Electronic Supplementary Information

Bridged and Fused Triazolic Energetic Frameworks with an Azo Building Block towards Thermally Stable and Applicable Propellent Ingredients

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Experimental Section

Safety precautions

Although no explosions or hazards were observed during the preparation and handling of these compounds, all are potentially explosive materials. Mechanical actions involving scraping must be avoided. In addition, all compounds must be synthesized on a small scale. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

General methods

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on 300/400 MHz (Bruker AVANCE 300/400) nuclear magnetic resonance spectrometers operating at 300/400, and 75/100 MHz, respectively. CD_3CN, $CDCl_3$, or d_6-DMSO were used as solvent and locking solvent. Chemical shifts for the ^{1}H and ^{13}C spectra are reported relative to Me_4Si. The decomposition (onset temperature) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a heating rate of 5 ºC min^{-1}. IR spectra were recorded using KBr pellets with a FTIR spectrometer (Thermo Nicolet AVATAR 370). Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM fall hammer and a BAM friction tester.

Synthesis of (*E*)-1,1'-(diazene-1,2-diylbis(3-nitro-1*H*-1,2,4-triazole-5,1-diyl))bis (propan-2-one) (**2**):

Method A: 1-(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)propan-2-one[1] (**1**) (0.185 g, 1.0 mmol) was dissolved in concentrated hydrochloric acid (2.5 mL). Potassium permanganate (0.197 g, 1.2 mmol) was dissolved in water (2.5 mL) and added dropwise to the reaction mixture. It was stirred for 48 hours at room temperature. The precipitate was filtered and dried to give 0.168 g (92%) of **2** as an orange solid.

Method B: Compound **1** (3.7 g, 20 mmol) was added to acetonitrile (40 mL) with stirring at 0-5 ºC. After dissolution, tert-butyl hypochlorite (5.52 ml, 60 mmol, 3.0 eq.) was added to the solution with stirring at 0-5 ºC. After 5 h, the solvent was evaporated and dried under vacuum to leave a yellow solid (5.05 g, 69 % yield).

T_d (onset): 221 ºC. ^{1}H NMR (d_6-acetone): δ = 5.98 (s, 4H), 2.46 (s, 6H) ppm; ^{13}C NMR: δ = 199.4, 161.8, 158.7, 59.4, 27.2 ppm; IR (KBr pellet): ῡ = 3003(m), 2951(w), 1734(s), 1556(w), 1501(s), 1463(m), 1420(w), 1365(m), 1341(m), 1319(s), 1184(m), 1158(m), 868(m), 850(w), 806(w), 745(w), 716(w), 629(w), 588(w), 496(w) cm^{-1}; elemental analysis (%) calcd. for $C_{10}H_{10}N_{10}O_6$ (366.25): C, 32.79; H, 2.75; N, 38.24; found: C, 33.03; H, 2.72; N, 38.10.

Synthesis of (*E*)-1,2-bis(3-nitro-1-(trinitromethyl)-1*H*-1,2,4-triazol-5-yl)diazene (**3**): Compound **2** (0.366 g , 1.0 mmol) was dissolved in sulfuric acid (98%, 1 mL) at 0 ºC. After cooling to -5 ºC, nitric acid (90%, 1 mL) was added dropwise. The reaction mixture was warmed slowly to room temperature and stirred for 72 h. The yellow

precipitate (**3**) was collected by filtration and dried giving 0.469 g (81%). T_d (onset): 175 ºC. ^{13}C NMR (CD_3CN): δ = 160.3, 159.9, 126.2 ppm; IR (KBr pellet): ῡ = 1732(w), 1646(s), 1626(s), 1601(s), 1569(s), 1520(m), 1454(w), 1385(m), 1348(m), 1332(w), 1307(s), 1274(s), 1185(m), 1029(m), 997(w), 845(s), 833(s), 792(s), 735(m), 702(w), 625(w), 588(w), 523(w), 489(w), 433(w) cm^{-1}; elemental analysis (%) calcd. for $C_6N_{16}O_{16}$ (552.16): C, 13.05; H, 0; N, 40.59; found: C, 13.34; H, 0.34; N, 40.38.

Synthesis of **4**: Compound **3** (0.138 g, 0.25 mmol) was added in batches to a solution of potassium iodide (0.166 g, 1 mmol) in methanol (3 mL) with stirring at 0 - 5 °C. After addition, the mixture was allowed to warm to room temperature. It was stirred for 4h, and the reaction mixture was maintained at – 20 °C for eight hours. The precipitate was collected by filtration and washed with methanol (2 mL) and then ethanol (7 mL) to give **4** (0.097 g, 84%) as a yellowish solid. T_d (onset) = 277 °C, ^{13}C NMR (d_6-DMSO) δ = 166.9, 166.1, 163.6, 160.3, 159.1, 156.7, 155.6, 148.3, 144.8, 143.4, 131.4 ppm; IR (KBr) ῡ = 1739(w), 1713(w), 1604(m), 1557(m), 1520(m), 1472(s), 1400(w), 1357(w), 1312(s), 1223(s), 1219(s), 1159(s), 1074(w), 1034(w), 1013(w), 891(m), 841(w), 830(w), 807(m), 768(w), 749(w), 737(m), 727(w), 672(w), 656(w), 611(w), 572(w), 459(w), 448(w), 438(w), 430(w) cm^{-1}; Elemental analysis (%): Calcd. for $C_6K_2N_{14}O_9$ (462.34): C, 15.59; H, 0.00; N, 36.36; found: C, 15.23; H, 0.183; N, 36.74.

Synthesis of **5**: To a solution of potassium hydroxide (0.044 g, 0.65 mmol) in ethanol (2 mL) was added a solution of hydroxylamine hydrochloride (0.076 g, 1.09 mmol) in water (0.5 mL). The solid potassium chloride was removed by filtration, and a solution of **3** (0.100 g, 0.18 mmol) in ethanol (2 mL) was added dropwise to the mother liquor with stirring for 0.5 h at 0–5 °C. Then the mixture was allowed to warm to room temperature and stirred for 6h. The precipitate was collected by filtration and washed with ethanol (2 mL) to give **5** (0.030 g, 35 %) as a pale yellow solid. T_d (onset) = 292 °C. ^{13}C NMR (d_6-DMSO) δ = 167.0, 160.3, 159.1, 148.3, 143.6, 131.5 ppm; IR (KBr) ῡ = 1732(m), 1602(m), 1557(m), 1521(w), 1472(s), 1423(m), 1362(w), 1327(w), 1311(s), 1270(m), 1215(s), 1158(s), 1097(w), 1034(m), 1014(m), 991(w), 897(m), 849(m), 818(m), 806(s), 765(w), 750(m), 737(w), 705(w), 655(w), 608(w), 566(w), 526(w), 466(w) cm^{-1}; Elemental analysis (%): Calcd. for $C_6K_2N_{14}O_{10}$ (478.34): C, 15.07; H, 0.00; N, 35.14; found: C, 15.34; H, 0.108; N, 35.86.

Synthesis of **7**: Compound **5** (0.0478 g, 0.1 mmol) was added to 5% sulfuric acid (1 mL). The reaction was stirred at room temperature for 0.5 h. The resulting solution was extracted with diethyl ether (5 × 5 mL). The organic solution was dried over anhydrous $MgSO_4$, and volatile solvent was removed by rotary evaporation to give **7** as a dark yellow solid (0.026 g, 65% yield). ^{1}H NMR (d_6-DMSO): δ = 7.87 (s, 1H) ppm; ^{13}C NMR (d_6-DMSO) δ = 166.8, 160.4, 159.0, 148.4, 143.3, 131.4 ppm; IR (KBr) ῡ = 3436(m), 2923(w), 1784(m), 1686(m), 1591(s), 1523(m), 1481(w), 1413(w), 1396(w), 1306(s), 806(s), 789(w), 778(w) cm^{-1}; elemental analysis (%): Calcd. for $C_6H_2N_{12}O_{10}$ (402.16): C, 17.92; H, 0.50; N, 41.80; found: C, 17.90; H, 0.91; N, 39.96。

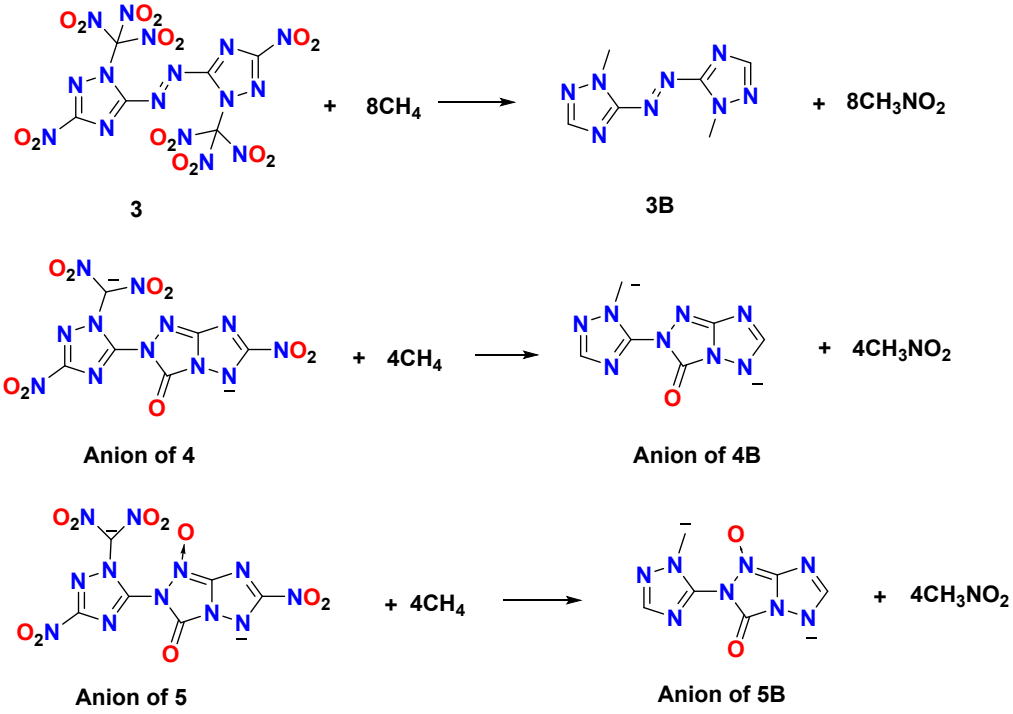
Synthesis of **8**: Compound **4** (0.0462 g, 0.1 mmol) was added to 5% sulfuric acid (1 mL). The reaction was stirred at room temperature for 0.5 h. The resulting solution was

extracted with diethyl ether (5 × 5 mL). The organic solution was dried over anhydrous $MgSO_4$, and then five drops 7 N ammonia methanol solution was added to the solution. After stirring for 5h at room temperature, the precipitate removed by filtration and dried in a vacuum. The product was obtained as a yellow solid (0.077 g, 73%). T_d (onset) = 175 °C, ^{1}H NMR (d_6-DMSO): δ = 7.12 (s, 4H) ppm; ^{13}C NMR (d_6-DMSO) δ = 163.2, 159.1, 157.0, 148.4, 143.4, 131.5 ppm; IR (KBr) ῡ = 3441(s), 3153(s), 1725(s), 1617(s), 1610(m), 1556(m), 1485(s), 1398(s), 1378(m), 1320(s), 1253(s), 1189(m), 1099(w), 1027(w), 1008(w), 893(m), 856(w), 815(m), 743(m), 690(w), 683(w) cm^{-1}; Elemental analysis (%): Calcd. for $C_6H_8N_{14}O_9$ (420.22): C, 17.15; H, 1.92; N, 46.67; found: C, 17.30; H, 2.59; N, 48.85.

