Supporting Information (SI)

Trinitromethyl- and Nitramino-Substituted Triazolo-Pyridazines: Synthesis and Energetic Performance

Sagar Nehe,[a‡] Abhishek Kumar Yadav,[a‡] Vikas D. Ghule,[b] Srinivas Dharavath[a*]

[a]Energetic Materials Laboratory, Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur-208016, Uttar Pradesh, India. orcid.org/ 0000-0003-0511-0607. E-mail: srinivasd@iitk.ac.in

[b]Department of Chemistry, National Institute of Technology Kurukshetra, Kurukshetra-136119, Haryana, India. orcid.org/0000-0002-0967-7777.

‡These authors contributed equally.

Table of Contents

Table of Contents

Caution! All the compounds investigated are potentially explosive, energetic materials. Although we have experienced no difficulties in syntheses 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) 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 and ^{13}C spectra. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and at a 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). Mass data was recorded using LC-MS (ESI)-Q-TOF (Agilent 6546) mass spectrometer. Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer in a helium atmosphere. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fall Hammer (OZM BFH-10) and a BAM Friction Tester (OZM FSKM-10) instrument.

Experimental Section:

***Ethyl 2-(6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)acetate (2)*:** Compound 3-chloro-6-hydrazineylpyridazine (2 g, 13.88 mmol) and 3-ethoxy-3-iminopropionic acid ethyl ester hydrochloride (3 g, 15.26 mmol) was taken in acetonitrile (50 mL). To this suspension, boron trifluoride diethyl etherate (0.4 mL, 3.88 mmol) was added gradually and the reaction mixture was stirred at room temperature for 12 hours. Insoluble solid was filtered out from the reaction mixture and the filtrate was concentrated using rotary evaporator to get pure light yellow coloured compound in 86% yield (2.9 g, 12.05 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.10 (d, 1H), 7.13 (d, 1H), 4.27 (s, 2H), 4.20 (q, 2H), 1.25 (t, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ(ppm) δ 167.10, 149.65, 144.49, 143.05, 126.45, 122.60, 61.97, 30.56, 14.15. IR (ATR, ZnSe, cm^{-1}): 3350, 2984, 1732, 1521, 1461, 1329, 1257, 1192, 1157, 1019, 948, 876, 816, 774, 669.

***6-chloro-3-(trinitromethyl)-[1,2,4]triazolo[4,3-b]pyridazine (3)*:** Compound 2 (500 mg, 2.07 mmol) was dissolved in concentrated H_2SO_4 (3.0 mL) and stirred at -5 °C for 15 minutes. Freshly prepared fuming HNO_3 (2.0 mL) was then added dropwise, ensuring the reaction temperature remained below 0 °C during the addition. After complete addition, the reaction mixture was stirred for 12 hours at room temperature and subsequently poured into ice-cold water (~50 g). The formed white precipitate was collected by filtration, washed with cold water (5.0 mL) and dried in air at room temperature to yield off-white solid compound 3 in 79% (500 mg). T_{dec} (5 °C min^{-1}): 126 °C (onset); ^1H NMR (500 MHz, DMSO-d6): (ppm) 8.00 (d, 1H), 8.92 (d, 1H); ^{13}C NMR (125 MHz, DMSO-d6): (ppm) 153.30, 147.76, 133.89, 128.60, 128.08, 127.69; IR (ATR ZnSe): υ 3075, 1593, 1522, 1448, 1329, 1279, 1184, 1112, 1075, 971, 943, 873, 796, 740 cm^{-1}.

General procedure for the synthesis of salts 4a-4c:

Hydrazine hydrate (113.53 mg, 2.268 mmol), hydroxylamine hydrate (74.84 mg, 2.268 mmol), and aqueous ammonia (38.55 mg, 2.268 mmol) were added slowly to compound 3 (500 mg, 1.512 mmol) in methanol at room temperature. The mixture was stirred for 5 hours at room temperature, after which the resulting precipitate was collected by filtration and then dried in air and isolated them in quantitative yields.

hydrazinium (6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)dinitromethanide (4a): Yield: (390 mg, 1.34 mmol, 88%) as a yellow solid. Td (onset): 194 °C. ^1H NMR (500 MHz, DMSO-d6): δ 8.525 (d, 1H), 7.54 (d, 1H), 7.07 (s, 5H); ^{13}C NMR (126 MHz, DMSO-d6) δ 149.34, 143.37, 142.71, 127.22, 123.16, 99.50; IR (ATR ZnSe): 3349, 3292, 1507, 1519, 1458, 1398, 1369, 1227, 1194, 1067, 992, 957, 936, 808 cm^{-1}.

hydroxyl ammonium (6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)dinitromethanide (4b): Yield: (395 mg, 1.35 mmol, 89%) as a pale yellow solid. Td (onset): 156 °C. ^1H NMR (500

MHz, DMSO-d6): δ 8.53 (d, 1H), 7.56 (d, 1H), 7.12 (s, 4H); ^{13}C NMR (126 MHz, DMSO-d6) δ 149.80, 143.89, 143.20, 127.72, 123.62, 100.27; IR (ATR ZnSe): 3208, 1519, 1465, 1431, 1194, 1137, 1121, 1070, 992, 818, 787, 745 cm^{-1}.

ammonium (6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)dinitromethanide (4c): Yield: (375 mg, 1.36 mmol, 90%) as a yellow solid. Td (onset): 197 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.52 (d, 1H), 7.55 (d, 1H), 7.08 (s, 4H); ^{13}C NMR (126 MHz, DMSO-d6) δ 149.38, 143.37, 142.73, 127.22, 123.19, 91.54; IR (ATR ZnSe): 3215, 1519, 1467, 1433, 1397, 1359, 1197, 1138, 1070, 993, 949, 818, 787, 745 cm^{-1}.

6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-amine (5): 3-chloro-6-hydrazineylpyridazine (2 g, 13.88 mmol) was placed in a round-bottom flask, and to this 8 mL of 1N HCl solution was added at room temperature. Further to this mixture, cyanogen bromide (1.61 gm, 15.26 mmol) was added at same temperature, and stirred for 24 hours. The reaction progress was monitored by TLC. After completion, the resulting precipitate was collected by filtration, washed with cold water, and dried in air to get pale yellow coloured pure compound 5 in 76 % yield (Yield: 1.8 gm 10.61 mmol). ^{1}H NMR (500 MHz, DMSO-d6): δ 8.32 (d, 1H), 7.56 (d, 1H), 6.69 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 150.14, 147.25, 139.19, 127.59, 126.25. IR (ATR ZnSe): 3072, 3018, 1681, 1545, 1488, 1391, 1344, 1290, 1189, 93 cm^{-1}.

s***N-(6-chloro-[1,2,4]triazolo[4,3-b]pyridazin-3-yl)nitramide (6):*** Compound 5 (500 mg, 2.94 mmol) was added portion-wise to the mixture of fuming nitric acid (2.0 mL) and 98% conc.

sulfuric acid (3 mL) in ice-water bath at 0 °C. After addition, the reaction mixture was stirred at the same temperature for 20 mins and further continued for 24 hrs at room temperature. After completion of the reaction, it was poured into crushed ice with stirring. The obtained precipitate was washed with water and dried in air to get an orange-coloured compound 6 in 86% yield (550 mg, 2.56 mmol). Td (onset): 353 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.73 (d, 1H), 7.85 (d, 1H). ^{13}C NMR (126 MHz, DMSO-d6) δ 161.10, 131.98, 131.16, 123.62, 120.56. IR (ATR ZnSe): 3075, 1524, 1440, 1337, 1267, 1163, 1097, 1068, 944, 818, 798, 770, 670, 617 cm^{-1}. HRMS (ESI-QTOF) m/z: calculated for $C_5H_3ClN_6O_2$ $[M-H]^-$ is 212.9933; Found 212.9932.

6-hydrazineyl-[1,2,4]triazolo[4,3-b]pyridazin-3-amine (7): Compound 6 (500 mg, 2.33 mmol) was gradually added to hydrazine monohydrate (80%) with continuous stirring and subsequently the mixture was heated at 100 °C for 12 hrs. Upon completion of the reaction, the mixture was cooled to room temperature. The formed precipitate was collected by filtration, washed thoroughly with cold water and ethanol, and dried in air to obtain pure compound 7 as an off-white solid in 70% yield (270 mg, 1.63 mmol). Td (onset): 183 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.19 (s, 1H), 7.63 (d, 1H), 7.51 (d, 1H), 7.08 (5.96, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 155.01, 149.73, 139.53, 123.58, 112.87. IR (ATR ZnSe): 3383, 3266, 3173, 3078, 1626, 1555, 1502, 1345, 1268, 1159, 1131, 1086, 1015, 960, 881, 821, 758, 661 cm^{-1}. HRMS (ESI-QTOF) m/z: calculated for $C_5H_7N_7$ $[M]^+$ 166.0836; Found 166.0843.

X-ray Crystallographic Data

A single crystal of suitable dimensions was used for X-ray data collection. Diffraction intensities were measured on a Bruker APEX-II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. Data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using SADABS (version 2.10). Using Olex2, the structure was solved with the ShelXT structure solution program by the intrinsic phasing method and refined with the ShelXL refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares procedures on F^2. The NO_2 group (compound 3; CCDC No. 2441110) attached to C12 was found to be disordered and was modelled accordingly. The thermal ellipsoid and packing diagrams of X-ray structures in the main article are plotted using Mercury 3.7 software.

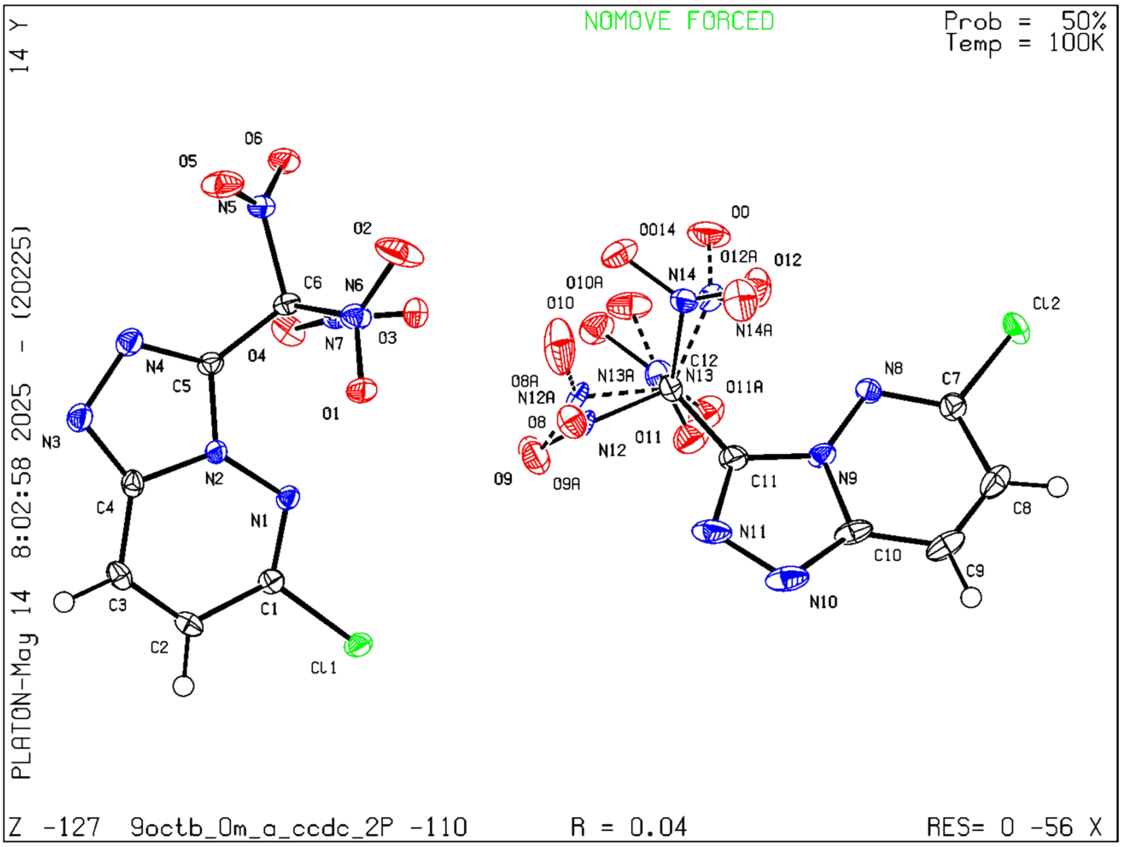


Figure S1: Molecular Structure of **3.**

Table S1 Crystal data and structure refinement for 3.

CCDC No.	2441110
Empirical formula	$C_6H_2ClN_7O_6$

Formula weight	303.60
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	9.1720(8)
b/Å	9.4996(9)
c/Å	13.2063(12)
α/°	104.376(3)
β/°	97.790(2)
γ/°	102.786(2)
Volume/Å^3	1064.67(17)
Z	4
ρ_{calc}g/cm^3	1.894
μ/mm^{-1}	0.406
F (000)	608.0
Crystal size/mm^3	0.33 × 0.22 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.108 to 56.738
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-17 \le l \le 17$
Reflections collected	22321
Independent reflections	5319 [R_{int} = 0.0445, R_{sigma} = 0.0356]
Data/restraints/parameters	5319/174/416
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0368, wR_2 = 0.0761
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.0820
Largest diff. peak/hole / e Å^{-3}	0.45/-0.48

Datablock 27jana_o_0m_a - ellipsoid plot

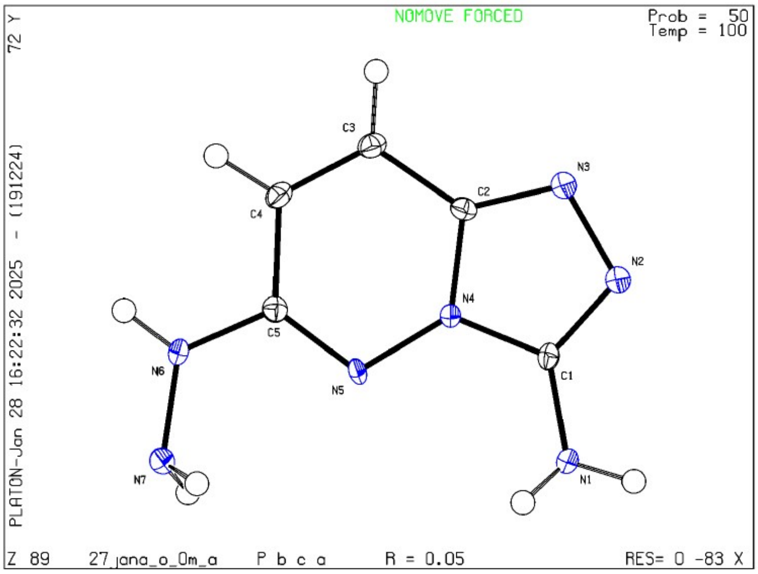


Figure S2: Molecular Structure of **7.**

Table S2 Crystal data and structure refinement for 7.

