Supporting Information for

New co-crystals/salts of gallic acid and substituted pyridines: an effect of *ortho*-substituents on the formation of an acid-pyridine heterosynthon

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Supplementary Figures:

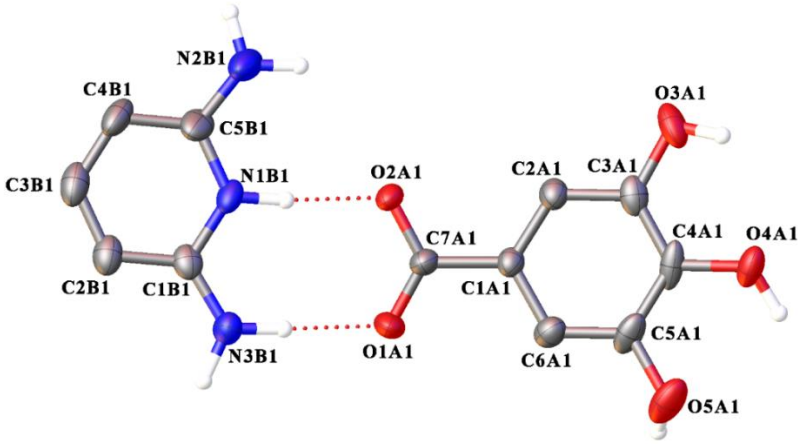


Figure S1. General view of the second symmetry-independent formula unit of the salt **4**. Hereinafter, non-hydrogen atoms are shown as thermal ellipsoids (p = 50%) and dashed lines stand for hydrogen bonds.

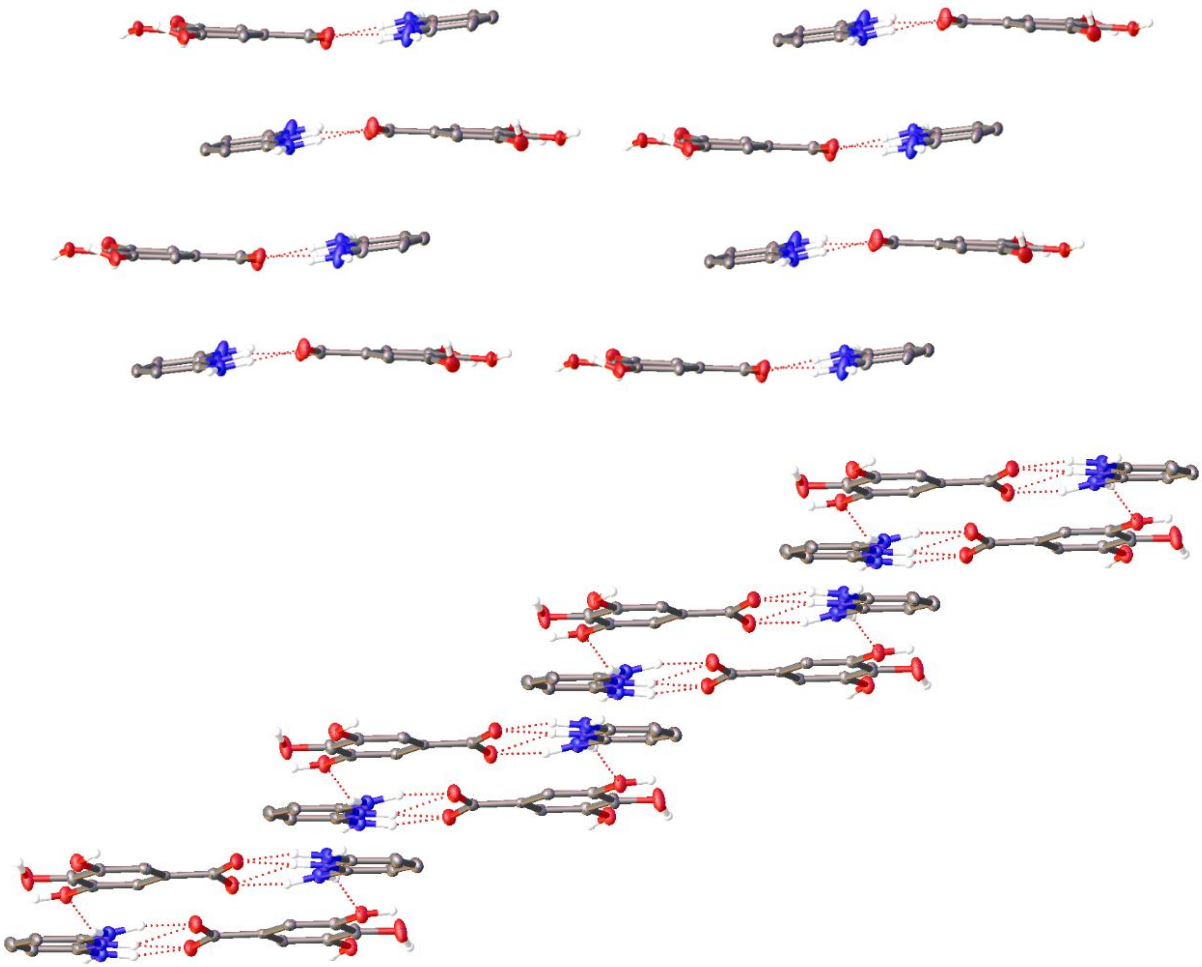


Figure S2. Fragments of the crystal packing in the salt **4** that are produced by the two-point (top) and the four-point (bottom) acid-pyridine heterosynthons.

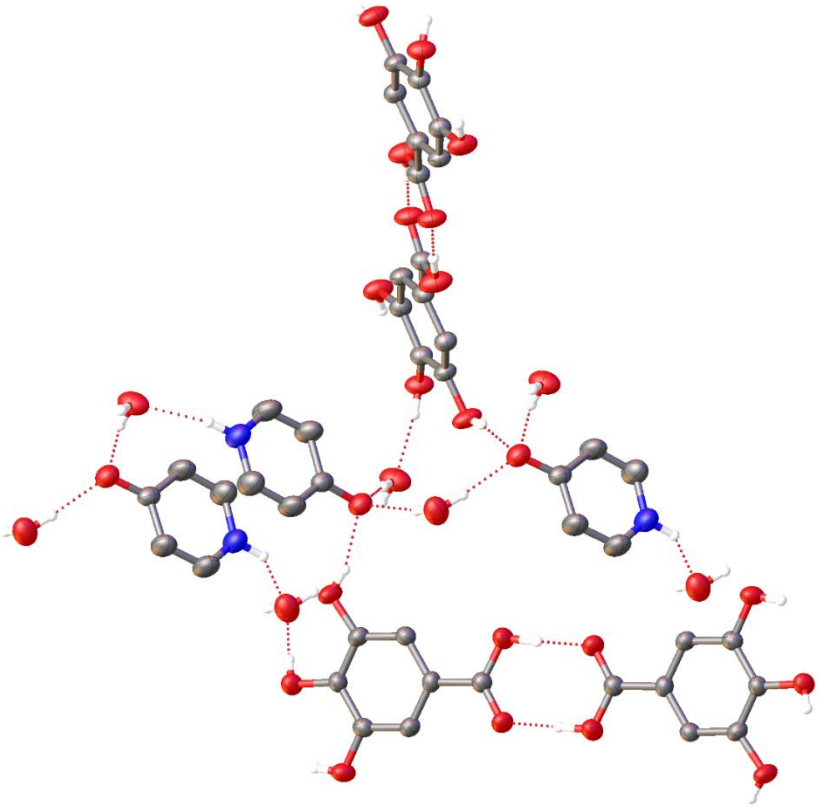


Figure S3. A fragment of the crystal packing in the co-crystal XUMHUL illustrating the formation of a centrosymmetric homosynthon from the molecules of gallic acid.

