Electronic Supplementary Information

Unravelling the Reactivity of the Azo Bridge in 3,3’-(5-Dinitromethyl-1,2,4-oxadiazolyl)- 4,4’-Azofurazanate in the Synthesis of Energetic Compounds

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Experimental section

Caution: All the nitrogen-rich compounds used are energetic materials and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and/or handling. Only small quantities should be prepared and studied.

General methods

^{1}H and ^{13}C spectra were recorded on a 400 MHz (Bruker AVANCE NEO 400) nuclear magnetic resonance spectrometer operating at 400.13, and 100.62 MHz, respectively. The chemical shifts in ^{13}C and ^{15}N NMR spectra are reported relative to Me_4Si and $MeNO_2$, respectively. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Discovery 25) at a scan rate of 5 ^{o}C min^{-1}. IR spectra were recorded using KBr pellets for solids on a Thermoscientific Summit PRO FT-IR. Densities were determined at 25 ^{o}C by employing a Micromeritics AccuPycII 1345 gas pycnometer. Elemental analyses were carried out using a Thermo Scientific FLASH 2000 elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fall hammer and a BAM friction tester, respectively.

4,4’-(5-Methyl dinitroacetate -1,2,4-oxadiazole)-3,3’-azofurazan (2)

To a solution of 3-amino-4-(5-acetoxymethyl-1,2,4-oxadiazole)furazan (0.84 g, 3.7 mmol) in chloroform (10 mL) was added concentrated HCl (10 mL). $KMnO_4$ (0.59g, 3.7 mmol) in H_2O (10 mL) was added slowly dropwise under stirring. After the addition was completed, the temperature was increased gradually to 50 °C and reacted for 3 h. The excess $KMnO_4$ was quenched with a few drops of 5% hydrogen peroxide solution until the solution became clear. The organic phase was separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 10 mL). The combined organic phase was dried with anhydrous Na_2SO_4. After the solvent was removed under vacuum, crude product **1** (0.81 g) was obtained as an orange oil. Concentrated H_2SO_4 (5 mL) was added to the oil and 100% HNO_3 (2.5 mL) was added dropwise while maintaining the temperature at -5 °C. The reaction mixture was stirred at 0 °C for 1 h, then for an additional 2h at room temperature. The yellow solid was collected by filtration, washed with trifluoroacetic acid (5 mL), and air dried to give compound **2**, (1.05 g, yield 90.5%). T_m: 110.5 °C; T_{dec}: 248.12 °C; IR (cm^{-1}) ν = 2974, 2891, 1780, 1598, 1567, 1439, 1400, 1338, 1296, 1276, 1247, 1162, 1095, 1070, 1033, 976, 959, 931, 916, 901, 851, 836, 802, 795, 766, 748, 713, 682, 643, 627, 583, 521. ^{1}H NMR (CD_3CN): 4.14 (6H, s, $-CH_3$); ^{13}C NMR (CD_3CN): δ 166.3, 162.9, 160.0, 155.3, 139.9, 110.8, 58.3; EA ($C_{14}H_6N_{14}O_{16}$, 626.28): Calcd, C: 26.85; H: 0.97; N: 31.31; Found, C: 26.79; H: 1.05; N: 30.88.

Diammonium 4,4’-(5-dinitromethyl-1,2,4-oxadiazole)-3,3’-azo-furazanate (3)

To a suspension of compound **2** (1.12 g, 1.8 mmol) in water (20 mL) was added concentrated aqueous ammonia (0.92g, 20 mmol). The reaction mixture was stirred at room temperature for 6 h, the solid was collected by filtration, and dried at 90 °C under vacuum to give compound **3** (0.72 g, yield 73.5%) as an orange solid. T_{dec}: 154.16 °C; IR (cm^{-1}) ν = 3225, 1552, 1496, 1418, 1351, 1291, 1230, 1163, 1079, 1033, 978, 926, 827, 770, 752, 703, 618, 482. ^{1}H NMR (DMSO-d$_6$): 7.21, 7.09, 6.96 (8H, s, -NH_4); ^{13}C NMR (DMSO-d$_6$): δ 122.9, 142.1, 158.6, 162.3, 172.8; ^{15}N NMR (DMSO-d6): -359.18, -136.97, -24.18, -17.73, 24.94, 44.00, 143.95; EA ($C_{10}H_8N_{16}O_{12}$, 544.27): Calcd, C: 22.07; H: 1.48; N: 41.18; Found, C: 21.91; H: 1.88; N: 40.11.

Dihydroxyammonium 4,4’-(5-dinitromethyl-1,2,4-oxadiazole)-3,3’-azo-furazanate (4)

Compound **3** (0.54g, 1 mmol) was suspended in water (15 mL) at 0 °C, then 50% H_2SO_4 (3 mL) was added slowly. After stirring for 10 minutes, the reaction mixture was extracted with ethyl ether (3×10 mL). The organic phase was combined and dried over anhydrous Na_2SO_4. After filtration 50% hydroxylamine solution (0.13g, 2 mmol) was added to the ether solution and stirred for 20 minutes. The precipitate was collected by filtration and dried under vacuum. Compound **4** was obtained as an orange solid (0.48 g, yield 83.0%). T_{dec}: 182.8 °C, IR (cm^{-1}) ν = 3152, 2696, 1599,1544, 1478, 1387, 1366, 1297, 1213, 1169, 1133, 1077, 1028, 1008, 976, 922, 897, 869, 833, 781, 753, 699, 609, 477. ^{1}H NMR (DMSO-d6): 8.72 (8H, s, -NH_3OH); ^{13}C NMR (DMSO-d6): δ 122.5, 141.8, 158.2, 161.9, 172.3; ^{15}N NMR (DMSO-d6): -299.09, -137.07, -24.24, -17.81, 24.94, 43.99, 143.93; EA ($C_{10}H_8N_{16}O_{14}$, 576.27): Calcd, C: 20.84; H: 1.40; N: 38.89; Found, C: 20.35; H: 1.86; N: 35.05.

Dihydrazinium 4,4’-(5-dinitromethyl-1,2,4-oxadiazole)-3,3’-hyrazinyl-furazanate (7)

To a solution of compound **2** (0.63 g, 1 mmol) in acetonitrile (8 mL) was added hydrazine monohydrate (0.5 g,10 mmol) in acetonitrile (5 mL). The reaction mixture was stirred at room temperature overnight; the precipitate was collected by filtration, dried under vacuum to give compound **7 (**0.56 g) as a yellow solid, yield 81.8%. T_{dec}: 208.8 °C; IR (cm^{-1}) ν = 3346, 3290, 3189, 1546, 1493, 1411, 1362, 1294, 1245, 1168, 1147, 1079, 976, 928, 828, 781, 749, 647, 582, 420. ^{1}H NMR (DMSO-d6): 4.78 (10H, br, -N_2H_5, -NH); ^{13}C NMR (DMSO-d6): δ 122.4, 136.2, 156.4, 158.8, 172.3; ^{15}N NMR (DMSO-d6): -332.96, -295.90, -139.23, -24.20, -22.93, -11.05, 36.17; EA ($C_{10}H_{12}N_{18}O_{12}$, 576.32): Calcd, C: 20.84; H: 2.10; N: 43.75; Found, C: 21.50; H: 2.63; N: 43.04.

X-ray Crystallography

Crystals of **2** was obtained by a recrystallization from solution of acetonitrile. Compound **5** was separated by column chromatography to obtain a pure product, the crystals of **5** suitable for single-crystal X-ray diffraction were grown by dissolving the compound in a minimum amount of methanol and let the solvent evaporated slowly.

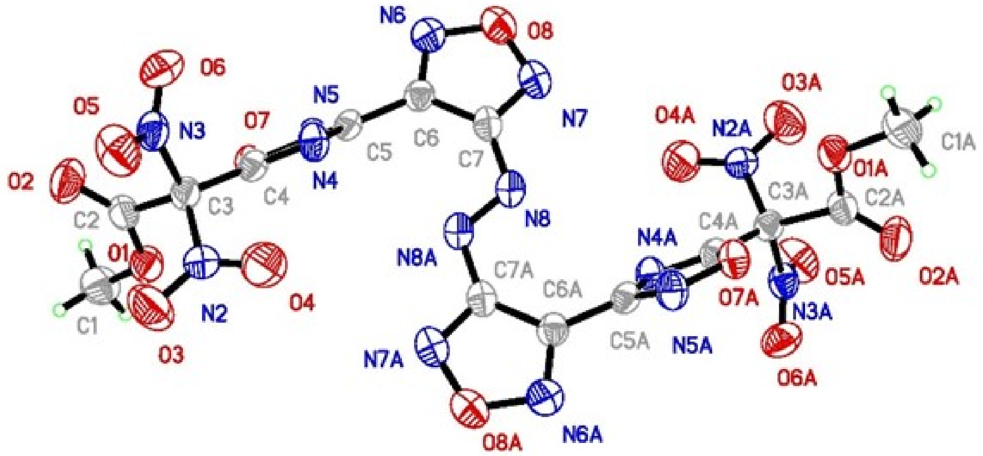


Figure S1. X-ray crystal structure of **2**.

