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

Supporting Information (SI)

Compounds based on 3-amino-4-(5-methyl-1,2,4-oxadiazol -3-yl)furazan as insensitive energetic materials

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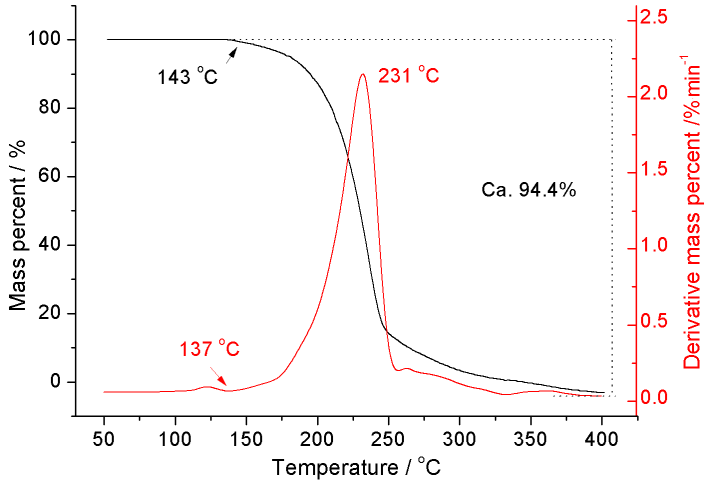

Fig. S1 TG and DTG curves of **1** under nitrogen with a heating rate of 5 °C min^{-1}.

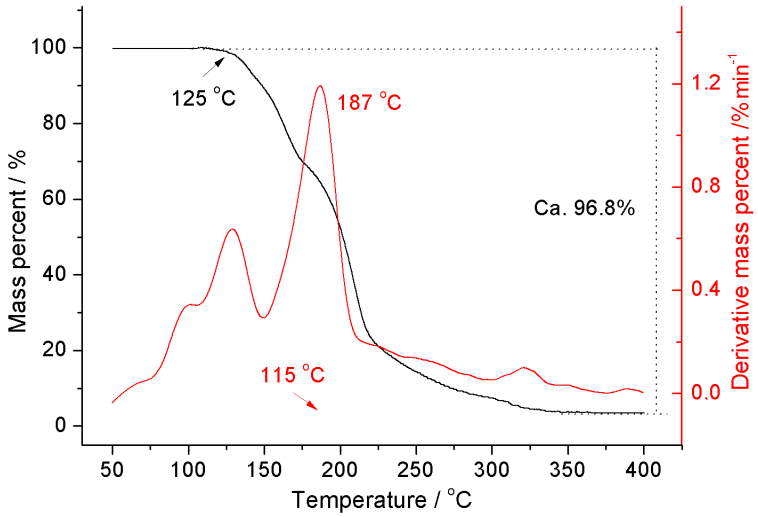

Fig. S2 TG and DTG curves of **2** under nitrogen with a heating rate of 5 °C min^{-1}.

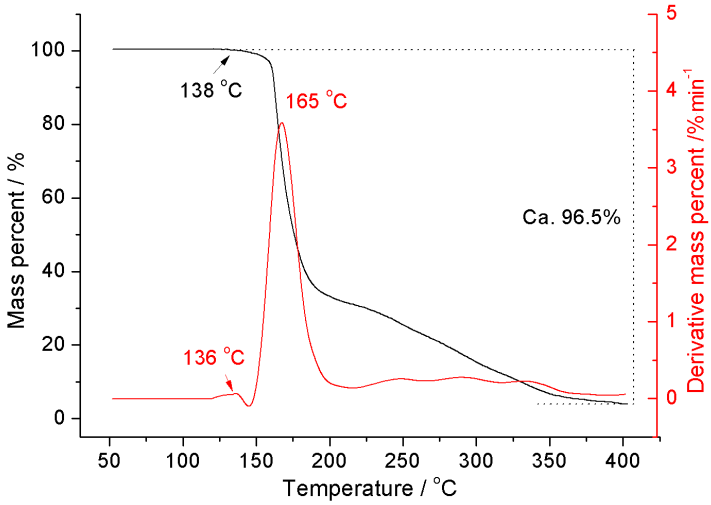

Fig. S3 TG and DTG curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}.

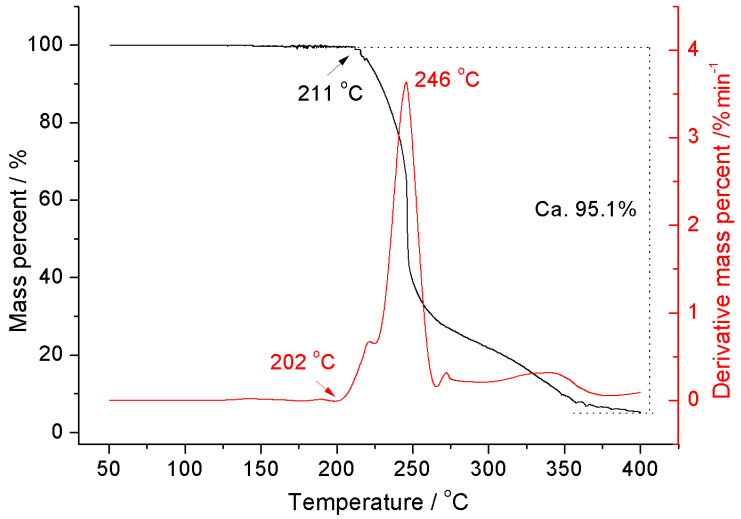

Fig. S4 TG and DTG curves of **4** under nitrogen with a heating rate of 5 °C min^{-1}.

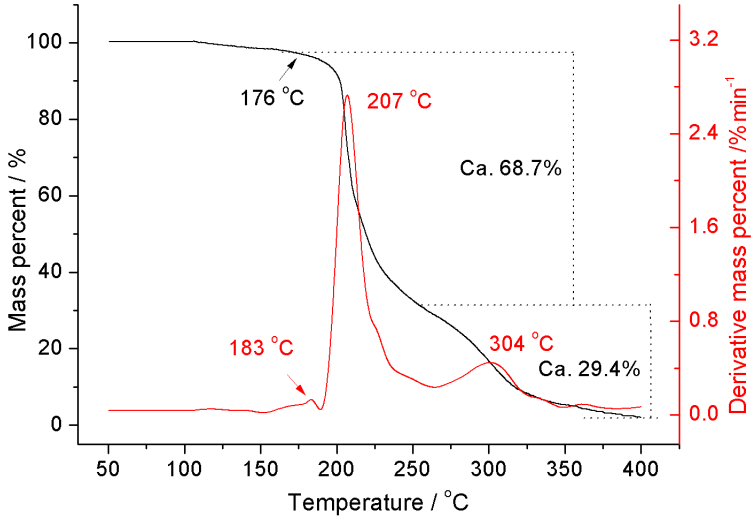

Fig. S5 TG and DTG curves of **5** under nitrogen with a heating rate of 5 °C min^{-1}.

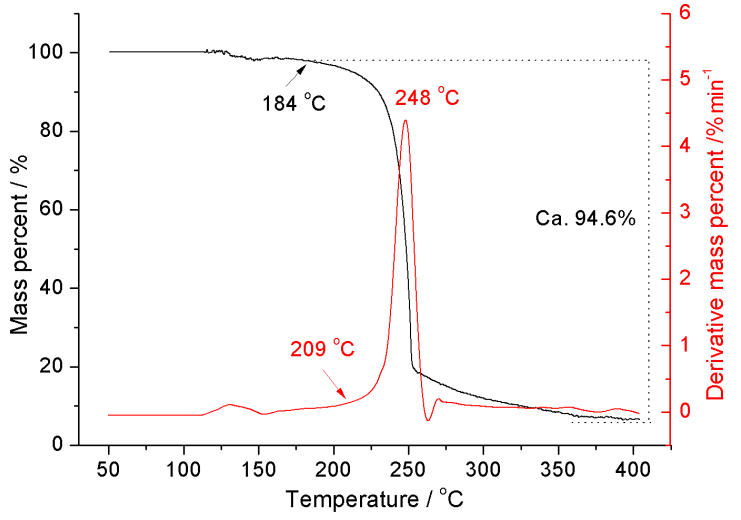

Fig. S6 TG and DTG curves of **6** under nitrogen with a heating rate of 5 °C min^{-1}.

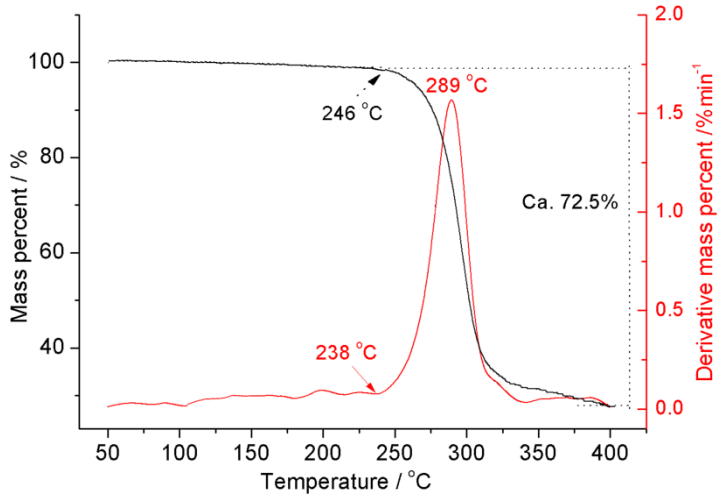

Fig. S7 TG and DTG curves of **7** under nitrogen with a heating rate of 5 °C min^{-1}.

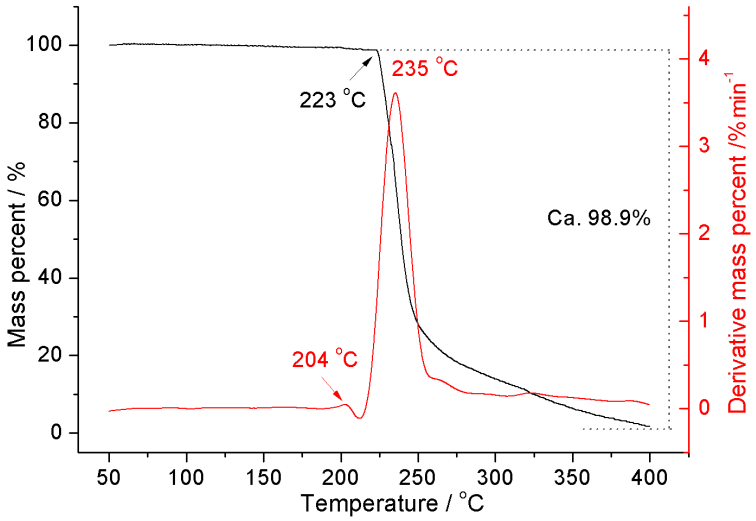

Fig. S8 TG and DTG curves of **8** under nitrogen with a heating rate of 5 °C min^{-1}.

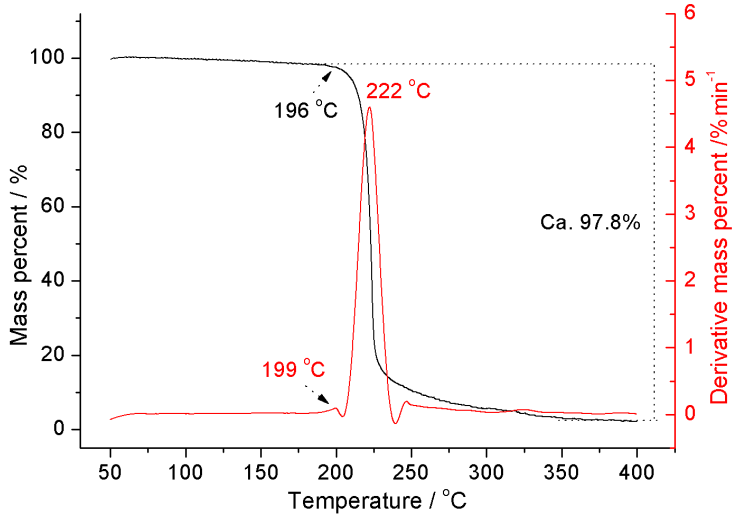

Fig. S9 TG and DTG curves of **9** under nitrogen with a heating rate of 5 °C min^{-1}.

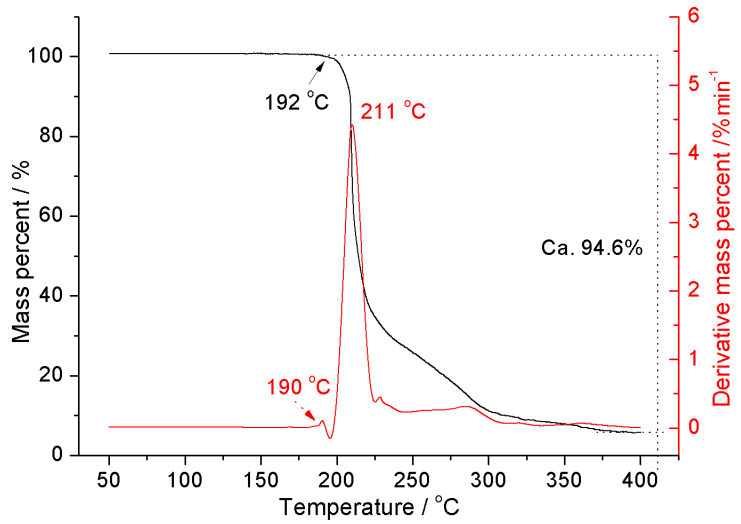

Fig. S10 TG and DTG curves of **10** under nitrogen with a heating rate of 5 °C min^{-1}.

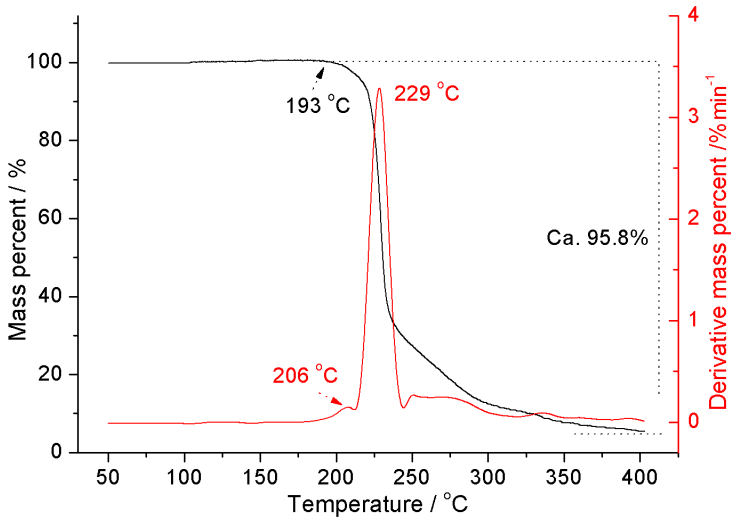

Fig. S11 TG and DTG curves of **11** under nitrogen with a heating rate of 5 °C min^{-1}.

