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

Supporting Information (SI)

Polynitro-1, 2, 4-triazole functionalized azo-furazans as high performance and insensitive energetic materials

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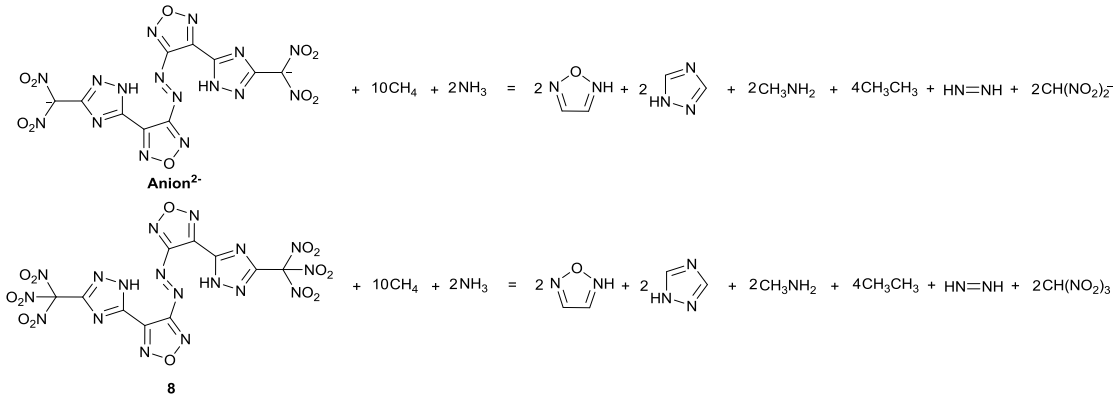
1. Computational data

All computations were carried out using the Gaussian09 program package.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[2] functional with the 6-311+G** basis set.[3] 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.[4] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

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 (Scheme S1).



Scheme S1. Isodesmic and tautomeric reactions to compute the HOF

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[5] or from the high-level computing such as CBS-4M.

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

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

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

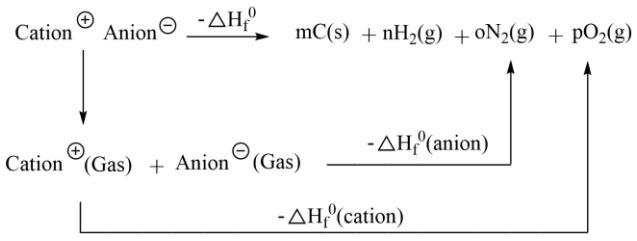


Fig. S1 Born−Haber cycle for the formation of energetic salts.

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. The equation for the lattice potential energy, U_{POT}, 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.

Table S1. *Ab initio* computational values of small molecules used in isodesmic and tautomeric reactions.

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
Anion^{2-}	-2010.078	504.14	80.92	707.56
8	-2420.063	575.08	97.28	1253.15
CH_4	-40.53	112.96	10.03	-74.6[e]
NH_3	-56.57	86.61	10.04	-45.9 [e]
CH_3NH_2	-95.87	161.37	11.61	-22.5 [e]
CH_3CH_3	-79.84	188.04	11.78	-84 [e]
NH=NH	-110.65	71.68	10	194.97 [e]
$CH(NO_2)^{2-}$	-449.00	100.12	18.42	-295.7 [e]
$CH(NO_2)_3$	-653.99	137.25	26.42	-13.4 [e]
1, 2, 5-Furazan	-262.06	115.16	11.82	215.72 [f]
1H-1, 2, 4-Triazole	-242.27	150.94	12.07	192.7 [f]

[a] Total energy calculated by B3LYP/6-311+G** method (a.u=2625.5 kJ mol^{-1}); [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.

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2. Crystallographic data and refinement parameters of 3

Table S2. Crystal data and structure refinement for **3**.

CCDC	1896042
Empirical formula	$C_{16}H_{16}N_{12}O_6$
Formula weight	472.41
Temperature/K	173
Crystal system	monoclinic
Space group	Cc
a/Å	5.0217(11)
b/Å	27.895(6)
c/Å	15.205(3)
α/°	90
β/°	97.057(5)
γ/°	90
Volume/Å^3	2113.8(8)
Z	4
ρ_{calc} g/cm^3	1.484
μ/mm^{-1}	0.118
F(000)	976.0
Crystal size/mm^3	0.19 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/ °	2.92 to 52.95
Index ranges	-6≤h≤6, -34≤k≤34, -16≤l≤18
Reflections collected	6766
Independent reflections	2796 [Rint = 0.0487, Rsigma = 0.0789]
Data/restraints/parameters	3648/650/329
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0487, wR_2 = 0.0995
Final R indexes [all data]	R_1 = 0.0896, wR_2 = 0.1173
Largest diff. peak/hole / e Å^{-3}	0.24/-0.20

Table S3. Bond Lengths for **3.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C14	1.322(6)	O2	N9	1.383(6)
O4	C15	1.453(6)	C12	C13	1.488(7)
O3	C14	1.207(6)	N6	C8	1.413(7)

N12	C12	1.337(6)	C14	C13	1.503(7)
N12	C11	1.367(6)	N5	C8	1.313(6)
O1	N4	1.396(5)	C8	C7	1.418(7)
O1	N5	1.360(6)	C11	C10	1.462(7)
N2	N1	1.353(5)	C5	C4	1.481(7)
N2	C6	1.344(6)	N8	C9	1.303(6)
N3	C5	1.365(6)	C10	N9	1.313(7)
N3	C6	1.328(6)	C10	C9	1.424(7)
N10	N11	1.358(5)	C7	C6	1.465(7)
N10	C11	1.323(7)	O6	C3	1.322(7)
N7	N6	1.248(5)	O6	C2	1.534(13)
N7	C9	1.416(7)	O6	C18	1.554(15)
N1	C5	1.330(6)	C3	C4	1.500(8)
N11	C12	1.330(6)	C15	C16	1.486(9)
O5	C3	1.178(7)	C2	C1	1.458(17)
N4	C7	1.327(6)	C18	C17	1.40(2)
O2	N8	1.374(6)			

Table S4. Bond Angles for **3.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O4	C15	117.3(4)	N1	C5	N3	113.8(4)
C12	N12	C11	102.5(4)	N1	C5	C4	122.6(5)
N5	O1	N4	111.9(4)	C9	N8	O2	104.6(4)
C6	N2	N1	109.3(4)	N9	C10	C11	121.2(5)
C6	N3	C5	102.9(4)	N9	C10	C9	108.9(5)
C11	N10	N11	101.9(4)	C9	C10	C11	129.9(5)
N6	N7	C9	111.8(4)	C12	C13	C14	113.5(4)
C5	N1	N2	103.4(4)	N4	C7	C8	108.4(5)
C12	N11	N10	111.1(4)	N4	C7	C6	115.4(5)
C7	N4	O1	104.5(4)	C8	C7	C6	136.2(5)
N8	O2	N9	112.3(4)	C10	N9	O2	104.5(4)
N12	C12	C13	126.6(4)	N2	C6	C7	126.4(4)
N11	C12	N12	109.6(4)	N3	C6	N2	110.6(4)
N11	C12	C13	123.8(4)	N3	C6	C7	123.0(4)
N7	N6	C8	114.2(4)	N7	C9	C10	126.3(4)
O4	C14	C13	109.9(4)	N8	C9	N7	123.9(5)
O3	C14	O4	124.7(5)	N8	C9	C10	109.8(5)

