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Electronic Supporting Information

A promising cation of 4-aminofurazan-3-carboxylic acid amidrazone in desensitizing energetic materials

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Table S1. Crystal data and structure refinement for **1 and 1a-1c**

CCDC number (compound name)	1916325(**1**)	1916327(**1a**·H_2O)	1916326(**1b**)	1916328(**1c**)
Empirical formula	$C_3H_6N_6O$	$C_3H_9N_7O_5$	$C_8H_{14}N_{20}O_4$	$C_9H_{14}N_{20}O_5$
Formula weight	142.14	223.17	454.39	482.40
Temperature(K)	173	293	293	173
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	P 1 21/c 1	P b c a	$P2_1/c$	P 1 n 1
Unit cell dimensions	a = 3.6422(9) Å, b= 21.241(4) Å, c=15.081(3) Å, α = 90°, β=95.90(8)°, γ = 90°	a = 6.8490(1) Å, b= 11.511(19) Å, c=22.982(4) Å α=90°; β= 90°;γ= 90 °	a =14.685(10) Å, b=7.065(5) Å, c=8.601(6) Å; α=90°;β= 93.63(15)° ;γ=90°	a = 6.8147(6) Å, b=14.324(11) Å, c=10.2906(8) Å; α=90°;β= 103.86(3)°;γ=90°
Volume	1160.5(4) Å^3	1181.8(5)Å^3	890.6(11) Å^3	975.26(14) Å^3
Z	8	8	2	2
Density	1.627	1.636	1.695	1.643
Mu (mm-1)	0.130	0.150	0.140	0.137
F(000)	592.0	928.0	468.0	496.0
h,k,lmax	5, 30, 21	8, 13, 27	17, 8, 10	9, 19, 13
Data completeness	0.993	1.00	0.994	0.93
Theta(max)	30.579	25.500	24.994	28.672
R(reflections)	0.0918 (2265)	0.0436 (1547)	0.0744 (1150)	0.0695 (3102)
wR2(reflections)	0.2745 (3547)	0.1148 (1683)	0.1776 (1565)	0.1771 (4700)
S	1.039	1.126	1.062	1.023
Npar	195	173	165	310

Table S2. Bond torsion angles of 1

Atom1	Atom2	Atom3	Atom4	Torsion(°)
N4	C3	N5	N6	-0.178(536)
N6	N5	C3	C2	178.899(297)
N3	C1	C2	C3	3.195(621)
N3	C1	N2	O1	177.457(331)
N4	C3	C2	N1	1.245(514)
C1	C2	C3	N1	179.598(625)

Table S3. Bond torsion angles of 1a

Atom1	Atom2	Atom3	Atom4	Torsion(°)
C2	N1	O1	N2	-0.31(17)
C1	N2	O1	N1	0.22(17)
O1	N2	C1	N3	177.87(15)
O1	N2	C1	C2	-0.05(16)
O1	N1	C2	C1	0.27(17)
O1	N1	C2	C3	179.75(13)
N2	C1	C2	N1	-0.14(18)
N3	C1	C2	N1	-177.99(16)
N2	C1	C2	C3	179.57(15)
N3	C1	C2	C3	2.6(3)
N5	N4	C3	N6	1.3(3)
N5	N4	C3	C2	179.75(13)
N1	C2	C3	N4	178.24(14)
C1	C2	C3	N4	-2.4(2)
N1	C2	C3	N6	-3.1(2)
C1	C2	C3	N6	176.28(15)

Table S4. Bond torsion angles of 1b

Atom1	Atom2	Atom3	Atom4	Torsion(°)
C3	N5	O2	N6	-0.7(3)
C2	N6	O2	N5	1.1(3)
O2	N6	C2	N7	175.2(3)
O2	N6	C2	C3	-0.9(3)
O2	N5	C3	C2	0.2(3)
O2	N5	C3	C4	179.9(2)
N6	C2	C3	N5	0.5(4)
N7	C2	C3	N5	175.5(3)
N6	C2	C3	C4	179.4(3)
N7	C2	C3	C4	4.6(5)
N9	N8	C4	N10	4.6(5)
N9	N8	C4	C3	177.3(3)

Table S5. Bond torsion angles of 1c

Atom1	Atom2	Atom3	Atom4	Torsion(°)
N6	N5	C3	N4	-0.270(1006)
N4	C3	C2	N2	-8.042(956)
C2	C1	N1	O1	0.198(713)
N3	C1	N1	O1	177.471(639)
N3	C1	C2	N2	177.310(689)
C1	C2	C3	N5	-4.072(1004)
N4	C3	C2	C1	176.002(665)
N2	C2	C3	N4	-8.042(956)

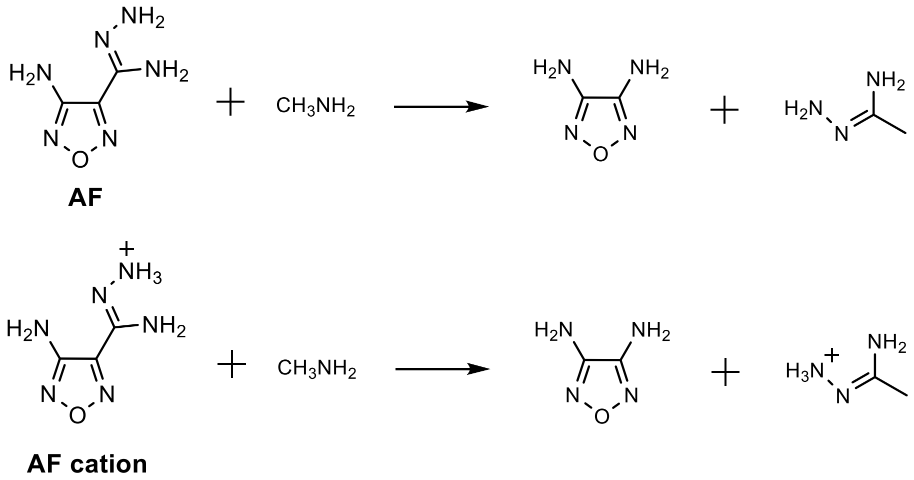
C2	C3	N5	N6	179.813(534)
N3	C1	C2	C3	-6.406(1205)
O1	N2	C2	C3	176.466(559)

