Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

3-R-4-(5-methyleneazide-1,2,4-oxadiazol-3-yl)furazan and its ionic salts as low-sensitivity and high-detonation energetic materials

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Computational details

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs[S1]. The geometric optimization and frequency analyses of the structures are based on available single-crystal structures and using the B3LYP functional with the 6–311+G** basis set. The geometrical were optimized with no constraints imposed under default convergence criteria. Total energy (E_0) and zero-point energy (ZPE) were calculated with vibrational frequency analysis. The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Based on a Born-Haber energy cycle (Scheme S1), the heat of formation of a salt can be simplified by the formula given in Equation (1):

H_f (salt, 298 K) = H_f (cation, 298K) + H_f (anion, 298K) –H_L (1)

where "H_L" is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins [S2]et al. [Eq. (2)]

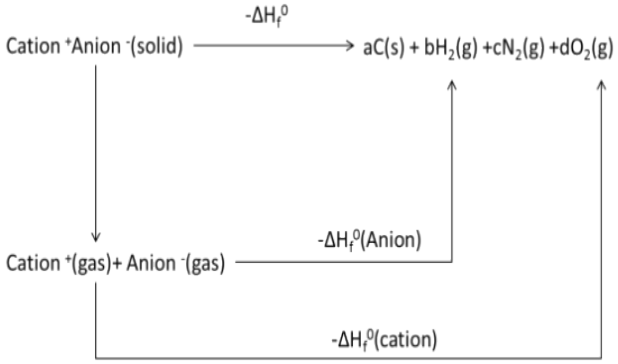
$H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

Where n_M and n_X depend on the nature of the ions, M_q^+ and X_p^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

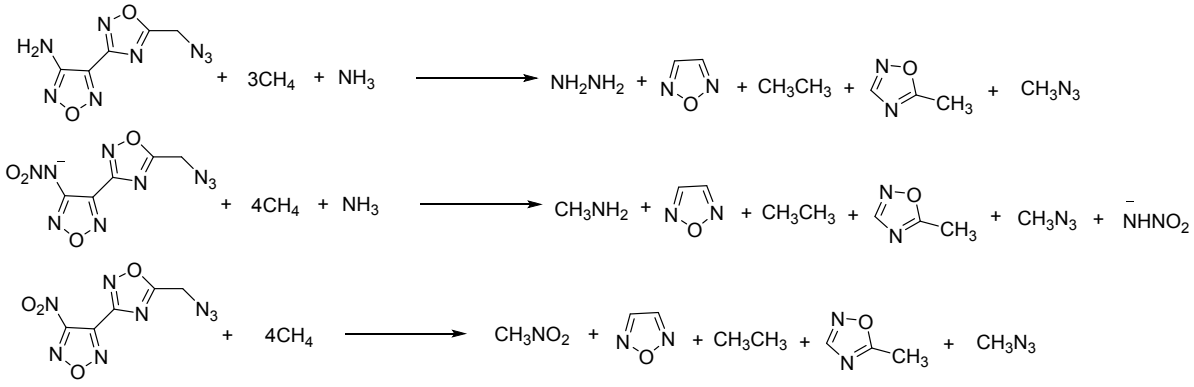
The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

U_{POT} [kJ mol^{-1}] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (3)

where ρ_m (g cm^{-3}) is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJmol^{-1}cm) and δ (kJ mol^{-1}) are assigned literature values.



Scheme S1. Born-Haber Cycle for the Formation of energetic salts



Scheme S2 Equivalent bond equation of 4-(1,2,4-oxadiazol-3-yl)furazan compounds

Crystallographic data

Table S1 Unit cell data of compounds **2** and **5**

	2	**5**
Formula	$C_5H_4N_8O_2$	$C_5H_6N_{10}O_4$
F_W (g mol^{-1})	208.16	270.20
Temperature (K)	296	296
Crystal system	orthorhombic	triclinic
Space group	P c a 21	P -1
Z	4	4
a(Å)	19.831(2)	8.2548(13)
b(Å)	5.3577(5)	10.4530(17)
c(Å)	7.8562(9)	13.508(2)
α(°)	90	93.199(5)
β(°)	90	99.554(4)
γ(°)	90	106.901(4)
V(Å^3)	834.71(15)	1093.1(3)
D_c (g cm^{-3})	1.656	1.642
μ(mm^{-1})	0.135	0.142
F(000)	424.0	552.0
Crystal size (mm^3)	0.22×0.21×0.01	0.2×0.18×0.01
Index ranges	-24＜h＜26 -7＜k＜6 -10＜l＜10	-10＜h＜10 -13＜k＜13 -17＜l＜17
θ(°)	3.308-28.253	2.423-27.552
Refl. Coll.	1984	4980
Independ. refl. [Rint]	1477	2573
R_1, wR_2 [I ＞2σ(I)]	0.0503, 0.1122	0.0688, 0.1551
R_1, wR_2 (all)	0.0796, 0.1215	0.1521, 0.1897
CCDC	2048721	2045479

Table S2 - Bond Distances of Compound **2**

bond	distances(Å)	bond	distances(Å)
O1-N1	1.402(4)	N6-N7	1.154(5)
O1-N2	1.362(4)	N6-C5	1.497(5)
O2-N3	1.413(4)	N7-N8	1.139(6)

O2-C4	1.334(4)	N5-H5A	0.8600
N1-C1	1.307(5)	N5-H5B	0.8600
N2-C2	1.300(5)	C1-C2	1.433(5)
N3-C3	1.288(5)	C2-C3	1.457(5)
N4-C3	1.377(4)	C4-C5	1.495(5)
N4-C4	1.281(4)	C5-H5C	0.9700
N5-C1	1.341(5)	C5-H5D	0.9700

Table S3 - Bond Angles of Compound **2**

N1-O1-N2	111.0(2)	N2-C2-C3	121.2(3)
N3-O2-C4	106.1(2)	C1-C2-C3	129.0(3)
O1-N1-C1	105.3(3)	N4-C3-C2	122.8(3)
O1-N2-C2	105.8(3)	N3-C3-N4	115.5(3)
O2-N3-C3	102.6(3)	N3-C3-C2	121.6(3)
C3-N4-C4	101.8(3)	O2-C4-N4	114.1(3)
N7-N6-C5	113.3(4)	O2-C4-C5	117.8(3)
N6-N7-N8	171.2(5)	N4-C4-C5	128.0(3)
H5A-N5-H5B	120.00	N6-C5-C4	109.8(4)
C1-N5-H5B	120.00	N6-C5-H5C	110.00
C1-N5-H5A	120.00	N6-C5-H5D	110.00
N5-C1 -C2	127.2(3)	C4-C5-H5C	110.00
N1-C1-C2	108.1(3)	C4-C5-H5D	110.00
N1-C1-N5	124.7(3)	H5C-C5-H5D	108.00
N2-C2-C1	109.7(3)		

Table S4 - Torsion Angles of Compound **2**

N2-O1-N1-C1	0.5(4)
N1-O1-N2-C2	-0.3(4)
C4-O2-N3-C3	0.2(4)
N3-O2-C4-N4	0.5(4)
N3-O2-C4-C5	-176.7(3)
O1-N1-C1-N5	179.7(4)
O1-N1-C1-C2	-0.5(4)
O1-N2-C2-C3	176.9(3)
O1-N2-C2-C1	0.0(4)
O2-N3-C3-N4	-0.8(4)
O2-N3-C3-C2	176.5(3)
C4-N4-C3-C2	-176.2(4)
C3-N4-C4-O2	-0.9(4)

