Electronic Supporting Information For

Trinitromethyl-Triazolone (TNMTO): A Highly Dense Oxidizer

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Table S1. Calculated Total Energy (E_0), Zero-point Energy (ZPE), values of Thermal Correction (H_T) and Enthalpy of Formation ($\Delta_f H°$ (g)) of the title compounds using B3LYP/6-31+G**//MP2/6-311++G** level of theory (Isodesmic).

Compounds	E_0 [Hartree/Particle]	ZPE [Hartree/Particle]	H_T [Hartree/Particle]	$\Delta_f H°$ (g) kJ/mol	$\Delta_f H_{sub}°$ kJ/mol	$\Delta_f H°$ (s) kJ/mol
CH_4	-40.3796224	0.044793	0.003812	-74.60[a]	----	----
CH_3NO_2	-244.4784821	0.049840	0.005298	-74.30[a]	----	----
CH_3CH_3	-79.5716305	0.074610	0.004428	-84.00[a]	----	----
TNE	-691.8636667	0.082007	0.011245	-91.63[a]	----	----
TO	-316.7572189	0.064231	0.005616	-25.87[a]	----	----
MTO	-355.9630511	0.091809	0.007306	-41.80[a]	----	----
NTO, 5	-520.8511701	0.066465	0.007992	-20.55[a](-25.57)[b]	47.75[c]	-68.30
TNMTO, 6	-968.2367424	0.097889	0.014696	-49.43[b]	15.04[c]	-64.47

[a] Obtained at G2 level. [b]Calculated using isodesmic equation as shown in Fig. S1. [c]Calculated using $\Delta H_{sub} = 0.188 \times T/kJmol^{-1}K^{-1}$

The gas-phase enthalpy of formation $\Delta_f H°(g)$ was predicted using Gaussian 03 program[1] according to isodesmic equation as shown in Figure S1.

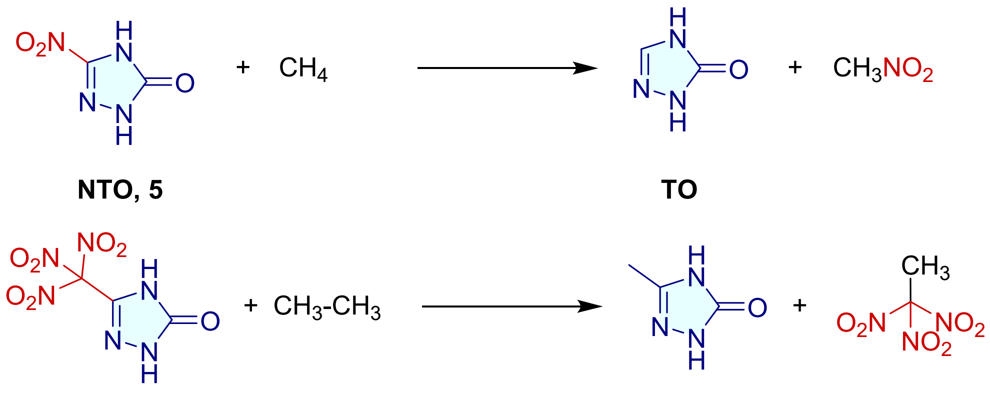


Fig. S1 Isodesmic reaction for TNMTO

Subsequently, for TNMTO, solid-phase enthalpy of formation $\Delta_f H°$ (s) were calculated by using equation 1.[2-4]

$$\Delta_f H°(s) = \Delta_f H°(g) - \Delta H_{sub} \tag{1}$$

Where, $\Delta_f H°(s)$ is solid phase enthalpy of formation, $\Delta_f H°(g)$ is gas phase enthalpy of formation and ΔH_{sub} is the enthalpy of sublimation.

The enthalpy of sublimation was estimated using equation 2 as per Trouton's rule.[5]

$$\Delta H_{sub} = 0.188 \times T/kJmol^{-1}K^{-1} \tag{2}$$

where, T, is either the melting point (mp) or the decomposition temperature (T_d), when no melting happens before decomposition.

The bond dissociation energies (BDEs) of compounds TNMTO and TNAA were estimated according to following equation 3.

$$\text{BDE [AB]} = E_0\,[\text{A.}] + E_0\,[\text{B.}] - E_0\,[\text{AB}] \quad (3)$$

where, BDE [AB] is bond dissociation energy and E_0 [A.] and E_0 [B.] are the energies of individual homolytic part and E_0 [AB] is the total energy of the individual molecule.

Table S2. The standard enthalpy of combustion $\Delta H_f^\circ{}_{(combust)}$ for the title compounds was calculated by following equation 8.

$\Delta_f H^\circ_{(combust)} = \Sigma\Delta_f H^\circ_{(products)} - \Sigma\Delta_f H^\circ_{(reactants)}$	(4)
RDX = $C_3H_6N_6O_6$ (s) + 1.5 O_2 (g) $\longrightarrow$ 3CO_2 (g) + 3H_2O (g) + 3N_2 (g)	(5)
NTO, 5 = $C_2H_2N_4O_3$ (s) + O_2 (g) $\longrightarrow$ 2CO_2 (g) + H_2O (g) + 2N_2 (g)	(6)
TNAA, 4 = $C_2HN_5O_9$ (s) $\longrightarrow$ 2CO_2 (g) + 0.5H_2O (g) + 2.5N_2 (g) + 2.25O_2	(7)
TNMTO, 6 = $C_3H_2N_6O_7$ (s) $\longrightarrow$ 3CO_2 (g) + H_2O (g) + 3N_2 (g)	(8)

The standard enthalpy of formation for CO_2 ($\Delta H_{f\,(CO2)}$ = -393.51 kJmol^{-1}); H_2O ($\Delta H_{f\,(H2O)}$ = -243.015 kJmol^{-1}).

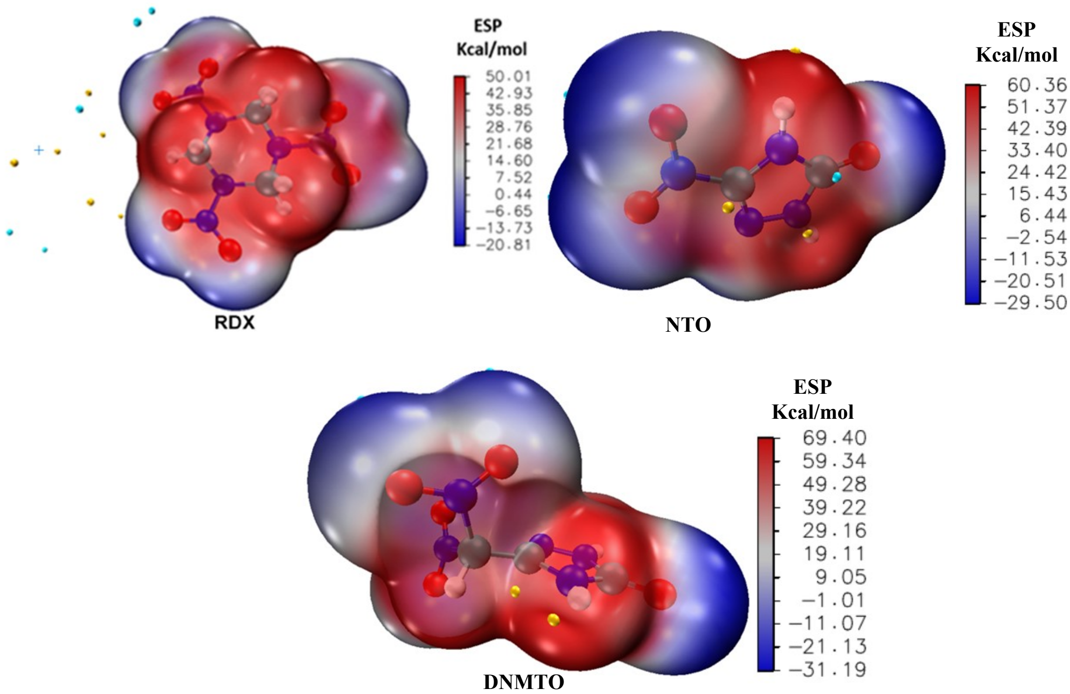
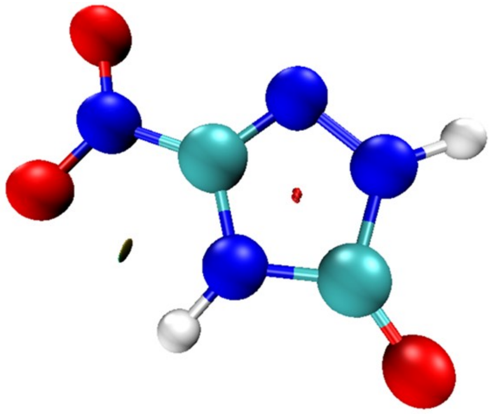
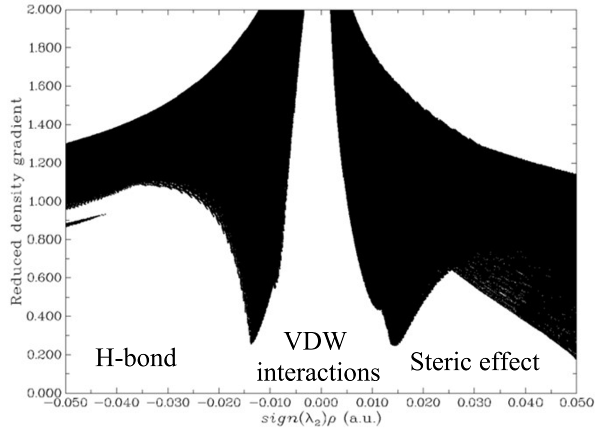
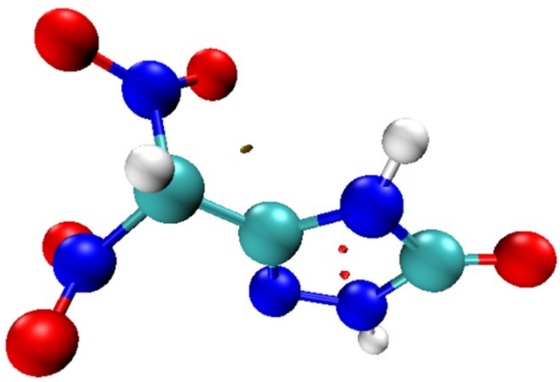


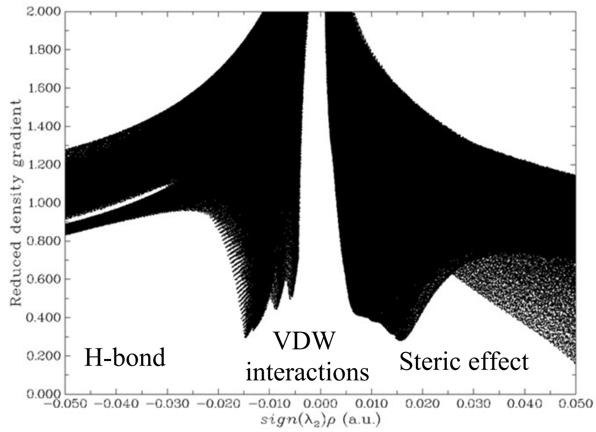
Fig. S2 Computed electrostatic potential (ESP) maps of RDX, NTO and DNMTO.





NTO, 5 **NTO, 5**





DNMTO, 10 **DNMTO, 10**

Fig. S3 Non-covalent interaction (NCI): Reduced density gradient (RDG) and scatter diagram of NTO and DNMTO.

Table S3. Comparison of the ratio of positive and negative ESPs and the surface area of ESPs of compounds and positive variance, total variance, balance of charges and product of total variance and balance of charges.

Compounds	A_{tot}[a] $Å^2$	A_{pos}[b] $Å^2$	A_{neg}[c] $Å^2$	$ratio_{pos}$ (%)	$ratio_{neg}$ (%)	$\sigma^2_{tot}\upsilon$[d] (kcal/mol)
TNMTO, 6	205.40	102.51	102.89	49.90	50.10	38.80
DNMTO, 10	187.12	87.93	99.19	46.99	53.01	45.12
TNT	221.89	128.42	93.47	57.88	42.12	22.48
NTO, 5	139.77	73.55	66.22	52.62	47.38	43.76
RDX	209.49	116.77	92.72	55.74	44.26	27.29

[a]SA_{tot} = Total surface area. [b]SA_{pos} = positive surface area. [c]SA_{neg} = Negative surface area. [d]Ratio of positive surface area [e d]Ratio of negative surface area. [g]Product of total variance and balance of charges.

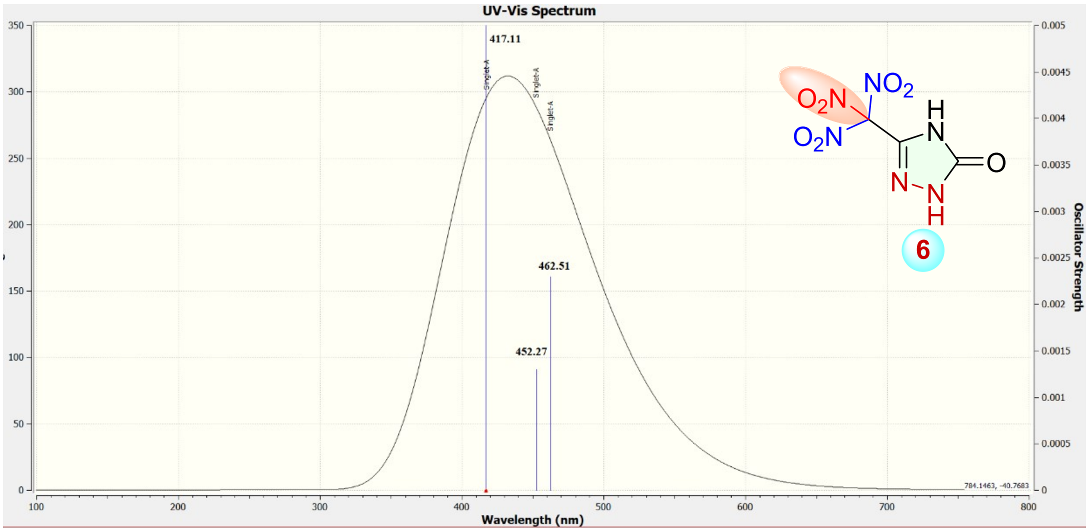


Fig. S4 Predicted UV-Visible spectrum of TNMTO at B3LYP/6-311++G(d,p) level.

EXPERIMENTAL SECTION

General Methods

All reagents and solvents were used as received unless otherwise specified (AKSci, Sigma-Aldrich, Acros Organics, VWR). The densities of the new compounds were measured at 25 °C with a Micromeritics Accupyc II 1340 gas pycnometer. Thermal stabilities (melting and decomposition points) were measured by heating individual samples from 35 to 400 °C at a heating rate of 5 °C min^{-1} and 10 °C min^{-1} on a Differential Scanning Calorimeter (DSC, TA Instruments Company, Model: Q2000) and thermogravimetric analysis (TGA, TA Instruments Company, Model: Q50). The FTIR spectra were recorded using KBr plates on a Thermo Nicolet AVATAR 370 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a 500 MHz (Brucker) nuclear magnetic resonance spectrometer operating at 500.19 and 125.77 MHz, respectively, using DMSO-d_6 as the solvent and locking solvent. The ^{15}N NMR spectra were recorded on a 500.19 MHz (Brucker 500) nuclear magnetic resonance operating at 50.70 MHz. As external standards, the chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) and nitromethane (^{15}N). Elemental analyses (C, H, N) were performed on a Vario Micro cube Elemental Analyser.

The crystals of compounds 6, 9 and 11.H_2O were mounted on a nylon loop with Paratone oil on an XtaLAB Synergy, Dualflex, HyPix diffractometer at 100 K. The structures were solved with the ShelXT[6-9] solution program using dual methods and Olex2.[10] The model was refined with ShelXL[6-9] using full matrix least squares minimization on F^2.

Caution!

The compounds studied are potentially high-energy materials. Therefore, it is strongly recommended that they should be synthesized in only small amounts and handled with extreme care.

5-(Trinitromethyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (6). Compound 10 (1.89 g, 10.0 mmol, 1.0 equiv.) was added in portions to pre-cooled 100% HNO_3 (18.9 g, 12.6 mL, 300.0 mmol, 30.0 equiv.), at -10 °C. The reaction mixture was maintained at that temperature for another 5 h. The HNO_3 was evaporated to leave a slightly yellow solid which was triturated with DCM to give pure 6 in excellent yield. White solid, 2.15 g, 90% yield, DSC (5 °C min^{-1}): $T_{d\ (onset)}$ = 80 °C. IR (KBr, υ, cm^{-1}) 3178 (s), 3053 (s), 2920 (s), 1715 (s), 1594 (s), 1476 (s), 1381 (s), 1278 (s), 1066 (s), 1031 (s), 944 (m), 803 (s), 777 (m), 735 (m); ^1H NMR (500.19 MHz, Acetone-d_6): δ 9.13 (br s, 1H), 12.35 (br s, 1H); ^{13}C NMR (125.77 MHz, CD_3CN): δ 125.8, 132.8, 155.1; Elemental analysis: calcd (%) for $C_3H_2N_6O_7$ (234.08): C 15.39, H 0.86, 35.90; found: C 15.30, H 1.46, N 34.77. The compound reacted slowly with CD_3CN, and acetone-d_6, reacted vigorously with D_2O, and DMSO-d_6 and subsequently decomposed with an exothermic reaction. It is stable in anhydrous DCM and $CHCl_3$ at room temperature however, TNMTO is partially soluble in DCM and $CHCl_3$.

2-(Dinitromethylene)-5,5-dinitro-2,5-dihydropyrimidine-4,6-diol (8). 4,6-Dihydroxy-2-methylpyrimidine 7 (8.0 g, 63.49 mmol, 1.0 equiv.) was added in portions to conc. H_2SO_4 (64.0

g, 24.0 mL, 65.30 mmol, 1.03 equiv.) at 0 °C. The mixture was cooled to -10 °C, and 100% HNO_3 (54.0 g, 36.0 mL, 85.71 mmol, 1.58 equiv.) was added. After 1.5 h, the white precipitate was filtered off, immediately washed with TFA (20 mL) and trifluoracetic anhydride (20 mL), and dried to give a white solid 8, Yield: 17.48 g, 90%, DSC (5 °C min^{-1}): $T_{d\ (onset)}$ = 86 °C. IR (KBr, υ, cm^{-1}) 3600 (s), 3518 (s), 3326 (s), 3197 (s), 3061 (s), 1628 (s), 1528 (s), 1401 (s), 1343 (s), 1290 (s), 1207 (s), 1154 (s), 1132 (s), 1037 (s), 895 (m), 812 (m), 794 (m), 747 (s), 724 (s); ^{1}H NMR (500.19 MHz, $CDCl_3$): δ 7.66 (br s, 2H); ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 98.8, 107.1, 125.0, 158.2. Elemental analysis: calcd (%) for $C_5H_2N_6O_{10}$ (306.10): C 19.62, H 0.66, 27.46; found: C 19.70, H 1.09, N 27.64.

Hydrazinium 3-dinitromethanide-1,2,4-triazolone (9). Compound 8 (4.590 g, 15.0 mmol, 1.0 equiv.) was added portion-wise to hydrazine hydrate (20 mL, 40% solution in water) at 0 °C. The resulting yellow mixture was stirred for another 5 h. The excess hydrazine was quenched with conc. HCl at 0°C, and the yellow precipitate was filtered off, washed with cold water, and dried to give pure 9 as a light-yellow solid. 2.85 g, 86%, DSC (5 °C min^{-1}): $T_{d\ (onset)}$ = 178 °C. IR (KBr, υ, cm^{-1}) 3342 (s), 3289 (s), 3068 (m), 2988 (m), 2882 (m), 2635 (m), 1721 (s), 1629 (m), 1575 (m), 1545 (m), 1509 (s), 1454 (m), 1419 (w), 1341 (m), 1247 (s), 1141 (s), 1102 (s), 1080 (m), 1041 (m), 965 (m), 746 (m), 680 (m); ^{1}H NMR (500.19 MHz, DMSO-d_6): δ 7.1 (br s, 5H), 11.21 (br s, 1H), 11.48 s, 1H); ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 124.6, 139.6, 156.3; Elemental analysis: calcd (%) for $C_3H_7N_7O_5$ (221.13): C 16.29, H 3.19, 44.34; found: C 16.22, H 3.14, N 44.34.

5-(Dinitromethyl)-2,4-dihydro-3H-1,2,4-triazol-3-one (10). Compound 9 (4.42 g, 20.0 mmol, 1.0 equiv.) was dissolved in acetonitrile (100 mL), and HCl (12M, 3.0 mL) was added at 0 °C. The resulting mixture was then heated at 60 °C for 1 h. The white precipitate was removed by filtration, washed with acetonitrile and the filtrate was dried under air to give compound 10 in pure form as a white solid, 3.0 g, 80%, DSC (5 °C min^{-1}): $T_{d\ (onset)}$ = 88 °C. IR (KBr, υ, cm^{-1}) 3175 (s), 3034 (s), 2954 (s), 1744 (s), 1697 (s), 1596 (s), 1515 (m), 1487 (m), 1383 (m), 1366 (m), 1325 (s), 1292 (m), 1235 (s), 1201 (s), 1127 (s), 1093 (s), 1039 (m), 1011 (m), 821 (m), 778 (m), 744 (m); ^{1}H NMR (500.19 MHz, acetone-d_6): δ 8.06 (s, 1H), 11.75 (s, 1H); ^{13}C NMR (125.77 MHz, acetone-d_6): δ 105.1, 134.9, 155.9; Elemental analysis: calcd (%) for $C_3H_3N_5O_5$ (189.09): C 19.06, H 1.60, 37.04; found: C 19.98, H 2.09, N 37.74.

