Interconversion between different stoichiometric forms of a three-component crystal *via* liquid-assisted grinding

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Experimental:

Chemicals were obtained from Sigma-Aldrich and used without further purification.

1 – Pamoic acid (200 mg, 0.51 mmol) and DABCO (60 mg, 0.53 mmol) were mixed in 8 ml THF. 1.8 ml of water were added to the mixture (yielding a 1:1 mole ratio water-THF solution), resulting in complete dissolution of the components. Colourless needle-shaped crystals were obtained from this solution.

2 – Pamoic acid (102 mg, 0.26 mmol) and DABCO (118 mg, 1.05 mmol) were dissolved in a 1:1 mole ratio mixture of THF-water. Colourless block crystals were afforded after approximately 2 months.

3 – Colourless block crystals were obtained from a seeded water-ethanol solution of powder obtained from a LAG experiment where pamoic acid (100 mg, 0.26 mmol) was ground together with DABCO (58 mg, 0.51 mmol, 1:2) and 3 drops of water (from a pipette). Crystals could also be obtained from an acetonitrile seeded solution. However, when the powder product was dissolved in acetone–H_2O or methanol we obtained only crystals of **1**.

Single-crystal X-ray intensity data were collected on a Bruker SMART Apex II X-ray diffractometer equipped with a Mo (λ= 0.71073 Å) fine-focus sealed tube and a 0.5 mm MonoCap collimator. Data were captured with a CCD (Charge-Coupled Device) area-detector. All data collections were carried out at 100 K using an Oxford Cryosystems cryostat (700 Series Cryostream Plus) attached to the diffractometer. Data collection and reduction were carried out using the Bruker software package APEX2,[1] using standard procedures. All structures were solved by direct methods using SHELXS-97[2] employed within the X-Seed[3,4] environment. Diagrams were generated using POV-Ray.[5]

PXRD patterns were collected using a PANalytical X'Pert Pro diffractometer with Bragg-Brentano geometry using CuKα radiation (λ = 1.5418 Å) at 45kV and 40 mA. Intensity data were captured with an X'Celerator detector with 2θ scans performed in the range 5-50° with a 0.0167 step size. Sample was spun at 4 revolutions per second.

Note on structure refinement: **3** – Hydrogen atom of the 25% occupancy DABCO could not be found in the electron density. The two hydrogen atoms attached to O9 (water molecule) were also not located in the electron density maps.

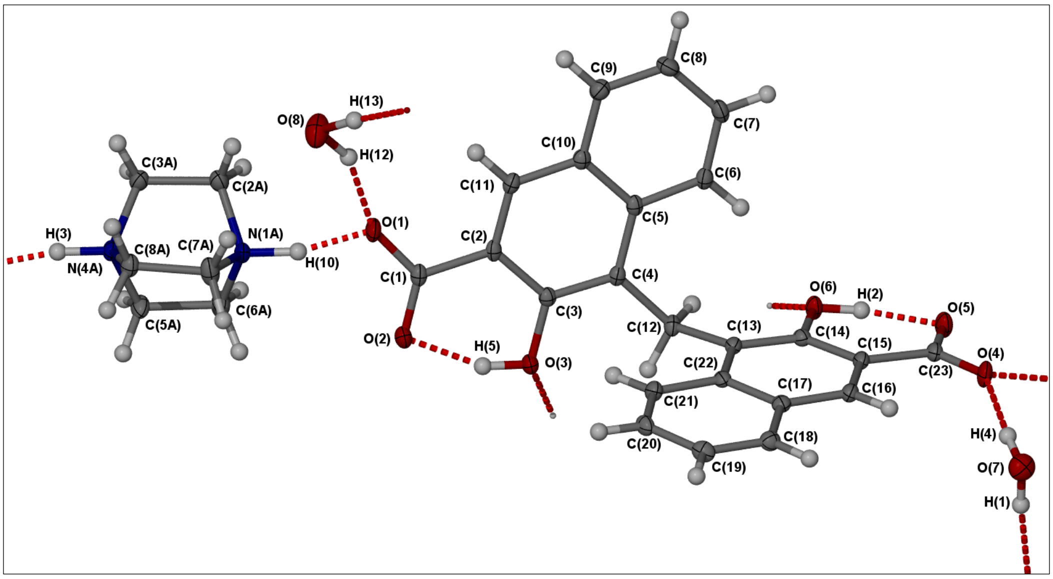

Figure S1 Thermal ellipsoid plot of the asymmetric unit of **1**.

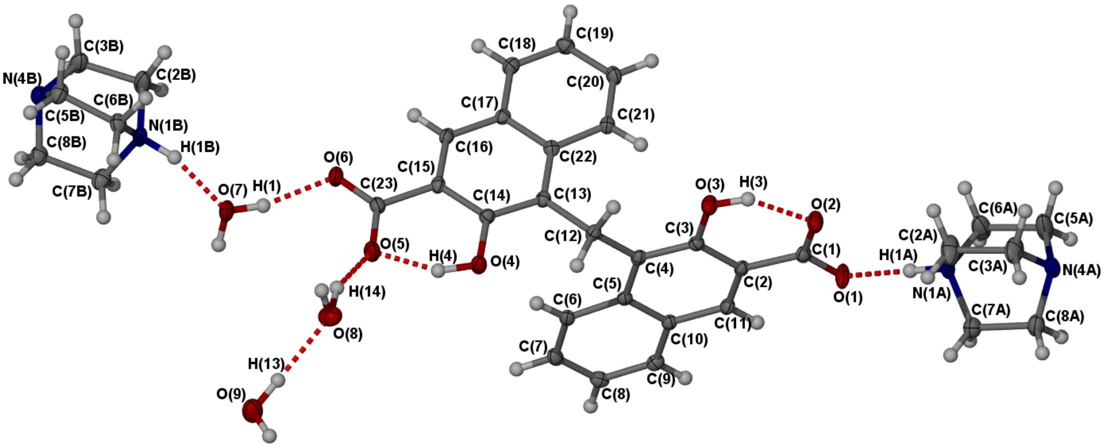

Figure S2 50% Thermal ellipsoid plot of **2**, only the ASU is shown.

