Supporting Information for

Tuning the magnetic properties of transition metal MOFs by the metal-oxygen condensation control: the relation between synthesis temperature, SBU nuclearity and carboxylate geometry

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Experimental

Synthesis of $[Co_2(hfipbb)_2(H_2hfipbb)]$ (3): This compound was obtained by reaction of 1 mmol of $CoCl_2 \cdot 6H_2O$ with 0.8 mmol of H_2hfipbb in 6 mL of water with addition of 0.05 mL of TEA. This mixture was heated in a Teflon-lined digestion bomb at 170 ºC during 6 days and then cooled to room temperature. Dark gray prismatic crystals were collected after washing with distilled water and acetone. In such conditions the obtained yield is 30.47 %. If the amount of TEA is augmented to 0.15 mL, the resultant yield is 57.26 % the obtained crystals being of bigger size.

The comparison between simulated and experimental XRD powder patterns (see Figures S1-S3) along with the results of elemental analysis allowed for verifying the purity of all compounds.

Table S1. Main crystallographic and refinement data for compound **3**.

	Compound 3
Formula	$[Co_2C_{51}H_{25}O_{12}F_{18}]$
Temperature (K)	273(2)
Molecular weight/gmol^{-}	1290.58
Crystal system	Monoclinic
Space Group	*P2/n*
a/Å	19.030(1)
b/Å	7.2336(5)
c/Å	20.500(1)
α/ º	90
β/ º	106.6290(10)
γ/ º	90
V/Å^3	2704.0(3)
Z	2
Calc. dens/g cm^{-3}	1.585
μ/mm^{-1}	0.735
Dimensions (mm)	0.6 x 0.4 x 0.2
Limiting indices	-22 < h < 22 -8 < k < 8 -24< l < 24
F(000)	1288
Refl. collected/unique with I > 2σ(I)	4666/3854
Refined parameters	379
Goodness-of-fit on F^2	1.058
R_1	0.0461
wR_2	0.1279
R-factor-all	0.0583

Table S2. Crystal data and Rietveld refinement values for compound **1a**.

Compound	**1a**
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a= 7.316(2) Å α = 90°
	b= 32.023(5)Å β = 99.91(2)°
	c= 16.533(3) Å γ = 90°
Profile Function	Pseudo-Voigt
U	0.31(7)
V	-0.07(1)
W	0.005(6)
NA	0.88(9)
NB	-0.02(1)
Zero Point	0.1052(8)
Asymmetry correction	Finger-Cox-Jephcoat
H/L	0.0141(2)
S/L	0.0146(2)
R_{wp}	0.0828
R_p	0.1996

Table S3. Crystal data and Rietveld refinement values for compound **1b**.

Compound	1b
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.127(1) Å α = 90°
	b = 31.803(4)Å β = 99.89(2)°
	c = 16.424(2) Å γ = 90°
Profile Function	Pseudo-Voigt
U	0.4(1)
V	-0.08(2)
W	0.0070(7)
NA	0.81(8)
NB	0.002(8)
Zero Point	0.1178(8)
Asymmetry correction	Finger-Cox-Jephcoat
H/L	0.0164(2)
S/L	0.0159(2)
R_{wp}	0.1444
R_p	0.2925

Table S4. Crystal data and Rietveld refinement values for compound **1c**.

Compound	**1c**
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a= 7.085(2) Å α = 90°
	b= 31.766(7)Å β = 99.78(4)°
	c= 16.404(4) Å γ = 90°
Profile Function	Pseudo-Voigt
U	2.9(3)
V	0.56(6)
W	0.032(2)
NA	0.92(8)
NB	-0.031(7)
Zero Point	0.107(2)
Asymmetry correctior	Finger-Cox-Jephcoat
H/L	0.01(1)
S/L	0.02(1)
R_{wp}	0.1516
R_p	0.2495

