

Supporting Information

Synthesis of novel insensitive heat-resistant explosive based on the fused-tricyclic skeleton

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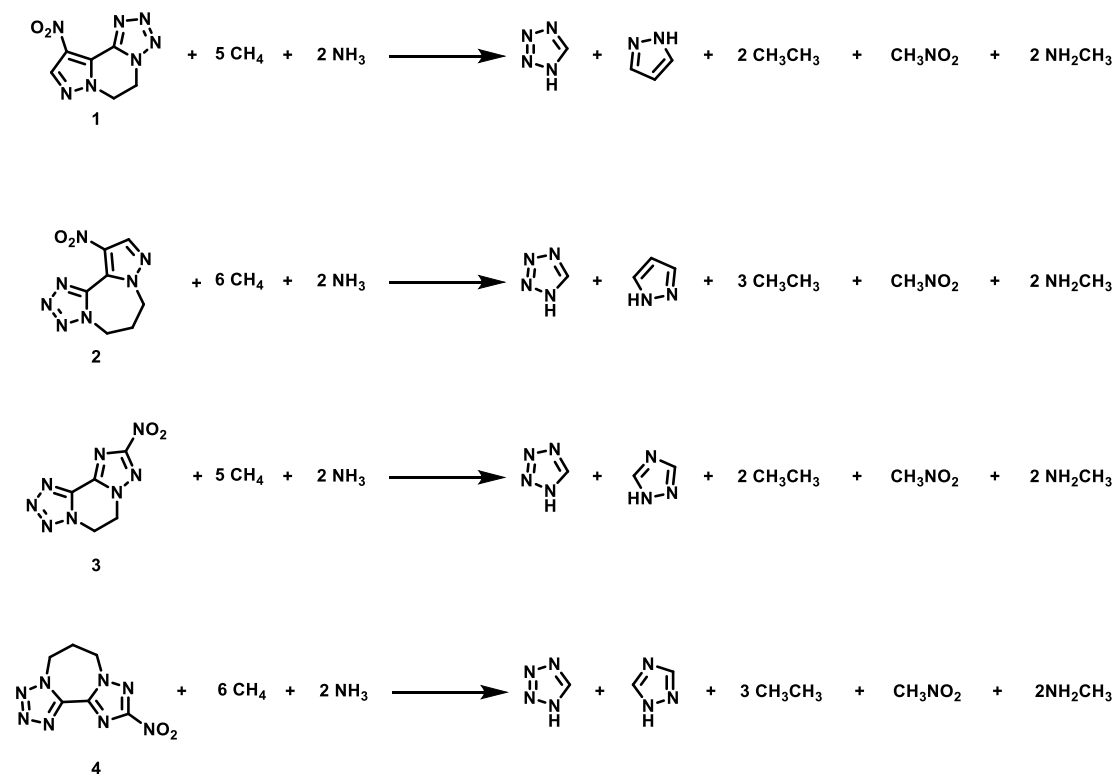
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1. Computational details




The calculation was performed by using the Gaussian 09 program package¹. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional² with 6-311+G** basis set^{3,4}. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heat of formation (HOF) of these compounds were computed through appropriate isodesmic reactions (Scheme S1). All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.



Scheme S1 Isodesmic and tautomeric reactions to compute the HOF.

Table S1 Total energy and heat of formation for the reference compounds

Compound	E ₀ /a.u.	ZPE/kJ.mol ⁻¹	H _T /kJ.mol ⁻¹	HOF/kJ.mol ⁻¹
CH ₄	-40.5339	112.26	10.04	-74.6
NH ₃	-56.5826	86.27	10.05	-45.9
CH ₃ CH ₃	-79.8565	187.31	11.79	-84
CH ₃ NO ₂	-245.0916	124.9	11.6	-74.3
CH ₃ NH ₂	-95.8938	160.78	11.64	-22.5

	-258.3241	117.69	11.8	334.3
	-226.2603	179.2	12.57	177.4
	-242.3204	150.39	12.06	192.7

