Electronic Supplementary Material (ESI) for CrystEngComm

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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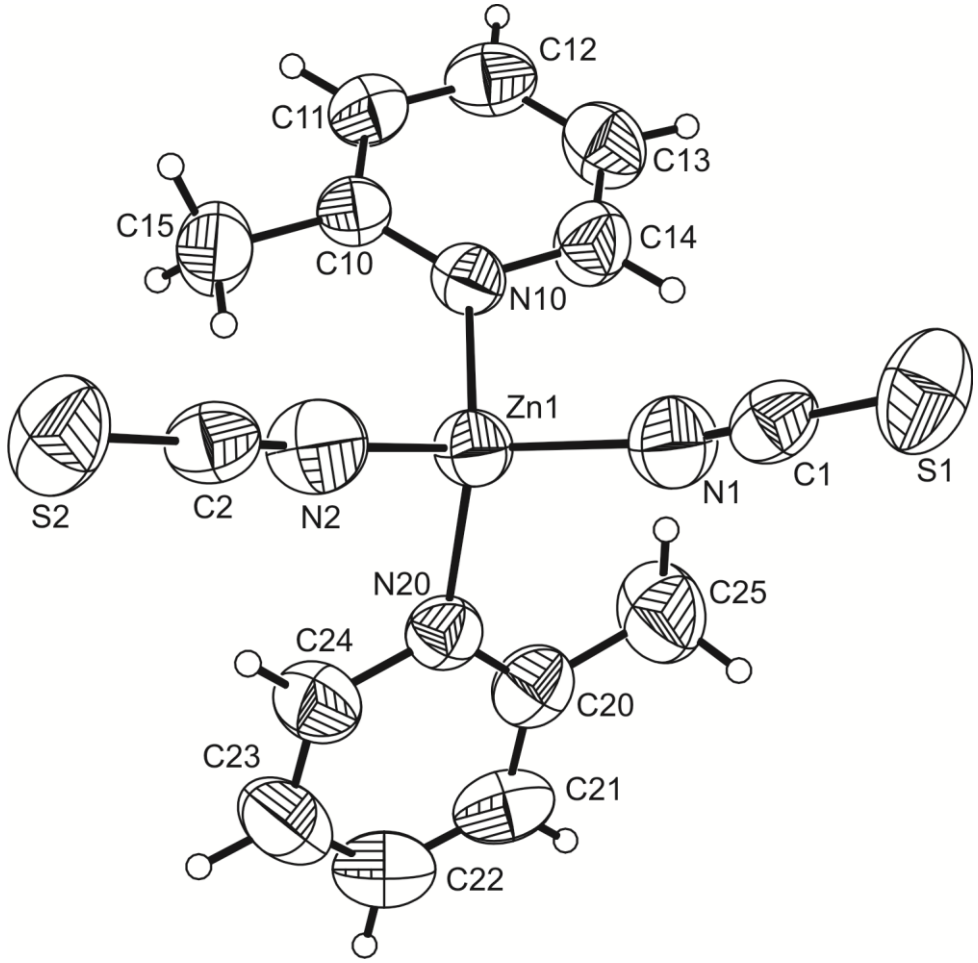

Figure S1. Crystal structure of $Zn(NCS)_2(2\text{-methylpyridine})_2$ (**1-Zn**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

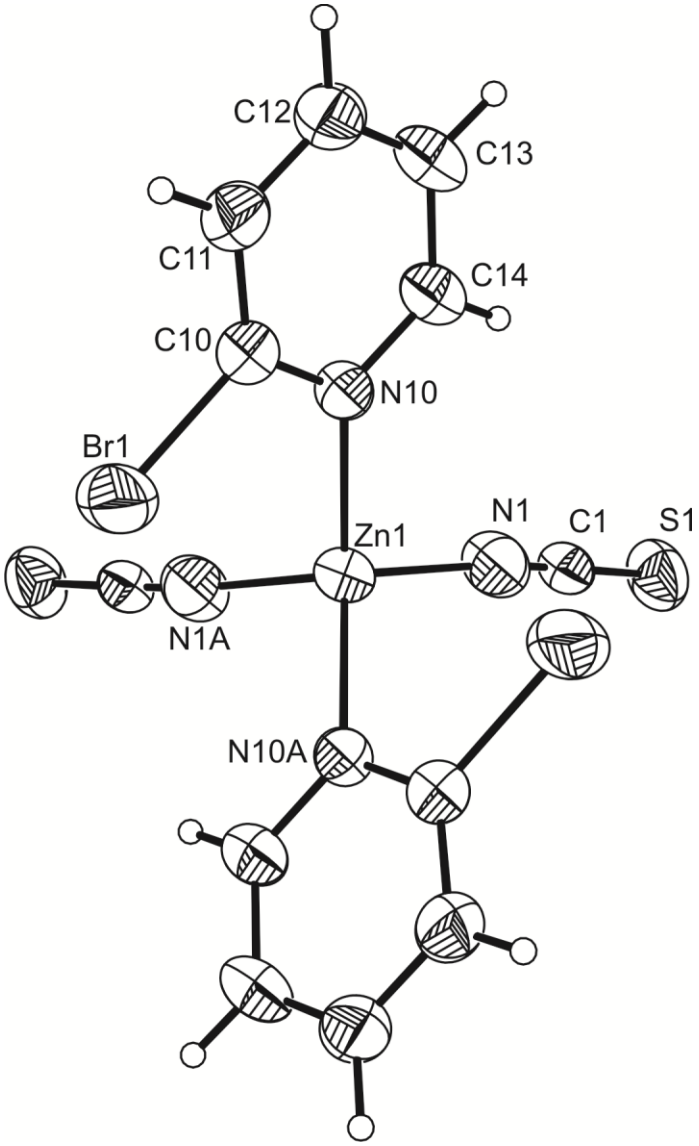

Figure S2. Crystal structure of $Zn(NCS)_2(2\text{-bromopyridine})_2$ (**2-Zn**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x + 1, y, -z + ½.

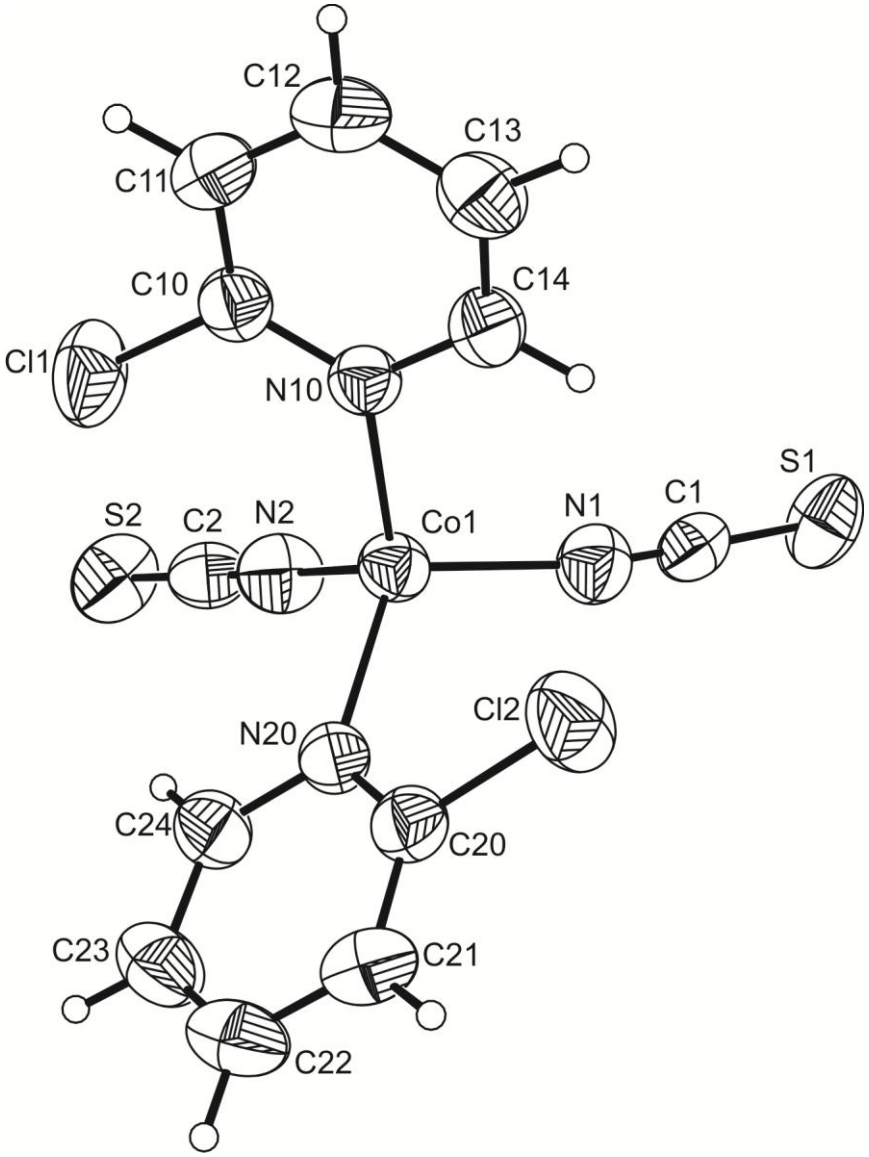

Figure S3. Crystal structure of $Co(NCS)_2$(2-chloropyridine)$_2$ (**3-Coα**) with view of the coordination sphere of the cobalt(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

