Supporting information for:

The thermal behaviour of benzoic acid : isonicotinamide binary co-crystals

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Table S1: Unit cell parameters calculated for BA:isoNCT at various temperatures. LeBail fits were performed using a C-centred cell in C2/c with and β = 96.917° in accordance with the literature.[1]

T / °C	a / Å	b / Å	c / Å	β / °	V / Å^3
-100[a]	22.379(4)	5.1507(8)	20.540(3)	96.927(2)	2350.3(5)
30	22.850(4)	5.1963(10)	20.559(7)	96.593(13)	2425.0(4)
60	23.029(4)	5.1916(10)	20.506(6)	96.314(16)	2436.8(4)
100	23.143(4)	5.2172(11)	20.437(6)	96.332(16)	2452.6(4)
150	23.315(6)	5.2209(11)	20.453(7)	96.31(2)	2474.7(4)
161	23.373(5)	5.2255(11)	20.431(6)	96.276(18)	2480.5(4)
166	23.376(6)	5.2194(14)	20.471(8)	96.26(2)	2482.7(5)

[a] Data from ref [1]

Table S2: Unit cell parameters calculated for BA_2:isoNCT at various temperatures. LeBail fits were performed using a primitive cell with α = 80.165°, β = 79.963° and γ = 89.973° in accordance with the literature.[2] Very limited changes in α, β, and γ are not reported here.

T / °C		a / Å	b / Å	c / Å	V / Å^3
-53[a]		10.032(4)	12.661(6)	14.354(6)	1768.1
32		10.841(4)	12.755(4)	14.587(5)	1965.9(7)
60		10.828(4)	12.753(4)	14.692(6)	1976.8(7)
100		10.845(5)	12.748(4)	14.860(5)	1997.3(7)
140		10.873(4)	12.743(4)	15.027(5)	2019.8(7)
150[b]		10.875(4)	12.745(4)	15.052(5)	2023.7(7)
150[c]	Phase 1	10.870(3)	12.788(2)	15.052(2)	2032.7(6)
	Phase 2	10.717(5)	12.753(2)	14.981(4)	1988.5(9)

[a] Values from ref [2]

[b] The results of fitting the pattern with a single phase

[c] The outcomes of a two-phase fit to the data collected at 150 °C.

