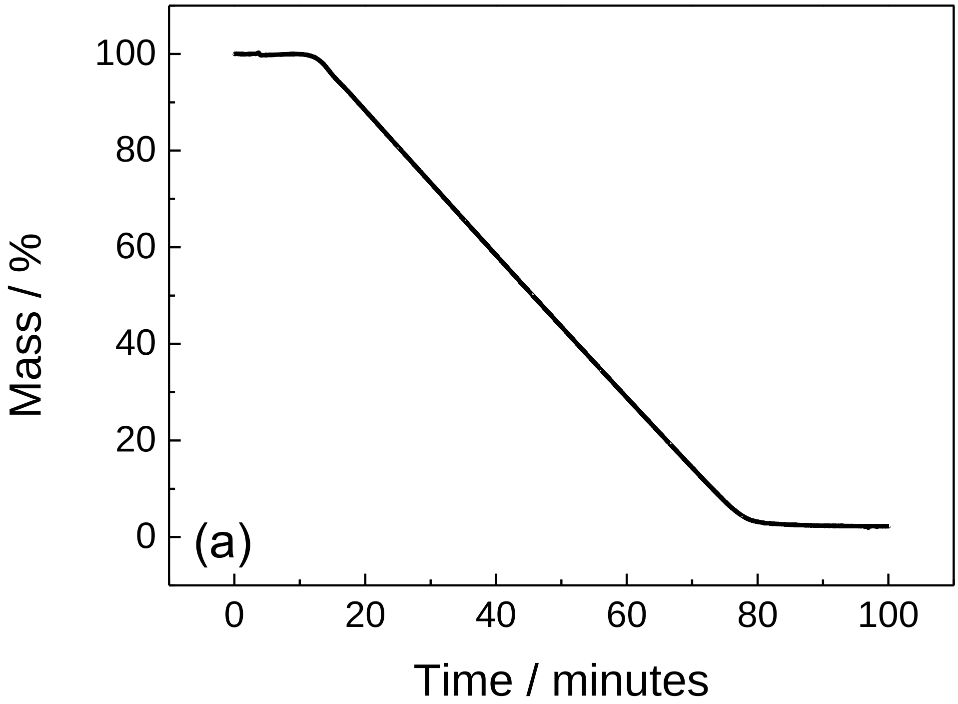


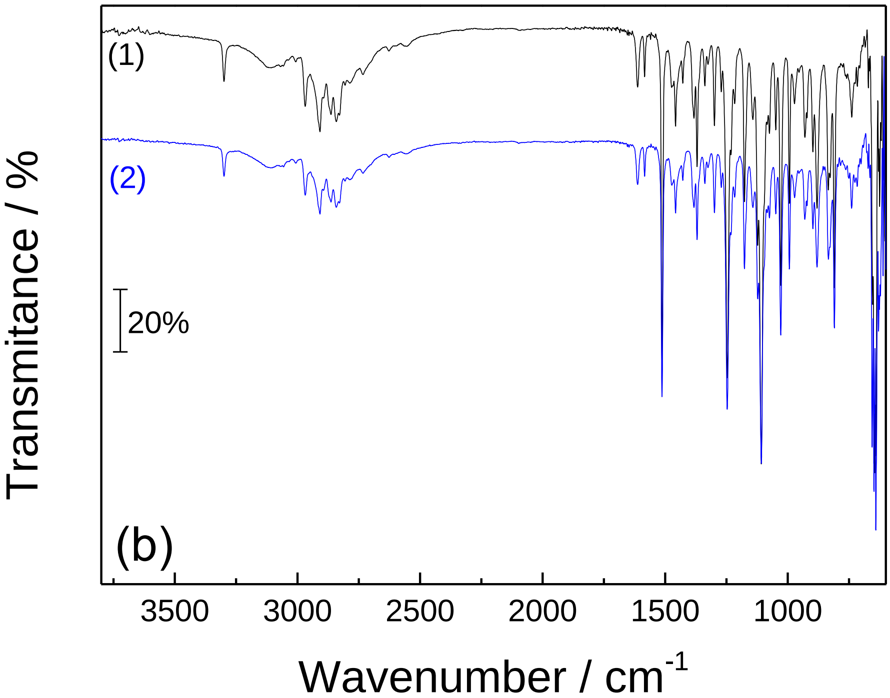


Figure S1. (a) TG curve of metoprolol, sample mass of 0.99 mg, in open *α*-alumina crucible, dry air (50 mL min^{-1}), heated up to 150 °C at 10 °C min^{-1} and kept in isotherm during 100 min; (b) (1) FTIR spectra of metoprolol base and (2) sublimated material collected in a glass tube.

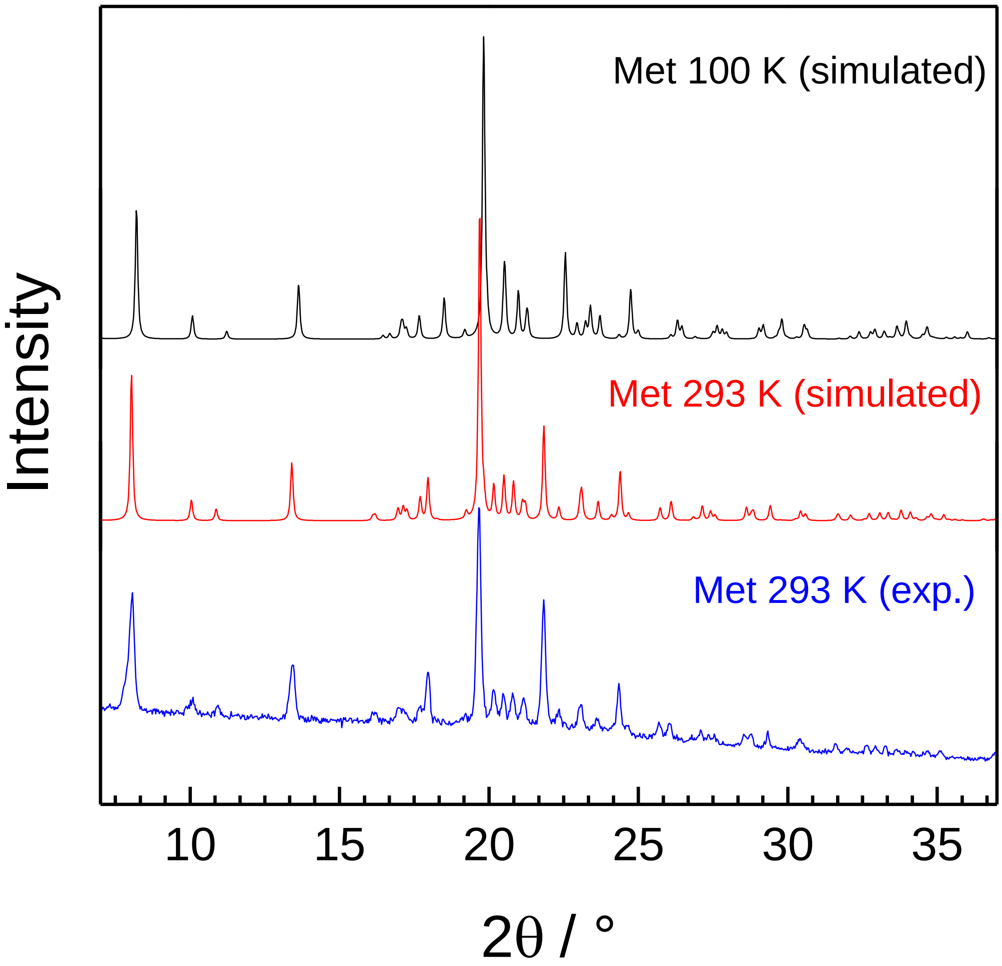


Figure S2. X-ray powder diffractogram of metoprolol, form I, simulated at 100 K [CCDC 1882466, Rossi, et. al., 2019] in comparison with form I experimental and simulated powder diffractograms (CCDC 1883843) at room temperature.

