SUPPORTING INFORMATION

Halogen bonding of the aldehyde oxygen atom in cocrystals of aromatic aldehydes and 1,4-diiodotetrafluorobenzene

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EXPERIMENTAL DETAILS

MECHANOCHEMICAL SYNTHESES

Synthesis of (**dmab**)$_2$(**tfib**)

A mixture of **dmab** (74.2 mg, 497 μmol) and **tfib** (99.9 mg, 248 μmol) was placed in a 10 mL stainless steel jar along with 25 μL of acetonitrile and two stainless steel balls 7 mm in diameter. The reaction mixture was then milled for 20 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz.

Synthesis of (**napht**)$_2$(**tfib**)

A mixture of **napht** (13.2 mg, 76.7 μmol) and **tfib** (30.9 mg, 76.8 μmol) was placed in a 10 mL stainless steel jar along with 10 μL of acetone and two stainless steel balls 7 mm in diameter. The reaction mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz.

Synthesis of (**dmb**)$_2$(**tfib**)

A mixture of **dmb** (40.0 mg, 240 μmol) and **tfib** (48.4 mg, 120 μmol) was placed in a 10 mL stainless steel jar along with 20 μL of nitromethane and two stainless steel balls 7 mm in diameter. The reaction mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz.

Synthesis of (**pca**)(**tfib**)

A mixture of **pca** (10.0 μL, 106 μmol) and **tfib** (40.2 mg, 100 μmol) was placed in a 10 mL stainless steel jar along with two stainless steel balls 7 mm in diameter. The reaction mixture was then milled for 15 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz.

Synthesis of (**van**)(**tfib**)

A mixture of **van** (20.0 mg, 131 μmol) and **tfib** (52.8 mg, 131 μmol) was placed in a 10 mL stainless steel jar along with 40 μL of nitromethane and a stainless steel ball 12 mm in diameter. The reaction mixture was then milled for 90 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz.

SOLUTION SYNTHESES

Synthesis of (**dmab**)$_2$(**tfib**)

A mixture of **dmab** (12.8 mg, 85.8 μmol) and **tfib** (17.2 mg, 42.8 μmol) was dissolved in 1.0 mL of hot tetrahydrofuran and left to crystallize at room temperature.

Solution synthesis of (**napht**)$_2$(**tfib**)

A mixture of **napht** (20.0 mg, 116 μmol) and **tfib** (23.3 mg, 58.0 μmol) was dissolved in 1.0 mL of hot methanol and left to crystallize at room temperature.

Synthesis of (**dmb**)$_2$(**tfib**)

A mixture of **dmb** (10.0 mg, 60.2 μmol) and **tfib** (24.2 mg, 60.2 μmol) was dissolved in 1.0 mL of hot nitromethane and left to crystallize at room temperature.

Solution synthesis of (**pca**)(**tfib**)

A mixture of **pca** (10.0 μL, 106 μmol) and **tfib** (40.2 mg, 100 μmol) was dissolved in 1.0 mL of hot acetone and left to crystallize at room temperature.

Synthesis of (**van**)(**tfib**)

A mixture of **van** (40.0 mg, 262 μmol) and **tfib** (105.6 mg, 262 μmol) was dissolved in 1.5 mL of hot methanol and left to crystallize at room temperature.

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 15.00.[1]

POWDER X-RAY DIFFRACTION EXPERIMENTS

PXRD experiments were performed on a PHILIPS PW 1840 X-ray diffractometer with Cu*K*α1 (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.[2]

SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of the prepared samples 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 295 K, except for the (**pca**)(**tfib**) cocrystal which decomposes at room temperature and its data was therefore collected at 150 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.[3] The structures were solved by direct methods and refined using the SHELXS, SHELXT and SHELXL programs, respectively.[4, 5] The structural refinement was performed on F^2 using all data. Alykl, aryl and hydroxyl group hydrogen atoms were placed in calculated positions and treated as riding on their parent atoms. All calculations were performed using the WINGX crystallographic suite of programs.[6] The molecular structures of compounds and their molecular packing projections were prepared by Mercury.[7]

References

1. STARe Evaluation Software Version 15.00, Mettler–Toledo GmbH, 2016.

2. 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.

3. Oxford Diffraction, Oxford Diffraction Ltd., Xcalibur CCD system, CrysAlis CCD and CrysAlis RED software, Version 1.170, 2003.

4. (a) G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122; (b) G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3–8.

5. G. M. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3–8.

6. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849–854.

7. 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.

Table S1. Crystal data and refinement details for the prepared cocrystals.

	(**dmab**)$_2$(**tfib**)	(**napht**)$_2$(**tfib**)	(**dmb**)$_2$(**tfib**)
Molecular formula	$C_{24}H_{22}F_4I_2N_2O_2$	$C_{28}H_{16}F_4I_2O_4$	$C_{24}H_{20}F_4I_2O_6$
M_r	700.23	746.21	734.20
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\,\bar{1}$	$P\,2_1/n$	$P\,2_1/n$
Crystal data:			
a / Å	8.1668(5)	9.8371(8)	8.2542(3)
b / Å	8.4423(6)	12.5539(10)	15.3640(5)
c / Å	10.8612(5)	21.3222(15)	10.5028(5)
α / °	100.288(5)	90	90
β / °	105.696(5)	96.397(7)	106.955(4)
γ / °	110.297(6)	90	90
V / Å^3	644.64(7)	2616.8(4)	1274.04(9)
Z	1	4	2
D_{calc} / g cm^{-3}	1.804	1.894	1.914
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.51 x 0.49 x 0.16	0.50 x 0.25 x 0.09	0.50 x 0.21 x 0.10
μ / mm^{-1}	2.491	2.465	2.535
F(000)	338	1432	708
Refl. collected/unique	6447 / 2799	16565 / 5691	13910 / 2778
Data/restraints/ parameters	156	345	165
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.471; –0.453	1.420; –0.946	0.292; –0.603
$R[F^2 > 4\sigma(F^2)]$	0.0308	0.060	0.0238
w$R(F^2)$	0.0773	0.133	0.0644
Goodness-of-fit, S	1.143	1.124	1.050

Table S1. Continued.

	(**van**)(**tfib**)	(**pca**)(**tfib**)
Molecular formula	$C_{14}H_8F_4I_2O_4$	$C_{12}H_5F_4I_2NO$
M_r	554.00	508.97
Crystal system	monoclinic	triclinic
Space group	$P\,2_1/c$	$P\,\bar{1}$
Crystal data:		
a / Å	7.6135(5)	4.2934(3)
b / Å	28.680(2)	6.2651(4)
c / Å	7.4414(7)	13.2828(8)
α / °	90	101.118(5)
β / °	98.956(7)	96.900(5)
γ / °	90	98.117(5)
V / Å^3	1605.1(2)	343.05(4)
Z	4	1
D_{calc} / g cm^{-3}	2.293	2.464
λ(MoK_α) / Å	0.71073	0.71073
T / K	295	150
Crystal size / mm^3	0.52 x 0.26 x 0.23	0.48 x 0.20 x 0.06
μ / mm^{-1}	3.970	4.623
F(000)	1032	234
Refl. collected/unique	10189 / 3498	2287 / 1462
Data/restraints/ parameters	209	112
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.536; –1.050	1.179; –2.195
$R[F^2 > 4\sigma(F^2)]$	0.0558	0.0361
w$R(F^2)$	0.1215	0.1042
Goodness-of-fit, S	1.196	1.137

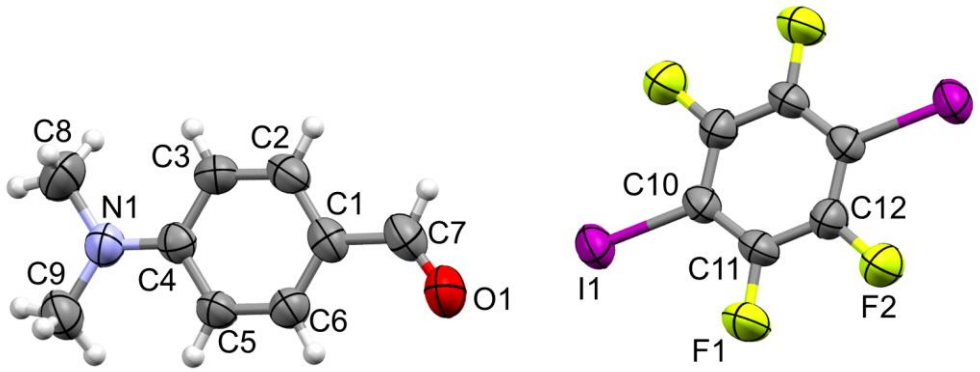

Figure S1. Molecular structure of (**dmab**)$_2$(**tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