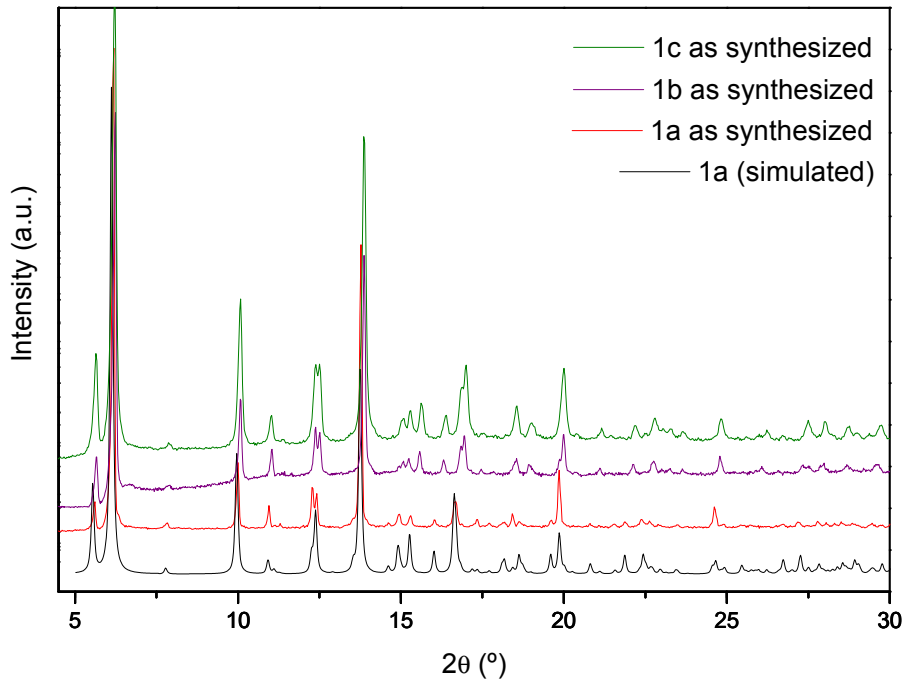


Figure S1. Comparison of simulated XRD powder pattern of compound **1a** with the corresponding experimental ones for **1a-c** compounds.

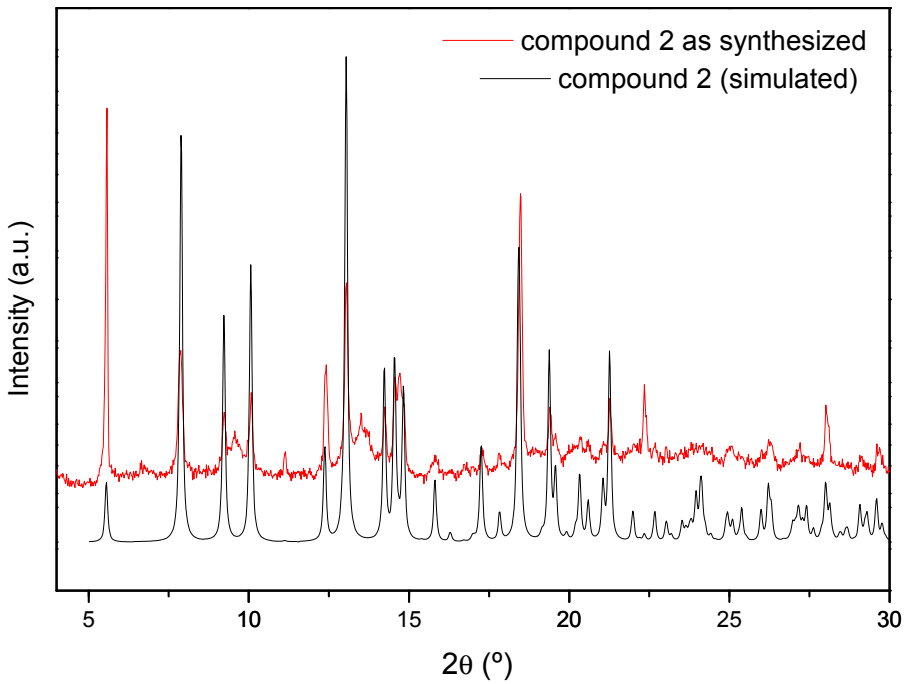


Figure S2. Comparison of simulated XRD powder pattern of compound 2 with the corresponding experimental one.

