Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

Supporting Information

Quantitative Determination of Activation Energies in Mechanochemical Reactions

Franziska Fischer[a], Klaus-Jürgen Wenzel[a], Klaus Rademann[a,b], Franziska Emmerling[a]

a. BAM Federal Institute for Materials Research and Testing, R.-Willstätter-Str. 11, 12489 Berlin,

b. Department of Chemistry, Humboldt-Universität zu Berlin, B.-Taylor-Str. 2, 12489 Berlin

KEYWORDS mechanochemistry, activation energy, in situ investigations, cocrystal

Table of contents

A Materials and Methods

Experimental detail. Ibuprofen (ibu), $C_{13}H_{18}O_2$, (99%, Alfa Aesar, Germany) and nicotinamide (na), $C_6H_6N_2O$, (≥ 99.5%, Sigma Aldrich, Germany) were purchased commercially and were used without further purification. Grinding was performed for all reactions (LAG and neat grinding) at 50 Hz for 40 min in a conventional ball mill (Pulverisette 23, Fritsch, Germany). In a typical experiment, the coolable stainless-steel jar subpart of a 10 mL vessel was pre-tempered with two steel balls of 10 mm diameter and 4 g in mass. Afterwards, the pre-tempered reactants were added in a stoichiometric ratio of 1:1 into the vessel for a total load of 1 g (0.6281 g ibuprofen and 0.3719 g nicotinamide). The vessel was directly sealed with a Makrolon top part. The nitrogen stream was turned on 30 s before milling in order to reach the required temperature quickly after starting the milling process. The temperature of the jar was controlled in the range of ± 1 K by adjusting the nitrogen stream. The experiments were conducted at the following temperatures: 282 K, 286 K, 290 K, 294 K, 298 K, and 302 K. Each experiment was repeated six times.

Raman Spectroscopy. Raman measurements were performed using a Raman RXN1™ Analyser (Kaiser Optical Systems, France). The spectra were collected using a contactless probe head (working distance 6.0 cm, spot size 1.0 mm). Raman spectra were recorded with an acquisition time of 5 s and 5 accumulations (NIR excitation radiation at λ = 785 nm and an irradiation of 6.6 W/cm^2).

Powder X-ray diffraction (PXRD). The milling synthesis of the ibu:na cocrystal was verified by PXRD (Figure S1). All PXRD experiments were carried out using a D8 diffractometer (Bruker AXS, Karlsruhe, Germany) in transmission geometry (Cu-$K_{\alpha1}$ radiation, λ = 1.54056 Å).

