Supporting Information

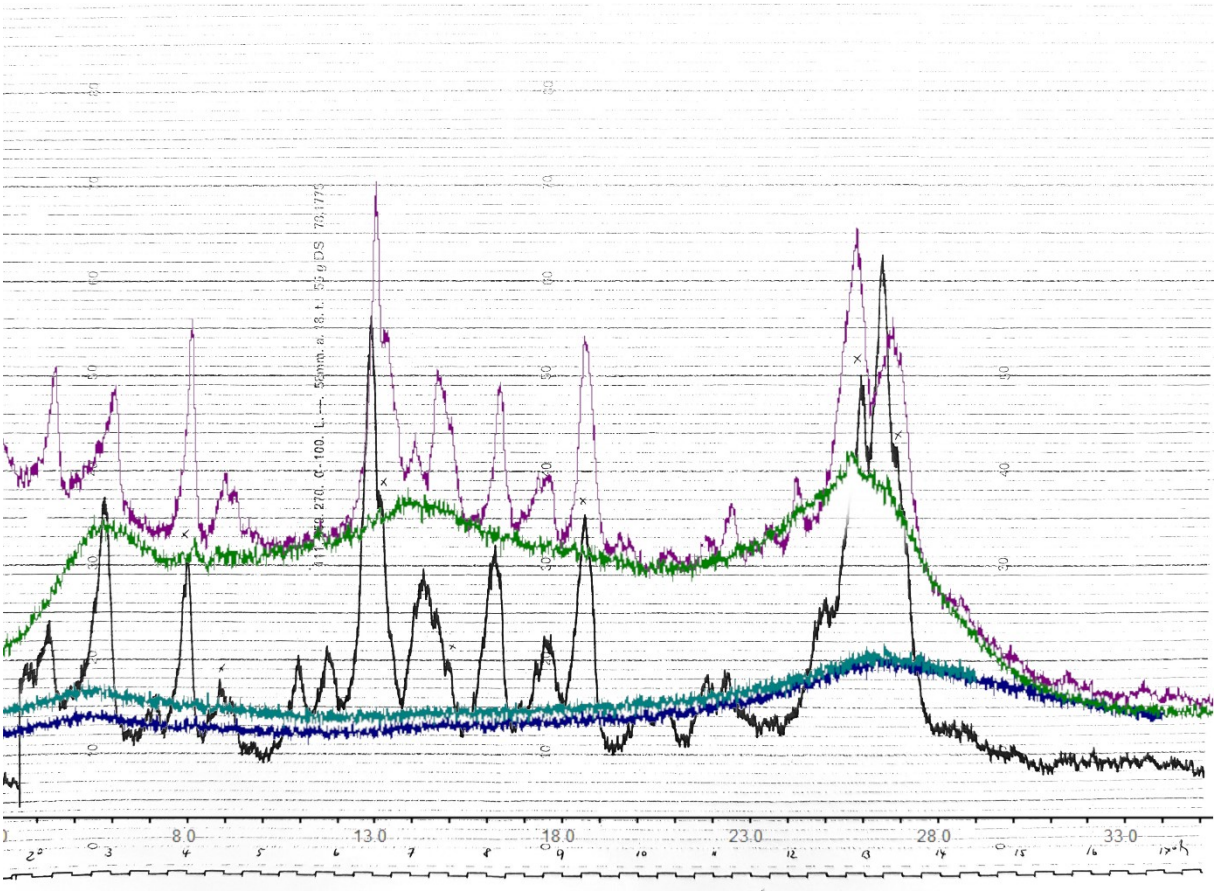

Figure S1: Overlay of the powder pattern showing β-P.R.5 (black) with powder patterns from the synthesis of P.R.5 (violet, green, turquoise and blue). The position of the humps in the amorphous powder patterns suggests that the samples are also β-P.R.5 (green, turquoise and blue).

