Electronic Supplementary Information

Bis(dinitropyrazolyl)methanes spruced up with hydroxyl group: High performance energetic salts with reduced sensitivity

Prachi Bhatia, [a] Krishna Pandey, [a] Priyanka Das, [a] and Dheeraj Kumar*[a]

[a] Energetic Materials Laboratory, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India. E-mail: dheeraj.kumar@cy.iitr.ac.in

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Caution!

Although no accidents were observed during the synthesis, handling, and characterization, all the compounds reported in this work are potentially explosive materials and may explode unpredictably under certain conditions. All the compounds must be synthesized only on a small scale (< 100 mg). Any mechanical actions involving grinding or scratching must be avoided. In addition, all the manipulations must be strictly carried out in a fume hood behind a polycarbonate safety shield. Eye

protection, a face shield, and leather gloves must be worn while handling these compounds.

1. General Methods

All reagents were purchased from Aldrich, TCI or GLR Innovations in analytical grade and were used as supplied, if not stated otherwise. ^{1}H, $^{13}C\{^{1}H\}$ NMR and ^{15}N spectra were recorded using a 500 MHz (JEOL ECZ500R/S1) NMR spectrometer operating at 500, 125 and 50.69 MHz, respectively. As external standards, chemical shifts in the ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si and ^{15}N NMR to ammonia. The melting point and decomposition temperatures were obtained on a differential scanning calorimeter (S11 6300 EXSTAR) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets for solids on a PerkinElmer FT-IR spectrometer. Densities were measured at room temperature by employing BELPycno L Ver1.15 gas pycnometer. High resolution mass spectra quadrupole time-of-flight (HRMS−QTOF) was obtained in ESI mode. Elemental analyses were carried out on an elementar model Vario-EI-III. The impact and friction sensitivity measurements were made using a standard BAM fall hammer (OZM) and a BAM Friction tester (FST ProEX).

Suitable crystals of **2** and **7** were obtained by slow evaporation of their saturated solutions in water. The single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.710 73 Å) sealed tube. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for the integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction. The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[1] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

2. Experimental Section

1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-ol) (2).

A suspension of disodium 3,5-dinitro-4-oxidopyrazol-1-ide (3.00 g, 14.85 mmol) was prepared in 15 mL DMF. To this solution, tetraethylammonium bromide (TEAB, 0.31 g, 1.49 mmol) and diiodomethane (9.94 g, 37.13 mmol) were added. The reaction mixture was heated to 70 °C and stirred for overnight. After being cooled, 30 mL cold water was added to the reaction mixture. A small amount of sodium thiosulfate solution was added to absorb the precipitate iodine, and the resultant mixture was stirred for 30 minutes. Without isolating the disodium salt **1**, acidification of the reaction mixture

with 2M H_2SO_4 to pH~1 was carried out. The obtained precipitate was filtered, and the filterate was extracted with ethyl acetate (3 x 100 mL), and washed with saturated brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to produce compound **2** as mustard colored solid. Yield: 1.73 g, 64%. T_m (5 °C min^{-1}): 108 °C (peak). T_{dec} (5 °C min^{-1}): 195 °C (onset). Density: 1.89 g cm^{-3}. ^1H NMR (DMSO-d_6, ppm): 7.20 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): δ 143.7, 137.7, 134.0, 67.1 ppm. ^{15}N NMR (DMSO-d_6, ppm): -199.6, -84.1, -34.1, -29.1. IR (ν, cm^{-1}): 3375, 2919, 2139, 1630, 1518, 1336, 1275, 1069, 908, 811, 649, 479. Elemental analysis for $C_7H_4N_8O_{10}$ (360.16): calcd C 23.34, H 1.12, N 31.11 %. Found: C 23.21, H 1.21, N 31.21 %. HRMS (ESI) m/z $[M - H]^-$ calcd for $C_7H_4N_8O_{10}$ 358.9972, found 359.0207.

Diammonium 1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-olate) (3).

Compound **2** (0.20 g, 0.55 mmol) was dissolved in acetonitrile (5 mL). To this solution, 1 mL of 28% aqueous ammonia solution was added, and the reaction mixture was stirred at -10 °C for 2 h. The precipitate obtained was filtered, washed with acetonitrile (2 x 2 mL) and dried in air to afford **3** as dark yellow colored solid. Yield: 204 mg, 93%. T_{dec} (5 °C min^{-1}): 204 °C (onset). Density: 1.85 g cm^{-3}. ^1H NMR (DMSO-d_6, ppm): 7.25 (s, 8H, NH_4^+), 6.99 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): δ 151.4, 146.7, 133.6, 67.9 ppm. ^{15}N NMR (DMSO-d_6, ppm): -362.3, -202.5, -74.0, -33.3, -25.8. IR (ν, cm^{-1}): 3431, 3125, 1621, 1395, 1357, 1265, 1093, 999, 905, 755, 647. Elemental analysis for $C_7H_{10}N_{10}O_{10}$ (394.22): calcd C 21.33, H 2.56, N 35.53 %. Found: C 21.38, H 2.66, N 35.60 %.

Dihydroxylammonium 1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-olate) (4).

Compound **2** (0.20 g, 0.55 mmol) was dissolved in acetonitrile (5 mL) and a solution of 50% aqueous hydroxylamine (37 mg, 1.11 mmol) in acetonitrile (1 mL) was added, and the reaction mixture was stirred at -10 °C for 2 h. The precipitate obtained was filtered, washed with acetonitrile (2 mL) and dried in air to obtain **4** as dark red colored solid. Yield: 211 mg, 89%. T_{dec} (5 °C min^{-1}): 171 °C (onset). Density: 1.82 g cm^{-3}. ^1H NMR (DMSO-d_6, ppm): 7.22 (s, 8H, NH_3OH), 6.99 (s, 2H, CH_2), $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): δ 151.3, 146.7, 133.7, 67.9 ppm. IR (ν, cm^{-1}): 3428, 3202, 2991, 2680, 1611, 1423, 1386, 1277, 1003, 855, 763, 647. Elemental analysis for $C_7H_{10}N_{10}O_{12}$ (426.22): calcd C 19.73, H 2.37, N 32.86 %. Found: C 19.91, H 2.42, N 32.81 %.

Dihydrazinium 1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-olate) (5).

Compound **2** (0.20 g, 0.55 mmol) was dissolved in acetonitrile (5 mL) and a solution of hydrazine monohydrate (56 mg, 1.11 mmol) in acetonitrile (1 mL) was added, and the reaction mixture was stirred at -10 °C for 2 h. The precipitate obtained was filtered, washed with acetonitrile (2 mL) and dried in air to afford **5** as dark green colored solid. Yield: 228 mg, 97%. T_{dec} (5 °C min^{-1}): 181 °C (onset). Density: 1.87 g cm^{-3}. ^1H NMR (DMSO-d_6, ppm): 6.99 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (DMSO-d_6, ppm): δ 151.3, 146.8, 133.7, 67.9 ppm. IR (ν, cm^{-1}): 3327, 3181, 3072, 2958, 1608, 1408, 1269, 1077, 1009,

967, 913, 792, 761, 647, 600, 527. Elemental analysis for $C_7H_{12}N_{12}O_{10}$ (424.25): calcd C 19.82, H 2.85, N 39.62 %. Found: C 19.75, H 2.96, N 39.52 %.

Di-3,6,7-Triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium 1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-olate) (6).

Compound **2** (0.20 g, 0.55 mmol) was dissolved in acetonitrile (5 mL) and to this solution, a suspension of 7H-[1,2,4]triazolo[4,3-b][1,2,4]triazole-3,6,7-triamine (0.17 g, 1.11 mmol) in acetonitrile (5 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The precipitate obtained was filtered, washed with acetonitrile (2 mL) and dried in air to yield **6** as brown colored solid. Yield: 319 mg, 86%. T_m (5 °C min^{-1}): 195 °C (peak).T_{dec} (5 °C min^{-1}): 216 °C (onset). Density: 1.79 g cm^{-3}. ^{1}H NMR (DMSO-d_6, ppm): 7.74 (s, 4H, N*H*$_2$), 7.09 (s, 4H, N*H*$_2$), 6.97 (s, 2H, C*H*$_2$), 5.75 (s, 4H, N*H*$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm): δ 159.9, 151.4, 147.7, 146.9, 141.5, 133.6, 67.8 ppm. ^{15}N NMR (DMSO-d_6, ppm): -333.0, -330.7, -327.5, -265.0, -205.5, -205.1, -192.9, -176.9, -175.9, -75.0, -34.8, -25.6. IR (ν, cm^{-1}): 3418, 3258, 3165, 3113, 1701, 1648, 1611, 1514, 1402, 1316, 1281, 1054, 973, 845, 758, 643. Elemental analysis for $C_{13}H_{16}N_{24}O_{10}$ (668.43): calcd C 23.36, H 2.41, N 50.29 %. Found: C 23.32, H 2.49, N 50.15 %.

Di-3,4,5-triamino-4H-1,2,4-triazol-1-ium 1,1'-methylenebis(3,5-dinitro-1H-pyrazol-4-olate) (7).

Compound **2** (0.20 g, 0.55 mmol) was dissolved in acetonitrile (5 mL) and to this solution, a suspension of 4H-1,2,4-triazole-3,4,5-triamine (0.13 mg, 1.11 mmol) in acetonitrile (5 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The precipitate obtained was filtered, washed with acetonitrile (2 mL) and dried in air to yield **7** as yellow colored solid. Yield: 317 mg, 98%. T_{dec} (5 °C min^{-1}): 211 °C (onset). Density: 1.75 g cm^{-3}. ^{1}H NMR (DMSO-d_6, ppm): 6.99 (s, 8H, N*H*$_2$), 6.97 (s, 2H, C*H*$_2$), 5.60 (s, 4H, N*H*$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, ppm): δ 151.3, 150.1, 147.0, 133.6, 67.9 ppm. IR (ν, cm^{-1}): 3420, 2903, 2513, 2130, 1696, 1667, 1411, 1258, 1010, 874, 797, 689, 647. Elemental analysis for $C_{11}H_{16}N_{20}O_{10}$ (588.38): calcd C 22.46, H 2.74, N 47.61 %. Found: C 22.37, H 2.79, N 47.52 %.

3. Crystal Structure Data

Table S1: Crystal data and structure refinement for Compound 2.

Identification code	dhhfhdhh_0m_a
Empirical formula	$C_7H_6N_8O_{11}$
Formula weight	378.20
Temperature/K	305(2)
Crystal system	monoclinic
Space group	$P2_1$

a/Å	9.9010(6)
b/Å	7.1701(4)
c/Å	10.0087(6)
α/°	90
β/°	109.195(2)
γ/°	90
Volume/Å^3	671.03(7)
Z	2
ρ_{calc}g/cm^3	1.872
μ/mm^{-1}	0.178
F(000)	384.0
Crystal size/mm^3	0.245 × 0.140 × 0.095
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.31 to 53.006
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 8, -12 ≤ l ≤ 12
Reflections collected	20668
Independent reflections	2788 [R_{int} = 0.0467, R_{sigma} = 0.0237]
Data/restraints/parameters	2788/1/245
Goodness-of-fit on F^2	0.794
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0925
Final R indexes [all data]	R_1 = 0.0331, wR_2 = 0.0963
Largest diff. peak/hole / e Å^{-3}	0.16/-0.20
Flack parameter	0.2(5)
CCDC	2293510

Table S2: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Compound 2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	1277(2)	-1409(3)	5434(3)	53.5(5)
O2	-124(3)	-221(4)	3499(3)	65.9(7)
O3	571(2)	3390(3)	2715.4(19)	47.1(5)
O4	2224(3)	6735(3)	3275(2)	51.2(5)
O5	4169(2)	6759(3)	5099(2)	53.0(5)
O6	1020(3)	5281(4)	9745(3)	56.3(6)
O7	1597(3)	8126(3)	10301(2)	49.7(5)
O8	3638.9(19)	9900(3)	9215(2)	38.6(4)
O9	5796(2)	9722(3)	7924(3)	57.6(6)
O10	6610(2)	6948(4)	7805(3)	53.4(6)
N1	913(2)	-151(4)	4571(2)	41.2(5)

N2	3043(3)	6034(3)	4362(2)	38.1(5)
N3	2807(2)	1701(3)	6036(2)	33.4(4)
N4	3380(2)	3366(3)	5993.4(19)	30.9(4)
N5	4099(2)	5418(3)	8000(2)	29.8(4)
N6	3038(2)	5030(3)	8498(2)	32.4(4)
N7	1707(2)	6673(3)	9731(2)	36.0(5)
N8	5702(2)	8021(4)	7939(2)	36.6(5)
C1	1738(3)	1548(4)	4833(2)	34.4(5)
C2	1557(3)	3135(4)	3966(2)	34.9(5)
C3	2651(2)	4283(4)	4757(2)	33.2(5)
C4	4559(2)	3933(4)	7238(2)	33.3(5)
C5	2754(2)	6629(4)	9007(2)	30.2(5)
C6	3596(2)	8132(4)	8833(2)	29.4(5)
C7	4471(2)	7258(3)	8191(2)	29.5(5)
O11	1078(3)	1436(3)	8682(3)	55.4(6)