CCDC No.	2441109
Empirical formula	$C_5H_7N_7$
Formula weight	165.18
Temperature/K	100
Crystal system	orthorhombic
Space group	Pbca
a/Å	6.9060(3
b/Å	12.1450(6)
c/Å	15.9930(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1341.39(11)
Z	8
ρ_{calc}g/cm^3	1.636
μ/mm^{-1}	0.119
F(000)	688.0
Crystal size/mm^3	0.33 × 0.22 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.178 to 56.918
Index ranges	$-9 \leq h \leq 9$, $-16 \leq k \leq 16$, $-18 \leq l \leq 21$
Reflections collected	20909
Independent reflections	1690 [R_{int} = 0.0465, R_{sigma} = 0.0196]
Data/restraints/parameters	1690/10/121
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1134
Final R indexes [all data]	R_1 = 0.0485, wR_2 = 0.1154
Largest diff. peak/hole / e Å^{-3}	0.40/-0.45

NMR, IR Spectra, HRMS & TG-DSC plots

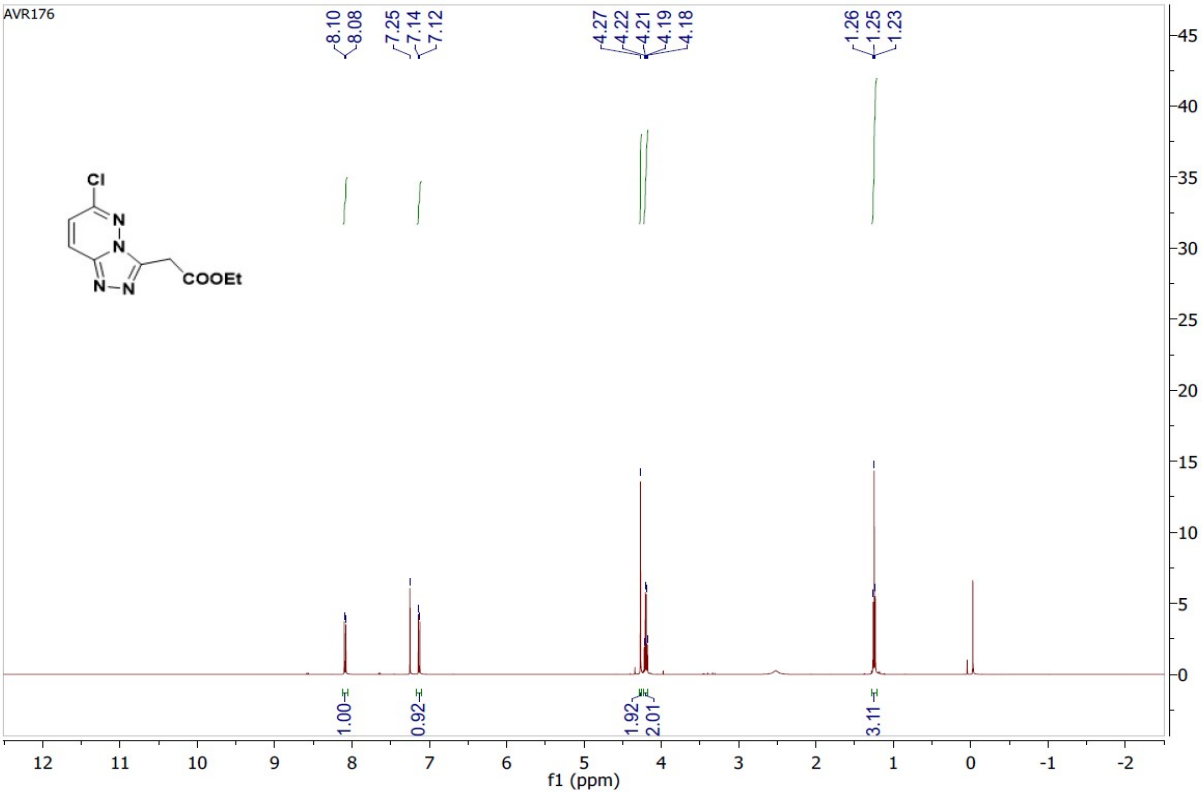


Figure S3: ^{1}H NMR spectrum of compound **2** in **CDCl$_3$** in 500 MHz**.**

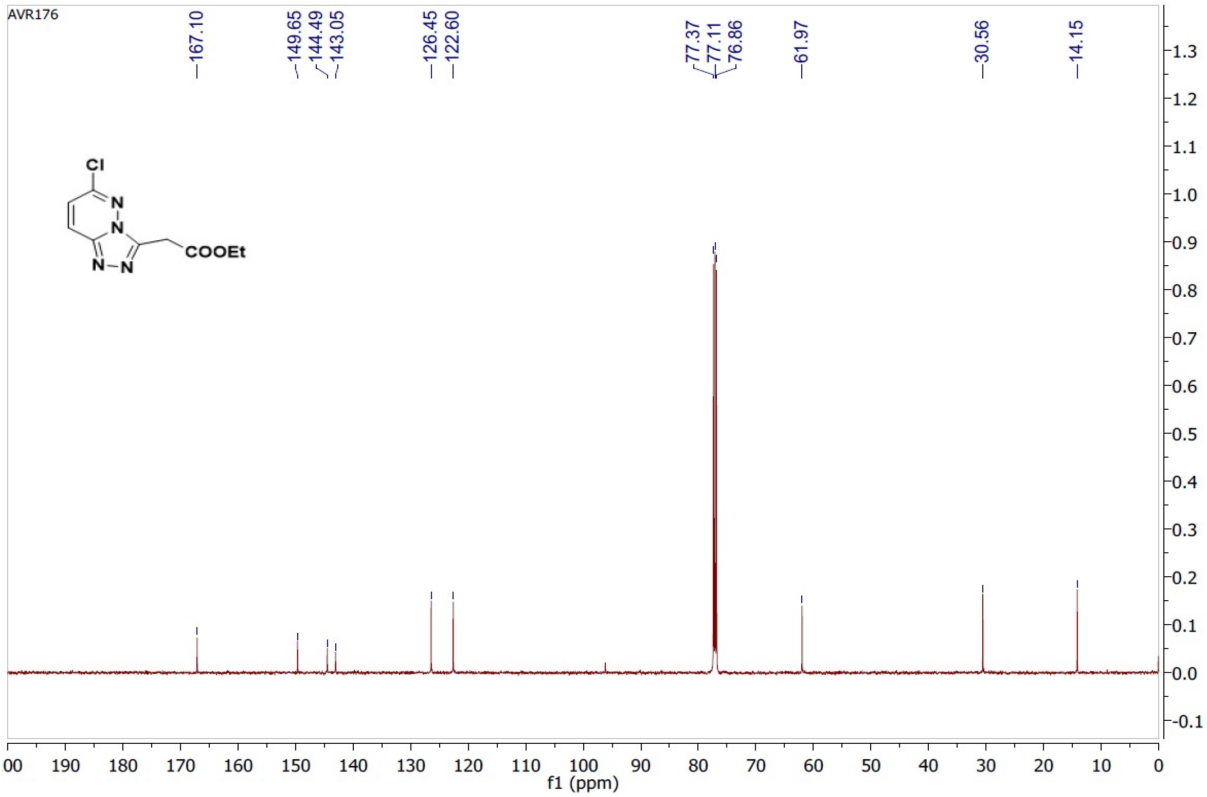


Figure S4: ^{13}C NMR spectrum of compound **2** in **CDCl$_3$** in 126 MHz.

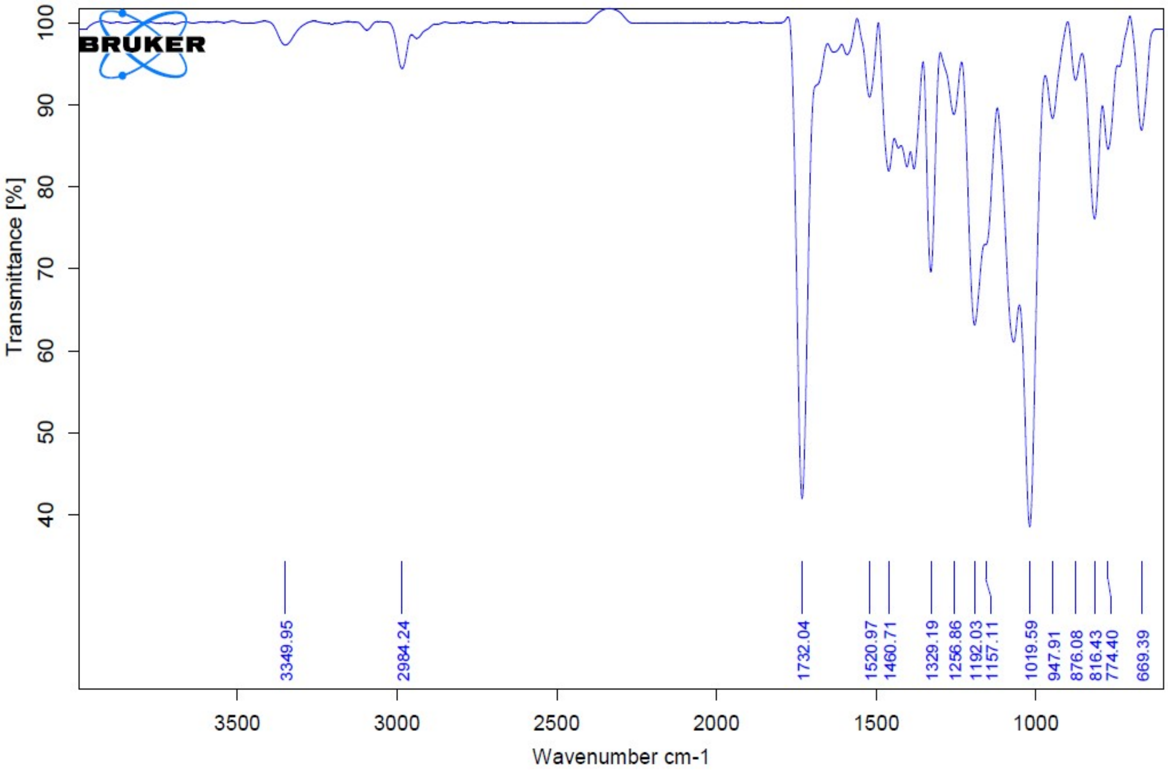


Figure S5: IR spectrum of compound **2.**

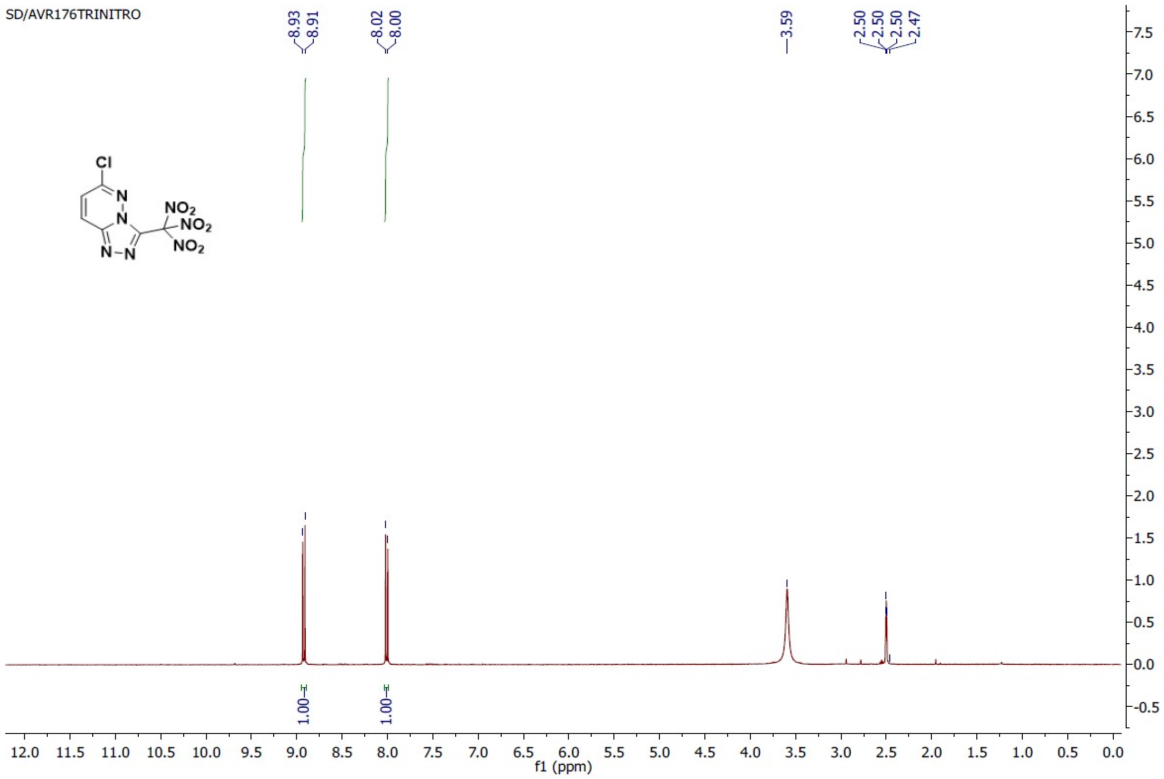


Figure S6: ^{1}H NMR spectrum of compound **3** in **DMSO-d_6** in 500 MHz**.**

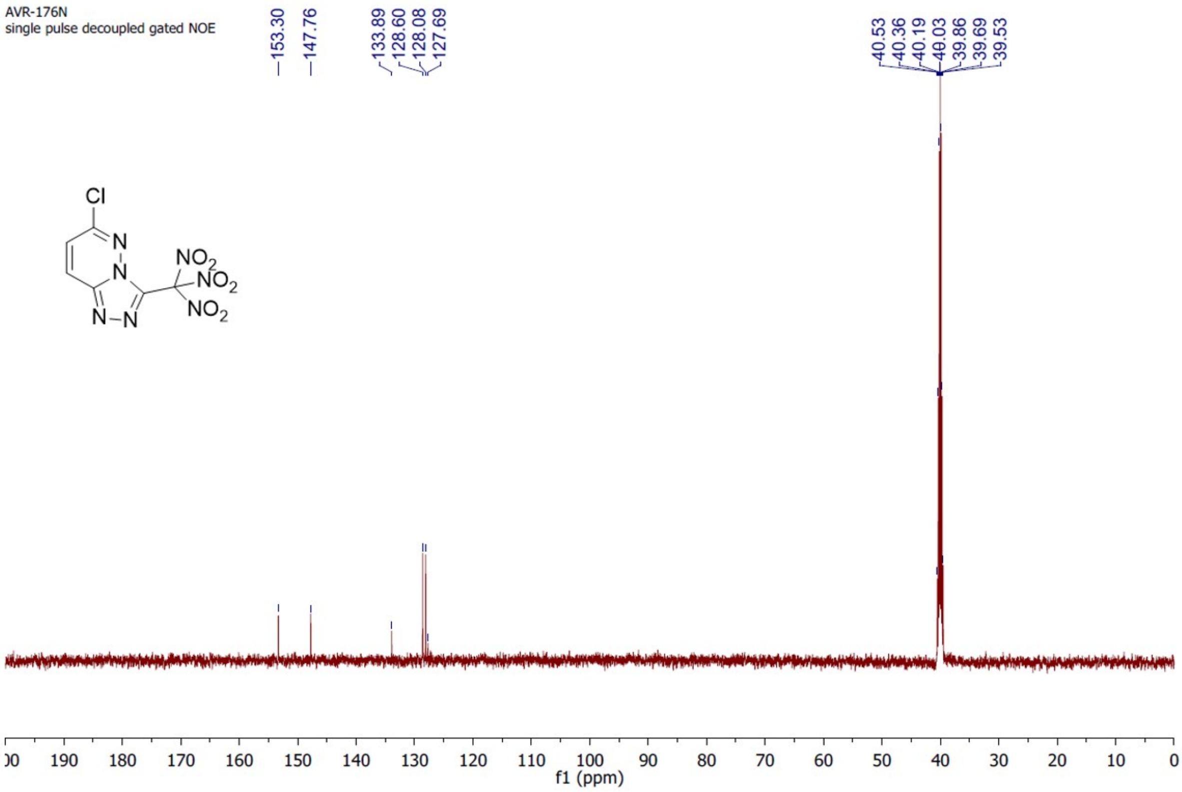


Figure S7: ^{13}C NMR spectrum of compound **3** in **DMSO-d_6** in 126 MHz.