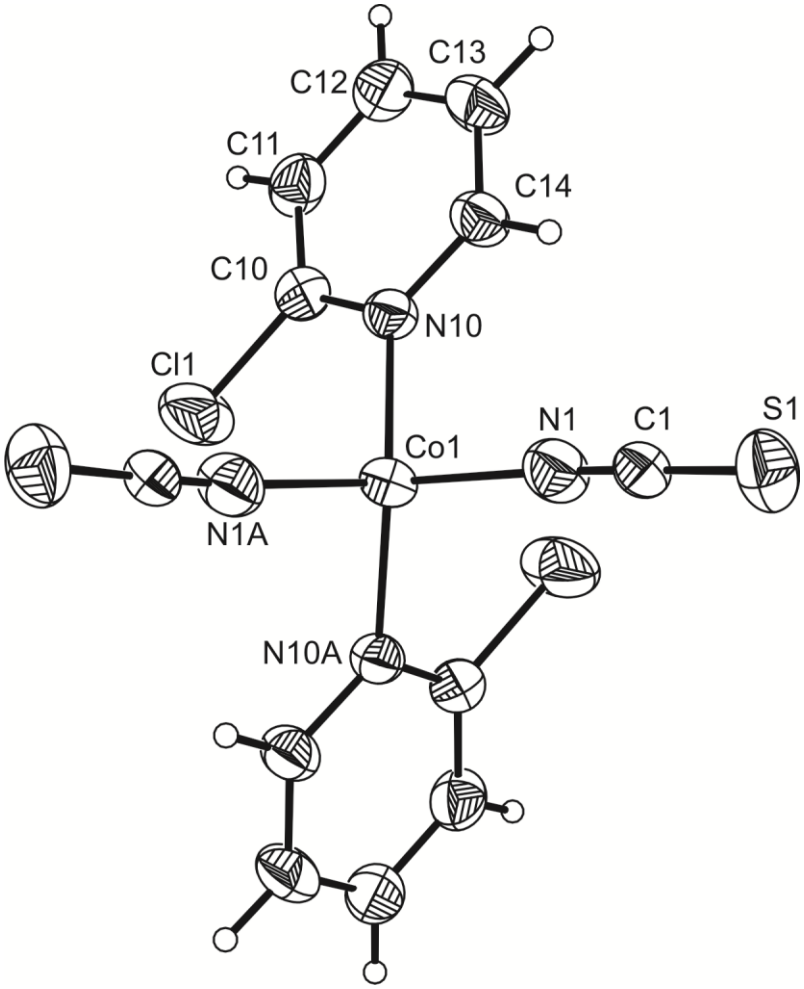

Figure S4. Crystal structure of $Co(NCS)_2(2\text{-chloropyridine})_2$ (**3-Coβ**) with view of the coordination sphere of the cobalt(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x, y, -z + ½.

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

compound	**3-Coβ**
Formula	$C_{12}H_8Cl_2CoN_4S_2$
MW / g·mol^{-1}	402.17
Crystal system	orthorhombic
Space group	*P*bcn
a /Å	11.2928(7)
b / Å	9.7123(5)
c / Å	15.1913(8)
V / Å^3	1666.17(16)
T / K	200
Z	4
D_{calc} / mg·m^3	1.603
μ / mm^{-1}	1.597
θ_{max} / °	28.03
Refl. collected	11189
Unique reflections	2005
R_{int}	0.0342
Refl. [F_0>4σ(F_0)]	1671
Parameters	97
R_1 [F_0>4σ(F_0)]	0.0312
wR_2	0.0799
GOF	1.036
$\Delta\rho_{max/min}$ / e·Å^{-3}	0.377 / -0.442

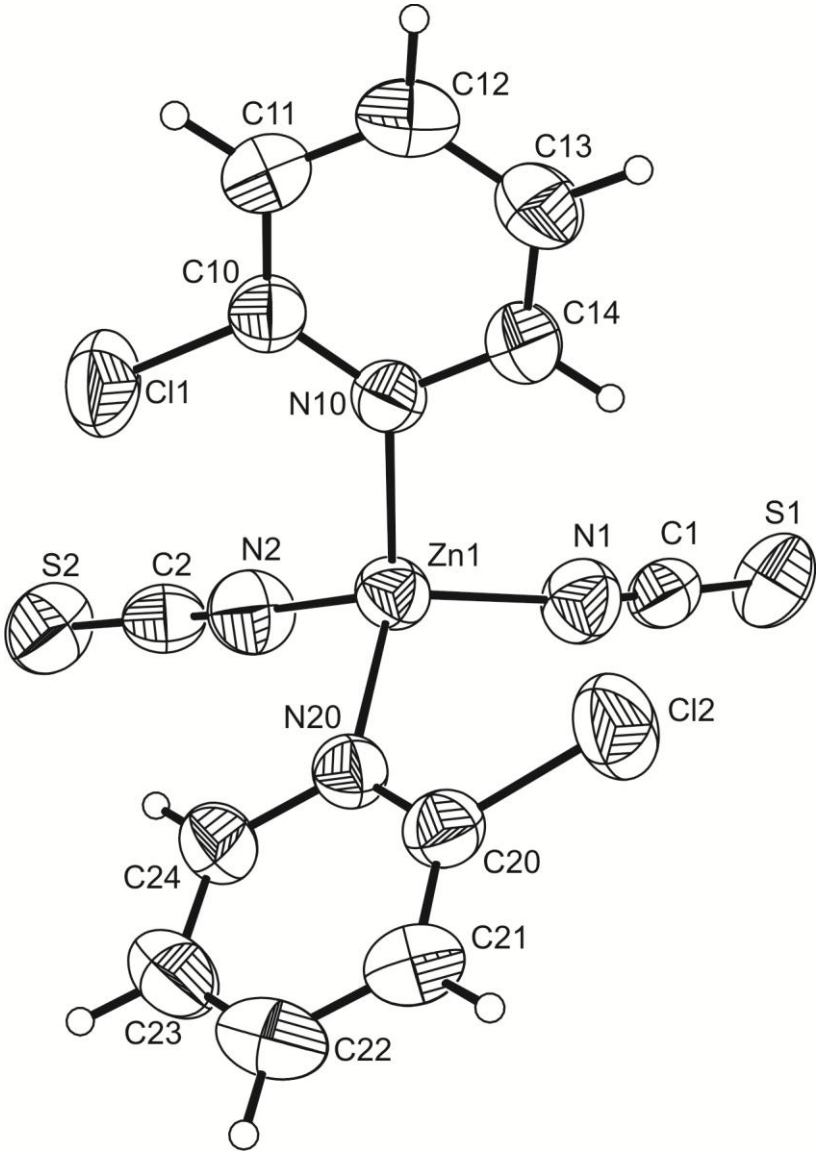

Figure S5. Crystal structure of $Zn(NCS)_2(2\text{-chloropyridine})_2$ (**3-Znα**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level.

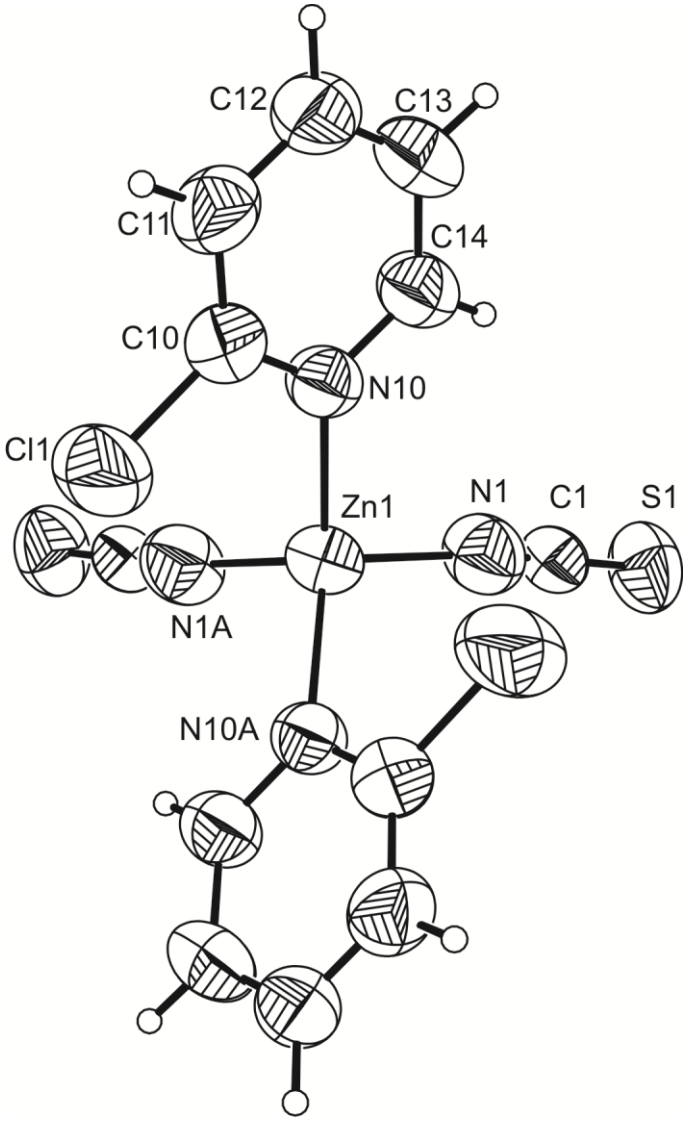

Figure S6. Crystal structure of $Zn(NCS)_2(2\text{-chloropyridine})_2$ (**3-Znβ**) with view of the coordination sphere of the zinc(II) cation with labeling and displacement ellipsoids drawn at 50 % probability level. Symmetry code: A = -x + 1, y, -z + 3/2.