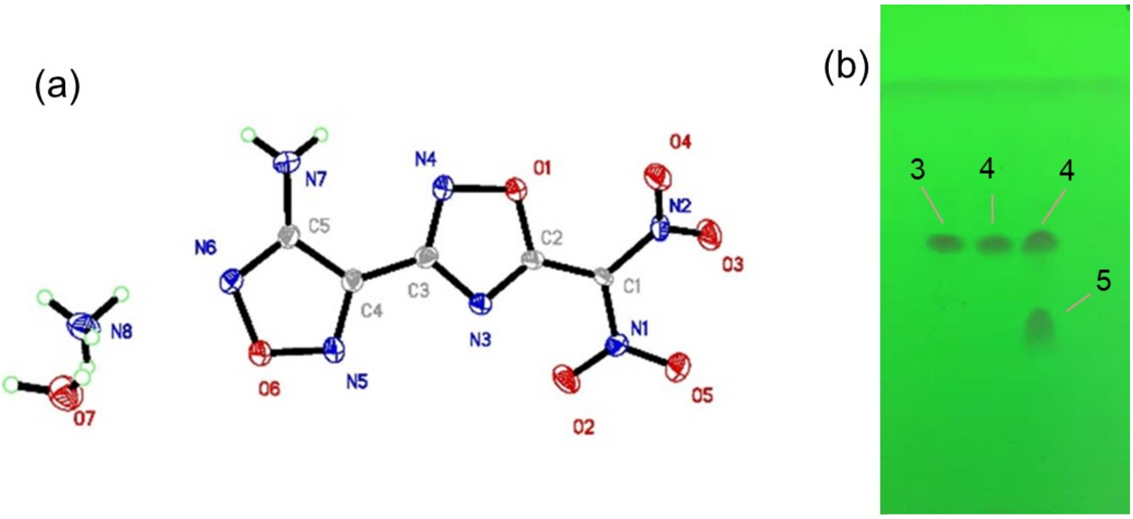


Figure S2. (a) X-ray crystal structure of **5**; (b) TLC result of reaction in methanol after 1 hour at room temperature. The left spot is compound **3**; The middle spot is compound **4**; Side product **5** and unreacted compound **4** are on the right.

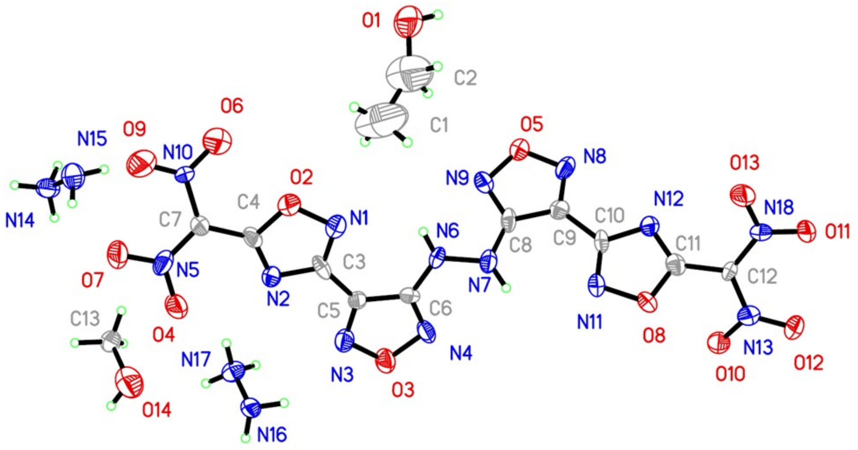


Figure S3. X-ray crystal structure of **7**·MeOH·EtOH**.**

In order to explain the abnormal solubility of **3** in typical solvents and water, the solvation free energies of **3** in different solvents were calculated using Gaussian 09 suite of programs.[1] The difference of Gibbs free energy (ΔGsolv) for **3** in solution and gas phases are given in Table S1. The more negative solvation free energy indicating the higher solubility,[2] solvation free energy of **3** in aqueous solution (-28.18 kcal mol^{-1}) compared to that in methanol (-43.39 kcal mol^{-1}), ethanol (-43.62 kcal mol^{-1}) or acetonitrile (-46.31 kcal mol^{-1}) suggesting a lower solubility of **3** in water than in methanol, ethanol or acetonitrile which is consistent with the experimental results.

Table S1. The solvation free energy of **3**.

Comp	3
$\Delta G_{\mathrm{solv,\ water}}$ [kcal/mol]	-28.17542306
$\Delta G_{\mathrm{solv,\ methanol}}$ [kcal/mol]	-43.39214951
$\Delta G_{\mathrm{solv,\ ethanol}}$ [kcal/mol]	-43.61792739
$\Delta G_{\mathrm{solv,\ acetonitrile}}$ [kcal/mol]	-46.31326852

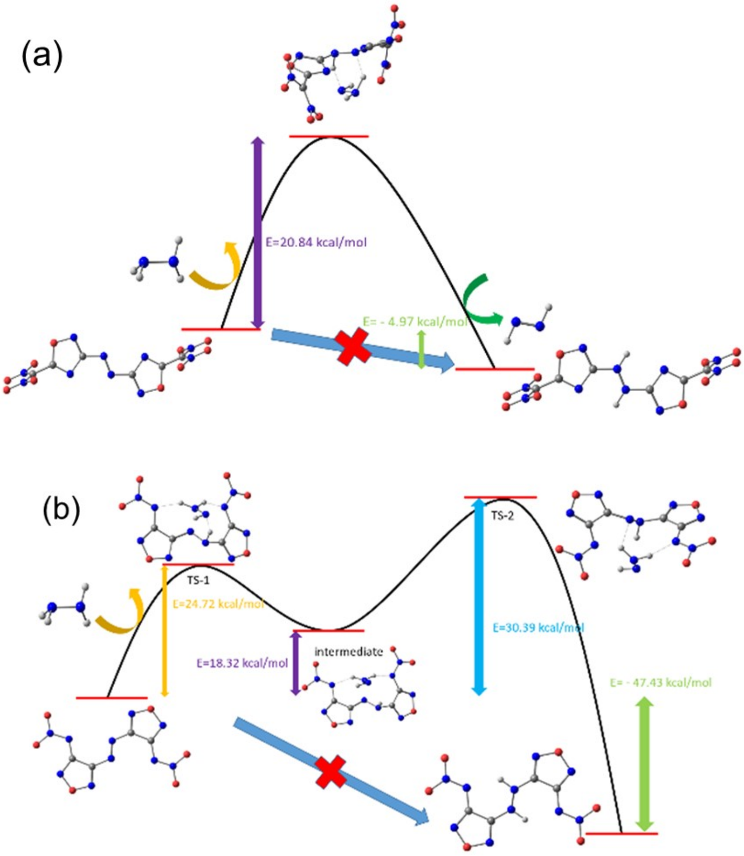


Figure S4. The failure of the azo double bond to single bond with the addition of hydrazine.

Table S2. Crystal data and structure refinement for **2** .

Identification code	**2**
CCDC number	2087553
Empirical formula	$C_{14}H_6N_{14}O_{16}$
Formula weight	626.33
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	5.843(3)
b/Å	7.177(3)
c/Å	14.405(6)
α/°	87.865(6)
β/°	88.438(6)
γ/°	80.502(6)
Volume/Å^3	595.2(4)
Z	1
ρ_{calc}g/cm^3	1.747
μ/mm^{-1}	0.161
F(000)	316.0
Crystal size/mm^3	0.120 × 0.110 × 0.090 mm^3

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.83 to 54.912
Index ranges	$-6 \leq h \leq 7$, $-9 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected	3668
Independent reflections	2632 [R_{int} = 0.0160]
Data/restraints/parameters	2632/1/200
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0438, wR_2 = 0.1529
Final R indexes [all data]	R_1 = 0.0514, wR_2 = 0.1661
Largest diff. peak/hole / e $Å^{-3}$	0.34/-0.31 e.$Å^{-3}$

Table S3. Crystal data and structure refinement for **3**·2 H_2O.