C3N4-C4-C5	176.0(4)
C4-N4-C3-N3	1.1(4)
N7-N6-C5-C4	-169.3(4)
N1-C1-C2-N2	0.3(5)
N1-C1-C2-C3	-176.3(4)
N5-C1-C2-C3	3.6(7)
N5-C1-C2-N2	-179.9(4)
C1-C2-C3-N3	-0.9(6)
C1-C2-C3-N4	176.2(4)
N2-C2-C3-N4	0.0(6)
N2-C2 -C3-N3	-177.1(4)
O2-C4 -C5 -N6	-60.0(4)
N4-C4-C5-N6	123.2(4)

Table S4 - Hydrogen Bonds of compound **2**

	D--H(Å)	H···A(Å)	D--H···A(Å)	D-H···A (°)
N5 -- H5A ... N4	0.8600	2.2800	3.121(4)	165.00
N5 -- H5B ... N3	0.8600	2.4500	3.016(5)	124.00
C5 -- H5C ... N1	0.9700	2.5300	3.472(5)	163.00

Table S5 - Bond Distances of Compound **5**

O1-N1	1.395(5)	N12-C8	1.376(4)
O1-N2	1.374(6)	N13-C8	1.290(4)
O2-N4	1.407(5)	N14-N15	1.150(5)
O2-C4	1.335(6)	N14-C10	1.518(5)
O3-N9	1.261(4)	N15-N16	1.146(7)
O4-N9	1.237(4)	N17-N18	1.314(3)
O5-N10	1.403(4)	N17-C6	1.373(4)
O5-N11	1.364(4)	N19-H19D	0.79(2)
O6-N13	1.401(4)	N19-H19A	0.795(19)
O6-C9	1.336(4)	N19-H19C	0.80(3)
O7-N18	1.244(4)	N19-H19B	0.79(3)
O8-N18	1.250(3)	N20-H20C	0.88(2)
N1-C1	1.315(5)	N20-H20D	0.91(3)
N2-C2	1.305(6)	N20-H20B	0.88(2)
N3-C3	1.380(5)	N20-H20A	0.88(2)
N3-C4	1.287(6)	C1-C2	1.427(6)
N4-C3	1.294(6)	C2-C3	1.447(6)
N5-N6	1.194(9)	C4-C5	1.470(7)
N5-C5	1.432(9)	C5-H5B	0.9700
N6-N7	1.124(9)	C-H5A	0.9700

N8-N9	1.306(4)	C6-C7	1.440(4)
N8-C1	1.370(5)	C7-C8	1.448(4)
N10-C6	1.310(4)	C9-C10	1.485(5)
N11-C7	1.302(4)	C10-H10A	0.9700
N12-C9	1.278(4)	C10-H10B	0.9700

Table S6 - Bond Angles of compound **5**

N1-O1-N2	111.3(3)	H19A-N19-H19D	110(3)
N4-O2-C4	106.9(3)	H19A-N19-H19C	108(3)
N10-O5-N11	111.3(2)	H20C-N20-H20D	108(2)
N13-O6-C9	106.5(2)	H20A-N20-H20C	111(2)
O1-N1-C1	104.8(4)	H20A-N20-H20B	111(3)
O1-N2-C2	105.6(3)	H20B-N20-H20D	107(2)
C3-N3-C4	103.0(3)	H20A-N20-H20D	108(3)
O2-N4-C3	103.1(3)	H20B-N20-H20C	111(2)
N6-N5-C5	115.0(6)	N1-C1-C2	108.9(4)
N5-N6-N7	166.0(9)	N1-C1 -N8	131.3(4)
N9-N8-C1	116.5(3)	N8-C1-C2	119.8(3)
O3-N9-N8	115.2(3)	C1-C2 -C3	130.5(4)
O4-N9-N8	125.1(3)	N2-C2-C1	109.4(4)
O3-N9-O4	119.7(3)	N2-C2-C3	120.1(4)
O5-N10-C6	105.2(3)	N3-C3-C2	125.2(4)
O5-N11-C7	105.8(3)	N3-C3-N4	114.3(4)
C8-N12-C9	102.4(3)	N4-C3-C2	120.5(4)
O6-N13-C8	103.0(2)	O2-C4-C5	119.2(4)
N15-N14 -C10	114.1(3)	O2-C4-N3	112.7(4)
N14-N15-N16	170.7(5)	N3-C4-C5	128.0(5)
N18-N17 -C6	116.2(2)	N5-C5-C4	108.8(5)
O7-N18-O8	120.4(2)	C4-C5-H5B	110.00
O8-N18-N17	123.3(3)	N5-C5-H5B	110.00
O7-N18-N17	116.3(2)	C4-C5-H5A	110.00
H19B-N19-H19D	112(3)	H5A-C5-H5B	108.00
H19A-N19-H19B	110(3)	N5-C5-H5A	110.00
H19B-N19-H19C	107(3)	N10-C6-C7	108.2(3)
H19C-N19-H19D	109(3)	N17-C6-C7	120.4(3)
N10-C6-N17	131.4(3)	O6-C9-C10	117.4(3)
N11-C7-C6	109.6(3)	N12-C9-C10	129.3(3)
N11-C7-C8	120.1(3)	N14-C10-C9	108.7(3)
C6-C7-C8	130.3(3)	C9-C10-H10A	110.00
N12-C8-C7	122.0(2)	C9-C10-H10B	110.00
N13-C8-C7	123.2(3)	H10A-C10-H10B	108.00
N12-C8-N13	114.8(3)	N14-C10-H10A	110.00

