Electronic Supplementary Material (ESI) for CrystEngComm

Co-crystal formation with 1,2,3,5-dithiadiazolyl radicals

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Electronic Supplementary Information

Powder X-ray diffraction

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO diffractometer in Bragg-Brentano geometry using an X'Celerator detector and Cu radiation source with a Ni filter. Samples were spun during data collection. Powder patterns were simulated and visualised in X'Pert HighScore Plus.[1] In all powder diffraction patterns, the *y*-axis gives intensity counts in arbitrary units.

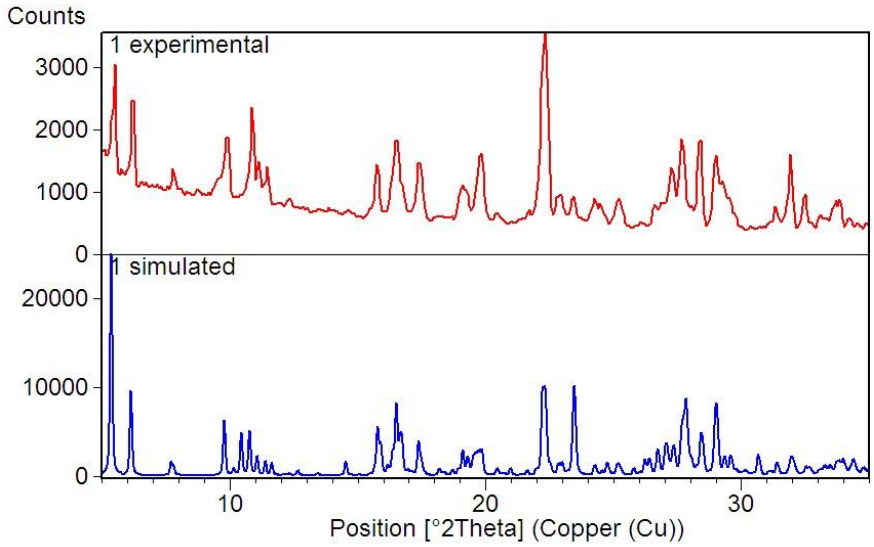


Fig. S1 Experimental and simulated PXRD patterns of **1**

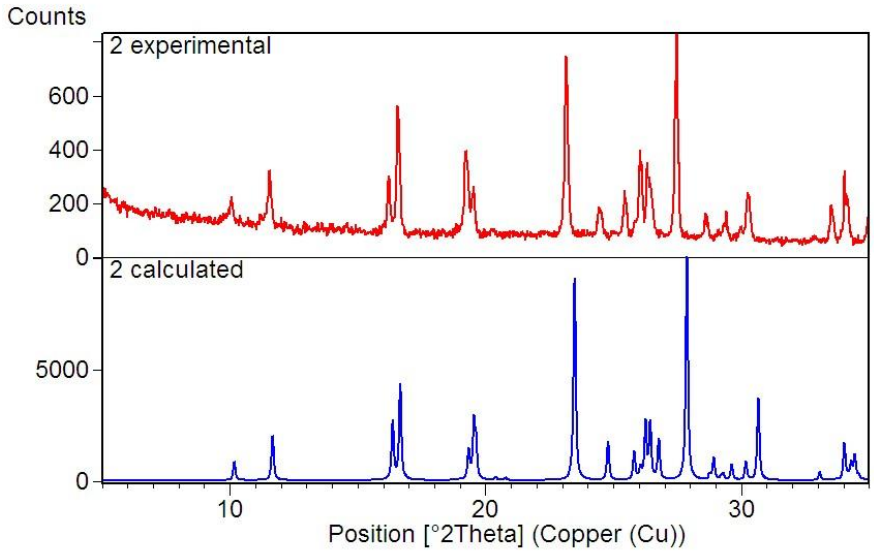


Fig. S2 Experimental and simulated PXRD patterns of **2**

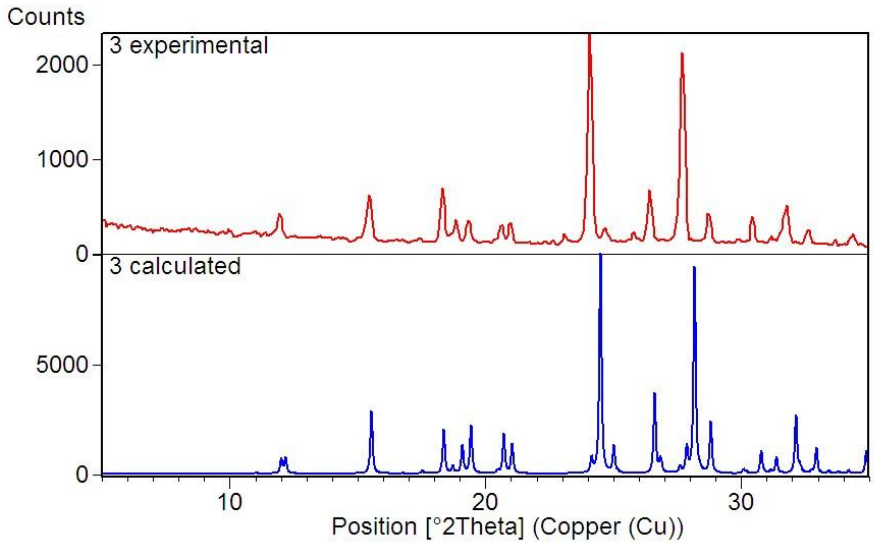


Fig. S3 Experimental and simulated PXRD patterns of **3**

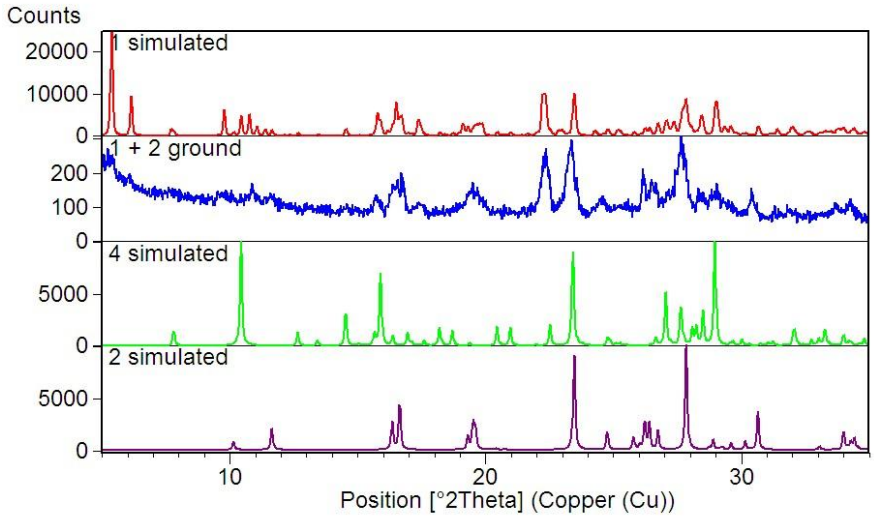


Fig. S4 PXRD for a ground mixture of **1** and **2**, showing that the product is a mixture of **1** and **2**, not co-crystal **4**.

