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Supporting Information

Isostructural materials of varying properties achieved via structurally equivalent donors and acceptors in halogen-bonded cocrystals

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EXPERIMENTAL DETAILS

COCRYSTALS OF **TFIB**:

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(**TMO**)

200 mg of **tfib** was placed in a 10 mL stainless steel grinding jar along with 51 µL **tmo** and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfib**)·(**tmo**).

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(**TOX**)

200 mg of **tfib** was placed in a 10 mL stainless steel grinding jar along with 47 µL **tox** and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfib**)·(**tox**).

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(MORPHOLINE)

200 mg of **tfib** was placed in a 10 mL stainless steel grinding jar along with 44 µL morpholine and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfib**)·(morpholine).

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(DIOXANE)

200 mg of **tfib** was placed in a 10 mL stainless steel grinding jar along with 45 µL dioxane and two 7 mm-diameter stainless steel grinding balls. The mixture was then

milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated incomplete conversion of the starting materials to (**tfib**)·(dioxane). According to relative intensities of XRPD peaks or reactant and product, using larger amount of dioxane led to a higher yield of the cocrystal. Upon standing at room temperature the obtained cocrystal decomposed to **tfib** within 15 minutes.

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(PIPERAZINE)

200 mg of an equimolar mixture of **tfib** and piperazine was placed in a 10 mL stainless steel grinding jar, along with 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfib**)·(piperazine).

MECHANOCHEMICAL REACTION OF **TFIB** AND DITHIANE

150 mg of **tfib** was placed in a 10 mL stainless steel grinding jar along with 23 mg of dithiane, 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 45 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to a yet unidentified product.

MECHANOCHEMICAL SYNTHESIS OF (**TFIB**)·(**DABCO**)

200 mg of an equimolar mixture of **tfib** and **dabco** was placed in a 10 mL stainless steel grinding jar, along with 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfib**)·(**dabco**).

COCRYSTALS OF **TFBB**:

MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(**TMO**)

200 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 66 µL **tmo** and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfbb**)·(**tmo**).

ATTEMPT OF MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(**TOX**)

200 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 63 µL **tox** and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30

minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfbb**)·(**tox**).

MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(MORPHOLINE)

200 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 60 µL morpholine, 20 µL acetonitrile and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 40 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfbb**)·(morpholine).

ATTEMPT OF MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(DIOXANE)

200 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 60 µL dioxane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated incomplete conversion of the starting materials to (**tfbb**)·(dioxane). According to relative intensities of XRPD peaks or reactant and product, using larger amount of dioxane led to a higher yield of the cocrystal. Upon standing at room temperature the obtained cocrystal decomposed to **tfib** within 15 minutes.

MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(PIPERAZINE)

120 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 34 mg of piperazine, 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfbb**)·(piperazine).

ATTEMPT OF MECHANOCHEMICAL REACTION OF **TFBB** AND DITHIANE

130 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 51 mg of dithiane, 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 40 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to a yet unidentified product.

MECHANOCHEMICAL SYNTHESIS OF (**TFBB**)·(**DABCO**)

130 mg of **tfbb** was placed in a 10 mL stainless steel grinding jar along with 48 mg of **dabco**, 50 µL nitromethane and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 40 minutes in a Retsch MM200 Shaker Mill. Analysis of the solid product via XRPD indicated complete conversion of the starting materials to (**tfbb**)·(**dabco**).

SYNTHESIS OF SINGLE CRYSTALS FOR X-RAY DIFFRACTION

SINGLE CRYSTALS OF (**TFIB**)·(**TMO**)

Single crystals were obtained by recrystallising 150 mg of (**tfib**)·(**tmo**) cocrystals obtained by grinding from 2 mL of hot nitromethane.

SINGLE CRYSTALS OF (**TFIB**)·(**TOX**)

Single crystals were grown by recrystallising 145 mg **tfib** from 0.67 mL **tox**.

SINGLE CRYSTALS OF (**TFIB**)·(PIPERAZINE)

Single crystals were grown by slow evaporation of a solution of 50 mg **tfib** and 12 mg piperazine in 3 mL chloroform.

SINGLE CRYSTALS OF (**TFIB**)·(MORPHOLINE)

Single crystals were obtained by recrystallising 50 mg **tfib** from a mixture of 0.75 mL morpholine and 1 mL acetonitrile.

SINGLE CRYSTALS OF (**TFIB**)·(DIOXANE)

Single crystals were synthesised by recrystallising 50 mg **tfib** from a mixture of 0.75 mL dioxane and 1 mL dichloromethane.

SINGLE CRYSTALS OF (**TFIB**)·(**DABCO**)

Single crystals were prepared from a solution of 100 mg **tfib** and 28 mg **dabco** in a 3:2 mixture of acetone and acetonitrile.

SINGLE CRYSTALS OF (**TFBB**)·(**TMO**)

Single crystals were obtained by recrystallising 90 mg of (**tfbb**)·(**tmo**) cocrystals obtained by grinding from 1 mL of hot nitromethane.

SINGLE CRYSTALS OF (**TFBB**)·(PIPERAZINE)

Single crystals were grown from a solution of 66 mg **tfbb** and 19 mg piperazine in a 1:10 mixture of acetonitrile and acetone.

SINGLE CRYSTALS OF (**TFBB**)·(MORPHOLINE)

Single crystals were obtained by recrystallising 50 mg **tfbb** from 1.05 mL of morpholine.

SINGLE CRYSTALS OF (**TFBB**)·(**DABCO**)

Single crystals were grown by crystallising 100 mg of **tfbb** and 36 mg **dabco** from a 1:1 mixture of acetonitrile and acetone.

X-RAY DIFFRACTION EXPERIMENTS

X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer equipped with an X'celerator RTMS detector, using Ni-filtered CuK_a radiation. Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems cryostream, using MoK_a radiation.

DIFFERENTIAL SCANNING CALORIMETRY EXPERIMENTS

DSC thermograms were obtained on a Mettler DSC822 DSC calorimeter, using samples with typical sizes between 5-15 mg. The sample was placed in a non-hermetically sealed aluminium pan. The measurements were performed in the temperature range 30-250 ^{o}C, with a heating rate of 10 ^{o}C min^{-1}, in a dynamic atmosphere of nitrogen gas.

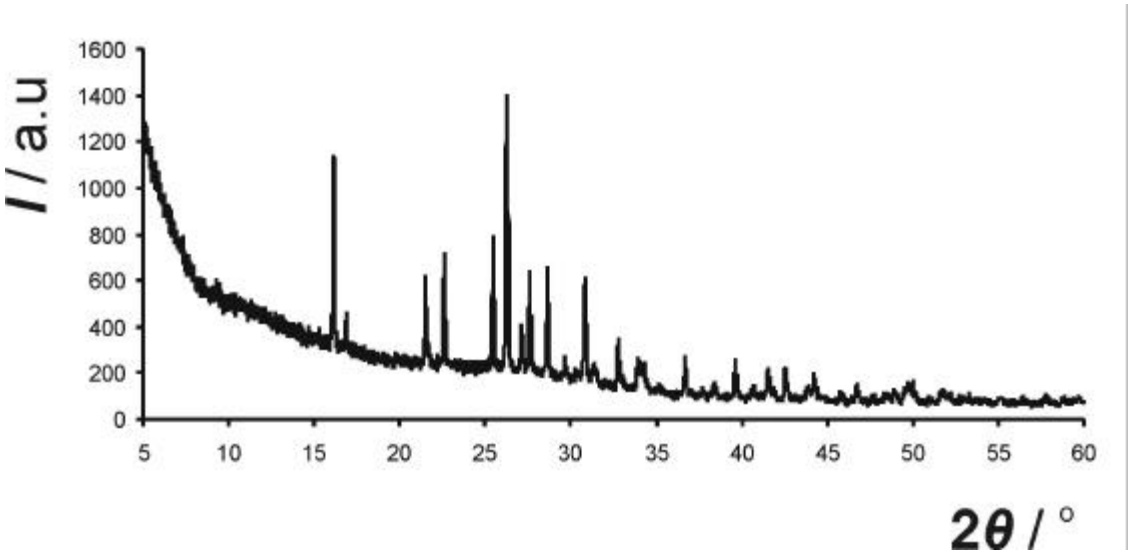

Figure S1. X-ray powder diffraction pattern for **tfib**.

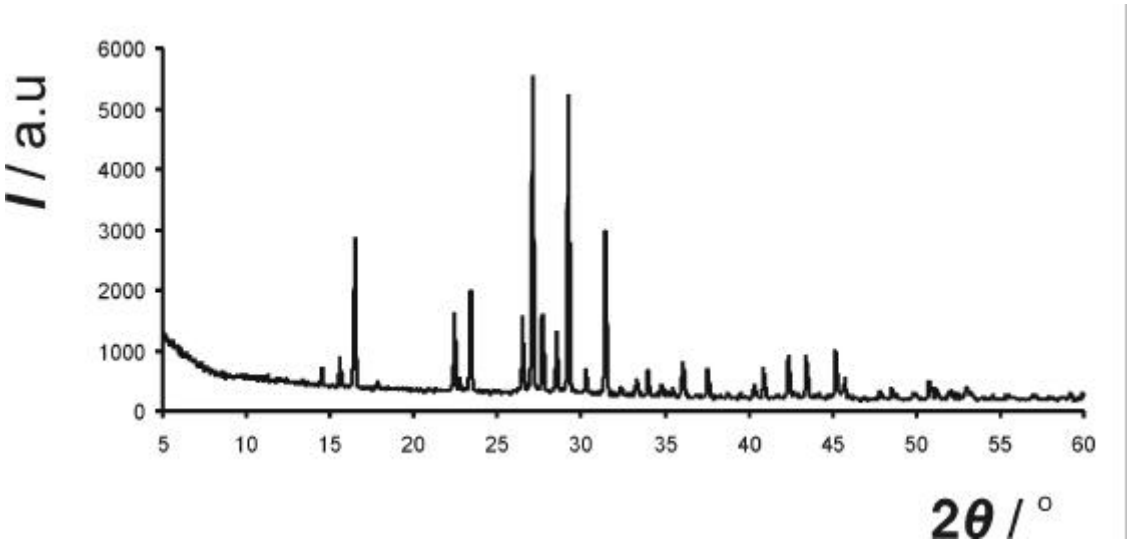

Figure S2. X-ray powder diffraction pattern for **tfbb**.

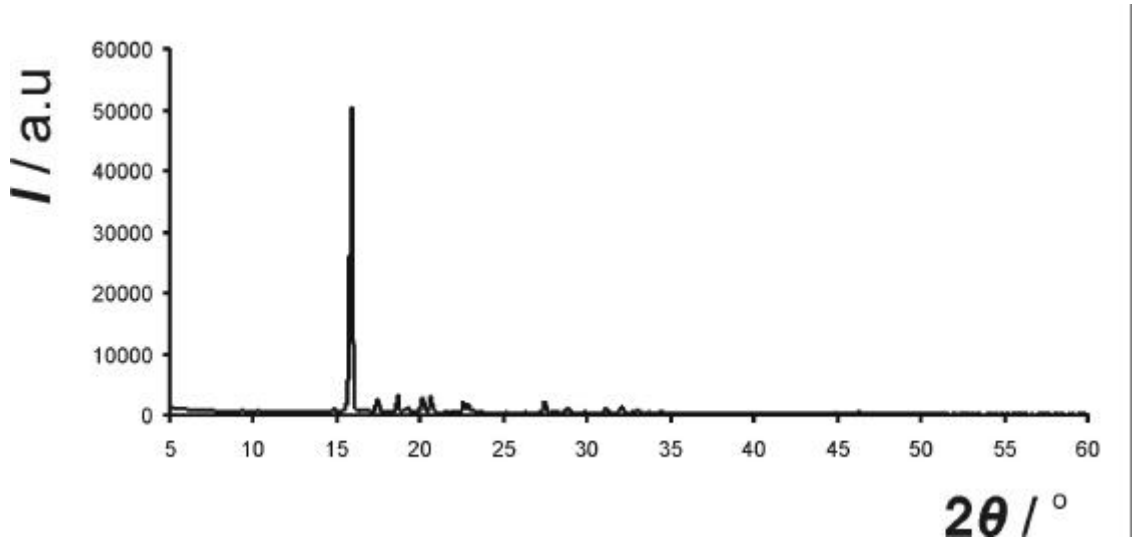

Figure S3. X-ray powder diffraction pattern for piperazine.

