CrystEngComm – Supporting Information for

A coloring tool for spiropyrans: Solid state metal-organic complexation versus salification

Vanessa Kristina Seiler,[a] Koen Robeyns,[a] Nikolay Tumanov,[b] Dominik Cinčić,[c] Johan Wouters,[b] Benoit Champagne,[b] and Tom Leyssens *[a]

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[a] *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, 1, Place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgium. E-mail: vanessa.seiler@uclouvain.be, koen.robeyns@uclouvain.be, tom.leyssens@uclouvain.be.*
[b] *Unité de Chimie Physique, Théorique et Structurale, UNamur, 61, rue de Bruxelles, B-5000 Namur, Belgium. E-Mail: nikolay.tumanov@unamur.be, johan.wouters@unamur.be, benoit.champagne@unamur.be.*
[c] *Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-1000 Zagreb, Croatia. E-mail: dominik@chem.pmf.hr.*

Experimental section
Synthesis

(Ia)
150.49 mg (0.543 mmol) of **SPH** and 76.04 mg (0.559 mmol) $ZnCl_2$ were separately dissolved in a total amount of 2 mL acetone in a round-bottom flask. After reflux heating for 10 min, an orange precipitate occurred. After cooling down, filtration of the precipitate with subsequent acetone and 1,4 dioxane washing yielded in 170.09 mg (76.1%) of the complex (Ia).

A 149.80 mg (0.540 mmol) **SPH** and 73.50 mg (0.540 mmol) $ZnCl_2$ Slurry in 2 mL acetone yielded orange precipitate after 1 day. The filtered and with acetone washed precipitate resulted in 193.56 mg (86.6%) of (Ia).

(Ib)
150.64 mg (0.543 mmol) of **SPH** and 123.20 mg (0.547 mmol) $ZnBr_2$ were separately dissolved in a total of 2 mL acetone in a round-bottom flask. After reflux heating for 10 min, an orange precipitate occurred. After cooling down the precipitate was filtered and washed with acetone an 1,4-dioxane yielding in 159.7 mg (58.7%) of the complex (Ib).

(IIa)
507.91 mg (1.55 mmol) **SPBenz** and 209.91 mg (1.54 mmol) $ZnCl_2$ were partially dissolved in 10 mL acetone. Reflux heating for 1h resulted in a red precipitate. After cooling down the precipitate was filtered and washed with acetone and 1,4-dioxane. 576.08 mg (76.6%) of the acetone solvate (IIa) was obtained.

(IIb)
500.07 mg (1.53 mmol) **SPBenz** and 346.50 mg (1.54 mmol) $ZnBr_2$ were partially dissolved in 10 mL acetone. Reflux heating for 1h resulted in a red precipitate. After cooling down the precipitate was filtered and washed with acetone and 1,4-dioxane. 490.70 mg (55.2%) of the acetone solvate (IIb) was obtained.

(IVa)
149.83 mg (0.465 mmol) **SPNO2** mixed with 65.65 mg (0.482 mmol) $ZnCl_2$ in 3 mL acetone were reflux heated for 10 min until orange precipitate occurred. The solution was left for cooling down. Washing of the precipitate with acetone and 1,4-dioxane yielded in 137.66 mg (63.9%) of the product (IVa).

(IVf)
150.41 mg (0.4657 mmol) **SPNO2** mixed with 160.55 mg (0.473 mmol) $ZnBr_2$ in 3 mL acetone were reflux heated for 10 min until orange precipitate occurred. The solution was left for cooling down. Washing of the precipitate with acetone and 1,4-dioxane yielded in 109.16 mg (42.5%) of the product (IVf).

(IVj)
A solution of 110.71 mg (0.465 mmol) $CoCl_2 \cdot 6H_2O$ in acetone was added to acetone solution of 150.46 mg (0.467 mmol) **SPNO2** and reflux heated until red/brown precipitate occurred (3 mL of acetone in total). Filtration of the precipitate and subsequent washing with acetone and 1,4-dioxane yielded in 183.38 mg (70.3%) of (IVj).

(IVk)
A slurry in 0.75 mL acetone with 249.99 mg (0.775 mmol) **SPNO2** and 92.20 mg (0.388 mmol) $CoCl_2 \cdot 6H_2O$ were left for stirring for 2 days and resulted in red-brown precipitate. Filtration and washing with acetone and 1,4-dioxane yielded in 104.04 mg (66.1%) of the product (IVk).

(IVm)
A slurry in 1.5 mL acetone with 150.50 mg (0.777 mmol) **SPNO2** and 186.40 mg (0.783 mmol) $CoCl_2 \cdot 6H_2O$ were left for stirring for 2 days and resulted in green precipitate. Filtration and washing with acetone and 1,4-dioxane yielded in 234.57 mg (69.9%) of the product (IVm).

Crystal packings

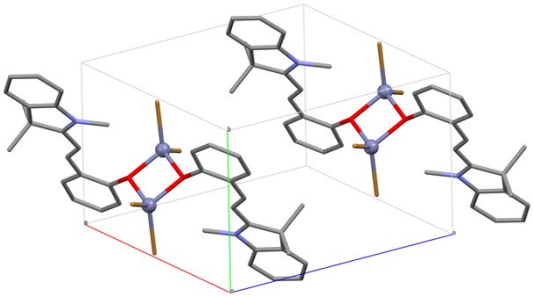

Figure S1: A partial packing diagram of **MCH** coordinated to $ZnBr_2$ (Ia) showing isolated dimers.

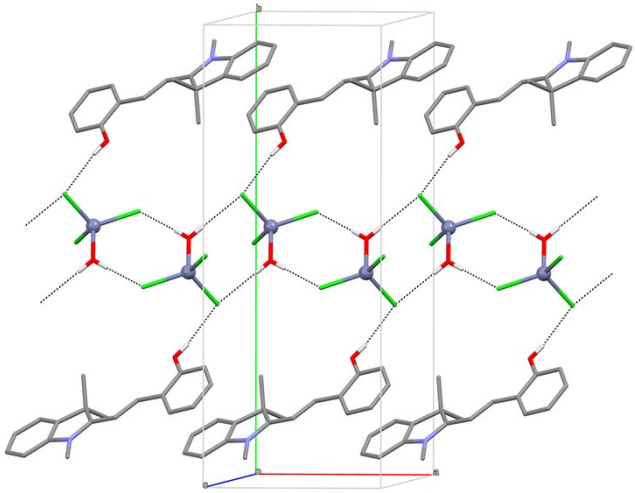

Figure S2: A partial packing diagram of **MCH** with $ZnCl_2$ forming the hydrate (Ic) with chains running along the *a* axis.

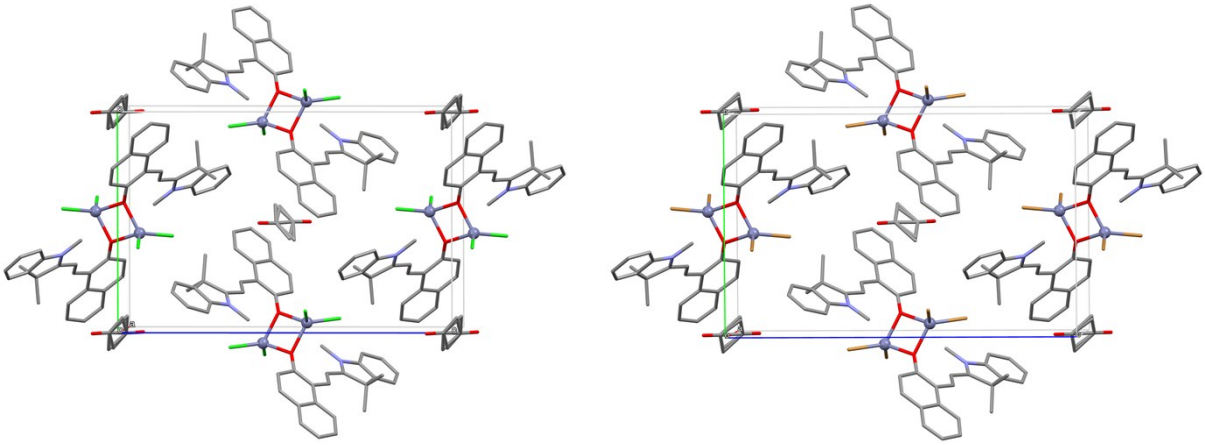

Figure S3: Partial packing diagrams of **MCBenz** coordinated to $ZnCl_2$ (IIa; left) and $ZnBr_2$ (IIb; right). Both packings show disordered acetone molecules over two positions.

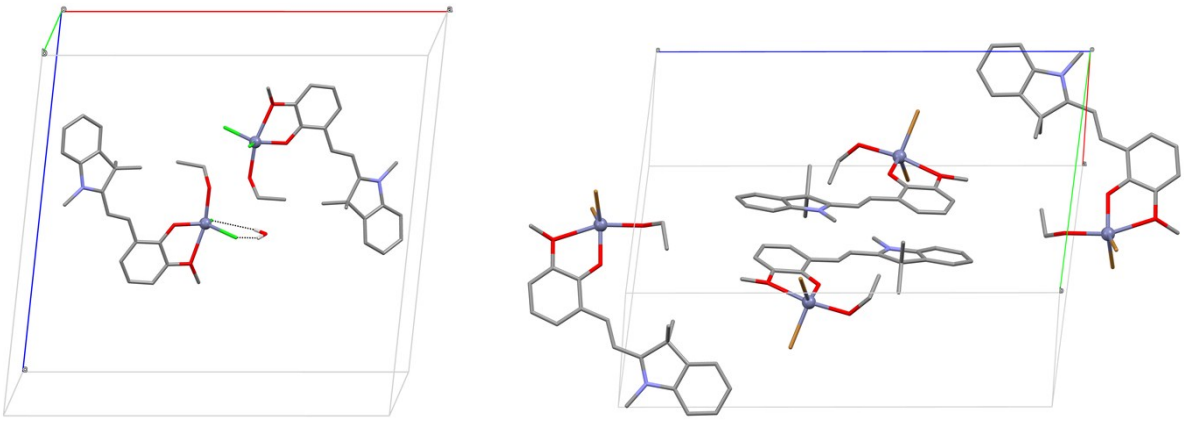

Figure S4: A partial packing diagram of **MCOMe** coordinated to $ZnCl_2$ (IIIa) and $ZnBr_2$ (IIIb) with ethanol and H_2O in the case of (IIIa) in the crystal structure. Hydrogen bonds are indicated as dashed lines. Only the main occupied site is shown.

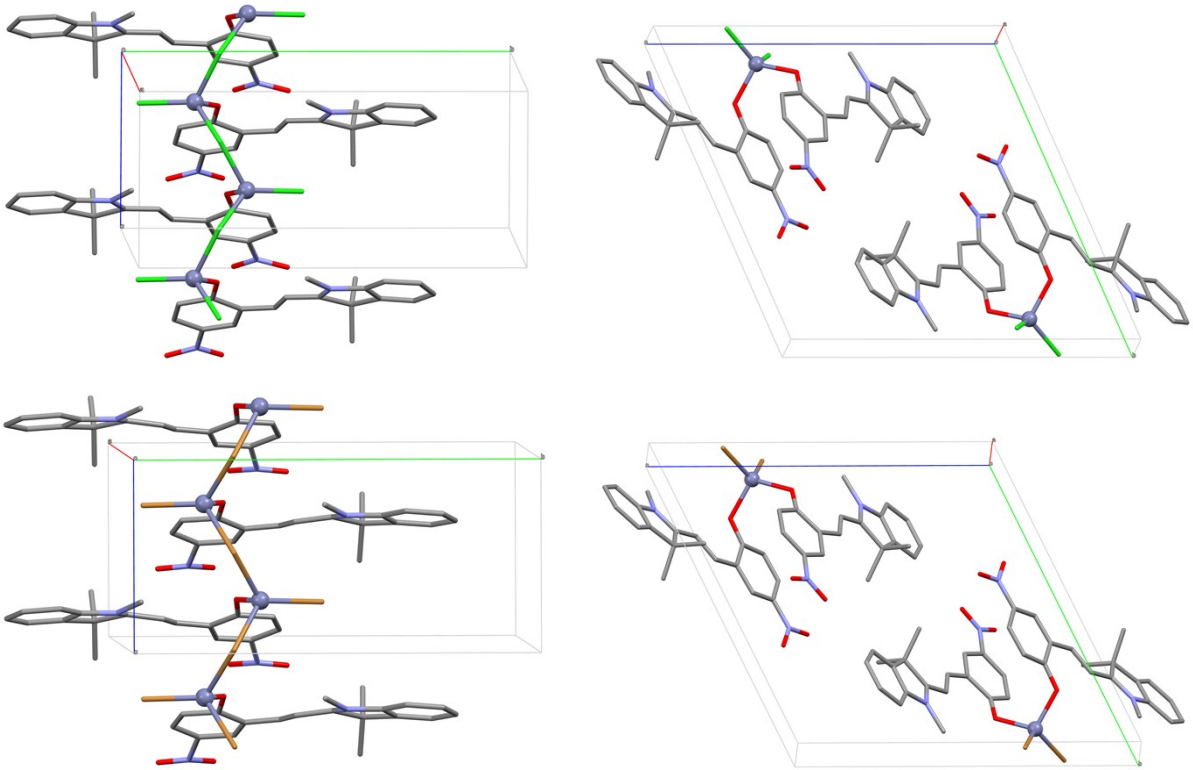

Figure S5: Partial packing diagrams of **MCNO2** coordinated to $ZnCl_2$ ((IVa); upper left) in a 1:1 ratio and in a 2:1 ratio ((IVb); upper right). Analogous for the isomorphous forms with $ZnBr_2$ ((IVf) and (IVg); below).

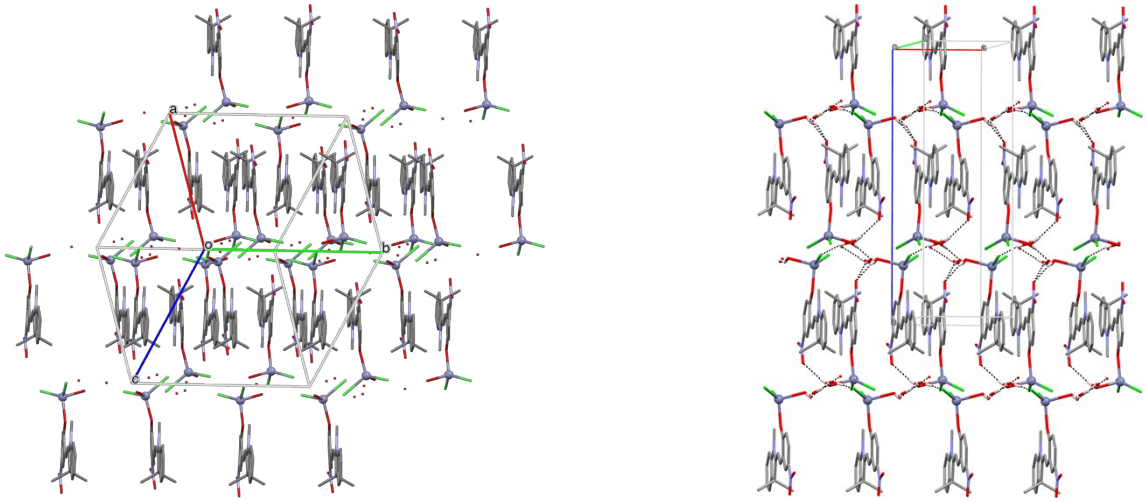

Figure S6: Two hydrate structures of **MCNO2** coordinated to $ZnCl_2$ in different ratios ((IVd) left; (IVe) right).