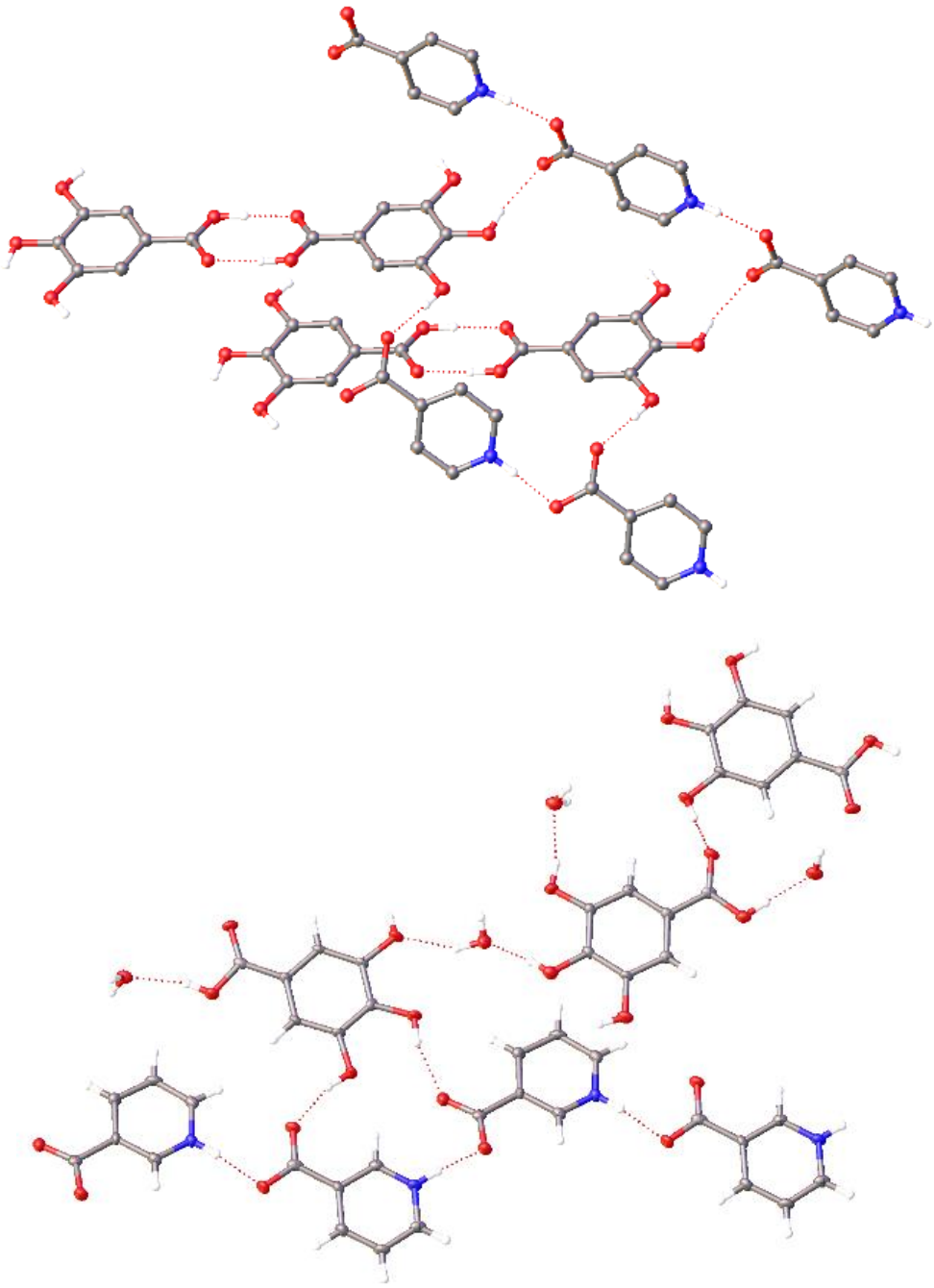


Figure S4. Fragments of the crystal packing in the co-crystals RUWGUM (top) and RUWHAT (bottom) illustrating the formation of hydrogen-bonded chains from the zwitterions of isonicotinic or nicotinic acid.

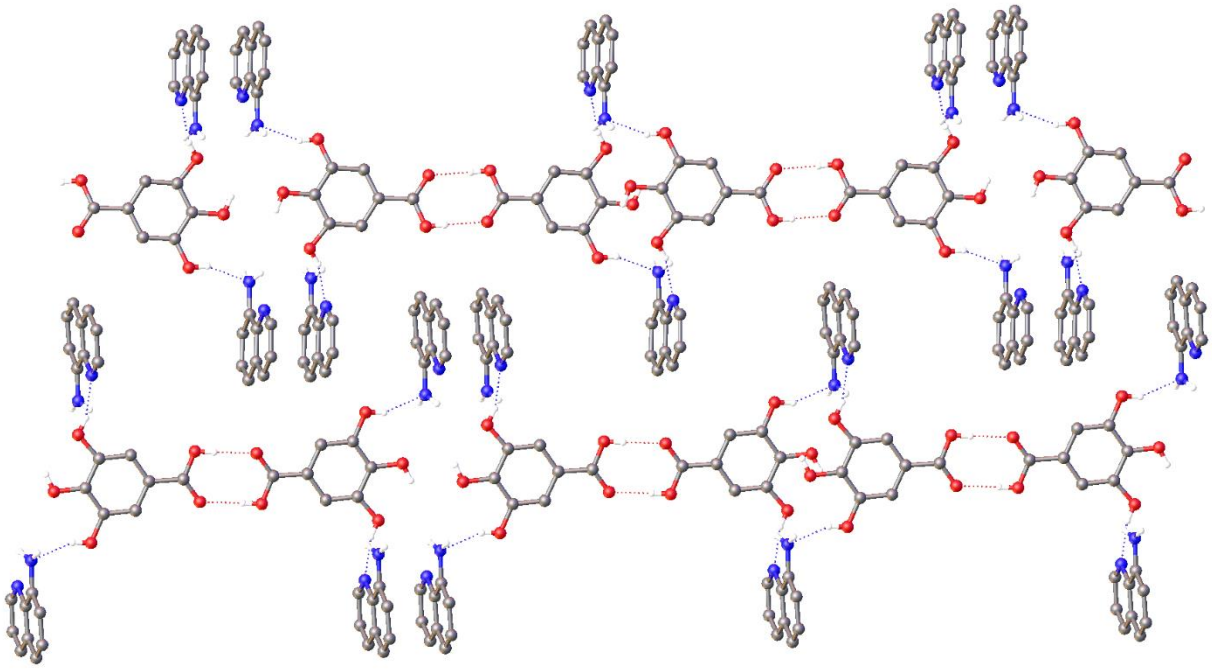
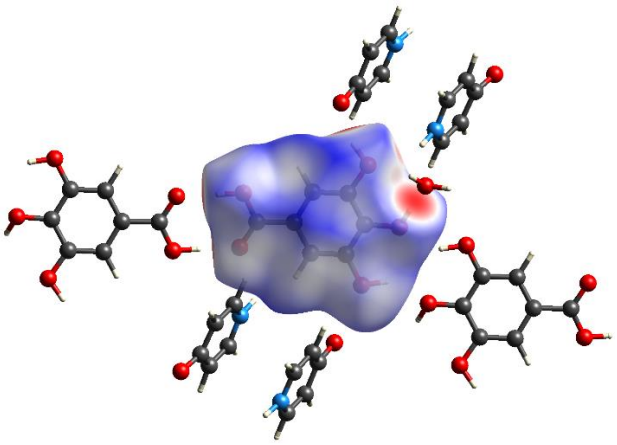
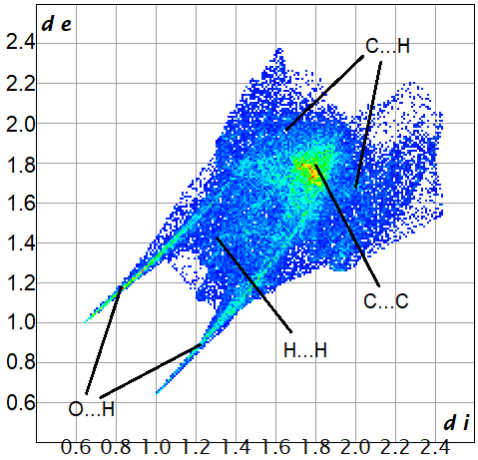
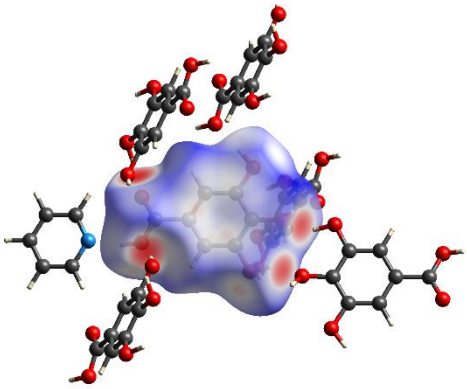


