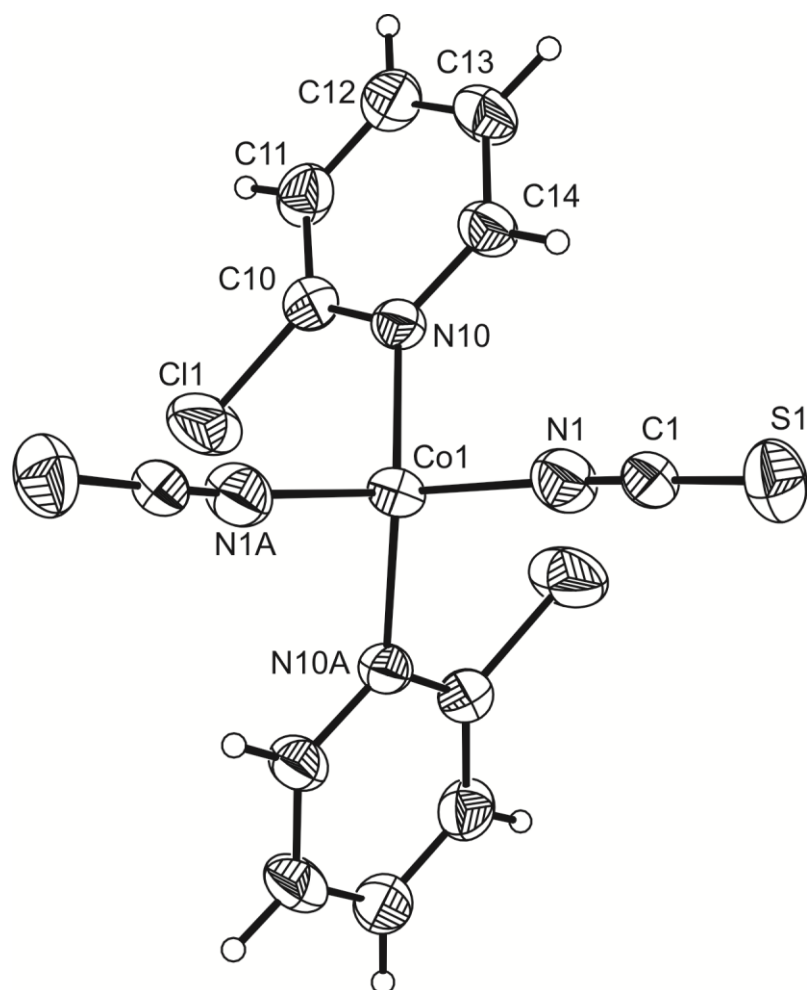


Figure S4. Crystal structure of $\text{Co}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Co β**) with view of the coordination sphere of the cobalt(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x, y, -z + 1/2.

Table S1. Selected crystal data on the structure determination from single crystal data for compound $\text{Co}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Co β**) at $T = 200$ K.

compound	3-Coβ
Formula	$\text{C}_{12}\text{H}_8\text{Cl}_2\text{CoN}_4\text{S}_2$
MW / $\text{g}\cdot\text{mol}^{-1}$	402.17
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
$a / \text{\AA}$	11.2928(7)
$b / \text{\AA}$	9.7123(5)
$c / \text{\AA}$	15.1913(8)
$V / \text{\AA}^3$	1666.17(16)
T / K	200
Z	4
$D_{\text{calc}} / \text{mg}\cdot\text{m}^{-3}$	1.603
μ / mm^{-1}	1.597
$\theta_{\text{max}} / ^\circ$	28.03
Refl. collected	11189
Unique reflections	2005
R_{int}	0.0342
Refl. [$F_0 > 4\sigma(F_0)$]	1671
Parameters	97
R_1 [$F_0 > 4\sigma(F_0)$]	0.0312
wR_2	0.0799
GOF	1.036
$\Delta\rho_{\text{max/min}} / \text{e}\cdot\text{\AA}^{-3}$	0.377 / -0.442

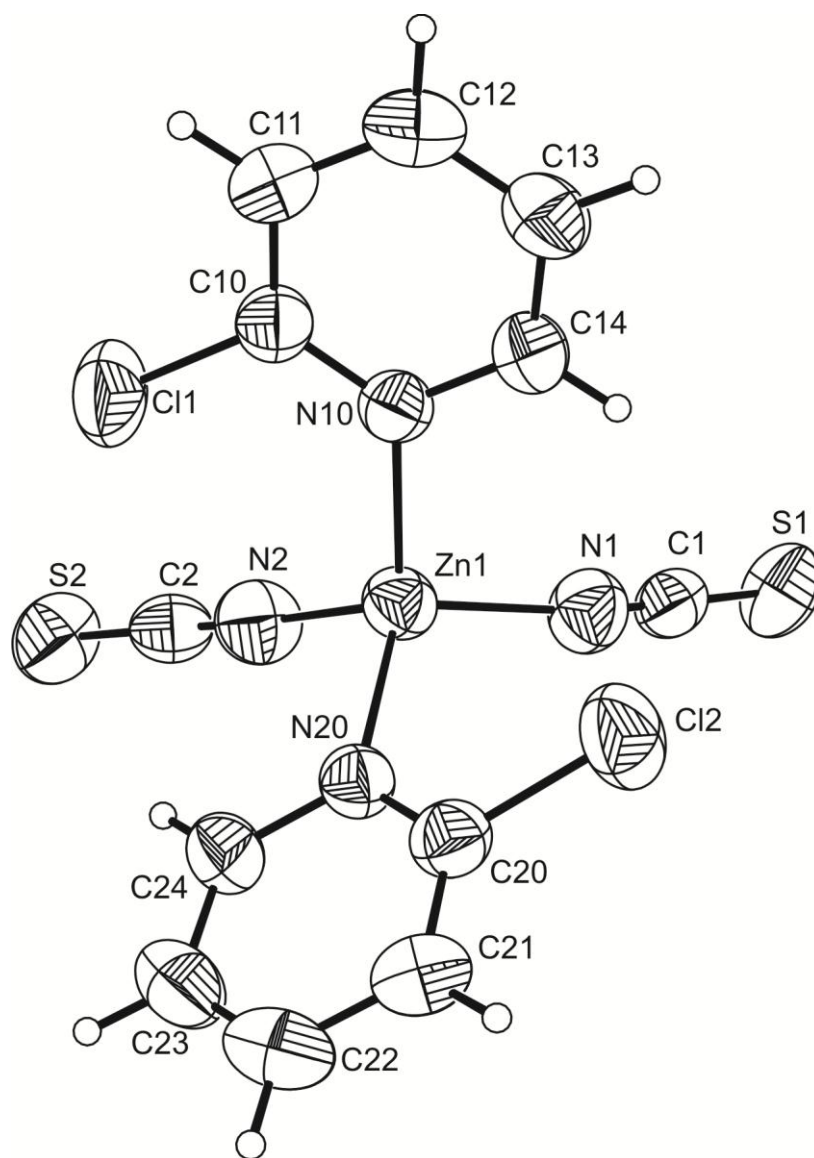


Figure S5. Crystal structure of Zn(NCS)₂(2-chloropyridine)₂ (**3-Znα**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