O6-C9-N12	113.3(3)	N14-C10-H10B	110.00

Table S7 - Torsion Angles of compound 5

N2-O1-N1-C1	0.1(4)	N1-O1-N2-C2	0.2(5)
C4-O2-N4-C3	0.4(5)	N4-O2-C4-C5	176.8(4)
N4-O2-C4-N3	-0.7(5)	N10-O5-N11-C7	-0.2(3)
N11-O5-N10-C6	-0.4(3)	N13-O6-C9-N12	0.1(3)
C9-O6-N13-C8	0.0(3)	N13-O6-C9-C10	-178.8(3)
O1-N1-C1-N8	-179.2(4)	O1-N1-C1-C2	-0.3(4)
O1-N2-C2-C3	179.6(4)	O1-N2-C2-C1	-0.4(5)
C3-N3-C4-C5	-176.5(5)	C4-N3-C3-N4	-0.4(5)
C3-N3-C4-O2	0.7(5)	C4-N3-C3-C2	177.7(4)
O2-N4-C3-N3	0.0(5)	O2-N4-C3-C2	-178.3(4)
N6-N5-C5-C4	166.2(6)	C1-N8-N9-O4	-4.8(5)
C1-N8-N9-O3	173.5(3)	N9-N8-C1-C2	-173.3(3)
N9-N8-C1-N1	5.5(6)	O5-N10-C6-C7	0.7(3)
O5-N10-C6-N17	-178.0(3)	O5-N11-C7-C8	179.1(2)
O5-N11-C7-C6	0.6(3)	C8-N12-C9-C10	178.5(3)
C9-N12-C8-N13	0.2(3)	C8-N12-C9-O6	-0.1(3)
C9-N12-C8-C7	-178.2(3)	O6-N13-C8-N12	-0.1(3)
O6-N13-C8-C7	178.2(2)	N15-N14-C10-C9	-128.6(4)
C6-N17-N18-O8	0.5(4)	C6-N17-N18-O7	-179.5(2)
N18-N17-C6-C7	176.6(2)	N18-N17-C6-N10	-4.8(5)
N1-C1-C2-N2	0.5(5)	N8-C1-C2-N2	179.5(3)
N1-C1-C2-C3	-179.5(4)	N8-C1-C2-C3	-0.5(6)
C1-C2-C3-N4	-159.6(4)	N2-C2-C3-N4	20.4(6)
C1-C2-C3-N3	22.4(7)	N2-C2-C3-N3	-157.6(4)
O2-C4-C5-N5	33.8(6)	N3-C4-C5-N5	-149.1(5)
N10-C6-C7-N11	-0.9(3)	N10-C6-C7-C8	-179.1(3)
N17-C6-C7-C8	-0.3(5)	N17-C6-C7-N11	178.0(3)
C6-C7-C8-N12	173.1(3)	C6-C7-C8-N13	-5.1(5)
N11-C7-C8-N13	176.8(3)	N11-C7-C8-N12	-5.1(4)
O6-C9-C10-N14	72.1(4)	N12-C9-C10-N14	-106.5(4)

Table S9 - Hydrogen Bonds of Compound **5**

	D--H(Å)	H···A(Å)	D--H···A(Å)	D-H···A (°)
N19 -- H19A ... N3	0.795(19)	2.298(19)	3.086(4)	172(3)
N19 -- H19B ... O7	0.79(3)	2.54(3)	3.017(4)	120(2)
N19 -- H19B ... N17	0.79(3)	2.30(3)	3.080(4)	173(3)
N19 -- H19C ... N11	0.80(3)	2.56(3)	3.305(4)	156(3)

N19 -- H19D ... O3	0.79(2)	2.17(2)	2.924(4)	160(3)
N20 -- H20B ... O3	0.88(2)	2.48(3)	3.043(3)	122(2)
N20 -- H20B ... O4	0.88(2)	2.09(2)	2.961(4)	168(2)
N20 -- H20B ... N9	0.88(2)	2.61(2)	3.376(4)	146(3)
N20 -- H20C ... O8	0.88(2)	1.97(2)	2.852(3)	177.2(19)
N20 -- H20C ... N18	0.88(2)	2.61(2)	3.405(3)	150(2)
N20 -- H20D ... O3	0.91(3)	1.92(3)	2.821(4)	174(2)
C5 -- H5A ... N11	0.9700	2.5500	3.514(6)	171.00
C5 -- H5B ... N16	0.9700	2.5700	3.360(8)	139.00
C10 -- H10B ... N8	0.9700	2.6100	3.541(5)	161.00

