**Supplementary Information**

**Single Crystal X-Ray Diffraction**

Single crystal diffraction data were collected on an Oxford Diffraction Gemini R Ultra diffractometer equipped with a Ruby CCD-detector with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å, graphite monochromator, mono-capillary collimator) for all compounds at 173 K using an Oxford Cryostream 700 cooler. Data reduction and cell refinement were carried out using *CrysAlisPro*.[1] Space group assignments were made using *XPREP*[2] and empirical absorption corrections[1] on all compounds. In all cases, the structures were solved in the WinGX[3] Suite of programs by direct methods using *SHELXS*-97[4] and refined using full-matrix least squares/difference Fourier techniques using *SHELXL*-97.[4] All non-hydrogen atoms were refined anisotropically. Thereafter, all hydrogen atoms attached to N and O atoms were located in the difference fourier map and their coordinates refined freely with isotropic parameters 1.5 times those of the heavy atoms to which they are attached. All C-H hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of the heavy atoms to which they are attached. Diagrams and publication material were generated using *ORTEP-3*[5], *PLATON*[6] and *DIAMOND*[7]. CCDC-753783-753786 contains the supplementary crystallographic data for structures **3-6** respectively while the cif file for **7** has not been deposited. These data can be obtained free of charge at www.ccdc.cam.ac.ul/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk]. The cif files for all compounds is given as supplementary information.

[1] *CrysAlisPro*, Oxford Diffraction Ltd., Version 1.171.33.34d (release 27-02-2009 CrysAlis171.NET).
[2] *XPREP2*, Bruker 2003, Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
[3] L. J. Farrugia, *J. Appl. Cryst.* **1999**, 32, 837-838.
[4] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112-122.
[5] L. J. Farrugia, *J. Appl. Cryst.* **30**, 565 (1997).
[6] A. L. Spek, *J. Appl. Crystallogr*. **2003**, 36, 7-13.
[7] K. Brandenburg, *J. Appl. Cryst*. **1999**, 32, 1028-1029.

**Powder X-Ray Diffraction**

Powder X-ray diffraction data for compounds **3-6** were collected on a Philips powder diffractometer using $CuK_{\alpha 1}$-radiation, graphite monochromator on diffracted beam and operating at 40 kV, 30 mA at 293 K. The measured powder patterns of **3** and **5** show preferred orientation effects due to the 2-D layering of the crystal packing, and the peak positions are shifted due to the temperature difference between the measured and calculated patterns.

## Cif Tables for co-crystal (nicotinic acid hydrazide)$_2$·(adipic acid) 3:

Table 1. Crystal data and structure refinement for **3**.

| | | |
|---|---|---|
| Identification code | 753783 | |
| Empirical formula | C18 H24 N6 O6 | |
| Formula weight | 420.43 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 13.1910(8) Å | α= 90°. |
| | b = 10.3449(5) Å | β= 102.230(6)°. |
| | c = 7.4635(4) Å | γ = 90°. |
| Volume | 995.35(9) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.403 Mg/m$^3$ | |
| Absorption coefficient | 0.107 mm$^{-1}$ | |
| F(000) | 444 | |
| Crystal size | 0.4 x 0.39 x 0.38 mm$^3$ | |
| Theta range for data collection | 3.16 to 25.50°. | |
| Index ranges | -15<=h<=13, -9<=k<=12, -8<=l<=9 | |
| Reflections collected | 6133 | |
| Independent reflections | 1840 [R(int) = 0.0273] | |
| Completeness to theta = 25.50° | 99.4 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.97 and 0.96 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1840 / 0 / 148 | |
| Goodness-of-fit on F$^2$ | 1.210 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0502, wR2 = 0.1285 | |
| R indices (all data) | R1 = 0.0618, wR2 = 0.1317 | |
| Largest diff. peak and hole | 0.295 and -0.229 e.Å$^{-3}$ | |

Table 2. Hydrogen bonds for **3** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...N(2) | 0.88(4) | 1.78(4) | 2.638(3) | 164(3) |
| C(3)-H(3)...O(3) | 0.95 | 3.18 | 3.705(3) | 117 |
| N(1)-H(1)...O(1)#2 | 0.88(3) | 2.18(3) | 3.040(3) | 165(3) |
| N(3)-H(3A)...O(1)#3 | 0.85(4) | 2.41(4) | 3.162(4) | 148(3) |
| N(3)-H(3B)...O(2)#4 | 0.88(4) | 2.54(4) | 3.360(4) | 155(3) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1 #2 -x+1,y+1/2,-z+3/2 #3 x,-y+1/2,z+1/2

