Electronic Supplementary Information

Finding Furoxan Rings

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Table of Contents

X-ray Crystallography of 3-5, and 8

A clear colorless block of dimensions 0.190 x 0.085 x 0.060 mm^3 for **3**; a colorless needle of dimensions 0.048 x 0.053 x 0.144 mm^3 for **4**; a clear colorless plate of dimensions 0.305 x 0.168 x 0.057 mm^3 for **5**; and a clear colorless chunk of dimensions 0.250 x 0.161 x 0.063 mm^3 for **8** were each mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoKα radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2014.3-0].[1] Data reduction was performed using *SAINT* [v7.68A][2] and *XPREP* [v2014/2].[3] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[4] The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WingX.[5] The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model (Table S1).

Table S1. Selected crystal parameters of **3-5** and **8**.

Empirical formula	$C_3KN_5O_7$ **3**	$C_3HN_5O_7$ **4**	$C_6N_8O_8$ **5**	$C_3H_4N_6O_8$ **8**
CCDC Number	1968919	1968921	1968922	1968920
Formula weight	257.18	219.09	312.14	252.12
Temperature/K	293(2)	173(2)	296(2)	296(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pna2_1$	$P2_12_12_1$	C2/c
a/Å	10.266(3)	18.1742(7)	6.754(3)	23.5598(10)
b/Å	7.180(2)	6.6529(3)	10.796(4)	6.4371(3)
c/Å	12.384(2)	6.1535(3)	15.179(6)	15.9786(7)
α/°	90	90	90	90
β/°	113.643(13)	90	90	130.7954(11)
γ/°	90	90	90	90
Volume/$Å^3$	836.2(4)	744.03(6)	1106.9(7)	1834.52(14)
Z	4	4	4	8
ρ_{calc} g/cm^3	2.043	1.956	1.873	1.826
μ/mm^{-1}	6.057	1.754	0.176	0.181
F(000)	512	440	624	1024
Crystal size/mm^3	0.190 x 0.085 x 0.060	0.048 x 0.053 x 0.144	0.305 x 0.168 x 0.057	0.250 x 0.161 x 0.063
θ range/°	4.702-74.484	4.866-74.655	2.315-30.018	2.284-30.019
Index ranges	$-12 \le h \le 12$ $-7 \le k \le 8$ $-12 \le l \le 15$	$-21 \le h \le 22$ $-8 \le k \le 8$ $-7 \le l \le 7$	$-9 \le h \le 9$ $-15 \le k \le 12$ $-21 \le l \le 21$	$-31 \le h \le 30$ $-9 \le k \le 9$ $-17 \le l \le 22$
Reflections collected	5640	6540	12914	10560

Independent reflections	1603 [R_{int} = 0.0324]	1465 [R_{int} = 0.0401]	3152 [R_{int} = 0.0302]	2596 [R_{int} = 0.0269]
Data/restraints/parameters	1603 / 0 / 146	1465/1/136	3152 / 0 / 199	2596 / 0 / 167
Goodness-of-fit on F^2	0.997	1.079	1.009	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0269, wR_2 = 0.0700	R_1 = 0.0436, wR_2 = 0.1113	R_1 =0.0376, wR_2 =0.0811	R_1 =0.0397, wR_2 =0.0918
Final R indexes [all data]	R_1 = 0.0276, wR_2 = 0.0705	R_1 =0.0445, wR_2 =0.1122	R_1 =0.0701, wR_2 =0.0933	R_1 =0.0771, wR_2 =0.1073
Largest diff. peak/hole / e $Å^{-3}$	0.301/-0.243	0.517/-0.195	0.234/-0.150	0.185/-0.221

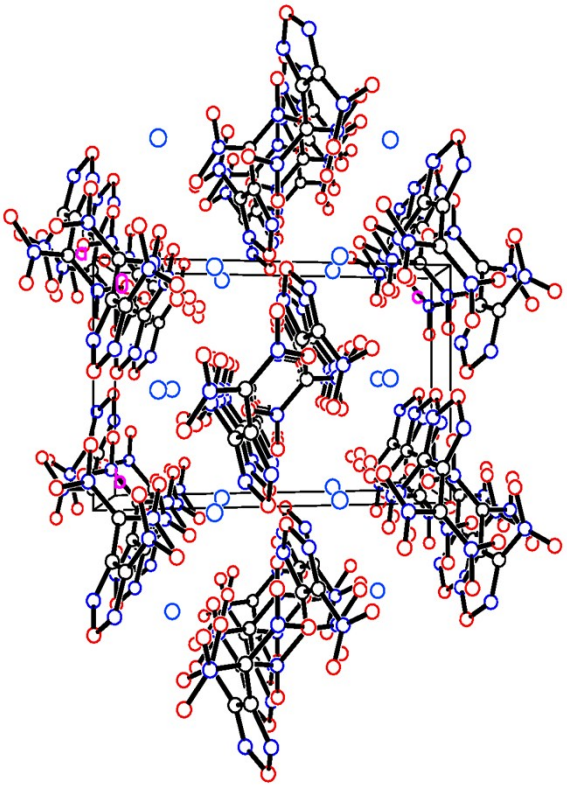


Figure S1. Unit cell view for **3** along *a* axis.

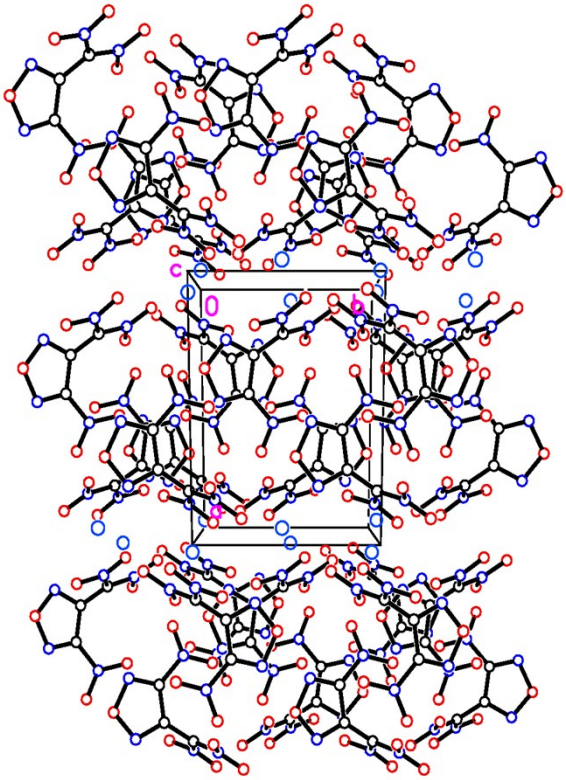


Figure S2. Unit cell view for **3** along *b* axis.

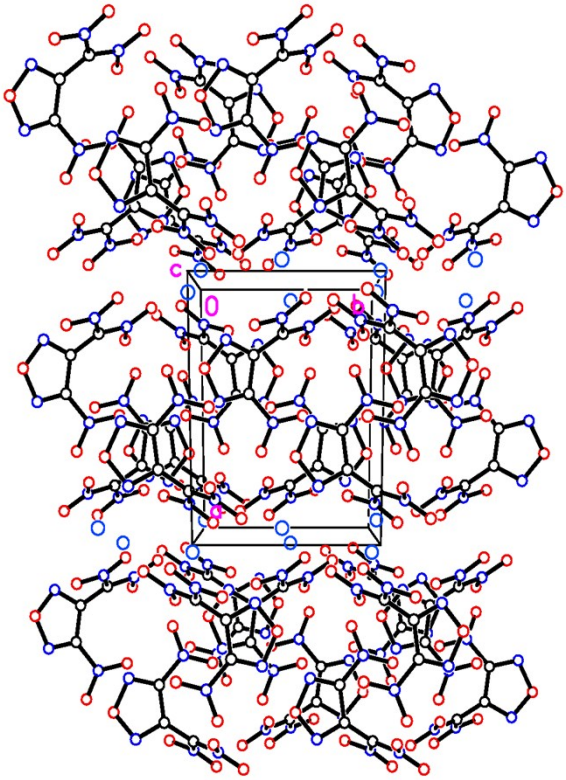


Figure S3. Unit cell view for **3** along *c* axis.

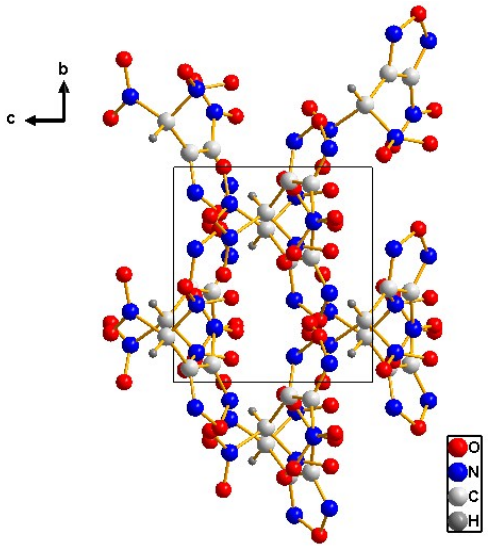


Figure S4. Unit cell view for **4** along *a* axis.

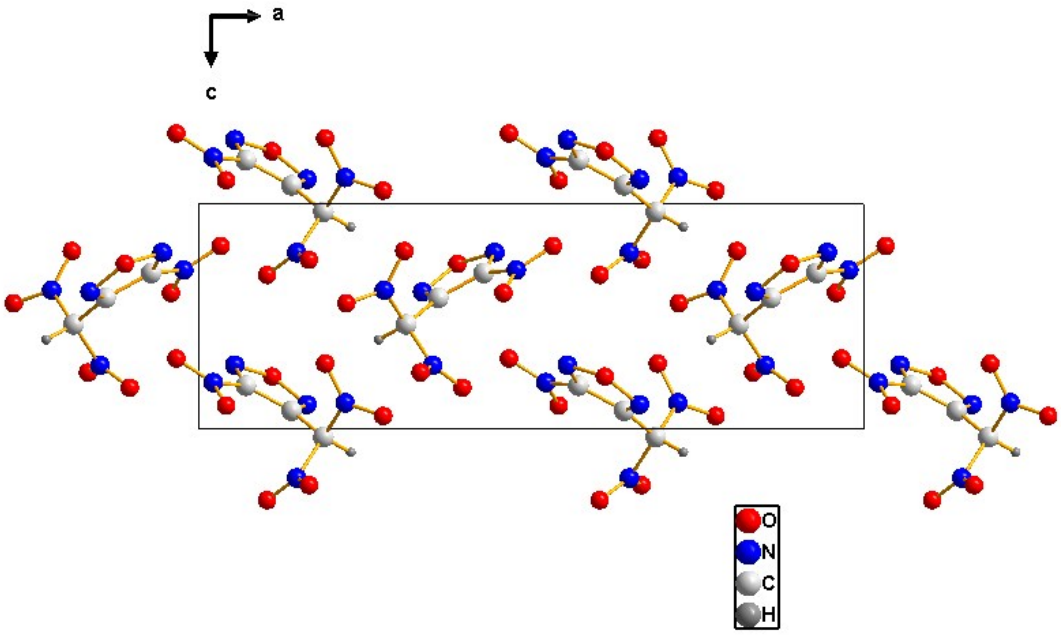


Figure S5. Unit cell view for **4** along *b* axis.

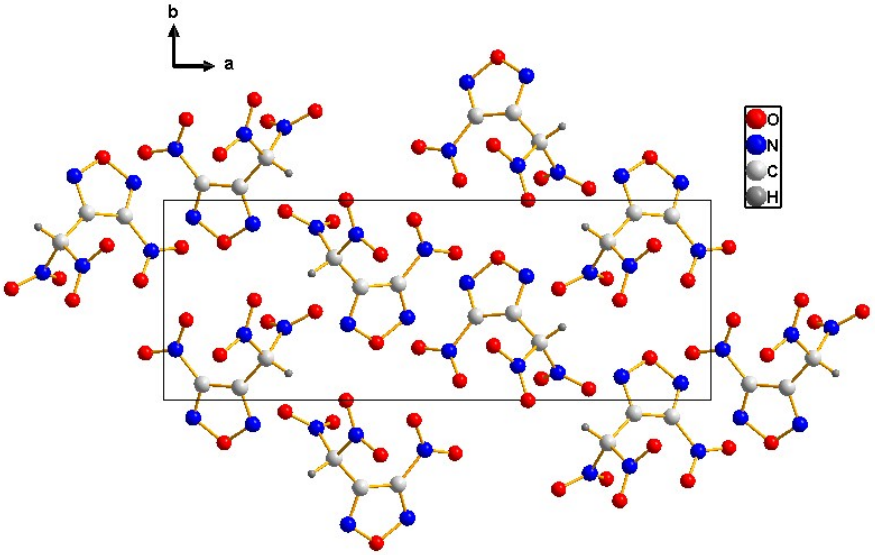


Figure S6. Unit cell view for **4** along *c* axis.

