Supplementary Information

Missing Puzzle in Crystal Engineering: 2-Pyridone and [1,3,5]-Triazine-2,4-diamine, Two Most Common Cyclic Hydrogen Bonding Sticky Sites, in a Single Core

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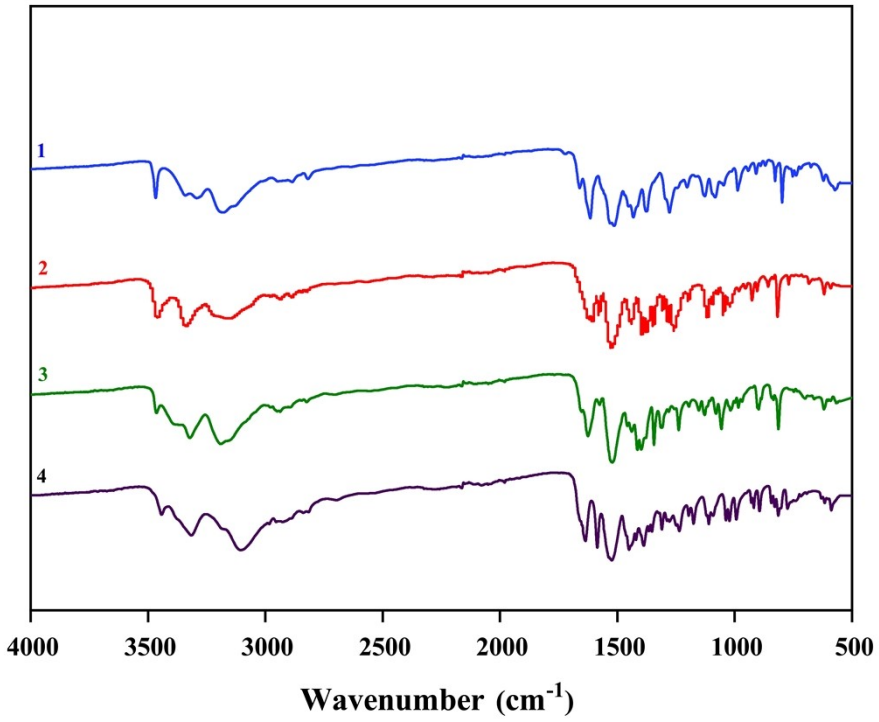

Fig. S1 Infrared spectra of **1-4**.

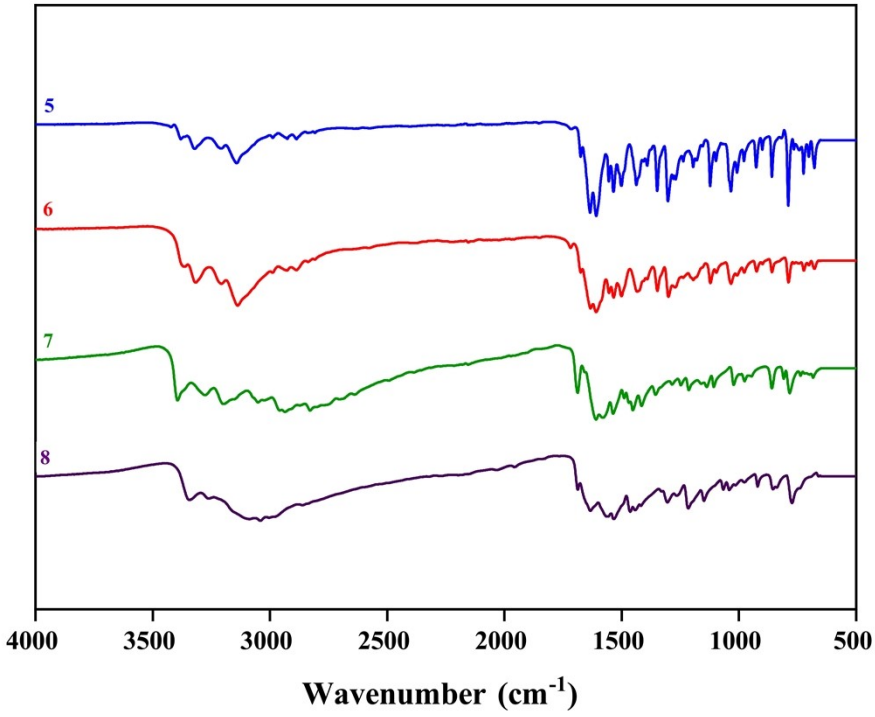

Fig. S2 Infrared spectra of **5-8**.

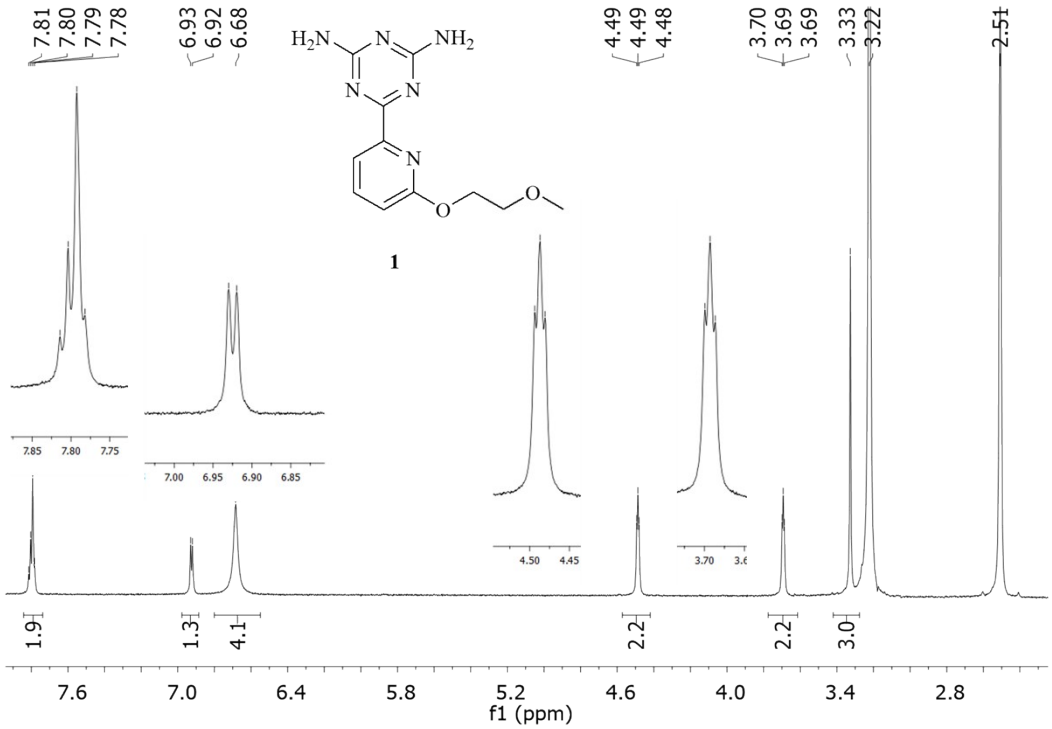

Fig. S3 ^{1}H NMR spectrum **1** in DMSO-d_6.

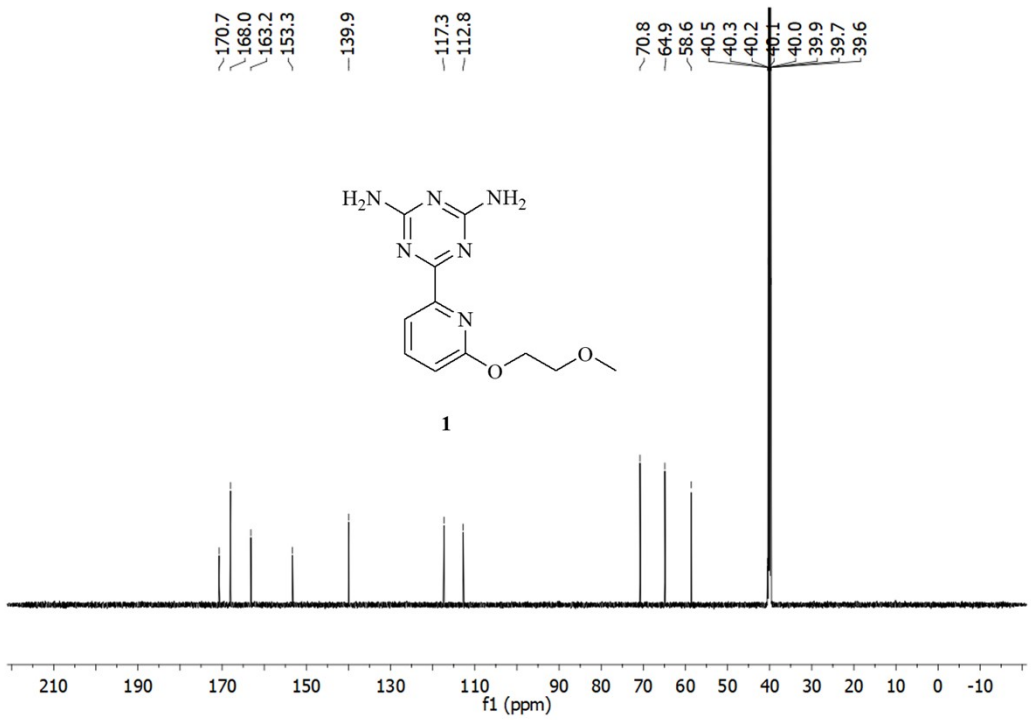

Fig. S4 ^{13}C NMR spectrum **1** in DMSO-d_6.

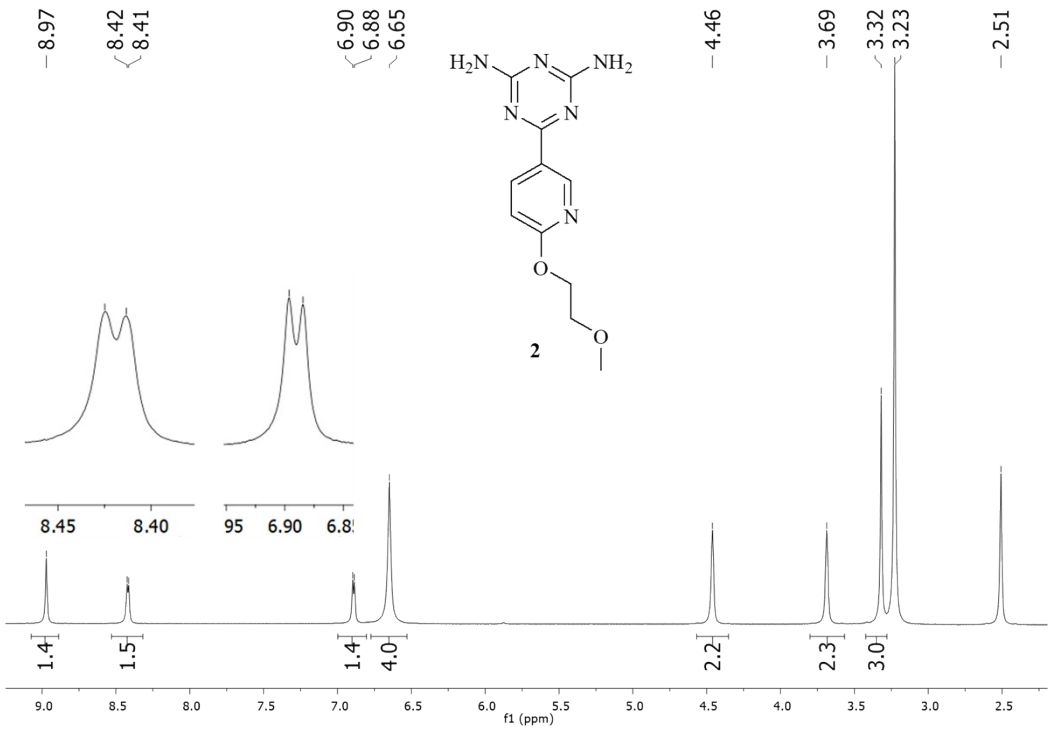

Fig. S5 ^{1}H NMR spectrum **2** in DMSO-d_6.