#4 -x+1,-y+1,-z+1

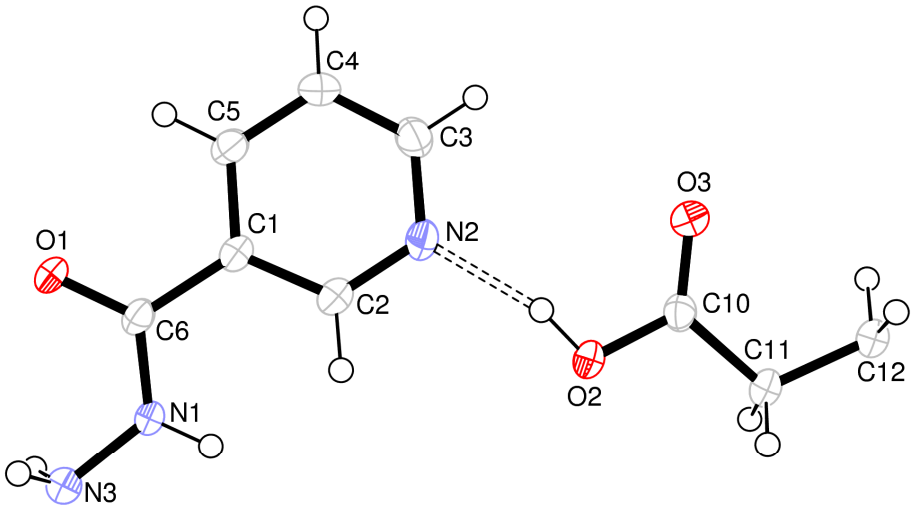


**Figure S1.** The asymmetric unit of **3** showing the atomic numbering scheme and 50% displacement ellipsoids.

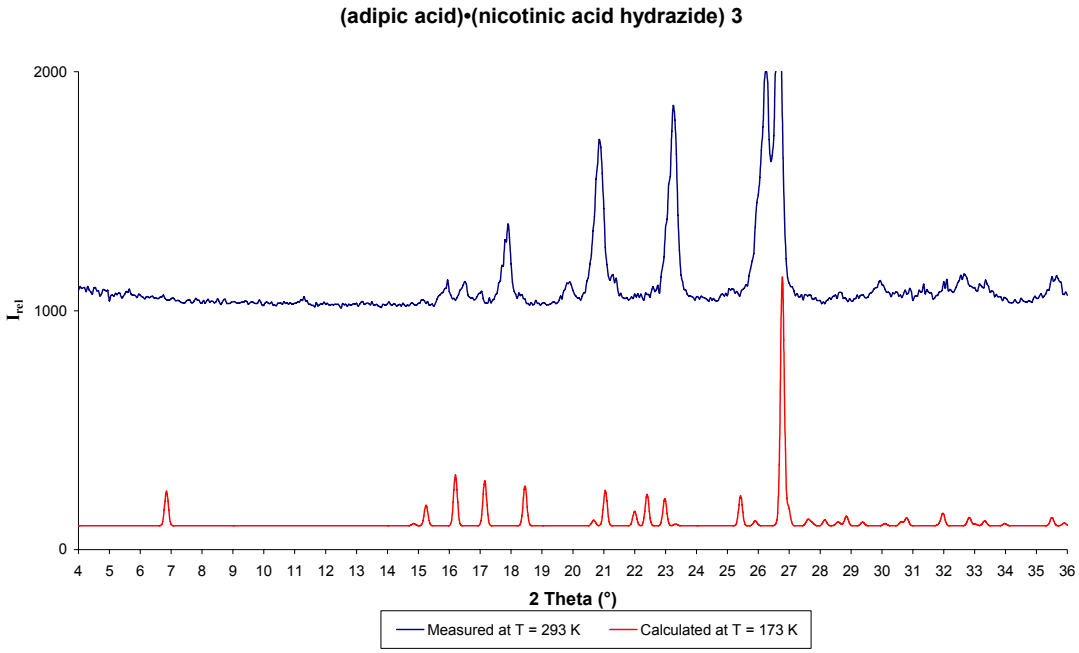


**Figure S2.** Comparative calculated and measured PXRD pattern for **3**.

## Cif Tables for co-crystal (*N*'-(propan-2-ylidene)nicotinohydrazide)$_2$·(adipic acid) **4:**

Table 3. Crystal data and structure refinement for **4**.