Synthesis of **9**: Compound **5** (0.0478 g, 0.1 mmol) was added to 5% sulfuric acid (1 mL). The reaction was stirred at room temperature for 0.5 h. The resulting solution was extracted with diethyl ether (5 × 5 mL). The organic solution was dried over anhydrous $MgSO_4$, and then five drops of 7 N ammonia in methanol was added to the solution. After stirring for 5h at room temperature, the solid was removed by filtration and dried in a vacuum. The product was obtained as a yellow solid (0.021 g, 45% yield). T_d (onset) = 202 °C, ^{1}H NMR (d_6-DMSO): δ = 7.09 (s, 4H) ppm; ^{13}C NMR (d_6-DMSO) δ = 166.9, 160.3, 159.1, 148.4, 143.3, 131.4 ppm; IR (KBr) ῡ = 3222(s), 1743(s), 1608(s), 1569(s), 1536(m), 1488(s), 1398(s), 1329(s), 1311(s), 1268(w), 1220(s), 1154(s), 1028(w), 1001(w), 902(m), 843(w), 824(m), 809(m), 740(m), 683(w) cm^{-1}; Elemental analysis (%): Calcd. for $C_6H_8N_{14}O_{10}$ (436.22): C, 16.52; H, 1.85; N, 44.95; found: C, 16.74; H, 2.01; N, 47.09.

Theoretical Calculations

The heats of formation were determined using isodesmic reactions (**Scheme S1**). The



Scheme S1. Isodesmic reactions to compute the heats of formation.

calculations were carried out using Gaussian 09 (Revision E.01) suite of programs.[2] The geometric optimization and frequency analyses of the structures were calculated at the M052X/6-31+G(d,p) level, and single energy points were calculated at the MP2/6-311++G(d,p) level. The heats of formation for **3B** and anions of **4B** and **5B** were obtained by an atomization approach using G2 ab initio method.[3] The heats of formation of other compounds in **Scheme S1** were obtained from the NIST WebBook.[4]

Table S1 The heats of formation (HOF) for **3 - 5**.[a]

Compounds	**ZPE**[b] (Hartree/Particle)	H_T[c] (Hartree/Particle)	**MP2-6-311++G**** (Hartree/Particle)	**HOF(gas)** (kJ mol^{-1})
3	0.188788	0.221476	-2302.23010	778.0
CH_4	0.044793	0.048605	-40.33281	-74.6[d]
CH_3NO_2	0.04984	0.055138	-244.42534	-81.0[d]
3B	0.16977	0.182657	-669.57476	606.3
Anion of **4**	0.137443	0.159153	-1558.79756	181.1
Anion of **4B**	0.124127	0.135935	-742.28708	575.2
Anion of **5**	0.14058	0.163596	-1633.78351	230.4
Anion of **5B**	0.127257	0.140439	-817.28352	597.0

[a] The enthalpy of sublimation was calculated by using Trouton's rule. Solid-state heats of formation of the resulting compounds were calculated with Equation (1) in which Tm is the melting temperature. $\Delta H_f = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - 188[J\ mol^{-1}\ K^{-1}] \times T_m$ (1). [b] Zero-point correction. [c] Thermal correction to enthalpy, i.e., $H_{298.15\,K} - H_{0\,K}$. [d] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL.

Crystallographic Data

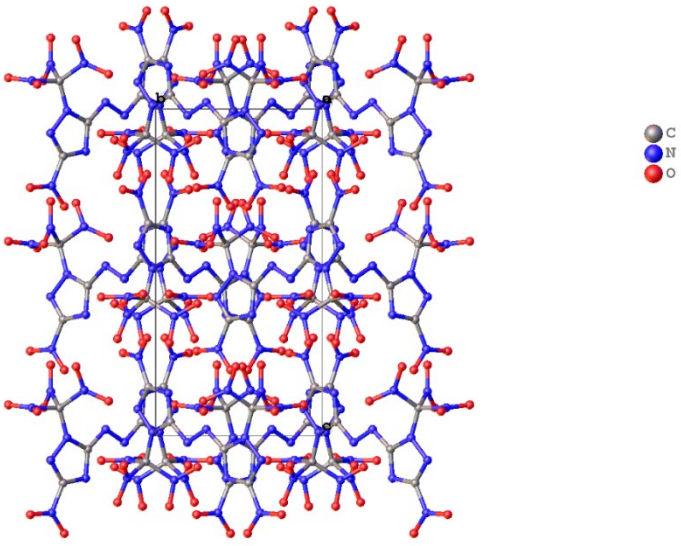


Figure S1. Packing diagram of **3**.

Table S2. Crystallographic data for compounds **3 - 5**.

Compound	**3**	**4**	**5**
CCDC number	2041417	2008399	2008400
Formula	$C_6N_{16}O_{16}$	$C_6K_2N_{12}O_9$	$C_6K_2N_{12}O_{10}$
$D_{calc.}$/ g cm^{-3}	1.966	2.070	2.131
Formula Weight	552.22	462.38	478.38
Size/mm^3	0.14×0.05×0.04	0.10×0.01×0.05	0.15×0.13×0.10
T/K	100.00(10)	271	291
Crystal System	orthorhombic	Monoclinic	Monoclinic
Space Group	$Pca2_1$	$P2_1/n$	$P2_1/n$
a/Å	16.8883(2)	5.7691(4)	5.7737(15)
b/Å	7.48894(9)	29.1794(18)	29.248(7)
c/Å	14.7517(2)	9.0054(7)	9.022(2)
α/°	90	90	90
β/°	90	101.820(3)	101.847(3)
γ/°	90	90	90
V/Å^3	1865.73(4)	1483.81(18)	1491.0(7)
Z	4	4	4
Wavelength/Å	1.54184	0.71073	0.71073
Q_{min}/°	5.238	2.414	2.41
Q_{max}/°	77.252	26.485	23.83
Indep't Refl's	3628	3006	3401
Refl's I≥2 *s*(I)	3501	2320	2554
Parameters	344	308	271
GooF	1.045	1.037	1.456
wR_2 (all data)	0.0779	0.0899	0.2213
R_1	0.0309	0.0407	0.0690

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
O1	6808.9(12)	11977(3)	2468.0(14)	25.3(4)
O2	5759.8(13)	10545(3)	2001.8(14)	26.0(4)
O3	3969.9(14)	4488(3)	7982.4(15)	29.0(5)
O4	3202.4(13)	2445(3)	7405.5(14)	25.4(4)
O5	6592.9(14)	7512(3)	5952.7(17)	31.8(5)
O6	6692.0(18)	9190(3)	7152.5(17)	42.7(6)
O7	5138.5(12)	11928(3)	5898.7(14)	27.2(4)
O8	5942.6(16)	12313(4)	7028.7(16)	43.9(6)
O9	7756.3(12)	10777(3)	5662.3(15)	29.3(5)
O10	7098.3(15)	13282(3)	5753.8(17)	33.8(5)
O11	3207.0(13)	7152(3)	3935.3(15)	29.3(5)
O12	2927.7(13)	5195(3)	2882.4(15)	31.6(5)

O13	4934.0(14)	3249(3)	4131.1(17)	37.7(5)
O14	4373.1(14)	3669(4)	2828.4(16)	39.0(6)
O15	3408(2)	1122(3)	4048.9(18)	47.2(7)
O16	2381.9(15)	2856(3)	4251.7(16)	41.8(6)
N1	5123.9(14)	8103(3)	5197.4(15)	19.4(5)
N2	4697.2(13)	6973(3)	4799.1(16)	19.8(5)
N3	6150.1(13)	10213(3)	4892.1(14)	16.6(4)
N4	6491.5(13)	11098(3)	4183.5(16)	18.0(4)
N5	5494.7(13)	9272(3)	3693.9(16)	19.5(5)
N6	3767.6(13)	4652(3)	5059.1(16)	17.2(4)
N7	3454.0(13)	3663(3)	5743.4(15)	18.7(4)
N8	4307.0(14)	5767(3)	6294.8(17)	20.0(5)
N9	6222.8(14)	11048(3)	2580.6(15)	19.6(5)
N10	3645.3(14)	3728(3)	7353.1(16)	20.7(5)
N11	6570.7(14)	8898(3)	6352.0(17)	23.5(5)
N12	5754.4(14)	11726(3)	6296.7(17)	22.5(5)
N13	7163.1(14)	11681(3)	5741.9(16)	23.6(5)
N14	3201.0(14)	5686(3)	3603.5(17)	21.9(5)
N15	4389.6(15)	3670(3)	3643.3(16)	22.2(5)
N16	3078.0(17)	2535(4)	4135.8(17)	29.9(6)
C1	5556.1(16)	9129(3)	4574.3(18)	18.0(5)
C2	6068.9(16)	10457(3)	3508.0(18)	17.1(5)
C3	4279.6(16)	5897(4)	5407.9(19)	17.9(5)
C4	3801.1(16)	4410(3)	6441.0(18)	17.3(5)
C5	6387.3(15)	10608(3)	5791.3(18)	18.0(5)
C6	3615.6(15)	4199(3)	4143.7(19)	18.3(5)

Table S4. Anisotropic Displacement Parameters ($\times 10^4$) for **3**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	24.1(10)	29.8(10)	22.0(10)	2.1(8)	2.3(8)	-7.9(8)
O2	30.2(11)	27.1(10)	20.7(10)	0.8(8)	-6.7(8)	-5.1(9)
O3	35.8(12)	33.0(12)	18.1(10)	-0.4(8)	-2.0(9)	-3.6(9)
O4	29.9(10)	23.6(10)	22.5(10)	4.8(8)	3.7(8)	-3.1(8)
O5	37.2(12)	23.7(10)	34.7(12)	0.3(9)	2.1(9)	6.7(9)
O6	66.5(17)	42.3(14)	19.2(11)	6.0(10)	-5.1(10)	4.5(12)
O7	24.3(10)	30.6(10)	26.6(11)	-0.1(9)	1.0(8)	7.7(8)
O8	46.0(15)	58.7(16)	27.1(12)	-23.8(11)	-4.6(11)	10.8(12)
O9	18.9(10)	46.1(12)	22.8(10)	-1.3(9)	0.1(8)	-1.4(9)
O10	43.8(13)	22.3(11)	35.4(12)	1.5(9)	-4.0(10)	-10.9(9)
O11	32.1(12)	24.6(11)	31.1(12)	-0.3(8)	0.0(9)	6.2(8)
O12	32.3(12)	36.7(12)	25.7(11)	3.3(9)	-8.1(9)	-5.0(9)

