Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Virtual assessment achieved two binary cocrystals based on a liquid and a solid pyridine derivative with modulated thermal stabilities

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PXRD patterns

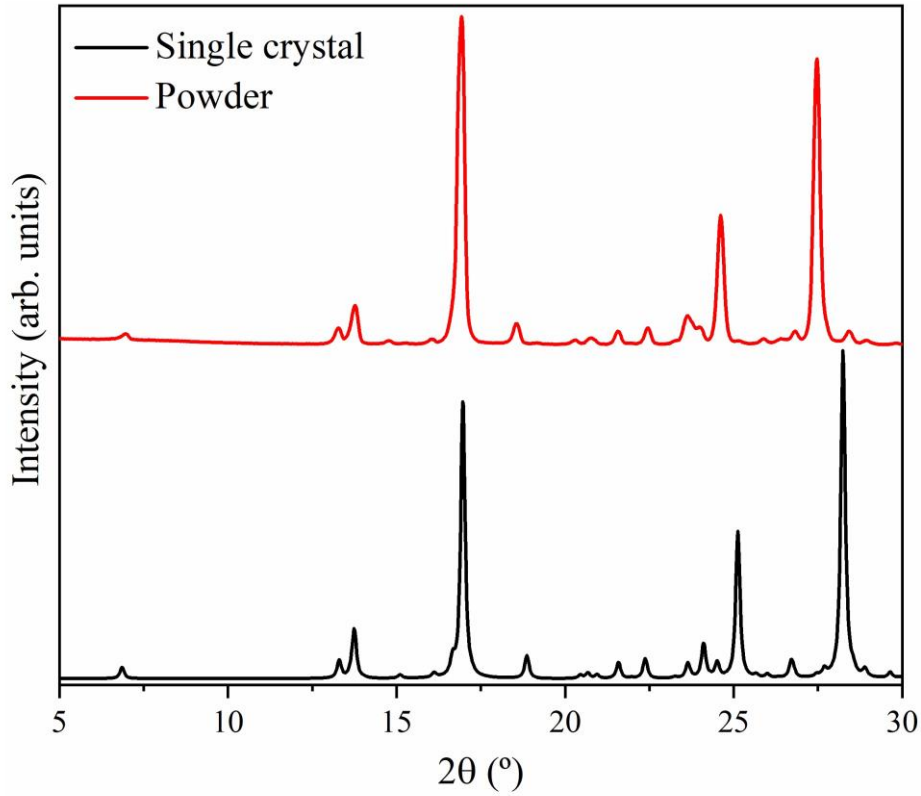


Figure S1. XRD pattern from the single crystal collected data at 100 K and powder XRD pattern at 298 K of cocrystal (HPip)(4-Acpy) (**1**).

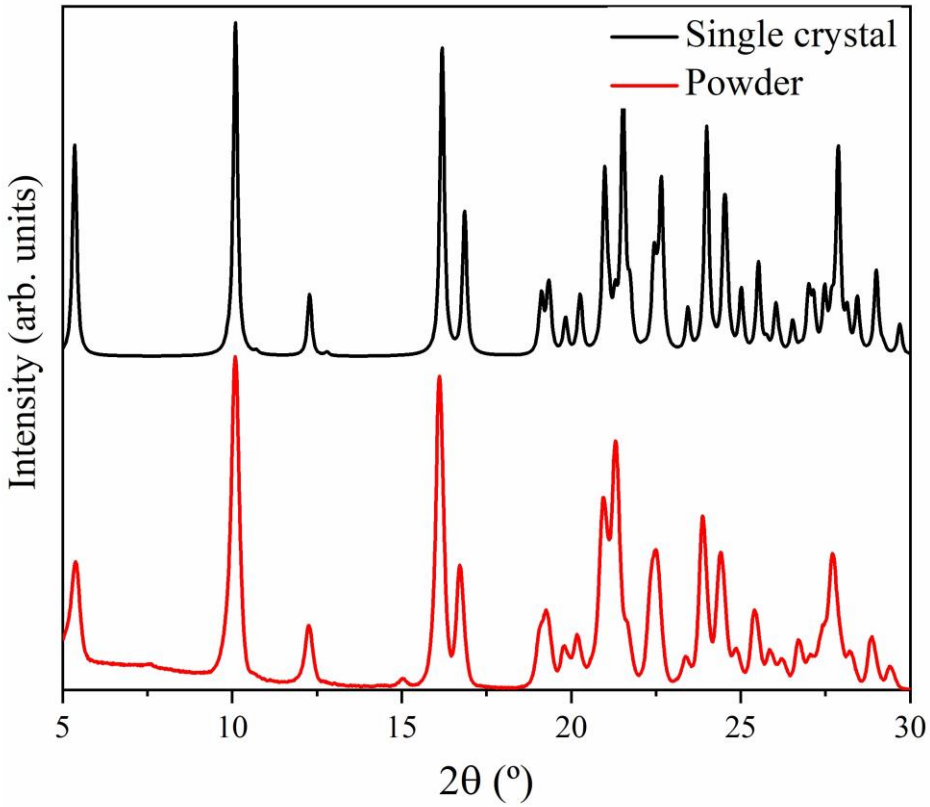


Figure S2. XRD pattern from the single crystal collected data at 100 K and powder XRD pattern at 298 K of cocrystal (HACA)(Pdon) (**2**).