Table S3: Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	54.6(12)	44.2(12)	62.3(12)	6.5(10)	20(1)	-7.9(10)
O2	54.0(13)	51.5(15)	70.7(16)	-6.1(11)	-8.5(11)	-10.7(11)
O3	47.6(10)	47.6(13)	36.6(9)	2.7(9)	1.1(8)	0.4(10)
O4	64.9(13)	45.3(11)	40.9(10)	10.1(9)	14.0(9)	6.6(11)
O5	56.4(12)	52.1(13)	48.3(11)	2.5(10)	14.2(9)	-16.3(11)
O6	58.0(12)	54.1(13)	71.7(15)	-11.1(12)	41.4(11)	-19.8(11)
O7	70.7(13)	38.4(11)	52.0(11)	1.0(9)	36.5(10)	7.8(10)
O8	38.9(9)	29.2(9)	45.9(10)	-6.9(7)	11.5(8)	-2.1(8)
O9	50.6(12)	39.3(12)	85.3(16)	9.0(11)	25.5(11)	-9.2(10)
O10	37.1(10)	52.1(13)	77.8(15)	-2.9(11)	28.1(10)	-2.8(10)
N1	34(1)	40.3(13)	48.5(12)	-6.9(10)	12.6(9)	-3.2(9)
N2	48.2(12)	36.1(12)	34.4(10)	-0.5(8)	19.5(10)	1.6(9)
N3	34.3(10)	30.9(11)	35.9(10)	-1.1(9)	12.7(8)	2.7(9)
N4	32.4(9)	29.6(10)	30.4(9)	-2.3(8)	10.0(7)	1.5(8)
N5	29.1(9)	29.1(10)	30.9(9)	-1.3(8)	9.5(7)	-0.4(8)
N6	33.7(10)	32.5(11)	32.1(10)	0.0(8)	12.5(7)	-3.9(9)
N7	36.3(10)	38.9(11)	34.9(10)	4.2(9)	14.5(8)	2.4(10)
N8	31.1(10)	40.7(12)	37.1(10)	2.2(9)	9.8(8)	-4.8(9)
C1	32.4(11)	34.6(12)	36.5(11)	-3.9(10)	11.9(9)	0.6(10)
C2	33.9(11)	38.9(13)	31.3(11)	-2.7(10)	9.9(9)	3.8(11)
C3	34.6(11)	36.0(12)	31.2(10)	-1.3(9)	14.0(9)	3.1(10)
C4	31.6(11)	32.2(13)	33.3(11)	-3.7(10)	6.7(9)	4.7(10)

C5	29.5(10)	33.2(12)	27.7(10)	0.7(9)	9.1(8)	-0.8(9)
C6	28.6(10)	31.1(11)	26(1)	1.5(9)	5.5(8)	-1.7(9)
C7	29.6(10)	29.3(11)	27.9(10)	0.8(9)	7.2(8)	-2.8(9)
O11	64.5(14)	33.4(12)	77.5(15)	3.1(11)	35.7(13)	4.2(10)

Table S4: Bond Lengths for Compound 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.219(3)	N4	C3	1.378(3)
O3	C2	1.322(3)	N4	C4	1.457(3)
O4	N2	1.230(3)	N5	C4	1.467(3)
O5	N2	1.231(3)	N5	C7	1.366(3)
O7	N7	1.210(3)	N6	N5	1.332(3)
O8	C6	1.321(3)	N6	C5	1.322(4)
O9	N8	1.224(4)	N7	O6	1.211(3)
O10	N8	1.224(3)	N7	C5	1.446(3)
N1	O2	1.218(3)	N8	C7	1.431(3)
N1	C1	1.442(4)	C2	C1	1.406(4)
N2	C3	1.408(3)	C3	C2	1.384(4)
N3	C1	1.321(3)	C5	C6	1.408(4)
N4	N3	1.328(3)	C7	C6	1.387(4)

Table S5: Crystal data and structure refinement for Compound 7.

Identification code	DK_PB_PSTOT_0249
Empirical formula	$C_{11}H_{16}N_{20}O_{10}$
Formula weight	588.379
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	32.034(3)
b/Å	5.3339(5)
c/Å	29.714(3)
α/°	90
β/°	121.034(3)
γ/°	90
Volume/Å^3	4350.3(7)
Z	8
ρ_{calc}g/cm^3	1.797
μ/mm^{-1}	0.157
F(000)	2418.3
Crystal size/mm^3	0.212 × 0.181 × 0.163
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	2.96 to 52.16
Index ranges	$-39 \leq h \leq 39$, $-6 \leq k \leq 6$, $-36 \leq l \leq 36$
Reflections collected	45335
Independent reflections	4306 [R_{int} = 0.0713, R_{sigma} = 0.0393]
Data/restraints/parameters	4306/5/415
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.0958
Final R indexes [all data]	R_1 = 0.0579, wR_2 = 0.1082
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.40
CCDC	2293511

Table S6: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 7. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	5593.8(5)	9080(3)	7513.5(6)	26.3(4)
O2	5528.1(6)	6837(3)	8088.4(6)	31.5(4)
O3	6154.9(5)	2600(3)	8521.8(5)	23.0(3)
O4	6895.1(6)	-745(3)	8601.2(6)	29.0(4)
O5	7274.3(7)	489(4)	8210.4(9)	62.0(7)
O6	7133.6(6)	11115(3)	6555.2(7)	41.0(5)
O7	6545.4(6)	10492(3)	5755.7(6)	33.6(4)
O8	5896.9(5)	6397(3)	5562.7(5)	23.5(3)
O9	5567.4(5)	2179(3)	5895.8(6)	27.0(4)
O10	5972.7(5)	1356(3)	6739.6(6)	28.0(4)
N1	5704.8(6)	7258(3)	7807.9(7)	22.8(4)
N2	6939.5(7)	672(4)	8295.0(7)	28.4(5)
N3	6251.8(6)	5899(3)	7540.7(7)	21.4(4)
N4	6580.7(6)	4116(3)	7677.2(7)	21.2(4)
N5	6618.4(6)	5188(3)	6915.2(7)	20.1(4)
N6	6852.9(6)	7173(3)	6884.4(7)	21.7(4)
N7	6775.2(6)	9929(4)	6223.8(7)	25.3(4)
N8	5907.0(6)	2601(3)	6352.6(7)	21.4(4)
C1	6057.0(7)	5533(4)	7841.2(8)	18.7(4)
C2	6252.7(7)	3420(4)	8188.5(8)	18.9(4)
C3	6597.2(7)	2578(4)	8058.2(8)	20.1(5)
C4	6851.2(8)	3811(5)	7401.9(9)	23.6(5)
C5	6609.3(7)	7833(4)	6381.8(8)	20.4(5)
C6	6194.3(7)	6270(4)	6046.5(8)	19.5(4)
C7	6223.0(7)	4548(4)	6427.2(8)	19.8(4)

N9	6884.4(6)	-2529(3)	10062.7(6)	18.7(4)
N10	7052.0(6)	766(3)	9731.0(7)	22.6(4)
N11	6621.9(6)	-414(3)	9357.0(7)	22.3(4)
N12	6918.5(7)	-4482(4)	10392.7(8)	23.9(4)
N13	7587.2(7)	-55(4)	10639.1(7)	24.1(4)
N14	6147.5(7)	-3913(4)	9309.1(8)	24.5(4)
C8	6523.7(7)	-2384(4)	9549.5(8)	19.3(4)
C9	7197.7(7)	-541(4)	10156.2(8)	19.2(4)
N15	5114.5(6)	11266(3)	3986.8(6)	18.6(4)
N16	5633.7(6)	9706(4)	4732.7(7)	23.2(4)
N17	5642.9(6)	8176(4)	4357.4(7)	24.7(4)
N18	4758.9(7)	12916(4)	3625.8(7)	22.2(4)
N19	5199.2(7)	8275(4)	3425.6(7)	23.7(4)
N20	5200.1(7)	13336(4)	4732.4(8)	25.8(4)
C10	5326.0(7)	9182(4)	3909.6(8)	20.1(5)
C11	5314.5(7)	11541(4)	4511.3(8)	20.0(5)

Table S7: Anisotropic Displacement Parameters ($Å^2×10^3$) for Compound 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	28.7(8)	22.4(8)	20.9(8)	5.5(7)	7.9(7)	6.8(7)
O2	34.7(9)	36(1)	31.8(9)	10.1(8)	22.8(8)	8.1(8)
O3	23.9(7)	26.4(8)	19.8(8)	1.9(6)	12.0(6)	6.8(7)
O4	33.4(9)	29.0(9)	27.0(9)	8.8(7)	17.3(7)	14.5(7)
O5	49.5(12)	82.3(16)	80.1(15)	44.0(11)	51.9(12)	54.8(13)
O6	33.3(9)	39.4(11)	34.7(10)	-18.2(8)	6.5(8)	3.0(8)
O7	34.5(9)	37.9(10)	24.3(9)	-7.1(8)	12.4(7)	8.1(8)
O8	23.0(7)	25.1(8)	16.4(8)	-2.5(6)	6.0(6)	1.8(6)
O9	23.0(8)	27.9(9)	25.0(8)	-6.3(7)	8.8(7)	-1.9(7)
O10	31.3(8)	25.9(9)	25.9(9)	-2.9(7)	14.1(7)	8.3(7)
N1	22.1(9)	23.4(10)	19.2(9)	2.5(8)	8.1(8)	2.1(8)
N2	25.6(10)	32.6(11)	28.7(11)	8.7(8)	15.1(9)	11.9(9)
N3	17.8(8)	23.5(10)	18.9(9)	1.9(7)	6.6(7)	4.2(8)
N4	16.6(8)	25.9(10)	19.8(9)	3.3(7)	8.4(7)	7.5(8)
N5	15.7(8)	23.4(10)	18.8(9)	-0.4(7)	7.2(7)	4.6(8)
N6	18.4(8)	24.9(10)	21.3(9)	-1.3(7)	9.9(7)	2.1(8)
N7	24.3(9)	25.1(10)	24.5(10)	-2.9(8)	11.2(8)	2.8(8)
N8	20.6(9)	21.1(10)	22.8(10)	0.5(7)	11.3(8)	0.8(8)
C1	18.2(10)	20.1(11)	16.6(10)	1.0(8)	8.2(8)	1.5(9)
C2	16.3(9)	19.8(11)	15.8(10)	-2.9(8)	4.9(8)	-0.6(9)
C3	17.8(10)	21.8(11)	17.3(10)	0.8(8)	6.7(8)	5.4(9)

C4	18.5(10)	31.0(13)	20.9(11)	2.3(9)	10.0(9)	7.5(10)
C5	18.5(10)	23.0(11)	19.4(11)	-1.2(9)	9.6(9)	2.5(9)
C6	17.4(10)	22.1(11)	19.2(11)	1.2(8)	9.6(9)	0.2(9)
C7	16.5(10)	21.2(11)	19.9(11)	0.1(8)	8.1(9)	0.5(9)
N9	20.3(8)	17.6(9)	18.5(9)	0.2(7)	10.1(7)	1.7(7)
N10	20.7(9)	23.5(10)	19.8(9)	-4.1(7)	7.7(8)	1.6(8)
N11	20.1(9)	25.1(10)	16.5(9)	-2.6(8)	5.8(7)	3.9(8)
N12	31.3(10)	19.4(10)	25.4(10)	4.9(8)	17.7(9)	6.7(8)
N13	24.2(10)	24.0(11)	18.9(10)	-1.4(8)	7.3(8)	5.2(8)
N14	25.4(10)	24.5(11)	22.8(10)	-4.5(8)	11.7(8)	-0.9(9)
C8	19.8(10)	18.9(11)	21.0(11)	2.9(8)	11.8(9)	1.5(9)
C9	20(1)	18.8(11)	19.8(11)	1.3(8)	10.9(9)	1.1(9)
N15	17.2(8)	20.0(9)	16.9(9)	1.7(7)	7.6(7)	1.3(7)
N16	23.2(9)	28.0(11)	15.5(9)	4.6(8)	7.9(8)	2.6(8)
N17	28.6(10)	26.2(10)	19.6(9)	7.3(8)	12.5(8)	3.4(8)
N18	20.3(9)	21.3(10)	19.3(10)	2.8(8)	6.1(8)	2.1(8)
N19	25.7(10)	26.4(11)	19.4(10)	8.0(8)	12.0(8)	2.0(8)
N20	22.4(10)	29.7(11)	17.9(10)	2.9(8)	5.0(8)	-4.3(9)
C10	19.9(10)	19.3(11)	22.3(11)	0.3(8)	11.8(9)	0.6(9)
C11	16.2(10)	24.2(12)	18.3(11)	-0.9(8)	8.1(8)	0.5(9)

Table S8: Bond Lengths for Compound 7.

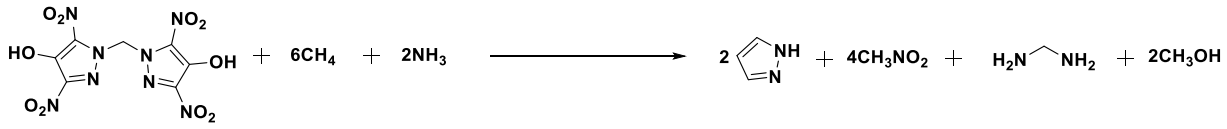
Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.231(2)	N8	C7	1.386(3)
O2	N1	1.246(2)	C1	C2	1.436(3)
O3	C2	1.261(2)	C2	C3	1.418(3)
O4	N2	1.246(2)	C5	C6	1.445(3)
O5	N2	1.225(2)	C6	C7	1.423(3)
O6	N7	1.234(2)	N9	N12	1.396(2)
O7	N7	1.229(2)	N9	C8	1.360(3)
O8	C6	1.251(2)	N9	C9	1.386(3)
O9	N8	1.247(2)	N10	N11	1.397(2)
O10	N8	1.248(2)	N10	C9	1.301(3)
N1	C1	1.419(3)	N11	C8	1.310(3)
N2	C3	1.391(3)	N13	C9	1.355(3)
N3	N4	1.319(2)	N14	C8	1.319(3)
N3	C1	1.341(3)	N15	N18	1.401(2)
N4	C3	1.377(3)	N15	C10	1.381(3)
N4	C4	1.475(3)	N15	C11	1.353(3)
N5	N6	1.328(2)	N16	N17	1.394(3)
N5	C4	1.441(3)	N16	C11	1.320(3)
N5	C7	1.389(3)	N17	C10	1.303(3)
N6	C5	1.327(3)	N19	C10	1.366(3)
N7	C5	1.418(3)	N20	C11	1.316(3)

4. Theoretical Study

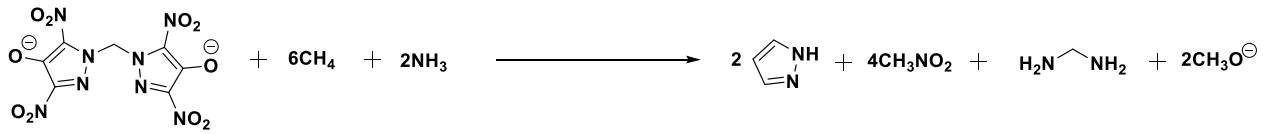
The heats of formation for energetic compounds **2-7** were obtained by using isodesmic reactions. The geometric optimization and frequency analyses of the structures were performed by using B3PW91/6-31G(d,p) level without any symmetry restriction as implemented in Gaussian 09 program.[2,3] All the optimized derivatives are confirmed to be true local energy minima on the potential energy surface without any imaginary frequencies. All calculated gas-phase enthalpies for covalent materials are converted to solid-phase values by subtracting the empirical heat of sublimation obtained based on the molecular surface properties.[4] For salts **3**–**7**, the solid phase heats of formation were calculated based on the Born–Haber energy cycle.[5,6]