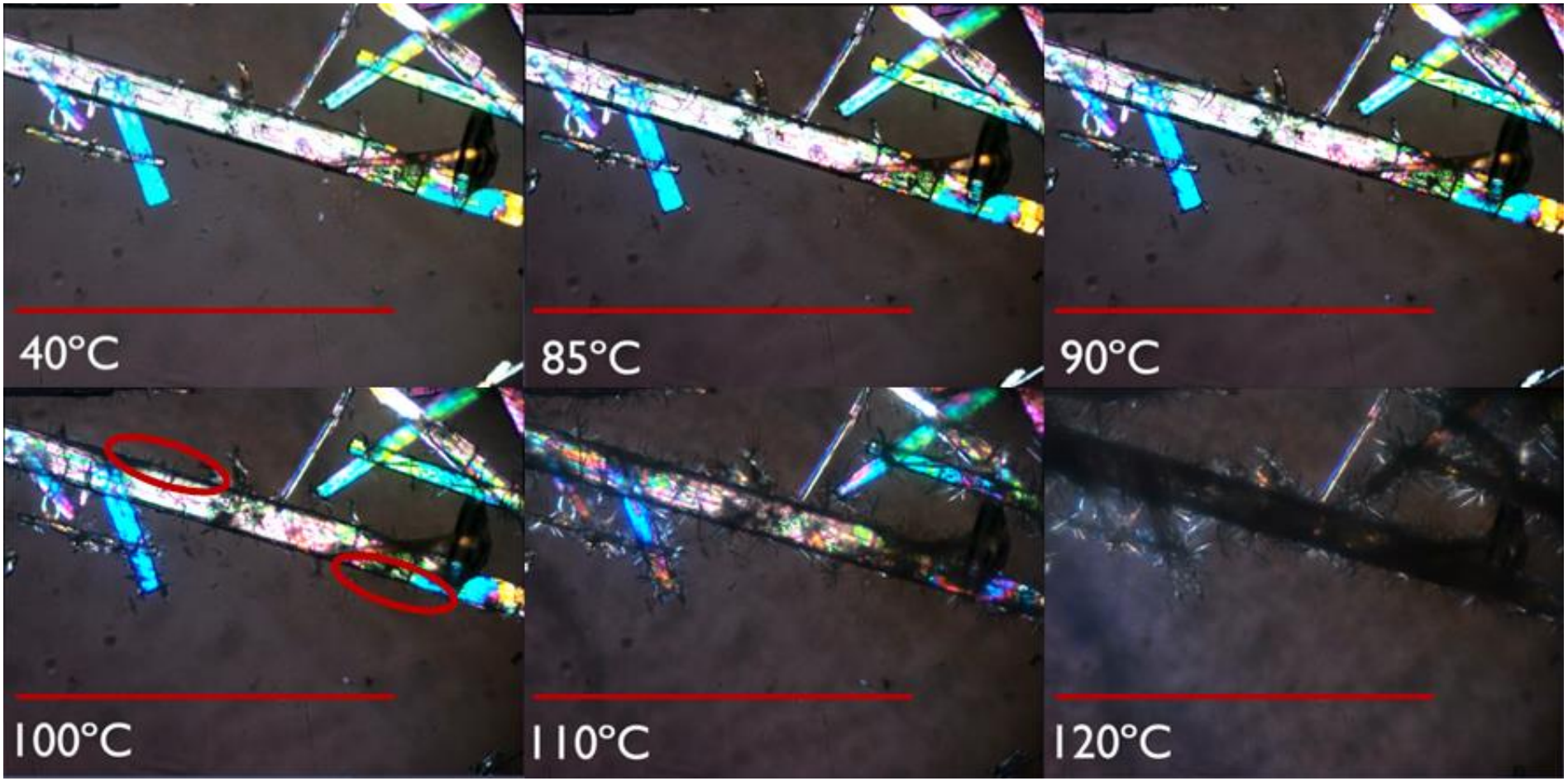


Figure S1: HSM data collected under crossed-polar conditions during the heating of BA_2:isoNCT at 5 °C min-1. The red bar in each image represents 1 µm. The rings in the 100 °C image highlight the needle-shaped crystals which are present on the surface of the large columnar crystals. This image is an enlargement of Figure 2 from the main manuscript.