Ammonium-6-(dinitromethylene)-1l²,3,5-triazinane-2,4-dione (11.H_2O). Compound 8 (4.590 g, 15.0 mmol, 1.0 equiv.) was added portion-wise to aqueous NH_3 (25 mL, 30% solution in water) at 0 °C. The resulting yellow mixture was stirred for 6 h. The yellow precipitate was filtered, washed with CH_3CN, and dried to give pure 11.H_2O as a light-yellow solid (3.48 g, 92%), DSC (5 °C min^{-1}): $T_{d\ (onset)}$ = 200 °C. IR (KBr, υ, cm^{-1}); ^{1}H NMR (500.19 MHz, DMSO-d_6): δ 6.64 (br s, 4H); ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 133.0, 157.5, 161.6; Elemental analysis: calcd (%) for $C_4H_8N_6O_7$ (252.14): C 19.05, H 3.20, 33.30; found: C 19.76, H 3.30, N 33.28.

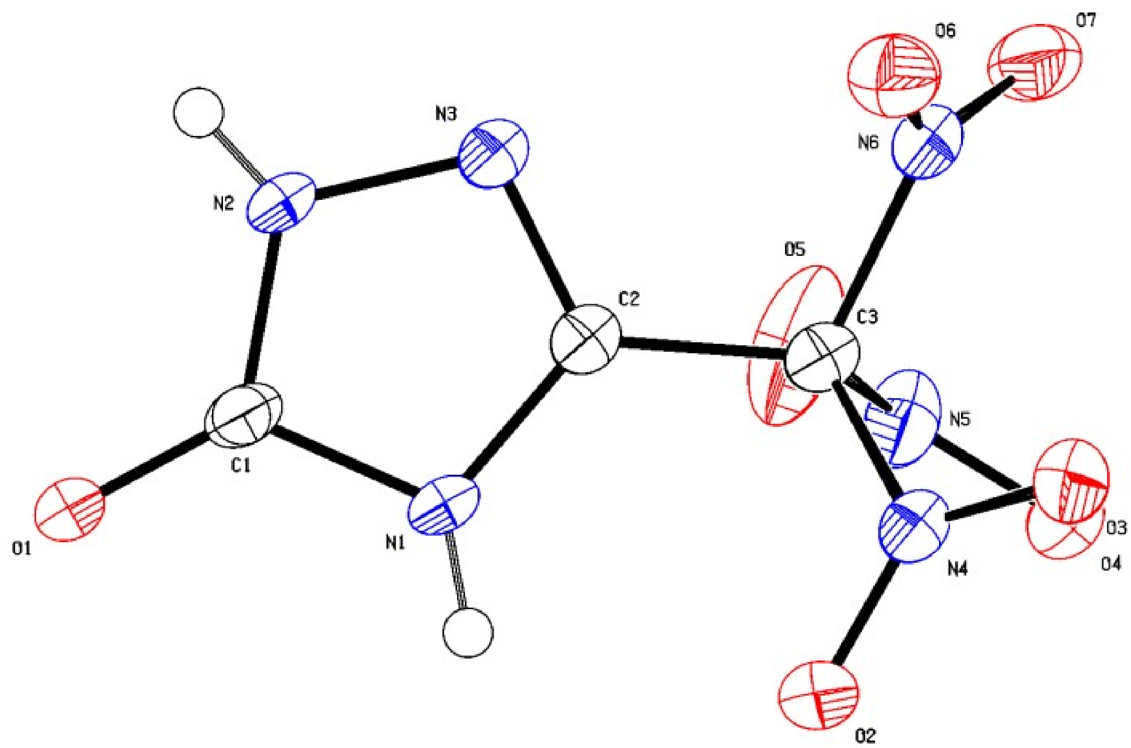


Fig. S5 Single crystal X-ray structure of TNMTO. Drawing at 50% ellipsoids with hetro-atoms labelled and the hydrogen atoms found and refined isotropically.

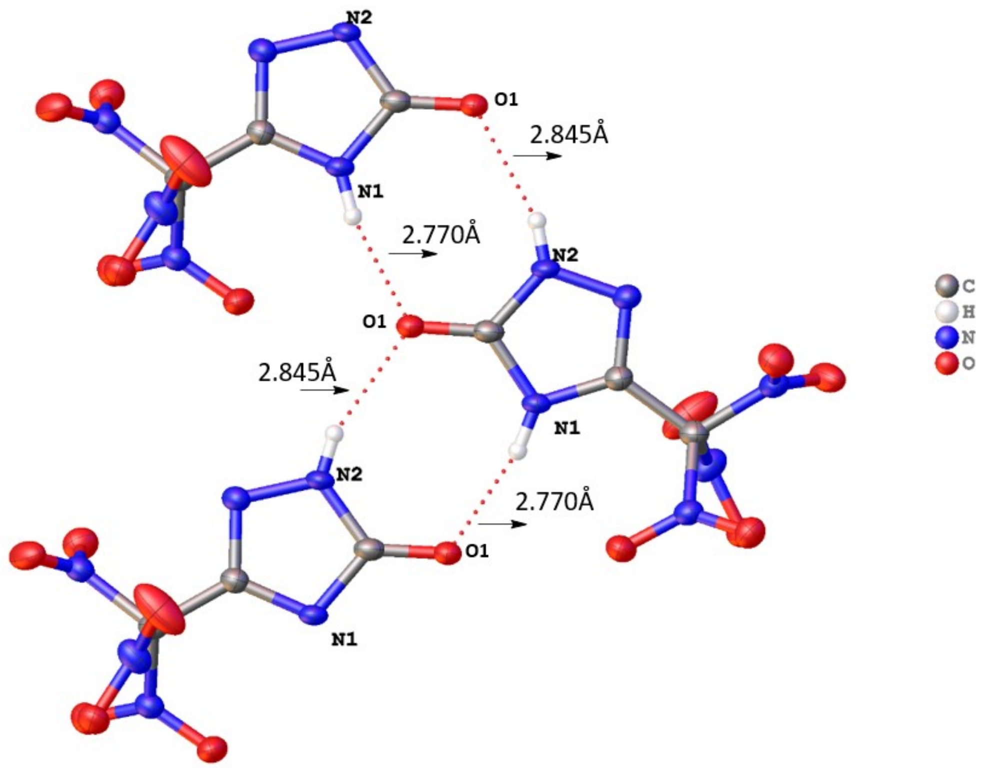


Fig. S6 The following hydrogen bonding interactions with a maximum D-D distance of 3.1 Å and a minimum angle of 110 ° are present in TNMTO: N1–O1_*1: 2.77 Å, N2–O1*_2: 2.845 Å.

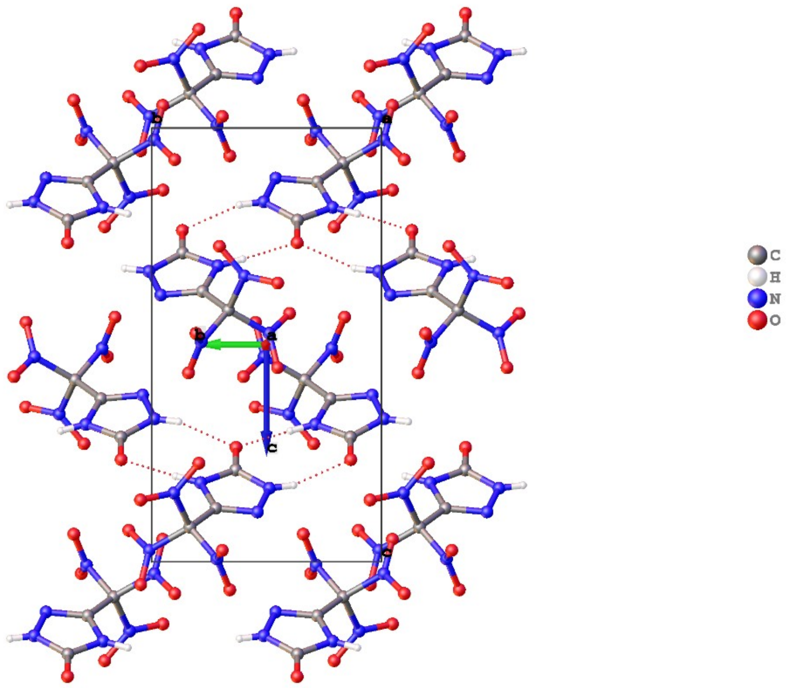


Fig. S7 Packing diagram of TNMTO viewed along a axis

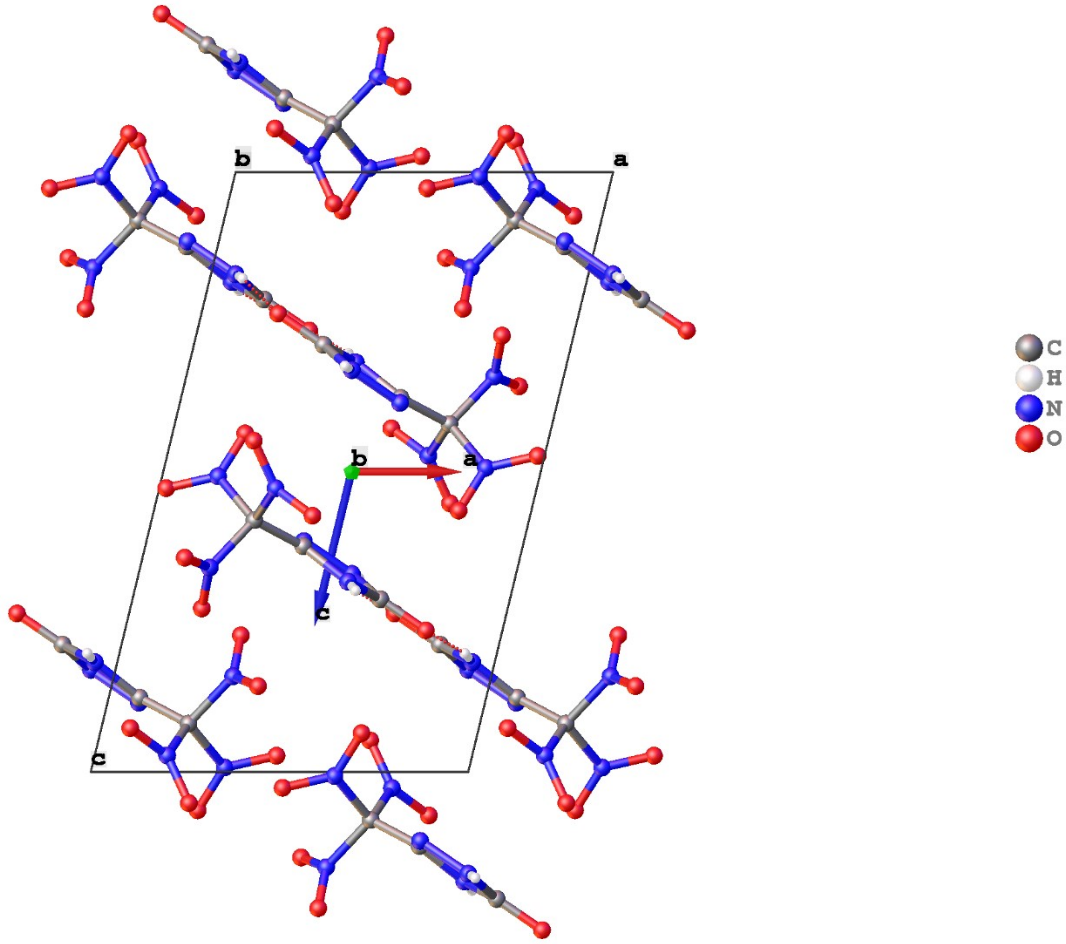


Fig. S8 Packing diagram of TNMTO viewed along the b axis

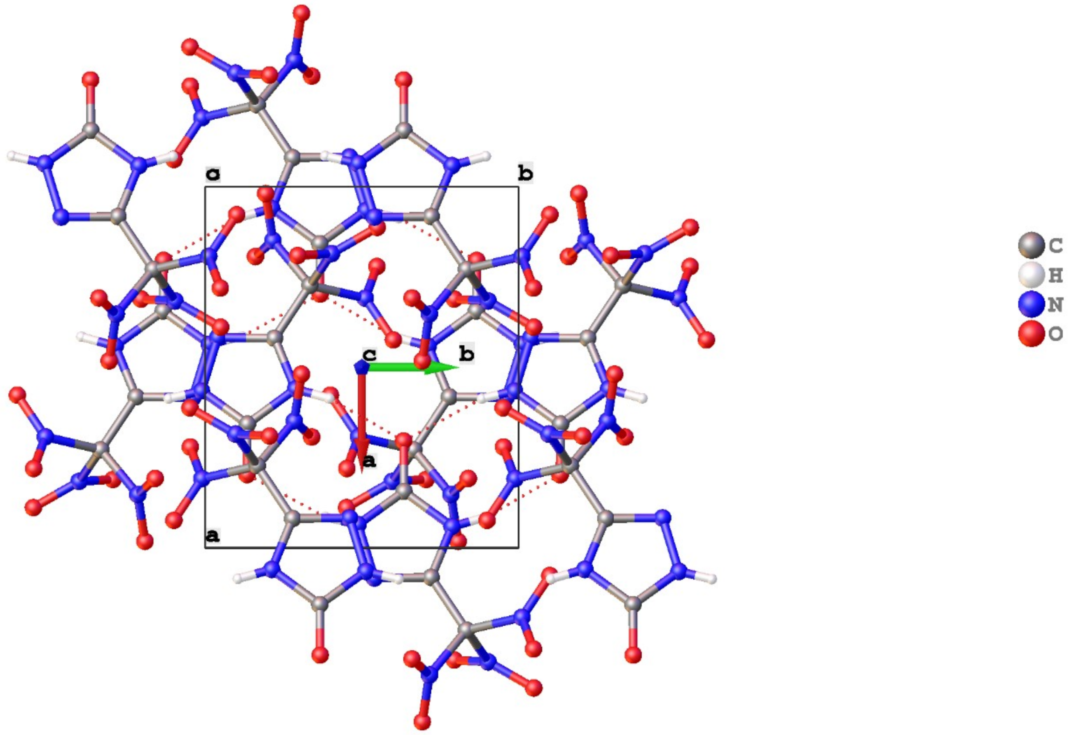


Fig. S9 Packing diagram of TNMTO viewed along the c axis

Table S4: Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for TNMTO. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	2032.7(17)	8668.2(19)	2359.4(11)	25.5(4)
O2	5765.4(18)	3997(2)	4271.4(13)	34.2(4)
O3	7798.8(17)	4521(2)	5522.7(12)	30.0(4)
O4	8881.4(18)	4511(2)	3571.0(13)	31.8(4)
O5	8103(3)	7051(3)	2724.6(16)	59.3(7)
O6	8074.7(19)	8398(2)	5643.1(12)	34.2(4)
O7	9816.7(19)	8072(2)	4732.0(15)	38.4(4)
N1	4405(2)	7122(2)	3172.0(13)	23.1(4)
N2	4351(2)	10124(3)	3300.4(14)	24.1(4)
N3	5833(2)	9602(2)	3847.3(14)	25.5(4)
N4	6920(2)	4891(2)	4729.3(14)	26.5(4)
N5	8157(2)	5966(3)	3407.7(15)	32.7(4)
N6	8519(2)	7842(3)	4929.8(15)	28.0(4)
C1	3433(2)	8655(3)	2877.9(16)	23.4(4)
C2	5814(2)	7789(3)	3762.2(16)	23.3(4)
C3	7277(2)	6660(3)	4196.4(16)	25.3(4)

Table S5: Bond Lengths in Å for TNMTO.

Atom	Atom	Length/Å
O1	C1	1.238(3)
O2	N4	1.216(2)
O3	N4	1.206(2)
O4	N5	1.200(2)
O5	N5	1.216(3)
O6	N6	1.207(3)
O7	N6	1.208(2)
N1	C1	1.373(3)
N1	C2	1.368(3)
N2	N3	1.361(2)
N2	C1	1.355(3)
N3	C2	1.297(3)
N4	C3	1.528(3)
N5	C3	1.545(3)
N6	C3	1.535(3)
C2	C3	1.484(3)

Table S6: Bond Angles in ° for TNMTO.

Atom	Atom	Atom	Angle/°
C2	N1	C1	106.41(17)
C1	N2	N3	113.16(17)
C2	N3	N2	103.42(16)
O2	N4	C3	113.98(17)
O3	N4	O2	127.85(19)
O3	N4	C3	118.16(17)
O4	N5	O5	128.3(2)
O4	N5	C3	117.07(18)
O5	N5	C3	114.42(18)
O6	N6	O7	128.3(2)
O6	N6	C3	115.19(17)
O7	N6	C3	116.49(19)
O1	C1	N1	127.48(19)
O1	C1	N2	128.54(19)
N2	C1	N1	103.97(17)
N1	C2	C3	125.92(18)
N3	C2	N1	113.01(17)
N3	C2	C3	120.78(18)
N4	C3	N5	105.24(16)
N4	C3	N6	108.38(16)
N6	C3	N5	105.88(16)
C2	C3	N4	113.67(17)
C2	C3	N5	112.59(18)
C2	C3	N6	110.62(17)

Table S7: Torsion Angles in ° for TNMTO.

Atom	Atom	Atom	Atom	Angle/°
O2	N4	C3	N5	-78.3(2)
O2	N4	C3	N6	168.83(17)
O2	N4	C3	C2	45.4(2)
O3	N4	C3	N5	100.4(2)
O3	N4	C3	N6	-12.5(2)
O3	N4	C3	C2	-135.9(2)
O4	N5	C3	N4	-25.9(2)
O4	N5	C3	N6	88.8(2)
O4	N5	C3	C2	-150.24(19)
O5	N5	C3	N4	158.6(2)
O5	N5	C3	N6	-86.7(2)
O5	N5	C3	C2	34.3(3)
O6	N6	C3	N4	-62.5(2)
O6	N6	C3	N5	-175.03(17)
O6	N6	C3	C2	62.7(2)
O7	N6	C3	N4	116.32(19)
O7	N6	C3	N5	3.8(2)
O7	N6	C3	C2	-118.4(2)
N1	C2	C3	N4	-49.9(3)
N1	C2	C3	N5	69.7(3)
N1	C2	C3	N6	-172.09(19)
N2	N3	C2	N1	1.2(2)
N2	N3	C2	C3	175.43(19)
N3	N2	C1	O1	178.4(2)
N3	N2	C1	N1	-0.5(2)
N3	C2	C3	N4	136.6(2)
N3	C2	C3	N5	-103.8(2)
N3	C2	C3	N6	14.4(3)
C1	N1	C2	N3	-1.5(2)
C1	N1	C2	C3	-175.4(2)
C1	N2	N3	C2	-0.4(2)
C2	N1	C1	O1	-177.8(2)
C2	N1	C1	N2	1.2(2)

Table S8: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TNMTO. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

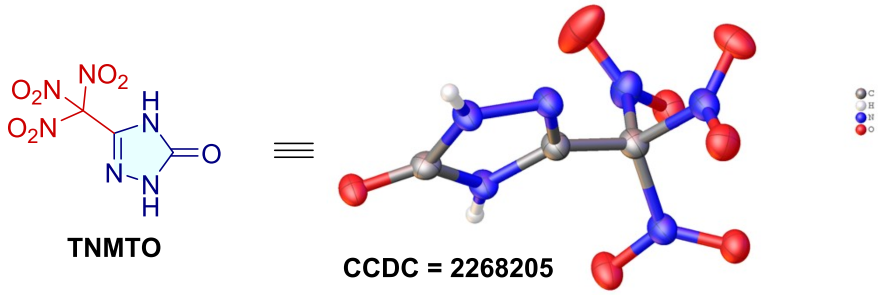
Atom	x	y	z	U_{eq}
H1	4150(30)	6040(50)	3020(20)	36(8)
H2	4140(30)	11170(50)	3230(20)	33(8)

Table S9: Hydrogen Bond information for TNMTO.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N1	H1	O1^1	0.81(3)	1.97(3)	2.770(2)	166(3)
N2	H2	O1^2	0.77(3)	2.11(3)	2.845(2)	161(3)

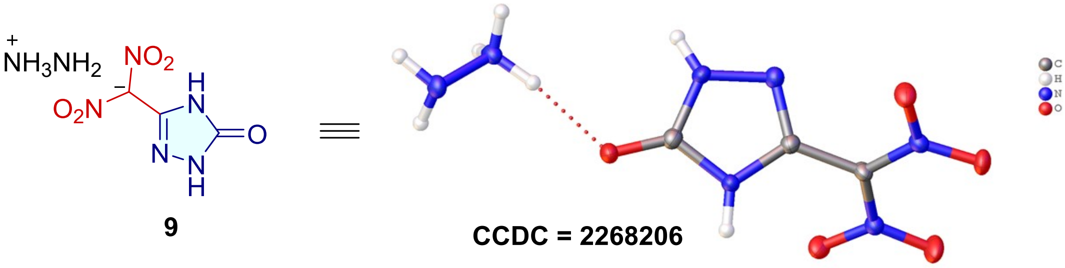
^{1}1/2-x,-1/2+y,1/2-z; ^{2}1/2-x,1/2+y,1/2-z

Table S10. Single crystal X-ray data and structure refinement for TNMTO.[6-10]



