SUPPORTING INFORMATION

Synthesis of an extended halogen-bonded metal-organic structure in a one-pot mechanochemical reaction that combines covalent, coordination and supramolecular synthesis

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Table of Contents

Experimental details	Materials, Solid-state synthesis, Solution synthesis, Thermal analysis, FTIR spectroscopy, Single-crystal X-ray diffraction experiments, Powder X-ray diffraction experiments	4
Table S1.	General and crystallographic data for Cu**(naap)$_2$·tfib**.	8
Figure S1.	Molecular structures of Cu**(naap)$_2$·tfib** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radius.	9
Figure S2.	PXRD pattern of pure **napht** reactant.	10
Figure S3.	PXRD pattern of pure **aap** reactant.	10
Figure S4.	PXRD pattern of pure copper acetate monohydrate.	11
Figure S5.	PXRD pattern of pure **tfib** reactant.	11
Figure S6.	PXRD patterns for mechanochemical and solution-based experiments involving **napht** and **aap**: a) **napht**, b) **aap**, c) compound **Hnaap** obtained by grinding in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA], d) compound **Hnaap** obtained by solution-based method, e) calculated pattern for compound **Hnaap**.	12
Figure S7.	PXRD patterns for mechanochemical and solution-based experiments involving compound **Hnaap** and copper acetate monohydrate: a) compound **Hnaap**, b) copper acetate monohydrate, c) acetic acid solvate of Cu**(naap)$_2$** obtained by grinding in ball mill for 50 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA], d) compound Cu**(naap)$_2$** obtained by solution-based method, e) acetic acid solvate of Cu**(naap)$_2$** after annealing at 200 °C for 30 min.	12
Figure S8.	PXRD patterns for mechanochemical and solution-based experiments involving compound Cu**(naap)$_2$** and **tfib**: a) compound Cu**(naap)$_2$**, b) **tfib**, c) compound Cu**(naap)$_2$·tfib** obtained by solution-based method, d) compound Cu**(naap)$_2$·tfib** obtained by grinding in ball mill for 50 min in the presence of a small quantity of nitromethane and e) calculated pattern for compound Cu**(naap)$_2$·tfib** .	13

Figure S9.	PXRD patterns for one-pot mechanochemical experiments: a) **napht**, b) **aap**, c) compound **Hnaap**, d) copper acetate monohydrate, e) **tfib**, f) compound Cu**(naap)$_2$·tfib** obtained by grinding of compound **Hnaap**, copper acetate monohydrate and **tfib** in ball mill for 50 min in the presence of a small quantity of nitromethane, g) compound Cu**(naap)$_2$·tfib** obtained by grinding of **napht**, **aap**, copper acetate monohydrate and **tfib** in ball mill for 60 min in the presence of a small quantity of nitromethane and h) calculated pattern for compound Cu**(naap)$_2$·tfib** .	13
Figure S10.	IR spectrum for pure **napht** reactant.	14
Figure S11.	IR spectrum for pure **aap** reactant.	14
Figure S12.	IR spectrum for pure **tfib** reactant.	15
Figure S13.	IR spectrum for **Hnaap** prepared by solution-based method.	15
Figure S14.	IR spectrum for **Hnaap** prepared by LAG.	16
Figure S15.	IR spectrum for Cu**(naap)$_2$** prepared by solution-based method.	16
Figure S16.	IR spectrum for the product of grinding of copper acetate monohydrate and compound **Hnaap**, i.e. the acetic acid solvate of compound Cu**(naap)$_2$**.	17
Figure S17.	IR spectrum for the product of grinding of copper acetate monohydrate and compound **Hnaap** after isothermal experiment at 200 °C.	17
Figure S18.	IR spectrum for Cu**(naap)$_2$·tfib** prepared by solution-based method.	18
Figure S19.	IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of compound Cu**(naap)$_2$** and **tfib**.	18
Figure S20.	IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of compound **Hnaap** and copper acetate monohydrate and **tfib**.	19
Figure S21.	IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of **napht**, **aap**, copper acetate monohydrate and **tfib**.	19
Figure S22.	DSC curve for pure **napht** reactant.	20
Figure S23.	DSC curve for pure **aap** reactant.	20
Figure S24.	TG (black) and DTA (red) curve for pure copper acetate monohydrate.	21
Figure S25.	DSC curve for pure **tfib** reactant.	21
Figure S26.	DSC curve for **Hnaap** synthesised by solution-based method.	22
Figure S27.	DSC curve for **Hnaap** synthesised by grinding in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% v/v of TEA].	22
Figure S28.	TG (black) and DTA (red) curve for **Hnaap** synthesised by solution-based method.	23
Figure S29.	TG (black) and DTA (red) curve for Cu**(naap)$_2$** obtained by solution-based method.	23
Figure S30.	TG (black) and DTA (red) curve for the product (i.e. the acetic acid solvate of compound Cu**(naap)$_2$**) obtained by grinding of copper acetate monohydrate and compound **Hnaap** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].	24
Figure S31.	TG curve of isothermal experiment at 200 °C for the product of grinding of copper acetate monohydrate and compound **Hnaap**, i.e. the acetic acid solvate of compound Cu**(naap)$_2$**.	24

Figure S32. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by solution-based method. 25

Figure S33. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of compound Cu**(naap)$_2$** and **tfib** in ball mill for 60 min in the presence of a small quantity of nitromethane. 25

Figure S34. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, compound **Hnaap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA]. 26

Figure S35. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, **napht**, **aap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA]. 26

Figure S36. DSC curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, **napht**, **aap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA]. 27

Figure S37. a) PXRD pattern of residue after TG experiment of compound Cu**(naap)$_2$** and b) calculated pattern for CuO. 28

Figure S38. a) PXRD pattern of residue after TG experiment of compound Cu**(naap)$_2$·tfib** and b) calculated pattern for CuO. 28

EXPERIMENTAL DETAILS

MATERIALS

The starting materials, 2-hydroxy-1-naphthaldehyde (**napht**) and 4-aminoacetophenone (**aap**) were obtained from Acros Organics; copper acetate monohydrate was obtained from Kemika; and 1,4-tetrafluoroiodobenzene (**tfib**) was obtained from Merck. **Napht** was recrystallised from methanol and all other materials were used without further purification. Solvents were purchased from Kemika and T.T.T., Zagreb.

BALL MILLING EXPERIMENTS

Synthesis of **Hnaap**

For LAG experiment equimolar quantities of **napht** (0.129 g, 0.75 mmol) and **aap** (0.101 g, 0.75 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 μL of a mixture of EtOH and TEA [5% *v*/*v* of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of acetic acid solvate of Cu**(naap)**$_2$

For LAG experiment, compound **Hnaap** (0.174 g, 0.60 mmol) and copper acetate monohydrate (0.060 g, 0.30 mmol) were placed in a 10 mL stainless steel grinding jar along with 35 μL of a mixture of EtOH and TEA [5% *v*/*v* of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of Cu**(naap)**$_2$**·tfib**

Single-step synthesis

For LAG experiment, compound Cu**(naap)**$_2$ (0.030 g, 0.047 mmol) and **tfib** (0.019 g, 0.047 mmol) were placed in a 5 mL stainless steel grinding jar along with 15 μL of nitromethane and two 4 mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

One-pot two-step synthesis

For LAG experiment, compound **Hnaap** (0.087 g, 0.30 mmol), copper acetate monohydrate (0.030 g, 0.15 mmol) and **tfib** (0.061 g, 0.15 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 μL of a mixture of EtOH and TEA [5% *v*/*v* of TEA] and two 7

mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

One-pot three-step synthesis

For LAG experiment, **napht** (0.052 g, 0.30 mmol), **aap** (0.041 g, 0.30 mmol), copper acetate monohydrate (0.030 g, 0.15 mmol) and **tfib** (0.061 g, 0.15 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 µL of a mixture of EtOH and TEA [5% *v*/*v* of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

SOLUTION SYNTHESIS

To monitor solid-state experiments, as well as to facilitate the characterisation of new materials by single-crystal X-ray diffraction, solid-state experiments were accompanied by conventional solution-based experiments. Crystal and molecular structures of **Hnaap** has been previously reported, CCDC code IXAPOM[1].

Synthesis of **Hnaap**

Equimolar quantities of **aap** (1.35 g, 0.01 mol) and **napht** (1.72 g, 0.01 mol), were dissolved in hot methanol (15 mL and 35 mL, respectively). The solutions were mixed and the resulting mixture left at room temperature. Orange precipitate appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with methanol.

Synthesis of Cu**(naap)**$_2$

A clear solution of copper acetate monohydrate (0.199 g, 0.001 mol) in 50 mL methanol was added to a solution of compound **Hnaap** (0.579 g, 0.002 mol) in 70 mL acetonitrile. The resultant mixture was refluxed for 3 h and the brown precipitate was separated from mother liquor by filtration, and washed with methanol.

Synthesis of Cu**(naap)**$_2$**·tfib**

Equimolar quantities of compound Cu**(naap)**$_2$ (0.64 g, 1.0 mmol) and **tfib** (0.40 g, 1.0 mmol), were dissolved in a hot mixture of ethanol and tetrahydrofurane (24 mL, 1:2). The resulting mixture left at room temperature. Brown crystals appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with methanol.

THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823^e module in sealed aluminium pans (40 μL), heated in flowing nitrogen (150 mL min^{-1}) at a rate of 10 °C min^{-1}. TG measurements were performed on a Mettler-Toledo TGA/SDTA 851^e module in sealed aluminium pans (40 μL), heated in flowing oygen (150 mL min^{-1}) at a rate of 10 °C min^{-1}. The data collection and analysis was performed using the program package STAR^e Software 9.01.[2]

FTIR SPECTROSCOPY

Infrared spectra were recorded on a PerkinElmer Spectrum Two FTIR spectrophotometer using a KBr pellet. The data collection and analysis was performed using the program package PerkinElmer Spectrum (version 10.4.2.279).

SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of Cu**(naap)$_2$·tfib** was determined by single crystal X-ray diffraction. Details of data collection and crystal structure refinement are listed in Table S1. The diffraction data were collected at 292 K for all compounds. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoKα (λ = 0.71073Å) radiation. The data sets were collected using the ω scan mode over the 2θ range up to 54°. Programs CrysAlis CCD[3] and CrysAlis RED[3] were employed for data collection, cell refinement, and data reduction. The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.[4] The structural refinement was performed on F^2 using all data. The hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and treated as riding on their parent atoms [C–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C)] while the others were located from the electron difference map. All calculations were performed using the WINGX crystallographic suite of programs.[5] The molecular structures of compounds are presented by ORTEP-3[6] and their molecular packing projections were prepared by Mercury.[7]

POWDER X-RAY DIFFRACTION EXPERIMENTS

PXRD experiments of the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with CuKα1 (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 3 to 50°

(2θ) with steps of 0.02°, and the measuring time was 0.5 to 1 s per step. The data collection and analysis was performed using the program package Philips X'Pert.[8]

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Table S1. General and crystallographic data for Cu**(naap)$_2$·tfib**.

	Compound Cu**(naap)$_2$·tfib**
Molecular formula	$(CuC_{38}H_{28}N_2O_4)(C_6F_4I_2)$
M_r	1042.02
Crystal system	triclinic
Space group	$P\ \bar{1}$
Crystal data:	
a / Å	8.093(5)
b / Å	9.502(5)
c / Å	12.751(5)
α / °	82.472(5)
β / °	82.927(5)
γ / °	86.586(5)
V / Å^3	963.8(9)
Z	1
D_{calc} / g cm^{-3}	1.795
λ(MoK_α) / Å	0.71073
T / K	295
Crystal size / mm^3	0.13x0.22x0.51
μ / mm^{-1}	2.235
$F(000)$	509
Refl. collected/unique	11870 / 4192
Data/restraints/parameters	259
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.363; −0.584
$R[F^2>4\sigma(F^2)]$	0.0363
$wR(F^2)$	0.0879
Goodness-of-fit, S	0.984

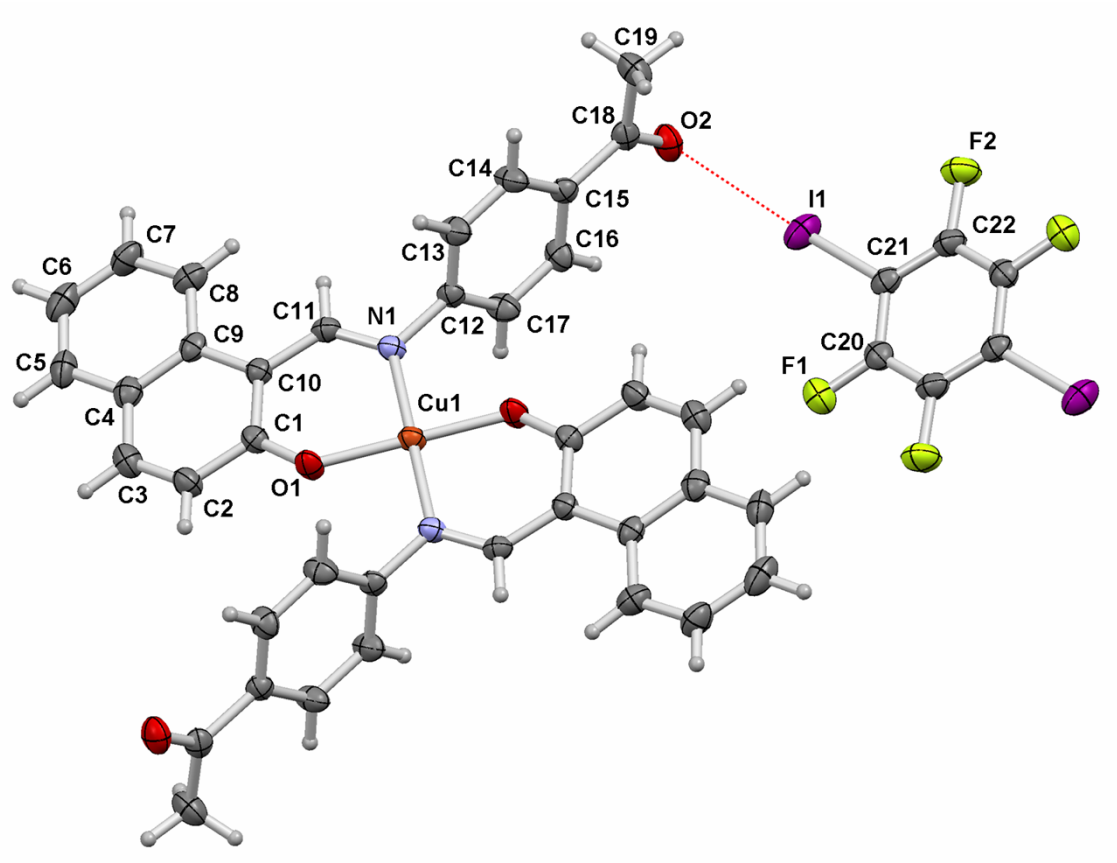

Figure S1. Molecular structures of Cu**(naap)$_2$·tfib** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radius.