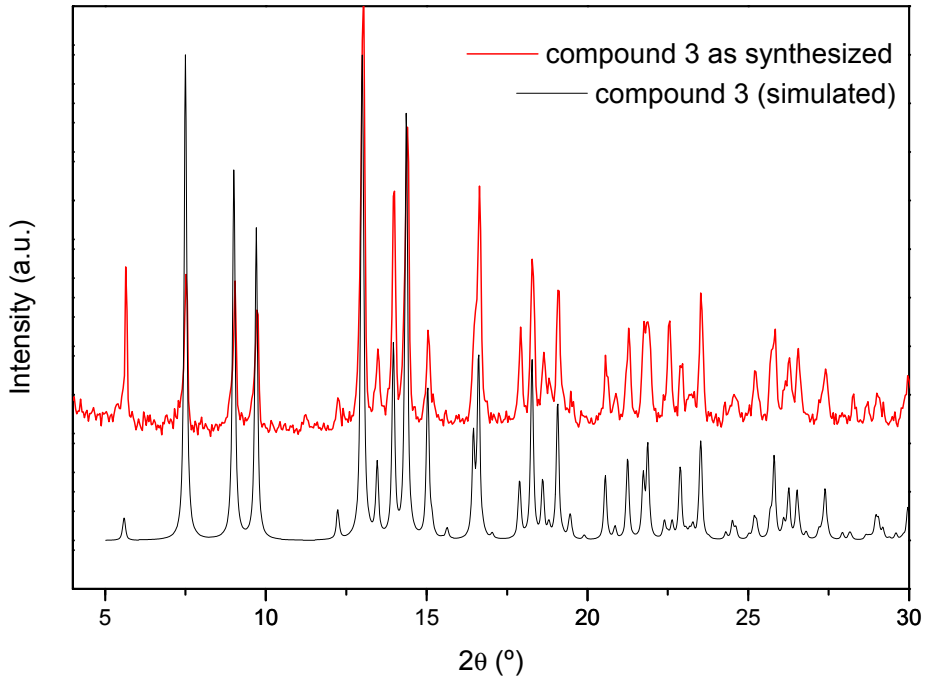


Figure S3. Comparison of simulated XRD powder pattern of compound **3** with the corresponding experimental one.

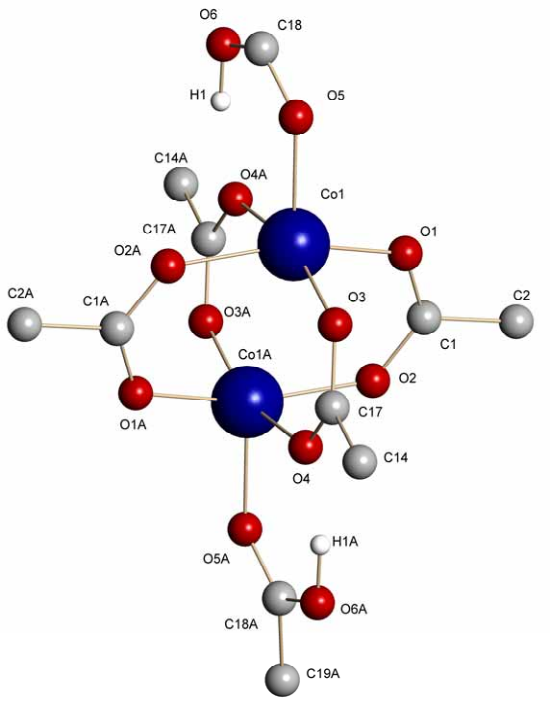


Figure S4. Coordination sphere of Co(II) ions in compound **3**.