FTIR-ATR and NMR spectroscopies

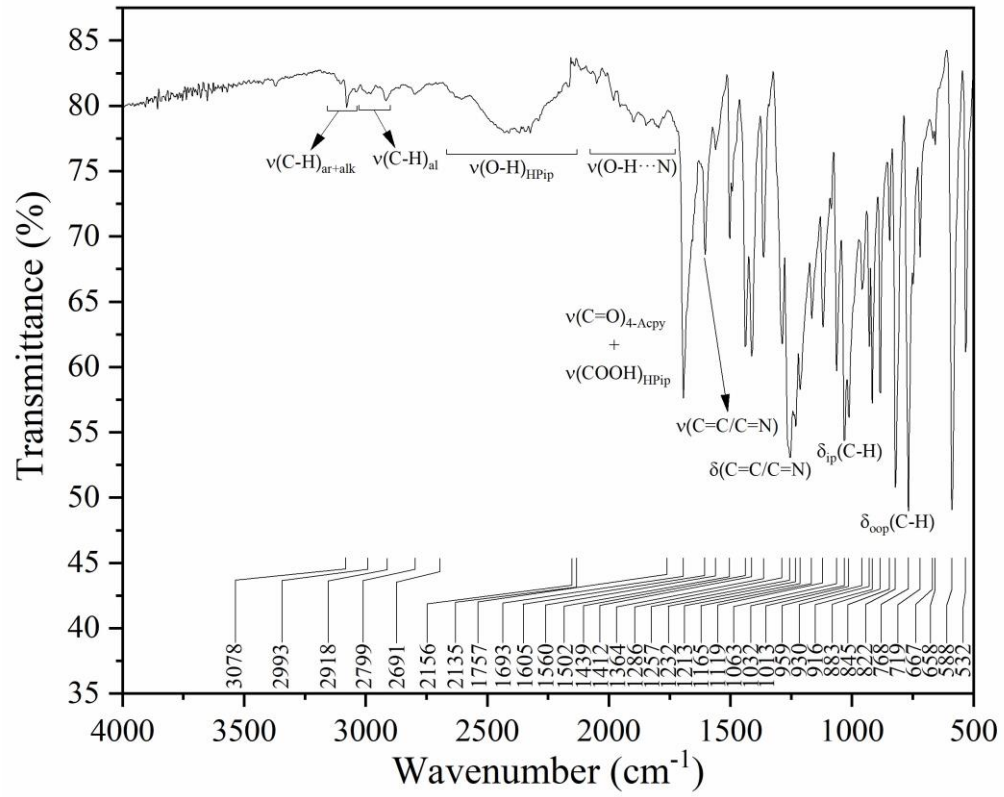


Figure S3. FTIR-ATR spectrum of cocrystal (HPip)(4-Acpy) (**1**).

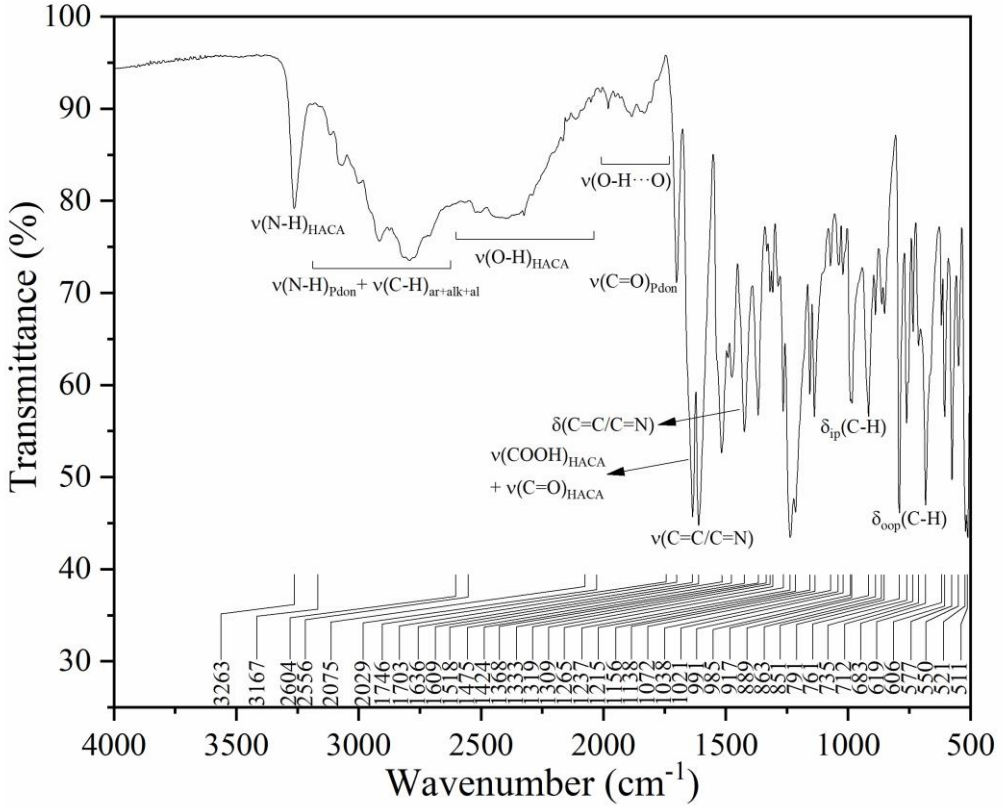


Figure S4. FTIR-ATR spectrum of cocrystal (HACA)(Pdon) (**2**).