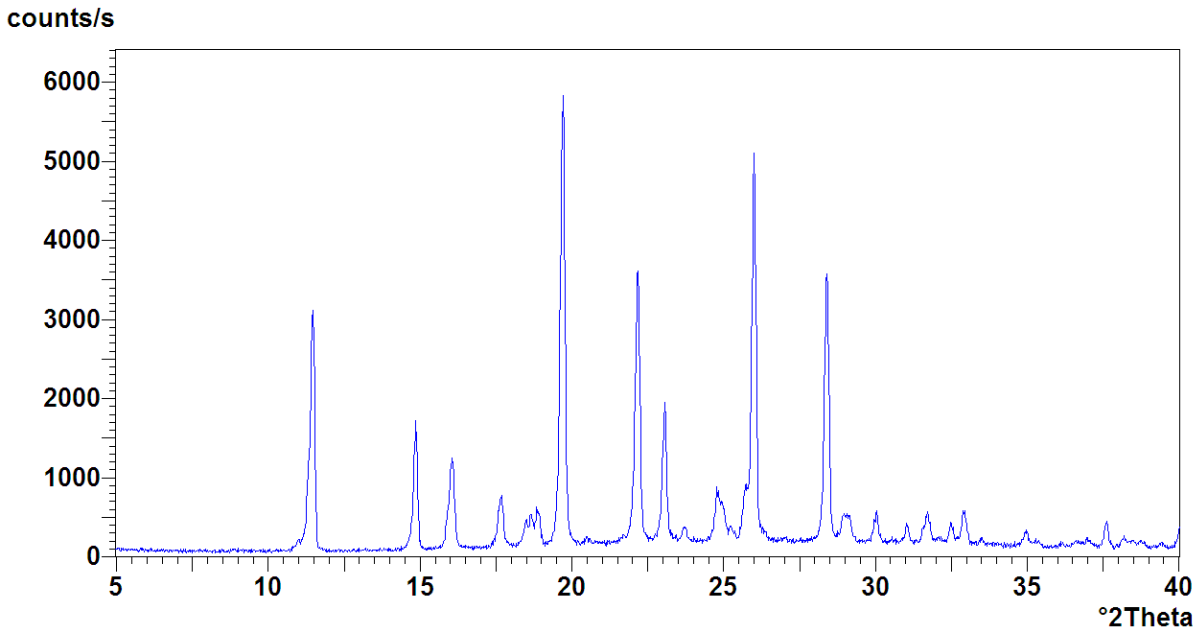

Figure S2. PXRD pattern of pure **napht** reactant.

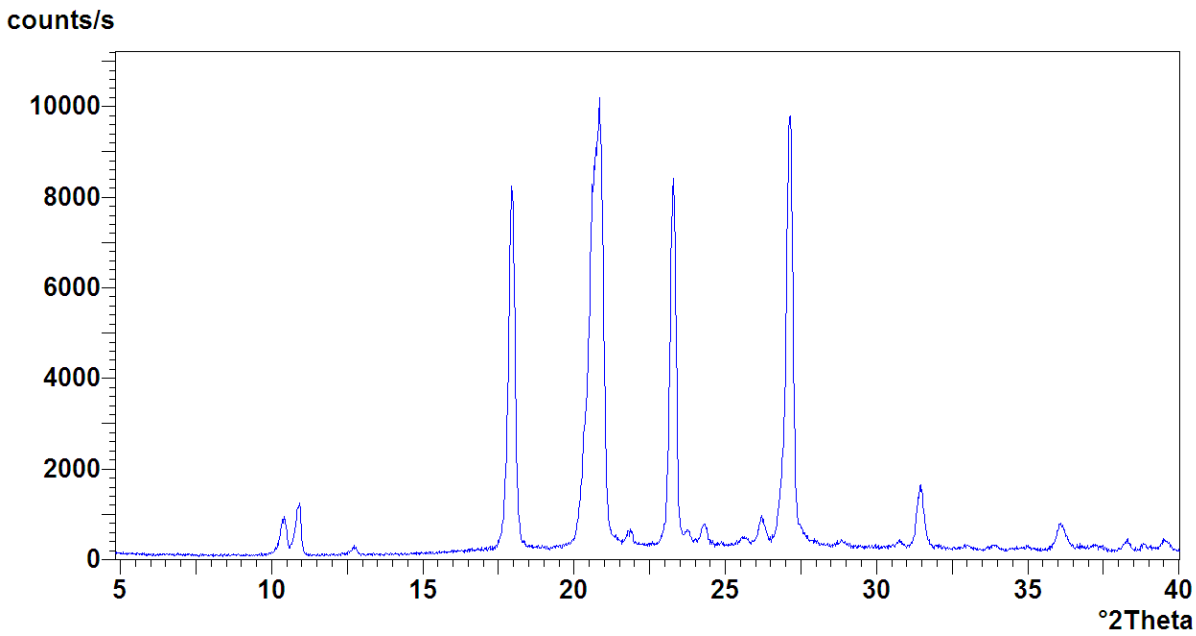

Figure S3. PXRD pattern of pure **aap** reactant.

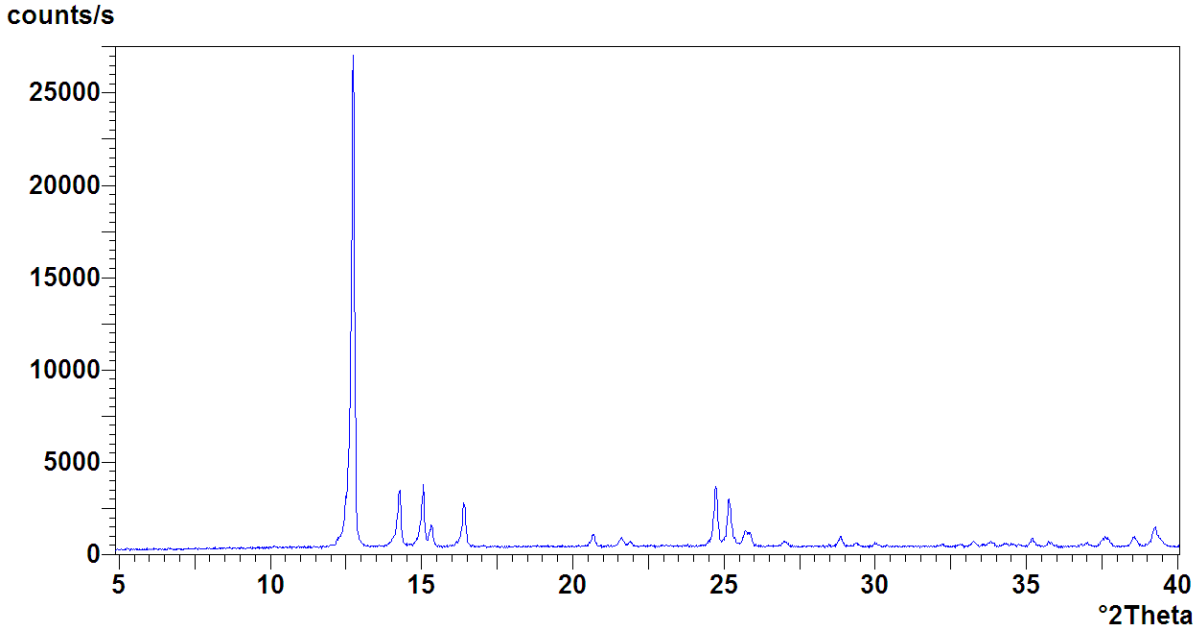

Figure S4. PXRD pattern of pure copper acetate monohydrate.

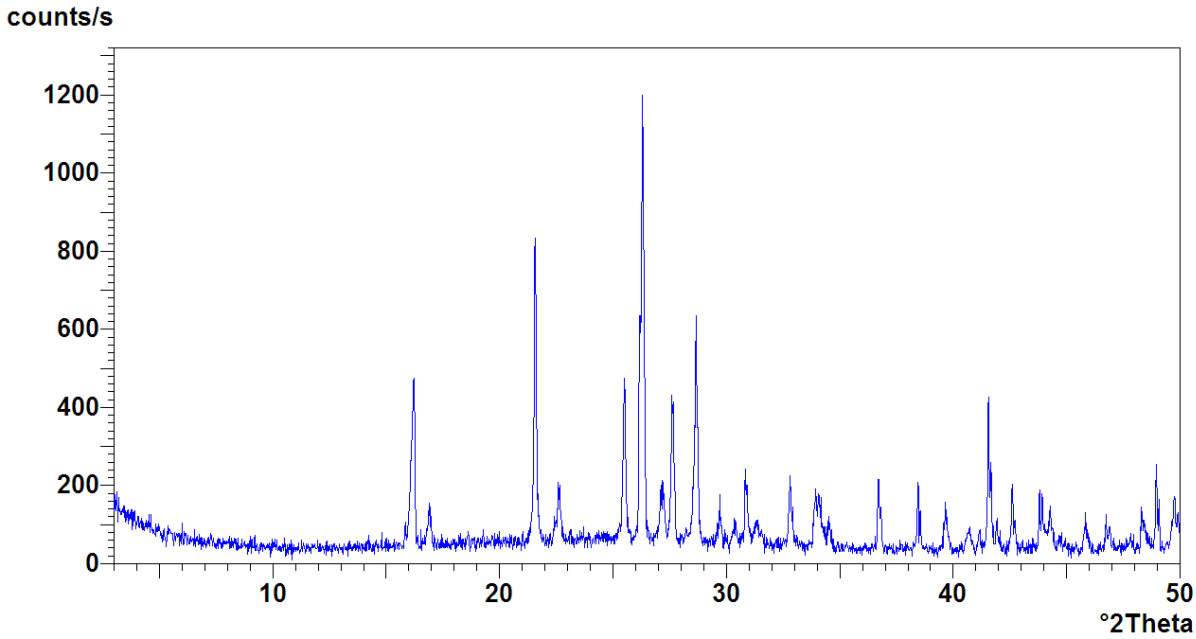

Figure S5. PXRD pattern of pure **tfib** reactant.

