Supporting Information (SI)

Exploring New Frontiers: Alliance of Pyrazole and Thiadiazole in Energetic Materials

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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 and ^{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. HRMS was recorded on a Quadrupole Time-of-Flight (Q-TOF) Mass Spectrometry 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). Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer in helium atmosphere. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fall hammer and a BAM friction tester. The single-crystal X-ray data collection was carried out using Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection.

Experimental Section:

***Synthesis of 5-(3-amino-1H-pyrazol-4-yl)-1,3,4-thiadiazol-2-amine (2)*:** To the solution of trifluoroacetic acid (TFA, 5 mL) taken in 50 mL of round bottom flask placed at room temperature, 3-amino-1*H*-pyrazole-4-carbonitrile (**1**) (200 mg, 1.85 mmol) was added slowly followed by the pinch-wise addition of thiosemicarbazide (202 mg, 2.21 mmol). The reaction mixture was then heated to 60 ˚C for 16 hours. Later, the reaction was stopped and allowed to cool down to room temperature. Aqueous NH_3 (25%) was then added dropwise to the reaction mixture till the white fume ceases and the formation of precipitate was observed. The newly formed precipitate was then filtered, washed with cold water, and dried in an oven at 50 ˚C. Light brown. Yield 80% (279 mg, 1.49 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 11.94 (s, 1H), 8.05 (br, 1H), 7.03 (s, 1H), 5.55 (br, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 171.77, 165.45, 151.76, 137.80, 128.34. IR (ATR, ZnSe, cm^{-1}): 759, 928, 974, 1039, 1317, 1486, 1598, 3124, 3316, 3405. HRMS (ESI-QTOF) m/z: calculated for $C_5H_6N_6S$ $[M+H]^+$ 183.0447; found 183.0449. Elemental analysis: (%) calculated for $C_5H_6N_6S{\cdot}0.3H_2O$ (187.60): C, 32.01; H, 3.55; N, 44.80; S, 17.09; found C, 32.49; H, 3.40; N, 44.60; S, 17.84.

***Synthesis of* (Z)-4-(5-(nitroimino)-4,5-dihydro-1,3,4-thiadiazol-2-yl)-1*H*-pyrazole-3-diazonium nitrate *(3)*:** To the ice-cooled solution 100% HNO_3 (6 mL) and 98% H_2SO_4 (9 mL) placed in ice bath, compound **2** (1000 mg, 5.48 mmol) was added slowly with uniform stirring. The reaction mixture was then stirred at the same temperature for 30 minutes and then at room temperature for the next 8 hours. The brownish solution was then poured into crushed ice and kept in the refrigerator for 15 minutes and later at ambient conditions for 12 hours. Dark orange

crystals were obtained, filtered, washed with water, and dried in oven. Dark orange. Yield 57% (936 mg, 3.10 mmol). T_d(onset): 145 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.19 (s, 1H), 7.70 (br). ^{13}C NMR (126 MHz, DMSO-d_6): 170.41, 151.14, 150.81, 133.46, 110.26. IR (ATR, ZnSe, cm^{-1}): 854, 1023, 1147, 1203, 1393, 1437, 1537, 1630, 1707, 2258, 3098, 3370. Elemental analysis: (%) calculated for $C_5H_3N_9O_5S$ (301.19): C, 19.94; H, 1.00; N, 41.85; S, 10.64; found C, 20.31; H, 1.28; N, 41.41; S, 11.13.

***Synthesis of Ammonium(5-(1H-pyrazol-4-yl)-1,3,4-thiadiazol-2-yl)(nitro)amide (4)*:** Compound **3** (100 mg, 0.33 mmol) was dissolved in methanol (5 mL) and aq. Ammonia or hydroxyl amine hydrate (1 mL) was added to it and stirred at room temperature for 12 hours. The formed precipitate was collected by filtration, washed with methanol, and dried in air to obtain pure product. Light brown. Yield 86 % (65 mg, 0.28 mmol). T_d(onset): 219 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.12 (s, 2H), 7.22 (br, 4H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 168.77, 154.13, 131.48, 113.35. IR (ATR, ZnSe, cm^{-1}): 658, 739, 850, 1015, 1086, 1124, 1259, 1329, 1436, 1461, 1576, 1695, 2835, 2974, 3099, 3211. Elemental analysis: (%) calculated for $C_5H_7N_7O_2S{\cdot}0.8H_2O$ (243.63): C, 24.65; H, 3.56; N, 40.25; S, 13.16; found C, 25.35; H, 3.16; N, 40.03; S, 13.64.

***Synthesis of hydrazinium 4-(5-(nitroamide)-1,3,4-thiadiazol-2-yl)-pyrazole-3-diazonium (5)*:** Compound **3** (100 mg, 0.28 mmol) was dissolved in methanol (5 mL), and hydrazine monohydrate (2 mL) was added into it and stirred at room temperature for 12 hours. The formed precipitate was collected by filtration, washed with methanol, and dried in air to obtain pure product. Dark brown. Yield 84% (76 mg, 0.283 mmol). T_d(onset): 171 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.30 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 169.55, 151.27,

143.91, 129.65, 103.92. IR (ATR, ZnSe, cm^{-1}): 660, 701, 742, 959, 1017, 1102, 1248, 1355, 1463, 1515, 1568, 2115, 2136, 3314. Elemental analysis: (%) calculated for $C_5H_6N_{10}O_2S$ (273.23): C, 22.22; H, 2.24; N, 5183; S, 11.86; found C, 21.50; H, 2.24; N, 51.83; S, 11.86.

***Synthesis of 5-(3-nitro-1H-pyrazol-4-yl)-1,3,4-thiadiazol-2-amine (6)*:** To the ice-cooled solution of hydrogen peroxide (3 mL) and conc. sulfuric acid (2 mL), compound 2 (100 mg, 0.54 mmol) was added pinch-wise and stirred at room temperature for 18 hours. The clear solution was then poured into crushed ice to obtain brownish precipitate, filtered, washed with water, and dried. Brown. Yield 65% (76 mg, 0.35 mmol). ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.54 (s, 1H), 6.03 (br, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 170.13, 151.48, 133.18, 107.85. IR (ATR, ZnSe, cm^{-1}): 610, 649, 700, 913, 968, 1022, 1100, 1152, 1328, 1372, 1518, 1586, 1624, 1645, 3126. HRMS (ESI-QTOF) m/z: calculated for $C_5H_4N_6O_2S$ $[M-H]^-$ 211.0044; found 211.0040. Elemental analysis: (%) calculated for $C_5H_4N_6O_2S{\cdot}2H_2O$ (248.21): C, 24.19; H, 3.25; N, 33.86. found C, 24.08; H, 2.75; N, 32.77.

***Synthesis of (Z)-N-(5-(3-nitro-1H-pyrazol-4-yl)-1,3,4-thiadiazol-2(3H)-ylidene)nitramide (7)*:** To the ice-cooled solution 100% HNO_3 (1 mL) placed in ice bath, compound **6** (121 mg, 0.57 mmol) was added slowly with uniform stirring. The reaction mixture was then stirred at the same temperature for 30 minutes and then at room temperature for the next 8 hours. The clear solution was then poured into crushed ice to obtain yellow precipitate, filtered, washed with water, and dried. Dark orange. Yield 74% (109 mg, 0.42 mmol). T_d(onset): 219 °C. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.58 (br, 1H), 8.68 (s, 1H), 6.59 (br, 1H). ^{13}C NMR (126 MHz, DMSO-d_6): δ(ppm) 170.98, 151.79, 149.78, 133.75, 106.75. IR (ATR, ZnSe, cm^{-1}): 656, 819, 926, 987, 1093, 1167, 1246, 1333, 1380, 1529, 3116, 3154. HRMS (ESI-QTOF)

m/z: calculated for $C_5H_3N_7O_4S$ $[M-H]^-$ 255.9894; found 255.9895. Elemental analysis: (%) calculated for $C_5H3N_7O_4S{\cdot}0.4H_2O$(264.39): C, 22.71; H, 1.45; N, 37.08; S, 12.13; found C, 23.10; H, 2.13; N, 37.10; S, 11.70.

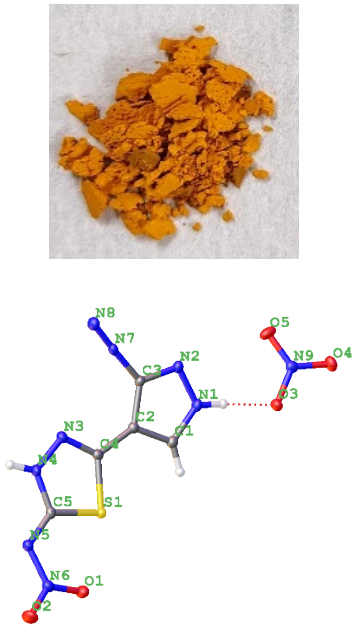


Figure S1: Crystal structure of compound **3.**

Table S1: Crystallographic data for compound **3.**

CCDC	2419626
Empirical formula	$C_5H_3N_9O_5S$
Formula weight	301.22
Temperature/K	100
Crystal system	monoclinic
Space group	P_{21}/n
a/Å	5.3298(2)
b/Å	13.0514(4)
c/Å	15.3353(5)
α/°	90
β/°	96.4230(10)
γ/°	90
Volume/Å3	1060.05(6)
Z	4
ρcalcg/cm3	1.887
μ/mm-1	0.351
F(000)	608.0
Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.108 to 56.778
Index ranges	-7 ≤ h ≤ 7, -17 ≤ k ≤ 17, -19 ≤ l ≤ 20
Reflections collected	22696
Independent reflections	2646 [Rint = 0.0315, Rsigma = 0.0167]

Data/restraints/parameters	2646/0/185
Goodness-of-fit on F2	1.058
Final R indexes [I>=2σ (I)]	R1 = 0.0259, wR2 = 0.0646
Final R indexes [all data]	R1 = 0.0277, wR2 = 0.0654
Largest diff. peak/hole / e Å-3	0.38/-0.26

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

Atom	**x**	**y**	**z**	**U(eq)**
S1	7353.2(5)	4318.3(2)	2633.5(2)	12.81(8)
O3	-404.2(16)	4295.2(6)	5830.5(6)	16.92(17)
O1	8376.4(17)	5527.0(7)	1451.9(6)	20.26(19)
O5	-192.5(17)	2914.6(7)	6639.5(6)	21.96(19)
O4	-2573.9(16)	4180.8(7)	6945.7(6)	20.12(19)
O2	11573.2(19)	5534.5(7)	687.8(7)	26.5(2)
N7	8208.1(18)	1776.9(7)	5011.0(6)	13.70(19)
N9	-1053.5(18)	3793.1(7)	6481.4(6)	14.35(19)
N2	4753.5(18)	2695.1(7)	5391.2(6)	14.39(19)
N5	11143.1(18)	4193.3(7)	1524.3(6)	15.2(2)
N4	10651.9(18)	2942.7(8)	2549.9(6)	15.17(19)
N1	3449.3(18)	3495.8(8)	5040.3(7)	14.73(19)
N3	9464.0(19)	2632.5(8)	3245.4(6)	15.26(19)
N6	10311.7(19)	5124.3(8)	1216.8(6)	16.6(2)
N8	9663(2)	1202.0(8)	5201.2(7)	19.3(2)
C3	6403(2)	2531.4(8)	4809.5(7)	13.0(2)
C2	6196(2)	3209.8(8)	4093.0(7)	12.9(2)
C5	9889(2)	3824.4(8)	2155.7(7)	13.0(2)
C4	7705(2)	3289.1(8)	3366.6(7)	13.0(2)
C1	4224(2)	3832.2(9)	4280.1(7)	14.7(2)

Table S3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h2a^*2U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
S1	12.94(13)	12.48(13)	13.52(14)	0.88(9)	3.67(10)	1.31(9)
O3	18.8(4)	17.6(4)	15.5(4)	2.3(3)	6.9(3)	2.0(3)
O1	21.0(4)	19.9(4)	20.9(4)	4.2(3)	6.8(3)	6.3(3)
O5	25.1(4)	12.7(4)	26.7(5)	2.2(3)	-3.6(4)	2.1(3)
O4	19.0(4)	24.0(4)	18.8(4)	-1.6(3)	8.8(3)	-0.9(3)
O2	30.9(5)	23.9(5)	27.6(5)	8.5(4)	15.7(4)	0.0(4)
N7	16.3(4)	13.4(4)	12.3(4)	-0.9(3)	5.6(3)	-0.6(4)
N9	14.9(4)	13.5(4)	14.3(5)	-0.8(3)	-0.1(3)	-2.6(3)
N2	15.1(4)	13.4(4)	15.0(5)	-1.4(4)	3.4(3)	0.7(3)
N5	17.6(5)	14.8(4)	14.1(5)	0.5(4)	5.2(4)	1.1(4)
N4	17.1(4)	16.1(5)	13.2(4)	0.8(4)	5.6(3)	4.4(4)
N1	13.9(4)	14.5(4)	16.3(5)	-1.4(4)	3.6(4)	2.2(3)
N3	18.1(5)	16.0(5)	12.1(4)	0.4(4)	3.7(4)	1.5(4)
N6	19.3(5)	16.2(5)	14.9(5)	0.4(4)	4.4(4)	-0.1(4)

N8	20.6(5)	18.8(5)	19.9(5)	1.7(4)	8.2(4)	3.7(4)
C3	14.0(5)	11.4(5)	14.0(5)	-0.5(4)	2.8(4)	0.8(4)
C2	13.6(5)	12.8(5)	12.2(5)	-1.1(4)	1.4(4)	-0.8(4)
C5	13.0(5)	14.3(5)	11.6(5)	-3.1(4)	1.5(4)	0.2(4)
C4	14.2(5)	13.1(5)	11.8(5)	-0.3(4)	1.3(4)	-1.3(4)
C1	14.6(5)	14.4(5)	15.1(5)	-0.2(4)	2.0(4)	0.8(4)

Table S4: Bond Lengths for compound **3**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
S1	C5	1.7322(11)	N2	C3	1.3380(14)
S1	C4	1.7482(11)	N5	N6	1.3595(14)
O3	N9	1.2738(13)	N5	C5	1.3271(14)
O1	N6	1.2464(13)	N4	N3	1.3614(13)
O5	N9	1.2486(13)	N4	C5	1.3417(15)
O4	N9	1.2445(13)	N1	C1	1.3528(15)
O2	N6	1.2325(13)	N3	C4	1.2986(14)
N7	N8	1.0948(14)	C3	C2	1.4058(15)
N7	C3	1.3870(14)	C2	C4	1.4489(15)
N2	N1	1.3346(13)	C2	C1	1.3838(15)

Table S5: Bond Angles for compound **3**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C5	S1	C4	87.33(5)	N7	C3	C2	127.82(10)
N8	N7	C3	177.09(12)	N2	C3	N7	117.12(10)
O5	N9	O3	119.89(10)	N2	C3	C2	114.87(10)
O4	N9	O3	119.37(10)	C3	C2	C4	130.10(10)
O4	N9	O5	120.73(10)	C1	C2	C3	101.70(9)
N1	N2	C3	101.99(9)	C1	C2	C4	128.13(10)
C5	N5	N6	113.96(9)	N5	C5	S1	130.86(9)
C5	N4	N3	117.64(9)	N5	C5	N4	119.21(10)
N2	N1	C1	113.97(9)	N4	C5	S1	109.88(8)
C4	N3	N4	108.80(9)	N3	C4	S1	116.25(8)
O1	N6	N5	121.65(9)	N3	C4	C2	122.31(10)
O2	N6	O1	122.50(10)	C2	C4	S1	121.36(8)
O2	N6	N5	115.85(10)	N1	C1	C2	107.48(10)