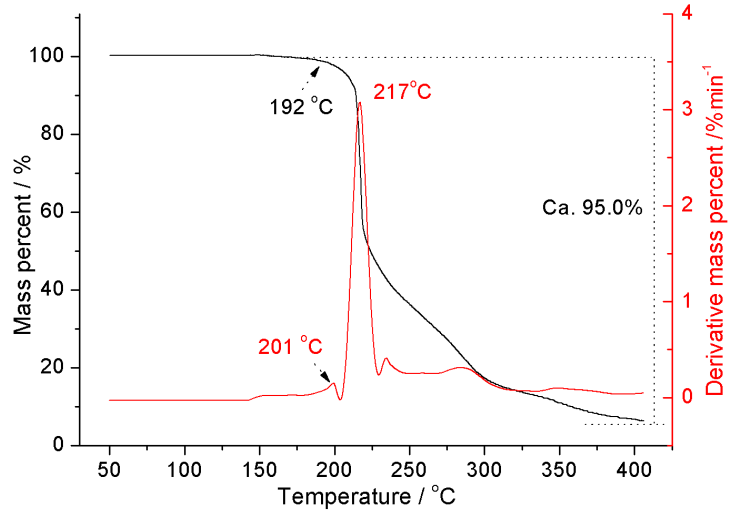

Fig. S12 TG and DTG curves of **12** under nitrogen with a heating rate of 5 °C min^{-1}.

2. Computational data

Computational data: Computations were performed by using the Gaussian09 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

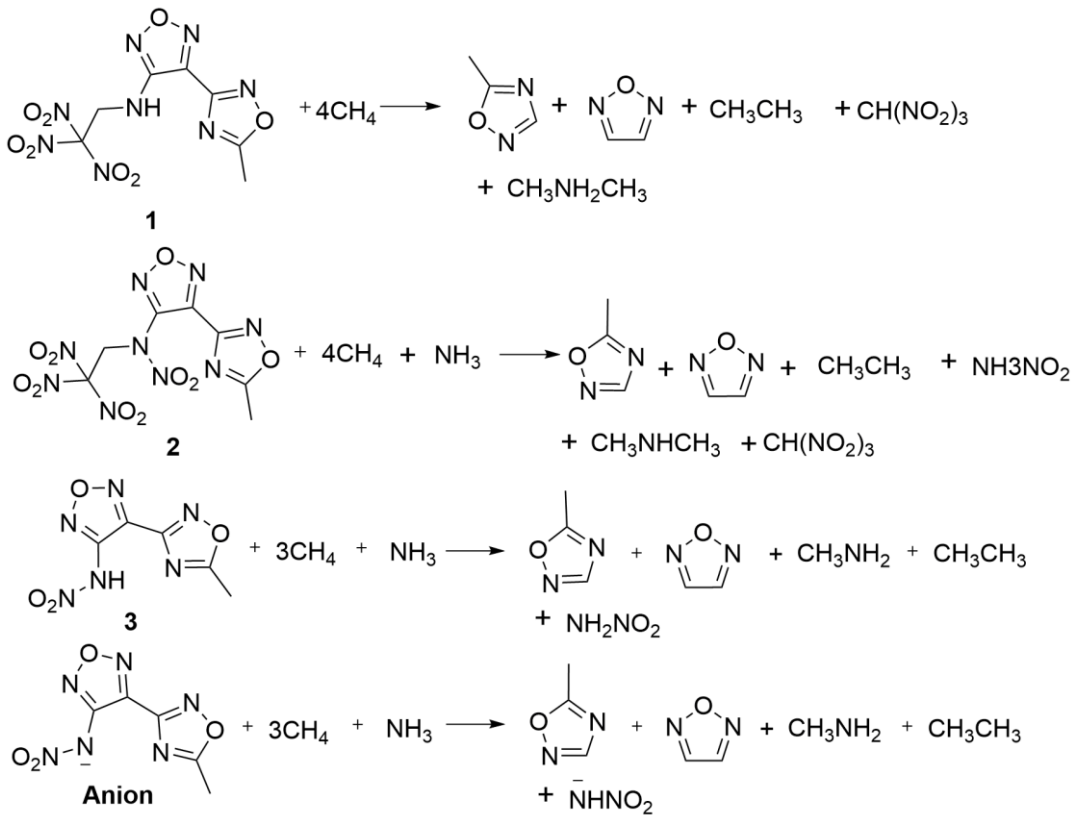

Fig. S13 Isodesmic and tautomeric reactions to compute the HOF.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to

derive the HOF of compounds **1-3**, are shown in Scheme 3. The heats of formation of the furazan and 5-methyl-1,2,4-oxadiazole ring used in the isodesmic reaction are 215.72 and 38.30 kJ mol^{-1}, respectively. The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).

$$\Delta H_{298} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R \quad (1)$$

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression, see Equation (2).

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation [(2)] is the PV work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation [(1)], apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments[6] or from the high-level computing such as CBS-4M.

Based on Born-Haber energy cycles, the heat of formation of a salt can be simplified and expressed as Equation (3), in which ΔH_L is the lattice energy of the salt. This quantity could be predicted by the formula suggested by Jenkins et al (Equation (4)), in which n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for the lattice potential energy, UPOT, takes the form of equation (5), where ρ_m (g cm^{-3}) is the density, M_m (g) is the chemical formula mass of the ionic material and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[7]

$$\Delta H_f^o \text{ (salt, 298 K)} = \Delta H_f^o\text{(cation, 298 K)} + \Delta H_f^o\text{(anion, 298 K)} - \Delta H_L \quad (3)$$

$$\Delta H_L = U_{POT} + [\, p(n_M/2-2) + q(n_X/2-2)]\, RT \quad (4)$$

$$U_{POT}\ (\text{kJ}\cdot\text{mol}^{-1}) = \gamma\,(\rho_m/M_m)1/3 + \delta \quad (5)$$

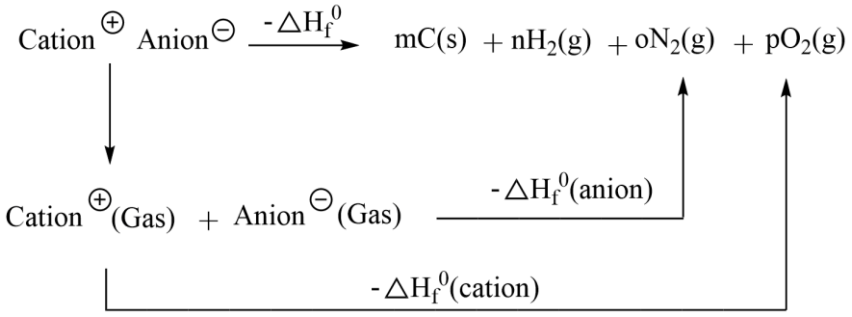

Fig. S14 Born-Haber Cycle for the Formation of Energetic Salts.

Table S1 *Ab initio* computational values of compounds **1-12**.

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
1	-1310.0769173	452.34	57.73	295.05
2	-1514.5884466	455.92	64.22	412.71
3	-822.3235213	299.92	36.04	355.76
anino	-821.8030073	264.37	32.47	173.33
hydroxylammonium	-132.0863674	137.02	11.32	691.11
ammonium	-56.9203229	124.71	9.98	636.74
guanidinium	-205.8352797	229.32	15.58	574.74
aminoguanidinium	-261.143676	266.25	17.03	756.62
hydrazinium	-112.2417207	172.94	12.04	763.05
3-amino-1,2,4-triazolium	-298.0616336	232.63	14.97	854.22
1,2,4-triazolium	-242.669331	184.02	12.27	823.20
5-aminotetrazolium	-314.0542798	203.21	15.63	1883.52
CH_4	-40.5339263	112.26	10.04	-74.60[e]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.40[e]
CH_3NHCH_3	-135.2095645	231.80	14.35	-18.80[e]
CH_3CH_3	-79.8565413	187.31	11.79	-84.00[e]
CH_3NH_2	-95.8938402	160.78	11.64	-22.5[e]
NH_3	-56.5826356	86.27	10.05	-45.90[e]
NH_2NO_2	-261.1248168	98.79	12.39	-3.90[e]
$NHNO_2^-$	-260.5730748	65.76	11.37	-120.22[f]
	-262.1183629	114.62	11.84	215.72[f]
	-301.4971523	185.97	16.36	38.29[f]

[a] Total energy calculated by B3LYP/6-31+G** method (a.u); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}); [e] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL; [f] calculated by CBS-4 Enthalpy.

3. Single-crystal X-ray diffraction analysis of compound 1

Table S2 Selected bond lengths [Å] for **1**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.402(3)	N5-C4	1.519(3)
O1-N2	1.372(3)	N6-C4	1.520(3)
O2-N4	1.217(3)	N7-C5	1.301(3)
O3-N4	1.211(3)	N8-C5	1.373(3)
O4-N5	1.209(3)	N8-C6	1.297(3)
O5-N5	1.213(3)	C1-C2	1.428(3)
O6-N6	1.215(3)	C2-C5	1.458(3)
O7-N6	1.220(3)	C3-C4	1.527(3)
O8-N7	1.405(3)	C6-C7	1.480(3)
O8-C6	1.343(3)	N3-C1	1.367(3)
N1-C1	1.310(3)	N3-C3	1.437(3)
N2-C2	1.302(3)	N4-C4	1.523(4)

Table S3 Selected bond angles [º] for **1**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	111.46(17)	C1-N3-H3	117.9(16)
N7-O8-C6	106.73(18)	N4-C4-N6	106.15(19)
O1-N1-C1	104.31(18)	N4-C4-N5	107.38(19)
O1-N2-C2	105.55(19)	N5-C4-C3	111.31(19)
C1-N3-C3	120.29(19)	N4-C4-C3	114.56(19)
O2-N4-O3	127.1(2)	N5-C4-N6	106.86(19)
O2-N4-C4	117.4(2)	N6-C4-C3	110.2(2)
O3-N4-C4	115.5(2)	N7-C5-C2	119.5(2)
O4-N5-O5	127.40(19)	N8-C5-C2	124.6(2)
O4-N5-C4	118.9(2)	N7-C5-N8	115.9(2)
O5-N5-C4	113.7(2)	N8-C6-C7	129.5(2)
O6-N6-O7	127.0(2)	O8-C6-N8	113.4(2)
O6-N6-C4	115.4(2)	O8-C6-C7	117.1(2)
O7-N6-C4	117.6(2)	N2-C2-C1	109.3(2)
O8-N7-C5	102.37(19)	N2-C2-C5	122.6(2)
C5-N8-C6	101.63(19)	C1-C2-C5	128.1(2)
N1-C1-N3	123.6(2)	N3-C3-C4	112.2(2)
N1-C1-C2	109.4(2)	C3-N3-H3	117.6(16)
N3-C1-C2	126.9(2)		

Table S4 Selected torsion angles for **1**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	0.6(3)	O6-N6-C4-N4	87.6(3)
N1-O1-N2-C2	-0.1(3)	O7-N6-C4-C3	144.1(2)

C6-O8-N7-C5	0.1(2)	O8-N7-C5-C2	179.3(2)
N7-O8-C6-C7	179.9(2)	O8-N7-C5-N8	-0.3(3)
N7-O8-C6-N8	0.1(3)	C5-N8-C6-C7	179.9(2)
O1-N1-C1-C2	-0.9(3)	C6-N8-C5-N7	0.4(3)
O1-N1-C1-N3	176.1(2)	C5-N8-C6-O8	-0.3(3)
O1-N2-C2-C5	178.4(2)	C6-N8-C5-C2	-179.2(2)
O1-N2-C2-C1	-0.4(3)	N3-C1-C2-N2	-176.0(3)
C3-N3-C1-N1	13.1(4)	N1-C1-C2-N2	0.9(3)
C1-N3-C3-C4	-108.4(3)	N1-C1-C2-C5	-177.9(2)
C3-N3-C1-C2	-170.5(2)	N3-C1-C2-C5	5.3(4)
O2-N4-C4-N6	0.4(3)	C1-C2-C5-N8	-158.8(2)
O3-N4-C4-N6	-178.74(19)	N2-C2-C5-N7	-157.0(3)
O3-N4-C4-N5	67.3(2)	N2-C2-C5-N8	22.6(4)
O2-N4-C4-N5	-113.7(2)	C1-C2-C5-N7	21.6(4)
O3-N4-C4-C3	-56.9(3)	N3-C3-C4-N5	-49.4(3)
O2-N4-C4-C3	122.2(2)	N3-C3-C4-N6	-167.7(2)
O5-N5-C4-N6	77.3(2)	N3-C3-C4-N4	72.7(3)
O4-N5-C4-C3	138.2(2)	O6-N6-C4-C3	-37.0(3)
O4-N5-C4-N4	12.1(3)	O6-N6-C4-N5	-158.1(2)
O5-N5-C4-C3	-43.0(3)	O7-N6-C4-N4	-91.4(3)
O5-N5-C4-N4	-169.16(19)	O7-N6-C4-N5	23.0(3)
O4-N5-C4-N6	-101.4(2)		

Table S5 Hydrogen bonds for **1** [Å and º].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N3-H3…N7	0.83(2)	2.46(2)	3.018(3)	125.7(19)
C3-H3A…N8	0.9900	2.6000	3.390(3)	137.00
C3-H3B…O5	0.9900	2.4300	3.382(3)	162.00
C3-H3B…N1	0.9900	2.4200	2.834(3)	104.00
C7-H7A…O4	0.9800	2.5500	3.311(3)	134.00
C7-H7C…O5	0.9800	2.5500	3.430(3)	149.00

4. Single-crystal X-ray diffraction analysis of compound 3

Table S6 Selected bond lengths [Å] for **3**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.392(4)	N5-C3	1.296(4)
O1-N2	1.375(4)	N6-C3	1.368(4)
O2-N4	1.214(4)	N6-C4	1.300(5)
O3-N4	1.235(4)	C1-C2	1.430(4)
O4-N5	1.416(4)	C2-C3	1.459(4)
O4-C4	1.341(4)	C4-C5	1.476(5)