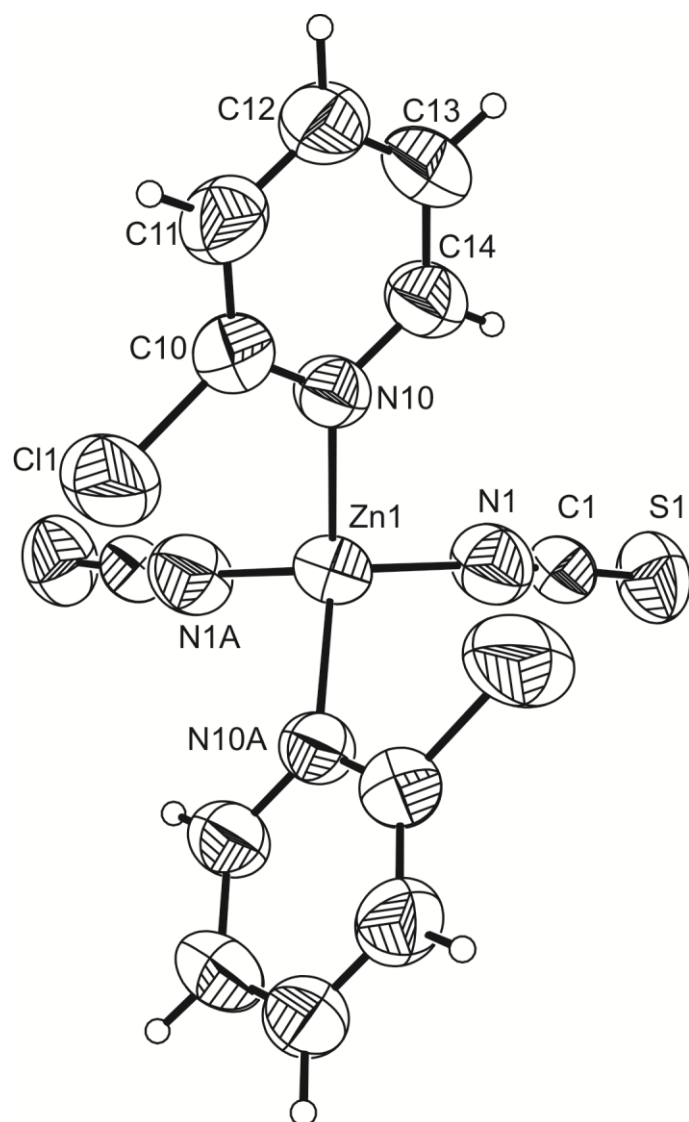


Figure S6. Crystal structure of Zn(NCS)₂(2-chloropyridine)₂ (**3-Znβ**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x + 1, y, -z + 3/2.

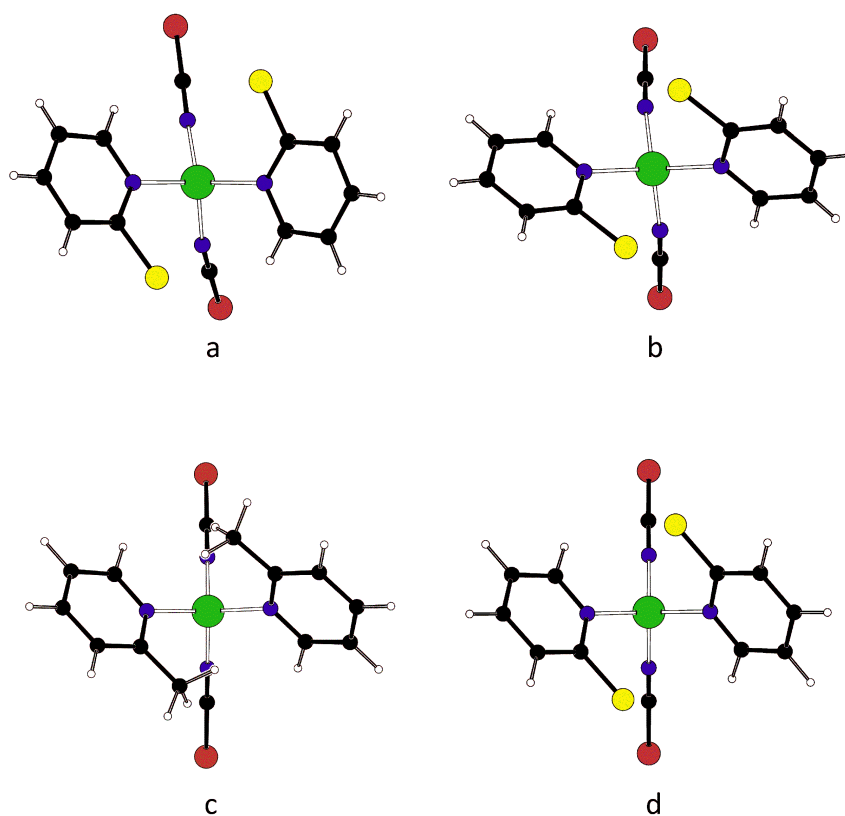


Figure S7. Comparison of molecular geometries: a) Molecule of **3-Zn α** as found in the crystal (space group $P2_12_12_1$); b) Molecule of **3-Zn β** (crystals in $Pbcn$); c) Molecule of **3-Zn α** after force field energy minimization; d) Molecule of **1-Zn** after force field energy minimization. Note the similarity between the experimentally determined molecular structure in $Pbcn$ (b) and the minimization results (c and d).

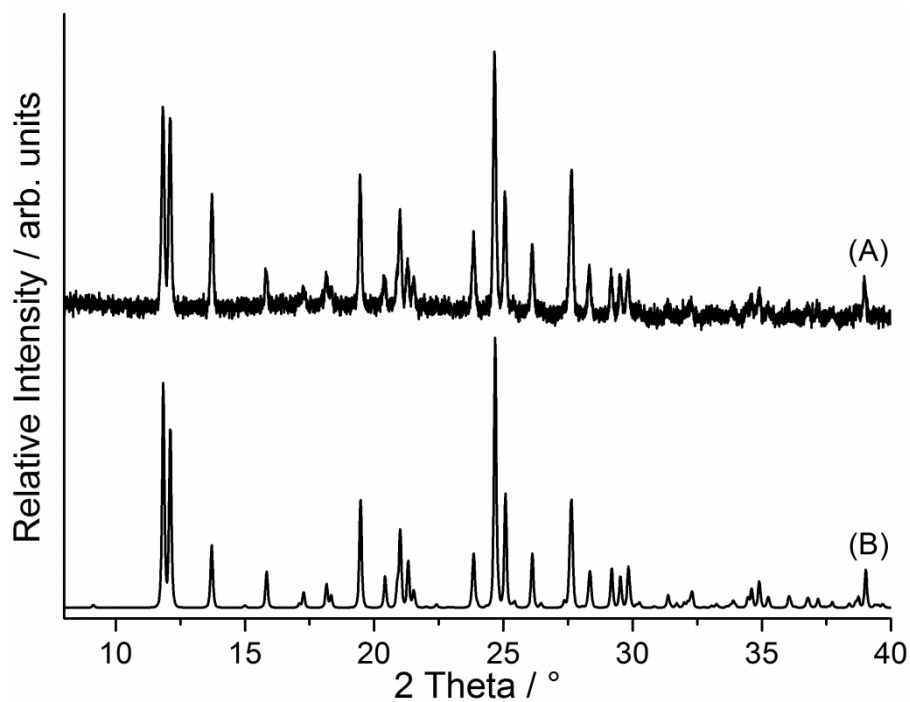


Figure S8. Experimental XRPD pattern of compound **1-Co** (A) and XRPD calculated from single crystal data of compound **1-Co** (B).

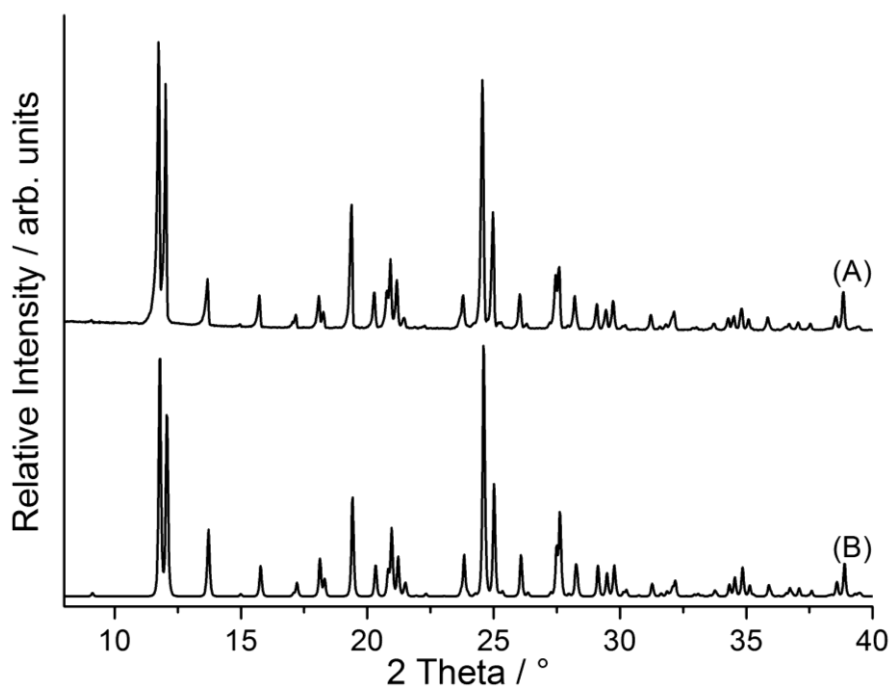


Figure S9. Experimental XRPD pattern of compound **1-Zn** (A) and XRPD calculated from single crystal data of compound **1-Zn** (B).

