Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information (SI)

Diazido Nitro Pyrazoles: Unlocking High-Performance Primary Explosive with Binder Capabilities

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Caution! All the compounds investigated are potentially explosive, energetic materials. Although we have experienced no difficulties in the synthesis and characterization of these compounds, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be always worn.

General Methods.

Reagents were purchased from Ak Scientifics, Acros Organics or Aldrich as analytical grade and were used as received. ^{1}H NMR, ^{13}C NMR spectra were recorded using JEOL DELTA (ECS) 500 (^{1}H, 500 MHz; ^{13}C, 126 MHz; 15N, 51 MHz) nuclear magnetic resonance spectrometer. DMSO-d_6 was employed as the solvent and locking solvent. Chemical shifts are given relative to $(CH_3)_4Si$ for ^{1}H, ^{13}C, and CH_3NO_2 for ^{15}N NMR. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and at heating rate of 5 °C min^{-1} on a differential scanning calorimeter (SDT650). IR spectra were recorded using Zn-Se pellets with ECO-ATR spectrometer (Bruker Alpha II). Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer in helium atmosphere. Heats of formation were experimentally determined by oxygen bomb calorimetry (Parr 6200 calorimeter). Impact and friction-sensitivity measurements were tested by employing a standard BAM Fall hammer and a BAM friction tester. The single-crystal X-ray data collection was carried out using Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

Experimental Section:

***Synthesis of 3,5-diazido-4-nitro-1H-pyrazole (2)*:** Conc. HCl (1.3 mL) was added to the suspension of 3,5-dihydrazineyl-4-nitro-1*H*-pyrazole (300 mg, 1.73 mmol) in distilled water (6 mL) and placed in ice bath. After 10 mins an aqueous solution of sodium nitrite (360 mg, 5.21 mmol in 1.5 mL H_2O) was added dropwise and the solution was left to stir at the same temperature for one hour and three hours at ambient temperature to obtain yellow coloured pure compound **2** in 52% yield (176 mg, 0.90 mmol). T_m/T_d(onset): 88/119 °C. ^1H NMR (500 MHz, DMSO-*d₆*): δ (ppm) 14.10 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ (ppm) 140.93, 115.68. MS (ESI) m/z: calculated for $C_3HN_9O_2$ [M-H]$^-$ 194.0180; Found 194.0188; IR (ATR, ZnSe, cm^{-1}): 791, 855, 1208, 1377, 1462, 1504, 1578, 2151, 3581. Elemental analysis: (%) calculated for $C_3HN_9O_2 \cdot 0.2H_2O$ (198.70): C, 18.13; H, 0.71; N, 63.44; found C, 19.11; H, 0.85; N, 62.65.

***Synthesis of 3,5-diazido-1-methyl-4-nitro-1H-pyrazole (3)*:** Compound **2** (300 mg, 1.73 mmol) was dissolved in acetonitrile (8 mL), and to this potassium carbonate was added. Further, methyl iodide was added dropwise to the above solution and heated to 40 °C with continuous stirring for 8 hours. The reaction mixture was then left to air dry, and the formed precipitate was washed with water (10 mL for 3 times) and dried in an oven at 50 °C to obtain brown coloured compound **3** in 65% yield (209 mg, 0.99 mmol). T_d(onset): 159 °C. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 4.38 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 150.01, 134.85, 37.37. MS (ESI) m/z: calculated for $C_4H_3N_9O_2$ [M+H]$^+$ 210.0482; Found 210.0486; IR (ATR, ZnSe, cm^{-1}): 776, 825, 988, 1144, 1194, 1314, 1431, 1494, 1622, 2126, 2166, 2889, 2958. Elemental analysis: (%) calculated for $C_4H_3N_9O_2 \cdot 0.2H_2O$ (212.73): C, 22.58; H, 1.61; N, 59.26; found C, 24.07; H, 1.75; N, 58.25.

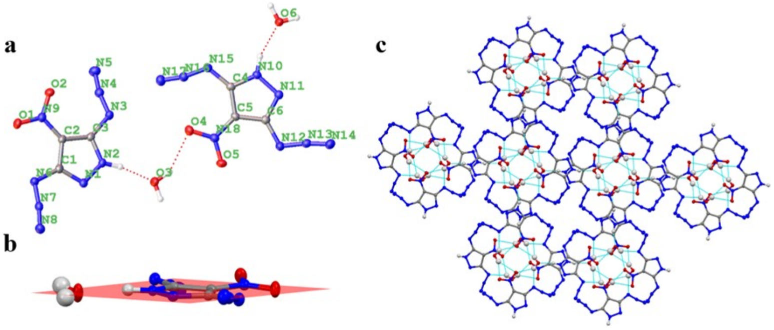


Figure S1: (**a**) Crystal structure, (**b**) planarity, and (**c**) crystal packing showing H-bonding interactions.

Table S1: Crystallographic data for 2.

CCDC No	2440016
Empirical formula	$C_6H_6N_{18}O_6$
Formula weight	426.29
Temperature/K	100
Crystal system	monoclinic
Space group	P2/n
a/Å	15.8138(6)
b/Å	6.4849(3)
c/Å	16.1635(6)
α/°	90
β/°	91.5980(10)
γ/°	90
Volume/Å3	1656.94(12)
Z	4
ρcalcg/cm3	1.709
μ/mm-1	0.150
F(000)	864.0
Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.042 to 56.594
Index ranges	-17 ≤ h ≤ 21, -8 ≤ k ≤ 8, -21 ≤ l ≤ 20
Reflections collected	27013
Independent reflections	4123 [Rint = 0.0404, Rsigma = 0.0263]
Data/restraints/parameters	4123/0/277
Goodness-of-fit on F2	1.066
Final R indexes [I>=2σ (I)]	R1 = 0.0417, wR2 = 0.1010
Final R indexes [all data]	R1 = 0.0529, wR2 = 0.1076
Largest diff. peak/hole / e Å-3	0.39/-0.23

Table S2: Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times10^3$) for **2**. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	**x**	**y**	**z**	**U(eq)**
O4	4476.0(8)	7290(2)	7814.0(7)	26.0(3)
O1	6872.4(8)	7443(2)	3351.0(7)	26.3(3)
O2	7270.8(7)	7013(2)	4634.0(7)	25.5(3)
O5	3188.9(8)	7505(2)	8229.3(7)	29.2(3)
O6	6232.3(8)	7459(2)	11568.1(7)	29.8(3)
O3	3556.5(8)	7474(2)	6222.3(7)	29.9(3)
N2	4739.1(8)	7613.8(19)	5074.7(8)	16.8(3)
N10	5104.6(8)	7610.1(19)	10288.8(8)	17.4(3)
N7	4454.3(8)	9115(2)	2728.7(8)	20.1(3)
N13	2714.4(8)	9135(2)	10603.8(8)	20.6(3)
N18	3956.2(9)	7412(2)	8373.0(8)	20.2(3)
N1	4461.8(8)	8061(2)	4285.8(8)	17.9(3)
N11	4316.4(8)	8058(2)	10577.2(8)	17.8(3)
N4	6574.7(8)	5912(2)	6028.4(8)	20.6(3)
N16	5918.1(8)	5964(2)	8456.7(8)	20.0(3)
N6	5144.2(8)	8342(2)	2988.1(8)	20.9(3)
N15	5891.6(8)	6874(2)	9139.4(8)	19.9(3)
N9	6716.2(8)	7281(2)	4091.6(8)	19.4(3)
N3	5887.6(8)	6846(2)	5933.9(8)	19.6(3)
N12	2940.6(9)	8367(2)	9928.1(8)	22.0(3)
N8	3882.7(9)	9822(2)	2416.5(9)	26.3(3)
N14	2423.2(9)	9831(2)	11162.7(9)	26.5(3)
N17	6076.2(9)	5158(2)	7866.9(9)	26.8(3)
N5	7165.8(9)	5089(2)	6244.0(9)	28.0(3)
C5	4267.3(10)	7473(2)	9196.3(9)	17.2(3)
C1	5148.6(10)	7944(2)	3840.8(9)	17.7(3)
C2	5870.4(9)	7419(2)	4335.3(9)	16.6(3)
C4	5109.2(10)	7264(2)	9475.8(9)	16.6(3)
C6	3811.7(10)	7967(2)	9913.5(9)	17.5(3)
C3	5567.0(10)	7224(2)	5139.1(9)	16.5(3)

Table S3: Anisotropic Displacement Parameters (Å$^2\times10^3$) for **2**. The Anisotropic displacement factor exponent takes the form:$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
O4	24.9(6)	36.5(7)	16.7(6)	2.1(5)	1.5(4)	-1.2(5)
O1	22.1(6)	37.1(7)	20.0(6)	2.1(5)	6.9(4)	2.1(5)
O2	16.3(6)	37.3(7)	22.7(6)	-0.3(5)	-0.3(4)	-1.3(5)
O5	18.4(6)	45.4(8)	23.6(6)	-2.5(5)	-4.5(5)	1.2(5)
O6	17.2(6)	55.1(9)	17.2(6)	-2.0(6)	0.5(4)	3.4(6)
O3	19.1(6)	53.3(9)	17.5(6)	0.9(6)	3.0(5)	0.6(6)
N2	17.5(6)	15.4(6)	17.5(6)	-0.7(5)	4.0(5)	-1.0(5)
N10	18.3(6)	16.1(6)	17.8(6)	0.3(5)	-1.4(5)	-0.7(5)
N7	21.8(7)	21.6(7)	16.9(6)	-0.8(5)	3.5(5)	-2.6(5)