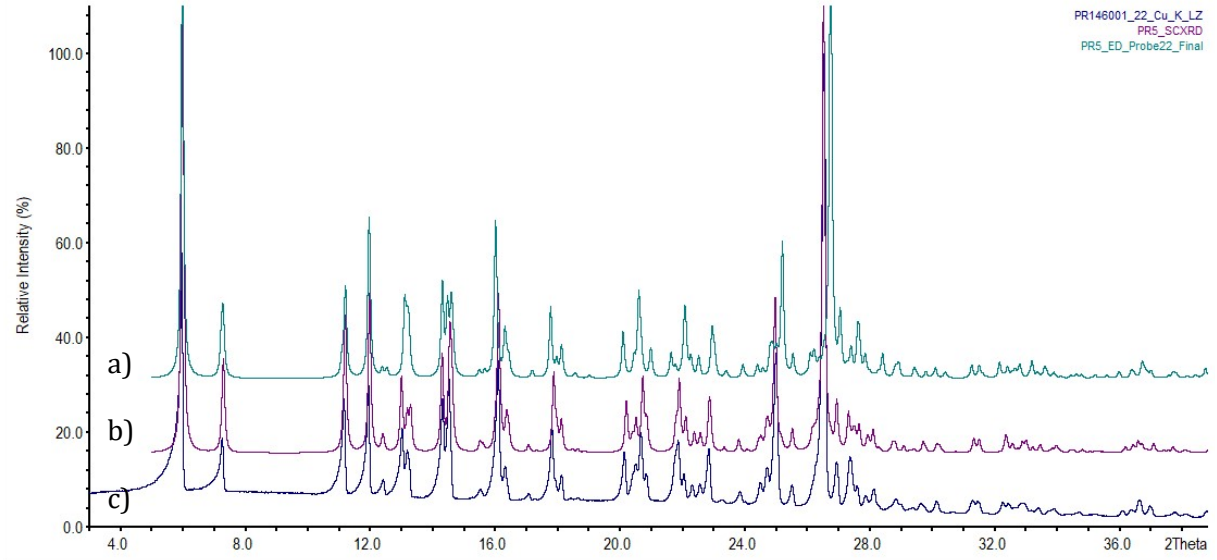

Figure S2: Comparison of the X-ray powder patterns of P.R.5 (a) simulated from the ED single-crystal data measured at -196 °C, (b) simulated from the XRD single-crystal data measured at 25°C ,(c) experimental X-ray powder pattern measured at 25 °C.

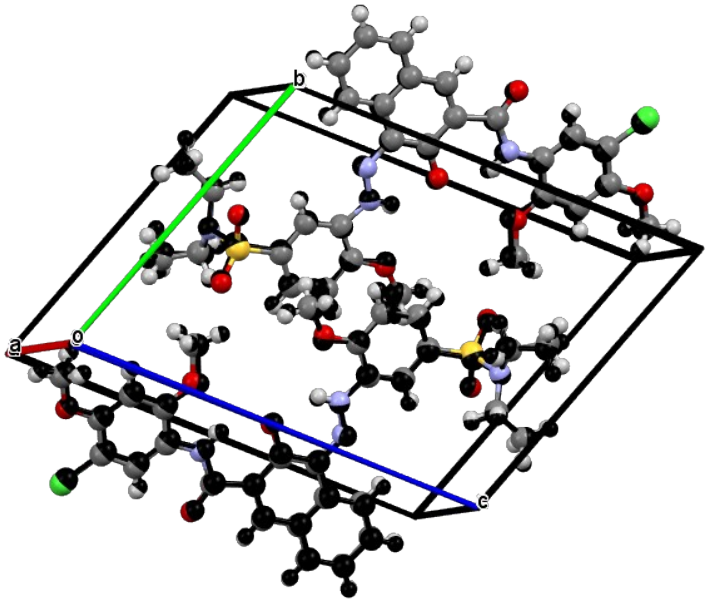

Figure S3: Superposition of the crystal structures from electron diffraction measured at -196 °C (coloured) and single crystal X-ray diffraction measured at 25 °C (black). Cell setting I, view direction [10 1 1]. The unit cell of the 25 °C data (cell setting II) has been transformed with (-1 0 0, -1 -1 0, 0 0 1) to match the setting of the -196 °C data (cell setting I).

Now that we have an X-ray structure and three ED structures, we can compare them. The RMSD between the X-ray structure and the kinematically refined ED structure from one dataset (CSD 2545237) is 0.162 Å; to the kinematically refined structure from the five-dataset merge (CSD 2544539) it is 0.157 Å; and to the dynamically refined structure it is 0.184 Å (2498247). All three differences fall within the tolerances accepted for a "correct structure model."

