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SUPPORTING INFORMATION

Mechanochemical and solution-based cocrystallization of 9,10-phenanthrenequinone and thiourea

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EXPERIMENTAL DETAILS

MATERIALS

The starting material, 9,10-phenanthrenequinone (**phen**) was obtained from Merck. Thiourea (**tu**), acetonitrile and benzene were obtained from Kemika. Ethanol was purchased from Gram-Mol.

MECHANOCHEMICAL SYNTHESIS

Equimolar quantities of **phen** (100.0 mg, 0.481 mmol) and **tu** (36.6 mg, 0.481 mmol) were placed in a 10 mL stainless steel jar along with 30 μL of acetonitrile and two stainless steel balls 7 mm in diameter. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency. The procedure was repeated for mixtures of **phen**:**tu** with molar ratios of 2:1 (100.0 mg, or 0.481 mmol, of **phen** to 18,3 mg, or 0.241 mmol, of **tu**) and 1:2 (100.0 mg, or 0.481 mmol, of **phen** to 73.2 mg, or 0.962 mmol, of **tu**).

SOLUTION SYNTHESIS

Equimolar quantities of **phen** (140 mg, 0.672 mmol) and **tu** (52.0 mg, 0.672 mmol), were dissolved in a hot mixture of ethanol and benzene (4.0 mL, 1:3). The resulting mixture was left at room temperature. Orange crystals appeared after half an hour, and were separated from the mother liquor by filtration.

THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823^{e} module. The samples were placed in sealed aluminium pans (40 μL) with three holes made on the top cover, and heated in flowing nitrogen (150 mL min^{-1}) from 25 °C to 500 °C at a rate of 10 °C min^{-1}. The data collection and analysis was performed using the program package STAR^{e} Software 9.01.[1]

FTIR SPECTROSCOPY

Infrared spectra in the range of 4000 to 400 cm^{-1} 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 (**phen**)(**tu**) were 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 293 K. 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 and CrysAlis RED were employed for data collection, cell refinement, and data reduction.[2] The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.[3] 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.[4] The molecular structures of compounds are presented by ORTEP-3,[5] and their molecular packing projections were prepared by Mercury.[6]

POWDER X-RAY DIFFRACTION EXPERIMENTS

PXRD experiments on 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 5 to 40° (2θ) with steps of 0.02 – 0.03°, and the measuring time was 0.2 – 0.5 s per step. Data collection and analysis was performed using the program package Philips X'Pert.[7]

References

1. STARe Software V.9.01., MettlerToledo GmbH, 2006.
2. Oxford Diffraction, Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis CCD and CrysAlis RED software, Version 1.170, 2003.
3. G. M. Sheldrick, *Acta Cryst. A64* **2008**,112.
4. L. J. Farrugia, WinGX, *J. Appl. Cryst.* **1999**, 32, 837.
5. L. J. Farrugia, ORTEP-3 for Windows, *J. Appl. Cryst.* **1997**, 30, 565.
6. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. v. d. Streek and P. A. Wood, *J. Appl. Crystallogr.* **2008**, 41, 466.
7. Philips X'Pert Data Collector 1.3e, Philips Analytical B. V. Netherlands, 2001; Philips X'Pert Graphic & Identify 1.3e Philips Analytical B. V. Netherlands, 2001; Philips X'Pert Plus 1.0, Philips Analytical B. V. Netherlands, 1999.

Table S1. General and crystallographic data for (**phen**)(**tu**).

	Compound (**phen**)(**tu**)
Molecular formula	$(C_{14}H_8O_2)(CH_4N_2S)$
M_r	284.3
Crystal system	orthorhombic
Space group	*P bcn*
Crystal data:	
a / Å	11.982(9)
b / Å	13.527(6)
c / Å	8.561(4)
α / °	90.00
β / °	90.00
γ / °	90.00
V / Å^3	1387.45(14)
Z	4
D_{calc} / g cm^{-3}	1.361
λ(MoK_α) / Å	0.71073
T / K	295
Crystal size / mm^3	0.53 x 0.77 x 0.32
μ / mm^{-1}	0.235
$F(000)$	592
Refl. collected/unique	6783 / 1502
Data/restraints/parameters	100
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.212; −0.185
$R[F^2>4\sigma(F^2)]$	0.037
$wR(F^2)$	0.094
Goodness-of-fit, S	0.946