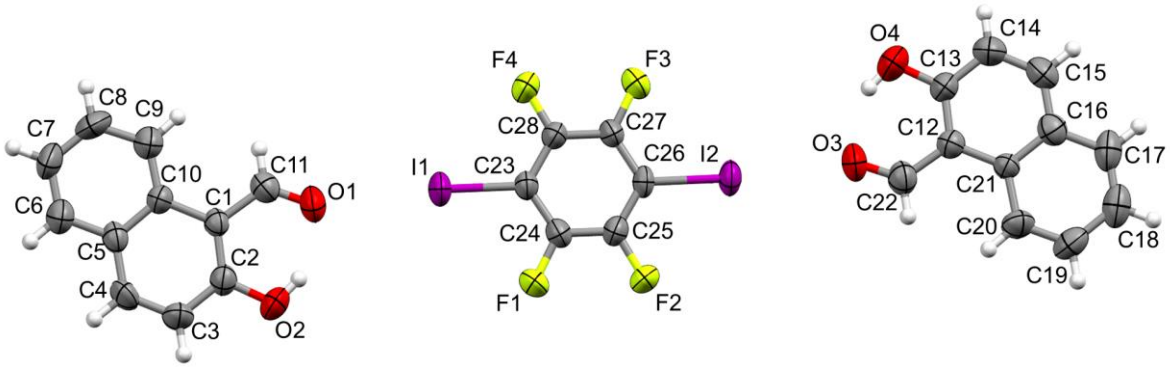

Figure S2. Molecular structure of (**napht**)$_2$(**tfib)** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

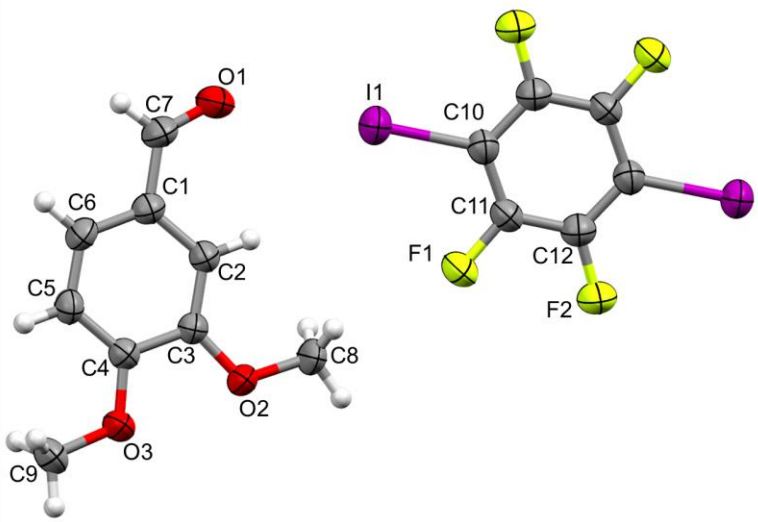

Figure S3. Molecular structure of (**dmb**)$_2$(**tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

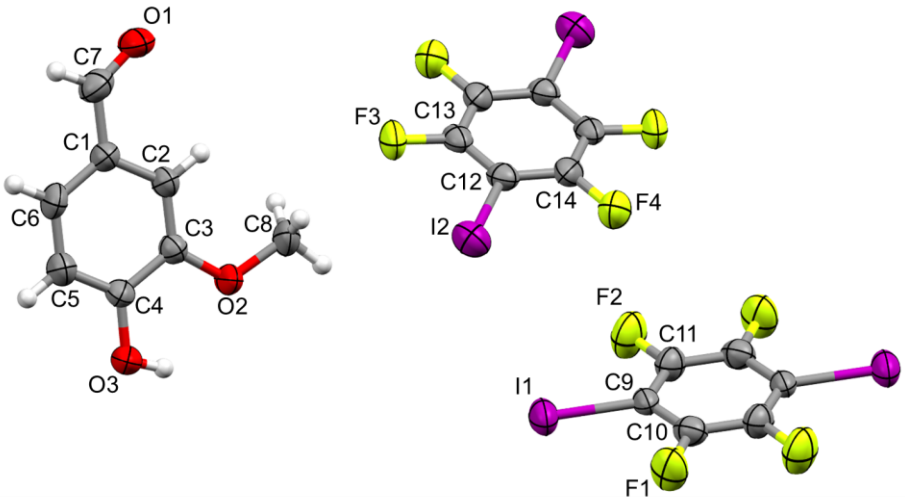

Figure S4. Molecular structure of (**van**)(**tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

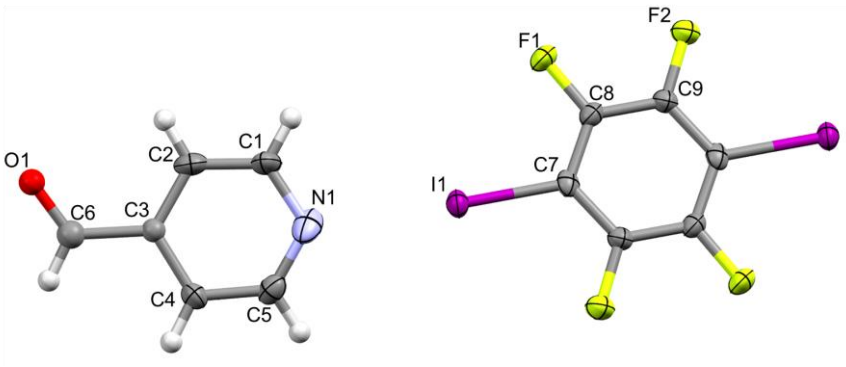

Figure S5. Molecular structure of (**pca**)(**tfib**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius.

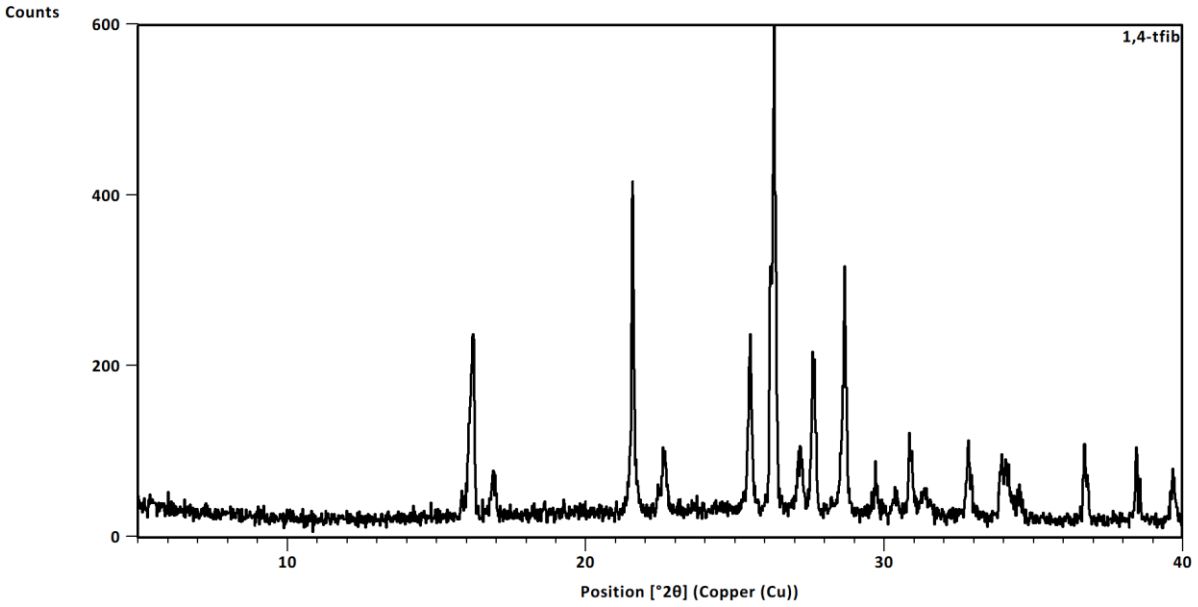

Figure S6. PXRD pattern of **tfib**.