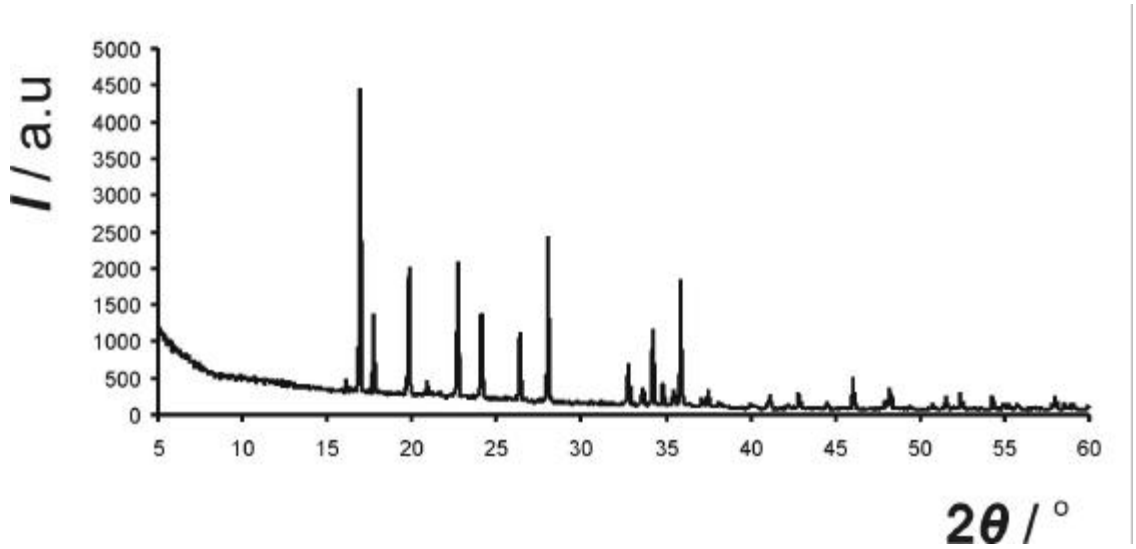

Figure S4. X-ray powder diffraction pattern for dithiane.

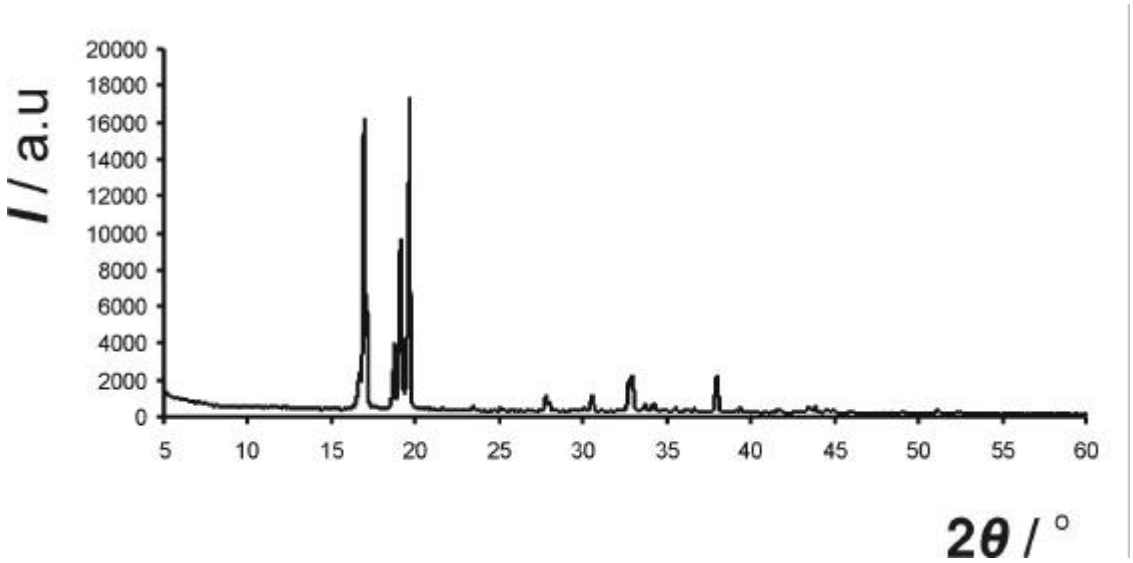

Figure S5. X-ray powder diffraction pattern for **dabco**.

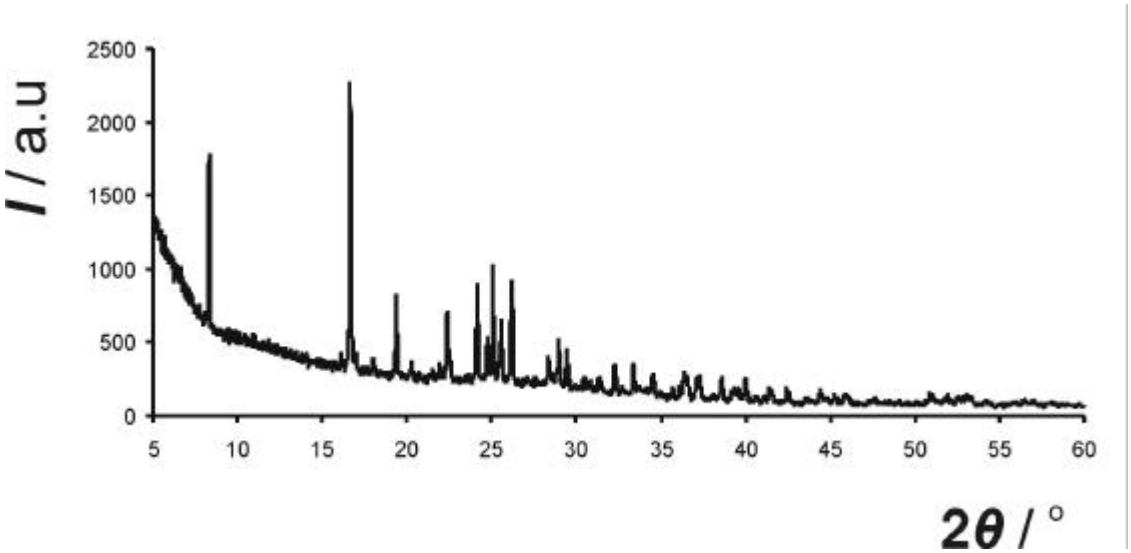

Figure S6. X-ray powder diffraction pattern of (**tfib**)·(**tmo**) obtained by grinding.

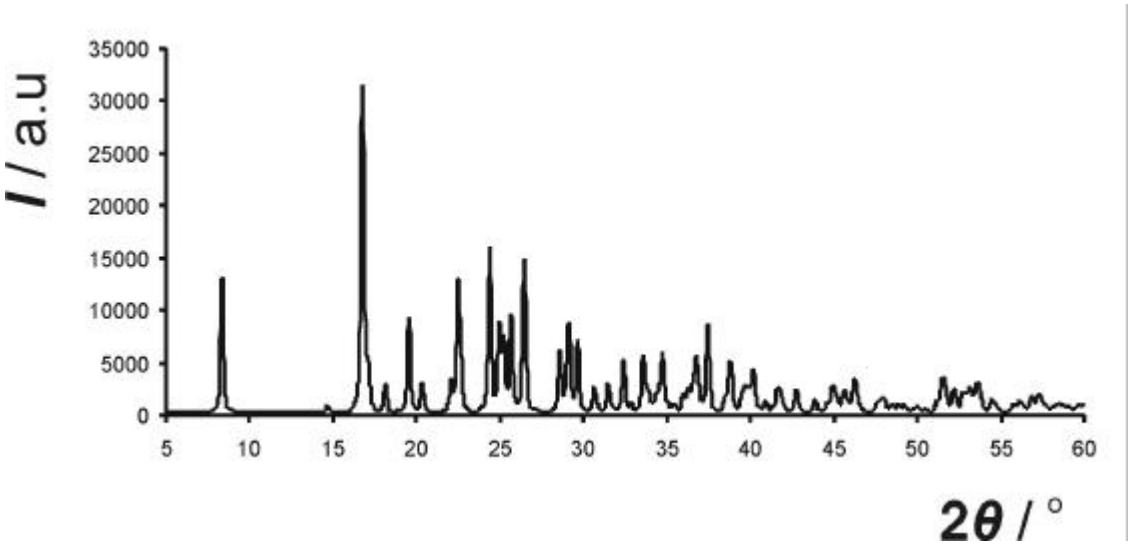

Figure S7. Simulated X-ray powder diffraction pattern for (**tfib**)$^{-}$(**tmo**).

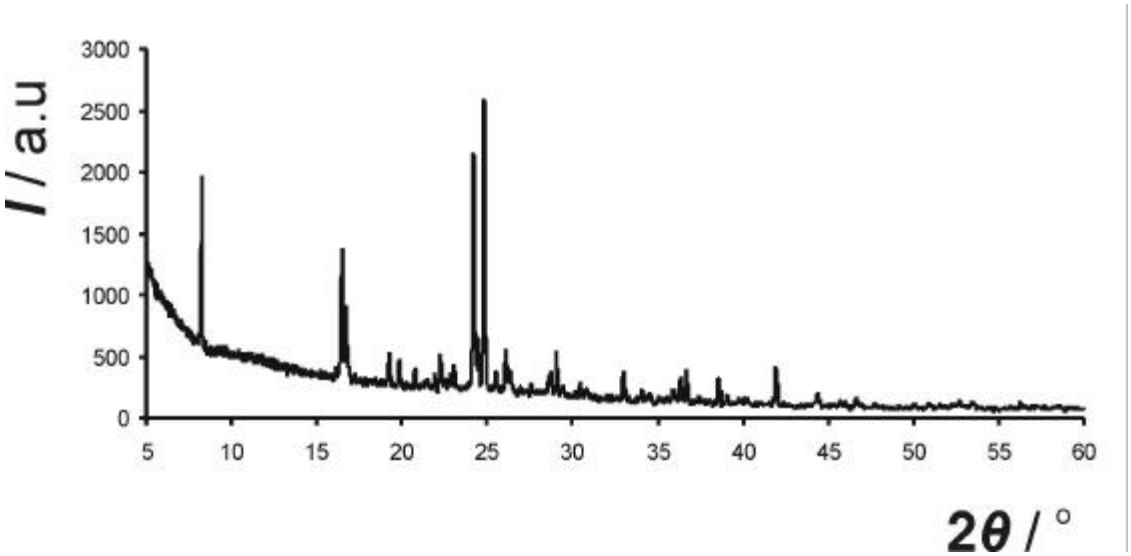

Figure S8. X-ray powder diffraction pattern of (**tfib**)·(**tox**) obtained by grinding.

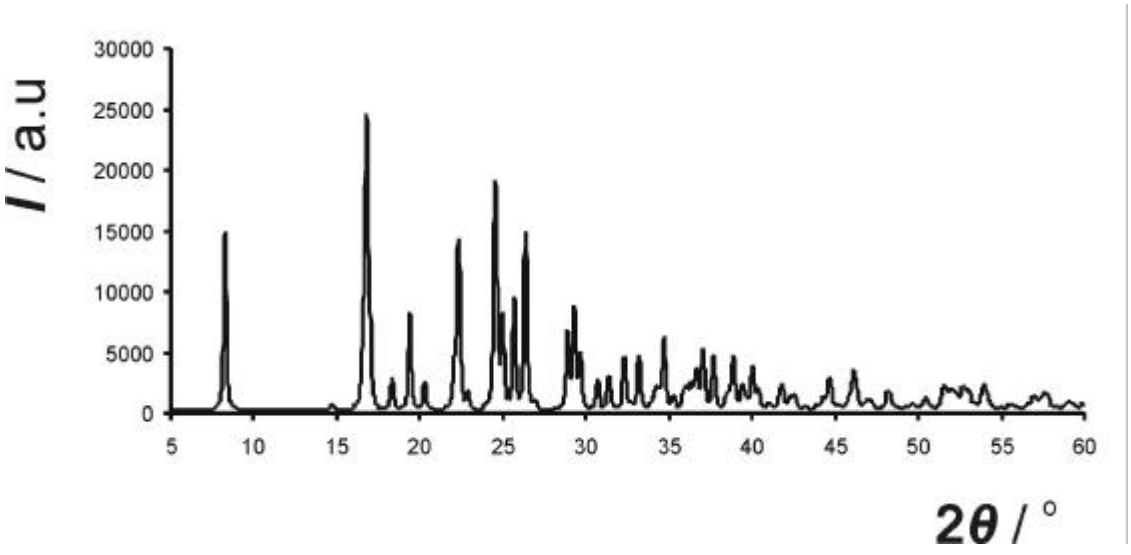

Figure S9. Simulated X-ray powder diffraction pattern for (**tfib**)·(**tox**).