Table S6: Torsion Angles for compound **3**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
N7	C3	C2	C4	2.4(2)	C3	C2	C4	S1	-170.78(10)
N7	C3	C2	C1	-174.69(11)	C3	C2	C4	N3	5.98(19)
N2	N1	C1	C2	0.46(13)	C3	C2	C1	N1	-0.31(12)
N2	C3	C2	C4	177.19(11)	C5	S1	C4	N3	-2.15(9)
N2	C3	C2	C1	0.10(13)	C5	S1	C4	C2	174.80(10)
N4	N3	C4	S1	0.81(12)	C5	N5	N6	O1	-7.14(15)

N4	N3	C4	C2	-176.11(10)	C5	N5	N6	O2	173.60(10)
N1	N2	C3	N7	175.53(9)	C5	N4	N3	C4	1.59(14)
N1	N2	C3	C2	0.15(13)	C4	S1	C5	N5	-174.38(12)
N3	N4	C5	S1	-3.19(13)	C4	S1	C5	N4	2.80(8)
N3	N4	C5	N5	174.37(10)	C4	C2	C1	N1	-177.48(11)
N6	N5	C5	S1	1.38(16)	C1	C2	C4	S1	5.59(17)
N6	N5	C5	N4	-175.58(10)	C1	C2	C4	N3	-177.65(11)
C3		N2		N1		C1		-0.37(12)	

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

Atom	x	y	z	U(eq)
H4	11876.73	2577.76	2365.41	18
H1A	3538.72	4393.09	3937.32	18
H1	2190(30)	3738(13)	5316(11)	28(4)

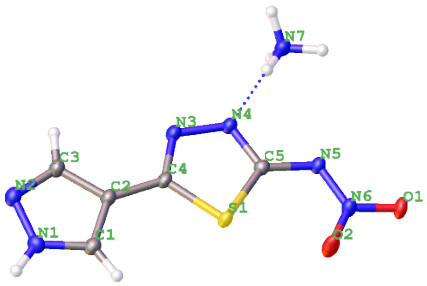


Figure S2: Crystal structure of compound **4.**

Table S8: Crystallographic data for compound **4.**

CCDC	2419625
Empirical formula	$C_5H_7N_7O_2S$
Formula weight	229.24
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	7.2255(3)
b/Å	8.2299(4)
c/Å	8.5296(3)
α/°	76.9840(10)
β/°	67.4560(10)
γ/°	79.1100(10)
Volume/Å3	453.44(3)
Z	2
ρcalcg/cm3	1.679
μ/mm-1	0.351
F(000)	236.0

Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.114 to 56.754
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -10 ≤ l ≤ 11
Reflections collected	7647
Independent reflections	2255 [Rint = 0.0268, Rsigma = 0.0264]
Data/restraints/parameters	2255/0/147
Goodness-of-fit on F2	1.068
Final R indexes [I>=2σ (I)]	R1 = 0.0329, wR2 = 0.0902
Final R indexes [all data]	R1 = 0.0360, wR2 = 0.0922
Largest diff. peak/hole / e Å-3	0.43/-0.34

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

Atom	x	y	z	U(eq)
S1	3071.1(5)	4375.3(4)	3750.5(4)	17.02(12)
O1	1376.3(16)	8710.3(13)	462.3(14)	22.9(2)
O2	691.6(16)	6522.0(16)	2501.4(17)	31.9(3)
N3	6936.8(18)	3914.0(15)	2714.2(16)	18.0(3)
N5	3919.2(18)	7018.3(15)	924.3(16)	17.2(3)
N4	6486.7(18)	5236.5(15)	1564.8(16)	17.6(3)
N7	8995.6(19)	7580.8(17)	-1051.8(17)	20.5(3)
N6	1964.4(19)	7386.3(16)	1334.0(17)	19.7(3)
N1	4715.6(19)	58.0(16)	7636.9(16)	20.1(3)
N2	6761(2)	-103.2(16)	6966.9(17)	22.1(3)
C2	5440(2)	1976.8(17)	5316.9(18)	16.9(3)
C4	5326(2)	3339.4(17)	3929.7(18)	16.1(3)
C5	4530(2)	5641.6(17)	1937.0(18)	15.8(3)
C3	7201(2)	1063.6(19)	5562(2)	20.4(3)
C1	3874(2)	1276.7(18)	6694.5(19)	19.1(3)

Table S10: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h2a^*2U_{11}+2hka^*b^*U_{12}+...]$.

Atom	U11	U22	U33	U23	U13	U12
S1	12.15(17)	15.35(18)	20.4(2)	0.78(13)	-5.21(13)	-0.11(12)
O1	21.3(5)	17.8(5)	29.0(6)	3.0(4)	-14.1(5)	1.6(4)
O2	14.0(5)	30.4(6)	39.3(7)	13.6(5)	-6.8(5)	-3.3(4)
N3	15.5(5)	16.7(6)	20.0(6)	-1.6(5)	-6.5(5)	1.2(4)
N5	15.4(6)	15.2(6)	19.7(6)	-0.9(5)	-6.7(5)	-0.1(4)
N4	14.9(5)	16.8(6)	18.8(6)	-1.0(5)	-5.7(4)	0.6(4)
N7	15.0(6)	22.5(6)	20.2(6)	-0.3(5)	-5.4(5)	0.6(5)
N6	16.7(6)	17.8(6)	22.7(6)	1.7(5)	-8.3(5)	-1.2(5)
N1	22.2(6)	17.5(6)	18.6(6)	0.0(5)	-6.3(5)	-3.8(5)

N2	21.3(6)	20.0(6)	24.5(7)	-1.7(5)	-10.1(5)	0.6(5)
C2	16.2(6)	14.8(6)	19.5(7)	-3.0(5)	-7.1(5)	0.6(5)
C4	14.7(6)	13.7(6)	19.3(7)	-3.7(5)	-6.5(5)	1.6(5)
C5	15.7(6)	14.7(6)	16.6(6)	-3.2(5)	-5.5(5)	-0.8(5)
C3	17.5(7)	19.7(7)	21.4(7)	-0.4(6)	-7.0(6)	0.6(5)
C1	18.2(6)	17.1(7)	21.9(7)	-4.2(5)	-7.4(6)	0.0(5)

Table S11: Bond Lengths for compound **4.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C4	1.7355(14)	N4	C5	1.3174(18)
S1	C5	1.7404(14)	N1	N2	1.3568(18)
O1	N6	1.2740(15)	N1	C1	1.3428(19)
O2	N6	1.2527(17)	N2	C3	1.328(2)
N3	N4	1.3717(16)	C2	C4	1.451(2)
N3	C4	1.3096(18)	C2	C3	1.4140(19)
N5	N6	1.3101(17)	C2	C1	1.384(2)
N5		C5		1.3738(17)	

Table S12: Bond Angles for compound **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	S1	C5	86.73(7)	C1	C2	C4	128.42(13)
C4	N3	N4	112.80(11)	C1	C2	C3	104.27(13)
N6	N5	C5	115.55(12)	N3	C4	S1	114.12(11)
C5	N4	N3	112.66(12)	N3	C4	C2	122.36(12)
O1	N6	N5	116.17(12)	C2	C4	S1	123.51(11)
O2	N6	O1	119.82(12)	N5	C5	S1	129.01(11)
O2	N6	N5	124.02(12)	N4	C5	S1	113.68(11)
C1	N1	N2	112.74(12)	N4	C5	N5	117.22(13)
C3	N2	N1	104.49(12)	N2	C3	C2	111.65(13)
C3	C2	C4	127.31(13)	N1	C1	C2	106.85(13)

Table S13: Torsion Angles for compound **4.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N3	N4	C5	S1	-0.94(16)	C4	C2	C1	N1	-179.87(14)
N3	N4	C5	N5	176.11(11)	C5	S1	C4	N3	-1.07(11)
N4	N3	C4	S1	0.79(16)	C5	S1	C4	C2	177.74(13)
N4	N3	C4	C2	-178.03(13)	C5	N5	N6	O1	176.47(12)
N6	N5	C5	S1	-3.33(19)	C5	N5	N6	O2	-3.7(2)
N6	N5	C5	N4	-179.85(12)	C3	C2	C4	S1	179.85(12)
N1	N2	C3	C2	-0.25(17)	C3	C2	C4	N3	-1.4(2)
N2	N1	C1	C2	-0.16(17)	C3	C2	C1	N1	0.00(16)
C4	S1	C5	N5	-175.50(14)	C1	N1	N2	C3	0.25(17)
C4	S1	C5	N4	1.12(11)	C1	C2	C4	S1	-0.3(2)
C4	N3	N4	C5	0.10(17)	C1	C2	C4	N3	178.40(14)

C4	C2	C3	N2	-179.97(14)	C1	C2	C3	N2	0.16(17)

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

Atom	x	y	z	U(eq)
H7A	8268.34	6864.01	-301.64	31
H7B	9304.69	8127.74	-470.81	31
H1	4015.7	-568.69	8586.91	24
H3	8534.11	1260.33	4813.51	24
H1A	2472.75	1596.82	6928.61	23
H7C	10090(40)	7010(30)	-1750(30)	46(6)
H7D	8290(40)	8290(30)	-1710(30)	45(6)

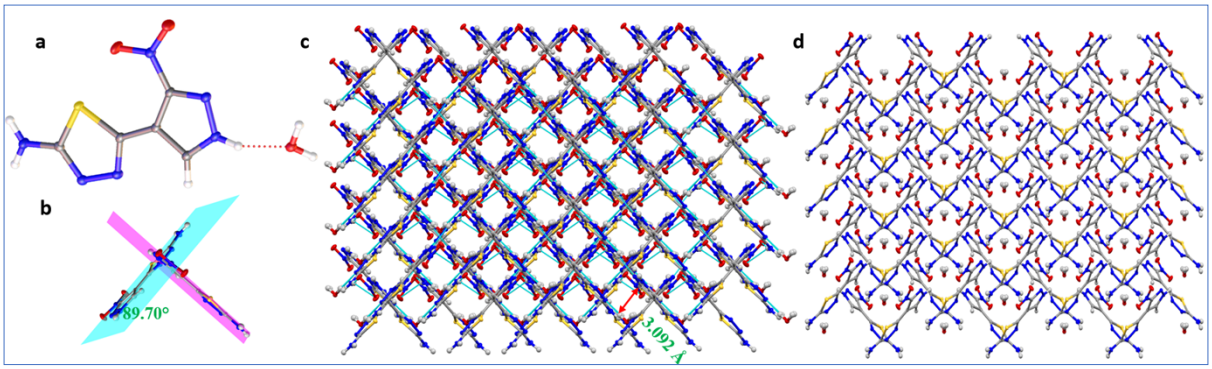


Figure S3: (a) crystal structure, (b) angle between the two molecules (crossed packing), (c, d) packing pattern along b- axis of compound **6**.

Table S15: Crystallographic data for compound **6**.

CCDC	2419623
Empirical formula	$C_5H_5N_6O_{2.5}S$
Formula weight	221.21
Temperature/K	100
Crystal system	monoclinic
Space group	*C2*
a/Å	13.6499(13)
b/Å	4.7759(5)
c/Å	13.2717(12)
α/°	90
β/°	110.836(2)
γ/°	90
Volume/Å3	808.61(14)
Z	4
ρcalcg/cm3	1.817
μ/mm-1	0.392
F(000)	452.0

Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.054 to 56.668
Index ranges	-18 ≤ h ≤ 18, -6 ≤ k ≤ 6, -17 ≤ l ≤ 17
Reflections collected	6398
Independent reflections	2021 [Rint = 0.0299, Rsigma = 0.0308]
Data/restraints/parameters	2021/1/139
Goodness-of-fit on F2	1.085
Final R indexes [I>=2σ (I)]	R1 = 0.0231, wR2 = 0.0549
Final R indexes [all data]	R1 = 0.0240, wR2 = 0.0555
Largest diff. peak/hole / e Å-3	0.21/-0.22
Flack parameter	-0.04(3)

Table S16: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **6**. Ueq is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S1	4790.8(3)	7685.9(10)	8458.2(3)	12.57(11)
O002	0	-1639(4)	5000	14.2(4)
O1	2745.8(13)	658(3)	9275.4(12)	22.4(4)
O2	3842.0(13)	3993(4)	9373.6(12)	24.6(4)
N6	3130.4(13)	2424(4)	8855.6(13)	14.5(3)
N5	6113.8(14)	11585(4)	8219.7(14)	16.0(4)
N3	3989.9(12)	7896(4)	6398.9(12)	13.6(3)
N1	1726.8(14)	1806(4)	6128.4(14)	13.3(3)
N2	1936.8(13)	1051(4)	7150.9(14)	13.2(3)
N4	4787.3(13)	9834(4)	6675.8(13)	13.2(3)
C2	3057.5(15)	4519(4)	7041.2(16)	11.2(4)
C3	2736.3(14)	2694(5)	7699.0(14)	12.0(3)
C5	5283.9(15)	9948(4)	7731.7(16)	12.1(4)
C1	2358.6(16)	3855(5)	6017.7(16)	13.3(4)
C4	3879.1(15)	6617(4)	7221.3(16)	11.6(4)

Table S17: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **6**. The Anisotropic displacement factor exponent takes the form:$-2\pi^2[h2a^*2U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
S1	13.8(2)	14.2(2)	8.49(19)	0.2(2)	2.38(15)	-3.0(2)
O002	16.4(10)	15.1(10)	10.8(9)	0	4.7(8)	0
O1	27.3(8)	24.9(9)	14.6(7)	1.9(7)	7.0(6)	-11.3(7)
O2	26.3(9)	31.1(9)	12.4(7)	-2.4(7)	1.8(6)	-16.3(7)
N6	15.5(7)	16.0(8)	11.9(7)	-0.5(7)	4.8(6)	-1.4(8)
N5	17.4(9)	18.0(8)	11.8(8)	-1.1(7)	4.0(7)	-5.4(7)
N3	12.9(7)	15.6(8)	11.1(7)	0.8(8)	2.9(6)	-1.6(8)
N1	12.7(8)	15.2(8)	10.5(8)	-1.0(6)	2.2(6)	-0.1(6)

N2	13.4(8)	14.3(8)	11.0(8)	-1.0(7)	3.4(6)	0.3(7)
N4	12.9(8)	14.0(8)	12.2(8)	1.1(7)	3.9(6)	-0.7(7)
C2	11.6(8)	12.0(8)	10.2(9)	-1.2(7)	4.1(7)	1.3(7)
C3	12.4(8)	13.3(8)	10.0(7)	-1.8(9)	3.3(6)	-0.8(9)
C5	12.6(9)	11.1(8)	14.1(9)	0.6(8)	6.6(7)	1.6(7)
C1	13.7(9)	14.5(9)	10.7(9)	-0.6(8)	3.3(7)	0.1(8)
C4	10.7(9)	12.5(8)	10.8(8)	-1.5(7)	2.8(7)	1.0(7)

Table S18: Bond Lengths for compound **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C5	1.735(2)	N1	N2	1.333(2)
S1	C4	1.747(2)	N1	C1	1.346(3)
O1	N6	1.227(2)	N2	C3	1.331(3)
O2	N6	1.226(2)	N4	C5	1.323(3)
N6	C3	1.440(2)	C2	C3	1.410(3)
N5	C5	1.339(3)	C2	C1	1.391(3)
N3	N4	1.375(2)	C2	C4	1.459(3)
N3		C4		1.306(3)	

Table S19: Bond Angles for compound **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	S1	C4	86.97(10)	N2	C3	N6	116.91(19)
O1	N6	C3	119.18(18)	N2	C3	C2	113.66(17)
O2	N6	O1	123.18(17)	C2	C3	N6	129.41(19)
O2	N6	C3	117.64(18)	N5	C5	S1	121.56(15)
C4	N3	N4	114.05(16)	N4	C5	S1	114.15(15)
N2	N1	C1	113.18(17)	N4	C5	N5	124.27(18)
C3	N2	N1	103.57(17)	N1	C1	C2	107.62(18)
C5	N4	N3	111.67(16)	N3	C4	S1	113.16(15)
C3	C2	C4	135.53(18)	N3	C4	C2	119.69(18)
C1	C2	C3	101.98(17)	C2	C4	S1	127.15(15)
C1		C2		C4		122.48(19)	

Table S20: Torsion Angles for compound **6**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N6	C3	N2	2.6(3)	C5	S1	C4	N3	0.40(16)
O1	N6	C3	C2	-179.1(2)	C5	S1	C4	C2	179.88(19)
O2	N6	C3	N2	-177.5(2)	C1	N1	N2	C3	-0.2(2)
O2	N6	C3	C2	0.8(3)	C1	C2	C3	N6	-177.7(2)
N3	N4	C5	S1	-0.6(2)	C1	C2	C3	N2	0.7(2)
N3	N4	C5	N5	177.69(18)	C1	C2	C4	S1	178.95(16)
N1	N2	C3	N6	178.25(18)	C1	C2	C4	N3	-1.6(3)
N1	N2	C3	C2	-0.3(2)	C4	S1	C5	N5	-178.20(18)
N2	N1	C1	C2	0.7(2)	C4	S1	C5	N4	0.11(16)

N4	N3	C4	S1	-0.8(2)	C4	N3	N4	C5	0.9(3)
N4	N3	C4	C2	179.66(17)	C4	C2	C3	N6	3.5(4)
C3	C2	C1	N1	-0.8(2)	C4	C2	C3	N2	-178.2(2)
C3	C2	C4	S1	-2.4(4)	C4	C2	C1	N1	178.28(18)
C3		C2		C4		N3		177.1(2)	

Table S21: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound **6.**

Atom	x	y	z	U(eq)
H00A	-171.55	-2740.49	5412.43	21
H00B	-36.11	-2639.07	4457.9	21
H5A	6362.28	12678.97	7833.44	19
H5B	6410.82	11567.8	8926.79	19
H1A	2331.93	4694.11	5359.47	16
H1	1220(20)	980(60)	5640(20)	20(7)

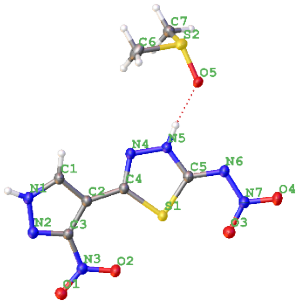


Figure S4: Crystal structure for compound **7.**

Table S22: Crystallographic data for compound **7**.

