SUPPORTING INFORMATION

Effect of atmosphere on solid-state amine-aldehyde condensations: gas-phase catalysts for solid-state transformations

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EXPERIMENTAL DETAILS

MATERIALS

The starting materials, 2-hydroxy-1-naphthaldehyde (**napht**), 2-aminobenzonitrile (**abn**) and 2-hydroxy-3-methoxybenzaldehyde (*ortho*-vanillin, **ovan**) were obtained from Acros Organics; 4-aminobenzonitrile (**4abn**), 4-hydroxy-3-methoxybenzaldehyde (vanillin, **van**) and 5-Amino-2-hydroxybenzoic acid (**5asa**) were 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.

SOLID-STATE SYNTHESIS

WATER VAPOUR DIGESTION EXPERIMENTS

Relative humidity conditions were achieved at ambient temperature (ca. 25 °C) within sealed glass desiccator jars containing NaOH for the 0% RH condition and an appropriate saturated aqueous salt solution: K_2CO_3 for 43% RH, NaCl for 75% RH and K_2SO_4 for 98% RH.[1] Relative humidity conditions were monitored with humidity-indicator cards (Sigma–Aldrich Co. Ltd.).

Synthesis of **1**

Equimolar quantities of **abn** (0.118 g, 1 mmol) and **napht** (0.172 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. Open glass vials containing 50–60 mg of powder (a mixture of solid reactants) were stored in the RH chambers (0%, 43%, 75% and 98% RH) at 25 °C. The efficiency of solid state reactions was compared by monitoring the reaction by PXRD for time periods of 1 day, 2 days, 3 days, 4 days, 8 days, 10 days and 18 days.

Synthesis of **2**

Equimolar quantities of **4abn** (0.118 g, 1 mmol) and **napht** (0.172 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. Open glass vials containing 70–80 mg of powder (a mixture of solid reactants) were stored in the RH chambers (0% and 98% RH) at 25 °C. The efficiency of solid state reactions was compared by monitoring the reaction by PXRD for time periods of 1 day, 2 days, 8 days, 4 weeks, 8 weeks, 11 weeks and 13 weeks.

Synthesis of **3**

Equimolar quantities of **4aba** (0.137 g, 1 mmol) and **napht** (0.172 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. Open glass vials containing 70–80 mg of

powder (a mixture of solid reactants) were stored in the RH chambers (0% and 98% RH) at 25 °C. The efficiency of solid state reactions was compared by monitoring the reaction by PXRD for time periods of 1 day, 2 days, 8 days, 4 weeks, 8 weeks, 11 weeks and 13 weeks.

Synthesis of **4**

Equimolar quantities of **ovan** (0.152 g, 1 mmol) and **5asa** (0.153 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. Open glass vials containing 70–80 mg of powder (a mixture of solid reactants) were stored in the RH chambers (0% and 98% RH) at 25 °C. The efficiency of solid state reactions was compared by monitoring the reaction by PXRD for time periods of 1 day, 5days, 8 days, 12 days, 15 days and 4 weeks.

Synthesis of **5**

Equimolar quantities of **napht** (0.172 g, 1 mmol) and **5asa** (0.153 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. Open glass vials containing 70–80 mg of powder (a mixture of solid reactants) were stored in the RH chambers (0% and 98% RH) at 25 °C. The efficiency of solid state reactions was compared by monitoring the reaction by PXRD for time periods of 1 day, 5days, 8 days, 12 days, 15 days and 4 weeks.

SOLVENT VAPOUR DIGESTION EXPERIMENTS

Synthesis of **4**

Equimolar quantities of **ovan** (0.152 g, 1 mmol) and **5asa** (0.153 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. 50–60 mg of mixture of solid reactants was placed in a 2 mL open test tube, and then exposed (at 25 °C) to EtOH (2 mL) vapour inside a 15 mL bottle, with no contact between the powder and the liquid. The bottle was tightly closed, but no vacuum was operated. The efficiency of solid state reactions under vapour of EtOH, was compared by monitoring the reaction by PXRD for time periods of 1 hour, 1 day and 3 days.

Synthesis of **5**

Equimolar quantities of **napht** (0.172 g, 1 mmol) and **5asa** (0.153 g, 1 mmol) were gently ground in an agate mortar at 25 °C for 10 min. 50–60 mg of mixture of solid reactants was placed in a 2 mL open test tube, and then exposed (at 25 °C) to solvent (2 mL) vapours inside a 15 mL bottle, with no contact between the powder and the liquid. The bottle was tightly closed, but no vacuum was operated. The efficiency of solid state reactions under vapour of EtOH, vapour of TEA and vapour mixture of EtOH and TEA (5% v/v of TEA) was compared by monitoring the reaction by PXRD.

BALL MILLING EXPERIMENTS

Synthesis of **4**

For NG experiment equimolar quantities of **ovan** (0.106 g, 0.7 mmol) and **5asa** (0.107 g, 0.7 mmol) were placed in a 10 mL stainless steel grinding jar with two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 5 and 30 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

For LAG experiment equimolar quantities of **ovan** (0.106 g, 0.7 mmol) and **5asa** (0.107 g, 0.7 mmol) were placed in a 10 mL stainless steel grinding jar along with 30 µL of EtOH and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 5 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of **5**

For NG experiment equimolar quantities of **napht** (0.106 g, 0.6 mmol) and **5asa** (0.094 g, 0.6 mmol) were placed in a 10 mL stainless steel grinding jar with two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 45 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

For LAG experiments equimolar quantities of **napht** (0.106 g, 0.6 mmol) and **5asa** (0.094 g, 0.6 mmol) were placed in a 10 mL stainless steel grinding jar along with 30 µL of solvent (EtOH, TEA and mixture of EtOH and TEA with 5% v/v of TEA) and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled in a Retsch MM200 Shaker Mill operating at 25 Hz frequency, 45 minutes for experiments with EtOH and mixture of EtOH/TEA and 20 minutes for experiment with TEA.

Synthesis of **6**

For NG experiment equimolar quantities of **van** (0.106 g, 0.7 mmol) and **5asa** (0.107 g, 0.7 mmol) were placed in a 10 mL stainless steel grinding jar with two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 30 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

For LAG experiments equimolar quantities of **van** (0.093 g, 0.6 mmol) and **5asa** (0.094 g, 0.6 mmol) were placed in a 10 mL stainless steel grinding jar along with 30 µL of solvent (EtOH, TEA and mixture of EtOH and TEA with 5% v/v of TEA) and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled in a Retsch MM200 Shaker Mill operating at 25 Hz frequency, 30 minutes for experiments with EtOH and mixture of EtOH/TEA and 20 minutes for experiment with TEA.

SOLUTION SYNTHESIS

To monitor solid-state experiments, as well as to facilitate the characterisation of new materials (for **5** and **6**) by single-crystal X-ray diffraction, solid-state experiments were accompanied by conventional solution-based experiments. Crystal and molecular structures of **1** (form II), **2**, **3** and **4** have been previously reported: for **1** CCDC deposition number 832330[2], for **2** CCDC code FOQZER[3], for **3** CCDC code DIWMAY[4] and for **4** CCDC code VIKLAD[5].

Synthesis of **1**

Equimolar quantities of **abn** (1.18 g, 0.01 mol) and **napht** (1.72 g, 0.01 mol) were dissolved in hot methanol (20 mL and 30 mL, respectively). The solutions were mixed and the resulting mixture left at room temperature. Yellow precipitate corresponding to polymorph **I** appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with methanol. Crystals of form **II** (compound **1**) were obtained by recrystallisation of form **I** from acetone.

Synthesis of **2**

Equimolar quantities of **4abn** (1.18 g, 0.01 mol) and **napht** (1.72 g, 0.01 mol), were dissolved in hot methanol (15 mL and 30 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 **3**

Equimolar quantities of **4aba** (1.37 g, 0.01 mol) and **napht** (1.72 g, 0.01 mol) were dissolved in hot methanol (10 mL and 30 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 **4**

Equimolar quantities of **ovan** (1.06 g, 7 mmol) and **5asa** (1.07 g, 7 mmol) were dissolved in hot ethanol (20 mL and 50 mL, respectively). The solution of **ovan** and suspension of **5asa** 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 ethanol.

Synthesis of **5**

Equimolar quantities of **napht** (0.53 g, 3 mmol) and **5asa** (0.47 g, 3 mmol) were dissolved in hot methanol (20 mL and 40 mL, respectively). The solution of **napht** and suspension of **5asa** 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 ethanol. Single crystals of **5** suitable for X-ray diffraction were obtained by recrystallisation from DMSO.

Synthesis of **6**

Equimolar quantities of **ovan** (1.06 g, 7 mmol) and **5asa** (1.07 g, 7 mmol) were dissolved in hot ethanol (20 mL and 50 mL, respectively). The solution of **van** and suspension of **5asa** were mixed and the resulting mixture left at room temperature. Dark yellow precipitate appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with ethanol.

THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823^e module in sealed aluminium pans (40 μL), heated in flowing nitrogen (200 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.[6]

FTIR SPECTROSCOPY

Infrared spectra were recorded on an EQUINOX 55 FTIR spectrophotometer using a KBr pellet. The data collection and analysis was performed using the program package OPUS 4.0.[7]

SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of **5** and **6(H_2O)** 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 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.[8] The data sets were collected using the ω scan mode over the 2θ range up to 54°. Programs CrysAlis CCD and CrysAlis RED[8] 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.[9] 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.[10] The molecular structures of compounds are presented by ORTEP-3[11] and their molecular packing projections were prepared by Mercury.[12]

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.[13]

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Table S1. General and crystallographic data for **5** and **6(H_2O)**.

	Compound 5	**Compound 6(H_2O)**
Molecular formula	$C_{18}H_{13}NO_4$	$C_{15}H_{15}NO_6$
M_r	307.305	305.287
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Crystal data:		
a / Å	10.4331(5)	11.0959(6)
b / Å	11.4045(5)	8.3683(4)
c / Å	11.4271(6)	14.7951(8)
α / °	90.00	90.00
β / °	97.021(4)	100.062(5)
γ / °	90.00	90.00
V / Å^3	1349.45(11)	1352.65(12)
Z	4	4
D_{calc} / g cm^{-3}	1.5126	1.499
λ(MoK_α) / Å	0.71073	0.71073
T / K	295	295
Crystal size / mm^3	0.09x0.19x0.21	0.15x0.16x0.17
μ / mm^{-1}	0.108	0.117
$F(000)$	640	640
Refl. collected/unique	7453 / 2910	7332 / 2932
Data/restraints/parameters	214	214
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.289; −0.230	0.373; −0.201
$R[F^2>4\sigma(F^2)]$	0.0549	0.0408
$wR(F^2)$	0.1459	0.0953
Goodness-of-fit, S	1.017	0.890

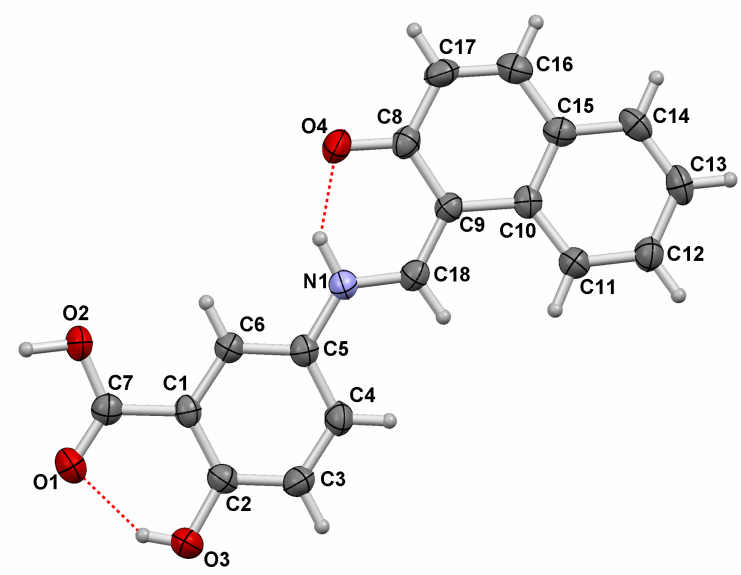

Figure S1. Molecular structures of **5** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radius.

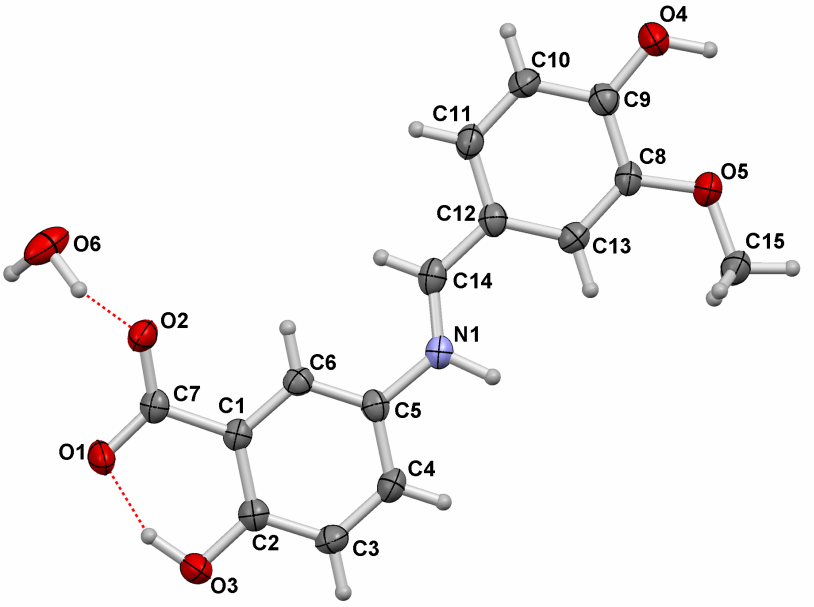

Figure S2. Molecular structures of **6(H_2O)** showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radius.

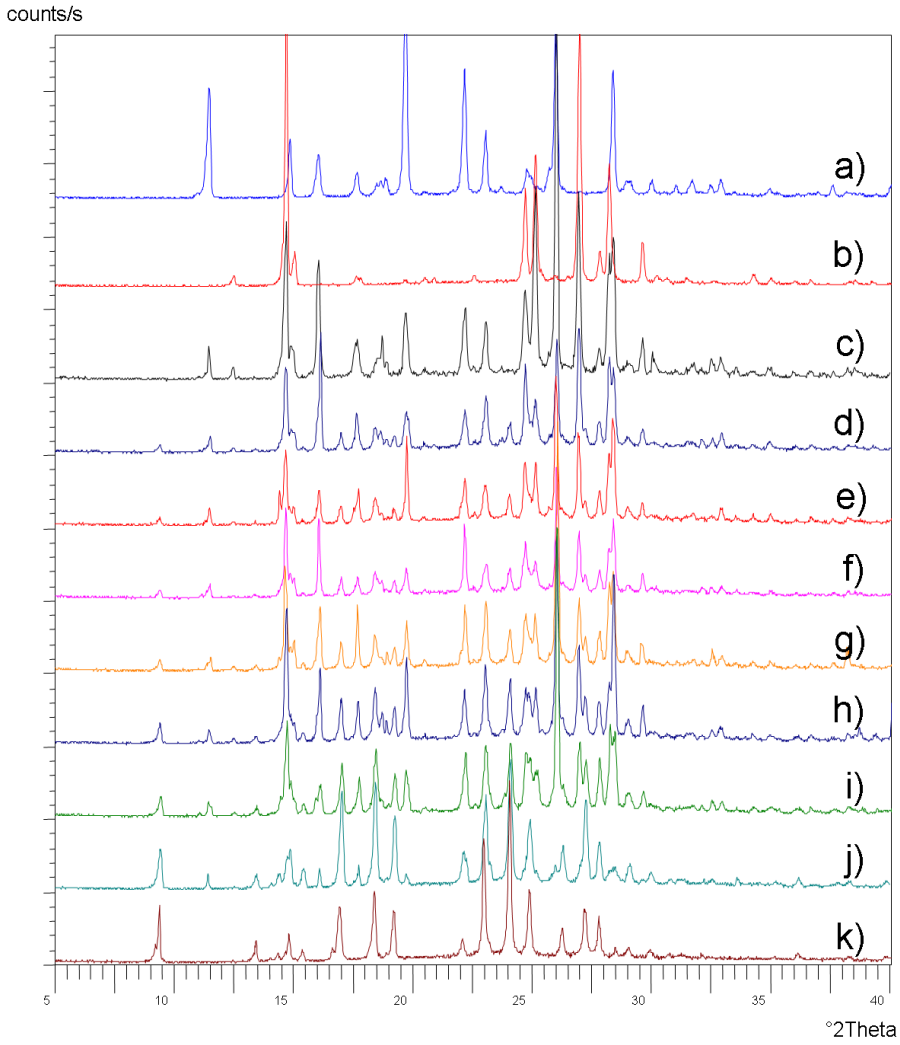

Figure S3. PXRD patterns for the product of ageing experiment at 0% RH for a mixture of **napht** and **abn**: a) pure **napht** reactant, b) pure **abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 3 days of ageing, g) 4 days of ageing, h) 8 days of ageing, i) 10 days of ageing, j) 18 days of ageing and k) **1** from solution.

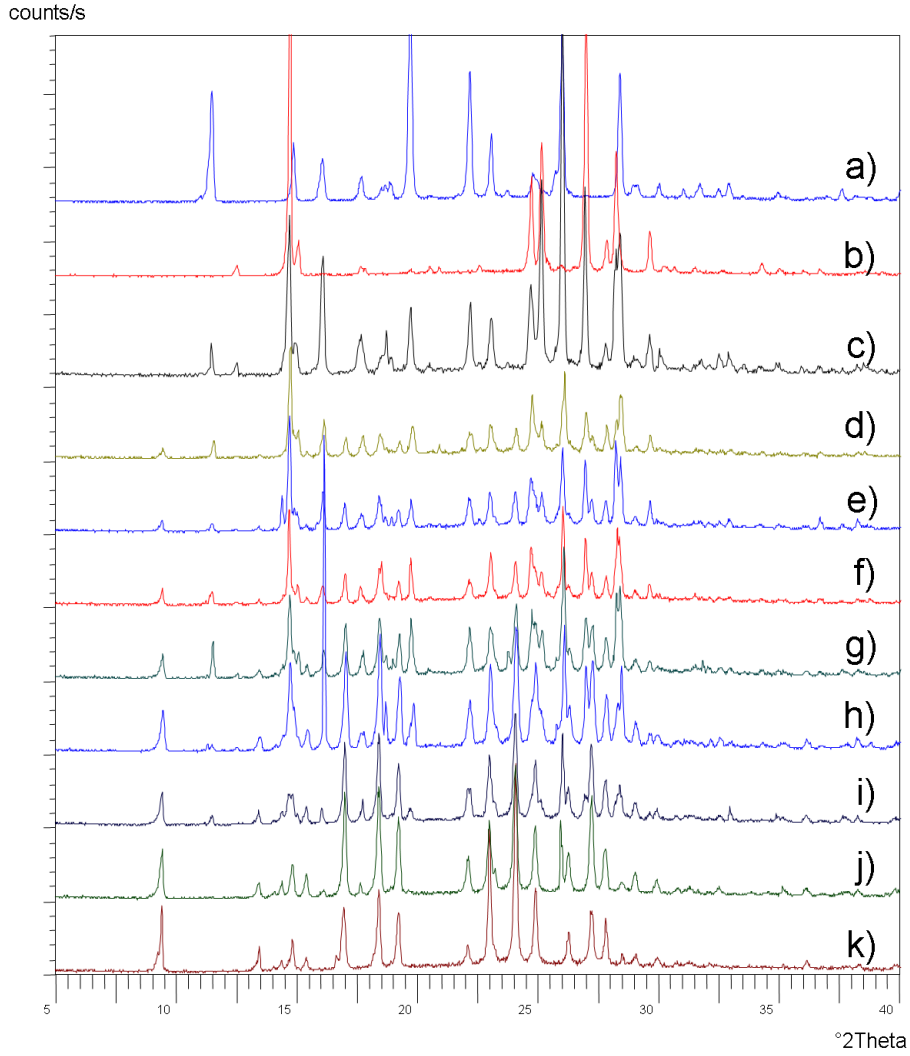

Figure S4. PXRD patterns for the product of ageing experiment at 43% RH for a mixture of **napht** and **abn**: a) pure **napht** reactant, b) pure **abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 3 days of ageing, g) 4 days of ageing, h) 8 days of ageing, i) 10 days of ageing, j) 18 days of ageing and k) **1** from solution.

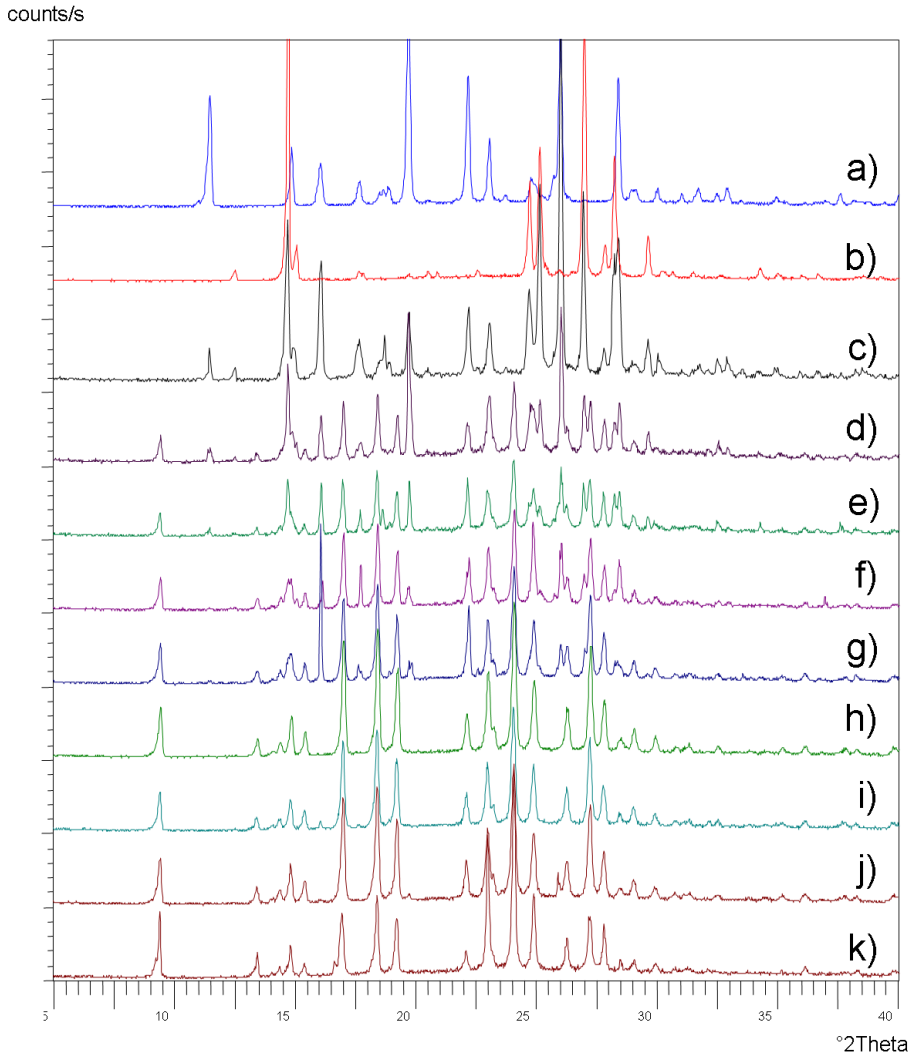

Figure S5. PXRD patterns for the product of ageing experiment at 75% RH for a mixture of **napht** and **abn**: a) pure **napht** reactant, b) pure **abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 3 days of ageing, g) 4 days of ageing, h) 8 days of ageing, i) 10 days of ageing, j) 18 days of ageing and k) **1** from solution.

