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Supporting information for article:

Clarifying the structures of imidines: using crystallographic characterization to identify tautomers and localized systems of π-bonding

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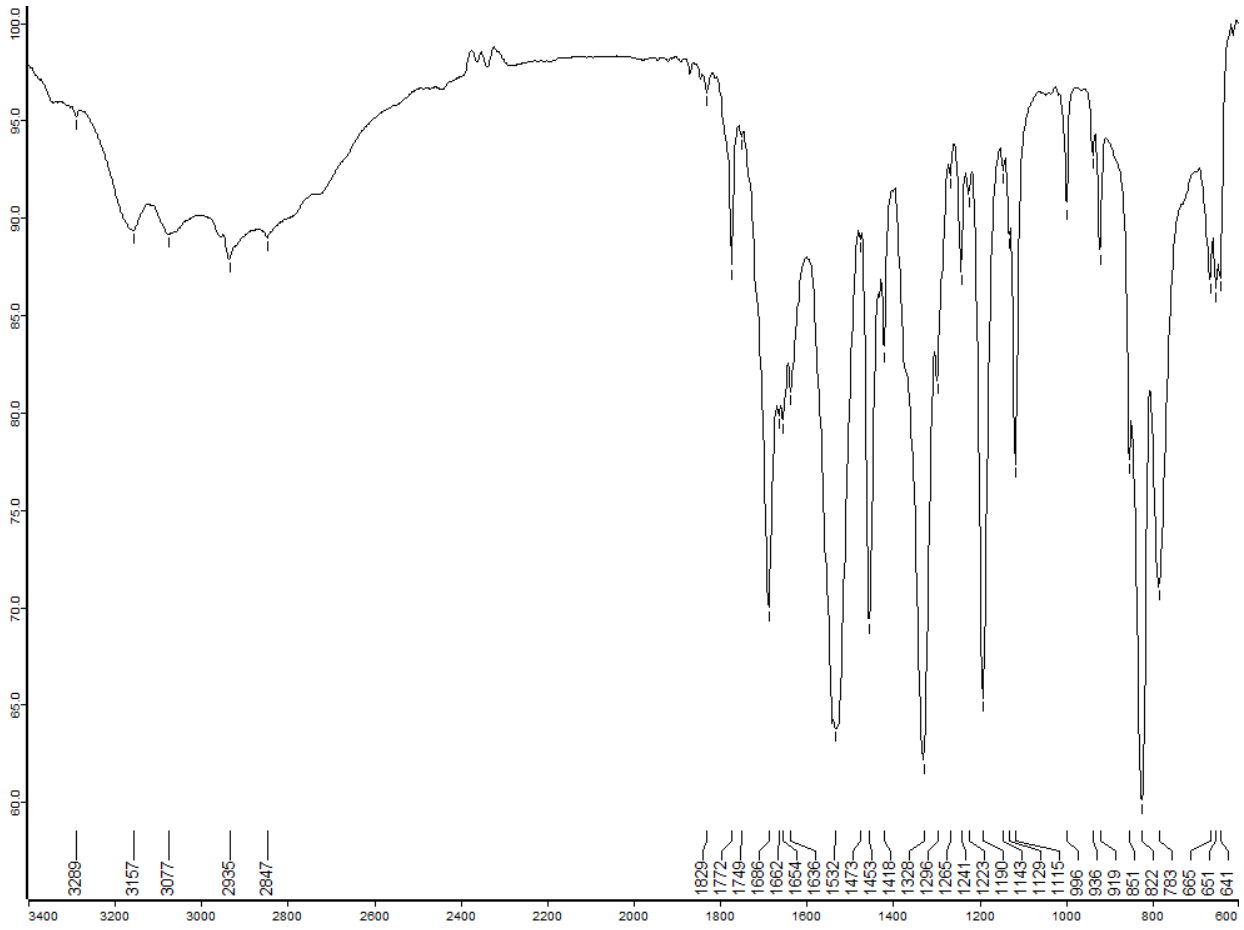
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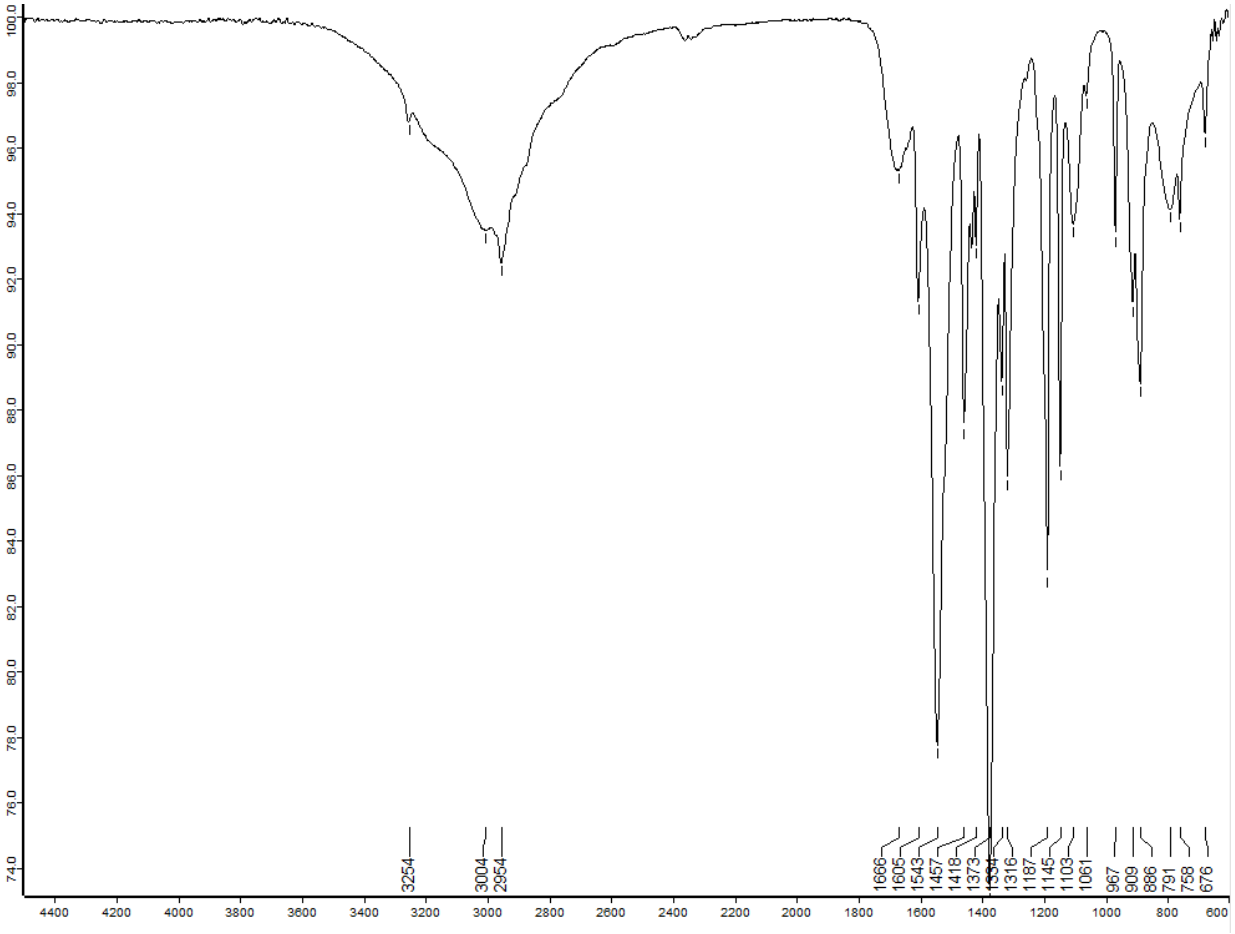
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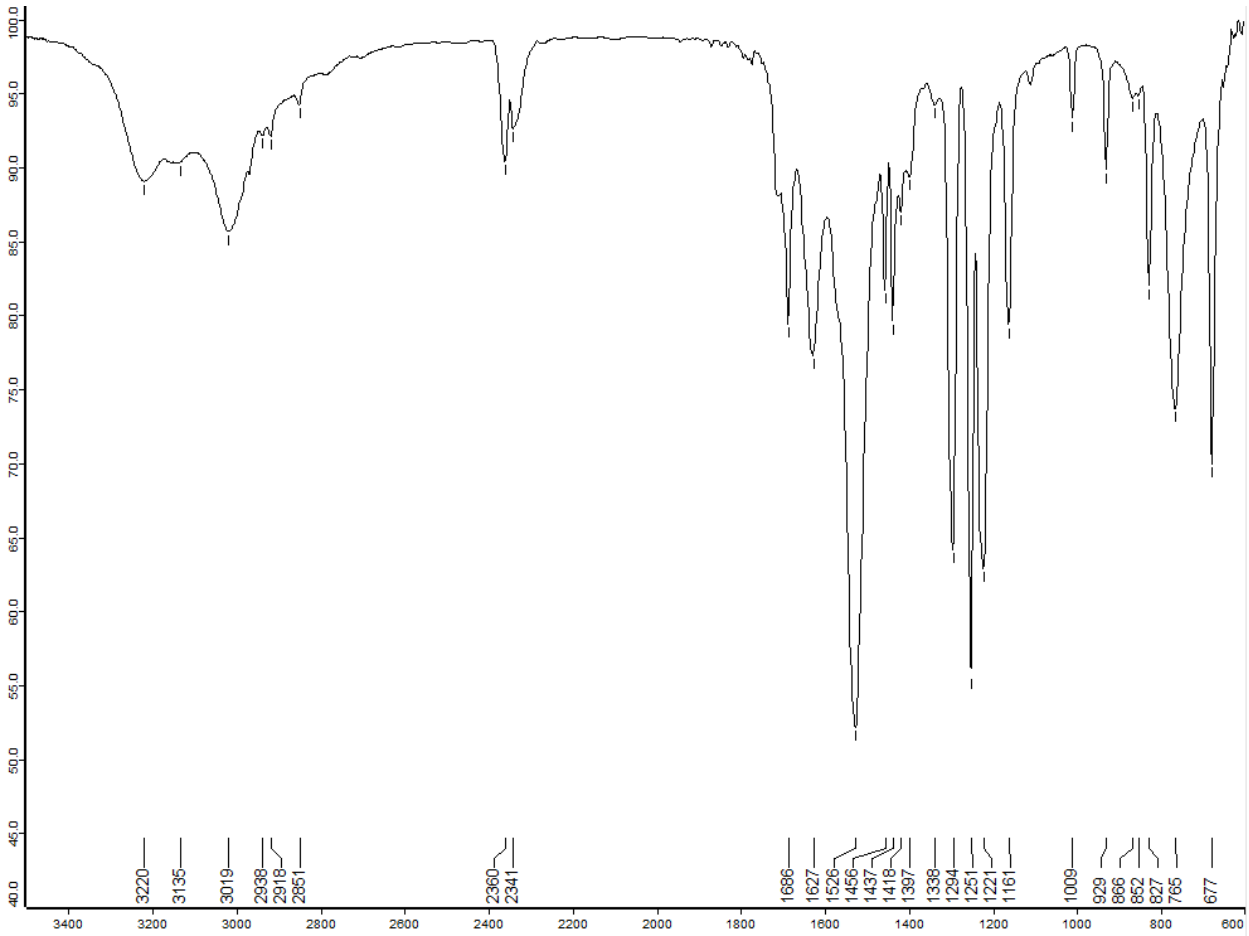
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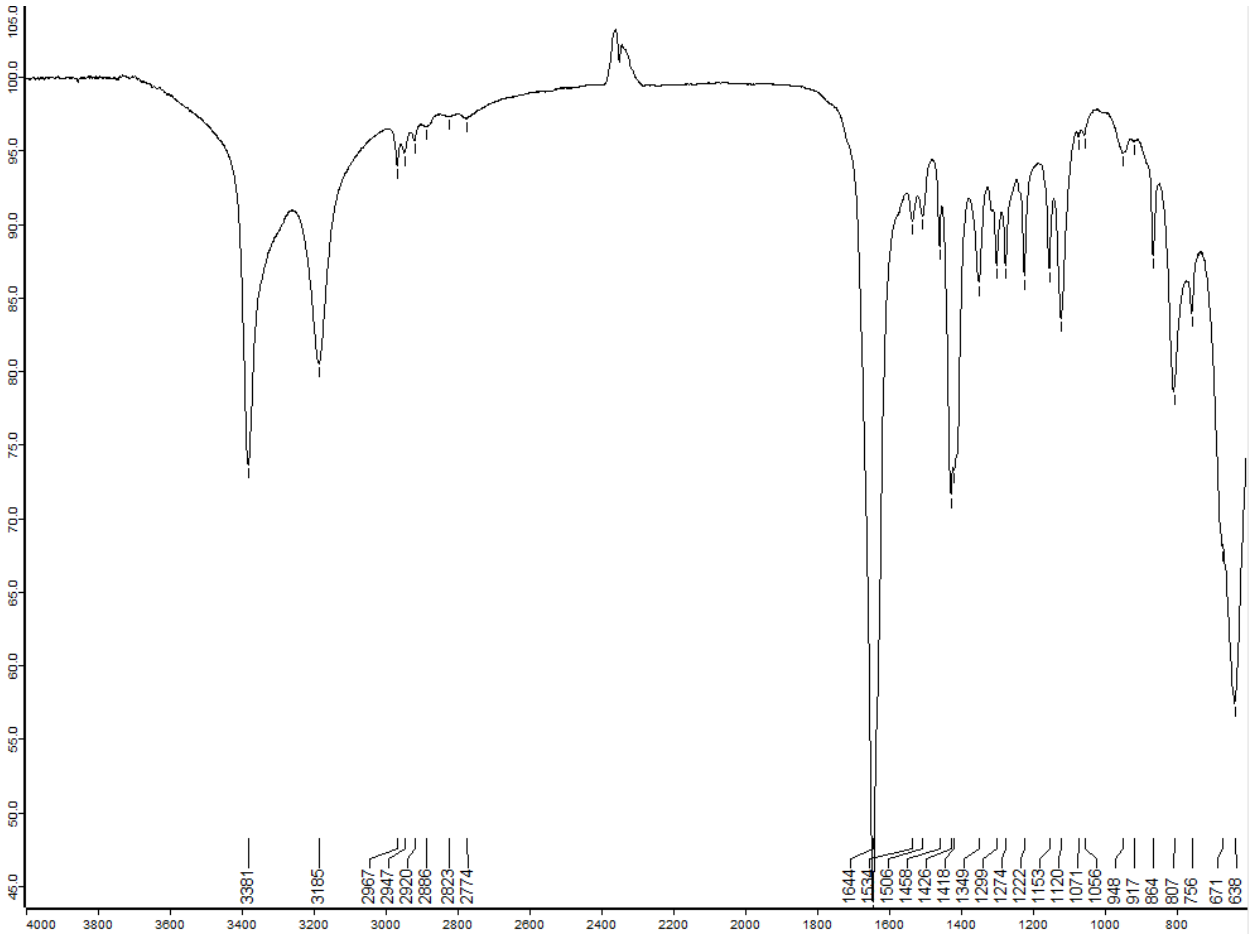
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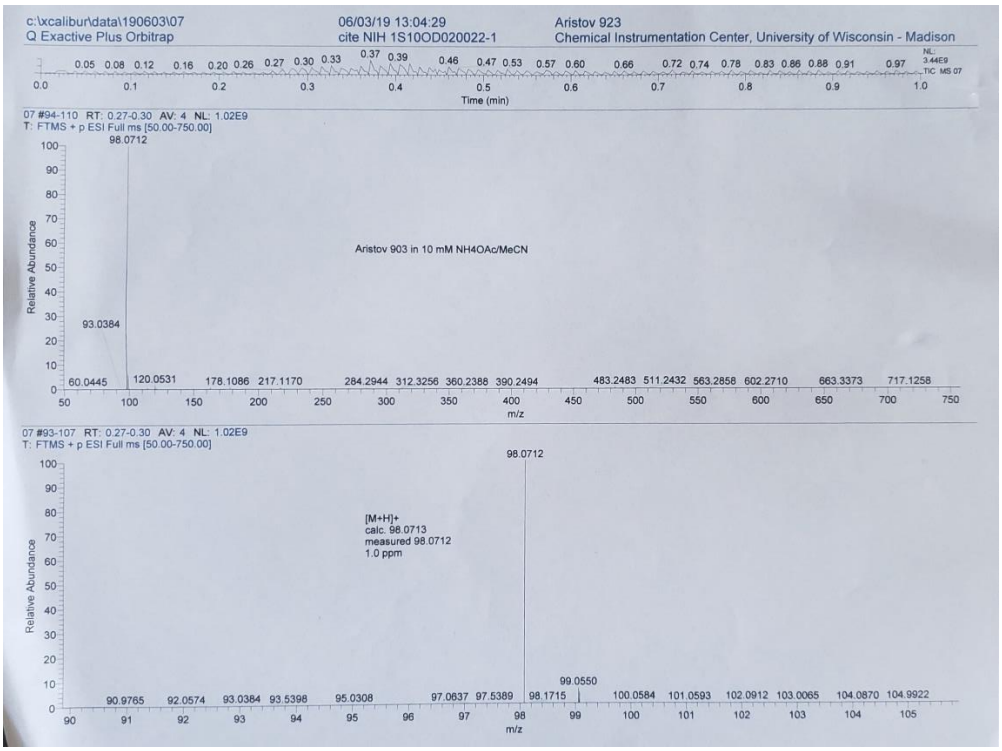

