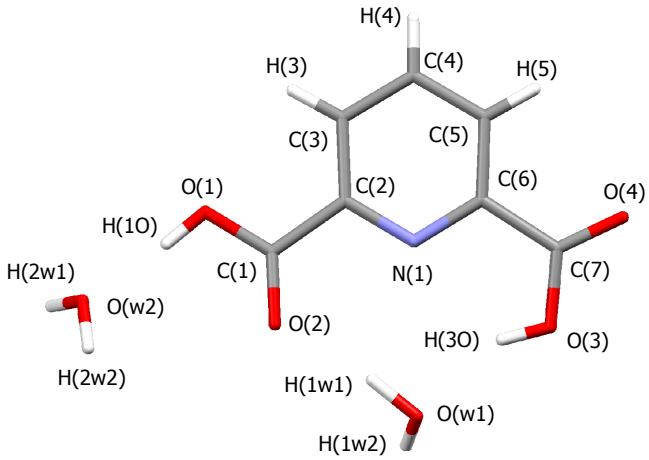
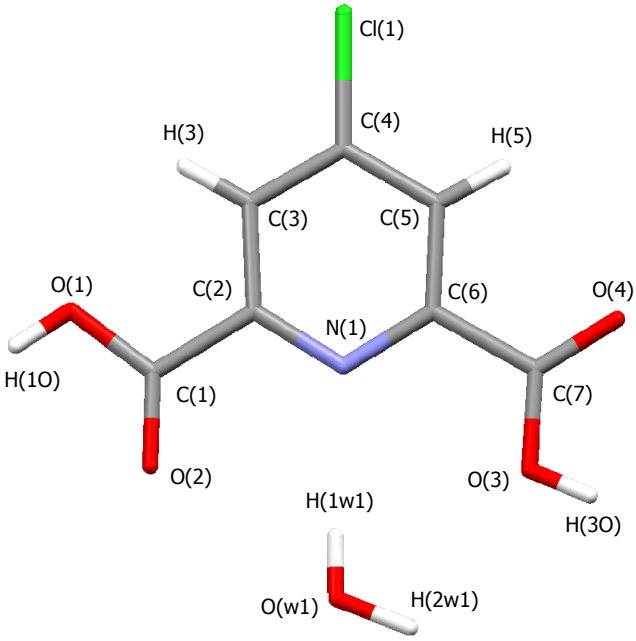
Polymorphism in pyridine-2,6-dicarboxylic acid: competition between "robust" synthons

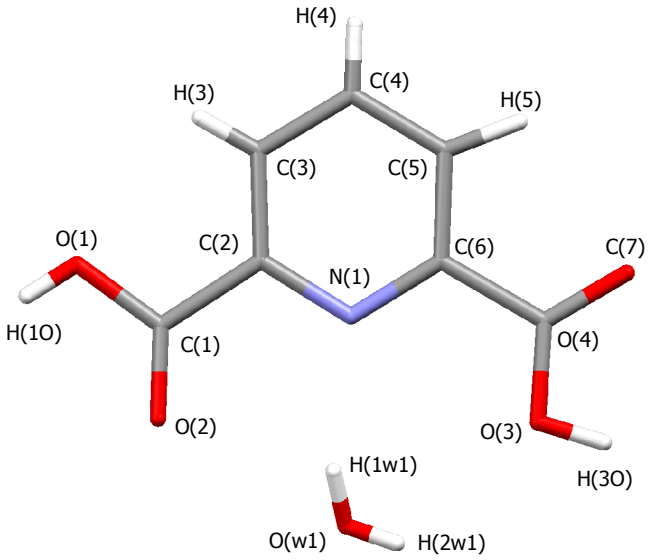
Supplementary data index:



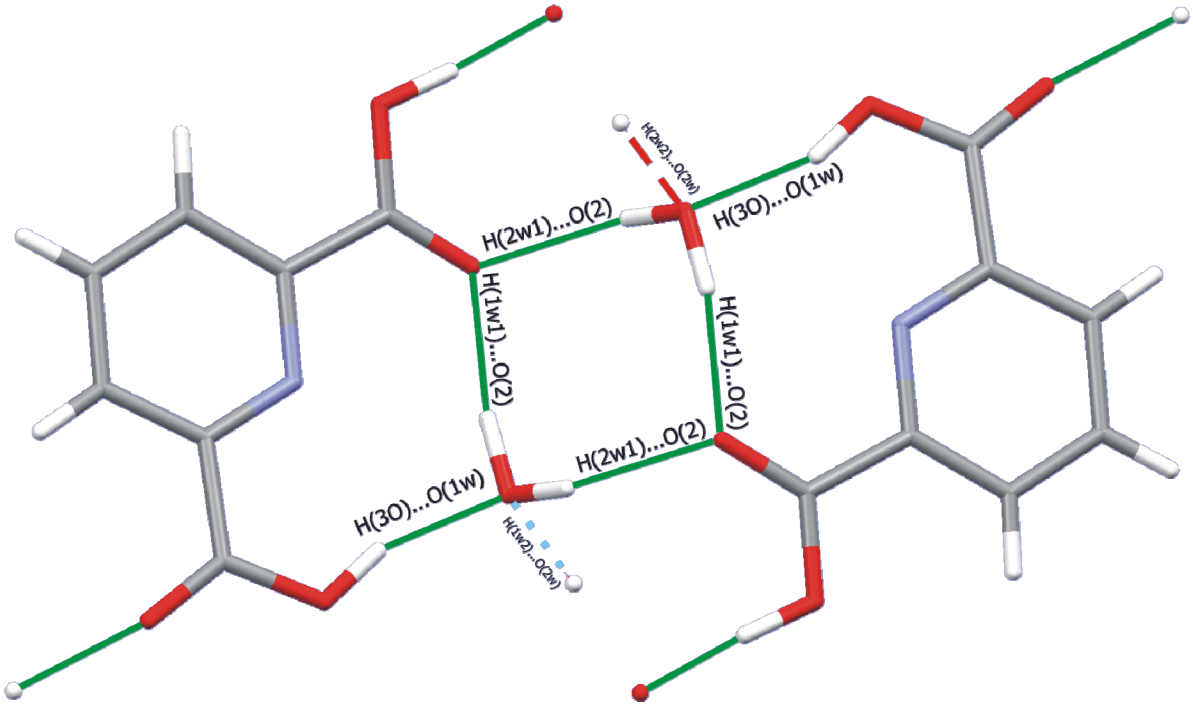
Supplementary Fig. 1 Crystal structure and numbering scheme of **4b**.



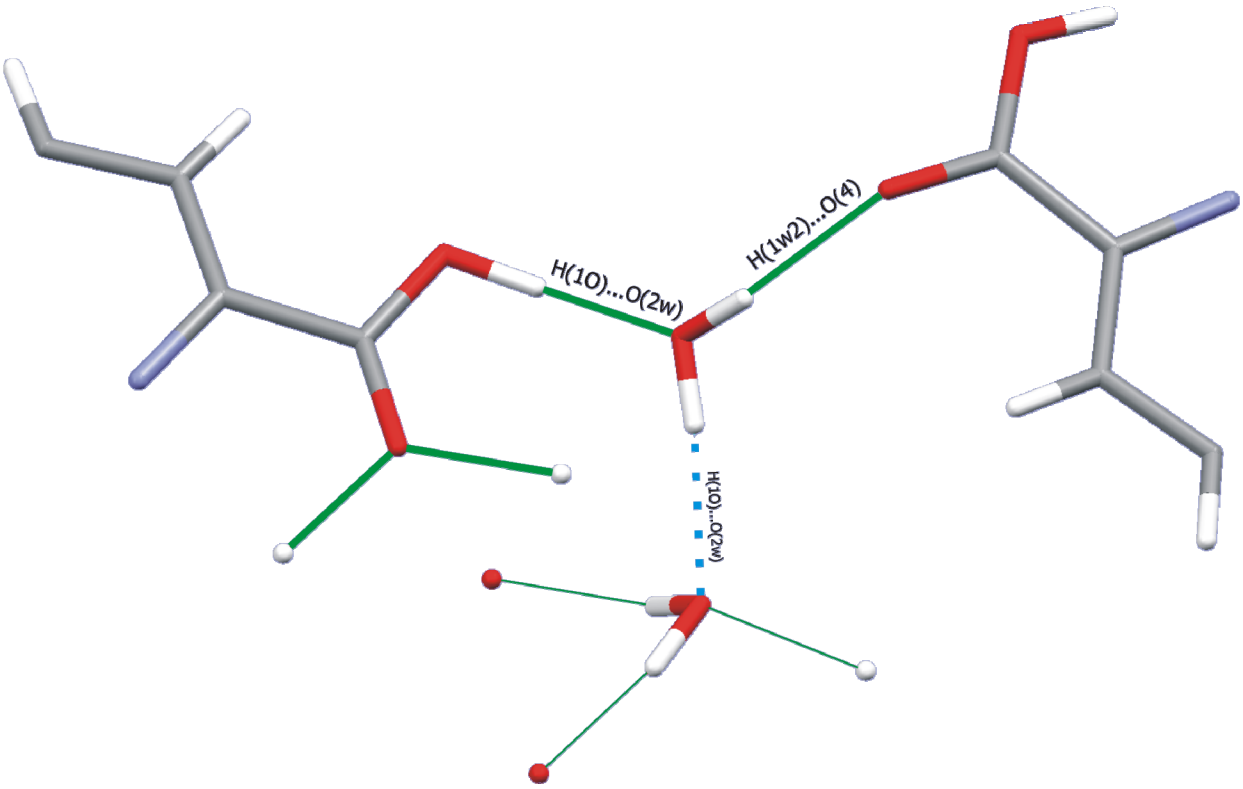
Supplementary Fig. 2 Crystal structure and numbering scheme of 4-chloropyridine-2,6-dicarboxylic acid mono-hydrate **6**.