O3	C14	C13	125.4(4)	C3	O6	C2	112.0(7)
C8	N5	O1	105.3(5)	C3	O6	C18	116.9(9)
N6	C8	C7	137.0(5)	O5	C3	O6	124.3(6)
N5	C8	N6	113.2(5)	O5	C3	C4	125.9(5)
N5	C8	C7	109.9(5)	O6	C3	C4	109.8(5)
N12	C11	C10	123.0(4)	O4	C15	C16	106.6(5)
N10	C11	N12	114.9(4)	C5	C4	C3	112.8(5)
N10	C11	C10	122.0(4)	C1	C2	O6	101.5(11)
N3	C5	C4	123.6(5)	C17	C18	O6	103.6(17)

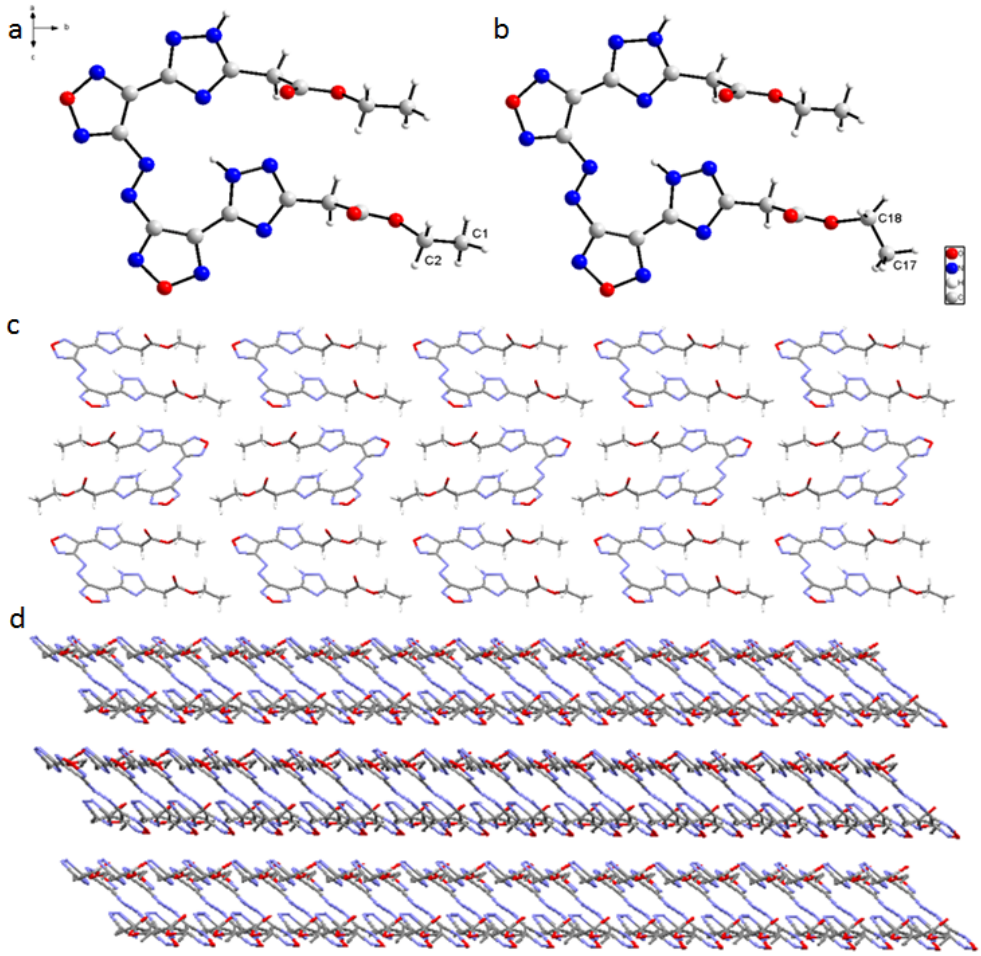

Fig. S2 Single-crystal X-ray structure of **3** (ellipsoids are set at 50% probability) (a) The part of the 2-fold disordered atoms with higher occupancy (0.50); (b) The part of the 2-fold disordered atoms with lower occupancy (0.50); (c) Stacking diagram of **3** (viewed along the *a*-axis); (d) Stacking diagram of **3** (viewed along the *b*-axis)

