Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 218–220

Di(propargyl)nitramine: synthesis and reactivity

**Pavel S. Gribov, Maria V. Mikhailova, Tatiana S. Kon’kova,
Yurii N. Matyushin and Aleksei B. Sheremetev**

CONTENTS

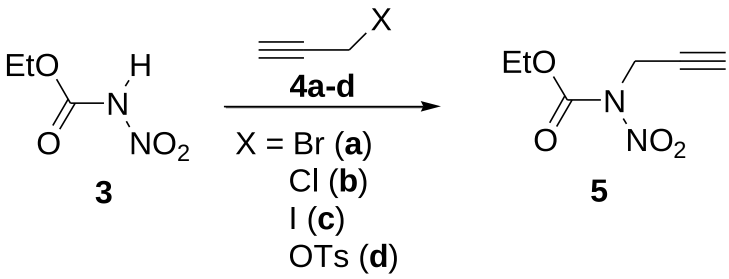
Experimental

IR spectra were recorded on a BrukerALPHA instrument in KBr pellets. ^{1}H, ^{13}C, and ^{14}N spectra were acquired on a Bruker AM-300 instrument (300.13, 75.47 and 21.69 MHz, respectively) in $CDCl_3$ or DMSO-d_6 at 299 K. The chemical shifts of ^{1}H and ^{13}C nuclei were reported relative to TMS, for ^{14}N – relative to $MeNO_2$, high-filed chemical shifts are given with a minus sign. High-resolution mass spectra with electrospray ionization were recorded on 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 Silicagel 60 F_{254} plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm).

Materials Most of the reagents and starting materials were purchased from commercial sources and used without additional purification. The starting ethyl nitrocarbamate (**3**)[S1] and propargyl tosylate (**4d**)[S2] were obtained published procedures.

Caution! Although we have encountered no difficulties during preparation and handling of these compounds, they are potentially explosive energetic materials. Manipulations must be carried out by using appropriate standard safety precautions.

Ethyl nitro(propargyl)carbamate (5)



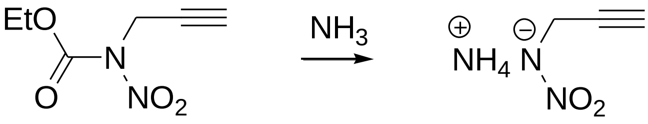
General procedure for the propargylation of ethyl nitrocarbamate (**3**). To a freshly prepared solution of compound **3** (0.4 g, 2.99 mmol) and 1 equiv of a base in a solvent (5 mL) was added dropwise the corresponding propargylation reagent **4a-d** (1-2 mmol). The mixture was stirred under the conditions shown in Table S1 until TLC analysis (1:4 MeCN / $CHCl_3$) indicated complete consumption of the starting material, then quenched with brine (50 mL) and extracted with EtOAc/hexane (1:1, 3×30 mL). The organic extracts were combined, dried with $MgSO_4$ and concentrated under vacuum to afford a yellow oil which was dissolved in CH_2Cl_2 (5 mL) and purified by a short silica gel column chromatography (CH_2Cl_2, R_f = 0.70) providing the title compound **5** as a light yellow liquid; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 3H, *J* = 7.2 Hz, CH_3), 2.25 (t, 1H, *J* = 2.3 Hz, CH), 4.30 (q, 2H, *J* = 10,7 Hz, $C\underline{H}_2CH_3$), 4.68 (d, 2H, *J* = 1,1 Hz, NCH_2). ^{13}C NMR ($CDCl_3$) δ 13.9, 38.8, 65.2, 65.1, 149.7. ^{14}N NMR ($CDCl_3$) δ -47.2 (NO_2). IR (KBr): 3294, 2989, 2942, 1775, 1746, 1583, 1424, 1376, 1324, 1289, 1237, 1200, 1180, 1154, 1072, 1008, 917, 875, 753, 688 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_6H_8N_3O_4Na$ $[M + Na]^+$ 195.0382, found 195.0377. Anal. calcd. for $C_6H_8N_2O_4$ (172.14): C 41.86, H 4.68, N 16.27. Found: C 42.01, H 4.74, N 16.19. The results are given in Table S1.

Table S1. Optimization of the reaction of ethyl nitrocarbamate (**3**) with **4a-d**

Entry	Reagent	Base (B)	**3** : **4** : **B**	Catalyst	Solvent	T, °C	Time, h	Isolated yield of **5**, %
1	**4a**	NEt_3	1:1.6:1	-	CH_2Cl_2	40	8	12
2	**4a**	NEt_3	1:1:1	-	DMF	25	24	30
3	**4a**	NEt_3	1:1:1	-	DMF	25	48	65
4	**4a**	NEt_3	1:1:1	-	DMF	25	72	67
5	**4a**	NEt_3	1:1:1	-	DMF	25	96	71
6	**4a**	NEt_3	1:1.5:1	-	DMF	25	96	71
7	**4a**	NEt_3	1:1:1	-	DMF	25	120	57
8	**4a**	NEt_3	1:1:1	-	CH_2Cl_2	25	96	27
9	**4a**	NEt_3	1:1:1	-	C_6H_6	25	96	25
10	**4a**	NEt_3	1:1:1	-	MeCN	25	96	43
11	**4a**	NEt_3	1:1:1	-	MeCN	25	160	55
12	**4a**	NEt_3	1:1:1	-	DMSO	25	96	57
13	**4a**	NEt_3	1:1:1	-	acetone	25	96	33
14	**4a**	NEt_3	1:1:1	-	THF	25	96	30
15	**4a**	NEt_3	1:1:1	-	MeOH	25	96	5
16	**4a**	K_2CO_3	1:1:0.5	-	DMF	25	96	69
17	**4a**	K_2CO_3	1:2:0.5	-	DMF	80	1	50
18	**4a**	K_2CO_3	1:2:0.5	-	DMF	80	2	63
19	**4a**	K_2CO_3	1:2:0.5	-	DMF	80	3	60
20	**4a**	NEt_3	1:1:1	-	MeCN	80	1	41
21	**4a**	NEt_3	1:1:1	-	MeCN	80	2	53
22	**4a**	NEt_3	1:1:1	-	MeCN	80	3	47
23	**4a**	NEt_3	1:1:1	KI	DMF	25	24	49
24	**4a**	NEt_3	1:1:1	KI	MeCN	80	1	47
25	**4a**	NEt_3	1:1:1	KI	MeCN	25	24	25
26	**4b**	NEt_3	1:1.1:1	-	DMF	25	96	0*
27	**4c**	NEt_3	1:1.1:1	-	DMF	25	96	0*
28	**4d**	NEt_3	1:1.1:1	-	DMF	25	48	67
29	**4d**	NEt_3	1:1.1:1	-	DMF	25	96	82
30	**4d**	NEt_3	1:1.1:1	-	DMF	25	120	77

* - a complex mixture of compounds

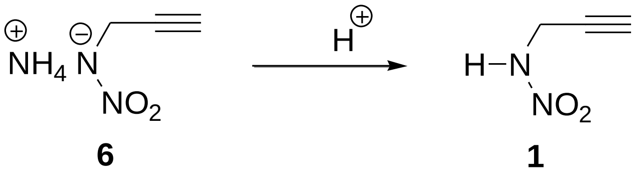
Ammonium nitro(propargyl)amide (6)



5 **6**

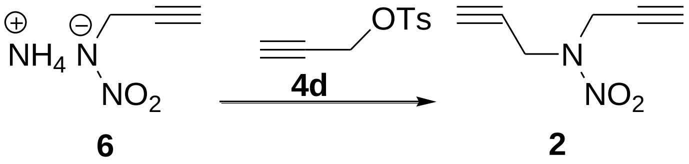
Compound **5** (0.65 g, 3.78 mmol) was dissolved in a mixture of dry diethyl ether (10 mL) and $CHCl_3$ (10 mL) and cooled to 10 °C. Excess gaseous ammonia was slowly bubbled through the solution for 1 h with stirring. The precipitate was isolated by filtration, washed with cold ether, and dried under vacuum to give salt **6** (0.43 g, 98%) as a white solid, mp 104-108°C (dec.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.86 (t, 1H, *J* = 2.5 Hz, CH), 3.85 (d, 2H, *J* = 1.3 Hz, CH_2), 7.09 (br s, 4H, NH_4^+),. ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.8, 72.2, 82.2. ^{14}N NMR (21 MHz, $CDCl_3$) δ -18.5 (NO_2), -358,7 (NH_4^+). IR (KBr): 3305, 3288, 3173, 1435, 1400, 1326, 1306, 1285, 1083, 955, 765, 716, 655, 634 cm^{-1}. Anal. calcd. for $C_3H_7N_3O_2$ (117.11): C 30.77, H 6.03, N 35.88; found C 30.84, H 6.11, N 35.74.

(Propargyl)nitramine (1)



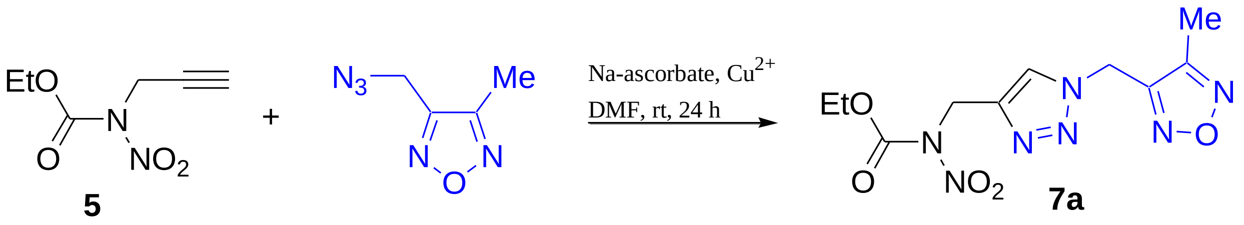
To a solution of salt **6** (0.2 g, 1.71 mmol) in EtOH (5 mL) was added 85% H_3PO_4 (0.15 mL) at room temperature. The mixture was diluted with diethyl ether (30 mL) and filtered through a short layer of silica gel. Evaporation left the crude product, which was purified by dilution with CH_2Cl_2 (20 mL) and filtration through a short layer of silica gel. The filtrate was concentrated *in vacuo* to give product **1** (0.15 g, 88%) as a light yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (t, 1H, *J* = 2.4 Hz, CH), 4.32 (s, 2H, CH_2), 8.84 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.0, 73.9, 75.5. ^{14}N NMR (21 MHz, $CDCl_3$) δ -31.1 (NO_2). IR (KBr): 3621 (уш), 3291, 3118, 1577, 1434, 1401, 1373, 1320, 1271, 1109, 1043, 938, 896, 776, 649 cm^{-1}. Anal. calcd. for $C_3H_4N_2O_2$ (100.08): C 36.01, H 4.03, N 27.99; found C 35.98, H 4.06, N 27.89.