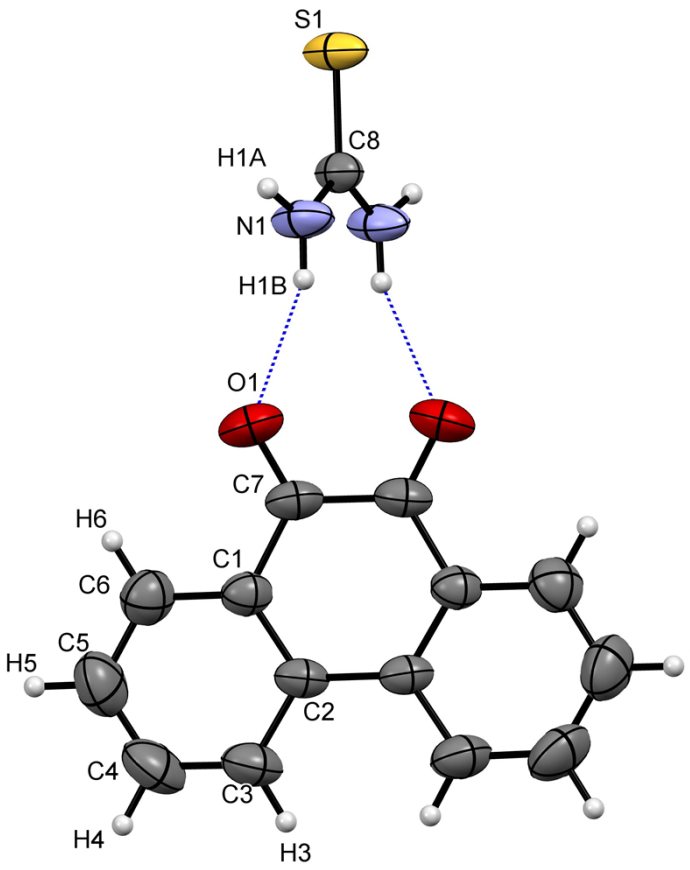

Figure S1. Molecular structure of (**phen**)(**tu**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 45 % probability level, hydrogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

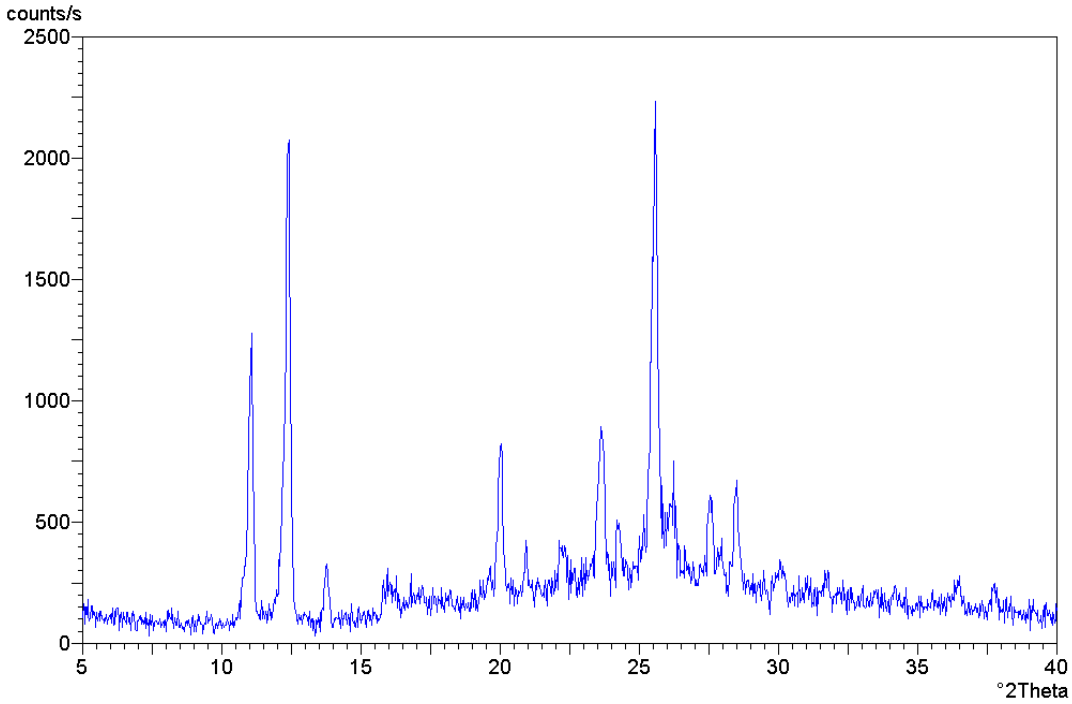

Figure S2. PXRD pattern of pure **phen** reactant.