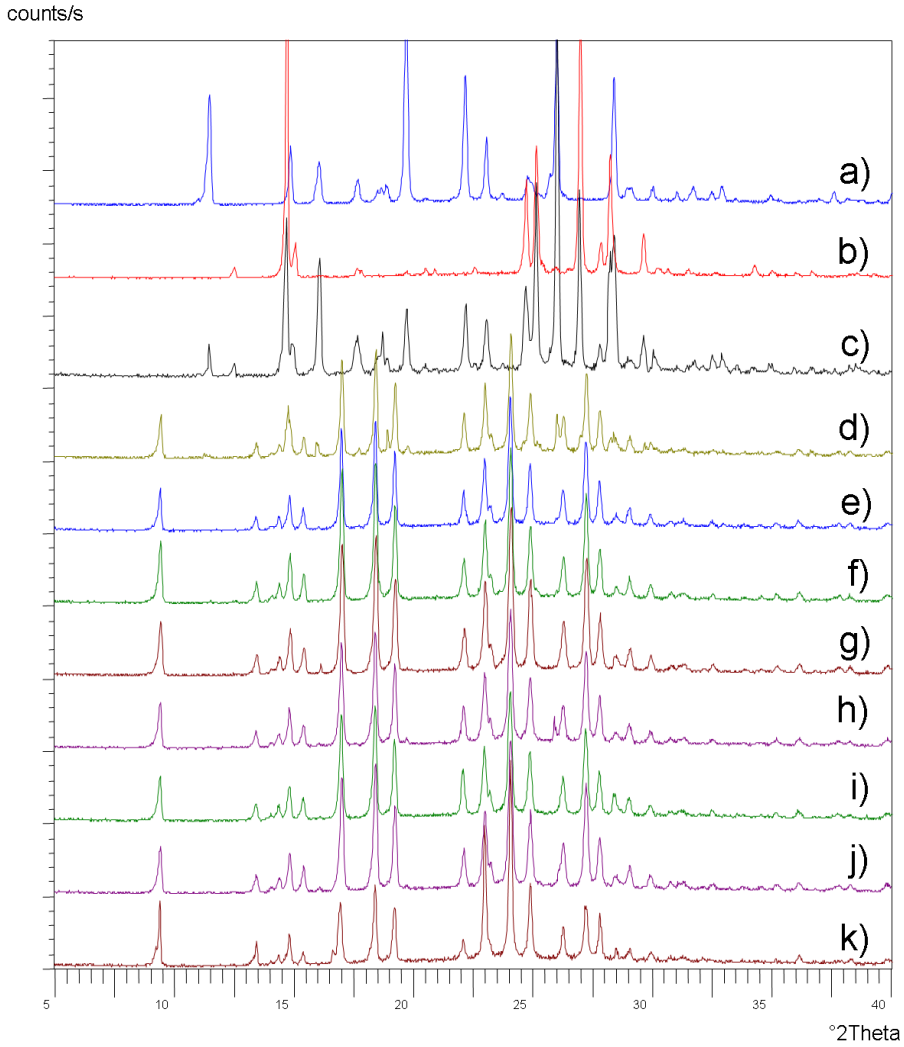

Figure S6. PXRD patterns for the product of ageing experiment at 98% RH for a mixture of **napht** and **abn**: a) pure **napht** reactant, b) pure **abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 3 days of ageing, g) 4 days of ageing, h) 8 days of ageing, i) 10 days of ageing, j) 18 days of ageing and k) **1** from solution.

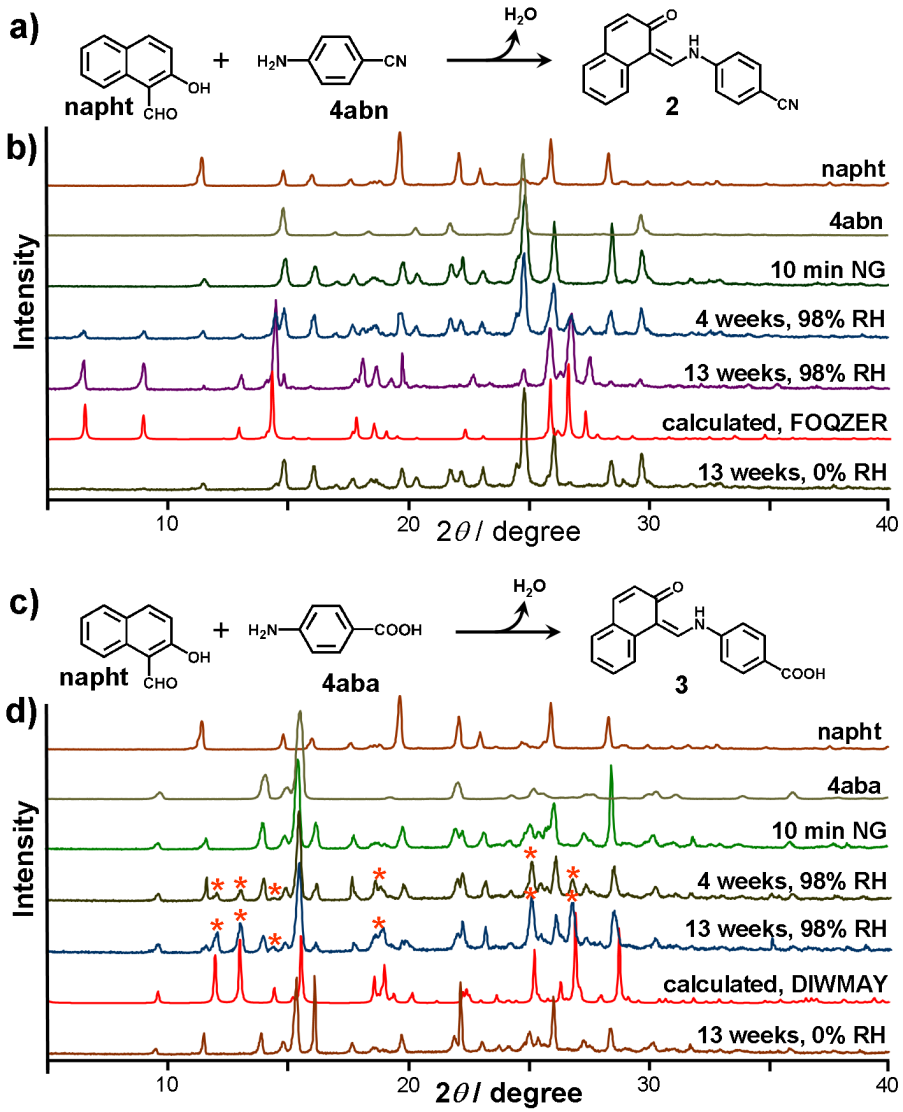

Figure S7. Reaction scheme of preparation of **2** (a) and relevant calculated and experimental PXRD patterns (b). Reaction scheme of preparation of 3 (c) and relevant calculated and experimental PXRD patterns (d). Characteristic reflections for 3 are indicated by "*".

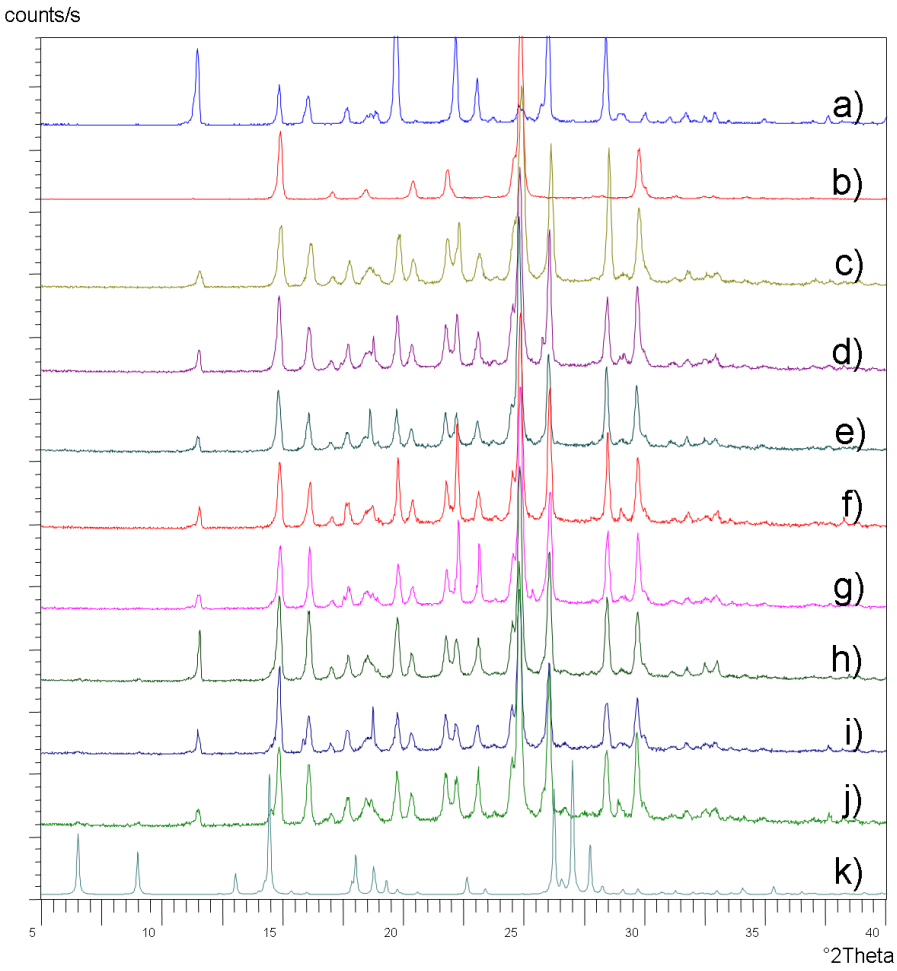

Figure S8. PXRD patterns for the product of ageing experiment at 0% RH for a mixture of **napht** and **4abn**: a) pure **napht** reactant, b) pure **4abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 8 days of ageing, g) 4 weeks of ageing, h) 8 weeks of ageing, i) 11 weeks of ageing, j) 13 weeks of ageing and k) calculated pattern of **2**.

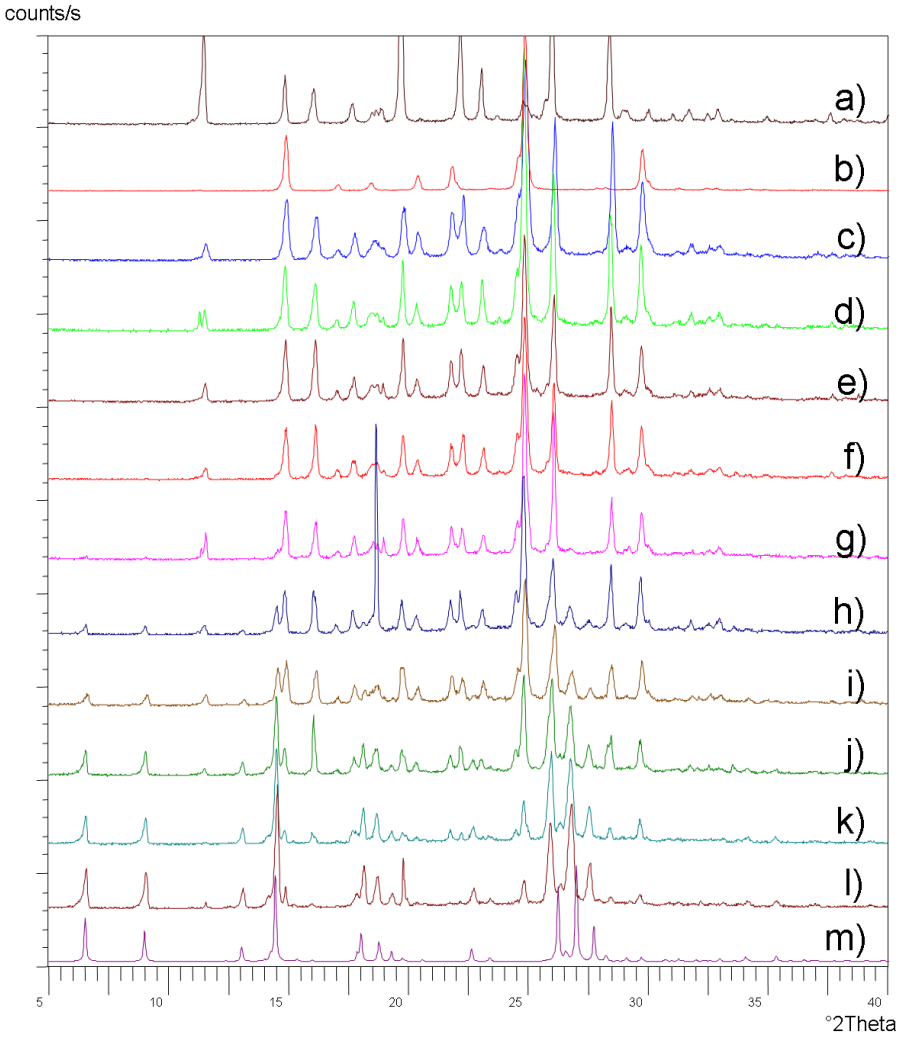

Figure S9. PXRD patterns for the product of ageing experiment at 98% RH for a mixture of **napht** and **4abn**: a) pure **napht** reactant, b) pure **4abn** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 4 days of ageing, g) 8 days of ageing, h) 21 days of ageing, i) 4 weeks of ageing, j) 8 weeks of ageing, k) 11 weeks of ageing, l) 13 weeks of ageing and m) calculated pattern of **2**.

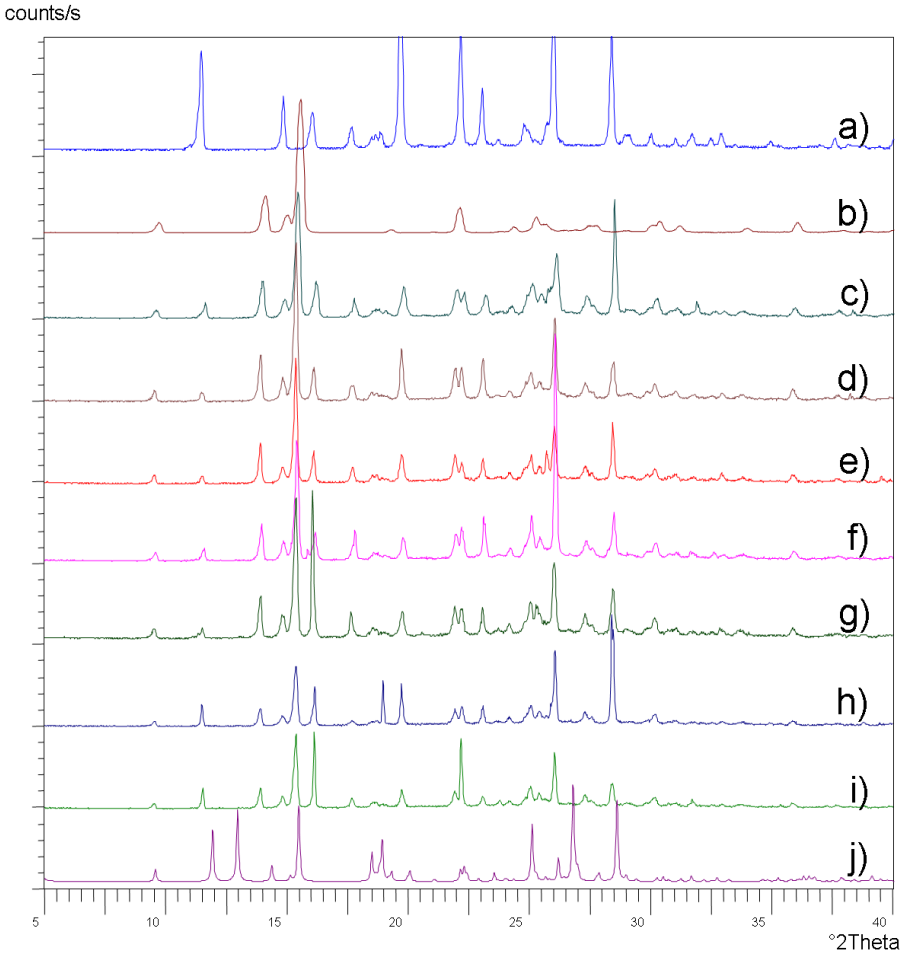

Figure S10. PXRD patterns for the product of ageing experiment at 0% RH for a mixture of **napht** and **4aba**: a) pure **napht** reactant, b) pure **4aba** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 4 weeks of ageing, g) 8 weeks of ageing, h) 11 weeks of ageing, i) 13 weeks of ageing and j) calculated pattern of **3**.

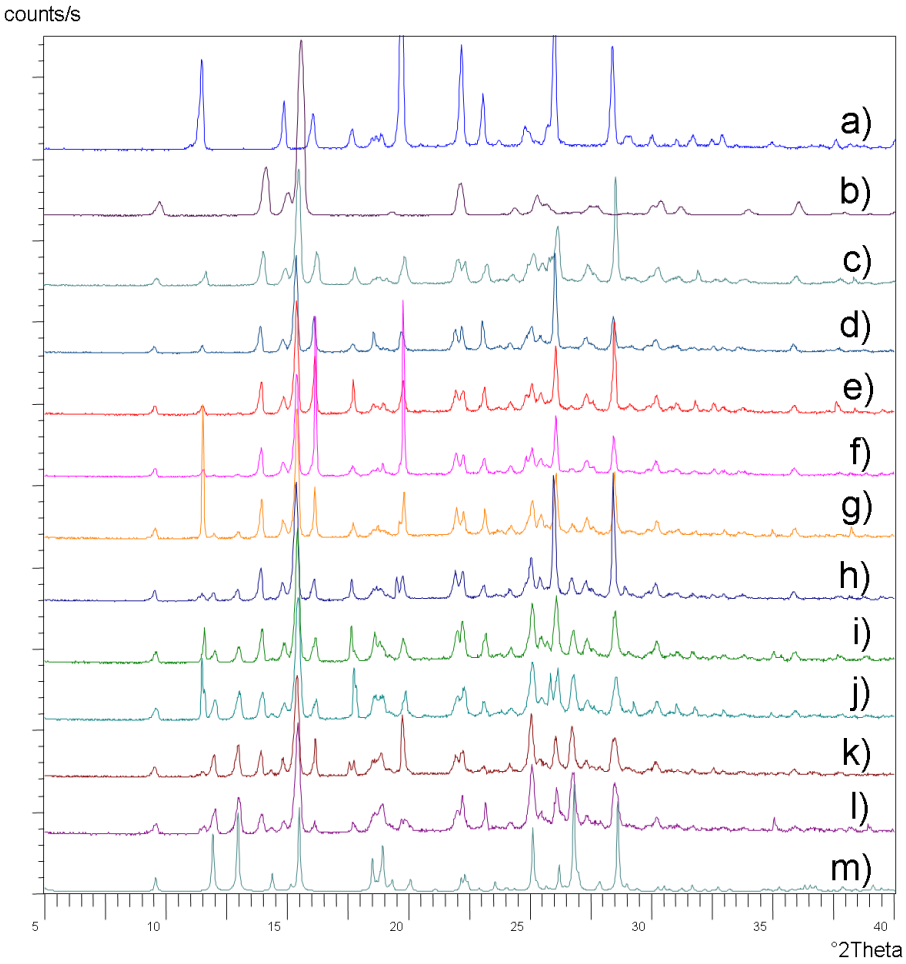

Figure S11. PXRD patterns for the product of ageing experiment at 98% RH for a mixture of **napht** and **4aba**: a) pure **napht** reactant, b) pure **4aba** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 2 days of ageing, f) 4 days of ageing, g) 8 days of ageing, h) 21 days of ageing, i) 4 weeks of ageing, j) 8 weeks of ageing, k) 11 weeks of ageing, l) 13 weeks of ageing and m) calculated pattern of **3**.

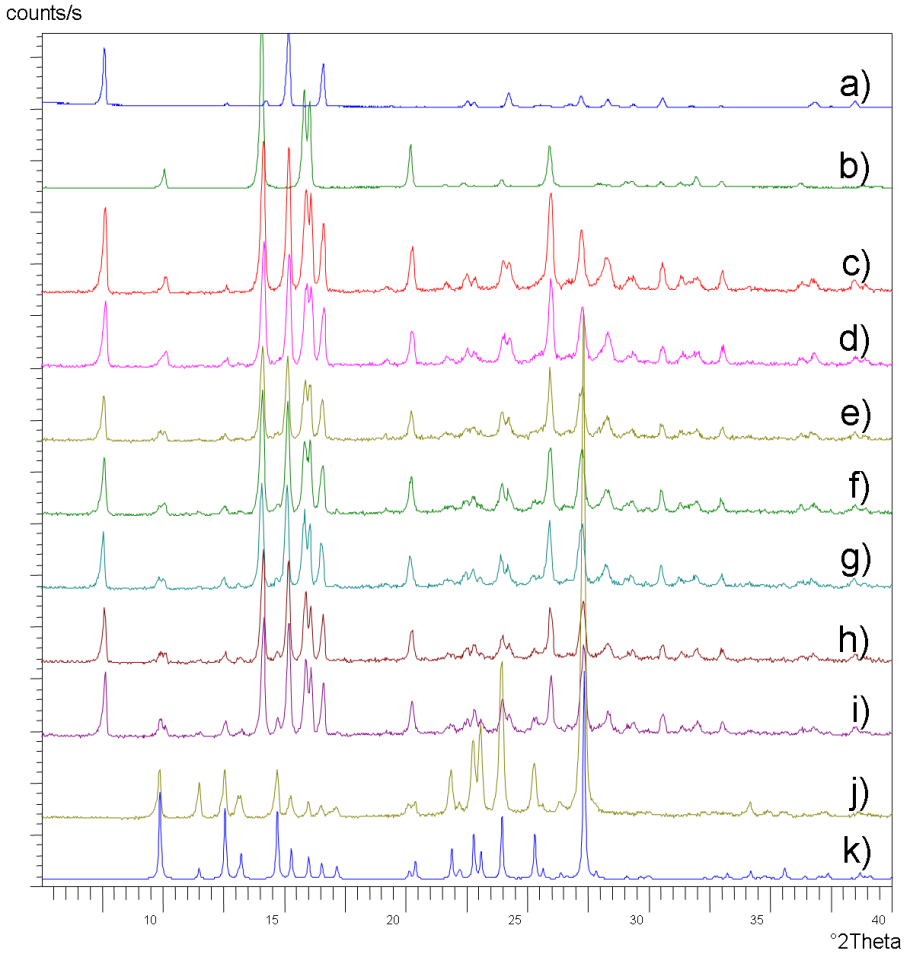

Figure S12. PXRD patterns for the product of ageing experiment at 0% RH for a mixture of **5asa** and **ovan**: a) pure **5asa** reactant, b) pure **ovan** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 5 days of ageing, f) 8 days of ageing, g) 12 days of ageing, h) 15 days of ageing, i) 4 weeks of ageing, j) **4** from solution and k) calculated pattern of **4**.

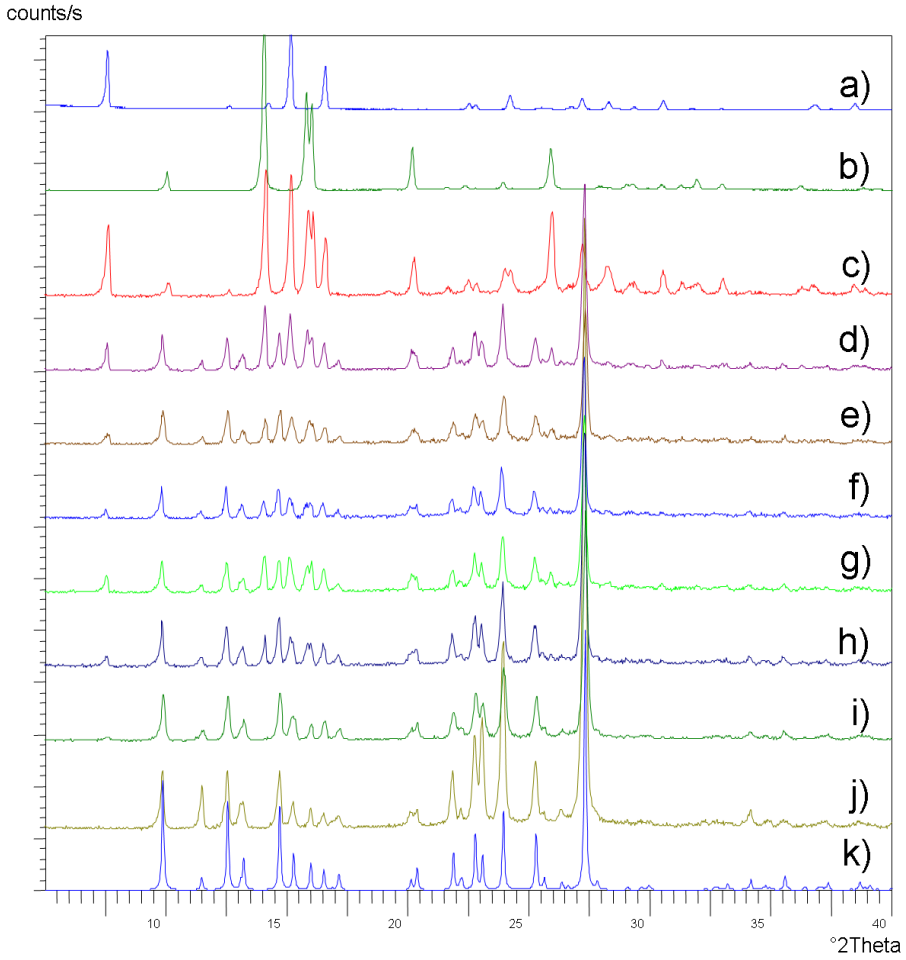

Figure S13. PXRD patterns for the product of ageing experiment at 98% RH for a mixture of **5asa** and **ovan**: a) pure **5asa** reactant, b) pure **ovan** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 5 days of ageing, f) 8 days of ageing, g) 12 days of ageing, h) 15 days of ageing, i) 4 weeks of ageing, j) **4** from solution and k) calculated pattern of **4**.