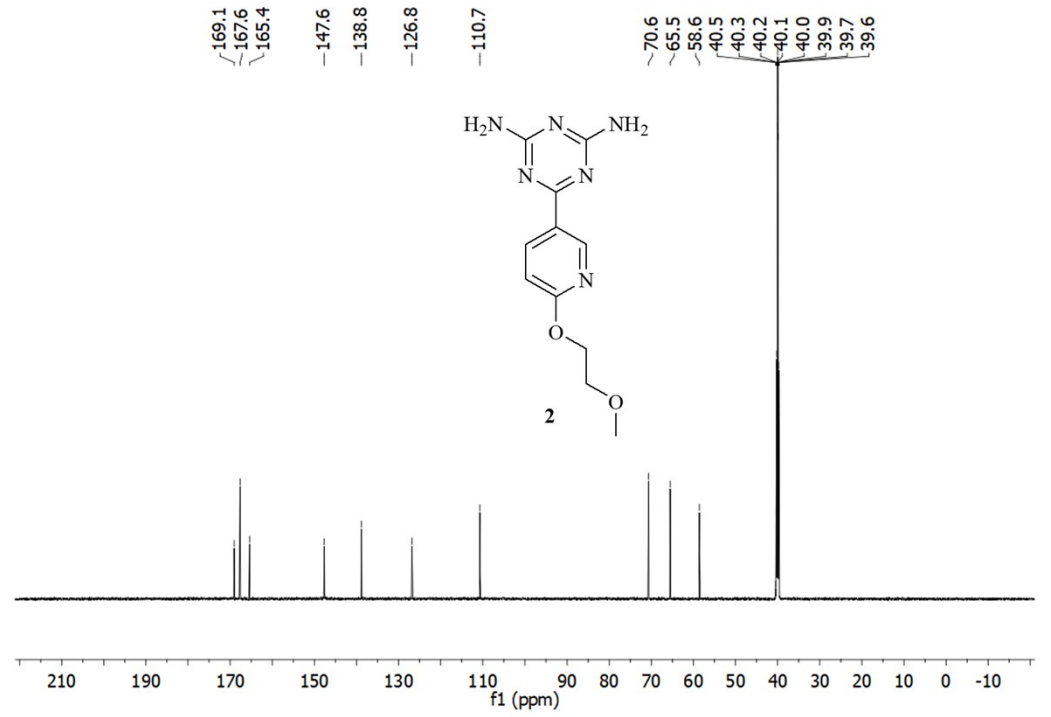

Fig. S6 ^{13}C NMR spectrum **2** in DMSO-d_6.

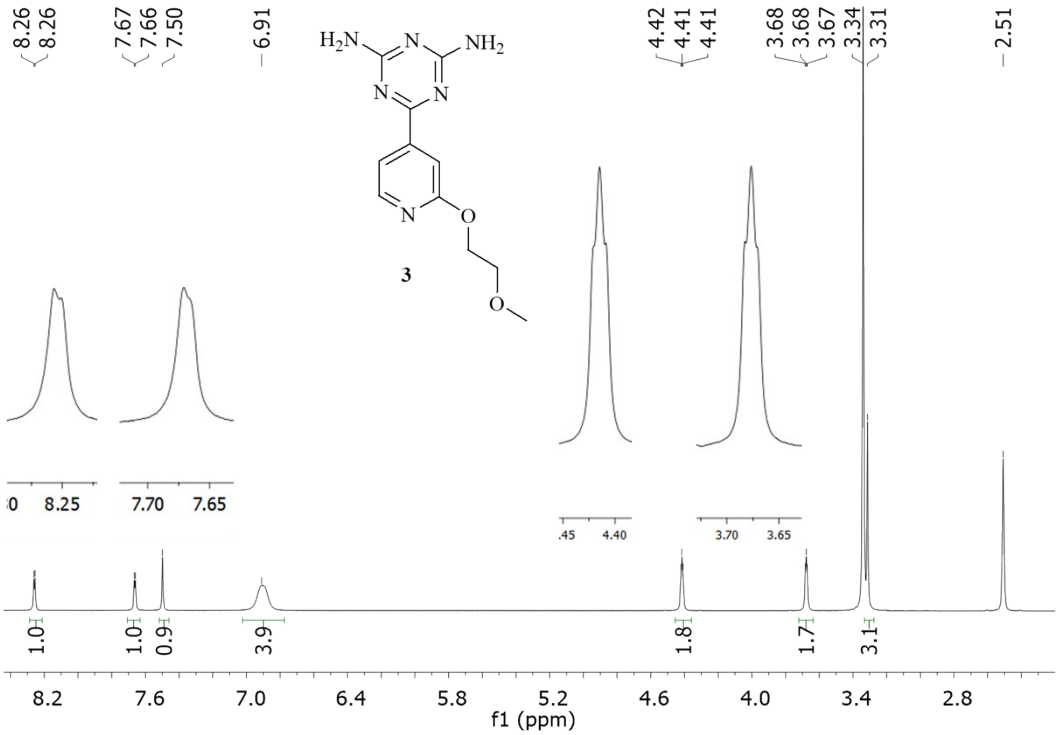

Fig. S7 ^{1}H NMR spectrum **3** in DMSO-d_6.

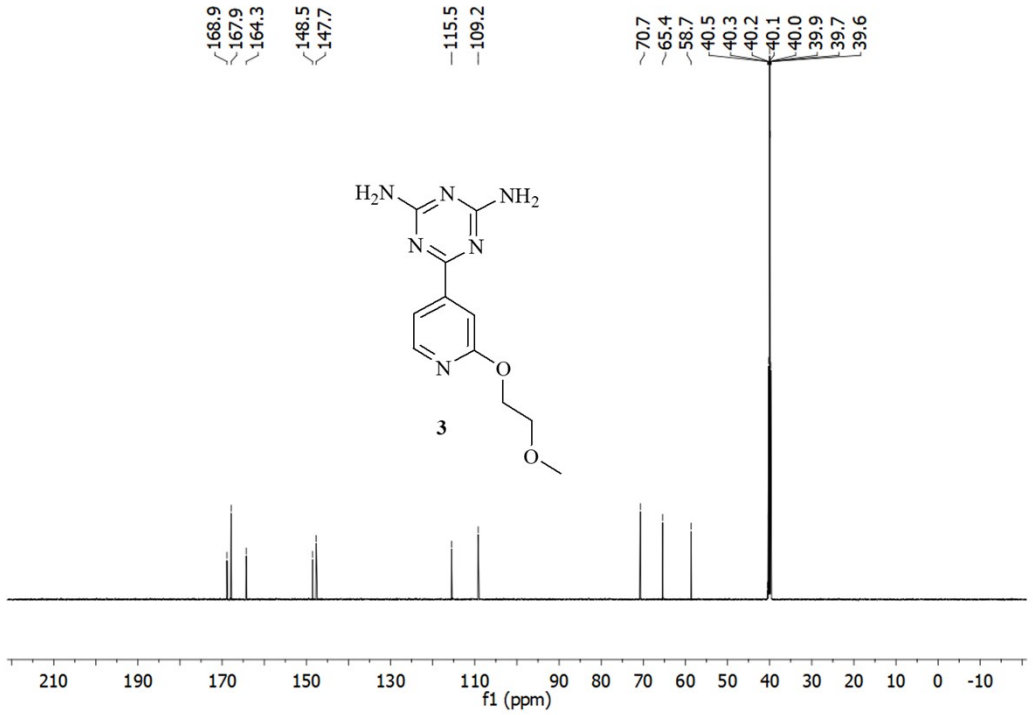

Fig. S8 ^{13}C NMR spectrum **3** in DMSO-d_6.

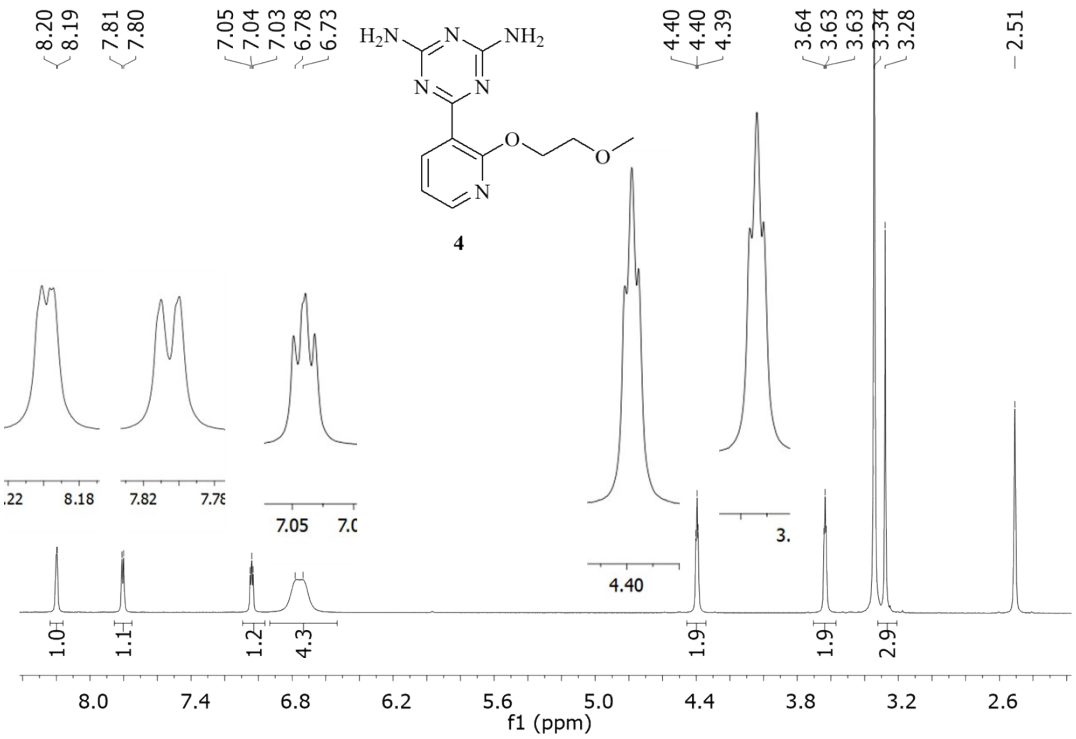

Fig. S9 ^{1}H NMR spectrum **4** in DMSO-d_6.

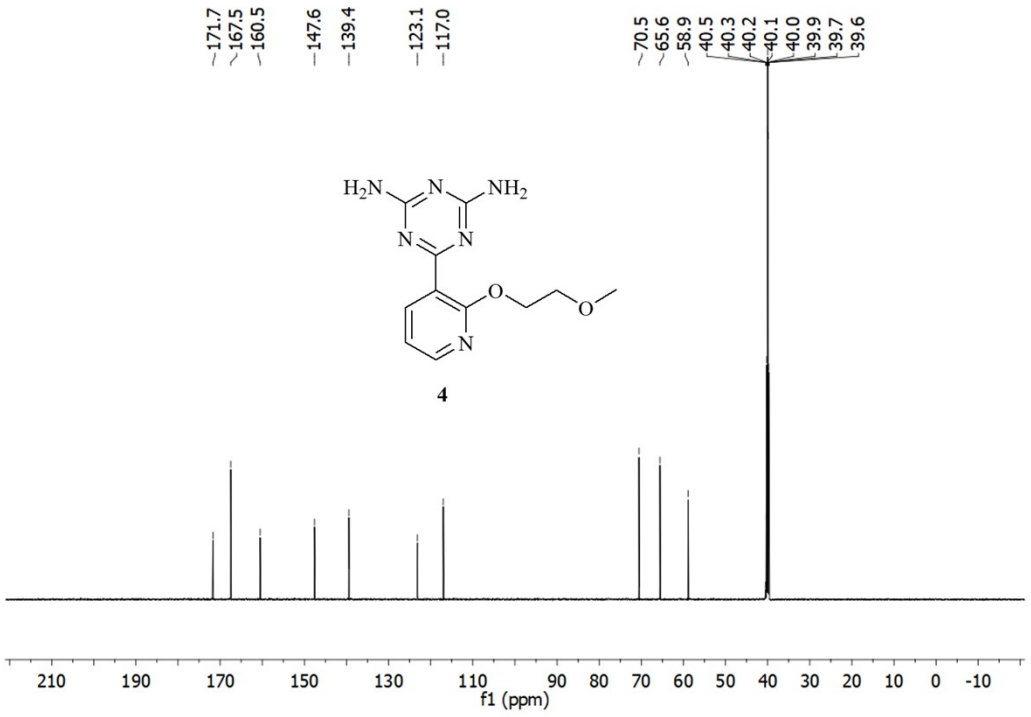

Fig. S10 ^{13}C NMR spectrum **4** in DMSO-d_6.