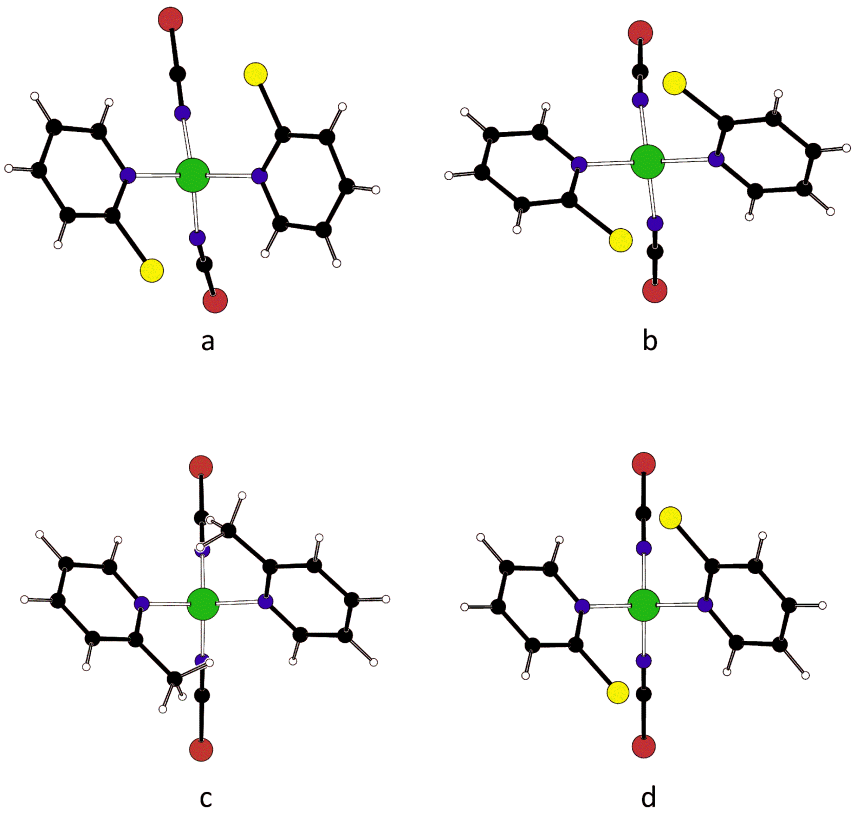

Figure S7. Comparison of molecular geometries: a) Molecule of **3-Znα** as found in the crystal (space group $P2_12_12_1$); b) Molecule of **3-Znβ** (crystals in *Pbcn*); c) Molecule of **3-Znα** after force field energy minimization; d) Molecule of **1-Zn** after force field energy minimization. Note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

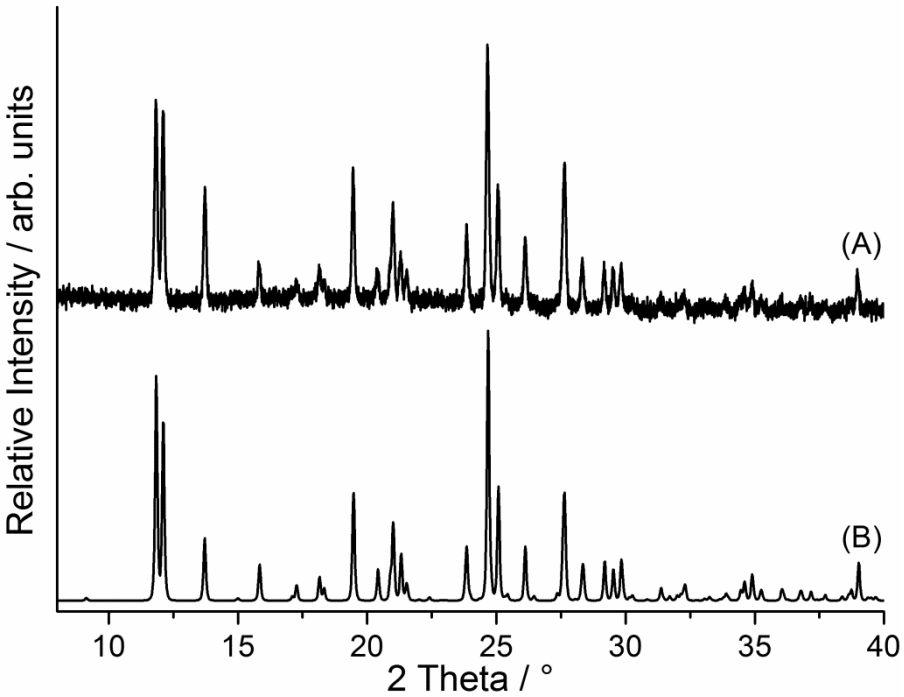

Figure S8. Experimental XRPD pattern of compound **1-Co** (A) and XRPD calculated from single crystal data of compound **1-Co** (B).

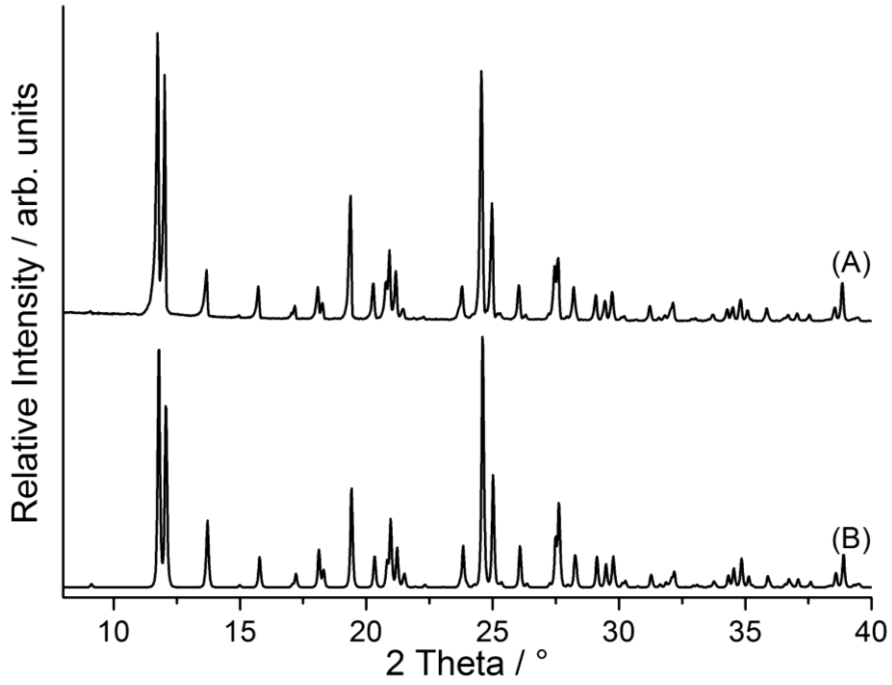

Figure S9. Experimental XRPD pattern of compound **1-Zn** (A) and XRPD calculated from single crystal data of compound **1-Zn** (B).

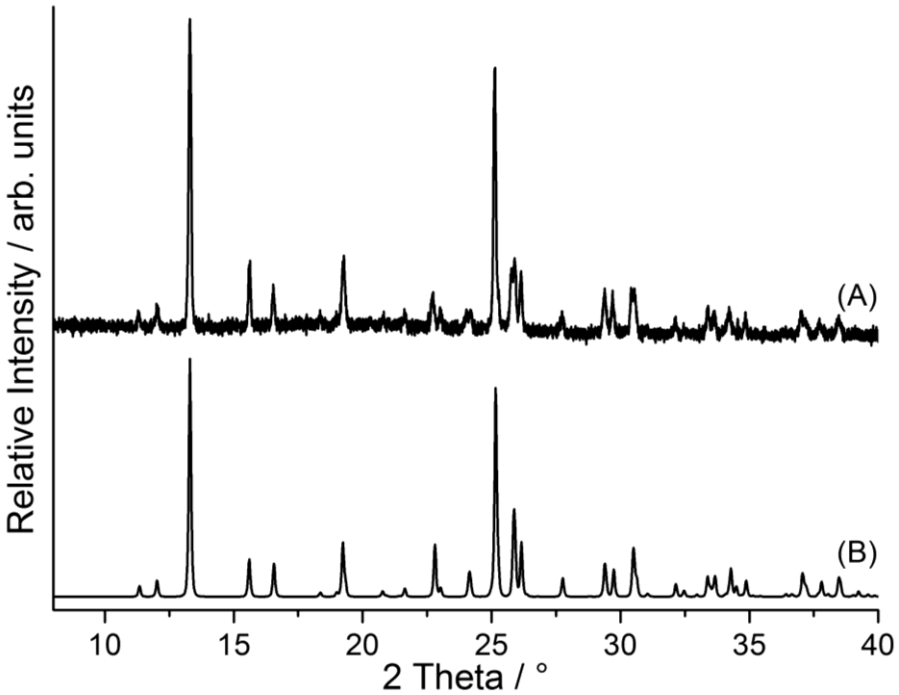

Figure S10. Experimental XRPD pattern of compound **2-Co** (A) and XRPD calculated from single crystal data of compound **2-Co** (B).