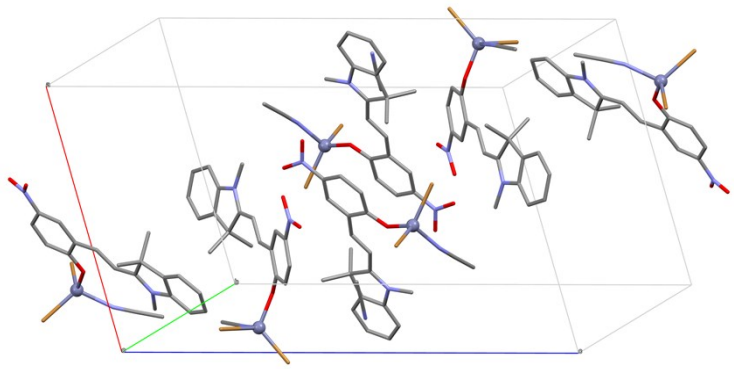

Figure S7: A partial packing diagram of **MCNO2** coordinated to $ZnBr_2$ with two acetonitrile molecules in the asymmetric unit (IVh); one coordinated to the metal center and one freely in the packing (not displayed).

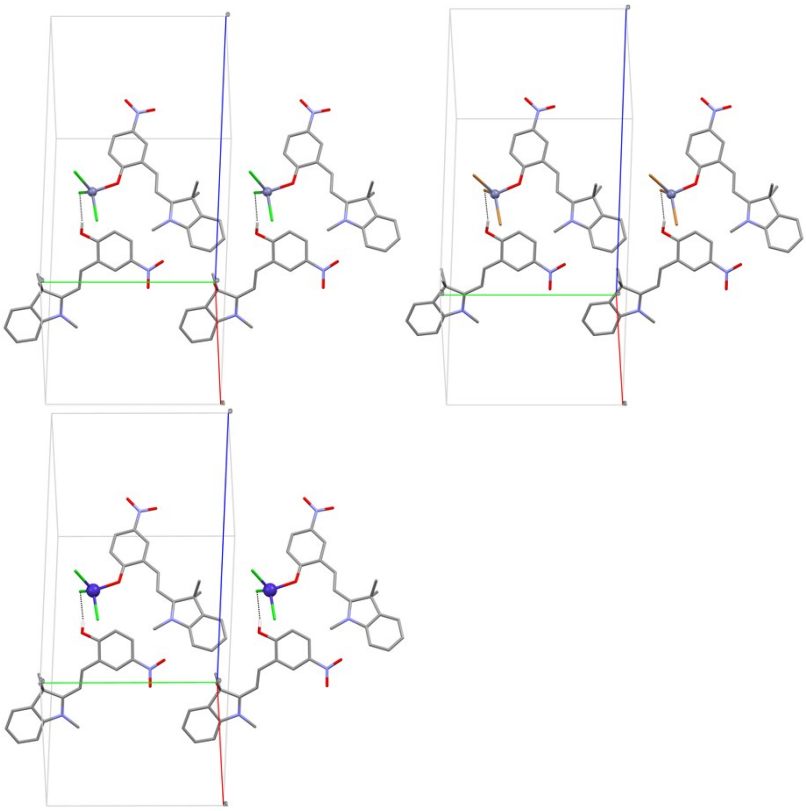

Figure S8: Partial packing diagrams of **MCNO2** with $ZnCl_2$ ((IVc); left), $ZnBr_2$ ((IVi); middle) and $CoCl_2$ ((IVk); right) showing their isomorphous structures with one protonated **MCNO2** molecule and one molecule coordinated to the metal center. Hydrogens bonds are indicated as dashed lines.

X-ray powder diffraction

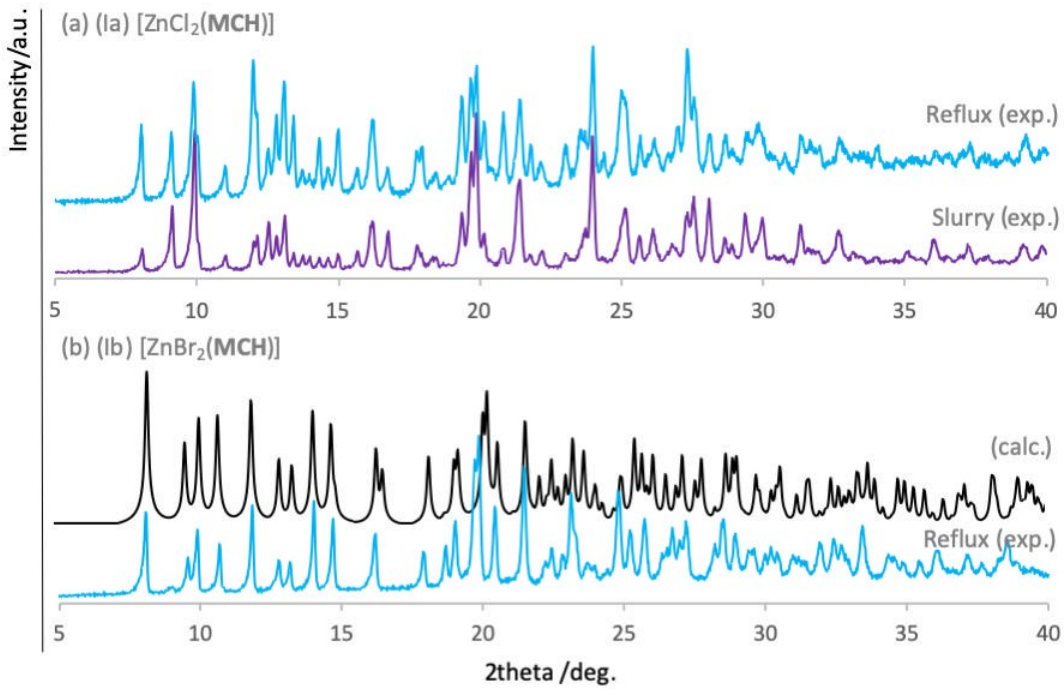

Figure S9: (a) X-ray powder diffraction patterns of (Ia) obtained by reflux (light blue curve) and by slurry (purple curve) in acetone. (b) The calculated powder X-Ray pattern of (Ib) (black curve) compared to the bulk material obtained by reflux (blue curve).

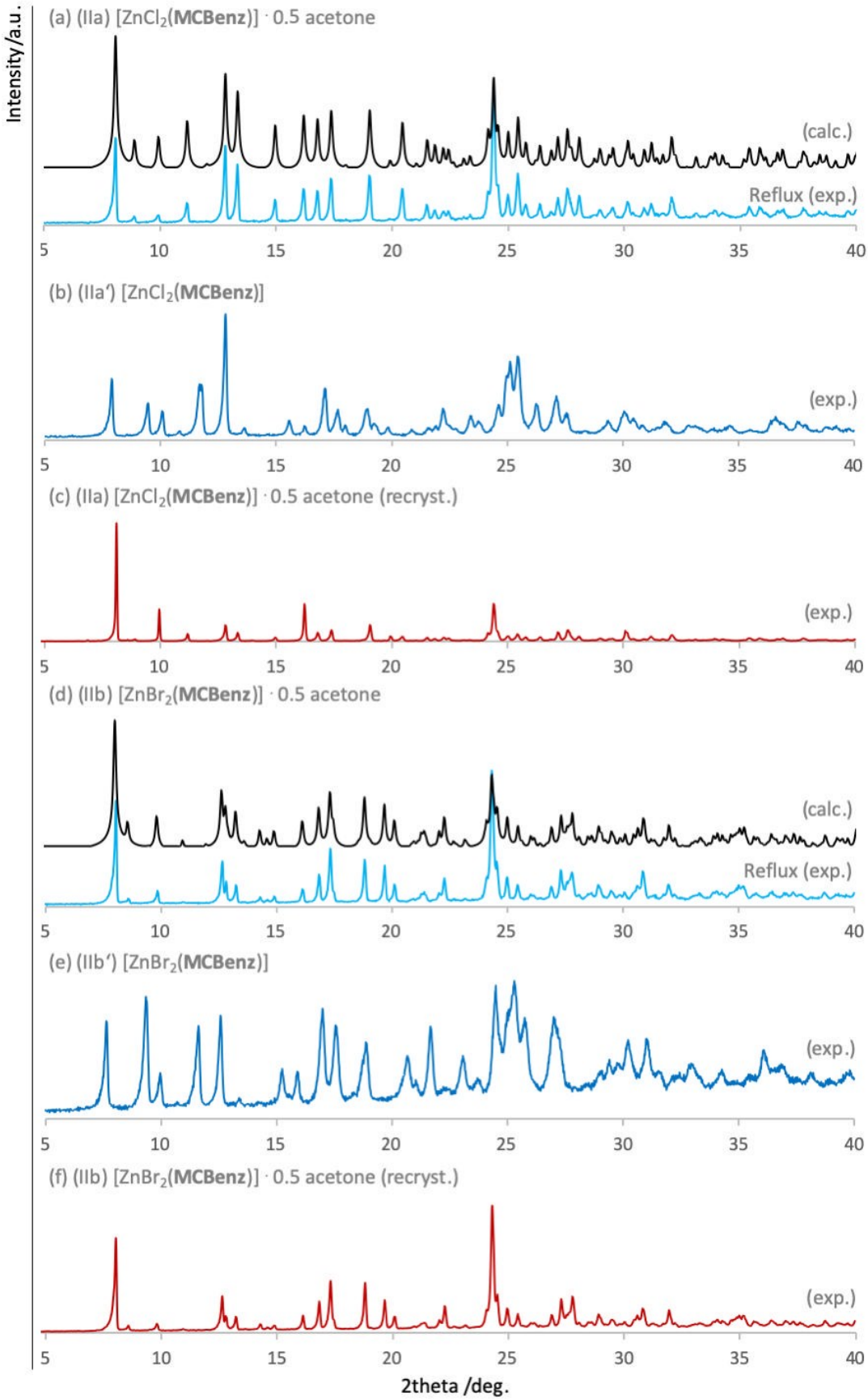

Figure S10: X-ray powder diffraction patterns of (IIa) and (IIb) comparing the calculated powder X-Ray patterns (black curves) with the from reflux obtained bulk material (light blue curves). In comparison the resulting ansolvate (IIa') and (IIb') after evaporation of acetone (dark blue curves) and the recrystallized solvates in an atmosphere of acetone (red curves).

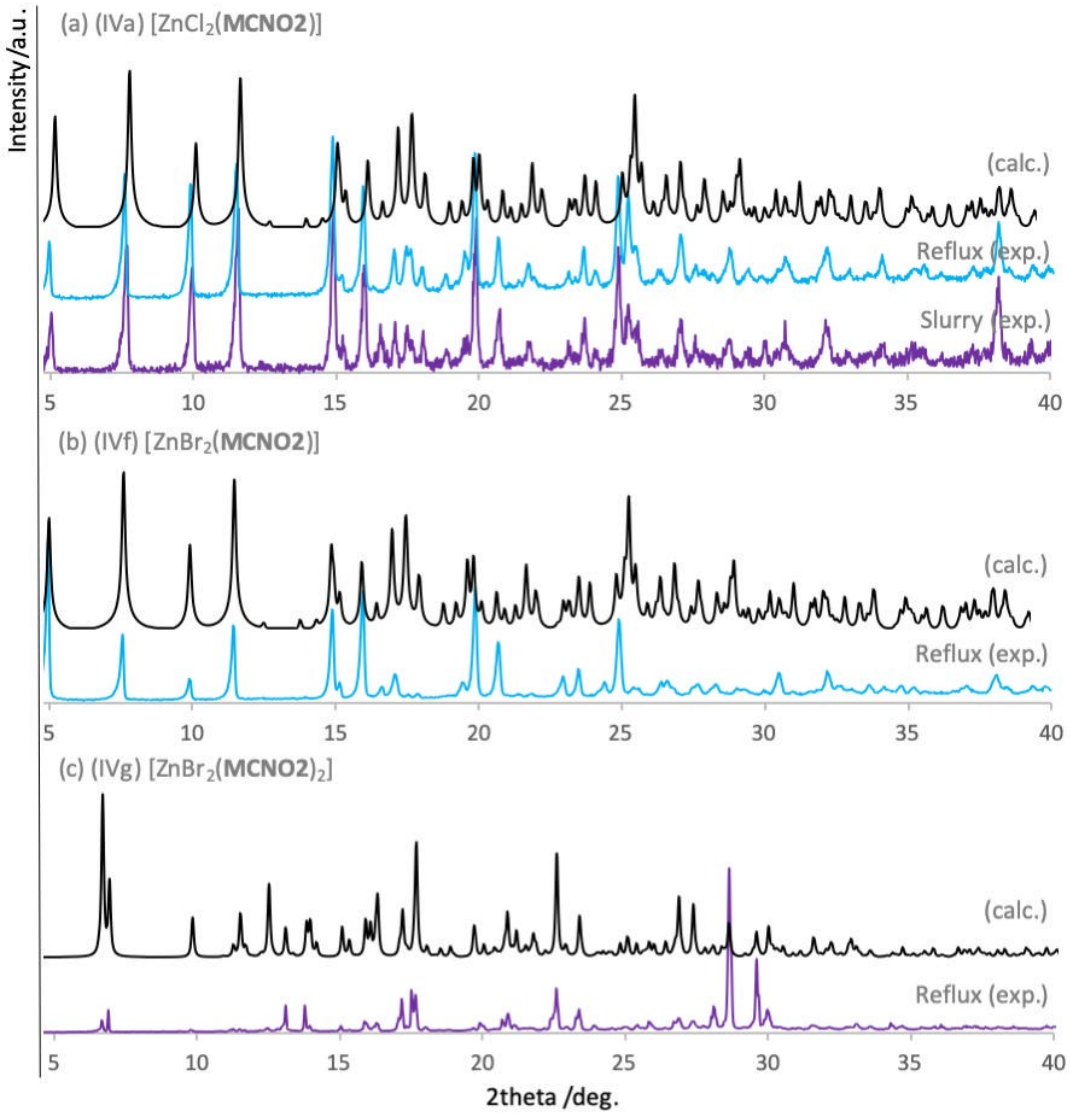

Figure S11: (a) X-ray powder diffraction patterns of (IVa) in comparison of the from single crystal calculated pattern (black curve) with the bulk material from reflux (light blue curve) and slurry (purple curve). (b) Comparison of the X-ray powder diffraction patterns of the from single calculated powder patterns (black curve) and the bulk material obtained from reflux (light blue curve). (c) Calculated powder x-ray patterns of (IVg) (black curve) in comparison with the bulk material obtained after evaporation of the filtrate from the reflux reaction of (IVf) (purple curve).

