

Electronic Supplementary Information

Asymmetric functionalized modification of bi(1,2,4-triazole) towards high-energy insensitive materials

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1 General methods

^1H and ^{13}C spectra were recorded using a 400 MHz nuclear magnetic resonance spectrometer Bruker AVANCE NEO 400 at a frequency of 400.13 MHz and 100.62 MHz, respectively. The melting and decomposition points were obtained at a heating rate of $10^\circ\text{C min}^{-1}$ and a flow rate of dry nitrogen gas of 50 mL min^{-1} using a Discovery DSC 25 differential scanning calorimeter from TA Instruments Co. IR spectra were recorded using a ThermoScientific Summit PRO FT-IR in KBr pellets that aim at solids. Densities were determined at 25°C by employing a Micromeritics AccuPycII 1345 gas pycnometer. Elemental analyses were carried out using a Thermo Scientific FLASH 2000 elemental analyzer. The impact and friction sensitivities were measured using a standard BAM fall hammer and a BAM friction tester, respectively.

2. Synthesis steps

Synthesis of compound **2**: At room temperature, 4.0 g ethyl-3-ethoxy-3-iminopropionate hydrochloride (EEIP) and 30 mL anhydrous acetonitrile were added to a 100 mL bottle, stir for half an hour, then 1.0 g of compound **1** and 6 mL of acetic acid were added in sequence, raise the temperature to 81°C , and reflux for another 12 hours. After the reaction was completed, it was cooled to the room temperature, and the solvent was removed under reduced pressure. 50 mL cold water is added, and the mixture was filtrated and dried to obtain yellow compound **2** (1.2 g, 69%). ^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 8.74 (s, 2H, C-H), 4.12 (q, $J = 8.0$ Hz, 2H, CH_2CH_3 -H), 3.94 (s, 2H, CH_2 -H), 1.19 (t, $J = 8.0$ Hz, 3H, CH_2CH_3 -H). ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 169.9, 143.9, 134.9, 121.6, 101.4, 59.6, 14.1. IR (cm^{-1}) $\nu = 2899, 1743, 1560, 1522, 1473, 1450, 1395, 1370, 1352, 1329, 1286, 1268, 1225, 1189, 1162, 1135, 1099, 1053, 1022, 978, 962, 937, 908, 876, 839, 763, 719, 707, 688, 675, 662, 654, 646, 641, 633, 602$. MS (m/z): calcd for: $\text{C}_8\text{H}_{10}\text{N}_6\text{O}_2$: 222.09 Found: 222.11. Elemental analysis calcd (%) for $\text{C}_8\text{H}_{10}\text{N}_6\text{O}_2$ (222.09): C 43.24, H 4.54, N 37.82 found: C 43.15, H 4.65, N 37.91.

Synthesis of compound **3**: At 0°C , compound **2** (1.0 g, mmol) was slowly added into 5 mL fuming nitric acid, maintained at this temperature for half an hour, and then returned to room temperature and continued reacting for 2 hours. After the reaction was completed, the reaction system was poured into ice water and large amounts of white solids are generated. Filter and

dry to obtain white solid of compound **3** (1.05 g, 75%). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 8.86 (s, 1H, C-H), 4.61 (q, *J* = 8.0 Hz, 2H, CH₂), 1.34 (t, *J* = 8.0 Hz, 3H, CH₃). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 156.3, 151.5, 148.1, 146.5, 136.9, 113.9, 66.8, 13.6. MS (*m/z*): calcd for: C₈H₈N₈O₆: 312.06 Found: 312.19. Elemental analysis calcd (%) for C₈H₈N₈O₆ (312.06): C 30.78, H 2.58, N 35.89 found: C 30.55, H 2.45, N 35.91.

Synthesis of compound **4**: 0.50 g compound **3** dissolved in 20 mL ethanol, methanolic ammonia (2.0 mol/L, 5 mL) solution was added, stirred for 2 hours, and filtered to obtain yellow solid (0.35 g, 85%). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 8.40 (s, 1H, C-H-H), 7.19 (s, 4H, NH₄⁺-H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 153.5, 149.4, 135.9, 125.6, 109.3. IR (cm⁻¹) ν = 3094, 1558, 1507, 1446, 1354, 1225, 1131, 1105, 1025, 990, 824, 742, 703, 631, 562, 546, 535, 520, 508, 493, 486, 478, 470, 462, 447, 435, 428, 417, 405, MS (*m/z*): calcd for: C₅H₇N₉O₄: 257.06 Found: 257.16. Elemental analysis calcd (%) for C₅H₇N₉O₄ (257.06): C 23.35, H 2.74, N 49.02 found: C 23.25, H 2.85, N 48.91.

Synthesis of compound **5**: 0.50 g compound **3** dissolved in 20 mL ethanol, 2 mL 50% hydroxylamine solution was added, stirred for 2 hours, and filtered to obtain yellow solid (0.37 g, 86%). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 8.42 (s, 1H, C-H-H), 7.10 (s, 4H, NH₃OH⁺-H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 152.7, 150.8, 129.0, 125.0, 118.1. IR (cm⁻¹) ν = 3234, 1533, 1499, 1443, 1373, 1239, 1099, 991, 742, 669, 493, 470, 447, 437, 417, 405. MS (*m/z*): calcd for: C₅H₇N₉O₅: 273.06. Found: 273.18. Elemental analysis calcd (%) for C₅H₇N₉O₄ (273.06): C 21.98, H 2.58, N 46.15, found: C 22.15, H 2.75, N 45.91.

Synthesis of compound **6**: 0.50 g compound **3** dissolved in 20 mL ethanol, 1 mL 85% hydrazine hydrate was added, stirred for 2 hours, and filtered to obtain yellow solid (0.38 g, 90%). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 8.37 (s, 1H, C-H-H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 151.3, 135.1, 126.5, 124.3, 105.0. IR (cm⁻¹) ν = 3853, 3735, 3649, 3629, 3243, 1684, 1653, 1559, 1541, 1507, 1234, 1096, 989, 462. MS (*m/z*): calcd for: C₅H₇N₉O₄: 272.07 Found: 272.17. Elemental analysis calcd (%) for C₅H₈N₁₀O₄ (272.07): C 22.06, H 2.96, N 51.46, found: C 22.15, H 3.15, N 51.21.

Synthesis of compound **TNBN**: At 0°C, compound **4** (0.50 g) was dissolved in 5 mL H₂SO₄, followed by slow addition of fuming nitric acid. After holding at this temperature for half an hour, the reaction warmed to room temperature for overnight. After the reaction was completed, the reacting

solution was poured into ice water to generate a large number of white solids. Filtered and dried to obtain compound **TNBN** (0.36 g, 72%). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 8.89 (s, 1H, C-H-H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 153.3, 151.0, 150.4, 148.5, 146.0. MS (*m/z*): calcd for: C₅H₃N₉O₆: 285.02 Found: 285.16. Elemental analysis calcd (%) for C₅H₃N₉O₆ (285.02): C 21.06, H 1.06, N 44.21 found: C 21.15, H 1.17, N 44.11.

3. Crystallographic data

Table S1 Crystal structure data and refined parameters of compounds **TNBN**.

compound	TNBN
Empirical formula	C ₅ H ₃ N ₉ O ₆
Formula weight	285.16
Temperature / K	117.40(14)
Crystal system	triclinic
Space group	P-1
a / Å, b / Å, c / Å	9.4075(6), 10.5966(7), 10.7909(7)
α/°, β/°, γ/°	75.498(6), 87.290(5), 88.701(5)
Volume / Å ³	1040.21(12)
Z	4
ρ _{calc} / mg mm ⁻³	1.821
μ / mm ⁻¹	0.166
F(000)	576
Crystal size / mm ³	0.21 × 0.18 × 0.13
2θ range for data collection	5.96 to 52°
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -10 ≤ l ≤ 13
Reflections collected	7528
Independent reflections	3978[R(int) = 0.0284 (inf-0.9Å)]
Data/restraints/parameters	3978/0/361
Goodness-of-fit on F ²	1.070
Final R indexes [<i>I</i> >2σ (<i>I</i>) i.e. F _o >4σ (F _o)]	R1 = 0.0427, wR2 = 0.0953
Final R indexes [all data]	R1 = 0.0539, wR2 = 0.1039
Largest diff. peak/hole / e Å ⁻³	0.236/-0.330
Flack Parameters	N
Completeness	0.9979
CCDC	2299438

Table S2 Bond lengths for compound **TNBN**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O7	N16	1.217(2)	O6	N9	1.215(2)
N13	C9	1.352(3)	O3	N8	1.214(2)
N13	C8	1.329(3)	N5	N6	1.353(2)
O11	N18	1.210(2)	N5	C4	1.325(3)