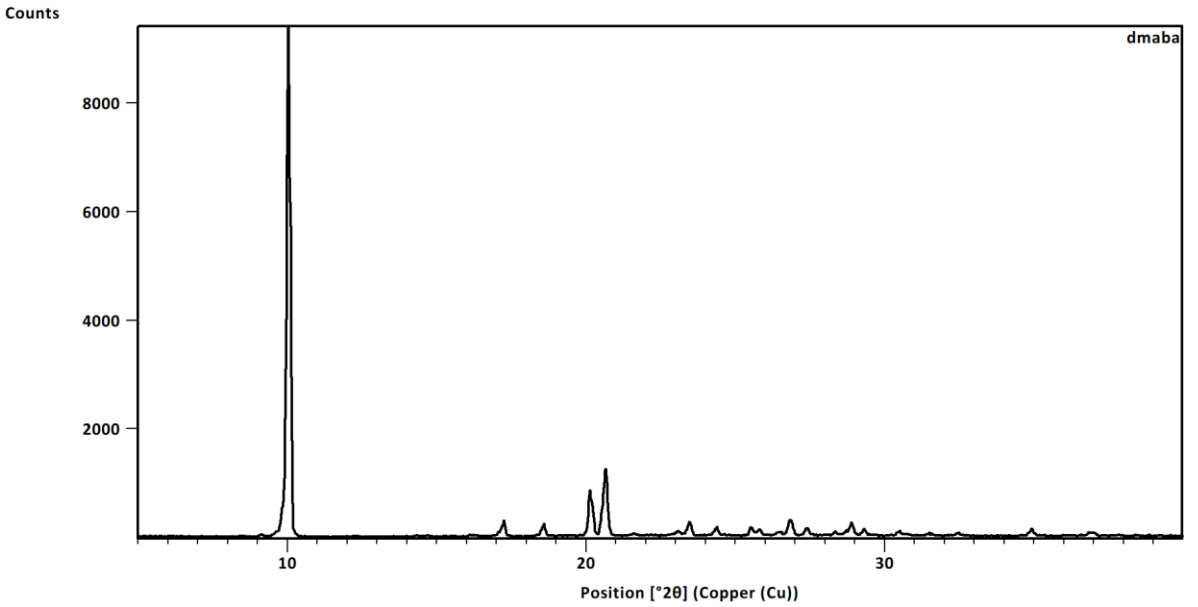

Figure S7. PXRD pattern of **dmab**.

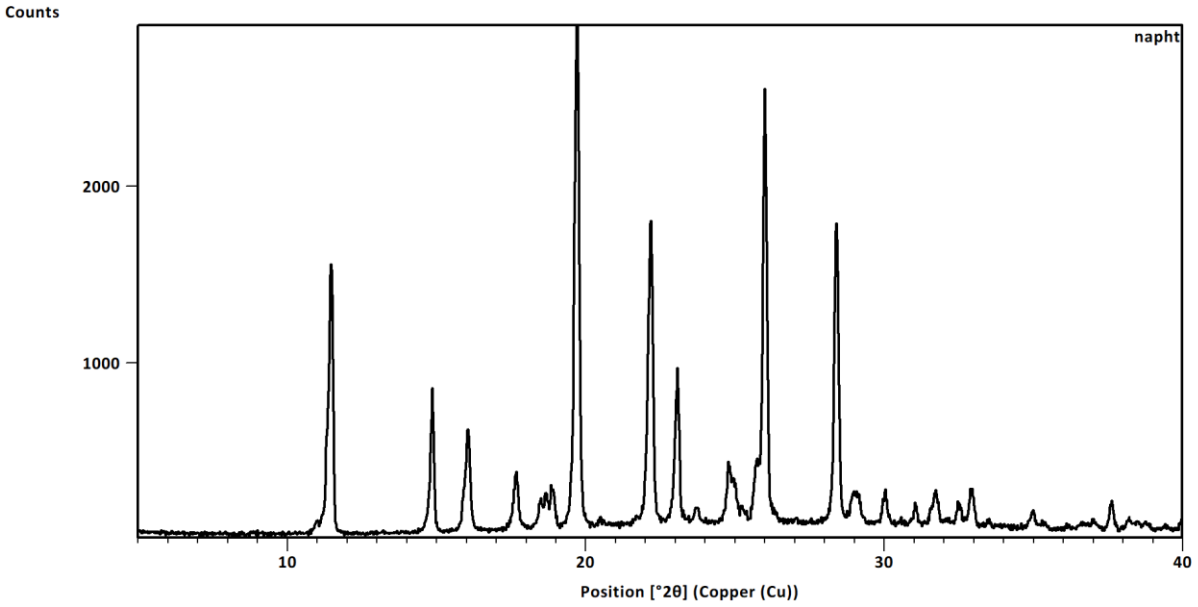

Figure S8. PXRD pattern of **napht**.

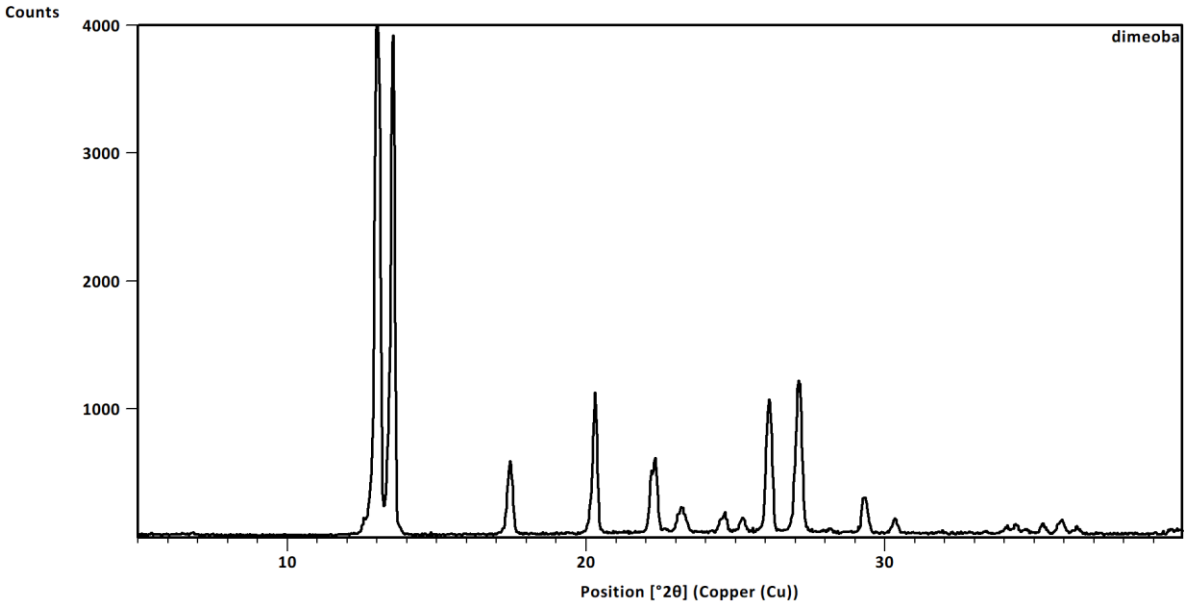

Figure S9. PXRD pattern of **dmb**.

