Supporting Information

Fused Pyrazolo[3,4-d] pyrimidine Nitrogen-rich Salts with Balanced Energetic Performance

Sagar Nehe,[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. E-mail: srinivasd@iitk.ac.in

[b]Department of Chemistry, National Institute of Technology Kurukshetra, Kurukshetra-136119, Haryana, India.

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Experimental Section:

Caution! The compounds in this work are energetic materials that could potentially explode under certain conditions (e.g., impact, friction, or electric discharge). Appropriate safety precautions, such as the use of shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as leather gloves) should be always taken when handling these materials.

General. All reagents were purchased from BLD Pharma or TCI, or Merck in analytical grade and were used as supplied. ^{1}H, $^{13}C\{^{1}H\}$, and ^{15}N NMR spectra were recorded JEOL DELTA (ECS) 500 (^{1}H, 500 MHz) and $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d6) nuclear magnetic resonance spectrometer. Chemical shifts for ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra are given with respect to external $(CH_3)_4Si$ (^{1}H and ^{13}C). [d6] DMSO was used as a locking solvent unless otherwise stated. IR spectra were recorded using Zn-Se pellets with an ECO-ATR spectrometer (Bruker Alpha II). A single crystal of suitable dimensions was used for data collection. Diffraction intensities were collected on a Bruker APEX-II CCD diffractometer, with graphite-monochromated Mo Kα (0.71073 Å) radiation at 100(2) K. Density was determined at room temperature by employing an Anton Par Ultra5000 gas pycnometer. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and a heating rate of 5 °C min^{-1} on a thermogravimetric differential scanning calorimeter (TGA-DSC (SDT-650)). HRMS was recorded on a Quadrupole Time-of-Flight Mass Spectrometry mass spectrometer and ESI-MS was recorded on Agilent mass spectrometer. Impact and friction sensitivity measurements were made using a standard BAM fall hammer and a BAM friction tester.

Experimental Section:

4,6-dihydrazineyl-2H-pyrazolo[3,4-d]pyrimidine **(1):** Compound **1** was synthesized according to the reported literature method.[1]

***diethyl 2,2'-(10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7-diyl)diacetate* (2):** Ethyl 3-ethoxy-3-iminopropanoate (6.52 g, 33.30 mmol) was dissolved in 10 mL of glacial acetic acid and to this compound **1** (2 g, 11.10 mmol) was added at room temperature. The reaction mixture was gradually heated to reflux and stirred for 12 hours. After completion, the excess solvent was removed using a rotary evaporator and water was added to it and sonicated to yield compound **2** as a brown solid. (Yield: 3 g, 8.05 mmol, 73 %). ^{1}H NMR (500 MHz, DMSO-d6): δ 14.18 (s, 1H), 8.91 (s, 1H), 4.52 (s, 2H), 4.44 (s, 2H), 4.15 – 4.10 (m, 4H), 1.18–1.13 (m, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ 167.8, 167.6, 144.2, 143.8, 143.1, 142.9, 141.3, 127.02, 95.8, 61.1, 32.4, 32.3, 13.9. IR (ATR ZnSe): 3202, 3054, 2943, 1739, 1709, 1646, 1587, 1472, 1379, 1297, 1202, 1027, 940, 877, 776, 735 cm^{-1}. Elemental Analysis Calcd for $C_{15}H_{16}N_8O_4$: C, 48.39; H, 4.33; N, 30.09. Found: C, 48.55; H, 4.36; N, 30.05.

***diethyl 2,2'-(10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7-diyl)bis(2,2-dinitroacetate)* (3):** Compound **2** (0.9 g, 2.42 mmol) was added portion-wise to the mixture of 100% nitric acid (2 mL) and 98% sulfuric acid (3 mL) in an ice-water bath at 0 °C. The reaction mixture was stirred at the same temperature for 20 minutes, then slowly warmed to room temperature and stirred for an additional 10 hours. Upon completion, the reaction mixture was slowly poured onto crushed ice with constant stirring. The resulting precipitate was collected by filtration, washed with water (10 mL), and air-dried to afford compound **3** as an off-white solid. (Yield: 1.2 g, 2.17 mmol, 90%). ^{1}H NMR (500 MHz, DMSO-d6) δ 14.71 (s, 1H), 9.27 (s, 1H), 4.68-4.62 (m, 4H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ 155.2, 154.9, 147.8, 144.4, 140.9, 137.8, 136.8, 129.0, 129.9, 118.5, 96.8, 68.3, 68.0, 13.43, 13.38 IR (ATR ZnSe): 1778, 1647, 1612, 1585, 1297, 1234, 1038, 944, 844, 815, 793, 738 cm^{-1}. Elemental Analysis Calcd for $C_{15}H_{12}N_{12}O_{12}$: C, 32.62; H, 2.19; N, 30.43. Found: C, 32.56; H, 2.57; N, 30.82. HRMS (ESI-QTOF) m/z: Calculated for $C_{15}H_{13}N_{12}O_{12}$ $(M+H)^+$ 553.0770. Found: 553.0777.

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

aqueous ammonia (23.13 mg, 1.35 mmol), hydroxylamine hydrate (69.31 mg, 1.35 mmol), and Hydrazine hydrate (67.92 mg, 1.35 mmol) were added slowly to compound 3 (500 mg, 0.90 mmol) in ethanol at room temperature. The mixture was stirred for 4 hours at same temperature, after which the resulting precipitate was collected by filtration and then dried in air and isolated the salts in quantitative yields.

diammonium 3,7-bis(dinitromethylene)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide **(4a):** Yield: (340.32 mg, 0.85 mmol, 85%) as a light brown solid. Td (onset): 193 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.94 (s, 1H), 7.63 (s, 8H); ^{13}C NMR (126 MHz, DMSO-d6): δ 143.7, 142.3, 141.8, 141.4, 140.7, 127.1, 122.6, 122.4, 95.7; ^{15}N NMR (50.5MHz, DMSO-d6): δ -25.73, -25.84, -30.34, -56.81, -63.74, -71.46, -85.12, -102.00, -115.17, -221.49, -225.56. IR (ATR ZnSe): 3128, 3031, 1634, 1583, 1474, 1396, 1209, 1126, 927, 814, 740 cm^{-1}. Elemental Analysis Calcd for $C_9H_{10}N_{14}O_8$: C, 24.44; H, 2.28; N, 44.34. Found: C, 24.70; H, 2.10; N, 44.55.

dihydroxyl ammonium 3,7-bis(dinitromethylene)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide **(4b):** Yield: (369.3 mg, 0.77 mmol, 75%) as a off white solid. Td (onset): 134 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 14.15 (s, 1H), 10.21 (s, 8H), 8.94 (s, 1H); ^{13}C NMR (126 MHz, DMSO-d6) δ 143.9, 142.5, 141.9, 1415, 140.8, 127.3, 122.7, 122.6, 96.8; IR (ATR ZnSe): 1643, 1585, 1533, 1473, 1215, 1134, 1097, 962, 821, 753 cm^{-1}. Elemental Analysis Calcd for $C_9H_{10}N_{14}O_{10}$ (0.2 H_2O): C, 22.62; H, 2.19; N, 41.04. Found: C, 22.20; H, 2.47; N, 40.90.

dihydrazinium 3,7-bis(dinitromethylene)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide **(4c):** Yield: (342.20 mg, 0.72 mmol,

80%) as a light yellow solid. Td (onset): 194 ºC. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.94 (s, 1H), 7.38 (s, 10H); ^{13}C NMR (126 MHz, DMSO-d6) δ 143.7, 142.4, 141.7, 141.4, 140.7, 127.1, 122.3, 122.4, 95.7; IR (ATR ZnSe): 3332, 3109, 1651, 1585, 1520, 1441, 1413, 1388, 1211, 1134, 1075, 959, 819, 735 cm^{-1}. Elemental Analysis Calcd for $C_9H_{12}N_{16}O_8$: C, 22.89; H, 2.56; N, 47.45. Found: C, 21.38; H, 2.54; N, 48.41.

triethyl 2,2',2''-(10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7,10-triyl)triacetate* (5)*: Compound **2** (800 mg, 2.15 mmol) was dissolved in a mixture of acetonitrile (10 mL) and water (5 mL) at room temperature. To this sodium carbonate (341.6 mg, 3.22 mmol) was added, and the reaction mixture was heated to 50 °C with stirring for 2 hours. The mixture was cool down, to this ethyl bromoacetate (717.6 mg, 4.297 mmol) was added and again the mixture was heated to 70 °C for 12 hours. Upon completion the reaction, the reaction mixture was concentrated under reduced pressure, and water was added. The resulting new precipitate was collected by filtration to afford a brown solid compound **5**. Yield: (689 mg, 1.50 mmol, 70%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.91 (s, 1H), 5.32 (s, 2H), 4.53 (s, 2H), 4.39 (s, 2H), 4.18 (q, 2H), 4.11 (m, 4H), 1.23 (t, 3H), 1.15 (m, 6H); ^{13}C NMR (126 MHz, DMSO-d6) δ 167.7, 167.5, 167,2, 144.4, 143.2, 143.1, 142.9, 140.9, 129.8, 96.7, 61.6, 61.1, 53.8, 32.4, 32.2, 14.0, 13.9; IR (ATR ZnSe): 2986, 1730, 1638, 1592, 1463,1400, 1377, 1329, 1246, 1214, 1019, 873, 777, 730, 656 cm^{-1}. Elemental Analysis Calcd for $C_{19}H_{22}N_8O_6$: C, 49.78; H, 4.87; N, 24.44. Found: C, 50.88; H, 5.17; N, 25.17.

***2,2',2''-(10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7,10-triyl)triacetic acid* (6):** Compound **5** (600 mg, 1.30 mmol) was dispersed in water (10 mL), and sodium hydroxide (523 mg, 13.08 mmol) was added to it at room temperature with stirring. The reaction mixture was then heated to 70 °C and maintained for 2 hours. Upon completion, the mixture was cooled to 10 °C and acidified with 2 N sulfuric acid. The resulting precipitate

was collected by filtration, washed with water, and dried at 50 °C to yield white coloured compound **6**. Yield: (367 mg, 0.98 mmol, 75%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.89 (s, 1H), 5.21 (s, 2H), 4.43 (s, 2H), 4.32 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d6) δ 169.1, 168.9, 168.7, 147.1, 143.5, 143.4, 129.6, 129.3, 124.3, 97.2, 32.3, 32.2; IR (ATR ZnSe): 3560, 3173,1728, 1642, 1597, 1495, 1402, 1305, 1271, 1217, 1181, 841, 809, 732, 700, 636 cm^{-1}. Elemental Analysis Calcd for $C_{13}H_{10}N_8O_6$ (1.4H_2O): C, 39.09; H, 3.23; N, 28.05. Found: C, 39.00; H, 3.449; N, 27.95.

2-(3,7-bis(trinitromethyl)-10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidin-10-yl)acetic acid **(7):** Compound **6** (500 mg, 1.33 mmol) was added slowly to a chilled mixture of 100% nitric acid (2 mL) and concentrated sulfuric acid (3 mL) in an ice-water bath at 0 °C. The reaction was maintained at this temperature for 20 minutes before being allowed to warm to room temperature and stirred for 12 hours. Upon completion, the reaction mixture was poured into crushed ice with stirring. The resulting precipitate was collected by filtration, washed with cold water, and dried in air to afford a reddish-yellow solid, compound **7**, rather than the fully nitrated 3,7,10-tris(trinitromethyl)-10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine (**7'**). Despite exploring various nitration conditions, attempts to obtain the fully nitrated compound **7'** were unsuccessful. Yield: (483 mg, 0.86 mmol, 88%) as a white solid. Td (onset): 114 ^{o}C and 191 ^{o}C. ^{1}H NMR (500 MHz, DMSO-d6): δ 9.31 (s, 1H), 5.28 (s, 2H); ^{13}C NMR (126 MHz, DMSO-d6) δ 167.9, 148.6, 145.3, 140.4, 134.8, 133.7, 131.9, 97.2, 54.5; IR (ATR ZnSe): 3738, 3679, 3555, 2982, 2896, 1624, 1594, 1407, 1283, 1225, 955, 840, 796 cm^{-1}. Elemental Analysis Calcd for $C_{11}H_4N_{14}O_{14}$: C, 23.75; H, 0.72; N, 35.25. Found: C, 24.09; H, 0.60; N, 34.31..

10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7-diamine **(8):** Compound **1** (1.5 g, 8.33 mmol) was dissolved in 15 mL of 1 N hydrochloric acid and stirred at room temperature for 15 minutes. Cyanogen bromide (2.2 g, 20.81 mmol) was then added, and the

mixture was heated to 70 °C in an oil bath and stirred for 15 hours. After completion of the reaction, the mixture was cooled to room temperature and neutralized with sodium carbonate. The resulting grey precipitate was collected by filtration, washed with water, and air-dried to yield pure compound **8** as a dark grey solid. (Yield: 1.6 g, 6.95 mmol, 83%). ^{1}H NMR (500 MHz, DMSO-d6): δ 8.60 (s, 1H), 6.58 (s, 2H), 6.42 (t, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 150.3, 148.9, 141.5, 138.4, 137.9, 125.6, 96.2. IR (ATR ZnSe): 3435, 3120, 1641, 1559, 1517, 1423, 1261, 792, 715 cm^{-1}. Elemental Analysis Calcd for $C_7H_6N_{10}$ (1.5H_2O): C, 33.39; H, 3.36; N, 55.62. Found: C, 33.35; H, 3.33; N, 55.65. HRMS (ESI-QTOF) m/z: Calculated for $C_7H_7N_{10}$ $(M+H)^+$ 231.0850. Found: 231.0853.

***N,N'-(9H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-3,7-diyl)dinitramide* (9):** Compound **8** (1.0 g, 4.34 mmol) was slowly added to 4 mL of 100% nitric acid in an ice-water bath at 0 °C with continuous stirring. The reaction mixture was maintained at this temperature for 20 minutes, then allowed to warm to room temperature and stirred for an additional 15 hours. Upon completion, the mixture was poured onto crushed ice with stirring. The resulting precipitate was collected by filtration, washed with cold water, and air-dried to obtain compound **9** as a reddish-yellow solid. (Yield: 1.21 g, 3.77 mmol, 87%). Td (onset): 213 ˚C. 1H NMR (500 MHz, DMSO-d6): δ 14.27 (s, 1H), 8.92 (s, 1H). 13C NMR (126 MHz, DMSO-d6) δ 148.7, 147.2, 140.9, 138.3, 137.3, 128.0, 95.4. IR (ATR ZnSe): 3256, 1633, 1595, 1562, 1514, 1485, 1373, 1318, 1257, 1206, 1120, 1074, 1046, 962, 851, 774, 726, 691, 650 cm^{-1}. Elemental Analysis Calcd for $C_7H_4N_{12}O_4$ (0.8H_2O): C, 25.13; H, 1.69; N, 50.23. Found: C, 25.11; H, 1.72; N, 50.23. HRMS (ESI-QTOF) m/z: Calculated for $C_7H_4N_{12}O_4Na$ $(M+Na)^+$ 343.0376. Found: 343.0365.

General procedure for the synthesis of salts 10a-10c:

aqueous ammonia (39.89 mg, 2.34 mmol), hydroxylamine hydrate (119.48 mg, 2.34 mmol), 5*H*-[1,2,4]triazolo[4,3-b][1,2,4]triazole-3,5,6-triamine (360.52 mg, 2.268 mmol) and were added slowly to compound 9 (500 mg, 1.56 mmol) in ethanol at room temperature. The mixture was stirred for 4 hours at room temperature, after which the resulting precipitate was collected by filtration and then dried in air and isolated them in quantitative yields.

diammonium (3Z,7Z)-3,7-bis(nitroimino)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide **(10a):** Yield: (481.48 mg, 1.36 mmol, 87%) as a light brown solid. Td (onset): 227 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.64 (s, 1H), 7.20 (s, 8H); ^{13}C NMR (126 MHz, DMSO-d6) δ 150.7, 149.4, 147.1, 141.2, 141.1, 125.3, 96.1; IR (ATR ZnSe): 2985, 2893, 1647, 1593, 1508, 1398, 1328, 1284, 1212, 852, 764, 721 cm^{-1}. Elemental Analysis Calcd for $C_7H_{10}N_{14}O_4$ (0.3 CH_3CN): C, 24.90; H, 3.00; N, 54.64. Found: C, 24.29; H, 3.04; N, 54.10.

dihydroxyl ammonium *(3Z,7Z)-3,7-bis(nitroimino)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide* **(10b):** Yield: (482.54 mg, 1.25 mmol, 80%) as a light yellow solid. Td (onset): 191 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.69 (s, 1H), 7.15 (s, 8H); ^{13}C NMR (126 MHz, DMSO-d6) δ 150.4, 149.3, 141.2, 140.8, 139.6, 125.8, 96.0; IR (ATR ZnSe): 3741, 2987, 2892, 2826, 1647, 1594, 1508, 1399, 1327, 1284, 1213, 1070, 989, 852, 763, 720 cm^{-1}. Elemental Analysis Calcd for $C_7H_{10}N_{14}O_6$ (0.8 H_2O): C, 20.98; H, 2.92; N, 48.94. Found: C, 20.43; H, 3.48; N, 49.39.

di (3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium) (3Z,7Z)-3,7-bis(nitroimino)-3H,7H,10H-pyrazolo[4,3-e]bis([1,2,4]triazolo)[4,3-a:4',3'-c]pyrimidine-2,6-diide **(10c):** Yield: (814.56 mg, 1.29 mmol, 83%) as a light brown solid. Td (onset): 254.93 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 13.83 (s, 1H), 8.70 (s, 1H), 7.79 (s, 4H), 7.11 (s, 4H), 5.75 (s, 4H); ^{13}C NMR (126 MHz, DMSO-d6) δ 159.6, 150.7, 149.4, 148.1, 142.1, 141.2, 141.1,

139.8, 125.4, 96.1; ^{15}N NMR (50.5MHz, DMSO-d6): δ -14.55, -15.33, -79.89, -86.33, -112.31, -131.10, -152.79, -177.44, -192.74, -201.90, -201.95, -205.13, -228.94, -264.54, -264.60, -287.44, -317.01, -326.97, -329.84, -331.89. IR (ATR ZnSe): 2988, 2893, 1634, 1562, 1486, 1319, 1216, 1069, 964, 780, 718 cm^{-1}. Elemental Analysis Calcd for $C_{13}H_{16}N_{28}O_4$ (0.5 H_2O): C, 24.49; H, 2.69; N, 61.52. Found: C, 24.77; H, 2.93; N, 61.06.

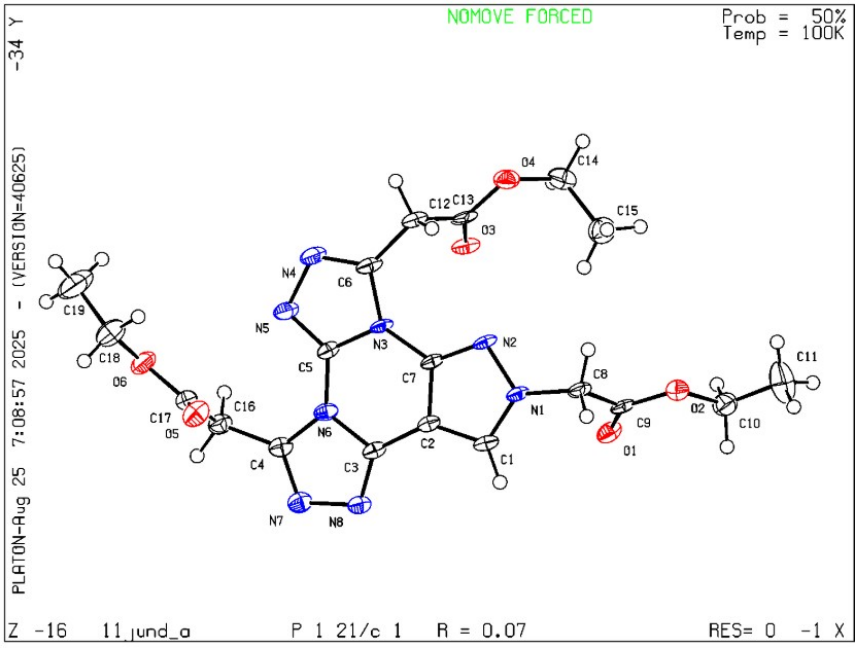


Figure S1: Molecular Structure of **5.**

Table 1 Crystal data and structure refinement for 5.

CCDC No.	2482600
Empirical formula	$C_{19}H_{22}N_8O_6$
Formula weight	458.437
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.810(4)

b/Å	18.242(5)
c/Å	8.351(2)
α/°	90
β/°	105.380(7)
γ/°	90
Volume/Å^3	2175.3(10)
Z	4
ρ_{calc}g/cm^3	1.400
μ/mm^{-1}	0.107
F(000)	960.5
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.3 to 50.1
Index ranges	-19 ≤ h ≤ 19, -24 ≤ k ≤ 24, -11 ≤ l ≤ 11
Reflections collected	30400
Independent reflections	3798 [R_{int} = 0.0725, R_{sigma} = 0.0486]
Data/restraints/parameters	3798/0/302
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0743, wR_2 = 0.1861
Final R indexes [all data]	R_1 = 0.0777, wR_2 = 0.1892
Largest diff. peak/hole / e Å^{-3}	0.63/-0.48

NMR, IR Spectra, HRMS & TG-DSC plots

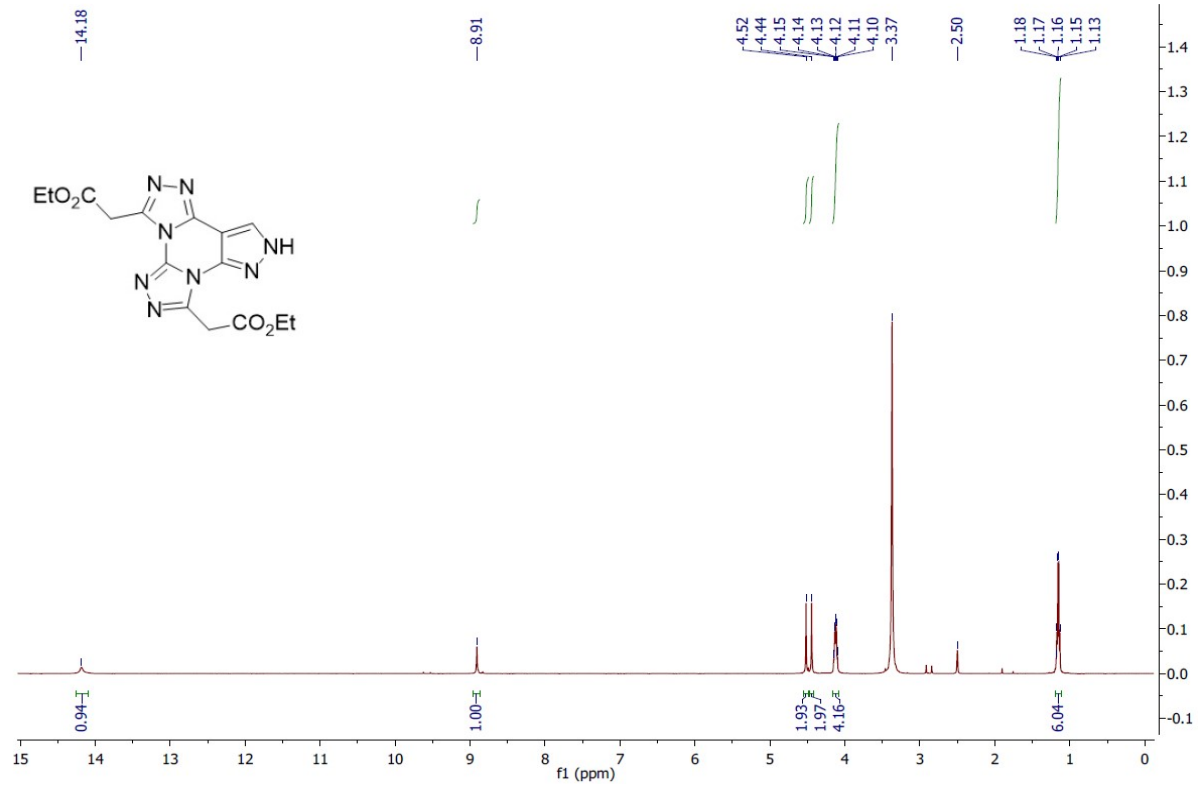


Figure S2: ^{1}H NMR spectrum of compound **2** in **DMSO-*d*$_6$** in 500 MHz**.**

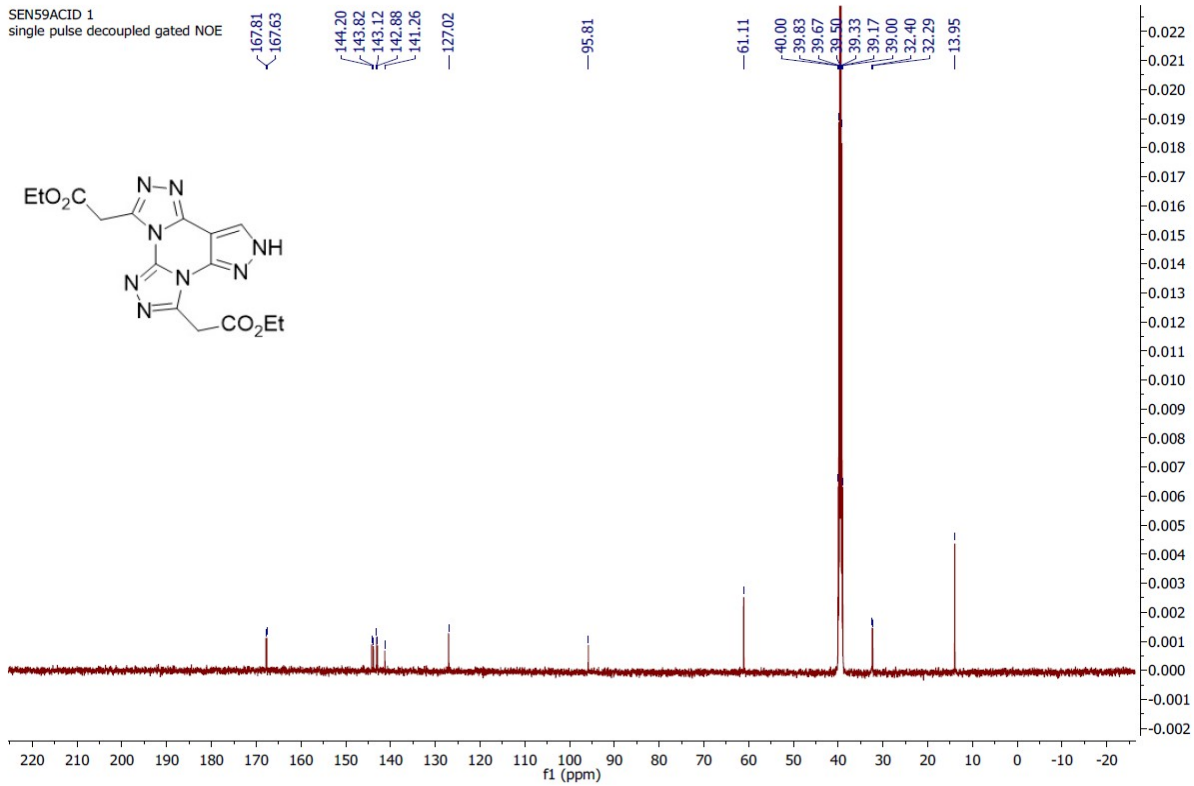


Figure S3: ^{13}C NMR spectrum of compound **2** in **DMSO-*d*$_6$** in 126 MHz.