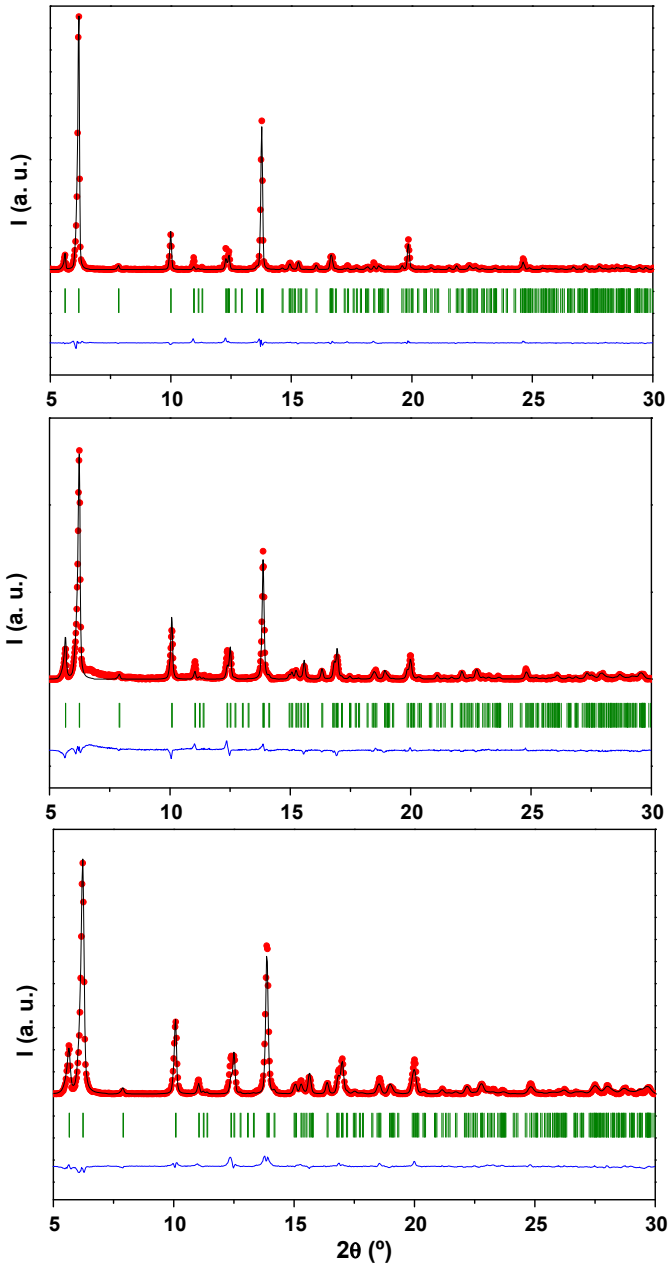


Figure S5. Rietveld analysis for compounds **1a** (up), **1b** (middle) and **1c** (down).

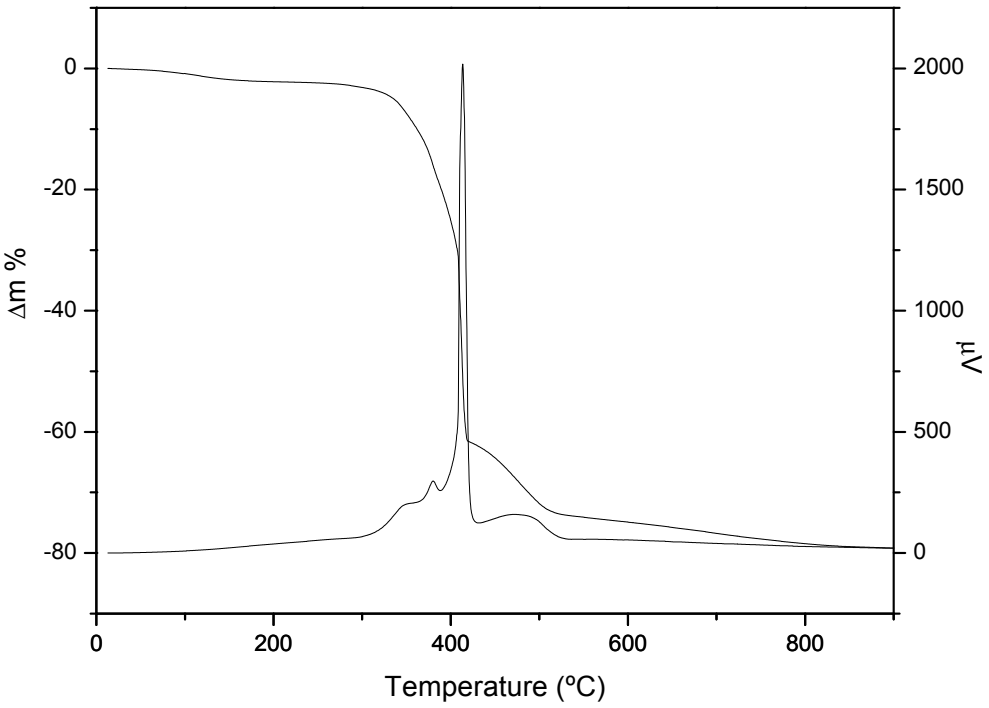


Figure S6. TGA/DTA curves for compound **1a**.