O10	N17	1.213(2)	O2	N7	1.217(2)
N14	N15	1.347(2)	N9	O5	1.212(2)
N14	C9	1.326(3)	N9	C5	1.525(3)
N15	C8	1.341(2)	O4	N8	1.217(2)
O12	N18	1.211(2)	N2	N3	1.361(2)
O9	N17	1.214(2)	N2	C1	1.321(3)
N17	C10	1.528(3)	N4	C4	1.355(3)
N16	O8	1.210(2)	N4	C3	1.327(3)
N16	C10	1.525(3)	N1	C1	1.328(3)
C9	C10	1.483(3)	N1	C2	1.362(3)
N10	C7	1.362(3)	O1	N7	1.210(2)
N10	C6	1.329(3)	N6	C3	1.335(3)
N11	N12	1.361(2)	N7	C5	1.537(3)
N11	C6	1.324(3)	N3	C2	1.320(3)
N18	C10	1.547(3)	N8	C5	1.537(3)
N12	C7	1.325(3)	C4	C5	1.490(3)
C7	C8	1.456(3)	C3	C2	1.467(3)

compound **TNBN**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O7	N16	1.217(2)	O6	N9	1.215(2)
N13	C9	1.352(3)	O3	N8	1.214(2)
N13	C8	1.329(3)	N5	N6	1.353(2)
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O10	N17	1.213(2)	O2	N7	1.217(2)
N14	N15	1.347(2)	N9	O5	1.212(2)
N14	C9	1.326(3)	N9	C5	1.525(3)
N15	C8	1.341(2)	O4	N8	1.217(2)
O12	N18	1.211(2)	N2	N3	1.361(2)
O9	N17	1.214(2)	N2	C1	1.321(3)
N17	C10	1.528(3)	N4	C4	1.355(3)
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N16	C10	1.525(3)	N1	C1	1.328(3)
C9	C10	1.483(3)	N1	C2	1.362(3)
N10	C7	1.362(3)	O1	N7	1.210(2)
N10	C6	1.329(3)	N6	C3	1.335(3)
N11	N12	1.361(2)	N7	C5	1.537(3)
N11	C6	1.324(3)	N3	C2	1.320(3)
N18	C10	1.547(3)	N8	C5	1.537(3)
N12	C7	1.325(3)	C4	C5	1.490(3)
C7	C8	1.456(3)	C3	C2	1.467(3)

4 ¹H NMR and ¹³C NMR, and IR Spectra

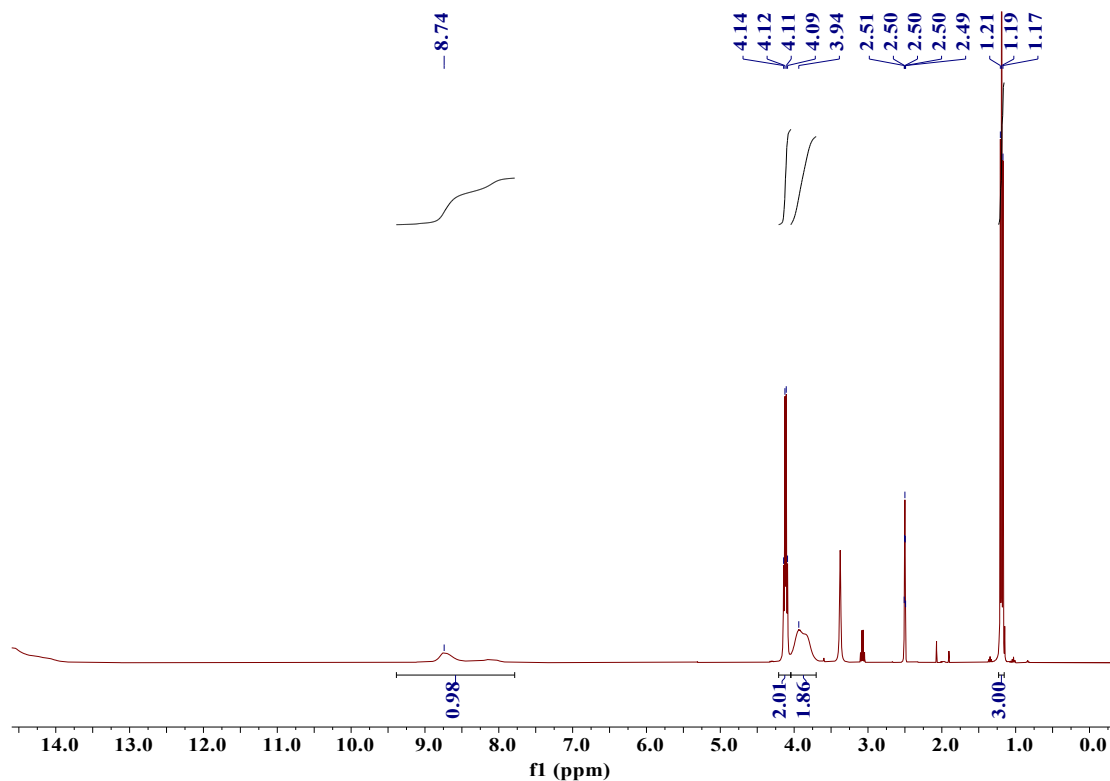


Figure S1. ¹H NMR spectrum of compound 2 in DMSO-*d*₆.

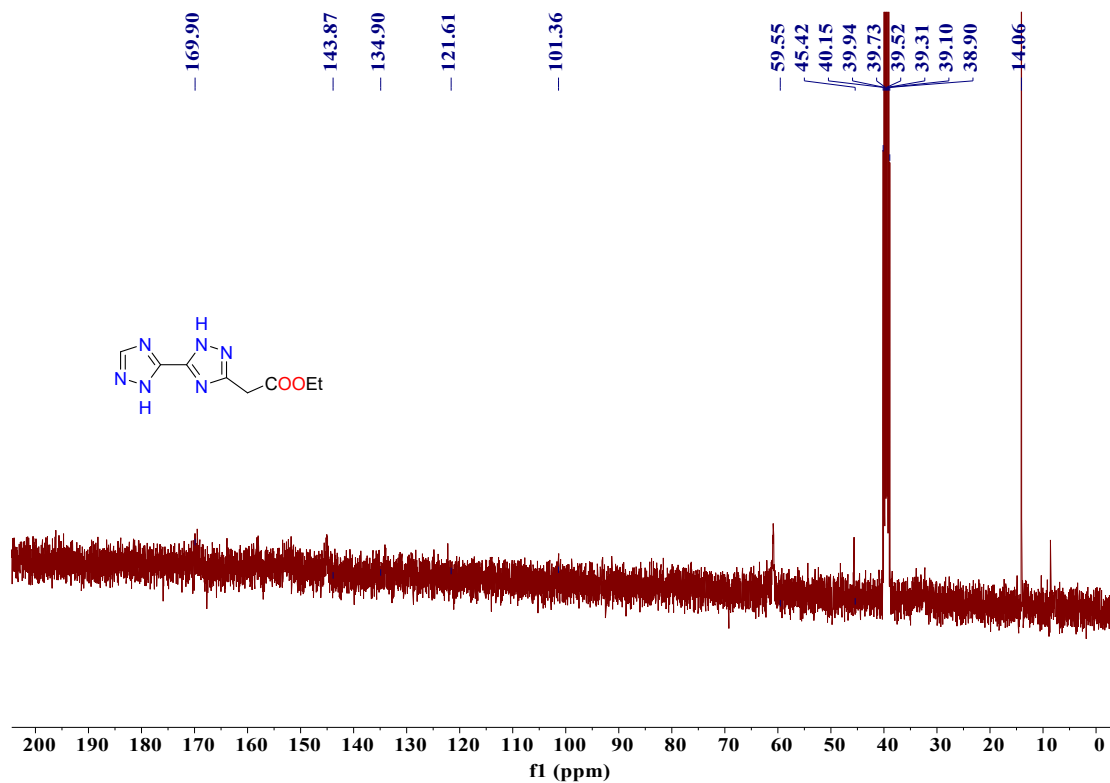


Figure S2. ¹³C NMR spectrum of compound 2 in DMSO-*d*₆.