N13	16.9(6)	21.7(7)	23.1(7)	1.5(5)	-0.3(5)	-0.9(5)
N18	20.6(7)	20.9(7)	19.0(7)	1.1(5)	-0.9(5)	-1.8(5)
N1	18.3(6)	16.9(6)	18.5(6)	-1.9(5)	1.8(5)	-1.7(5)
N11	19.1(6)	15.5(6)	18.9(6)	0.8(5)	1.6(5)	-1.0(5)
N4	20.6(7)	20.6(7)	20.7(7)	0.5(5)	2.0(5)	-2.5(5)
N16	20.0(7)	19.6(7)	20.4(7)	2.4(5)	0.8(5)	-0.6(5)
N6	18.8(7)	25.8(7)	18.2(6)	0.1(5)	0.8(5)	1.6(5)
N15	19.5(7)	20.7(7)	19.4(6)	-1.8(5)	-0.6(5)	-0.3(5)
N9	20.0(7)	18.3(6)	20.0(7)	-1.0(5)	2.8(5)	-0.9(5)
N3	19.7(7)	20.6(7)	18.6(6)	0.2(5)	2.6(5)	2.1(5)
N12	19.2(7)	27.3(7)	19.6(7)	-2.0(5)	0.5(5)	-1.1(6)
N8	24.9(7)	33.5(8)	20.4(7)	2.2(6)	-0.2(6)	3.0(6)
N14	20.6(7)	32.3(8)	26.5(7)	-2.7(6)	2.1(6)	2.0(6)
N17	28.2(8)	29.5(8)	22.9(7)	-2.1(6)	1.7(6)	1.6(6)
N5	24.3(7)	29.2(8)	30.4(8)	4.6(6)	-0.3(6)	1.9(6)
C5	19.0(7)	15.2(7)	17.2(7)	1.2(5)	-1.1(6)	-2.4(5)
C1	18.7(7)	15.5(7)	19.0(7)	-2.6(6)	2.2(6)	-1.6(6)
C2	16.0(7)	14.3(7)	19.6(7)	-1.6(5)	2.5(6)	-1.2(5)
C4	18.8(7)	12.2(6)	18.7(7)	1.7(5)	-1.0(6)	-2.1(5)
C6	19.7(8)	14.0(7)	18.8(7)	1.1(5)	0.7(6)	-2.1(6)
C3	16.5(7)	12.9(7)	20.1(7)	-2.0(5)	2.7(6)	-2.3(5)

Table S4: Bond Lengths for **2**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O4	N18	1.2409(18)	N11	C6	1.320(2)
O1	N9	1.2334(18)	N4	N3	1.2498(19)
O2	N9	1.2351(18)	N4	N5	1.123(2)
O5	N18	1.2304(18)	N16	N15	1.2533(19)
N2	N1	1.3679(18)	N16	N17	1.1214(19)
N2	C3	1.335(2)	N6	C1	1.402(2)
N10	N11	1.3739(18)	N15	C4	1.388(2)
N10	C4	1.333(2)	N9	C2	1.408(2)
N7	N6	1.2616(19)	N3	C3	1.390(2)
N7	N8	1.1210(19)	N12	C6	1.403(2)
N13	N12	1.2613(19)	C5	C4	1.401(2)
N13	N14	1.1204(19)	C5	C6	1.419(2)
N18	C5	1.406(2)	C1	C2	1.417(2)
N1	C1	1.321(2)	C2	C3	1.403(2)

Table S5: Bond Angles for **2**.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C3	N2	N1	113.64(12)	N18	C5	C6	127.40(14)
C4	N10	N11	113.57(13)	C4	C5	N18	127.36(14)
N8	N7	N6	172.33(15)	C4	C5	C6	104.96(13)
N14	N13	N12	172.01(16)	N1	C1	N6	122.88(14)
O4	N18	C5	118.00(13)	N1	C1	C2	111.60(13)

O5	N18	O4	122.37(13)	N6	C1	C2	125.50(14)
O5	N18	C5	119.62(14)	N9	C2	C1	127.90(14)
C1	N1	N2	104.38(12)	C3	C2	N9	127.26(14)
C6	N11	N10	104.39(12)	C3	C2	C1	104.66(13)
N5	N4	N3	168.93(16)	N10	C4	N15	116.49(13)
N17	N16	N15	169.03(16)	N10	C4	C5	105.69(13)
N7	N6	C1	112.35(13)	N15	C4	C5	137.79(14)
N16	N15	C4	118.85(13)	N11	C6	N12	123.36(14)
O1	N9	O2	122.91(14)	N11	C6	C5	111.39(14)
O1	N9	C2	118.94(13)	N12	C6	C5	125.23(14)
O2	N9	C2	118.15(13)	N2	C3	N3	115.93(13)
N4	N3	C3	119.48(13)	N2	C3	C2	105.71(13)
N13	N12	C6	112.95(13)	N3	C3	C2	138.28(14)

Table S6: Torsion Angles for **2.**

A	**B**	**C**	**D**	**Angle/˚**	**A**	**B**	**C**	**D**	**Angle/˚**
O4	N18	C5	C4	-5.0(2)	N1	C1	C2	N9	-175.68(14)
O4	N18	C5	C6	168.02(15)	N1	C1	C2	C3	-0.18(17)
O1	N9	C2	C1	-7.2(2)	N11	N10	C4	N15	177.78(12)
O1	N9	C2	C3	178.28(15)	N11	N10	C4	C5	-0.54(17)
O2	N9	C2	C1	172.45(15)	N4	N3	C3	N2	159.58(14)
O2	N9	C2	C3	-2.1(2)	N4	N3	C3	C2	-24.0(3)
O5	N18	C5	C4	175.92(15)	N16	N15	C4	N10	159.25(14)
O5	N18	C5	C6	-11.1(2)	N16	N15	C4	C5	-23.2(3)
N2	N1	C1	N6	-178.65(14)	N6	C1	C2	N9	3.1(3)
N2	N1	C1	C2	0.12(16)	N6	C1	C2	C3	178.55(14)
N10	N11	C6	N12	-178.78(14)	N9	C2	C3	N2	175.70(14)
N10	N11	C6	C5	-0.25(16)	N9	C2	C3	N3	-0.9(3)
N7	N6	C1	N1	10.1(2)	N17	N16	N15	C4	-175.6(8)
N7	N6	C1	C2	-168.50(15)	N5	N4	N3	C3	-175.6(8)
N13	N12	C6	N11	10.7(2)	C1	C2	C3	N2	0.16(16)
N13	N12	C6	C5	-167.65(15)	C1	C2	C3	N3	-176.45(18)
N18	C5	C4	N10	174.60(14)	C4	N10	N11	C6	0.50(16)
N18	C5	C4	N15	-3.2(3)	C4	C5	C6	N11	-0.05(17)
N18	C5	C6	N11	-174.30(14)	C4	C5	C6	N12	178.44(15)
N18	C5	C6	N12	4.2(3)	C6	C5	C4	N10	0.34(16)
N1	N2	C3	N3	177.39(12)	C6	C5	C4	N15	-177.41(17)
N1	N2	C3	C2	-0.10(17)	C3	N2	N1	C1	-0.01(17)

Table S7: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2**.

Atom	**x**	**y**	**z**	**U(eq)**
H6A	6769.13	7438.69	11551.08	45
H6B	6130.11	7599.41	12078.16	45
H3A	3627.66	7460.52	6745.5	45

H3B	3026.65	7635.65	6145.11	45
H2	4403.27	7585.67	5499.65	20
H10	5562.69	7557.04	10610	21

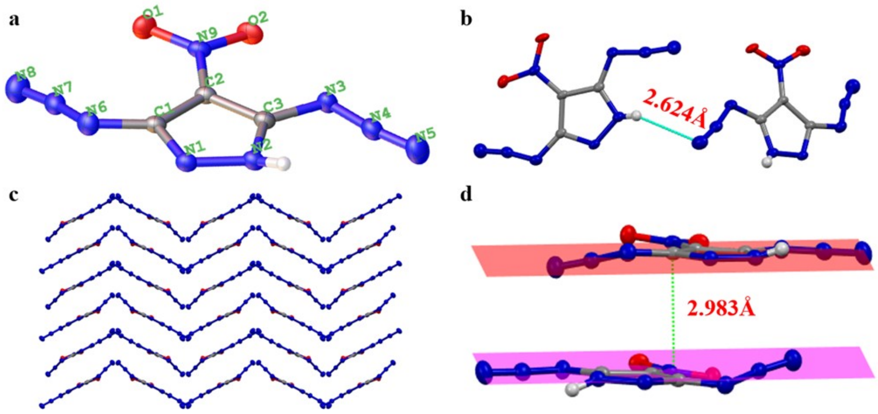


Figure S2: (**a**) Crystal structure, (**b**) Hydrogen bonding distance, (**c**) wave-like crystal packing along the c-axis, and (d) inter-layer separation between two planes.

Table S8: Crystallographic data for 2 (without water).