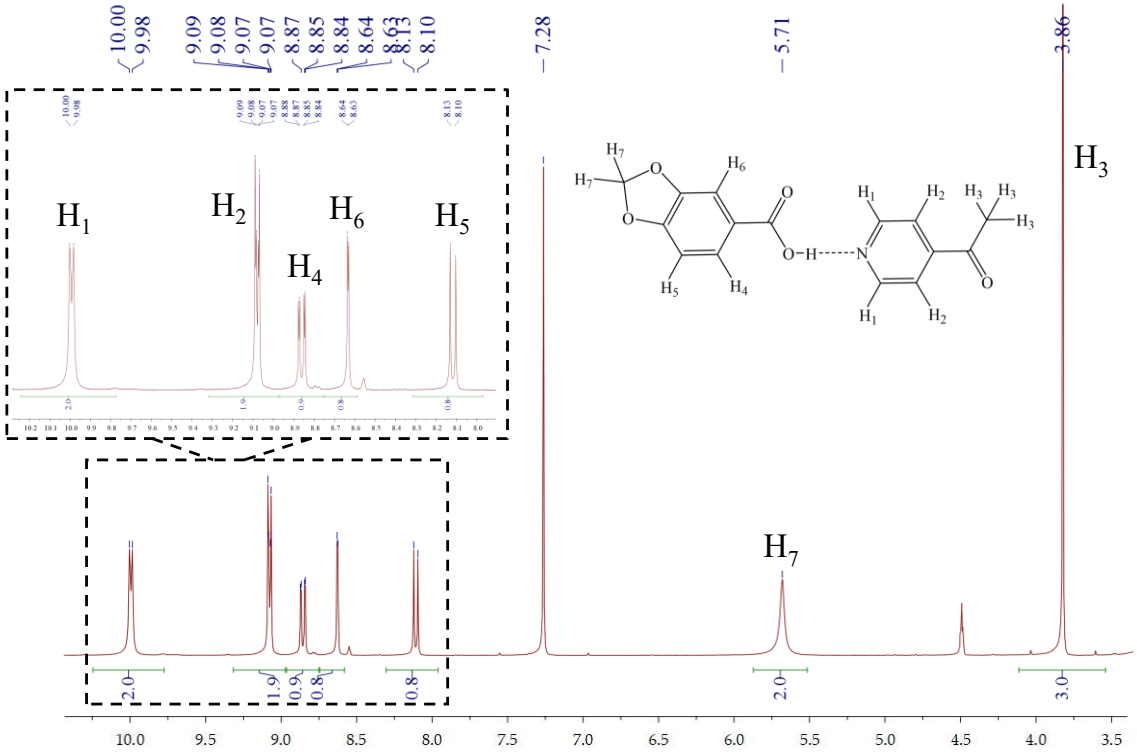


Figure S5. ^{1}H NMR spectrum of cocrystal (HPip)(4-Acpy) (**1**) recorded at 298 K in CD_3OD.

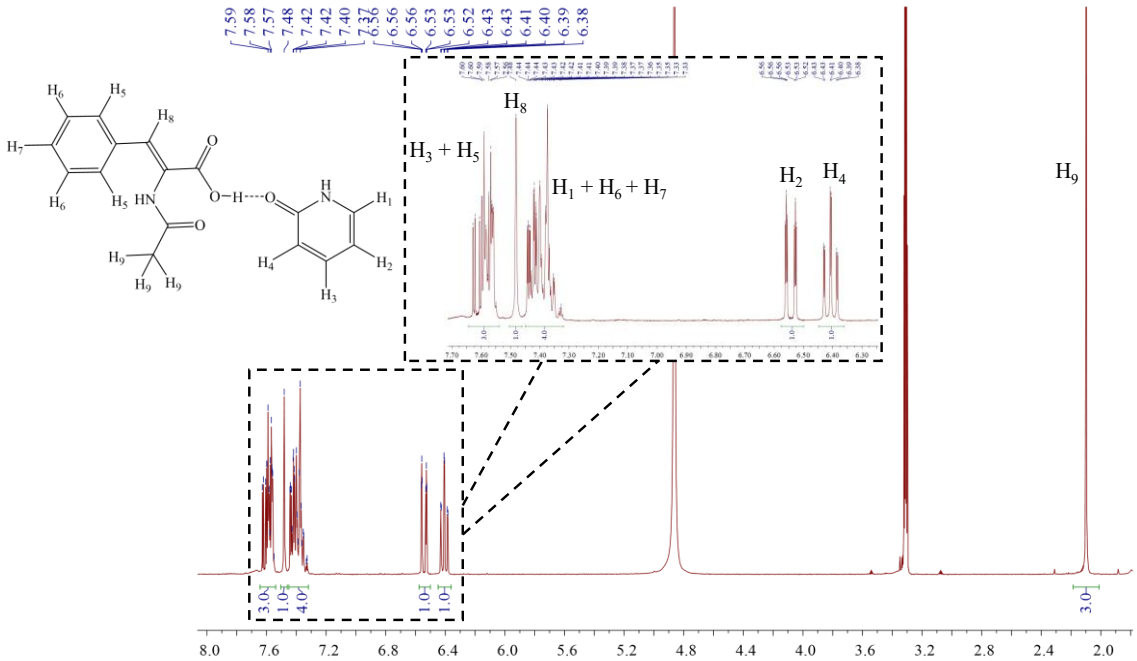


Figure S6. ^{1}H NMR spectrum of cocrystal (HACA)(Pdon) (**2**) recorded at 298 K in CD_3OD.