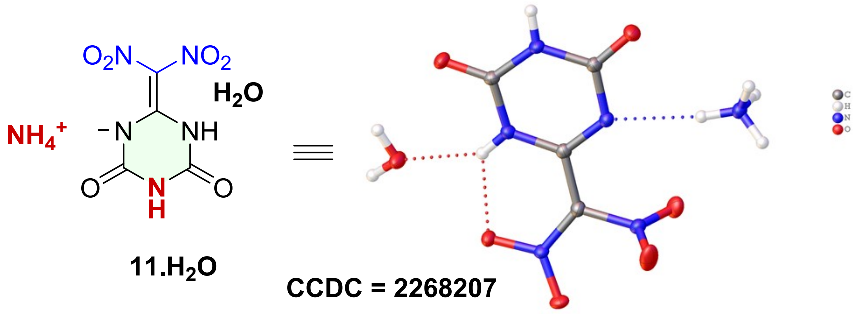
Formula	$C_3H_2N_6O_7$ (CCDC = 2268205)
$D_{calc.}$/ g cm^{-3}	1.902
m/mm^{-1}	1.682
Formula Weight	234.11
Colour	yellow
Shape	needle-shaped
Size/mm^3	0.11×0.04×0.02
T/K	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	8.4982(2)
b/Å	7.1276(2)
c/Å	13.8819(4)
a/°	90
b/°	103.573(3)
g/°	90
V/Å^3	817.37(4)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	5.585
Q_{max}/°	80.393
Measured Refl's.	8681
Indep't Refl's	1751
Refl's I≥2 s(I)	1461
R_{int}	0.0436
Parameters	153
Restraints	0
Largest Peak	0.488
Deepest Hole	-0.402
GooF	1.055
wR_2 (all data)	0.1356
wR_2	0.1274
R_1 (all data)	0.0551
R_1	0.0459

Table S11. Single crystal X-ray data and structure refinement for compound 9.[6-10]



Formula	$C_3H_7N_7O_5$ (CCDC = 2268206)
$D_{calc.}$/ g cm^{-3}	1.899
μ/mm^{-1}	1.554
Formula Weight	221.16
Colour	yellow
Shape	needle-shaped
Size/mm^3	0.17×0.02×0.01
T/K	100.15
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	3.63691(18)
b/Å	17.1203(9)
c/Å	12.4539(6)
$\alpha/^\circ$	90
$\beta/^\circ$	94.177(4)
$\gamma/^\circ$	90
V/Å^3	773.38(7)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
$\Theta_{min}/^\circ$	4.398
$\Theta_{max}/^\circ$	81.103
Measured Refl's.	8241
Indep't Refl's	1657
Refl's I≥2 σ(I)	1318
R_{int}	0.0797
Parameters	164
Restraints	0
Largest Peak	0.325
Deepest Hole	-0.318
GooF	1.077
wR_2 (all data)	0.1229
wR_2	0.1107
R_1 (all data)	0.0623
R_1	0.0452

Table S12. Single crystal X-ray data and structure refinement for compound 11.H_2O.[6-10]



Formula	$C_4H_8N_6O_7$ (CCDC = 2268207)
$D_{calc.}$/ g cm^{-3}	1.788
m/mm^{-1}	1.507
Formula Weight	252.16
Colour	yellow
Shape	block-shaped
Size/mm^3	0.11×0.07×0.06
T/K	100.00(10)
Crystal System	monoclinic
Flack Parameter	0.6(4)
Hooft Parameter	0.2(2)
Space Group	*Ia*
a/Å	8.26070(10)
b/Å	9.13530(10)
c/Å	12.5011(2)
a/°	90
b/°	96.6790(10)
g/°	90
V/Å^3	936.98(2)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	6.014
Q_{max}/°	80.141
Measured Refl's.	5189
Indep't Refl's	1465
Refl's I≥2 s(I)	1424
R_{int}	0.0309
Parameters	187
Restraints	2
Largest Peak	0.148
Deepest Hole	-0.218
GooF	1.065
wR_2 (all data)	0.0765
wR_2	0.0756
R_1 (all data)	0.0295
R_1	0.0286

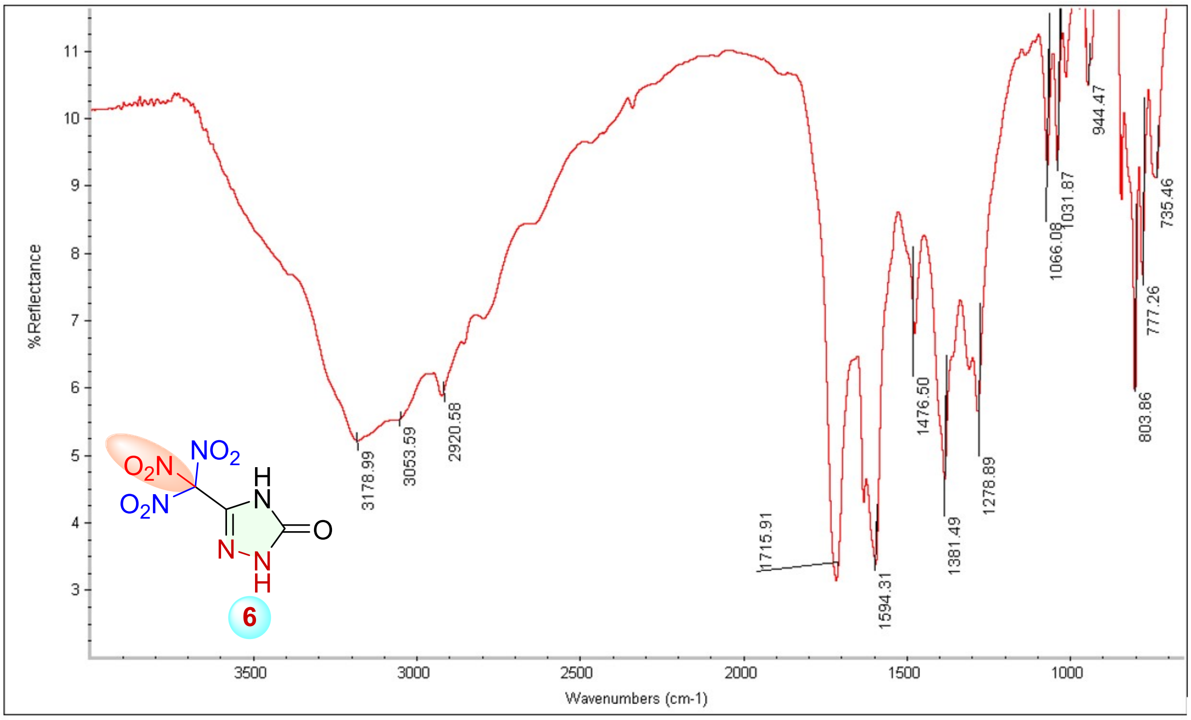


Fig. S10 FTIR-Spectrum of Compound 6.

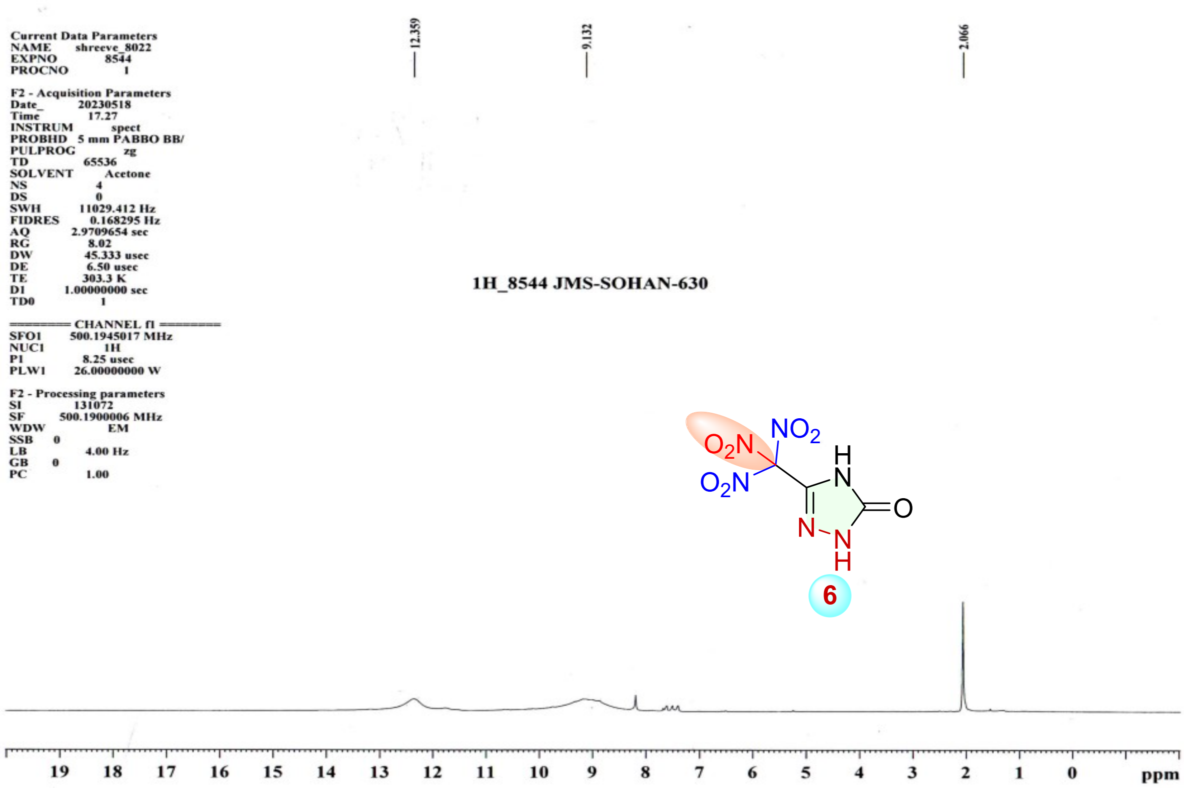


Fig. S11 ^{1}H NMR Spectrum of Compound 6 (500.19 MHz).

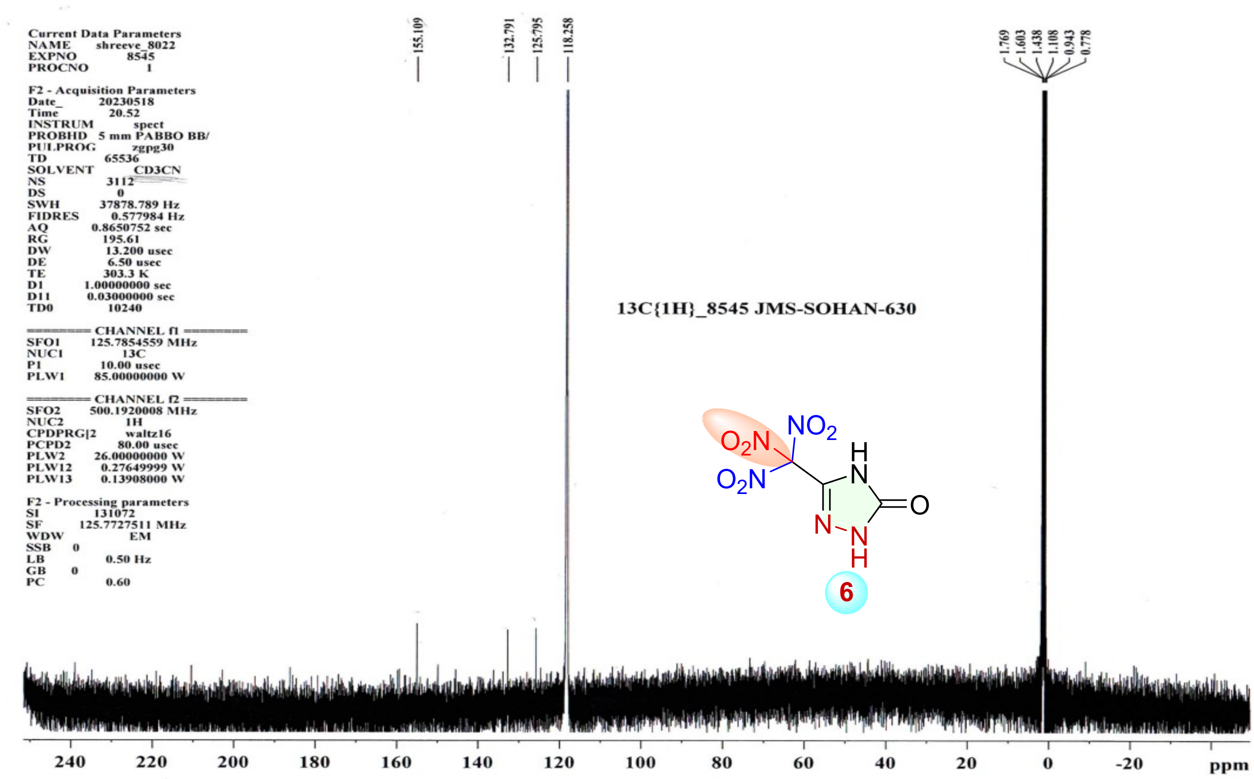


Fig. S12 ^{13}C NMR Spectrum of Compound 6 (125.77 MHz).

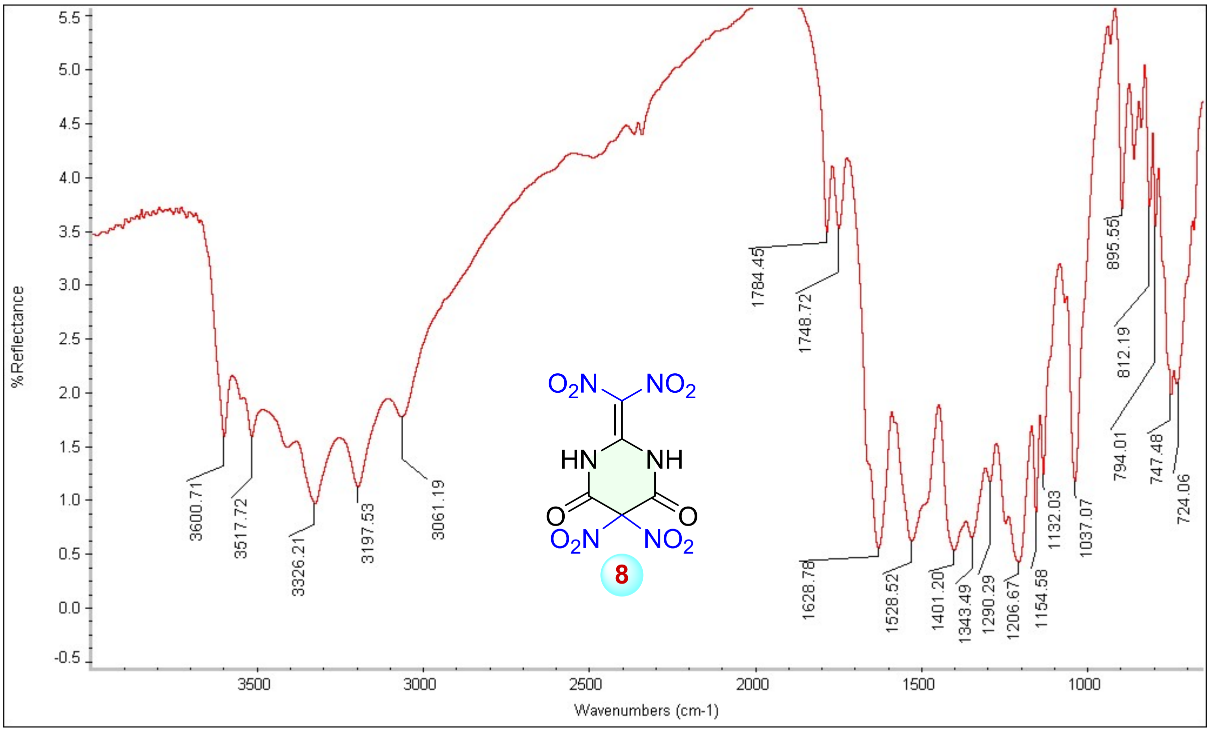


Fig. S13 FTIR-Spectrum of Compound 8.

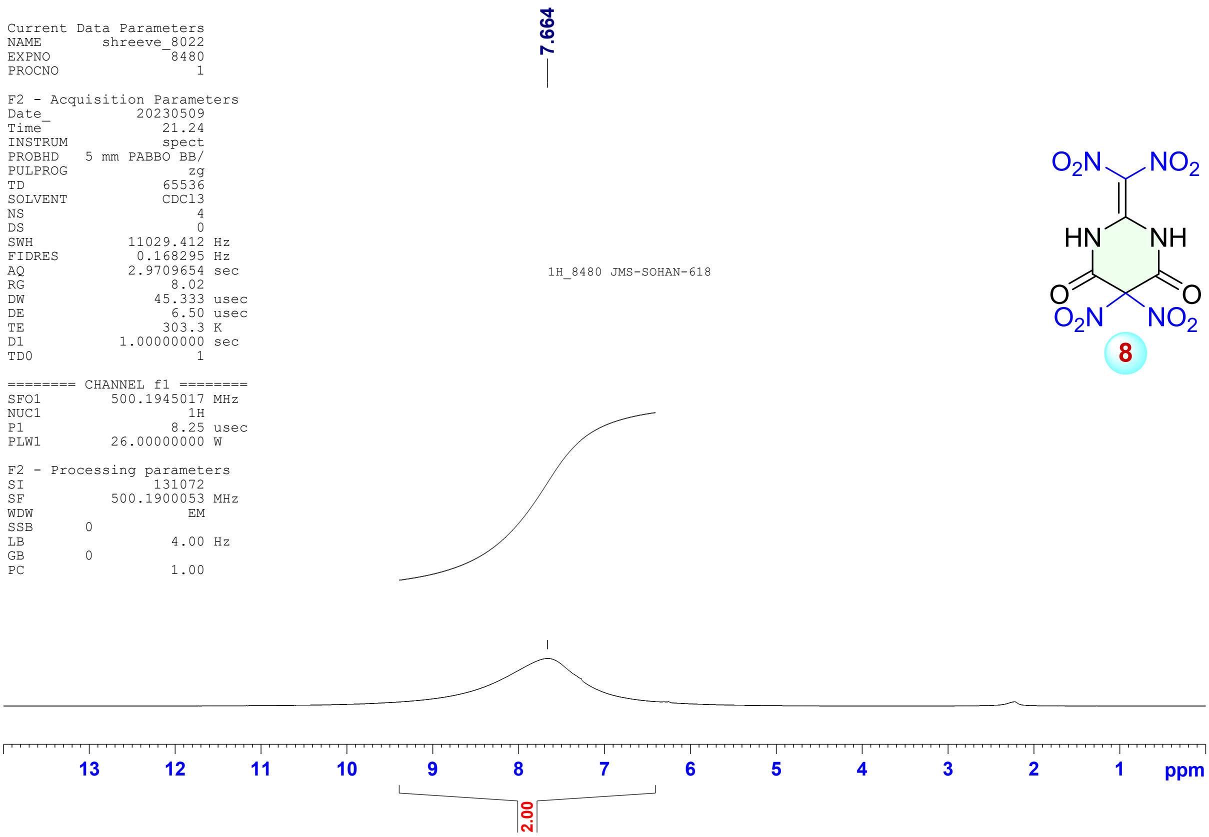


Fig. S14 ^{1}H NMR Spectrum of Compound 8 (500.19 MHz).

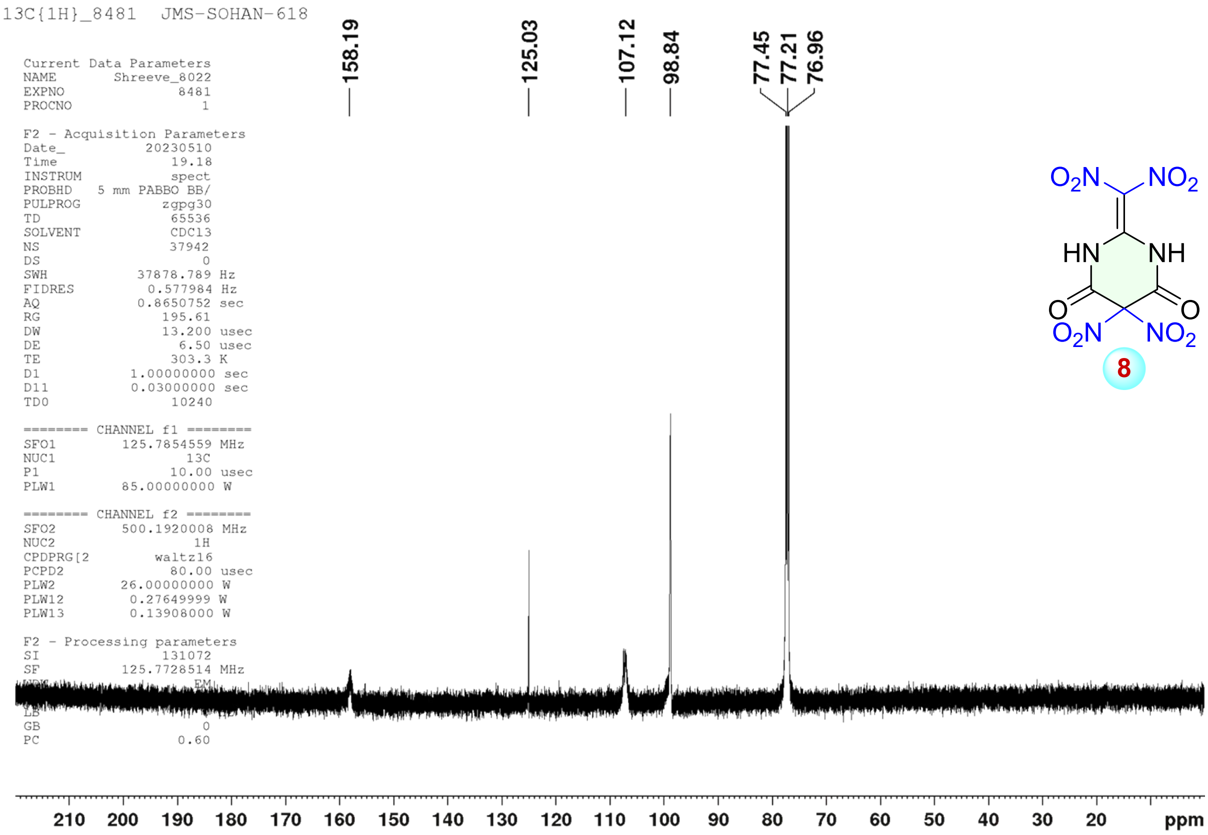


Fig. S15 ^{13}C NMR Spectrum of Compound 8 (125.77 MHz).