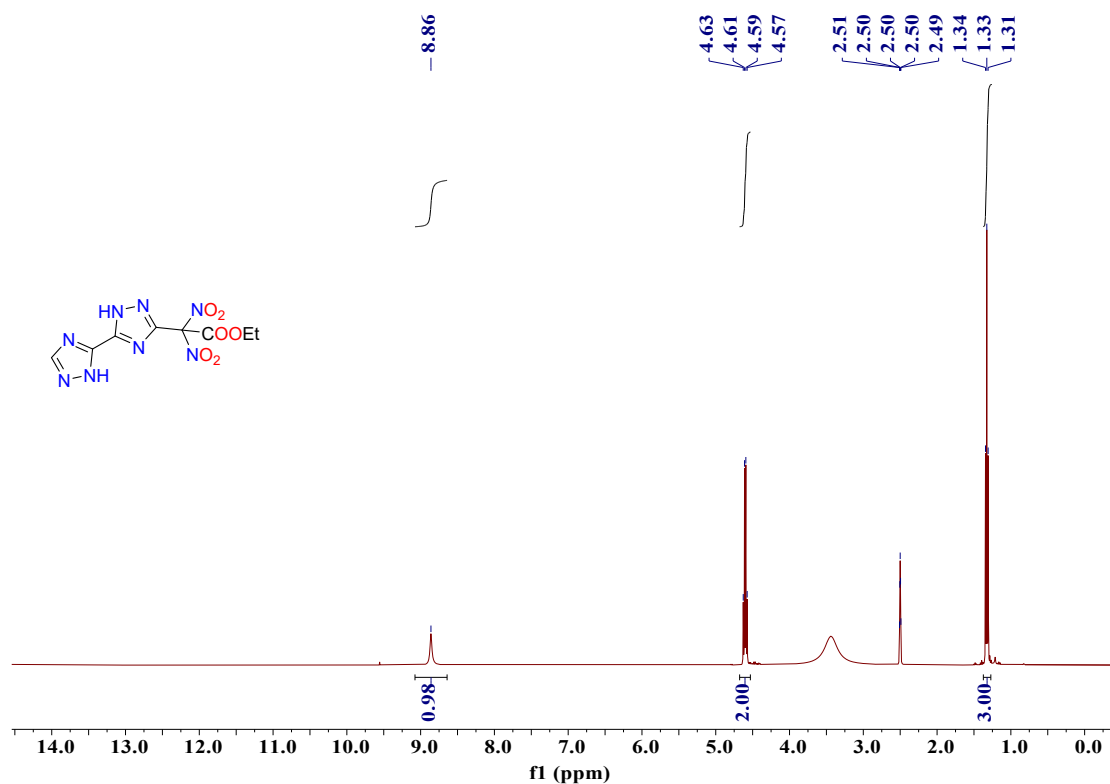


Figure S3. ¹H NMR spectrum of compound 3 in DMSO-*d*₆.

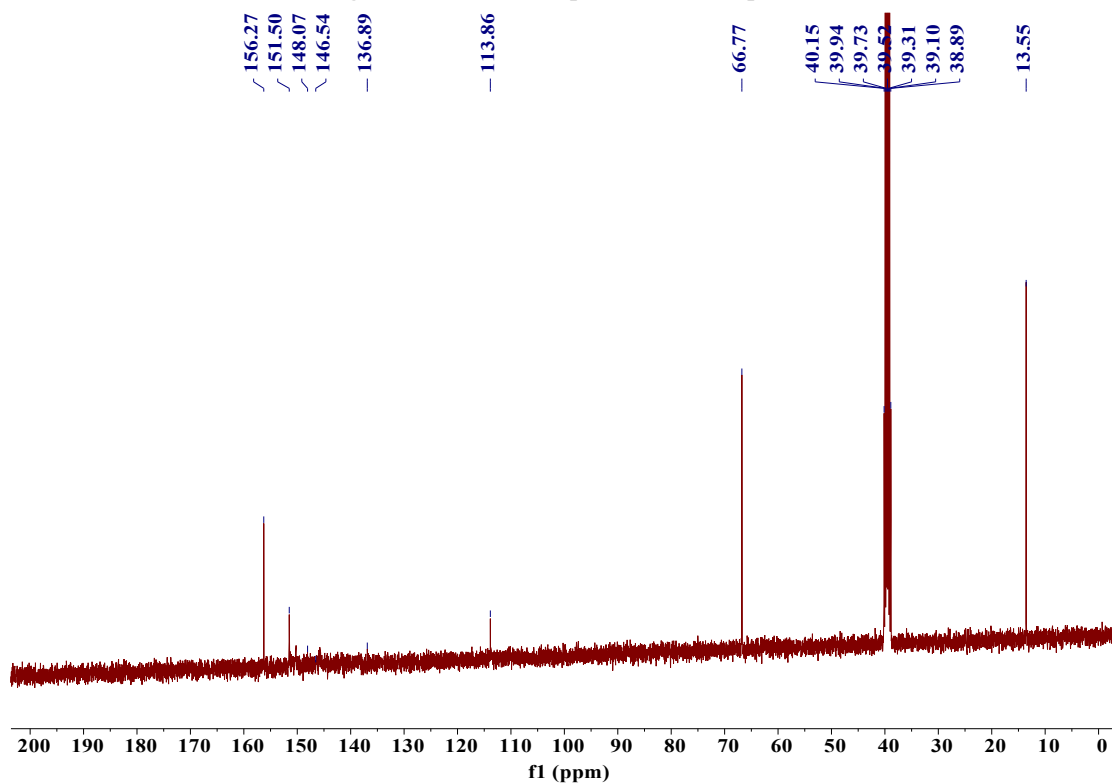


Figure S4. ¹³C NMR spectrum of compound 3 in DMSO-*d*₆.

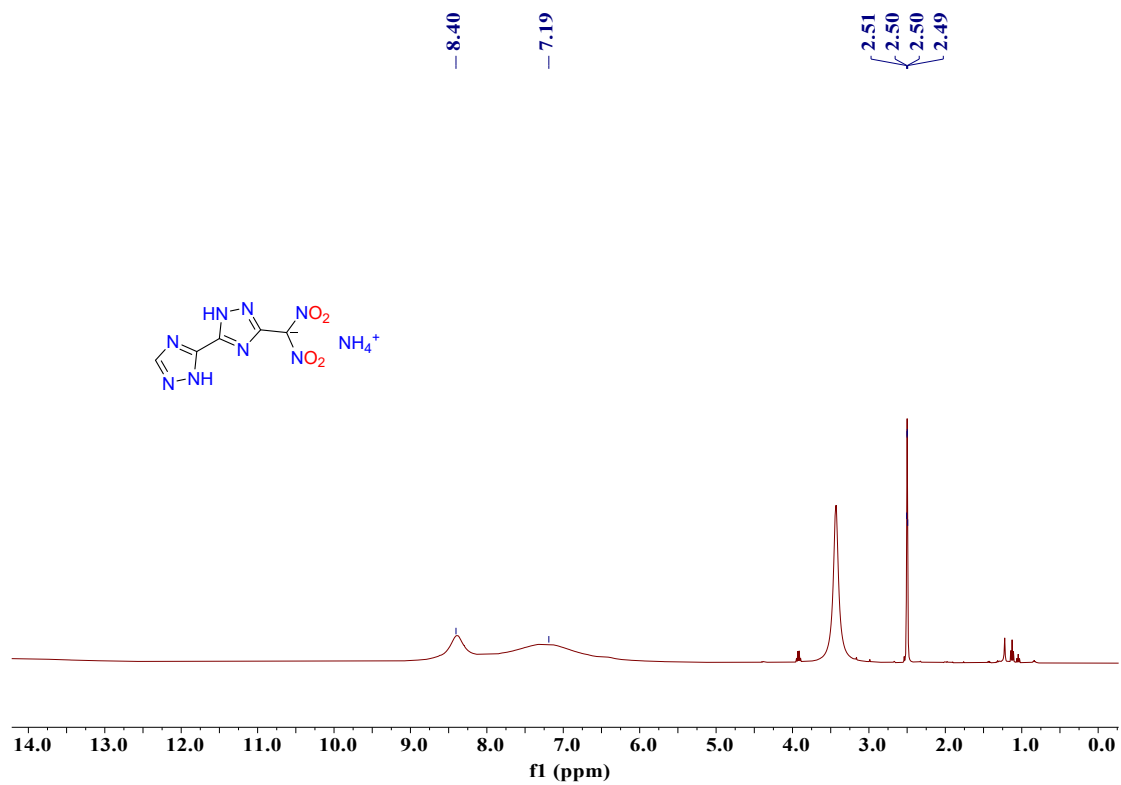


Figure S5. ^1H NMR spectrum of compound 4 in DMSO- d_6 .