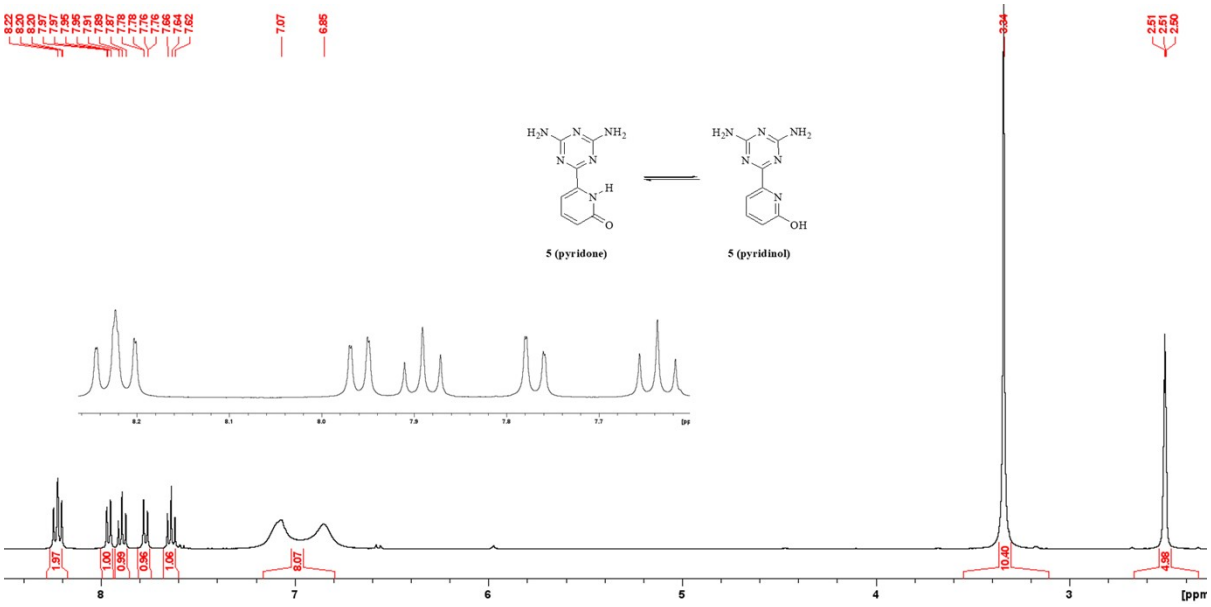

Fig. S11 ^{1}H NMR spectrum **5** in DMSO-d_6.

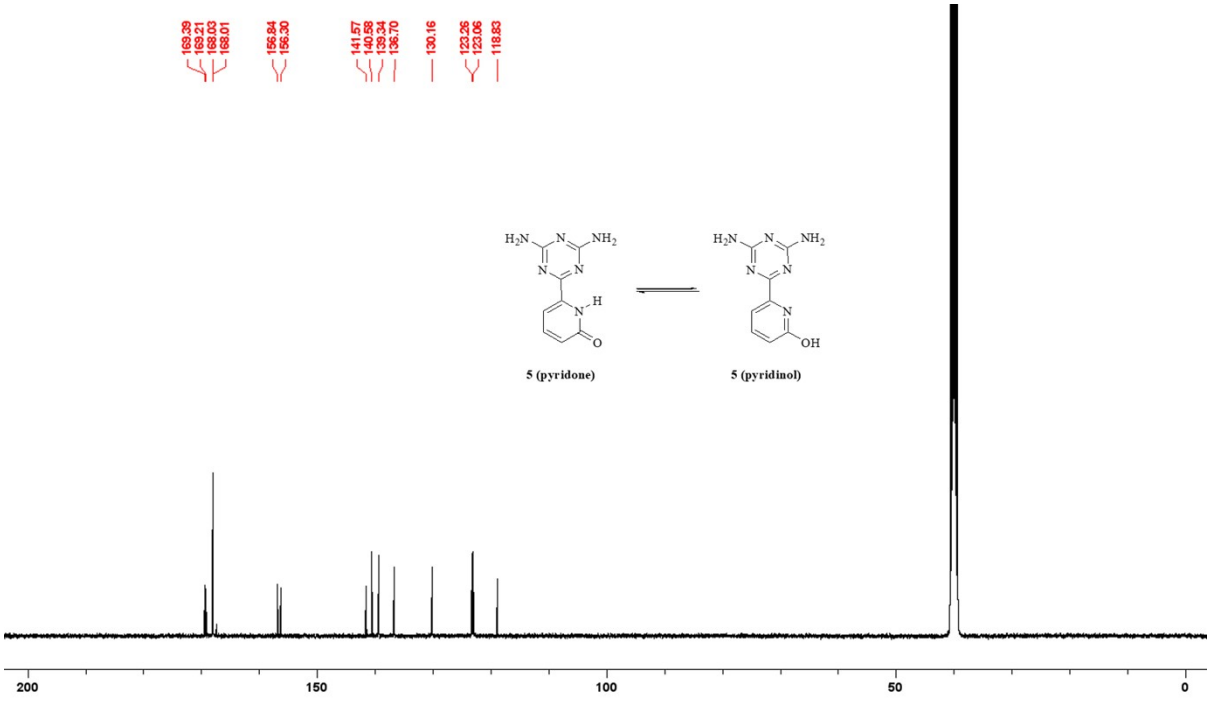

Fig. S12 ^{13}C NMR spectrum **5** in DMSO-d_6.

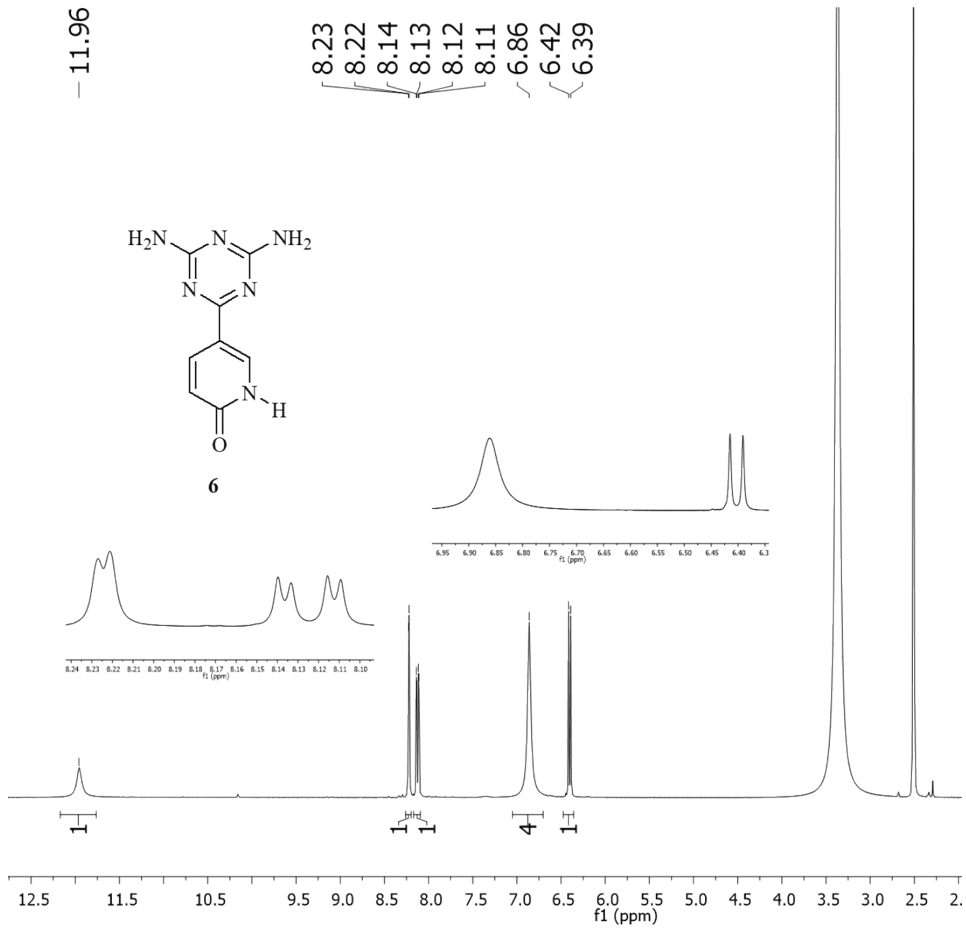

Fig. S13 ^{1}H NMR spectrum **6** in DMSO-d_6.

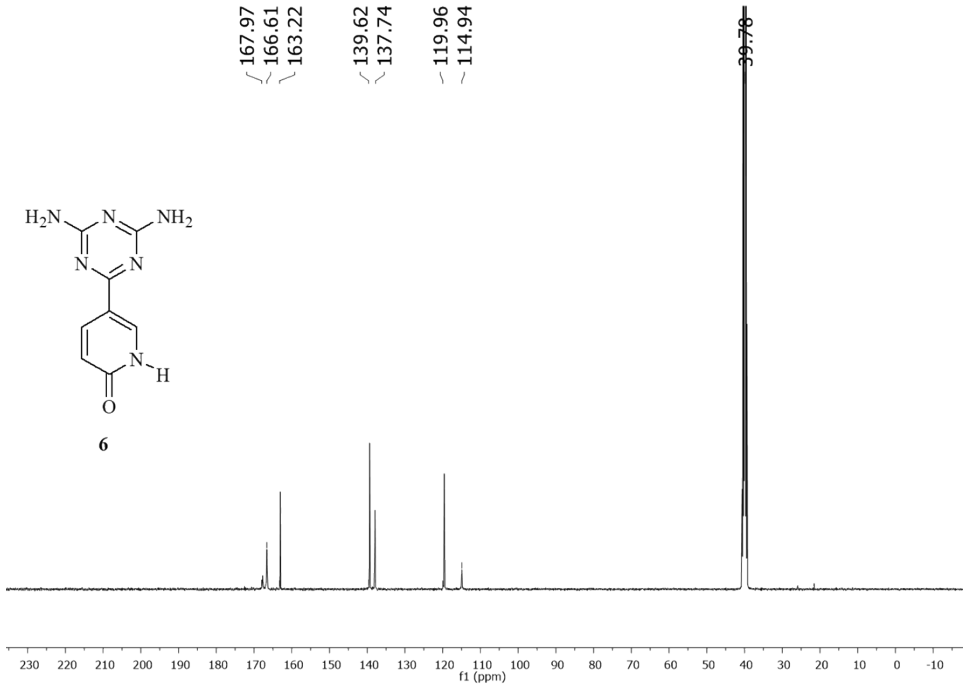

Fig. S14 ^{13}C NMR spectrum **6** in DMSO-d_6.