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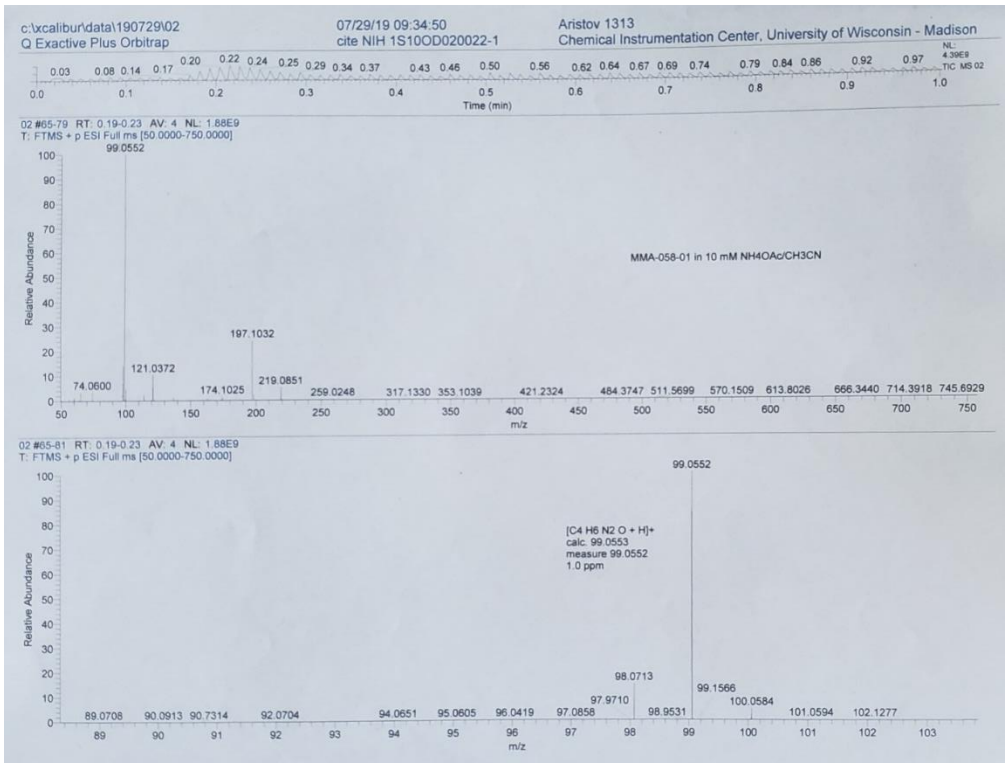
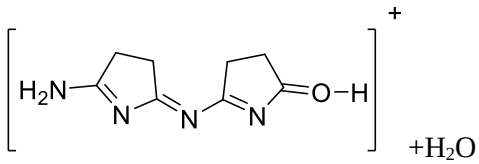