CCDC No	2445030
Empirical formula	$C_3HN_9O_2$
Formula weight	195.13
Temperature/K	100
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	14.4561(9)
b/Å	6.9477(5)
c/Å	7.1889(5)
α/°	90
β/°	90
γ/°	90
Volume/Å3	722.03(9)
Z	4
ρ calcg/cm3	1.795
μ/mm-1	0.153
F(000)	392.0
Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.864 to 58.45
Index ranges	$-19 \le h \le 19$, $-9 \le k \le 9$, $-9 \le l \le 9$
Reflections collected	10980
Independent reflections	1949 [Rint = 0.0359, Rsigma = 0.0247]
Data/restraints/parameters	1949/1/131
Goodness-of-fit on F2	1.146

Final R indexes [I>=2σ (I)]	R1 = 0.0346, wR2 = 0.0879
Final R indexes [all data]	R1 = 0.0381, wR2 = 0.0910
Largest diff. peak/hole / e Å-3	0.39/-0.20
Flack parameter	-0.1(7)

Table S9: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times 10^3$) for **2**. Ueq is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O2	-5060.2(13)	-2517(3)	-1935(3)	24.4(4)
O1	-3751.8(12)	-3524(3)	-3082(3)	26.2(4)
N9	-4547.5(15)	-2899(3)	-3260(3)	18.7(4)
N2	-5867.0(14)	-1550(3)	-7322(3)	19.6(4)
N6	-3684.7(14)	-3819(3)	-7451(3)	23.2(4)
N1	-5085.8(14)	-2391(3)	-8050(3)	17.8(4)
N3	-6384.5(14)	-963(3)	-4210(3)	22.5(4)
N7	-3208.1(14)	-4879(3)	-6409(3)	22.6(4)
N4	-7073.9(15)	-164(3)	-4949(3)	23.8(4)
N8	-2705.4(16)	-5859(4)	-5708(4)	32.6(5)
C2	-4905.3(14)	-2589(3)	-5043(4)	16.5(4)
N5	-7727.2(16)	571(4)	-5392(3)	33.9(6)
C3	-5754.0(16)	-1687(3)	-5504(3)	17.8(4)
C1	-4488.3(16)	-3021(3)	-6771(3)	16.9(4)

Table S10: Anisotropic Displacement Parameters ($Å^2\times 10^3$) for **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h2a*2U_{11}+2hka*b*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
O2	32.0(9)	31.5(9)	9.8(7)	-0.3(7)	1.5(7)	-3.4(8)
O1	25.9(9)	32.7(9)	20.0(8)	1.5(8)	-5.8(7)	5.1(7)
N9	24.6(10)	18.5(9)	12.9(9)	-0.3(7)	-2.2(8)	-4.0(7)
N2	23.4(10)	20.8(9)	14.6(9)	-1.4(7)	-0.8(7)	0.0(7)
N6	24.9(10)	28.0(10)	16.6(8)	0.9(8)	2.9(8)	1.1(8)
N1	21.2(10)	20.0(9)	12.2(8)	0.4(7)	-0.7(7)	-1.2(7)
N3	22.8(9)	28.7(11)	16.0(8)	-4.8(8)	-1.4(8)	3.6(8)
N7	22.0(9)	23.8(9)	22.1(9)	-2.1(9)	3.0(8)	-0.6(8)
N4	27.3(10)	24.5(9)	19.7(9)	-4.2(9)	1.1(9)	1.9(8)
N8	30.8(12)	35.1(12)	31.9(12)	3.8(10)	-0.3(10)	6.8(10)
C2	20.5(9)	17.8(9)	11.2(9)	1.1(9)	-0.8(9)	-3.1(7)
N5	35.9(13)	36.9(12)	28.8(13)	-1.9(10)	-1.7(10)	12.5(10)
C3	21.4(10)	18.1(10)	14.0(9)	-0.6(7)	-1.5(8)	-1.4(8)
C1	20.5(11)	17.5(10)	12.8(10)	0.3(8)	-1.6(8)	-3.1(8)

Table S11: Bond Lengths for **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O2	N9	1.236(3)	N1	C1	1.335(3)
O1	N9	1.236(3)	N3	N4	1.259(3)
N9	C2	1.399(3)	N3	C3	1.396(3)
N2	N1	1.375(3)	N7	N8	1.116(3)
N2	C3	1.320(3)	N4	N5	1.119(3)
N6	N7	1.256(3)	C2	C3	1.417(3)
N6	C1	1.377(3)	C2	C1	1.413(3)

Table S12: Bond Angles for **2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	N9	O1	123.6(2)	N9	C2	C3	127.1(2)
O2	N9	C2	116.8(2)	N9	C2	C1	127.95(19)
O1	N9	C2	119.54(19)	C1	C2	C3	104.9(2)
C3	N2	N1	104.16(19)	N2	C3	N3	123.6(2)
N7	N6	C1	119.1(2)	N2	C3	C2	111.7(2)
C1	N1	N2	114.1(2)	N3	C3	C2	124.6(2)
N4	N3	C3	113.2(2)	N6	C1	C2	139.3(2)
N8	N7	N6	169.8(3)	N1	C1	N6	115.7(2)
N5	N4	N3	171.5(3)	N1	C1	C2	105.1(2)

Table S13: Torsion Angles for **2**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	N9	C2	C3	7.5(3)	N1	N2	C3	C2	0.5(3)
O2	N9	C2	C1	-175.6(2)	N7	N6	C1	N1	-161.5(2)
O1	N9	C2	C3	-172.4(2)	N7	N6	C1	C2	20.3(4)
O1	N9	C2	C1	4.6(3)	N4	N3	C3	N2	-0.1(3)
N9	C2	C3	N2	177.3(2)	N4	N3	C3	C2	177.6(2)
N9	C2	C3	N3	-0.6(3)	C3	N2	N1	C1	-0.8(3)
N9	C2	C1	N6	0.6(4)	C3	C2	C1	N6	178.0(3)
N9	C2	C1	N1	-177.8(2)	C3	C2	C1	N1	-0.3(2)
N2	N1	C1	N6	-178.11(18)	C1	N6	N7	N8	176.3(13)
N2	N1	C1	C2	0.7(2)	C1	C2	C3	N2	-0.2(2)
N1	N2	C3	N3	178.5(2)	C1	C2	C3	N3	-178.1(2)

Table S14: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2**.

Atom	x	y	z	U(eq)
H2	-6210(150)	-700(300)	-7700(400)	590(180)

NMR, IR Spectra, HRMS & TGA-DSC plots for 2 and 3.