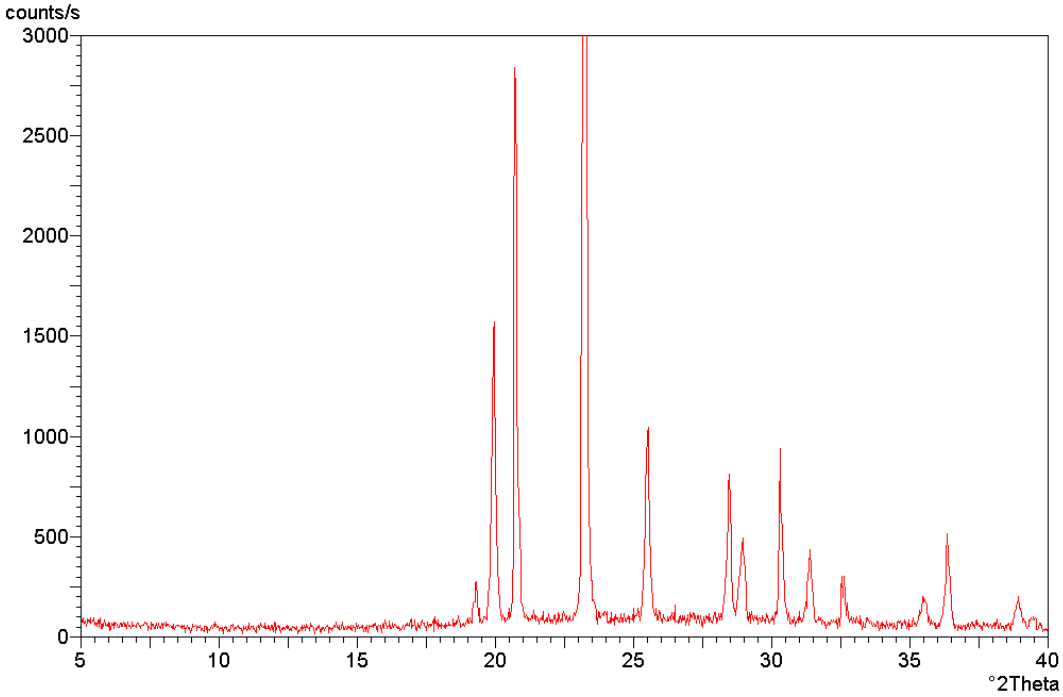

Figure S3. PXRD pattern of pure **tu** reactant.