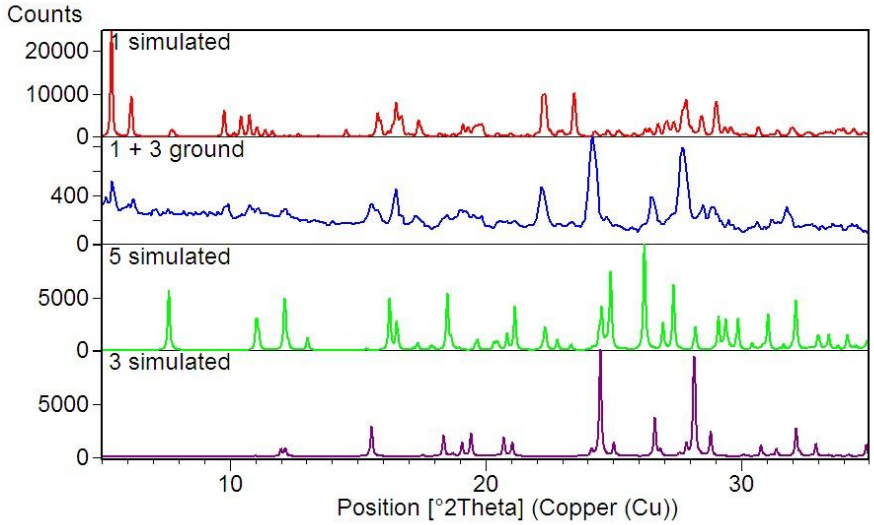
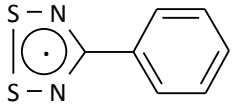
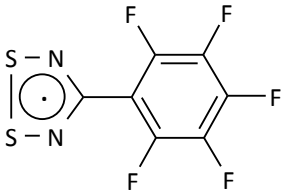
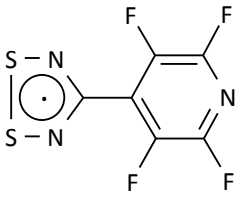
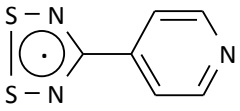
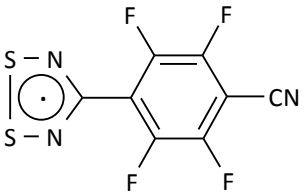
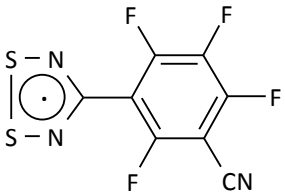
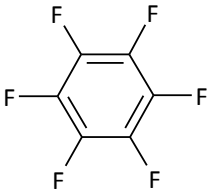
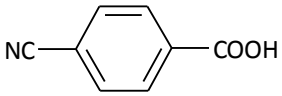
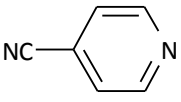
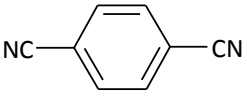
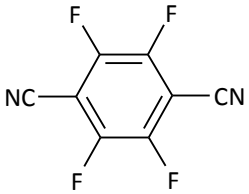
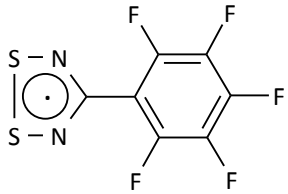
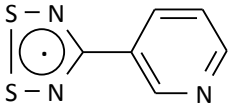
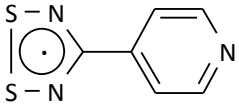
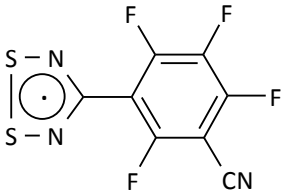
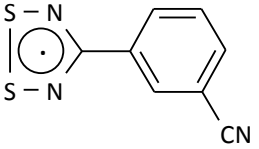
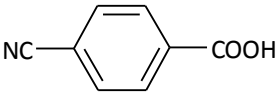
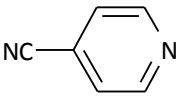
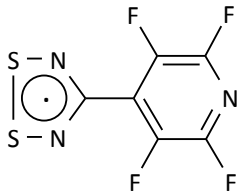
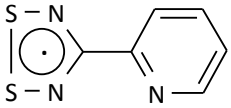
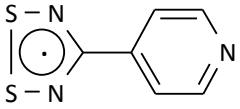
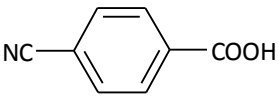


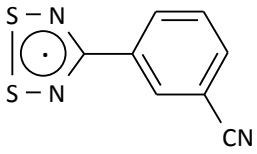
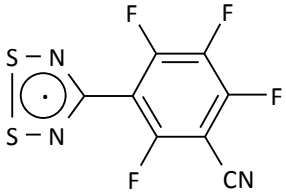
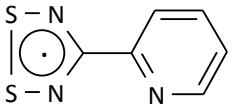
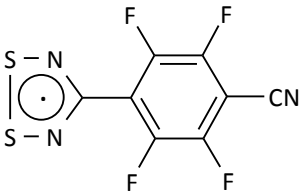
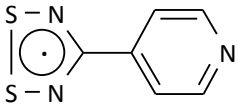
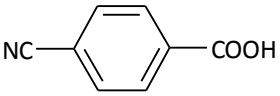
Fig. S5 PXRD for a ground mixture of **1** and **3**, showing that the product is a mixture of **1** and **3**, not co-crystal **5**.