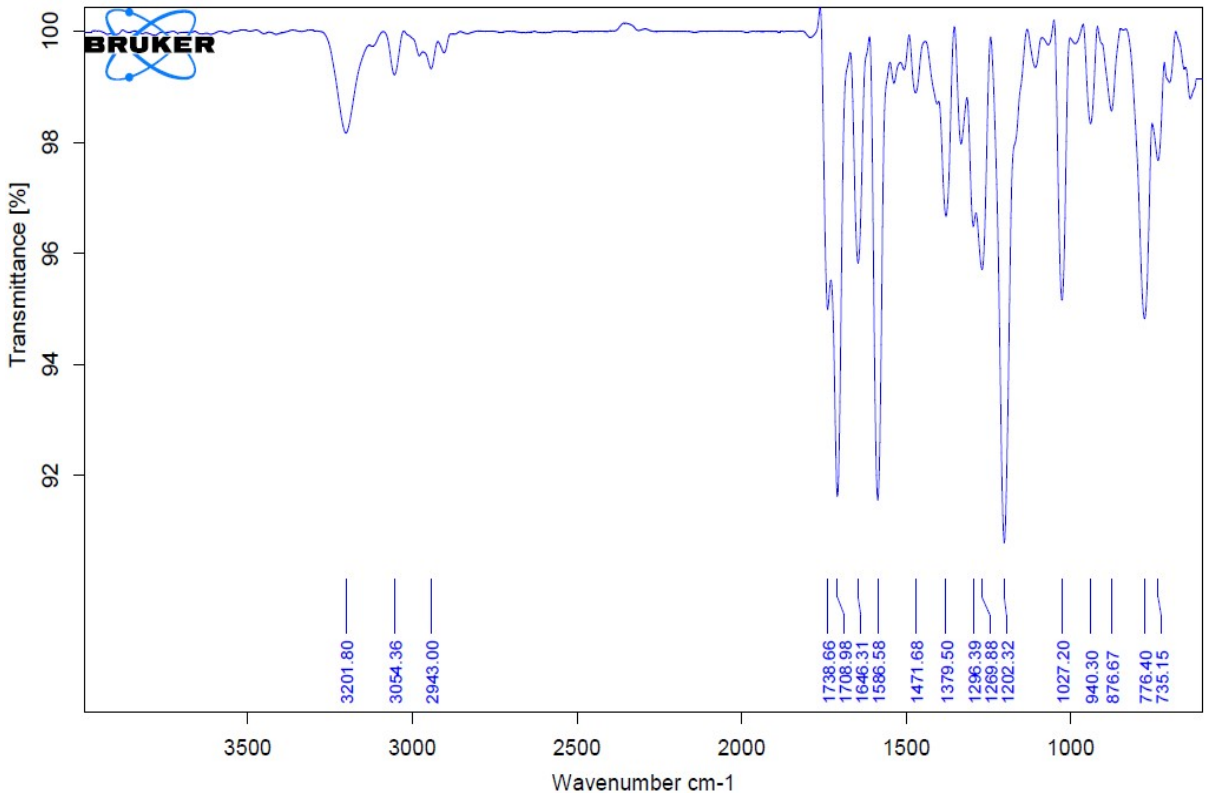


Figure S4: IR spectrum of compound **2.**

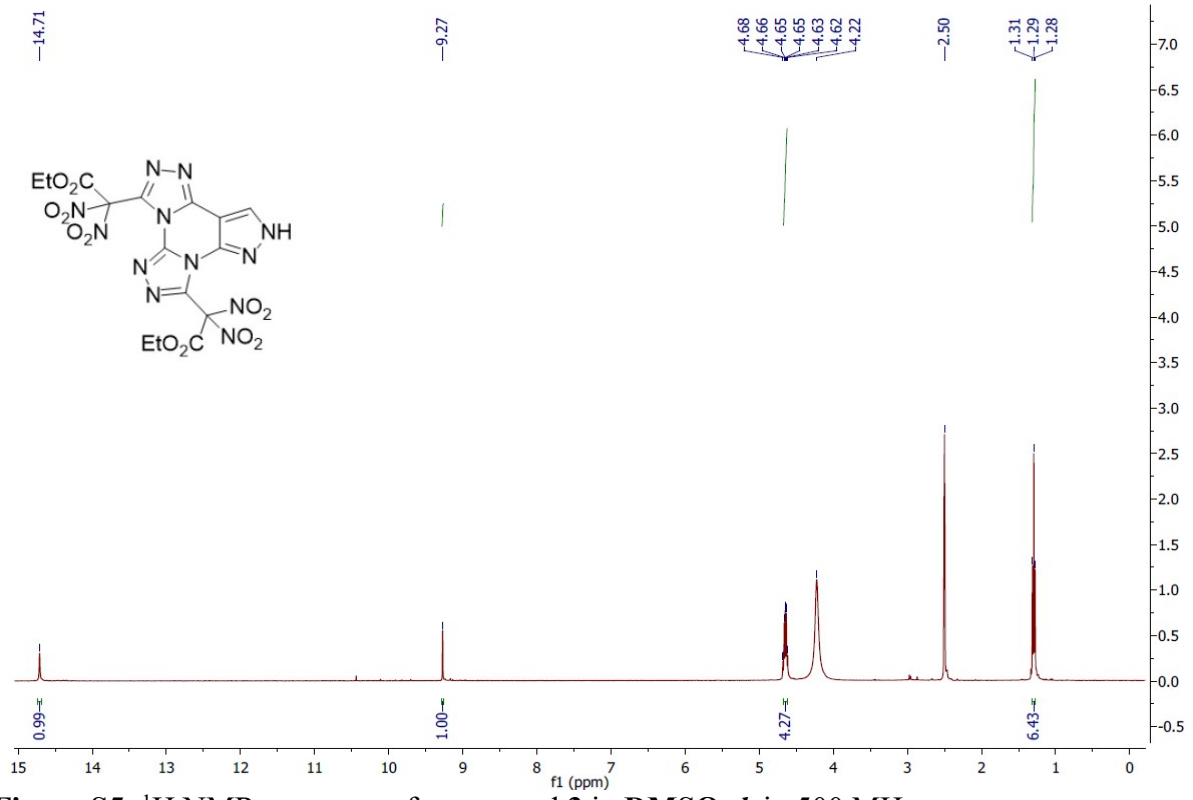


Figure S5: ^{1}H NMR spectrum of compound **3** in **DMSO-*d*$_6$** in 500 MHz**.**

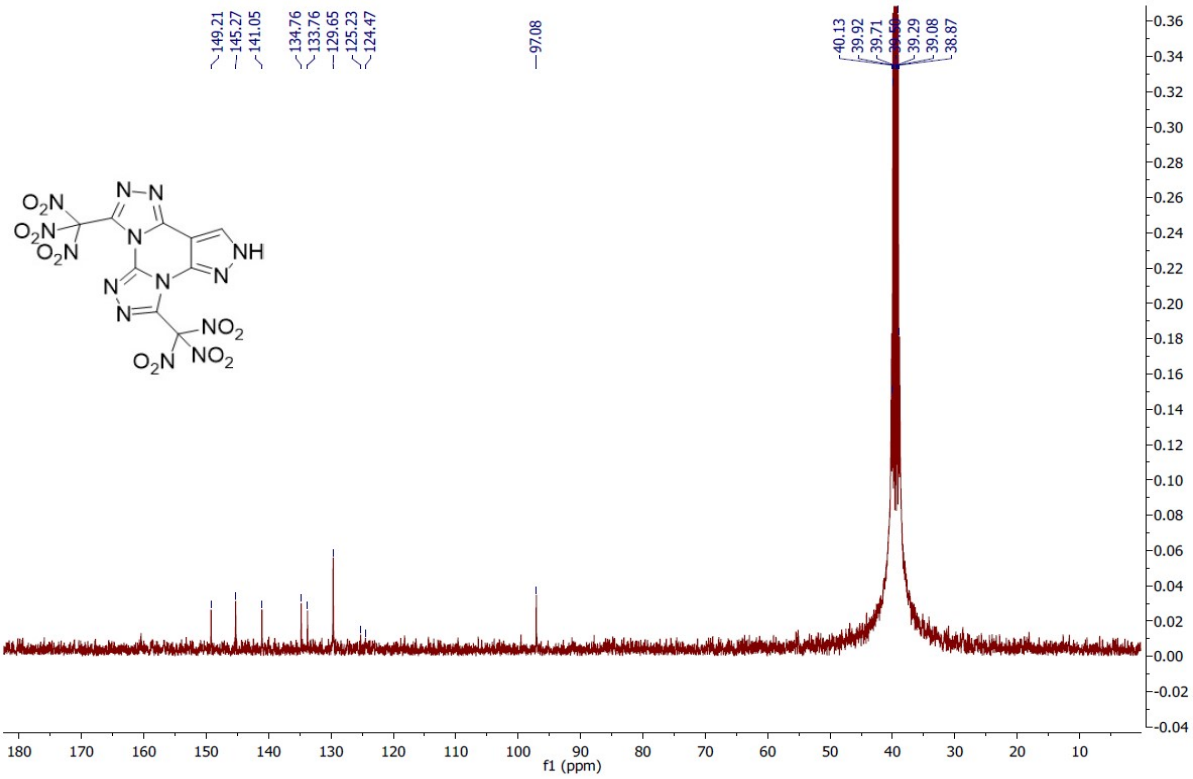


Figure S6: ^{13}C NMR spectrum of compound **3** in **DMSO-*d*$_6$** in 126 MHz.

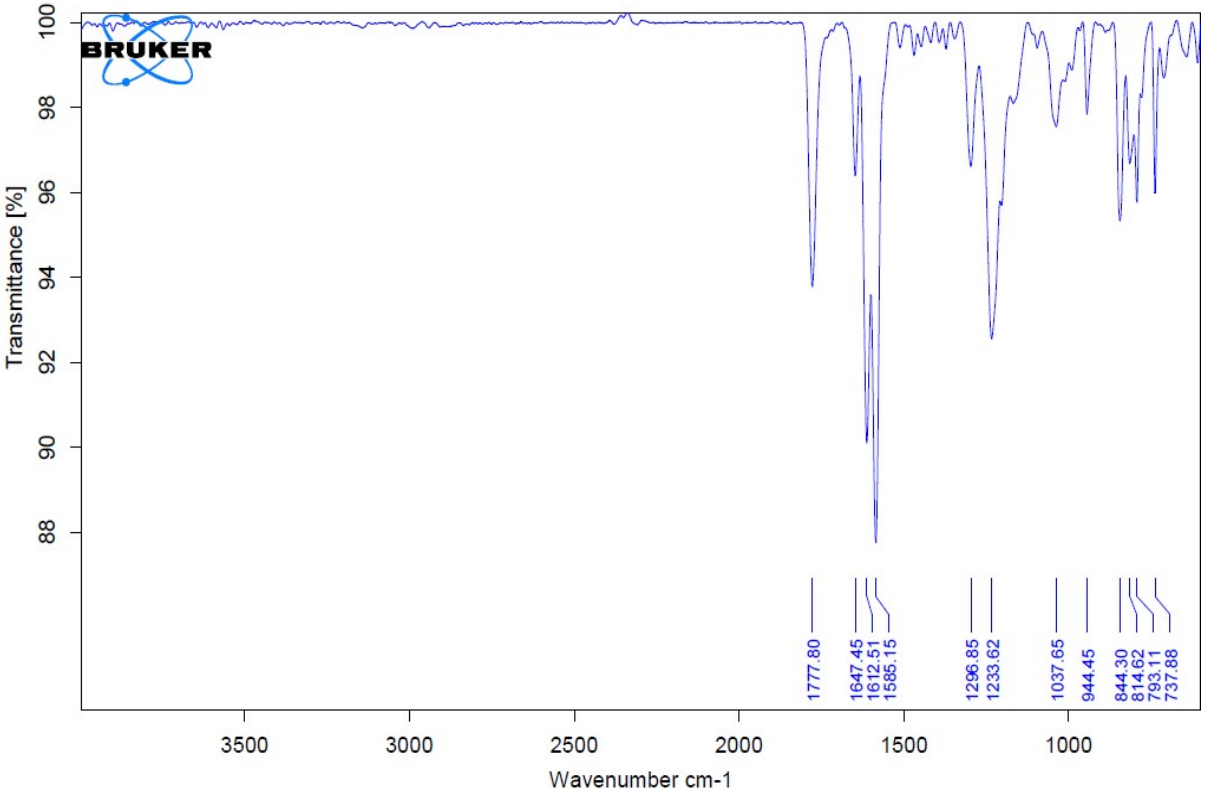


Figure S7: IR spectrum of compound **3.**

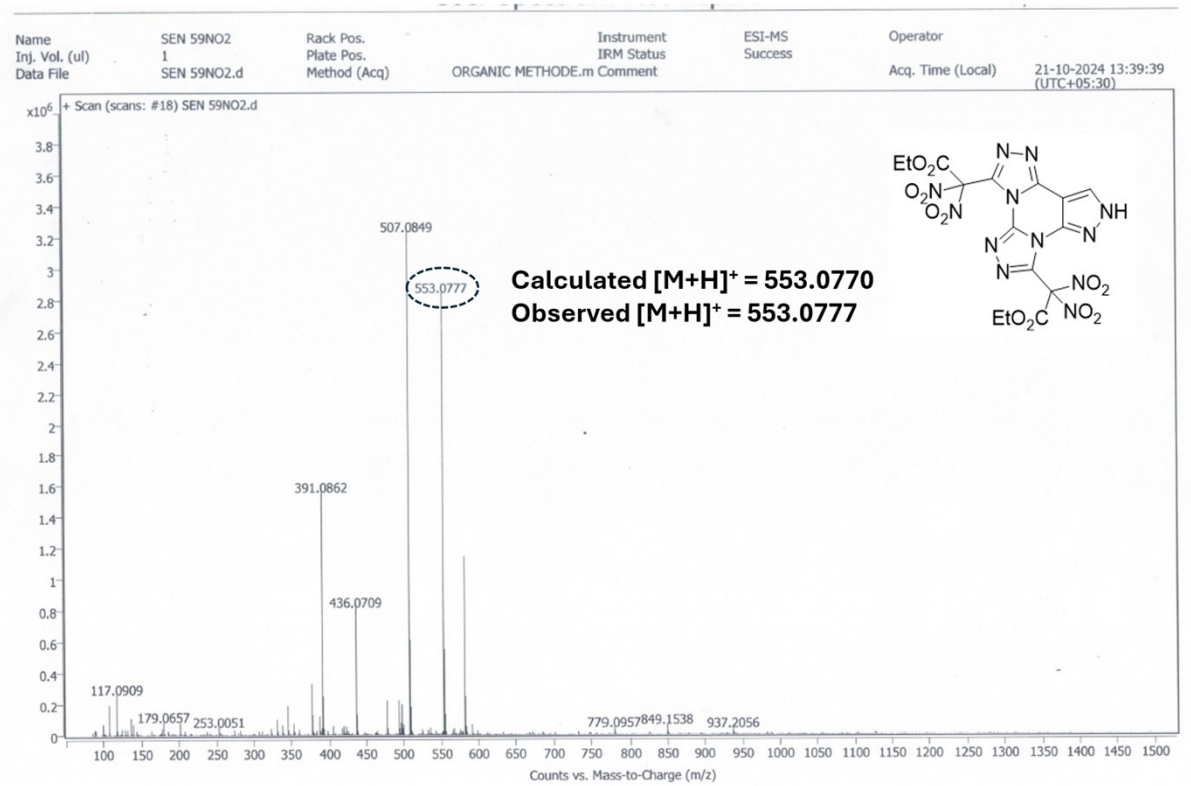


Figure S8: Mass spectrum of compound **3**.

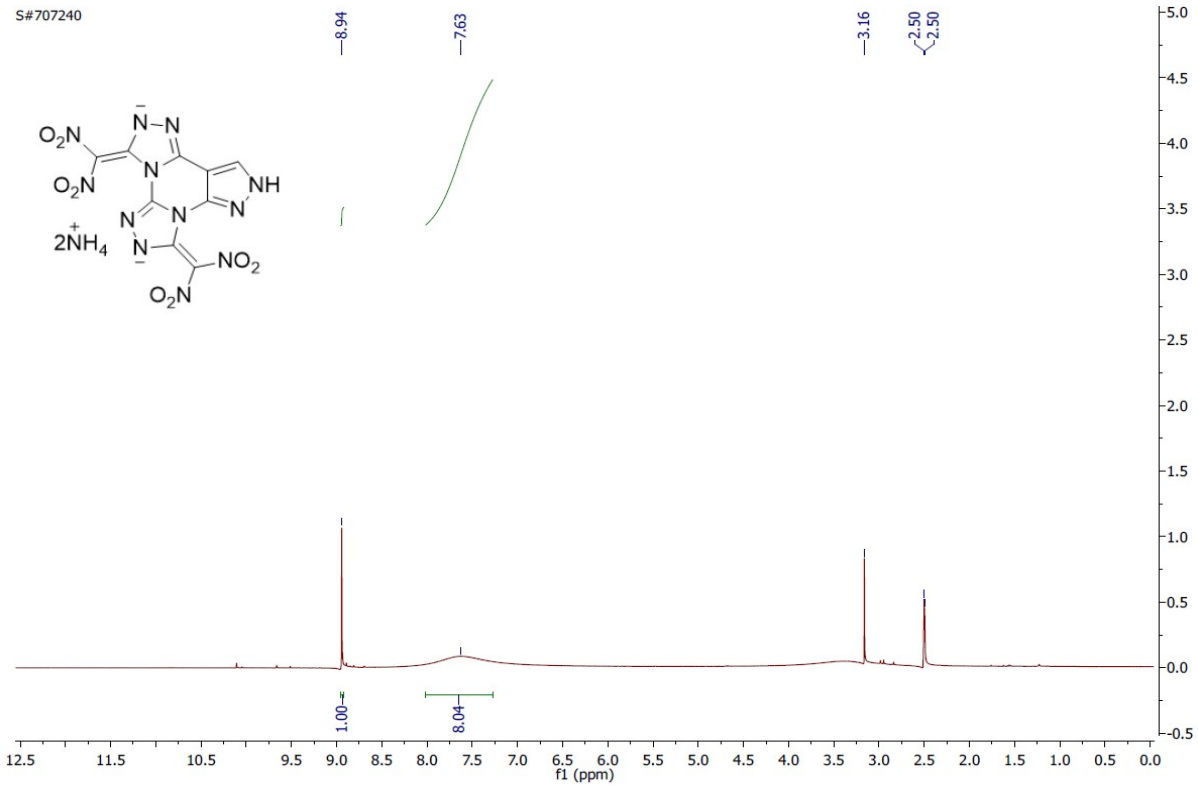


Figure S9: ^{1}H NMR spectrum of compound **4a** in **DMSO-*d*$_6$** in 500 MHz**.**

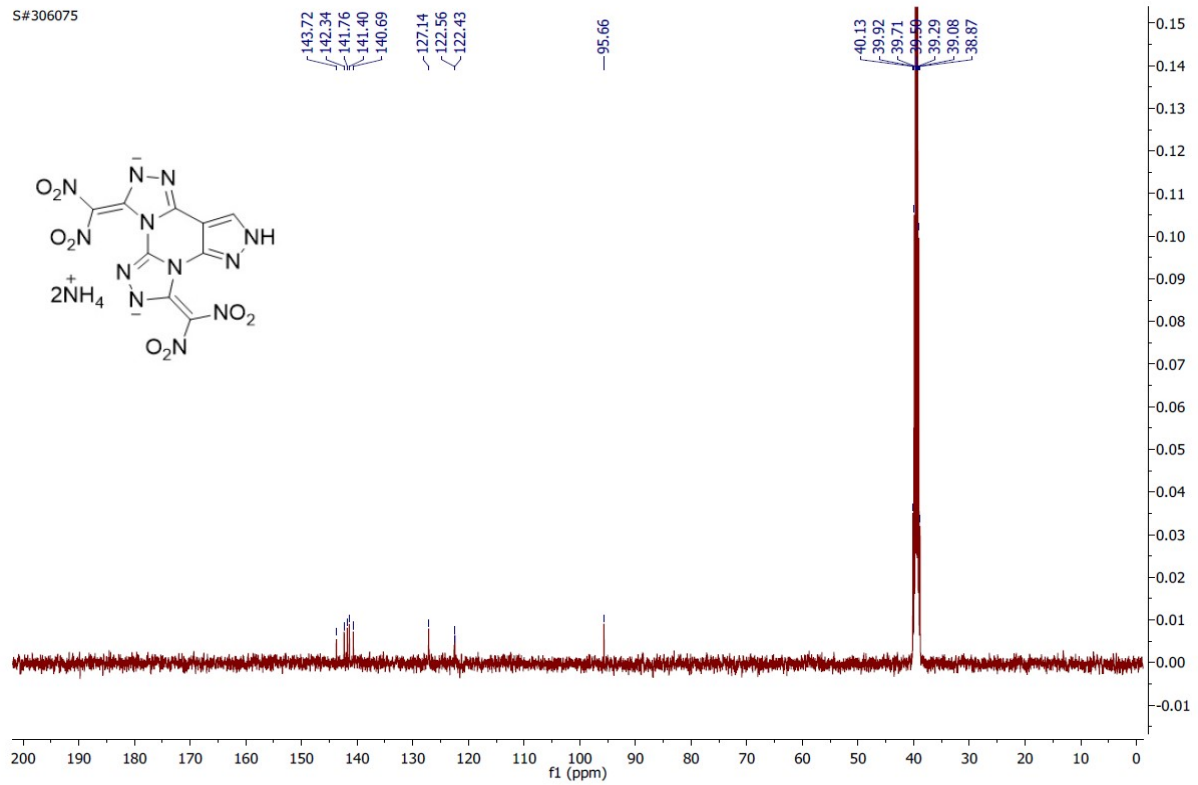


Figure S10: ^{13}C NMR spectrum of compound **4a** in **DMSO-*d*$_6$** in 126 MHz.