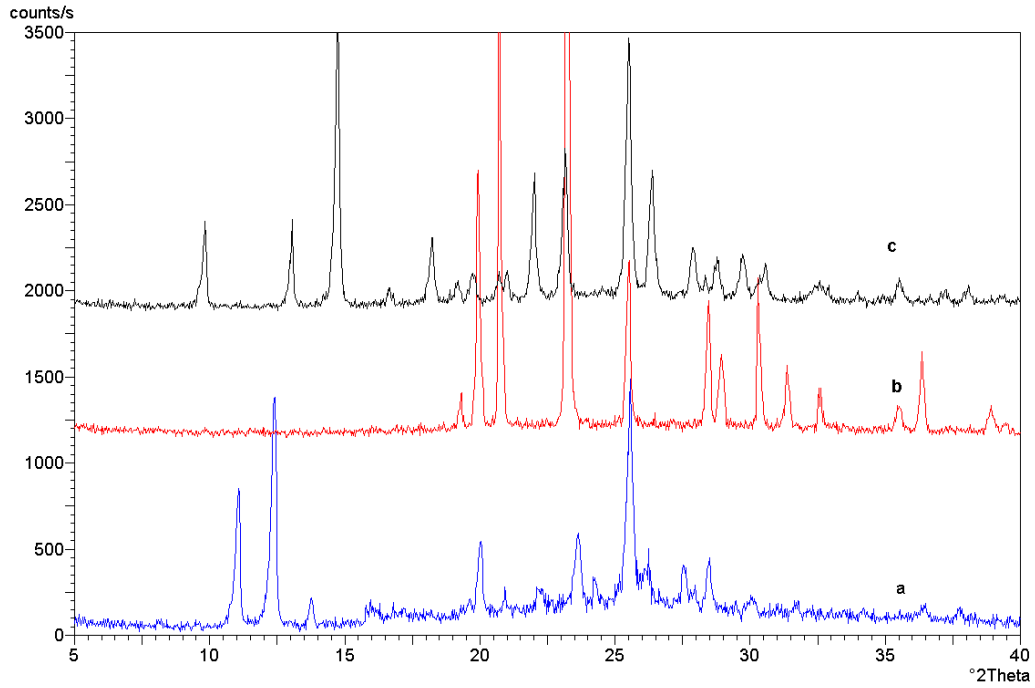

Figure S4. PXRD patterns of: a) **phen**, b) **tu**, c) product obtained by grinding an equimolar amount of **phen** and **tu** in a ball mill for 30 min in the presence of acetonitrile.

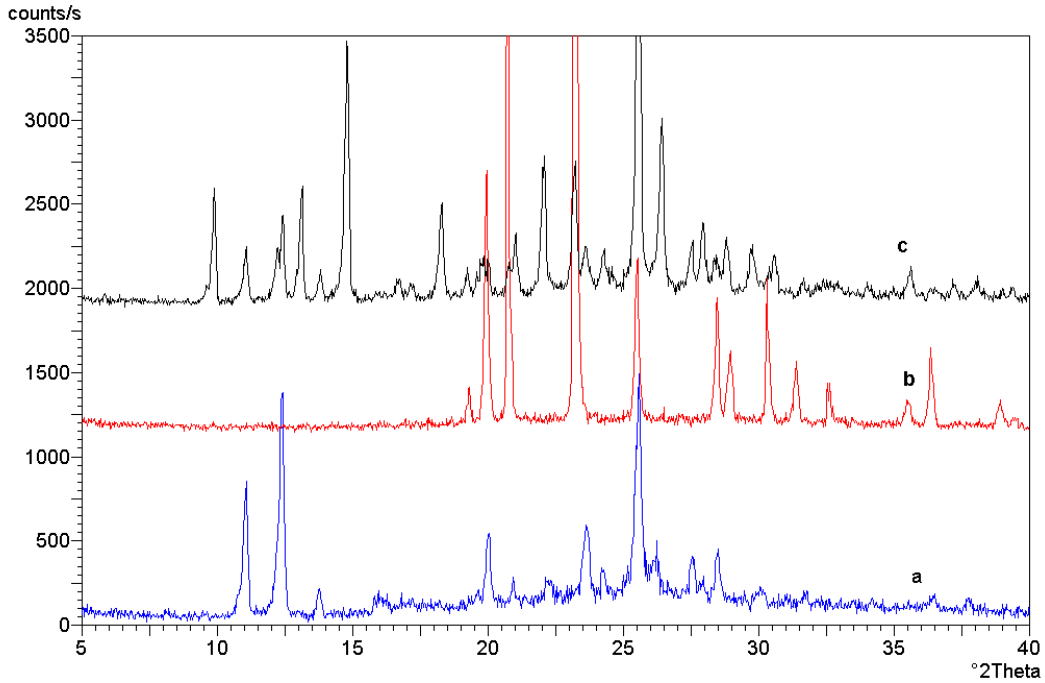

Figure S5. PXRD patterns of: a) **phen**, b) **tu**, c) product obtained by grinding a mixture with a 2:1 molar ratio of **phen** to **tu** in a ball mill for 15 min in the presence of 15 μL of acetonitrile.