CCDC	2419624
Empirical formula	$C_7H_9N_7O_5S_2$
Formula weight	335.33
Temperature/K	100
Crystal system	monoclinic
Space group	P_{21}/c
a/Å	9.3112(3)
b/Å	16.9168(5)
c/Å	8.2596(3)
α/°	90
β/°	90.7140(10)
γ/°	90
Volume/Å3	1300.92(7)
Z	4
ρcalcg/cm3	1.712
μ/mm-1	0.446
F(000)	688.0

Crystal size/mm3	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.488 to 56.632
Index ranges	-12 ≤ h ≤ 12, -22 ≤ k ≤ 22, -11 ≤ l ≤ 11
Reflections collected	19845
Independent reflections	3225 [Rint = 0.0379, Rsigma = 0.0255]
Data/restraints/parameters	3225/0/200
Goodness-of-fit on F2	1.056
Final R indexes [I>=2σ (I)]	R1 = 0.0421, wR2 = 0.1090
Final R indexes [all data]	R1 = 0.0541, wR2 = 0.1214
Largest diff. peak/hole / e Å-3	0.88/-0.48

Table S23: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **7**. Ueq is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S1	7063.8(5)	7140.2(3)	5243.6(6)	23.14(14)
S2	1406.9(6)	7085.2(3)	9489.5(7)	29.34(16)
O5	2574.4(17)	7550.3(9)	8614(2)	31.4(4)
O1	9682.4(18)	5171.8(9)	2461(2)	33.2(4)
O2	8790.3(19)	6281.5(9)	3297(2)	37.3(4)
O3	7254.6(19)	8630.5(10)	4894(2)	36.4(4)
O4	6123(2)	9574.1(10)	6127(2)	41.0(4)
N2	8224(2)	4373.0(10)	4656(2)	26.6(4)
N5	4841(2)	7049.1(10)	6936(2)	25.5(4)
N4	5203.9(19)	6277.3(10)	6719(2)	26.2(4)
N3	8895(2)	5555.4(11)	3340(2)	27.6(4)
N1	7301(2)	4169.5(11)	5816(2)	26.2(4)
N7	6298(2)	8868.5(11)	5807(2)	29.6(4)
N6	5375.6(19)	8358.4(10)	6530(2)	25.8(4)
C3	8027(2)	5147.0(12)	4507(3)	24.0(4)
C2	6984(2)	5450.4(12)	5565(3)	23.8(4)
C1	6541(2)	4780.4(12)	6387(3)	24.8(4)
C4	6362(2)	6228.5(11)	5859(3)	22.3(4)
C5	5689(2)	7593.4(12)	6283(2)	22.6(4)
C7	88(2)	6841.4(13)	8011(3)	31.0(5)
C6	2150(3)	6122.9(15)	9781(3)	37.2(6)

Table S24: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound **7**. The Anisotropic displacement factor exponent takes the form:$-2\pi^2[h2a^*2U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
S1	24.1(3)	15.3(2)	30.2(3)	-0.69(17)	7.85(19)	-0.08(18)
S2	31.9(3)	23.2(3)	33.3(3)	-5.1(2)	13.9(2)	-6.7(2)
O5	29.1(8)	15.9(7)	49.6(10)	-3.3(6)	17.7(7)	-4.7(6)

O1	33.3(8)	24.5(8)	42.1(9)	-5.3(7)	15.7(7)	-1.2(7)
O2	41.3(10)	17.7(8)	53.6(11)	0.0(7)	22.6(8)	-1.4(7)
O3	36.8(9)	23.6(8)	49.4(10)	-0.6(7)	20.3(7)	0.0(7)
O4	44.2(10)	16.5(8)	63.1(12)	-3.2(7)	22.8(9)	-1.9(7)
N2	26.4(9)	18.4(8)	35.2(10)	-1.6(7)	7.0(7)	-0.3(7)
N5	23.5(9)	16.0(8)	37.3(10)	-0.7(7)	10.2(7)	1.0(7)
N4	24.7(9)	15.4(8)	38.8(10)	-0.6(7)	8.5(7)	1.3(7)
N3	26.9(9)	19.8(8)	36.1(10)	-2.4(7)	8.9(7)	-1.9(7)
N1	28.3(9)	16.1(8)	34.4(10)	0.6(7)	7.4(7)	-0.1(7)
N7	30.7(10)	18.9(9)	39.5(11)	-0.5(7)	11.0(8)	0.4(7)
N6	26.7(9)	15.5(8)	35.4(10)	-0.2(7)	7.5(7)	-0.3(7)
C3	23.2(10)	18.4(9)	30.5(11)	-2.0(8)	6.6(8)	-1.8(7)
C2	23.2(10)	17.0(9)	31.4(11)	0.1(8)	5.6(8)	0.8(7)
C1	25.7(10)	16.5(9)	32.4(11)	-0.6(8)	5.8(8)	1.1(8)
C4	22.5(9)	16.1(9)	28.4(10)	-0.5(7)	4.5(8)	0.2(7)
C5	24.1(10)	17.6(9)	26.1(10)	-1.0(7)	3.9(8)	0.2(8)
C7	26.3(11)	21.5(10)	45.3(13)	-0.3(9)	10.5(9)	0.9(8)
C6	39.9(13)	26.9(12)	44.8(14)	11.0(10)	-4.3(11)	-8.3(10)

Table S25: Bond Lengths for compound **7**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C4	1.753(2)	N5	N4	1.361(2)
S1	C5	1.730(2)	N5	C5	1.332(3)
S2	O5	1.5309(16)	N4	C4	1.301(3)
S2	C7	1.770(3)	N3	C3	1.442(3)
S2	C6	1.784(3)	N1	C1	1.341(3)
O1	N3	1.224(2)	N7	N6	1.360(2)
O2	N3	1.233(2)	N6	C5	1.343(3)
O3	N7	1.241(2)	C3	C2	1.411(3)
O4	N7	1.234(2)	C2	C1	1.387(3)
N2	N1	1.340(3)	C2	C4	1.460(3)
N2		C3		1.328(3)	

Table S26: Bond Angles for compound **7**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	S1	C4	88.00(10)	C5	N6	N7	113.91(17)
O5	S2	C7	106.54(10)	N2	C3	N3	117.17(18)
O5	S2	C6	104.84(11)	N2	C3	C2	113.36(18)
C7	S2	C6	98.35(11)	C2	C3	N3	129.46(19)
C3	N2	N1	103.34(17)	C3	C2	C4	135.14(19)
C5	N5	N4	117.42(18)	C1	C2	C3	102.54(18)
C4	N4	N5	109.98(17)	C1	C2	C4	122.31(19)
O1	N3	O2	124.02(19)	N1	C1	C2	107.25(19)
O1	N3	C3	119.15(18)	N4	C4	S1	114.64(15)
O2	N3	C3	116.83(17)	N4	C4	C2	118.78(18)
N2	N1	C1	113.51(18)	C2	C4	S1	126.51(15)

O3	N7	N6	121.50(18)	N5	C5	S1	109.93(15)
O4	N7	O3	122.77(19)	N5	C5	N6	118.29(18)
O4	N7	N6	115.73(18)	N6	C5	S1	131.77(16)

Table S27: Torsion Angles for compound **7**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
O1	N3	C3	N2	5.6(3)	N1	N2	C3	C2	0.1(2)
O1	N3	C3	C2	-175.5(2)	N7	N6	C5	S1	1.2(3)
O2	N3	C3	N2	-174.4(2)	N7	N6	C5	N5	-179.65(19)
O2	N3	C3	C2	4.5(3)	C3	N2	N1	C1	0.2(3)
O3	N7	N6	C5	5.9(3)	C3	C2	C1	N1	0.5(2)
O4	N7	N6	C5	-173.7(2)	C3	C2	C4	S1	-16.7(4)
N2	N1	C1	C2	-0.4(3)	C3	C2	C4	N4	166.5(2)
N2	C3	C2	C1	-0.4(3)	C1	C2	C4	S1	165.42(18)
N2	C3	C2	C4	-178.6(2)	C1	C2	C4	N4	-11.4(3)
N5	N4	C4	S1	-0.7(2)	C4	S1	C5	N5	-1.49(16)
N5	N4	C4	C2	176.45(19)	C4	S1	C5	N6	177.7(2)
N4	N5	C5	S1	1.5(3)	C4	C2	C1	N1	179.0(2)
N4	N5	C5	N6	-177.81(19)	C5	S1	C4	N4	1.31(18)
N3	C3	C2	C1	-179.3(2)	C5	S1	C4	C2	-175.6(2)
N3	C3	C2	C4	2.5(4)	C5	N5	N4	C4	-0.5(3)
N1		N2		C3		N3		179.23(18)	

Table S28: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound **7**.

Atom	x	y	z	U(eq)
H1A	5831.85	4758.24	7202.03	30
H7A	-362.62	7326.53	7601.45	46
H7B	-644.76	6503.47	8498.15	46
H7C	539.84	6559.1	7115.49	46
H6A	2413.12	5899.45	8730.74	56
H6B	1438.86	5781.22	10294.82	56
H6C	3007.81	6159.59	10477.15	56
H1	7270(30)	3698(19)	6150(30)	38(8)
H5	4090(40)	7177(19)	7510(40)	49(9)

NMR, IR Spectra, HRMS & TG-DSC plots for compounds 2-7.

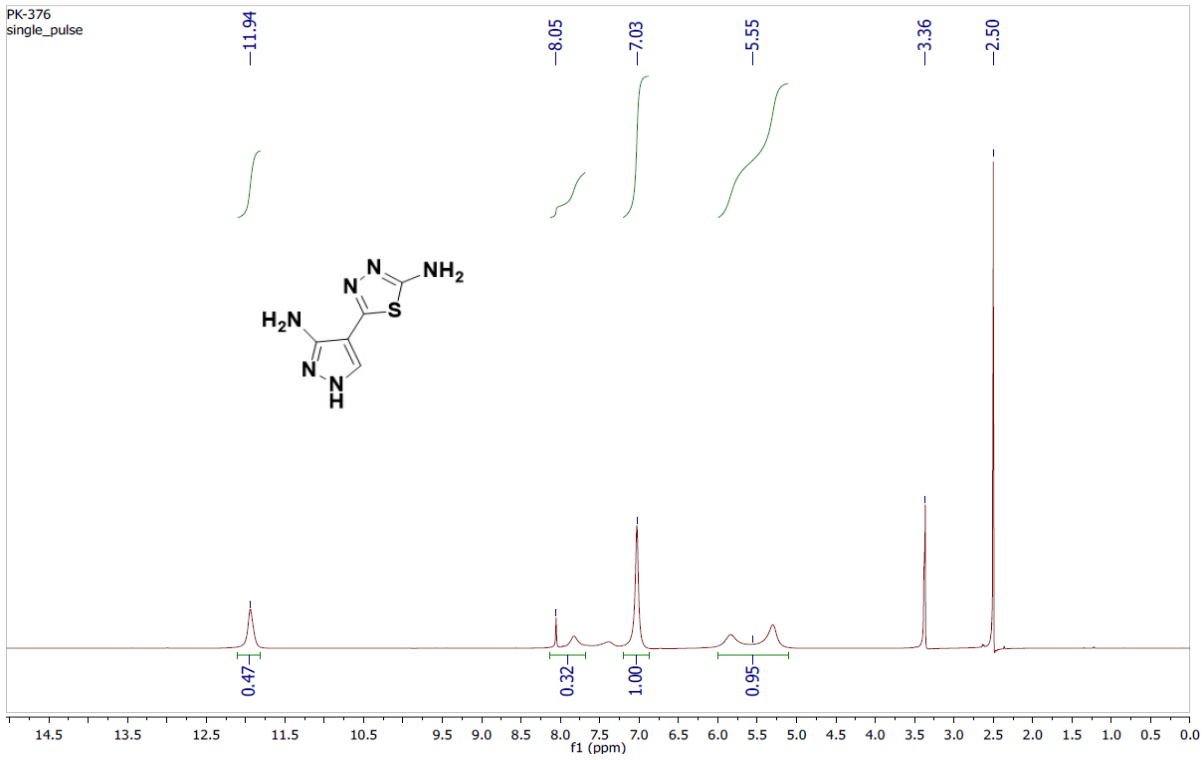


Figure S5: ^{1}H NMR spectrum of compound **2** in **DMSO-*d*$_6$**.