Table S6. Intermolecular hydrogen bonds of crystal 1 and 1a-1c

Comp.	D-H···A	D-H(Å)	H···A(Å)	D-H···A(Å)	∠D-H···A(°)
1	N10H10A···N8	0.886	2.209	3.031	154.28
	N12H12A···N5	1.056	2.219	3.255	166.21
	N6-H6A···O2	0.882	2.465	3.181	138.59
	N10-H10B···N1	0.886	2.335	3.040	136.51
	N10-H10B···N7	0.886	2.425	2.277	105.78
1a	N3-H3A···O3	0.876	2.203	3.076	173.63
	N5-H5C···O5	0.932	1.881	2.811	176.80
	O5-H7···O3	0.830	2.010	2.837	174.23
	N6-H6A···O5	0.861	2.082	2.900	158.31
	O5-H8···O4	0.792	2.209	2.963	159.41
	N5-H5B···O3	0.892	2.077	2.924	158.36
	N6-H6B···O2	0.763	2.198	2.954	170.92
1b	N9-H9A···N3	0.875	2.489	3.091	126.52
	N9-H9A···N4	0.875	2.471	2.862	107.74
	N9-H9A···O1	0.875	2.119	2.835	138.65
	N9-H9B···O1	0.814	2.048	2.842	164.90
	N10-H10B···O1	0.921	1.892	2.800	168.26
	N10-H10A···N2	0.911	2.303	3.213	177.64
1c	N10-H10A···O5	0.880	2.193	3.013	154.89
	N12-H12C···N17	0.910	2.295	2.999	134.00
	N12-H12C···N15	0.910	2.311	3.036	136.51
	N6-H6A···N17	0.910	2.060	2.884	149.89
	N6-H6A···N4	0.910	2.491	2.727	95.12
	N4-H4A···N17	0.890	2.499	3.205	148.38
	N4-H4A···N18	0.890	2.355	3.281	162.45
	N12-H12B···N19	0.910	1.983	2.837	155.68
	N12-H12B···N18	0.910	2.457	3.338	163.02
	N6-H6B···N20	0.910	1.928	2.829	170.16
	N4-H4B···N1	0.880	2.120	2.986	167.85
	N12-H12A···O4	0.910	2.030	2.814	143.39
	N12-H12A···N13	0.910	2.183	2.942	140.42

Theoretical calculations

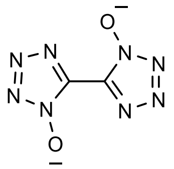
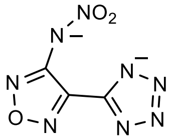
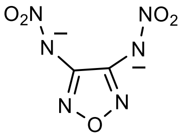
As mentioned in the manuscript, the gas phase heats of formation for all newly prepared neutral compounds were obtained using isodesmic reactions (Scheme S1). The geometric optimization and frequency analysis of the structures were calculated using B3LYP function with 6-31+G** basis set.[1] All of the optimized structures were checked to be true local energy minima on the potential energy surface without imaginary frequencies. Single-point energies based on the optimized structures were calculated at the MP2/6-311++G** set.[2] Atomization energies for frame molecules or ions were obtained by employing the G2 *ab initio* method.[3] The conversion of gas phase enthalpies to solid phase values for neutral compounds was done by subtracting the empirical heat of sublimation obtained based on Trouton's rule. The heats of formation of other compounds in Scheme S1 were determined from the NIST WebBook.[4]



Scheme S1. Isodesmic reactions for calculating heats of formation for 1 and its anion

Table S7. Enthalpies of the gas-phase species (NIST value and G2 method).[3,4]

M	ΔH_f° (kJ mol^{-1})
AF	329.1
AF cation	1024.2

$NO3$ anion	-307.9[5]
	587.7[6]
	472.1[7]
	263.3[8]

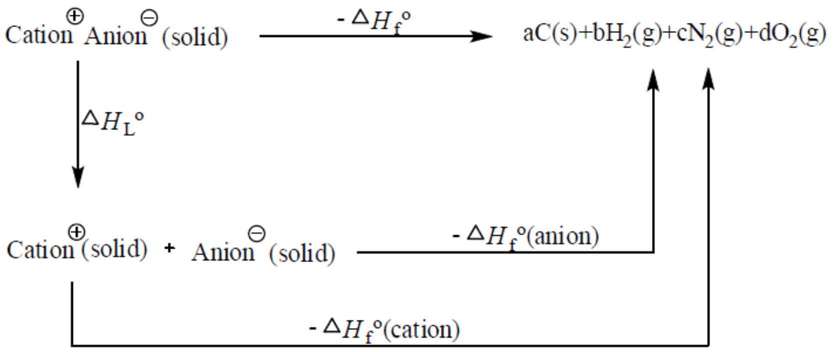
Based on the literature, the heat of sublimation is estimated with Trouton's rule.[9] The solid phase heats of formation of neutral compounds were calculated with equation (1), in which T_d represents the decomposition temperature.

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188[\mathrm{J\ mol^{-1}\ K^{-1}}] \times T_d \qquad (1)$$

Based on the Born-Haber energy cycle (Scheme 1), the heat of formation of a salt can be simplified according to equation (2), where ΔH_L is the lattice energy of the salt.

$$\Delta H_f^o(\text{ionic salt, 298K}) = \Delta H_f^o(\text{cation, 298K}) + \Delta H_f^o(\text{anion, 298K}) - \Delta H_L \quad (2)$$

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (3)], [10] where U_{POT} is the lattice potential energy and nM and nX depend on the nature of the ions Mp^{+} and Xq^{-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.



Scheme 1. Born-Haber energy cycle

$$\Delta H_L = U_{POT} + [p(\mathrm{nM}/2-2) + q(\mathrm{nX}/2-2)]RT \qquad (3)$$

The equation for the lattice potential energy, U_{POT}, takes the form of equation (4), where ρm is the density (g cm^{-3}), Mm is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ^{-1}mol^{-1}cm) and δ (kJ^{-1}mol^{-1}) are assigned literature values.

$$U_{POT}\ (\mathrm{kJ^{-1}mol^{-1}}) = \gamma\ (\rho\mathrm{m}/M\mathrm{m})^{1/3} + \delta \qquad (4)$$