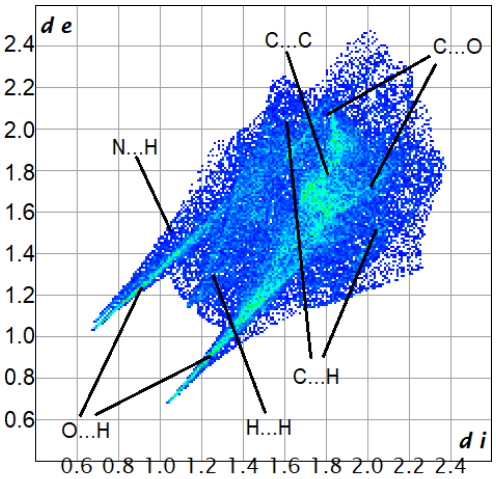
Figure S5. A fragment of the crystal packing in the salt AYIWEM illustrating the formation of hydrogen-bonded dimers from the molecules of gallic acid.



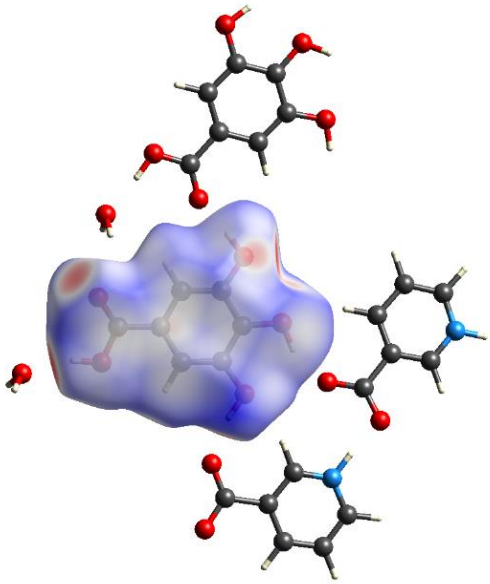


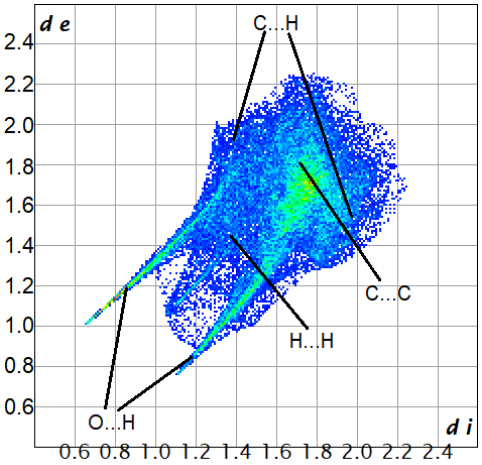
XUMHUL



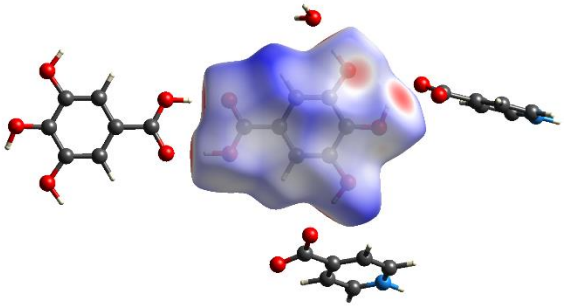


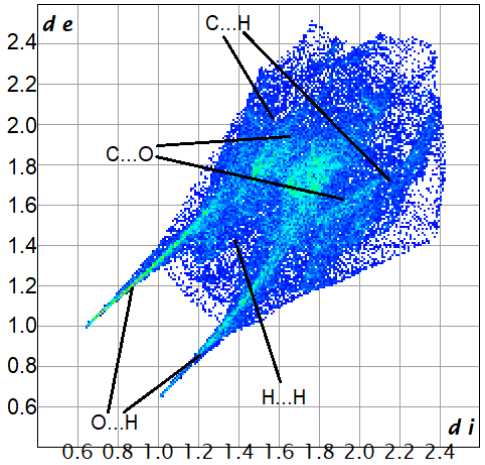
YAHTUY



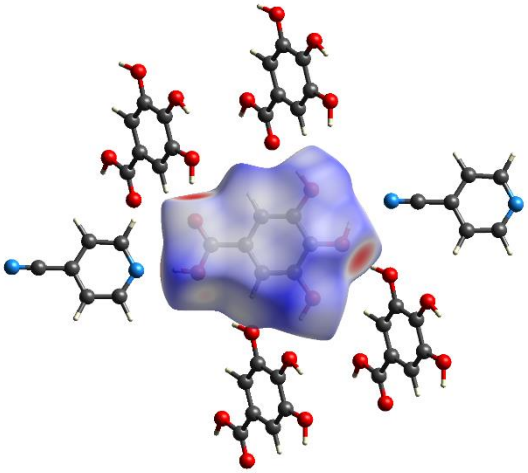


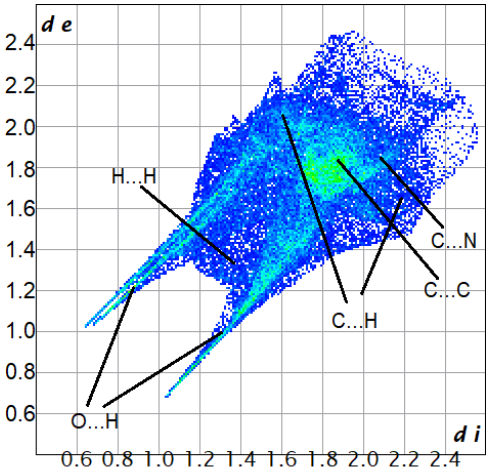
RUWHAT



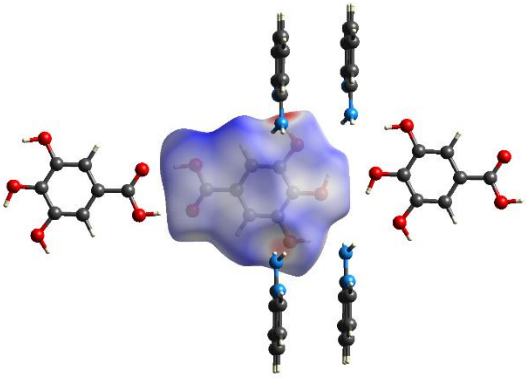


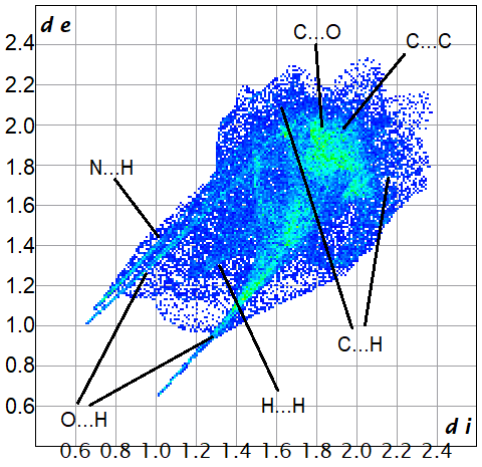
RUWGUM



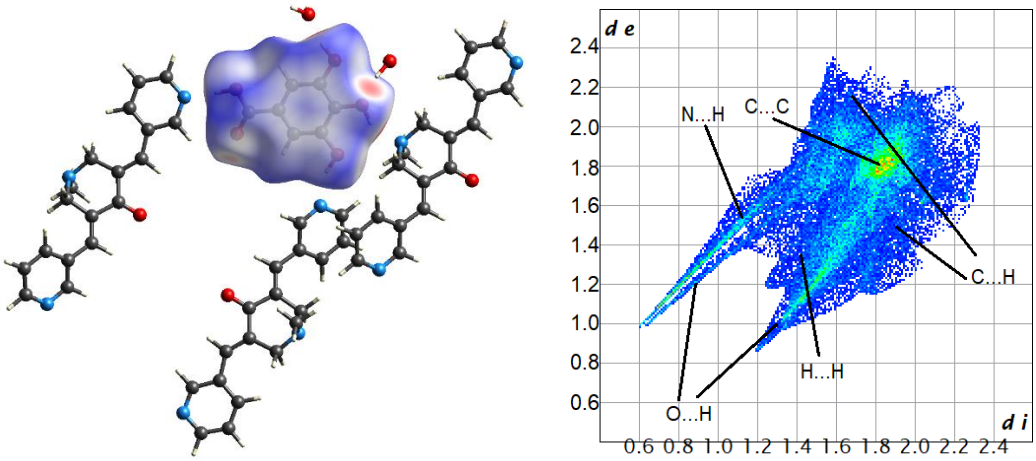


LALVED

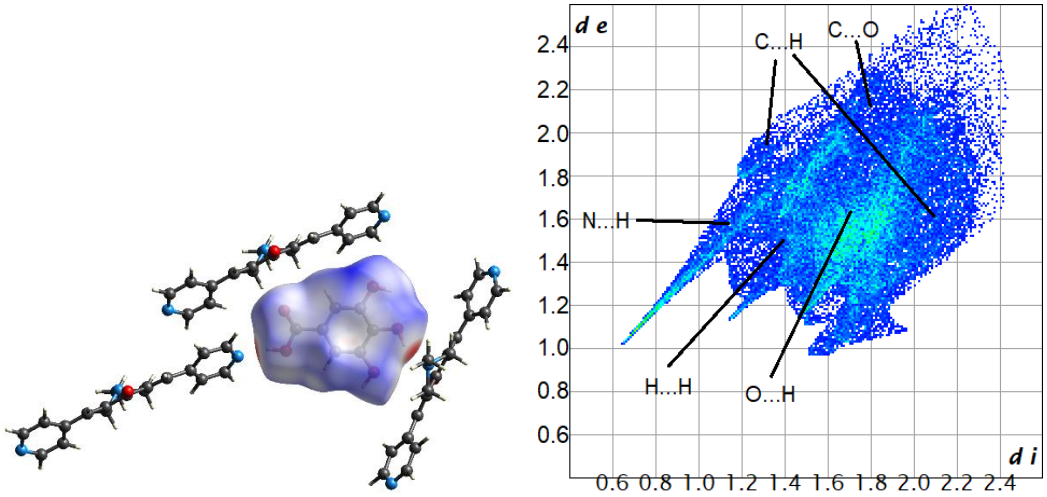




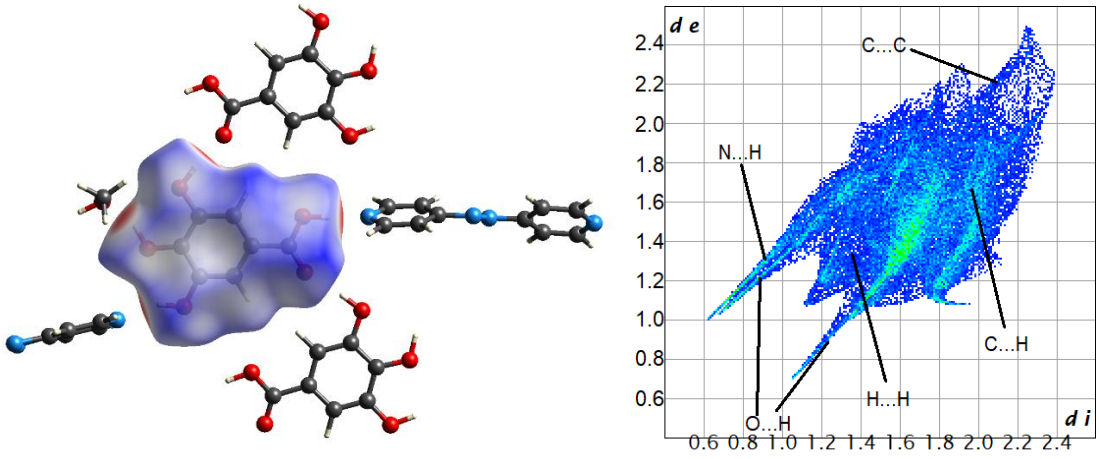
AYIWEM



TUZFAX



TUZFEB



LEFPUJ

Figure S6. Hirshfeld surfaces (left) of the molecule of gallic acid and their 2D fingerprint plots (right), as generated by Crystal Explorer [1], in other co-crystals of gallic acid and pyridine-containing compounds from CSD identified by their RefCodes.

