Electronic Supporting Information

High-performing, insensitive and thermally stable energetic materials from zwitterionic gem-dinitromethyl substituted C-C bonded 1,2,4-triazole and 1,3,4-oxadiazole

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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 heavy leather gloves) should be always taken when handling these materials.

General. All reagents were purchased from AKSci or TCI or Merck in analytical grade and were used as supplied. ^{1}H NMR and ^{13}C NMR, ^{15}N NMR spectra were recorded JEOL DELTA (ECS) 500 (1H, 500 MHz; 13C, 126 MHz) nuclear magnetic resonance spectrometer. Chemical shifts for 1H NMR and 13C NMR spectra are given with respect to external (CH3)4Si (1H and 13C). [D6] DMSO was used as a locking solvent unless otherwise stated. IR spectra were recorded using Zn-Se pellets with a 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 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 differential scanning calorimeter (DSC, Mettler). 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.

Synthesis of ethyl 5-amino-1,3,4-oxadiazole-2-carboxylate (2): Hydrazine hydrate (80%, 4 mL) was added dropwise in the solution of diethyl oxalate (15 g, 102 mmol) in ethanol (25 mL) at -20 °C. The reaction mixture was stirred at same temp for 35 min and solid was filtered. To the filtrate, cyanogen bromide (8.25 g, 77.8 mmol) and water (8 mL) was added and stirred at room temp for 2 hrs. The formed precipitated was collected by filtration, washed with diethyl ether (50 mL) and dried under vacuum to obtained ethyl 5-amino-1,3,4-oxadiazole-2-carboxylate (**2**) as a white solid. Yield (5.6 g, 35.64 mmol, 35%). ^{1}H NMR (500 MHz, DMSO-d6): δ 7.77 (s, 2H), 4.33 (q, 2H), 1.30 (t, 3H). ^{13}C NMR (126 MHz, DMSO-d6) δ 165.59, 154.56, 150.80, 62.49, 14.41. IR (ATR ZnSe): 3307, 3099, 2982, 1726, 1653, 1581, 1432, 1370, 1307, 1145, 1073, 1043, 999, 843, 741, 681 cm^{-1}.

Synthesis of 5-amino-1,3,4-oxadiazole-2-carbohydrazide (3): Hydrazine hydrate (80%, 5 mL) was added dropwise in to the suspension of compound **2** (1g, 6.36 mmol) in EtOH (12 mL) and reflux it at 80 °C for 8 hrs. The reaction mixture was cooled to room temperature and the resulting precipitate was collected by filtration and washed with ethanol to give 5-amino-1,3,4-oxadiazole-2-carbohydrazide (**3**) as a white solid. Yield (0.81 g, 5.66 mmol, 90%). T_m (onset): 92 °C. T_d (onset): 242 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 10.02 (s, 1H), 7.49 (s, 2H), 4.57 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 165.02, 153.68, 152.46. IR (ATR ZnSe): 3436, 3296, 3168, 3119, 2949, 2909, 2858, 1654, 1578, 1420, 1399, 1218, 1123, 1039, 994, 939, 871, 812, 720, 623 cm^{-1}. Elemental Analysis Calcd for $C_3H_5N_5O_2(0.6H_2O)$: C, 23.41; H, 4.06; N, 45.50. Found: C, 23.12; H, 4.48; N, 45.01.

Synthesis of ethyl 2-(5-(5-amino-1,3,4-oxadiazol-2-yl)-1H-1,2,4-triazol-3-yl)acetate (4): Ethyl 3-ethoxy-3-iminopropanoate (4 g, 20.44 mmol) was dissolved in acetonitrile (30 mL)

and Et_3N (2 mL) was added with stirring at room temperature for 30 mins. After that **3** (1 g, 6.98 mmol) and glacial acetic acid (6 mL) was added and refluxed the reaction mixture for 12 hrs. The reaction was cool down to room temperature and solvent was evaporated using rotary evaporate and added water in the residue. This mixture was sonicated and isolated newly formed solid cream color compound **4.** Yield (1.41 g, 5.93 mmol, 85%). ^{1}H NMR (500 MHz, DMSO-d6): δ 7.36 (s, 2H), 4.12 (s, 2H), 3.98 (s, 2H), 1.20 (t, 3H). ^{13}C NMR (126 MHz, DMSO-d6) δ 168.50, 167.07, 164.43, 151.91, 150.24, 61.59, 32.76, 14.47. IR (ATR ZnSe): 3313, 3103, 2979, 1729, 1645, 1452, 1373, 1256, 1168, 1026, 924, 779, 673 cm^{-1}. HRMS (ESI) m/z $(M+H)^+$ Calcd for $C_8H_{10}N_6O_3$: 239.0887 Found: 239.0892. Elemental Analysis Calcd for $C_8H_{10}N_6O_3$: C, 40.34; H, 4.23; N, 35.28. Found: C, 40.35; H, 4.26; N, 35.66.

Synthesis of (5-(5-iminio-4,5-dihydro-1,3,4-oxadiazol-2-yl)-1H-1,2,4-triazol-3-yl)dinitromethanide (5): Compound **4** (500 mg, 1.8781 mmol) was added in portions to the mixture of fuming nitric acid (2.5 mL) and 3 mL conc. sulfuric acid (98%) in ice-water bath at 0 °C. After addition, the reaction mixture was stirred at same temperature for 20 mins and continued for 12 hrs at room temperature. Mixture was poured into crushed ice and stirred it 30 min at room temp and then kept into the fridge for overnight. The obtained crystals (suitable for single crystal XRD) were filtered, washed with cold water and dried in air to get yellow coloured compound **5.** Yield (0.40 g, 1.57 mmol, 75%). T_d (onset): 132 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.76 (s, 1H), 4.54 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 163.06, 154.62, 151.86, 148.84, 146.30. IR (ATR ZnSe): 3497, 3401, 3279, 2924, 1720, 1650, 1522, 1471, 1354, 1276, 1190, 1131, 1077, 983, 826, 733 cm^{-1}. Elemental Analysis Calcd for $C_5H_4N_8O_5$ (H_2O): C, 21.91; H, 2.21; N, 40.87. Found: C, 21.77; H, 2.35; N, 39.83.

General procedure for the synthesis of salts 6-8

Hydrazine hydrate (45 mg, 0.898 mmol), hydroxylamine hydrate (30 mg, 0.908 mmol), 7H-[1,2,4]triazolo[4,3-b][1,2,4]triazole-3,6,7-triamine (TATOT) (133 mg, 0.862 mmol) was added slowly with stirring to a solution of **4** (100 mg, 0.390 mmol) in methanol (3 mL) at 25 °C. The reaction mixture was stirred for 6 h at room temperature, and newly formed precipitated were collected by filtration and dried with high vacuum to get desired products with quantitative yields.

Di hydrazinium 5-(5-amino-1,3,4-oxadiazol-2-yl)-3-(dinitromethaneidyl)-1,2,4-triazol-1-ide (6): Yield (106 mg, 0.331 mmol, 85%) as yellow solid. T_d (onset): 200 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 7.27 (s, 2H), 5.34 (s, 10H). ^{13}C NMR (126 MHz, DMSO-d6) δ 164.25, 152.78, 150.87, 149.88, 124.98. IR (ATR ZnSe): 3382, 3337, 3267, 3121, 2922, 2853, 1651, 1602, 1512, 1412, 1235, 1192, 1074, 1005, 936, 822, 739, 663 cm^{-1}. Elemental Analysis Calcd for $C_5H_{12}N_{12}O_5$: C, 18.75; H, 3.78; N, 52.49. Found: C, 19.31; H, 4.11; N, 52.88.

Dihydroxyl ammonium 5-(5-amino-1,3,4-oxadiazol-2-yl)-3-(dinitromethaneidyl)-1,2,4-triazol-1-ide (7): Yield (100 mg, 0.310 mmol, 80%) as yellow solid. T_d (onset): 186 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 7.28 (s, 2H), 4.10 (s, 6H). ^{13}C NMR (126 MHz, DMSO-d6) δ163.82, 152.13, 150, 149.48, 124.16. IR (ATR ZnSe): 3739, 3613, 3482, 3371, 3271, 3129, 3036, 2786, 1657, 1525, 1403, 1282, 1192, 1127, 972, 825, 733 cm^{-1}.

Di (3,6,7-triamino-7H-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium) 5-(5-amino-1,3,4-oxadiazol-2-yl)-3-(dinitromethaneidyl)-1,2,4-triazol-1-ide (8): Yield (193 mg, 0.341 mmol, 88%) as yellow solid. Td (onset): 243 °C. ^{1}H NMR (500 MHz, DMSO-d6): δ 7.32 (s, 2H), 6.69 (s, 8H) 5.65 (s, 4H). ^{13}C NMR (126 MHz, DMSO-d6) δ 170.28, 164.39, 159.65, 152.36, 150, 148.91, 143.10, 124.17. IR (ATR ZnSe): 3364, 3318, 3140, 2894, 2356, 1655, 1530, 1484, 1403, 1358, 1211, 1097, 1047, 975, 906, 831, 780, 737, 667 cm^{-1}. Elemental Analysis Calcd for $C_{11}H_{16}N_{24}O_5$: C, 23.41; H, 2.86; N, 59.56. Found: C, 22.74; H, 3.34; N, 60.05.

Synthesis of 5-(3-amino-1H-1,2,4-triazol-5-yl)-1,3,4-oxadiazol-2-amine (9): A suspension of aminoguanidine sulphate (6.28 g, 25.50 mmol), NaOMe (1.37 g, 25.35 mmol) and anhydrous MeOH (12 mL) was cooled below 0 °C and compound **2** (1 g, 6.36 mmol) was added slowly to it. The reaction mixture was refluxed for 24 hrs and cooled to 10 °C and subsequently poured into the ice water (~25 mL). Mixture was acidified to pH 4-5 with 37% HCl. The newly obtained precipitated was filtered, washed with water, and dried in air to get the product **9** as a yellow solid. Yield (0.85 g, 5.09 mmol, 80%) as yellow solid. ^{1}H NMR (500 MHz, DMSO-d6): δ 8.42 (s, 1H), 7.35 (s, 2H) 7.16 (s, 2H). ^{13}C NMR (126 MHz, DMSO-d6) δ 162.78, 156.60, 151.37, 147.06. IR (ATR ZnSe): 3342, 3101, 2922, 2852, 1651, 1589, 1435, 1364, 1192, 1093, 1041, 903, 814, 735 cm^{-1}. HRMS (ESI) m/z (M+H)$^{+}$ Calcd for $C_4H_5N_7O$: 168.0634 Found: 168.0625.

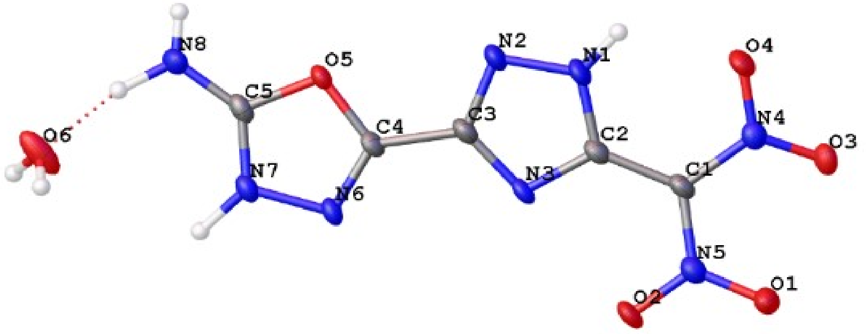


Figure S1: Molecular Structure of **5**.

Table S1: Crystallographic data for **5**.

CCDC No.	2237463
Empirical formula	$C_5H_6N_8O_6$
Formula weight	274.18
Temperature/K	100
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	14.4122(14)
b/Å	12.1358(12)
c/Å	5.6687(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	991.48(17)
Z	4
ρ_{calc}g/cm^3	1.837
μ/mm^{-1}	0.167
F(000)	560.0
Crystal size/mm^3	0.11 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.388 to 56.532
Index ranges	$-19 \leq h \leq 19$, $-15 \leq k \leq 16$, $-7 \leq l \leq 7$
Reflections collected	12485
Independent reflections	2463 [R_{int} = 0.0627, R_{sigma} = 0.0537]
Data/restraints/parameters	2463/1/190
Goodness-of-fit on F^2	1.118
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.0990
Final R indexes [all data]	R_1 = 0.0843, wR_2 = 0.1085
Largest diff. peak/hole / e Å^{-3}	0.26/-0.25
Flack parameter	-0.4(10)

Table S2. Fractional Atomic Coordinates (×10^4) and Equivalent IsotropicDisplacement Parameters (Å^2×10^3) for 5. Ueq is defined as1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O5	3899.2(18)	6536(2)	9075(5)	22.1(7)
O3	234.4(19)	3362(3)	849(6)	27.9(7)
O4	225.3(19)	4707(3)	3300(6)	37.2(9)
O1	1735(2)	3115(3)	-1422(6)	40.1(10)
N6	4776(2)	5647(3)	6458(6)	21.8(9)
N4	656(2)	4060(3)	2003(7)	23.8(8)
O2	2992(2)	3691(3)	229(6)	36.8(10)
N5	2134(2)	3625(3)	218(7)	26.8(9)
N3	3013(2)	4853(3)	4172(6)	21.3(8)
N8	5023(3)	7326(3)	11423(7)	27.8(9)
O6	6797(2)	7877(4)	10992(7)	46.4(11)
N7	5328(2)	6216(3)	8054(7)	21.8(8)
N1	1665(2)	5439(4)	5387(7)	28.9(10)
N2	2275(2)	5930(4)	6842(7)	28.4(9)
C5	4802(3)	6725(4)	9624(8)	22.0(10)
C2	2097(3)	4804(4)	3777(8)	21.6(10)
C1	1632(3)	4149(4)	1991(9)	22.8(9)
C4	3947(3)	5872(4)	7134(9)	21.0(9)
C3	3069(3)	5541(4)	6030(8)	22.7(9)

Table S3. Anisotropic Displacement Parameters (Å2×103) for 5. TheAnisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
O5	9.4(13)	32.8(17)	24.0(16)	-5.9(14)	-1.5(12)	-0.7(12)
O3	18.0(14)	37(2)	28.9(17)	-3.9(16)	-2.7(13)	-7.7(14)
O4	12.0(15)	58(2)	41(2)	-20.9(19)	-2.4(15)	4.6(15)
O1	17.0(15)	65(3)	38(2)	-27(2)	-3.4(15)	2.7(16)
N6	10.6(16)	30(2)	25(2)	-2.7(18)	-3.7(15)	-0.9(15)
N4	18.7(17)	30(2)	22.7(17)	-2.3(17)	-3.6(17)	0.8(16)
O2	8.8(14)	64(3)	38.1(19)	-16.5(18)	-0.3(14)	-0.1(15)
N5	15.5(16)	37(2)	28(2)	-5.9(18)	-1.7(16)	1.8(16)
N3	7.8(14)	30(2)	25.9(19)	-0.4(18)	-1.6(14)	0.8(14)
N8	15.8(17)	39(2)	28(2)	-10(2)	2.8(17)	-4.4(17)
O6	17.3(15)	73(3)	49(3)	29(2)	-0.5(17)	-1.1(17)
N7	12.0(15)	29(2)	24.4(19)	0.1(17)	-2.6(15)	-1.2(16)
N1	10.0(16)	45(3)	32(2)	-11.3(19)	-4.2(16)	1.6(16)
N2	10.5(16)	46(3)	29(2)	-10.9(19)	-1.9(15)	-1.2(17)
C5	11.9(18)	28(2)	26(2)	4(2)	-2.2(16)	-1.9(17)
C2	12.0(18)	29(2)	24(2)	-1(2)	-0.6(17)	3.0(17)
C1	11.1(18)	33(3)	24(2)	-2(2)	0.5(18)	1.8(18)
C4	11.1(18)	28(2)	23(2)	-0.7(19)	-3.3(18)	3.3(18)
C3	10.9(18)	32(2)	25(2)	-1(2)	0.7(17)	0.3(17)