Di(propargyl)nitramine (2)



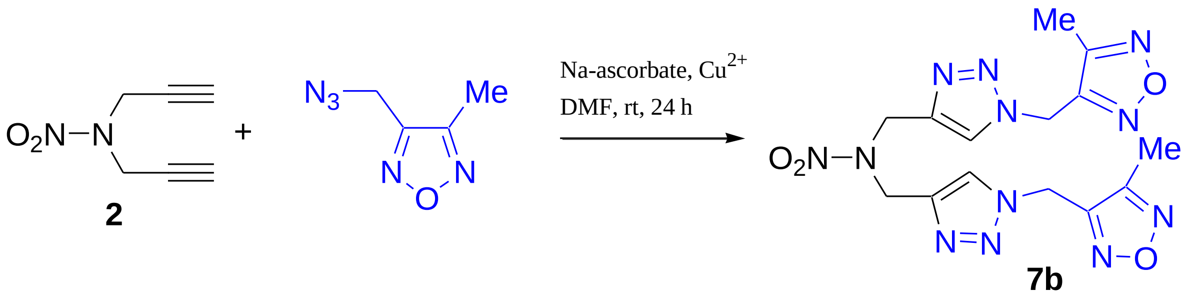
Salt **6** (0.3 g, 2.56 mmol), propargyl tosylate **4d** (0.54 g, 2.56 mmol) and DMF (5 mL) were stirred together at 60 °C for 0.5 h. The reaction mixture was cooled to 10 °C, diluted with water (50 mL) and then extracted with EtOAc-hexane (1:1; 5×40 mL). The organic extracts were combined, dried with $MgSO_4$ and concentrated under vacuum to afford a yellow oil which was dissolve in CH_2Cl_2 (5 mL) and purified via a short silica gel column (CH_2Cl_2, R_f = 0.75) providing the title compound **2** (0.43 g, 82%) as a light yellow liquid, bp 75°C (1.5 mbar) or 186 °C (1 bar); ^{1}H NMR ($CDCl_3$) δ 2.42 (t, 1H, *J* = 2.4 Hz, CH), 4.67 (d, 2H, *J* = 1.2 Hz, CH_2). ^{13}C NMR ($CDCl_3$) δ 39.7, 74.7, 74.8. ^{14}N NMR ($CDCl_3$) δ -30.8 (NO_2). IR (KBr): 3290, 2995, 1532, 1439, 1421, 1373, 1284, 1176, 1091, 952, 924, 844, 765, 682, 651 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_6H_6N_2O_2Na$ $[M + Na]^+$ 161.0327, found 161.0321. Anal. calcd. for $C_6H_6N_2O_2$ (138.13): C 52.17, H 4.38, N 20.28; found C 52.25, H 4.41, N 20.15.

Ethyl ((1-((4-methylfurazan-3-yl)methyl)-1*H*-1,2,3-triazol-4-yl)methyl)(nitro)carbamate (7a).



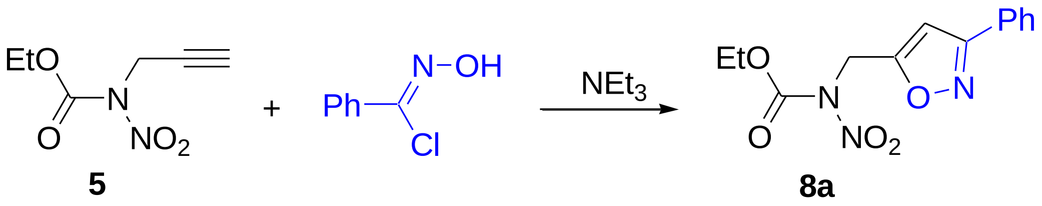
To a vigorously stirred solution of alkyne **5** (0.3 g, 1.74 mmol) and 3-azidomethyl-4-methylfurazan (0.24 g, 1.74 mmol) in DMF (5 mL) $CuSO_4{\cdot}5H_2O$ (0.02 g, 0.087 mmol) was added followed by sodium ascorbate (0.03 g, 0.174 mmol). The mixture was stirred for 24 h at room temperature and then diluted with H_2O (50 mL) and extracted using EtOAc/hexane (1:1, 5×40 mL). Combined organic layers were washed with H_2O (15 mL) and filtered through anhydrous sodium sulfate, and concentrated on a rotary evaporator to give **8a** (0.41 g, 75%) as yellow oil. ^{1}H NMR ($CDCl_3$) δ 1,25 (t, 3H, *J* = 7.1 Hz, $CH_2C\underline{H}_3$), 2.27 (s, 3H, CH_3), 4.32 (q, 2H, *J* = 10,7 Hz, $C\underline{H}_2CH_3$), 5.30 (s, 2H, CH_2NNO_2), 5.95 (s, 2H, Furazan-CH_2-Tr), 8.29 (s, 1H, CH (Triazole)). ^{13}C NMR ($CDCl_3$) δ 7.5, 13.7, 42.1, 44.4, 64.6, 124.6, 141.3, 149.8, 151.2, 151.3. ^{14}N NMR ($CDCl_3$) δ -43.9 (NO_2). Anal. calcd. for $C_{10}H_{13}N_7O_5$ (311.25): C 38.59, H 4.21, N 31.50; found C 38.50, H 4.23, N 31.40.

N,N-Bis((1-((4-methylfurazan-3-yl)methyl)-1*H*-1,2,3-triazol-4-yl)methyl)nitramine (7b)



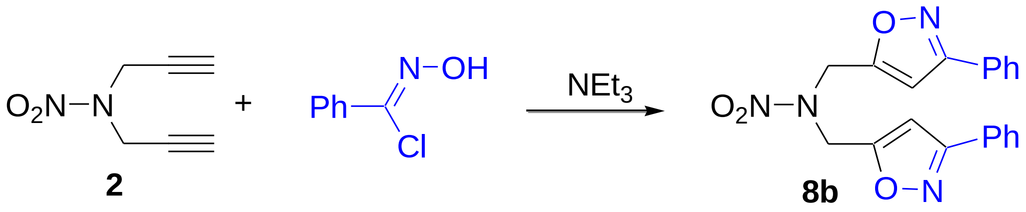
The procedure is the same as for **7a** except that 2 equiv of 3-azidomethyl-4-methylfurazan and 1 equiv of compound **2** were used. A single product was obtained with slight impurities, which were removed by passing through a silica gel column with methanol–dichloromethane (1 : 20) as the eluent to give **7b** (62%) as a white solid, mp 100-102°C; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H, CH_3), 5.13 (s, 2H, CH_2NNO_2), 5.95 (s, 2H, Furazan-CH_2), 8.27 (s, 1H, CH (Triazole)). ^{13}C NMR ($CDCl_3$) δ 7.5, 42.1, 46.5, 124.9, 141.2, 151.1, 151.3. ^{14}N NMR ($CDCl_3$) δ -30.5 (NO_2). IR (KBr): 3116, 3076, 3008, 1583, 1512, 1448, 1297, 1277, 1224, 1171, 1132, 1049, 935, 899, 848, 802, 780 cm^{-1}. Anal. calcd. for $C_{14}H_{16}N_{12}O_4$ (416.34): C 40.39, H 3.87, N 40.37; found C 40.42, H 3.93, N 40.24.

Ethyl nitro((3-phenylisoxazol-5-yl)methyl)carbamate (8a)



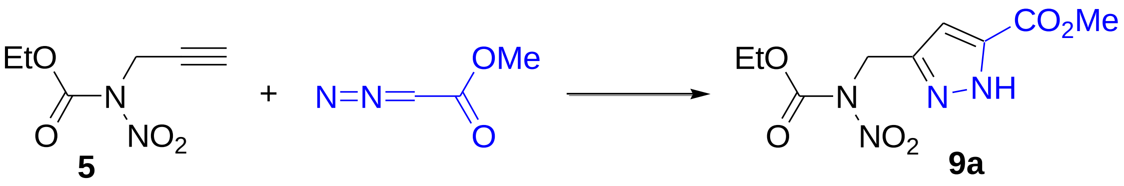
A solution of compound **5** (0.2 g, 1.16 mmol) and *N*-hydroxybenzenecarboximidoyl chloride (0.271 g, 1.74 mmol) in dichloromethane (10 mL) was cooled in an ice bath. Triethylamine (0.175 g, 1.74 mmol), dissolved in dichloromethane (15 mL), was added to the solution via syringe pump over 1 h. The reaction mixture was concentrated by rotary evaporation, and purified by flash chromatograpy (EtOAc/hexane 1:7) to afford product **9a** (0.23 g, 45% yield) as yellow oil; ^{1}H NMR ($CDCl_3$) δ 1,41 (t, 3H, *J* = 7.1 Hz, $CH_2C\underline{H}_3$), 4.45 (q, 2H, *J* = 10.7 Hz, $C\underline{H}_2CH_3$), 5.41 (s, 2H, $C\underline{H_2}$), 6.62 (s, 1H, $CH_{isoxazole}$), 7.46 (t, 3H, *J* = 3.1 Hz, CH_{Ar}), 7.78 (q, 2H, *J* = 4.6 Hz, CH (Ar)). ^{13}C NMR ($CDCl_3$) δ 14.1, 44.0, 65.6, 101.9, 126.9, 128.5, 129.0, 130.4, 149.9, 162.8, 165.7. ^{14}N NMR ($CDCl_3$) δ -47.6 (NO_2). FT−IR (KBr): 3135, 2987, 2361, 2341, 1777, 1745, 1583, 1471, 1444, 1421, 1410, 1375, 1329, 1292, 1254, 1235, 1180, 1156, 1069,998, 932 cm^{-1}. Anal. calcd. for $C_{13}H_{13}N_3O_5$ (291.26): C 53.61, H 4.50, N 14.43; found C 53.57, H 4.44, N 14.32.