N1-C1	1.304(4)	N3-C1	1.383(4)
N2-C2	1.302(4)	N3-N4	1.359(4)

Table S7 Selected bond angles [°] for **3**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	111.5(2)	C1-C2-C3	129.3(3)
N5-O4-C4	106.4(3)	N5-C3-N6	115.2(3)
O1-N1-C1	104.5(3)	N5-C3-C2	120.8(3)
O1-N2-C2	105.6(3)	N6-C3-C2	124.0(3)
N4-N3-C1	123.4(3)	N4-N3-H3	115.0(19)
O2-N4-O3	125.9(3)	C1-N3-H3	120.3(19)
O2-N4-N3	119.4(3)	N6-C4-C5	129.4(3)
O3-N4-N3	114.8(3)	O4-C4-N6	112.8(3)
O4-N5-C3	102.9(3)	O4-C4-C5	117.8(3)
C3-N6-C4	102.7(3)	N3-C1-C2	124.4(3)
N1-C1-N3	126.0(3)	N2-C2-C1	108.8(3)
N1-C1-C2	109.6(3)	N2-C2-C3	121.9(3)

Table S8 Selected torsion angles [°] for **3**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	-0.6(3)	C3-N6-C4-O4	0.6(4)
N1-O1-N2-C2	0.2(3)	C3-N6-C4-C5	179.3(4)
N5-O4-C4-C5	-179.3(3)	C4-N6-C3-N5	-0.7(4)
C4-O4-N5-C3	0.0(3)	N3-C1-C2-C3	1.4(5)
N5-O4-C4-N6	-0.4(4)	N1-C1-C2-N2	-0.6(4)
O1-N1-C1-C2	0.7(3)	N1-C1-C2-C3	-178.3(3)
O1-N1-C1-N3	-179.0(3)	N3-C1-C2-N2	179.1(3)
O1-N2-C2-C3	178.1(3)	N2-C2-C3-N5	178.4(3)
O1-N2-C2-C1	0.2(4)	C1-C2-C3-N5	-4.2(5)
C1-N3-N4-O3	175.4(3)	C1-C2-C3-N6	175.6(3)
C1-N3-N4-O2	-3.5(4)	N2-C2-C3-N6	-1.8(5)
N4-N3-C1-N1	23.3(5)	O4-N5-C3-C2	-179.8(3)
N4-N3-C1-C2	-156.3(3)	C4-N6-C3-C2	179.6(3)
O4-N5-C3-N6	0.4(3)		

Table S9 Hydrogen bonds for **3** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N3-H3…N5	0.88(3)	2.54(3)	2.953(4)	110(2)
N3-H3…N6	0.88(3)	2.00(3)	2.862(4)	168(2)

C5-H5B…O2	0.9800	2.5400	3.430(5)	150.00

5. Single-crystal X-ray diffraction analysis of compound 4

Table S10 Selected bond lengths [Å] for **4**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.394(3)	N6-C4	1.279(4)
O1-N2	1.370(3)	C1-C2	1.427(4)
O2-N4	1.229(3)	C2-C3	1.453(4)
O3-N4	1.264(3)	C4-C5	1.464(4)
O4-N5	1.400(3)	O5-N7	1.399(3)
O4-C4	1.337(4)	N3-N4	1.316(3)
N1-C1	1.312(4)	N3-C1	1.365(4)
N2-C2	1.285(4)	N5-C3	1.285(4)
N6-C3	1.368(4)		

Table S11 Selected bond angles [º] for **4**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	111.1(2)	N6-C3-C2	121.9(2)
N5-O4-C4	106.1(2)	O4-C4-N6	113.5(3)
O1-N1-C1	105.0(2)	O4-C4-C5	116.7(2)
O1-N2-C2	105.6(2)	N6-C4-C5	129.9(3)
N4-N3-C1	116.3(2)	C1-C2-C3	129.7(3)
O2-N4-O3	119.9(2)	N5-C3-N6	115.2(2)
O2-N4-N3	125.1(2)	N5-C3-C2	122.9(2)
O3-N4-N3	115.1(2)	N1-C1-C2	108.1(2)
O4-N5-C3	103.1(2)	N3-C1-C2	120.9(2)
C3-N6-C4	102.2(2)	N2-C2-C1	110.2(2)
N1-C1-N3	131.0(2)	N2-C2-C3	120.1(2)

Table S12 Selected torsion angles [º] for **4**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	-0.3(3)	O4-N5-C3-C2	179.8(2)
N1-O1-N2-C2	0.5(3)	C4-N6-C3-C2	-179.7(3)
N5-O4-C4-C5	-179.3(2)	C3-N6-C4-O4	-0.3(3)
C4-O4-N5-C3	-0.1(3)	C3-N6-C4-C5	179.2(3)
N5-O4-C4-N6	0.2(3)	C4-N6-C3-N5	0.2(3)
O1-N1-C1-C2	0.0(3)	N3-C1-C2-C3	0.2(5)
O1-N1-C1-N3	-179.6(3)	N1-C1-C2-N2	0.3(3)

O1-N2-C2-C3	179.3(2)	N1-C1-C2-C3	-179.4(3)
O1-N2-C2-C1	-0.5(3)	N3-C1-C2-N2	179.9(3)
C1-N3-N4-O3	-177.3(2)	N2-C2-C3-N5	-176.0(3)
C1-N3-N4-O2	2.3(4)	C1-C2-C3-N5	3.6(5)
N4-N3-C1-N1	-6.9(4)	C1-C2-C3-N6	-176.5(3)
N4-N3-C1-C2	173.7(2)	N2-C2-C3-N6	3.9(4)
O4-N5-C3-N6	-0.1(3)		

Table S13 Hydrogen bonds for **4** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O5-H5…O3	0.83(3)	1.84(3)	2.667(3)	178(4)
O5-H5…N3	0.83(3)	2.59(3)	3.150(3)	126(3)[i]
O5-H5…N4	0.83(3)	2.61(3)	3.377(3)	155(3) [i]
N7-H7A…O3	0.90(2)	1.97(2)	2.791(3)	152(2)
N7-H7A…N4	0.90(2)	2.59(2)	3.342(3)	141.6(17)
N7-H7B…O5	0.90(2)	2.43(2)	2.897(3)	112.8(16)
N7-H7B…N3	0.90(2)	2.52(2)	3.108(3)	124.3(17) [i]
N7-H7B…N5	0.90(2)	2.19(2)	2.999(3)	149.6(18) [i]
N7-H7C…O2	0.910(19)	2.29(2)	2.770(3)	112.8(16)
N7-H7C…N1	0.910(19)	2.08(2)	2.919(3)	153(2) [i]
C5-H5C…N6	0.9800	2.5700	3.539(4)	169.00 [i]

Symmetry codes: [i] 1/2-x,1/2-y,-z

6. Single-crystal X-ray diffraction analysis of compound **7**·H_2O

Table S14 Selected bond lengths [Å] for **7**·H_2O.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.397(5)	N3-N4	1.303(5)
O1-N2	1.387(5)	N3-C1	1.375(5)
O2-N4	1.256(5)	N5-C3	1.295(5)
O3-N4	1.257(4)	N6-C4	1.297(6)
O4-N5	1.417(5)	N6-C3	1.385(5)
O4-C4	1.345(5)	C1-C2	1.439(6)
N1-C1	1.310(6)	C2-C3	1.468(5)
N2-C2	1.292(6)	C4-C5	1.480(6)

Table S15 Selected bond angles [°] for **7**·H_2O.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	110.8(3)	O2-N4-N3	117.1(3)
N5-O4-C4	106.5(3)	O3-N4-N3	124.8(3)

O1-N1-C1	105.5(3)	O4-N5-C3	102.7(3)
O1-N2-C2	105.5(3)	C3-N6-C4	101.9(3)
N4-N3-C1	117.7(3)	N3-C1-C2	119.3(4)
O2-N4-O3	118.2(3)	N1-C1-C2	108.2(4)
N5-C3-C2	123.1(4)	N1-C1-N3	132.4(4)
N6-C3-C2	121.3(3)	N2-C2-C3	120.8(4)
O4-C4-C5	117.3(4)	N2-C2-C1	110.0(4)
N6-C4-C5	129.3(4)	C1-C2-C3	129.2(4)
O4-C4-N6	113.4(4)	N5-C3-N6	115.6(3)

Table S16 Selected torsion angles [º] for **7**·H_2O.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	-0.3(4)	N1-O1-N2-C2	0.1(4)
O1-N1-C1-C2	0.4(4)	C4-O4-N5-C3	-0.6(4)
O1-N2-C2-C3	178.5(4)	N5-O4-C4-C5	-177.1(4)
O1-N2-C2-C1	0.1(5)	N5-O4-C4-N6	0.2(5)
C1-N3-N4-O3	-1.4(6)	O1-N1-C1-N3	177.9(4)
C1-N3-N4-O2	178.7(4)	N4-N3-C1-N1	6.8(7)
N1-C1-C2-N2	-0.3(5)	N4-N3-C1-C2	-175.9(4)
N1-C1-C2-C3	-178.5(4)	O4-N5-C3-N6	0.8(5)
N3-C1-C2-N2	-178.2(4)	O4-N5-C3-C2	178.4(4)
N2-C2-C3-N5	178.5(4)	C4-N6-C3-C2	-178.3(4)
C1-C2-C3-N5	-3.6(7)	C3-N6-C4-O4	0.2(5)
C1-C2-C3-N6	173.9(4)	C3-N6-C4-C5	177.1(4)
N2-C2-C3-N6	-4.1(6)	C4-N6-C3-N5	-0.7(5)
N3-C1-C2-C3	3.6(7)		

Table S17 Hydrogen bonds for **7**·H_2O [Å and º].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
O5-H5D…O2	0.81(4)	2.11(3)	2.878(4)	159(5)
O5-H5D…N3	0.81(4)	2.62(4)	2.993(4)	110(4)
O5-H5E…N5	0.83(3)	2.19(3)	3.011(5)	168(4)
C5-H5A…N6	0.9800	2.6100	3.560(6)	165.00

7. Single-crystal X-ray diffraction analysis of compound 9

Table S18 Selected bond lengths [Å] for **9**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.402(2)	C4-C5	1.479(3)
O1-N2	1.377(3)	N7-C6	1.337(3)

O2-N4	1.256(3)	N8-N9	1.408(3)
O3-N4	1.253(3)	N8-C6	1.321(3)
O4-N5	1.412(3)	N10-C6	1.320(3)
O4-C4	1.346(3)	N6-C3	1.377(3)
N1-C1	1.315(3)	N6-C4	1.295(3)
N2-C2	1.302(3)	C1-C2	1.443(3)
N3-N4	1.326(3)	C2-C3	1.461(3)
N3-C1	1.383(3)	N5-C3	1.304(3)

Table S19 Selected bond angles [º] for **9**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-N2	111.14(17)	N9-N8-C6	118.3(2)
N5-O4-C4	106.47(17)	N7-C6-N8	118.7(2)
O1-N1-C1	105.09(18)	N7-C6-N10	121.2(2)
O1-N2-C2	105.89(17)	N8-C6-N10	120.09(19)
N4-N3-C1	116.0(2)	N2-C2-C3	120.69(19)
O2-N4-O3	120.15(19)	C1-C2-C3	130.0(2)
O2-N4-N3	116.4(2)	N5-C3-N6	115.1(2)
O3-N4-N3	123.38(19)	N5-C3-C2	122.40(19)
O4-N5-C3	102.82(17)	N6-C3-C2	122.5(2)
C3-N6-C4	102.38(19)	O4-C4-N6	113.22(19)
N1-C1-N3	130.3(2)	O4-C4-C5	117.6(2)
N1-C1-C2	108.52(19)	N6-C4-C5	129.2(2)
N3-C1-C2	120.9(2)	N2-C2-C1	109.3(2)

Table S20 Selected torsion angles [º] for **9**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N2-O1-N1-C1	0.8(3)	N9-N8-C6-N10	-4.0(4)
N1-O1-N2-C2	-0.5(3)	C3-N6-C4-O4	-0.1(3)
N5-O4-C4-C5	178.8(2)	C3-N6-C4-C5	-178.9(3)
C4-O4-N5-C3	0.4(3)	C4-N6-C3-N5	0.4(3)
N5-O4-C4-N6	-0.1(3)	N3-C1-C2-C3	5.4(4)
O1-N1-C1-C2	-0.8(3)	N1-C1-C2-N2	0.5(3)
O1-N1-C1-N3	173.4(3)	N1-C1-C2-C3	-179.8(3)
O1-N2-C2-C3	-179.8(2)	N3-C1-C2-N2	-174.3(2)
O1-N2-C2-C1	0.0(3)	N2-C2-C3-N5	-178.5(3)
C1-N3-N4-O3	7.5(4)	C1-C2-C3-N5	1.8(4)
C1-N3-N4-O2	-175.3(2)	C1-C2-C3-N6	-176.9(3)
N4-N3-C1-N1	21.6(4)	N2-C2-C3-N6	2.8(4)
N4-N3-C1-C2	-164.8(2)	N9-N8-C6-N7	178.9(2)
O4-N5-C3-N6	-0.5(3)	C4-N6-C3-C2	179.2(2)
O4-N5-C3-C2	-179.2(2)		

Table S21 Hydrogen bonds for **9** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N7-H7A…N2	0.87(2)	2.40(2)	3.155(3)	144.2(19)[i]
N7-H7B…N3	0.89(2)	2.20(2)	3.084(3)	169(2) [i]
N8-H8…O2	0.87(2)	2.02(2)	2.884(3)	169(2)
N9-H9B…O3	0.876(17)	2.41(2)	3.024(3)	127.4(18)
N9-H9B…N1	0.876(17)	2.367(17)	3.223(3)	165.8(19) [i]
N10-H10A…N9	0.874(16)	2.28(2)	2.653(3)	105.8(18)
N10-H10A…N6	0.874(16)	2.261(17)	3.108(3)	163(2)
N10-H10B…O3	0.88(2)	2.08(2)	2.944(3)	169(2)