NMR spectra data of all compounds

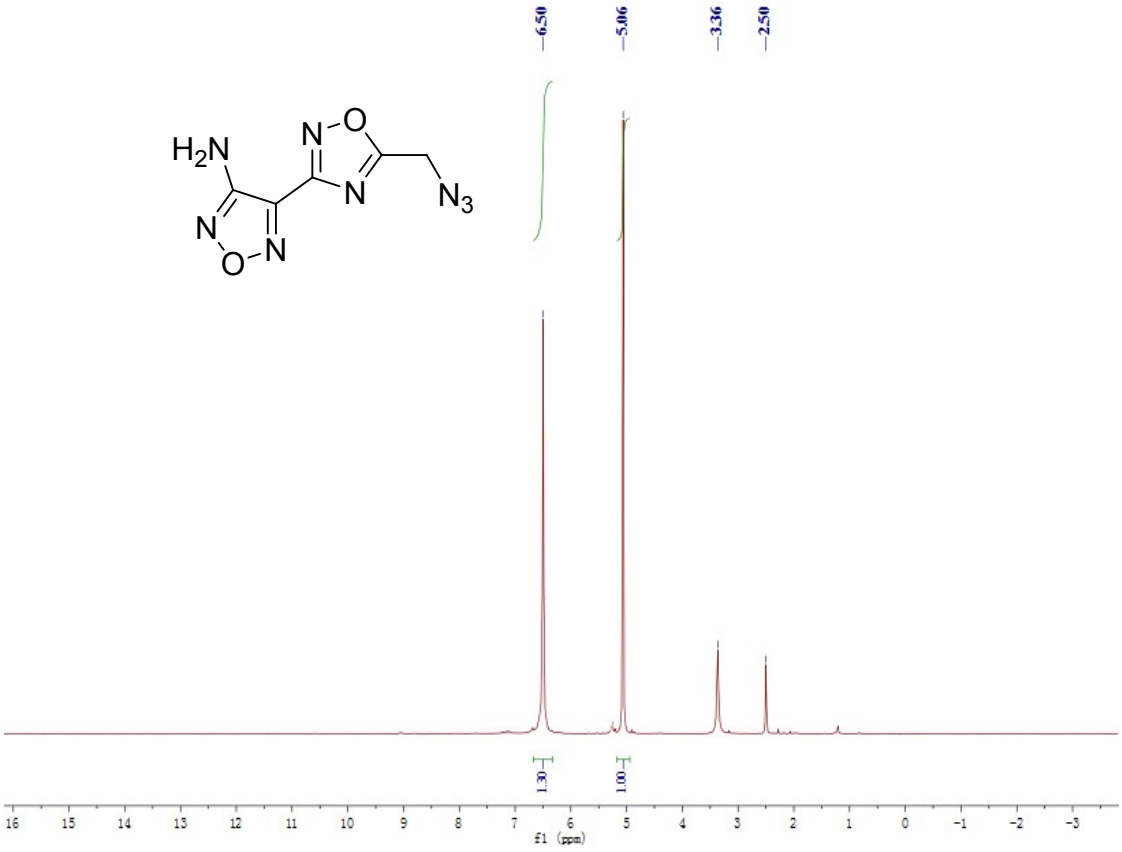


Figure S1 ^{1}H NMR for compound **2**

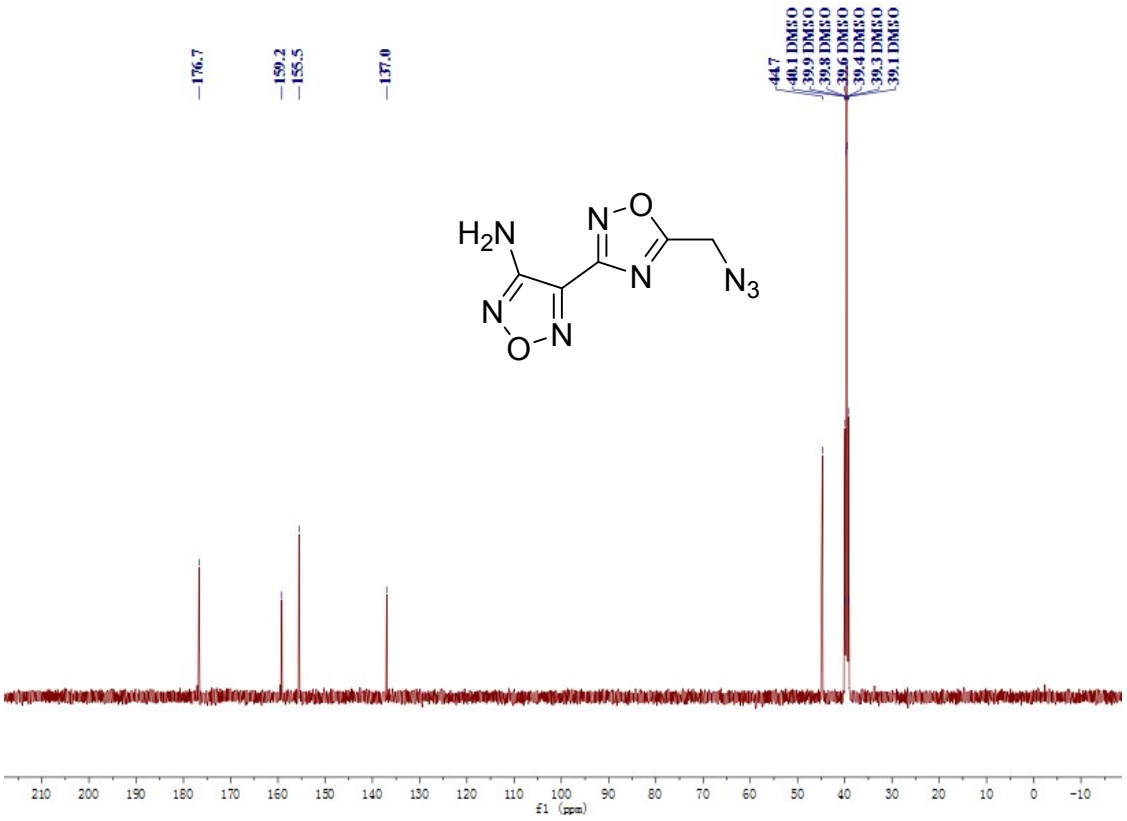


Figure S2 ^{13}C NMR for compound **2**