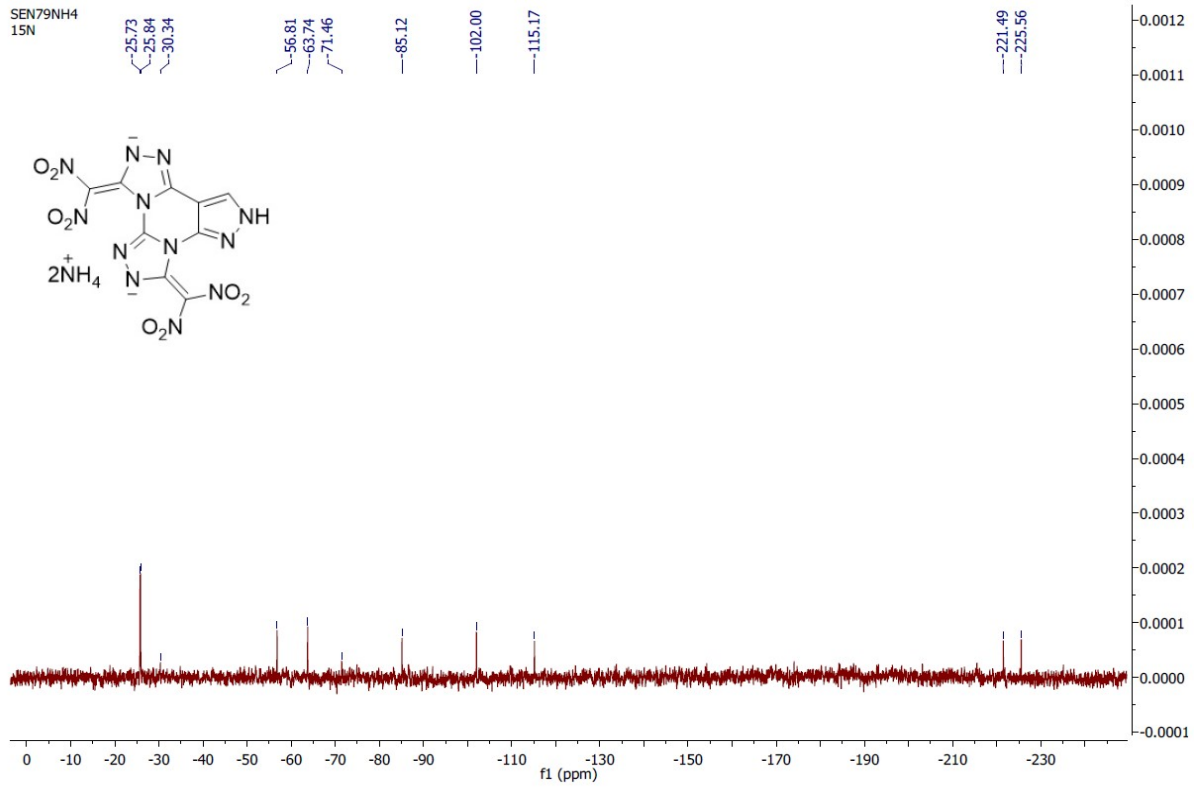


Figure S11: ^{15}N NMR spectrum of compound **4a** in **DMSO-*d*$_6$** in 50.5 MHz.

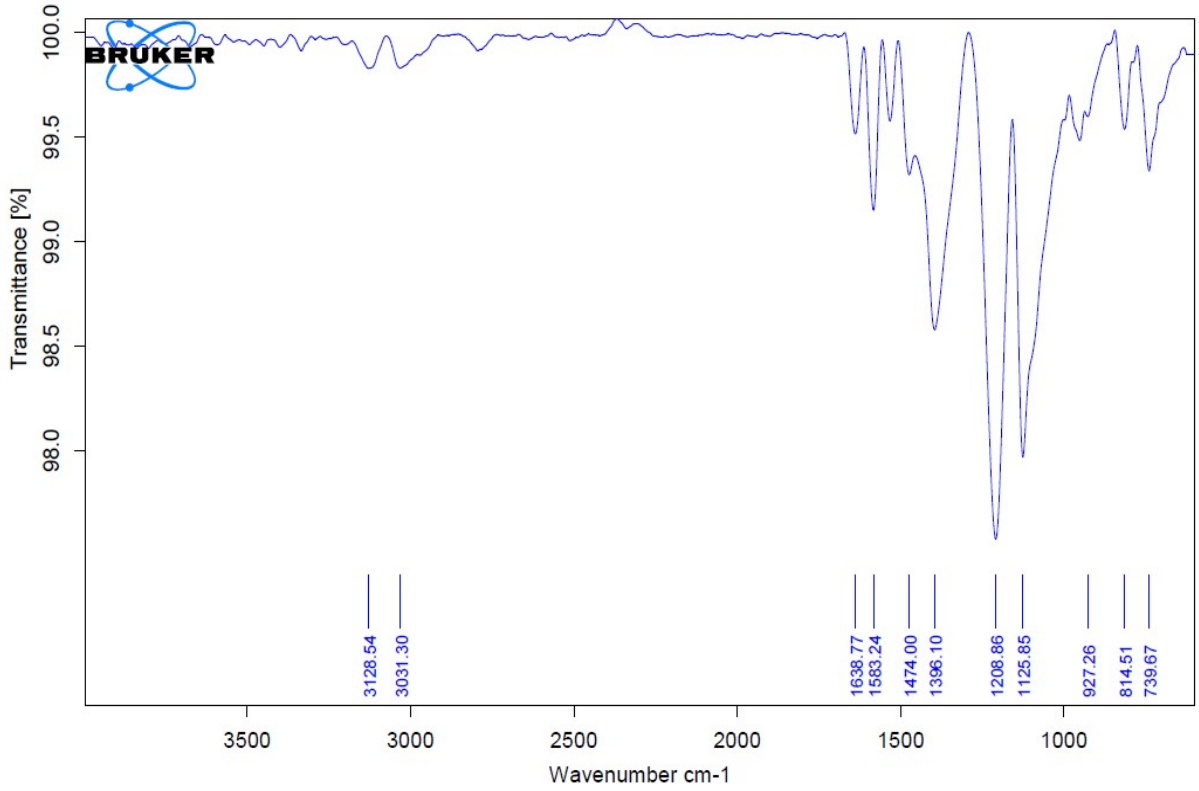


Figure S12: IR spectrum of compound **4a**.

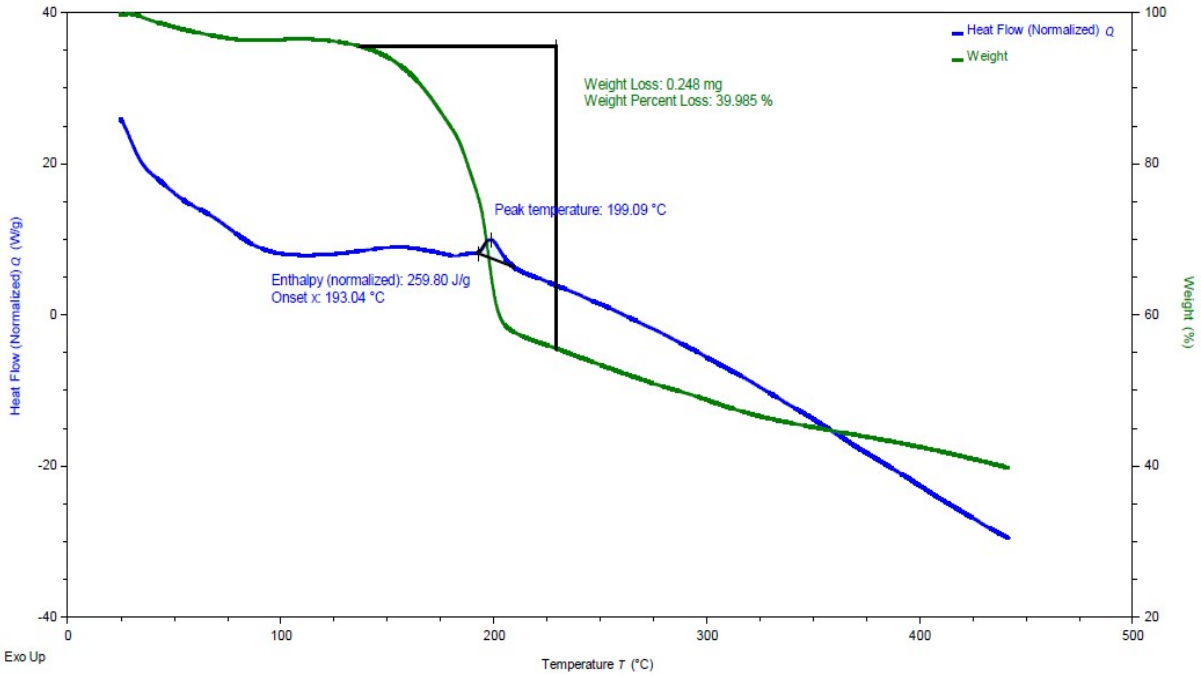


Figure S13: DSC spectra of compound **4a** at a heating rate of 5 ˚C min^{-1}.

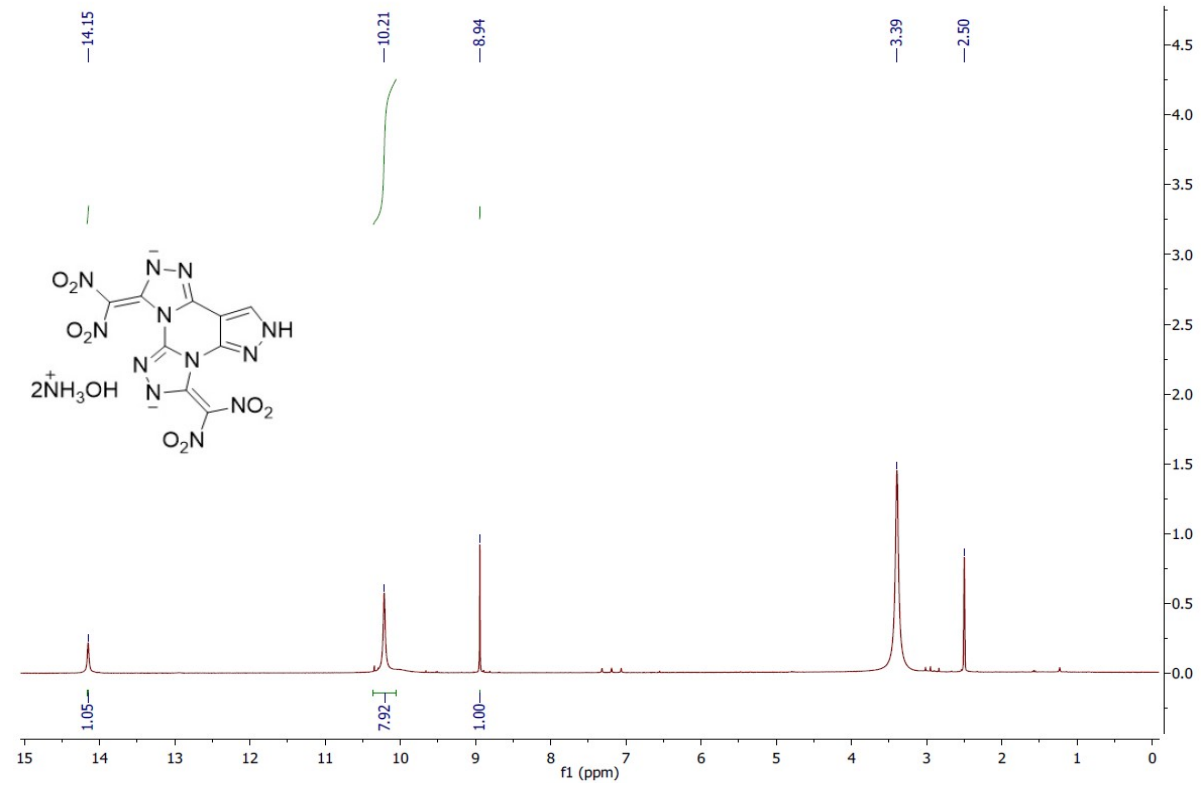


Figure S14: ^{1}H NMR spectrum of compound **4b** in **DMSO-*d*$_6$** in 500 MHz**.**

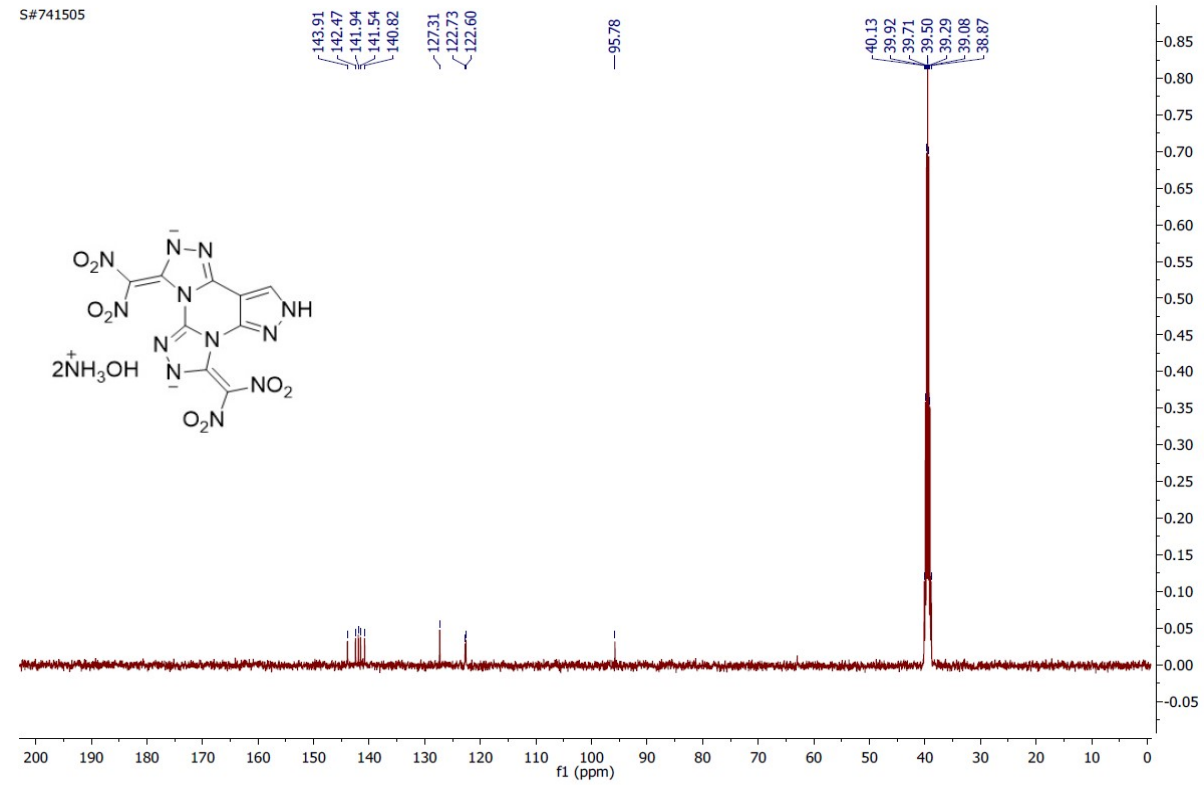


Figure S15: ^{13}C NMR spectrum of compound **4b** in **DMSO-*d*$_6$** in 126 MHz.

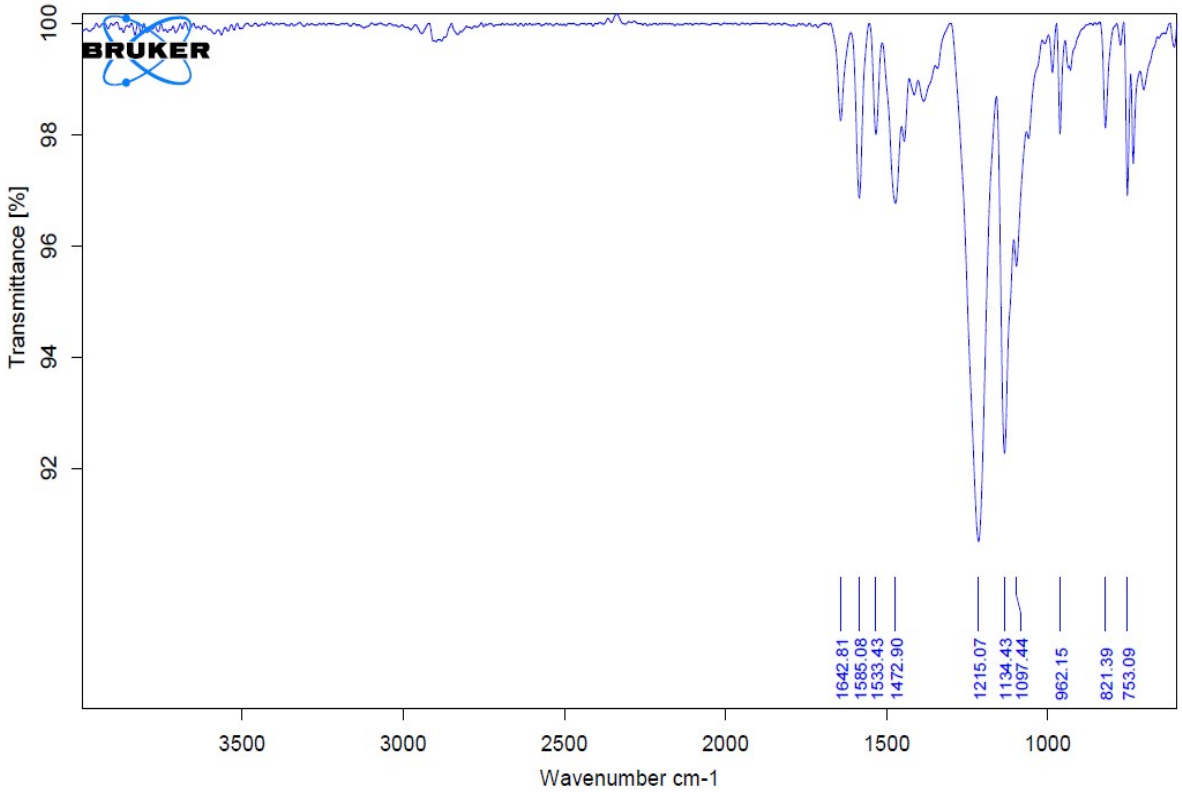


Figure S16: IR spectrum of compound **4b**.

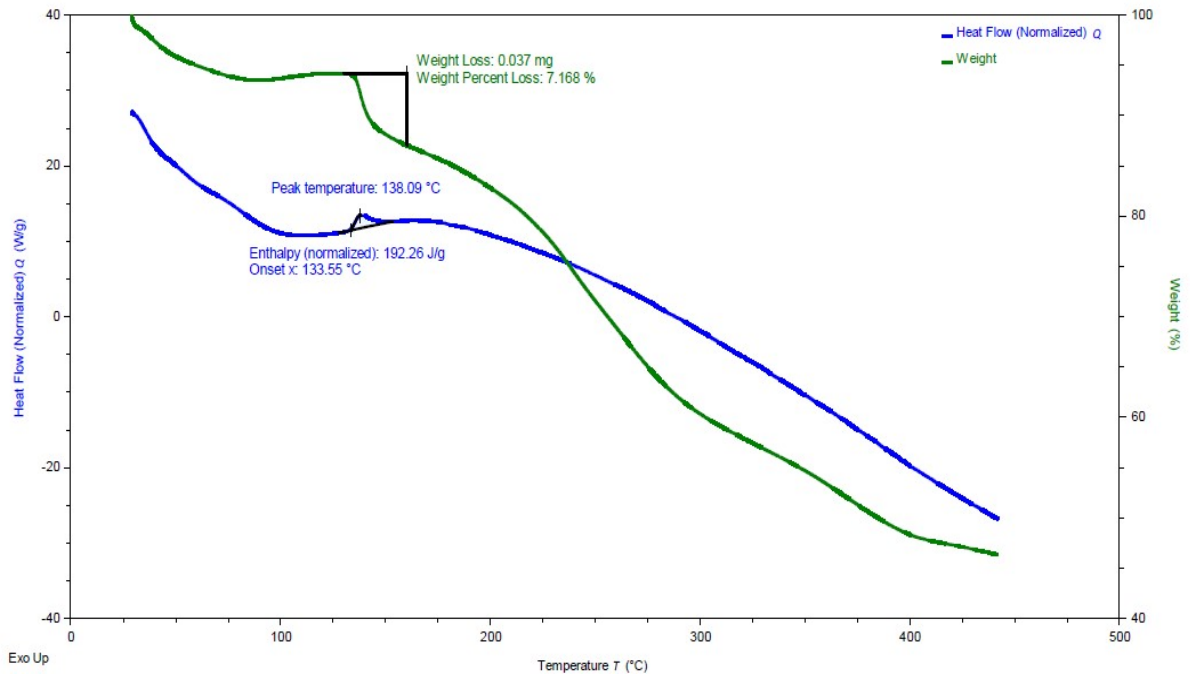


Figure S17: DSC spectra of compound **4b** at a heating rate of 5 ˚C min^{-1}.

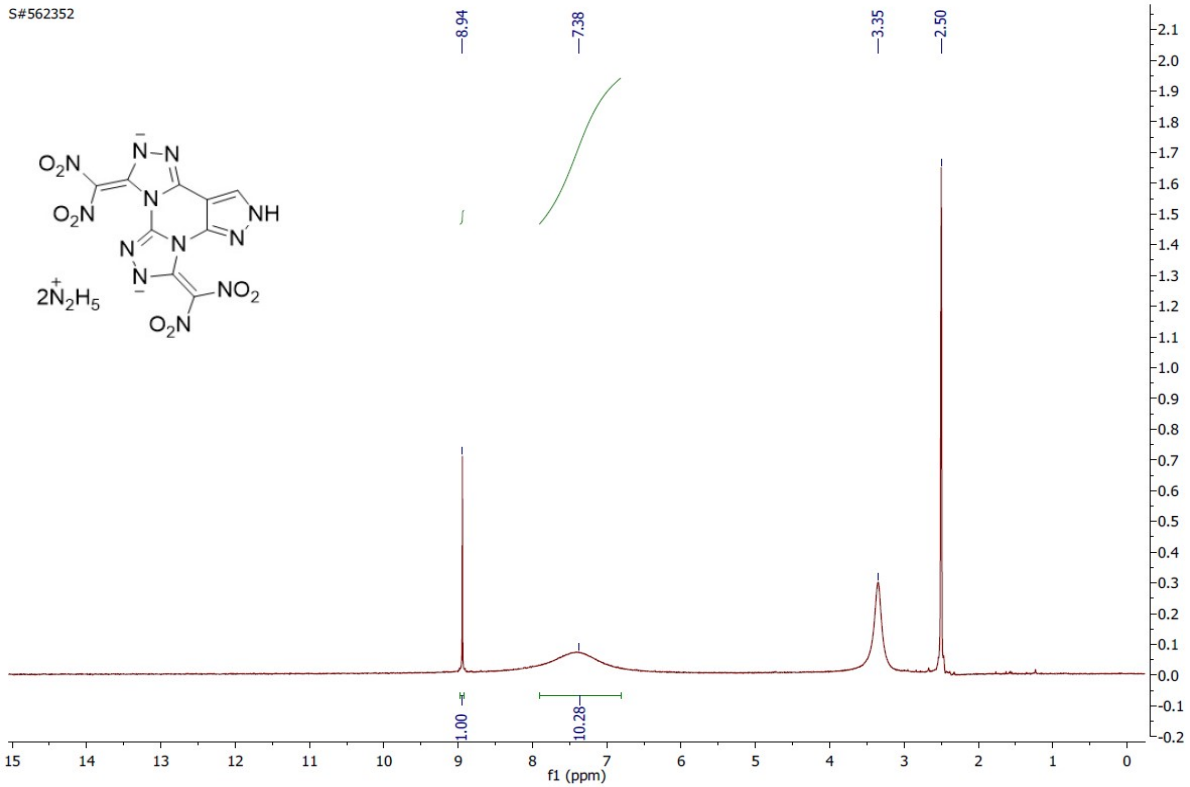


Figure S18: ^{1}H NMR spectrum of compound **4c** in **DMSO-*d*$_6$** in 500 MHz**.**

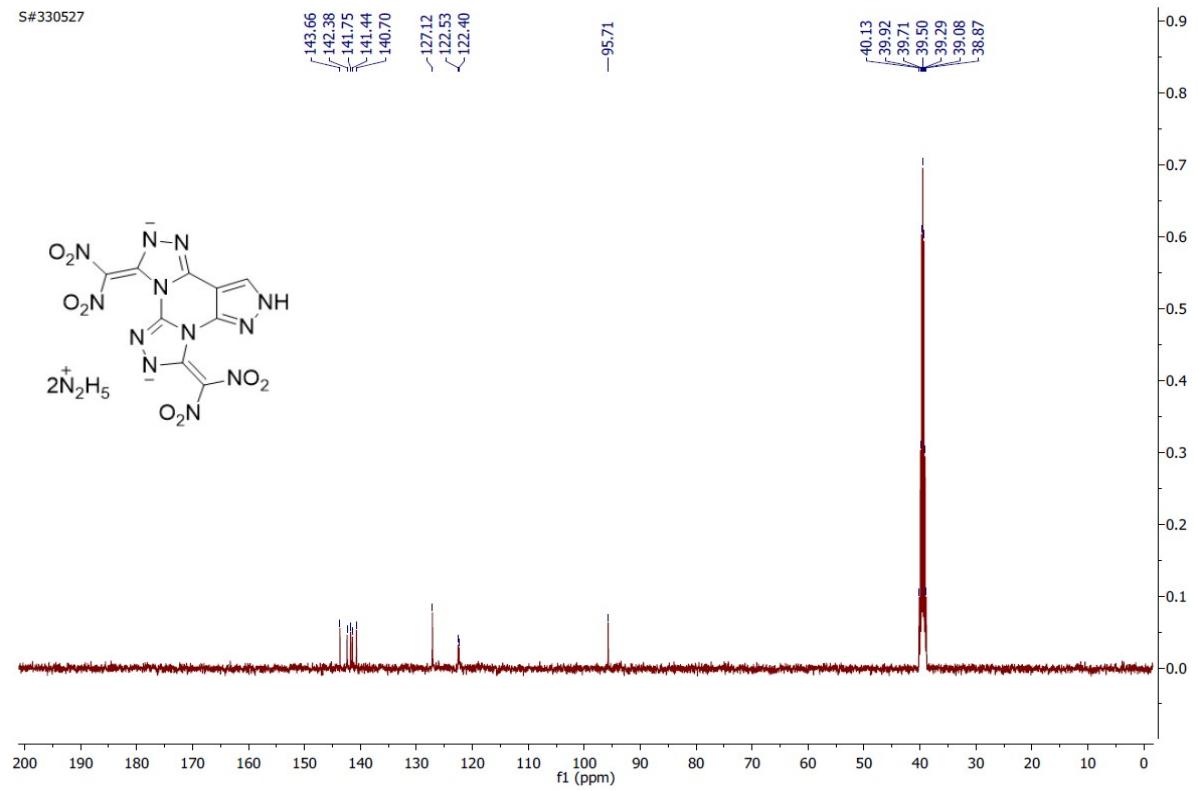


Figure S19: ^{13}C NMR spectrum of compound **4c** in **DMSO-*d*$_6$** in 126 MHz.