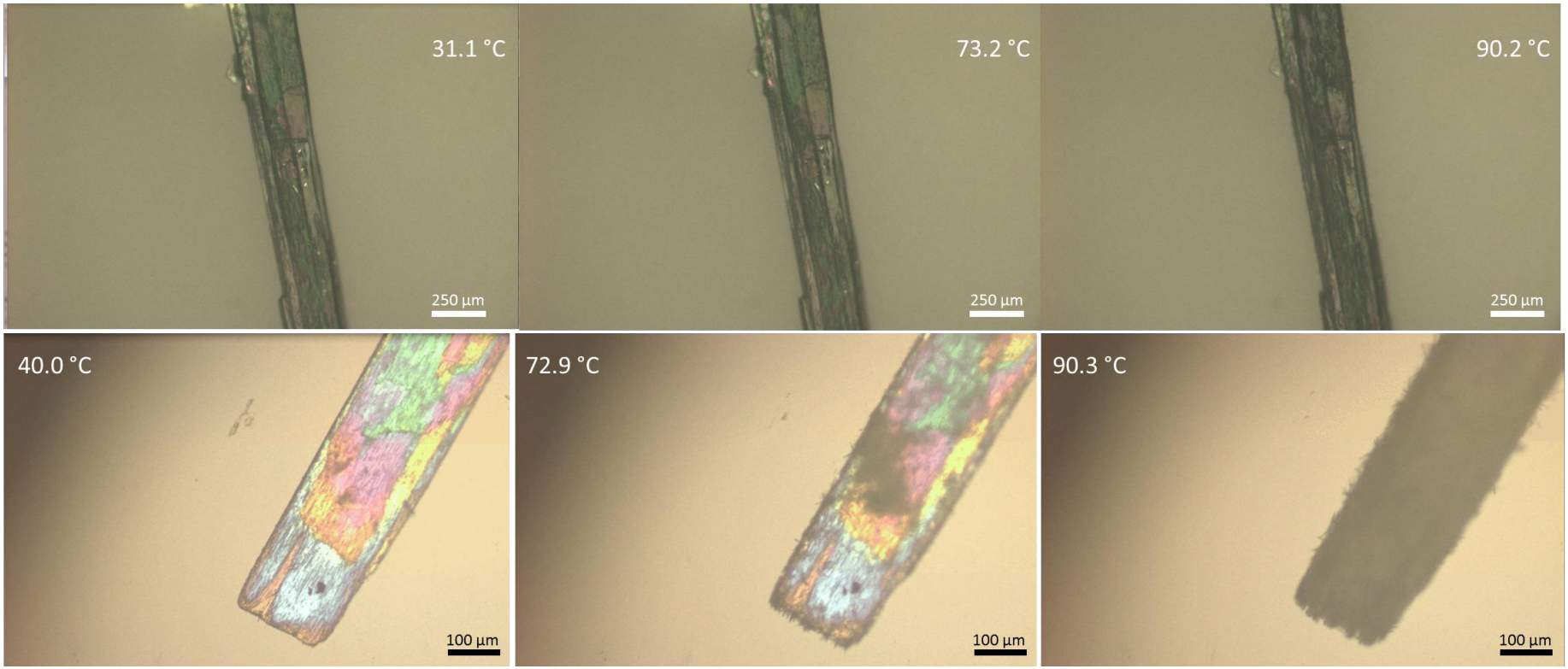


Figure S2: Hot stage microscopy data recorded at different heating rates on crystals of BA_2:isoNCT. Top: heating at 10 °C min^{-1}; bottom: heating at 2 °C min^{-1}

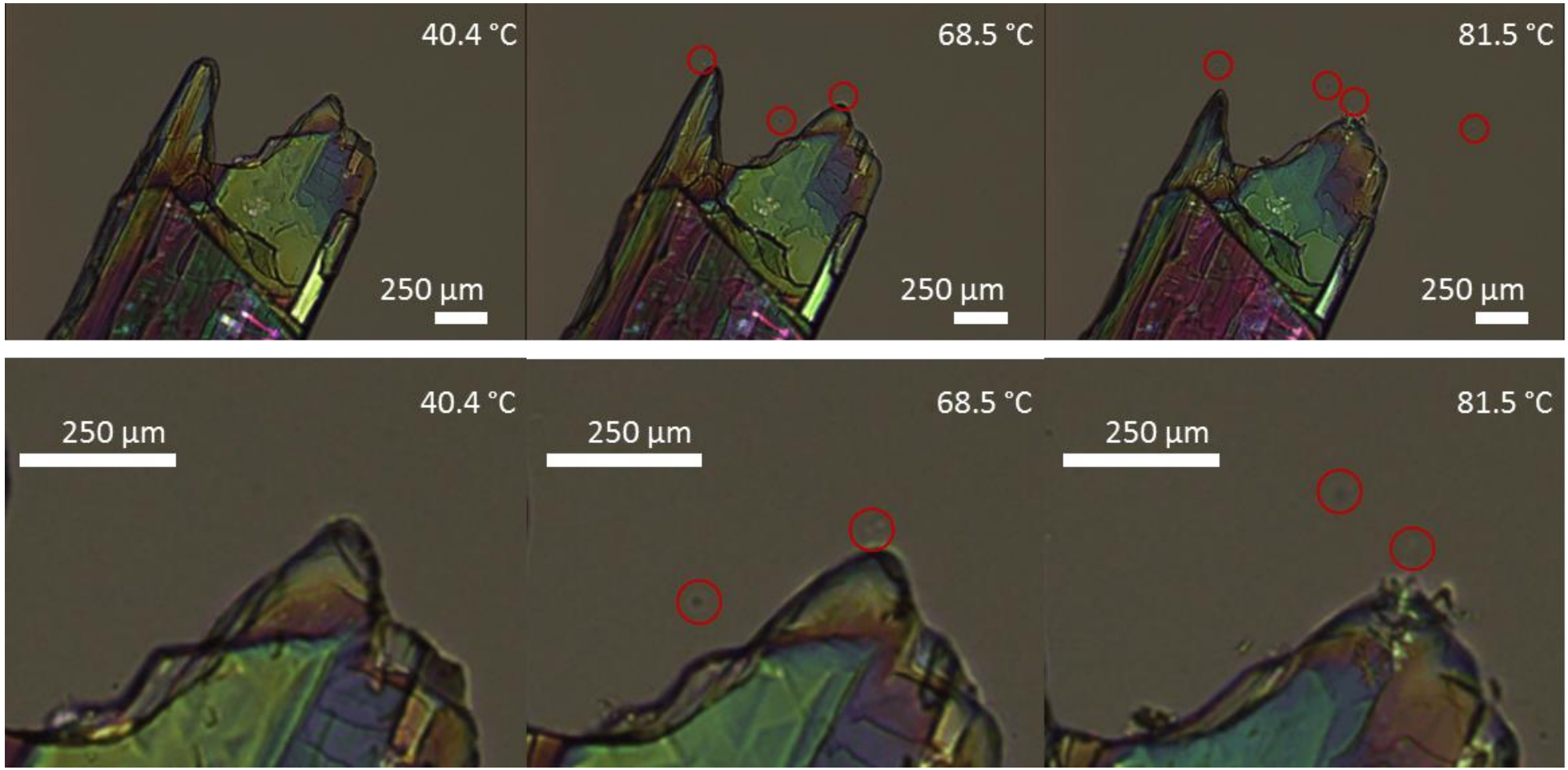
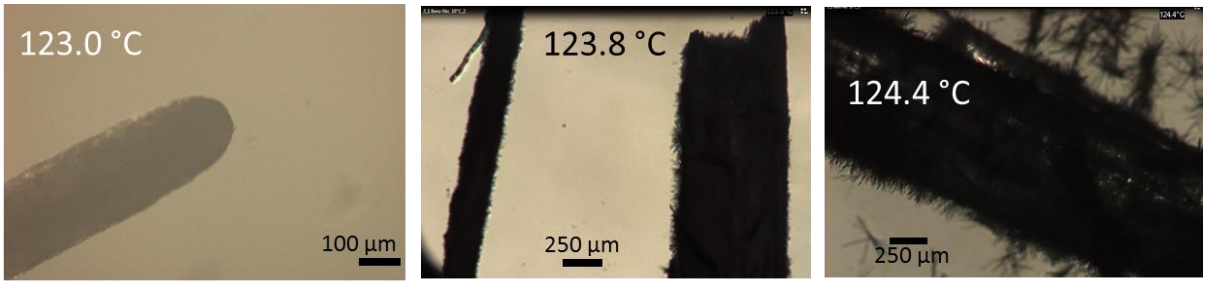