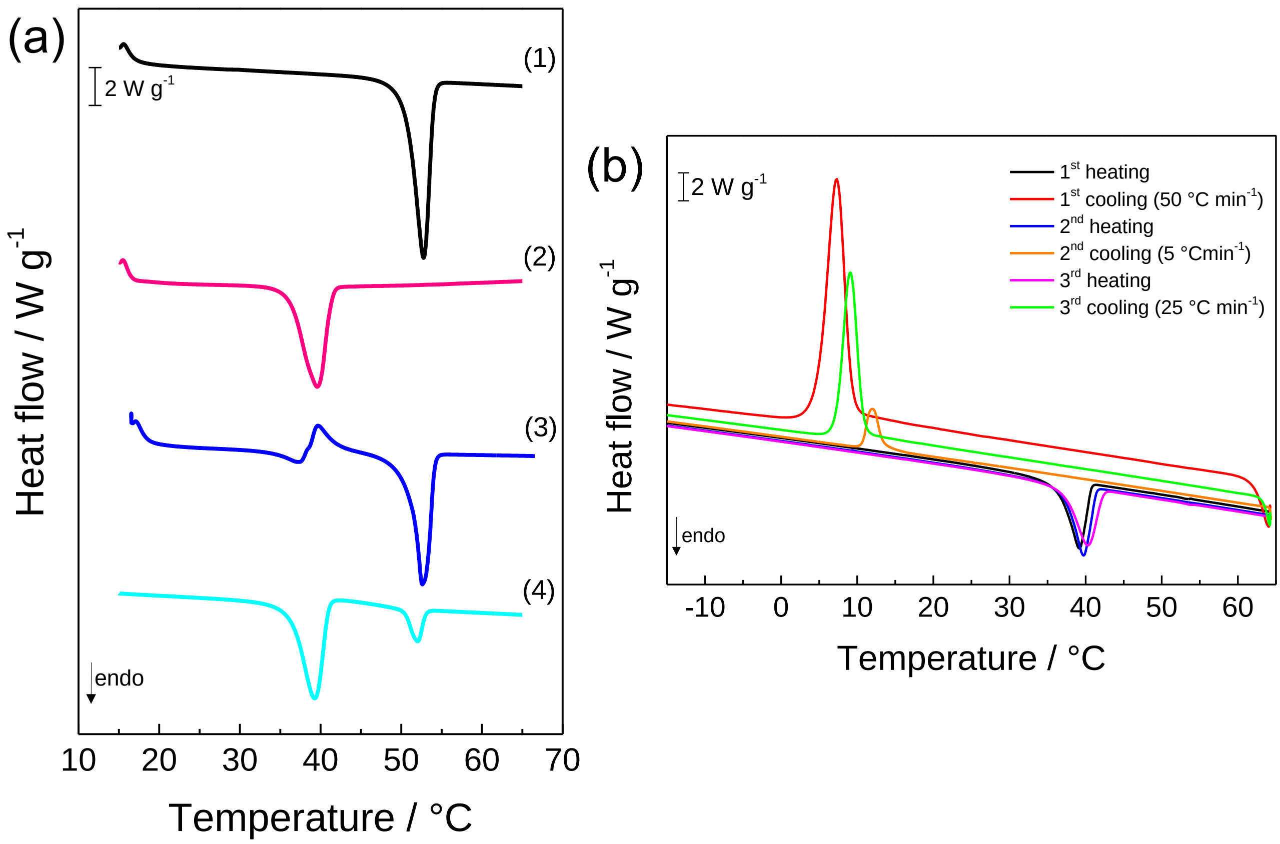


Figure S3. Examples of metoprolol DSC curves: (a) Heating runs: (1) first heating; (2) after cooling at 5 °C min^{-1} ; (3) after cooling for 2h30 on the fridge; (4) after another cooling on DSC at 5 °C min^{-1}; and (b) other sample with subsequent cycles: at heating rate of 10 °C min^{-1} and different cooling hates: 50 °C min^{-1} on the 1st cooling, 5 °C min^{-1} on the 2nd cooling and 25 °C min^{-1} on the 3rd cooling.