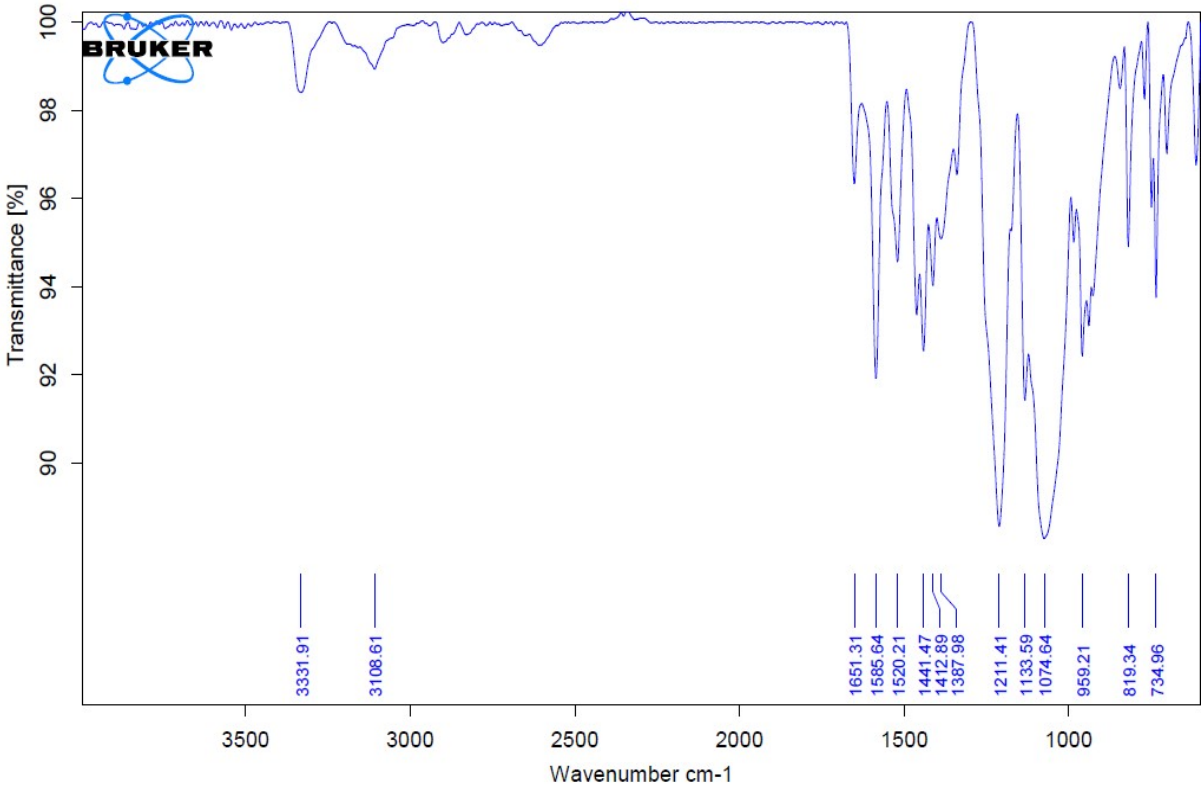


Figure S20: IR spectrum of compound **4c.**

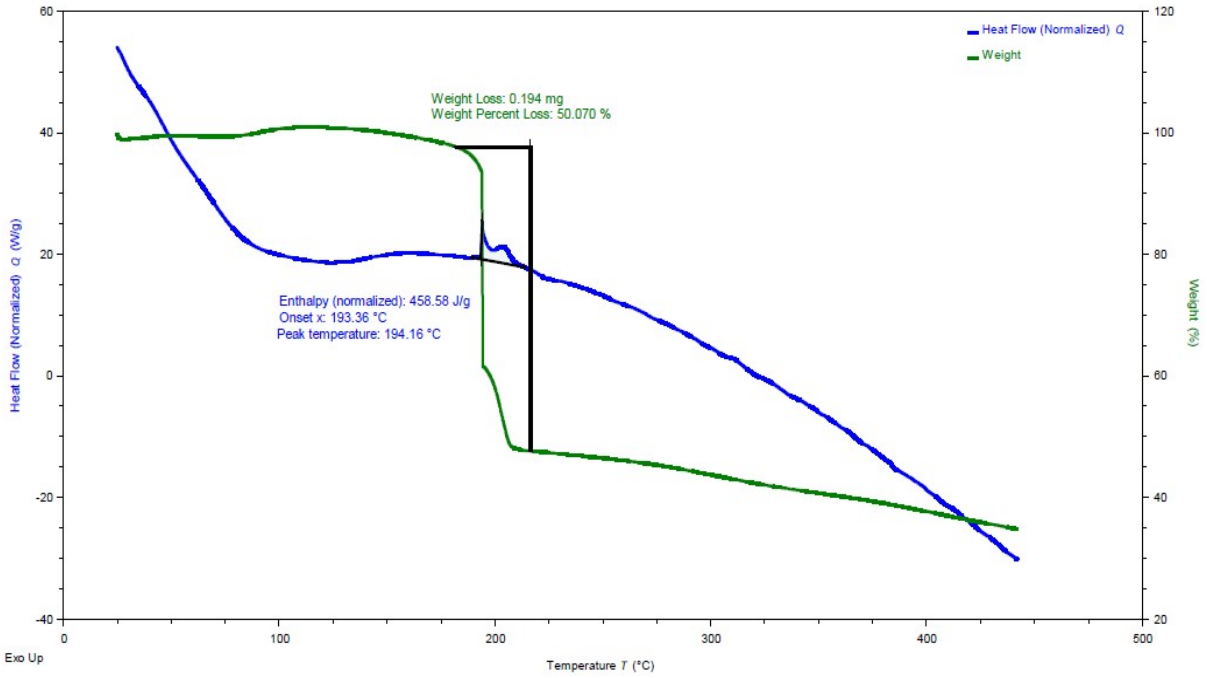


Figure S21: DSC spectra of compound **4c** at a heating rate of 5 ˚C min^{-1}.

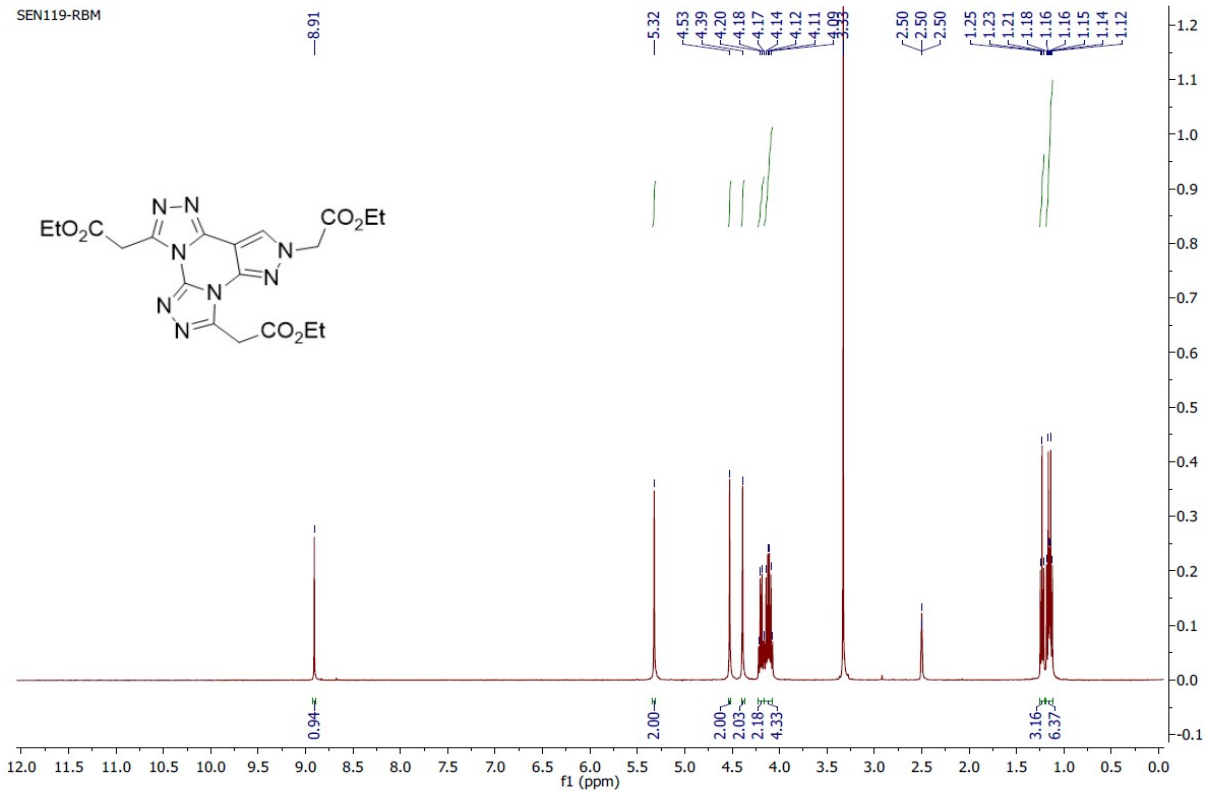


Figure S22: ^{1}H NMR spectrum of compound **5** in **DMSO-*d*$_6$** in 500 MHz**.**

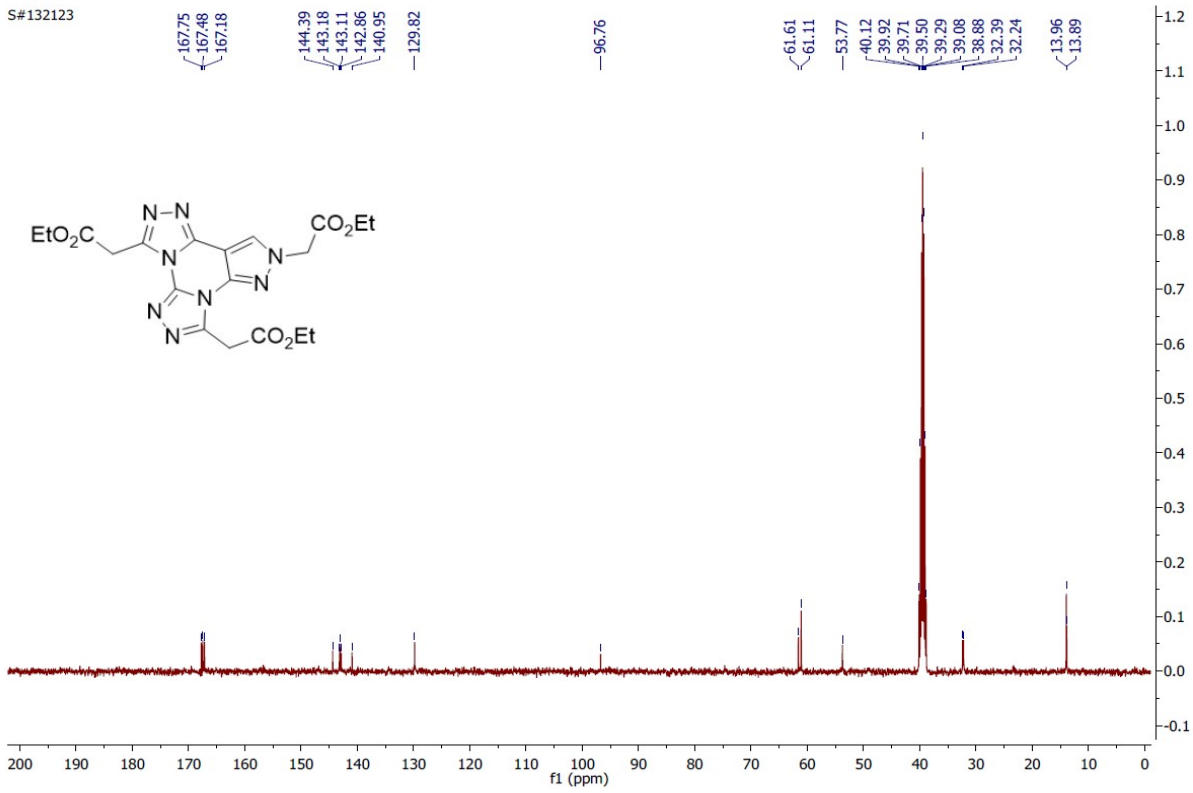


Figure S23: ^{13}C NMR spectrum of compound **5** in **DMSO-*d*$_6$** in 126 MHz

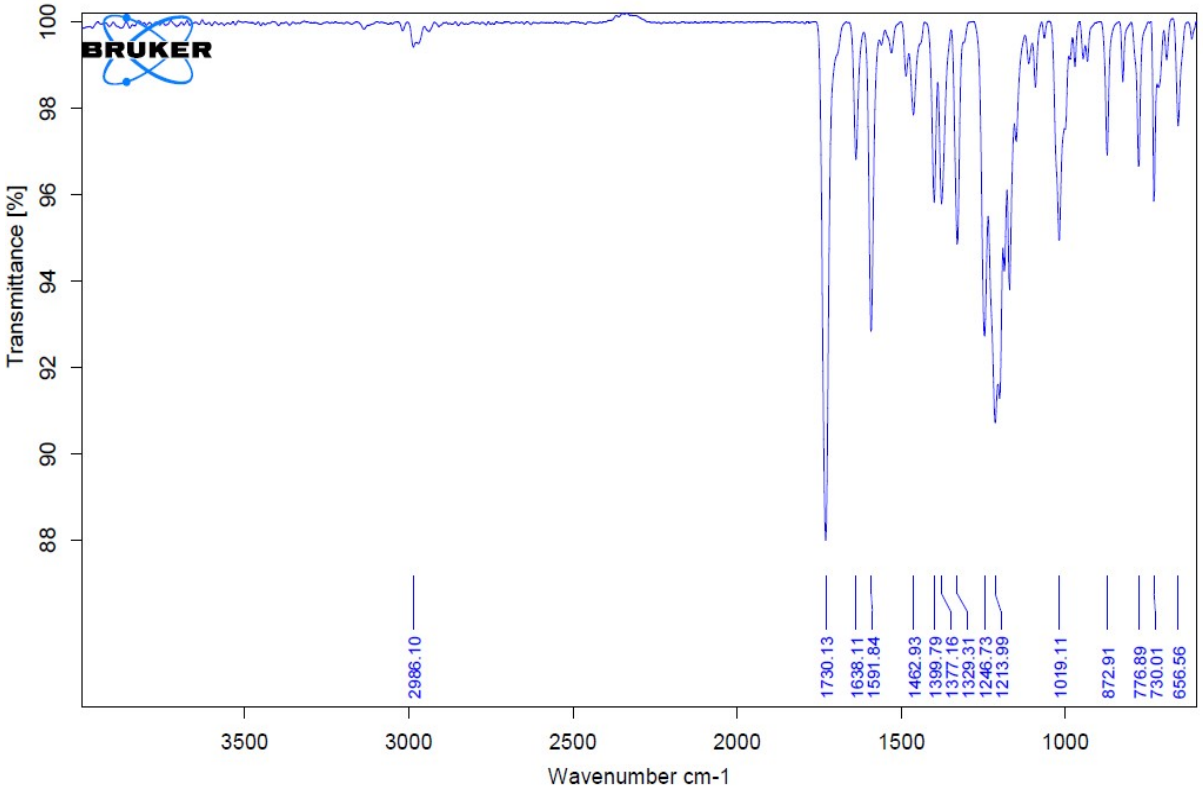


Figure S24: IR spectrum of compound **5.**

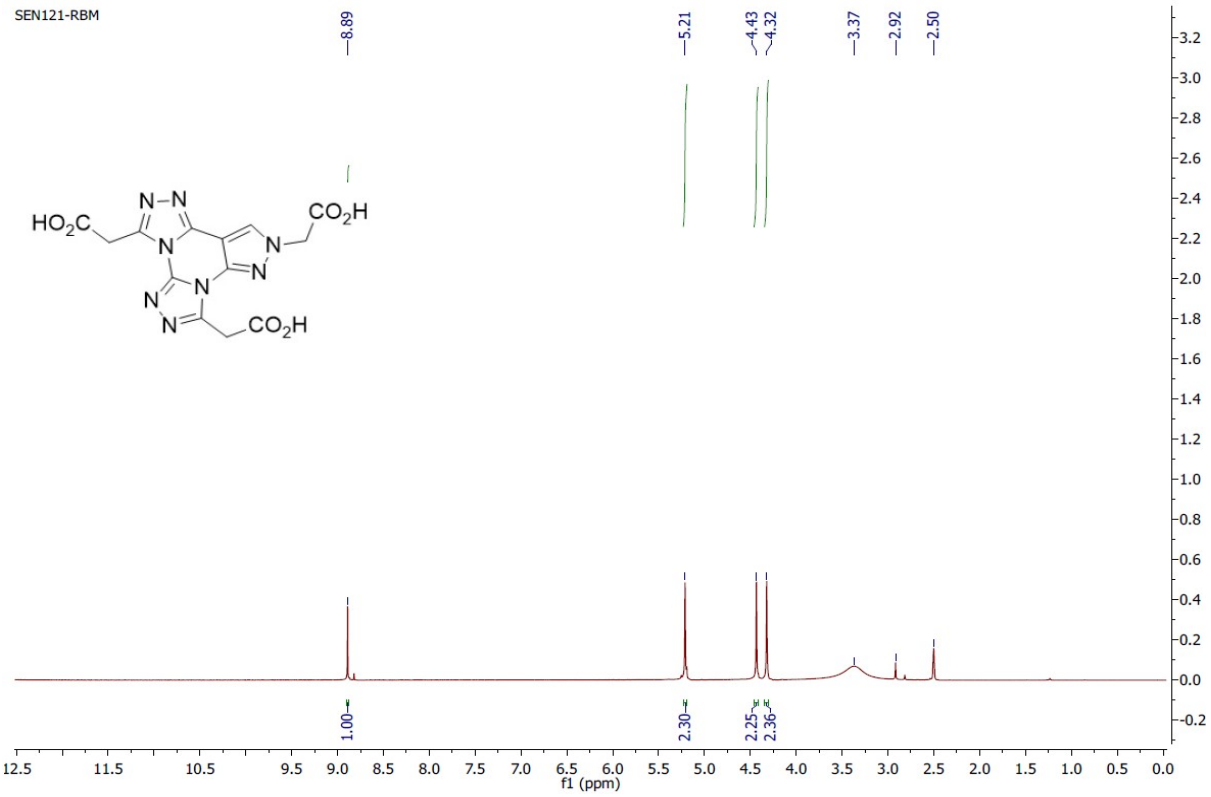


Figure S25: [1]H NMR spectrum of compound **6** in **DMSO-*d*$_6$** in 500 MHz**.**

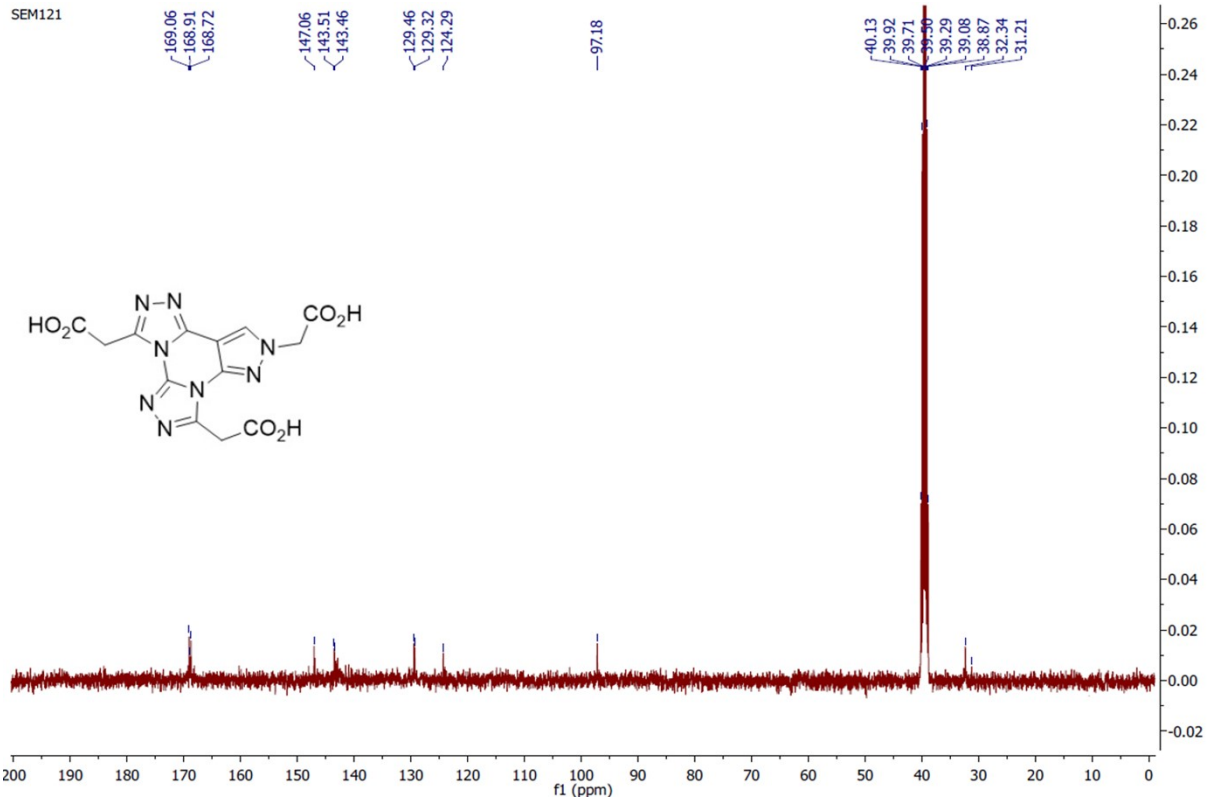


Figure S26: [13]C NMR spectrum of compound **6** in **DMSO-*d*$_6$** in 126 MHz.