| | | |
|---|---|---|
| Identification code | 753784 | |
| Empirical formula | C12 H16 N3 O3 | |
| Formula weight | 250.28 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 5.0880(2) Å | α= 90°. |
| | b = 38.9970(16) Å | β= 94.128(4)°. |
| | c = 6.3470(2) Å | γ = 90°. |
| Volume | 1256.08(8) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.323 Mg/m$^3$ | |
| Absorption coefficient | 0.097 mm$^{-1}$ | |
| F(000) | 532 | |
| Crystal size | 0.45 x 0.2 x 0.06 mm$^3$ | |
| Theta range for data collection | 3.13 to 25.50°. | |
| Index ranges | -5<=h<=6, -40<=k<=47, -7<=l<=7 | |
| Reflections collected | 6687 | |
| Independent reflections | 2321 [R(int) = 0.0252] | |
| Completeness to theta = 25.50° | 99.2 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.99 and 0.97 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2321 / 0 / 171 | |
| Goodness-of-fit on F$^2$ | 1.190 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0664, wR2 = 0.1253 | |
| R indices (all data) | R1 = 0.0756, wR2 = 0.1278 | |
| Largest diff. peak and hole | 0.212 and -0.227 e.Å$^{-3}$ | |

Table 4. Hydrogen bonds for **4** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...N(2) | 0.94(4) | 1.73(4) | 2.672(3) | 177(4) |
| C(2)-H(2A)...O(3) | 0.95 | 2.66 | 3.286(4) | 124 |
| N(1)-H(1)...O(1)#2 | 0.90(3) | 2.18(3) | 3.066(3) | 170(3) |
| C(3)-H(3)...O(3)#3 | 0.95 | 2.50 | 3.264(4) | 138 |
| C(4)-H(4)...O(3)#4 | 0.95 | 2.51 | 3.361(4) | 149 |
| C(7)-H(7C)...N(3)#2 | 0.98 | 2.43 | 3.325(4) | 151 |
| C(9)-H(9B)...N(3)#5 | 0.98 | 2.68 | 3.595(4) | 156 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2 #2 x-1,y,z #3 x,y,z-1 #4 x+1,y,z-1