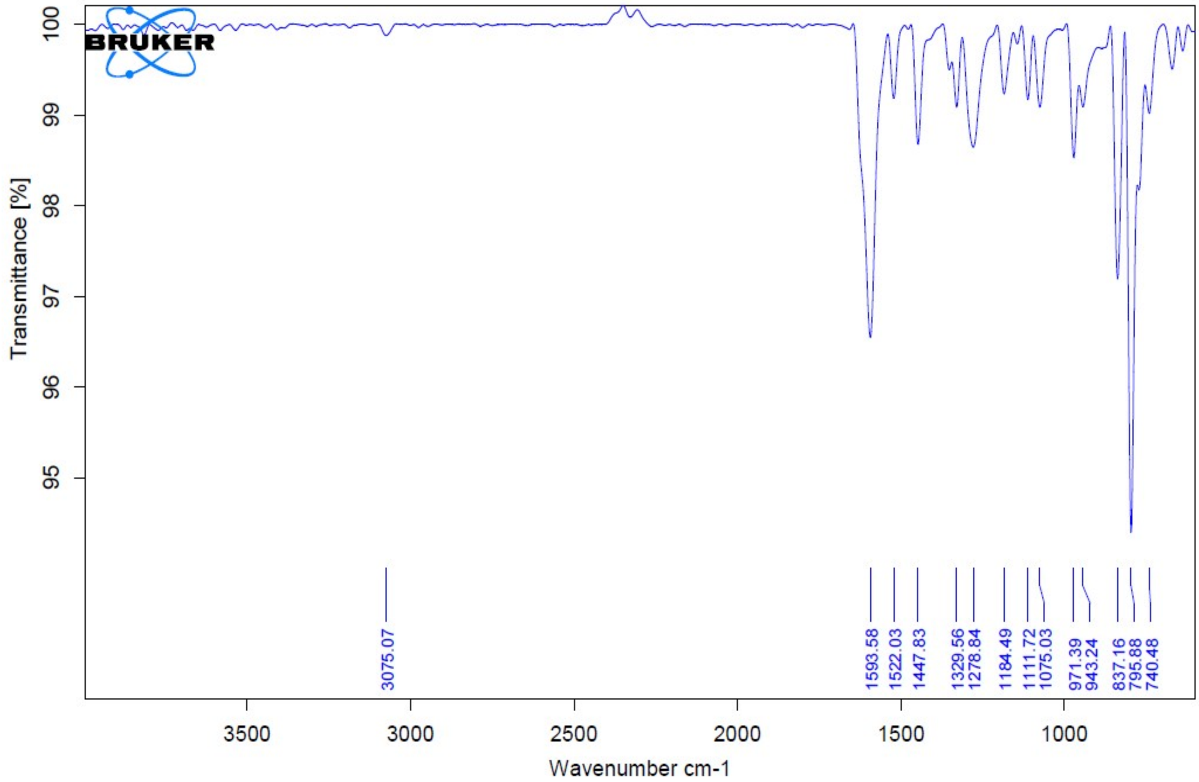


Figure S8: IR spectrum of compound **3.**

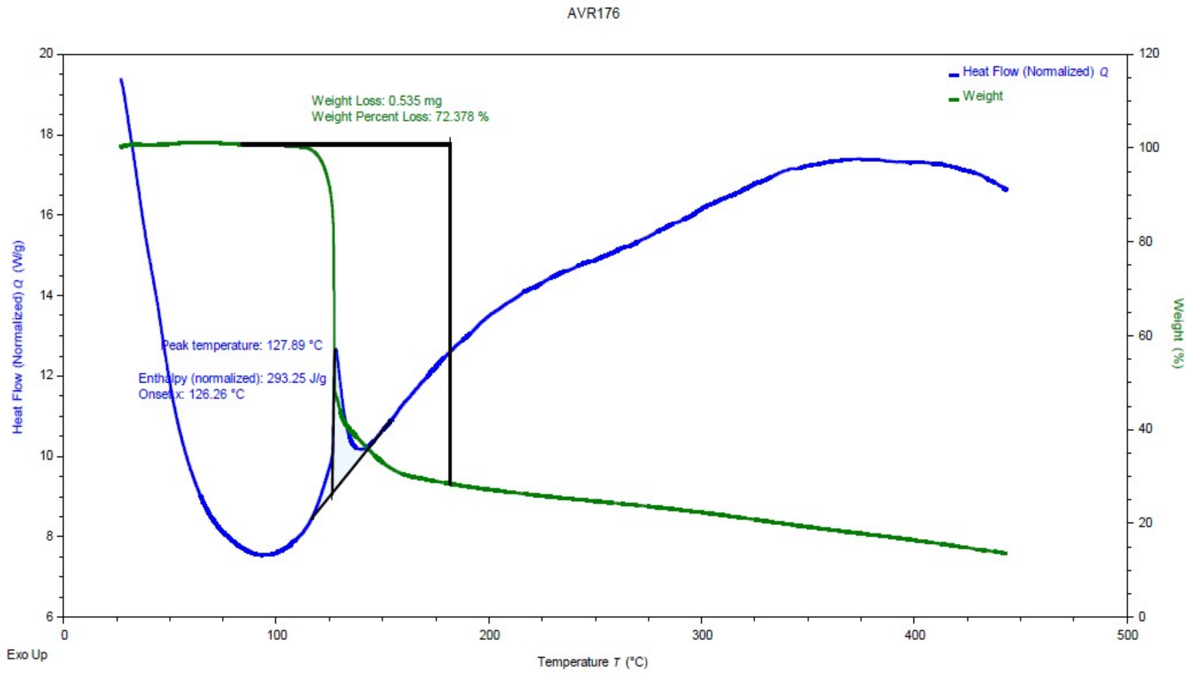


Figure S9: DSC spectra of compound **3** at heating rate 5 °C min^{-1}**.**

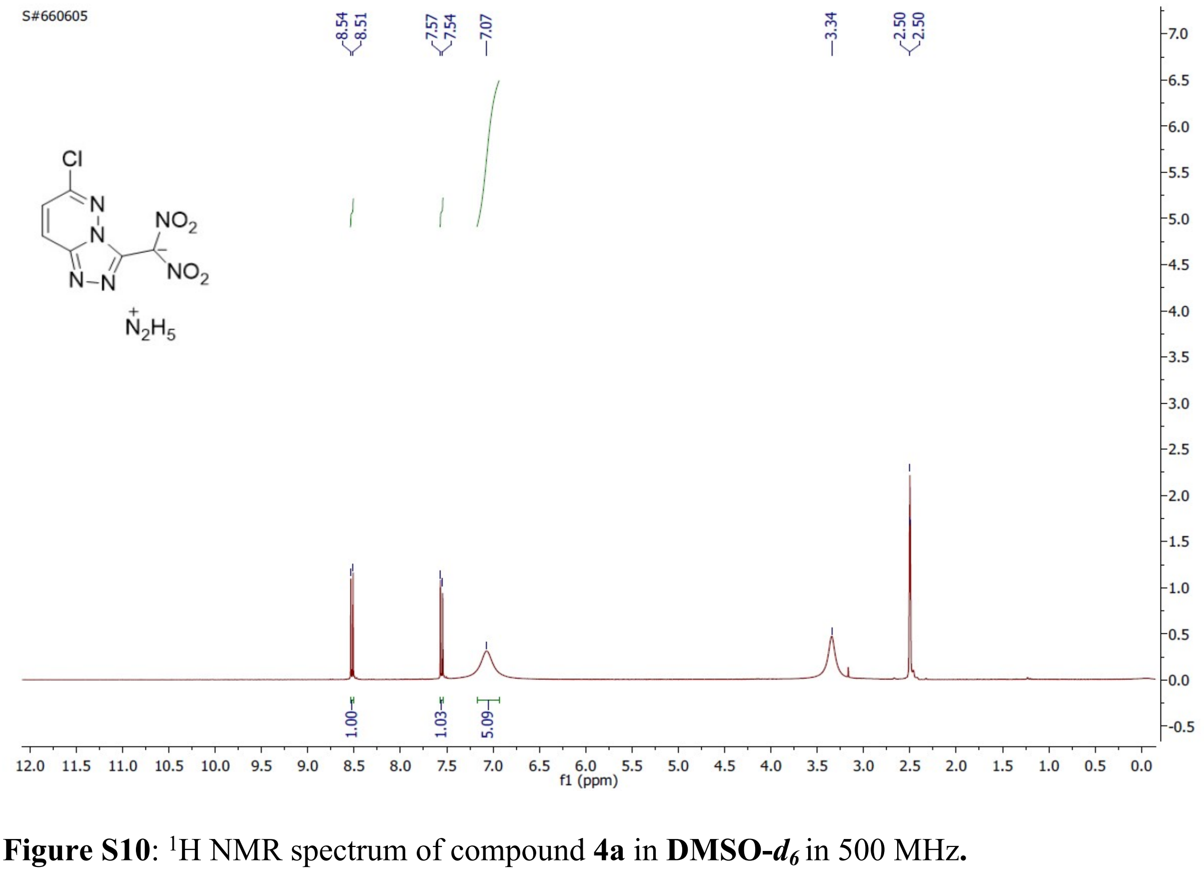


Figure S10: ^{1}H NMR spectrum of compound **4a** in **DMSO-d_6** in 500 MHz**.**

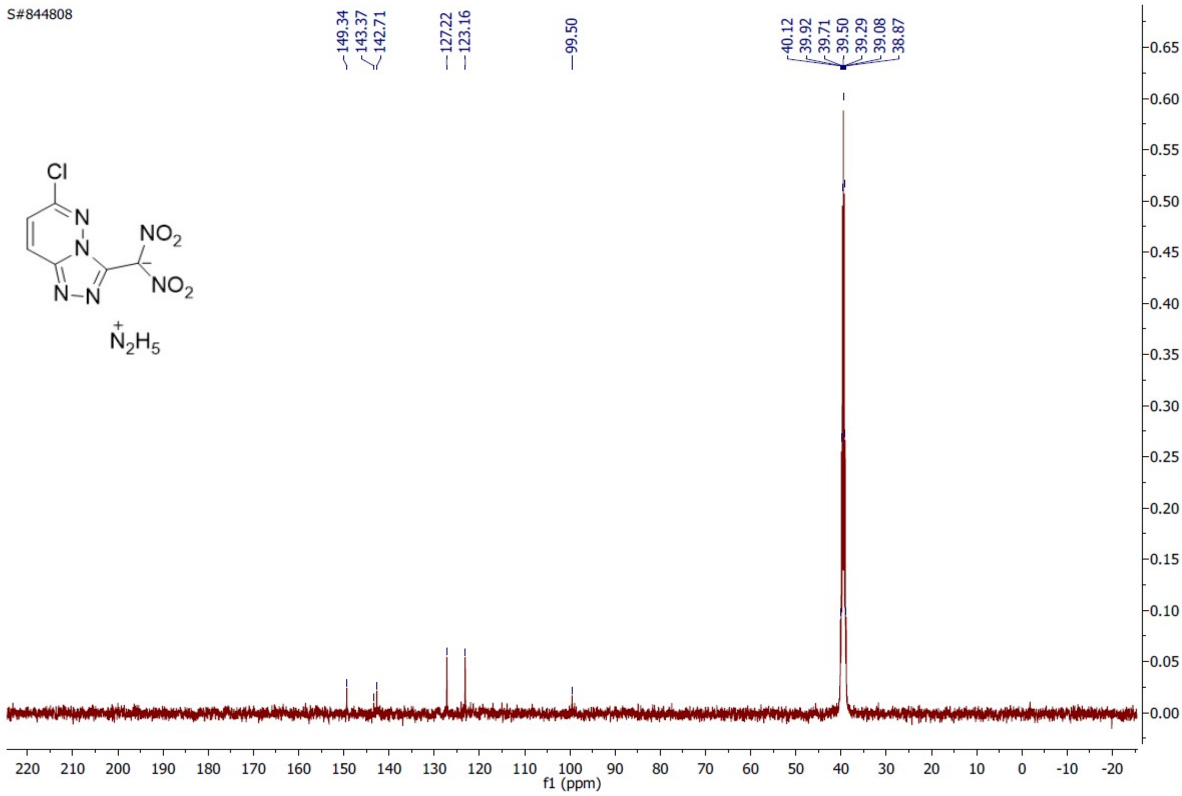


Figure S11: ^{13}C NMR spectrum of compound **4a** in **DMSO-*d*$_6$** in 126 MHz.

