Supporting Information

Evaluation of the formation pathways of cocrystal polymorphs in liquid-assisted synthesis

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1. Solid-state NMR

^{1}H MAS NMR spectra were recorded on a Bruker AVANCE 400 spectrometer using a 2.5 mm double-bearing MAS probe (Bruker Biospin) and applying a spinning speed of 20 kHz. The ^{1}H MAS NMR spectra were recorded with a $\pi/2$ pulse lengths of 3.7 µs, a recycle delay of 5 s and an accumulation number of 256. Existent background signals were suppressed with a phase-cycled depth pulse sequence according to Cory and Ritchey.[40]

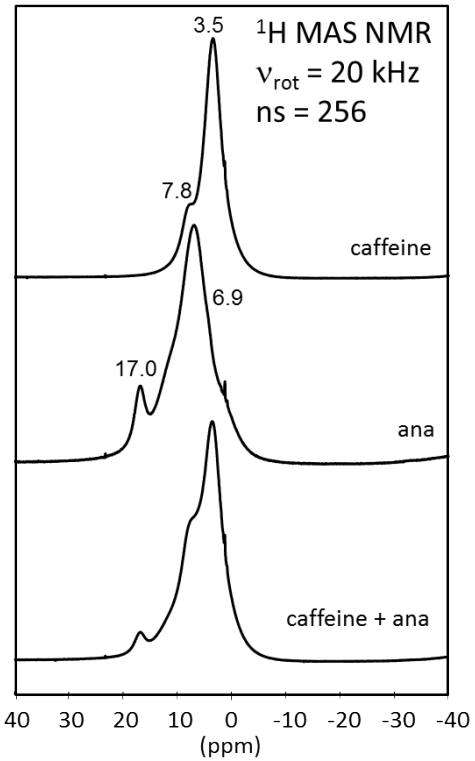

Fig. S 1 ^{1}H magic angle spinning (MAS) NMR spectra of caffeine (above), anthranilic acid (ana) and the superimposed spectra of the reactants (below) without the spinning sidebands.

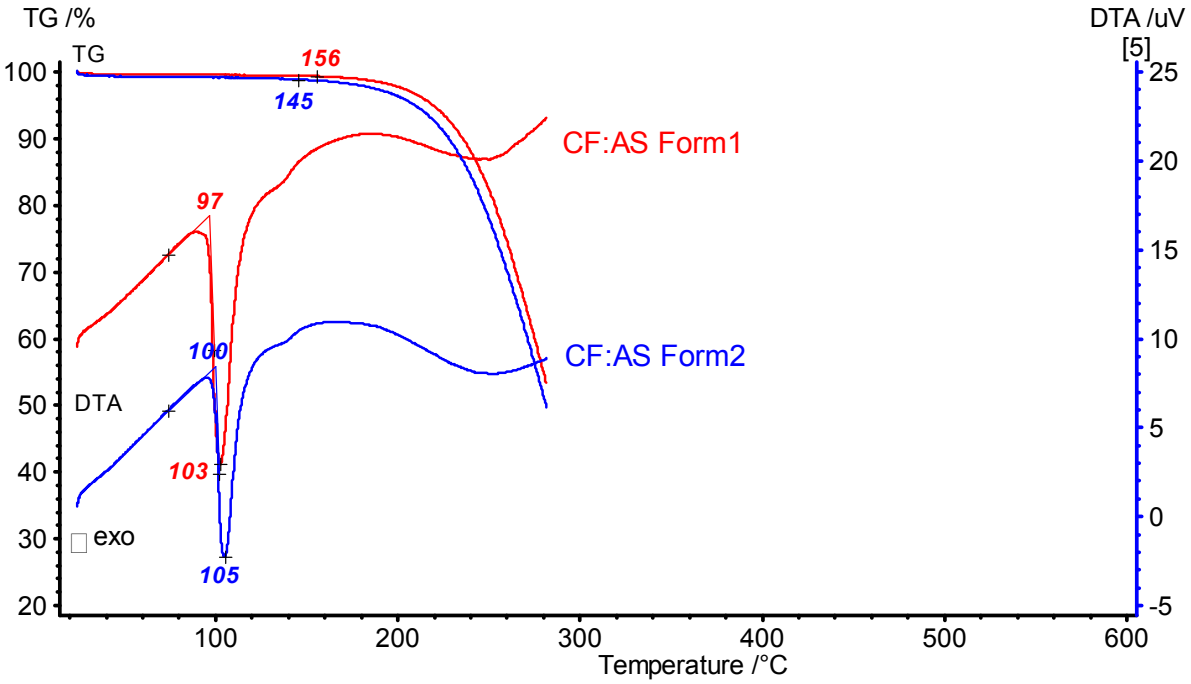

Fig. S 2 DTA/TG measurements of the of cf:ana cocrystal form I (red) and form II (blue).