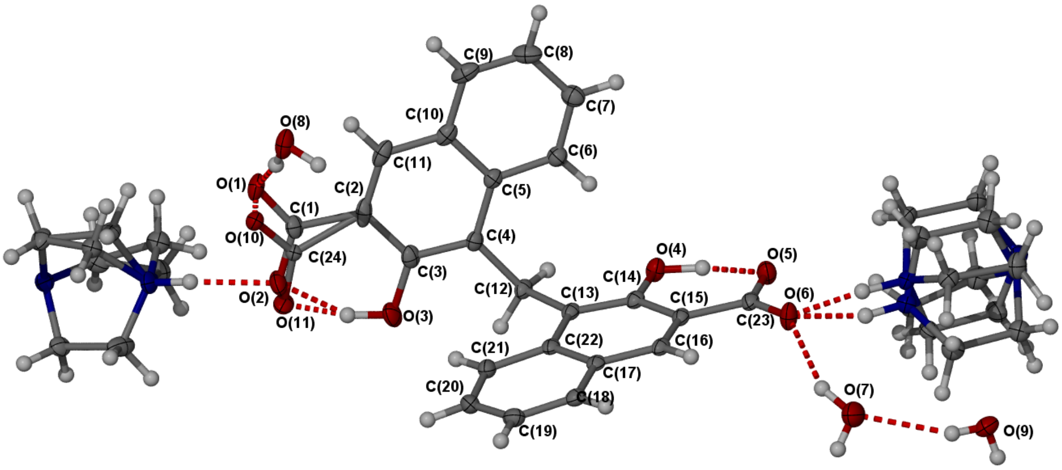

Figure S3 Thermal ellipsoid (50%) plot of the ASU of **3**

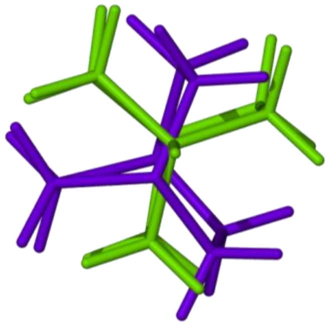

Figure S4 Capped-stick representation of the two disordered DABCO cations – green indicates the position of 75% occupancy, purple indicates that of 25% occupancy.

Selected crystallographic data for **1**, **2** and **3** are given in Table S1. Hydrogen bonding parameters are given in tables S2-4.

Table S1 Selected crystallographic data for structures **1**-**3**.

	1	**2**	**3**
Stoichiometry acid : base :H_2O	1:2:2	1:2:3	1:2:3
Chemical Formula	$C_{29}H_{32}N_2O_8$	$C_{35}H_{46}N_4O_9$	$C_{35}H_{46}N_4O_9$
Formula Weight	536.57	666.76	666.76
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a /Å	15.3417(10)	13.8658(4)	11.419(3)
b /Å	12.4564(8)	9.0624(3)	18.531(4)
c /Å	13.9070(9)	26.4347(9)	17.890(4)
β /°	110.8180(10)	95.548(2)	122.434(3)
Z	4	4	4
Temperature / K	100(2)	100(2)	100(2)
Calculated Density / g cm^{-3}	1.435	1.340	1.377
μ / mm^{-1}	0.105	0.097	0.099
Independent Reflections	5393	7912	7864
R_{int}	0.0186	0.0497	0.0258
$R1$ [I > $2\sigma(I)$]	0.0381	0.0490	0.0587

Table S2 Hydrogen bonding parameters for **1**

	***D*—H (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
O7—H7W2···O4$^{\text{i}}$	0.86 (2)	2.9064 (15)	168 (2)
O4—H4···O5	0.90 (2)	2.5127 (13)	158 (2)
N4A—H4A···O6$^{\text{ii}}$	1.01 (2)	2.5461 (13)	170.5 (18)
N4A—H4A···O5$^{\text{ii}}$	1.01 (2)	3.3069 (14)	129.4 (14)
O7—H7W1···O6	0.84 (2)	2.8914 (15)	166.7 (19)
O3—H3···O2	0.90 (2)	2.5315 (13)	157 (2)
N1A—H1A···O1	1.07 (2)	2.5389 (14)	165 (2)
N1A—H1A···O2	1.07 (2)	3.4808 (14)	134.7 (16)
O8—H8W1···O1	1.06 (3)	2.7978 (15)	155 (2)
O8—H8W2···O3$^{\text{iii}}$	1.000 (18)	2.8579 (14)	174 (3)
Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*+1, −*y*+3/2, *z*−1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2			

Table S3 Hydrogen bonding parameters for **2**

	***D*—H (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
O8—H8W1···O1$^{\text{i}}$	0.91 (3)	2.7003 (18)	173 (2)
N1A—H1A···O1	0.95 (2)	2.6573 (19)	176 (2)
O3—H3···O2	0.92 (3)	2.5260 (16)	154 (2)
N1B—H1B···O7	0.98 (2)	2.6684 (19)	164 (2)
O7—H7W1···O6	0.91 (3)	2.6875 (18)	170 (3)
O9—H9W2···O6$^{\text{ii}}$	0.88 (3)	2.848 (2)	175 (2)
O4—H4···O5	0.95 (2)	2.5026 (16)	157 (2)
O8—H8W2···O5	0.91 (3)	2.811 (2)	160 (2)
O9—H9W1···O8	0.92 (3)	2.842 (2)	174 (2)
O7—H7W2···O9$^{\text{iii}}$	0.90 (3)	2.813 (2)	171 (3)
Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, *y*−1, *z*; (iii) −*x*, *y*+1/2, −*z*+1/2			

Table S4 Hydrogen bonding parameters for **3**

	***D*—H (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
N1C—H1C···O6	0.93	2.640 (6)	164
N1C—H1C···O5	0.93	3.193 (6)	120
O7—H7W2···O8$^{\text{i}}$	0.83	2.7470 (17)	166
O4—H4···O5	0.99 (2)	2.5038 (14)	156 (2)
N1A—H1A···O2	0.94 (2)	2.731 (2)	152 (2)
N1A—H1A···O10	0.94 (2)	2.841 (5)	141.7 (19)
N1A—H1A···O11	0.94 (2)	2.869 (9)	141.0 (19)
N1A—H1A···O1	0.94 (2)	3.2027 (19)	129.0 (17)
N1B—H1B···O6	1.00 (3)	2.6962(19)	175 (2)
N1B—H1B···O5	1.00 (3)	3.1775 (19)	121.6 (18)
O8—H8W2···N4A$^{\text{ii}}$	0.89 (2)	2.8753 (16)	170 (2)
O7—H7W1···O6	0.92 (3)	2.8428 (16)	155 (2)
O3—H3···O2	0.95 (3)	2.565 (2)	153 (2)
O9—H9W2···O7$^{\text{iii}}$	0.75 (3)	2.903 (2)	158 (3)
O8—H8W1···O1	0.87 (2)	2.8192 (19)	164 (2)
O8—H8W1···O10	0.87 (2)	3.018 (6)	177 (2)
O9—H9W1···O4	0.72 (3)	2.899 (2)	149 (3)
Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) −*x*−1, *y*+1/2, −*z*−1/2; (iii) −*x*, *y*−1/2, −*z*+1/2			

LAG experiments:

Grinding was performed manually with an agate mortar and pestle.

1 – Pamoic acid (100 mg, 0.257 mmol) and DABCO (29 mg, 0.258 mmol) were ground together with 5 drops of water from a pipette (Figure S5).

3 – Pamoic acid (100 mg, 0.257 mmol) and DABCO (58 mg, 0.517 mmol) were ground together with 5 drops of water from a pipette (Figure S6).

Stepwise experiments: Pamoic acid (100 mg, 0.257 mmol) was ground together with DABCO (29 mg, 0.258 mmol) and 3 drops of water to yield **1**. A PXRD pattern was then recorded. To this was added 0.1 equivalents of DABCO (2.9 mg 0.026 mmol) with 3 drops of water followed by PXRD analysis. This process was repeated until a 1:2 molar ratio of pamoic acid to DABCO was achieved.