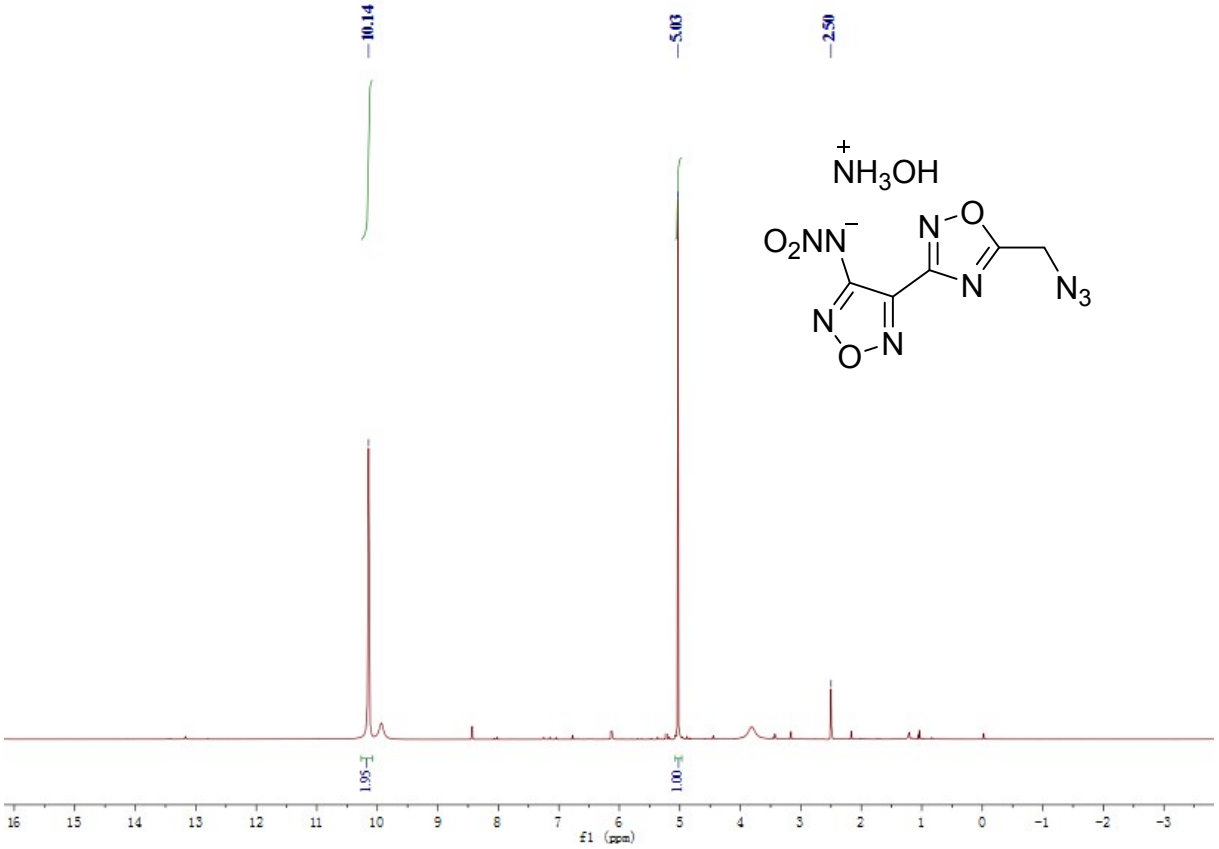


Figure S3 ^{1}H NMR for compound **4**

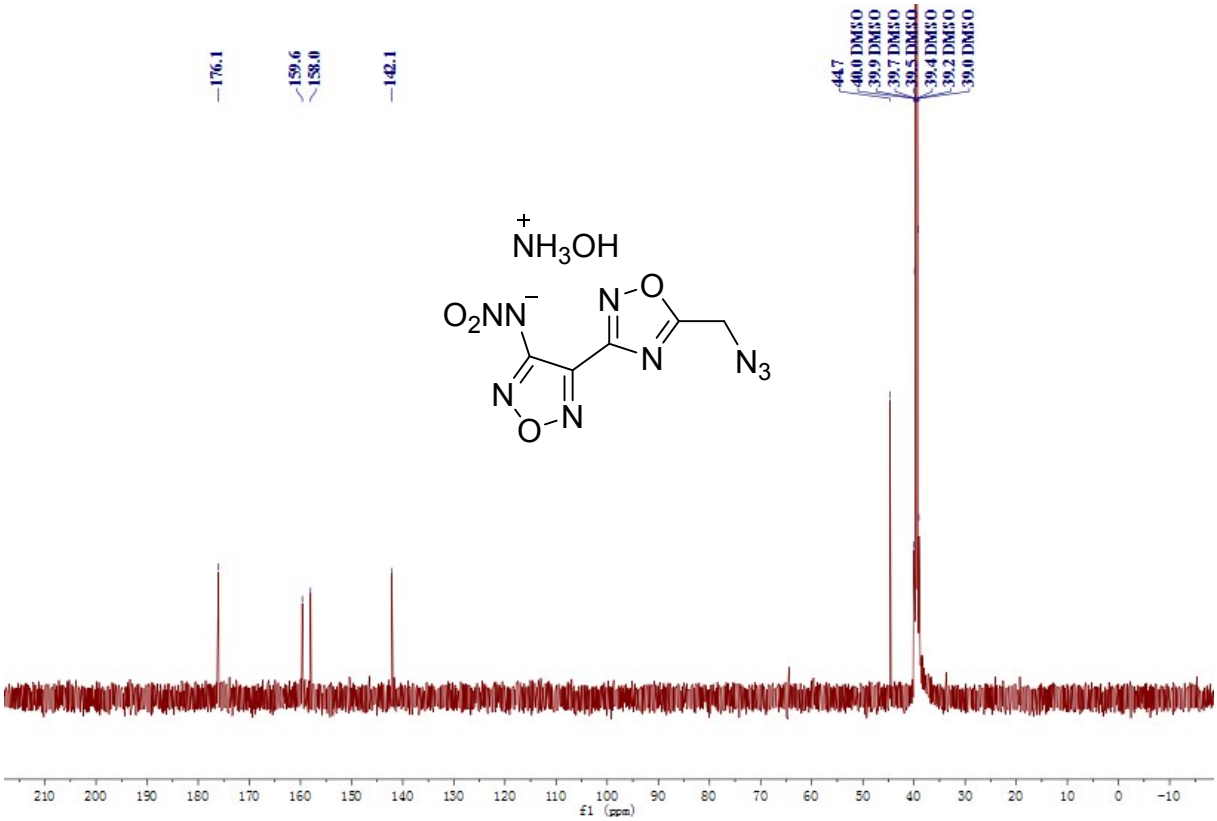


Figure S4 ^{13}C NMR for compound **4**

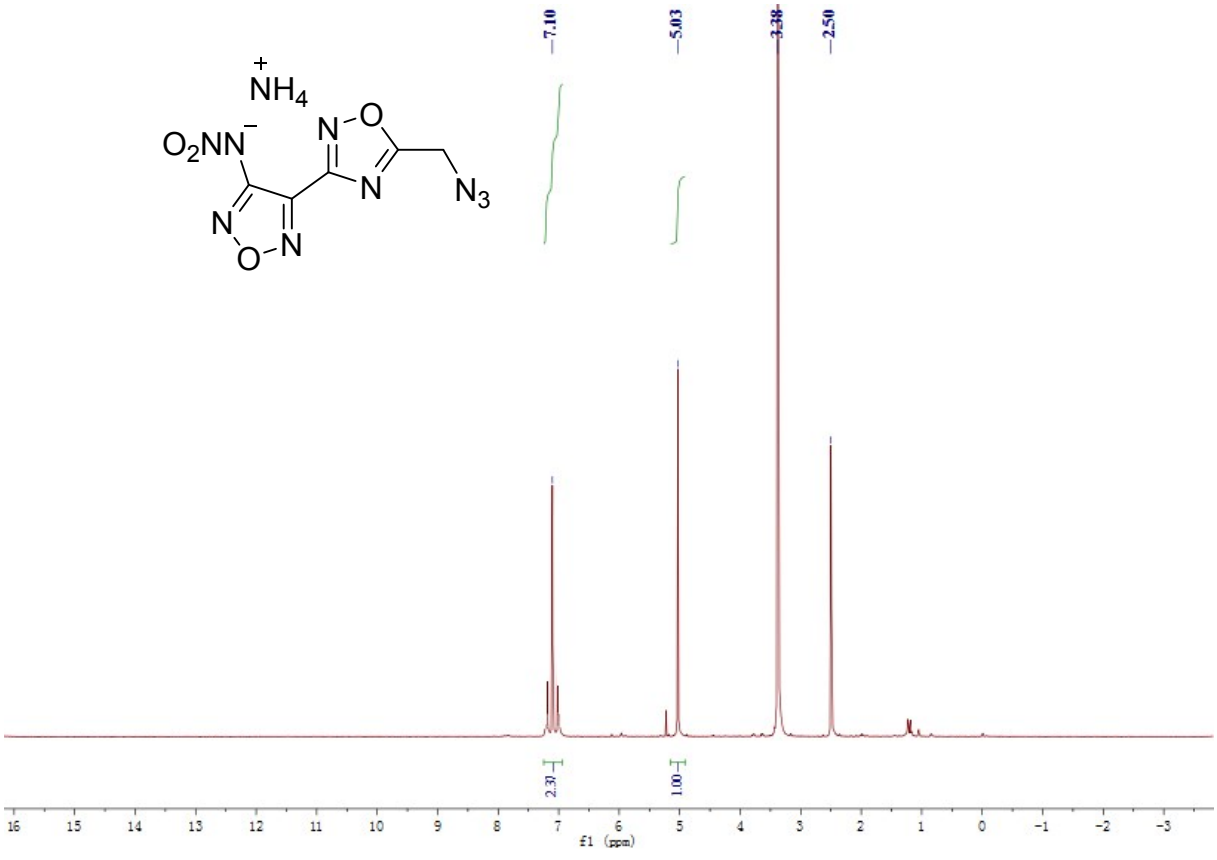


Figure S5 ^{1}H NMR for compound **5**