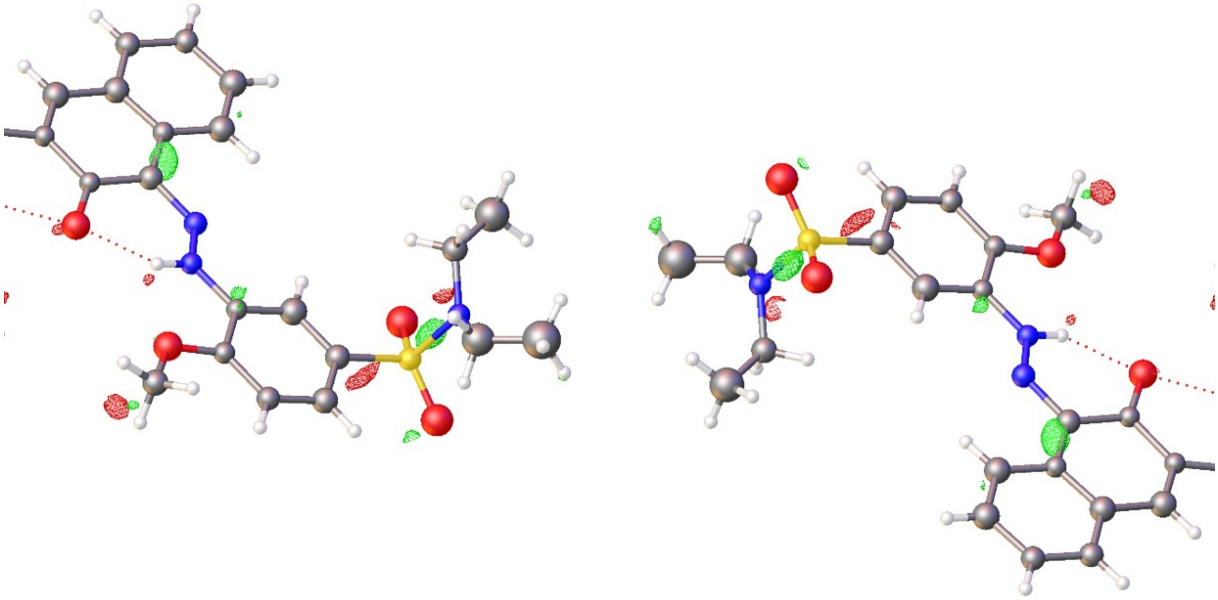

Figure S4: Difference electron density in the region of the void (centre), according to ED data (positive density shown in green, negative density in red, contour level: 0.3 1/A^3).

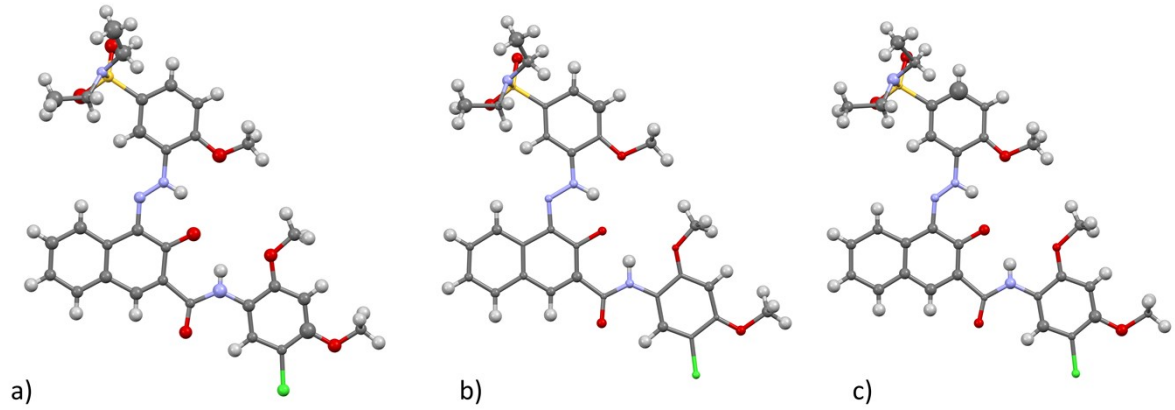

Figure S5: Molecular structure of P.R.5, ED data from a) kinematic refinement, b) dynamic refinement, c) merged data set. The sizes of the atoms correspond to the atomic displacement parameters

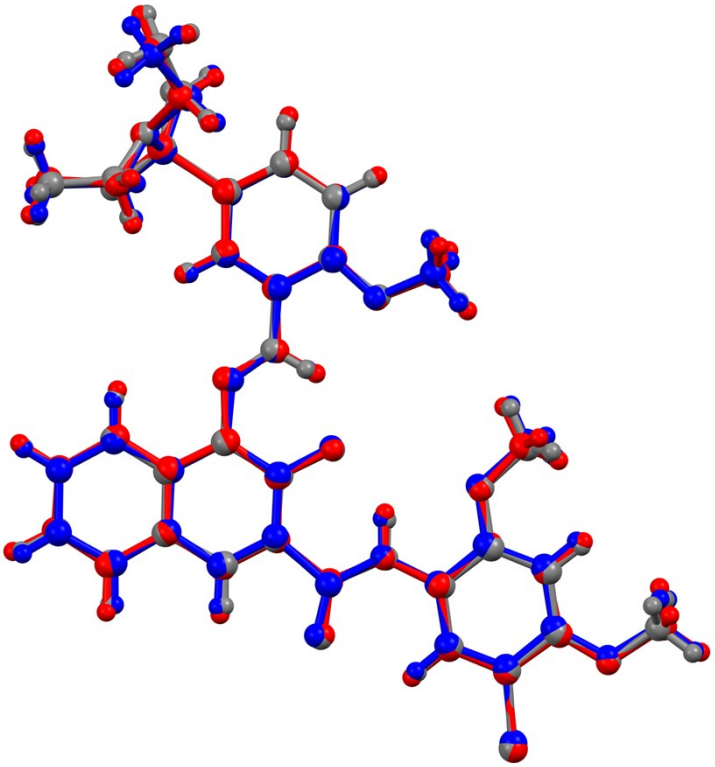

Figure S6: Superposition of the molecular structures from electron diffraction obtained using a kinematic refinement (grey), dynamic refinement (red) and kinematic refinement of the merged data set (blue).