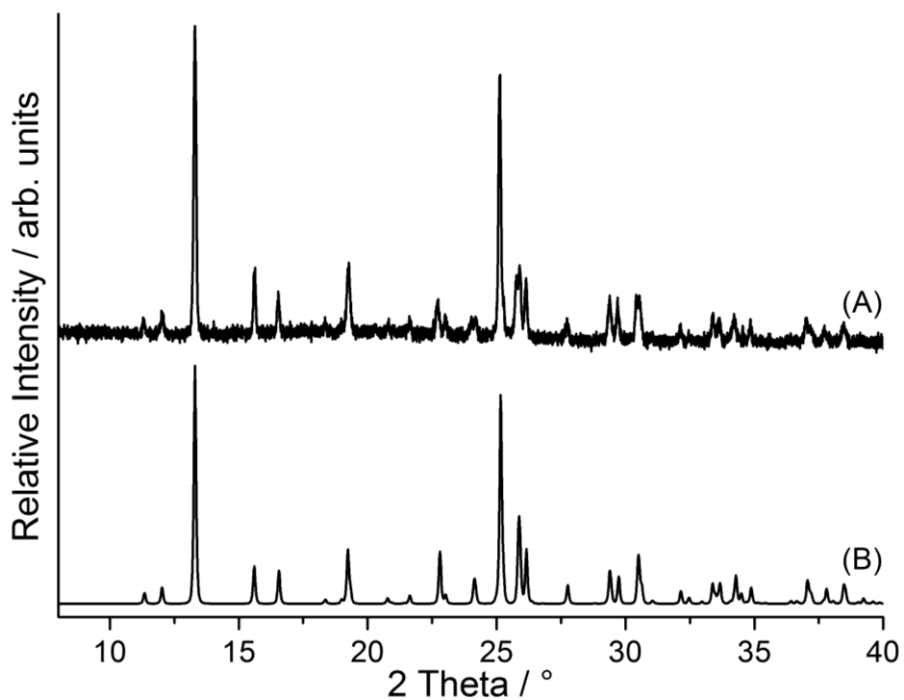


Figure S10. Experimental XRPD pattern of compound **2-Co** (A) and XRPD calculated from single crystal data of compound **2-Co** (B).

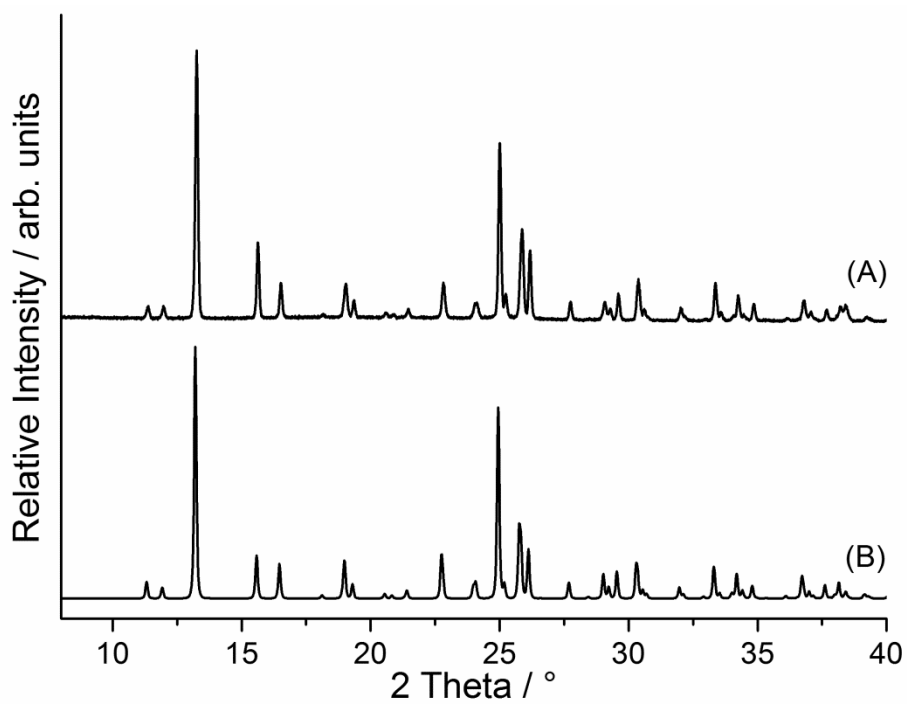


Figure S11. Experimental XRPD pattern of compound **2-Zn** (A) and XRPD calculated from single crystal data of compound **2-Zn** (B).

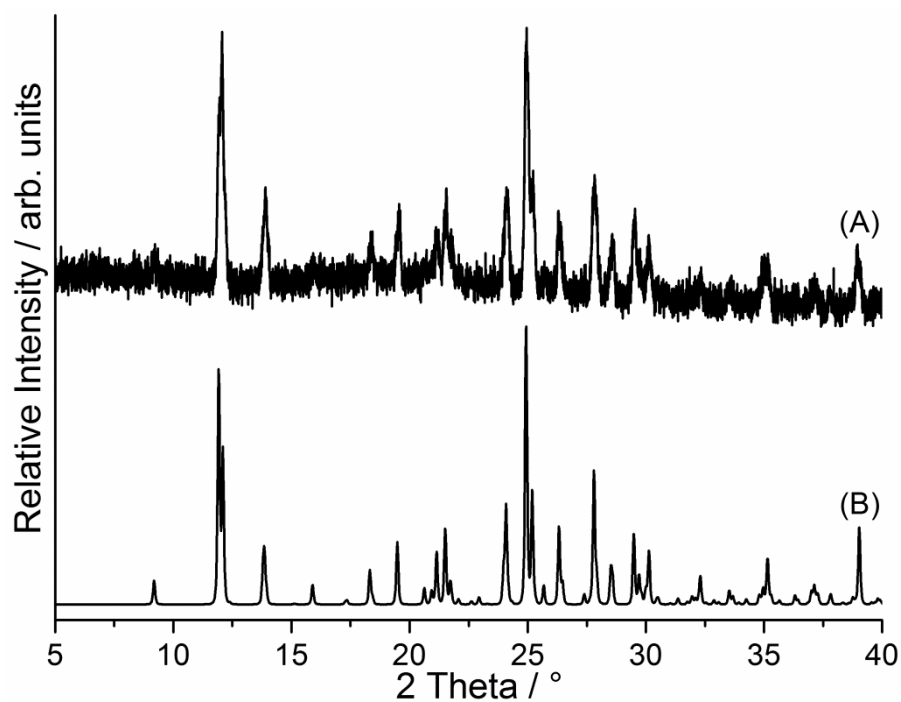


Figure S12. Experimental XRPD pattern of compound **3-Co α** (A) and XRPD calculated from single crystal data of compound **3-Co α** (B).