B X-ray powder diffraction patterns and crystal structure of compounds

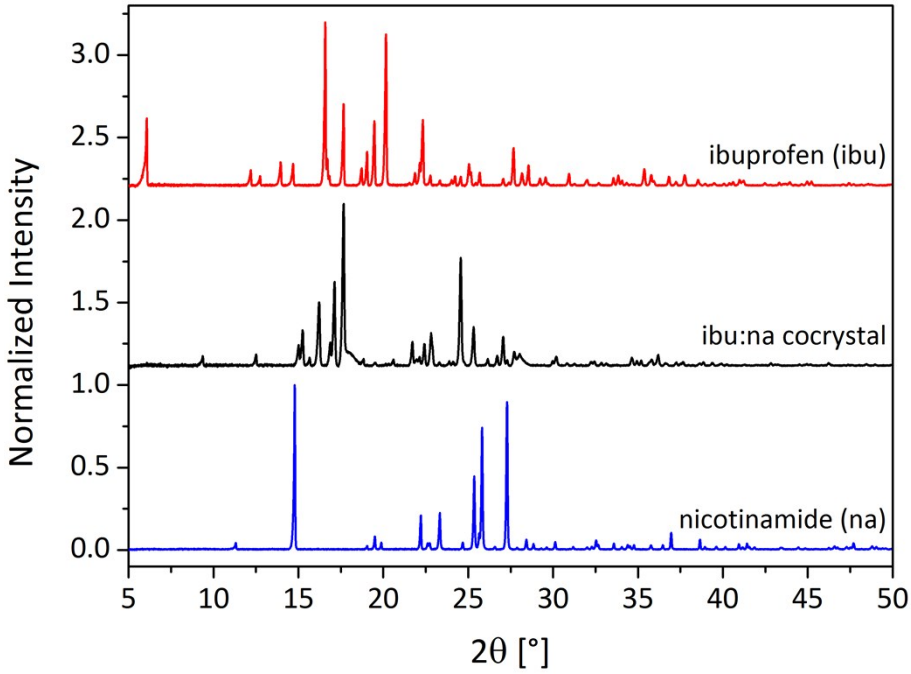

Fig. S1 XRD patterns of the ibu:na cocrystal (black) and the respective reactants ibu (red) and na (blue).

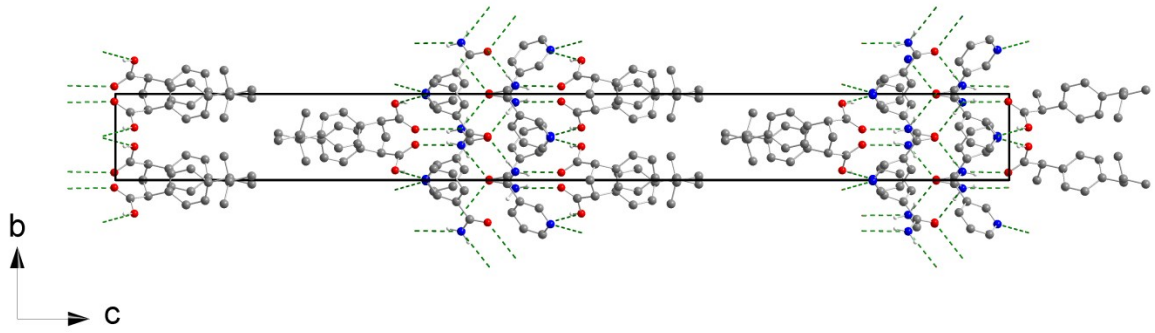

Fig. S2 Crystal structure of the ibu:na cocrystal along the a-axis.

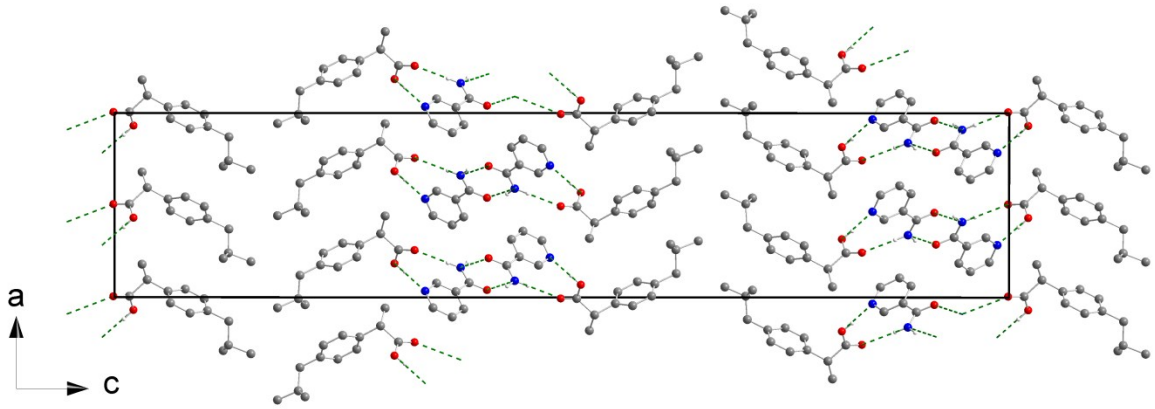

Fig. S3 Crystal structure of the ibu:na cocrystal along the b-axis.