Interconversion experiments: Grinding pamoic acid (100 mg, 0.257 mmol) with DABCO (29 mg, 0.258 mmol) and 3 drops of water yielded a sample of **1**. To this light yellow powder a further 29 mg of DABCO (0.258 mmol) was added with 3 drops of water and ground until a powder product was afforded, which was subsequently analysed by PXRD and confirmed to be **3**. This product was then ground together with pamoic acid (100 mg, 0.257 mmol) and 3 drops of water which yielded **1**. This was followed by grinding with DABCO (58 mg, 0.517 mmol) and 3 drops of water. This product was then ground with a further 200 mg pamoic acid (0.515 mmol) and 6 drops of water, and finally with 116 mg DABCO (1.03 mmol) and 6 drops of water.

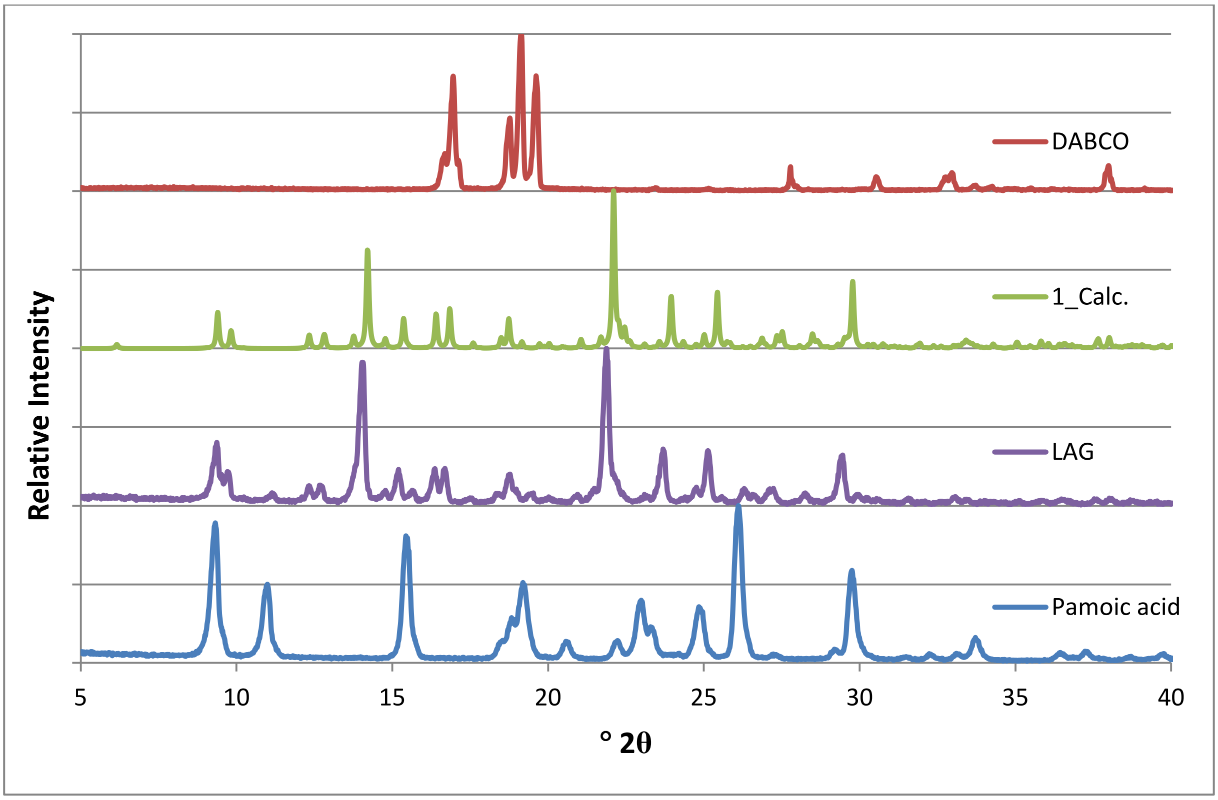

Figure S5 PXRD patterns for the LAG experiment involving pamoic acid and DABCO in a 1:1 stoichiometry with H_2O versus the simulated pattern from single crystal data (**1**_calc.). The experimental patterns for DABCO and pamoic acid are included for comparison purposes.

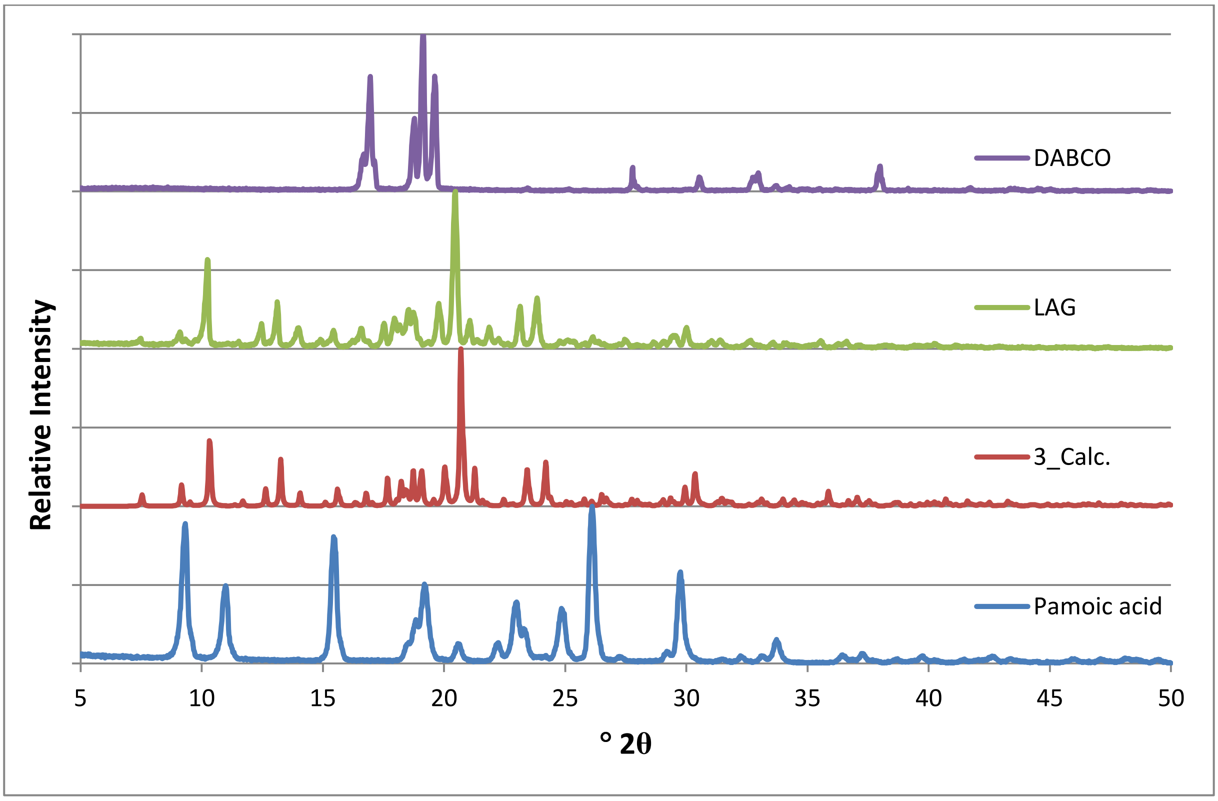

Figure S6 PXRD pattern obtained on grinding of pamoic acid and DABCO in a 1:2 ratio with 5 drops of water (LAG). This pattern is compared to that calculated from the single-crystal data of **3** which was obtained by seeding a water-ethanol solution with the LAG product. Experimental patterns for pamoic acid and DABCO are included for comparison.