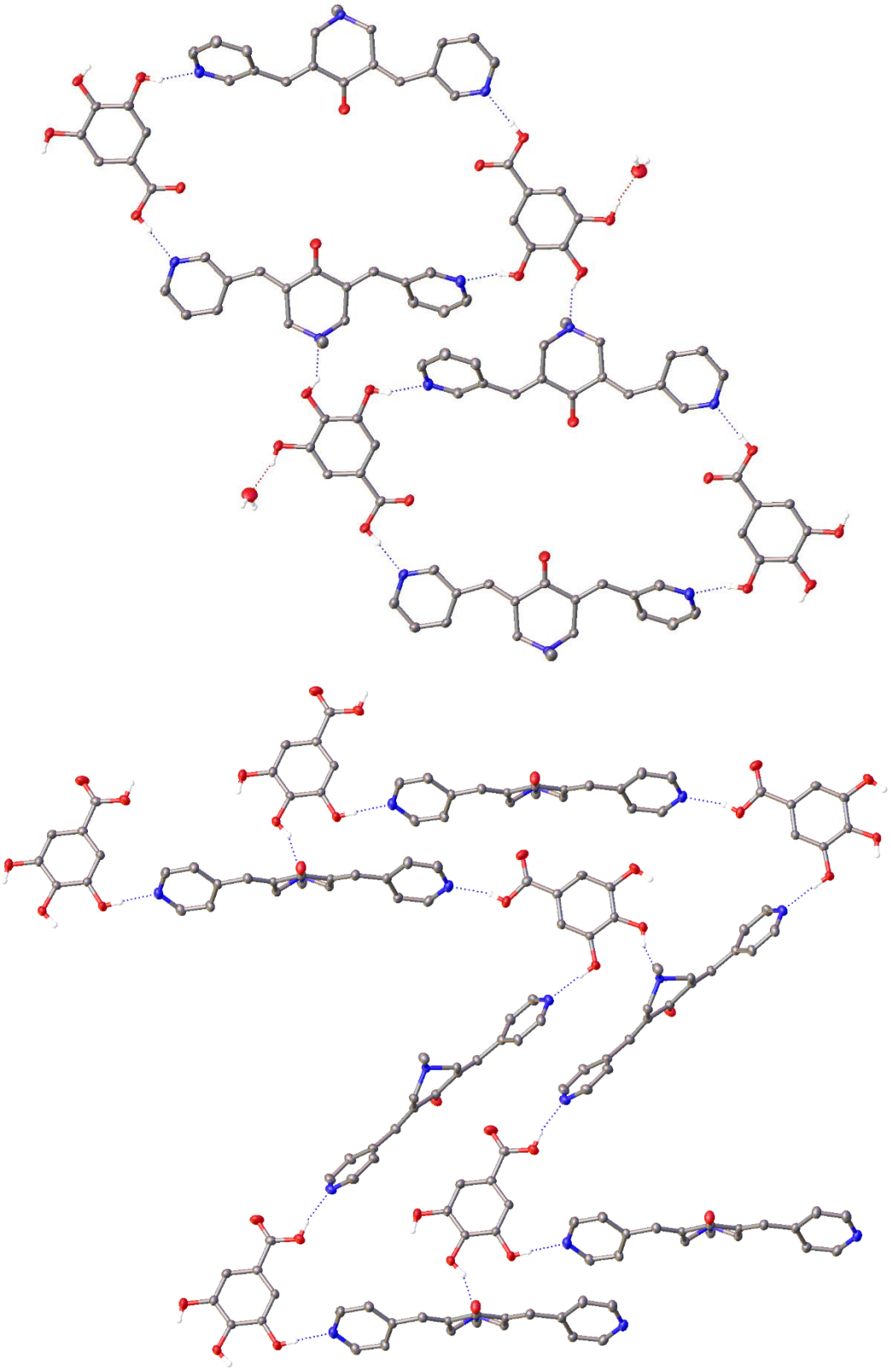


Figure S7. Fragments of the crystal packing in the co-crystals TUZFAX (top) and TUZFEB (bottom) illustrating the formation of hydrogen-bonded layers from the molecules of gallic acid and of an appropriate pyridine-containing compound.

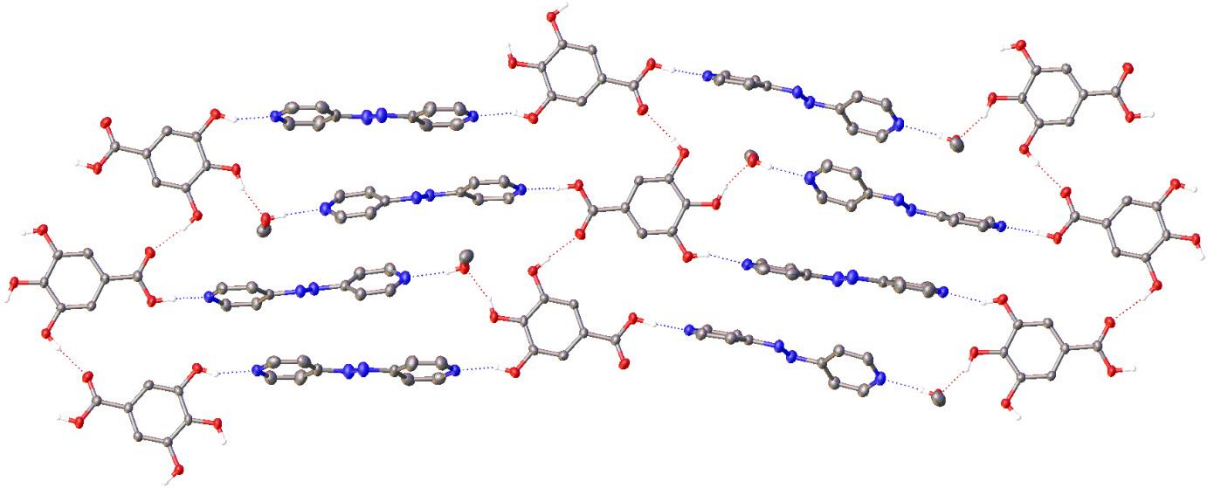


Figure S8. A fragment of the crystal packing in the co-crystal LEFPUJ illustrating the formation of hydrogen-bonded layers with the alternating