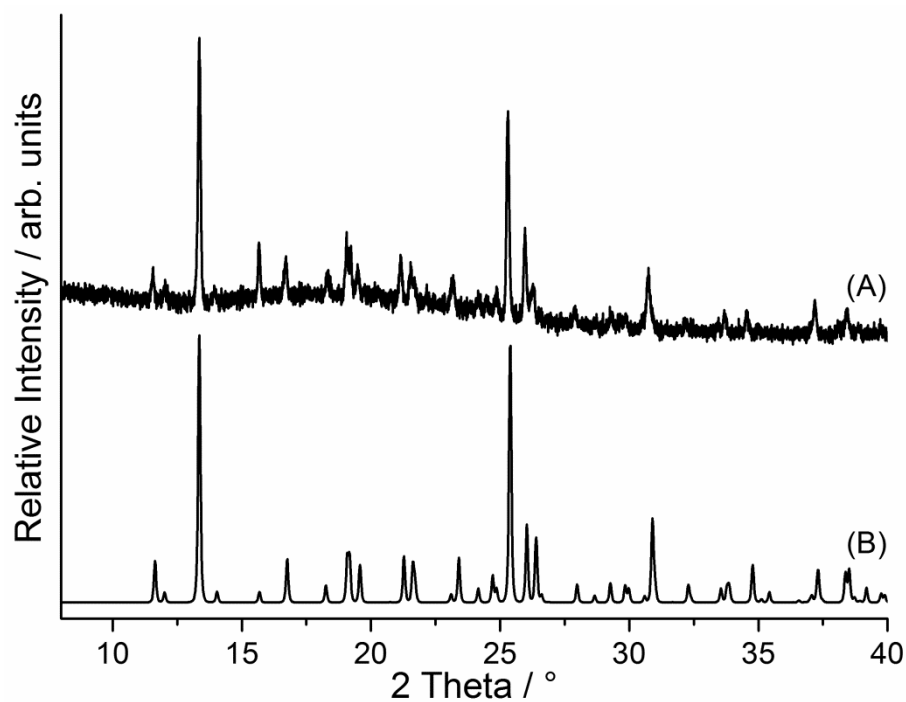


Figure S13. Experimental XRPD pattern of compound **3-Co β** (A) and XRPD calculated from single crystal data of compound **3-Co β** (B).

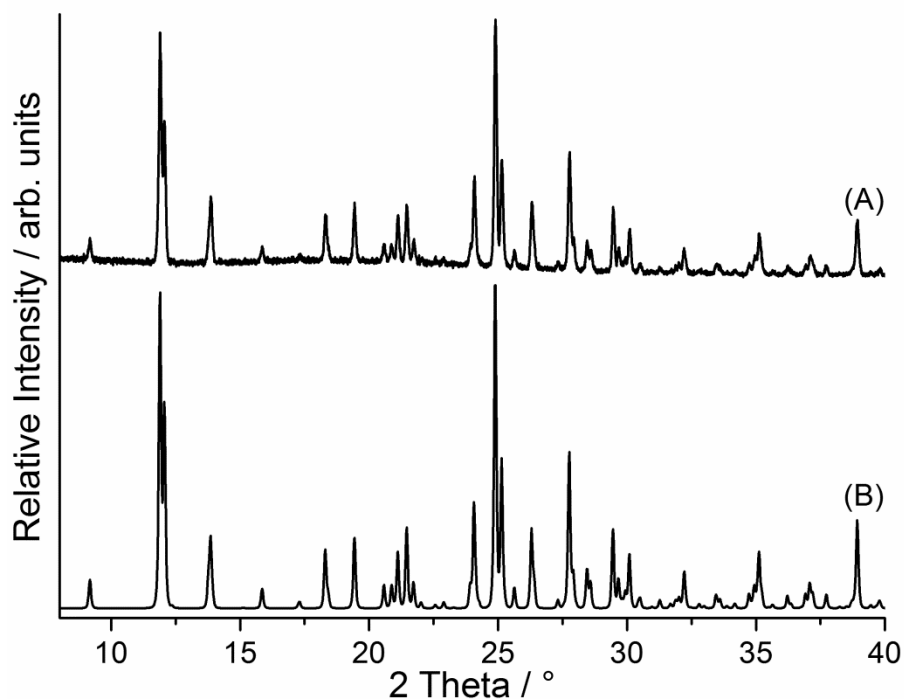


Figure S14. Experimental XRPD pattern of compound **3-Zn α** (A) and XRPD calculated from single crystal data of compound **3-Zn α** (B).

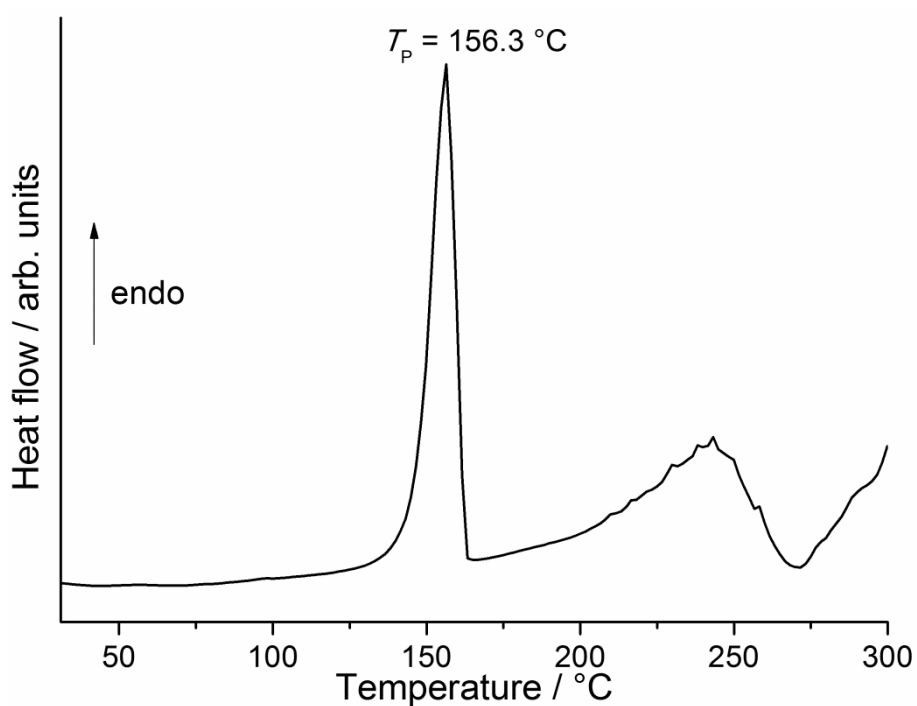


Figure S15. Differential scanning calorimetry (DSC) measurement for compound **1-Co**.

Heating rate $3\text{ °C}\cdot\text{min}^{-1}$; N_2 atmosphere; T_p = peak temperature ($^{\circ}\text{C}$).

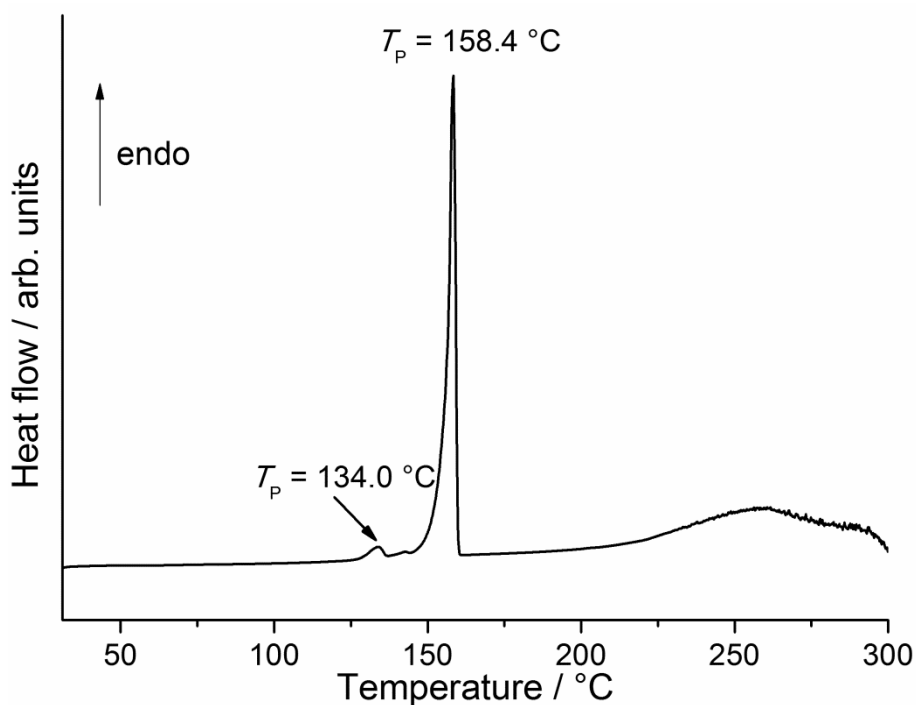


Figure S16. Differential scanning calorimetry (DSC) measurement for compound **1-Zn**.

Heating rate $3\text{ °C}\cdot\text{min}^{-1}$; N_2 atmosphere; T_p = peak temperature ($^{\circ}\text{C}$).