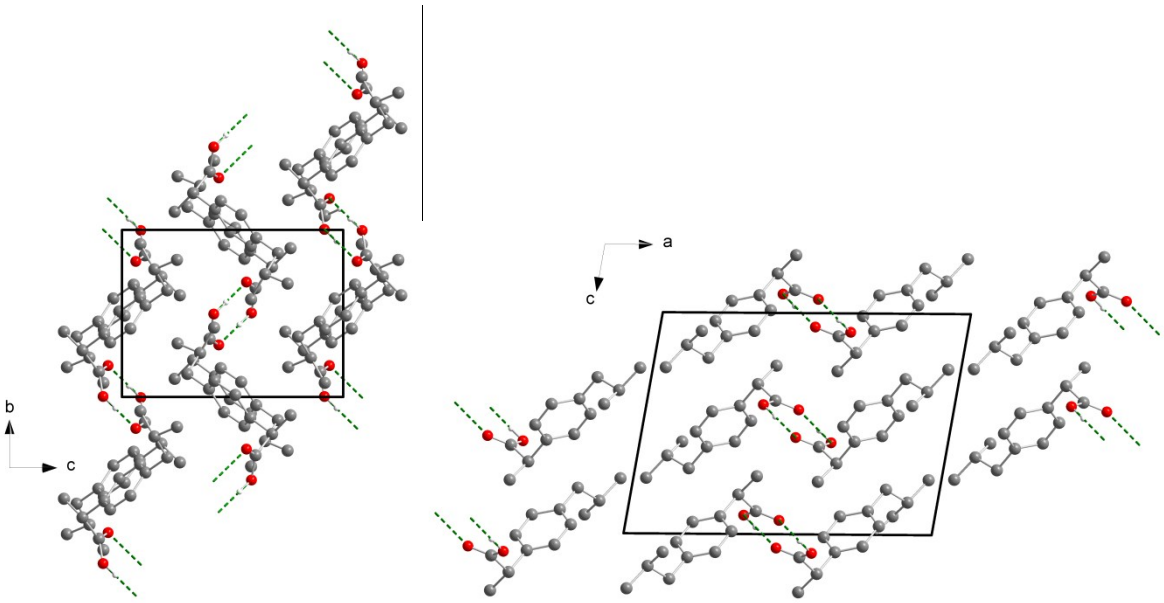

Fig. S4 Crystal structure of the reactant ibu along the a- and the b-axis.

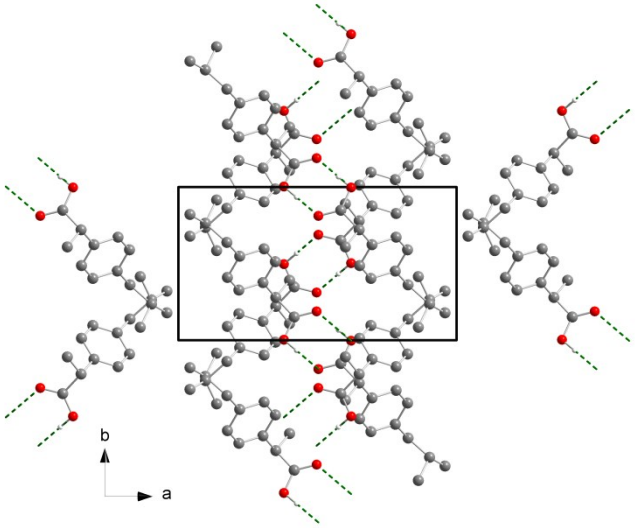

Fig. S5 Crystal structure of the reactant ibu along the c-axis.