Figure S3: HSM data recorded on a crystal of BA_2:isoNCT immersed in oil. Gas bubbles are circled in red. The bottom row shows enlargements of the top.



(a) **(b)**

Figure S4: HSM data recorded on crystals of BA_2:isoNCT at T > 122 °C (the melting point of BA). Data were obtained at **(a)** 2 and **(b)** 10 °C min^{-1}.

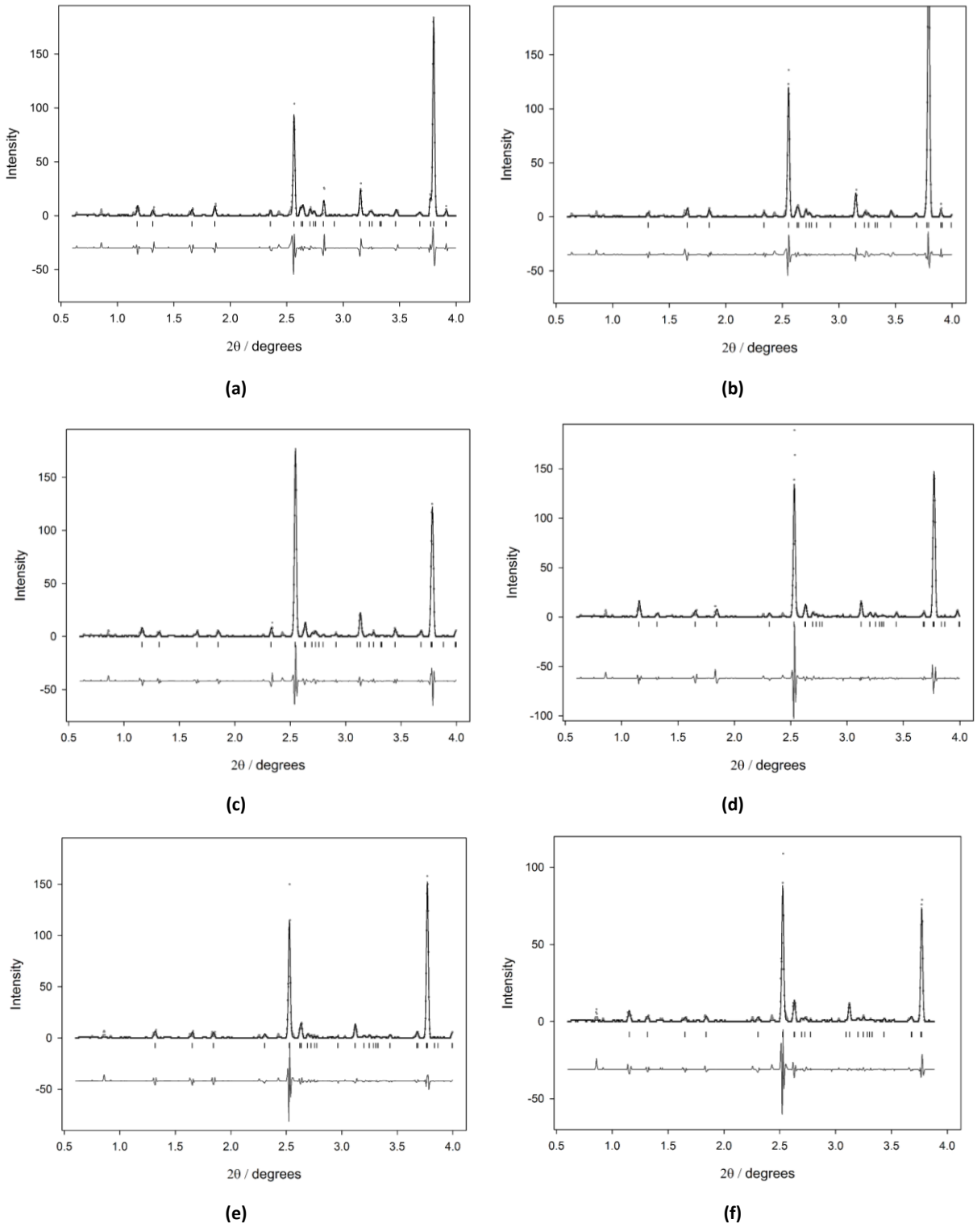


Figure S5: Partial Rietveld fits to the X-ray diffraction data collected on the 1:1 BA:isoNCT co-crystal **(a)** 30; **(b)** 60; **(c)** 100; **(d)** 150; **(e)** 161; and, **(f)** 166 °C. Dots show the observed data, and tick marks the calculated reflections; the upper line is the fit to the data, and the lower line is the difference. A 3-term cosine Fourier series was used to fit the background. The unit cell parameters were refined. A single Gaussian peak shape, and a single U_{iso} for all the non-H atoms, were employed. The initial data were background-subtracted to remove a large amorphous background arising due to the glassy C vessel used for heating, and thus the background is constant in these patterns.