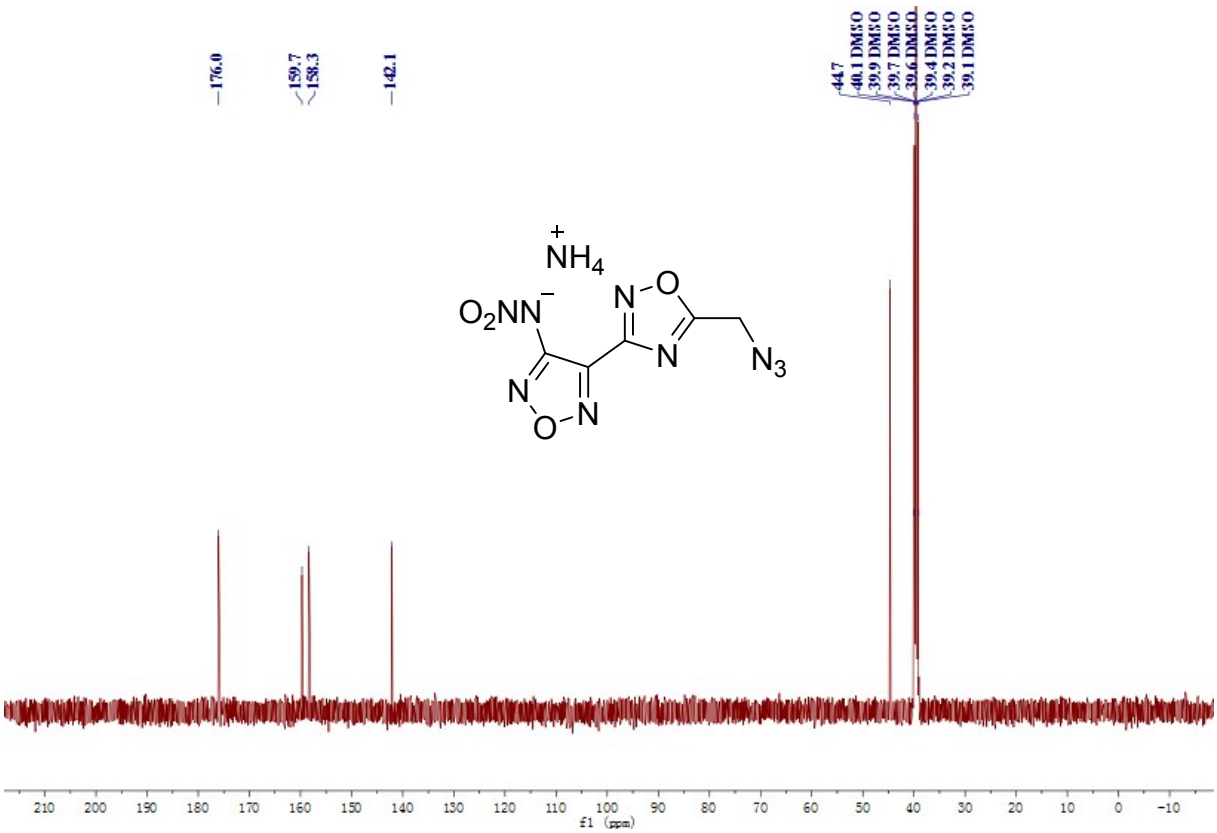


Figure S6 ^{13}C NMR for compound **5**

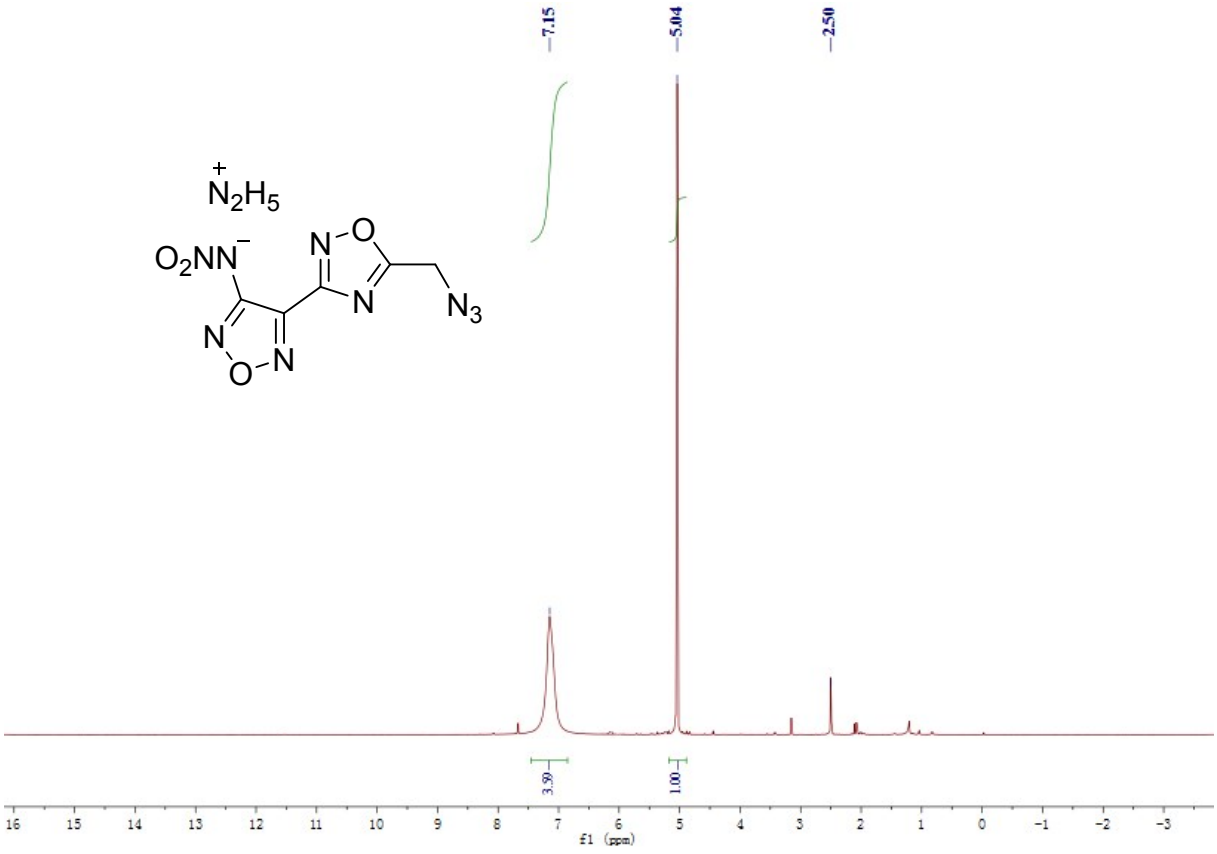


Figure S7 ^{1}H NMR for compound **6**

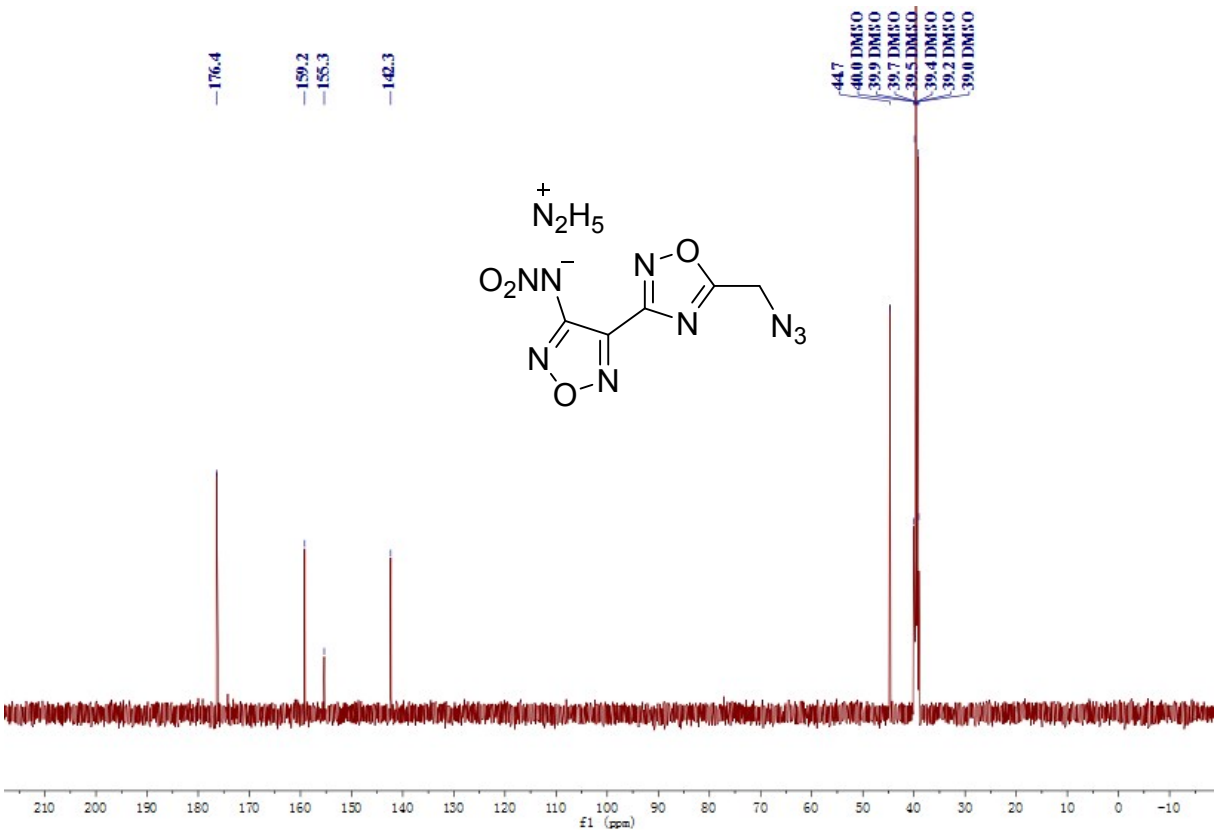