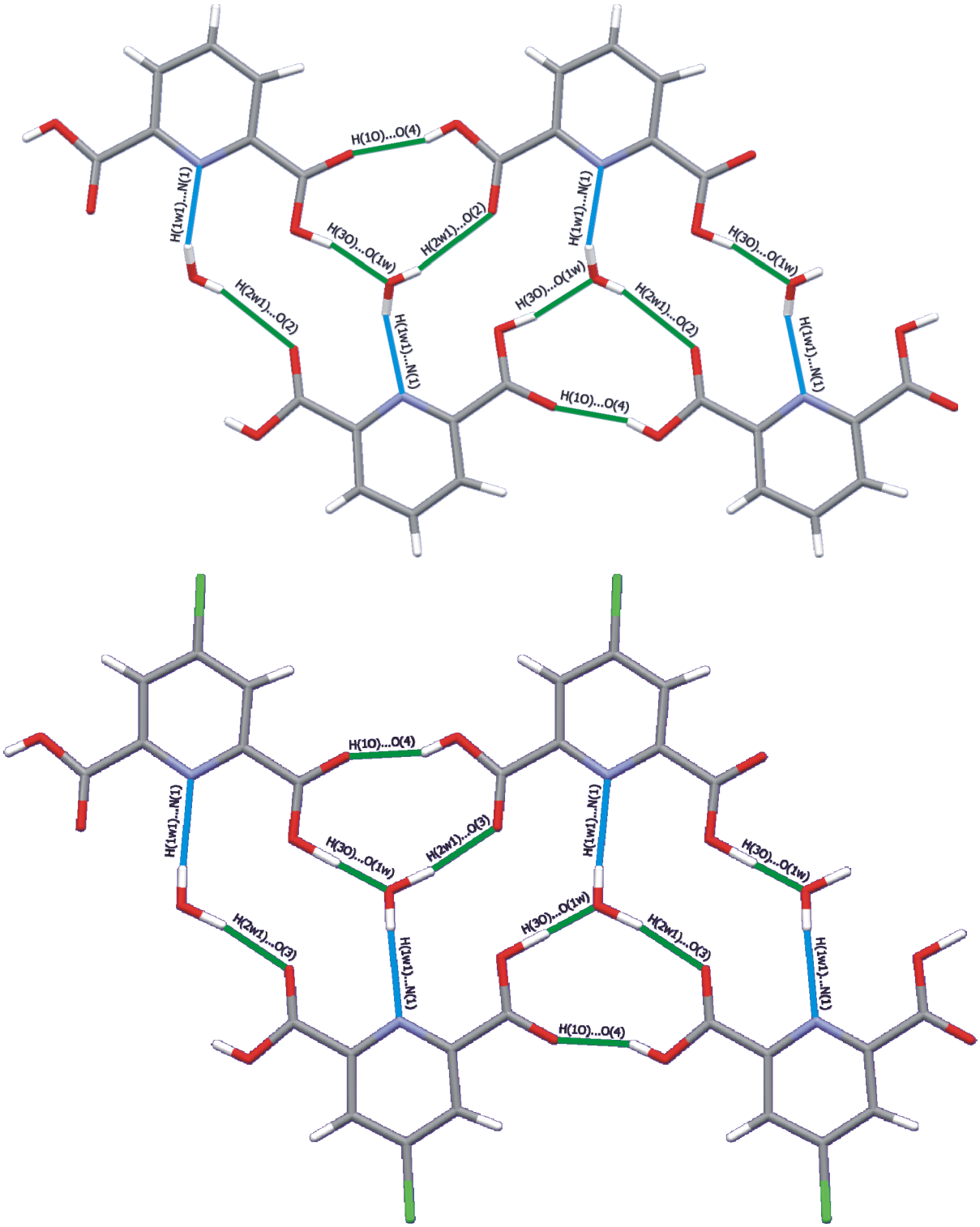
Supplementary Fig. 3 Crystal structure and numbering scheme* of dipicolinic acid mono-hydrate.[4] *(revised order for consistency within this publication).