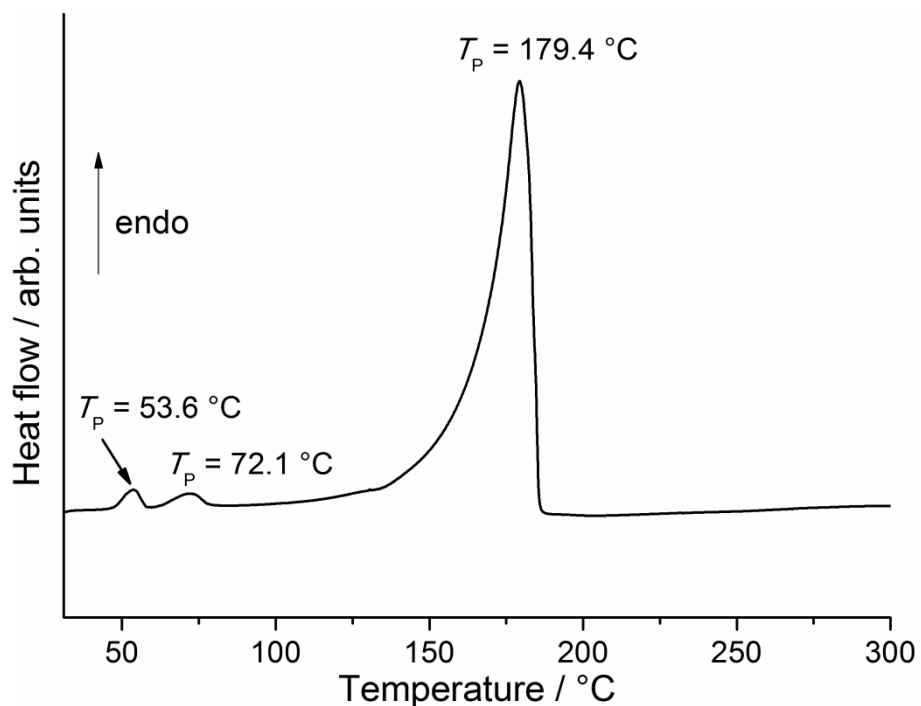


Figure S17. Differential scanning calorimetry (DSC) measurement for compound **2-Co**.

Heating rate $3\text{ °C}\cdot\text{min}^{-1}$; N_2 atmosphere; T_p = peak temperature ($^{\circ}\text{C}$).

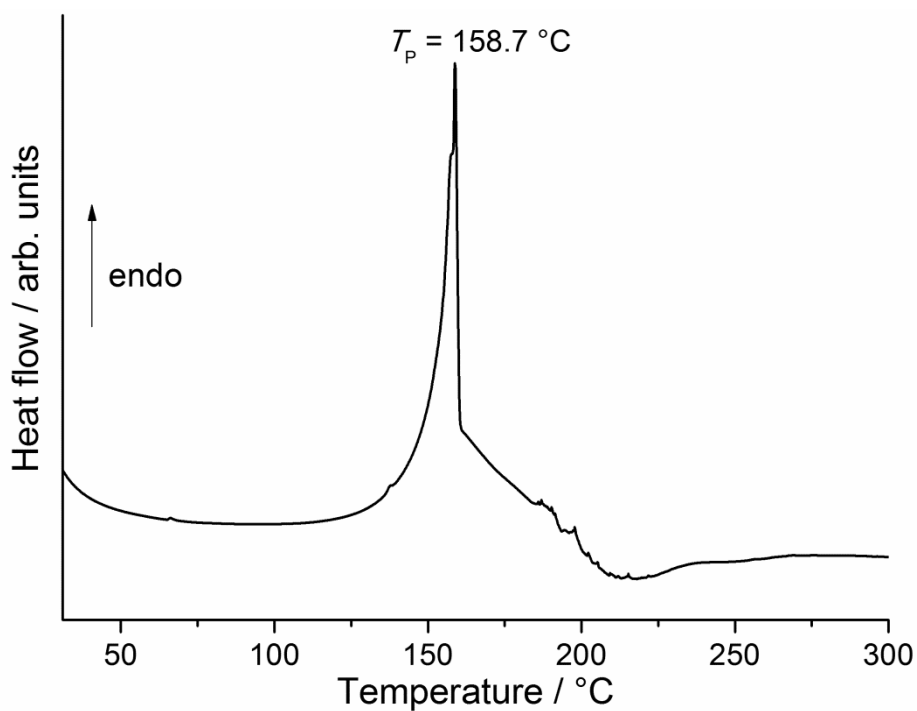


Figure S18. Differential scanning calorimetry (DSC) measurement for compound **2-Zn**.
Heating rate $3\text{ °C}\cdot\text{min}^{-1}$; N_2 atmosphere; T_p = peak temperature ($^{\circ}\text{C}$).

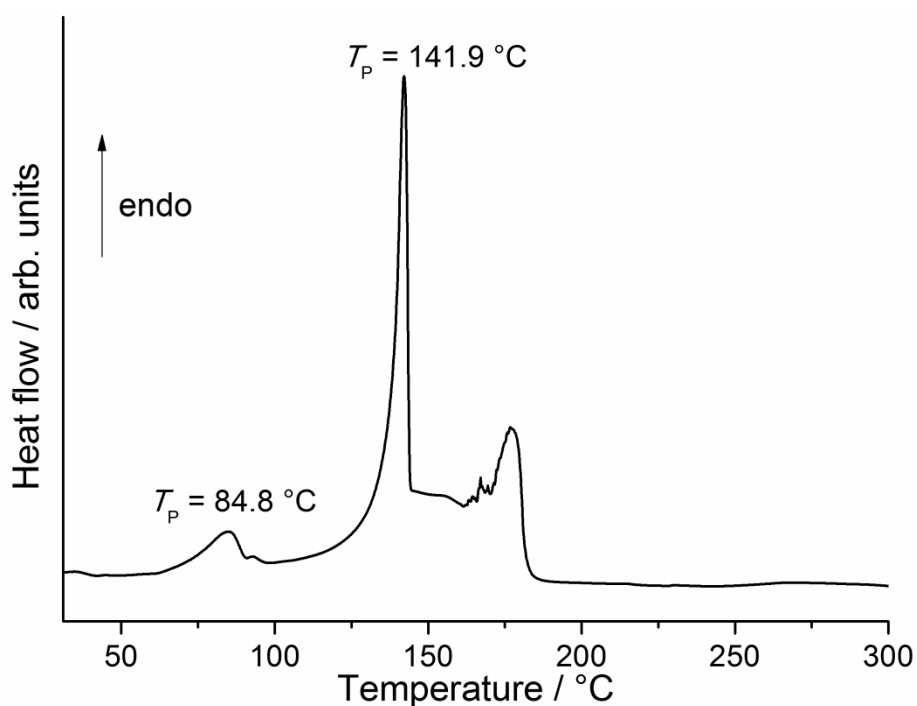


Figure S19. Differential scanning calorimetry (DSC) measurement for compound **3-Coβ**.
Heating rate $3\text{ °C}\cdot\text{min}^{-1}$; N_2 atmosphere; T_p = peak temperature ($^{\circ}\text{C}$).

