Electronic Supplementary Information

Mono-N-oxidation of Heterocycle-Fused Pyrimidines

Yongxing Tang,* †[a,b] Kejia Li, †[a] Ajay Kumar Chinnam,[b] Richard J. Staples,[c] and Jean'ne M. Shreeve*[b]

[a] Dr. Y. Tang, K. Li, Nanjing University of Science and Technology, Nanjing, 210094 (China)

[b] Dr. Y. Tang, Prof. J. M. Shreeve, Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343 USA. Fax: (+1) 208-885-5173 E-mail: jshreeve@uidaho.edu

[c] Dr. A. K. Chinnam, Dr. R. J. Staples, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

† These authors contributed equally to this work.

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Crystal Structure Packing Diagrams

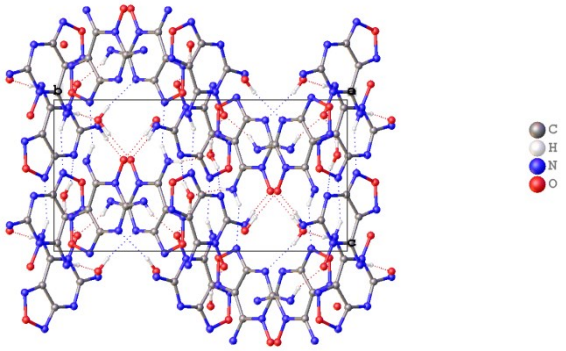

Figure S1. The packing diagram of **2**·H_2O viewed along *a* axis.

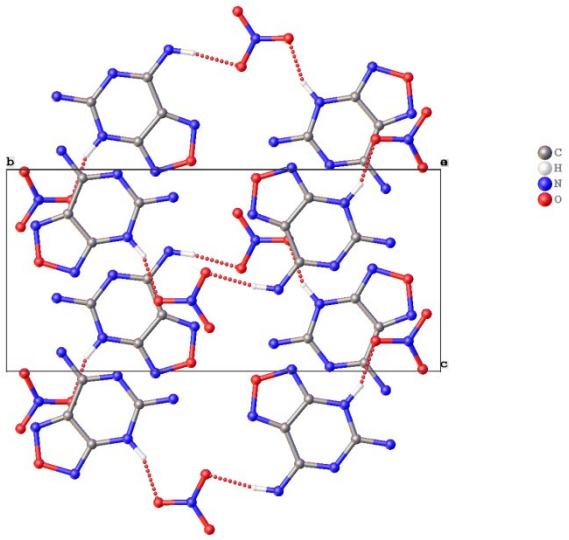

Figure S2. The packing diagram of **3** viewed along *a* axis.

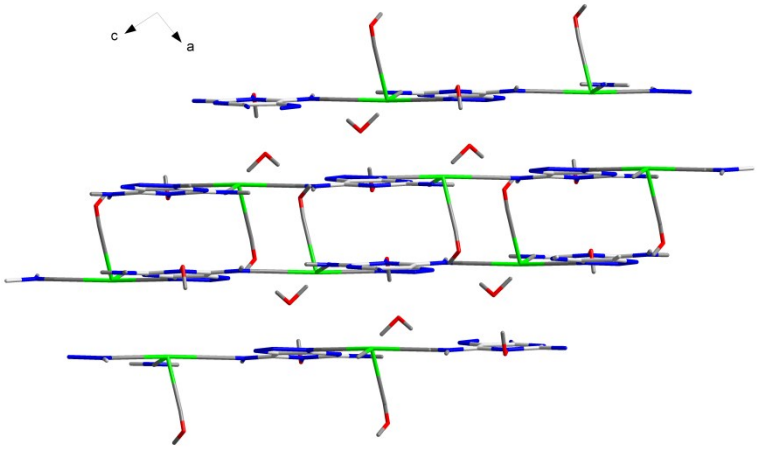

Figure S3. The packing diagram of **5**·HCl·$2H_2O$ viewed along *b* axis.

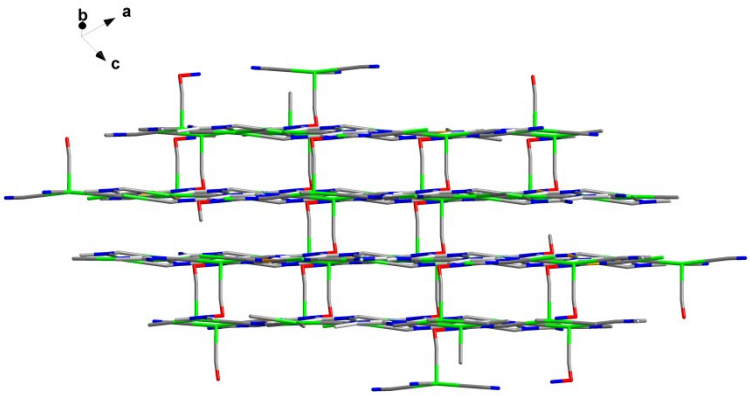

Figure S4. The packing diagram of **7**·2HCl viewed along *b* axis.