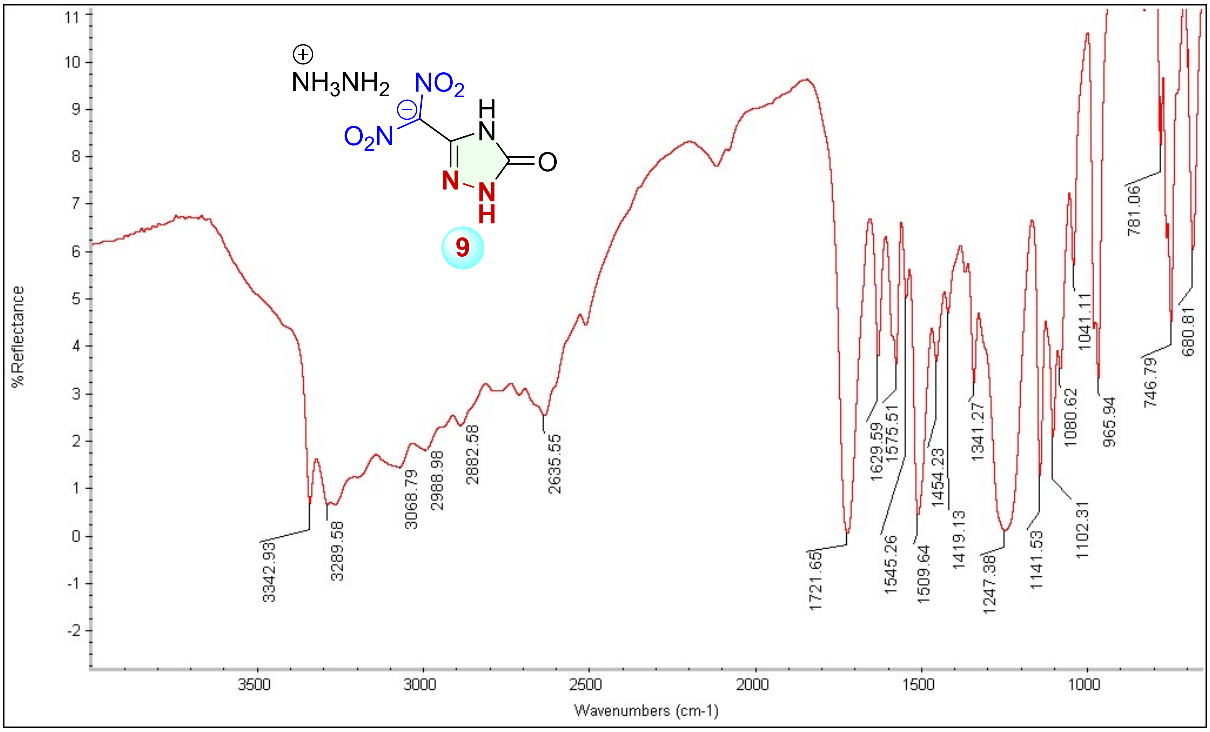


Fig. S16 FTIR-Spectrum of Compound 9.

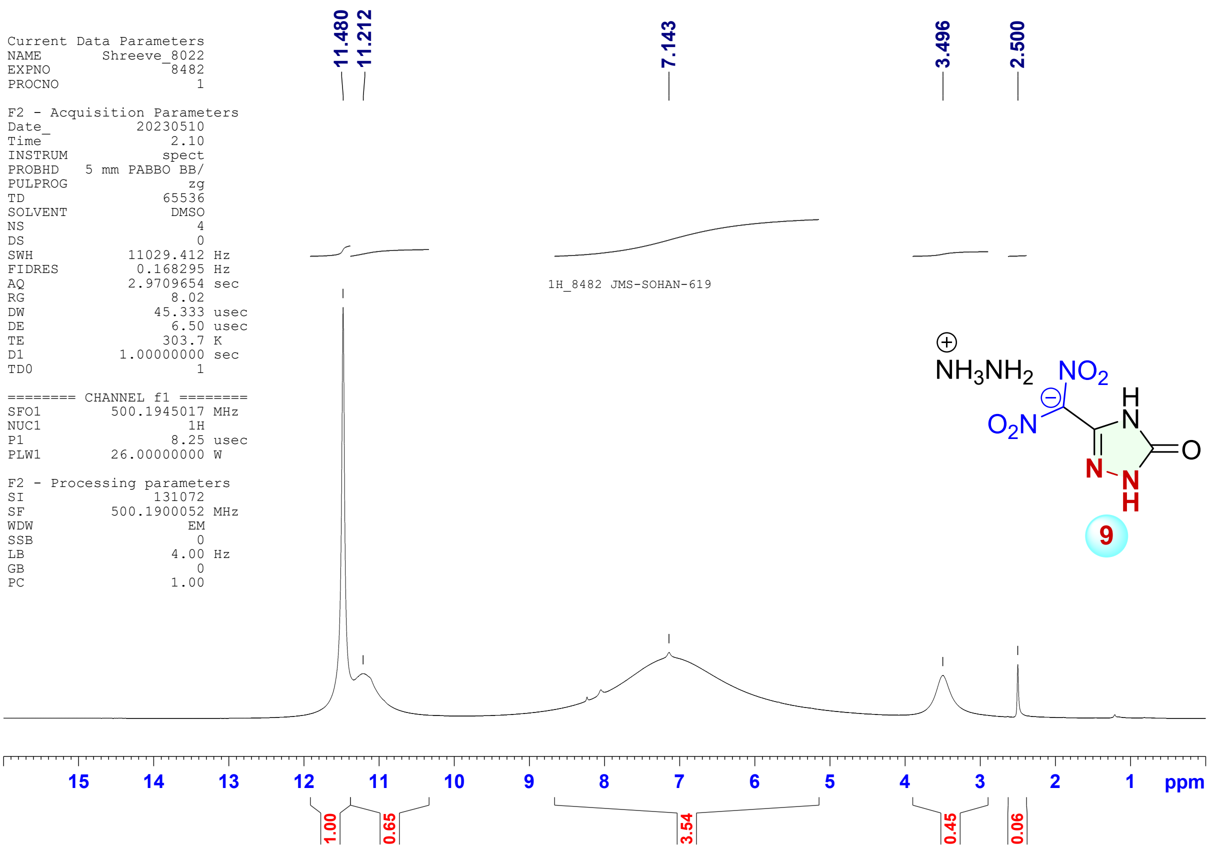


Fig. S17 [1]H NMR Spectrum of Compound 9 (500.19 MHz).

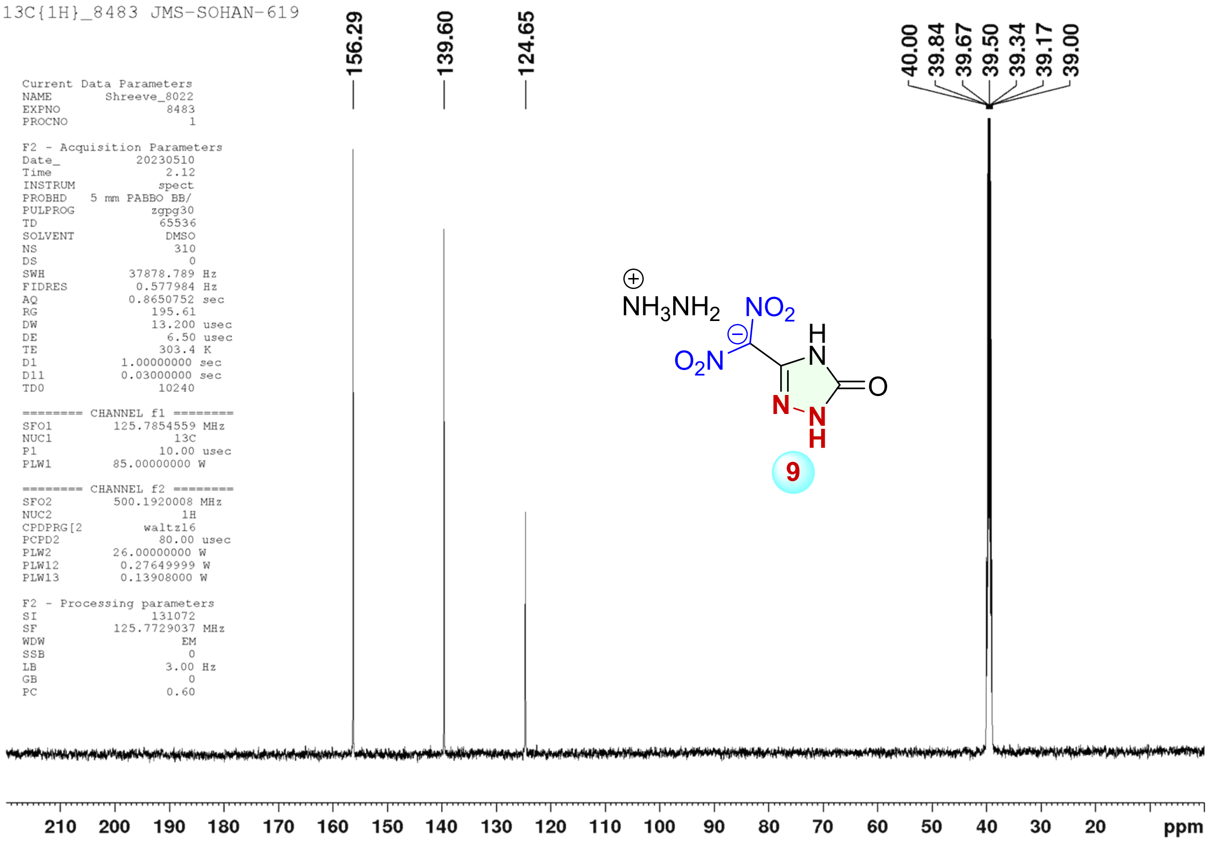


Fig. S18 ^{13}C NMR Spectrum of Compound 9 (125.77 MHz).

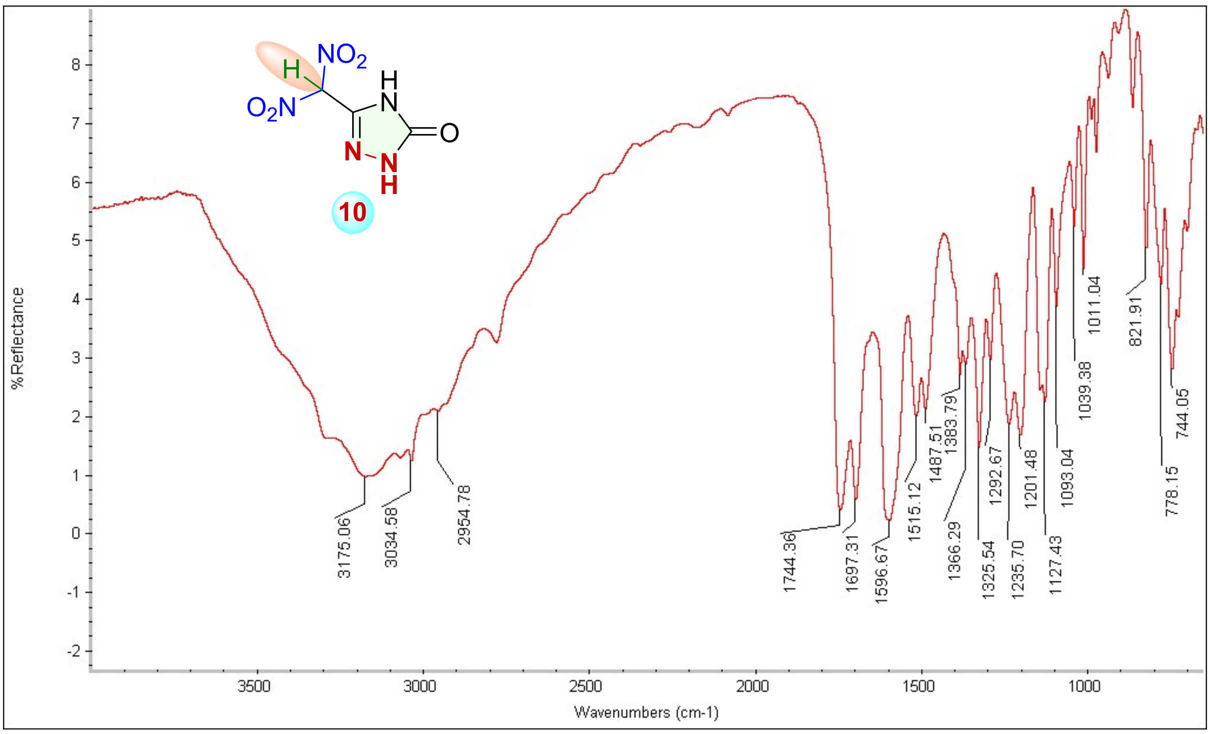


Fig. S19 FTIR-Spectrum of Compound 10.

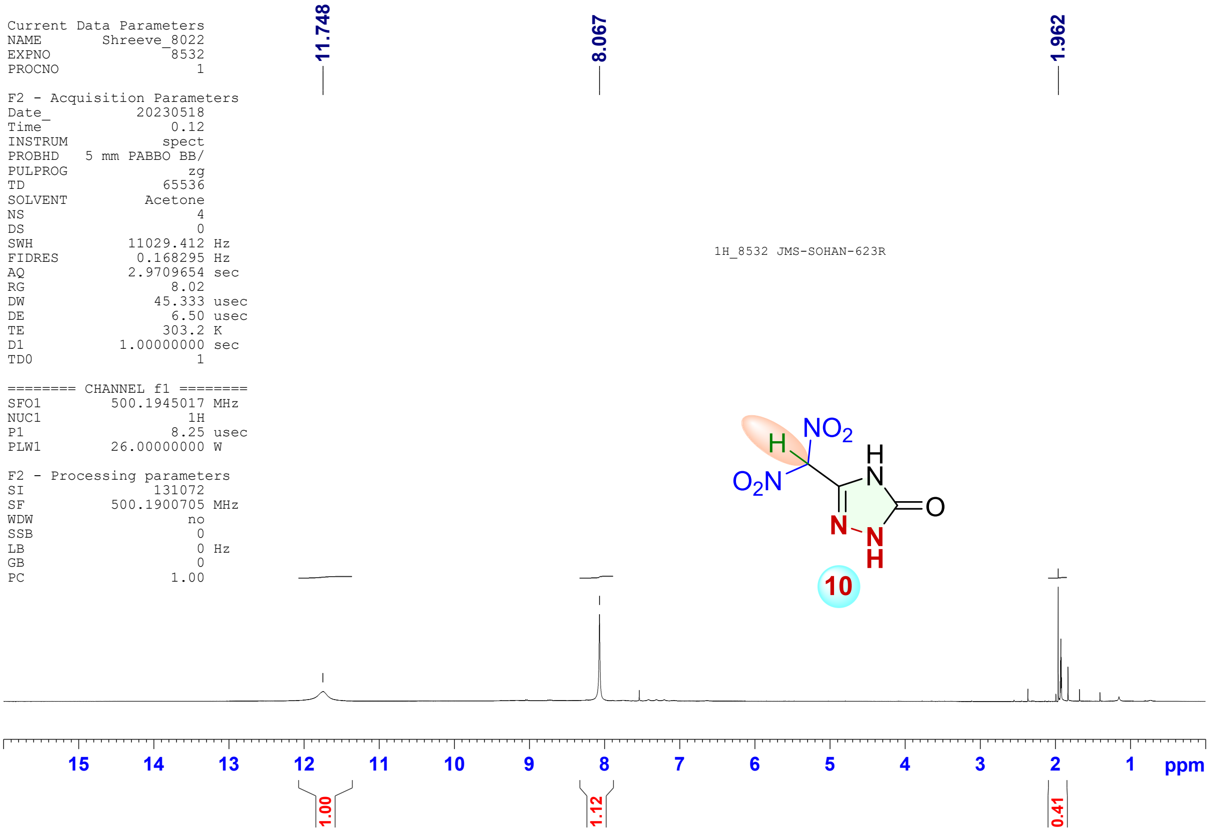


Fig. S20 ^{1}H NMR Spectrum of Compound 10 (500.19 MHz).

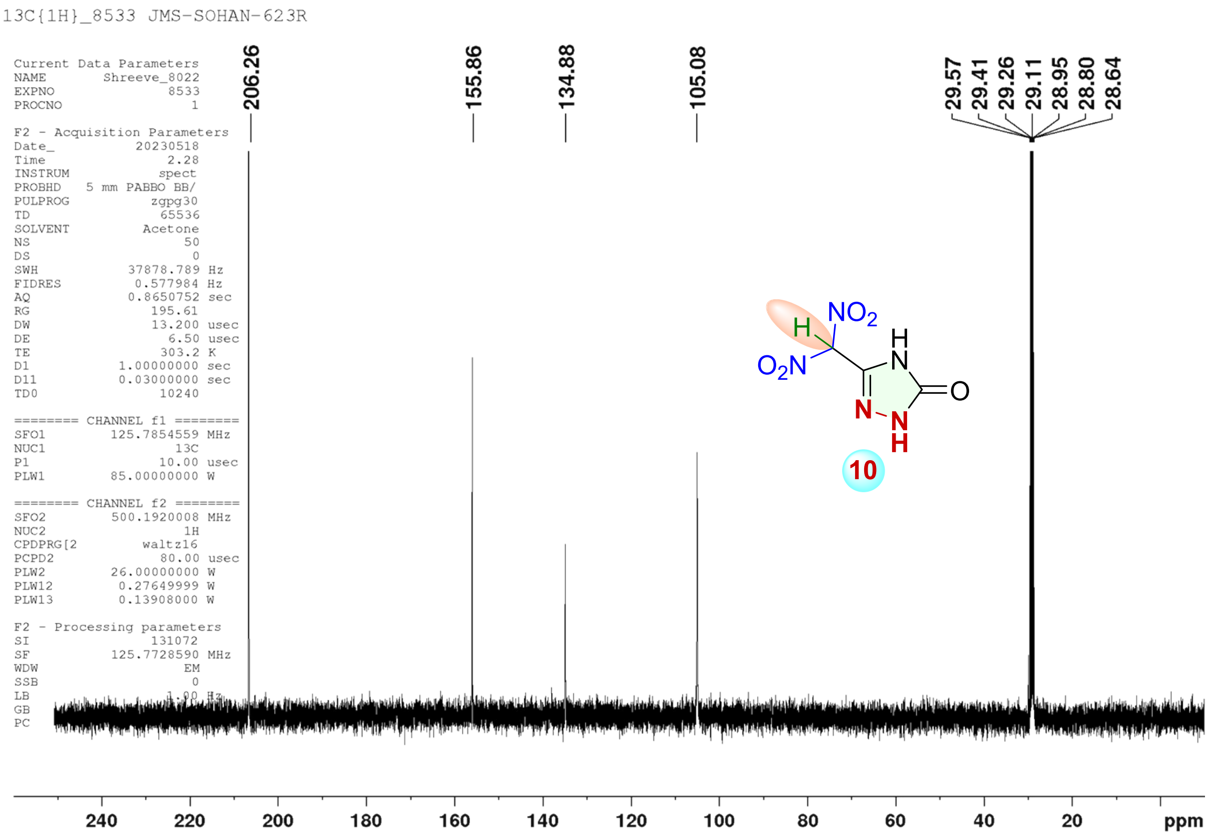


Fig. S21 ^{13}C NMR Spectrum of Compound 10 (125.77 MHz).