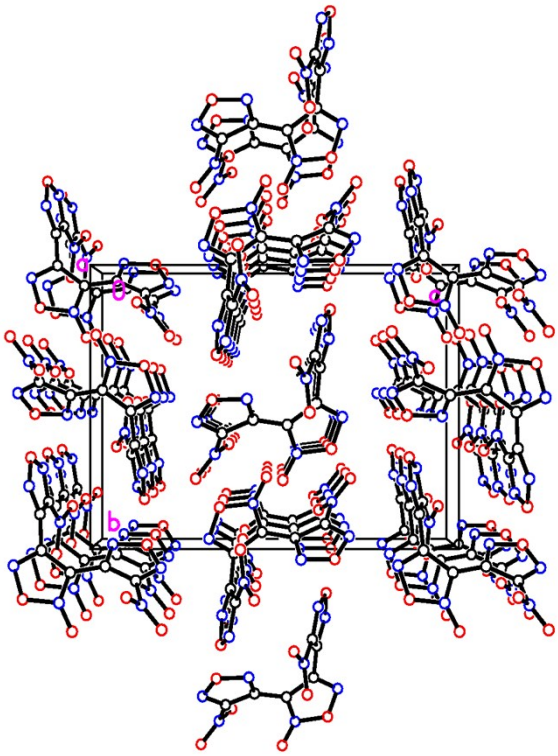


Figure S7. Unit cell view for **5** along *a* axis.

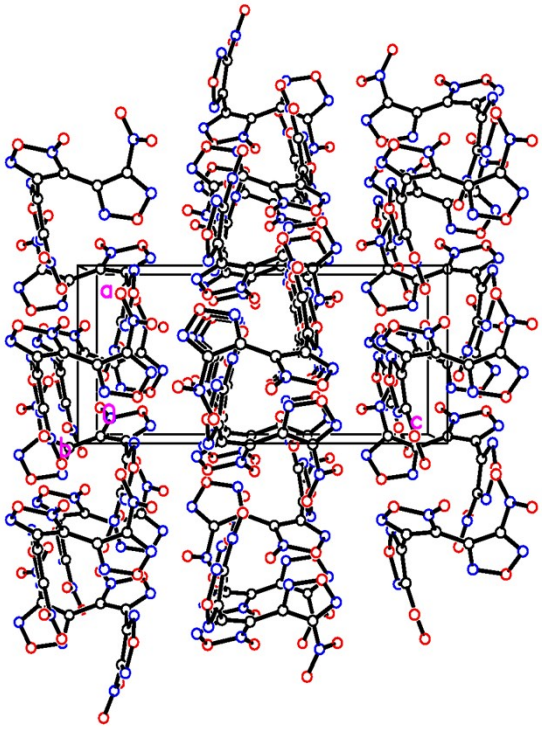


Figure S8. Unit cell view for **5** along *b* axis.

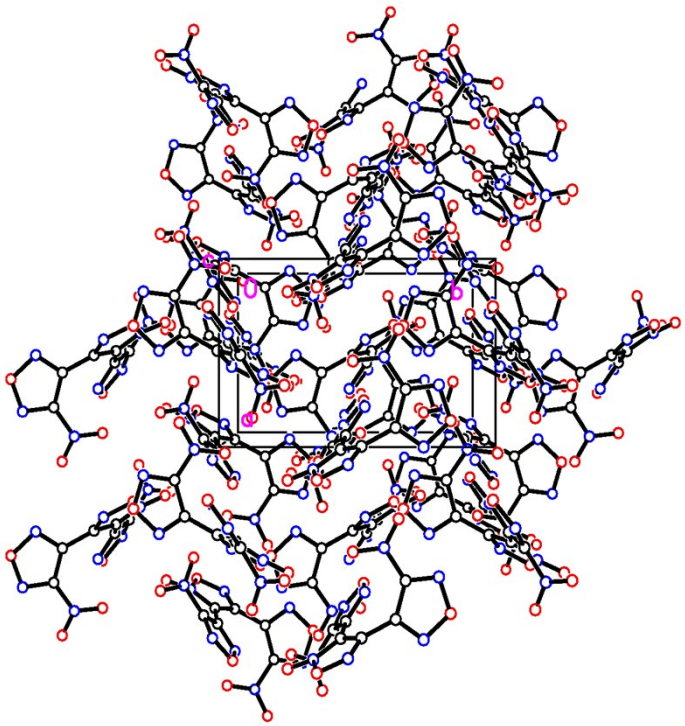


Figure S9. Unit cell view for **5** along *c* axis.

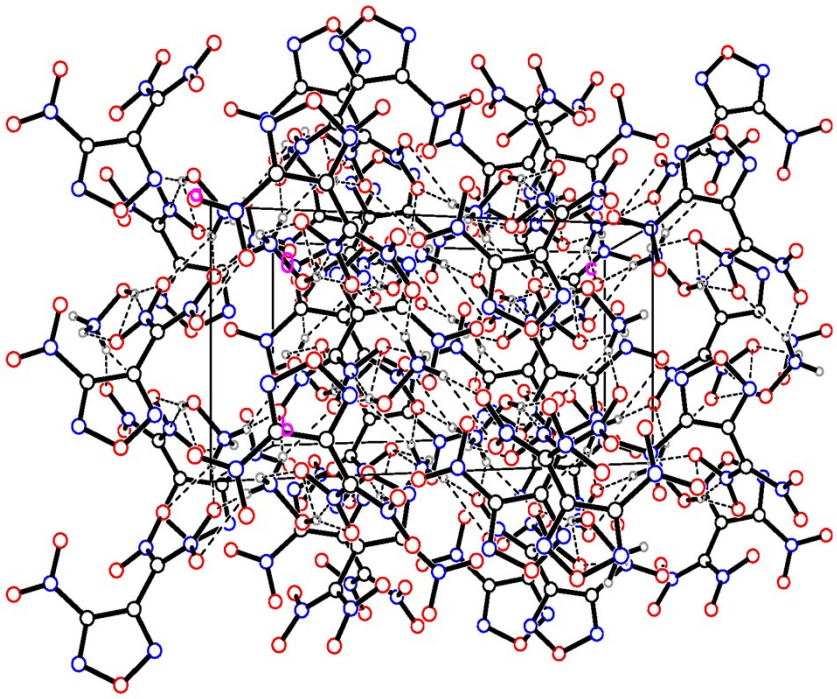


Figure S10. Unit cell view for **8** along *a* axis, hydrogen bonds are marked as dotted lines.

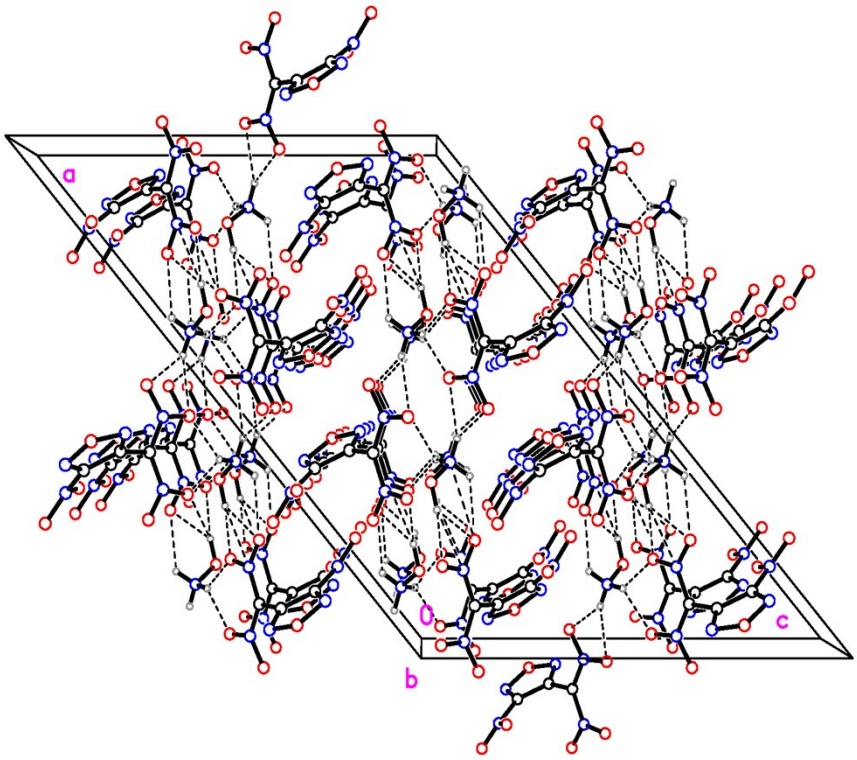


Figure S11. Unit cell view for **8** along *b* axis, hydrogen bonds are marked as dotted lines.

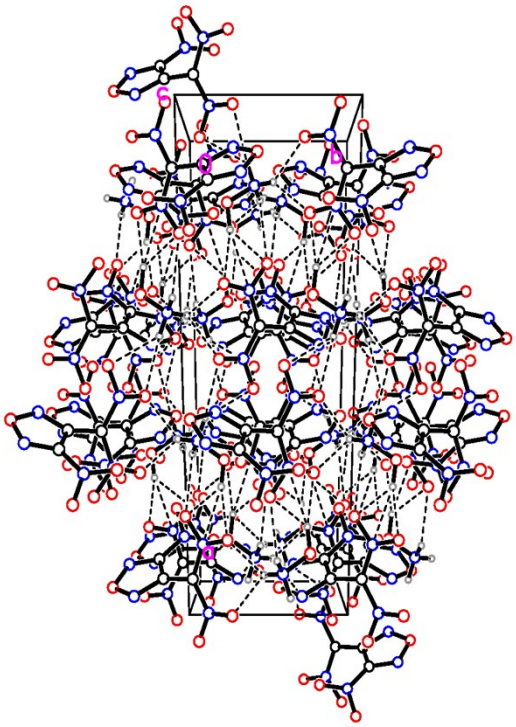


Figure S12. Unit cell view for **8** along *c* axis, hydrogen bonds are marked as dotted lines.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1764(1)	3327(2)	7295(1)	39(1)
O(2)	750(1)	6017(2)	6796(1)	37(1)
N(3)	1488(1)	4748(2)	6658(1)	25(1)
C(4)	2018(2)	4809(2)	5799(1)	25(1)
N(5)	1724(1)	6234(2)	4987(1)	26(1)
O(6)	1012(1)	7621(2)	5009(1)	37(1)
O(7)	2198(1)	6029(2)	4215(1)	41(1)
C(8)	2828(2)	3217(2)	5674(1)	26(1)
N(9)	2233(2)	1677(2)	5157(1)	39(1)
O(10)	3328(1)	496(2)	5238(1)	47(1)
N(11)	4626(2)	1310(2)	5834(2)	43(1)
C(12)	4318(2)	2949(2)	6088(1)	31(1)
N(13)	5431(1)	4261(3)	6728(1)	41(1)
O(14)	6529(1)	3644(3)	7466(1)	60(1)
O(15)	5162(2)	5888(2)	6475(2)	64(1)
K(16)	536(1)	9763(1)	6754(1)	30(1)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O(1)	54(1)	29(1)	36(1)	8(1)	20(1)	3(1)
O(2)	44(1)	28(1)	52(1)	-1(1)	32(1)	5(1)
N(3)	25(1)	22(1)	28(1)	-2(1)	11(1)	-2(1)
C(4)	24(1)	23(1)	28(1)	0(1)	10(1)	2(1)
N(5)	23(1)	27(1)	25(1)	0(1)	7(1)	-2(1)
O(6)	40(1)	29(1)	39(1)	8(1)	13(1)	10(1)

O(7)	49(1)	48(1)	33(1)	3(1)	24(1)	-1(1)
C(8)	25(1)	27(1)	27(1)	-1(1)	10(1)	1(1)
N(9)	32(1)	30(1)	52(1)	-9(1)	15(1)	3(1)
O(10)	41(1)	35(1)	67(1)	-15(1)	23(1)	7(1)
N(11)	35(1)	45(1)	52(1)	-5(1)	19(1)	10(1)
C(12)	26(1)	36(1)	32(1)	-2(1)	12(1)	4(1)
N(13)	26(1)	58(1)	40(1)	-9(1)	13(1)	-4(1)
O(14)	25(1)	99(1)	48(1)	4(1)	5(1)	-2(1)
O(15)	48(1)	48(1)	85(1)	-16(1)	14(1)	-11(1)
K(16)	34(1)	25(1)	30(1)	0(1)	13(1)	3(1)

Table S4. Bond lengths [Å] and angles [°] for **3**.

O(1)-N(3)	1.2509(17)	C(8)-C(12)	1.418(2)
O(2)-N(3)	1.2401(17)	N(9)-O(10)	1.3795(18)
N(3)-C(4)	1.376(2)	O(10)-N(11)	1.369(2)
C(4)-N(5)	1.381(2)	N(11)-C(12)	1.290(2)
C(4)-C(8)	1.458(2)	C(12)-N(13)	1.448(2)
N(5)-O(6)	1.2412(18)	N(13)-O(15)	1.212(3)
N(5)-O(7)	1.2429(18)	N(13)-O(14)	1.214(2)
C(8)-N(9)	1.300(2)		
O(2)-N(3)-O(1)	120.58(13)	C(12)-C(8)-C(4)	130.27(14)
O(2)-N(3)-C(4)	122.43(12)	C(8)-N(9)-O(10)	106.21(13)
O(1)-N(3)-C(4)	116.99(12)	N(11)-O(10)-N(9)	111.42(12)
N(3)-C(4)-N(5)	123.23(13)	C(12)-N(11)-O(10)	103.89(13)
N(3)-C(4)-C(8)	118.47(13)	N(11)-C(12)-C(8)	111.73(15)
N(5)-C(4)-C(8)	118.07(13)	N(11)-C(12)-N(13)	120.66(15)
O(6)-N(5)-O(7)	121.84(13)	C(8)-C(12)-N(13)	127.61(15)
O(6)-N(5)-C(4)	122.47(13)	O(15)-N(13)-O(14)	126.35(18)
O(7)-N(5)-C(4)	115.69(13)	O(15)-N(13)-C(12)	115.94(14)
N(9)-C(8)-C(12)	106.73(14)	O(14)-N(13)-C(12)	117.71(18)
N(9)-C(8)-C(4)	122.96(13)		

Table S5. Torsion angles [°] for **3**.