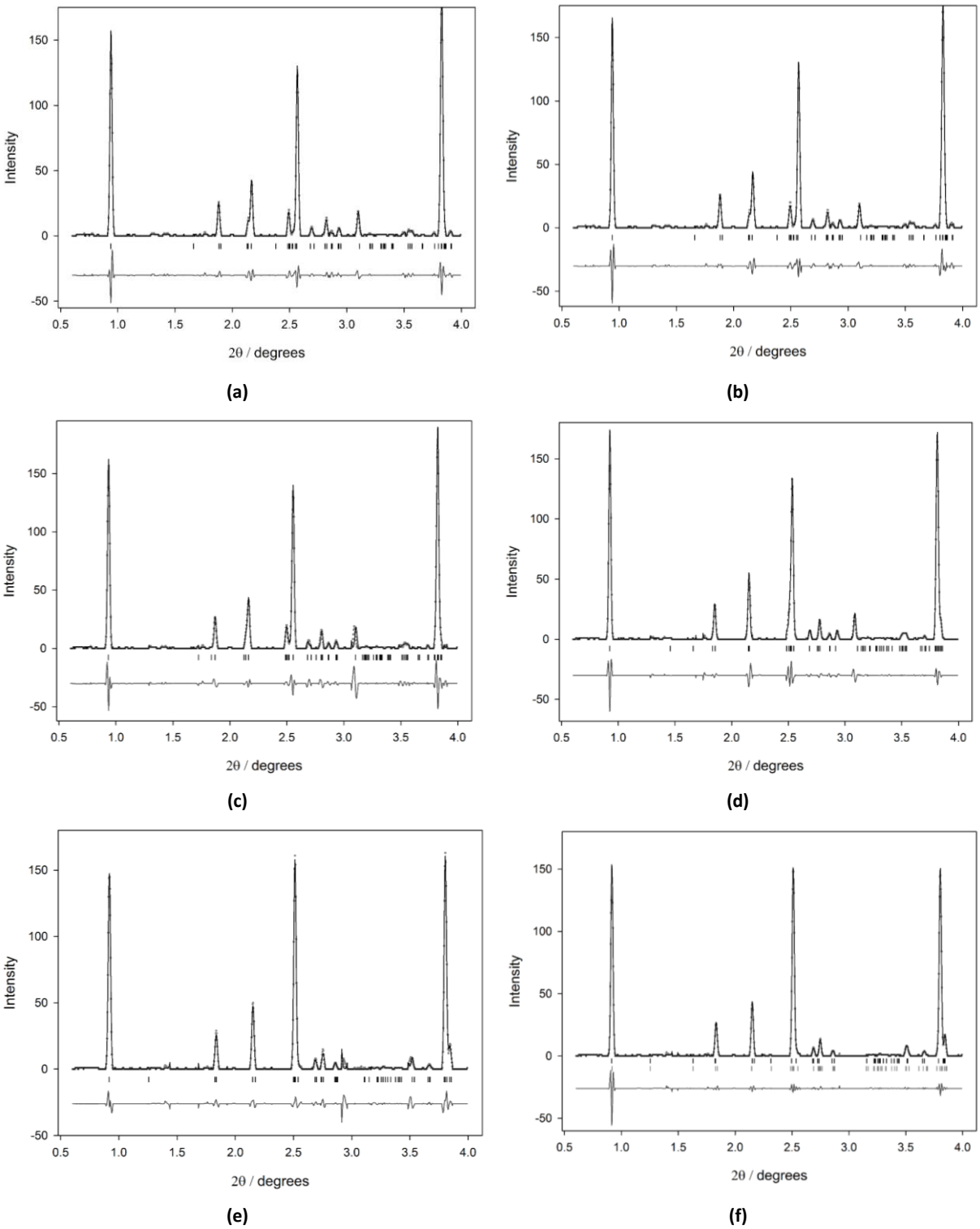


Figure S6: Partial Rietveld fits to the X-ray diffraction data collected on the 2:1 BA:isoNCT co-crystal **(a)** 30; **(b)** 32; **(c)** 60; **(d)** 100; **(e)** 140; and, **(f)** 150 °C. Dots show the observed data, and tick marks the calculated reflections; the upper line is the fit to the data, and the lower line is the difference. A 3-term cosine Fourier series was used to fit the background. The unit cell parameters were refined. A single Gaussian peak shape, and a single U_{iso} for all the non-H atoms, were employed. Note that in (f) there are two sets of tick marks, corresponding to two different phases (see main text). The initial data were background-subtracted to remove a large amorphous background arising due to the glassy C vessel used for heating, and thus the background is constant in these patterns.