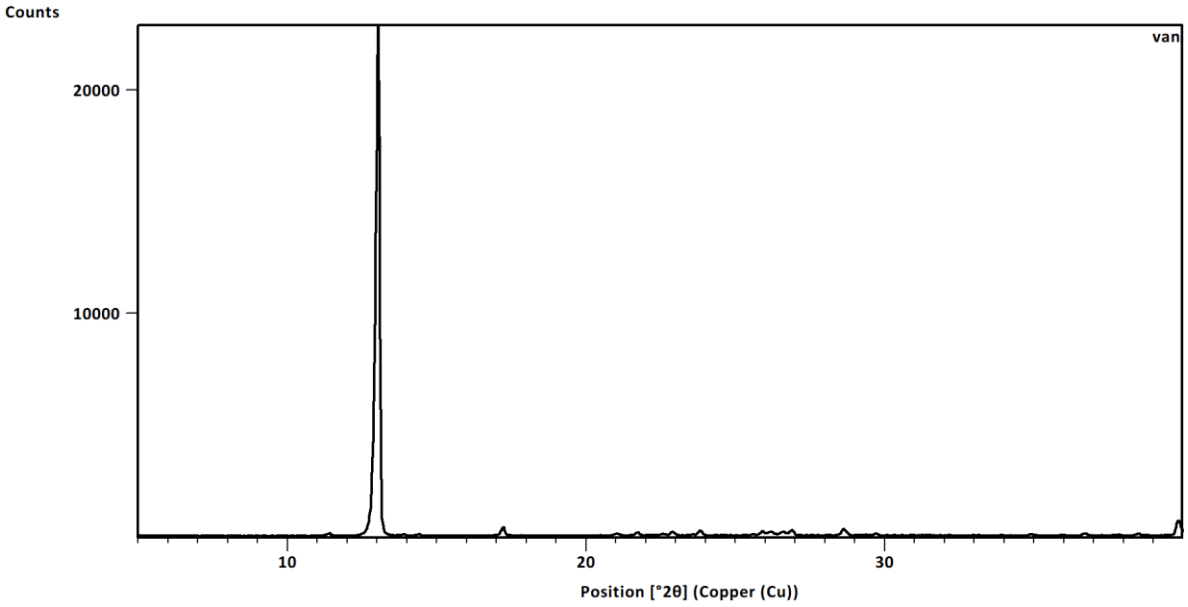

Figure S10. PXRD pattern of **van.**

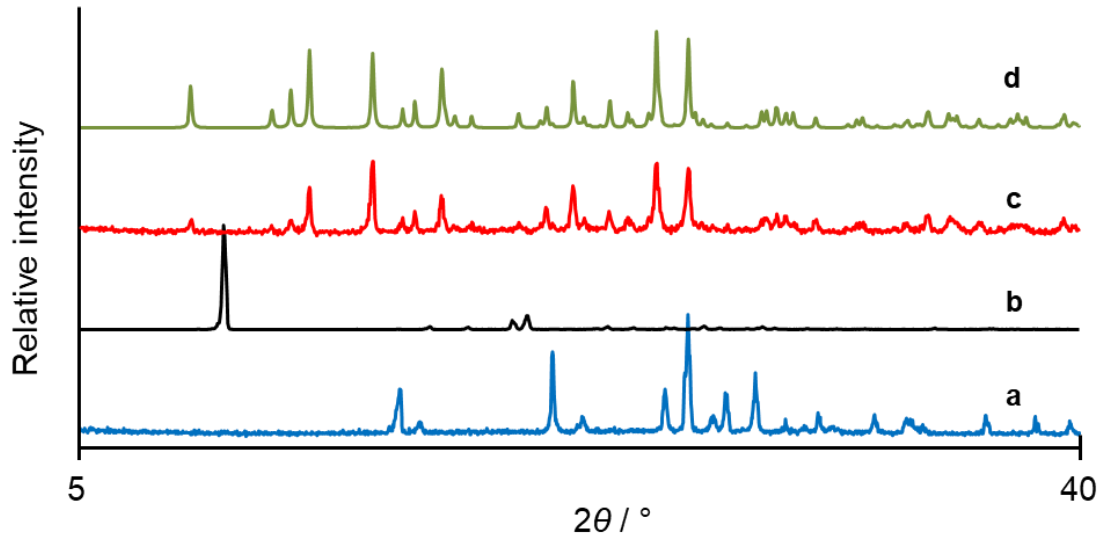

Figure S11. PXRD patterns of: a) **tfib**, b) **dmab**, c) product obtained by grinding **tfib** and **dmab** in a 1:2 stoichiometric ratio, d) calculated pattern from (**dmab**)$_2$(**tfib**) single crystal data.

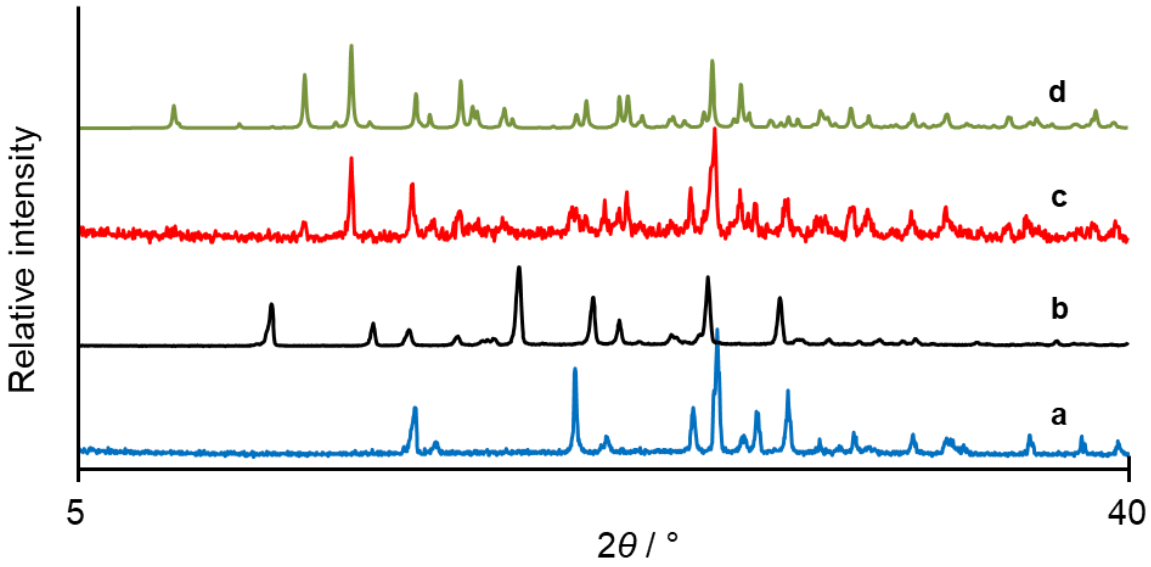

Figure S12. PXRD patterns of: a) **tfib**, b) **napht**, c) product obtained by grinding **tfib** and **napht** in a 1:2 stoichiometric ratio, d) calculated pattern from (**napht**)$_2$(**tfib**) single crystal data

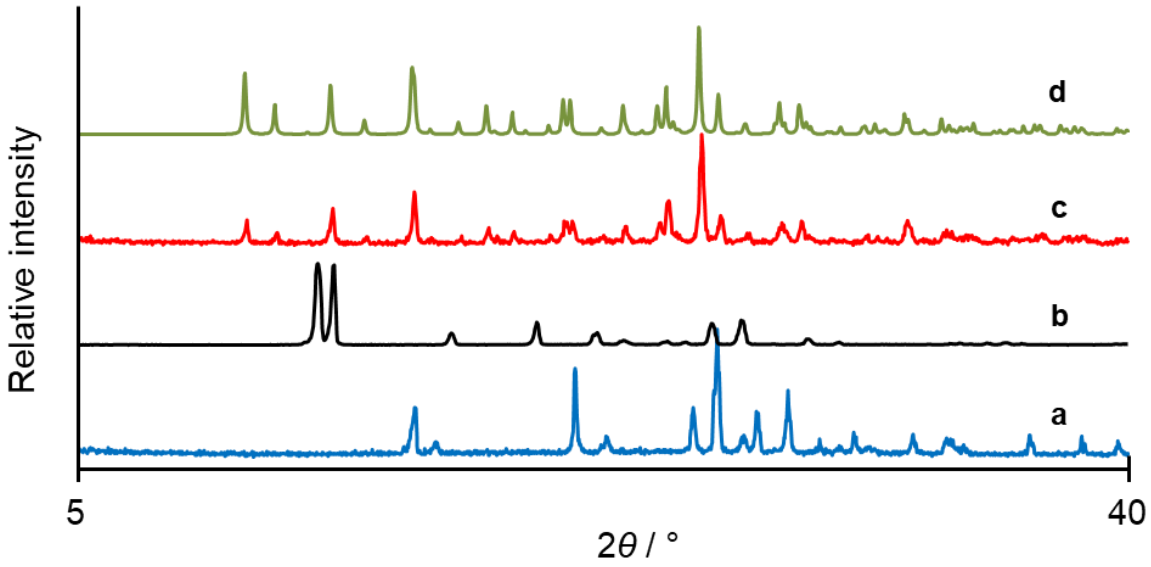

Figure S13. PXRD patterns of: a) **tfib**, b) **dmb**, c) product obtained by grinding **tfib** and **dmb** in a 1:2 stoichiometric ratio, d) calculated pattern from (**dmb**)$_2$(**tfib**) single crystal data.