Isodesmic Reactions:

Compounds 2



Anion for compounds 3-7



5. NMR Data

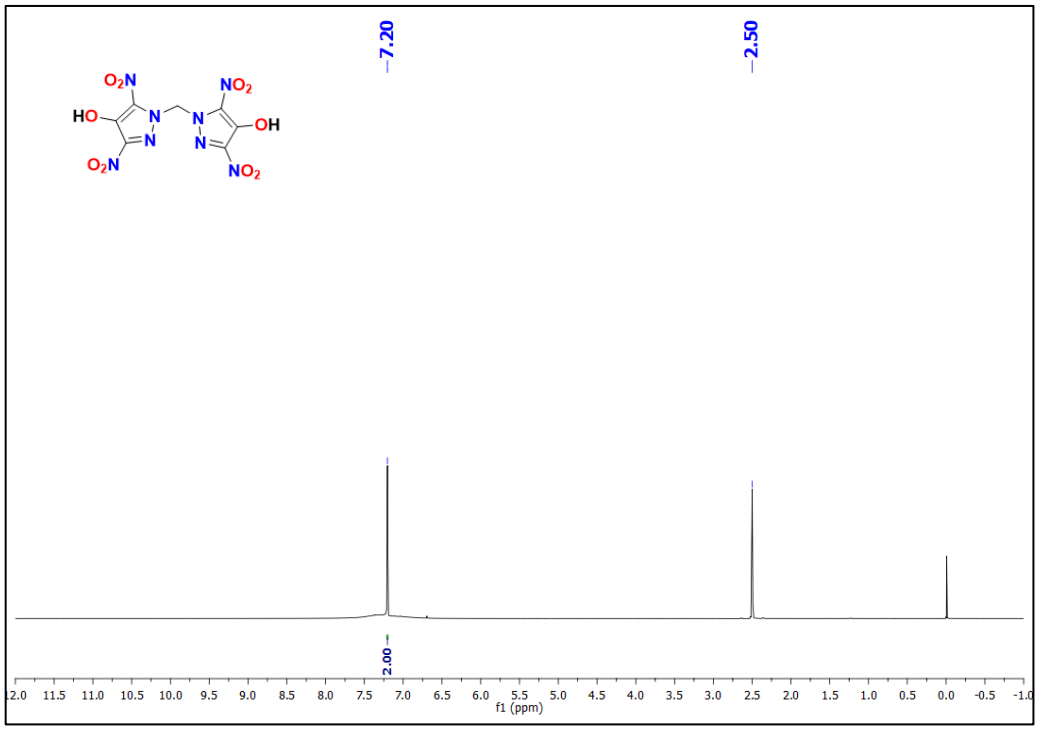


Fig.S1: ^{1}H NMR Spectra of compound **2**

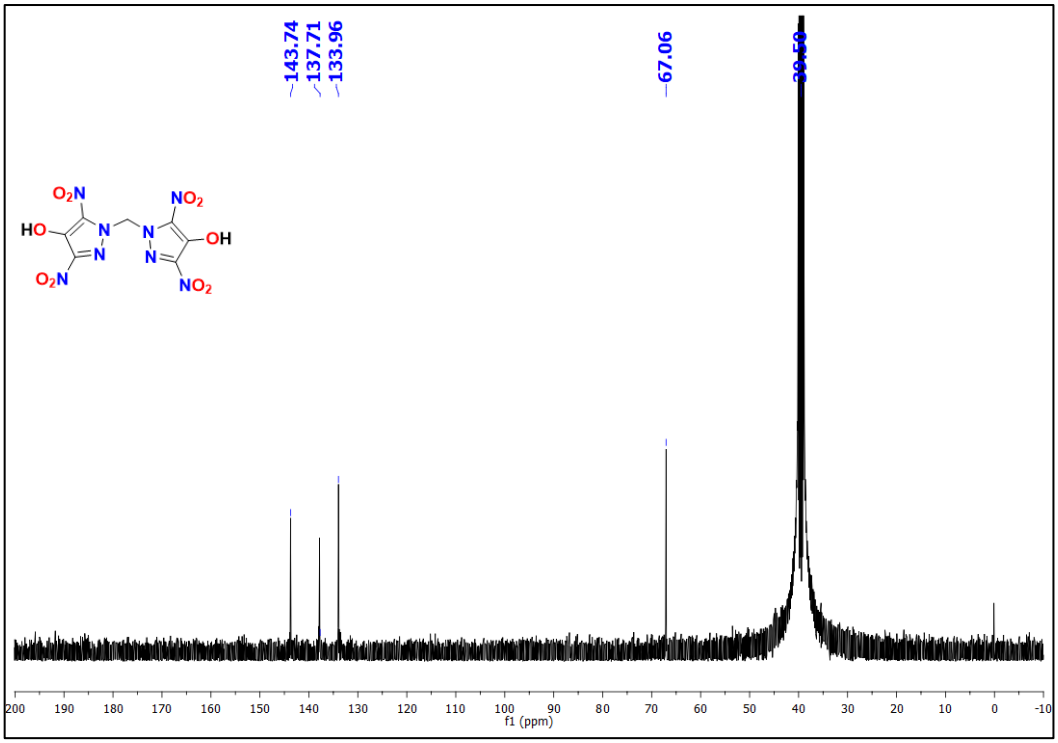


Fig.S2: $^{13}C\{^{1}H\}$ NMR Spectra of compound **2**

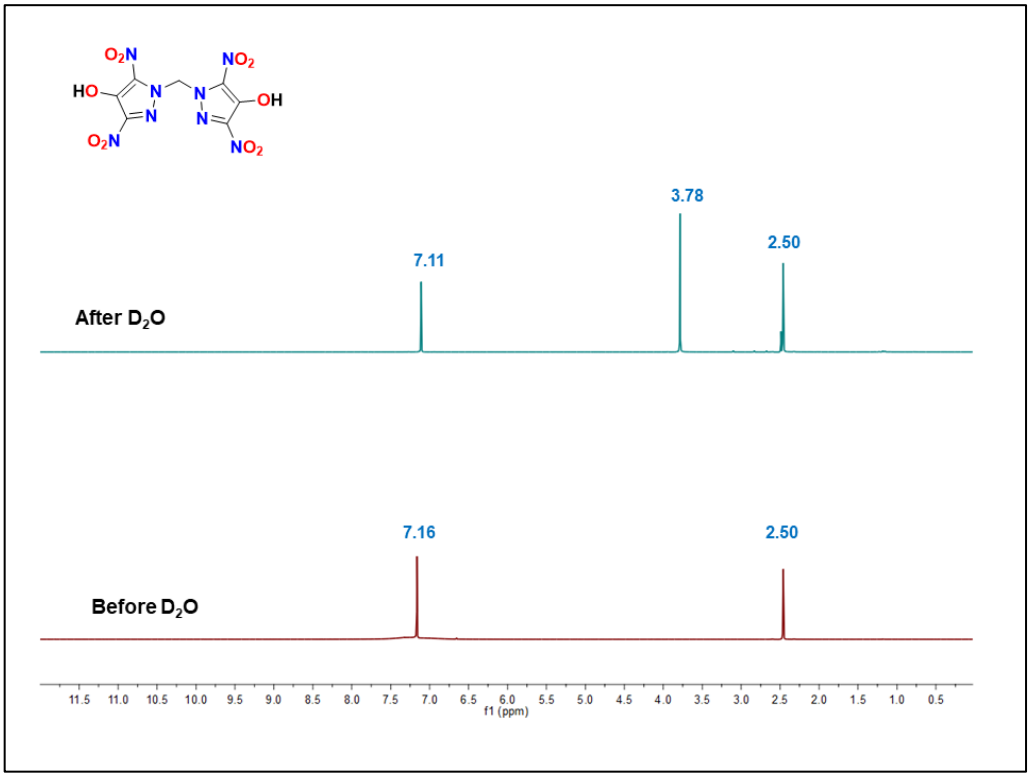


Fig.S3: D_2O Exchange Spectra of compound **2**

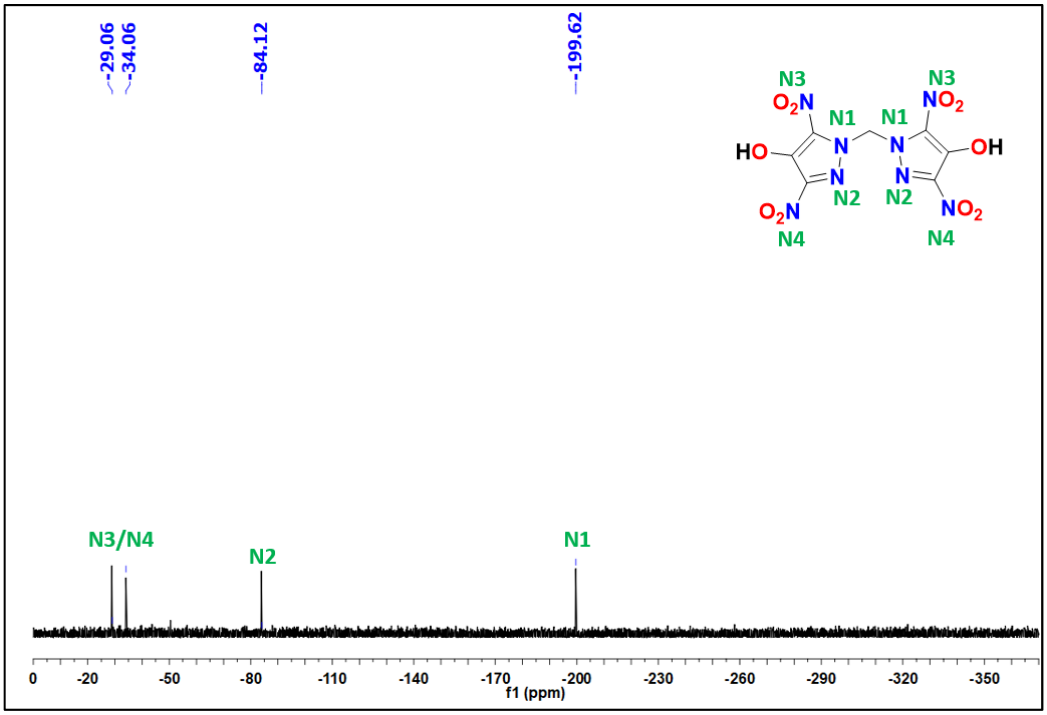


Fig.S4: ^{15}N NMR Spectra of compound **2**

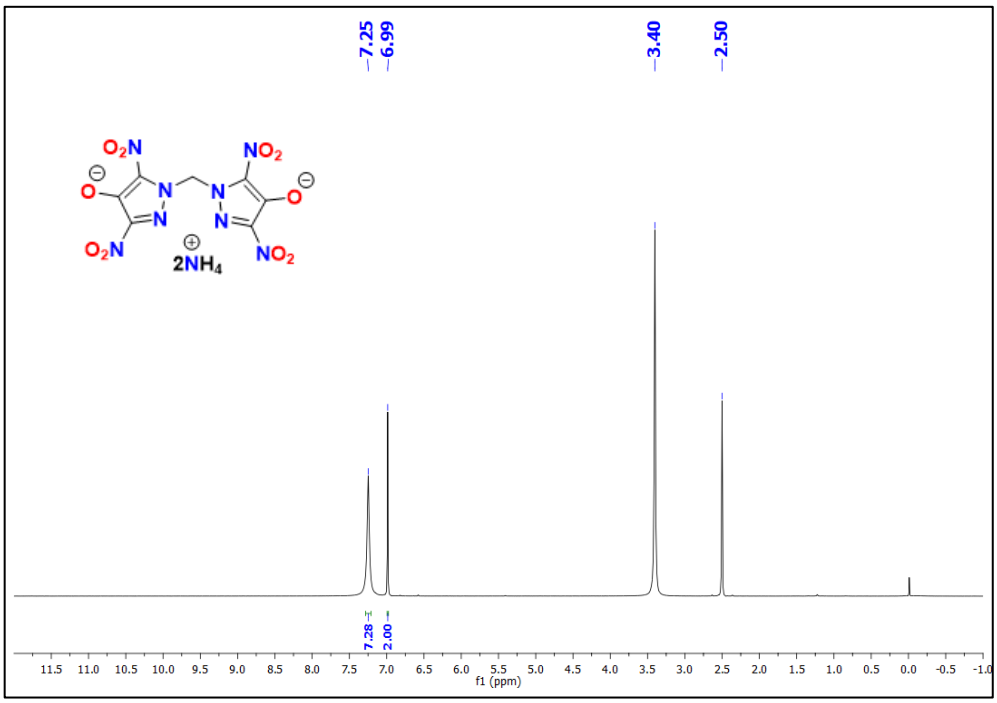


Fig.S5: ^{1}H NMR Spectra of compound **3**

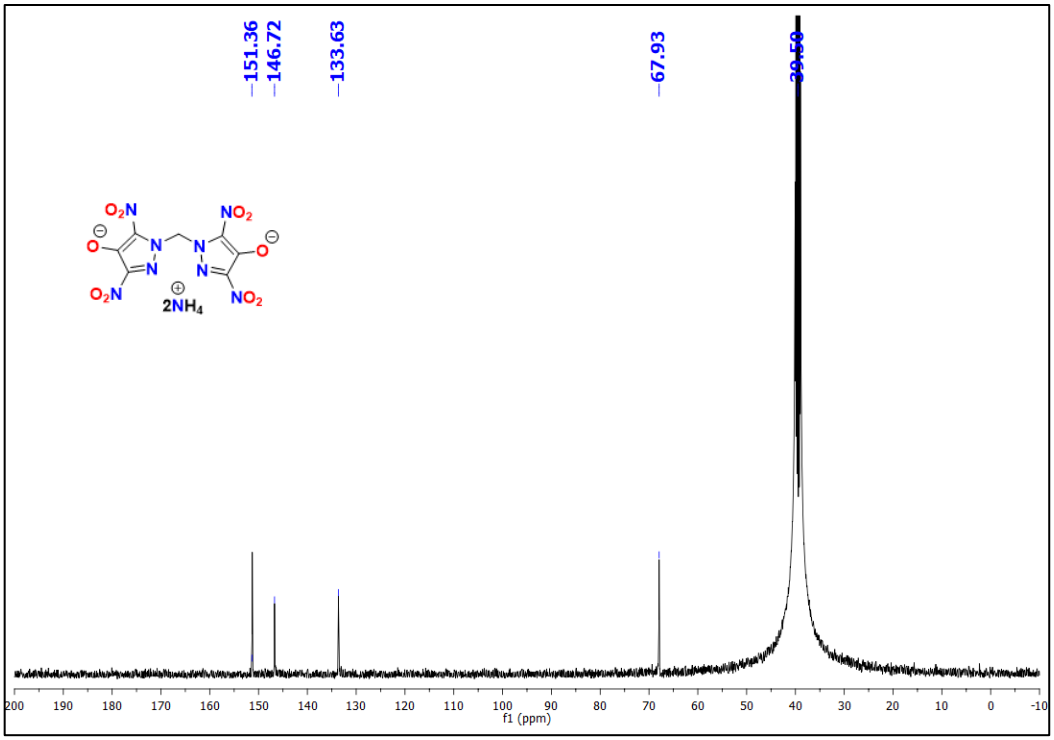


Fig.S6: $^{13}C\{^{1}H\}$ NMR Spectra of compound **3**

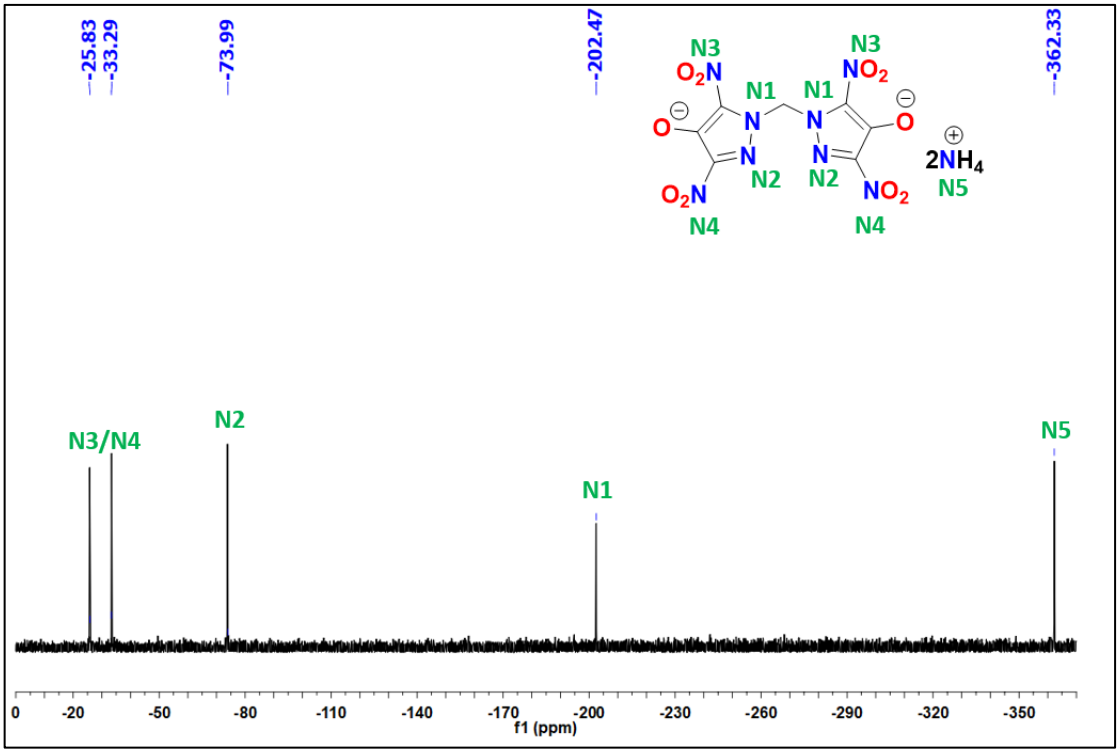


Fig.S7: ^{15}N NMR Spectra of compound **3**