Crystal Structure Analysis

Table S1. Crystal data and structure refinement for **2**·H_2O**.**

Identification code	**2**·H_2O
CCDC number	2040723
Formula	$C_4H_6N_6O_3$
$D_{calc.}$/ g cm^{-3}	1.448
μ/mm^{-1}	1.084
Formula Weight	186.15
Colour	yellow
Shape	needle
Size/mm^3	0.20×0.03×0.03
T/K	100.00(11)
Crystal System	tetragonal
Space Group	$P4_2/n$
a /Å	14.9237(4)
b /Å	14.9237(4)
c /Å	7.6656(3)
α /°	90
β /°	90
γ /°	90
V/Å^3	1707.26(11)
Z	8
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_{α}
Θ_{min}/°	4.189
Θ_{max}/°	77.434
Measured Refl's.	9080
Indep't Refl's	1775
Refl's I≥2 σ(I)	1559
R_{int}	0.0505
Parameters	120
Restraints	0
Largest Peak	0.250
Deepest Hole	-0.267
GooF	1.144
wR_2 (all data)	0.1497
wR_2	0.1468
R_1 (all data)	0.0670
R_1	0.0613

Table S2. Bond lengths [Å] and angles [°] for **2**·H_2O**.**

Atom	Atom	Length/Å
O1	N3	1.394(3)
O1	N4	1.381(3)
O2	N1	1.342(2)
N1	C1	1.412(3)
N1	C4	1.333(3)
N2	C1	1.333(3)
N2	C2	1.355(3)
N3	C2	1.319(3)
N4	C3	1.302(3)
N5	C1	1.306(3)
N6	C4	1.308(3)
C2	C3	1.415(3)
C3	C4	1.446(3)

Atom	Atom	Atom	Angle/°
N4	O1	N3	112.26(18)
O2	N1	C1	117.34(19)
C4	N1	O2	118.06(19)
C4	N1	C1	124.4(2)
C1	N2	C2	113.9(2)
C2	N3	O1	104.3(2)
C3	N4	O1	103.7(2)
N2	C1	N1	123.6(2)
N5	C1	N1	114.0(2)
N5	C1	N2	122.4(2)
N2	C2	C3	125.4(2)
N3	C2	N2	126.2(2)
N3	C2	C3	108.4(2)
N4	C3	C2	111.3(2)
N4	C3	C4	129.8(2)
C2	C3	C4	119.0(2)
N1	C4	C3	113.6(2)
N6	C4	N1	120.8(2)
N6	C4	C3	125.7(2)

Table S3. Torsion angles [°] for **2**·H_2O**.**

Atom	Atom	Atom	Atom	Angle/°
O1	N3	C2	N2	-179.8(3)
O1	N3	C2	C3	0.4(3)
O1	N4	C3	C2	0.4(4)
O1	N4	C3	C4	-179.9(3)
O2	N1	C1	N2	177.4(2)
O2	N1	C1	N5	-2.3(3)
O2	N1	C4	N6	1.3(4)
O2	N1	C4	C3	-179.0(2)
N2	C2	C3	N4	179.7(3)
N2	C2	C3	C4	-0.1(4)
N3	O1	N4	C3	-0.1(4)
N3	C2	C3	N4	-0.5(4)
N3	C2	C3	C4	179.8(3)
N4	O1	N3	C2	-0.2(4)
N4	C3	C4	N1	-176.9(3)
N4	C3	C4	N6	2.8(5)
C1	N1	C4	N6	176.4(2)
C1	N1	C4	C3	-3.8(3)
C1	N2	C2	N3	178.5(3)
C1	N2	C2	C3	-1.7(4)
C2	N2	C1	N1	0.8(3)
C2	N2	C1	N5	-179.6(2)
C2	C3	C4	N1	2.8(4)
C2	C3	C4	N6	-177.5(3)
C4	N1	C1	N2	2.2(4)
C4	N1	C1	N5	-177.4(2)

Table S4. Hydrogen bond information for **2**·H_2O.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N5	H5A	O2[1]	0.86	1.92	2.759(2)	163.6
N6	H6A	N3[2]	0.86	2.26	3.013(3)	146.1
N6	H6B	O1W[3]	0.86	1.88	2.720(3)	166.7
O1W	H1WA	O2[4]	0.85	1.88	2.694(2)	161.0
O1W	H1WB	N2[5]	0.85	2.06	2.869(3)	159.0

[1]1-y,1/2+x,1/2+z; [2]+x,+y,-1+z; [3]1-x,1-y,-1-z; [4]-1/2+y,1-x,1/2+z; [5]-1/2+y,1-x,-1/2+z

Table S5. Crystal data and structure refinement for **3.**

Identification code	**3**
CCDC number	2040720
Formula	$C_4H_5N_7O_4$
$D_{calc.}$/ g cm^{-3}	1.859
μ/mm^{-1}	1.452
Formula Weight	215.15
Colour	colourless
Shape	plate
Size/mm^3	0.16×0.10×0.04
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a /Å	6.1448(3)
b /Å	16.4016(6)
c /Å	7.6331(3)
α /°	90
β /°	92.289(3)
γ /°	90
V/Å^3	768.68(6)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_{α}
Θ_{min}/°	5.394
Θ_{max}/°	77.136
Measured Refl's.	4461
Indep't Refl's	1526
Refl's I≥2 σ(I)	1336
R_{int}	0.0430
Parameters	156
Restraints	0
Largest Peak	0.292
Deepest Hole	-0.331
GooF	1.069
wR_2 (all data)	0.1140
wR_2	0.1096
R_1 (all data)	0.0458
R_1	0.0409

Table S6. Bond lengths [Å] and angles [°] for **3**.