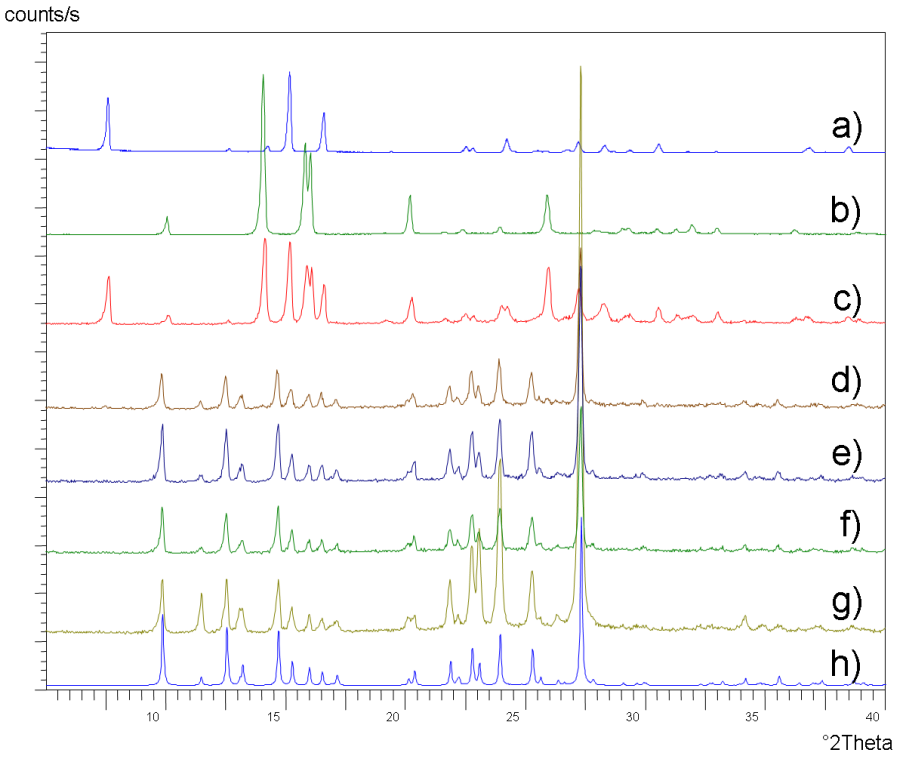

Figure S14. PXRD patterns for the product of vapour digestion experiment in EtOH vapour for a mixture of **5asa** and **ovan**: a) pure **5asa** reactant, b) pure **ovan** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 hour of ageing, e) 1 day of ageing, f) 3 days of ageing, g) **4** from solution and h) calculated pattern of **4**.

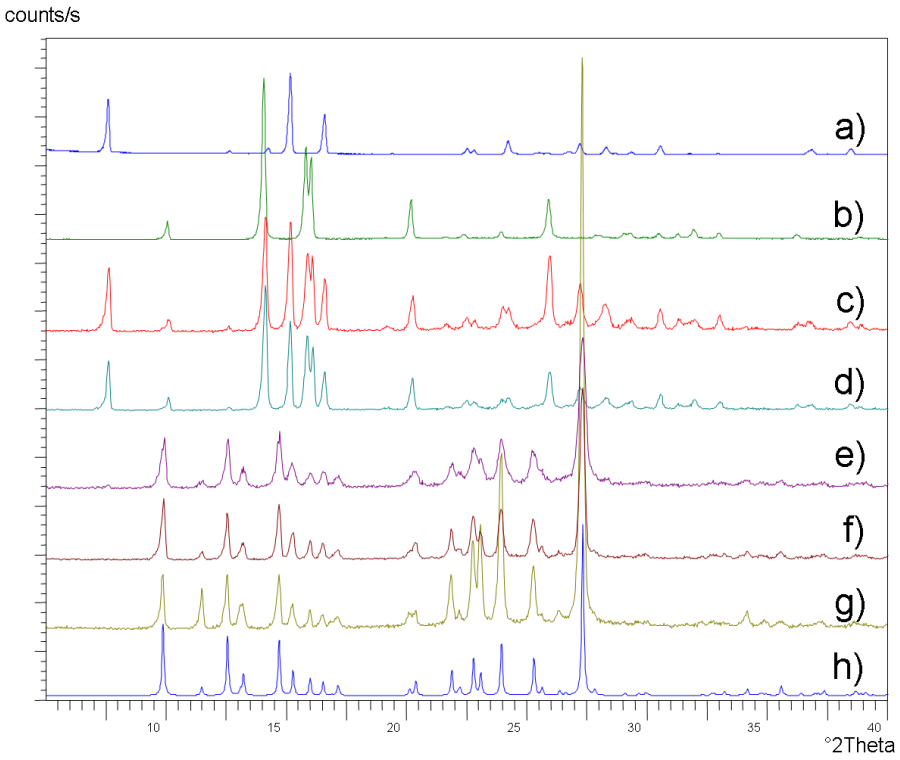

Figure S15. PXRD patterns for the product of grinding experiments for a mixture of **5asa** and **ovan**: a) pure **5asa** reactant, b) pure **ovan** reactant, c) mixture of reactants after 10 min neat grinding in mortar at room conditions, d) neat grinding in ball mill for 5 min, e) neat grinding in ball mill for 30 min, f) liquid-assisted grinding in ball mill for 5 min in the presence of EtOH, g) **4** from solution and h) calculated pattern of **4**.

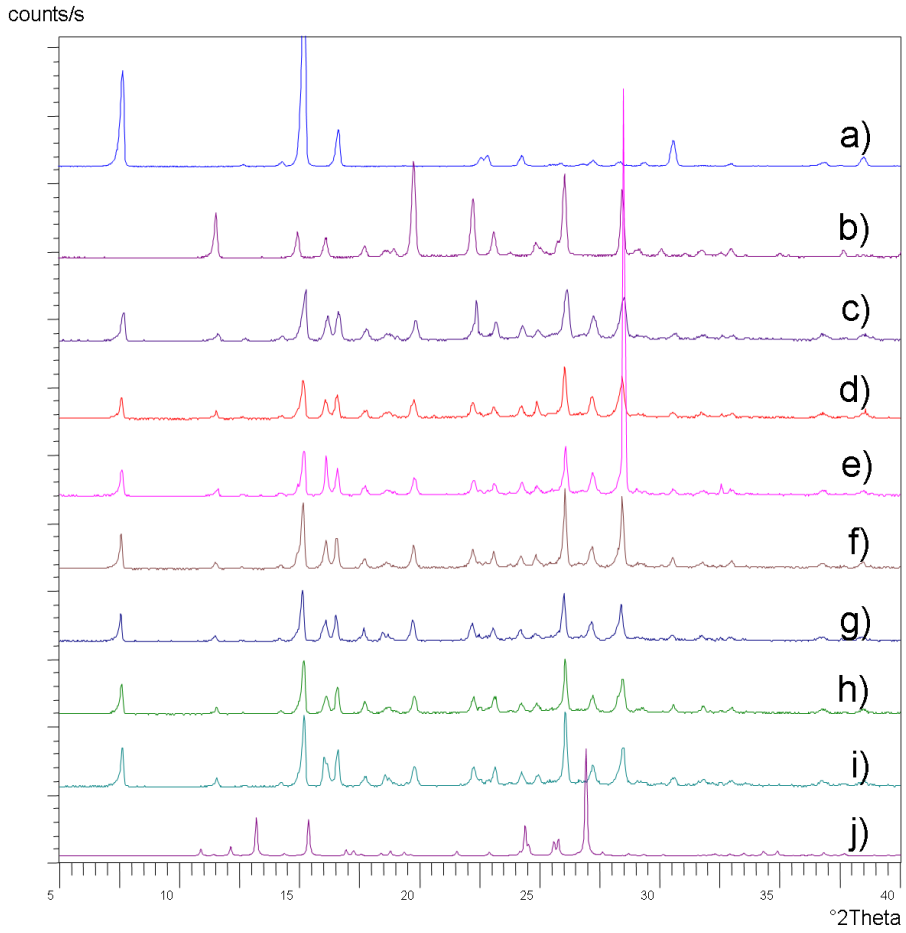

Figure S16. PXRD patterns for the product of ageing experiment at 0% RH for a mixture of **5asa** and **napht**: a) pure **5asa** reactant, b) pure **napht** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 5 days of ageing, f) 8 days of ageing, g) 12 days of ageing, h) 15 days of ageing, i) 4 weeks of ageing and j) calculated pattern of **5**.

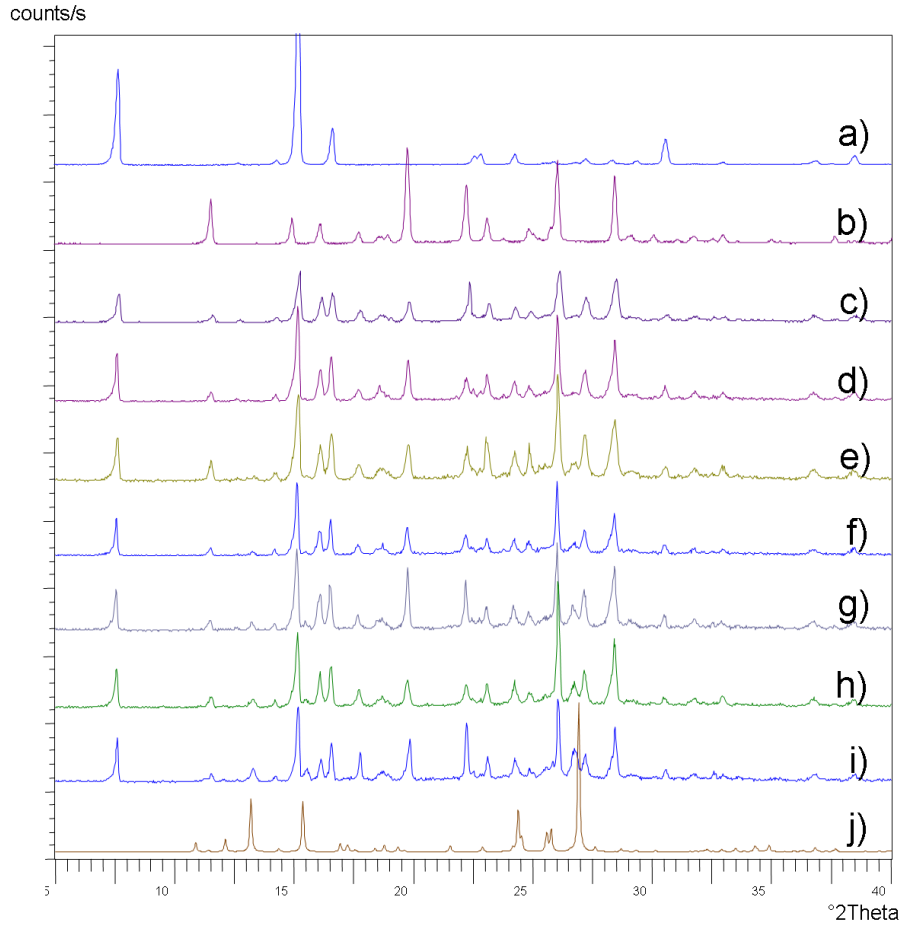

Figure S17. PXRD patterns for the product of ageing experiment at 98% RH for a mixture of **5asa** and **napht**: a) pure **5asa** reactant, b) pure **napht** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 day of ageing, e) 5 days of ageing, f) 8 days of ageing, g) 12 days of ageing, h) 15 days of ageing, i) 4 weeks of ageing and j) calculated pattern of **5**.

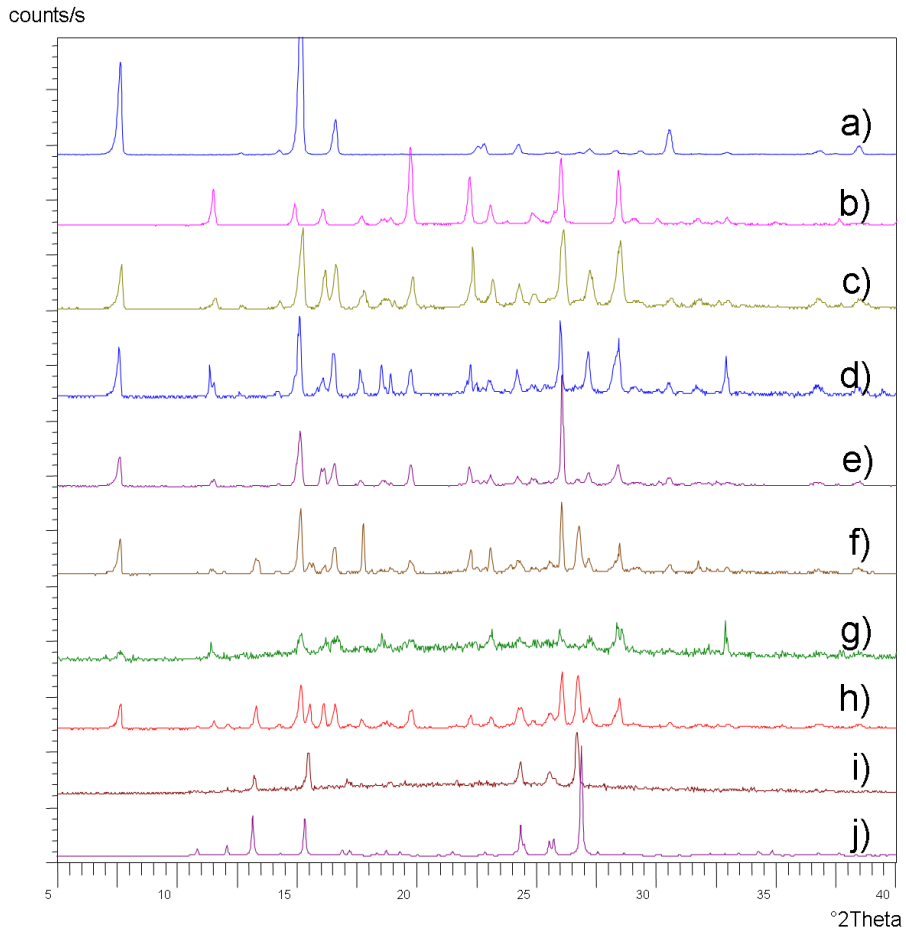

Figure S18. PXRD patterns for the product of vapour digestion experiments for a mixture of **5asa** and **napht**: a) pure **5asa** reactant, b) pure **napht** reactant, c) mixture of reactants after 10 min neat grinding at room conditions, d) 1 hour of ageing in EtOH vapour, e) 1 day of ageing in EtOH vapour, f) 15 days of ageing in EtOH vapour, g) 1 hour of ageing in TEA vapour, h) 1 hour ageing in a vapour mixture of EtOH and TEA [5% *v*/*v* of TEA], i) 1 day ageing in a vapour mixture of EtOH and TEA [5% *v*/*v* of TEA] and j) calculated pattern of **5**.

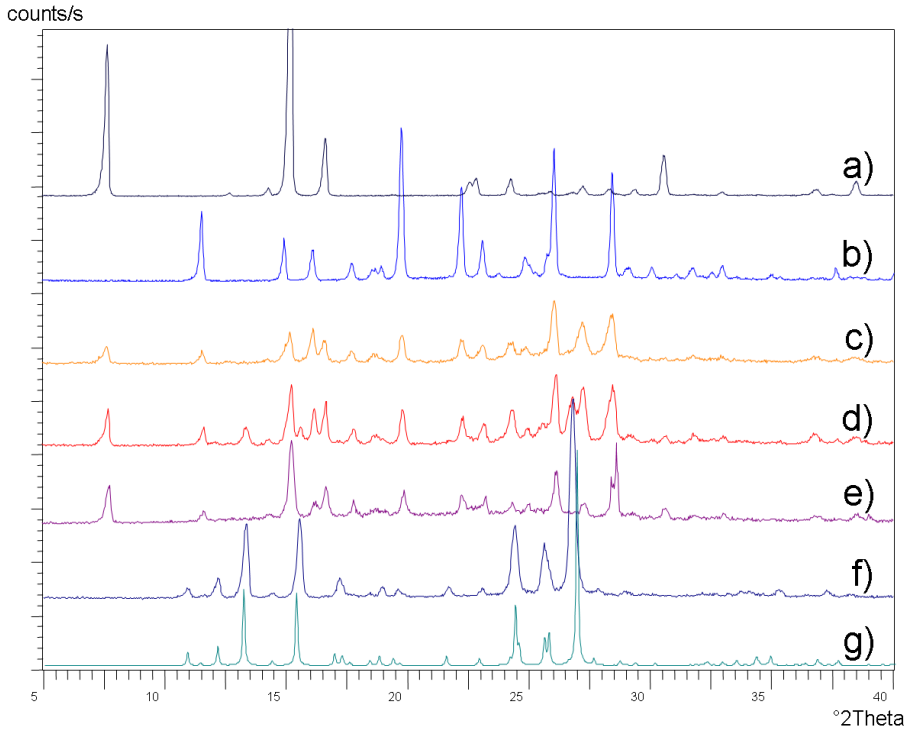

Figure S19. PXRD patterns for the product of grinding experiments for a mixture of **5asa** and **napht**: a) pure **5asa** reactant, b) pure **napht** reactant, c) neat grinding in ball mill for 45 min, d) liquid-assisted grinding in ball mill for 45 min in the presence of EtOH, e) liquid-assisted grinding in ball mill for 20 min in the presence of TEA, f) liquid-assisted grinding in ball mill for 45 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA] and g) calculated pattern of **5**.

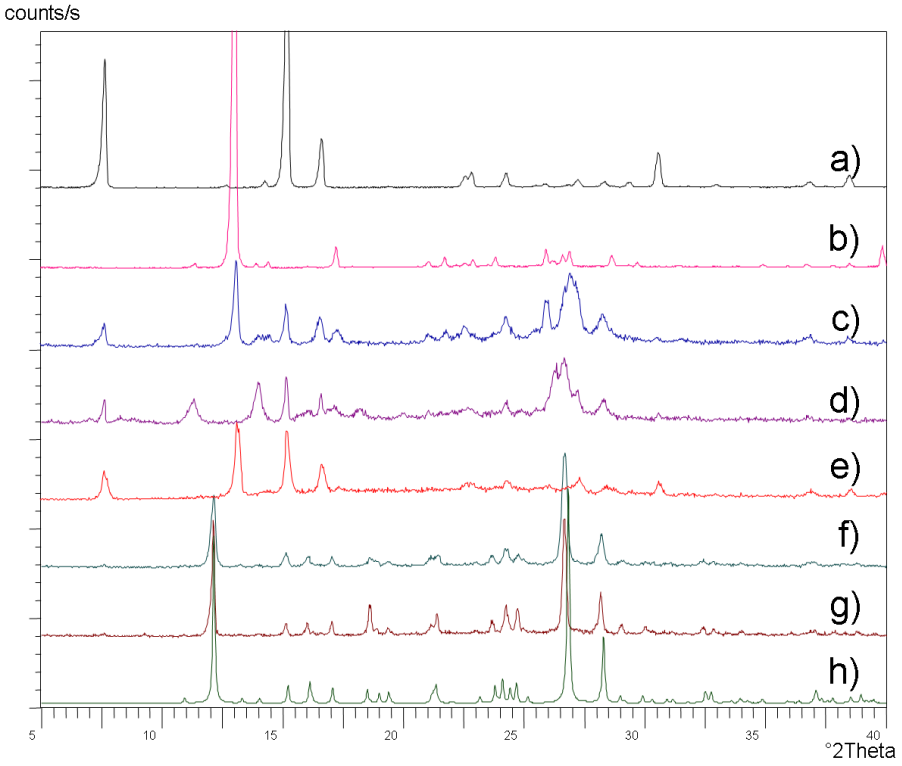

Figure S20. PXRD patterns for the product of grinding experiments for a mixture of **5asa** and **van**: a) pure **5asa** reactant, b) pure **van** reactant, c) neat grinding in ball mill for 30 min, d) liquid-assisted grinding in ball mill for 30 min in the presence of EtOH, e) liquid-assisted grinding in ball mill for 20 min in the presence of TEA, f) liquid-assisted grinding in ball mill for 30 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA], g) **6(H$_2$O)** from solution and h) calculated pattern of **6(H$_2$O)**.

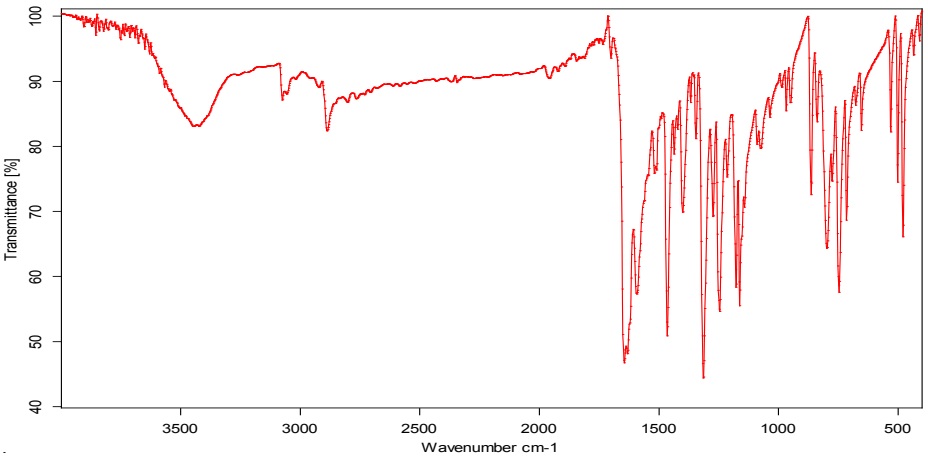

Figure S21. IR spectrum for pure **napht** reactant.

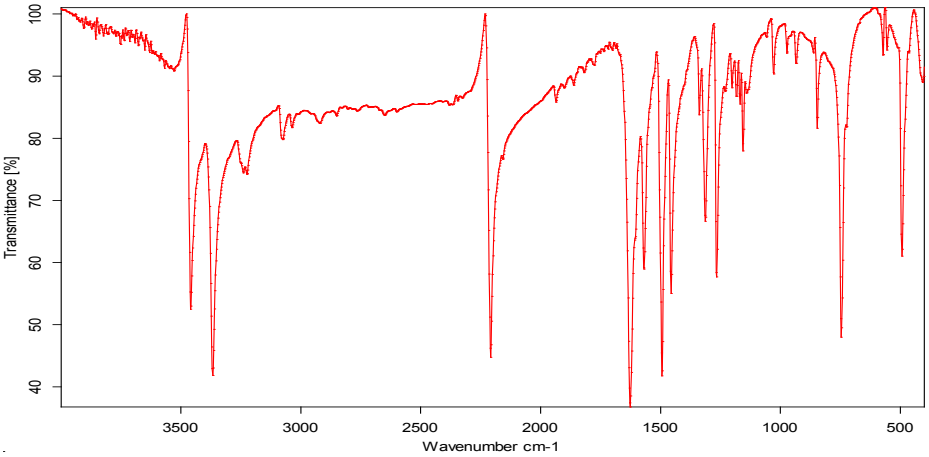

Figure S22. IR spectrum for pure **abn** reactant.

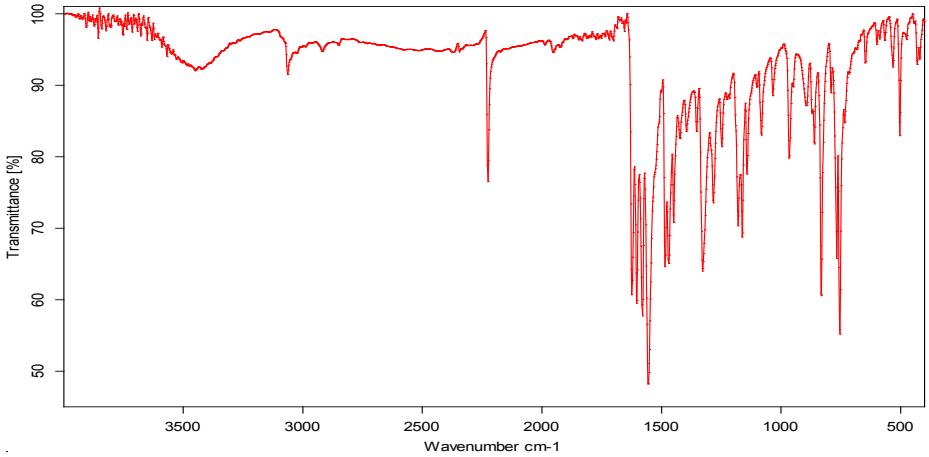

Figure S23. IR spectrum for **1** prepared by solution-based method.