Table S4. Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O5	C5	1.358(5)	N3	C2	1.340(5)
O5	C4	1.366(5)	N3	C3	1.346(6)

O3	N4	1.231(5)	N8	C5	1.293(6)
O4	N4	1.242(5)	N7	C5	1.322(5)
O1	N5	1.256(5)	N1	N2	1.345(5)
N6	N7	1.389(5)	N1	C2	1.347(6)
N6	C4	1.284(5)	N2	C3	1.321(5)
N4	C1	1.412(5)	C2	C1	1.451(6)
O2	N5	1.239(4)	C4	C3	1.468(5)
N5	C1	1.392(6)			

Table S5. Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5	O5	C4	103.6(3)	N7	C5	O5	108.4(4)
C4	N6	N7	103.4(3)	N3	C2	N1	108.5(4)
O3	N4	O4	120.3(3)	N3	C2	C1	126.5(4)
O3	N4	C1	122.8(4)	N1	C2	C1	124.9(4)
O4	N4	C1	116.9(4)	N4	C1	C2	119.9(4)
O1	N5	C1	121.5(3)	N5	C1	N4	119.1(4)
O2	N5	O1	119.4(4)	N5	C1	C2	121.0(3)
O2	N5	C1	119.0(4)	O5	C4	C3	117.5(3)
C2	N3	C3	102.5(3)	N6	C4	O5	114.4(4)
C5	N7	N6	110.1(3)	N6	C4	C3	128.1(4)
N2	N1	C2	111.5(4)	N3	C3	C4	123.7(4)
C3	N2	N1	101.2(4)	N2	C3	N3	116.3(4)
N8	C5	O5	120.8(4)	N2	C3	C4	120.0(4)
N8	C5	N7	130.8(4)				

Table S6. Torsion Angles for 5.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O5	C4	C3	N3	-177.1(4)	N7	N6	C4	C3	176.6(4)
O5	C4	C3	N2	3.5(6)	N1	N2	C3	N3	0.6(5)
O3	N4	C1	N5	16.0(7)	N1	N2	C3	C4	180.0(4)
O3	N4	C1	C2	-165.6(4)	N1	C2	C1	N4	-6.4(7)
O4	N4	C1	N5	-166.0(4)	N1	C2	C1	N5	172.0(4)
O4	N4	C1	C2	12.5(7)	N2	N1	C2	N3	1.0(6)
O1	N5	C1	N4	3.1(7)	N2	N1	C2	C1	178.7(4)
O1	N5	C1	C2	-175.4(4)	C5	O5	C4	N6	-0.2(5)
N6	N7	C5	O5	-1.8(5)	C5	O5	C4	C3	-177.9(4)
N6	N7	C5	N8	178.7(5)	C2	N3	C3	N2	0.0(5)
N6	C4	C3	N3	5.5(8)	C2	N3	C3	C4	-179.4(4)
N6	C4	C3	N2	-173.8(5)	C2	N1	N2	C3	-0.9(5)
O2	N5	C1	N4	-179.0(4)	C4	O5	C5	N8	-179.2(4)
O2	N5	C1	C2	2.6(7)	C4	O5	C5	N7	1.2(4)
N3	C2	C1	N4	171.0(4)	C4	N6	N7	C5	1.5(5)
N3	C2	C1	N5	-10.6(7)	C3	N3	C2	N1	-0.6(5)
N7	N6	C4	O5	-0.8(5)	C3	N3	C2	C1	-178.2(5)

Table S7. Hydrogen Atom Coordinates (Å×104) andIsotropic Displacement Parameters (Å2×103) for 5.

Atom	*x*	*y*	*z*	U(eq)
H8A	4630(40)	7620(40)	12280(90)	33
H6A	7194.11	7441.66	11589.38	70
H6B	6999.88	8123.74	9686.88	70
H1	1040(40)	5650(50)	5380(110)	54(18)
H8B	5700(30)	7580(40)	11470(90)	39(14)
H7	6050(50)	5970(50)	8220(150)	100(20)

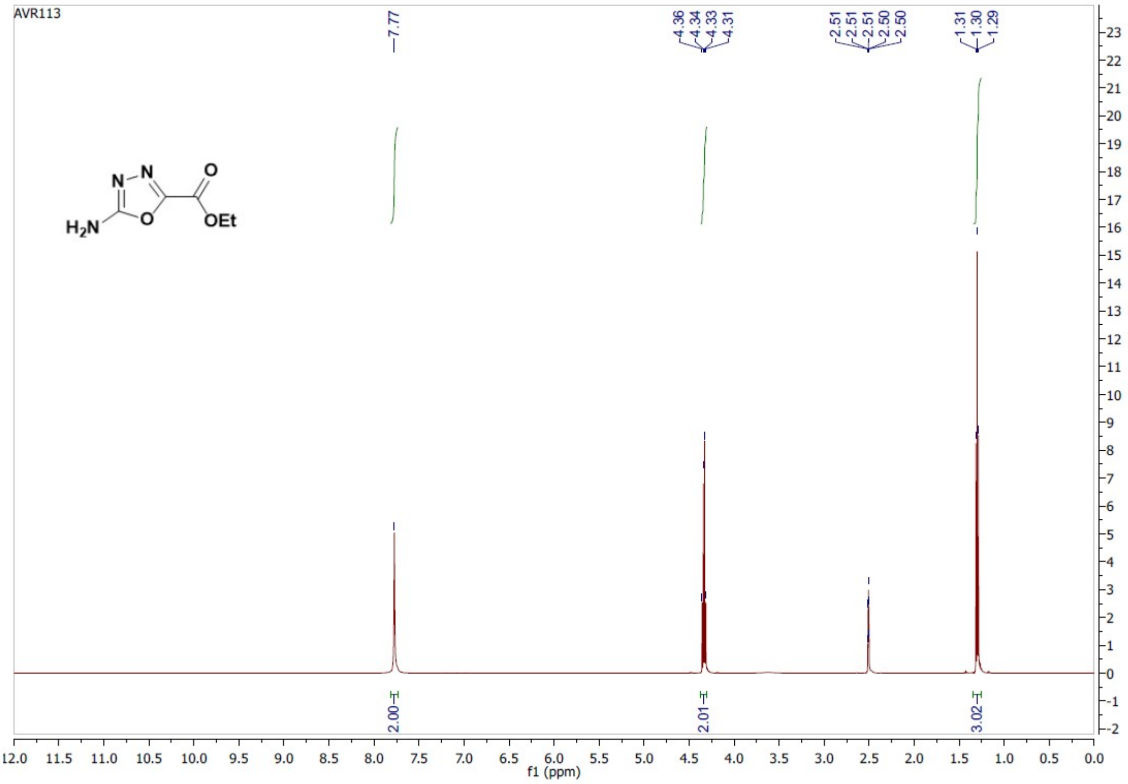


Figure S2: ^{1}H NMR Spectrum of Compound 2 (recorded in d_6-DMSO).

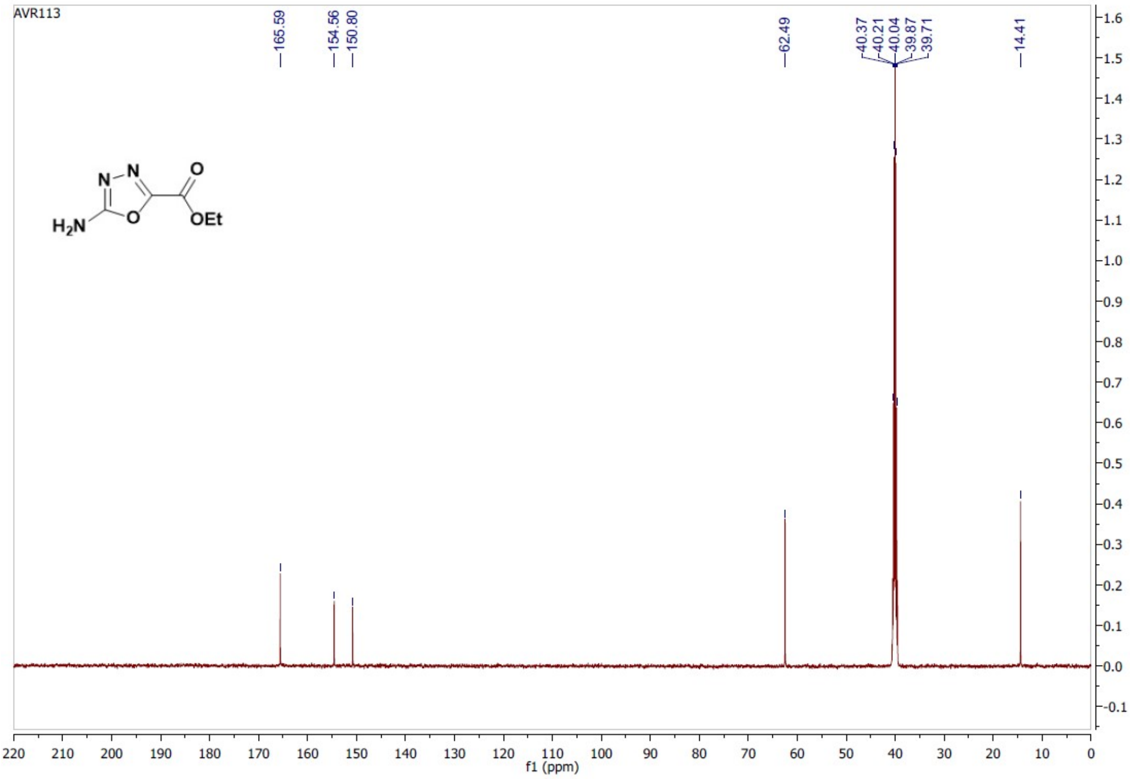


Figure S3: ^{13}C NMR Spectrum of Compound 2 (recorded in *d*$_6$-DMSO).

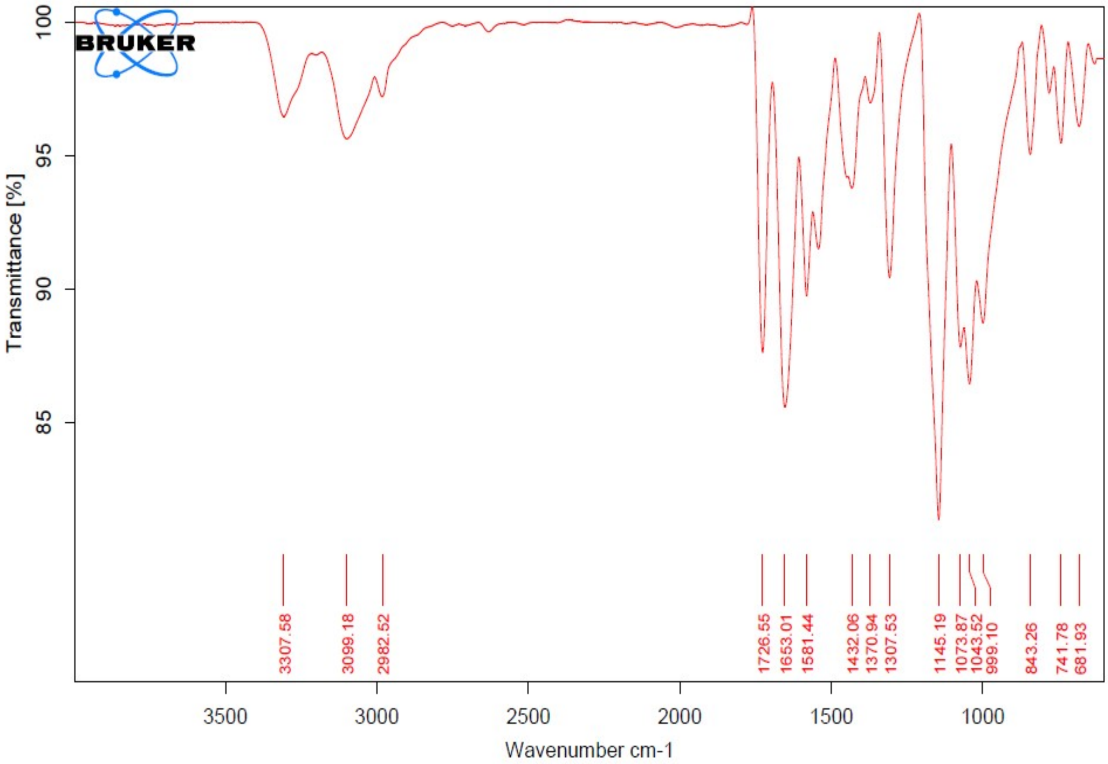


Figure S4: IR Spectrum of Compound 2.

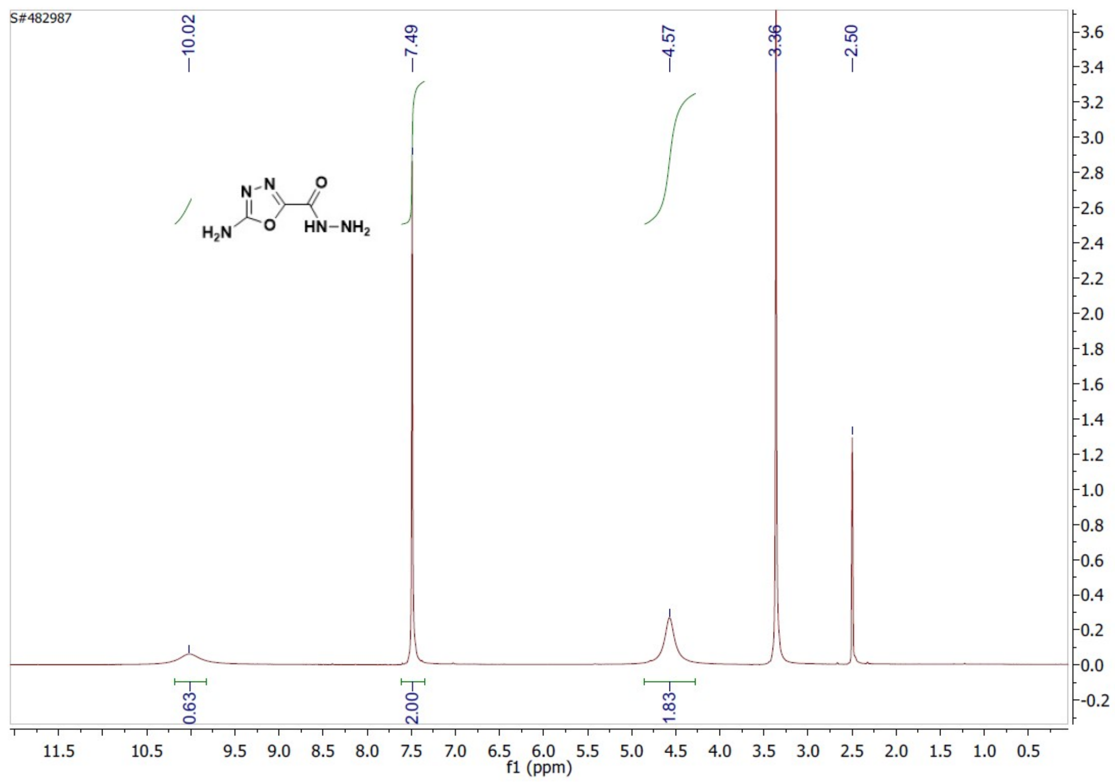


Figure S5: ^{1}H NMR Spectrum of Compound 3 (recorded in d_6-DMSO).