The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

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

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

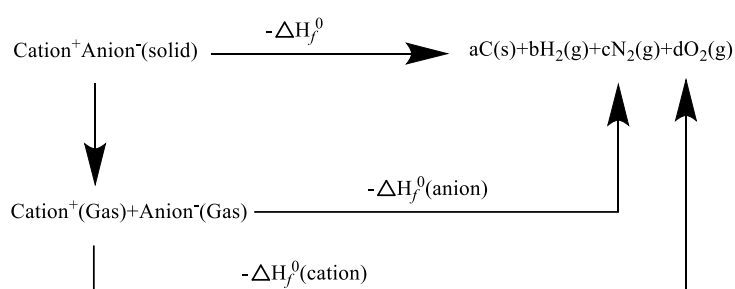
$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

ΔE_0 = the change in total energy between the products and the reactants at 0 K; ΔZPE = the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T = the thermal correction from 0 to 298 K; $\Delta(PV) = \Delta nRT$. For the isodesmic reactions $\Delta n = 0$, so $\Delta(PV) = 0$.

On the left side of Equation (2), apart from target compound all the others are called reference compounds. The HOF of reference compounds are available either from experiments or from high level computing such as CBS-4M.

Based on a Born-Haber energy cycle (Scheme S2), the heats of formation of the salts were obtained by Equation (3):

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



Scheme S2 Born-Haber cycle for the formation of energetic salts

Where ΔH_L is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al. as given in Equation (4):

$$\Delta H_L = UPOT + [p(nM/2-2) + q(nX/2-2)] RT \quad (4)$$

Where n_M and n_X depend on the nature of the ions M_{p+} and X_{q-} , respectively, 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 UPOT takes the form of equation (5):

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

ρ_m = the density ($\text{g}\cdot\text{cm}^{-3}$), M_m = the chemical formula mass of the ionic material.

2. The experiment and crystallographic data

General methods

Reagents were purchased from Aldrich and Acros Organics and are used as received. ^1H and ^{13}C NMR spectra are recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300 and 75.0 MHz, respectively. The decomposition points are obtained on a differential scanning calorimeter at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. IR spectra are recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities are determined at $25\text{ }^\circ\text{C}$ by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements are made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data are calculated by program package EXPLO5 (version 6.01).

X-ray crystallography

The data for **1-4** were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 1.54178\text{ nm}$) or CuK α ($\lambda = 0.71073\text{ nm}$) at 193 K. The data collection and the initial unit cell refinement are performed by using APEX2 (v2010.3-0). Data Reduction is performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections are applied by using the SADABS (v2008/1) program. The structures are solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL-2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands are included using a riding model. The crystallographic data and CCDC numbers for these compounds are summarized in Table S2.

Table S2 Crystallographic Data for **1-4**

Compound	1	2	3	4
CCDC	2356449	2356448	2326589	2326592
Formula	C ₆ H ₅ N ₇ O ₂	C ₇ H ₇ N ₇ O ₂	C ₅ H ₄ N ₈ O ₂	C ₆ H ₆ N ₈ O ₂
Formula weight	207.17	221.20	208.16	222.19
Temperature/K	233	223	198	193
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /n	P2 ₁ /n
a/Å	6.3809(6)	6.7579(3)	6.3057(2)	14.5684(4)
b/Å	10.3716(8)	8.4422(4)	9.7520(3)	9.3480(3)
c/Å	12.1362(10)	16.3524(6)	13.0730(4)	15.0235(4)
α/°	90	90	90	90
β/°	91.201(6)	90	94.800(2)	117.776(2)
γ/°	90	90	90	90
Volume/Å ³	803.00(12)	932.93(7)	801.08(4)	1810.24(10)
Z	4	4	4	4
ρ _{calc} / mg·mm ⁻³	1.714	1.575	1.726	1.631
μ/mm ⁻¹	1.176	1.052	1.220	1.120
F (000)	424.0	456.0	424.0	912.0
Crystal size /mm ³	0.12×0.11×0.1	0.13×0.11×0.1	0.11×0.1×0.09	0.13×0.11×0.1
2θ/°	11.222 to 136.502	11.796 to 136.676	11.334 to 136.03	11.572 to 136.478
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -19 ≤ l ≤ 19	-7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15	-17 ≤ h ≤ 12, - 11 ≤ k ≤ 11, - 14 ≤ l ≤ 18
Reflections collected	8695	8704	7173	13050
Independent reflections	8695 [R _{int} =?, R _{sigma} = 0.0892]	1700 [R _{int} = 0.0510, R _{sigma} = 0.0312]	1700 [R _{int} = 0.0528, R _{sigma} = 0.0302]	1700 [R _{int} = 0.0427, R _{sigma} = 0.0324]
Data/restraints/par ameters	8695/0/137	1700/0/145	1452/6/155	3240/18/299
Goodness-of-fit on F ²	1.039	1.049	1.078	1.073
Final R indexes [I ≥ 2σ (I)]	R1 = 0.0575, wR2 = 0.1583	R1 = 0.0378, wR2 = 0.0986	R1 = 0.0314, wR2 = 0.0771	R1 = 0.0423, wR2 = 0.1139