#5 x-1/2,-y+1/2,z+1/2

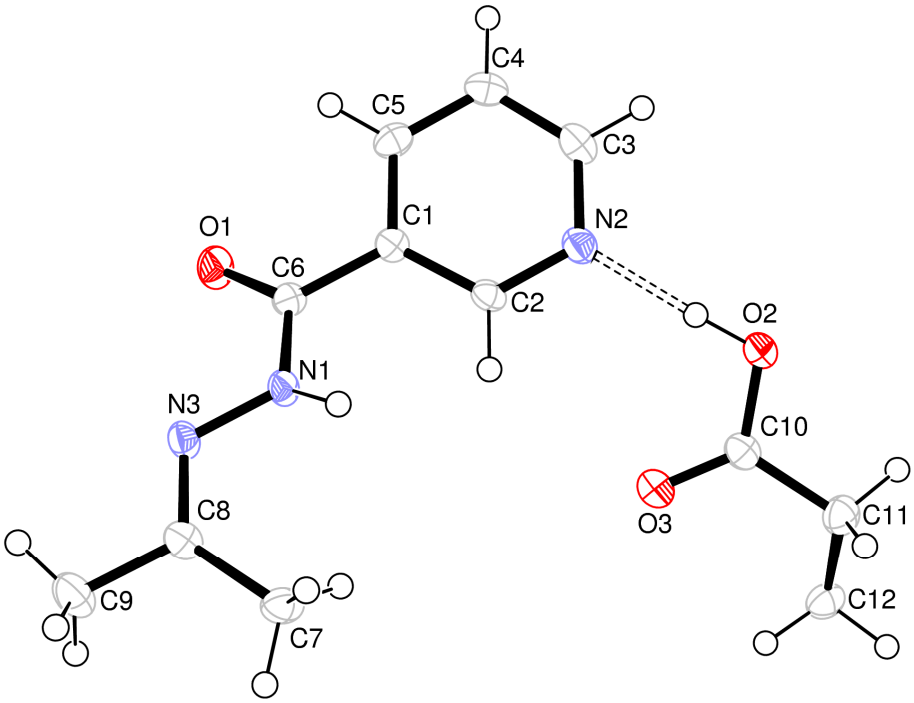


**Figure S3.** The asymmetric unit of **4** showing the atomic numbering scheme and 50% displacement ellipsoids.

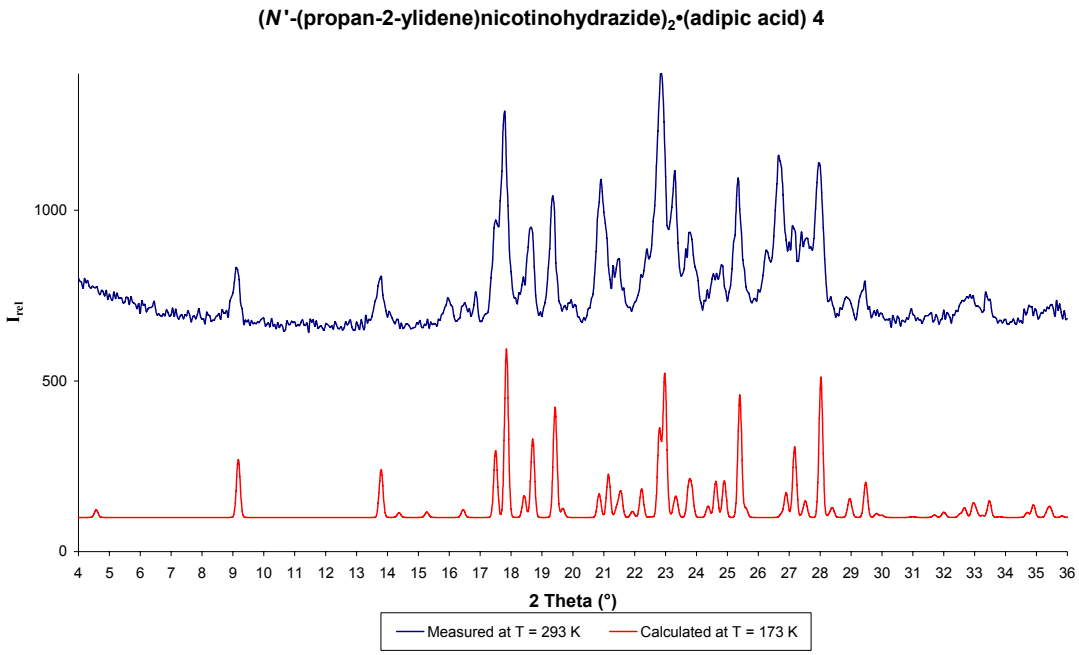


**Figure S4.** Comparative calculated and measured PXRD pattern for **4**.

## Cif Tables for co-crystal (nicotinic acid hydrazide)·(succinic acid) 5:

Table 5. Crystal data and structure refinement for **5**.

| | | |
|---|---|---|
| Identification code | 753785 | |
| Empirical formula | C16 H20 N6 O6 | |
| Formula weight | 392.38 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 8.0830(4) Å | α= 90°. |
| | b = 26.5860(10) Å | β= 104.449(4)°. |
| | c = 8.0970(4) Å | γ = 90°. |
| Volume | 1684.97(13) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.547 $Mg/m^3$ | |
| Absorption coefficient | 0.121 $mm^{-1}$ | |
| F(000) | 824 | |
| Crystal size | 0.2 x 0.21 x 0.24 $mm^3$ | |
| Theta range for data collection | 3.02 to 25.50°. | |
| Index ranges | -9<=h<=9, -32<=k<=26, -8<=l<=9 | |
| Reflections collected | 11280 | |
| Independent reflections | 3131 [R(int) = 0.0358] | |
| Completeness to theta = 25.50° | 99.8 % | |
| Absorption correction | Multiscan | |
| Max. and min. transmission | 0.99 and 0.93 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3131 / 0 / 277 | |
| Goodness-of-fit on $F^2$ | 1.027 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0359, wR2 = 0.0904 | |
| R indices (all data) | R1 = 0.0489, wR2 = 0.0946 | |
| Largest diff. peak and hole | 0.166 and -0.249 $e.Å^{-3}$ | |