O(2)-N(3)-C(4)-N(5)	-3.1(2)	N(3)-C(4)-C(8)-C(12)	-99.55(19)
O(1)-N(3)-C(4)-N(5)	175.82(13)	N(5)-C(4)-C(8)-C(12)	85.7(2)
O(2)-N(3)-C(4)-C(8)	-177.61(13)	C(12)-C(8)-N(9)-O(10)	-0.69(18)
O(1)-N(3)-C(4)-C(8)	1.35(19)	C(4)-C(8)-N(9)-O(10)	-178.37(14)
N(3)-C(4)-N(5)-O(6)	3.7(2)	C(8)-N(9)-O(10)-N(11)	1.1(2)
C(8)-C(4)-N(5)-O(6)	178.22(13)	N(9)-O(10)-N(11)-C(12)	-1.0(2)
N(3)-C(4)-N(5)-O(7)	-175.17(14)	O(10)-N(11)-C(12)-C(8)	0.53(19)
C(8)-C(4)-N(5)-O(7)	-0.68(19)	O(10)-N(11)-C(12)-N(13)	-179.75(15)
N(3)-C(4)-C(8)-N(9)	77.5(2)	N(9)-C(8)-C(12)-N(11)	0.1(2)
N(5)-C(4)-C(8)-N(9)	-97.22(19)	C(4)-C(8)-C(12)-N(11)	177.56(16)
N(9)-C(8)-C(12)-N(13)	-179.59(16)	C(8)-C(12)-N(13)-O(15)	-33.7(2)
C(4)-C(8)-C(12)-N(13)	-2.1(3)	N(11)-C(12)-N(13)-O(14)	-34.1(2)
N(11)-C(12)-N(13)-O(15)	146.63(18)	C(8)-C(12)-N(13)-O(14)	145.57(17)

Table S6. Bond lengths [Å] and angles [°] for **4**.

O1-N1	1.358(4)	O1-N2	1.366(4)
O2-N3	1.205(4)	O3-N3	1.213(4)
O4-N4	1.216(4)	O5-N4	1.212(4)
O6-N5	1.221(4)	O7-N5	1.221(4)

N1-C1	1.281(5)	N2-C2	1.308(5)
N3-C1	1.461(4)	N4-C3	1.540(5)
N5-C3	1.496(5)	C1-C2	1.426(5)
C2-C3	1.490(5)	C3-H3	1.0000
N1-O1-N2	112.0(3)	C1-N1-O1	104.8(3)
C2-N2-O1	105.7(3)	N4-C3-H3	107.8
N5-C3-H3	107.8	C2-C3-H3	107.8
N5-C3-N4	107.8(3)	C2-C3-N4	113.7(3)
C2-C3-N5	111.6(3)	C1-C2-C3	134.1(3)
N2-C2-C3	118.9(3)	N2-C2-C1	106.8(3)
C2-C1-N3	128.2(3)	N1-C1-N3	121.1(3)
N1-C1-C2	110.7(3)	O7-N5-C3	116.9(3)
O6-N5-C3	118.6(3)	O6-N5-O7	124.5(3)
O4-N4-C3	113.6(3)	O5-N4-C3	117.6(3)
O5-N4-O4	128.7(4)	O3-N3-C1	115.4(3)
O2-N3-C1	117.3(3)	O2-N3-O3	127.2(3)

Table S7. Torsion angles [°] for **4**.

N2-O1-N1-C1	0.0(4)	N1-O1-N2-C2	0.3(4)
O1-N1-C1-C2	-0.3(4)	O1-N1-C1-N3	178.4(3)
O2-N3-C1-N1	2.7(5)	O3-N3-C1-N1	-176.2(4)
O2-N3-C1-C2	-178.8(4)	O3-N3-C1-C2	2.3(5)
O1-N2-C2-C1	-0.5(4)	O1-N2-C2-C3	175.7(3)
N1-C1-C2-N2	0.5(4)	N3-C1-C2-N2	-178.1(3)
N1-C1-C2-C3	-174.8(4)	N3-C1-C2-C3	6.6(6)
N2-C2-C3-N5	-107.3(4)	C1-C2-C3-N5	67.5(5)
N2-C2-C3-N4	130.5(3)	C1-C2-C3-N4	-54.7(5)
O6-N5-C3-C2	-21.9(4)	O7-N5-C3-C2	156.2(3)
O6-N5-C3-N4	103.7(3)	O7-N5-C3-N4	-78.2(4)
O5-N4-C3-C2	145.6(3)	O4-N4-C3-C2	-37.1(4)
O5-N4-C3-N5	21.3(4)	O4-N4-C3-N5	-161.4(3)

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1635(4)	6280(3)	3776(2)	86(1)
O(2)	3336(5)	7453(3)	2915(2)	124(1)
N(3)	3141(5)	6607(3)	3425(2)	65(1)
C(4)	4893(4)	5879(2)	3625(2)	45(1)
N(5)	5997(4)	5486(3)	2993(2)	62(1)
O(6)	7387(3)	4746(2)	3393(1)	61(1)
N(7)	7106(3)	4720(2)	4290(1)	44(1)
C(8)	5564(3)	5414(2)	4444(2)	35(1)
C(9)	4892(3)	5595(2)	5337(1)	35(1)
N(10)	3847(3)	6574(2)	5586(1)	45(1)
O(11)	3245(3)	7503(2)	5222(1)	66(1)
O(12)	3419(3)	6429(2)	6509(1)	57(1)
N(13)	4250(3)	5335(2)	6784(1)	52(1)
C(14)	5127(3)	4858(2)	6099(1)	37(1)
C(15)	6116(4)	3649(2)	6180(2)	39(1)
N(16)	5126(4)	2674(2)	6421(2)	58(1)
O(17)	6487(4)	1724(2)	6438(2)	71(1)
N(18)	8332(4)	2122(2)	6200(2)	59(1)
C(19)	8100(4)	3293(2)	6041(2)	42(1)

N(20)	9785(3)	4044(2)	5800(2)	52(1)
O(21)	11250(3)	3524(3)	5525(2)	84(1)
O(22)	9581(3)	5154(2)	5894(1)	65(1)

Table S9 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
O(1)	67(2)	95(2)	97(2)	-10(2)	-10(2)	23(2)
O(2)	149(3)	105(2)	117(2)	56(2)	-39(2)	20(2)
N(3)	81(2)	58(2)	57(1)	4(1)	-26(2)	9(2)
C(4)	57(2)	37(1)	40(1)	3(1)	-6(1)	-1(1)
N(5)	81(2)	64(2)	40(1)	7(1)	4(1)	2(2)
O(6)	69(1)	71(1)	42(1)	-3(1)	12(1)	12(1)
N(7)	50(1)	44(1)	37(1)	-1(1)	5(1)	2(1)
C(8)	40(1)	27(1)	39(1)	-1(1)	0(1)	-2(1)
C(9)	35(1)	30(1)	41(1)	-3(1)	-1(1)	1(1)
N(10)	49(1)	37(1)	50(1)	-8(1)	-5(1)	8(1)
O(11)	80(2)	42(1)	76(2)	-4(1)	-14(1)	20(1)
O(12)	59(1)	59(1)	53(1)	-18(1)	9(1)	12(1)
N(13)	56(1)	56(2)	44(1)	-4(1)	6(1)	5(1)
C(14)	38(1)	40(1)	34(1)	-3(1)	2(1)	-2(1)
C(15)	45(1)	40(1)	31(1)	4(1)	-1(1)	-1(1)
N(16)	65(2)	46(1)	63(1)	16(1)	8(1)	-4(1)
O(17)	88(2)	43(1)	83(1)	24(1)	4(1)	2(1)
N(18)	66(2)	48(1)	63(2)	9(1)	-9(1)	12(1)
C(19)	47(1)	43(1)	36(1)	2(1)	-6(1)	3(1)
N(20)	43(1)	63(2)	49(1)	0(1)	-9(1)	0(1)
O(21)	41(1)	106(2)	105(2)	-10(2)	3(1)	11(1)
O(22)	63(1)	59(1)	71(1)	0(1)	-3(1)	-16(1)

Table S10. Bond lengths [Å] and angles [°] for **5**.

O(1)-N(3)	1.202(3)	O(2)-N(3)	1.204(4)
N(3)-C(4)	1.453(4)	C(4)-N(5)	1.288(4)
C(4)-C(8)	1.415(3)	N(5)-O(6)	1.374(3)
O(6)-N(7)	1.375(3)	N(7)-C(8)	1.304(3)
C(8)-C(9)	1.442(3)	C(9)-N(10)	1.326(3)
C(9)-C(14)	1.412(3)	N(10)-O(11)	1.215(3)
N(10)-O(12)	1.439(3)	O(12)-N(13)	1.372(3)
N(13)-C(14)	1.303(3)	C(14)-C(15)	1.471(3)
C(15)-N(16)	1.300(3)	C(15)-C(19)	1.411(4)
N(16)-O(17)	1.377(3)	O(17)-N(18)	1.366(3)
N(18)-C(19)	1.297(3)	C(19)-N(20)	1.444(3)
N(20)-O(21)	1.212(3)	N(20)-O(22)	1.215(3)
O(1)-N(3)-O(2)	126.9(3)	O(1)-N(3)-C(4)	115.9(3)
O(2)-N(3)-C(4)	117.1(3)	N(5)-C(4)-C(8)	110.6(2)
N(5)-C(4)-N(3)	119.6(2)	C(8)-C(4)-N(3)	129.5(2)
C(4)-N(5)-O(6)	104.9(2)	N(5)-O(6)-N(7)	110.86(19)
C(8)-N(7)-O(6)	106.01(19)	N(7)-C(8)-C(4)	107.6(2)
N(7)-C(8)-C(9)	119.8(2)	C(4)-C(8)-C(9)	132.6(2)
N(10)-C(9)-C(14)	106.0(2)	N(10)-C(9)-C(8)	122.9(2
C(14)-C(9)-C(8)	131.1(2)	O(11)-N(10)-C(9)	135.0(2)
O(11)-N(10)-O(12)	117.7(2)	C(9)-N(10)-O(12)	107.3(2)
N(13)-O(12)-N(10)	107.95(17)	C(14)-N(13)-O(12)	106.4(2)
N(13)-C(14)-C(9)	112.3(2)	N(13)-C(14)-C(15)	119.3(2)

C(9)-C(14)-C(15)	128.3(2)	N(16)-C(15)-C(19)	108.0(2)
N(16)-C(15)-C(14)	120.6(2)	C(19)-C(15)-C(14)	131.3(2)
C(15)-N(16)-O(17)	105.4(2)	N(18)-O(17)-N(16)	111.72(19)
C(19)-N(18)-O(17)	104.2(2)	N(18)-C(19)-C(15)	110.6(2)
N(18)-C(19)-N(20)	120.0(3)	C(15)-C(19)-N(20)	129.3(2)
O(21)-N(20)-O(22)	126.1(3)	O(21)-N(20)-C(19)	118.1(3)
O(22)-N(20)-C(19)	115.8(2)		

Table S11. Torsion angles [°] for **5**.