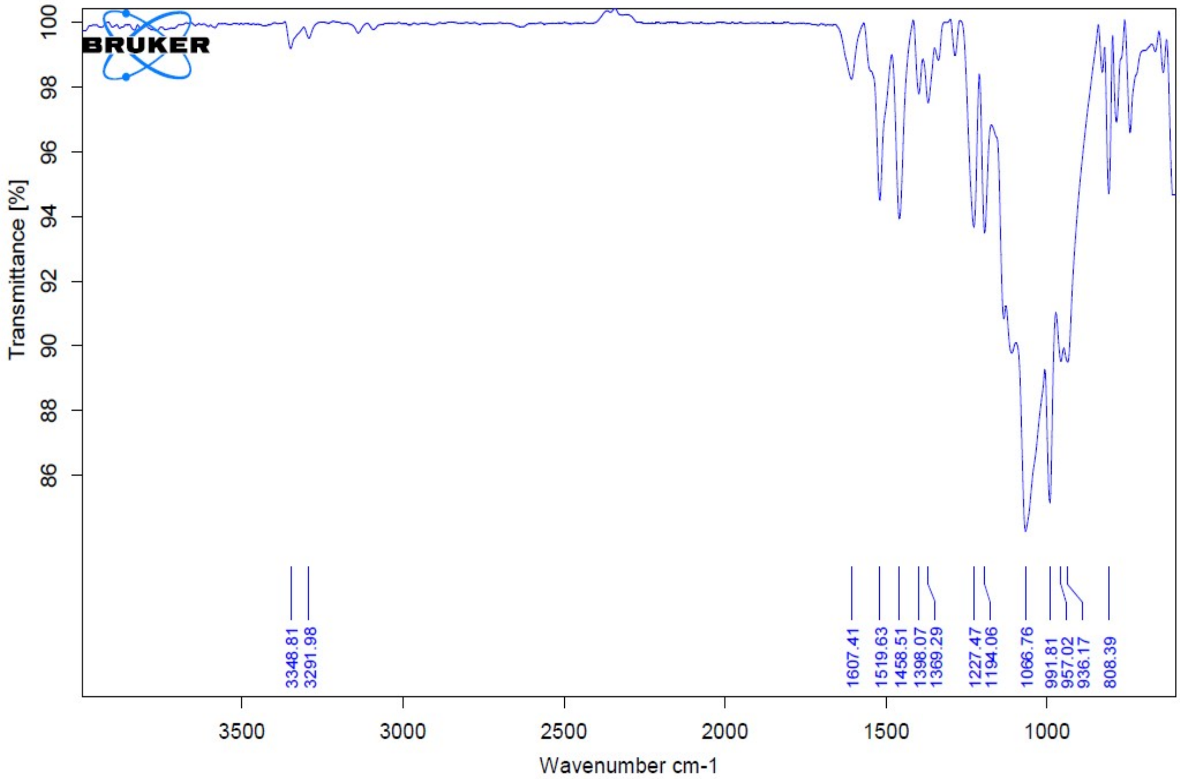


Figure S12: IR spectrum of compound **4a.**

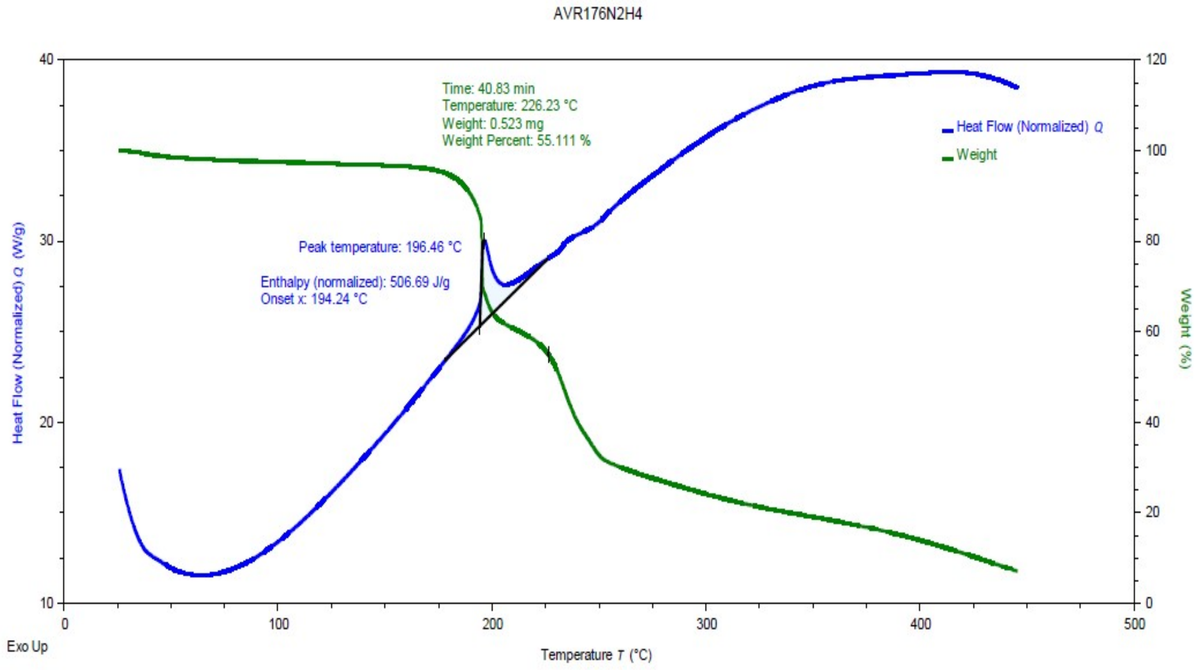


Figure S13: DSC spectra of compound **4a** at heating rate 5 °C min^{-1}.

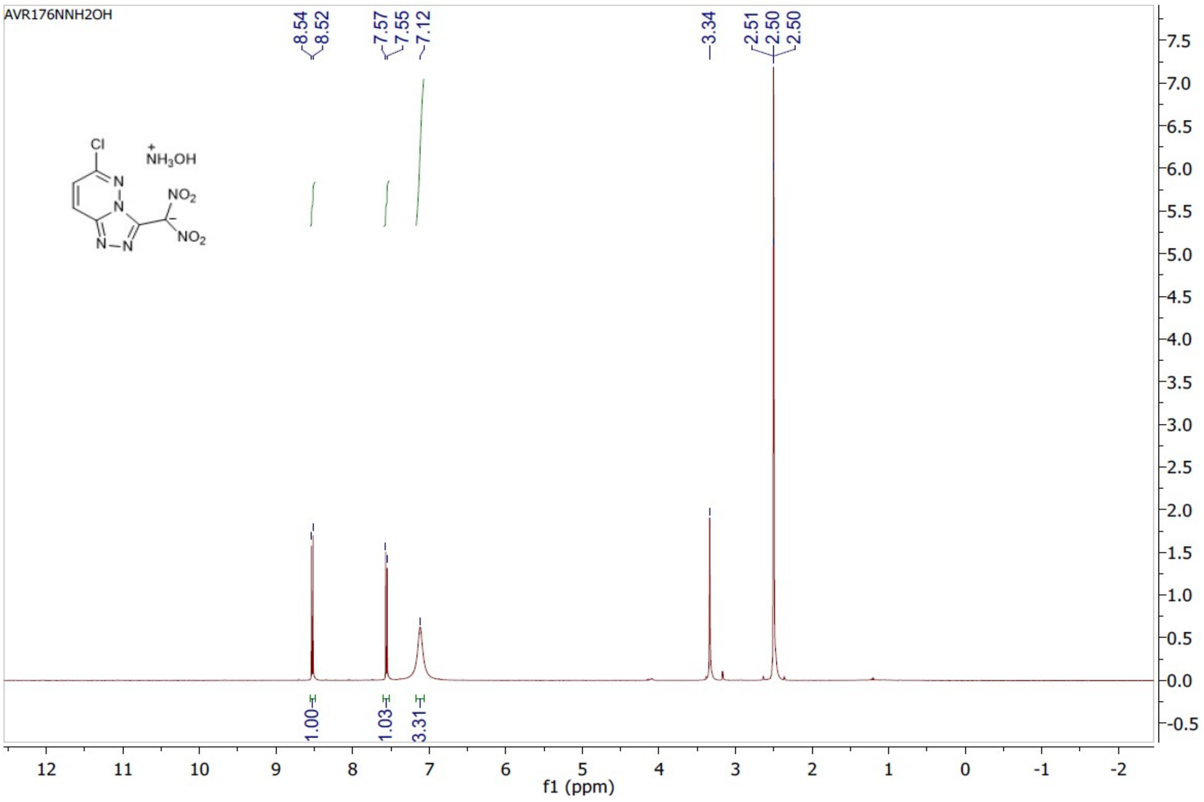


Figure S14: ^{1}H NMR spectrum of compound **4b** in **DMSO-d_6** in 500 MHz.

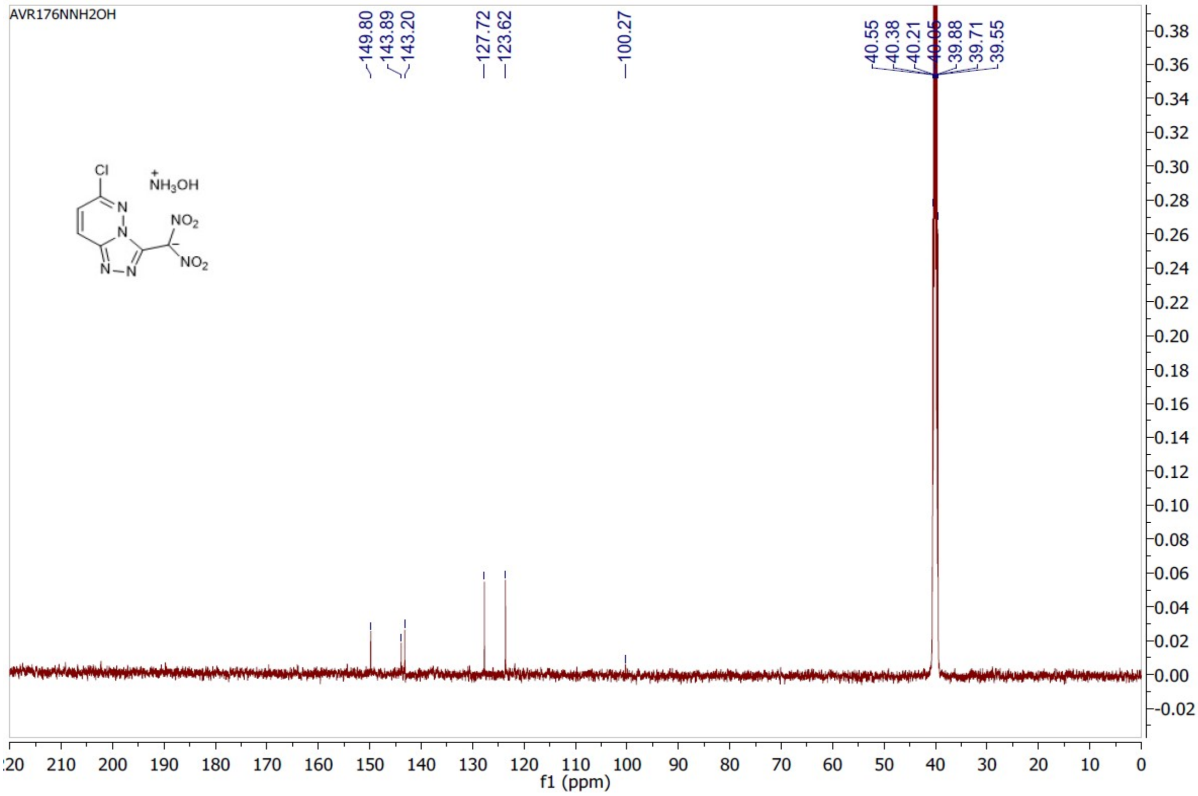


Figure S15: ^{13}C NMR spectrum of compound **4b** in **DMSO-d_6** in 126 MHz**.**