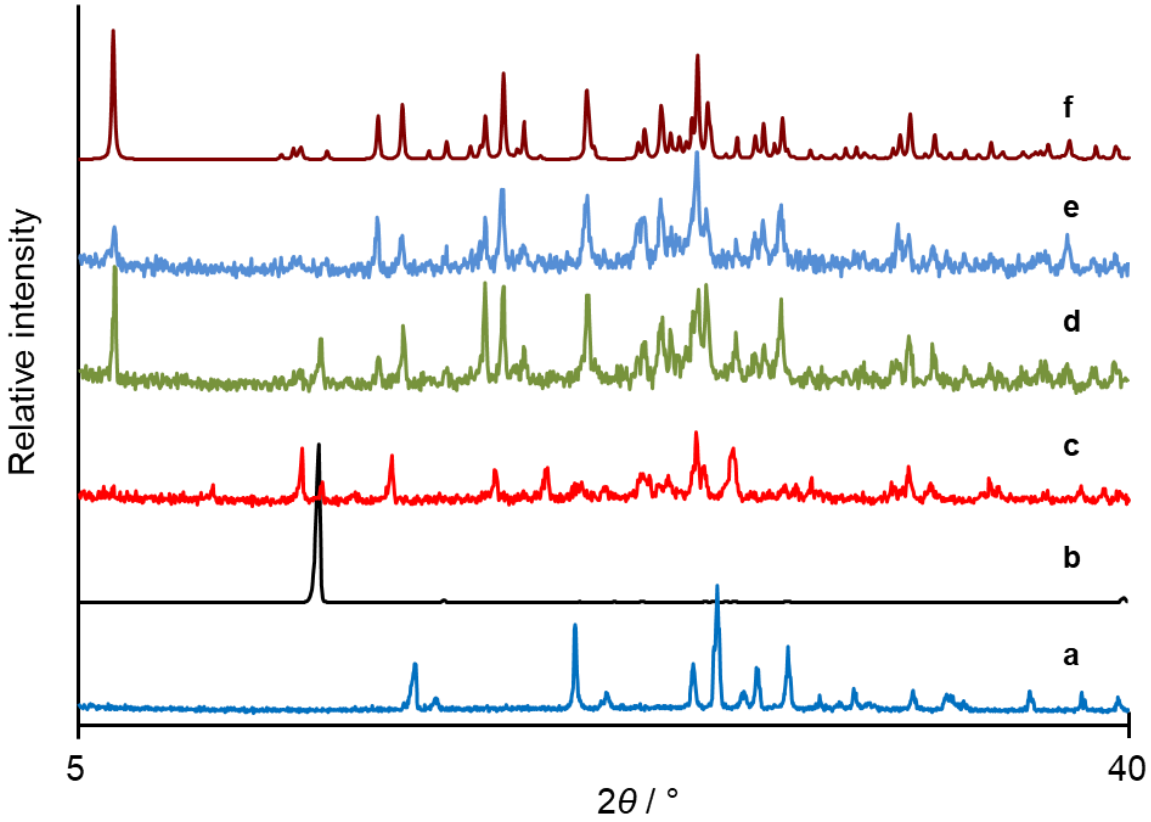

Figure S14. PXRD patterns of: a) **tfib**, b) **van,** c) product obtained by grinding **tfib** and **van** in a 1:1 stoichiometric ratio for 15 minutes, d) product obtained by heating the grinding product (c) at 90 °C for 15 minutes, e) product obtained by grinding **tfib** and **van** in a 1:1 stoichiometric ratio for 90 minutes, f) calculated pattern from (**van**)(**tfib**) single crystal data.

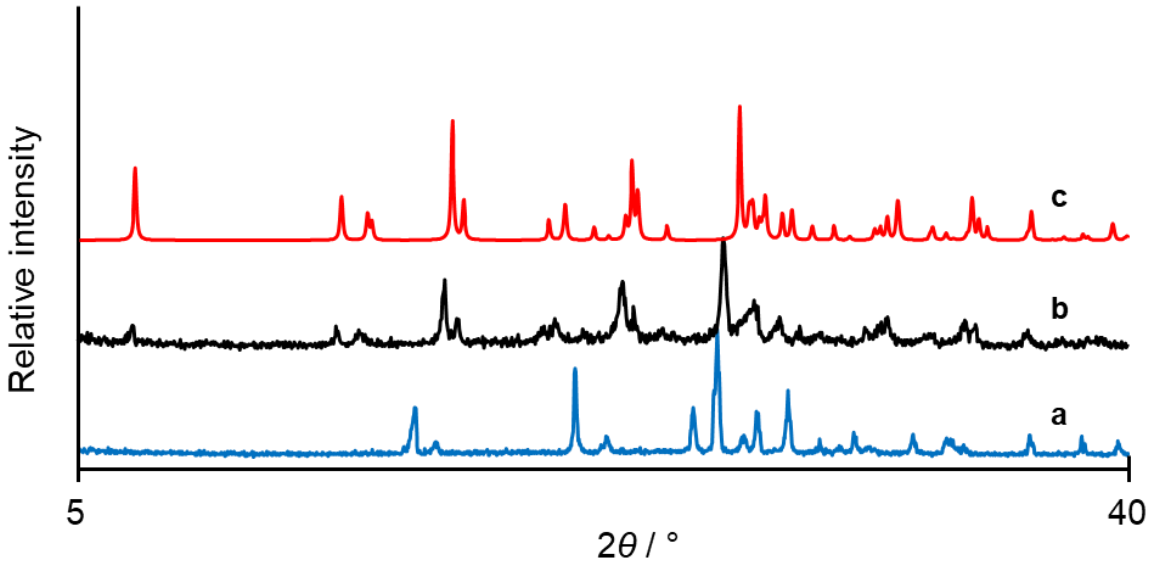

Figure S15. PXRD patterns of: a) **tfib**, b) product obtained by grinding **tfib** and **pca** in a 1:1 stoichiometric ratio, c) calculated pattern from (**pca**)(**tfib**) single crystal data.

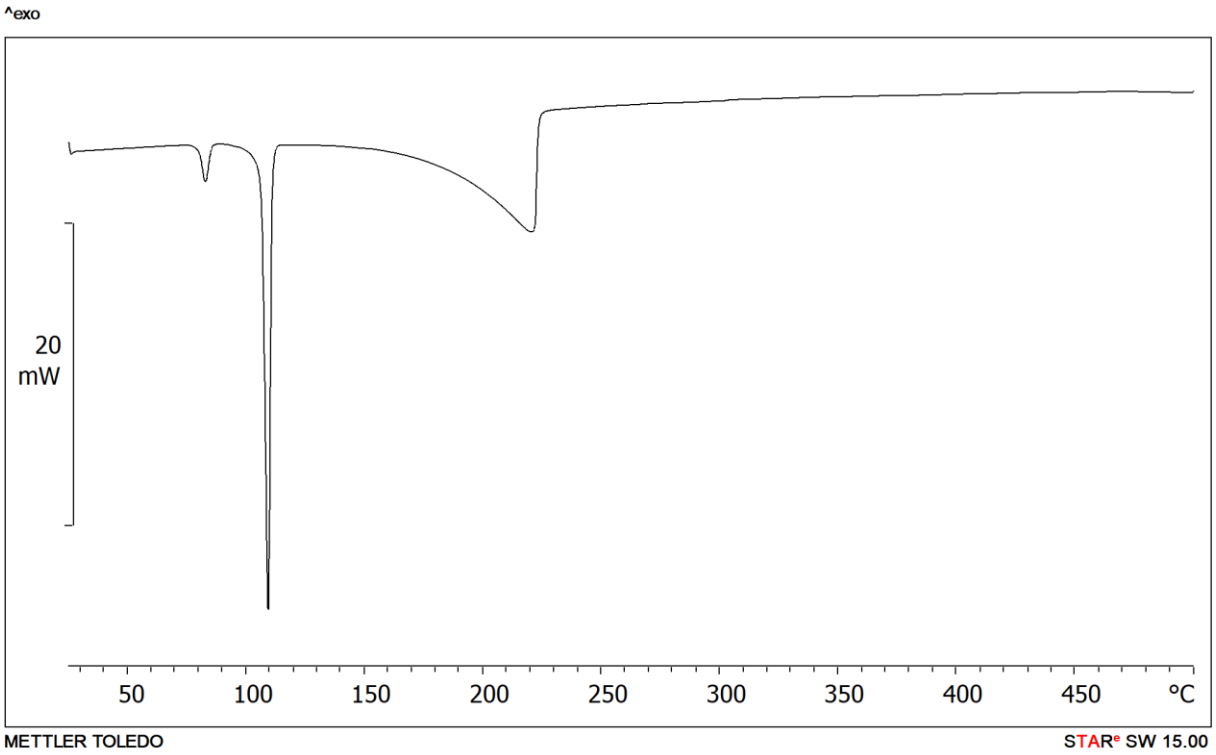

Figure S16. DSC curve of **tfib**.