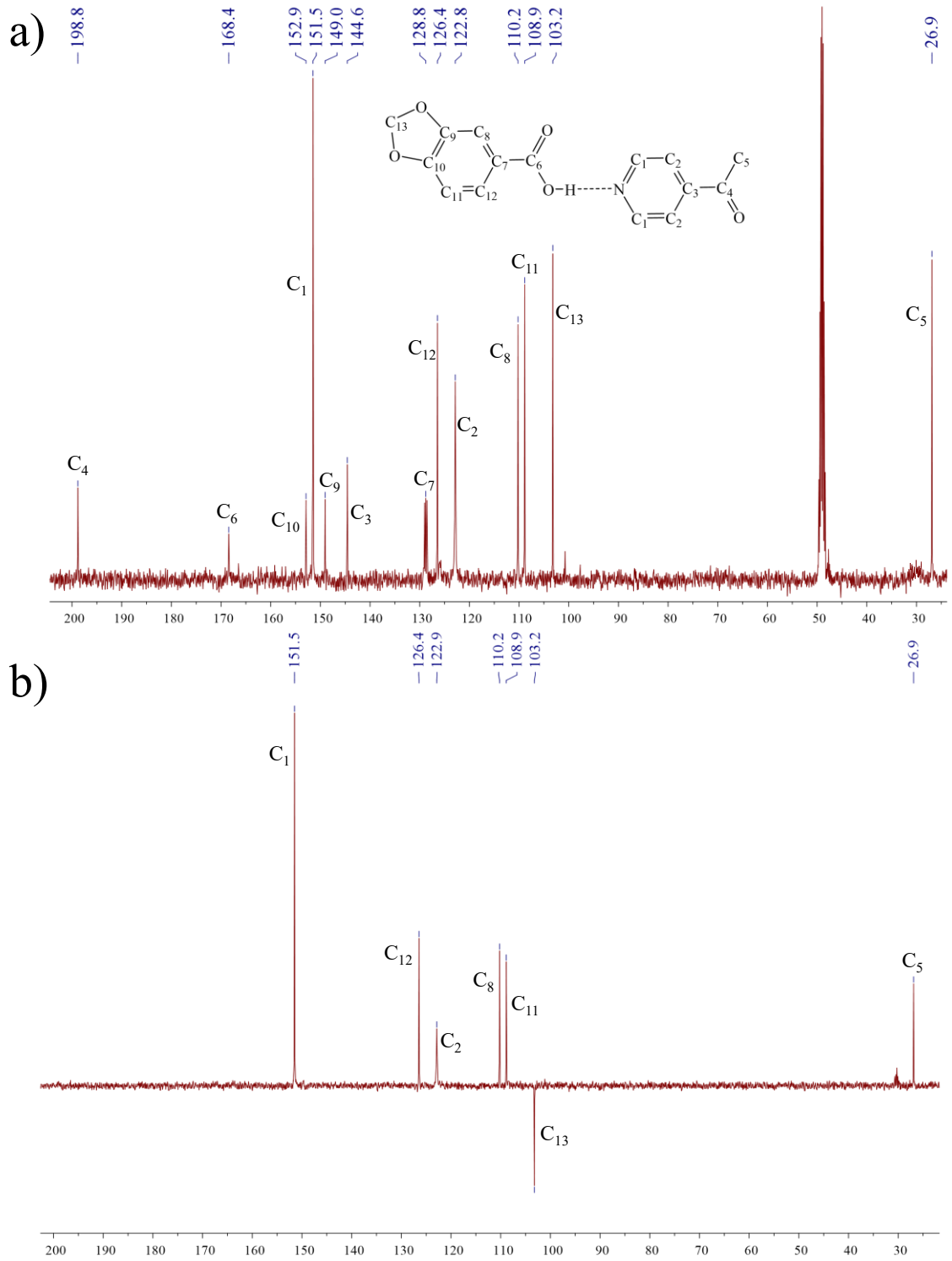


Figure S7. (a) $^{13}C\{^{1}H\}$ and (b) DEPT-135 NMR spectra of cocrystal (HPip)(4-Acpy) (**1**) recorded at 298 K in CD_3OD.

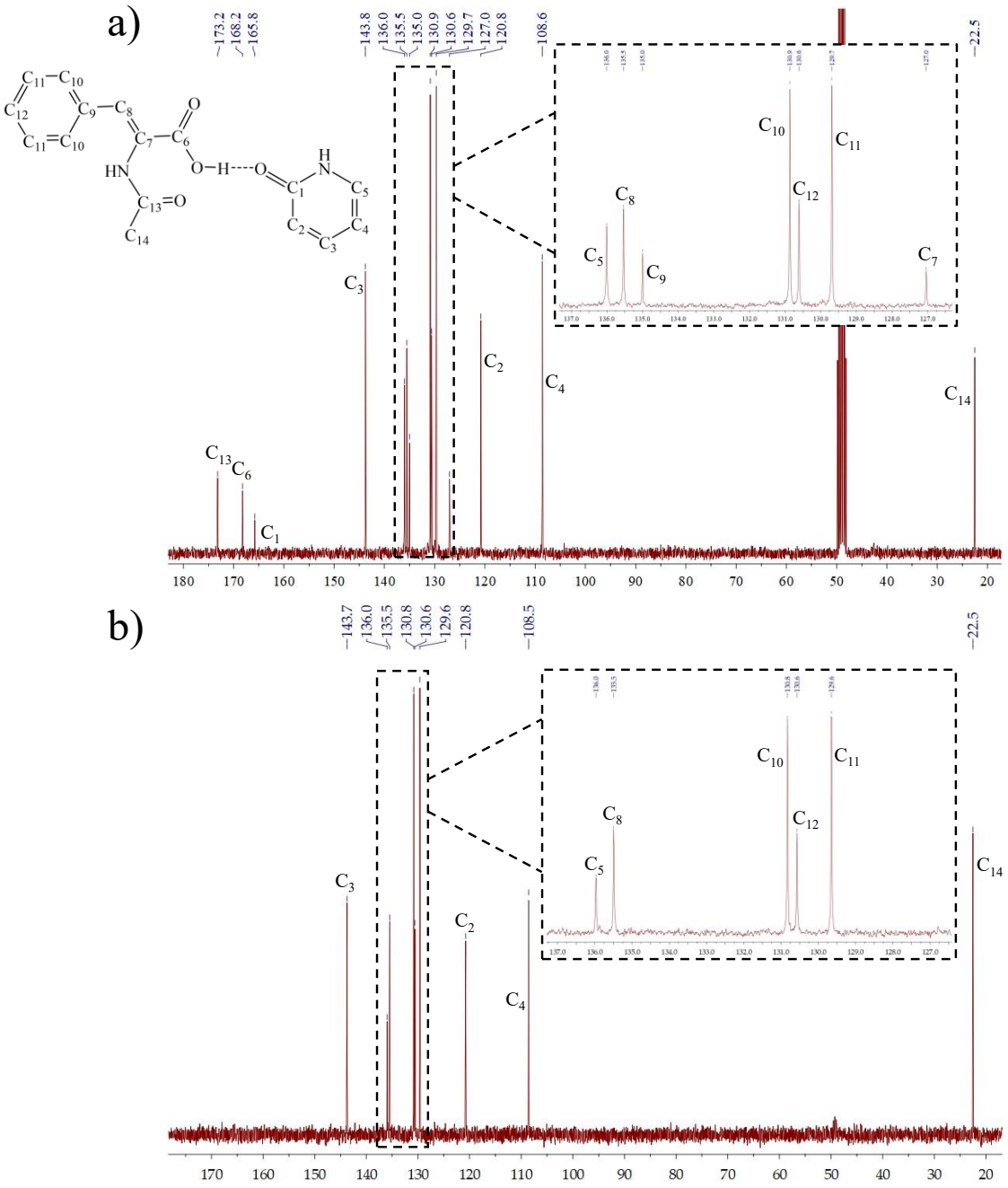


Figure S8. (a) $^{13}C\{^{1}H\}$ and (b) DEPT-135 NMR spectra of cocrystal (HACA)(Pdon) (**2**) recorded at 298 K in CD_3OD.

