Electronic Supplementary Information

Energetic Multifunctionalized Nitro/nitramino Isomeric Pyrazole-Tetrazole Hybrids: Enhancing Density and Detonation Properties through Hydrogen Bonding and π-π Interactions

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Contents

1. General Experimental

All reagents (analytical grade) were purchased from AK Scientific or VWR and were used as supplied. ^{1}H, ^{13}C, ^{14}N, and ^{15}N NMR spectra were recorded using a 500 MHz (Bruker Advance) NMR spectrometer operating at 500.19 125.78, 36.14, and 50.69 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C NMR spectra are reported relative to Me_4Si solvent resonance as internal standard and ^{14}N and ^{15}N NMR spectra to nitromethane as an external standard. Abbreviations for multiplicities and descriptors are: s = singlet, br = broad signal, m = multiplet and q = quartet. 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. For mass spectrometry, a Waters Q-ToF Premier quadrupole-time of flight mass spectrometer was used.

Single crystals of **H_2DNP-5T**, **11-DMA** and **4** suitable for single-crystal X-ray analysis were obtained by the evaporation of their saturated solutions in acetonitrile-methanol, DMF-AcOH, and water-methanol, respectively. Yellow crystals of **H_2DNP-5T**, **11-DMA** and **4** with dimensions 0.21 × 0.15 × 0.05 mm^3, 0.15 × 0.04 × 0.02 mm^3 and 0.24 × 0.16 × 0.07 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 steady 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 F2. 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 **H_2DNP-5T, 11-DMA,** and **4** in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers **CCDC** 2352179, 2352181, and 2352182, 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).

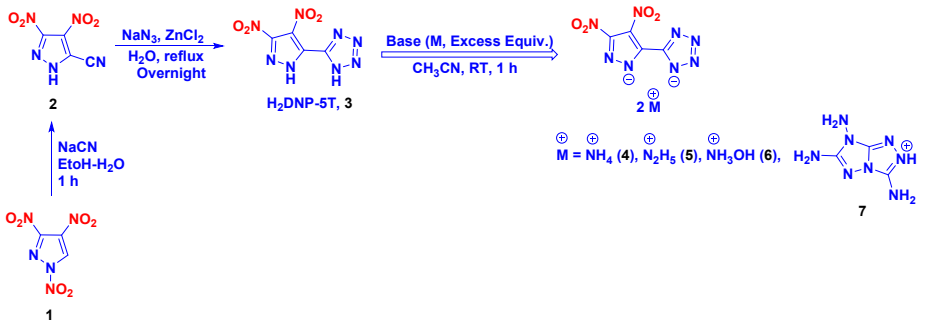
2. Experimental Section

***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: 1,3,4-Trinitro-1*H*-pyrazole was prepared according to the literature.[S4]

Synthesis of compound 2. 5-Cyano-3,4-dinitropyrazole was prepared from 1,3,4-trinitropyrazole according to the modified reported method (Scheme S1).[S5] Trinitropyrazole (3.05 g, 15 mmol) in ether (30 mL) was slowly added to the solution of NaCN (7.35 g, 150 mmol) in EtOH (200 mL) and H_2O (75 mL) at ~20 °C. The reaction mixture was stirred for 1 h and then acidified with stirring in 20% H_2SO_4 to pH 2-3. The Na_2SO_4 that formed was filtered off, and the solvent was evaporated in vacuo. The residue was extracted with ethyl acetate to yield compound **2** in 91% yield. The characterization data was matched with reported literature data.

Safety Precautions and Neutralization of Sodium Cyanide: Sodium cyanide (NaCN) is highly toxic. Perform all operations in a fume hood with the sash lowered. Use appropriate PPE, including a lab coat, long pants, closed-toed shoes, goggles, and double nitrile gloves. Inspect gloves before use, change them regularly, and wash hands after removal. Use suitable materials like polypropylene and keep containers tightly closed. Neutralize spills with a sodium hypochlorite solution.



Scheme S1: Synthesis of compound **2**, H_2DNP-**5T** (**3**) and its ionic derivatives, **4**, **5**, **6**, and **7**.

Synthesis of H_2DNP-5T (3). Into an oven-dried round bottomed flask (100 mL) was added compound **2** (1.83 g, 10 mmol), sodium azide (0.78 g, 12 mmol), zinc chloride (1.63 g, 12 mmol), and distilled water (25.0 mL). The mixture was maintained at reflux for overnight. Then it was cooled to room temperature and treated with 2N hydrochloric acid (50 mL) and extracted with ethyl acetate (2 x 50 mL). The organic phase was dried with anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The resulting solid was washed with water and the product was filtered to obtain a pale yellow powder, **H_2DNP-5T**.

H_2DNP-5T: Yellow Solid; Yield: 71%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 11.68 (br, 2H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 149.3, 147.9, 129.5, 125.3 ppm. FTIR (cm^{-1}) ῡ 3448, 3066, 2817, 2691, 2150, 1593, 1568, 1524, 1463, 1399, 1373, 1331, 1142, 979, 832. Elemental analysis: Calcd (%) for $C_4H_2N_8O_4$ (226.11): C, 21.25; H, 0.89; N, 49.56; Found: C 21.59, H 1.26, N 50.5.

General procedure for the synthesis for compounds 4-7.

H_2DNP-5T (**3**) (400 mg, 1.77 mmol) was dissolved in acetonitrile (10 mL) and aqueous ammonia (510 µl, 2 equiv), hydrazine monohydrate (173 µl, 2 equiv), hydroxylamine (50%, 217 µl, 2 equiv), or TATOT (0.545 g, 2 equiv) was added to the reaction mixture at 0 °C. The

reaction mixture was stirred for 1 h at room temperature. The product which precipitated in the reaction mixture was filtered and washed with acetonitrile and dried in air (Scheme S1).

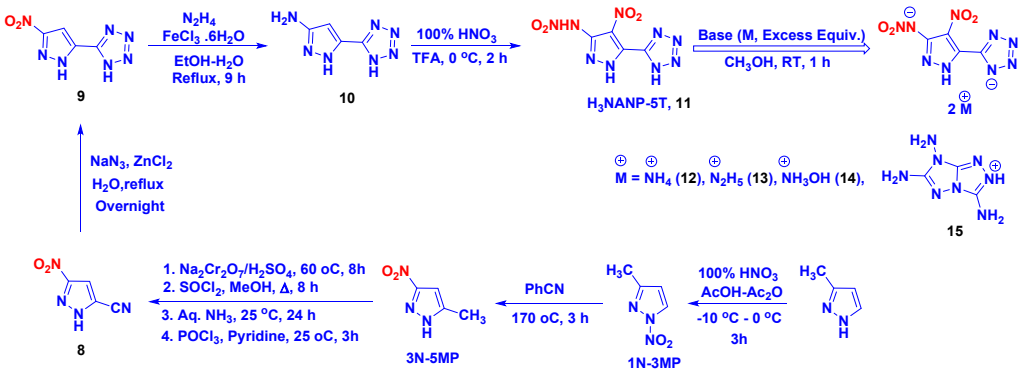
4: Yellow Solid; Yield: 86%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.35 (br, 8H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 154.2, 149.4, 139.5, 125.6 ppm. FTIR (cm^{-1}) ῡ 3297, 3248, 2721, 1495, 1429, 1402, 1345, 1313, 1261, 1195, 1140, 1125, 980, 852, 819. Elemental analysis: Calcd (%) for $C_4H_8N_{10}O_4$ (260.17): C, 18.47; H, 3.10; N, 53.84; Found: C 18.63, H 4.08, N 53.85.

5: Yellow Solid; Yield: 89%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.12 (br, 10H) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 154.1, 149.2, 138.9, 125.6 ppm. FTIR (cm^{-1}) ῡ 3348, 2919, 2625, 1595, 1528, 1482, 1411, 1375, 1342, 1321, 1276, 1190, 1088, 972, 926, 851, 818. Elemental analysis: Calcd (%) for $C_4H_{10}N_{12}O_4$ (290.20): C, 16.56; H, 3.47; N, 57.92; Found: C 16.81, H 3.86, N 57.58.

6: Yellow solid; Yield: 82%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 8.20 (br, 8H) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 151.2, 149.1, 135.2, 125.2 ppm. FTIR (cm^{-1}) ῡ 3149, 2940, 2603, 1600, 1528, 1491, 1345, 1318, 1280, 1245, 1219, 1142, 1003, 985, 852, 817. Elemental analysis: Calcd (%) for $C_4H_8N_{10}O_6$ (292.17): C, 16.44; H, 2.76; N, 47.94; Found: C 17.27, H 2.95 N 48.07.

7: Yellow solid; Yield: 84%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.29 (s, 4H), 6.92 (s, 4H), 5.70 (s, 4H) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 159.5, 149.6, 149.5, 147.9, 142.0, 133.7, 125.2 ppm. FTIR (cm^{-1}) ῡ 3363, 3311, 3073, 2716, 1693, 1653, 1538, 1515, 1499, 1375, 1352. Elemental analysis: Calcd (%) for $C_{10}H_{14}N_{24}O_4$ (534.39): C, 22.48; H, 2.64; N, 62.91; Found: C 22.82, H 2.91 N 62.82.

Synthesis of 1N-3MP: 100% nitric acid (6 mL) was added dropwise to a stirred solution of 3-methyl-1*H*-pyrazole (8.59 g, 126 mmol) in glacial acetic acid (32 mL) that had been cooled to -10 °C using an ice-salt bath. Voluminous precipitate was formed. Acetic anhydride was added (17 mL) was added dropwise and the resultant mixture was stirred at 0 °C temperature for 3 hours. The mixture was poured onto ice and the precipitate was isolated by filtration. The characterization data was matched with reported literature data. Yield: 71% (Scheme S2).



Scheme S2: Synthesis of compound **H$_3$NANP-5T** (**11**) and its ionic derivatives **12**, **13**, **14**, and **15**.

Synthesis of 3N-5MP. 1-Nitro-3-methyl-1*H*-pyrazole (**1N-3MP)** (3 g, 23.6 mmol) was dissolved in benzonitrile (30 mL) at room temperature. The mixture was heated to 170 °C for 3 h. After cooling and the addition of hexane, the product was precipitated and collected by filtration and washed with hexane (2.4 g, 80%). The characterization data matched the reported literature data.[S6]

Synthesis of compound 8: 3-Nitro-1*H*-pyrazole-5-carbonitrile was prepared according to the reported literature.[S7]

Synthesis of compound 9: Into an oven-dried round-bottomed flask (100 mL) was added compound **8** (1.38 g, 10 mmol), sodium azide (0.78 g, 12 mmol), zinc chloride (1.63 g, 12 mmol), and distilled water (25.0 mL). The mixture was maintained at reflux for overnight. Then it was cooled to room temperature and treated with 2N hydrochloric acid (50 mL) and extracted with ethyl acetate (2 x 50 mL). The organic phase was dried with anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The resulting solid was washed with water and the product was filtered to obtain the desired product as white powder in 87% yield. The characterization data matched the reported literature data.[S8]

Synthesis of compound 10: 5-(1*H*-tetrazol-5-yl)-1*H*-pyrazol-3-amine was prepared according to the literature method.[S8]

Synthesis of H_3NANP-5T (11). A solution of amine **10** (1.0 g, 6.62 mmol) in TFA (15 mL) was cooled to 5–10 °C and treated by dropwise addition of 100% HNO_3 (1.5 mL). The mixture was maintained at 0–5 °C for 2 h, and the precipitate that formed was filtered off, washed with TFA (2 ml) and dried in air.

H_3NANP-5T: Cream color solid; Yield: 91%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 11.64 (br, 3H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 147.1, 139.7, 130.2, 125.3 ppm. Elemental analysis: Calcd (%) for $C_4H_3N_9O_4$ (241.13): C, 19.92; H, 1.25; N, 52.28; Found: C 20.24, H 1.91, N 51.35.

General procedure for the synthesis for compounds 12-15.

H_3NANP-5T (300 mg, 1.24 mmol) was dissolved in methanol (10 mL). Then aqueous ammonia (1 mL), hydrazine monohydrate (350 µl), hydroxylamine (50%, 152 µl, 2 equiv), or TATOT HCl (0.473 g, 2 equiv) was added to the reaction mixture at 0 °C. The mixture was stirred for 1 h at room temperature. The product precipitated and was filtered and washed with methanol and dried in air.

12: Yellow Solid; Yield: 92%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.62 (br, 9H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 153.7, 146.1, 139.2, 120.9 ppm. FTIR (cm^{-1}) ῡ 3316, 3014, 1583, 1545, 1405, 1350, 1328, 1288, 1188, 1172, 1073, 1014, 972, 816, 757, 659. Elemental analysis: Calcd (%) for $C_4H_9N_{11}O_4$ (275.19): C, 17.46; H, 3.30; N, 55.99; Found: C 17.52, H 3.255, N 54.58.

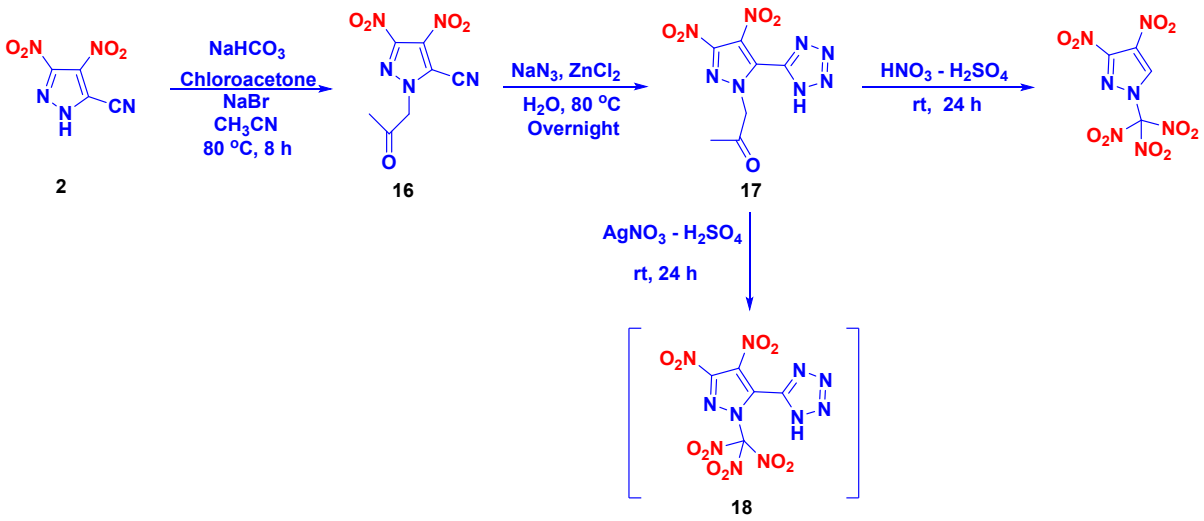
13: Yellow Solid; Yield: 94%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.34 (br), 3.54 (br) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 153.4, 146.0, 138.7, 120.8 ppm. FTIR (cm^{-1}) ῡ 3553, 3269, 2632, 1616, 1528, 1540, 1454, 1419, 1374, 1300, 1214, 1098, 1018, 971, 868, 816, 766, 658.

Elemental analysis: Calcd (%) for $C_4H_{11}N_{13}O_4$ (305.22): C, 14.86; H, 4.05; N, 56.33; Found: C 14.94, H 3.45, N 56.55.

14: Yellow solid; Yield: 84%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 8.40 (br, 9H) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 151.8, 146.2, 136.2, 120.3 ppm. FTIR (cm^{-1}) ῡ 3316, 2912, 2696, 1572, 1527, 1459, 1374, 1328, 1291, 1195, 1152, 1088. 1006, 974, 821, 745. Elemental analysis: Calcd (%) for $C_4H_9N_{11}O_6$ (307.19): C, 15.64; H, 2.95; N, 50.16; Found: C 16.05, H 2.93 N 50.19.

15: Yellow solid; Yield: 88%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 7.09 (s, 4H), 6.87 (s, 4H) 5.68 (s, 4H) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 159.4, 149.7, 148.0, 146.7, 142.0, 133.5 ppm. FTIR (cm^{-1}) ῡ 3443. 3286, 3176, 2744, 1716, 1700, 1650, 1591, 1537, 1506, 1461, 1356, 1300, 1196, 1065, 1015, 972, 844, 762. Elemental analysis: Calcd (%) for $C_{10}H_{15}N_{25}O_4$ (549.40): C, 21.86; H, 2.75; N, 63.74; Found: C 21.59, H 3.02 N 63.3.

Synthesis of 16. To a 100 mL round bottom flask, compound **2** (1.2 g, 6.55 mmol) was added and dissolved in dry acetonitrile (20 mL). To this, sodium bicarbonate (0.55 g, 6.55 mmol) was added in portions. The mixture was maintained at room temperature for 1 hour. After, NaBr (0.81 g, 7.86 mmol) and chloroacetone (0.73 g, 7.89 mmol) were added in one portion. The mixture was maintained at reflux for 8 hours. After completion of the reaction, the solvent was evaporated by blowing air. The residue was redissolved in water and stirred. The precipitate was filtered and dried to obtain the product in 73% yield (Scheme S3).



Scheme S3: Synthetic scheme for **16, 17** and **18**.

16: Yellow solid; Yield: 73%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 5.81 (s, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 198.7, 146.0, 129.8, 117.9, 106.2, 62.5, 27.0 ppm. FTIR (cm^{-1}) ῡ 3350, 2996, 2942, 2260, 1734, 1559, 1528, 1490, 1462, 1400, 1343, 1329, 1175, 1088, 908, 850, 820, 765, 642. Elemental analysis: Calcd (%) for $C_7H_5N_5O_5$ (239.15): C, 35.16; H, 2.11; N, 29.29; Found: C 34.88, H 2.11, N 28.95.

Synthesis of 17. Into an oven-dried round bottomed flask (100 mL) was added compound **16** (2.39 g, 10 mmol), sodium azide (0.78 g, 12 mmol), zinc chloride (1.63 g, 12 mmol), and

distilled water (25.0 mL). The mixture was maintained at reflux overnight. After that, it was cooled to room temperature and treated with 2N hydrochloric acid to maintain the pH~3. The colorless precipitate was formed and collected by filtration. The solid compound was washed with excess amounts of water and dried at room temperature to give white solid 17 (2.32 g, 82%).

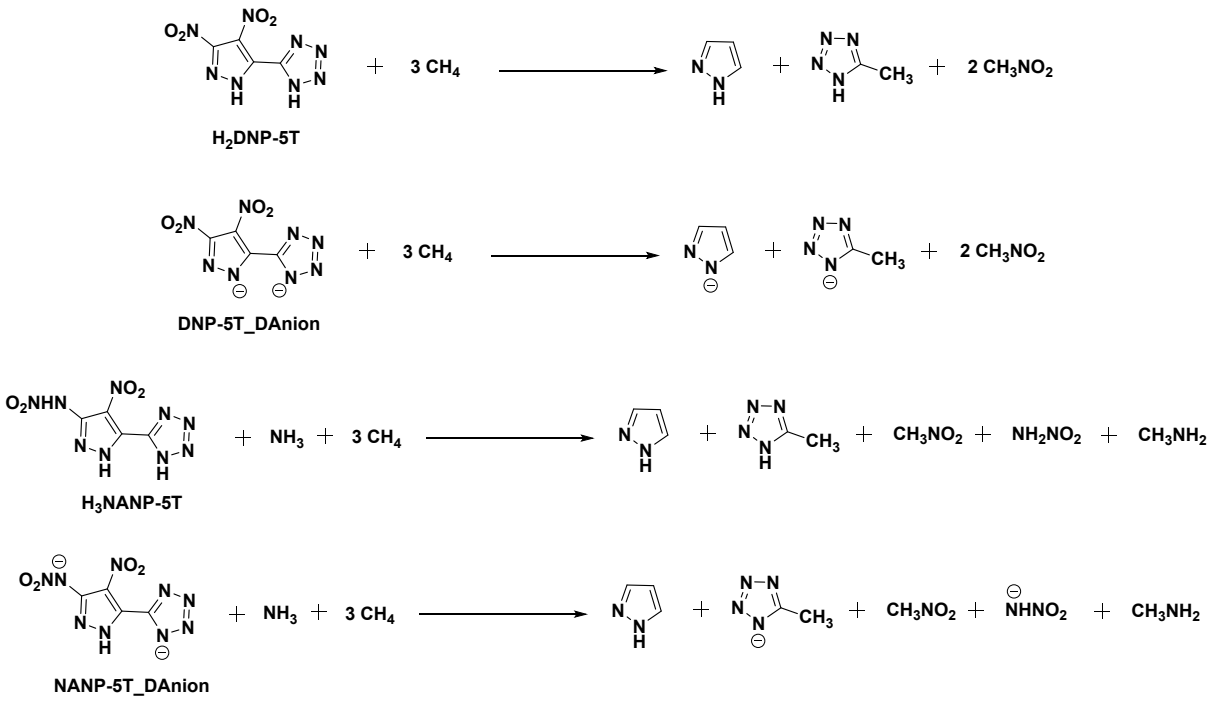
17: Orange solid; Yield: 82%; ^{1}H NMR (500.19 MHz, DMSO-d_6) δ 5.75 (s, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 199.7, 149.4, 145.4, 130.4, 125.6, 62.6, 26.9 ppm. FTIR (cm^{-1}) ῡ 3117, 3000, 2950, 1728, 1556, 1535, 1499, 1478, 1360, 1337, 1312, 1174, 1121, 1050, 1039, 902, 813, 800. Elemental analysis: Calcd (%) for $C_7H_6N_8O_5$ (282.18): C, 29.80; H, 2.14; N, 39.71; Found: C 29.38, H 2.29, N 39.73.

Synthesis of 18. Compound **17** (0.56g, 2 mmol) was added portion wise to the nitrating mixture of conc. H_2SO_4 (10 mL) and silver nitrate (2.7g, 16 mmol) at 0 ^{o}C. The mixture was stirred at room temperature for 24 h. After that, the reaction mixture was poured slowly into ice-cold distilled water. The colourless precipitate (mixture of product and silver sulphate) was formed and collected by filtration. The product was confirmed by ESI and NMR analysis.

18: ^{13}C NMR (125.78 MHz, DMSO-d_6) δ 149.3, 146.5, 135.2, 132.6, 124.7 ppm. ^{14}N NMR (36.14 MHz, DMSO-d_6) δ -29.3, -40.3 ppm. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_5N_{11}O_{10}$ 373.9829, found: 373.9839.

3. Theoretical study and isodesmic reactions

The HOFs (heats of formation) 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.[S8] The atomization energies for cations were calculated by using the G^{2}ab *initio* method.[S9] 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.[S10] All calculated gas-phase enthalpies for covalent materials are converted to solid phase values by subtracting the empirical heat of sublimation obtained based on Trouton's rule.[S11]



Scheme S4: Isodesmic Reactions.

4. X-Ray Crystallographic Data

Table S1. Crystal data and structure refinement for compounds **H2DNP-5T**, **11-DMA**, **and 4**.

Compound	**H2DNP-5T (3)**	**11-DMA**	**4**
CCDC	2352179	2352181	2352182
Formula	$C_4H_2N_8O_4$	$C_6H_{10}N_{10}O_4$	$C_4H_8N_{10}O_4$
$D_{calc.}$/ g cm^{-3}	1.847	1.703	1.712
m/mm^{-1}	1.456	1.251	1.312
Formula Weight	226.14	286.24	260.20
Color	yellow	yellow	yellow
Shape	irregular-shaped	needle-shaped	block-shaped
Size/mm^3	0.21×0.15×0.05	0.15×0.04×0.02	0.24×0.16×0.07
T/K	100.00(10)	100.00(10)	100.00(10)
Crystal System	monoclinic	triclinic	monoclinic
Space Group	P21/n	P-1	$P2_1/n$
a/Å	8.62863(11)	6.0120(3)	8.04522(10)
b/Å	9.67955(12)	9.7746(3)	9.82848(11)
c/Å	9.75493(13)	9.9277(4)	12.90621(14)
α/°	90	80.652(3)	90
β/°	93.4845(12)	76.157(4)	98.3666(11)

γ/°	90	84.914(3)	90
V/Å^3	813.238(18)	558.18(4)	1009.66(2)
Z	4	2	4
Z'	1	1	1
Wavelength/Å	1.54184	1.54184	1.54184
Radiation type	Cu K$_a$	Cu K$_a$	Cu K$_a$
Q_{min}/°	6.448	4.591	5.681
Q_{max}/°	80.322	77.364	77.635
Measured Refl's.	6003	6256	11895
Indep't Refl's	1741	2274	2117
Refl's I≥2 s(I)	1590	1870	1987
R_{int}	0.0301	0.0343	0.0344
Parameters	153	199	195
Restraints	0	0	0
Largest Peak	0.297	0.517	0.324
Deepest Hole	-0.295	-0.294	-0.274
GooF	1.073	1.056	1.065
wR_2 (all data)	0.0916	0.1371	0.0889
wR_2	0.0889	0.1280	0.0874
R_1 (all data)	0.0366	0.0567	0.0354
R_1	0.0339	0.0469	0.0336

Table S2: Hydrogen Bond information for **H_2DNP-5T (3)**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N1	H1	N6[1]	0.906(19)	1.960(19)	2.7928(15)	152.1(16)
N3	H3	N2[2]	0.89(2)	2.06(2)	2.9350(16)	167.9(18)

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

Table S3: Hydrogen Bond information for **4**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
N10	H10A	N5[1]	0.92(2)	1.90(2)	2.8100(16)	172.5(17)
N10	H10B	O3[2]	0.89(2)	2.11(2)	2.9732(15)	162.6(19)
N10	H10C	N1[3]	0.94(2)	1.93(2)	2.8650(15)	169.3(18)
N9	H9B	N3	0.91(2)	2.01(2)	2.8861(16)	162.7(17)
N9	H9C	N2[4]	0.89(2)	2.07(2)	2.9485(16)	172.0(17)

––––

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

5. NMR spectra (^{1}H, ^{13}C, ^{14}N and ^{15}N), IR spectra, and DSC of compounds

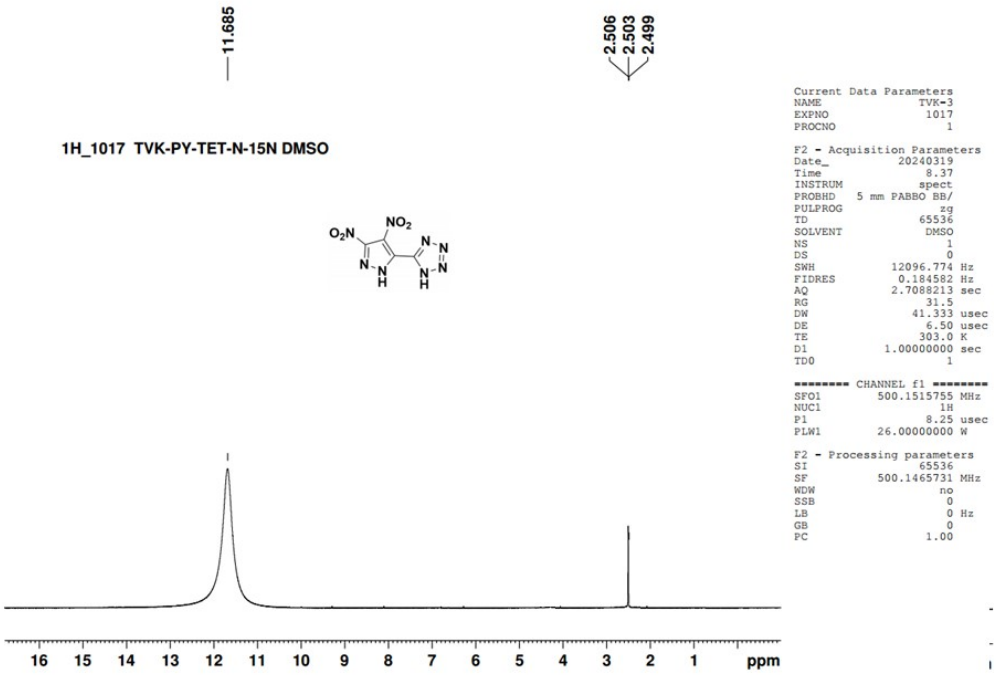

Figure S1: ^{1}H NMR spectrum of **3** in dimethyl sulfoxide-d_6.

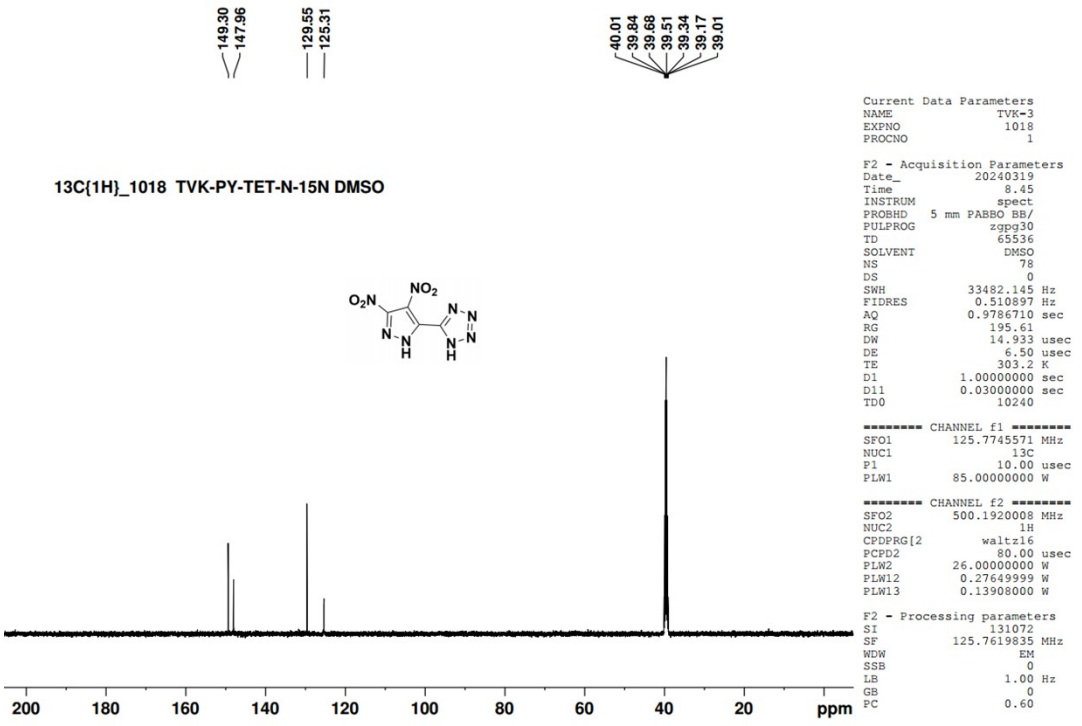

Figure S2: ^{13}C NMR spectrum of **3** in dimethyl sulfoxide-d_6.

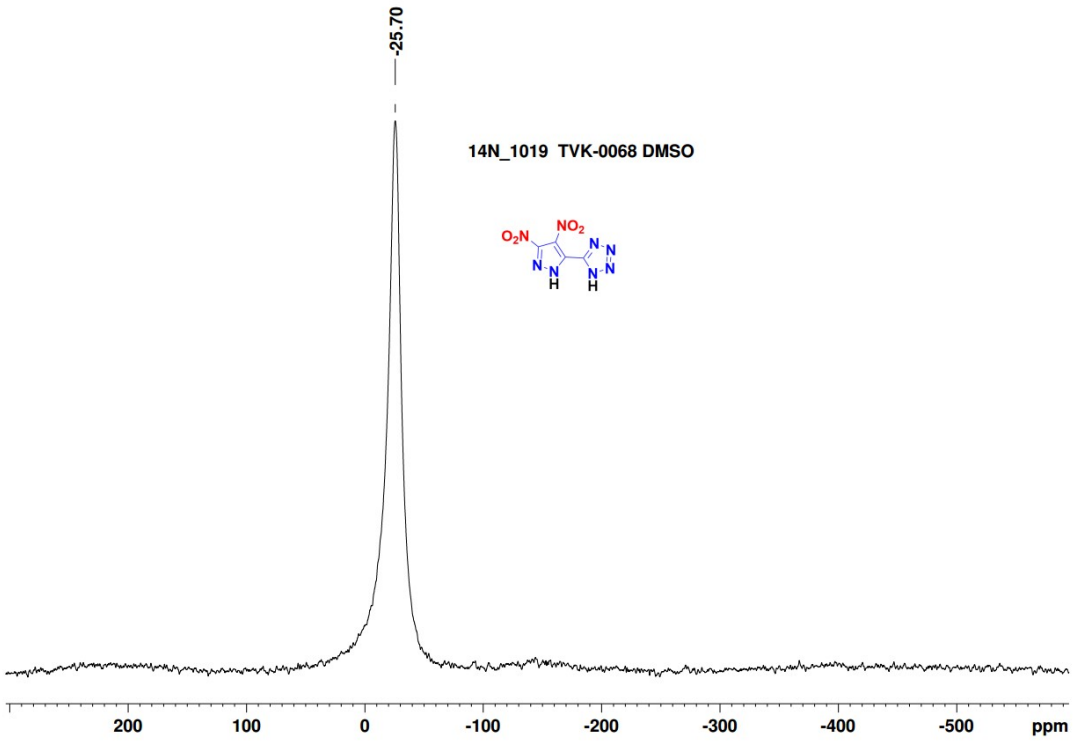

Figure S3: ^{14}N NMR spectrum of **3** in dimethyl sulfoxide-d_6.

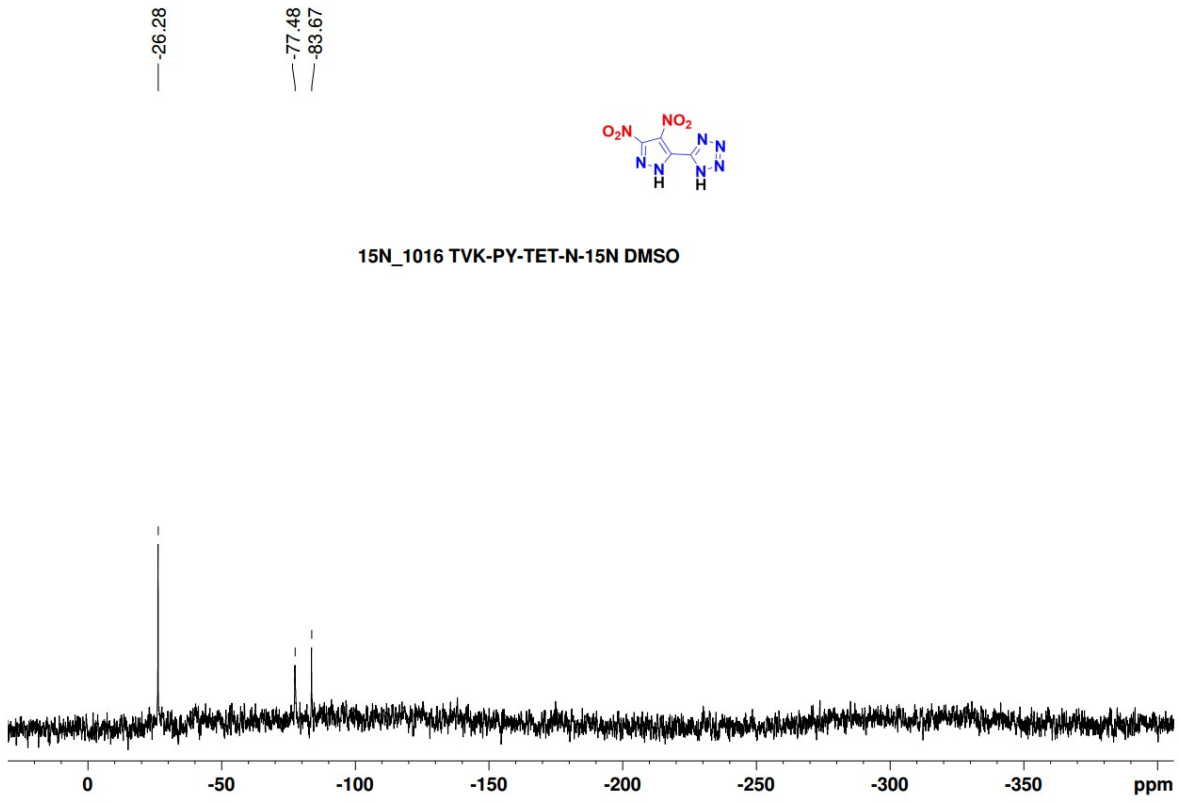

Figure S4: ^{15}N NMR spectrum of **3** in dimethyl sulfoxide-d_6.

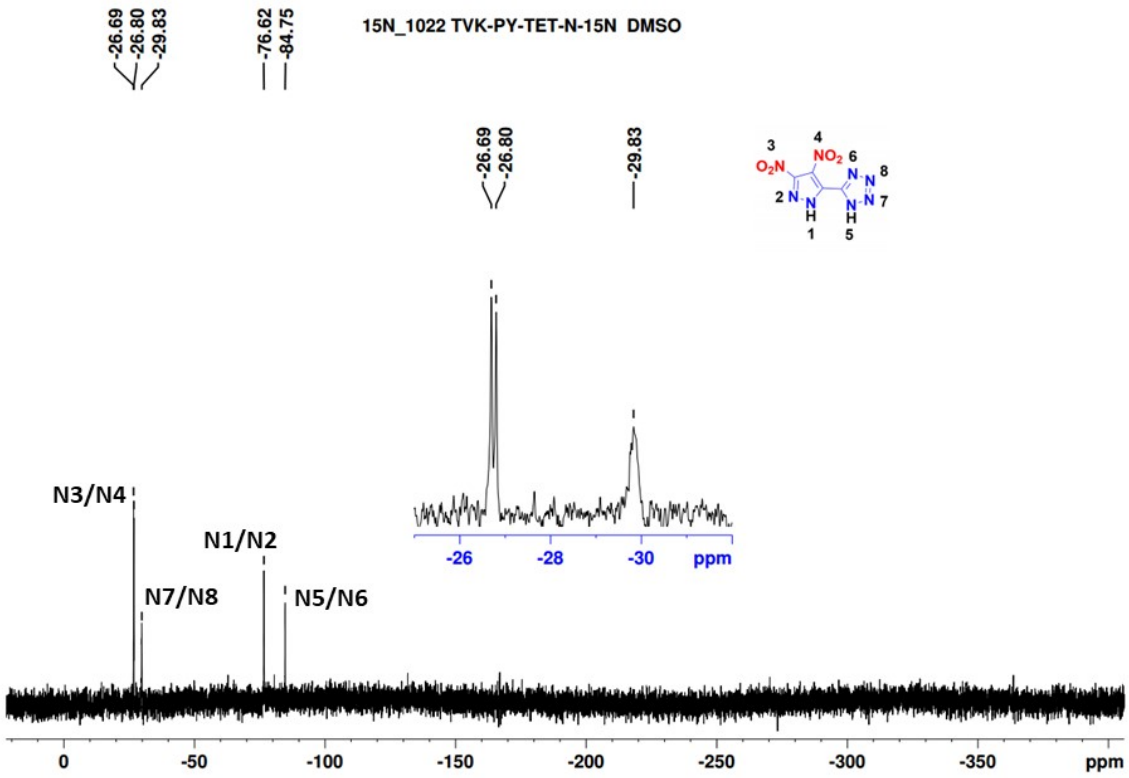

Figure S5: ^{15}N NMR spectrum of **3** in dimethyl sulfoxide-d_6 (D_2O Exchange).

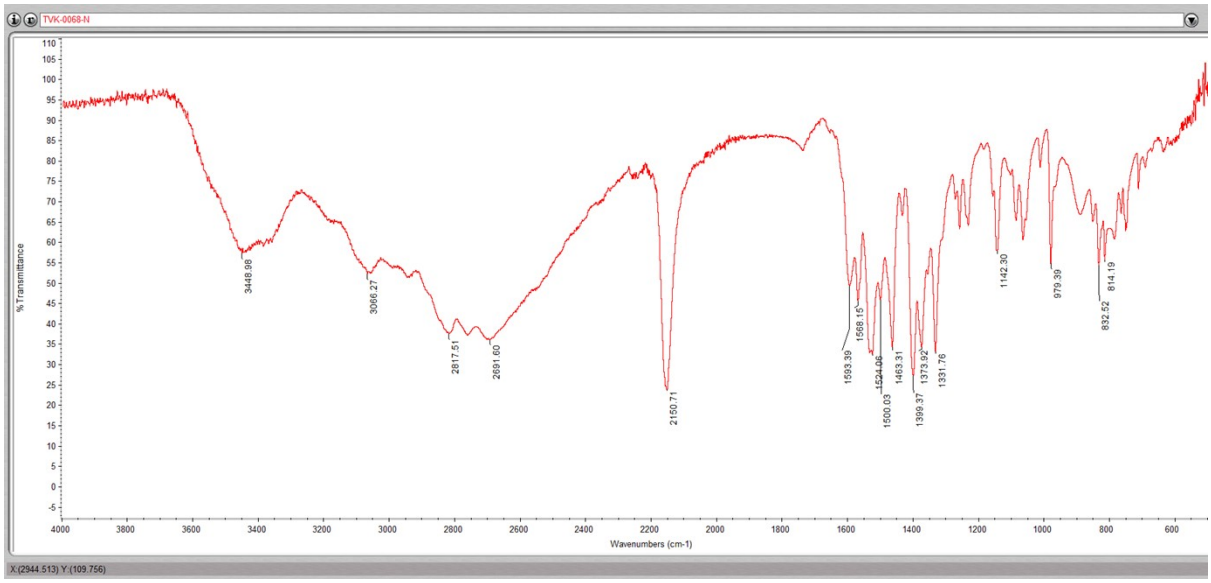

Figure S3: IR spectrum of **3**.

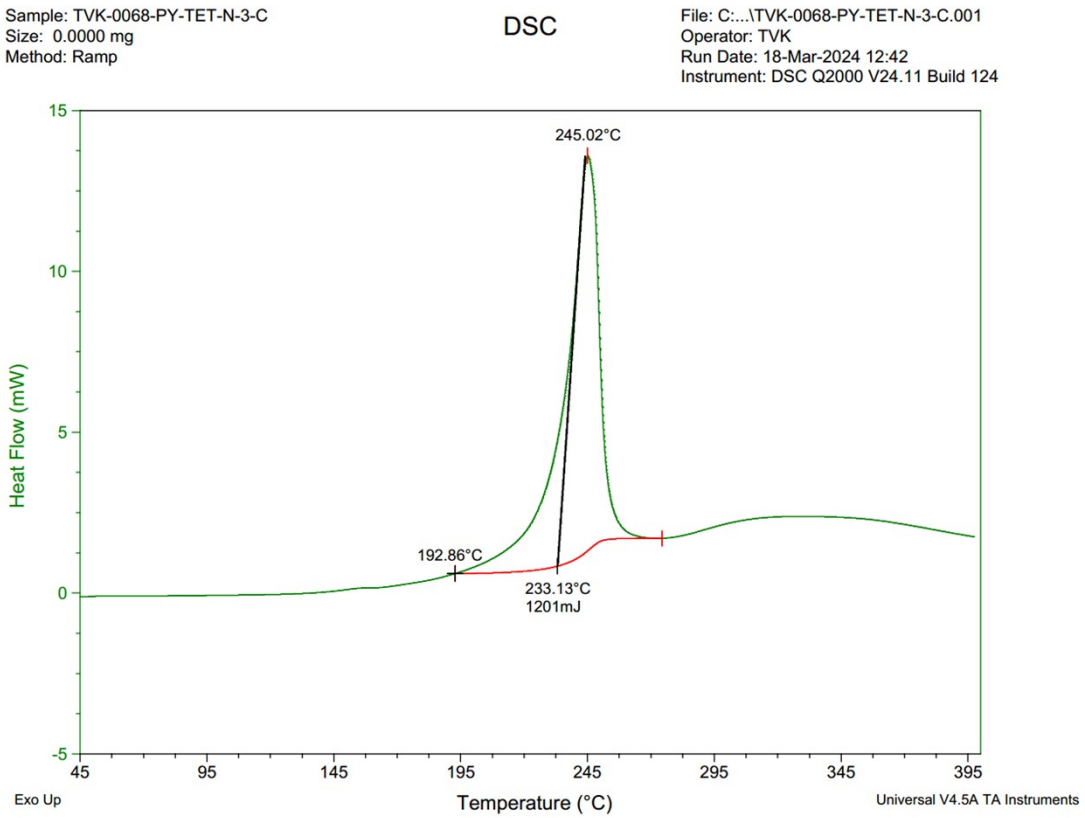

Figure S4: Thermal behavior of **3** at 5 °C/min.

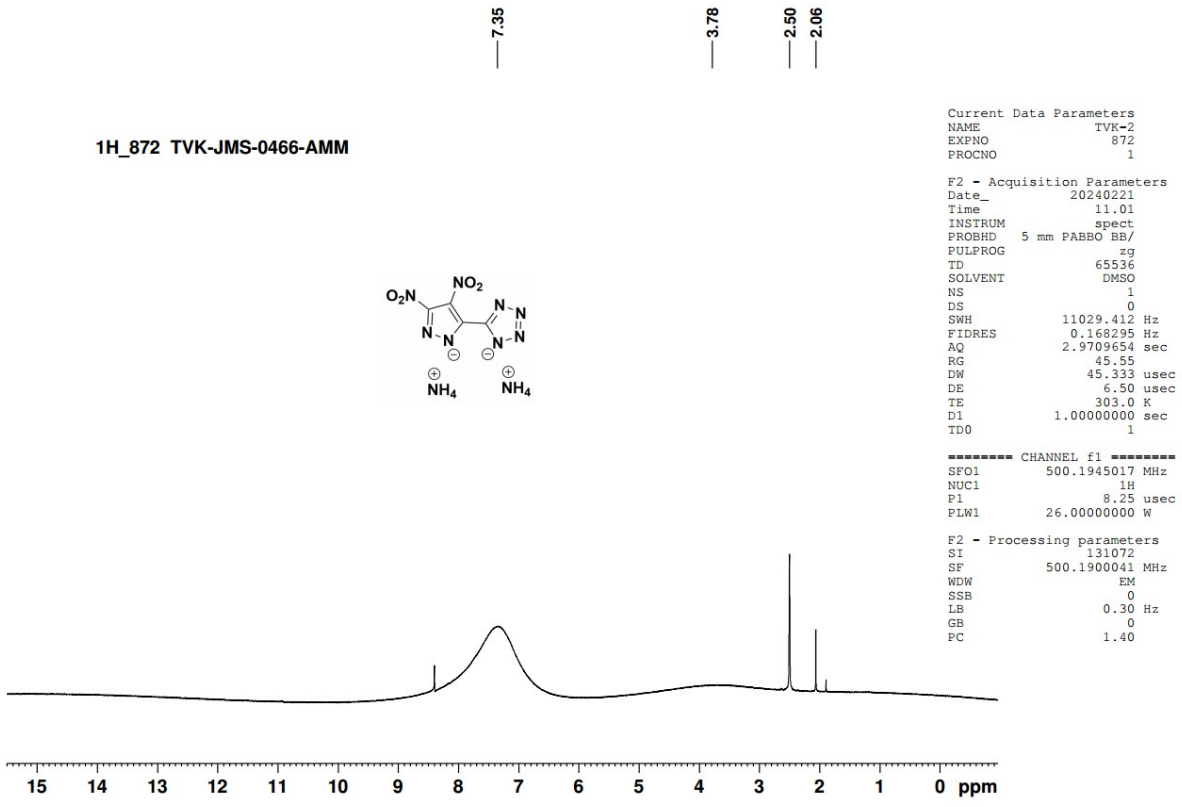

Figure S5: ^{1}H NMR spectrum of **4** in dimethyl sulfoxide-d_6.

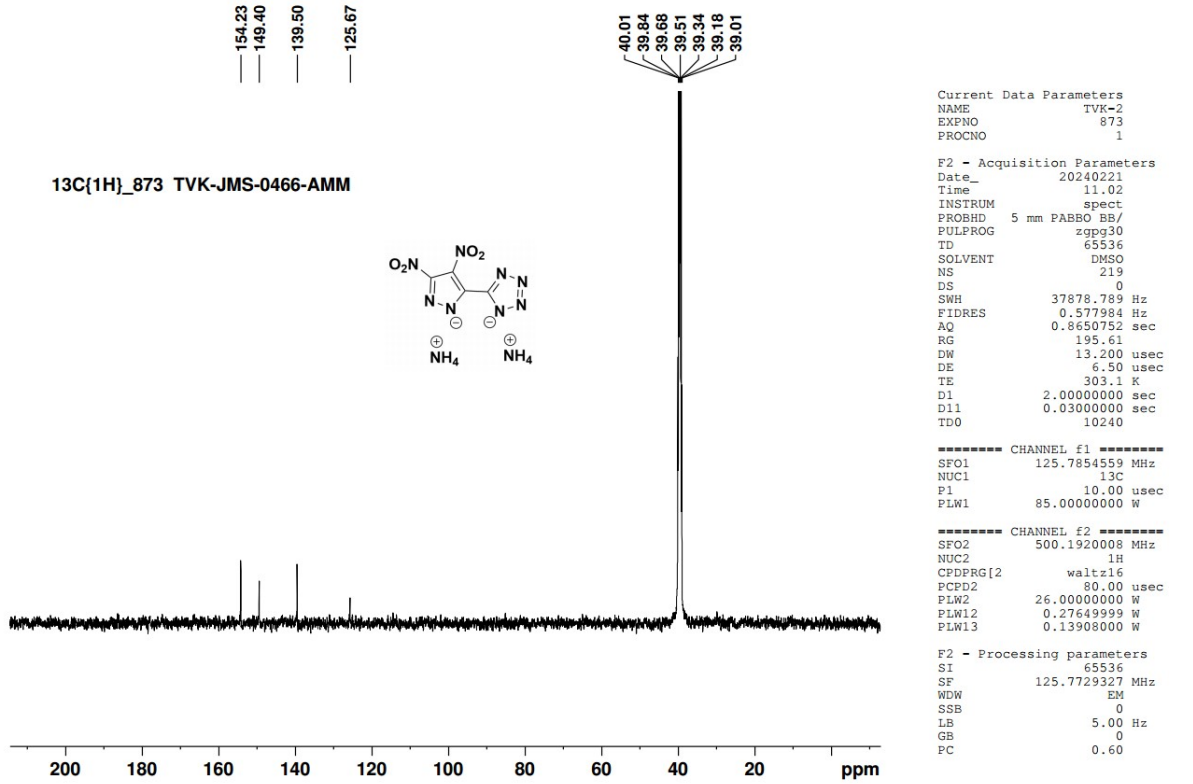

Figure S6: ^{13}C NMR spectrum of **3** in dimethyl sulfoxide-d_6.

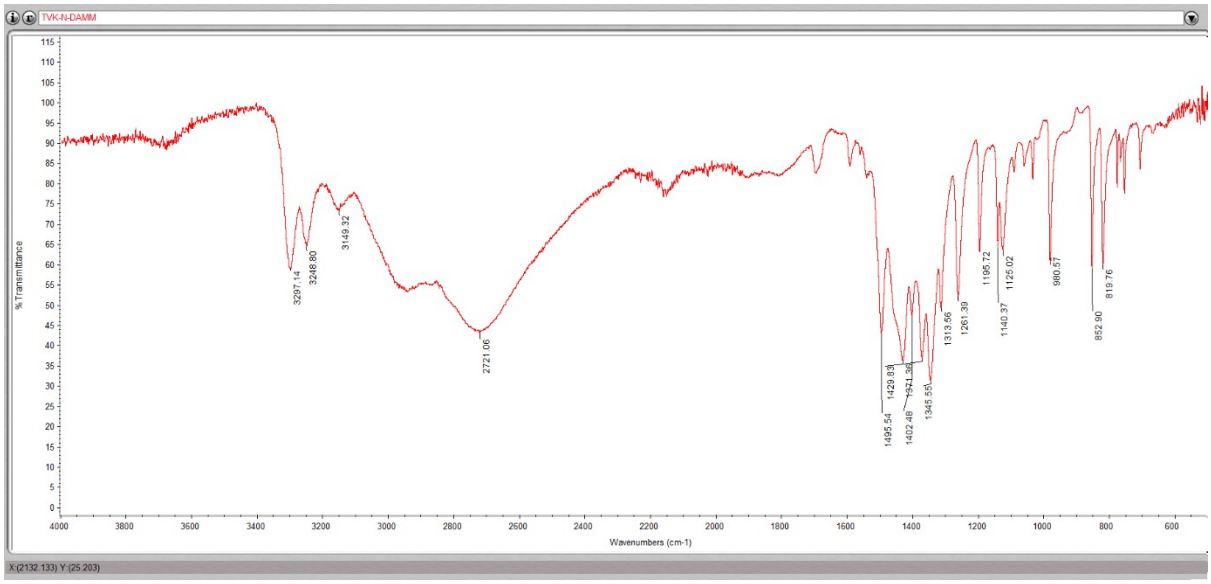

Figure S7: IR spectrum of **4**.

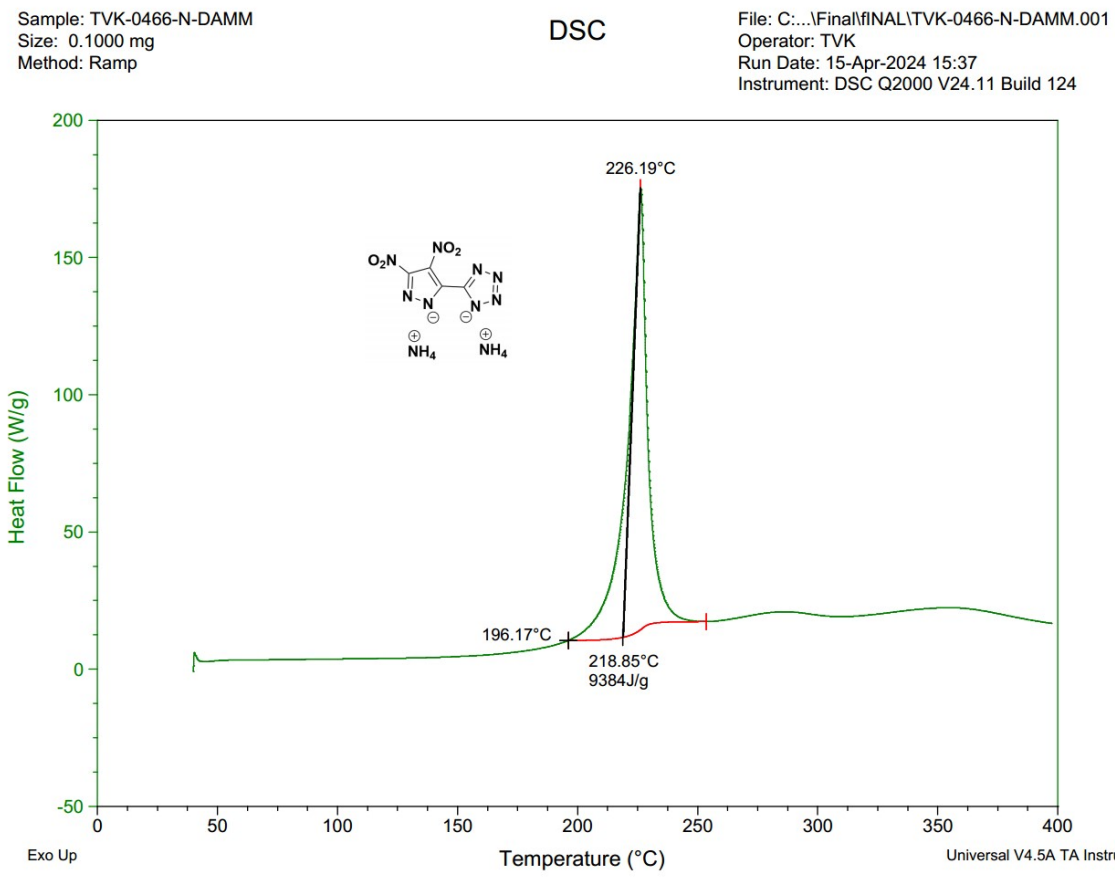

Figure S8: Thermal behavior of **4** at 5 °C/min.

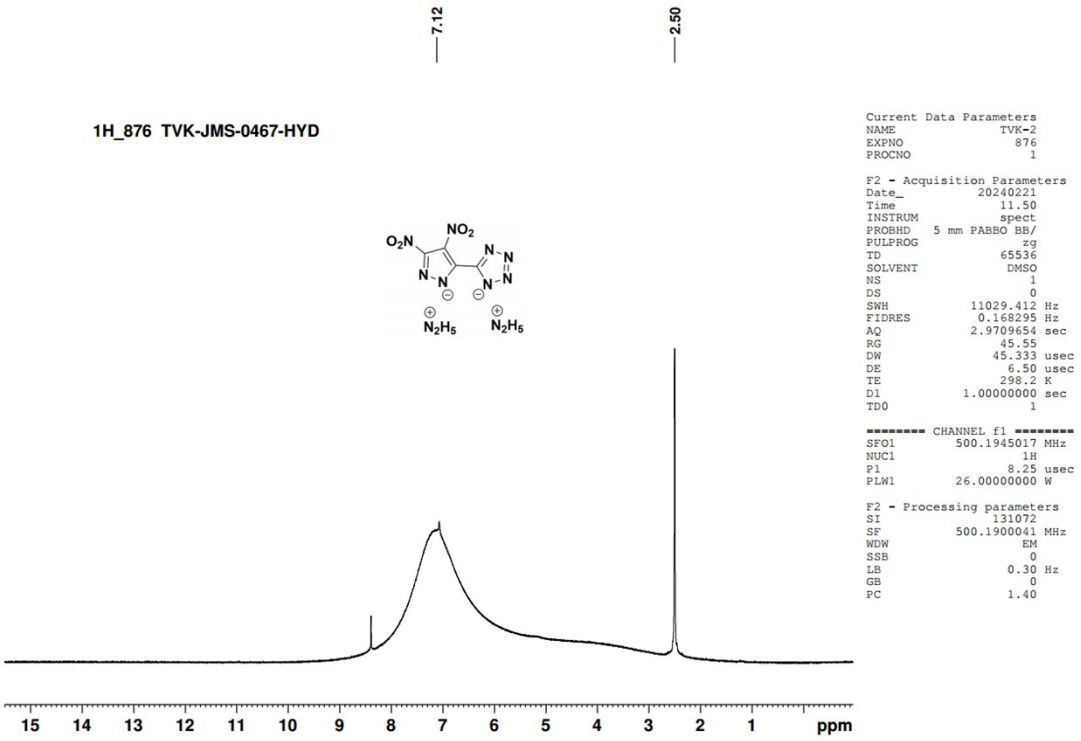

Figure S9: ^{1}H NMR spectrum of **5** in dimethyl sulfoxide-d_6.

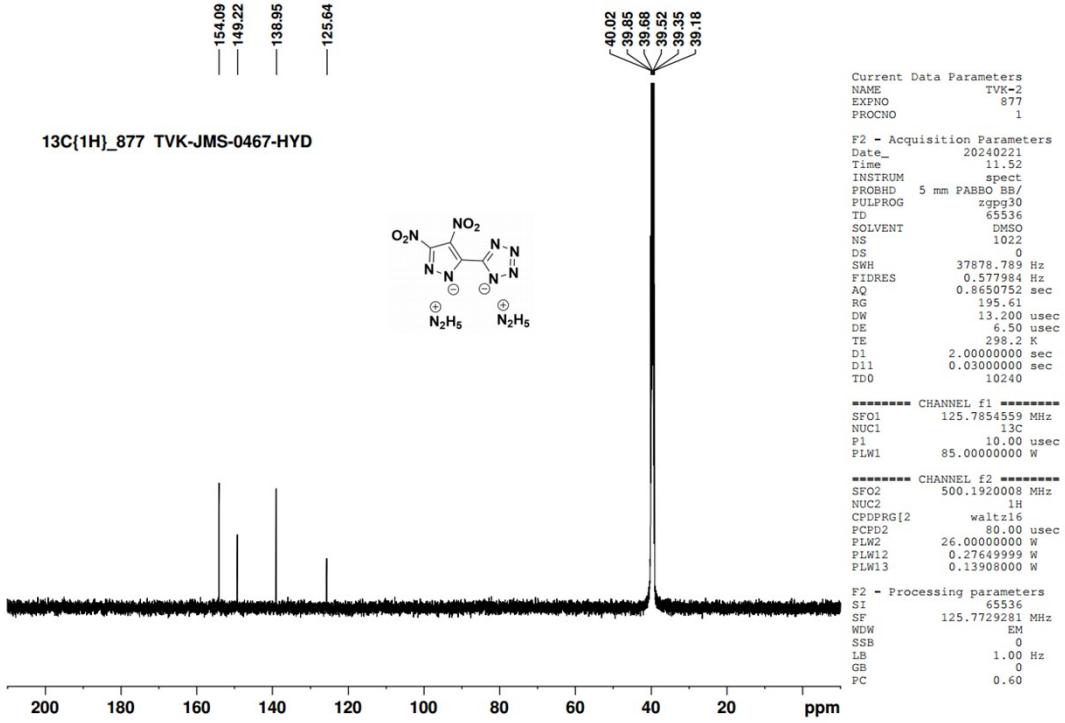

Figure S10: ^{13}C NMR spectrum of **5** in dimethyl sulfoxide-d_6.

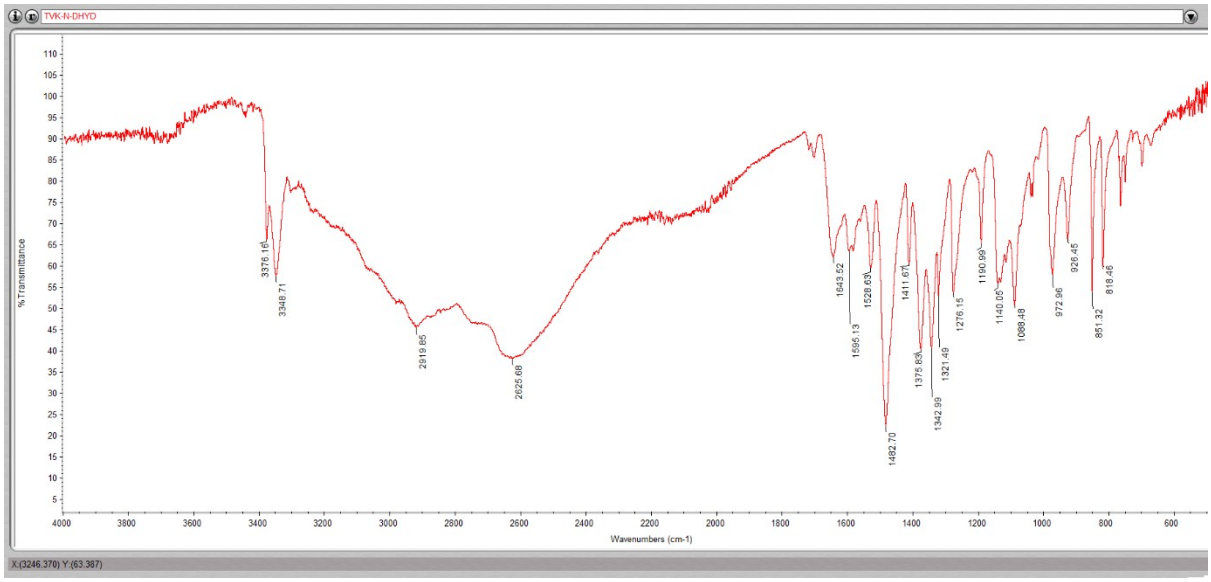

Figure S11: IR spectrum of **5**.

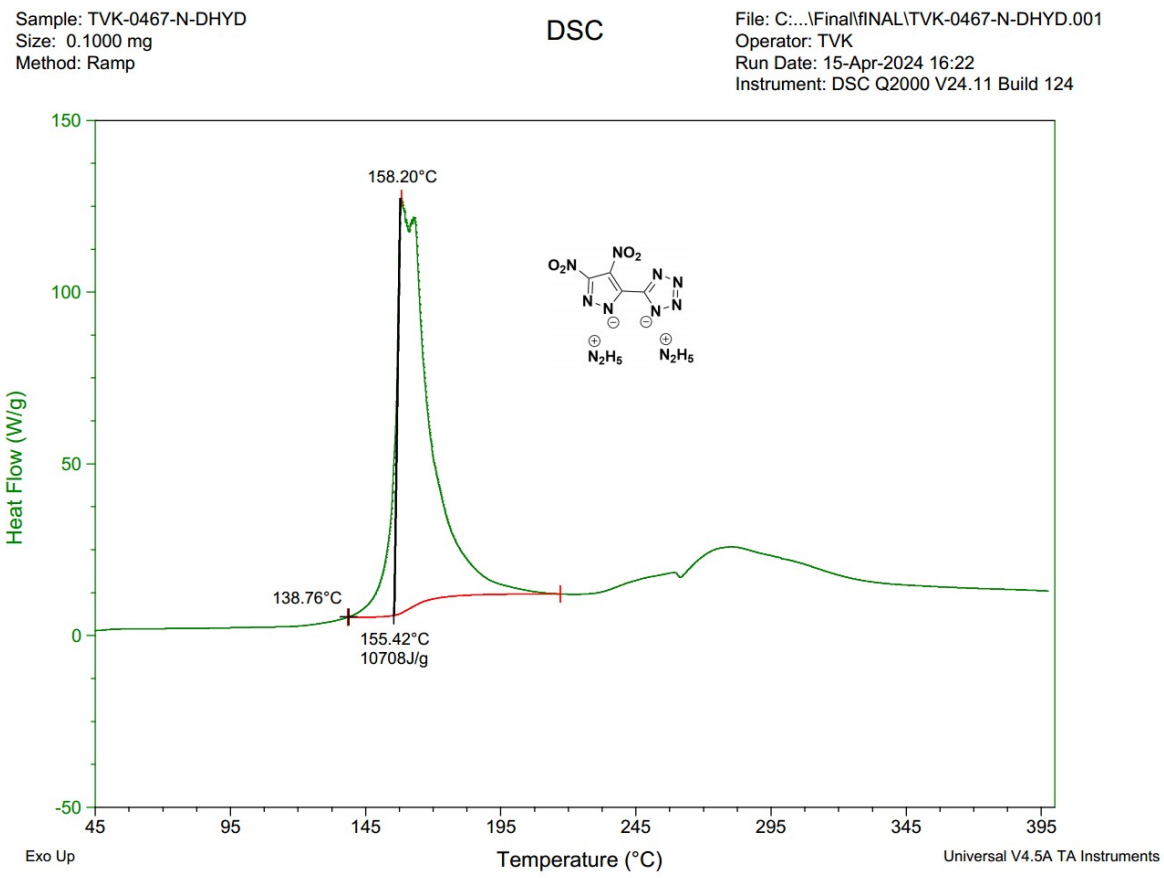

Figure S12: Thermal behavior of **5** at 5 °C/min.

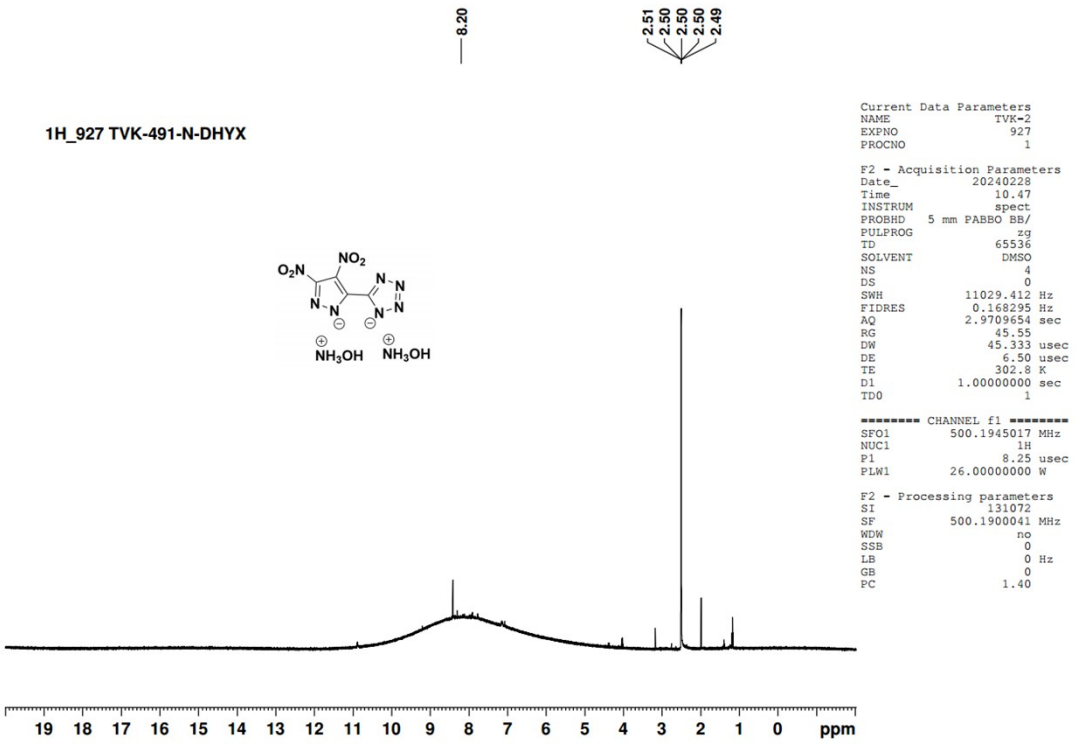

Figure S13: ^{1}H NMR spectrum of **6** in dimethyl sulfoxide-d_6.

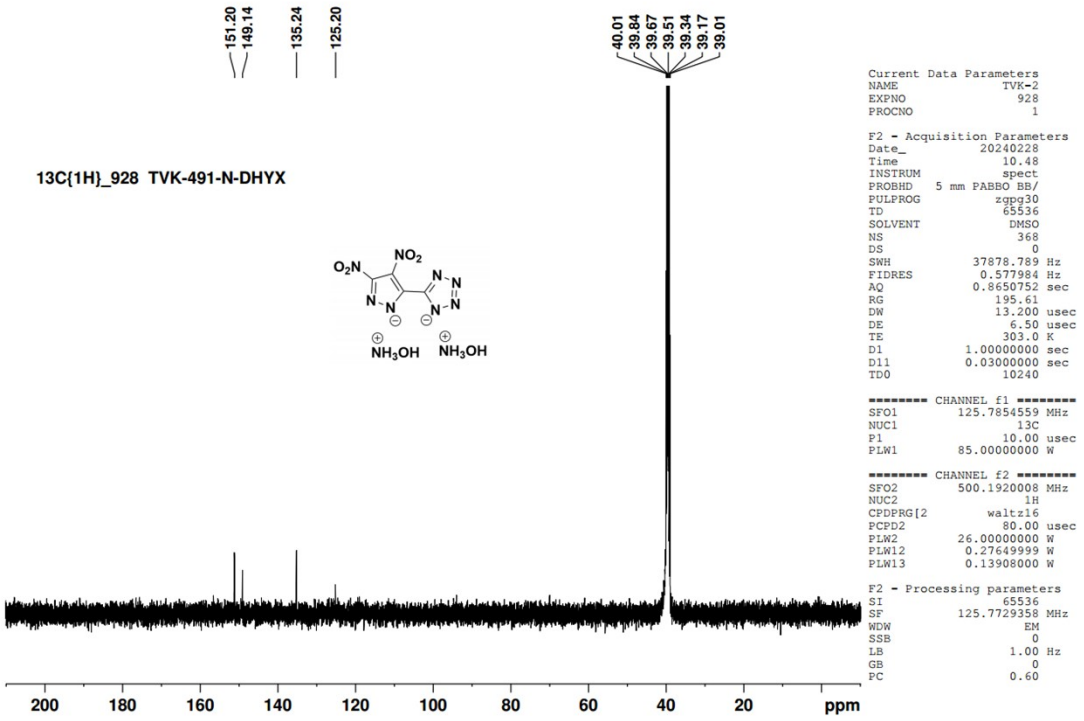

Figure S14: ^{13}C NMR spectrum of **6** in dimethyl sulfoxide-d_6.

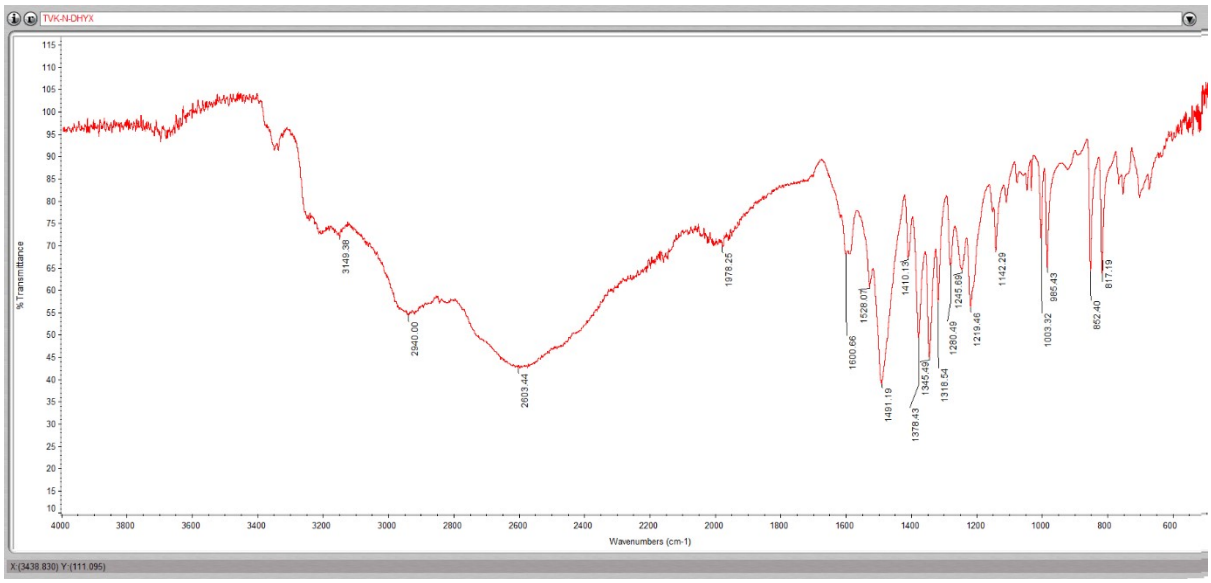

Figure S15: IR spectrum of **6**.

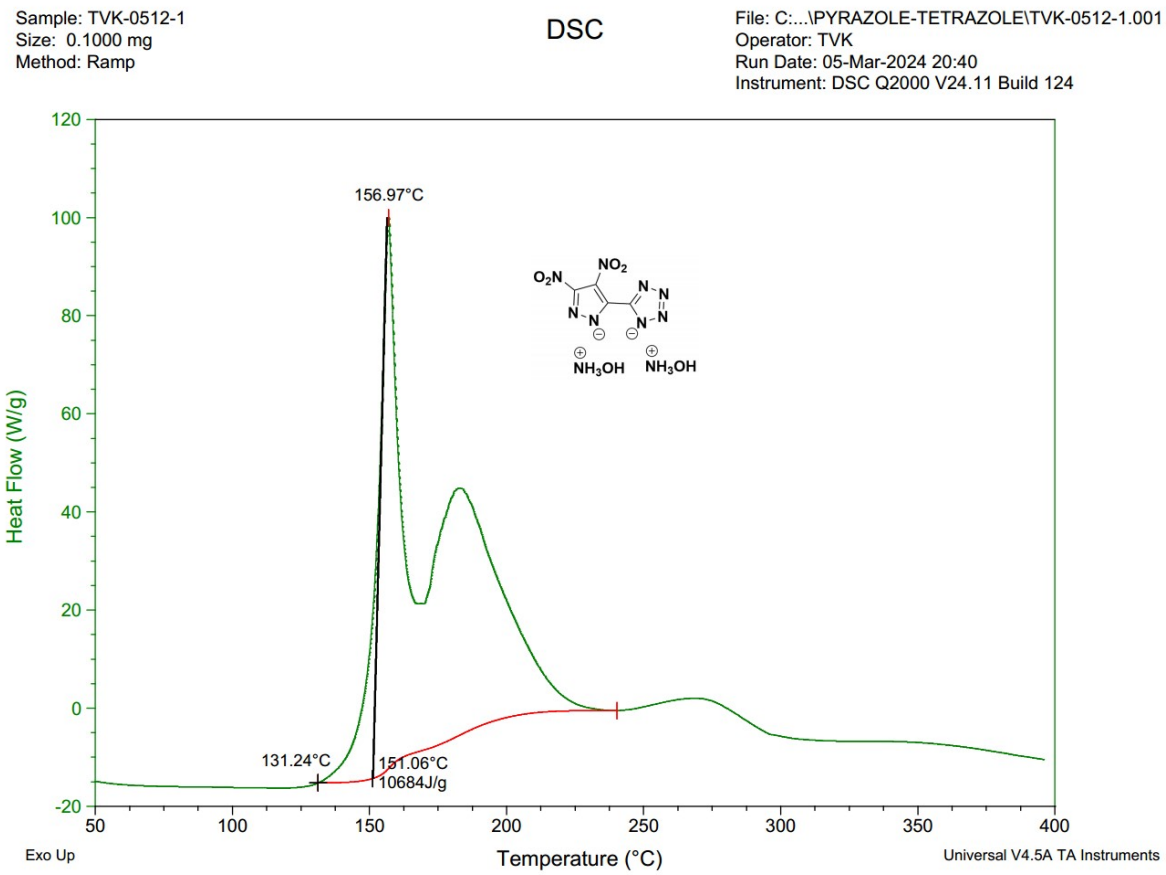

Figure S16: Thermal behavior of **6** at 5 °C/min.

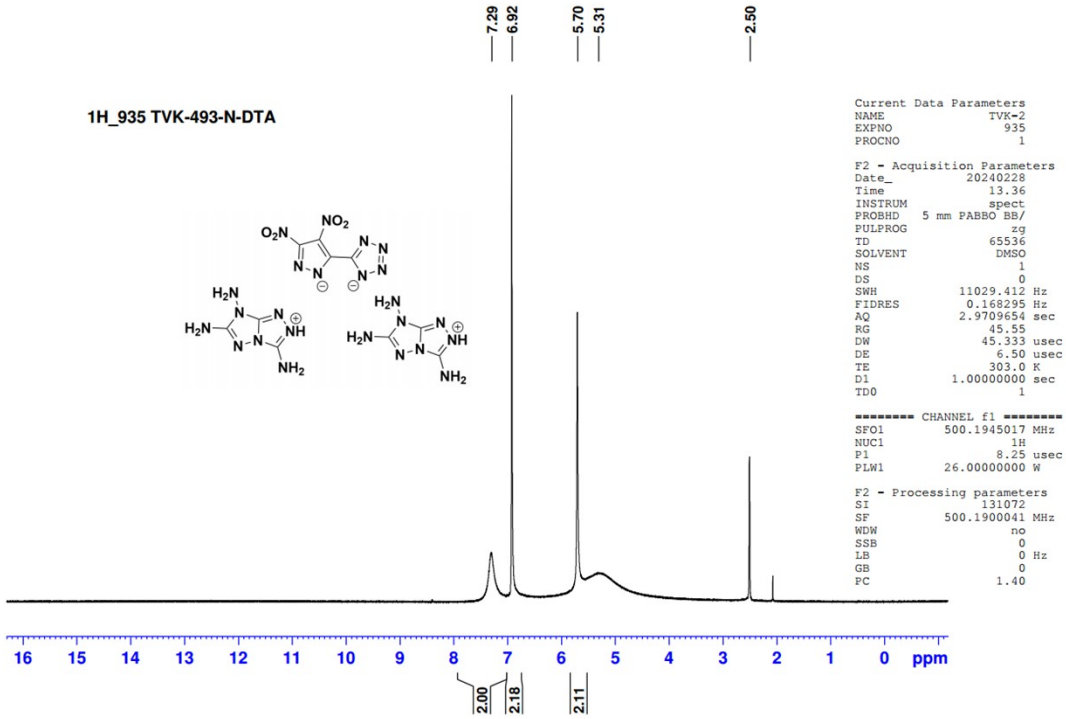

Figure S17: [1]H NMR spectrum of **7** in dimethyl sulfoxide-d_6.

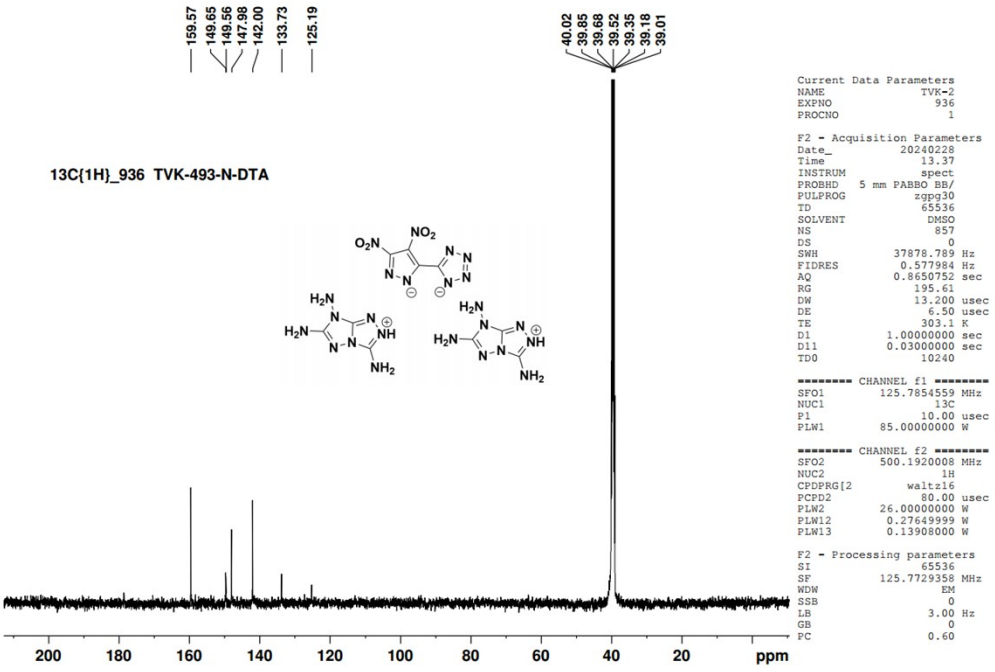

Figure S18: [13]C NMR spectrum of **7** in dimethyl sulfoxide-d_6.

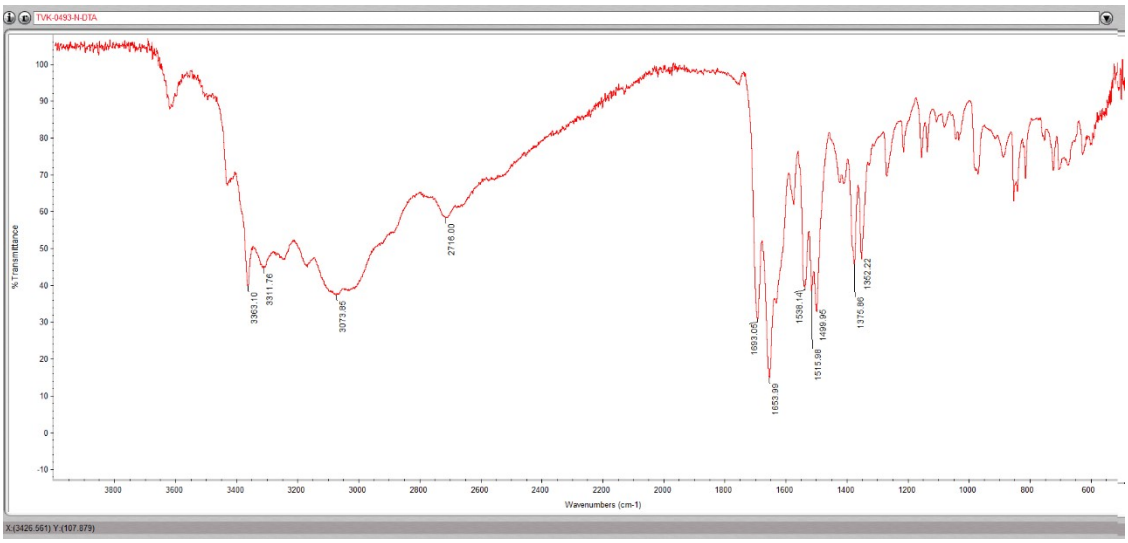

Figure S19: IR spectrum of **7**.

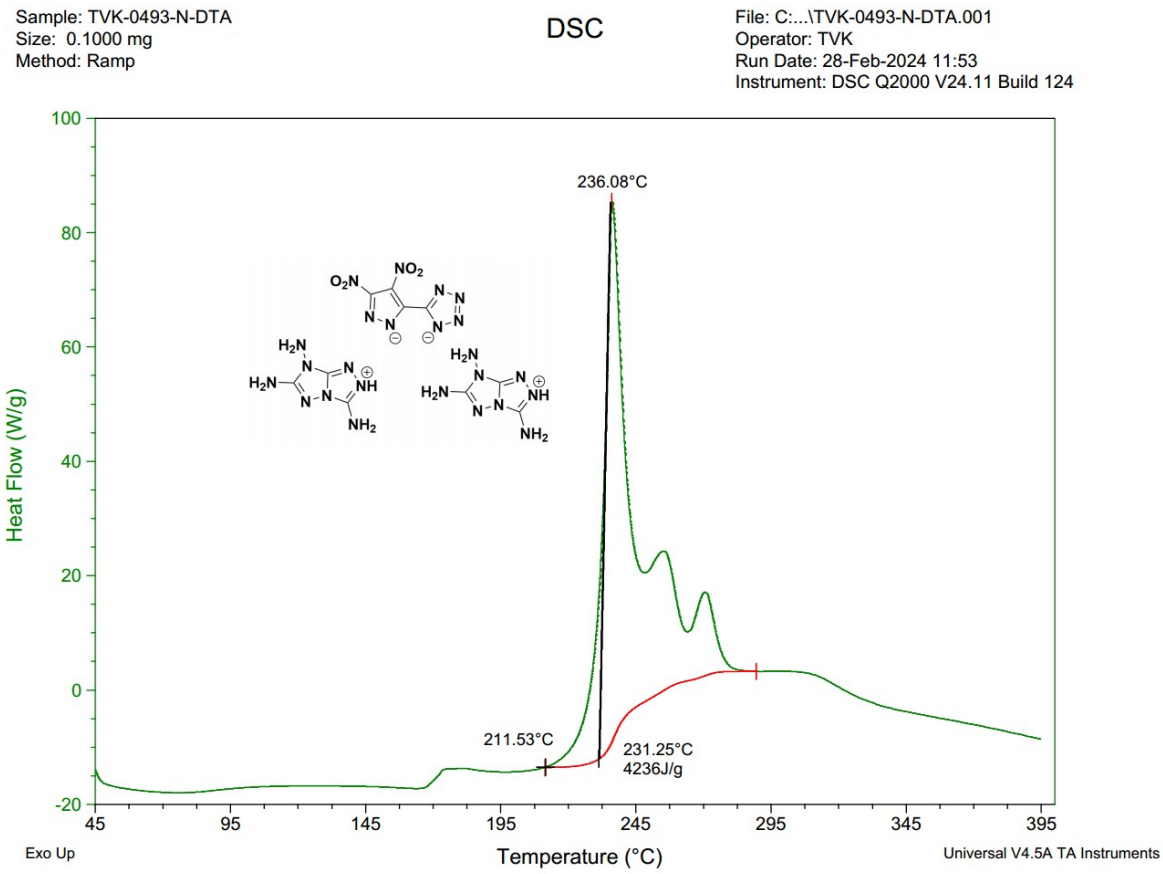

Figure S20: Thermal behavior of **7** at 5 °C/min.

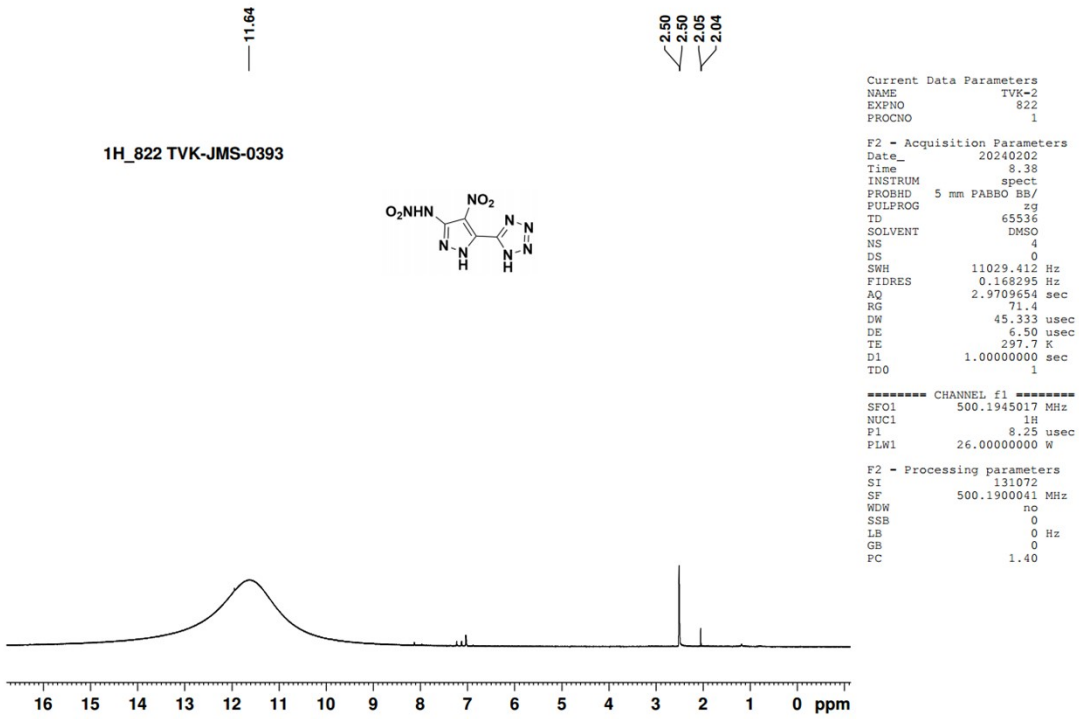

Figure S21: [1]H NMR spectrum of **11** in dimethyl sulfoxide-d_6.

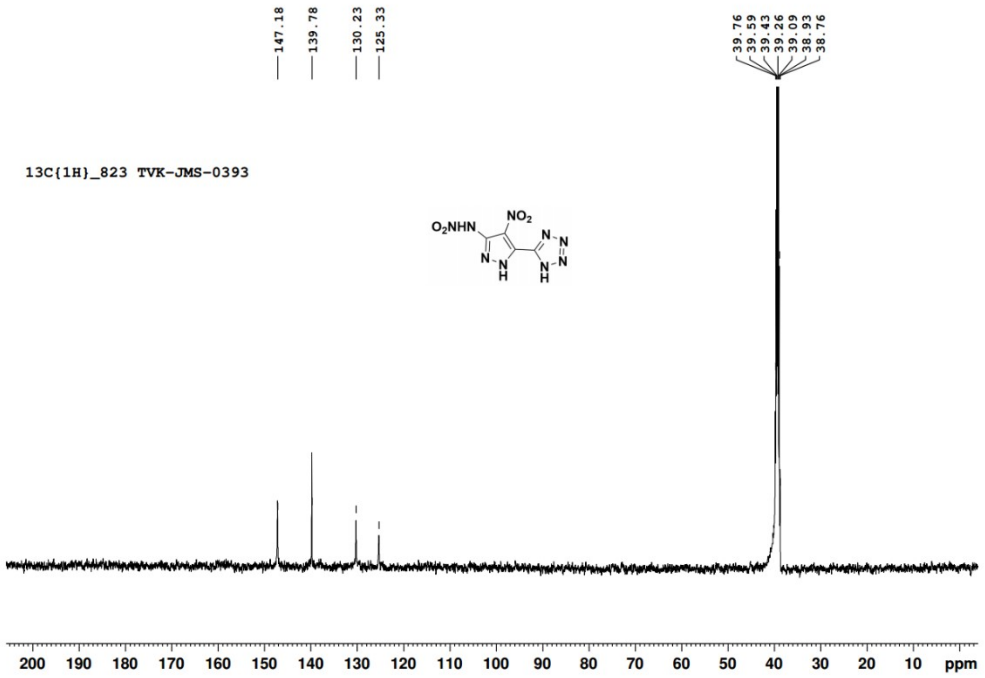

Figure S22: [13]C NMR spectrum of **11** in dimethyl sulfoxide-d_6.

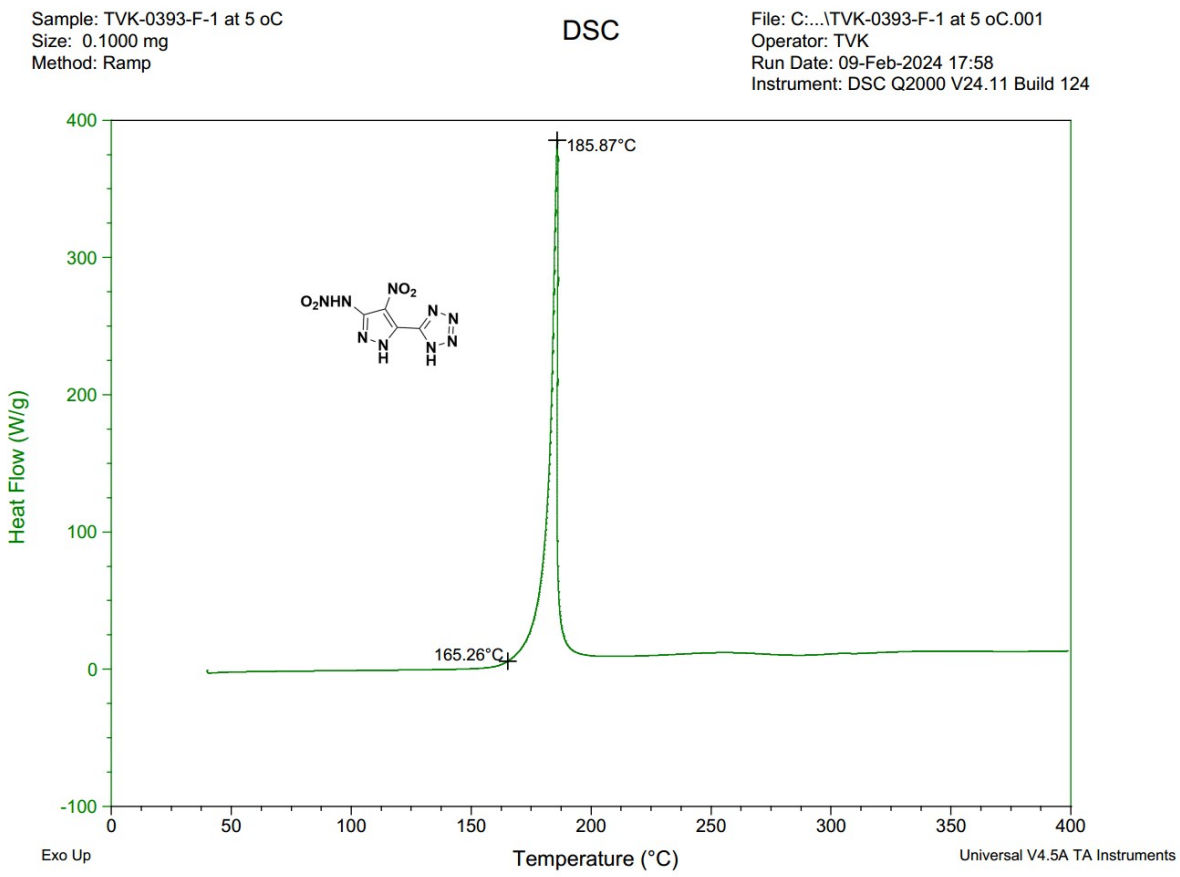

Figure S23: Thermal behavior of **11** at 5 °C/min.

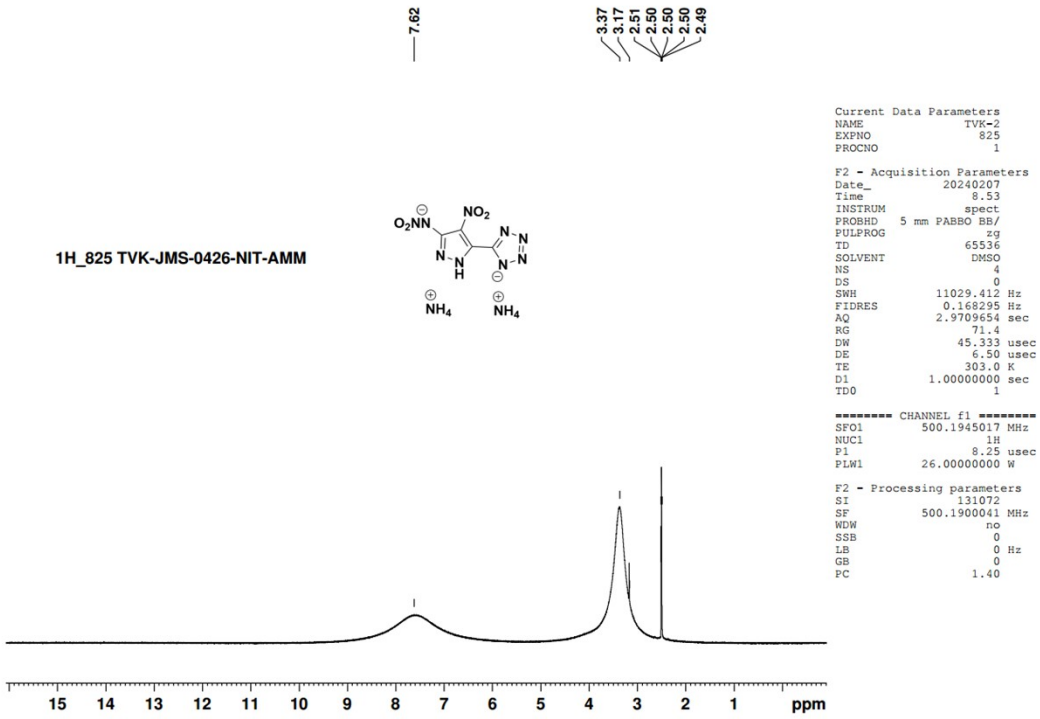

Figure S24: [1]H NMR spectrum of **12** in dimethyl sulfoxide-d_6.

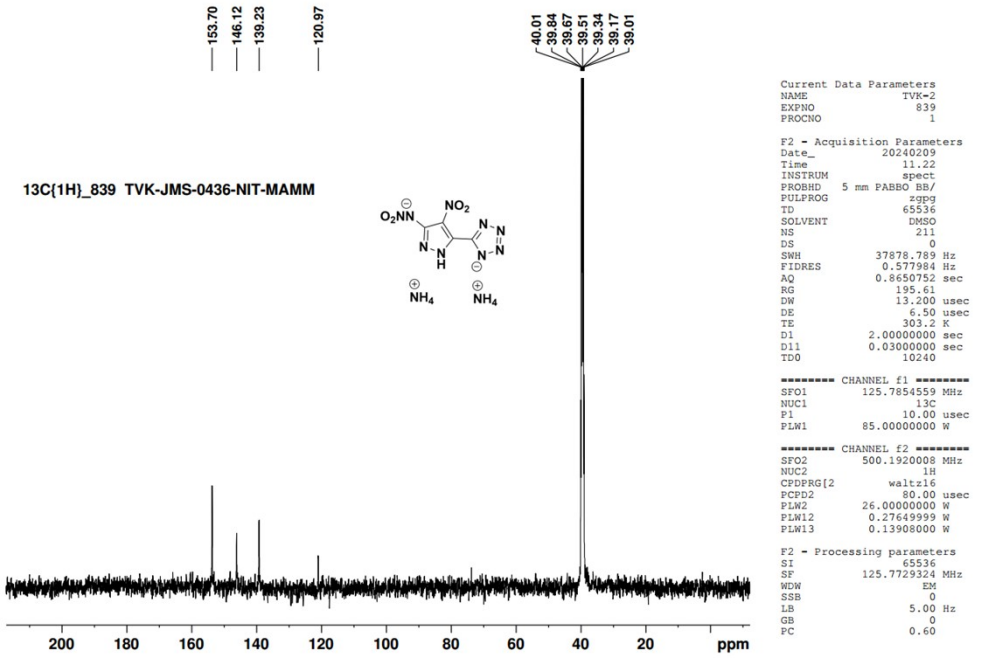

Figure S25: [13]C NMR spectrum of **12** in dimethyl sulfoxide-d_6.

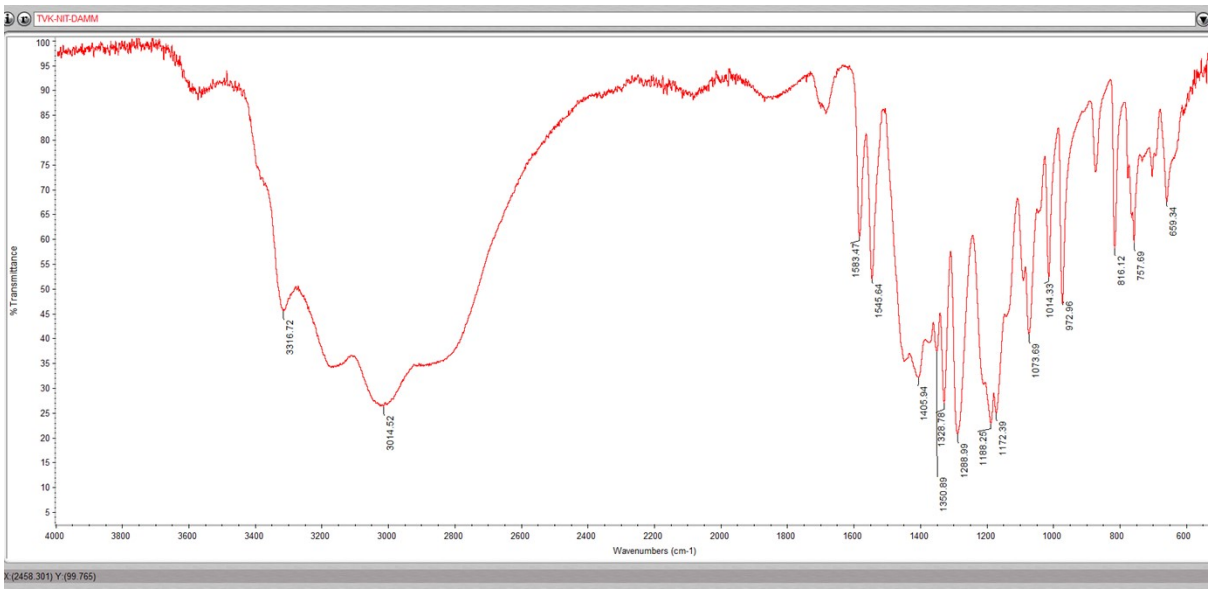

Figure S26: IR spectrum of **12**.

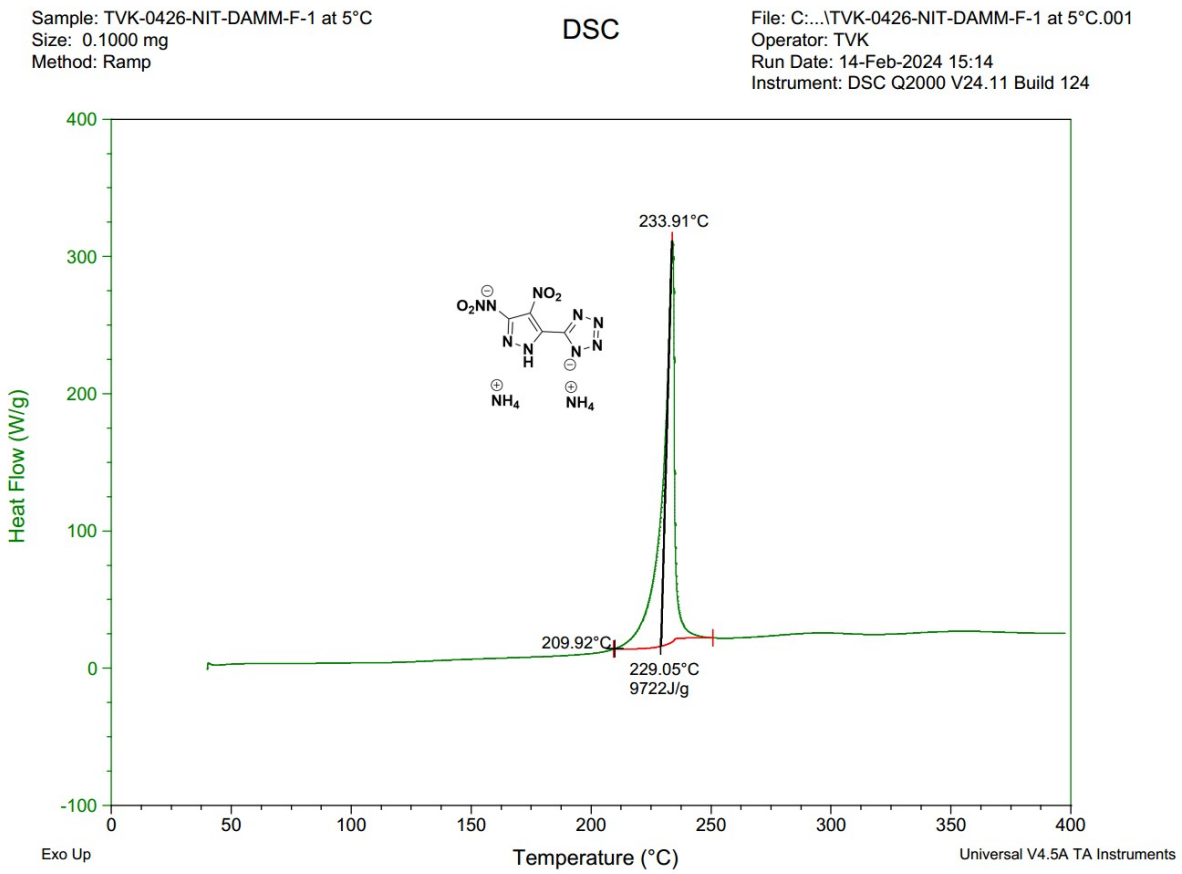

Figure S27: Thermal behavior of **12** at 5 °C/min.

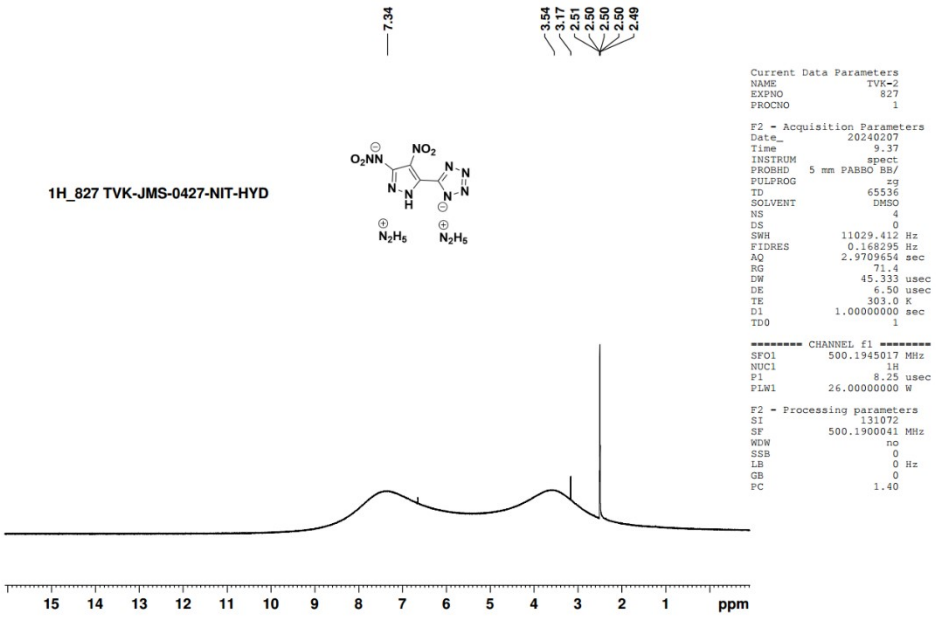

Figure S28: [1]H NMR spectrum of **13** in dimethyl sulfoxide-d_6.

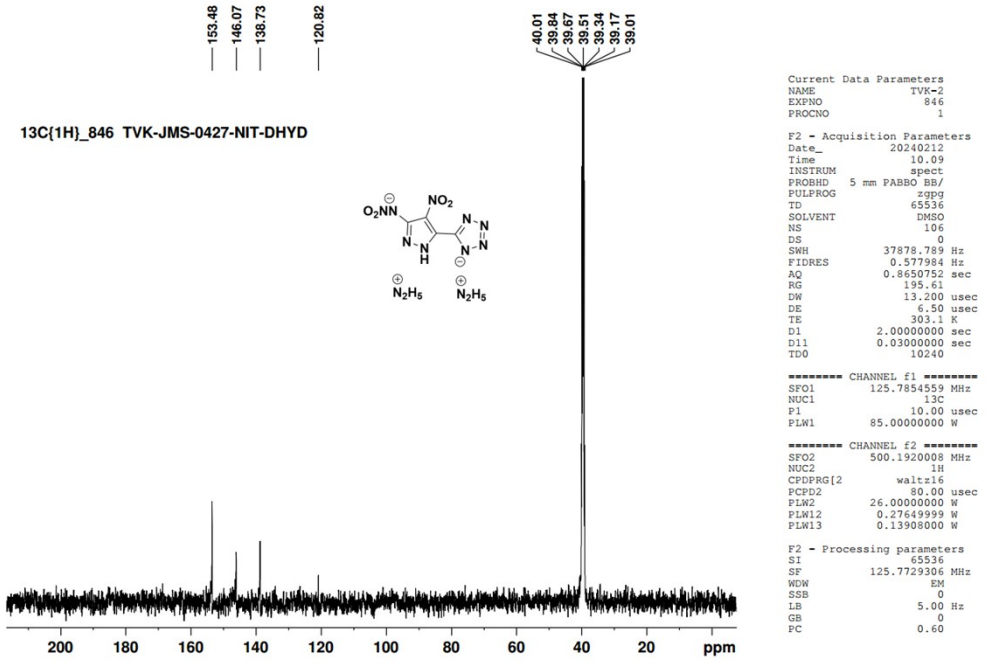

Figure S29: [13]C NMR spectrum of **13** in dimethyl sulfoxide-d_6.

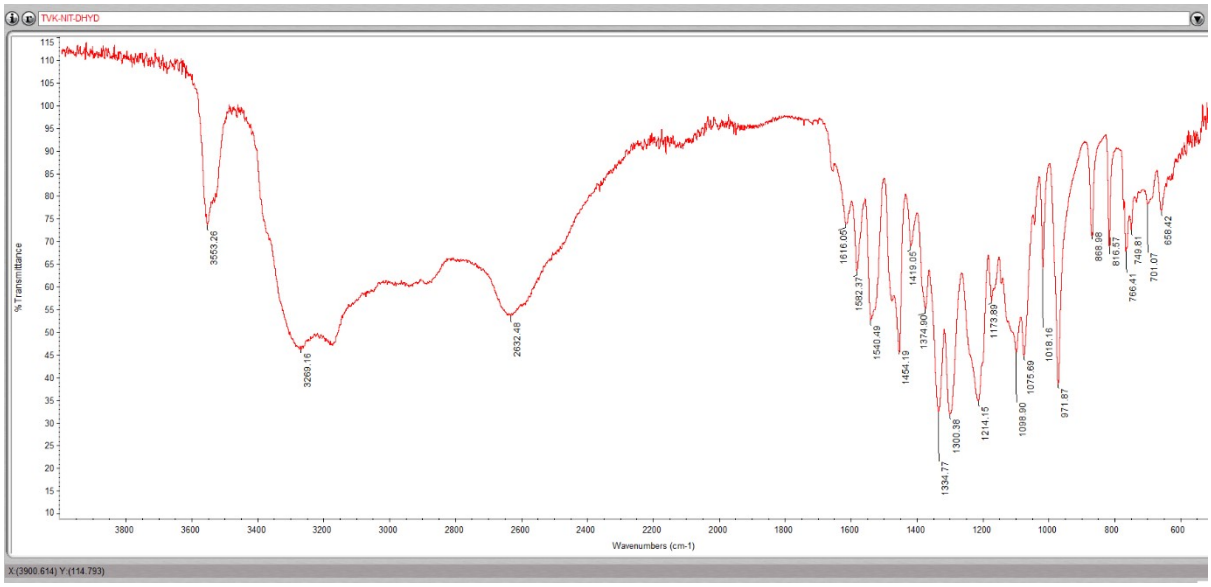

Figure S30: IR spectrum of **13**.

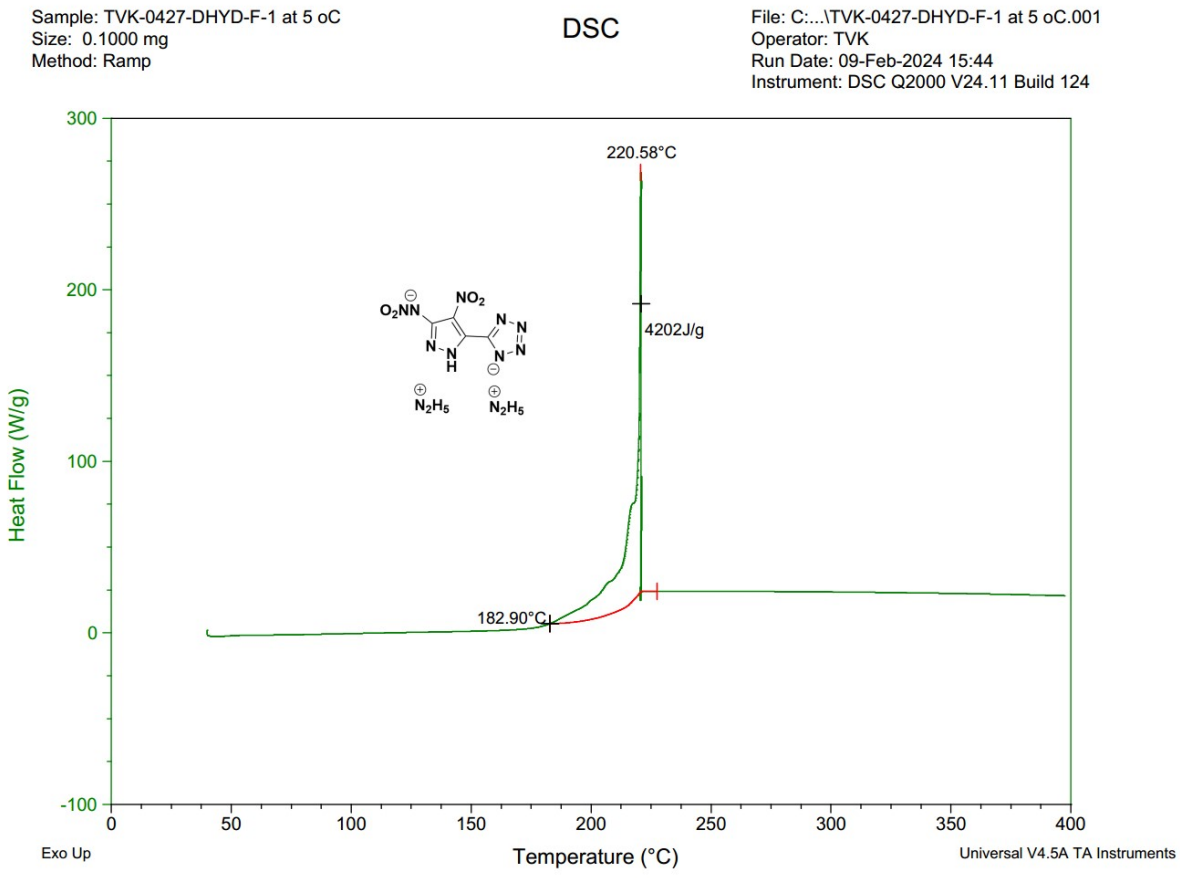

Figure S31: Thermal behavior of **13** at 5 °C/min.

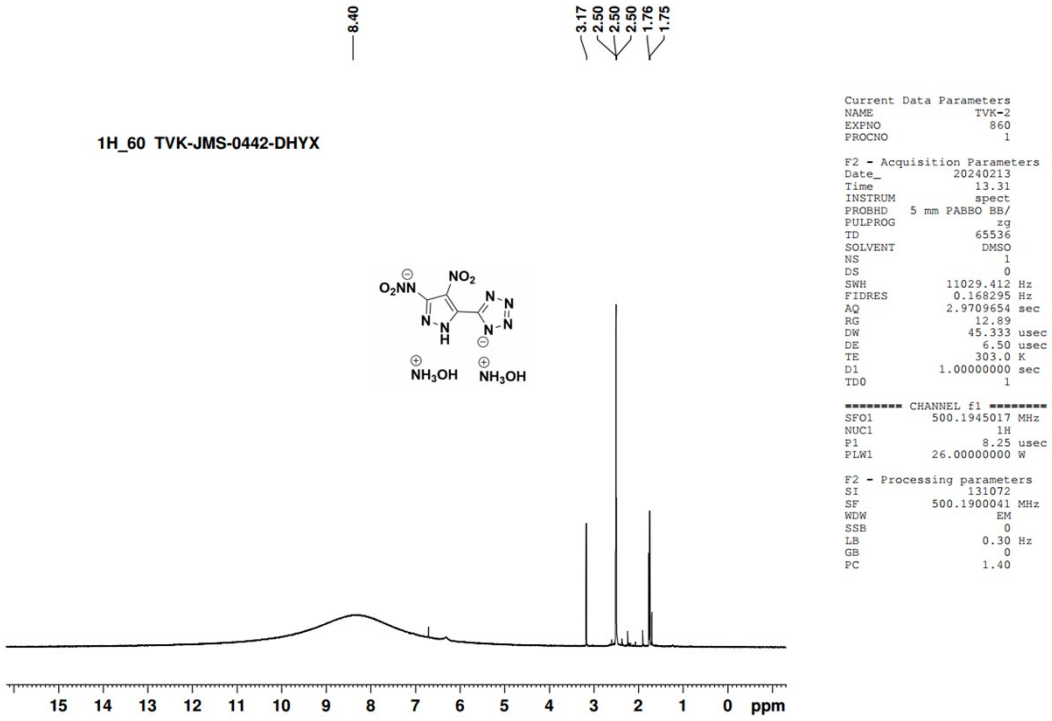

Figure S32: [1]H NMR spectrum of **14** in dimethyl sulfoxide-d_6.

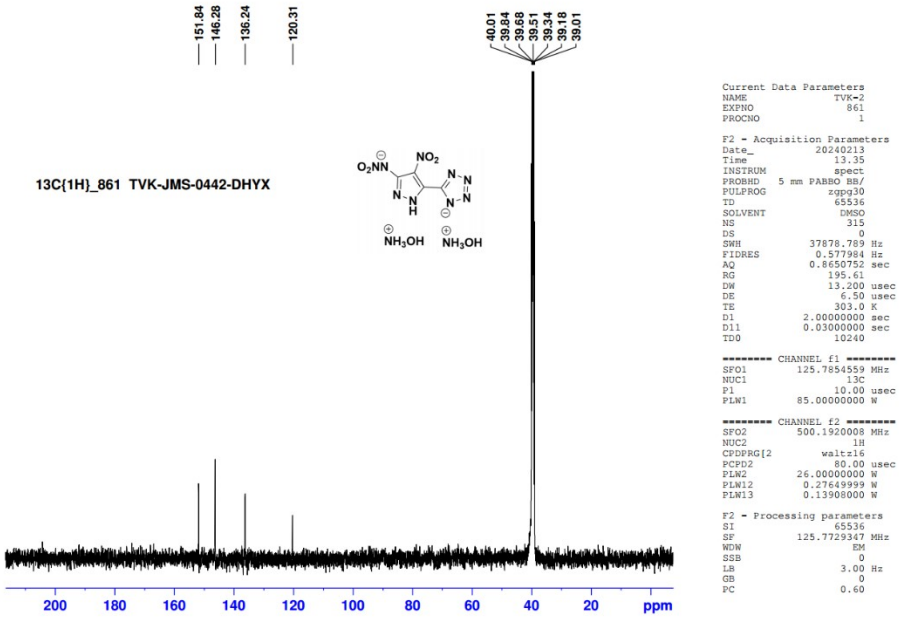

Figure S33: [13]C NMR spectrum of **14** in dimethyl sulfoxide-d_6.

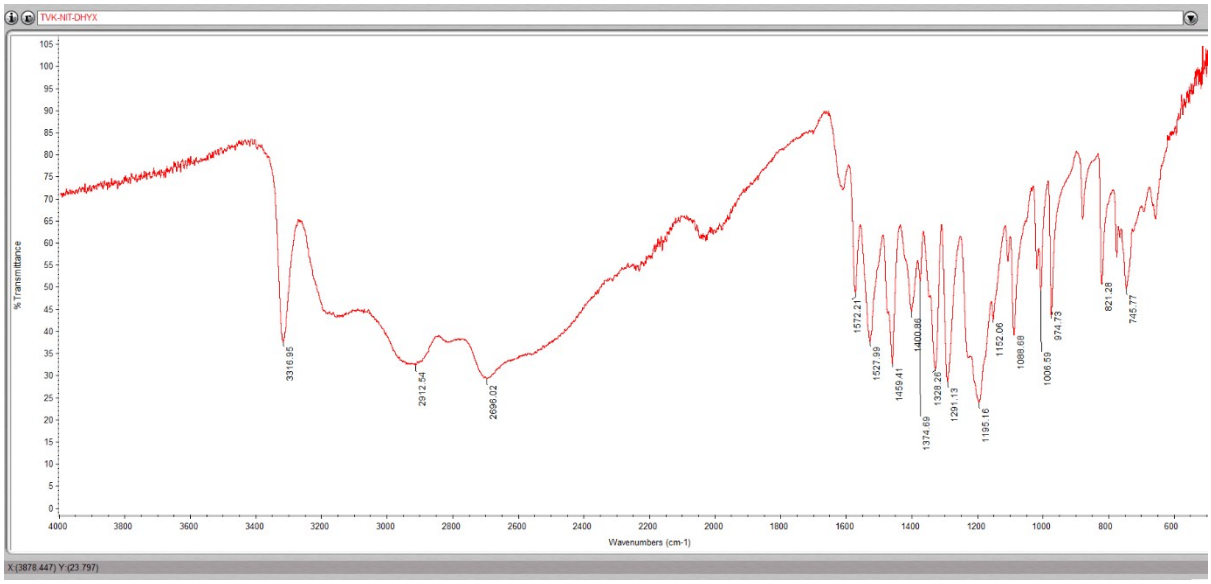

Figure S34: IR spectrum of **14**.

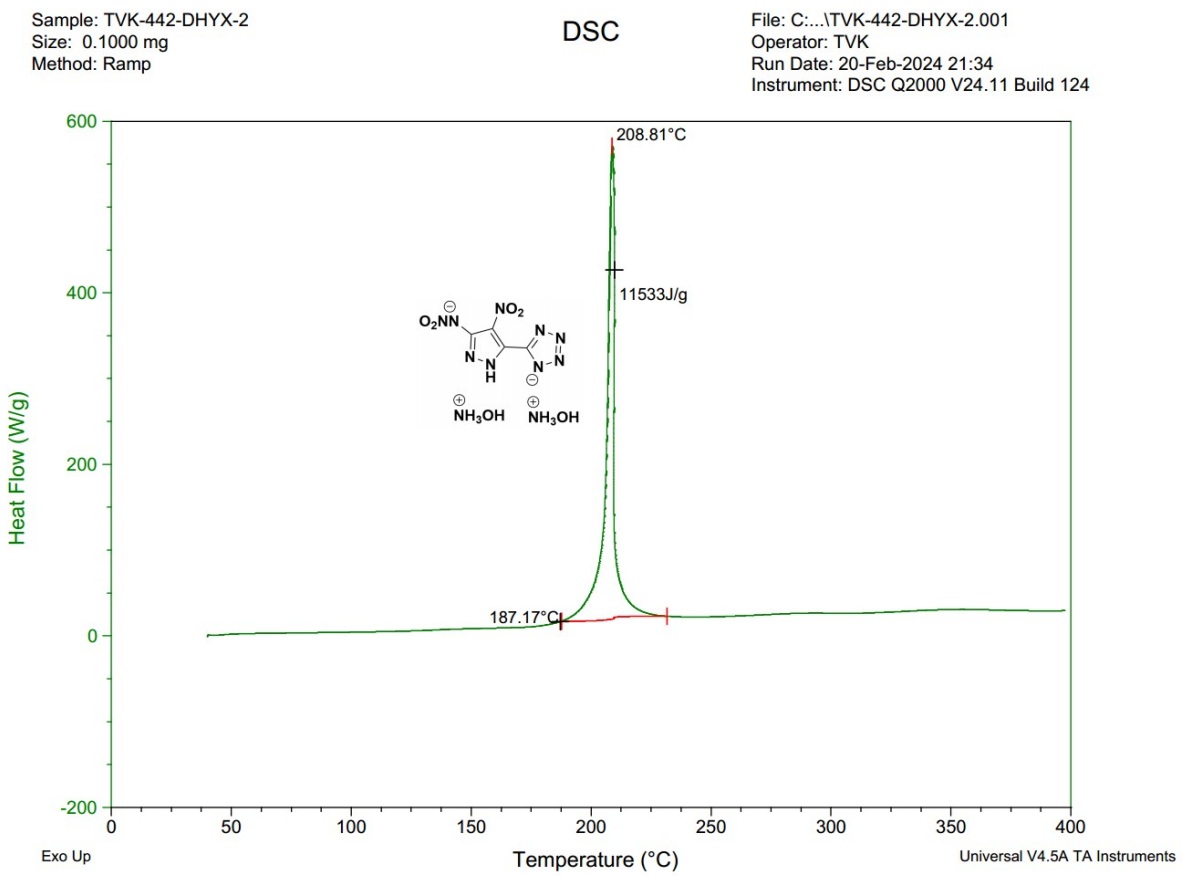

Figure S35: Thermal behavior of **14** at 5 °C/min.

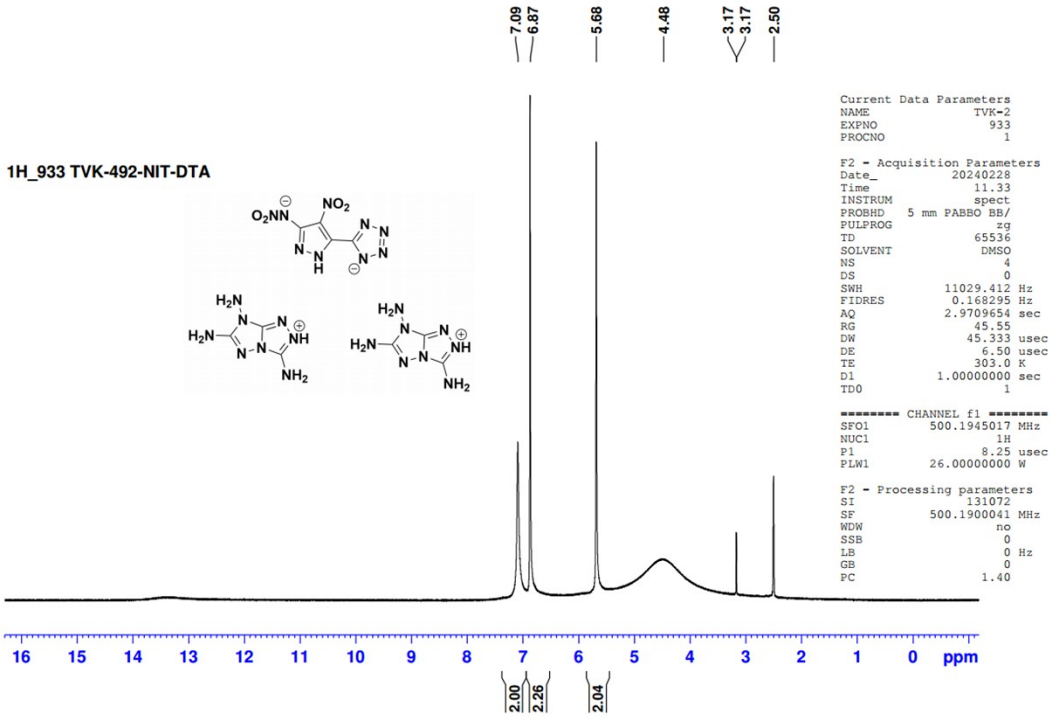

Figure S36: [1]H NMR spectrum of **15** in dimethyl sulfoxide-d_6.

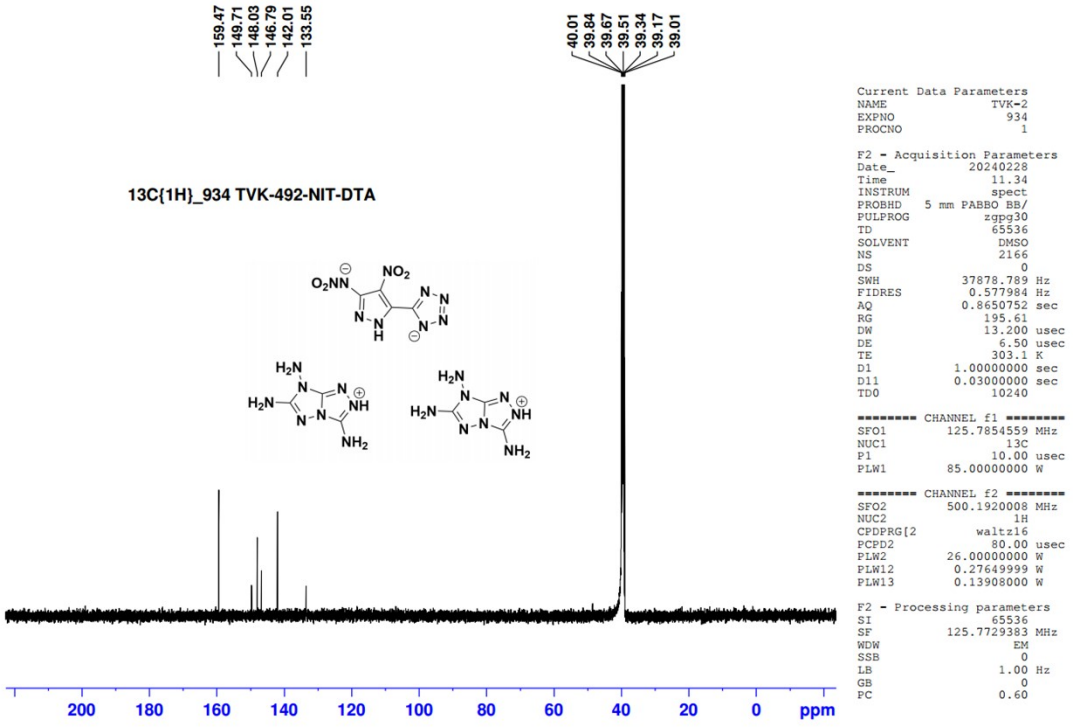

Figure S37: ^{13}C NMR spectrum of **15** in dimethyl sulfoxide-d_6.

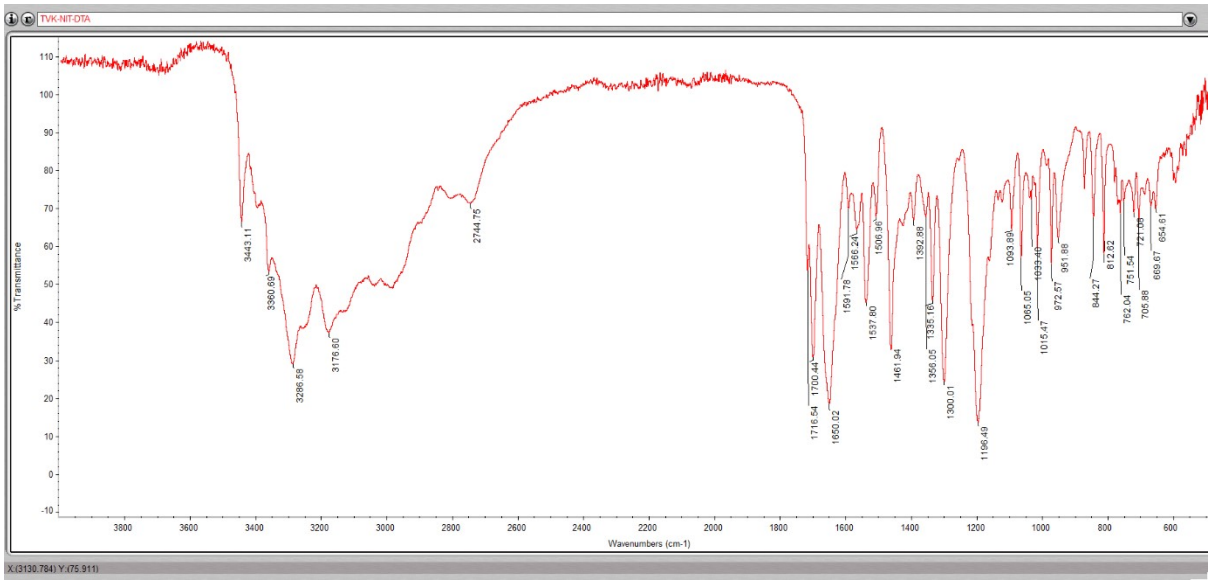

Figure S38: IR spectrum of **15**.

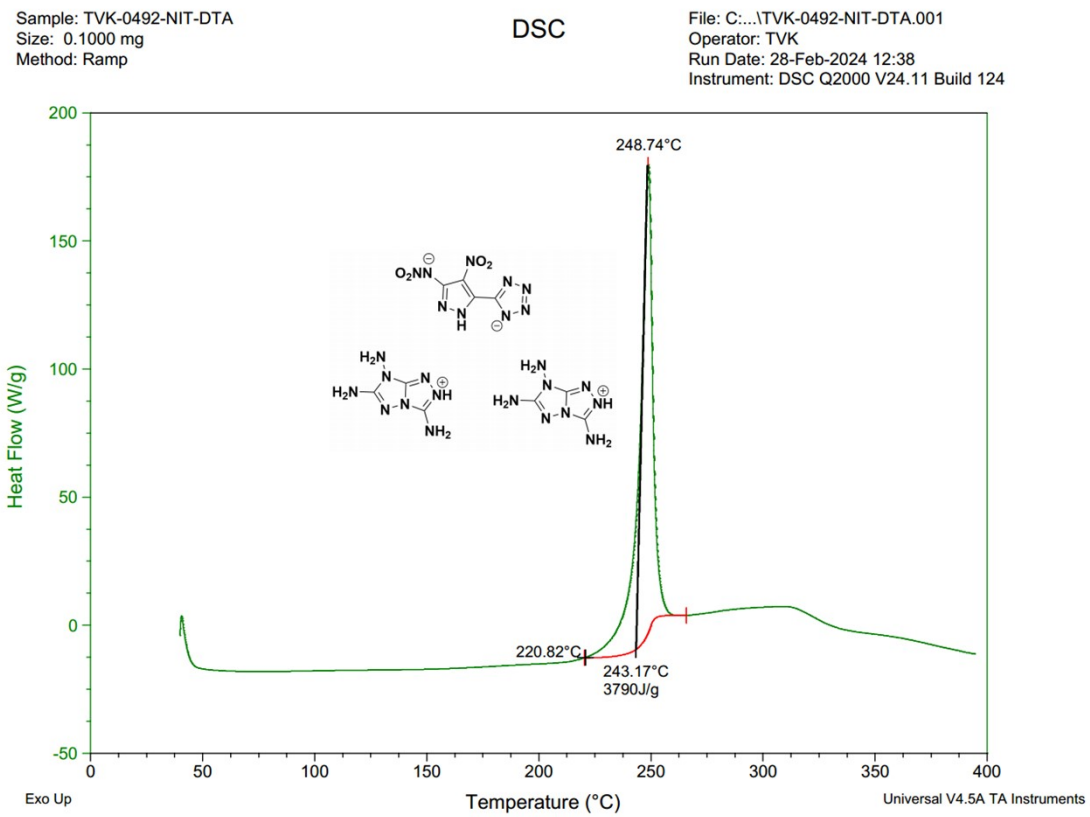

Figure S39: Thermal behavior of **15** at 5 °C/min.

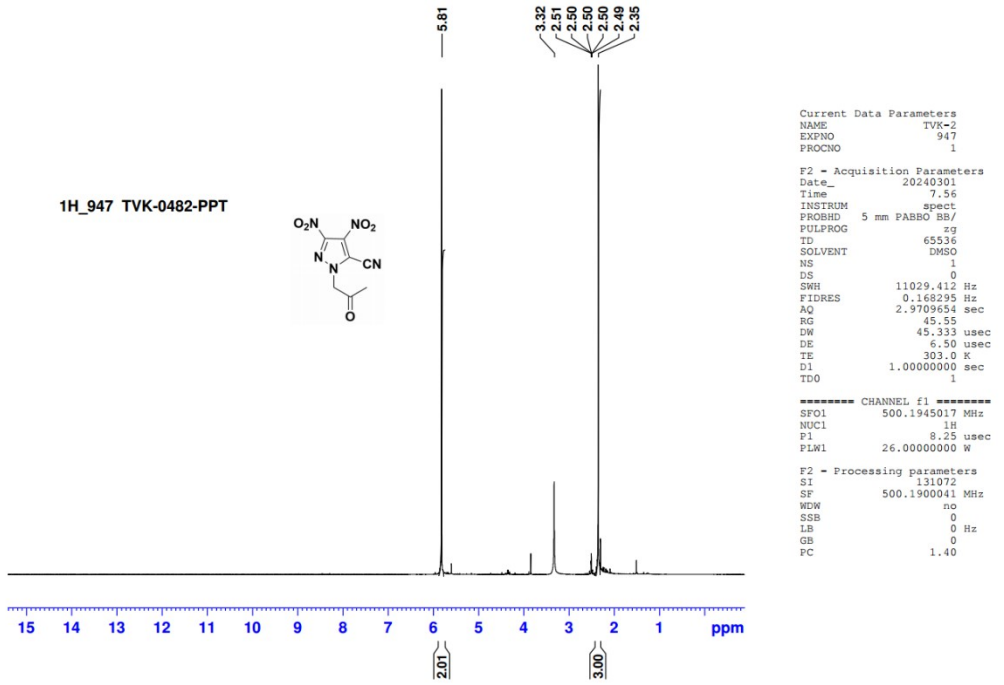

Figure S40: [1]H NMR spectrum of **16** in dimethyl sulfoxide-d_6.

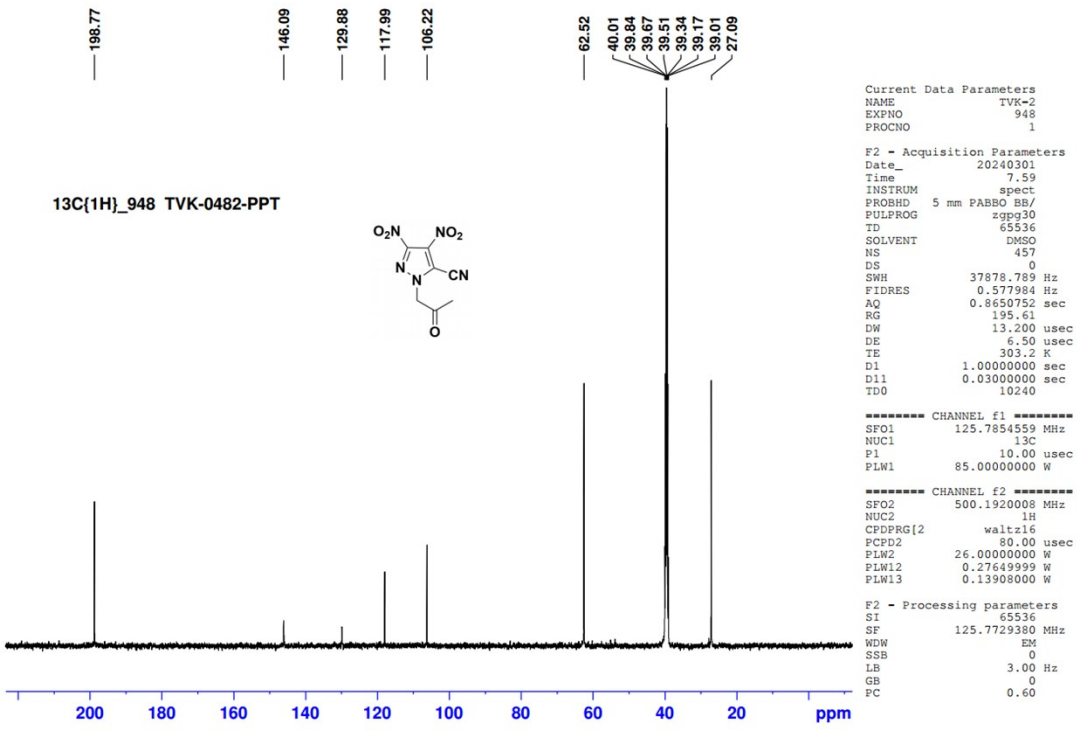

Figure S41: [13]C NMR spectrum of **16** in dimethyl sulfoxide-d_6.

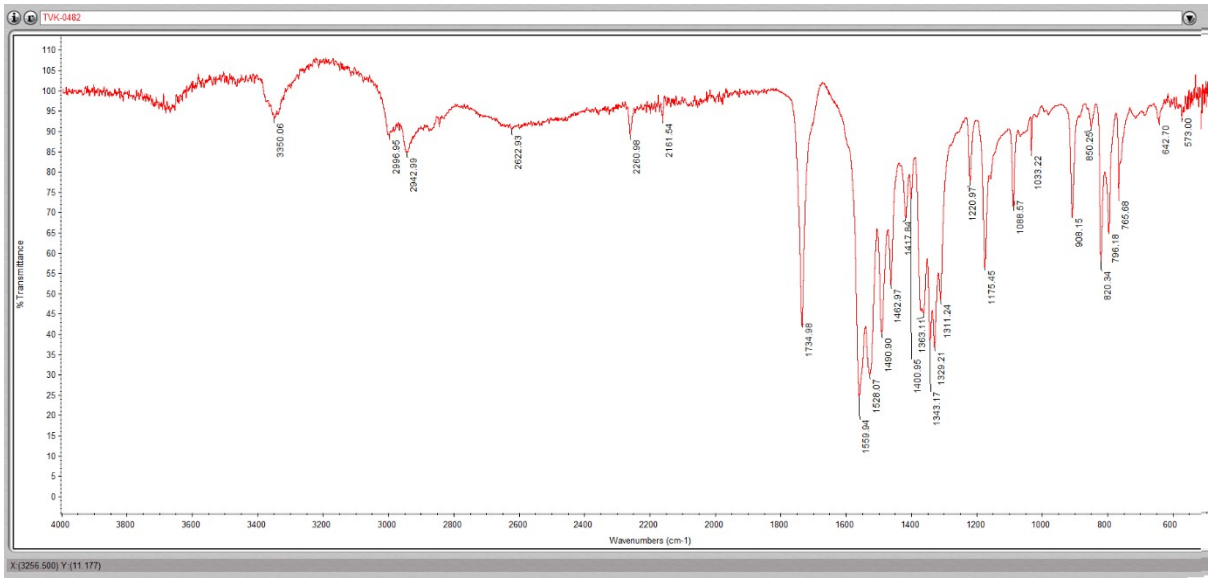

Figure S42: IR spectrum of **16**.

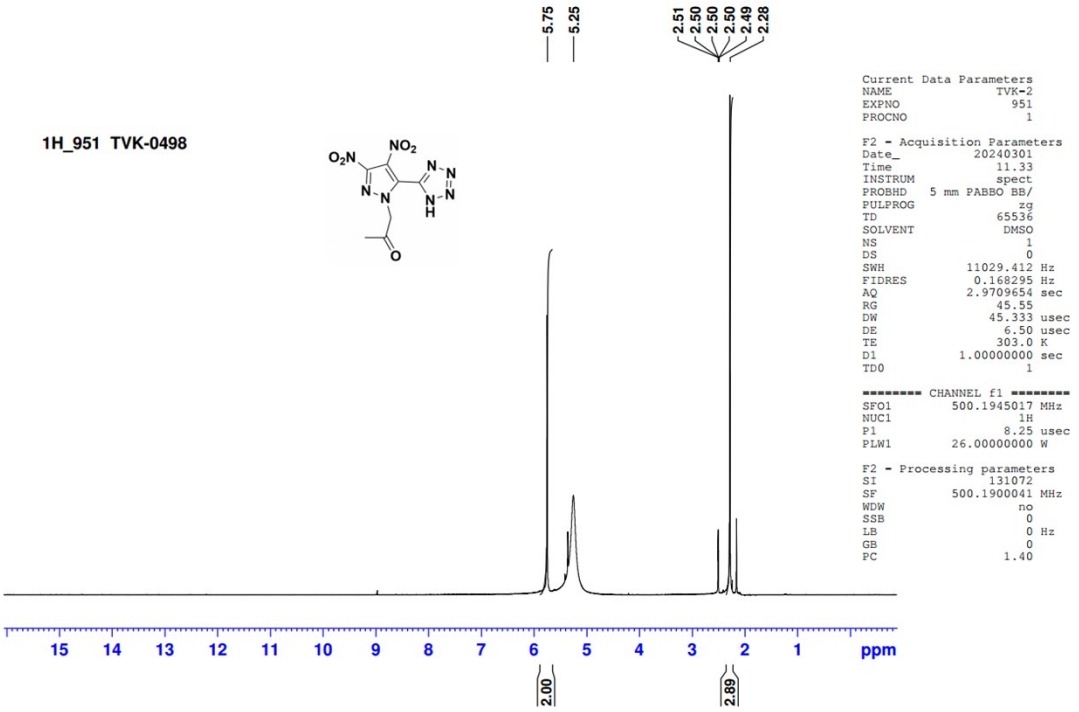

Figure S43: [1]H NMR spectrum of **17** in dimethyl sulfoxide-d_6.

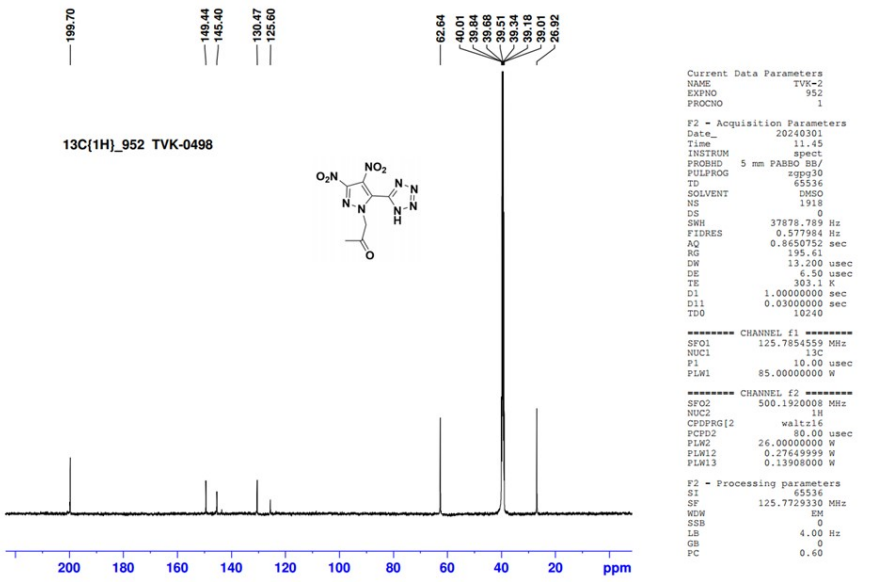

Figure S44: [13]C NMR spectrum of **17** in dimethyl sulfoxide-d_6.

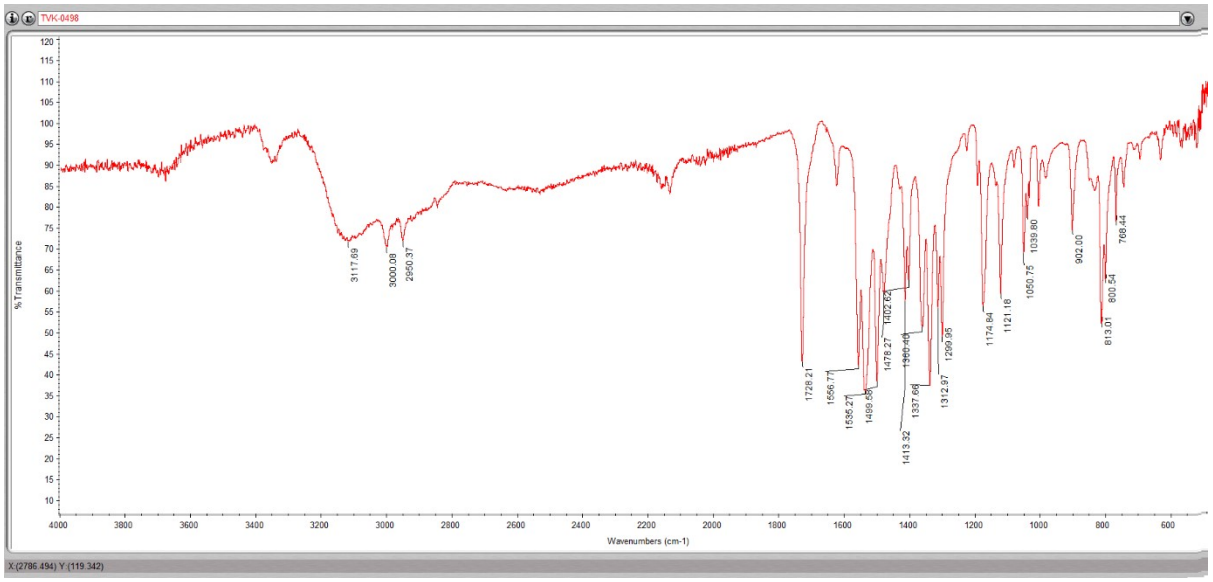

Figure S45: IR spectrum of **17**.

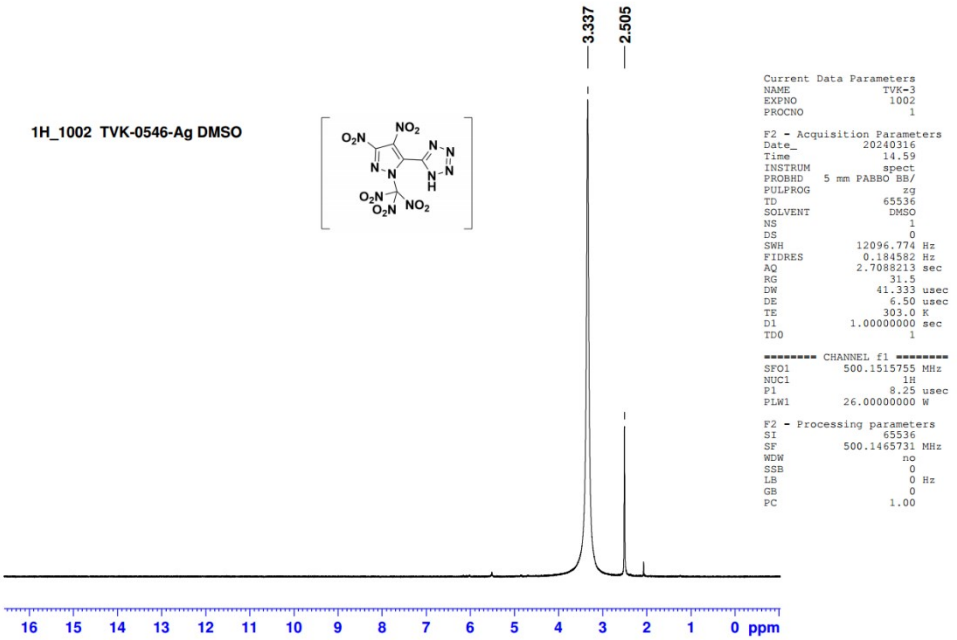

Figure S46: [1]H NMR spectrum of **18** in dimethyl sulfoxide-d_6.

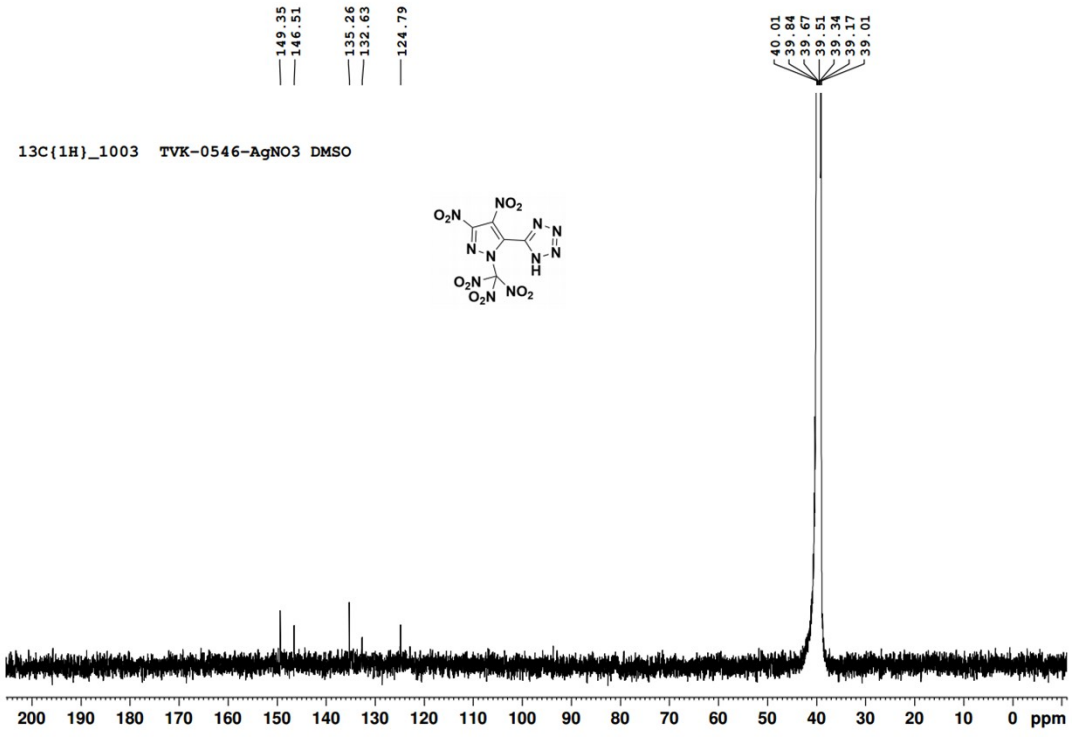

Figure S47: [13]C NMR spectrum of **18** in dimethyl sulfoxide-d_6.

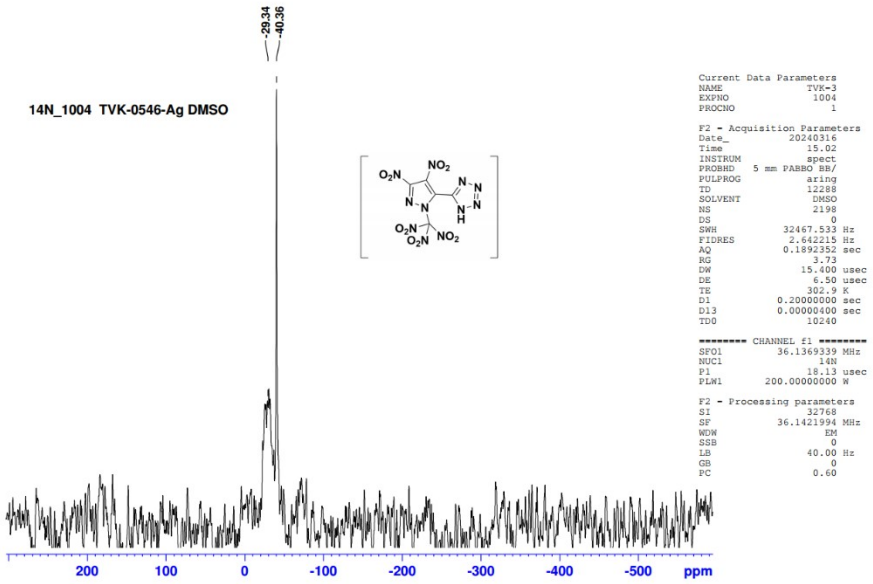

Figure S48: ^{14}N NMR spectrum of **18** in dimethyl sulfoxide-d_6.

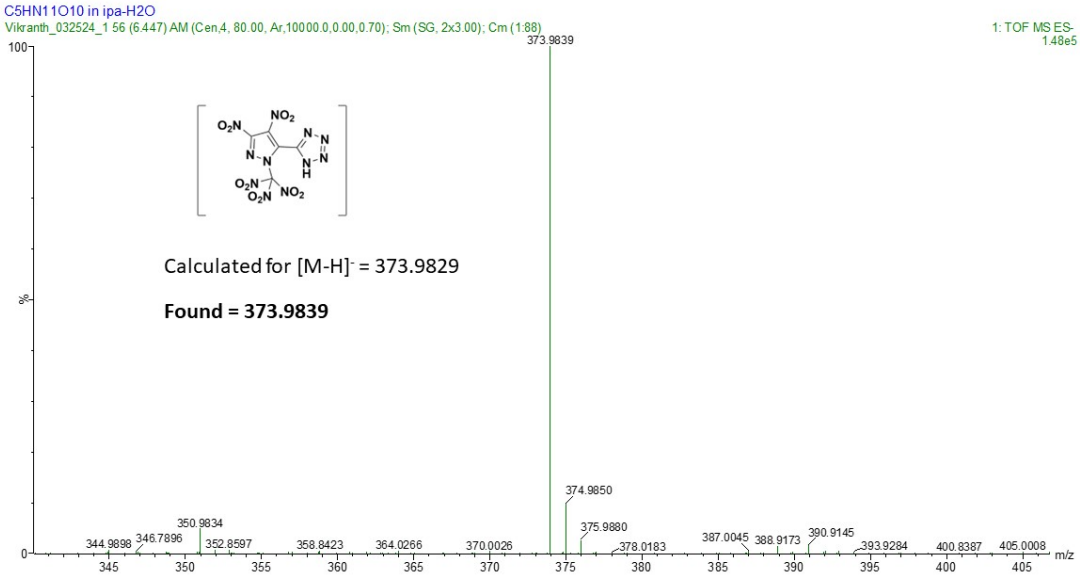

Figure S49: ESI of **18**.

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