3. Mass spectrum

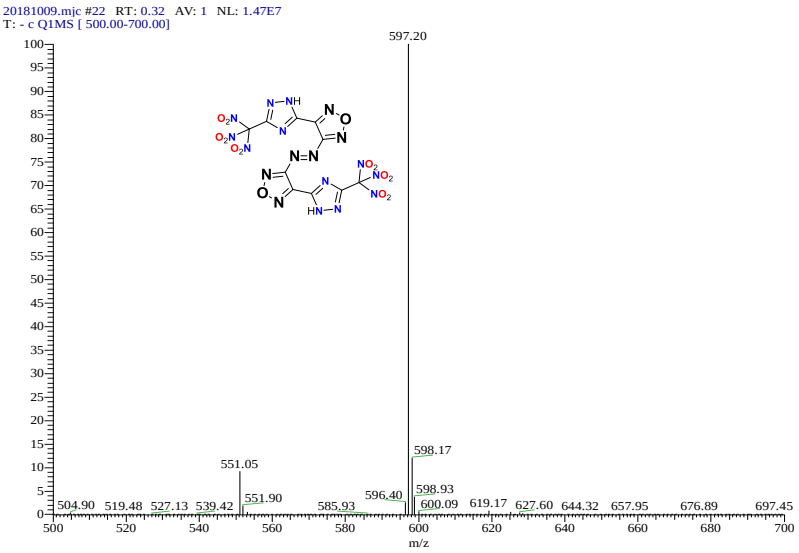

Fig.S3 Mass spectrum of **8.**

4. ^{1}H NMR , ^{13}C NMR spectra

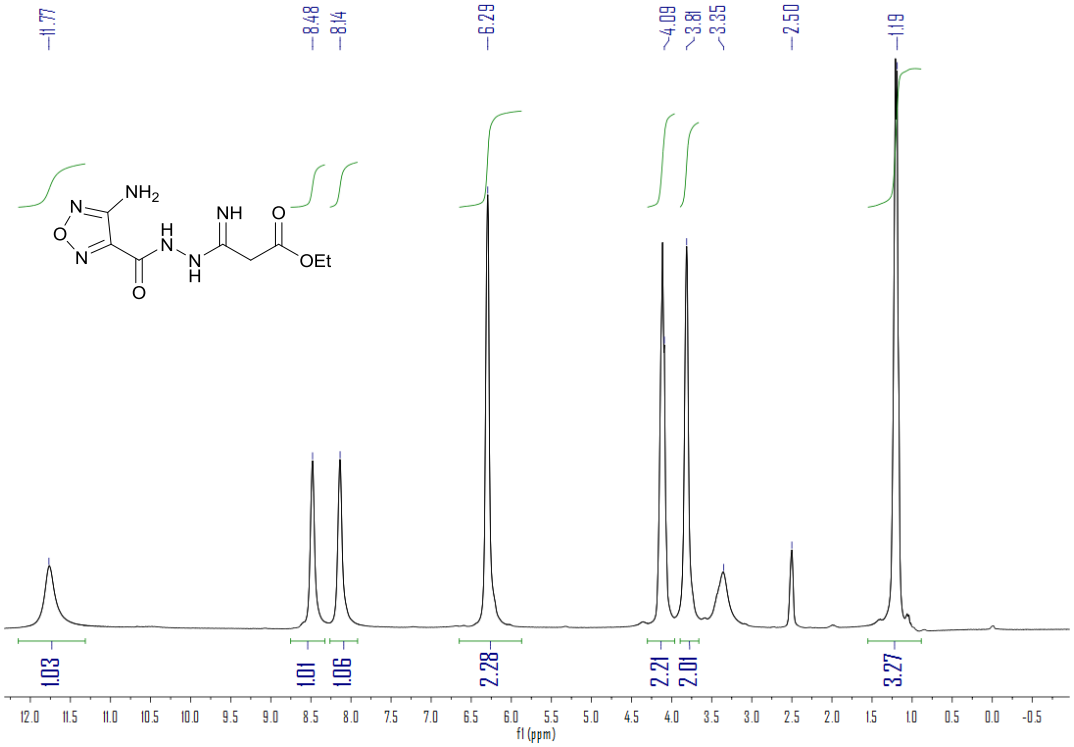

Fig. S4 ^{1}H-NMR spectra (300 MHz) of **1** in DMSO-d_6 at 25 ℃

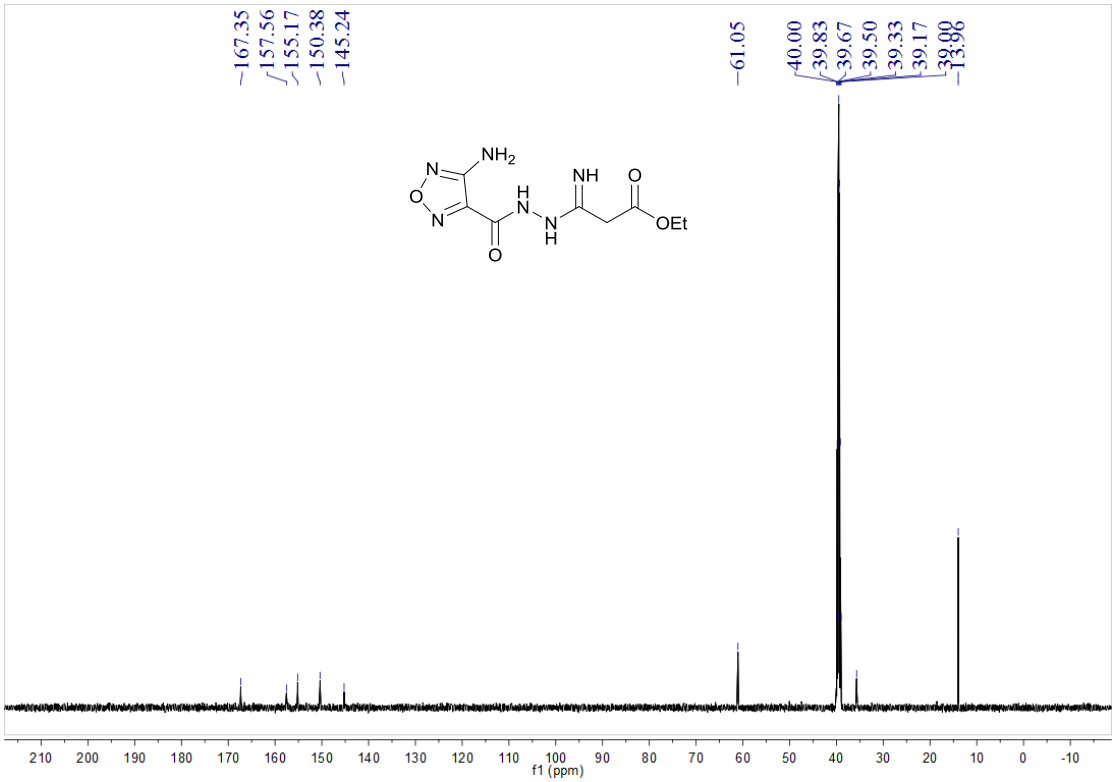

Fig. S5 ^{13}C-NMR spectra (126 MHz) of **1** in DMSO-d_6 at 25 ℃