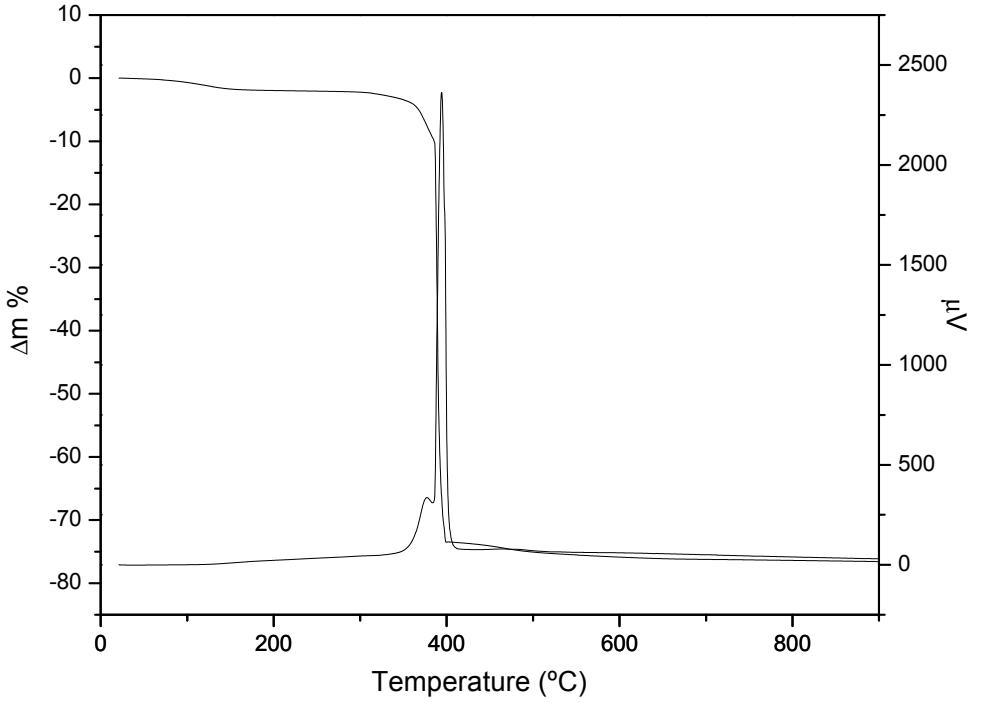


Figure S7. TGA/DTA curves for compound **1b**.

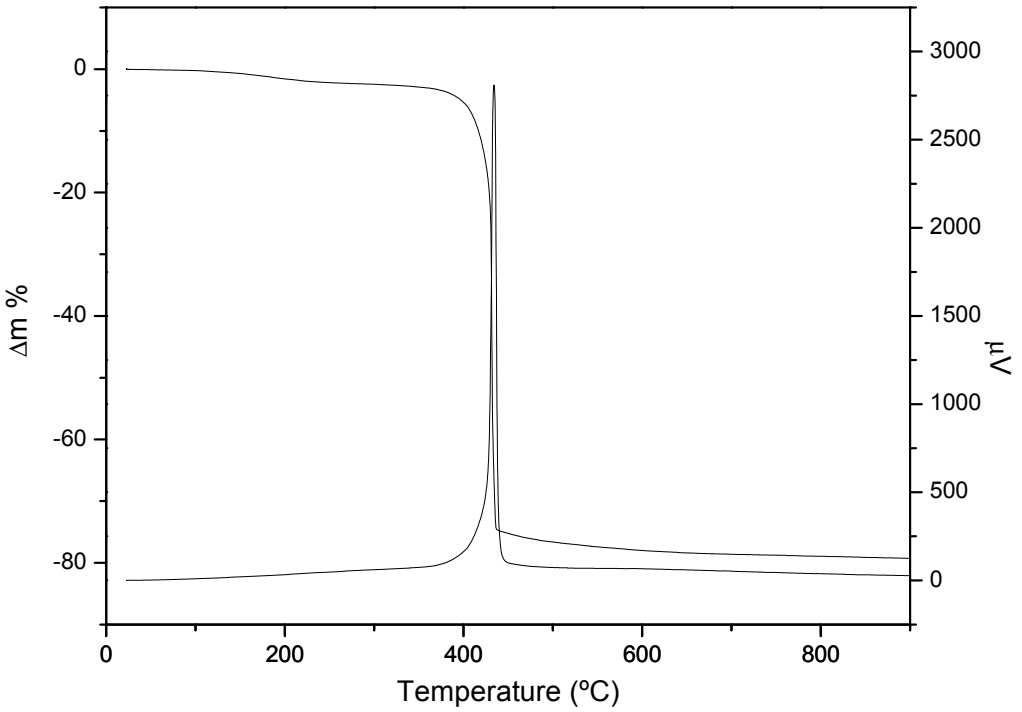
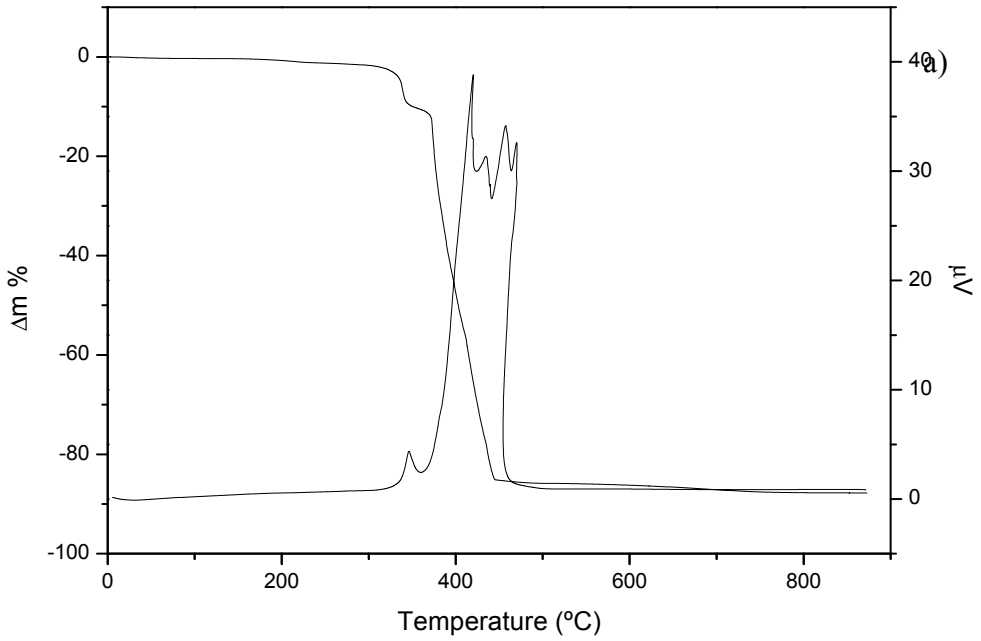