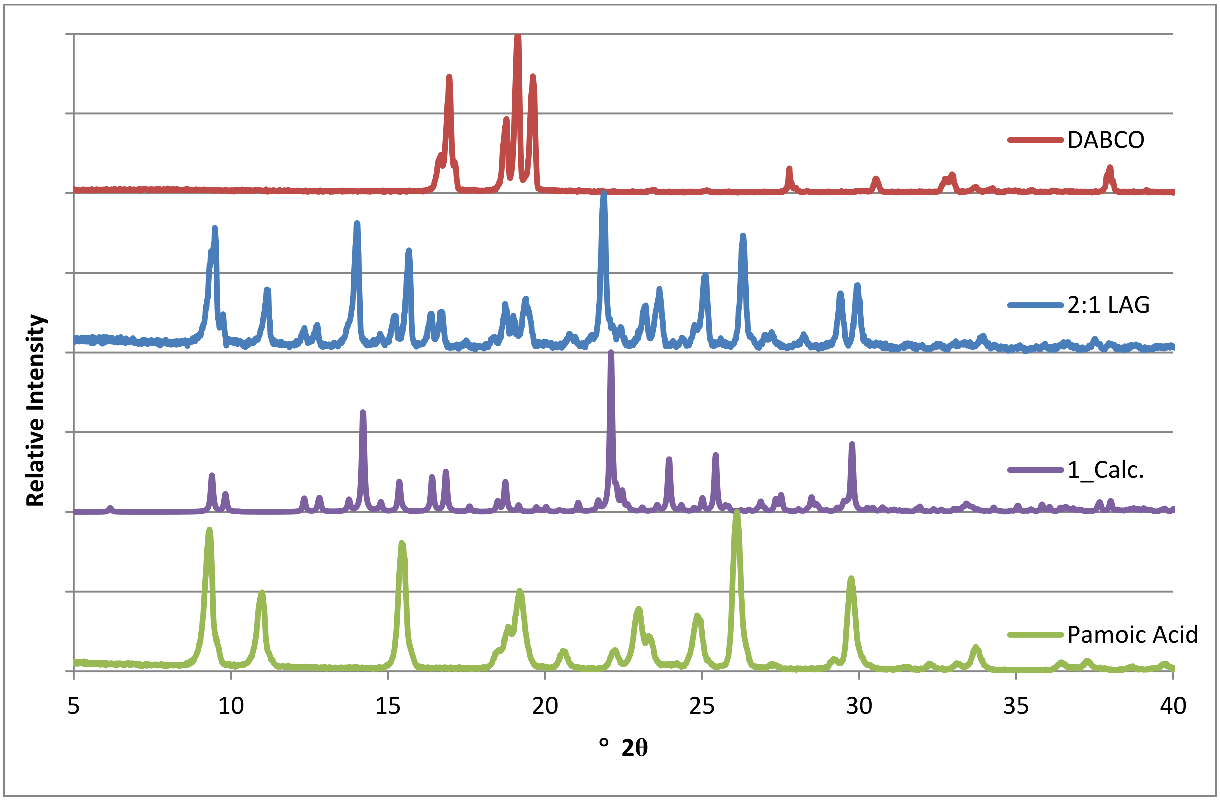

Figure S7 PXRD patterns for the LAG experiment involving pamoic acid and DABCO in a 2:1 stoichiometry with H_2O versus the simulated pattern from single-crystal data (1_Calc.). The experimental patterns for pamoic acid and DABCO are included for comparison purposes.

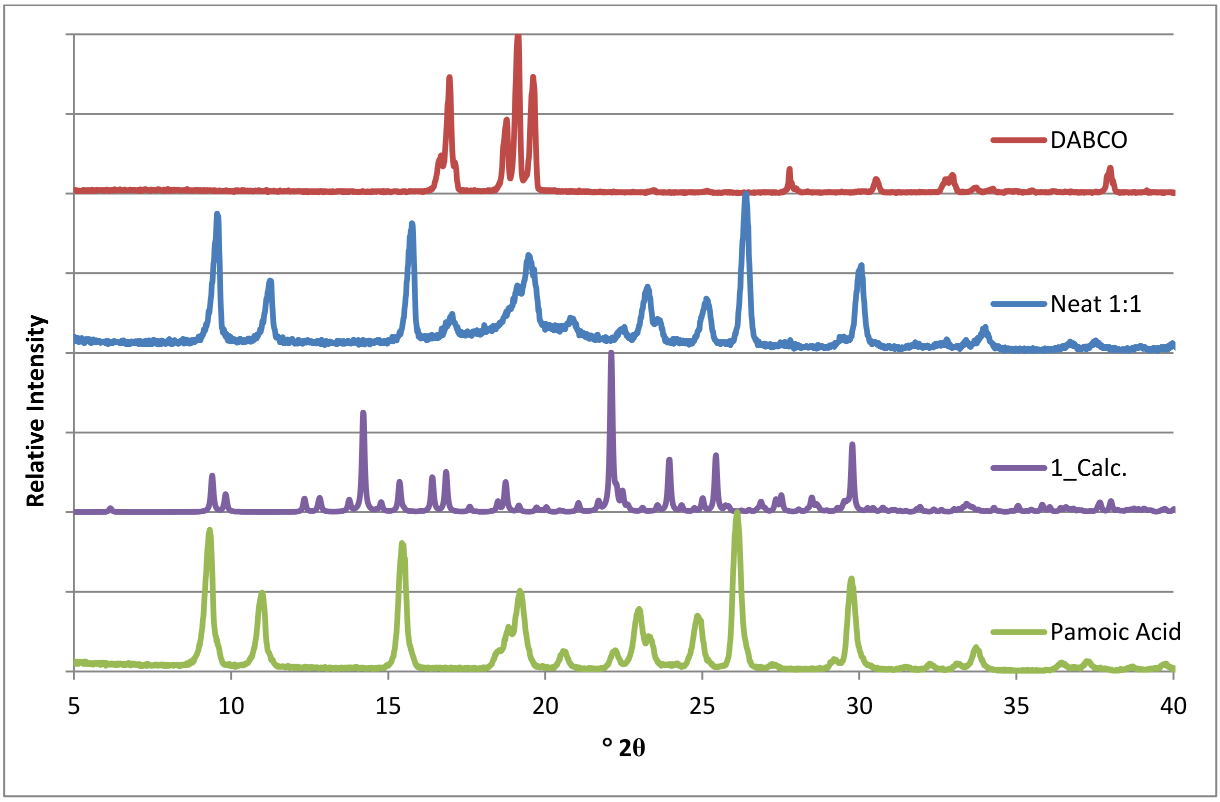

Figure S8 PXRD patterns for the neat grinding experiment involving pamoic acid and DABCO in a 1:1 stoichiometry versus the simulated pattern from single-crystal data (1_Calc.). The experimental patterns for pamoic acid and DABCO are included for comparison purposes.