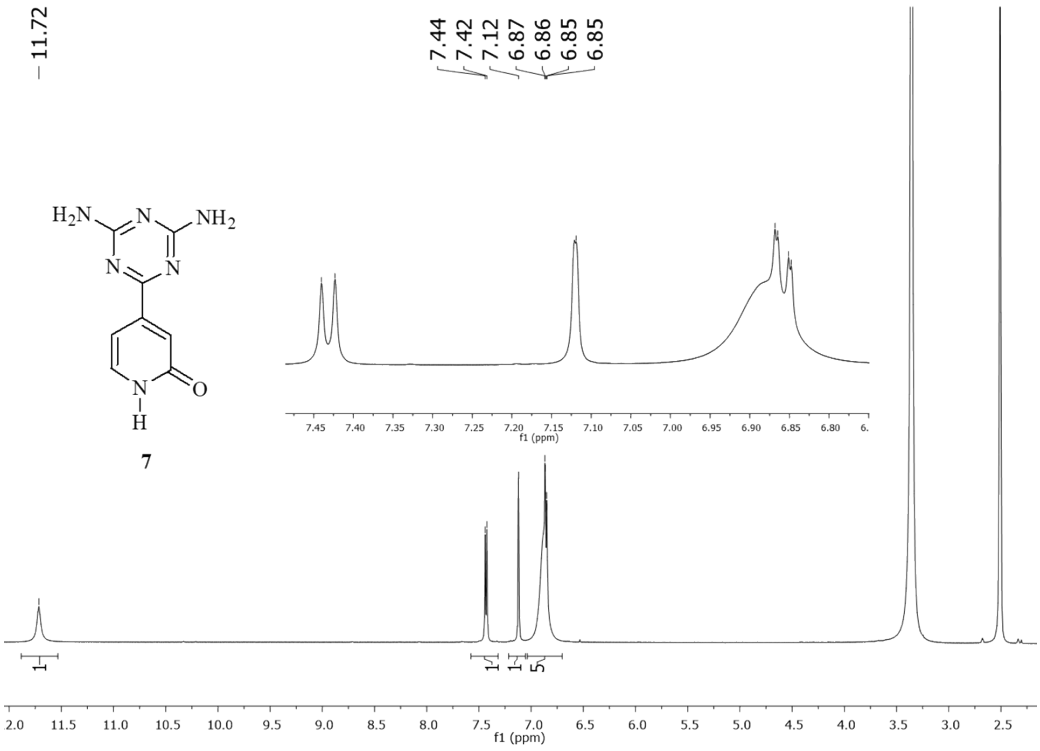

Fig. S15 ^{1}H NMR spectrum **7** in DMSO-d_6.

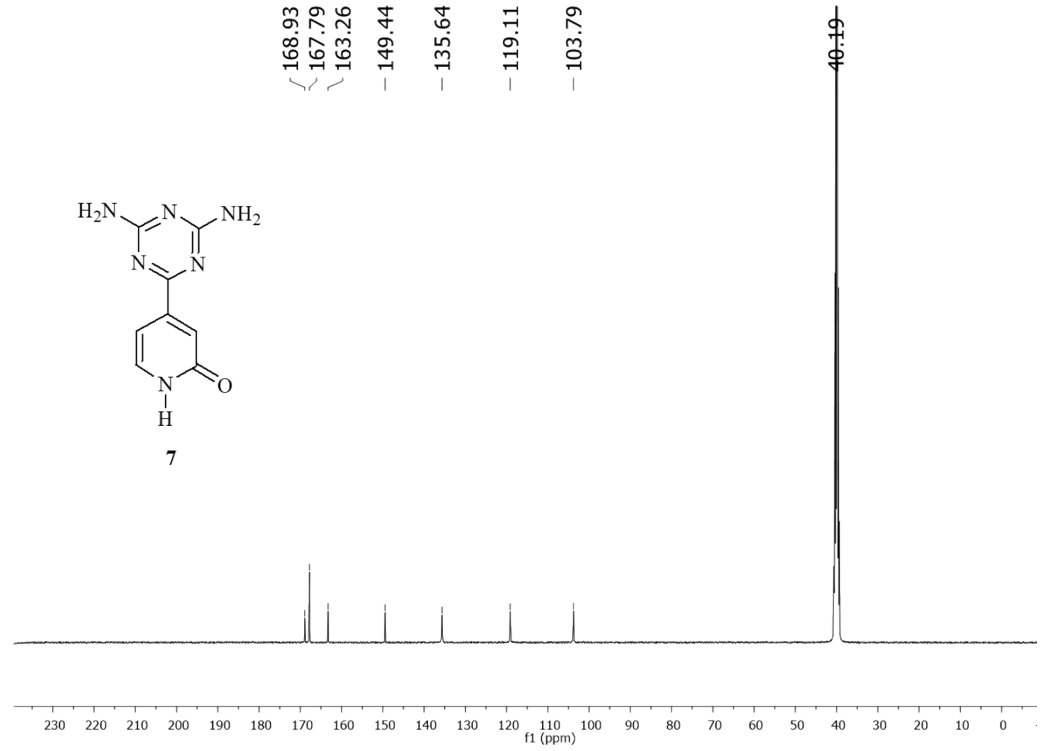

Fig. S16 ^{13}C NMR spectrum **7** in DMSO-d_6.

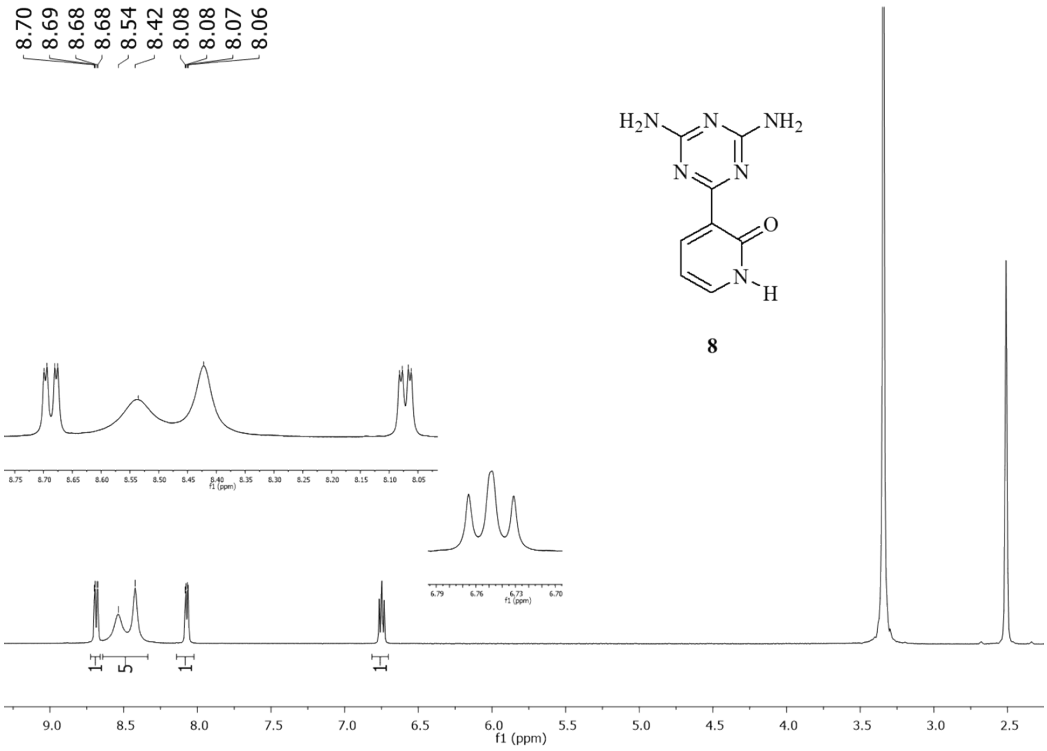

Fig. S17 ^{1}H NMR spectrum **8** in DMSO-d_6.

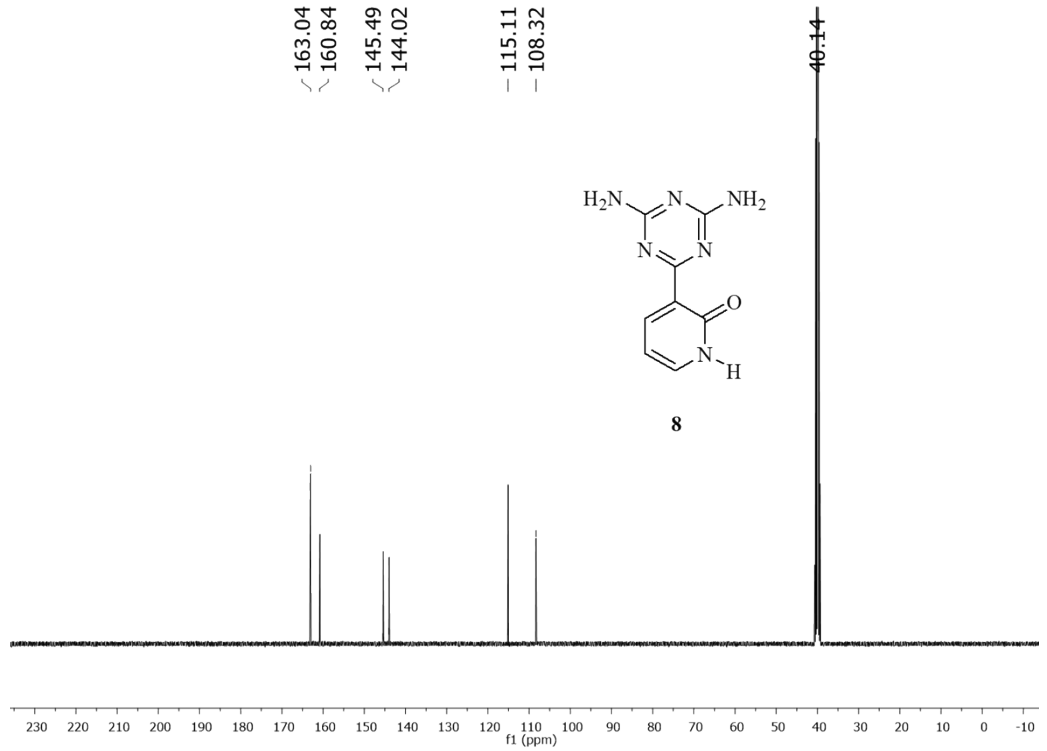

Fig. S18 ^{13}C NMR spectrum **8** in DMSO-d_6.