Table 6. Hydrogen bonds for **5** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...N(2A) | 0.93(2) | 1.62(2) | 2.540(2) | 170(2) |
| C(3A)-H(3A)...O(3) | 0.95 | 2.87 | 3.446(2) | 121 |
| O(4)-H(4)...N(2B) | 0.94(2) | 1.60(2) | 2.541(2) | 171(2) |
| C(3B)-H(3B)...O(5) | 0.95 | 2.81 | 3.404(2) | 122 |
| N(1A)-H(1A)...O(1B)#1 | 0.84(2) | 2.08(2) | 2.914(2) | 172(2) |
| N(3A)-H(3AB)...O(4)#2 | 0.88(2) | 2.50(2) | 3.036(2) | 120(1) |
| N(3A)-H(3AB)...O(3)#3 | 0.88(2) | 2.55(2) | 3.213(2) | 133(1) |
| N(3A)-H(3AA)...O(5)#4 | 0.80(2) | 2.57(2) | 3.212(2) | 139(2) |
| N(1B)-H(1B)...O(1A)#5 | 0.83(2) | 2.06(2) | 2.885(2) | 170(2) |
| N(3B)-H(3BA)...O(2)#6 | 0.87(2) | 2.43(2) | 2.995(2) | 123(1) |
| N(3B)-H(3BB)...O(1B)#7 | 0.85(2) | 2.17(2) | 2.991(2) | 163(2) |
| C(2A)-H(2A)...O(1B)#1 | 0.95 | 2.28 | 3.219(2) | 171 |
| C(2B)-H(2B)...O(1A)#5 | 0.95 | 2.26 | 3.167(2) | 159 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z+3/2 #2 -x+1,y+1/2,-z+1/2 #3 -x+1,-y+1,-z