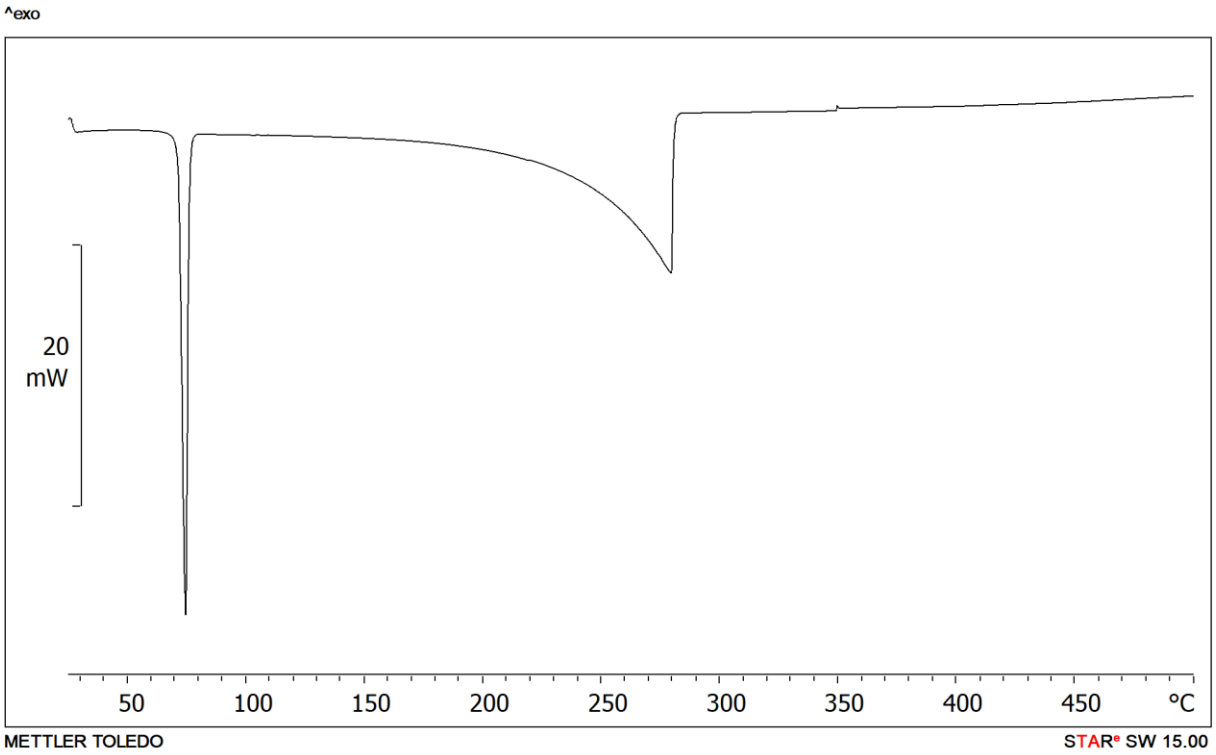

Figure S17. DSC curve of **dmab**.

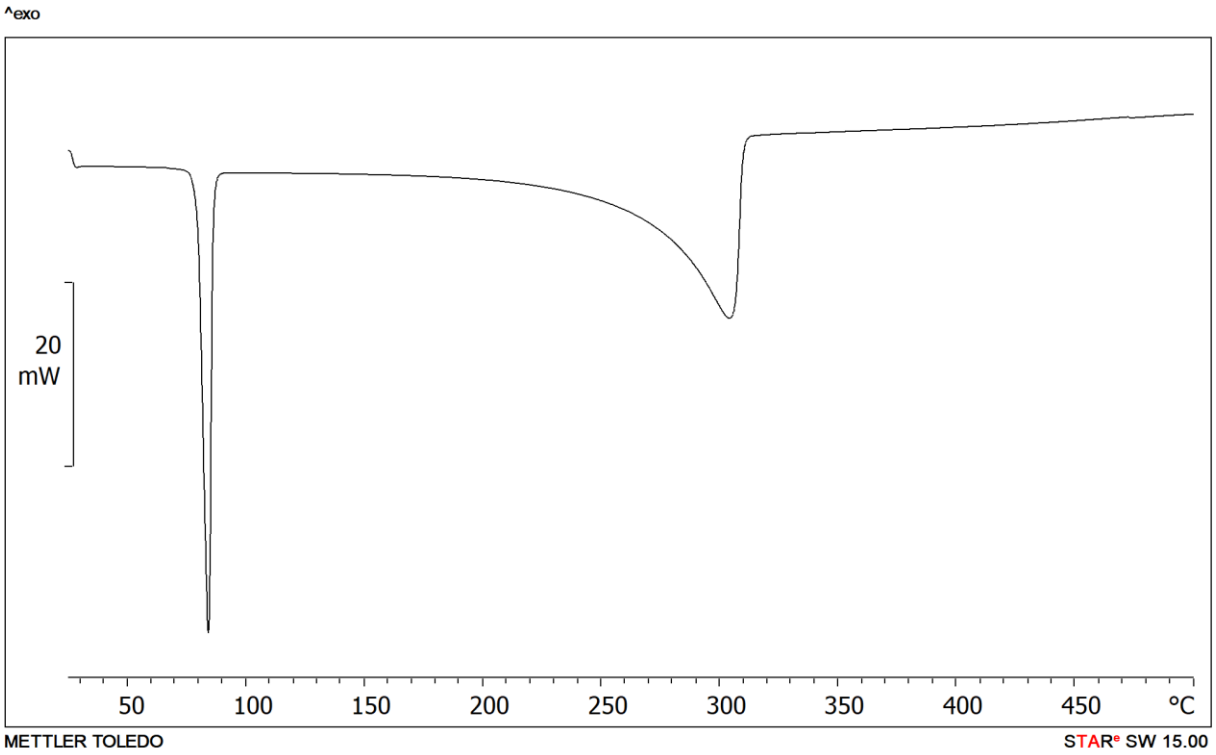

Figure S18. DSC curve of **napht**.

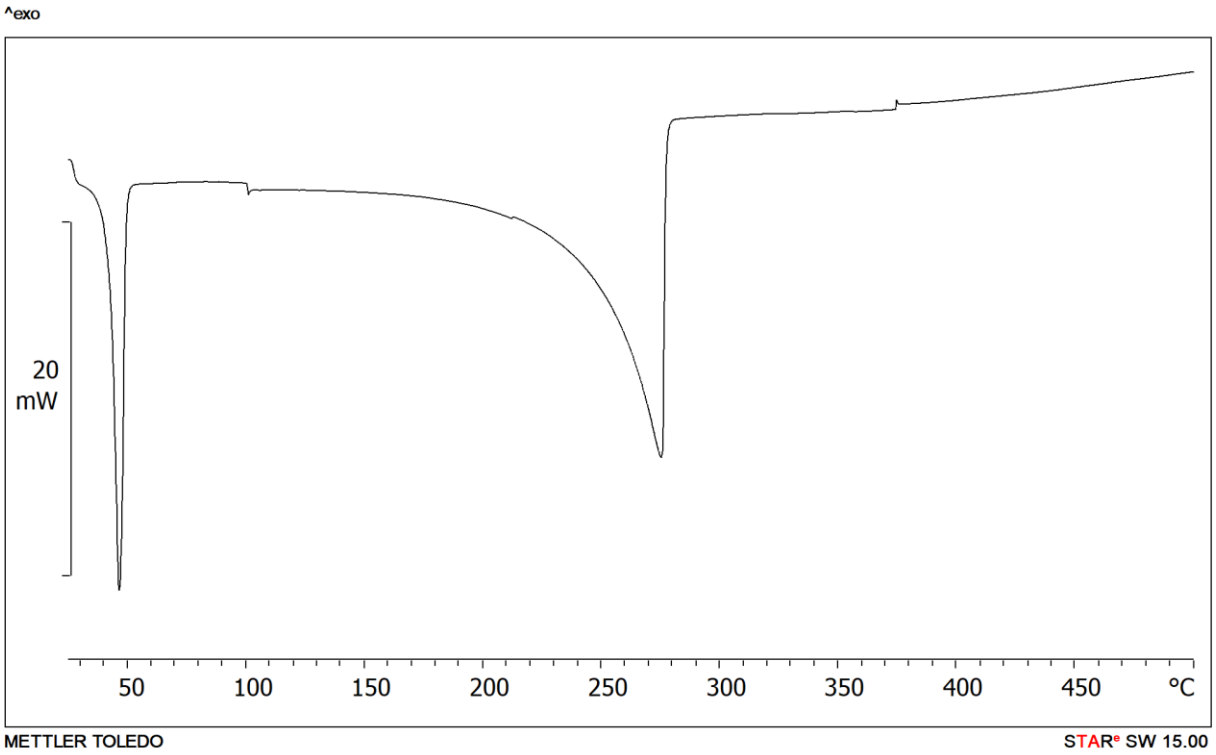

Figure S19. DSC curve of **dmb**.