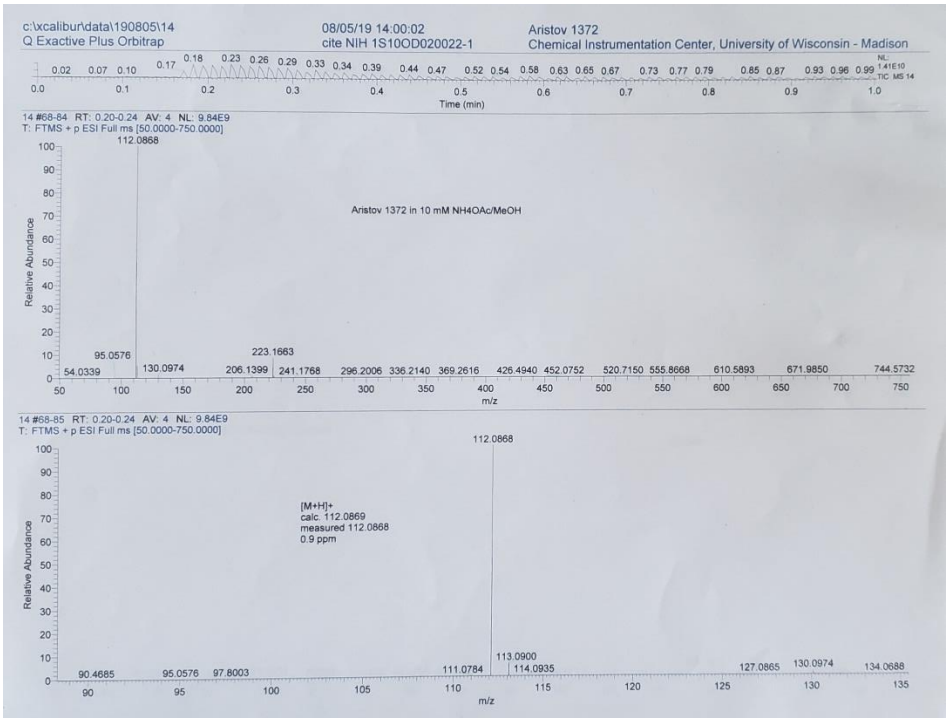
ESI (*m*/*z*): ([$C_8H_{10}N_4O$](H_2O)+H]$^+$) 197.1032



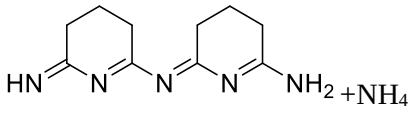
+H_2O

ESI (*m*/*z*): ([HNNO5+Na]$^+$) 121.0372

2



ESI (*m*/*z*): ($[C_{10}H_{15}N_5]+NH_4]^+$) 223.17



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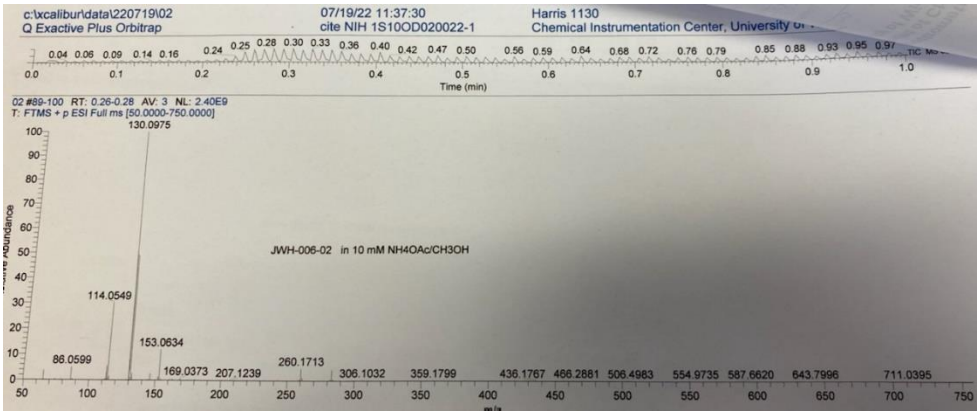
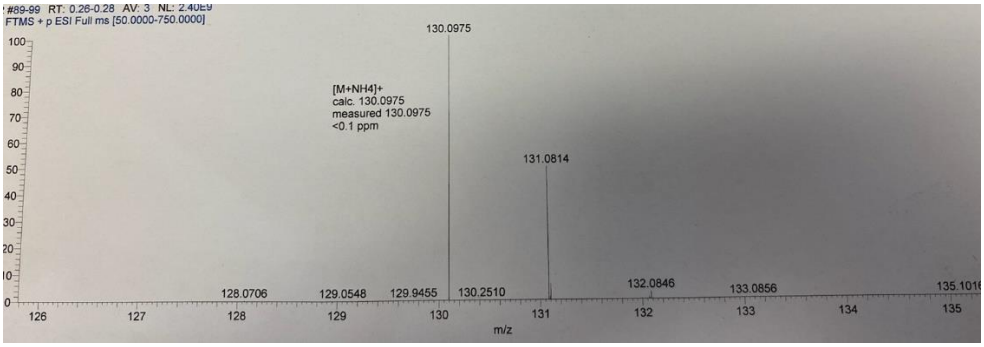
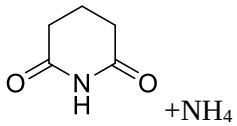




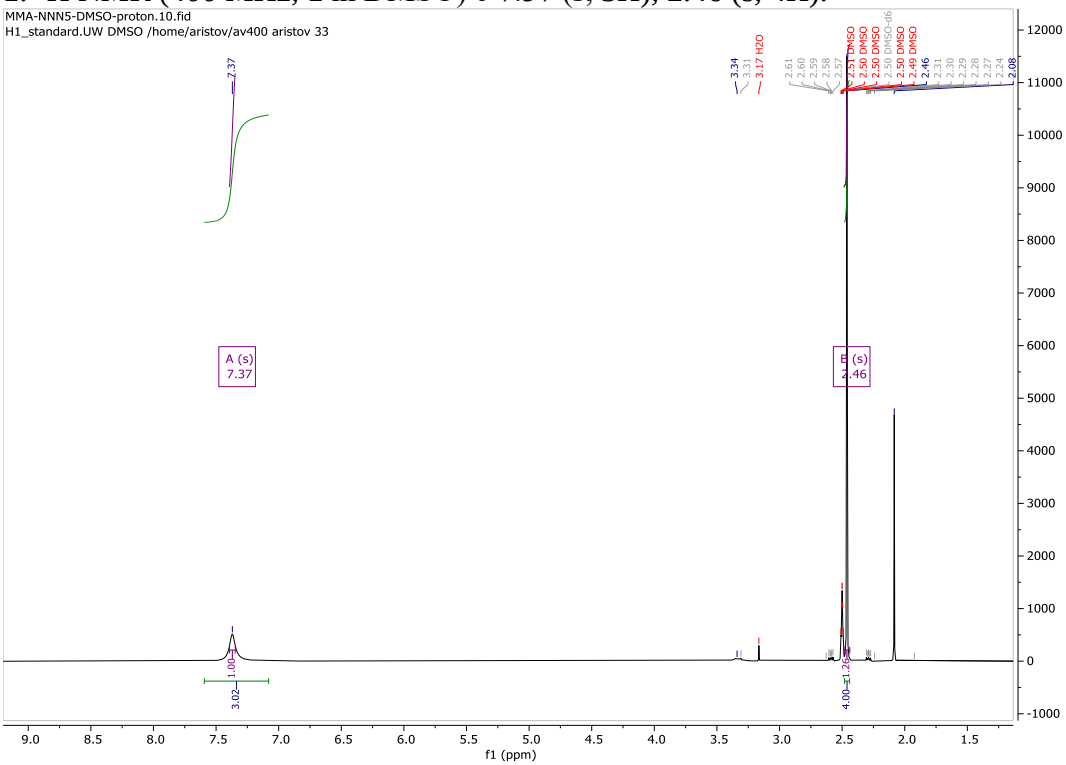
ESI (*m*/*z*): ([HONO6]+NH_4)$^+$) 131.0814