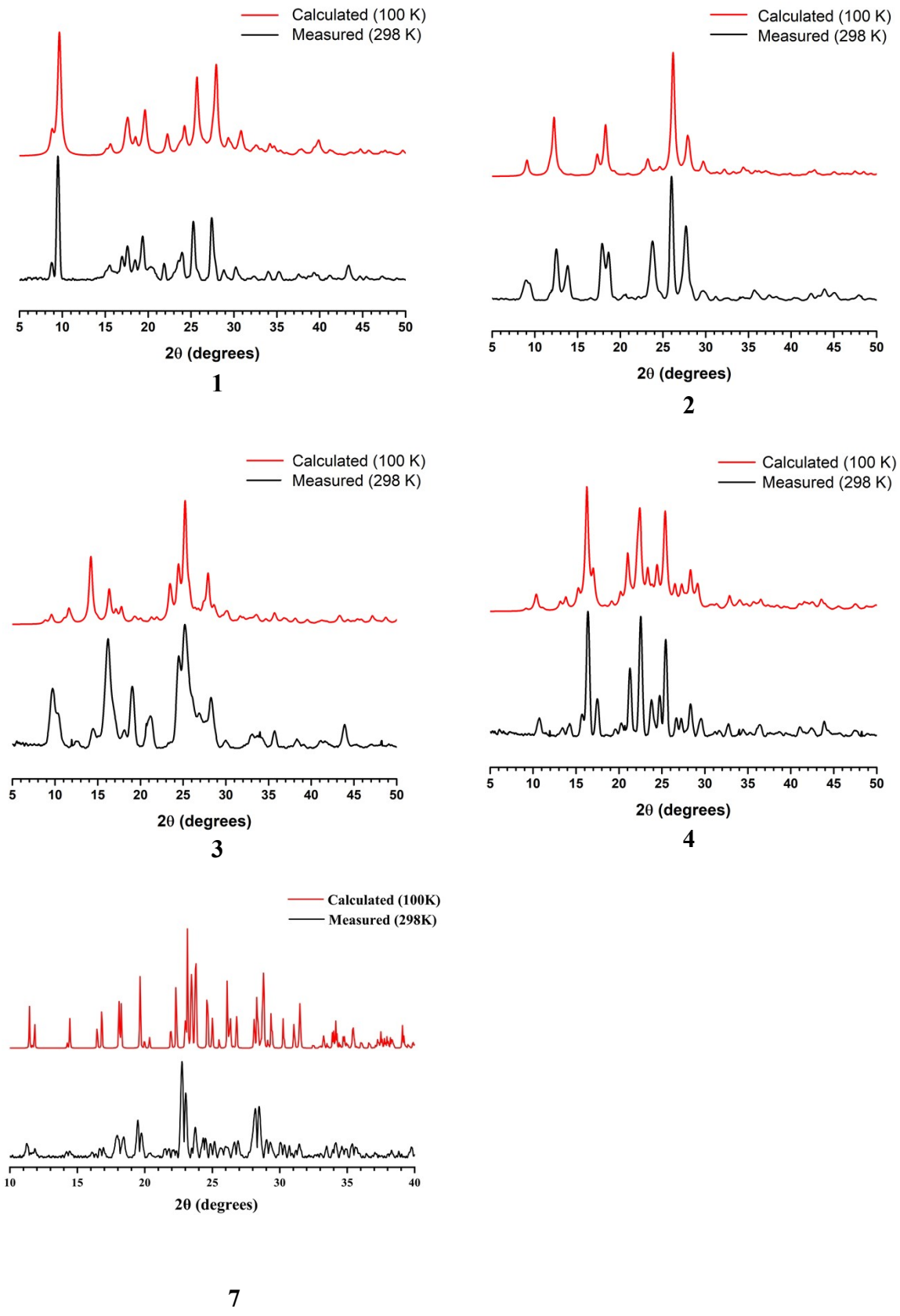

Fig. S19 PXRD of **1-4** and **5** and **7**. Comparison of the measured powder X-ray diffraction (in black) with simulated patterns (in red) calculated from single-crystal structures.

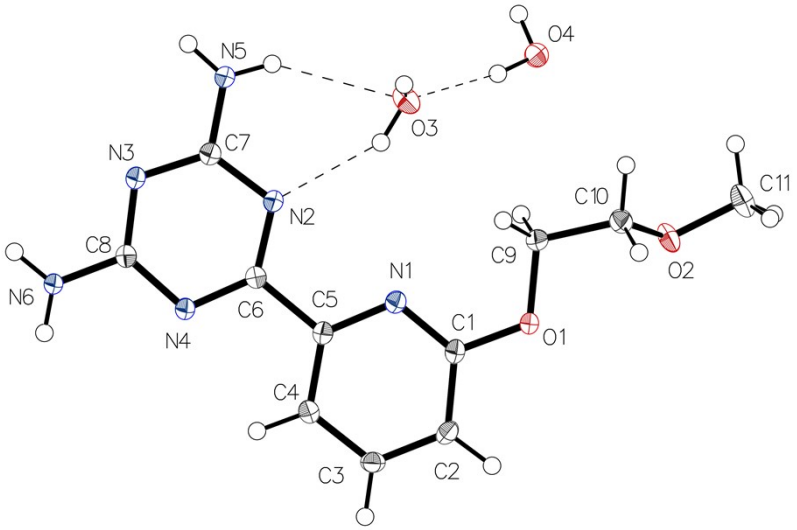

Fig. S20 Thermal atomic displacement ellipsoid plot of the structure of **1** grown from slow evaporation of water. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

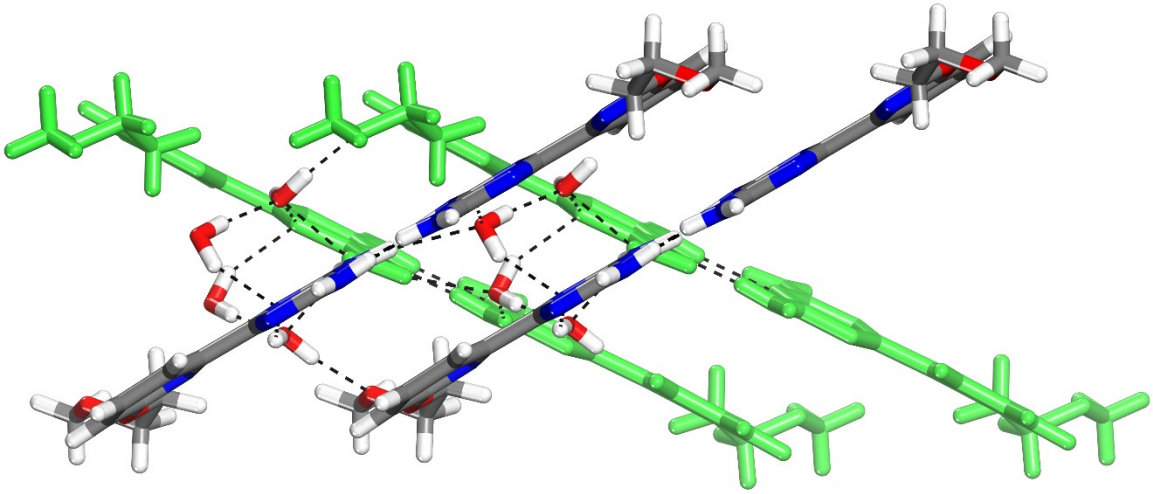

Fig. S21 View showing hydrogen bonding between two adjacent layers in crystal of **1**, with one layer highlighted in green for clarity. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

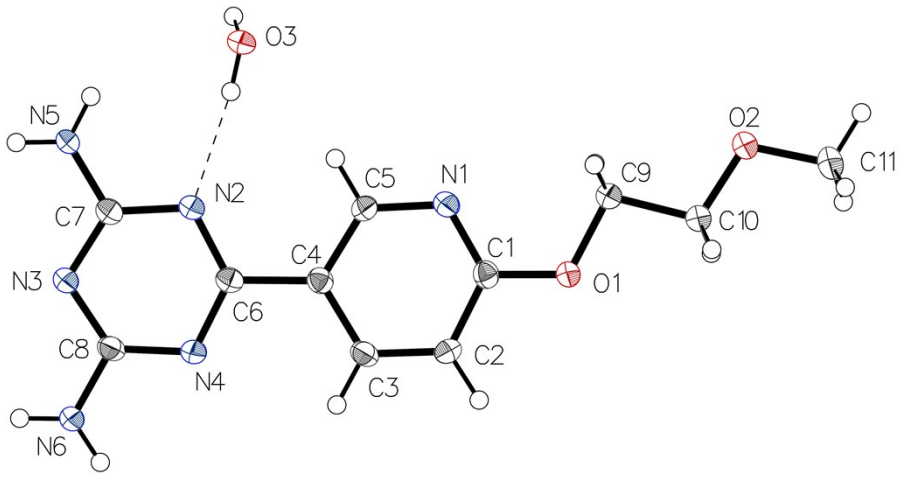

Fig. S22 Thermal atomic displacement ellipsoid plot of the structure of **2** grown from slow evaporation of water. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

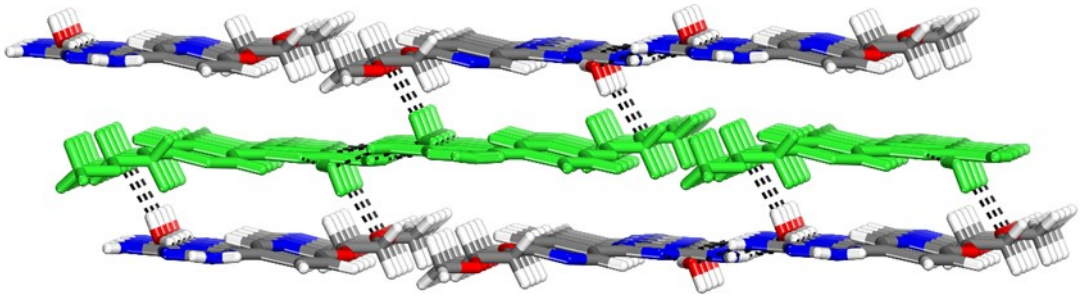

Fig. S23 View showing the adjacent stacking of layers in crystal of **2**. For clarity one layer is marked in green. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

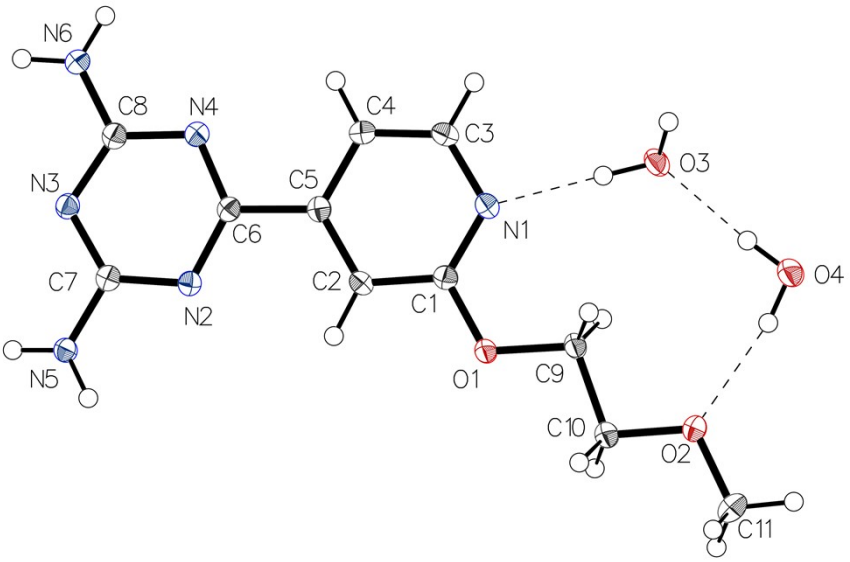

Fig. S24 Thermal atomic displacement ellipsoid plot of the structure of **3** grown from slow evaporation of water. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

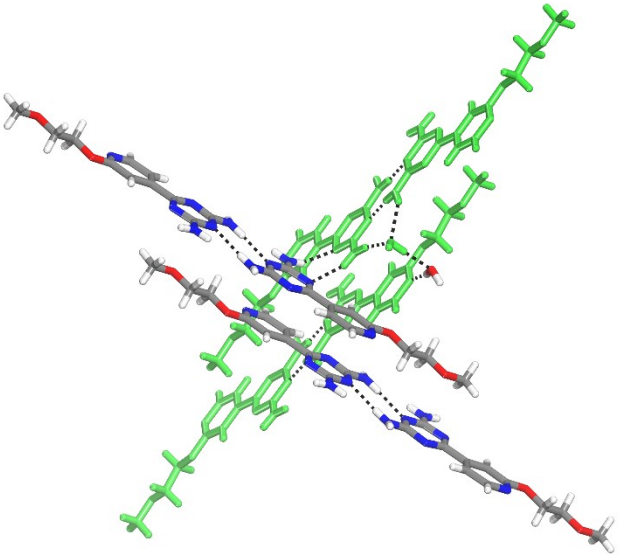

Fig. S25 View showing hydrogen bonding between adjacent layers in crystal of **3**, one layer highlighted in green for clarity. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