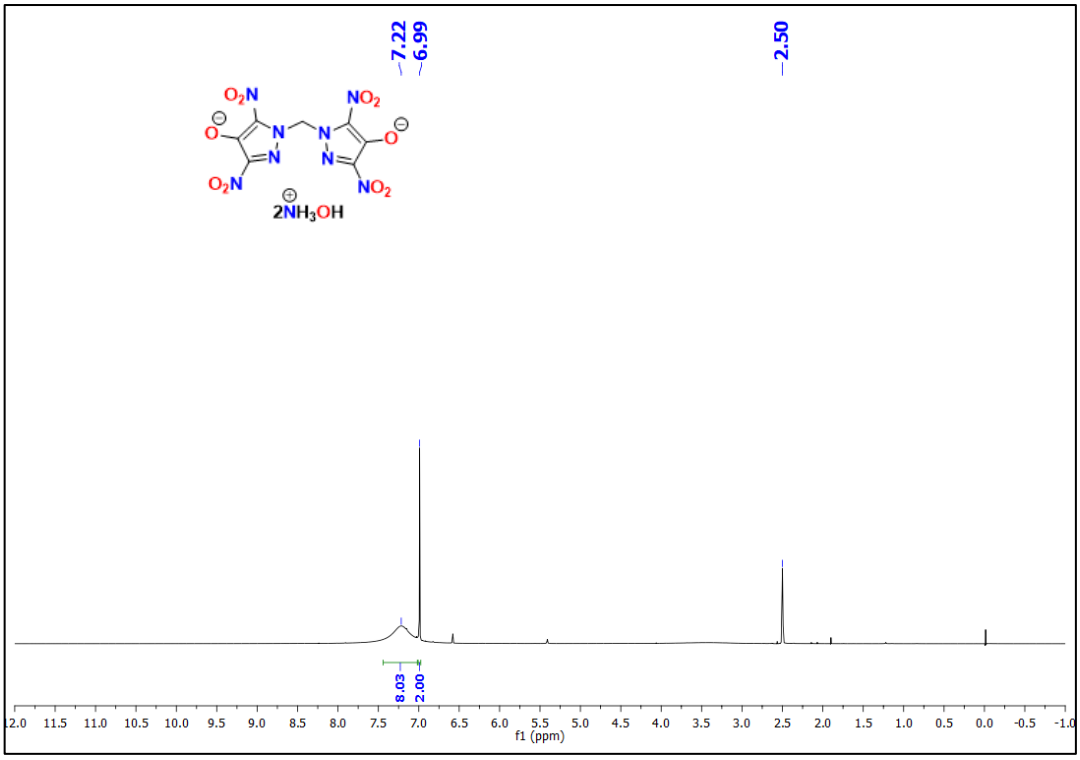


Fig.S8: ^{1}H NMR Spectra of compound **4**

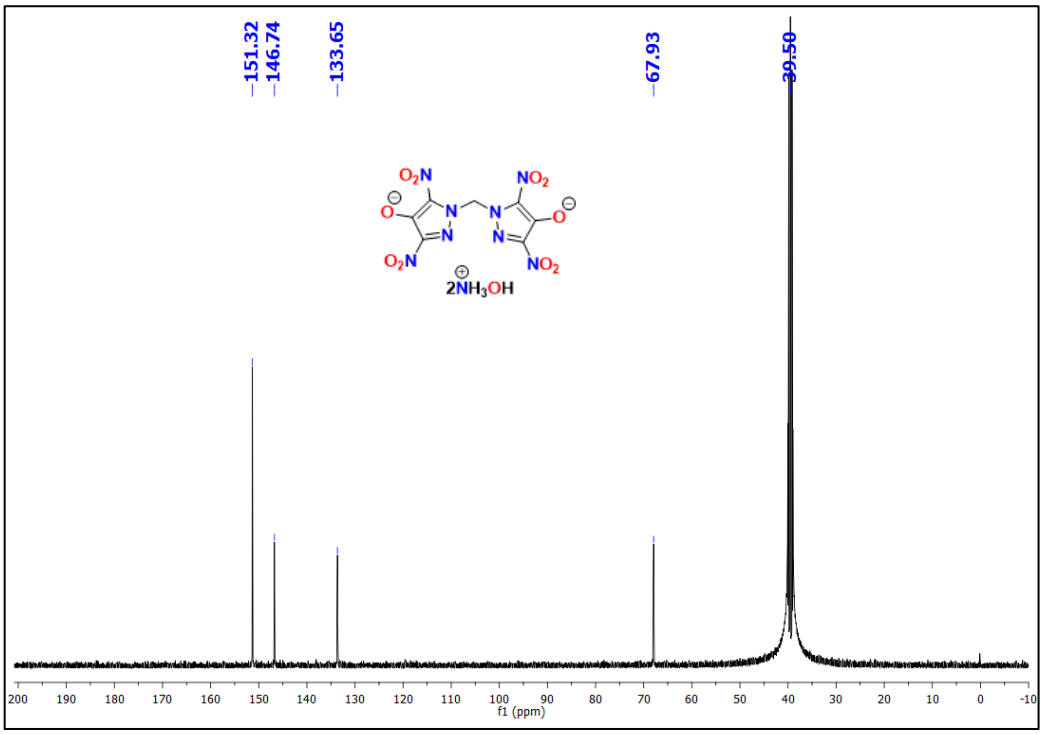


Fig.S9: ^{13}C{^{1}H} NMR Spectra of compound **4**

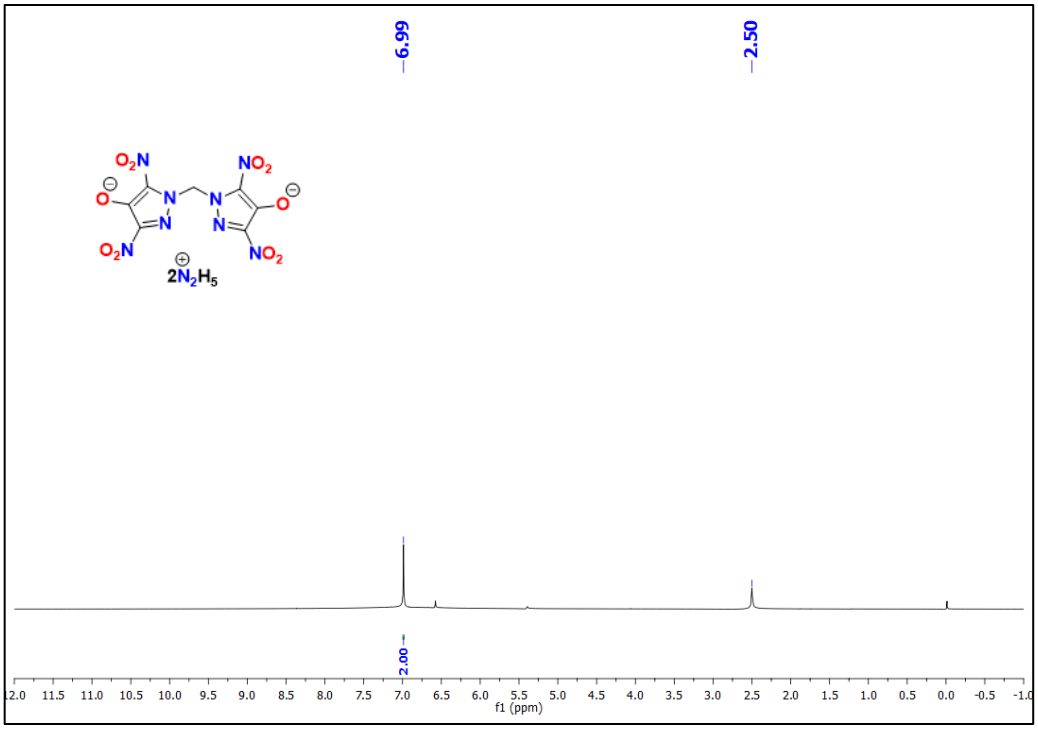


Fig.S10: ^{1}H NMR Spectra of compound **5**

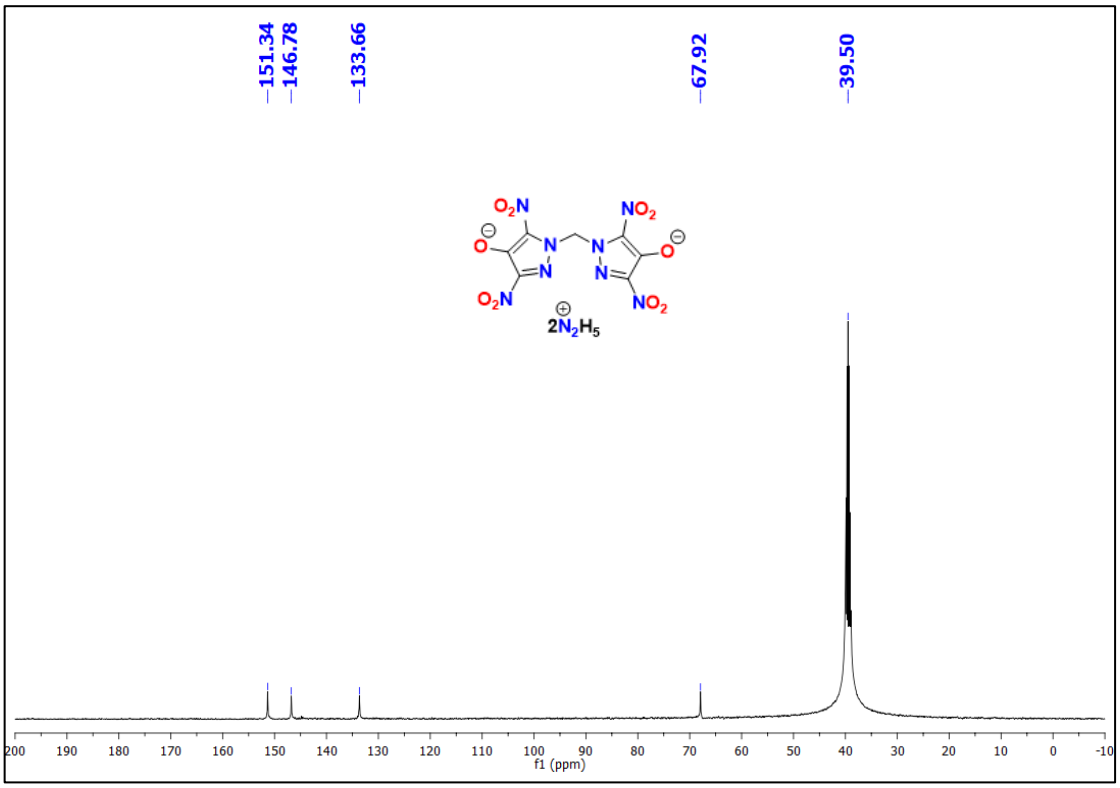


Fig.S11: ^{13}C{^{1}H} NMR Spectra of compound **5**

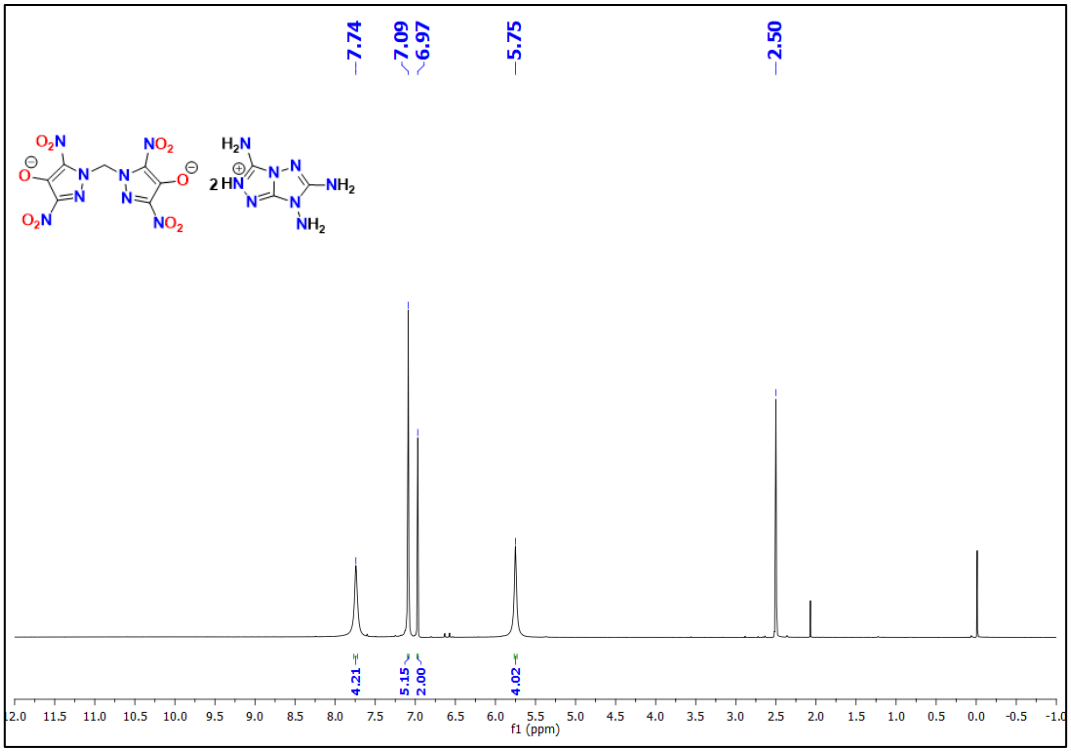


Fig.S12: ^{1}H NMR Spectra of compound **6**

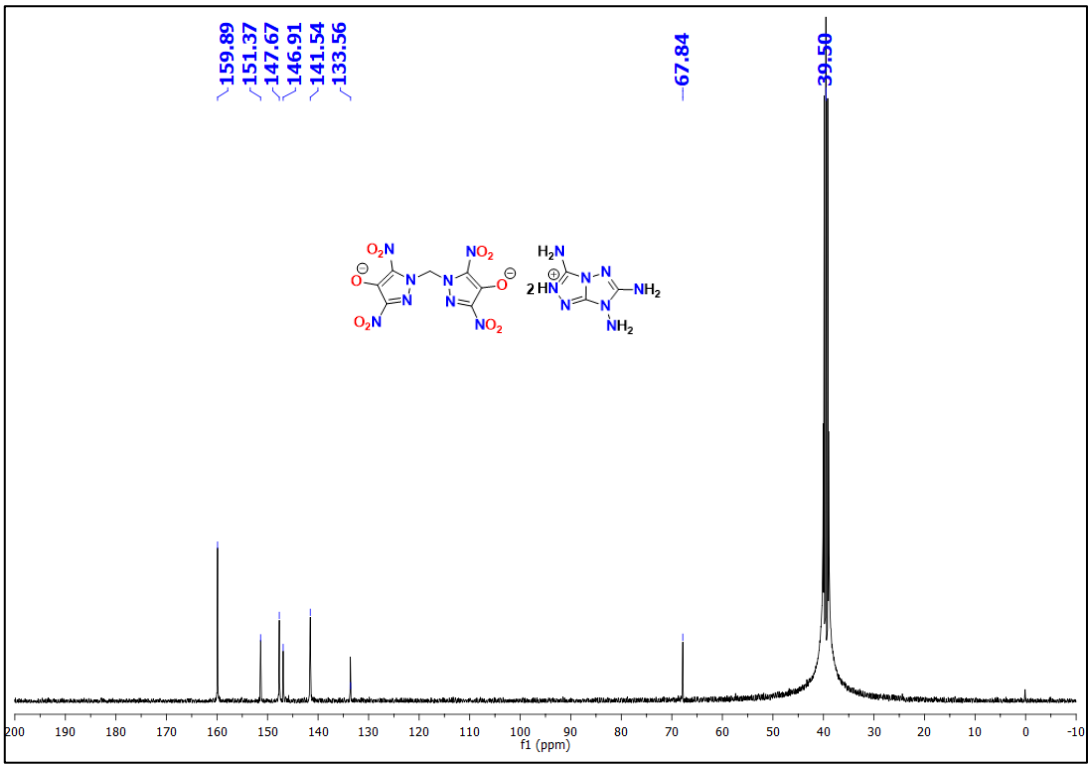


Fig.S13: ^{13}C{^{1}H} NMR Spectra of compound **6**

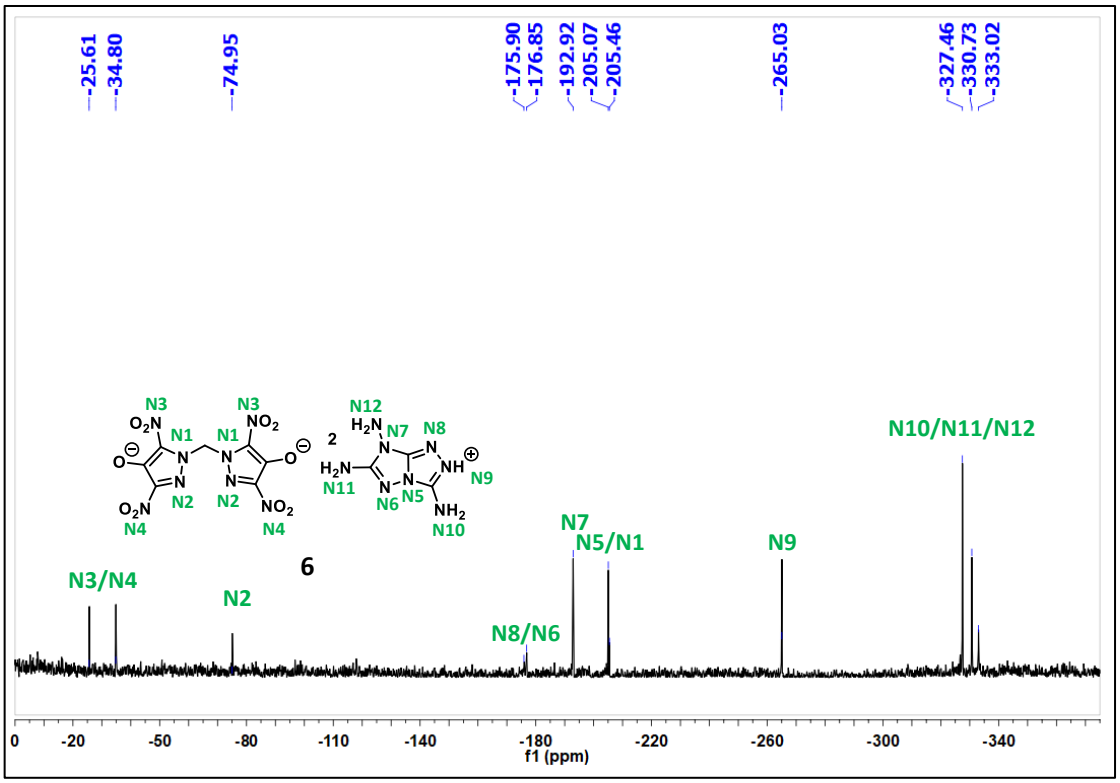


Fig.S14: ^{15}N NMR Spectra of compound **6**

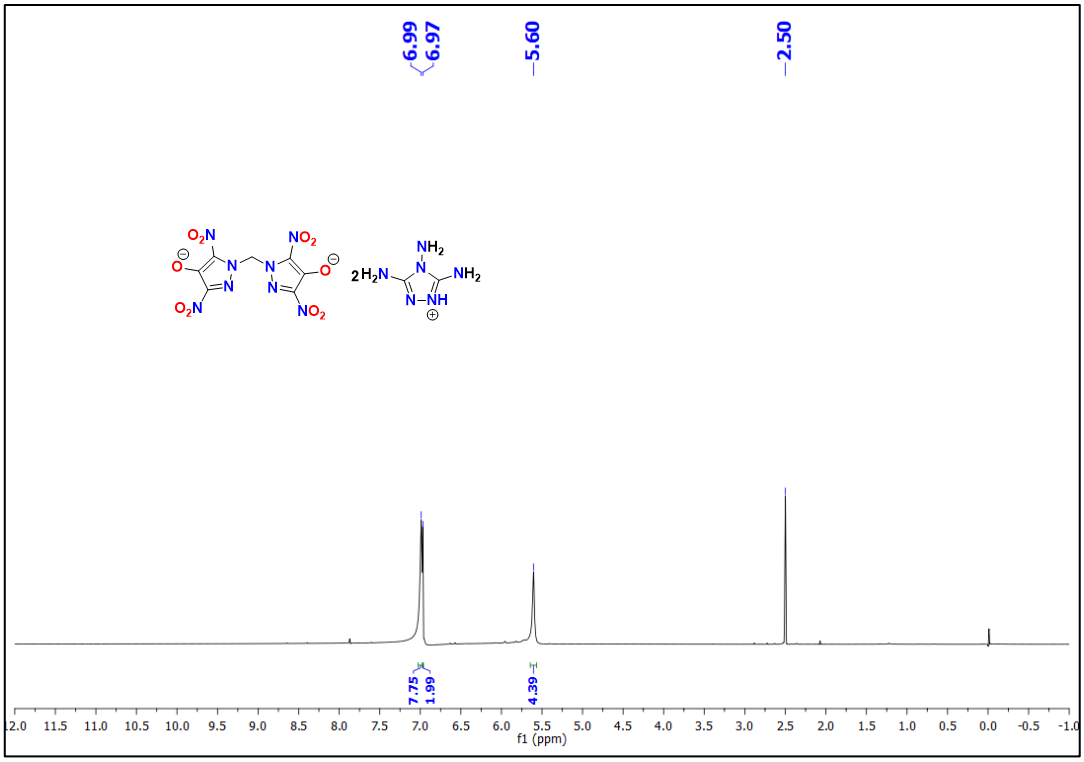


Fig.S15: ^{1}H NMR Spectra of compound **7**