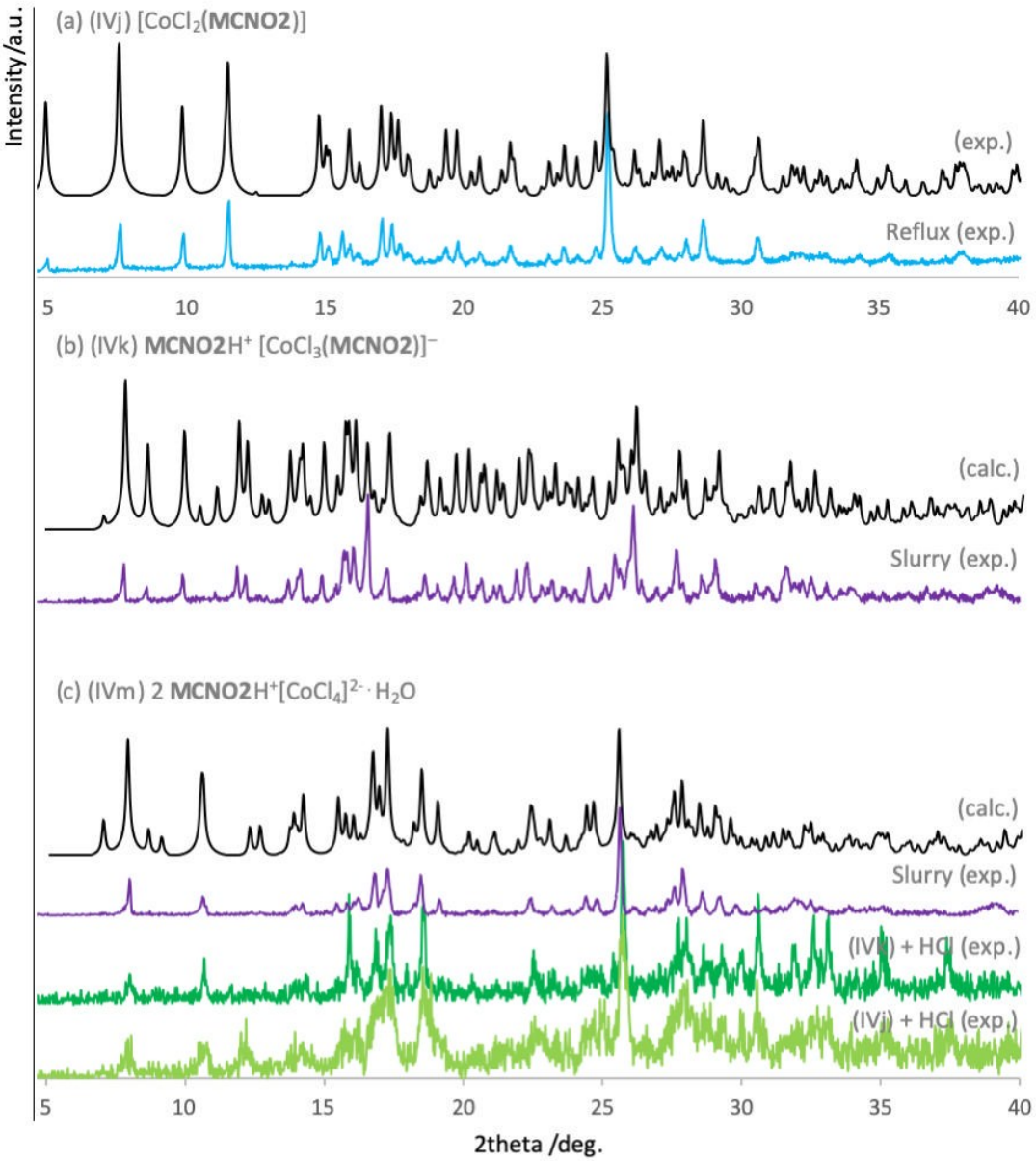

Figure S12: (a) X-ray powder diffraction patterns of the from reflux obtained product (light blue curve) compared to the from single crystal calculated x-ray pattern of (IVj) (black curve). (b) Calculated powder x-ray patterns of (IVk) (black curve) compared to the bulk material obtained by a 1:1 Slurry of **SPNO2** with $CoCl_2 \cdot 6H_2O$ (purple curve). (c) Calculated powder x-ray patterns of (IVm) (black curve) compared to the bulk material obtained by a 2:1 Slurry of **SPNO2** with $CoCl_2 \cdot 6H_2O$ (purple curve). Obtained product of (IVk) and (IVj) after exposure to an atmosphere of HCl (green curves).

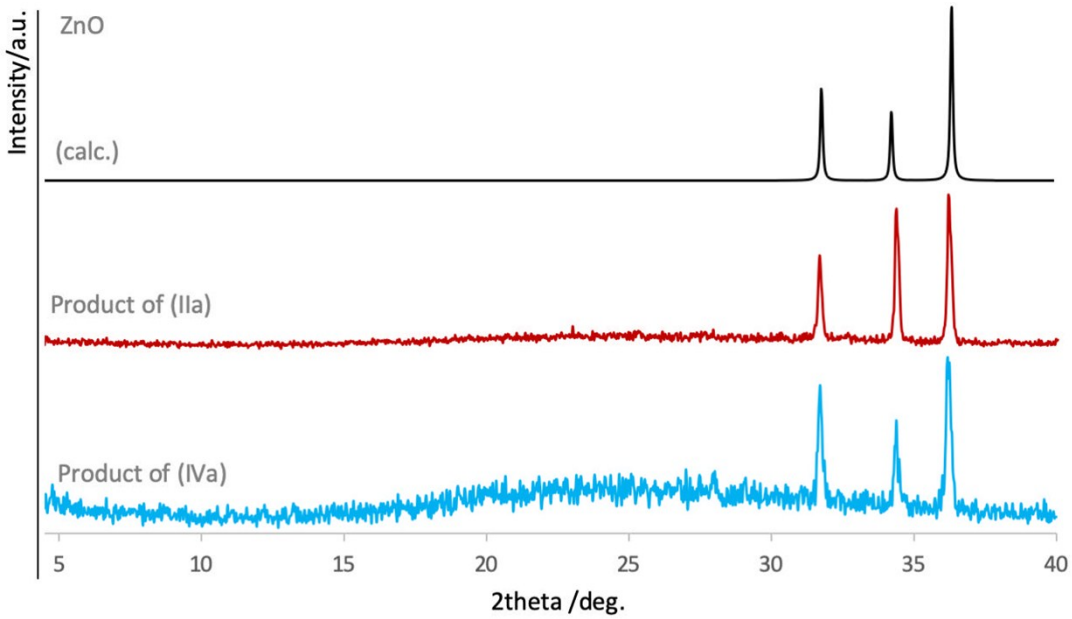

Figure S13: X-ray powder diffraction patterns of the obtained ZnO products obtained after burning (IIa), and (IVi) under oxygen flow in comparison of the simulated powder patterns of ZnO.

NMR

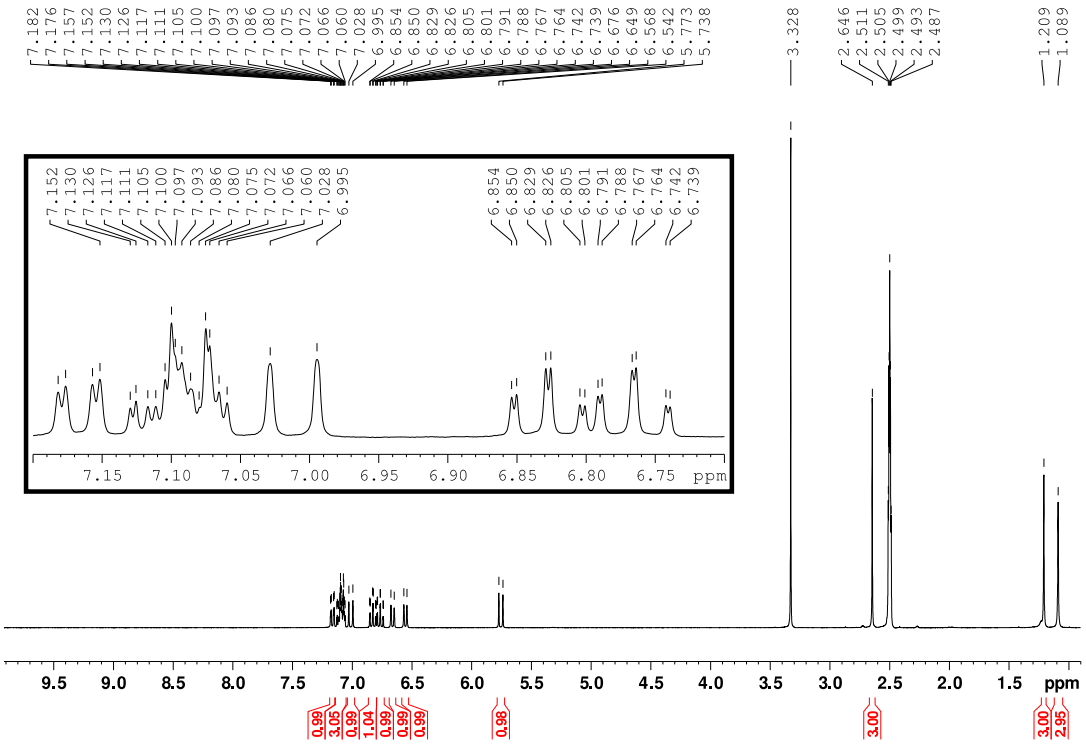

Figure S14: ^{1}H-NMR of **SPH** in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present.

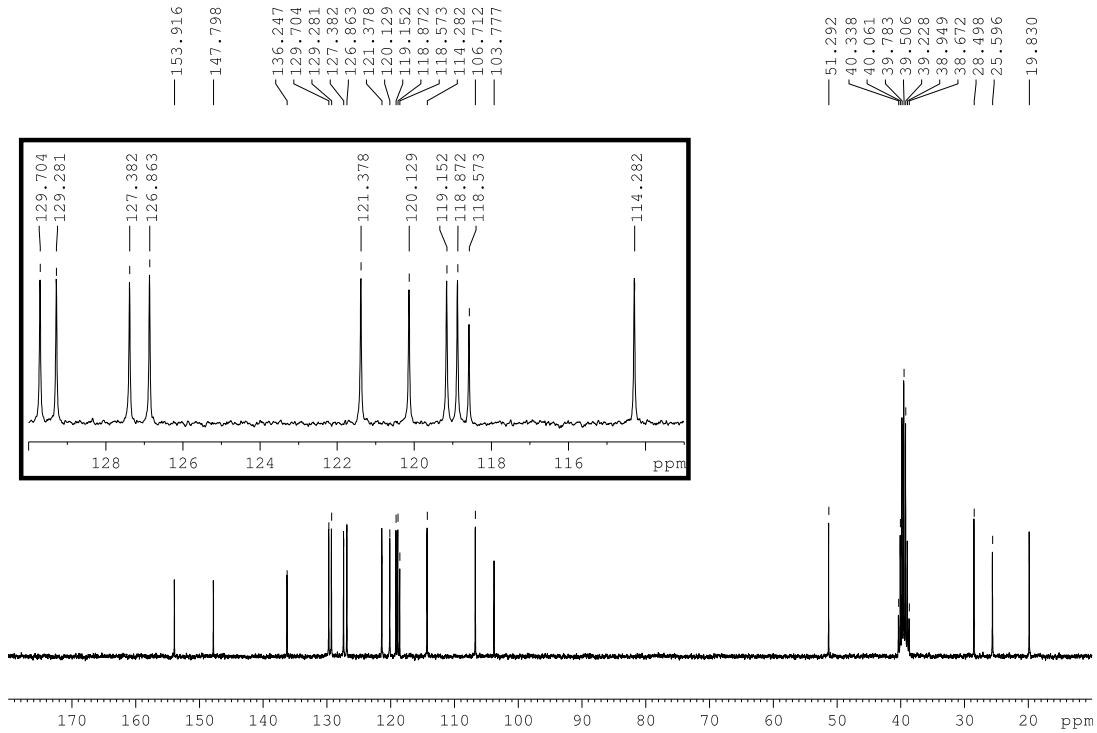

Figure S15: ^{13}C-NMR of **SPH** in DMSO-d_6 (δ (ppm): 39.51).

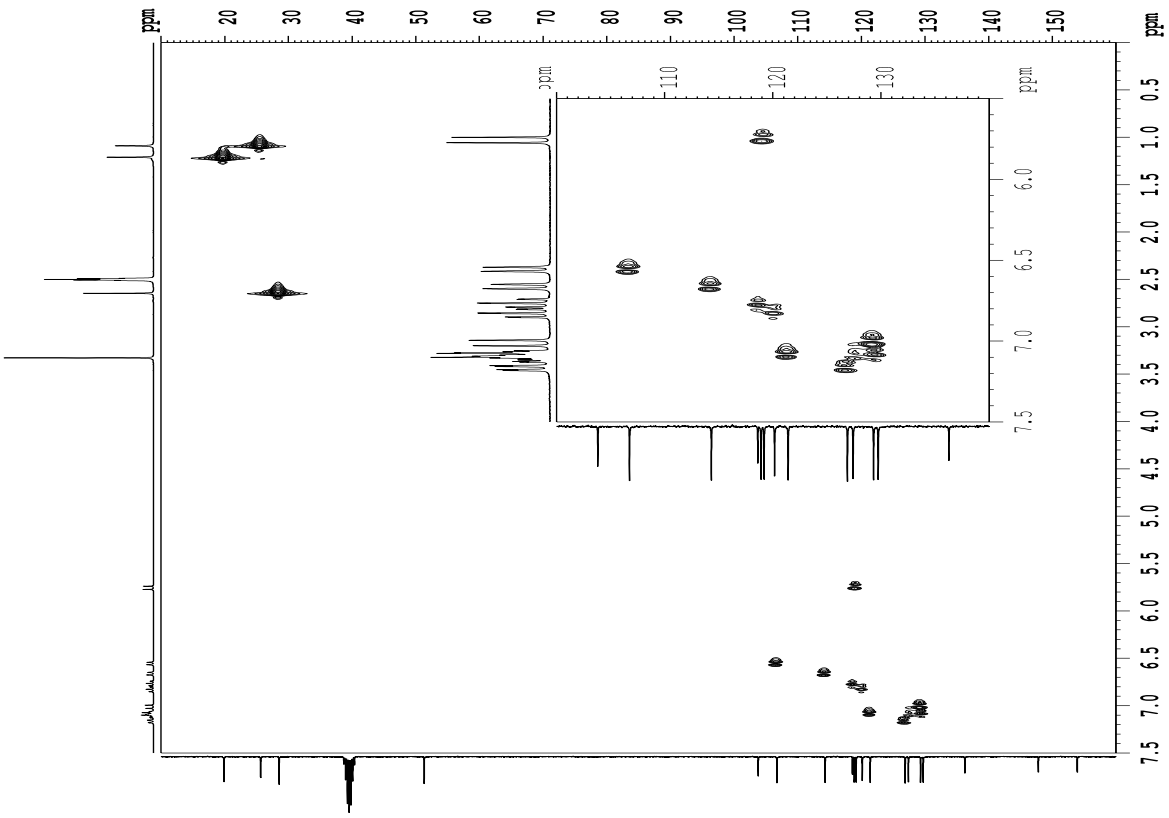

Figure S16: HMQC-NMR of **SPH** in DMSO-d_6 (δ (ppm): 2.50/39.51).