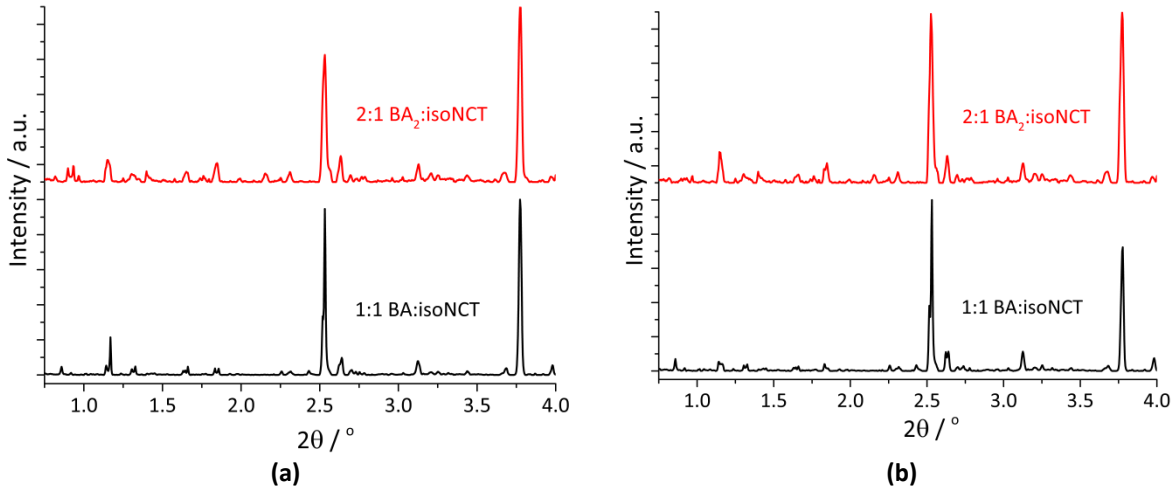


Figure S7: The XRD patterns obtained when the 2:1 and 1:1 co-crystals are heated to **(a)** 161 and **(b)** 166 °C. To facilitate comparisons, the intensities of the reflections in each pattern have been normalised to the most intense reflection.

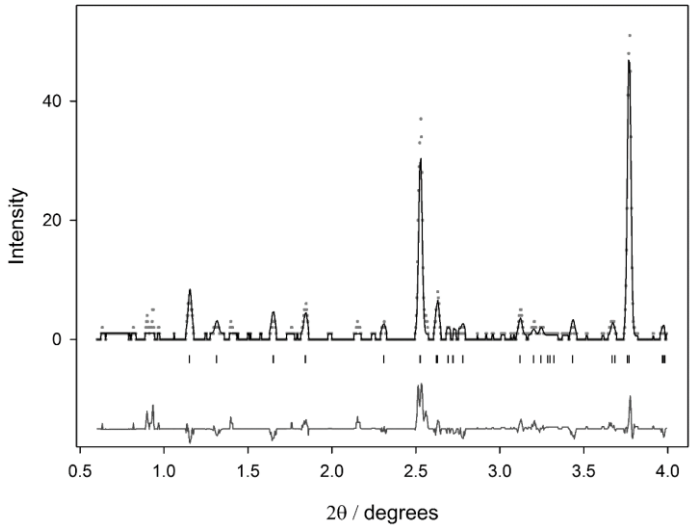


Figure S8: Partial Rietveld fit to the X-ray diffraction data collected at 161 °C from the 2:1 BA_2:isoNCT co-crystal. Dots show the observed data, the upper line is the fit to the data, and the lower line is the difference. A 3-term cosine Fourier series was used to fit the background. The unit cell parameters were refined. A single Gaussian peak shape, and a single U_{iso} for all the non-H atoms, were employed.

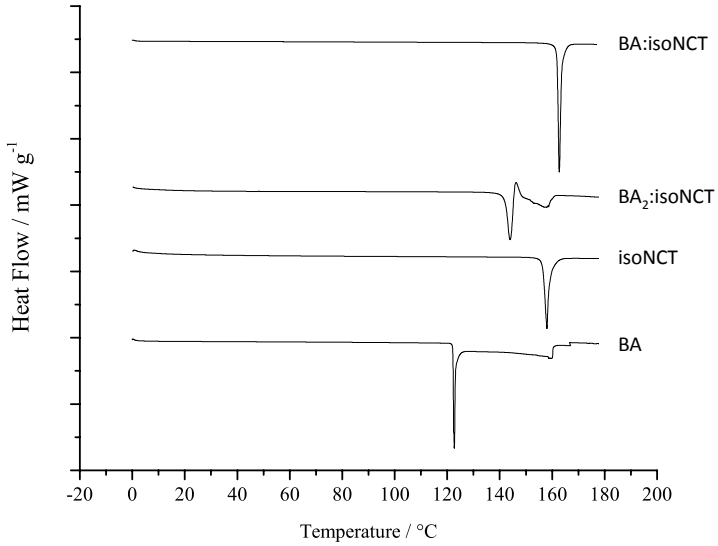


Figure S9: DSC data for the raw materials and co-crystals. Data were collected at heating rates of 10 °C min^{-1}.