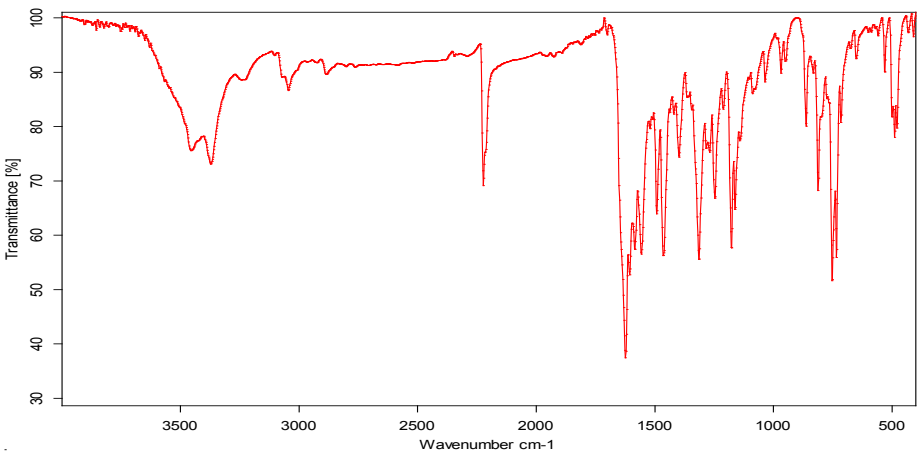

Figure S24. IR spectrum for the product obtained by ageing a mixture of **napht** and **abn** at 0% RH for 7 days.

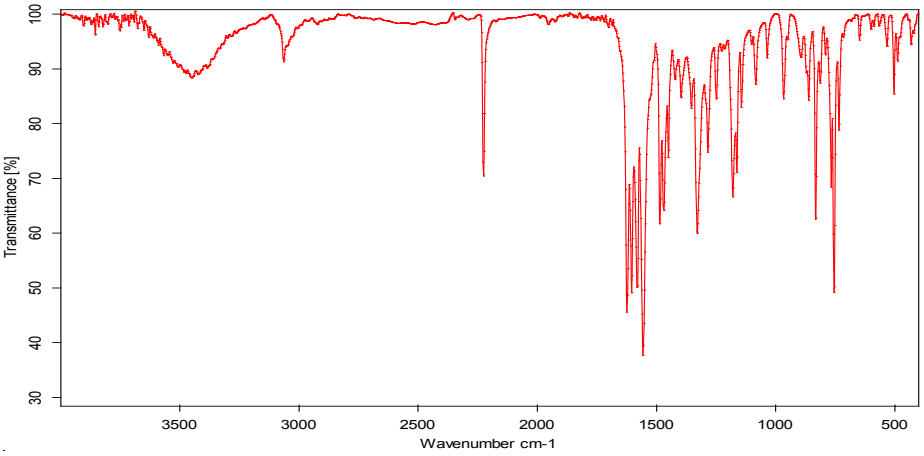

Figure S25. IR spectrum for the product obtained by ageing a mixture of **napht** and **abn** at 98% RH for 7 days.

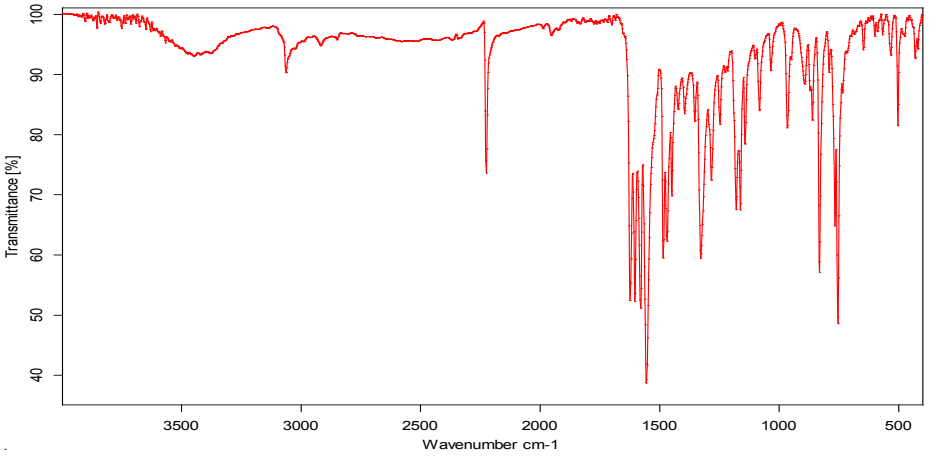

Figure S26. IR spectrum for the product obtained by ageing a mixture of **napht** and **abn** at 98% RH for 18 days.

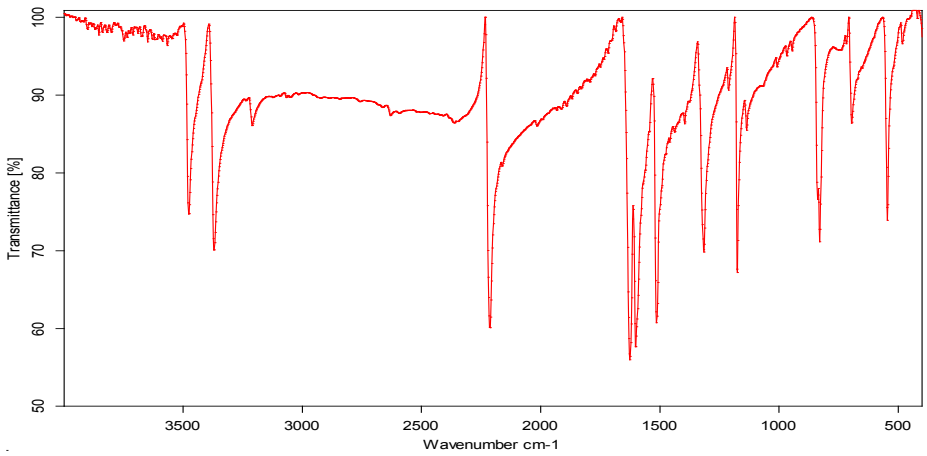

Figure S27. IR spectrum for pure **4abn** reactant.

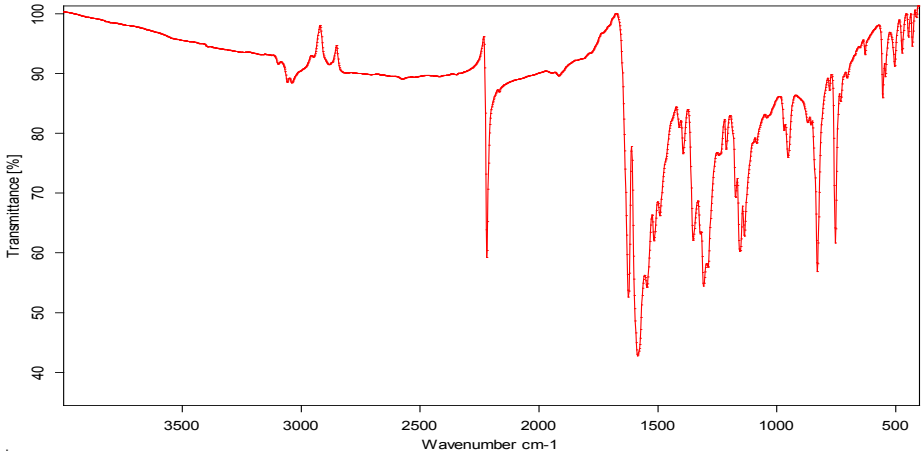

Figure S28. IR spectrum for **2** prepared by solution-based method.

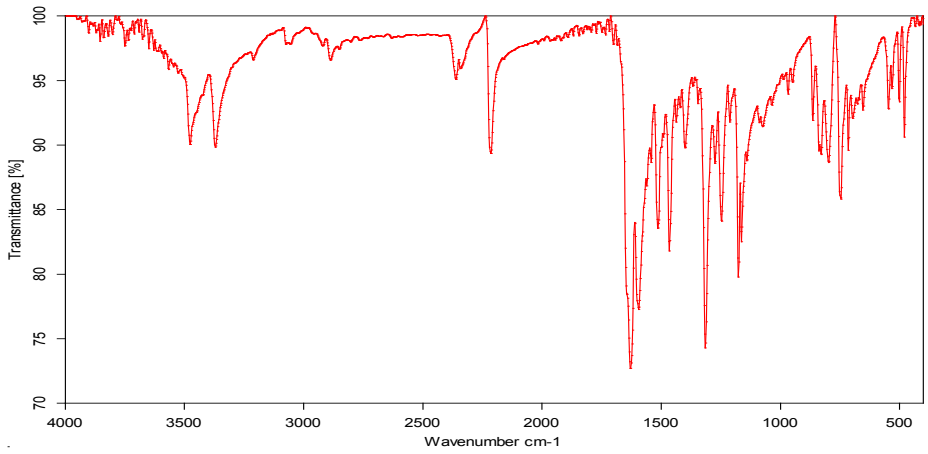

Figure S29. IR spectrum for the product obtained by ageing a mixture of **napht** and **4abn** at 0% RH for 13 weeks.

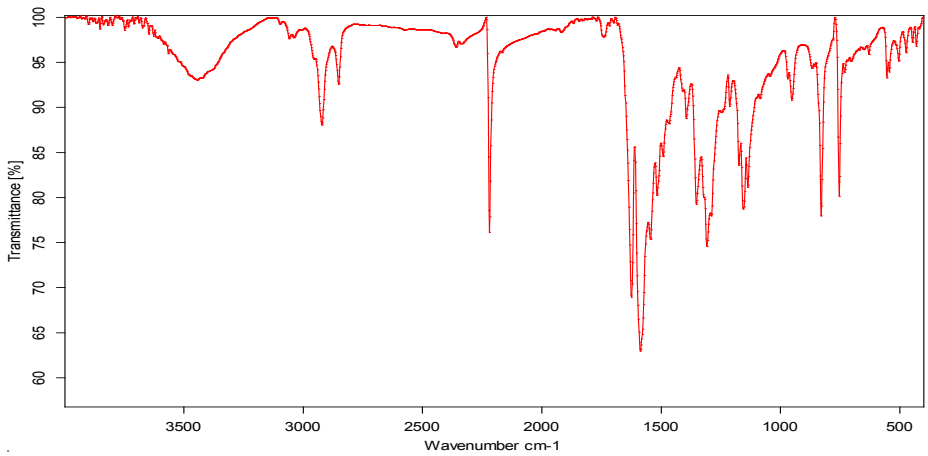

Figure S30. IR spectrum for the product obtained by ageing a mixture of **napht** and **4abn** at 98% RH for 13 weeks.

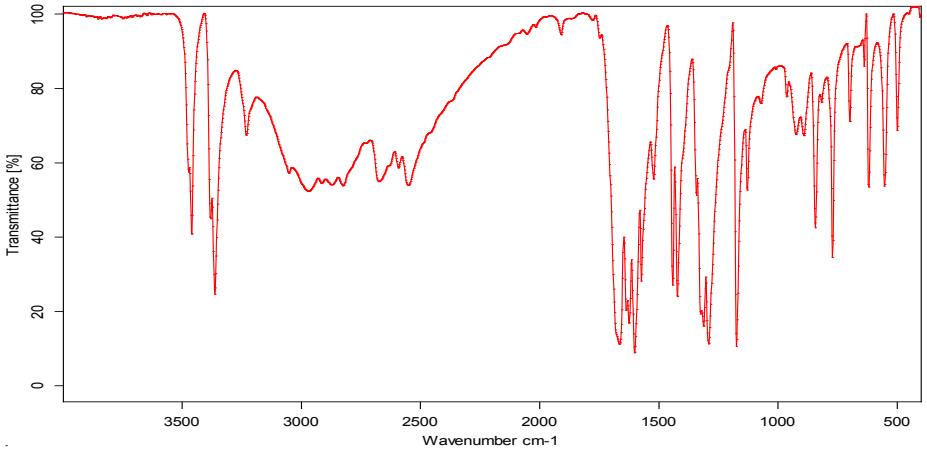

Figure S31. IR spectrum for pure **4aba** reactant.

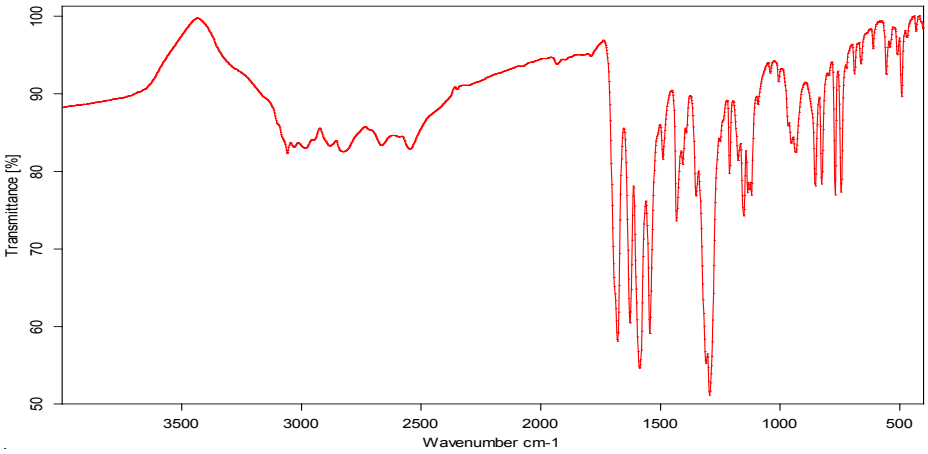

Figure S32. IR spectrum for **3** prepared by solution-based method.

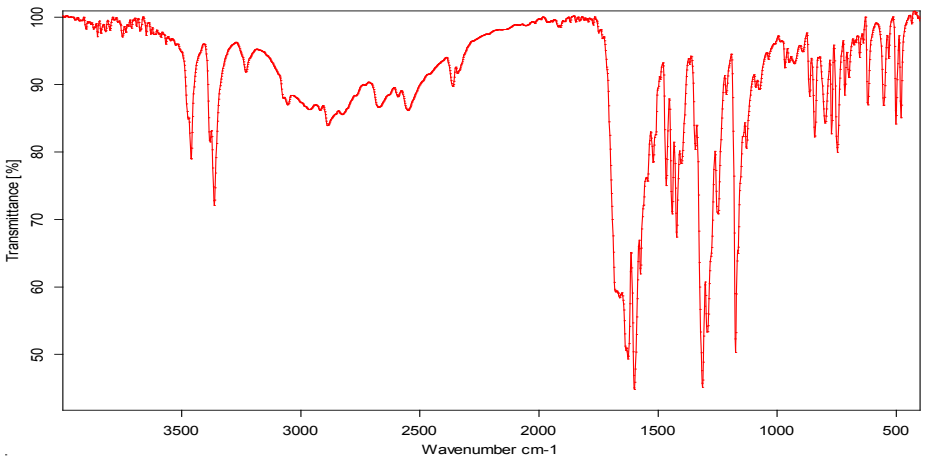

Figure S33. IR spectrum for the product obtained by ageing a mixture of **napht** and **4aba** at 0% RH for 13 weeks.

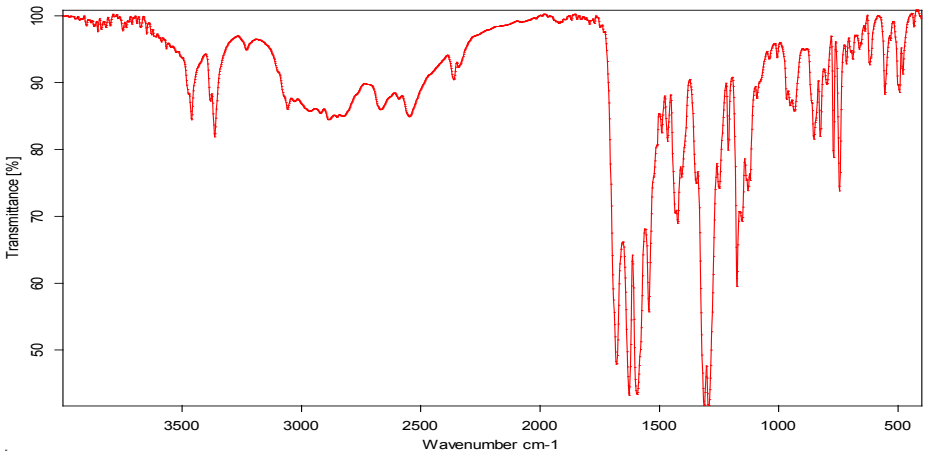

Figure S34. IR spectrum for the product obtained by ageing a mixture of **napht** and **4aba** at 98% RH for 13 weeks.

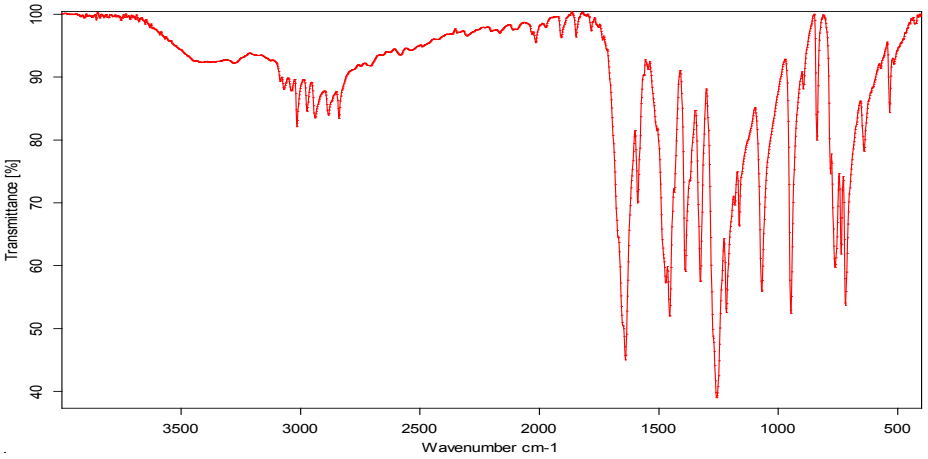

Figure S35. IR spectrum for pure **ovan** reactant.

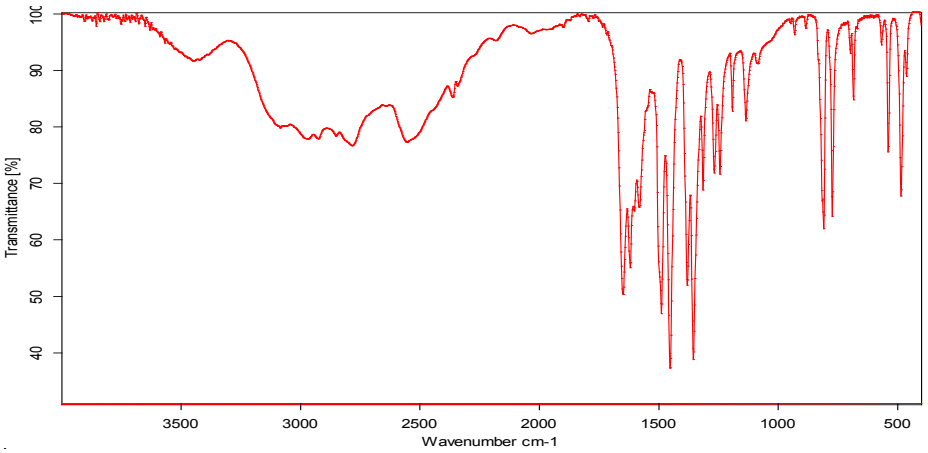

Figure S36. IR spectrum for pure **5asa** reactant.

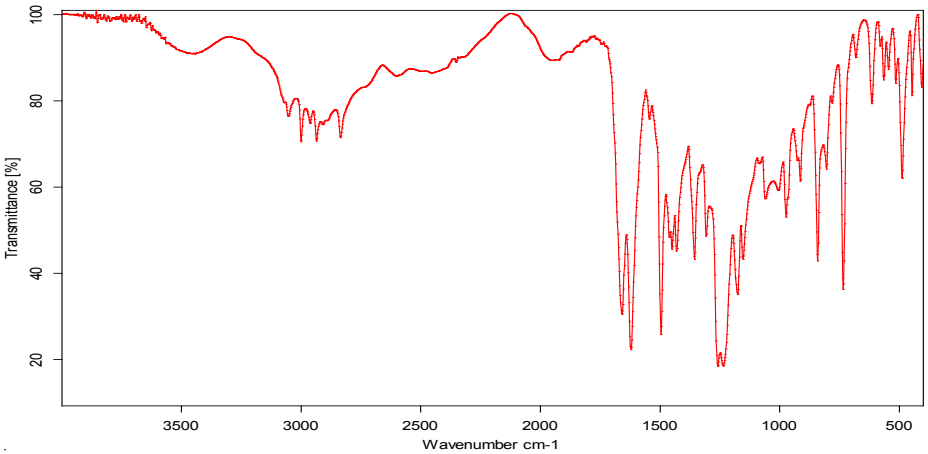

Figure S37. IR spectrum for **4** prepared by solution-based method.

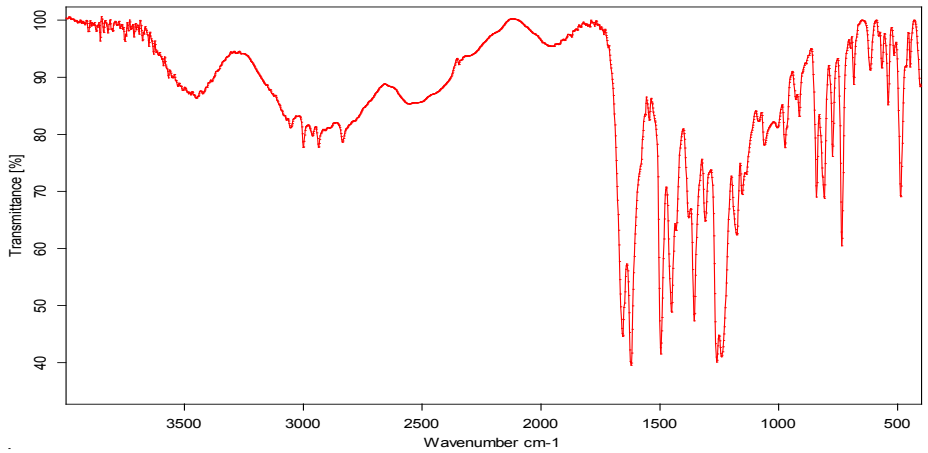

Figure S38. IR spectrum for the product obtained by ageing a mixture of **5asa** and **ovan** at 0% RH for 5 months.

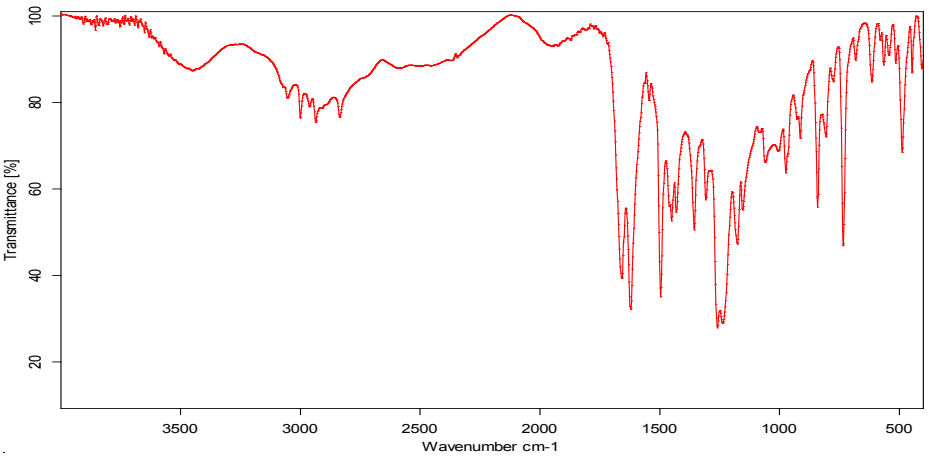

Figure S39. IR spectrum for the product obtained by ageing a mixture of **5asa** and **ovan** at 98% RH for 5 months.

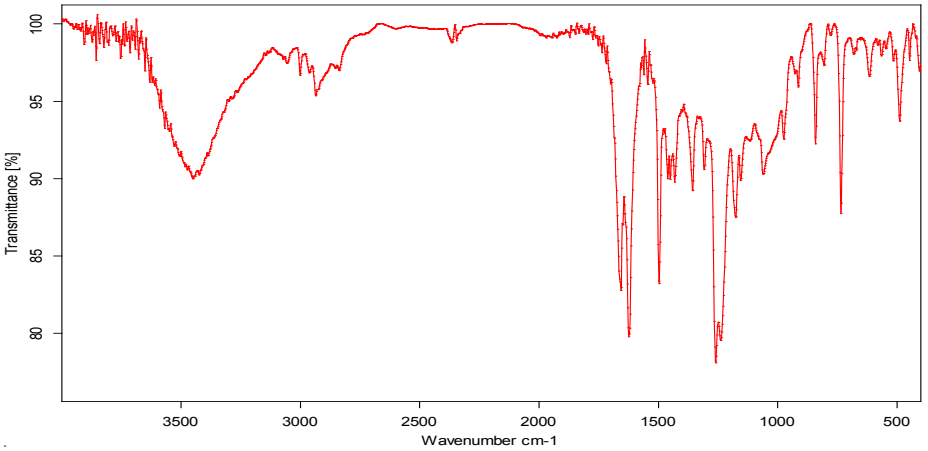

Figure S40. IR spectrum for the product obtained by ageing a mixture of **5asa** and **ovan** in EtOH vapour for 1 hour.