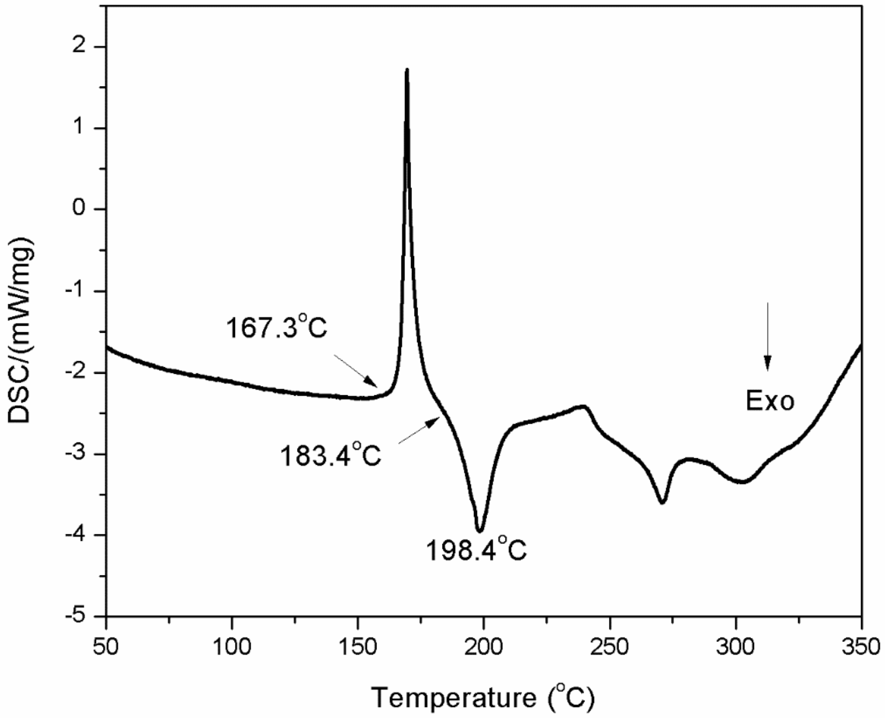


Figure S1. The DSC curve of 1

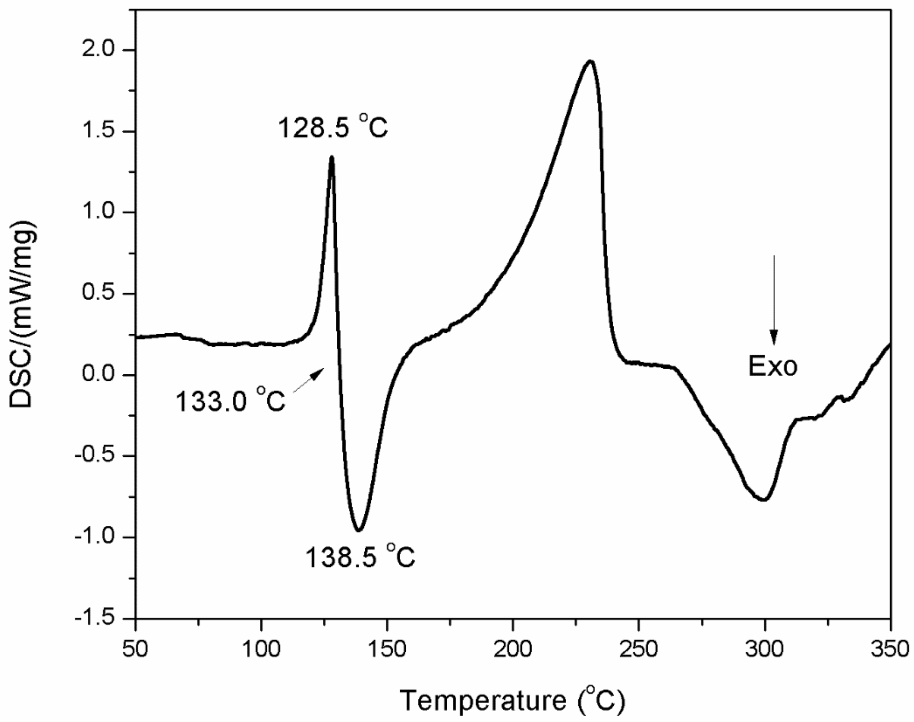


Figure S2. The DSC curve of 1a

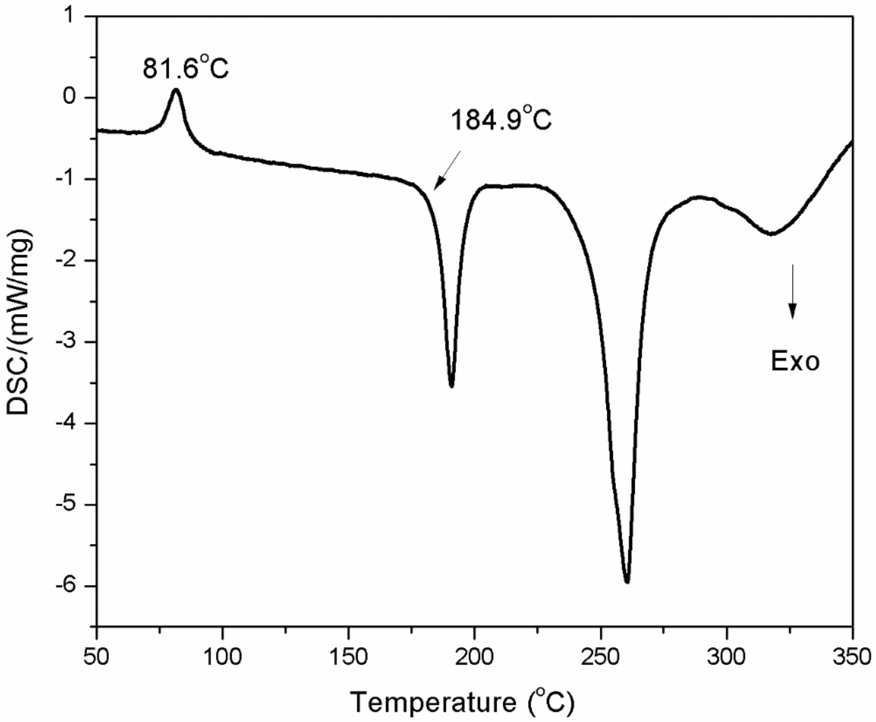


Figure S3. The DSC curve of 1b

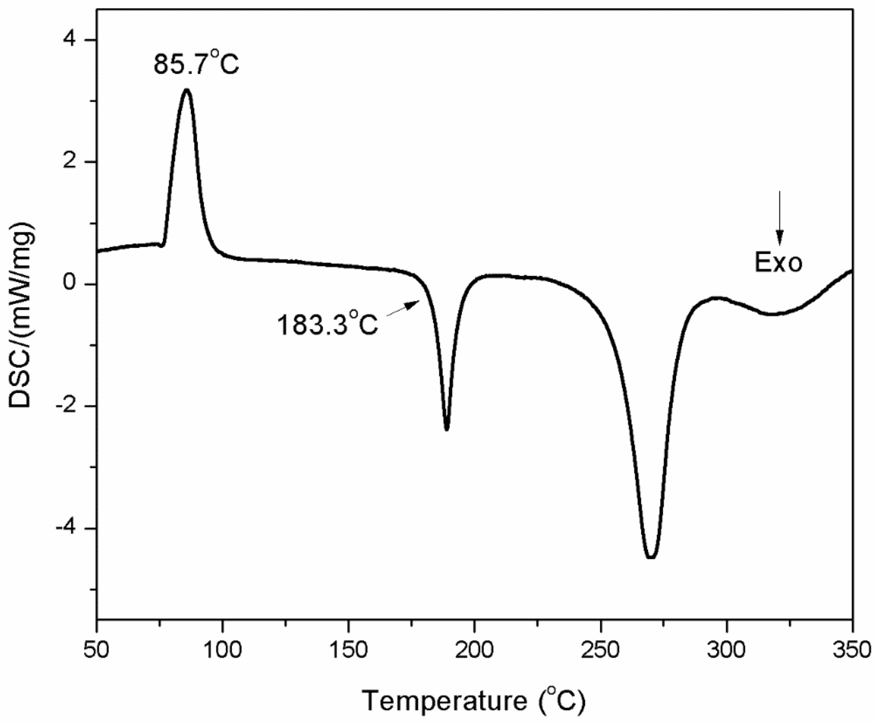


Figure S4. The DSC curve of 1c

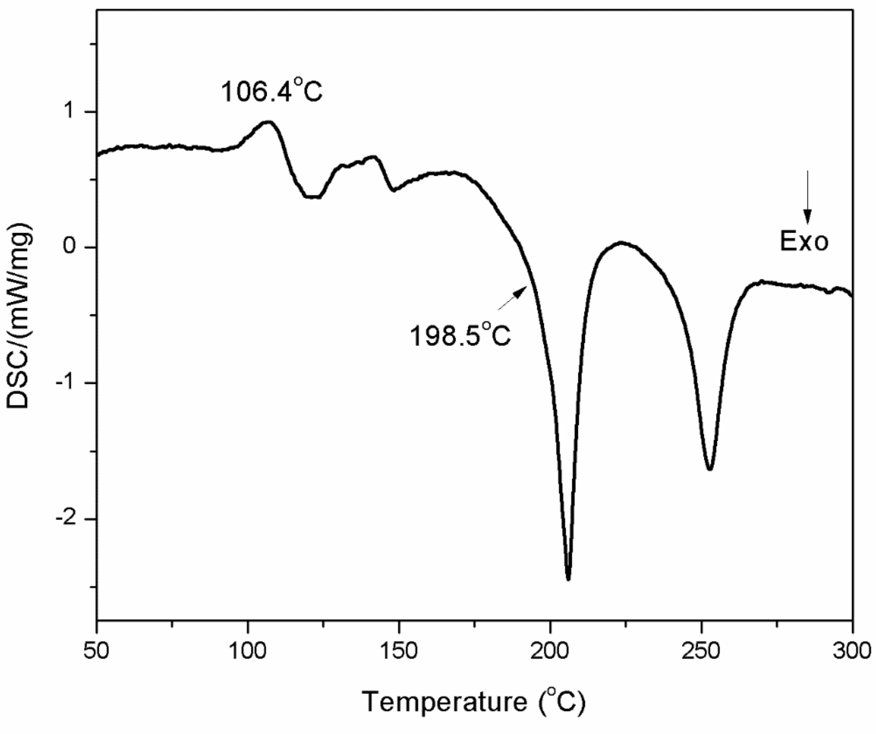