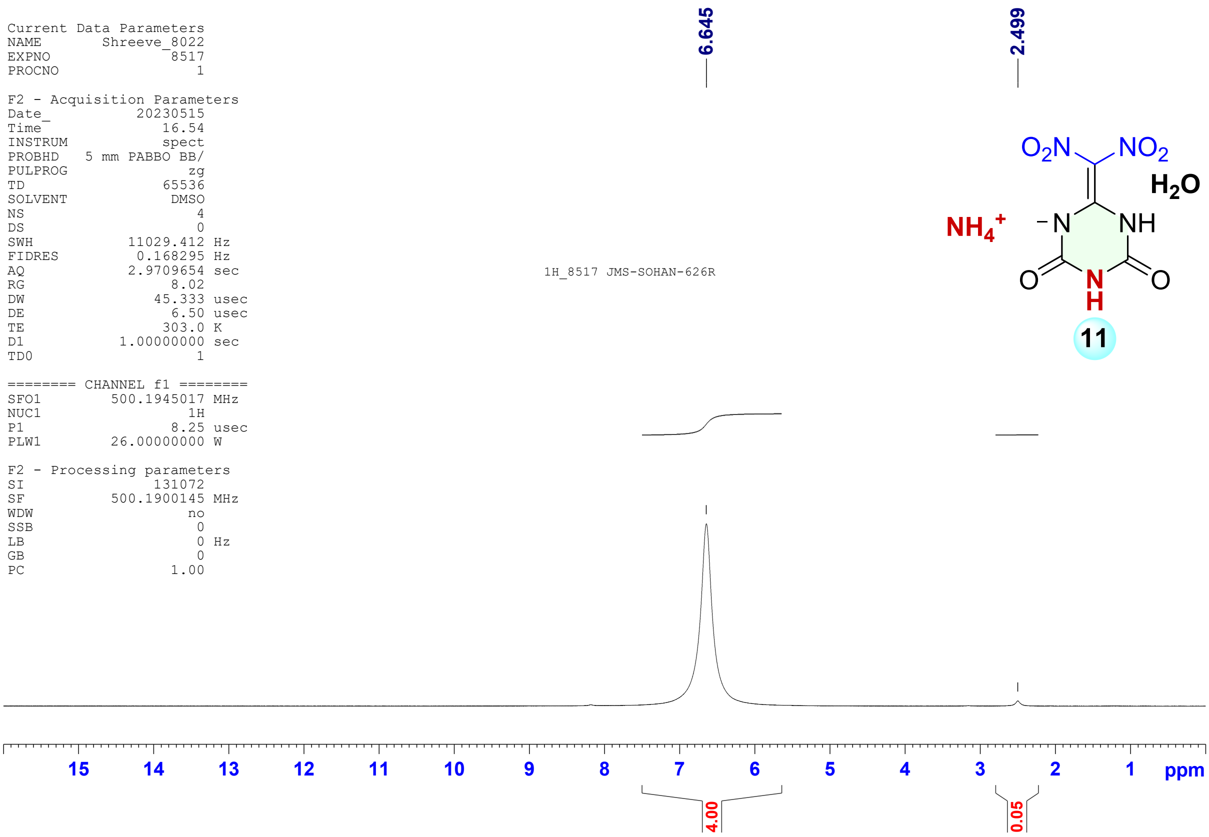


Fig. S22 ^{1}H NMR Spectrum of Compound 11.H_2O (500.19 MHz).

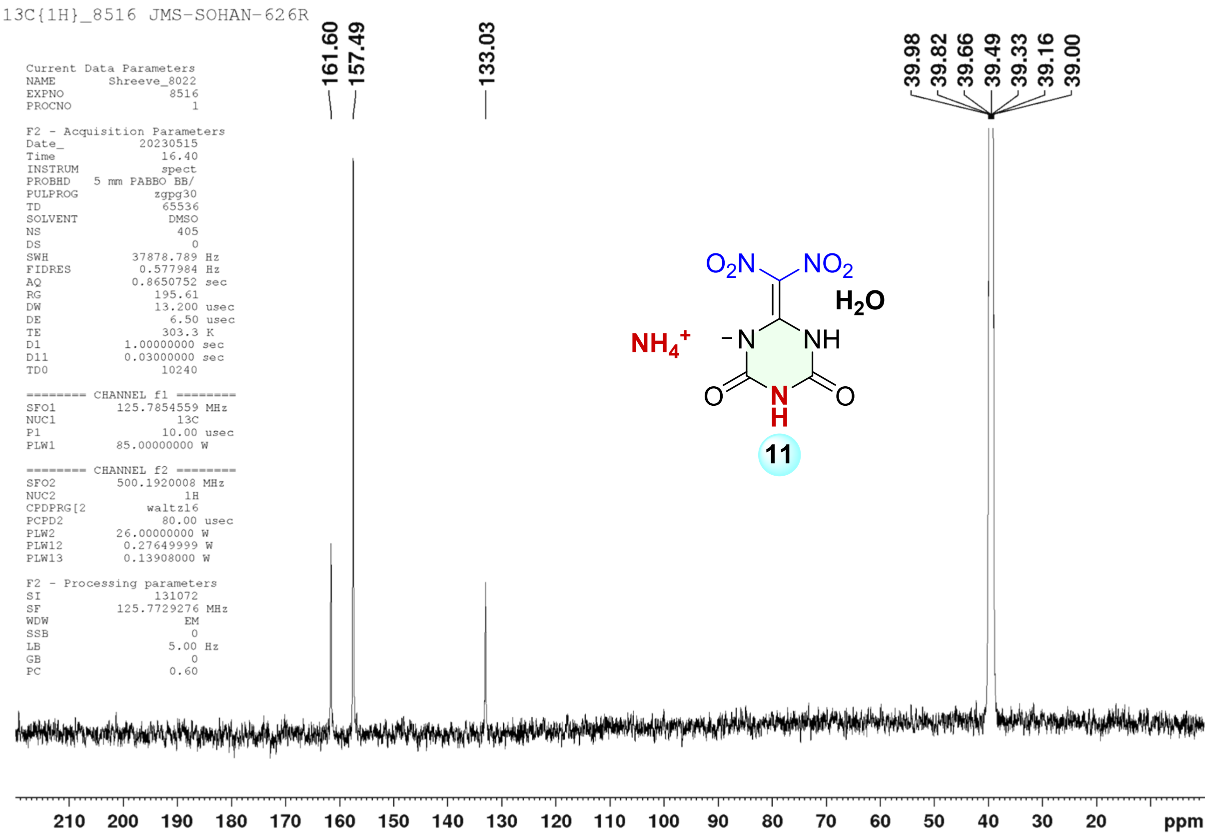


Fig. S23 ^{13}C NMR Spectrum of Compound 11.H_2O (125.77 MHz).

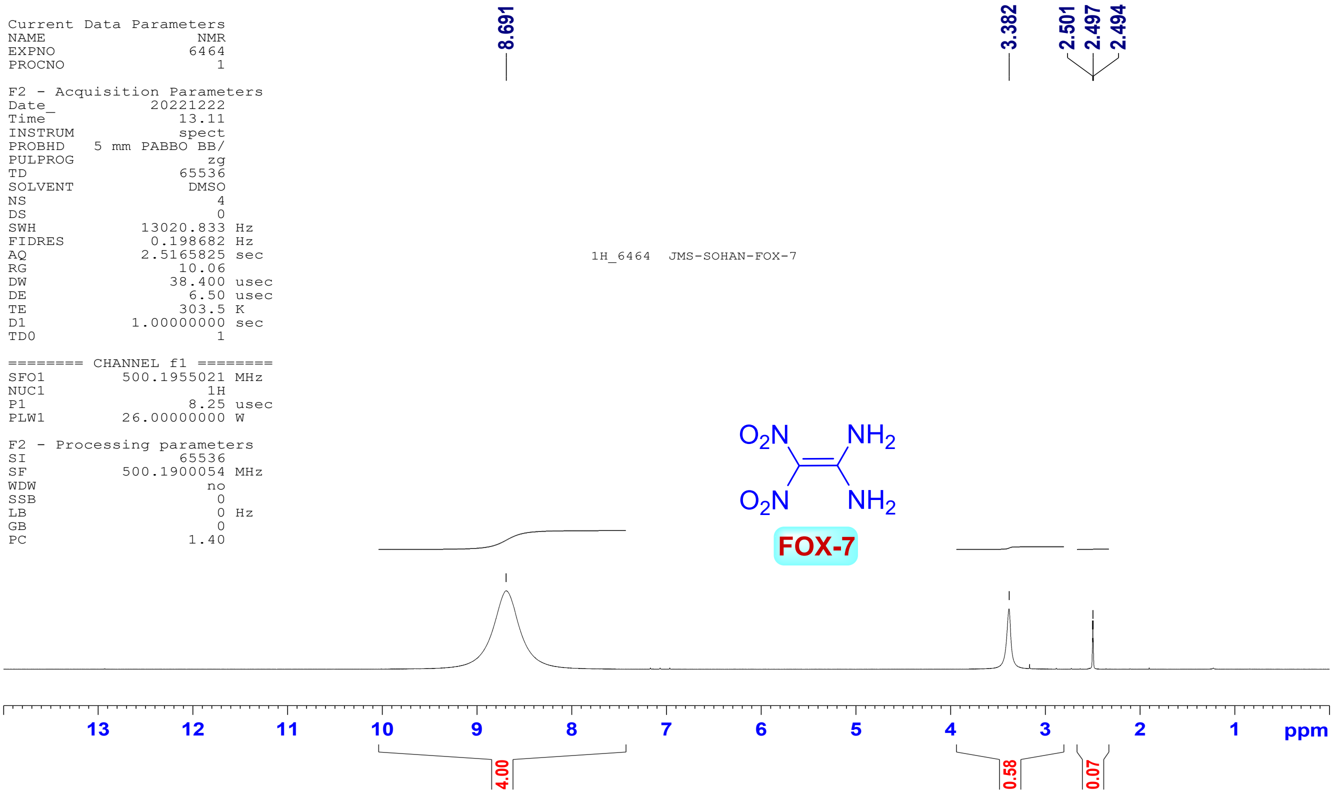


Fig. S24 ^{1}H NMR Spectrum of FOX-7 (500.19 MHz).

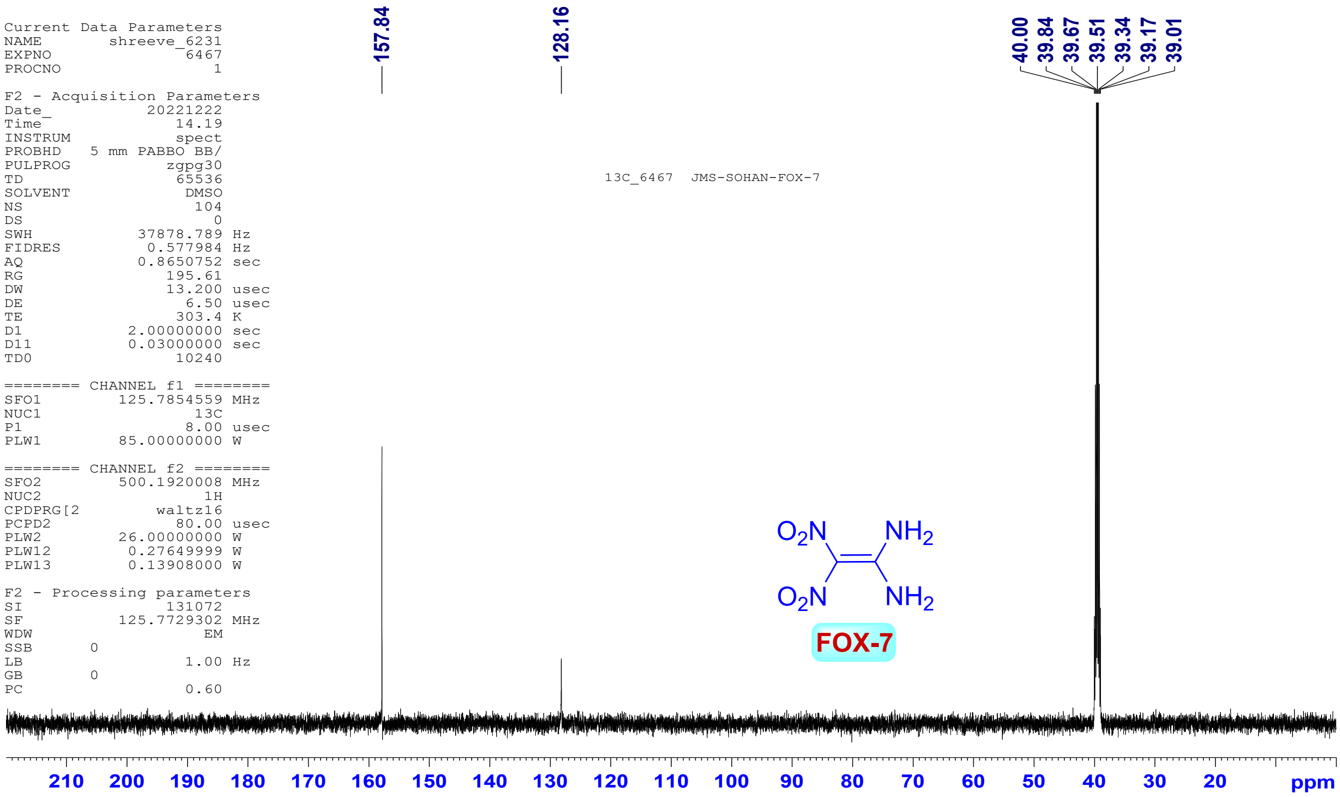


Fig. S25 ^{13}C NMR Spectrum of FOX-7 (125.77 MHz).