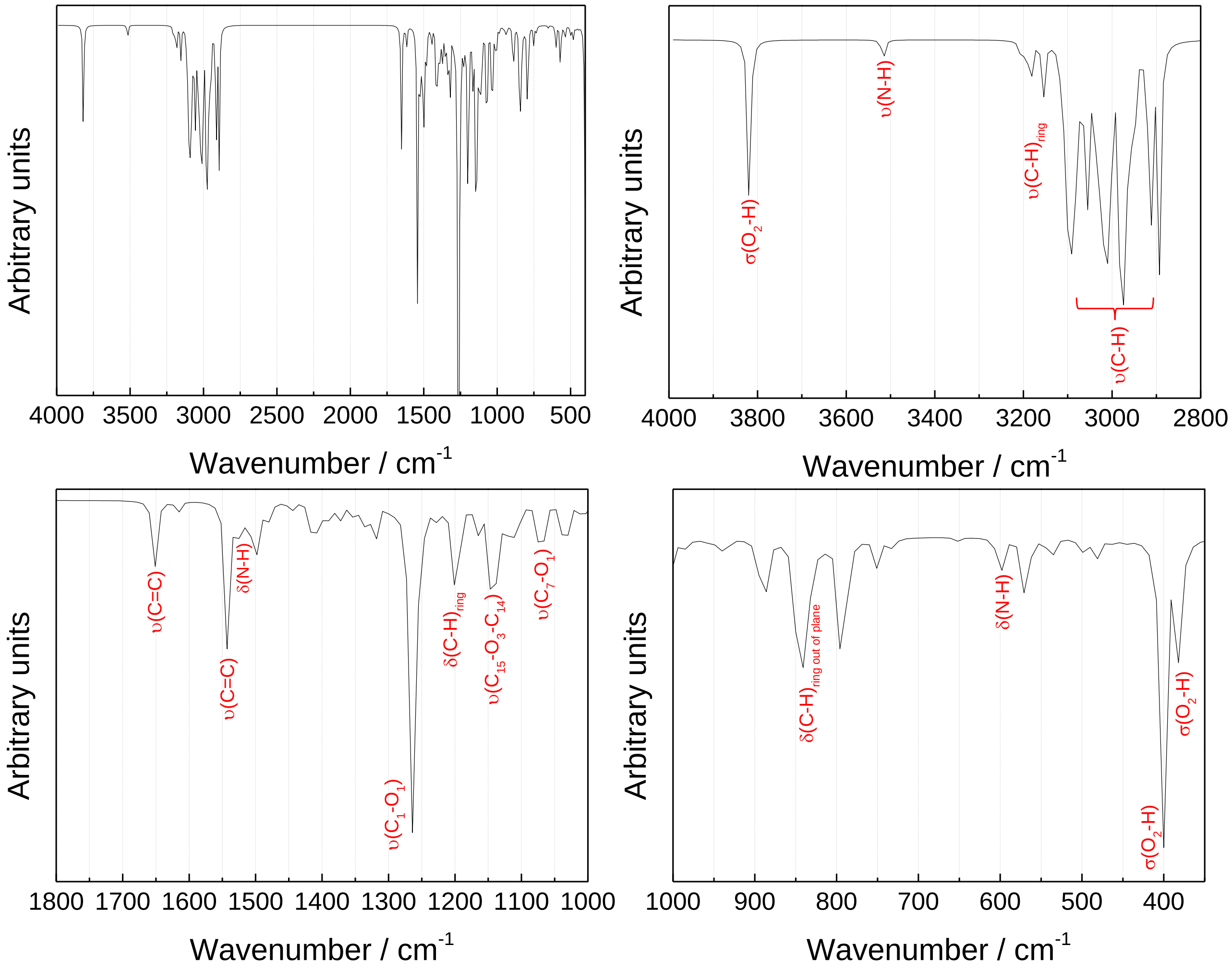


Figure S4. Simulated FTIR spectrum for metoprolol isolated molecule.