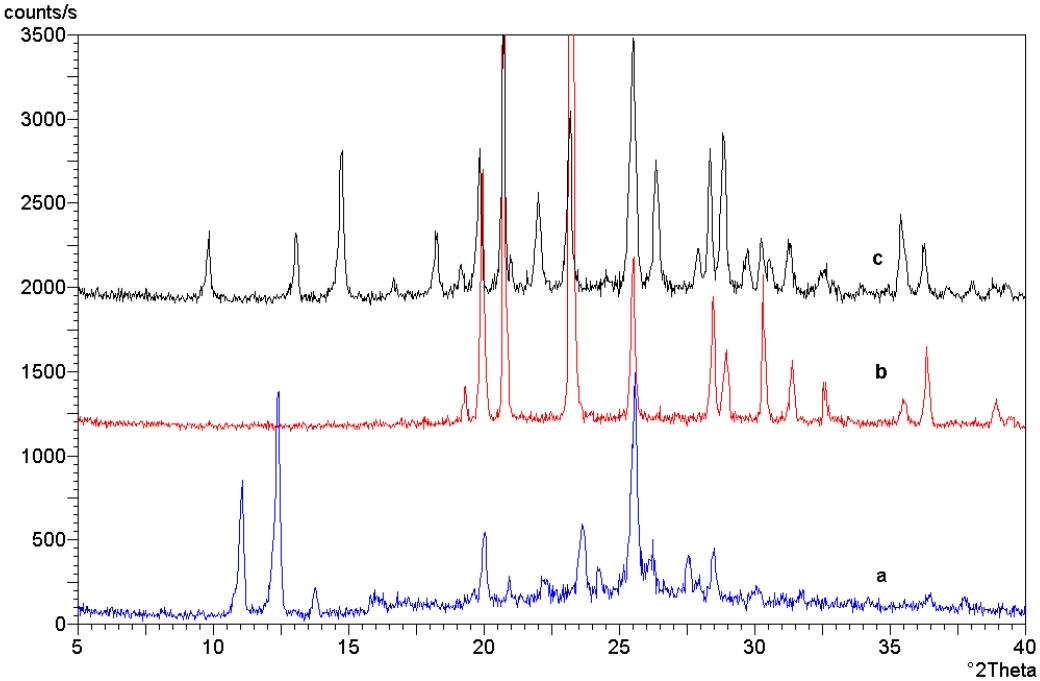

Figure S6. PXRD patterns of: a) **phen**, b) **tu**, c) product obtained by grinding a mixture with a 1:2 molar ratio of **phen** to **tu** in a ball mill for 15 min in the presence of 15 μL of acetonitrile.

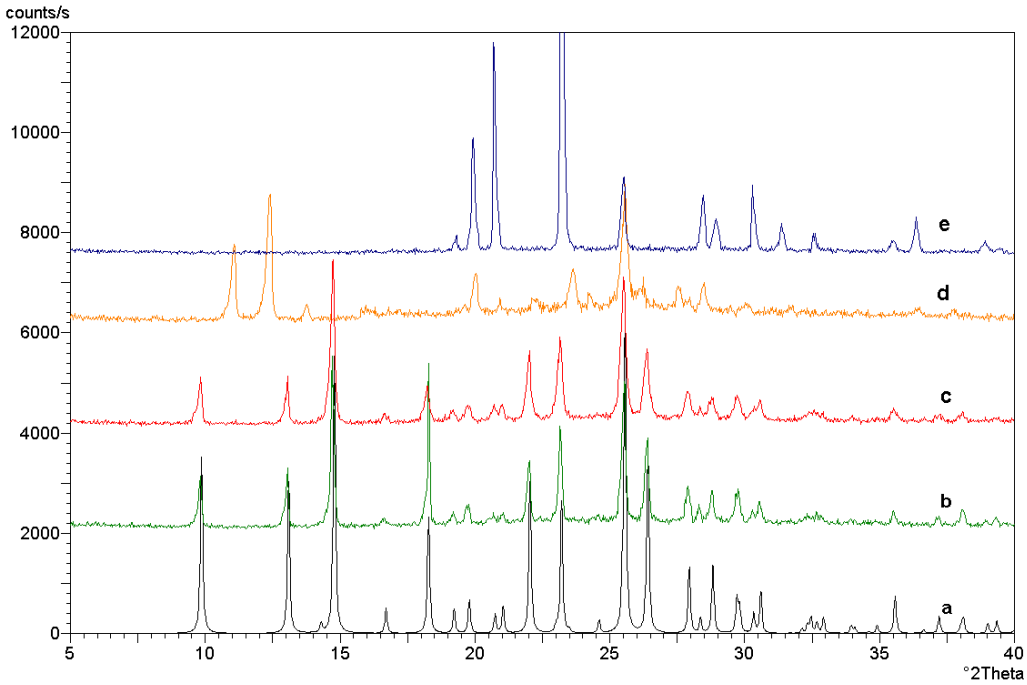

Figure S7. PXRD patterns for mechanochemical and solution-based experiments involving **phen** and **tu**: a) **calculated** pattern of cocrystal (**phen**)(**tu**), b) (**phen**)(**tu**) obtained by solution synthesis, c) (**phen**)(**tu**) obtained by mechanochemical synthesis, d) **phen**, e) **tu**.