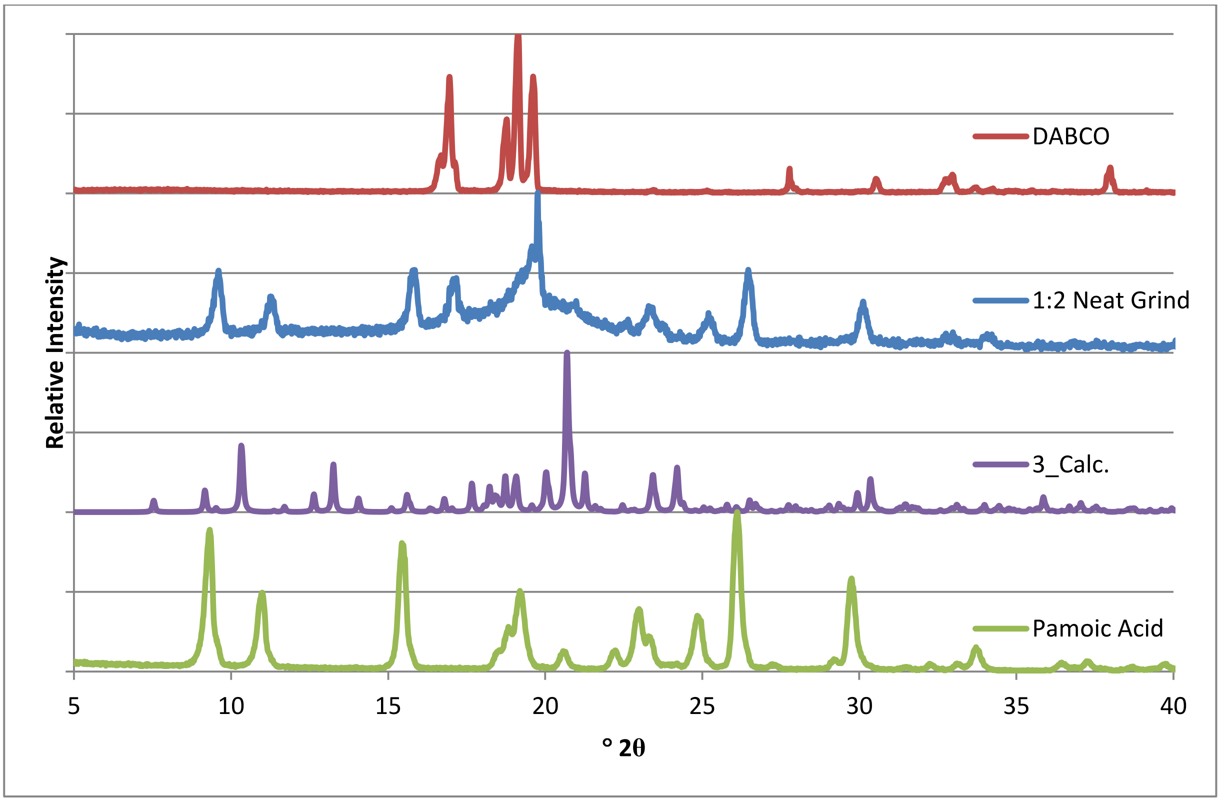

Figure S9 PXRD patterns for the neat grinding experiment involving pamoic acid and DABCO in a 1:2 stoichiometry versus the pattern simulated from single-crystal data (3_Calc.). The experimental patterns for pamoic acid and DABCO are included for comparison purposes.

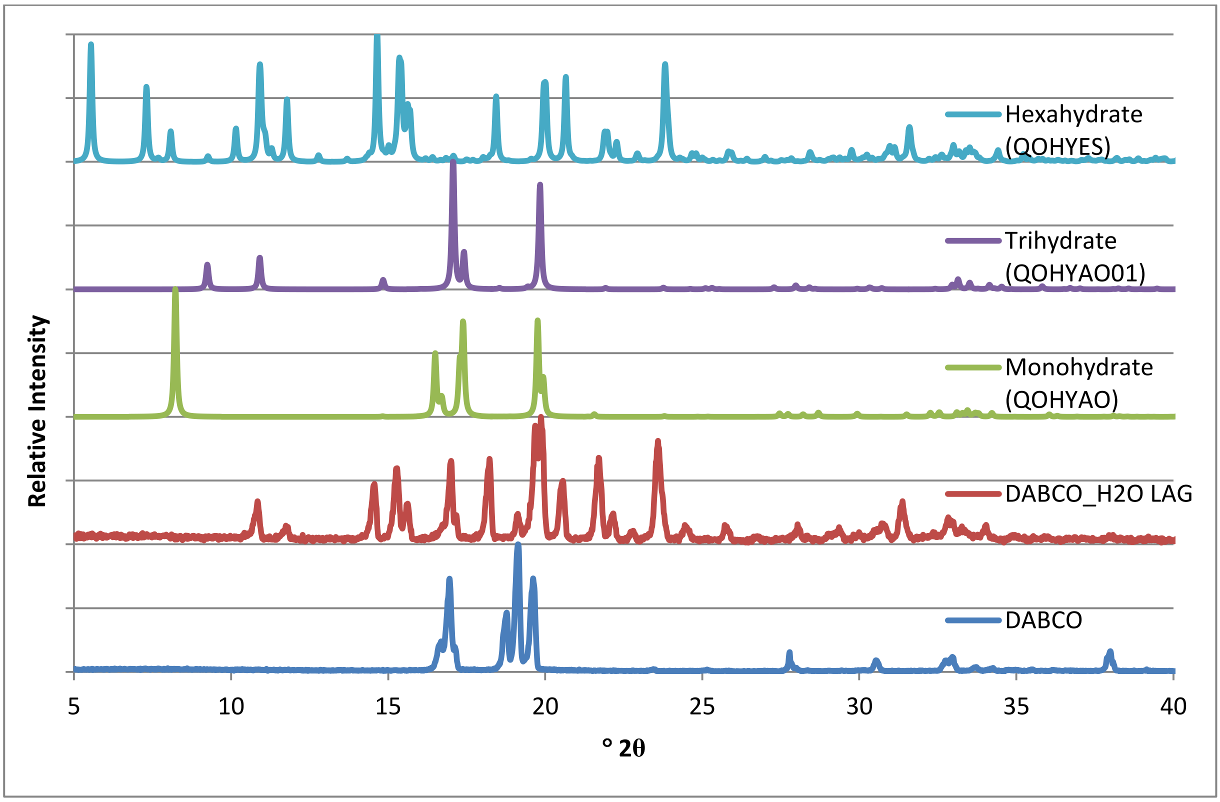

Figure S10 PXRD patterns for the LAG experiment involving DABCO and H_2O versus data obtained from the Cambridge Structural Database (monohydrate, trihydrate, hexahydrate). The experimental pattern for DABCO is included for comparison.