Figure S8 ^{13}C NMR for compound **6**

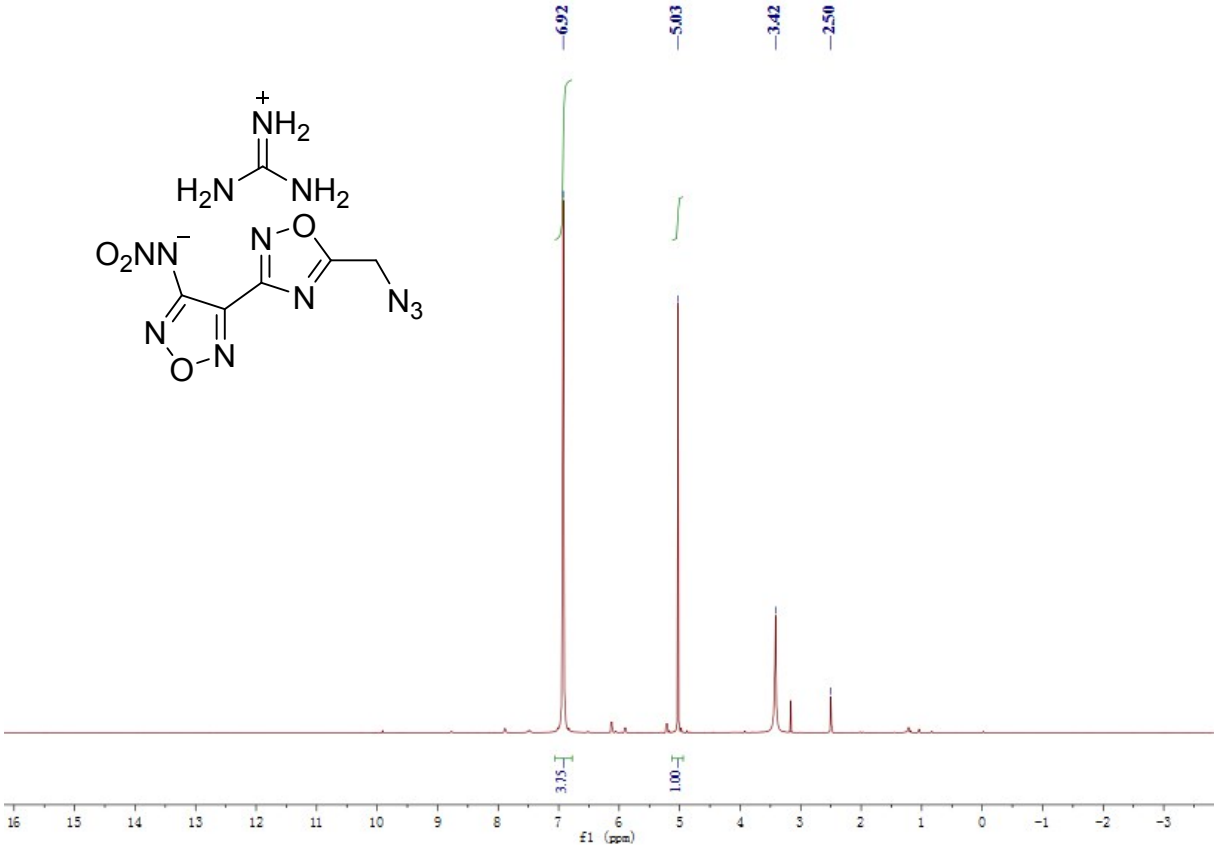


Figure S9 ^{1}H NMR for compound **7**

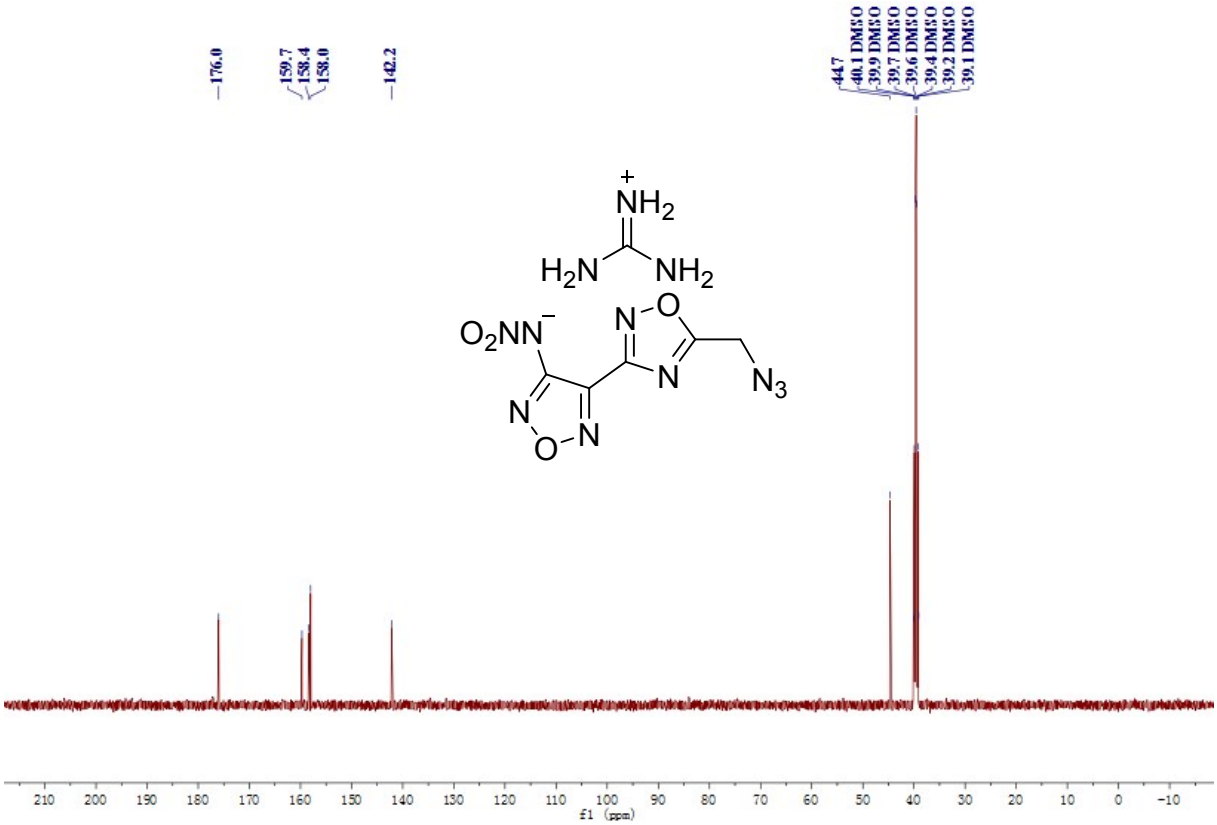


Figure S10 ^{13}C NMR for compound **7**