Atom	Atom	Length/Å
O1	N3	1.4033(18)
O1	N4	1.3739(18)
N1	C1	1.364(2)
N1	C4	1.370(2)
N2	C3	1.324(2)
N2	C4	1.356(2)
N3	C1	1.303(2)
N4	C2	1.303(2)
N5	C4	1.306(2)
N6	C3	1.312(2)
C1	C2	1.407(2)
C2	C3	1.465(2)
O2	N7	1.2605(19)
O3	N7	1.2588(18)
O4	N7	1.2444(18)

Atom	Atom	Atom	Angle/°
N4	O1	N3	111.68(12)
C1	N1	C4	117.41(14)
C3	N2	C4	120.95(14)
C1	N3	O1	103.60(12)
C2	N4	O1	104.70(13)
N1	C1	C2	121.11(14)
N3	C1	N1	128.65(15)
N3	C1	C2	110.24(15)
N4	C2	C1	109.78(14)
N4	C2	C3	132.15(15)
C1	C2	C3	118.07(15)
N2	C3	C2	118.38(14)
N6	C3	N2	121.12(15)
N6	C3	C2	120.50(15)
N2	C4	N1	124.01(15)
N5	C4	N1	117.67(15)
N5	C4	N2	118.32(15)
O3	N7	O2	119.07(13)
O4	N7	O2	120.35(13)
O4	N7	O3	120.57(13)

Table S7. Torsion angles [°] for **3**.

Atom	Atom	Atom	Atom	Angle/°
O1	N3	C1	N1	178.79(14)
O1	N3	C1	C2	-0.61(16)
O1	N4	C2	C1	-0.12(17)
O1	N4	C2	C3	179.63(16)
N1	C1	C2	N4	-178.96(13)
N1	C1	C2	C3	1.3(2)
N3	O1	N4	C2	-0.26(17)
N3	C1	C2	N4	0.50(19)
N3	C1	C2	C3	-179.29(14)
N4	O1	N3	C1	0.55(16)
N4	C2	C3	N2	177.65(16)
N4	C2	C3	N6	-2.4(3)
C1	N1	C4	N2	-1.7(2)
C1	N1	C4	N5	178.69(14)
C1	C2	C3	N2	-2.6(2)
C1	C2	C3	N6	177.34(14)
C3	N2	C4	N1	0.3(2)
C3	N2	C4	N5	179.90(14)
C4	N1	C1	N3	-178.54(15)
C4	N1	C1	C2	0.8(2)
C4	N2	C3	N6	-178.06(14)
C4	N2	C3	C2	1.9(2)

Table S8. Hydrogen bond information for **3**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N1	H1	O2	0.93(3)	1.83(3)	2.7047(19)	157(3)
N6	H6A	O3[1]	0.91(2)	2.00(2)	2.8875(19)	163(2)

[1]1/2-x,-1/2+y,3/2-z

Table S9. Crystal data and structure refinement for **5**·HCl·2H_2O**.**

Identification code	**5·HCl·2H_2O**
CCDC number	2040721
Formula	$C_4H_{10}ClN_7O_3$
$D_{calc.}$/ g cm^{-3}	1.610
μ/mm^{-1}	3.531
Formula Weight	239.64
Colour	yellow
Shape	plate
Size/mm^3	0.21×0.15×0.05
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a /Å	8.3157(4)
b /Å	9.2267(4)
c /Å	12.9583(6)
α /°	90
β /°	95.961(4)
γ /°	90
V/Å^3	988.87(7)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_{α}
Θ_{min}/°	5.898
Θ_{max}/°	77.347
Measured Refl's.	11264
Indep't Refl's	2044
Refl's I≥2 σ(I)	1862
R_{int}	0.0557
Parameters	176
Restraints	0
Largest Peak	0.417
Deepest Hole	-0.439
GooF	1.080
wR_2 (all data)	0.1168
wR_2	0.1129
R_1 (all data)	0.0448
R_1	0.0417

Table S10. Bond lengths [Å] and angles [°] for **5**·HCl·2H_2O**.**

Atom	Atom	Length/Å
O1	N1	1.377(2)
N1	C1	1.365(3)
N1	C2	1.399(3)
N2	C2	1.332(3)
N2	C3	1.343(3)
N3	N4	1.363(2)
N3	C3	1.348(3)
N4	N5	1.307(2)
N5	C4	1.364(3)
N6	C1	1.307(3)
N7	C2	1.315(3)
C1	C4	1.420(3)
C3	C4	1.382(3)

Atom	Atom	Atom	Angle/°
O1	N1	C2	117.19(16)
C1	N1	O1	117.20(16)
C1	N1	C2	125.59(17)
C2	N2	C3	113.46(16)
C3	N3	N4	109.89(17)
N5	N4	N3	108.98(16)
N4	N5	C4	107.18(16)
N1	C1	C4	112.43(17)
N6	C1	N1	119.94(19)
N6	C1	C4	127.63(19)
N2	C2	N1	121.75(18)
N7	C2	N1	116.23(18)
N7	C2	N2	122.00(18)
N2	C3	N3	127.89(18)
N2	C3	C4	127.96(19)
N3	C3	C4	104.16(17)
N5	C4	C1	131.51(18)
N5	C4	C3	109.79(18)
C3	C4	C1	118.70(18)