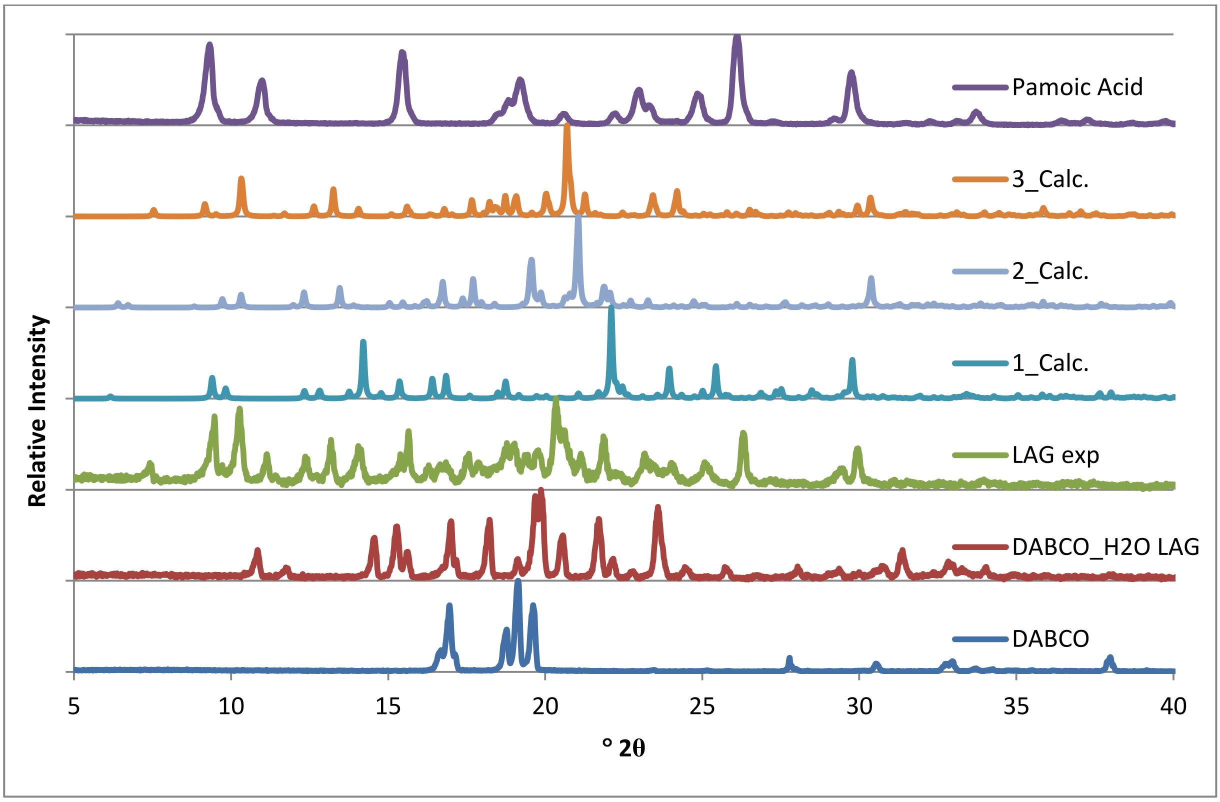

Figure S11 PXRD patterns for the LAG experiment involving the hydrated DABCO (DABCO_H2O LAG) with pamoic acid in a 2:1 stoichiometry with no further addition of water, versus the simulated single-crystal data (**1**, **2** and **3**). The experimental patterns for DABCO and pamoic acid are included for comparison purposes.

DSC Data

Differential Scanning Calorimetry (DSC) was carried out using a TA Instruments Q100 system under a N_2 gas purge (flow rate of 50.0 ml/min) coupled to a RCS cooling unit. Samples were placed in aluminium pans that were non-hermetically sealed with vented aluminium lids, and were heated from 25 °C to 170 °C at a heating rate of 10 °C/min.