Attempted synthesis of further co-crystals

Table S1 Combinations of co-crystal formers used in attempts to produce DTDA-containing co-crystals

co-crystal former 1	co-crystal former 2	result
		crystals of **4**
		crystals of **5**
		crystals of co-crystal former 1
		multiple crystal forms – needles, blocks blocks are co-crystal former 1
		crystals of co-crystal former 1 two separate bands of crystals
		crystals of dithiatetrazocine – unwanted product
		no crystals
		components crystallised separately
		components crystallised separately

		components crystallised separately
		crystals of co-crystal former 1
		crystals of co-crystal former 1
		two bands of sublimed material – no crystals
		two separate bands of crystals
		crystals of co-crystal former 1
		crystals do not diffract appear to be a mixture of the two co-crystal formers
		crystals of co-crystal former 1
		crystals of co-crystal former 1
		no crystals

		no crystals
		two crystal forms no crystals suitable for diffraction
		no crystals

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was was carried out using a TA Instruments Q100 system under a N_2 gas purge, with a flow rate of 50.0 ml min^{-1}. The ramp rate was 10 °C min^{-1}, and the cooling rate was 5 °C min^{-1}. Samples were placed in aluminium pans that were non-hermetically sealed with non-vented aluminium lids. Analysis was carried out using TA Instruments Universal Analysis 2000.[2]

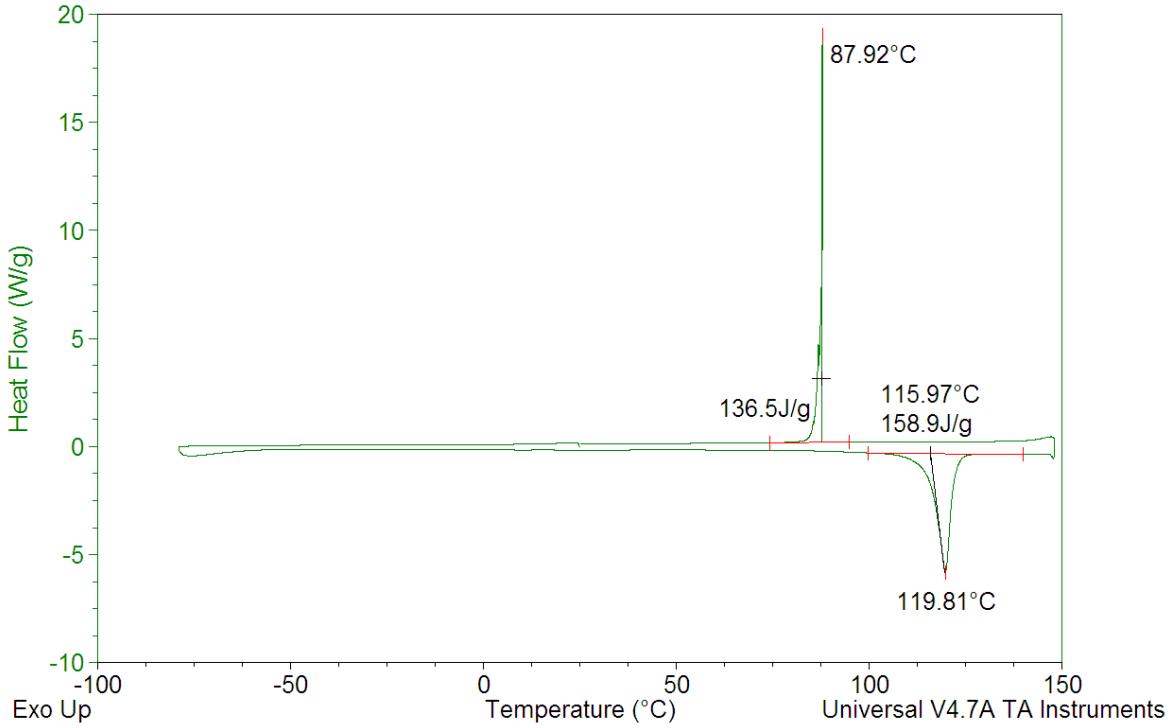


Fig. S6 DSC trace of **1**.