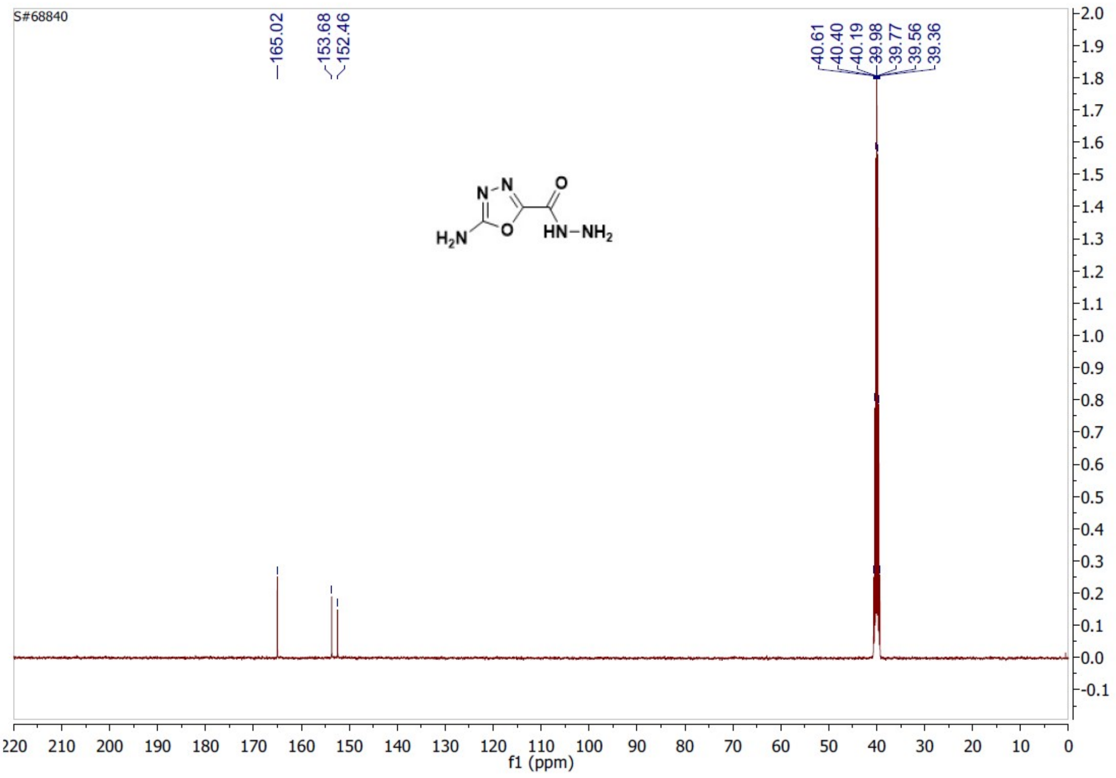


Figure S6: ^{13}C NMR Spectrum of Compound 3 (recorded in d_6-DMSO).

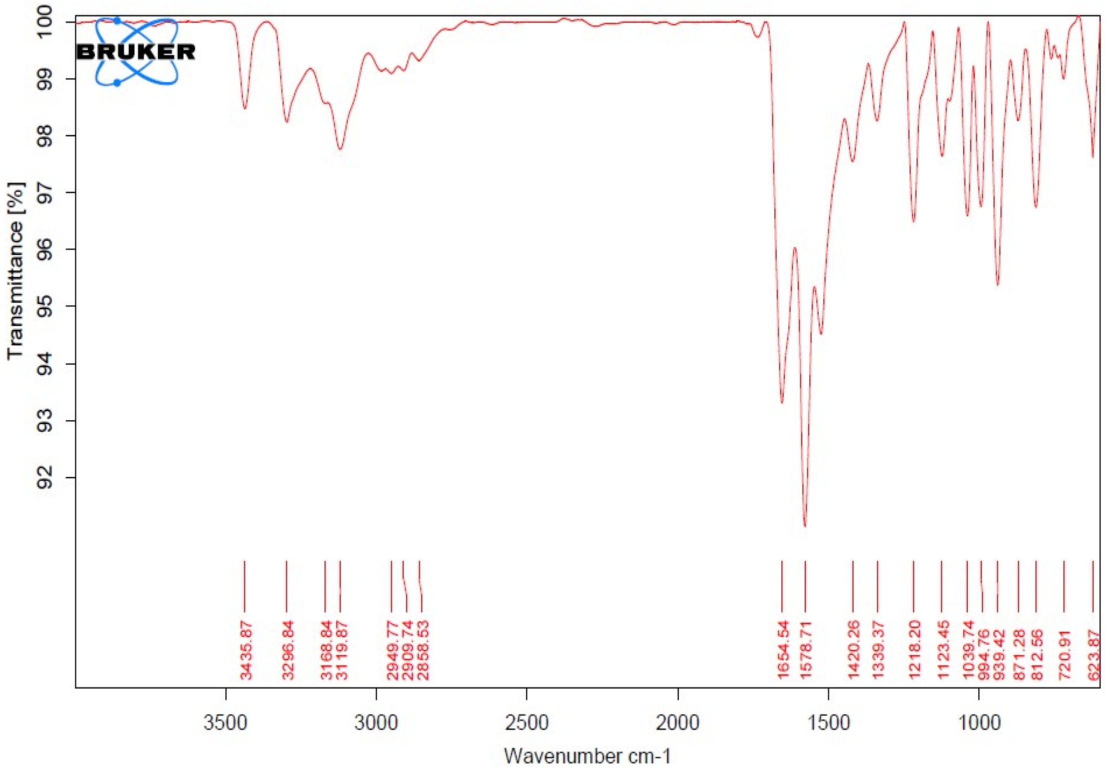


Figure S7: IR Spectrum of Compound 3.

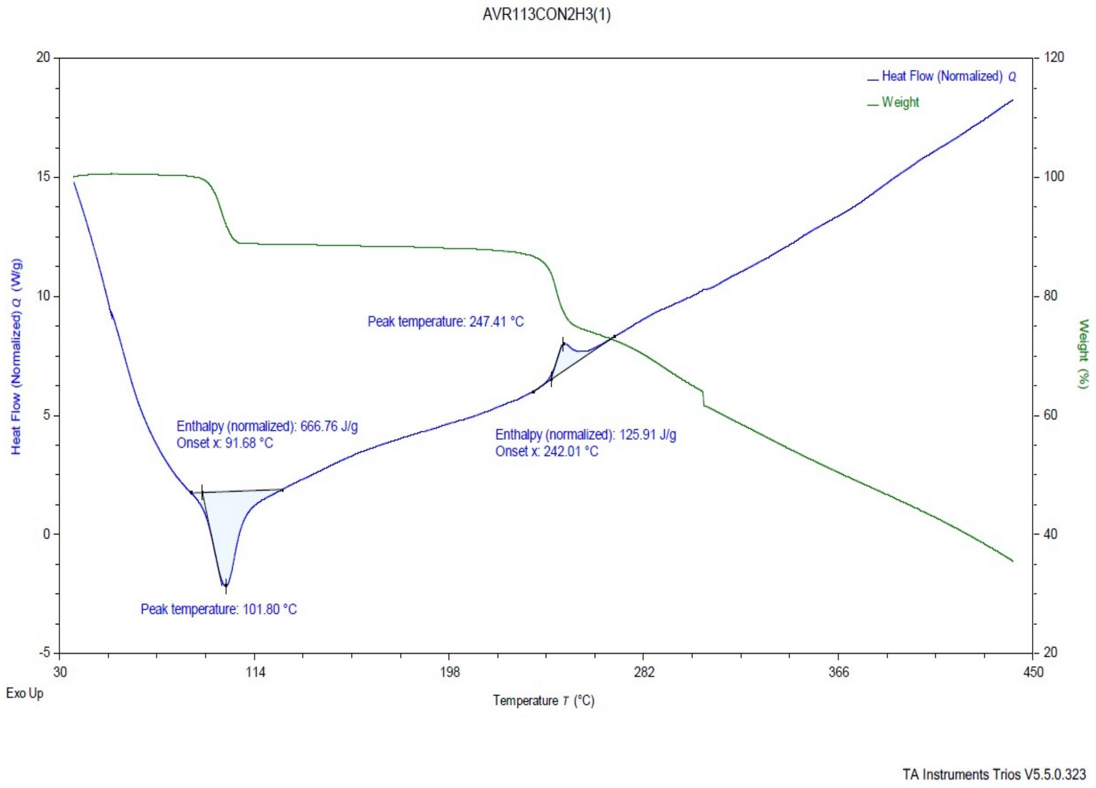


Figure S8. DSC Plot of Compound 3 at Heating rate 5 ^{o}C min^{-1}.

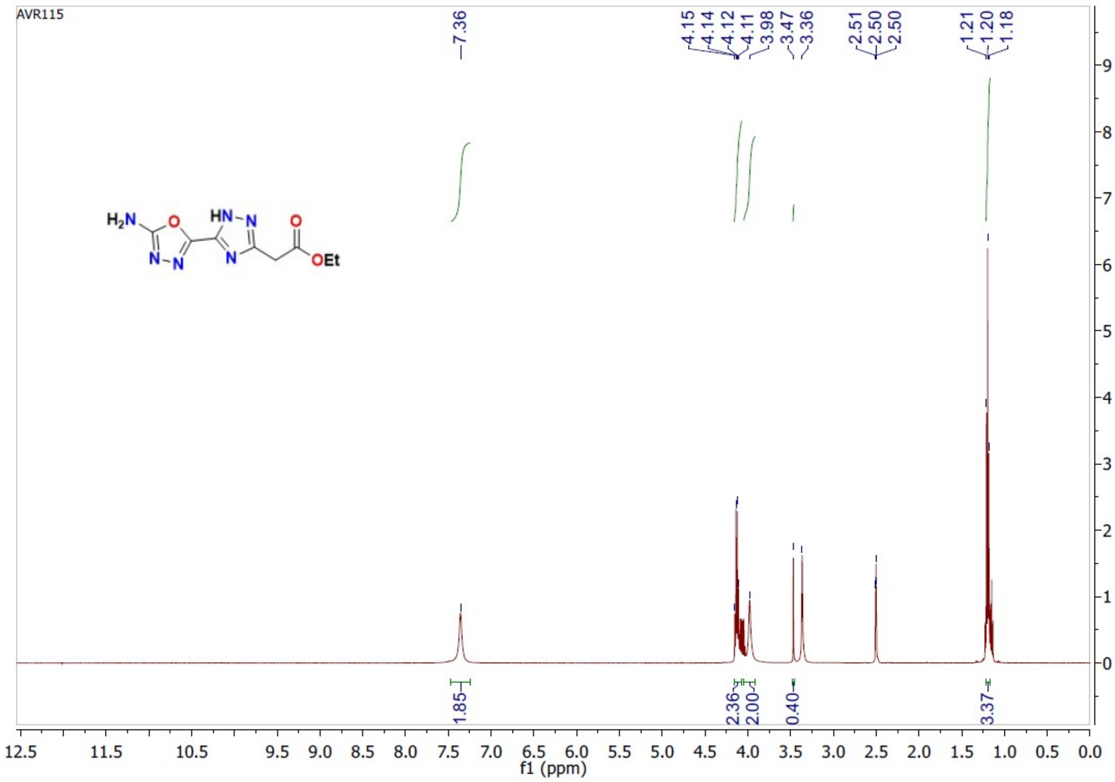


Figure S9: ^{1}H NMR Spectrum of Compound 4 (recorded in d_6-DMSO).

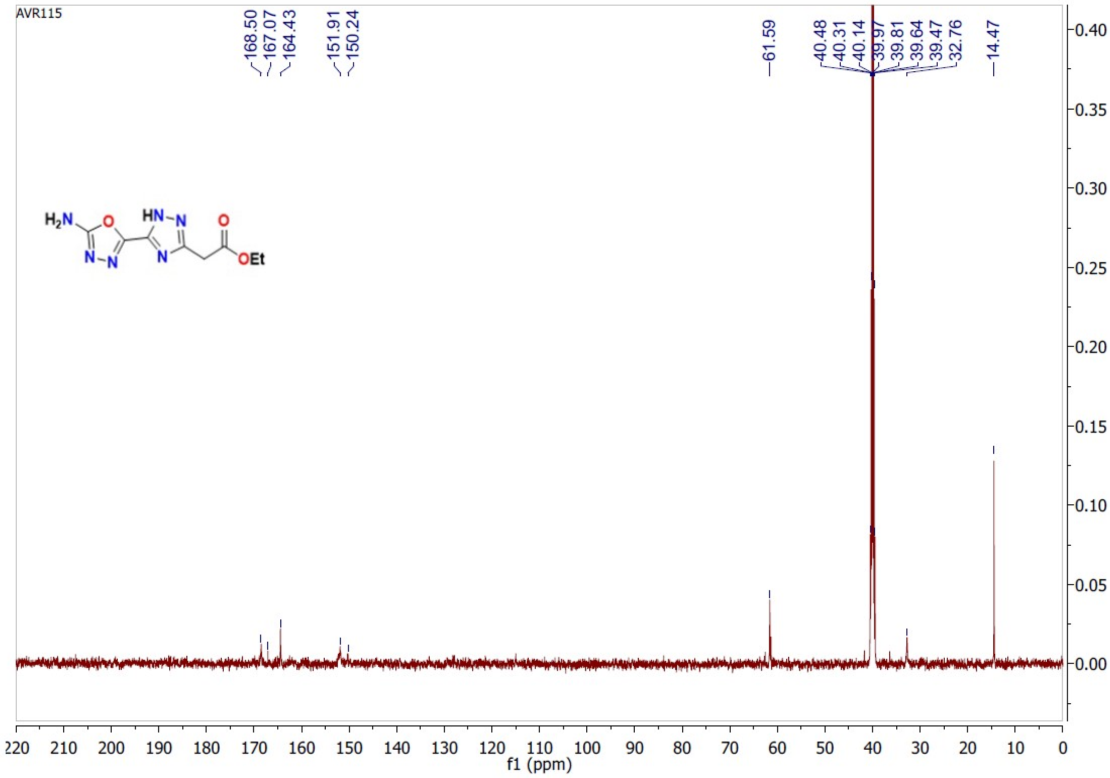


Figure S10: ^{13}C NMR Spectrum of Compound 4 (recorded in d_6-DMSO).