Identification code	**3**·2 H2O
CCDC number	2087554
Empirical formula	C10H12N16O14
Formula weight	580.36
Temperature/K	153 K
Crystal system	monoclinic
Space group	P 2_1/c
a/Å	5.0442(10)
b/Å	13.949(3)
c/Å	15.122(3)
α/°	90
β/°	92.06(3)
γ/°	90
Volume/Å3	1063.3(4)
Z	2
ρ_{calc}g/cm3	1.813
μ/mm-1	0.168
F(000)	592.0
Crystal size/mm^3	0.13 x 0.12 x 0.1 mm^3
2Θ range for data collection/°	3.066 to 27.482
Index ranges	-6<=h<=6, -17<=k<=18, -19<=l<=19
Reflections collected	7140
Independent reflections	2425 [Rint = 0.0449]
Data/restraints/parameters	2545 / 18 / 191
Goodness-of-fit on F^2	1.158
Final R indexes [I>=2σ (I)]	R1 = 0.0594, wR2 = 0.1384
Final R indexes [all data]	R1 = 0.0669, wR2 = 0.1430
Largest diff. peak/hole / e $Å^{-3}$	0.322 and -0.242 e.$Å^{-3}$

Table S4. Crystal data and structure refinement for **4.**

Identification code	**4**
CCDC number	2087555
Empirical formula	C10H8N16O14
Formula weight	576.32
Temperature/K	296 K
Crystal system	monoclinic
Space group	$P\ 2_1/c$
a/Å	11.796(3)
b/Å	7.4634(18)
c/Å	11.526(3)
α/°	90
β/°	96.659(4)
γ/°	90
Volume/Å3	1007.9(4)
Z	2
ρ_{calc}g/cm3	1.899
μ/mm-1	0.176
F(000)	584.0
Crystal size/mm^3	0.13 ×0.11 ×0.10
2Θ range for data collection/°	3.476 to 54.99
Index ranges	$-15 \le h \le 13$, $-9 \le k \le 9$, $-14 \le l \le 8$
Reflections collected	6023
Independent reflections	2309 [Rint = 0.0383]
Data/restraints/parameters	2309/0/184
Goodness-of-fit on F^2	0.965
Final R indexes [I>=2σ (I)]	R1 = 0.0463, wR$_2$ = 0.1347
Final R indexes [all data]	R1 = 0.0740, wR$_2$ = 0.1603
Largest diff. peak/hole / e Å^{-3}	0.23 and -0.22 e.Å^{-3}

Table S5. Crystal data and structure refinement for **7**·EtOH·MeOH**.**

Identification code	**7**·EtOH·MeOH
CCDC number	2094944
Empirical formula	$C_{13}H_{22}N_{18}O_{14}$
Formula weight	654.49
Temperature/K	170.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	3.6502(5)
b/Å	17.024(3)
c/Å	41.865(6)

α/°	90
β/°	92.467(4)
γ/°	90
Volume/Å^3	2599.1(7)
Z	2
ρ_{calc} g/cm^3	1.673
μ/mm^{-1}	0.149
F(000)	1352.0
Crystal size/mm^3	0.12 × 0.11 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.392 to 49.976
Index ranges	$-4 \le h \le 4$, $-16 \le k \le 20$, $-49 \le l \le 47$
Reflections collected	15885
Independent reflections	4650 [R_{int}= 0.1504, R_{sigma}= 0.1728]
Data/restraints/parameters	4650/16/409
Goodness-of-fit on F^2	0.973
Final R indexes [I>=2σ (I)]	R_1= 0.0969, wR_2= 0.2272
Final R indexes [all data]	R_1= 0.2090, wR_2= 0.2758
Largest diff. peak/hole / e Å^{-3}	0.55/-0.63

Table S6. Crystal data and structure refinement for **5·H$_2$O**

Identification code	**5·H$_2$O**
CCDC number	2087557
Empirical formula	$C_5H_8N_8O_7$
Formula weight	292.19
Temperature/K	163.15
Crystal system	monoclinic
Space group	P2$_1$/c
a/Å	13.575(3)
b/Å	11.854(2)
c/Å	6.6963(13)
α/°	90
β/°	98.79(3)
γ/°	90
Volume/Å^3	1064.9(4)
Z	4
ρ_{calc}g/cm^3	1.823
μ/mm^{-1}	0.168
F(000)	600.0
Crystal size/mm^3	0.13 × 0.03 × 0.02 mm^3
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.036 to 54.958
	$-17 \leq h \leq 17$, $-15 \leq k \leq 15$, $-8 \leq l \leq 8$
Index ranges	
Reflections collected	2399
Independent reflections	2399 [R_{int}= ?]
Data/restraints/parameters	2399/0/182
Goodness-of-fit on F^2	1.144
Final R indexes [I>=2σ (I)]	R_1= 0.0884, wR_2= 0.1737
Final R indexes [all data]	R_1= 0.1085, wR_2= 0.1851
Largest diff. peak/hole / e Å^{-3}	0.36/-0.42 e.Å^{-3}

^{1}H NMR , ^{13}C NMR and ^{15}N NMR spectra

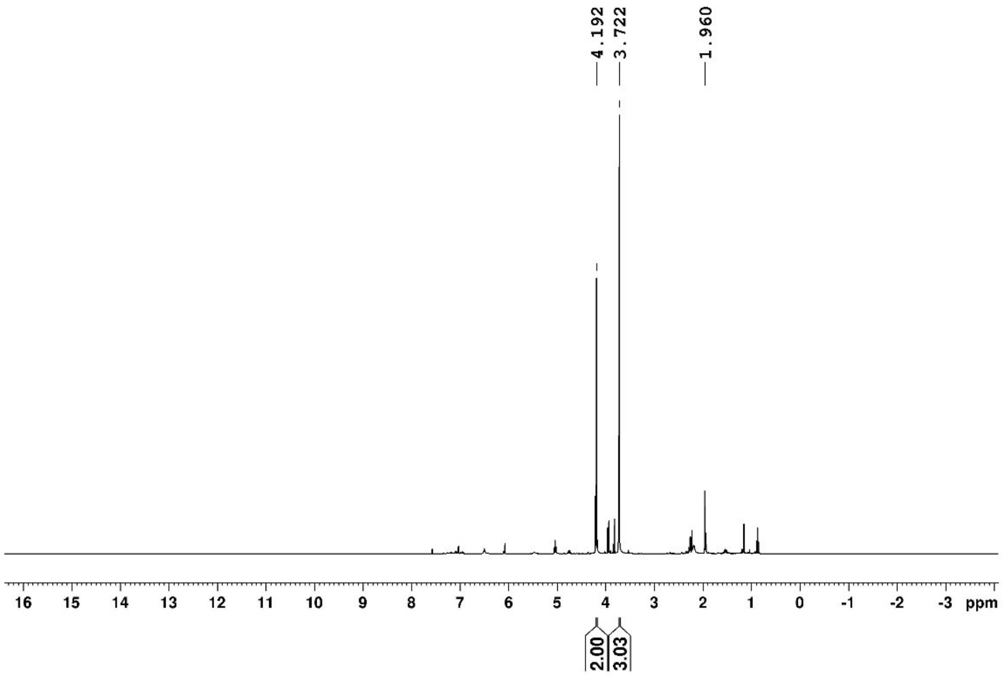


Figure S5. ^{1}H NMR of **1** with some unknown impurities.

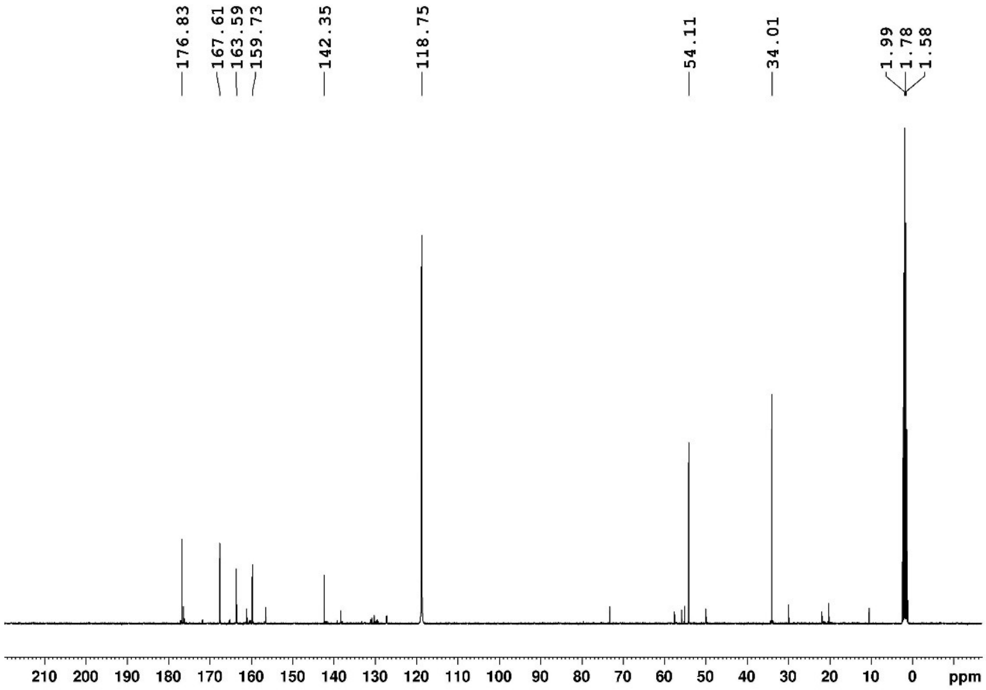


Figure S6. ^{13}C NMR of **1** with some unknown impurities.