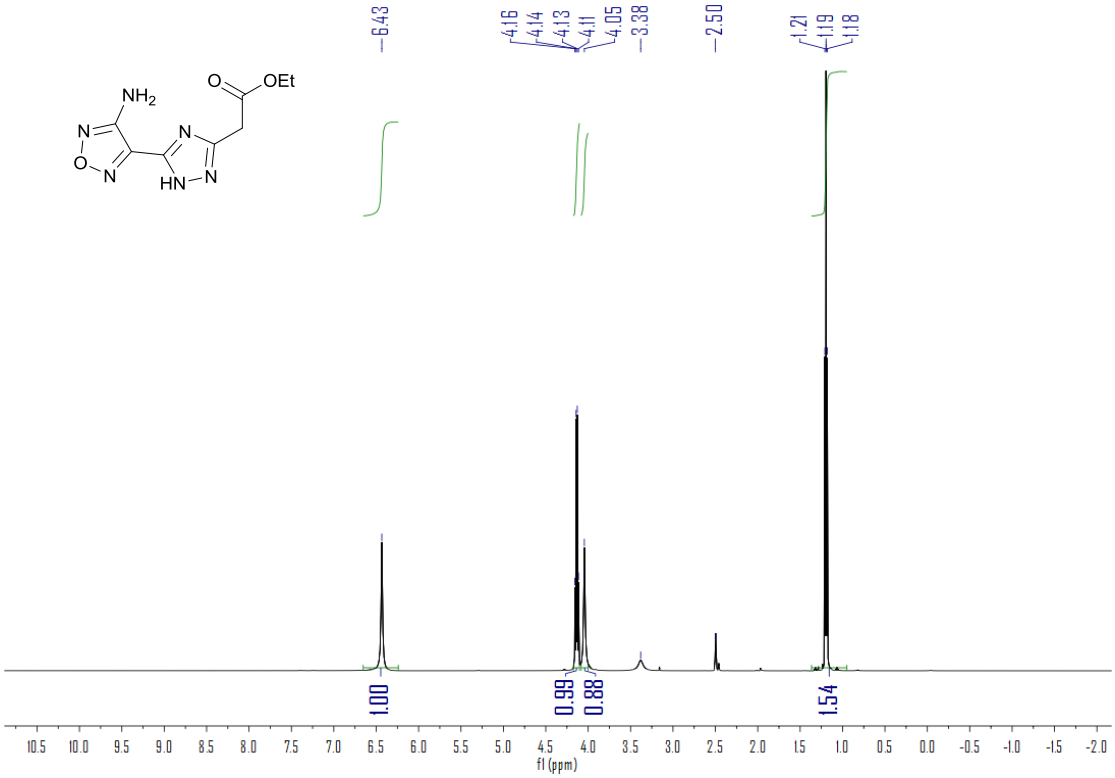

Fig. S6 ^{1}H-NMR spectra (300 MHz) of **2** in DMSO-d_6 at 25 ℃

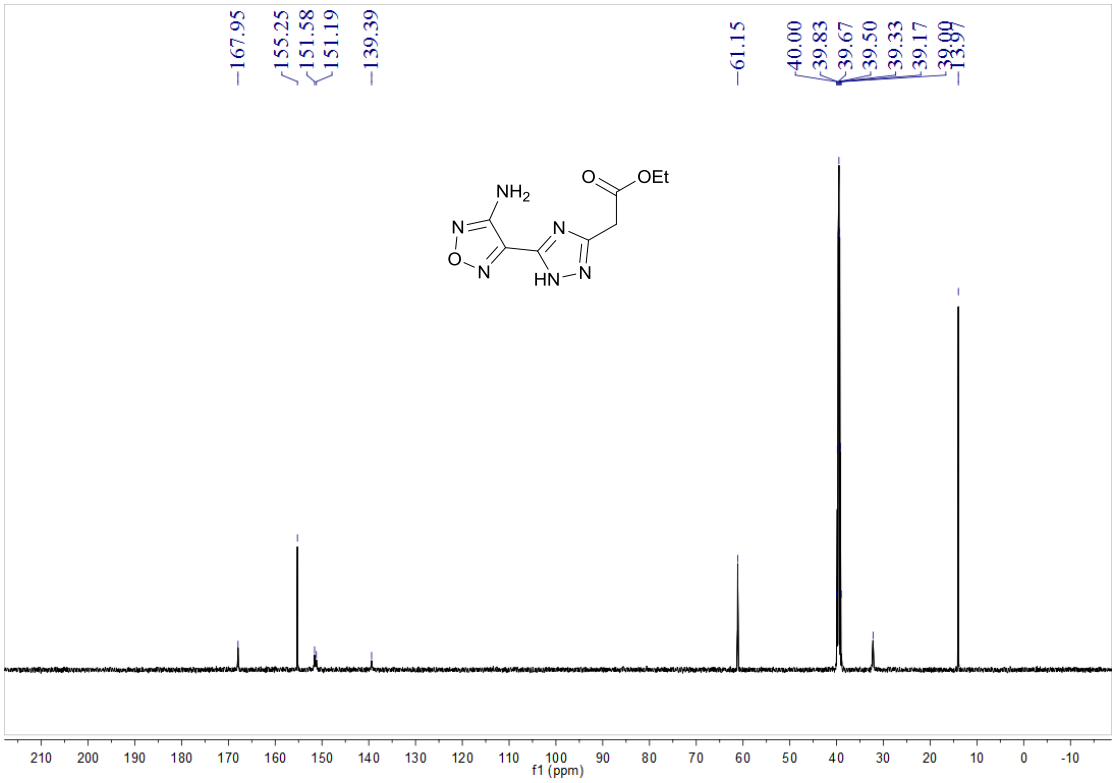

Fig. S7 ^{13}C-NMR spectra (126 MHz) of **2** in DMSO-d_6 at 25 ℃

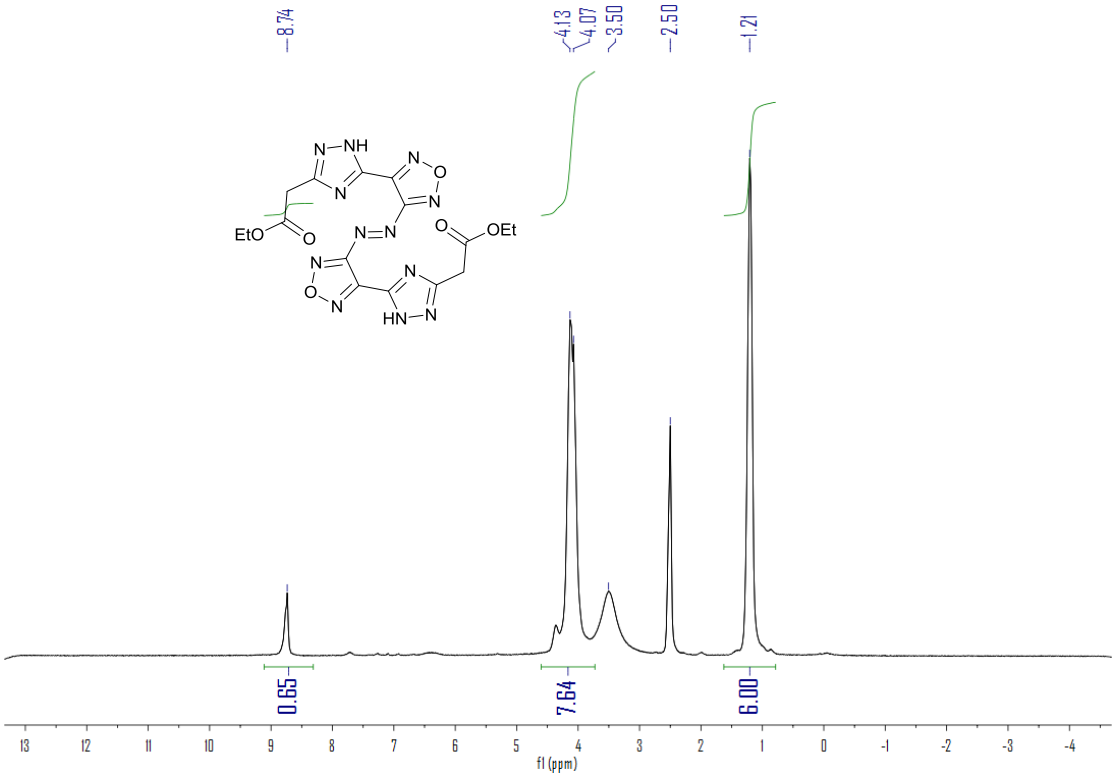