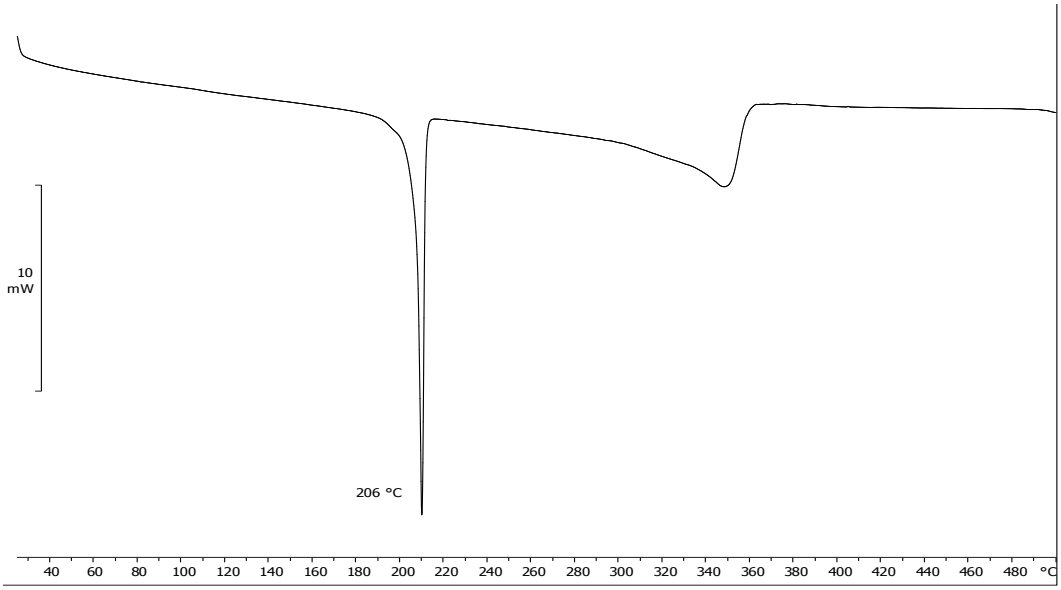

Figure S8. DSC curve of the pure **phen** reactant.

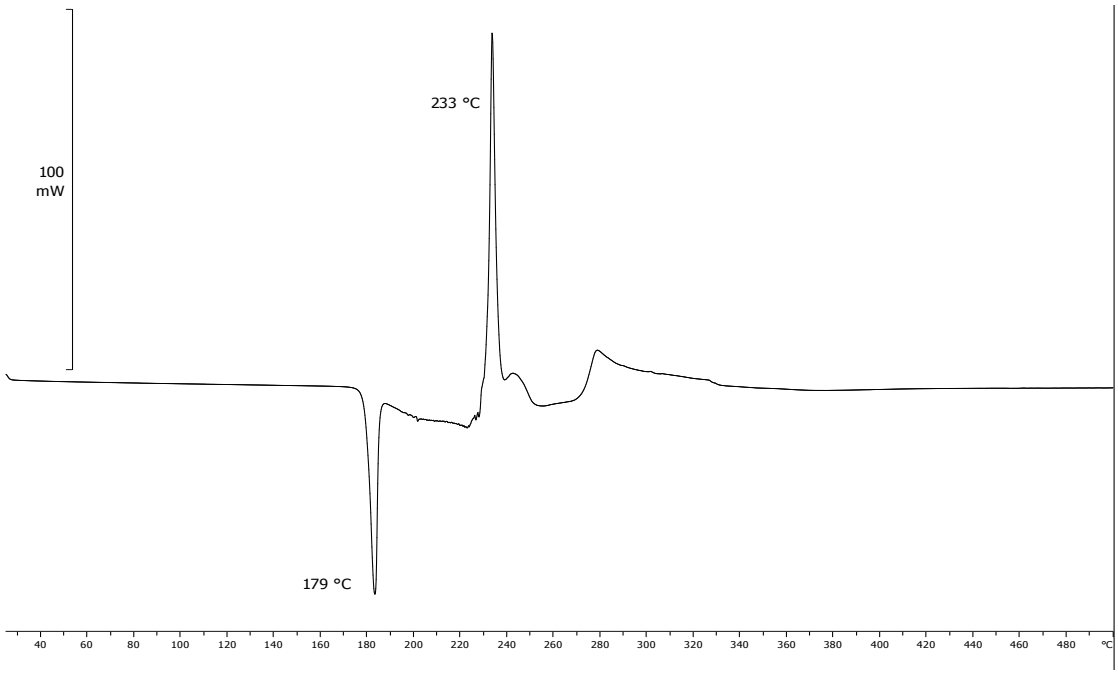

Figure S9. DSC curve of the pure **tu** reactant.