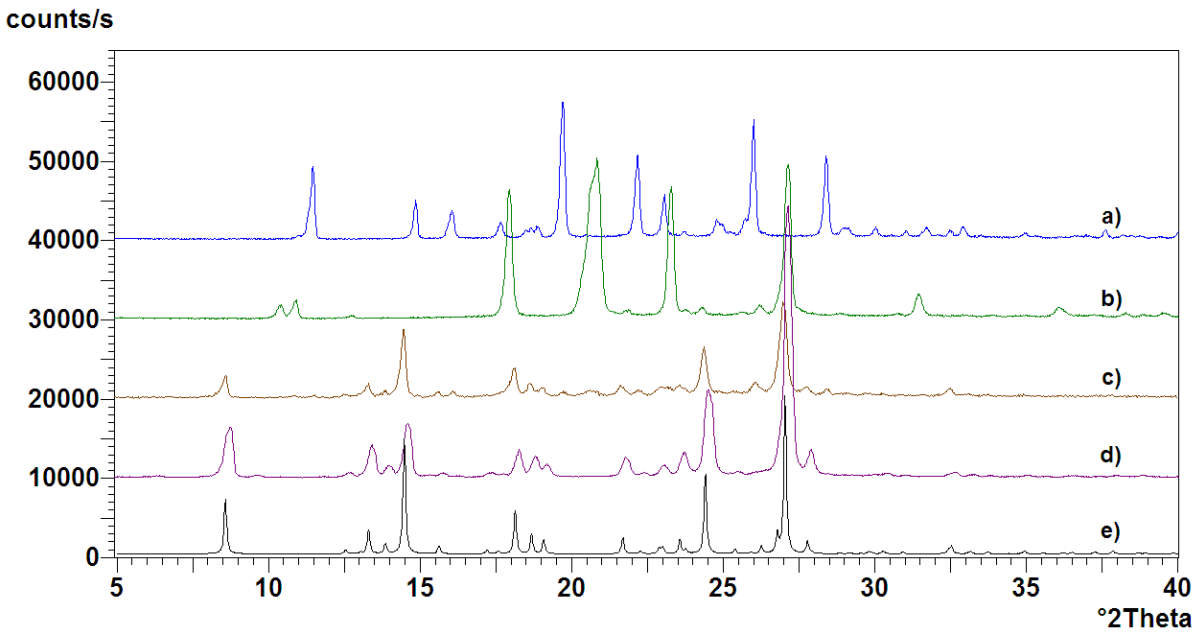

Figure S6. PXRD patterns for mechanochemical and solution-based experiments involving **napht** and **aap**: a) **napht**, b) **aap**, c) compound **Hnaap** obtained by grinding in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA], d) compound **Hnaap** obtained by solution-based method, e) calculated pattern for compound **Hnaap**.

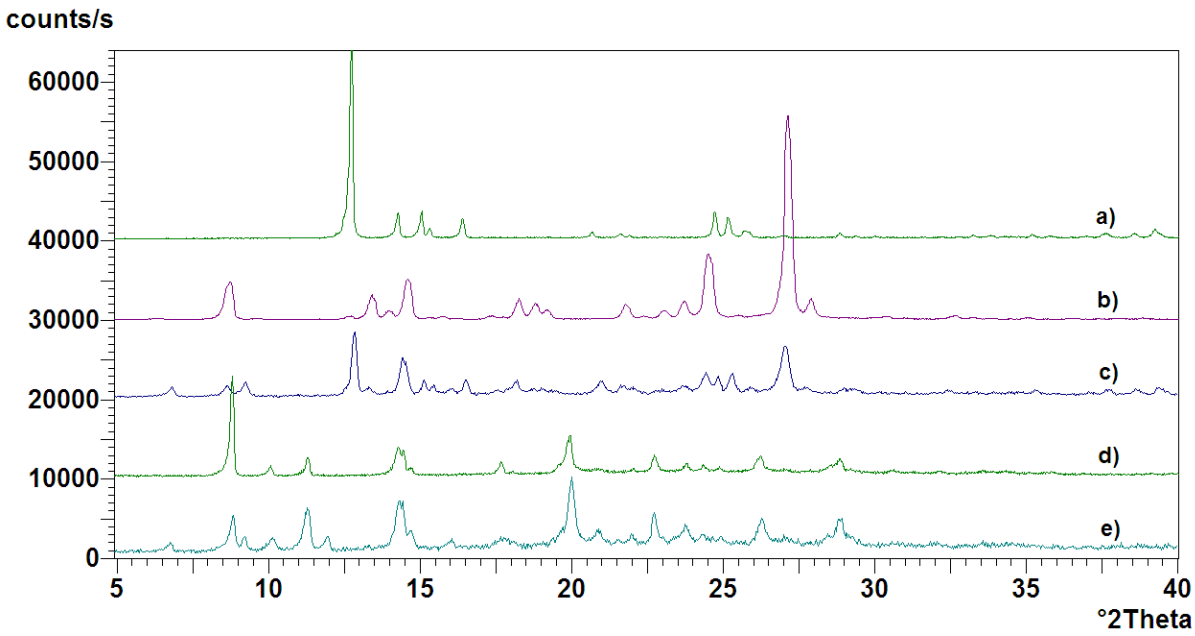

Figure S7. PXRD patterns for mechanochemical and solution-based experiments involving compound **Hnaap** and copper acetate monohydrate: a) compound **Hnaap**, b) copper acetate monohydrate, c) acetic acid solvate of Cu**(naap)$_2$** obtained by grinding in ball mill for 50 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA], d) compound Cu**(naap)$_2$** obtained by solution-based method, e) acetic acid solvate of Cu**(naap)$_2$** after annealing at 200 °C for 30 min.

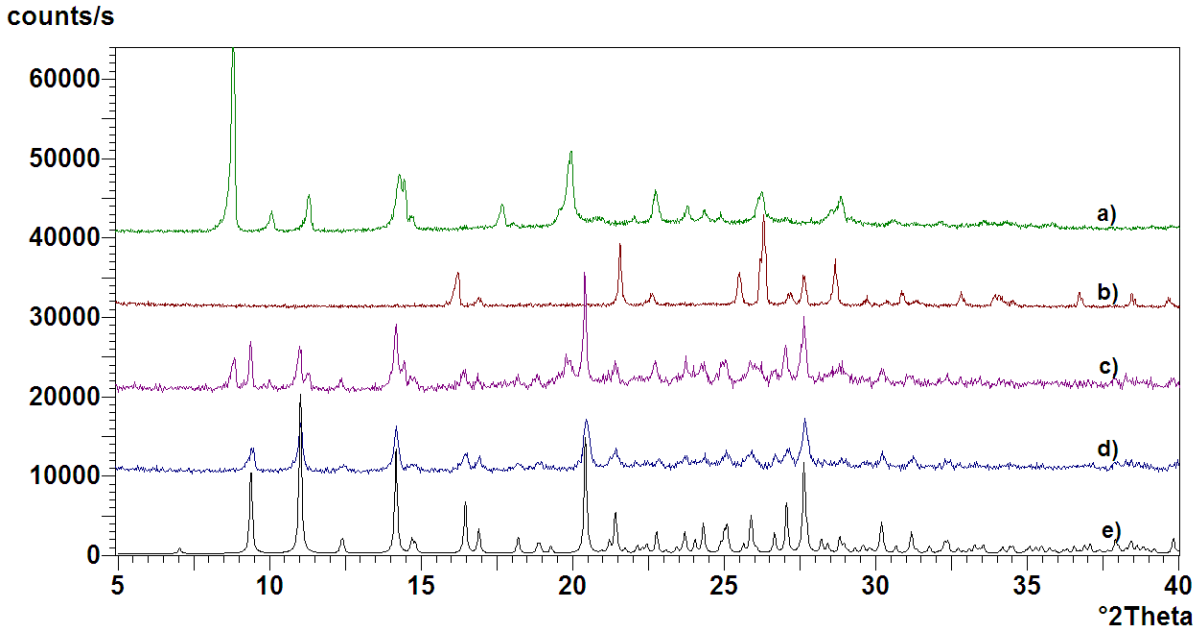

Figure S8. PXRD patterns for mechanochemical and solution-based experiments involving compound Cu**(naap)$_2$** and **tfib**: a) compound Cu**(naap)$_2$**, b) **tfib**, c) compound Cu**(naap)$_2$·tfib** obtained by solution-based method, d) compound Cu**(naap)$_2$·tfib** obtained by grinding in ball mill for 50 min in the presence of a small quantity of nitromethane and e) calculated pattern for compound Cu**(naap)$_2$·tfib**.

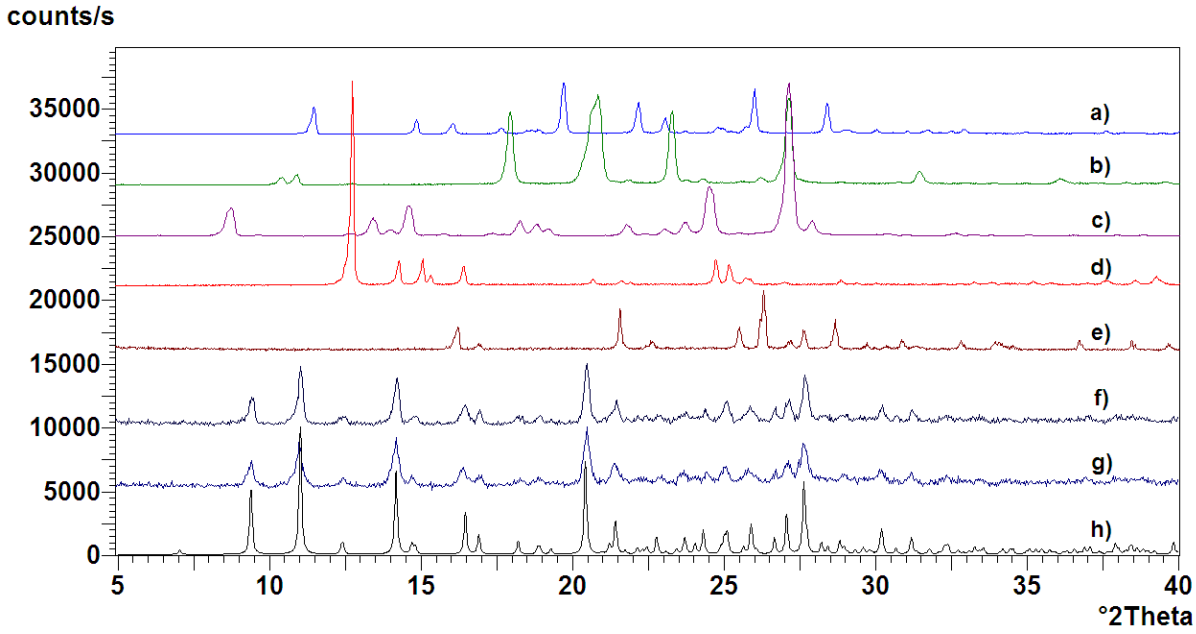

Figure S9. PXRD patterns for one-pot mechanochemical experiments: a) **napht**, b) **aap**, c) compound **Hnaap**, d) copper acetate monohydrate, e) **tfib**, f) compound Cu**(naap)$_2$·tfib** obtained by grinding of compound **Hnaap**, copper acetate monohydrate and **tfib** in ball mill for 50 min in the presence of a small quantity of nitromethane, g) compound Cu**(naap)$_2$·tfib** obtained by grinding of **napht**, **aap**, copper acetate monohydrate and **tfib** in ball mill for 60 min in the presence of a small quantity of nitromethane and h) calculated pattern for compound Cu**(naap)$_2$·tfib**.

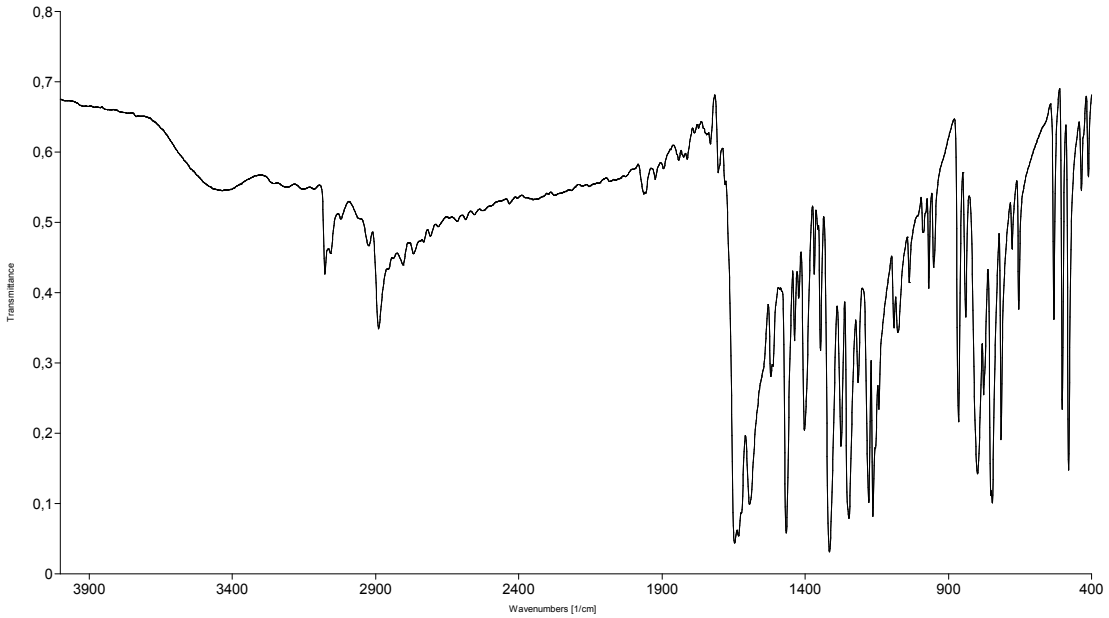

Figure S10. IR spectrum for pure **napht** reactant.

