

## Supporting information – experimental procedures

In the setup (Scheme 1), reactor volume and volume of the cathode compartment including tubing are 0.001 and 0.0002 m<sup>3</sup> respectively. A direct current density of 300 A·m<sup>-2</sup> resulted in a potential difference over the module of 11 V. Volumetric flow rate through the cathode compartment was 5·10<sup>-6</sup> m<sup>3</sup>/s. Buffered standard solutions containing mineral salts representing fermentation conditions<sup>1</sup> were used.

Batch experiments: During 1 hour a standard solution, initially containing 0.45 g/l CA and 3 g/l NBA, was circulated through the module.

Continuous experiment: The initial contents of the reactor were based on the standard solution with 3.1 g/l NBA. The feed, added to the reactor with a flow rate of 0.24 l/hour, was based on the standard solution with 3 g/l NBA and 1.15 g/l CA. The duration of the continuous experiment was 8 hours.

Solution samples were filtered using 0.45 µm filters and analyzed using HPLC (278 nm, C18 column, flow rate 1.5 ml/min).

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<sup>1</sup> K. Nijkamp, N. van Luijk, J. A. M. de Bont, J. Wery, *Appl. Microbiol. Biotechnol.* **2005**, *69*, 170-177.

## Supporting information – HR-XRPD

A co-crystalline powder sample of Cinnamic acid (CA) and 3-Nitrobenzamide (NBA) was prepared using a solvent mediated transformation<sup>1</sup>. 1066 mg of CA, 239 mg of NBA and 10 ml of ethanol were added in a crystallizer of sufficient volume. The suspension was stirred. After 24 hours at room temperature the crystals were collected by filtration and dried under vacuum. The yield was around 390 mg co-crystals.

The powder data were collected on D8 Advance Diffractometer<sup>2</sup> using Cu K<sub>α1</sub> radiation (1.54056 Å) with germanium monochromator at Room Temperature. The data were collected from 1.5 to 27.5°  $\theta$  with 0.01577°  $\theta$  steps on a solid state LynxEye detector. The sample was measured in 8 mm long glass capillary with 0.3 mm outer diameter.

The diffraction pattern was indexed using TOPAS<sup>3</sup> to a triclinic cell and based on the symmetry of the molecules the centrosymmetric P-1 space group was assigned. During the cell refinement process several peaks with relatively low intensity could not be indexed. All these peaks did belong to two polymorphs of CA (CSD refcodes CINMAC and CINMAC06 (CCDC, October 2009)), which suggested that the crystalline material was a mixture of the CA:NBA co-crystal and two polymorphs of CA. This information was used in the quantitative Rietveld<sup>4</sup> refinement, which showed that the crystalline material consisted of w/w 96.2(8)% of CA:NBA, 2.4(5)% of CINMAC06 and 1.4(3)% of CINMAC (Figure 1).

The CA:NBA co-crystal structure consists of packed centrosymmetrical hydrogen-bonded tetramers. In the tetramer (figure 2) the amide-carboxylic acid synthon hydrogen binds CA and NBA. In turn twins of hydrogen bonded CA and NBA are connected through two hydrogen bonds between the amide H-atoms of NBA and the non-protonated O-atom of the carboxylic acid of CA.