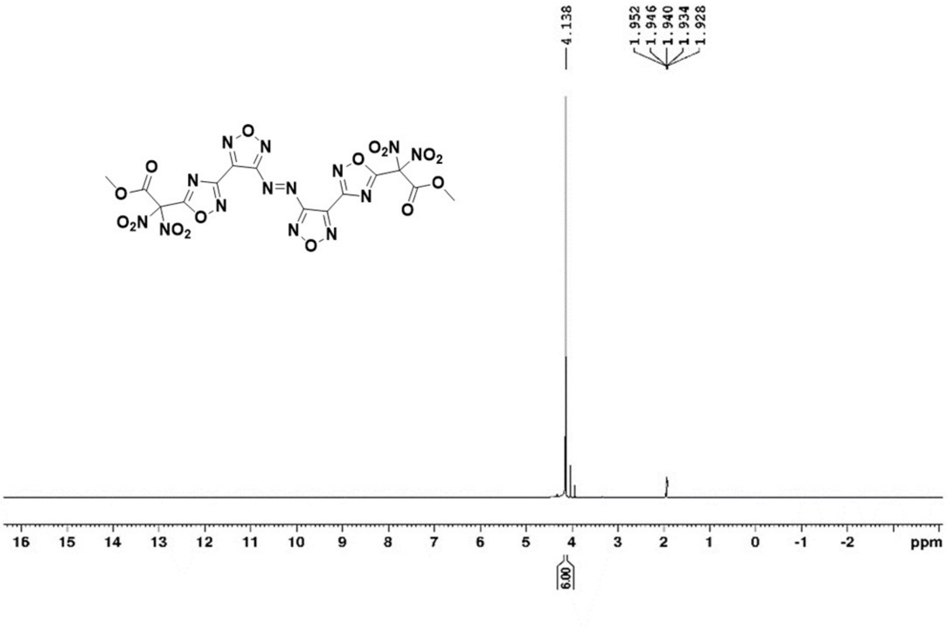


Figure S7. ^{1}H NMR of **2**.

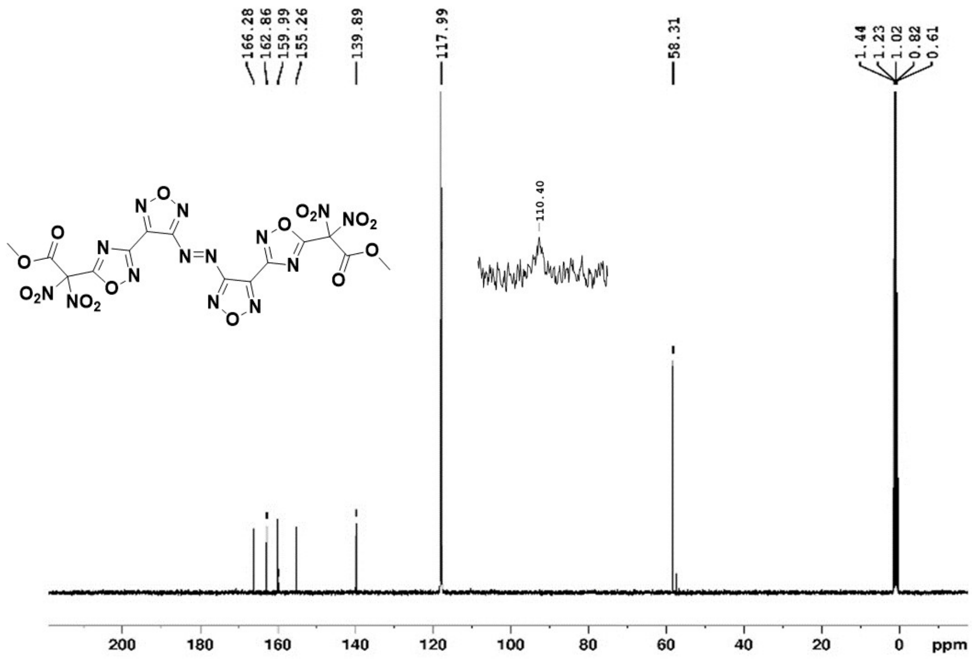


Figure S8. ^{13}C NMR of **2**.

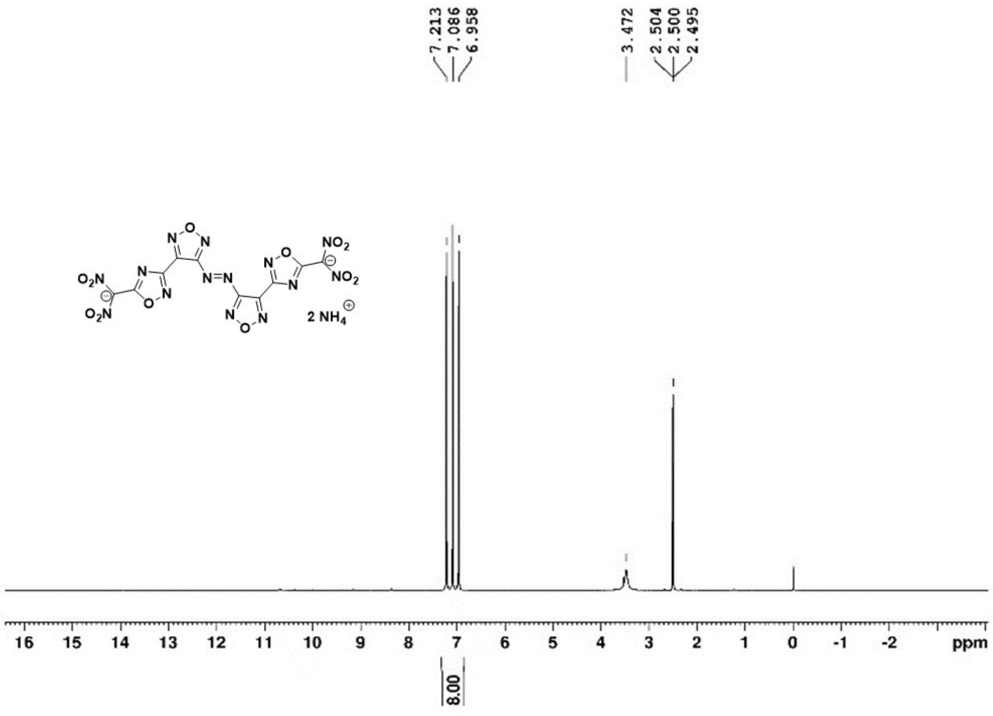


Figure S9. ^{1}H NMR of **3**.