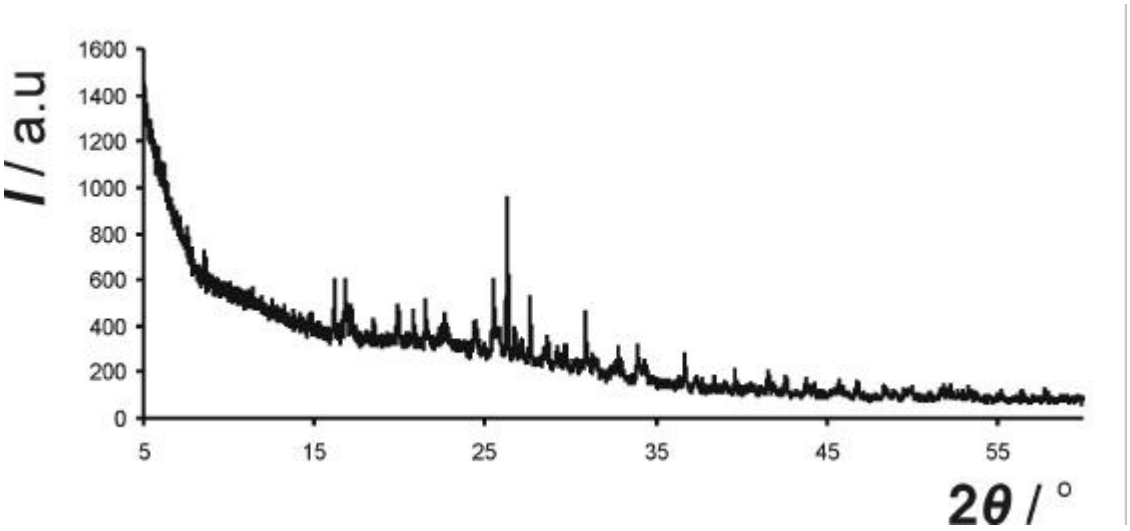

Figure S10. X-ray powder diffraction pattern of (**tfib**)·(dioxane) obtained by grinding.

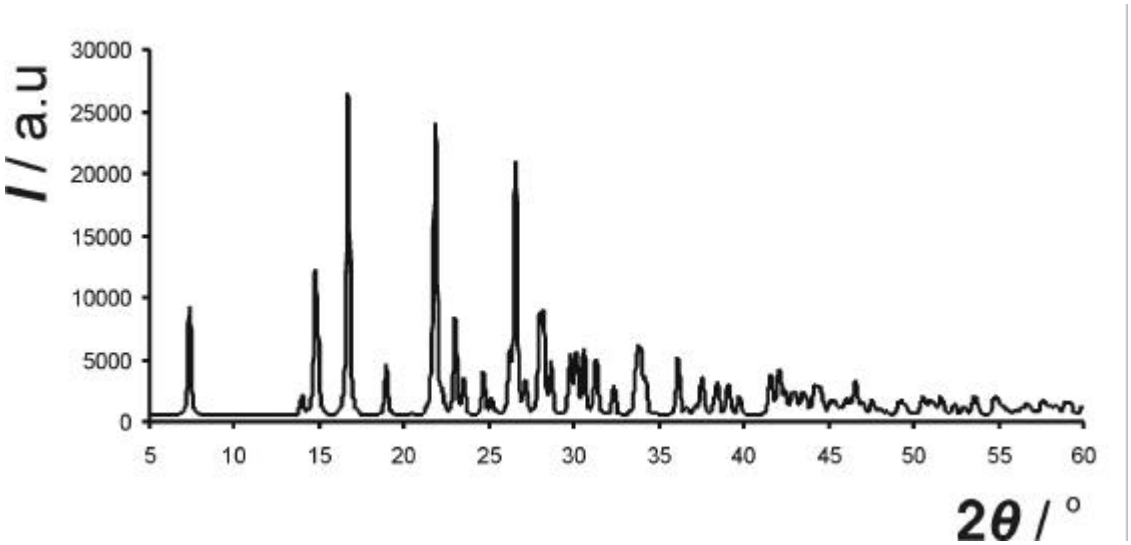

Figure S11. Simulated X-ray powder diffraction pattern for (**tfib**)·(dioxane).

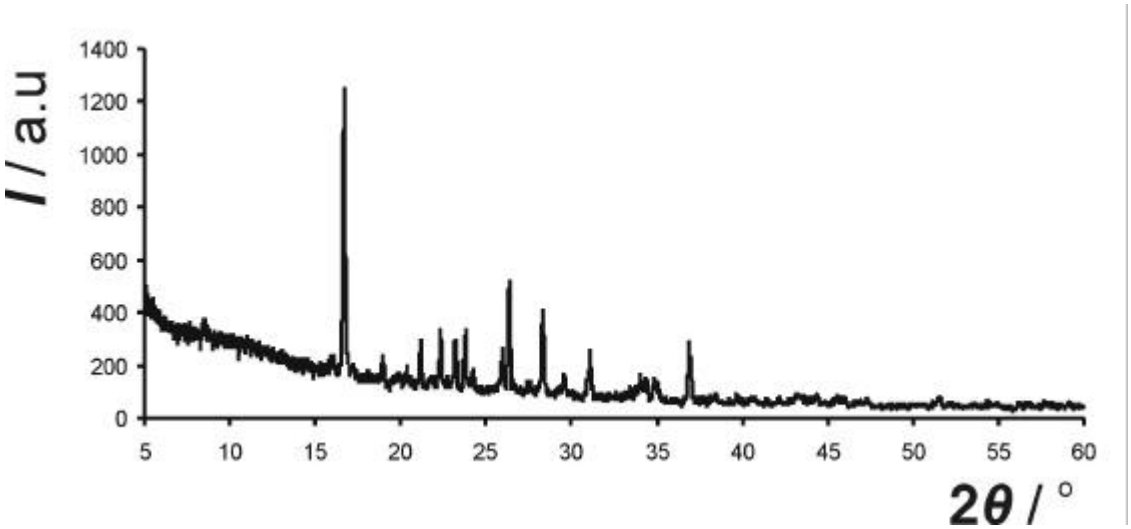

Figure S12. X-ray powder diffraction pattern of the product obtained by liquid-assisted grinding of dithiane and **tfib**.

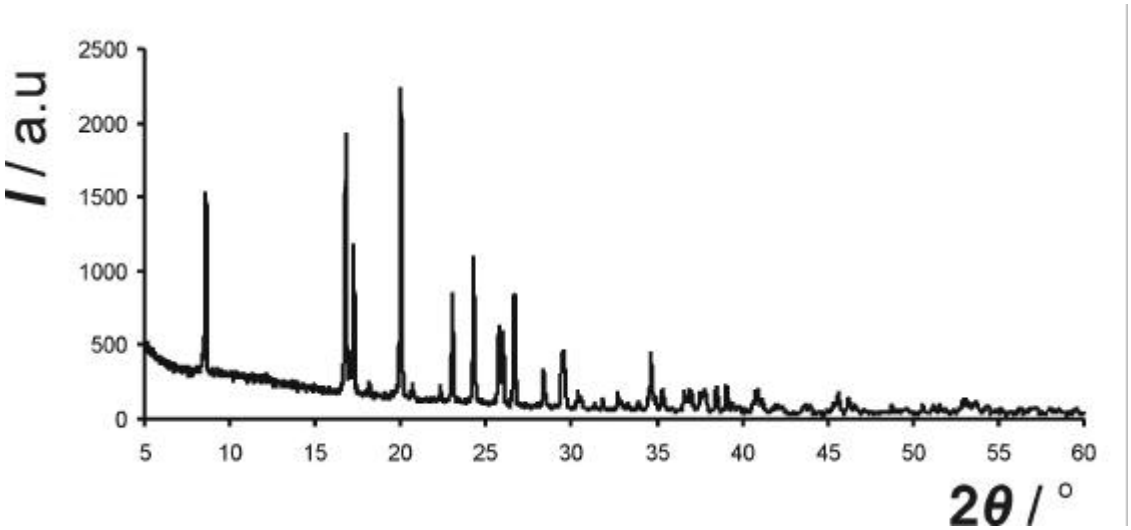

Figure S13. X-ray powder diffraction pattern of (**tfib**)$^{-}$(piperazine) obtained by liquid-assisted grinding.

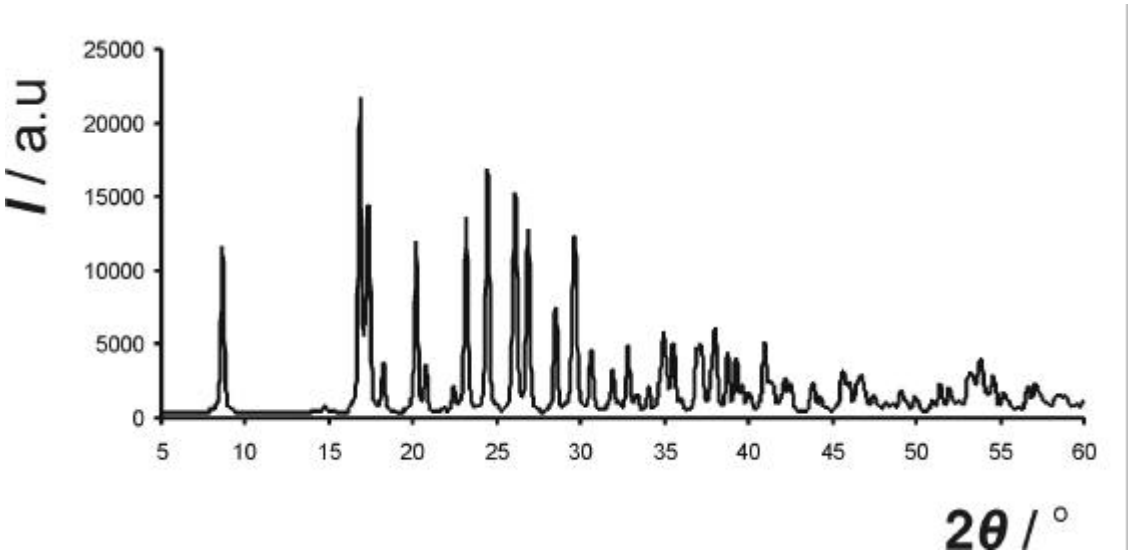

Figure S14. Simulated X-ray powder diffraction pattern for (**tfib**)$^{-}$(piperazine).

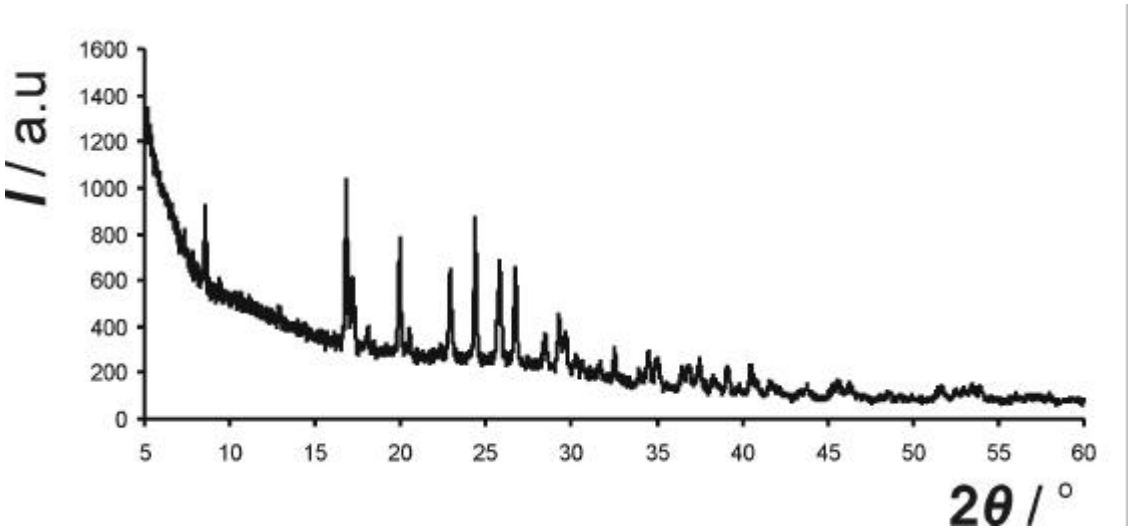

Figure S15. X-ray powder diffraction pattern of (**tfib**)·(morpholine) obtained by liquid-assisted grinding.