Symmetry codes: [i] x,-1+y,z

8. ^{1}H NMR and ^{13}C NMR spectra of compounds 1-12

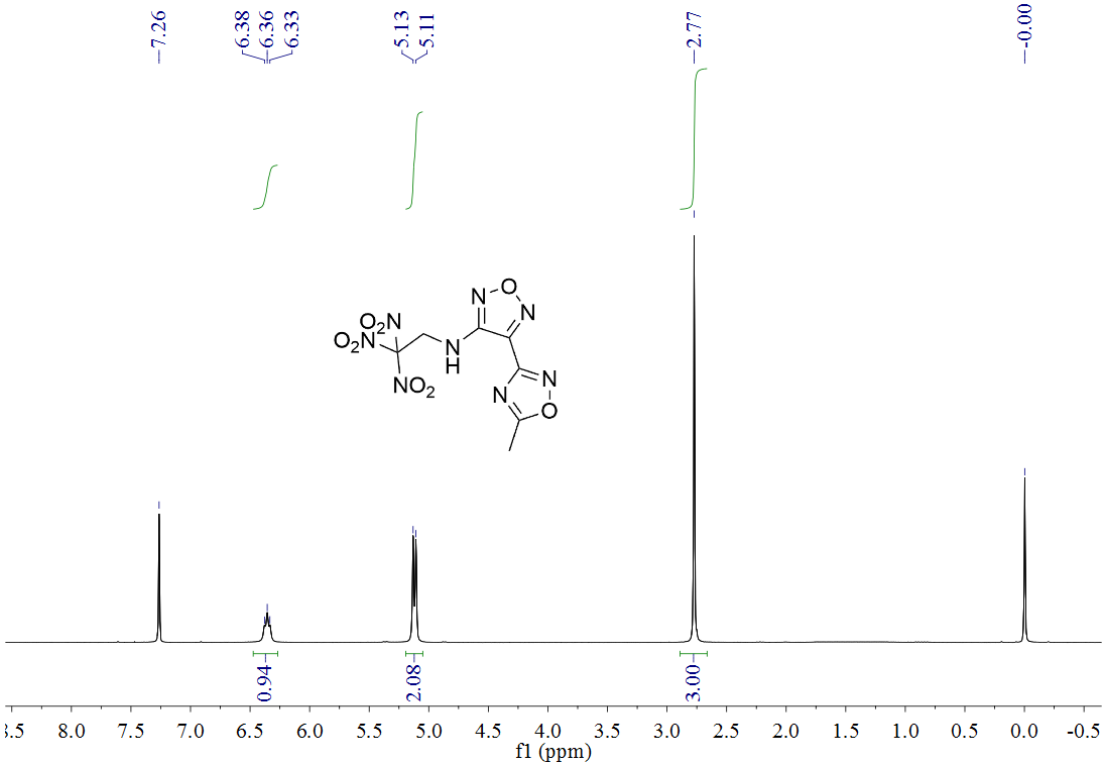

Fig. S15 ^{1}H-NMR spectrum of **1** in $CDCl_3$.

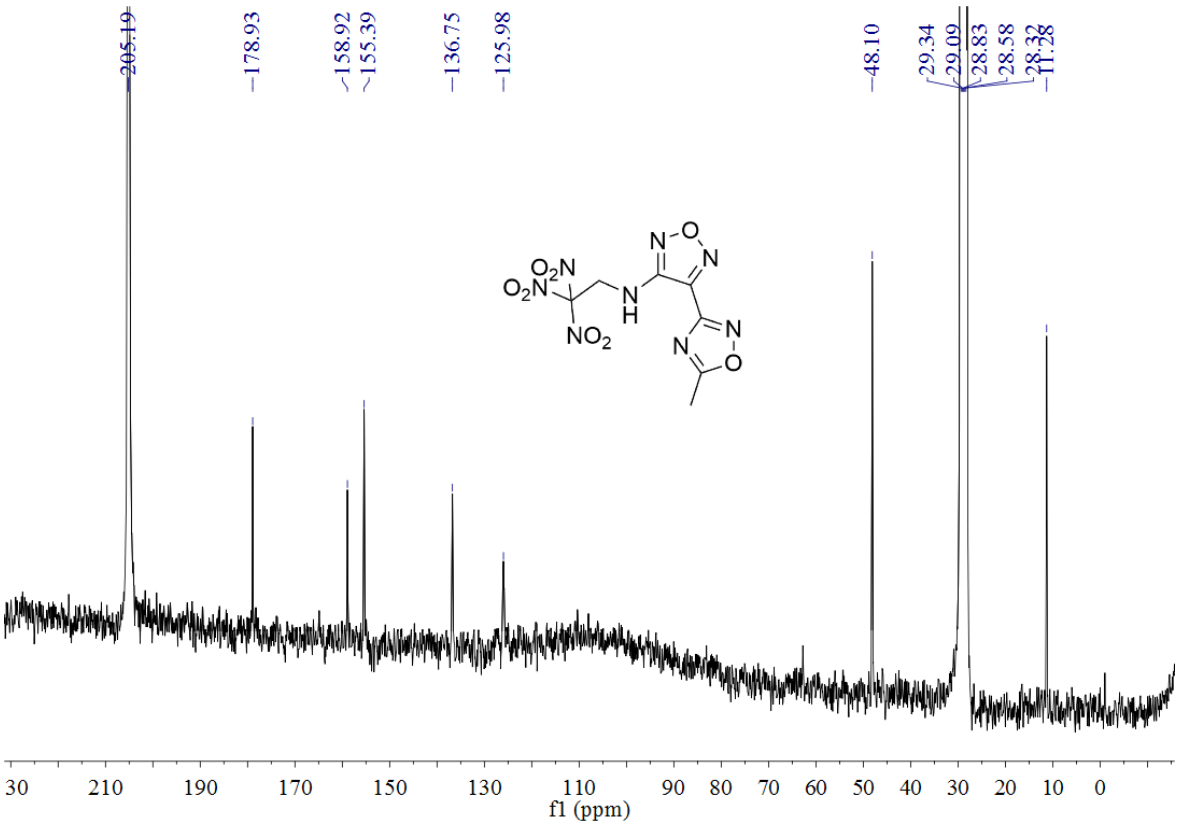

Fig. S16 ^{13}C-NMR spectrum of **1** in d_6-acetone.

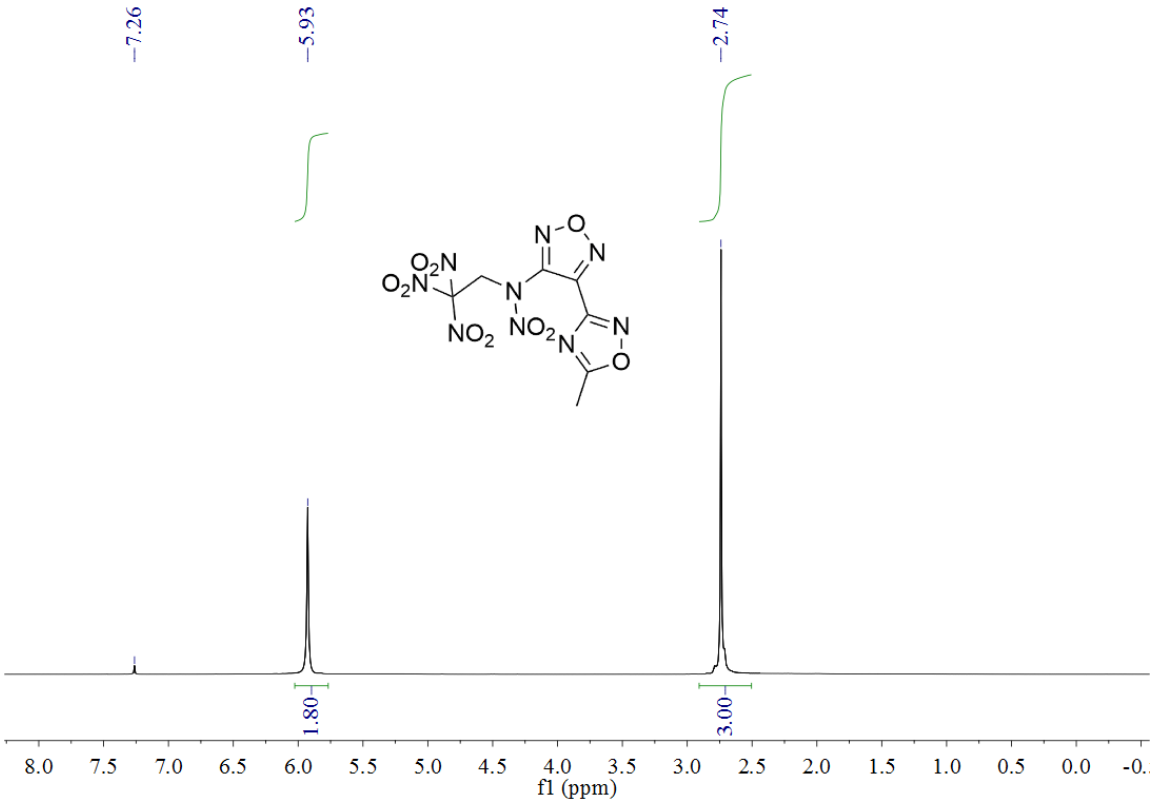

Fig. S17 ^{1}H-NMR spectrum of **2** in $CDCl_3$.

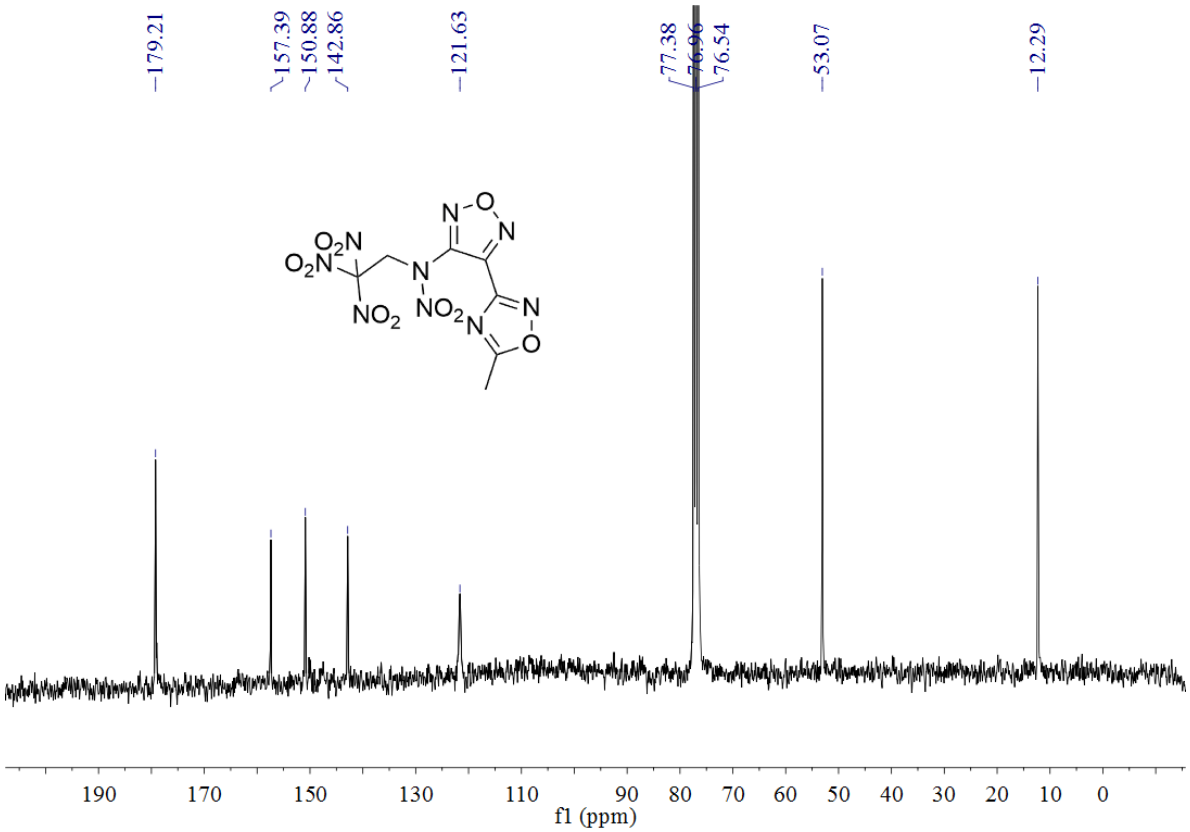

Fig. S18 ^{13}C-NMR spectrum of **2** in d_6-acetone.

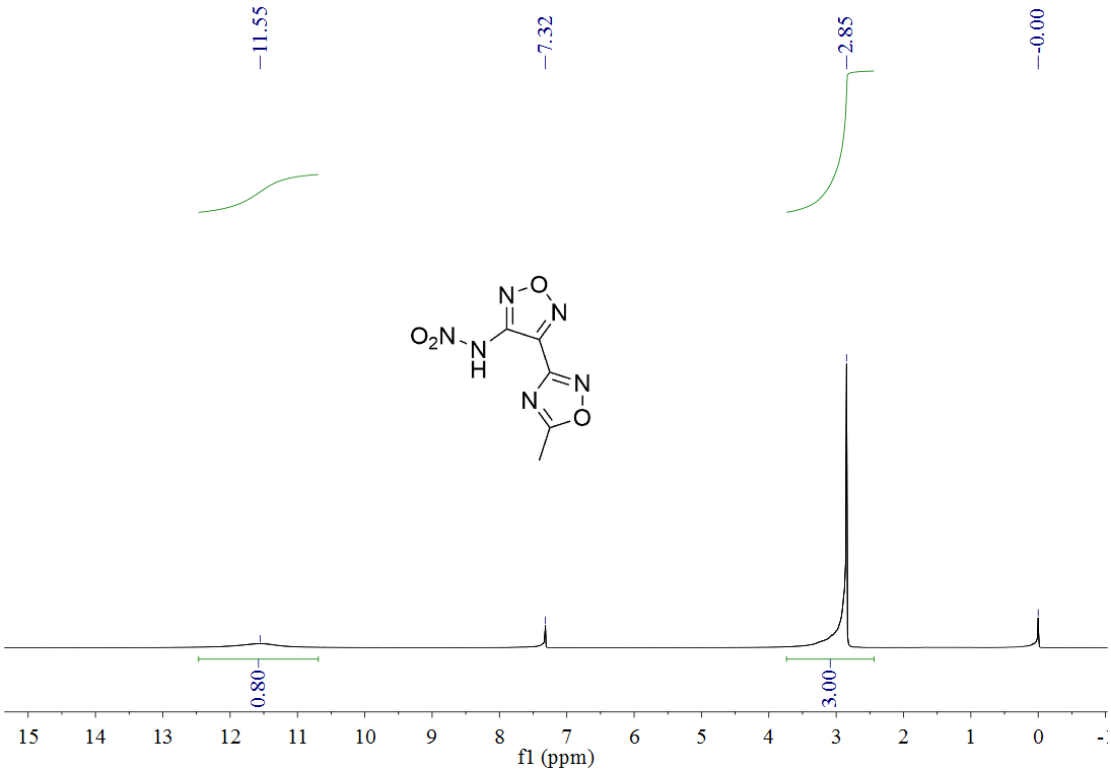

Fig. S19 ^{1}H-NMR spectrum of **3** in $CDCl_3$.