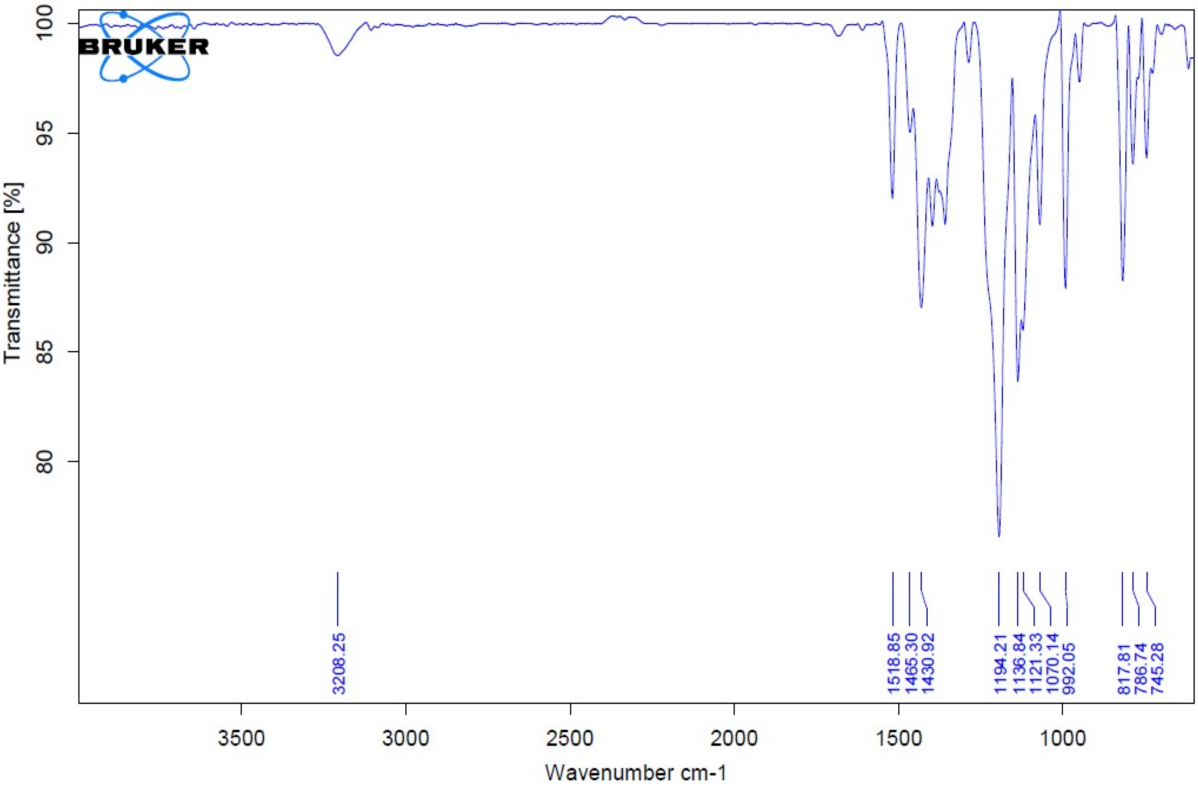


Figure S16: IR spectrum of compound **4b.**

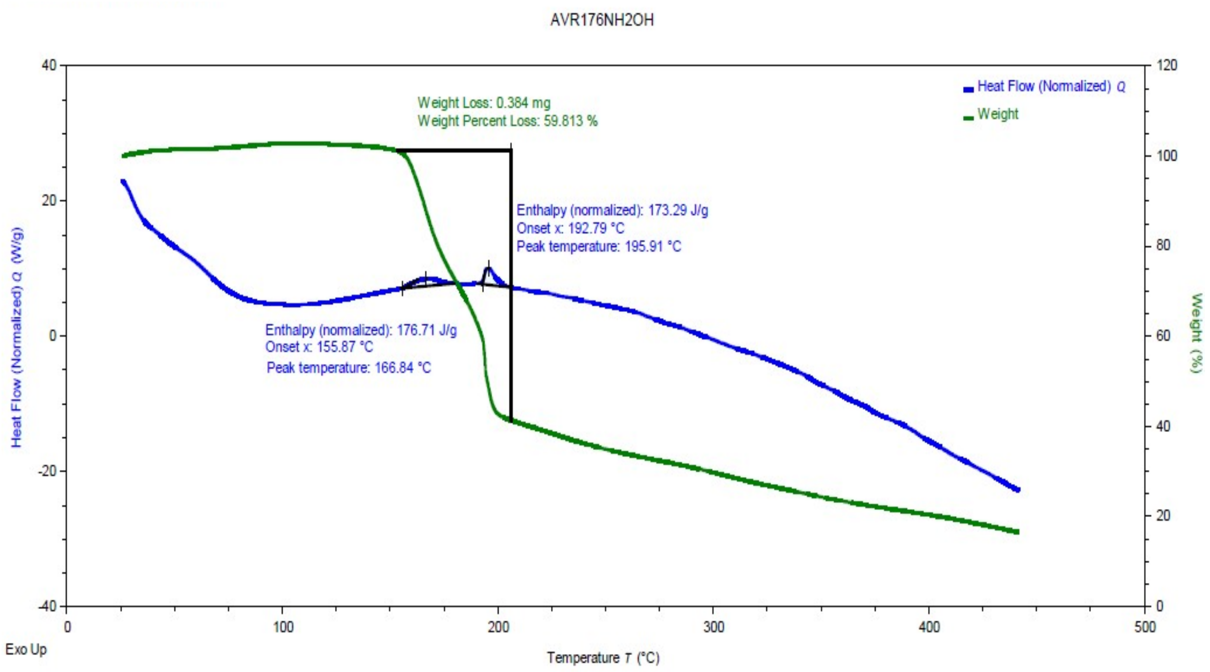


Figure S17: DSC spectra of compound **4b** at heating rate 5 °C min^{-1}**.**

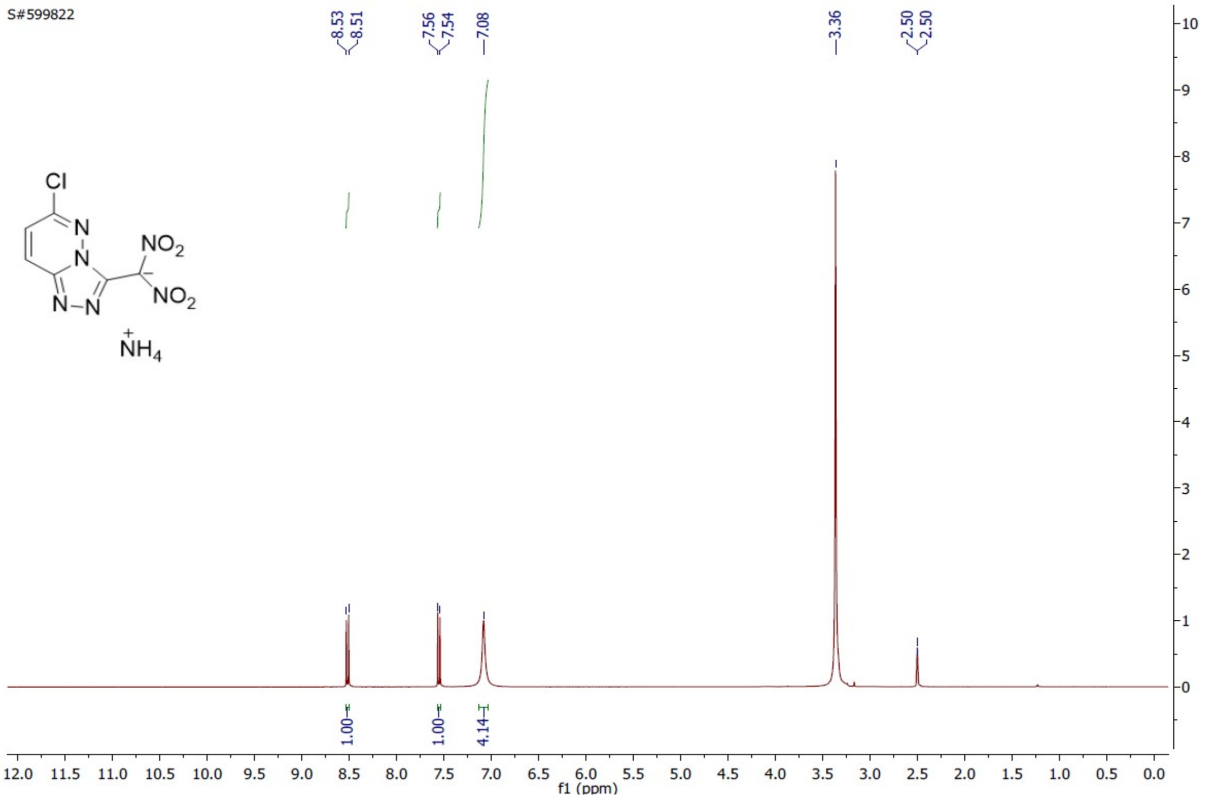


Figure S18: ^{1}H NMR spectrum of compound **4c** in **DMSO-d_6** in 500 MHz.

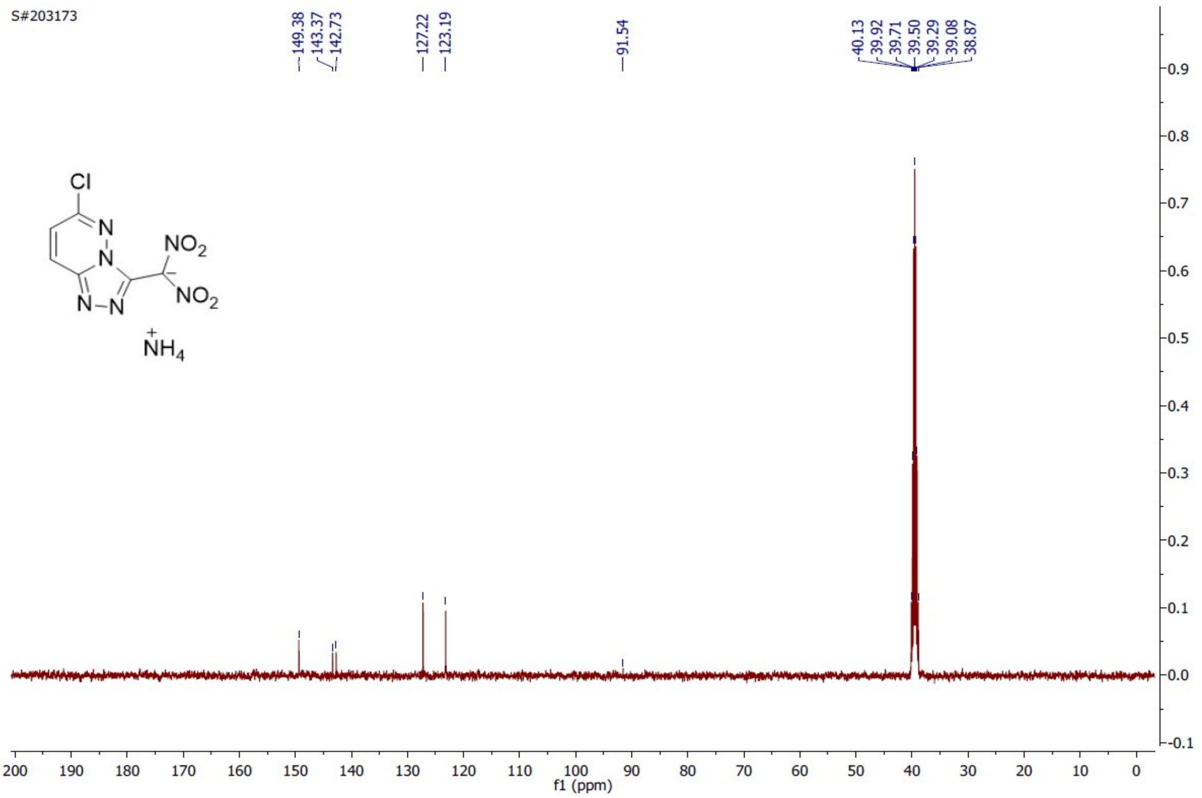


Figure S19: ^{13}C NMR spectrum of compound **4c** in **DMSO-d_6** in 126 MHz.

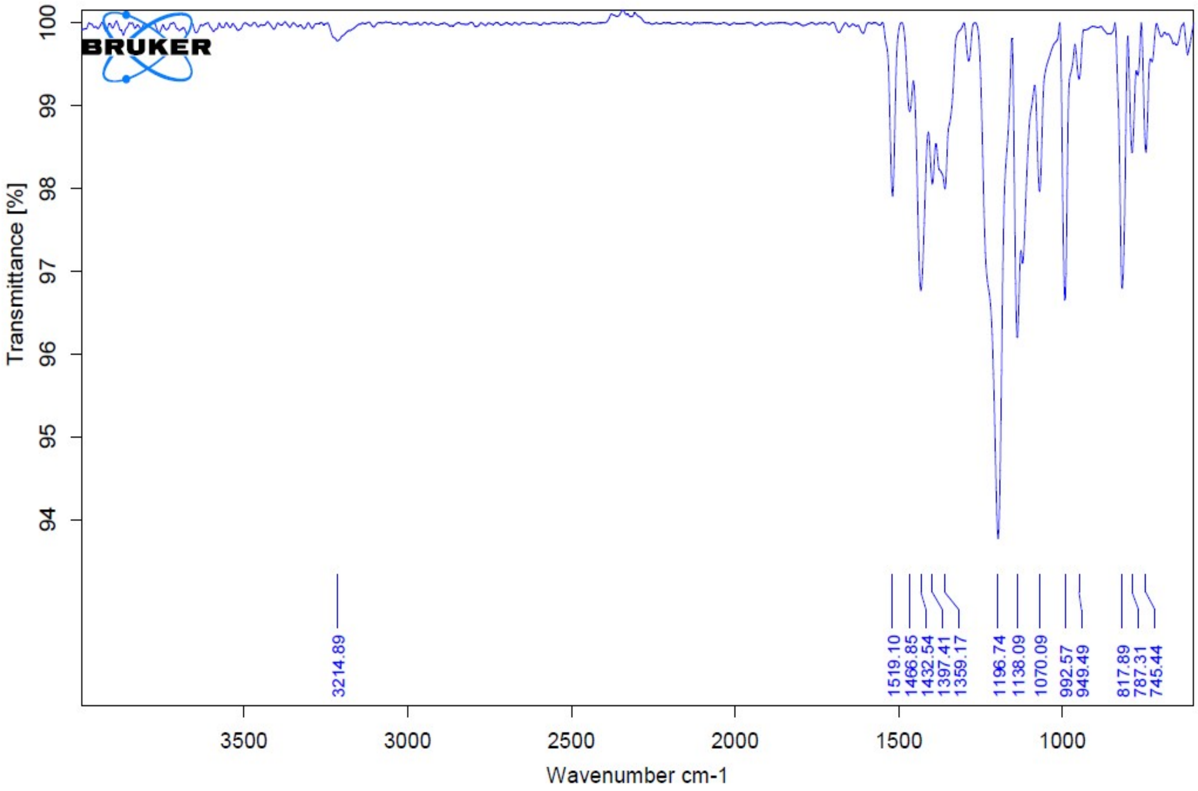


Figure S20: IR spectrum of compound **4c.**

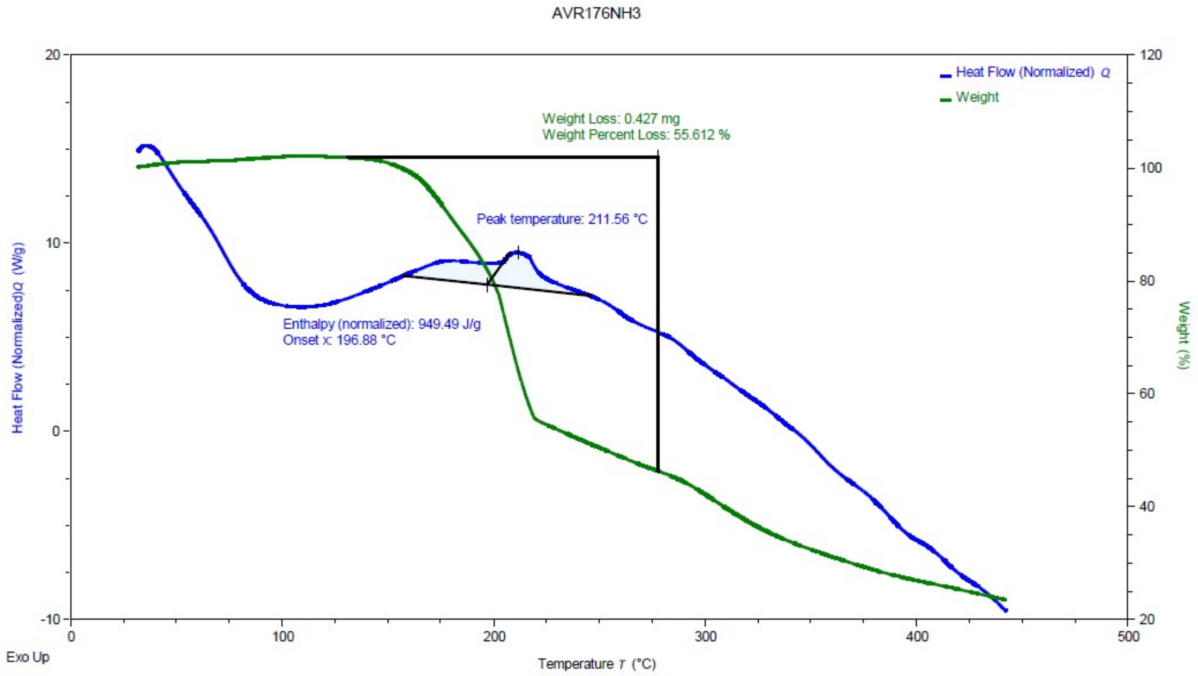


Figure S21: DSC spectra of compound **4c** at heating rate 5 °C min^{-1}**.**

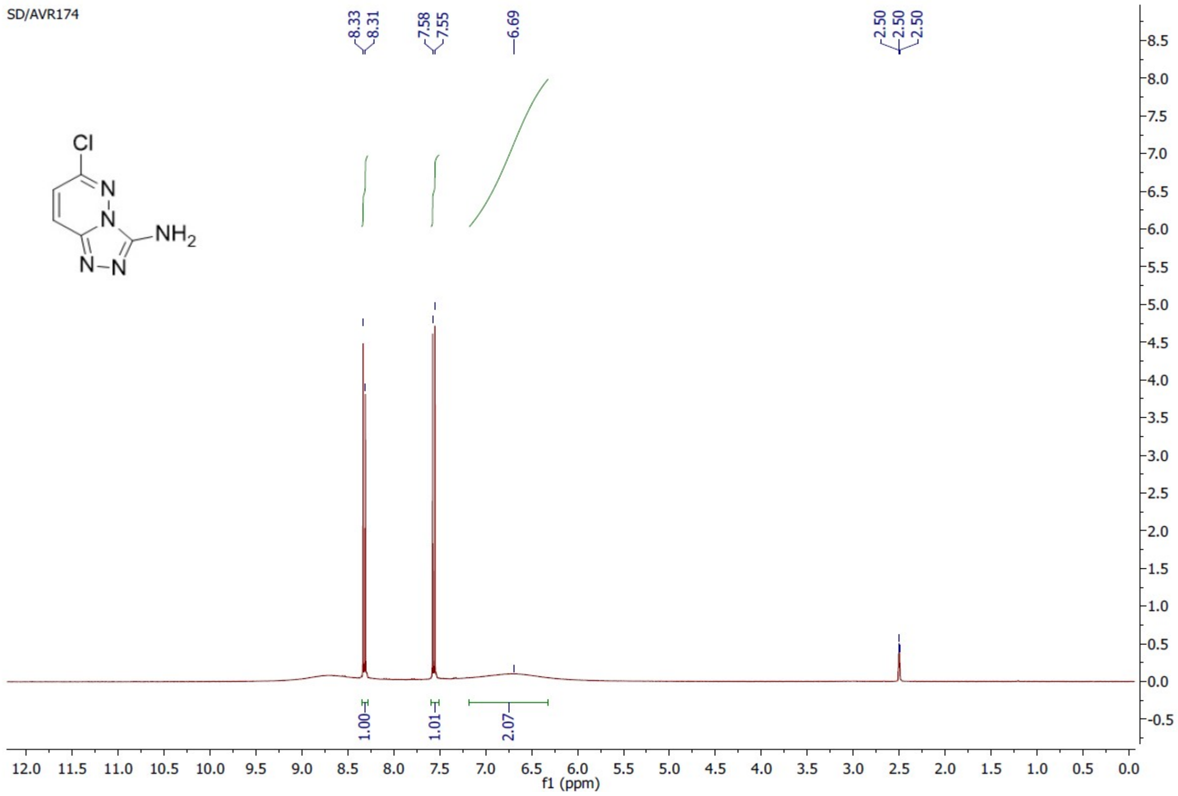


Figure S22: ^{1}H NMR spectrum of compound **5** in **DMSO-d_6** in 500 MHz.