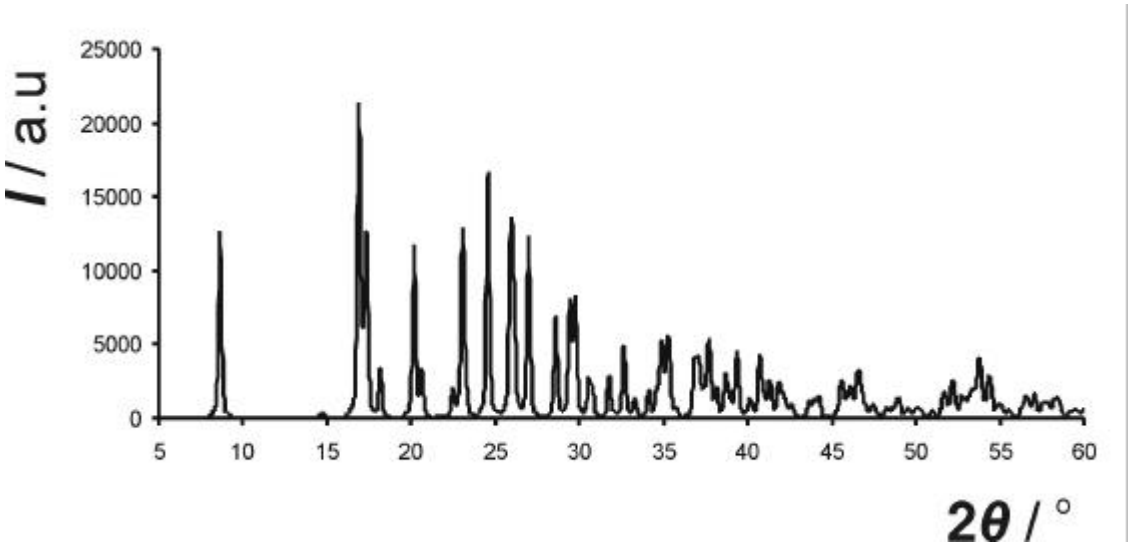

Figure S16. Simulated X-ray powder diffraction pattern for (**tfib**)$^-$(morpholine).

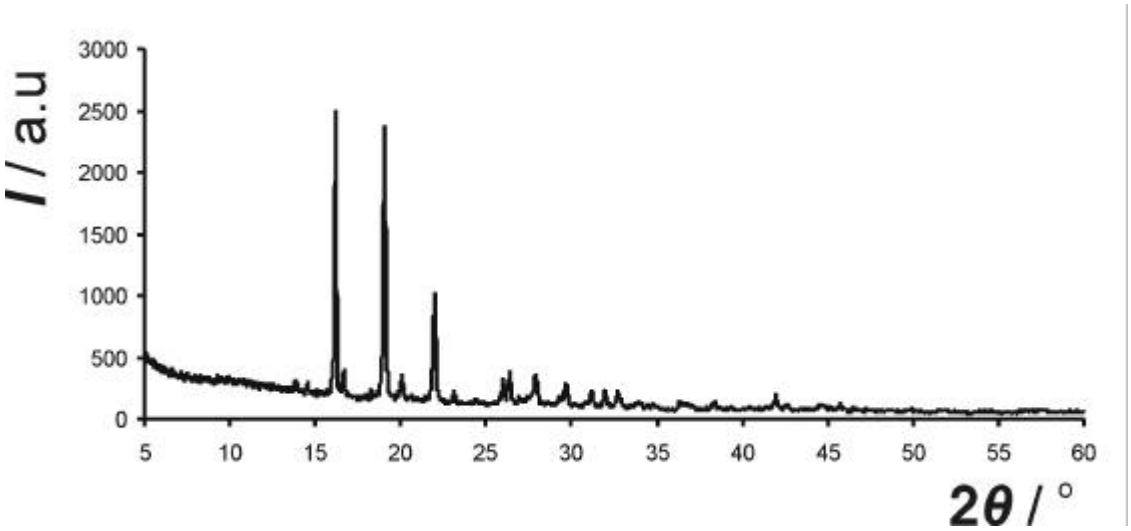

Figure S17. X-ray powder diffraction pattern of (**tfib**)$^-$(dabco) obtained by liquid-assisted grinding.

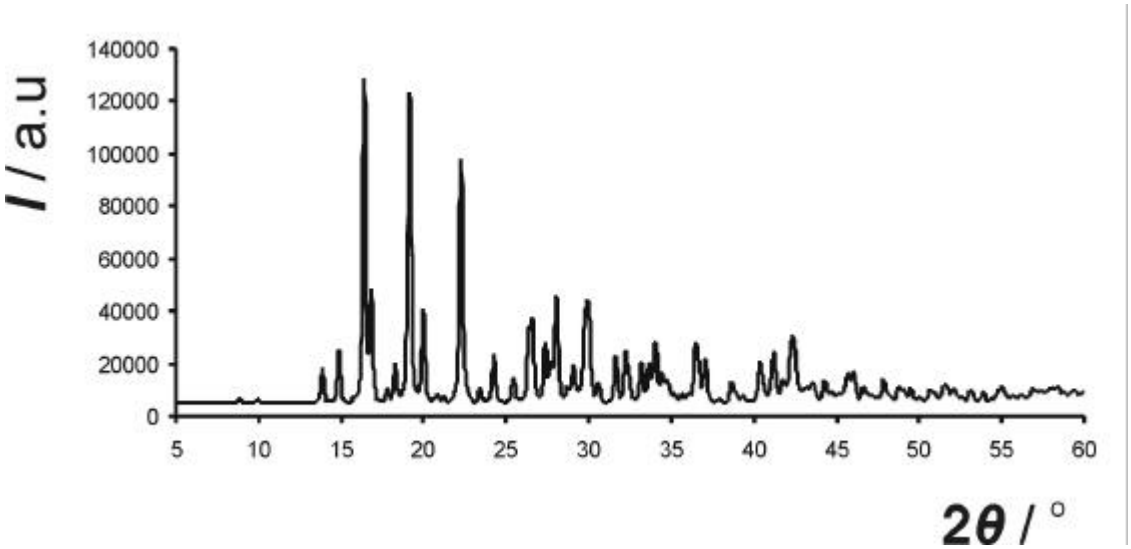

Figure S18. Simulated X-ray powder diffraction pattern for (**tfib**)·(dabco).

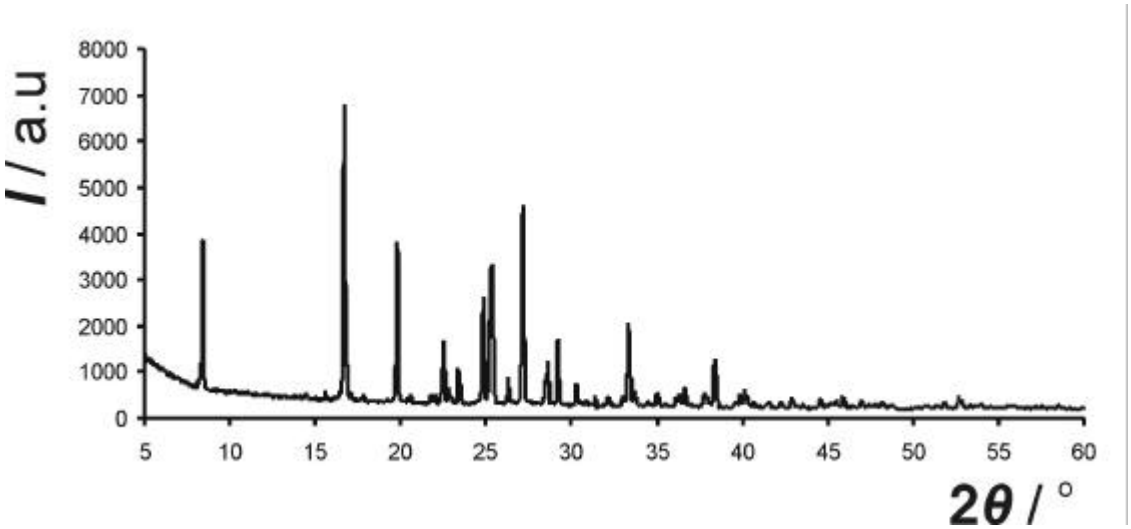

Figure S19. X-ray powder diffraction pattern of (**tfbb**)$^{-}$(**tmo**) obtained by grinding.

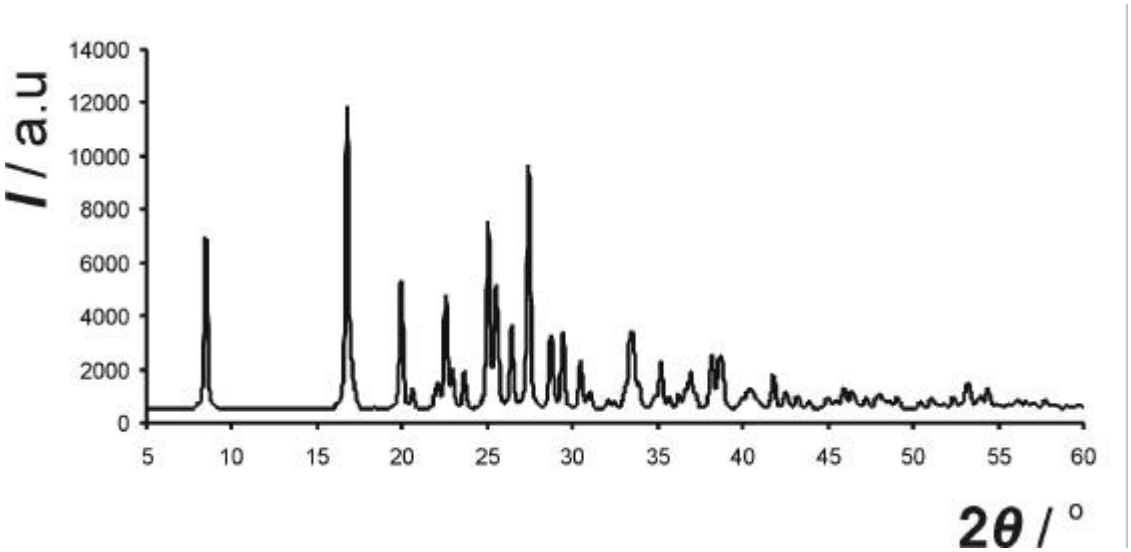

Figure S20. Simulated X-ray powder diffraction pattern for (**tfbb**)$^{-}$(**tmo**).