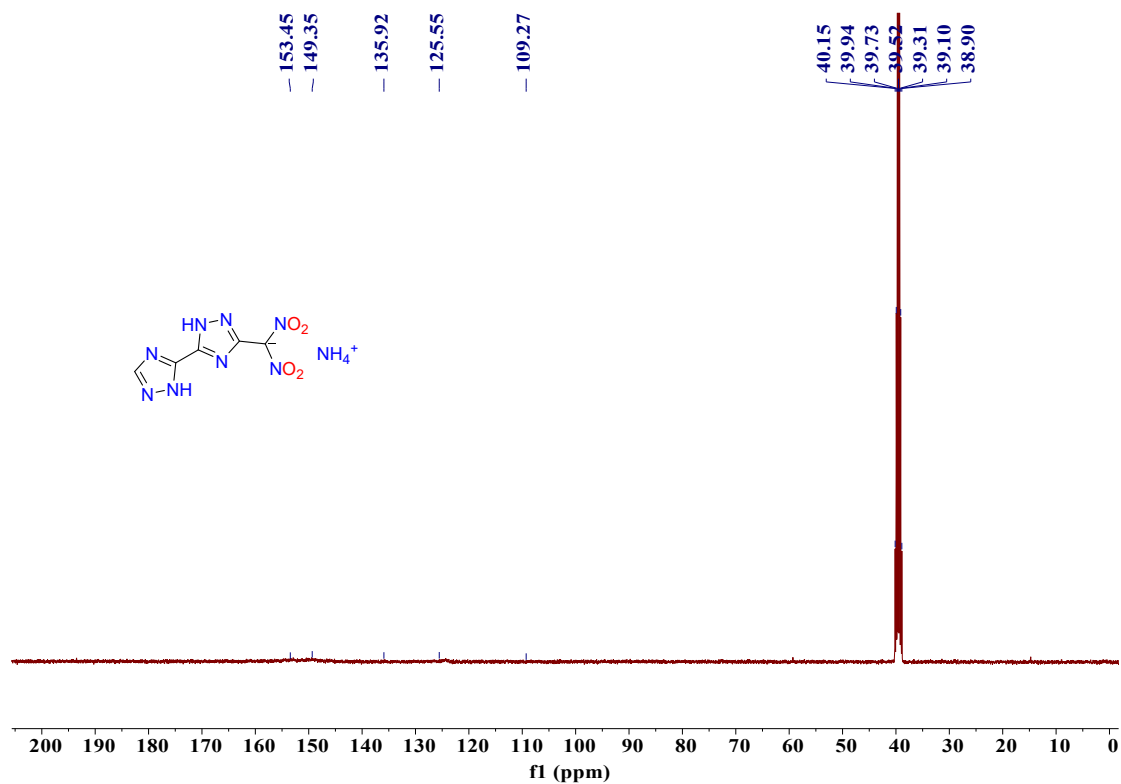


Figure S6. ^{13}C NMR spectrum of compound 4 in DMSO- d_6 .

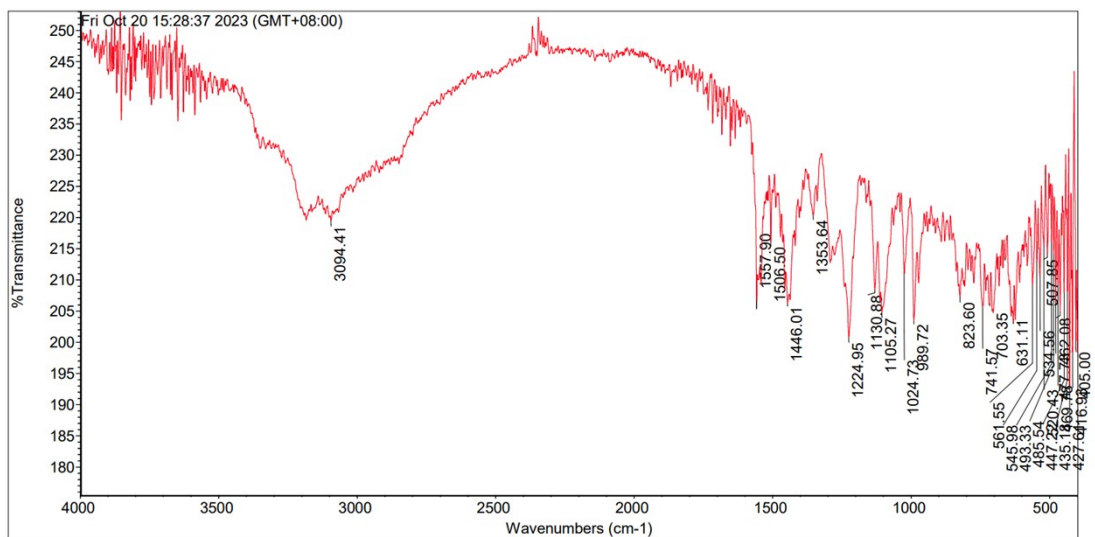


Figure S7. IR spectrum of compound 4.

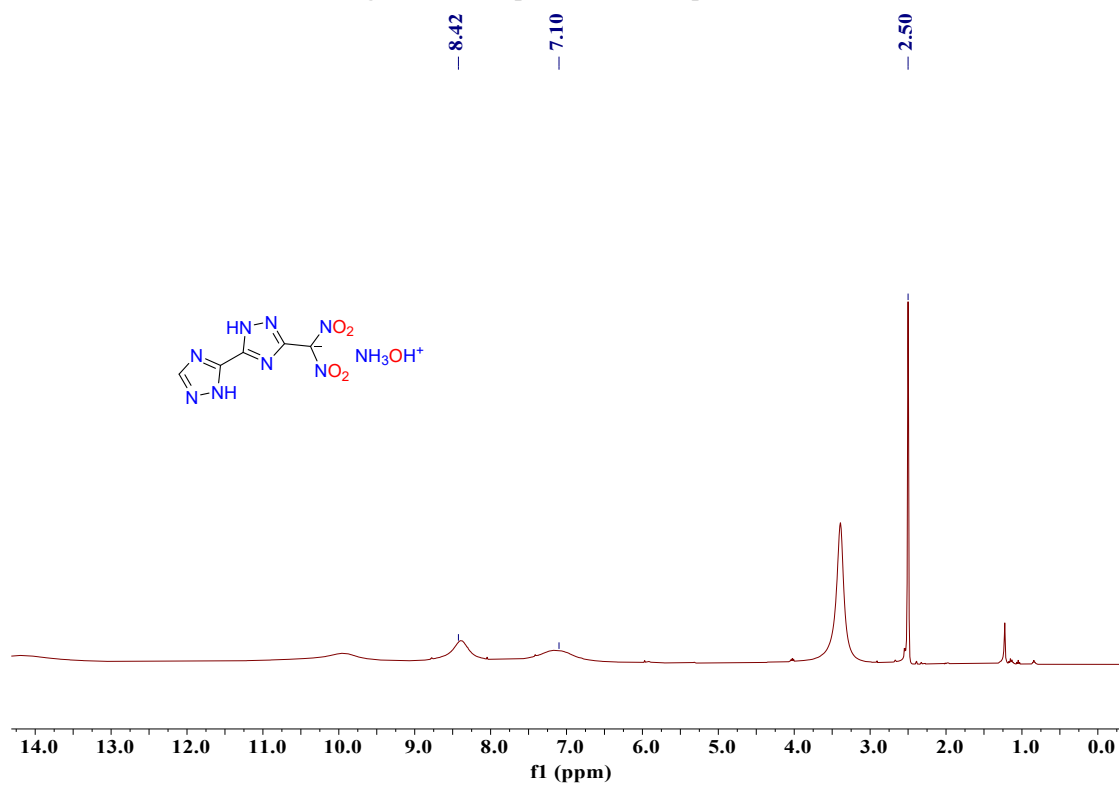


Figure S8. ^1H NMR spectrum of compound 5 in $\text{DMSO-}d_6$.