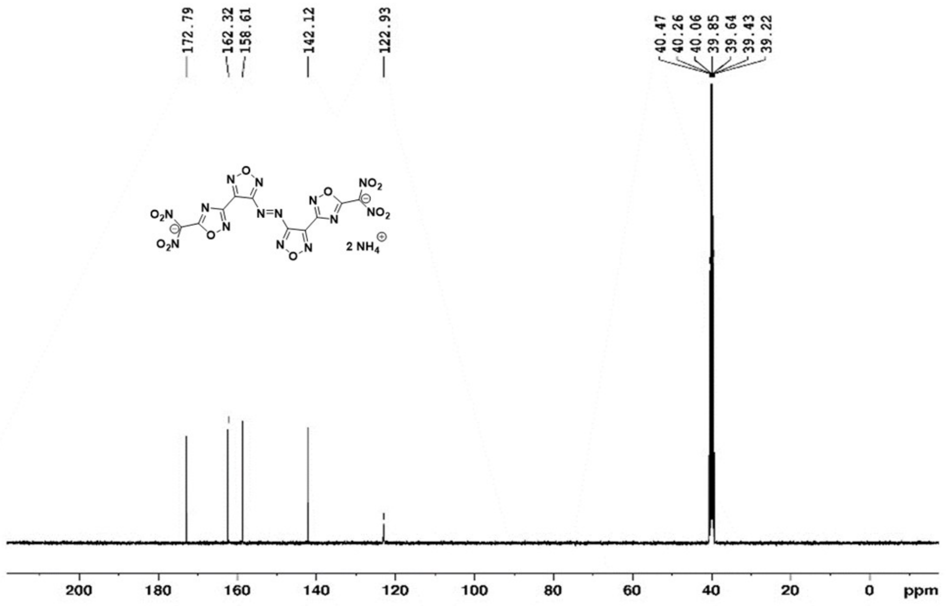


Figure S10. ^{13}C NMR of **3**.

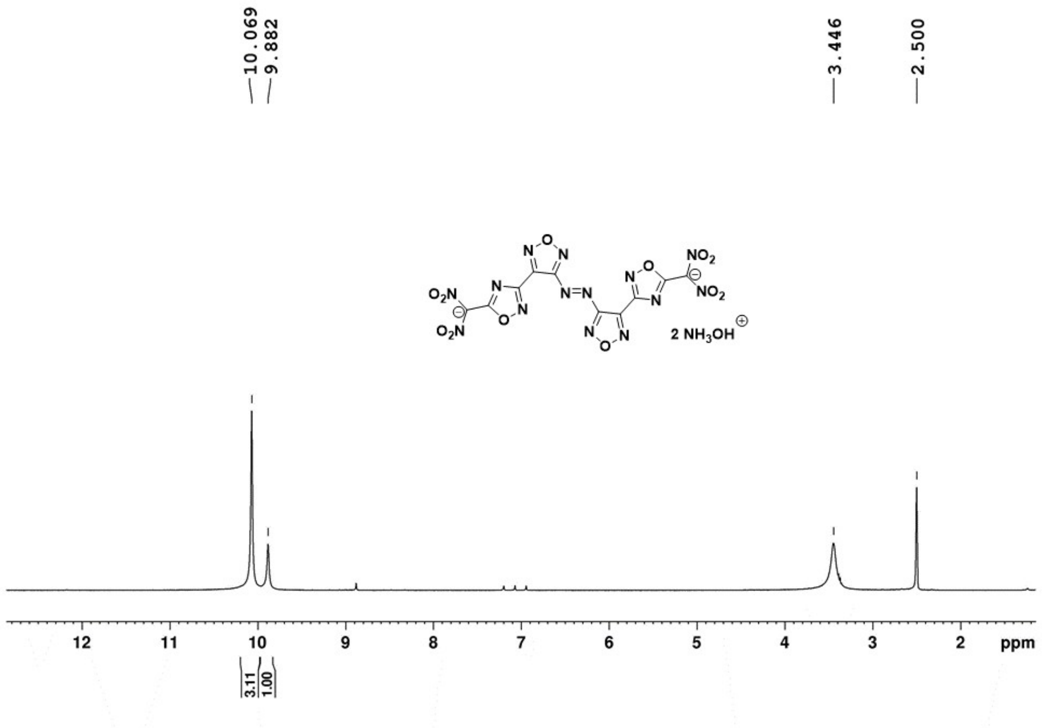


Figure S11. ^{1}H NMR of **4**.

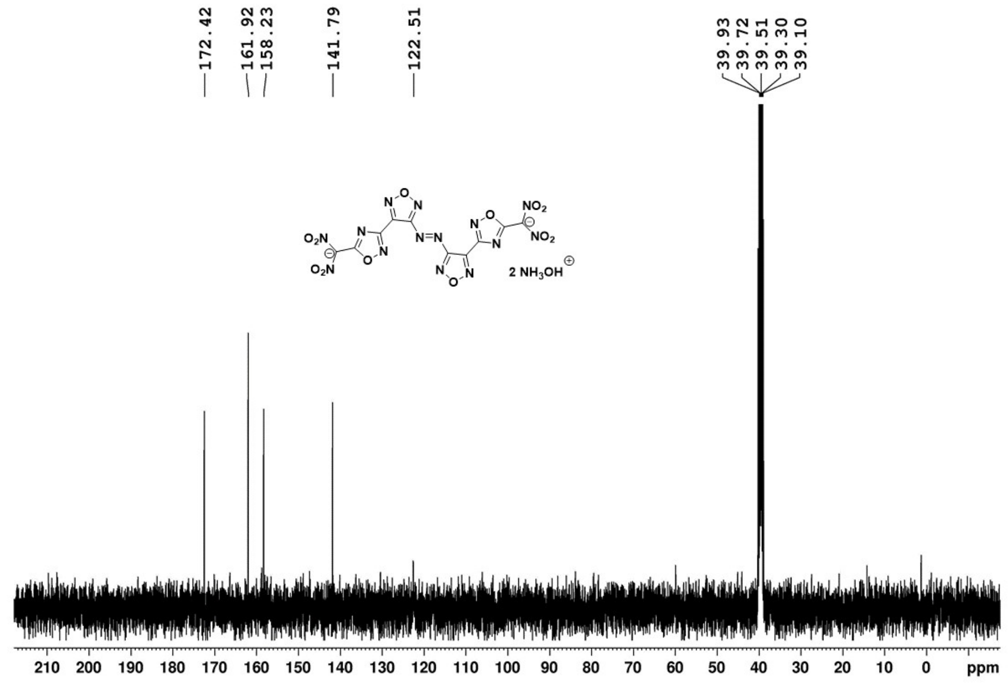


Figure S12. ^{13}C NMR of **4**.

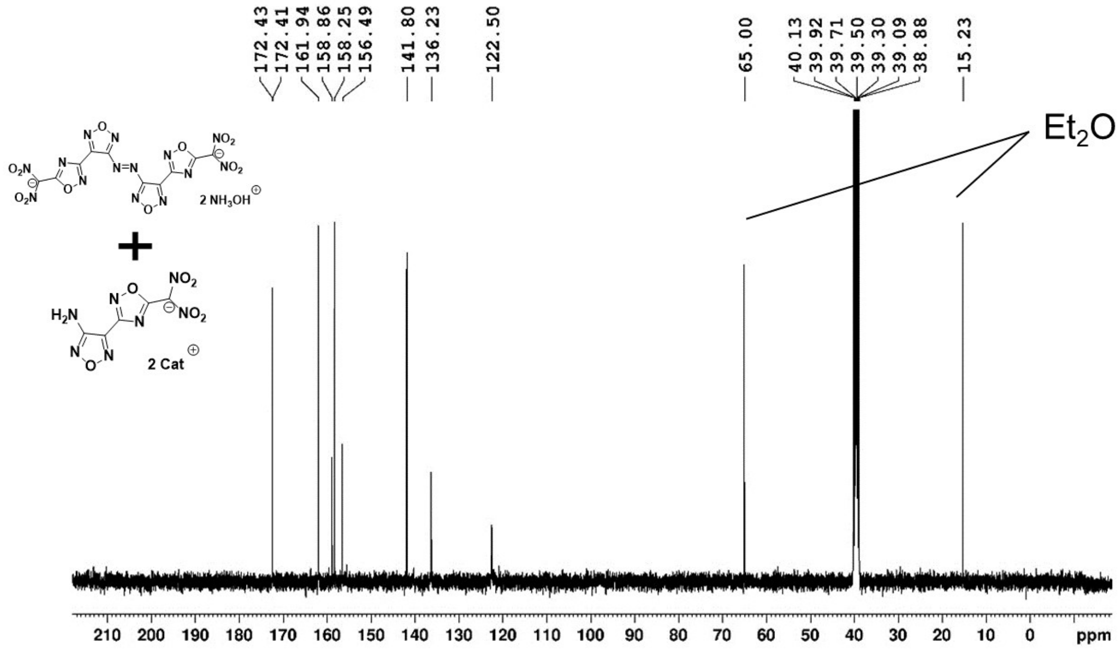


Figure S13. ^{13}C NMR of **4** and **5**.