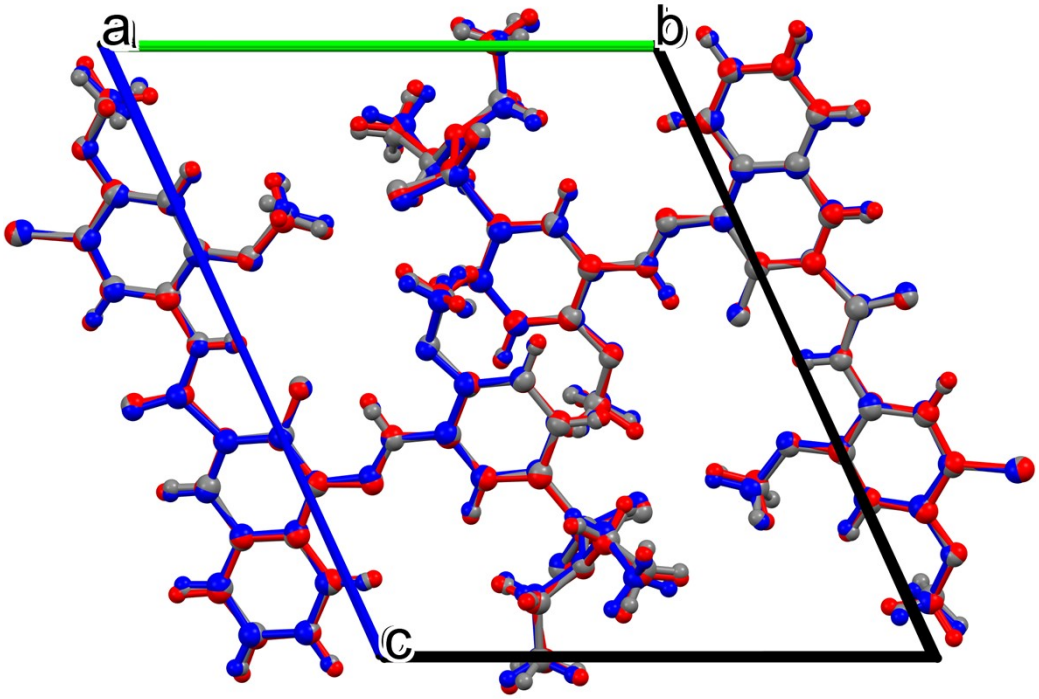

Figure S7: Superposition of the crystal structures from electron diffraction obtained using a kinematic refinement (grey), dynamic refinement (red) and kinematic refinement of the merged data set (blue).

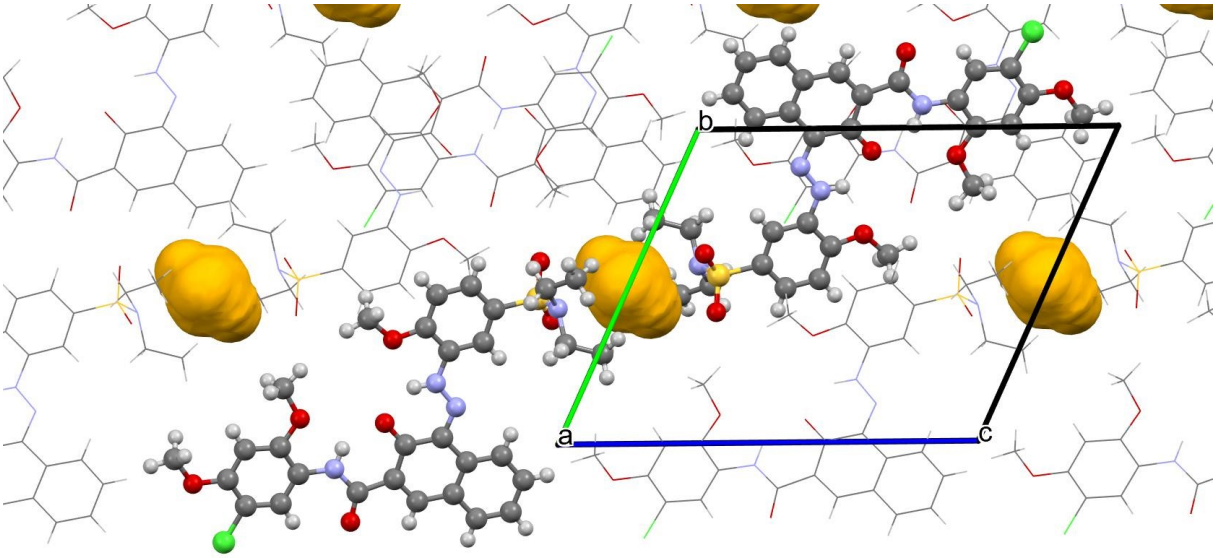

Figure S8: Void (in yellow) between the SO_2NEt_2 groups in the crystal structure of α-P.R.5 (data from SCXRD, cell setting I). Two molecules are highlighted. View direction [-100].

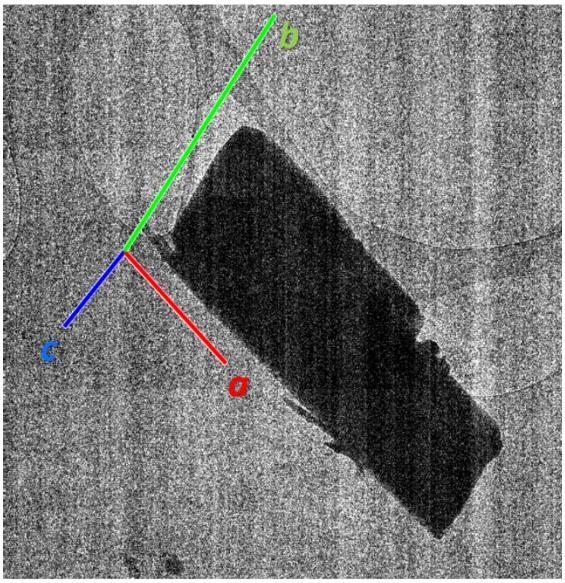

Figure S9: P.R.5, α-phase. Morphology (TEM) and lattice directions (ED). a and b are parallel to the supporting carbon film, c points outwards.