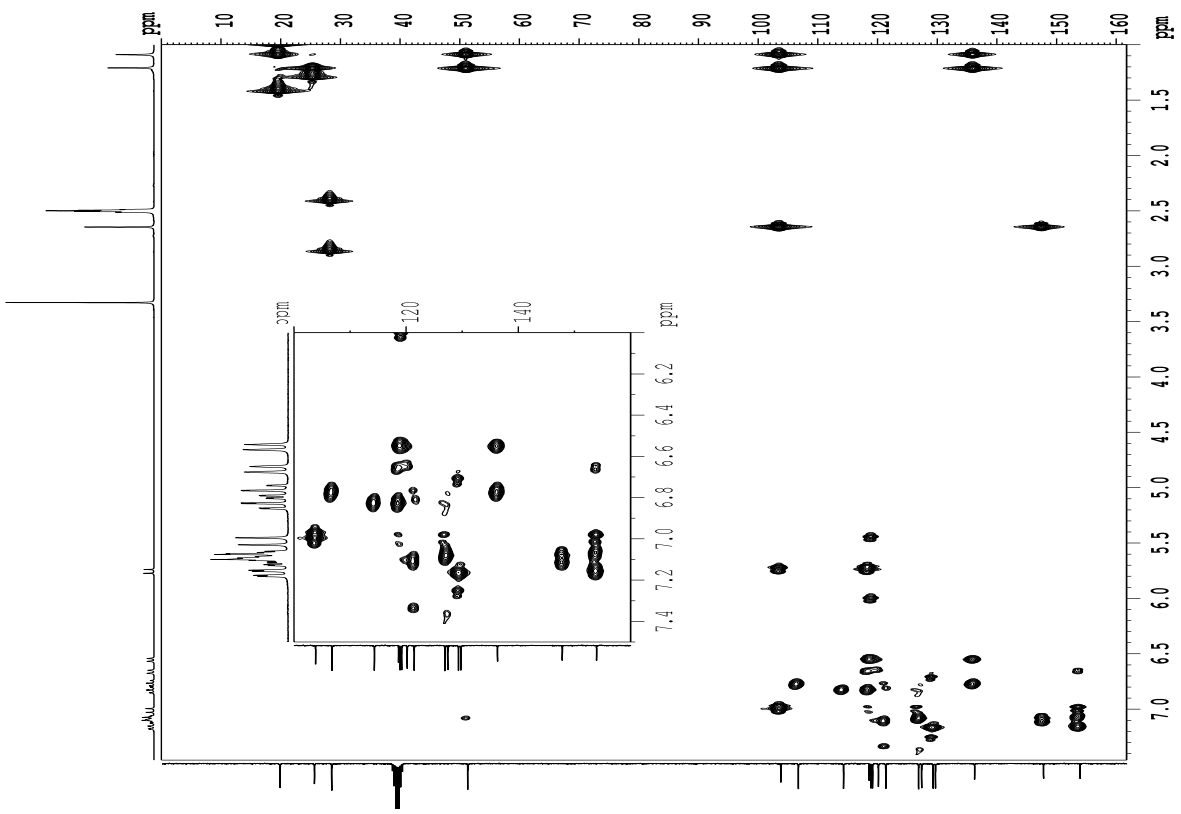

Figure S17: HMBC-NMR of **SPH** in DMSO-d_6 (δ (ppm): 2.50/39.51).

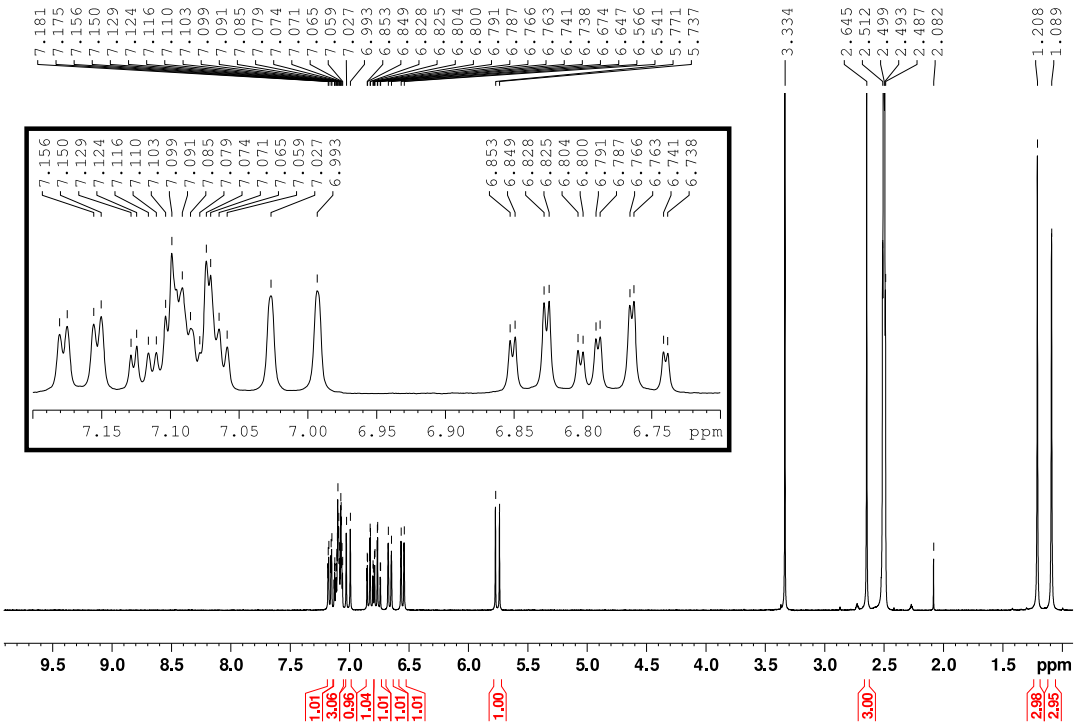

Figure S18: ^{1}H-NMR of (Ia) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) acetone (δ (ppm): 2.08) present.

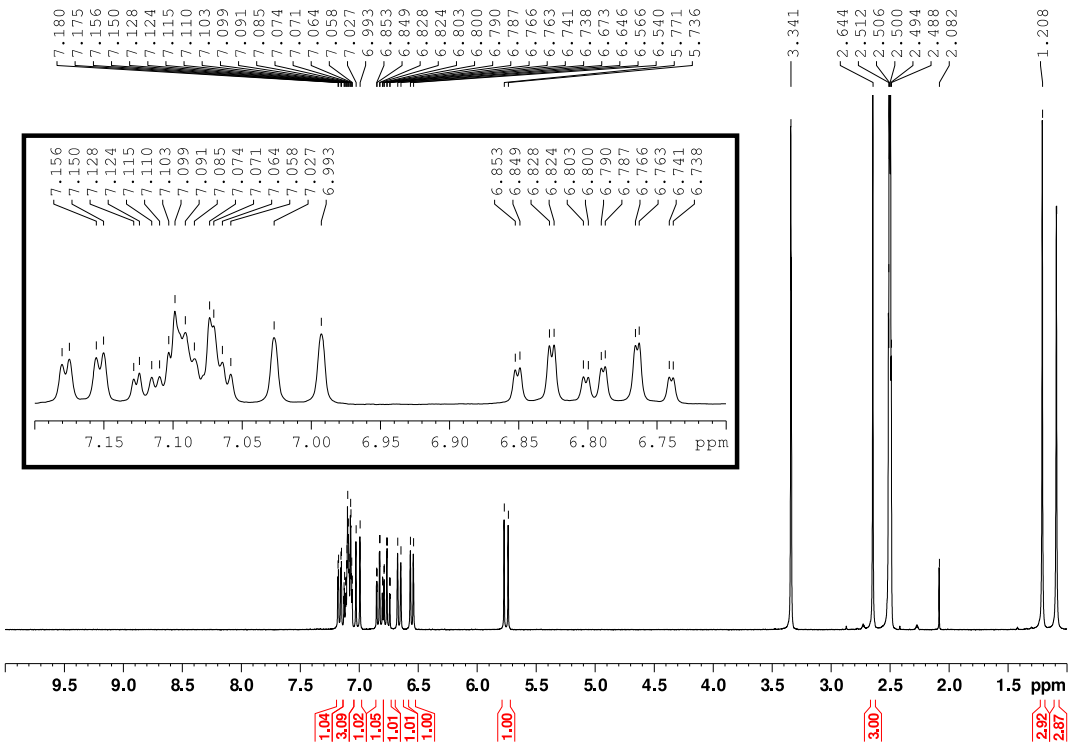

Figure S19: ^{1}H-NMR of (Ib) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.34) and acetone (δ (ppm): 2.08) present.

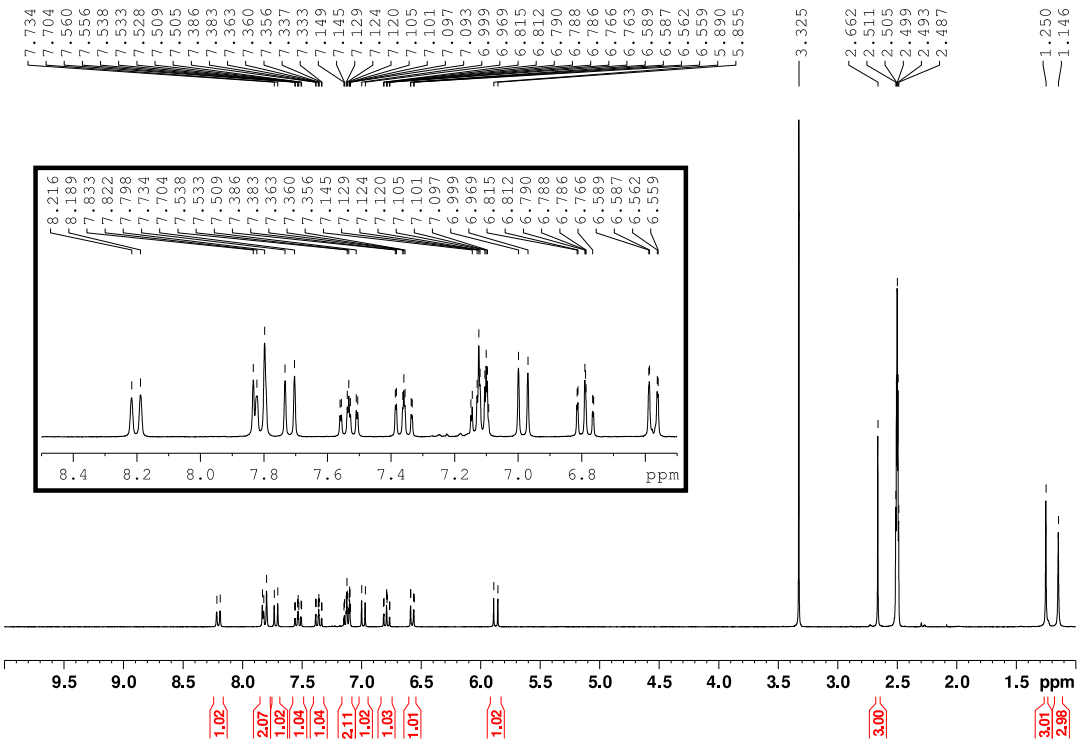

Figure S20: ^{1}H-NMR of **SPBenz** in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present.

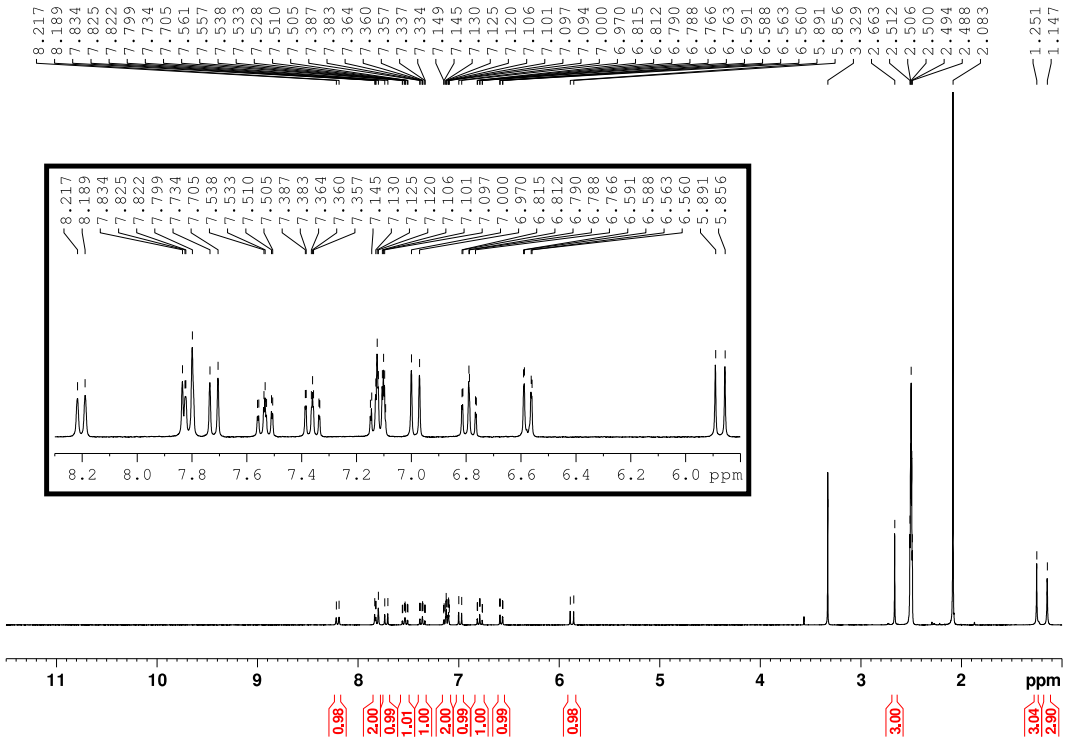

Figure S21: ^{1}H-NMR of (IIa) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present. The acetone signal (δ (ppm): 2.08) derives from the solvate.

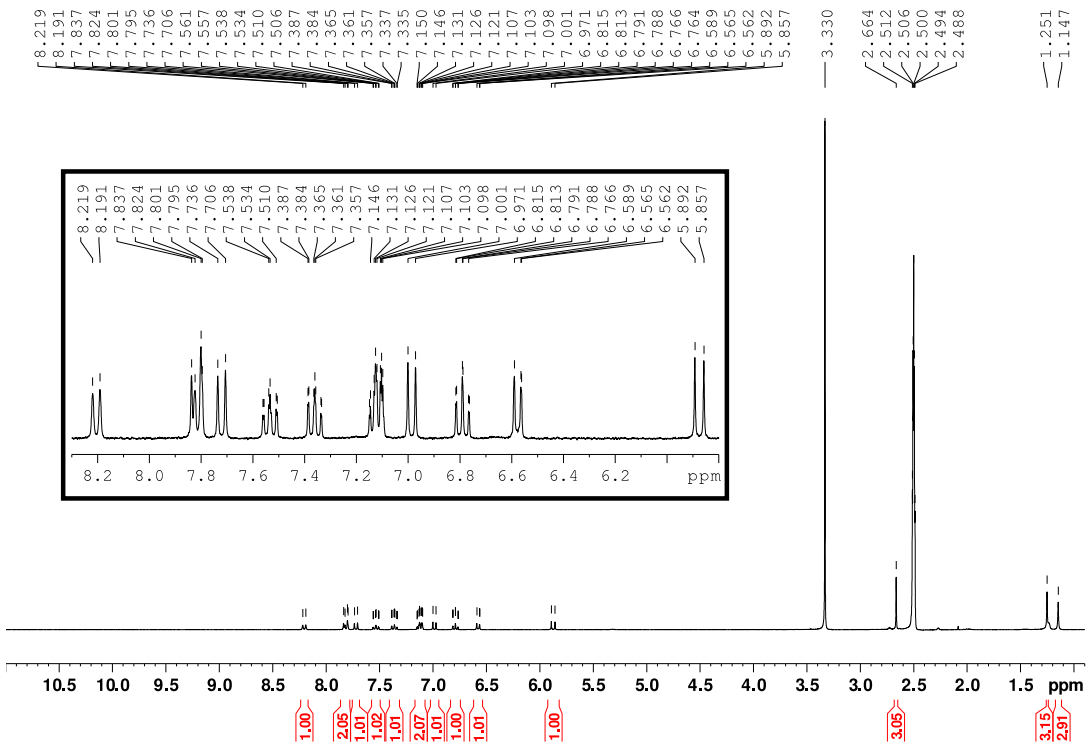

Figure S22: ^{1}H-NMR of the ansolvate (IIa') in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present.