O13	38.4(12)	45.2(13)	29.6(12)	4.7(11)	2.8(10)	24.2(10)
O14	36.5(12)	62.1(17)	18.3(11)	-4.8(11)	6.3(9)	-3.2(11)
O15	91(2)	19.4(11)	30.9(13)	-5.4(10)	17.3(13)	-16.5(12)
O16	38.1(14)	63.1(15)	24.2(12)	10.3(11)	-7.0(10)	-30.1(12)
N1	22.0(11)	17.6(10)	18.6(11)	-1.4(8)	3.5(9)	-3.8(9)
N2	20.3(11)	18.5(10)	20.4(11)	-1.4(9)	1.7(9)	-4.1(8)
N3	17.7(10)	17.3(10)	14.8(11)	-0.9(8)	1.7(8)	-2.8(8)
N4	18.8(10)	16.9(10)	18.3(11)	1.8(9)	2.8(9)	0.1(8)
N5	21.0(11)	19.6(11)	18.0(11)	-1.6(9)	0.5(9)	-0.6(9)
N6	19.7(10)	17.0(10)	14.8(10)	-0.8(8)	1.9(8)	-3.9(8)
N7	20.7(11)	17.3(10)	18.0(11)	2.5(9)	3.5(9)	0.6(8)
N8	22.3(11)	19.4(11)	18.4(11)	-1.5(9)	1.2(8)	-1.1(9)
N9	23.1(11)	20.1(11)	15.4(11)	0.1(8)	0.4(9)	-0.1(9)
N10	22.5(11)	21.2(11)	18.5(11)	0.5(9)	1.5(9)	3.4(9)
N11	23.5(12)	26.5(12)	20.4(12)	5.3(10)	0.8(9)	1.3(9)
N12	24.9(11)	21.6(11)	21.0(12)	-3.5(9)	1.6(9)	1.9(9)
N13	24.1(12)	29.2(13)	17.4(11)	-0.1(9)	-3.3(9)	-6.9(10)
N14	19.9(11)	24.8(12)	21.2(12)	2.8(9)	-2.1(9)	-2.4(9)
N15	30.3(13)	18.5(11)	17.9(11)	-1.6(9)	1.9(9)	2.2(9)
N16	42.8(16)	33.1(14)	13.9(12)	-1.1(11)	1.5(11)	-19.6(12)
C1	20.3(12)	17.0(12)	16.8(13)	-2.5(10)	2.8(9)	-3.1(9)
C2	18.6(12)	17.0(12)	15.6(12)	-1.3(10)	2.1(9)	-0.4(9)
C3	18.3(12)	16.5(12)	19.0(13)	-1.8(10)	1.7(10)	-0.9(10)
C4	19.4(12)	15.1(12)	17.4(13)	-0.6(9)	2.1(10)	1.8(9)
C5	19.6(12)	19.1(12)	15.3(13)	-1.9(10)	0.3(10)	-1.5(10)
C6	22.8(12)	16.6(11)	15.5(12)	0.8(10)	0.7(10)	-3.7(9)

Table S5. Bond Lengths in Å for **3**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O1	N9	1.221(3)	N3	C1	1.373(3)
O2	N9	1.218(3)	N3	C5	1.417(3)
O3	N10	1.219(3)	N4	C2	1.316(4)
O4	N10	1.220(3)	N5	C1	1.307(4)
O5	N11	1.194(3)	N5	C2	1.343(4)
O6	N11	1.218(4)	N6	N7	1.359(3)
O7	N12	1.204(3)	N6	C3	1.372(3)
O8	N12	1.209(3)	N6	C6	1.416(4)
O9	N13	1.215(3)	N7	C4	1.310(4)
O10	N13	1.204(3)	N8	C3	1.313(4)
O11	N14	1.203(3)	N8	C4	1.345(3)
O12	N14	1.216(3)	N9	C2	1.461(3)
O13	N15	1.209(3)	N10	C4	1.463(3)
O14	N15	1.202(3)	N11	C5	1.556(3)

O15	N16	1.202(4)	N12	C5	1.549(3)
O16	N16	1.212(4)	N13	C5	1.539(3)
N1	N2	1.258(3)	N14	C6	1.538(4)
N1	C1	1.403(3)	N15	C6	1.553(4)
N2	C3	1.398(3)	N16	C6	1.542(3)
N3	N4	1.365(3)			

Table S6. Bond Angles in º for **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N2	N1	C1	111.1(2)	O13	N15	C6	115.1(2)
N1	N2	C3	112.2(2)	O14	N15	O13	127.8(3)
N4	N3	C1	109.5(2)	O14	N15	C6	117.1(2)
N4	N3	C5	119.8(2)	O15	N16	O16	129.7(3)
C1	N3	C5	130.5(2)	O15	N16	C6	116.0(3)
C2	N4	N3	100.0(2)	O16	N16	C6	114.2(3)
C1	N5	C2	101.5(2)	N3	C1	N1	118.7(2)
N7	N6	C3	109.7(2)	N5	C1	N1	130.9(3)
N7	N6	C6	120.5(2)	N5	C1	N3	110.4(2)
C3	N6	C6	129.4(2)	N4	C2	N5	118.5(2)
C4	N7	N6	100.2(2)	N4	C2	N9	120.1(2)
C3	N8	C4	101.1(2)	N5	C2	N9	121.3(2)
O1	N9	C2	116.4(2)	N6	C3	N2	118.0(2)
O2	N9	O1	127.0(2)	N8	C3	N2	131.7(3)
O2	N9	C2	116.7(2)	N8	C3	N6	110.2(2)
O3	N10	O4	126.5(2)	N7	C4	N8	118.8(2)
O3	N10	C4	117.1(2)	N7	C4	N10	119.5(2)
O4	N10	C4	116.3(2)	N8	C4	N10	121.7(2)
O5	N11	O6	129.0(3)	N3	C5	N11	112.5(2)
O5	N11	C5	117.4(2)	N3	C5	N12	111.6(2)
O6	N11	C5	113.7(2)	N3	C5	N13	107.8(2)
O7	N12	O8	128.1(3)	N12	C5	N11	109.0(2)
O7	N12	C5	115.4(2)	N13	C5	N11	106.6(2)
O8	N12	C5	116.4(2)	N13	C5	N12	109.1(2)
O9	N13	C5	114.6(2)	N6	C6	N14	113.8(2)
O10	N13	O9	129.1(3)	N6	C6	N15	111.2(2)
O10	N13	C5	116.2(2)	N6	C6	N16	107.9(2)
O11	N14	O12	129.4(3)	N14	C6	N15	108.8(2)
O11	N14	C6	116.5(2)	N14	C6	N16	108.3(2)
O12	N14	C6	114.0(2)	N16	C6	N15	106.6(2)

Table S7. Bond Lengths in Å for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.227(3)	N7	C2	1.372(3)

O2	N1	1.226(3)	N7	C6A	1.396(6)
O3	N5	1.245(3)	N7	N12B	1.445(12)
O4	N5	1.239(3)	N7	C6B	1.391(12)
O5	N6	1.244(3)	N7	N12A	1.441(5)
O6	N6	1.242(3)	N8A	N9	1.383(5)
O7A	C6A	1.237(6)	N8A	C5A	1.370(10)
O7B	C6B	1.229(13)	N8A	C6A	1.342(8)
O9	N11	1.228(4)	N8B	C5B	1.35(3)
O10	N11	1.222(5)	N8B	C6B	1.343(16)
N1	C1	1.455(3)	N8B	N10	1.387(16)
N2	C2	1.324(3)	N9	C7	1.337(4)
N2	C1	1.347(3)	N9	C5B	1.392(11)
N3	N4	1.376(3)	N10	C7	1.331(4)
N3	C2	1.358(3)	N10	C5A	1.365(8)
N3	C3	1.393(3)	N11	C7	1.469(4)
N4	C1	1.301(3)	N12A	C5A	1.339(7)
N5	C3	1.379(3)	N12B	C5B	1.34(2)
N6	C3	1.373(3)			

Table S8. Bond Angles in º for **4**.

Atom	**Atom**	**Atom**	**Angle/º**	**Atom**	**Atom**	**Atom**	**Angle/º**
O1	N1	O2	125.0(2)	C5A	N10	C7	101.8(4)
O1	N1	C1	117.3(2)	N8B	N10	C7	89.0(6)
O2	N1	C1	117.6(2)	O10	N11	C7	116.7(3)
C1	N2	C2	100.4(2)	O9	N11	O10	125.5(3)
N4	N3	C2	108.87(19)	O9	N11	C7	117.8(3)
N4	N3	C3	121.66(19)	N7	N12A	C5A	98.5(5)
C2	N3	C3	129.2(2)	N7	N12B	C5B	98.4(11)
N3	N4	C1	100.4(2)	N1	C1	N4	120.0(2)
O3	N5	O4	122.1(2)	N2	C1	N4	119.1(2)
O3	N5	C3	117.0(2)	N1	C1	N2	120.7(2)
O4	N5	C3	121.0(2)	N3	C2	N7	123.7(2)
O5	N6	O6	121.8(3)	N2	C2	N3	111.2(2)
O5	N6	C3	121.8(2)	N2	C2	N7	125.1(2)
O6	N6	C3	116.4(2)	N3	C3	N6	117.3(2)
N12A	N7	C2	119.5(2)	N5	C3	N6	124.9(2)
N12A	N7	C6A	115.6(3)	N3	C3	N5	117.8(2)
C2	N7	C6A	124.8(3)	N8A	C5A	N10	105.1(4)
N12B	N7	C2	116.9(5)	N8A	C5A	N12A	113.6(6)
C2	N7	C6B	128.5(5)	N10	C5A	N12A	141.2(7)
N12B	N7	C6B	114.5(7)	N9	C5B	N12B	149.1(16)
N9	N8A	C5A	116.3(5)	N8B	C5B	N12B	114.5(11)
N9	N8A	C6A	132.1(5)	N8B	C5B	N9	96.3(12)

C5A	N8A	C6A	111.5(5)	O7A	C6A	N7	126.3(5)
C5B	N8B	C6B	110.9(13)	O7A	C6A	N8A	132.9(5)
N10	N8B	C5B	126.3(10)	N7	C6A	N8A	100.8(4)
N10	N8B	C6B	122.7(13)	O7B	C6B	N7	127.2(9)
N8A	N9	C7	94.3(3)	N7	C6B	N8B	101.8(11)
C5B	N9	C7	105.9(8)	O7B	C6B	N8B	131.0(12)
N9	C7	N10	122.5(3)	N10	C7	N11	120.5(3)
N9	C7	N11	116.9(3)				

Table S9. Torsion Angles in ° for **4**.