chains of the molecules of gallic acid and of 1,2-bis(pyridin-4-yl)diazene.

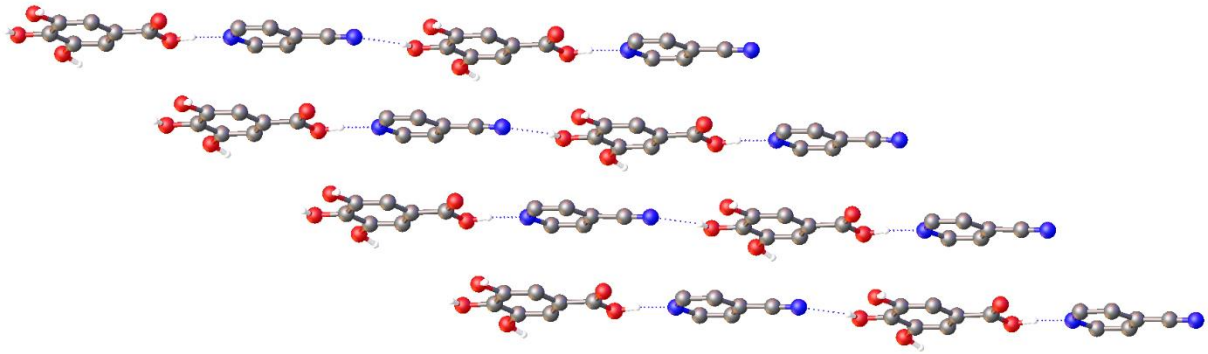


Figure S9. A fragment of the crystal packing in the co-crystal LALVED illustrating the formation of hydrogen-bonded chains from the molecules of gallic acid and 4-cyanopyridine.

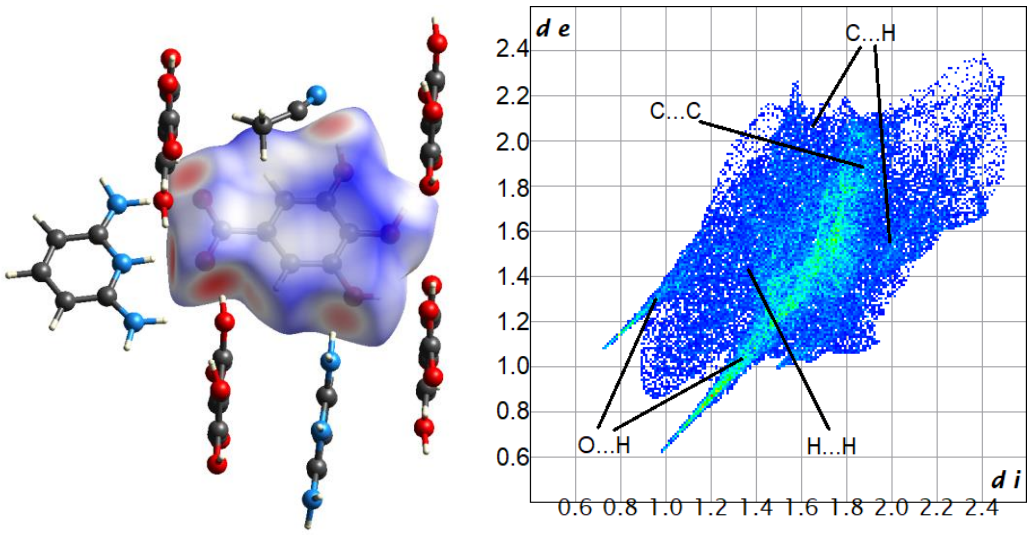
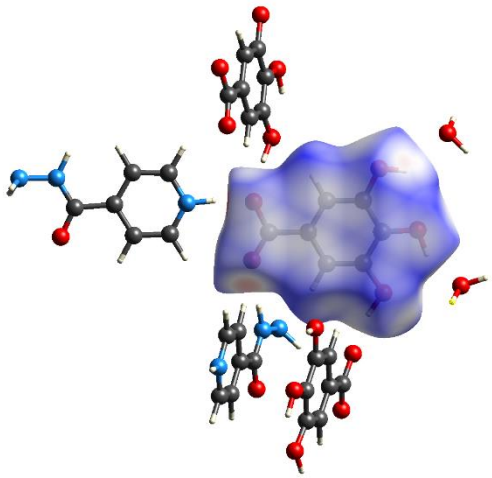
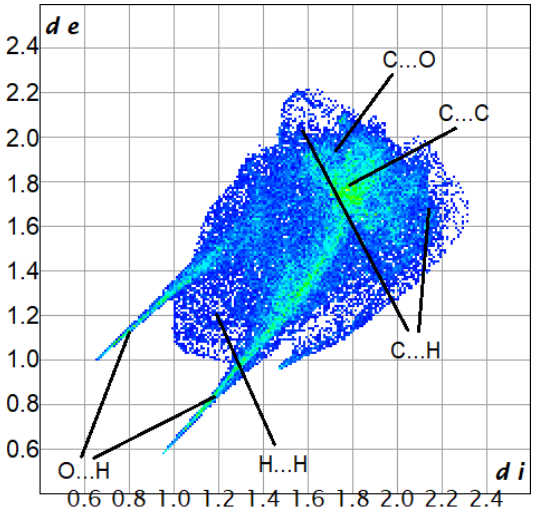
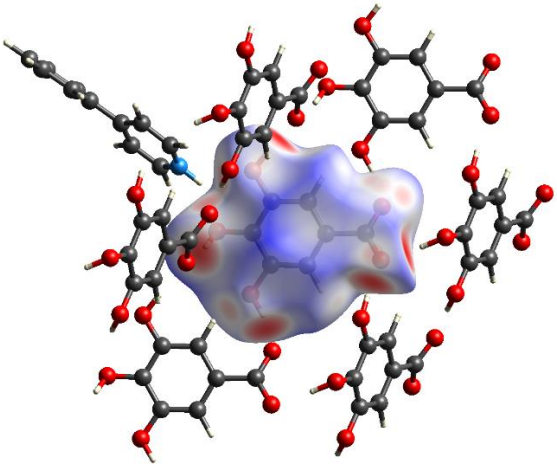