Figure S5. The DSC curve of 1d

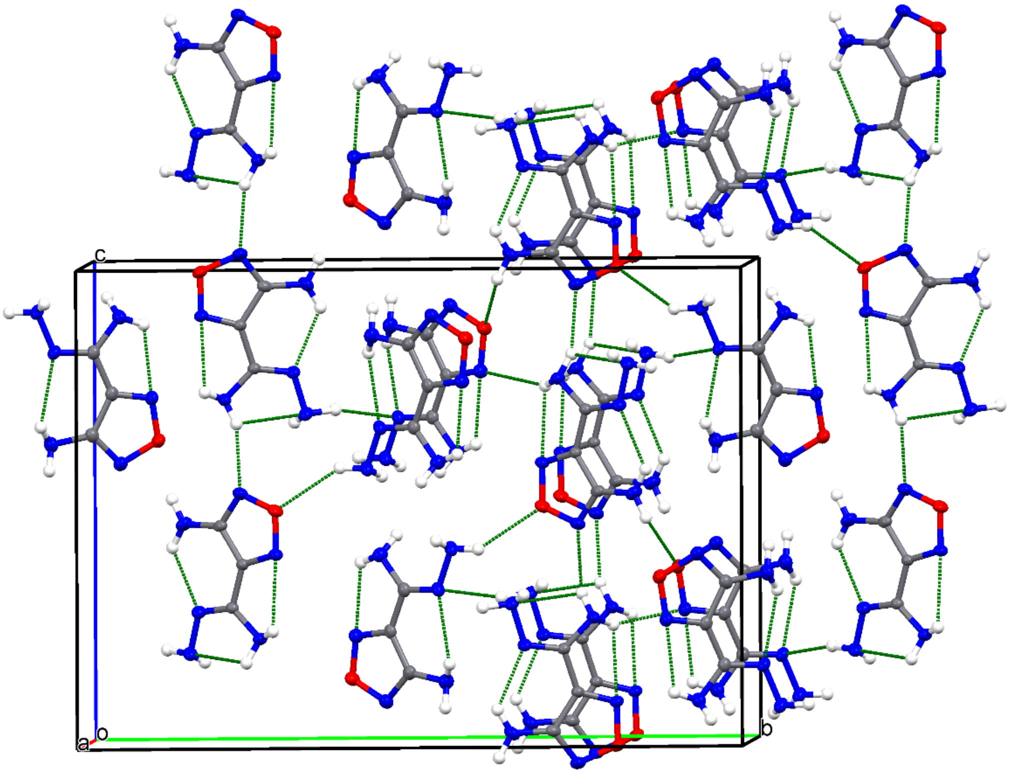


Figure S6. The packing mode of 1 from the a-axis

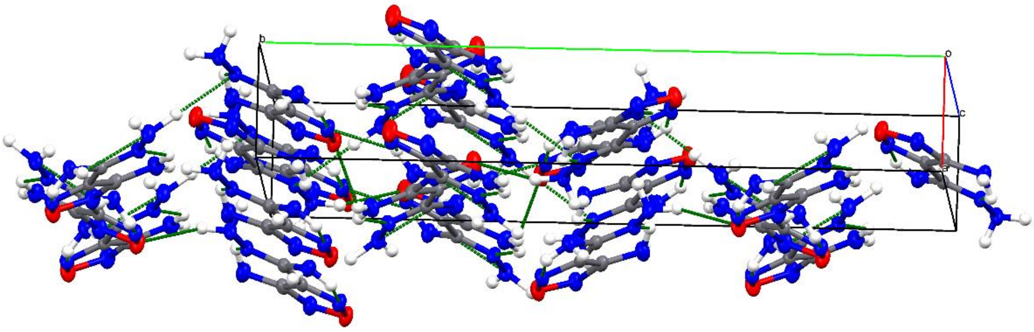


Figure S7. The packing mode of 1 from the c-axis

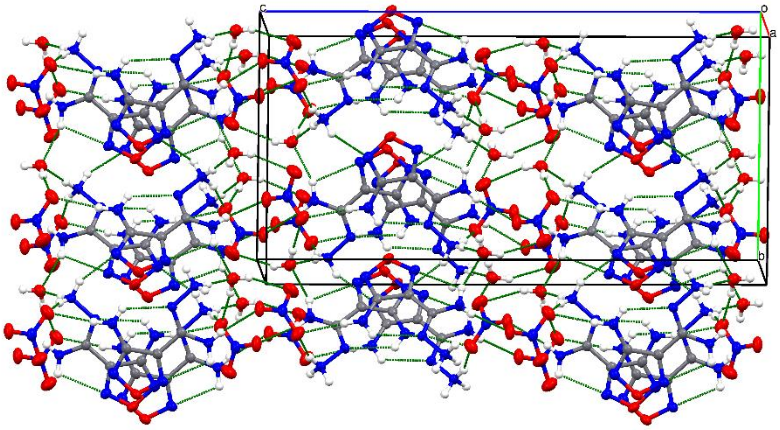


Figure S8. The packing mode of 1a from the a-axis

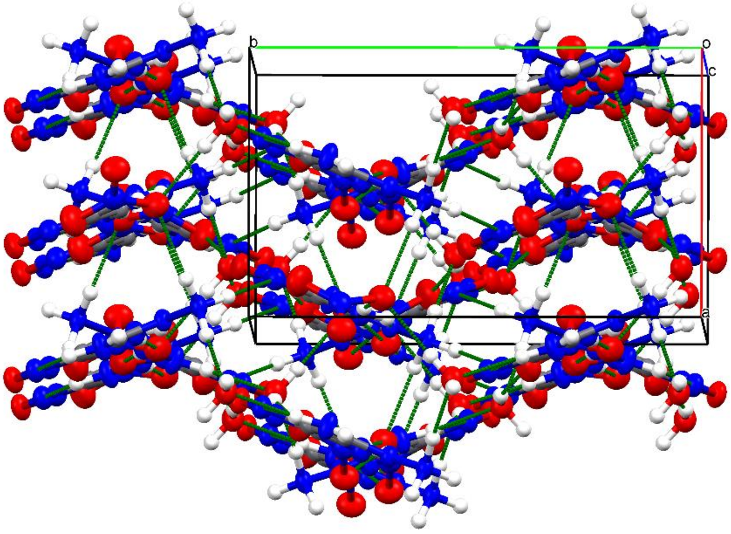