O(1)-N(3)-C(4)-N(5)	130.5(3)	O(2)-N(3)-C(4)-N(5)	-48.1(4)
O(1)-N(3)-C(4)-C(8)	-43.6(4)	O(2)-N(3)-C(4)-C(8)	137.8(3)
C(8)-C(4)-N(5)-O(6)	0.7(3)	N(3)-C(4)-N(5)-O(6)	-174.5(2)
C(4)-N(5)-O(6)-N(7)	-0.9(3)	N(5)-O(6)-N(7)-C(8)	0.8(3)
O(6)-N(7)-C(8)-C(4)	-0.3(3)	O(6)-N(7)-C(8)-C(9)	-179.0(2)
N(5)-C(4)-C(8)-N(7)	-0.2(3)	N(3)-C(4)-C(8)-N(7)	174.3(3)
N(5)-C(4)-C(8)-C(9)	178.3(3)	N(3)-C(4)-C(8)-C(9)	-7.2(5)
N(7)-C(8)-C(9)-N(10)	155.7(2)	C(4)-C(8)-C(9)-N(10)	-22.6(4)
N(7)-C(8)-C(9)-C(14)	-24.8(4)	C(4)-C(8)-C(9)-C(14)	156.9(3)
C(14)-C(9)-N(10)-O(11)	178.5(3)	C(8)-C(9)-N(10)-O(11)	-1.9(4)
C(14)-C(9)-N(10)-O(12)	-0.6(3)	C(8)-C(9)-N(10)-O(12)	179.0(2)
O(11)-N(10)-O(12)-N(13)	-179.2(2)	C(9)-N(10)-O(12)-N(13)	0.0(3)
N(10)-O(12)-N(13)-C(14)	0.6(3)	O(12)-N(13)-C(14)-C(9)	-1.1(3)
O(12)-N(13)-C(14)-C(15)	-178.2(2)	N(10)-C(9)-C(14)-N(13)	1.1(3)
C(8)-C(9)-C(14)-N(13)	-178.5(2)	N(10)-C(9)-C(14)-C(15)	177.9(2)
C(8)-C(9)-C(14)-C(15)	-1.7(4)	N(13)-C(14)-C(15)-N(16)	59.0(3)
C(9)-C(14)-C(15)-N(16)	-117.6(3)	N(13)-C(14)-C(15)-C(19)	-120.9(3)
C(9)-C(14)-C(15)-C(19)	62.5(4)	C(19)-C(15)-N(16)-O(17)	0.6(3)
C(14)-C(15)-N(16)-O(17)	-179.4(2)	C(15)-N(16)-O(17)-N(18)	-0.4(3)
N(16)-O(17)-N(18)-C(19)	0.0(3)	O(17)-N(18)-C(19)-C(15)	0.3(3)
O(17)-N(18)-C(19)-N(20)	177.5(2)	N(16)-C(15)-C(19)-N(18)	-0.6(3)
C(14)-C(15)-C(19)-N(18)	179.3(2)	N(16)-C(15)-C(19)-N(20)	-177.4(2)
C(14)-C(15)-C(19)-N(20)	2.5(4)	N(18)-C(19)-N(20)-O(21)	19.5(4)
C(15)-C(19)-N(20)-O(21)	-163.9(3)	N(18)-C(19)-N(20)-O(22)	-160.8(2)
C(15)-C(19)-N(20)-O(22)	15.8(4)		

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4780(1)	5895(2)	1112(1)	76(1)
O(2)	5359(1)	7890(2)	806(1)	56(1)
N(3)	5370(1)	6481(2)	1344(1)	43(1)
C(4)	6020(1)	5519(2)	2220(1)	36(1)
N(5)	6718(1)	6131(2)	2625(1)	38(1)
O(6)	6829(1)	7605(2)	2250(1)	59(1)
O(7)	7257(1)	5089(2)	3416(1)	46(1)
C(8)	5991(1)	3720(2)	2742(1)	41(1)
N(9)	5655(1)	1996(2)	2211(1)	67(1)
O(10)	5785(1)	633(2)	2990(1)	79(1)
N(11)	6207(1)	1537(3)	4009(2)	64(1)
C(12)	6327(1)	3392(3)	3852(1)	44(1)
N(13)	6761(1)	4856(3)	4765(1)	65(1)
O(14)	6697(1)	6664(2)	4533(1)	63(1)
O(15A)	7312(3)	4346(11)	5712(5)	87(2)
O(15B)	6931(4)	3958(11)	5610(5)	107(2)

N(16)	6242(1)	834(2)	710(1)	36(1)
O(17)	6601(1)	2417(2)	1493(1)	68(1

Table S13 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **8**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	$\mathbf{U_{11}}$	$\mathbf{U_{22}}$	$\mathbf{U_{33}}$	$\mathbf{U_{23}}$	$\mathbf{U_{13}}$	$\mathbf{U_{12}}$
O(1)	31(1)	90(1)	87(1)	34(1)	31(1)	6(1)
O(2)	42(1)	56(1)	53(1)	22(1)	23(1)	6(1)
N(3)	33(1)	44(1)	44(1)	8(1)	22(1)	4(1)
C(4)	30(1)	37(1)	38(1)	7(1)	21(1)	3(1)
N(5)	32(1)	39(1)	39(1)	5(1)	23(1)	3(1)
O(6)	41(1)	63(1)	65(1)	26(1)	30(1)	-2(1)
O(7)	30(1)	51(1)	46(1)	12(1)	20(1)	8(1)
C(8)	35(1)	40(1)	47(1)	6(1)	26(1)	3(1)
N(9)	74(1)	47(1)	64(1)	6(1)	38(1)	-12(1)
O(10)	85(1)	53(1)	86(1)	16(1)	50(1)	-12(1)
N(11)	72(1)	60(1)	77(1)	27(1)	56(1)	17(1)
C(12)	48(1)	43(1)	51(1)	15(1)	37(1)	17(1)
N(13)	75(1)	69(1)	46(1)	11(1)	38(1)	34(1)
O(14)	72(1)	61(1)	66(1)	-6(1)	49(1)	0(1)
O(15A)	90(3)	89(3)	40(2)	13(2)	24(2)	30(3)
O(15B)	157(6)	90(3)	53(3)	14(2)	59(4)	29(4)
N(16)	35(1)	38(1)	36(1)	6(1)	23(1)	5(1)
O(17)	47(1)	71(1)	81(1)	-31(1)	39(1)	-7(1)

Table S14. Bond lengths [Å] and angles [°] for **8**.

O(1)-N(3)	1.2388(17)	O(2)-N(3)	1.2386(17)
N(3)-C(4)	1.3741(18)	C(4)-N(5)	1.3725(18)
C(4)-C(8)	1.455(2)	N(5)-O(6)	1.2379(17)
N(5)-O(7)	1.2503(15)	C(8)-N(9)	1.304(2)
C(8)-C(12)	1.408(2)	N(9)-O(10)	1.385(2)
O(10)-N(11)	1.364(2)	N(11)-C(12)	1.289(2)
C(12)-N(13)	1.453(2)	N(13)-O(14)	1.200(2)
N(13)-O(15A)	1.232(6)	N(13)-O(15B)	1.269(6)
N(16)-O(17)	1.3910(18)	N(16)-H(16A)	0.8900
N(16)-H(16B)	0.8900	N(16)-H(16C)	0.8900
O(17)-H(17)	0.96(3)		
O(2)-N(3)-O(1)	120.26(13)	O(2)-N(3)-C(4)	122.74(13)
O(1)-N(3)-C(4)	117.00(13)	N(5)-C(4)-N(3)	123.07(13)
N(5)-C(4)-C(8)	116.66(12)	N(3)-C(4)-C(8)	120.24(13)
O(6)-N(5)-O(7)	120.27(12)	O(6)-N(5)-C(4)	123.96(12)
O(7)-N(5)-C(4)	115.77(12)	N(9)-C(8)-C(12)	107.18(15)
N(9)-C(8)-C(4)	122.67(15)	C(12)-C(8)-C(4)	130.03(15)
C(8)-N(9)-O(10)	105.66(15)	N(11)-O(10)-N(9)	111.30(14)
C(12)-N(11)-O(10)	104.17(15)	N(11)-C(12)-C(8)	111.69(17)
N(11)-C(12)-N(13)	120.36(16)	C(8)-C(12)-N(13)	127.95(15)
O(14)-N(13)-O(15A)	117.2(4)	O(14)-N(13)-O(15B)	131.1(4)
O(14)-N(13)-C(12)	117.06(15)	O(15A)-N(13)-C(12)	123.1(4)
O(15B)-N(13)-C(12)	107.4(4)	O(17)-N(16)-H(16A)	109.5
O(17)-N(16)-H(16B)	109.5	H(16A)-N(16)-H(16B)	109.5
O(17)-N(16)-H(16C)	109.5	H(16A)-N(16)-H(16C)	109.5
H(16B)-N(16)-H(16C)	109.5	N(16)-O(17)-H(17)	104.4(15)

Table S15. Torsion angles [°] for **8**.

O(2)-N(3)-C(4)-N(5)	4.8(3)	C(12)-C(8)-N(9)-O(10)	0.1(2)
O(1)-N(3)-C(4)-N(5)	-174.40(16)	C(4)-C(8)-N(9)-O(10)	176.60(15)
O(2)-N(3)-C(4)-C(8)	-173.03(15)	C(8)-N(9)-O(10)-N(11)	-0.2(2)
O(1)-N(3)-C(4)-C(8)	7.8(2)	N(9)-O(10)-N(11)-C(12)	0.3(2)
N(3)-C(4)-N(5)-O(6)	0.7(2)	O(10)-N(11)-C(12)-C(8)	-0.18(19)
C(8)-C(4)-N(5)-O(6)	178.56(15)	O(10)-N(11)-C(12)-N(13)	179.46(15)
N(3)-C(4)-N(5)-O(7)	-179.08(14)	N(9)-C(8)-C(12)-N(11)	0.0(2)
C(8)-C(4)-N(5)-O(7)	-1.2(2)	C(4)-C(8)-C(12)-N(11)	-176.10(16)
N(5)-C(4)-C(8)-N(9)	-116.76(18)	N(9)-C(8)-C(12)-N(13)	-179.56(16)
N(3)-C(4)-C(8)-N(9)	61.2(2)	C(4)-C(8)-C(12)-N(13)	4.3(3)
N(5)-C(4)-C(8)-C(12)	58.9(2)	N(11)-C(12)-N(13)-O(14)	-161.46(17)
N(3)-C(4)-C(8)-C(12)	-123.19(18)	C(8)-C(12)-N(13)-O(14)	18.1(3)
N(11)-C(12)-N(13)-O(15A)	37.7(4)	N(11)-C(12)-N(13)-O(15B)	-2.4(4)
C(8)-C(12)-N(13)-O(15A)	-142.7(4)	C(8)-C(12)-N(13)-O(15B)	177.2(4)

Table S16. Hydrogen coordinates (x 104) and isotropic displacement parameters (Å2x 103) for **8**.

	x	y	z	U(eq)
H(16A)	6511	501	519	54
H(16B)	5790	1264	115	54
H(16C)	6196	-274	994	54
H(17)	7123(16)	2240(40)	1860(20)	103

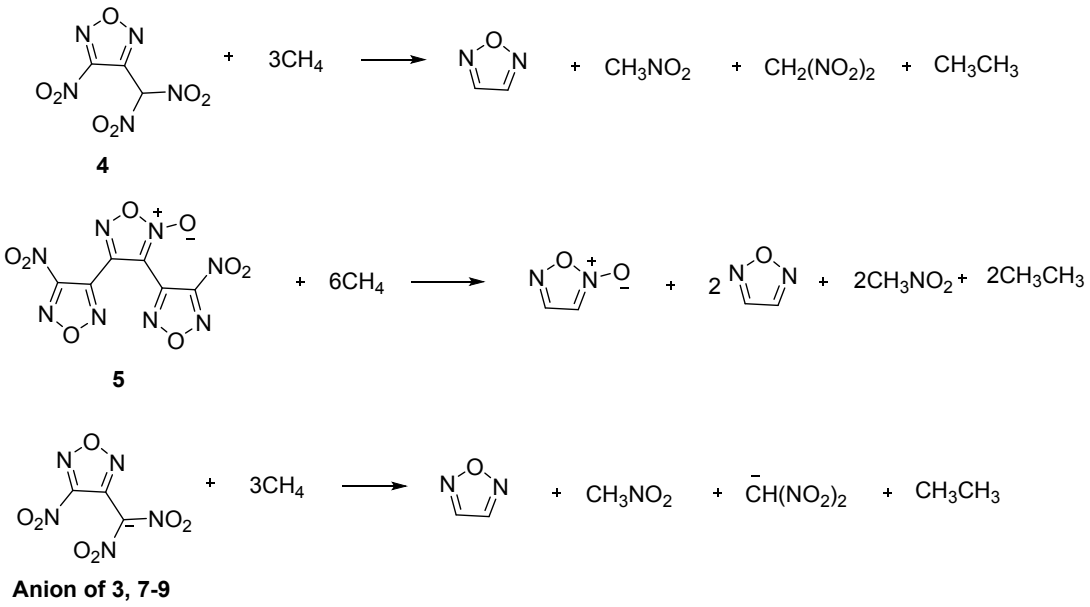
Table S17. Hydrogen bonds for **8** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(16)-H(16A)...O(7)#1	0.89	2.22	2.8697(16)	129.2
N(16)-H(16B)...O(2)#4	0.89	2.14	2.9715(17)	155.2
N(16)-H(16B)...O(1)#4	0.89	2.36	3.0895(18)	139.8
N(16)-H(16C)...O(2)#5	0.89	2.15	2.8920(18)	141.1
N(16)-H(16C)...O(6)#5	0.89	2.05	2.8007(16)	141.3
O(17)-H(17)...O(7)#1	0.96(3)	2.26(3)	2.9987(18)	133(2)
O(17)-H(17)...O(6)#1	0.96(3)	1.89(3)	2.8318(18)	165(2)
O(17)-H(17)...N(5)#1	0.96(3)	2.39(3)	3.3257(18)	164(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,y-1/2,-z+1/2 #2 x,-y+1,z-1/2 #3 x,-y,z-1/2
#4 -x+1,-y+1,-z #5 x,y-1,z

Theoretical calculations

The heats of formation for **4**, **5** and anion of **3**, **7-9** were determined using isodesmic reactions (Scheme S1). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[6] The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level,[7] and single energy points were calculated at the MP2/6-311++G** level.[8] The heats of formation for the cations were obtained by an atomization approach using G2 ab initio method.[9] The heats of formation of other compounds in Scheme S1 were obtained from the NIST WebBook.[10]



Scheme S1. Isodesmic reactions.