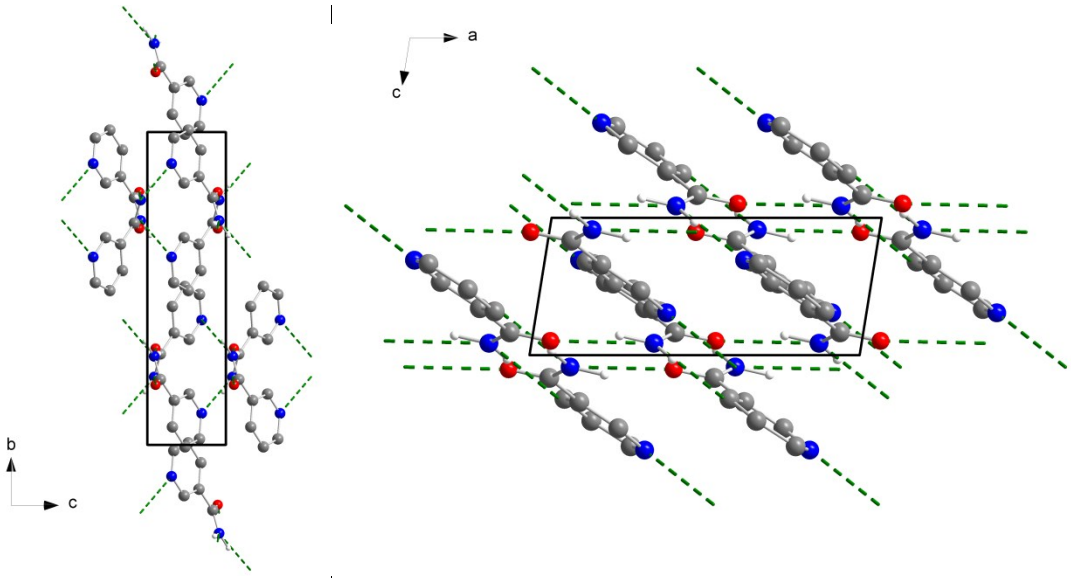

Fig. S6 Crystal structure of the reactant na along the a- and the b-axis.

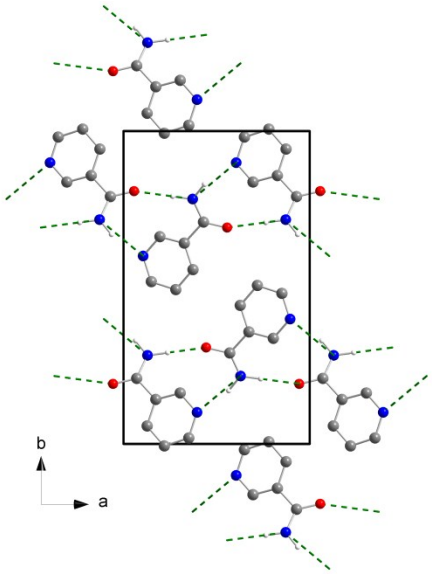

Fig. S7 Crystal structure of the reactant na along the c-axis.