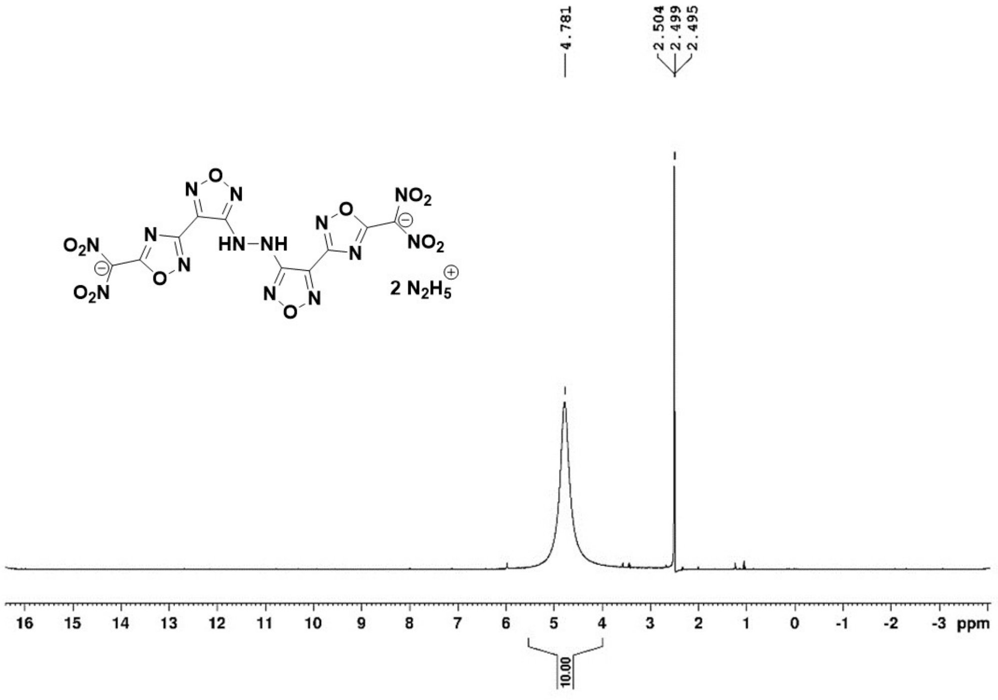


Figure S14. ^{13}C NMR of **7**.

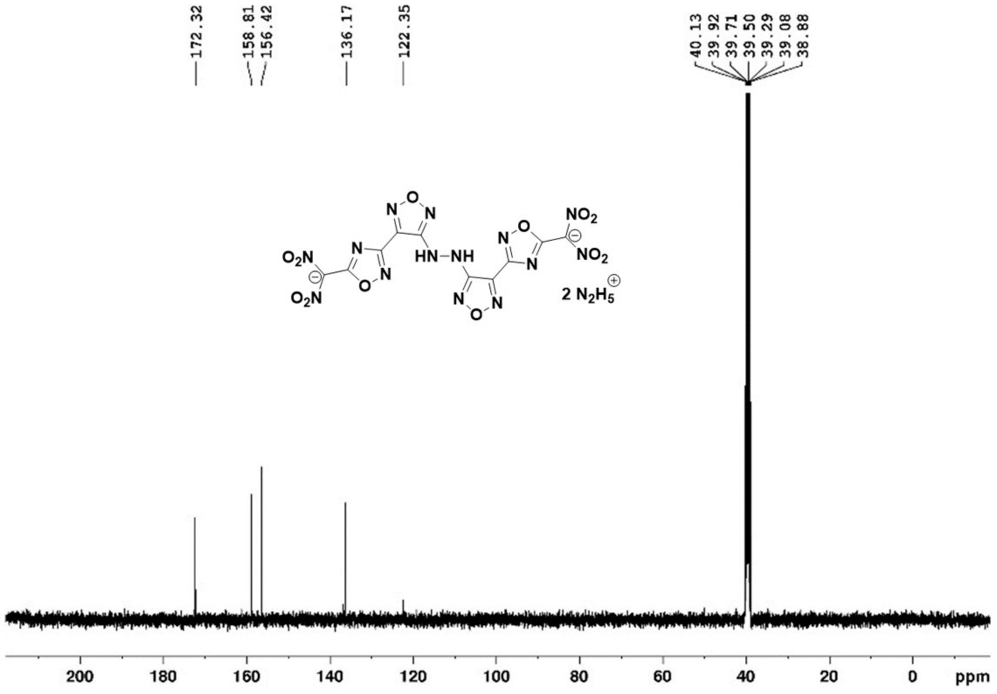


Figure S15. ^{13}C NMR of **7**.

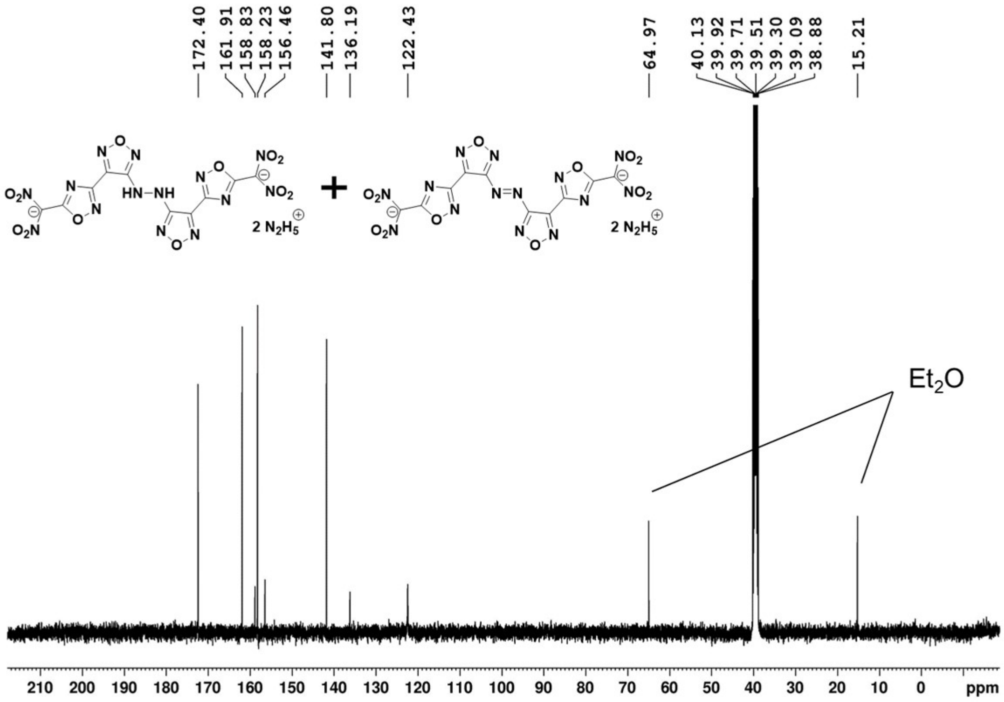


Figure S16. ^{13}C NMR of **6** and **7**.