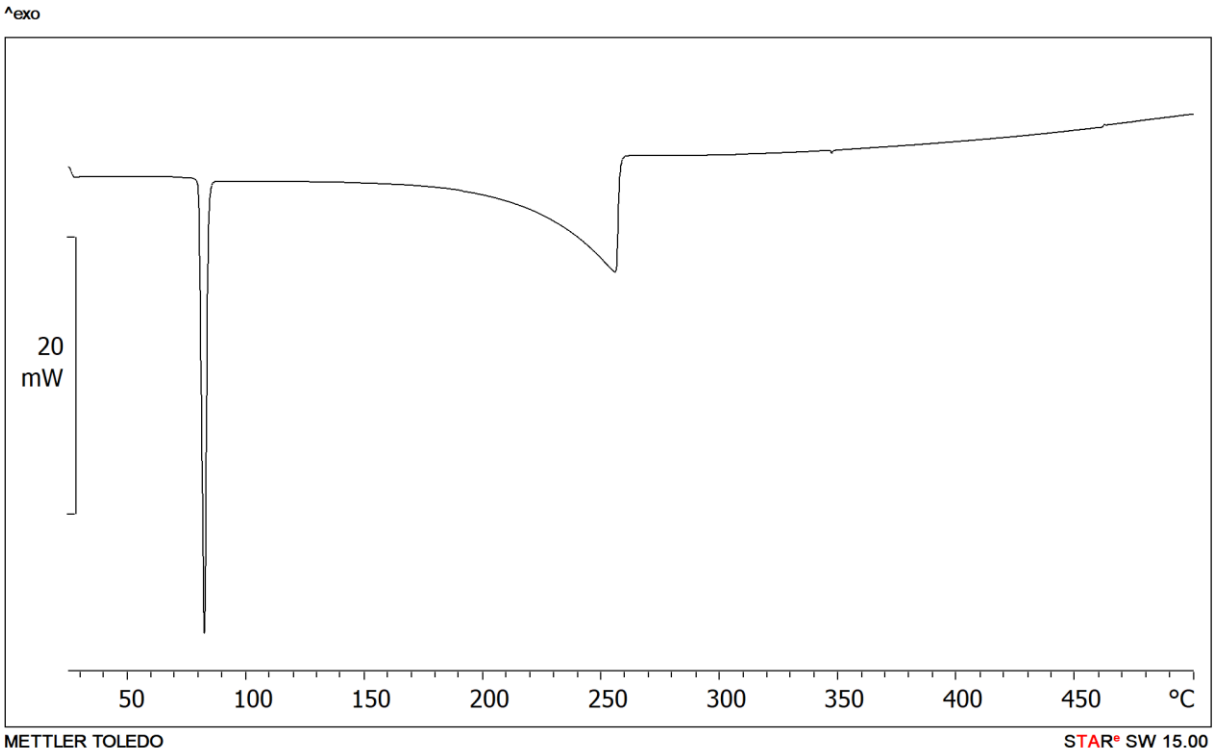

Figure S20. DSC curve of **van**.

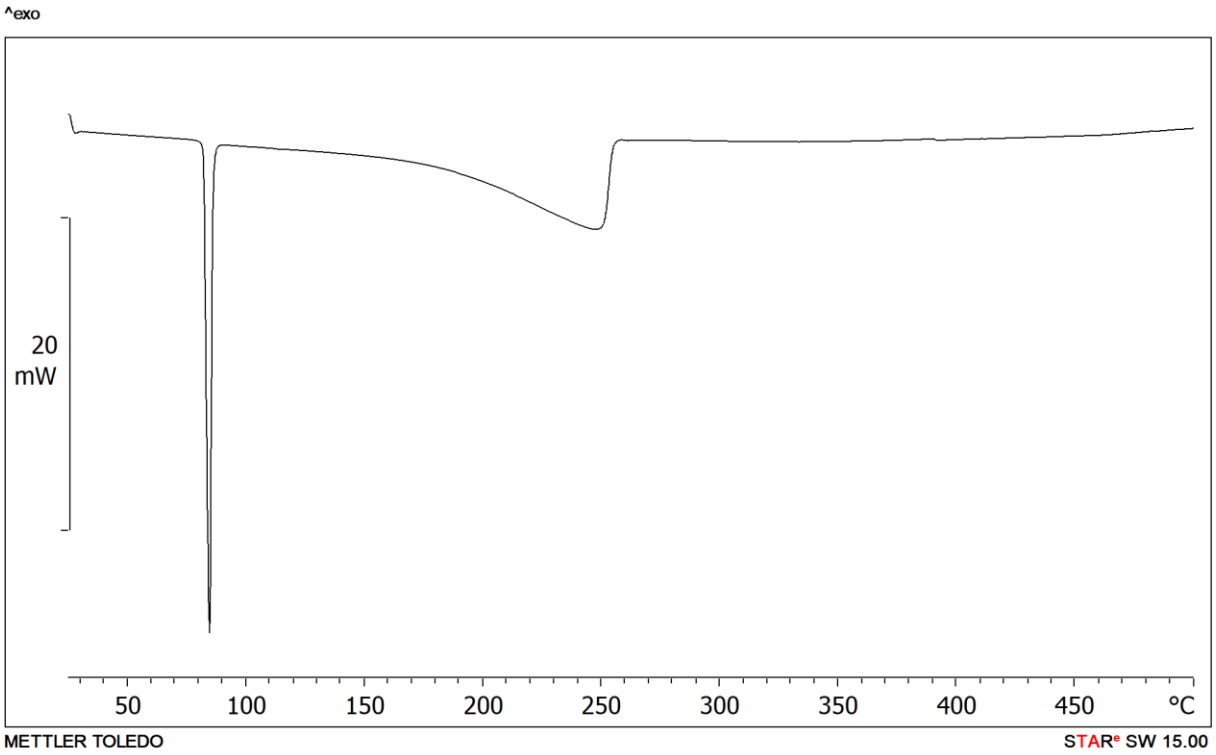

Figure S21. DSC curve of (**dmab**)$_2$(**tfib**).

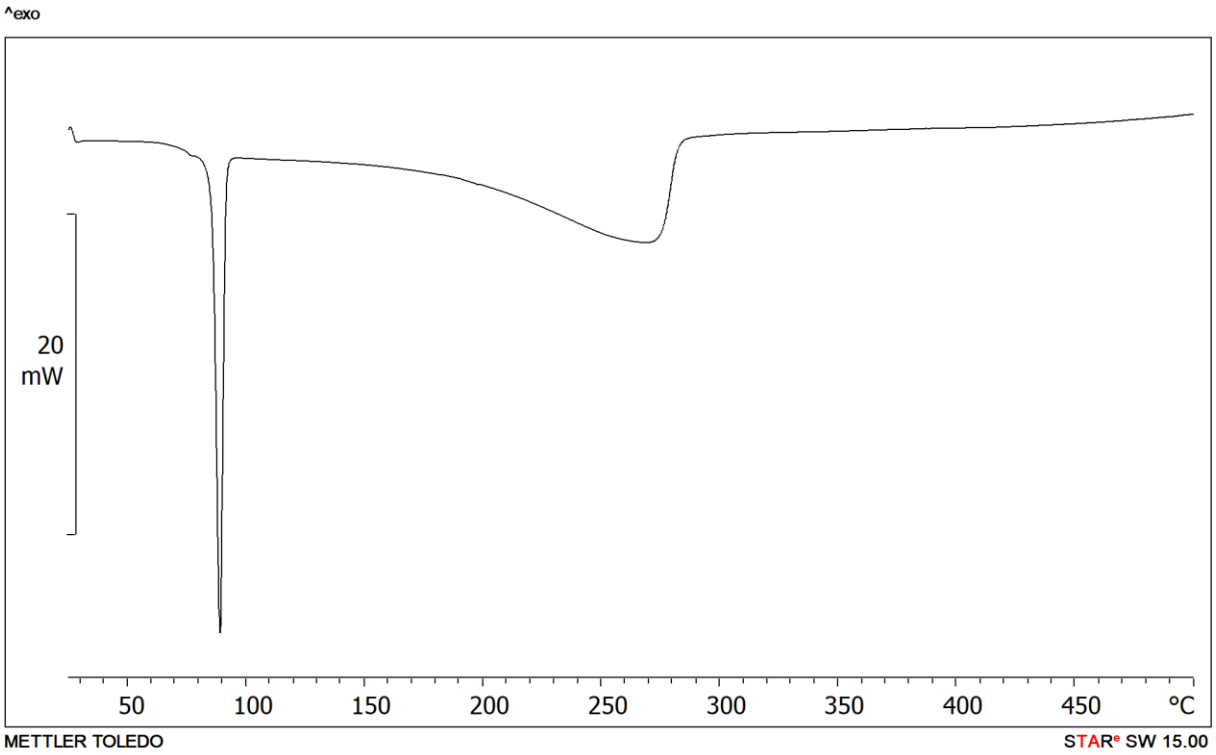

Figure S22. DSC curve of (**napht**)$_2$(**tfib**).