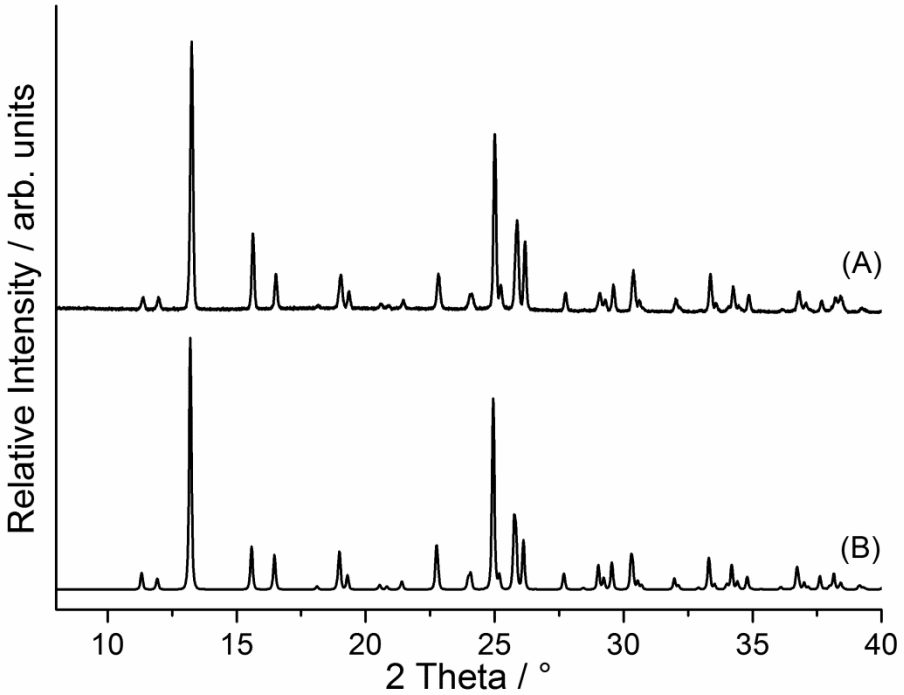

Figure S11. Experimental XRPD pattern of compound **2-Zn** (A) and XRPD calculated from single crystal data of compound **2-Zn** (B).

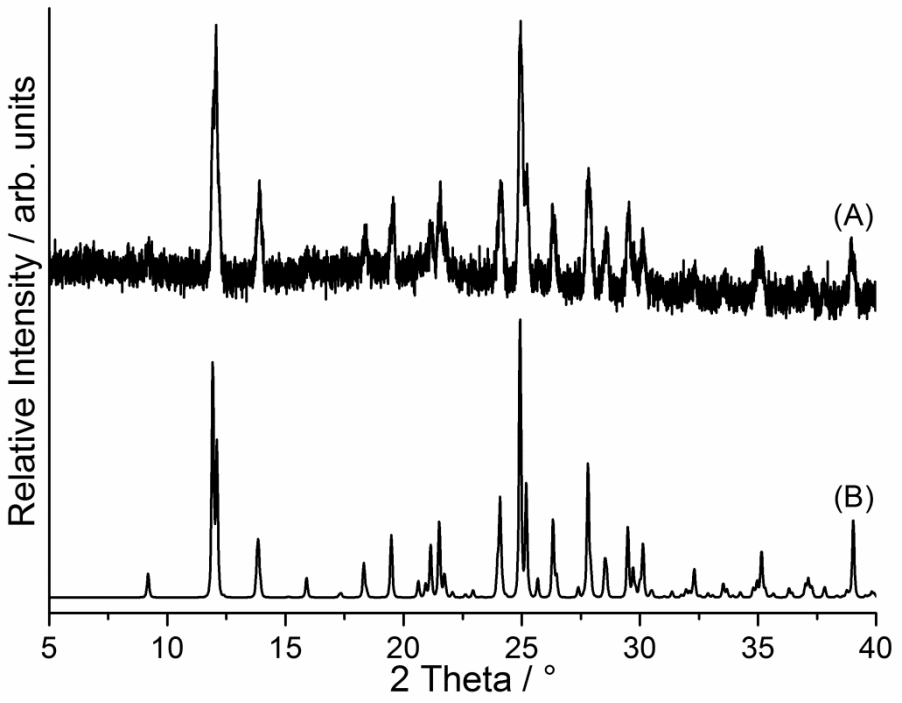

Figure S12. Experimental XRPD pattern of compound **3-Coα** (A) and XRPD calculated from single crystal data of compound **3-Coα** (B).

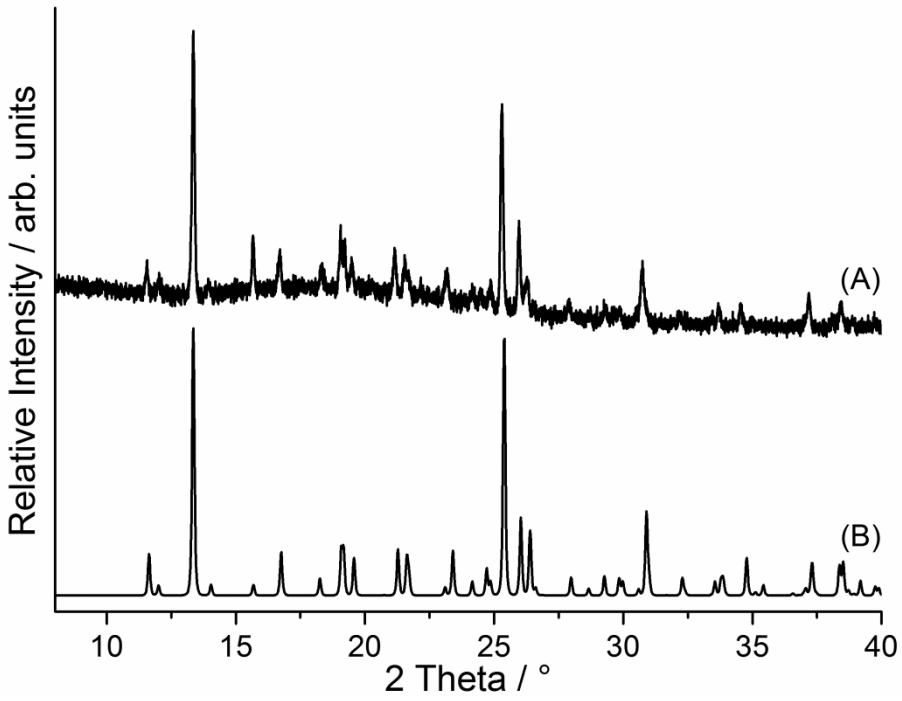

Figure S13. Experimental XRPD pattern of compound **3-Coβ** (A) and XRPD calculated from single crystal data of compound **3-Coβ** (B).

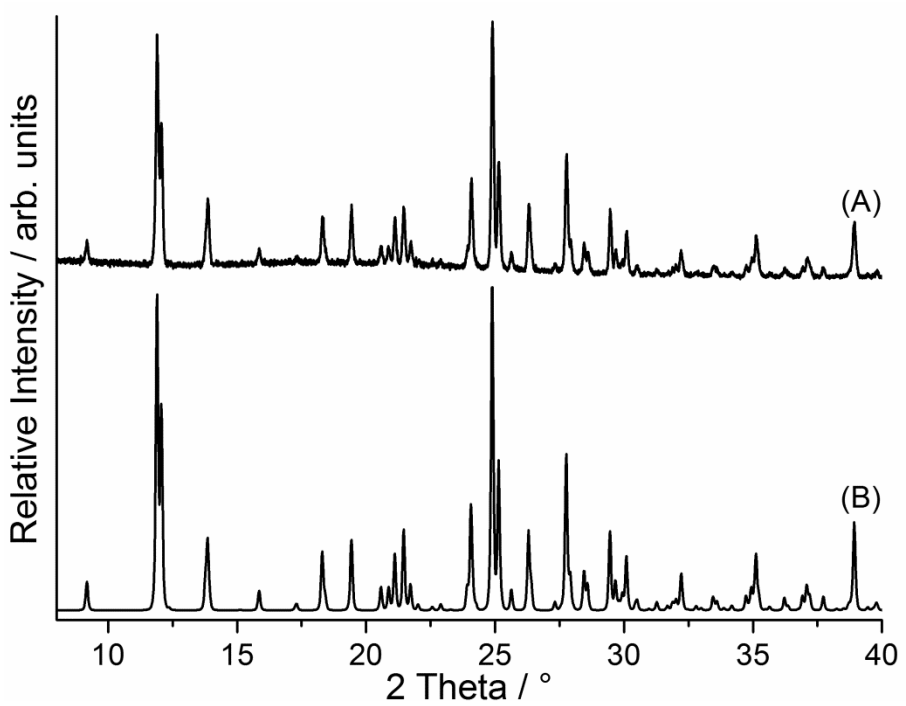

Figure S14. Experimental XRPD pattern of compound **3-Znα** (A) and XRPD calculated from single crystal data of compound **3-Znα** (B).