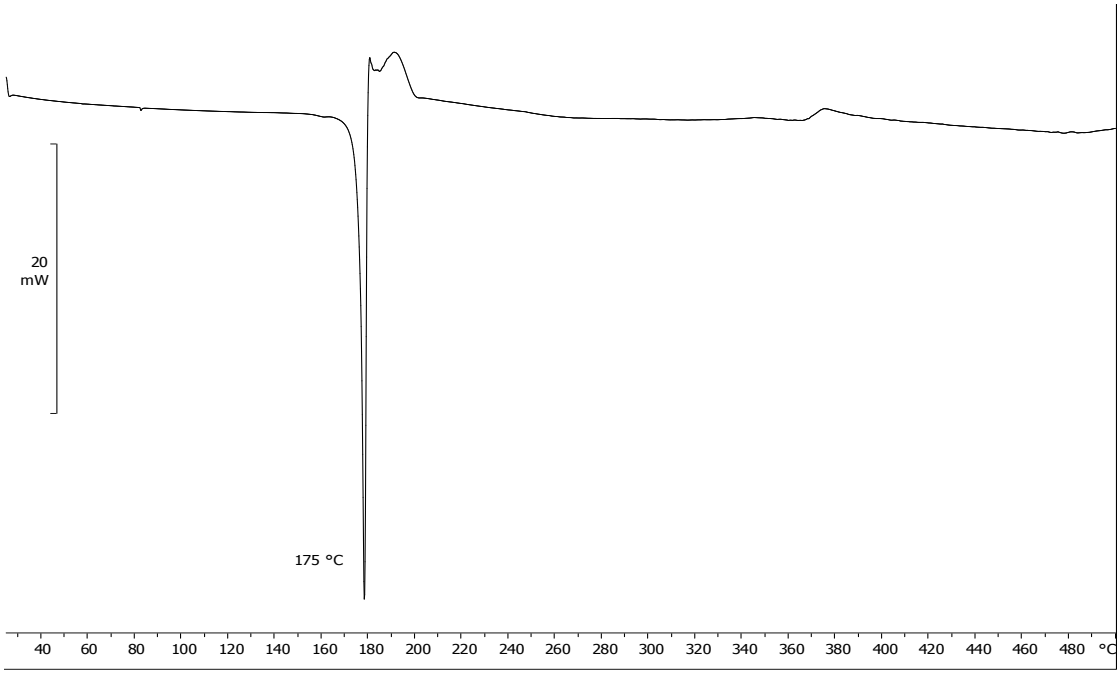

Figure S10. DSC curve of the (**phen**)(**tu**) cocrystal obtained by solution synthesis.

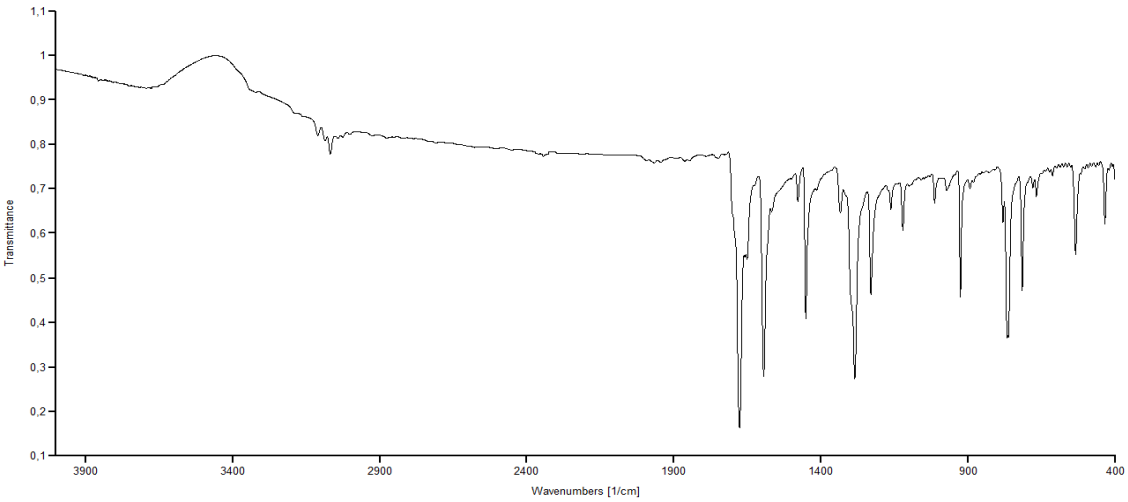

Figure S11. IR spectrum of the pure **phen** reactant.