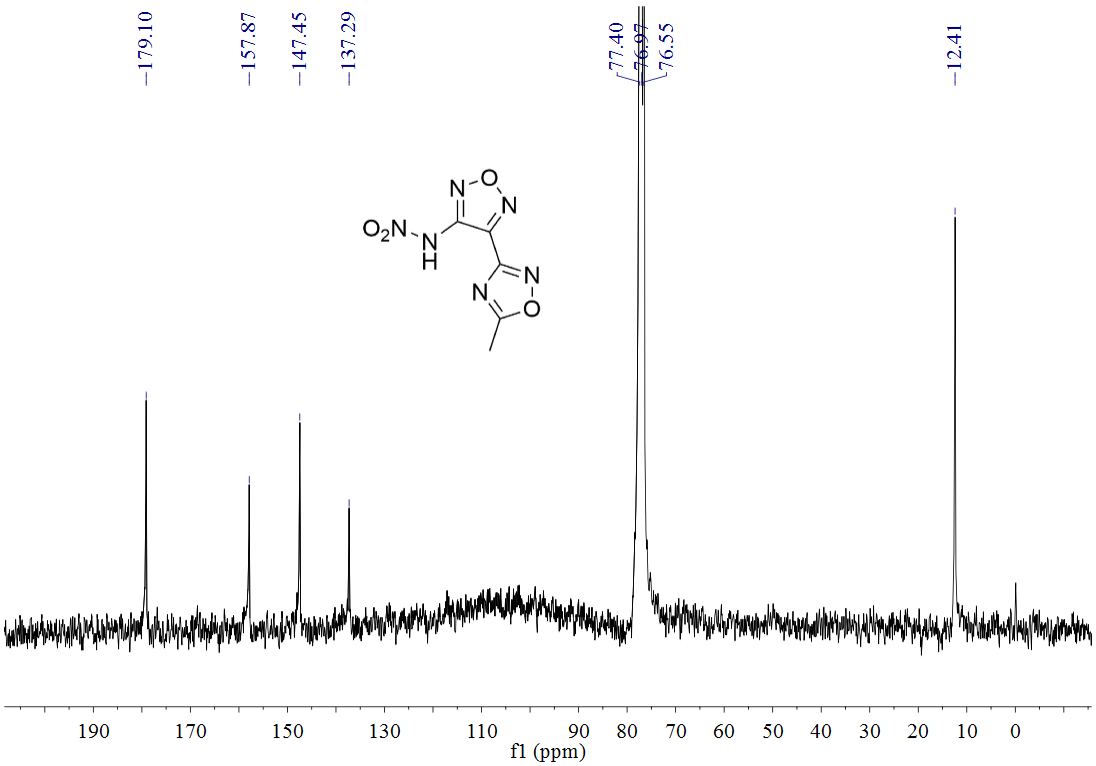

Fig. S20 ^{13}C-NMR spectrum of **3** in $CDCl_3$.

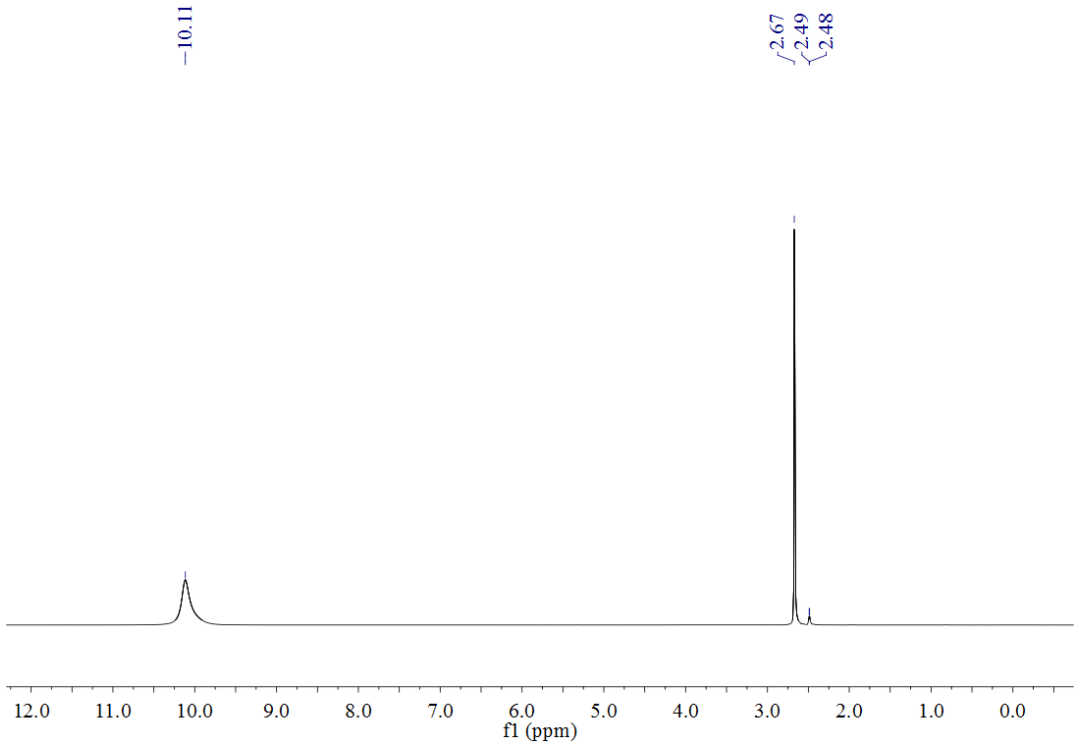

Fig. S21 ^{1}H-NMR spectrum of **4** in d_6-DMSO.

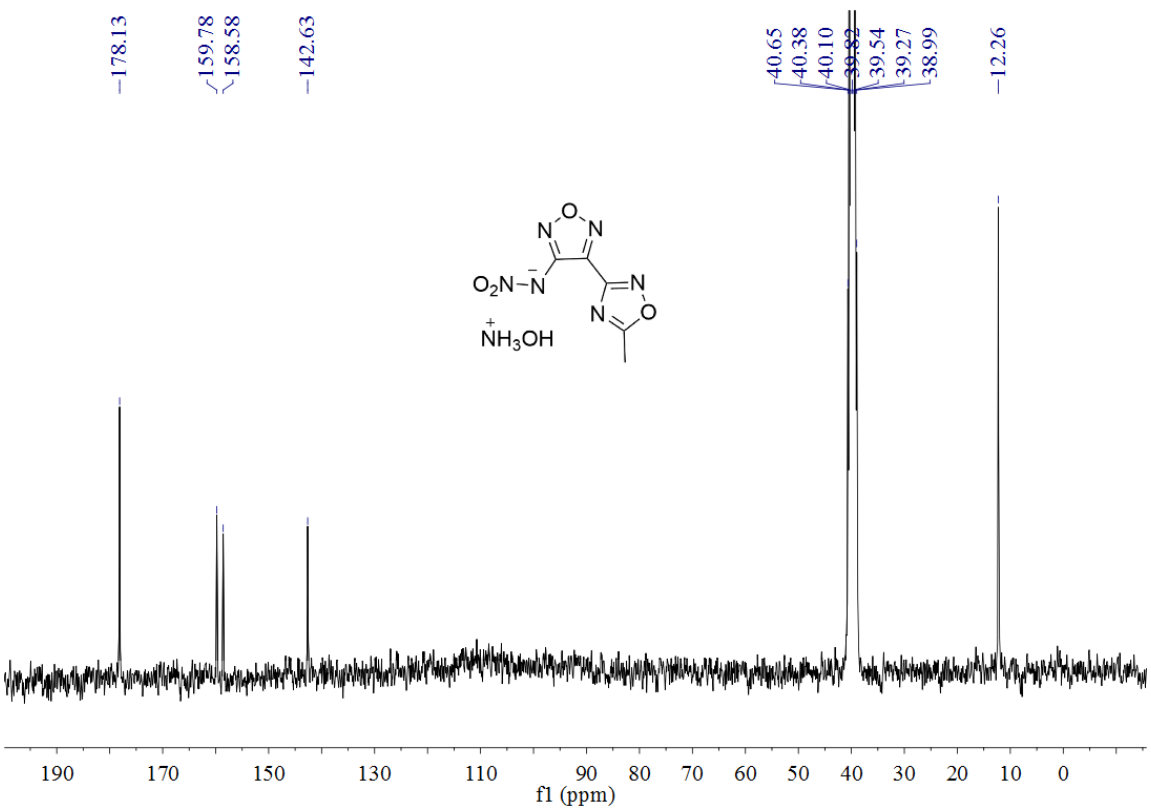

Fig. S22 ^{13}C-NMR spectrum of **4** in d_6-DMSO.

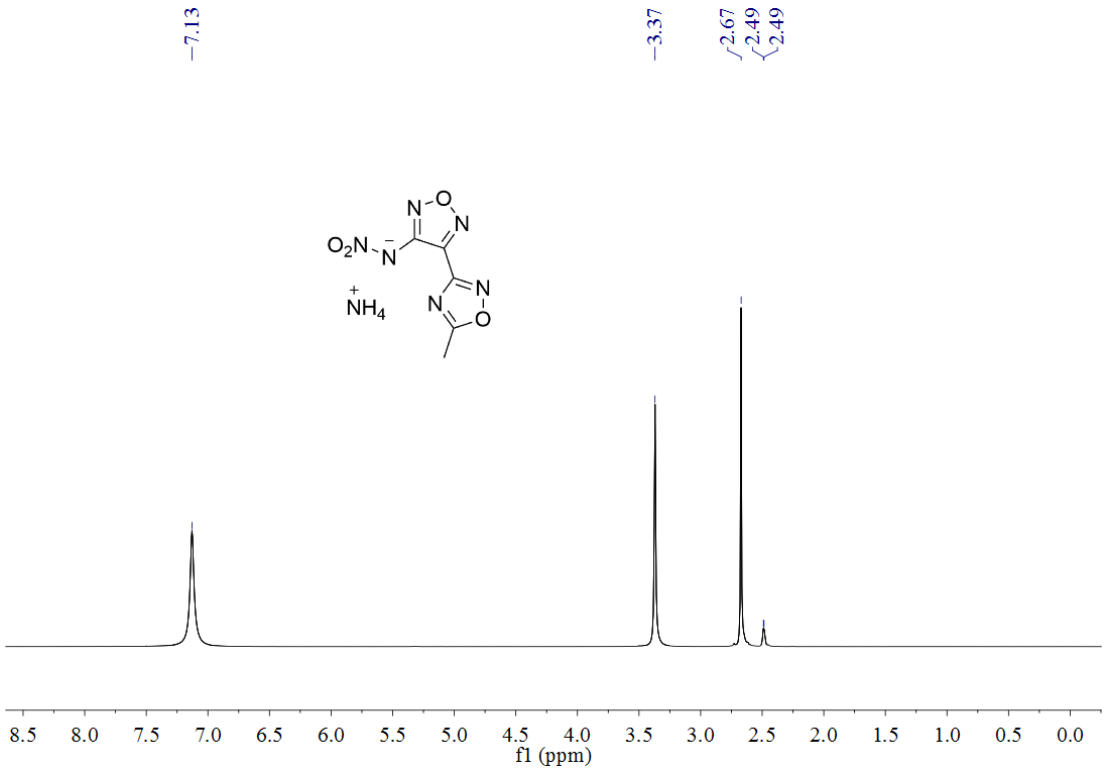

Fig. S23 ^{1}H-NMR spectrum of **5** in d_6-DMSO.

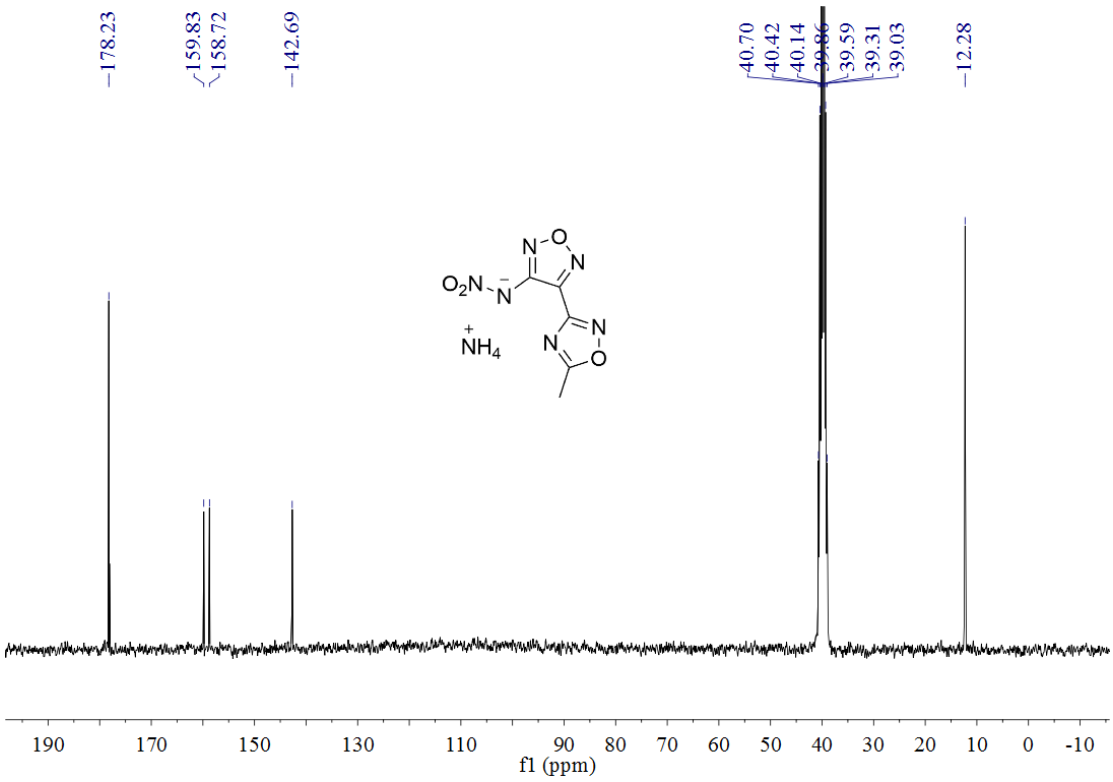

Fig. S24 ^{13}C-NMR spectrum of **5** in d_6-DMSO.