N,N-Bis((3-phenylisoxazol-5-yl)methyl)nitramine (8b)



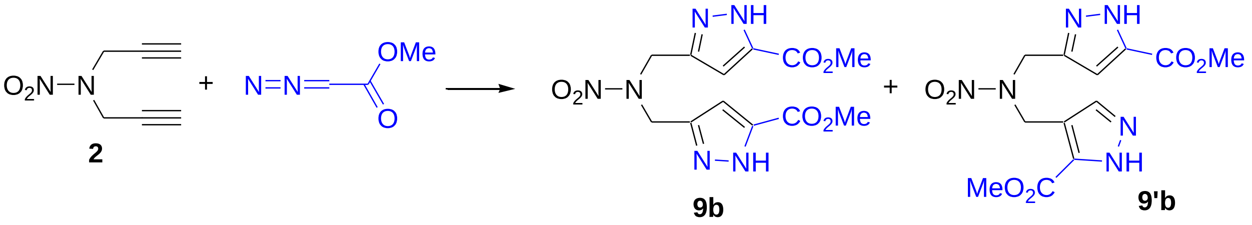
The procedure is the same as for **8a** except that 2 equiv of phenyl hydroximoyl chloride and 1 equiv of compound **2** were used. The product **8b** (69%) was obtained as a white solid, mp 148-150°C; ^{1}H NMR ($CDCl_3$) δ 5.23 (s, 2H, CH_2NNO_2), 6.71 (s, 1H, $CH_{isoxazole}$), 7.47 (s, 1H, CH_{Ar}), 7.48 (d, 2H, *J* = 1.3 Hz, CH_{Ar}), 7.81 (q, 2H, *J* = 4.7 Hz, CH_{Ar}). ^{13}C NMR ($CDCl_3$) δ 46.3, 102.9, 126.9, 128.3, 129.1, 130.5, 163.0, 164.9. ^{14}N NMR ($CDCl_3$) δ -33.6 (NO_2). IR (KBr): 3437, 3125, 1611, 1533, 1469, 1445, 1429, 1411, 1344, 1277, 1079, 992, 940, 767, 694 cm^{-1}. Anal. calcd. for $C_{20}H_{16}N_4O_4$ (376.37): C 63.83, H 4.29, N 14.89; found C 63.95, H 4.31, N 14.81.

Methyl 3-(*N*-ethoxycarbonyl-*N*-nitro)aminomethyl)-1*H*-pyrazole-5-carboxylate (9a)



Compound **5** (0.3 g, 1.74 mmol) was mixed with methyl diazoacetate (0.27 g, 2.61 mmol) in dichloroethane (5 mL) and refluxed for 36 h. The crude products were purified by flash column chromatography (EtOAc/hexane, 1:3). Product **9a** (0.37 g, 79% yield) was obtained as a white solid, mp 121-123°C. ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 3H, *J* = 7.1 Hz, $CH_2C\underline{H}_3$), 3.87 (s, 3H, CH_3), 4.49 (q, 2H, *J* = 10.7 Hz, $C\underline{H}_2CH_3$), 4.99 (s, 2H, CH_2), 6.85 (s, 1H, $CH_{pyrazole}$), 12.48 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$) δ 13.8, 41.9, 52.2, 65.1, 110.5, 143.0, 144.9, 148.8, 161.1. ^{14}N NMR ($CDCl_3$) δ -27.5 (NO_2). FT−IR (KBr): 3522, 3199, 3004, 2960, 2880, 2703, 2493, 1767, 1713, 1633, 1579, 1470, 1452, 1090, 1017, 944, 920, 866, 784, 767 cm^{-1}. Anal. calcd. for $C_9H_{12}N_4O_6$ (272.21): calcd. C 39.71, H 4.44, N 20.58; found C 39.78, H 4.47, N 20.50.

Dimethyl 3,3'-((nitroazanediyl)bis(methylene))bis(1*H*-pyrazole-5-carboxylate) (9b)



Compound **2** (0.2 g, 1.45 mmol) was mixed with methyl diazoacetate (0.37 g, 3.63 mmol) in dichloroethane (5 mL) and refluxed for 110 h (TLC analysis). After the mixture was cooled to room temperature, the white solid which separated was collected by filtration and washed with $CHCl_3$ (10 mL) to give the product as a mixture of isomers **9b** and **9'b** (0.26 g, 49%), mp 180-184°C.

For **9b**: ^{1}H NMR (DMSO-d_6) δ 3.77 (s, 3H, CH_3), 5.02 (s, 2H, CH_2NNO_2), 6.66 (d, 2H, *J* = 7.5 Hz, $CH_{pyrazole}$), 13.64 (br. s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ 46.2, 51.5, 107.2, 133.9, 143.1, 159.3. ^{14}N NMR (DMSO-d_6) δ -28.9 (NO_2). IR (KBr): 3252 (уш), 3138, 2994, 2956, 1720, 1523, 1467, 1411, 1361, 1289, 1273, 1252, 1170, 1025, 1005, 928, 911, 819, 785, 761 cm^{-1}. Anal. calcd. for $C_{14}H_{18}N_6O_6$ (366.33): C 45.90, H 4.95, N 22.94; found C 46.00, H 4.99, N 22.88.

For **9'b**: ^{1}H NMR (DMSO-d_6) δ 3.82 (s, 3H, CH_3), 5.07 (s, 2H, CH_2NNO_2), 6.76 (d, 2H, *J* = 4.4 Hz, $CH_{pyrazole}$), 14.02 (d, 1H, *J* = 11.2 Hz, NH). ^{13}C NMR (DMSO-d_6) δ 48.6, 48.8, 52.1, 108.0, 138.2, 146.7, 146.9, 162.3.

Calorimetric measurements

The main method for determining the enthalpy of formation of energetic compounds is combustion calorimetry. The measurements were performed on a precision automatic combustion calorimeter with an isothermal shell (created specifically for the combustion of energetic materials by the Laboratory of Thermodynamics of High-Energy Systems of the N. N. Semenov Federal Research Center of Chemical Physics, Russian Academy of Sciences).[S3] Basic design features of the calorimeter used in this study: 1) small heat equivalent (~500 cal·degree^{-1}) with a large volume of bomb (200 cm^3); 2) easy maintenance of the calorimeter bomb; 3) continuously thermostatted shell; 4) A liquid sealed calorimetric vessel with a jacket, permanently attached to the shell (a calorimeter with a constant volume of a thermofor delivering a constant heat equivalent); 5) low measurement error. The calorimeter measures the thermal effect of the combustion reaction of compounds with an extended error of 0.01–0.02%. Calibration of the calorimeter was carried out with the reference benzoic acid (the K-1 brand produced by the D. I. Mendeleev Institute of Metrology). The combustion energy of benzoic acid under standard conditions was 6322.6±1.2 cal·g^{-1}. The absence of a systematic error in calorimetric measurements was controlled by burning secondary reference compounds, namely, succinic and hippuric acids, whose combustion energies on this calorimeter were 3020.3±0.6 cal·g^{-1} (0.02%) and 5631.4±3.4 cal·g^{-1} (0.06%), respectively. The combustion energy of dimethyl phthalate used as an excipient under standard conditions was 5737.7±1.3 cal g^{-1}, as determined by us in a separate experiment. The test oily samples, which are a mixture of the target di(propargyl)nitramine (**2**) and the excipient, were burned in a platinum crucible. A sample of **2** and dimethyl phthalate (the excipient) were weighed on Bunge microanalytic scales with an error of 2×10^{-6} g. The weighed sample was placed in a calorimetric bomb and filled with oxygen. The initial oxygen pressure during combustion of each sample was about 30 atm (3 MPa). Before the experiment, 1 mL of distilled water was injected into the bomb to create a saturated vapor pressure and dissolve the nitrogen oxides formed during combustion.

The samples were ignited with a cotton thread, which in turn was ignited by incandescent platinum wire (diameter 0.3 mm) with a dosed pulse of current supplied from a special device. The combustion energy of dimethyl phthalate under standard conditions was 5737.7±1.3 cal·g^{-1}. The combustion energy of cotton yarn was measured in a series of seven experiments and amounted to 3968.9 ±1.6 cal·g^{-1}. When determining the combustion energy, corrections for the thermal effects of nitric acid formation, for the heat exchange of a calorimetric vessel with an isothermal shell, as well as for the combustion energy of the auxiliary compound and cotton thread were taken into account. A detailed procedure for preparing samples and conducting an incineration experiment was described earlier.[S4]

For thermochemical experiments several samples of compound **2** have been obtained and purified by different methods. The purity of the samples was at least 99.5% (HPLC).

The combustion energy ($-\Delta U'_{\mathrm{B}}$, cal·g^{-1}) under calorimetric bomb conditions for the compound **2** is given in Table S2.

Table S2. Determination of the combustion energy of **di(propargyl)nitramine** (**2**).

N	m, g	ΔT, °C	Q, cal	q_a, cal	q_i, cal	q_N, cal	q_{cot}, cal	$-\Delta U'_B$, cal·g^{-1}
1	0.073238	2.56826	1380.67	906.64	7.24	1.10	8.67	6240.2
2	0.070562	2.31812	1246.20	788.52	7.20	1.05	8.78	6244.6
3	0.070811	2.30317	1238.16	779.25	7.26	1.05	8.59	6242.1
4	0.071268	2.26812	1219.32	757.58	7.28	1.05	8.79	6238.7
5	0.075012	2.38637	1282.89	797.68	7.24	1.13	8.51	6243.4
$-\Delta U'_B = 6241.8 \pm 2.7$ cal·g^{-1}								

N – the ordinal number of the experiment;
m – weight of the sample in vacuum, g;
ΔT – the corrected temperature rise for the calorimeter, degrees;
Q – the amount of heat measured in the experiment, cal;
q_a – heat of the combustion of the auxiliary compound - dimethyl phthalate, cal;
q_i – ignition energy, cal;
q_N – correction for the formation of nitric acid, cal;
q_{cot} – a heat generation from combustion of the cotton thread, cal;
$\Delta U'_B$ – combustion energy of a compound in the bomb, cal·g^{-1}.