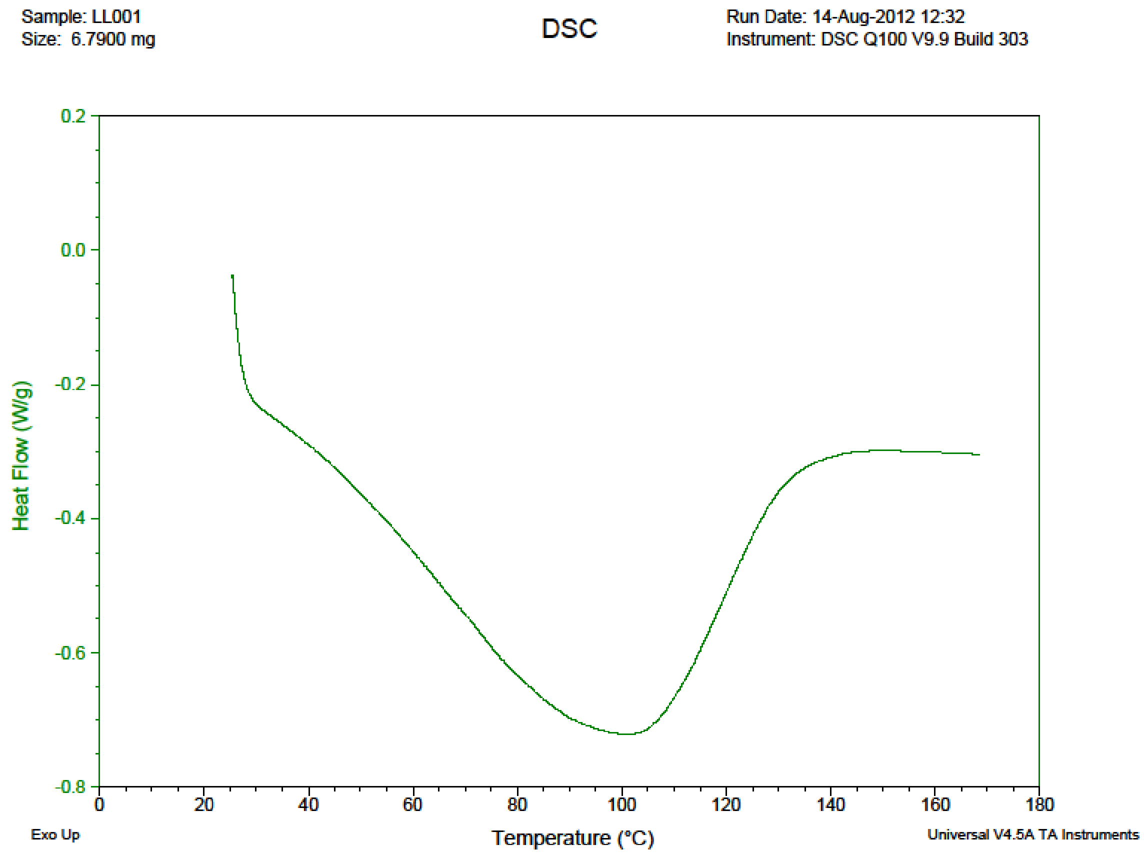

Figure S12 DSC trace of **1**

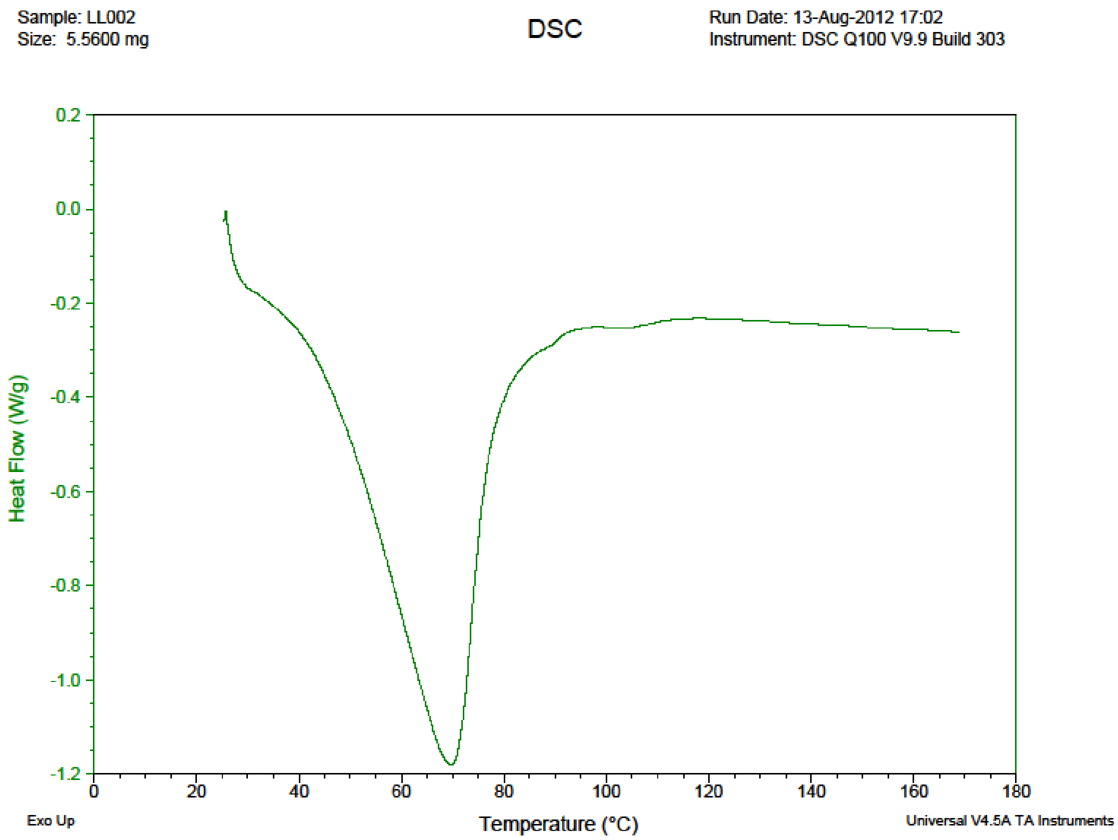

Figure S13 DSC trace of **2**

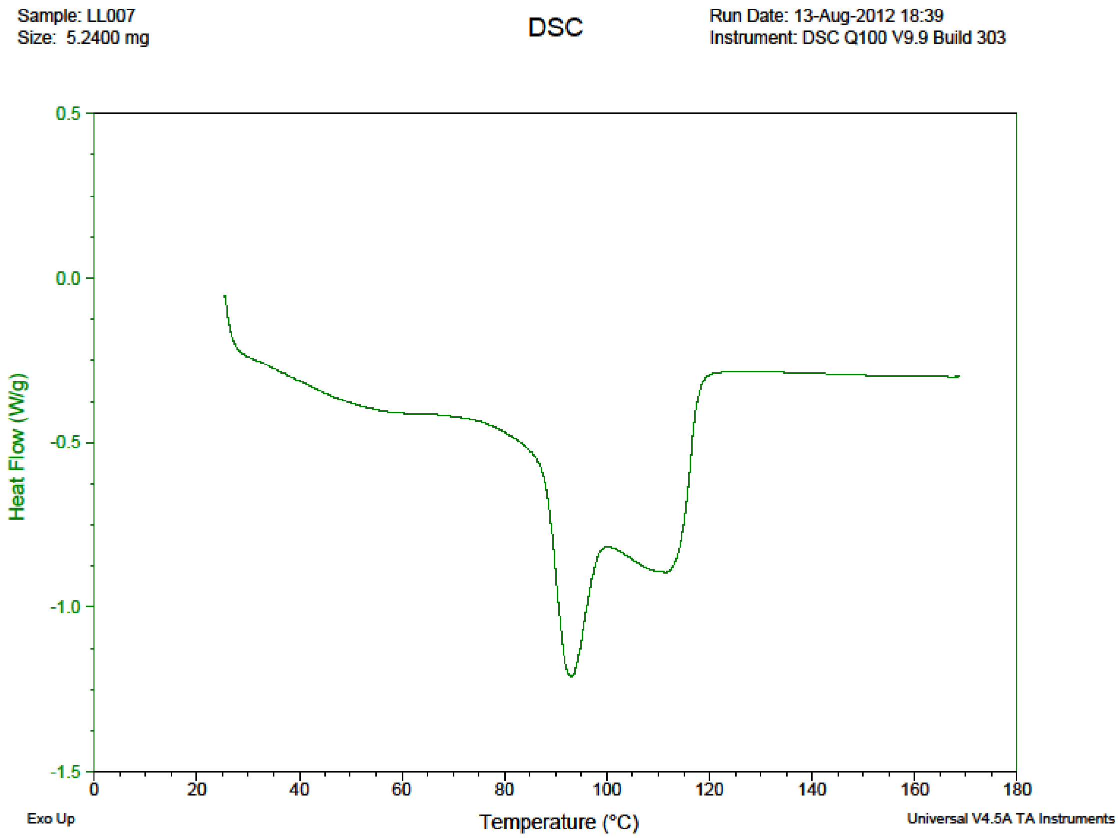

Figure S14 DSC trace of **3**.

TGA Data

TGA data were collected on a Perkin Elmer TGA 7 with a heating rate of 10 °C/min.