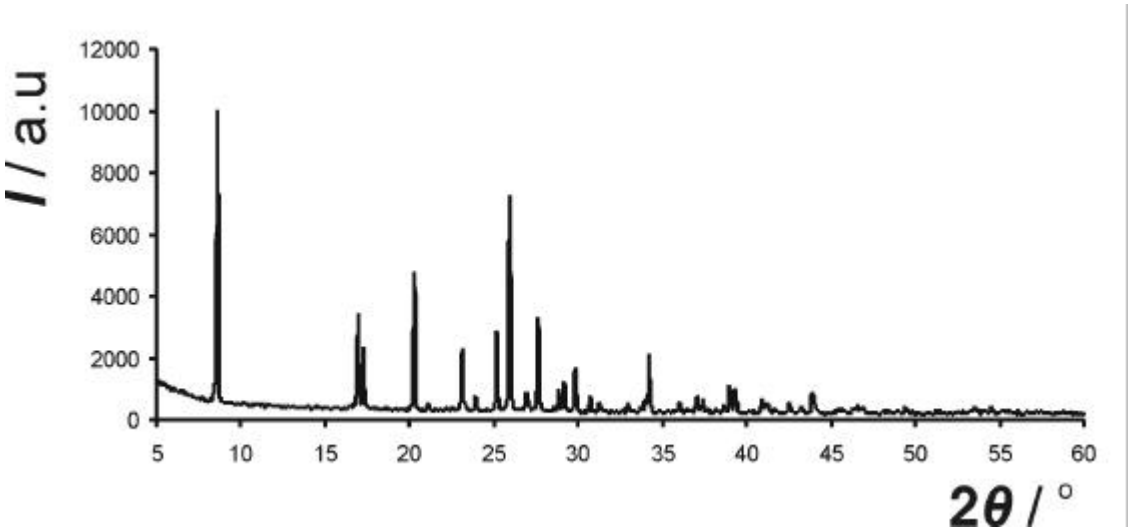

Figure S21. X-ray powder diffraction pattern of (**tfbb**)$^-$(morpholine) obtained by liquid-assisted grinding.

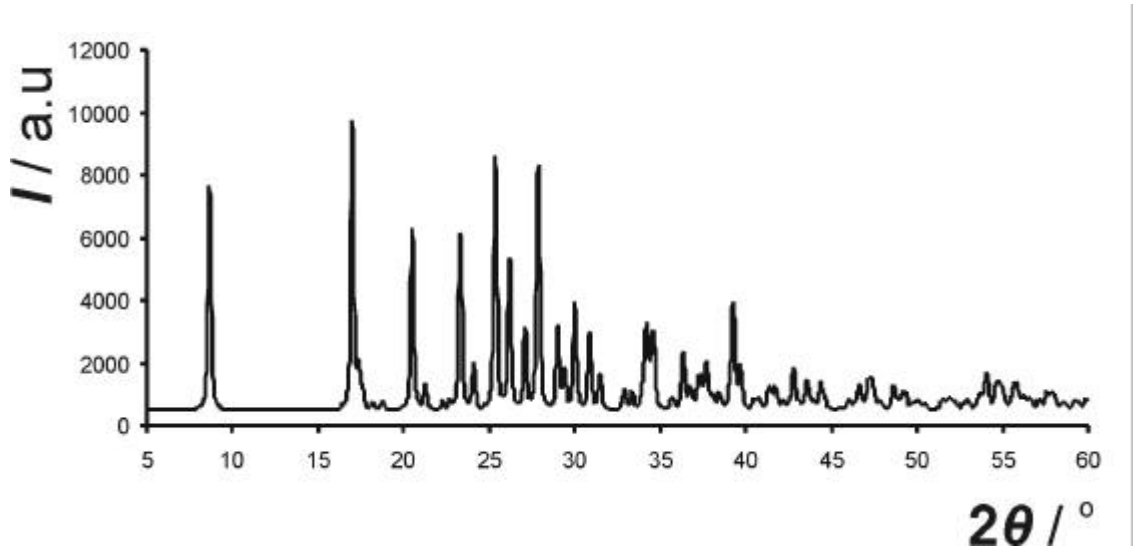

Figure S22. Simulated X-ray powder diffraction pattern for **(tfbb)**$^{-}$(morpholine).

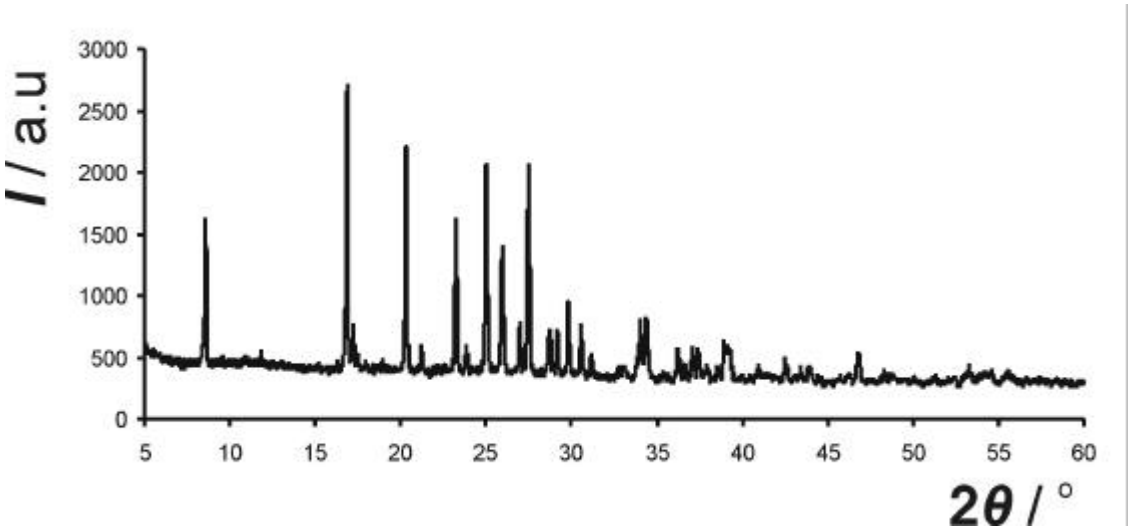

Figure S23. X-ray powder diffraction pattern of (**tfbb**)·(piperazine) obtained by liquid-assisted grinding.

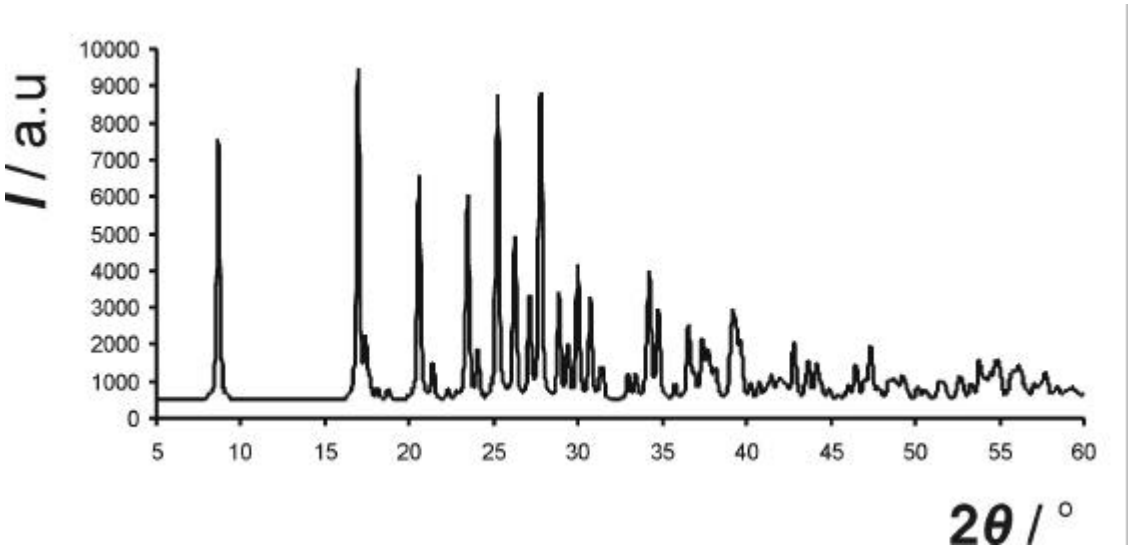

Figure S24. Simulated X-ray powder diffraction pattern of (**tfbb**)$_2$(piperazine).

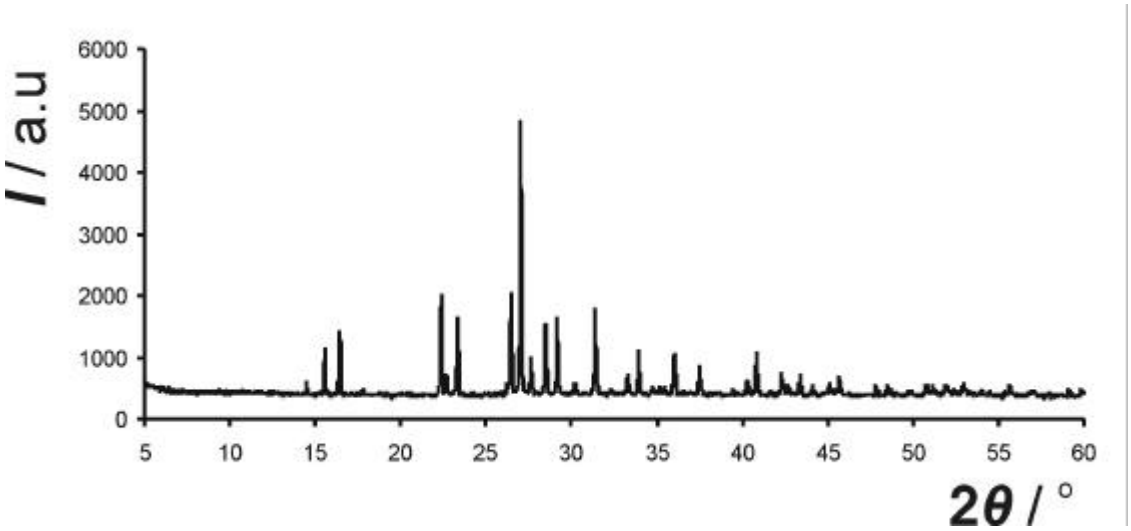

Figure S25. X-ray powder diffraction pattern of a 1:1 mixture of **tfbb** and **tox** after grinding.

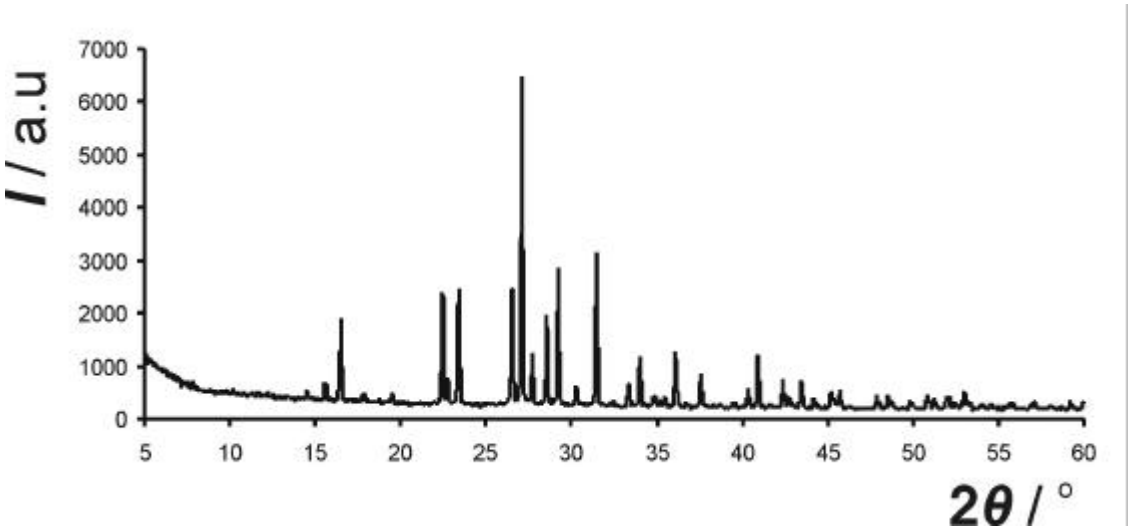

Figure S26. X-ray powder diffraction pattern of a 1:1 mixture of **tfbb** and dioxane after grinding.