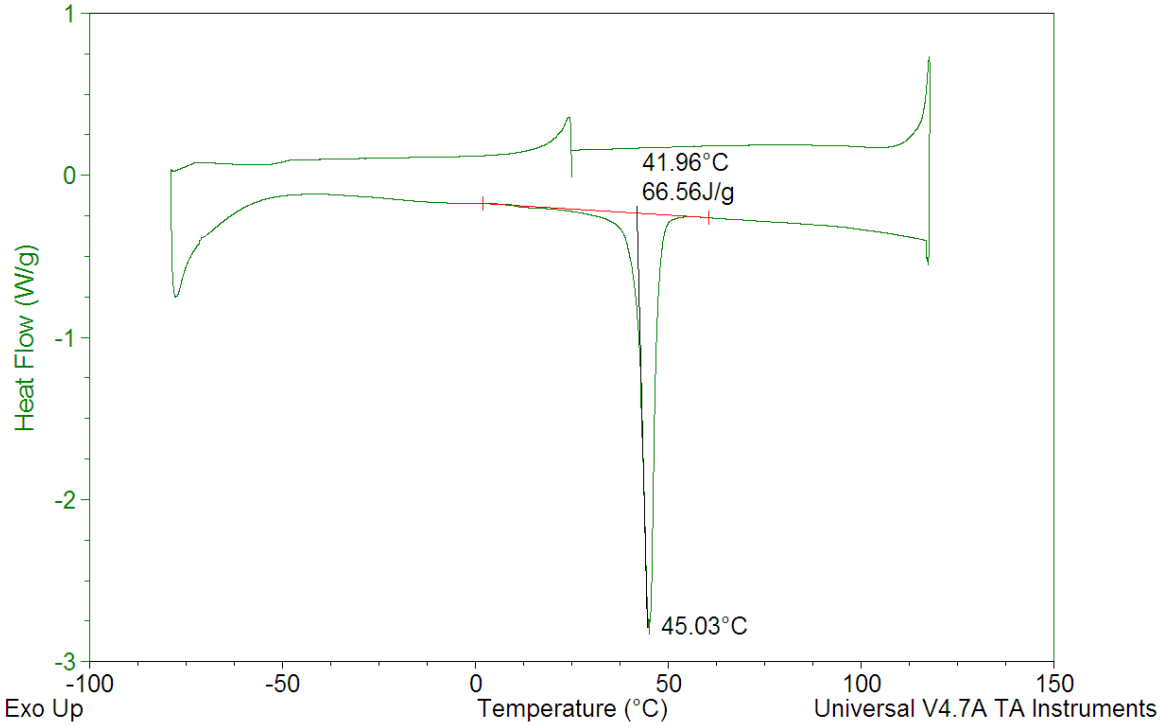


Fig. S7 DSC trace of **2**.

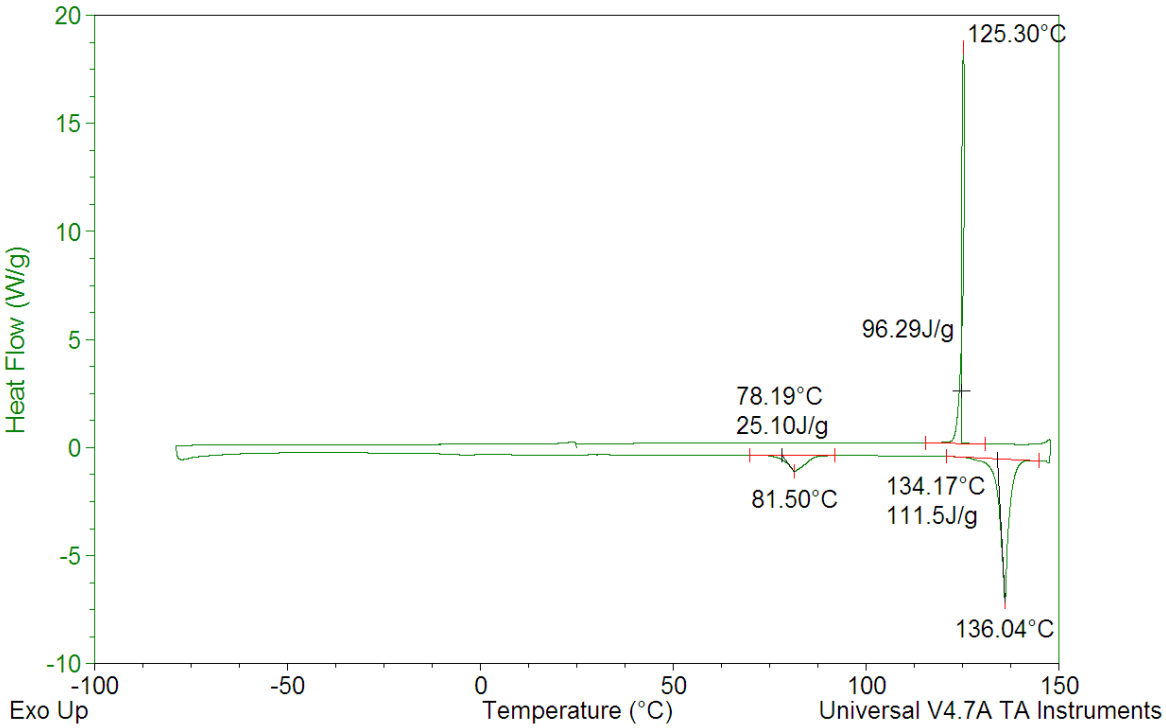


Fig. S8 DSC trace of **3**.