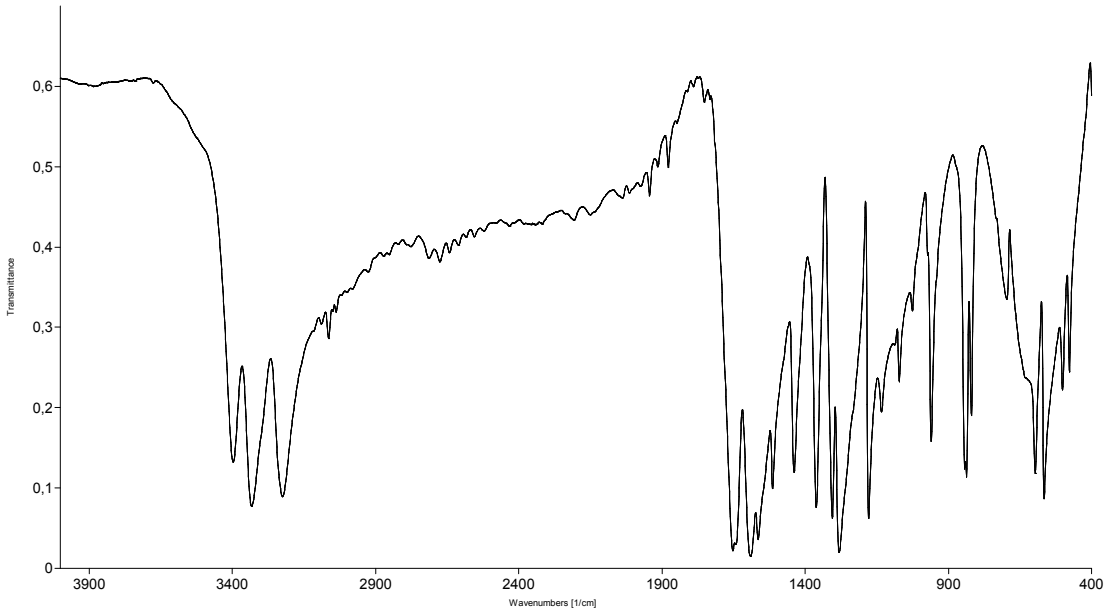

Figure S11. IR spectrum for pure **aap** reactant.

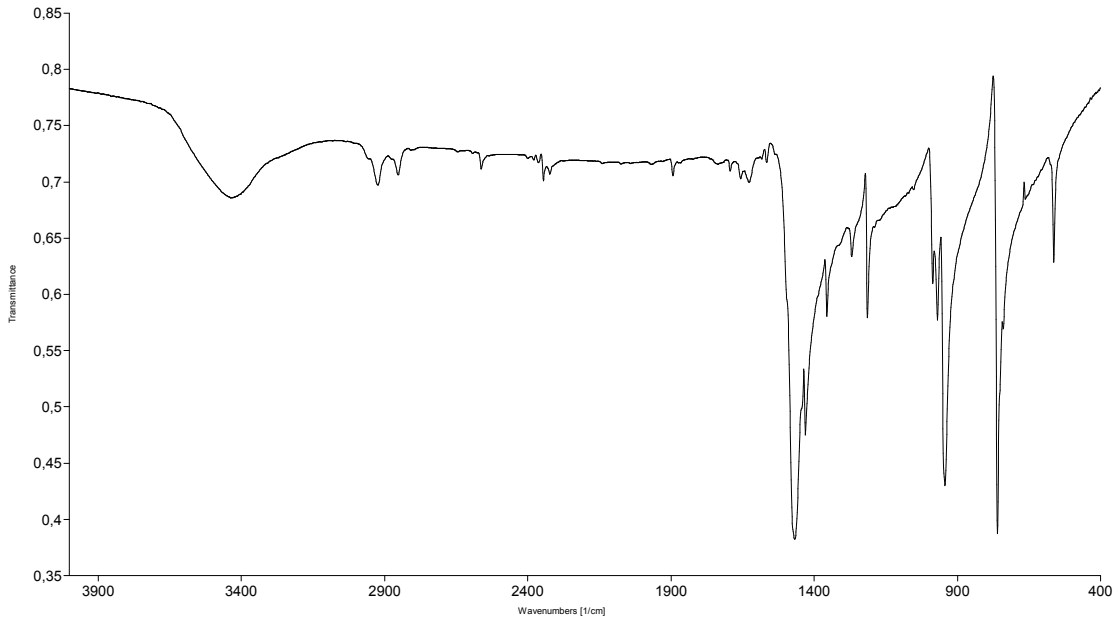

Figure S12. IR spectrum for pure **tfib** reactant.

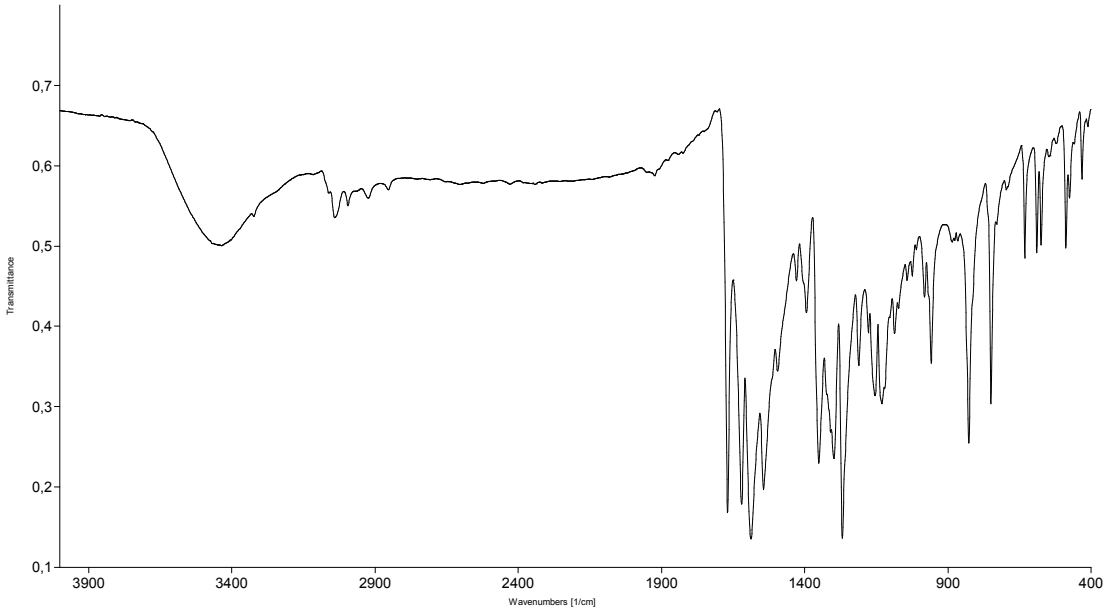

Figure S13. IR spectrum for **Hnaap** prepared by solution-based method.

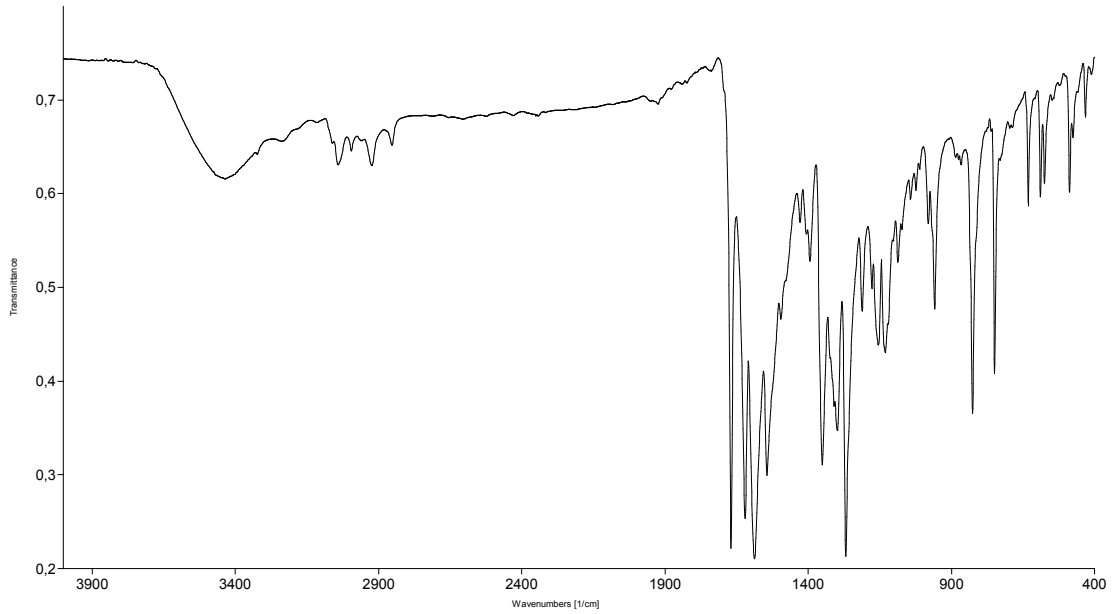

Figure S14. IR spectrum for **Hnaap** prepared by LAG.

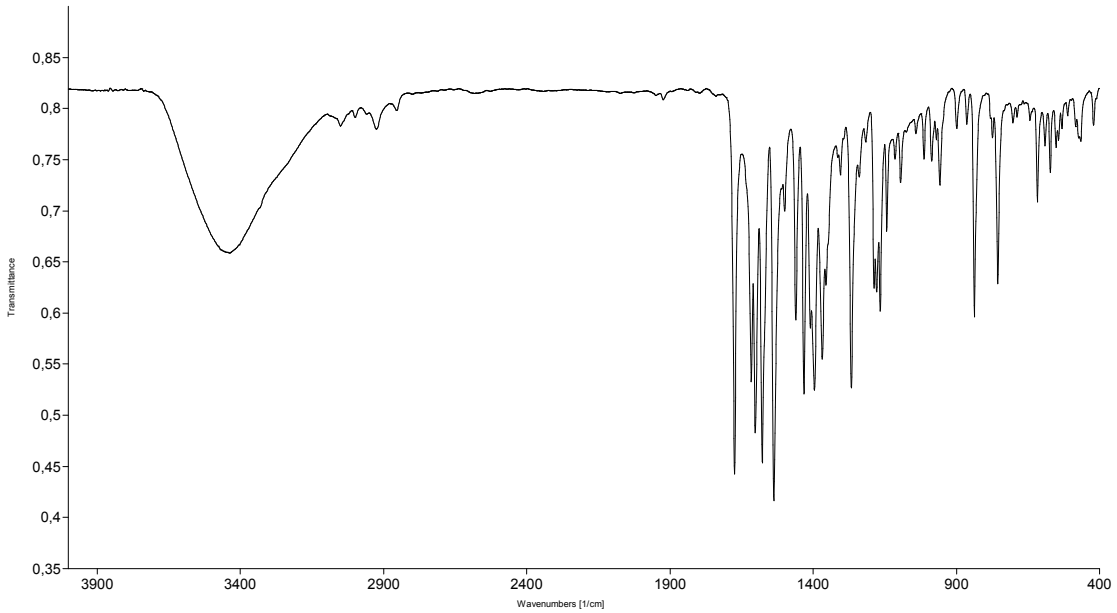

Figure S15. IR spectrum for Cu**(naap)$_2$** prepared by solution-based method.

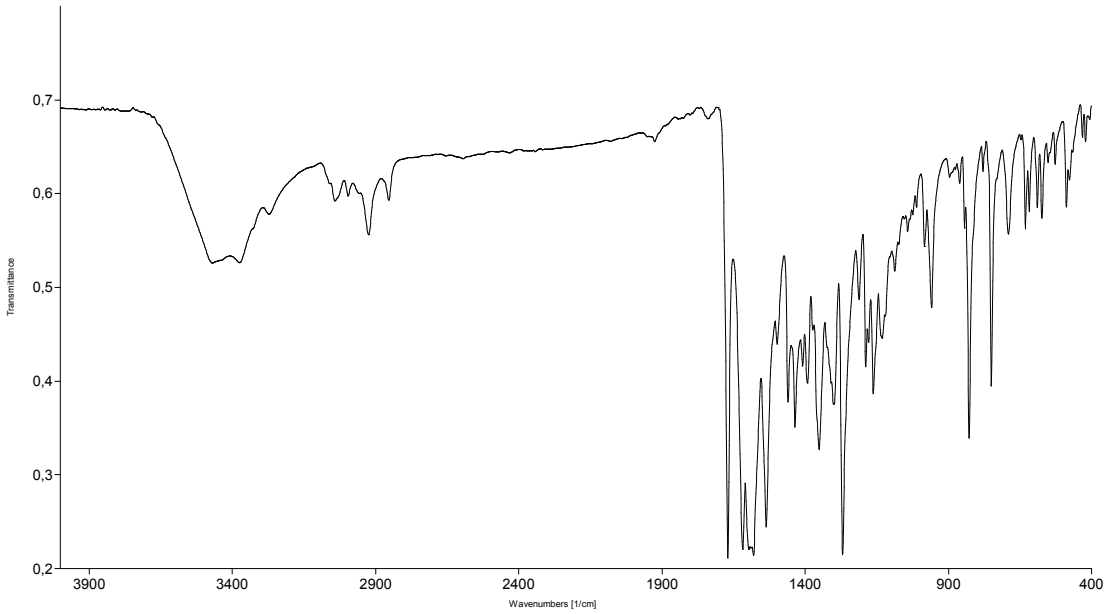

Figure S16. IR spectrum for the product of grinding of copper acetate monohydrate and compound **1**, i.e. the acetic acid solvate of compound Cu**(naap)$_2$**.