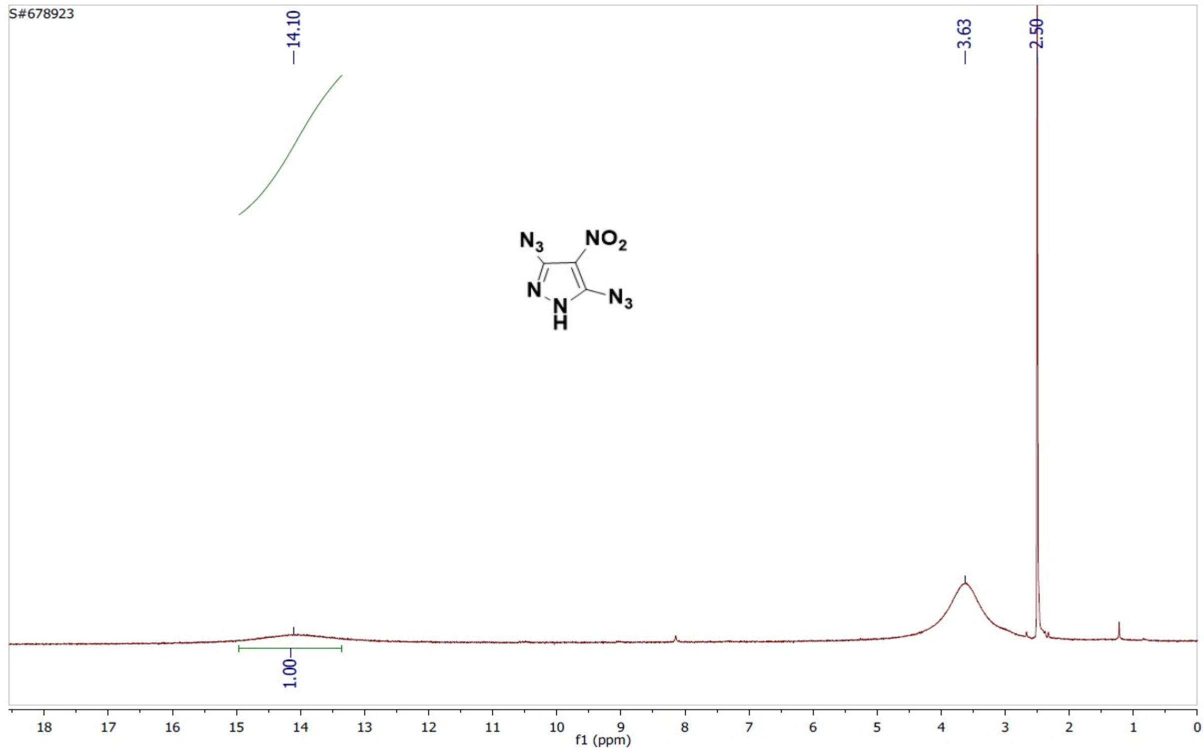


Figure S3: ^{1}H NMR spectrum of compound **2** in **DMSO-d_6.**

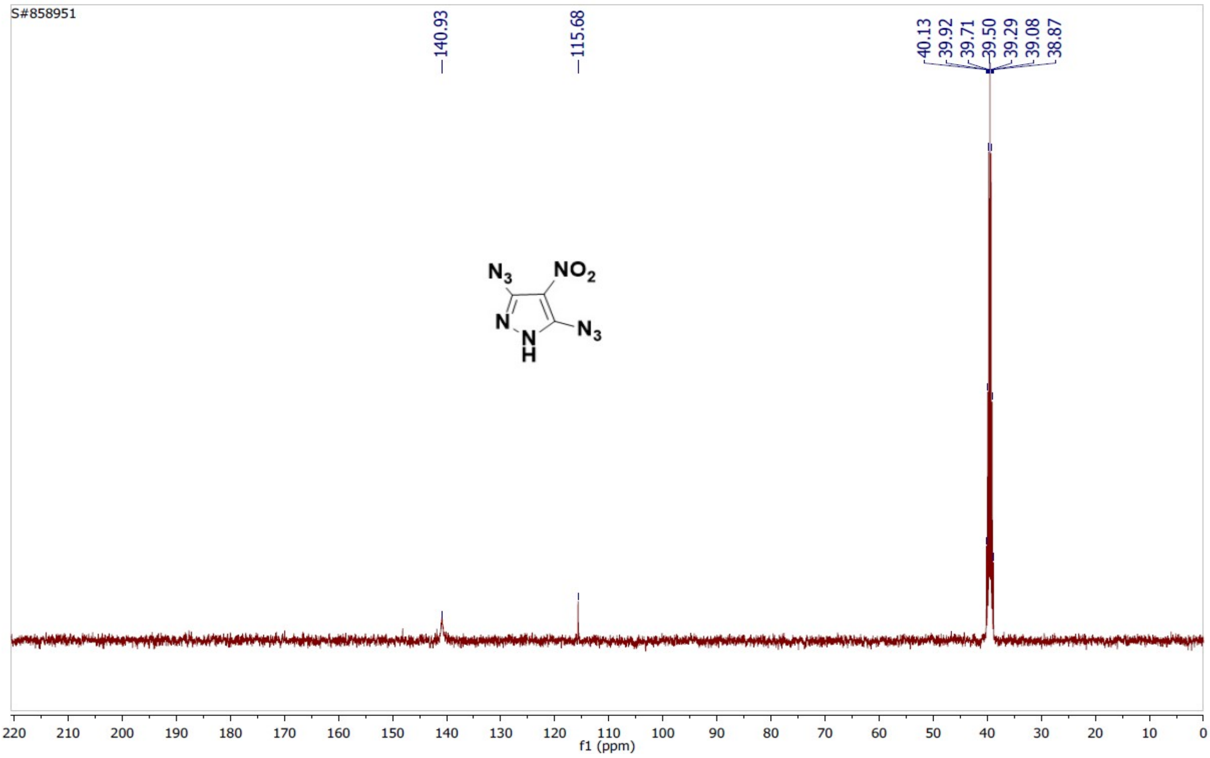


Figure S4: ^{13}C NMR spectrum of compound **2** in **DMSO-d_6.**

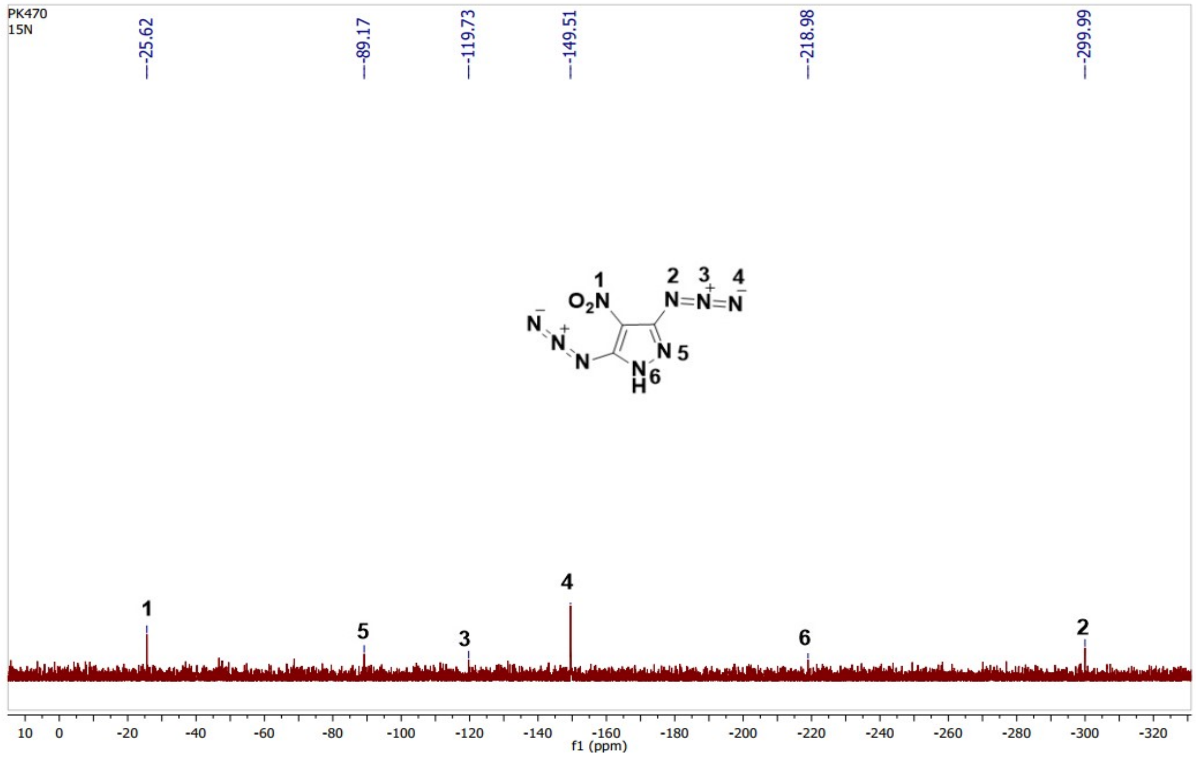


Figure S5: ^{15}N NMR spectrum of compound **2** in **DMSO-*d*$_6$.**

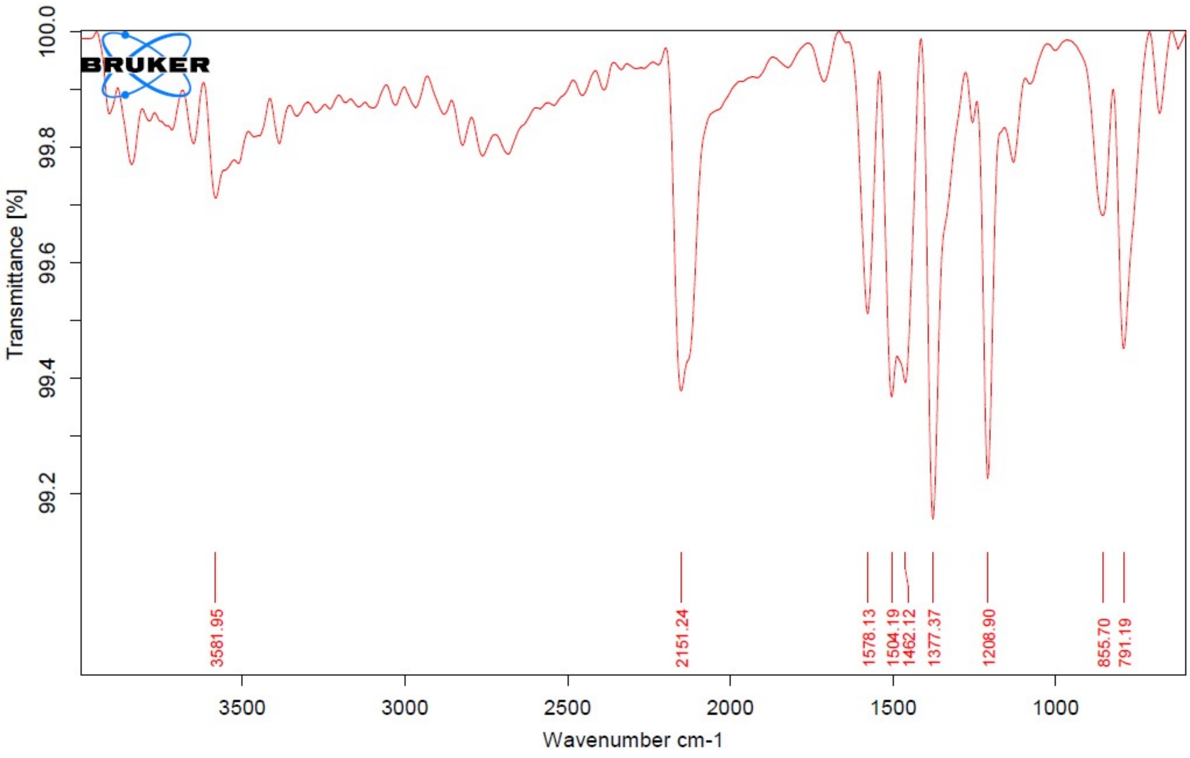
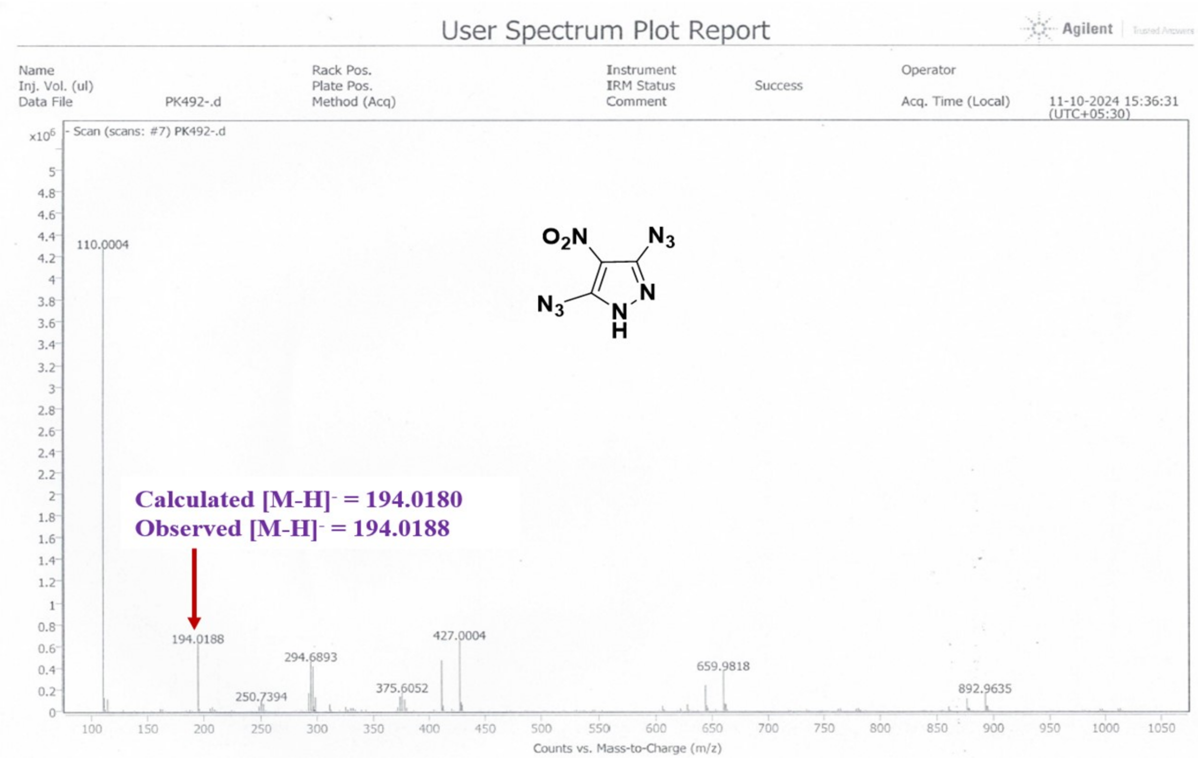