Hirshfeld Surface Analysis

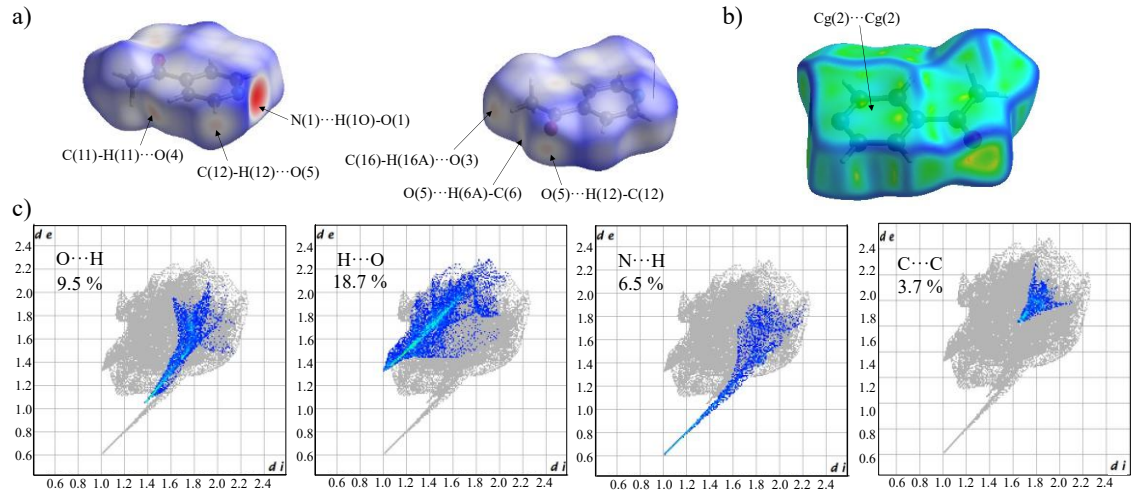


Figure S9. Hirshfeld surfaces of 4-Acpy in cocrystal **1** mapped with (a) d_{norm} and (b) curvedness representations. (c) 2D fingerprint plots of 4-Acpy in cocrystal **1**. Relevant supramolecular interactions have been highlighted in the Hirshfeld surface representations.

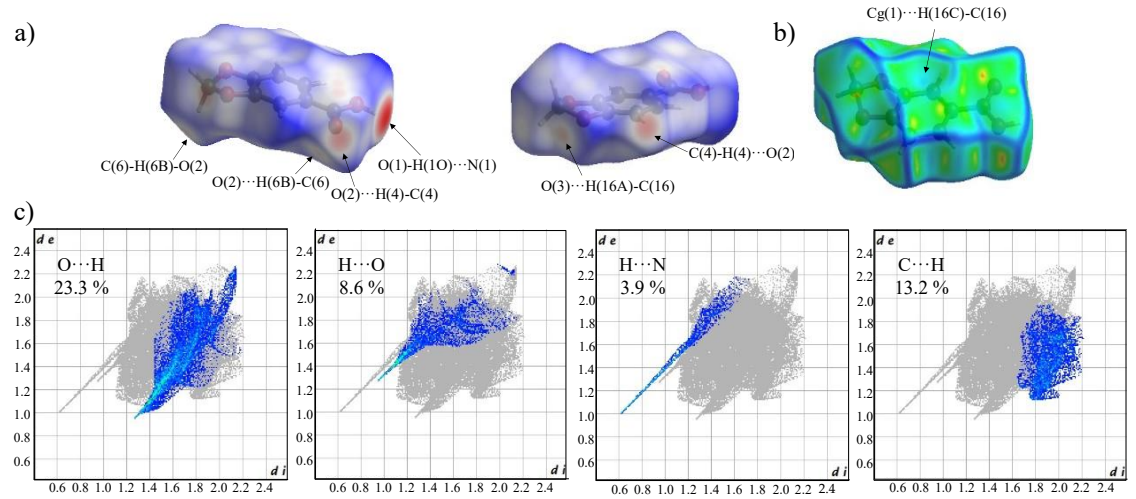


Figure S10. Hirshfeld surfaces of HPip in cocrystal **1** mapped with (a) d_{norm} and (b) curvedness representations. (c) 2D fingerprint plots of HPip in cocrystal **1**. Relevant supramolecular interactions have been highlighted in the Hirshfeld surface representations.

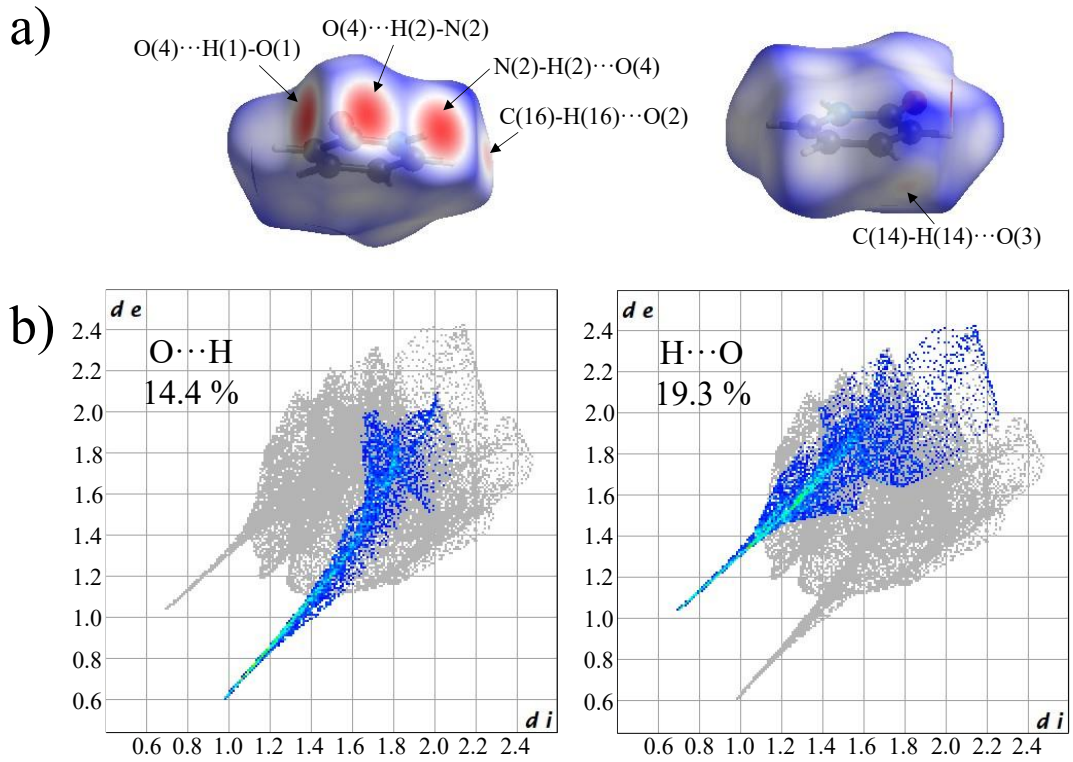


Figure S11. (a) Hirshfeld surfaces mapped with d_{norm} of Pdon in **2**. (b) 2D fingerprint plots of Pdon in cocrystal **2**. Relevant supramolecular interactions have been highlighted in the Hirshfeld surface representations.