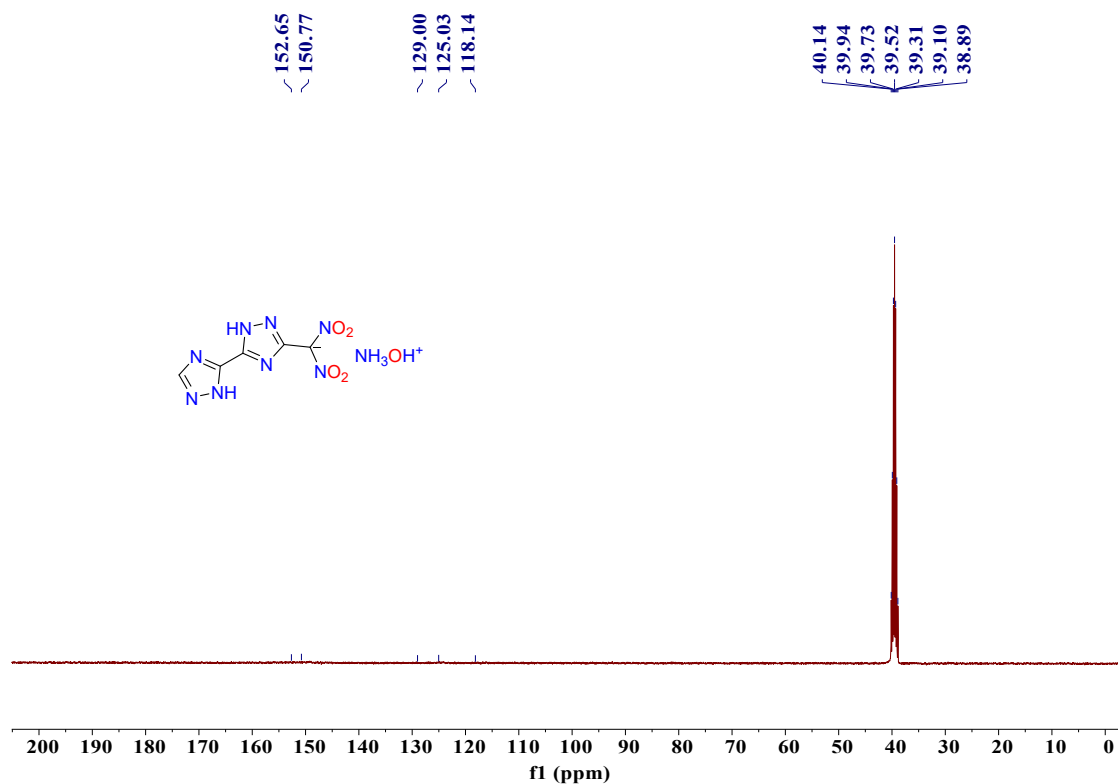


Figure S9. ^{13}C NMR spectrum of compound 5 in DMSO- d_6 .

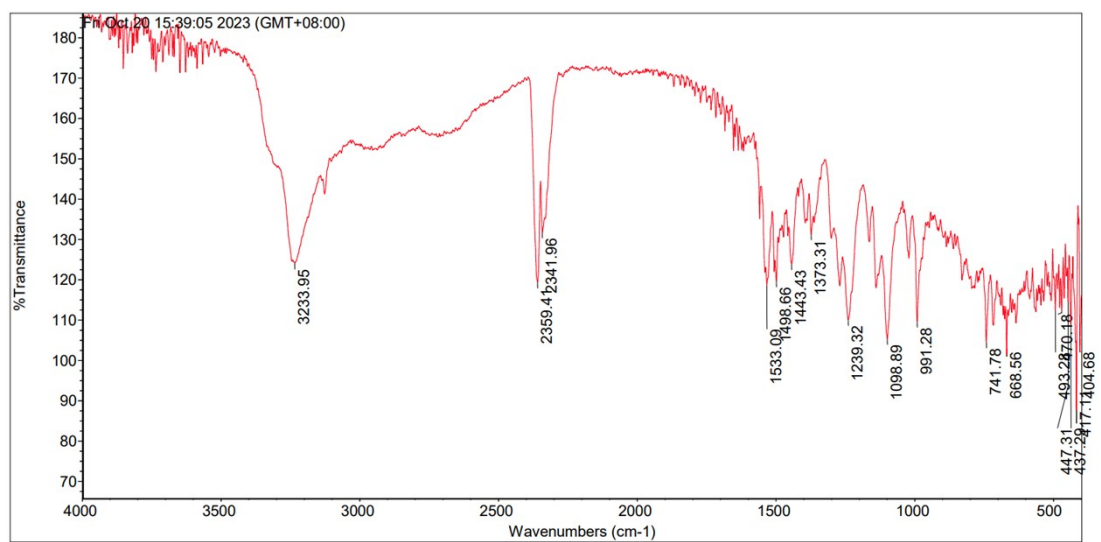


Figure S10. IR spectrum of compound 5.

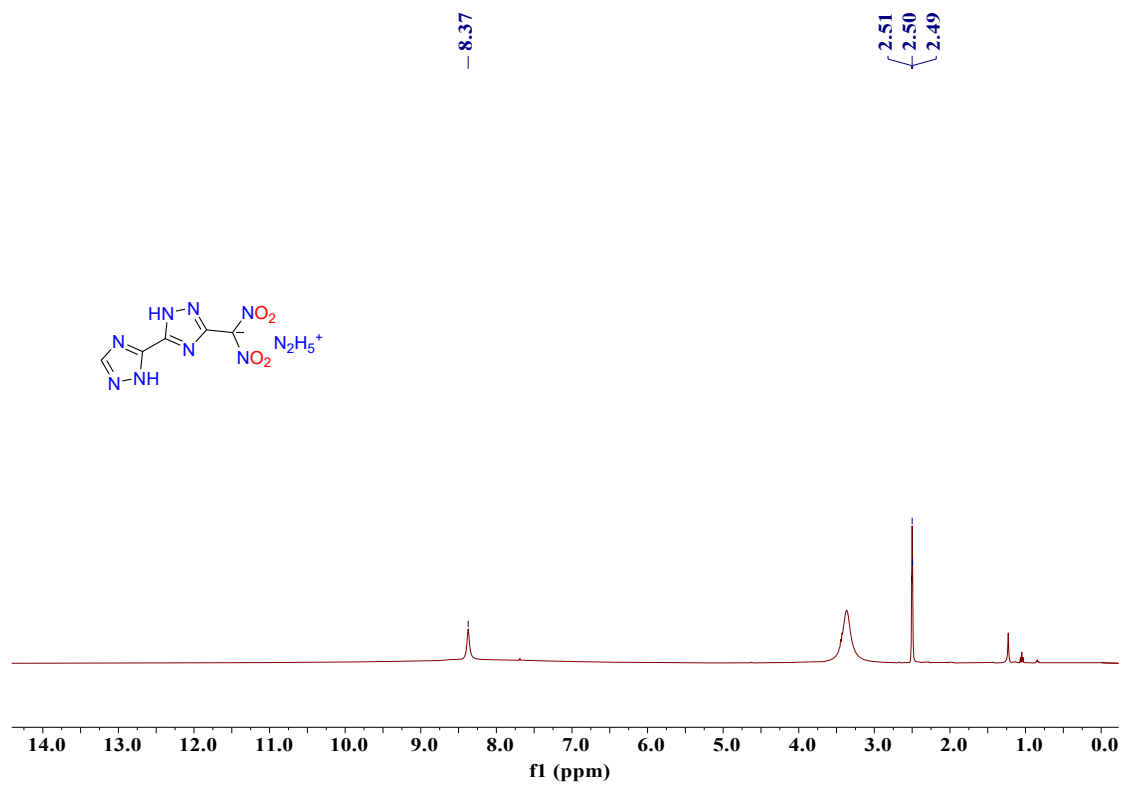


Figure S11. ¹H NMR spectrum of compound 6 in DMSO-*d*₆.