#4 -x+1,-y+1,-z+1 #5 -x+1,y-1/2,-z+1/2 #6 -x+2,y-1/2,-z+3/2

#7 -x+3,-y,-z+2

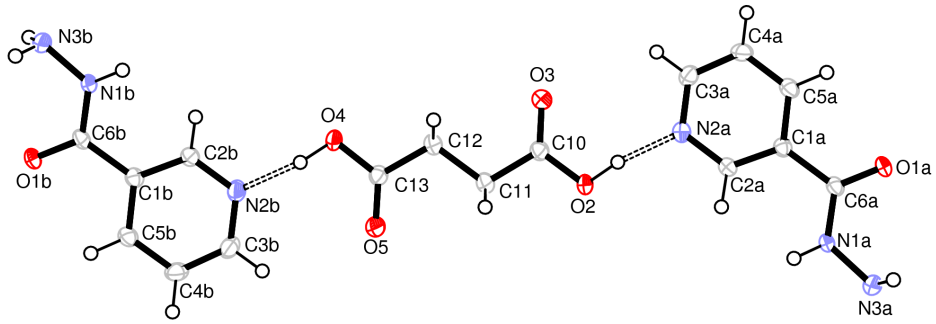


**Figure S5.** The asymmetric unit of **5** showing the atomic numbering scheme and 50% displacement ellipsoids.

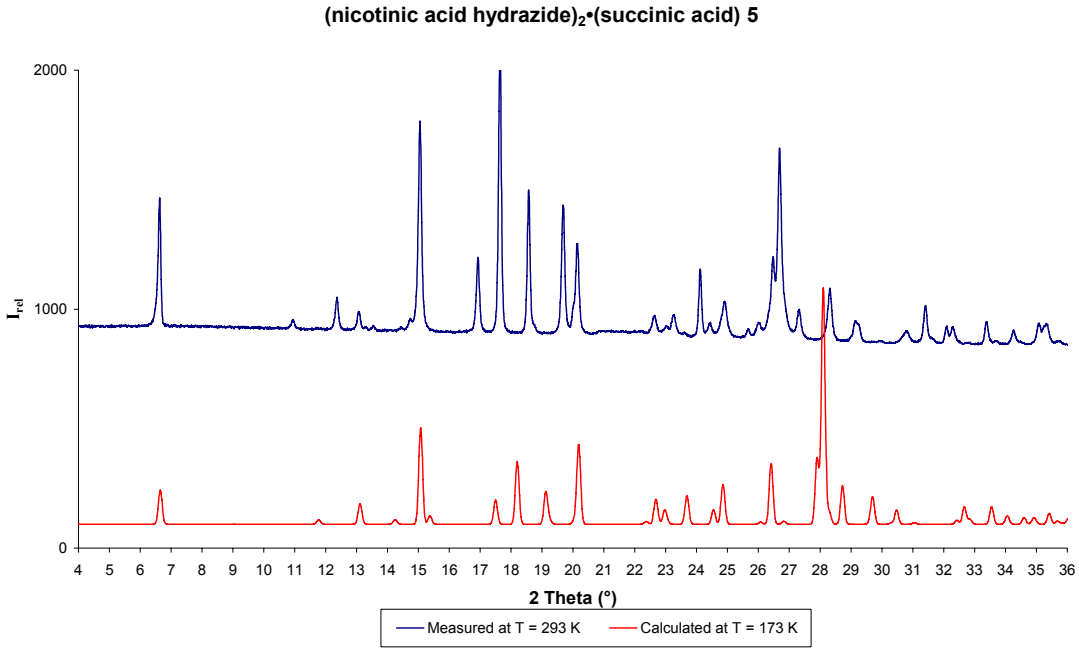


**Figure S6.** Comparative calculated and measured PXRD pattern for **5**.

## Cif Tables for co-crystal (*N*'-(propan-2-ylidene)nicotinohydrazide)$_2$•(sebacic acid) 6:

Table 7. Crystal data and structure refinement for **6**.

| | | |
|---|---|---|
| Identification code | 753786 | |
| Empirical formula | C28 H40 N6 O6 | |
| Formula weight | 556.66 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 5.07070(10) Å | α= 90°. |
| | b = 44.5556(8) Å | β= 94.587(2)°. |
| | c = 6.39920(10) Å | γ = 90°. |
| Volume | 1441.13(4) Å$^3$ | |
| Z | 2 | |
| Density (calculated) | 1.283 Mg/m$^3$ | |
| Absorption coefficient | 0.092 mm$^{-1}$ | |
| F(000) | 596 | |
| Crystal size | 0.36 x 0.24 x 0.2 mm$^3$ | |
| Theta range for data collection | 1.83 to 25.29°. | |
| Index ranges | -5<=h<=6, -52<=k<=53, -7<=l<=7 | |
| Reflections collected | 10132 | |
| Independent reflections | 2595 [R(int) = 0.0259] | |
| Completeness to theta = 25.29° | 99.3 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.98 and 0.96 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2595 / 0 / 189 | |
| Goodness-of-fit on F$^2$ | 0.995 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0806, wR2 = 0.1912 | |
| R indices (all data) | R1 = 0.0834, wR2 = 0.1933 | |
| Largest diff. peak and hole | 0.705 and -0.677 e.Å$^{-3}$ | |

Table 8. Hydrogen bonds for **6** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(2)-H(2)...N(2) | 0.89(5) | 1.80(5) | 2.684(3) | 179(5) |
| C(2)-H(2A)...O(3) | 0.95 | 2.71 | 3.332(3) | 124 |
| N(1)-H(1)...O(1)#2 | 0.86(4) | 2.20(4) | 3.046(3) | 171(3) |
| C(3)-H(3)...O(3)#3 | 0.95 | 2.57 | 3.362(4) | 141 |
| C(4)-H(4)...O(3)#4 | 0.95 | 2.56 | 3.414(4) | 150 |
| C(7)-H(7C)...N(3)#2 | 0.98 | 2.41 | 3.307(3) | 151 |
| C(9)-H(9B)...N(3)#5 | 0.98 | 2.68 | 3.610(4) | 158 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+2 #2 x-1,y,z #3 x,y,z-1 #4 x+1,y,z-1