C Raman data of compounds

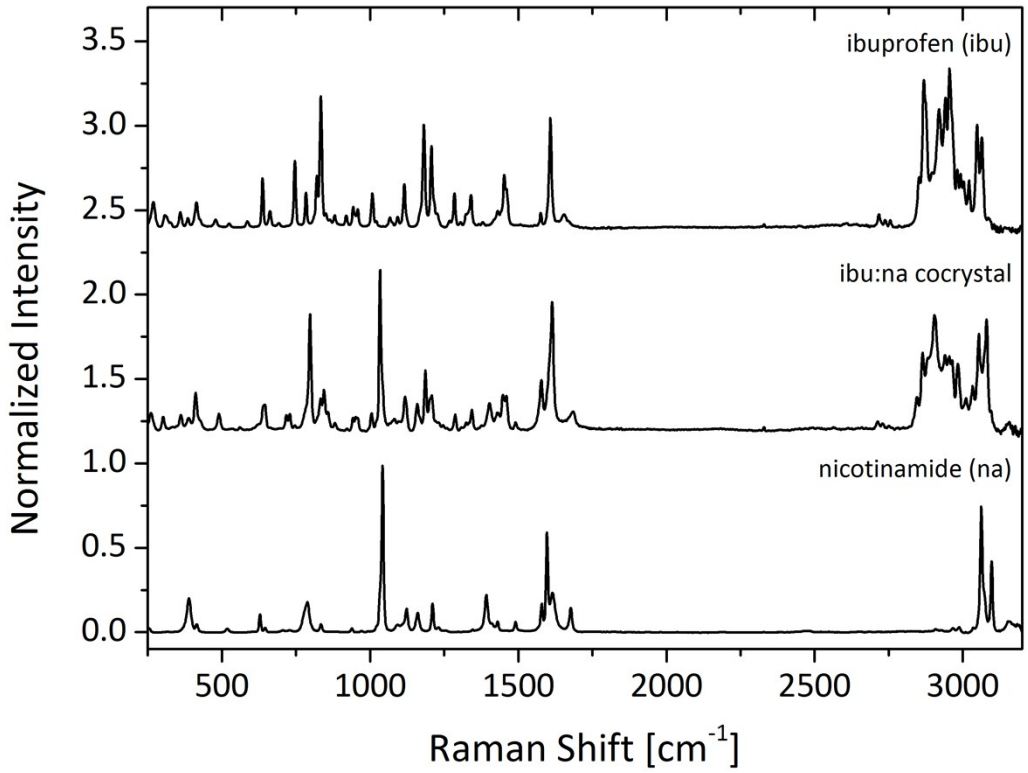

Fig. S8 Raman spectra of the ibu:na cocrystal and the reactants ibu and na.

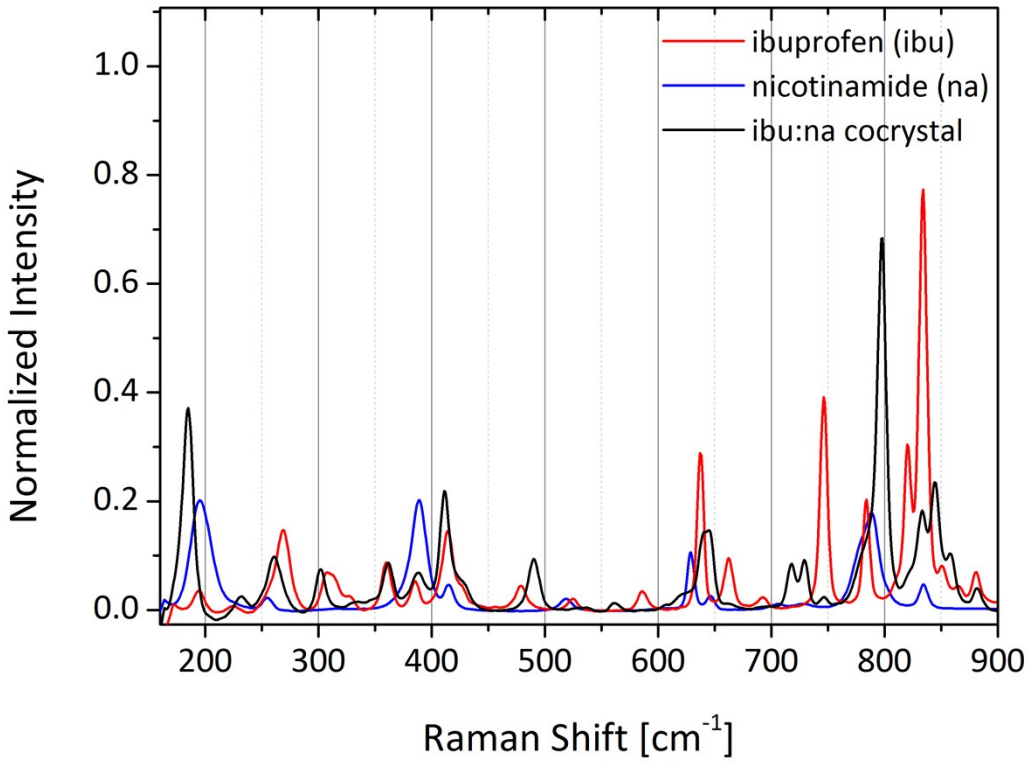

Fig. S9 Zoomed Raman spectra of the ibu:na cocrystal and the reactants ibu and na.