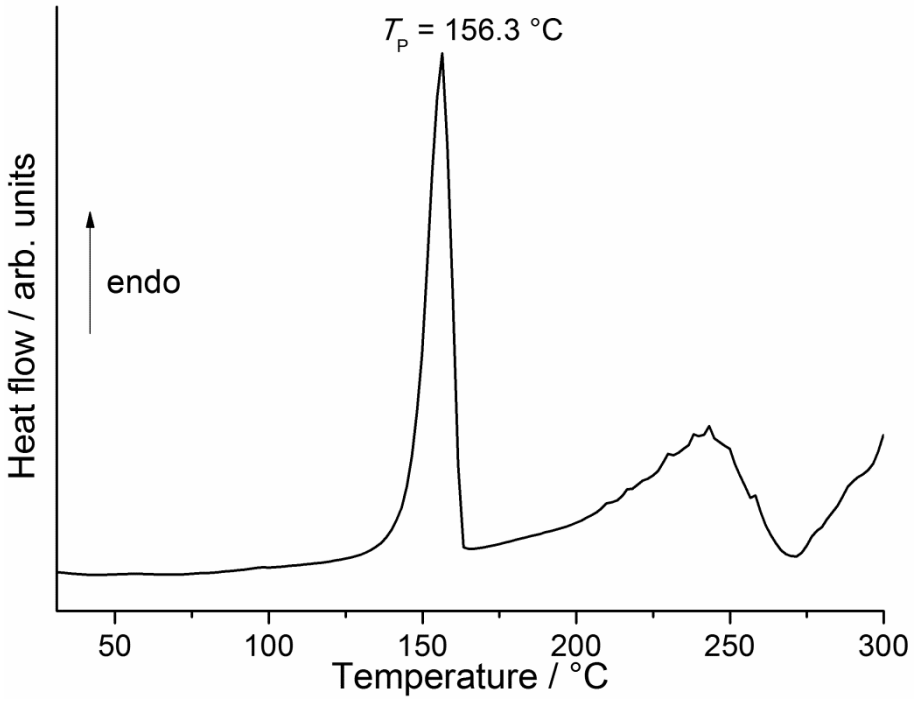

Figure S15. Differential scanning calorimetry (DSC) measurement for compound **1-Co**. Heating rate 3 °C·min^{-1}; N_2 atmosphere; T_P = peak temperature (°C).

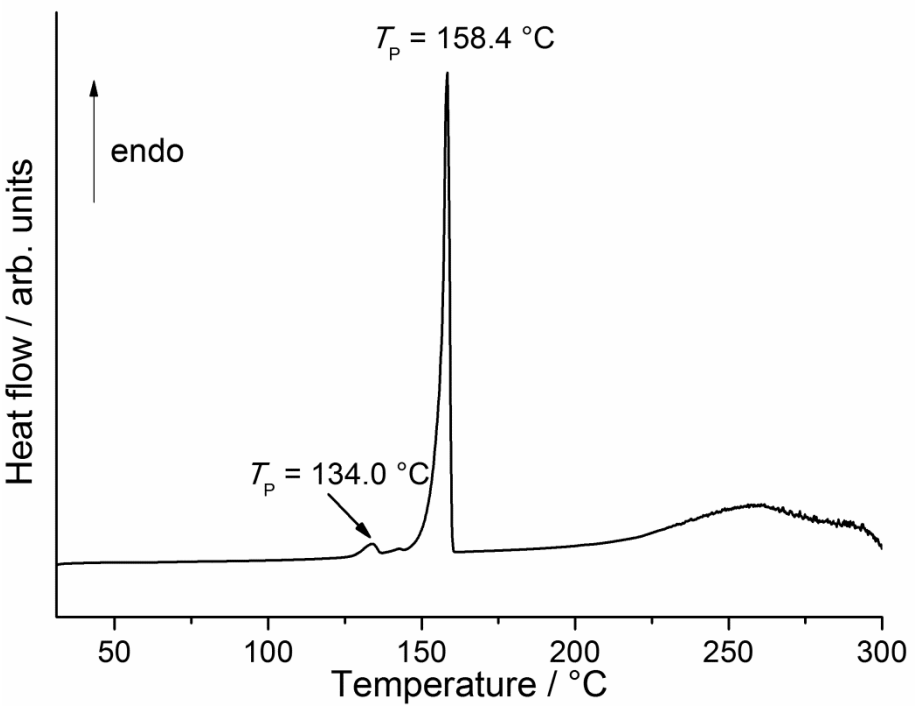

Figure S16. Differential scanning calorimetry (DSC) measurement for compound **1-Zn**. Heating rate 3 °C·min^{-1}; N_2 atmosphere; T_P = peak temperature (°C).

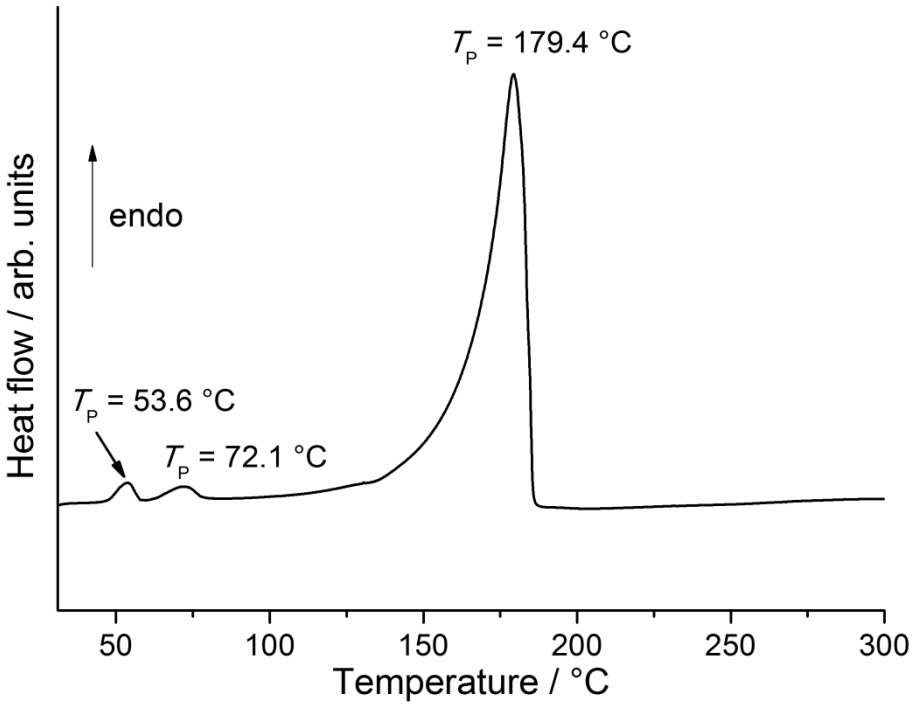

Figure S17. Differential scanning calorimetry (DSC) measurement for compound **2-Co**. Heating rate 3 °C·min^{-1}; N_2 atmosphere; T_P = peak temperature (°C).

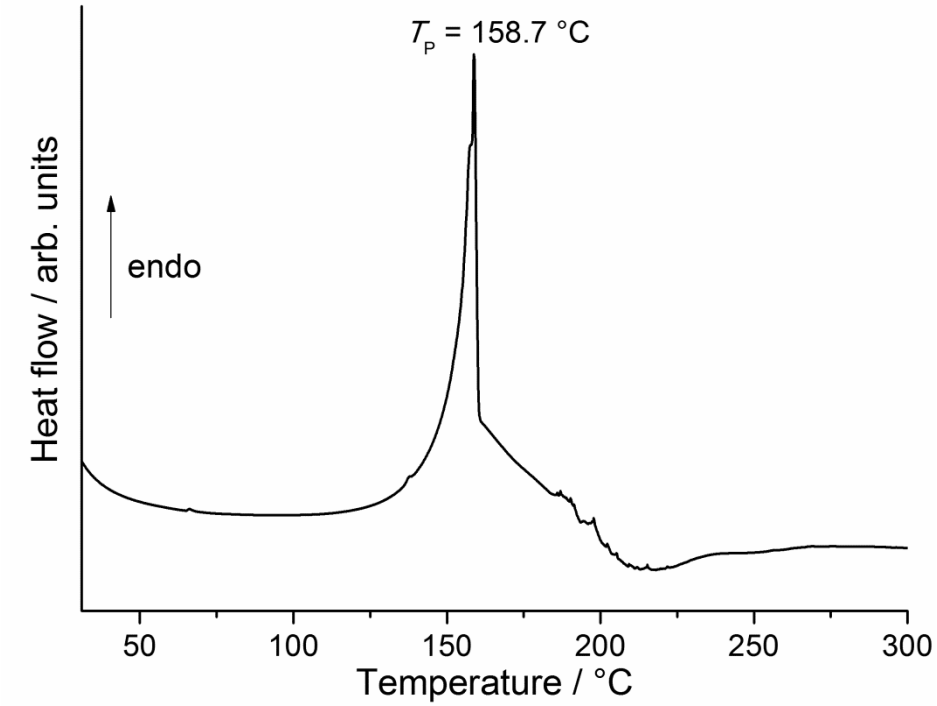

Figure S18. Differential scanning calorimetry (DSC) measurement for compound **2-Zn**. Heating rate 3 °C·min^{-1}; N_2 atmosphere; T_P = peak temperature (°C).