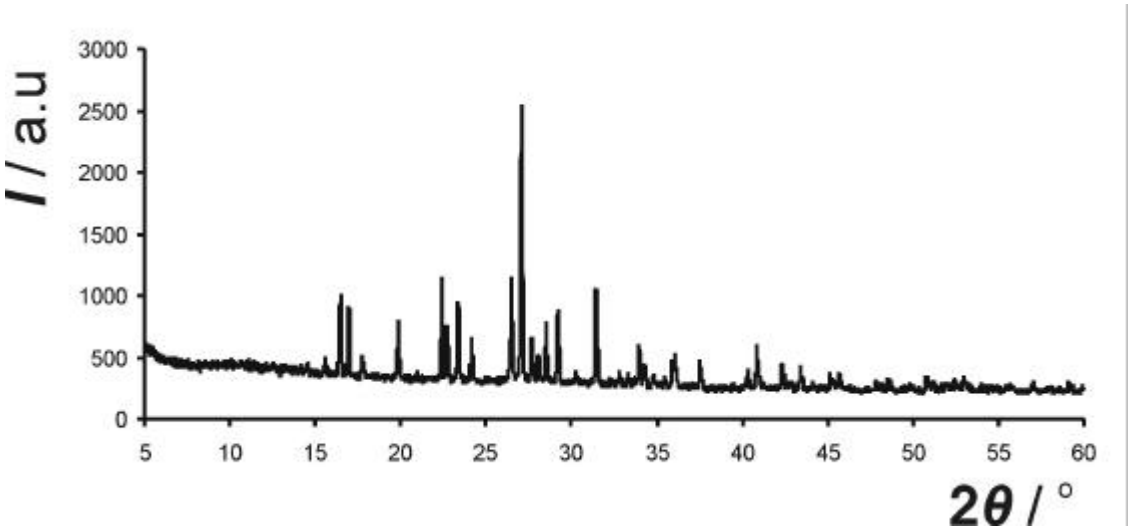

Figure S27. X-ray powder diffraction pattern of a 1:1 mixture of **tfbb** and dithiane after liquid-assisted grinding.

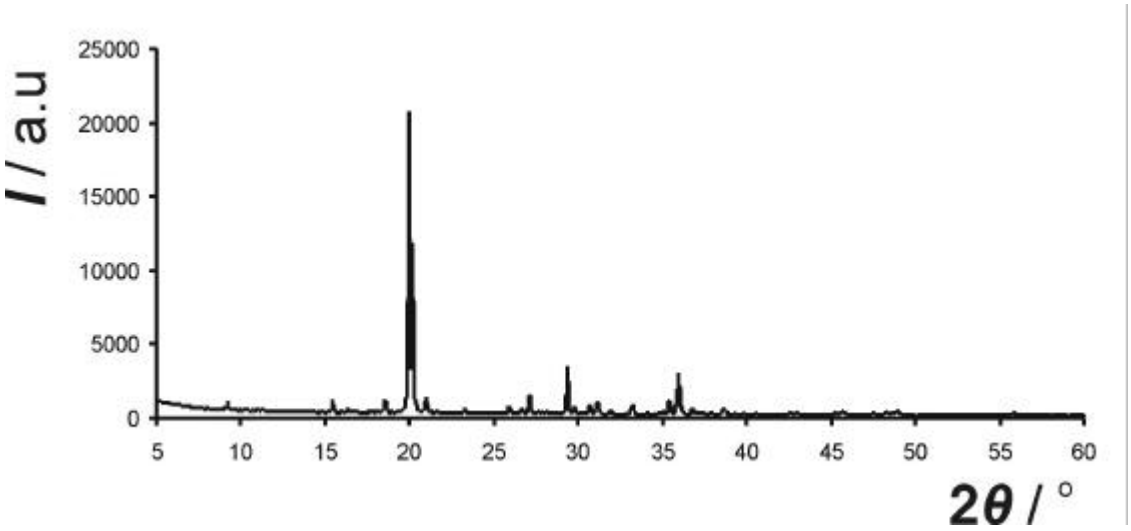

Figure S28. X-ray powder diffraction pattern of (**tfbb**)·(**dabco**) obtained by liquid-assisted grinding.

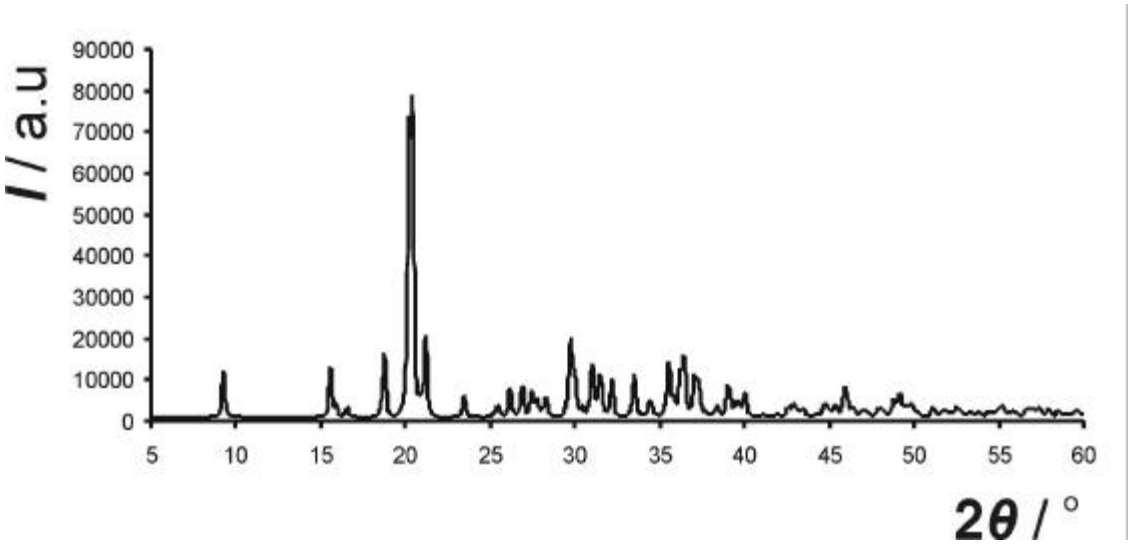

Figure S29. Simulated X-ray powder diffraction pattern of (**tfbb**)·(**dabco**).

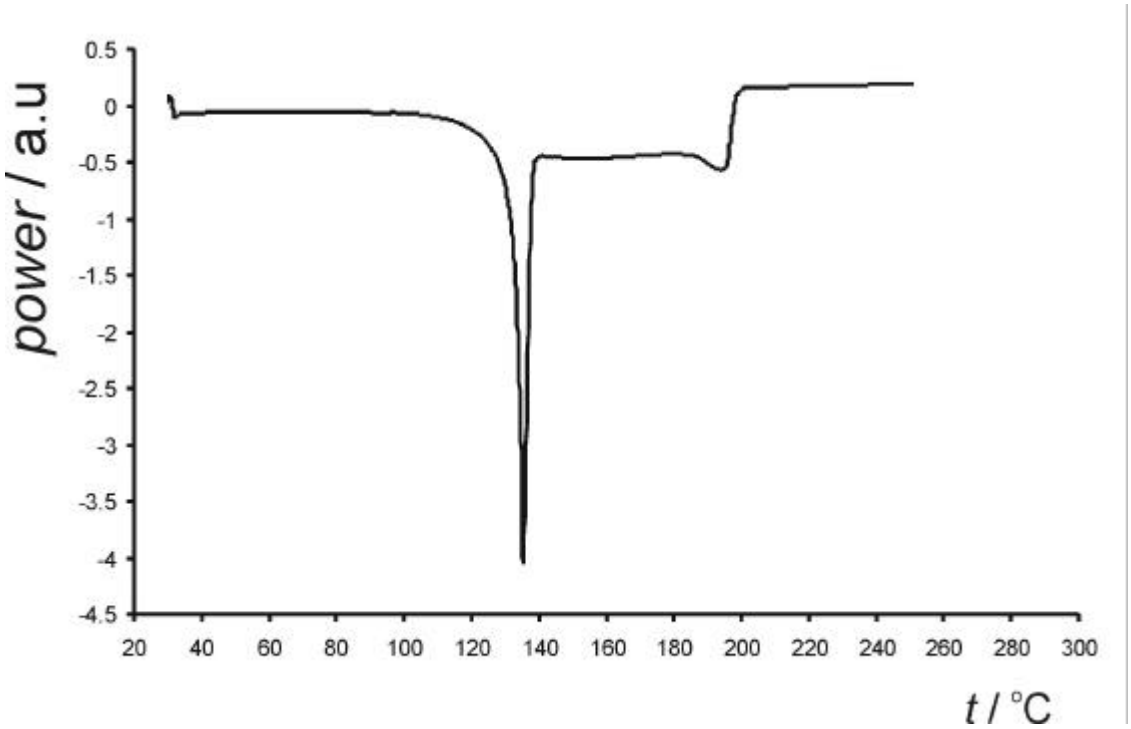

Figure S30. DSC thermogram for the cocrystal (**tfib**)·(**tmo**).

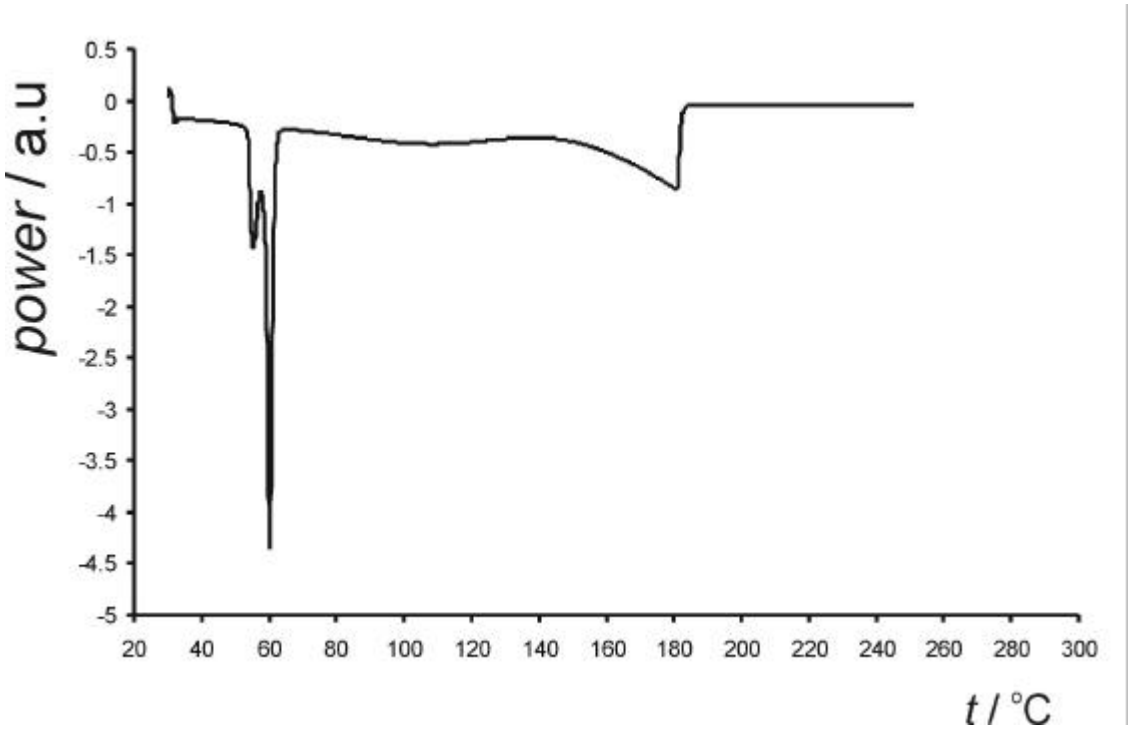

Figure S31. DSC thermogram for the cocrystal (**tfib**)·(**tox**).