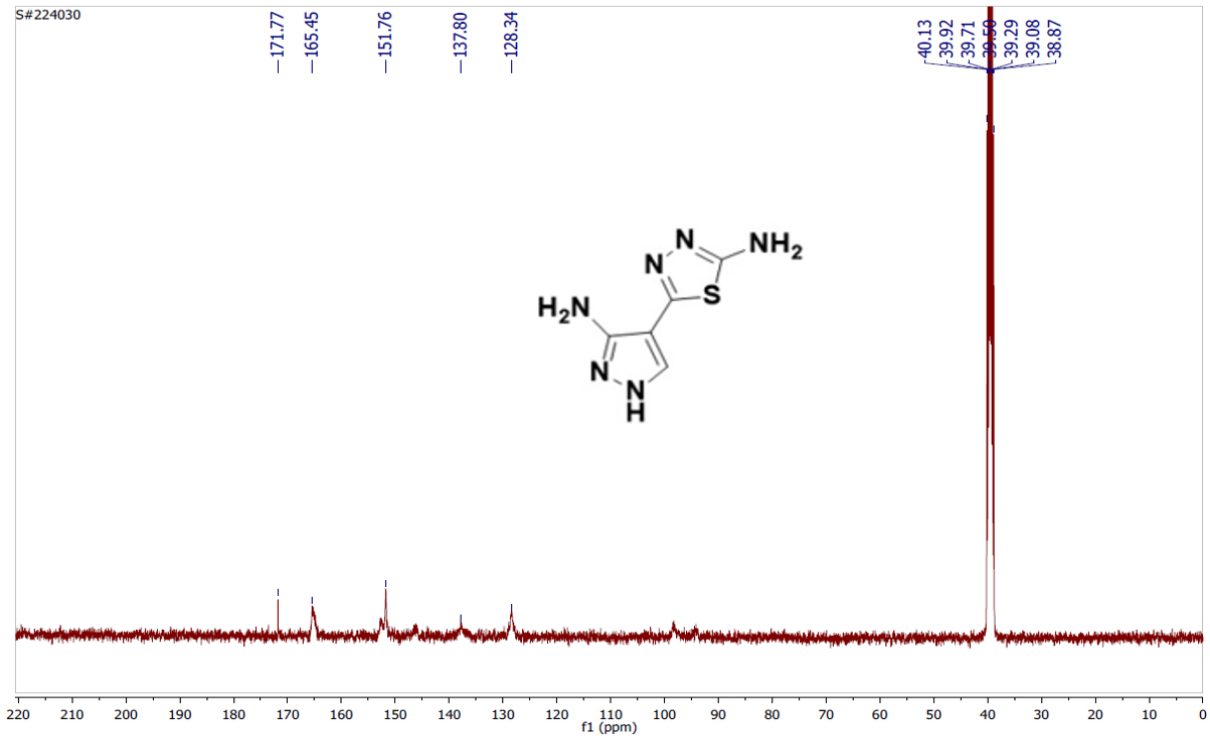


Figure S6: ^{13}C NMR spectrum of compound **2** in **DMSO-*d*$_6$**.

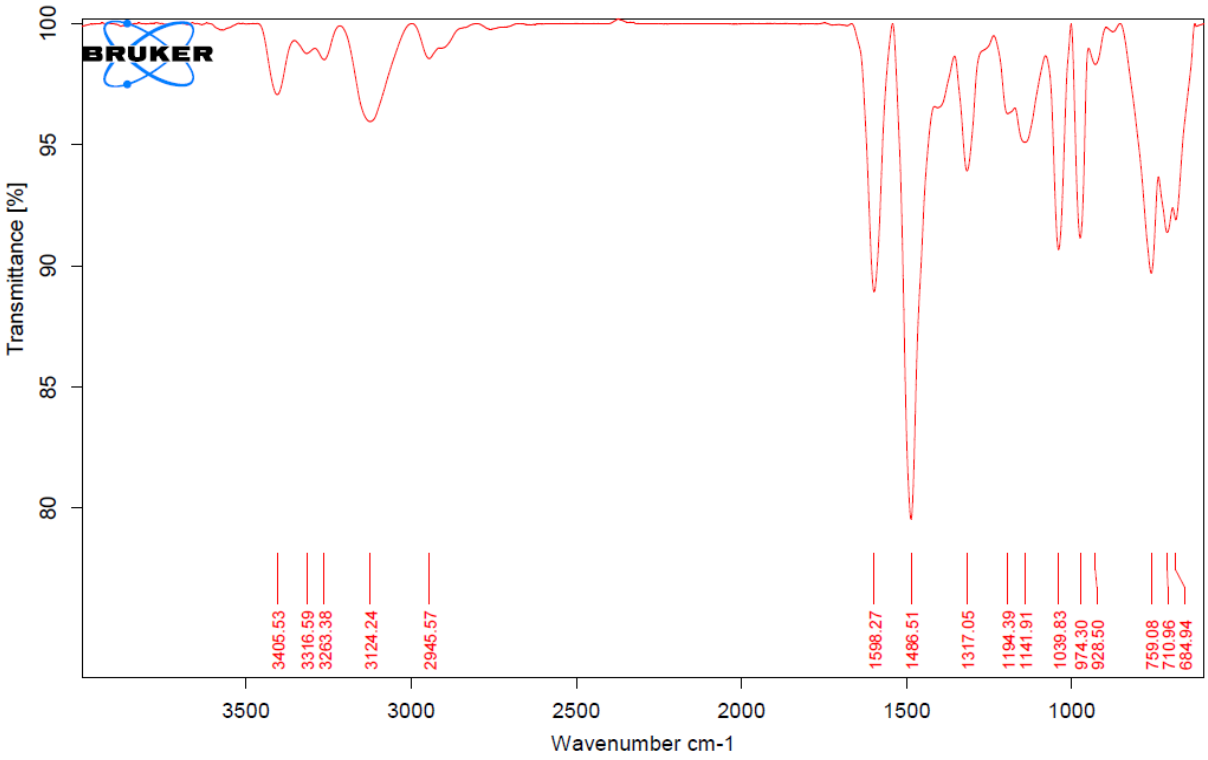


Figure S7: IR spectrum of compound **2.**

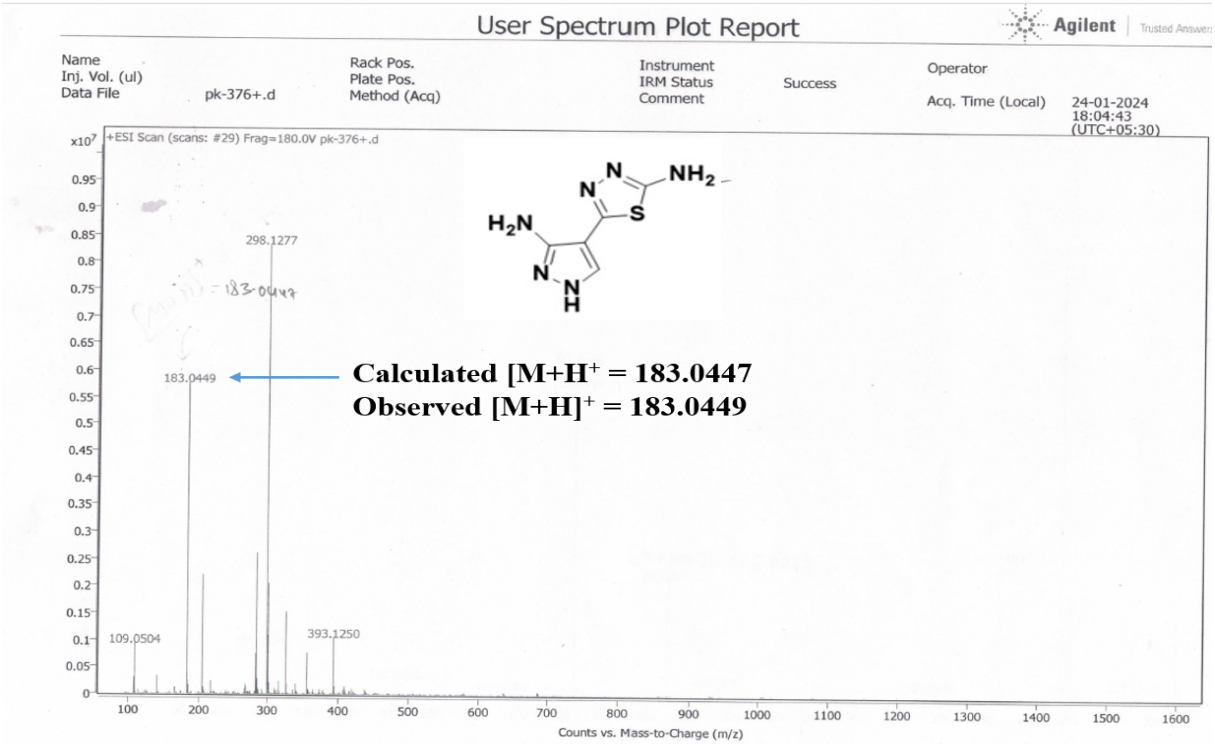


Figure S8: HRMS spectrum of compound **2.**

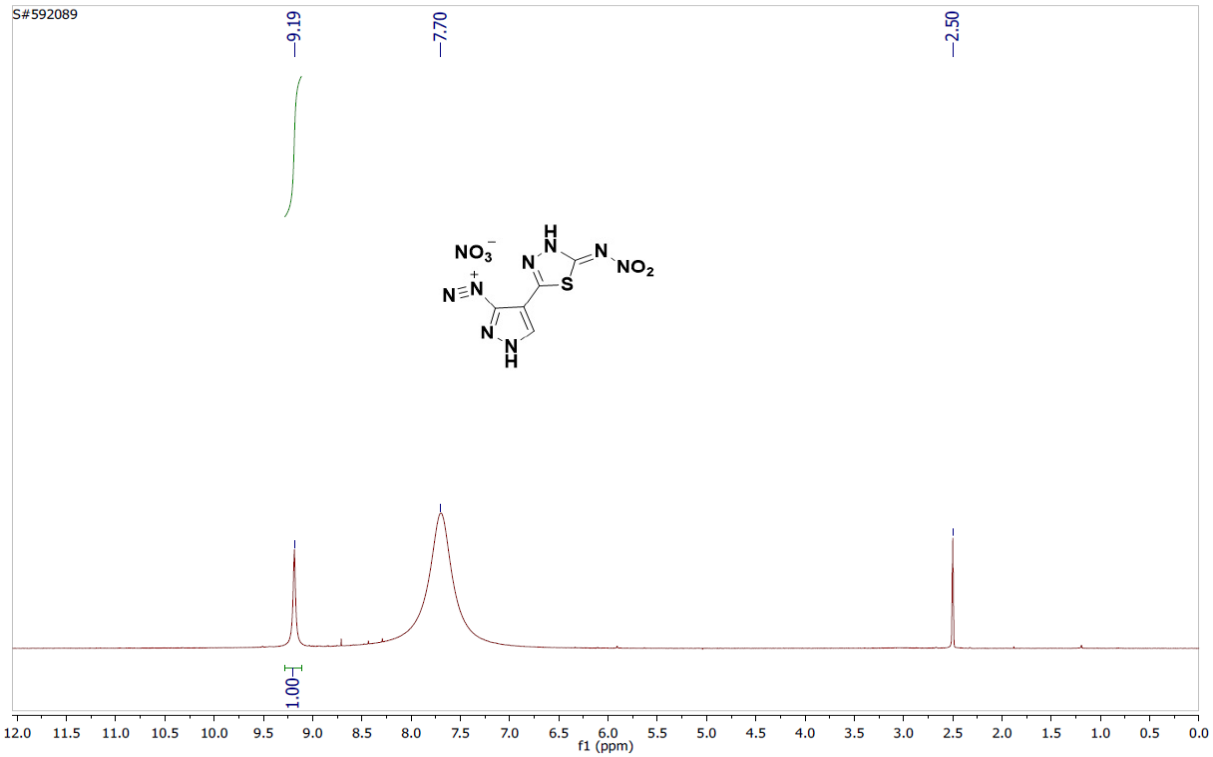


Figure S9: ^{1}H NMR spectrum of compound **3** in **DMSO-*d*$_6$**.