Supplementary Fig. 4 Enlarged **Fig**. **4**

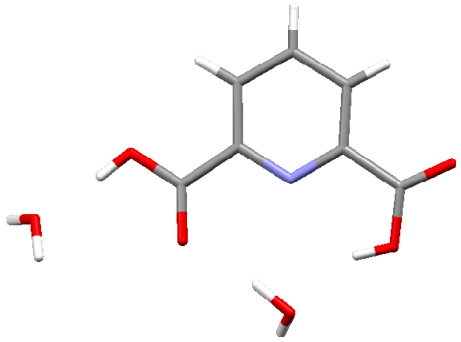


Supplementary Fig. 5 Enlarged **Fig**. **5**



Supplementary Fig. 6 Enlarged **Fig**. **6**

Supplementary Table 1. Crystal data and structure refinement of **4b**.



Identification code	**4b**	
Empirical formula	$C_7H_9NO_6$	
Formula weight	203.15	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = **3.65790(10) Å**	α = **90°**
	b = **11.0577(4) Å**	β = **93.0200(10)°**
	c = **21.5478(10) Å**	γ = **90°**
Volume	**870.35(6) Å^3**	
Z	4	
Density (calculated)	1.550 Mg / m^3	
Absorption coefficient	0.138 mm^{-1}	
$F(000)$	424	
Crystal	Plate; Colourless	
Crystal size	0.34 × 0.32 × 0.12 mm^3	
θ range for data collection	3.39 – 27.48°	
Index ranges	$-4 \le h \le 4$, $-14 \le k \le 14$, $-27 \le l \le 27$	
Reflections collected	9977	
Independent reflections	1969 [R_{int} = 0.0812]	
Completeness to θ = 27.48°	98.8 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9836 and 0.9545	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1969 / 0 / 145	
Goodness-of-fit on F^2	1.013	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0466, $wR2$ = 0.0927	
R indices (all data)	$R1$ = 0.0929, $wR2$ = 0.1119	
Largest diff. peak and hole	0.241 and –0.238 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: All carbon hydrogen atoms fixed at idealized positions, with a riding model and fixed thermal parameters [U_{ij} = 1.2U_{ij} (eq) for the atom to which they are bonded] were used for subsequent refinements.

Supplementary Table 2. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
C1	7737(5)	2559(2)	4778(1)	19(1)	1
C2	6046(5)	3096(2)	4193(1)	18(1)	1
C3	5900(5)	4334(2)	4084(1)	21(1)	1
C4	4354(5)	4742(2)	3521(1)	24(1)	1
C5	2921(5)	3910(2)	3094(1)	22(1)	1
C6	3096(5)	2692(2)	3251(1)	20(1)	1
C7	1393(5)	1751(2)	2824(1)	24(1)	1
N1	4663(4)	2282(1)	3782(1)	19(1)	1
O1	8888(4)	3364(1)	5189(1)	26(1)	1
O2	8008(4)	1468(1)	4855(1)	26(1)	1
O3	1490(4)	615(1)	3015(1)	30(1)	1
O4	−127(4)	2016(1)	2328(1)	31(1)	1
O1W	4469(4)	−296(1)	4079(1)	29(1)	1
O2W	1966(4)	2587(2)	1154(1)	32(1)	1

Supplementary Table 3. Bond lengths [Å] and angles [°].

C1–O2	1.221(2)	C6–N1	1.332(2)
C1–O1	1.311(2)	C6–C7	1.502(3)
C1–C2	1.497(3)	C7–O4	1.215(2)
C2–N1	1.342(2)	C7–O3	1.322(2)
C2–C3	1.389(3)	O1–H1O	0.8400
C3–C4	1.386(3)	O3–H3O	0.8400
C3–H3	0.9500	O1W–H1W1	0.96(3)
C4–C5	1.384(3)	O1W–H2W1	0.88(3)
C4–H4	0.9500	O2W–H1W2	0.84(3)
C5–C6	1.390(2)	O2W–H2W2	0.90(3)
C5–H5	0.9500		

O2–C1–O1	123.87(17)	C4–C5–H5	120.9
O2–C1–C2	122.33(16)	C6–C5–H5	120.9
O1–C1–C2	113.80(15)	N1–C6–C5	123.42(16)
N1–C2–C3	122.67(17)	N1–C6–C7	115.91(16)
N1–C2–C1	114.40(15)	C5–C6–C7	120.65(17)
C3–C2–C1	122.93(16)	O4–C7–O3	120.37(17)
C4–C3–C2	118.56(17)	O4–C7–C6	121.92(17)
C4–C3–H3	120.7	O3–C7–C6	117.68(17)
C2–C3–H3	120.7	C6–N1–C2	117.95(15)
C5–C4–C3	119.24(17)	C1–O1–H1O	109.5
C5–C4–H4	120.4	C7–O3–H3O	109.5
C3–C4–H4	120.4	H1W1–O1W–H2W1	104(2)
C4–C5–C6	118.12(17)	H1W2–O2W–H2W2	109(2)