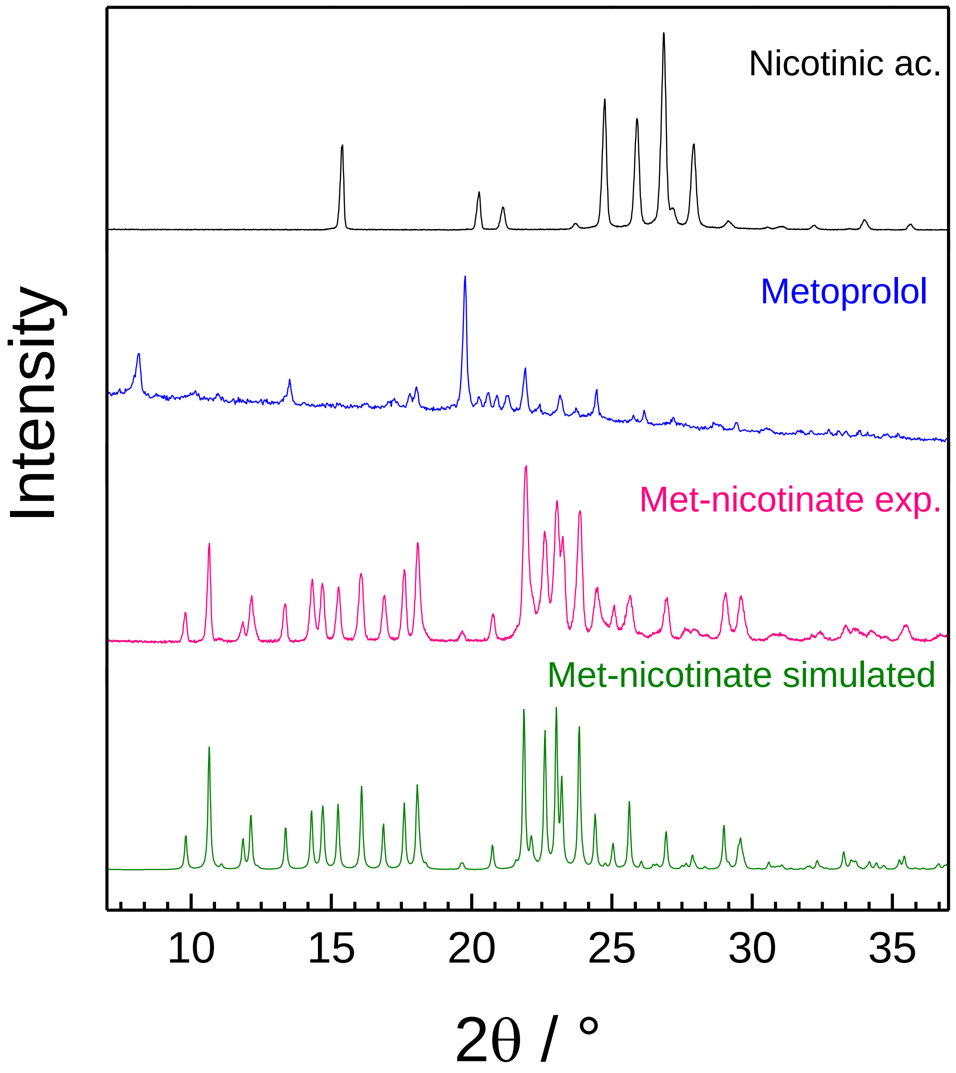


Figure S5. X-ray powder diffractograms of nicotinic acid, metoprolol base (Form I), and metoprolol nicotinate experimental and simulated.