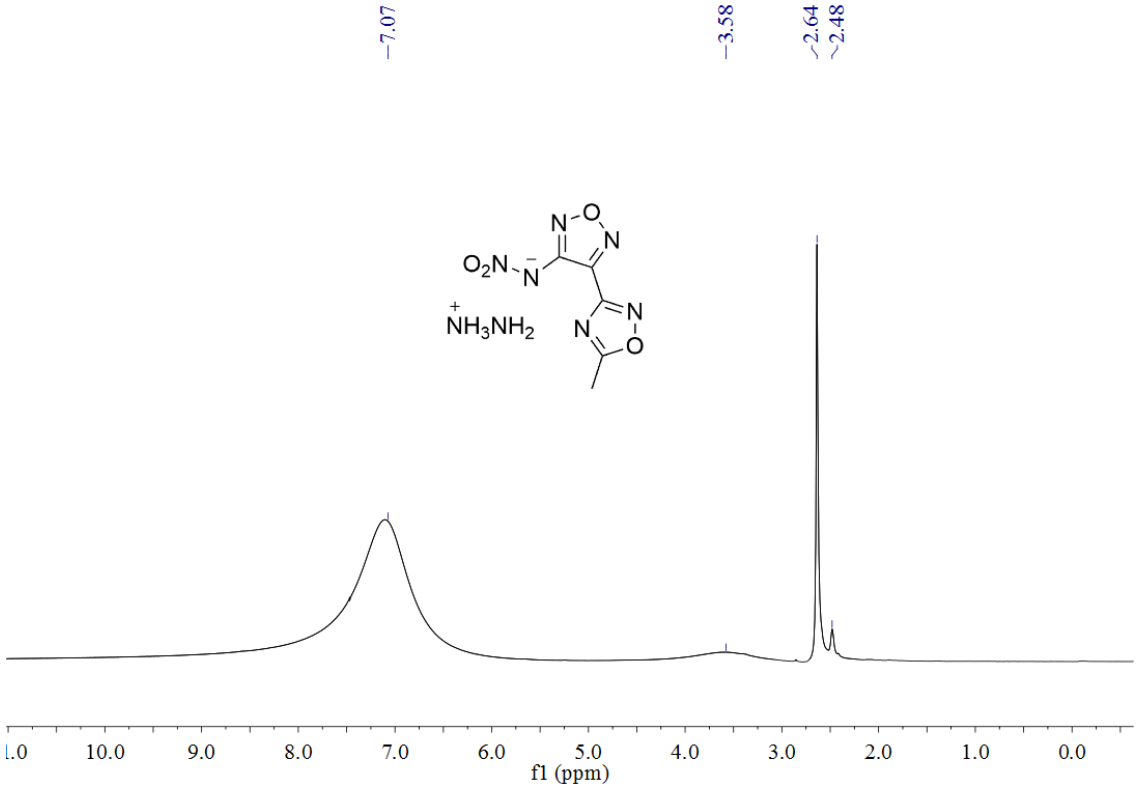

Fig. S25 ^{1}H-NMR spectrum of **6** in d_6-DMSO.

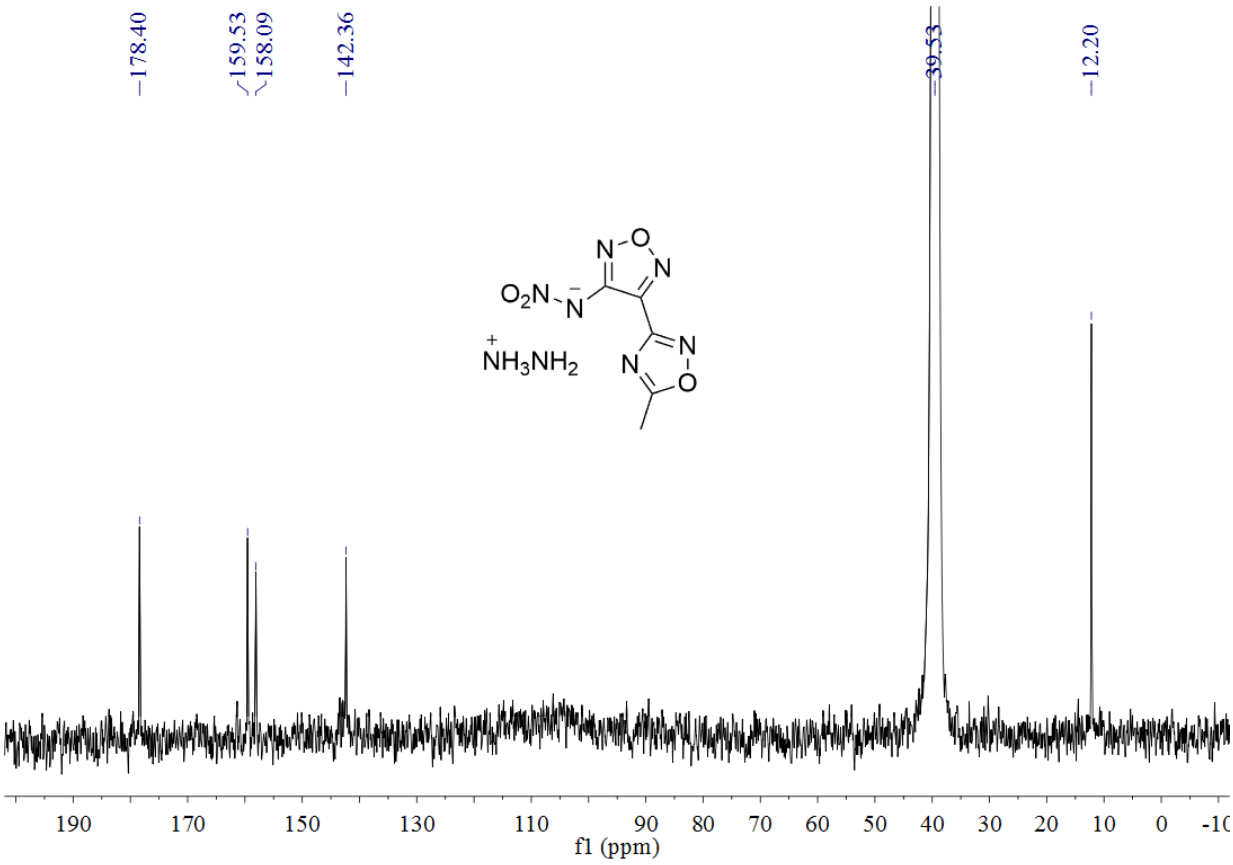

Fig. S26 ^{13}C-NMR spectrum of **6** in d_6-DMSO.

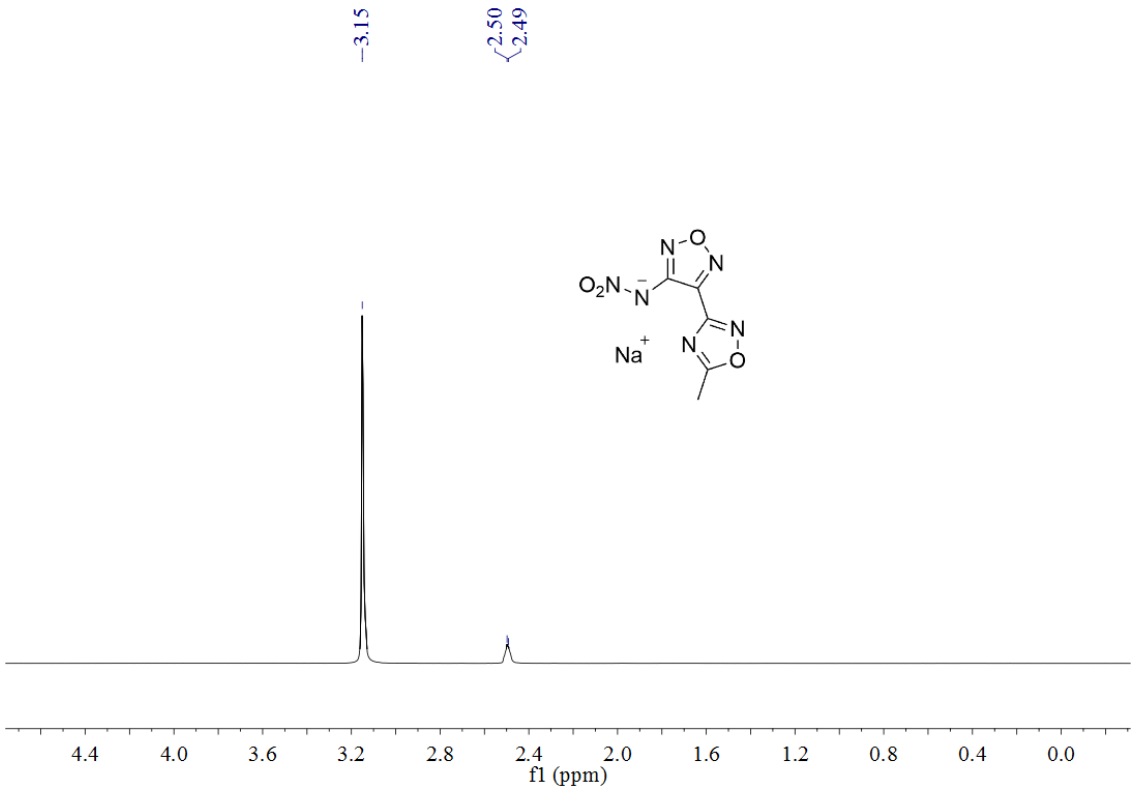

Fig. S27 ^{1}H-NMR spectrum of **7** in d_6-DMSO.

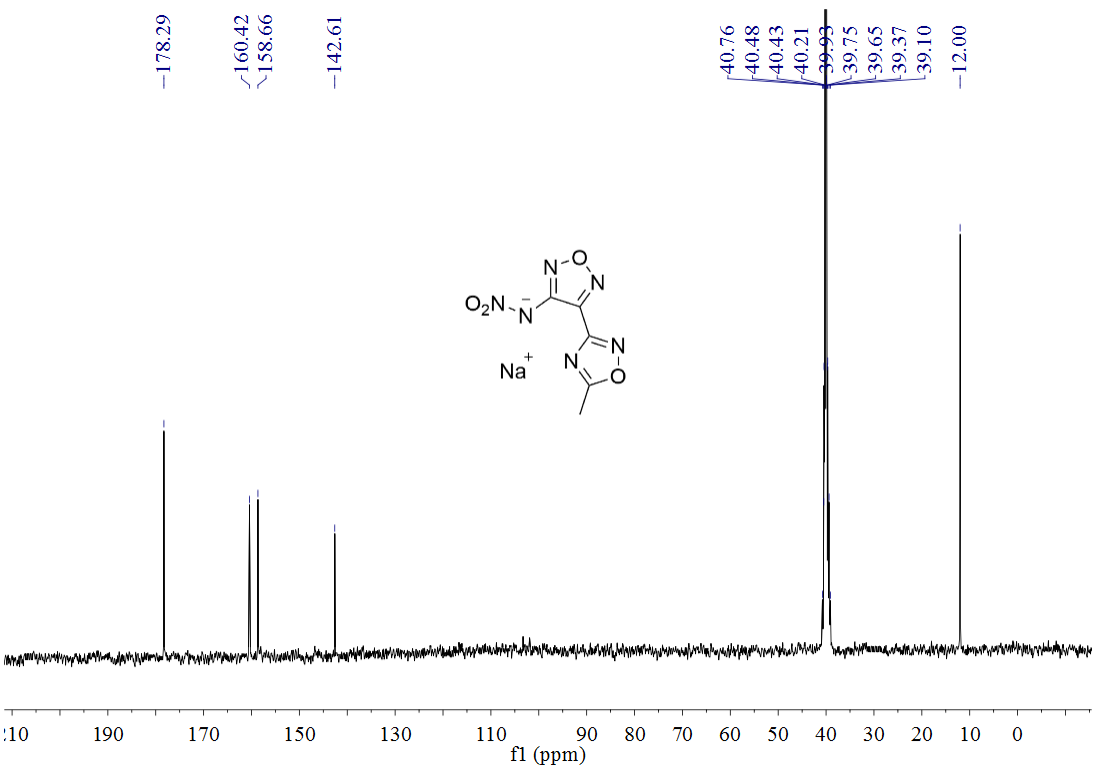

Fig. S28 ^{13}C-NMR spectrum of **7** in d_6-DMSO.

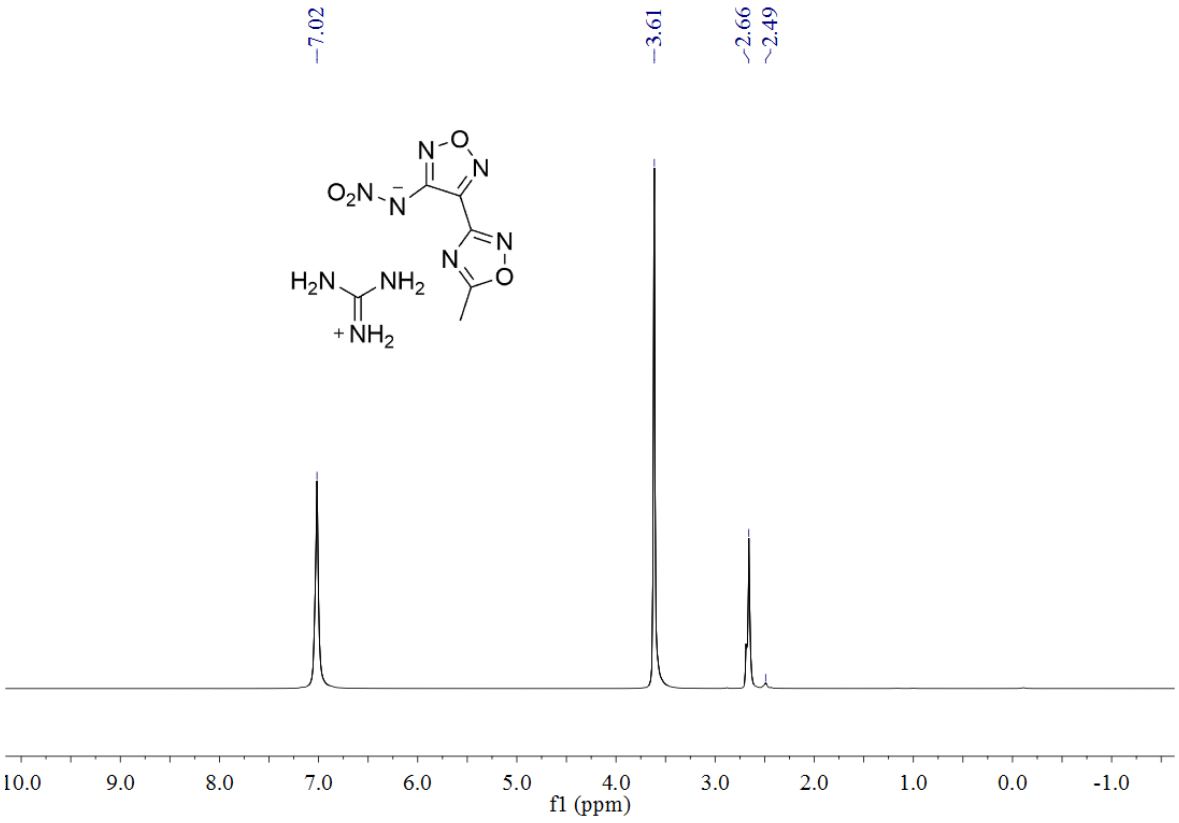

Fig. S29 ^{1}H-NMR spectrum of **8** in d_6-DMSO.