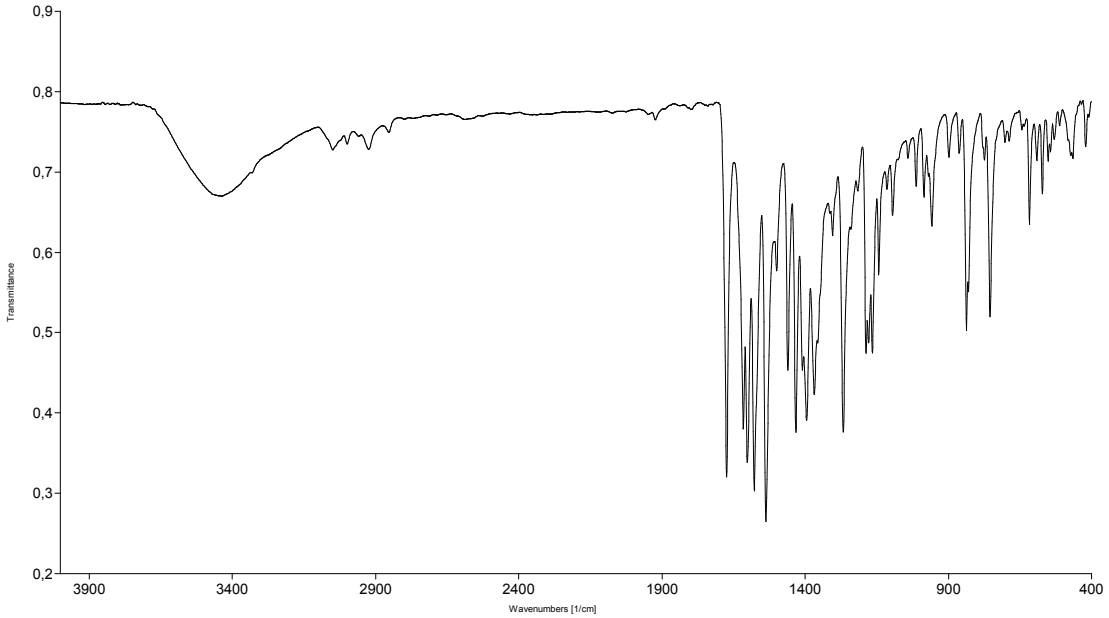

Figure S17. IR spectrum for the product of grinding of copper acetate monohydrate and compound **Hnaap** after isothermal experiment at 200 °C.

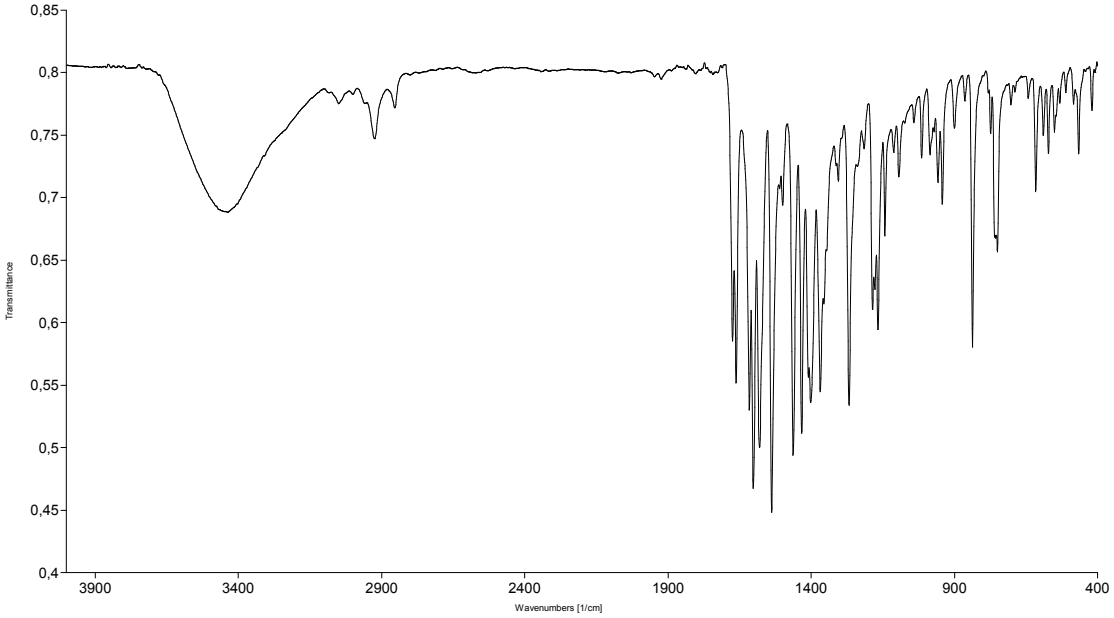

Figure S18. IR spectrum for Cu**(naap)$_2$·tfib** prepared by solution-based method.

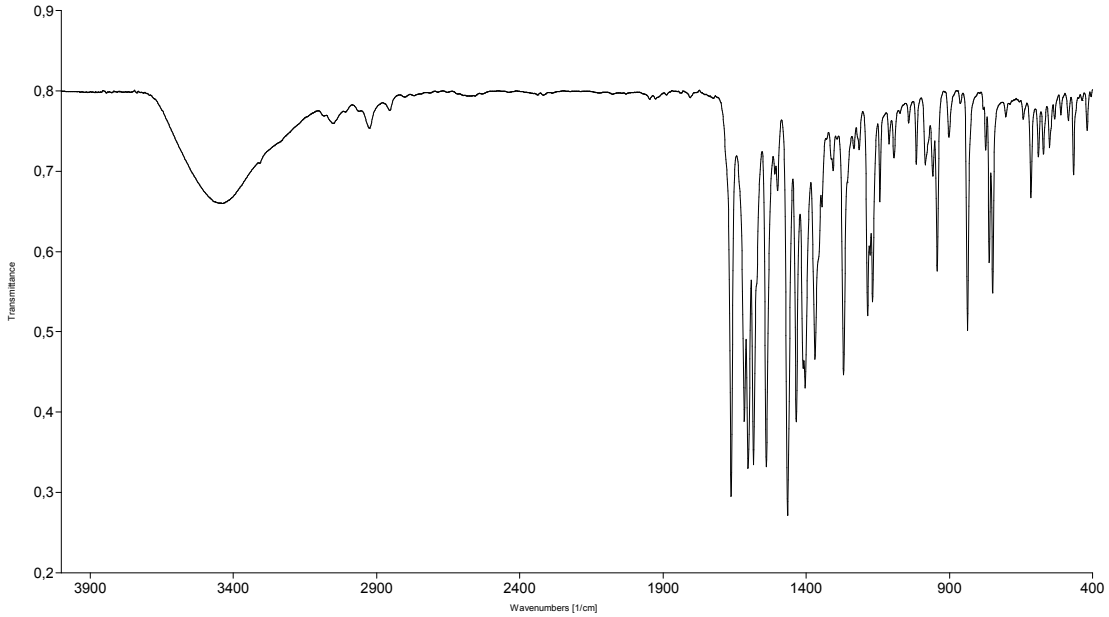

Figure S19. IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of compound Cu**(naap)$_2$** and **tfib**.

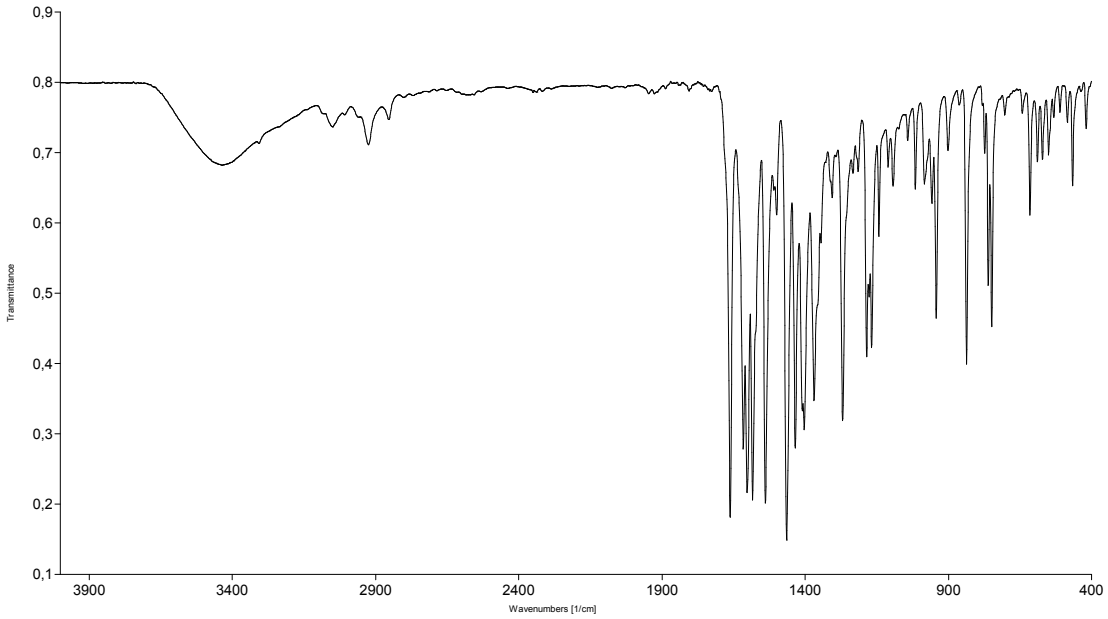

Figure S20. IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of compound **Hnaap** and copper acetate monohydrate and **tfib**.

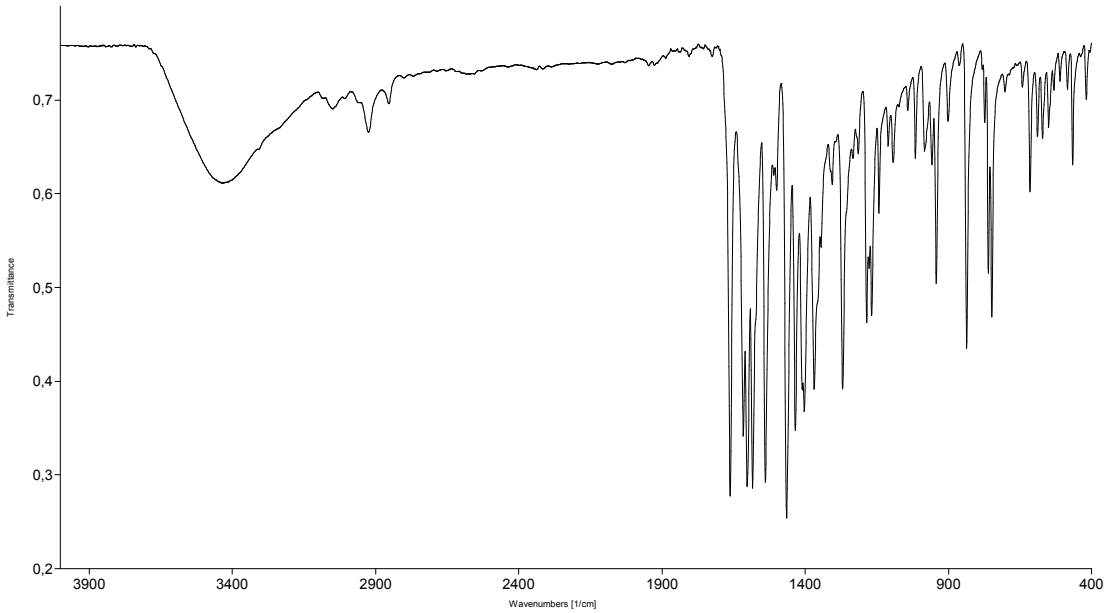

Figure S21. IR spectrum for Cu**(naap)$_2$·tfib** prepared by grinding of **napht**, **aap**, copper acetate monohydrate and **tfib**.

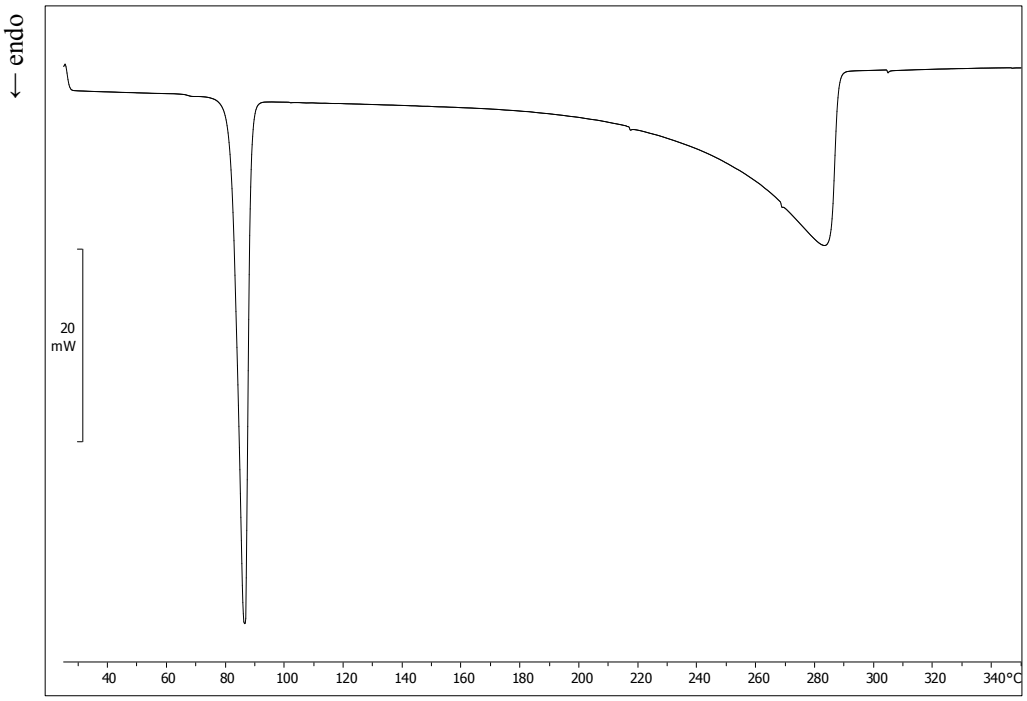

Figure S22. DSC curve for pure **napht** reactant.