Fig. S8 ^{1}H-NMR spectra (300 MHz) of **3** in DMSO-d_6 at 25 ℃

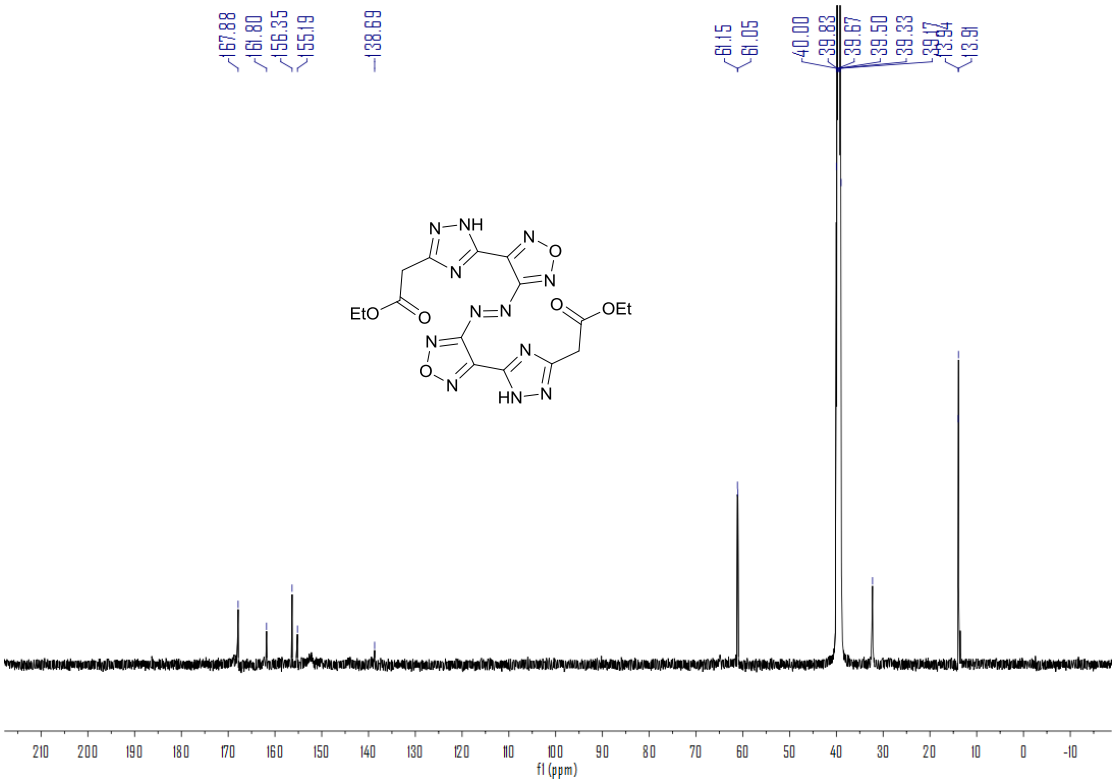

Fig. S9 ^{13}C-NMR spectra (126 MHz) of **3** in DMSO-d_6 at 25 ℃

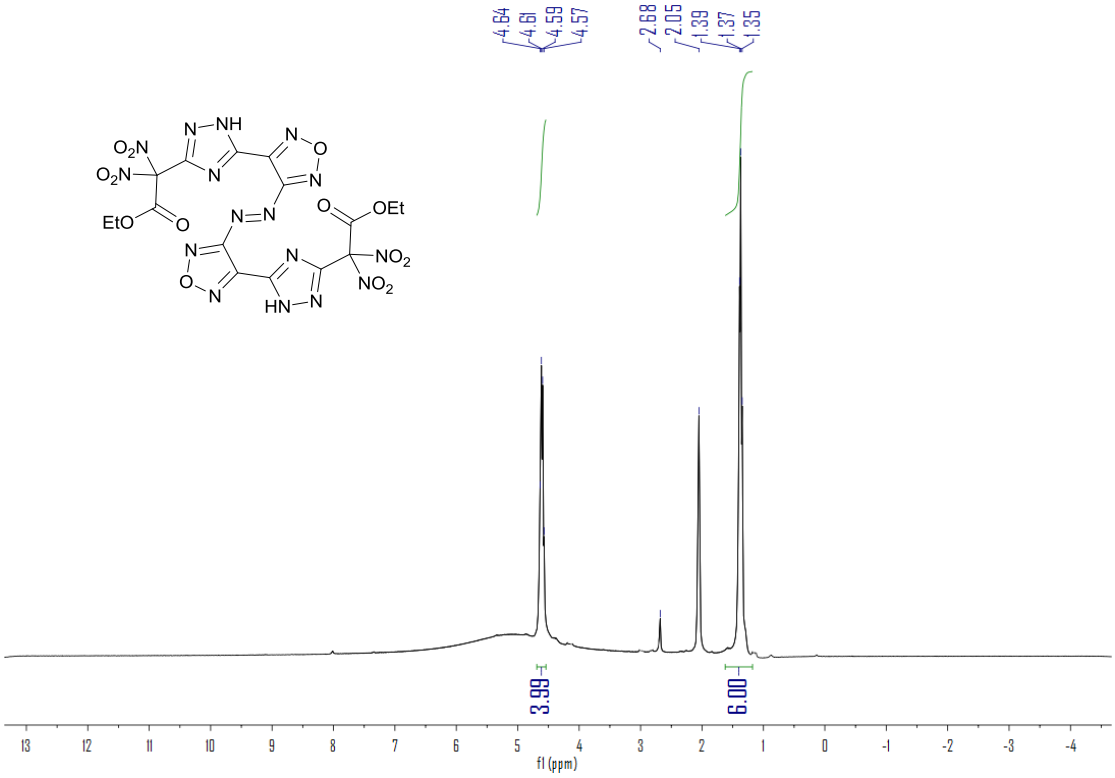

Fig. S10 ^{1}H-NMR spectra (300 MHz) of **4** in Acetone-d_6 at 25 ℃

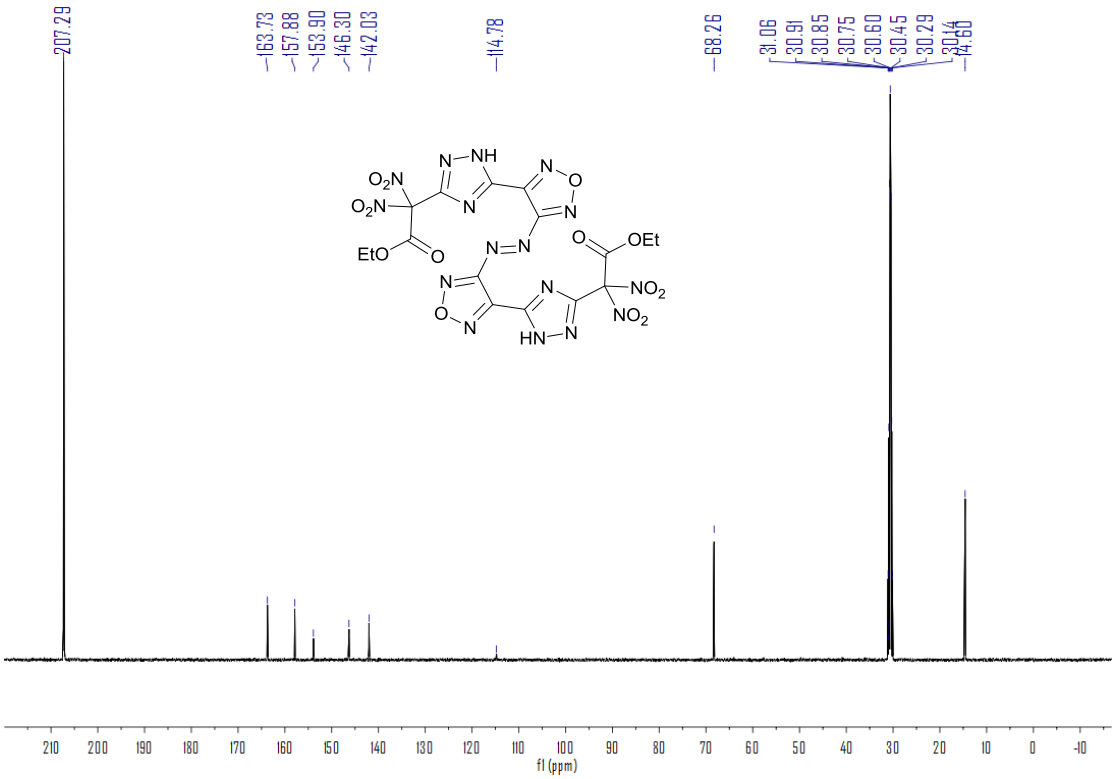