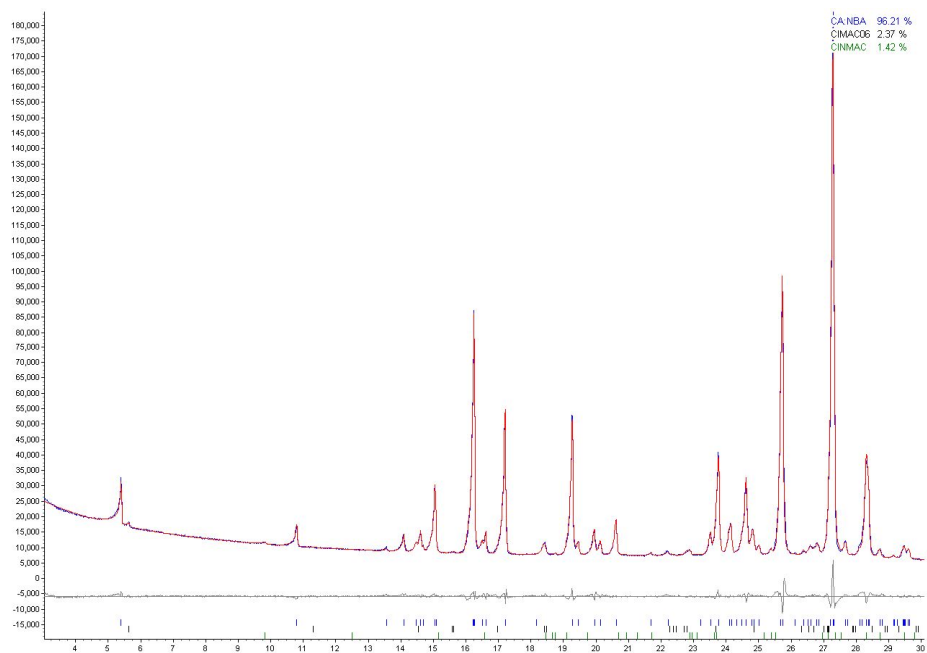


Figure 1: The High Resolution XRPD pattern of the CA:NBA co-crystal sample. The crystalline sample consisted of w/w 96.2(8)% of CA:NBA, 2.4(5)% of CINMAC06 and 1.4(3)% of CINMAC.

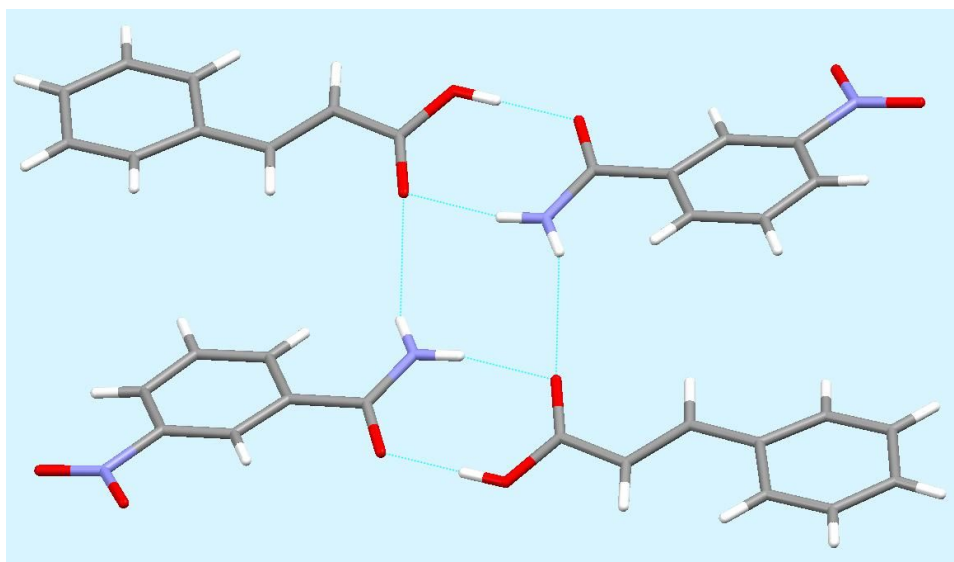


Figure 2: The centrosymmetrical hydrogen-bonded tetramer in the Crystal structure of the 1:1 co-crystal of cinnamic acid (CA) and 3-nitrobenzamide (NBA)

## References

1. J.H. ter Horst, P. W. Cains, *Cryst. Growth Des.* **2008**, *8*, 2537-2542.
2. *DIFFRAC plus XRD Commander*, version 2.3; Kienle, M.; Jacob, M. Bruker AXS GmbH: Karlsruhe, Germany, 2003.
3. Coelho, A. A. *Topas user manual*; Version 3.1 ed.; Bruker AXS GmbH: Karlsruhe, Germany, 2003.
4. Rietveld, H. M. *J.Appl.Crystallogr.* **1969**, *2*, 65-71.