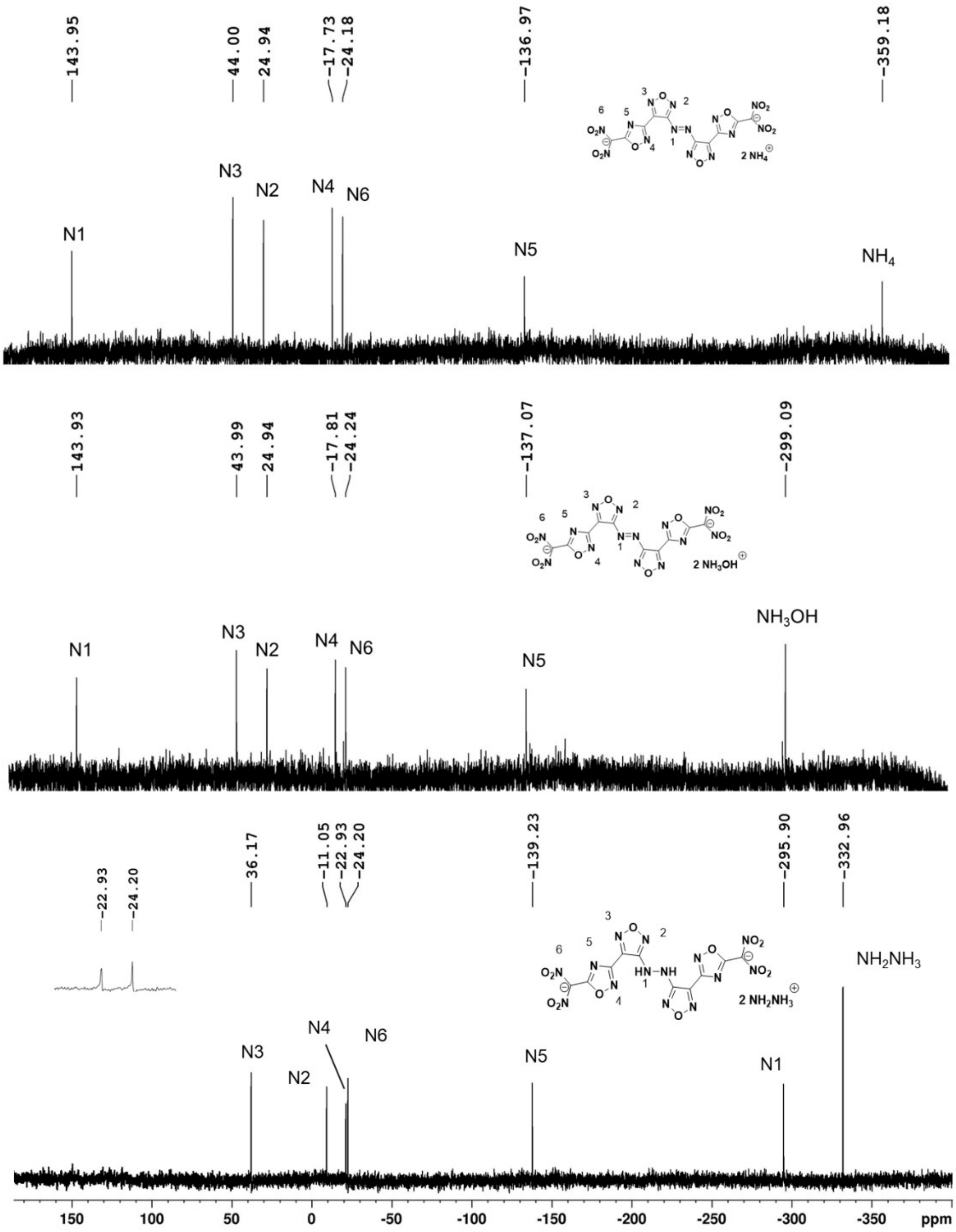


Figure S17. ^{15}N NMR spectra of (a) **3**, (b) **4** and (c) **7**.

Differential scanning calorimetry (DSC) scans

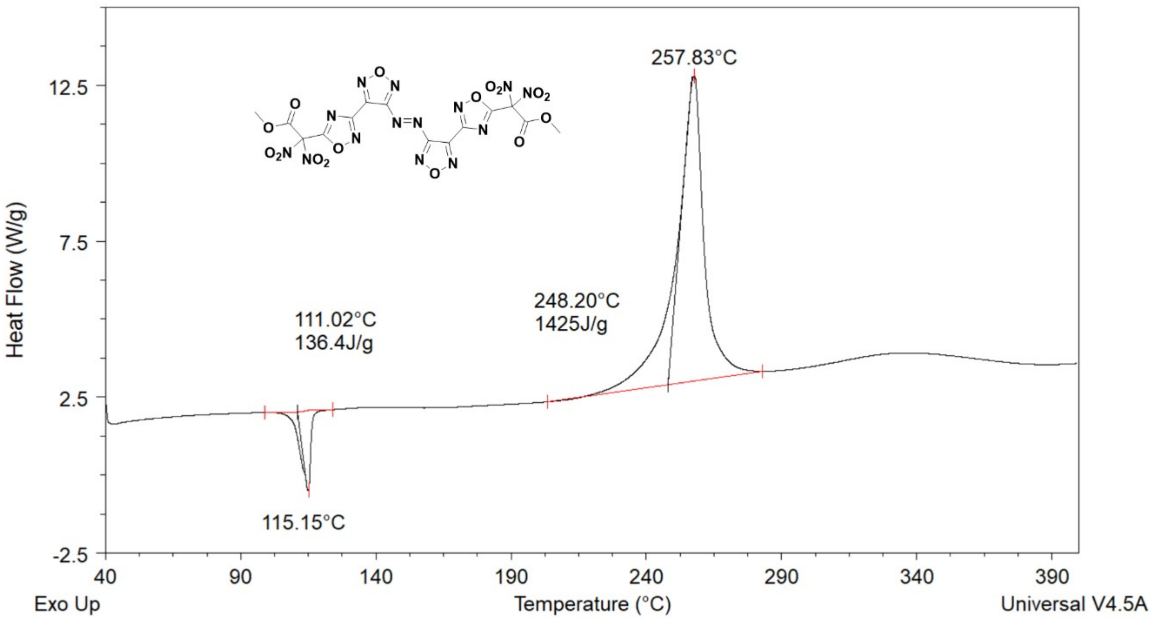


Figure S18. DSC curves of **2** under nitrogen with a heating rate of 5 °C min^{-1}

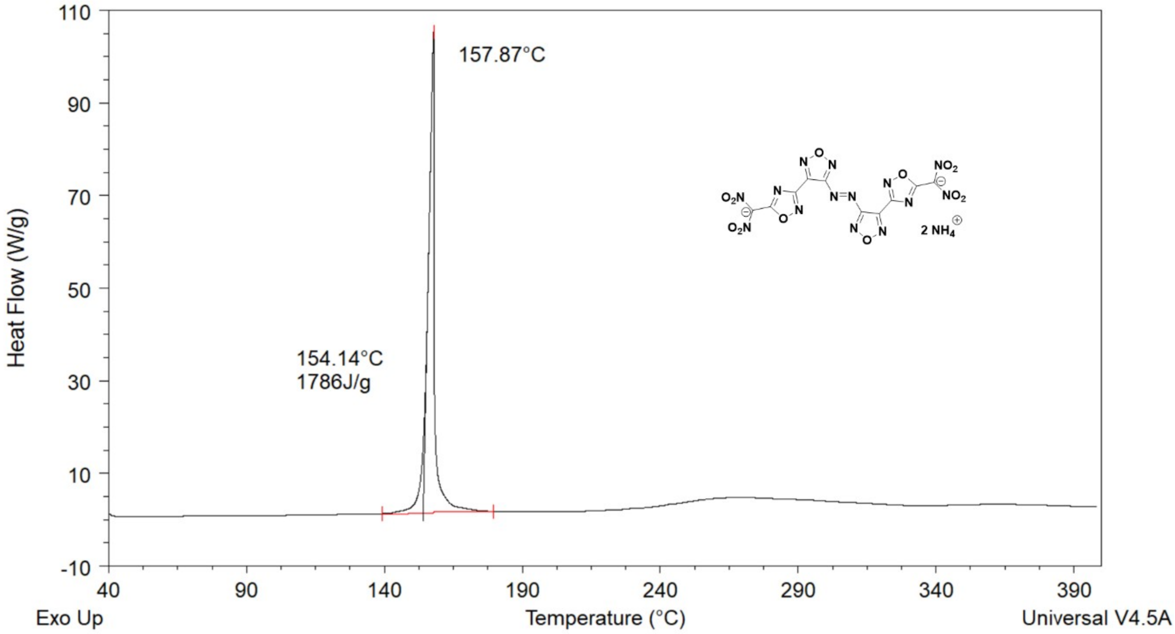


Figure S19. DSC curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}

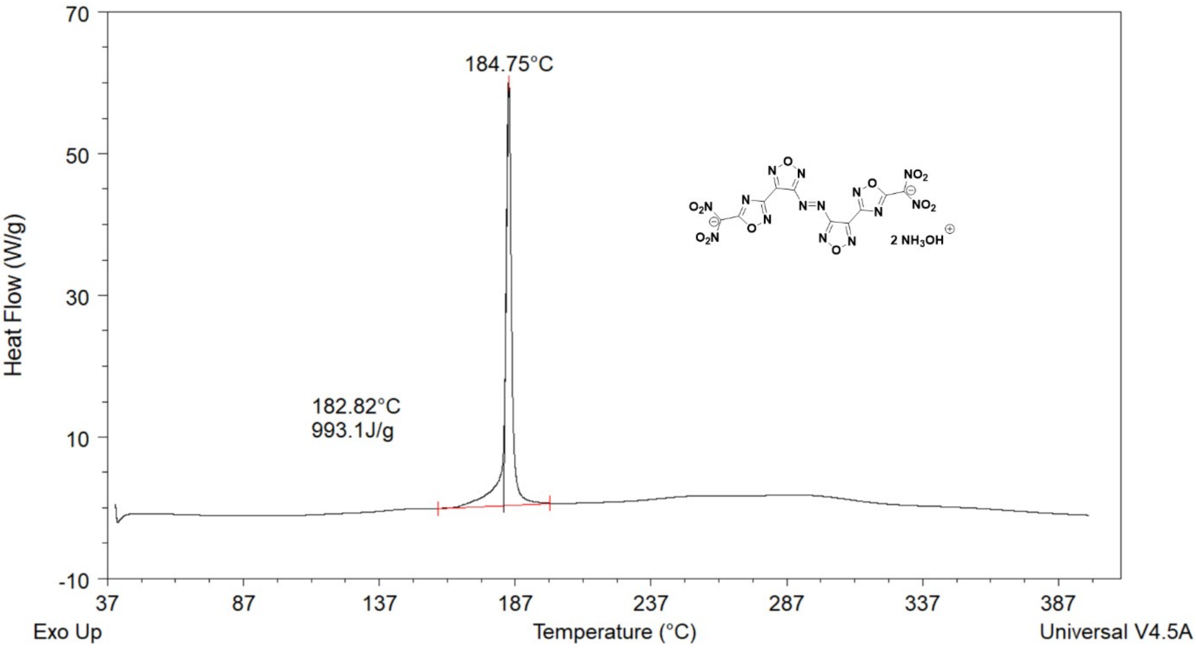


Figure S20. DSC curves of **4** under nitrogen with a heating rate of 5 °C min^{-1}