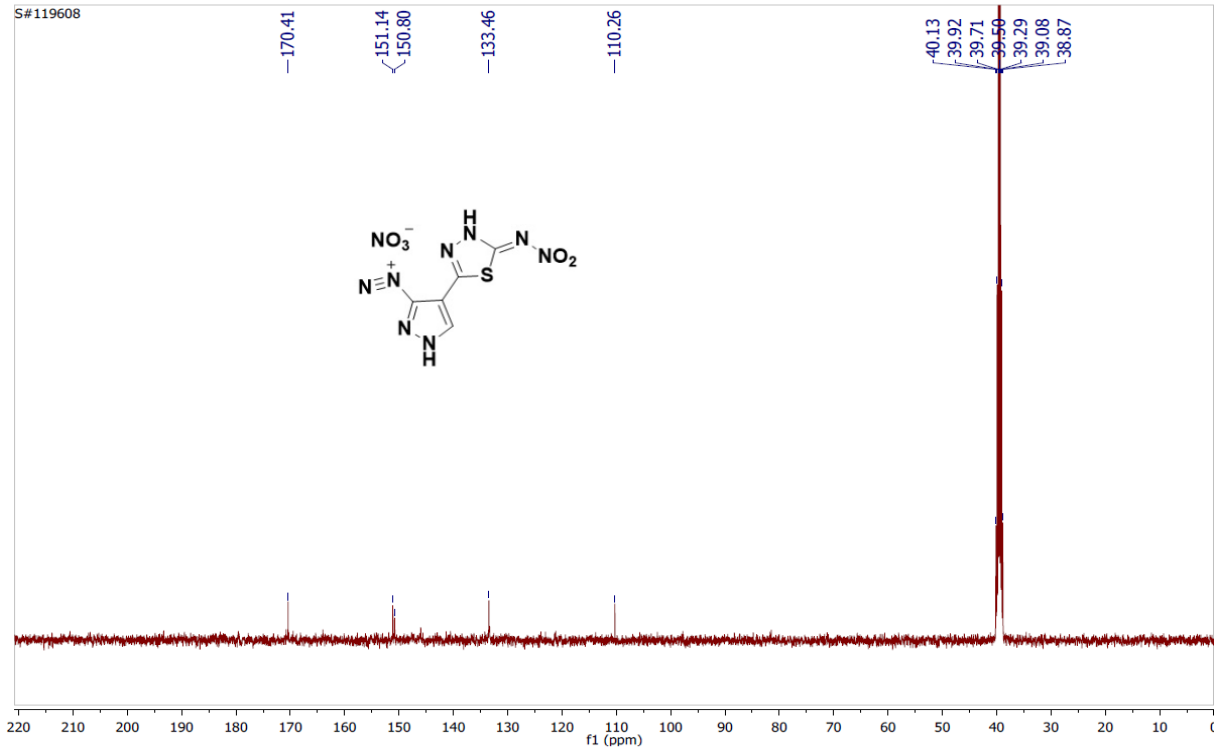


Figure S10: ^{13}C NMR spectrum of compound **3** in **DMSO-*d*$_6$.**

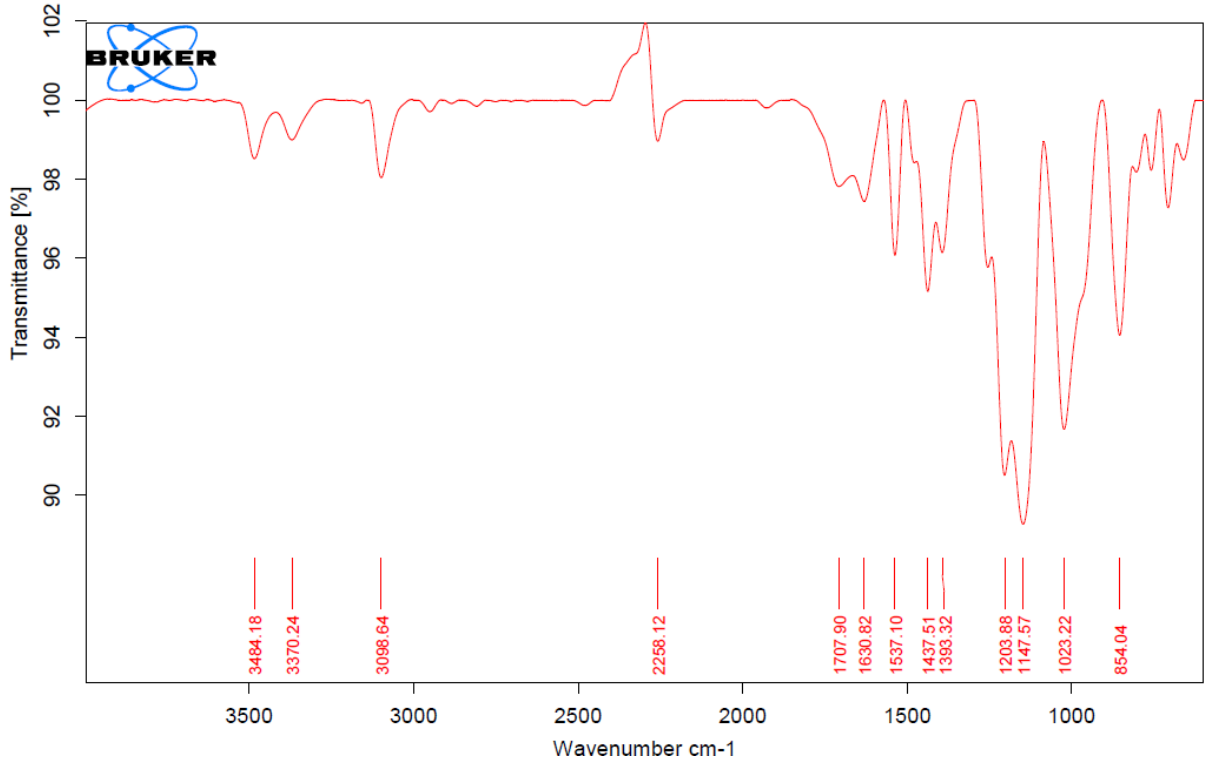


Figure S11: IR spectrum of compound **3.**

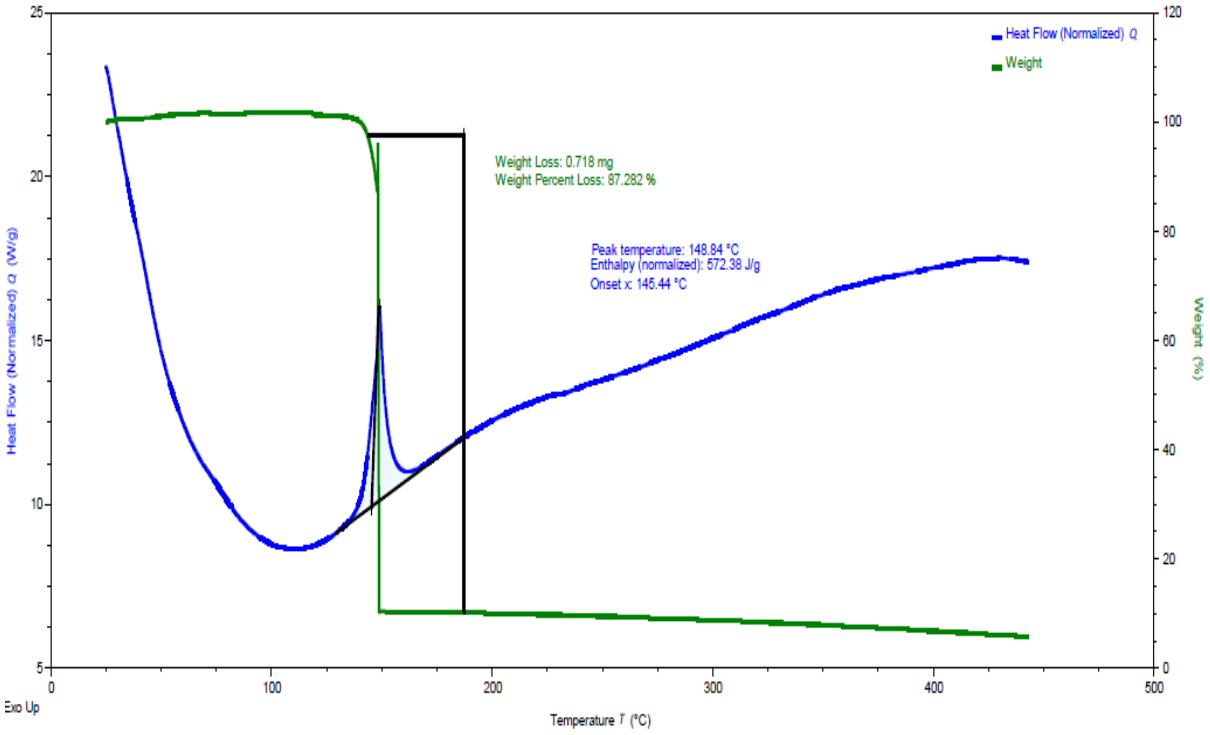


Figure S12: DSC spectrum of compound **3** at heating rate 5 ^{o}C min^{-1}**.**

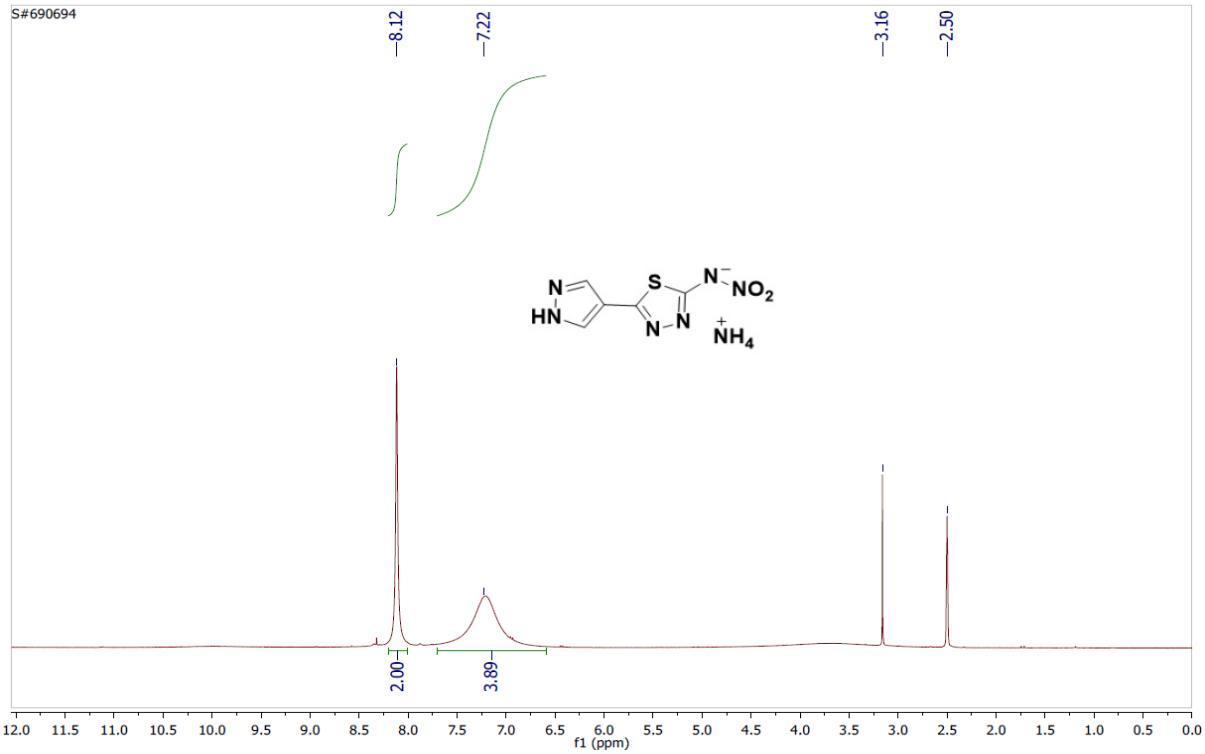


Figure S13: ^{1}H NMR spectrum of compound **4** in **DMSO-*d*$_6$.**