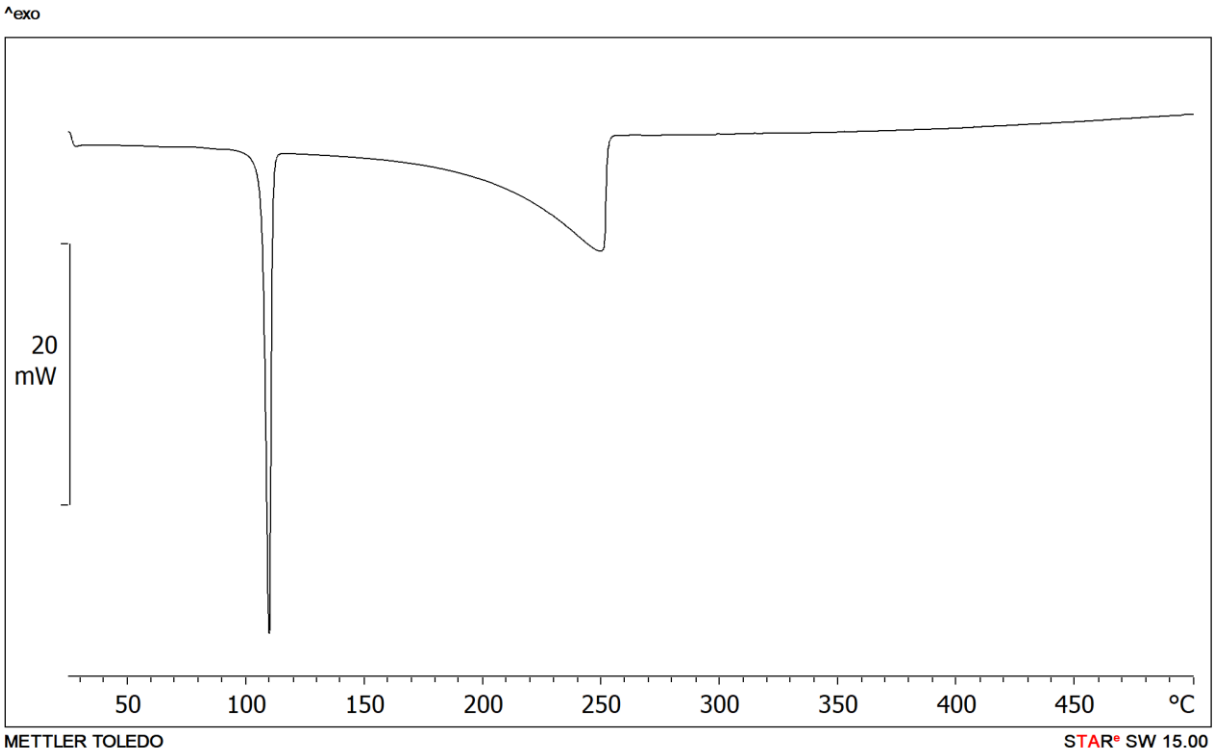

Figure S23. DSC curve of (**dmb**)$_2$(**tfib**).

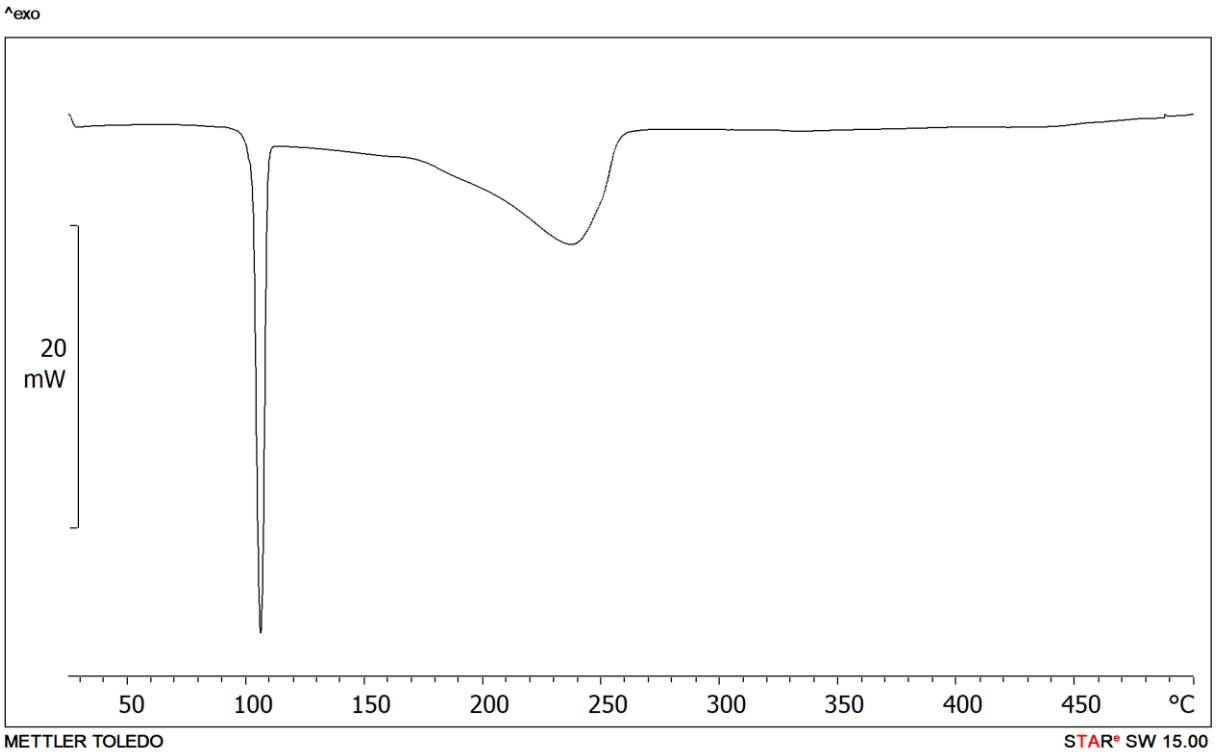

Figure S24. DSC curve of (**van**)(**tfib**).

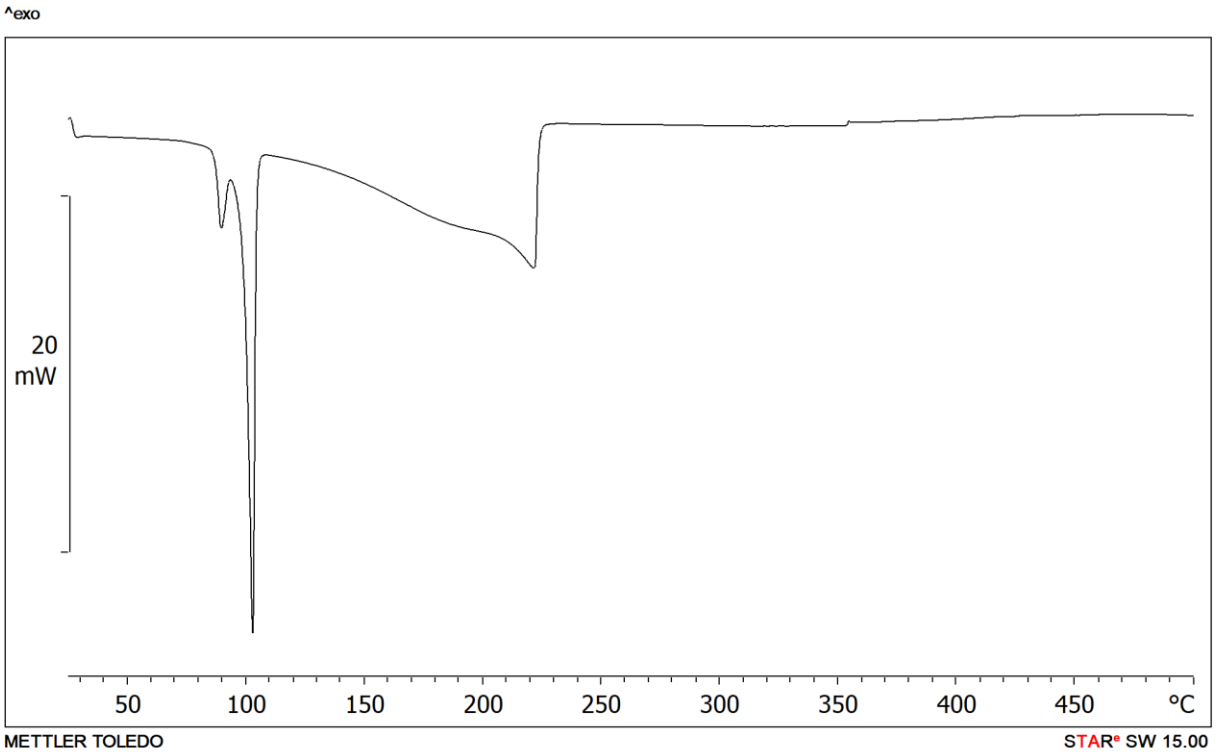

Figure S25. DSC curve of (**pca**)(**tfib**).