Figure S9. The packing mode of 1a from the c-axis

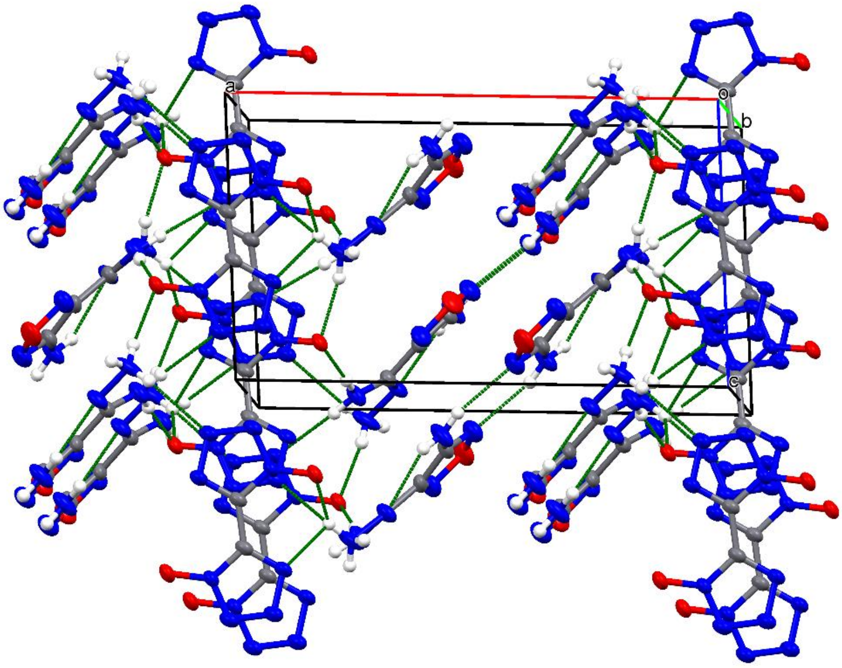


Figure S10. The packing mode of 1b from the b-axis

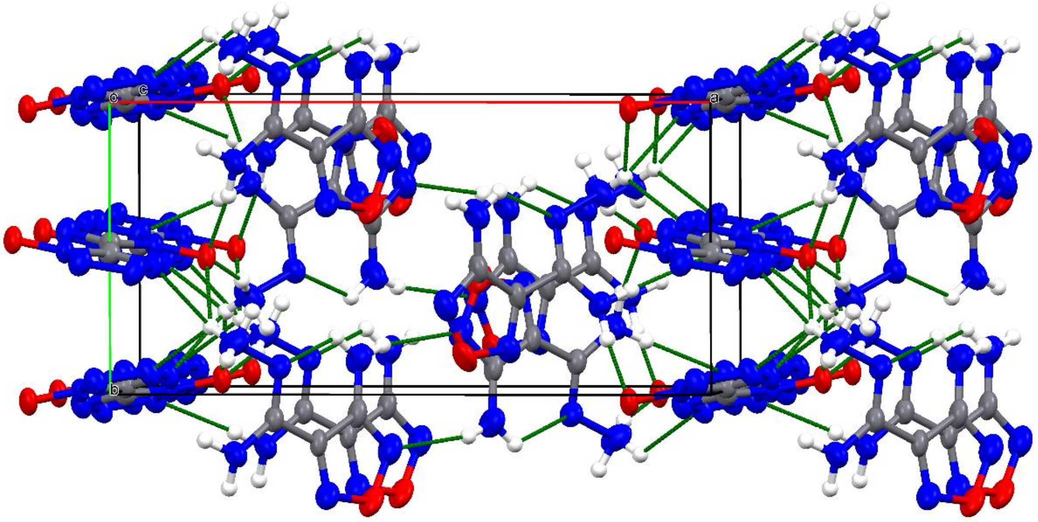


Figure S11. The packing mode of 1b from the c-axis

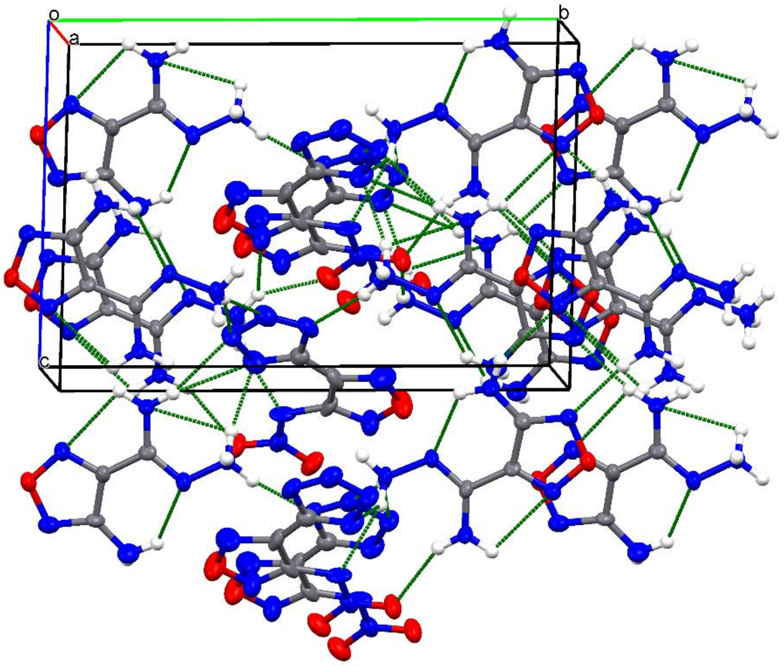


Figure S12. The packing mode of 1c from the a-axis