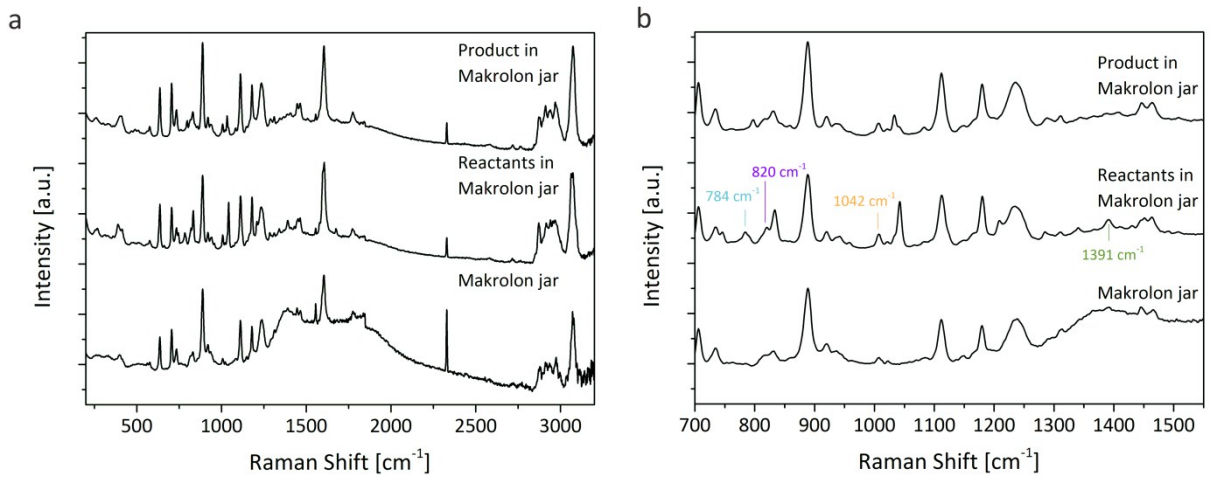

Fig. S10 a) Raman spectra of the empty grinding jar, the ibu:na cocrystal and the reactants ibu and na with the grinding jar background. b) Zoomed Raman spectra.