Figure S8. TGA/DTA curves for compound **1c**.



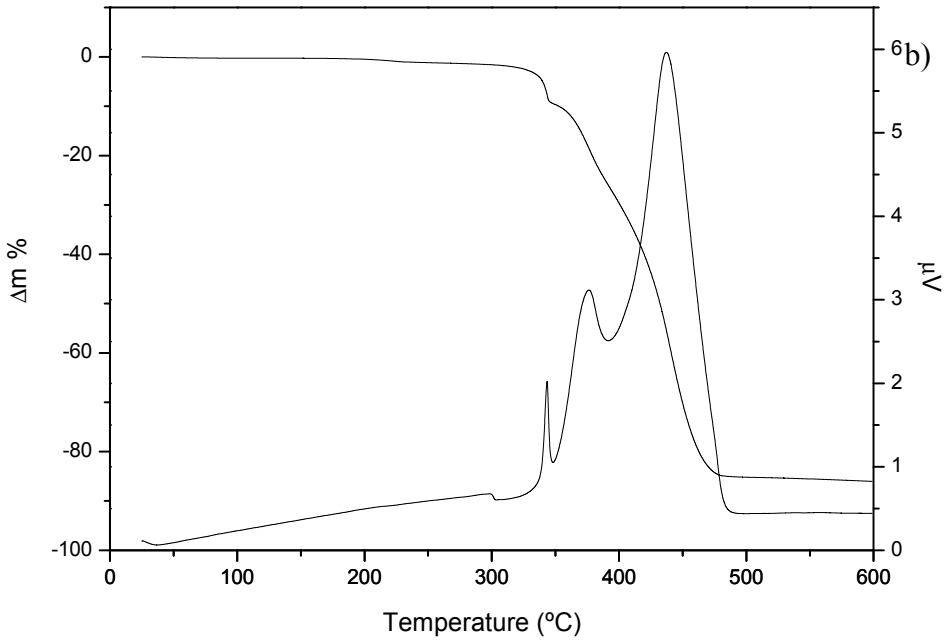


Figure S9. TGA/DTA curves for compound **2** in the ranges of (a) 25-900 ºC, heating rate 10ºC/min, and (b) 25-600 ºC, heating rate 5ºC/min.