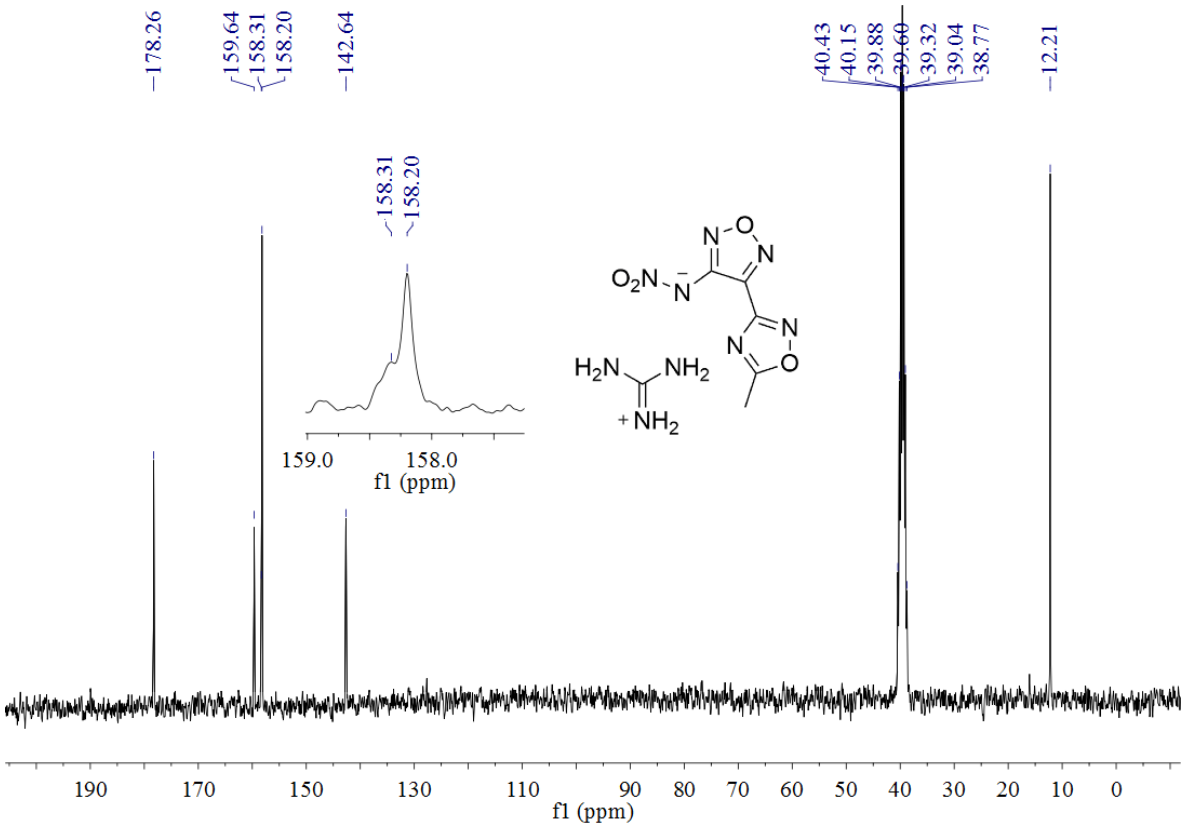

Fig. S30 ^{13}C-NMR spectrum of **8** in d_6-DMSO.

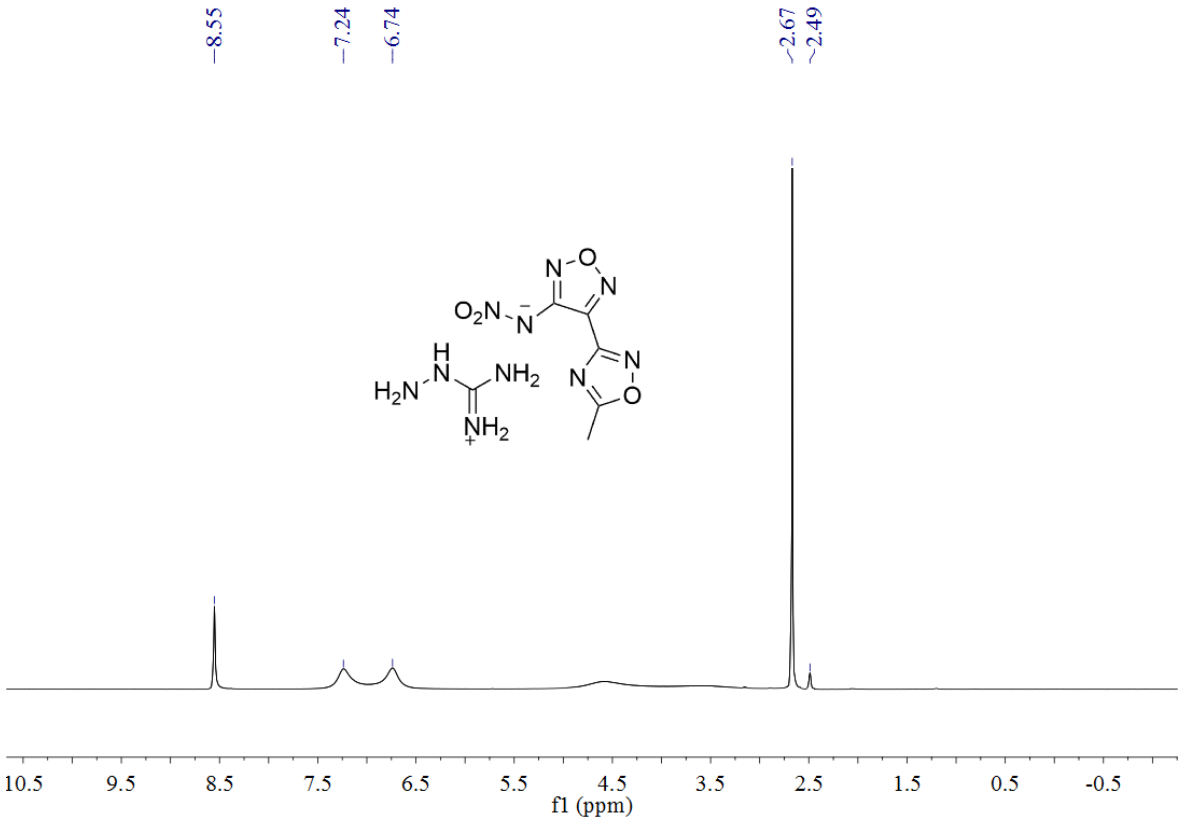

Fig. S31 ^{1}H-NMR spectrum of **9** in d_6-DMSO.

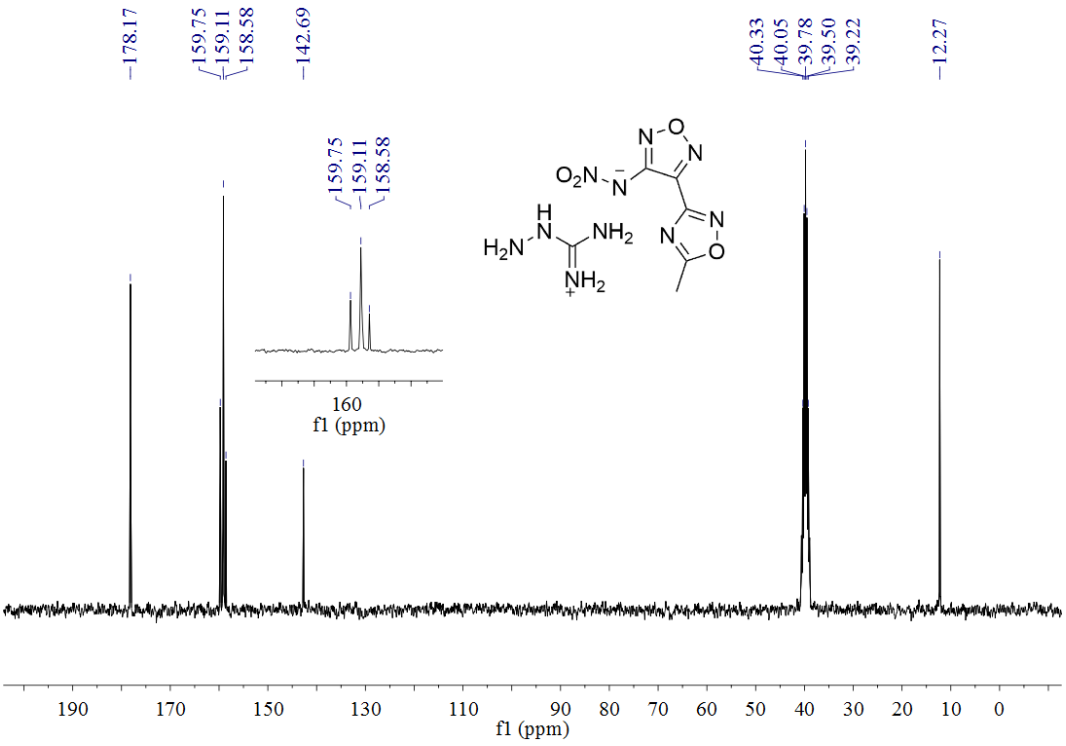

Fig. S32 ^{13}C-NMR spectrum of **9** in d_6-DMSO.

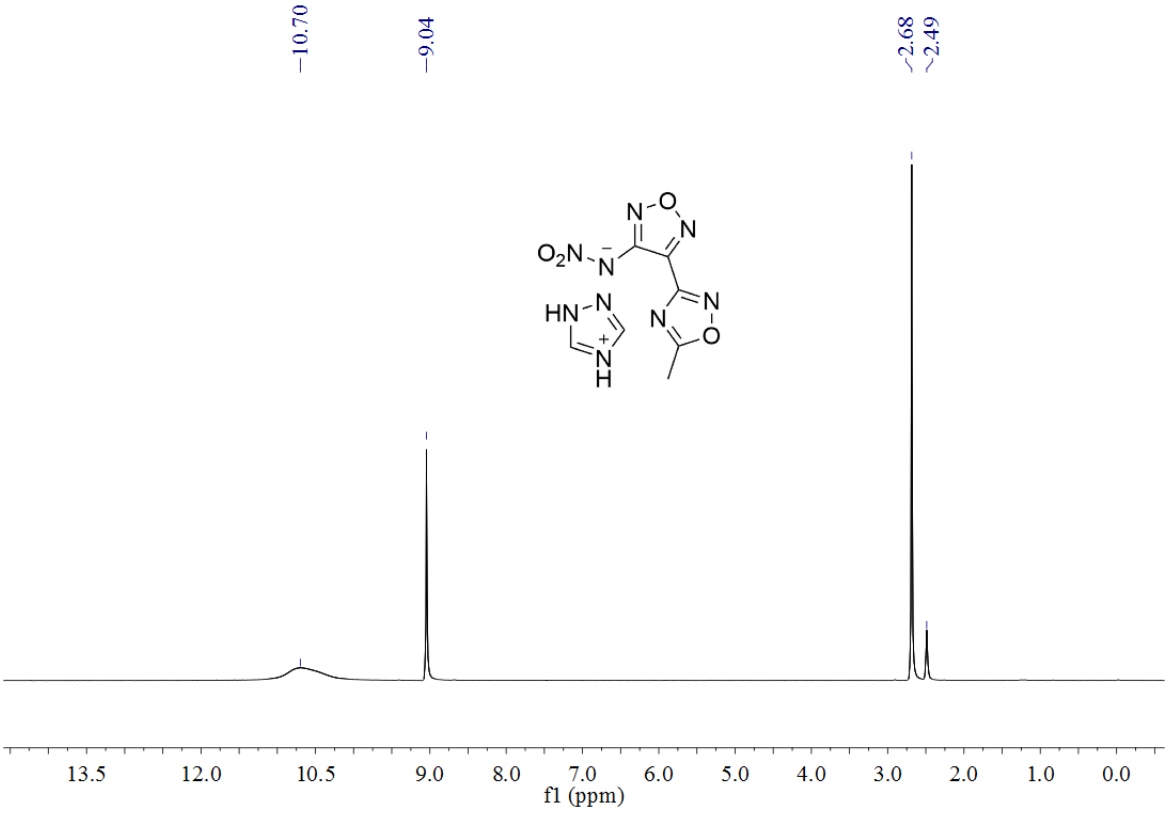

Fig. S33 ^{1}H-NMR spectrum of **10** in d_6-DMSO.