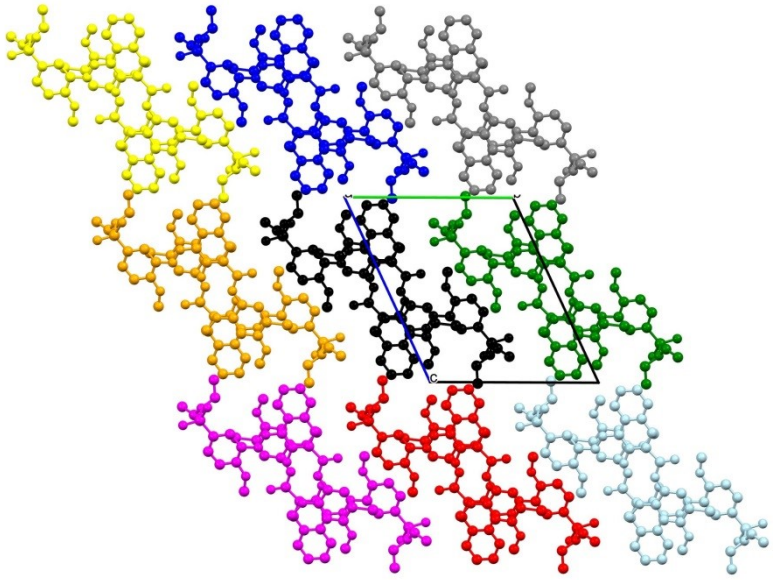

Figure S10: Arrangement of the molecular stacks. View direction [-100]. Hydrogen atoms omitted for clarity.

Void: Calculation method

The size of the void was determined using the tools within the program Mercury from CCDC.

This "void" is defined as the space in the unit cell, which is big enough to hold a spherical "probe" of given radius. As probe radius we used the default value of 1.2 Å. As grid spacing we used the smallest possible value (0.1 Å). Nevertheless, the resulting void volume depends slightly on the unit cell setting. The two different cell settings used for P.R.5 are given in Table 1 in the main text.

The crystal structure determined by ED at -196 °C (cell setting I) shows a void with a volume of 36.4 Å. The X-ray data measured at 295 K result in a void of 37.8 Å^3 when using the cell setting I, and of 40.0 Å^3 when using the unit cell setting II. In all cases, there is only one void per unit cell.

In cell setting I (ED and SCXRD) the void is located at an inversion centre at (0.5, 0.5, 0), in cell setting II at an inversion centre at (0,0,0) (see Figure S11).

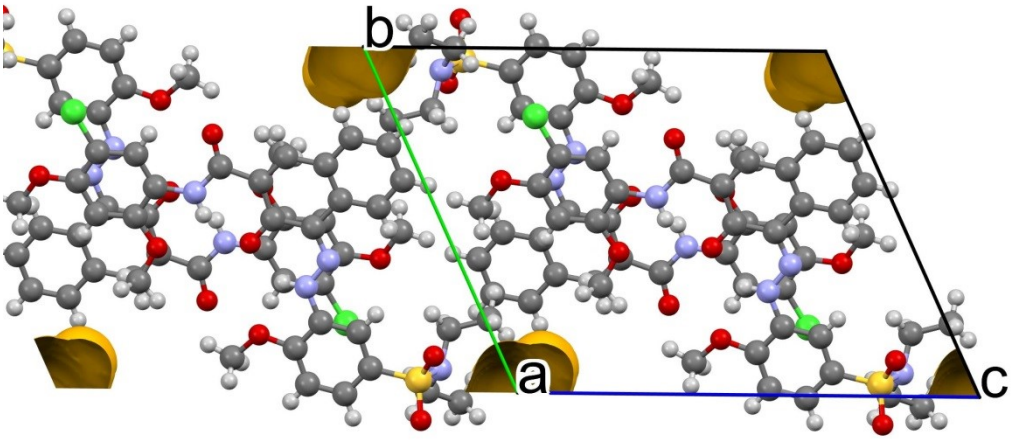

Figure S11: Void in the P.R.5 crystal structure, SCRXD structure, cell setting II.