D Temperature-dependent data

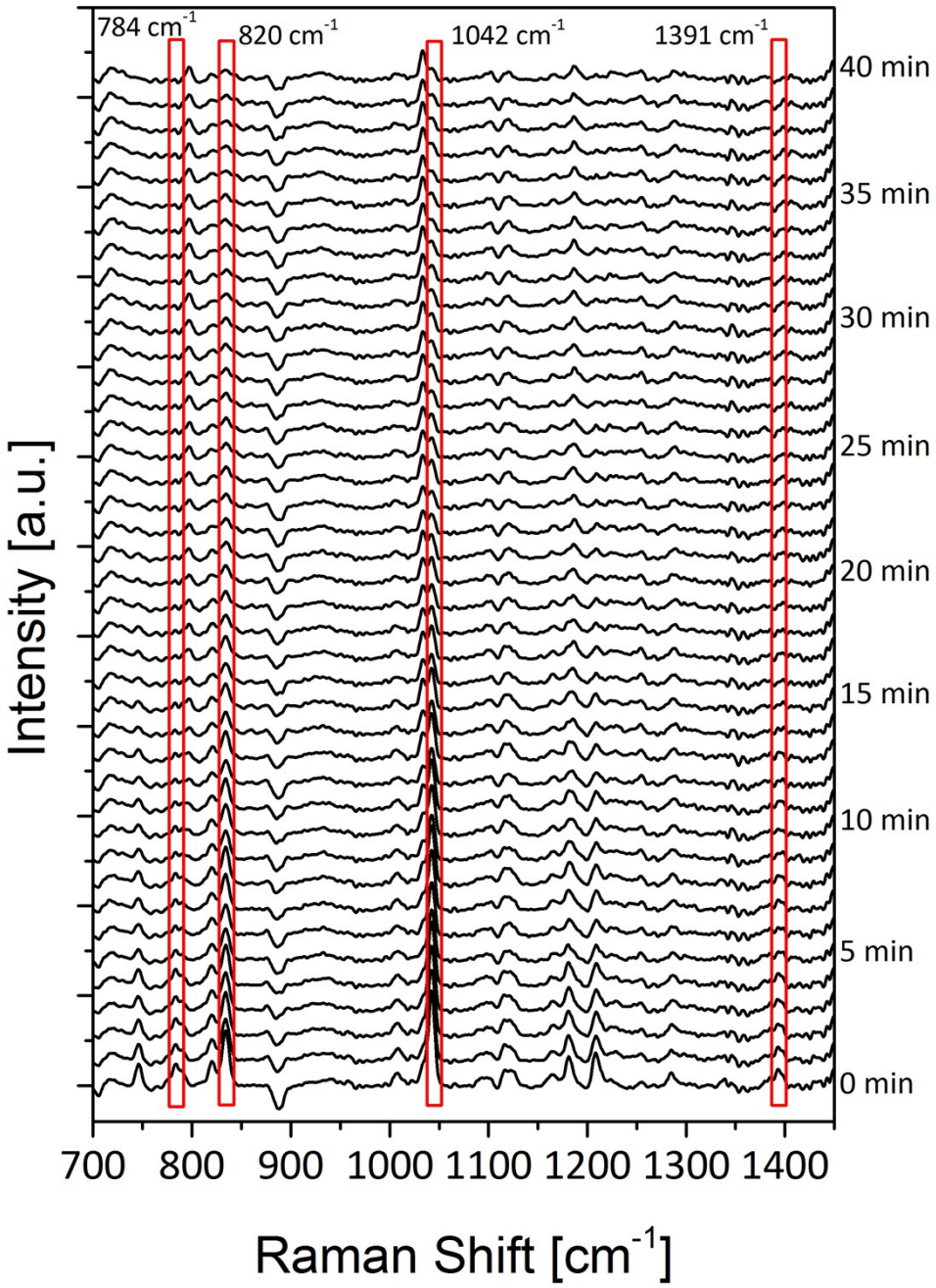

Fig. S11 Time-dependent and background corrected Raman spectra of the ibu:na synthesis. Milling synthesis was performed at 50 Hz for 40 min at 286 K.

Table S1 | Temperature-dependent rate constants obtained at different Raman signals. sd. = standard deviation.

T [K]	784 cm^{-1}		820 cm^{-1}		1042 cm^{-1}		1391 cm^{-1}	
	k [min^{-1}]	sd.	k [min^{-1}]	sd.	k [min^{-1}]	sd.	k [min^{-1}]	sd.
282	0.073	0.009	0.027	0.005	0.037	0.002	0.031	0.001
286	0.086	0.008	0.029	0.002	0.038	0.004	0.035	0.003
290	0.103	0.007	0.030	0.002	0.042	0.004	0.039	0.005
294	0.106	0.017	0.032	0.004	0.044	0.001	0.046	0.003
298	0.113	0.007	0.034	0.009	0.049	0.007	0.049	0.014
302	0.129	0.027	0.035	0.008	0.057	0.003	-	-

E Arrhenius equations

(S1) $$k = A\, e^{-\frac{E_a}{(RT)}}$$

(S2) $$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + ln(A)$$

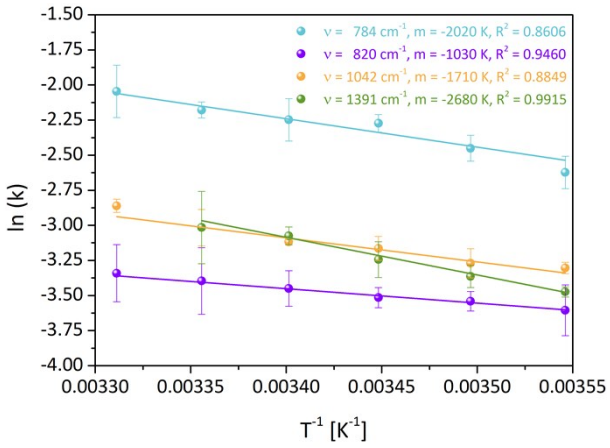

Fig. S12 Arrhenius plots according to the temperature-dependent rate constants determined based on the Raman signal at 784 cm^{-1}, 820 cm^{-1}, 1042 cm^{-1}, and 1391 cm^{-1}.