Final R indexes [all data]	R1 = 0.0789, wR2 = 0.1739	R ₁ = 0.0442, wR ₂ = 0.1013	R1 = 0.0431, wR2 = 0.0825	R1 = 0.0495, wR2 = 0.1196
Largest diff./ peak/hole/e Å ⁻³	0.37/-0.41	0.40/-0.21	0.19/-0.17	0.30/-0.20

Table S3 Hydrogen bonds present in **1-4**

Compound	D-H...A	<i>d</i> (D-H)/Å	<i>d</i> (H...A)/Å	<i>d</i> (D...A)/Å	<(DHA)/(°)
1	C1-H1A...N4	0.9800	2.4600	3.098(4)	122.0
	C1-H1B...N6	0.9800	2.6000	3.528(4)	157.0
2	C1-H1...O1	0.9400	2.4900	3.321(4)	147.0
	C5-H5A...O2	0.9800	2.4200	3.328(4)	155.0
3	C4B-H4BB...O1	0.9900	2.54	3.157(4)	120.0
	C5B-H5BA...N3	0.9900	2.53	3.369(13)	143.0
4	C5-H5B...N10	0.9900	2.58	3.283(3)	128.0
	C6-H6A...N15	0.9900	2.56	3.372(3)	140.0

3. ^1H and ^{13}C NMR spectra for all new compounds

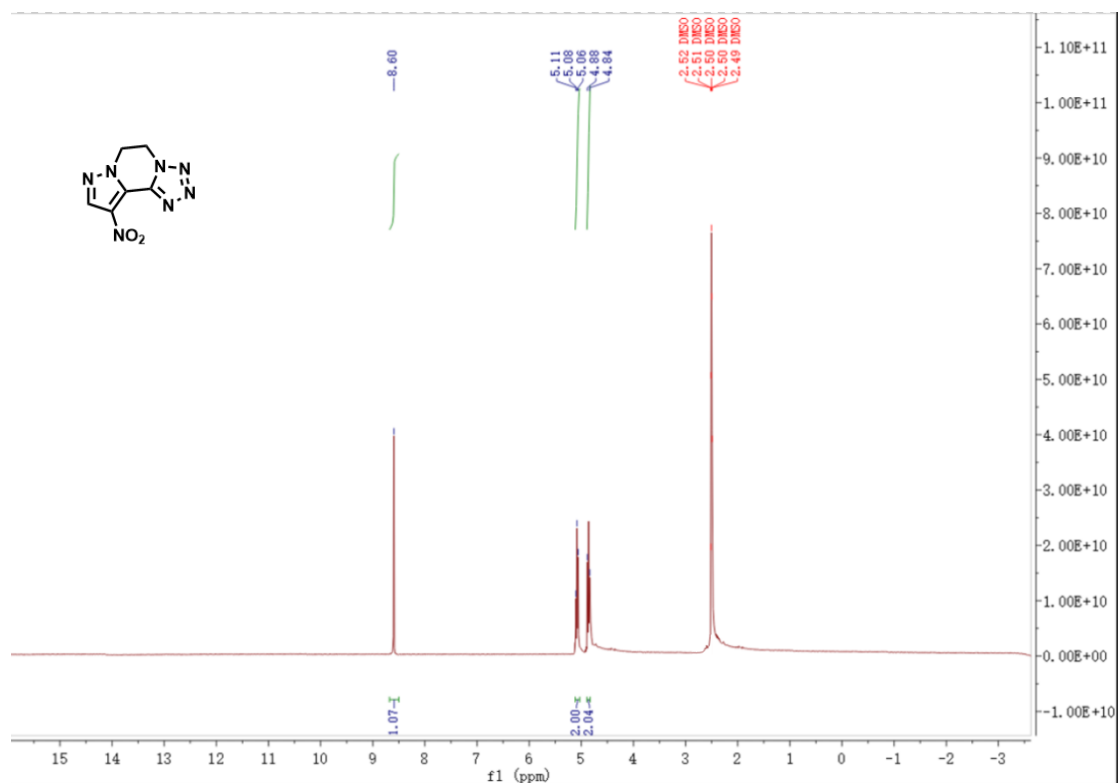


Figure S1 ^1H NMR spectra (300 MHz) of 1 in [D6] DMSO at 25 °C

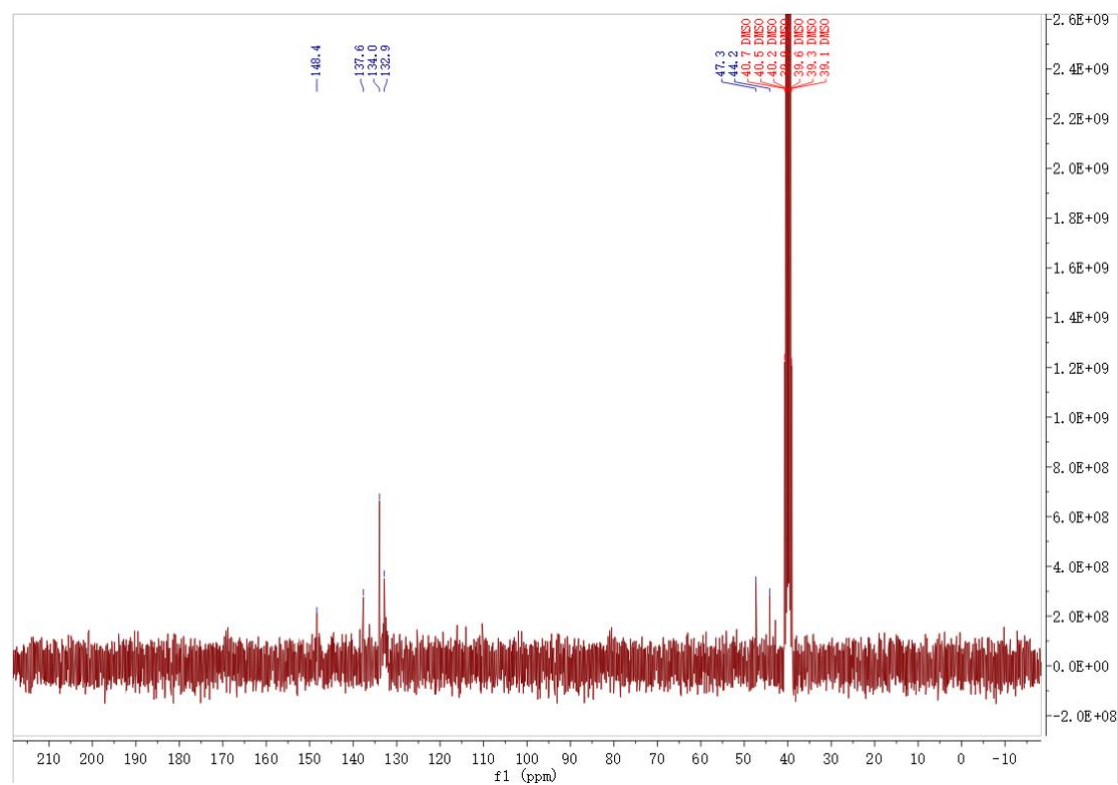


Figure S2 ^{13}C NMR spectra (75 MHz) of 1 in [D6] DMSO at 25 °C.