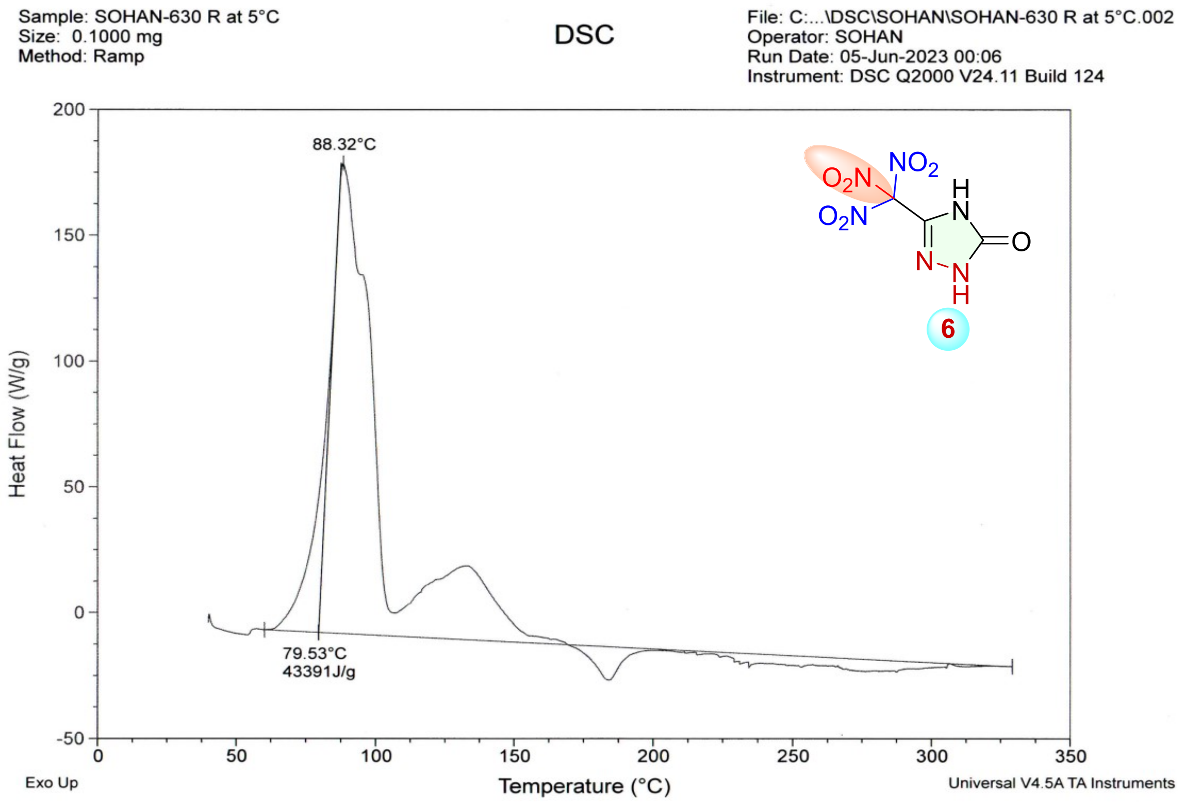


Fig. S26 DSC of compound 6 at 5 °C min^{-1}

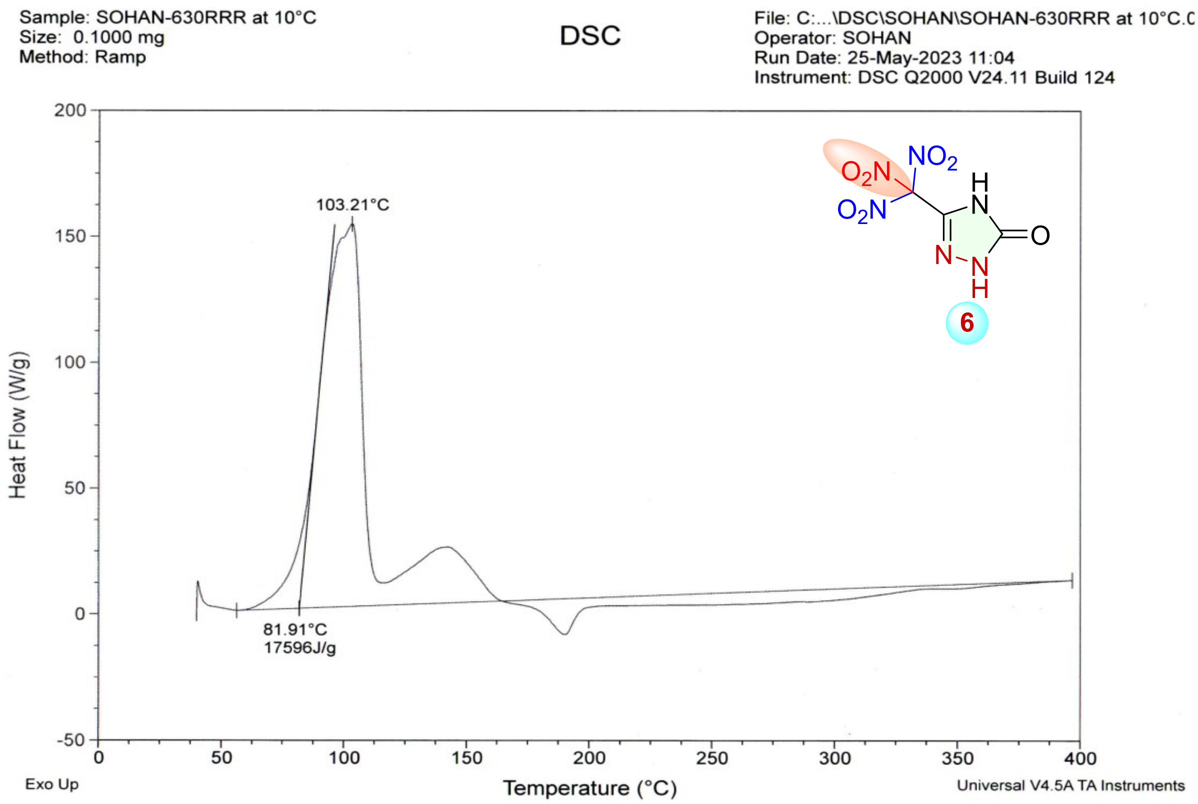


Fig. S27 DSC of compound 6 at 10 °C min^{-1}

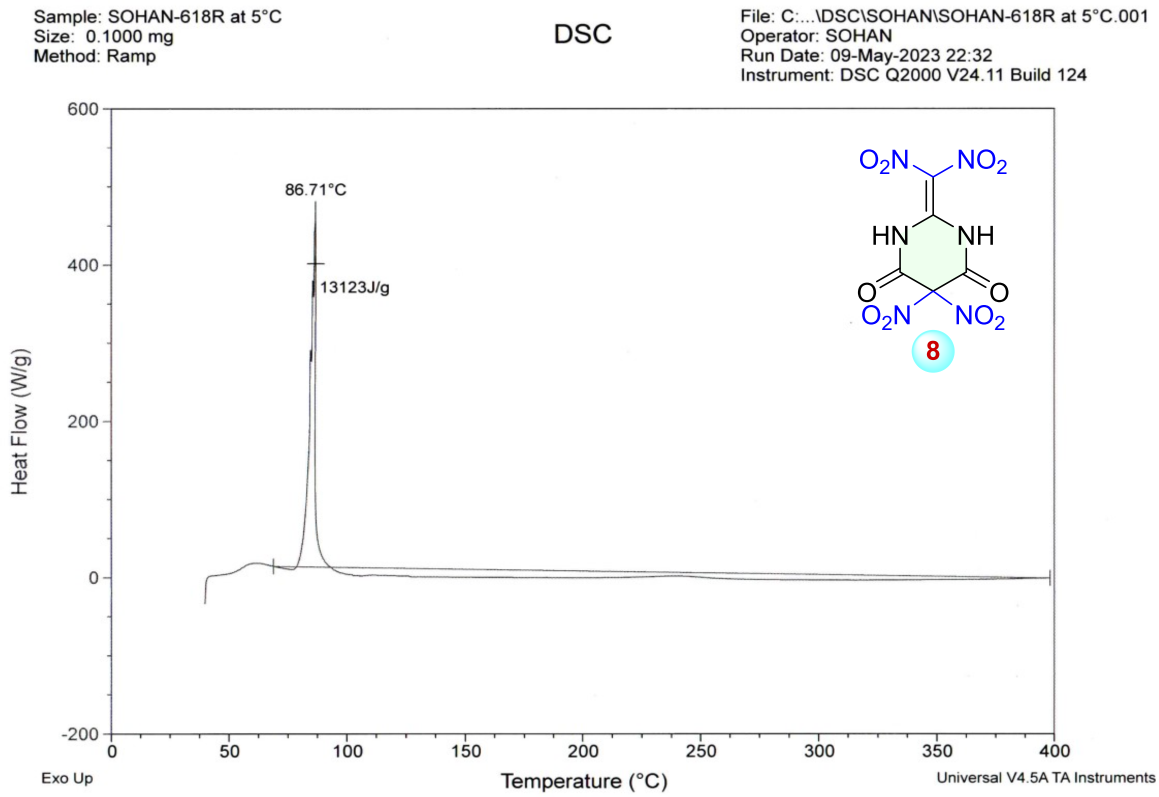


Fig. S28 DSC of compound 8 at 5 °C min^{-1}

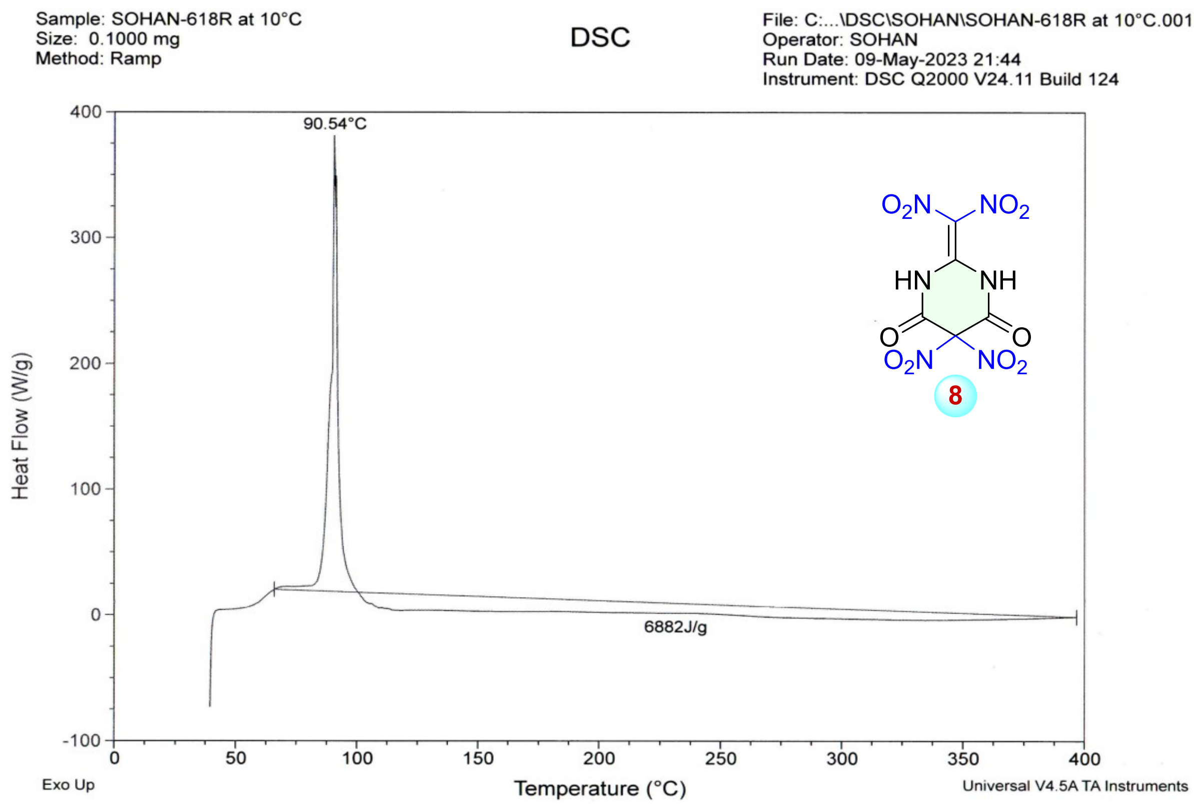


Fig. S29 DSC of compound 8 at 10 °C min^{-1}

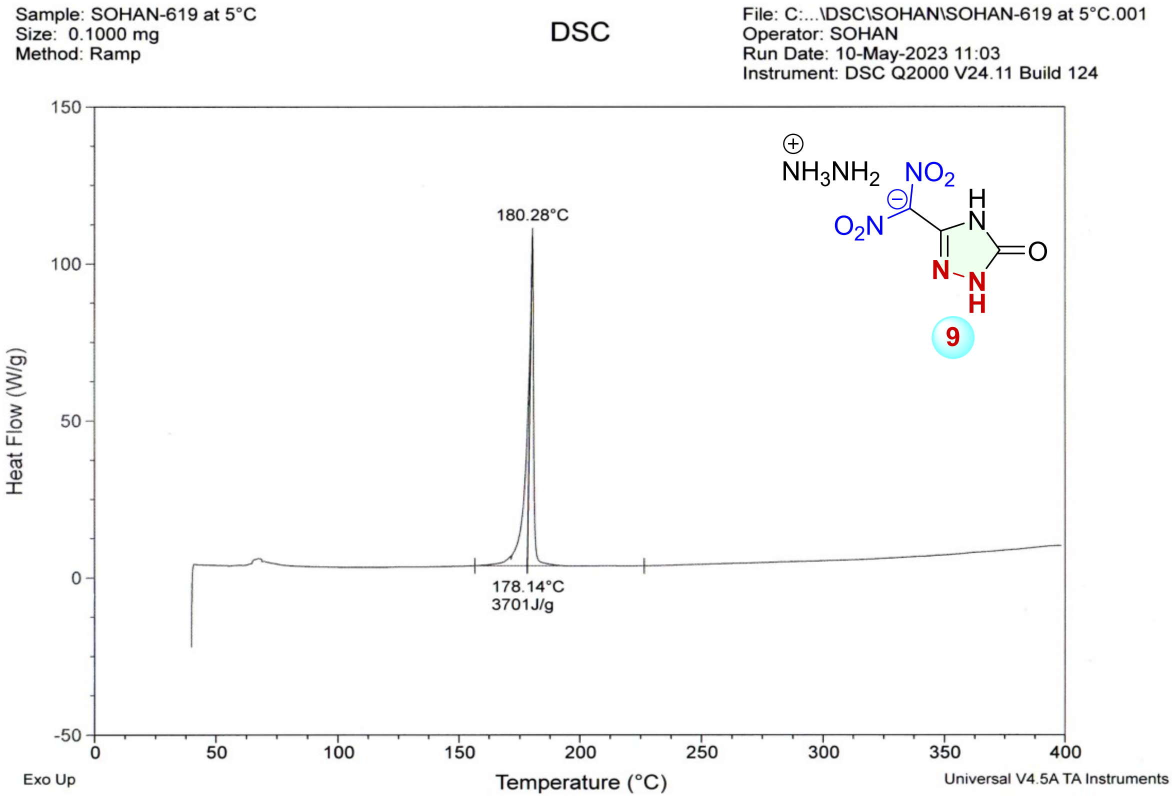


Fig. S30 DSC of compound 9 at 5 °C min^{-1}

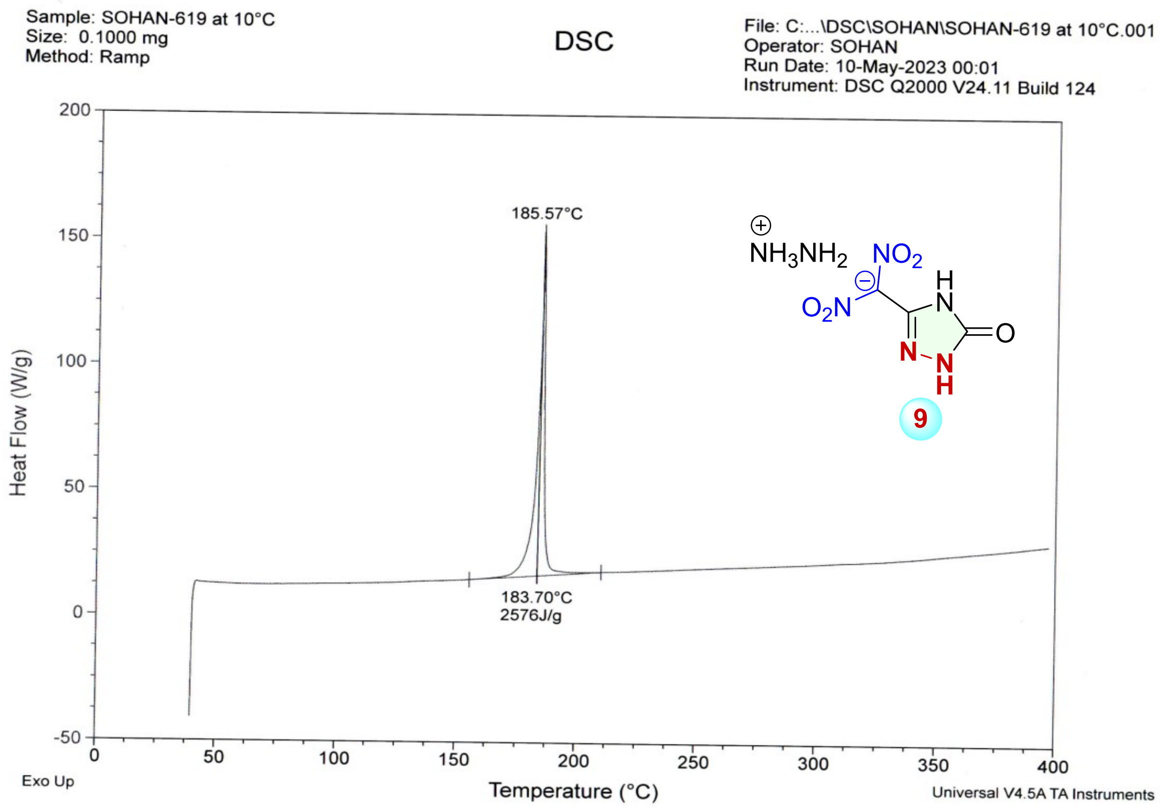


Fig. S31 DSC of compound 8 at 10 °C min^{-1}

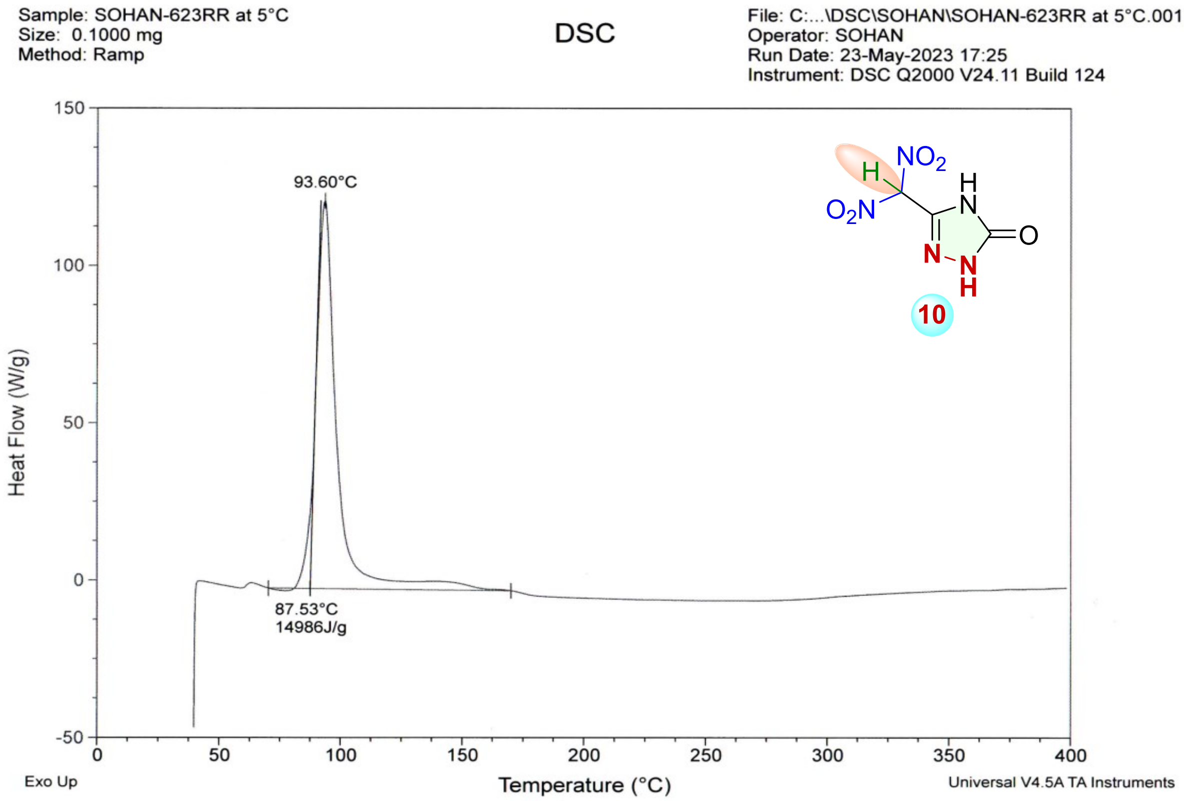


Fig. S32 DSC of compound 10 at 5 °C min^{-1}

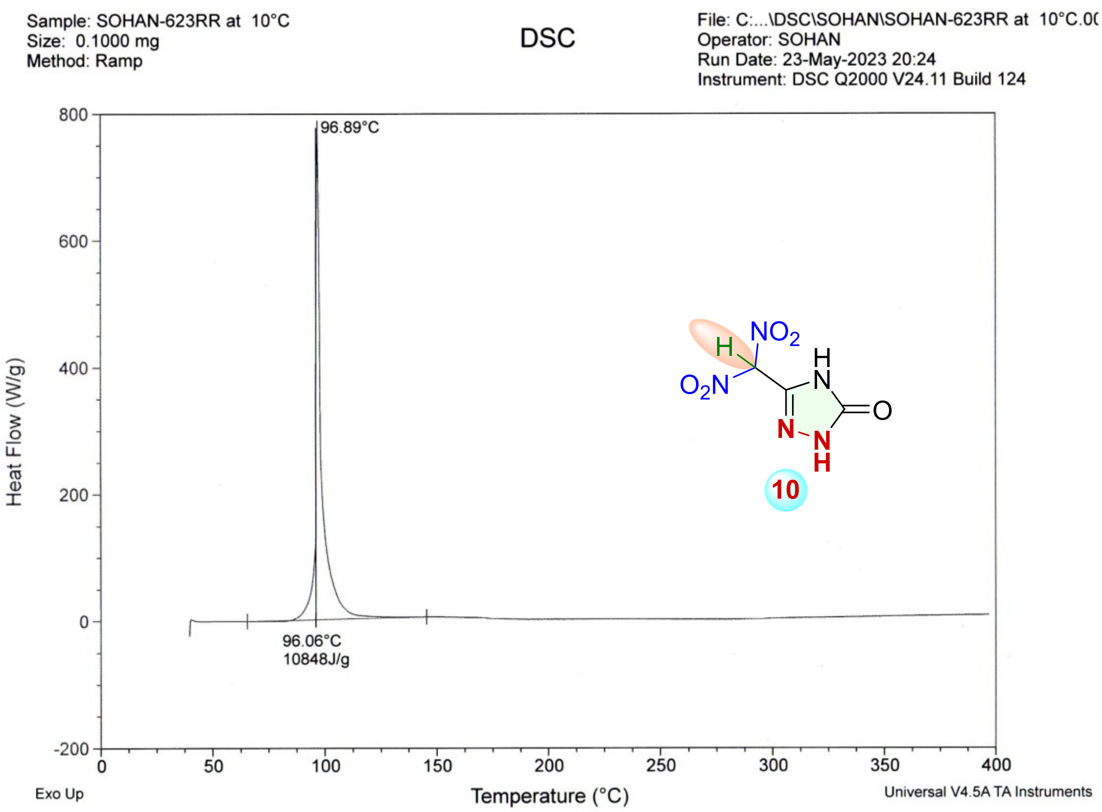


Fig. S33 DSC of compound 10 at 10 °C min^{-1}

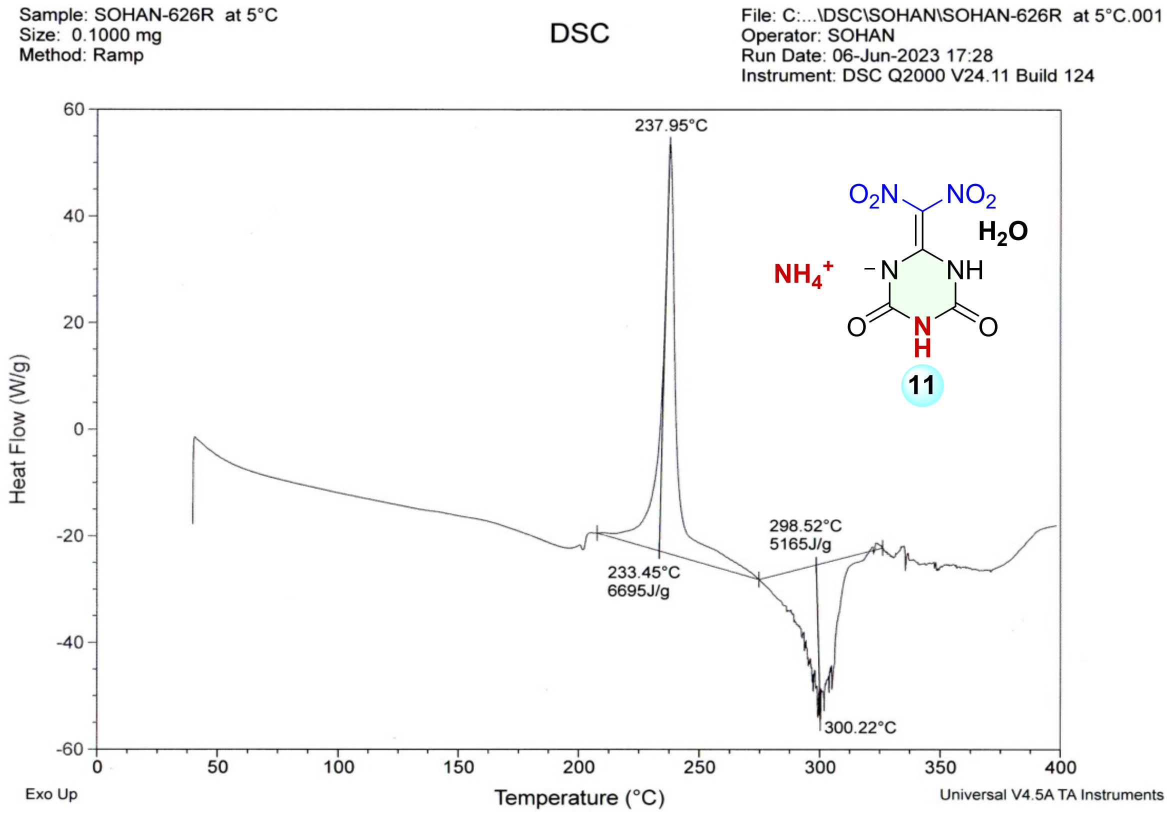