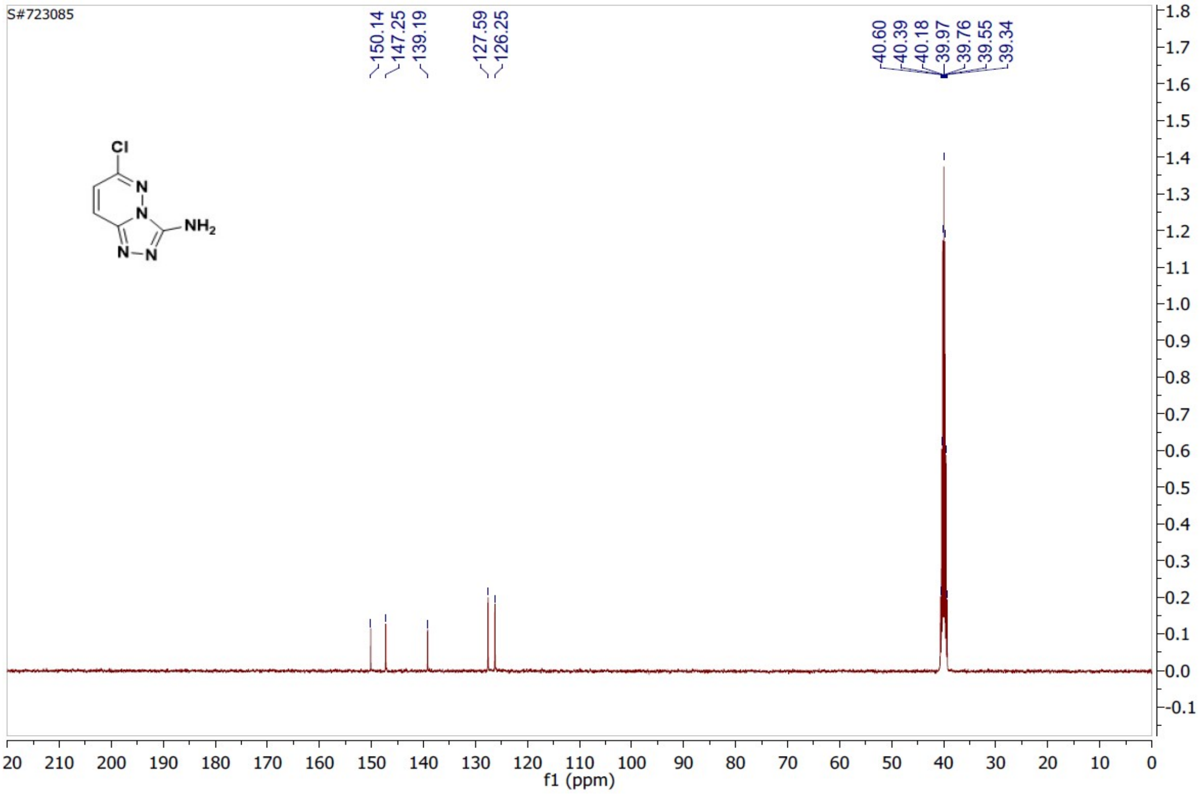


Figure S23: ^{13}C NMR spectrum of compound **5** in **DMSO-*d₆*** in 126 MHz.

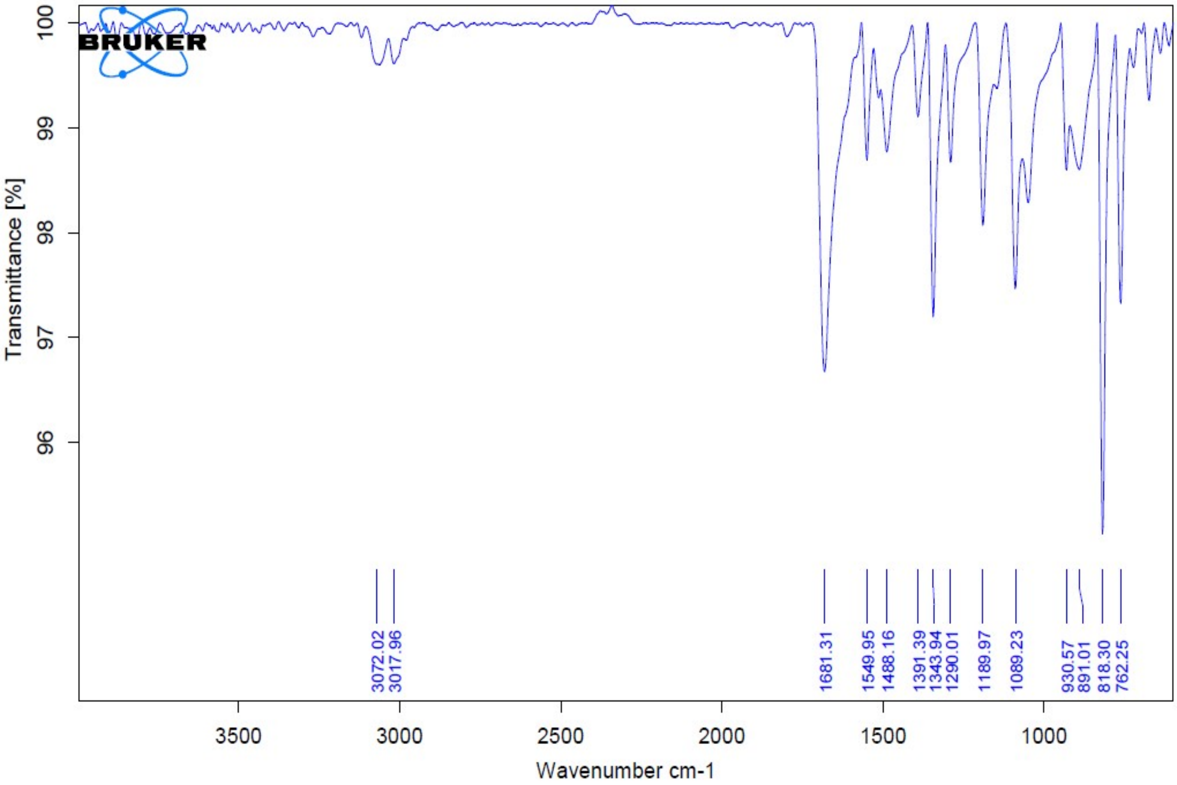


Figure S24: IR spectrum of compound **5.**

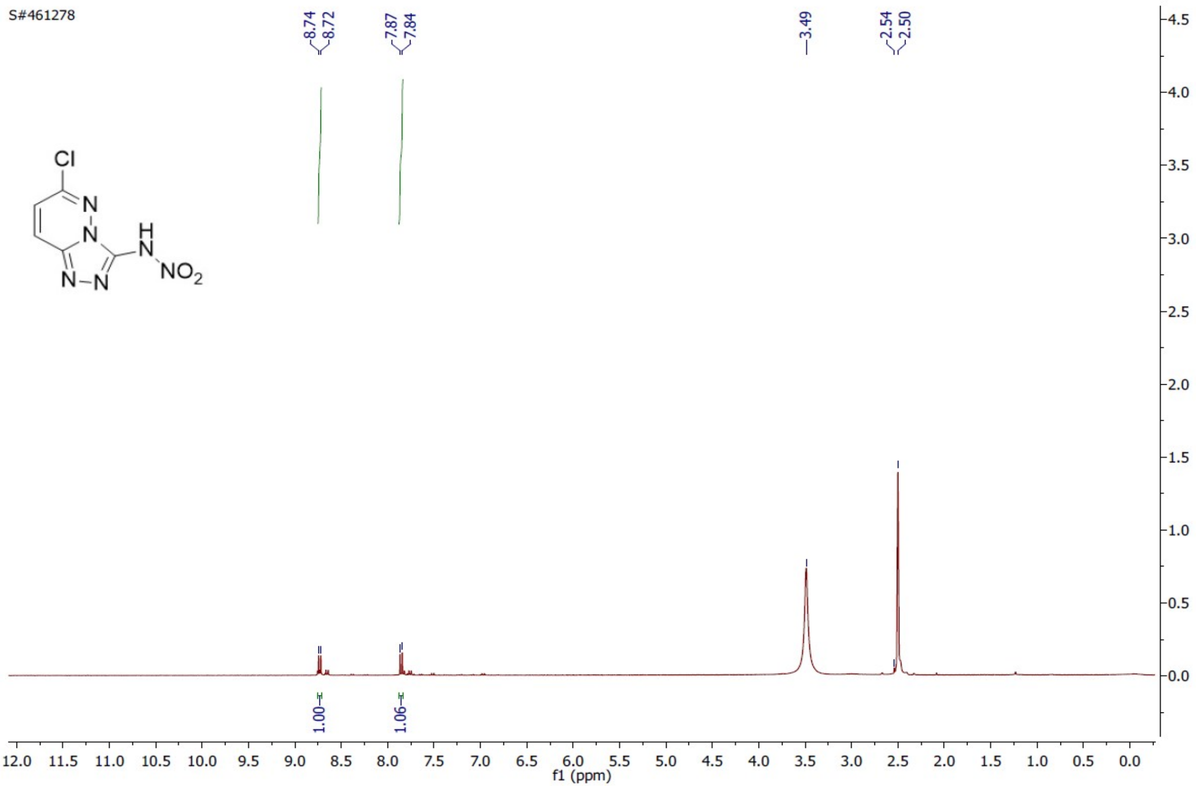


Figure S25: ^{1}H NMR spectrum of compound **6** in **DMSO-*d₆*** in 500 MHz.

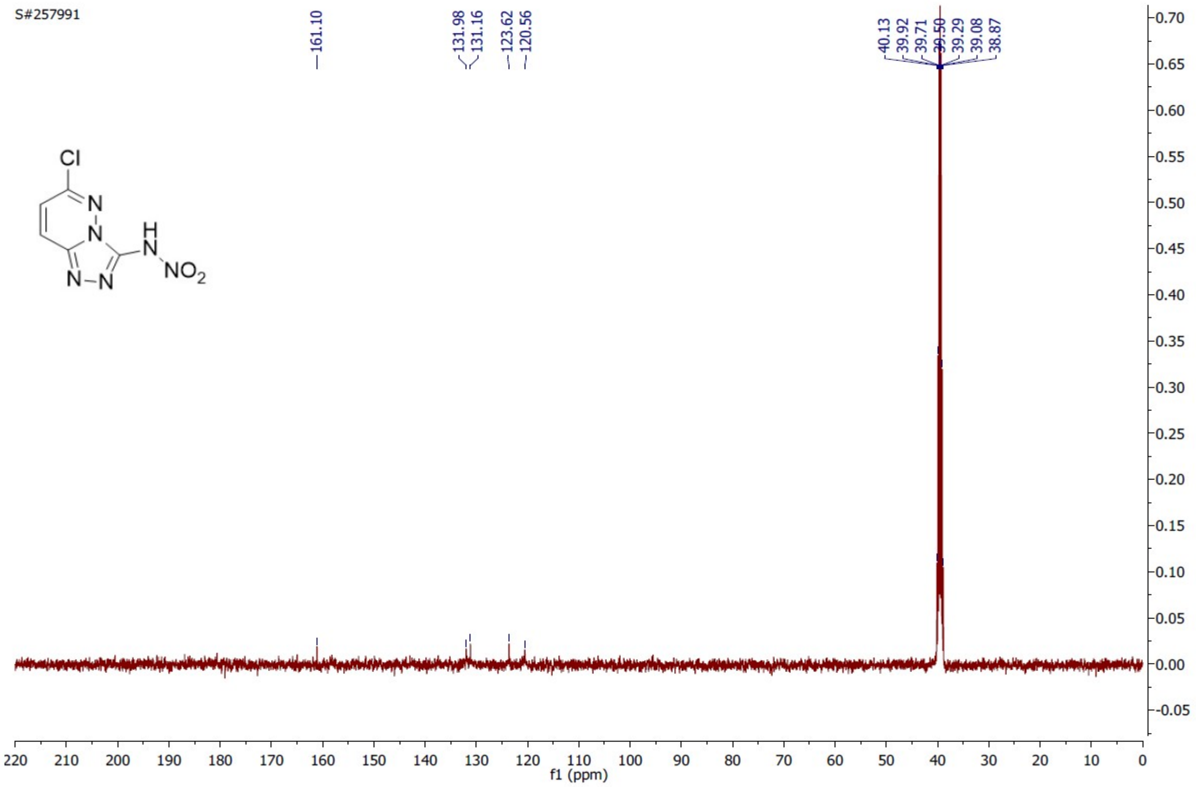


Figure S26: ^{13}C NMR spectrum of compound **6** in **DMSO-*d₆*** in 126 MHz**.**