Reaction of combustion of compound **2** proceeds in accordance with the stoichiometry presented by equation (I):

$$C_6H_6N_2O_{2(l)} + 6.5O_{2(g)} = 6CO_{2(g)} + 3H_2O_{(l)} + N_{2(g)} \qquad \text{(I)},$$

where the subscripts *g* and *l* correspond to the gaseous and liquid states, respectively, in this and subsequent equations.

The enthalpy of formation of compound **2** for the standard state was calculated from the corresponding enthalpy of combustion in accordance with the stoichiometry of the reaction (I):

$$\Delta H^\circ_f[C_6H_6N_2O_2]_{(l)} = 6\Delta H^\circ_f[CO_2]_{(g)} + 3\,\Delta H^\circ_f[H_2O]_{(l)} - \Delta H^\circ_c \qquad \text{(II)},$$

where ΔH°_c – the standard enthalpy of combustion of the compound **2**, kcal·mol^{-1}, and ΔH°_f – the standard enthalpy of its formation, kcal·mol^{-1}.

$$\Delta H^\circ_c = -861.3 \pm 0.4 \text{ kcal·mol}^{-1}$$

$$\Delta H^{\circ}_{\mathrm{f}}\ [\mathrm{C_6H_6N_2O_2}]_{(l)} = \mathbf{92.0 \pm 0.4}\ \mathrm{kcal{\cdot}mol^{-1}}$$

When calculating the standard enthalpy of formation of the studied compound **2**, the reference values of the enthalpies of formation of combustion products were used[S5]:

$$\Delta H^{\circ}_{\mathrm{f}}[\mathrm{CO_2}]_{(\mathrm{g})} = -94.051 \pm 0.031\ \mathrm{kcal{\cdot}mol^{-1}}$$

$$\Delta H^{\circ}_{\mathrm{f}}[\mathrm{H_2O}]_{(\mathrm{l})} = -68.315 \pm 0.009\ \mathrm{kcal{\cdot}mol^{-1}}$$

References

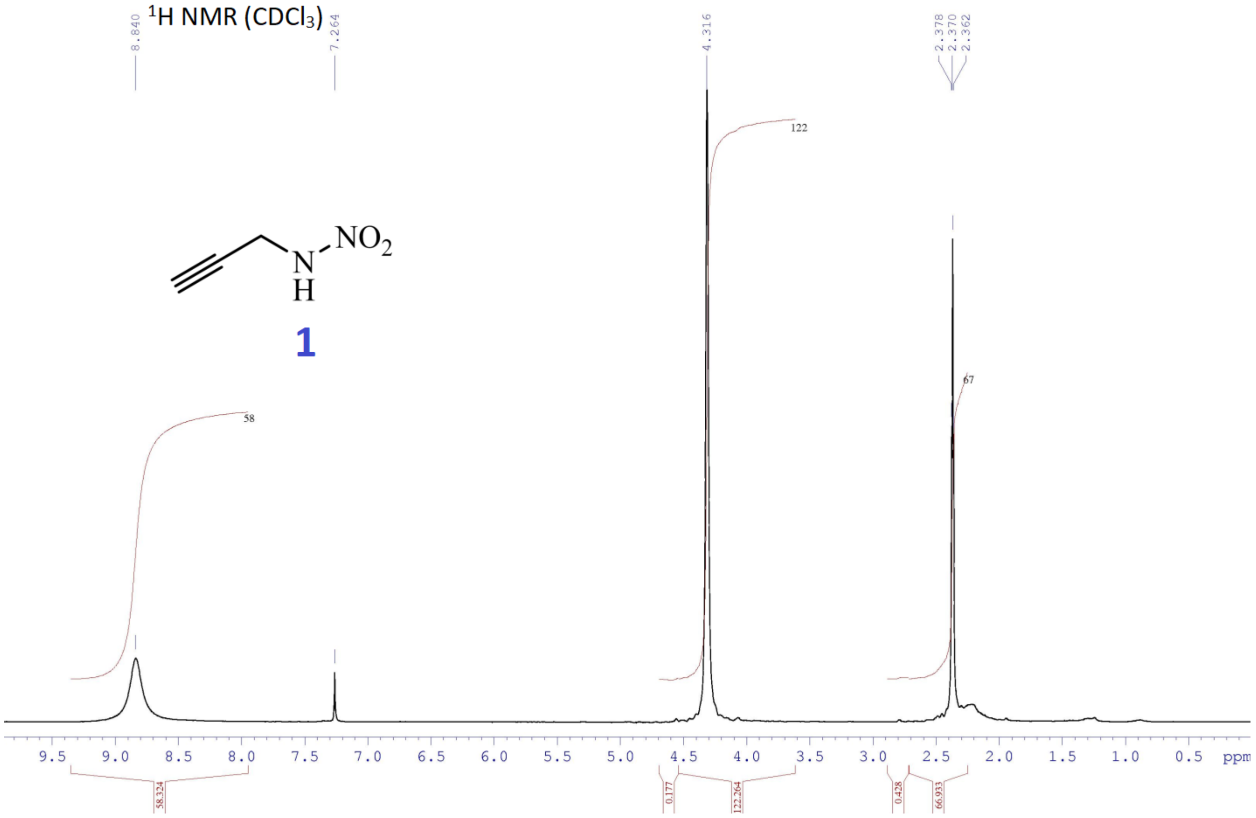
S1. O. A. Luk’yanov, I. K. Kozlova, O. P. Shitov, Yu. V. Konnova, I. V. Kalinina and V. A. Tartakovsky, *Russ. Chem. Bull.*, 1996, **45**, 863 (*Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 908).

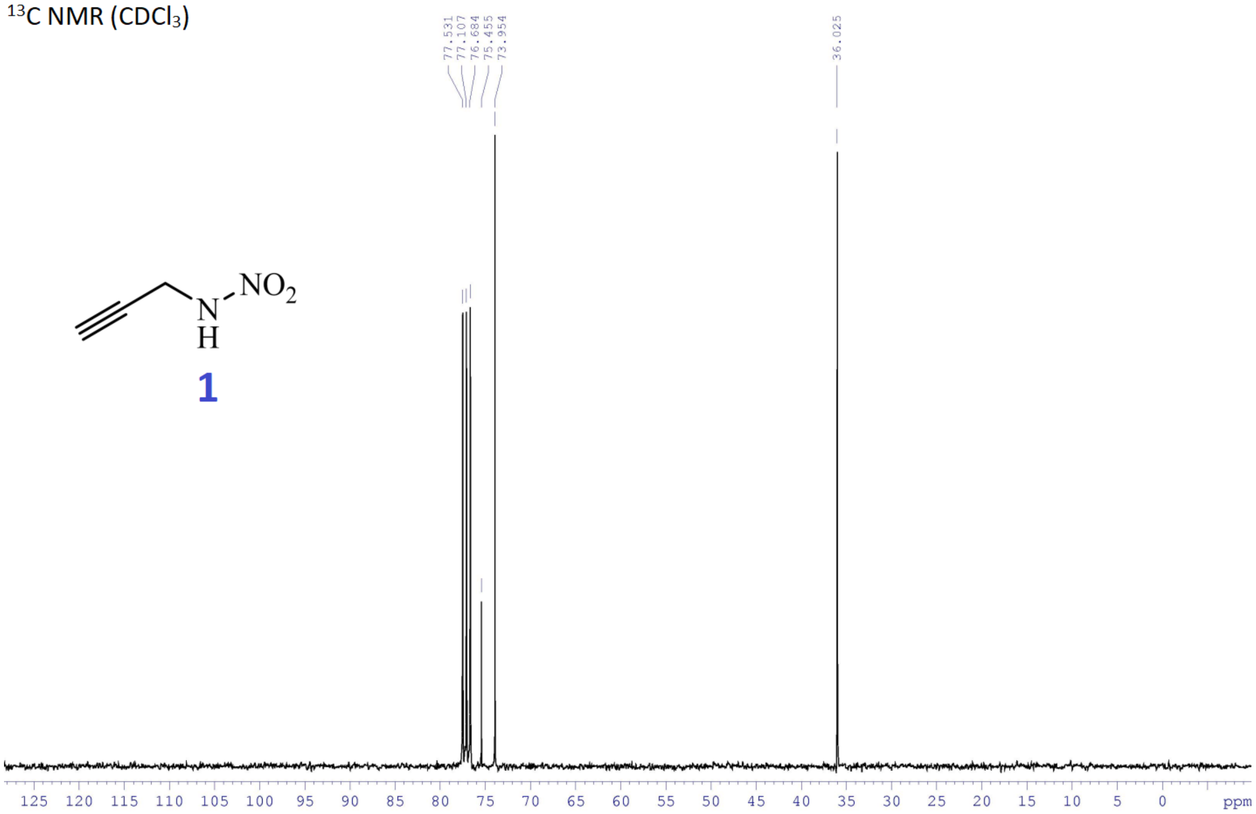
S2. R. Srinivasan, M. Uttamchandani and S. Q. Yao, *Org. Lett.*, 2006, **8**, 713.

S3. Ya. O. Inozemtsev, A. B. Vorob’ev, A. V. Inozemtcev and Yu. N. Matyushin, *Gorenie i* V*zryv* (*Combustion and Explosion*), 2014, **7** (3), 260 (in Russian).