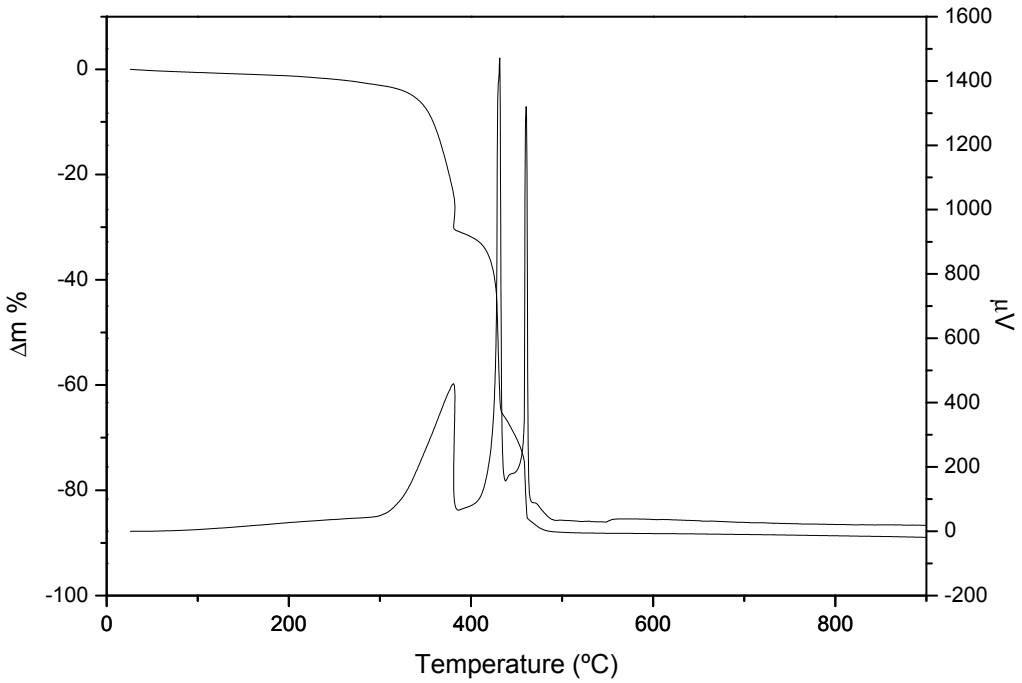


Figure S10. TGA/DTA curves for compound **3**.

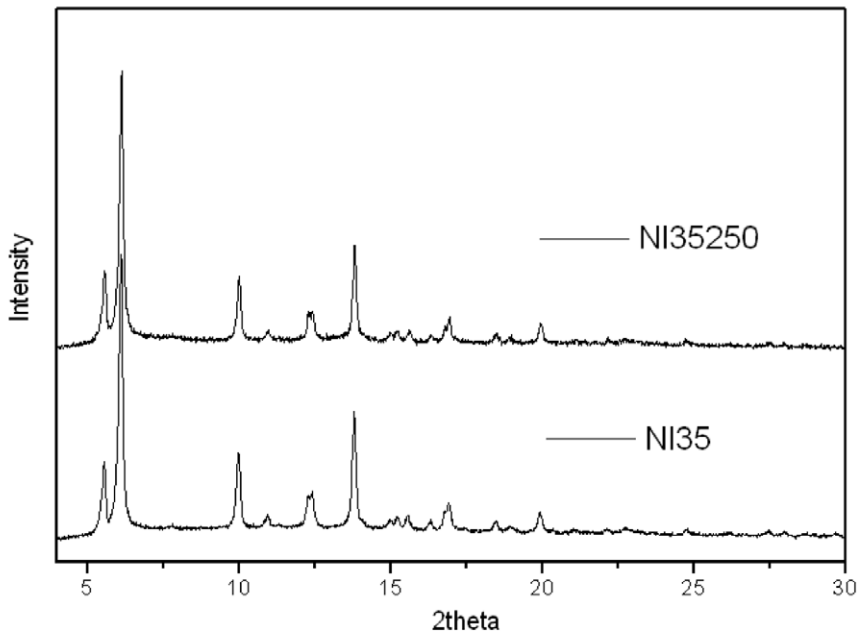


Figure S11. XRPD of structure type **1** as synthesized and after heating up to 250º C (for Ni compound)