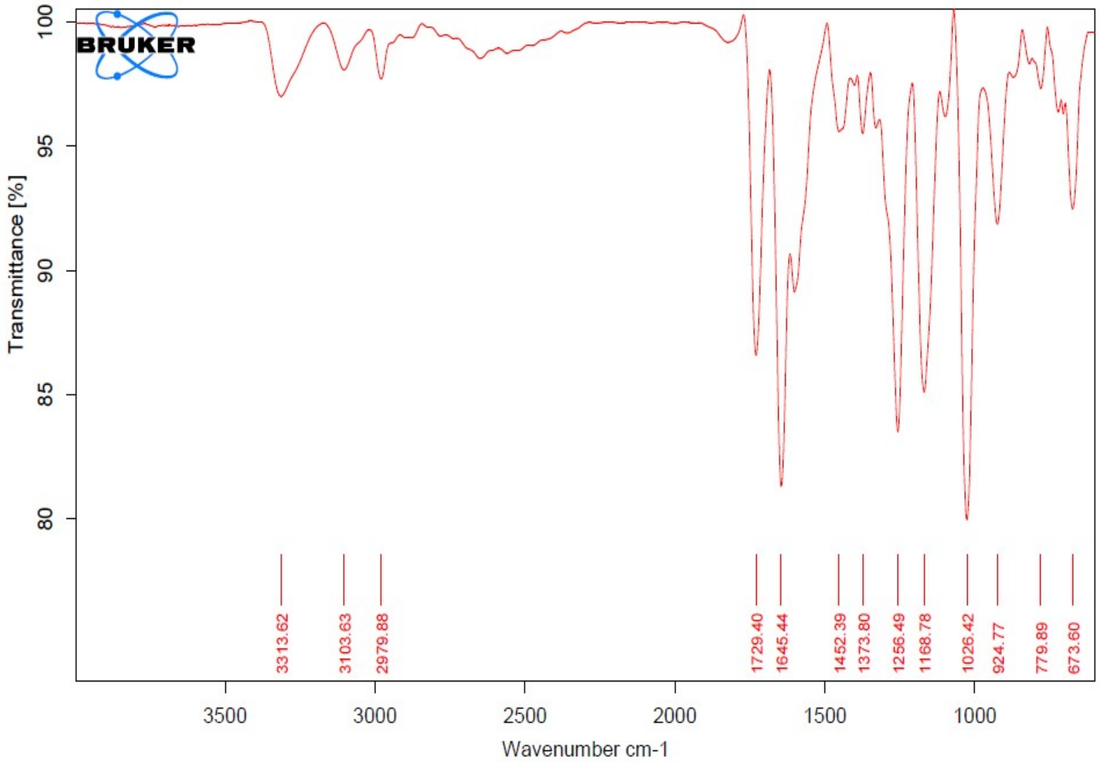
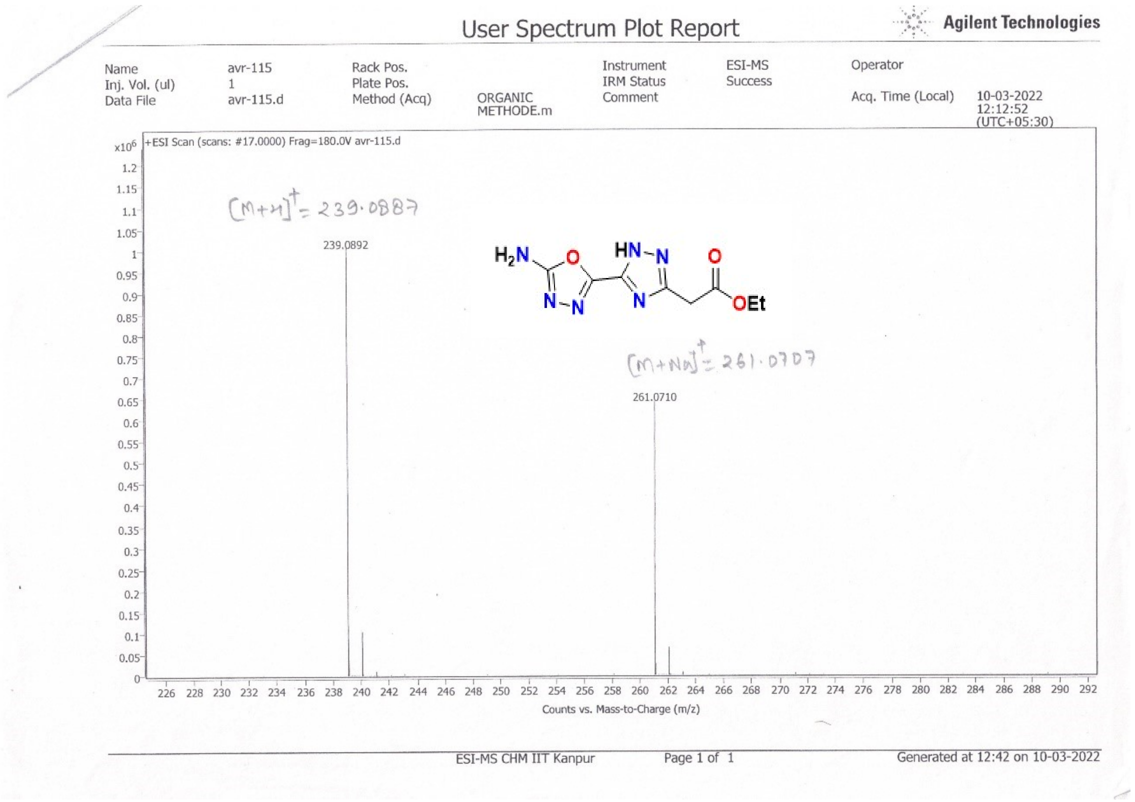


Figure S11: IR Spectra of Compound 4.



User Spectrum Plot Report

Agilent Technologies

Name	avr-115	Rack Pos.		Instrument	ESI-MS	Operator	
Inj. Vol. (ul)	1	Plate Pos.		IRM Status	Success		
Data File	avr-115.d	Method (Acq)	ORGANIC METHODE.m	Comment		Acq. Time (Local)	10-03-2022 12:12:52 (UTC+05:30)

+ESI Scan (scans: #17.0000) Frag=180.0V avr-115.d

$[M+H]^+ = 239.0887$

$[M+Na]^+ = 261.0707$

ESI-MS CHM IIT Kanpur Page 1 of 1 Generated at 12:42 on 10-03-2022

Figure S12: Mass Spectrum of Compound 4.

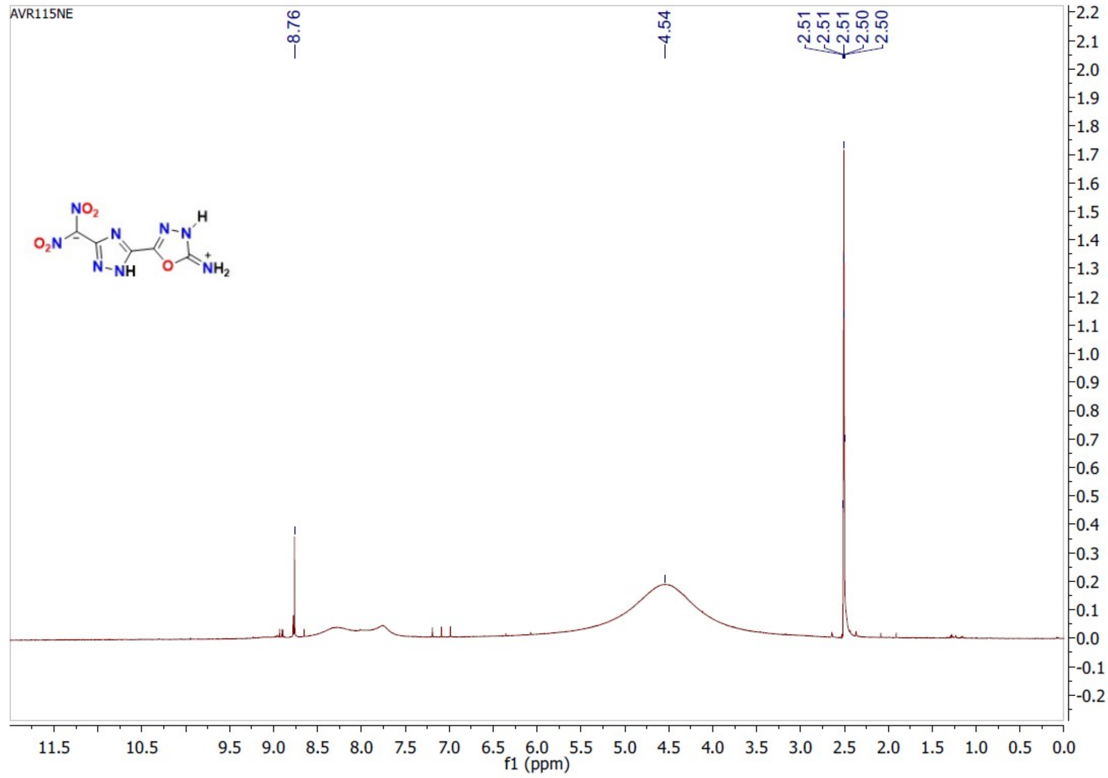


Figure S13: ^{1}H NMR Spectrum of Compound 5 (recorded in d_6-DMSO).

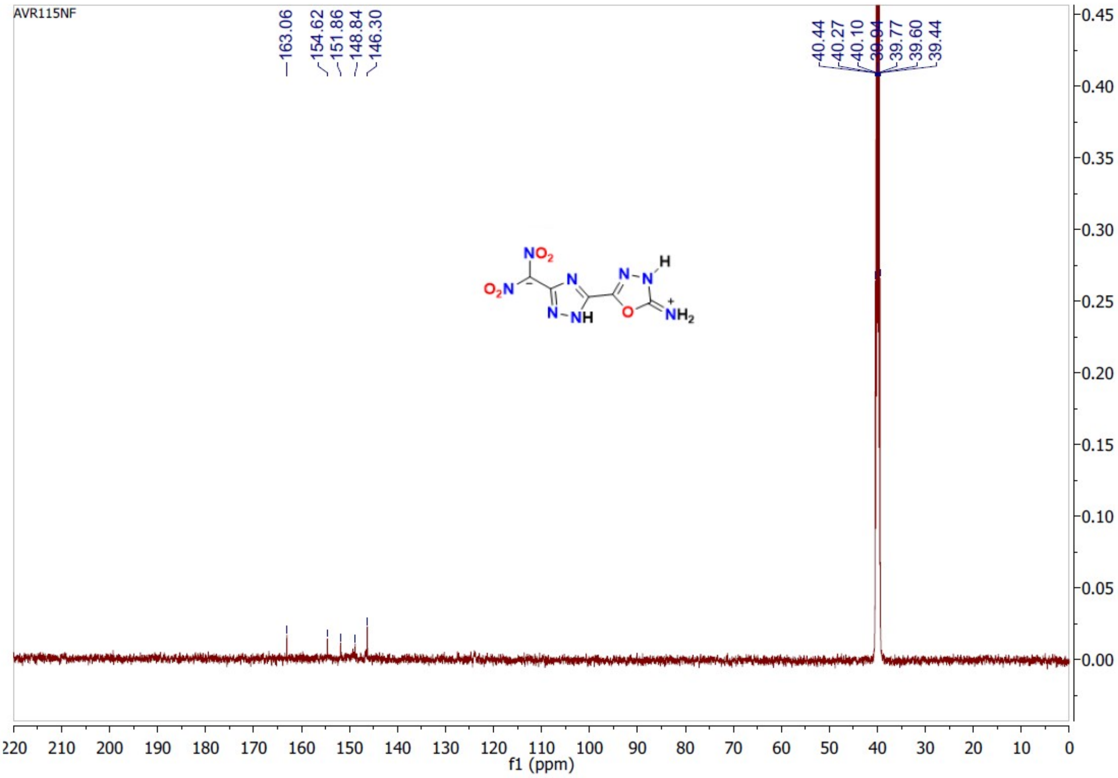


Figure S14: ^{13}C NMR Spectrum of Compound 5 (recorded in d_6-DMSO).

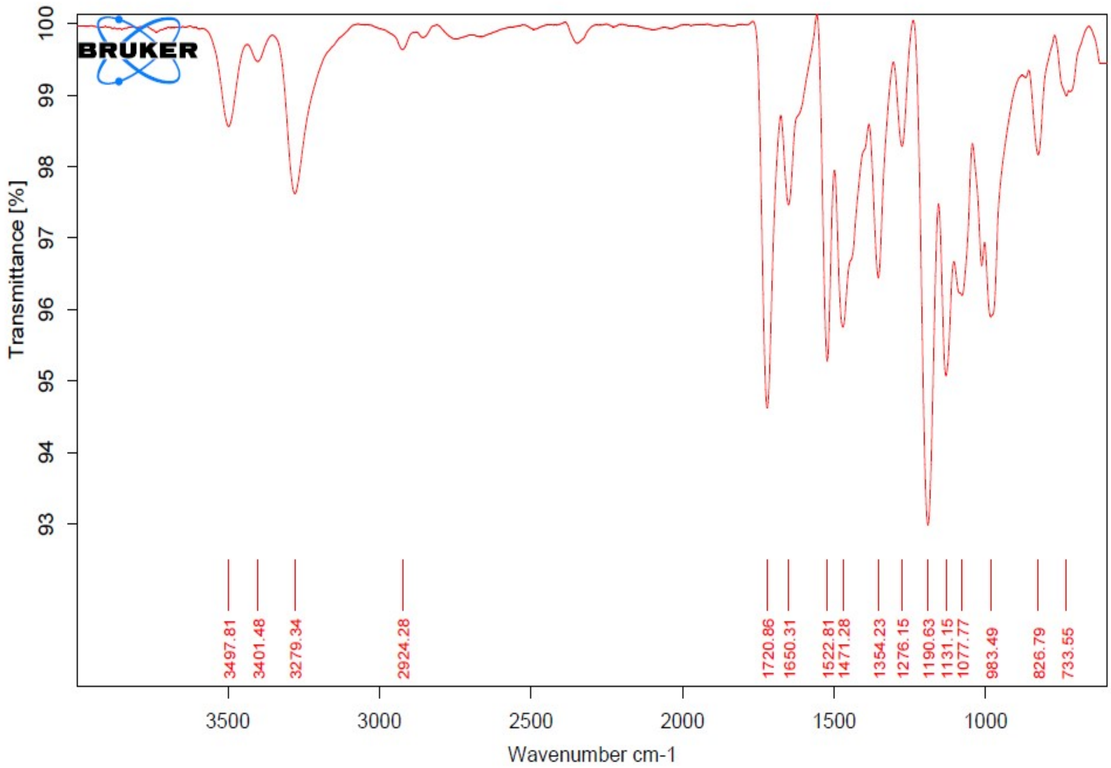


Figure S15: IR Spectrum of Compound 5.

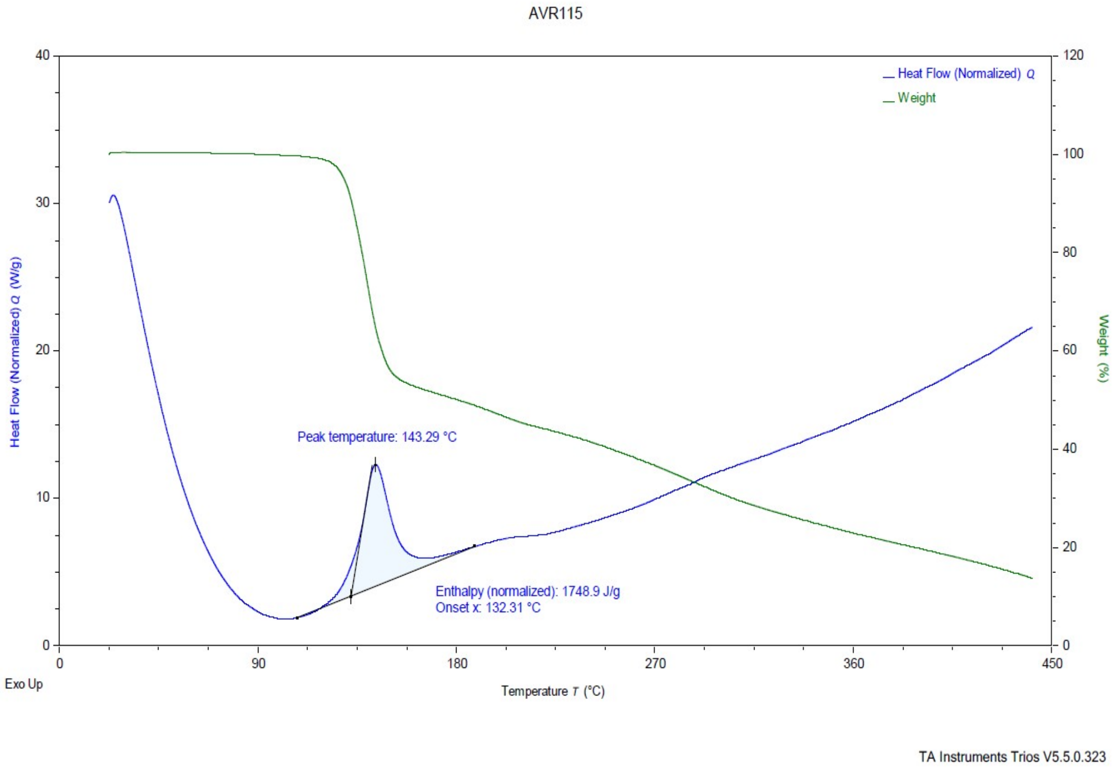


Figure S16. DSC Plot of Compound 5 at Heating rate 5 °C min^{-1}.