Fig. S11 ^{13}C-NMR spectra (126 MHz) of **4** in Acetone-d_6 at 25 ℃

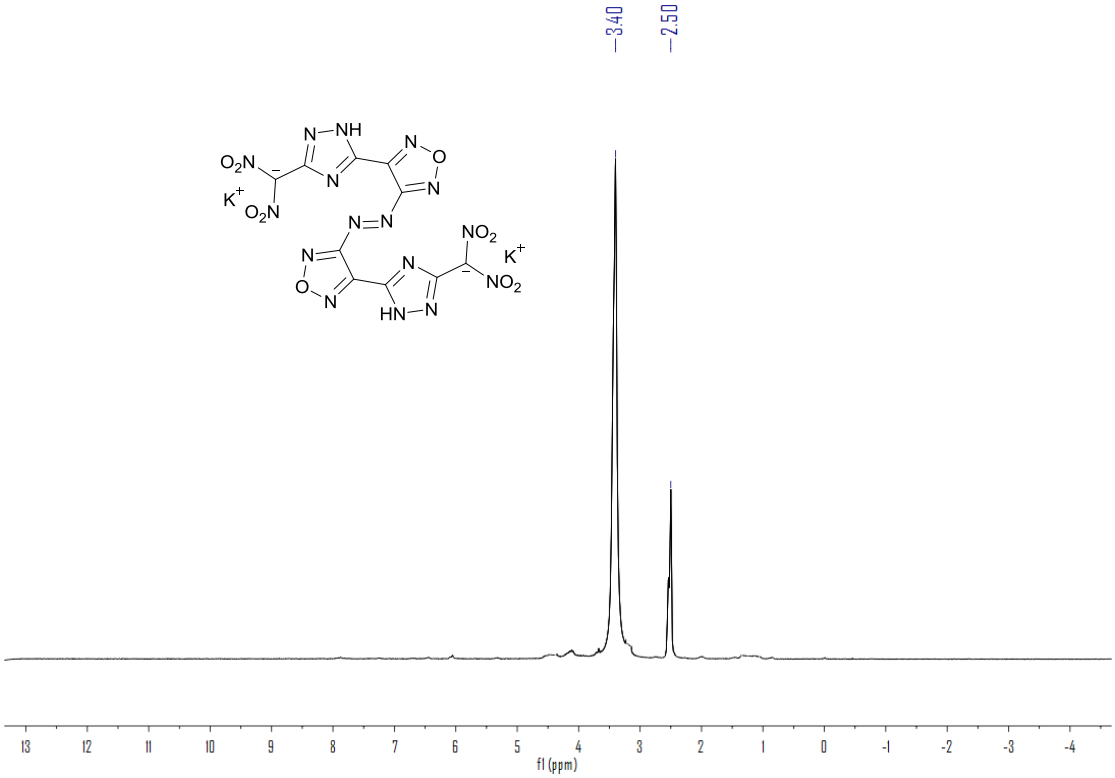

Fig. S12 ^{1}H-NMR spectra (300 MHz) of **5** in DMSO-d_6 at 25 ℃

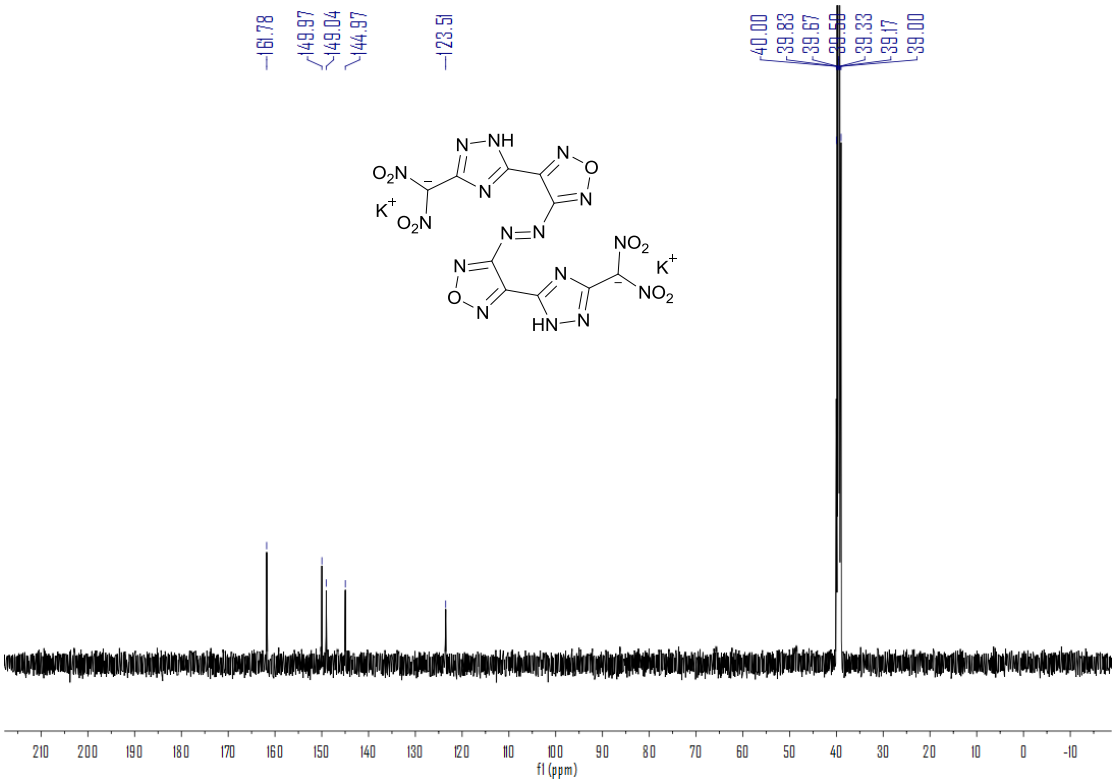

Fig. S13 ^{13}C-NMR spectra (126 MHz) of **5** in DMSO-d_6 at 25 ℃

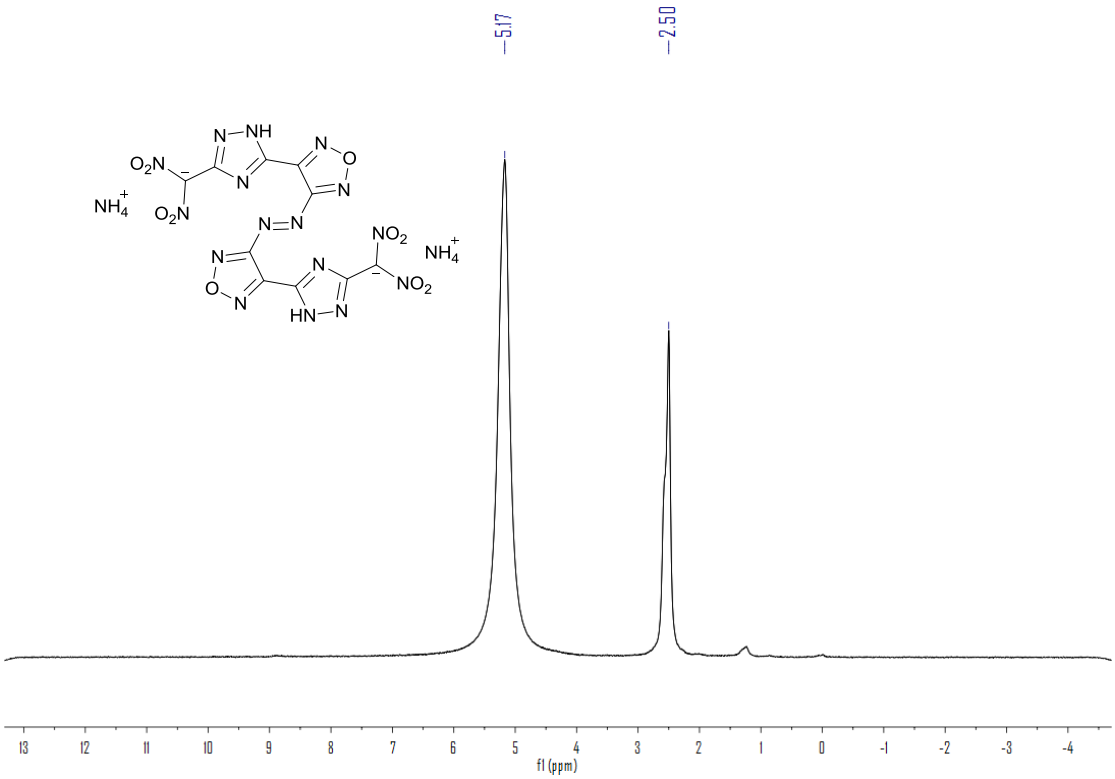