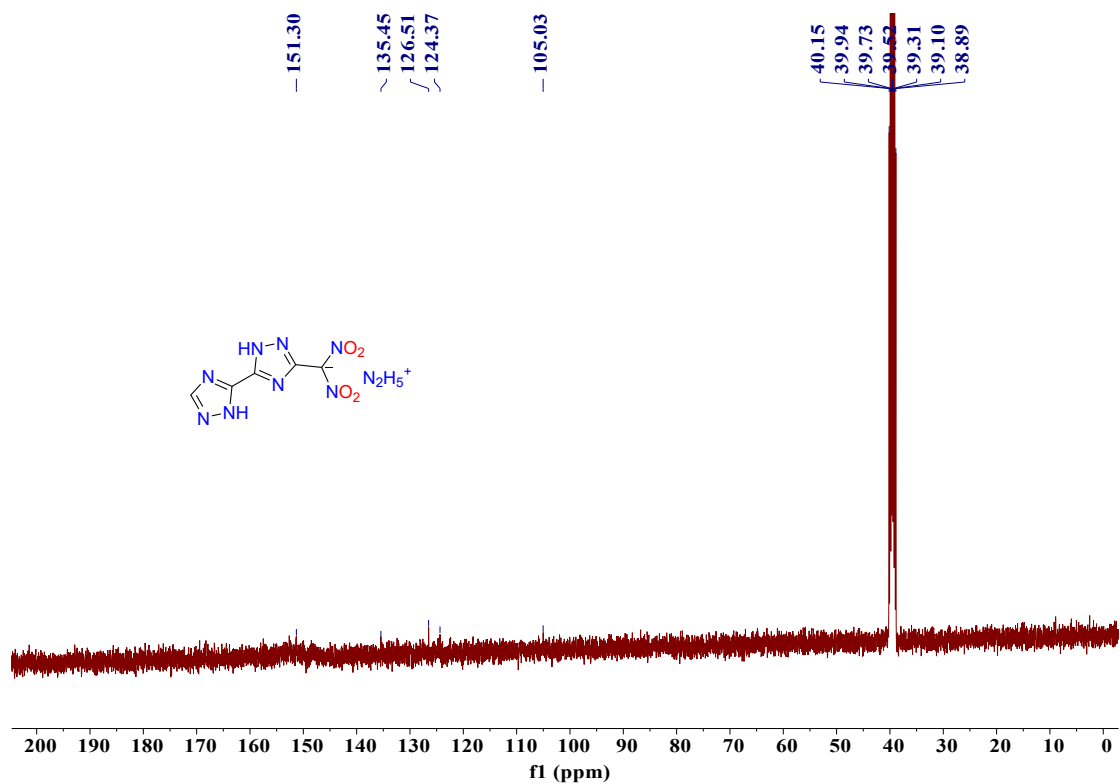


Figure S12. ¹³C NMR spectrum of compound 6 in DMSO-*d*₆.

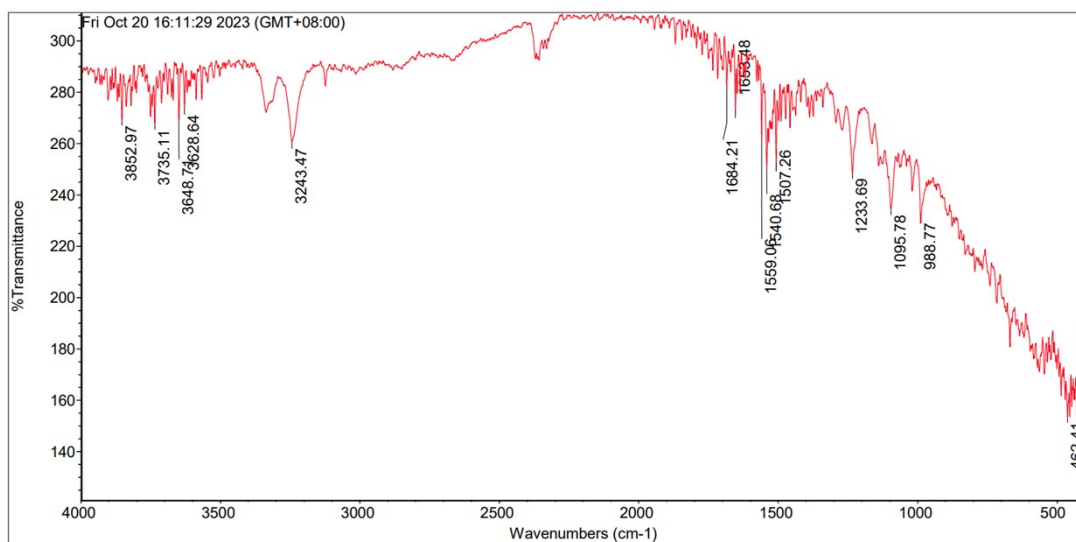


Figure S13. IR spectrum of compound 6.

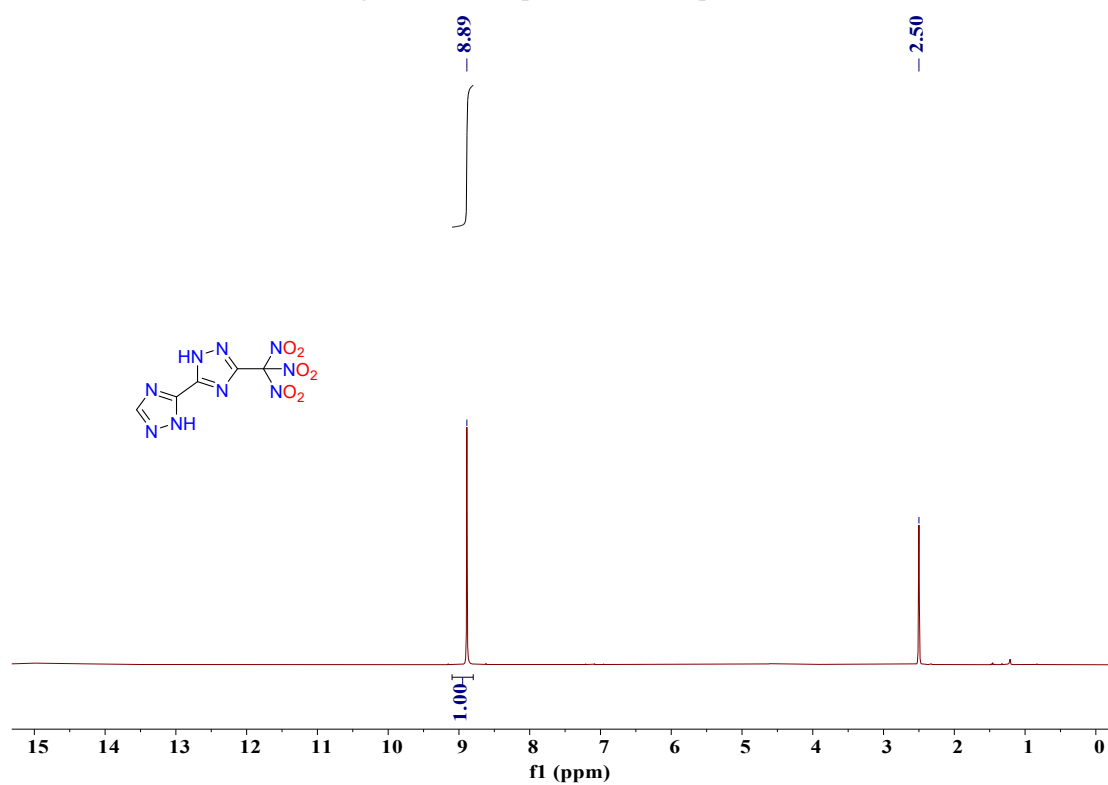


Figure S14. ^1H NMR spectrum of TNBN in $\text{DMSO-}d_6$.

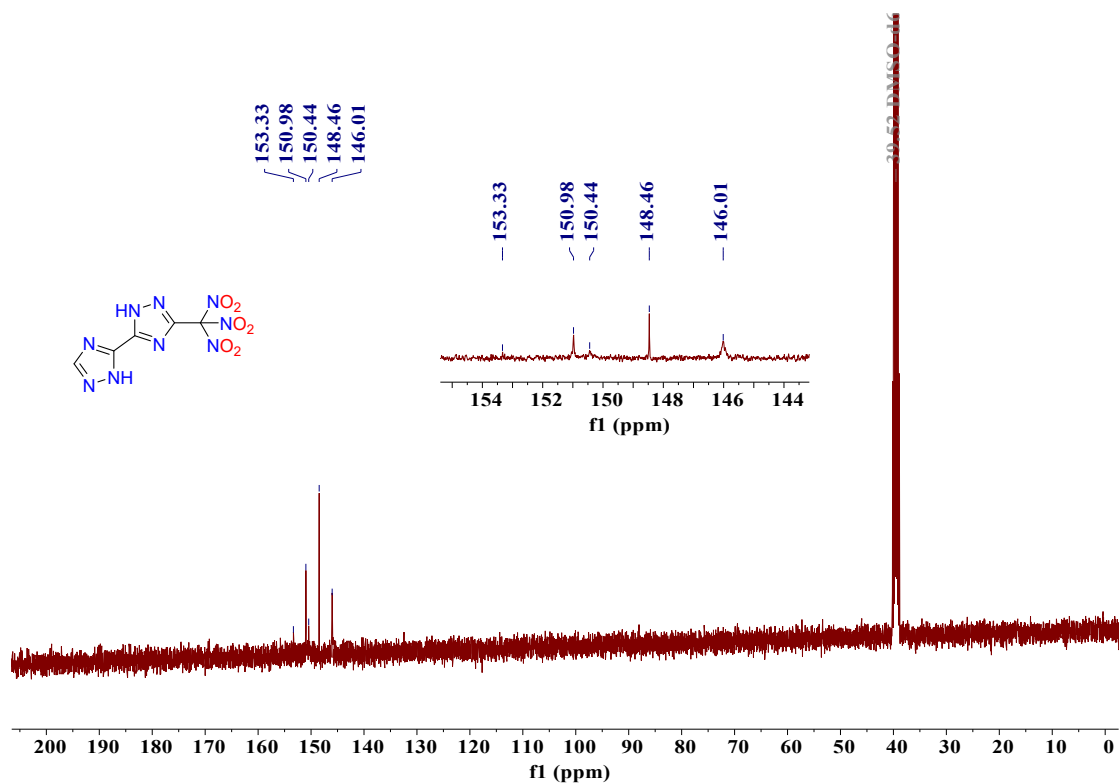


Figure S15. ^{13}C NMR spectrum of TNBN in $\text{DMSO-}d_6$.