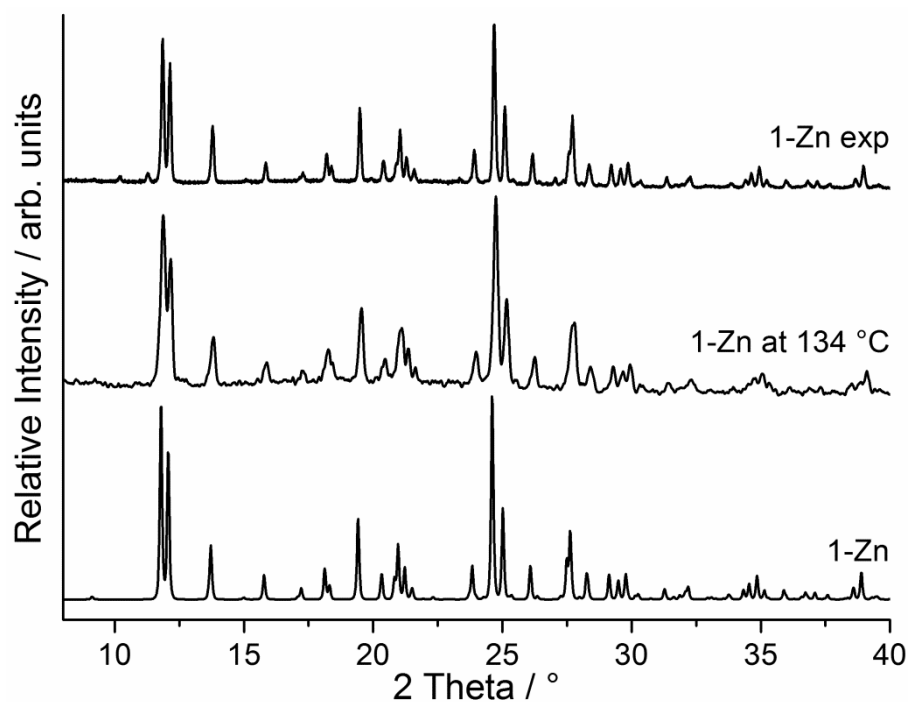


Figure S20. Experimental XRPD of compound **1-Zn** (top) and the intermediate, which were obtained at 134 °C in the DSC measurement of compound **1-Zn** (middle) as well as XRPD calculated from single crystal data of **1-Zn** (bottom).

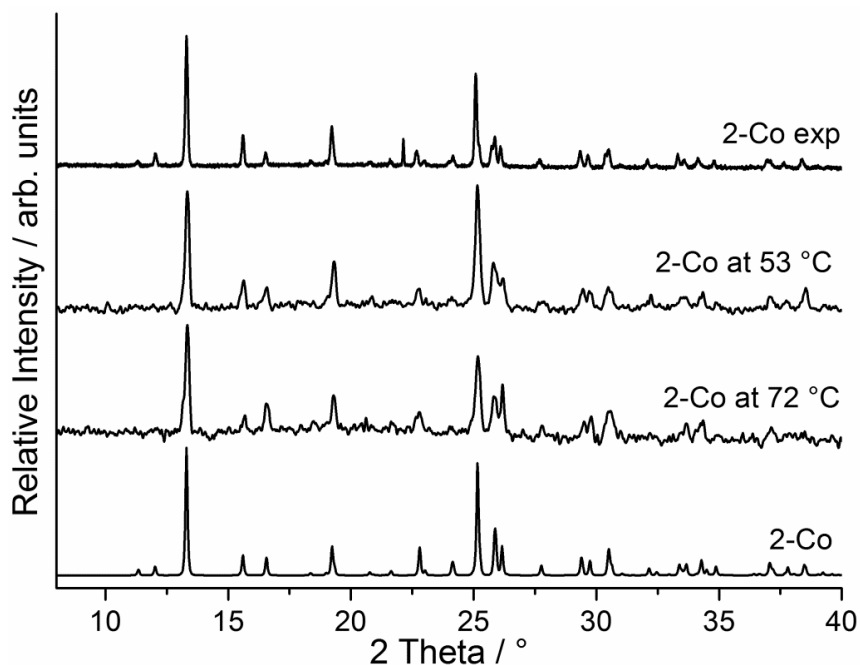


Figure S21. Experimental XRPD of compound **2-Co** (top) and the intermediate, which were obtained at 53 °C and 72 °C in the DSC measurement of compound **2-Co** (middle) as well as XRPD calculated from single crystal data of **2-Co** (bottom).

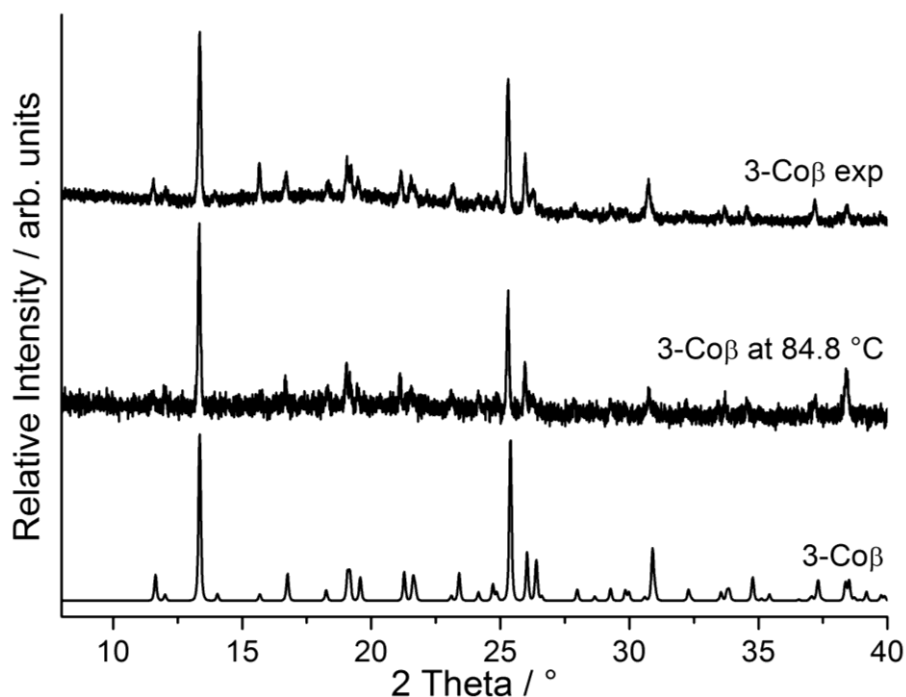


Figure S22. Experimental XRPD of compound **3-Coβ** (top) and the intermediate, which were obtained at 84.8 °C in the DSC measurement of compound **3-Coβ** (middle) as well as XRPD calculated from single crystal data of **3-Coβ** (bottom).

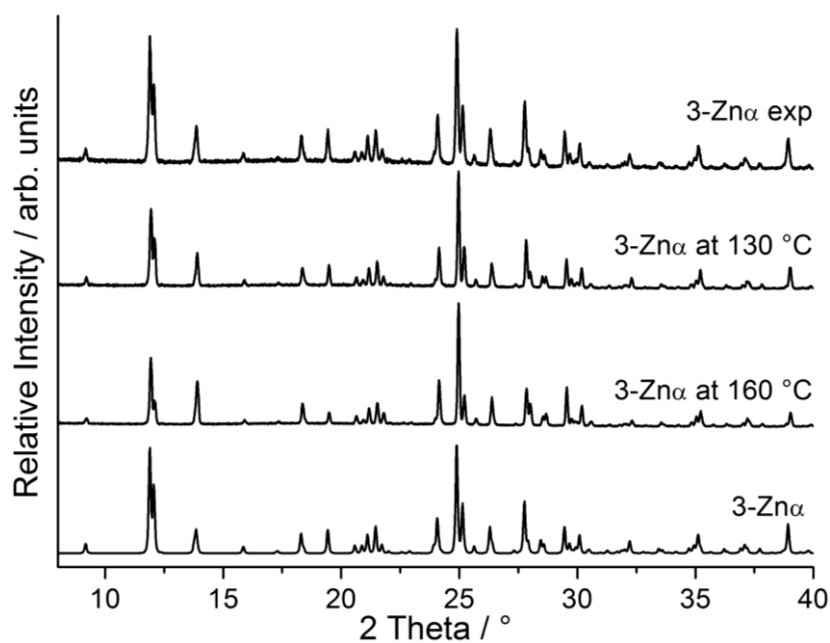


Figure S23. Experimental XRPD of the residues which were obtained after heating **3-Znα** at 130 °C and at 160 °C for three days in methanol and experimental and calculated powder pattern of **3-Znα**.