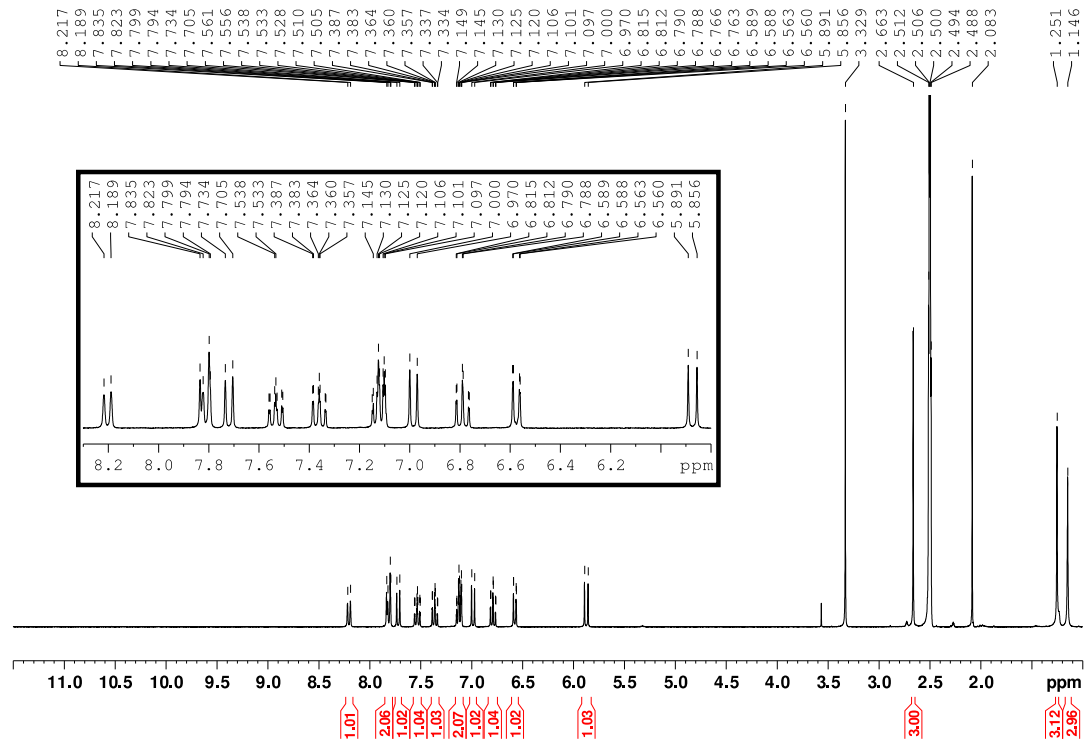

Figure S23: ^{1}H-NMR of (IIb) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present. The acetone signal (δ (ppm): 2.08) derives from the solvate.

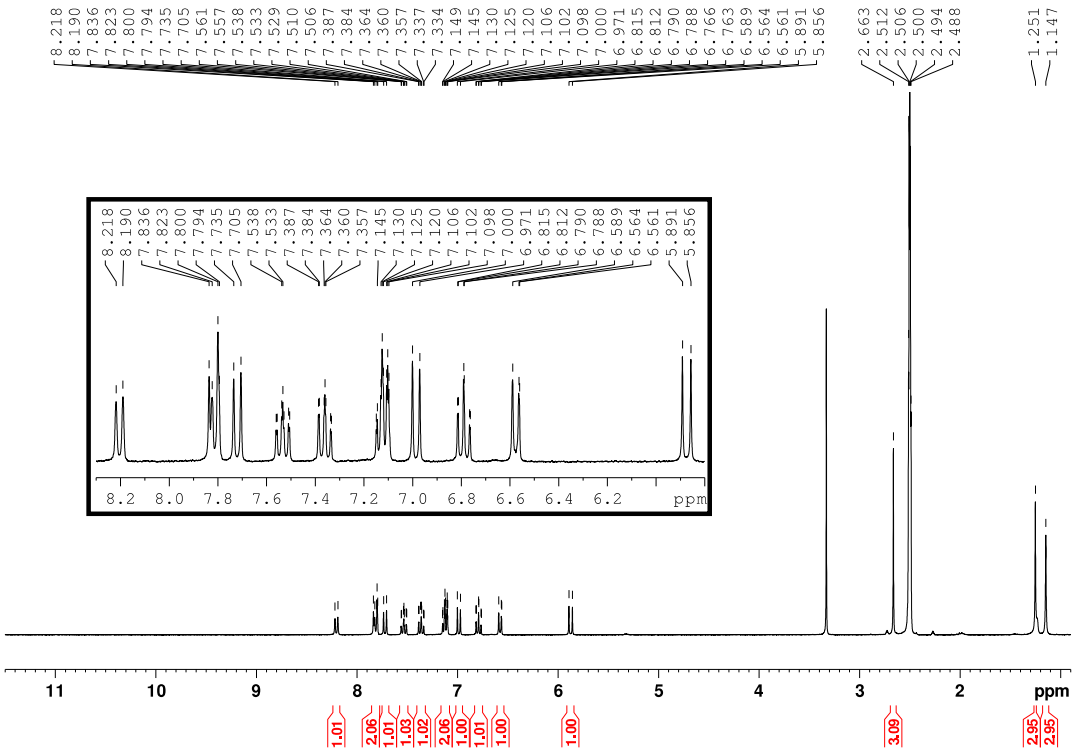

Figure S24: ^{1}H-NMR of the ansolvate (IIb') in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present.

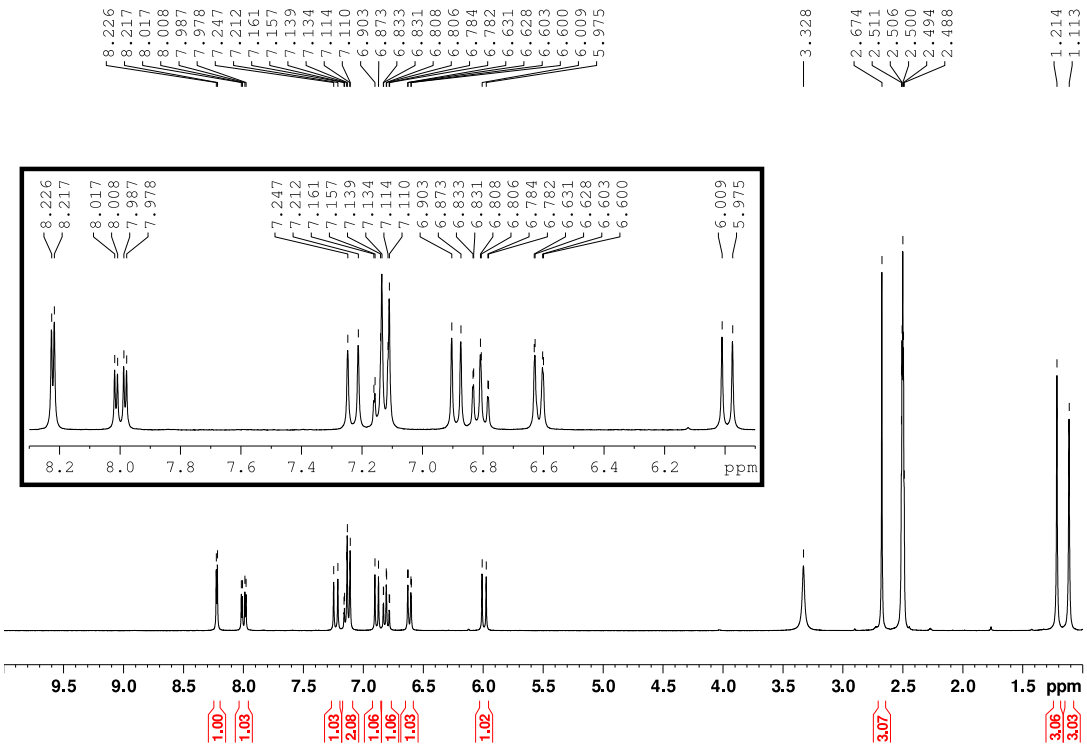

Figure S25: ^{1}H-NMR of **SPNO2** in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) present.

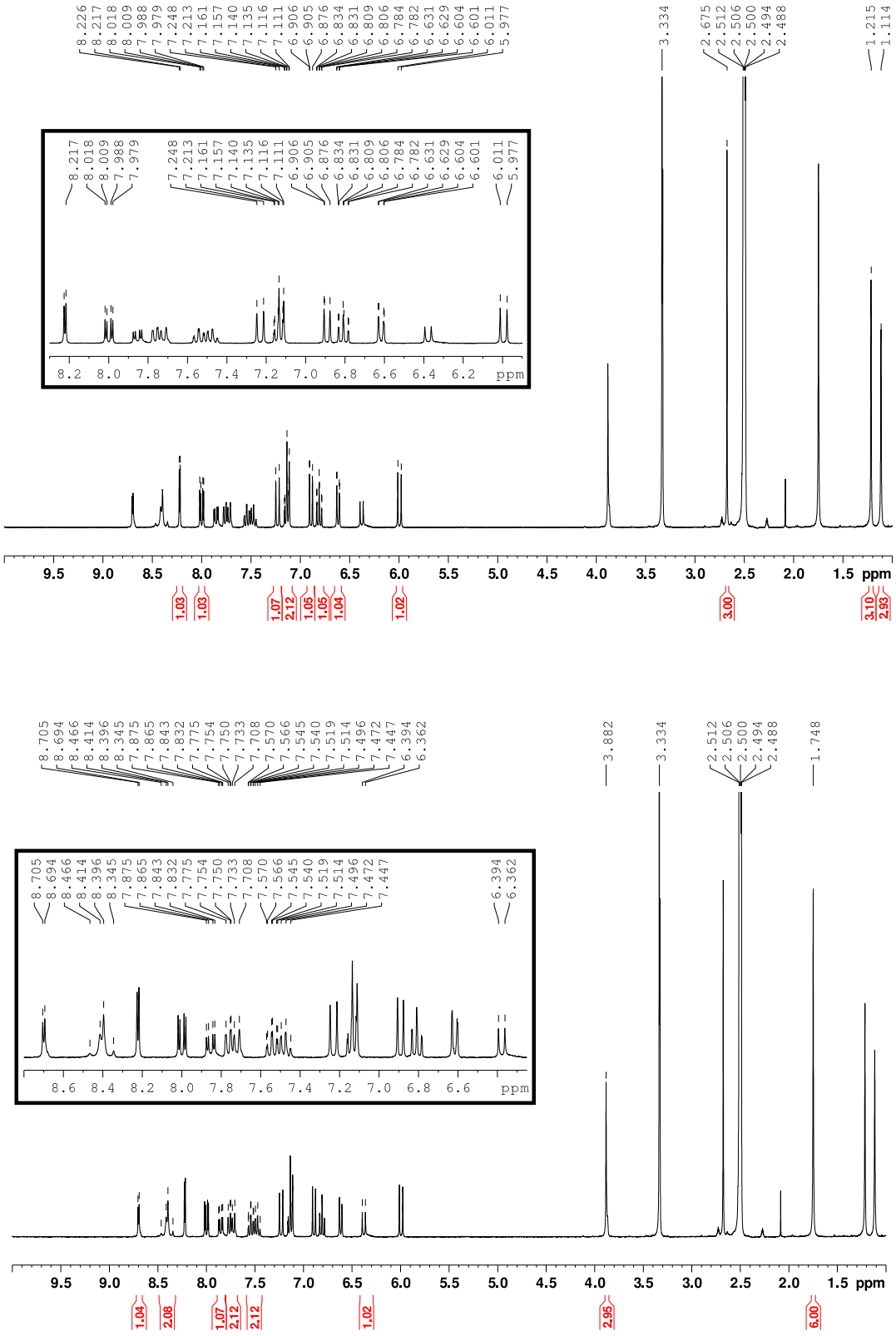

Figure S26: ^{1}H-NMR of (IVa) in DMSO-d_6 (δ (ppm): 2.50) showing the *SP* (highlighted in the spectra below) and *MC* form (highlighted in the upper spectra) of **SPNO2**/**MCNO2**. Traces of H_2O (δ (ppm): 3.33) and acetone (δ (ppm): 2.08) present.

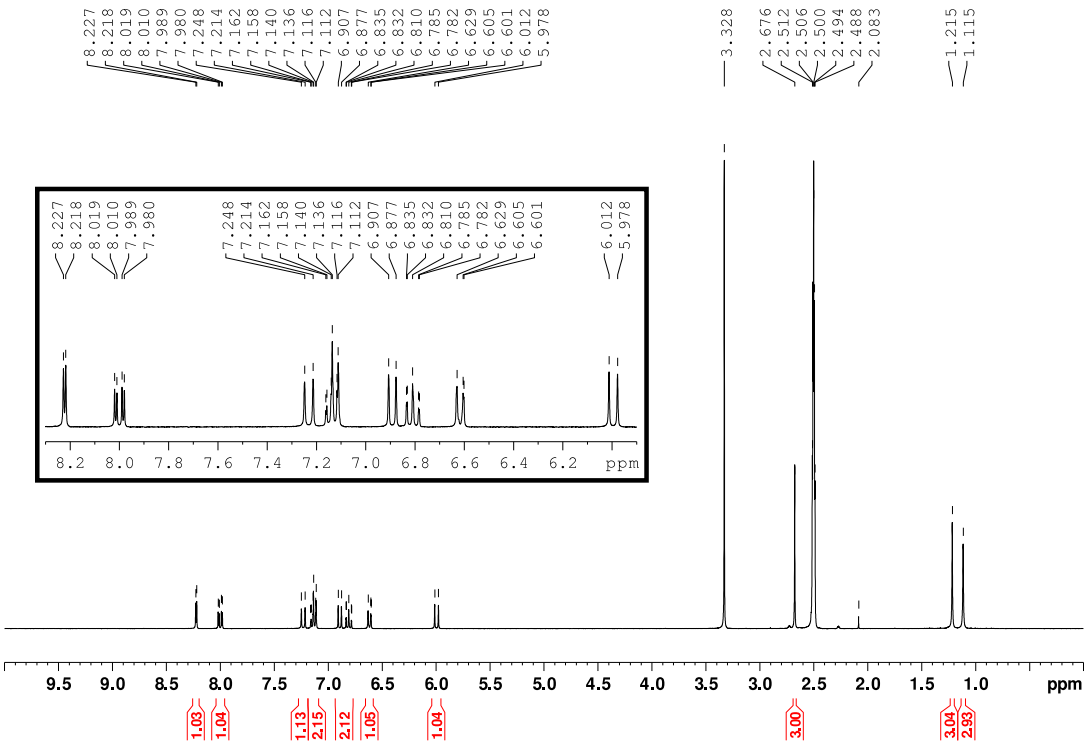

Figure S27: ^{1}H-NMR of (IVa) in DMSO-d_6 (δ (ppm): 2.50) showing only the *SP* form) of **SPNO2**/**MCNO2** after exposing to sunlight. Traces of H_2O (δ (ppm): 3.33) and acetone (δ (ppm): 2.08) present.

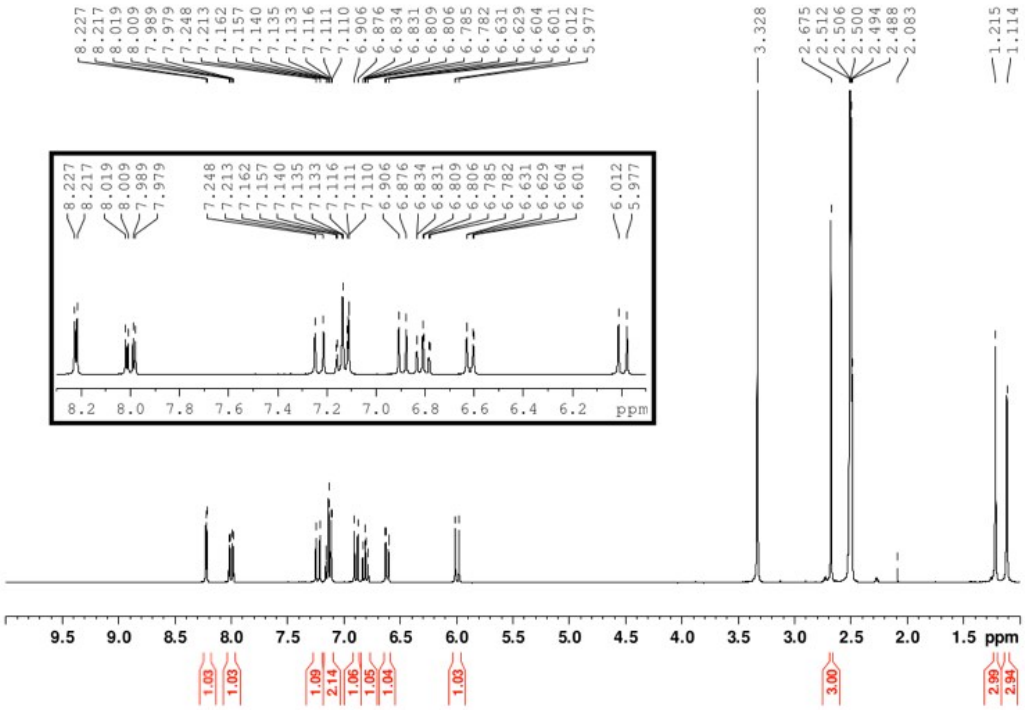

Figure S28: ^{1}H-NMR of (IVf) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.33) and acetone (δ (ppm): 2.08) present.