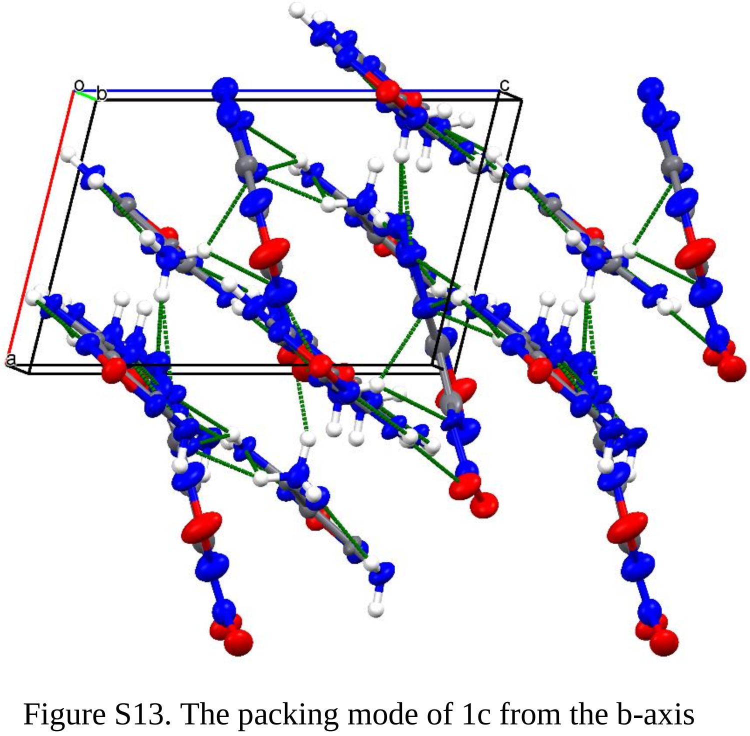


Figure S13. The packing mode of 1c from the b-axis

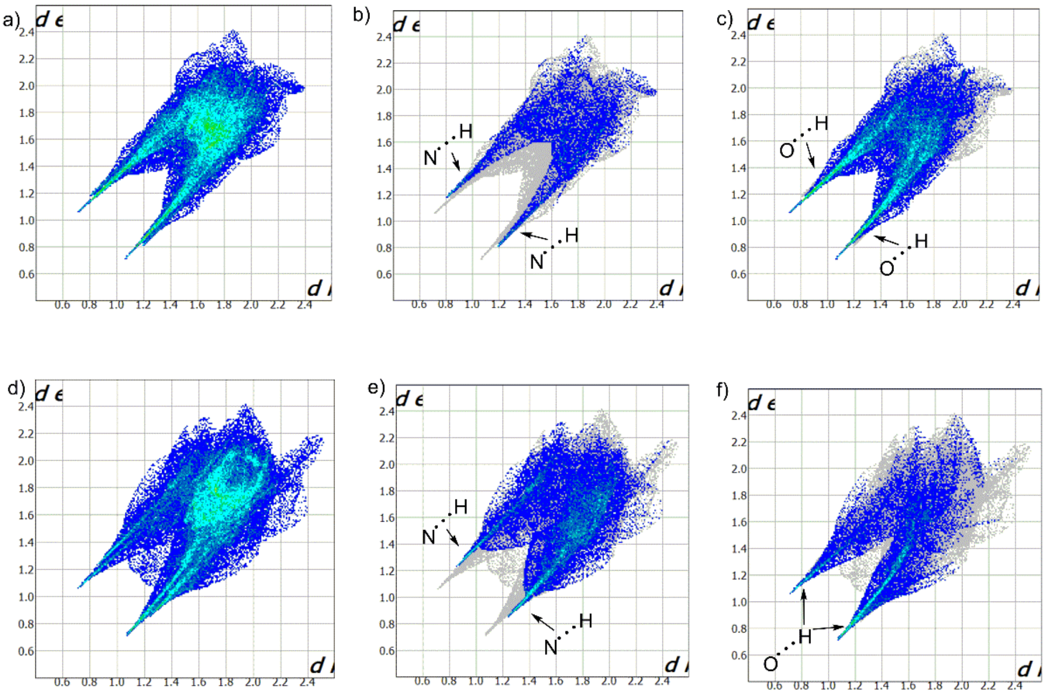


Figure S14. a) the total weak interactions of 1a; b) the N-H weak interactions of 1a; c) the O-H weak interactions of 1a; d) the total weak interactions of 1b; e) the N-H weak interactions of 1b; f) the O-H weak interactions of 1b.