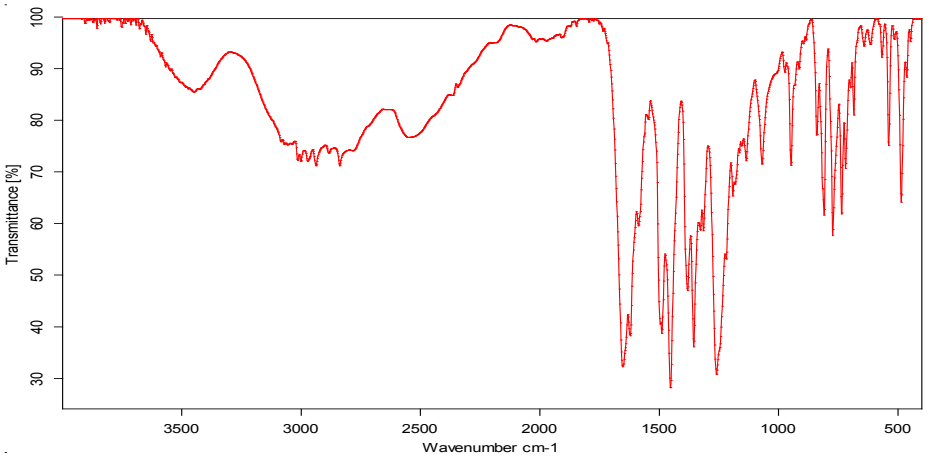

Figure S41. IR spectrum for the product obtained by neat grinding of **5asa** and **ovan** in ball mill for 5 min.

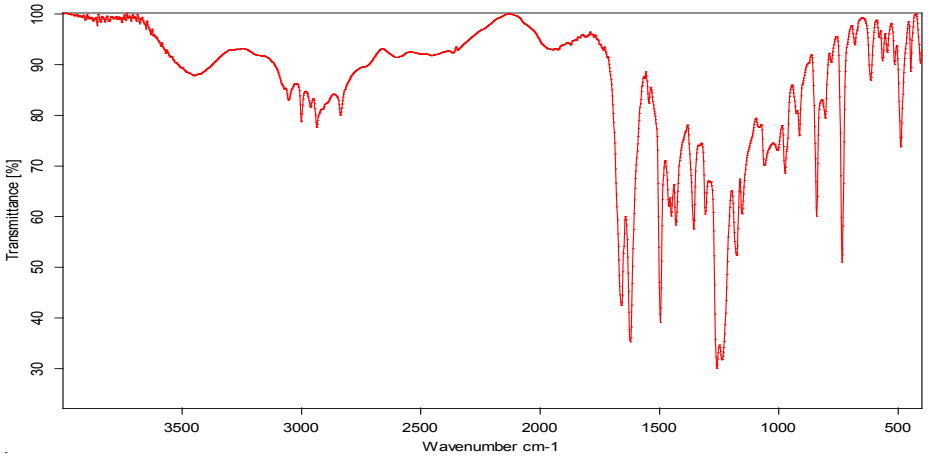

Figure S42. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **ovan** in ball mill for 5 min in the presence of EtOH.

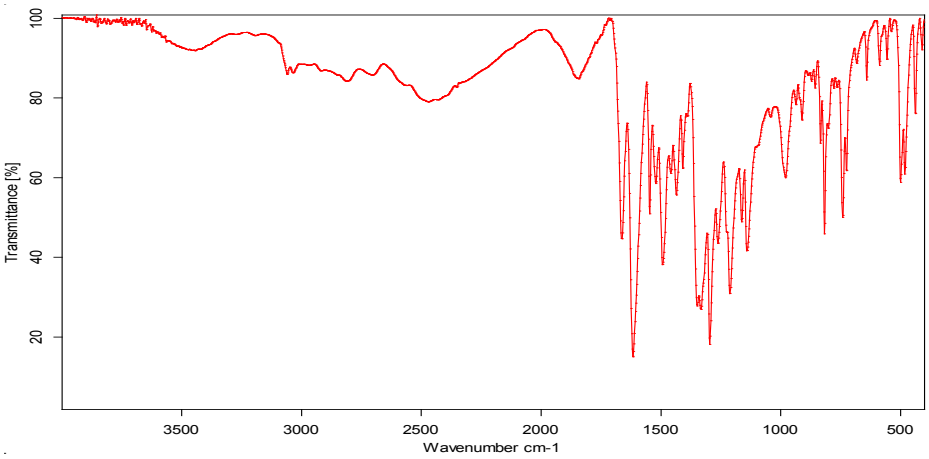

Figure S43. IR spectrum for **5** prepared by solution-based method.

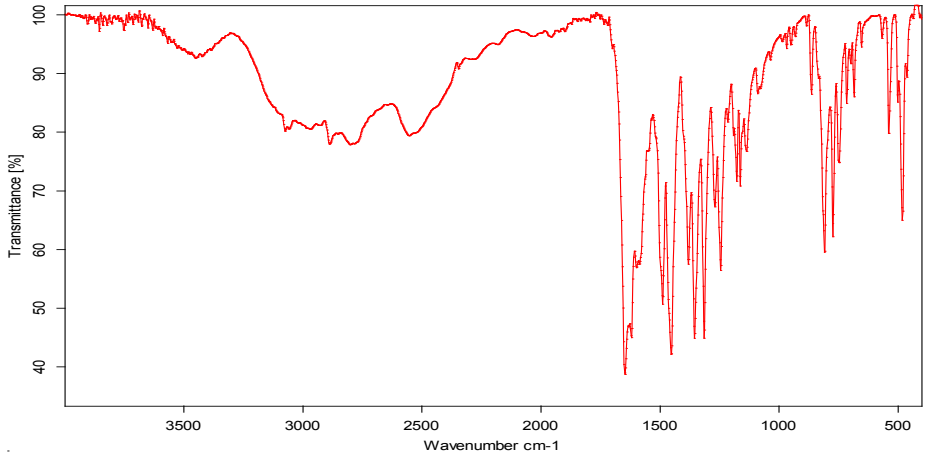

Figure S44. IR spectrum for the product obtained by ageing a mixture of **5asa** and **napht** at 0% RH for 5 months.

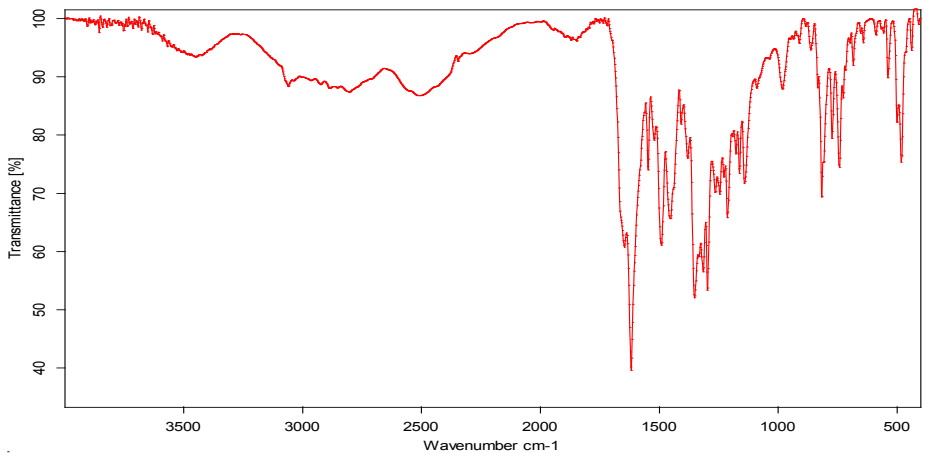

Figure S45. IR spectrum for the product obtained by ageing a mixture of **5asa** and **napht** at 98% RH for 5 months.

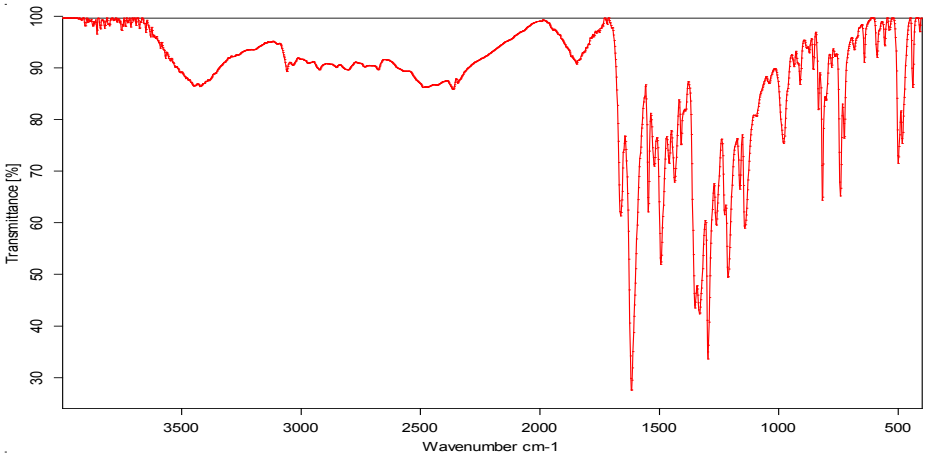

Figure S46. IR spectrum for the product obtained by ageing a mixture of **5asa** and **napht** in a vapour mixture of EtOH and TEA (5% *v*/*v* of TEA) for 1 day.

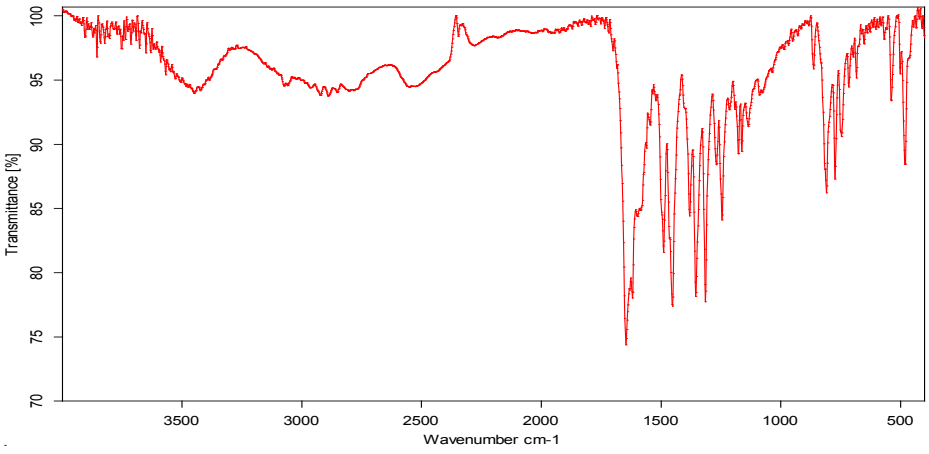

Figure S47. IR spectrum for the product obtained by neat grinding of **5asa** and **napht** in ball mill for 45 min.

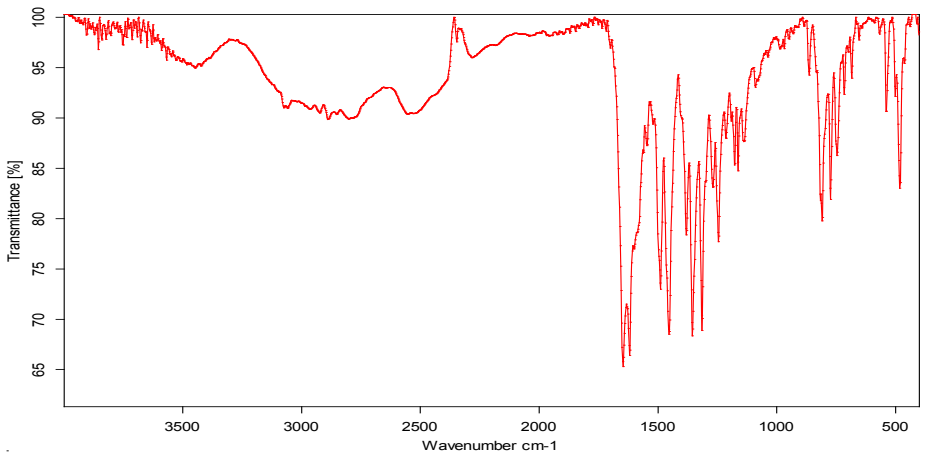

Figure S48. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **napht** in ball mill for 45 min in the presence of EtOH.

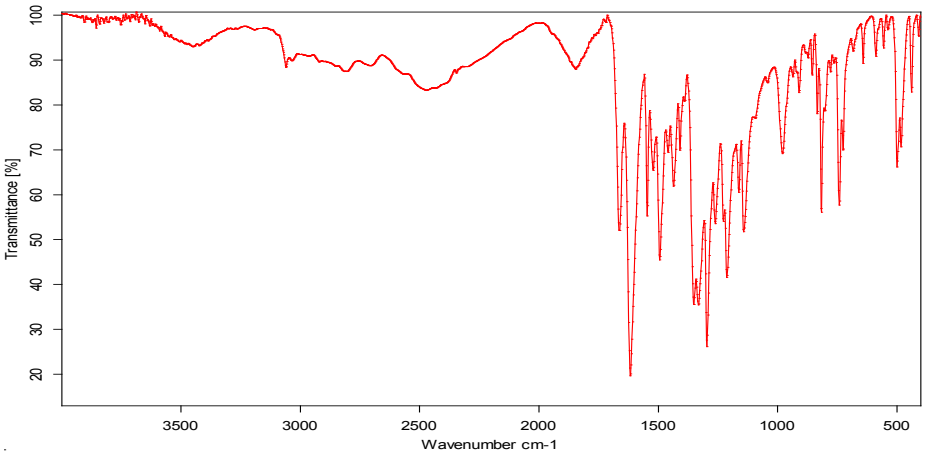

Figure S49. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **napht** in ball mill for 45 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

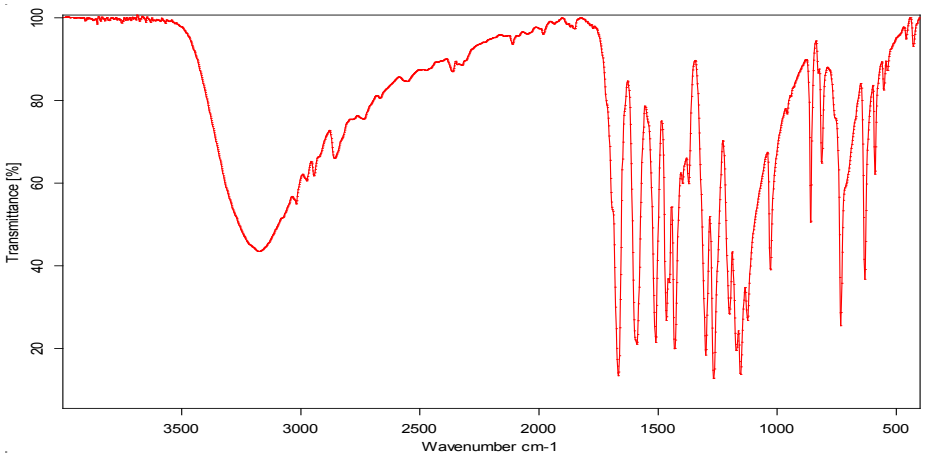

Figure S50. IR spectrum for pure **van** reactant.

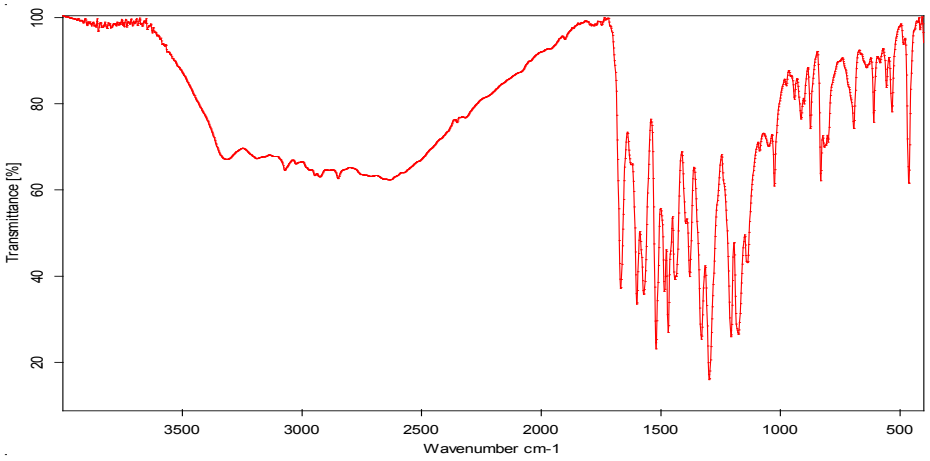

Figure S51. IR spectrum for **6(H_2O)** prepared by solution-based method.

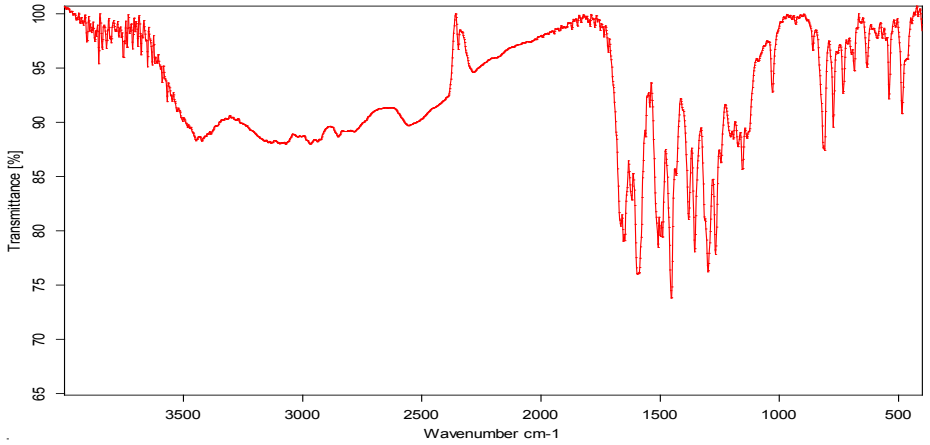

Figure S52. IR spectrum for the product obtained by neat grinding of **5asa** and **van** in ball mill for 30 min.

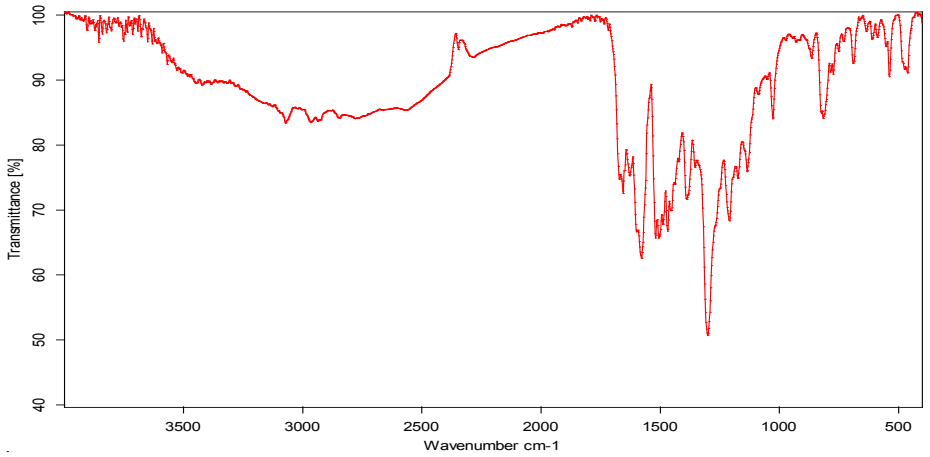

Figure S53. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 30 min in the presence of EtOH.

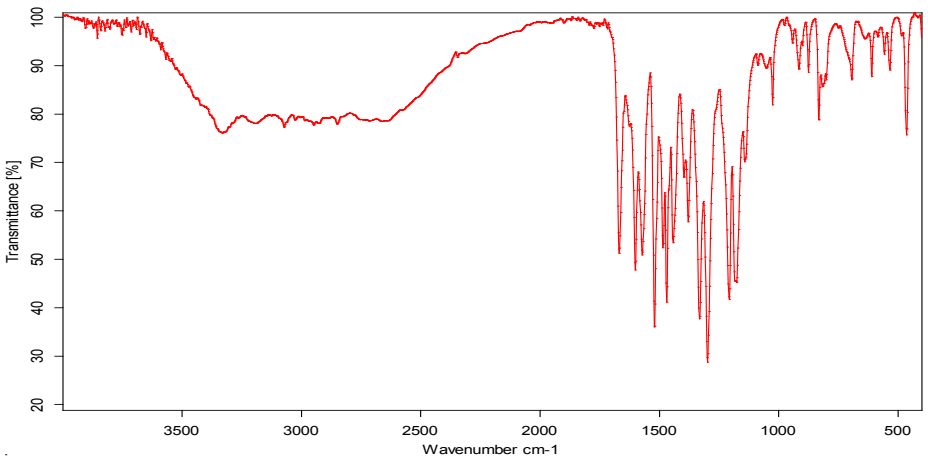

Figure S54. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 30 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

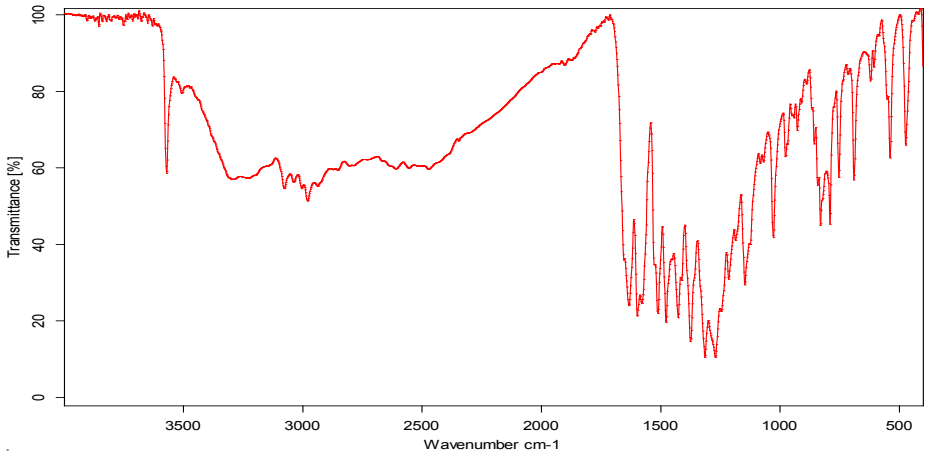

Figure S55. IR spectrum for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 30 min in the presence of TEA.

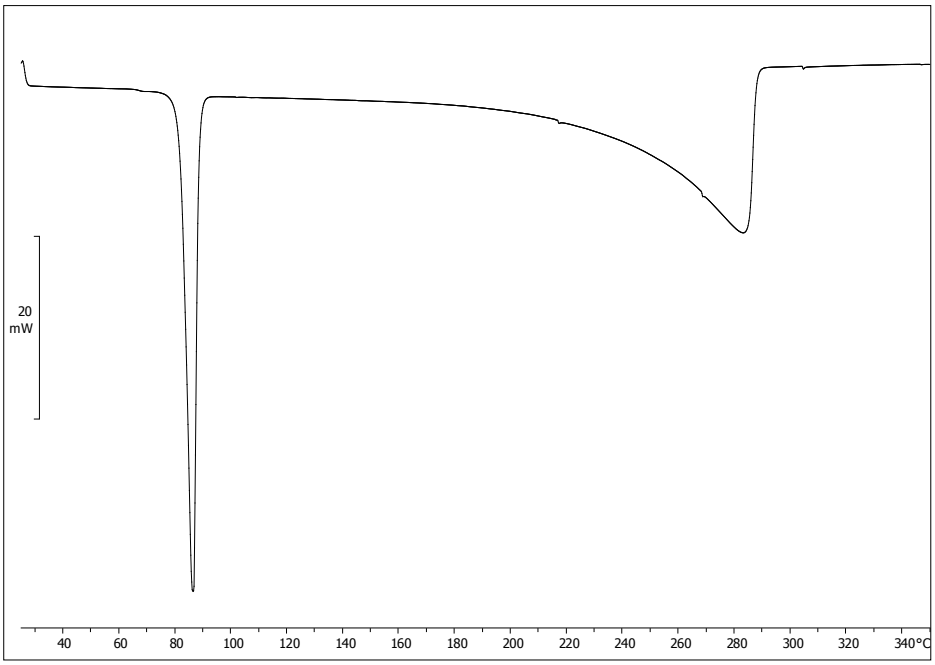

Figure S56. DSC curve for pure **napht** reactant.