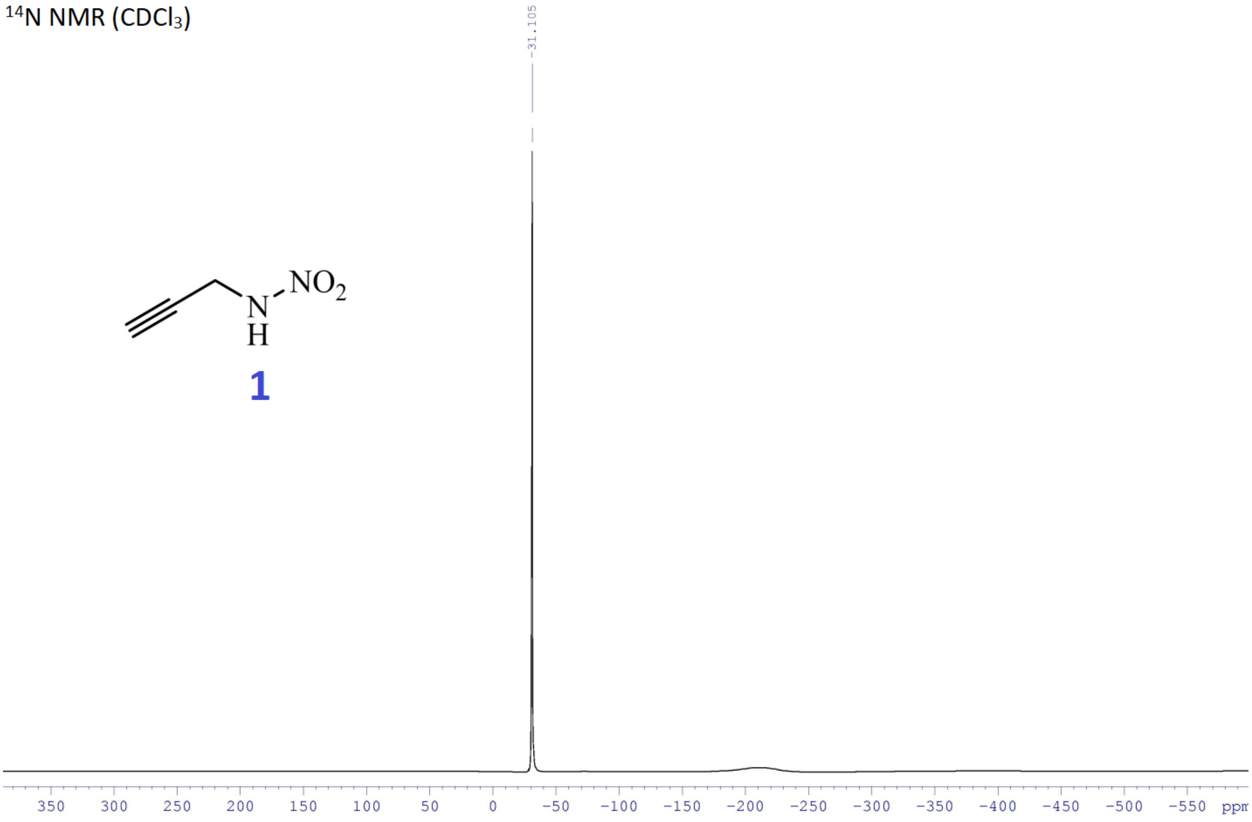
S4. T. S. Kon’kova, E. A. Miroshnichenko, Yu. N. Matyushin, A. B. Vorob’ev, Ya. O. Inozemtsev, I. L. Dalinger, T. K. Shkineva and S. A. Shevelev, *Gorenie i Vzryv,* (*Combustion and Explosion*), 2015, **8** (2), 175 (in Russian).

S5. CODATA Key Values for Thermodynamics, eds. J. D. Cox, D. D. Wagman and V. A. Medvedev, Hemisphere Publishing Corp., New York, 1989.

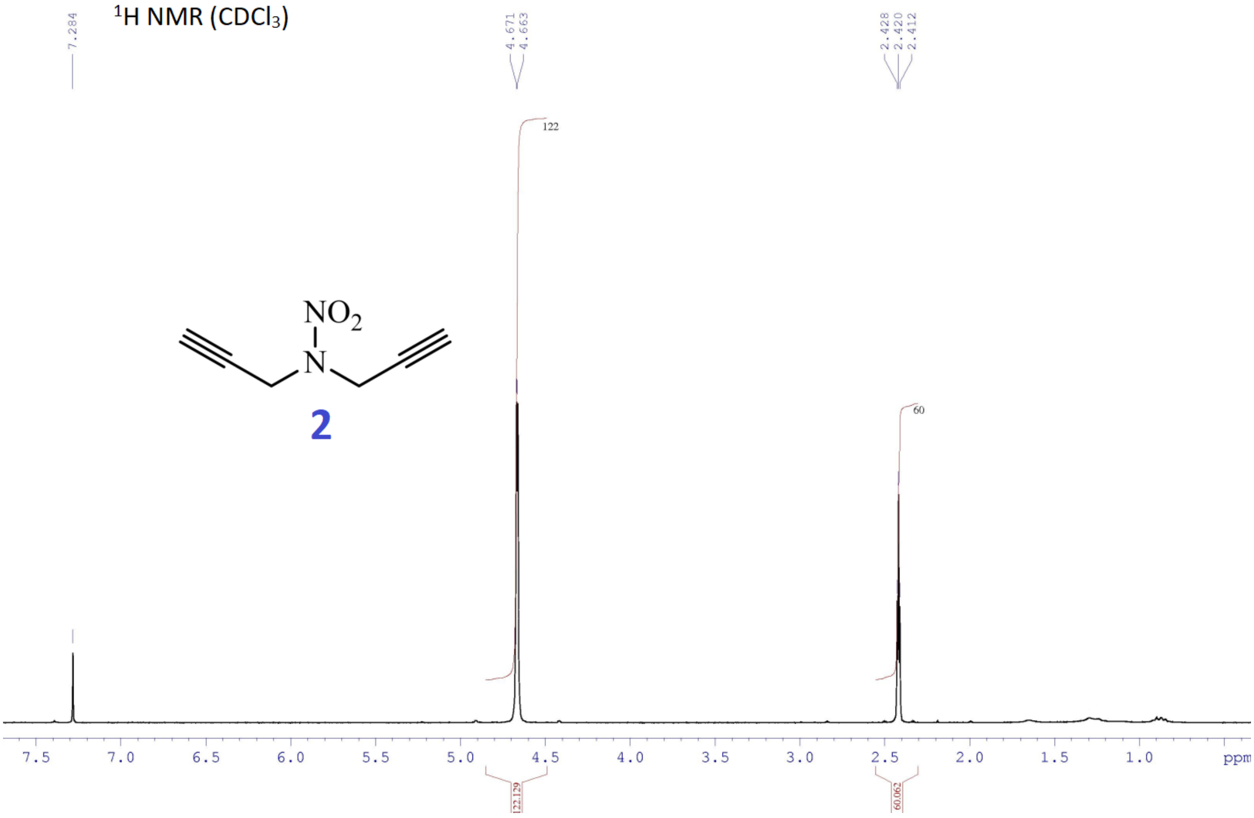

^1H NMR ($CDCl_3$)
8.840
7.264
4.316
2.378
2.370
2.362
122
67
58
NO$_2$
N
H
1
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
58.324
0.177
122.264
0.428
66.933


^{13}C NMR ($CDCl_3$)
77.531
77.107
76.684
75.455
73.954
36.025
NO$_2$
N
H
1
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm

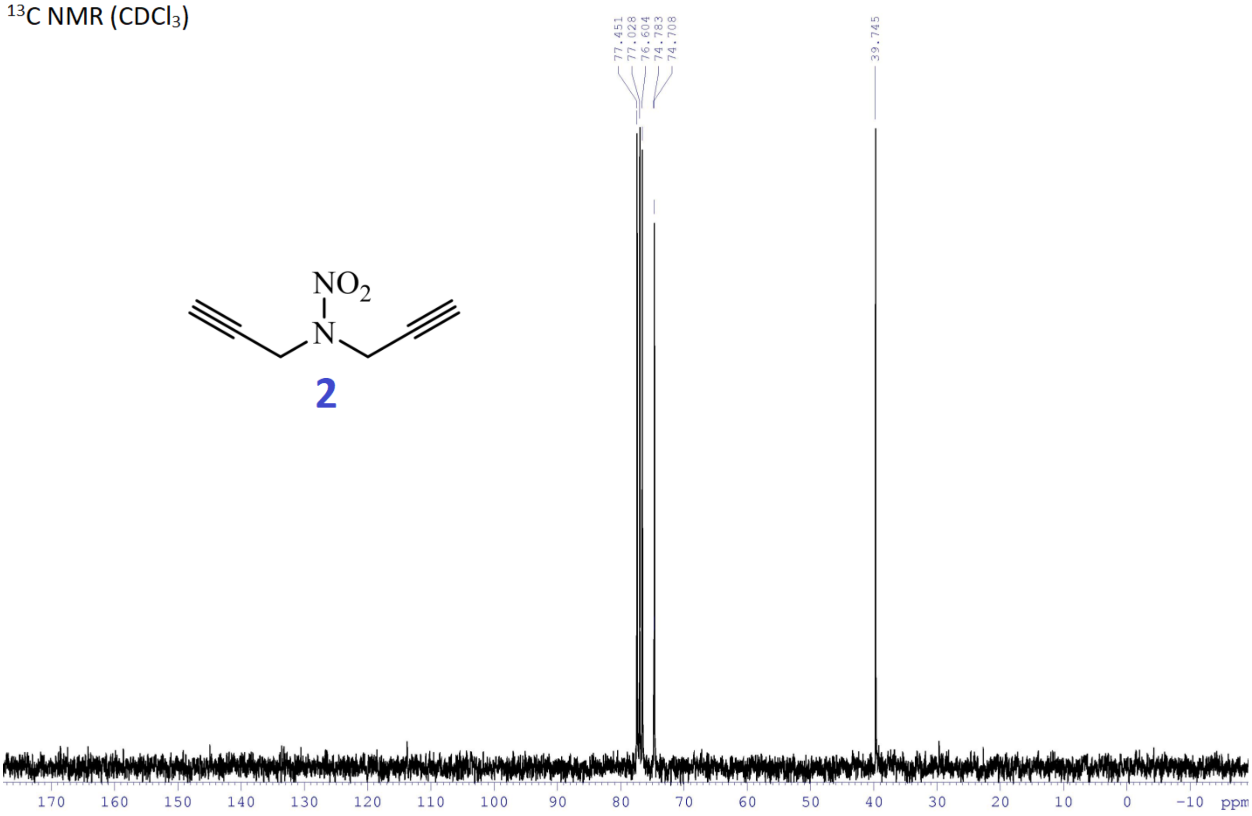
^{14}N NMR (CDCl$_3$)