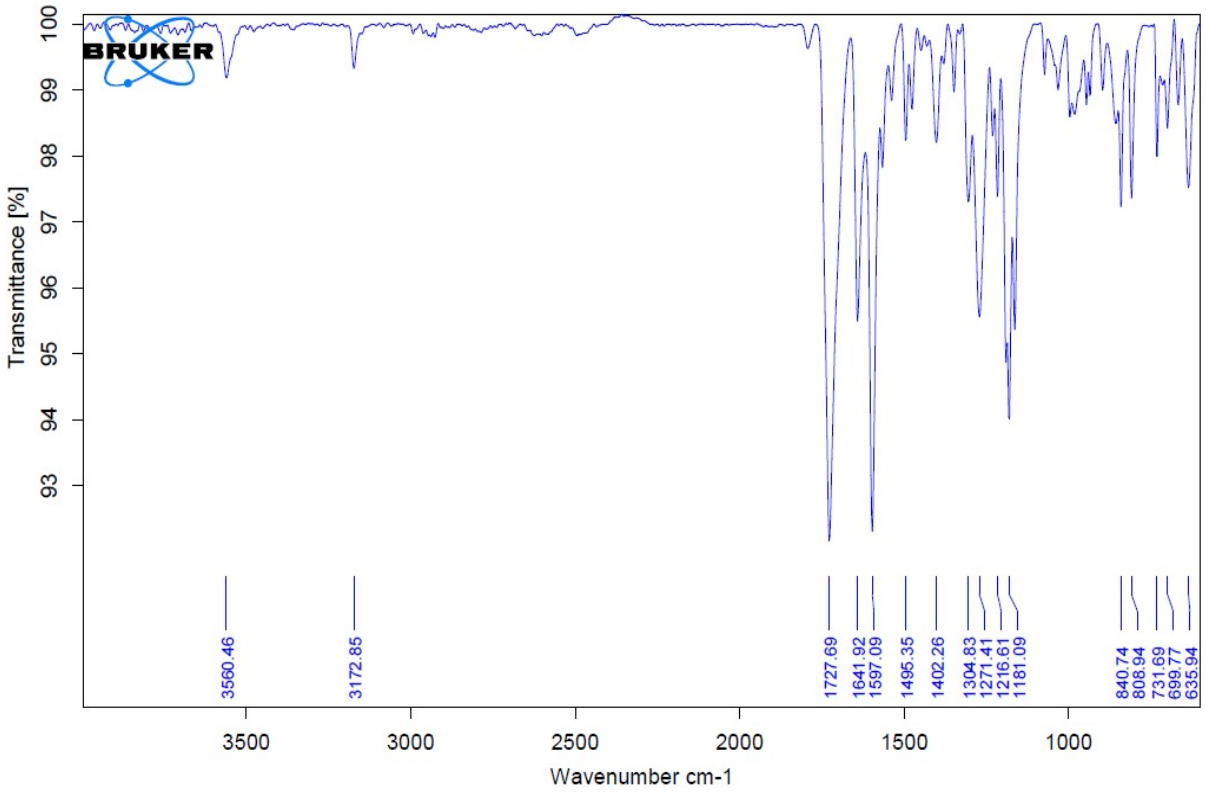


Figure S27: IR spectrum of compound **6.**

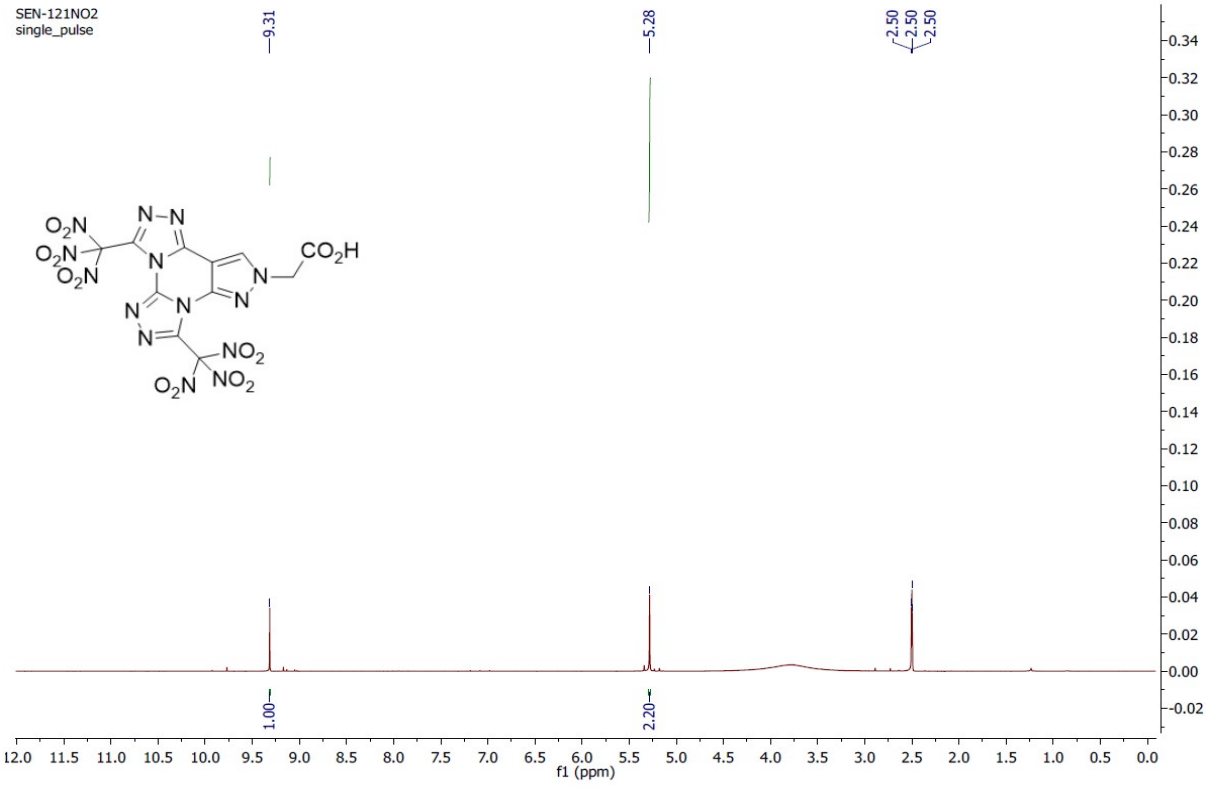


Figure S28: ^{1}H NMR spectrum of compound **7** in **DMSO-*d*$_6$** in 500 MHz**.**

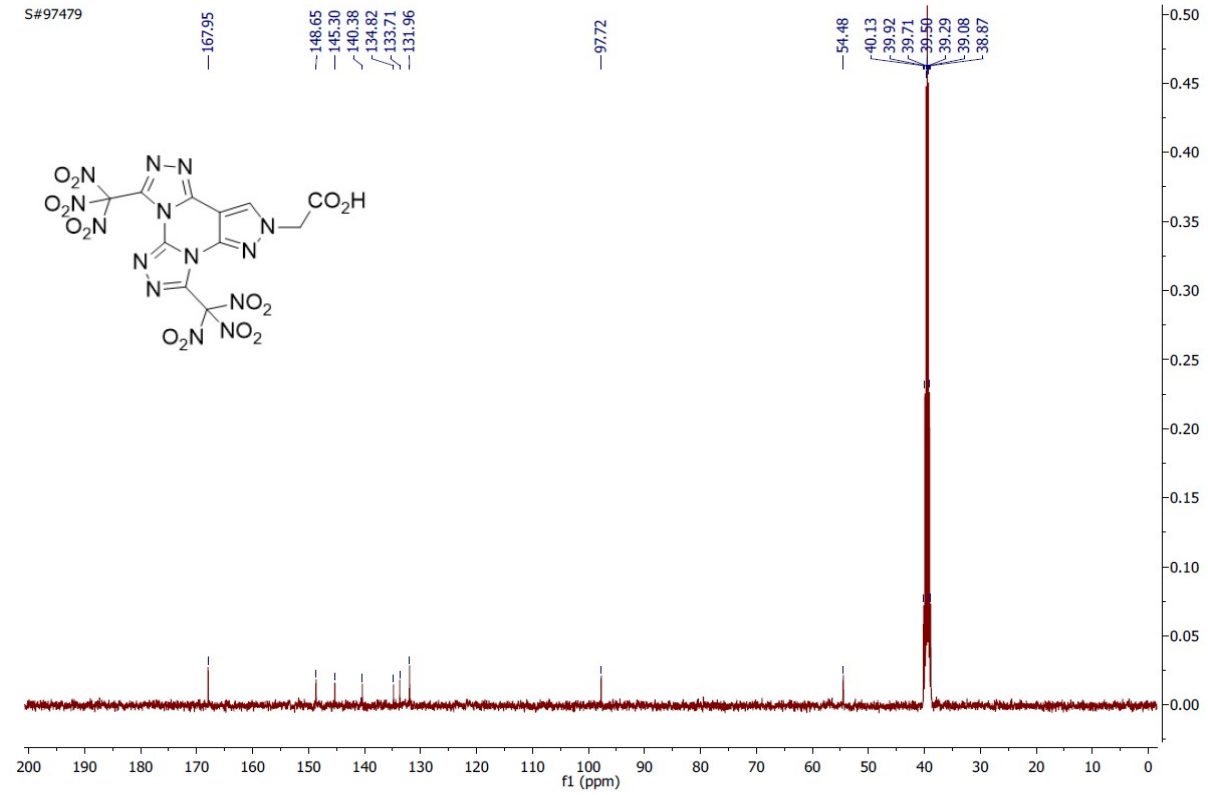


Figure S29: ^{13}C NMR spectrum of compound **7** in **DMSO-*d*$_6$** in 126 MHz.

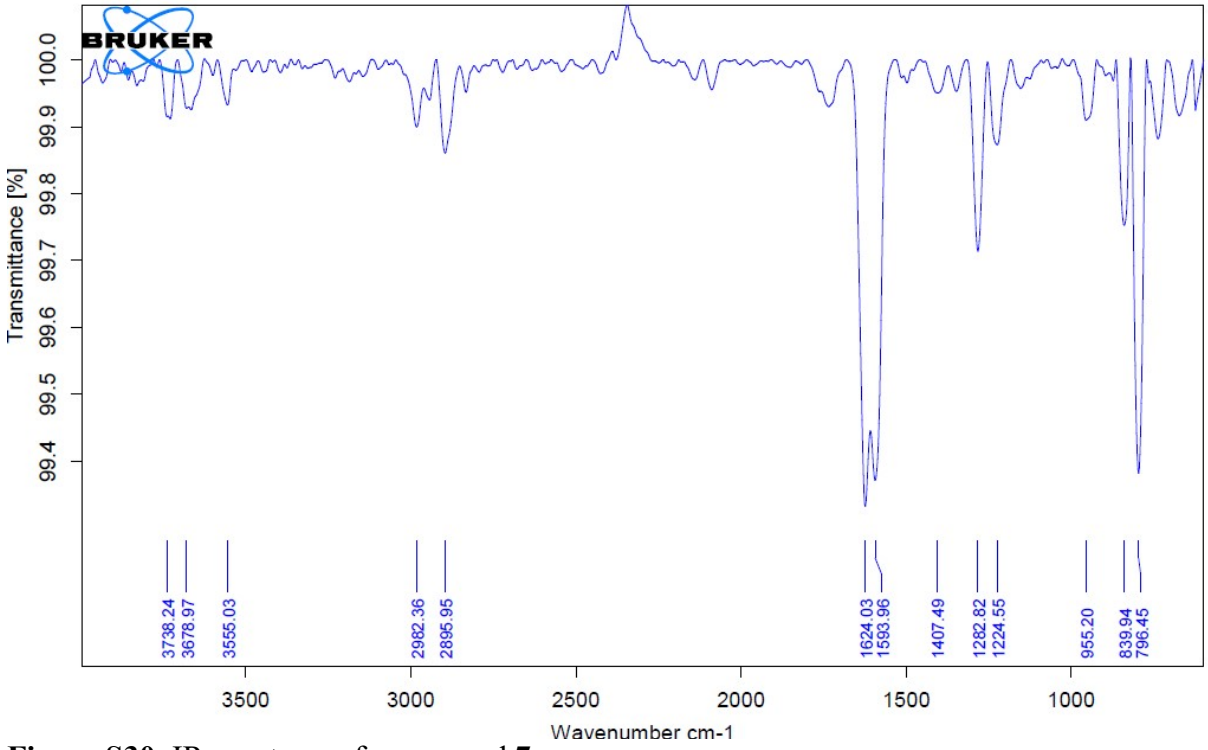


Figure S30: IR spectrum of compound **7.**

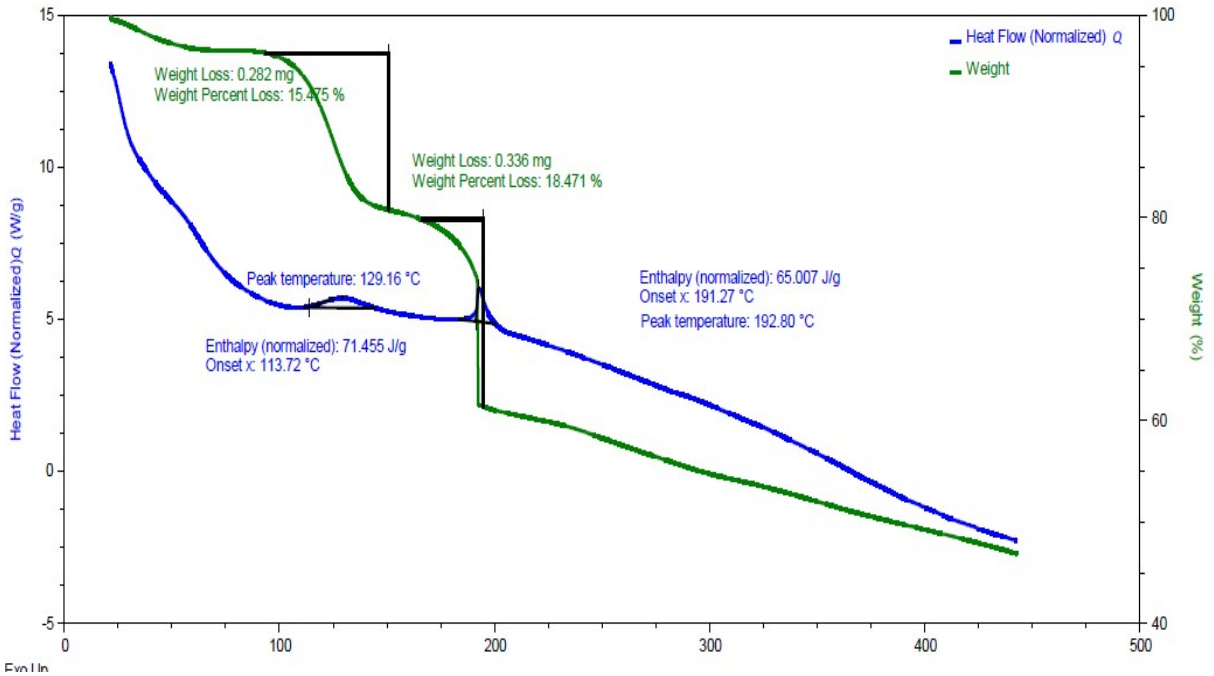


Figure S31: DSC spectra of compound **7** at a heating rate of 5 ˚C min^{-1}.

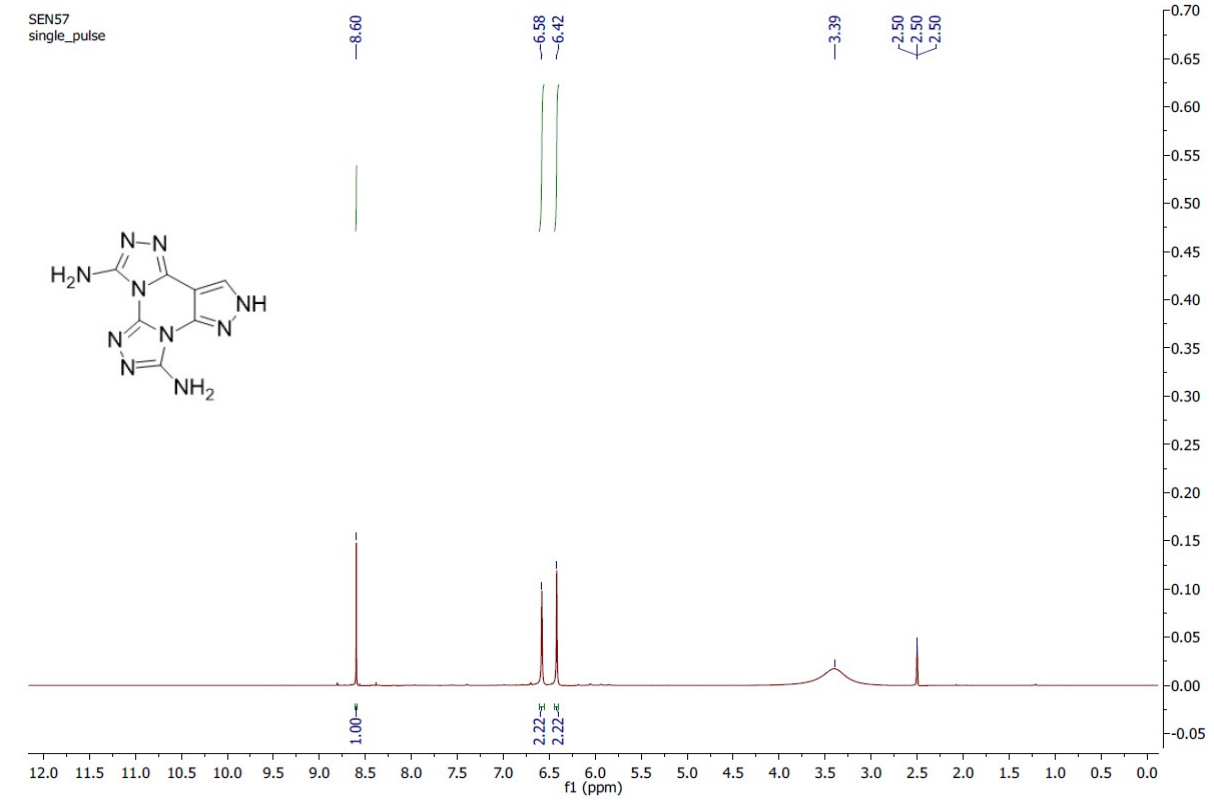


Figure S32 ^{1}H NMR spectrum of compound **8** in **DMSO-*d*$_6$** in 500 MHz**.**

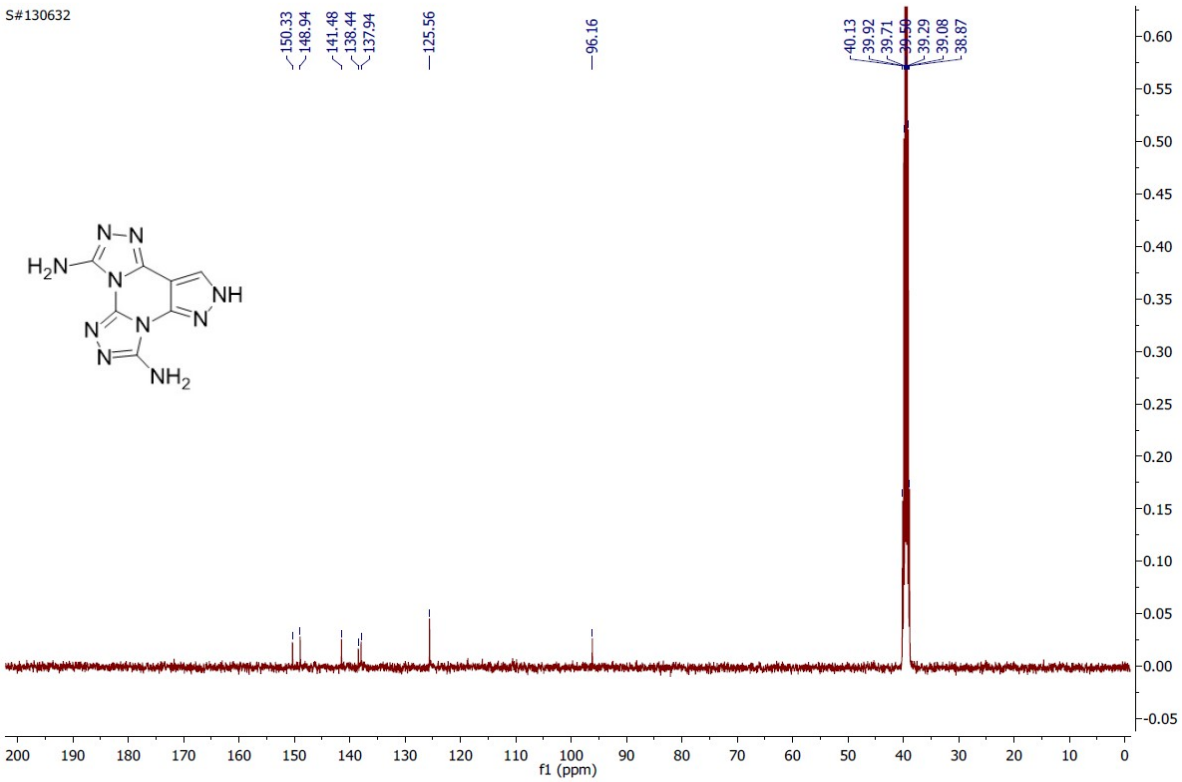


Figure S33: ^{13}C NMR spectrum of compound **8** in **DMSO-*d*$_6$** in 126 MHz.

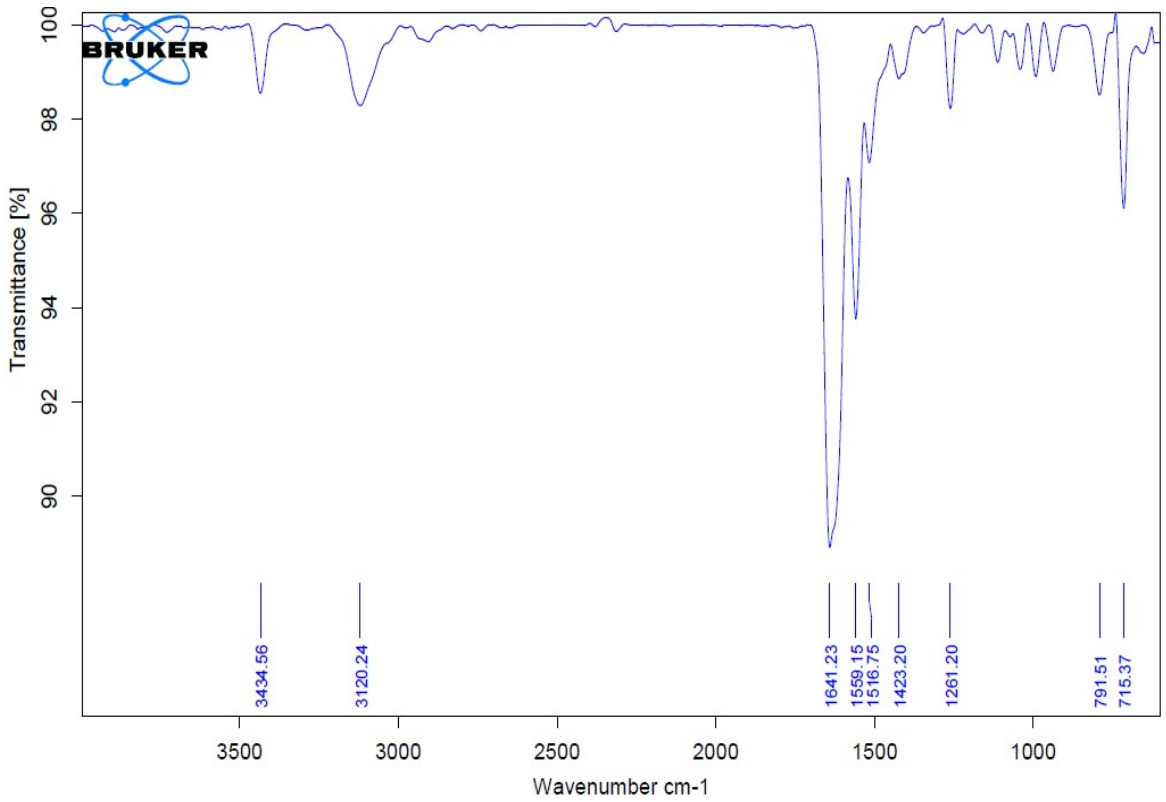


Figure S34: IR spectrum of compound **8**.