Figure S6: IR spectrum of compound **2.**


User Spectrum Plot Report

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Rack Pos.
Plate Pos.
Method (Acq)
Instrument
IRM Status Success
Comment
Operator
Acq. Time (Local) 11-10-2024 15:36:31 (UTC+05:30)

Figure S7: Mass spectra of compound **2.**

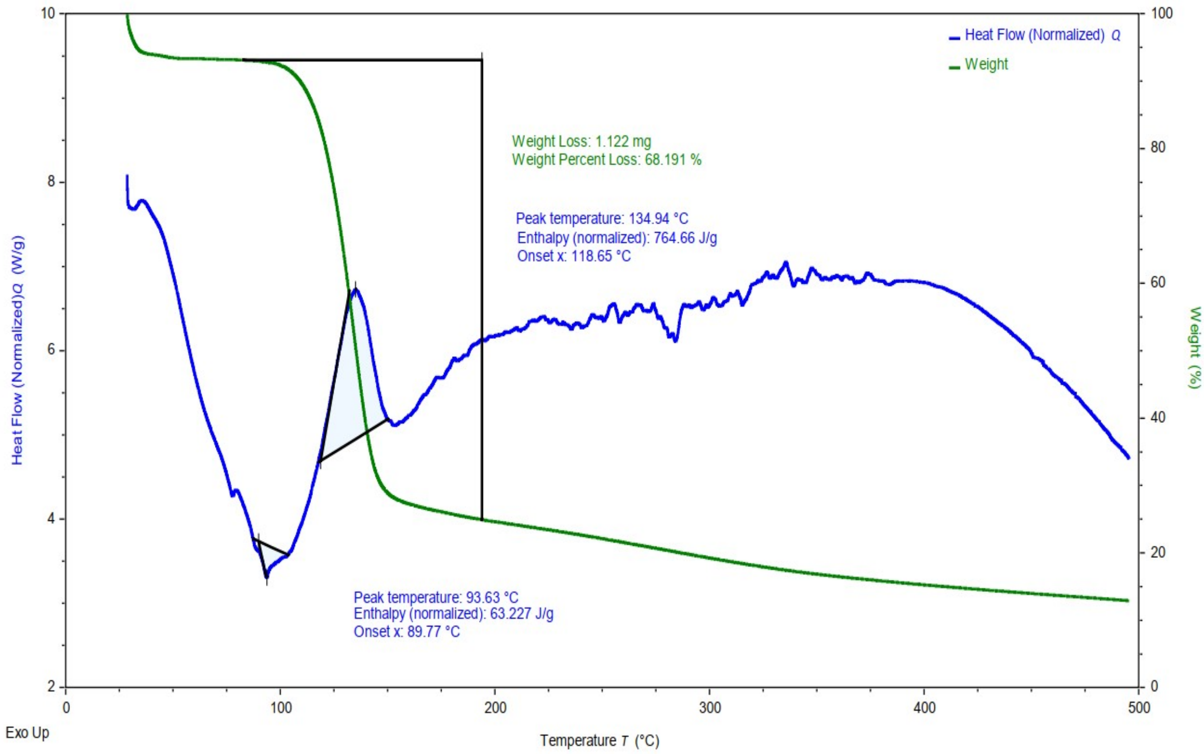


Figure S8: TGA-DSC spectra of compound **2** at a heating rate of 5 °C min^{-1}.