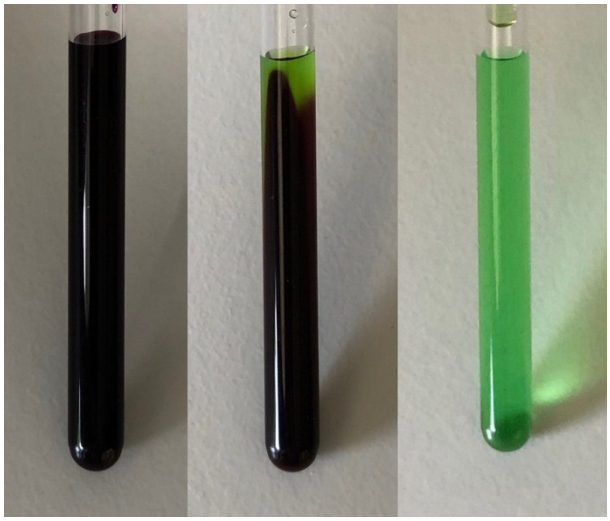

Figure S29: NMR tube of (IVj) in DMSO-d_6 directly after dissolution (left), after exposing for several seconds to sunlight (middle) and exposing to sunlight until complete discoloration.

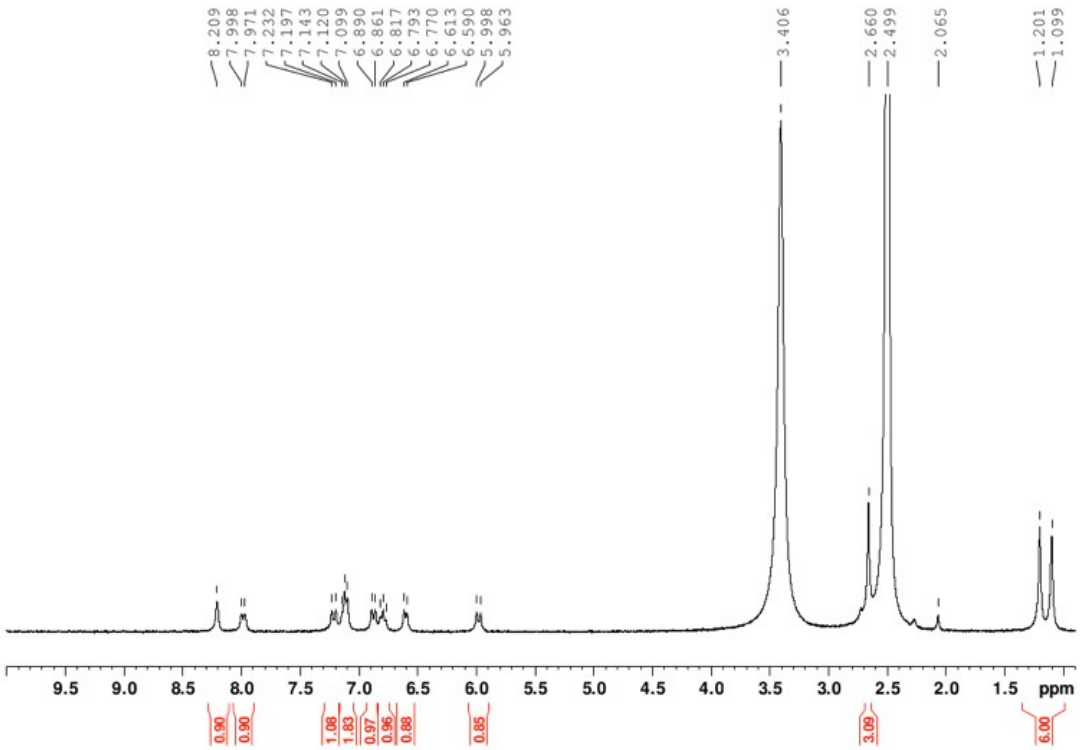

Figure S30: ^{1}H-NMR of (IVj) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.41) and acetone (δ (ppm): 2.07) present.

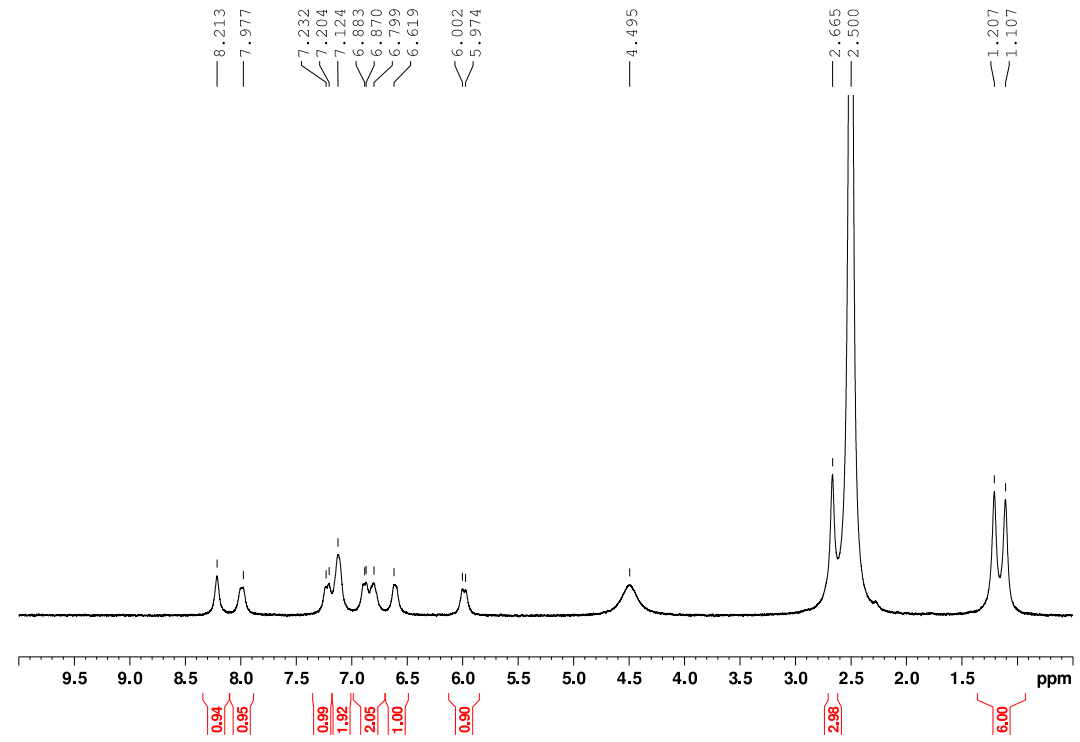

Figure S31: ^{1}H-NMR of (IVk) in DMSO-d_6 (δ (ppm): 2.50).

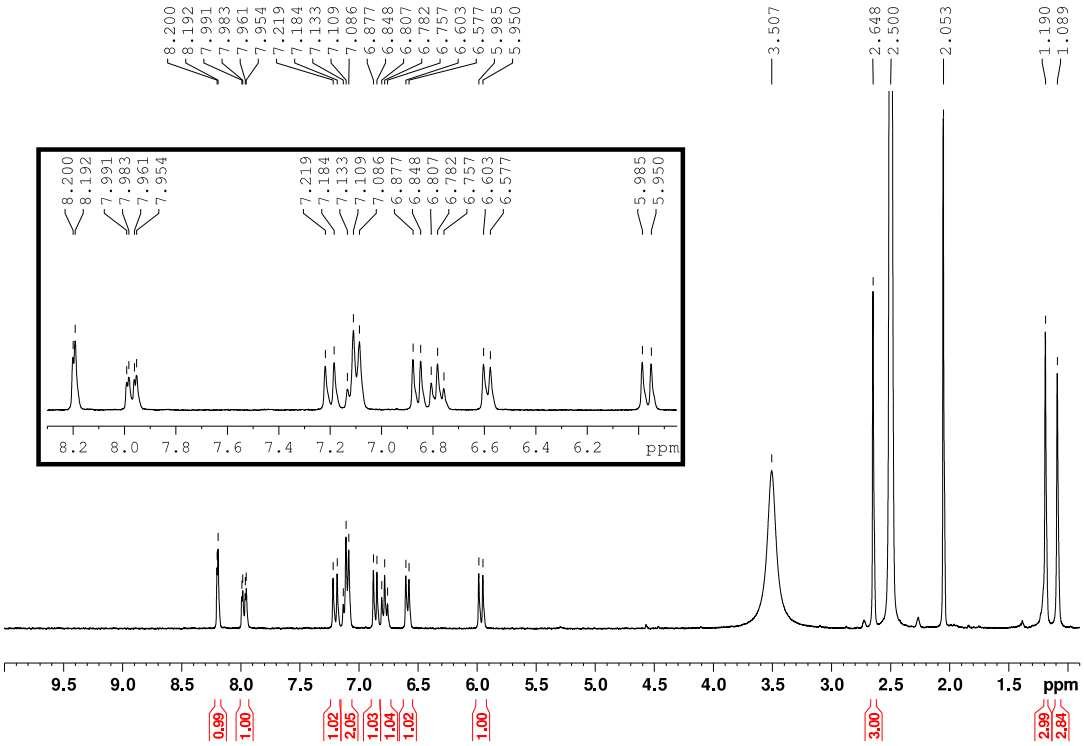

Figure S32: ^{1}H-NMR of (IVm) in DMSO-d_6 (δ (ppm): 2.50). Traces of H_2O (δ (ppm): 3.51) and acetone (δ (ppm): 2.05) present.

Diffuse reflectance spectroscopy

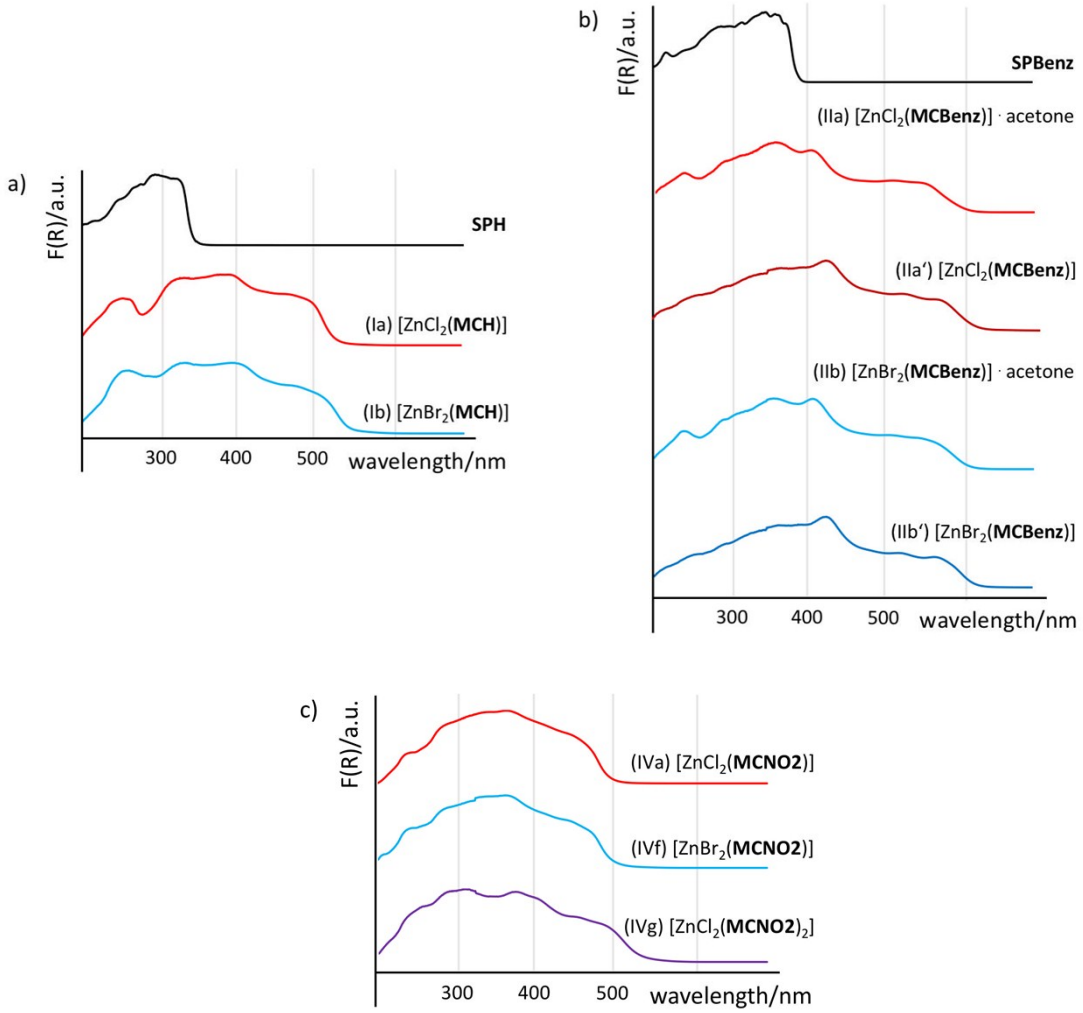

Figure S33: Diffuse reflectance spectroscopy of the parent spiropyran compounds, a) **SPH/MCH**, b) **SPBenz/MCBenz** and c) **SPNO2/MCNO2**, as well as their formed complexes with $ZnCl_2$/$ZnBr_2$.