Symmetry transformations used to generate equivalent atoms:

Supplementary Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	18(1)	23(1)	17(1)	−3(1)	2(1)	−3(1)
C2	14(1)	24(1)	17(1)	0(1)	2(1)	−1(1)
C3	19(1)	21(1)	23(1)	−3(1)	2(1)	−3(1)
C4	24(1)	19(1)	29(1)	4(1)	1(1)	1(1)
C5	20(1)	28(1)	19(1)	6(1)	−1(1)	2(1)
C6	17(1)	25(1)	18(1)	−1(1)	0(1)	0(1)
C7	21(1)	30(1)	19(1)	−1(1)	1(1)	0(1)
N1	18(1)	22(1)	17(1)	−1(1)	1(1)	−2(1)
O1	35(1)	26(1)	18(1)	0(1)	−8(1)	−2(1)
O2	36(1)	19(1)	22(1)	1(1)	−4(1)	−2(1)
O3	41(1)	24(1)	24(1)	−4(1)	−7(1)	−4(1)
O4	33(1)	40(1)	18(1)	0(1)	−7(1)	−2(1)
O1W	39(1)	22(1)	25(1)	0(1)	−1(1)	−3(1)
O2W	42(1)	33(1)	21(1)	1(1)	−2(1)	−7(1)

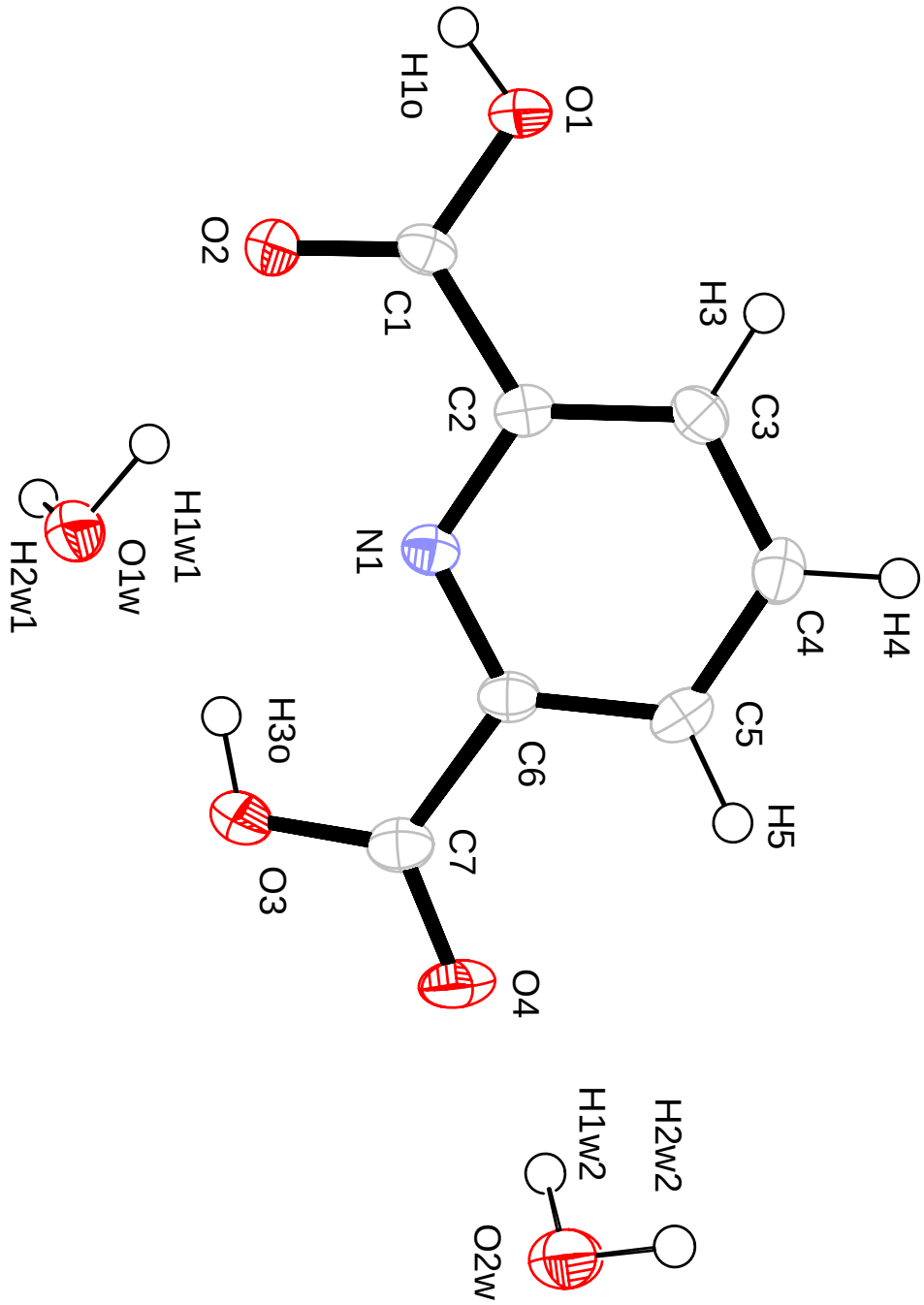
Supplementary Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	x	y	z	U_{eq}	*S.o.f.*
H3	6840	4889	4389	25	1
H4	4278	5582	3430	29	1
H5	1849	4165	2705	27	1
H1O	9778	3011	5507	40	1
H3O	2532	578	3371	45	1
H1W1	5650(80)	360(30)	4307(14)	73(9)	1
H1W2	1120(80)	2510(20)	1506(15)	58(9)	1
H2W1	3030(80)	−620(30)	4348(15)	74(10)	1
H2W2	2820(70)	3350(20)	1115(12)	51(8)	1