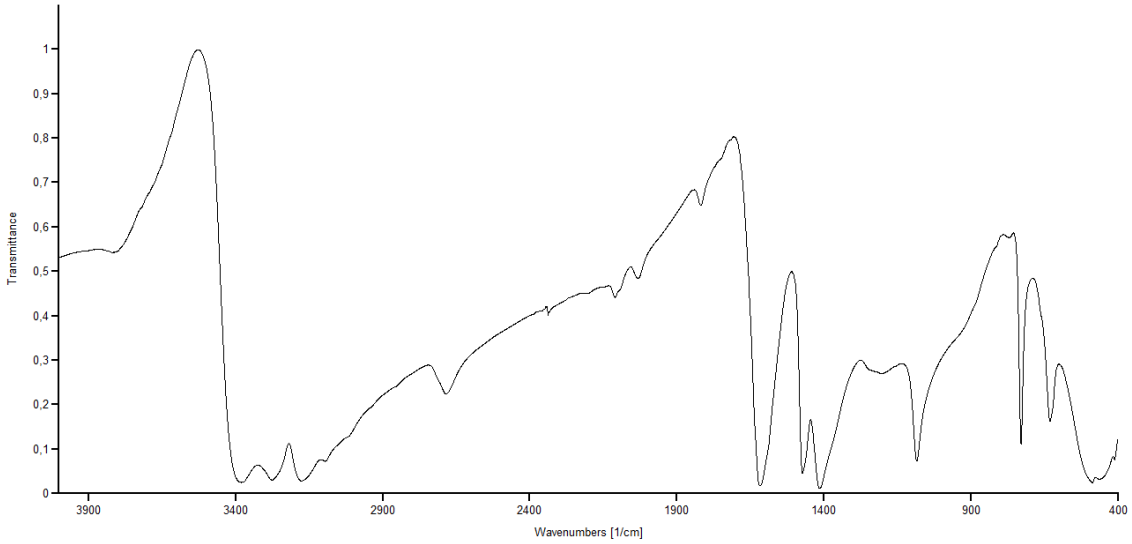

Figure S12. IR spectrum of the pure **tu** reactant.

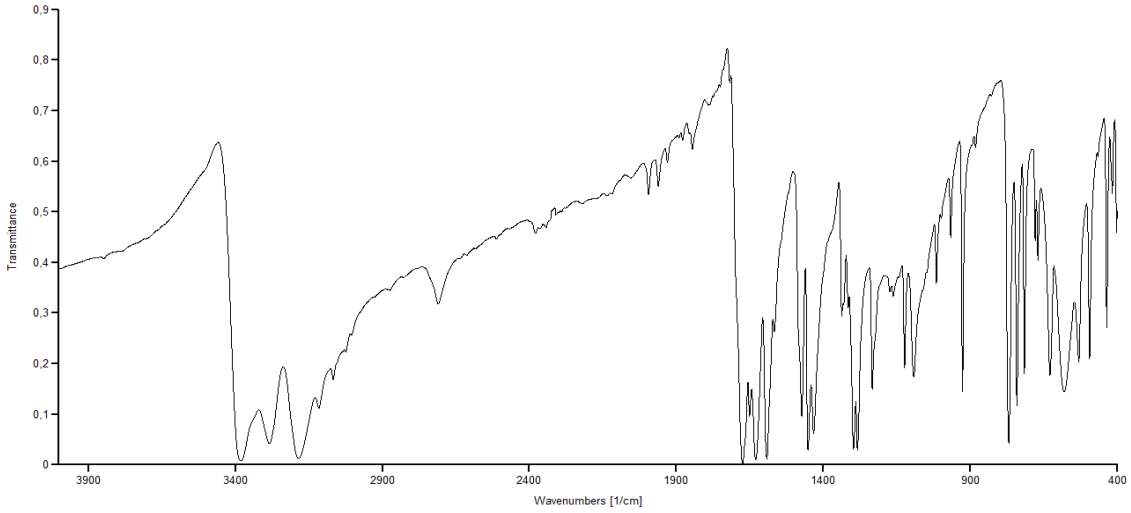

Figure S13. IR spectrum of the (**phen**)(**tu**) cocrystal.