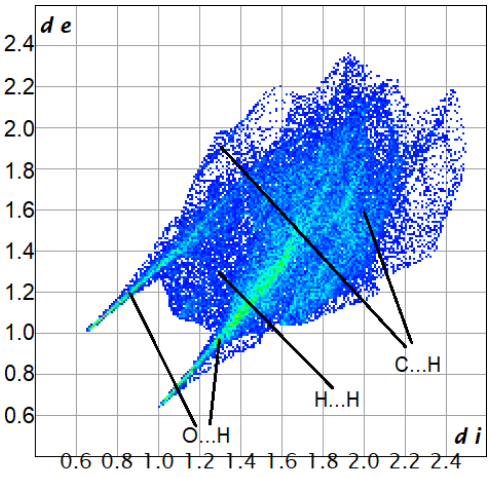
Figure S10. Hirshfeld surface (left) of the second symmetry-independent gallate anion in the salt **4** and its 2D fingerprint plot (right).



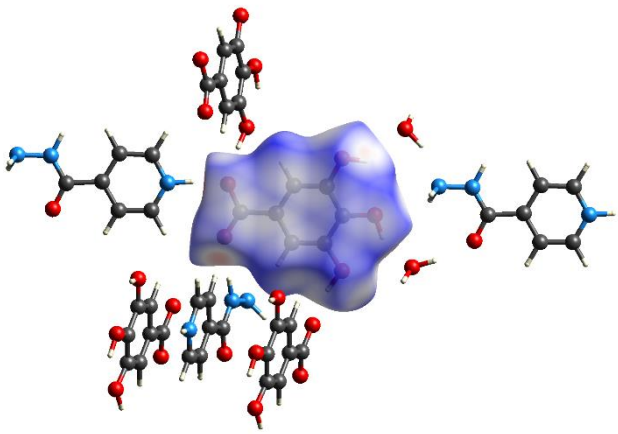


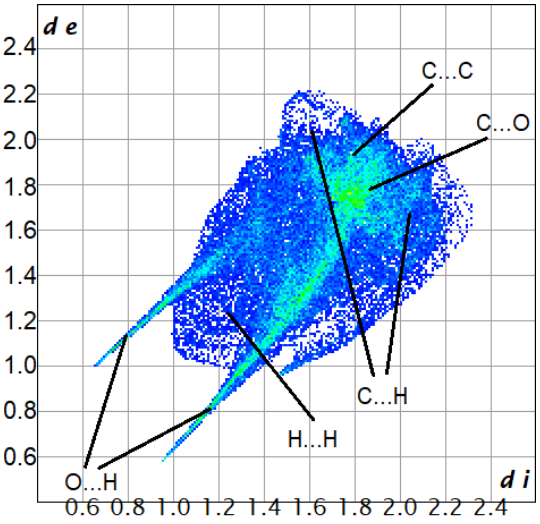
XUMKAU



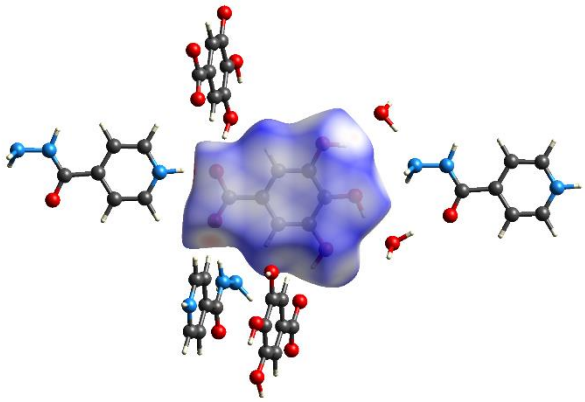


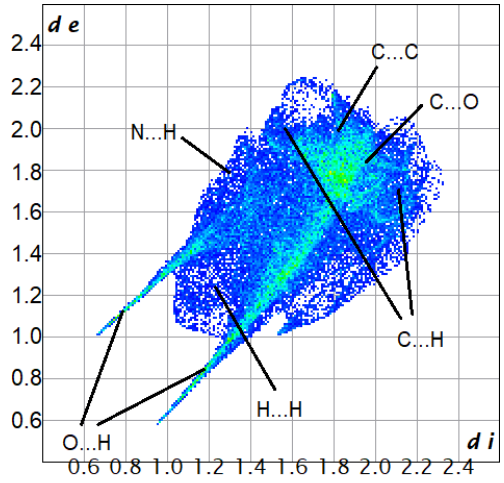
TICZIQ



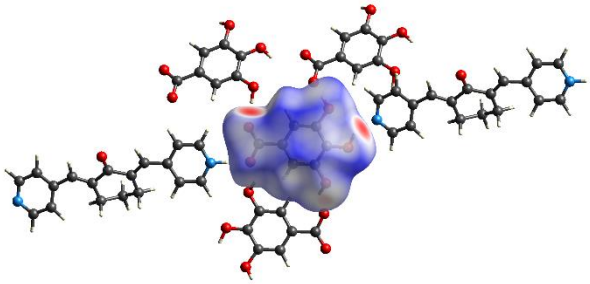


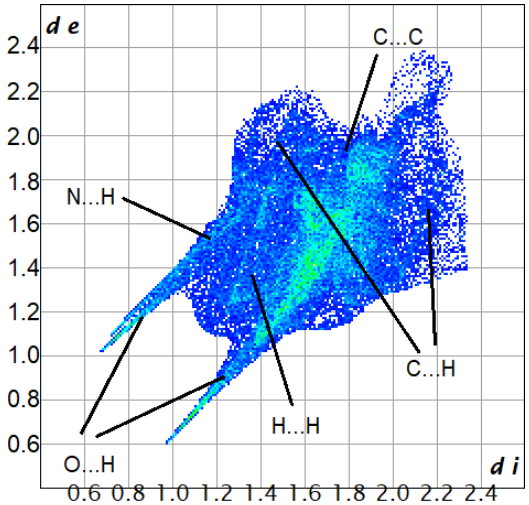
LODHIX



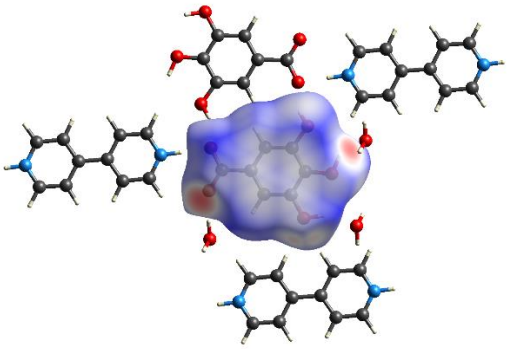


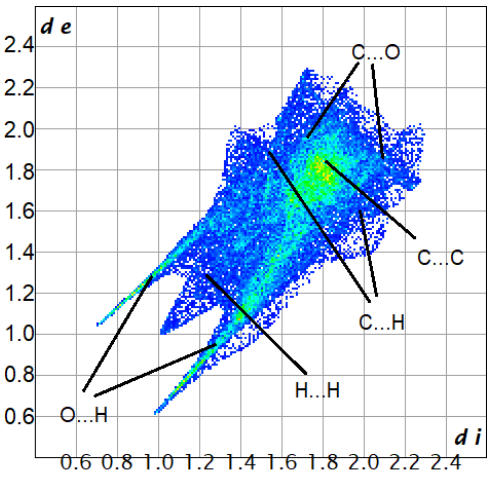
LODHOD



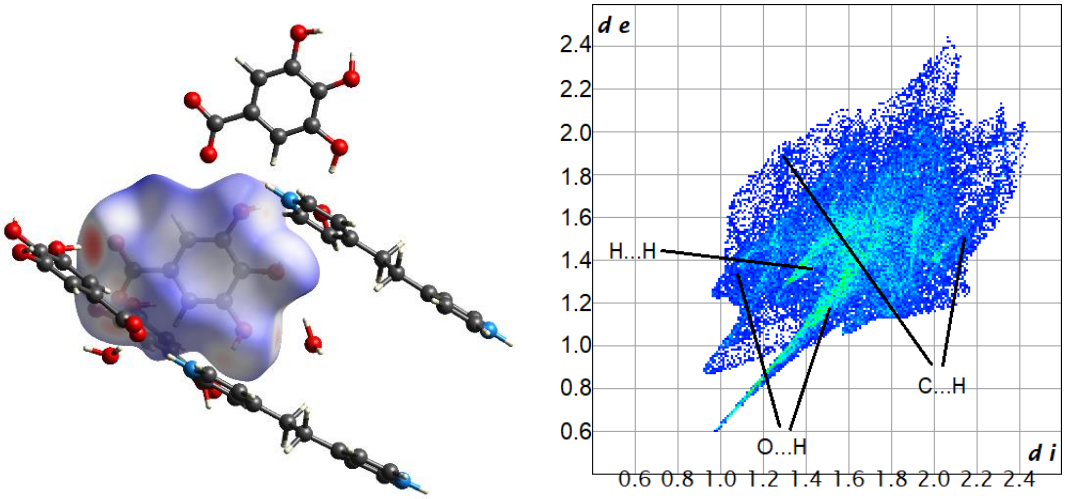


TUZDUP





EHUGOE



DUTJET

Figure S11. Hirshfeld surfaces (left) of the gallate anion and their 2D fingerprint plots (right) in other salts of gallic acid and pyridine-containing compounds from CSD identified by their RefCodes. X-ray diffraction data for LODHIX and LODHOD are collected from the same salt at 100 K and at room temperature, respectively.