Table S11. Torsion angles [°] for **5**·HCl·2H_2O**.**

Atom	Atom	Atom	Atom	Angle/°
O1	N1	C1	N6	-1.8(3)
O1	N1	C1	C4	177.39(16)
O1	N1	C2	N2	-174.72(17)
O1	N1	C2	N7	4.3(2)
N1	C1	C4	N5	179.75(19)
N1	C1	C4	C3	-1.0(3)
N2	C3	C4	N5	-179.75(18)
N2	C3	C4	C1	0.8(3)
N3	N4	N5	C4	0.0(2)
N3	C3	C4	N5	0.3(2)
N3	C3	C4	C1	-179.16(17)
N4	N3	C3	N2	179.78(18)
N4	N3	C3	C4	-0.2(2)
N4	N5	C4	C1	179.1(2)
N4	N5	C4	C3	-0.2(2)
N6	C1	C4	N5	-1.1(4)
N6	C1	C4	C3	178.17(19)
C1	N1	C2	N2	3.9(3)
C1	N1	C2	N7	-177.10(18)
C2	N1	C1	N6	179.55(18)
C2	N1	C1	C4	-1.2(3)
C2	N2	C3	N3	-178.43(19)
C2	N2	C3	C4	1.6(3)
C3	N2	C2	N1	-3.8(3)
C3	N2	C2	N7	177.33(18)
C3	N3	N4	N5	0.1(2)

Table S12. Hydrogen bond information for **5**·HCl·2H_2O **.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N6	H6A	O2	0.87(3)	1.97(3)	2.830(2)	170(3)
N7	H7B	O2[1]	0.87(3)	2.05(3)	2.881(2)	160(3)
O2	H2B	N4[2]	0.81(4)	2.26(4)	3.016(2)	155(3)
O3	H3A	N5[3]	0.84(3)	2.08(3)	2.827(2)	148(2)
O3	H3B	N2	0.92(4)	1.90(4)	2.778(2)	158(4)
O1	H1	O3[4]	0.91(4)	1.59(4)	2.494(2)	171(3)

[1]-1/2+x,1/2-y,1/2+z; [2]+x,-1+y,+z; [3]-1/2+x,3/2-y,1/2+z; [4]3/2-x,-1/2+y,3/2-z

Table S13. Crystal data and structure refinement for **7**·2HCl**.**

Identification code	**7**·2HCl
CCDC number	2040722
Formula	$C_5H_8Cl_2N_6O$
$D_{calc.}$/ g cm^{-3}	1.715
μ/mm^{-1}	6.167
Formula Weight	239.07
Colour	colourless
Shape	needle
Size/mm^3	0.17×0.05×0.02
T/K	100.01(10)
Crystal System	triclinic
Space Group	P-1
a /Å	6.3903(2)
b /Å	7.8053(2)
c /Å	9.9575(2)
α /°	79.811(2)
β /°	75.385(2)
γ /°	76.143(2)
V/Å^3	463.01(2)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_{α}
Θ_{min}/°	4.625
Θ_{max}/°	77.349
Measured Refl's.	11036
Indep't Refl's	1884
Refl's I≥2 σ(I)	1717
R_{int}	0.0661
Parameters	155
Restraints	0
Largest Peak	0.439
Deepest Hole	-0.529
GooF	1.136
wR_2 (all data)	0.1123
wR_2	0.1098
R_1 (all data)	0.0431
R_1	0.0400

Table S14. Bond lengths [Å] and angles [°] for **7**·2HCl**.**

Atom	Atom	Length/Å
O1	N1	1.385(3)
N1	C1	1.391(4)
N1	C5	1.371(4)
N2	C1	1.329(4)
N2	C2	1.335(4)
N3	C2	1.370(4)
N3	C3	1.340(4)
N4	C3	1.326(4)
N4	C4	1.392(3)
N5	C1	1.321(4)
N6	C5	1.309(4)
C2	C4	1.384(4)
C4	C5	1.403(4)

Atom	Atom	Atom	Angle/°
O1	N1	C1	118.0(2)
C5	N1	O1	116.3(2)
C5	N1	C1	125.3(2)
C1	N2	C2	113.5(2)
C3	N3	C2	109.0(2)
C3	N4	C4	107.6(2)
N2	C1	N1	121.8(2)
N5	C1	N1	117.3(2)
N5	C1	N2	120.9(3)
N2	C2	N3	126.0(2)
N2	C2	C4	127.8(2)
N3	C2	C4	106.2(2)
N4	C3	N3	109.8(2)
N4	C4	C5	133.6(3)
C2	C4	N4	107.4(2)
C2	C4	C5	118.8(2)
N1	C5	C4	112.4(2)
N6	C5	N1	120.5(2)
N6	C5	C4	127.1(3)