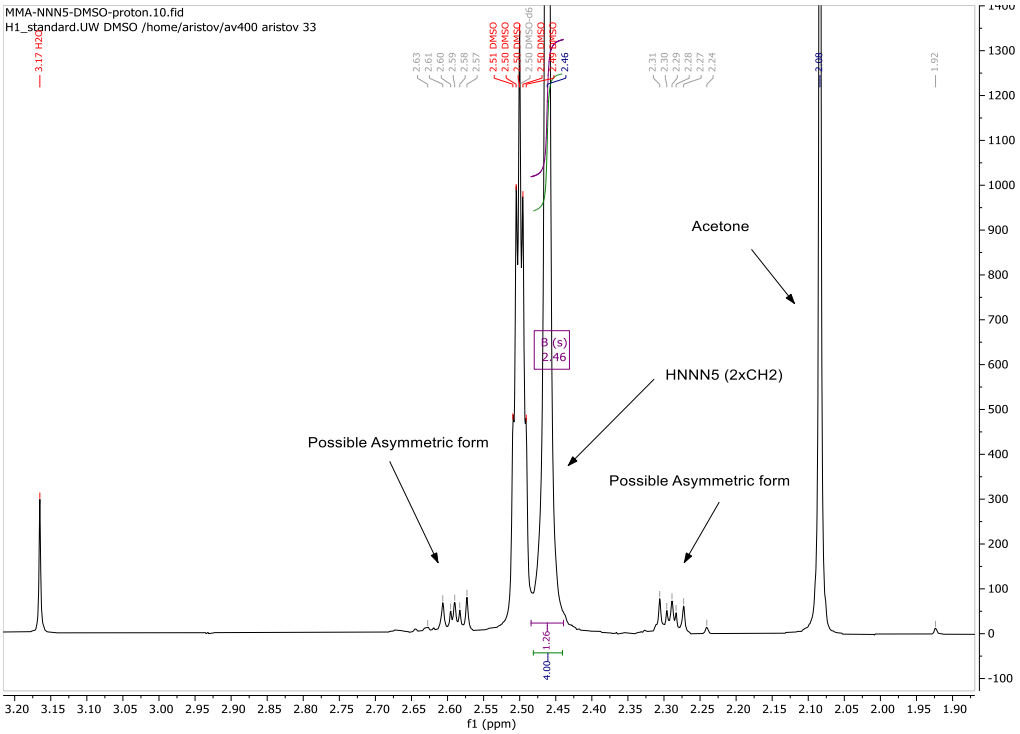


+NH_4

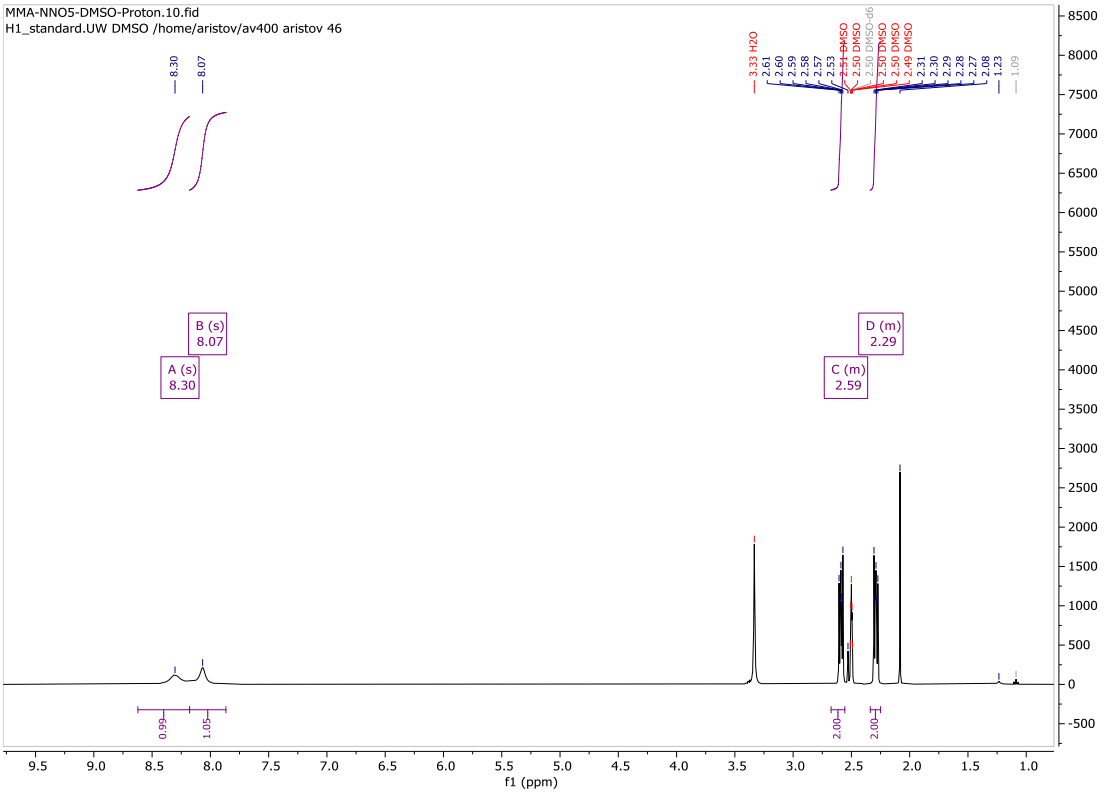
NMR Data:

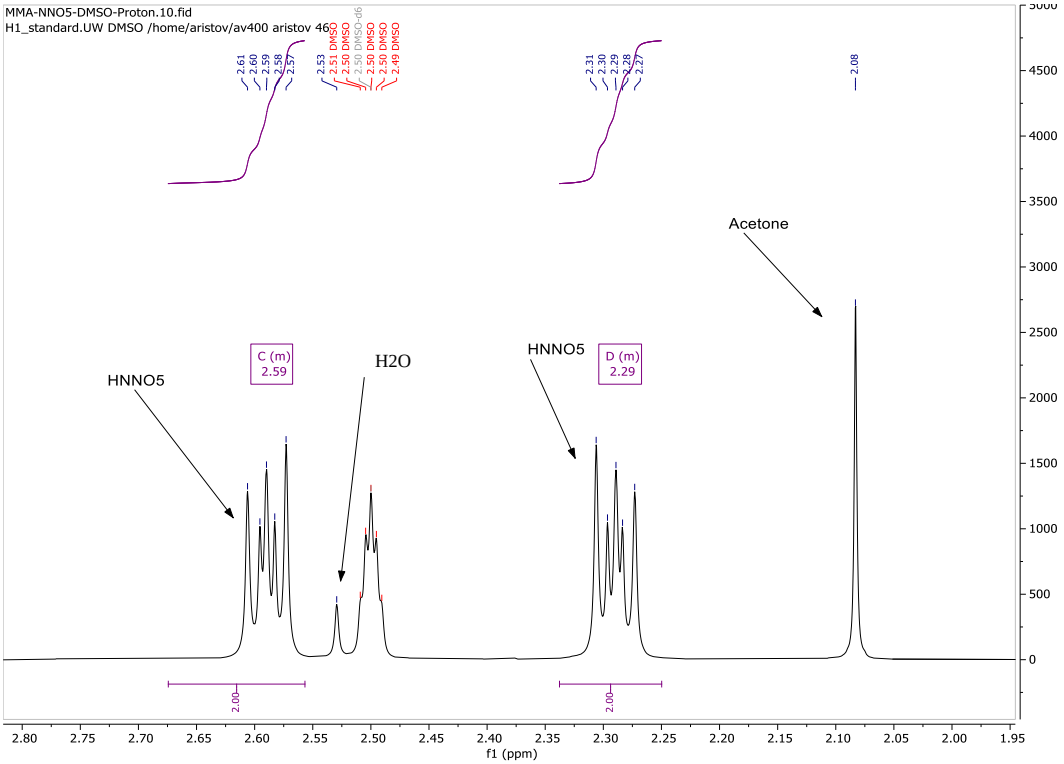
1: ^{1}H NMR (400 MHz, **1** in DMSO) δ 7.37 (s, 3H), 2.46 (s, 4H).



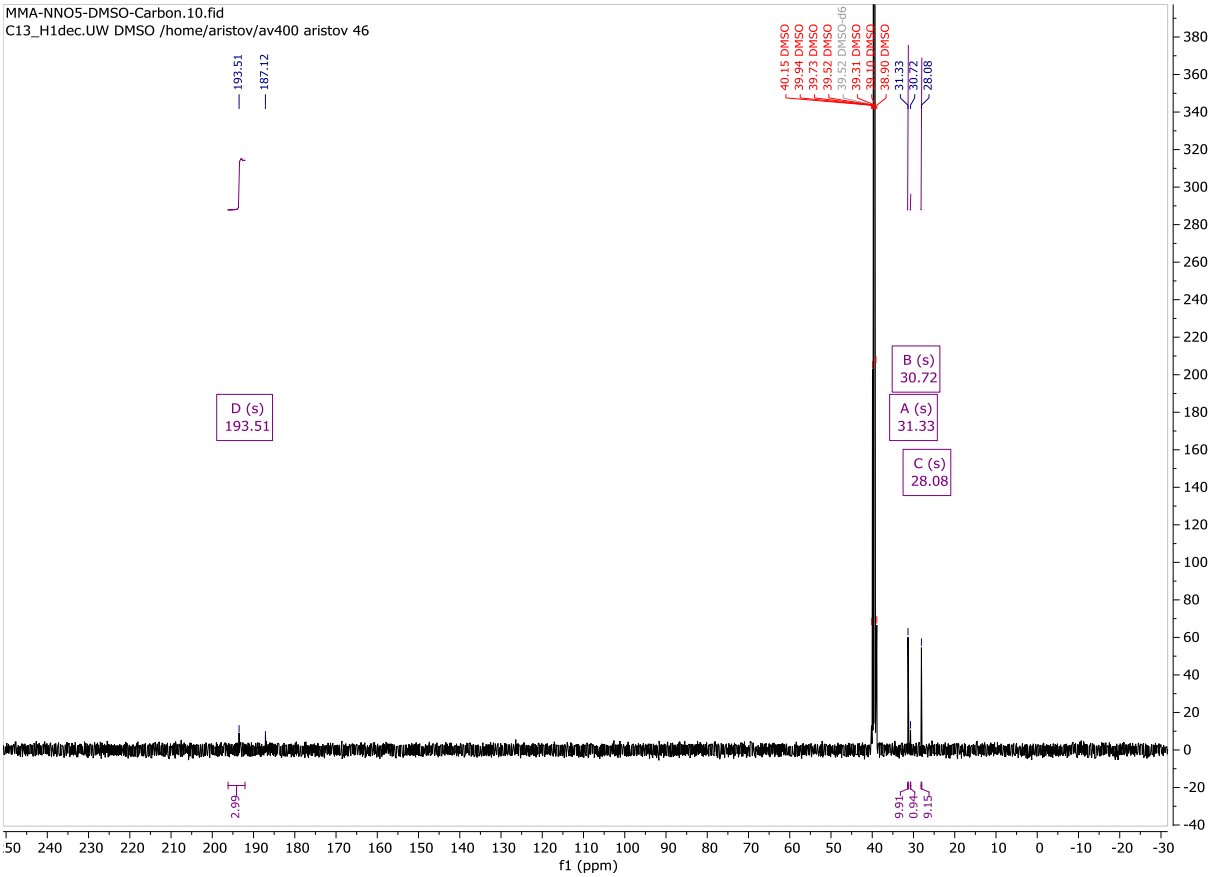


3: ^{1}H NMR (400 MHz, **3** DMSO) δ 8.30 (s, 1H), 8.07 (s, 1H), 2.67 – 2.56 (m, 2H), 2.34 – 2.25 (m, 2H).