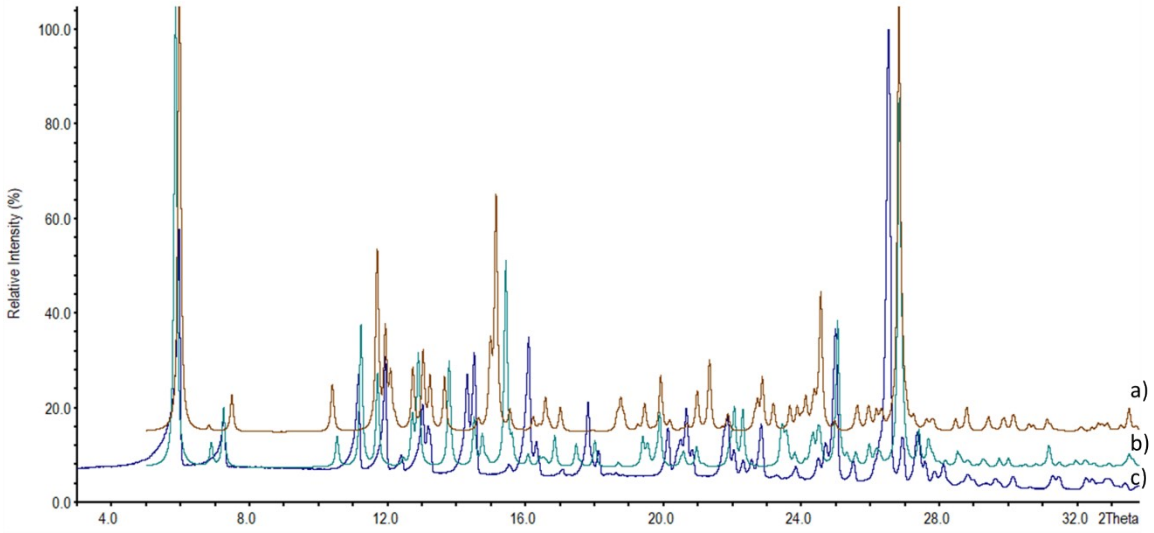

Figure S12: Hypothetical monohydrate and hemihydrate phases of α-P.R.5 a) Simulated powder pattern of a calculated structure containing two water molecules per unit cell. b) Simulated powder pattern of a calculated structure containing one water molecule per unit cell. c) Best powder pattern of P.R.5, sample obtained by heating the commercial product in chlorobenzene.

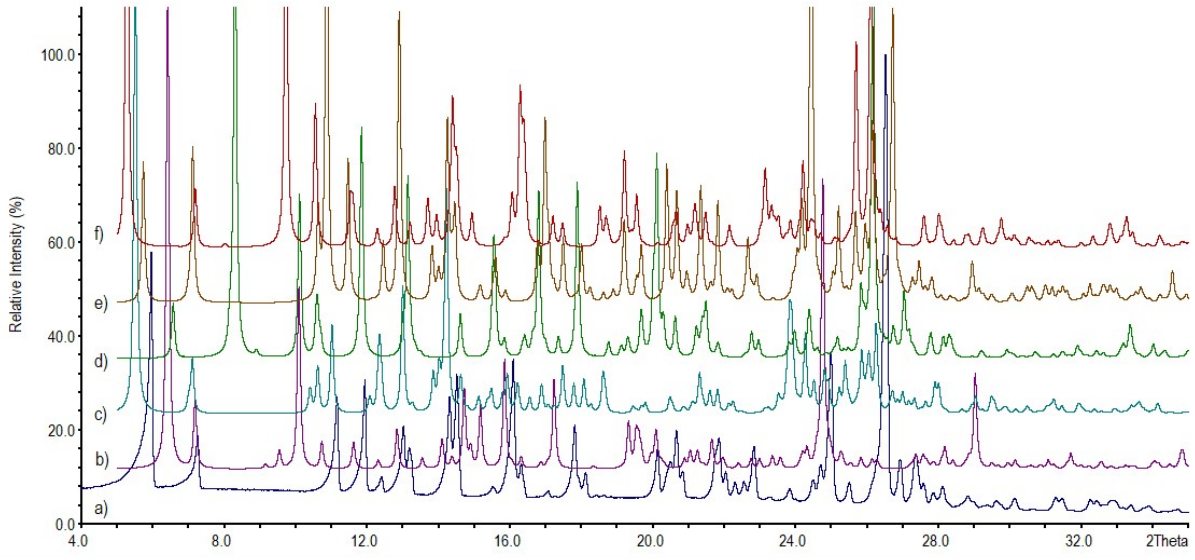

Figure S13: X-ray powder pattern of P.R.5 and mixed crystals a) Best powder pattern of P.R.5. b) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the N,N-dipropyl derivative in a 1:1 ratio. c) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the N-ethyl-N-propyl derivative in a 1:1 ratio. d) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the N-methylpiperazine derivative in a 1:1 ratio. e) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the morpholene derivative in a 1:1 ratio. f) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the piperidine derivative in a 1:1 ratio.