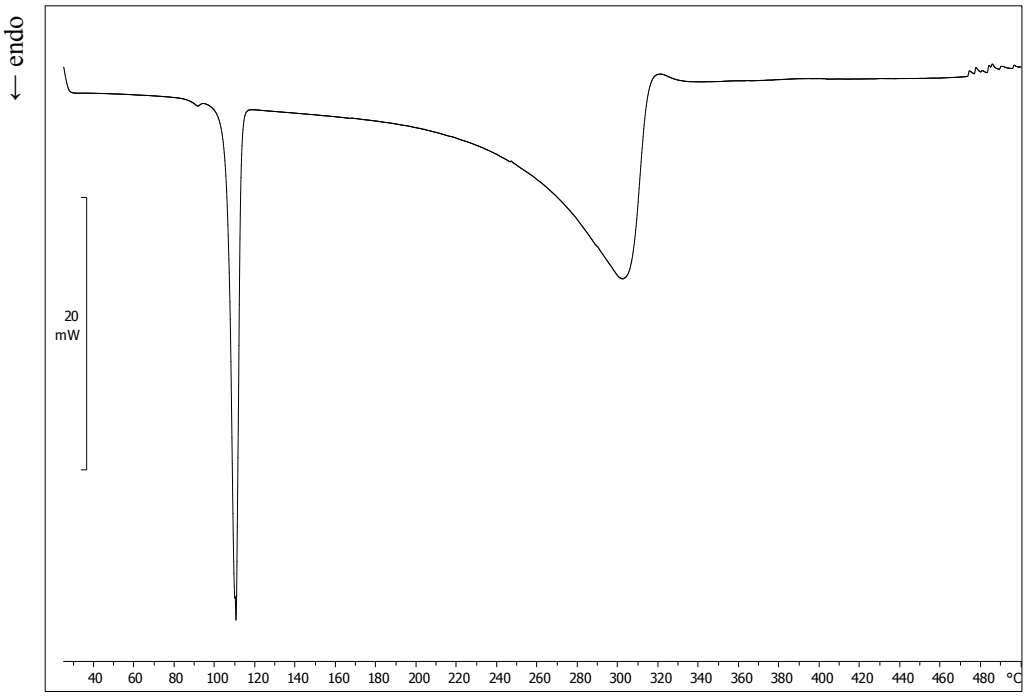

Figure S23. DSC curve for pure **aap** reactant.

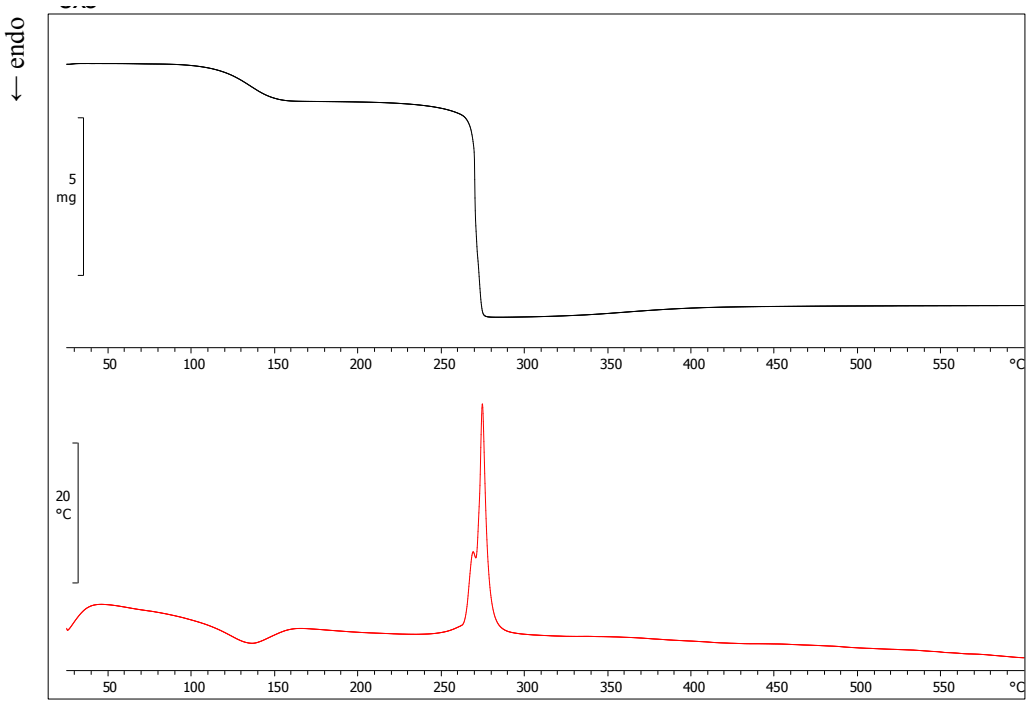

Figure S24. TG (black) and DTA (red) curve for pure copper acetate monohydrate.

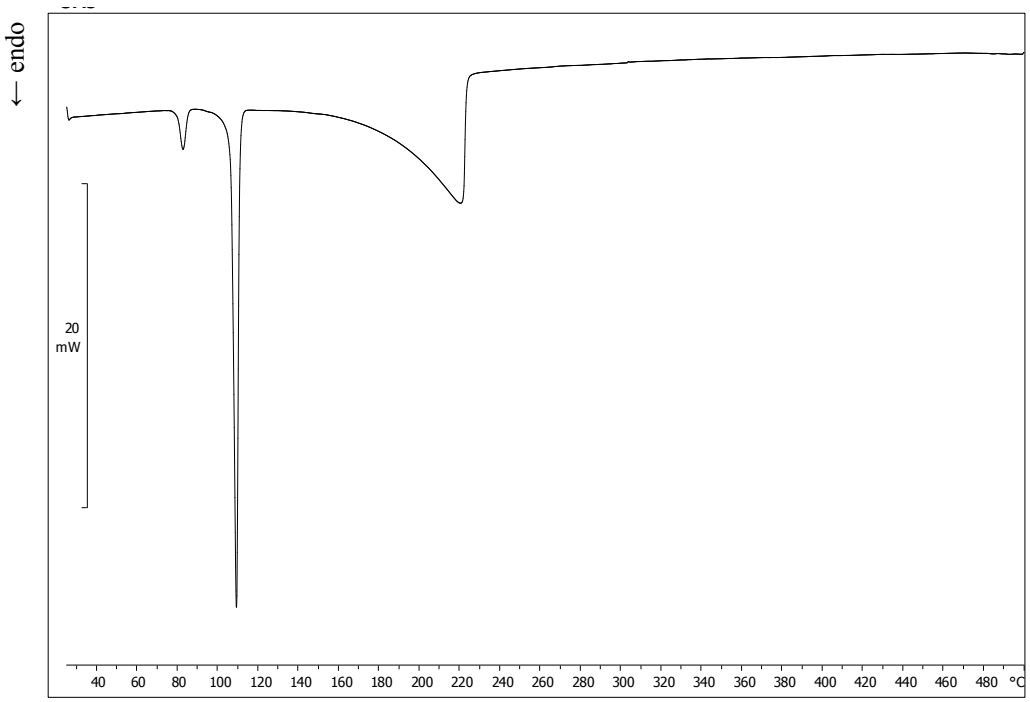

Figure S25. DSC curve for pure **tfib** reactant.

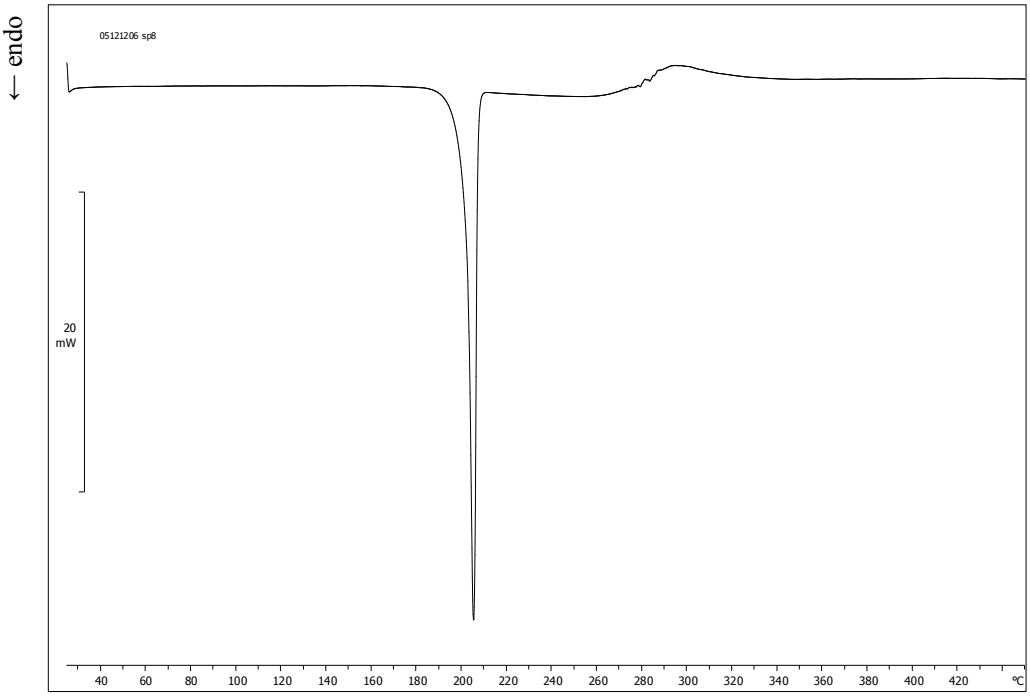

Figure S26. DSC curve for **Hnaap** synthesised by solution-based method.

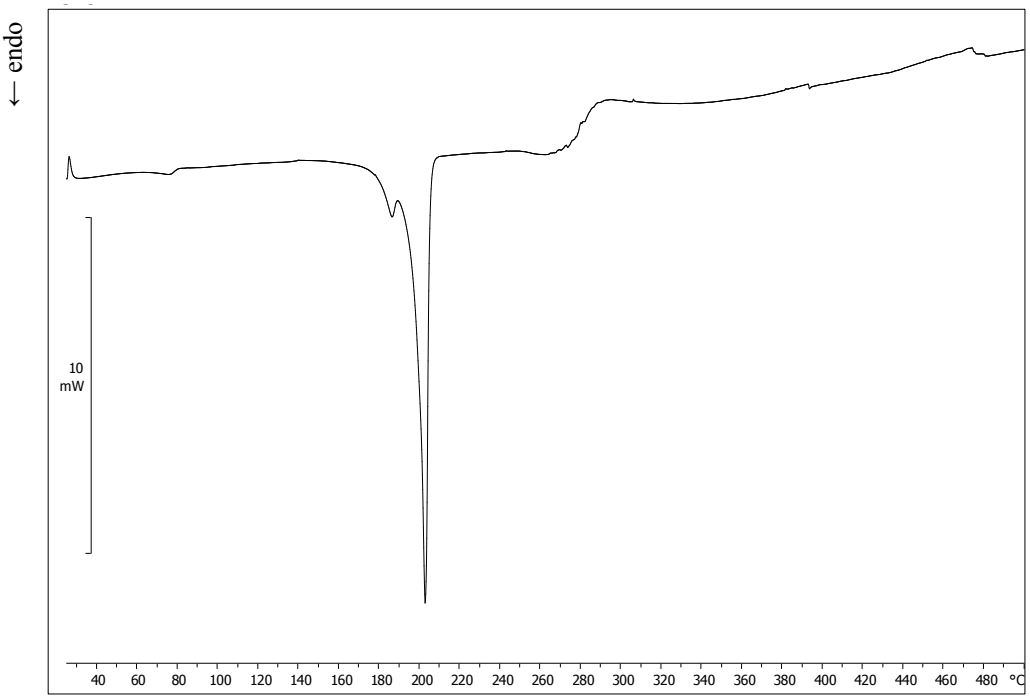

Figure S27. DSC curve for **Hnaap** synthesised by grinding in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

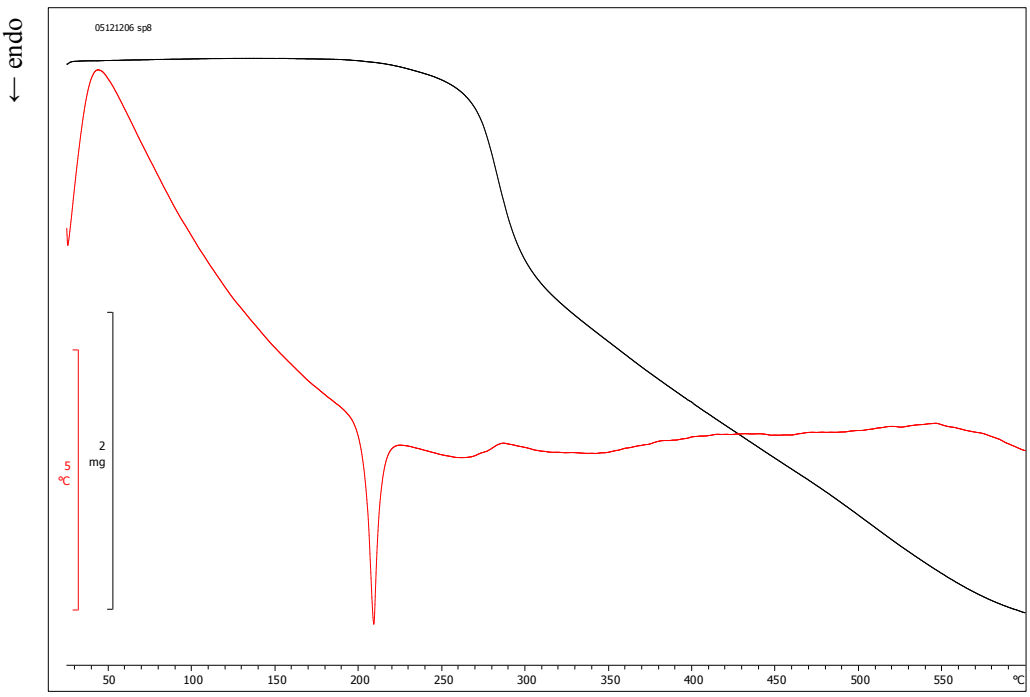

Figure S28. TG (black) and DTA (red) curve for **Hnaap** synthesised by solution-based method.