Supplementary Table 6. Hydrogen bonds [Å and °].

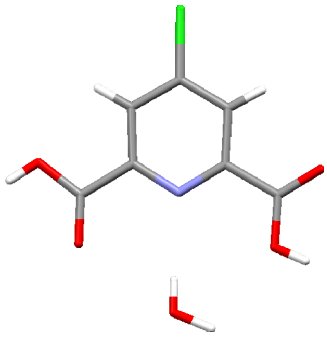
D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
O3–H3O···O1W	0.84	1.91	2.6835(19)	152.4
O1–H1O···O2W^{i}	0.84	1.70	2.539(2)	173.5
O1W–H1W1···O2	0.96(3)	1.88(3)	2.8372(19)	171(2)
O1W–H2W1···O2^{ii}	0.88(3)	2.01(3)	2.827(2)	154(3)
O2W–H2W2···O1W^{iii}	0.90(3)	1.86(3)	2.738(2)	165(2)
O2W–H1W2···O4	0.84(3)	1.93(3)	2.755(2)	167(3)

Symmetry transformations used to generate equivalent atoms:
(i) x+1,–y+1/2,z+1/2 (ii) –x+1,–y,–z+1 (iii) –x+1,y+1/2,–z+1/2



Supplementary Fig. 7 Ortep Plot (including numbering scheme) of **4b**:

Supplementary Table 7. Crystal data and structure refinement of **6**.



Identification code	**6**	
Empirical formula	$C_7H_6ClNO_5$	
Formula weight	219.58	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = **5.1793(2) Å**	α = **90°**
	b = **9.4760(3) Å**	β = **94.289(2)°**
	c = **8.5004(3) Å**	γ = **90°**
Volume	**416.02(3) Å^3**	
Z	2	
Density (calculated)	1.753 Mg / m^3	
Absorption coefficient	0.454 mm^{-1}	
F(000)	224	
Crystal	Plate; Colourless	
Crystal size	0.20 × 0.18 × 0.03 mm^3	
θ range for data collection	3.22 – 27.48°	
Index ranges	$-6 \le h \le 6$, $-12 \le k \le 12$, $-10 \le l \le 11$	
Reflections collected	5401	
Independent reflections	1880 [R_{int} = 0.0491]	
Completeness to θ = 27.48°	99.7 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	0.9865 and 0.9147	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1880 / 1 / 138	
Goodness-of-fit on F^2	1.063	
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1$ = 0.0294, $wR2$ = 0.0717	
R indices (all data)	$R1$ = 0.0316, $wR2$ = 0.0735	
Absolute structure parameter	0.28(5)	
Largest diff. peak and hole	0.212 and –0.319 e Å^{-3}	

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). J. Appl. Cryst. 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement**: *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. **276**: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction**: *SORTAV* (R. H. Blessing, Acta Cryst. A**51** (1995) 33–37; R. H. Blessing, J. Appl. Cryst. **30** (1997) 421–426). S**tructure solution**: *SHELXS97* (G. M. Sheldrick, Acta Cryst. (1990) A**46** 467–473). S**tructure refinement**: *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details: All carbon hydrogen atoms fixed at idealized positions, with a riding model and fixed thermal parameters [U_{ij} = 1.2U_{ij} (eq) for the atom to which they are bonded] were used for subsequent refinements.