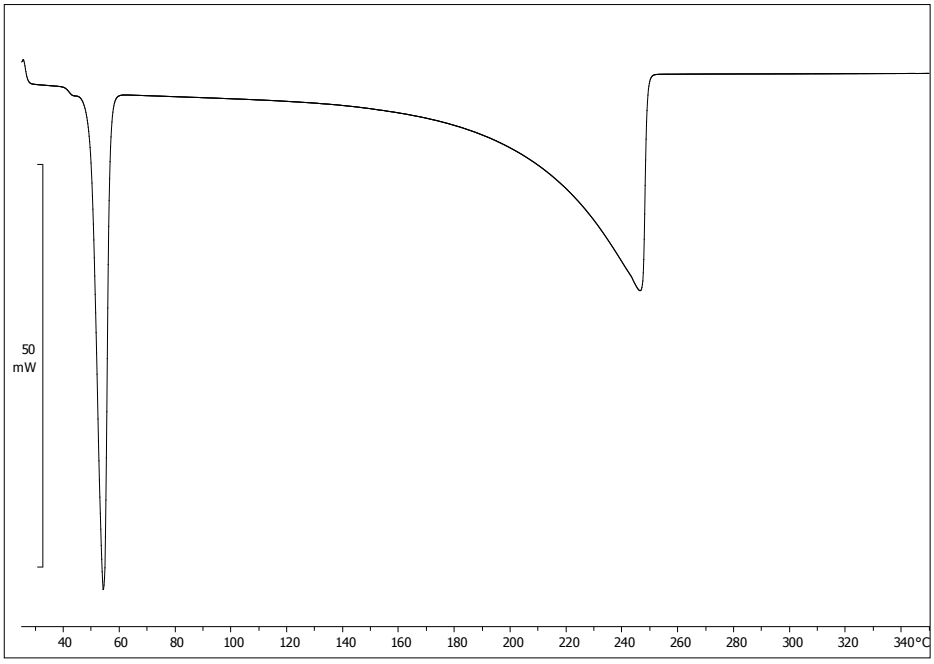

Figure S57. DSC curve for pure **abn** reactant.

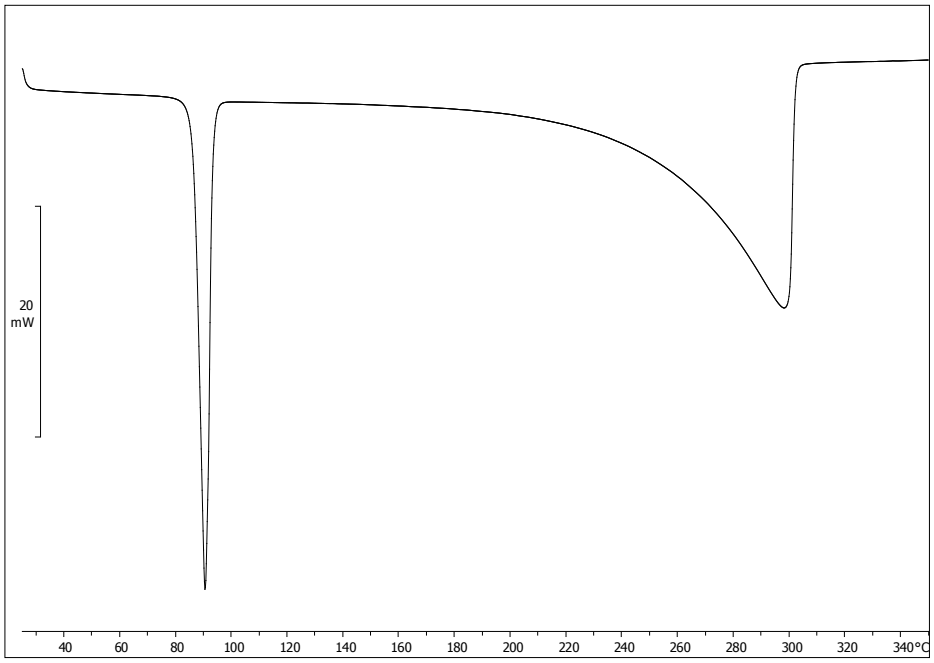

Figure S58. DSC curve for pure **4abn** reactant.

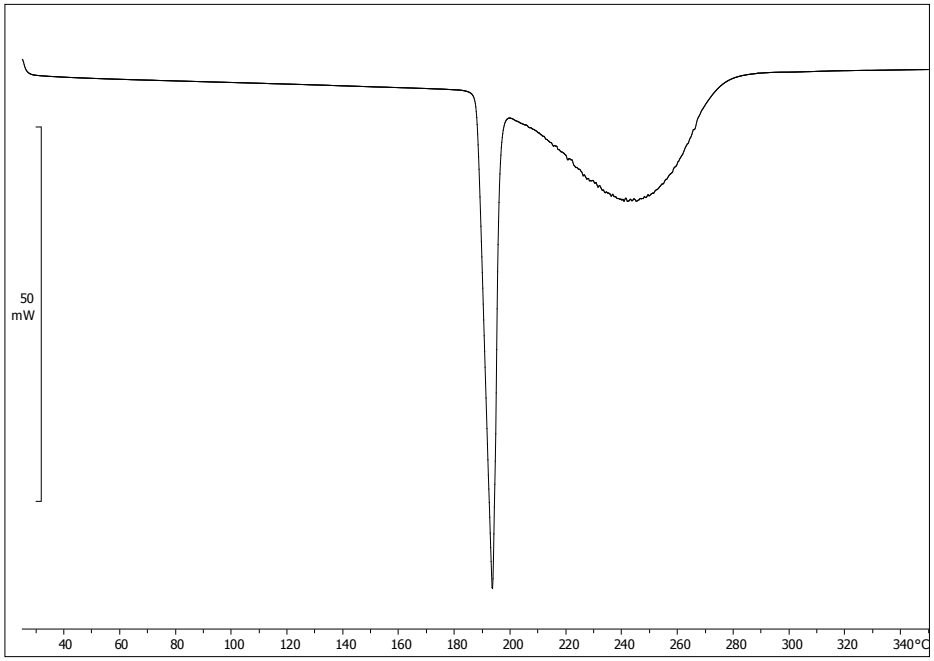

Figure S59. DSC curve for pure **4aba** reactant.

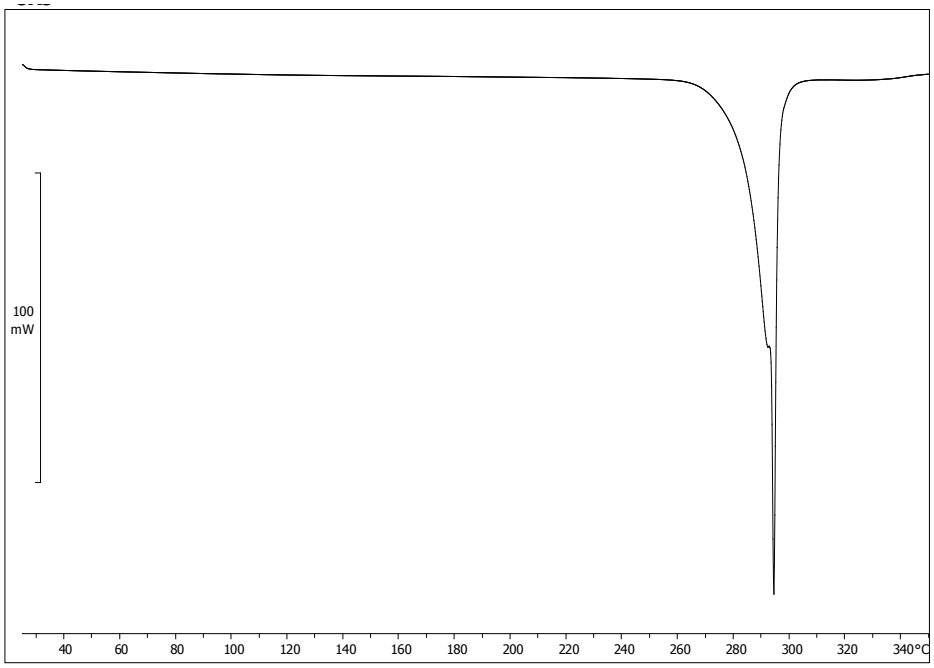

Figure S60. DSC curve for pure **5asa** reactant.

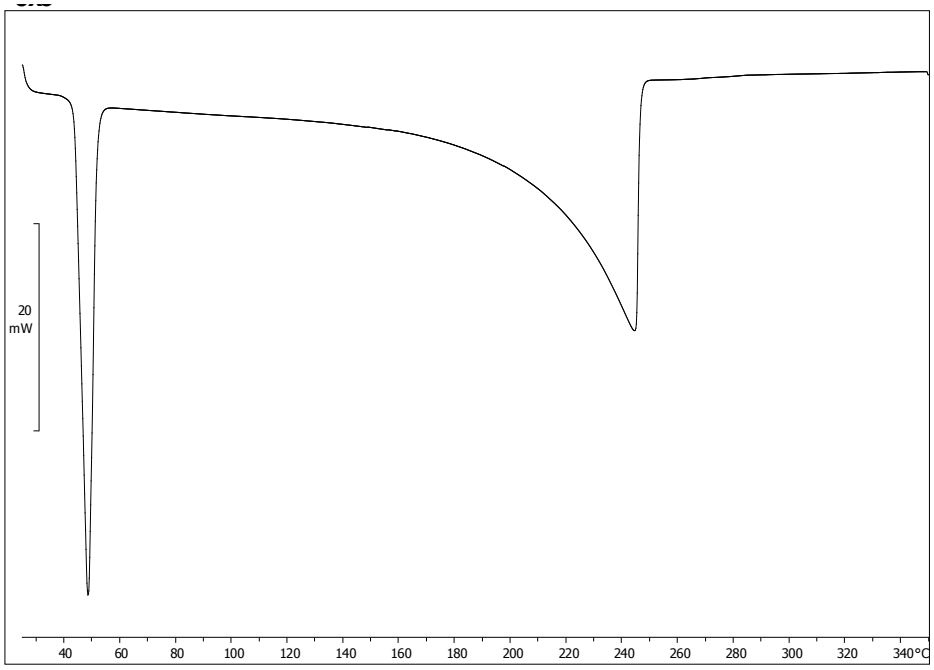

Figure S61. DSC curve for pure **ovan** reactant.

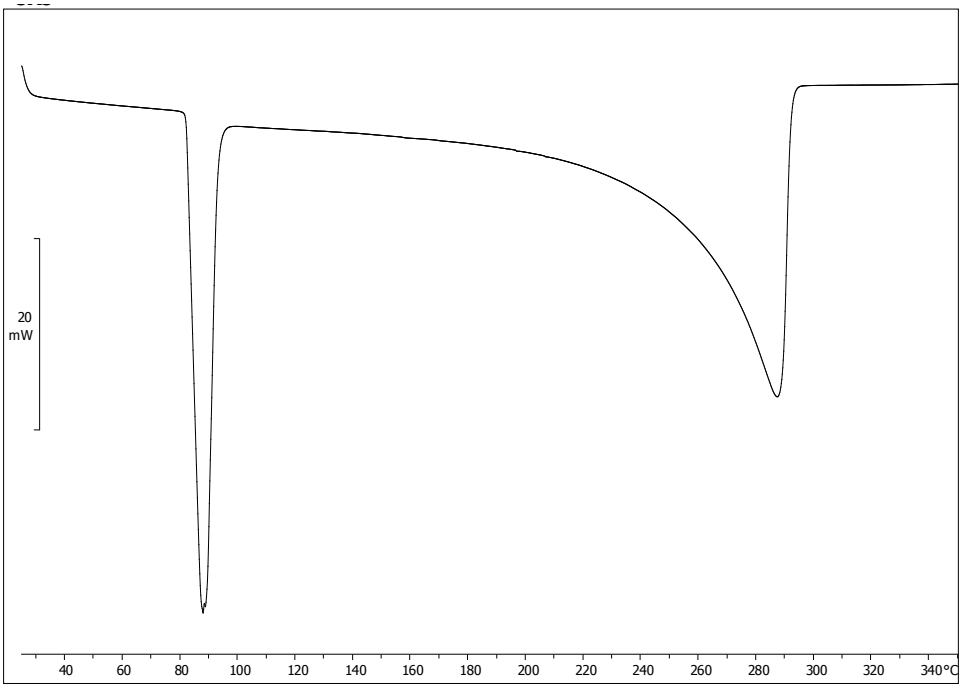

Figure S62. DSC curve for pure **van** reactant.

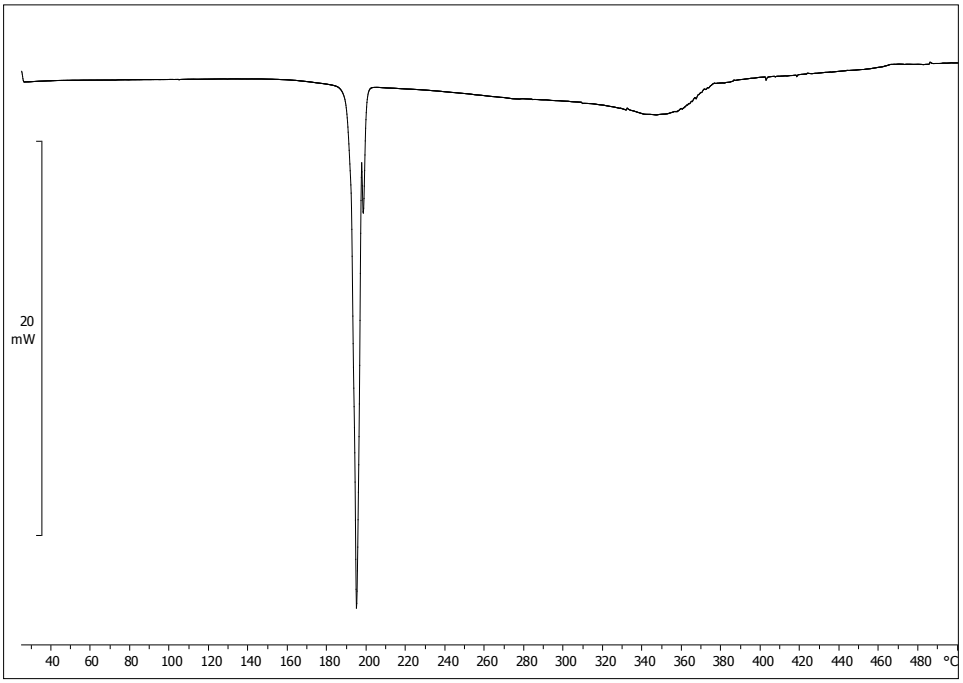

Figure S63. DSC curve for **1** synthesised by solution-based method.

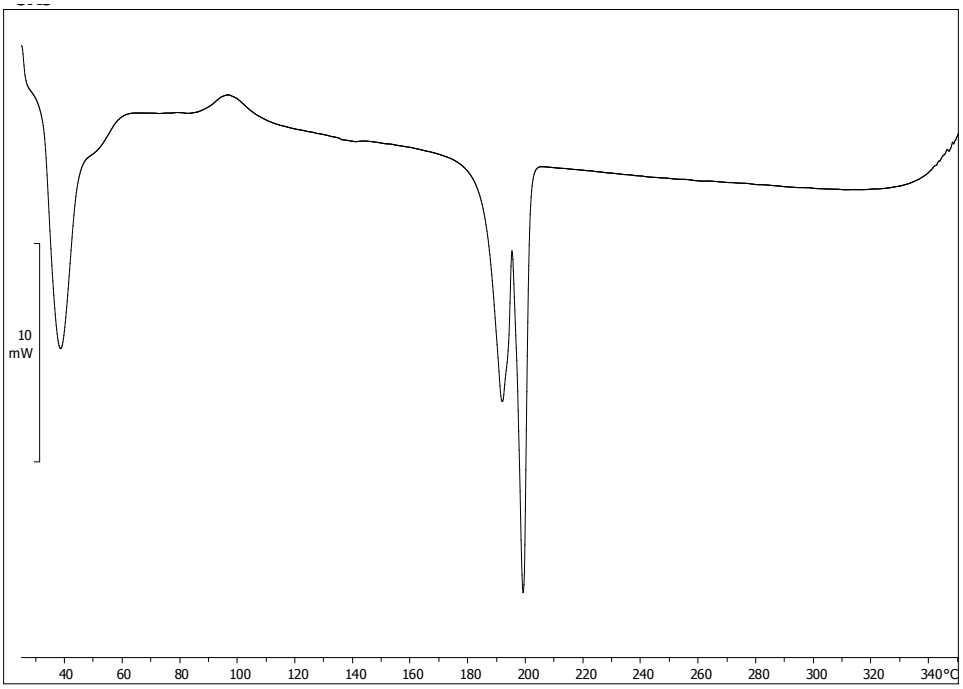

Figure S64. DSC curve for the product obtained by ageing a mixture of **napht** and **abn** at 0% RH for 3 days.

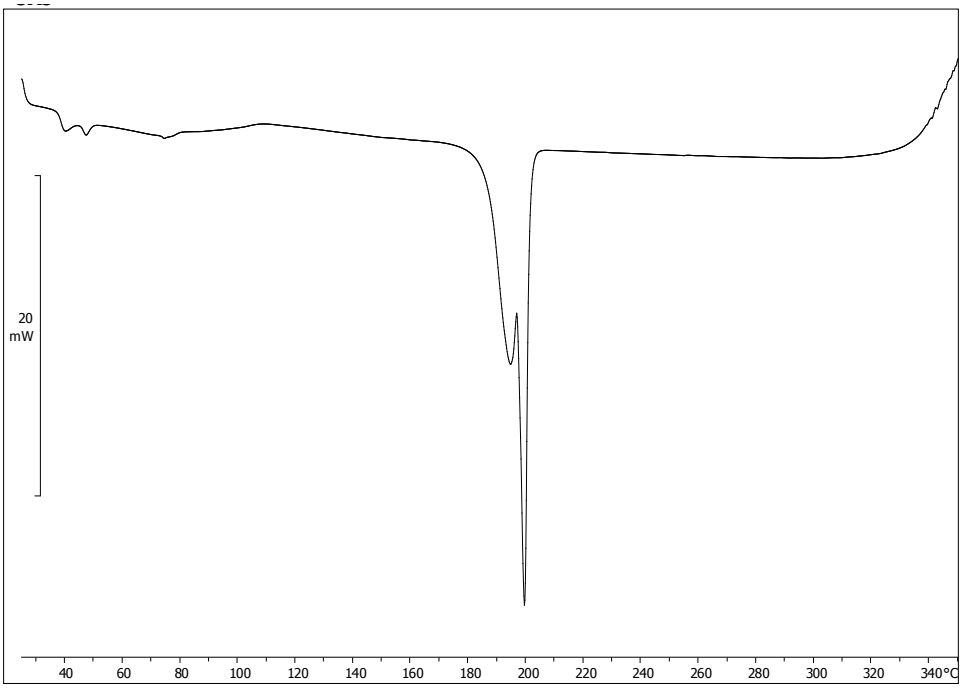

Figure S65. DSC curve for the product obtained by ageing a mixture of **napht** and **abn** at 98% RH for 3 days.

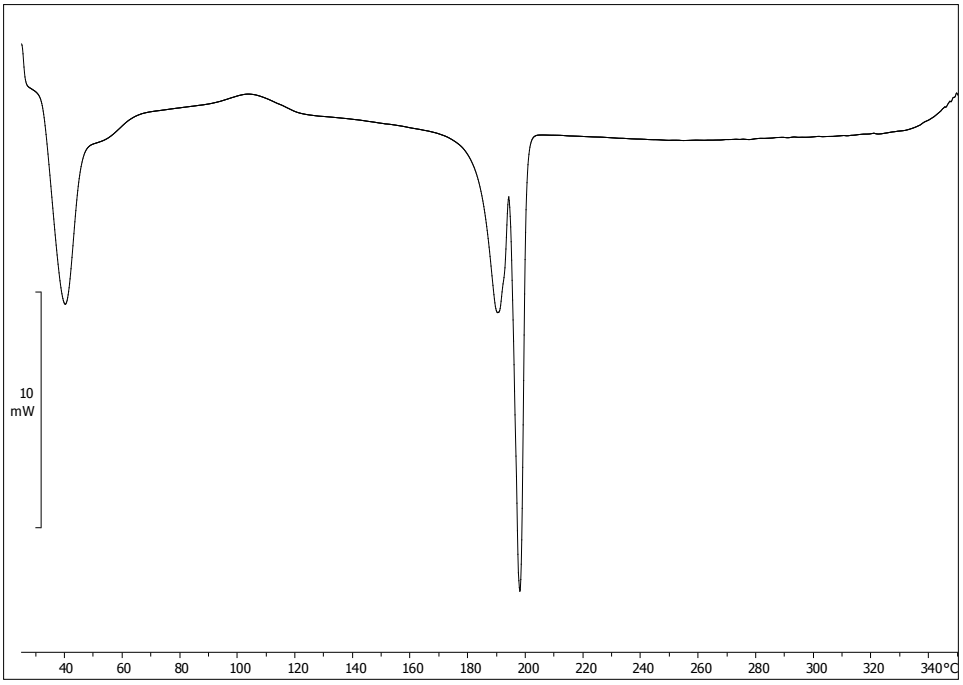

Figure S66. DSC curve for the product obtained by ageing a mixture of **napht** and **abn** at 0% RH for 7 days.

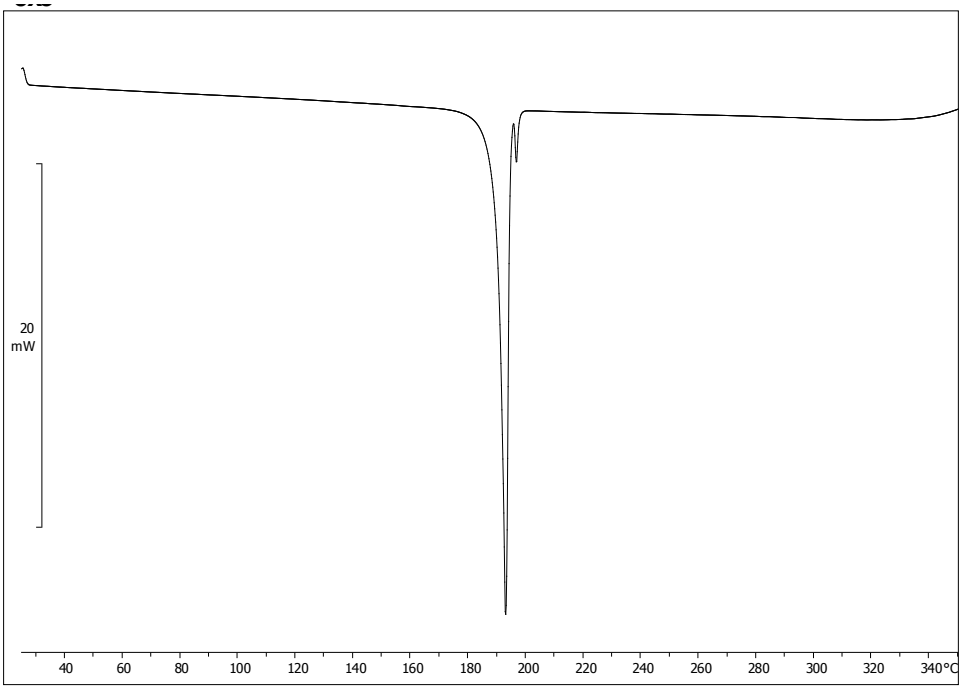

Figure S67. DSC curve for the product obtained by ageing a mixture of **napht** and **abn** at 98% RH for 7 days.

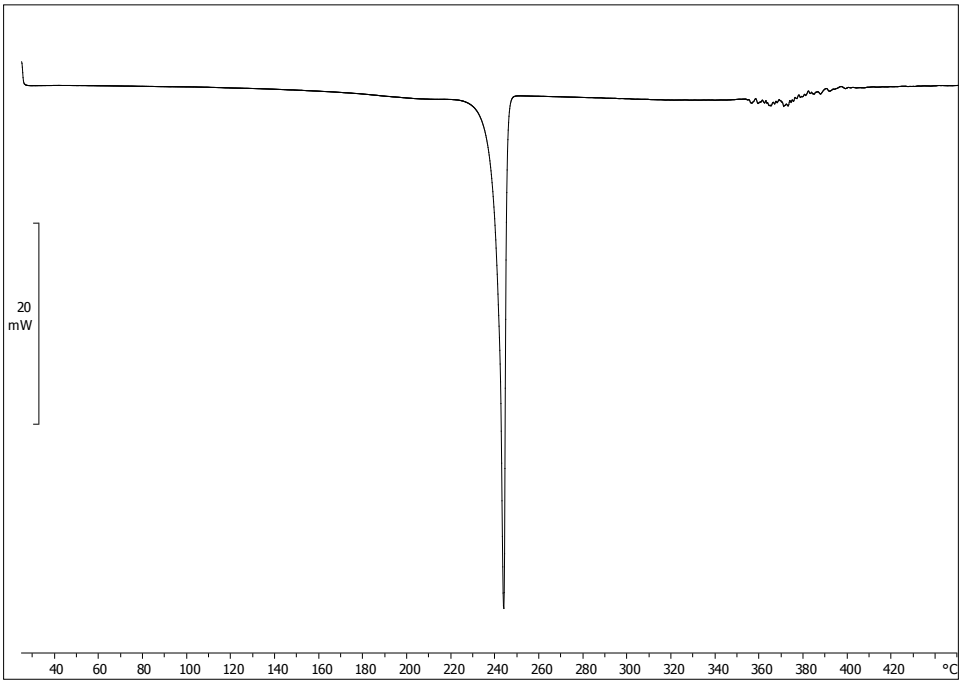

Figure S68. DSC curve for **2** synthesised by solution-based method.