#5 x-1/2,-y+1/2,z+1/2

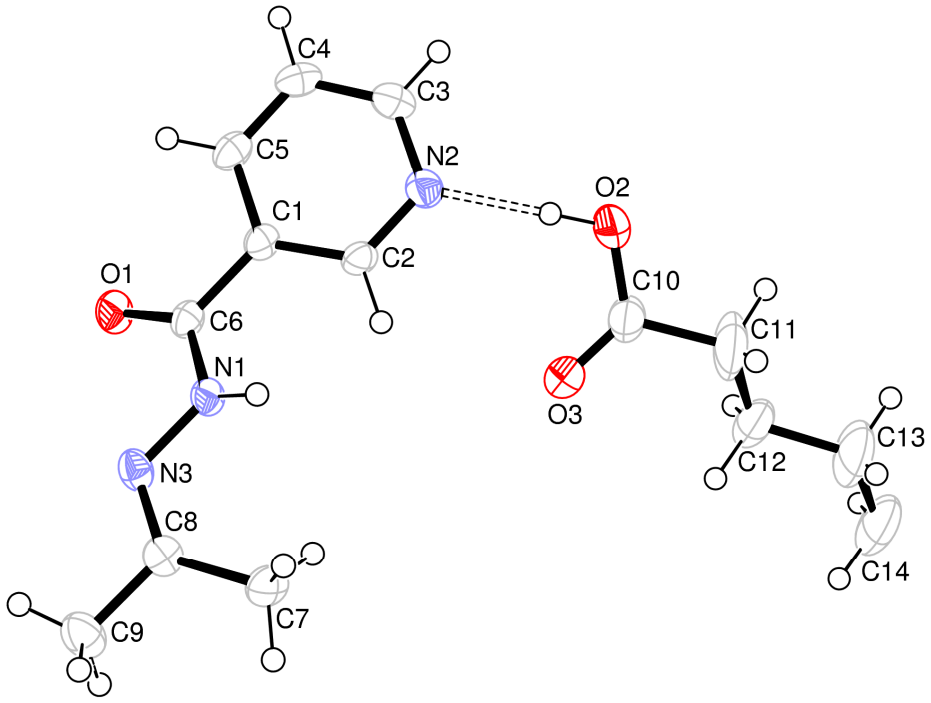


**Figure S7.** The asymmetric unit of **6** showing the atomic numbering scheme and 50% displacement ellipsoids.

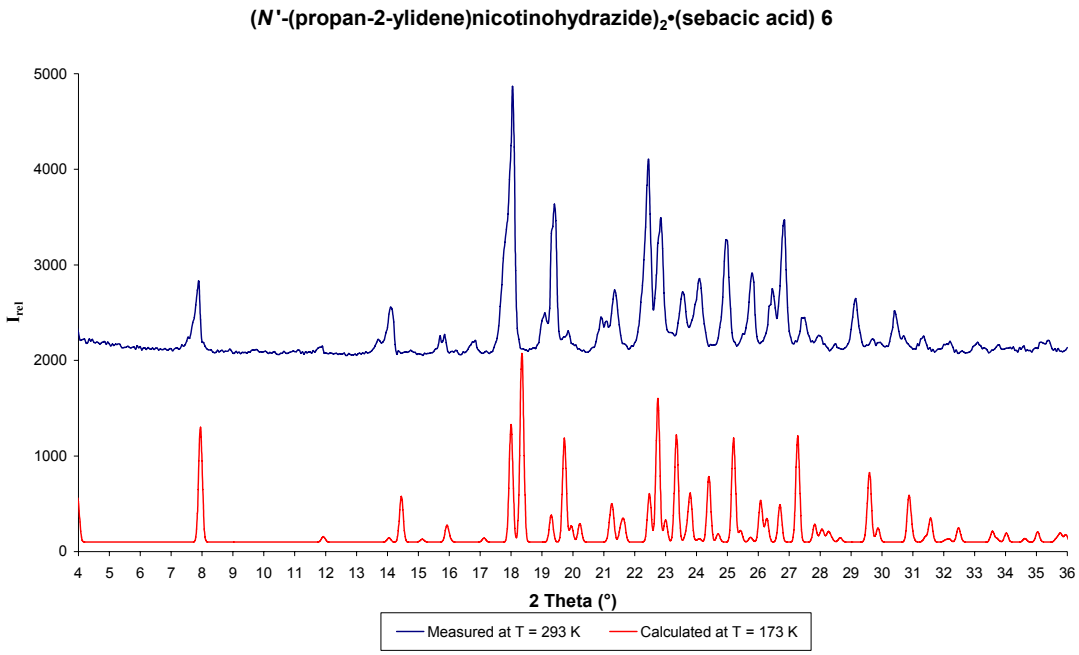


**Figure S8.** Comparative calculated and measured PXRD pattern for **6**.

## Cif Tables for co-crystal (*N*'-(propan-2-ylidene)nicotinohydrazide) 7:

Table 9. Crystal data and structure refinement for **7**.

| | | |
|---|---|---|
| Identification code | 9vnp289_p | |
| Empirical formula | C9 H11 N3 O | |
| Formula weight | 177.21 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/n | |
| Unit cell dimensions | a = 7.4276(15) Å | α= 90°. |
| | b = 17.979(4) Å | β= 116.07(3)°. |
| | c = 7.5801(15) Å | γ = 90°. |
| Volume | 909.2(3) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.295 $Mg/m^3$ | |
| Absorption coefficient | 0.089 $mm^{-1}$ | |
| F(000) | 376 | |
| Crystal size | 0.37 x 0.27 x 0.22 $mm^3$ | |
| Theta range for data collection | 3.20 to 25.50°. | |
| Index ranges | -8<=h<=8, -20<=k<=21, -9<=l<=7 | |
| Reflections collected | 5713 | |
| Independent reflections | 1687 [R(int) = 0.0309] | |
| Completeness to theta = 25.50° | 99.6 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.99 and 0.94 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 1687 / 0 / 123 | |
| Goodness-of-fit on $F^2$ | 1.027 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0425, wR2 = 0.1001 | |
| R indices (all data) | R1 = 0.0648, wR2 = 0.1074 | |
| Largest diff. peak and hole | 0.209 and -0.183 $e.Å^{-3}$ | |