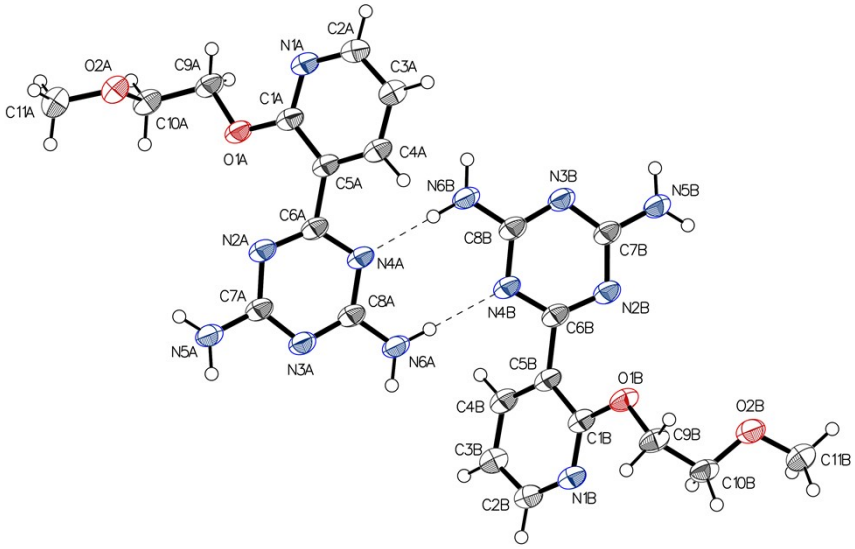

Fig. S26 Thermal atomic displacement ellipsoid plot of the structure of **4** grown from slow evaporation of water. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

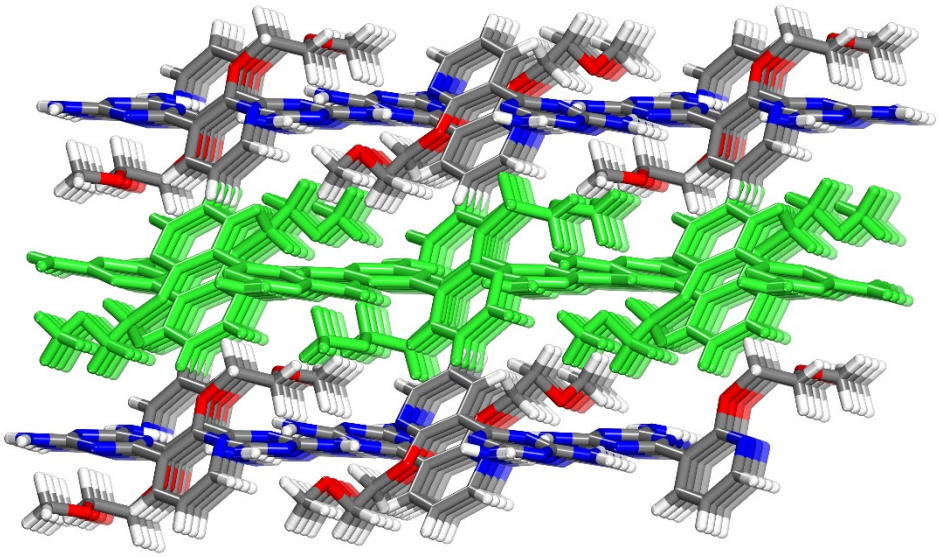

Fig. S27 View showing the packing of layers in crystal of **4**. For clarity one layer is marked in green. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

Table S1 Hydrogen-bond geometry (Å, º) in structure of **1**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
O3—H3*A*···O2^{i}	0.849(15)	2.243(16)	3.0282(12)	153.9(19)
O3—H3*B*···N2	0.847(14)	2.165(16)	2.9143(13)	147.4(17)
O4—H4*A*···O3	0.865(13)	1.977(14)	2.8357(12)	171.7(16)
O4—H4*B*···N2^{ii}	0.849(15)	2.243(16)	3.0282(12)	153.9(19)
N6—H6*A*···O4^{iii}	0.861(12)	2.287(14)	2.9830(13)	138.0(13)
N6—H6*B*···N3^{iv}	0.864(13)	2.102(13)	2.9635(14)	174.6(14)
N5—H5*A*···O4^{v}	0.856(13)	2.315(14)	3.1519(13)	165.8(14)
N5—H5*B*···O3	0.845(13)	2.422(14)	3.1484(13)	144.5(14)

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1, *y*, −*z*+1/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) −*x*+3/2, −*y*−1/2, −*z*+1; (v) −*x*+1, *y*−1, −*z*+1/2.

Table S2 Hydrogen-bond geometry (Å, º) in structure of **2**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N5—H5*A*···O3^{i}	0.85(2)	2.27(2)	2.9380(18)	134.8(19)
N5—H5*B*···N3^{ii}	0.84(2)	2.22(2)	3.0547(19)	173.5(18)
N6—H6*A*···O3^{iii}	0.86(2)	2.13(2)	2.9826(18)	168.5(18)
N6—H6*B*···N1^{iii}	0.87(2)	2.32(2)	3.0822(19)	147.3(18)
O3—H3*A*···N2	0.83(2)	2.01(2)	2.8408(17)	173(2)
O3—H3*B*···O2^{iv}	0.86(3)	1.97(3)	2.8235(17)	169(2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) −*x*+1, −*y*, −*z*+2; (iii) *x*, *y*−1, *z*; (iv) −*x*+1, −*y*+2, −*z*+1.

Table S3 Hydrogen-bond geometry (Å, º) in structure of **3**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N5—H5*A*···N2^{i}	0.876(12)	2.280(12)	3.0880(12)	153.4(12)
N5—H5*B*···O4^{ii}	0.881(12)	2.135(12)	3.0041(12)	169.1(13)
N6—H6*A*···O4^{iii}	0.879(12)	2.291(13)	2.9780(13)	134.9(12)
N6—H6*B*···N3^{iv}	0.892(12)	2.110(13)	3.0005(13)	175.9(14)
O3—H3*A*···N1	0.879(14)	1.930(14)	2.7983(10)	169.1(17)
O4—H4*A*···O2	0.872(15)	2.051(15)	2.9105(12)	168.4(17)
O4—H4*B*···O3	0.864(14)	1.908(14)	2.7711(12)	176.0(16)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) *x*−1, −*y*+1, *z*−1/2; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iv) −*x*+1/2, −*y*+1/2, −*z*+1.

Table S4 Hydrogen-bond geometry (Å, º) in structure of **4**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N5*A*—H5*AA*···O2*A*^{i}	0.892(14)	2.457(18)	3.1347(16)	133.1(17)
N5*A*—H5*AB*···N2*A*^{i}	0.896(14)	2.042(14)	2.9372(18)	176(2)
N6*A*—H6*AA*···N4*B*	0.896(13)	2.103(13)	2.9976(18)	176.8(17)
N6*A*—H6*AB*···N1*B*^{ii}	0.898(13)	2.303(15)	3.1199(16)	151.2(17)
N5*B*—H5*BB*···N2*B*^{iii}	0.894(14)	2.099(14)	2.9904(18)	174.5(19)
N6*B*—H6*BA*···N1*A*^{iv}	0.894(13)	2.142(14)	2.9882(17)	157.7(16)
N6*B*—H6*BB*···N4*A*	0.902(13)	2.078(13)	2.9764(18)	174.3(17)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*, −*y*+1, −*z*+2; (iii) −*x*, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+2, −*z*+1.

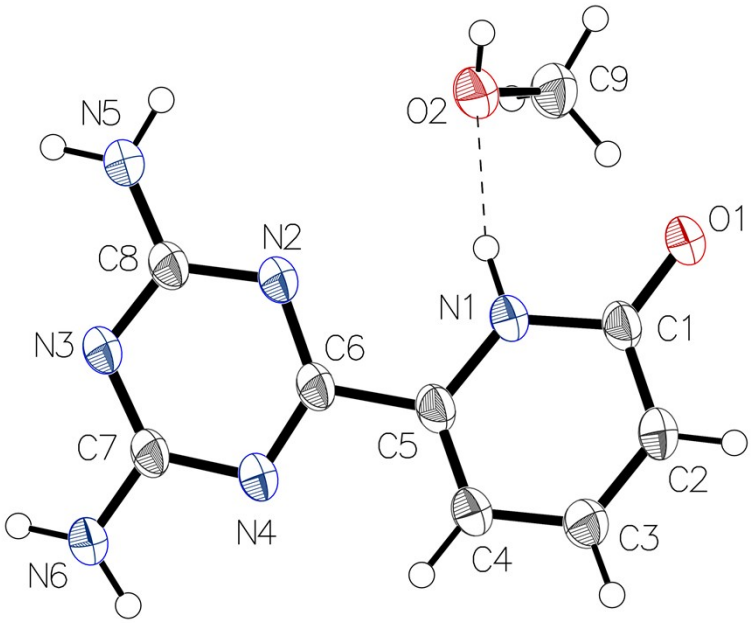

Fig. S28 Thermal atomic displacement ellipsoid plot of the structure of **5** grown from slow evaporation of methanol. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

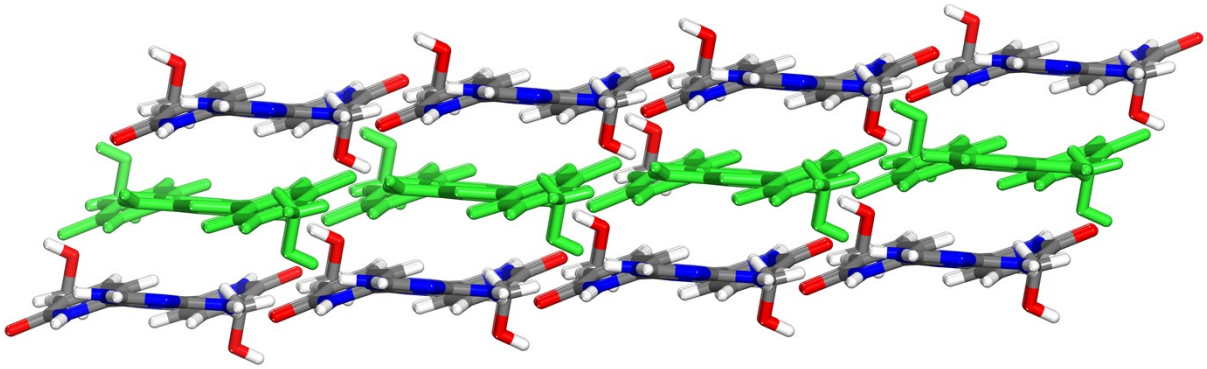

Fig. S29 View showing the packing of layers in crystal of **5**. For clarity one layer is marked in green. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

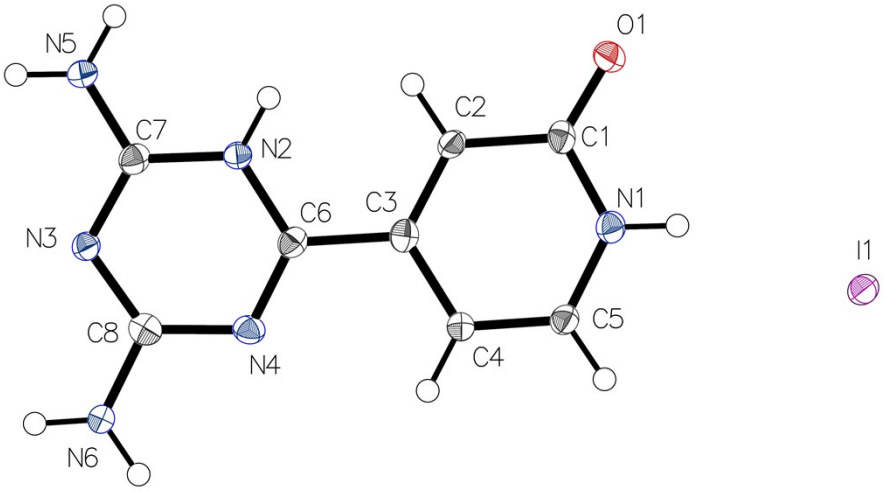

Fig. S30 Thermal atomic displacement ellipsoid plot of the structure of **7** grown slow evaporation of acetic acid. The ellipsoids of non-hydrogen atoms are drawn at 50% probability level and hydrogen atoms are represented by a sphere of arbitrary size.