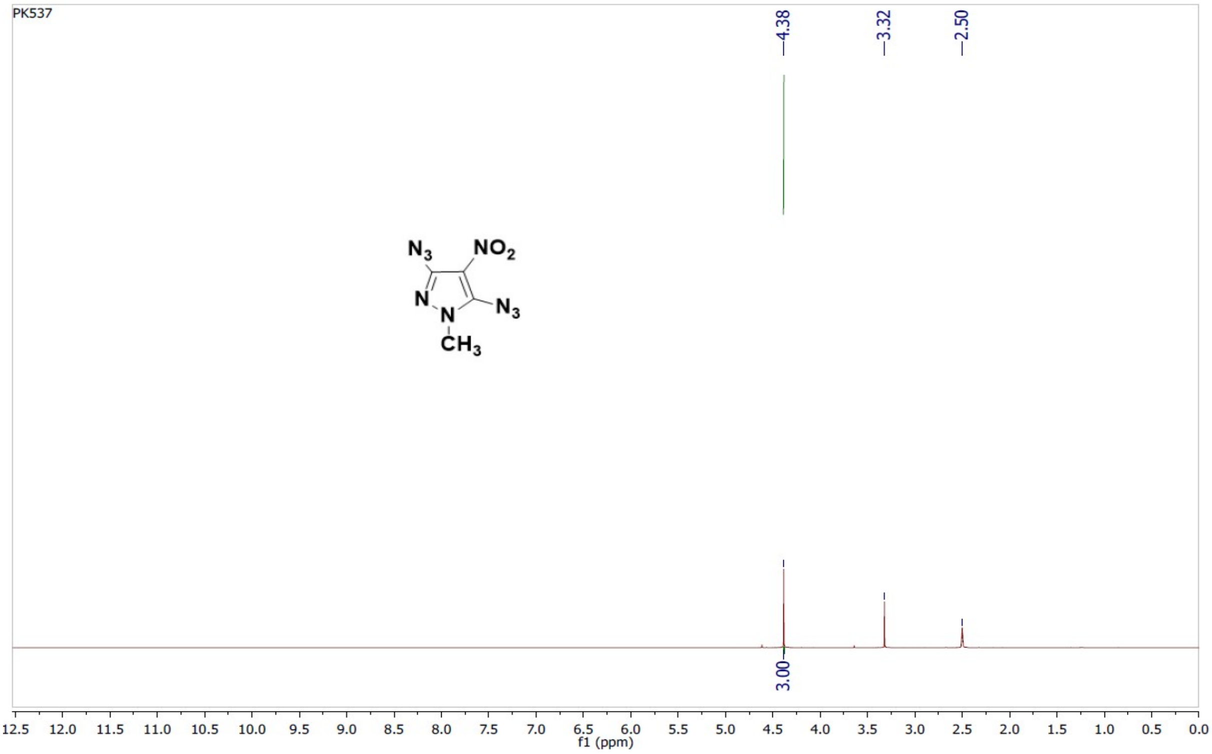


Figure S9: ^{1}H NMR spectrum of compound **3** in **DMSO-*d*$_6$.**

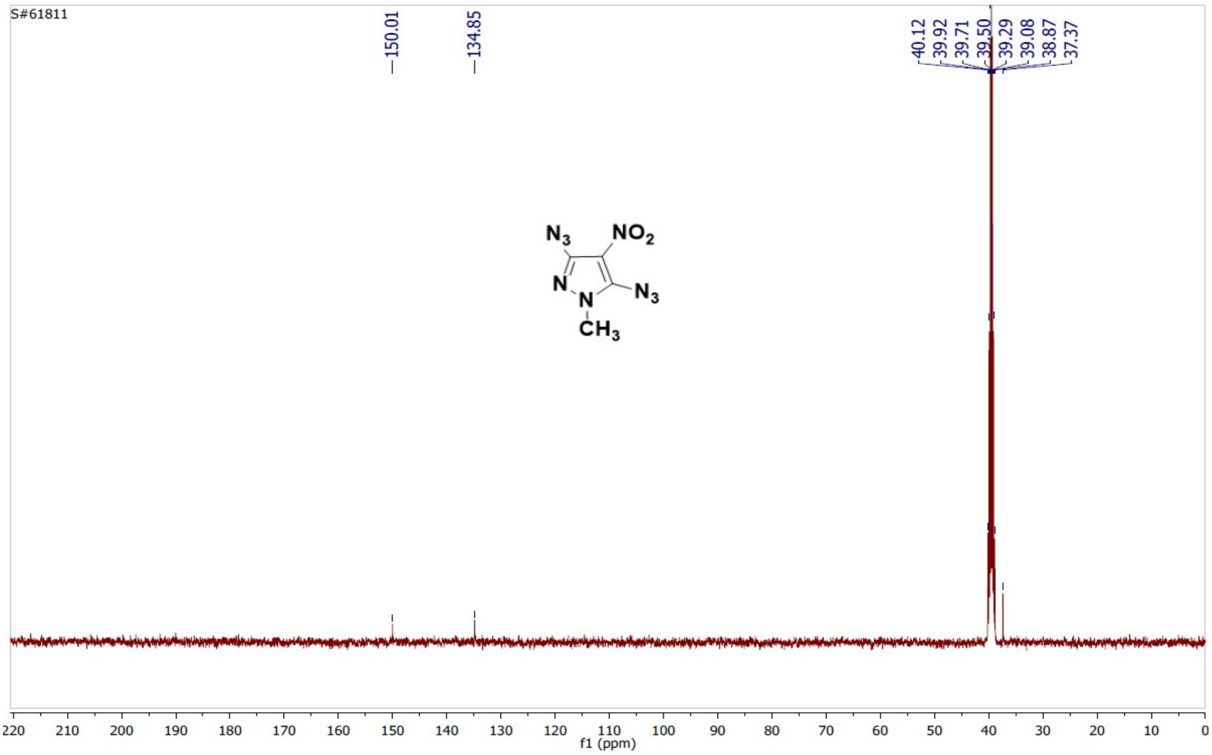


Figure S10: ^{13}C NMR spectrum of compound **3** in **DMSO-*d*$_6$.**

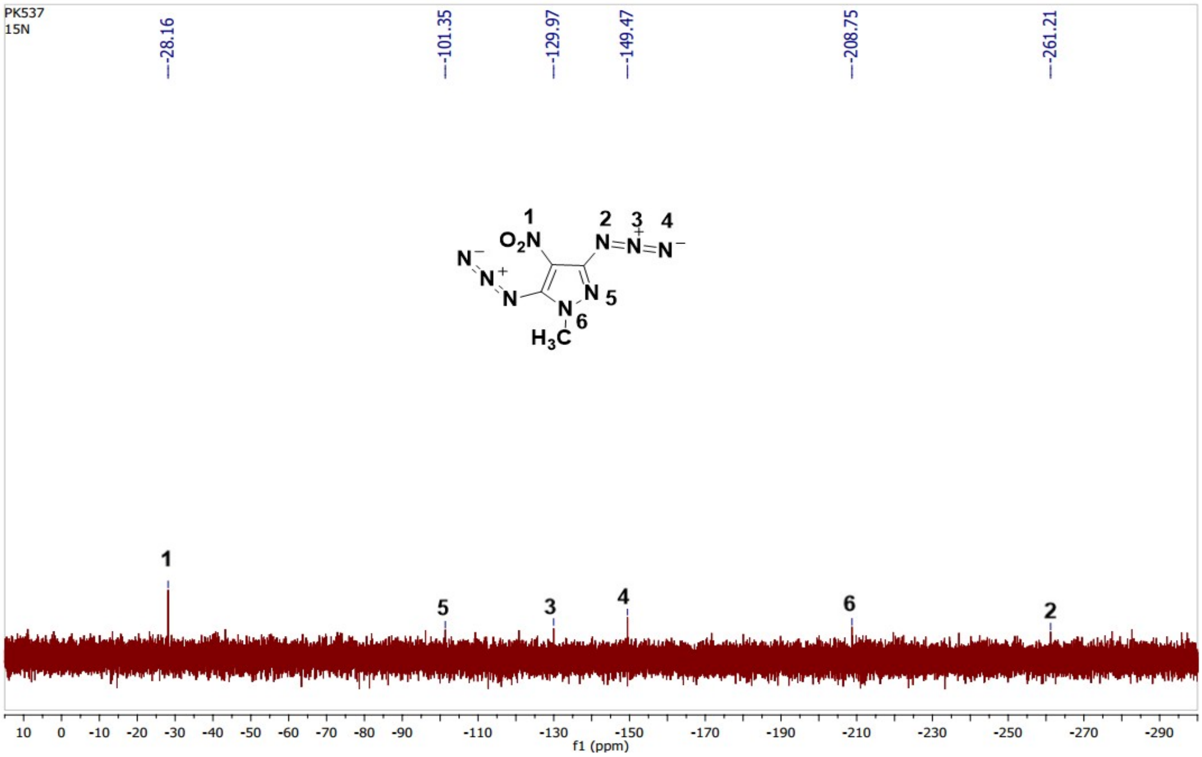


Figure S11: ^{15}N NMR spectrum of compound **3** in **DMSO-d_6.**

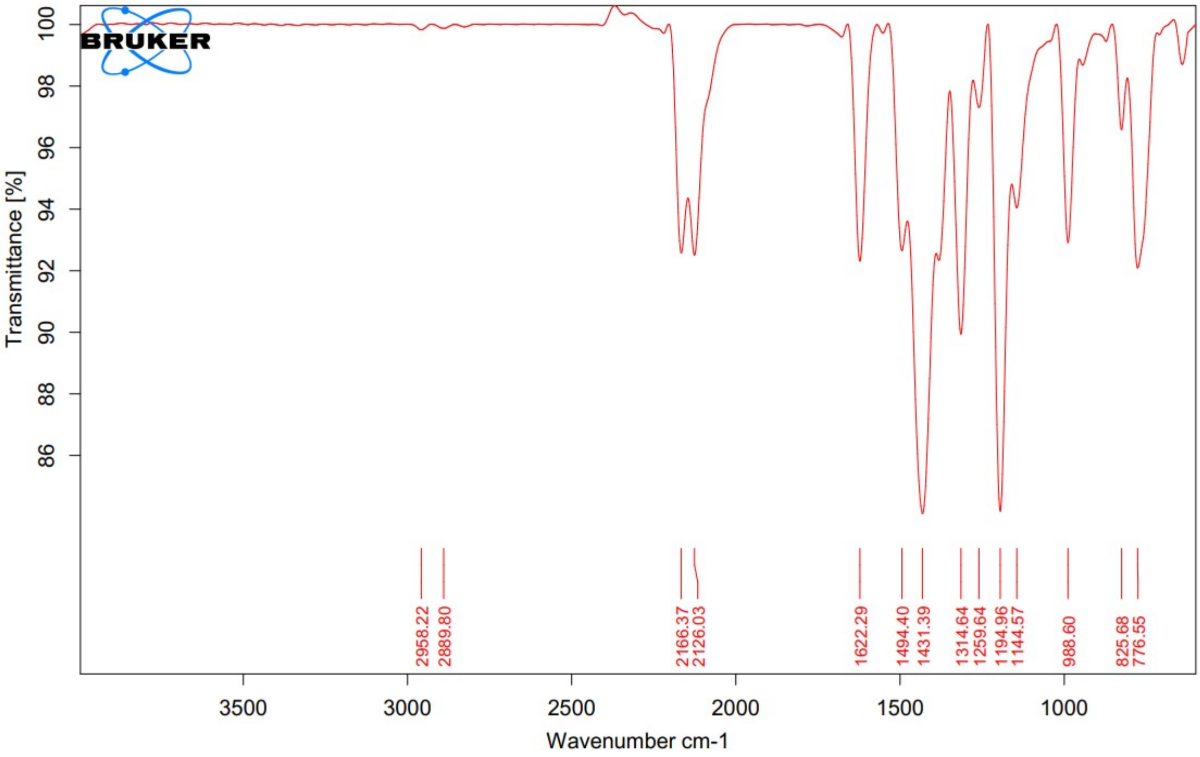
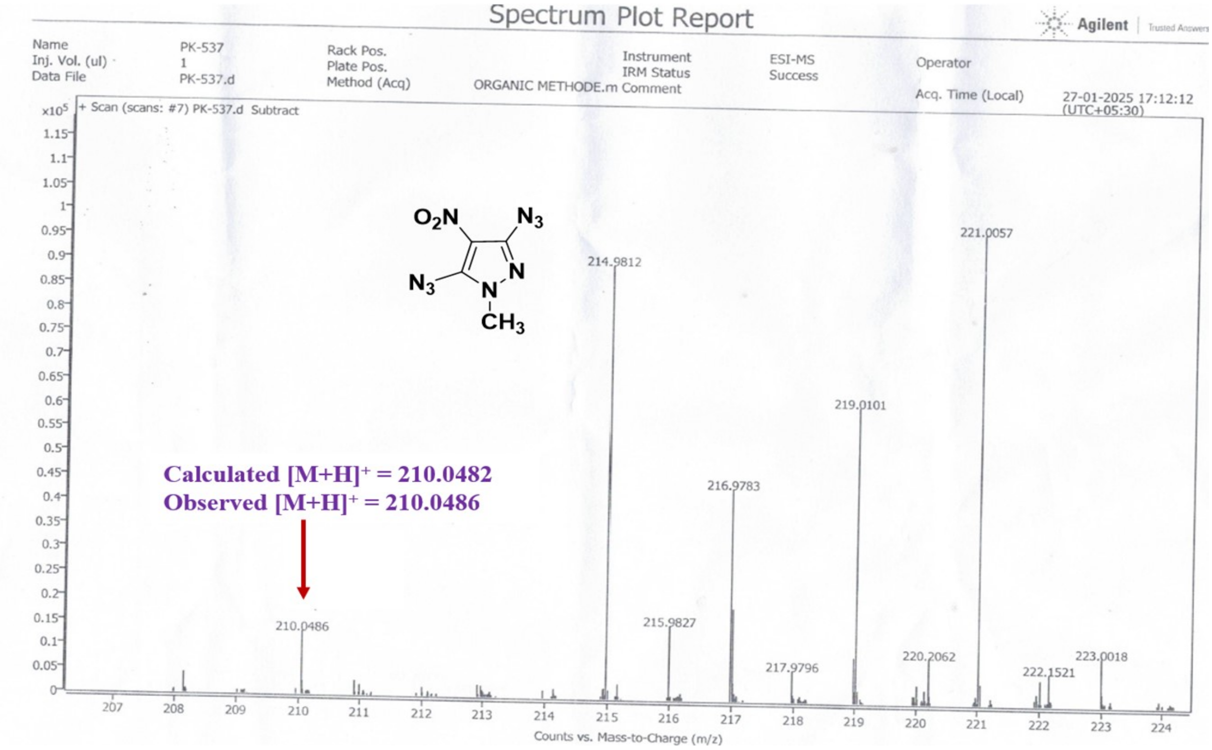