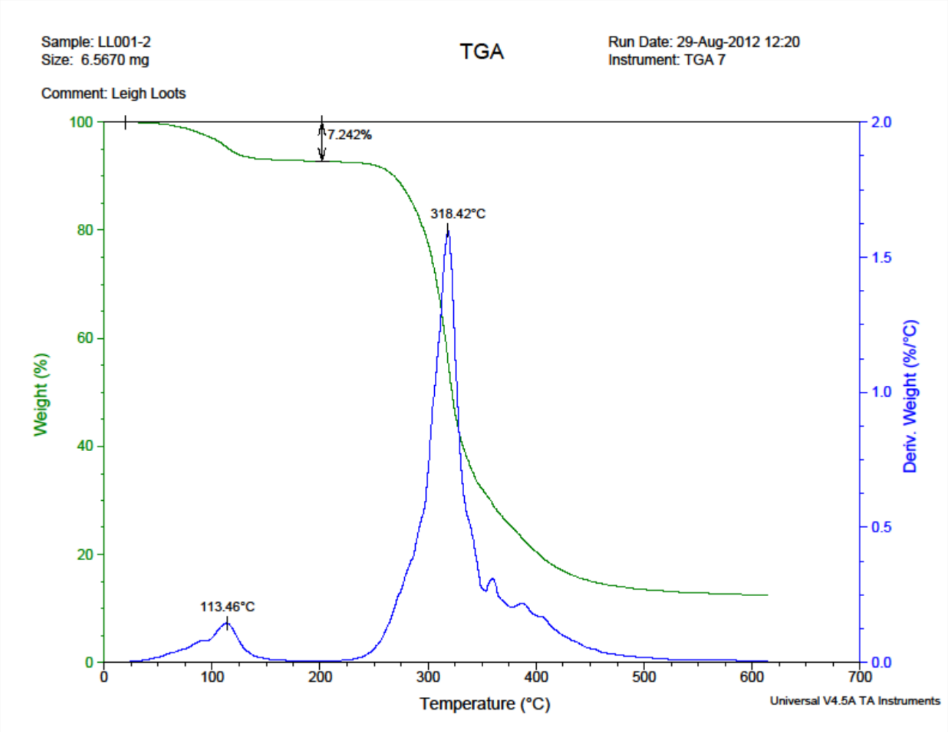

Figure S15 TGA results for **1**

Calculated percentage mass loss for **1** is 6.7%.

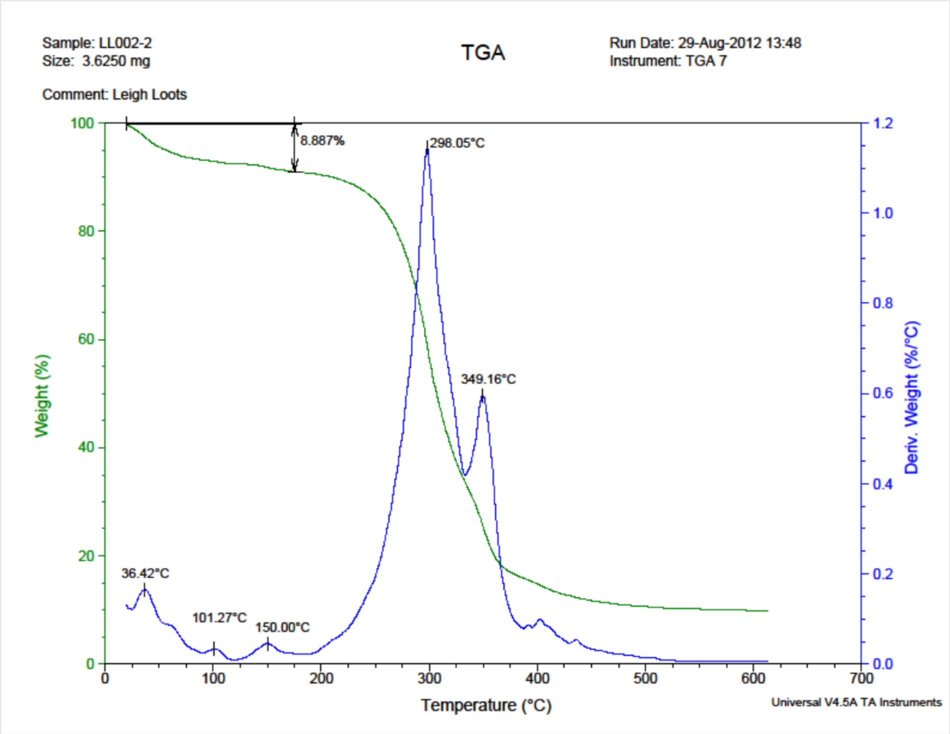

Figure S16 TGA results for **2**

Calculated percentage mass loss for **2** is 8.1%.

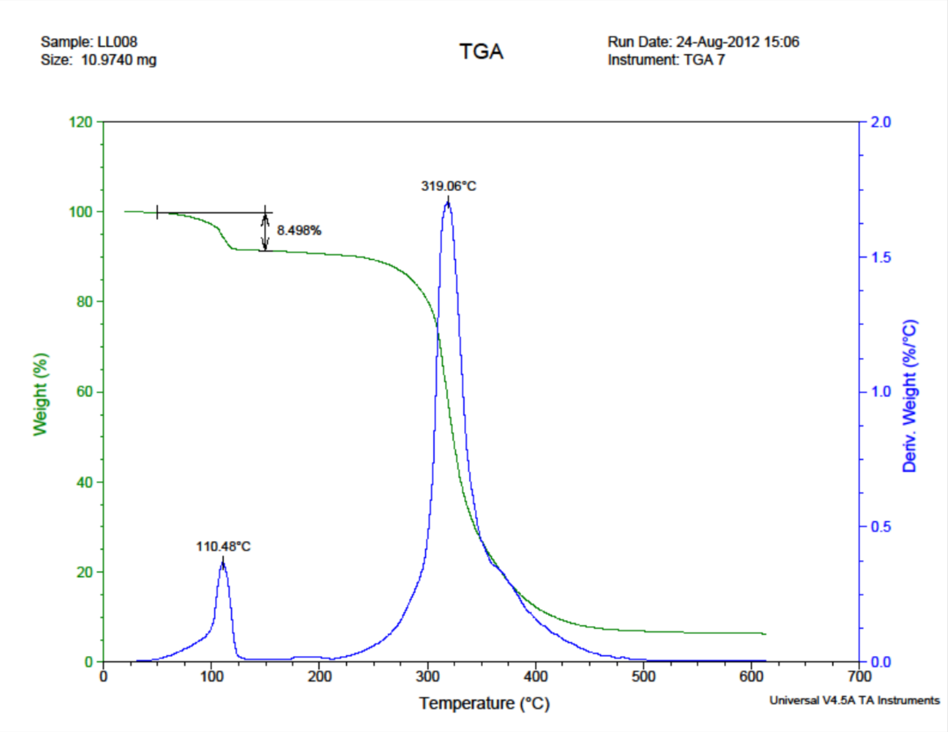

Figure S17 TGA results for **3**

Calculated percentage mass loss for **3** is 8.1%.

References:

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