Atom	**Atom**	**Atom**	**Atom**	**Angle/º**
O1	N1	C1	N2	-13.2(4)
O1	N1	C1	N4	172.1(2)
O2	N1	C1	N2	164.0(2)
O2	N1	C1	N4	-10.7(4)
C2	N2	C1	N1	-173.4(2)
C2	N2	C1	N4	1.3(3)
C1	N2	C2	N3	-1.6(3)
C1	N2	C2	N7	178.0(2)
C2	N3	N4	C1	-0.6(3)
C3	N3	N4	C1	174.1(2)
N4	N3	C2	N2	1.5(3)
N4	N3	C2	N7	-178.1(2)
C3	N3	C2	N2	-172.7(2)
C3	N3	C2	N7	7.8(4)
N4	N3	C3	N5	80.6(3)
N4	N3	C3	N6	-102.1(3)
C2	N3	C3	N5	-106.0(3)
C2	N3	C3	N6	71.4(3)
N3	N4	C1	N1	174.3(2)
N3	N4	C1	N2	-0.5(3)
O3	N5	C3	N3	-5.1(4)
O3	N5	C3	N6	177.8(2)
O4	N5	C3	N3	174.9(2)
O4	N5	C3	N6	-2.3(4)
O5	N6	C3	N3	-172.5(2)
O5	N6	C3	N5	4.7(4)
O6	N6	C3	N3	6.9(4)
O6	N6	C3	N5	-176.0(3)
C2	N7	N12A	C5A	175.7(3)
C6A	N7	N12A	C5A	-0.2(4)
N12A	N7	C2	N2	-145.2(3)
N12A	N7	C2	N3	34.3(4)

C6A	N7	C2	N2	30.2(4)
C6A	N7	C2	N3	-150.3(3)
N12A	N7	C6A	O7A	178.2(4)
N12A	N7	C6A	N8A	-0.1(5)
C2	N7	C6A	O7A	2.7(7)
C2	N7	C6A	N8A	-175.7(3)
C5A	N8A	N9	C7	0.0(4)
C6A	N8A	N9	C7	176.0(5)
N9	N8A	C5A	N10	-0.8(5)
N9	N8A	C5A	N12A	176.3(4)
C6A	N8A	C5A	N10	-177.6(4)
C6A	N8A	C5A	N12A	-0.5(6)
N9	N8A	C6A	O7A	6.1(10)
N9	N8A	C6A	N7	-175.8(4)
C5A	N8A	C6A	O7A	-177.8(6)
C5A	N8A	C6A	N7	0.4(5)
N8A	N9	C7	N10	0.9(4)
N8A	N9	C7	N11	-178.0(3)
C7	N10	C5A	N8A	1.2(4)
C7	N10	C5A	N12A	-174.6(7)
C5A	N10	C7	N9	-1.4(4)
C5A	N10	C7	N11	177.4(3)
O9	N11	C7	N9	-10.4(4)
O9	N11	C7	N10	170.8(3)
O10	N11	C7	N9	168.7(3)
O10	N11	C7	N10	-10.2(4)
N7	N12A	C5A	N8A	0.4(5)
N7	N12A	C5A	N10	175.9(6)

Table S10. Bond Lengths in Å for **5**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N5	1.239(5)	N3	C3	1.401(5)
O2	N5	1.230(5)	N4	C1	1.309(5)
O3	N6	1.236(5)	N5	C3	1.373(5)
O4	N6	1.233(5)	N6	C3	1.372(6)
O5	N1	1.225(5)	N7	N8	1.411(5)
O6	N1	1.229(5)	N7	C2	1.376(5)
O7	N8	1.121(7)	N7	C4	1.409(5)
O8	C4	1.172(5)	N8	C5	1.336(5)
O9	N12	1.209(8)	N9	N10	1.378(5)
O10	N12	1.220(7)	N9	C4	1.354(5)
N1	C1	1.456(5)	N9	C5	1.366(5)
N2	C1	1.339(5)	N10	C6	1.335(7)

N2	C2	1.313(5)	N11	C5	1.349(6)
N3	N4	1.376(5)	N11	C6	1.331(6)
N3	C2	1.364(5)	N12	C6	1.461(7)

Table S11. Bond Angles in º for **5**.

Atom	Atom	Atom	Angle/º	Atom	Atom	Atom	Angle/º
O5	N1	O6	125.8(4)	N9	N10	C6	97.7(4)
O5	N1	C1	117.6(3)	C5	N11	C6	99.3(4)
O6	N1	C1	116.6(3)	O9	N12	O10	124.3(5)
C1	N2	C2	101.0(3)	O9	N12	C6	117.9(5)
N4	N3	C2	108.8(3)	O10	N12	C6	117.8(5)
N4	N3	C3	122.0(3)	N1	C1	N2	121.4(3)
C2	N3	C3	128.9(3)	N1	C1	N4	119.4(3)
N3	N4	C1	100.1(3)	N2	C1	N4	119.0(3)
O1	N5	O2	122.4(4)	N2	C2	N3	111.0(3)
O1	N5	C3	116.5(3)	N2	C2	N7	125.5(3)
O2	N5	C3	121.1(4)	N3	C2	N7	123.5(3)
O3	N6	O4	122.1(4)	N3	C3	N5	118.0(4)
O3	N6	C3	121.3(3)	N3	C3	N6	16.9(3)
O4	N6	C3	116.6(3)	N5	C3	N6	125.1(3)
N8	N7	C2	122.2(3)	O8	C4	N7	130.4(4)
N8	N7	C4	116.0(3)	O8	C4	N9	130.5(4)
C2	N7	C4	121.7(3)	N7	C4	N9	99.1(3)
O7	N8	N7	137.7(5)	N8	C5	N9	112.2(3)
O7	N8	C5	122.2(5)	N8	C5	N11	137.2(4)
N7	N8	C5	100.1(3)	N9	C5	N11	110.5(4)
N10	N9	C4	136.4(4)	N10	C6	N11	121.7(4)
N10	N9	C5	110.8(3)	N10	C6	N12	117.4(4)
C4	N9	C5	112.7(3)	N11	C6	N12	120.9(5)

Table S12. Torsion Angles in ° for **5**.

Atom	Atom	Atom	Atom	Angle/º
O5	N1	C1	N2	163.7(4)
O5	N1	C1	N4	-10.3(5)
O6	N1	C1	N2	-14.0(5)
O6	N1	C1	N4	172.1(4)
C2	N2	C1	N1	-172.7(3)
C2	N2	C1	N4	1.3(5)
C1	N2	C2	N3	-1.8(4)
C1	N2	C2	N7	178.4(4)
C2	N3	N4	C1	-0.9(4)
C3	N3	N4	C1	174.2(3)

N4	N3	C2	N2	1.8(4)
N4	N3	C2	N7	-178.3(3)
C3	N3	C2	N2	-172.9(4)
C3	N3	C2	N7	7.0(6)
N4	N3	C3	N5	79.9(5)
N4	N3	C3	N6	-101.6(4)
C2	N3	C3	N5	-106.1(5)
C2	N3	C3	N6	72.4(5)
N3	N4	C1	N1	173.9(3)
N3	N4	C1	N2	-0.2(5)
O1	N5	C3	N3	-5.1(6)
O1	N5	C3	N6	176.6(4)
O2	N5	C3	N3	175.3(4)
O2	N5	C3	N6	-3.1(7)
O3	N6	C3	N3	-173.6(4)
O3	N6	C3	N5	4.8(7)
O4	N6	C3	N3	5.7(6)
O4	N6	C3	N5	-175.9(4)
C2	N7	N8	O7	-2.6(8)
C2	N7	N8	C5	175.2(3)
C4	N7	N8	O7	-178.1(6)
C4	N7	N8	C5	-0.3(4)
N8	N7	C2	N2	-145.2(4)
N8	N7	C2	N3	35.0(5)
C4	N7	C2	N2	30.0(6)
C4	N7	C2	N3	-149.8(4)
N8	N7	C4	O8	177.7(4)
N8	N7	C4	N9	0.1(4)
C2	N7	C4	O8	2.2(7)
C2	N7	C4	N9	-175.4(3)
O7	N8	C5	N9	178.6(5)
O7	N8	C5	N11	0.4(4)
N7	N8	C5	N9	176.3(5)
N7	N8	C5	N11	175.9(5)
C4	N9	N10	C6	0.8(4)
C5	N9	N10	C6	7.5(8)
N10	N9	C4	O8	-174.8(4)
N10	N9	C4	N7	-177.5(4)
C5	N9	C4	O8	0.2(4)
C5	N9	C4	N7	175.9(3)
N10	N9	C5	N8	-1.1(5)
N10	N9	C5	N11	-0.4(5)
C4	N9	C5	N8	-177.4(3)
C4	N9	C5	N11	-0.4(5)

N9	N10	C6	N11	-177.5(4)
N9	N10	C6	N12	-2.6(8)
C6	N11	C5	N8	-175.1(5)
C6	N11	C5	N9	0.8(4)
C5	N11	C6	N10	-0.3(5)
C5	N11	C6	N12	176.8(4)
O9	N12	C6	N10	168.5(4)
O9	N12	C6	N11	-8.7(7)
O10	N12	C6	N10	-12.1(6)
O10	N12	C6	N11	170.7(4)

NMR and IR spectra and DSC plots of 2 – 5, 7 - 9

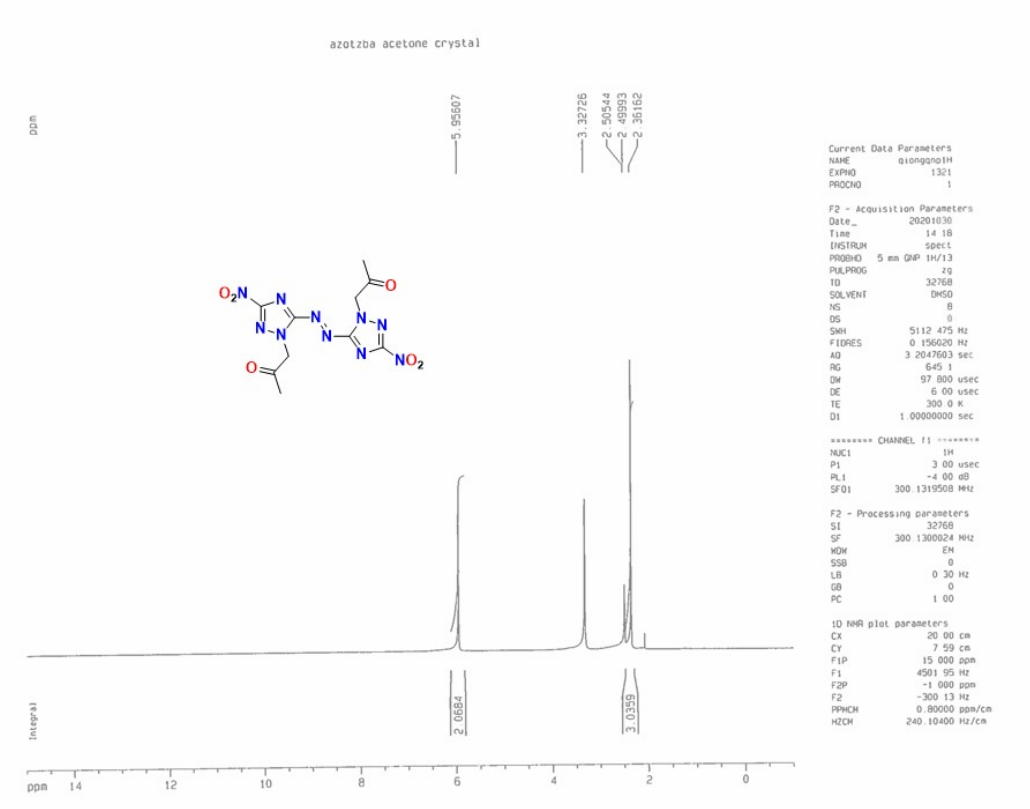


Figure S2 ^{1}H-NMR spectrum of **2** in d_6-DMSO.