Fig. S14 ^{1}H-NMR spectra (300 MHz) of **6** in DMSO-d_6 at 25 ℃

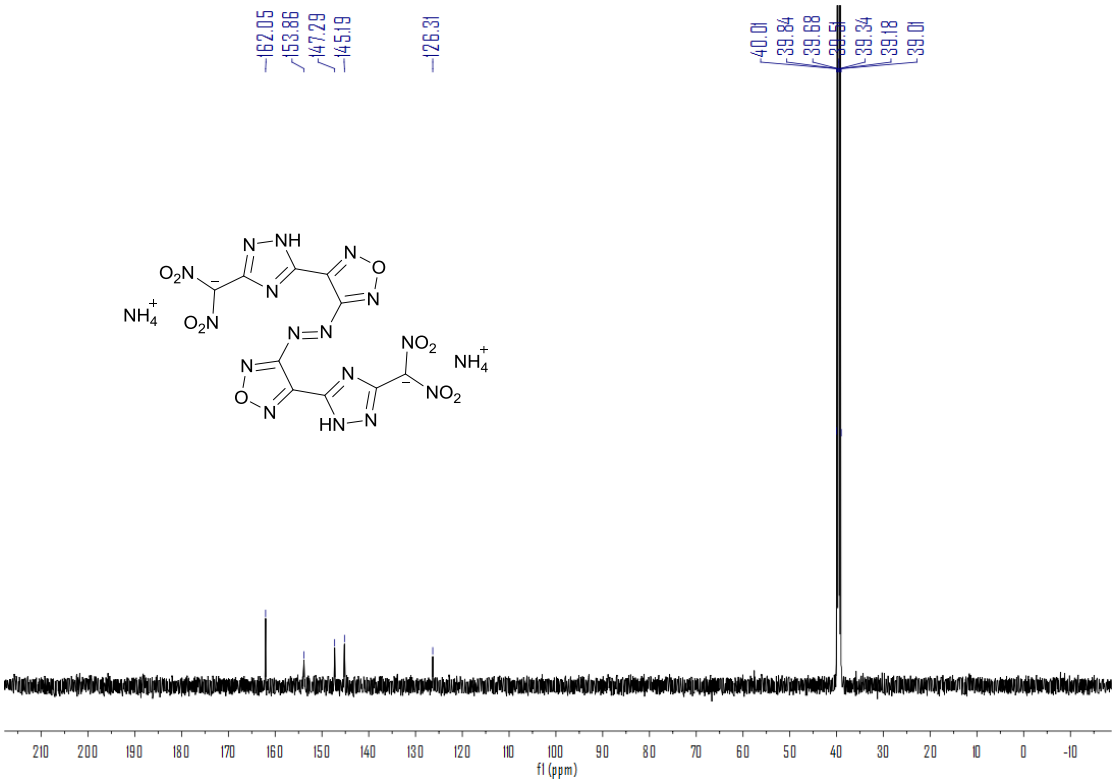

Fig. S15 ^{13}C-NMR spectra (126 MHz) of **6** in DMSO-d_6 at 25 ℃

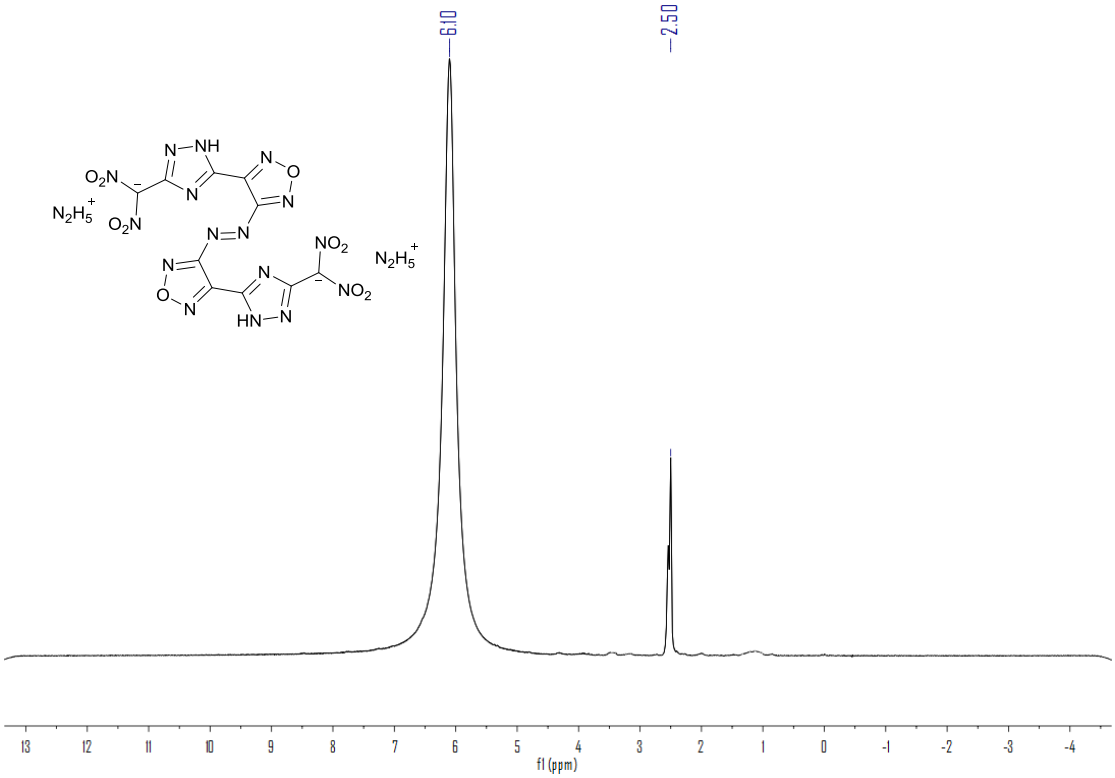

Fig. S16 ^{1}H-NMR spectra (300 MHz) of **7** in DMSO-d_6 at 25 ℃