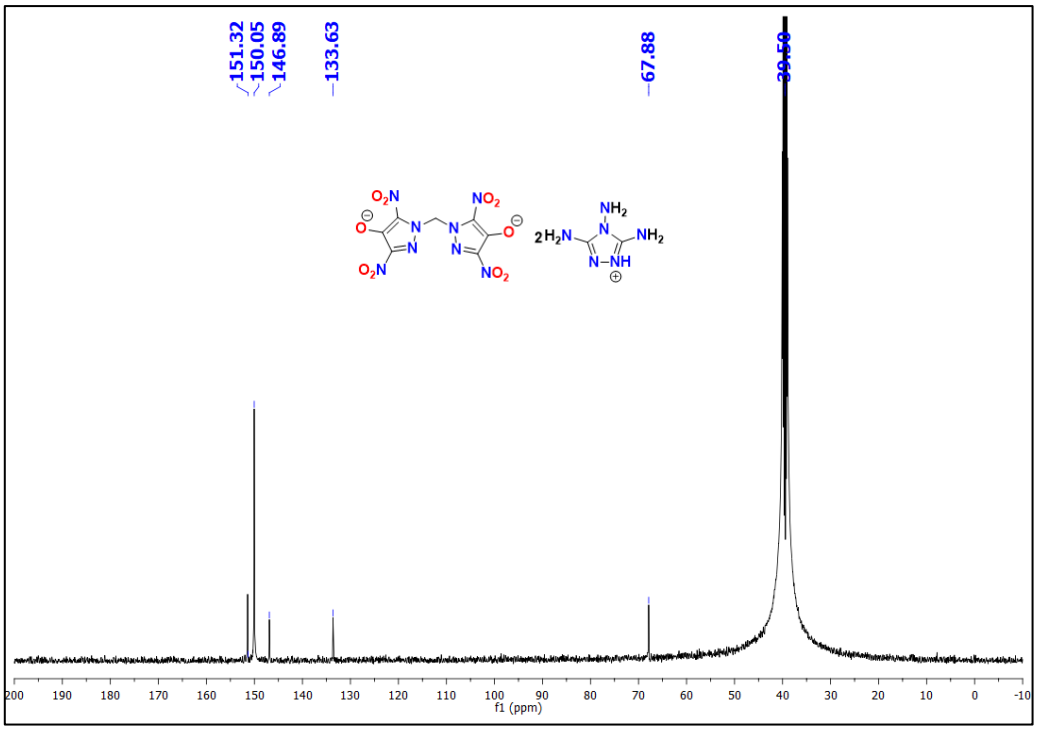


Fig.S16: ^{13}C{^{1}H} NMR Spectra of compound **7**

6. IR Data

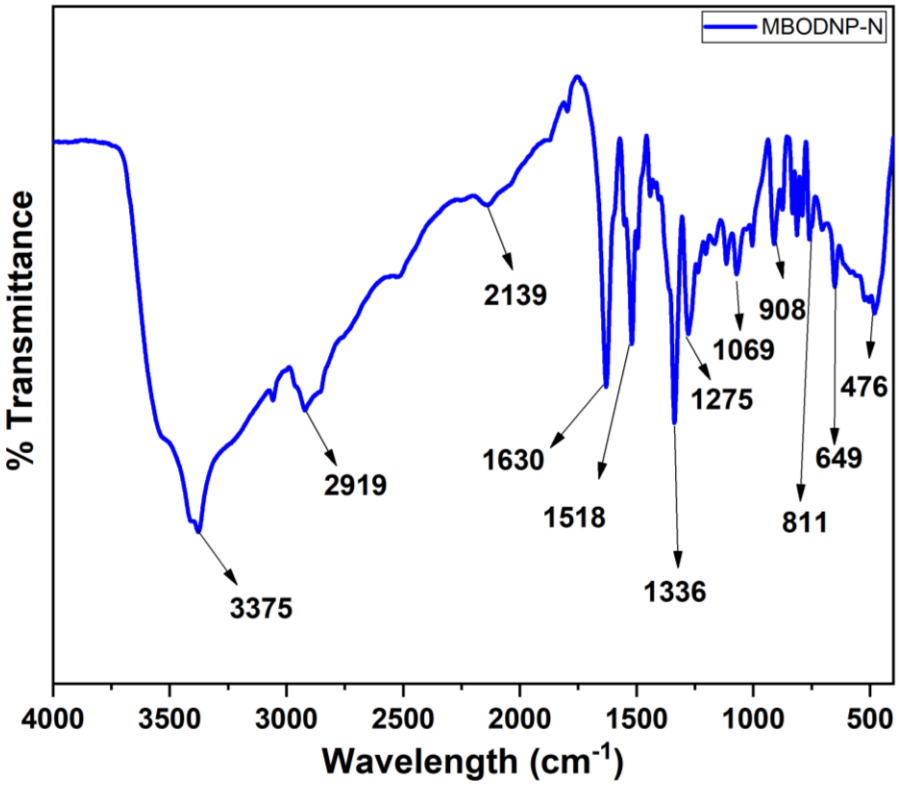


Fig.S17: IR Spectra of compound **2**

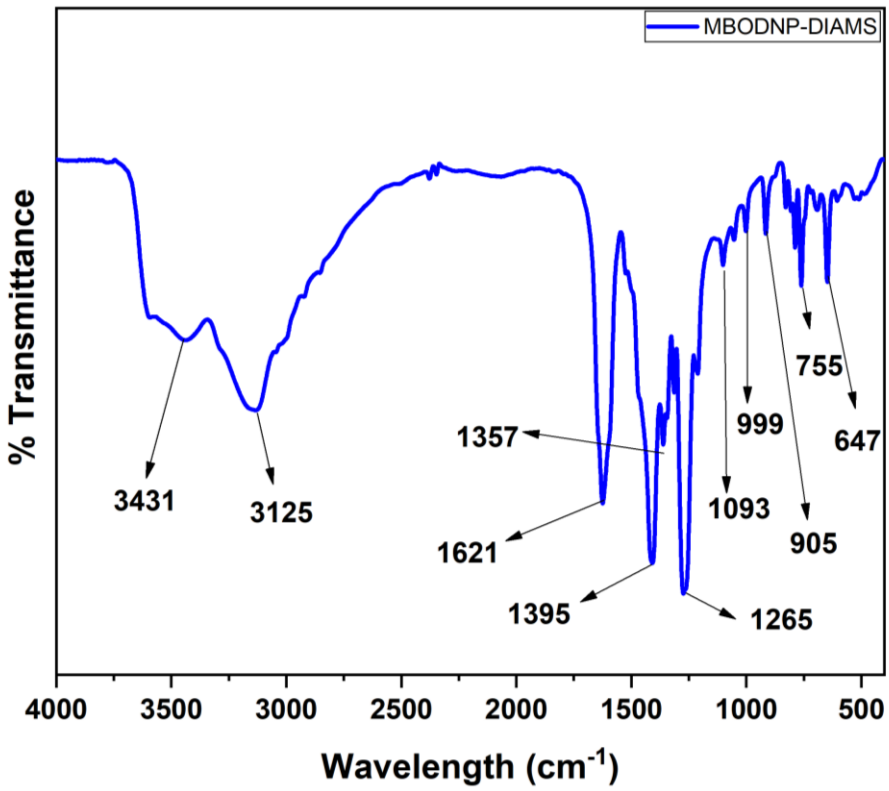


Fig.S18: IR Spectra of compound **3**

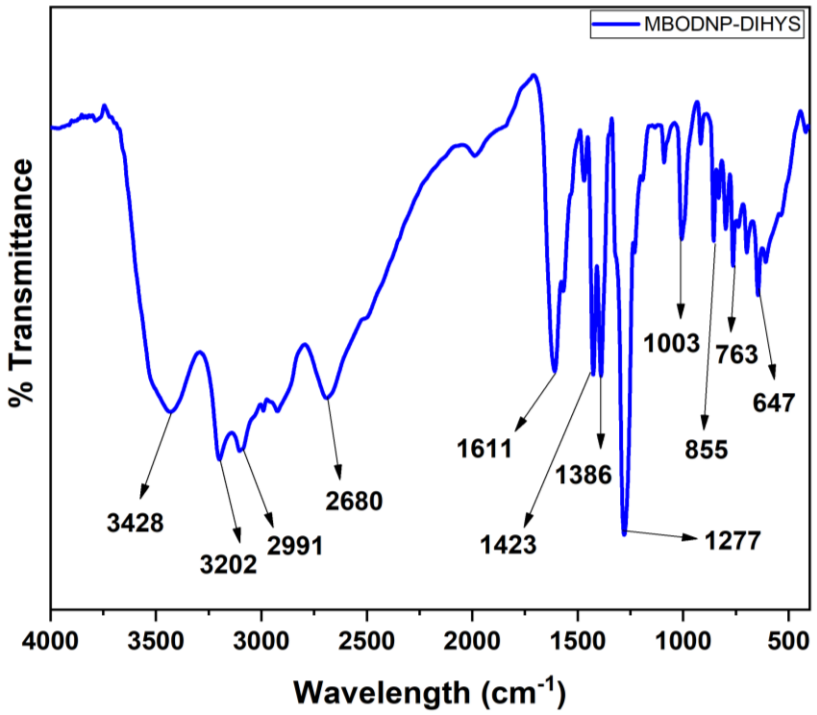


Fig.S19: IR Spectra of compound **4**

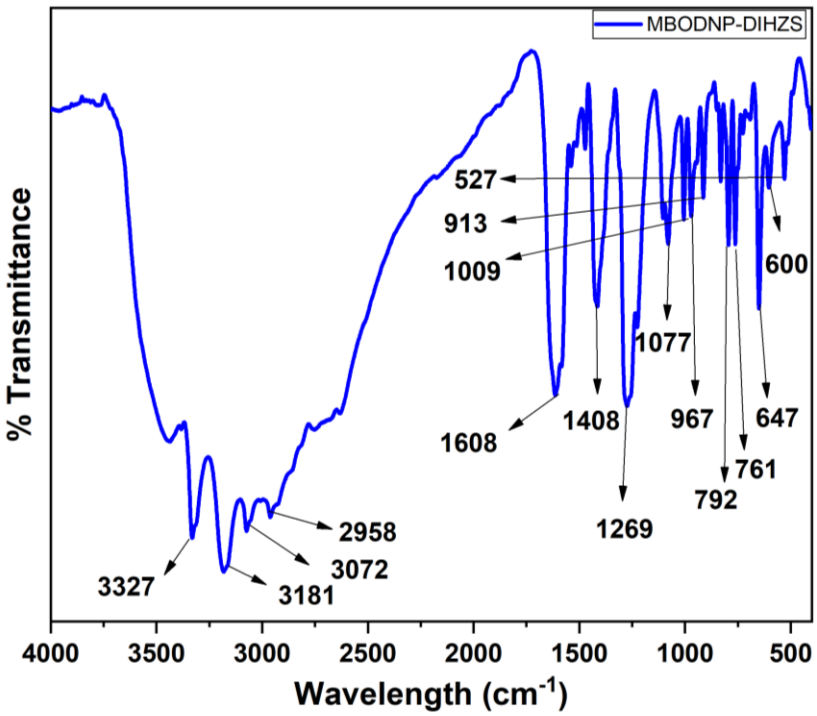


Fig.S20: IR Spectra of compound **5**

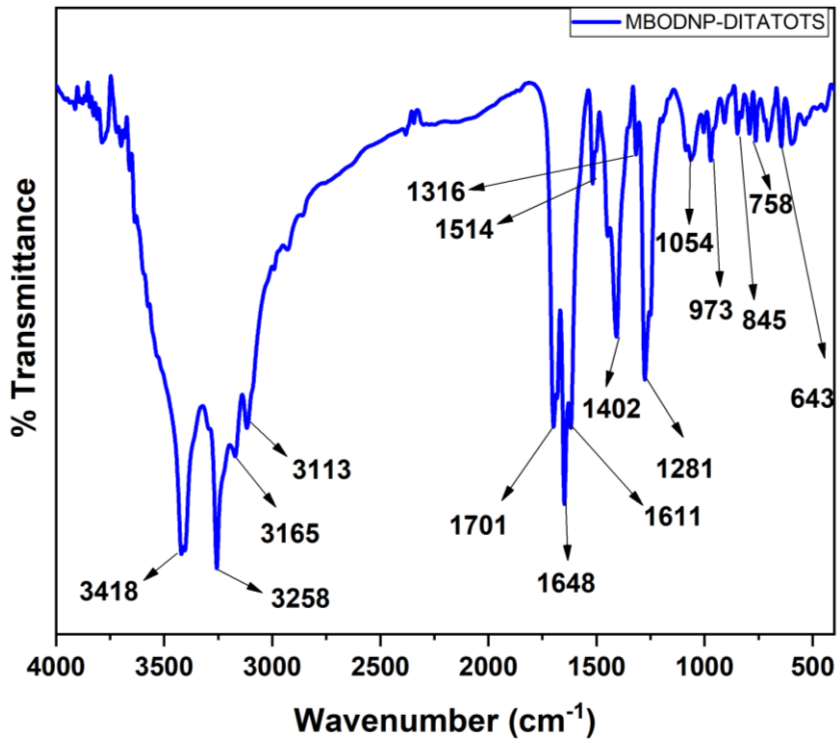


Fig.S21: IR Spectra of compound **6**

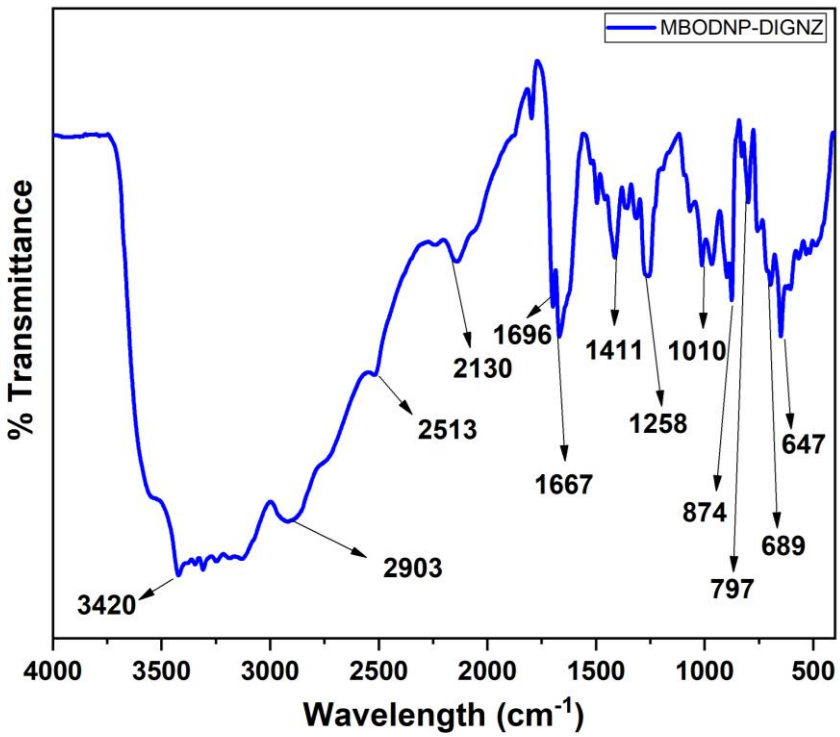


Fig.S22: IR Spectra of compound **7**

7. DSC Data

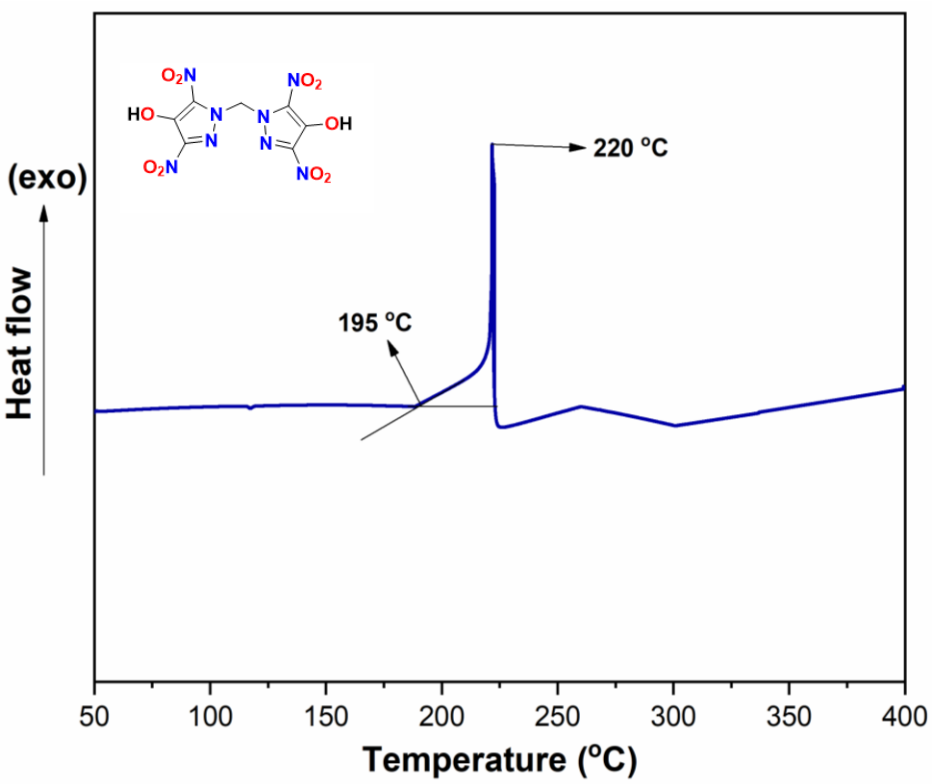


Fig.S23: DSC Spectra of compound **2**

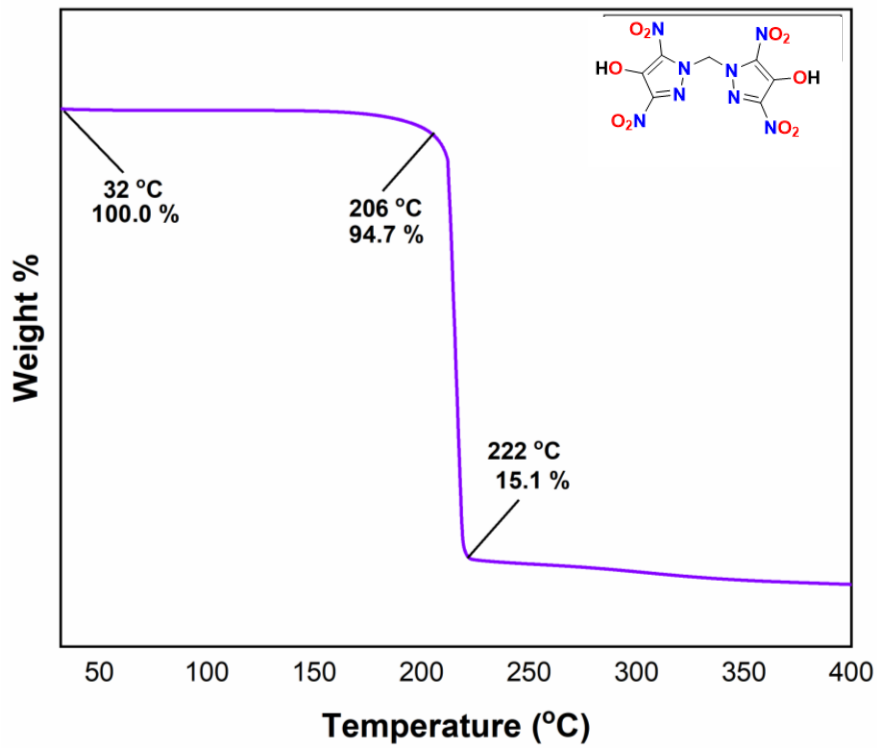