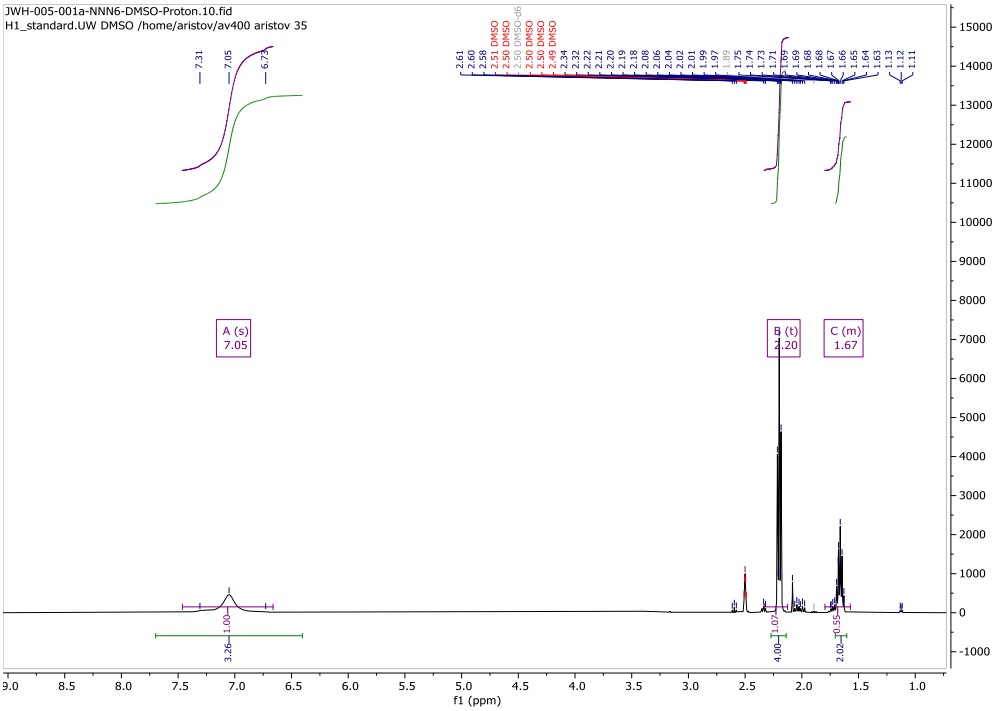


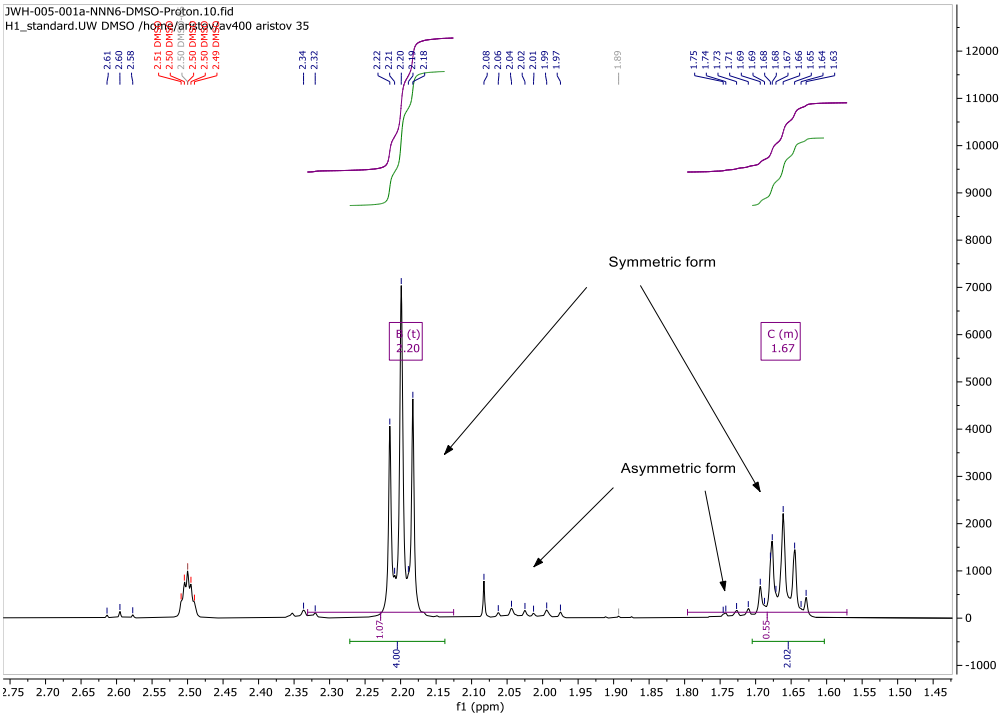


3: ^{13}C NMR (101 MHz, **3** in DMSO) δ 193.51, 31.33, 30.72, 28.08.

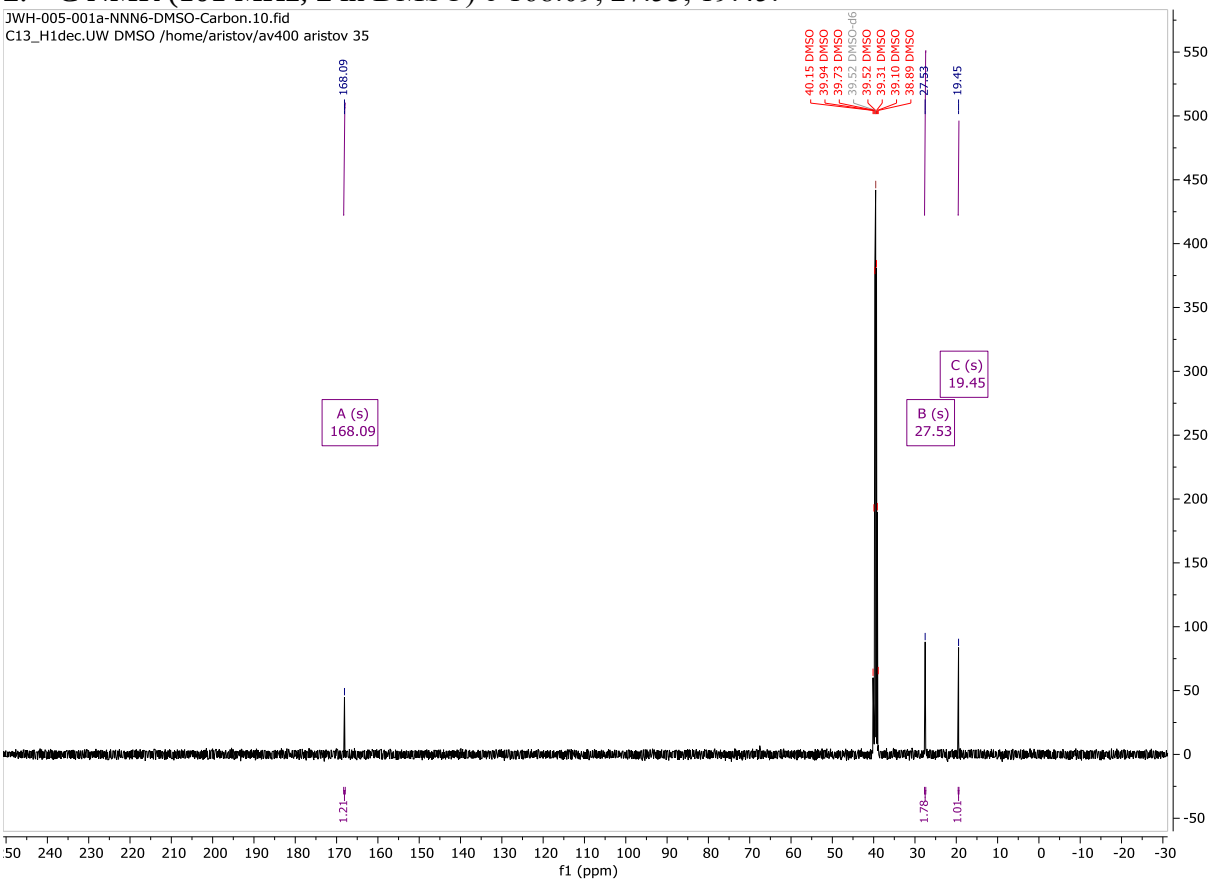


2: ^{1}H NMR (400 MHz, **2** in DMSO) δ 7.05 (s, 3H), 2.20 (t, *J* = 6.5 Hz, 4H), 1.80 – 1.57 (q, 2H).