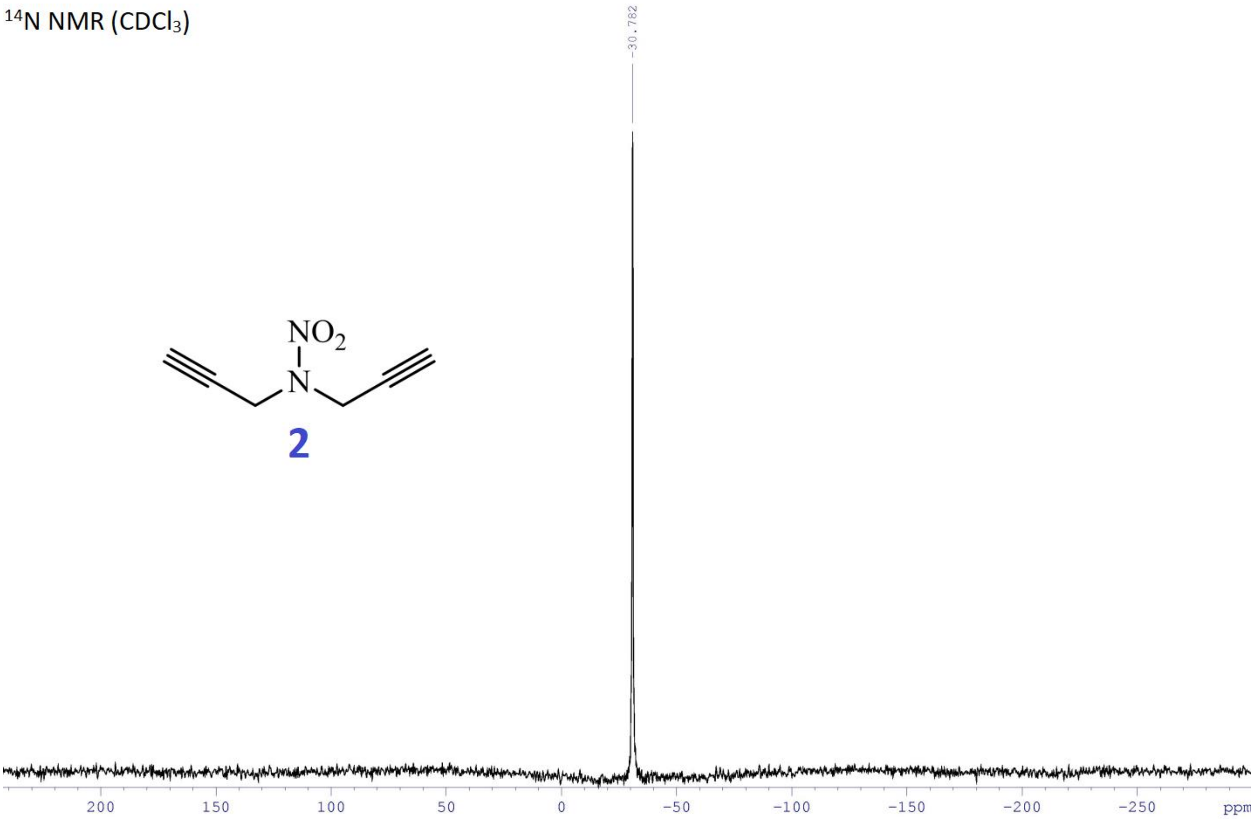
^{1}H NMR (CDCl$_3$)



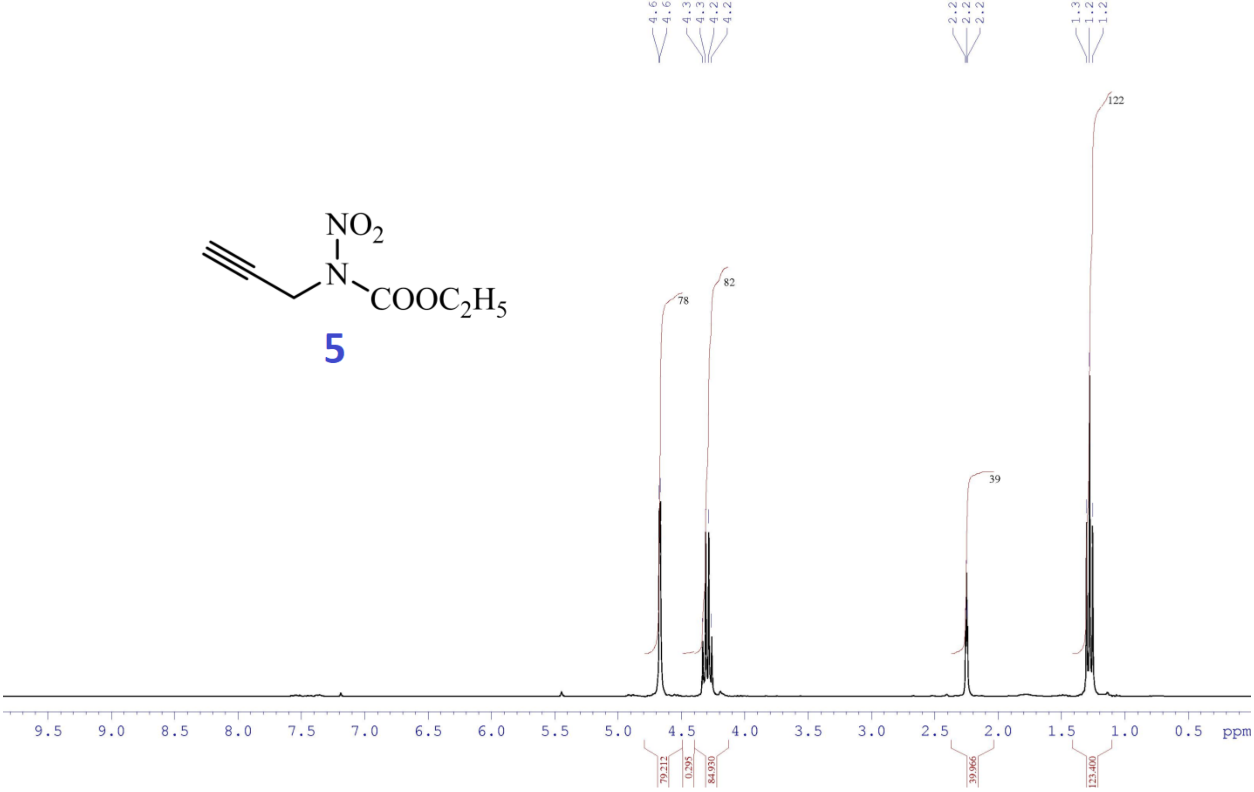
^{13}C NMR (CDCl$_3$)



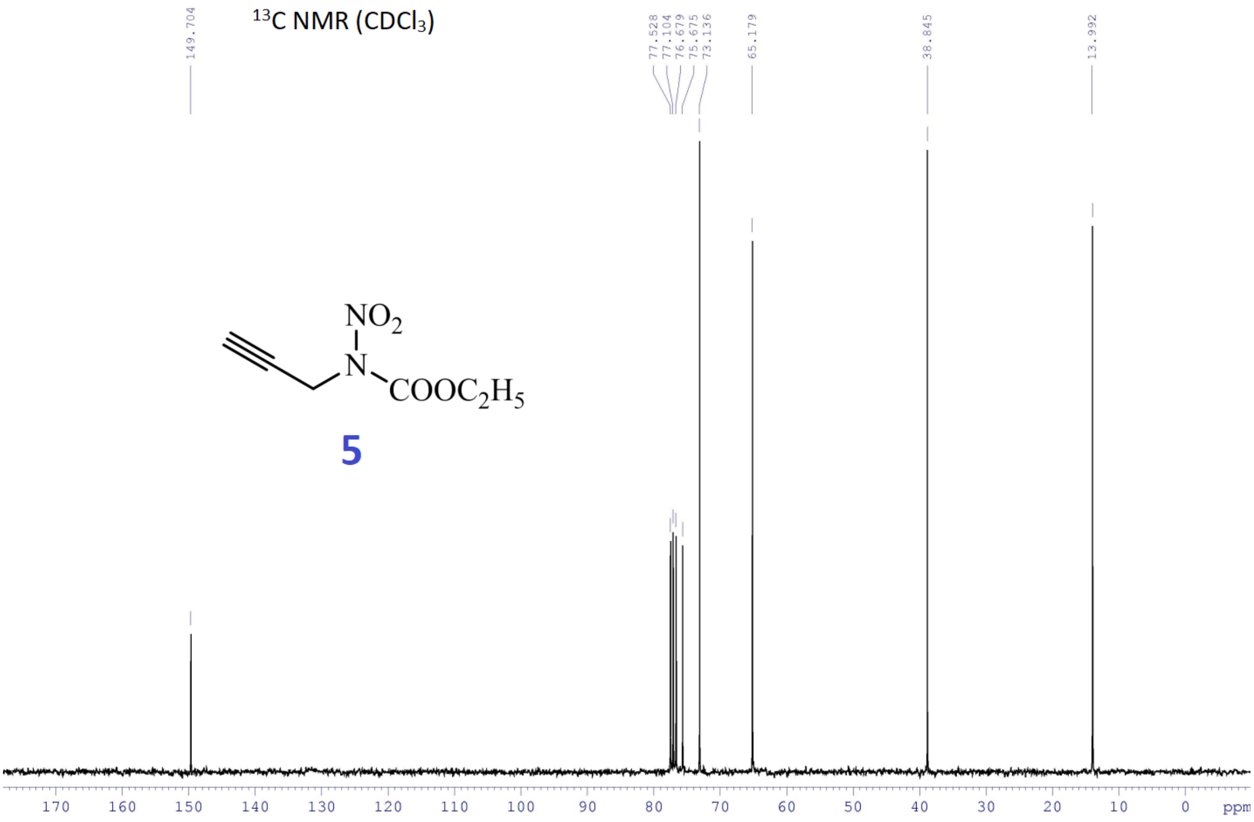
^{14}N NMR (CDCl$_3$)