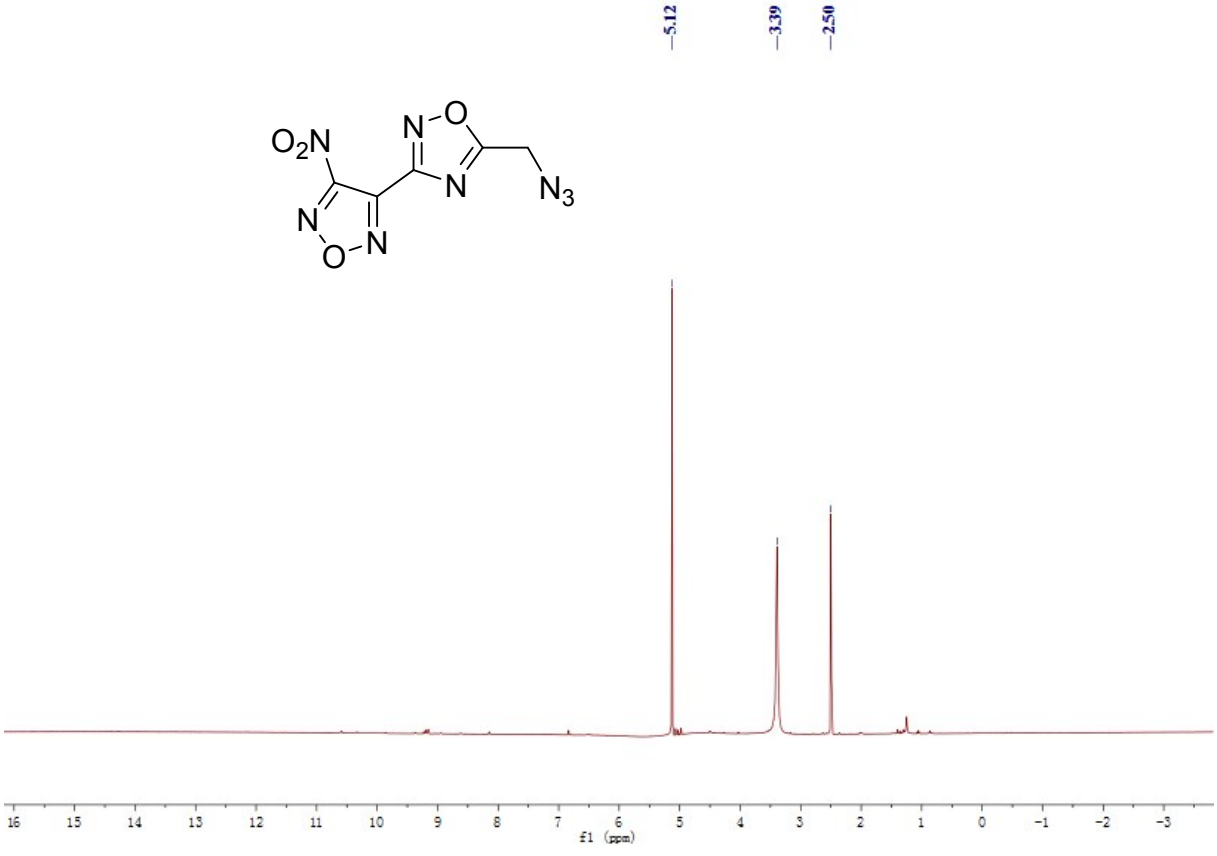


Figure S11 ^{1}H NMR for compound **8**

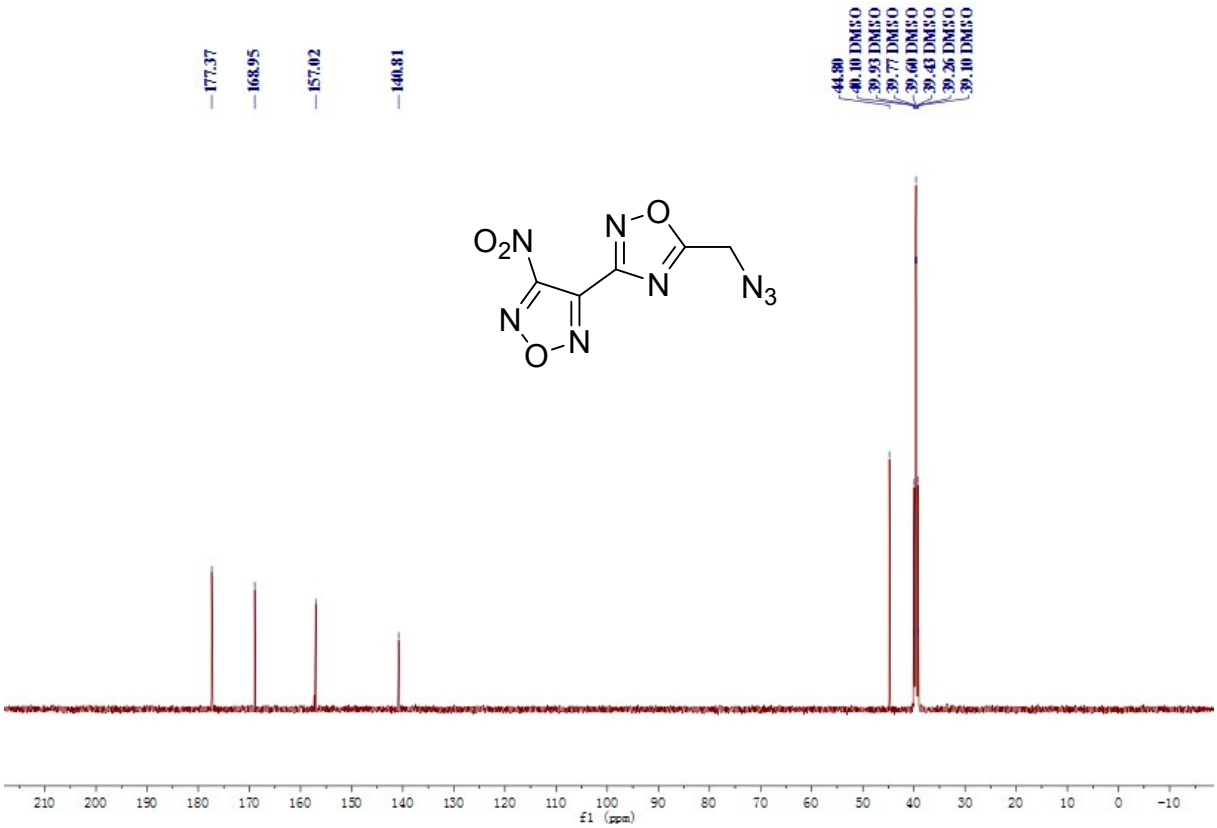


Figure S12 ^{13}C NMR for compound **8**

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