Table 10. Hydrogen bonds for **7** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)...O(1)#1 | 0.91(2) | 1.96(2) | 2.869(2) | 177(2) |
| C(9)-H(9B)...N(2)#2 | 0.98 | 2.73 | 3.685(2) | 167 |

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+1/2,z-1/2 #2 -x+3/2,y-1/2,-z+3/2

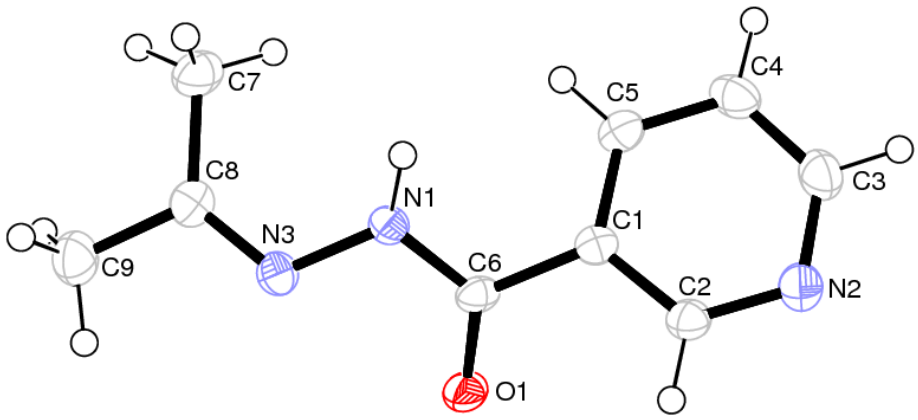


**Figure S9.** The asymmetric unit of **7** showing the atomic numbering scheme and 50% displacement ellipsoids.

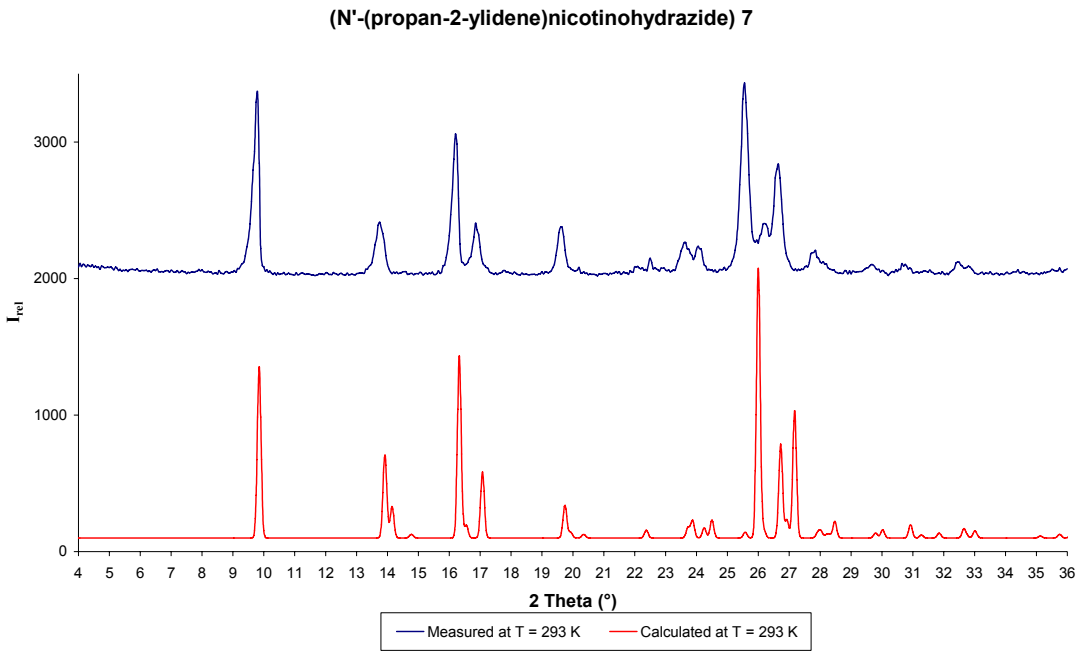


**Figure S10.** Comparative calculated and measured PXRD pattern for **7**.