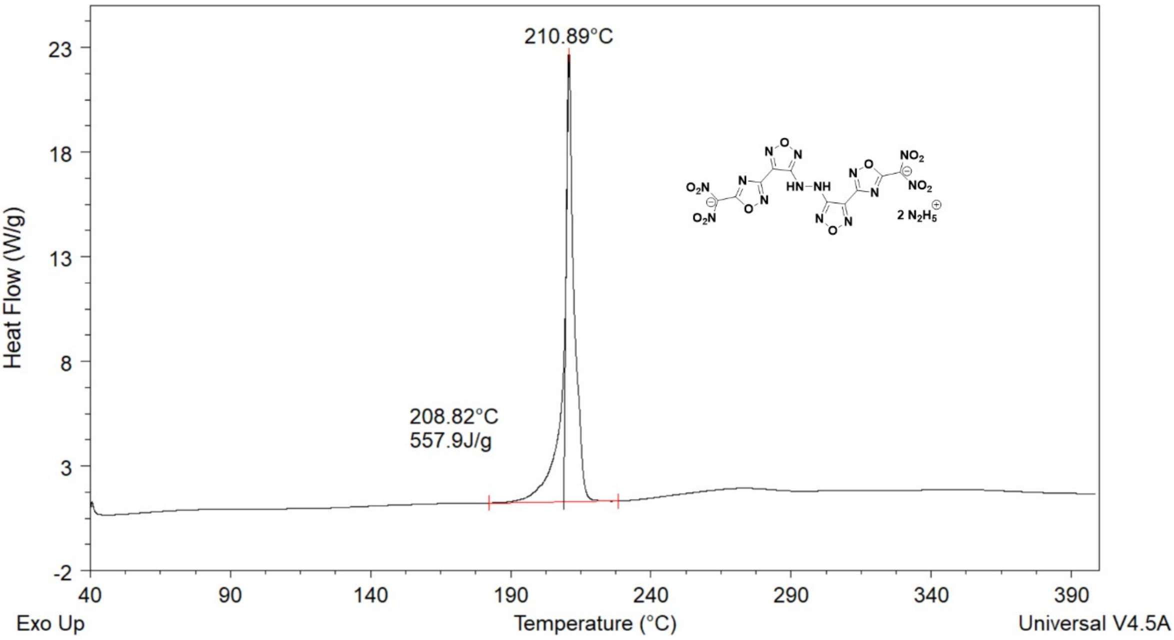
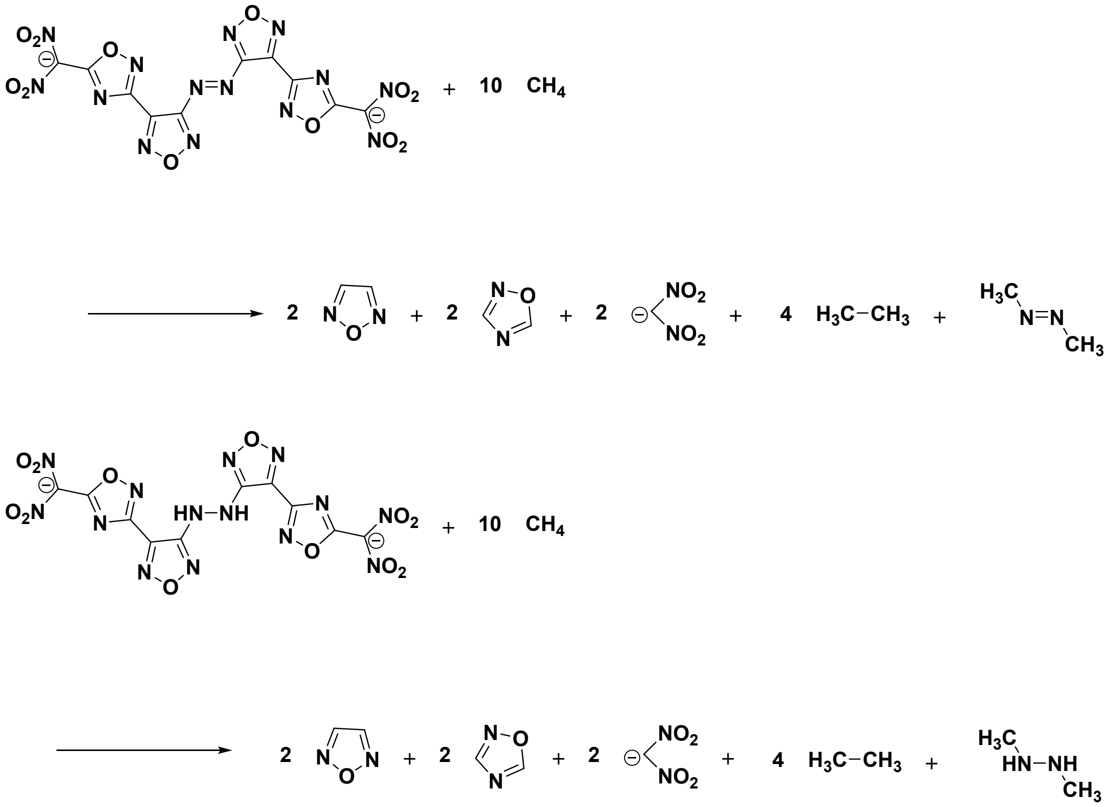


Figure S21. DSC curves of **7** under nitrogen with a heating rate of 5 °C min^{-1}

Gaussian Calculations



Scheme S1. Isodesmic reactions for calculating heats of formation for the anions of **3, 4** and **7**.

The heats of formation for **3**, **4** and **7** were calculated by Gaussian 09 (Revision E.01) suite of programs using the isodesmic reactions shown in Scheme S1. All of the structures were optimized by means of theB3LYP-D3BJ functional using 6-31+G(d,p) basis set, all of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies, and the single point energy was calculated at the M062X/def2QZVPP level.[3]

Table S7. Calculated (B3LYP-D3BJ/ 6-31+G(d,p) // M062x/def2QZVPP) total energy(E_0), zero-point energy (*ZPE*), values of the correction (H_r), and heats of formation (HOF) for anions.

	ZPE	Hr	E_0	Corrected E_0	HOF (KJ mol^{-1})
1, 2, 4-oxadiazole	0.046573	0.050946	-262.108905	-262.05982	86.15[b]
Furazan	0.045772	0.05019	262.0633126	-262.01495	196.75[b]
$CH(NO_2)_2^-$	0.039791	0.046669	449.0152272	-448.97015	-232.98[b]
CH_3CH_3	0.074962	0.079382	-79.8143982	-79.73801	-84[a]
N_2H_2	0.028522	0.032322	110.6471796	-110.61600	200.41[b]
NH_2NH_2	0.053112	0.057732	111.8673581	-111.81175	110.61[b]
CH3NH2	0.064305	0.068654	-95.8543147	-95.78823	-23[a]
CH4	0.045014	0.048823	-40.5062133	-40.45919	-74.6[a]

NH3	0.034517	0.038327	-56.5578458	-56.52090	-45.9[a]
3 (Anion)	0.173757	0.20367	2049.705644	-2049.50892	996.91[b]
7 (Anion)	0.199549	0.229663	2051.005917	-2050.78424	698.22[b]
NH_4^+	-	-	-	-	632.02[b]
NH_3OH^+	-	-	-	-	669.53[b]
$NH_2NH_3^+$	-	-	-	-	764.82[b]

[a] Data from NIST, [b] Calculated from G2.

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