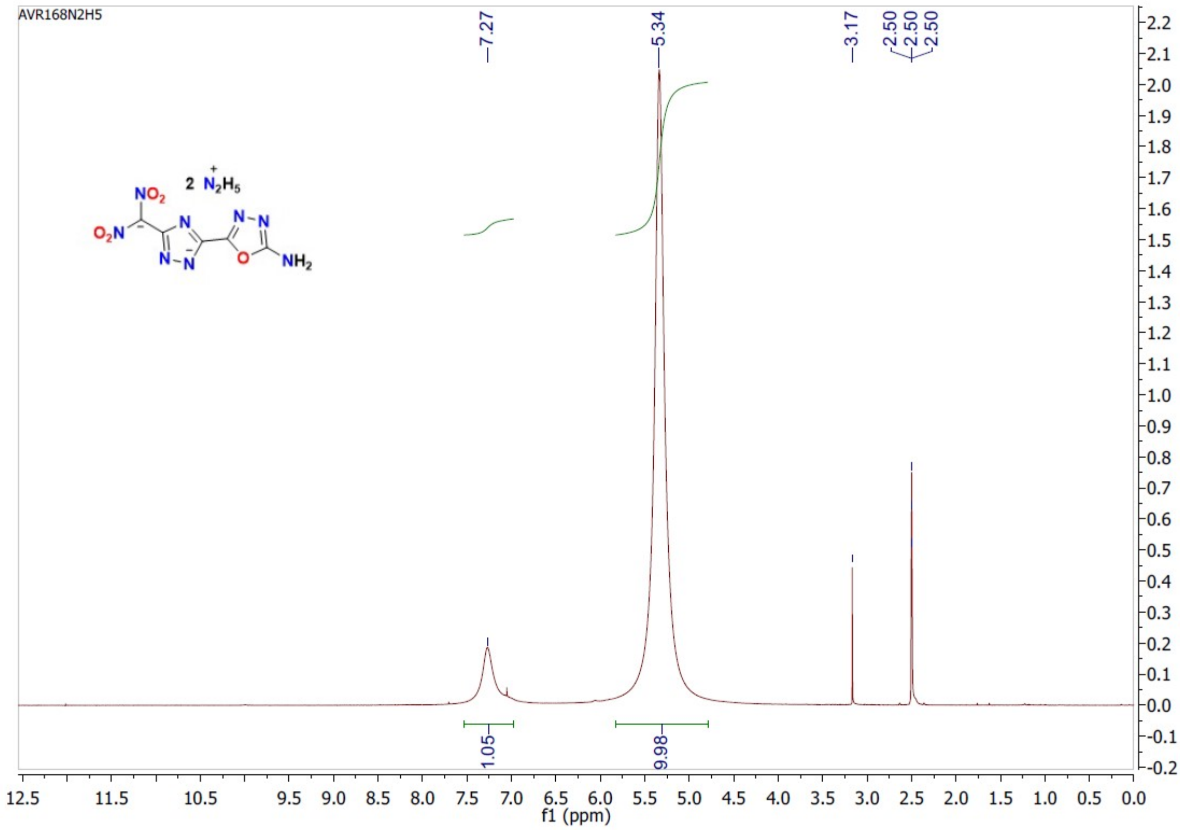


Figure S17: ^{1}H NMR Spectra of Compound 6 (recorded in *d_6*-DMSO).

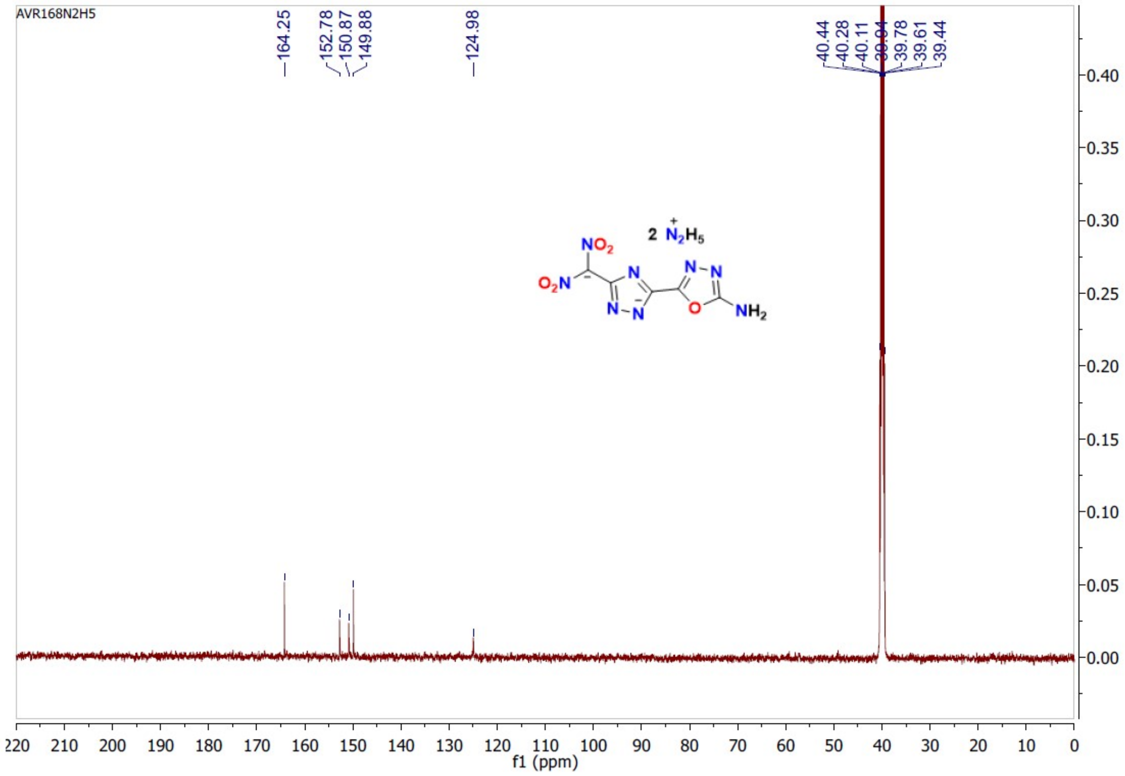


Figure S18: ^{13}C NMR Spectrum of Compound 6 (recorded in *d_6*-DMSO).

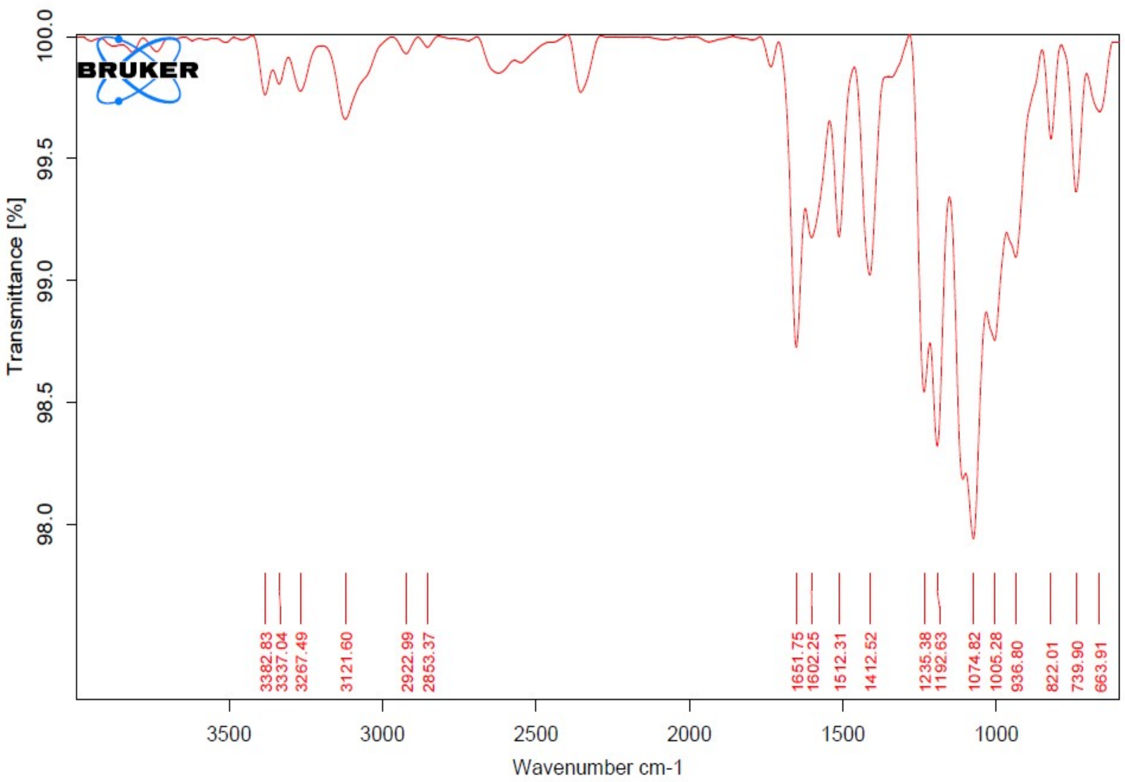


Figure S19: IR Spectra of Compound 6.

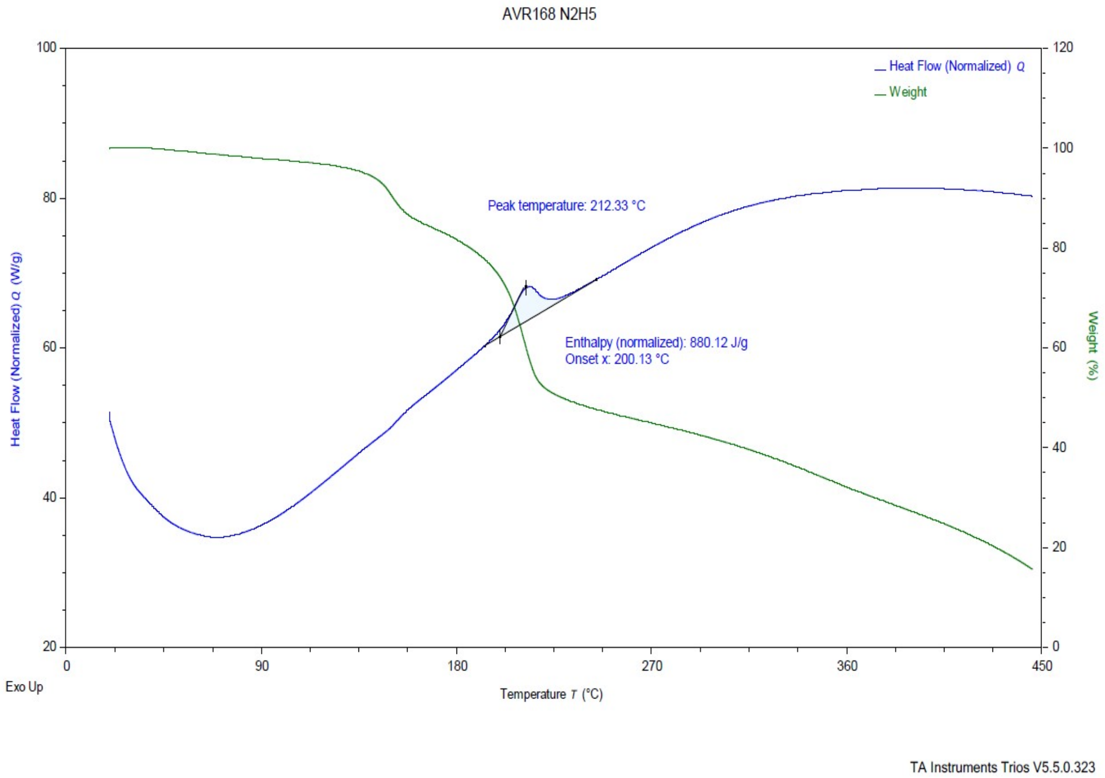


Figure S20. DSC Plot of Compound 6 at Heating rate 5 ^{o}C min^{-1}.

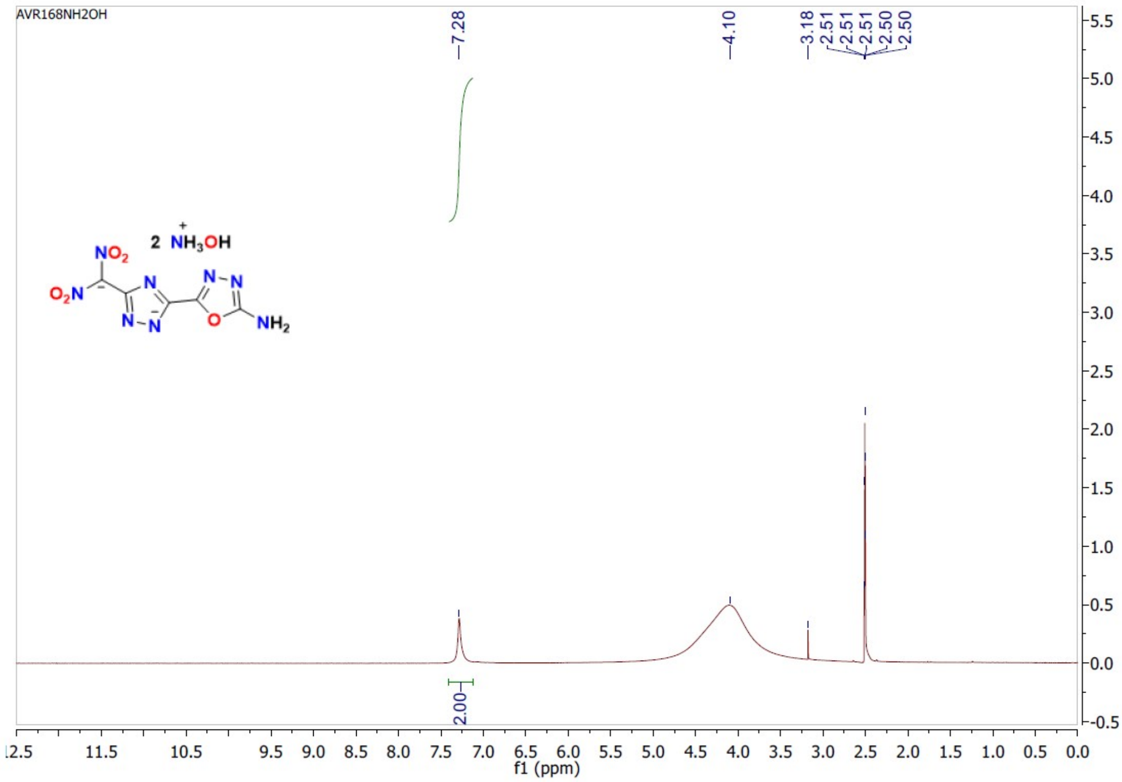


Figure S21: ^{1}H NMR Spectrum of Compound 7 (recorded in d_6-DMSO).