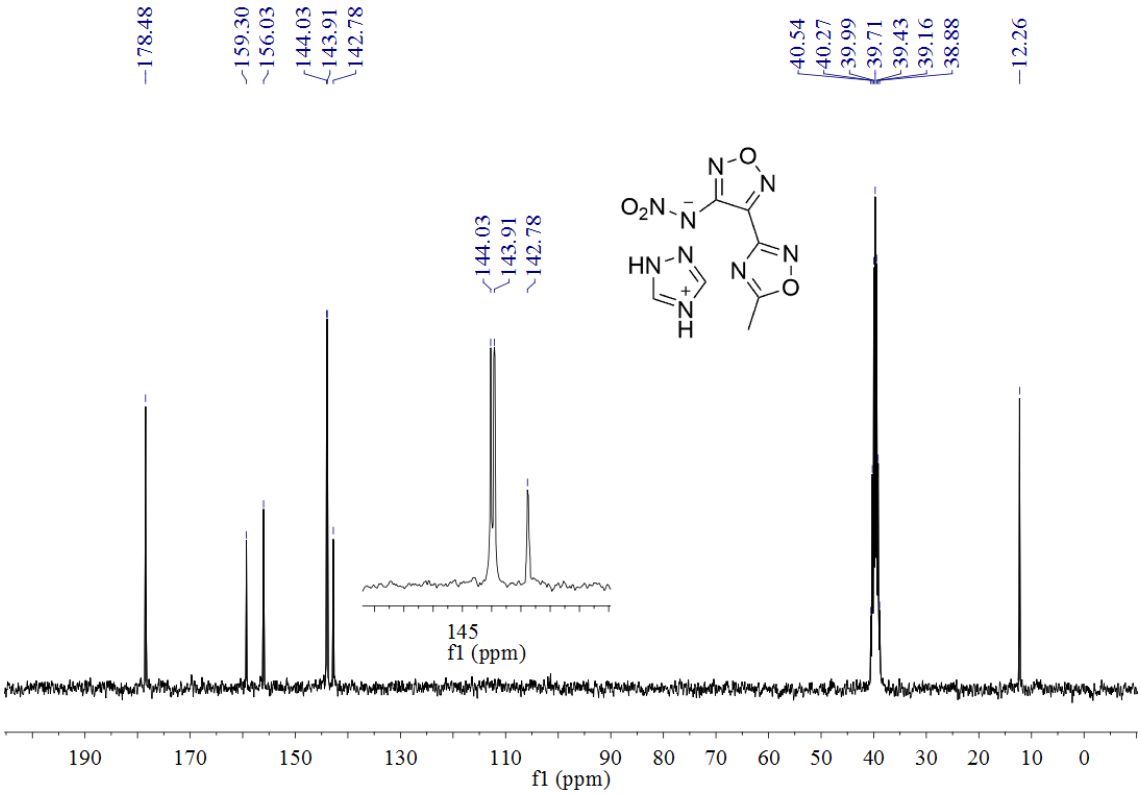

Fig. S34 ^{13}C-NMR spectrum of **10** in d_6-DMSO.

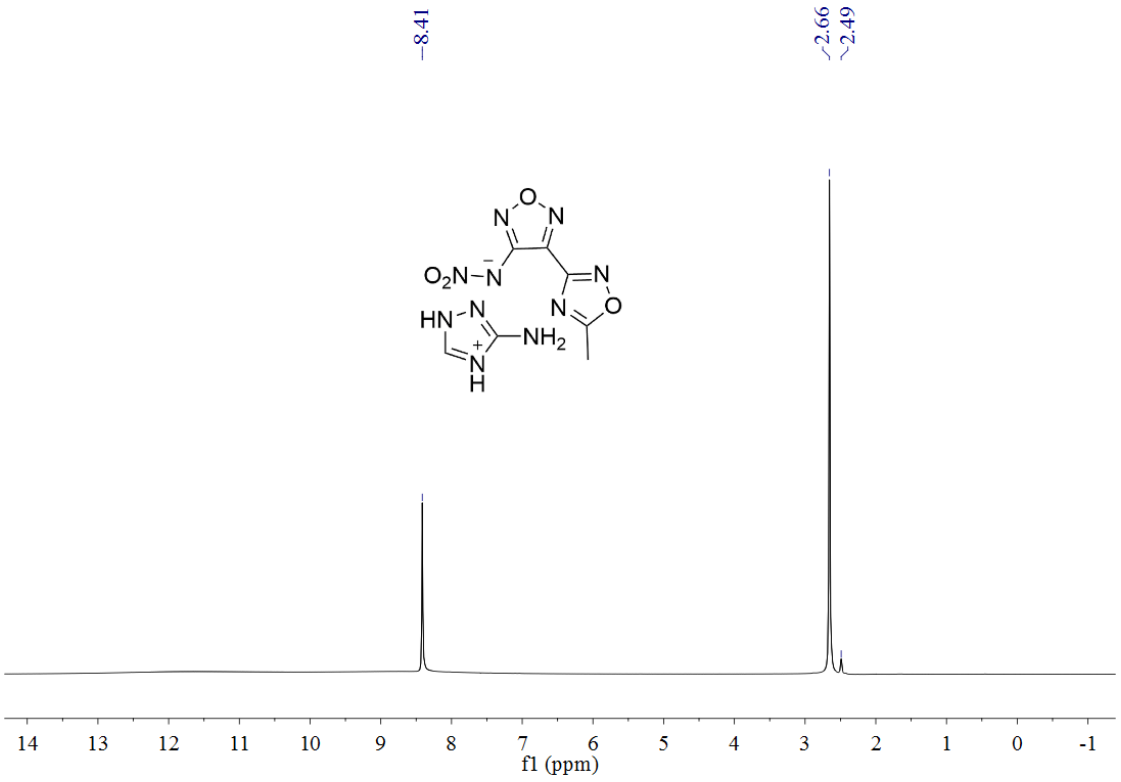

Fig. S35 ^{1}H-NMR spectrum of **11** in d_6-DMSO.

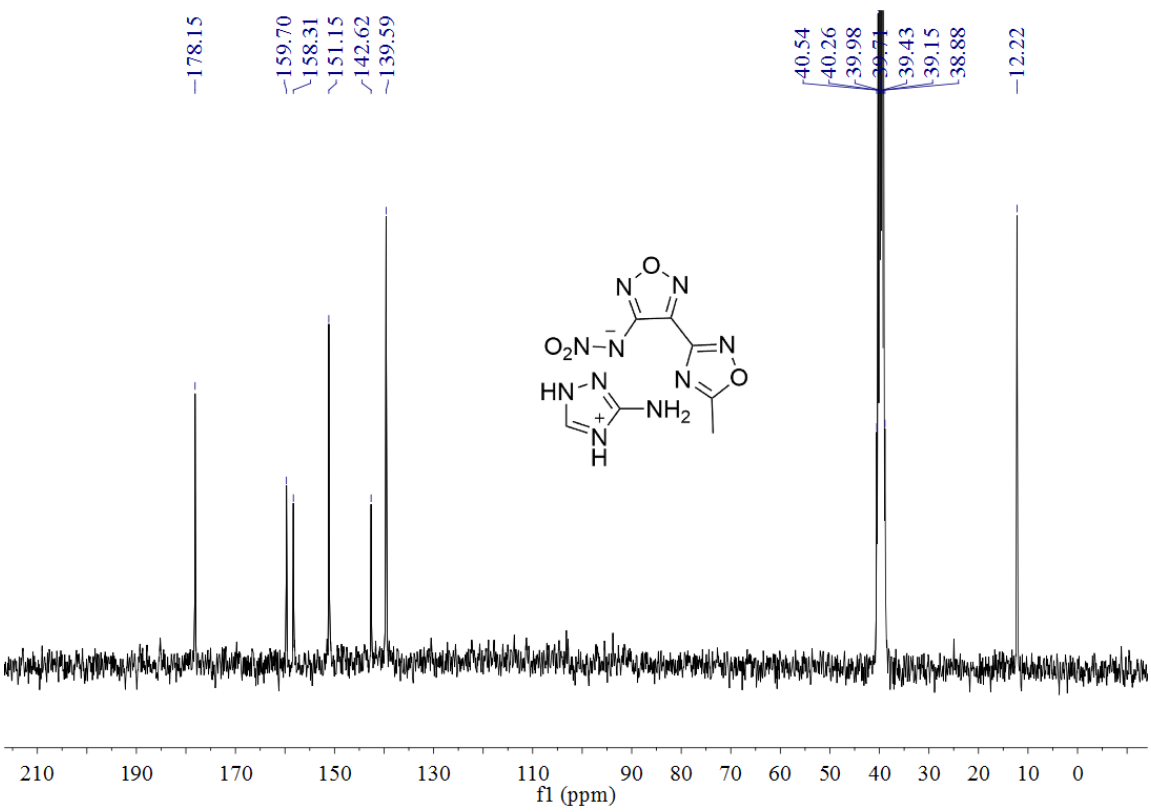

Fig. S36 ^{13}C-NMR spectrum of **11** in d_6-DMSO.

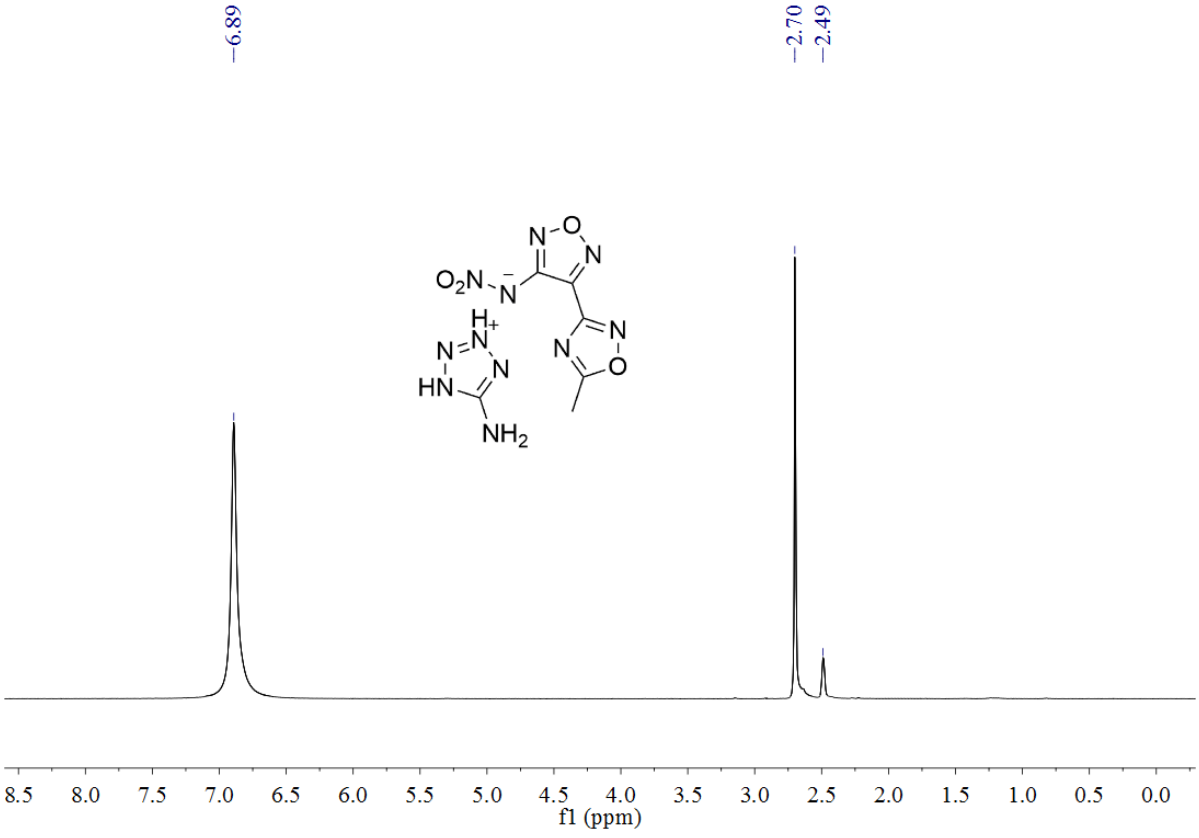

Fig. S37 ^{1}H-NMR spectrum of **12** in d_6-DMSO.

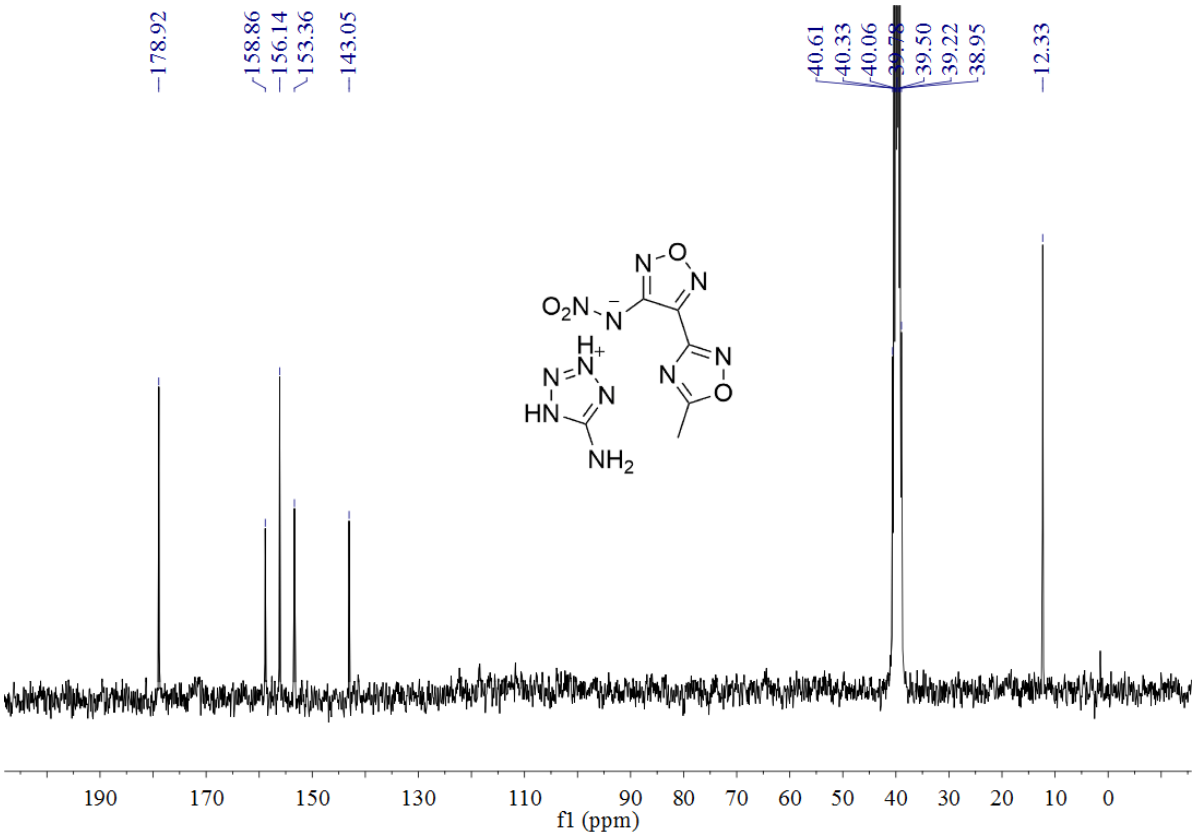

Fig. S38 ^{13}C-NMR spectrum of **12** in d_6-DMSO.

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