Thermal gravimetric analysis

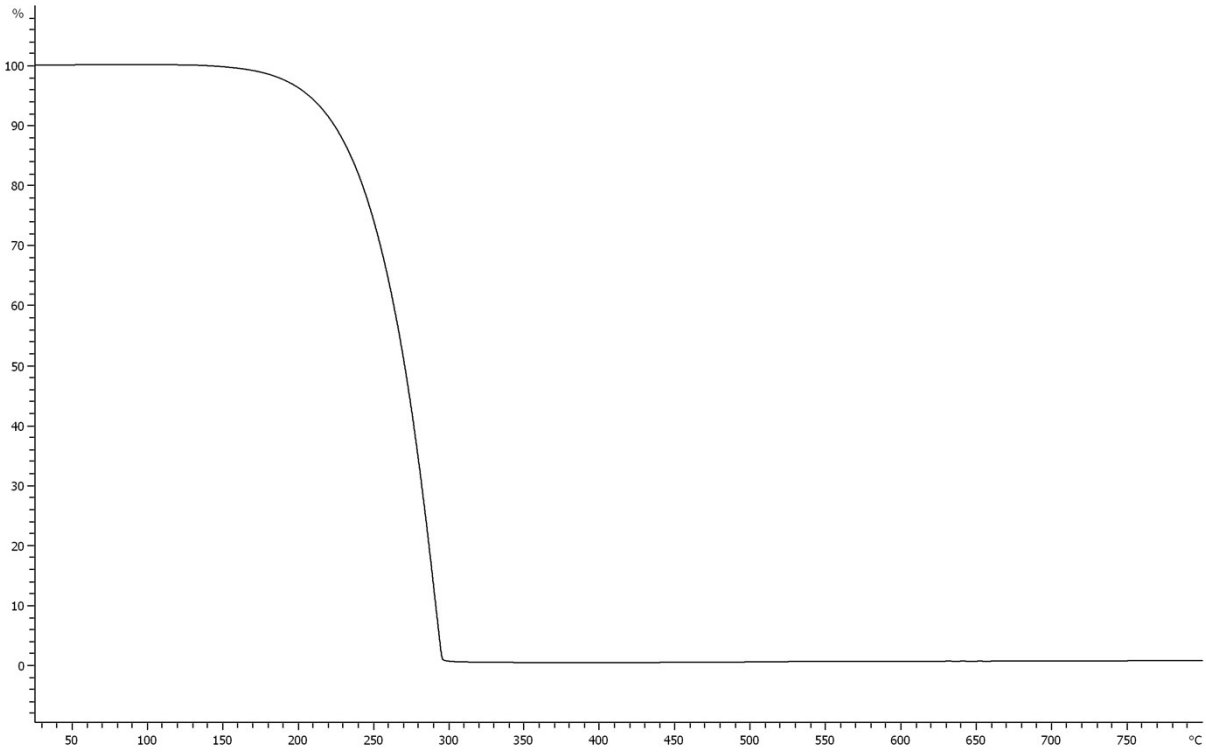

Figure S34: TGA analysis of **SPH**. (25-800 °C; 10°C/min; N_2)

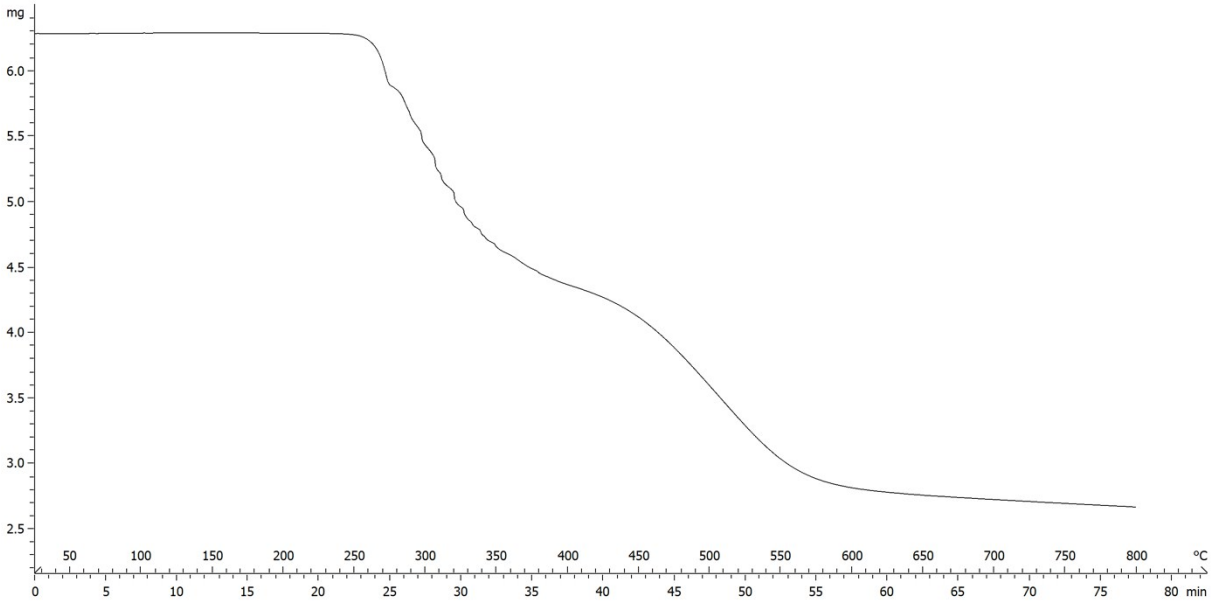

Figure S35: TGA analysis of **MCH** coordinated to $ZnCl_2$ (Ia). (25-800 °C; 10°C/min; N_2)

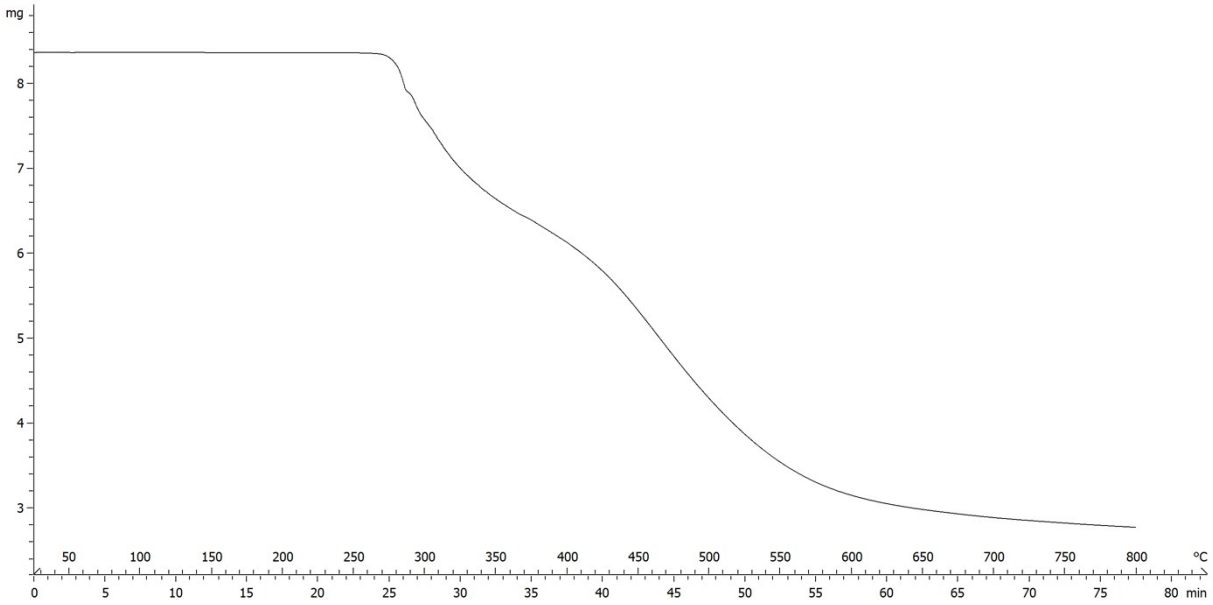

Figure S36: TGA analysis of **MCH** coordinated to $ZnBr_2$ (Ib). (25-800 °C; 10°C/min; N_2)

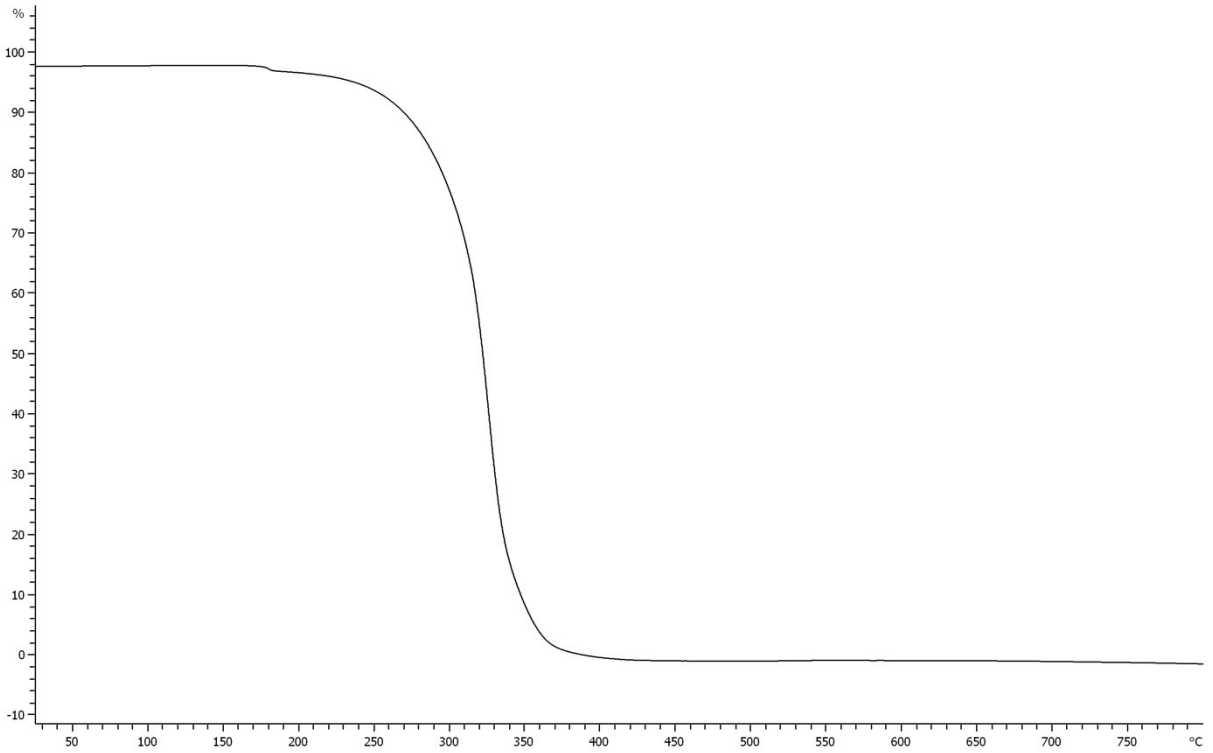

Figure S37: TGA analysis of **SPBenz**. (25-800 °C; 10°C/min; N_2)

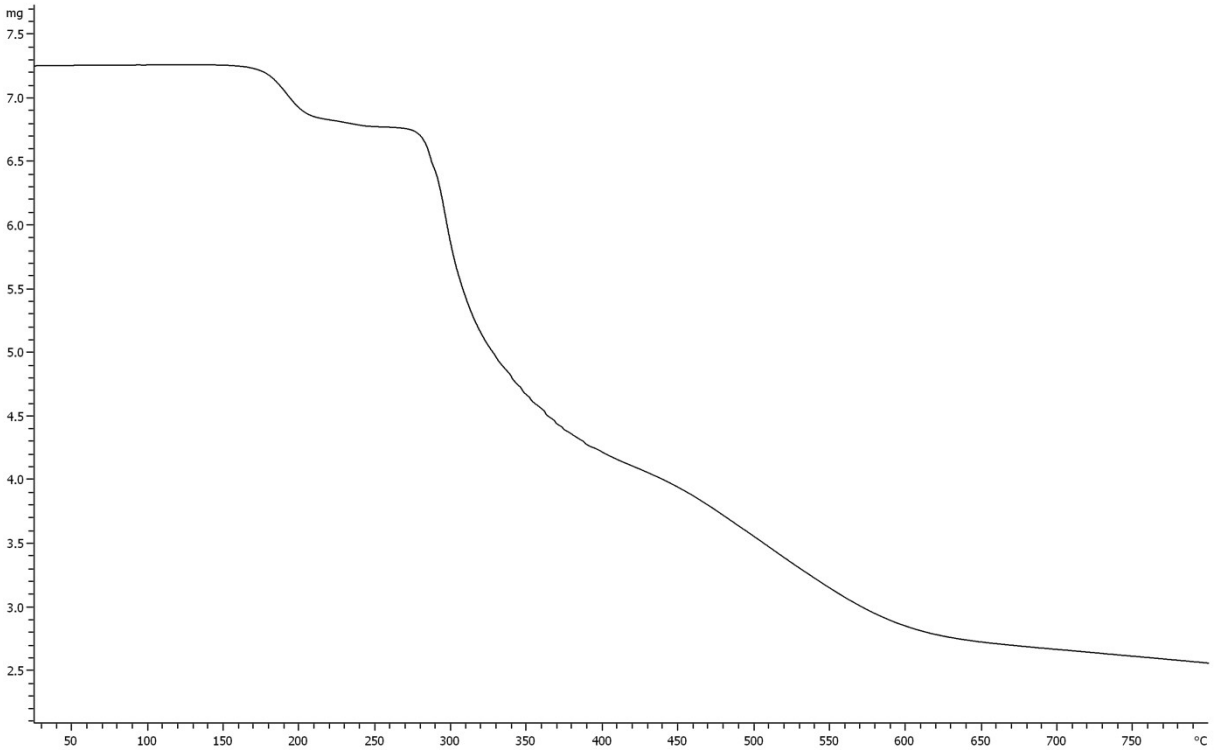

Figure S38: TGA analysis of **MCBenz** coordinated to $ZnCl_2$ (IIa) showing the loss of acetone starting around 150°C. (25-800 °C; 10°C/min; N_2)

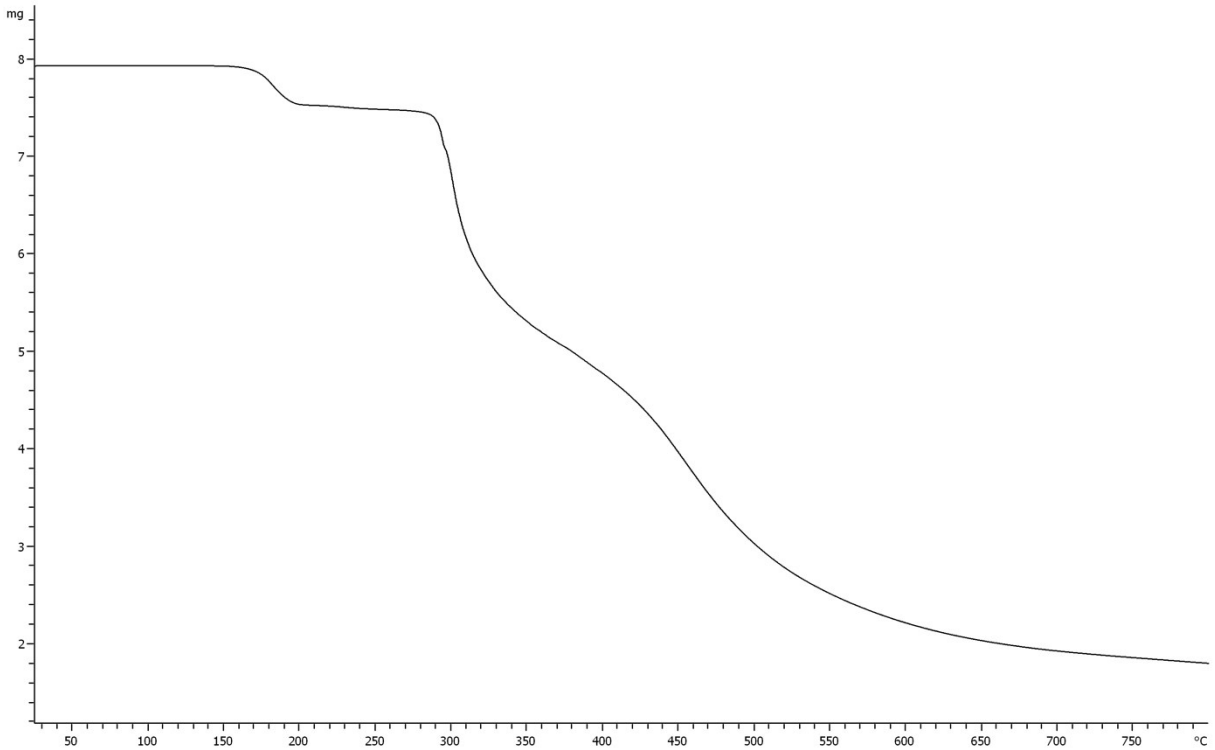

Figure S39: TGA analysis of **MCBenz** coordinated to $ZnBr_2$ (IIb) showing the loss of acetone starting around 147°C. (25-800 °C; 10°C/min; N_2)