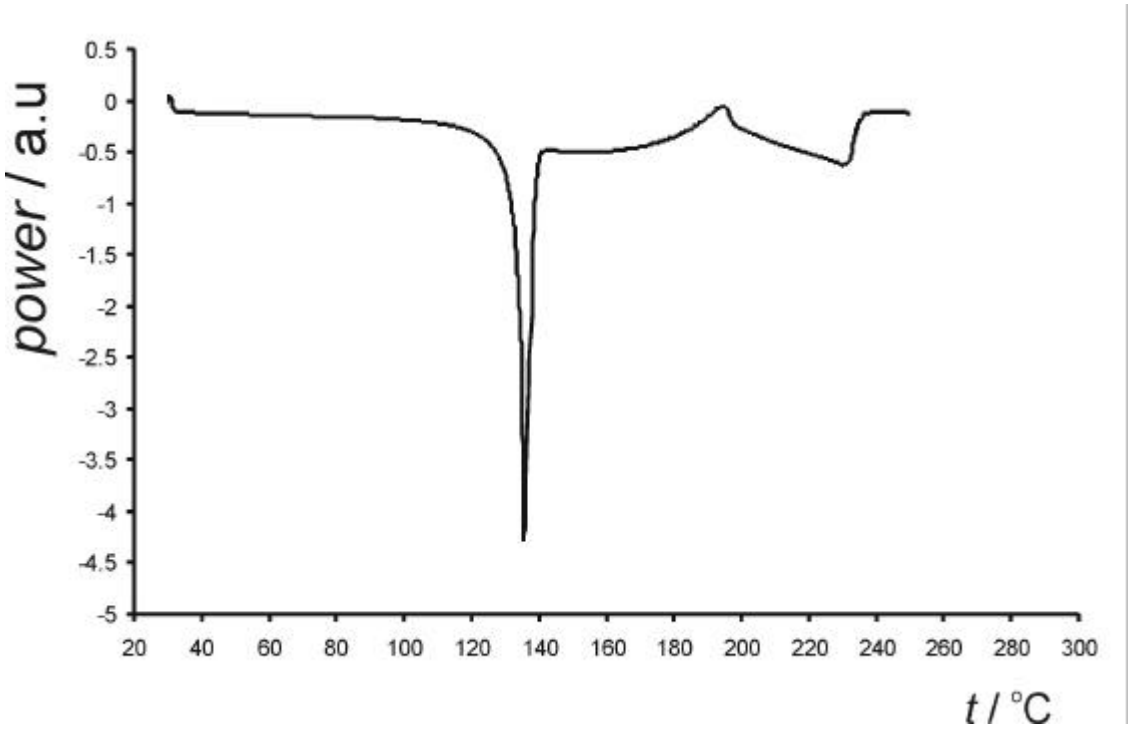

Figure S32. DSC thermogram for the cocrystal (**tfib**)·(morpholine).

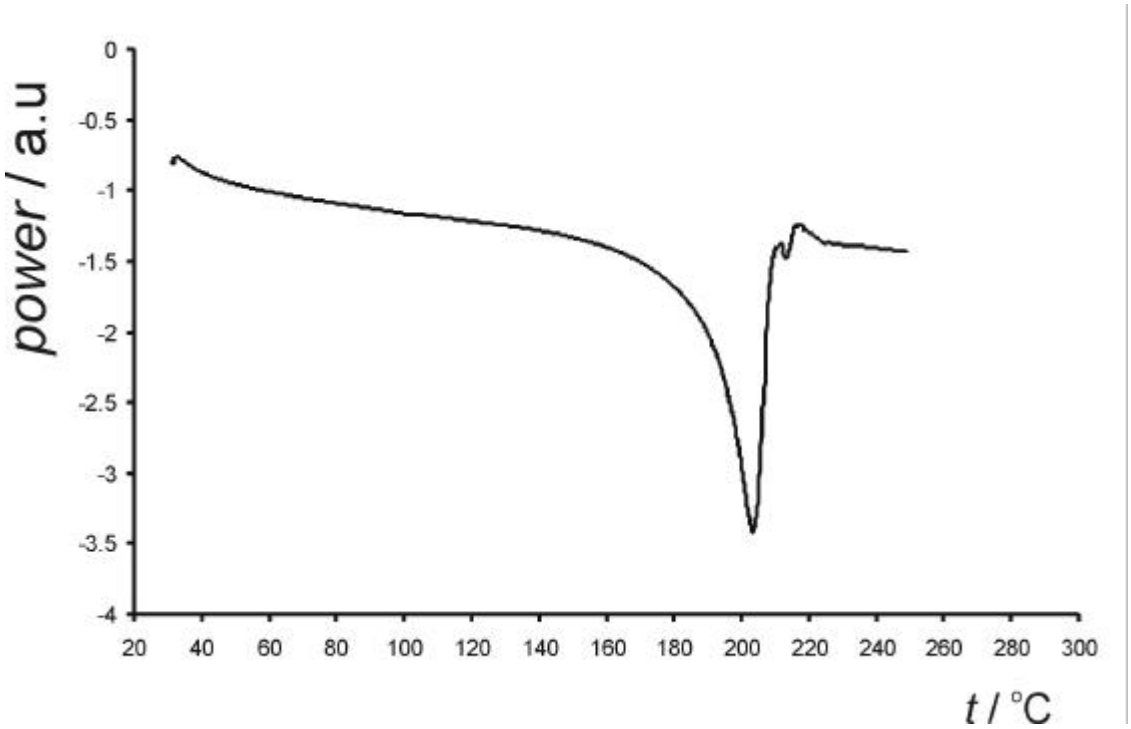

Figure S33. DSC thermogram for the cocrystal (**tfib**)·(piperazine).

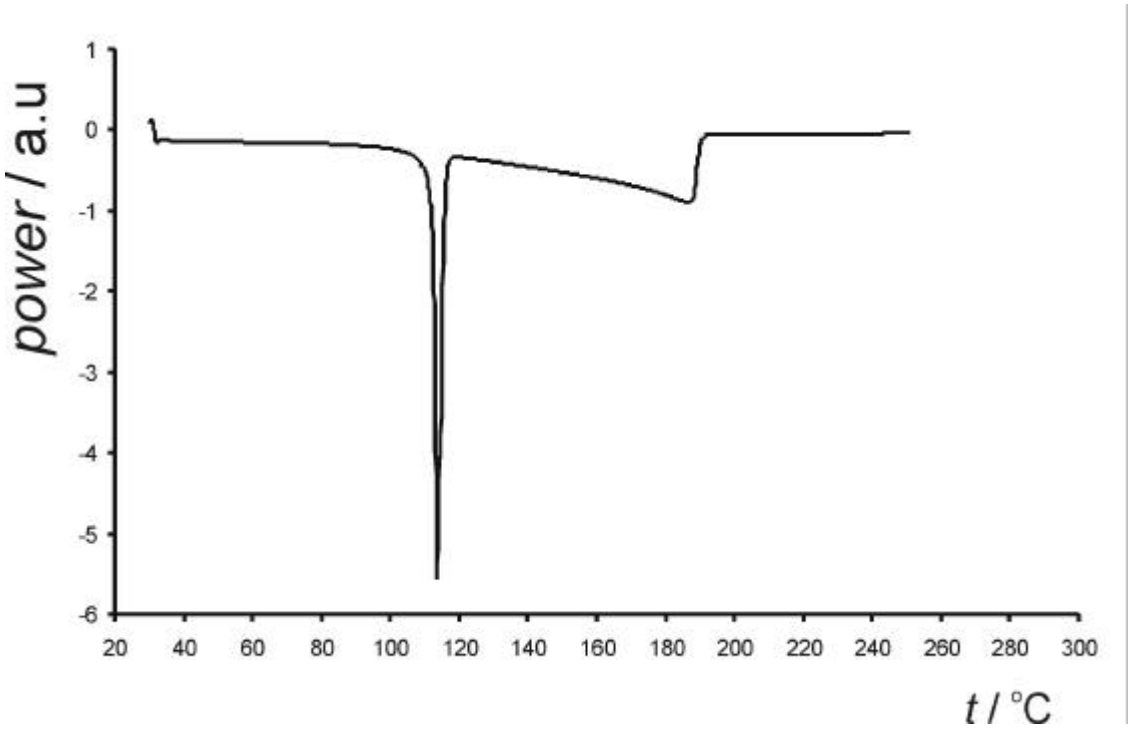

Figure S34. DSC thermogram for the cocrystal of **tfib**·and dithiane.

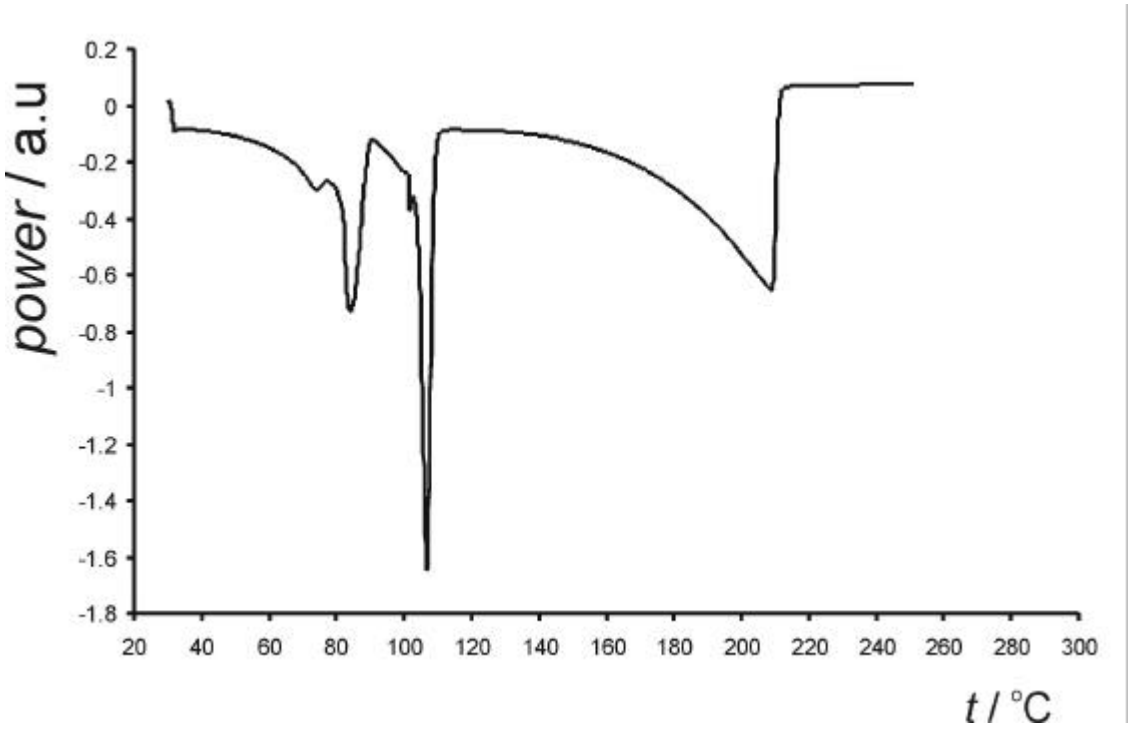

Figure S35. DSC thermogram for the cocrystal of **tfib**·and dioxane.

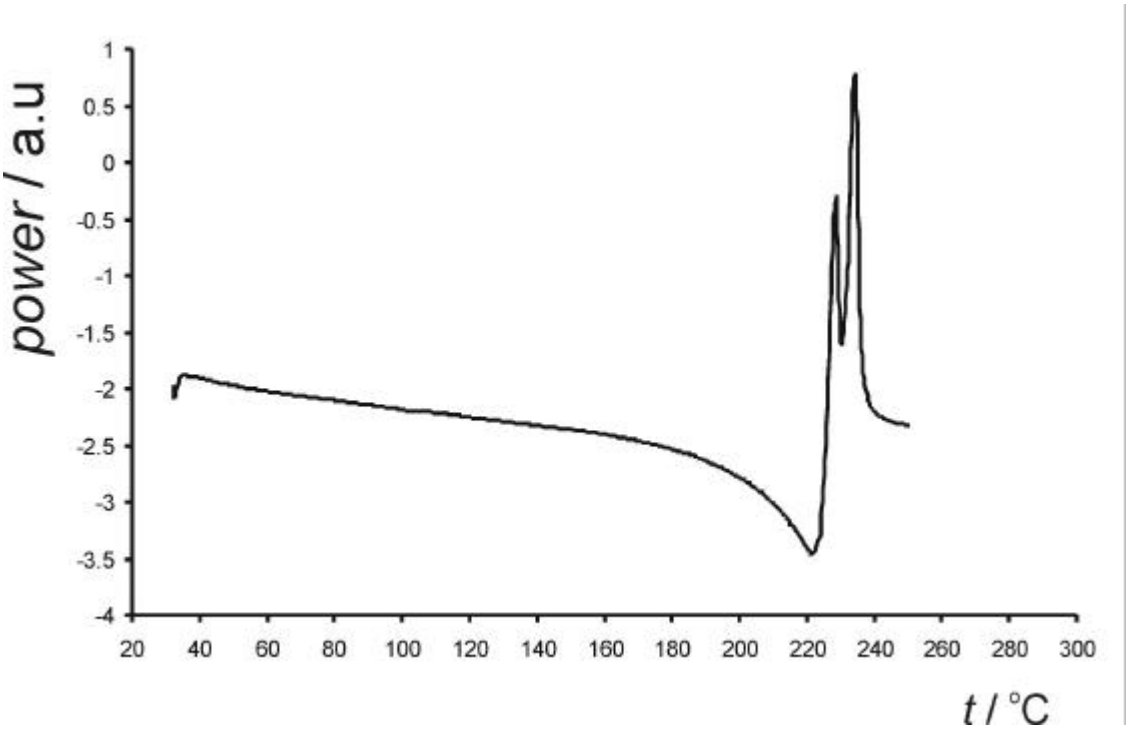

Figure S36. DSC thermogram for the cocrystal (**tfib**)·(**dabco**).