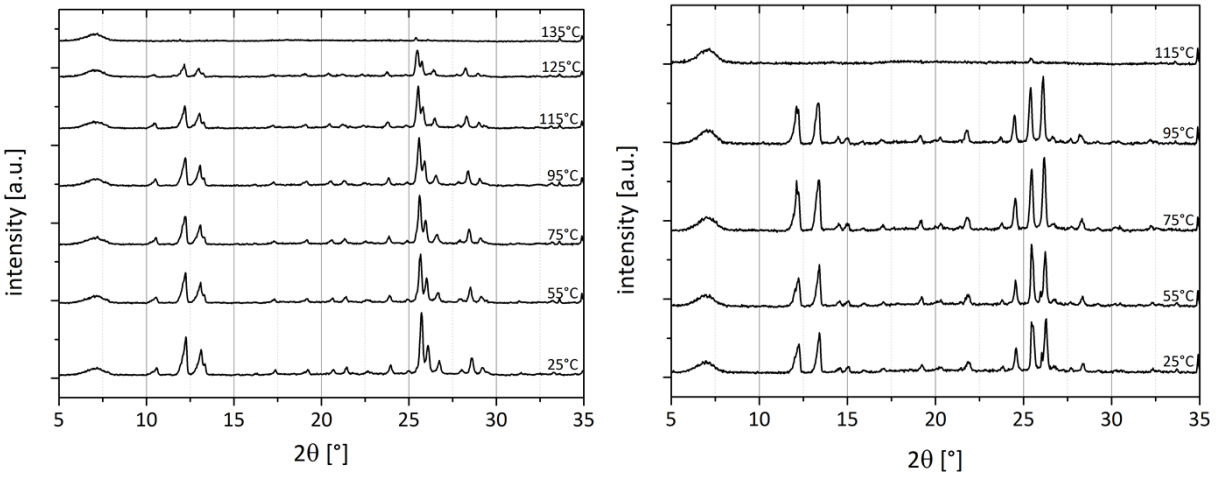

Fig. S 3 Temperature dependent PXRD patterns of the cf:ana cocrystal form I (left) and form II (right). The reflections, which remain in the diffraction pattern of melt are based on the sample holder and the Kapton foil.

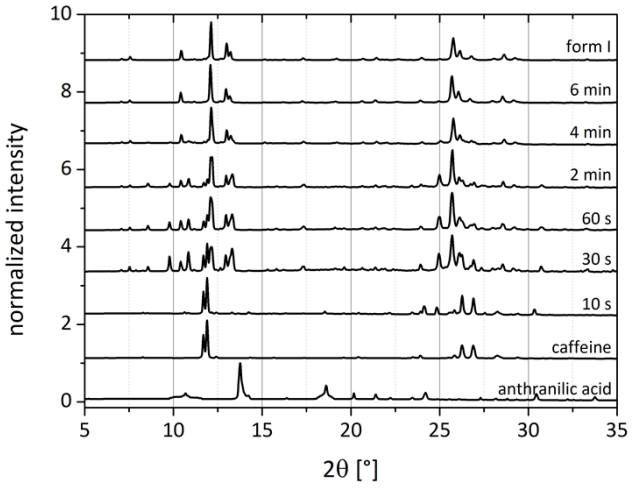

Fig. S 4 XRD patterns of the cf:ana cocrystal (form I) after different milling time intervals. Dioxane was used in the grinding process.

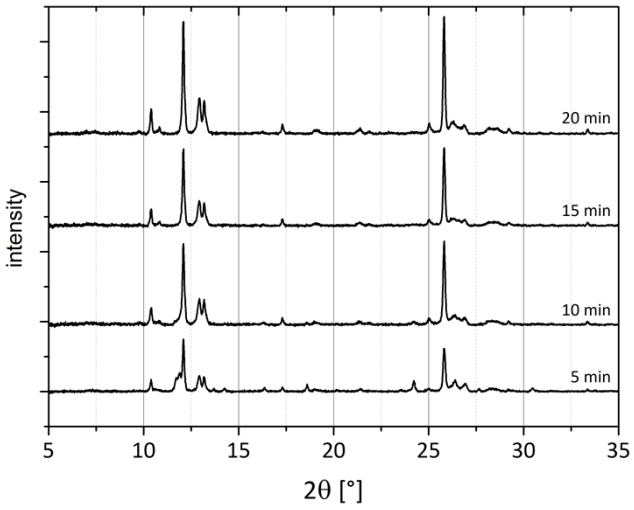

Fig. S 5 XRD patterns of the cf:ana cocrystal (form I) after different milling time intervals during neat grinding.