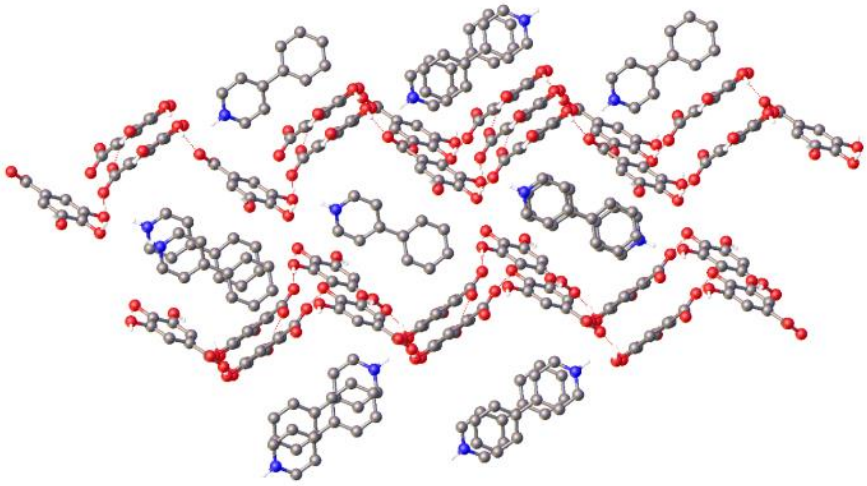


Figure S12. A fragment of the crystal packing in the salt TICZIQ illustrating the formation of hydrogen-bonded corrugated layers from the gallate anions.

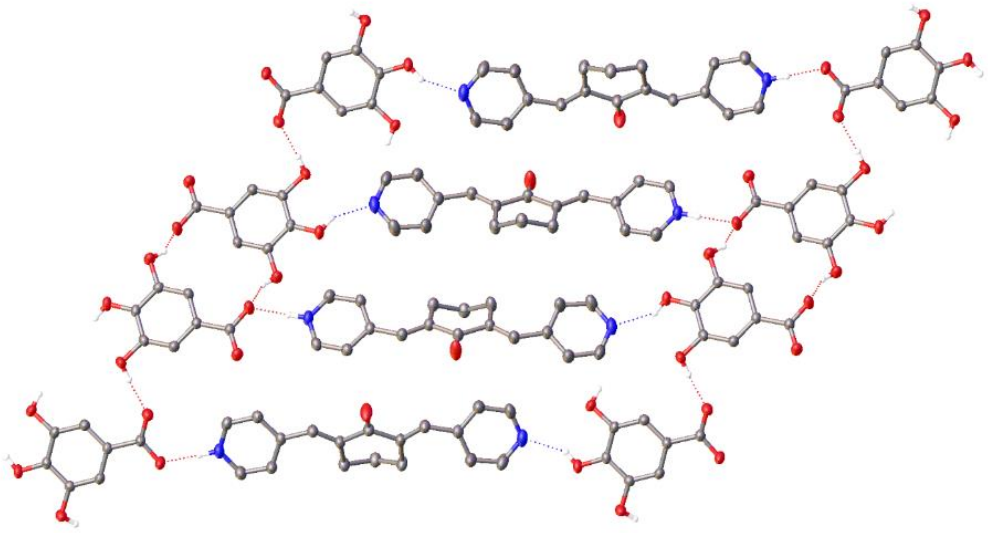
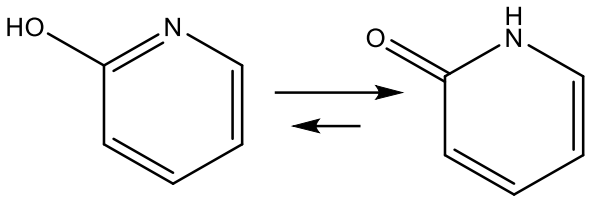


Figure S13. A fragment of the crystal packing in the co-crystal TUZDUP illustrating the formation of hydrogen-bonded layers.

Supplementary Schemes:



2-hydroxypyridine pyridone-2

Scheme S1. Keto-enol equilibrium of **2-OH-Py** favoring its keto-form, pyridone-2.

Supplementary Tables:

Table S1. Contributions (%) of various interactions into the Hirschfeld surface of the molecule of gallic acid in other co-crystals of gallic acid identified by their RefCodes in CSD.