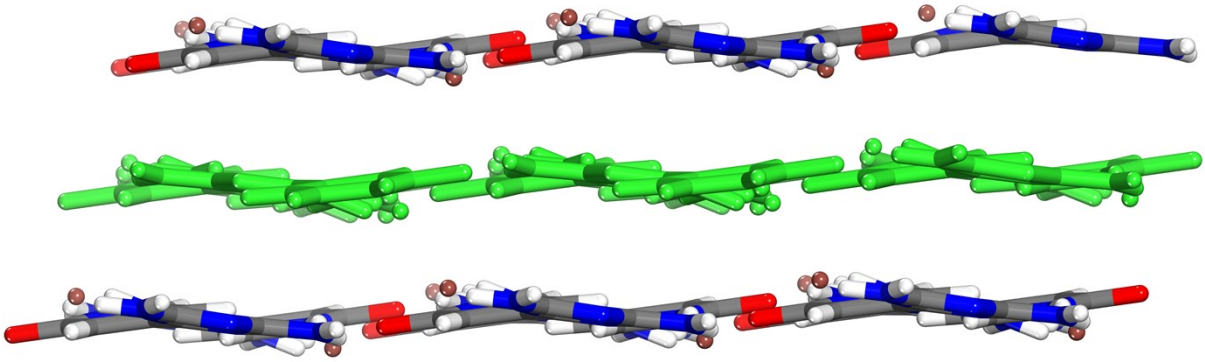

Fig. S31 View showing the packing of layers in crystal of **7**. For clarity one layer is marked in green. Hydrogen bonds are represented by dashed lines. Unless stated otherwise, carbon atoms are shown in grey, hydrogen atoms in white, oxygen atoms in red and nitrogen atoms in blue.

Table S5 Hydrogen-bond geometry (Å, º) in structure of **5**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N6—H6*A*···O1^{i}	0.906(13)	2.307(19)	3.037(2)	137(2)
N6—H6*B*···O1^{ii}	0.906(13)	2.071(15)	2.961(2)	167(2)
N5—H5*A*···N3^{iii}	0.906(13)	2.087(13)	2.991(3)	176(3)
N1—H1· O2	0.906(13)	2.027(15)	2.907(2)	164(2)
N5—H5*B*···O1^{iv}	0.906(13)	2.00(2)	2.764(2)	141(3)
O2—H2A···N2^{iv}	0.851(2)	2.099(11)	2.928(2)	165(4)

Symmetry codes: (i) 1-x,1-y,1-z; (ii) 1+x,+y,1+z; (iii) 1-x,-y,2-z; (iv) -x,-y,1-z.

Table S6 Hydrogen-bond geometry (Å, º) in structure of **7**

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N1—H1···I1	0.88	2.64	3.469(5)	158.5
N2—H2···I1^{i}	0.88	2.74	3.497(4)	145.1
N5—H5*A*···N3^{ii}	0.88	2.18	3.061(7)	178.4
N5—H5B···O1^{iii}	0.88	2.22	2.828(6)	125.6
N6—H6A···O1^{iv}	0.88	1.97	2.843(6)	169.7
N6—H6B···I1^{iv}	0.88	3.02	3.736(4)	139.8

Symmetry codes: (i) 1-x,1-y,2-z; (ii) -x,2-y,1-z; (iii) 1-x,2-y,2-z; (iv) -1+x,+y,-1+z.

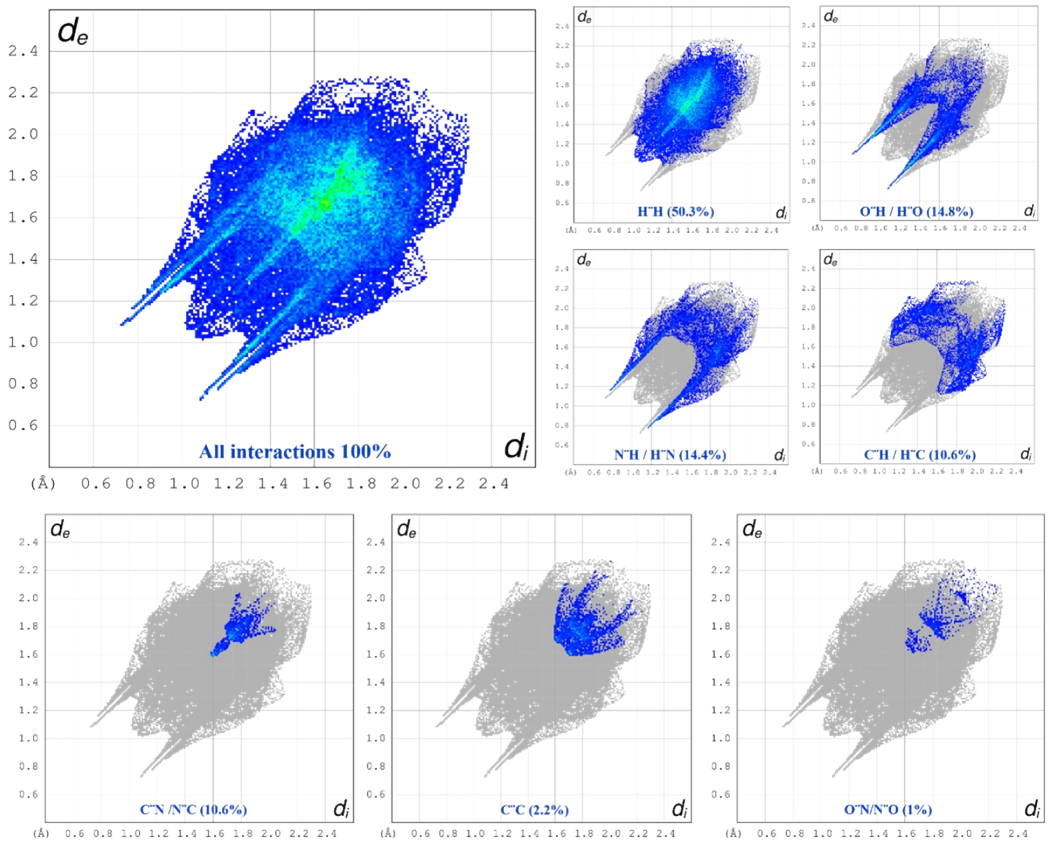

Fig. S32 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **1**.

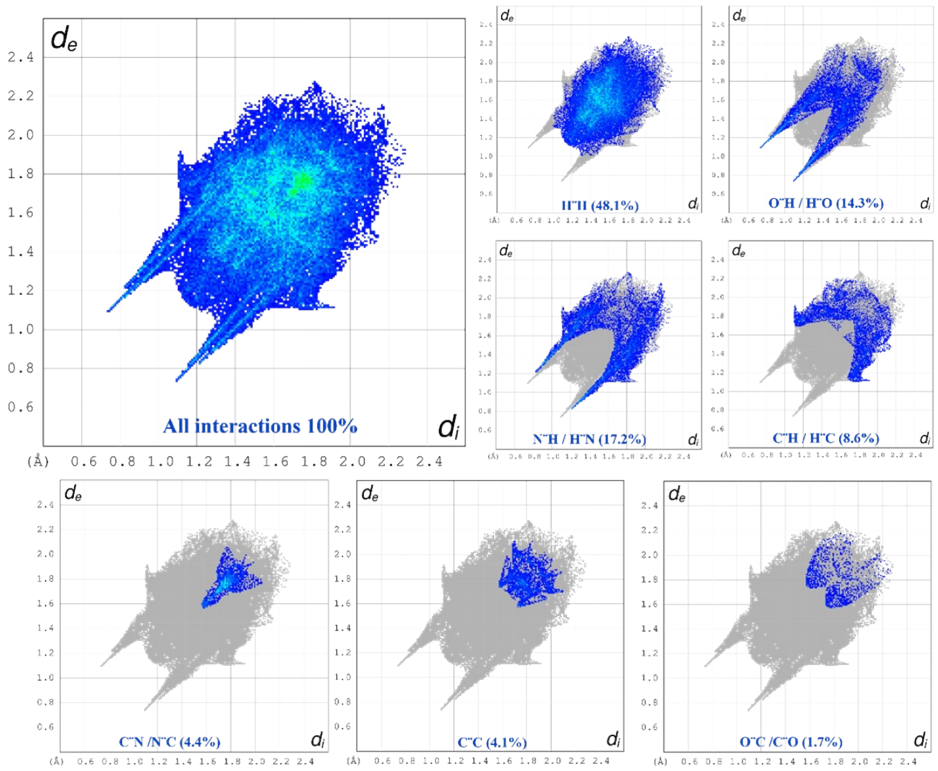

Fig. S33 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **2**.

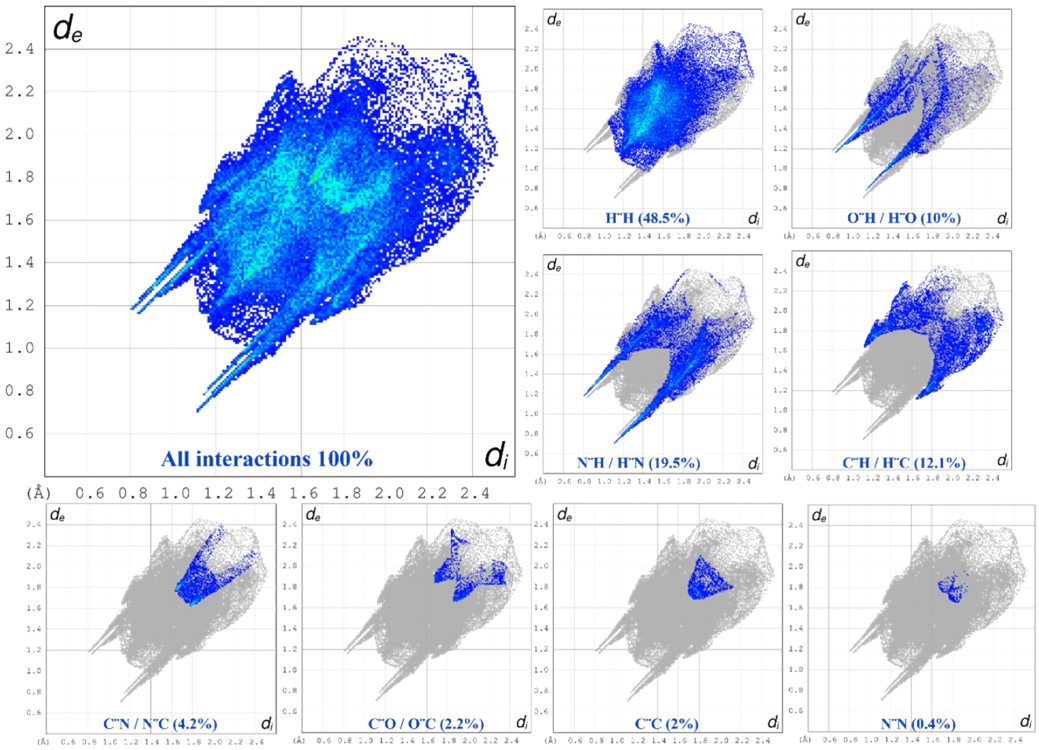

Fig. S34 (a) Molecular Hirshfeld d_{norm}, d_i and d_e surfaces mapped and (b) 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **3**.