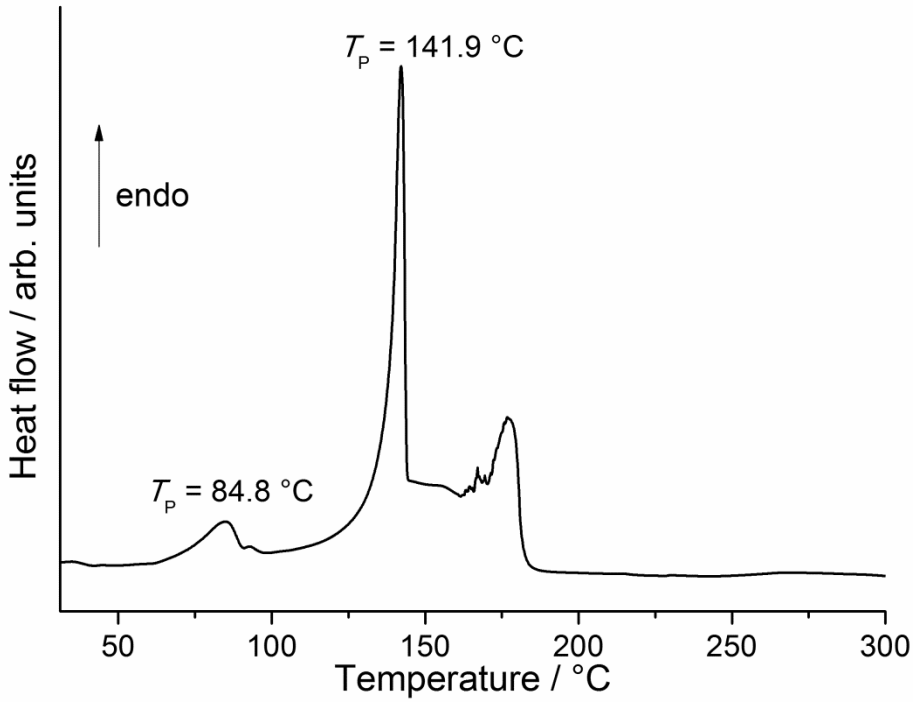

Figure S19. Differential scanning calorimetry (DSC) measurement for compound **3-Coβ**. Heating rate 3 °C·min^{-1}; N_2 atmosphere; T_P = peak temperature (°C).

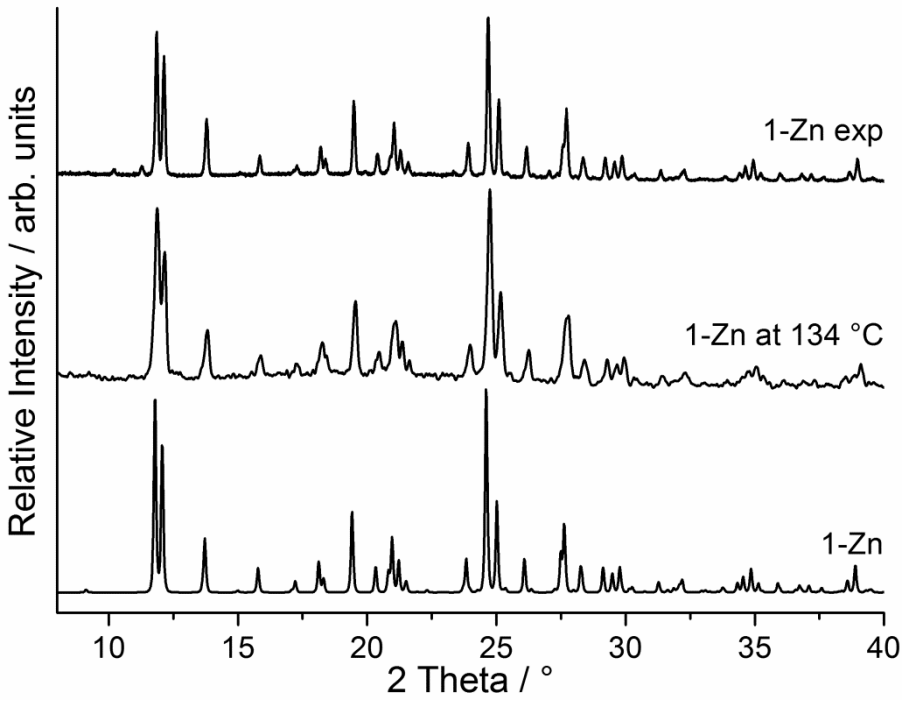

Figure S20. Experimental XRPD of compound **1-Zn** (top) and the intermediate, which were obtained at 134 °C in the DSC measurement of compound **1-Zn** (middle) as well as XRPD calculated from single crystal data of **1-Zn** (bottom).

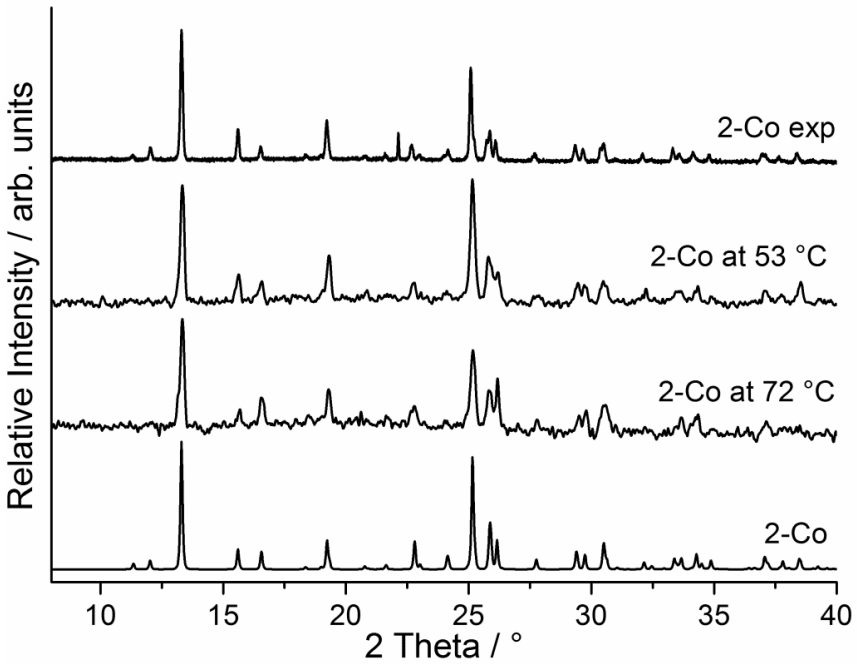

Figure S21. Experimental XRPD of compound **2-Co** (top) and the intermediate, which were obtained at 53 °C and 72 °C in the DSC measurement of compound **2-Co** (middle) as well as XRPD calculated from single crystal data of **2-Co** (bottom).

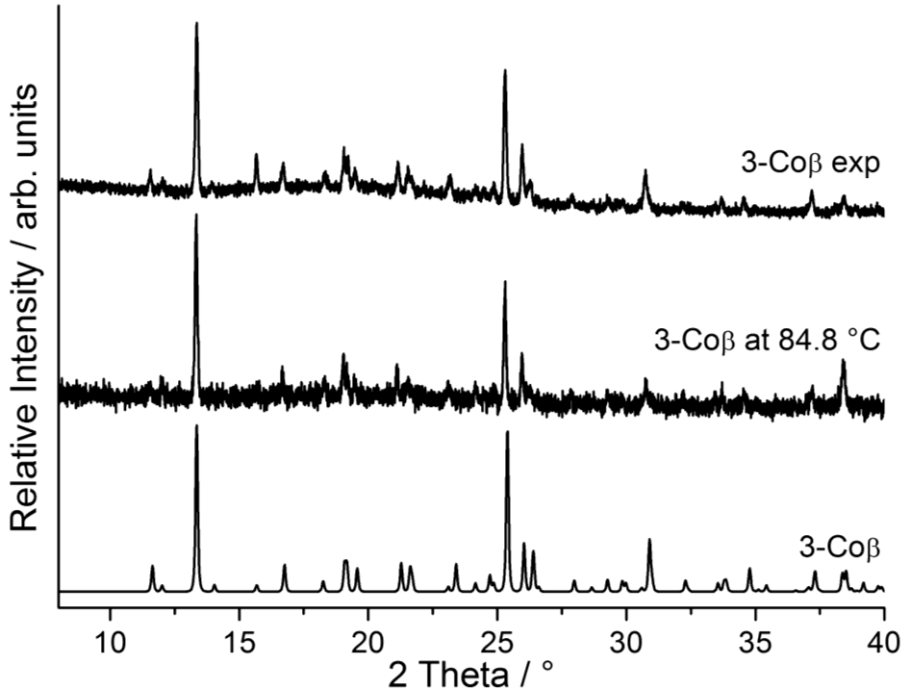

Figure S22. Experimental XRPD of compound **3-Coβ** (top) and the intermediate, which were obtained at 84.8 °C in the DSC measurement of compound **3-Coβ** (middle) as well as XRPD calculated from single crystal data of **3-Coβ** (bottom).