Fig.S24: Thermogravimetric analysis of compound **2**

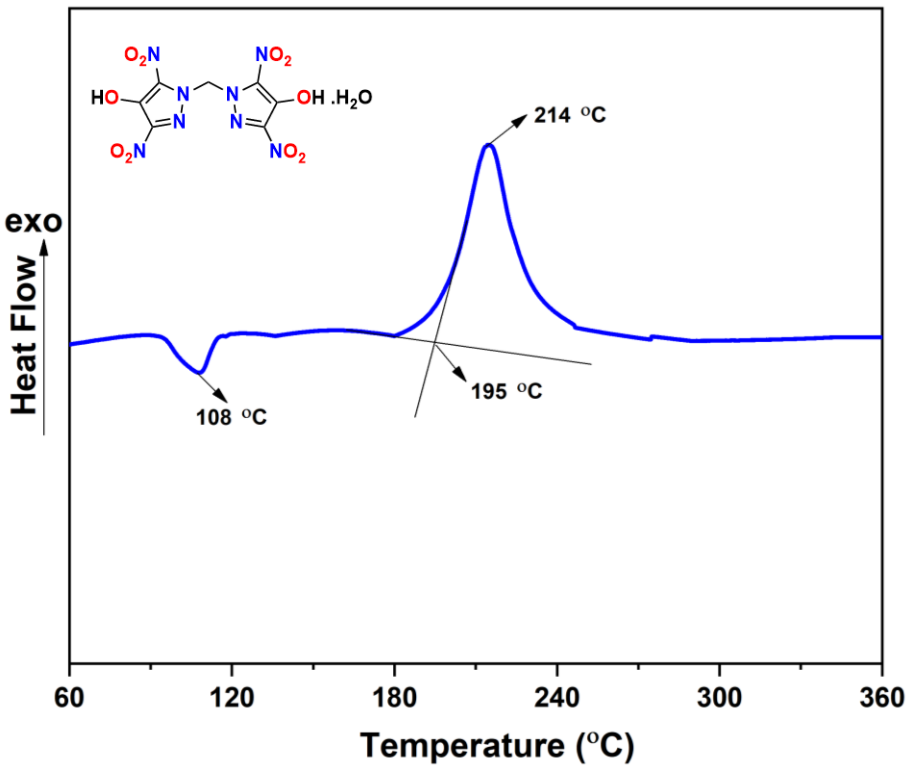


Fig.S25: DSC Spectra of compound **2.H$_2$O**

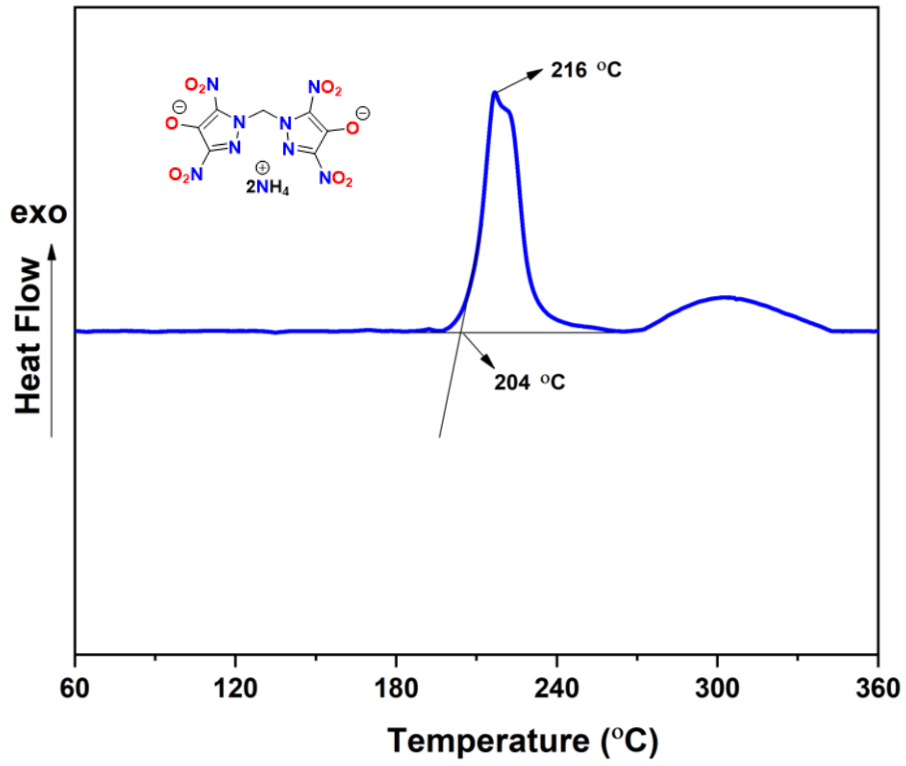


Fig.S26: DSC Spectra of compound **3**

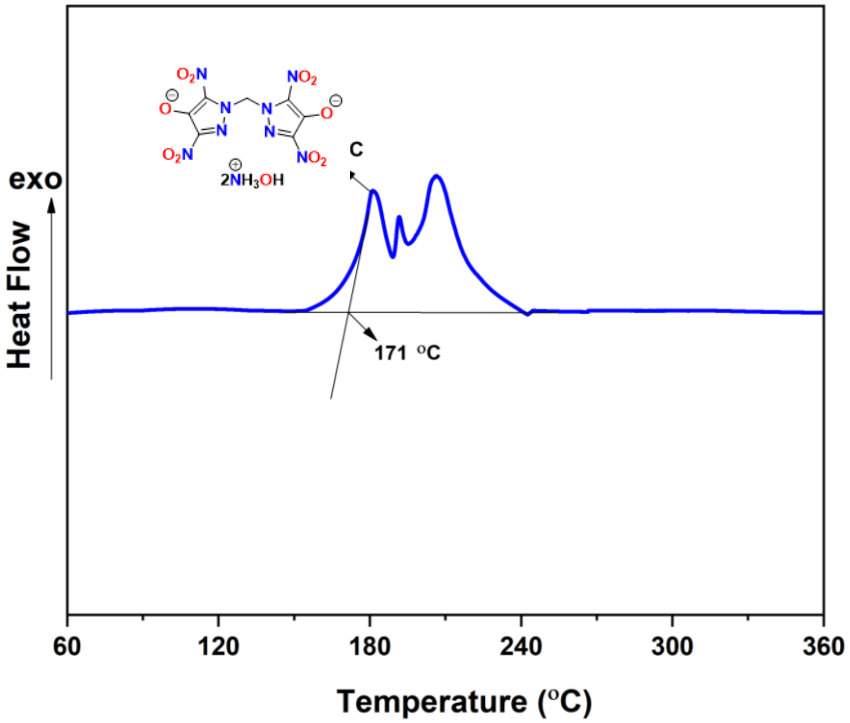


Fig.S27: DSC Spectra of compound **4**

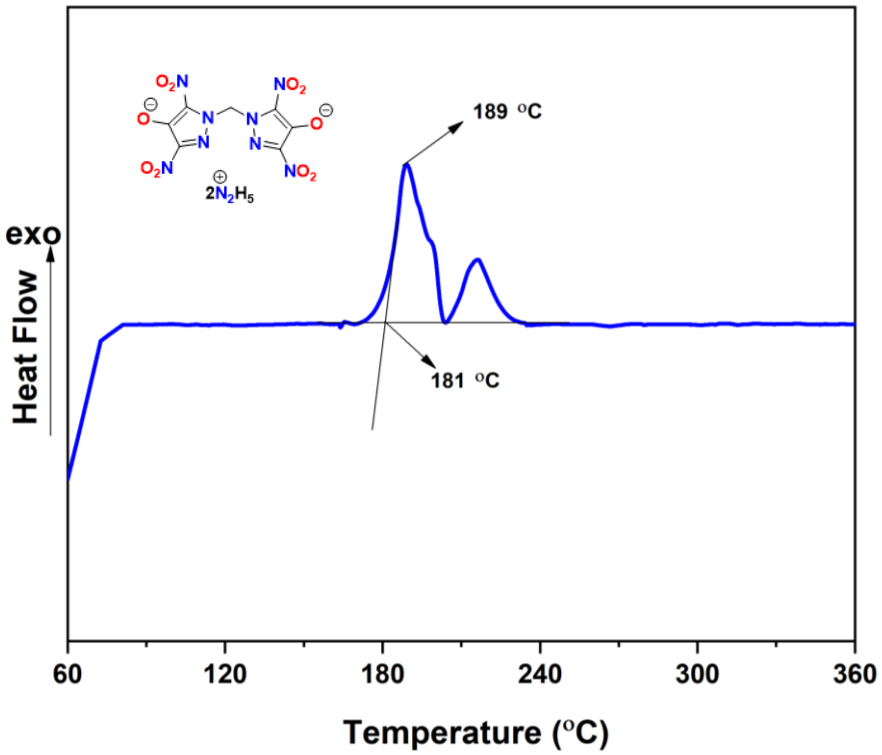


Fig.S28: DSC Spectra of compound **5**

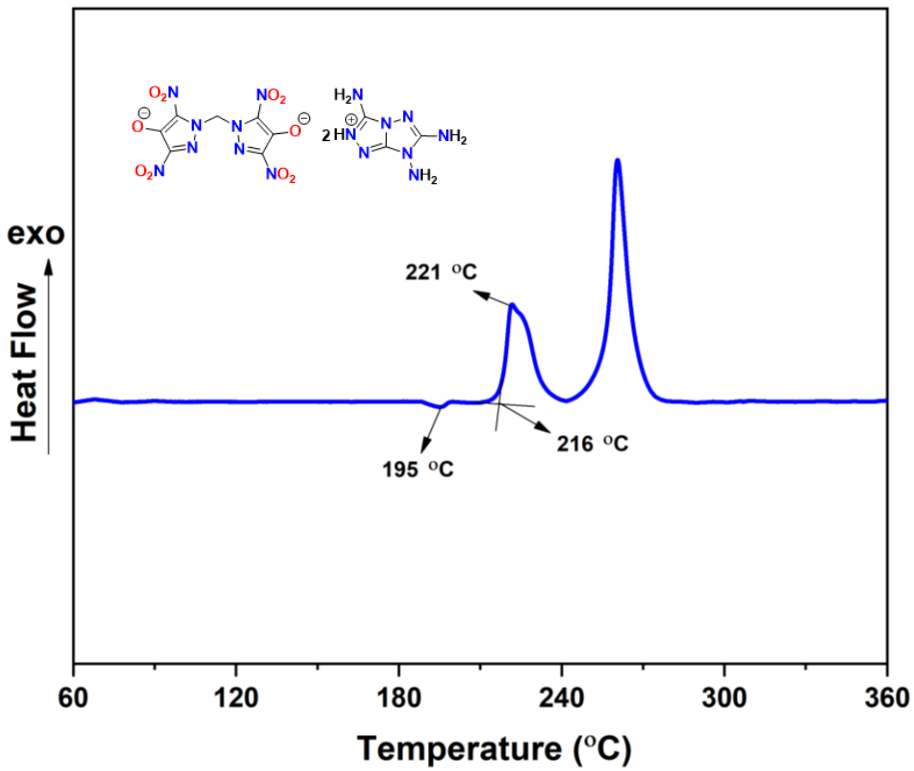


Fig.S29: DSC Spectra of compound **6**

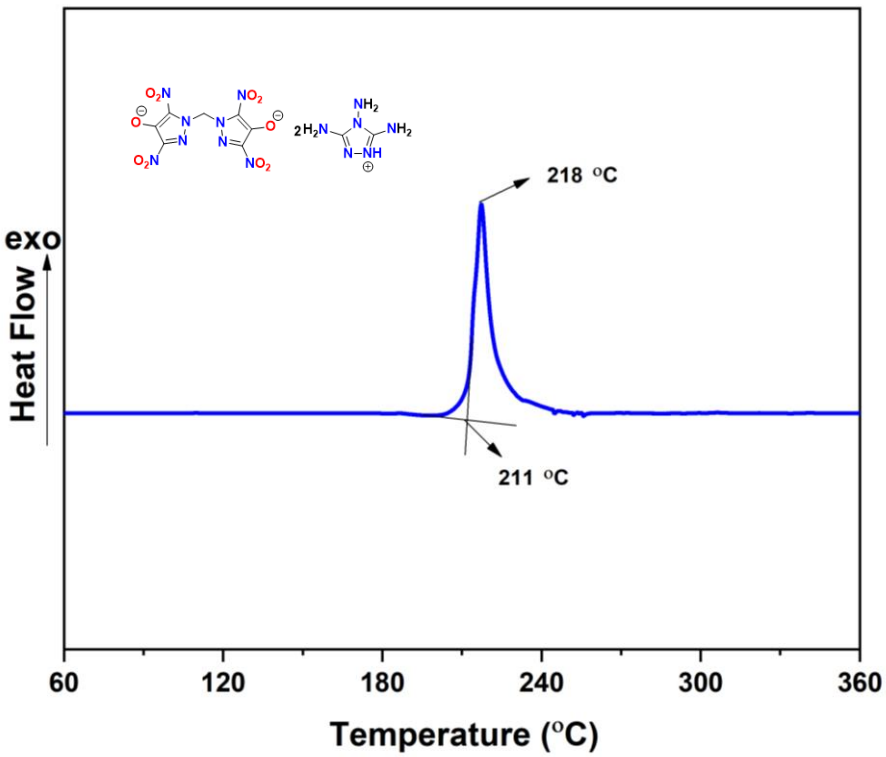


Fig.S30: DSC Spectra of compound **7**

8. Mass Spectra

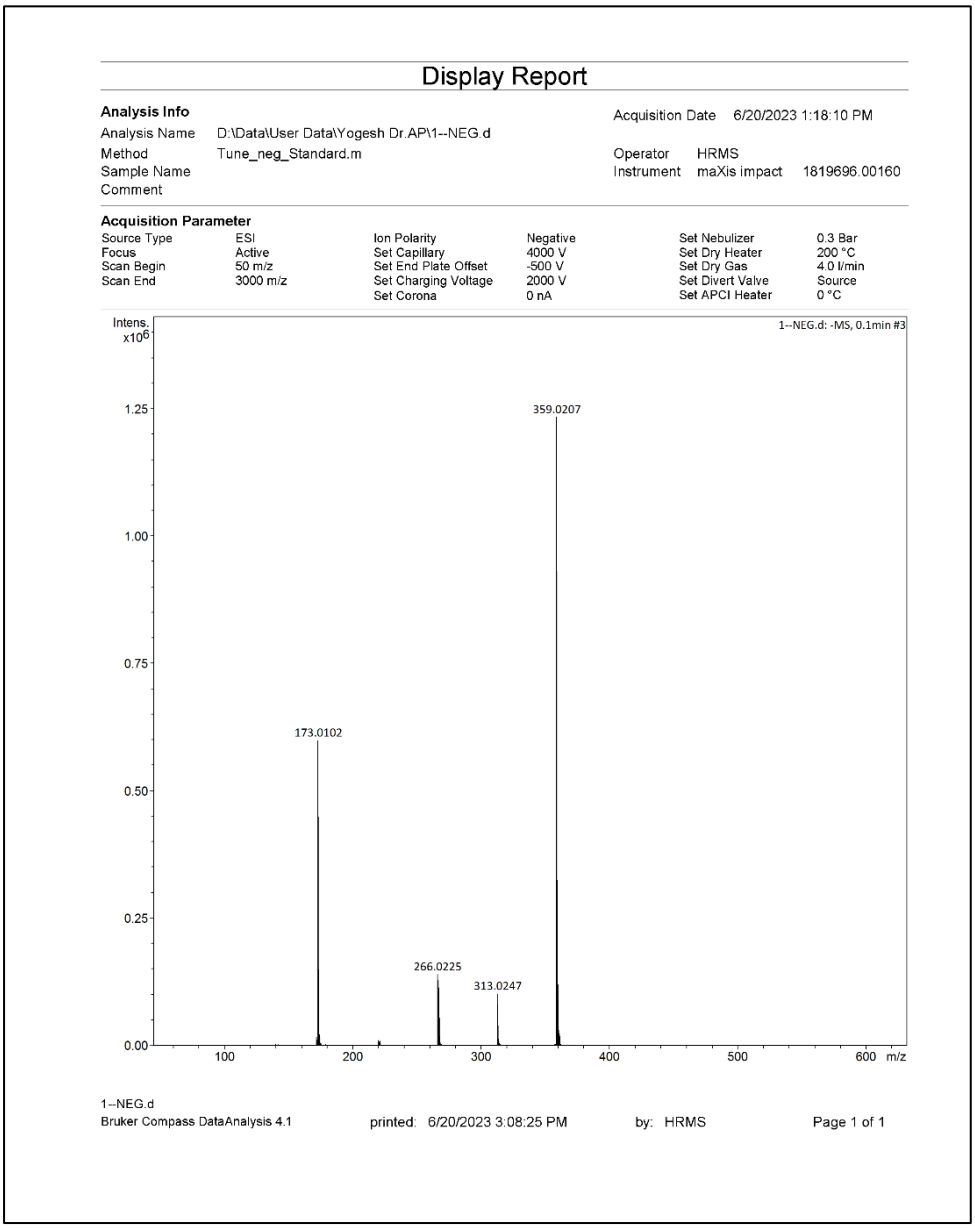


Fig.S31: Mass Spectra of compound **2**

9. Crystal Packing Diagram

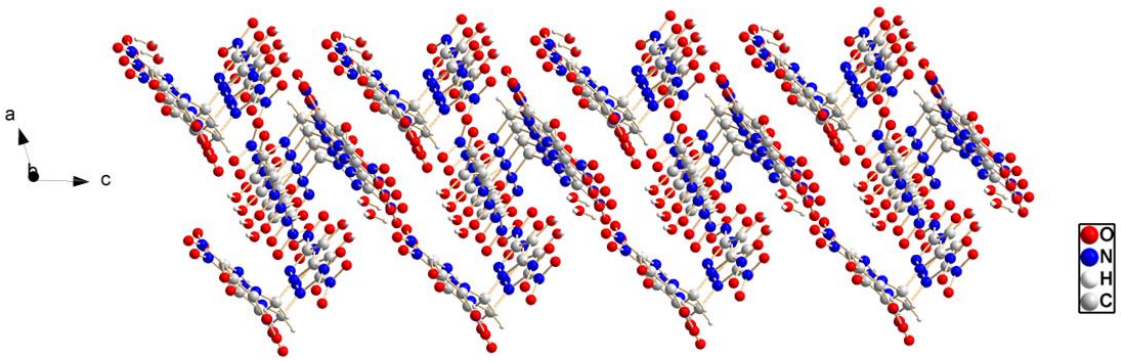