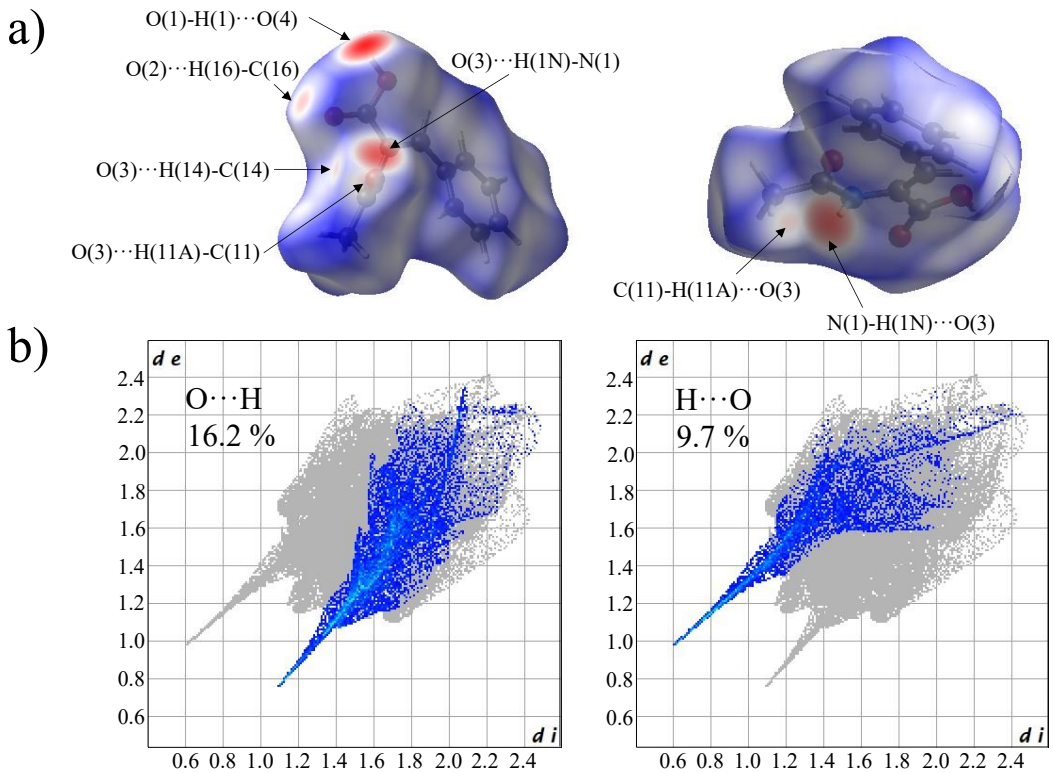


Figure S12. (a) Hirshfeld surfaces mapped with d_{norm} of HACA in **2**. (b) 2D fingerprint plots of HACA in cocrystal **2**. Relevant supramolecular interactions have been highlighted in the Hirshfeld surface representations.

Topological Analysis

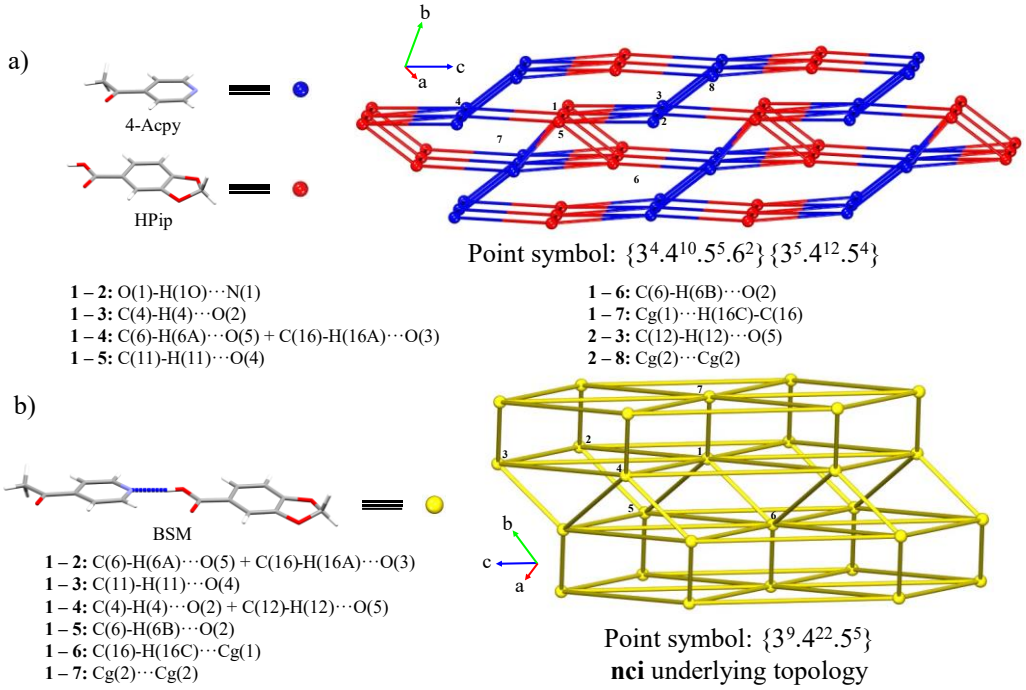


Figure S13. Schematic representation of the underlying topologies of cocrystal **1** considering (a) HPip and 4-Acpy as nodes. (b) BSM as node. The list of supramolecular interactions associated to each edge is provided for both simplifications.