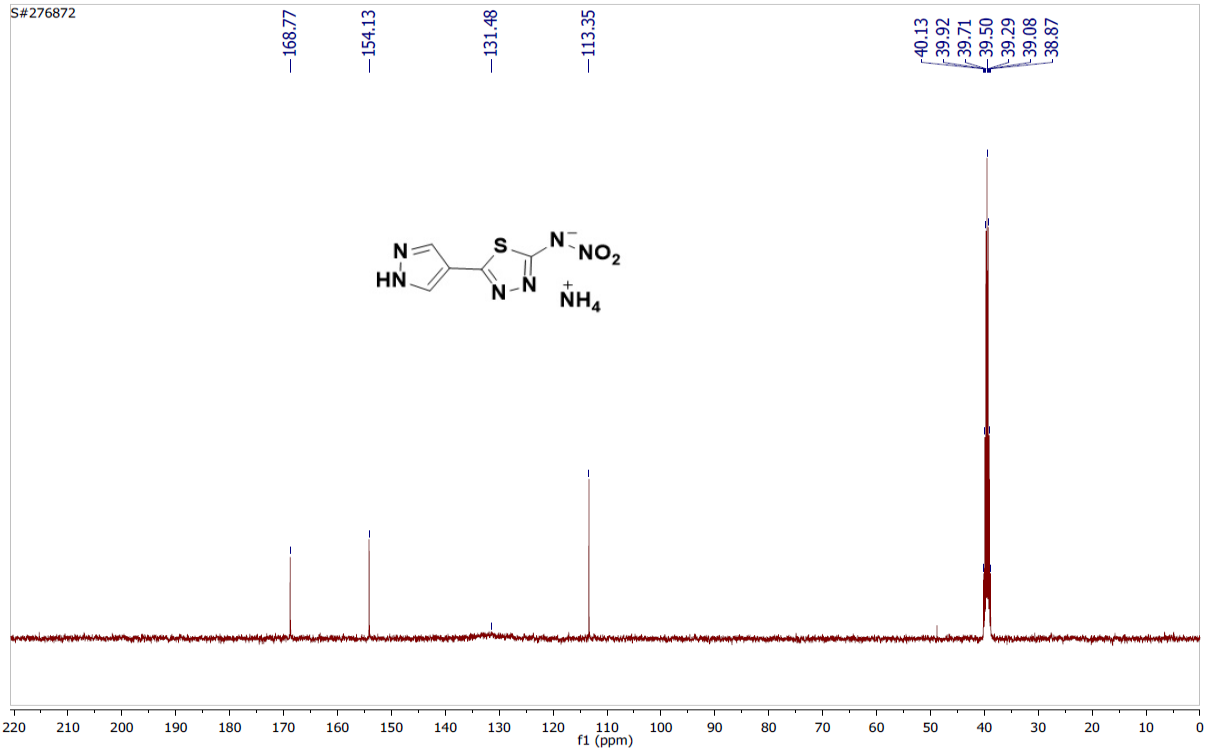


Figure S14: ^{13}C NMR spectrum of compound **4** in **DMSO-*d*$_6$.**

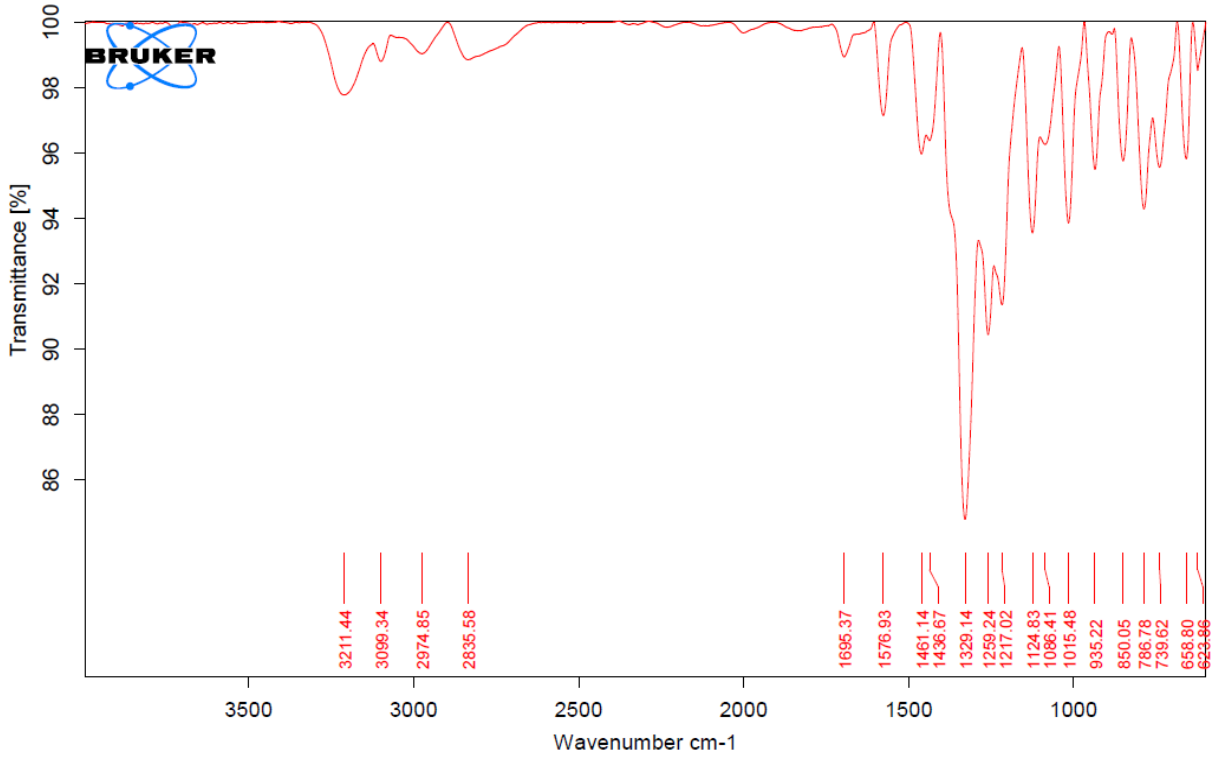


Figure S15: IR spectrum of compound **4.**

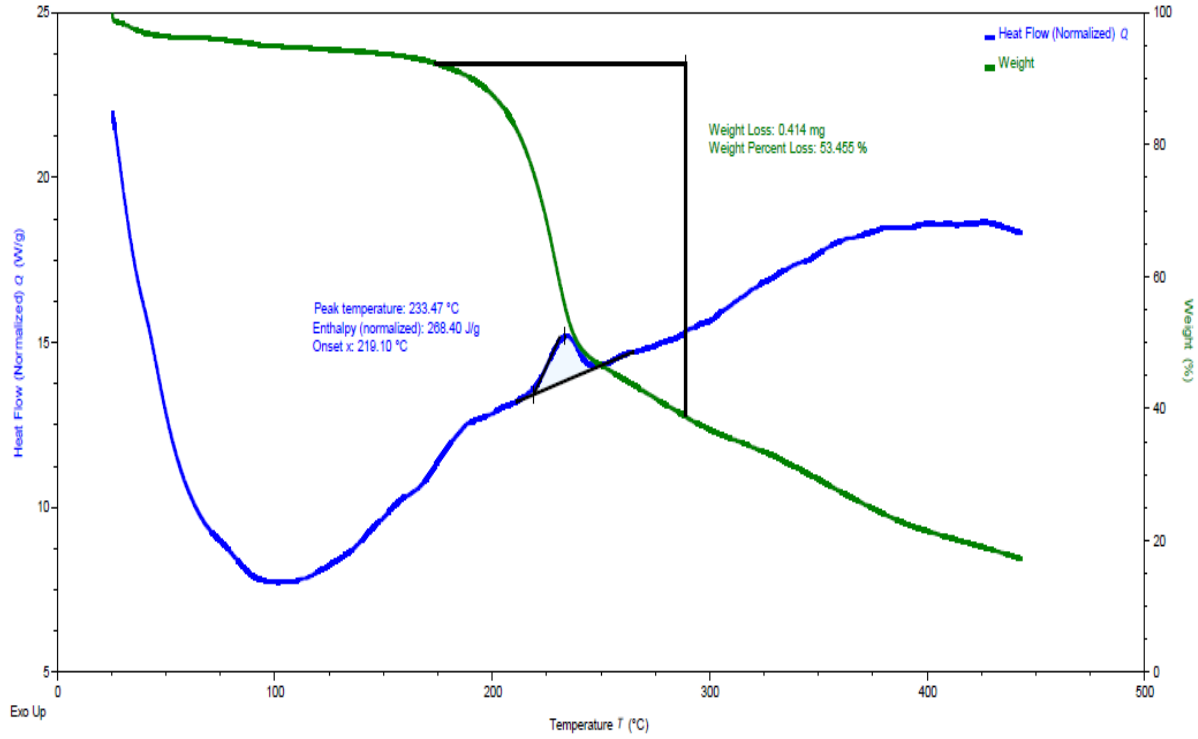


Figure S16: DSC spectrum of compound **4** at heating rate 5 ^{o}C min^{-1}**.**

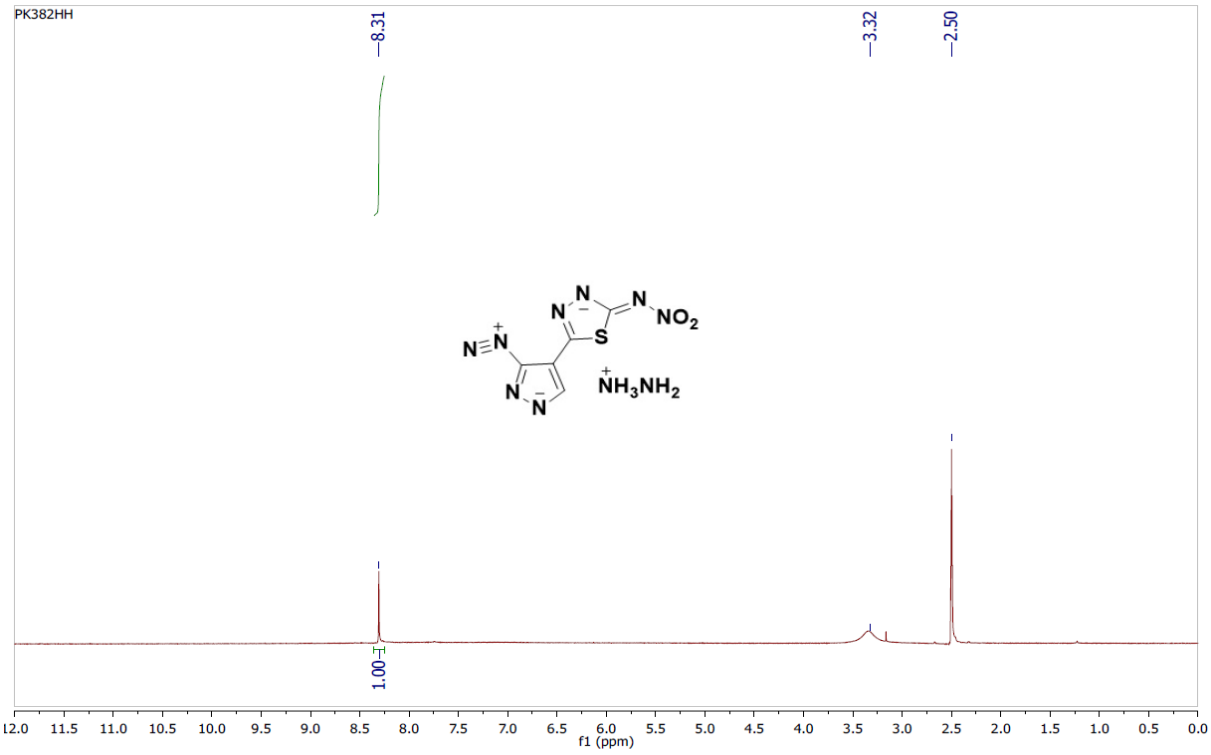


Figure S17: ^{1}H NMR spectrum of compound **5** in **DMSO-*d*$_6$**.