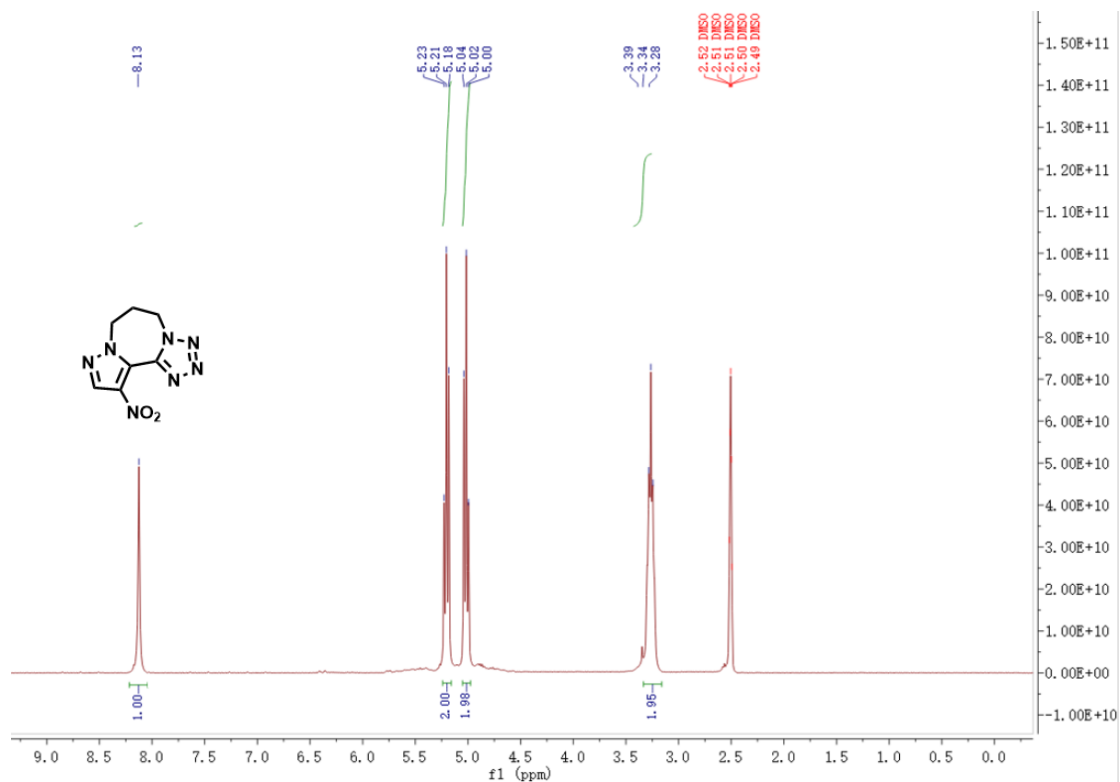


Figure S3 ¹H NMR spectra (300 MHz) of **2** in [D₆] DMSO at 25 °C

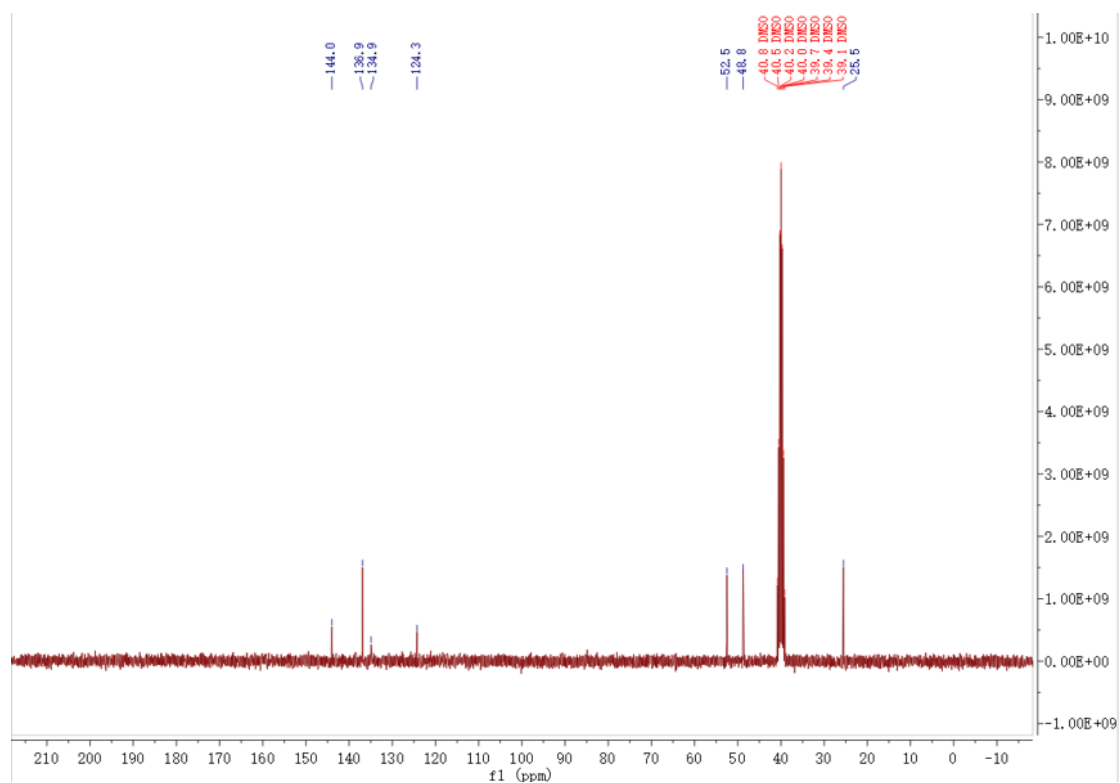