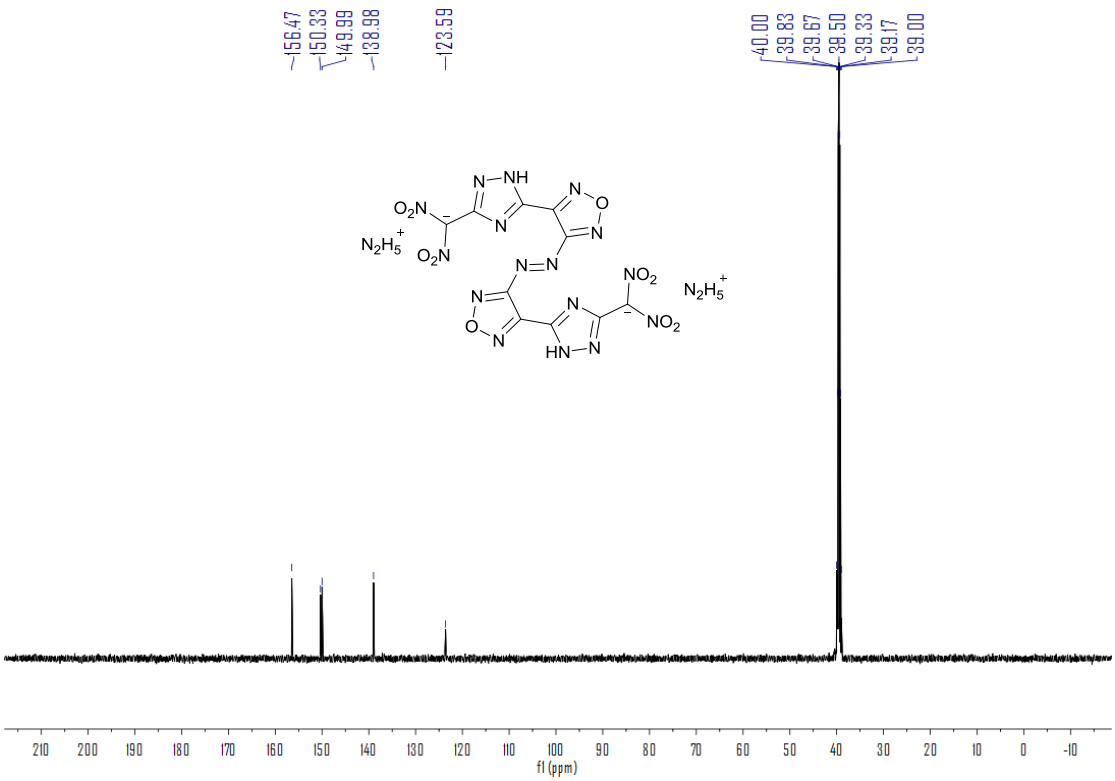

Fig. S17 ^{13}C-NMR spectra (126 MHz) of **7** in DMSO-d_6 at 25 ℃

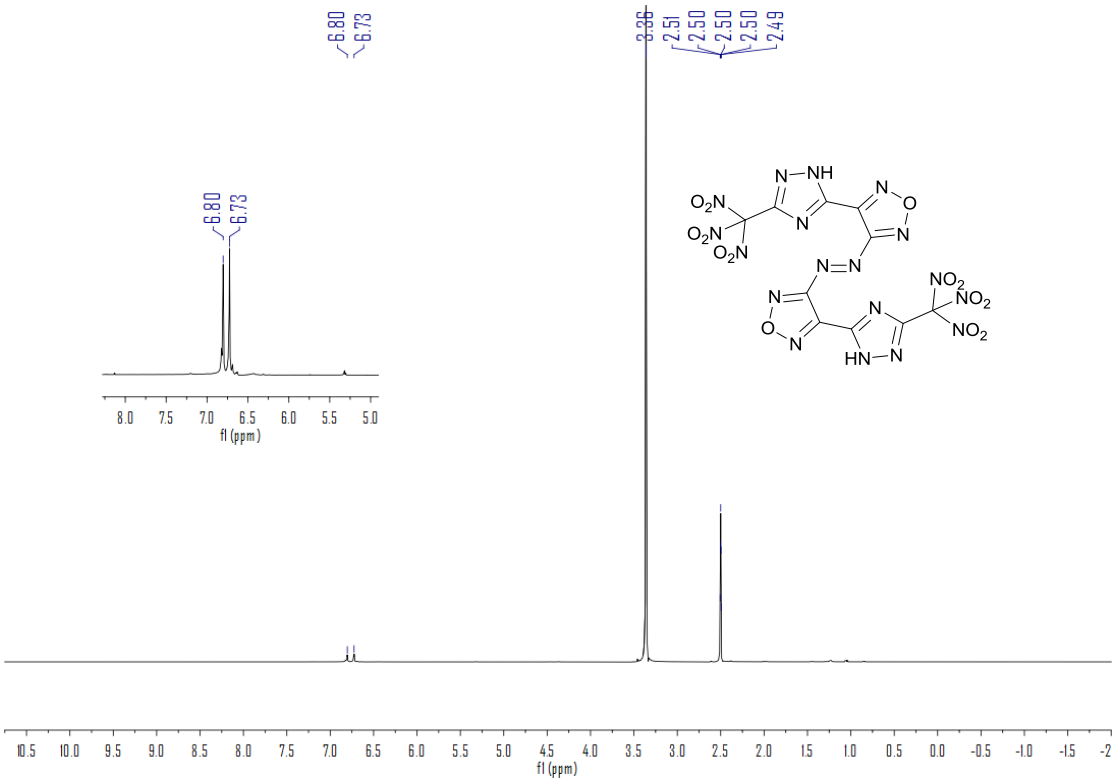

Fig. S18 ^{1}H-NMR spectra (500 MHz) of **8** in DMSO-d_6 at 25 ℃

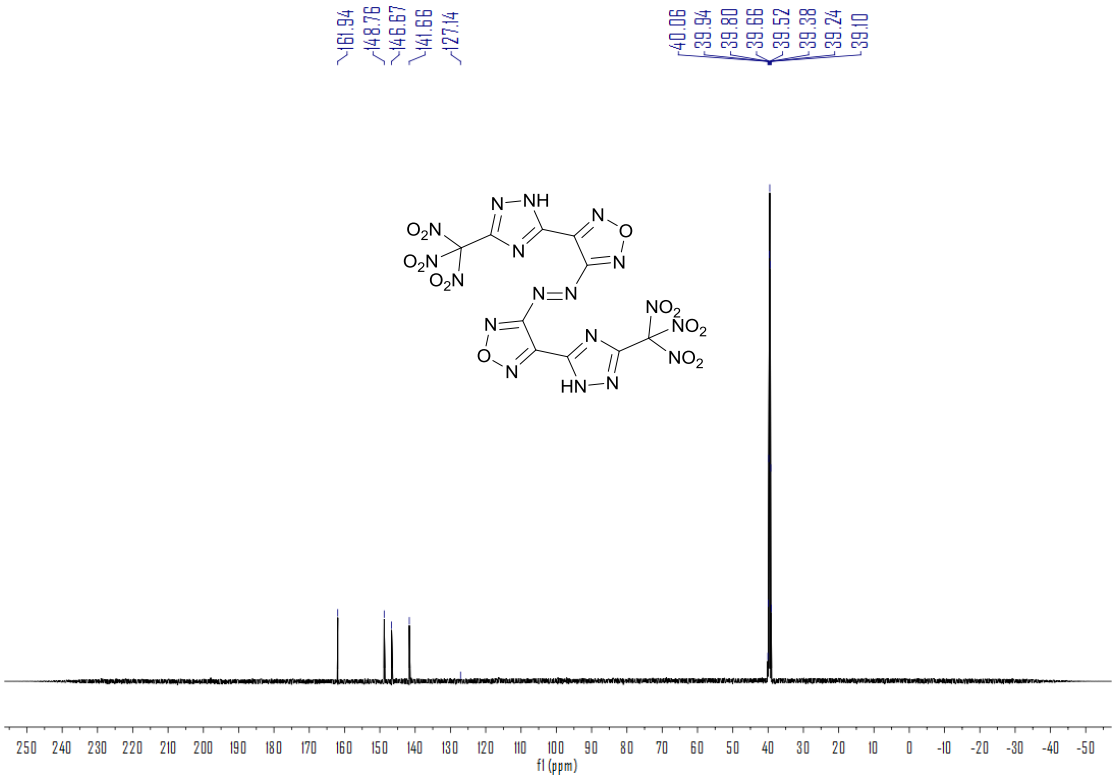

Fig. S19 ^{13}C-NMR spectra (126 MHz) of **8** in DMSO-d_6 at 25 ℃