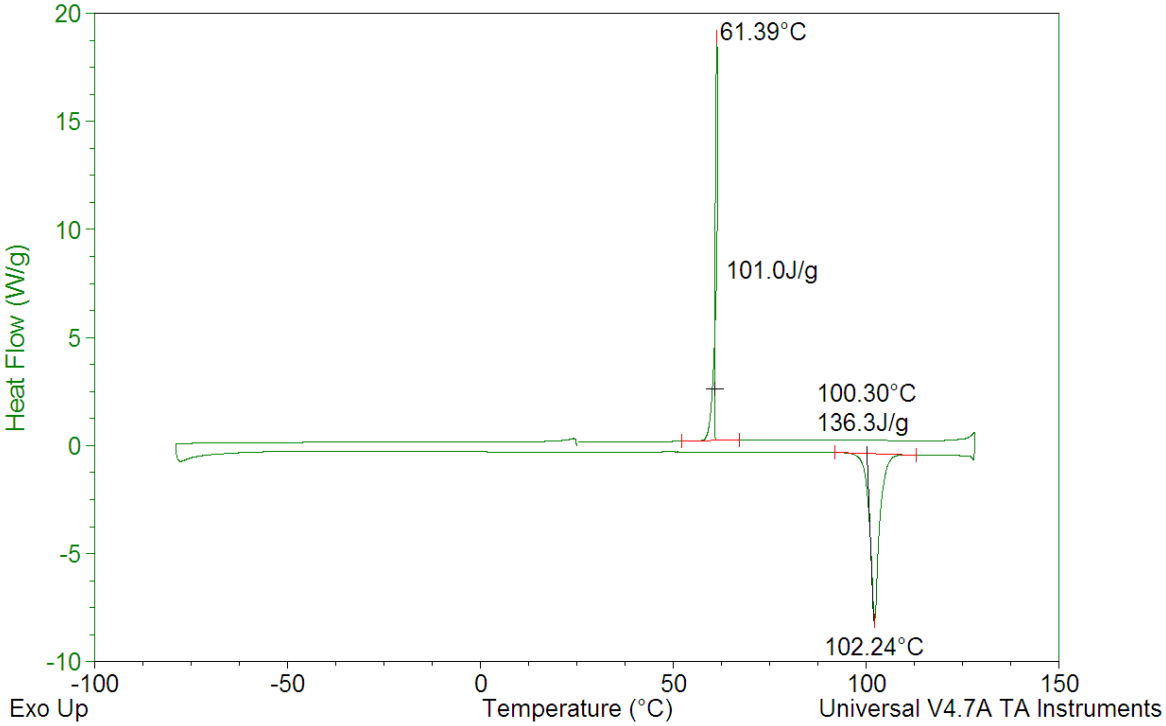


Fig. S9 DSC trace of co-crystal **4**.