Table S15. Torsion angles [°] for **7**·2HCl**.**

Atom	Atom	Atom	Atom	Angle/°
O1	N1	C1	N2	-179.2(2)
O1	N1	C1	N5	2.3(4)
O1	N1	C5	N6	-3.5(4)
O1	N1	C5	C4	176.4(2)
N2	C2	C4	N4	-180.0(3)
N2	C2	C4	C5	-4.7(4)
N3	C2	C4	N4	0.2(3)
N3	C2	C4	C5	175.4(2)
N4	C4	C5	N1	175.2(3)
N4	C4	C5	N6	-4.9(5)
C1	N1	C5	N6	-176.2(3)
C1	N1	C5	C4	3.7(4)
C1	N2	C2	N3	-178.1(3)
C1	N2	C2	C4	2.1(4)
C2	N2	C1	N1	3.4(4)
C2	N2	C1	N5	-178.2(3)
C2	N3	C3	N4	-0.3(3)
C2	C4	C5	N1	1.5(4)
C2	C4	C5	N6	-178.6(3)
C3	N3	C2	N2	-179.8(3)
C3	N3	C2	C4	0.0(3)
C3	N4	C4	C2	-0.4(3)
C3	N4	C4	C5	-174.6(3)
C4	N4	C3	N3	0.5(3)
C5	N1	C1	N2	-6.7(4)
C5	N1	C1	N5	174.9(3)

Table S16. Hydrogen bond information for **7**·2HCl**.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	Cl1	0.94(5)	2.01(5)	2.944(2)	172(4)
N4	H4	Cl2	0.85(4)	2.30(4)	3.095(2)	154(3)