Fig. S34 DSC of compound 11.H_2O at 5 °C min^{-1}

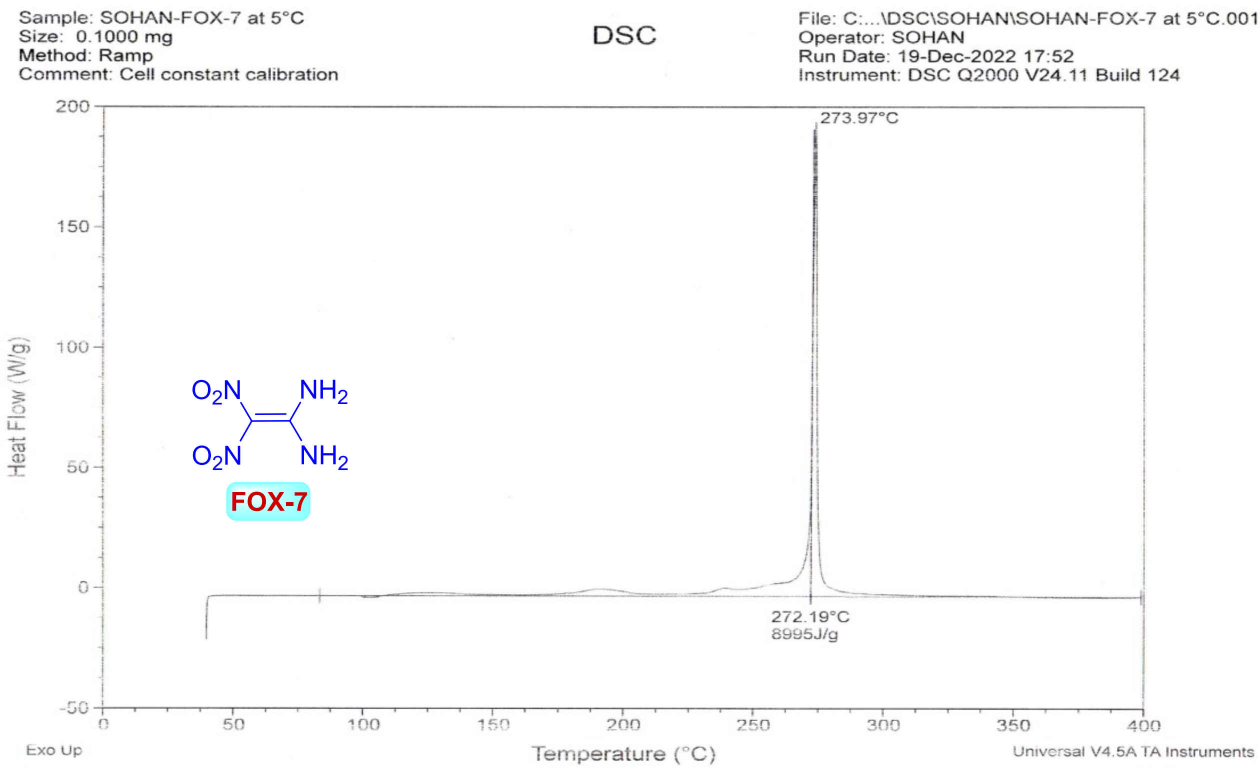


Fig. S35 DSC of compound FOX-7 at 5 °C min^{-1}

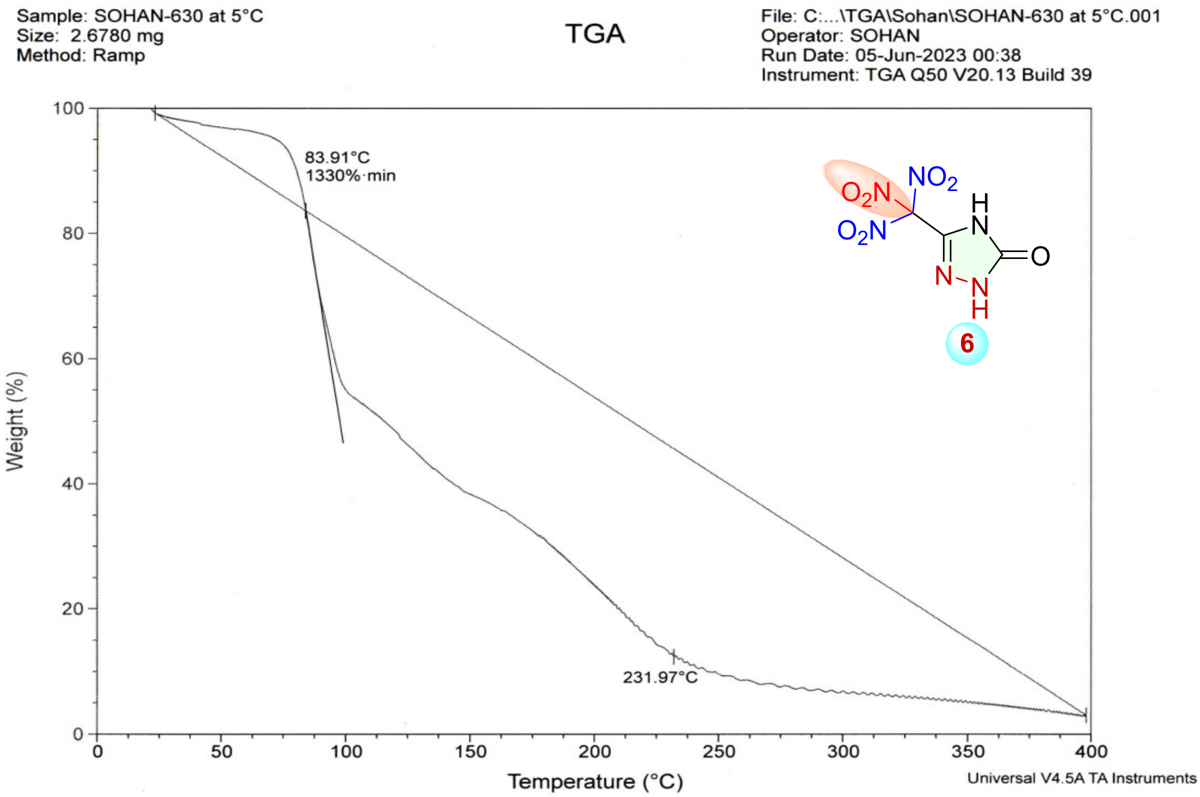


Fig. S36 TGA of compound 6 at 5 °C min^{-1}

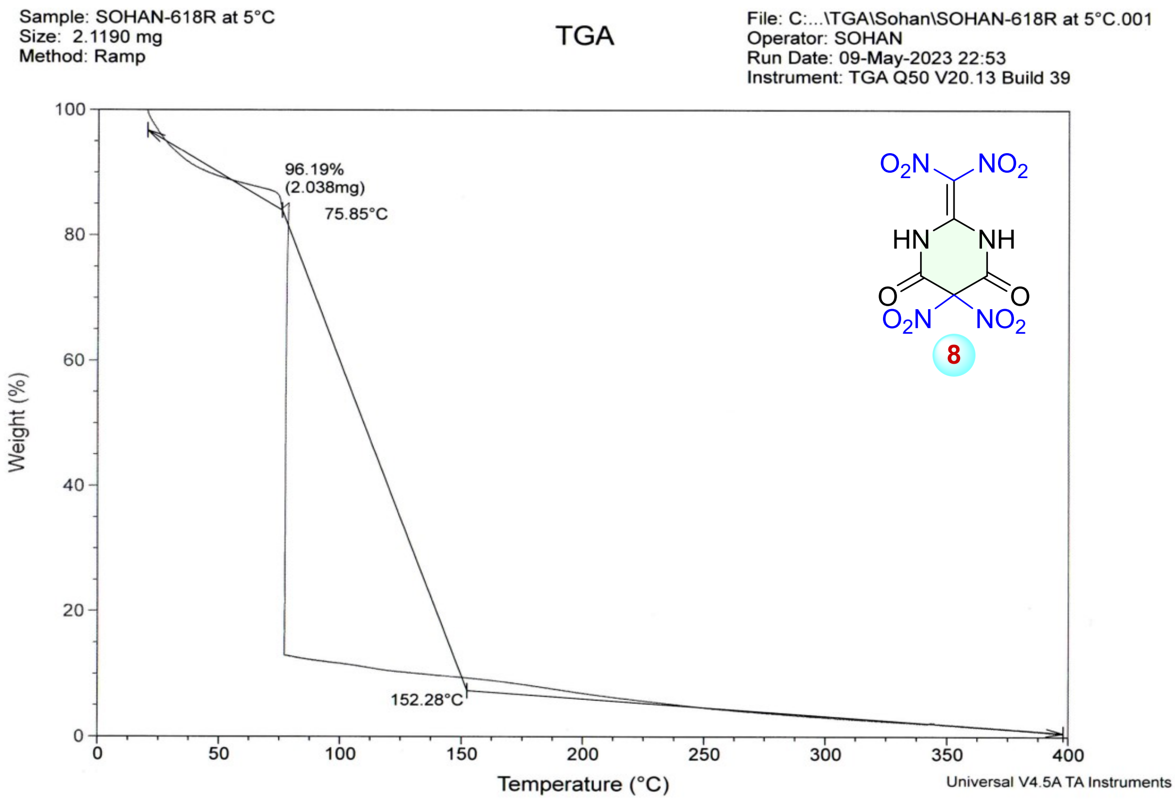


Fig. S37 TGA of compound 8 at 5 °C min^{-1}

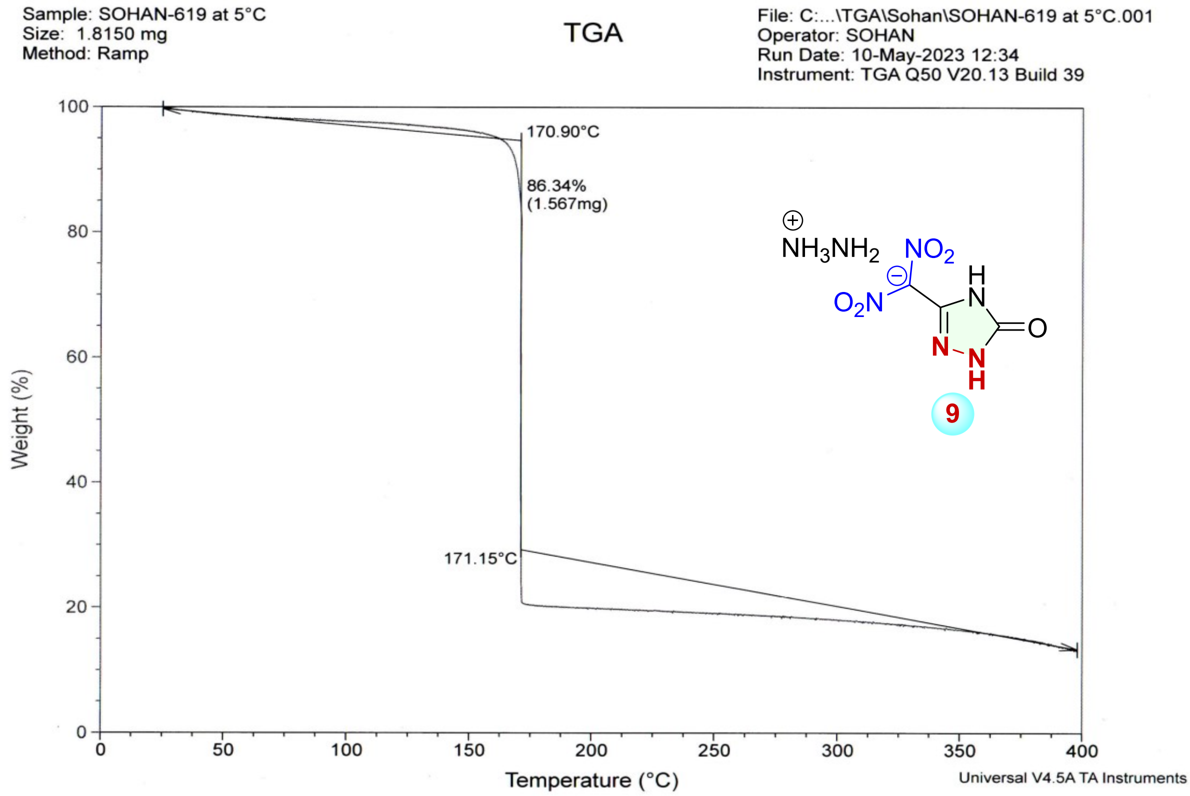


Fig. S38 TGA of compound 9 at 5 °C min-1

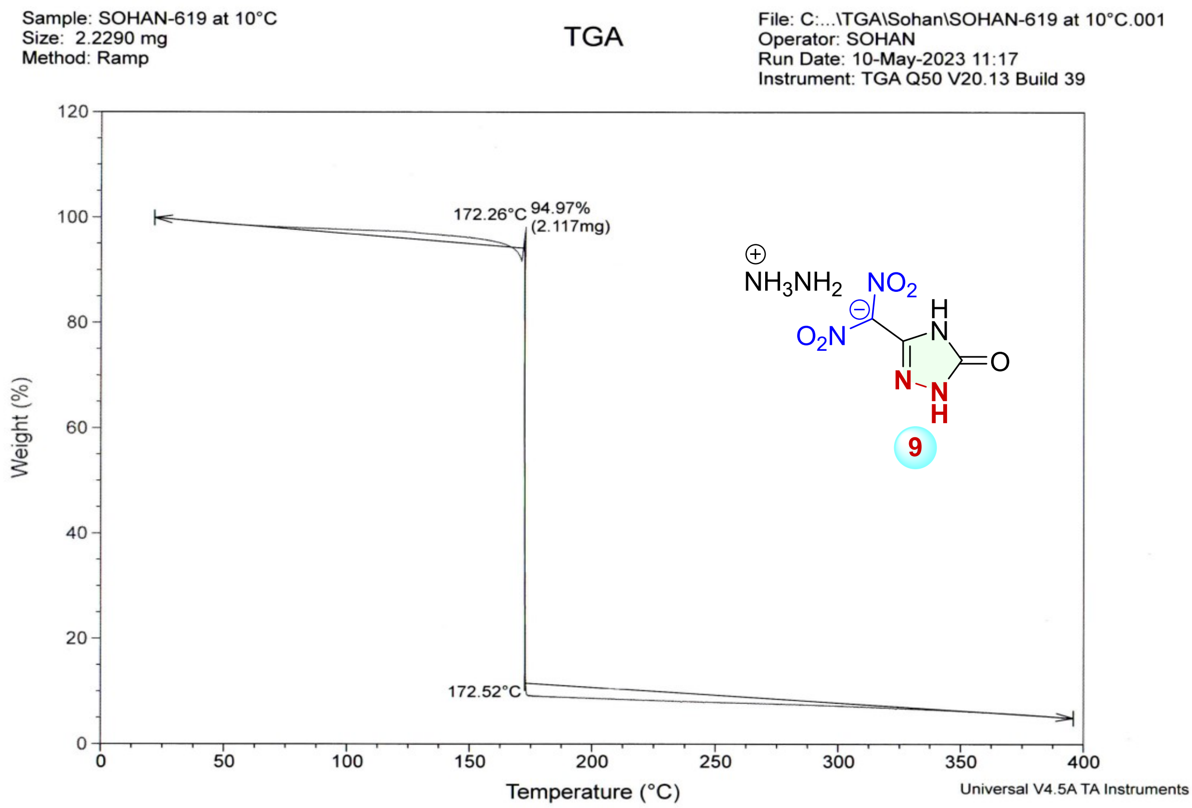


Fig. S39 TGA of compound 9 at 5 °C min-1

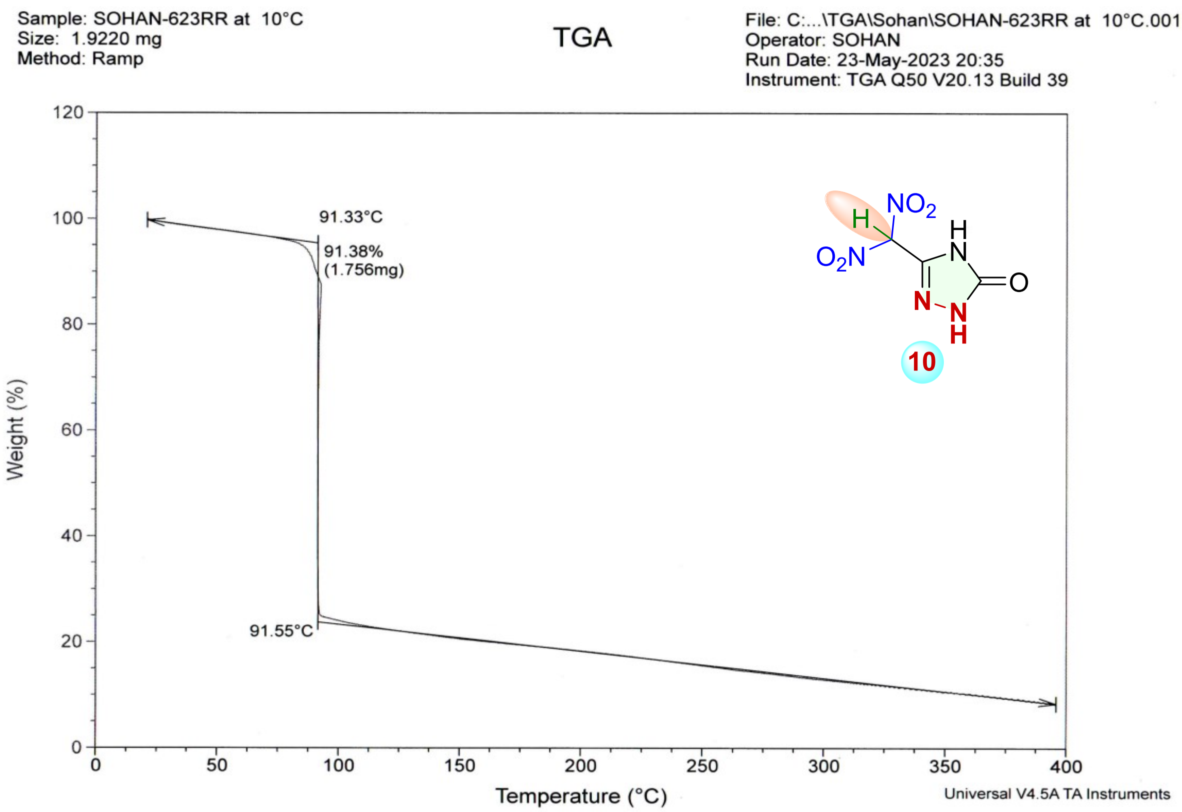


Fig. S40 TGA of compound 10 at 5 °C min^{-1}

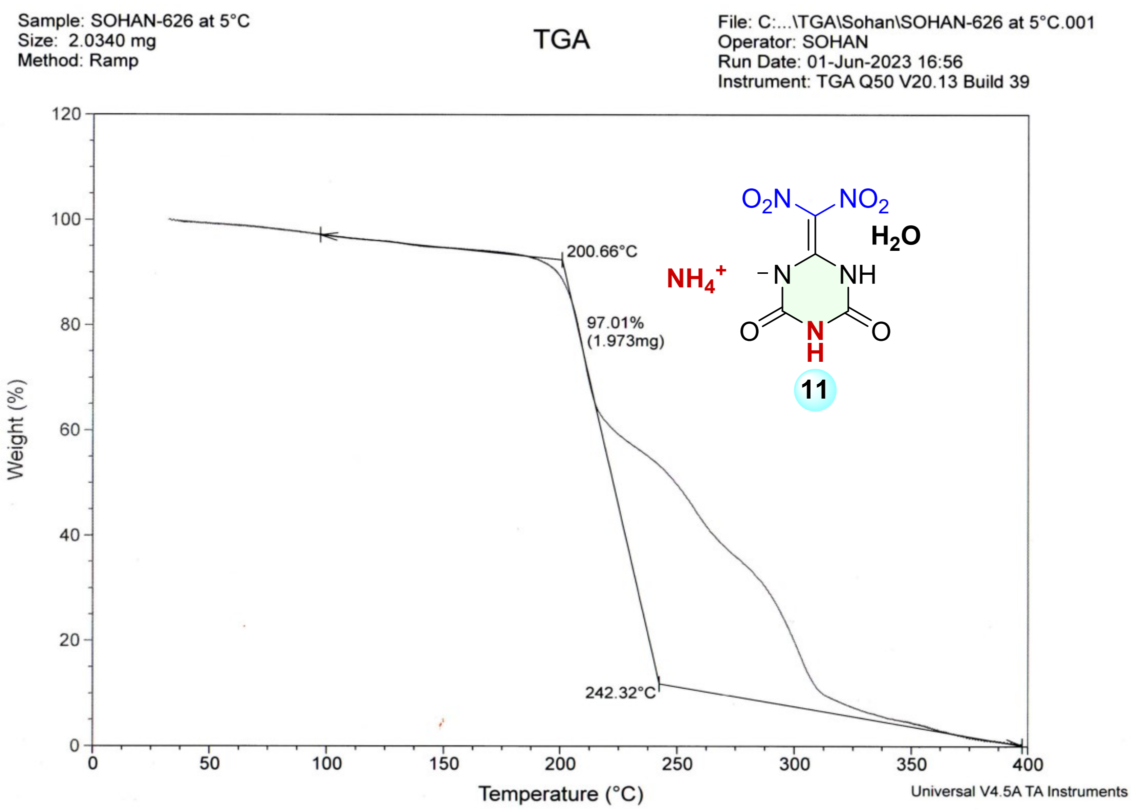


Fig. S41 TGA of compound 11.H_2O at 5 °C min^{-1}

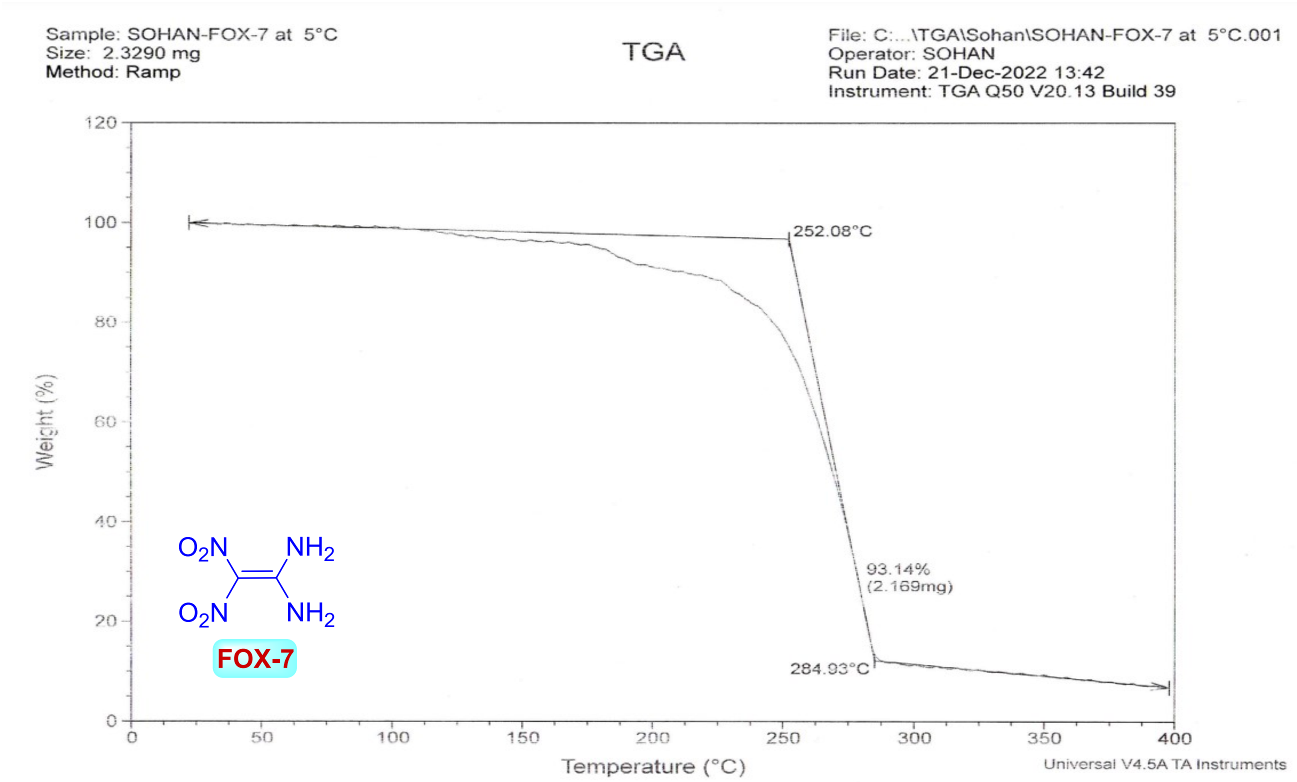
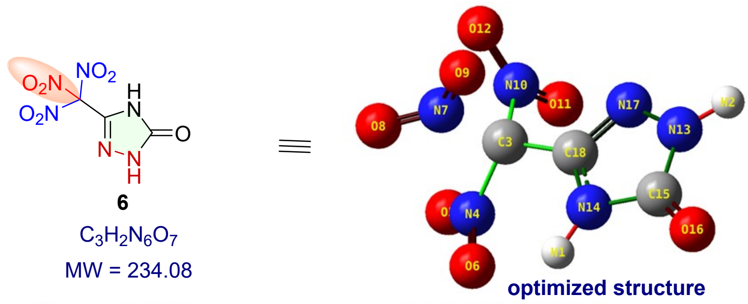