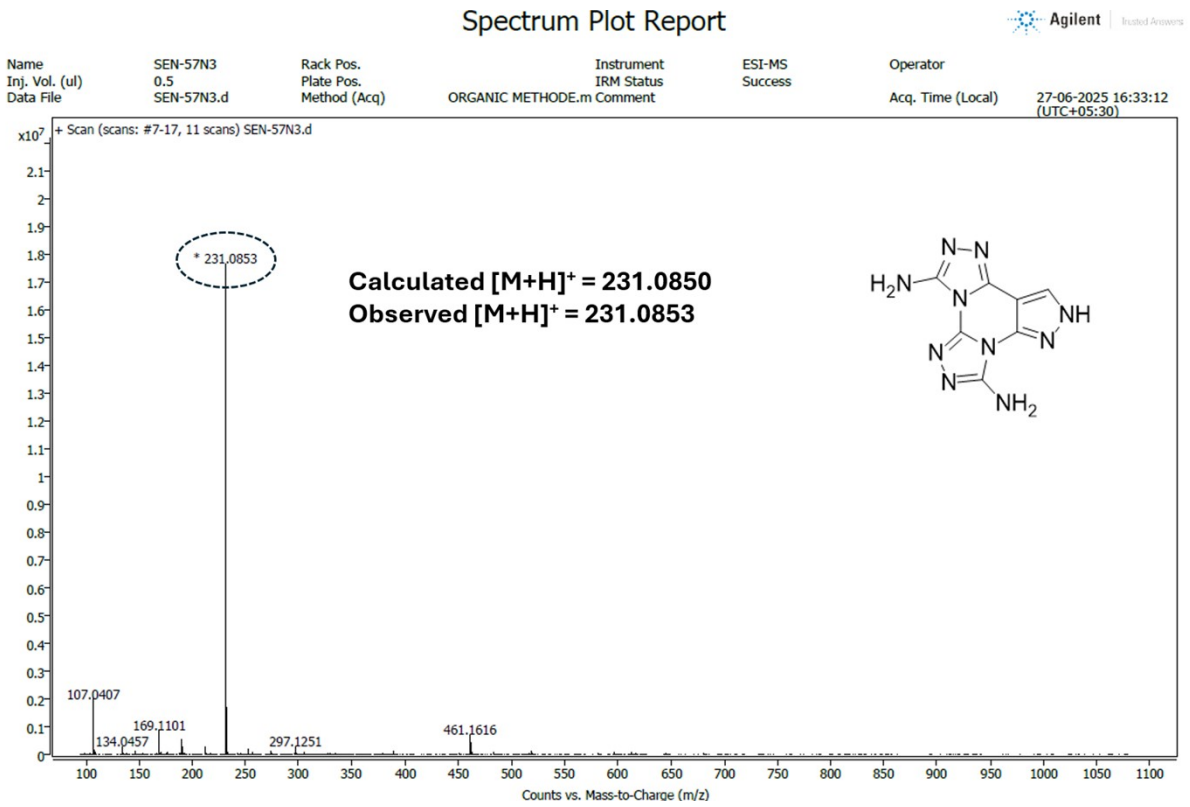


Figure S35: Mass spectra of compound **8**.

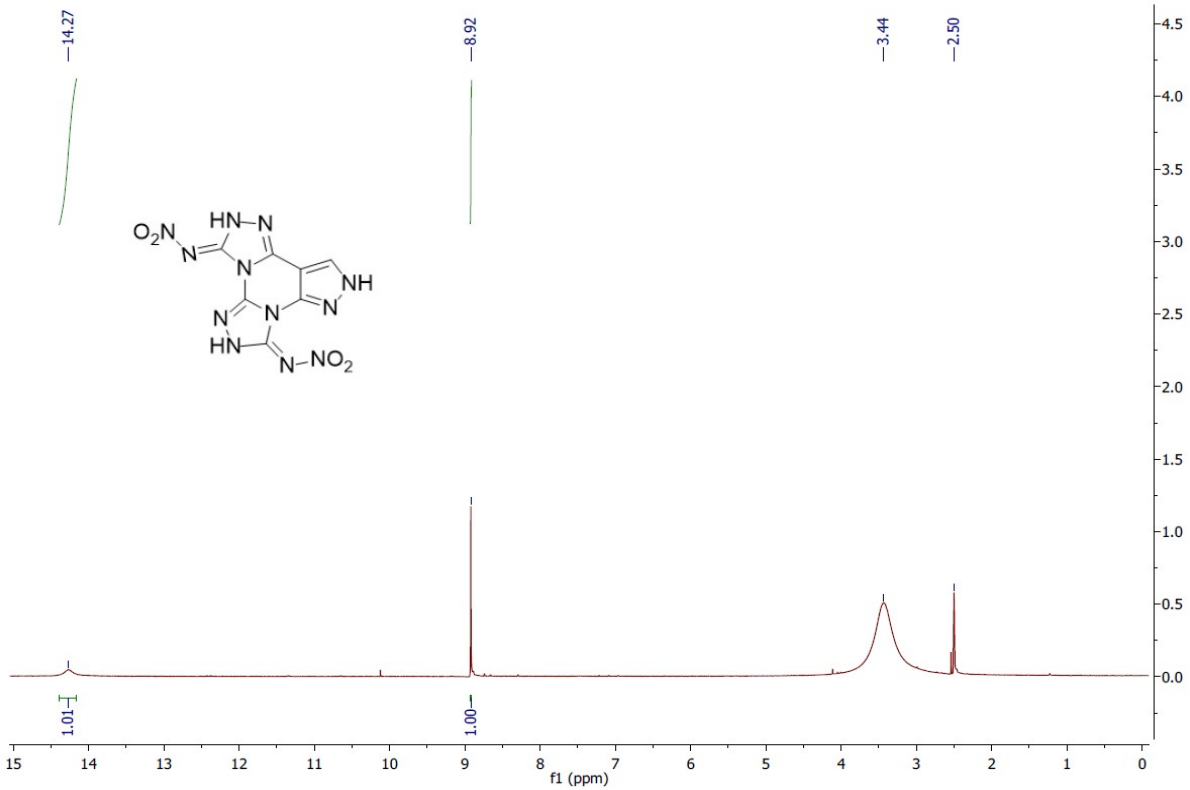


Figure S36: ^{1}H NMR spectrum of compound **9** in **DMSO-*d*$_6$** in 500 MHz**.**

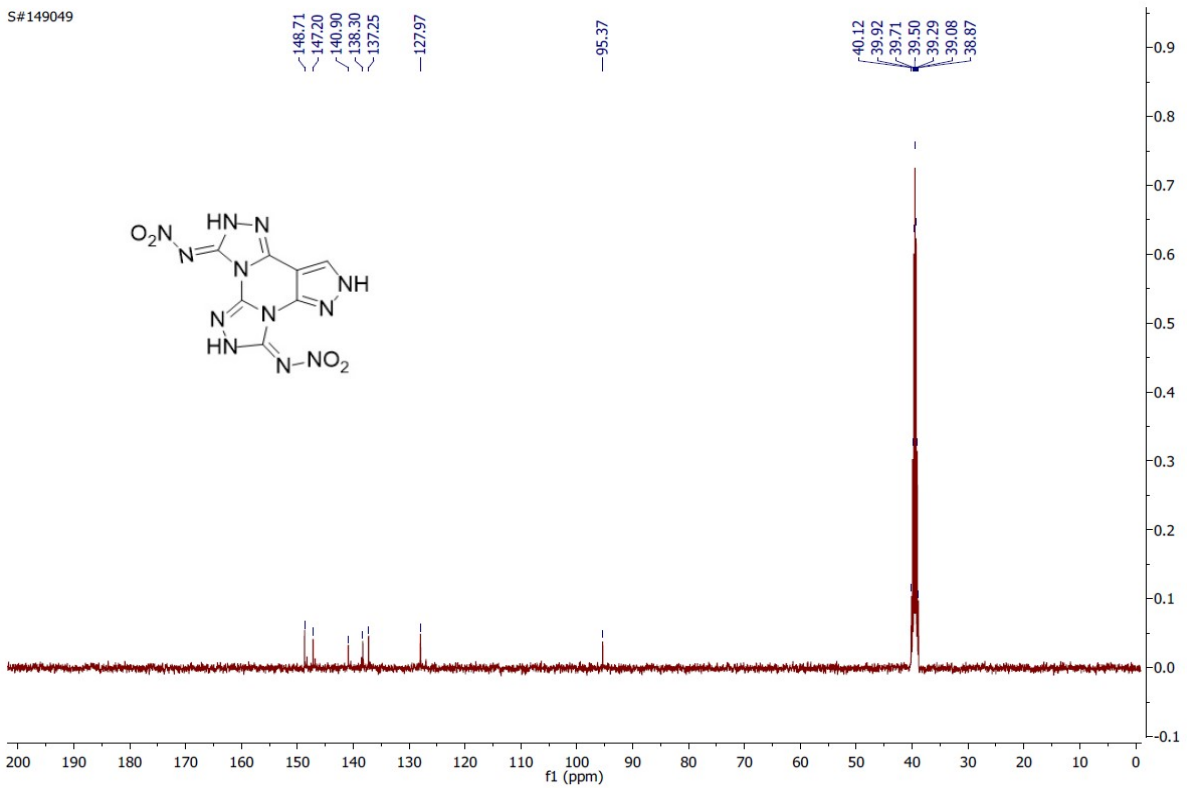


Figure S37: ^{13}C NMR spectrum of compound **9** in **DMSO-*d*$_6$** in 126 MHz.

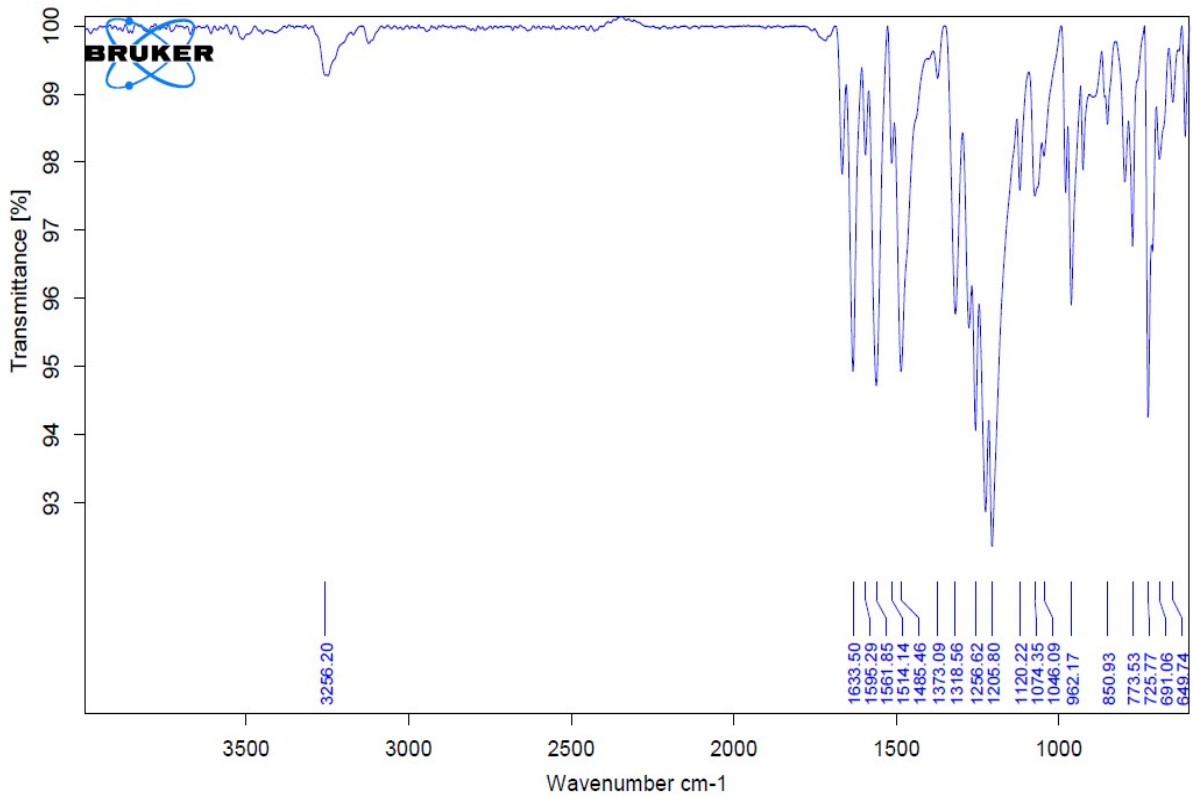


Figure S38: IR spectrum of compound **9**.

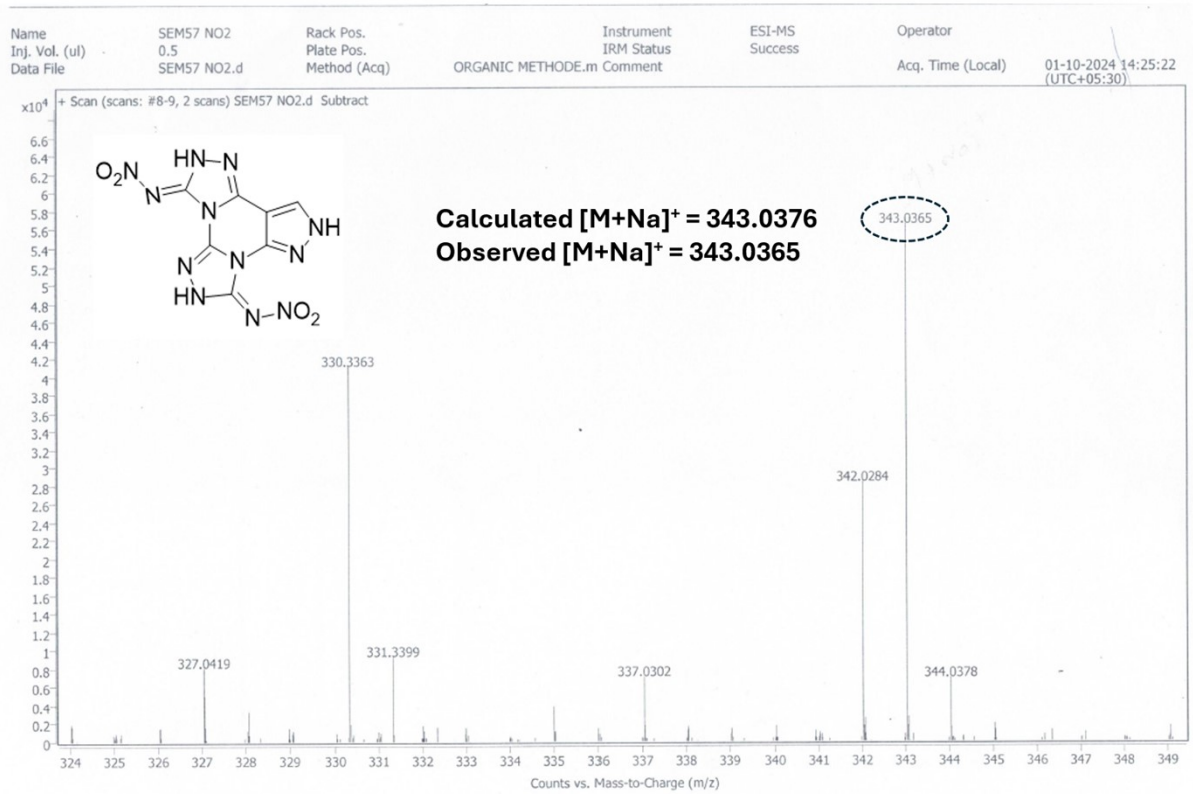


Figure S39: Mass spectrum of compound **9**.

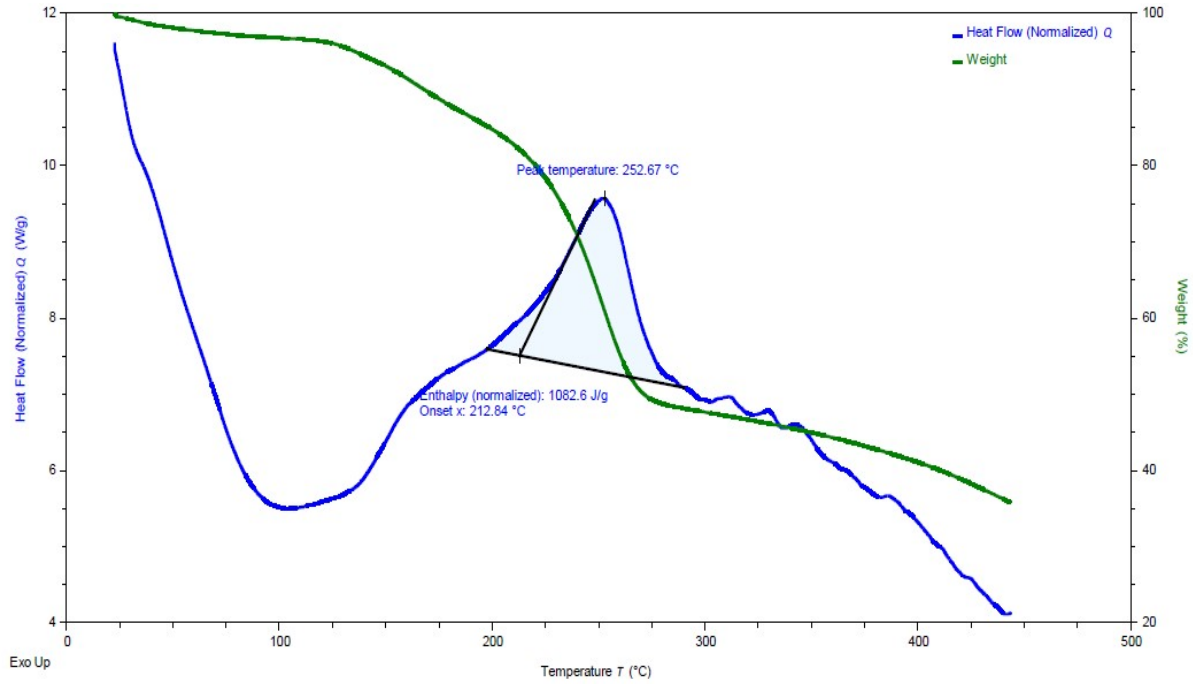


Figure S40: DSC spectra of compound **9** at a heating rate of 5 ˚C min^{-1}.

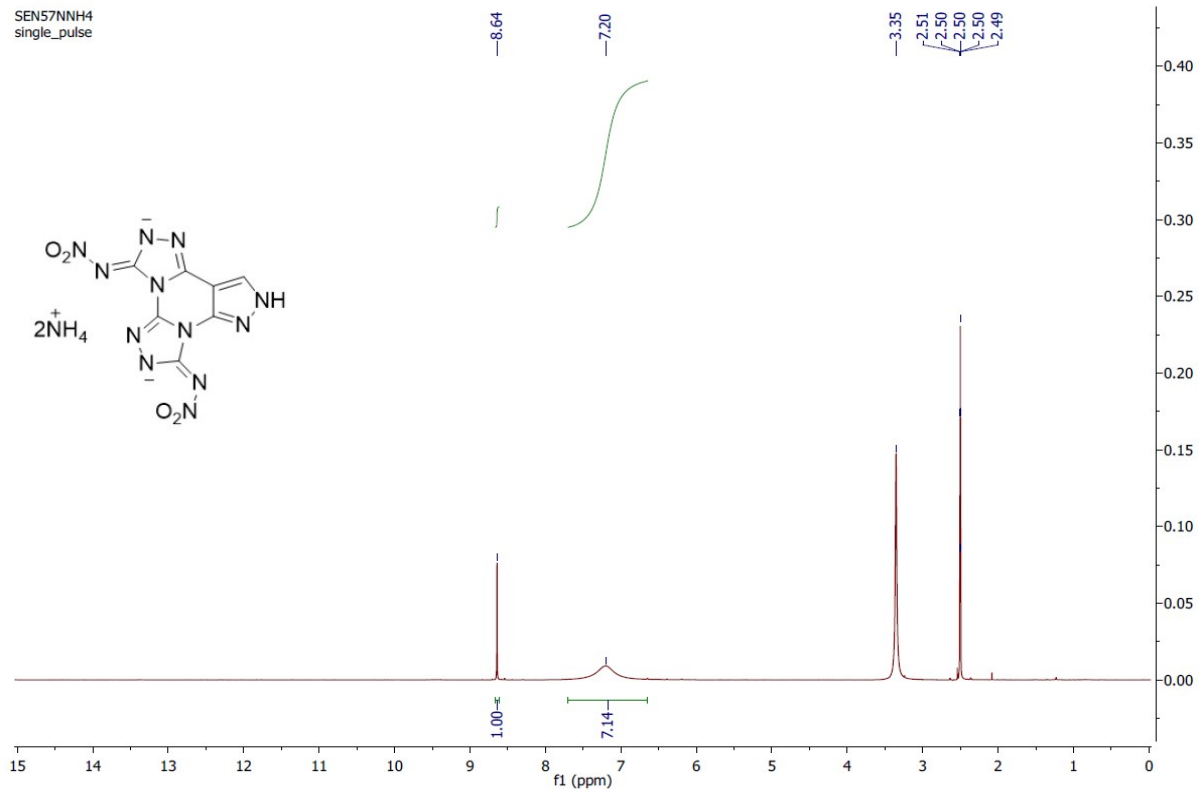


Figure S41: [1]H NMR spectrum of compound **10a** in **DMSO-*d*$_6$** in 500 MHz**.**

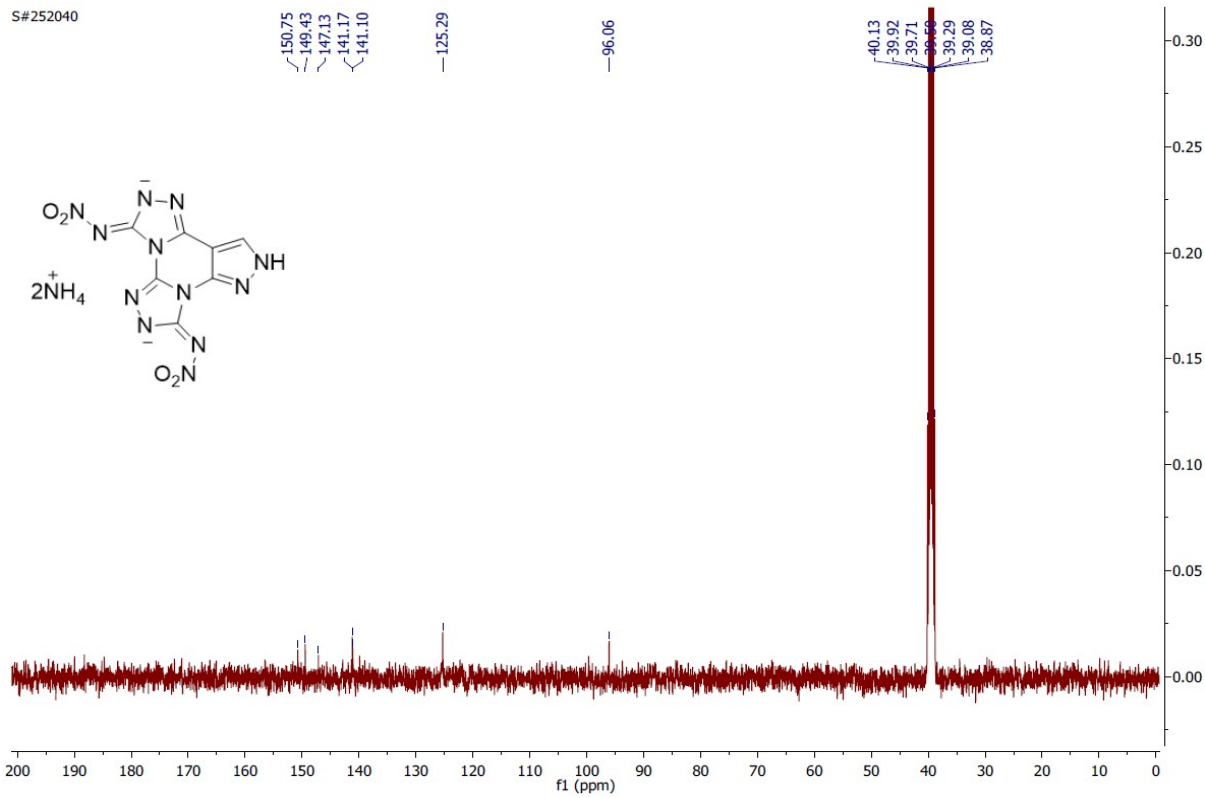


Figure S42: [13]C NMR spectrum of compound **10a** in **DMSO-*d*$_6$** in 126 MHz.