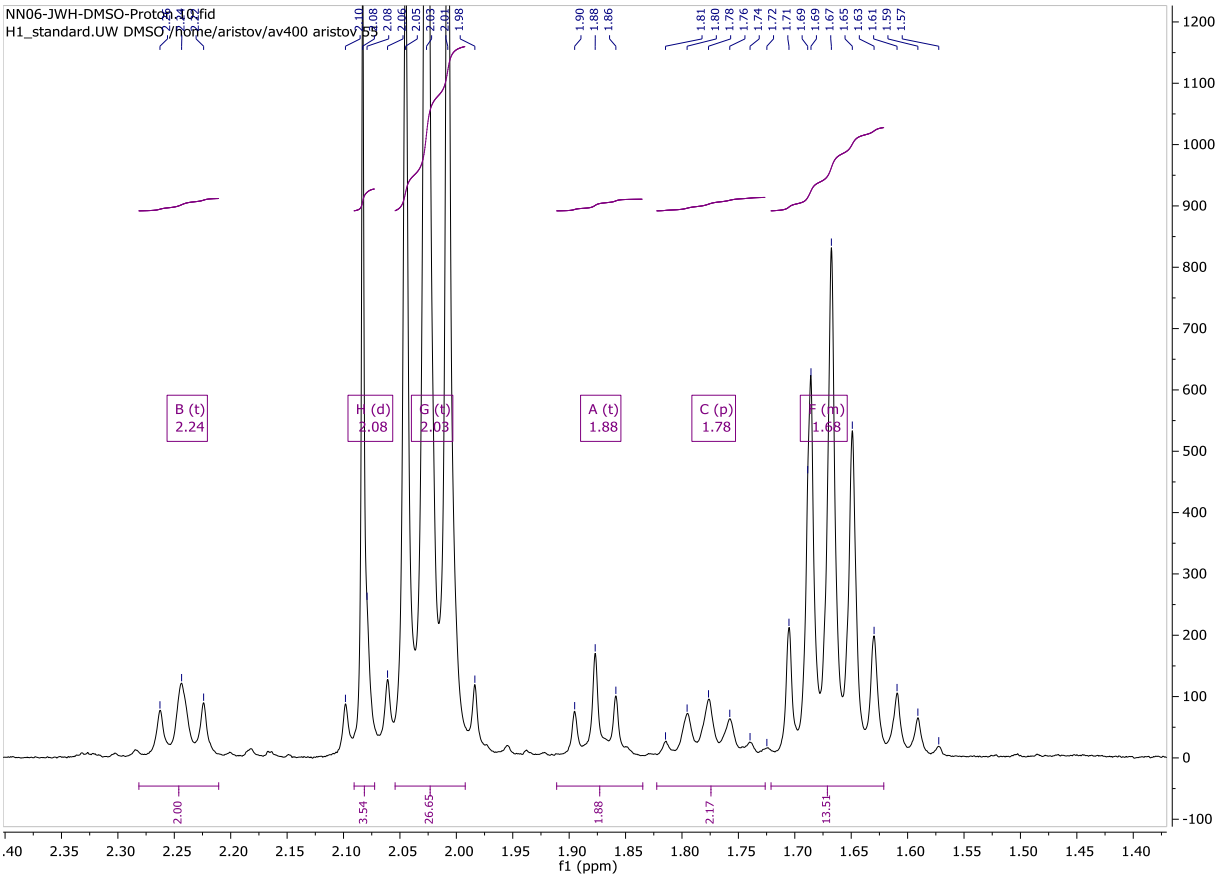


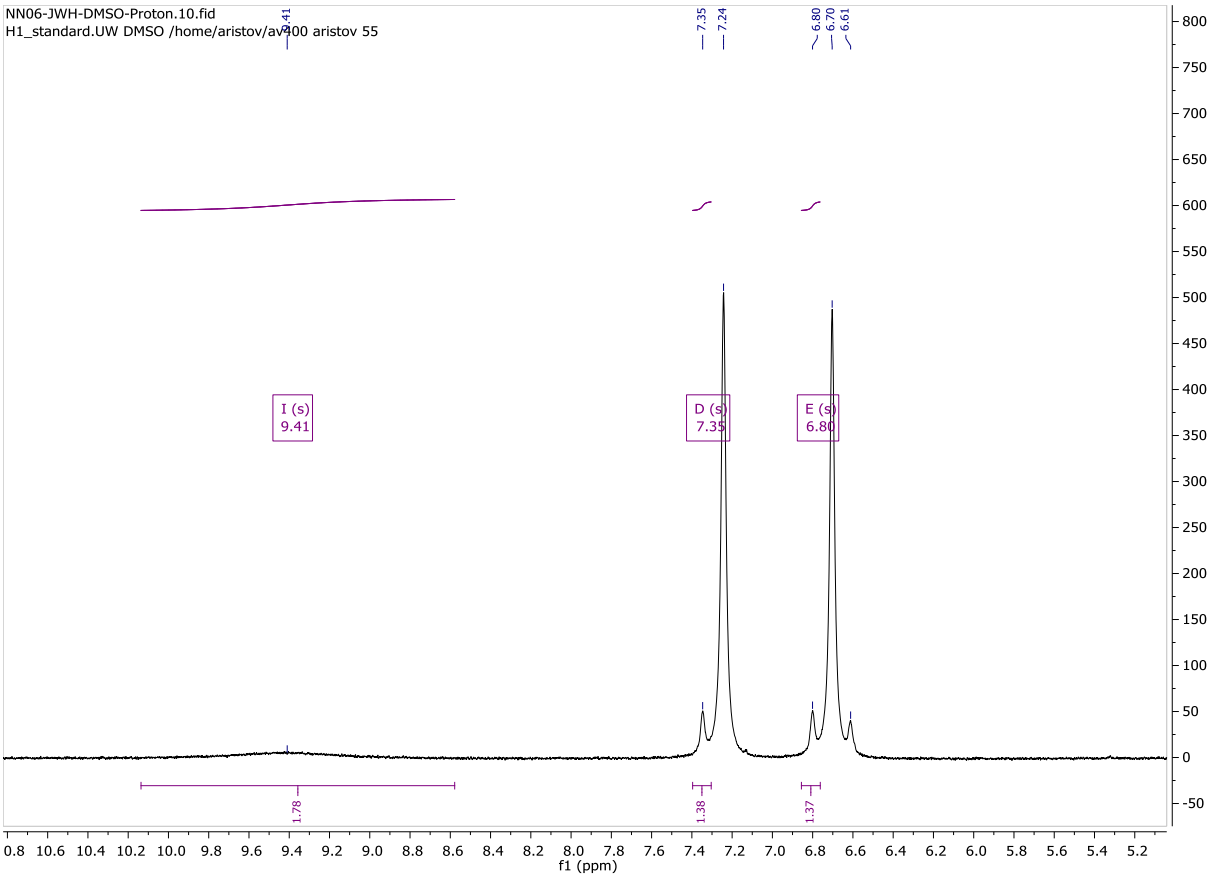


2: ^{13}C NMR (101 MHz, **2** in DMSO) δ 168.09, 27.53, 19.45.



4: ^{1}H NMR (400 MHz, **4** DMSO-d_6) δ, 7.35 (s, 1H), 6.80 (s, 1H), 2.24 (t, J = 7.7 Hz, 2H), 1.88 (t, J = 7.3 Hz, 2H), 1.78 (p, J = 7.4 Hz, 2H). The remaining peaks are either unreacted starting material, **3**, or glutarimide.

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D (s)
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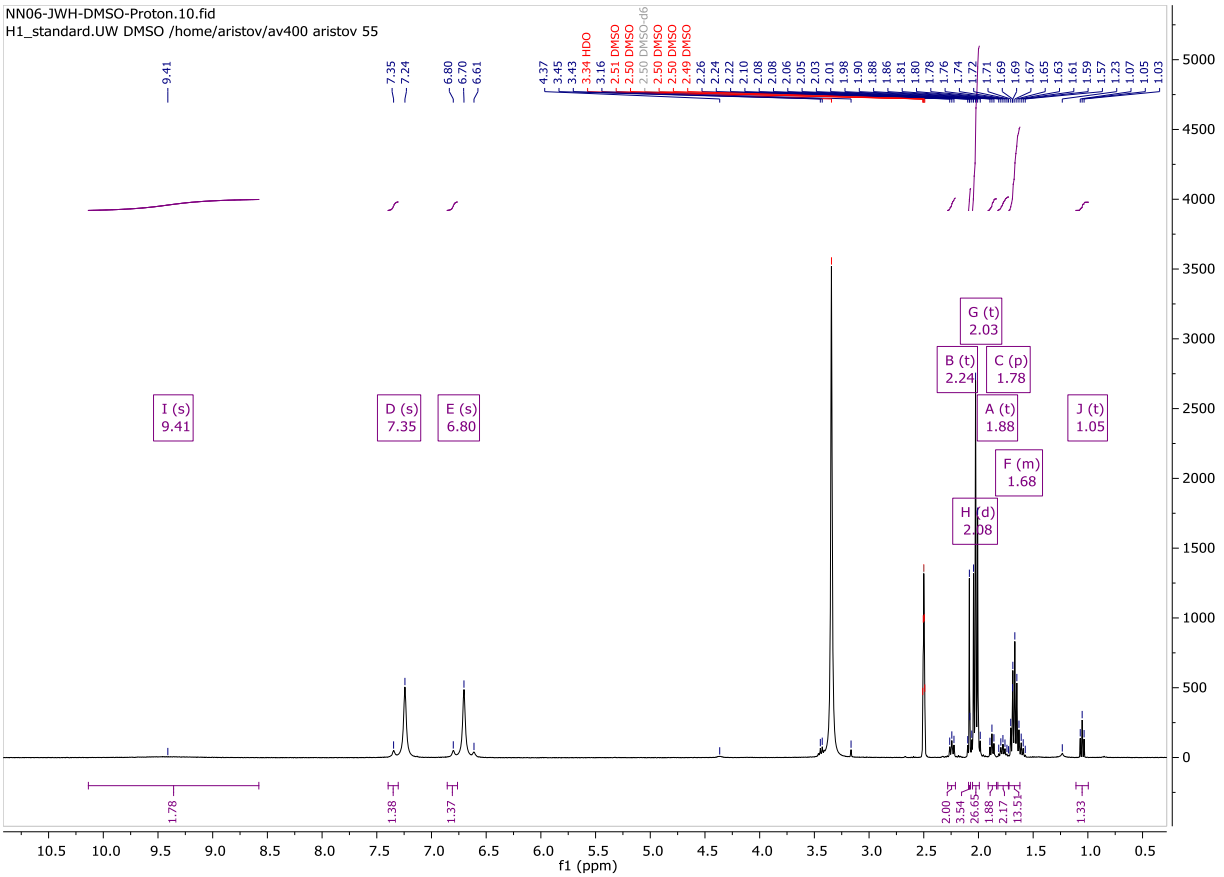
E (s)
6.80
1.78
1.38
1.37
f1 (ppm)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D (s) 7.35
E (s) 6.80
G (t) 2.03
B (t) 2.24
C (p) 1.78
A (t) 1.88
J (t) 1.05
F (m) 1.68
H (d) 2.08
f1 (ppm)

Calculations:

Table S1. XYZ coordinates from the optimized asymmetric structure of **1**.

Atom	X	Y	Z
C	0.649857	1.277596	-0.00554
C	-0.87957	1.208895	0.007742
C	-1.165	-0.29754	-0.00051
N	0.036009	-1.01282	-0.00076
C	1.005749	-0.19268	0.001706
N	2.298247	-0.57871	0.049523
H	2.487487	-1.54654	-0.09035
H	3.013518	0.059235	-0.21267
N	-2.28135	-0.86433	-0.00814
H	-3.02497	-0.18848	-0.00903
H	-1.30665	1.666701	0.89213
H	-1.32716	1.683164	-0.85749
H	1.050836	1.764418	-0.88898
H	1.070304	1.774916	0.861671

Table S2. XYZ coordinates from the optimized symmetric structure of **1**.

Atom	X	Y	Z
C	0.738432	1.272389	0.093736
C	-0.78701	1.239713	-0.0961
C	-1.1574	-0.23124	-0.00404
N	0.025415	-0.93835	0.000991
C	1.175065	-0.17634	0.005833
N	2.371288	-0.54612	-0.03507
H	2.465645	-1.54601	-0.07787
H	0.017593	-1.93459	0.010076
N	-2.27434	-0.79566	0.041777
H	-3.02215	-0.12755	0.023393
H	-1.32447	1.814511	0.647444
H	-1.08008	1.609986	-1.07252
H	1.255905	1.862327	-0.64936
H	1.016463	1.655097	1.068347

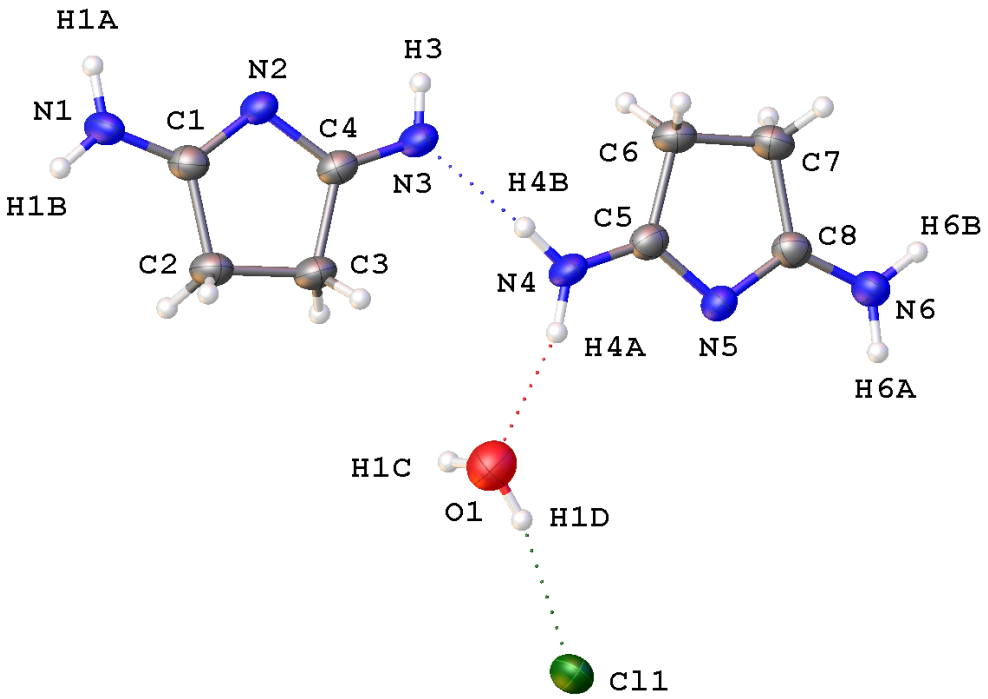

Figure S1. A molecular drawing of the structure of **1**•HCl shown with 50% probability ellipsoids.