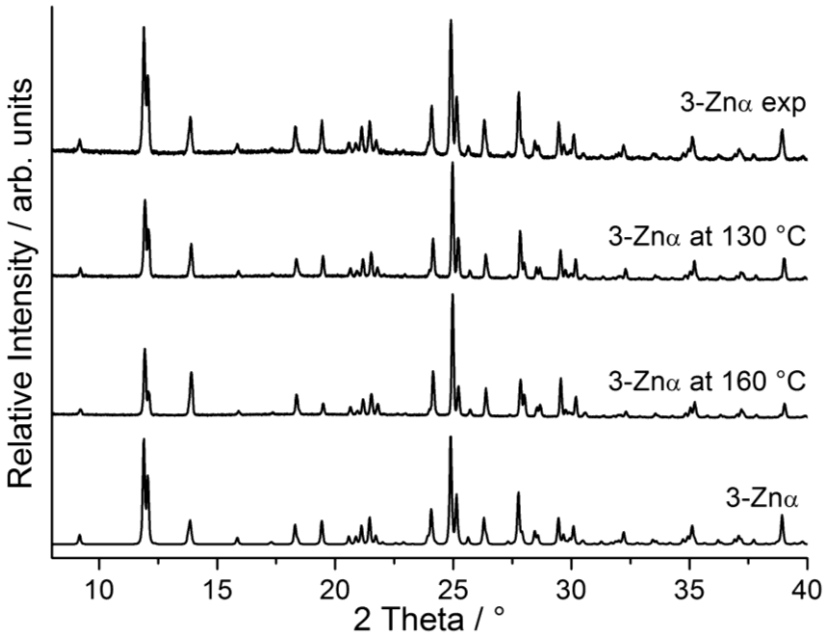

Figure S23. Experimental XRPD of the residues which were obtained after heating **3-Znα** at 130 °C and at 160 °C for three days in methanol and experimental and calculated powder pattern of **3-Znα**.

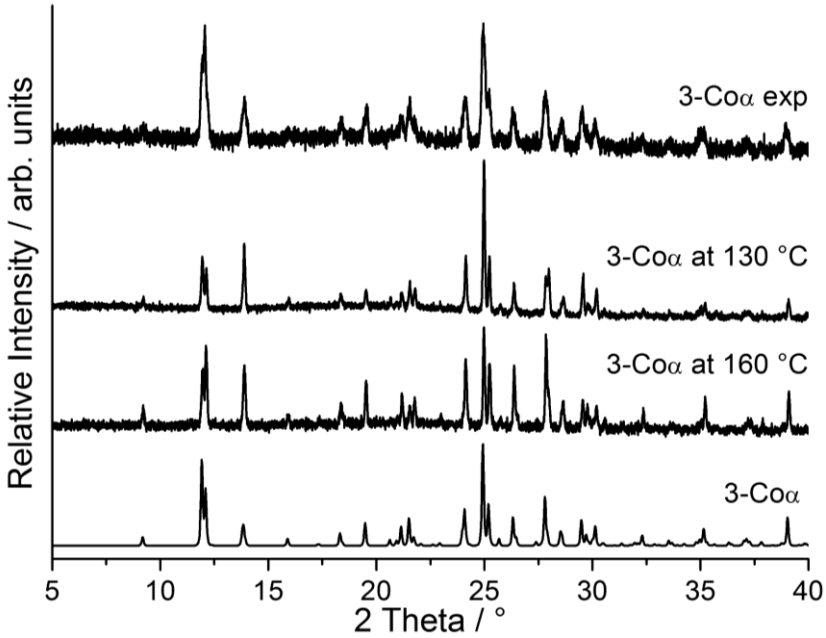

Figure S24. Experimental XRPD of the residues which were obtained after heating **3-Coα** at 130 °C and at 160 °C for three days in methanol and experimental and calculated powder pattern of **3-Coα**.

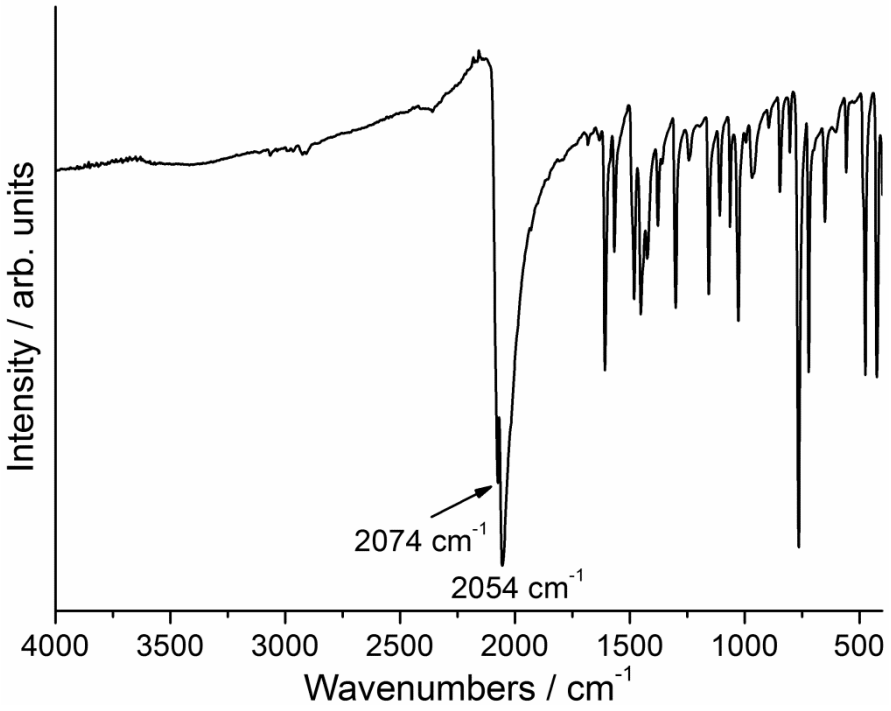

Figure S255. IR spectrum of $Co(NCS)_2(2\text{-methylpyridine})_2$ (**1-Co**).

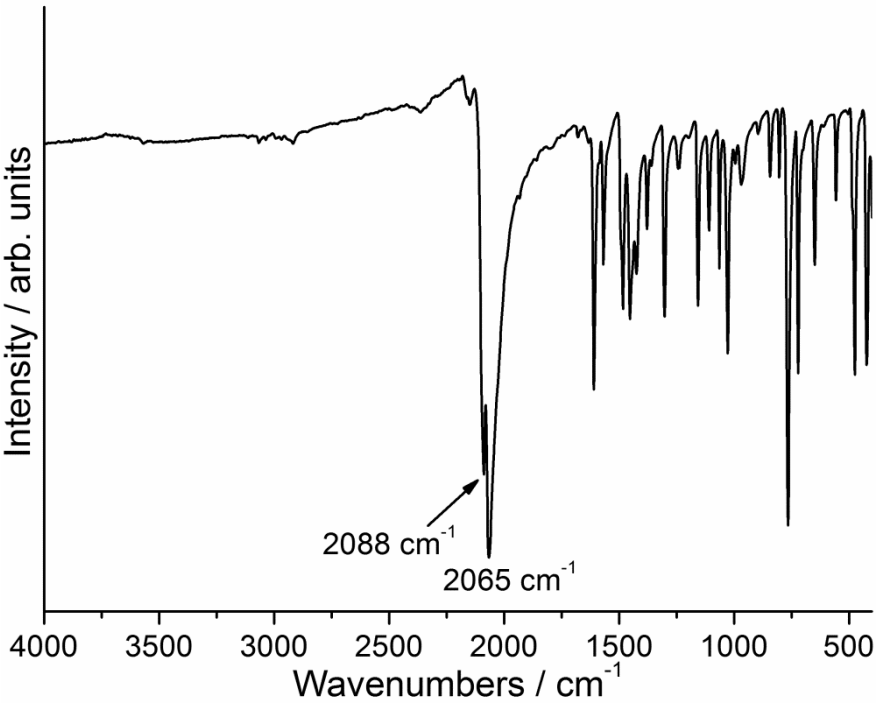

Figure S266. IR spectrum of $Zn(NCS)_2(2\text{-methylpyridine})_2$ (**1-Zn**).

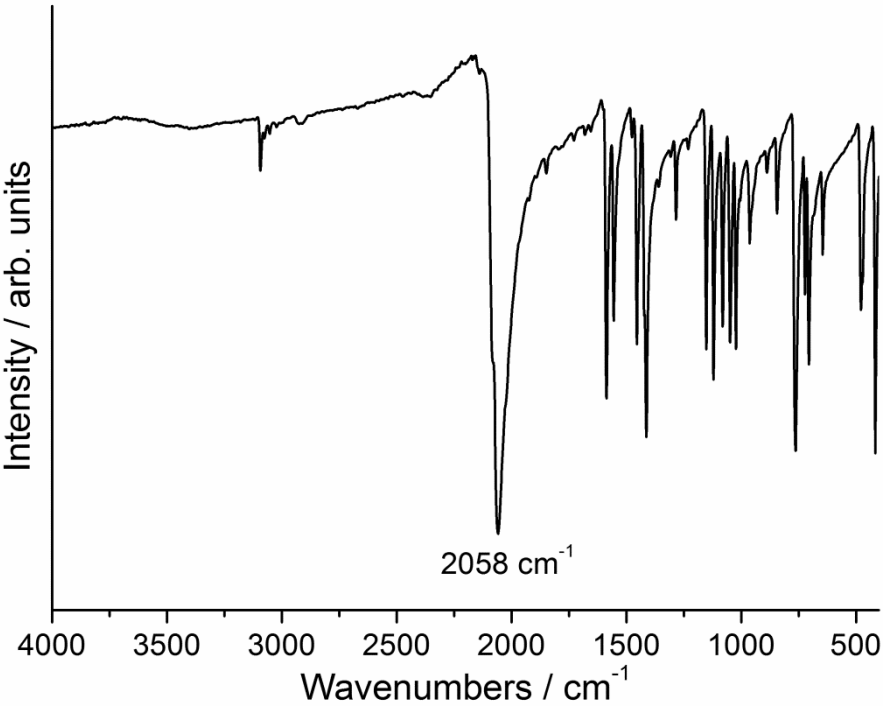

Figure S277. IR spectrum of $Co(NCS)_2(2\text{-bromopyridine})_2$ (**2-Co**).