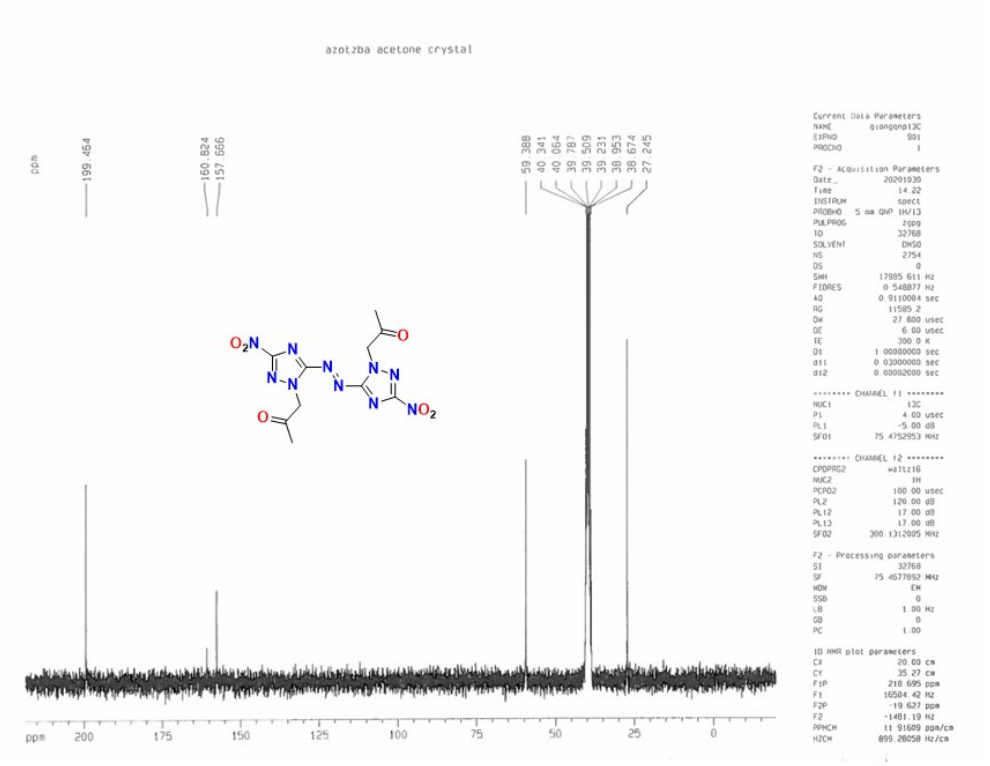


Figure S3 ^{13}C-NMR spectrum of **2** in d_6-DMSO.

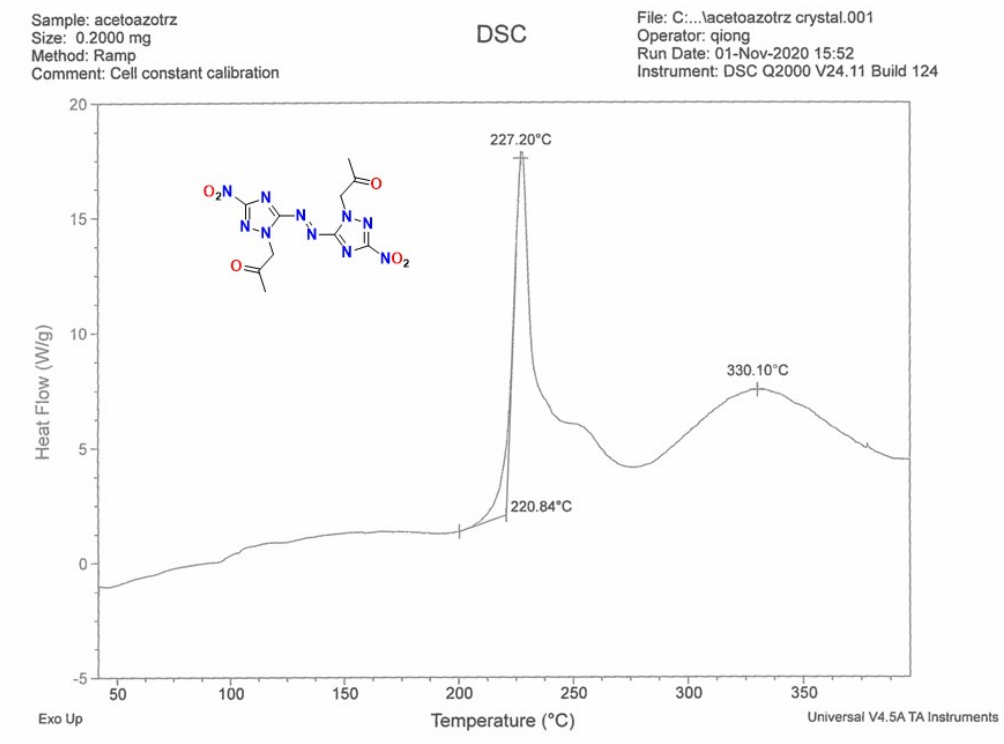


Figure S4 DSC plot of **2**.

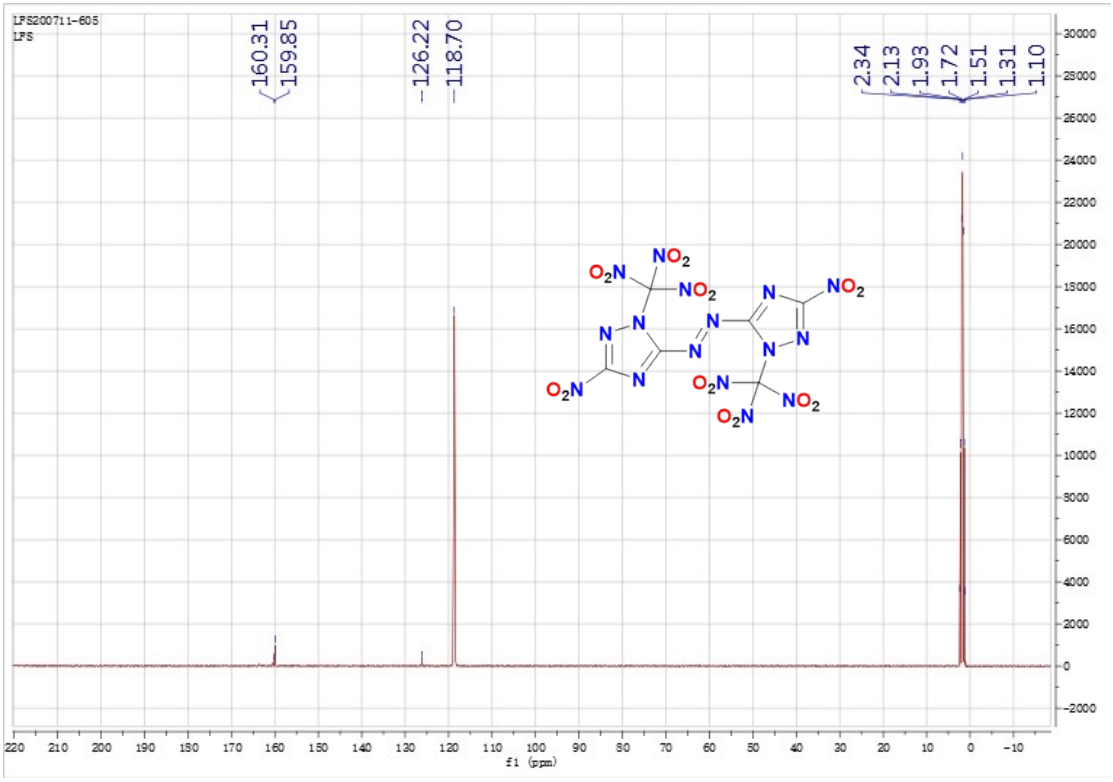


Figure S5 ^{13}C-NMR spectrum of **3** in CD_3CN.

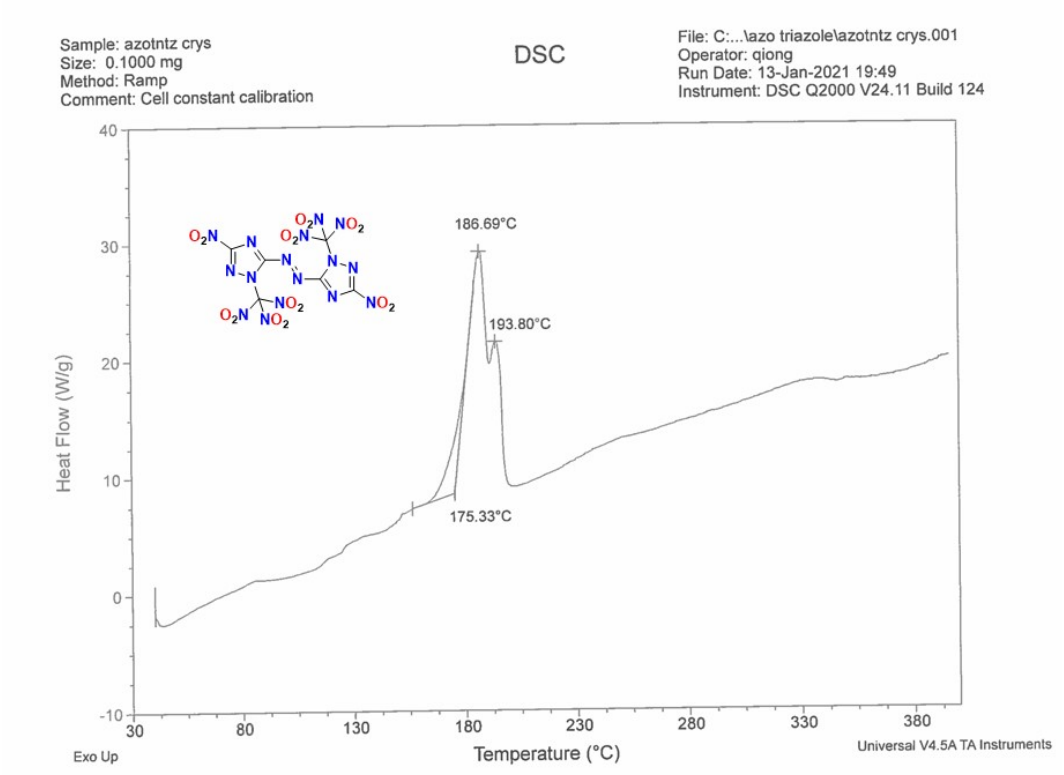


Figure S6 DSC plot of **3**.