Supplementary Table 8. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
Cl1	5315(1)	−18023(1)	−10390(1)	20(1)	1
C5	1930(4)	−16892(2)	−8480(3)	17(1)	1
C3	2088(4)	−19410(2)	−8572(3)	15(1)	1
N1	−899(3)	−18259(2)	−6951(2)	15(1)	1
O2	−2625(3)	−20915(2)	−6144(2)	25(1)	1
O1	377(3)	−21882(1)	−7579(2)	24(1)	1
O4	−410(3)	−14555(2)	−7357(2)	25(1)	1
C6	−4(4)	−17023(2)	−7445(2)	14(1)	1
O3	−3035(3)	−15832(1)	−5950(2)	23(1)	1
C4	2964(3)	−18109(2)	−9053(2)	16(1)	1
C7	−1197(4)	−15680(2)	−6887(3)	15(1)	1
C2	159(4)	−19422(2)	−7518(2)	16(1)	1
C1	−868(4)	−20816(2)	−6984(2)	15(1)	1
O1W	−4877(3)	−23512(2)	−5214(2)	29(1)	1

Supplementary Table 9. Bond lengths [Å] and angles [°].

Cl1–C4	1.7282(16)	O1–C1	1.319(2)
C5–C4	1.376(3)	O1–H1	0.8400
C5–C6	1.387(3)	O4–C7	1.220(2)
C5–H5	0.9500	C6–C7	1.506(3)
C3–C4	1.386(3)	O3–C7	1.295(3)
C3–C2	1.391(3)	O3–H3A	0.8400
C3–H3	0.9500	C2–C1	1.506(3)
N1–C2	1.337(2)	O1W–H1WB	0.79(3)
N1–C6	1.339(2)	O1W–H1WA	1.01(4)
O2–C1	1.202(2)		
C4–C5–C6	117.96(16)	C5–C4–Cl1	120.37(14)
C4–C5–H5	121.0	C3–C4–Cl1	119.89(14)
C6–C5–H5	121.0	O4–C7–O3	125.3(2)
C4–C3–C2	117.68(18)	O4–C7–C6	118.7(2)
C4–C3–H3	121.2	O3–C7–C6	115.95(16)
C2–C3–H3	121.2	N1–C2–C3	123.96(17)
C2–N1–C6	116.58(14)	N1–C2–C1	116.81(17)
C1–O1–H1	109.5	C3–C2–C1	119.23(17)
N1–C6–C5	124.07(17)	O2–C1–O1	125.56(18)
N1–C6–C7	118.72(17)	O2–C1–C2	123.21(17)
C5–C6–C7	117.19(17)	O1–C1–C2	111.22(18)
C7–O3–H3A	109.5	H1WB–O1W–H1WA	112(3)
C5–C4–C3	119.74(14)		

Symmetry transformations used to generate equivalent atoms:

Supplementary Table 10. Anisotropic displacement parameters [$Å^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl1	20(1)	19(1)	24(1)	2(1)	12(1)	−1(1)
C5	20(1)	12(1)	19(1)	2(1)	1(1)	−4(1)
C3	17(1)	10(1)	19(1)	−1(1)	6(1)	1(1)
N1	17(1)	10(1)	17(1)	0(1)	4(1)	1(1)
O2	29(1)	13(1)	34(1)	1(1)	19(1)	−1(1)
O1	32(1)	8(1)	33(1)	1(1)	17(1)	−1(1)
O4	32(1)	11(1)	35(1)	0(1)	16(1)	0(1)
C6	17(1)	13(1)	14(1)	0(1)	4(1)	0(1)
O3	27(1)	11(1)	33(1)	−1(1)	16(1)	2(1)
C4	16(1)	17(1)	15(1)	2(1)	6(1)	1(1)
C7	17(1)	11(1)	17(1)	−1(1)	2(1)	−1(1)
C2	17(1)	10(1)	20(1)	2(1)	1(1)	−1(1)
C1	18(1)	9(1)	19(1)	−2(1)	5(1)	1(1)
O1W	33(1)	13(1)	44(1)	1(1)	26(1)	1(1)