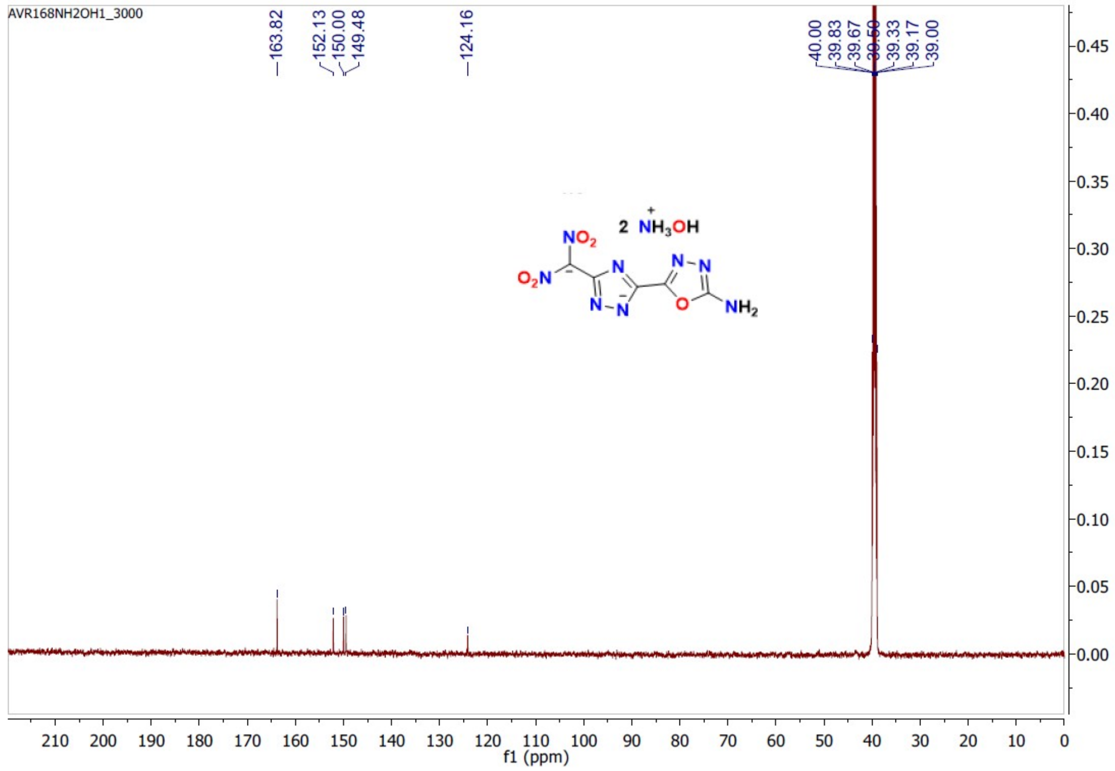


Figure S22: ^{13}C NMR Spectrum of Compound 7 (recorded in d_6-DMSO).

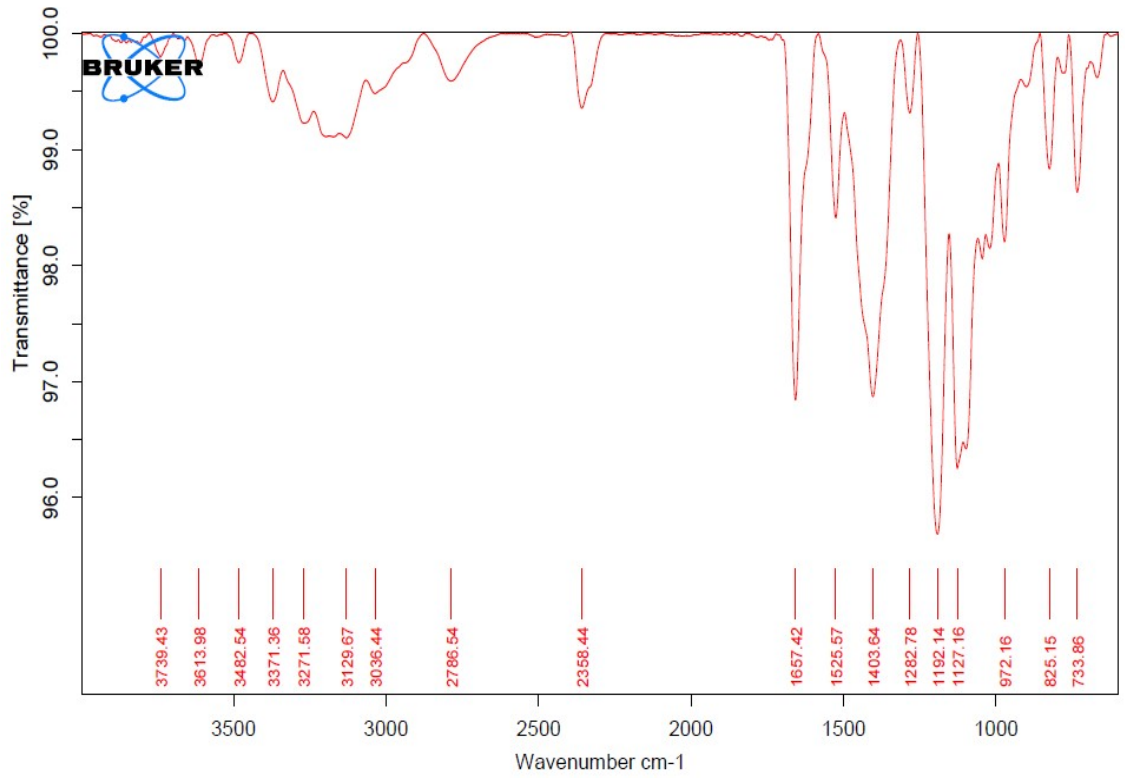


Figure S23: IR Spectra of Compound 7.

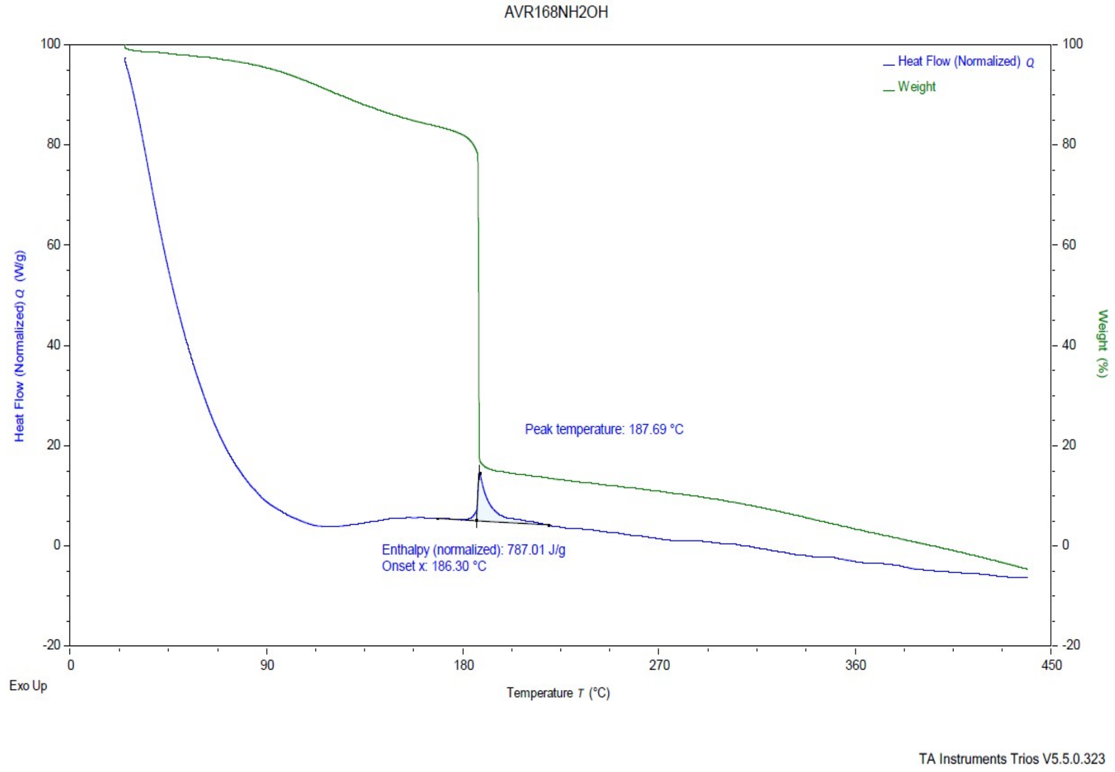


Figure S24. DSC Plot of Compound 7 at Heating rate 5 °C min^{-1}.

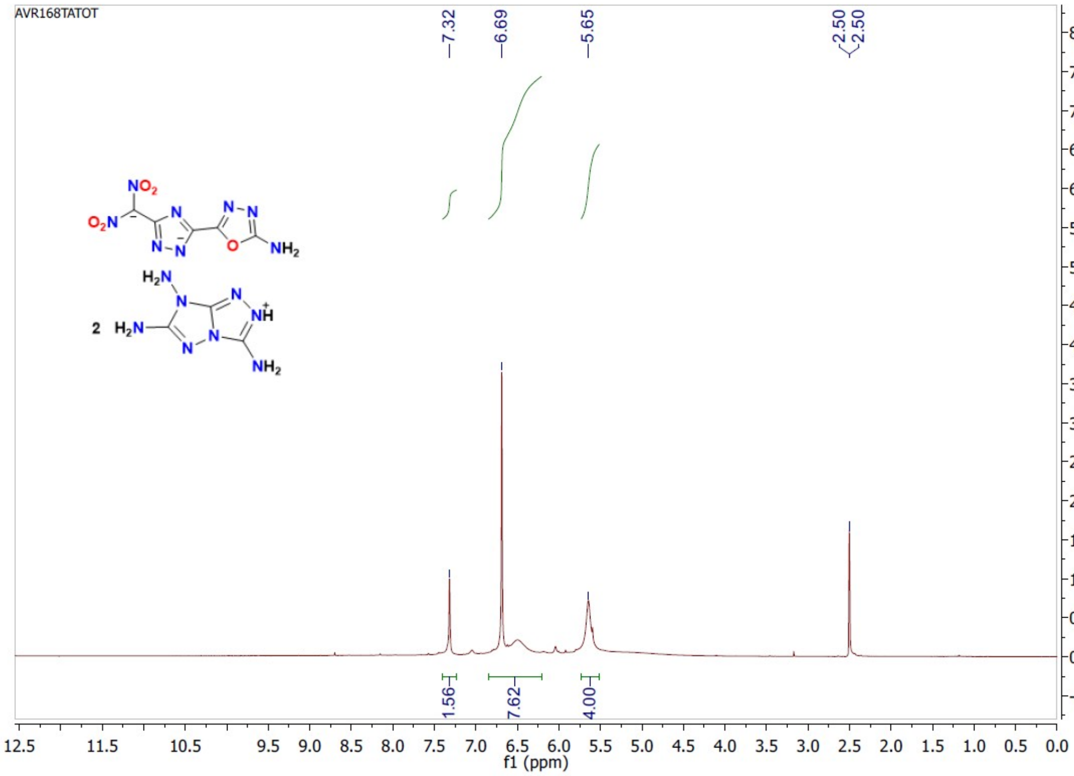


Figure S25: ^{1}H NMR Spectrum of Compound 8 (recorded in d_6-DMSO).

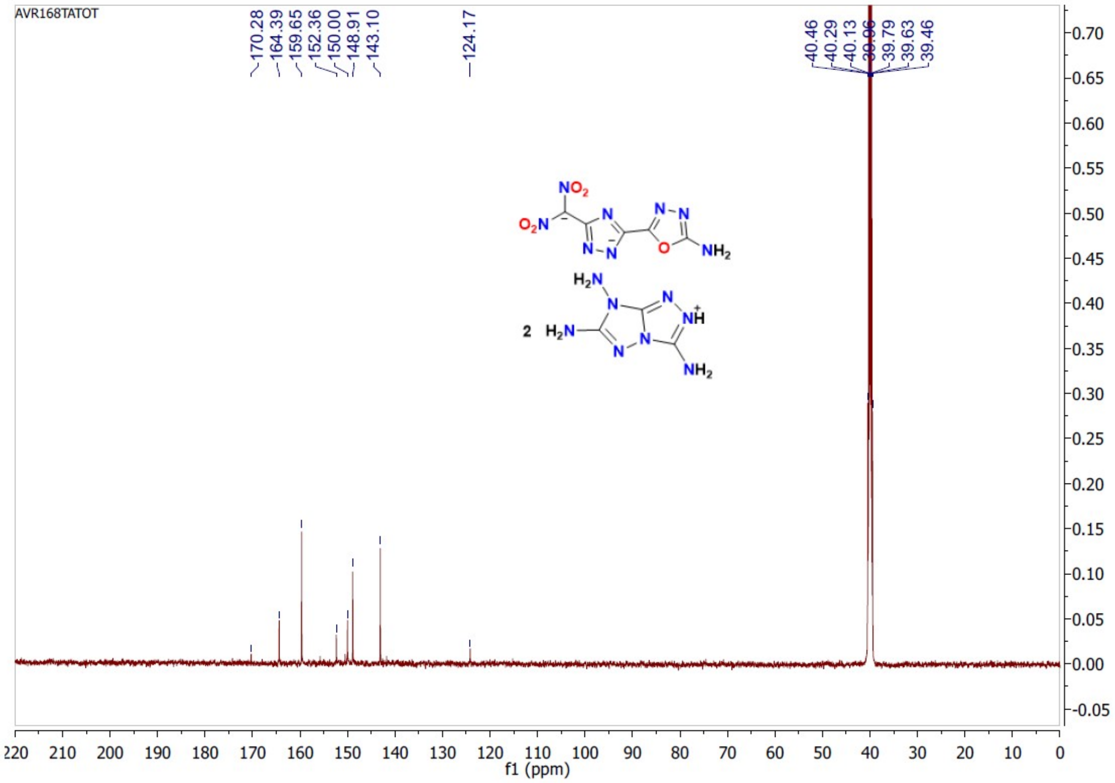


Figure S26: ^{13}C NMR Spectrum of Compound 7 (recorded in d_6-DMSO).

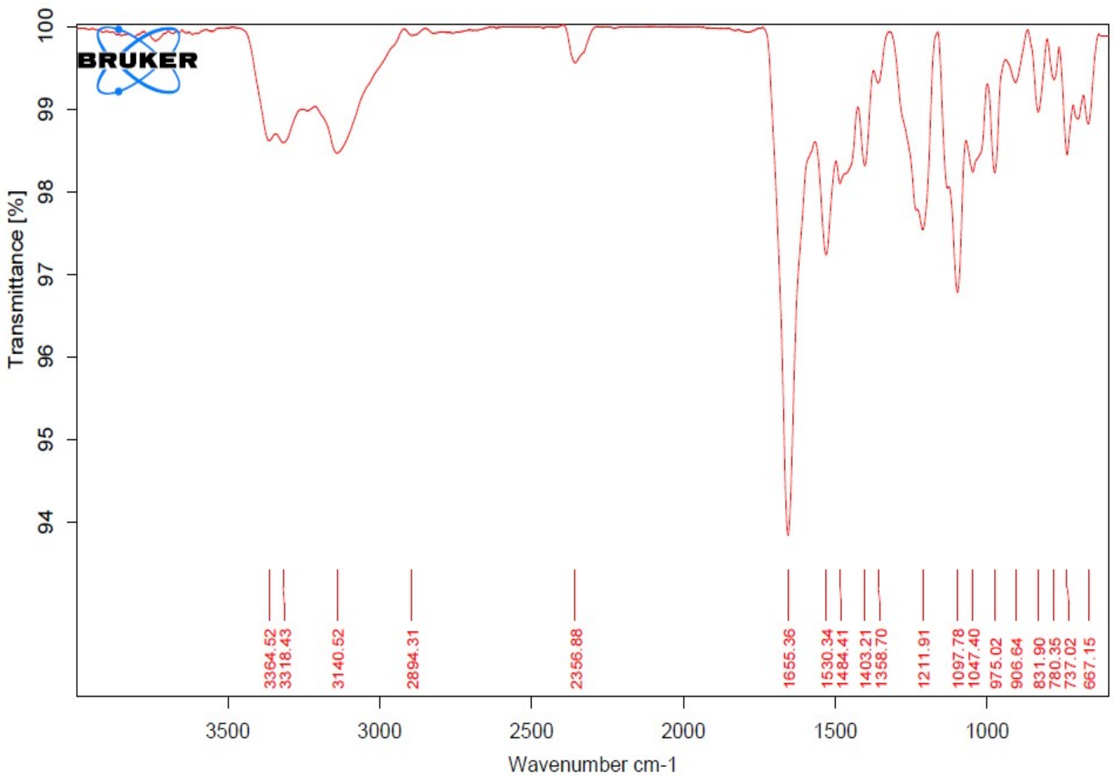


Figure S27: IR Spectrum of Compound 8.