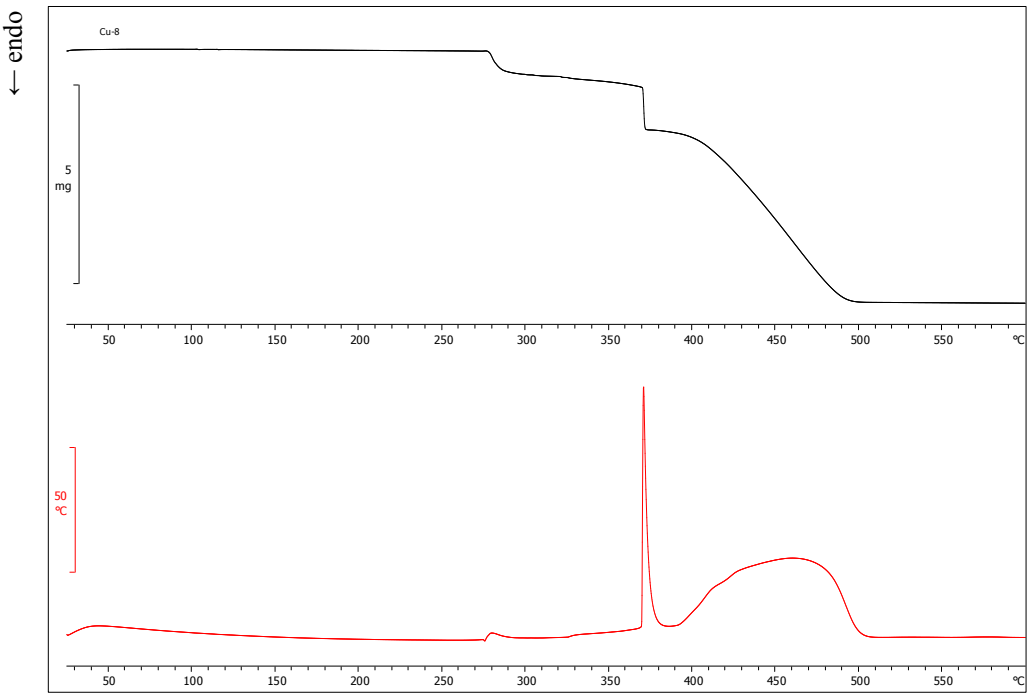

Figure S29. TG (black) and DTA (red) curve for Cu**(naap)$_2$** obtained by solution-based method.

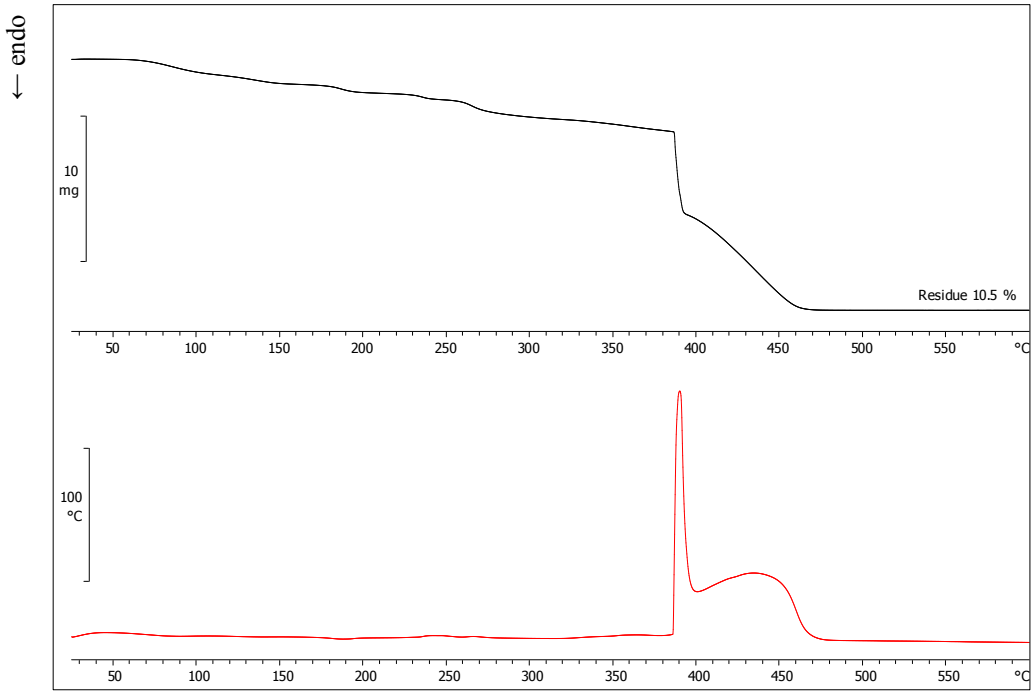

Figure S30. TG (black) and DTA (red) curve for the product (i.e. the acetic acid solvate of compound Cu**(naap)$_2$**) obtained by grinding of copper acetate and compound **Hnaap** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

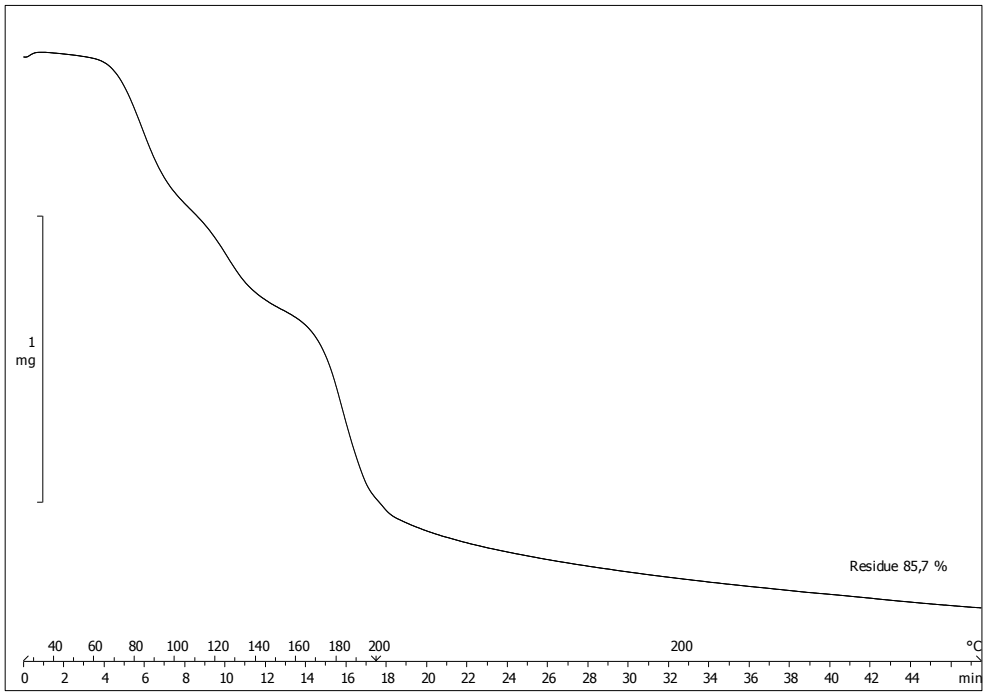

Figure S31. TG curve of isothermal experiment at 200 °C for the product of grinding of copper acetate monohydrate and compound **Hnaap**, i.e. the acetic acid solvate of compound Cu**(naap)$_2$**.

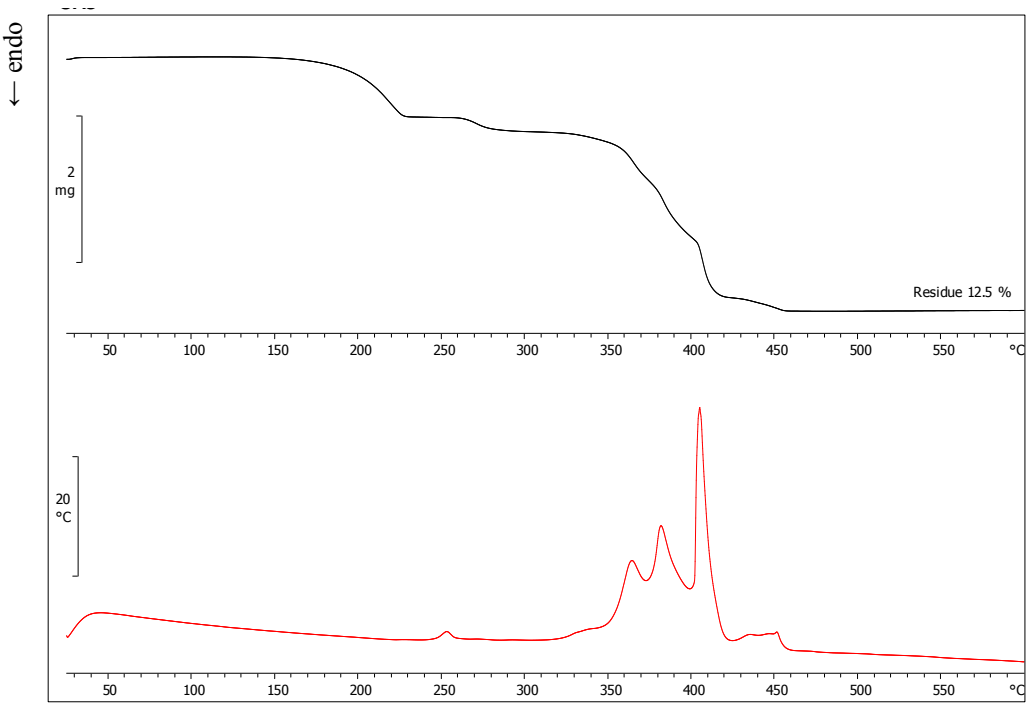

Figure S32. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by solution-based method.

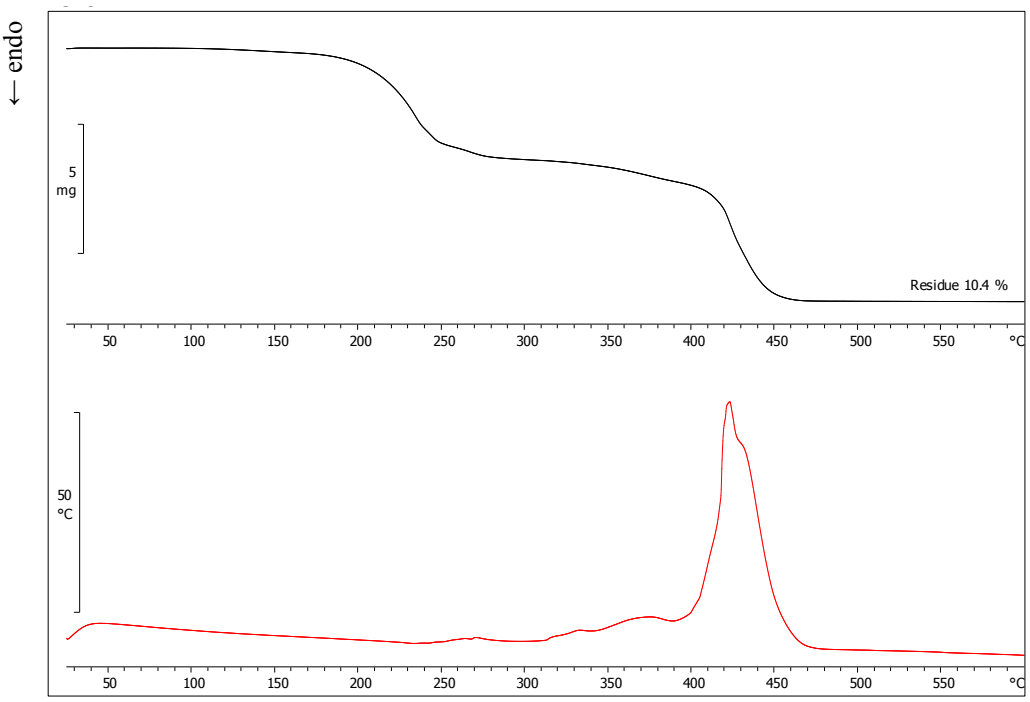

Figure S33. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of compound Cu**(naap)$_2$** and **tfib** in ball mill for 60 min in the presence of a small quantity of nitromethane.