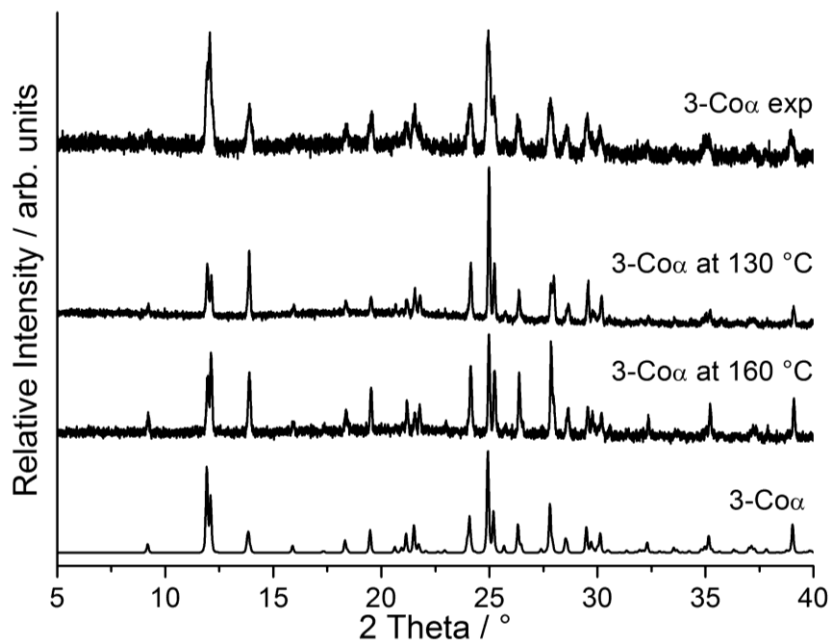


Figure S24. Experimental XRPD of the residues which were obtained after heating **3-Coα** at 130 °C and at 160 °C for three days in methanol and experimental and calculated powder pattern of **3-Coα**.

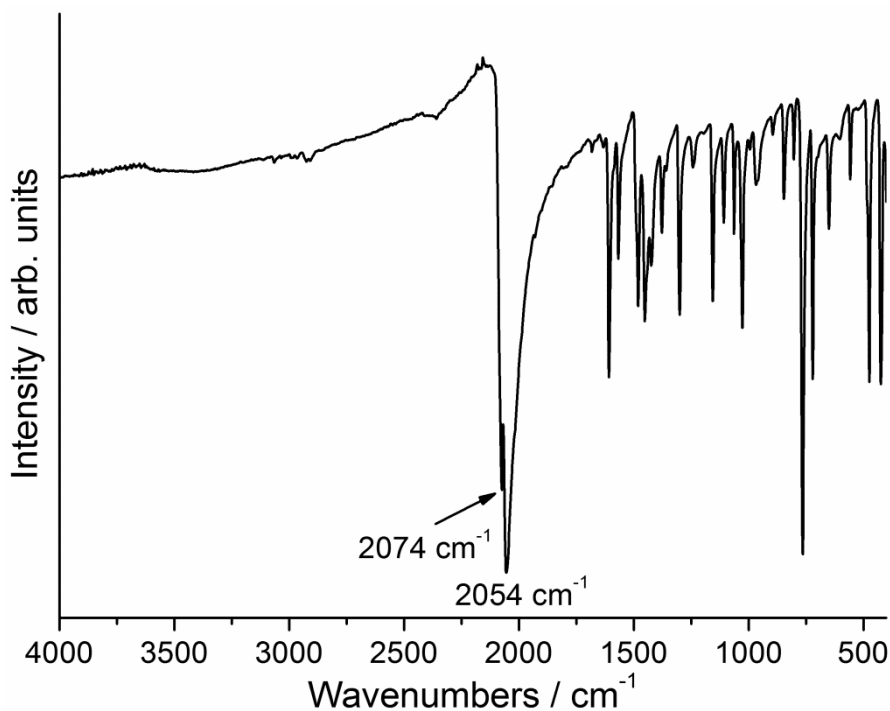


Figure S255. IR spectrum of $\text{Co}(\text{NCS})_2(2\text{-methylpyridine})_2$ (**1-Co**).

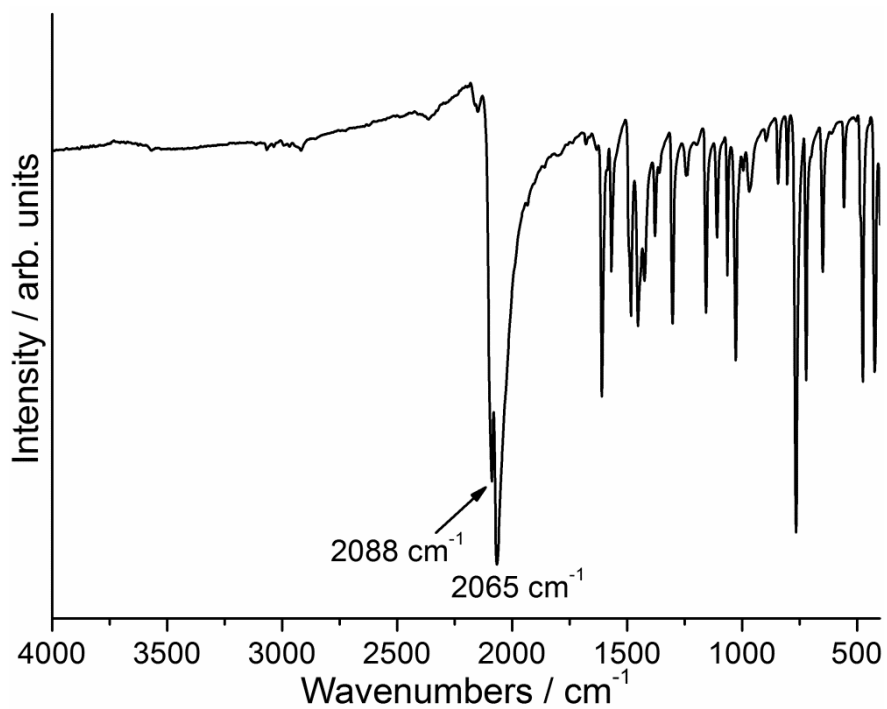


Figure S266. IR spectrum of Zn(NCS)₂(2-methylpyridine)₂ (**1-Zn**).

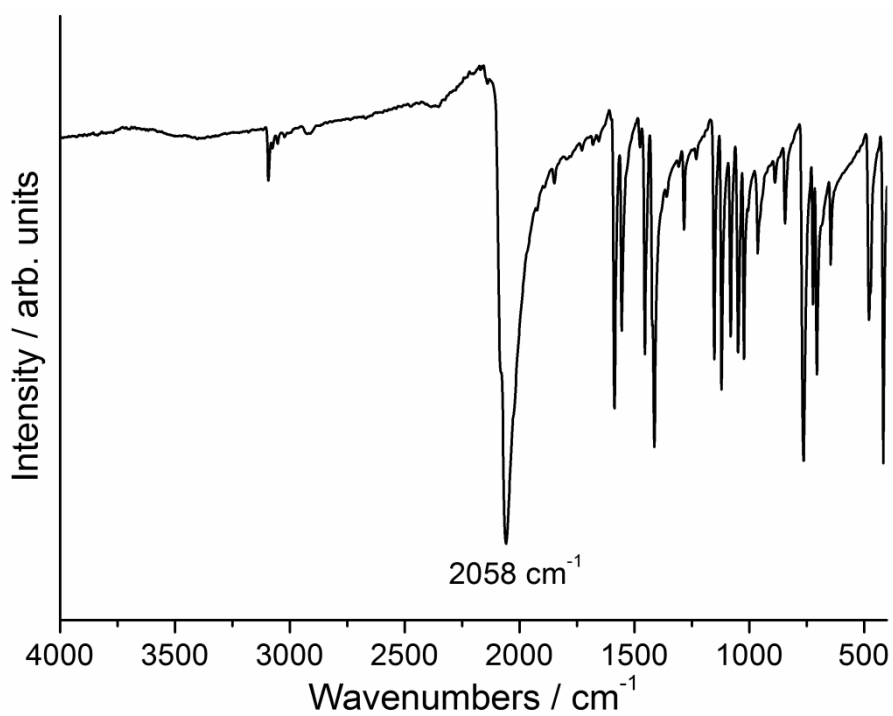


Figure S277. IR spectrum of Co(NCS)₂(2-bromopyridine)₂ (**2-Co**).