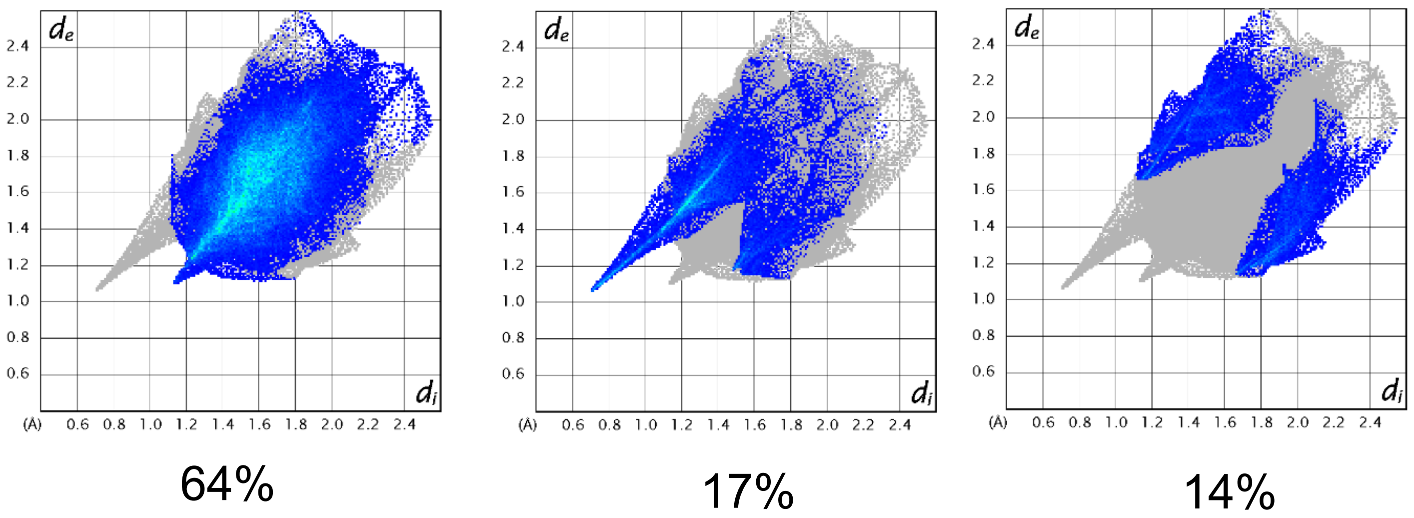


Figure S6. Fingerprint plots for the metoprolol cation in metoprolol nicotinate broken down into contributions from H···H (left), H···O (middle) and H···C (right) close contacts.