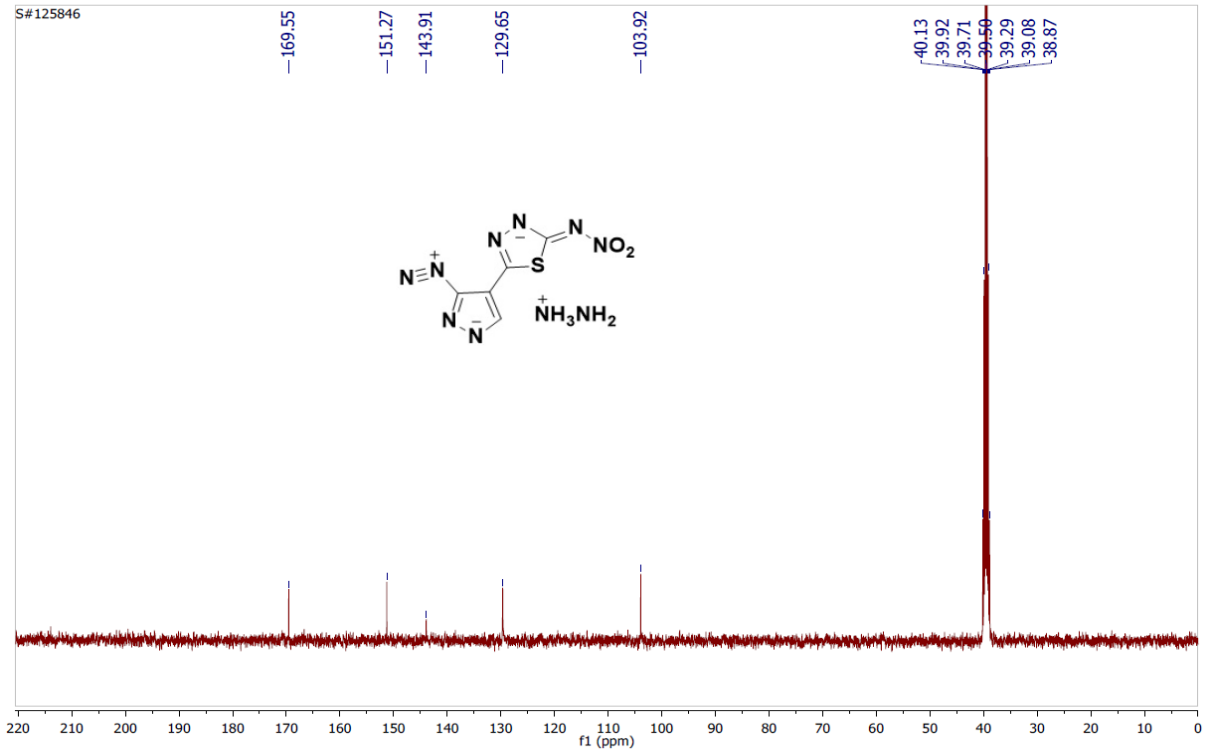


Figure S18: ^{13}C NMR spectrum of compound **5** in **DMSO-*d*$_6$.**

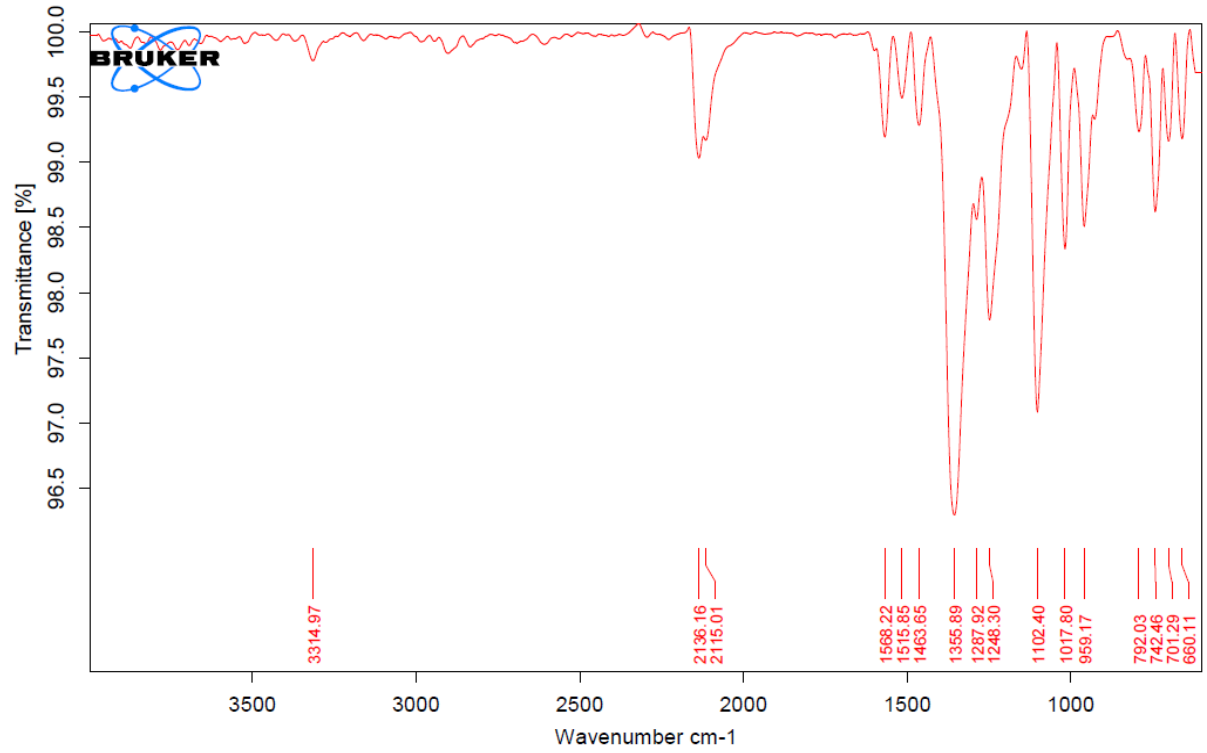


Figure S19: IR spectrum of compound **5.**

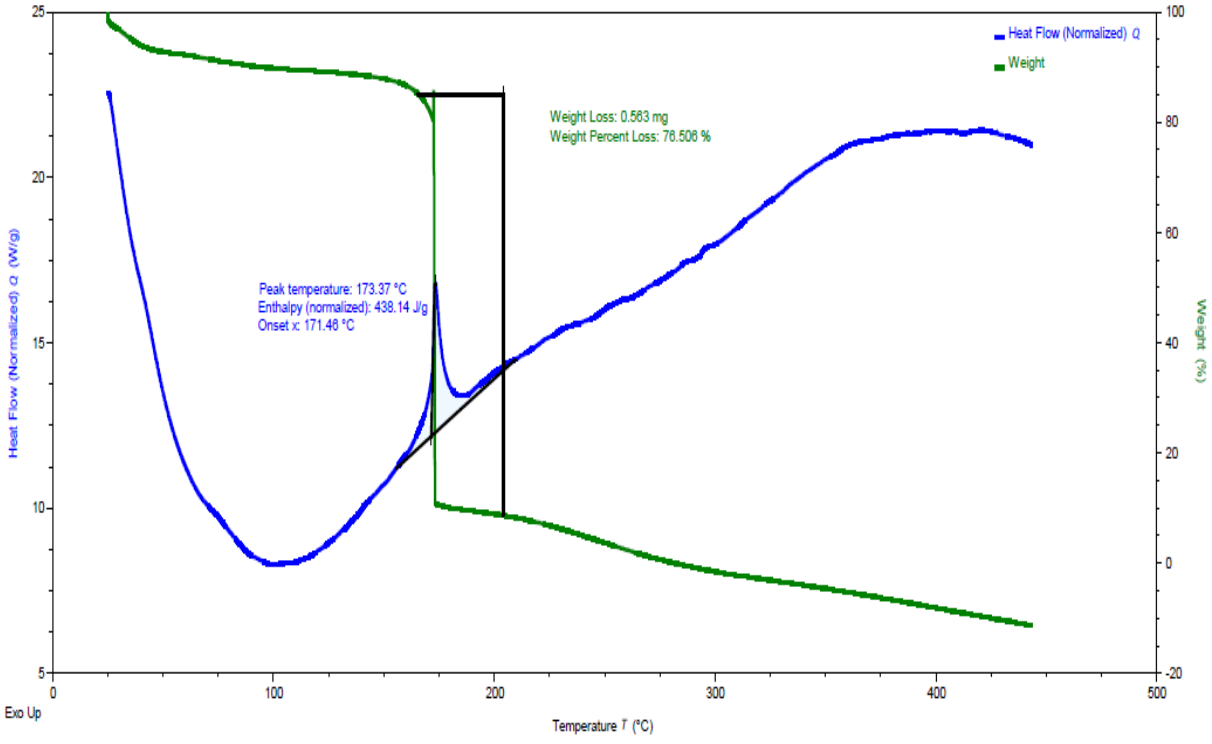


Figure S20: DSC spectrum of compound **5** at heating rate 5 ^{o}C min^{-1}**.**

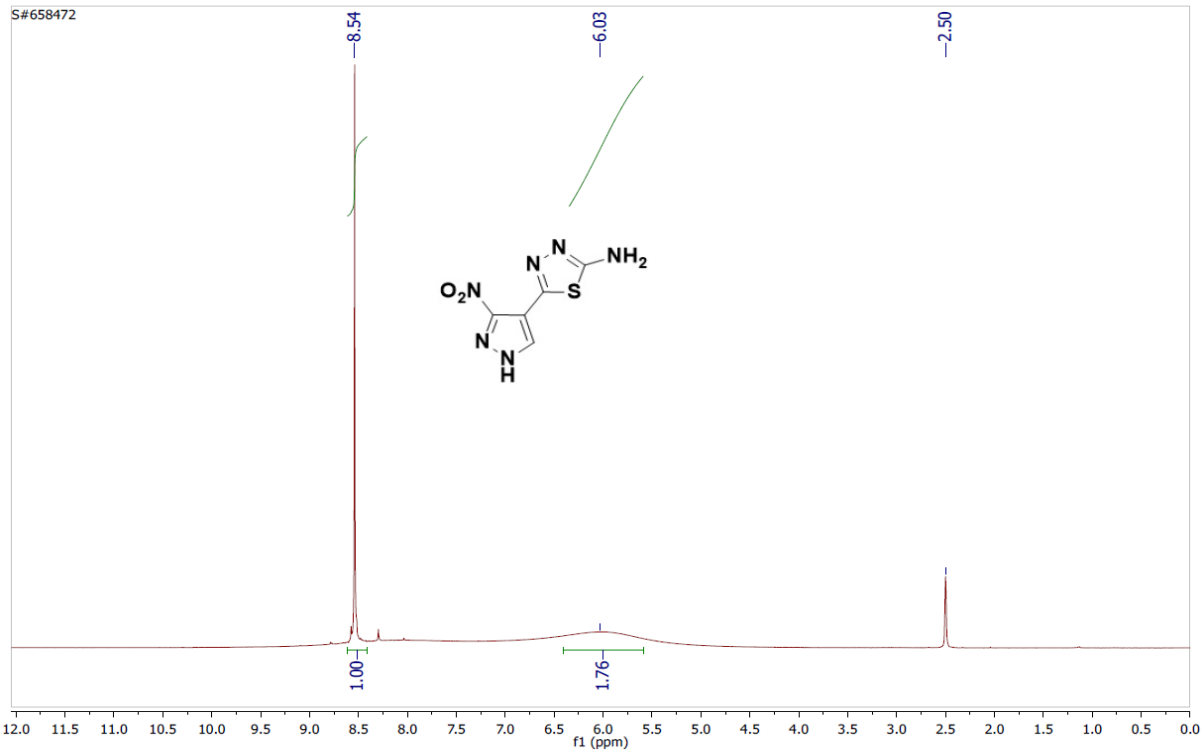


Figure S21: ^{1}H NMR spectrum of compound **6** in **DMSO-*d*$_6$.**

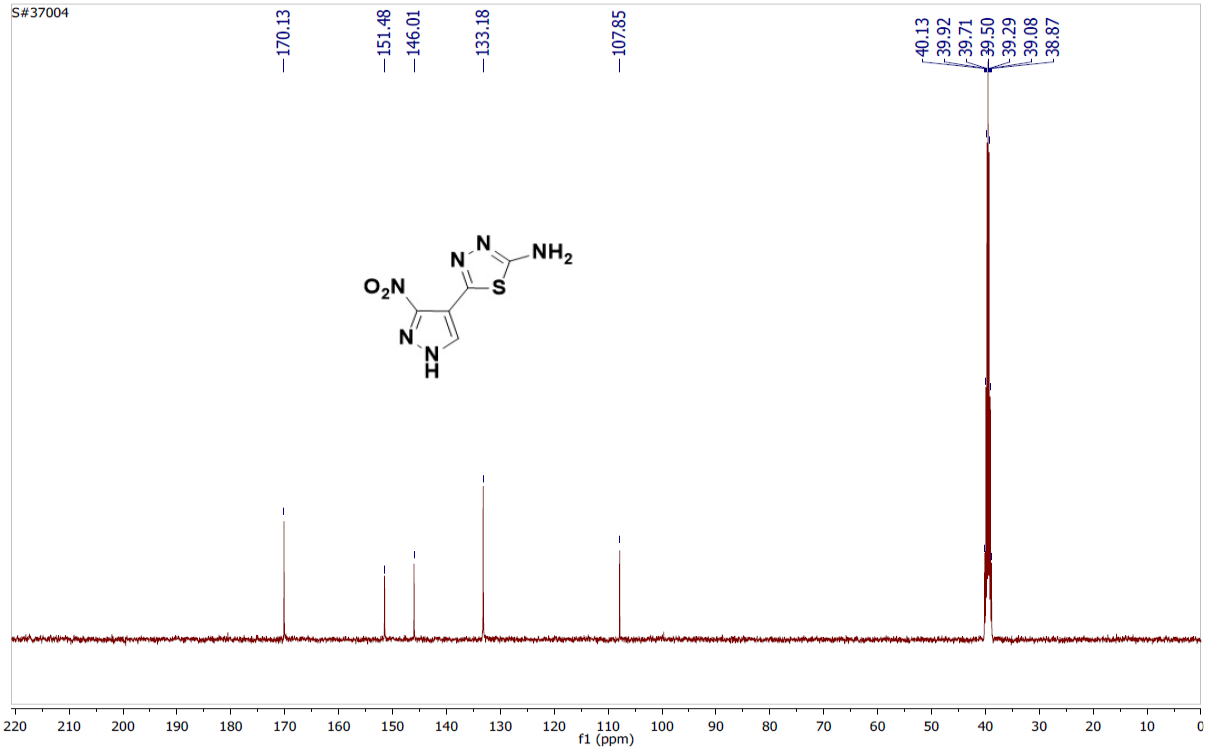


Figure S22: ^{13}C NMR spectrum of compound **6** in **DMSO-*d*$_6$.**

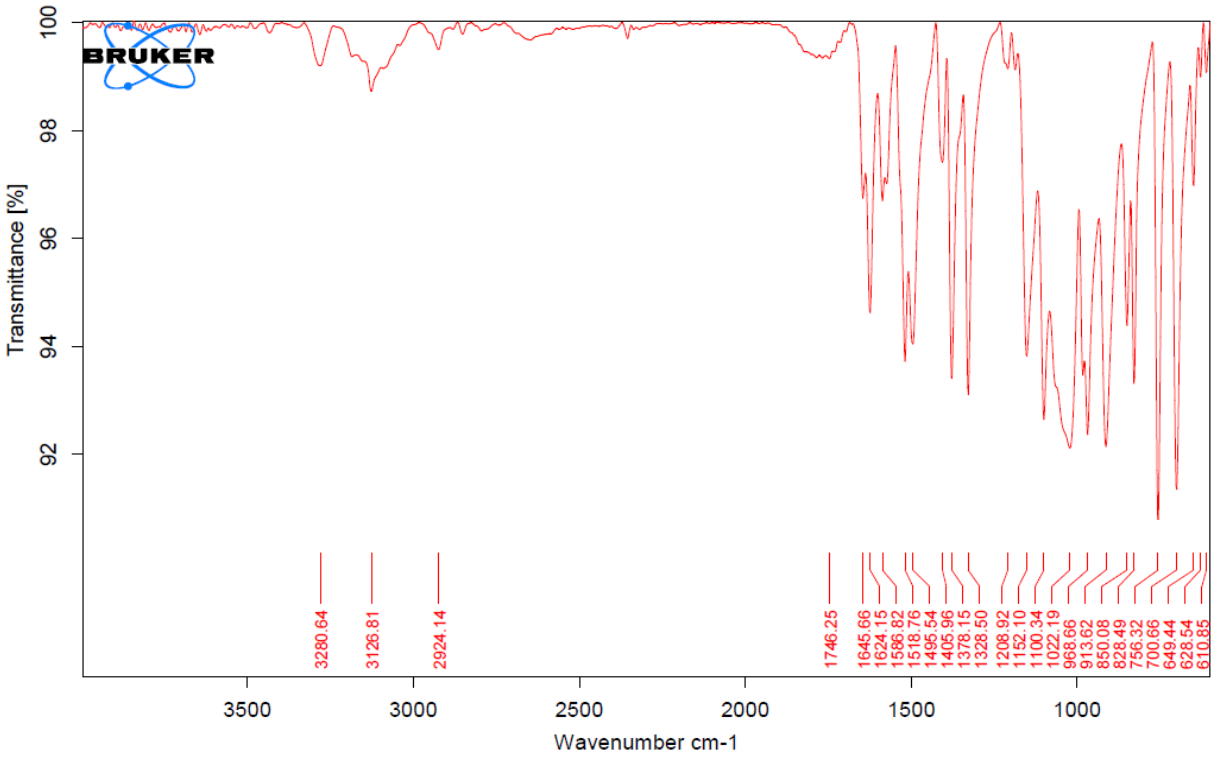


Figure S23: IR spectrum of compound **6.**

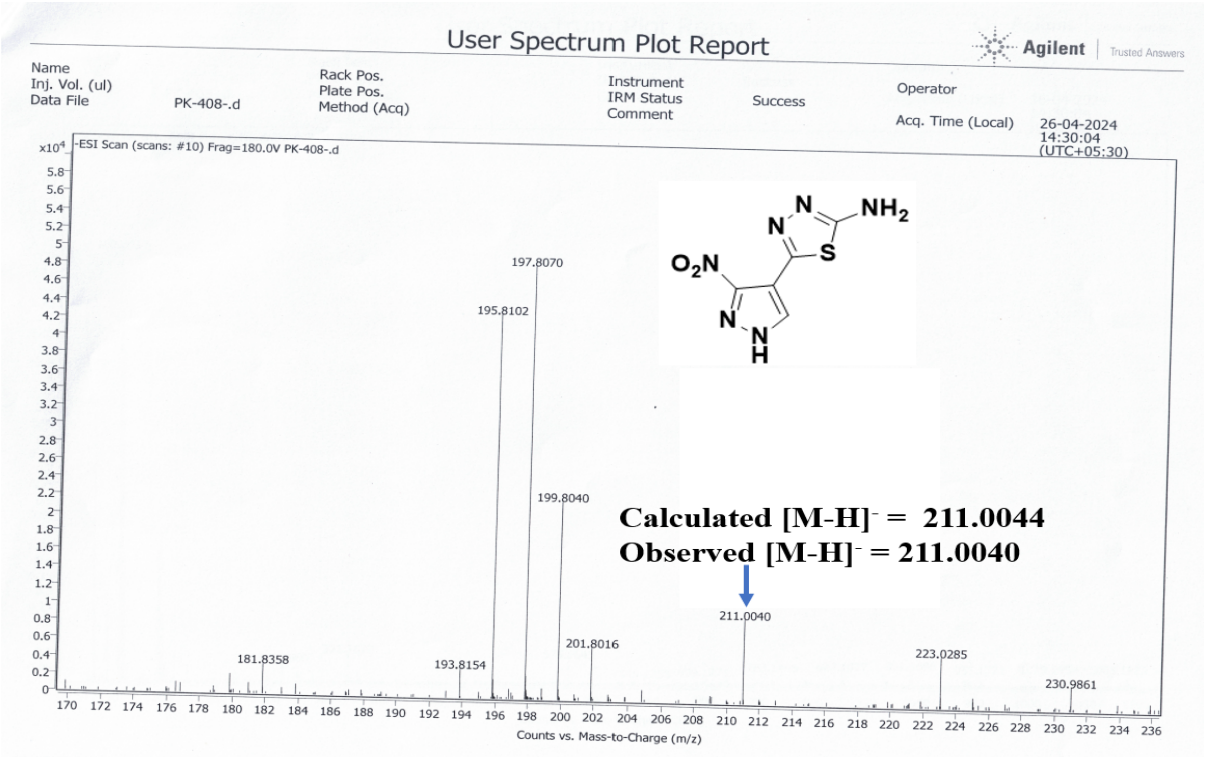


Figure S24: HRMS spectrum of compound **6.**

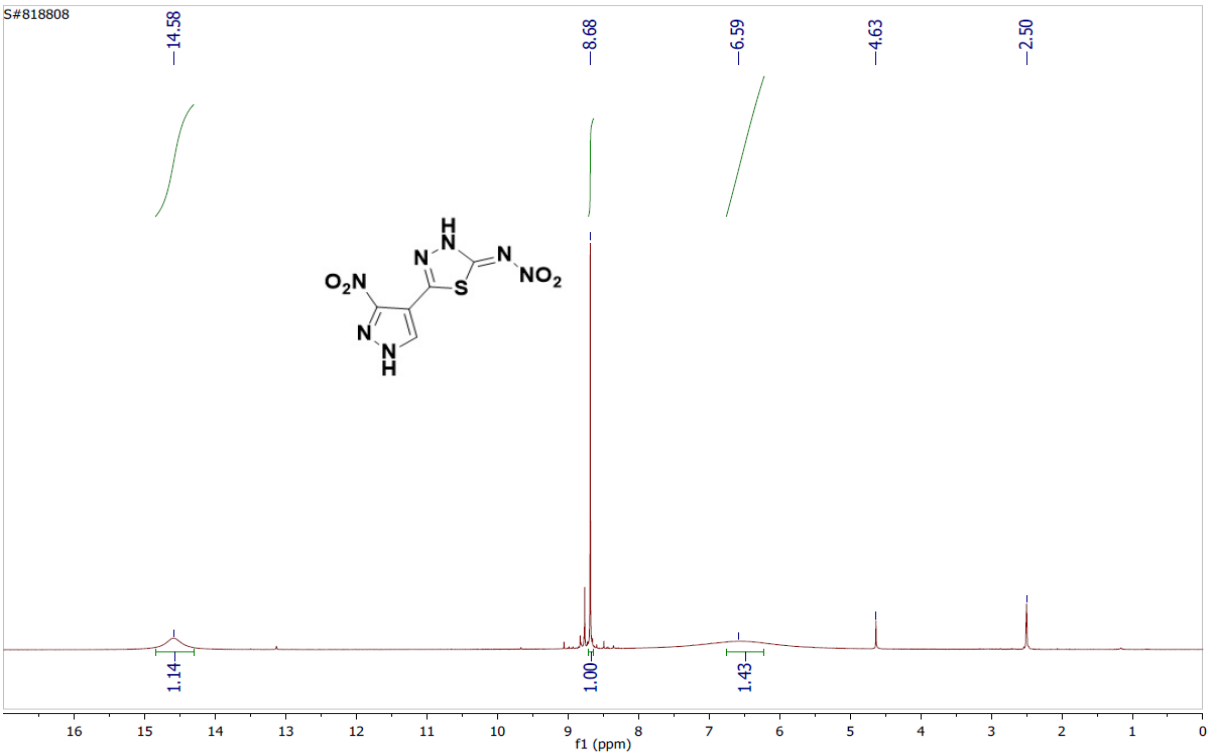


Figure S25: ^{1}H NMR spectrum of compound **7** in **DMSO-*d*$_6$**.