Fig.S32: Ball and stick packing diagram for **2.H_2O** viewed along b axis.

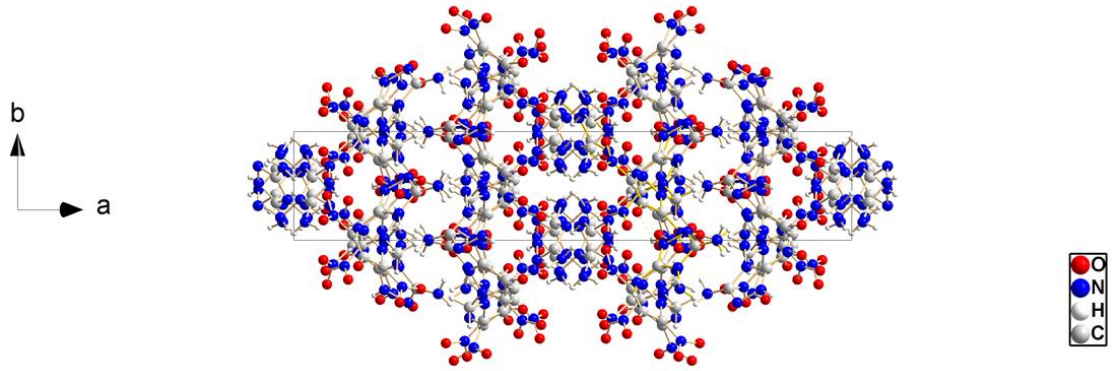


Fig.S33: Ball and stick packing diagram for **7** viewed along c axis.

10. ^{15}N NMR Analysis

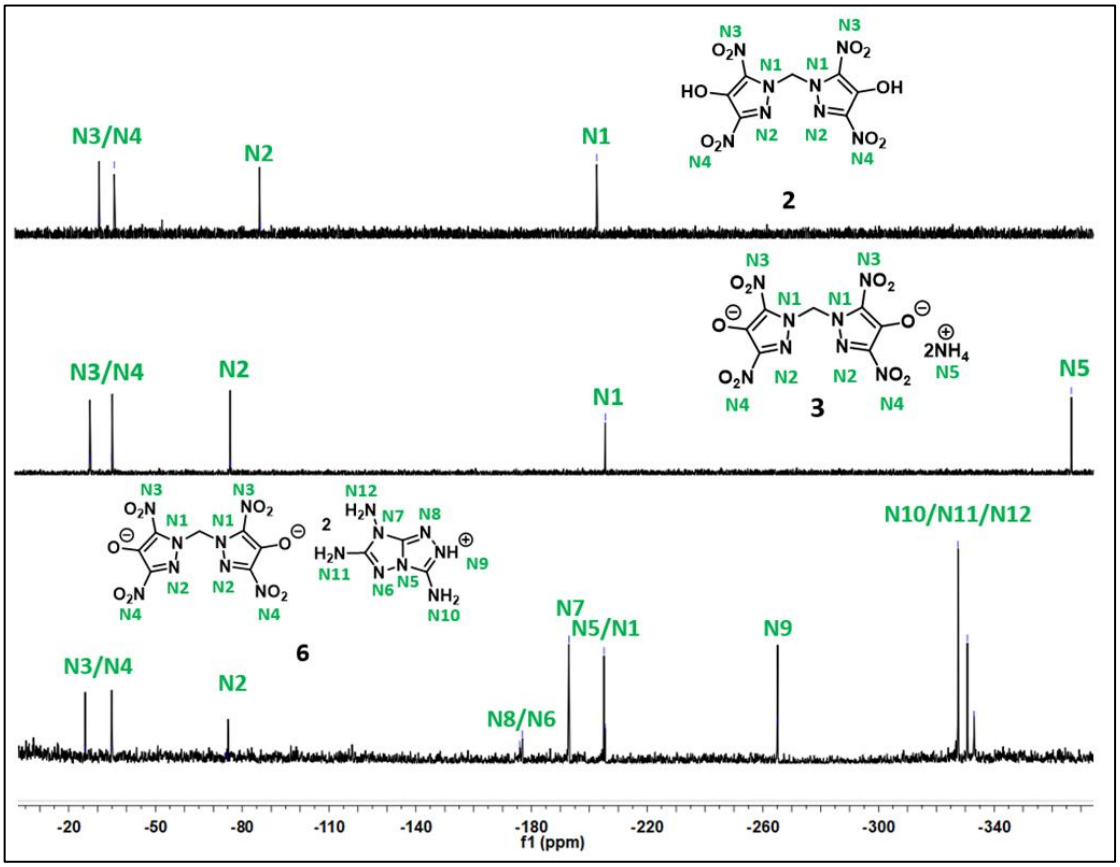


Fig.S34: ^{15}N NMR spectra of compounds **2**, **3**, and **6**

The ^{15}N NMR spectral analysis for compounds **2**, **3**, and **6** was done by taking nitromethane as a reference (Fig. S34). The peaks of the nitrogens of the nitro groups fall in the range of -25.6 ppm to -34.8 ppm. After formation of anion in salts **3** and **6**, an upfield shift is observed in N1 (from -199.6 ppm in **2** to -202.5 in **3** and -205.5 ppm in **6**, whereas N2 observed a downfield shift (from -84.1 ppm in **2** to -74.0 in **3** and -75.0 ppm in **6**). Peak of the ammonium cation in **3** was found to be at -362.3 ppm, and amino groups in the cation of **6** showed peaks in the range of -333.0 and -327.5 ppm.

References:

1 SMART: Bruker Molecular Analysis Research Tools, version 5.618, Bruker Analytical X-ray Systems, Madison, WI, 2000.

2 R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

3 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 09, Revision E.01, Gaussian, Inc., Wallingford, CT, 2013.

4 E. F. C. Byrd and B. M. Rice, J. Phys. Chem. A, 2006, 110, 1005–1013.

5 H. D. B. Jenkins, D. Tudela and L. Glasser, Inorg. Chem., 2002, 41, 2364–2367.

6 V. D. Ghule, J. Phys. Chem. C, 2013, 117, 16840–16849.