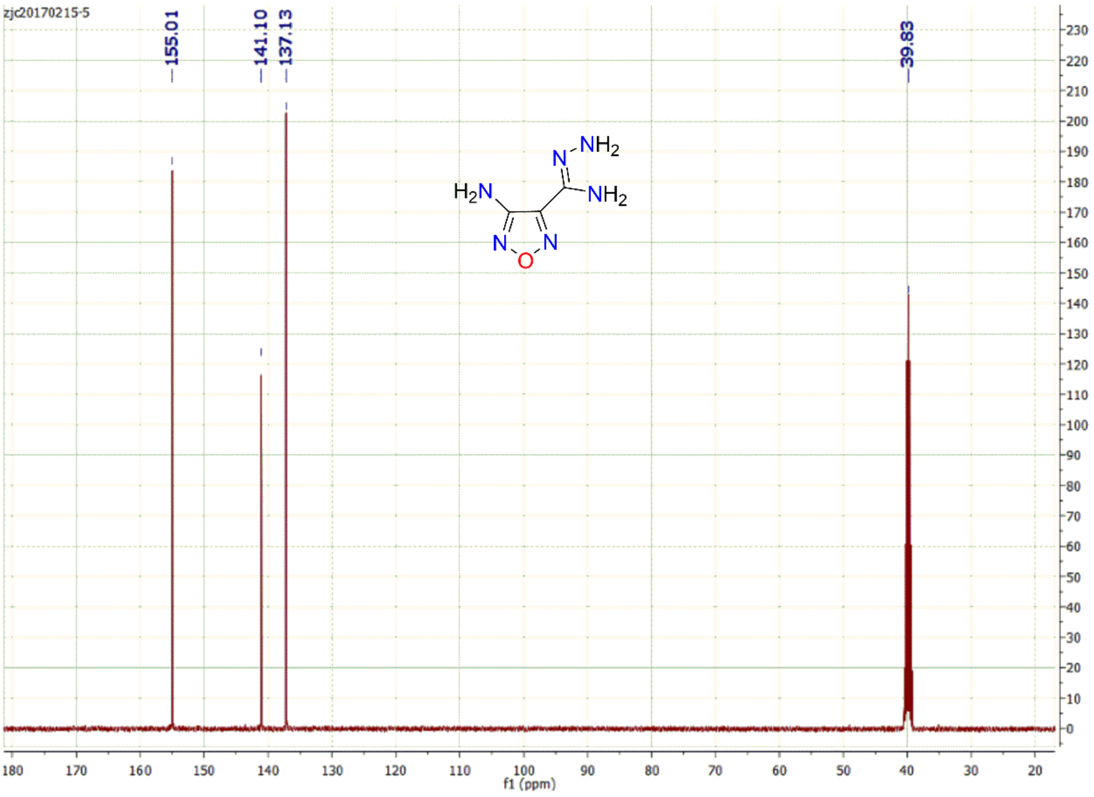


Figure S15. ^{13}C of compound 1

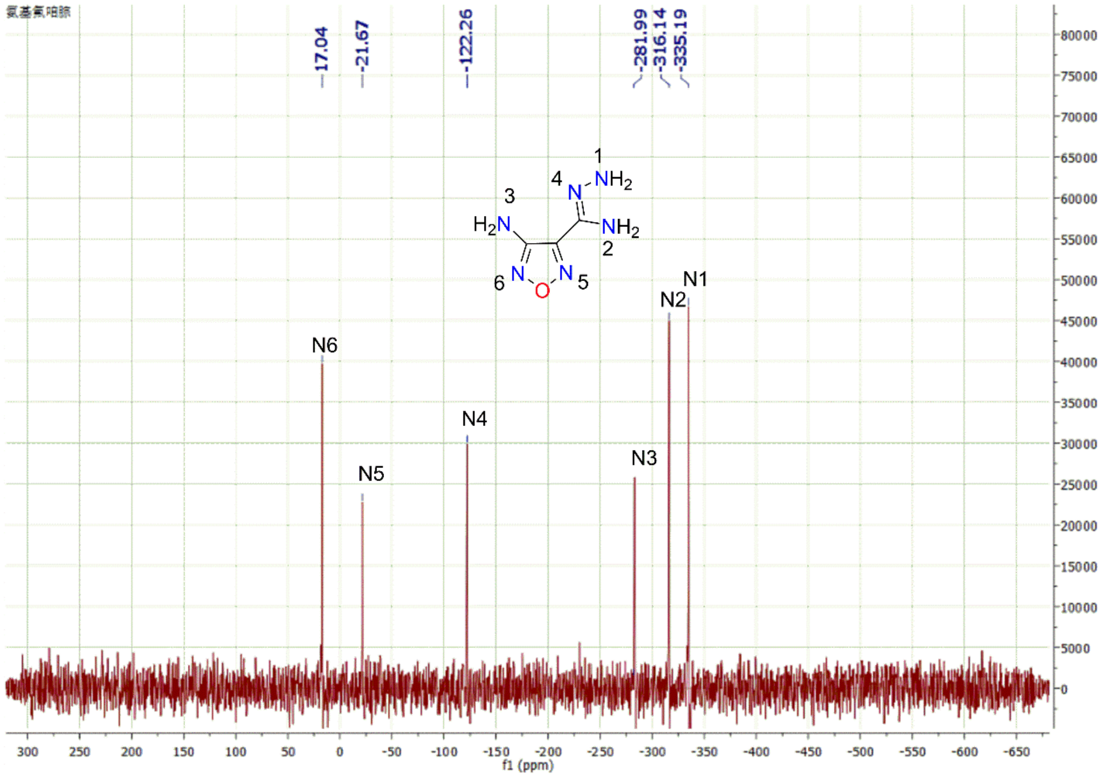


Figure S16. ^{15}N of compound 1

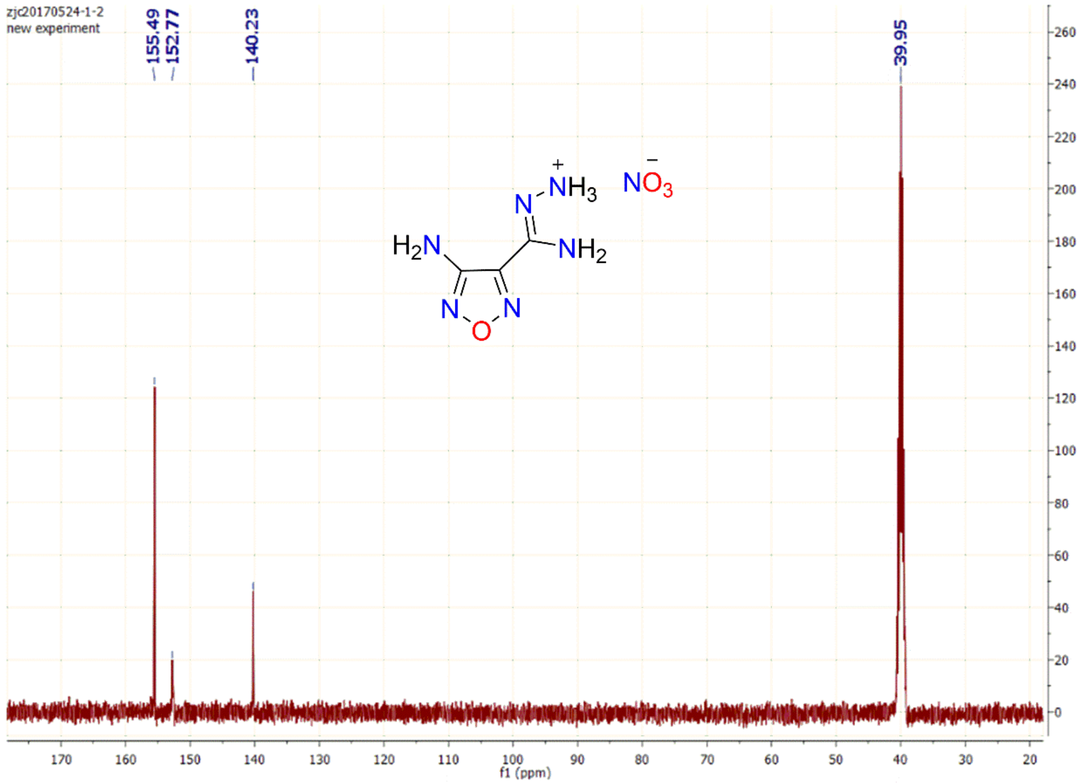


Figure S17. ^{13}C of compound 1a

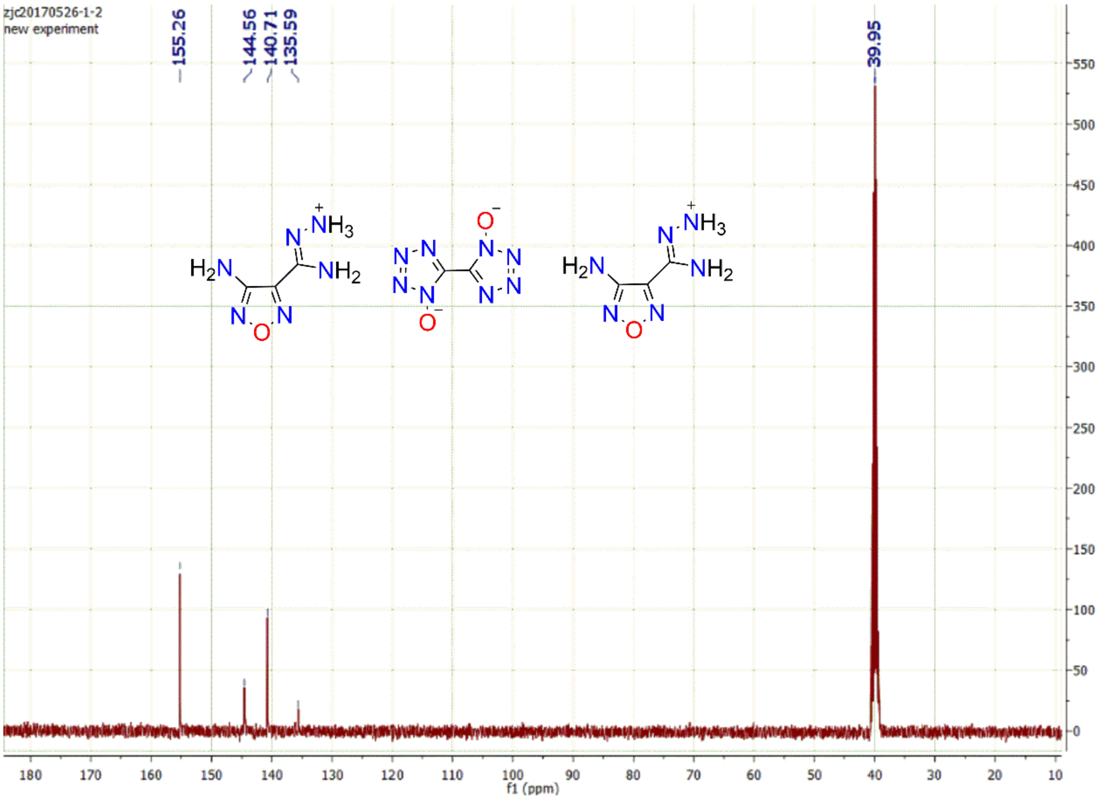