Figure S4 ¹³C NMR spectra (75 MHz) of **2** in [D₆] DMSO at 25 °C.

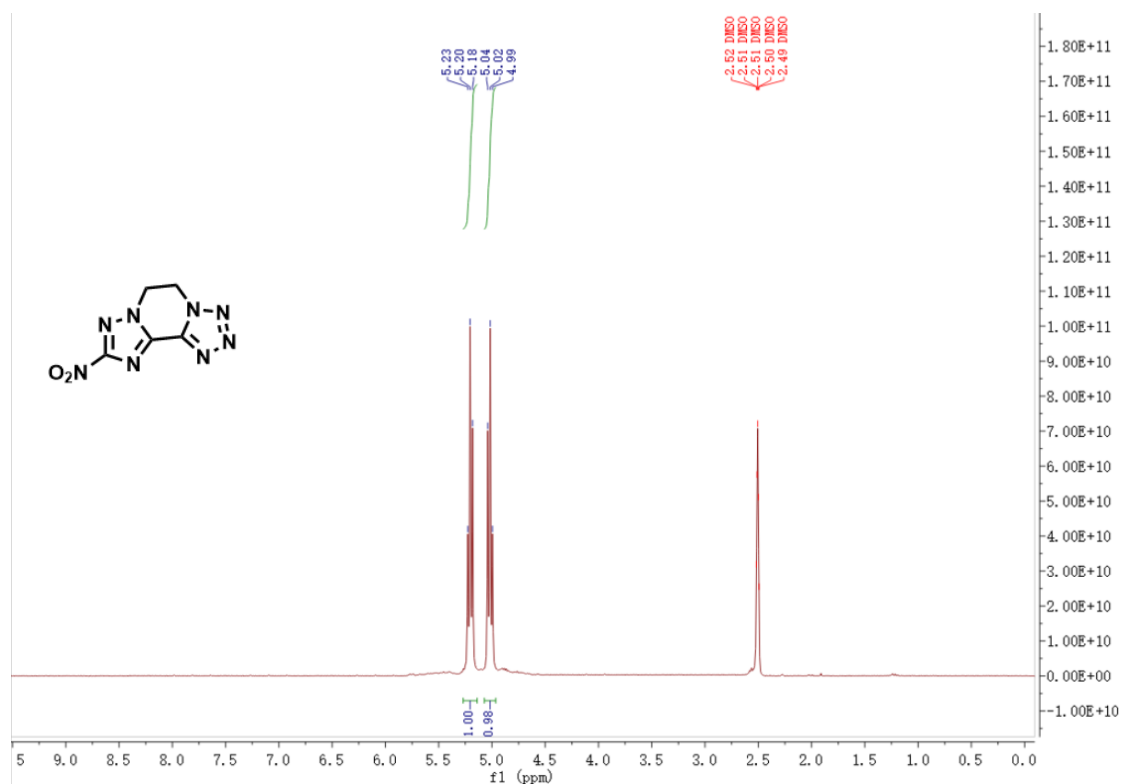


Figure S5 ^1H NMR spectra (300 MHz) of **3** in $[\text{D}_6]$ DMSO at 25 $^\circ\text{C}$