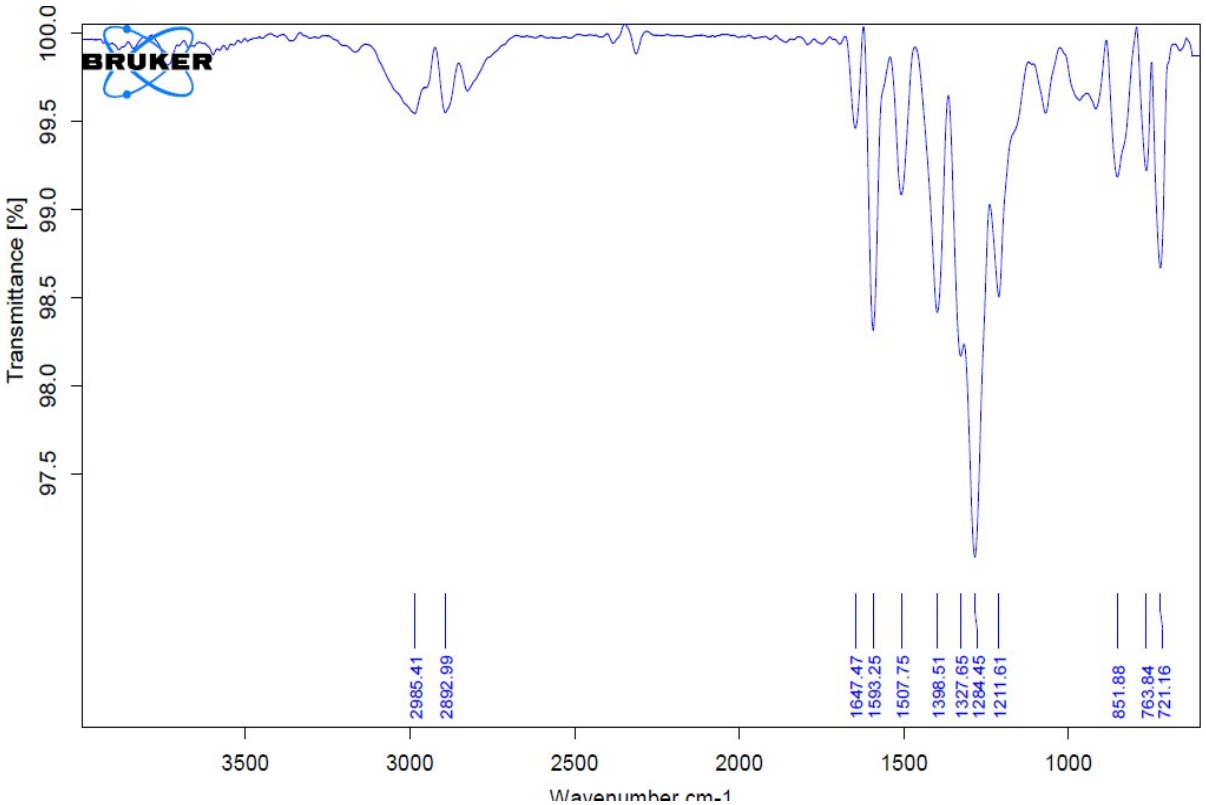


Figure S43: IR spectrum of compound **10a**.

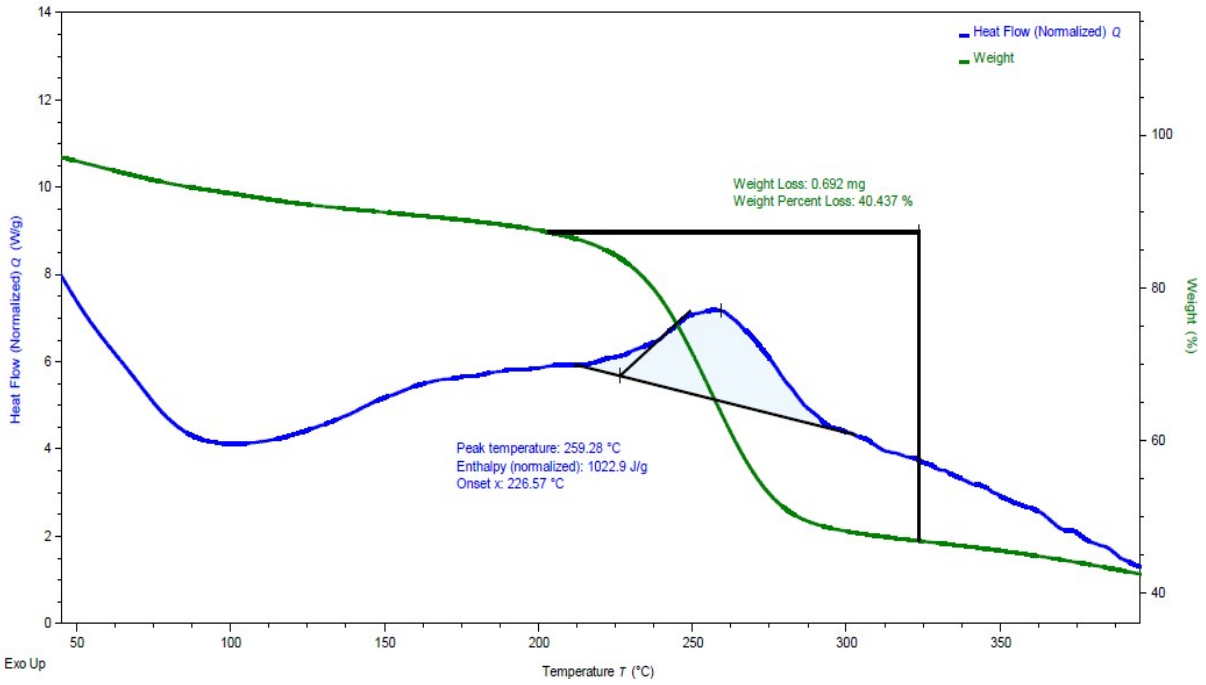


Figure S44: DSC spectra of compound **10a** at a heating rate of 5 ˚C min^{-1}.

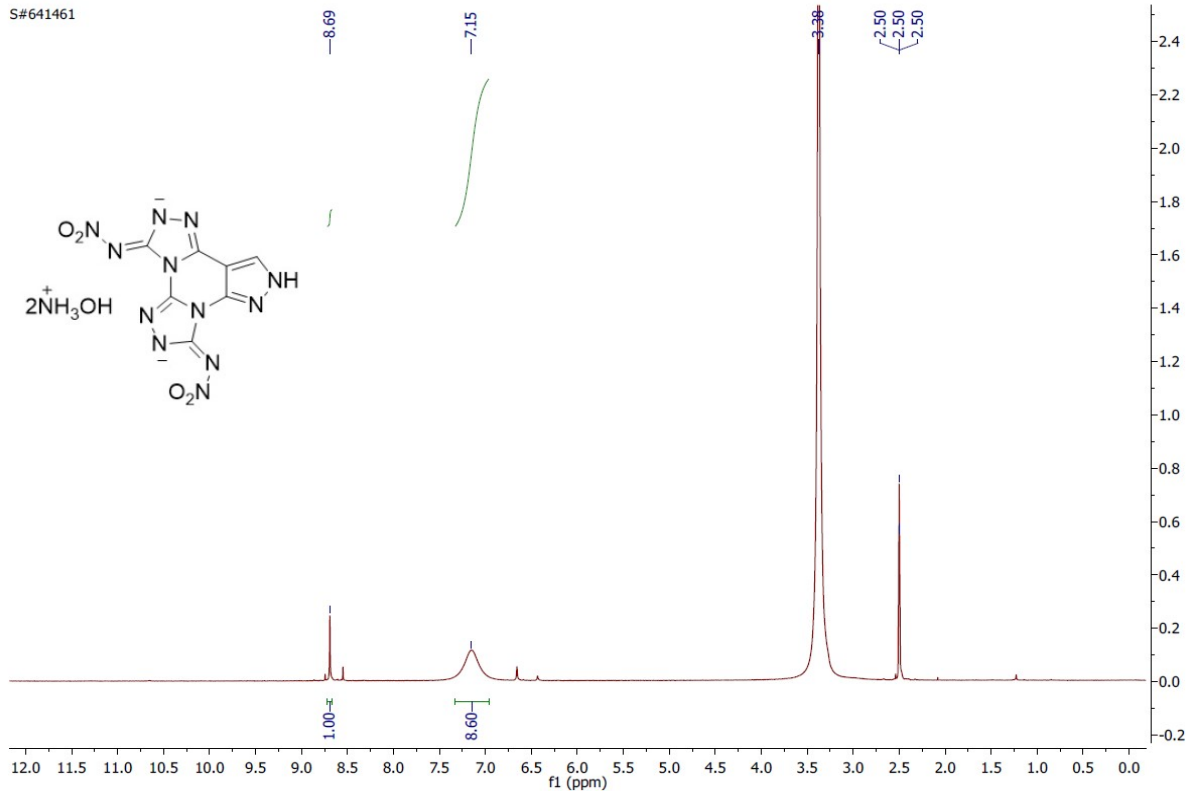


Figure S45: [1]H NMR spectrum of compound **10b** in **DMSO-*d*$_6$** in 500 MHz**.**

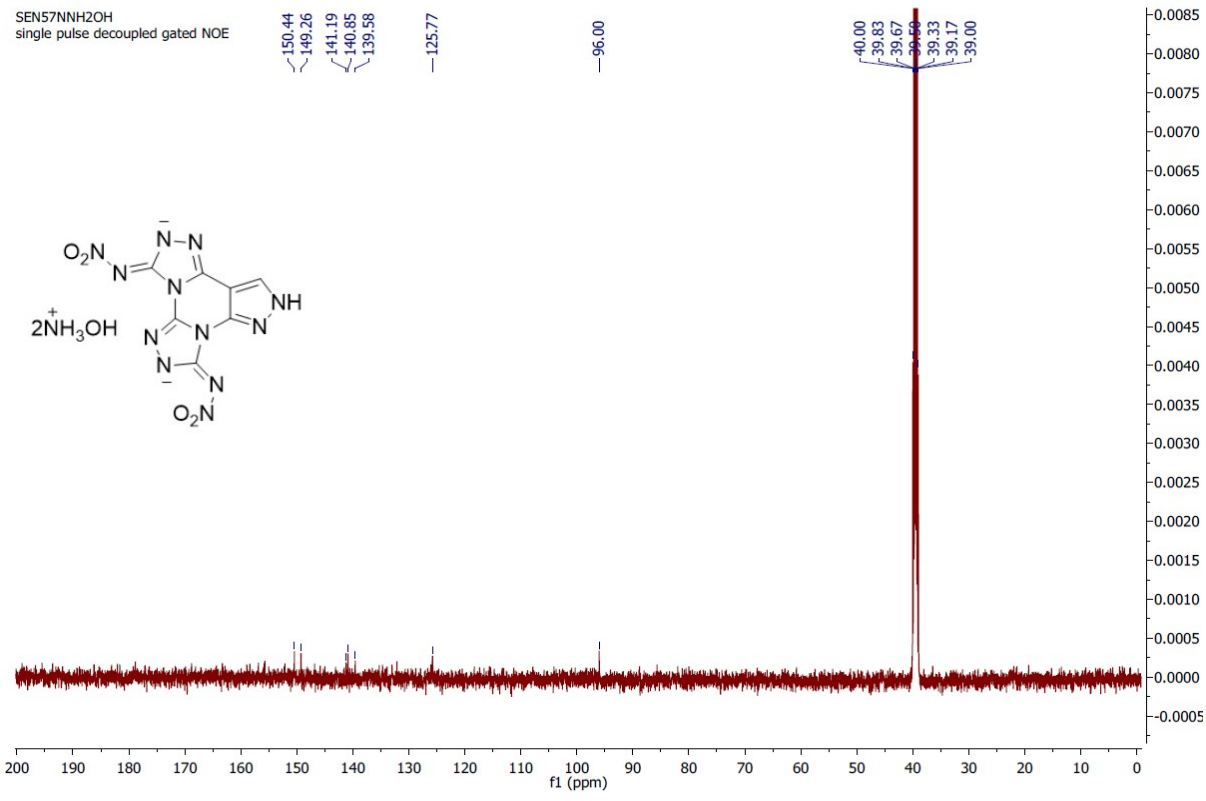


Figure S46: [13]C NMR spectrum of compound **10b** in **DMSO-*d*$_6$** in 126 MHz.

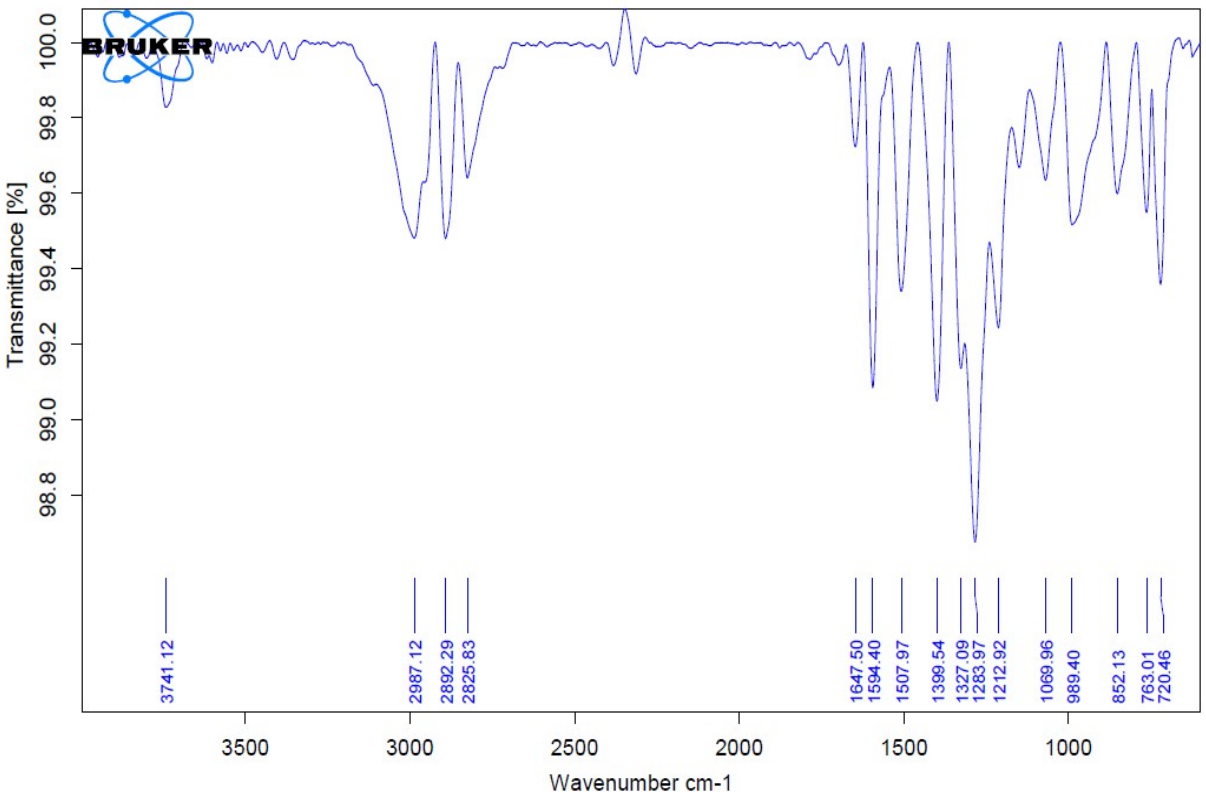


Figure S47: IR spectrum of compound **10b**.

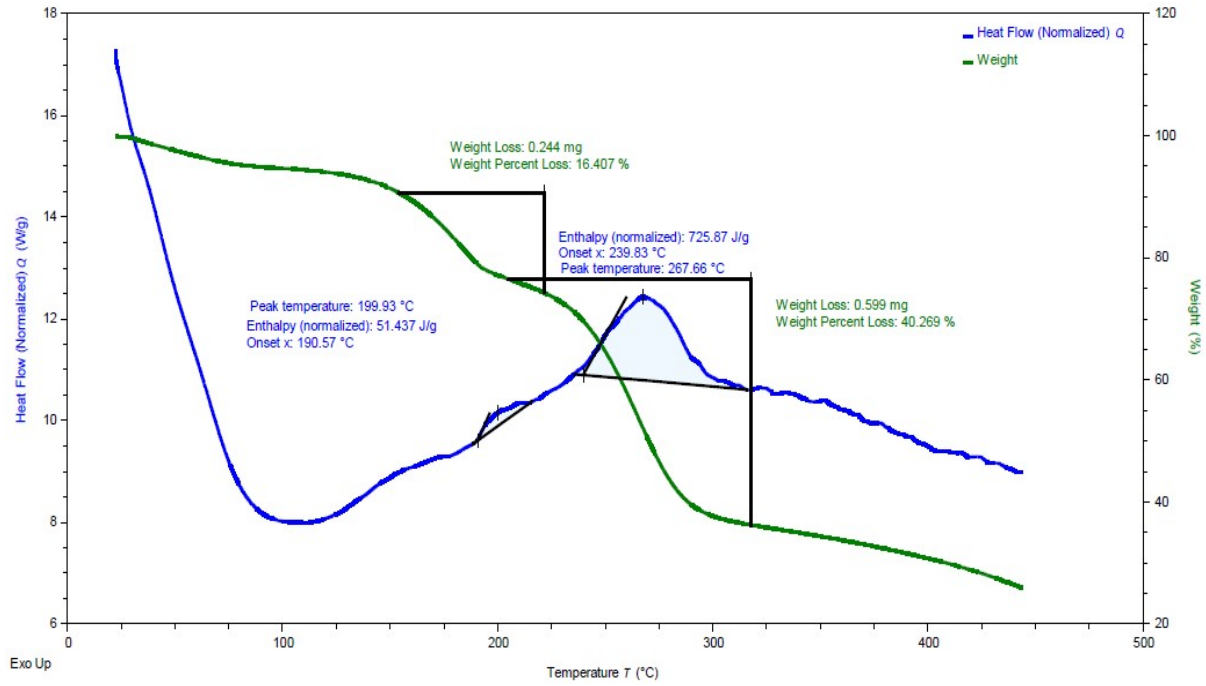


Figure S48: DSC spectra of compound **10b** at a heating rate of 5 ˚C min^{-1}.

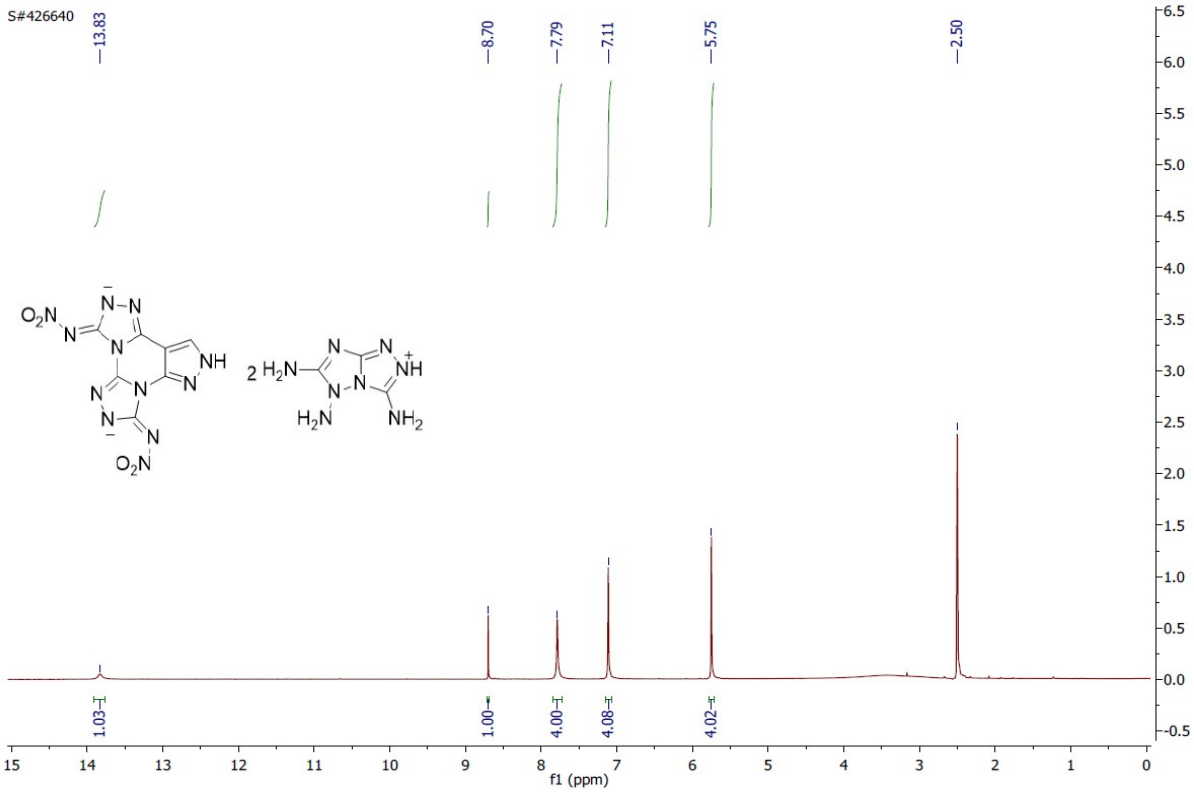


Figure S49: ^{1}H NMR spectrum of compound **10c** in **DMSO-*d*$_6$** in 500 MHz**.**

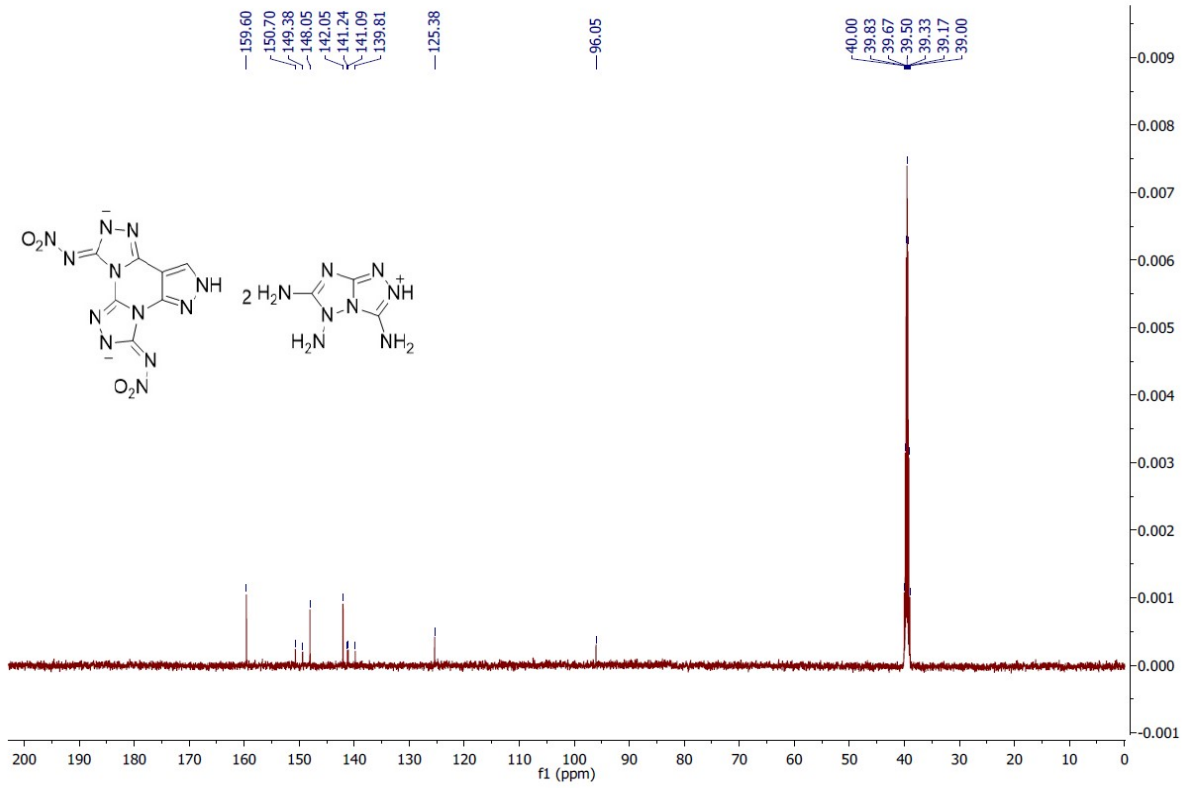


Figure S50: ^{13}C NMR spectrum of compound **10c** in **DMSO-*d*$_6$** in 126 MHz.