Figure S18. ^{13}C of compound 1b

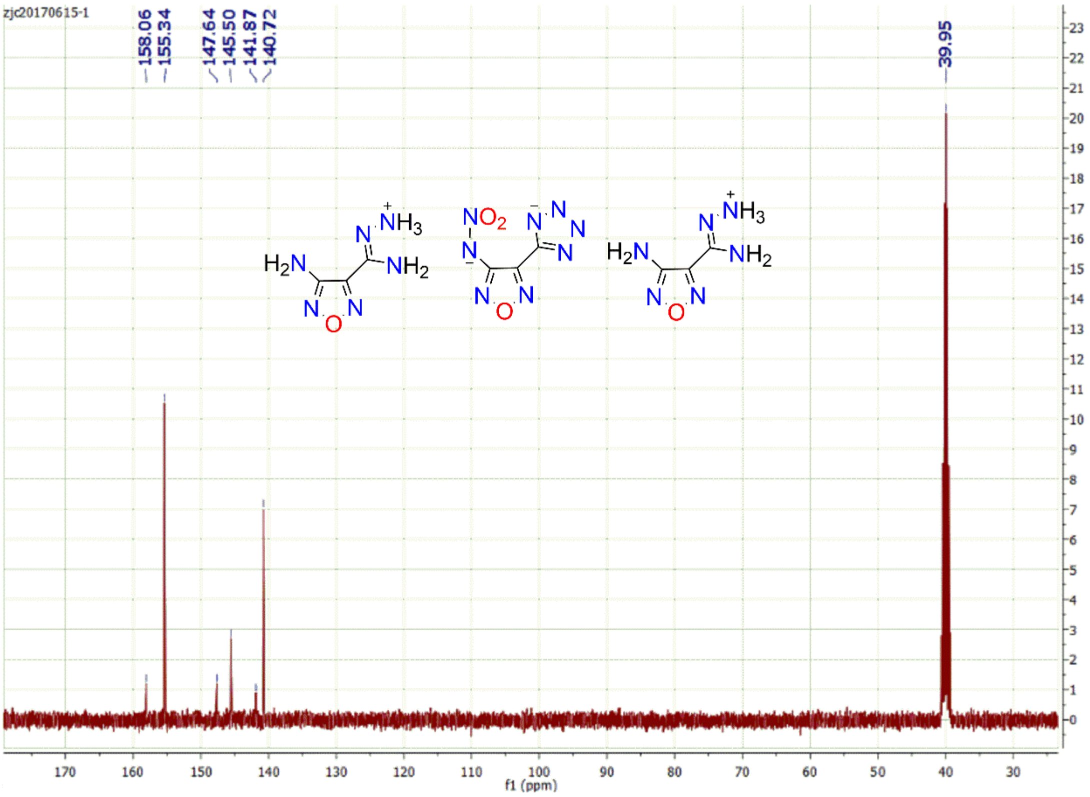


Figure S19. ^{13}C of compound 1c

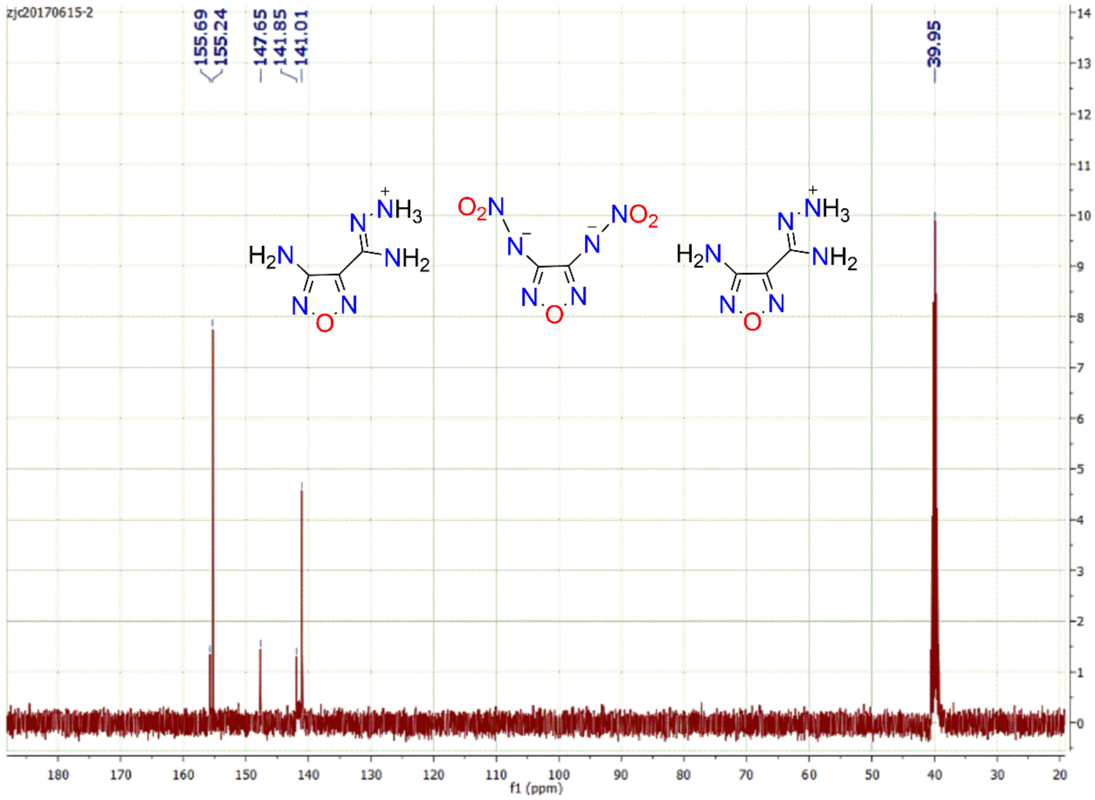


Figure S20. ^{13}C of compound 1d

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