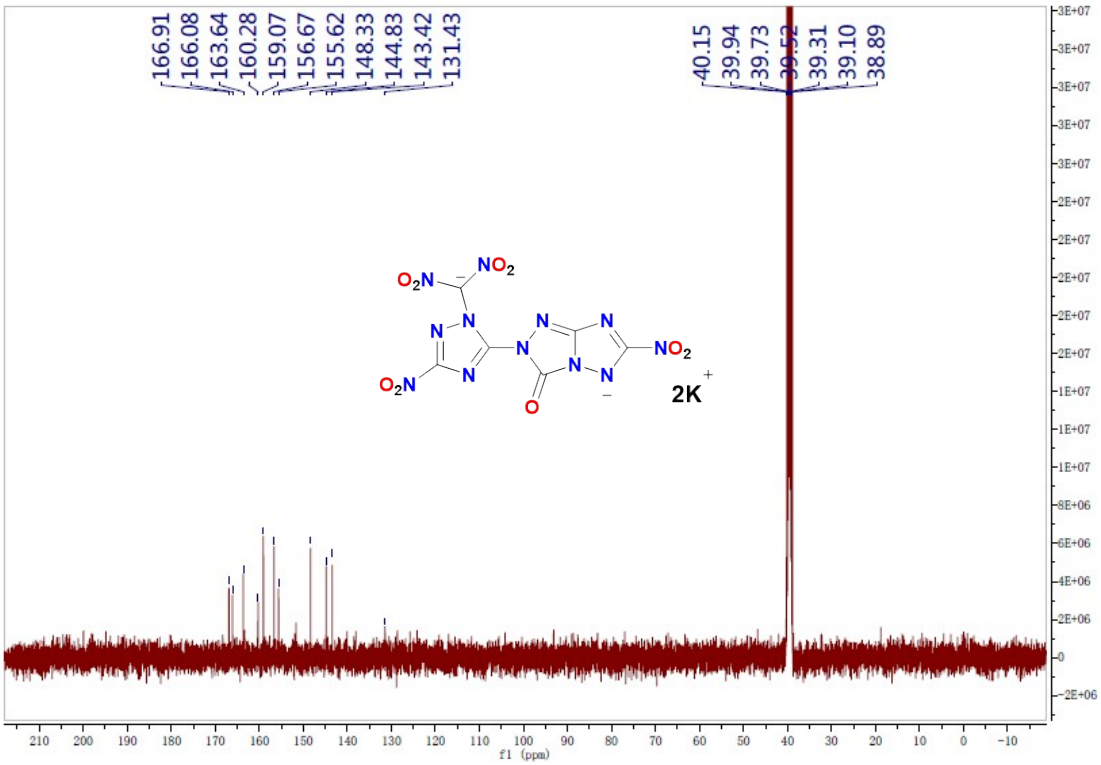


Figure S7 ^{13}C-NMR spectrum of **4** in d_6-DMSO.

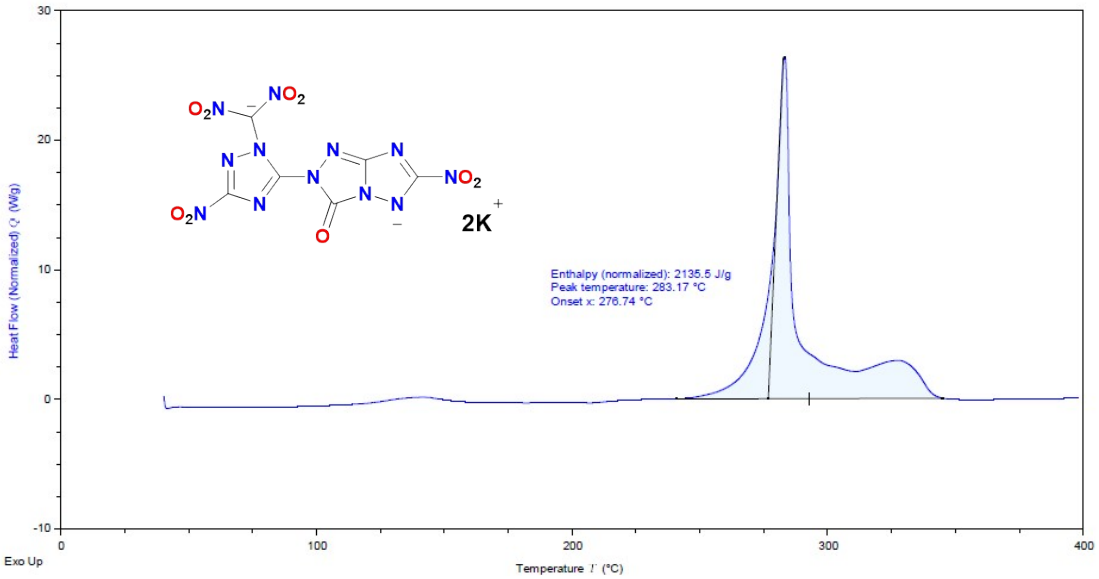


Figure S8 DSC plot of **4**.

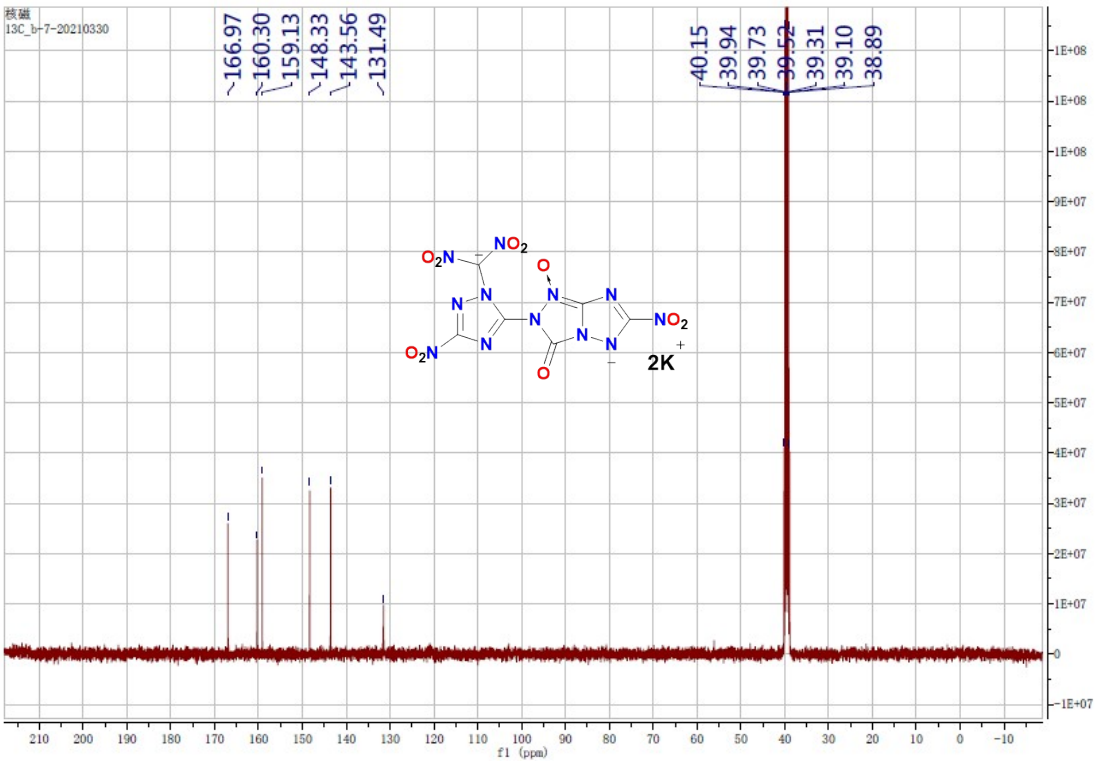


Figure S9 ^{13}C-NMR spectrum of **5** in d_6-DMSO.

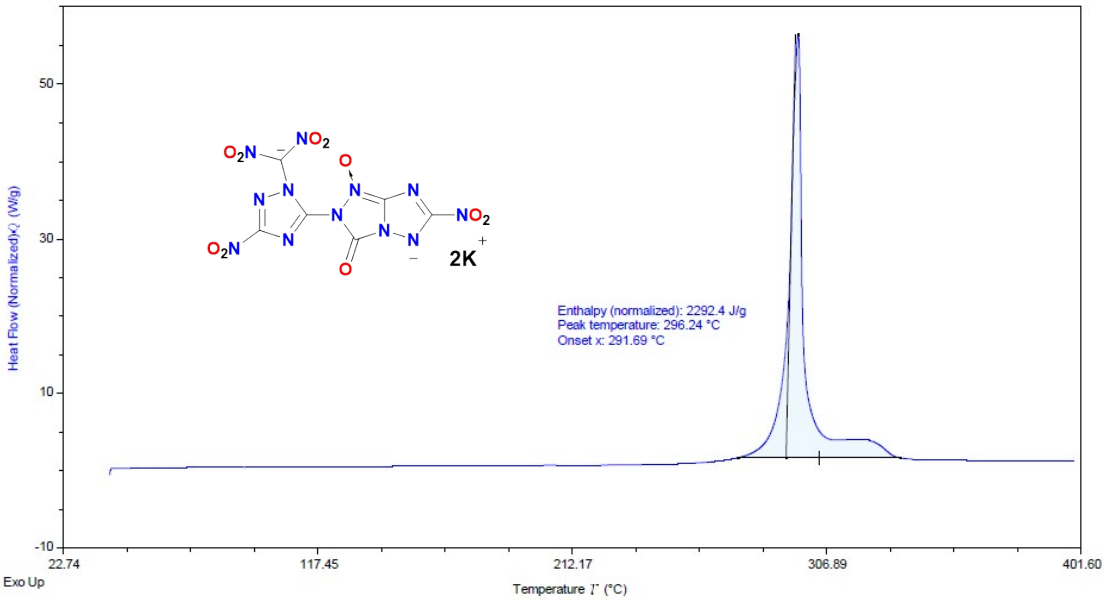


Figure S10 DSC plot of **5**.

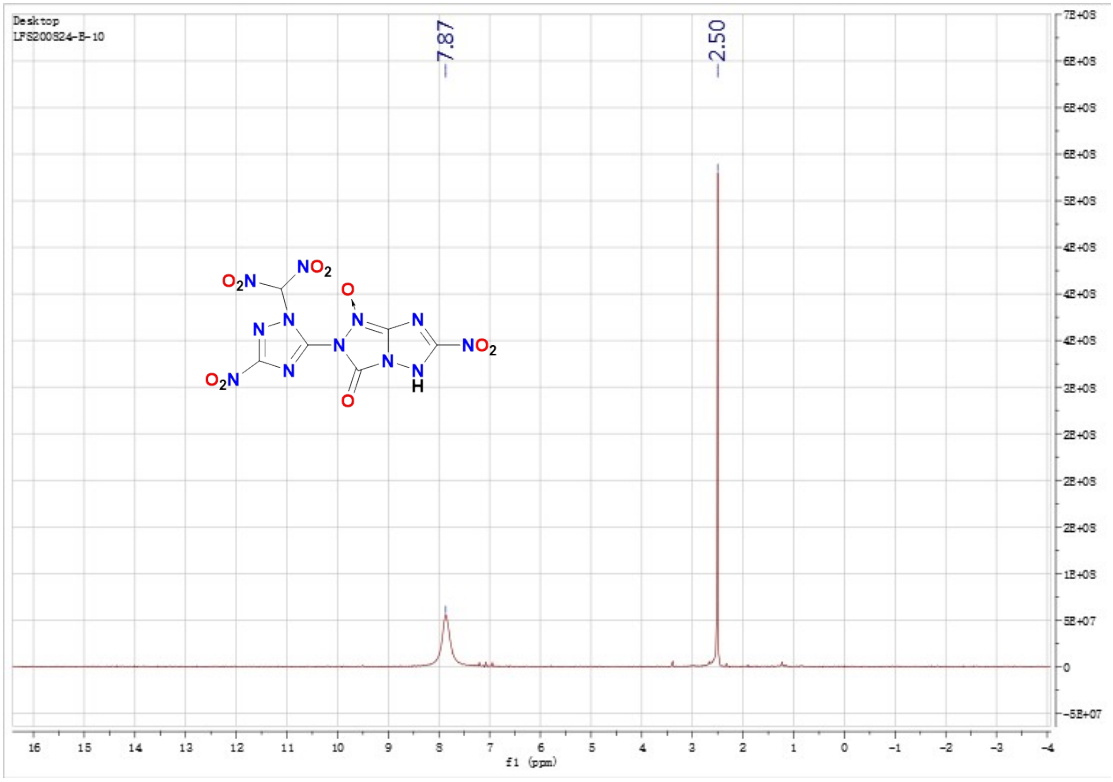


Figure S11 ^{1}H NMR spectrum of **7** in d_6-DMSO.