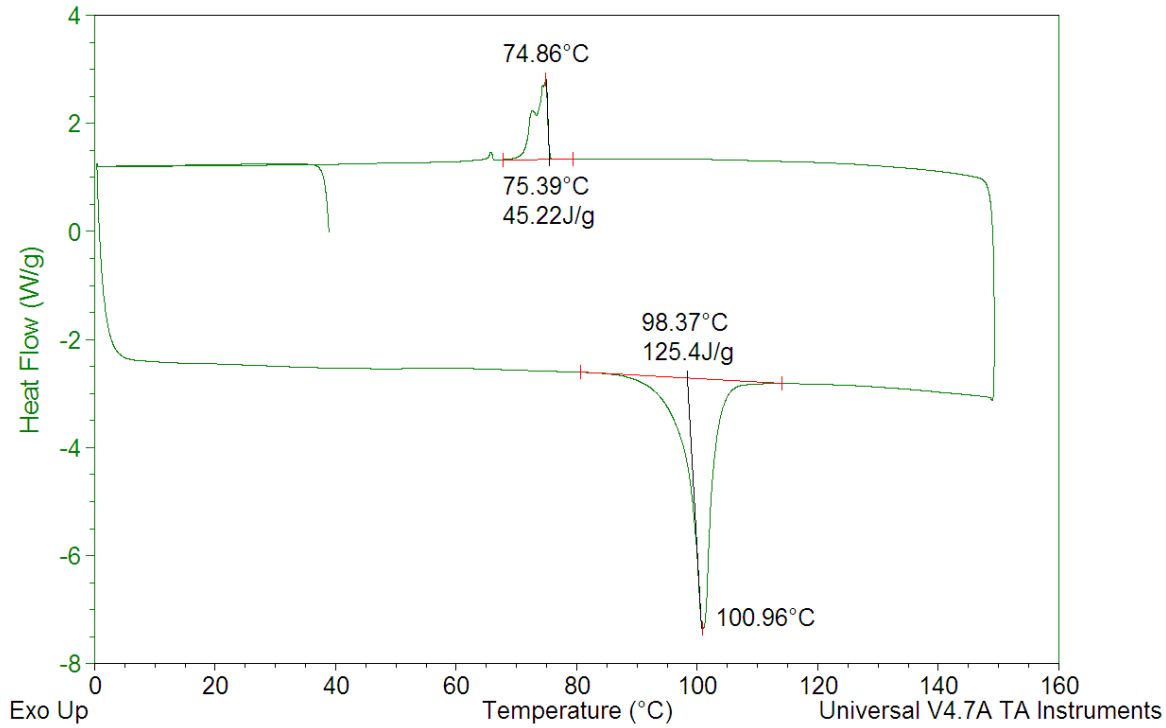


Fig. S10 DSC trace of co-crystal **5**.