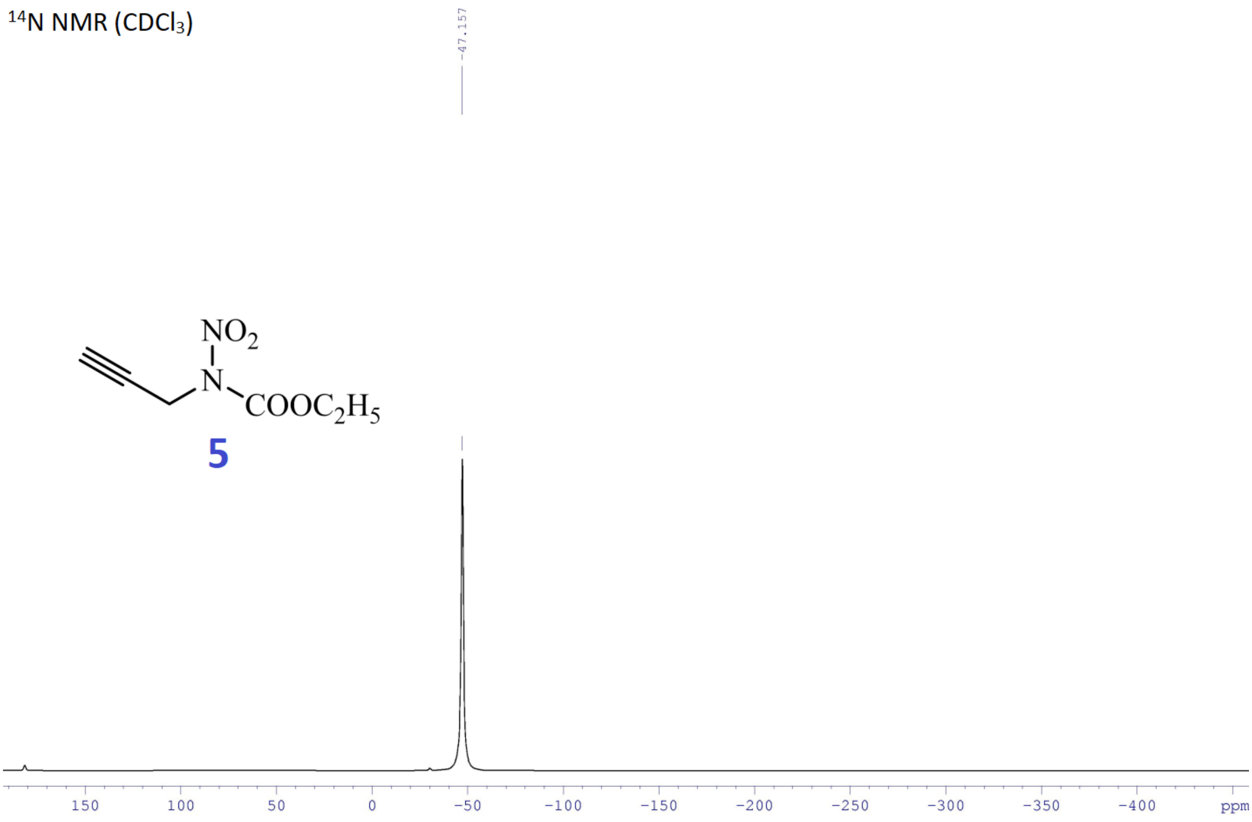
^{1}H NMR (CDCl$_3$)



^{13}C NMR (CDCl$_3$)

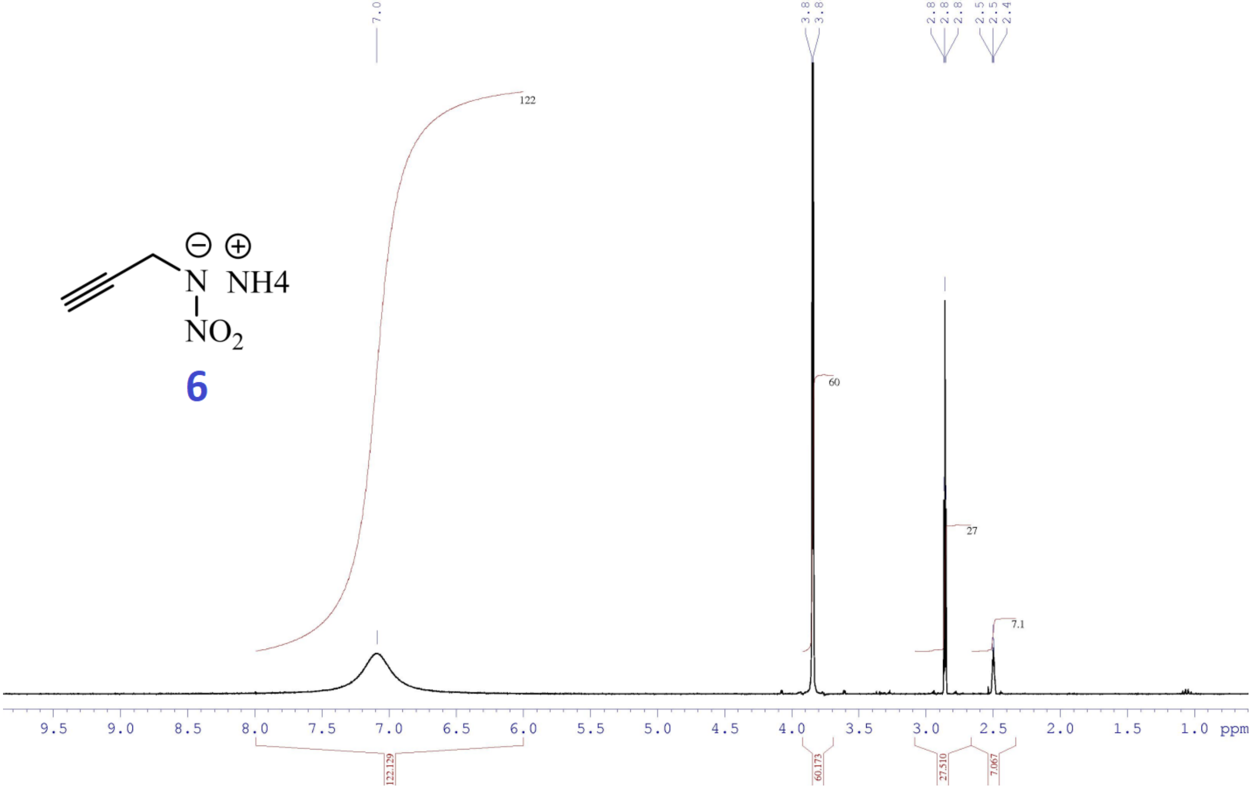


^{14}N NMR (CDCl$_3$)



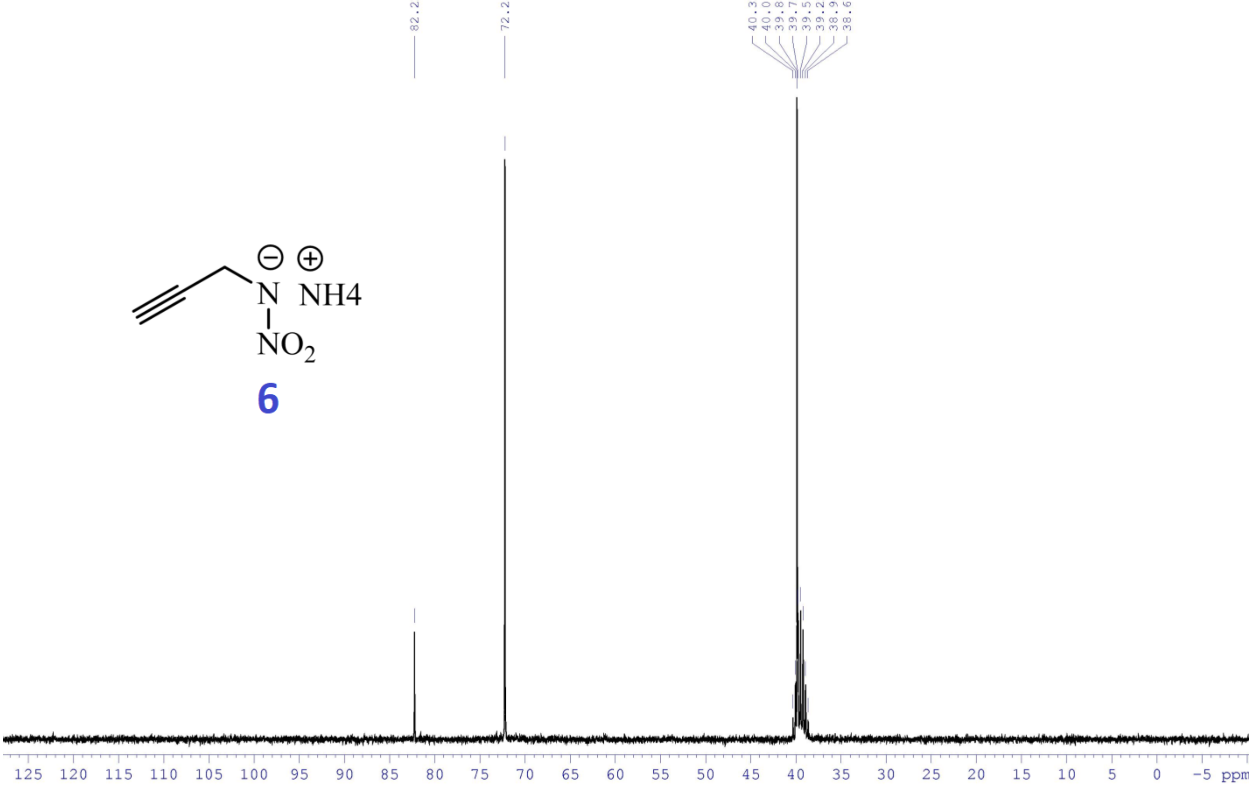
5

^{1}H NMR (DMSO-d6)