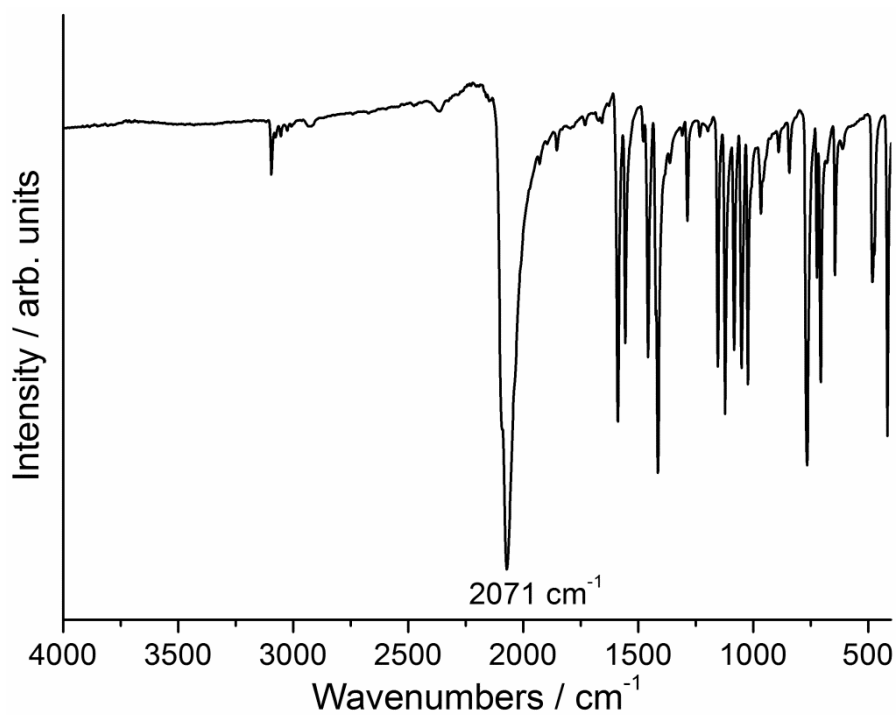


Figure S288. IR spectrum of $\text{Zn}(\text{NCS})_2(2\text{-bromopyridine})_2$ (**2-Zn**).

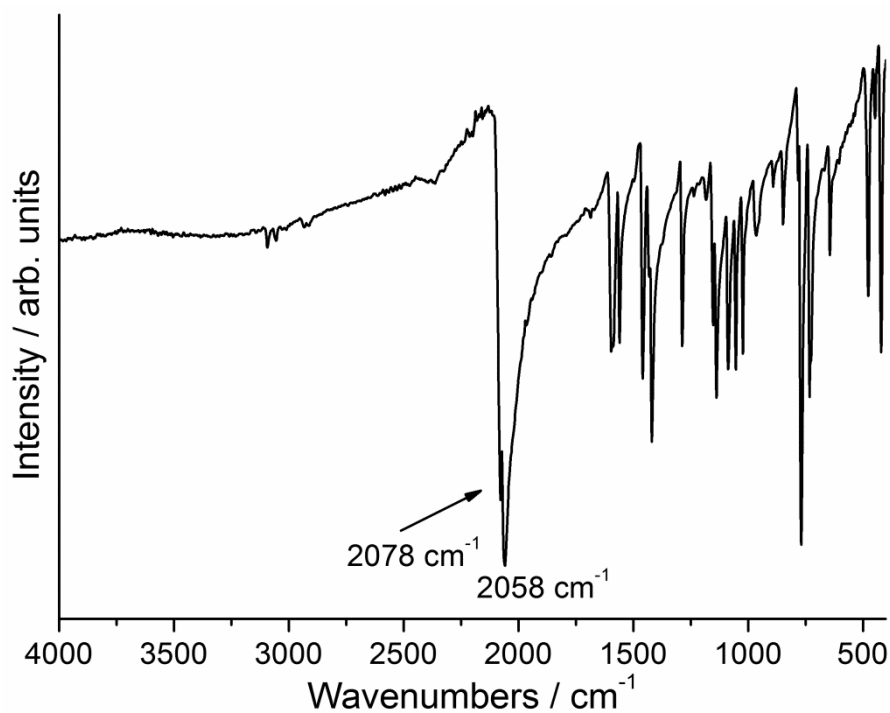


Figure S29. IR spectrum of $\text{Co}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Co α**).

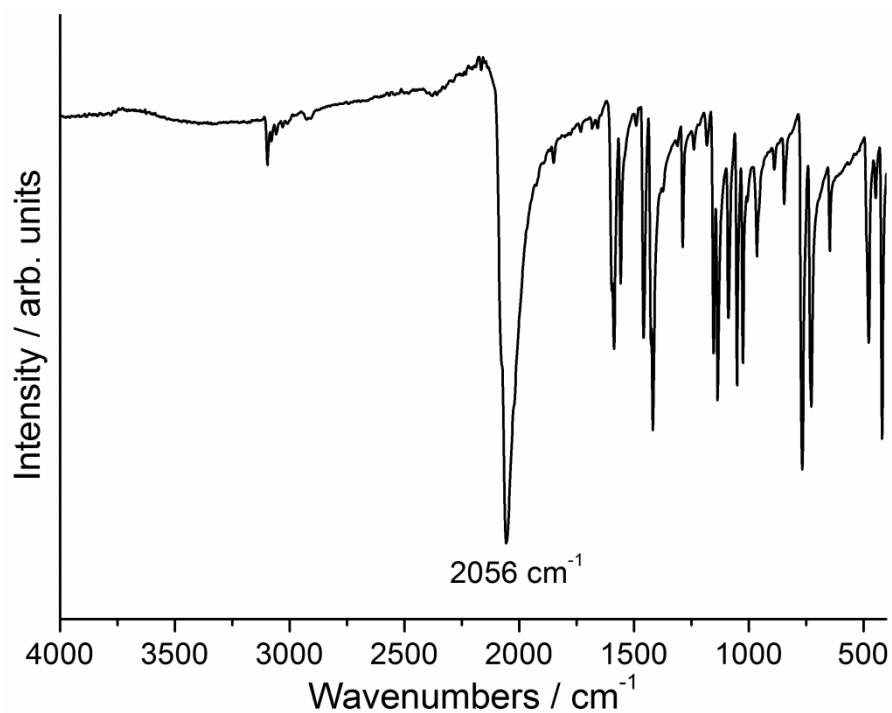


Figure S30. IR spectrum of $\text{Co}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Coβ**).

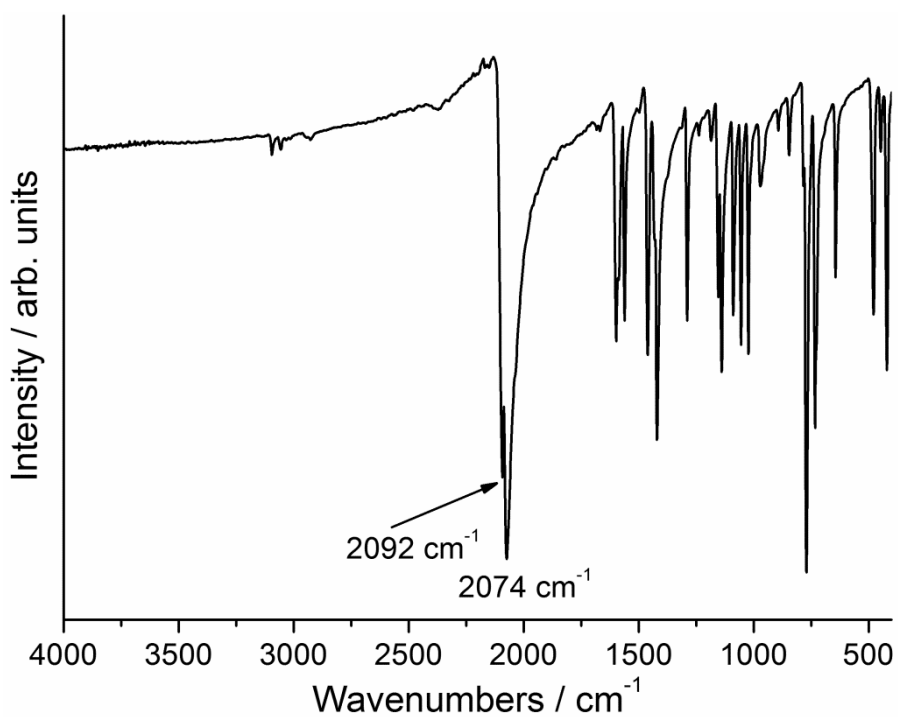


Figure S291. IR spectrum of $\text{Zn}(\text{NCS})_2(2\text{-chloropyridine})_2$ (**3-Znα**).