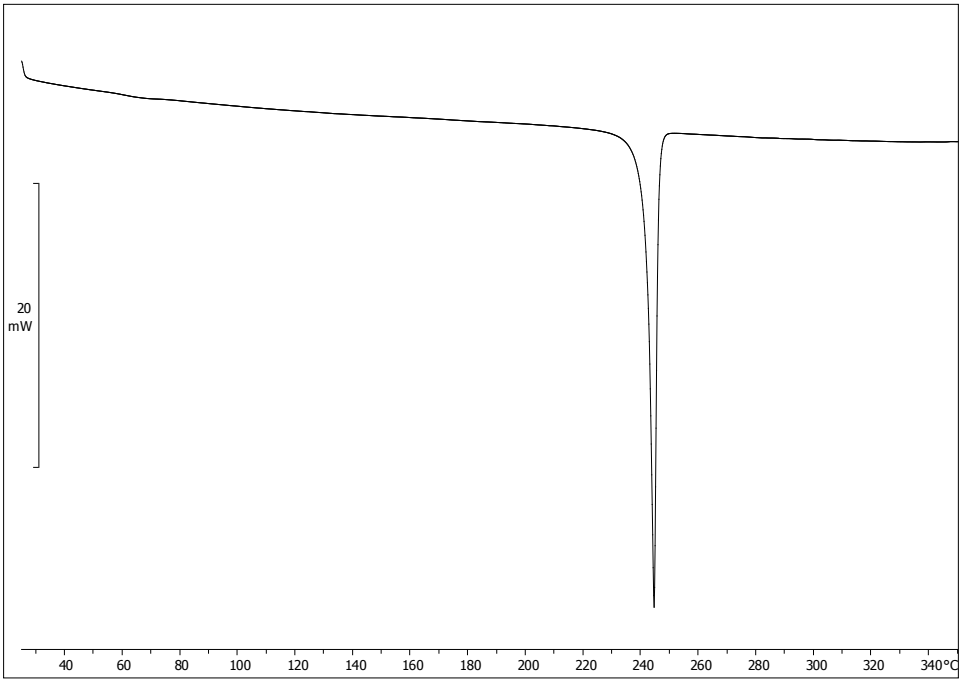

Figure S69. DSC curve for the product obtained by ageing a mixture of **napht** and **4abn** at 98% RH for 13 weeks.

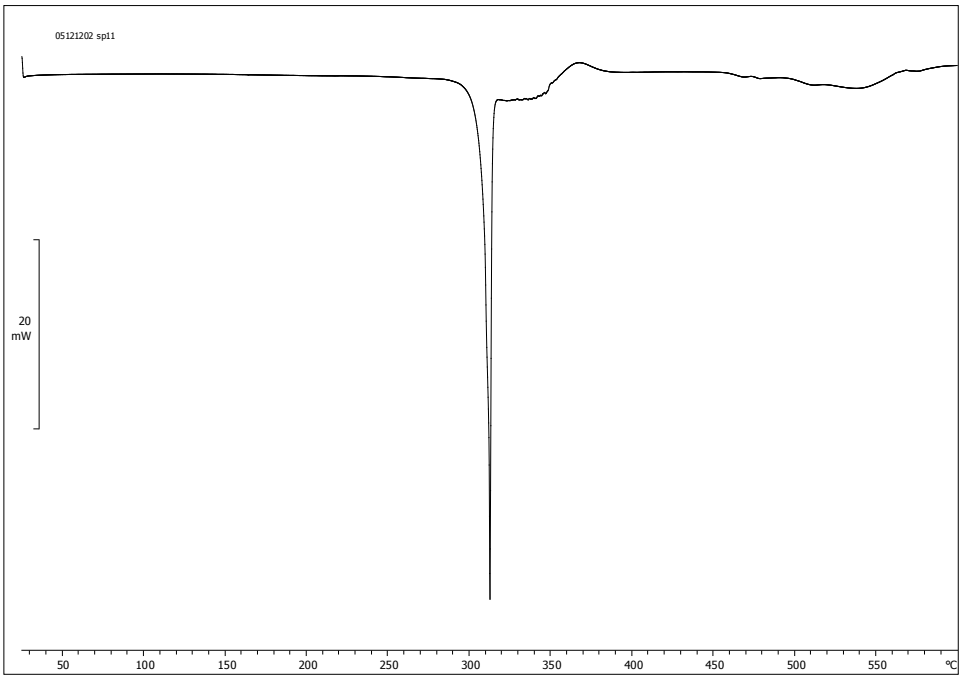

Figure S70. DSC curve for **3** synthesised by solution-based method.

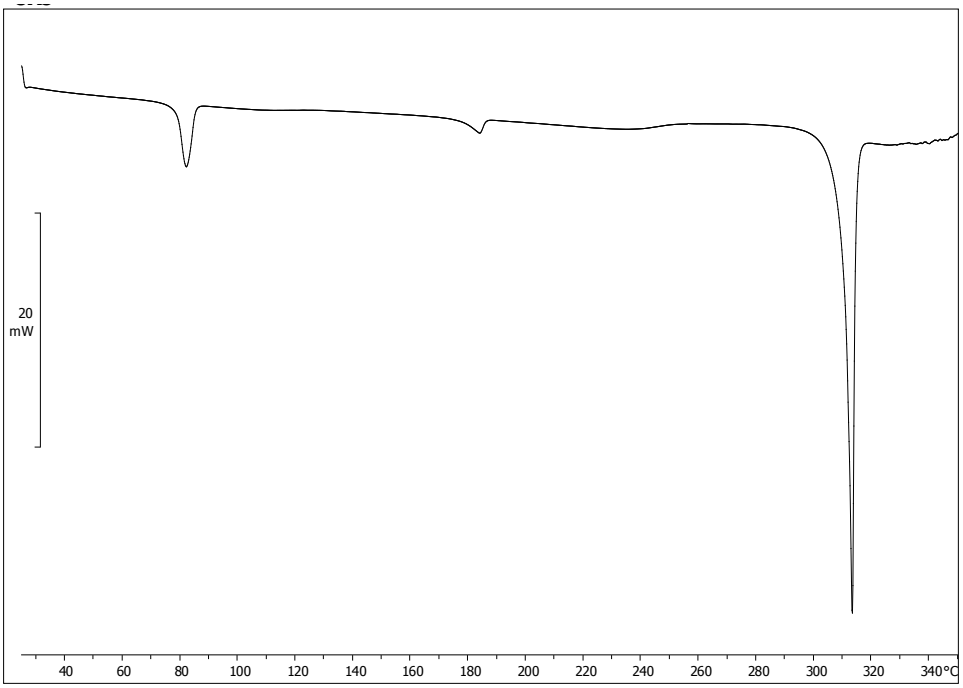

Figure S71. DSC curve for the product obtained by ageing a mixture of **napht** and **4aba** at 98% RH for 13 weeks.

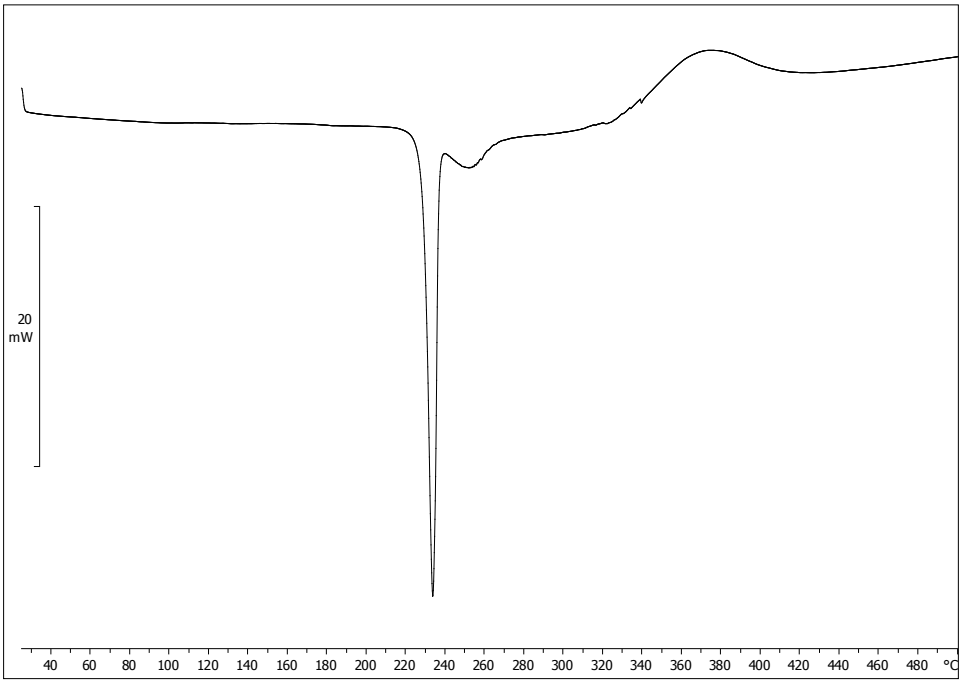

Figure S72. DSC curve for **4** synthesised by solution-based method.

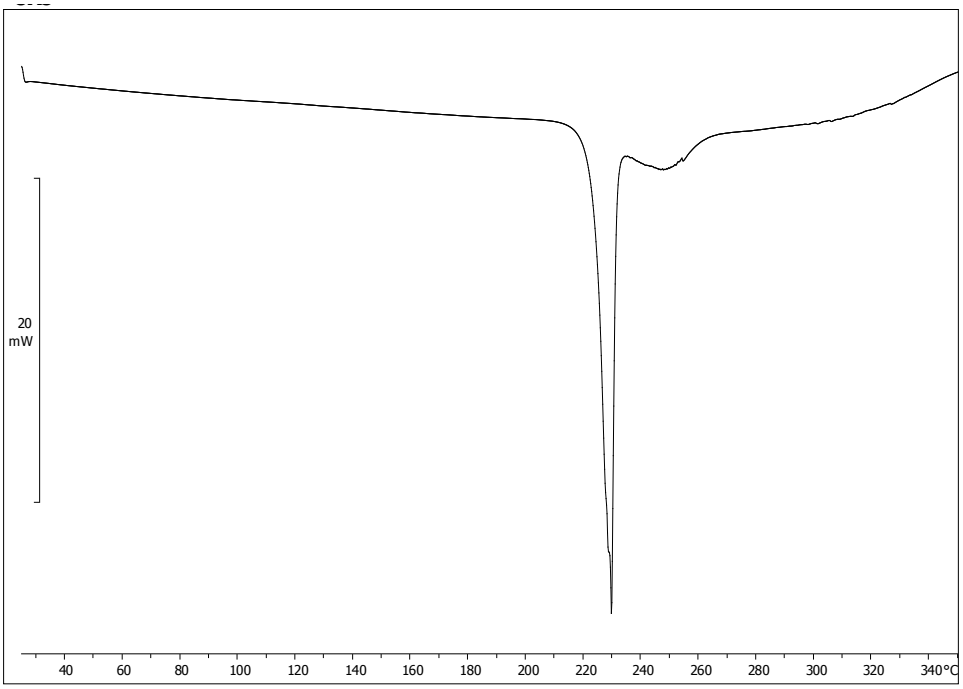

Figure S73. DSC curve for the product obtained by ageing a mixture of **5asa** and **ovan** at 98% RH for 5 months.

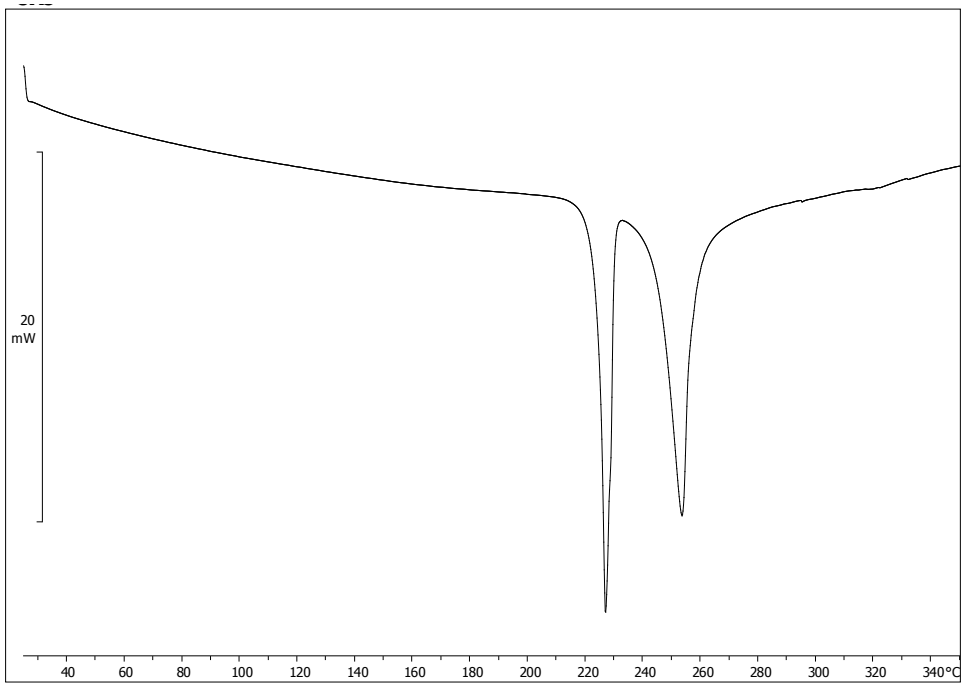

Figure S74. DSC curve for the product obtained by ageing a mixture of **5asa** and **ovan** at 0% RH for 5 months.

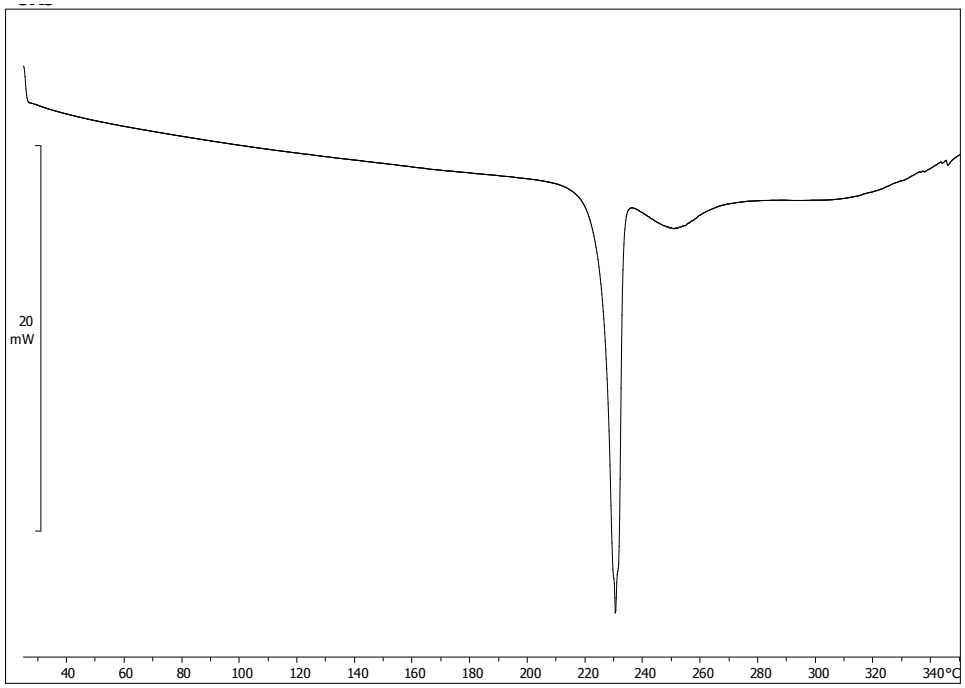

Figure S75. DSC curve for the product obtained by ageing a mixture of **5asa** and **ovan** in EtOH vapour for 1 hour.

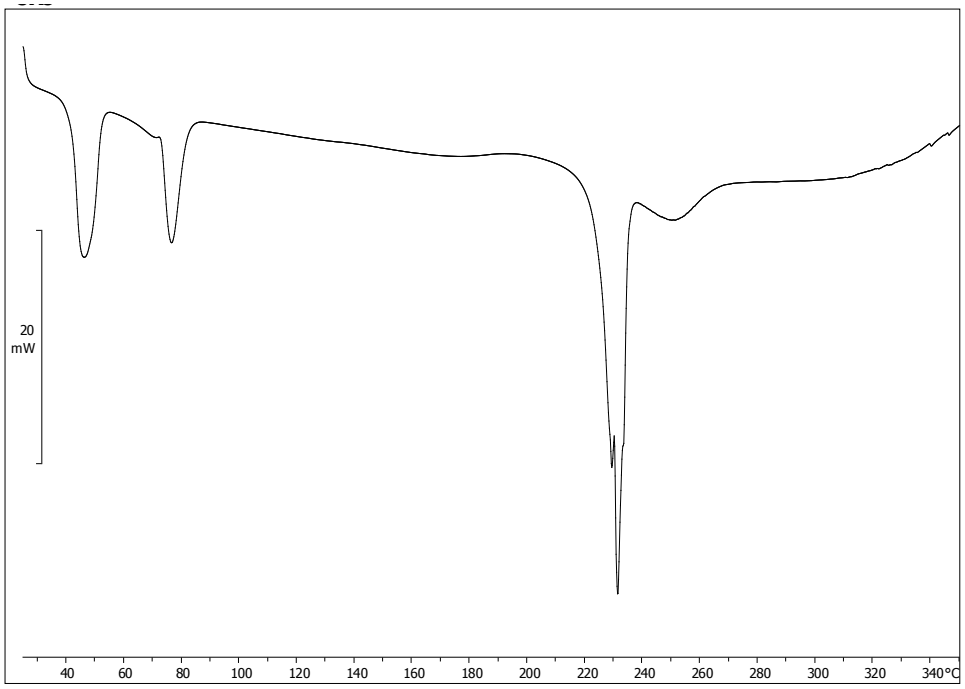

Figure S76. DSC curve for the product obtained by neat grinding of **5asa** and **ovan** in ball mill for 5 min.

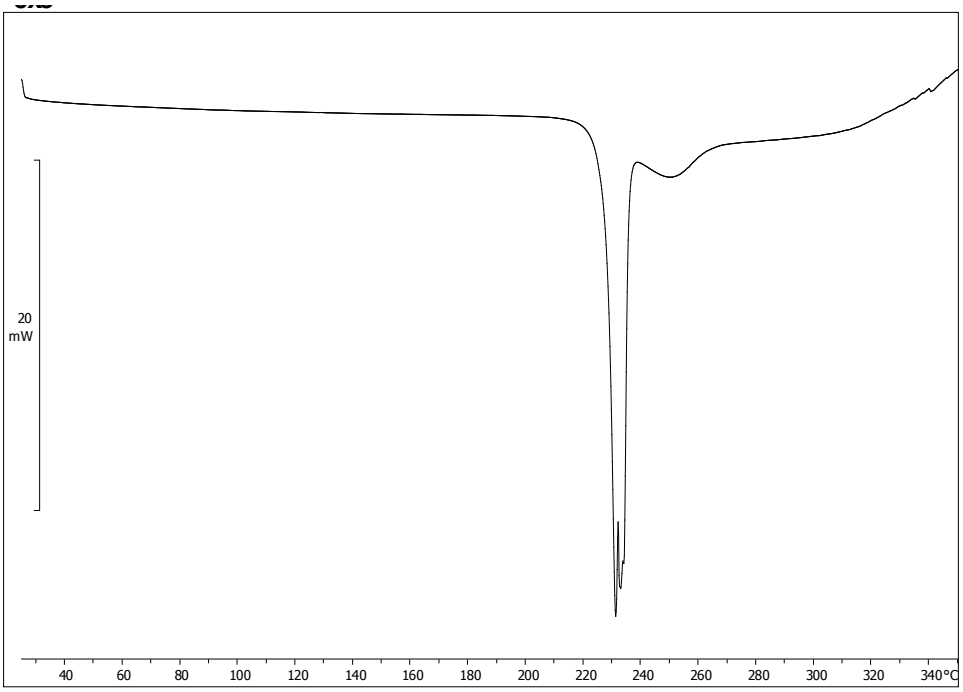

Figure S77. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **ovan** in ball mill for 5 min in the presence of EtOH.

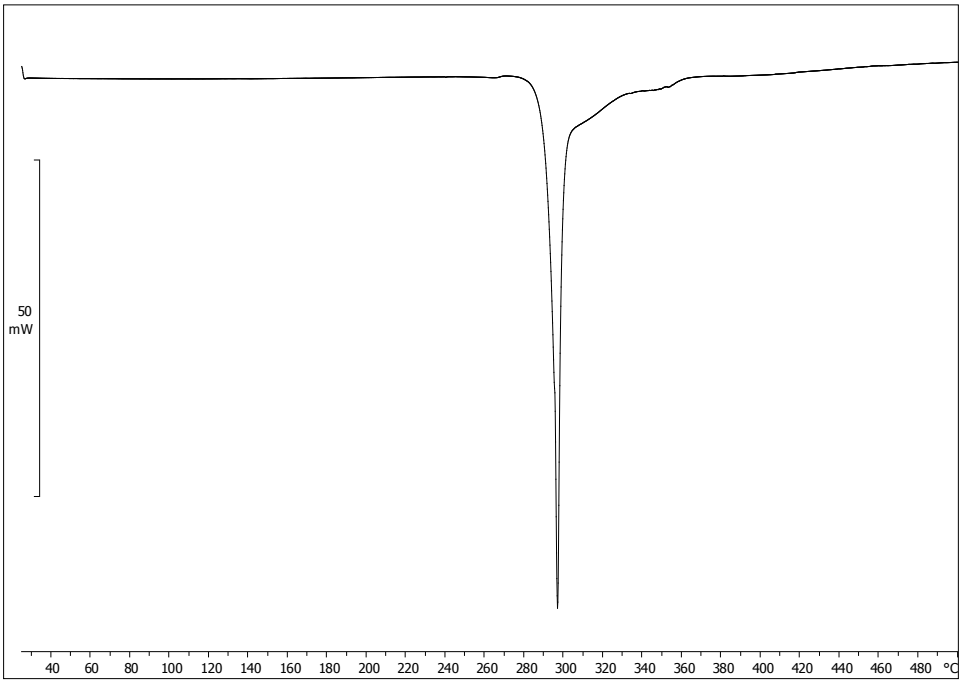

Figure S78. DSC curve for **5** synthesised by solution-based method.

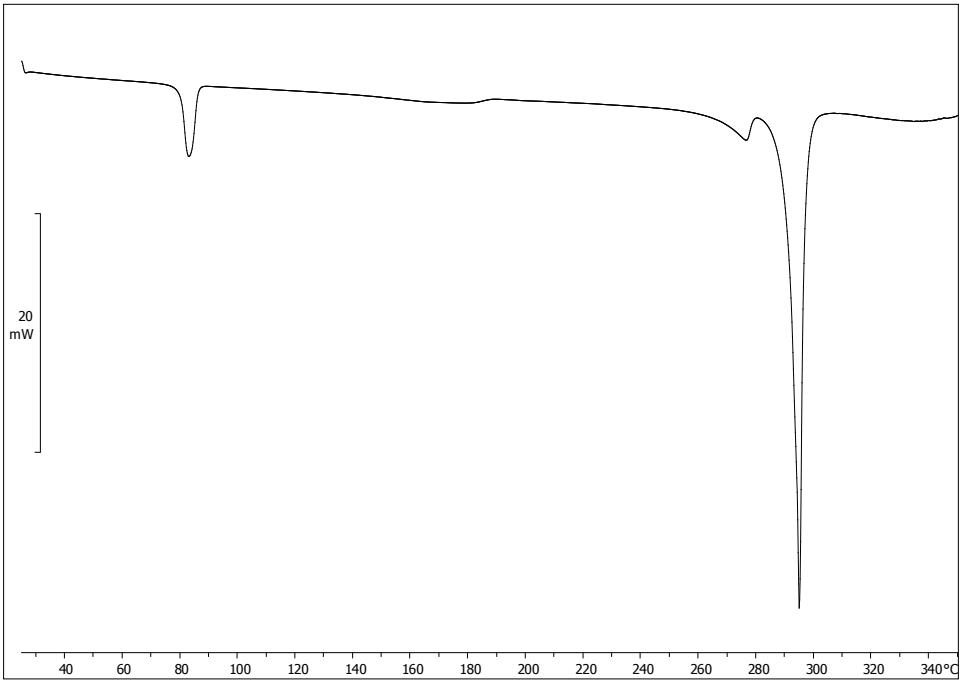

Figure S79. DSC curve for the product obtained by ageing a mixture of **5asa** and **napht** at 98% RH for 5 months.