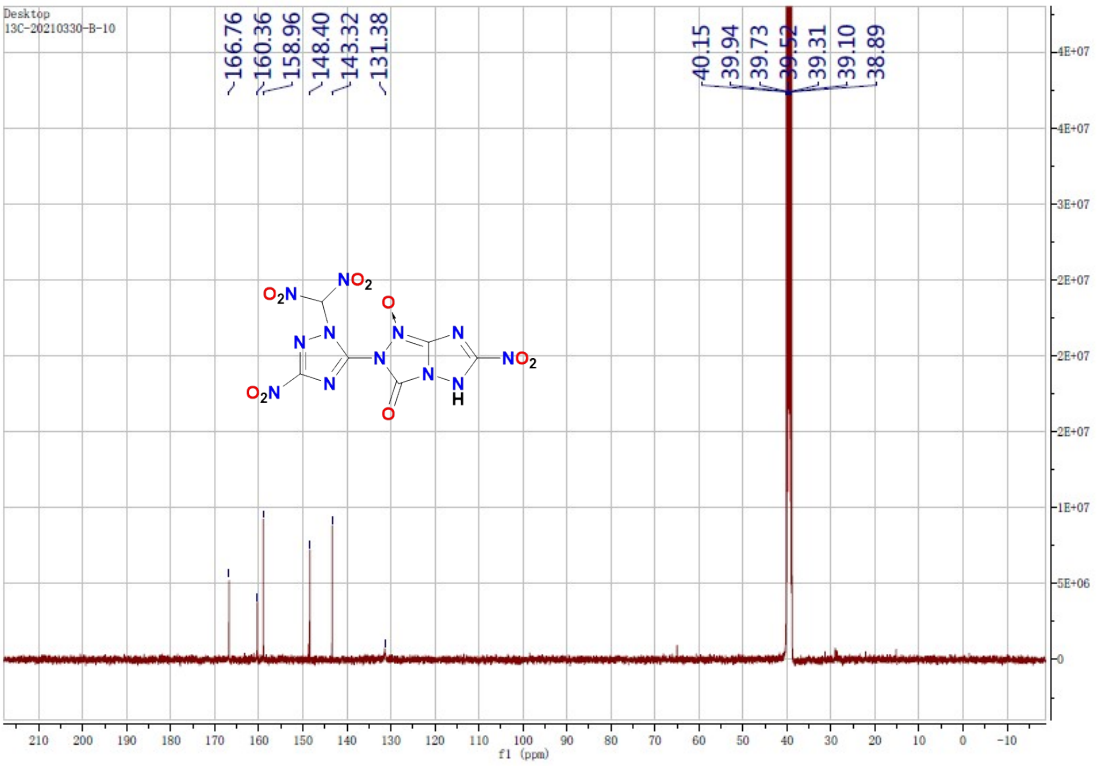


Figure S12 ^{13}C NMR spectrum of **7** in d_6-DMSO.

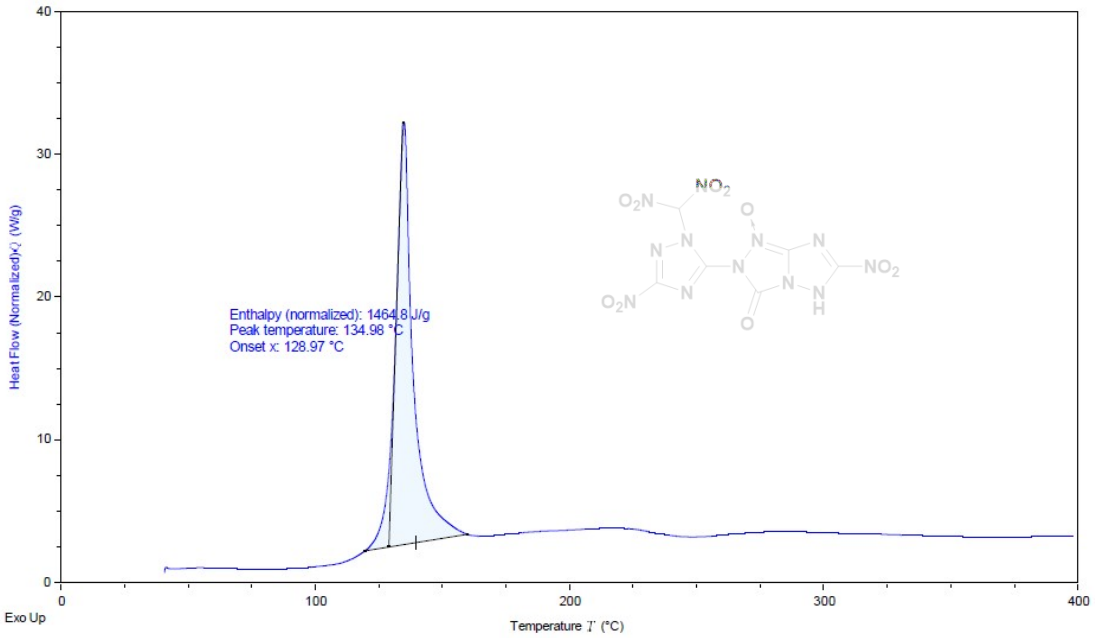


Figure S13 DSC plot of **7**.

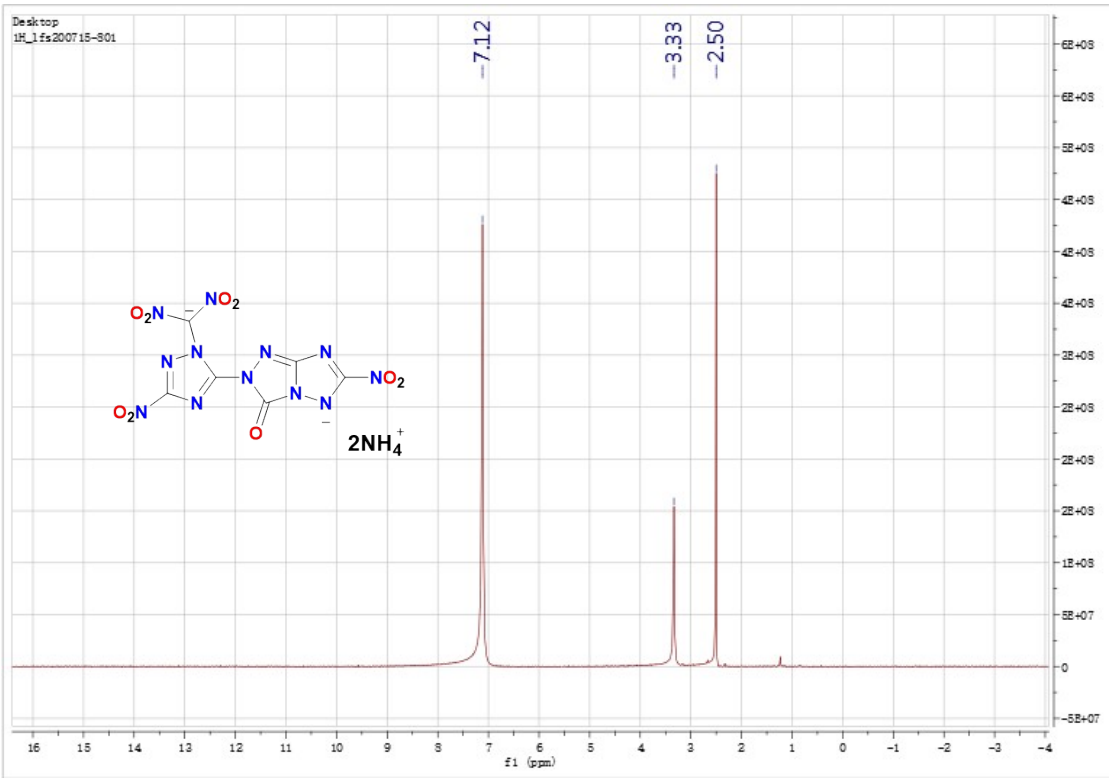


Figure S14 ^{1}H NMR spectrum of **8** in d_6-DMSO.

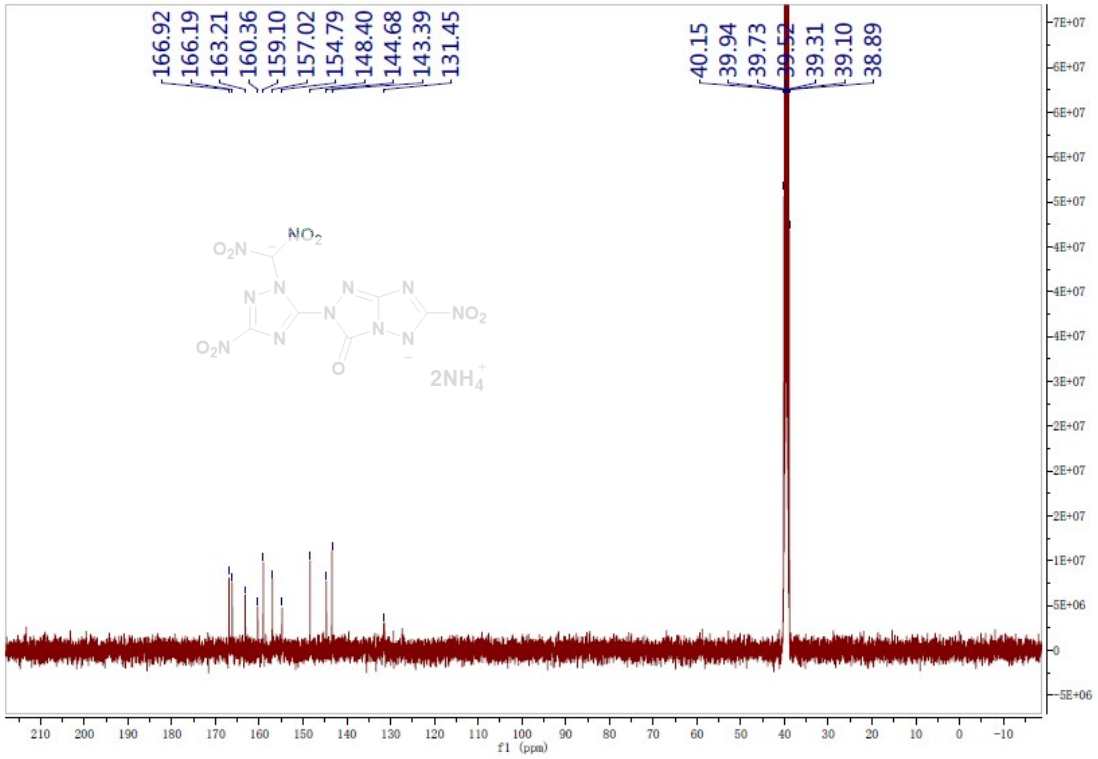


Figure S15 ^{13}C NMR spectrum of **8** in d_6-DMSO.