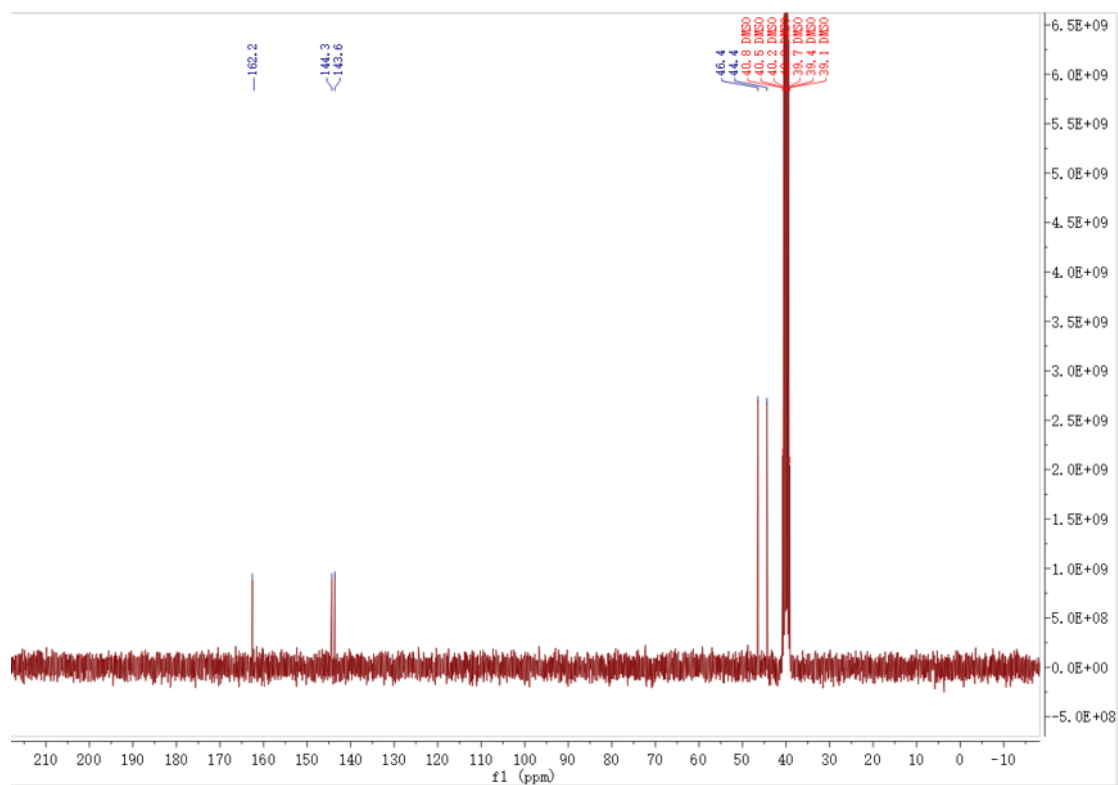


Figure S6 ^{13}C NMR spectra (75 MHz) of **3** in $[\text{D}_6]$ DMSO at 25 $^\circ\text{C}$.