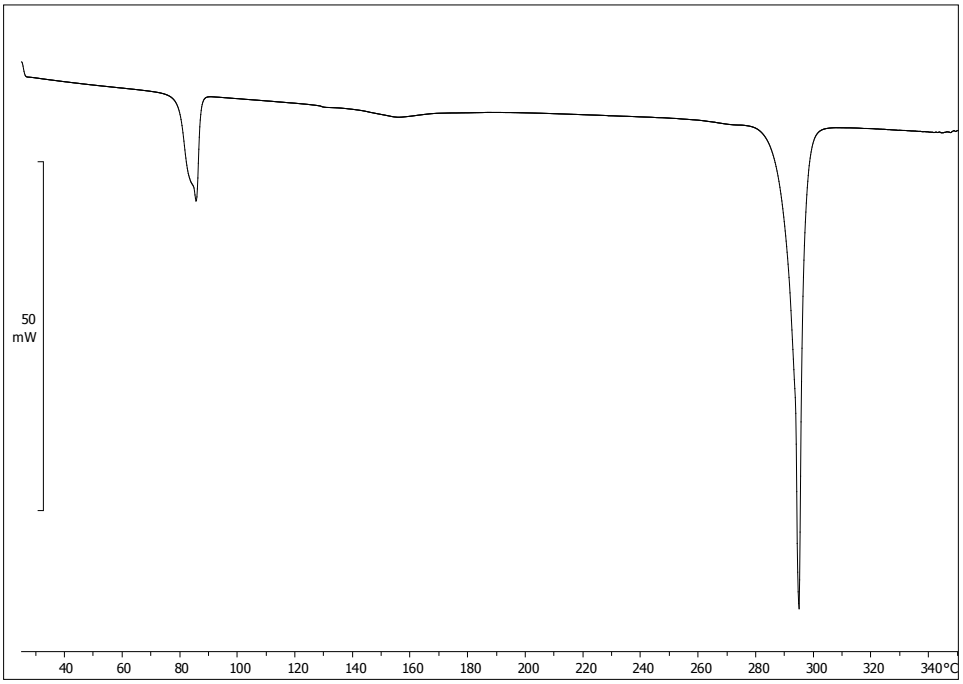

Figure S80. DSC curve for the product obtained by ageing a mixture of **5asa** and **napht** at 0% RH for 5 months.

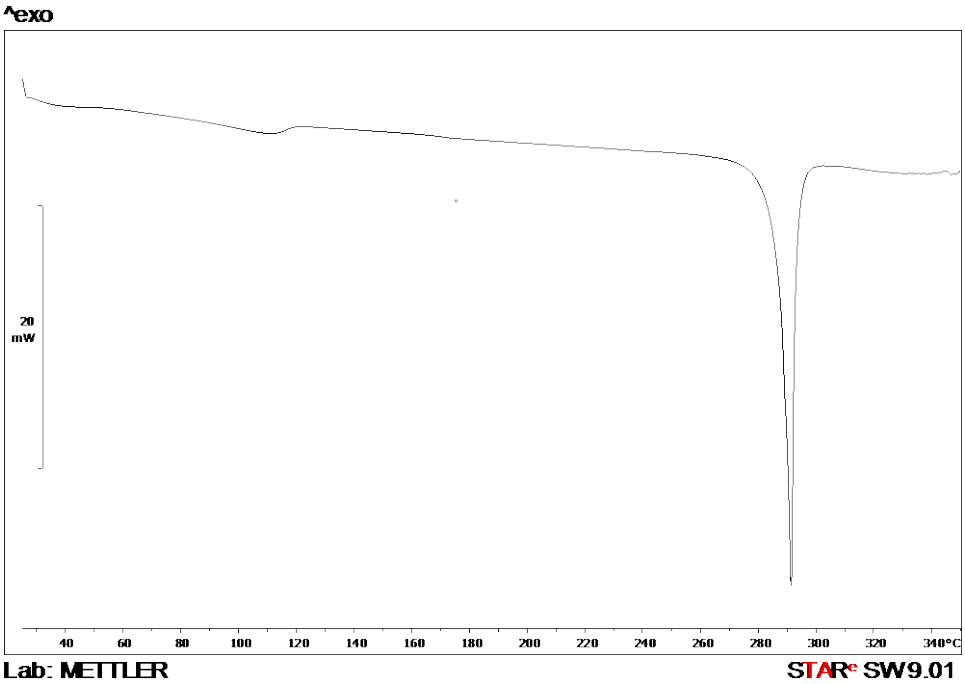

Figure S81. DSC curve for the product obtained by ageing a mixture of **5asa** and **napht** in a vapour mixture of EtOH and TEA (5% *v*/*v* of TEA) for 1 day.

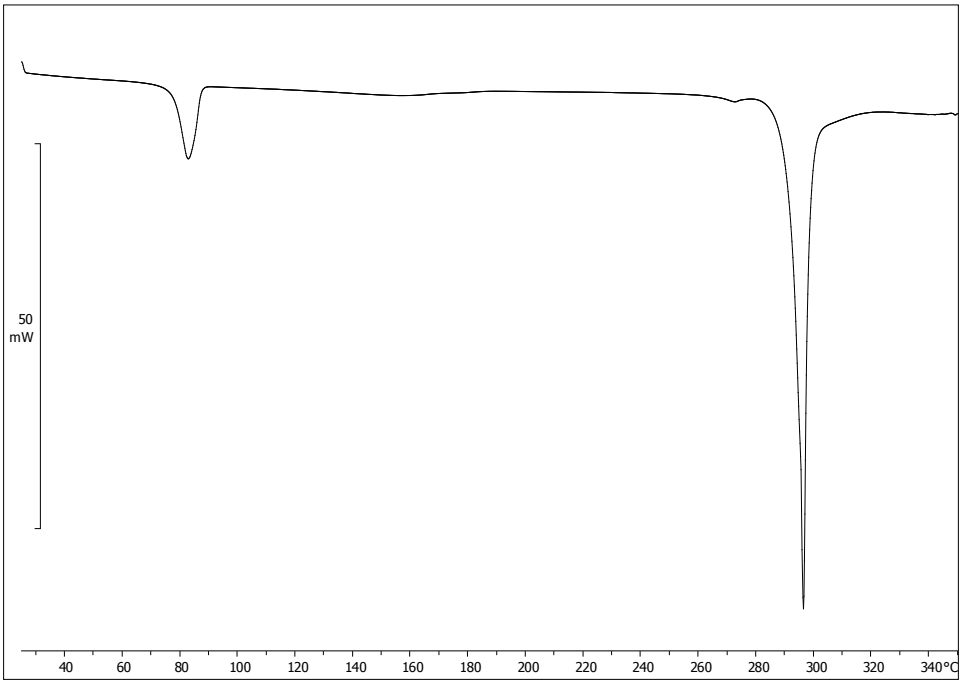

Figure S82. DSC curve for the product obtained by neat grinding of **5asa** and **napht** in ball mill for 45 min.

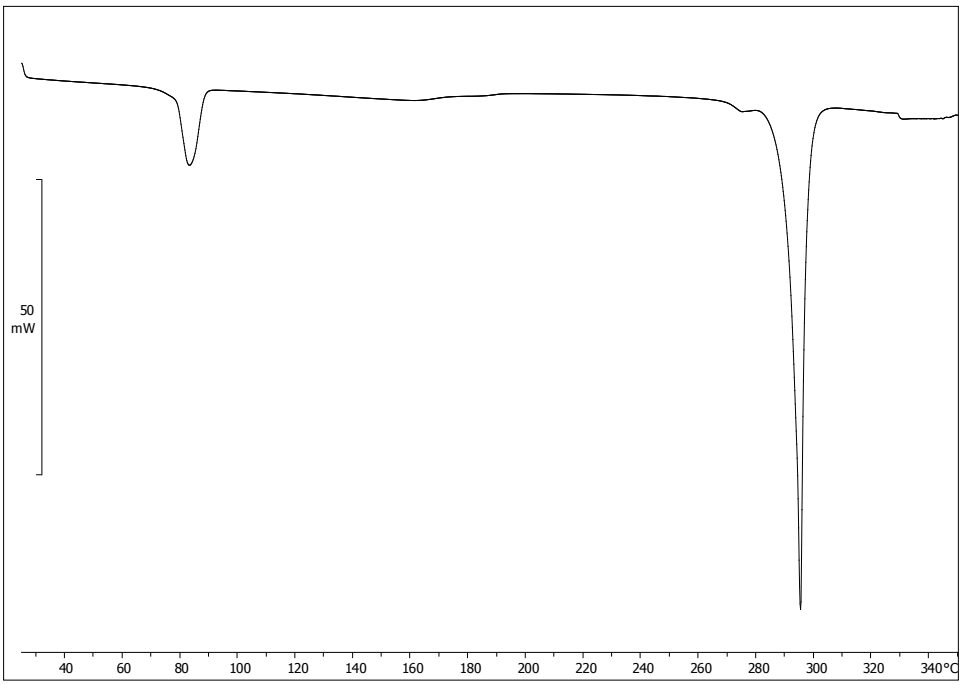

Figure S83. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **napht** in ball mill for 45 min in the presence of EtOH.

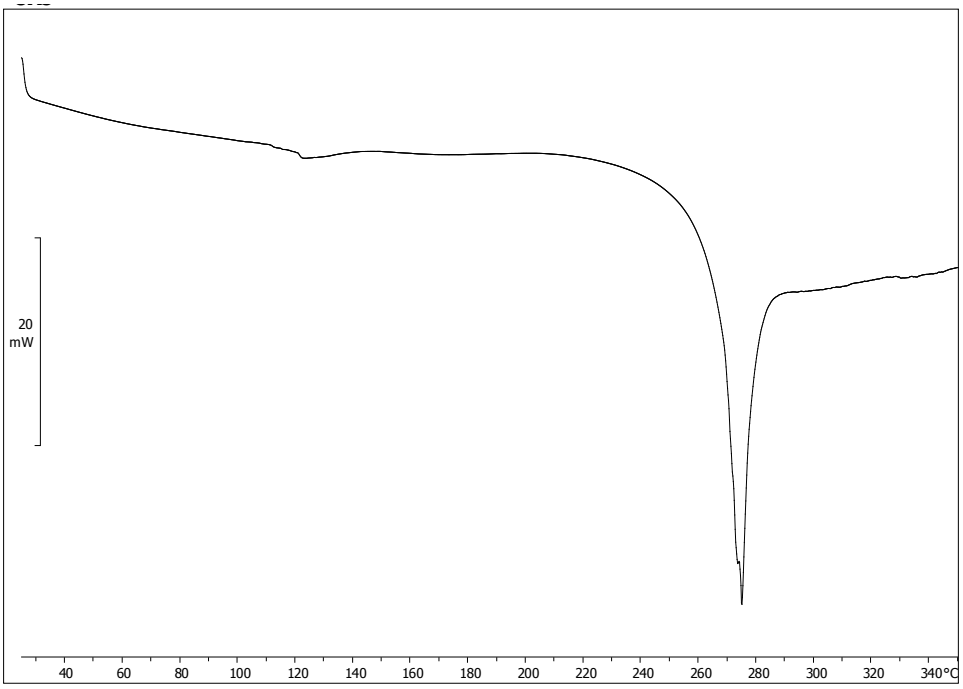

Figure S84. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **napht** in ball mill for 20 min in the presence of TEA.

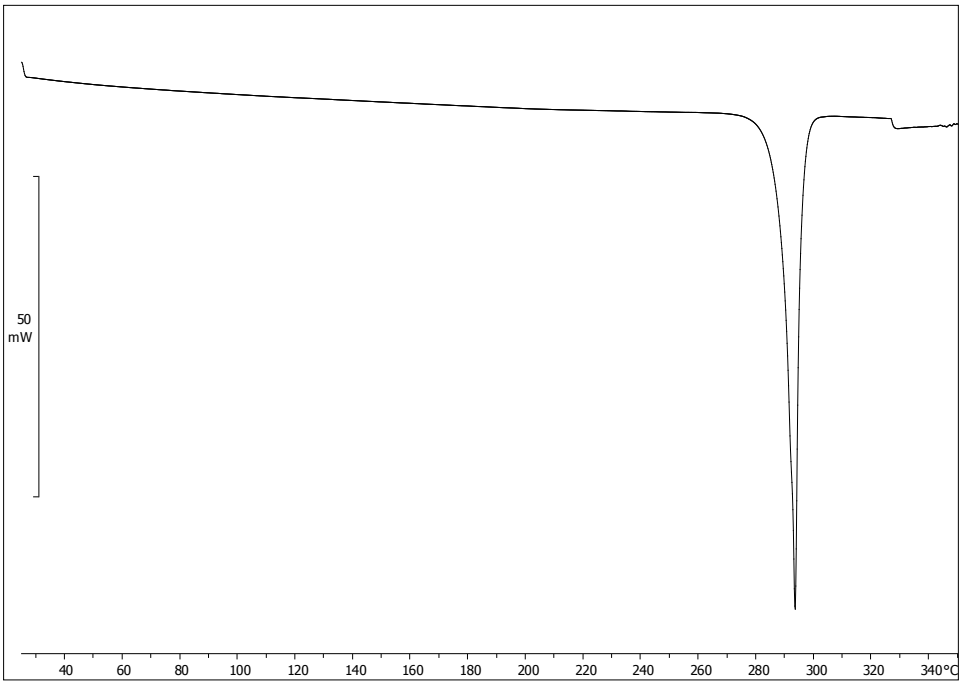

Figure S85. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **napht** in ball mill for 45 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA].

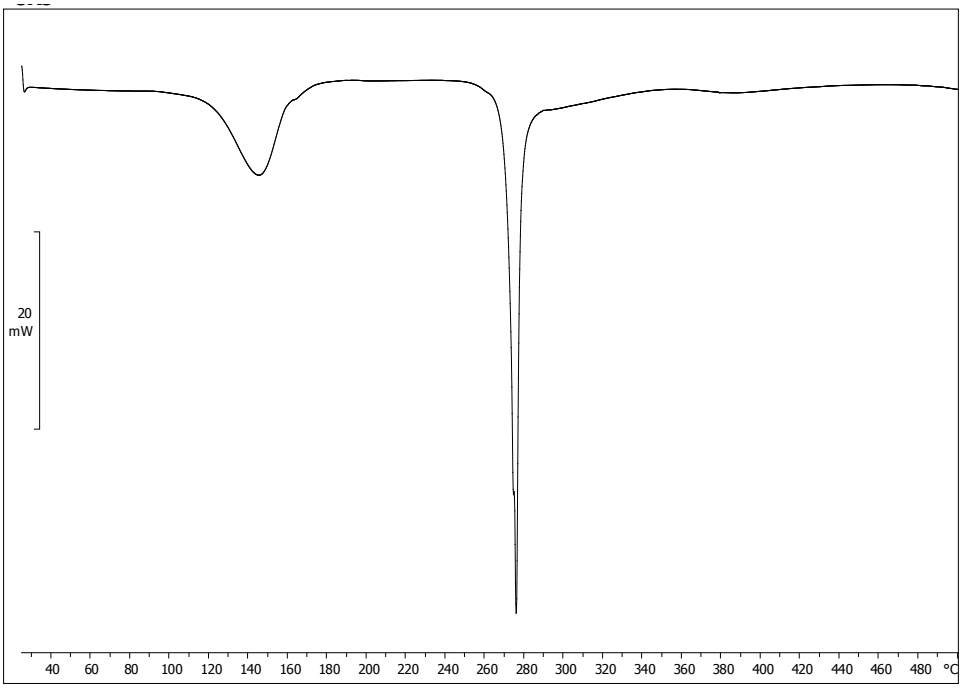

Figure S86. DSC curve for **6(H_2O)** synthesised by solution-based method.

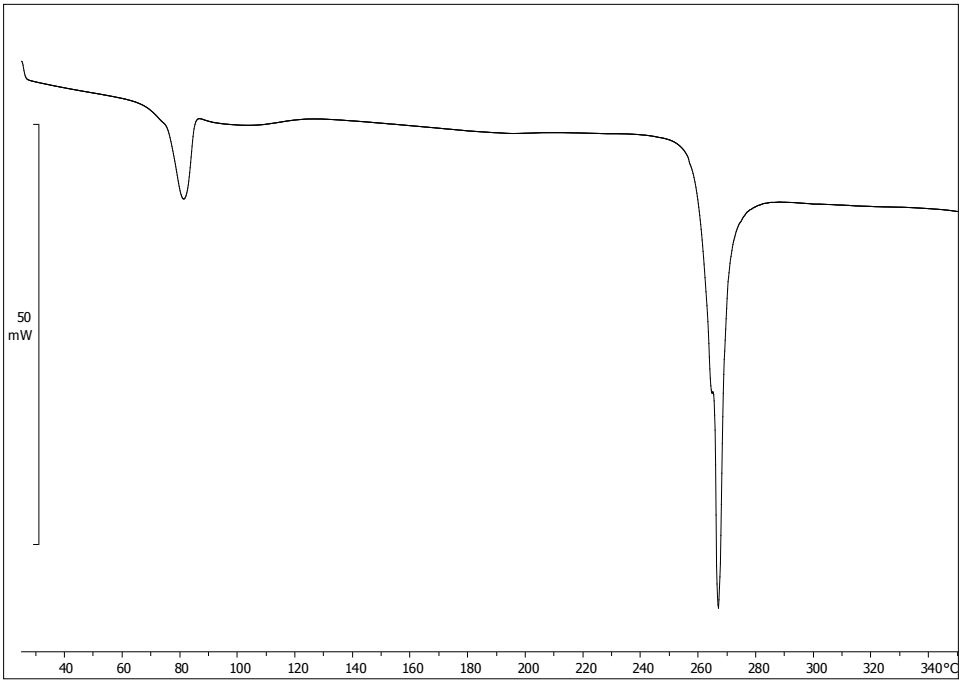

Figure S87. DSC curve for the product obtained by neat grinding of **5asa** and **van** in ball mill for 30 min.

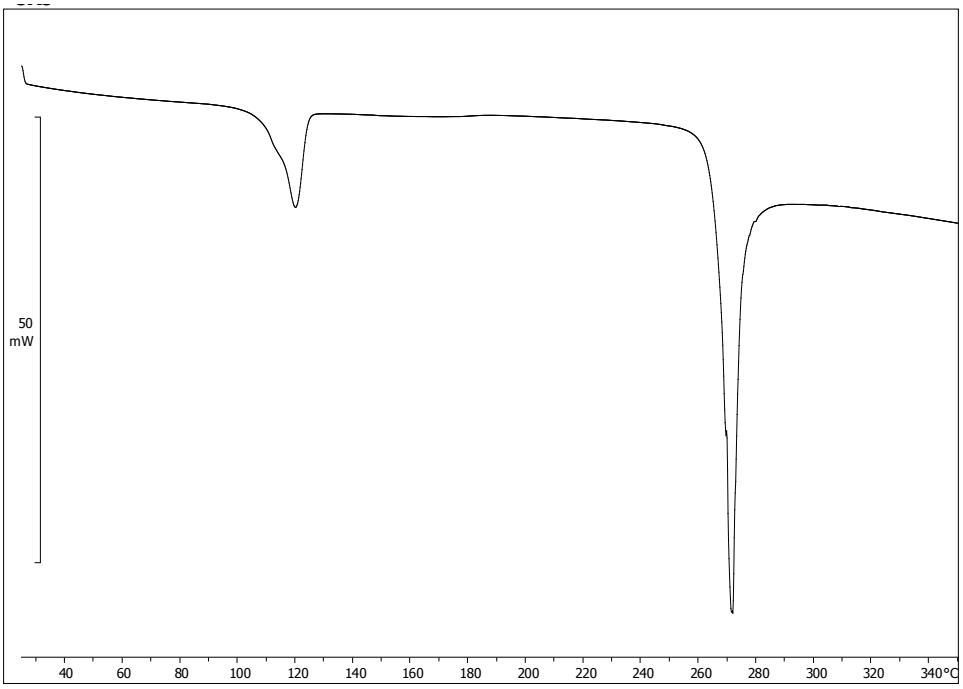

Figure S88. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 30 min in the presence of EtOH.

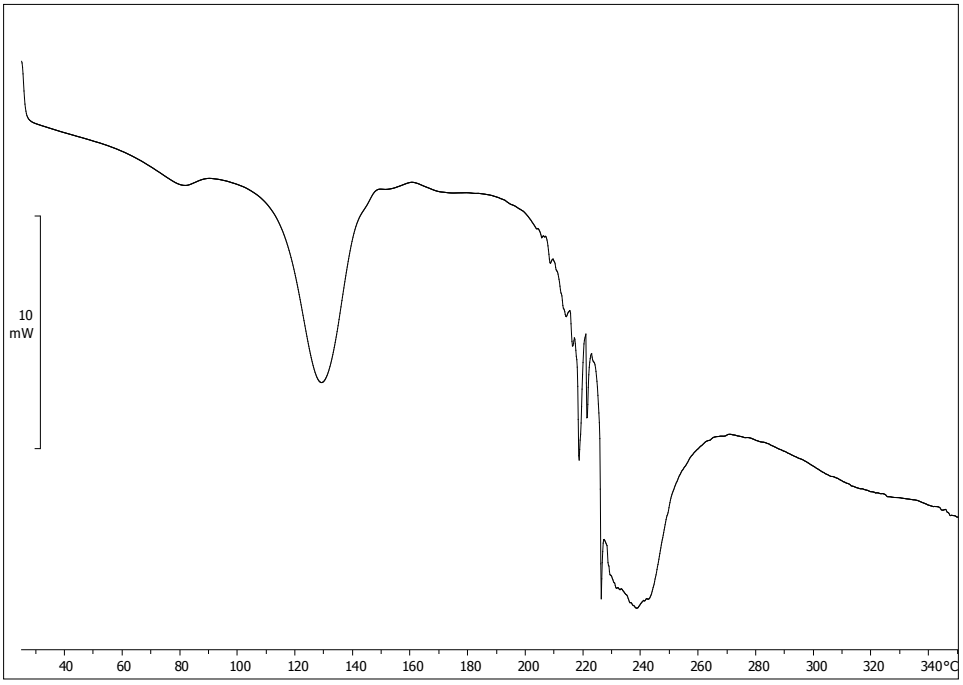

Figure S89. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 20 min in the presence of TEA.

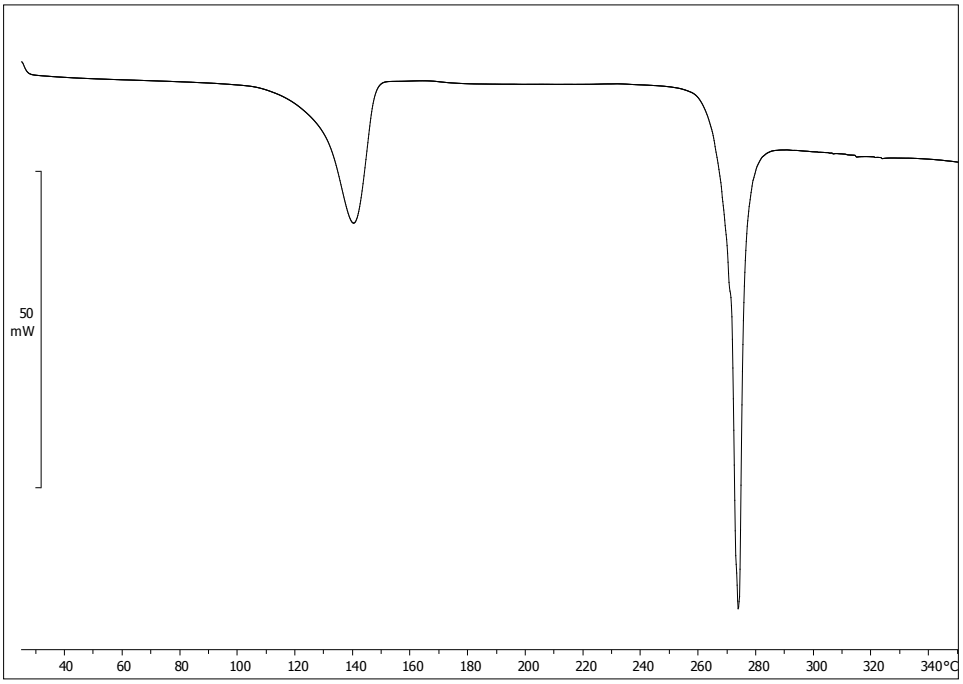

Figure S90. DSC curve for the product obtained by liquid-assisted grinding of **5asa** and **van** in ball mill for 30 min in the presence of a mixture of EtOH and TEA [5% *v*/*v* of TEA].