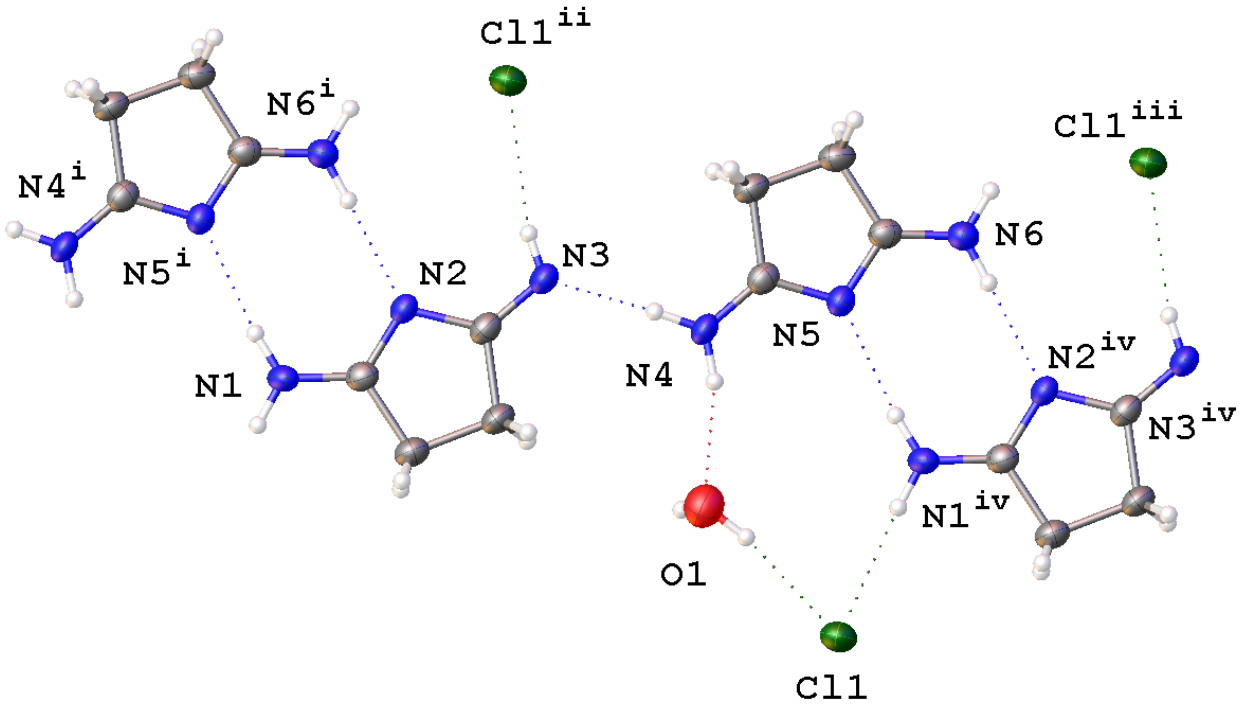

Figure S2. A molecular drawing of **1**•HCl shown with 50% probability ellipsoids, with emphasis placed on the layered hydrogen bonding system. [Symmetry code: i: 1/2+X,-1/2+Y,+Z; ii: 1/2+X,1/2+Y,+Z ; iii: -1/2+X,1/2+Y,+Z ; iv: +X,1+Y,+Z.]

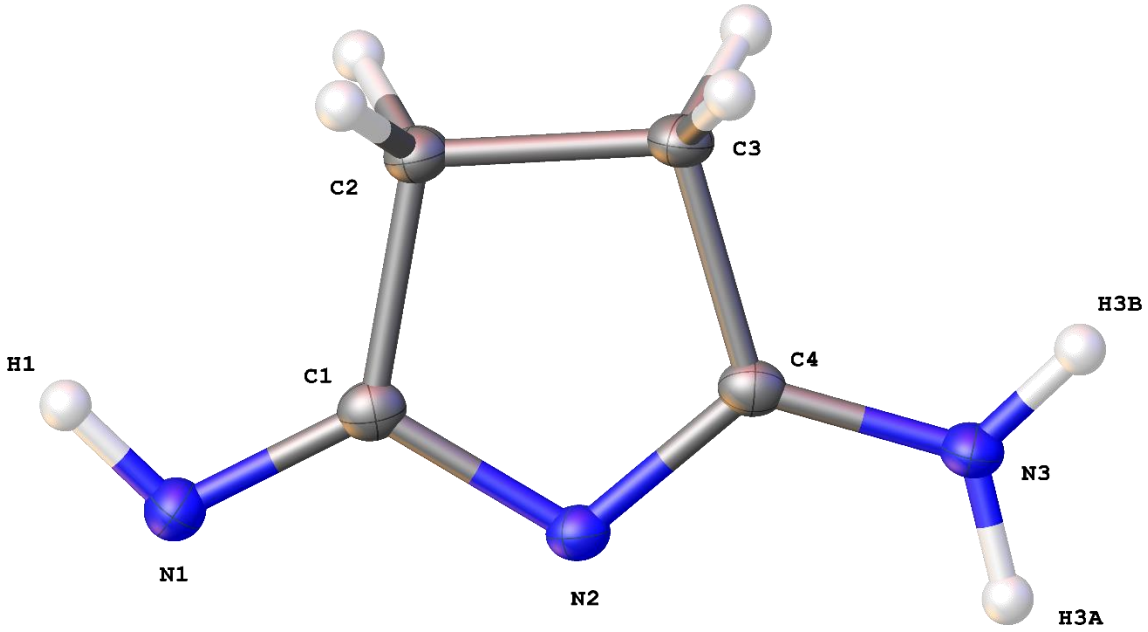

Figure S3. A molecular drawing of **1** shown with 50% probability ellipsoids.

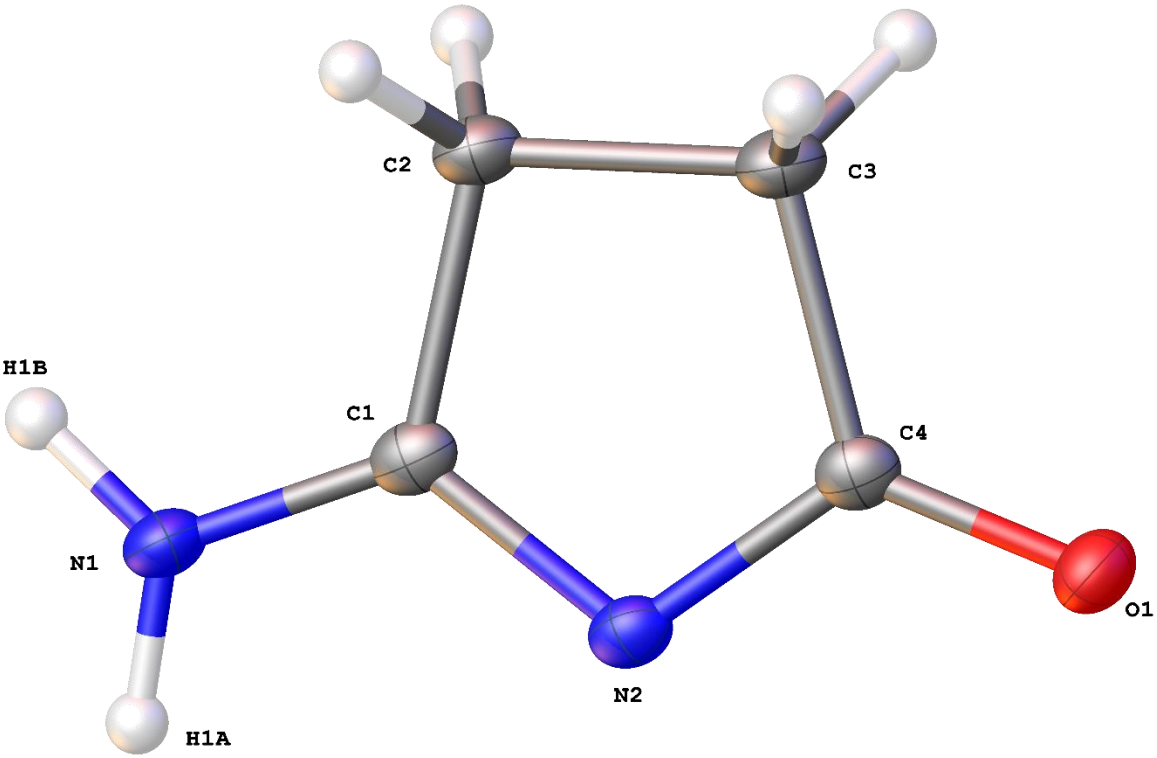

Figure S4. A molecular drawing of **3** shown with 50% probability ellipsoids.

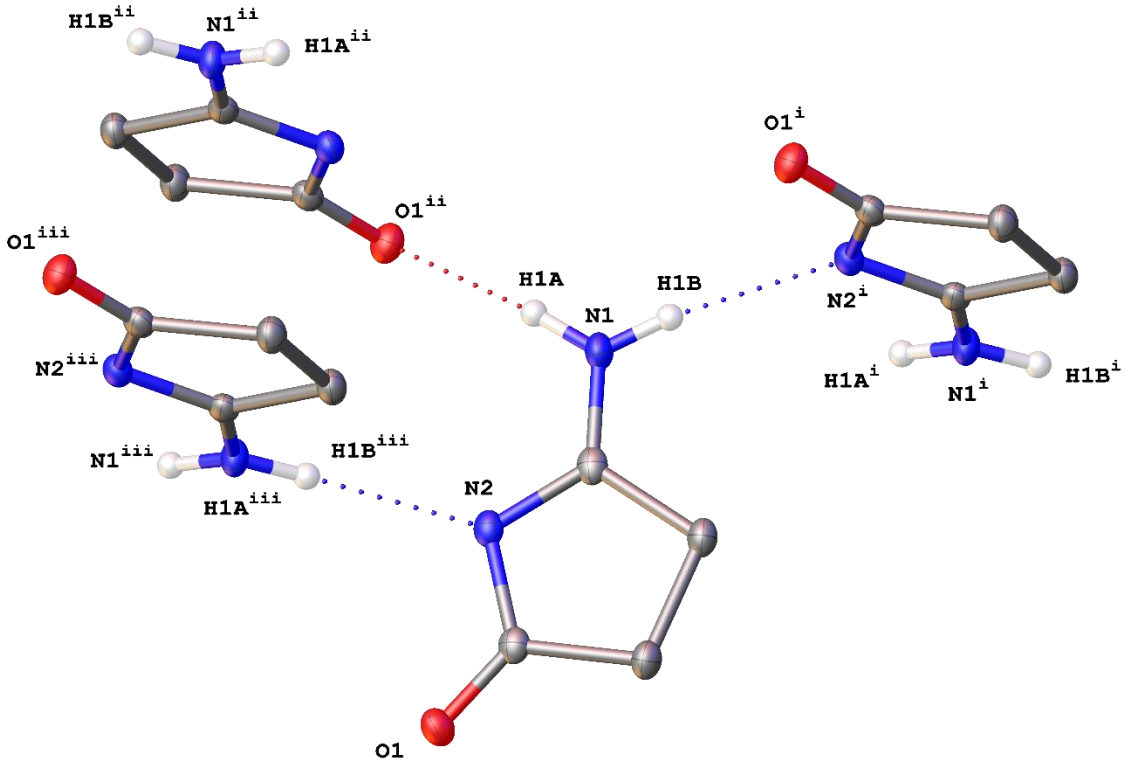

Figure S5. A molecular drawing of **3** shown with 50% probability ellipsoids with emphasis placed on the hydrogen bonding interactions. All H atoms not participating in hydrogen bonding interactions are omitted. [Symmetry code: i = -1/2+X,1/2-Y,-1/2+Z; ii = 3/2-X,-1/2+Y,3/2-Z; iii = 1/2+X,1/2-Y,1/2+Z.]