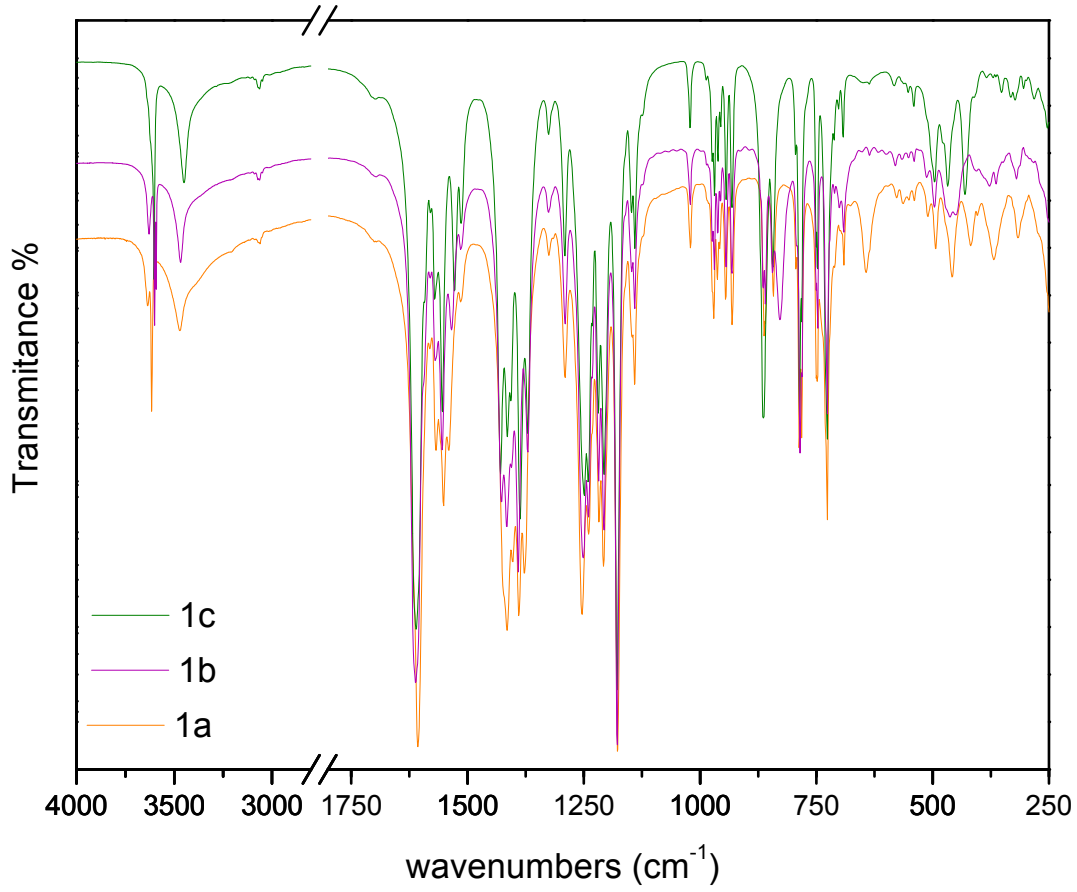


Figure S12. FTIR spectra of compounds **1a-c**.

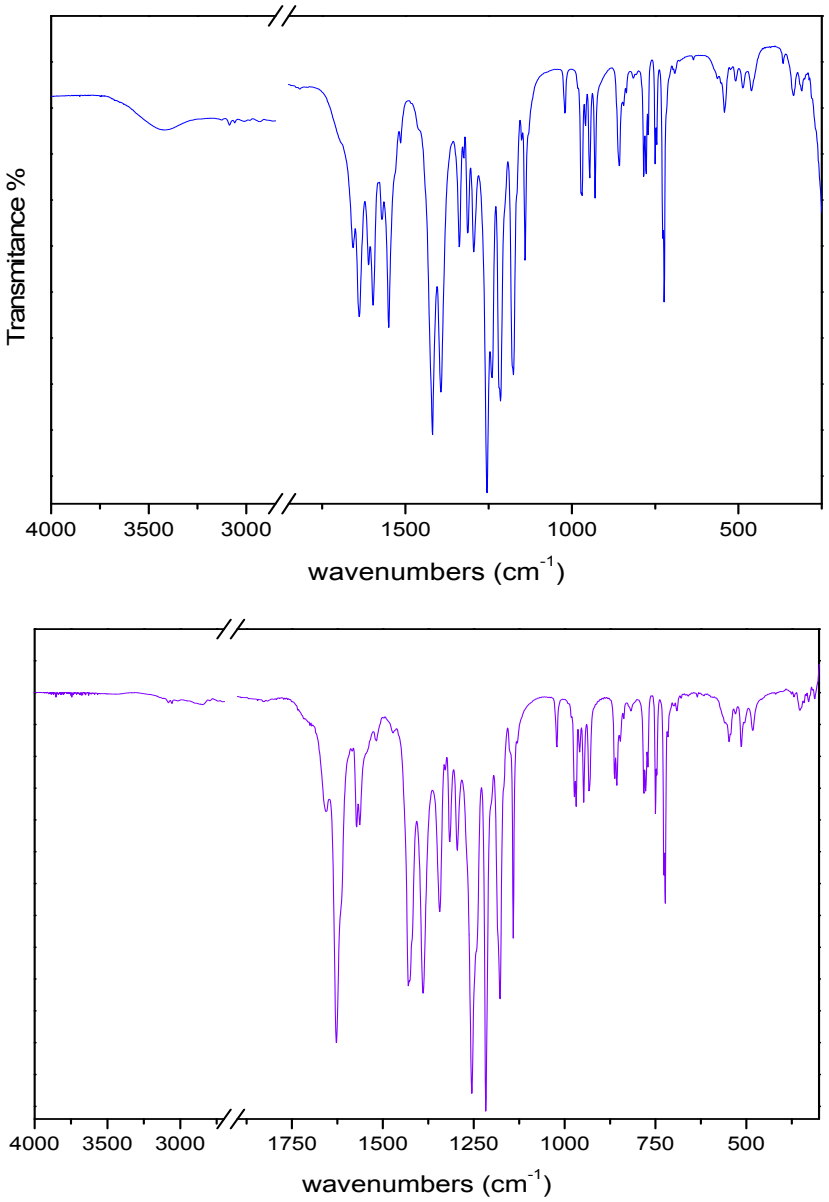


Figure S13. FTIR spectra of compounds **2** (up) and **3** (down).