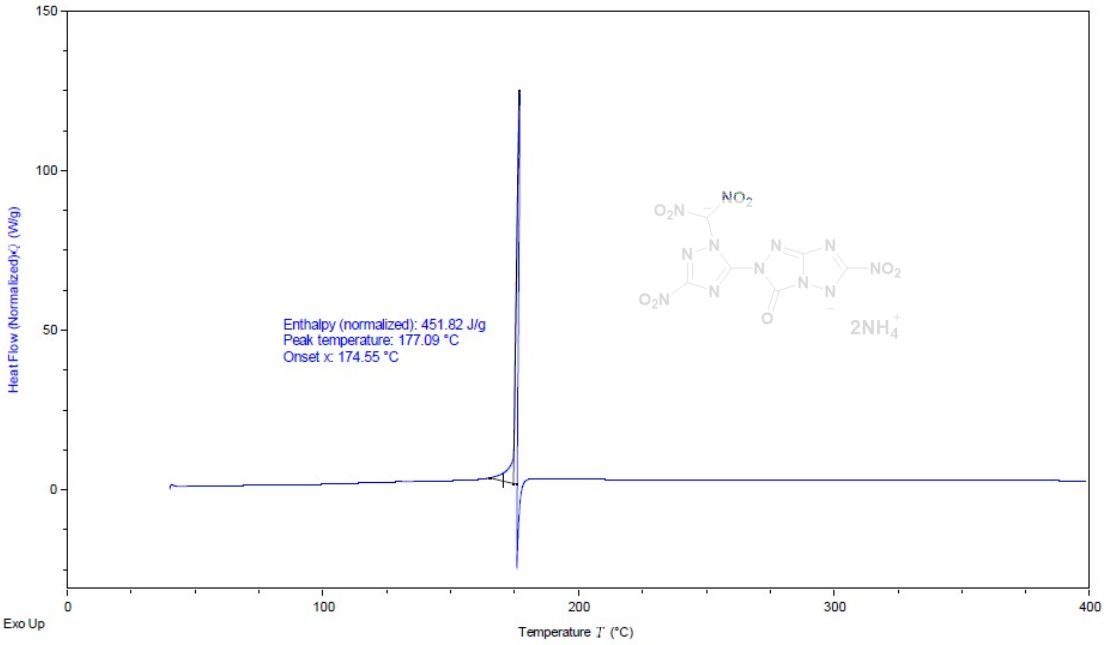


Figure S16 DSC plot of **8**.

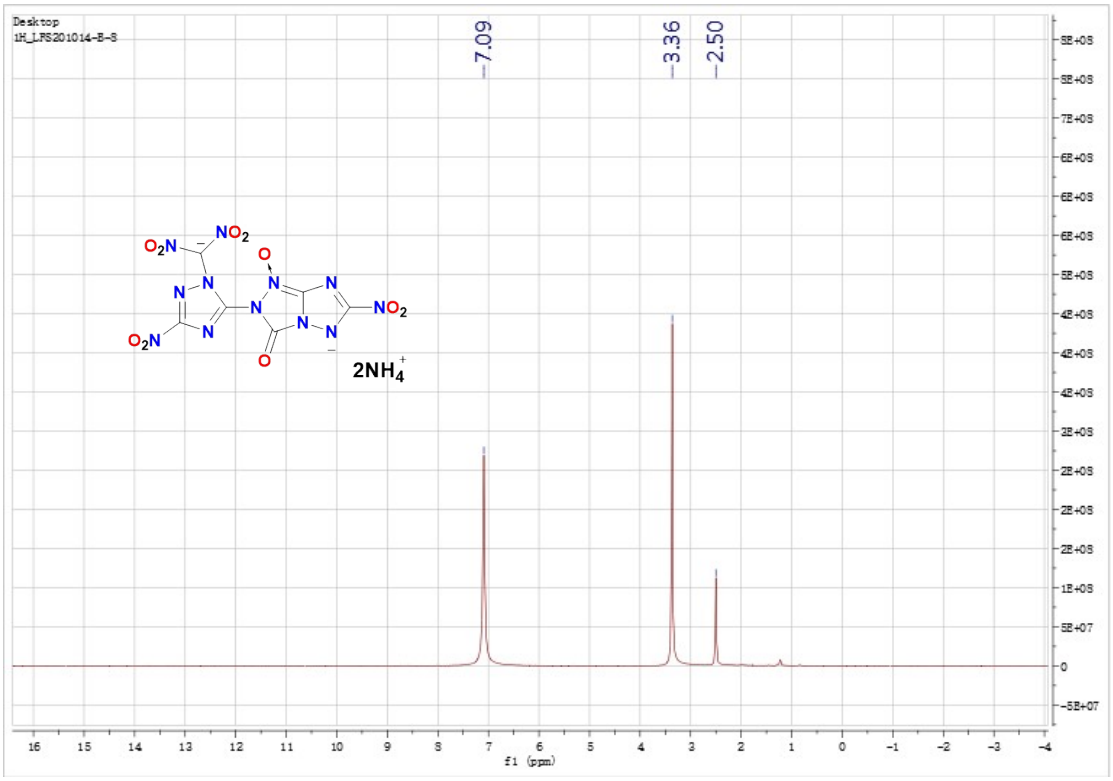


Figure S17 ^{1}H NMR spectrum of **9** in d_6-DMSO.

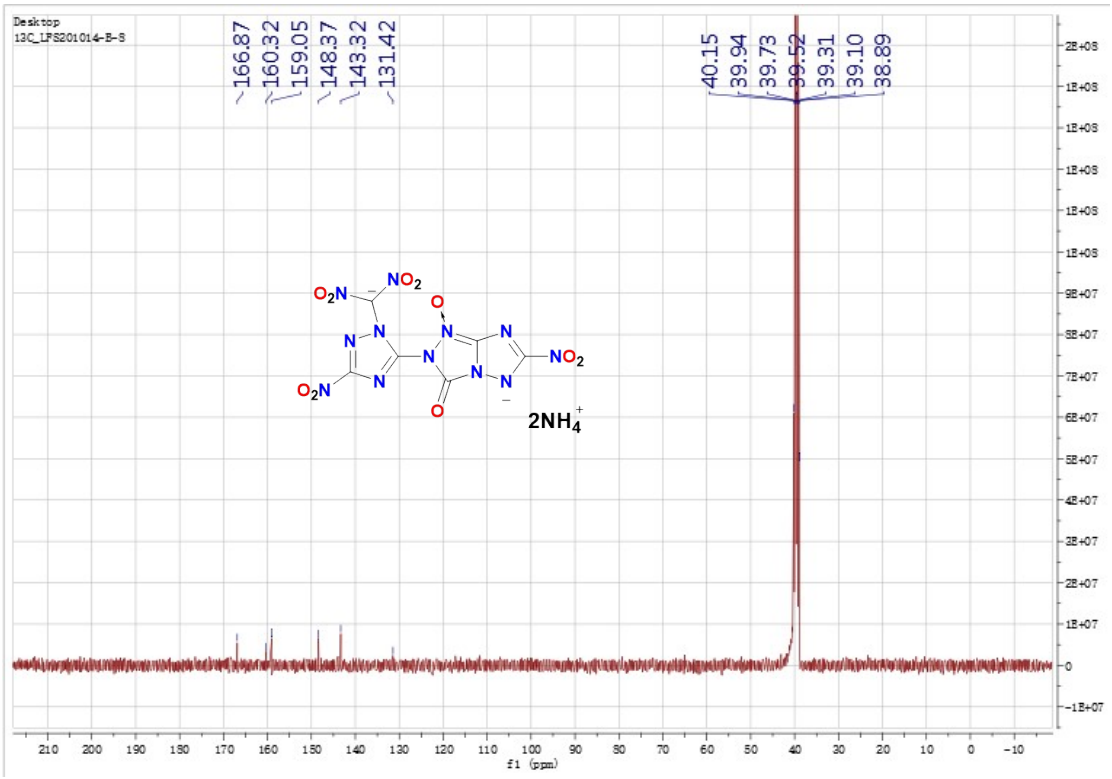


Figure S18 ^{13}C NMR spectrum of **9** in d_6-DMSO.

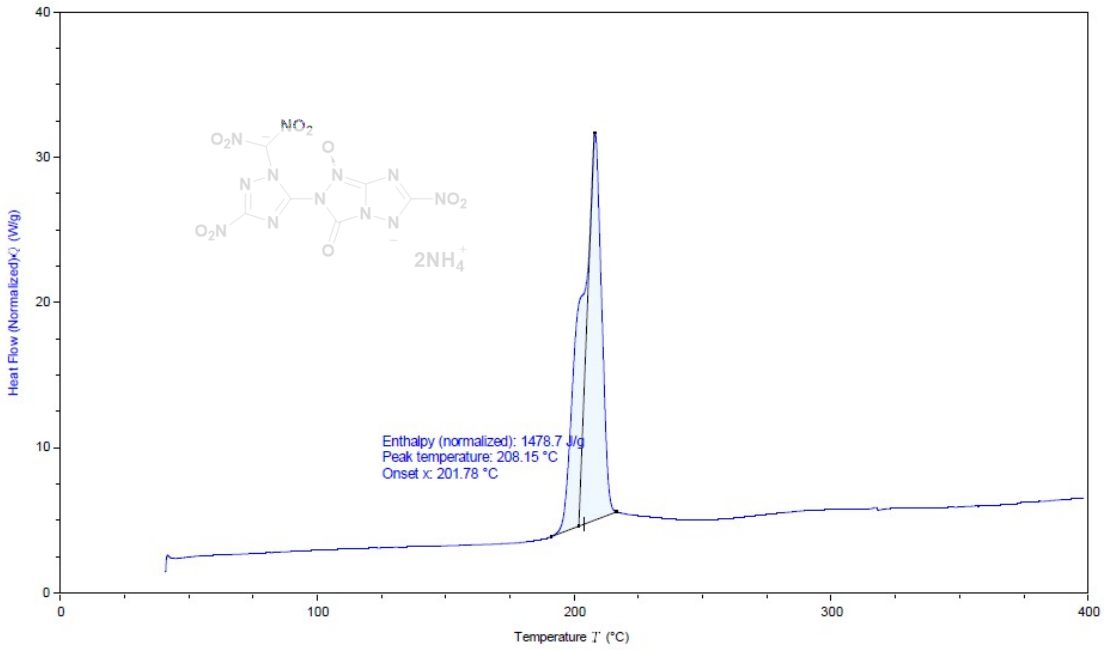


Figure S19 DSC plot of **9**.

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