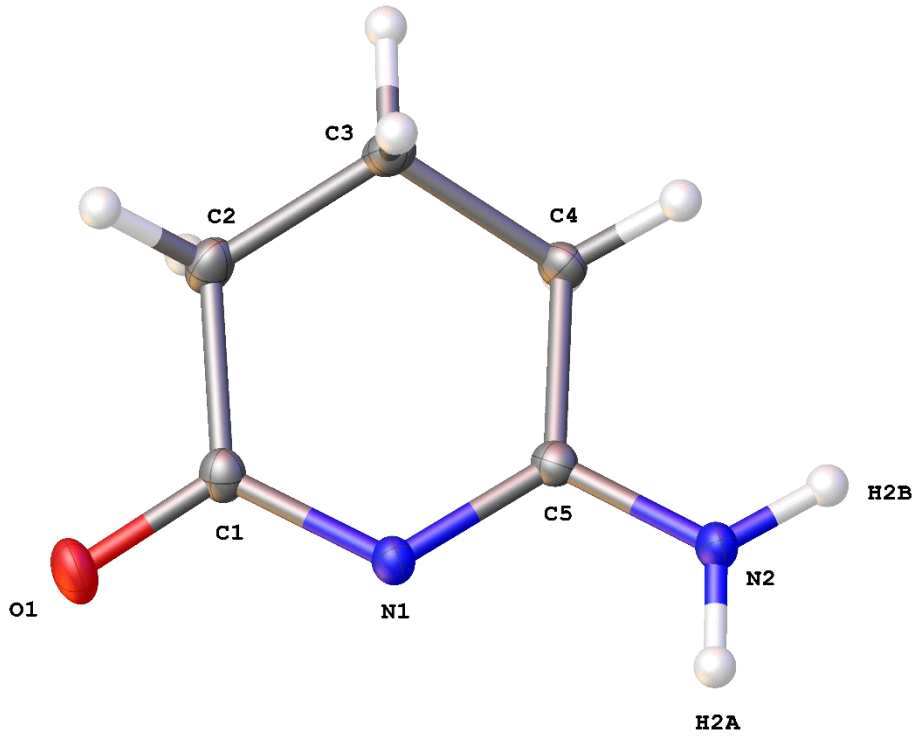

Figure S6. A molecular drawing of **4** shown with 50% probability ellipsoids.

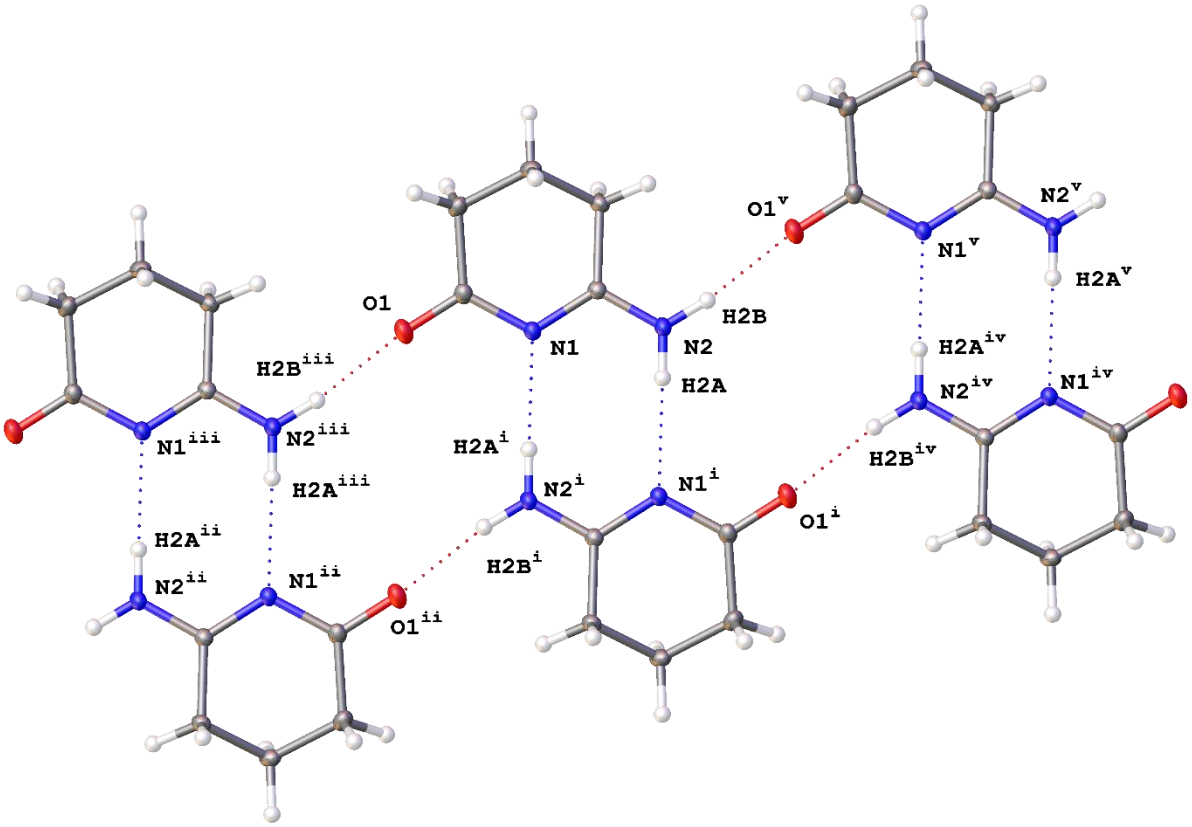

Figure S7. A molecular drawing of **4** shown with 50% probability ellipsoids. Emphasis is placed on the hydrogen bonding system. [Symmetry codes: i=-X,1-Y,1-Z; ii=-X,2-Y,1-Z; iii=+X,1+Y,+Z; iv=-X,-Y,1-Z; v=+X,-1+Y,+Z.]

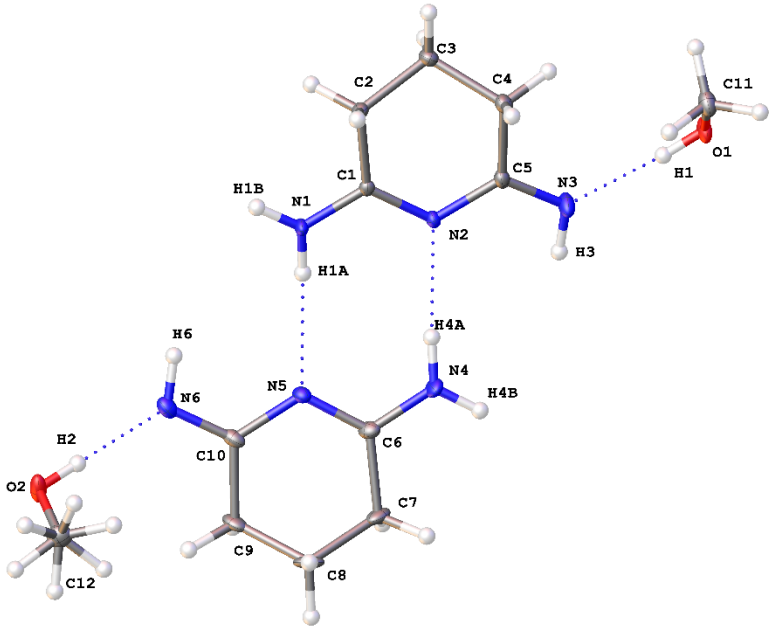

Figure S8. A molecular drawing of the major component of **2** shown with 50% probability ellipsoids.

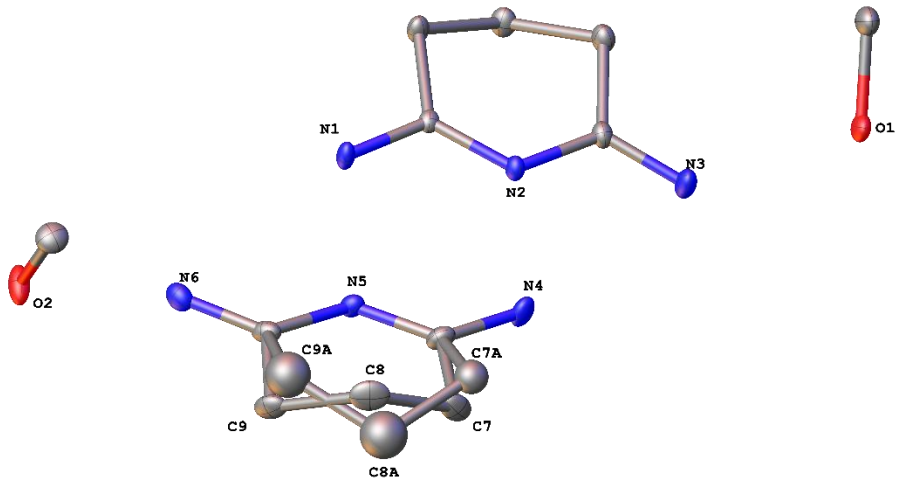

Figure S9. A molecular drawing of **2** shown with 50% probability ellipsoids. All Hydrogen atoms were omitted for clarity. Emphasis was placed on the disordered portion of the ring.