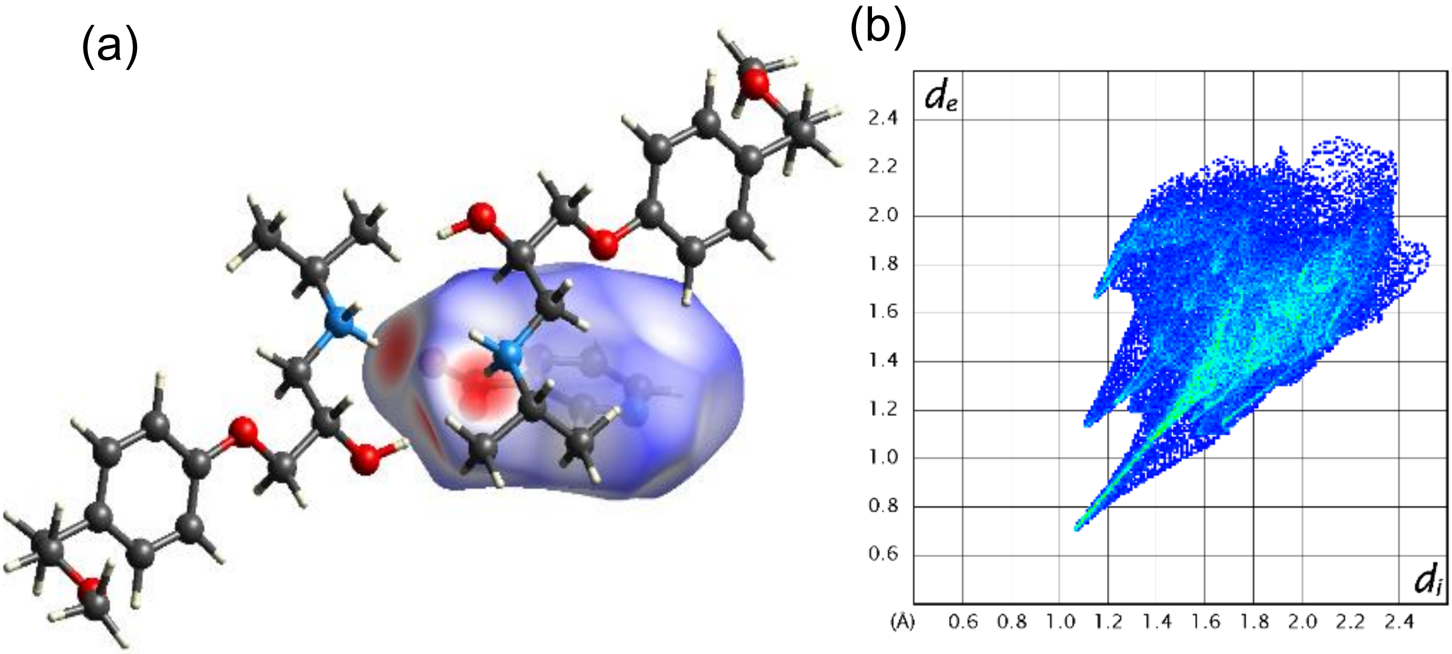
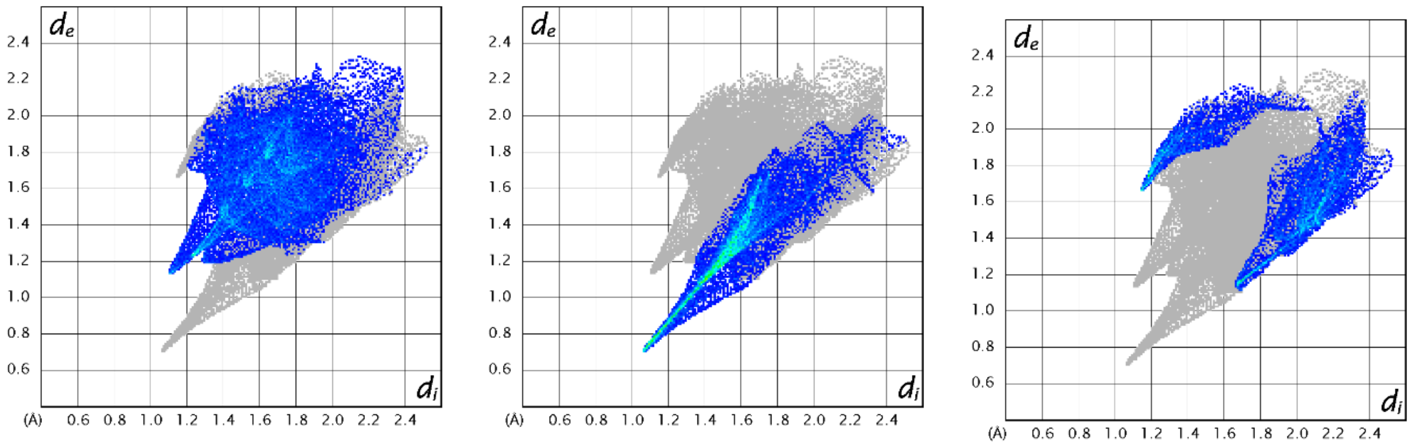