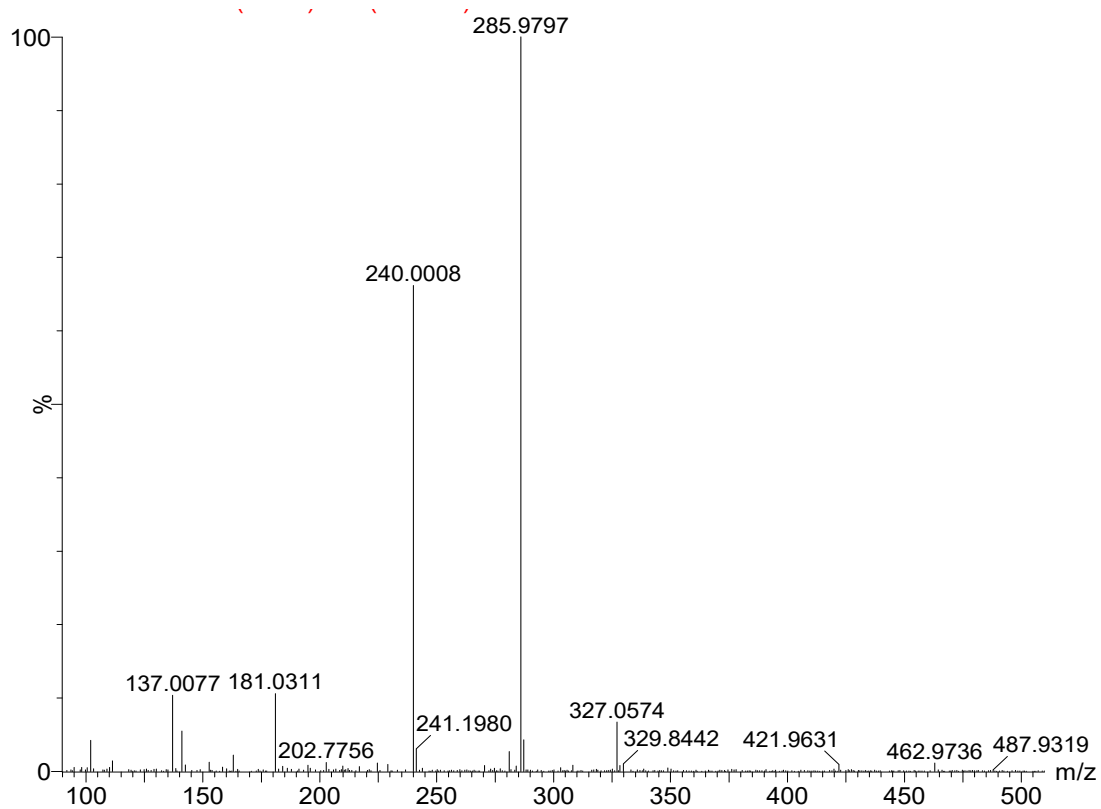


Figure S16. Mass spectrum of TNBN.

5. DSC curve

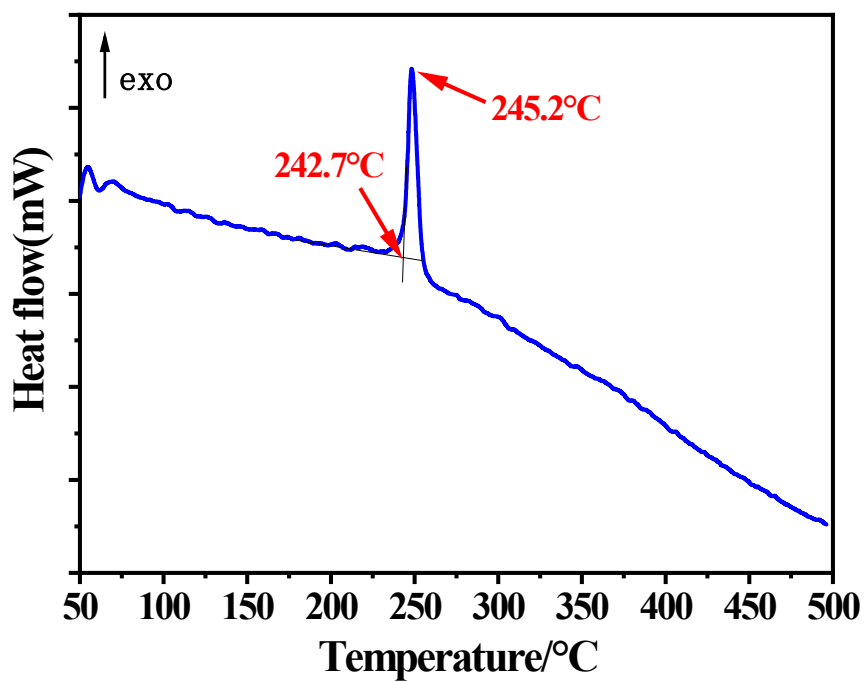


Figure S17. the DSC curves of compounds 4.

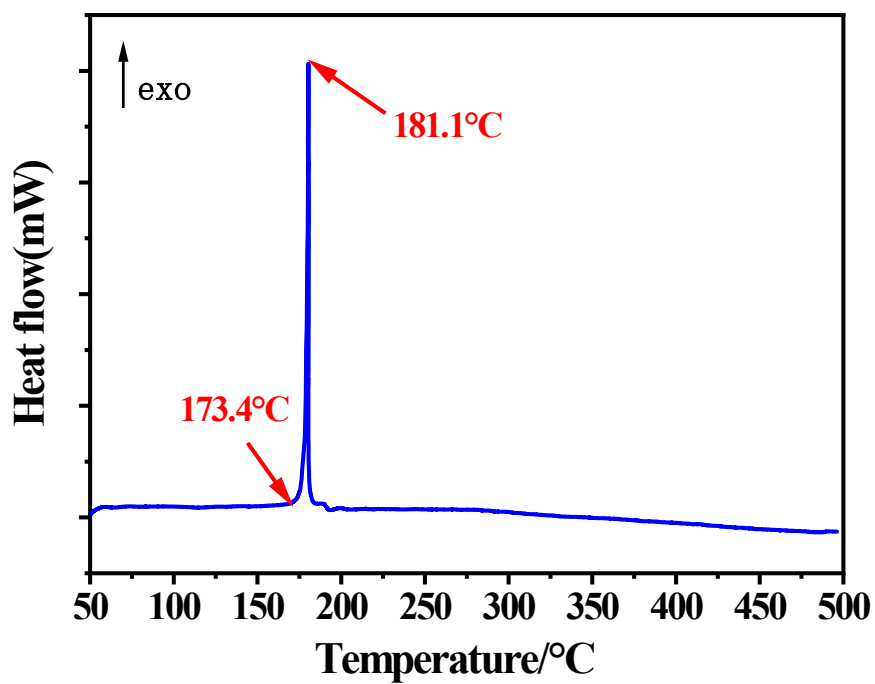


Figure S18. the DSC curves of compounds 5.