Figure S12: IR spectrum of compound **3.**



Spectrum Plot Report

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Plate Pos.
Method (Acq) ORGANIC METHODE.m
Instrument ESI-MS
IRM Status Success
Comment
Operator
Acq. Time (Local) 27-01-2025 17:12:12 (UTC+05:30)

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Calculated $[M+H]^+ = 210.0482$
Observed $[M+H]^+ = 210.0486$

Figure S13: Mass spectra of compound **3.**

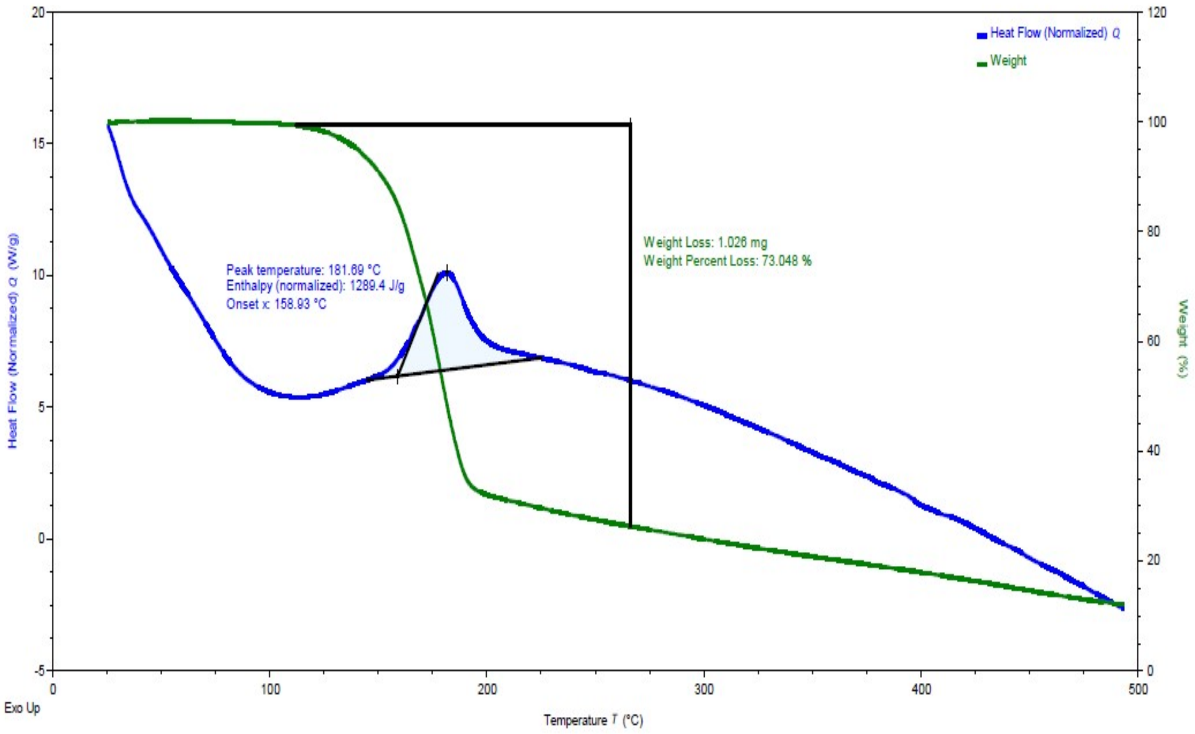


Figure S14: TGA-DSC spectra of compound **3** at a heating rate of 5 ^{o}C min^{-1}.

Heats of combustion: The heat of combustion is a vital indicator for estimating the energetic properties of explosive materials. The constant-volume combustion energy of the assynthesized compound was determined by a precise oxygen bomb calorimetry (Parr 6200 calorimeter). Approximately 120 mg of the compound and a well-defined amount of benzoic acid were taken in a mass ratio of 1:3 to make a palette. The bomb calorimeter was calibrated using the certified 1 gm benzoic acid palette under an oxygen environment. The sample was sealed in a bomb, which subsequently burned in the pure oxygen atmosphere.

The experimental result of the combustion energy ($\Delta_c U$) of **$C_3HN_9O_2$** is -2296.76 cal g $^{-1}$.
The enthalpy of combustion ($\Delta_c H$) is calculated to be –1859.4005 kJ mol^{-1}, based on the equation $\Delta_c H = \Delta_c U + \Delta nRT$, where $\Delta n = ng$ (products) – ng (reactants), R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K (ng is the total molar number of gases in the products or reactants). The combustion equation is as follows:
$C_3HN_9O_2(s) + 9/4O_2(g) = 3CO_2(g) + 0.5H_2O\ (l) + 9/2N_2(g)$
The standard molar enthalpy ($\Delta_f H$) of formation for the combustion products, H_2O (l, –285.83 kJ mol^{-1}), and CO_2 (g, –393.51 kJ mol^{-1}) were obtained from the literature.[1,2] According to Hess's law, the standard molar enthalpy of formation ($\Delta_f H$) at 298.15 K is calculated to be 535.95 kJ mol^{-1}.

$\Delta_f H[C_3HN_9O_2, s] = 3\Delta_f H[CO_2, g] + 0.5\Delta_f H[H_2O, l] - \Delta_c H[C_3HN_9O_2, s]$

The experimental result of the combustion energy ($\Delta_c U$) of **$C_4H_3N_9O_2$** is -2378.15 cal g $^{-1}$.
The enthalpy of combustion ($\Delta_c H$) is calculated to be –2068.3166 kJ mol^{-1}, based on the equation $\Delta_c H = \Delta_c U + \Delta nRT$, where $\Delta n = ng$ (products) – ng (reactants), R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K (ng is the total molar number of gases in the products or reactants). The combustion equation is as follows:
$C_4H_3N_9O_2(s) + 15/4O_2(g) = 4CO_2(g) + 9/2N_2(g) + 3/2H_2O(l)$
The standard molar enthalpy ($\Delta_f H$) of formation for the combustion products, H_2O (l, –285.83 kJ mol^{-1}), CO_2 (g, –393.51 kJ mol^{-1}) were obtained from the literature.[1,2] According to Hess's law, the standard molar enthalpy of formation ($\Delta_f H$) at 298.15 K is calculated to be 65.21 kJ mol^{-1}.

$\Delta_f H[C_4H_3N_9O_2, s] = 4\Delta_f H[CO_2, g] + 3/2\Delta_f H[H_2O, l] - \Delta_c H[C_4H_3N_9O_2, s]$

Computational Details:

Computations were carried out using the Gaussian 09 program suite.[3] The structure optimizations are performed with M06-2X/def2-TZVPP level of theory and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were found. Heat of formation (HOF) is a measure of energy content of an energetic material that can decompose, ignite and explode by heat or impact. It enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure, heat of detonation and specific impulse. However, it is impractical to determine the HOF of novel energetic materials because of their unstable intermediates and unknown combustion mechanism. Gas-phase heats of formation for neutral compound and anion were calculated using the Gaussian-4 (G4) composite method, see Table S**16**.

The usage of the HOF_{Gas} in the calculation of detonation properties slightly overestimates the values of detonation velocity and detonation pressure, and hence, the solid phase HOF (HOF_{Solid}) has been calculated which can efficiently reduce the errors. The HOF_{Solid} is calculated as the difference between HOF_{Gas} and heat of sublimation (HOF_{Sub}) as,

$$\mathrm{HOF}_{\mathrm{Solid}} = \mathrm{HOF}_{\mathrm{Gas}} - \mathrm{HOF}_{\mathrm{Sub}} \qquad (1)$$

The heat of sublimation (HOF_{Sub}), which is required to convert the HOF_{Gas} to the HOF_{Solid}, was calculated from Equation (2),[4]

$$HOF_{Sub} = 0.000267\,A^2 + 1.650087\,\left(v\sigma_{tot}^2\right)^{0.5} - 2.966078 \qquad (2)$$

Where A represents the surface area of the 0.001 electrons/bohr^3 isosurface of electronic density, v denotes the degree of balance between the positive and negative surface potentials, and σ_{tot}^2 is the electrostatic potential variance. These molecular surface properties were obtained using the Multiwfn program[5] and listed in Table **S17**.

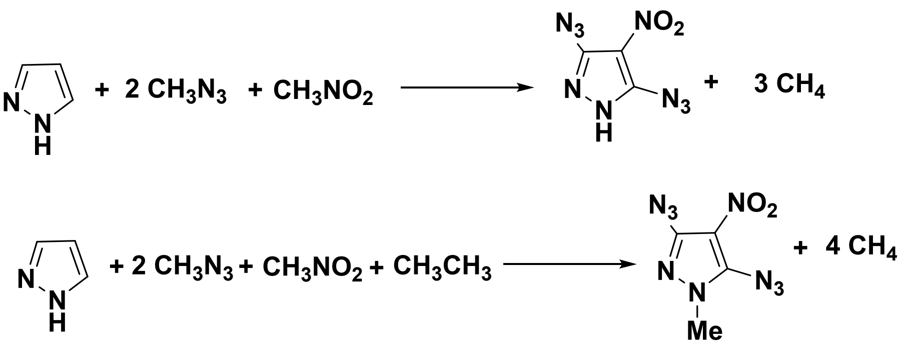


Figure S15. Designed isodesmic reactions for the prediction of HOF_{gas} of compounds **2** and **3**.