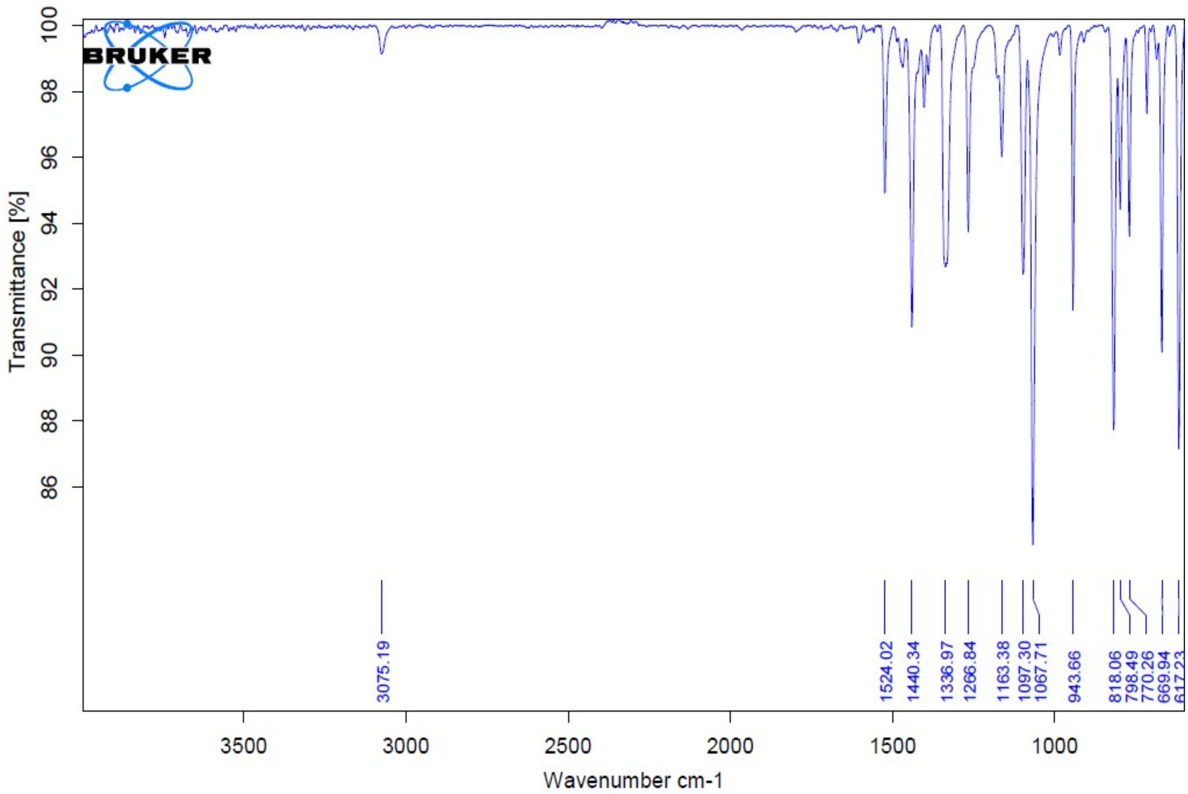
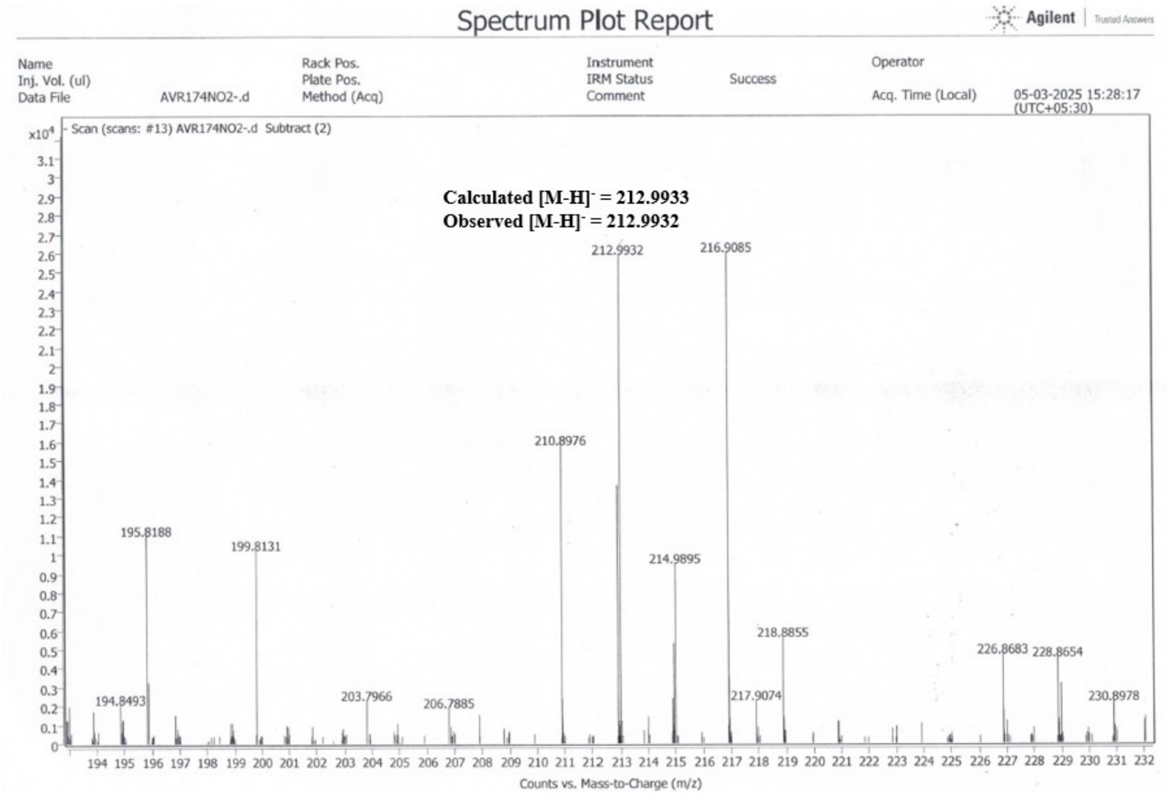


Figure S27: IR spectrum of compound **6.**



Calculated [M-H]$^-$ = 212.9933
Observed [M-H]$^-$ = 212.9932

Figure S28: Mass spectrum of compound **6.**

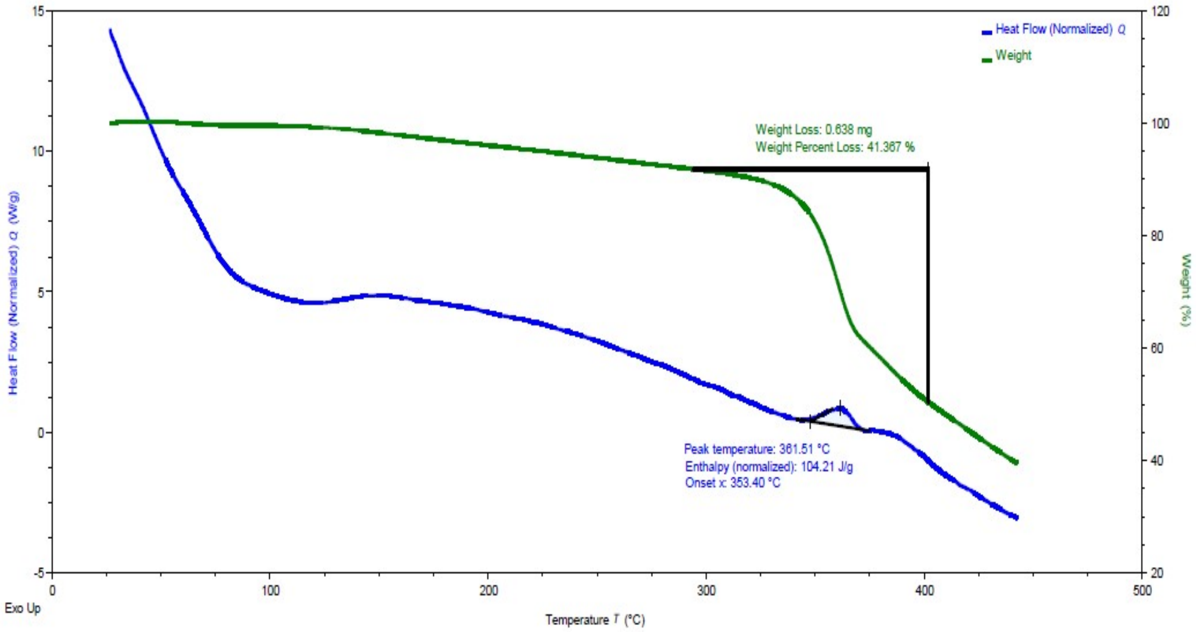


Figure S29: DSC spectra of compound **6** at heating rate 5 °C min^{-1}**.**

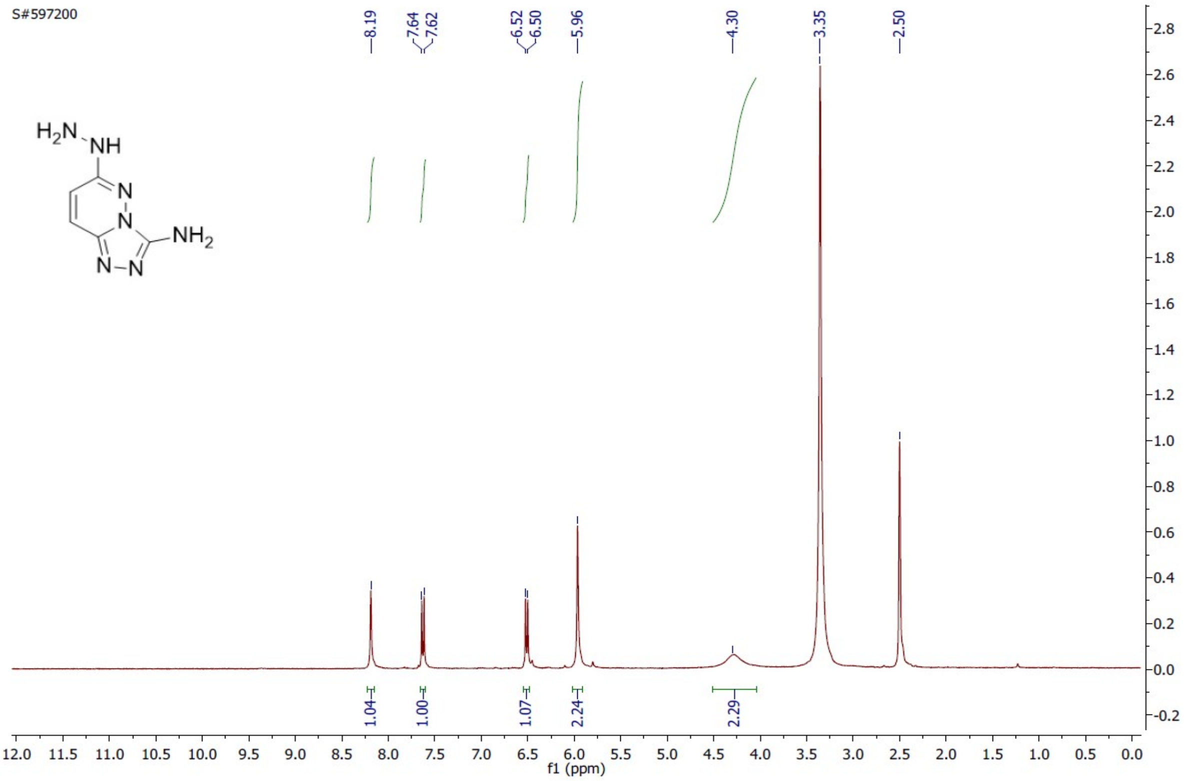


Figure S30: ^{1}H NMR spectrum of compound **7** in **DMSO-$\boldsymbol{d_6}$** in 500 MHz.

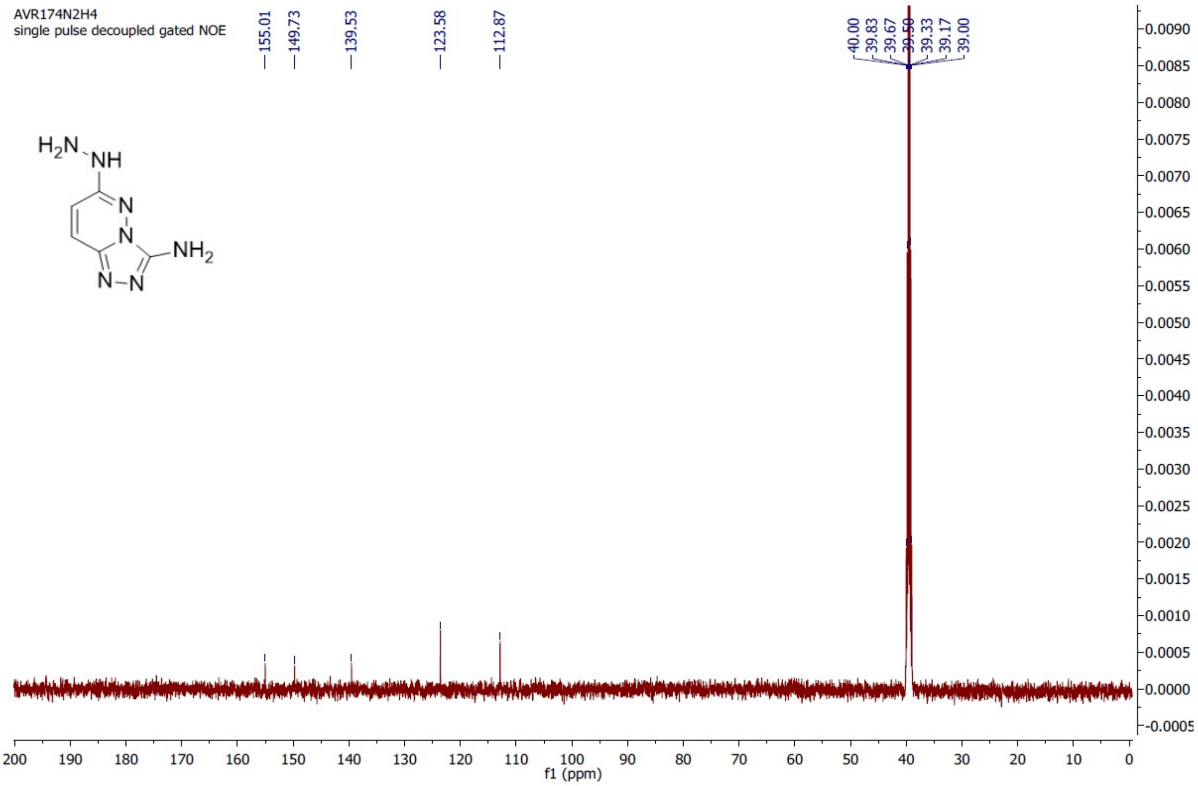


Figure S31: ^{13}C NMR spectrum of compound **7** in **DMSO-d_6** in 126 MHz**.**