Table S18 The heats of formation (HOF) for **4**, **5** and anion of **3**, **7-9**.[a]

Compounds	**ZPE** [Hartree/Particle]	**Hcorr** [Hartree/Particle]	**Mp-6-311++g**** [Hartree/Particle]	**HoF(gas)** [kJ mol^{-1}]
4	0.080872	0.094275	-912.9127531	134.9521803
5	0.10615	0.123935	-1265.157924	602.3225537
Anion of **3**, **7-9**	0.067759	0.080944	-912.4077036	-58.47370814

[a] The enthalpy of sublimation was calculated by using Trouton's rule. Solid-state heats of formation of the resulting compounds were calculated with Equation (1) in which Tm is the melting temperature. $\Delta H_f = \Delta H_f(g) - \Delta H_{sub} = \Delta Hf(g) - 188[J\ mol^{-1}\ K^{-1}] \times T_m$ (1).

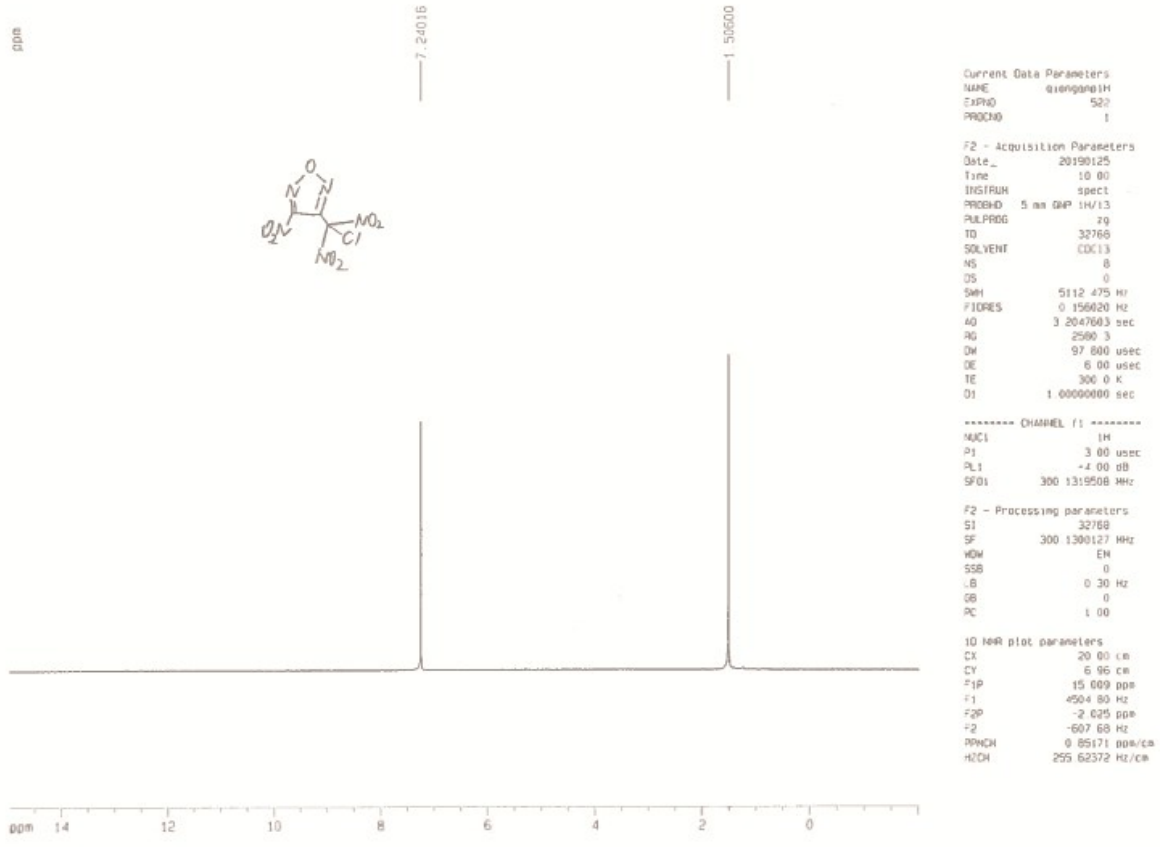


Figure S13. ^{1}H NMR spectrum of **2**

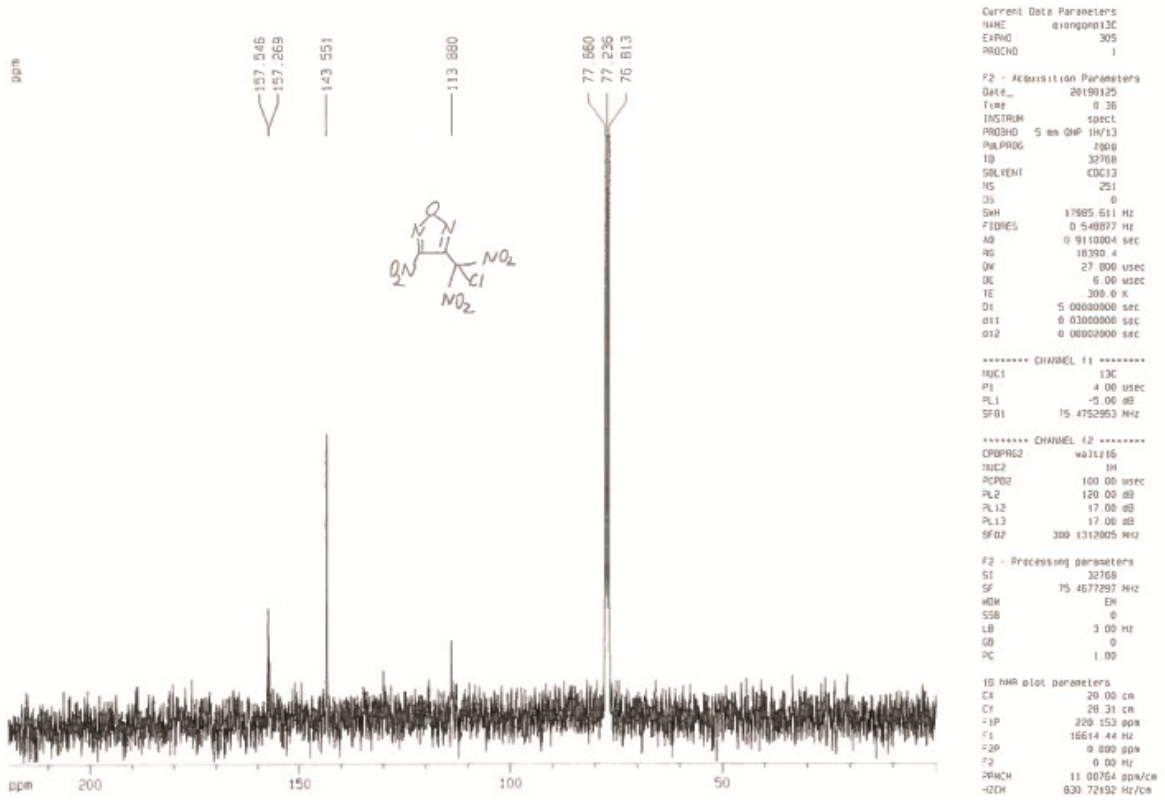


Figure S14. ^{13}C NMR spectrum of **2**

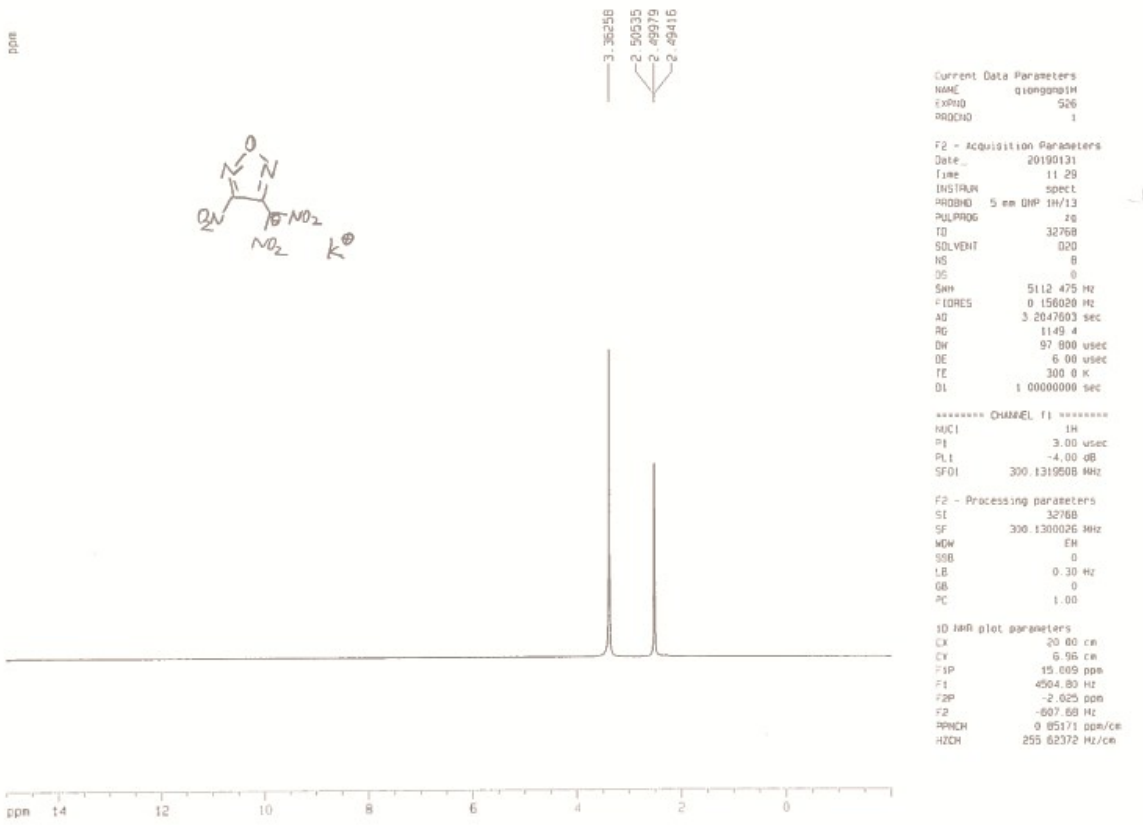


Figure S15. ^{1}H NMR spectrum of **3**

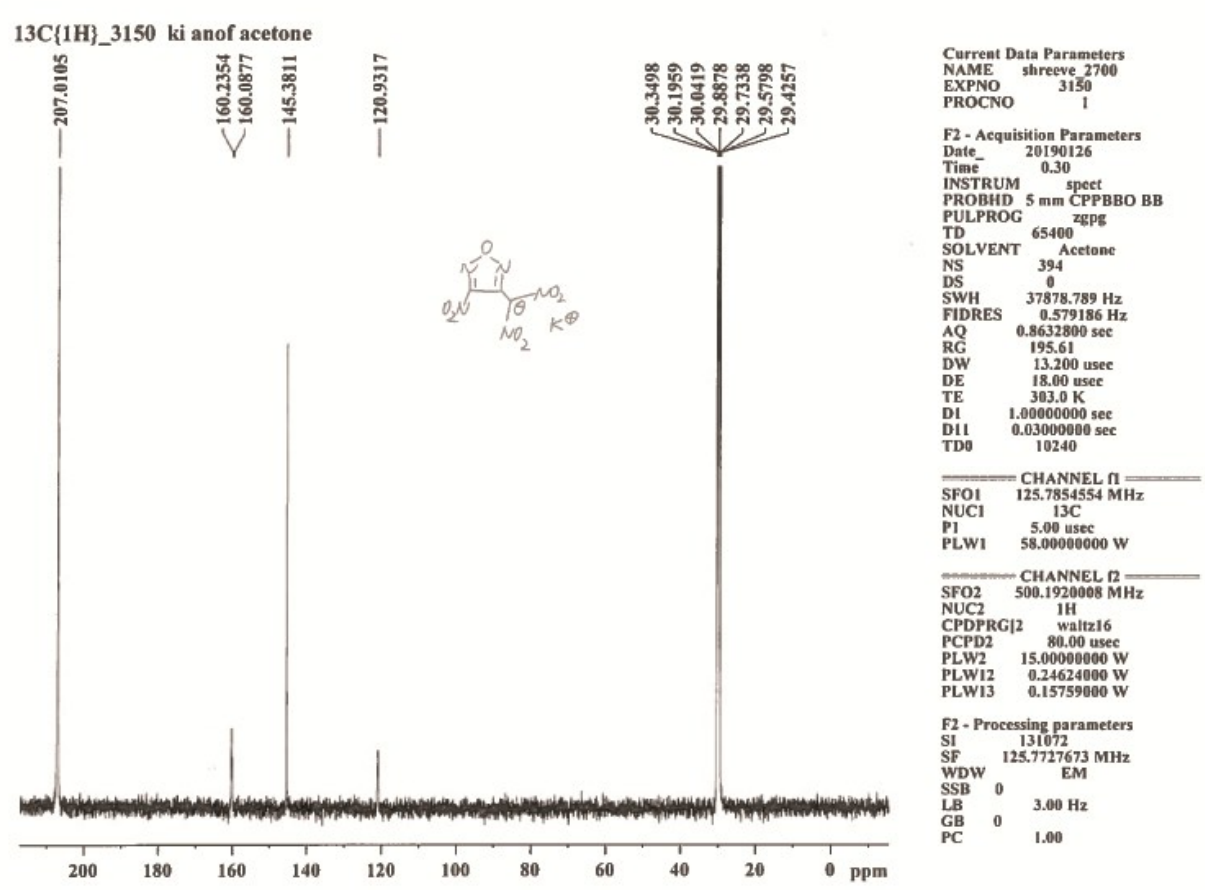


Figure S16. ^{13}C NMR spectrum of **3**