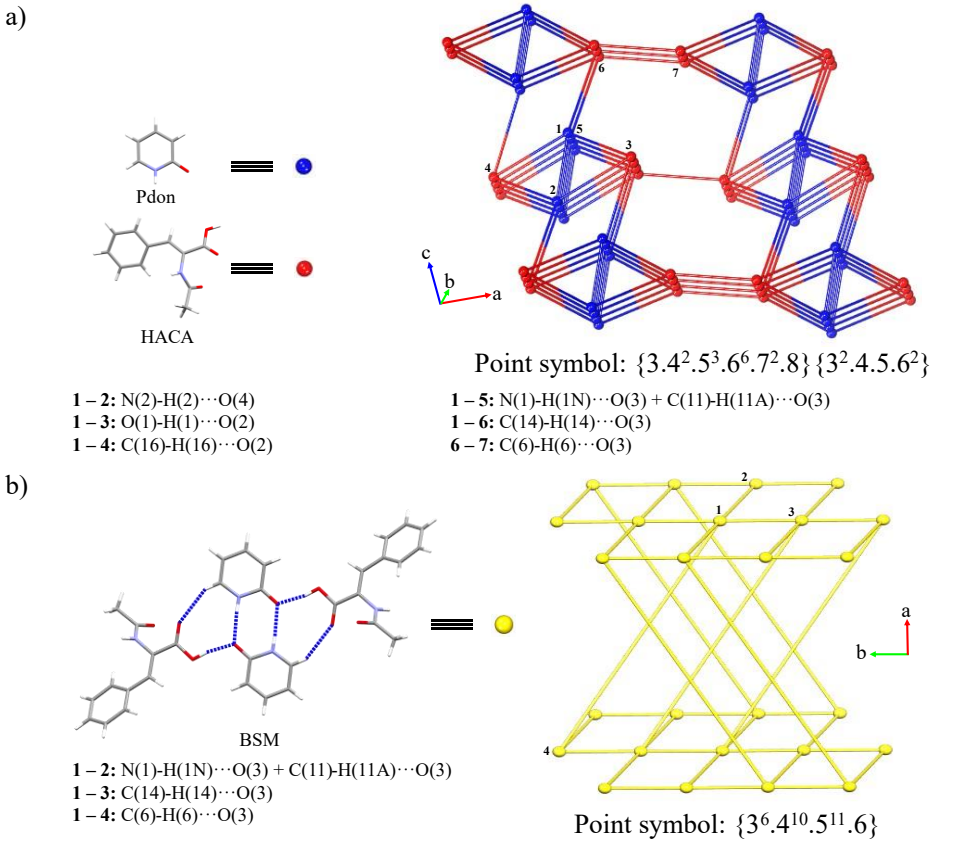


Figure S14. Schematic representation of the underlying topologies of cocrystal **2** considering (a) HACA and Pdon as nodes. (b) BSM as node. The list of supramolecular interactions associated to each edge is provided for both simplifications.

Cambridge Structural Database results

Table S1. CSD results of the selected cocrystal structures presenting the acid···4-Acpy heterosynthon.

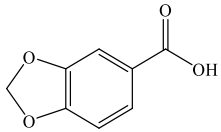
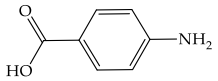
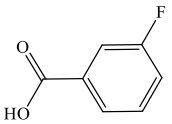
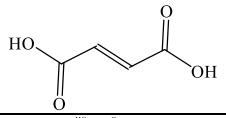
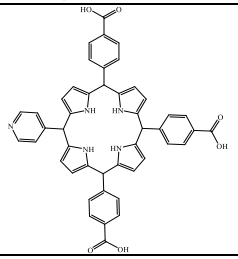
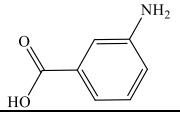
CSD Code	Coformer	Strong Synthons	Dimensionality considering strong synthons	Weak interactions	Dimensionality considering weak interactions	Ref
		Acid···Pyridine	0D dimer	C-H···O C-H···π π··· π	3D	This work
FEXSEJ		Acid···Pyridine Amine···Amine Acid···Amine	2D	C-H···O	3D	1
HOLIAU06		Acid···Pyridine	0D dimer	C-H···O π··· π	3D	2
HOLIAU07		Acid···Pyridine	0D dimer	C-H···O C-H···π π··· π	3D	
HOZBOO		Acid···Pyridine	0D trimer	C-H···O π··· π	3D	3
RIGLAV		Acid···Pyridine	1D	C-H···O	3D	4
KEBCON		Acid···Pyridine Acid···Amine	2D	C-H···O π··· π	3D	5

Table S2. CSD results of the selected cocrystal structures presenting the Pdon···Pdon homosynton supported by Pdon···acid heterosynthons.

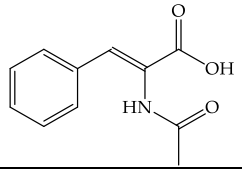
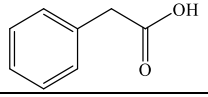
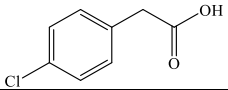
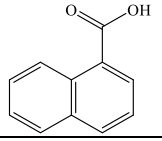
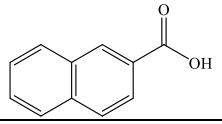
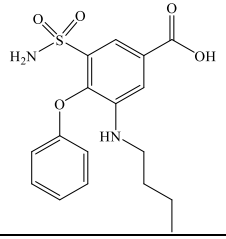
CSD Code	Coformer	Strong Synthons	Dimensionality considering strong synthons	Weak interactions	Dimensionality considering weak interactions	Ref
		Pdon···Acid Amide···Amide	2D	-	-	This work
AHASUX		Pdon···Acid	0D tetramer	C-H···O	2D	6
AHATAE		Pdon···Acid	0D tetramer	C-H···O and π···π	3D	
AHATEI		Pdon···Acid	0D tetramer	C-H···O and π···π	1D	
AHATIM		Pdon···Acid	0D tetramer	C-H···O and C-H···π	3D	
FEDFUS		Pdon···Acid, Sulfonamide··· Sulfonamide	2D	-	-	7