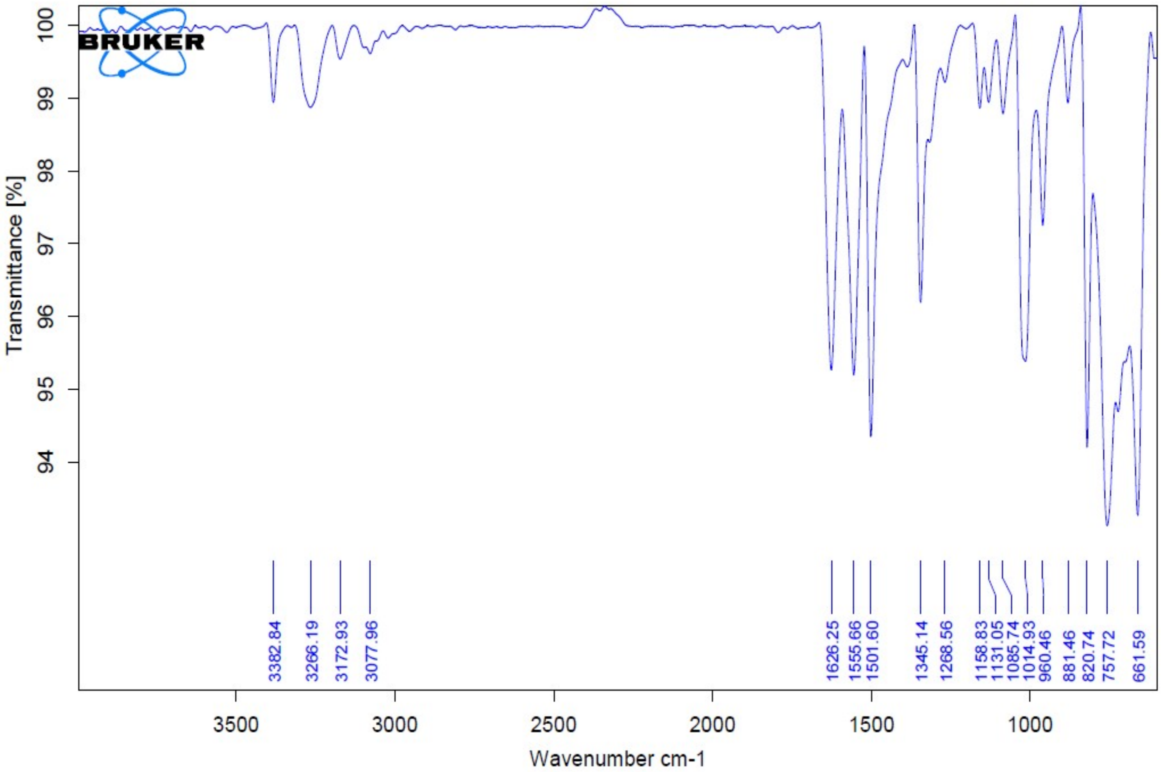
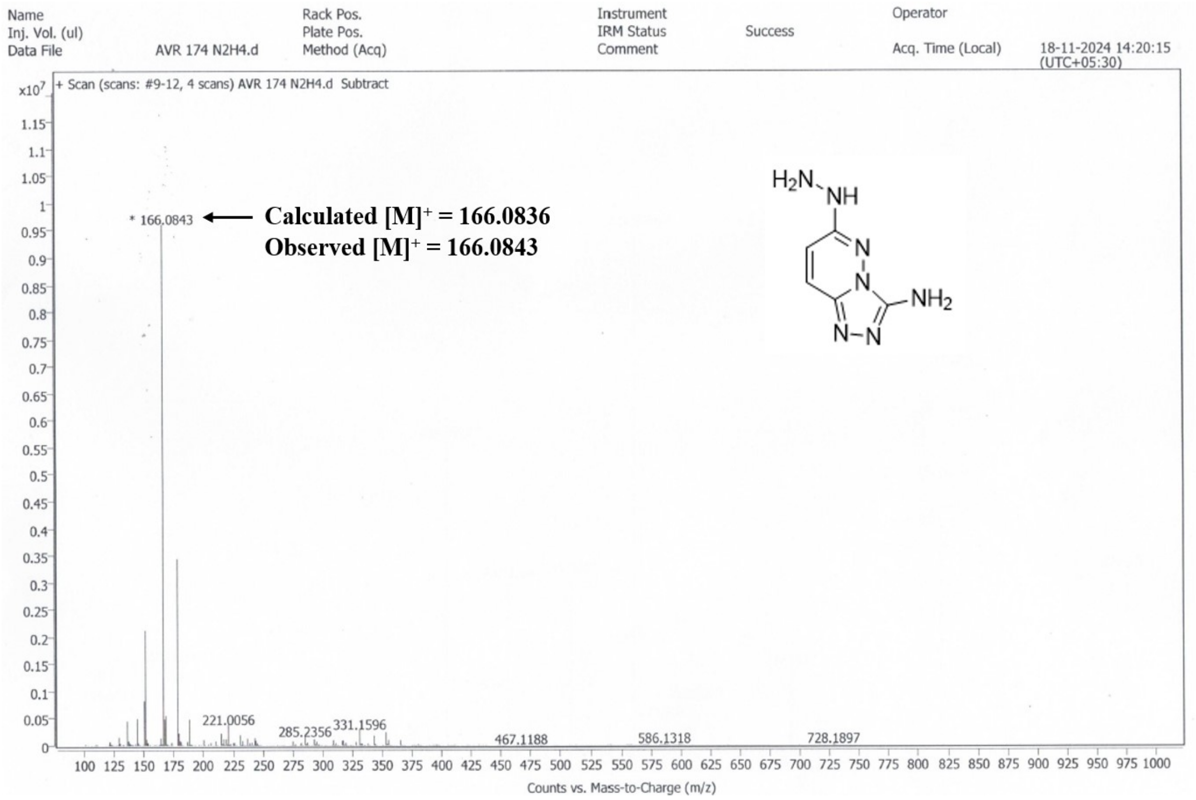


Figure S32: IR spectrum of compound **7.**



Name
Inj. Vol. (ul)
Data File AVR 174 N2H4.d
Rack Pos.
Plate Pos.
Method (Acq)
Instrument
IRM Status Success
Comment
Operator
Acq. Time (Local) 18-11-2024 14:20:15 (UTC+05:30)

Figure S33: Mass spectrum of compound **7.**

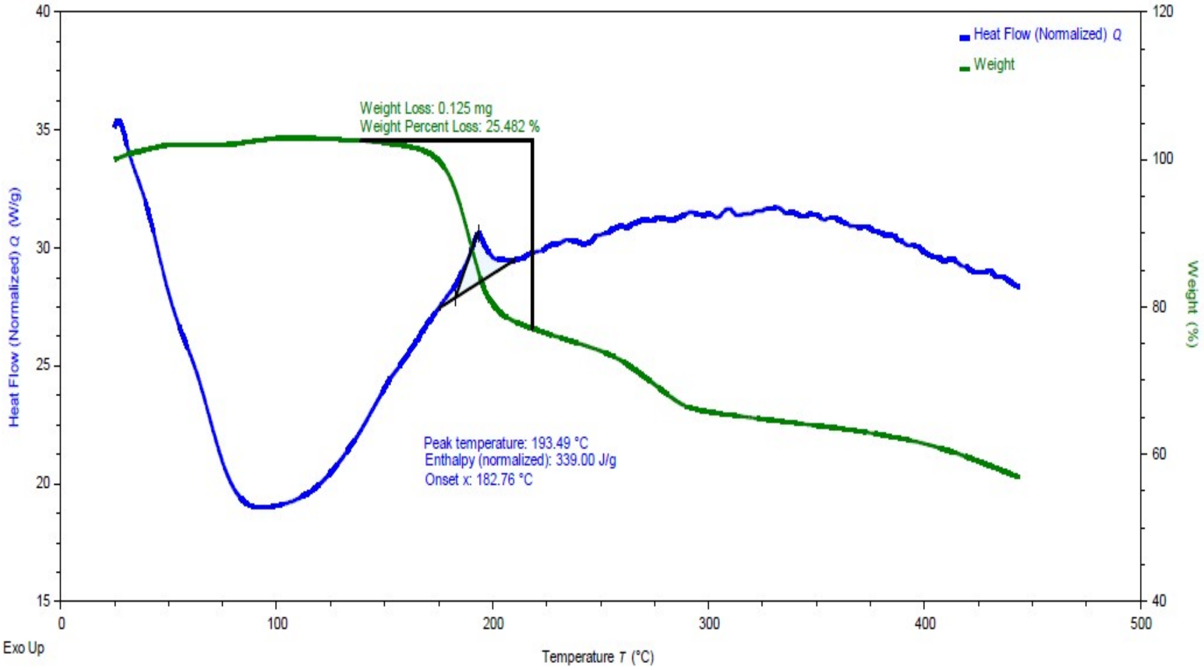


Figure S34: DSC spectra of compound **7** at heating rate 5 ^{o}C min^{-1}**.**

Computational details

Computations were carried out using the Gaussian 09 program suite.[1] 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 designed isodesmic reactions (see Figure S35). Calculated total energies and related data for reference compounds and target compounds is listed in Tables S3 and S4. 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,

$$HOF_{Solid} = HOF_{Gas} - HOF_{Sub} \tag{1}$$

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

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

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[3] and listed in Table S5.

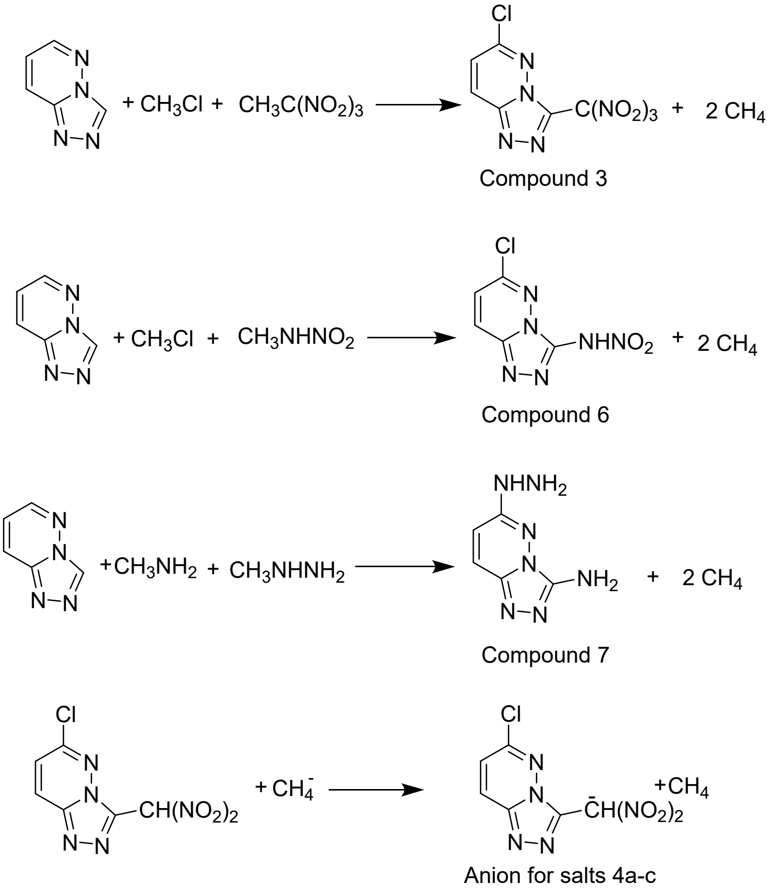


Figure S35. Isodesmic reactions designed to compute gas phase heats of formation and heats of formation for anionic components.

Based on the Born–Haber cycle (shown in Figure S36), the heat of formation of an ionic compound can be simplified by subtracting the lattice energy of the salt (H_L) from the total heat of formation of salt (see Table S6) *i.e.* sum of the heats of formation of the cation and anion as shown in equation (3).

$$\text{HOF (salt, 298 K)} = \text{HOF (cation, 298 K)} + \text{HOF (anion, 298 K)} - H_L \qquad (3)$$

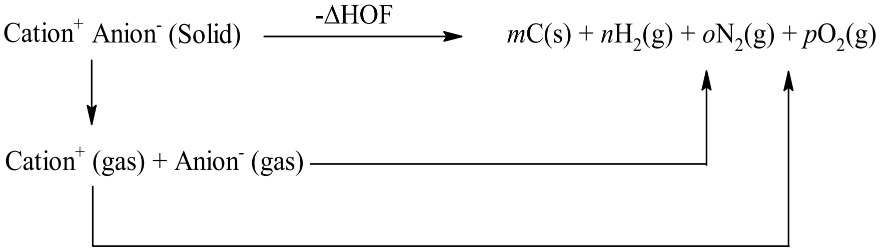


Figure S36. Born-Haber cycle for the formation of energetic salts.

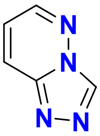
Lattice potential energy is the energy associated with the process in which a crystalline solid lattice, M_pX_q is converted into its constituent gaseous ions, $_pM^{q+}$ (g) and $_qX^{p-}$ (g). The lattice energy can be predicted with reasonable accuracy by using Jenkins' equation (4).[4]

$$\mathrm{H_L} = U_{\mathrm{POT}} + [p(\frac{n_M}{2} - 2) + q(\frac{n_X}{2} - 2)]RT \tag{4}$$

where nM and nX depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. When lattice potential energy (U_{POT}), is incorporated and made part of a Born–Haber cycle, it needs to be converted into a lattice enthalpy term. This lattice enthalpy (H_L) involves correction of the U_{POT} term by an appropriate number of RT terms.

Table S3. Calculated total energies at 298K (E_0), zero-point energies (ZPE), and thermal corrections (H_T) and experimental HOF_{gas} of reference compounds used isodesmic reaction at the M06-2X/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_3NO_2	-244.955044	0.0506	0.0053	-81
NH_3	-56.513648	0.0345	0.0038	-45.94
CH_3CH_3	-79.727235	0.075	0.0045	-84
CH_3Cl	-500.057158	0.038	0.0040	-81.9
CH_3^-	-39.782152	0.0285	0.0039	145.14
CH_3NH_2	-95.776504	0.0644	0.0044	-23.5
CH_3NHNH_2	-151.134206	0.0811	0.0052	98.65[a]
$CH_3CH(NO_2)_2$	-488.554783	0.0827	0.0085	-101.77[a]
$CH_3C(NO_2)_3$	-693.214881	0.0846	0.0109	-69.85[a]

	-411.775221	0.0953	0.0065	439.16[a]

[a]Calculated using G4 method.

Table S4. Calculated total energies (E_0), zero-point energies (ZPE), and thermal corrections (H_T) for target compounds 3, 6, and 7 and anion for salts 4a-c at the M06-2X/def2-TZVPP level.

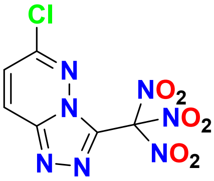
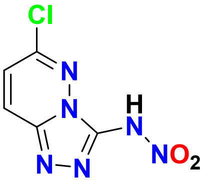
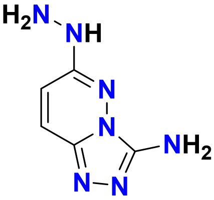
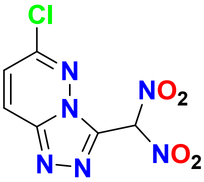
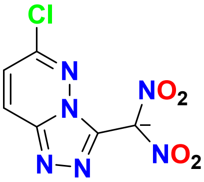
Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF_{gas}/HOF_{anion} (kJ/mol)**	**HOF_{Sub} (kJ/mol)**
	-1524.131967	0.1214	0.0168	-36.5	119.81
	-1131.207188	0.1052	0.0115	486.6	108.93
	-577.774295	0.1466	0.0108	678.4	112.9
	-1319.656754	0.1197	0.0143	-56.3	-
	-1319.162737	0.1064	0.0140	-300.8	-

Table S5. Calculated molecular surface properties of compounds 3, 6, and 7.

Compd.	**Surface area ($Å^2$)**	**Volume ($Å^3$)**	**σ_{tot}^2 (kcal/mol)**	**ν**

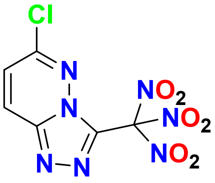
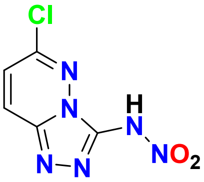
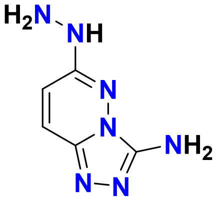
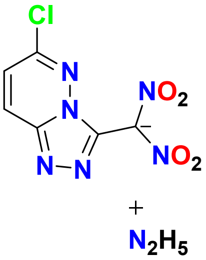
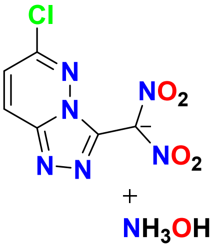
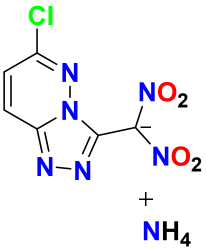
	250.43	268.04	175.27	0.1664
	205.38	204.75	216.03	0.2365
	187.75	186.30	334.28	0.2340

Table S6. Energy content of salts 4a-c.

Compd.	**HOF$_c$^{a}**	**HOF$_a$^{b}**	**U$_{Pot}$^{c}**	**H$_L$^{d}**	**HOF$_{salt}$^{e}**
	769.5	-300.8	467.9	472.8	-4.14
	675.6	-300.8	462.7	467.6	-92.8
	636.8	-300.8	473.7	478.7	-142.7

[a]Heat of formation of cation (kJ mol^{-1}). HOF$_c$ data for cations is obtained from Ref. 5. [b]Heat of formation of anion (kJ mol^{-1}). [c]Lattice potential energy (kJ mol^{-1}). [d]Lattice energy (kJ mol^{-1}). [e]Heat of formation of salt (kJ mol^{-1}).

References:

1 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.

2 E. F. C. Byrd and B. M. Rice, *J. Phys. Chem. A* 2006, **110**, 1005-1013.

3 T. Lu and F. Chen, *J. Comput. Chem*, 2012, **33**, 580–592.

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