Contacts	**XUMHUL**	**YAHTUY**	**RUWHAT***	**RUWGUM**	**LALVED**	**AYIWEM**	**TUZFAX**	**TUZFEB**	**LEFPUJ**	**Average**
O…H	44.8	40.2	42.9	43.5	40.3	34.7	37.6	30.7	38.6	39.3
N…H	0.0	4.2	0.6	0.3	9.1	4.5	9.5	9.8	7.3	5.0
C…H	12.9	14.2	15.3	17.5	11.9	10.6	11.8	20.9	18.5	14.8
H…H	27.6	29.6	24.4	22.8	19.6	32.7	27.4	33.1	30.6	27.5
C…C	6.2	4.4	5.4	2.9	8.0	6.0	9.7	0.8	0.4	4.9
O…O	2.4	2.3	1.4	3.4	2.9	1.8	0.4	0.0	0.4	1.7
C…N	0.0	0.2	0.5	0.5	3.8	0.0	0.8	0.0	1.2	0.8
C…O	6.0	4.3	9.2	8.6	4.0	9.8	1.9	4.6	0.6	5.4
N…O	0.0	0.5	0.4	0.4	0.4	0.0	0.9	0.1	2.6	0.6

*For systems with several symmetry-independent molecules of gallic acid, the mean values are given.

Table S2. The parameters of the hydrogen bond O-H…N in the heterosynthon acid-pyridine in the co-crystals of gallic acid identified by their RefCodes in CSD.

Compound	**N…O, Å**	**NHO, °**
XUMHUL	-	-
YAHTUY	2.730(5)	168.8(2)
RUWGUM	-	-
RUWHAT	-	-
LALVED	2.636(2)	171(4)
AYIWEM	-	-
TUZFAX	2.587(2)	177.24(11)
TUZFEB	2.691(2)	163.45(10)
LEFPUJ	2.623(3)	174(2)
Average	**2.653**	**170.9**

Table S3. The parameters of the hydrogen bond N-H…O in the heterosynthon acid-pyridine in the gallate salts identified by their RefCodes in CSD.

Compound	**N…O, Å**	**NHO, °**
XUMKAU	2.642(3)	179(2)
TICZIQ	2.9421(19)	122(3)
LODHIX*	2.544(4) (2.576(4))	173(4) (173(4))
LODHOD*	2.551(5) (2.564(5))	172(6) (177(7))
TUZDUP	2.5997(18)	177.6(4)
EHUGOE	2.6134(15)	179(2)
DUTJEI*	2.571(5) (2.514(6))	162.9(3) (166.4(3))
Average**	**2.612 [2.575]**	**168.2 [173.3]**

*The values for the second symmetry-independent gallate anion are given in parentheses.

**The value in the brackets is an average with TICZIQ excluded, as it features an unfavorable geometry of the hydrogen bond with the two components of the acid-pyridine heterosynthon twisted relative to each other (Fig. S12 of SI).

Table S4. The parameters of the hydrogen bond N-H…O in the heterosynthon acid-pyridine in the co-crystals **1**, **2** and **3** and in the salts **4** and **5** together with the appropriate average values.

Compound	**N…O, Å**	**NHO, °**
1	2.941(8)	154.7(2)
2	2.798(2)	175.82(9)
3	2.739(2)	160.73(17)
Average	**2.826**	**163.75**
4*	3.002(5) and 3.009(5) (2.766(4))	143.74(18) and 150.4(2) (165.0(2))
5	3.034(2)	124.28(11)
Average	**2.950**	**145.9**

*The values for the second symmetry-independent gallate anion are given in parentheses.

Table S5. Contributions (%) of various interactions into the Hirschfeld surface of the gallate anion in other gallate salts identified by their RefCodes in CSD.

Contacts	**XUMKAU**	**TICZIQ***	**LODHIX***	**LODHOD***	**TUZDUP**	**EHUGOE**	**DUTJEI***	**Average**
O…H	45.8	54.5	45.6	46.7	44.2	46.2	50.7	47.7
N…H	0.6	0.0	0.7	0.7	3.1	0.4	0.0	0.8
C…H	12.7	19.0	10.3	8.3	15.9	6.8	15.3	12.6
H…H	25.8	24.8	26.3	26.9	25.0	26.0	25.4	25.7
C…C	5.2	0.0	8.1	10.4	6.2	13.3	4.6	6.8
O…O	2.9	0.1	1.9	0.9	0.7	1.3	2.0	1.4
C…N	1.5	0.1	1.1	0.8	0.5	0.5	0.8	0.8
C…O	6.6	1.7	5.5	4.4	2.6	5.3	1.0	3.9
N…O	0.2	0.1	0.7	1.1	1.7	0.3	0.3	0.6

*For systems with several symmetry-independent gallate anions, the mean values of interactions are given. X-ray diffraction data for LODHIX and LODHOD are collected from the same salt at 100 K and at room temperature, respectively.

Table S6. ΔpKa values for **1-5** and for other two-component systems based on gallic acid identified by their RefCodes in CSD.*****

Compound		pKa*	ΔpKa	Predicted	Experimental
GA	-	4.33		-	-
	2-OH-Py**	12.02	7.69	Salt	Co-crystals (from acetonitrile kept for six days and four weeks, respectively)
	2,6-NH_2-Py	6.13	1.8	Both co-crystal and salt are possible	Salt (from acetonitrile kept for six days)
	2,6-CH_2OH-Py	13.03	8.7	Salt	Salt (from acetonitrile kept for three weeks)
	2-COOH-quinoline	1.2	-3.13	Co-crystal	Co-crystal (from methanol kept for ten days)
XUMHUL [10.1016/j.molstruc.2020.127828]			0.86	Both co-crystal and salt are possible	Co-crystal (from methanol and kept for 4-5 days)
YAHTUY [10.1107/S1600536811043868]			0.9	Both co-crystal and salt are possible	Co-crystal
RUWHAT [10.1021/cg100484a]			-2.13	Co-crystal	Co-crystal (from methanol kept for three days at RT)
RUWGUM [10.1021/cg100484a]			-2.38	Co-crystal	Co-crystal (from water-methanol (1:3) kept for seven days at RT)
LALVED [10.1016/j.molstruc.2020.129279]			-2.41	Co-crystal	Co-crystal (from water-methanol (1:1) refluxed for 1 h and kept overnight at RT)
AYIWEM [10.5517/ccdc.csd.ccx8q84]			-0.24	Both co-crystal and salt are possible	Co-crystal
TUZFAX [10.1016/j.molstruc.2016.02.025]			-0.45	Both co-crystal and salt are possible	Co-crystal (from CH_2Cl_2-methanol

			(1:1) kept for nine days at RT)
TUZFEB [10.1016/j.molstruc.2016.02.025]	-0.45	Both co-crystal and salt are possible	Co-crystal (from CH_2Cl_2-methanol (1:1) kept for seven days at RT)
LEFPUJ [10.1107/S1600536812031029]	-2.4	Co-crystal	Co-crystal (from methanol kept for weeks at RT)
XUMKAU [10.1016/j.molstruc.2020.127828]	4.82	Salt	Salt (from methanol kept for 4-5 days)
TICZIQ [10.1039/C3CE40499D]	1.12	Both co-crystal and salt are possible	Salt (from methanol)
LODHIX [10.1021/cg4018807]	7.07	Salt	Salt (from methanol-water)
LODHOD [10.1080/15421406.2013.763335]	7.07	Salt	Co-crystal (from ethanol-water)
TUZDUP [10.1016/j.molstruc.2016.02.025]	-0.8	Both co-crystal and salt are possible	A salt and a co-crystal (from CH_2Cl_2-methanol (1:1) kept for five days at RT)
EHUGOE [10.1524/ncrs.2010.0308]	-1.06	Both co-crystal and salt are possible	Salt (from water-ethanol (1:2) kept at pH = 6-7 for six days at RT)
DUTJEI [10.1107/S1600536810027169]	-2.4	Co-crystal	Salt (from ethanol-water (2:1), refluxed for 30 min and kept for one week at RT)

*pKa values are taken as-is from Sci-Finder database (Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02).

In the solid state, **2-OH-Py exists only as the keto-tautomer [2; 3].

Supplementary References:

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