Electronic Supplementary Information

Isomer-Driven Pyrazole Frameworks: Structural and Zwitterionic Insights for Advanced Energetics

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1. General Experimental

All reagents (analytical grade) were purchased from AK Scientific or VWR and were used as supplied. ^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded using a 500 MHz (Bruker Advance) NMR spectrometer operating at 500.19 125.78, and 36.14 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si as internal standard and ^{14}N spectra to nitromethane as an external standard. The decomposition temperatures (onset) were obtained on a differential scanning calorimeter (TA Instruments Company, Q2000) at a scan rate of 5 °C min^{-1}. Infra-red spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The room temperature densities were measured at 25 °C by employing a gas pycnometer (Micromeritics AccuPyc II 1340). The impact and friction sensitivities were determined by using a standard BAM drop hammer and BAM friction tester. Elemental analyses were carried out on a Vario Micro cube Elemental Analyzer.

The crystal structure of **5** was determined through electron diffraction of a powder sample, showcasing the utility of this method for characterizing complex energetic materials when single-crystal growth is challenging. Suitable single crystals of **8** and **11** were obtained for SC-XRD analysis through slow evaporation of their saturated solutions in methanol.

Experimental Procedure for Data Collection of 5: A portion of the crystalline sample was carefully crushed between two glass slides to make grains thin enough for micro-ED. A 3mm Cu TEM grid with continuous carbon film was dropped into this powder to gather grains. Data was collected on a Rigaku XtaLAB Synergy-ED electron diffractometer, configured with an electron source operating at 200kV and a HyPix-ED detector.

Yellow crystals of **8**, and **7a** with dimensions 0.23 × 0.06 × 0.01 mm^3, and 0.11 × 0.04 × 0.01 mm^3, respectively, were selected and mounted on nylon loops with Paratone oil on a XtaLAB Synergy, Dualflex, HyPix diffractometer. The crystals were kept at a constant T = 100 K during data collection.

The structures were solved with the ShelXT[S1] solution program using dual methods and by using Olex2.[S2] The model was refined with ShelXL[S3] using full matrix least squares minimization on F^2. The packing coefficient was calculated using Platon version 90622. The value of the Packing Index for a given structure (as an INS or CIF file) was determined by selecting the 'CALC K.P.I.' function from the PLATON main menu.

Crystallographic data (including the structure factor files) for structures **5, 8,** and **11** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers **CCDC** 2407425, 2407426, and 2407427, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2. Experimental Section

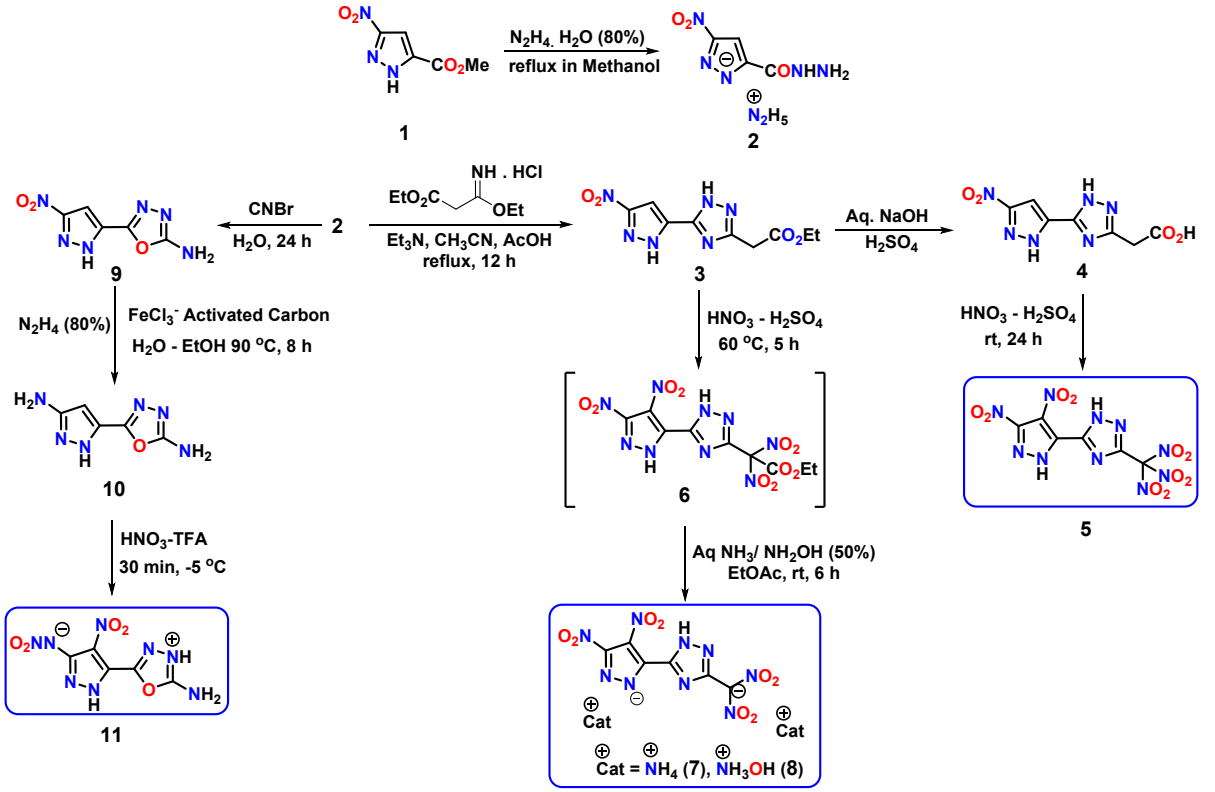
***Caution*.** All the compounds prepared are energetic materials and sensitive towards external stimuli. Mechanical actions involving scratching or scraping must be avoided. While we have not encountered any issues in the handling of these compounds, proper protective measures

(face shield, eye protection, apron and leather gloves) should be taken at all times. In addition, all of the energetic compounds were prepared only on a small scale and handled using a plastic spatula.

Synthesis of compound 1: methyl 3-nitro-1*H*-pyrazole-5-carboxylate was prepared according to the literature procedure.[S4]

Synthesis of compound 2. In an oven-dried 100 mL round-bottomed flask, 3-nitro-1*H*-pyrazole-5-carboxylic acid methyl ester (2.5 g, 14.6 mmol) was dissolved in methanol (40 mL). Hydrazine hydrate (80%, 9 mL) was added dropwise to the solution with stirring. The reaction mixture was heated at reflux at 80 °C for 12 hours. After completion, the solution was cooled and refrigerated overnight, resulting in a yellow crystalline precipitate. The precipitate was collected by filtration, washed three times with cold ethanol (10 mL each), and dried under reduced pressure to yield compound **2** as a yellow solid.

2: Yellow Solid; Yield: 85%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.08 (s, 1H), 5.49 (br, 5H + H_2O) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 162.1, 157.4, 144.9, 101.4 ppm. FTIR (cm^{-1}) ῡ 3312, 3246, 3092, 2545, 1617, 1531, 1456, 1360, 132, 1265, 1148, 1115, 1081, 1010, 987, 964, 875, 815. Elemental analysis: Calcd (%) for $C_4H_9N_7O_3$ (203.08): C, 23.65; H, 4.47; N, 48.26; Found: C 23.72, H 4.25, N 48.51.



Scheme S1: Isomer-driven synthesis of compounds **5**, **11**, and energetic salts **7** and **8** from the key precursor, hydrazinium 3-nitro-1*H*-pyrazole-5-carbohydrazide (**2**).

Synthesis of 3. Ethyl 3-ethoxy-3-iminopropanoate (6 g, 30.7 mmol) was dissolved in ethanol (15 mL), followed by the addition of triethylamine (3 mL, 21.5 mmol) with stirring at room temperature for 1 hour. Compound **2** (1.8 g, 8.87 mmol) and glacial acetic acid (30 mL) were then added to the reaction mixture. The resulting solution was refluxed at 110 °C for 12 hours.

After cooling to room temperature, most of the solvent was evaporated under reduced pressure. The residue was treated with water to induce recrystallization. The precipitate was collected by filtration, washed with cold water, and dried to afford compound **3** as a pale-yellow solid.

3: Pale-yellow solid; Yield: 75%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 14.76 (br, 1H), 14.38 (br, 1H), 7.29 (s, 1H), 4.16-4.11(q, 2H), 4.00 (s, 2H), 1.21-1.18 (t, 3H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 168.0, 156.5, 152.2, 151.3, 137.3, 99.5, 61.1, 32.2, 13.9 ppm. FTIR (cm^{-1}) ῡ 3220, 3111, 2852, 1723, 1535, 1474, 1454, 1381, 1247, 1208, 1178, 1057, 1028, 1000, 876, 792. Elemental analysis: Calcd (%) for $C_9H_{10}N_6O_4$ (266.08): C, 40.61; H, 3.79; N, 31.57; Found: C 40.67, H 3.92, N 31.86.

Synthesis of 4. Compound **3** (2 g, 7.5 mmol) was dissolved in an aqueous solution of sodium hydroxide (1.2 g, 30 mmol in 25 mL of distilled water). The reaction mixture was stirred at 80 °C for 1 hour. After cooling to 0 °C, concentrated sulfuric acid was added dropwise until the pH reached 1, and the mixture was stirred at room temperature. A white precipitate formed, which was filtered, washed thoroughly with cold water, and dried at room temperature to yield pure compound **4**.

4: White solid; Yield: 82%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 14.31 (br, 2H), 7.29 (s, 1H), 3.89 (s, 2H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 170.0, 156.5, 153.2, 151.3, 137.2, 99.5, 33.3 ppm. ^{14}N NMR (36.14 MHz, DMSO-d_6) δ -23.5 ppm. FTIR (cm^{-1}) ῡ 3357, 3141, 3067, 2886, 1723, 1684, 1532, 1450, 1358, 1226, 1184, 1156, 1007, 1023, 912, 853, 824. Elemental analysis: Calcd (%) for $C_7H_6N_6O_4$ (238.05): C, 35.30; H, 2.54; N, 35.29; Found: C 35.38, H 2.62, N 35.49.

Synthesis of 5. Compound **4** (0.24 g, 2 mmol) was gradually added to a chilled mixture of concentrated nitric acid (3 mL) and concentrated sulfuric acid (3 mL) maintained at −10 °C using an ice-salt bath. The reaction mixture was stirred at this temperature for 30 minutes and then allowed to gradually warm to room temperature, where it was stirred continuously for 24 hours. After completion, the reaction mixture was poured onto crushed ice and stirred for 30 minutes. The resulting precipitate was collected by filtration, thoroughly washed with ice-cold water followed by trifluoroacetic acid, and dried to yield the product as a white solid.

5: White solid; Yield: 84%; ^{1}H NMR (500.19 MHz, acetonitrile-d_3) δ 13.50 (br, 2H) ppm. ^{13}C NMR (125.78 MHz, acetone-d_6) δ 150.4, 149.9, 146.2, 130.2, 125.9, 103.1 ppm. ^{14}N NMR (36.14 MHz, acetone-d_6) δ -27.3, -28.2. -33.7 ppm. FTIR (cm^{-1}) ῡ 3307, 1617, 1598, 1560, 1537, 1513, 1416, 1369, 1280, 1193, 1130, 1084, 976, 957, 844, 813. Elemental analysis: Calcd (%) for $C_6H_2N_{10}O_{10}$ (374.00): C, 19.26; H, 0.54; N, 37.44; Found: C 19.25, H 0.70, N 37.46.

General procedure for the synthesis for compounds 7 and 8.

Compound **3** (0.24 g, 2 mmol) was carefully added to a chilled mixture of 100% nitric acid (2 mL) and concentrated sulfuric acid (2 mL), maintained at −10 °C in an ice-salt bath. The reaction was stirred at this temperature for 30 minutes, then gradually warmed to room temperature and further heated to 60 °C for 5 hours. Upon completion, the reaction mixture was poured onto crushed ice and stirred for an additional 30 minutes.

The resulting mixture was extracted with ethyl acetate (10 mL), and the organic layer was washed with cold brine solution (3 × 10 mL) and dried over anhydrous sodium sulfate. The dried organic phase was then treated with an excess of aqueous ammonia (for compound **7**) or hydroxylamine (50%) (for compound **8**) and stirred at room temperature for 6 hours. The precipitated yellow solids were filtered, washed with small amounts of ethyl acetate, and dried to yield compounds **7** and **8**, respectively.

7: Yellow solid; Yield: 81%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 5.59 (br, 8H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 152.0, 150.7, 149.3, 137.0, 125.7, 125.2 ppm. ^{14}N NMR (36.14 MHz, DMSO-d_6) δ 17.4, -22.2, -362.9 ppm. FTIR (cm^{-1}) ῡ 3215, 1534, 1411, 1364, 1347, 1326, 1266, 1209, 1152, 1121, 1002, 968, 852, 817. Elemental analysis: Calcd (%) for $C_6H_9N_{11}O_8$ (363.06): C, 19.84; H, 2.50; N, 42.42; Found: C 19.83, H 2.81, N 42.61.

8: Yellow solid; Yield: 77%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 10.26 (br, 8H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 152.1, 150.3, 149.0, 136.5, 125.6, 125.1 ppm. FTIR (cm^{-1}) ῡ 3321, 2980, 2665, 1612, 1519, 1458, 1375, 1336, 1268, 1205, 1134, 1106, 1000, 984, 852, 832, 818. Elemental analysis: Calcd (%) for $C_6H_9N_{11}O_{10}$ (395.05): C, 18.24; H, 2.30; N, 38.99; Found: C 18.29, H 2.61, N 39.21.

Synthesis of 9: Cyanogen bromide (0.43 g, 4.05 mmol) was added to an aqueous solution of compound **2** (0.55 g, 2.7 mmol) in 10 mL of water at room temperature. The reaction mixture was stirred continuously at room temperature for 24 hours. Upon completion, the resulting precipitate was collected by filtration, thoroughly washed with water, and dried to obtain pure compound **9** as a yellow solid.

9: Yellow solid; Yield: 69%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 15.18 (br, 1H), 7.49 (s, 2H), 7.35 (s, 1H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 161.1, 156.3, 149.0, 130.6, 100.7 ppm. FTIR (cm^{-1}) ῡ 3447, 3342, 3147, 2602, 1664, 1620, 1427, 1384, 1329, 1234, 1187, 1079, 1032, 985, 936, 827. Elemental analysis: Calcd (%) for $C_5H_4N_6O_3$ (196.03): C, 30.62; H, 2.06; N, 42.85; Found: C 30.78, H 2.31, N 42.71.

Synthesis of 10. A mixture of nitro derivative **9** (0.2 g, 1 mmol), hydrazine hydrate (0.2 mL, 4 mmol), $FeCl_3 \cdot 6H_2O$ (1.4 mg), and activated carbon (0.18 g) in a 1:1 ethanol-water solution (6 mL) was refluxed for 9 hours. After cooling, the activated carbon was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was dissolved in water and acidified with hydrochloric acid to adjust the pH to 3-4. The resulting gray precipitate was collected by filtration, washed with cold water, and air-dried to yield compound **10**.

10: Gray solid; Yield: 65%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 11.93 (br s, 1H), 7.04 (s, 2H), 5.63 (s, 1H), 5.20 (s, 2H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 163.1, 154.4, 149.1, 137.3, 86.0 ppm. FTIR (cm^{-1}) ῡ 3165, 3094, 2990, 1658, 1626, 1586, 1433, 1388, 1239, 1142, 1083, 1031, 994, 947, 859. Elemental analysis: Calcd (%) for $C_5H_6N_6O$ (166.06): C, 36.15; H, 3.64; N, 50.58; Found: C 35.78, H 3.80, N 50.87

Synthesis of 11. A solution of diamine **10** (0.2 g, 1.2 mmol) in trifluoroacetic acid (TFA, 4 mL) was cooled to -5 °C. Concentrated nitric acid (1.2 mL) was added dropwise while maintaining the temperature. The reaction mixture was stirred at this temperature for 30 minutes. Afterward, the solvent was removed by air evaporation, and ice-cold water was added to the residue with

stirring. The resulting precipitate was collected by filtration, washed with cold water (2 mL), and air-dried to obtain compound **11**.

11: Yellow solid; Yield: 74%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.76 (br, 2H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 164.2, 148.7, 140.6, 129.3, 124.5 ppm. ^{14}N NMR (36.14 MHz DMSO-d_6) δ -25.4 ppm. FTIR (cm^{-1}) ῡ. 3565, 3352, 3290, 1716, 1544, 1462, 1436, 1351, 1293, 1189, 1111, 1040, 1018, 974, 943, 868. Elemental analysis: Calcd (%) for $C_5H_4N_8O_5$ (256.03): C, 23.45; H, 1.57; N, 43.75; Found: C 23.27, H 1.72, N 43.70.

3. Theoretical Study and Isodesmic reactions

The heat of formation (HOF) for all compounds were calculated by using isodesmic reactions. The single crystal structures were used for the geometric optimization and frequency analyses using the B3LYP functional with the 6-31+G** basis set. The single-point energies were obtained at the MP2/6-311++G** level.[S5] The atomization energies for cations were calculated by using the G^{2}ab *initio* method.[S6] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. In case of the energetic salts, the solid-phase heats of formation were obtained based on a Born–Haber energy cycle (1).[S7]

Based on the Born−Haber energy cycle (Figure S1), the solid phase heat of formation of ionic compounds can be simplified by equation 1

$$HOF\ (salt, 298\ K) = HOF\ (cation, 298\ K) + HOF\ (anion, 298\ K) - \Delta H_L \quad (1)$$

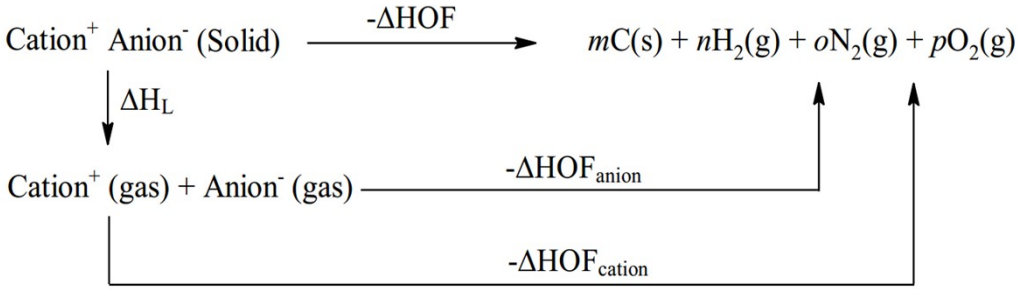


Figure S1: Born-Haber cycle for the formation of energetic salts.

In eq 1, the lattice energy (ΔH_L) of energetic salts could be predicted by using the formula suggested by the literature [equation 2].

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

in which n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form [equation 3]:

$$U_{POT}/kJ\ mol^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

in which ρ_m (g cm^{-3}) is the density, M_m is the chemical formula mass of the ionic compound, g (or Mg), and values for the coefficients γ/kJ mol^{-1} cm) and δ/kJ mol^{-1} are taken from the literature.[S7]

Gas-phase heat of formation to solid state heat of formation

All calculated gas-phase enthalpies (HOF_{Gas}) for covalent materials are converted to solid phase (HOF_{Solid}) (4) values by subtracting the empirical heat of sublimation (HOF_{Sub}) obtained based on Trouton's rule according to equation 5 (T represents either the melting point of the decomposition temperature when no melting occurs prior to decomposition).[S8]

$$HOF_{Solid} = HOF_{Gas} - HOF_{Sub} \quad (4)$$

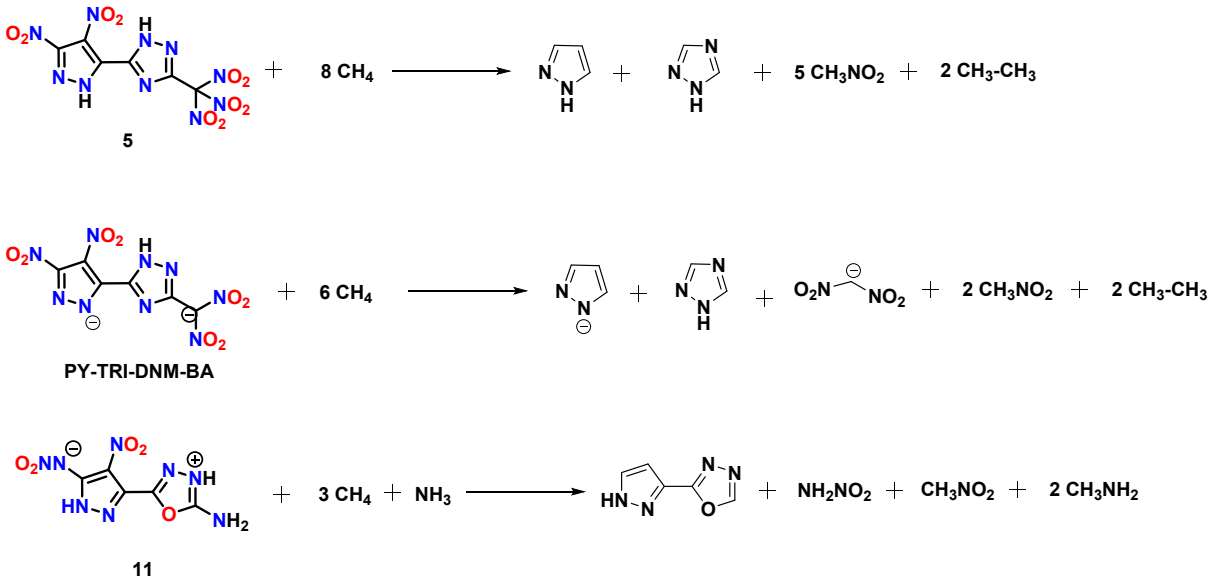
$$HOF_{Sub} = 188/Jmol^{-1}K^{-1} \text{ X T} \quad (5)$$

HOF_{Sub} (For Compound **5**) = 0188 * (273 + 163.9) = 82.13 ~ 82 kJ/mol

HOF_{Sub} (For Compound **11**) = 0188 * (273 + 242.7) = 96.9 ~ 97 kJ/mol

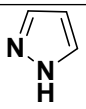
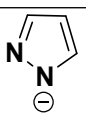
Table S1: Solid state heat of formation for 5 and 11 using Trouton's rule.

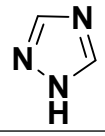
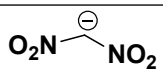
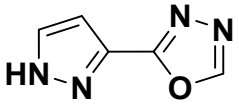
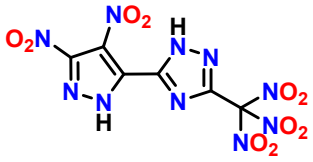
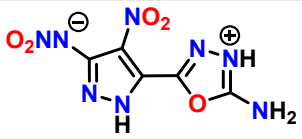
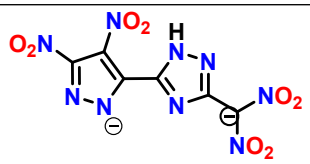
Compound	HOF_{Gas}) kJ/mol	HOF_{Sub} kJ/mol	HOF_{Solid} kJ/mol
5	449	82	367
11	514.7	97	417.7



Scheme S2: Isodesmic Reactions.

Table S2: Calculated zero-point energy (ZPE), values of the correction (H_{Corr}), total energy (E_o) and the gas-state heat of formation.

Compound	**ZPE**	**H_{Corr}**	**E_0**	**Corrected E_0**	**HOF_{gas} (kJ/mol)**
	0.071265	0.075955	-225.6230236	-225.54992	179.4
	0.056611	0.061165	-25.0498361	-224.99094	124.2

	0.059886	0.064393	-241.6632438	-241.60125	190.3
	0.039729	0.046609	-448.0309286	-447.9859088	-232.9[S9]
	0.098366	0.106444	-485.9481235	-485.845614	250.8
 5	0.152301	0.173698	-1525.765744	-1525.59813	449.0
 11	0.136455	0.1528	-1004.502143	-1004.354801	514.7
 PY-TRI-DNM-BA	0.121957	0.141405	-1320.609045	-1320.4725	82.6

4. X-Ray Crystallographic Data

Table S3. Crystal data and structure refinement for compounds **5**, **8, and 11**.

Compound	**5**	**8**	**11**
CCDC	2407425	2407426	2407427
Formula	$C_6H_2N_{10}O_{10}$	$C_6H_9N_{11}O_{10}$	$C_5H_4N_8O_5$
$D_{calc.}$/ g cm^{-3}	1.933	1.905	1.946
μ/mm^{-1}	0.000	1.593	1.535
Formula Weight	374.14	395.24	256.16
Color	colorless	yellow	yellow
Shape	plate-shaped	needle-shaped	irregular-shaped
Size/mm^3		0.23×0.06×0.01	0.11×0.04×0.01
***T*/K**	**298.00(10)**	**100.00(10)**	**100.00(10)**
Crystal System	monoclinic	triclinic	monoclinic
Space Group	$P2_1/n$	P-1	$I2/a$
a/Å	6.8861(19)	7.3911(5)	13.9776(7)
b/Å	22.50(2)	7.7664(4)	6.1067(3)
c/Å	8.314(2)	12.5111(8)	20.5048(11)

α/°	90	87.103(5)	90
β/°	93.94(3)	78.941(6)	92.102(5)
γ/°	90	77.912(5)	90
V/Å^3	1285.4(12)	689.16(8)	1749.04(16)
Z	4	2	8
Z'	1	1	1
Wavelength/Å	0.0251	1.54184	1.54184
Radiation type	electron	Cu K_a	Cu K_a
Q_{min}/°	0.064	3.600	4.315
Q_{max}/°	0.863	80.268	79.978
Measured Refl's.	14630	8761	5381
Indep't Refl's	2324	2857	1736
Refl's I≥2 s(I)	1116	2286	1320
R_{int}	0.3464	0.0609	0.0590
Parameters	244	271	179
Restraints	204	2	0
Largest Peak	0.237	0.512	0.296
Deepest Hole	-0.194	-0.740	-0.272
GooF	1.289	1.081	1.053
wR_2 (all data)	0.4822	0.2278	0.1194
wR_2	0.4398	0.2136	0.1091
R_1 (all data)	0.2726	0.0872	0.0619
R_1	0.2089	0.0725	0.0428

Table S4: Hydrogen Bond information for **5**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N3	H3	O7	1.03(6)	1.99(6)	2.781(18)	132(3)
N3	H3	N5[1]	1.03(6)	2.13(5)	2.872(12)	127(4)

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[1]1+x,+y,+z

Table S5: Hydrogen Bond information for **8**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N5	H5	O4[1]	0.96(6)	2.20(6)	3.013(4)	141(5)
N5	H5	O5	0.96(6)	2.02(6)	2.540(4)	112(4)
O10A	H10A	O1[2]	0.84	1.99	2.823(5)	172.4
N11A	H11A	O8[3]	0.91	1.22	2.01(4)	141.3
N11A	H11A	N9[3]	0.91	2.36	2.98(4)	125.3
N11A	H11B	O8	0.91	2.38	2.84(3)	111.2
N11A	H11C	O7	0.91	1.51	2.28(4)	139.6
N11A	H11C	N9	0.91	2.22	2.86(3)	127.0
N11A	H11C	O9	0.91	2.30	2.94(4)	127.6
O9	H9	N3	0.87(5)	1.95(5)	2.812(4)	173(5)
N10	H10C	N2	0.83(6)	1.92(6)	2.741(4)	172(5)

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N10	H10D	N1[2]	0.91(4)	1.91(5)	2.815(4)	172(4)
O10	H10	O7	0.84	2.31	2.79(3)	117.1
O10	H10	O9	0.84	1.70	2.52(3)	163.2
N11	H11D	O2[4]	0.98	1.86	2.746(6)	148.4
N11	H11E	O10[5]	0.98	2.18	2.96(3)	135.4
N11	H11E	N11[5]	0.98	1.26	2.205(13)	159.3
N11	H11F	O7	0.98	1.79	2.573(6)	134.4

––––

[1]-x,1-y,1-z; [2]2-x,-y,1-z; [3]2-x,1-y,-z; [4]1+x,+y,-1+z; [5]2-x,-y,-z

5. NMR spectra (^{1}H, ^{13}C, and ^{14}N), IR spectra, and DSC of compounds

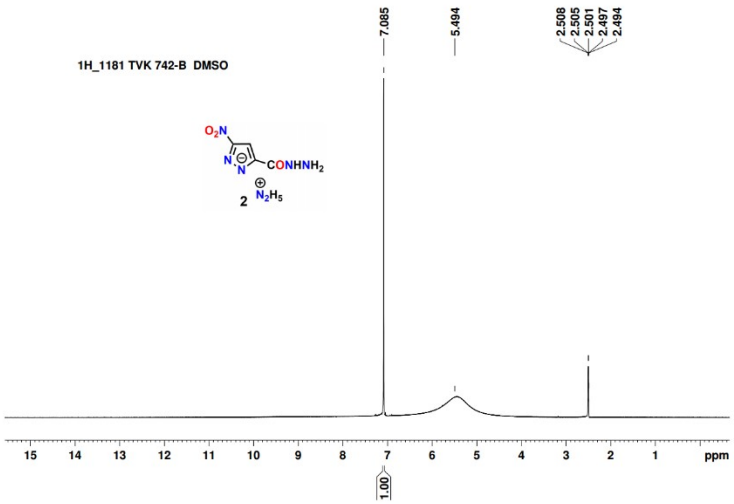

Figure S2: ^{1}H NMR spectrum of **2** in dimethyl sulfoxide-d_6.

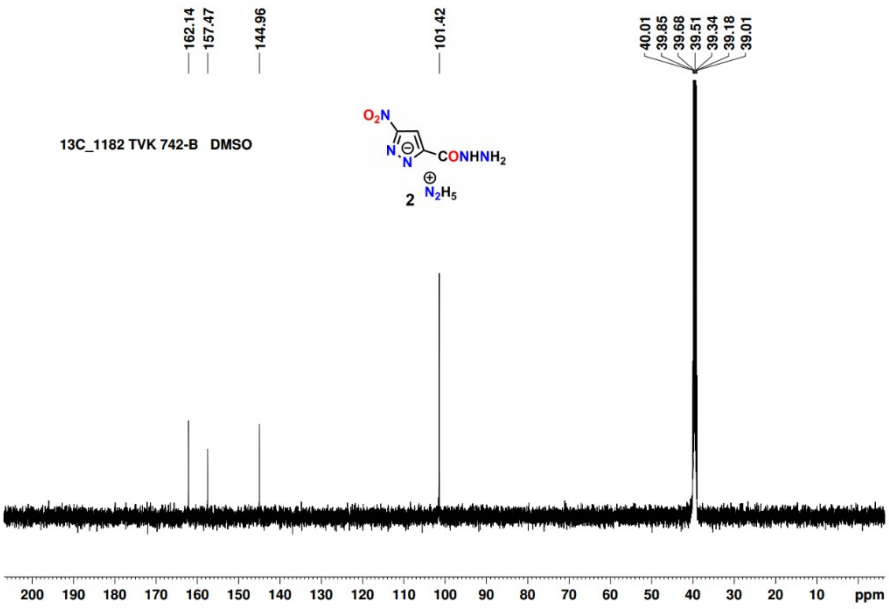

Figure S3: ^{13}C NMR spectrum of **2** in dimethyl sulfoxide-d_6.

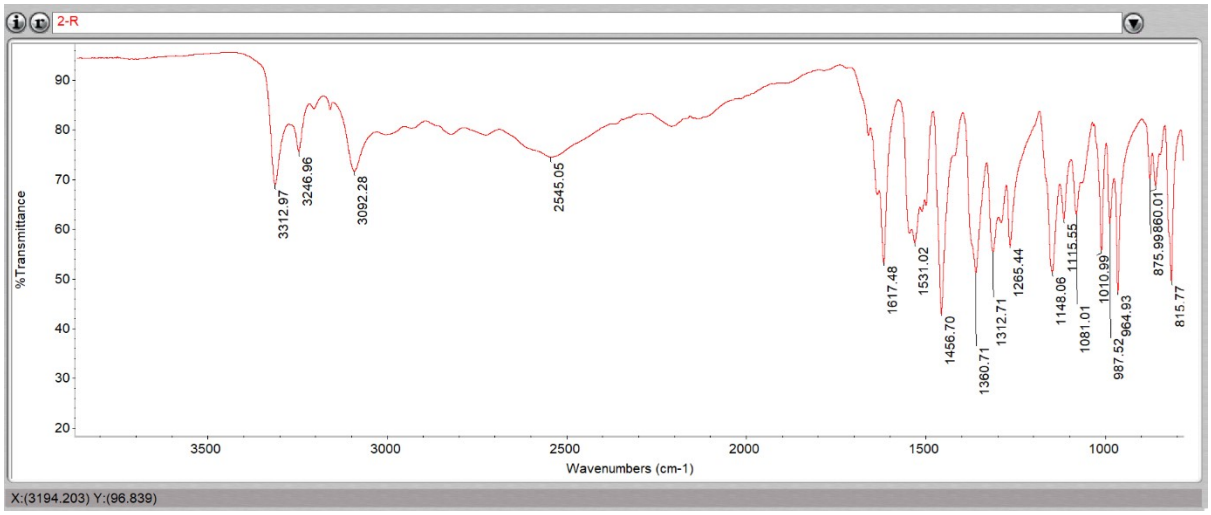

Figure S4: IR spectrum of **2**.

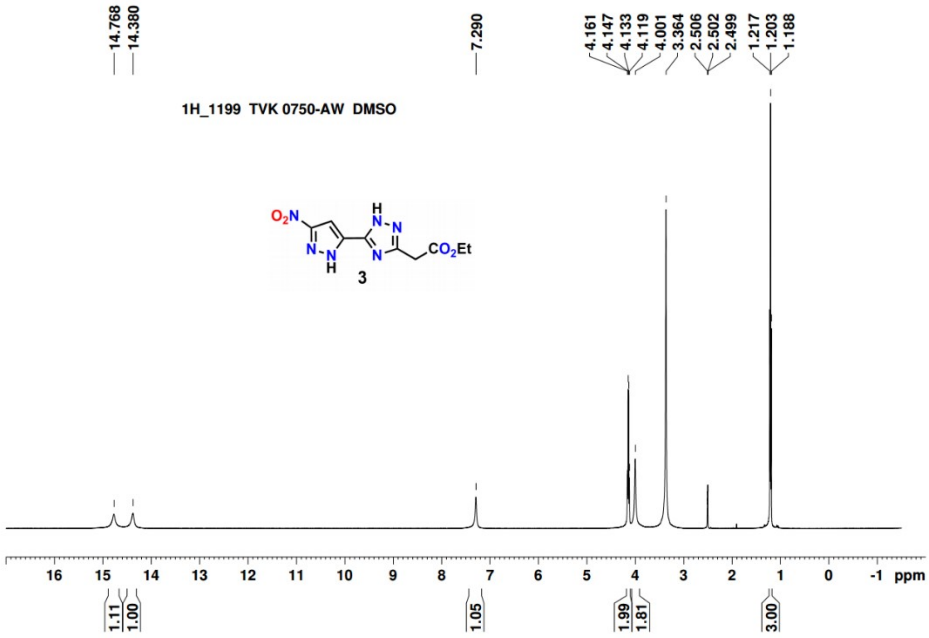

Figure S5: ^{1}H NMR spectrum of **3** in dimethyl sulfoxide-d_6.

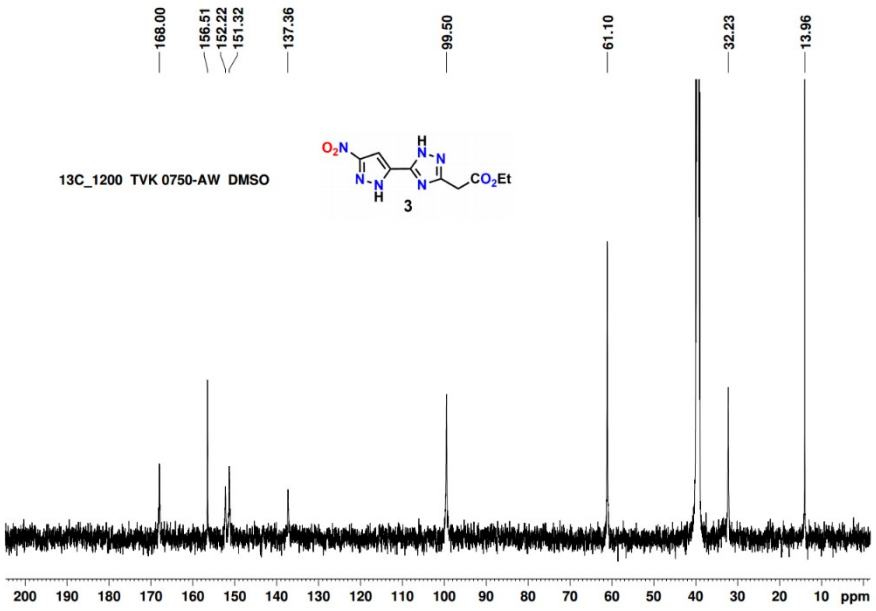

Figure S6: ^{13}C NMR spectrum of **3** in dimethyl sulfoxide-d_6.

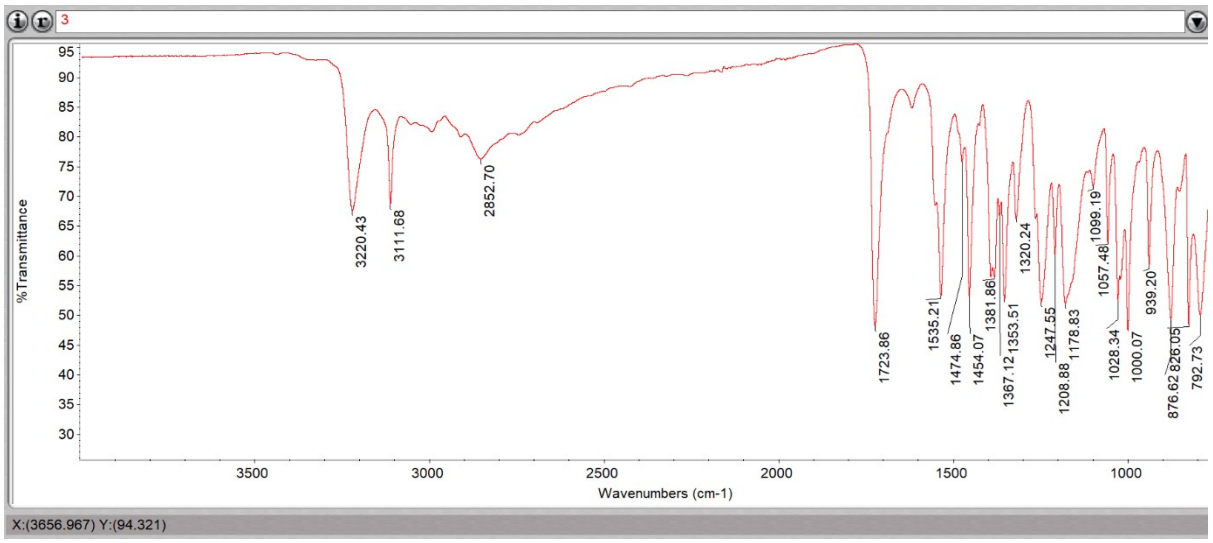

Figure S7: IR spectrum of **3**.

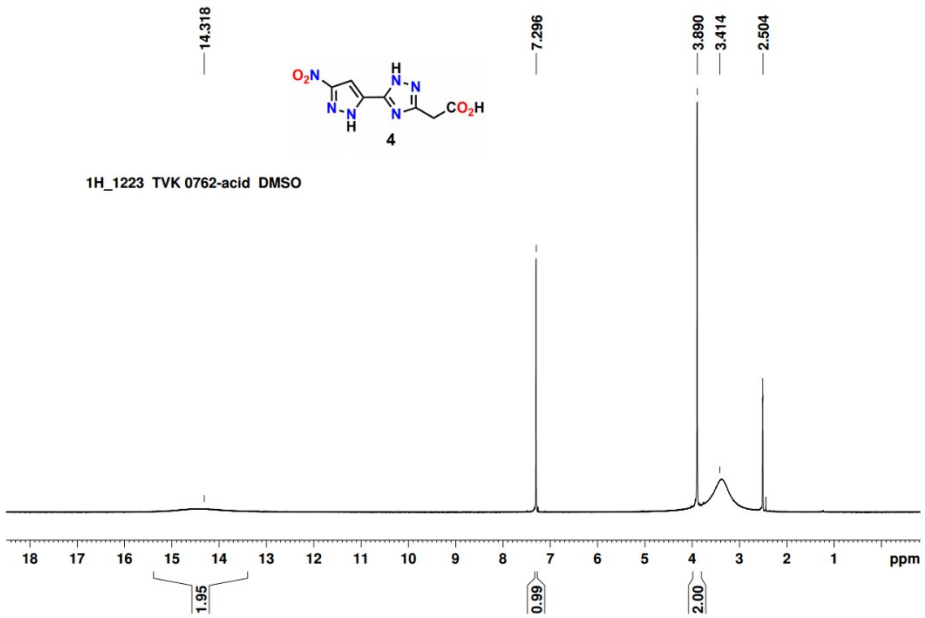

Figure S8: ^{1}H NMR spectrum of **4** in dimethyl sulfoxide-d_6.

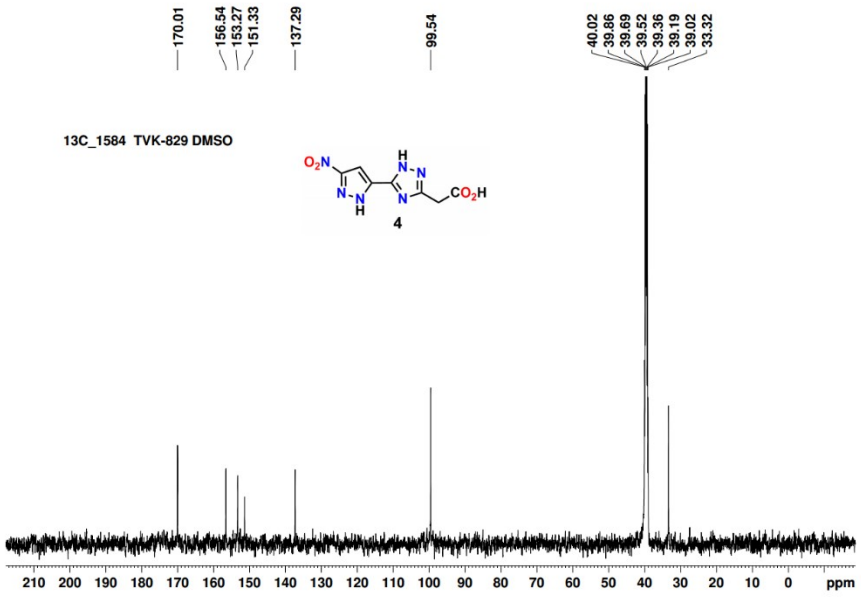

Figure S9: ^{13}C NMR spectrum of **4** in dimethyl sulfoxide-d_6.

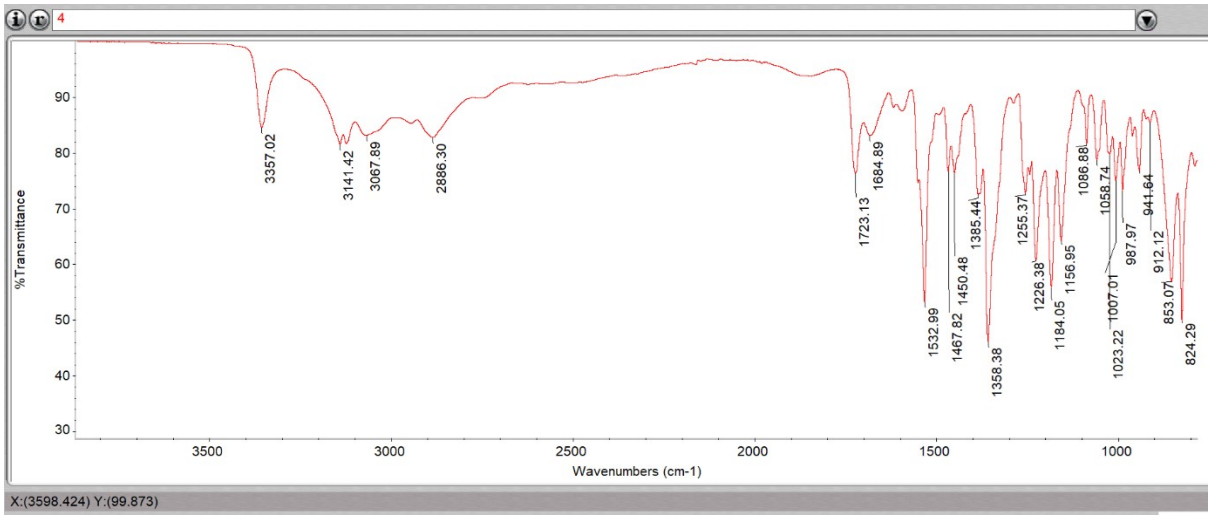

Figure S10: IR spectrum of **4**.

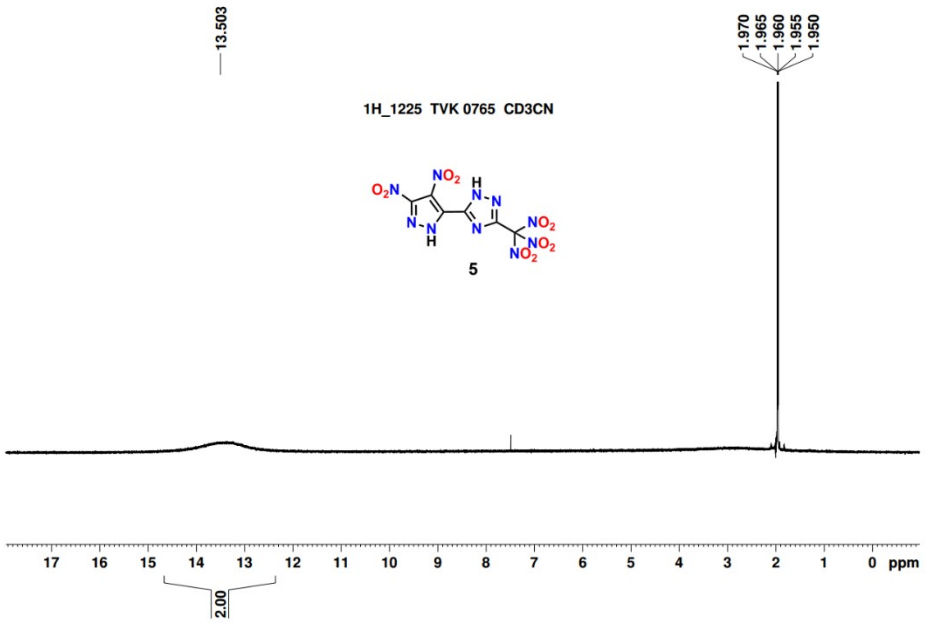

Figure S11: ^{1}H NMR spectrum of **5** in acetonitrile-d_3.

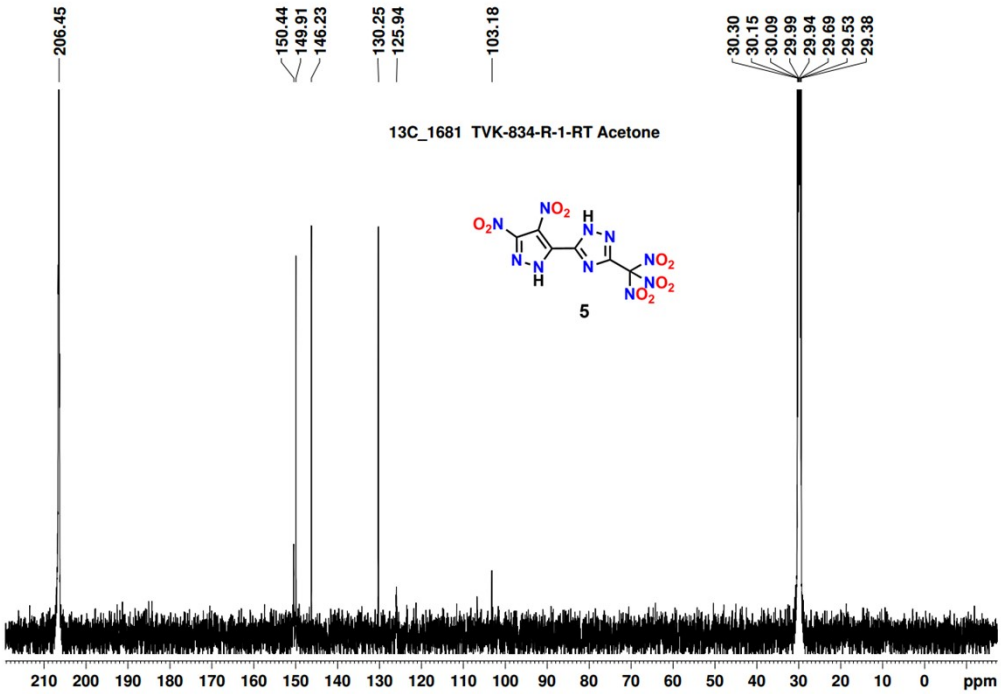

Figure S12: ^{13}C NMR spectrum of **5** in acetone-d_6.

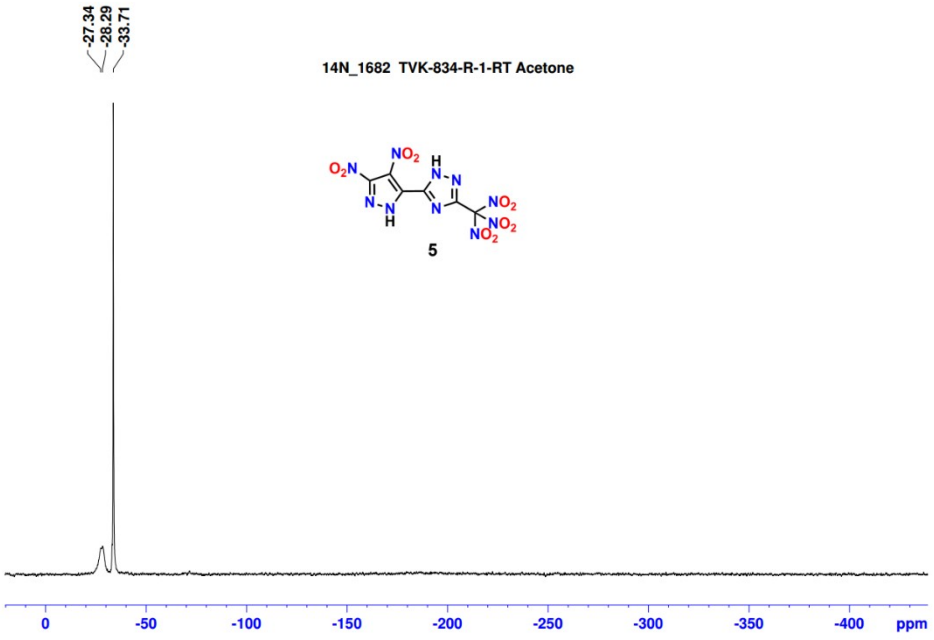

Figure S13: ^{14}N NMR spectrum of **5** (acetone-d_6; 36.14 MHz).

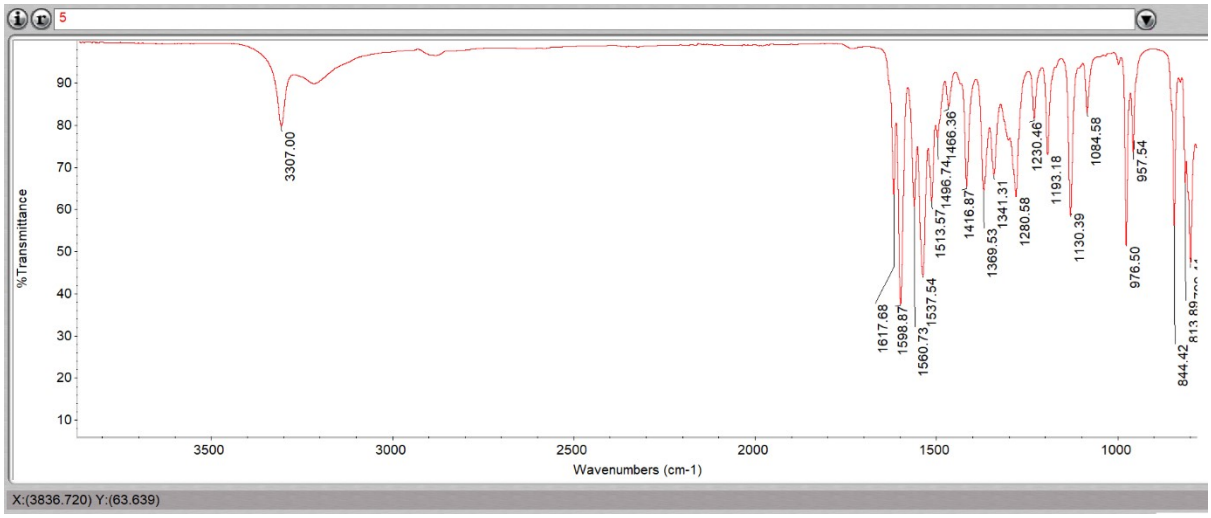

Figure S14: IR spectrum of **5**.

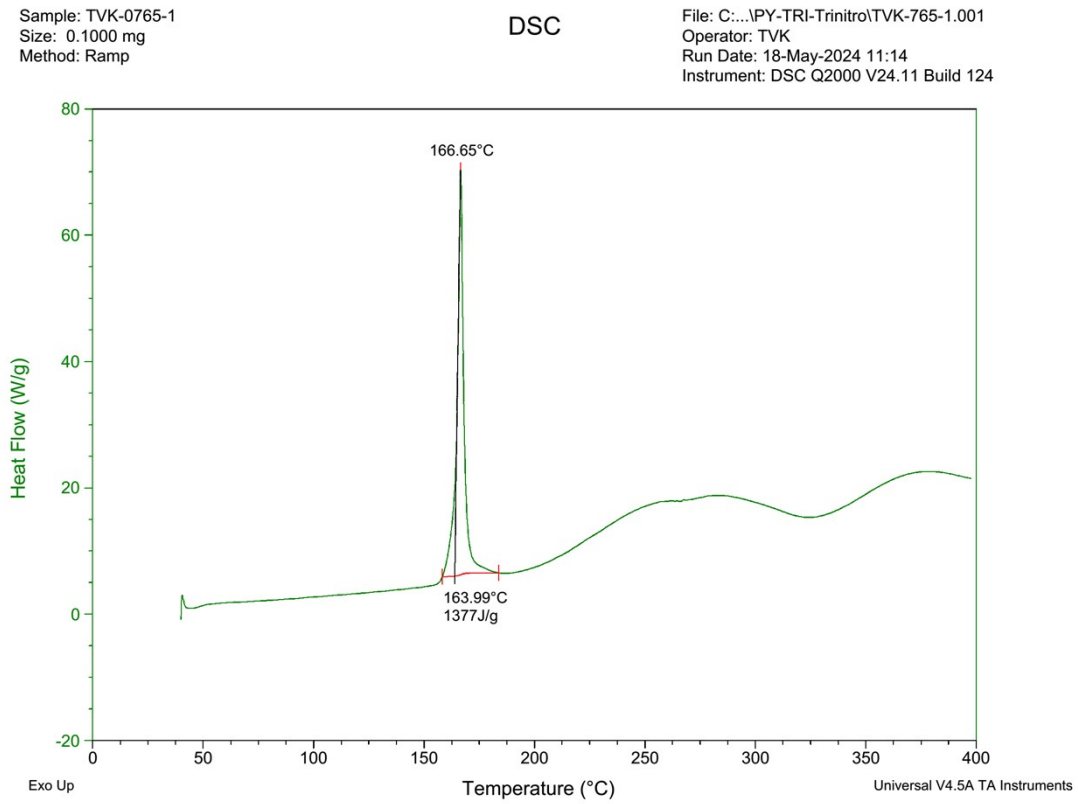

Figure S15: Thermal behavior of **5** at 5 °C/min.

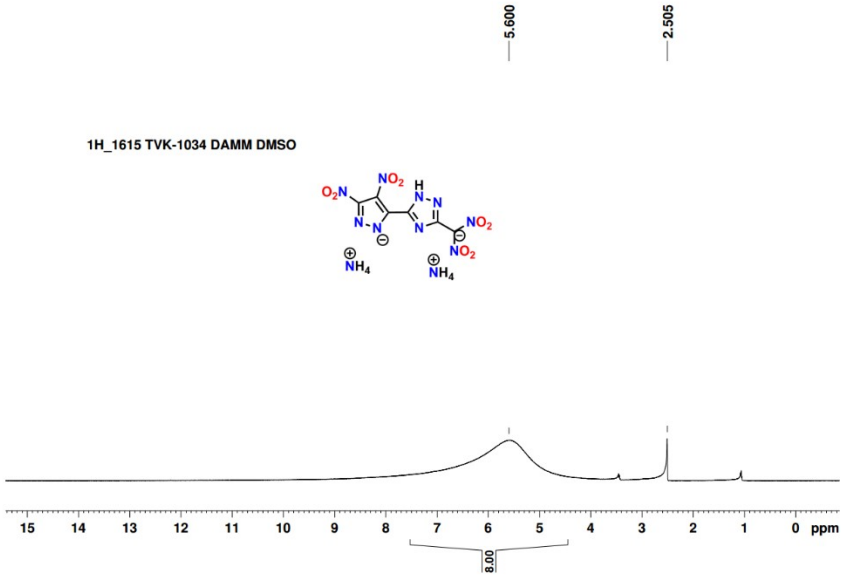

Figure S16: ^{1}H NMR spectrum of 7 in dimethyl sulfoxide-d_6.

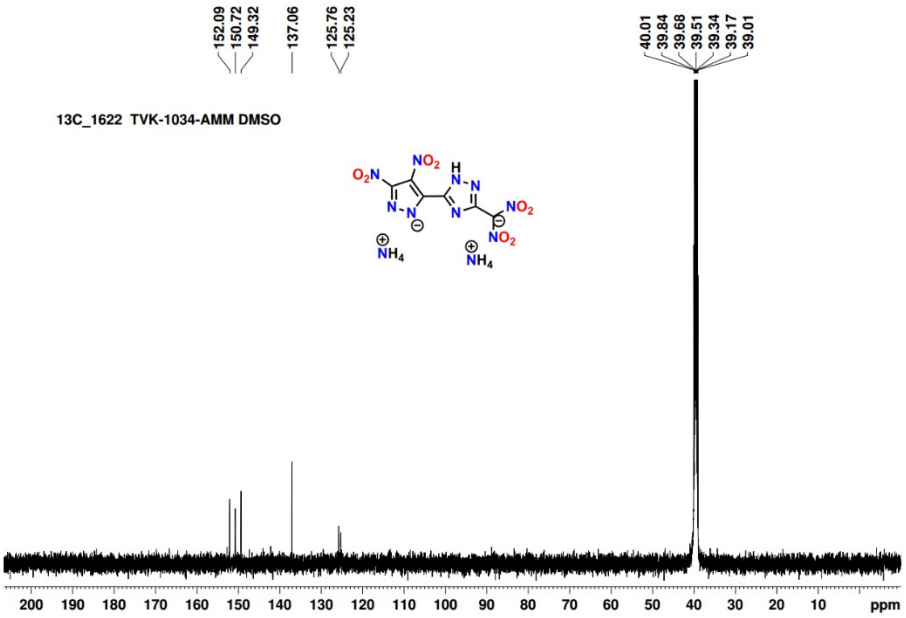

Figure S17: ^{13}C NMR spectrum of **7** in dimethyl sulfoxide-d_6.

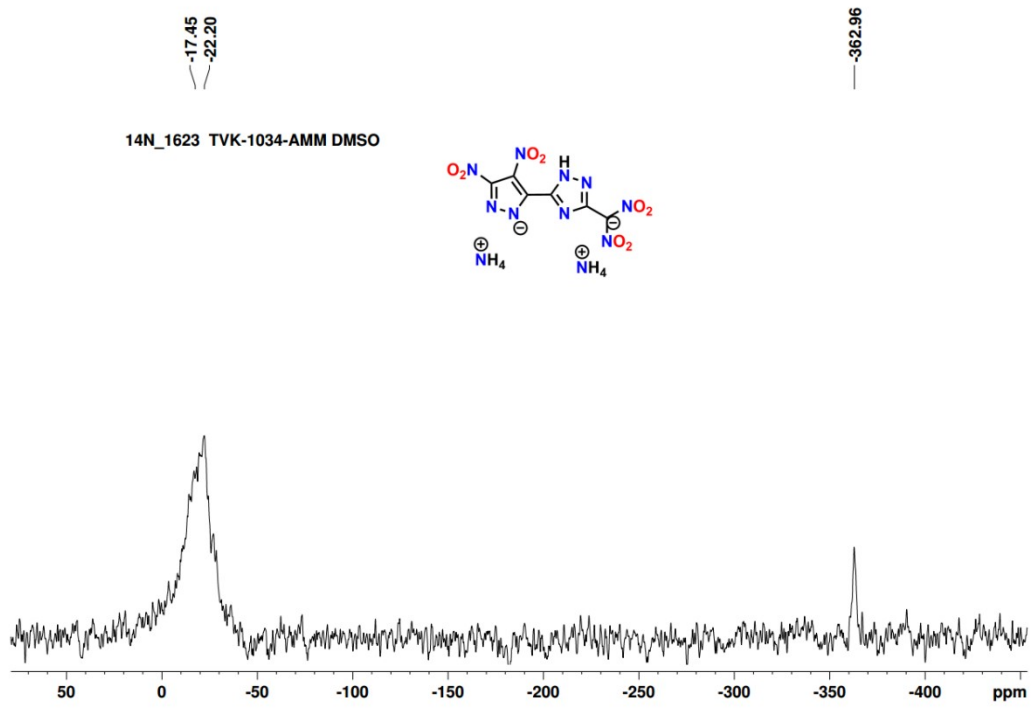

Figure S18: $^{14}4$ NMR spectrum of **7** in dimethyl sulfoxide-d_6.

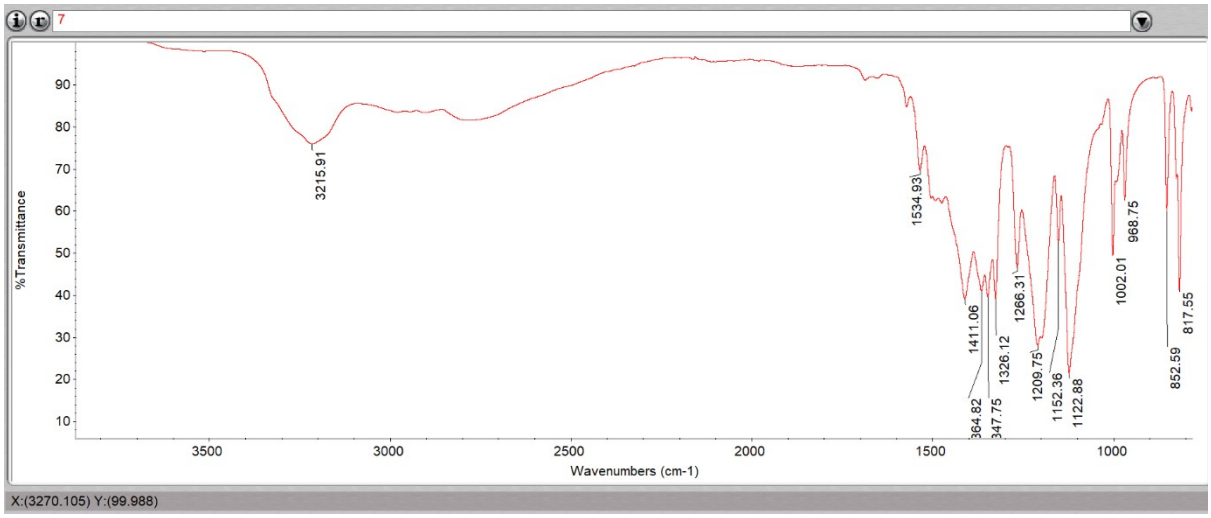

Figure S19: IR spectrum of **7**.

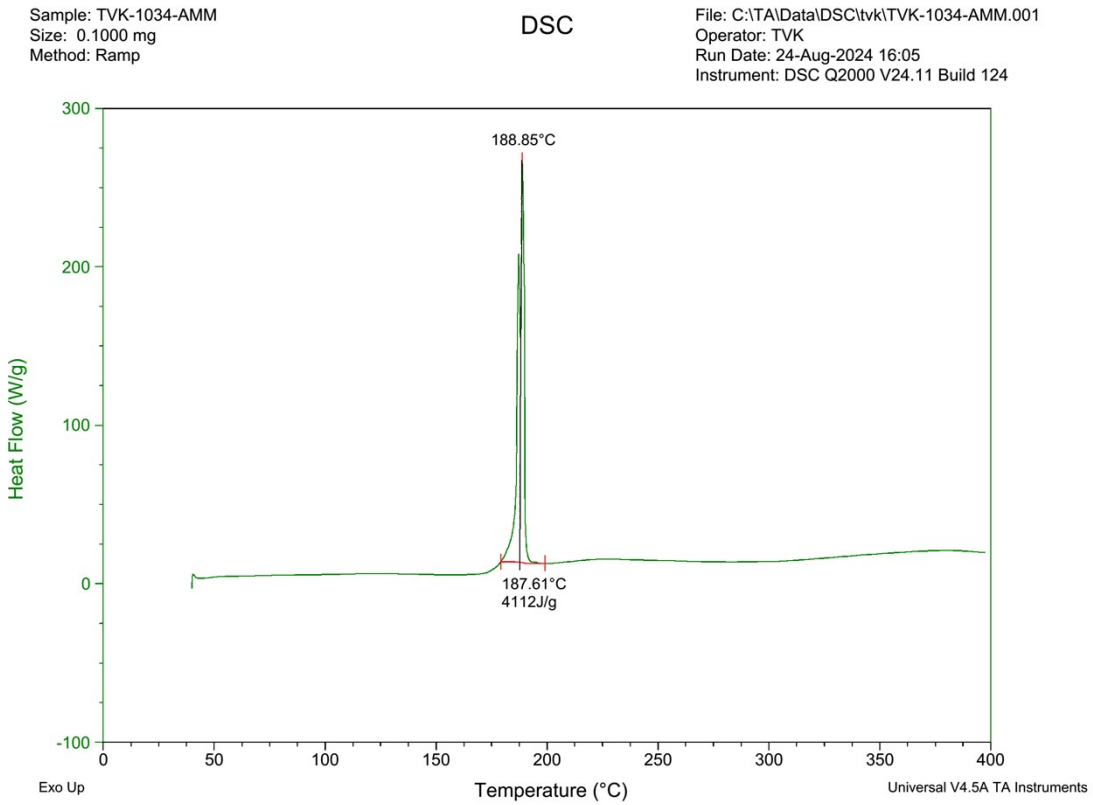

Figure S20: Thermal behavior of **7** at 5 °C/min.

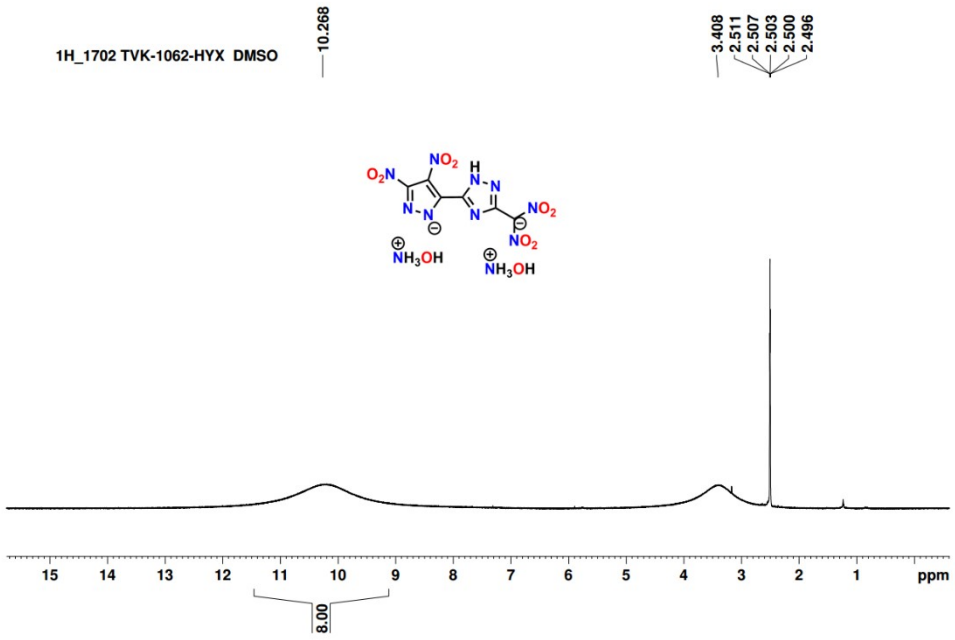

Figure S21: ^{1}H NMR spectrum of **8** in dimethyl sulfoxide-d_6.

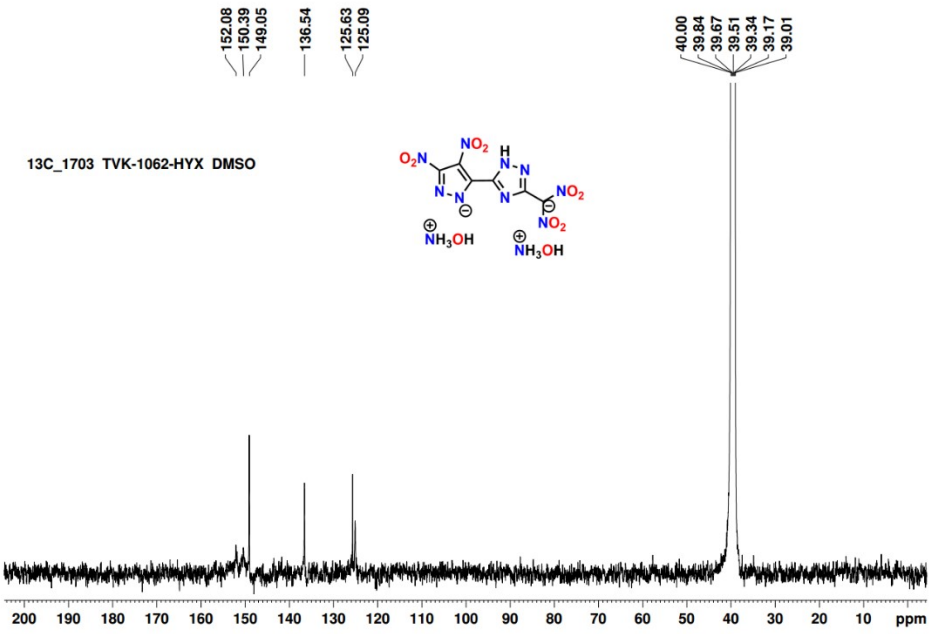

Figure S22: ^{13}C NMR spectrum of **8** in dimethyl sulfoxide-d_6.

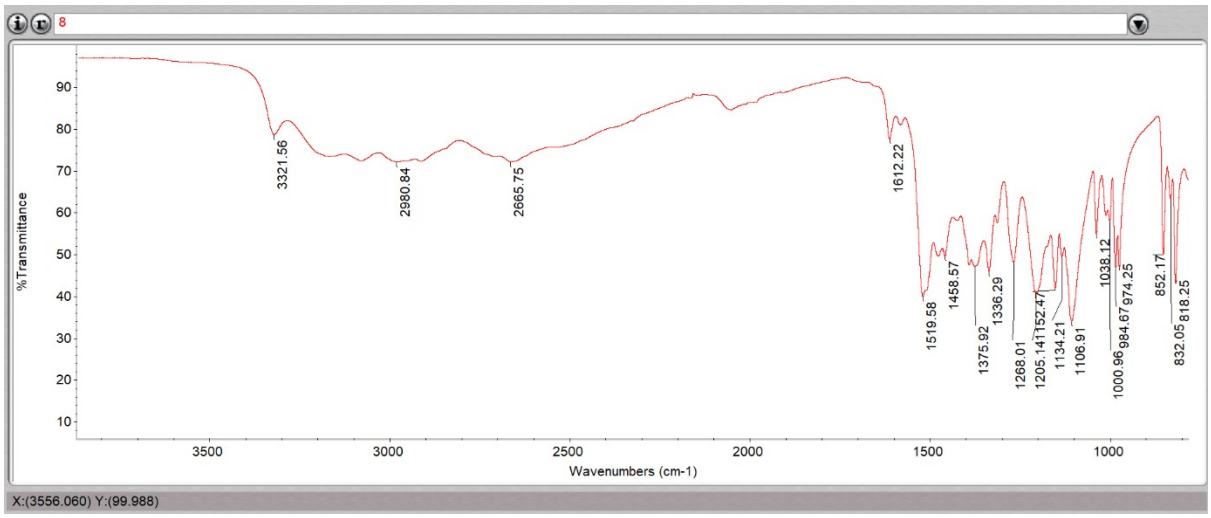

Figure S23: IR spectrum of **8**.

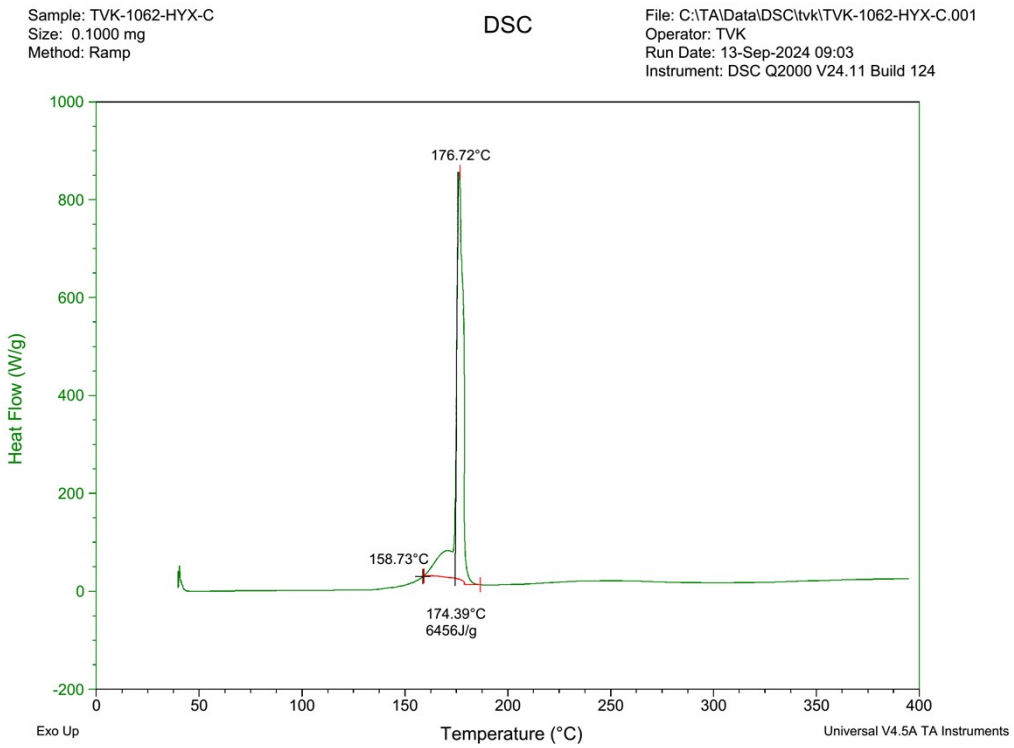

Figure S24: Thermal behavior of **8** at 5 °C/min.

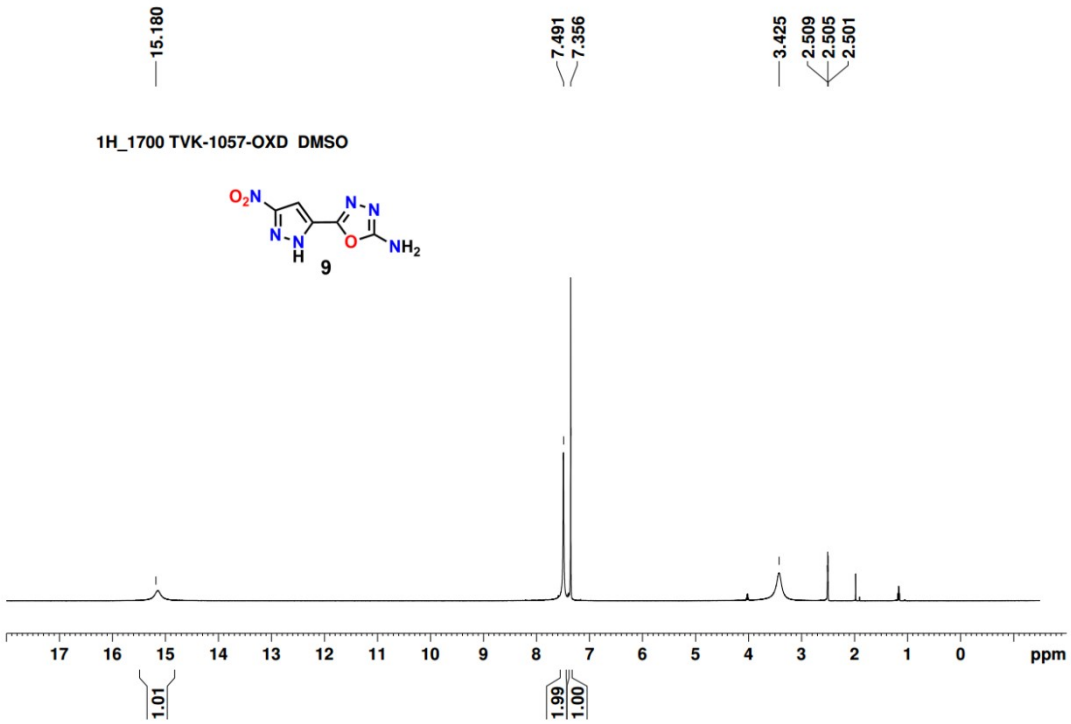

Figure S25: ^{1}H NMR spectrum of **9** in dimethyl sulfoxide-d_6.

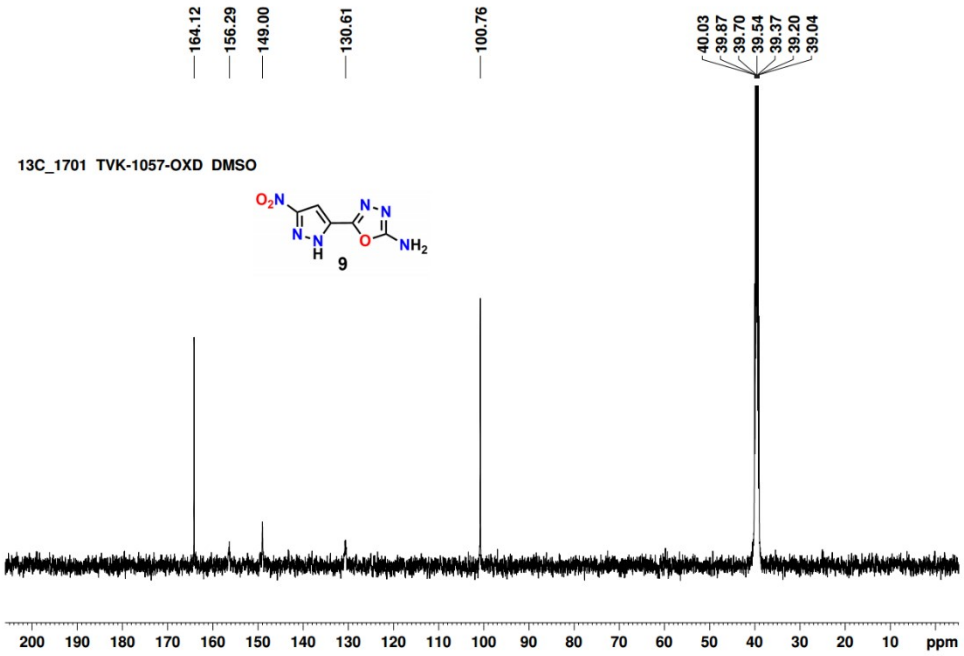

Figure S26: ^{13}C NMR spectrum of **9** in dimethyl sulfoxide-d_6.

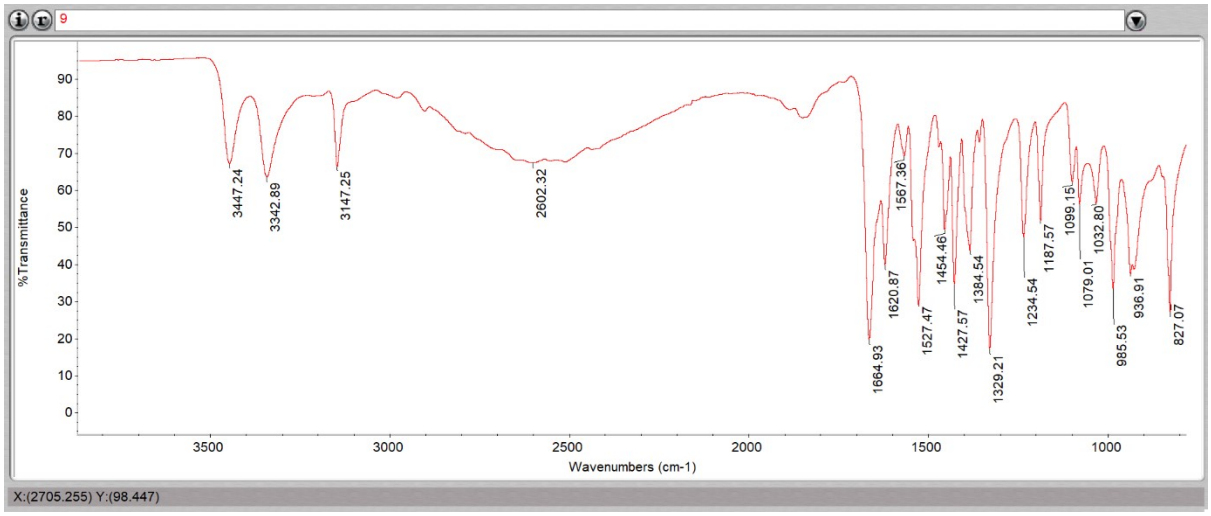

Figure S27: IR spectrum of **9**.

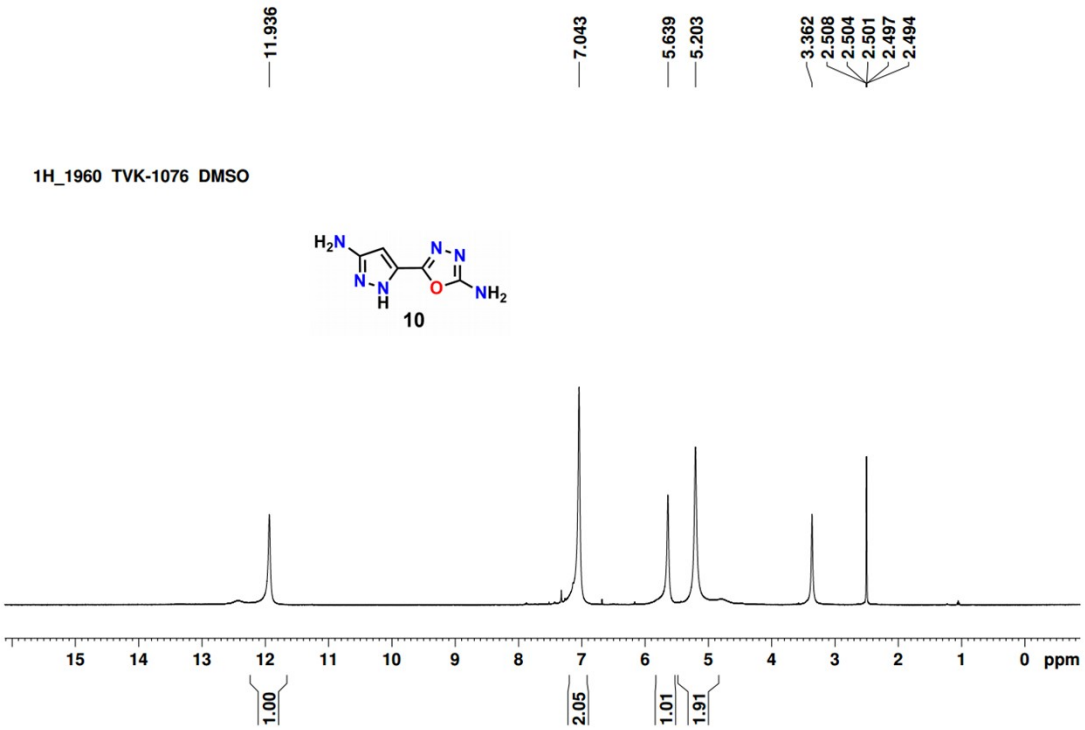

Figure S28: [1]H NMR spectrum of **10** in dimethyl sulfoxide-d_6.

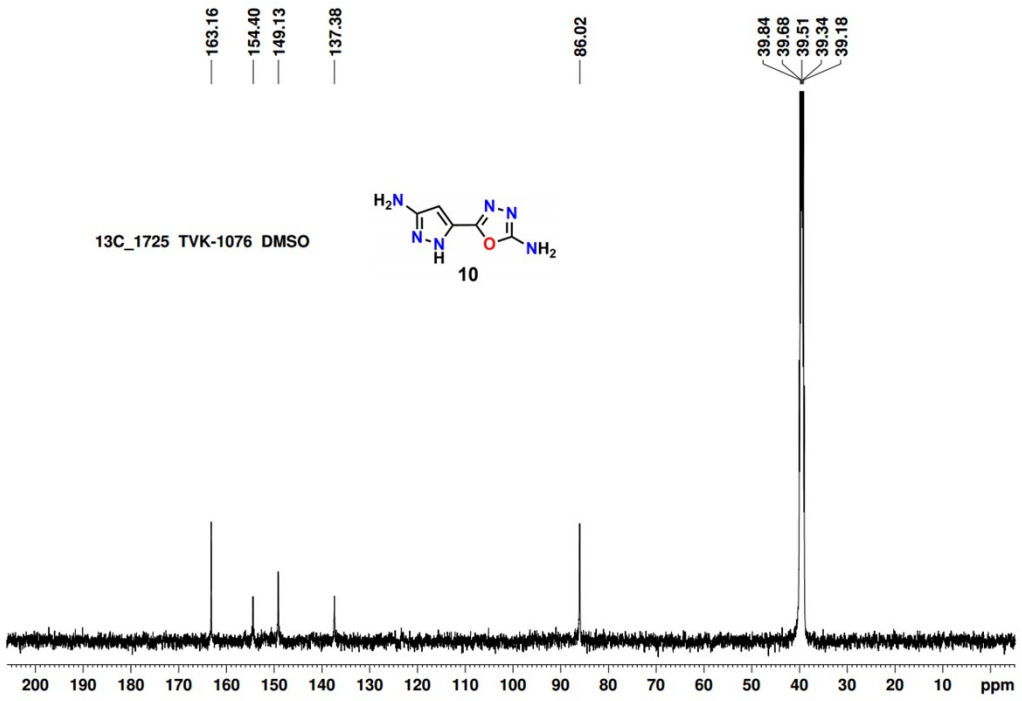

Figure S29: [13]C NMR spectrum of **10** in dimethyl sulfoxide-d_6.

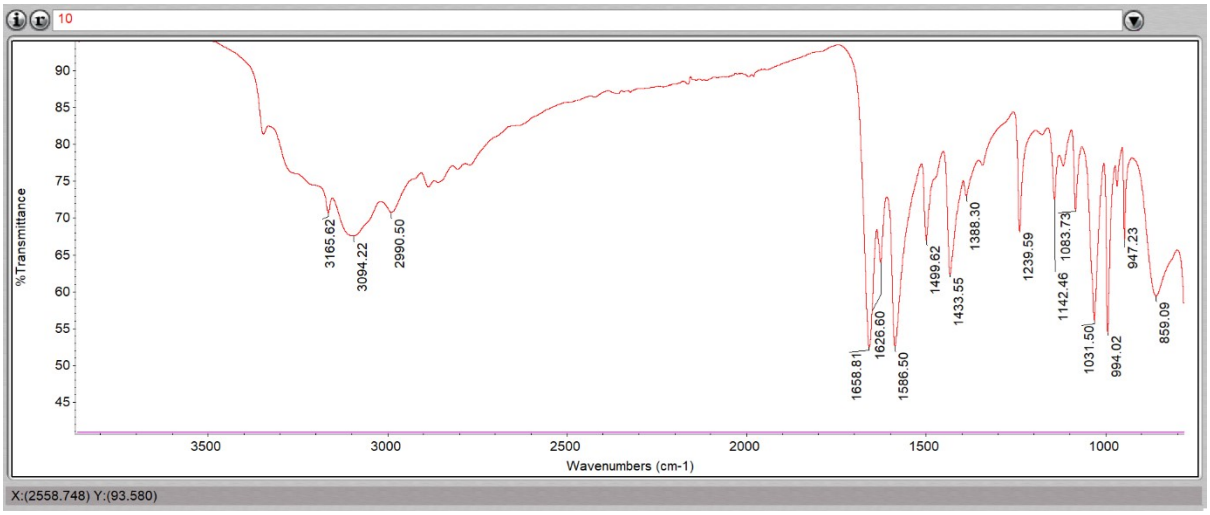

Figure S30: IR spectrum of **10**.

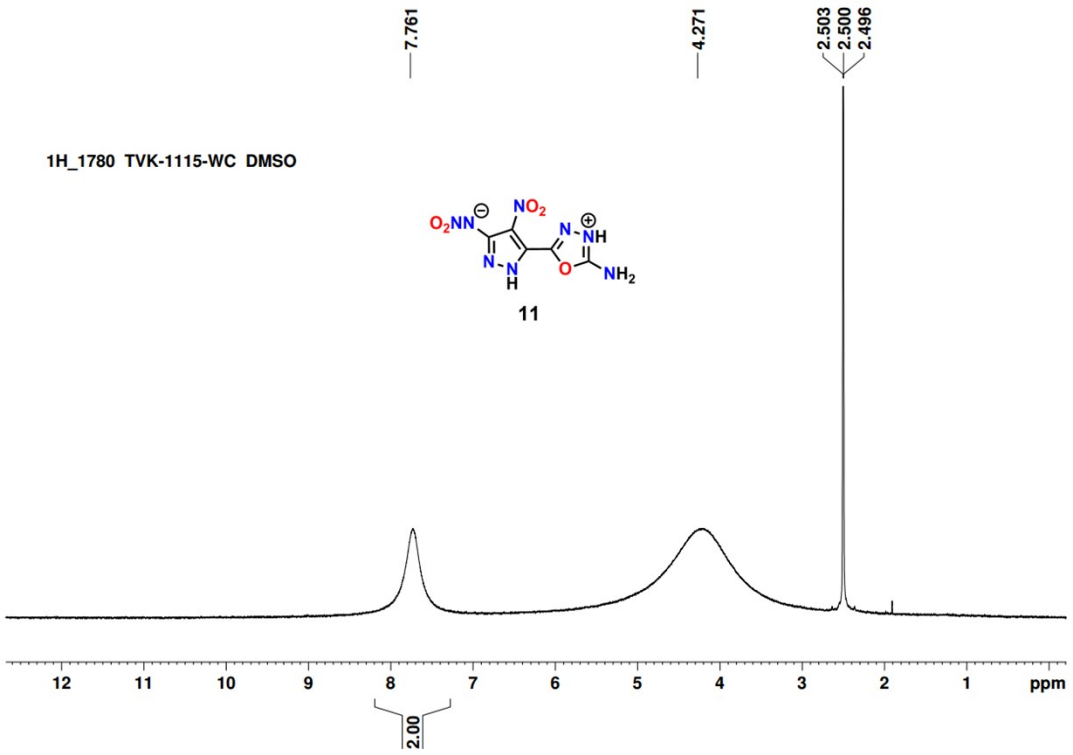

Figure S31: ^{1}H NMR spectrum of **11** in dimethyl sulfoxide-d_6.

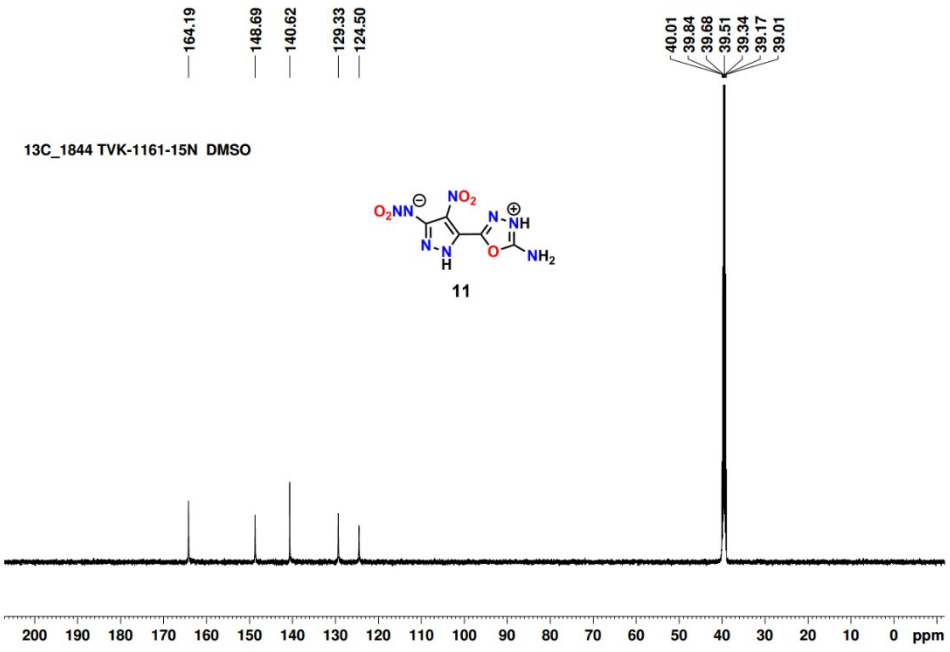

Figure S32: ^{13}C NMR spectrum of **11** in dimethyl sulfoxide-d_6.

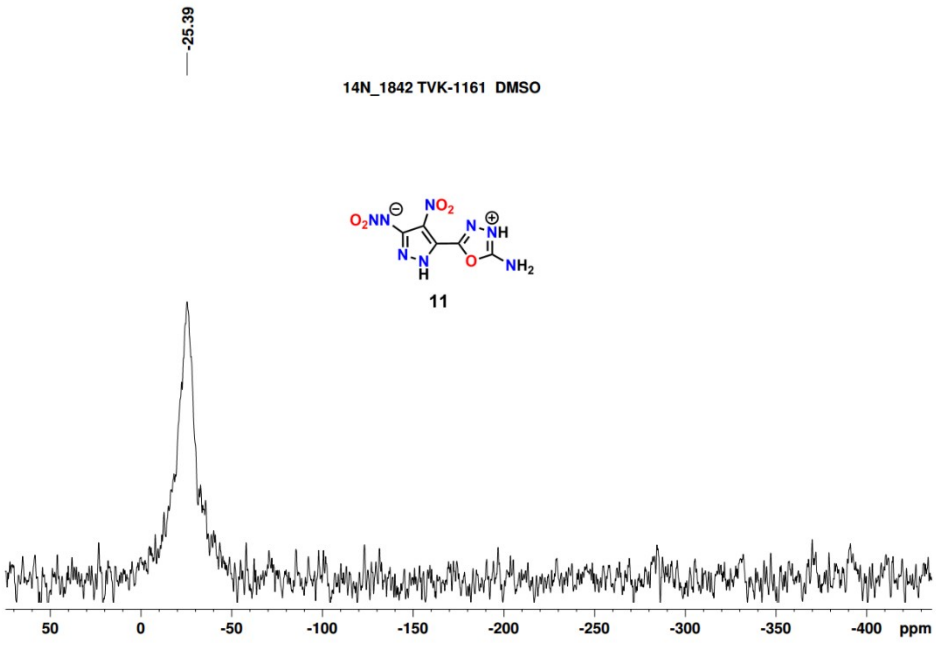

Figure S33: ^{14}N NMR spectrum of **11** in dimethyl sulfoxide-d_6.

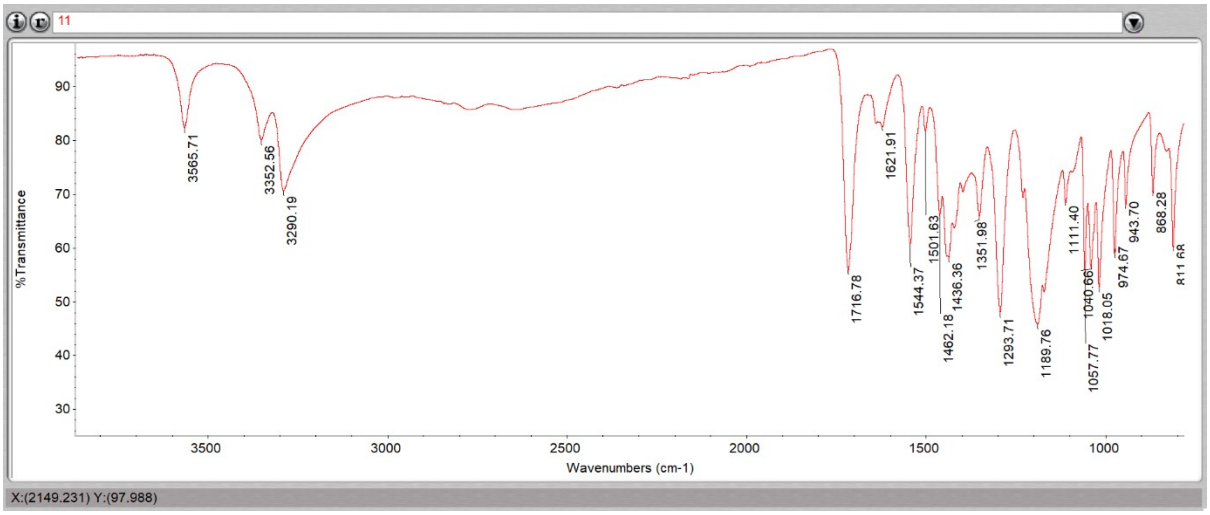

Figure S34: IR spectrum of **11**.

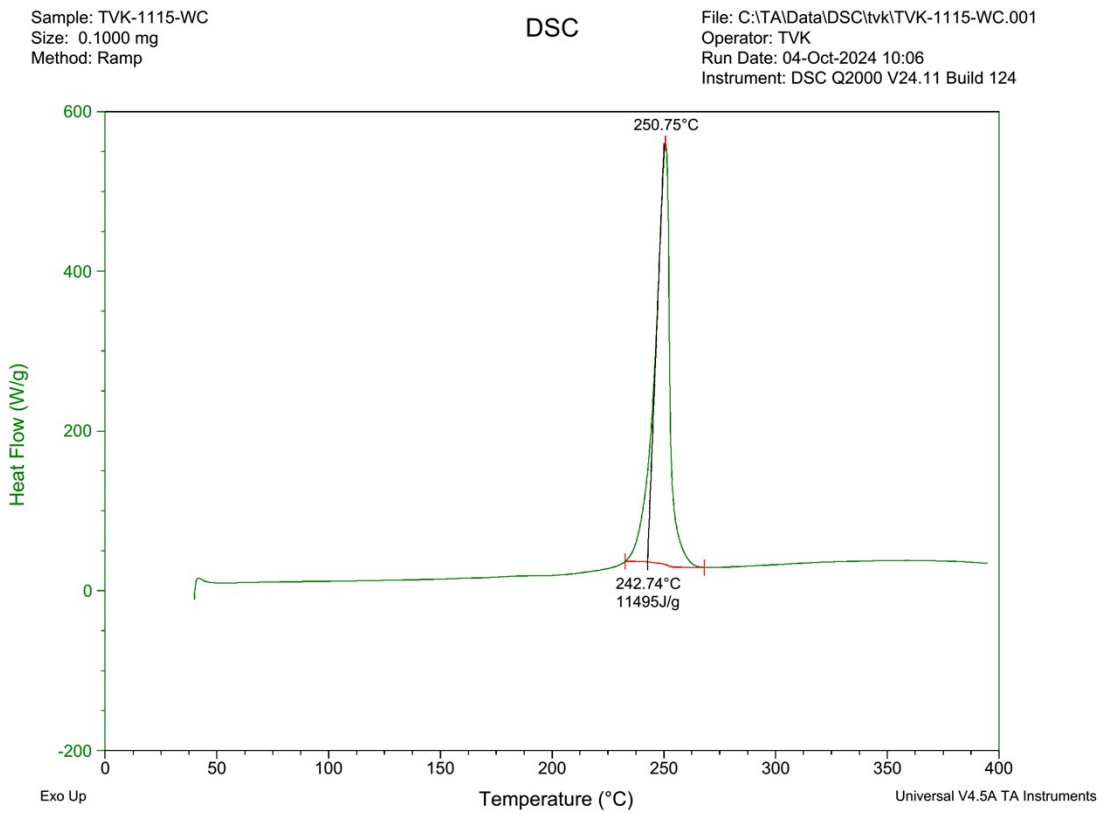

Figure S35: Thermal behavior of **11** at 5 °C/min.

6. References

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