NMR Spectrum of **2.**

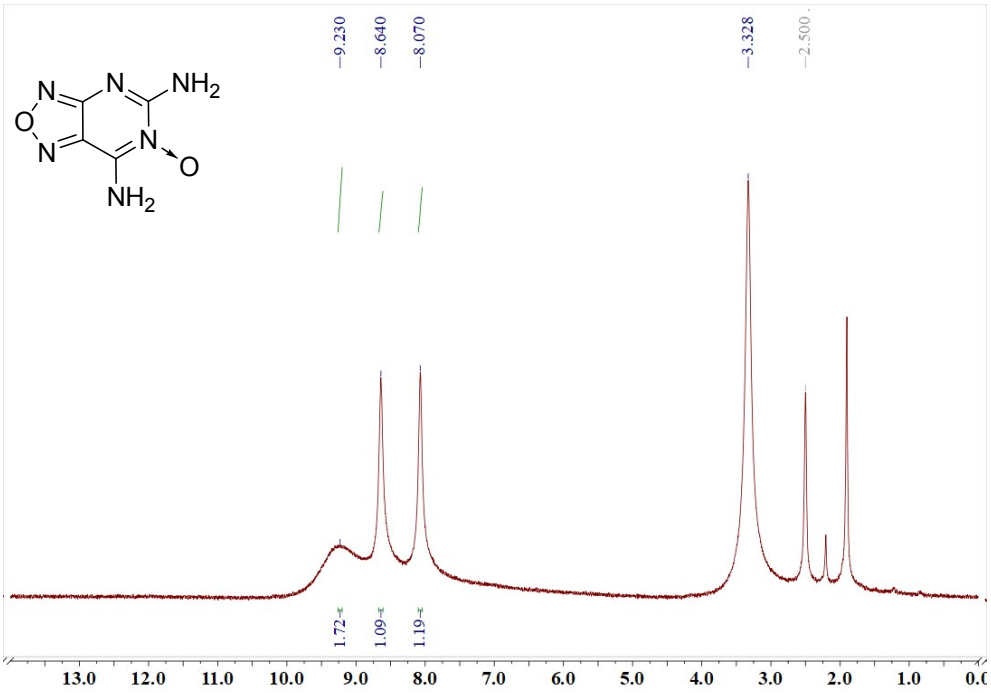

Figure S5. ^{1}H NMR Spectrum of **2**

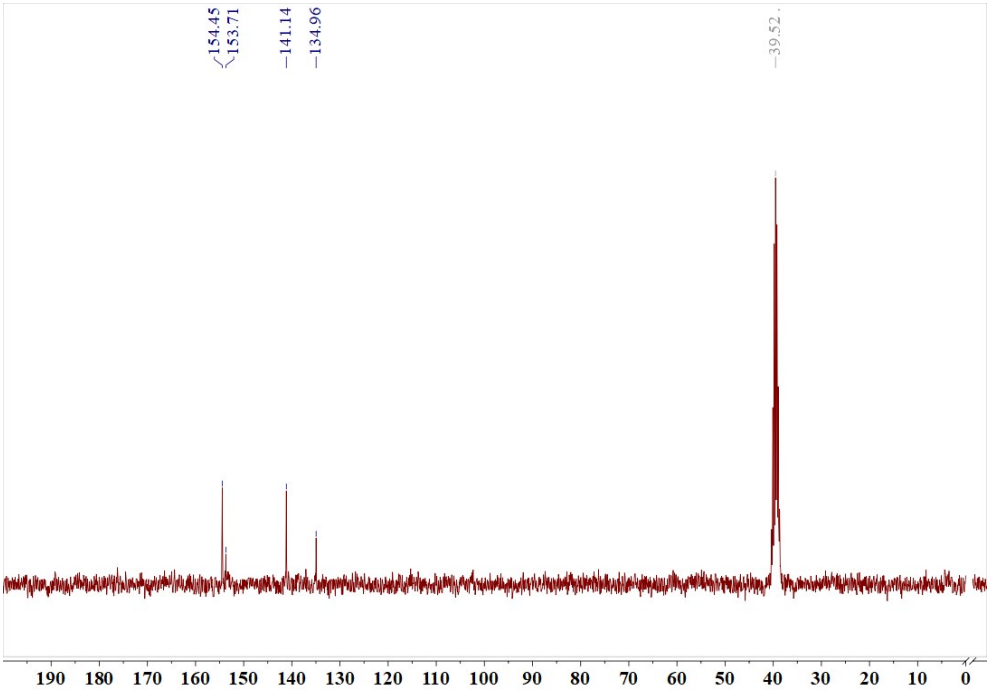

Figure S6. ^{13}C NMR Spectrum of **2**

NMR Spectrum of **3**

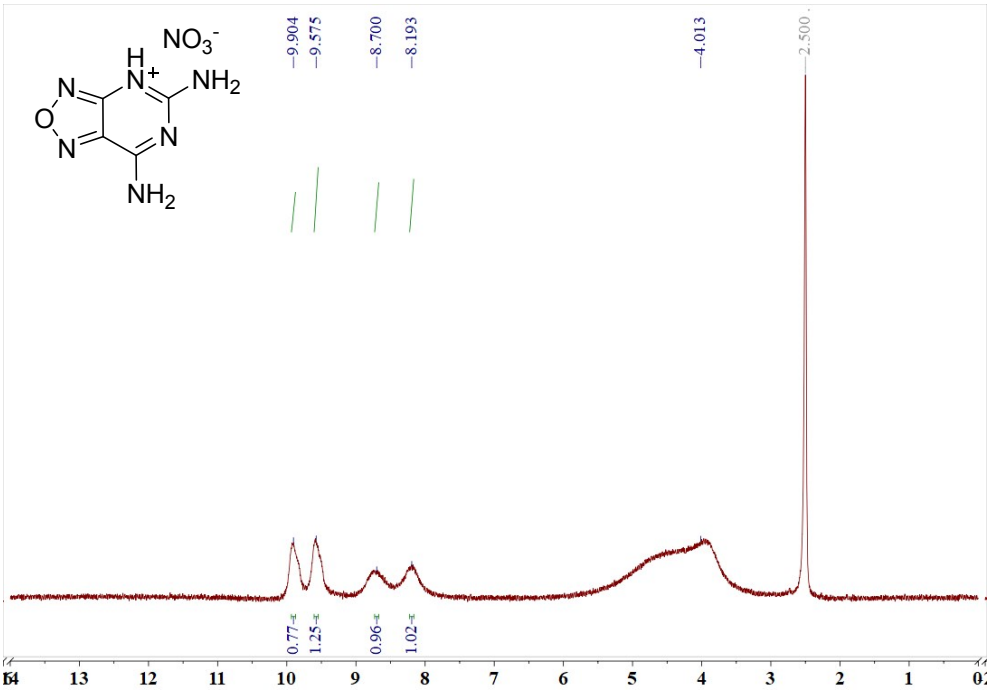