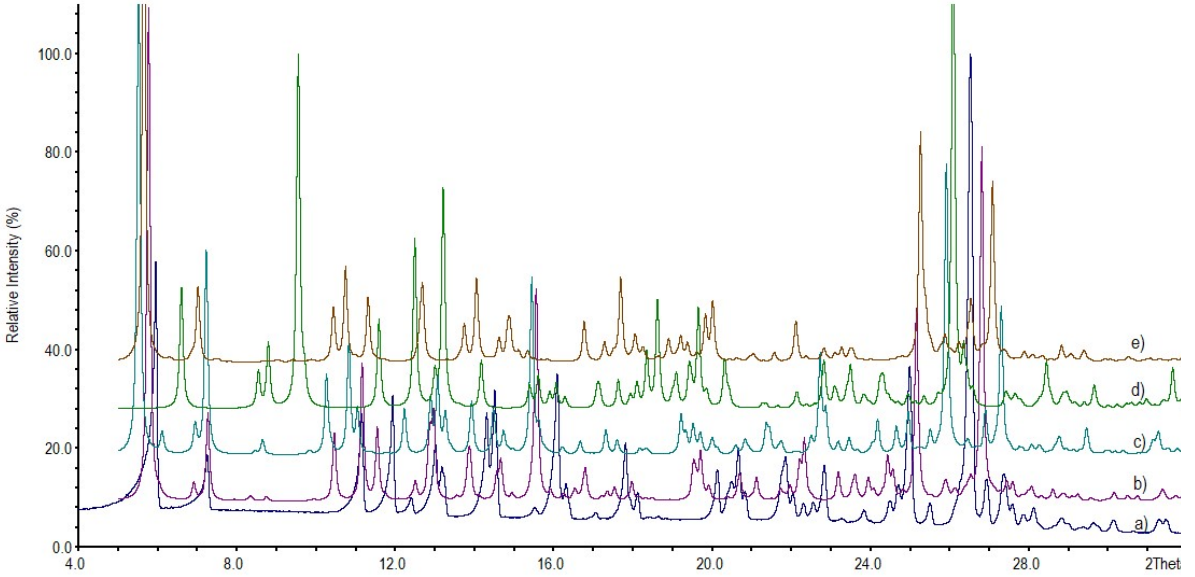

*Figure S14: X-ray powder pattern of P.R.5 and mixed crystals a) Best powder pattern of P.R.5. b) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the phenylamide derivative in a 3:1 ratio. c) Simulated powder pattern of a calculated mixed crystal containing P.R.5, iso-P.R.5 (**3**), the phenylamide derivative (**2**) and P.R.146 in a 1:1:1:1 ratio. d) Simulated powder pattern of a calculated mixed crystal containing P.R.5 and the phenylamide derivative (**2**) in a 1:1 ratio. e) Simulated powder pattern of a calculated mixed crystal containing P.R.5, iso-P.R.5 (**3**), the phenylamide derivative (**2**) and P.R.146 in a 9:3:3:1 ratio.*

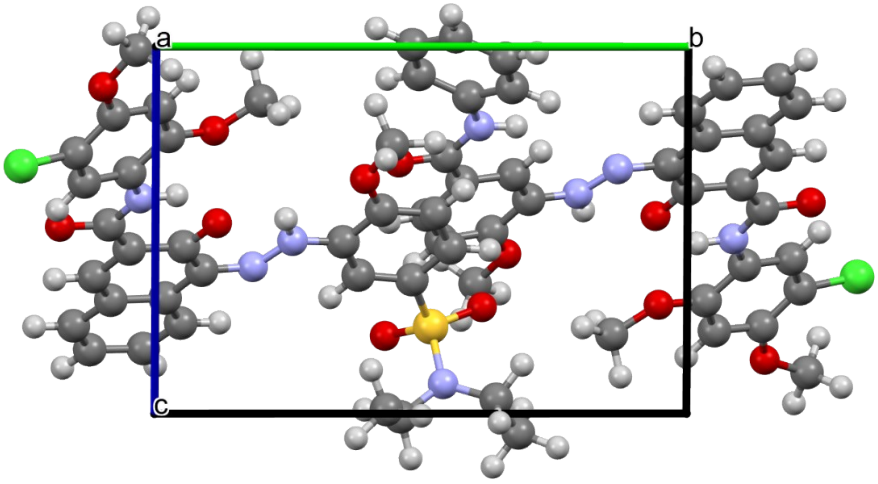

Figure S15: Modelled crystal structure for a mixed crystal containing P.R.5 and the phenylamide derivative in a 1:1 ratio (shown coloured by atom type).

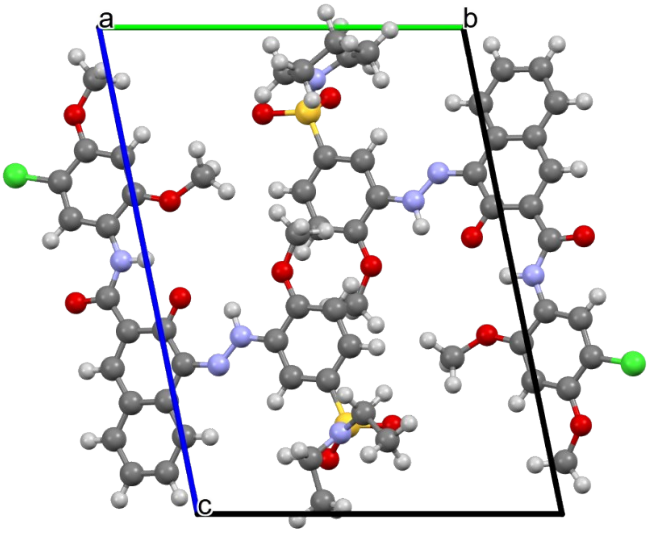

Figure S16: Modelled crystal structure for a mixed crystal containing P.R.5 and the piperidine derivative in a 1:1 ratio (shown coloured by atom type).