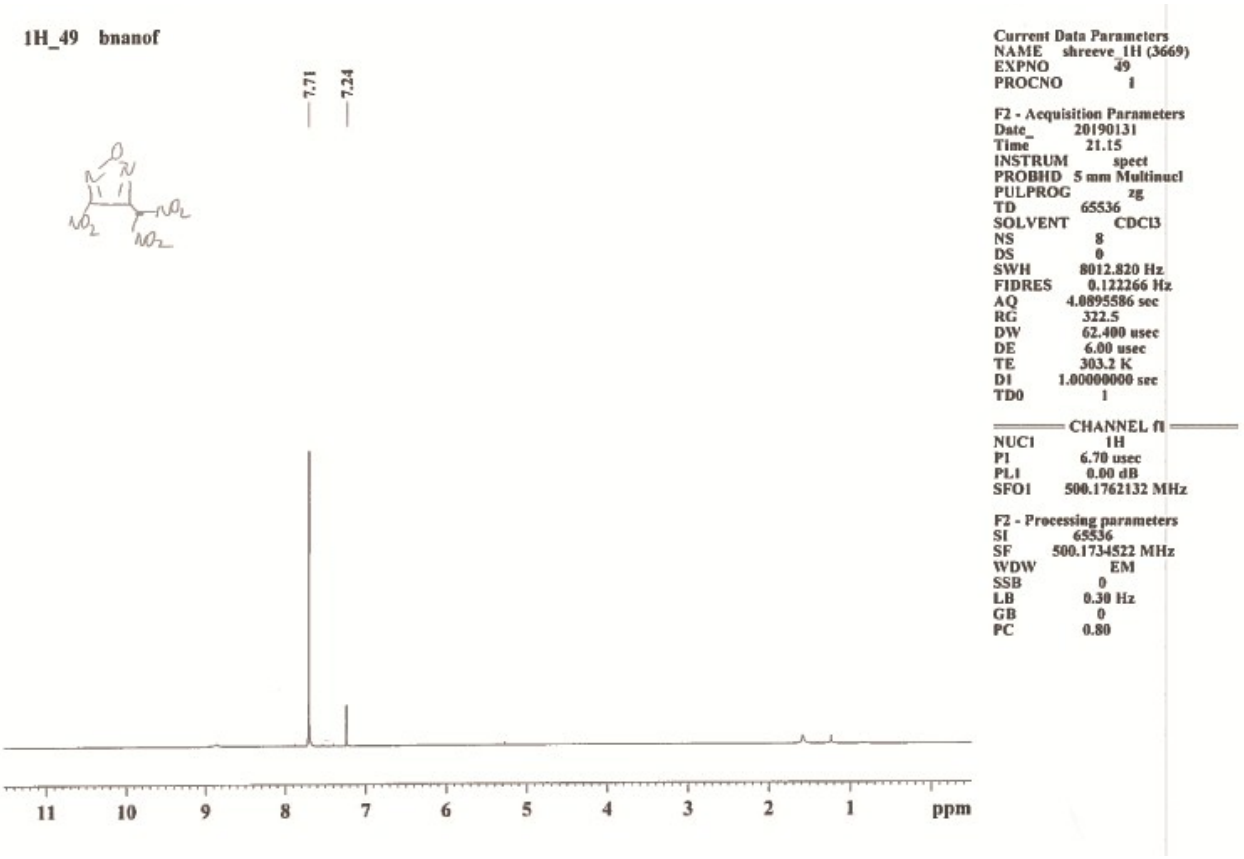


Figure S17. ^{1}H NMR spectrum of **4**

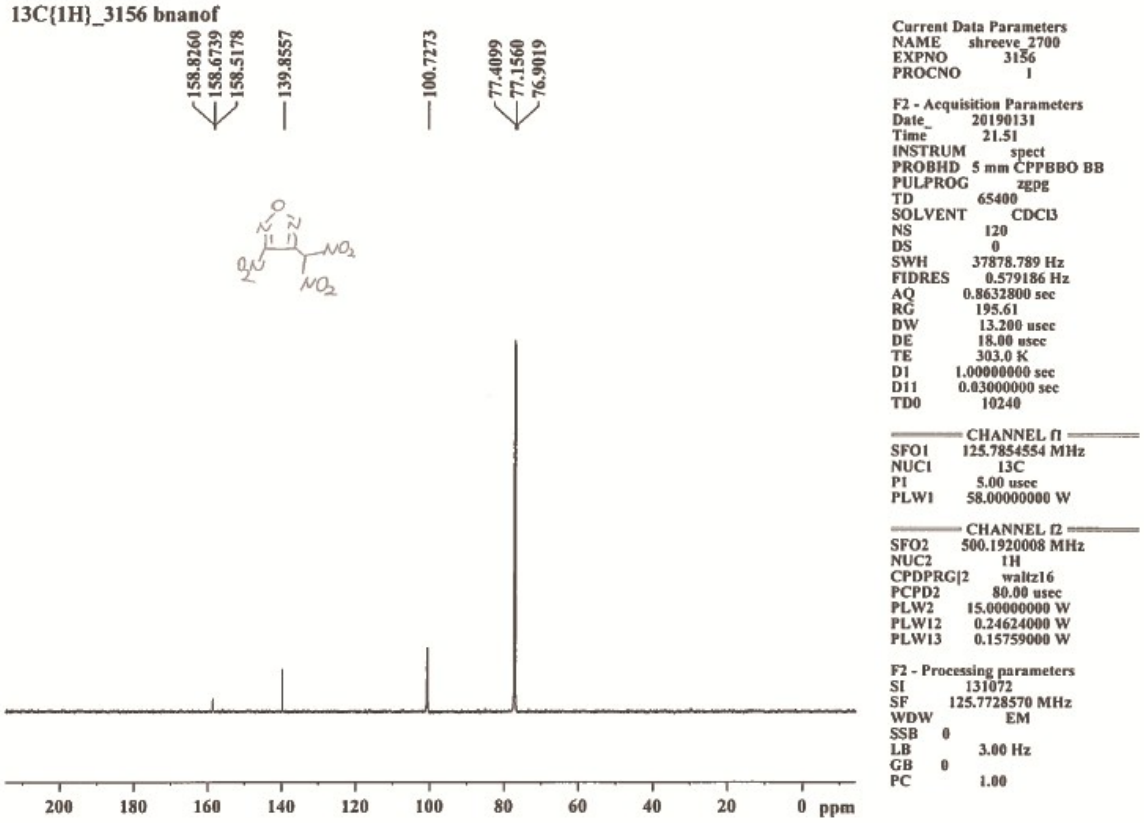


Figure S18. ^{13}C NMR spectrum of **4**

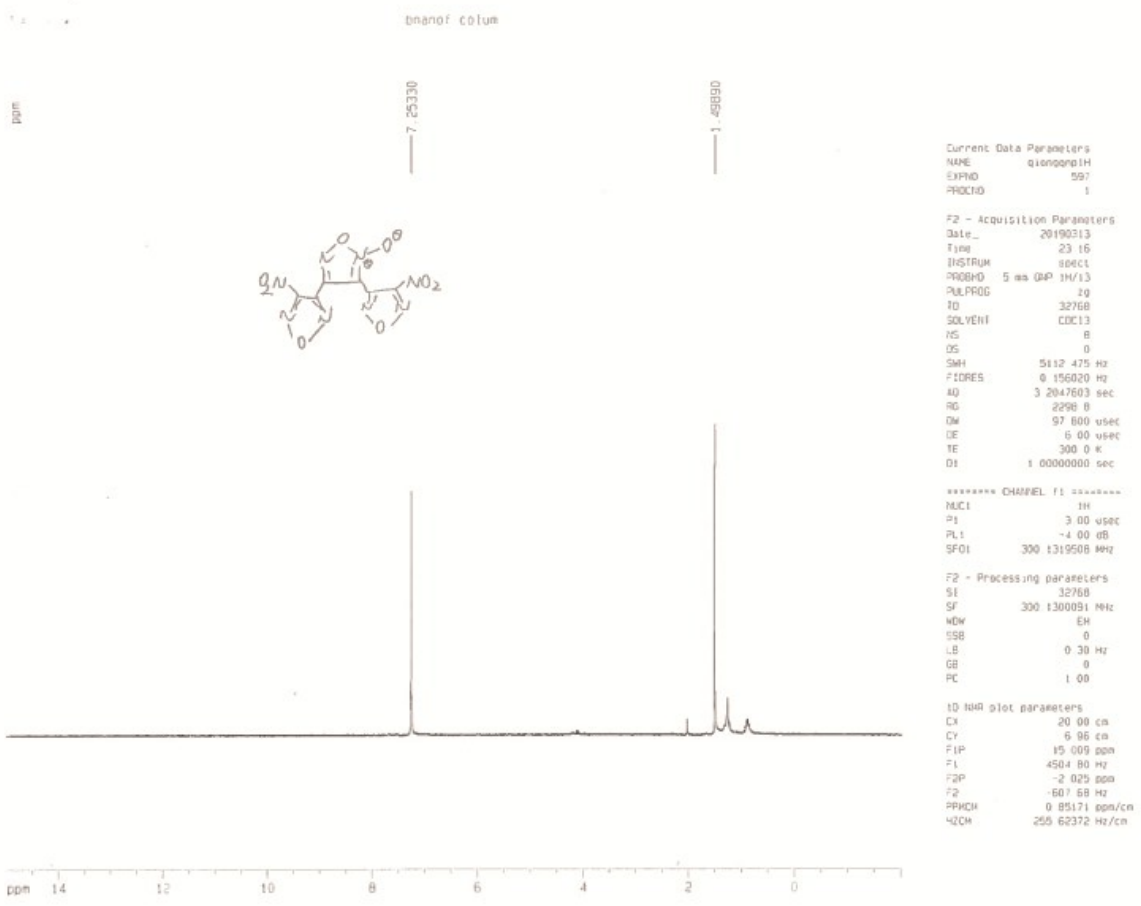


Figure S19. ^{1}H NMR spectrum of **5**

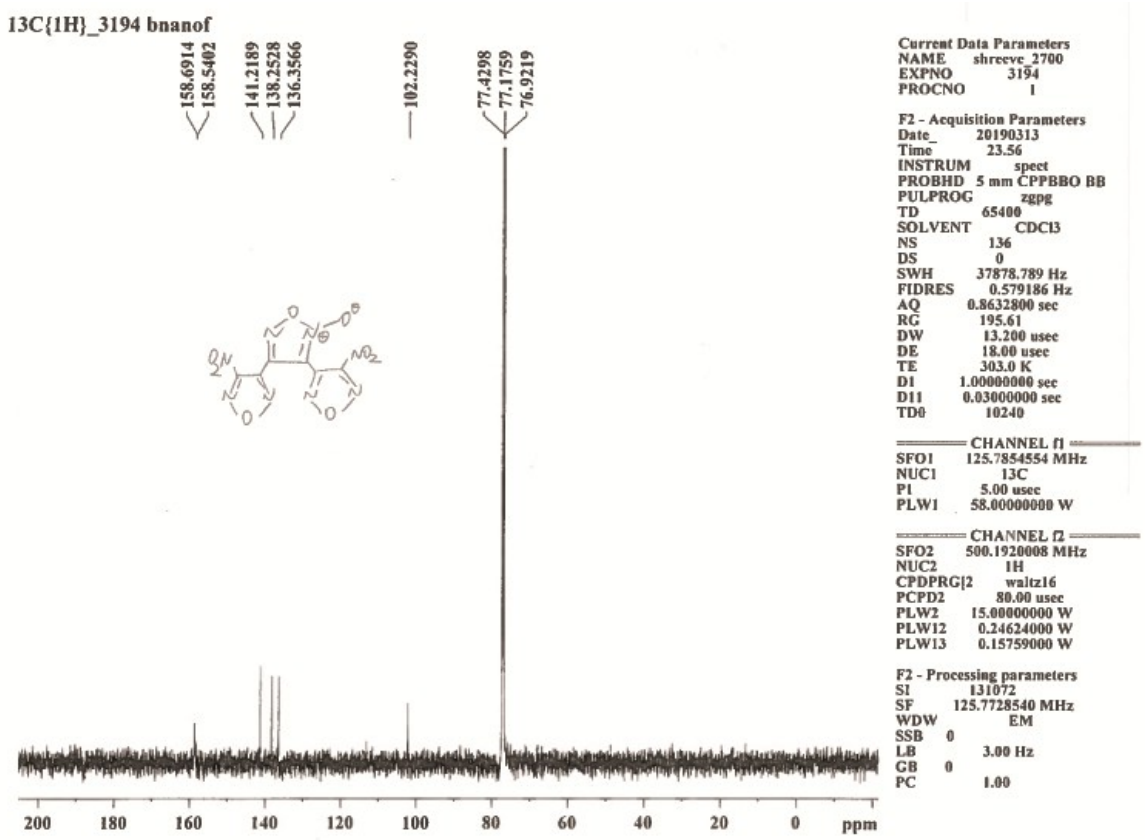


Figure S20. ^{13}C NMR spectrum of **5**

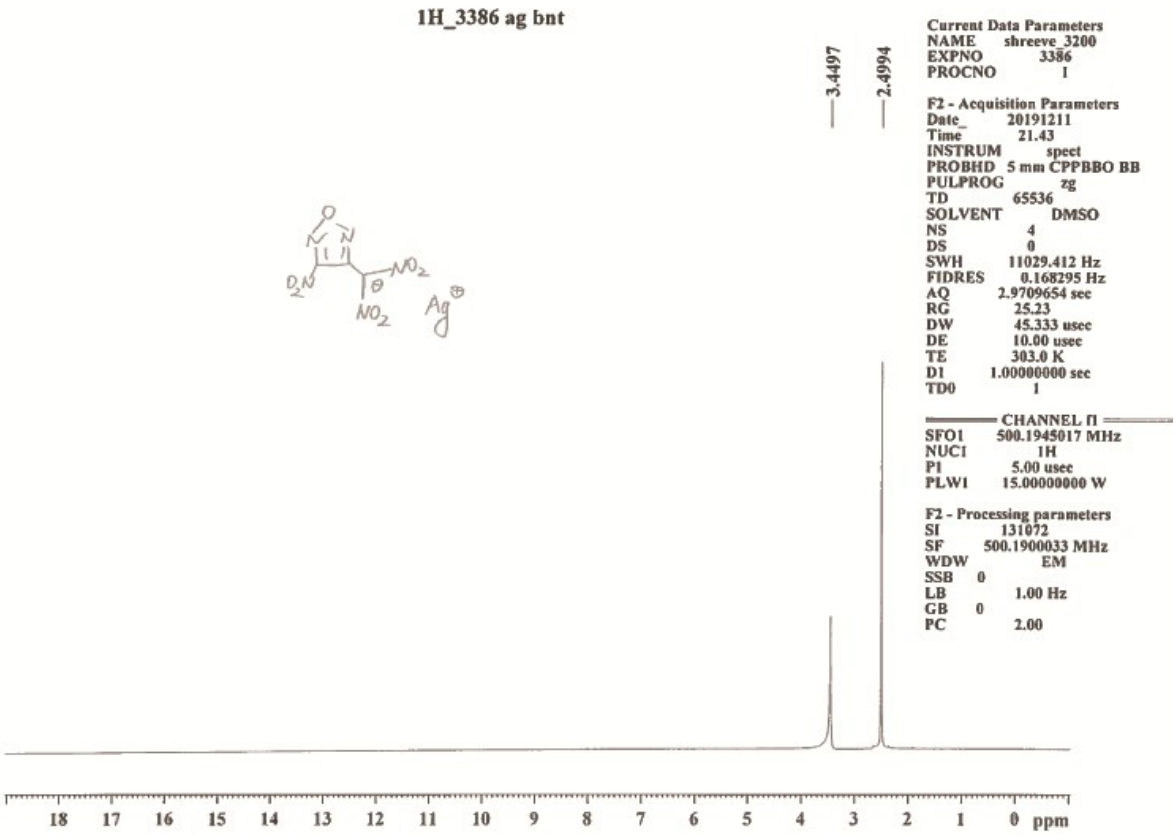


Figure S21. ^{1}H NMR spectrum of **6**

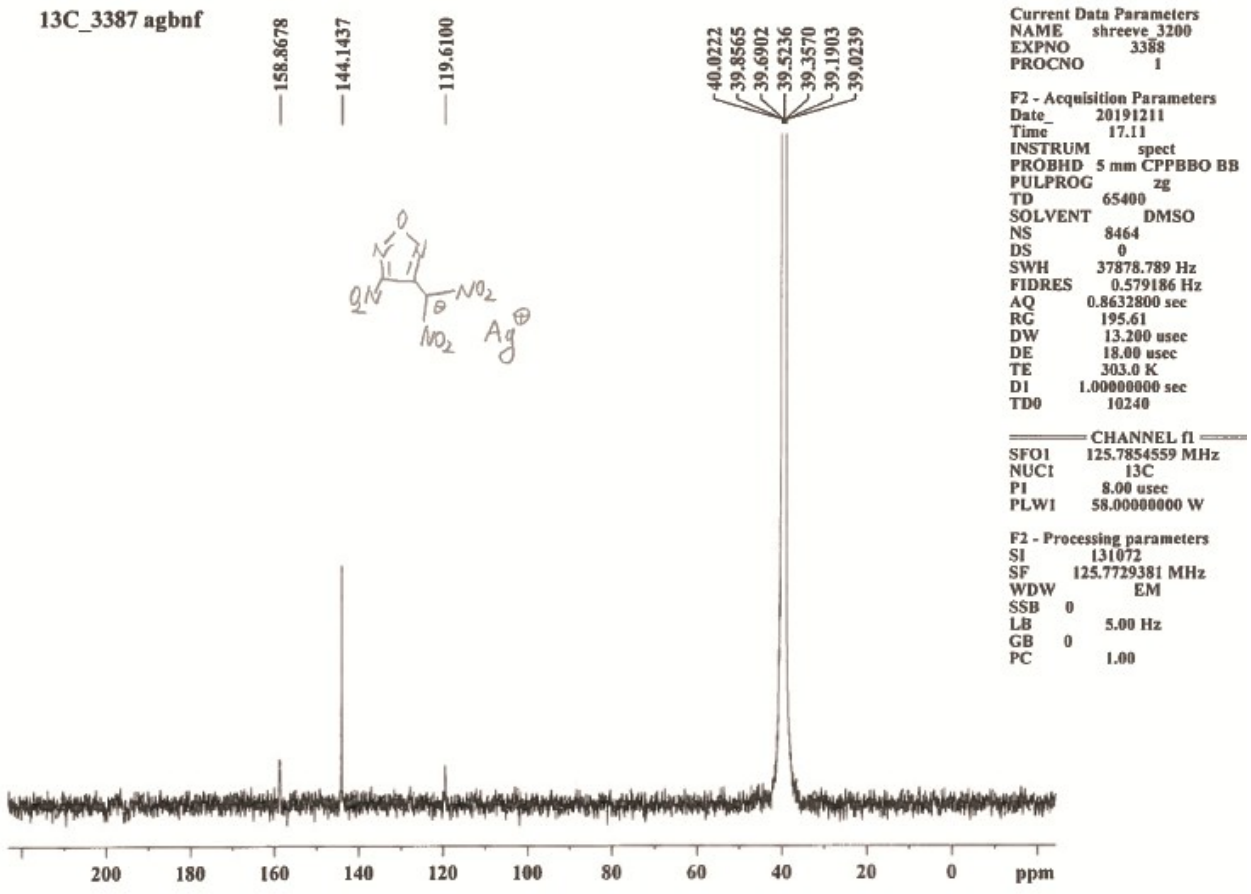


Figure S22. ^{13}C NMR spectrum of **6**

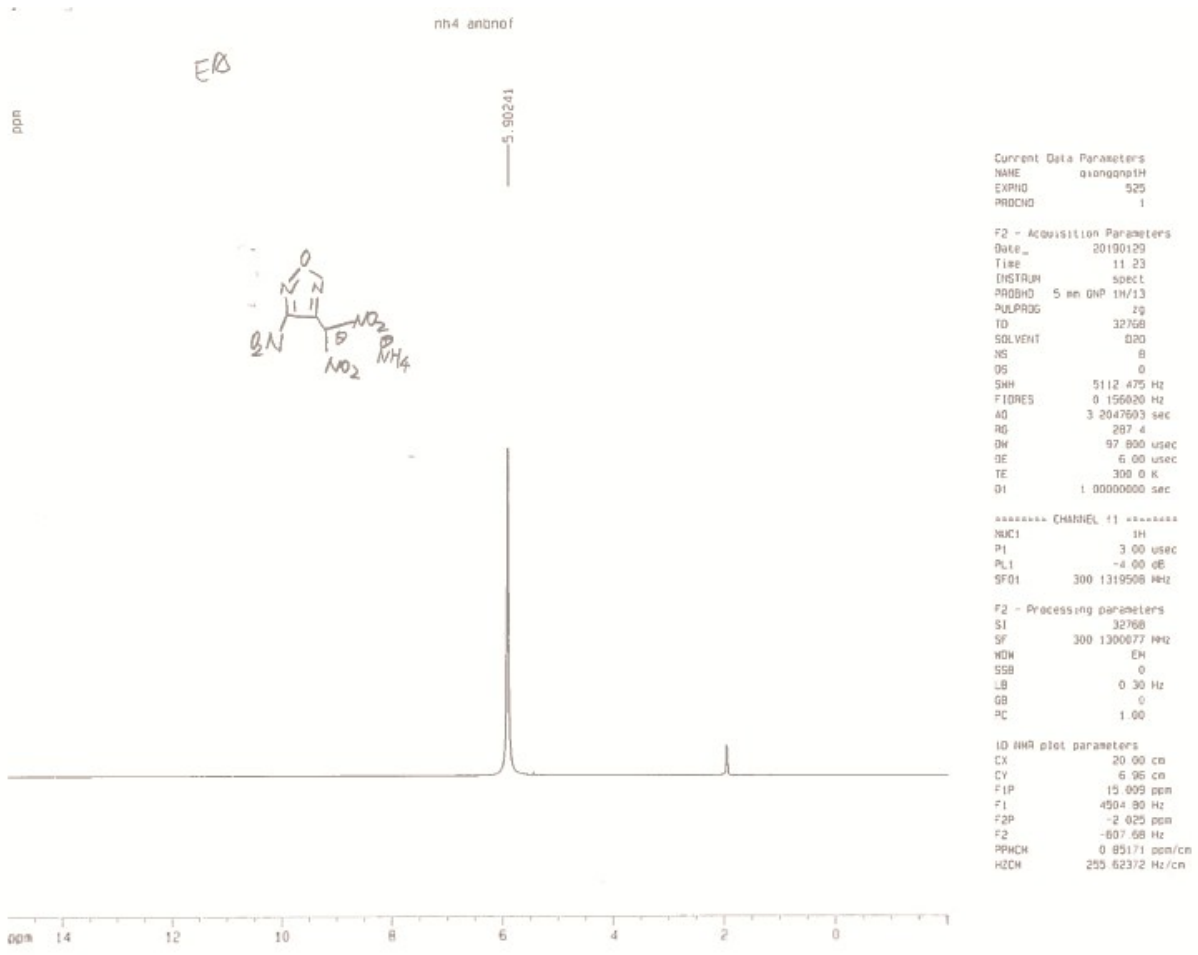