Table S2. *Cont.*

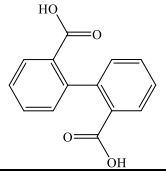
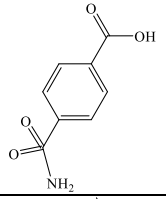
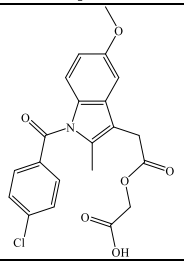
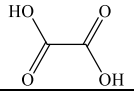
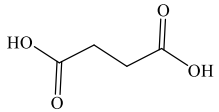
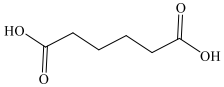
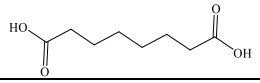
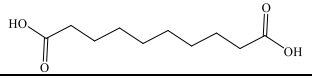
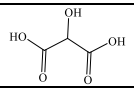
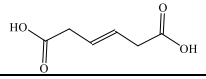
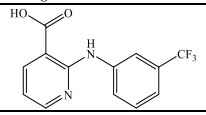
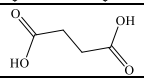
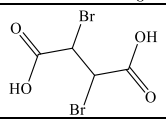
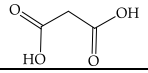
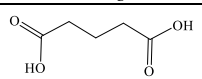
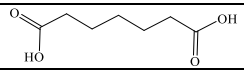
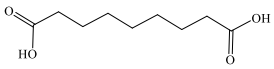
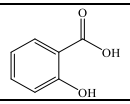
CSD Code	Coformer	Strong Synthons	Dimensionality considering strong synthons	Weak interactions	Dimensionality considering weak interactions	Ref
FOTYET		Pdon···Acid	1D	-	-	8
FURWIA02		Pdon···Acid, Sulfonamide··· Sulfonamide, Sulfonamide···Acid	3D	-	-	9
KARFER		Pdon···Acid	0D tetramer	C-H···O	3D	10
QIMHOJ01		Pdon···Acid	1D	C-H···O	2D	11
NISTAK		Pdon···Acid	1D	C-H···O	3D	
NISVUJ	 + H_2O	Pdon···Acid, H_2O···H_2O, H_2O···Acid	3D	-	-	

Table S2. *Cont.*

CSD Code	Coformer	Strong Synthons	Dimensionality considering strong synthons	Weak interactions	Dimensionality considering weak interactions	Ref
NITGUS		Pdon···Acid	1D	C-H···O	3D	11
NITQIQ		Pdon···Acid	1D	C-H···O	2D	
PAHYUT		Pdon···Acid, Acid···Alcohol	2D	-	-	12
QIMHUP		Pdon···Acid	1D	-	-	13
RIQXEX		Pdon···Acid	0D tetramer	π···π	1D	14
XASCUP		Pdon···Acid	1D	C-H···O	3D	15
XASDAW		Pdon···Acid	1D	C-H···O	2D	
XUNHET		Pdon···Acid	1D	C-H···O	2D	16
XUNHIX		Pdon···Acid, Acid···Acid	1D	C-H···O	3D	
XUNHOD		Pdon···Acid	1D	-	-	
XUNHUJ		Pdon···Acid, Acid···Acid	1D	C-H···O	3D	
YOYXUI		Pdon···Acid	0D tetramer	C-H···O, π···π	3D	17

Energy Frameworks

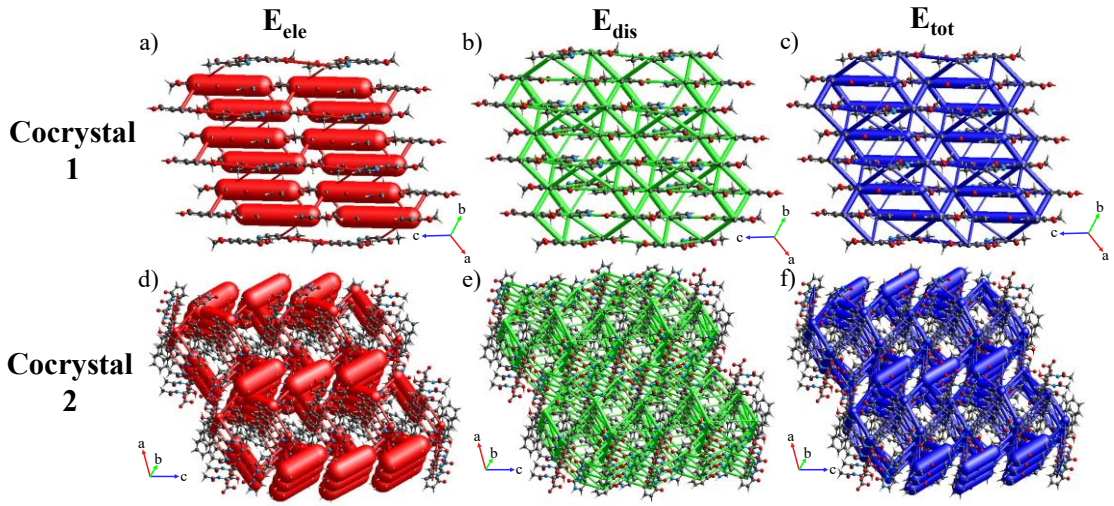


Figure S15. Energy frameworks (E_{ele}, E_{dis}, E_{tot}) for cocrystals (a-c) **1** and (d-f) **2**. All the diagrams use the same energy cylinder scale factor of 150 and an energy cut-off of -7.80 KJ/mol within a 3×1×2 (**1**) and a 2×3×2 (**2**) unit cells.

Table S3. Contribution energies (electrostatic, E_{ele}; polarization, E_{pol}; dispersion, E_{dis}; repulsion, E_{rep}), total energies (E_{tot}) and lattice energies (E_{latt}) of cocrystals **1** and **2**[a].

Structure	Molecule	E_{ele}	E_{pol}	E_{dis}	E_{rep}	E_{tot}	E_{latt}
Cocrystal 1	HPip	-173.8	-30.5	-194.5	168.2	-230.6	-211.0
	4-Acpy	-147.9	-26.5	-163.2	146.3	-191.3	
Cocrystal 2	HACA	-247.9	-53.4	-125.2	185.8	-240.7	-274.2
	Pdon	-226.2	-50.8	-223.7	193.1	-307.6	

[a]Energies are given in KJ/mol

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