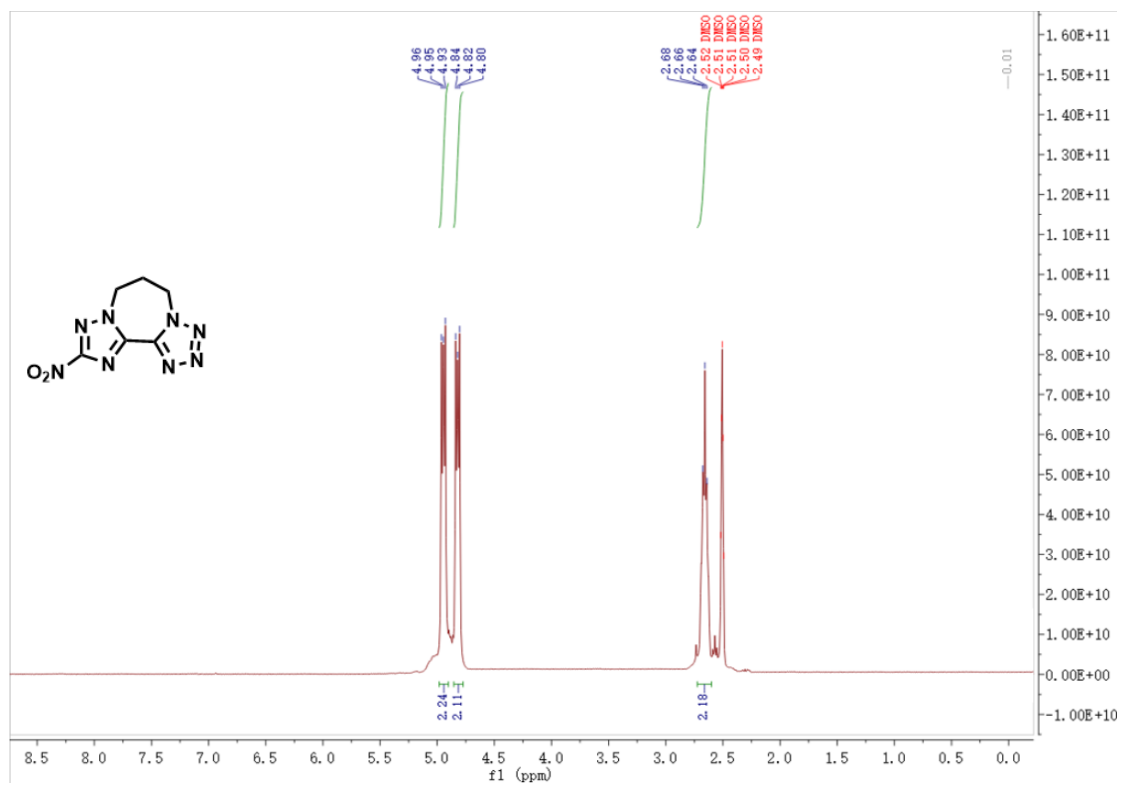


Figure S7 ^1H NMR spectra (300 MHz) of **4** in [D₆] DMSO at 25 °C

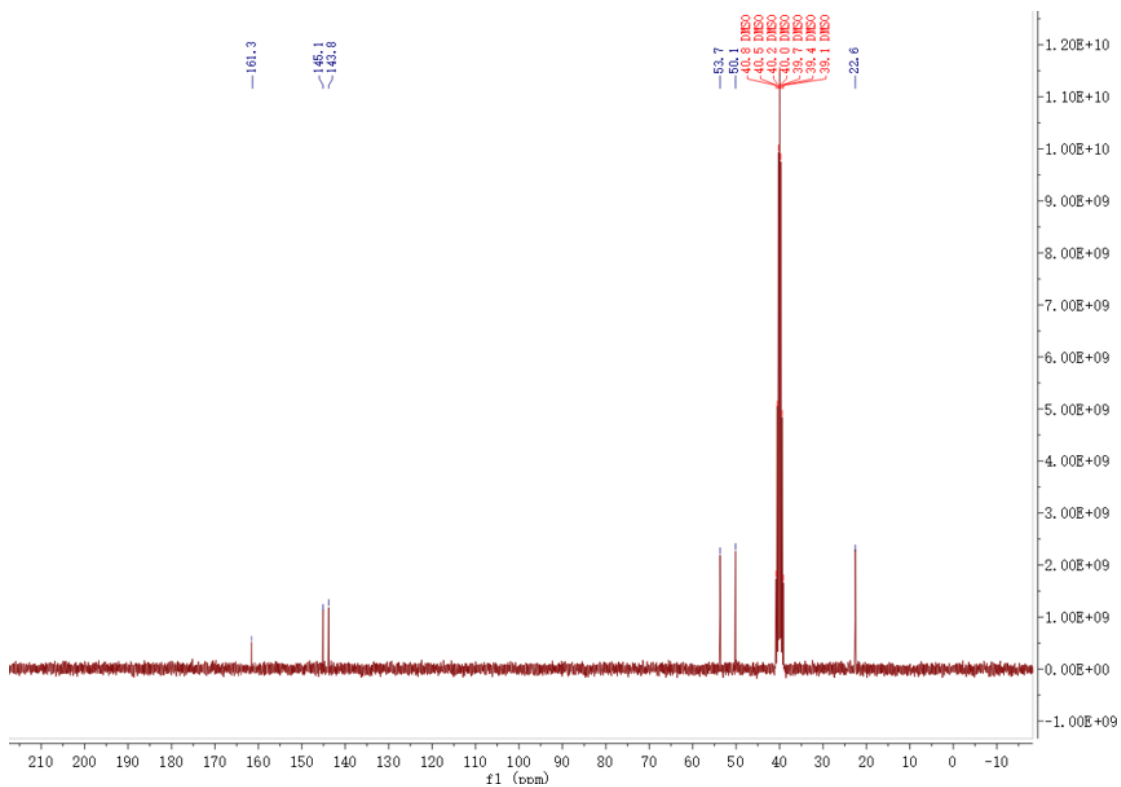


Figure S8 ^{13}C NMR spectra (75 MHz) of **4** in [D₆] DMSO at 25 °C.