Fig. S42 TGA of compound FOX-7 at 5 °C min^{-1}

Table S13. Cartesian coordinates (in Å) for optimized structure of compound 6 obtained using the B3LYP/6-311++G(d,p) level of theory



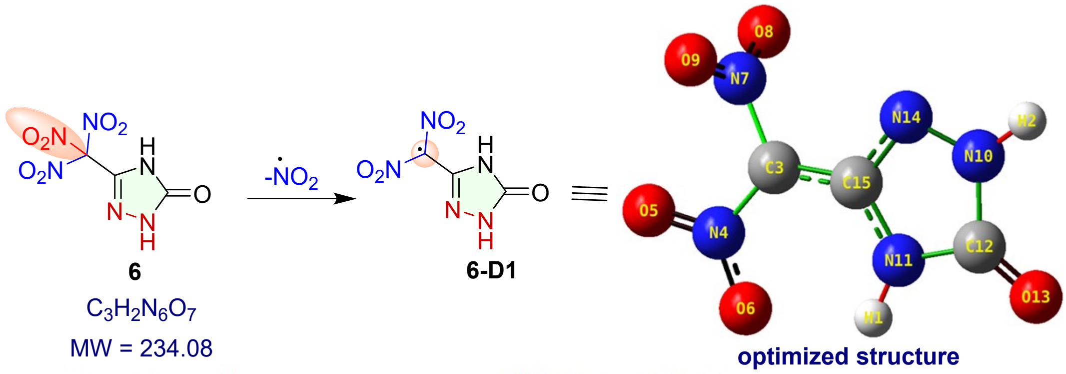

```
Zero-point correction=                           0.097753 (Hartree/Particle)
Thermal correction to Energy=                    0.111470
Thermal correction to Enthalpy=                  0.112414
Thermal correction to Gibbs Free Energy=         0.056015
Sum of electronic and zero-point Energies=          -970.442062
Sum of electronic and thermal Energies=             -970.428346
Sum of electronic and thermal Enthalpies=           -970.427401
Sum of electronic and thermal Free Energies=        -970.483801
```

Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z
1	H	-0.001367	4.334601	0.062278
2	H	0.829129	6.852583	-3.063359
3	C	-2.109598	6.299167	0.185123
4	N	-2.838334	5.009304	0.634443
5	O	-4.041143	5.014146	0.656434
6	O	-2.087475	4.105848	0.963063
7	N	-1.638105	6.980014	1.543516
8	O	-2.315724	6.747190	2.516325
9	O	-0.653865	7.671811	1.453880
10	N	-3.144603	7.253918	-0.464646
11	O	-3.657119	6.827539	-1.470876
12	O	-3.335113	8.310339	0.093174
13	N	0.429464	6.406913	-2.252024
14	N	0.001453	5.108857	-0.584404

15	C	0.956049	5.295414	-1.594947
16	O	1.953298	4.662553	-1.832741
17	N	-0.733435	6.858987	-1.731132
18	C	-0.978142	6.060208	-0.735905

Number of imaginary frequencies at the B3LYP/6-311++G(d,p) level = 0

Table S14. Cartesian coordinates (in Å) for optimized structure of compound 6-D1 obtained using the B3LYP/6-311++G(d,p) level of theory

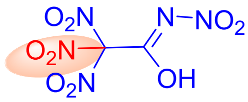



```
Zero-point correction=                           0.084027 (Hartree/Particle)
Thermal correction to Energy=                    0.094870
Thermal correction to Enthalpy=                  0.095814
Thermal correction to Gibbs Free Energy=         0.045040
Sum of electronic and zero-point Energies=          -765.289016
Sum of electronic and thermal Energies=             -765.278174
Sum of electronic and thermal Enthalpies=           -765.277229
Sum of electronic and thermal Free Energies=        -765.328003
```

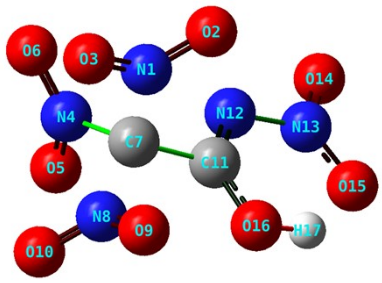
Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z
1	H	-0.216997	4.298060	0.004686
2	H	1.050832	6.857733	-2.962600
3	C	-2.313046	6.137974	-0.288097
4	N	-2.799960	5.286427	0.737363
5	O	-3.922378	5.495801	1.176801
6	O	-2.043872	4.373875	1.108273
7	N	-3.205757	7.246398	-0.679880
8	O	-3.850401	7.091975	-1.700321
9	O	-3.211257	8.216340	0.054411
10	N	0.521191	6.389577	-2.240233
11	O	-0.131605	5.031188	-0.686721
12	C	0.952808	5.248959	-1.529088
13	O	1.987409	4.649920	-1.644678
14	N	-0.682696	6.837203	-1.892183
15	C	-1.088831	5.985806	-0.919997

Number of imaginary frequencies at the B3LYP/6-311++G(d,p) level = 0

Table S15. Cartesian coordinates (in Å) for optimized structure of compound TNAA, 4 obtained using the B3LYP/6-311++G(d,p) level of theory



≡



TNAA, 4

$C_2HN_5O_9$

MW = 239.06

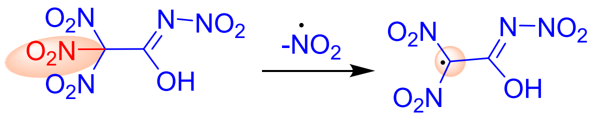
optimized structure

```
Zero-point correction=                           0.081330 (Hartree/Particle)
Thermal correction to Energy=                    0.095638
Thermal correction to Enthalpy=                  0.096582
Thermal correction to Gibbs Free Energy=         0.037574
Sum of electronic and zero-point Energies=          -1027.326554
Sum of electronic and thermal Energies=             -1027.312245
Sum of electronic and thermal Enthalpies=           -1027.311301
Sum of electronic and thermal Free Energies=        -1027.370309
```

Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z
1	N	-4.318756	1.426156	0.462412
2	O	-4.132852	2.379699	1.183437
3	O	-5.347684	0.835749	0.241015
4	N	-3.200147	1.202725	-1.806394
5	O	-2.236794	0.871448	-2.457519
6	O	-4.215946	1.738721	-2.175780
7	C	-3.069615	0.877930	-0.293051
8	N	-3.128234	-0.669579	-0.081946
9	O	-3.271271	-0.991917	1.074768
10	O	-3.035113	-1.373130	-1.056051
11	C	-1.773451	1.487745	0.237378
12	N	-1.518739	2.657702	-0.246077
13	N	-0.349155	3.312636	0.233589
14	O	-0.160202	4.409794	-0.208011
15	O	0.393148	2.734608	1.053347
16	O	-1.129657	0.756464	1.099494
17	H	-0.325692	1.292069	1.360786

Number of imaginary frequencies at the B3LYP/6-311++G(d,p) level = 0

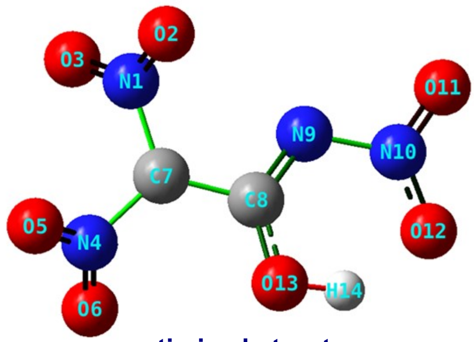
Table S16. Cartesian coordinates (in Å) for optimized structure of compound TNAA-D1 obtained using the B3LYP/6-311++G(d,p) level of theory



TNAA, 4

TNAA-D1

≡



$C_2HN_5O_9$

MW = 239.06

optimized structure

```
Zero-point correction=                           0.067022 (Hartree/Particle)
Thermal correction to Energy=                    0.078763
Thermal correction to Enthalpy=                  0.079707
Thermal correction to Gibbs Free Energy=         0.025540
Sum of electronic and zero-point Energies=           -822.157072
Sum of electronic and thermal Energies=              -822.145331
Sum of electronic and thermal Enthalpies=            -822.144386
Sum of electronic and thermal Free Energies=         -822.198553
```

Center Number	Atomic Symbol	Coordinates (Angstroms) X	Y	Z
1	N	-4.259286	1.666861	0.122107
2	O	-4.323775	1.355089	1.294158
3	O	-5.107927	2.223926	-0.549429
4	N	-3.196461	0.415366	-1.701345
5	O	-3.973092	-0.511820	-1.539226
6	O	-2.557801	0.678113	-2.705358
7	C	-3.025259	1.315285	-0.575705
8	C	-1.738291	1.843872	-0.167633
9	N	-1.816405	2.899505	0.603828
10	N	-0.596721	3.454259	1.063327
11	O	-0.707752	4.329928	1.877061
12	O	0.489481	3.038621	0.609584
13	O	-0.691824	1.197951	-0.616406
14	H	0.102990	1.715301	-0.313394

Number of imaginary frequencies at the B3LYP/6-311++G(d,p) level = 0

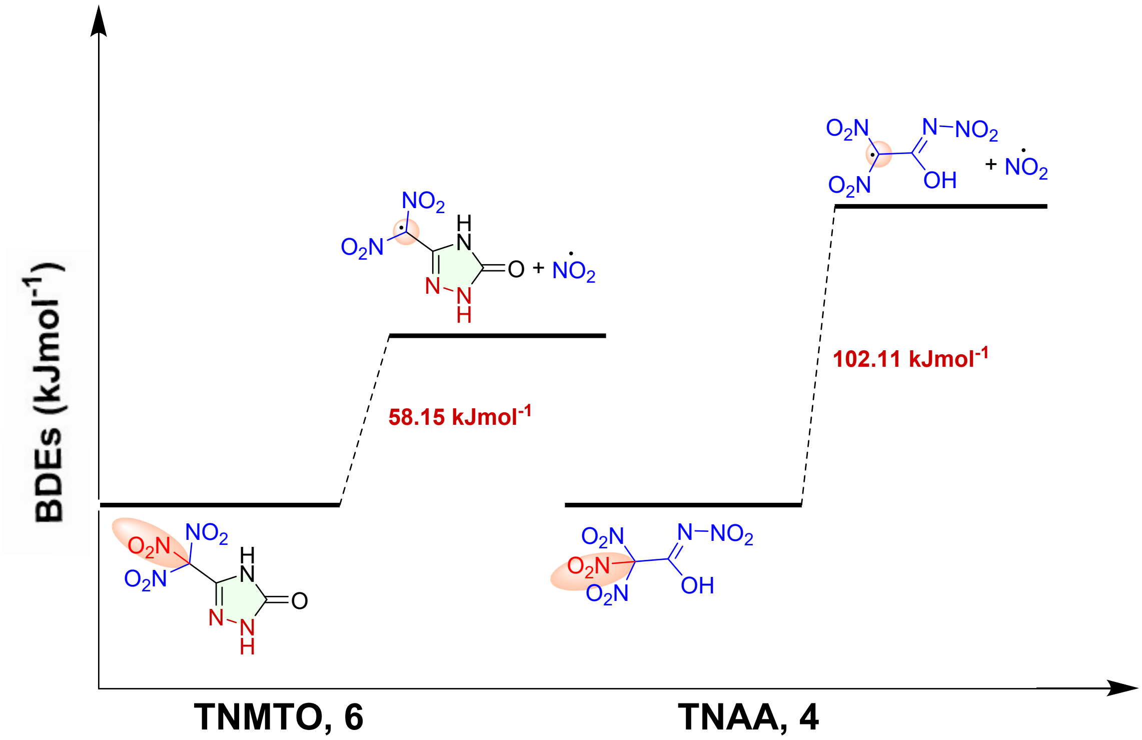


Fig. S43 Comparison of bond dissociation energies (BDEs), calculated at B3LYP/6-311++ G (d,p) level

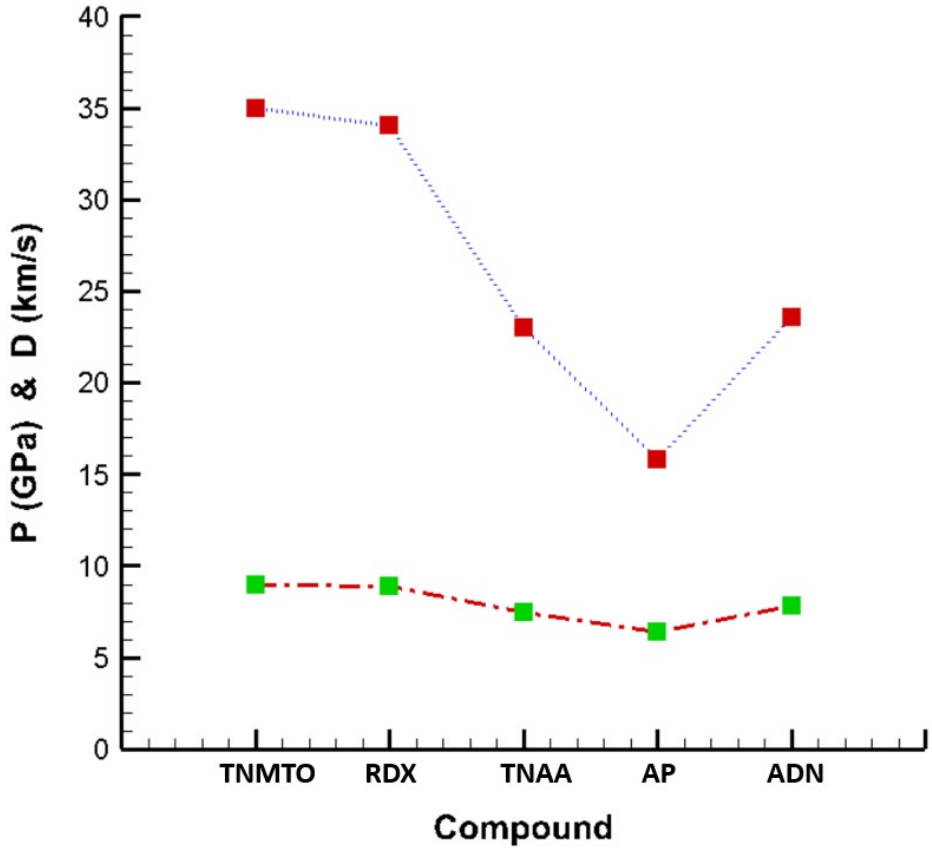


Fig. S44 Comparison of detonation velocity and detonation pressure.

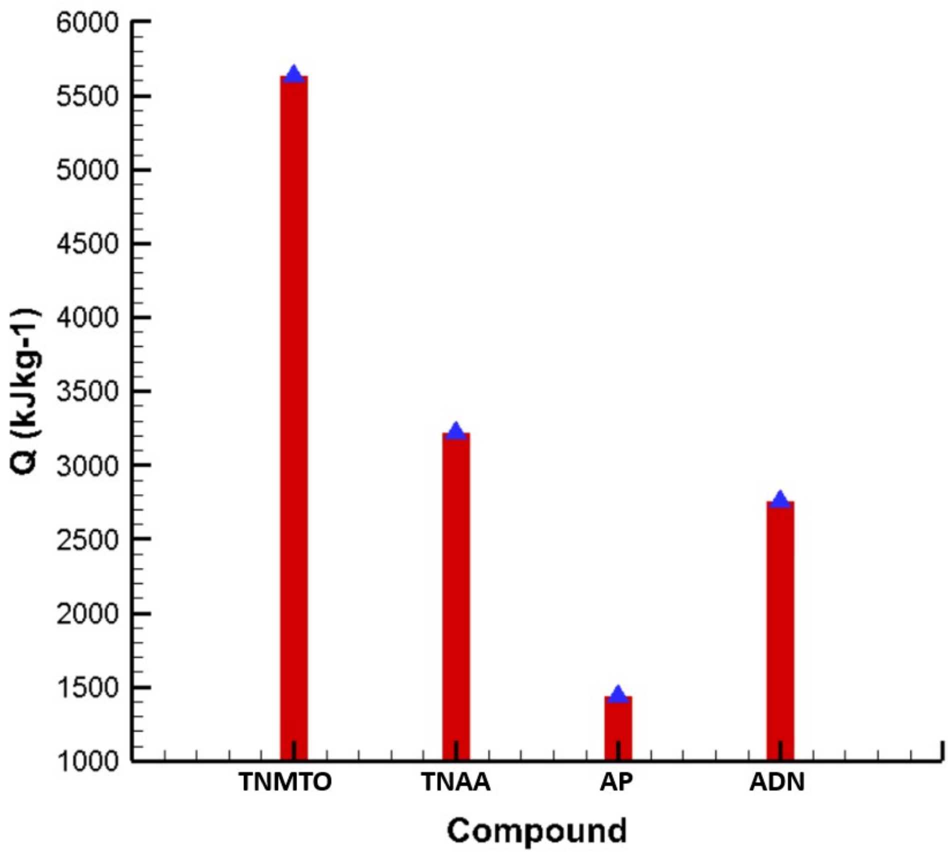


Fig. S45 Comparison of heat of detonation (Q).

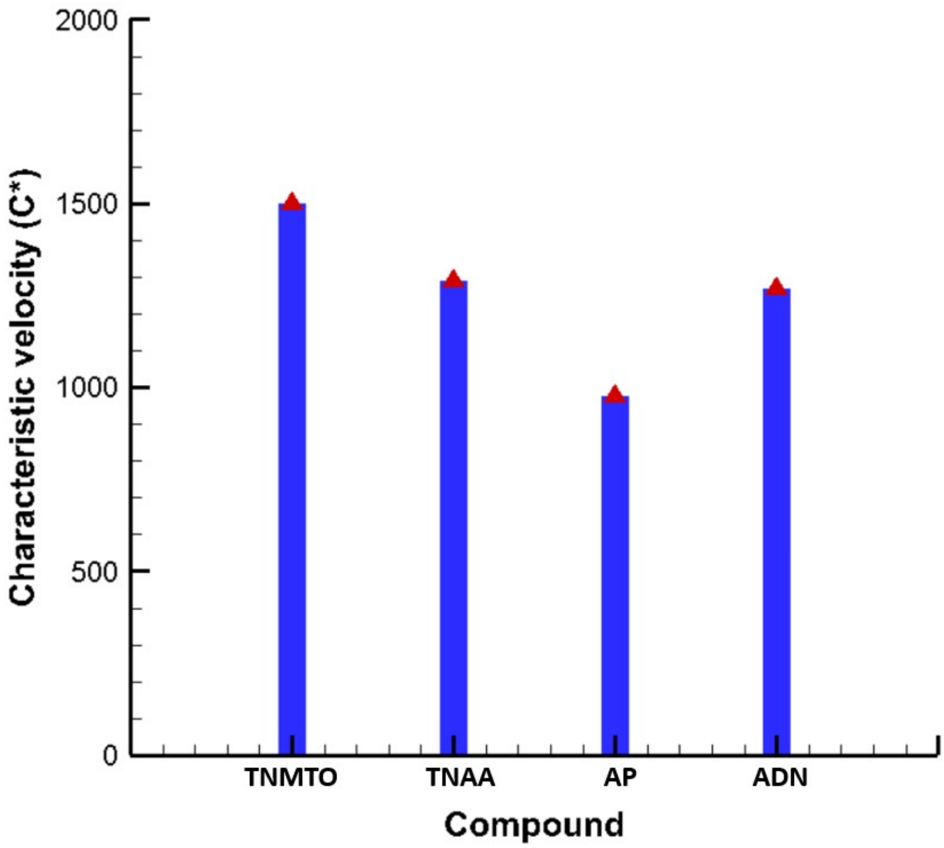


Fig. S46 Comparison of characteristic velocity (C*).

REFERENCES

1. 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. L. Caricato, X., 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, J. A. Montgomery, Jr., 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, N. J. 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Revision D.01 ed., Gaussian, Inc., Wallingford, CT, 2003.
2. P. W. Atkins, Physical Chemistry, Oxford University press: Oxford 1982.
3. M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, Empirical correlations between thermodynamic properties and intermolecular forces, *J. Am. Chem. Soc.,* 1995, 117, 5013–5015
4. H. Gao, C. Ye, C. M. Piekarski and J. M. Shreeve, Computational characterization of energetic salts, *J. Phys. Chem. C,* 2007, 111, 10718–10731.

5. M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, Empirical correlations between thermodynamic properties and intermolecular forces, *J. Am. Chem. Soc.*, 1995, 117, 5013-5015.
6. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr. Sect. A Found. Adv*., 2015, C71, 3-8.
7. G. M. Sheldrick, A short history of *ShelX, Acta Cryst.,* 2008, *A64*, 112-122.
8. Twin reference: S. Parsons, Introduction to twinning *Acta Cryst.,* 2003, D59, 1995-2003.
9. (a) CrysAlisPro Software System, Rigaku Oxford Diffraction, 2020. (b) G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst*., 2015, A71, 3-8.
10. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2 A complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.,* 2009, 42, 339-341.