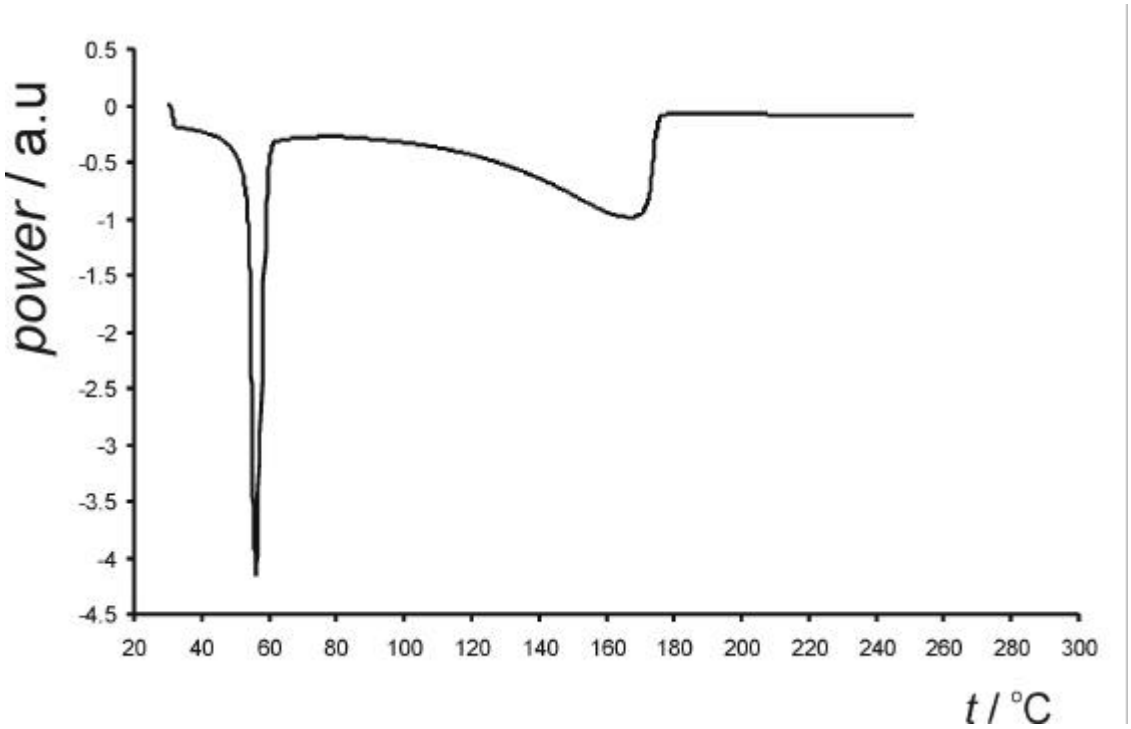

Figure S37. DSC thermogram for the cocrystal (**tfbb**)·(**tmo**).

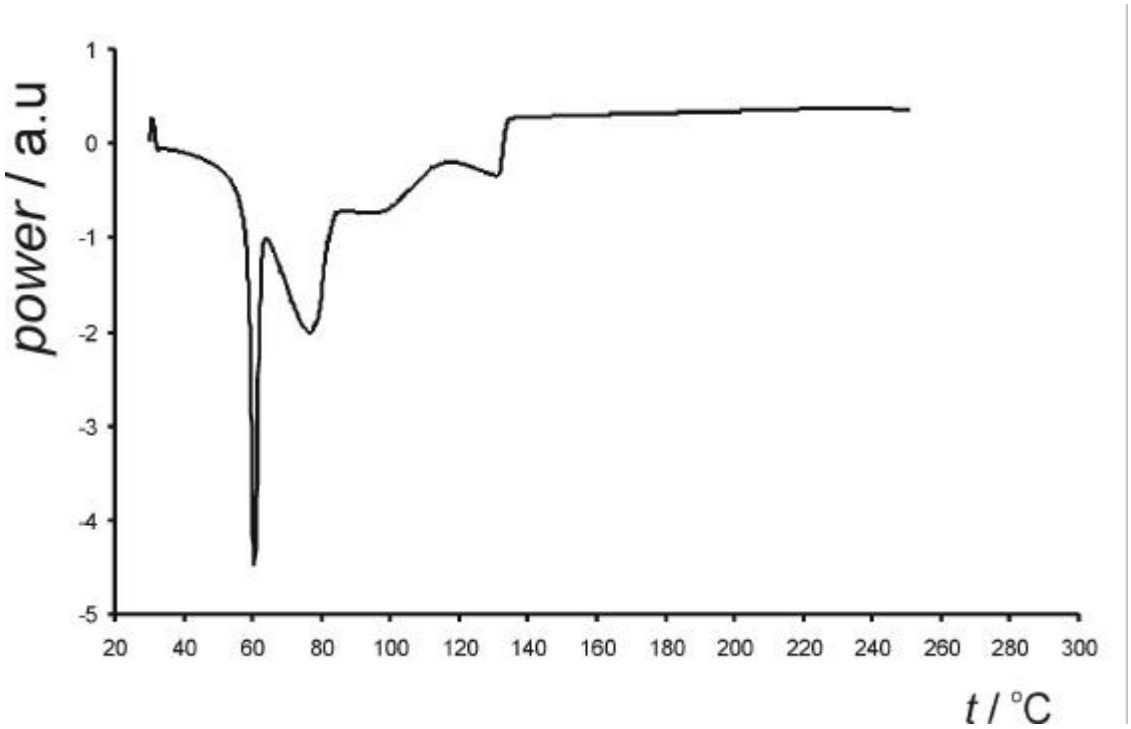

Figure S38. DSC thermogram for the cocrystal (**tfbb**)·(morpholine).

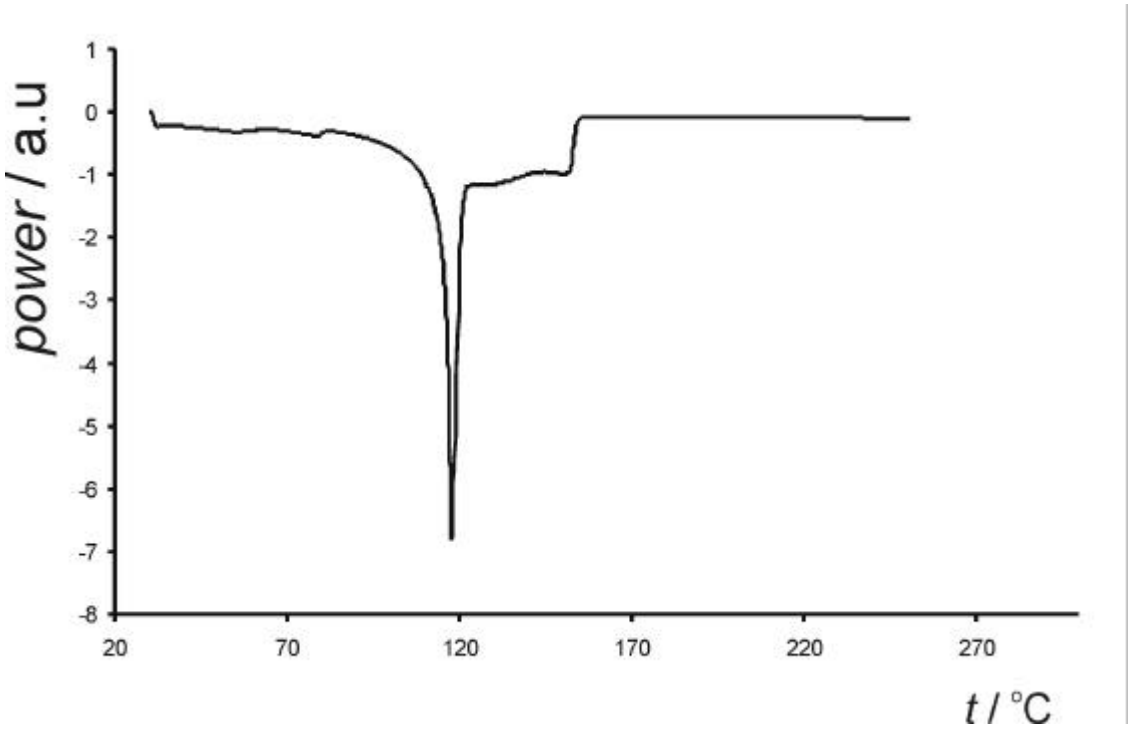

Figure S39. DSC thermogram for the cocrystal (**tfbb**)·(piperazine).

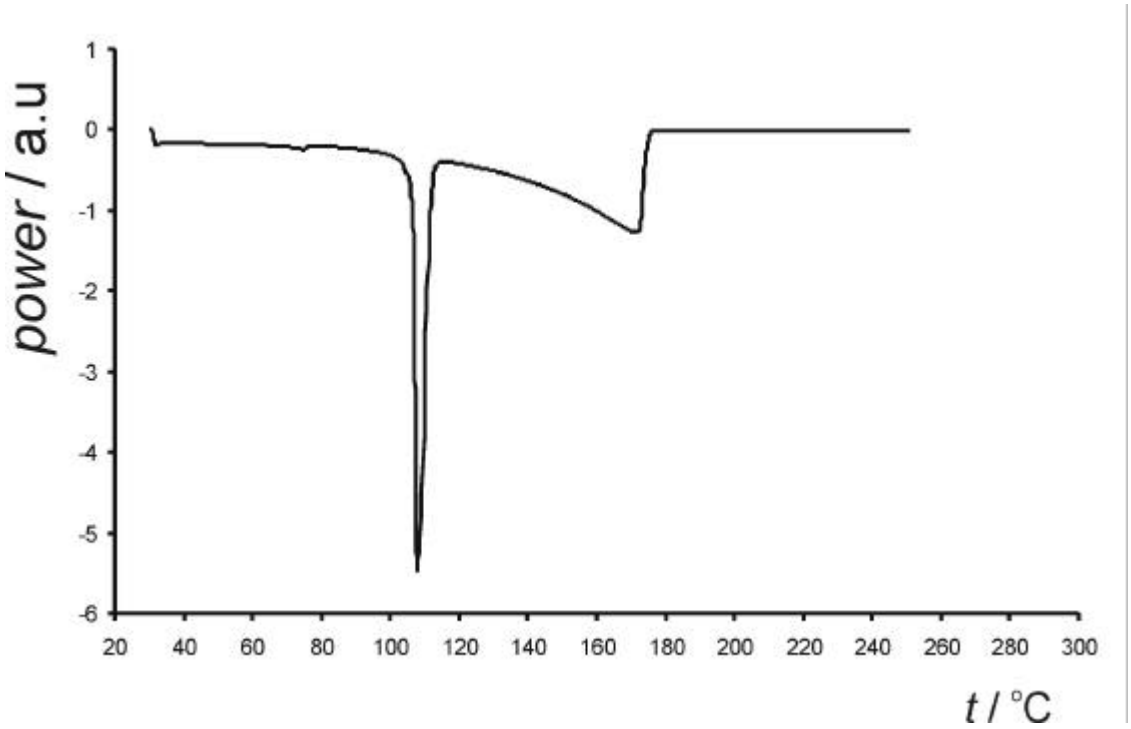

Figure S40. DSC thermogram for the cocrystal (**tfbb**)·(**dabco**).