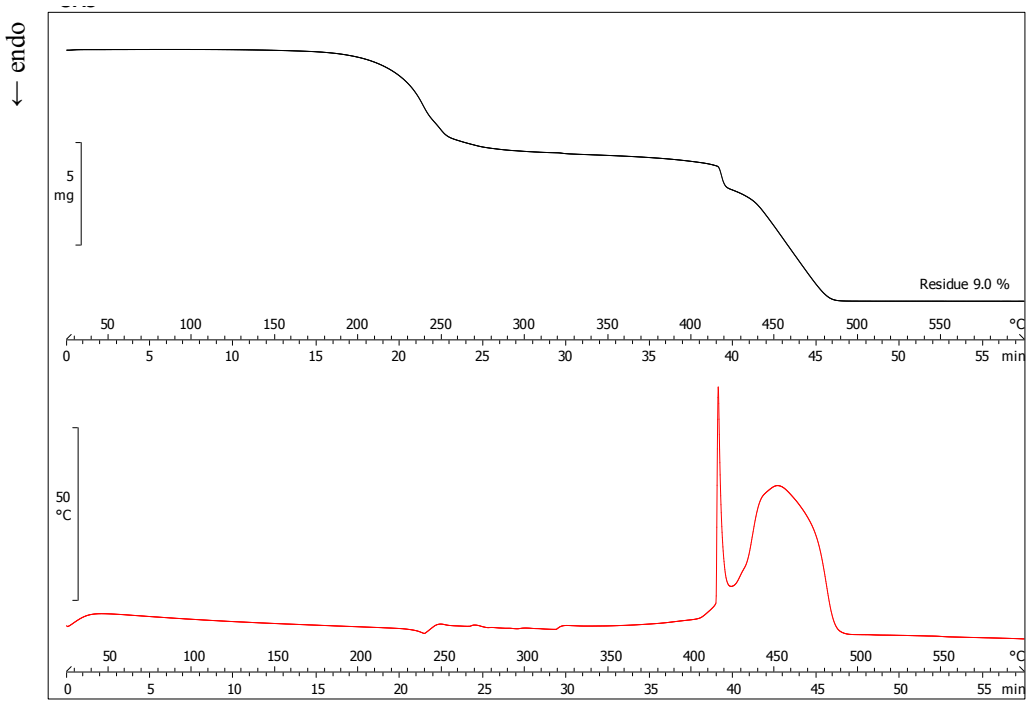

Figure S34. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, compound **Hnaap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

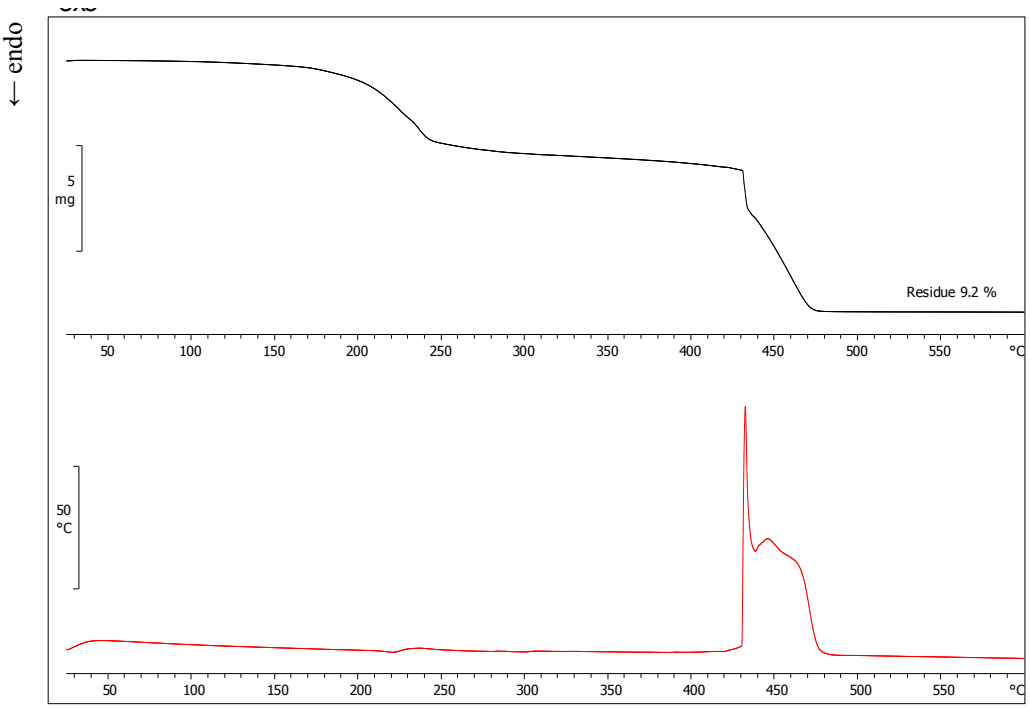

Figure S35. TG (black) and DTA (red) curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, **napht**, **aap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

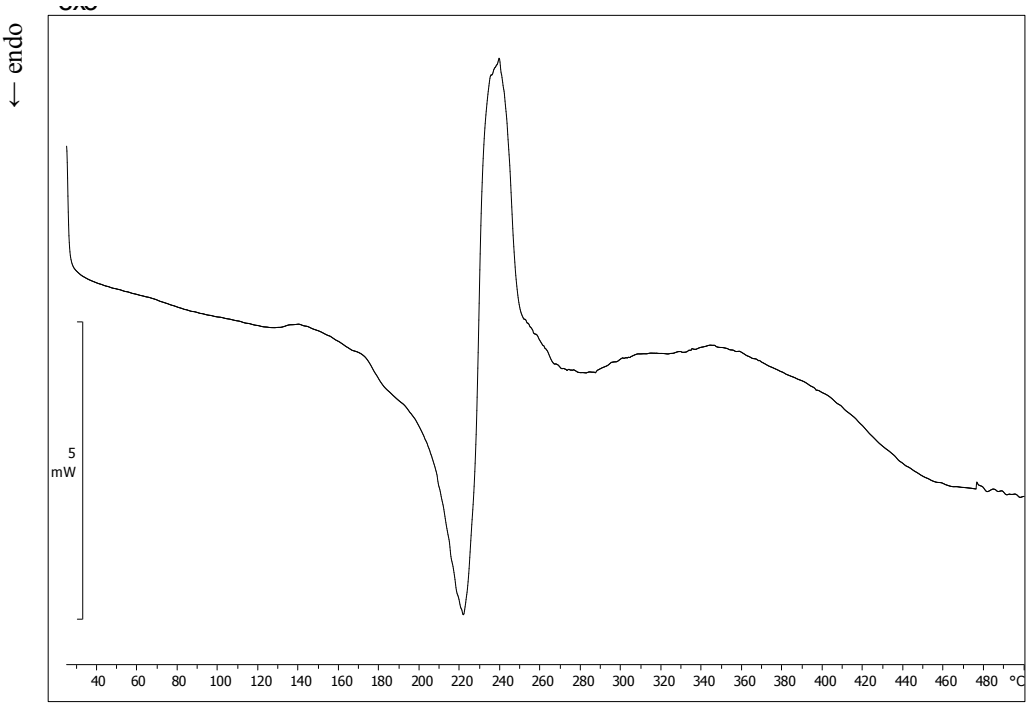

Figure S36. DSC curve for Cu**(naap)$_2$·tfib** obtained by grinding of copper acetate monohydrate, **napht**, **aap** and **tfib** in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

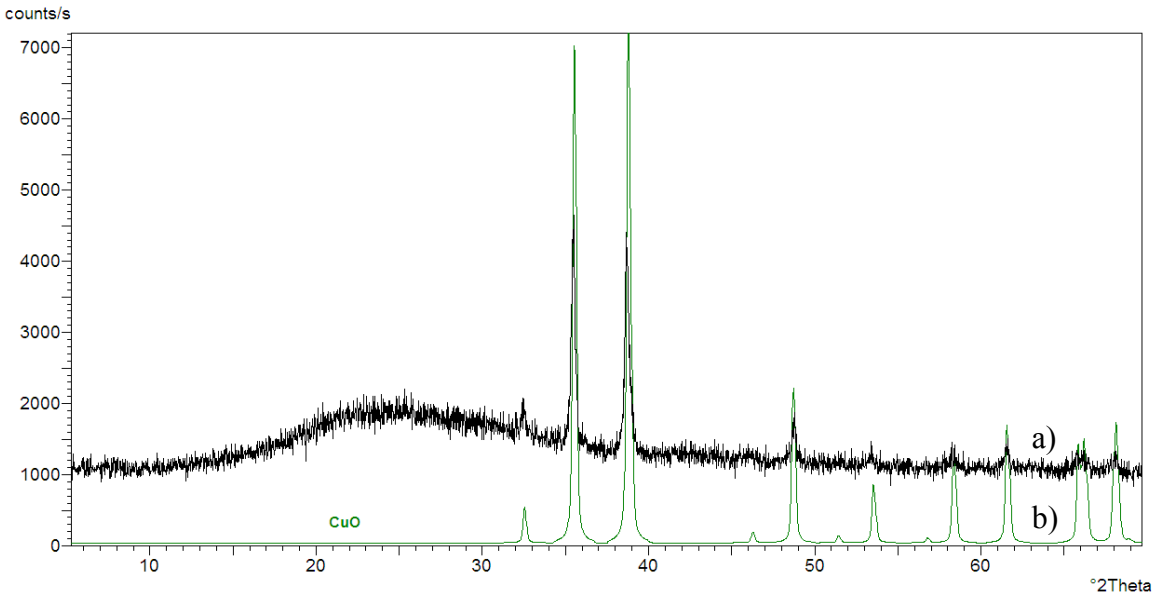

Figure S37. a) PXRD pattern of residue after TG experiment of compound Cu**(naap)$_2$** and b) calculated pattern for CuO.

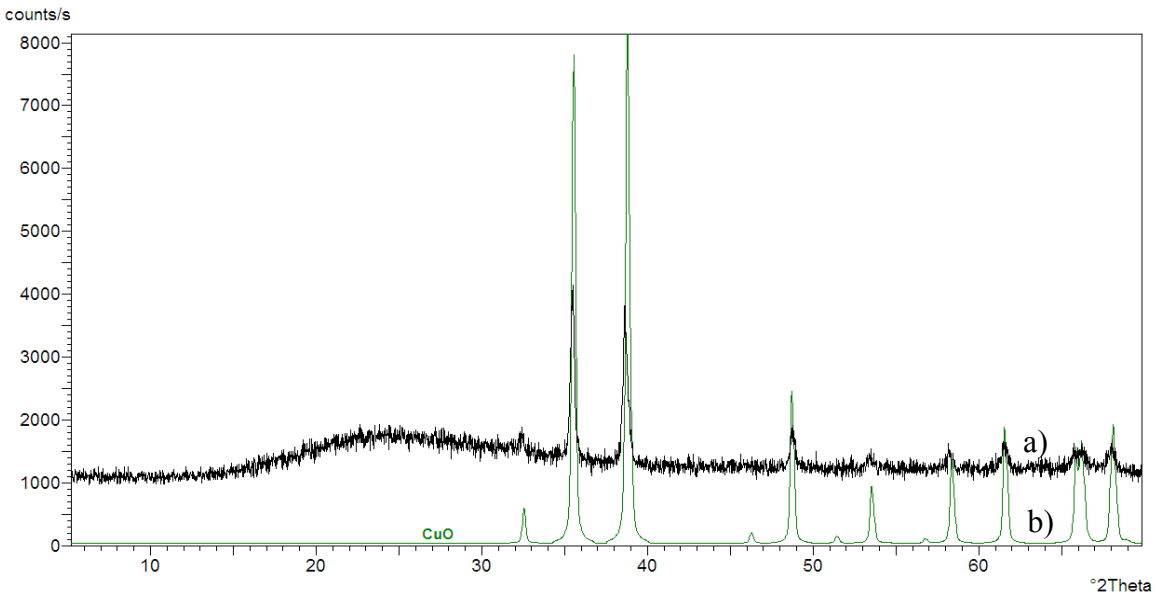

Figure S38. a) PXRD pattern of residue after TG experiment of compound Cu**(naap)$_2$·tfib** and b) calculated pattern for CuO.