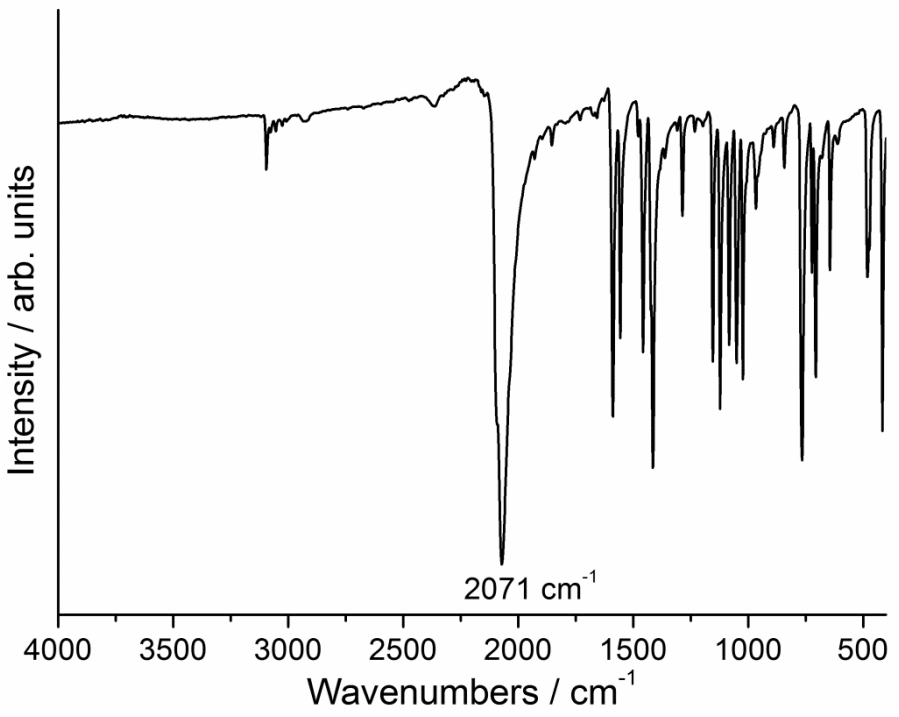

Figure S288. IR spectrum of $Zn(NCS)_2(2\text{-bromopyridine})_2$ (**2-Zn**).

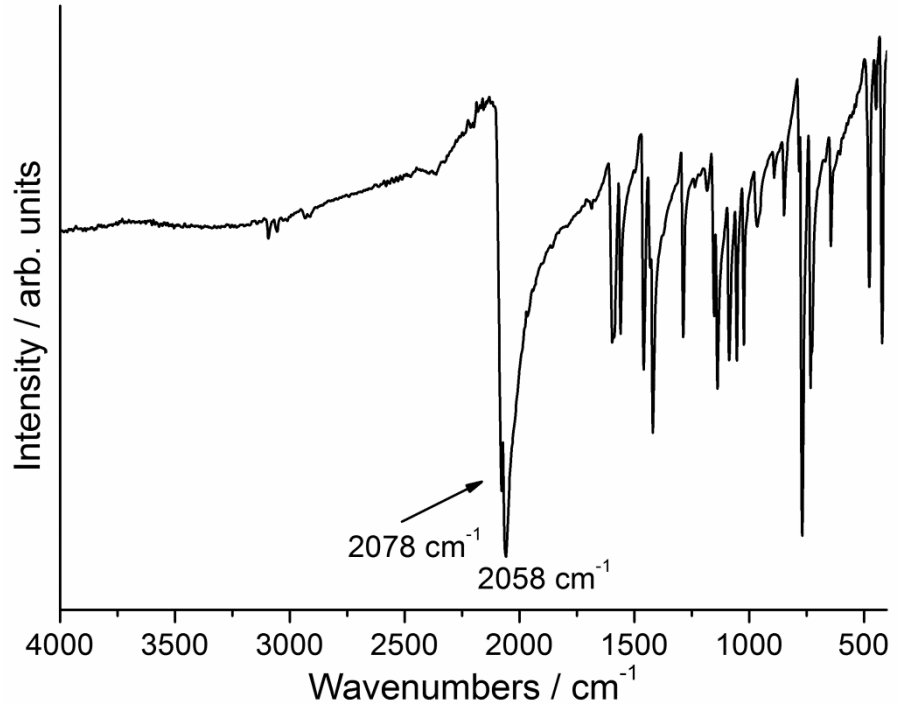

Figure S29. IR spectrum of $Co(NCS)_2(2\text{-chloropyridine})_2$ (**3-Coα**).

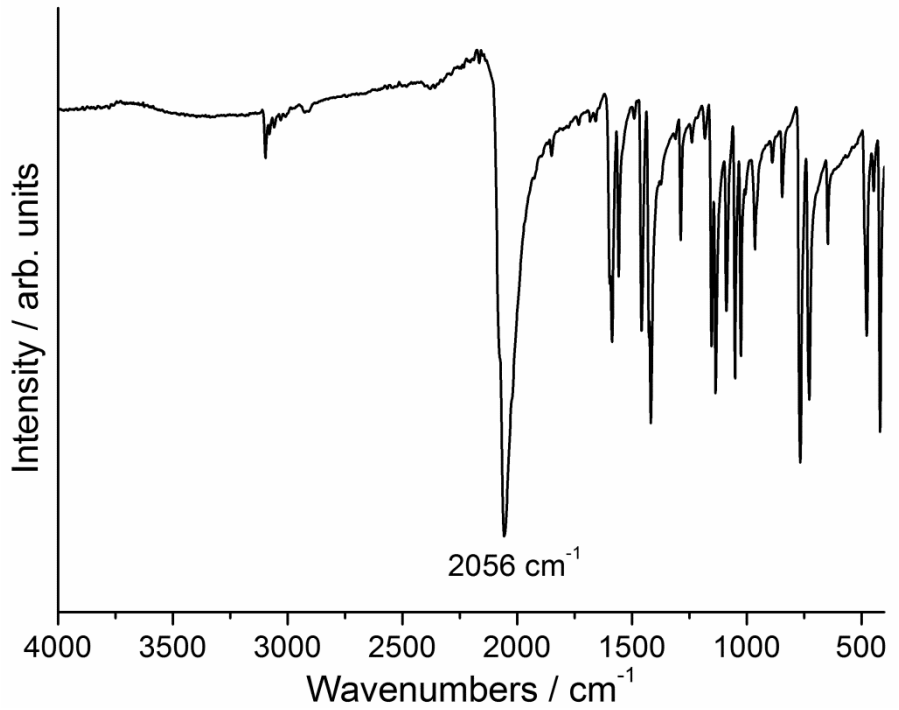

Figure S30. IR spectrum of $Co(NCS)_2(2\text{-chloropyridine})_2$ (**3-Coβ**).

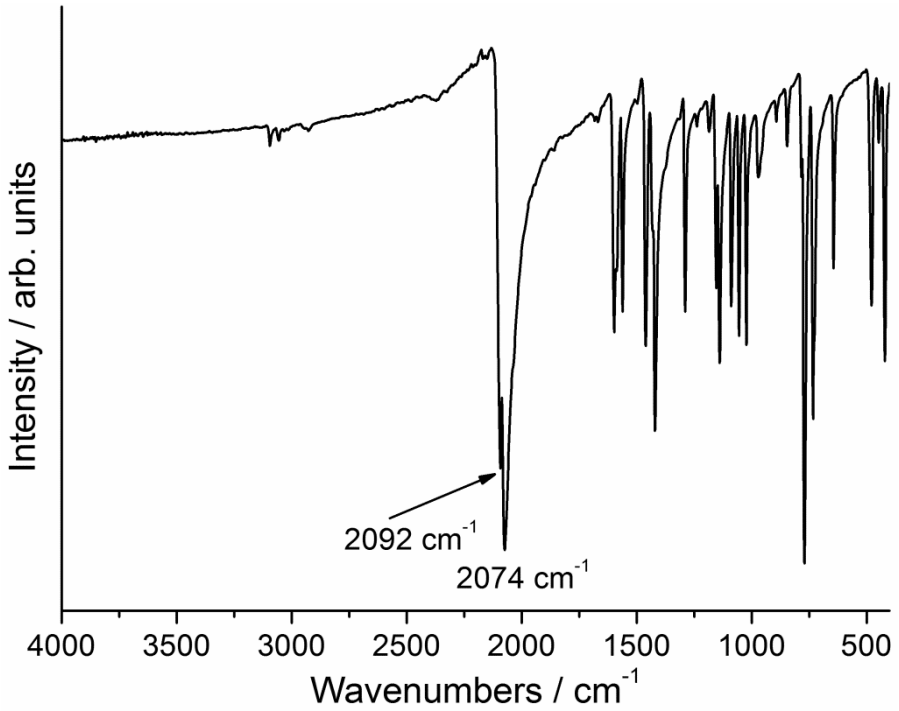

Figure S291. IR spectrum of $Zn(NCS)_2(2\text{-chloropyridine})_2$ (**3-Znα**).