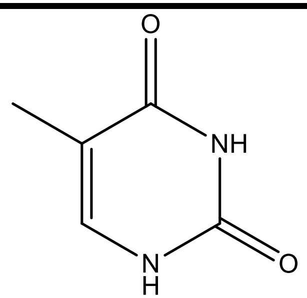
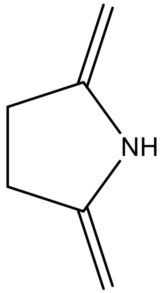
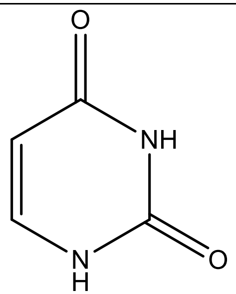
Figure S7. (a) d_{norm} surfaces of the nicotinate anion in the metoprolol nicotinate crystal lattices. Neighboring counterions associated with close contacts are also shown; (b) Fingerprint for the nicotinate anion in metoprolol nicotinate.

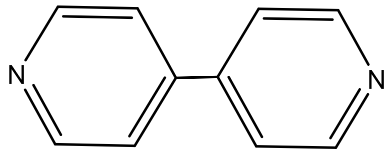
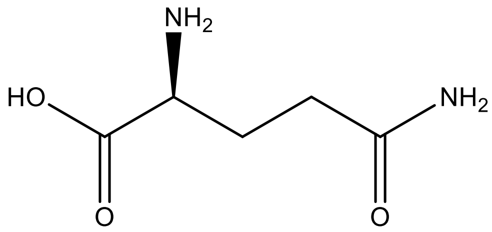
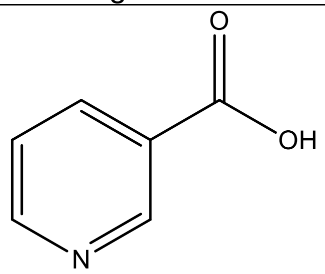
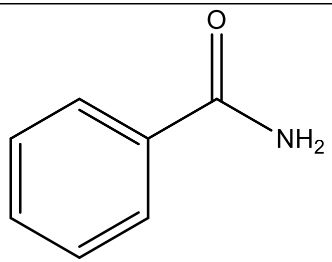
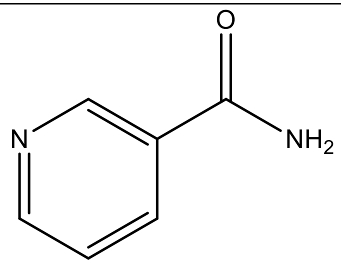


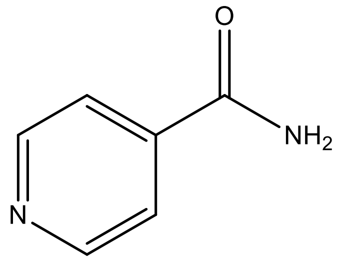
41% 25% 20%

Figure S8. Fingerprint plots for the nicotinate anion in metoprolol nicotinate broken down into contributions from H···H (left), H···O (middle) and H···C (right) close contacts.

Table S1. Molecular structure of the coformers tested in this work

Coformador	**pka**	**Brand**	**Result**
 thymine	9.7	Sigma >99.5%	x
 succinamide	9.5	Sigma >99%	x
 uracil	9.4	Fluka ≥99%	x

 4,4-bipiridil	4.3	Fluka >99%	x
 L-glutamine	9.1		x
 Nicotinic acid	2.0 4.9	Sigma ≥99%	Salt
 benzamide	23.3	Sigma >98%	x
 nicotinamide	3.4	Sigma >99%	x

 isonicotinamide	3.7	Sigma >99%	x