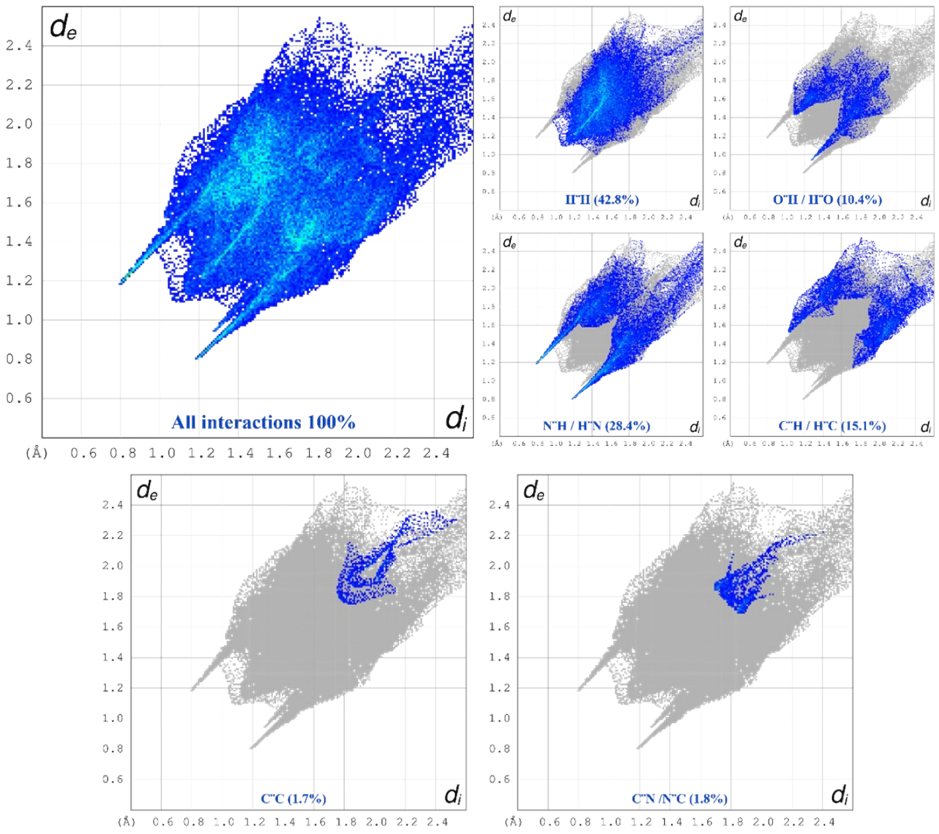

Fig. S35 (a) Molecular Hirshfeld d_{norm}, d_i and d_e surfaces mapped and (b) 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **4**.

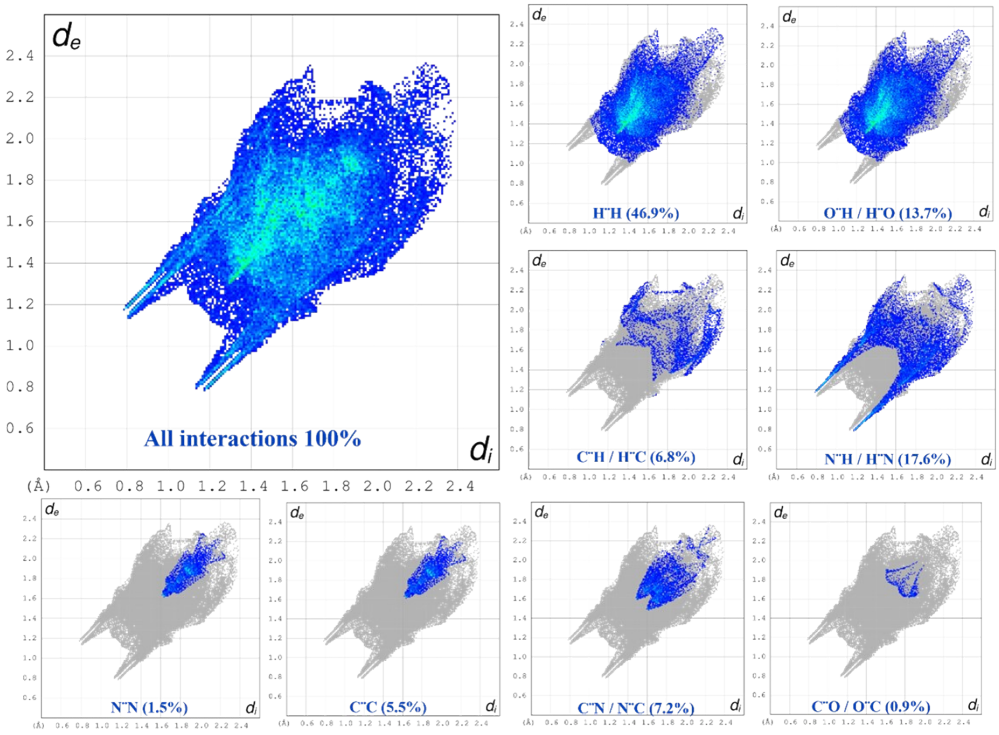

Fig. S36 (a) Molecular Hirshfeld d_{norm}, d_i and d_e surfaces mapped and (b) 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **5**.

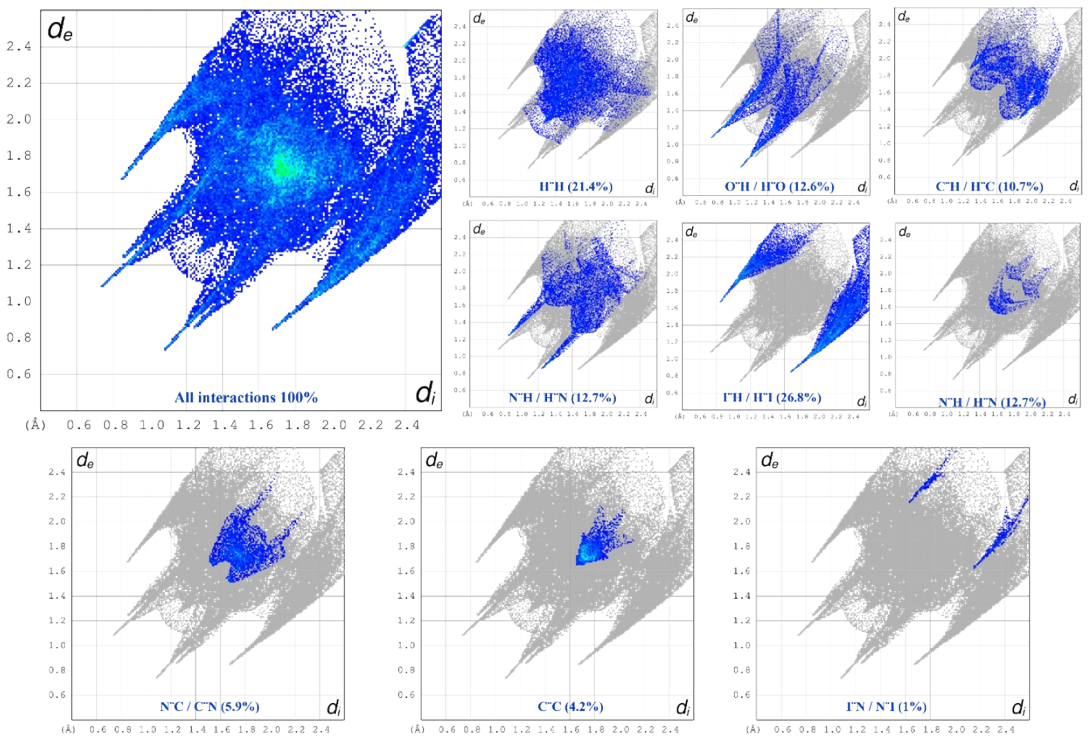

Fig. S37 (a) Molecular Hirshfeld d_{norm}, d_i and d_e surfaces mapped and (b) 2D fingerprint plots with relative contributions in percentage of various intermolecular contacts to HS area for **7**.

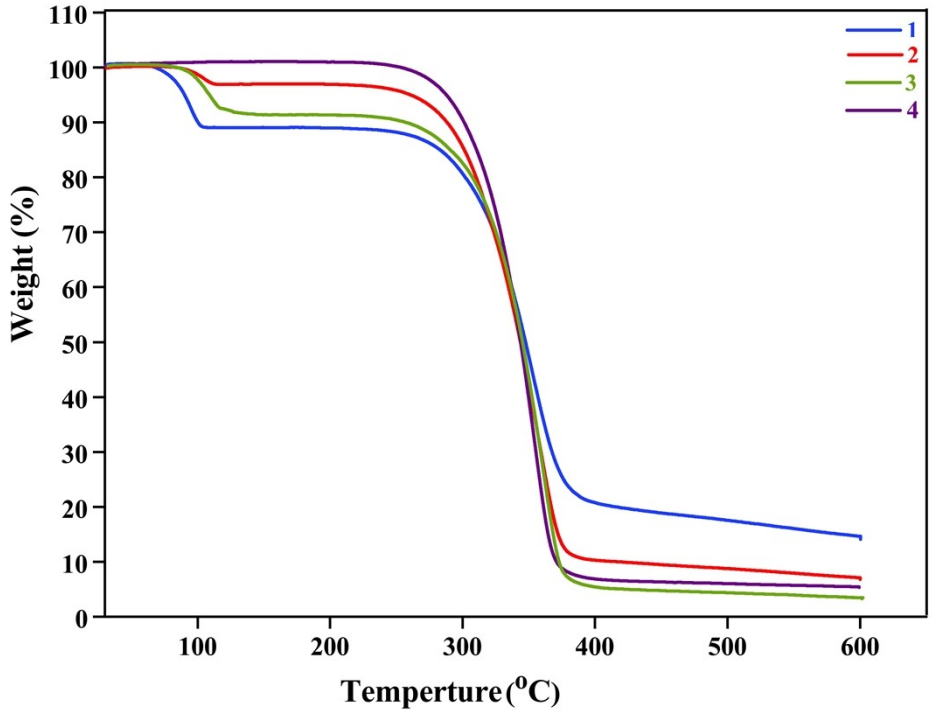

Fig. S38 Thermogravimetric analysis curves of **1-4**.

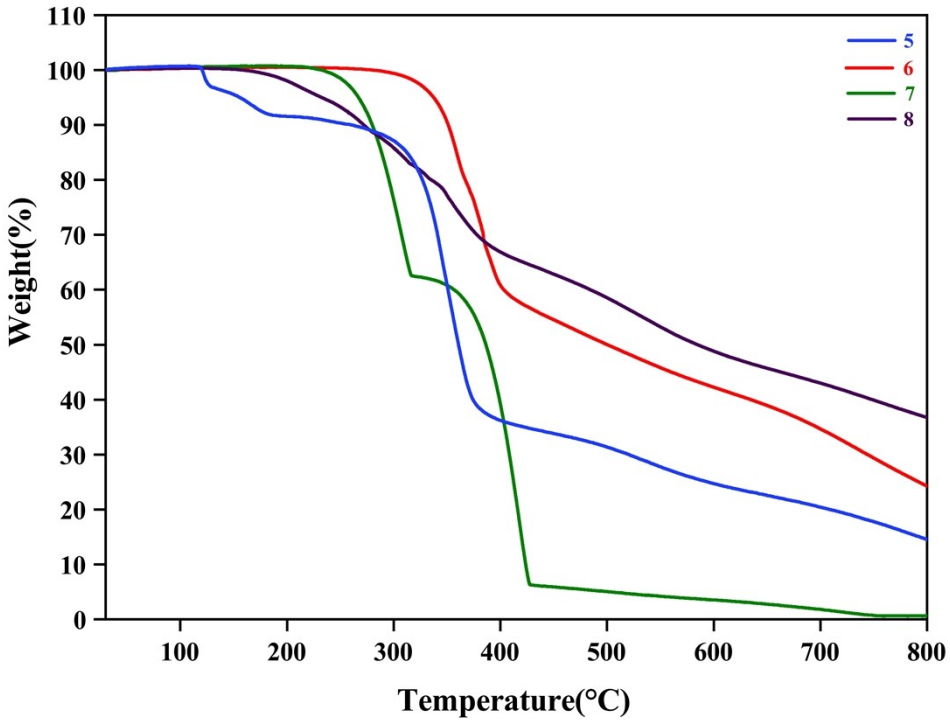

Fig. S39 Thermogravimetric analysis curves of **5-8**.