Figure S7. ^{1}H NMR Spectrum of **3**

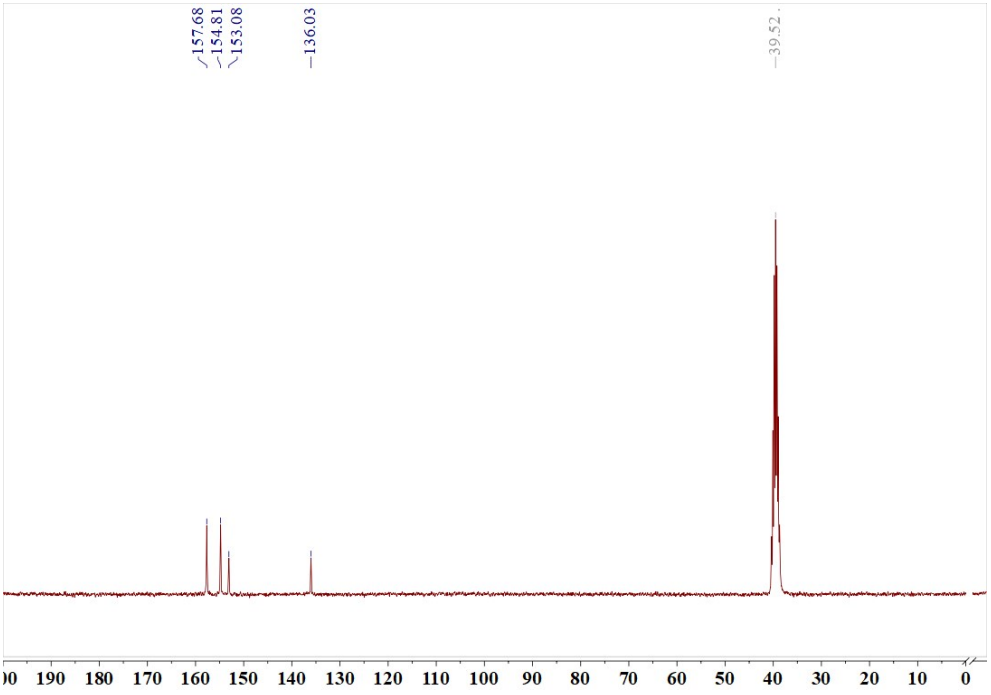

Figure S8. ^{13}C NMR Spectrum of **3**

NMR Spectrum of **5**

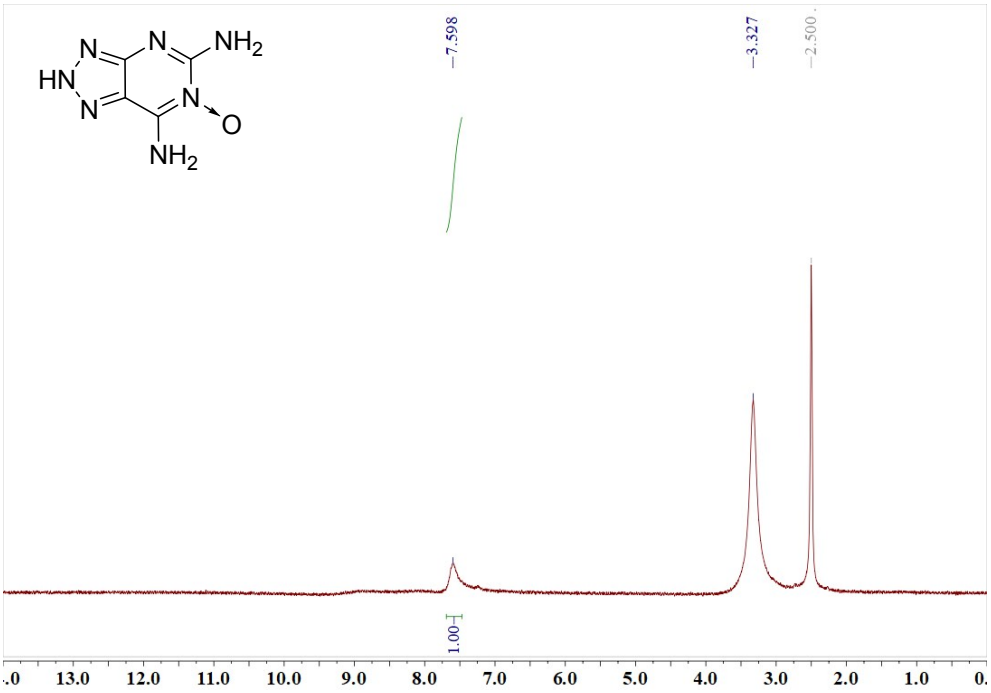

Figure S9. ^{1}H NMR Spectrum of **5**

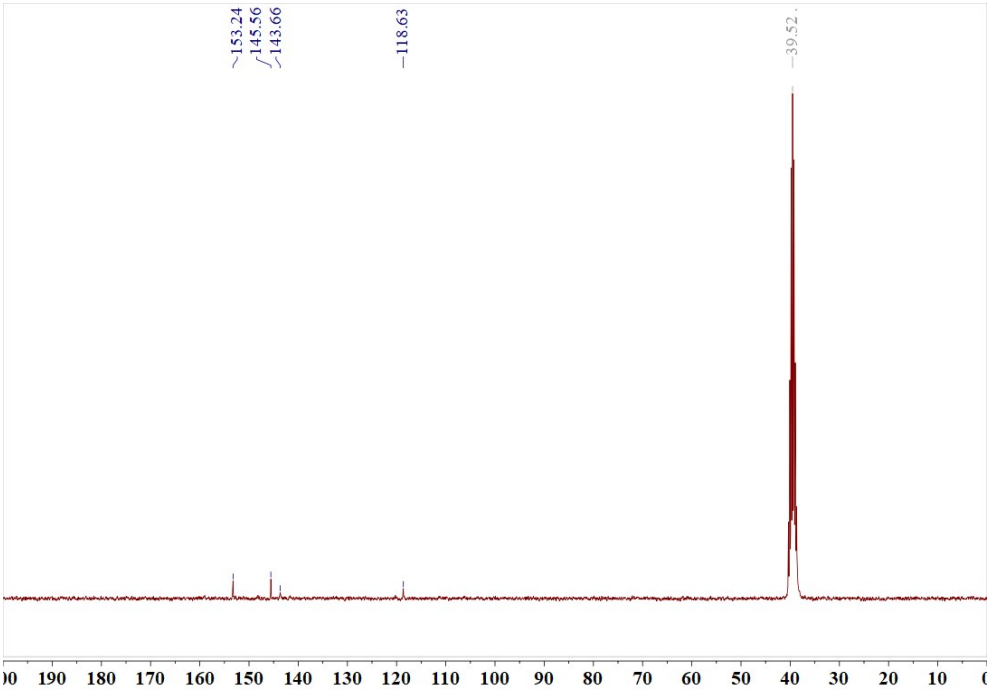