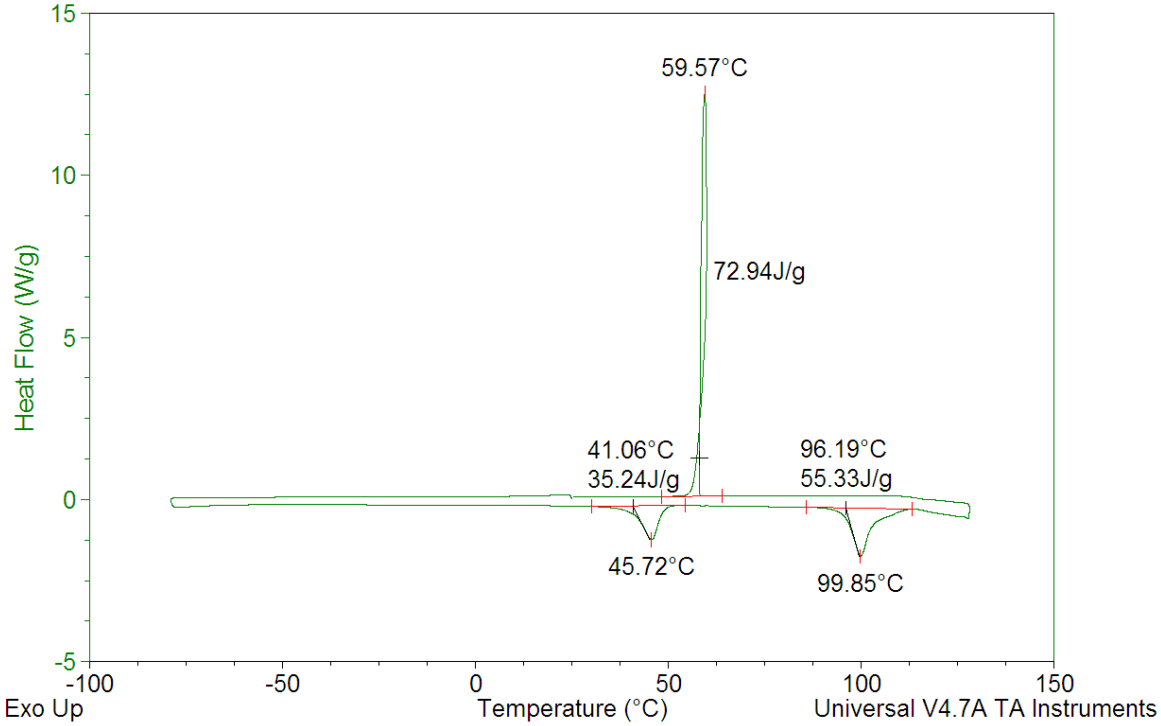


Fig. S11 DSC trace of 1:1 mixture of **1** and **2**

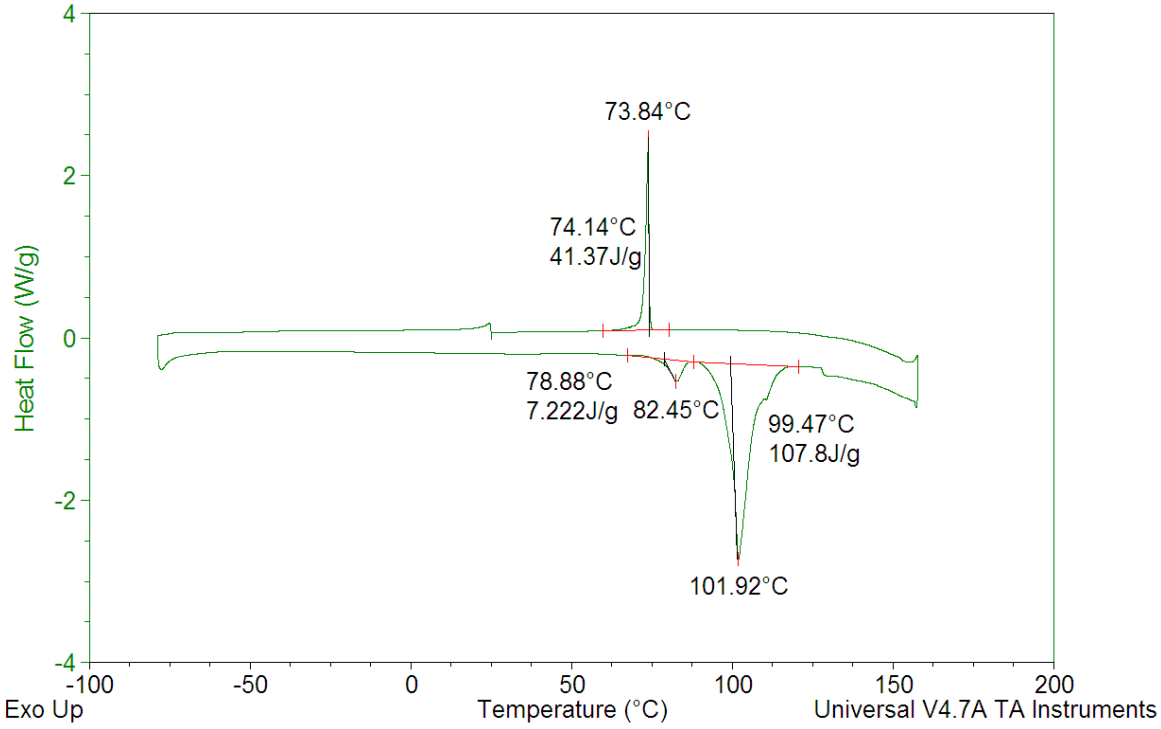


Fig. S12 DSC trace of 1:1 mixture of **1** and **3**

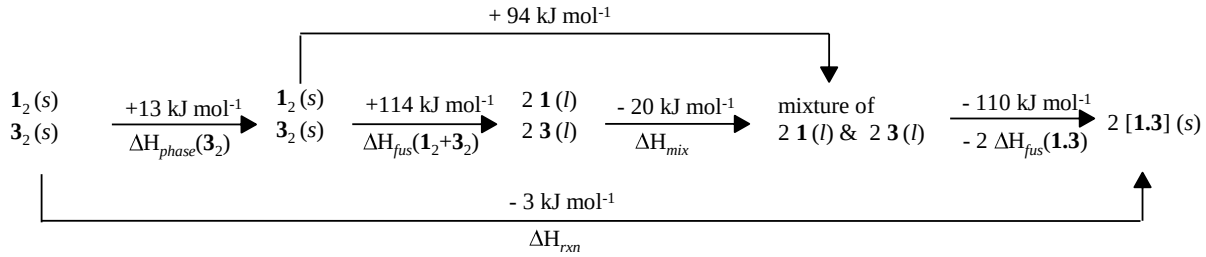


Fig. S13 Thermodynamic estimate of ΔH_{rxn} for formation of co-crystal **5** from $(\mathbf{1})_2$ and $(\mathbf{3})_2$.

References

1 X'Pert HighScore Plus, 2009, PANalytical B. V., Almelo, The Netherlands.
2 TA Instruments Universal Analysis 2000 version 4.7A, 1998-2009, TA Instruments – Waters LLC.