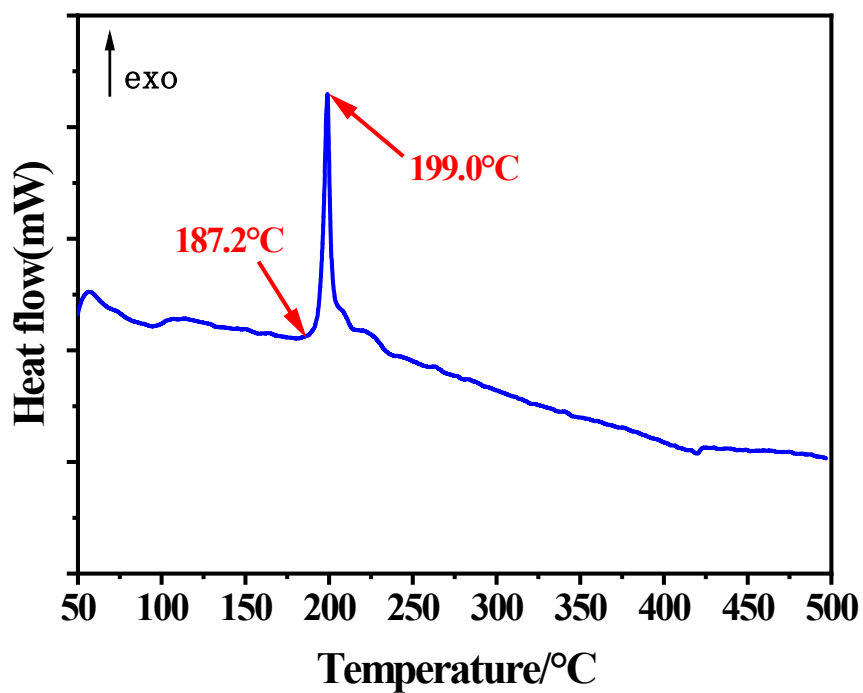


Figure S19. the DSC curves of compounds 6.

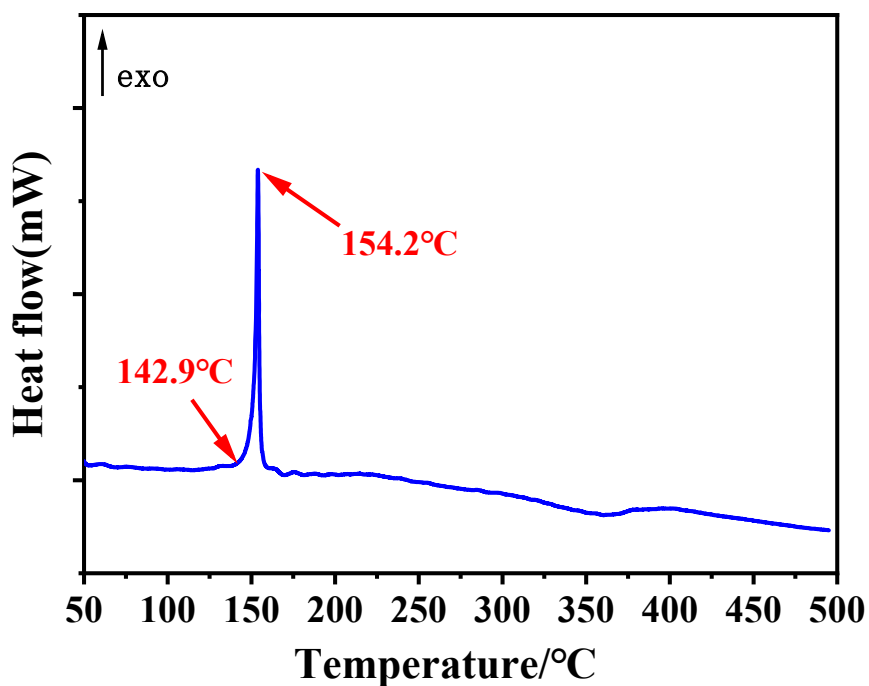


Figure S20. the DSC curves of compounds TNBN.

6. Calculation of formation enthalpy

Table S4 Cartesian coordinates of the optimized anions of compounds 4, 5 and 6.

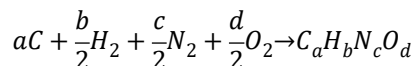
atom	a/ Å	b/ Å	c/ Å
C	-1.78920400	-0.83992600	0.09039000
C	-1.21129300	1.16843800	0.00471500
N	-2.12652600	0.34058100	-0.48898300
H	-2.33131900	-1.75890700	-0.08740800
H	0.39634200	0.87387400	1.34004200
C	-1.04973700	2.58041100	-0.24667500
N	-0.11263500	3.34528800	0.27990600
H	-2.63523100	3.00626600	-1.59696600
C	-0.37634600	4.57735700	-0.25523600
N	-1.84008600	3.31160800	-1.05856100
N	-1.42825700	4.58871800	-1.07891100
N	-0.38717700	0.49349000	0.82941300
N	-0.74058600	-0.80531900	0.90058900
C	0.40715700	5.77753000	0.03535600
N	0.02878400	6.54126800	1.13459600
O	0.63397700	7.56591100	1.47056200
O	-0.97181300	6.11819900	1.76359500
N	1.51366200	6.03273100	-0.76799600
O	1.71740800	5.19715200	-1.68245500
O	2.24657900	7.01362000	-0.59573200

Table S5 Cartesian coordinates of TNBN.

atom	a/ Å	b/ Å	c/ Å
O	-4.19105100	15.48673100	11.89392500
N	-4.72744500	16.18769000	11.06215900
O	-5.66283100	16.94306500	11.20472600
C	-4.11289400	16.06136100	9.66365200
N	-4.18915000	14.55588900	9.32449100
N	-5.00653500	16.80042500	8.64864300
C	-2.73857000	16.62149100	9.60092100
O	-5.19971400	13.99361300	9.69083300
O	-3.25019400	14.09299800	8.71559100
O	-5.65545900	16.12303700	7.88127300
O	-4.95974400	18.00770600	8.73250100
N	-2.02245200	16.90061100	10.68108000
N	-2.15067800	16.88621200	8.41083200
N	-0.89801200	17.36896500	10.13456700
C	-0.97458000	17.35927900	8.78173700
H	-0.12392500	17.68075300	10.70489200
C	0.13101900	17.82752000	7.96506600
N	1.27553100	18.28682100	8.55008300
N	0.12244600	17.84786000	6.63980300
C	2.01688700	18.61009700	7.51067200
N	1.33808300	18.35205200	6.37386400

H	3.01667900	19.02020300	7.53311400
H	1.62248800	18.48582200	5.41487200

Both **TNBN** and the anions of compounds 4, 5 and 6 were subjected to geometric optimization and vibration analysis at the B3PW91/6-31G** level, and higher precision single point energy calculations were performed again at M062X/def2TZVP. Add the high-precision single point energy and the enthalpy correction obtained from vibration analysis to obtain the corresponding enthalpy of the structure. The calculation principle of the enthalpy of molecular formation is as follows:



By definition, the enthalpy of formation is the reaction enthalpy of the above equation. The enthalpy of reaction is determined by calculating the difference between the enthalpy of the products and the enthalpy of the reactants. To calculate the enthalpy of each species involved in the reaction, quantum chemistry computational programs such as Gaussian or ORCA can be used. Carbon is a solid at room temperature, but the enthalpy value obtained from quantum chemistry calculation corresponds to its formation in the gaseous state. Subtracting the sublimation enthalpy ($H_{sub}(C)$) from the enthalpy value ($H(C)$) obtained from quantum chemistry calculation is necessary to determine the enthalpy of carbon in its stable phase (solid). In summary, the formula for calculating the enthalpy of formation using the definition method is as follows:

$$\Delta_f H_m^\theta = \Delta_r H_m^\theta = H(C_aH_bN_cO_d) - a[H(C) - H_{sub}(C)] - \frac{b}{2}H(H_2) - \frac{c}{2}H(N_2) - \frac{d}{2}H(O_2)$$

All the enthalpy values provided above are enthalpies at 298 K. The enthalpy represented by $H(C_aH_bN_cO_d)$ corresponds to the enthalpy of a single molecule. Therefore, the final result denotes the gas-phase enthalpy of formation of the compound at 298 K.

The enthalpy of formation of anion is calculated using the same principle, while the enthalpy of cation formation is found in the NIST manual. Then, based on Jenkins' empirical formula, the lattice energy of the ionic salt was calculated.

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

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

Finally, according to the Born Haber cycle, the enthalpy of ion salt formation can be calculated using the following formula:

$$\Delta_f H_m^\theta(\text{salt}) = \Delta_f H_m^\theta(\text{cation}) + \Delta_f H_m^\theta(\text{anion}) - \Delta H_L$$

Table S6 The enthalpy of formation of the energetic salts (4, 5 and 6) and compound **TNBN**.

Compound	$\Delta_f H_m^\theta(\text{cation})$	$\Delta_f H_m^\theta(\text{anion})$	H_L	$\Delta_f H_m^\theta(\text{cmp, air})$	$\Delta_{\text{sub}} H_m^\theta(\text{kJ/mol})$	$\Delta_f H_m^\theta(\text{cmp, solid})$
4	641.8	116.4	489.6	–	–	268.6
5	681.5	116.4	479.8	–	–	318.1
6	759.9	116.4	476.2	–	–	400.1
TNBN	–	–	–	575.8	164.1	411.7