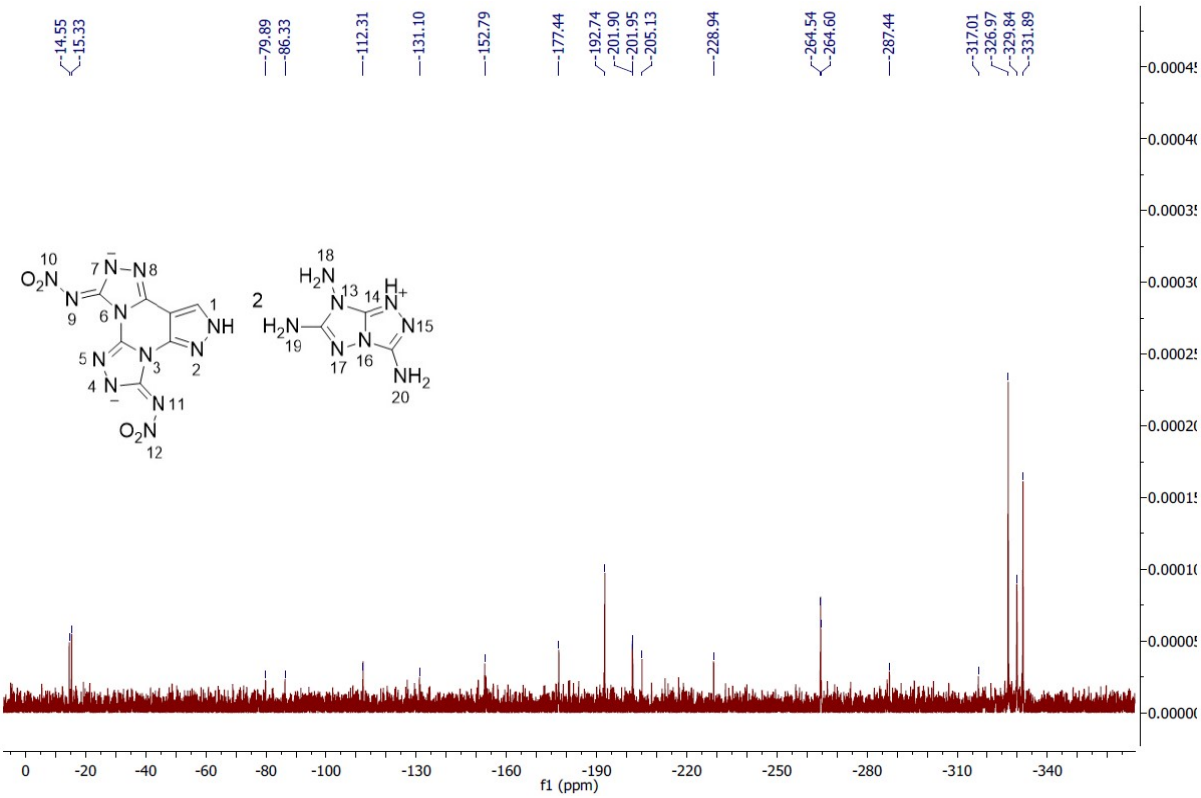


Figure S51: ^{15}N NMR spectrum of compound **10c** in **DMSO-*d*$_6$** in 50.5 MHz.

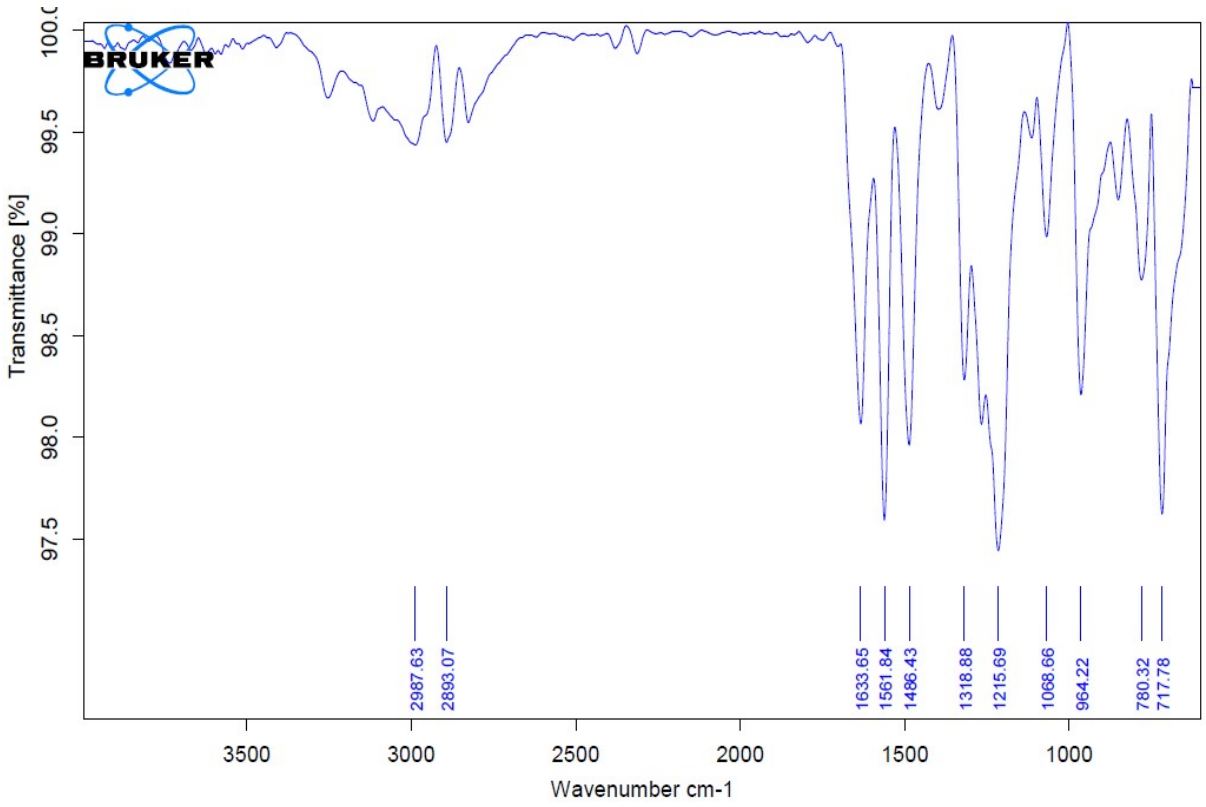


Figure S52: IR spectrum of compound **10c**.

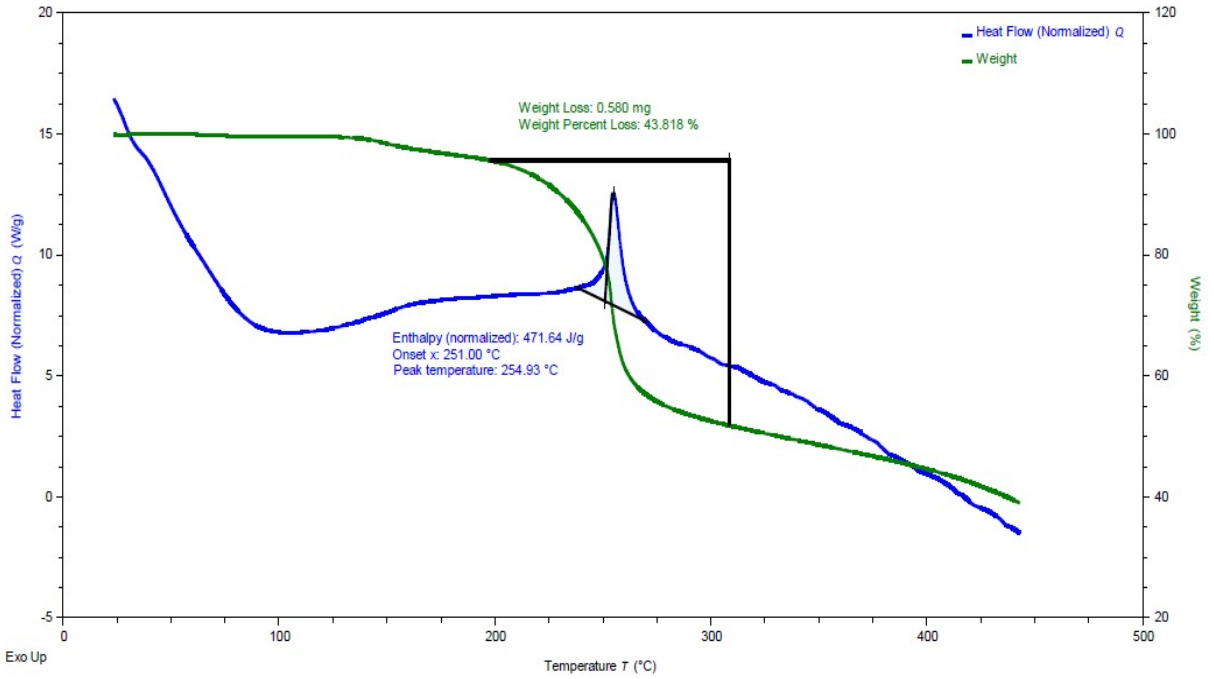


Figure S53: DSC spectra of compound **10c** at a heating rate of 5 ˚C min^{-1}.

Computational details:

Computations were carried out using the Gaussian 09 program suite.[2] The structure optimizations are performed with B3LYP/6-31G(d,p) 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 the 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 mechanisms. Heats of formation for anions were calculated using the designed isodesmic reactions (see **Figure S54**). Calculated total energies and related data for reference compounds and target compounds are listed in **Tables S2** and **S3**.

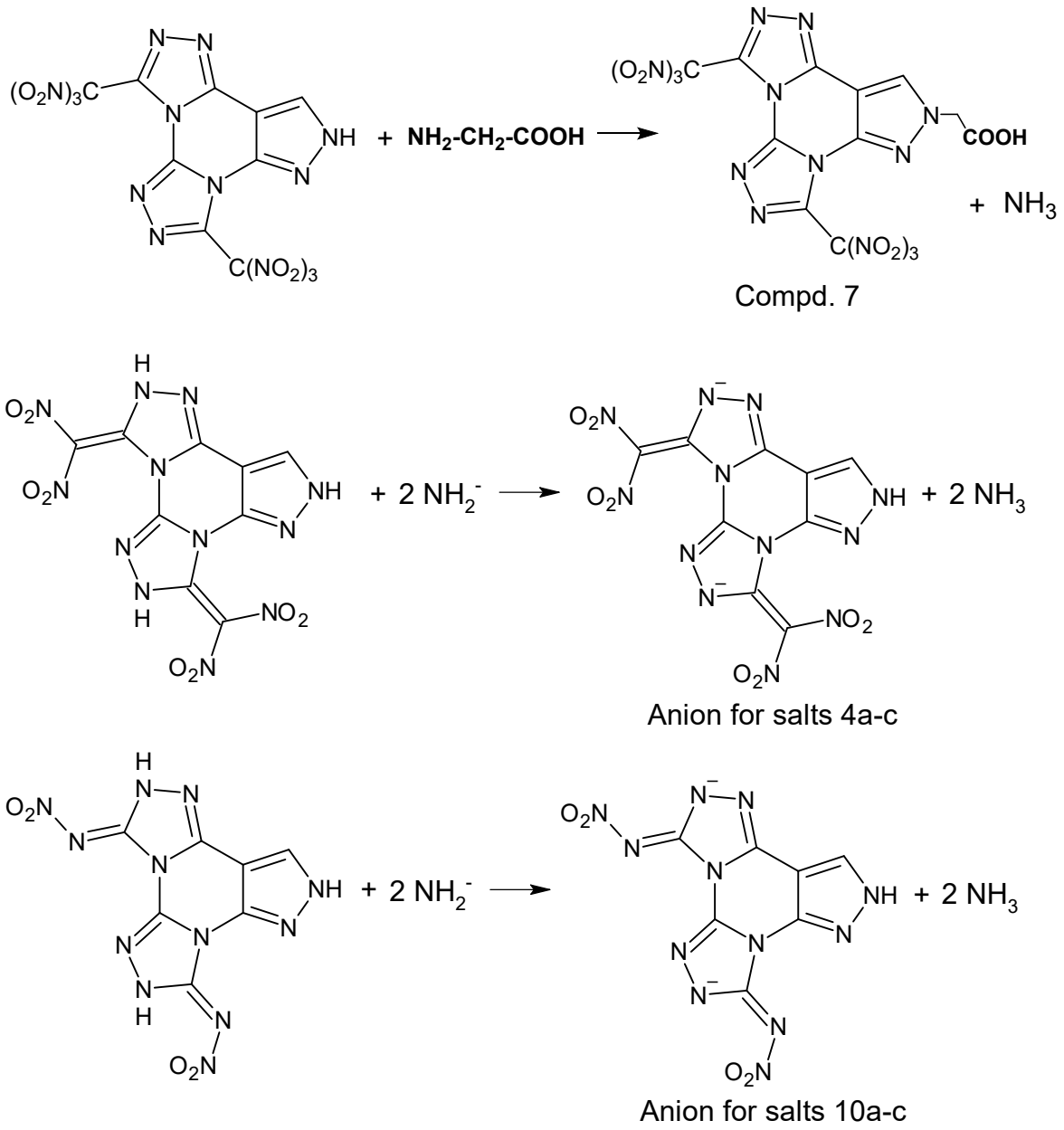


Figure S54. Designed isodesmic reactions to compute heats of formation for anionic components in salts **4a-c** and **10a-c**.

The computed HOF_{Gas} value for compound **7** using the isodesmic reaction approach is 469.4 kJ/mol. The use of HOF_{Gas} in the calculation of detonation properties slightly overestimates the values of detonation velocity and detonation pressure. Therefore, the solid phase HOF (HOF_{Solid}) for compound **7** has been calculated, which can efficiently reduce these errors. The HOF_{Solid} is calculated as the difference between HOF_{Gas} and heat of sublimation (HOF_{Sub}) as,

$$HOF_{Solid} = HOF_{Gas} - HOF_{Sub} \quad (1)$$

The heat of sublimation (HOF_{Sub}), which is required to convert the HOF_{Gas} to the HOF_{Solid}, was calculated from Equation (2)[3]

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

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. The computed heat of sublimation for compound **7** using equation (2) is 244.6 kJ/mol. The molecular surface properties of compound 7, obtained from the Multiwfn program, are listed in **Table S4**.

Based on the Born–Haber cycle (shown in **Figure S55**), 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 S5**) *i.e.* sum of the heats of formation of the cation and anion as shown in equation (3).

HOF (salt, 298 K) = HOF (cation, 298 K) + HOF (anion, 298 K) - H_L (3)

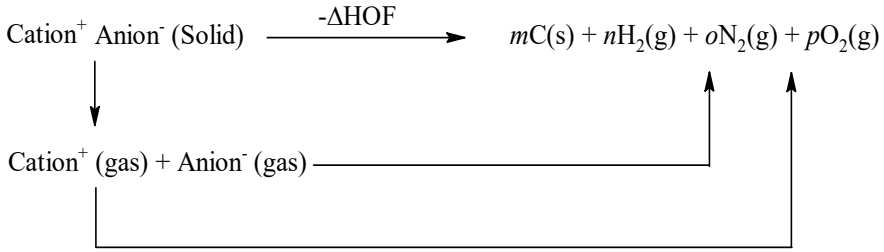


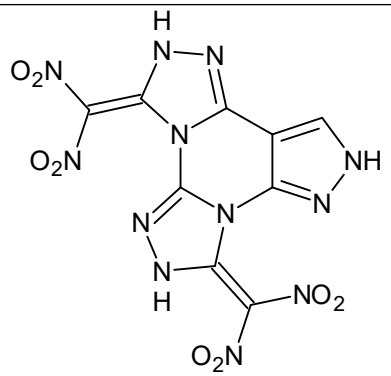
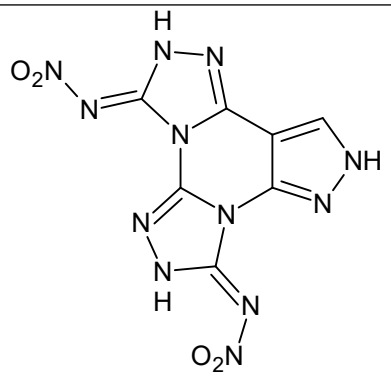
Figure S55. Born-Haber cycle for the formation of energetic salts.

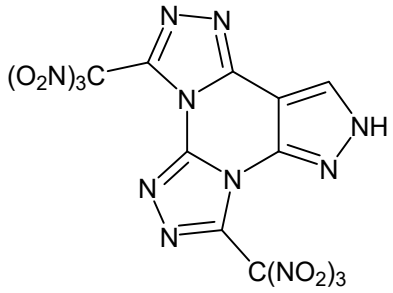
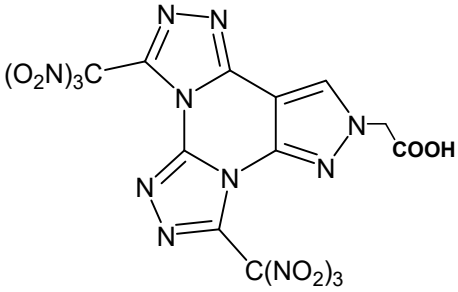
Lattice potential energy is the energy associated with the process in which a crystalline solid lattice, M_pX_q is converted into its constituent gaseous ions, ${}_pM^{q+}$ (g) and ${}_qX^{p-}$ (g). The lattice energy can be predicted with reasonable accuracy by using Jenkins' equation (4).[4]

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

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 correcting the U_{POT} term with an appropriate number of RT terms.

Table S2. Calculated total energies at 298K (E_0), zero-point energies (ZPE), and thermal corrections (H_T), and experimental/computed HOF_{Gas} of reference/target compounds used in isodesmic reactions.

Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF_{gas} (kJ/mol)**
NH_2-Anion	-55.826758	0.0178	0.0038	111.75[a]
NH_3	-56.51952	0.0344	0.0038	-45.94
	-1603.441445	0.1959	0.0228	828.0
	-1226.568636	0.1671	0.0171	879.9

	-2012.358217	0.196	0.0291	854.3
	-2240.203010	0.2393	0.0335	469.4
NH_2CH_2COOH	-284.34894	0.0801	0.0065	-390.5

[a]Calculated using G4 method.

Table S3. Calculated total energies (E_0), zero-point energies (ZPE), and thermal corrections (H_T) for anions.

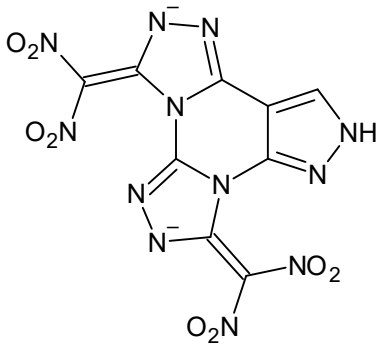
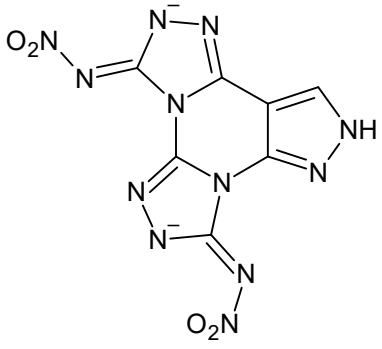
Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF_{anion} (kJ/mol)**
	-1602.386753	0.1692	0.0228	274.8
	-1225.440286	0.1404	0.0175	495.8

Table S4. Calculated molecular surface properties of compound **7**.

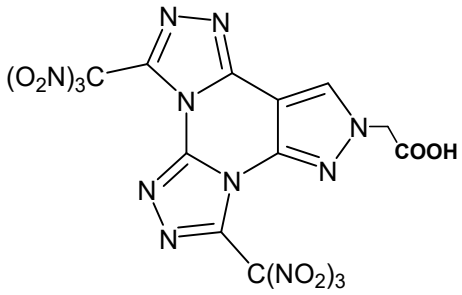
Compd.	Surface area (Å²)	Volume (Å³)	σ^2_{tot} (kcal/mol)	Balance Parameter (ν)
	421.06	473.83	260.52	0.0936

Table S5. Energy content of salts 4a-c and 10a-c.

Compd.	HOF_c[a]	HOF_a[b]	U_{Pot}[c]	H_L[d]	HOF_{salt}[e]
4a	636.8	274.8	1138.3	1150.7	397.68
4b	675.6	274.8	1130.2	1142.6	483.30
4c	769.5	274.8	1143.8	1156.2	657.50
10a	636.8	495.8	1231.1	1243.5	525.85
10b	675.6	495.8	1199.3	1211.7	635.26
10c	1112.0	495.8	1012.8	1025.2	1694.61

[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}).

Table S6. Optimized coordinates of compound **7** at B3LYP/6-31G(d,p) level of theory.

6	0.471332000	2.150985000	0.481870000
6	1.211210000	0.951872000	0.346761000
6	-0.958552000	2.121243000	0.388020000
7	0.545678000	-0.254616000	0.123965000

7	-1.547030000	0.878357000	0.156204000
6	-0.826060000	-0.298446000	0.048947000
6	1.450334000	3.106843000	0.711083000
7	2.513142000	1.116432000	0.477514000
7	-1.882577000	3.053211000	0.475747000
7	-3.094263000	2.441965000	0.303499000
6	-2.900145000	1.158819000	0.112705000
6	0.903100000	-1.583094000	-0.015211000
7	-0.170310000	-2.328597000	-0.153394000
7	-1.270426000	-1.520044000	-0.115284000
6	-3.997146000	0.187160000	-0.107510000
6	2.283195000	-2.121529000	-0.000818000
7	2.230031000	-3.674480000	0.012594000
8	1.949497000	-4.177317000	-1.054943000
8	2.463125000	-4.211527000	1.077359000
7	-5.357666000	0.919414000	0.064576000
8	-5.918901000	0.763224000	1.130839000
8	-5.701064000	1.584566000	-0.890551000
7	-3.976808000	-0.966800000	0.947687000
8	-4.549070000	-1.994077000	0.663453000
8	-3.407709000	-0.675142000	1.985943000
7	-4.011539000	-0.416832000	-1.531898000
8	-5.020748000	-1.010586000	-1.850600000
8	-3.007329000	-0.222101000	-2.198780000

7	3.121364000	-1.726502000	-1.240192000
8	4.112944000	-2.394384000	-1.451167000
8	2.701954000	-0.774267000	-1.879072000
7	3.062520000	-1.681403000	1.278032000
8	2.353162000	-1.489705000	2.249783000
8	4.269470000	-1.600185000	1.197806000
1	1.379619000	4.171844000	0.869136000
7	2.635047000	2.448588000	0.708620000
6	4.641262000	3.340984000	-0.521187000
8	5.813292000	3.613491000	-0.594018000
8	3.784699000	3.320694000	-1.555932000
1	4.296881000	3.534232000	-2.355228000
6	3.967541000	3.014111000	0.812718000
1	4.603550000	2.304969000	1.344221000
1	3.916792000	3.932954000	1.402948000

Table S7. Optimized coordinates of anion for salts 4a-c at B3LYP/6-31G(d,p) level of theory.

6	0.326952000	2.520706000	-0.428487000
6	1.298166000	1.576505000	-0.118994000
6	-1.048554000	2.108965000	-0.465741000
7	0.989283000	0.240815000	0.058520000
7	-1.330940000	0.782078000	-0.143813000
6	-0.340585000	-0.162081000	0.104069000
6	1.057305000	3.732736000	-0.494217000

7	2.349305000	3.548598000	-0.233018000
7	2.488956000	2.206064000	-0.025340000
7	-2.159769000	2.772034000	-0.685564000
7	-3.203782000	1.886903000	-0.502511000
6	-2.726661000	0.702931000	-0.179960000
6	1.710054000	-0.942053000	0.270125000
7	0.851228000	-1.921315000	0.461277000
7	-0.438291000	-1.441801000	0.348687000
1	0.681365000	4.722137000	-0.714656000
1	3.268968000	1.818032000	0.516927000
6	3.147723000	-1.140108000	0.117761000
6	-3.526773000	-0.484164000	0.101368000
7	4.058662000	-0.458848000	0.896740000
8	3.558429000	0.434719000	1.673736000
8	5.287131000	-0.621212000	0.830791000
7	3.583174000	-2.080457000	-0.862265000
8	4.692447000	-2.625781000	-0.767053000
8	2.798801000	-2.308308000	-1.803328000
7	-4.002493000	-1.227740000	-0.980966000
8	-4.807428000	-2.164838000	-0.839918000
8	-3.566941000	-0.885900000	-2.111964000
7	-3.815996000	-0.759327000	1.438687000
8	-3.263802000	0.003689000	2.277884000
8	-4.563817000	-1.688597000	1.785994000

Table S8. Optimized coordinates of anion for salts 10a-c at B3LYP/6-31G(d,p) level of theory.

6	0.482922000	2.114338000	0.020557000
6	1.392907000	1.023684000	-0.101884000
6	-0.932968000	1.878345000	-0.050150000
7	0.894005000	-0.256747000	-0.278875000
7	-1.366301000	0.566474000	-0.202688000
6	-0.475436000	-0.498542000	-0.385022000
6	1.298411000	3.221560000	0.146378000
7	2.576550000	2.750589000	0.073754000
7	2.664523000	1.400383000	-0.070038000
7	-1.949593000	2.707145000	-0.019271000
7	-3.098524000	1.949571000	-0.141938000
6	-2.772638000	0.663749000	-0.245454000
6	1.488957000	-1.505059000	-0.560895000
7	0.525223000	-2.371042000	-0.813439000
7	-0.711950000	-1.735706000	-0.705401000
7	-3.670887000	-0.328374000	-0.529167000
7	2.828285000	-1.740265000	-0.757702000
7	-3.743982000	-1.289653000	0.402913000
8	-3.073263000	-1.228116000	1.466797000
8	-4.544077000	-2.225190000	0.184444000
7	3.604018000	-1.495062000	0.305159000
8	3.122412000	-1.154920000	1.419230000

8	4.838650000	-1.644697000	0.147937000
1	1.066796000	4.268367000	0.269173000
1	3.430935000	3.265368000	0.199239000

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