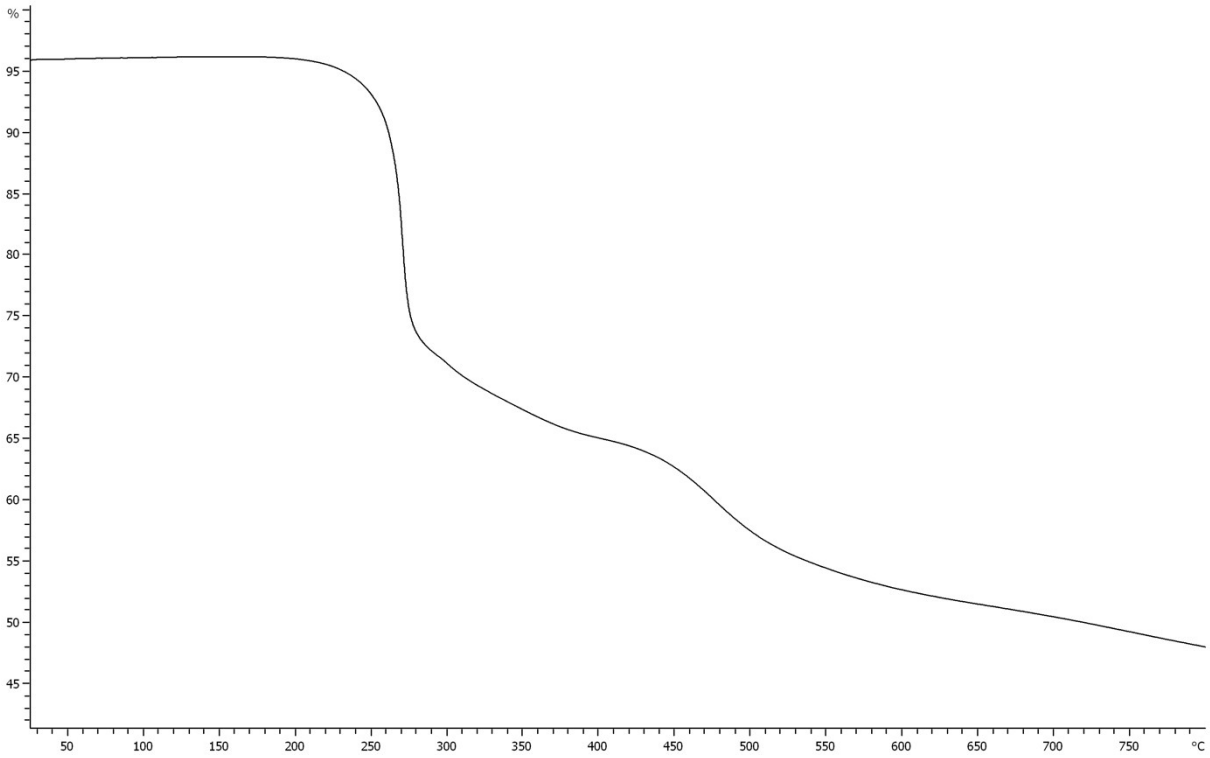

Figure S40: TGA analysis of **SPNO2**. (25-800 °C; 10°C/min; N_2)

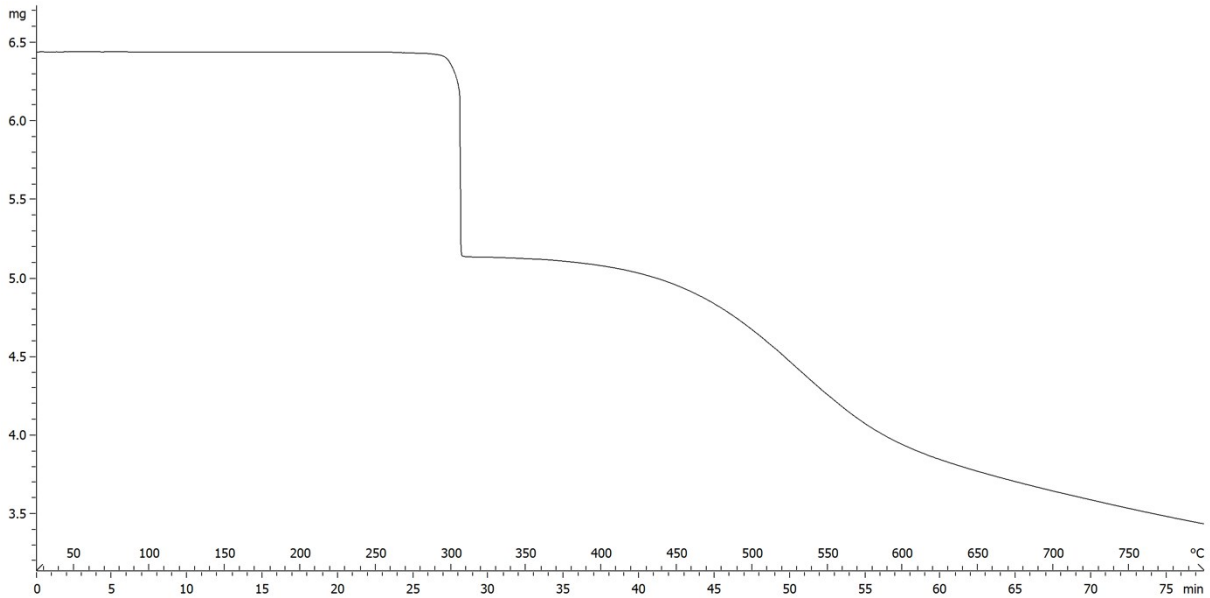

Figure S41: TGA analysis of **MCNO2** coordinated to $ZnCl_2$ (IVa). (25-800 °C; 10°C/min; N_2)

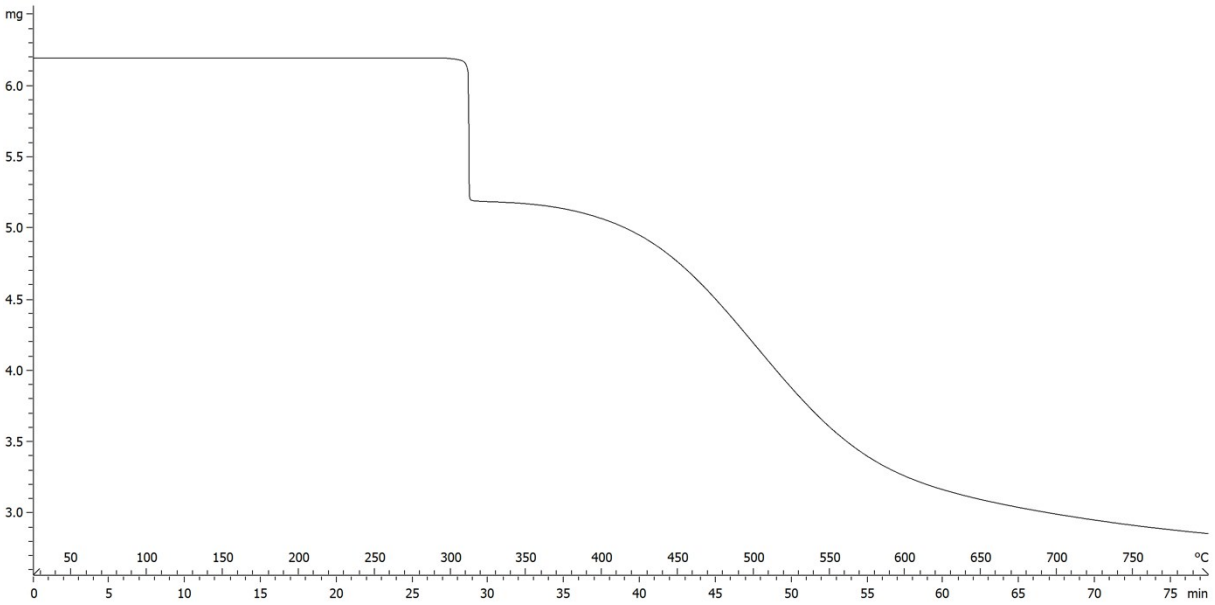

Figure S42: TGA analysis of **MCNO2** coordinated to $ZnBr_2$ (IVf). (25-800 °C; 10°C/min; N_2)

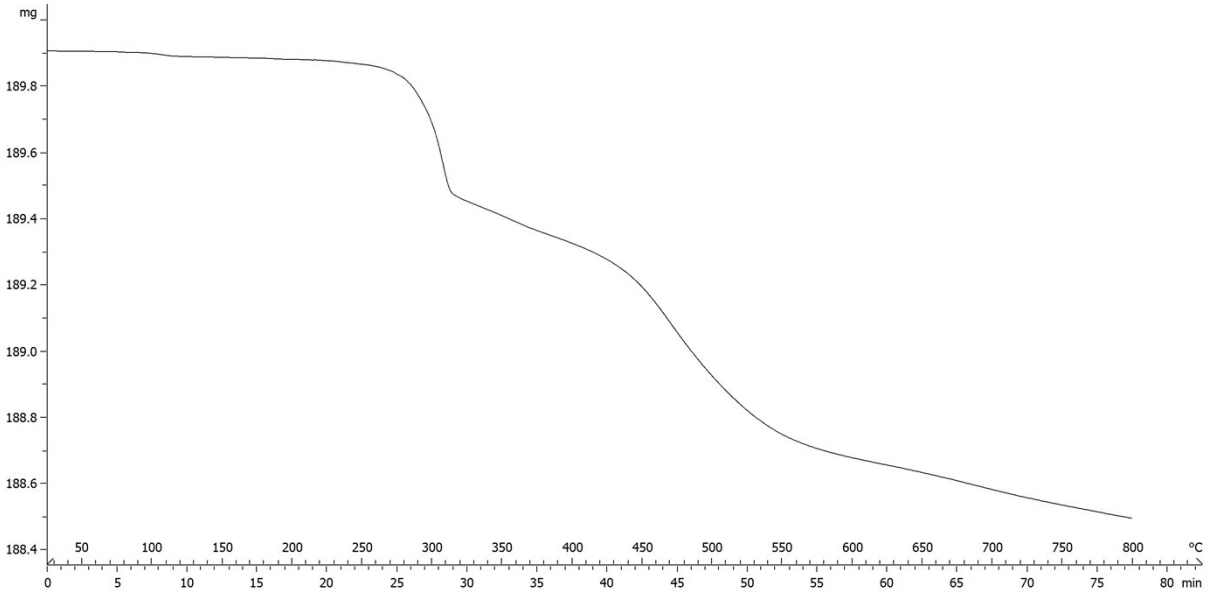

Figure S43: TGA analysis of **MCNO2** coordinated to $CoCl_2$ (IVj). (25-800 °C; 10°C/min; N_2)

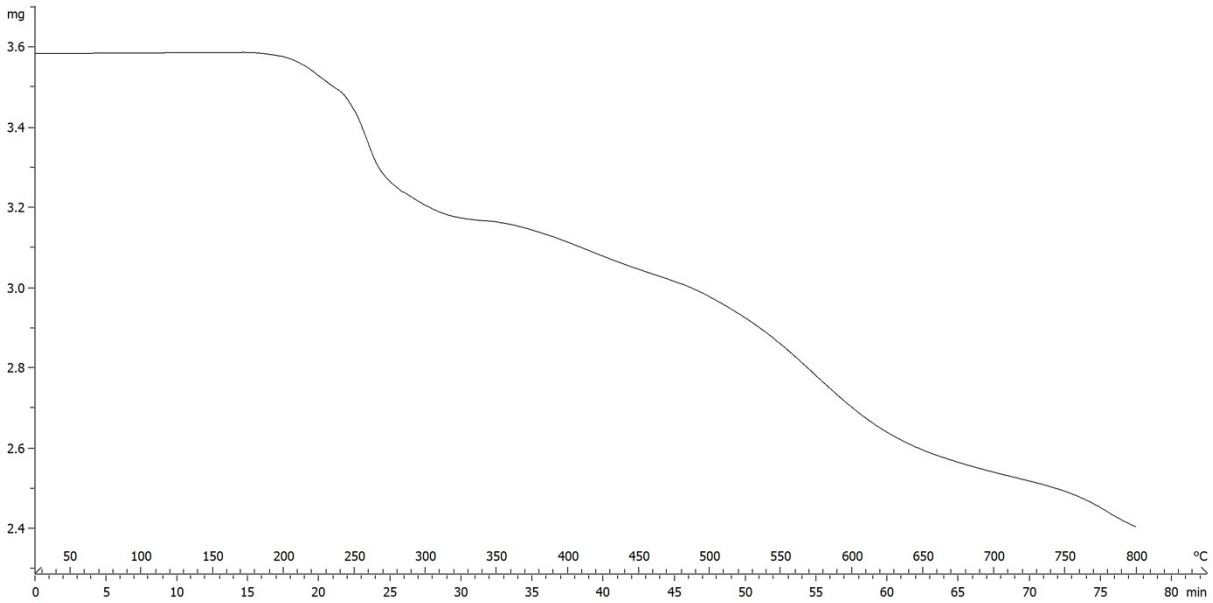

Figure S44: TGA analysis of **MCNO2** with $CoCl_2$ forming the mix form (IVk). (25-800 °C; 10°C/min; N_2)

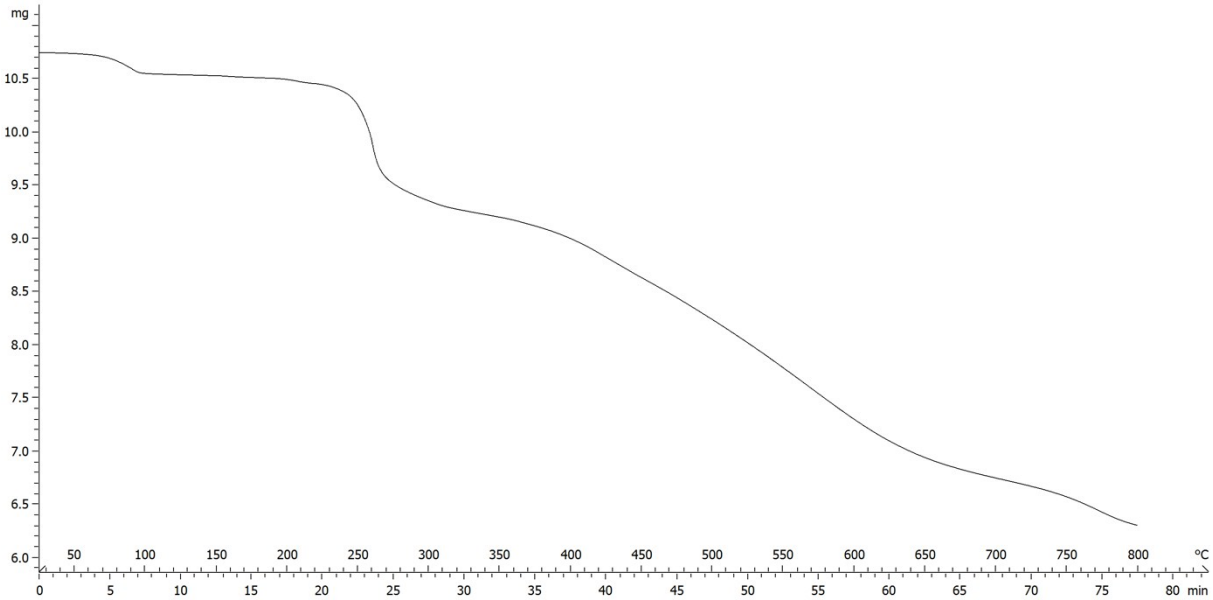

Figure S45: TGA analysis of **MCNO2** with $CoCl_2$ forming the hhydrated salt (IVm). (25-800 °C; 10°C/min; N_2)