Figure S10. ^{13}C NMR Spectrum of **5**

NMR Spectrum of **7**

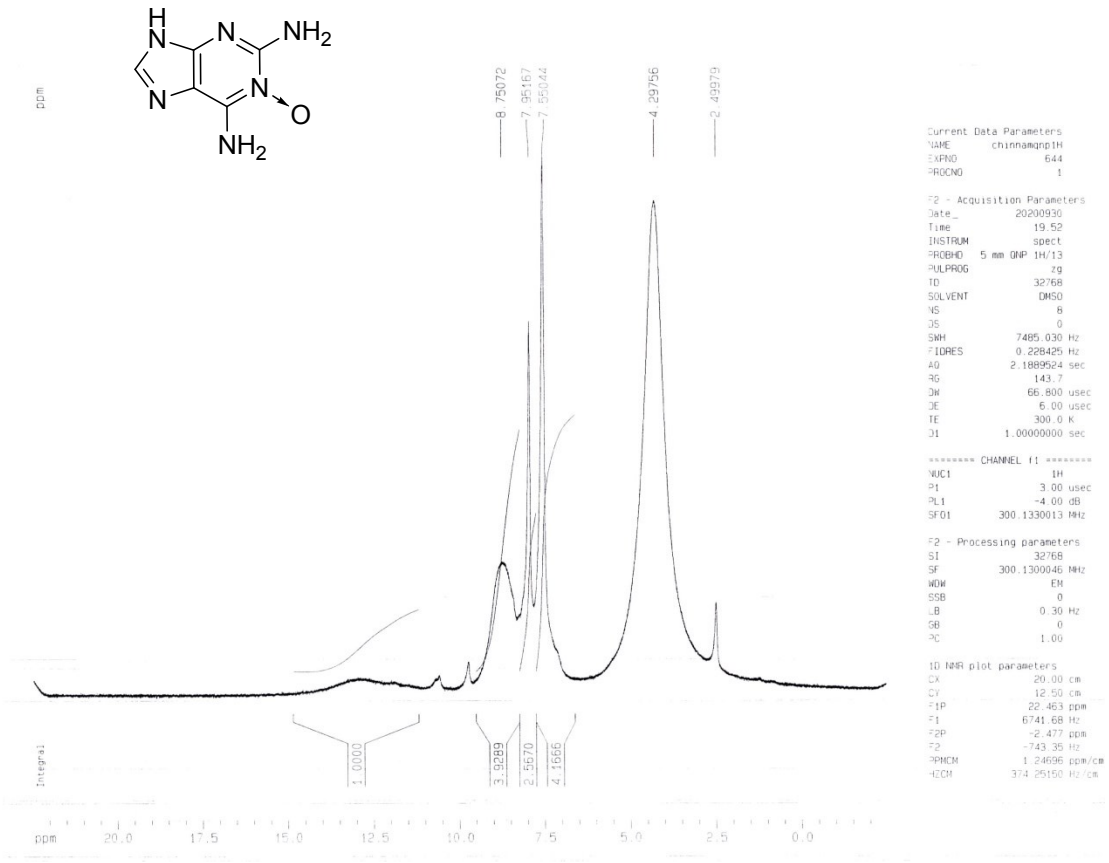

Figure S11. ^{1}H NMR Spectrum of **7**

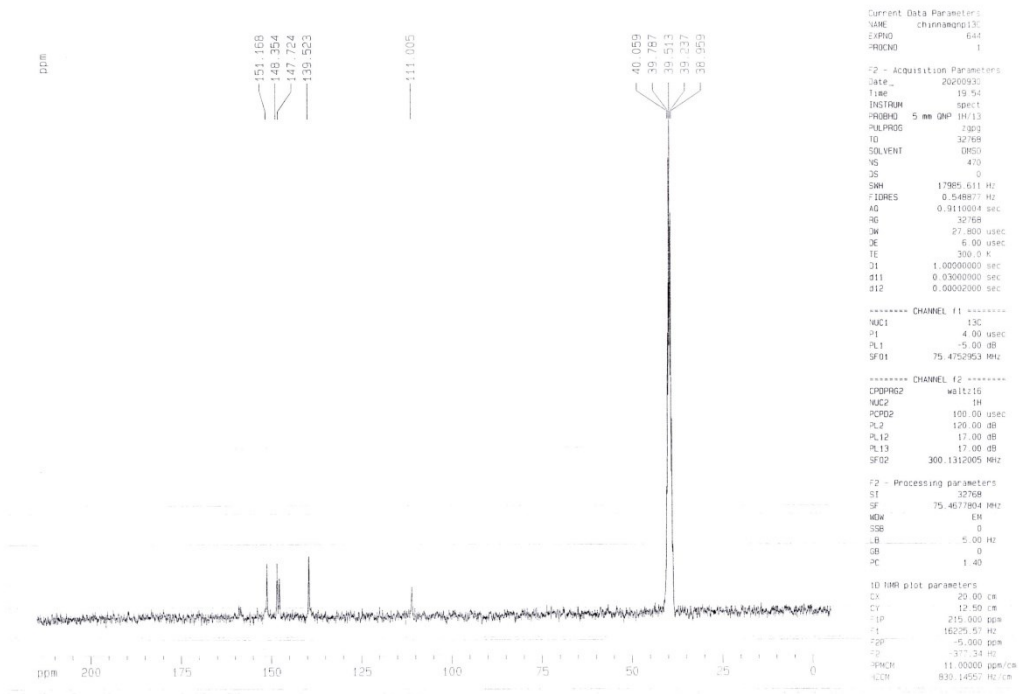

Figure S12 ^{13}C NMR Spectrum of **7**

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