Table S15: Calculated total energies at 298K (E_0), zero point energies (ZPE), thermal corrections (H_T), and experimental HOF$_{gas}$ of reference compounds used isodesmic reaction at the M062X/def2-TZVPP level.

Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF$_{gas}$ (kJ/mol)**
CH_4	-40.453065	0.0449	0.0038	-74.8
CH_3CH_3	-79.727235	0.075	0.0045	-84
CH_3NO_2	-244.955044	0.0506	0.0053	-81
CH_3N_3	-204.029671	0.051	0.0054	298
Pyrazole-1H	-226.136343	0.0722	0.0046	179.4

Table S16. Calculated total energies at 298K (E_0), zero-point energies (ZPE), thermal corrections (H_T), and experimental HOF$_{gas}$ of target compounds at the M062X/def2-TZVPP level.

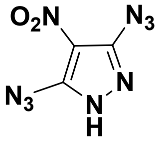
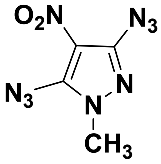
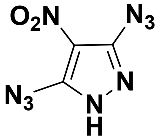
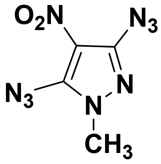
Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF$_{gas}$**
	-757.798526	0.082158	0.093504	900.4425
	-797.075815	0.110508	0.124248	883.0536

Table S17. Calculated molecular surface properties and heat of sublimation of target compounds.

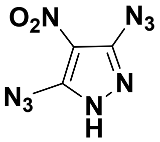
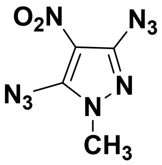
Compd.	**Surface area (Å^2)**	**Volume (Å^3)**	**$\sigma_{tot}{}^2$ (kcal/mol)^2**	**v**	**HOF$_{Sublimation}$ (kJ/mol)**
	191.80981	185.23984	229.74925	0.24195360	105.03
	211.64341	207.93499	175.92575	0.23744520	107.12

In energetic materials, generally, C-NO_2, N-NO_2 and O-NO_2 are the weakest bond which easily ruptures on applying external stimuli. Hence, we have calculated the bond dissociation energy (BDE) of longest C-NO_2 bond using following equation at B3LYP/6-31G(d,p) level,

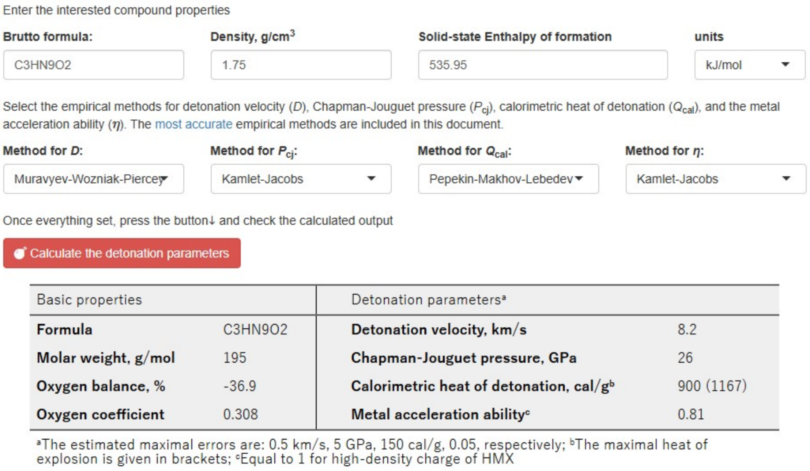
$$BDE = [E_{R1} + E_{R2}] - E_{R1-R2}$$

where E_{R1-R2}, E_{R1} and E_{R2} are the total energies with zero-point energy correction of the precursor and the corresponding radicals produced by bond dissociation (see **Table S18**).

Table S18. Calculated total energies (E_0) of R-NO_2, R, and NO_2 at the B3LYP/6-31G(d,p) level, used in the prediction of bond dissociation energies.

Compounds	**E_0 (a.u.)**			**BDE (kJ mol^{-1})**
	R-NO_2	**R**	**NO_2**	
	-757.798526	-552.571393	-205.060445	437.63
	-797.075815	-591.888371	-205.060445	333.43

Energetic properties calculated using the method provided by the Predictive Laboratory of Energetic Materials (PILEM).[7]



Enter the interested compound properties

Brutto formula: C3HN9O2

Density, g/cm^3: 1.75

Solid-state Enthalpy of formation: 535.95

units: kJ/mol

Select the empirical methods for detonation velocity (*D*), Chapman-Jouguet pressure (P_{cj}), calorimetric heat of detonation (Q_{cal}), and the metal acceleration ability (η). The most accurate empirical methods are included in this document.

Method for *D*: Muravyev-Wozniak-Piercey

Method for P_{cj}: Kamlet-Jacobs

Method for Q_{cal}: Pepekin-Makhov-Lebedev

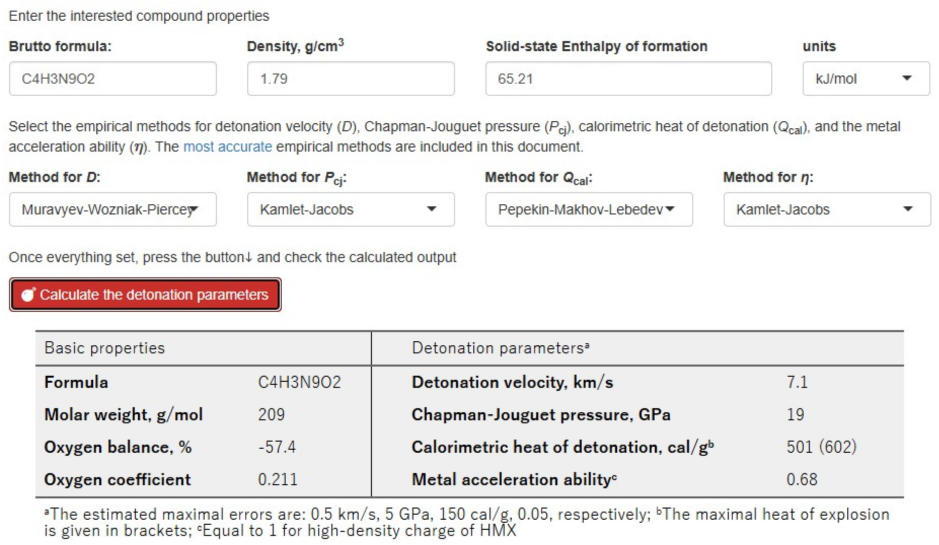
Method for η: Kamlet-Jacobs

Once everything set, press the button↓ and check the calculated output

Basic properties		Detonation parameters[a]	
Formula	C3HN9O2	**Detonation velocity, km/s**	8.2
Molar weight, g/mol	195	**Chapman-Jouguet pressure, GPa**	26
Oxygen balance, %	-36.9	**Calorimetric heat of detonation, cal/g[b]**	900 (1167)
Oxygen coefficient	0.308	**Metal acceleration ability[c]**	0.81

[a]The estimated maximal errors are: 0.5 km/s, 5 GPa, 150 cal/g, 0.05, respectively; [b]The maximal heat of explosion is given in brackets; [c]Equal to 1 for high-density charge of HMX

Figure **S16**: Energetic properties for compound **2**.



Enter the interested compound properties

Brutto formula: C4H3N9O2

Density, g/cm^3 1.79

Solid-state Enthalpy of formation 65.21

units kJ/mol

Select the empirical methods for detonation velocity (D), Chapman-Jouguet pressure (P_{cj}), calorimetric heat of detonation (Q_{cal}), and the metal acceleration ability (η). The most accurate empirical methods are included in this document.

Method for D: Muravyev-Wozniak-Piercey

Method for P_{cj}: Kamlet-Jacobs

Method for Q_{cal}: Pepekin-Makhov-Lebedev

Method for η: Kamlet-Jacobs

Once everything set, press the button↓ and check the calculated output

Basic properties		Detonation parameters[a]	
Formula	C4H3N9O2	**Detonation velocity, km/s**	7.1
Molar weight, g/mol	209	**Chapman-Jouguet pressure, GPa**	19
Oxygen balance, %	-57.4	**Calorimetric heat of detonation, cal/g[b]**	501 (602)
Oxygen coefficient	0.211	**Metal acceleration ability[c]**	0.68

[a]The estimated maximal errors are: 0.5 km/s, 5 GPa, 150 cal/g, 0.05, respectively; [b]The maximal heat of explosion is given in brackets; [c]Equal to 1 for high-density charge of HMX

Figure **S17**: Energetic properties for compound **3**.

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3. Gaussian 09, Revision E.01, M. J.Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian*, Inc., Wallingford CT, **2013**.
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5. Lu, T.; Chen, F.; *J. Comput. Chem.* **2012**, *33*, 580.
6. Jenkins, H. D. B.; Tudela, D.; Glasser, L. Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements. *Inorg. Chem.* **2002**, 41, 2364-2367.
7. Muravyev, N. V.; Wozniak, D. R.; Piercey, D. G. Progress and performance of energetic materials: open dataset, tool, and implications for synthesis. *J. Mater. Chem. A*, **2022**, *10*, 11054-11073.