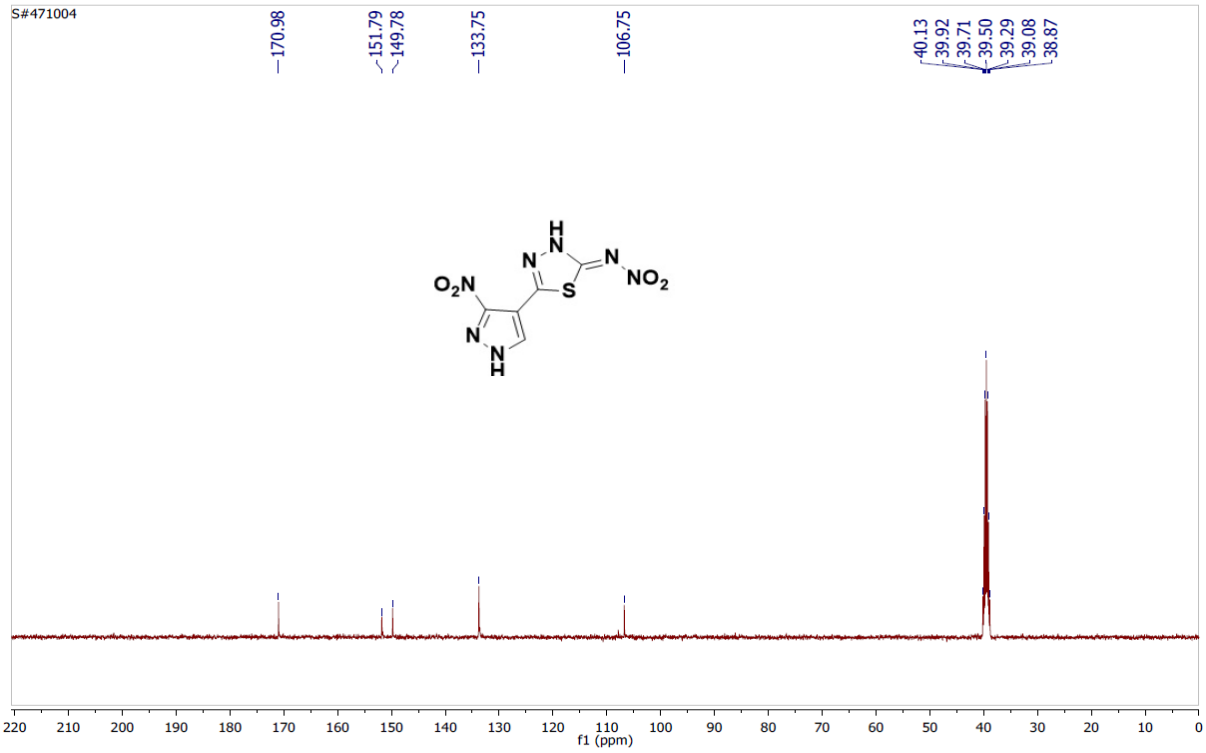


Figure S26: ^{13}C NMR spectrum of compound **7** in **DMSO-*d*$_6$.**

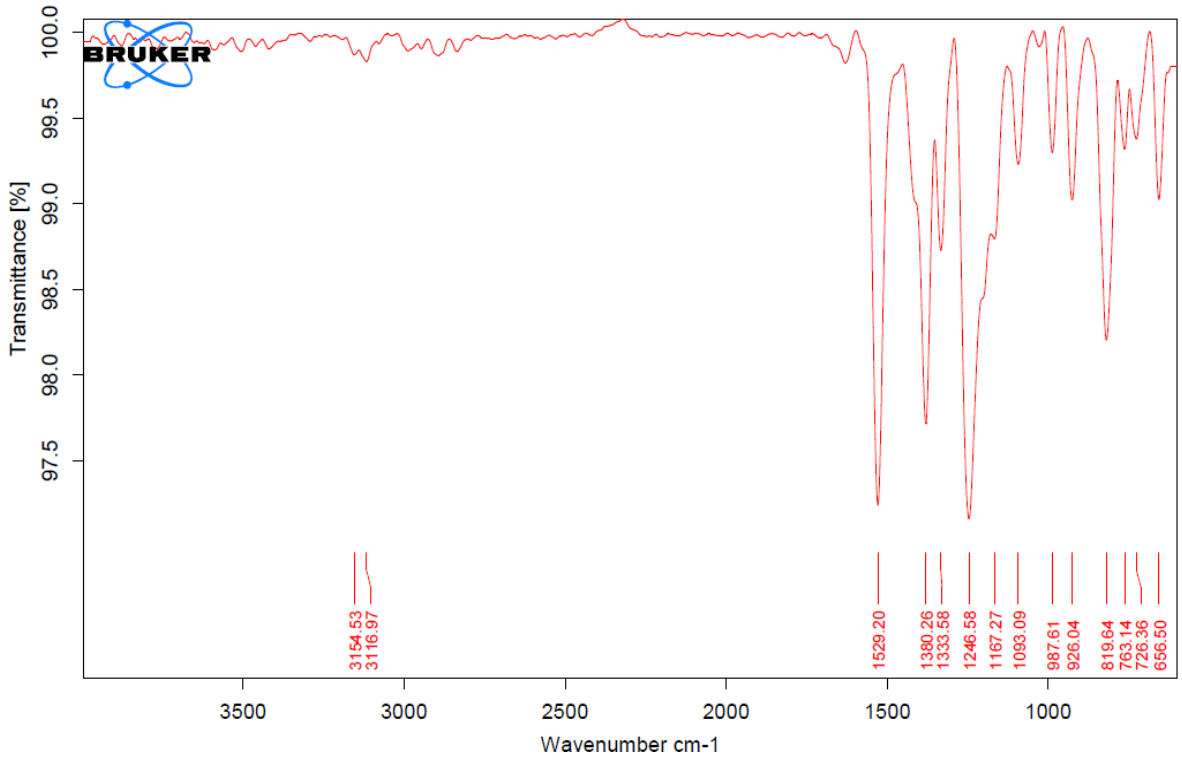


Figure S27: IR spectrum of compound **7.**

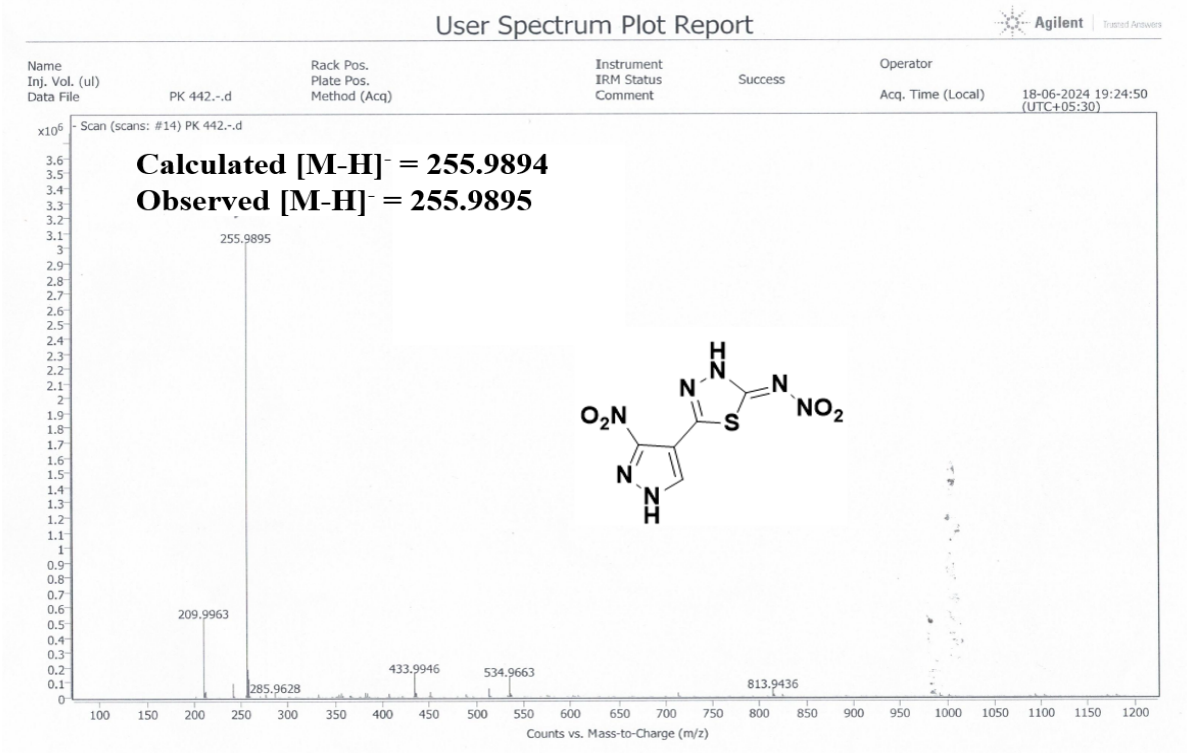


Figure S28: HRMS spectrum of compound **7.**

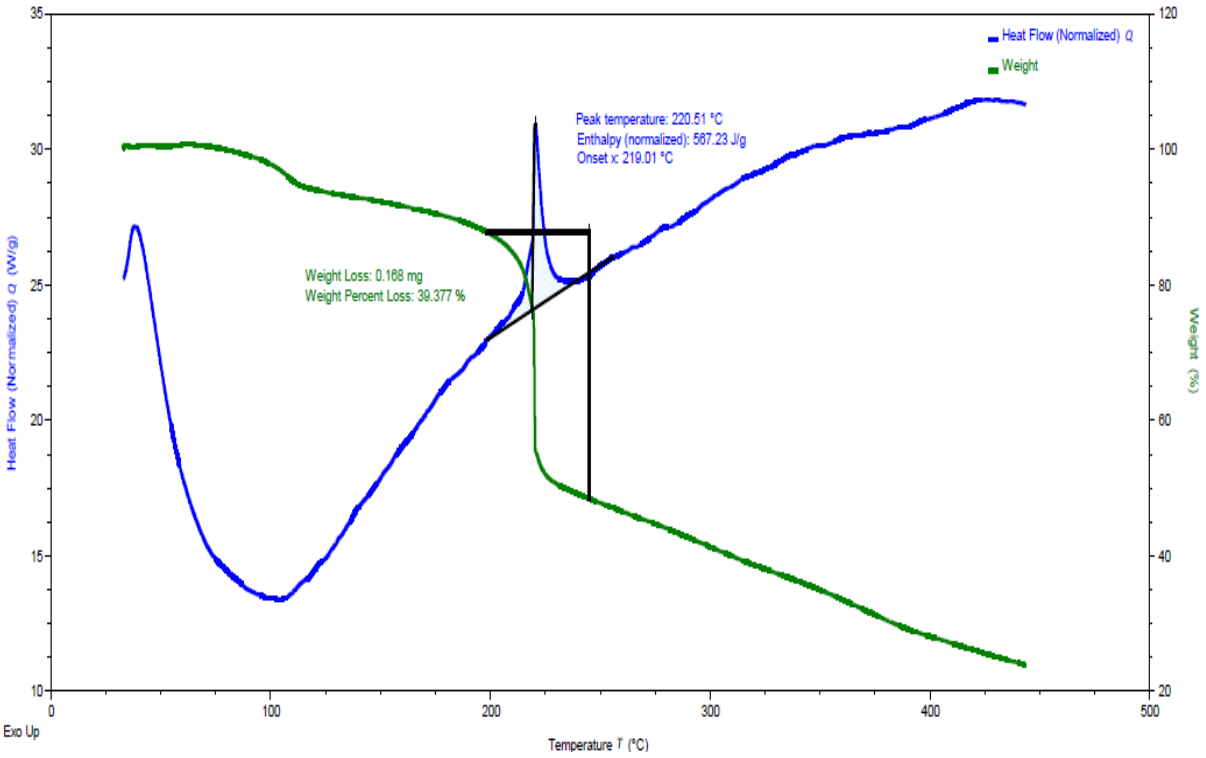


Figure S29: DSC spectrum of compound **7.**

Hot needle (HN) test: The hot needle (HN) test was carried out to gain insight into the energetic performance of the newly synthesized compounds. A hot needle ignites the compound **3** (10 mg), and the subsequent events were recorded with a high-speed camera (Phantom VEO 710 with 7000 fps). The ignition delay (ID) time, defined as the time required to inflame the compound after contact with the hot needle, was measured and revealed in Figure S29. Interestingly, compound **3** exhibits rapid ignition delay time, which begins at 13ms, and the flame vanished at 326ms having faint luminous flame.

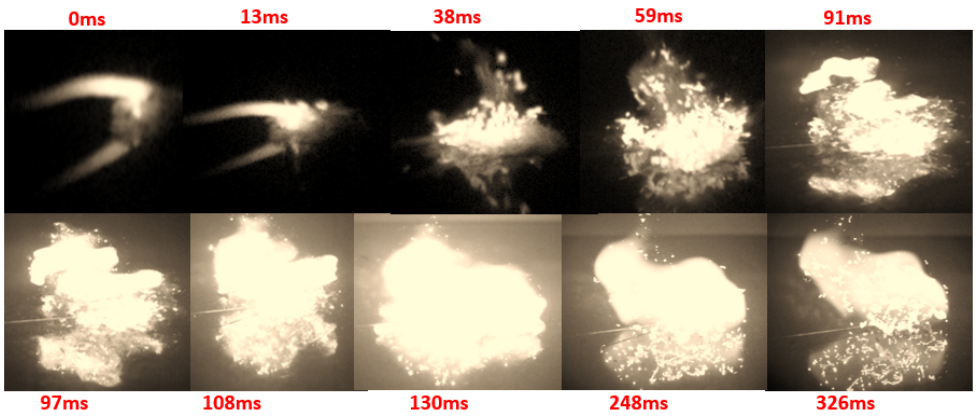


Figure S30: Hot needle (HN) test for compound **3**.

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 S31). Calculated total energies and related data for reference compounds and target compounds is listed in Tables S29 and S30. 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,

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

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

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

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. These molecular surface properties were obtained using the Multiwfn program[3] and listed in Table S31.

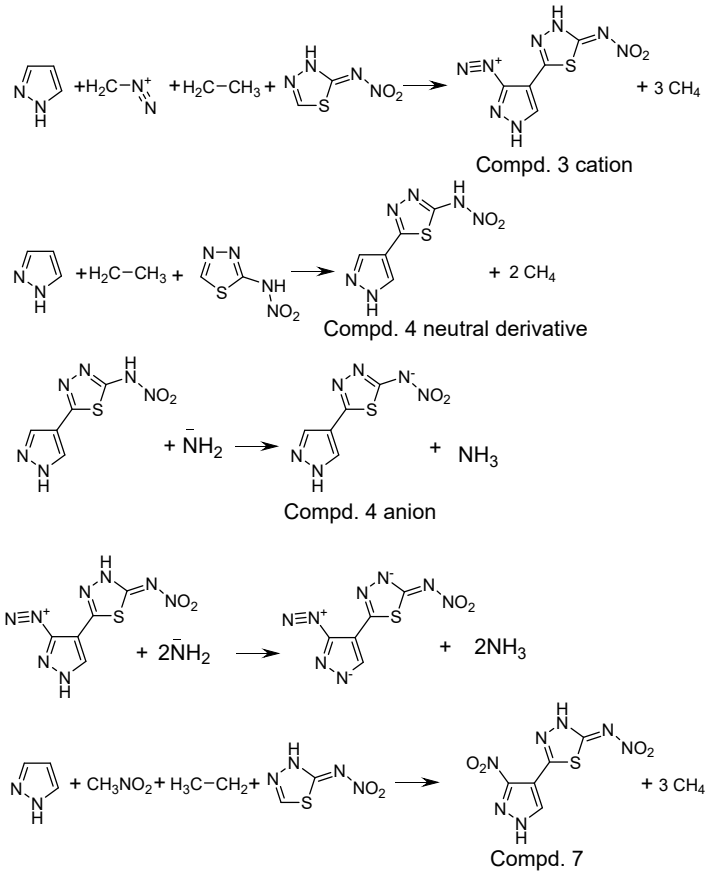


Figure S31. Isodesmic reactions designed to compute gas phase heats of formation and heats of formation for anionic components.

Based on the Born–Haber cycle (shown in Figure S32), 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 S32) *i.e.* sum of the heats of formation of the cation and anion as shown in equation (3).

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

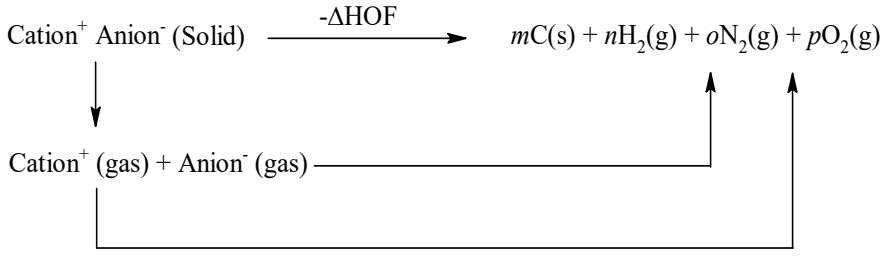


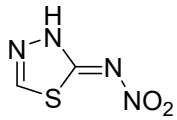
Figure S32. Born-Haber cycle for the formation of energetic salts.

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 correction of the U_{POT} term by an appropriate number of RT terms.

Table S29. 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
NH3	-56.513648	0.0345	0.0038	-45.94
CH_3CH_3	-79.727235	0.075	0.0045	-84
NH_2^-	-55.856335	0.0186	0.0038	111.75
	-844.845816	0.0644	0.0080	294.61[a]
Pyrazole	-226.118697	0.0722	0.0046	179.4
CH_3NHNH_2	-151.134206	0.0811	0.0052	98.65[a]

[a]Calculated using G4 method.

Table S30. Calculated total energies (E_0), zero-point energies (ZPE), and thermal corrections (H_T) for target compounds and their anions 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)**

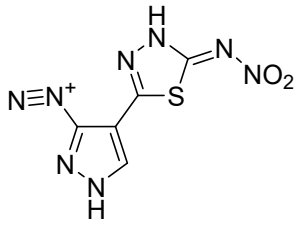
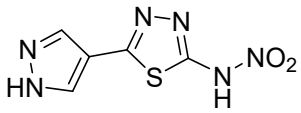
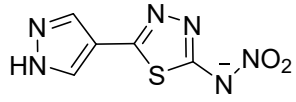
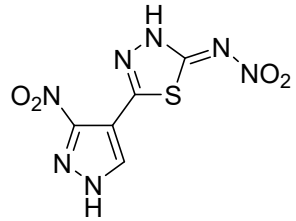
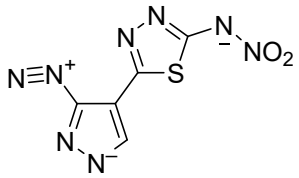
	-1178.387856	0.1159	0.0136	1463.8	-
	-1069.80307	0.1165	0.0123	494.4	-
	-1069.303113	0.1034	0.0117	239.0	-
	-1274.301125	0.1202	0.0144	497.9	128.69
	-1177.552319	0.0885	0.0132	521.3	-

Table S31. Calculated molecular surface properties of compound 7.

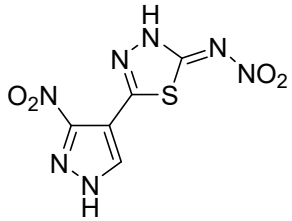
Compd.	**Surface area (Å²)**	**Volume (Å³)**	σ_{tot}^{2} **(kcal/mol)**	***v***
	234.77	238.95	357.60	0.1752

Table S32. Energy content of salts 3-5.

Compd.	**HOF_c[a]**	**HOF_a[b]**	**U_{Pot}[c]**	**H_L[d]**	**HOF_{salt}[e]**
3	1463.8	-314.38	465.97	470.93	678.49
4	636.8	239.0	483.2	488.2	387.6

5	769.5	521.3	474.5	479.4	811.35

[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}).

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