Figure S23. ^{1}H NMR spectrum of **7**

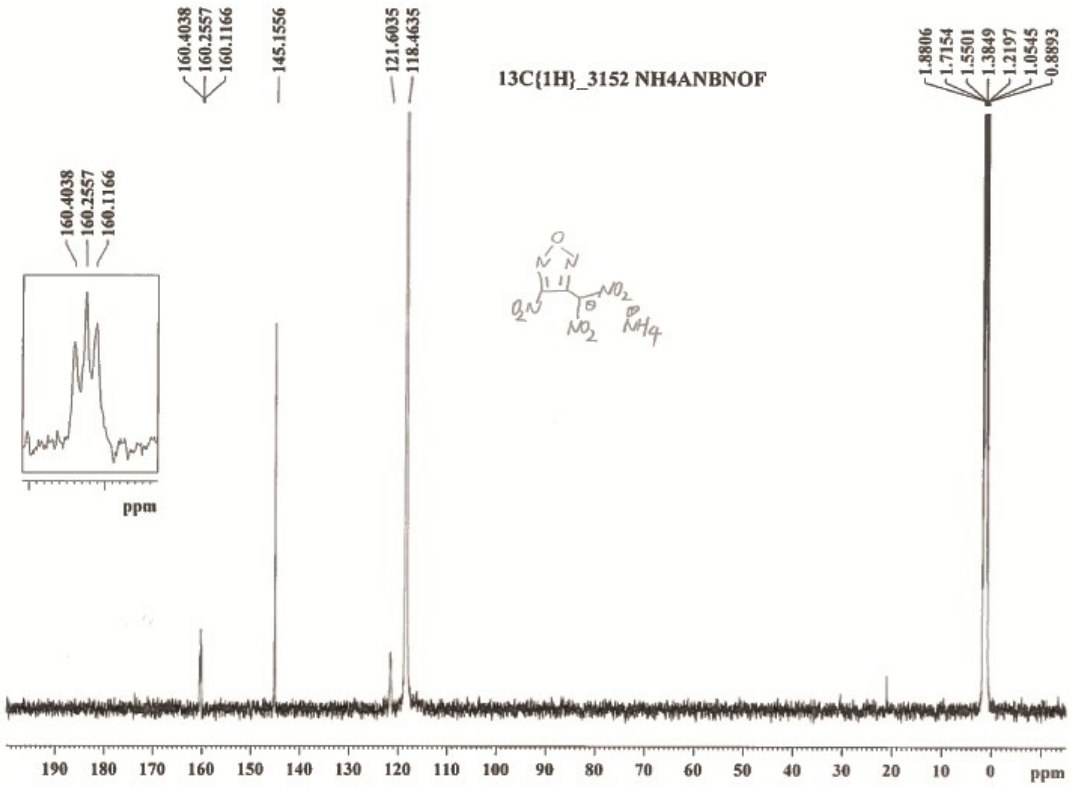


Figure S24. ^{13}C NMR spectrum of **7**

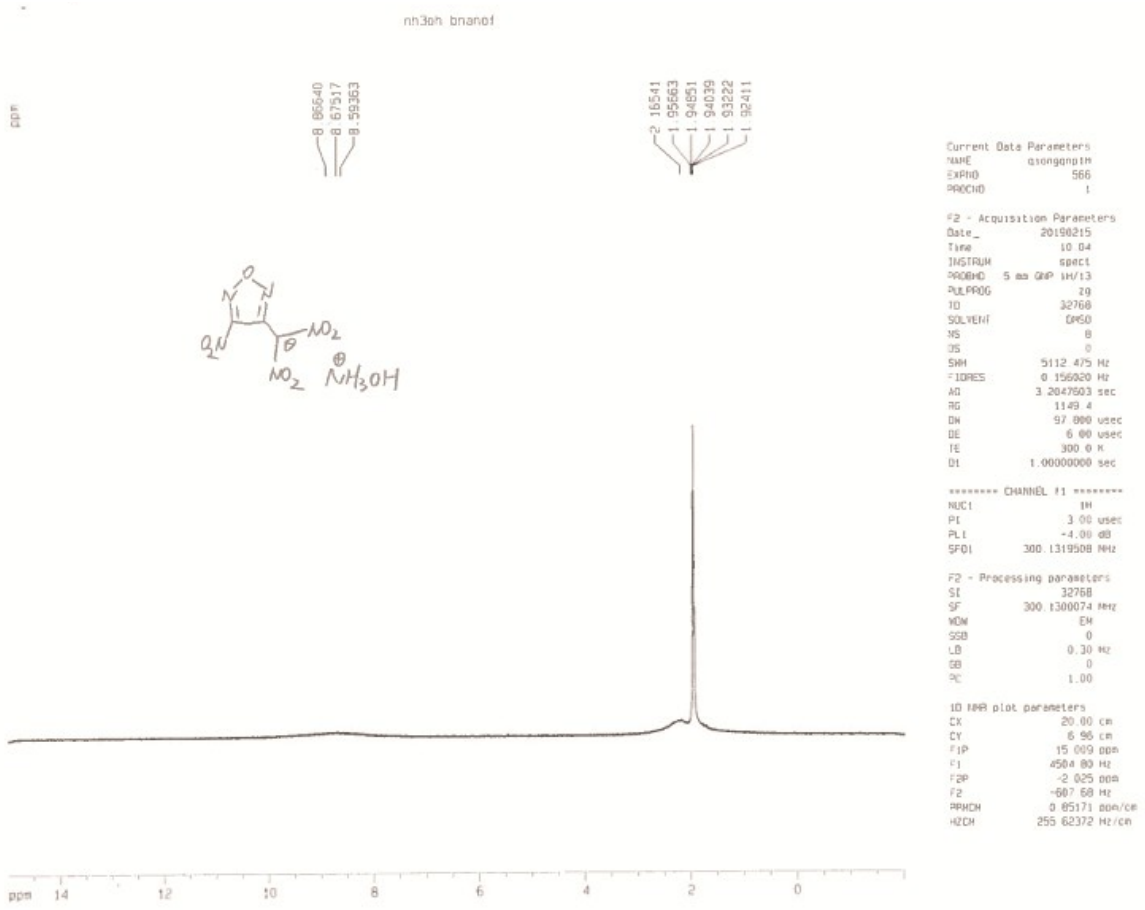


Figure S25. ^{1}H NMR spectrum of **8**

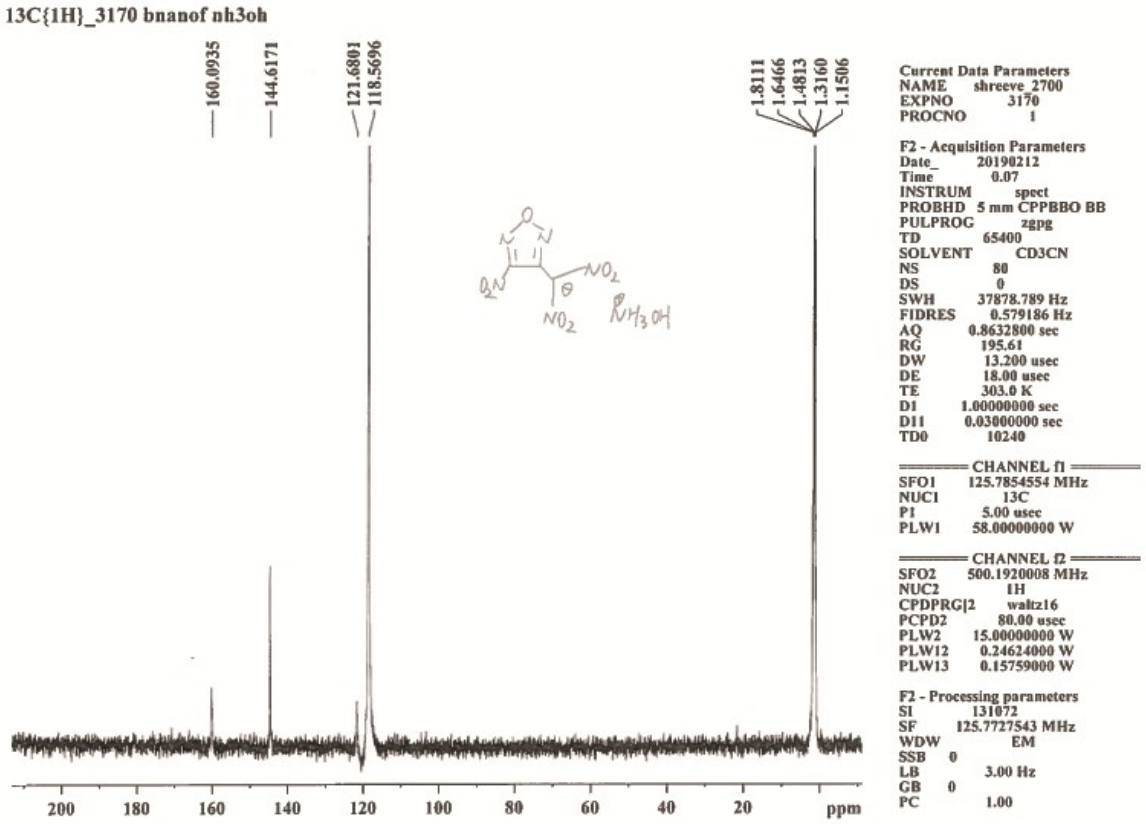


Figure S26. ^{13}C NMR spectrum of **8**

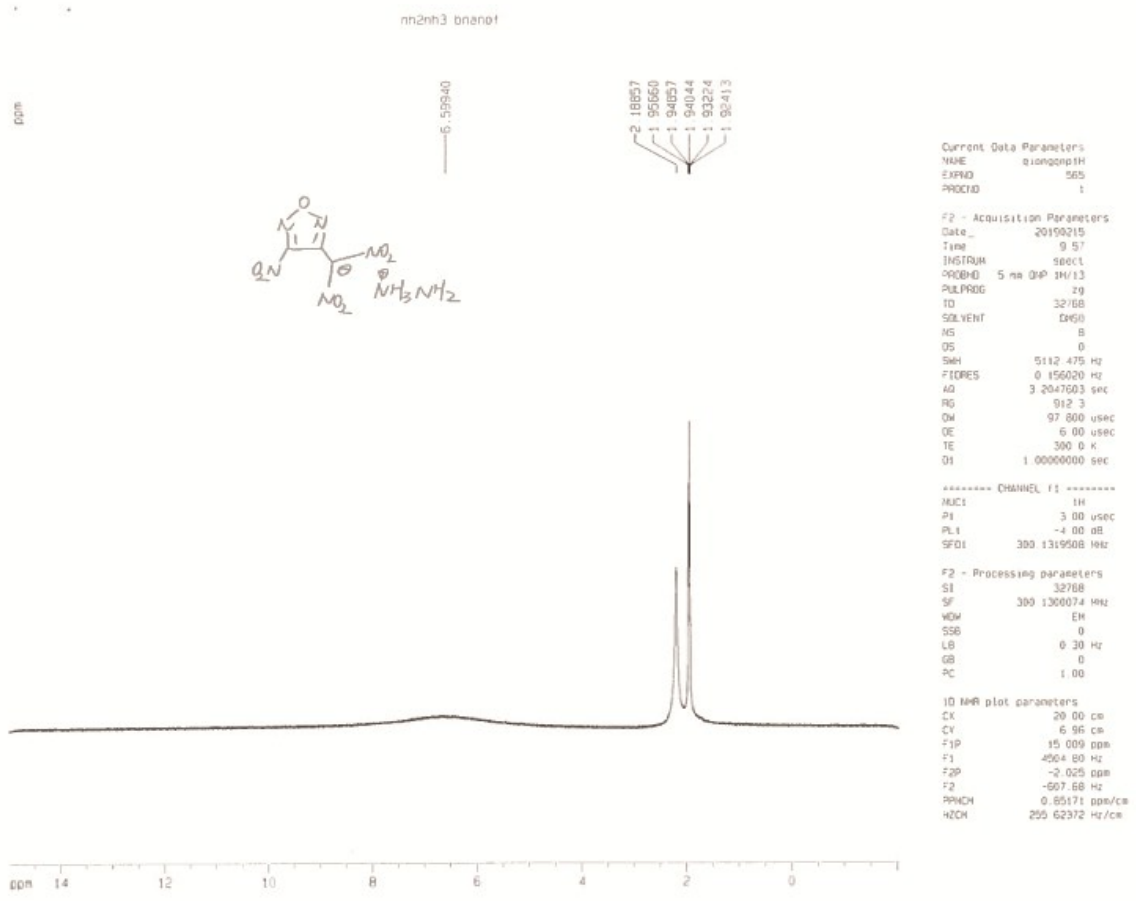


Figure S27. ^{1}H NMR spectrum of **9**

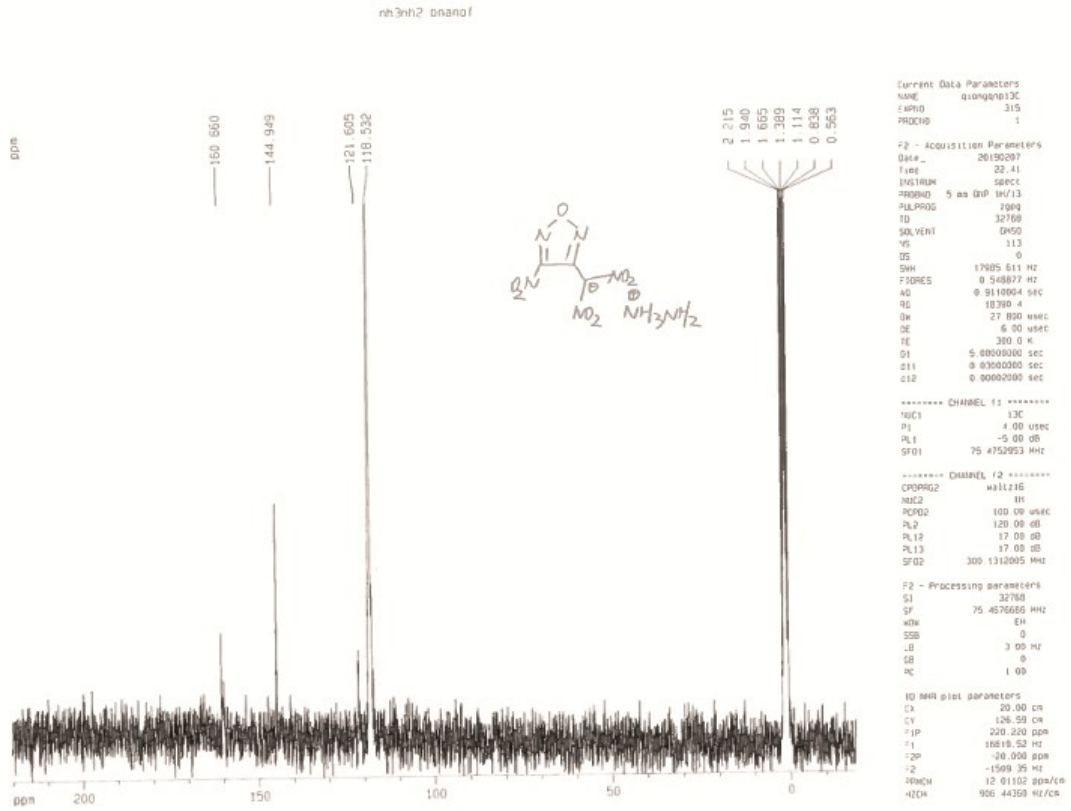


Figure S28. ^{13}C NMR spectrum of **9**

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