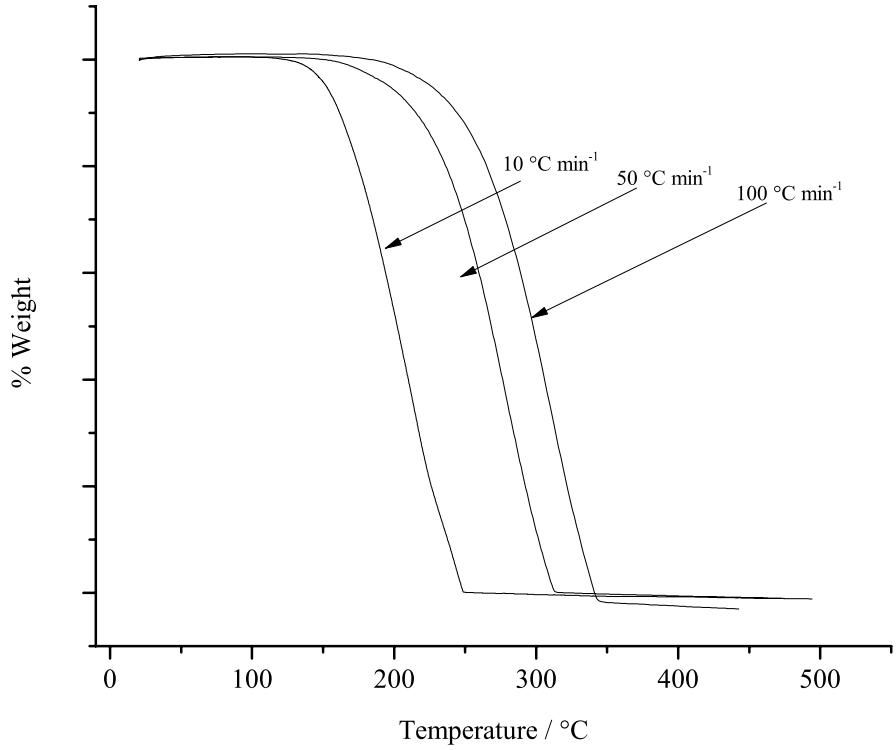


Figure S10: Weight loss as a function of temperature for BA_2:isoNCT at different heating rates.

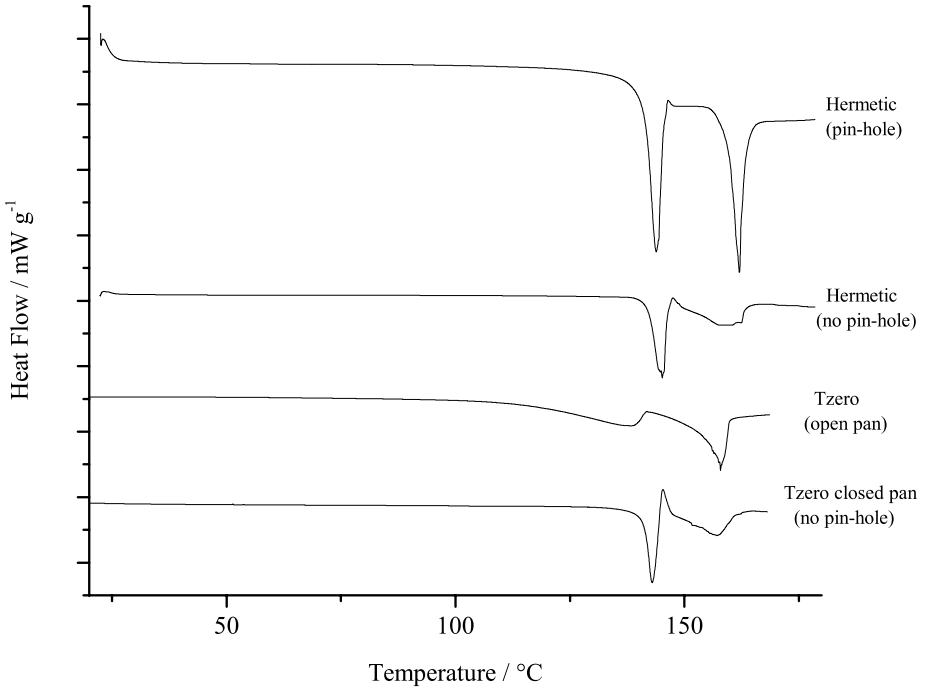


Figure S11: DSC thermograms of BA_2:isoNCT co-crystals heated in different pan types at 10°C min^{-1}.

References

(1) Aakeröy, C. B.; Beatty, A. M.; Helfrich, B. A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 3240-3242.
(2) Seaton, C. C.; Parkin, A.; Wilson, C. C.; Blagden, N. *Cryst. Growth Des.* **2009**, *9*, 47-56.