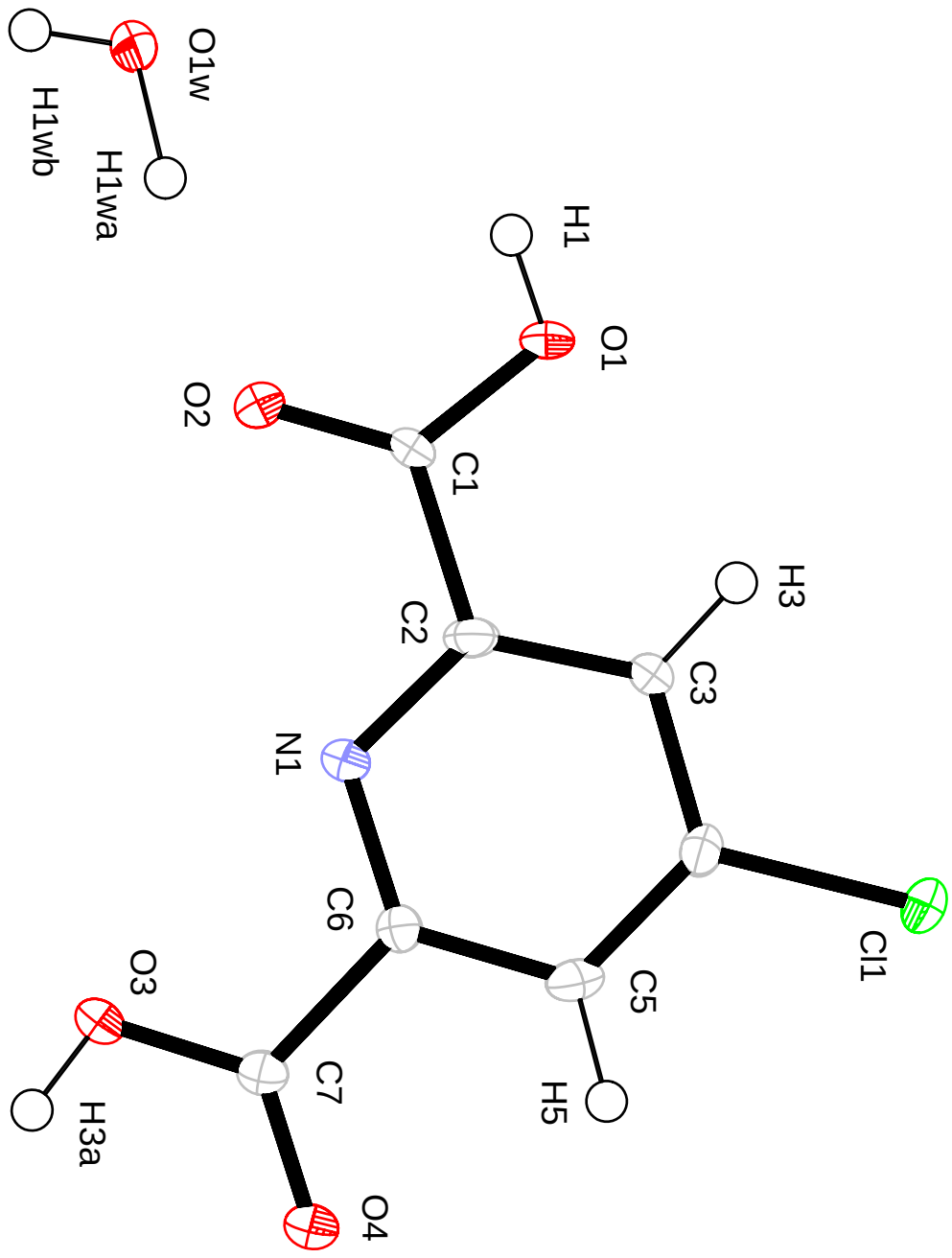
Supplementary Table 11. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H5	2521	−15991	−8784	20	1
H3	2781	−20263	−8949	18	1
H1	−317	−22644	−7336	35	1
H3A	−3656	−15038	−5752	34	1
H1WB	−6050(50)	−23470(40)	−4670(30)	42(8)	1
H1WA	−4200(60)	−22540(40)	−5470(30)	50(9)	1

Supplementary Table 12. Hydrogen bonds [Å and °].

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*DHA*)
O1–H1···O4^{i}	0.84	1.81	2.5747(17)	150.3
O3–H3A···O1W^{ii}	0.84	1.66	2.494(2)	175.4
O1W–H1WB···N1^{iii}	0.79(3)	2.19(3)	2.972(2)	175(3)
O1W–H1WB···O2^{iii}	0.79(3)	2.53(3)	2.901(2)	111(3)
O1W–H1WA···O1	1.01(4)	3.14(3)	3.828(2)	126(2)

Symmetry transformations used to generate equivalent atoms:
(i) x,y−1,z (ii) x,y+1,z (iii) −x−1,y−1/2,−z−1



Supplementary Fig. 7 Ortep Plot (including numbering scheme) of **6**: