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Unusual formation of 4-diazo-3-nitriminopyrazoles upon acid nitration of pyrazolo[3,4-*d*][1,2,3]triazoles

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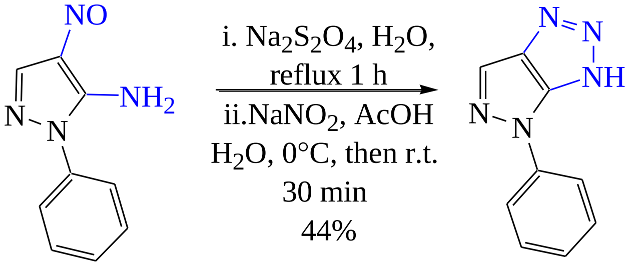
1. Experimental Section.

IR spectra were recorded on a Bruker Alpha FT-IR spectrometer for samples in KBr pellets. ^{1}H, ^{13}C, ^{14}N and ^{15}N spectra were recorded on a Bruker AM-300 instrument (300.13, 75.47 and 21.69 MHz, respectively) and Bruker AV 600 (600.1, 150.9, 43.4 MHz, respectively) in DMSO-d$_6$ or acetone-d$_6$ at 299 K. All chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C) and to MeNO$_2$ (^{14}N, ^{15}N), high-filed chemical shifts are given with a minus sign. High-resolution mass spectra with electrospray ionization were measured with a Bruker MicroOTOF II instrument. Elemental analysis was performed on a PerkinElmer 2400 Series II instrument. The reaction progress and purity of the obtained compounds were controlled by TLC on Merck Silica gel 60 F254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Most of the reagents and starting materials were purchased from commercial sources and used without additional purification. The starting 4-nitroso-1-phenyl-1*H*-pyrazol-5-amine[S1] and 6-methyl-4-phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole[S2] were synthesized according to the published procedure.

Thermal analysis measurements were conducted using the Netzsch STA 449F3 apparatus. Samples of 0.5-2.0 mg were loaded in standard aluminum crucibles, covered with pierced lids and heated at constant 5 K min^{-1} rate up to 550 °C. Argon flow (70 mL min^{-1}) was purged through the furnace. Impact and friction sensitivities were obtained in accordance with STANAG standards, the details can be found elsewhere.[S3] Impact sensitivity tests were performed using BAM-type machine according to STANAG 4489.[S4] The reported values (IS) are the drop energies corresponding to 50 % probability of explosion obtained with Bruceton analysis. Friction sensitivity was evaluated in agreement with STANAG 4487.[S5] Reported quantity (FS) is the friction force corresponding to 50 % probability of explosion obtained with Bruceton analysis.

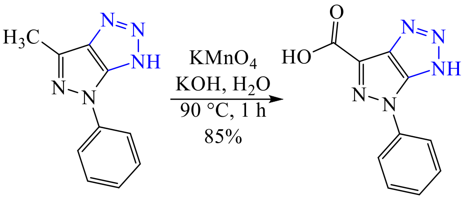
X-ray diffraction study

Single crystal X-ray diffraction experiments for compounds **2b** and **2c** were carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 100 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package.[S6] The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program.[S7]



1a

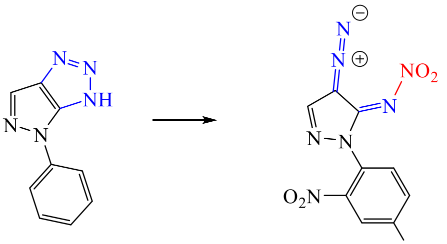
4-Phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole (1a). A mixture of 0.927 g (4.93 mmol) 4-nitroso-1-phenyl-1*H*-pyrazol-5-amine and 1.715 g (9.86 mmol) Na$_2$S$_2$O$_4$ in 38 ml H$_2$O was refluxed 1 h. The solution was extracted with ethyl acetate (3×15 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure to get brown oil of 0.467 g 1-phenyl-4,5-diaminopyrazole. The resulting oil was used without further purification. It was dissolved in 0.46 ml (8.05 mmol) AcOH and 5 ml H_2O, cooled to 0°C and treated with solution of 0.2 g (2.89 mmol) $NaNO_2$ in 0.6 ml H_2O. The reaction mixture was stirred under the same conditions for 5 min, then stirred for 30 min at 20°C. The precipitate that formed was filtered off and washed with water. The filtrate was extracted with ethyl acetate (3×15 ml) and dried over Na_2SO_4. The solvent was removed under reduced pressure. Both portions of the crude compound were recrystallized from H_2O to give 0.459 g (45%), red needles, mp = 234°C. IR (KBr), ν: 3050, 2926, 2781, 1598, 1542, 1500, 1441, 1143, 1040, 983, 825, 750, 684, 607, 505 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ:15.79 (1H, br. s, NH); 8.15 (1H, s, H^3-pyrazole); 8.01 (2H, d, J=8, $H^{2,6}$ – Ph); 7.57 (2H, t, J=15.5, $H^{3,5}$ – Ph); 7.27 (1H, t, J = 14.6, H^4 – Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 138.7; 129.8; 125.0; 116.2; Found, *m/z*: 186.0776 $[M+H]^+$. $C_9H_7N_5^+$. Calculated, *m/z*: 186.0774.



1b **1c**

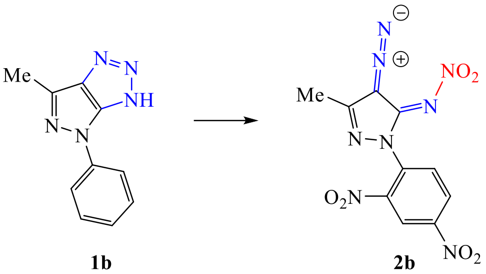
4-Phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole-6-carboxylic acid (1c). 6-Methyl-4-phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole **1b** (4.84 g, 2.4 mmol) and KOH (1.74 g, 3.1 mmol) were dissolved in warm H_2O (200 ml), then $KMnO_4$ (18.5 g, 11.7 mmol) was added maintaining the temperature at 90-95°C. The mixture was boiled for 2 h, then cooled to the room temperature and filtered. The precipitate was washed with hot water. The filtrate was acidified with HCl to pH=1 and the new precipitate was filtered off. Yield 4.72 g (85%), white powder, mp = 216-217 °C. IR (KBr), ν: 3209, 2574, 1935, 1719, 1597, 1453, 1135, 743, 648, 503 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 16.34 (1H, br.s., NH); 8.12 (2H, d, J = 6,9, $H^{2,6}$ – Ph); 7.63 (2H, t, J = 15.7, $H^{3,5}$ – Ph); 7,39 (1H, t, J = 14.6, H^4 – Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 160.2; 136.9; 128.7; 125.4; 116.2; Found, *m/z*: 252.0492 $[M+Na]^+$. $C_{10}H_6N_5NaO_2^+$. Calculated, *m/z*: 252.0492.

Nitration of 4-phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazoles 1a-c. General method. A solution 4-phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole **1a-c** (1.5 mmol) in conc H_2SO_4 (4 ml) and HNO_3 (1 ml, *d* 1.5 g cm^{-3}) was stirred at 20°C for 96 h (for **1a**), 48 h (for **1b**) or 5 h (for **1c**). The reaction mixture was poured into ice cold H_2O (20 ml), the precipitate that formed was filtered off, washed with H_2O, and air-dried.



1a **2a**

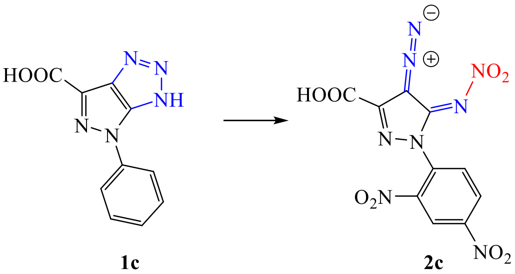
(3*E*)-4-Diazo-2-(2,4-dinitrophenyl)-*N*-nitro-2,4-dihydro-3*H*-pyrazol-3-imine (2a)
Yield 0.68 g (70%), beige powder, mp = 184 °C (H_2O-MeOH). IR (KBr), ν: 3128, 3088, 3061, 2201, 1609, 1544, 1513, 1476, 1391, 1371, 1348, 1242, 1189, 1176, 1097, 909, 835, 772, 742 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.89 (1H, d, H^3 – Ph); 8.81 (1H, s, H^3-pyrazole); 8.73 (1H, d, J=8.9, H^5 – Ph); 8.13 (1H, d, J=8.8, H^6 – Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 154.5; 147.4; 144.1; 142.6; 134.0; 130.8; 128.9; 121.3; 80.0; ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -17.8 (C-NO_2); -144.2 (-N_2^+); Found, *m/z*: 343.0147 $[M+Na]^+$. $C_9H_4N_8NaO_6^+$. Calculated, *m/z*: 343.0146.



1b **2b**

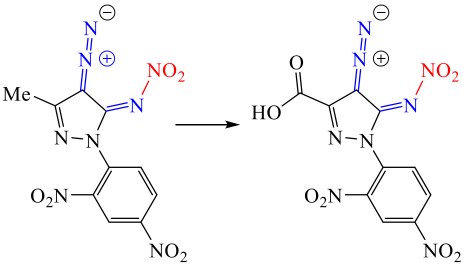
(3*E*)-4-Diazo-2-(2,4-dinitrophenyl)-5-methyl-*N*-nitro-2,4-dihydro-3*H*-pyrazol-3-imine (2b). Yield 1.398 g (55%), yellow powder, mp = 213 °C (EtOAc). IR (KBr), ν: 3443, 2193, 1613, 1543, 1343, 1240, 1114, 846, 718, 513 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.87 (1H, d, J=2.7, H^3 – Ph); 8.71 (1H, dd, J=8.9, H^5 – Ph); 8.10 (1H, d, J=8.8, H^6 – Ph); 2.52 (3H, s, CH_3); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 154.6; 151.2; 147.2; 143.9; 133.9; 130.6; 128.9; 121.2; 80.2; 12.3; ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -18.5 (C-NO_2); -146.6 (-N_2^+); ^{15}N NMR (21.7 MHz, DMSO-d_6) δ: -16.1, -16.8, -18.3; -33.1; -91.1; -131.2; -146.3; -204.1. Found, *m*/*z*: 335.0485 $[M+H]^+$. $C_{10}H_7N_8O_6^+$. Calculated, *m*/*z*: 335,0483. Elemental analysis calcd (%) for $C_{10}H_6N_8O_6$ (286,99) (%): C, 35.95; H, 1.69; N, 33.30. Found (%): C, 35.94; H, 1.81; N, 33.53.

(5*E*)-4-Diazo-1-(2,4-dinitrophenyl)-5-nitroimino-4,5-dihydro-1*H*-pyrazole-3-carboxylic acid (2c).



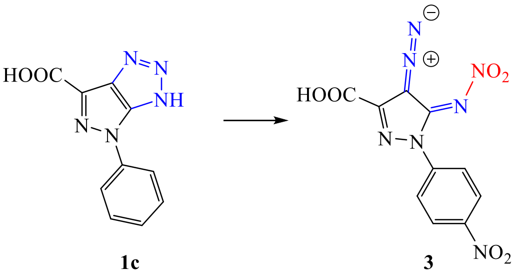
1c **2c**

Method A. According to the general method from compound **1c**. Yield 1.124 g (42%), beige powder, m.p. 190°C (decomp., H_2O-MeOH).



2b **2c**

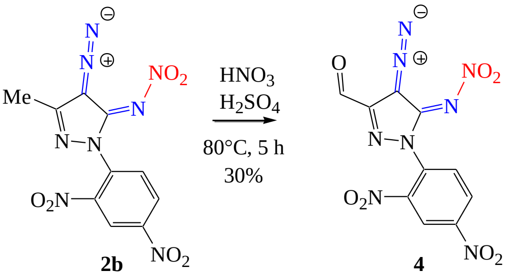
Method B. Oxidation of compound **2b**. To a solution of nitramide 1.67 g (5 mmol) **2b** in conc. H_2SO_4 (17 ml) was added $Na_2Cr_2O_7$•$2H_2O$ (2.59 g, 8 mmol) at 40°C. The reaction mixture was stirred at 55°C for 1 h, cooled to 20°C and poured into ice cold H_2O (70 ml). The precipitate that formed was filtered off, washed with H_2O, and air-dried. Yield 0.83 g (46%), beige powder, mp = 205 °C (H_2O-MeOH). IR (KBr), ν: 3604, 3434, 3119, 2193, 1953, 1727, 1512, 1353, 1237, 1047, 985, 853, 773, 452 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.92 (1H, d, H^3 – Ph); 8.78 (1H, dd, J=8.6, H^5 – Ph); 8.16 (1H, d, J=8.7, H^6 – Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 159.3; 155.6; 147.9; 144.1; 142.9; 133.6; 131.2; 129.3; 121.4; 80.0; ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -19.5 (NO_2); Found, *m*/*z*: 365.0227 $[M+H]^+$. $C_{10}H_5N_8O_8^+$. Calculated, *m*/*z*: 365.0225.



1c **3**

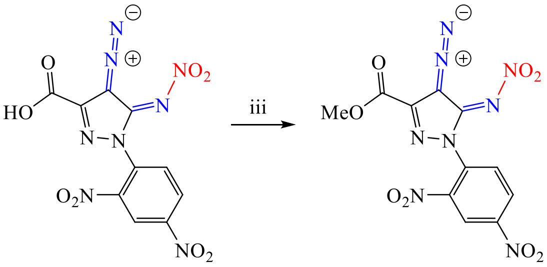
(5*E*)-4-Diazo-5-(nitroimino)-1-(4-nitrophenyl)-4,5-dihydro-1*H*-pyrazole-3-carboxylic acid (3).

A solution of 4-phenyl-3,4-dihydropyrazolo[3,4-*d*][1,2,3]triazole-6-carboxylic acid (**1c**) (1.3 mmol) in HNO_3 (3 ml, *d* 1.5 g cm^{-3}) was stirred at 20°C for 3 h. The mixture was poured into ice cold H_2O (25 ml), the precipitate that formed was filtered off, washed with H_2O, and air-dried. Yield 0.259 g (62%), yellow powder, mp = 158 °C (decomp., H_2O-MeOH). IR (KBr), ν: 3601; 3437; 2192; 1727; 1509; 1385; 1304; 1237;1045; 984; 857; 771 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.45 (2H, d, J=9.1, $H^{2,6}$ – Ph); 8.09 (2H, d, J=9.1, $H^{3,5}$ – Ph); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 159.6; 155.5; 146.7; 142.2; 142.1; 131.2; 129.9; 129.3; 125.7; 124.7; 79.9; ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -17.9 (C-NO_2); -160.5 (-N_2^+); Found, *m*/*z*: 342.0196 $[M+H]^+$. $C_{10}H_5N_7O_6Na^+$. Calculated, *m*/*z*: 342.0194.



2b **4**

(5*E*)-4-Diazo-1-(2,4-dinitrophenyl)-5-(nitroimino)-4,5-dihydro-1*H*-pyrazole-3-carbaldehyde (4).
A solution of nitramide **2b** 1.33 g (4 mmol) in 100% H_2SO_4 (5.64 ml) and HNO_3 (1 ml, *d* 1.5 g cm^{-3}) was stirred at 80°C for 5 h. The reaction mixture was poured into ice cold H_2O (20 ml), the precipitate that formed was filtered off, washed with H_2O, and air-dried. Yield 0.4 g (30 %), beige powder, mp = 168°C. IR (KBr), ν: 3084, 2882, 2361, 2196, 1700, 1612, 1545, 1430, 1349, 1229, 1055, 984, 740, 547, 421 cm^{-1}; ^1H NMR (300 MHz, acetone-d_6) δ: 10.04 (1H, s, $C\underline{H}O$); 9.01 (1H, d, *J* = 2.6 Hz, H^3 – Ph); 8.84 (1H, dd, J=8.8, H^5 – Ph); 8.23 (1H, d, J=8.7, H^6 – Ph); ^{13}C NMR (75.5 MHz, acetone-d_6) δ: 184.3; 155.8; 154.6; 148.1; 144.1; 133.4; 131.2; 129.5; 121.5; 85.9; ^{14}N NMR (21.7 MHz, acetone-d_6) δ: -21.2 (C-NO_2); Found, *m*/*z*: 381.0538 $[M+H]^+$. $C_{10}H_4N_8O_7^+$. Calculated, *m*/*z*: 381.0538.

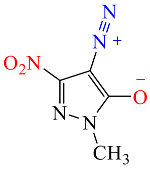
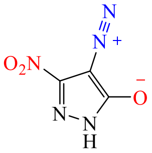
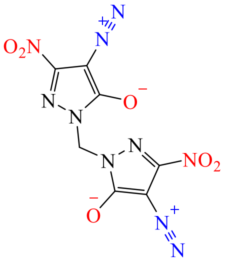
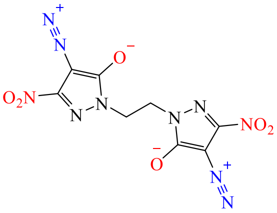
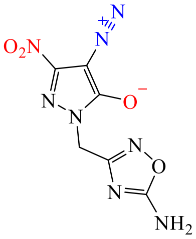


2c **5**

Methyl (5*E*)-4-diazo-1-(2,4-dinitrophenyl)-5-(nitroimino)-4,5-dihydro-1*H*-pyrazole-3-carboxylate (5)
A suspension of acid (**2b**) 0.15 g (0.4 mmol) in 3 ml CH_3OH was added 0.1 мл (1.4 моль) $SOCl_2$. Reaction mixture refluxed 20 h. The solvent was removed under reduced pressure. A crude compound was recrystallized from EtOH. Yield 0.08 g (51%), yellow powder, T_m=148 °C. IR (KBr), ν: 3120, 2198, 1728, 1613, 1546, 1511, 1500, 1349, 1325, 1044, 855, 746 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ: 8.92 (1H, s, H^3 – Ph); 8.77 (1H, д, J=7, H^5 – Ph); 8.15 (1H, д, J=8.7, H^6 – Ph); 3.98 (3H, c, $COO\underline{CH_3}$); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 158.2; 155.6; 147.9; 144.1; 141.3; 133.4; 131.2; 129.3; 121.5; 80.1; 53.6; ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -19.5 (C-NO_2); -155 (-N_2^+); Found, *m*/*z*: 379.0387 $[M+H]^+$. $C_{11}H_7N_8O_8^+$. Calculated, *m*/*z*: 379.0387.

2. Energetic properties.

Table S1. Energetic properties of 3-nitro-4-diazopyrazolones in comparison with 4-diazopyrazol-3-nitrimines **2a,b.**

Compound	mp /°C [a]	T_d /°C [b]	d^3, [c] /g cm^{-3}	Δ_fH /kJ mol^{-1} (kJ g^{-1})[d]	D[e] /km s^{-1}	P, GPa[f]	IS, J[g]	FS, N[h]
2a	184	184	1.675*	577 (1.79)	7.4	27	3.6±0.6	190
2b	213	213	1.629	517 (1.55)	7.1	25	5	320
 S8	127	228	1.63	177 (1.05)	7.4	21.7	22	-
 S9	-	155	1.77	129.1 (0.83)	8.1	26.4	2.5	5<
 S10	194	226	1.732	497 (1.55)	8.0	26	1.5	40
 S11	-	247	1.72	441.9 (1.32)	7.8	24.2	20	80
 S12		120.6		380.7 (1.51)	8.0	28.1	9.8	120

[a] Melting point. [b] Decomposition temperature measured at a heating rate of 5 °C min^{-1}. [c] Density from X-ray analysis at room temperature. *Density measured by using a gas pycnometer (25°C). [d] Calculated enthalpy of the formation for solid state. [e] Detonation velocity. [f] Detonation pressure. [g] Impact sensitivity (STANAG 4489). [h] Friction sensitivity (STANAG 4487).

3. Spectra of compounds.

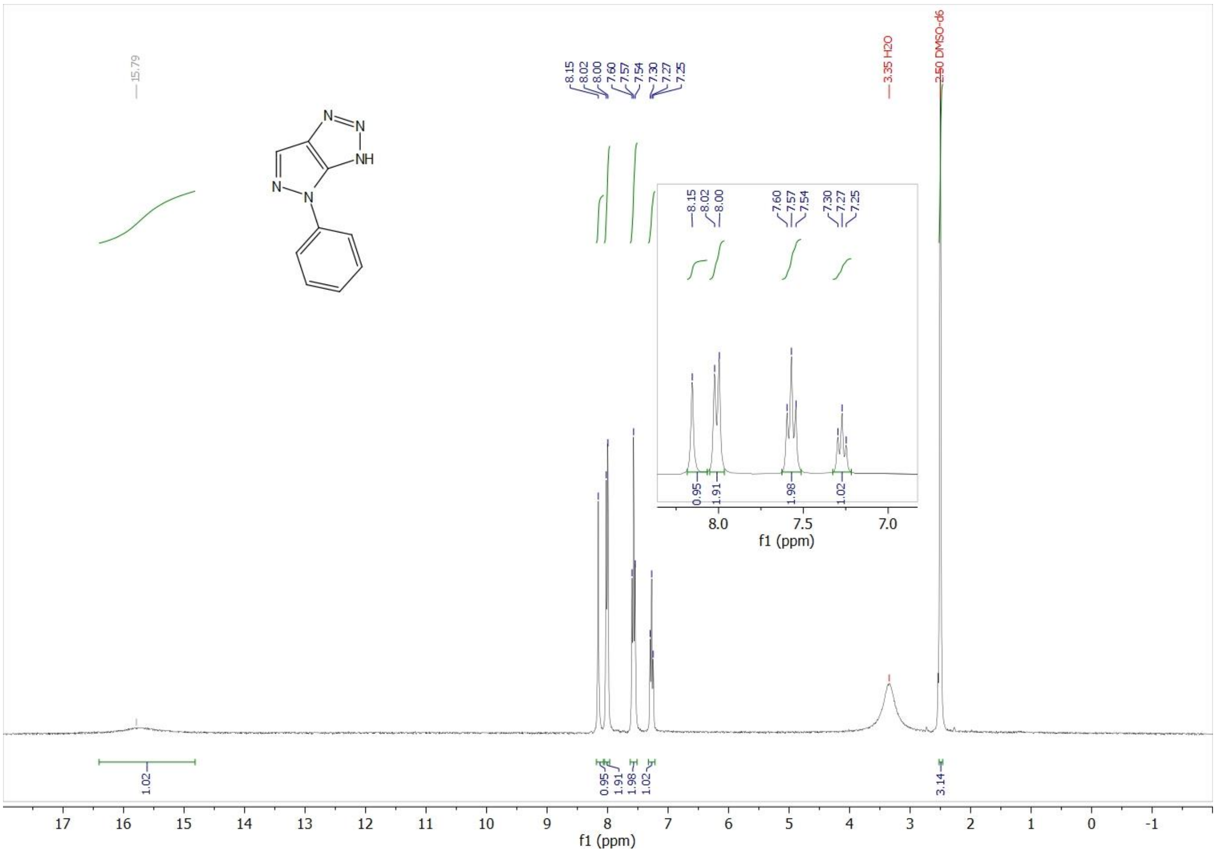


Fig S1. ^{1}H NMR spectrum of compound **1a** in DMSO-d_6.

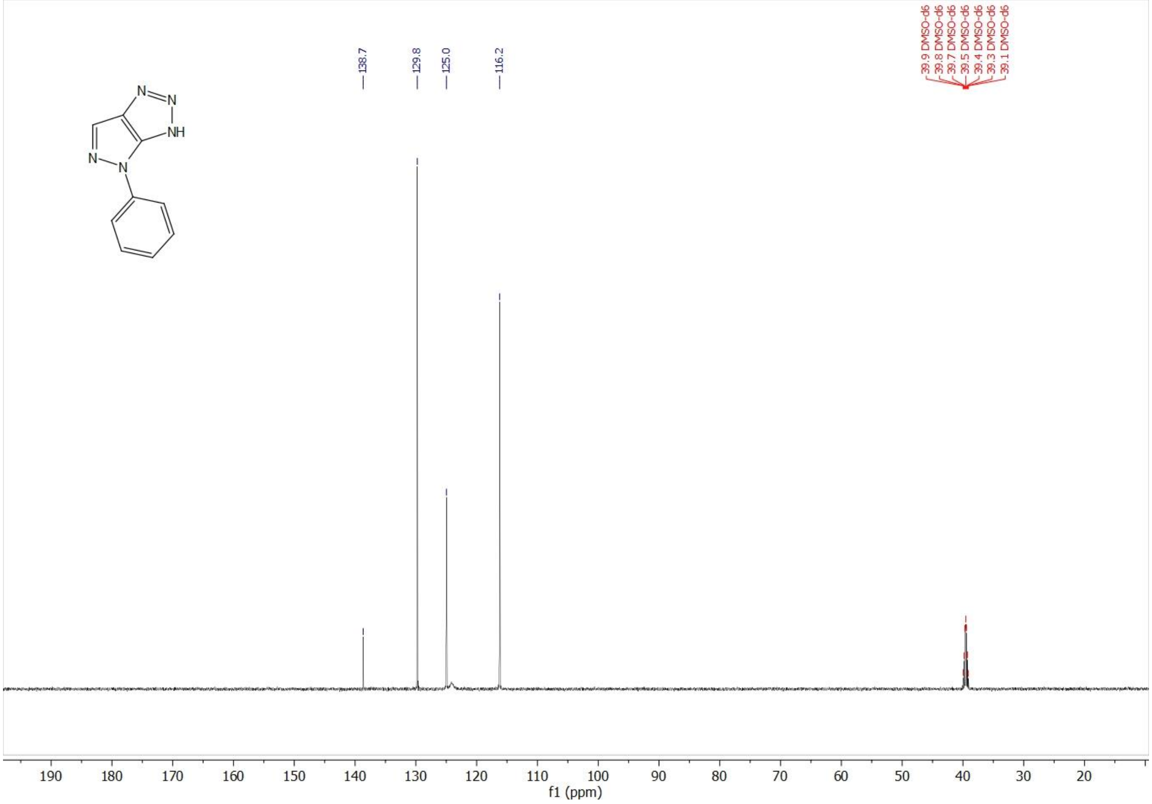


Fig S2. ^{13}C NMR spectrum of compound **1a** in DMSO-d_6.

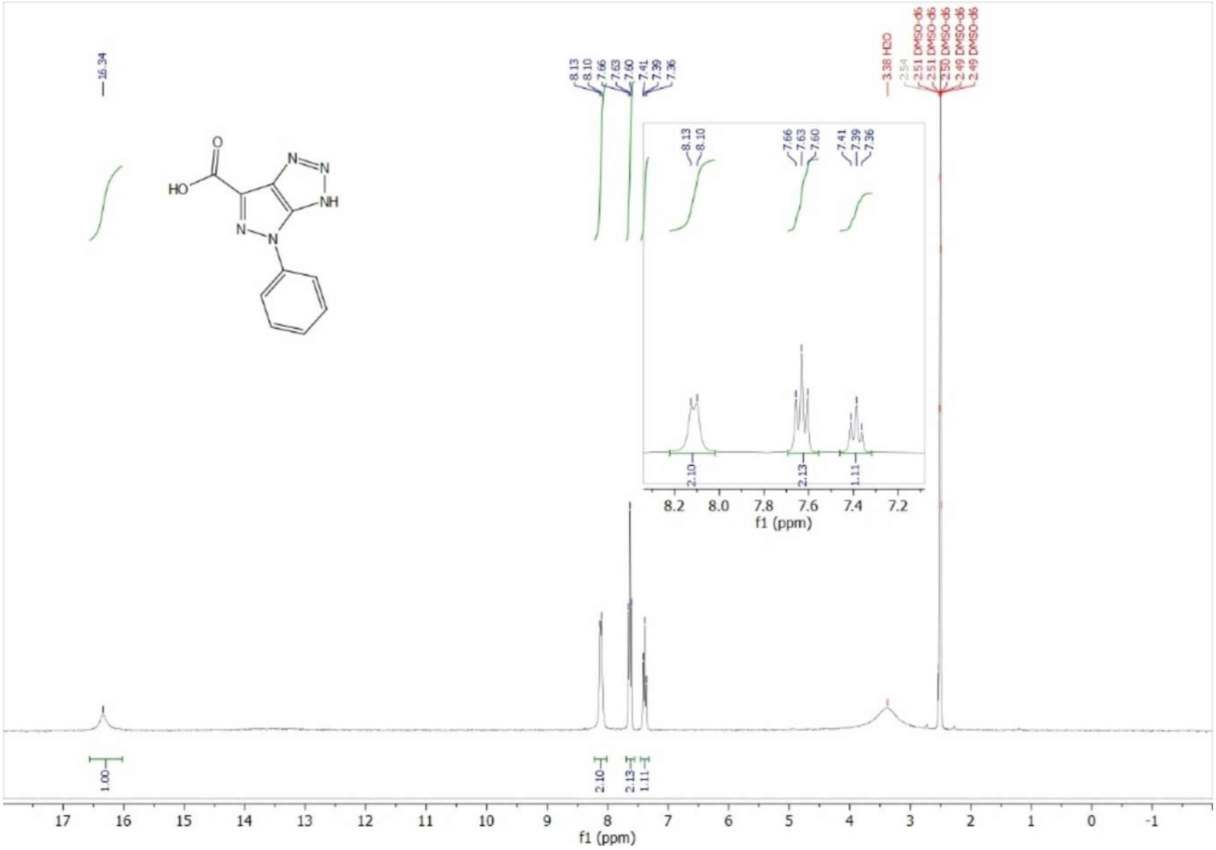


Fig S3. ^{1}H NMR spectrum of compound **1c** in DMSO-d$_6$.

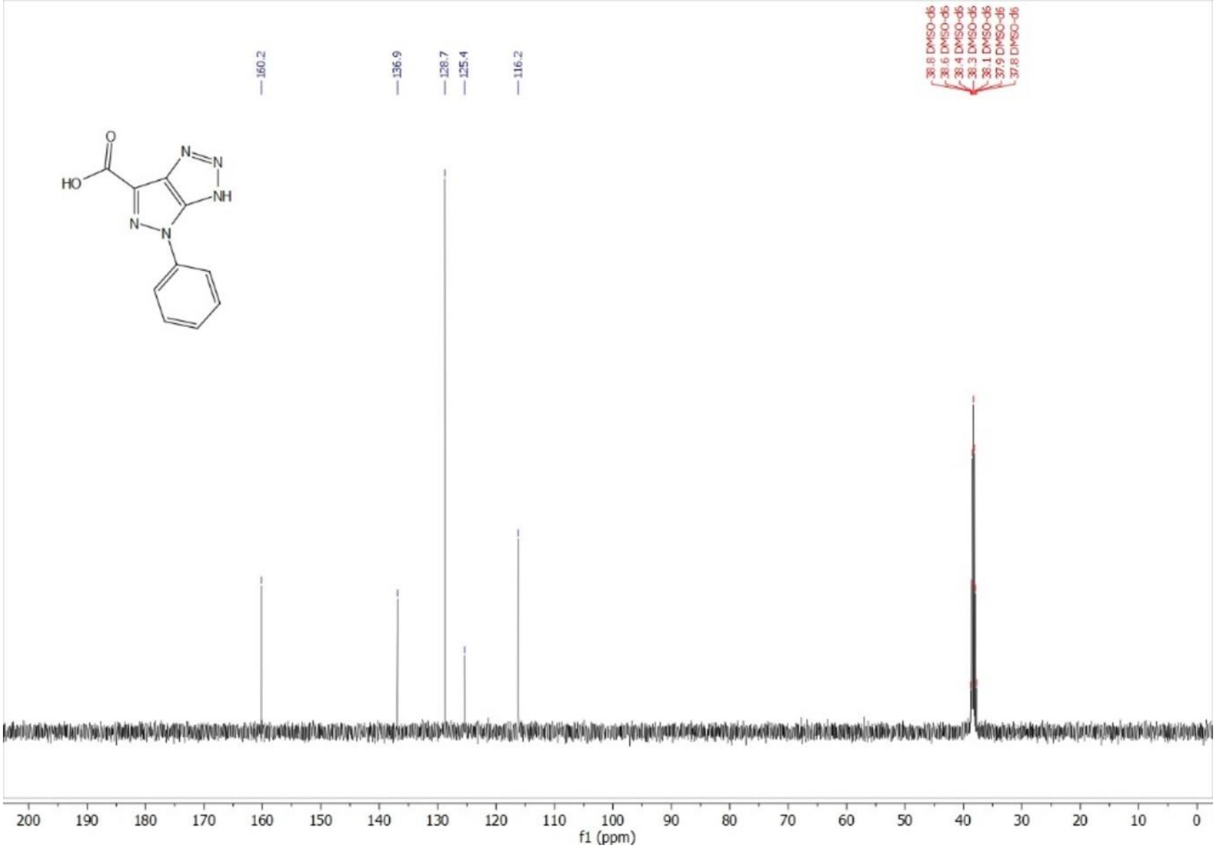


Fig S4. ^{13}C NMR spectrum of compound **1c** in DMSO-d$_6$.

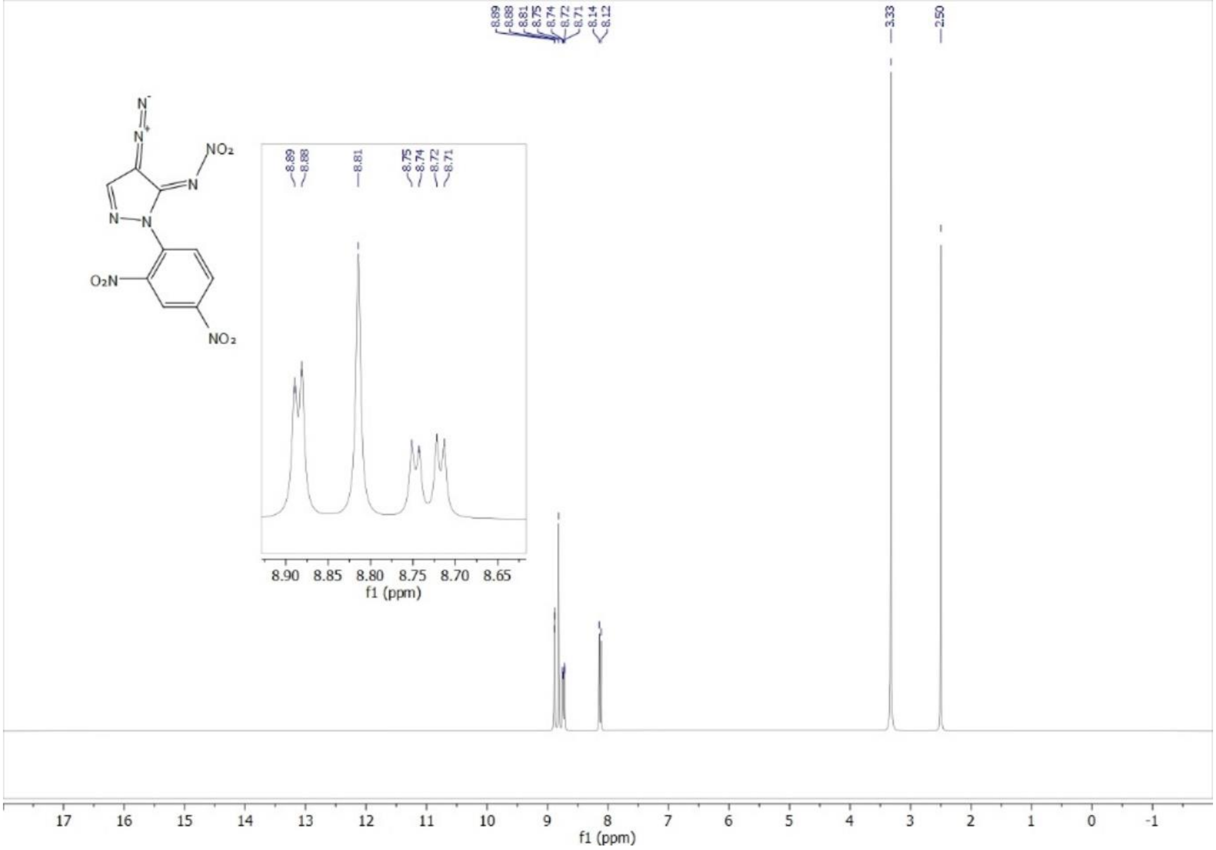


Fig S5. ^{1}H NMR spectrum of compound **2a** in DMSO-d$_6$.

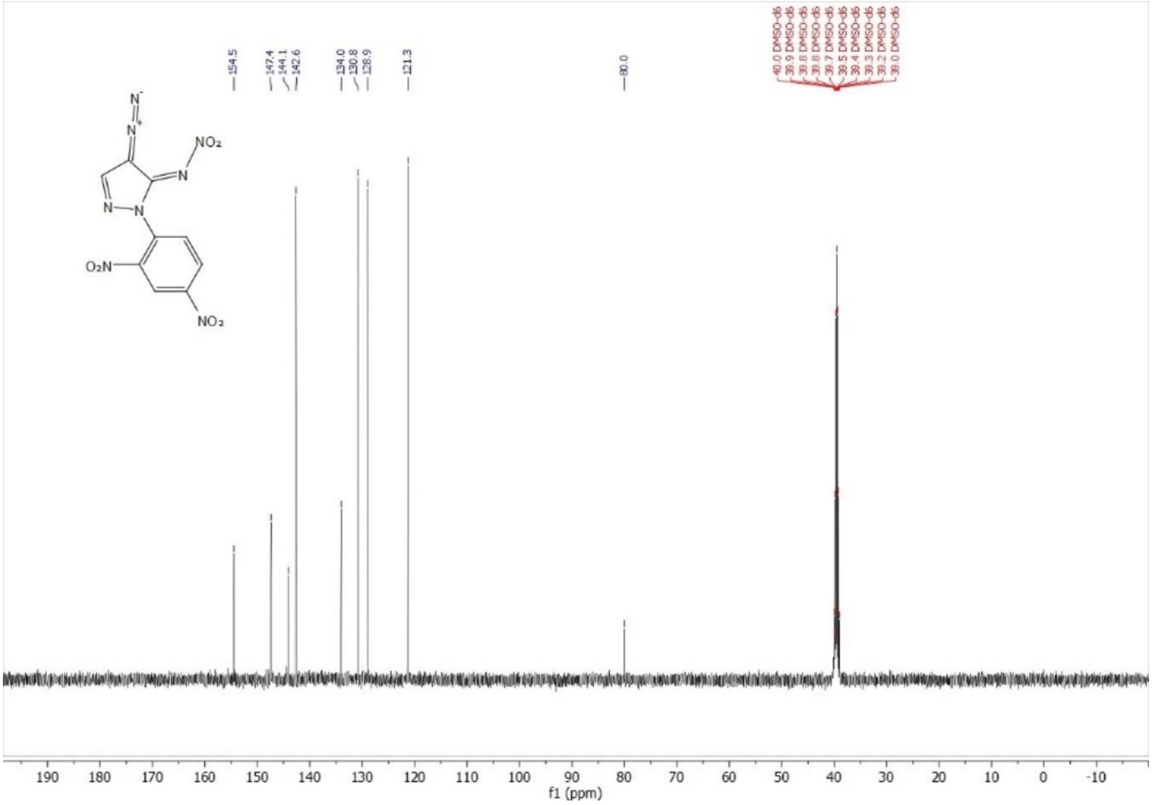


Fig S6. ^{13}C NMR spectrum of compound **2a** in DMSO-d$_6$.

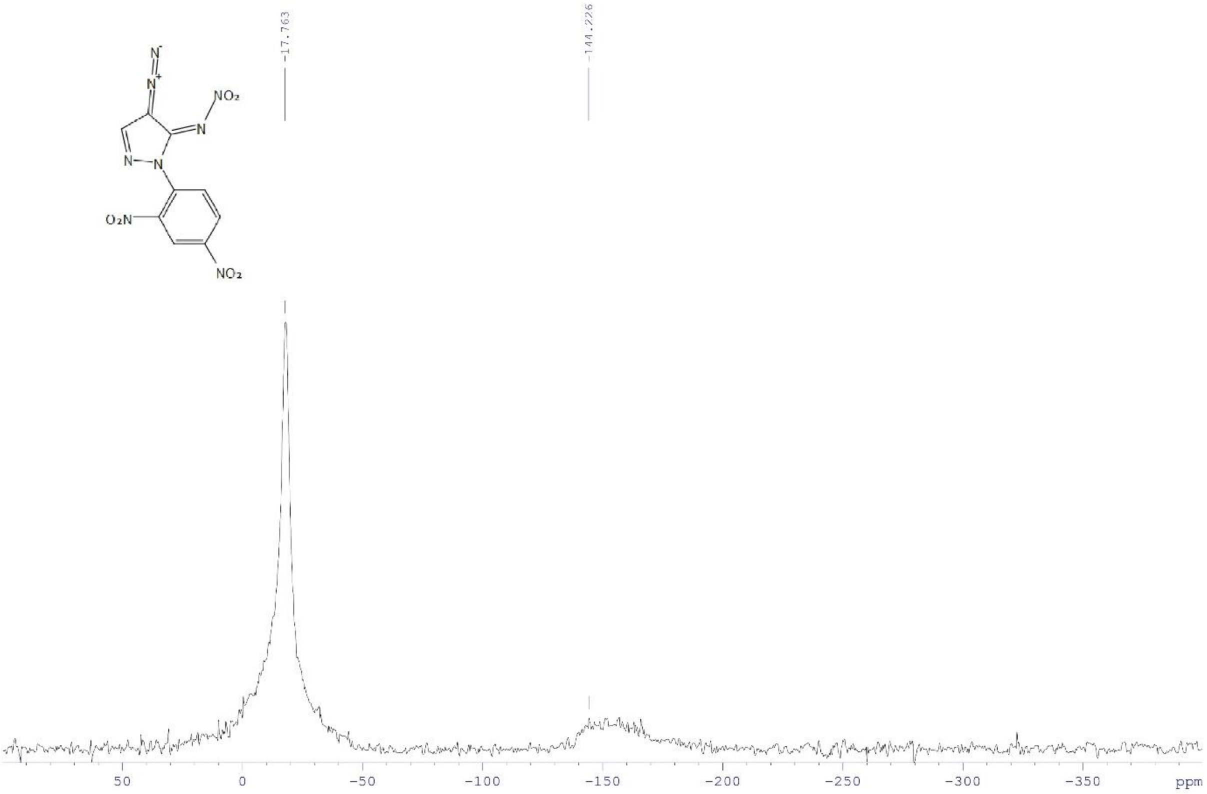


Fig S7. ^{14}N NMR spectrum of compound **2a** in DMSO-d$_6$.

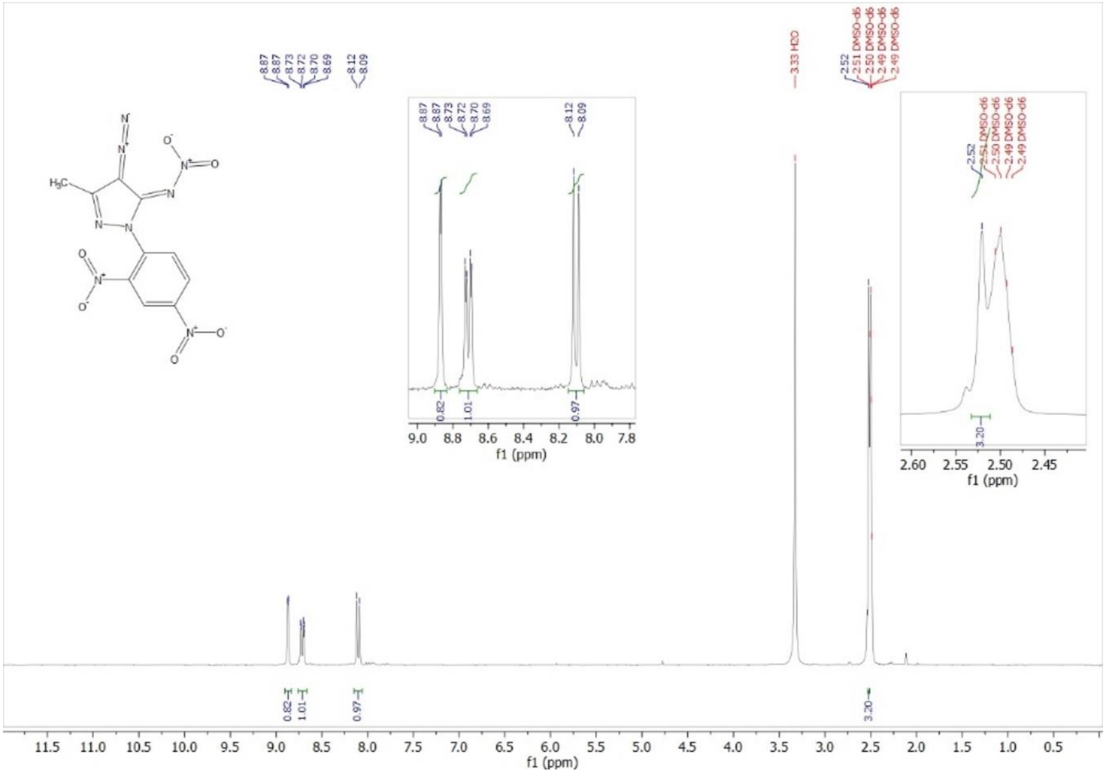


Fig S8. ^{1}H NMR spectrum of compound **2b** in DMSO-d$_6$.

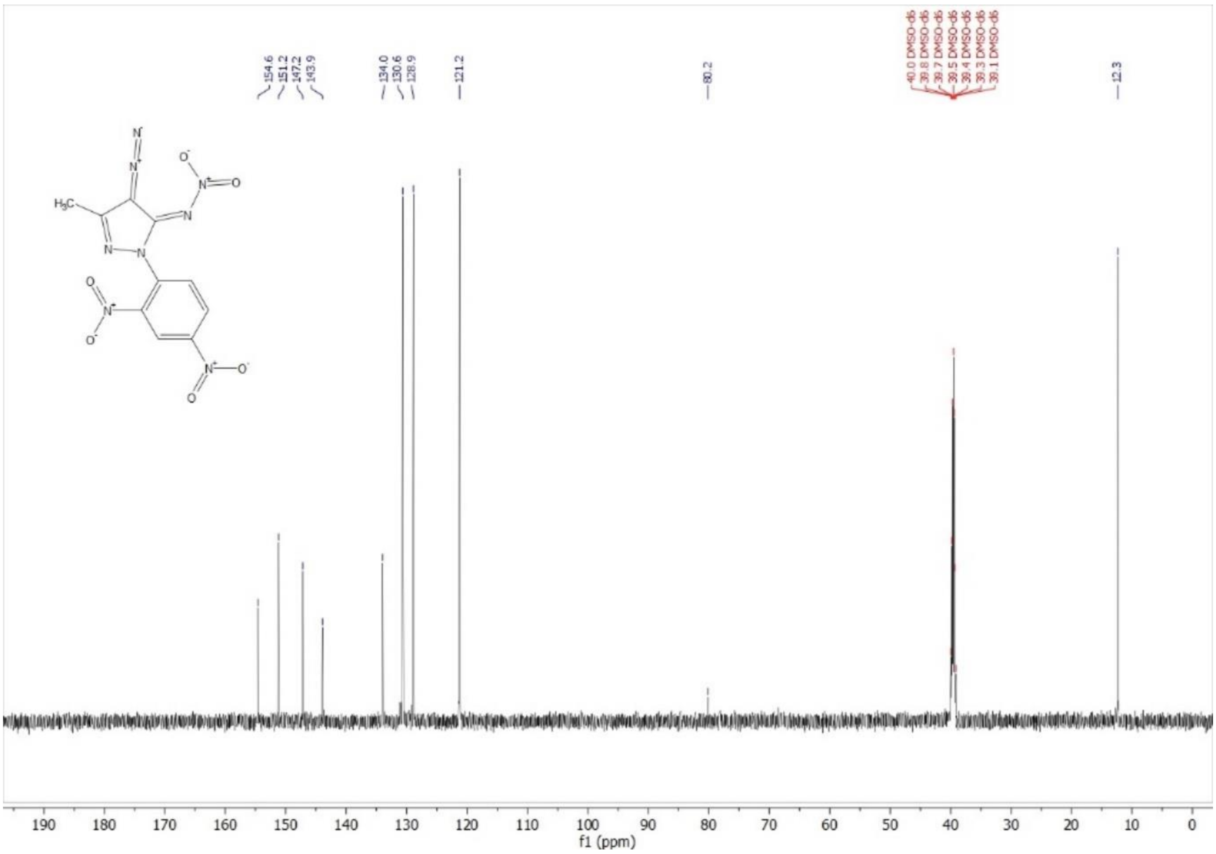


Fig S9. ^{13}C NMR spectrum of compound **2b** in DMSO-d$_6$.

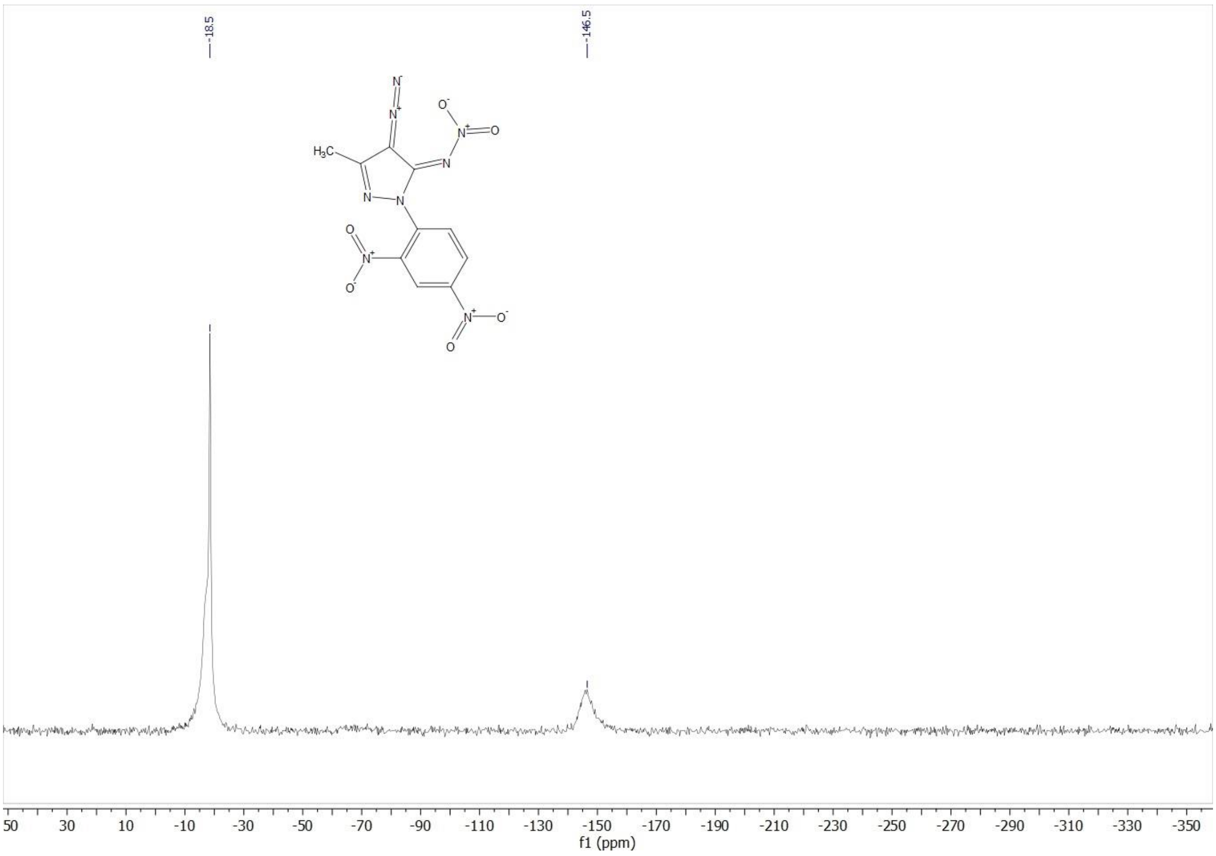


Fig S10. ^{14}N NMR spectrum of compound **2b** in DMSO-d$_6$.

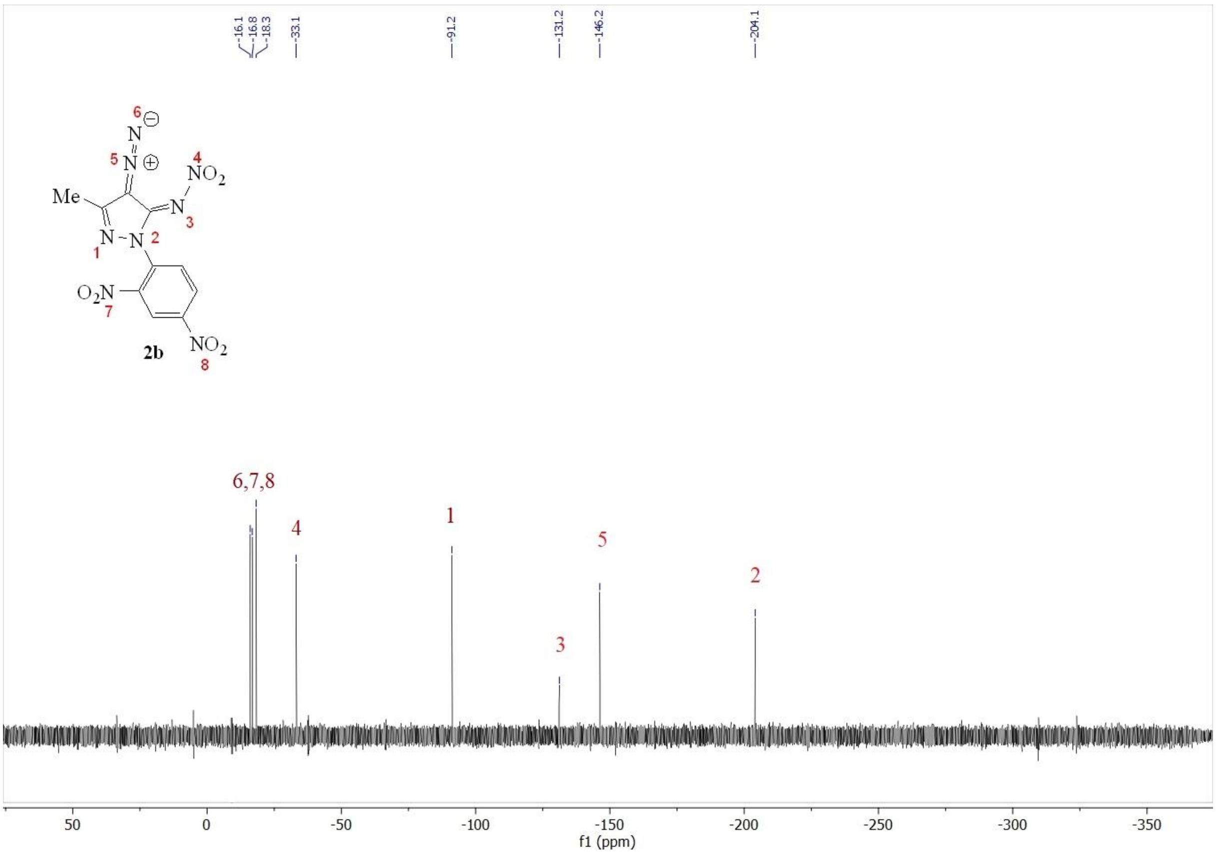


Fig S11. ^{15}N NMR spectrum of compound **2b** in DMSO-d$_6$.

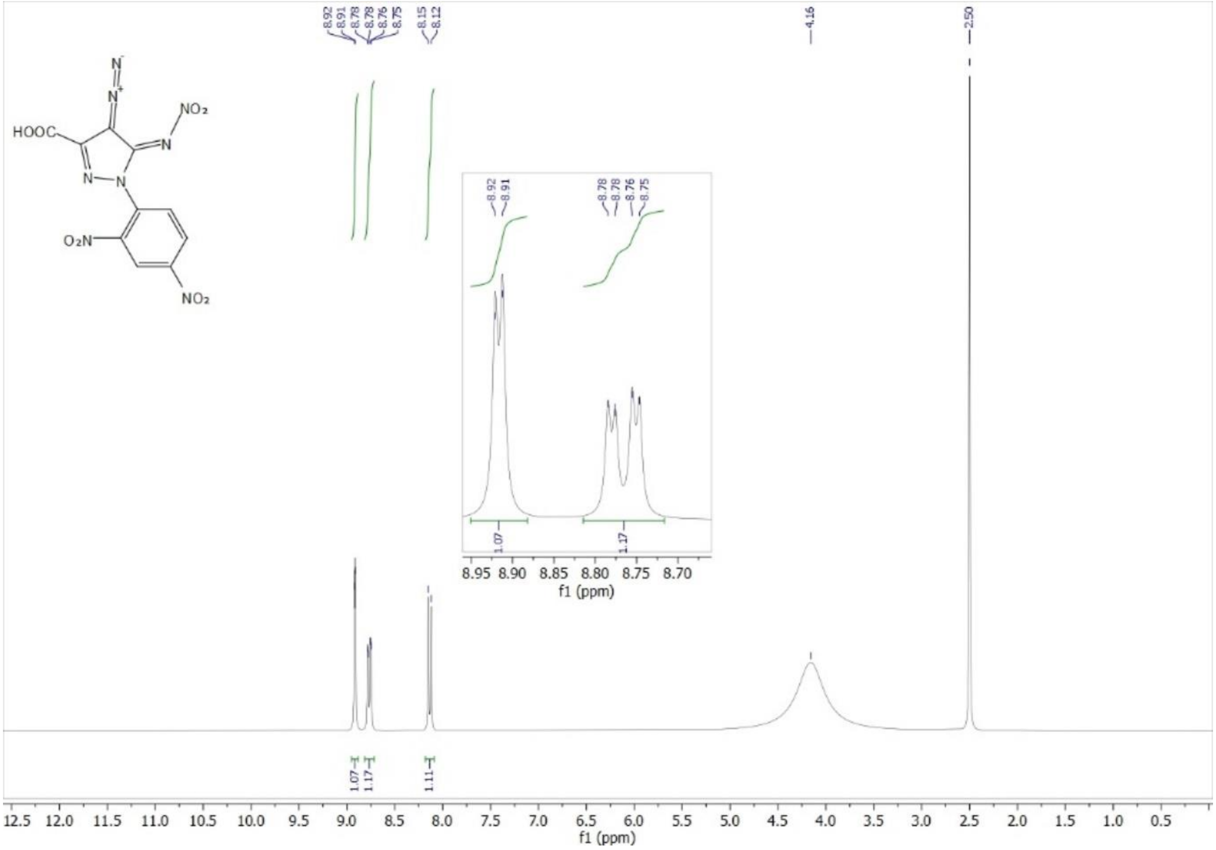


Fig S12. ^{1}H NMR spectrum of compound **2c** in DMSO-d$_6$.

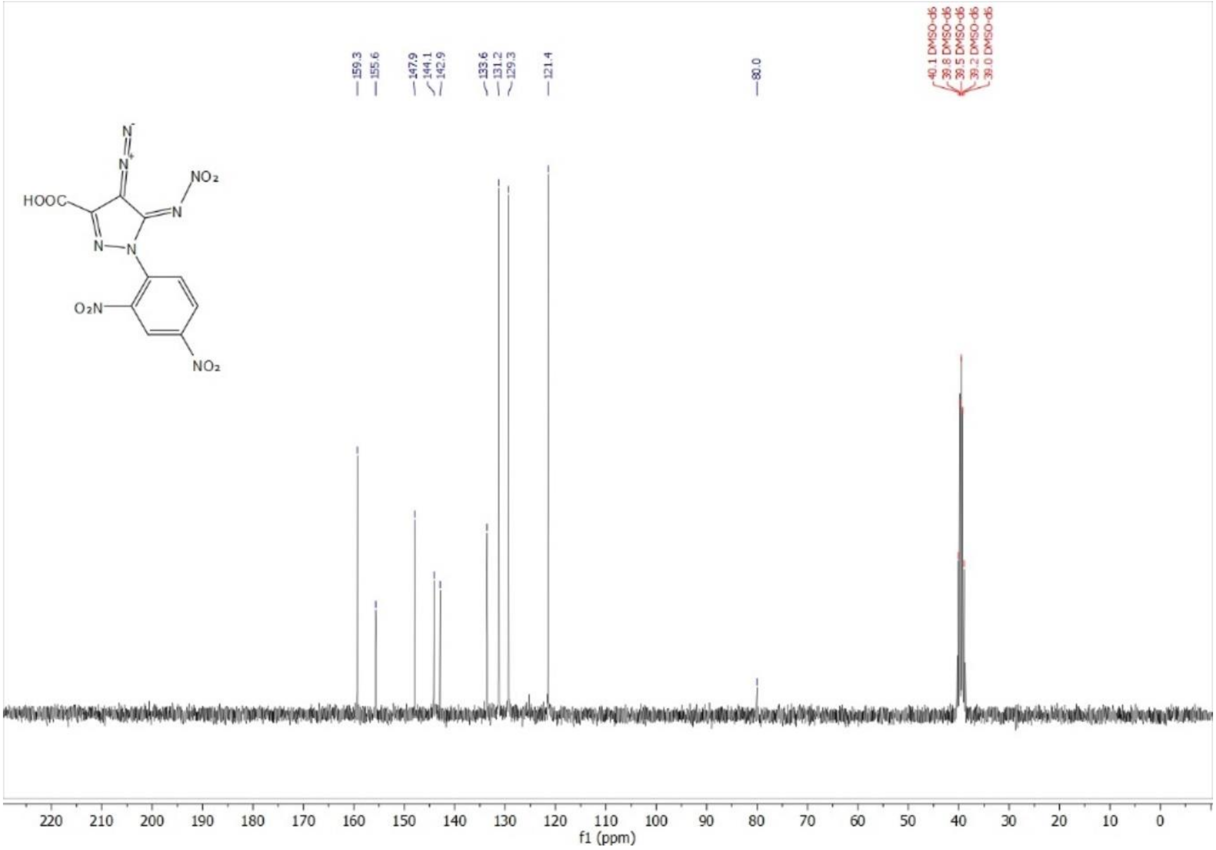


Fig S13. ^{13}C NMR spectrum of compound **2c** in DMSO-d$_6$.

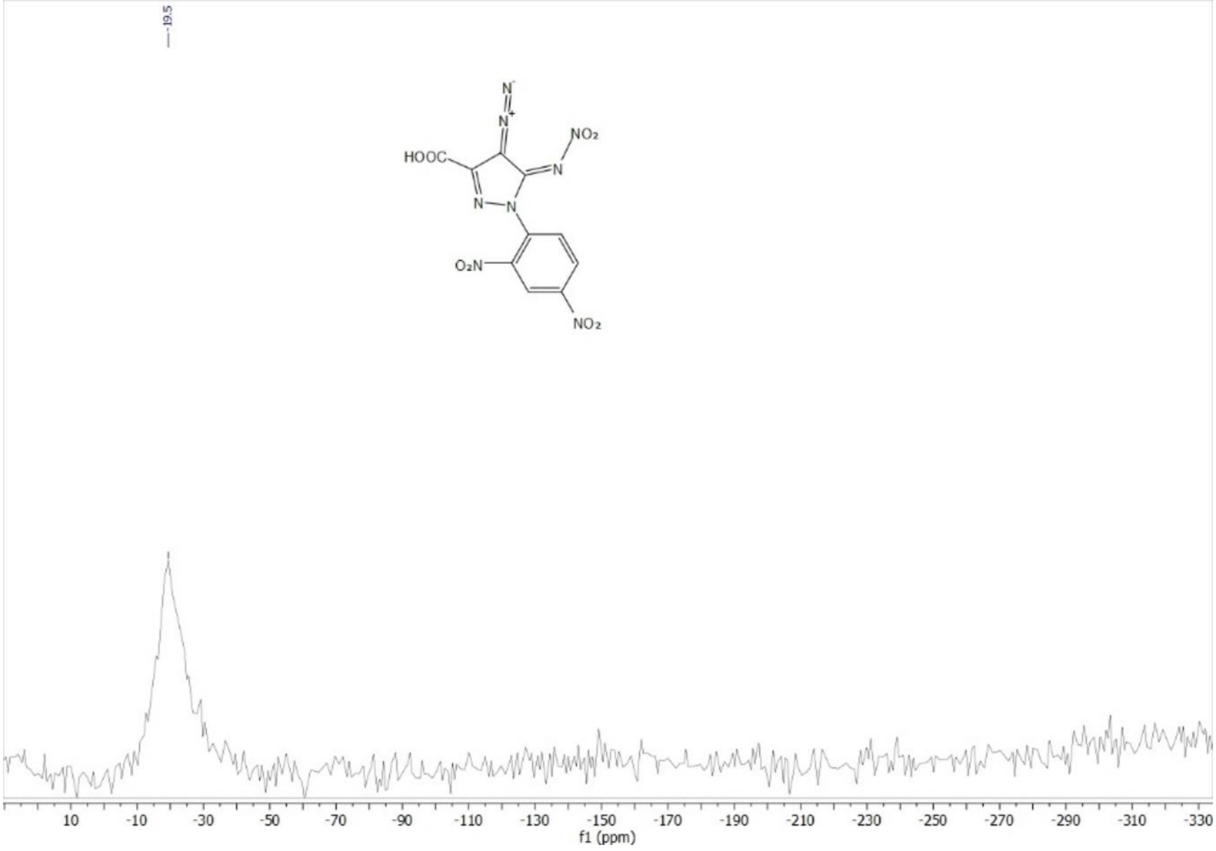


Fig S14. ^{14}N NMR spectrum of compound **2c** in DMSO-d$_6$.

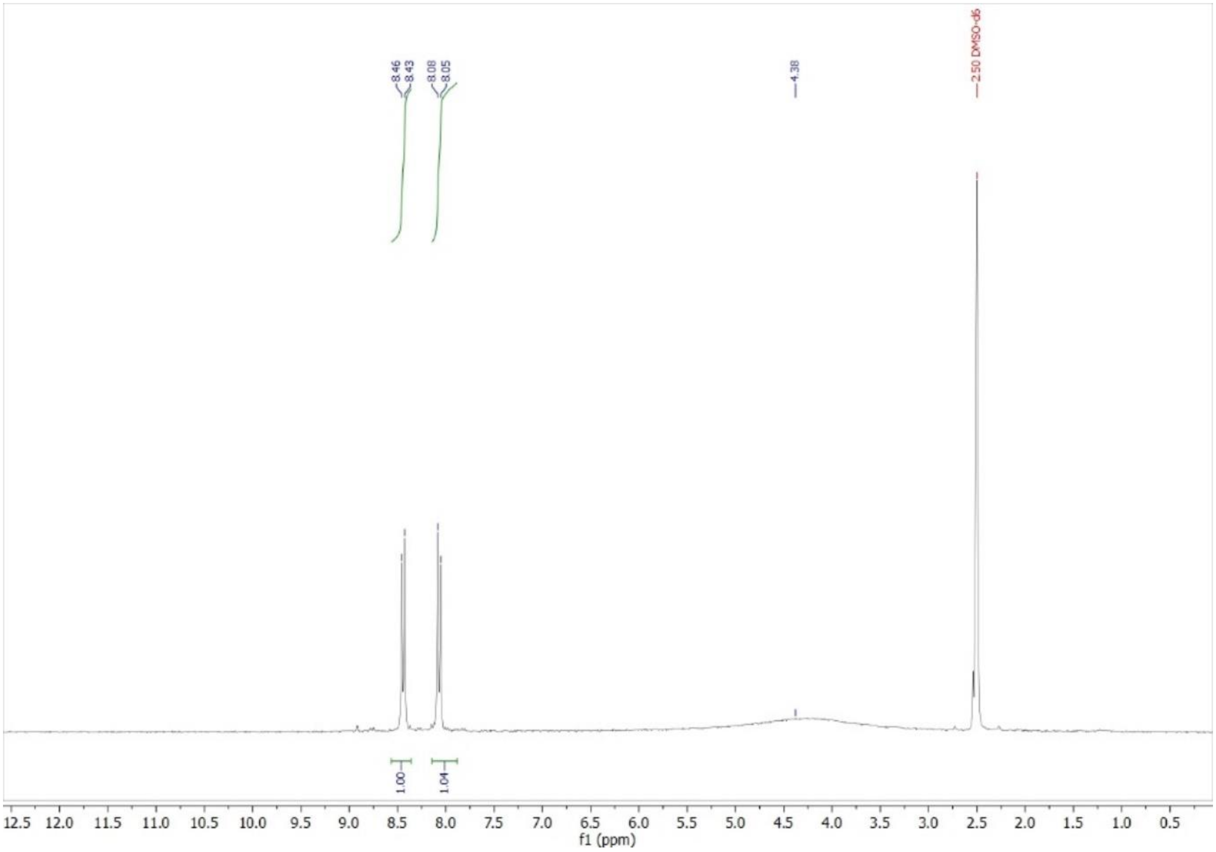


Fig S15. ^{1}H NMR spectrum of compound **3** in DMSO-d$_6$.

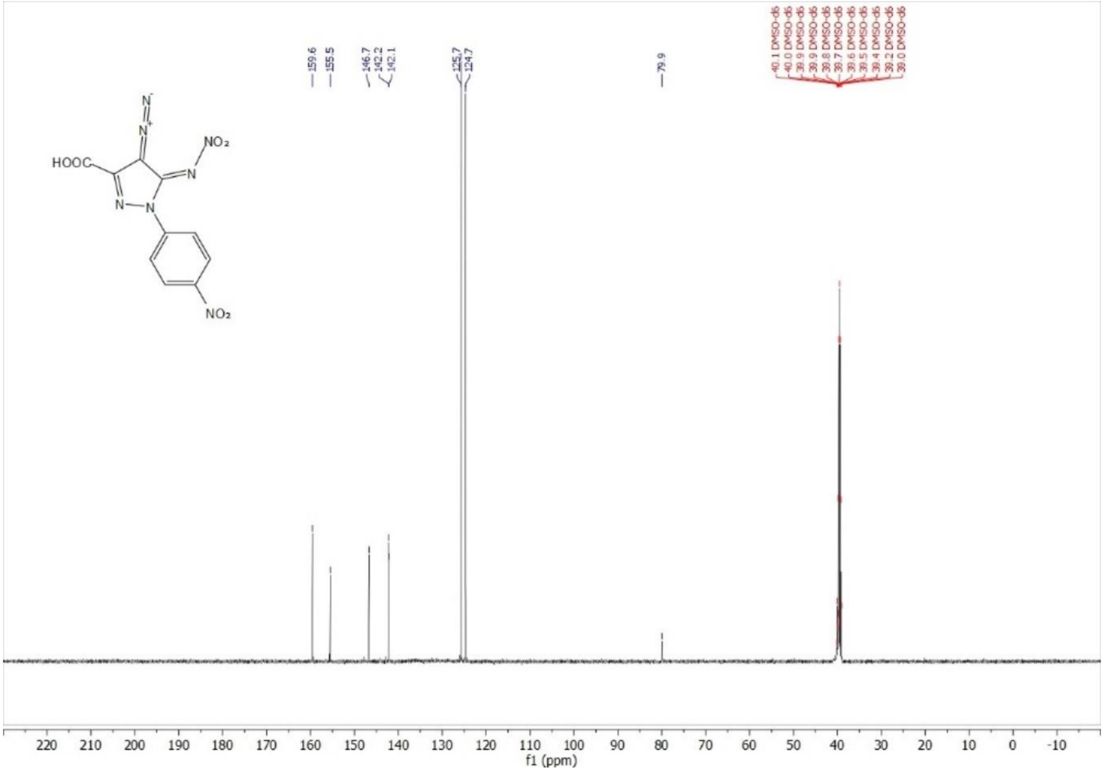


Fig S16. ^{13}C NMR spectrum of compound **3** in DMSO-d$_6$.

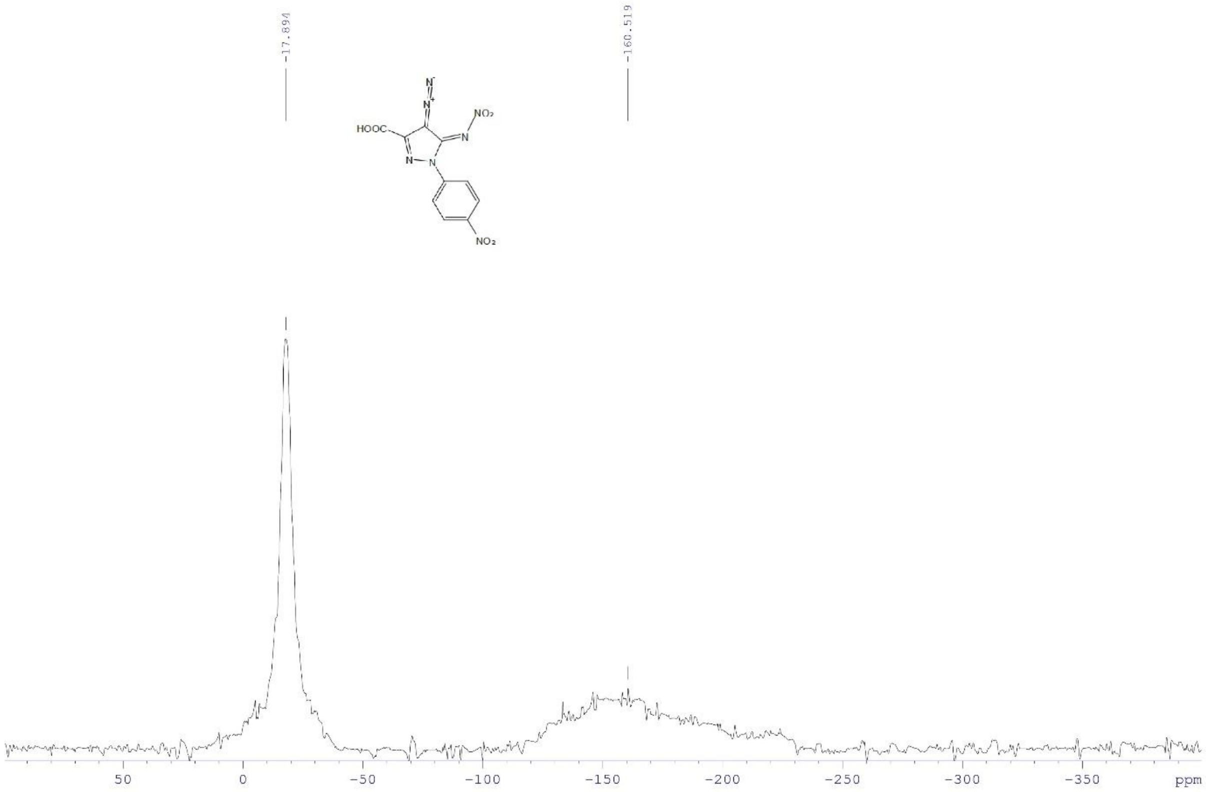


Fig S17. ^{14}N NMR spectrum of compound **3** in DMSO-d$_6$.

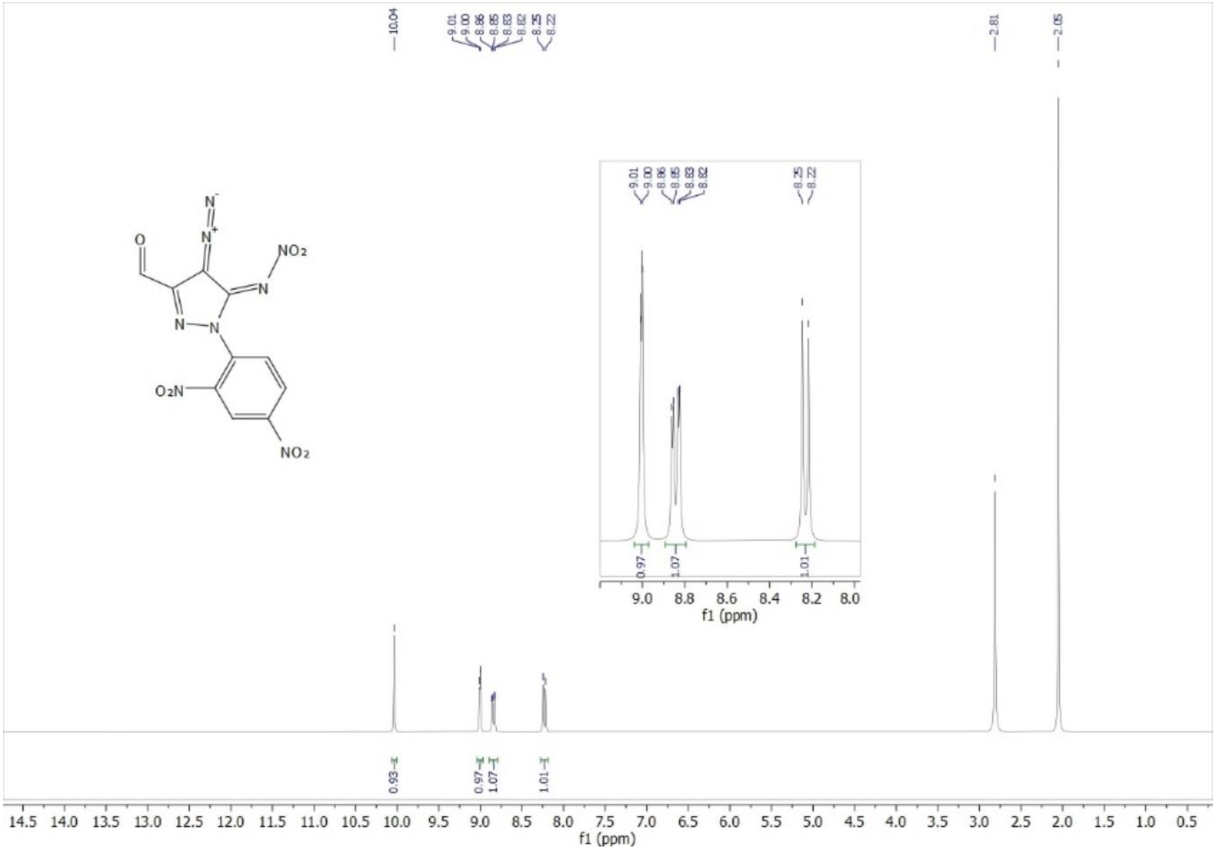


Fig S18. ^{1}H NMR spectrum of compound **4** in acetone-d$_6$.

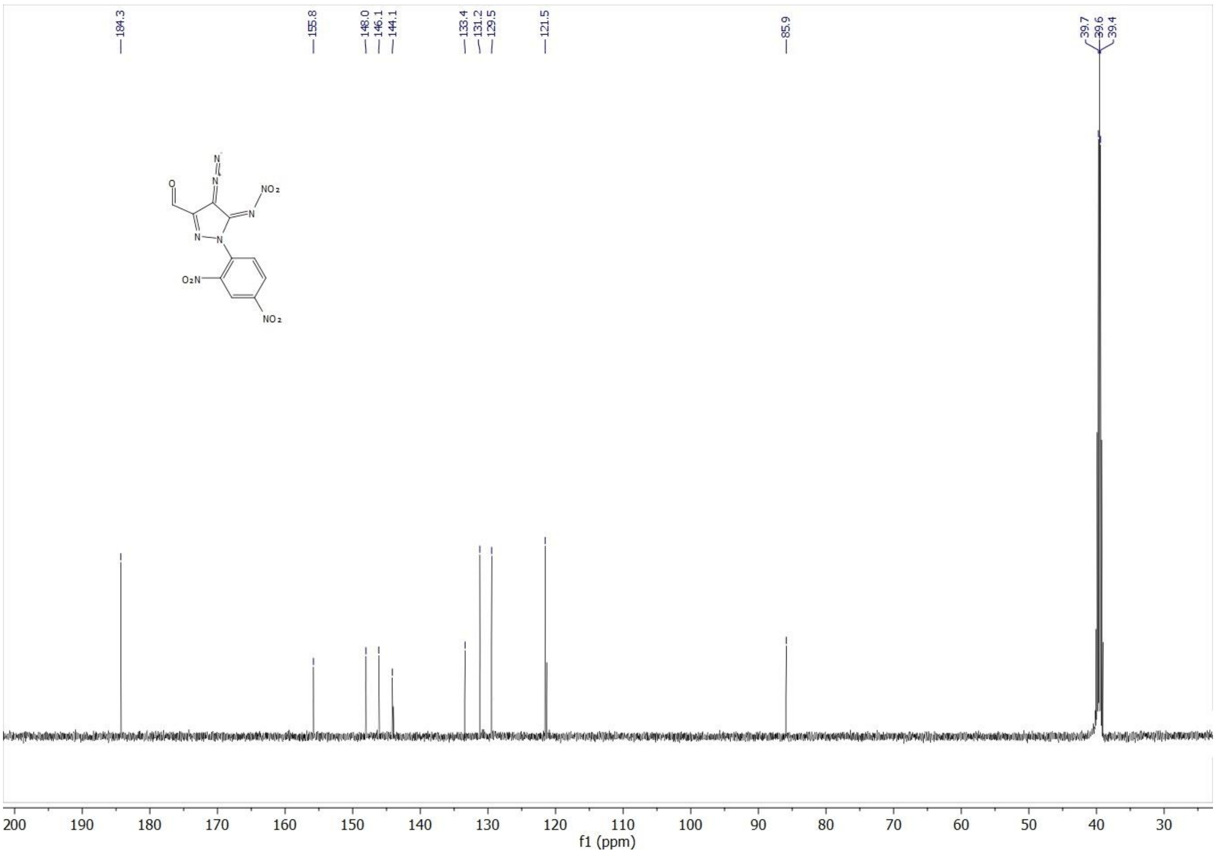


Fig S19. ^{13}C NMR spectrum of compound **4** in acetone-d$_6$.

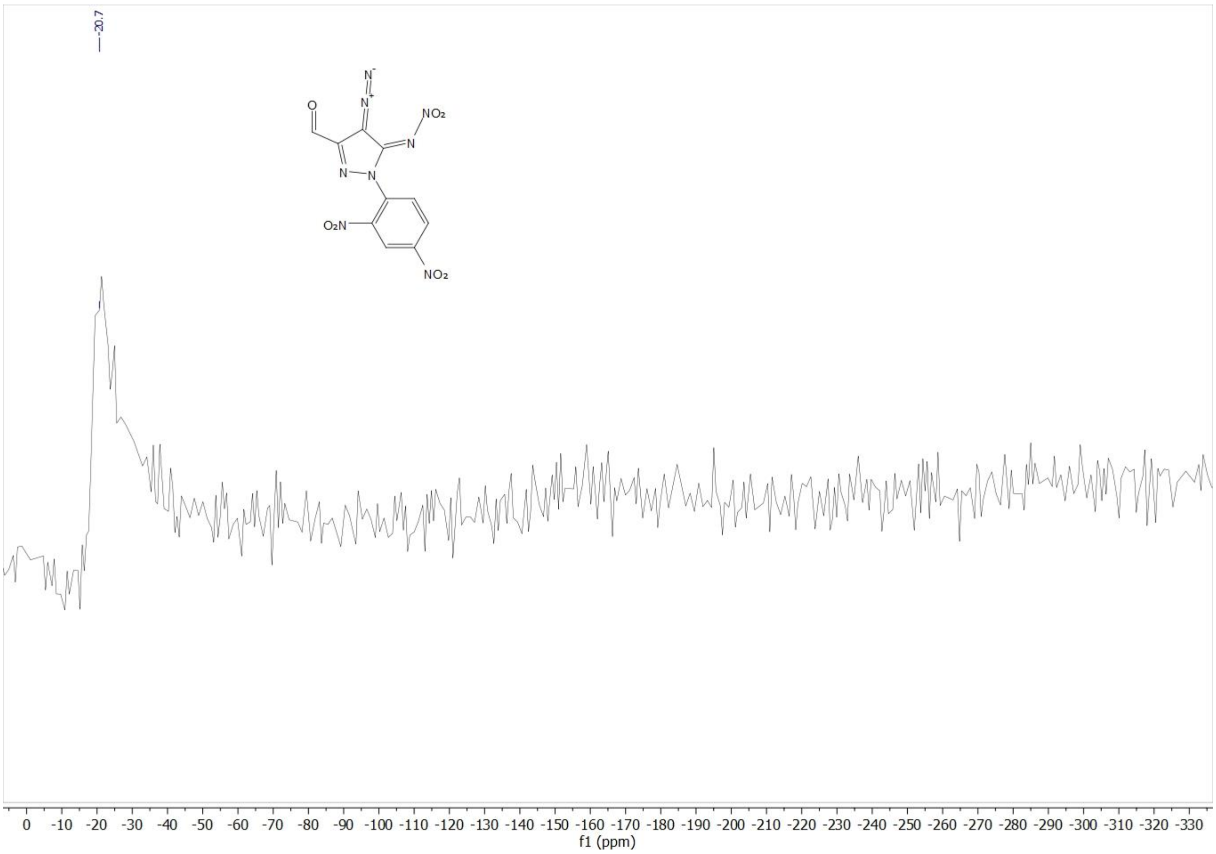


Fig S20. ^{14}N NMR spectrum of compound **4** in acetone-d$_6$.

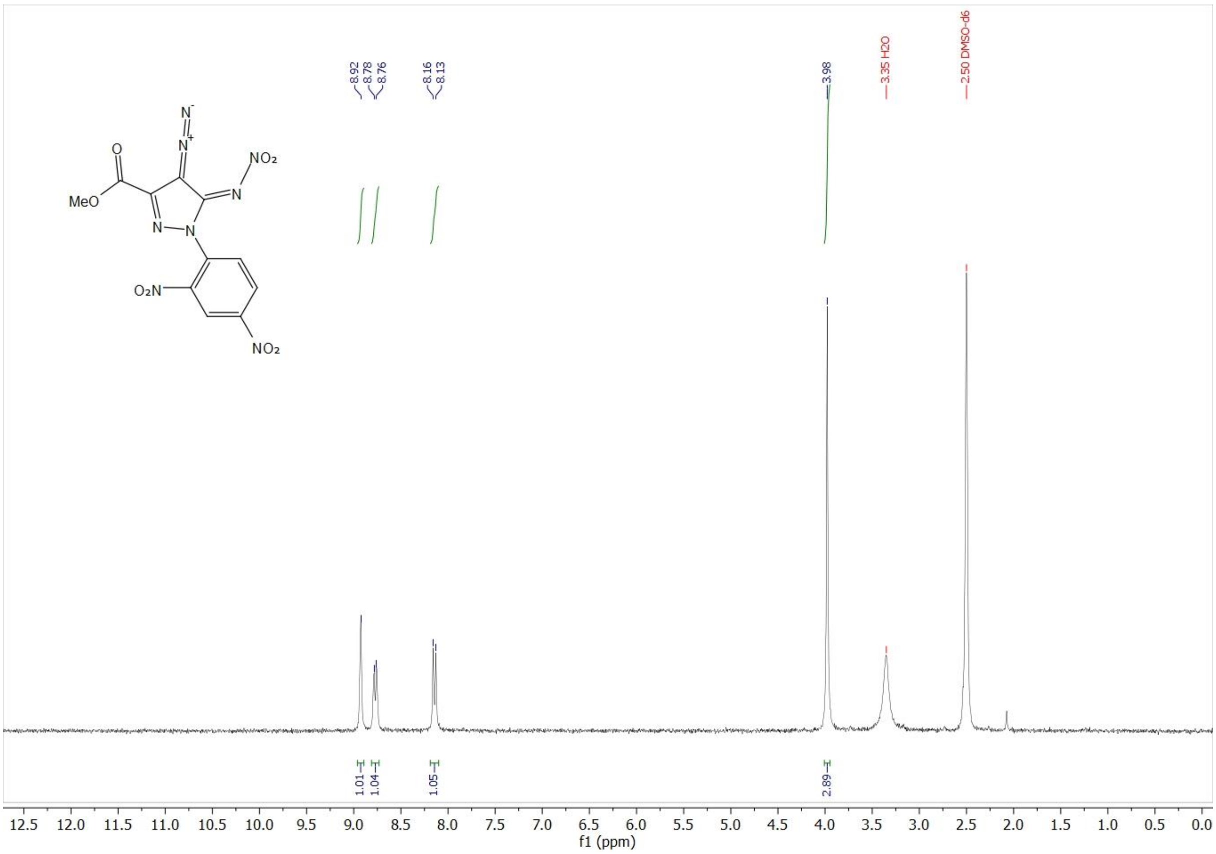


Fig S21. ^{1}H NMR spectrum of compound **5** in DMSO-d$_6$.

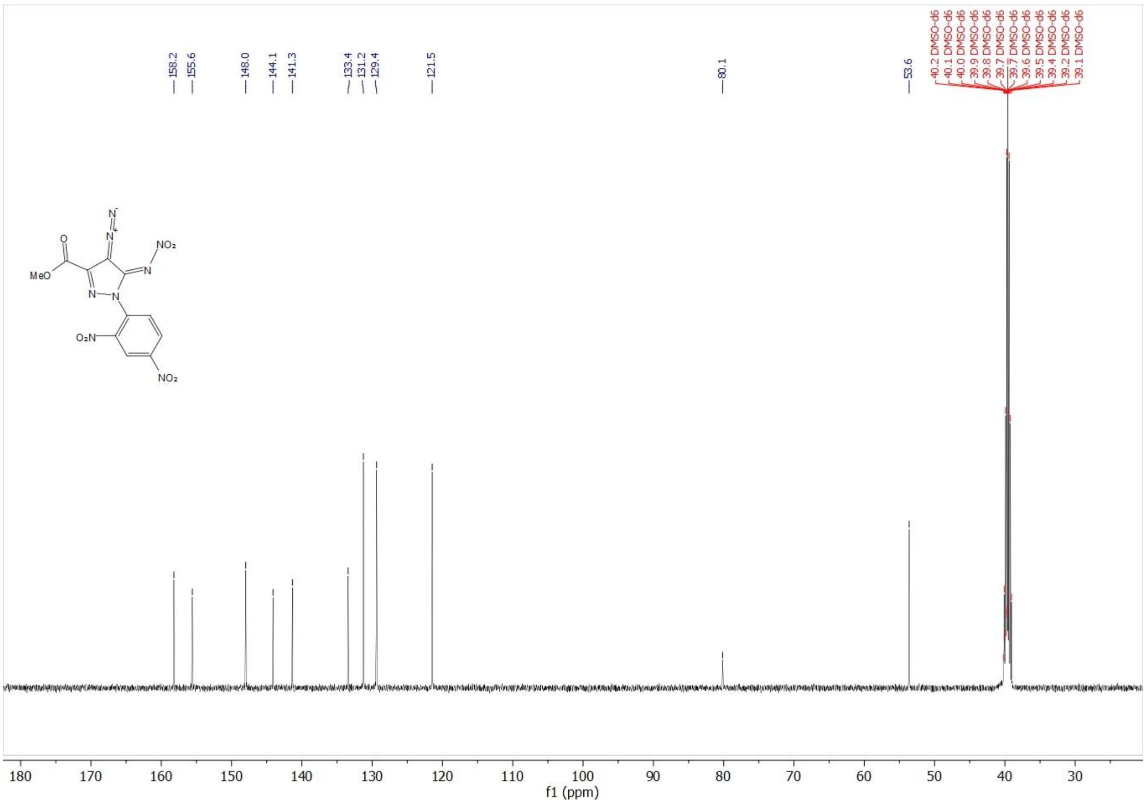


Fig S22. ^{13}C NMR spectrum of compound **5** in DMSO-d$_6$.

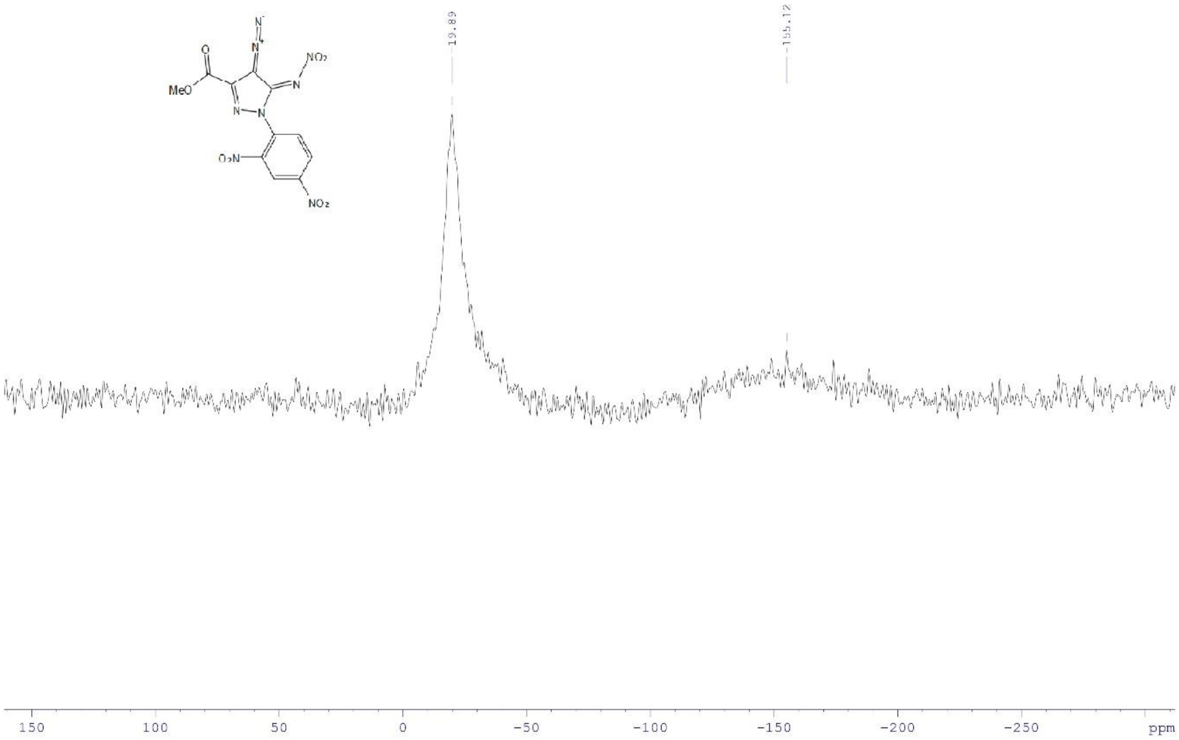


Fig S23. ^{14}N NMR spectrum of compound **5** in DMSO-d_6.

4. Thermal analysis of compounds

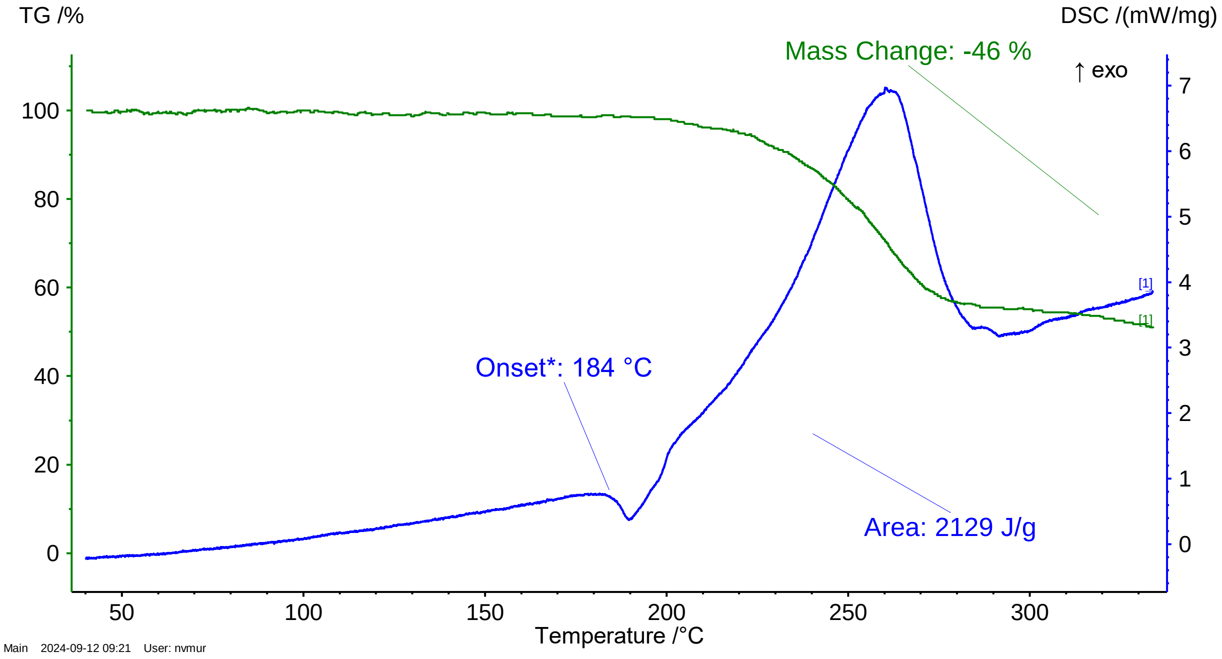


Fig S24. DSC (blue curve) and TGA (green curve) signals for linearly heated **2a**.

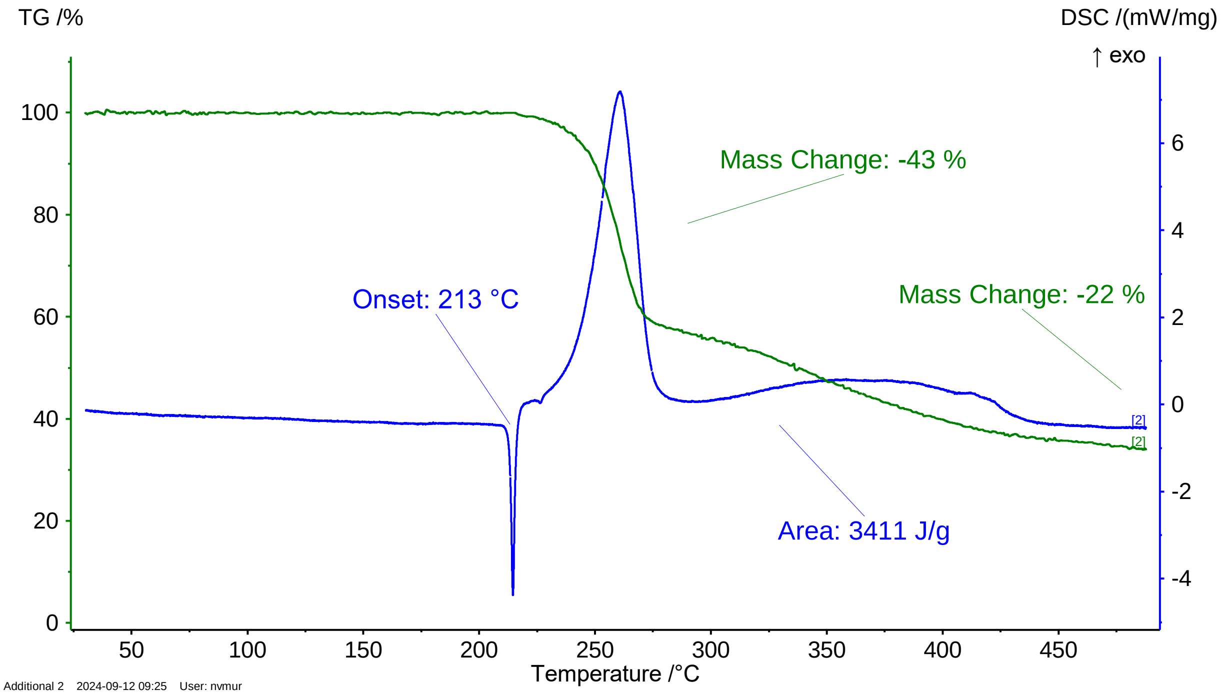


Fig S25. DSC (blue curve) and TGA (green curve) signals for linearly heated **2b**.

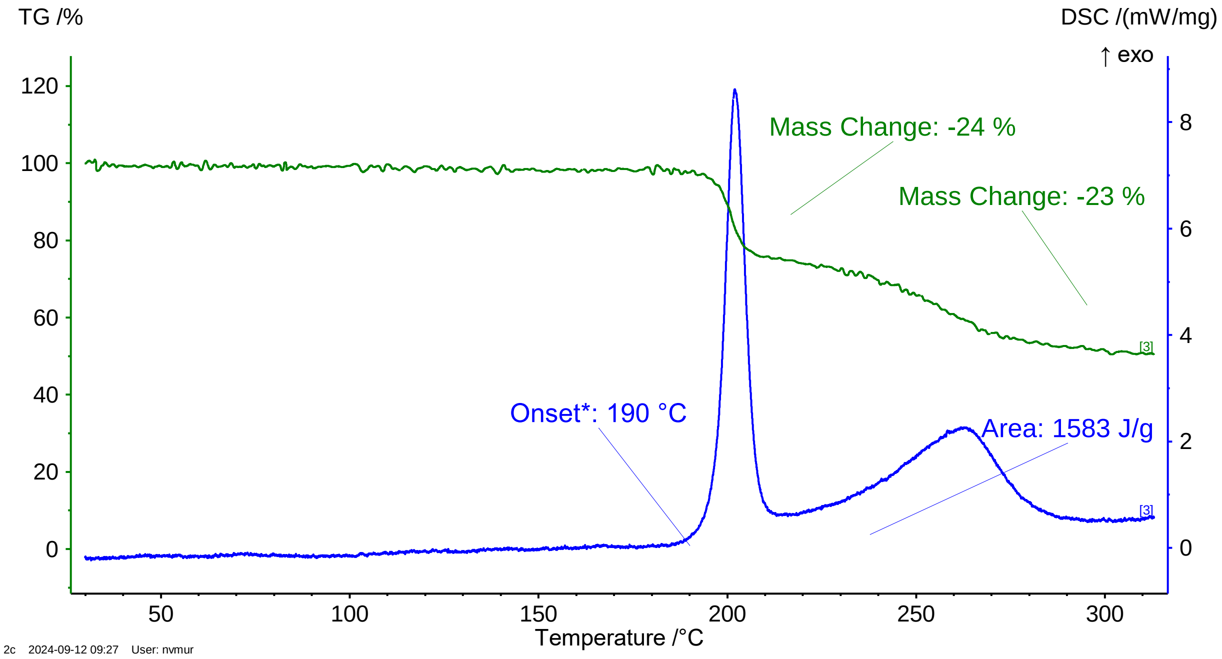


Fig S26. DSC (blue curve) and TGA (green curve) signals for linearly heated **2c**.

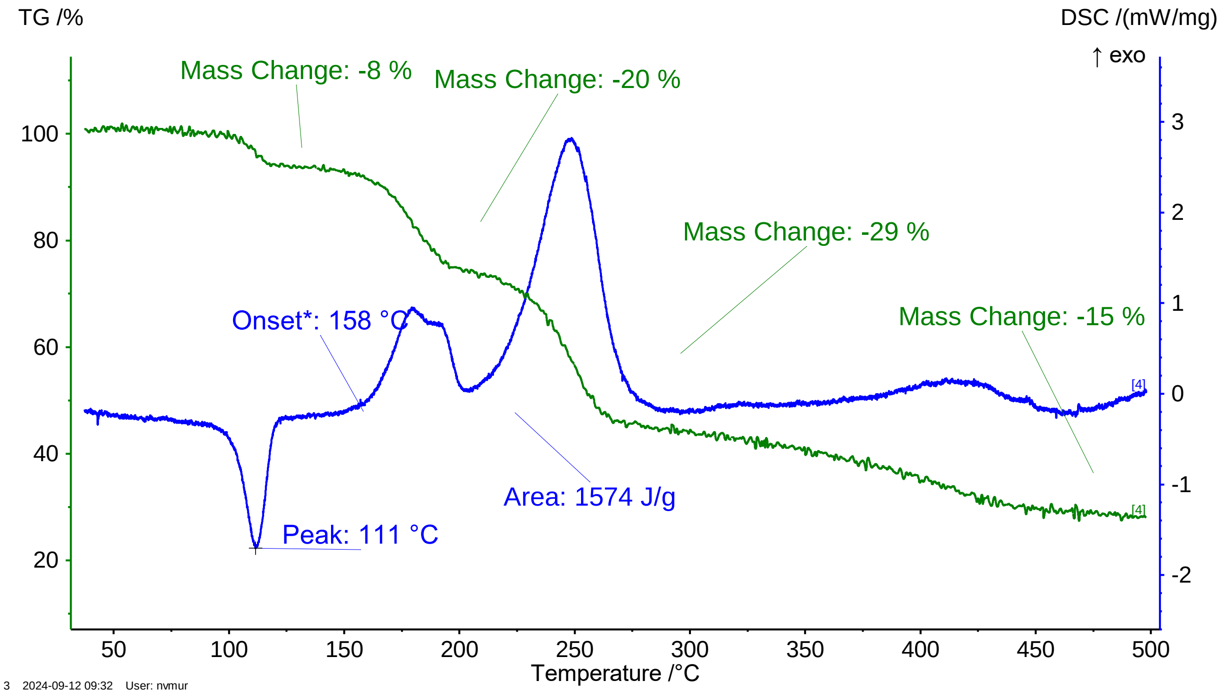


Fig S27. DSC (blue curve) and TGA (green curve) signals for linearly heated **3**. Mass spectrometric analysis of the gas phase show that first endotherm at 111°C is associated with the water loss, whereas the following exotherm is accompanied by release of the decomposition products (N_2O, NO_2).

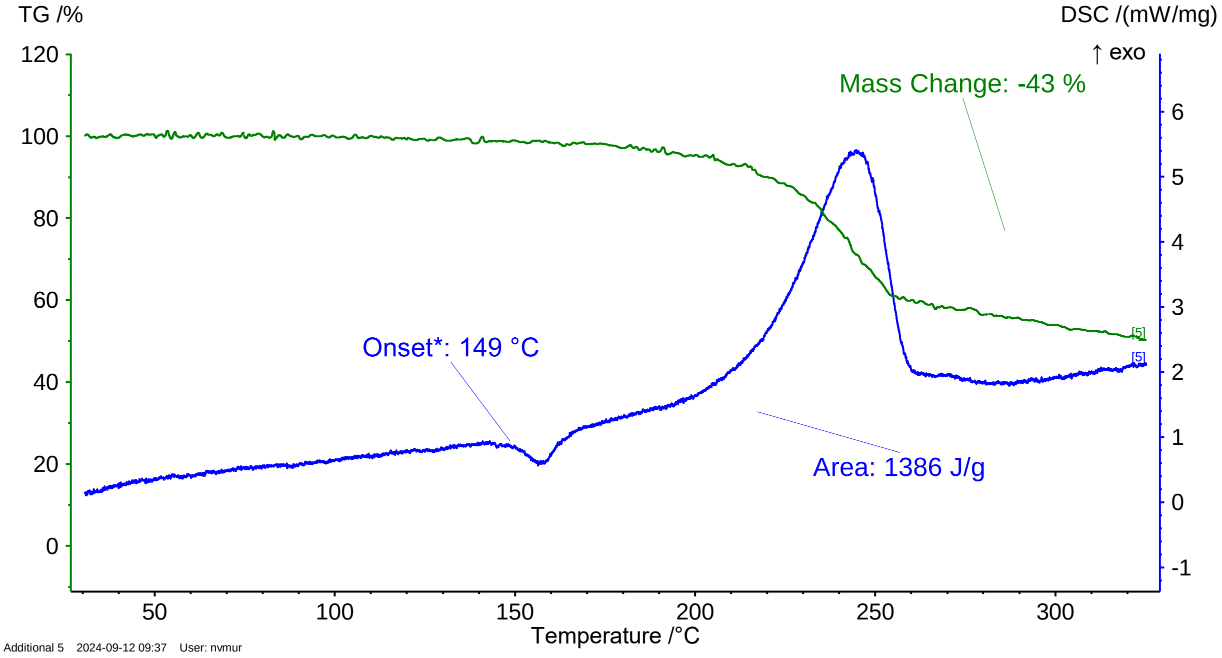


Fig S28. DSC (blue curve) and TGA (green curve) signals for linearly **5**.

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