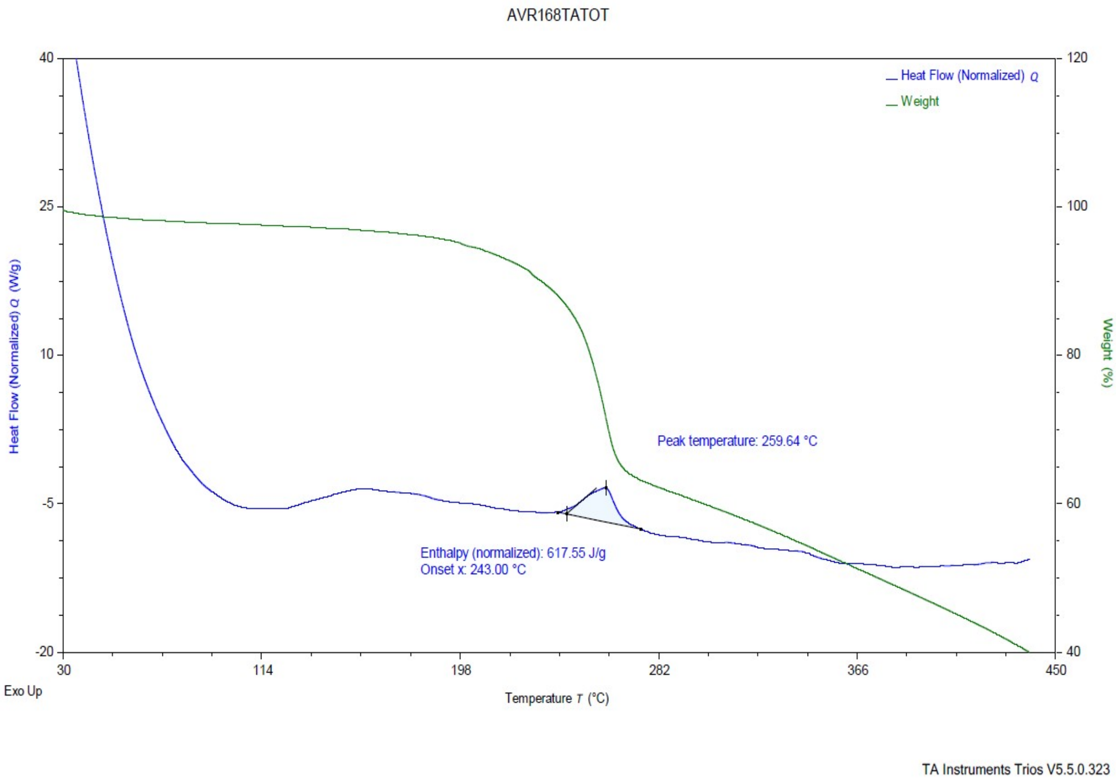


Figure S28. DSC Plot of Compound 8 at Heating rate 5 ^{o}C min^{-1}.

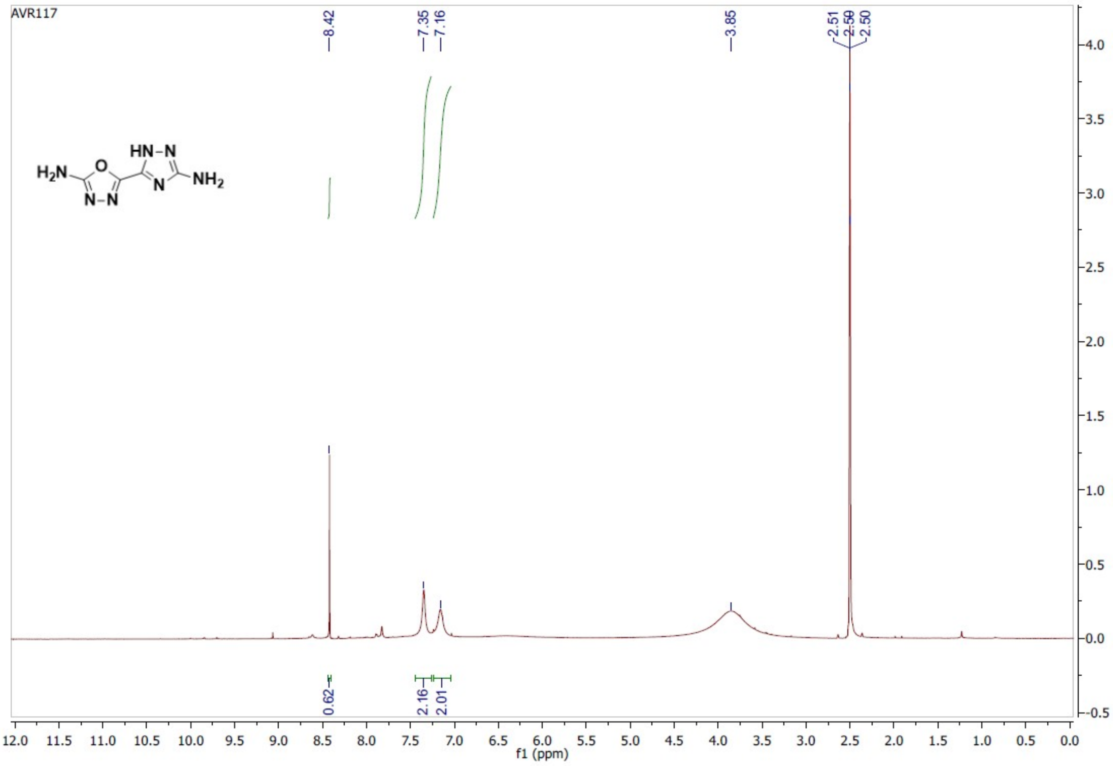


Figure S29: ^{1}H NMR Spectrum of Compound 9 (recorded in d_6-DMSO).

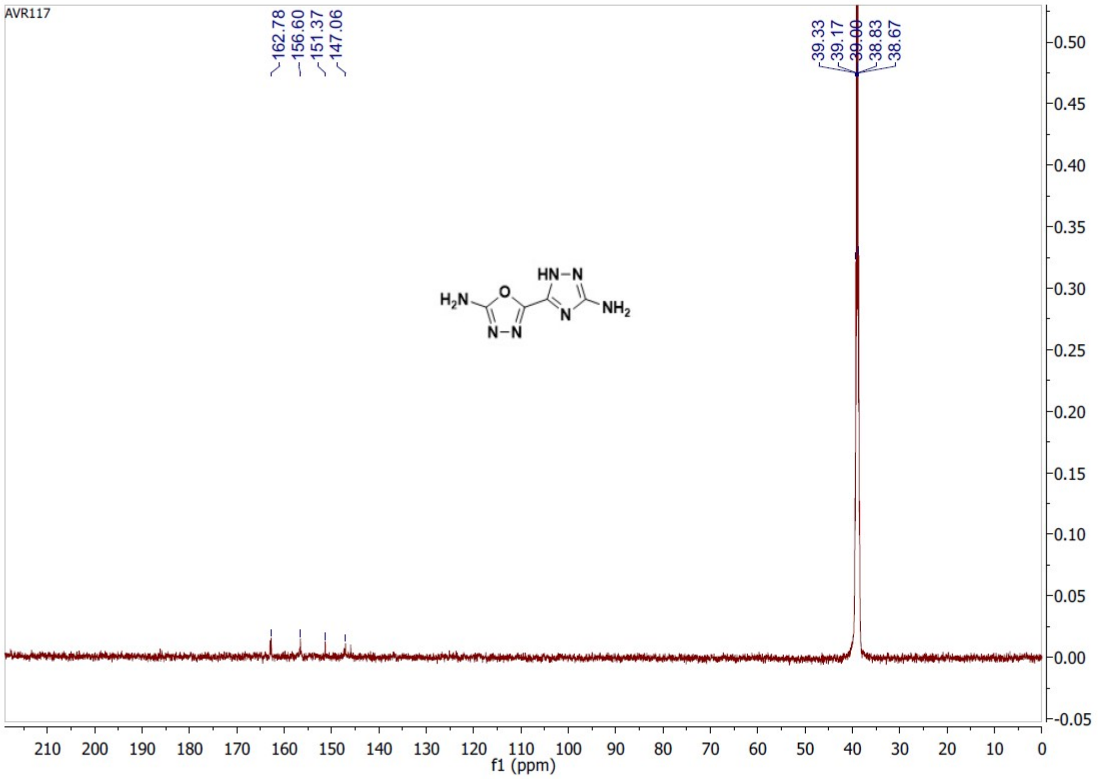


Figure S30: ^{13}C NMR Spectrum of Compound 9 (recorded in d_6-DMSO).

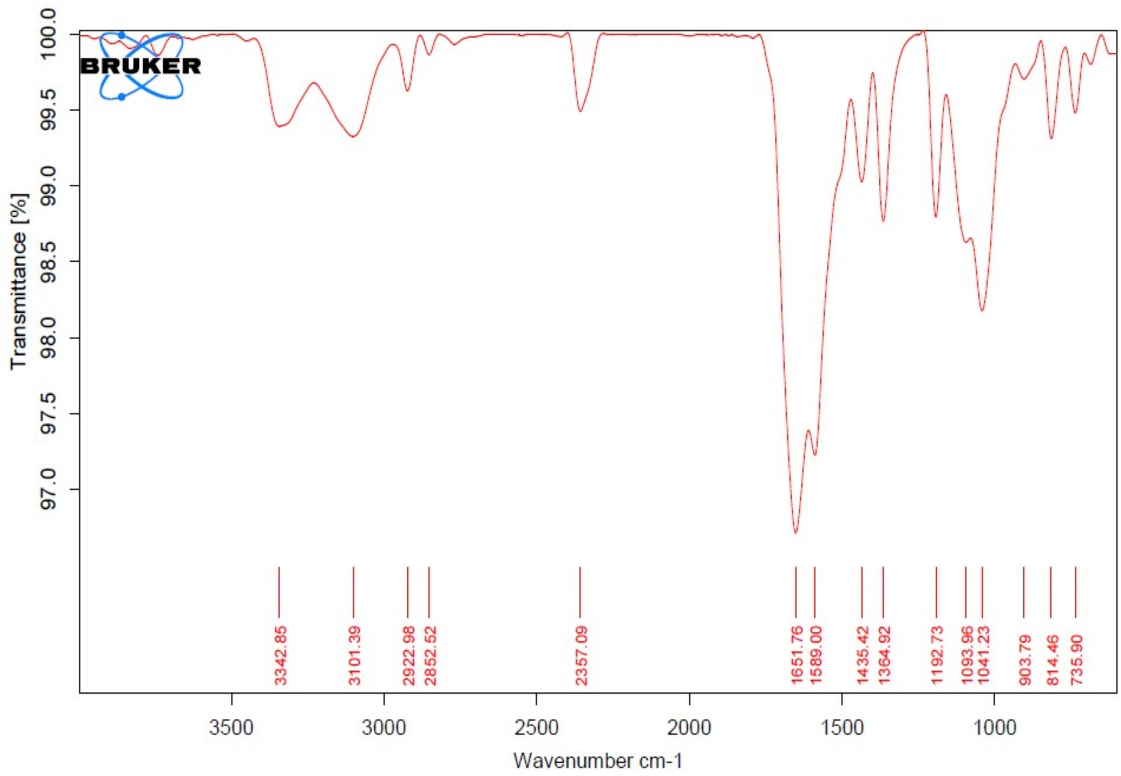
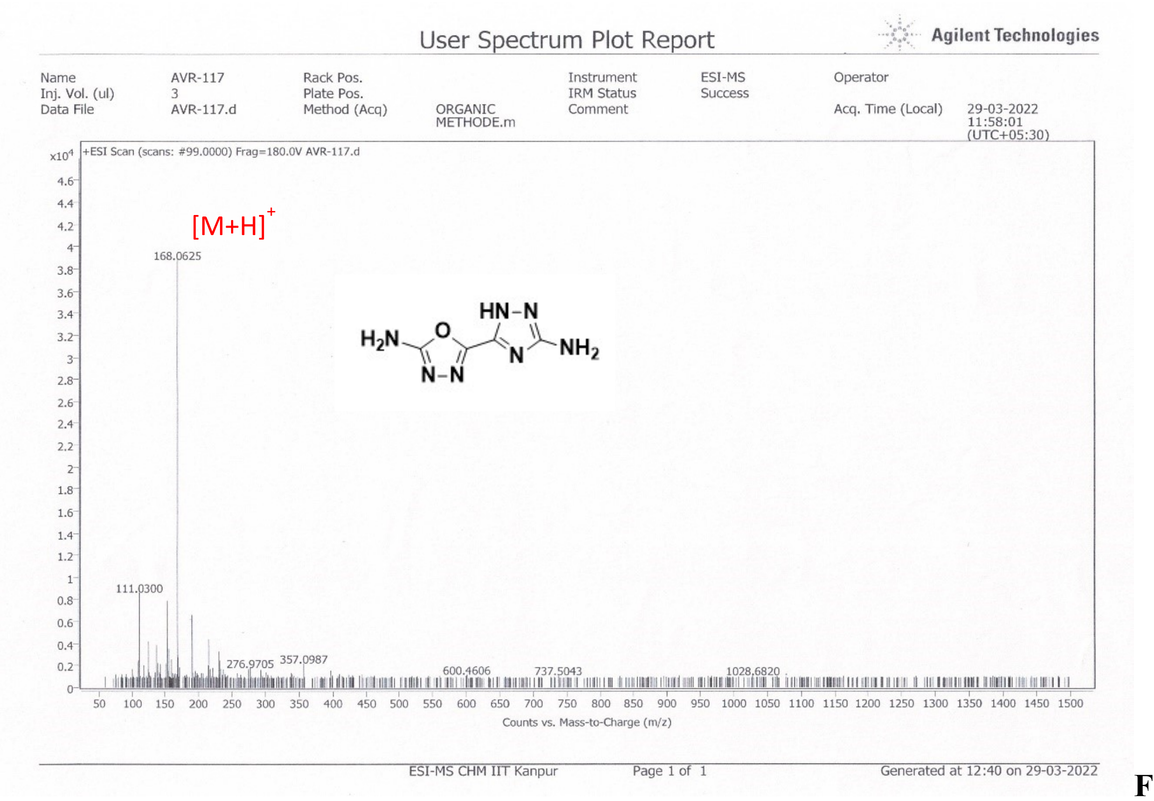


Figure S31: IR Spectrum of Compound 9.


User Spectrum Plot Report

Agilent Technologies

Name	AVR-117	Rack Pos.		Instrument	ESI-MS	Operator	
Inj. Vol. (ul)	3	Plate Pos.		IRM Status	Success		
Data File	AVR-117.d	Method (Acq)	ORGANIC METHODE.m	Comment		Acq. Time (Local)	29-03-2022 11:58:01 (UTC+05:30)

+ESI Scan (scans: #99.0000) Frag=180.0V AVR-117.d

ESI-MS CHM IIT Kanpur Page 1 of 1 Generated at 12:40 on 29-03-2022

Figure S32: Mass Spectrum of Compound 9.

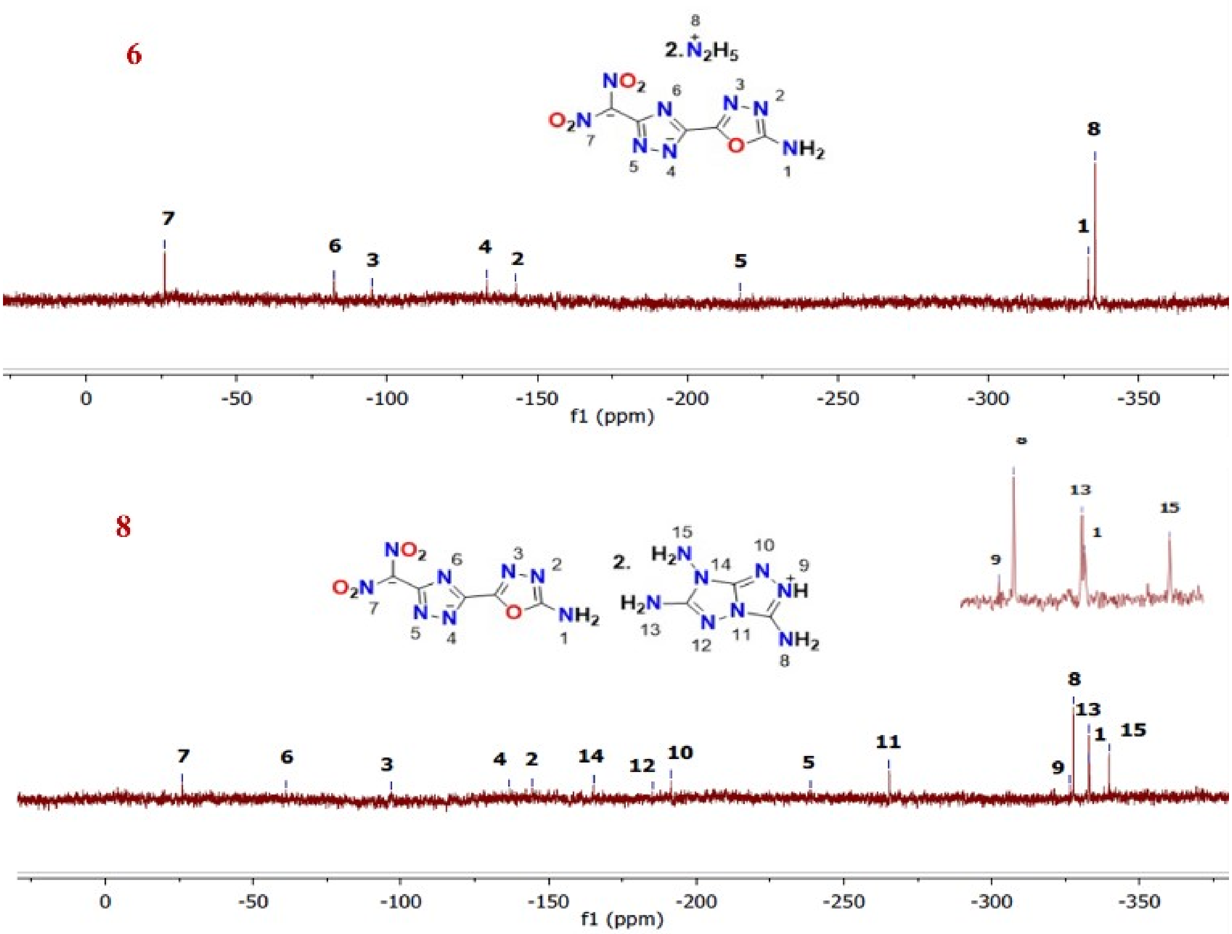


Figure S33. **^{15}N NMR (proton decoupled) spectrum of compounds 6 and 8 (recorded in *d_6*-DMSO with 8192 scans).**

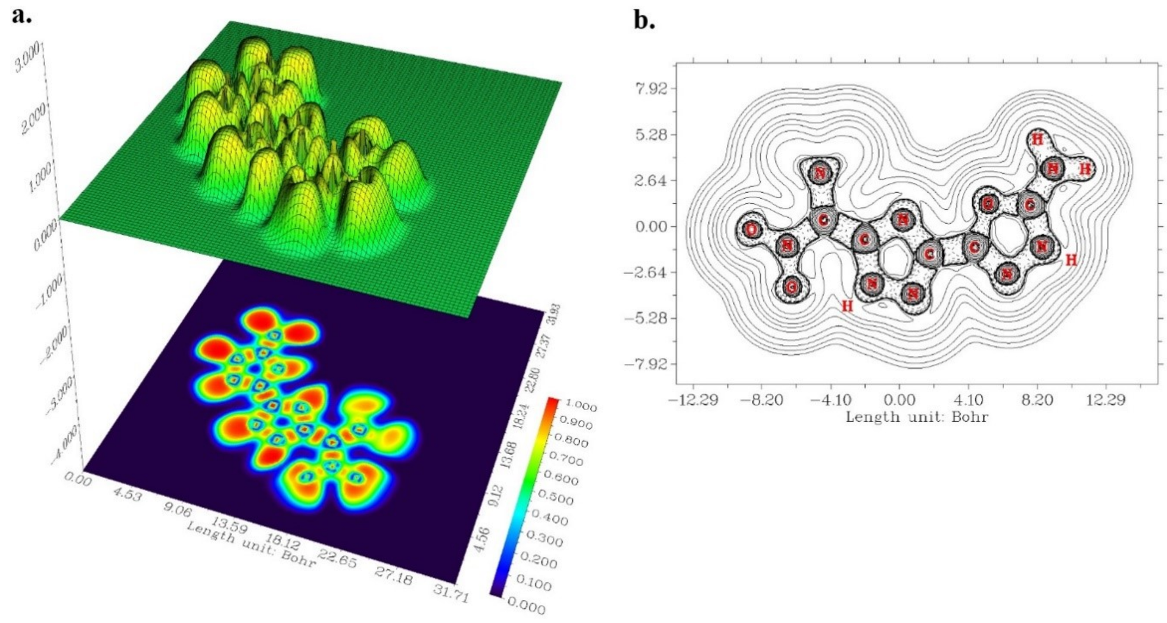


Figure S34. a. Shaded surface plot with projection showing effect of electron localization function and b. contour map of electron density Laplacian of compound **5**.

Computational Details

Computations were carried out using the Gaussian 09 program suite.[1] The structure optimizations are performed with B3PW91 functional with 6-31G(d,p) basis set and characterized to be true local energy minima on the potential energy surface and no imaginary frequencies were found. Isodesmic reactions have been designed to predict the gas phase HOF (HOF_{gas}) and shown in Figure S35. The total energies (E_0), zero point correction (ZPE), thermal corrections (H_T), and the experimental/calculated HOF values of the reference compounds used in isodesmic reactions and other derivatives are given in Tables S8 and S9. The usage of 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}) can effectively reduce the errors. The HOF_{solid} is calculated as the difference between HOF_{gas} and heat of sublimation (HOF_{sub}) as,

$$\mathrm{HOF}_{solid} = \mathrm{HOF}_{gas} - \mathrm{HOF}_{sub} \quad (1)$$

HOF_{sub} depend on the molecular surface properties and calculated using equation (2) proposed by Politzer et al.,[2]

$$HOF_{sub} = 4.4307\ x\ 10^{-4}A^2 + 2.0599\left(v\sigma_{tot}^2\right)^{0.5} - 2.4825 \quad (2)$$

where A represent 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 molecular surface properties (see Table S10) were obtained using the Multiwfn program.[3] The HOF of energetic salts were predicted using Born–Haber cycle (Figure S36) and can be simplified by the equation (3),

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

in above equation, H_L is the lattice energy of the salts (see Table S11), which can be predicted by using the formula proposed by Jenkins et al.[4]

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

The nature of the cation M_p^+ and anion X_q^- decide n_M and n_X values, respectively and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. U_{POT} is the lattice potential energy, calculated using the density (ρ in g/cm^3) and the chemical formula mass (M in g/mol) of the ionic salt.

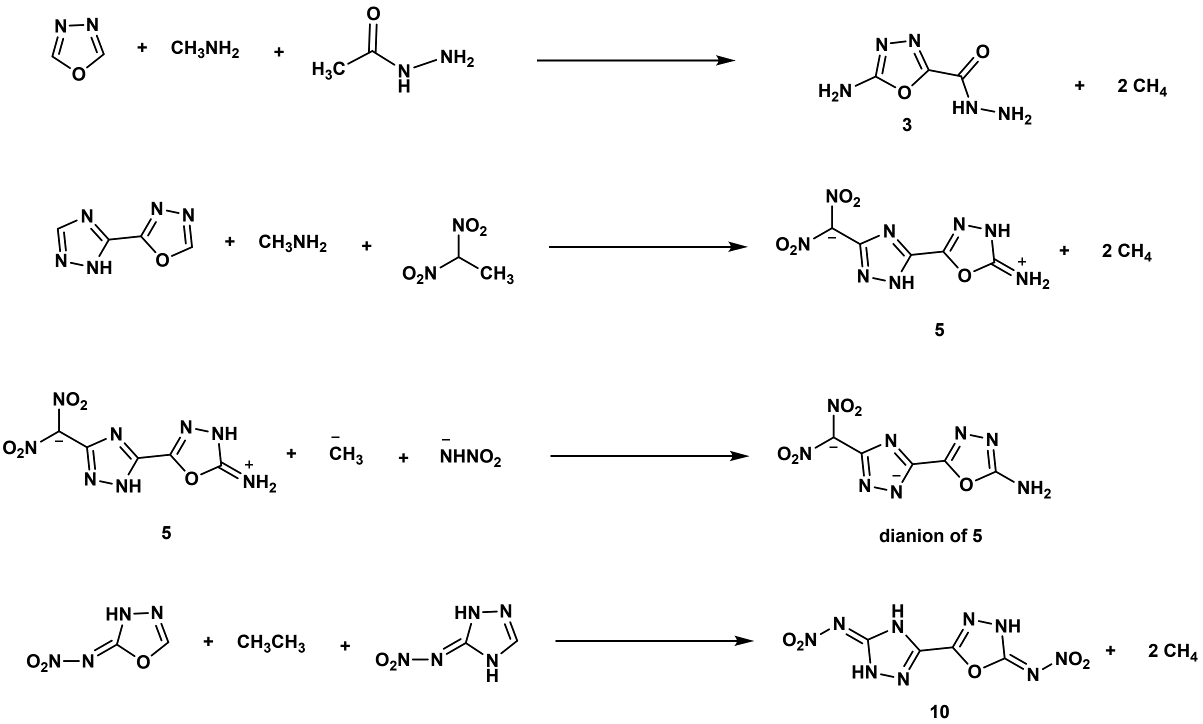


Figure S35. Designed isodesmic reactions for the prediction of HOF_{gas} of compounds **3**,**5**, **10** and corresponding anion.

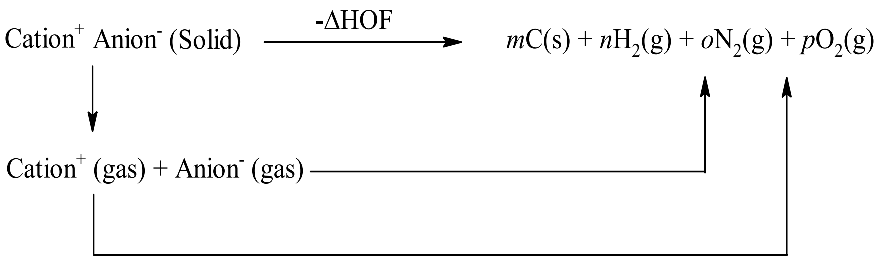
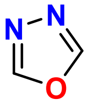
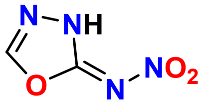
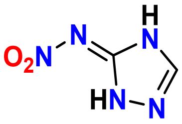
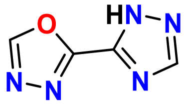
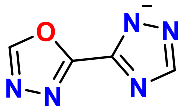


Figure S36. Born-Haber cycle for the formation of energetic salts.

Table S8. 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 B3PW91/6-31G(d,p) level.

Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**	**HOF_{gas} (kJ/mol)**
CH_3NO_2	-244.866526	0.0502	0.0053	-81
CH_3NH_2	-95.759911	0.0644	0.0043	-23.5
CH_4	-40.459807	0.045	0.0039	-74.8
NH_2NO_2	-260.8979	0.0399	0.0046	-6
$NHNO_2$ anion	-260.334021	0.0268	0.0042	-103.24[a]
CH3 anion	-39.749553	0.0279	0.0039	145.14[a]
CH3-CH3	-79.730113	0.075	0.0044	-84
	-261.945517	0.0468	0.0043	63.6
	-521.666459	0.0671	0.0076	111.88[a]
	-501.819085	0.0802	0.0077	242.44[a]
$CH_3C(O)NHNH_2$	-264.346634	0.0915	0.0074	-120.01[a]
	-502.874452	0.0874	0.0079	276.44[a]
	-502.338431	0.0736	0.0076	116.13[a]
$CH_3CH(NO_2)_2$	-488.544782	0.0817	0.0087	-101.77[a]

[a]Calculated using G4 method.

Table S9. Calculated total energies at 298K (E_0), zero point energies (ZPE), and thermal corrections (H_T) and experimental HOF_{gas} of target compounds at the B3PW91/6-31G(d,p) level.

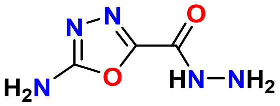
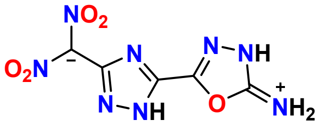
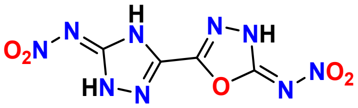
Compd.	**E_0 (a.u.)**	**ZPE (au)**	**H_T (au)**
	-541.166467	0.1078	0.0106
	-1006.282937	0.1376	0.016
	-1022.299959	0.1265	0.0152

Table S10. Calculated molecular surface properties and heat of sublimation of target compounds.

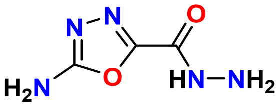
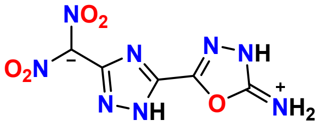
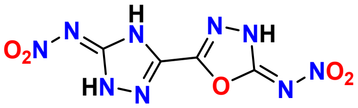
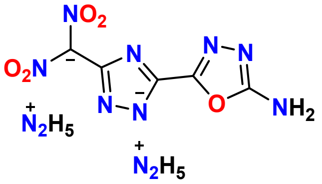
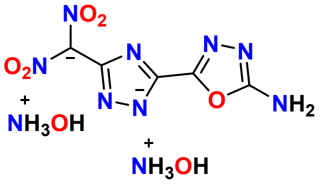
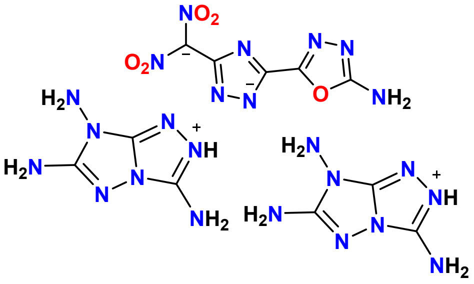
Compd.	**Surface area (Å^2)**	**Volume (Å^3)**	**σ_{tot}^2 (kcal/mol)^2**	**v**	**$HOF_{Sublimation}$ (kJ/mol)**
	162.32	149.09	385.10	0.2498	109.61
	243.60	238.42	478.21	0.1649	140.08
	237.56	229.96	352.31	0.1939	132.58

Table S11. Energy content of salts **6-8**.

Salt	**HOF$_c$**[a]	**HOF$_a$**[b]	**U$_{Pot}$**[c]	**H$_L$**[d]	**HOF$_{salt}$**[e]
	769.5	59.16	1293.6	1306.05	292.10
	675.6	59.16	1312.84	1325.23	85.12
	1112.0	59.16	1044.84	1057.23	1225.9

[a] Heat of formation of cation (kJ mol^{-1}). [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}).

Reference:

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.
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