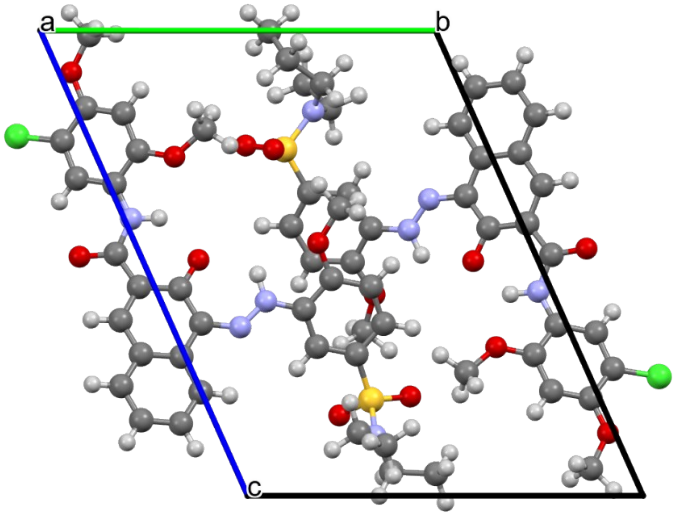

Figure S17: Modelled crystal structure for a mixed crystal containing P.R.5 and the N-ethyl-N-propyl derivative in a 1:1 ratio (shown coloured by atom type).

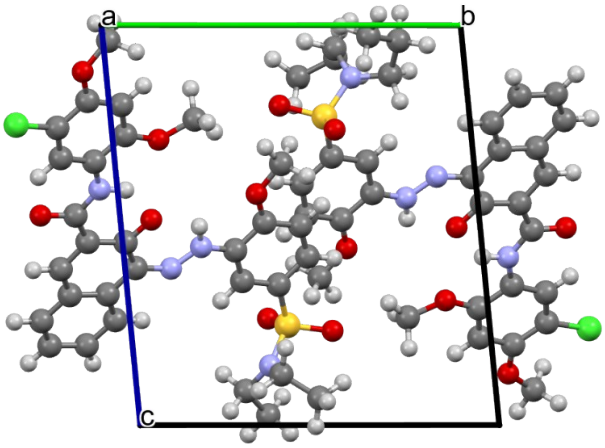

Figure S18: Modelled crystal structure for a mixed crystal containing P.R.5 and the N,N-dipropyl derivative in a 1:1 ratio (shown coloured by atom type).

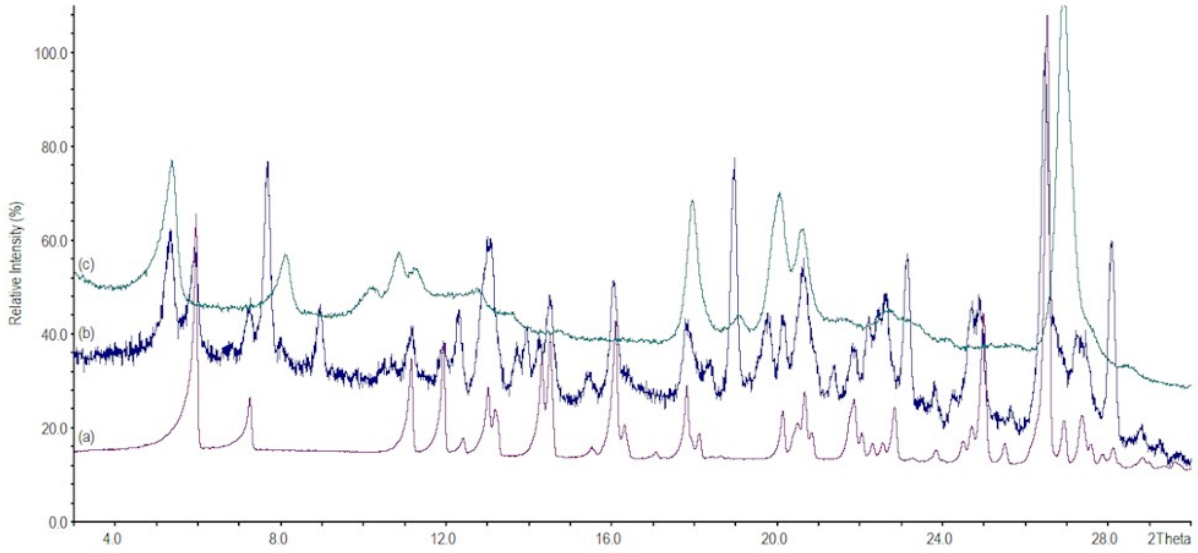

*Figure S19: Powder patterns of (a) P.R.5, (b) A mixed crystal of a cosynthesis of P.R.5 and of (**2**) in a 1:1 ratio and a subsequent trichlorobenzene finish, (c) P.R.146.*