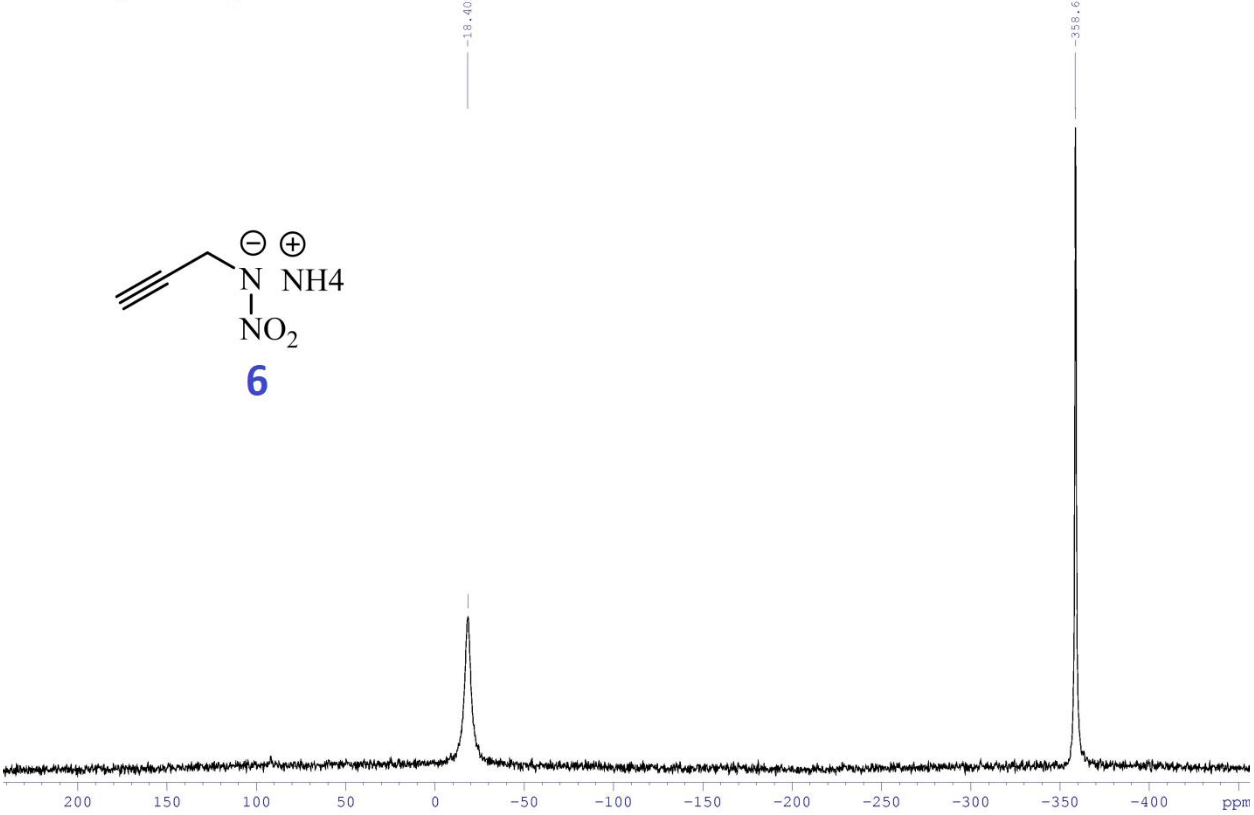
6

^{13}C NMR (DMSO-d6)

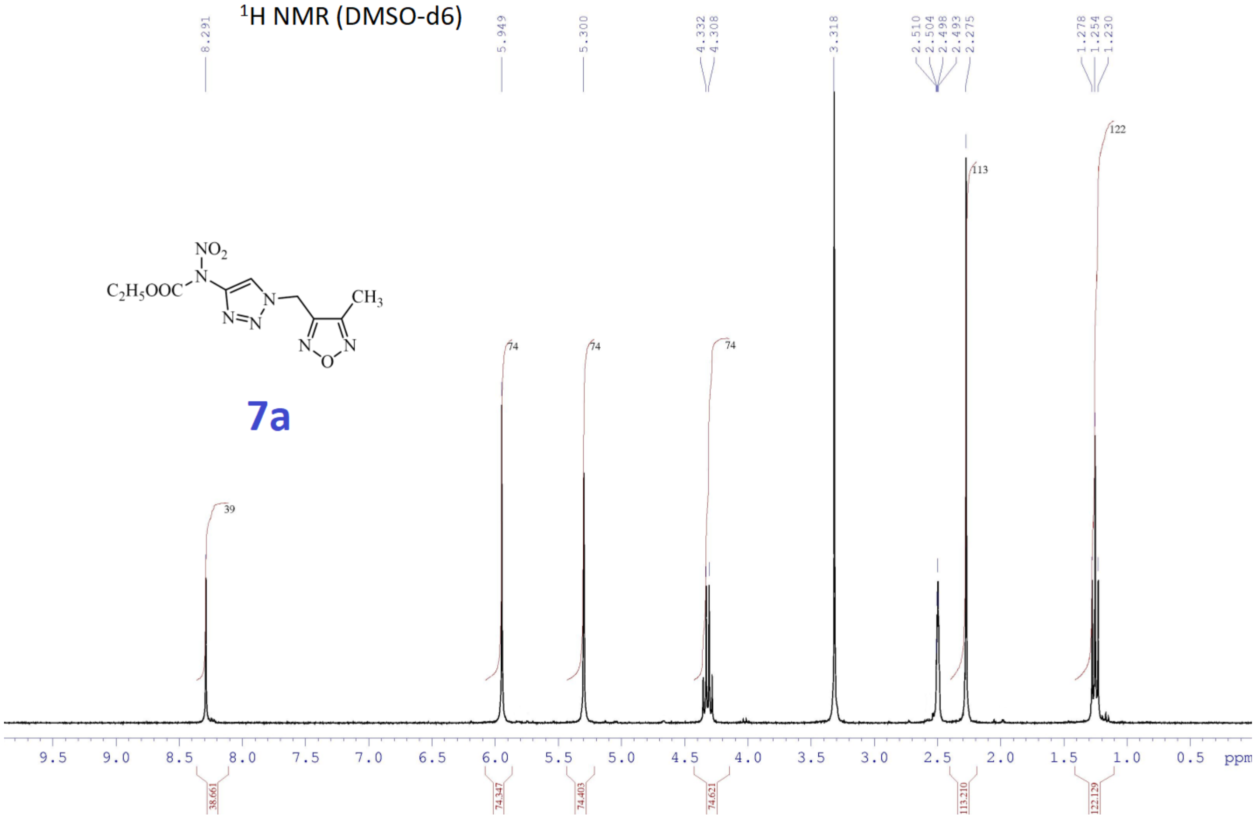


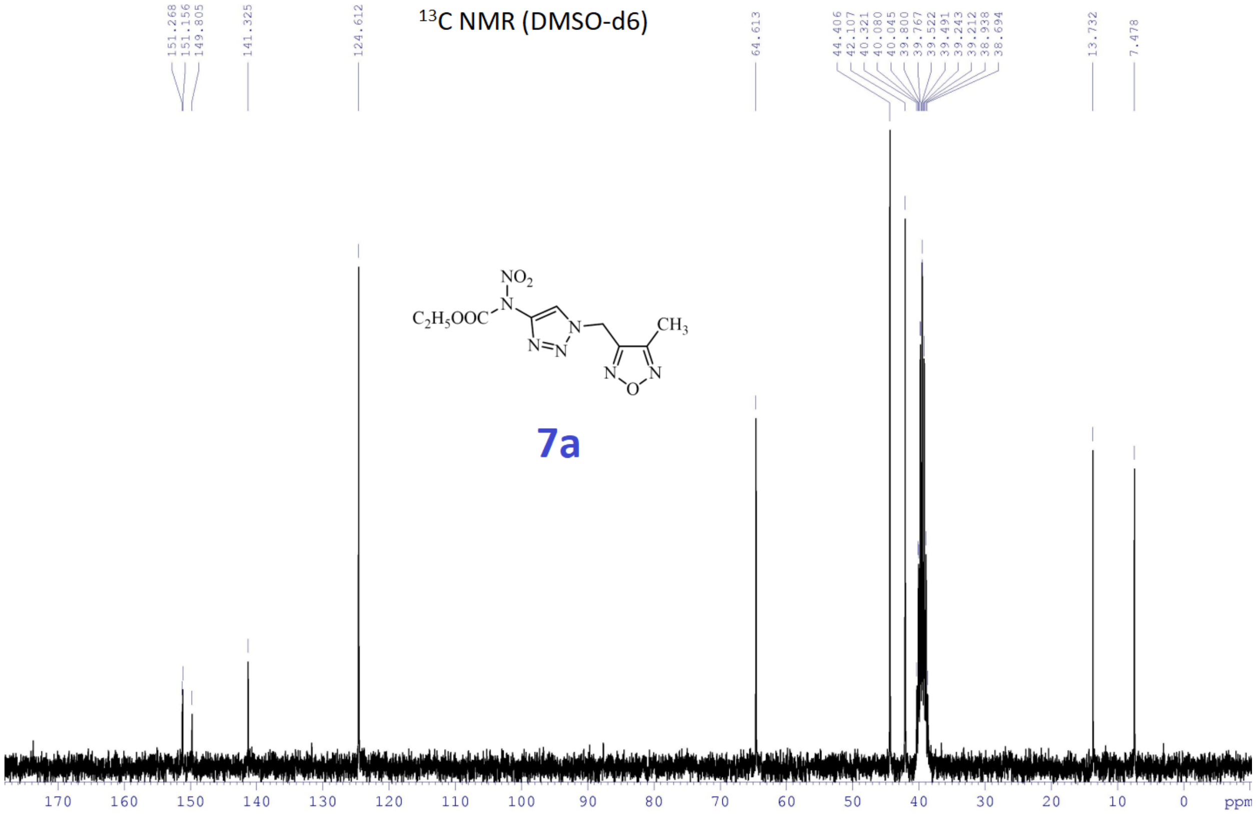
6

^{14}N NMR (DMSO-d6)

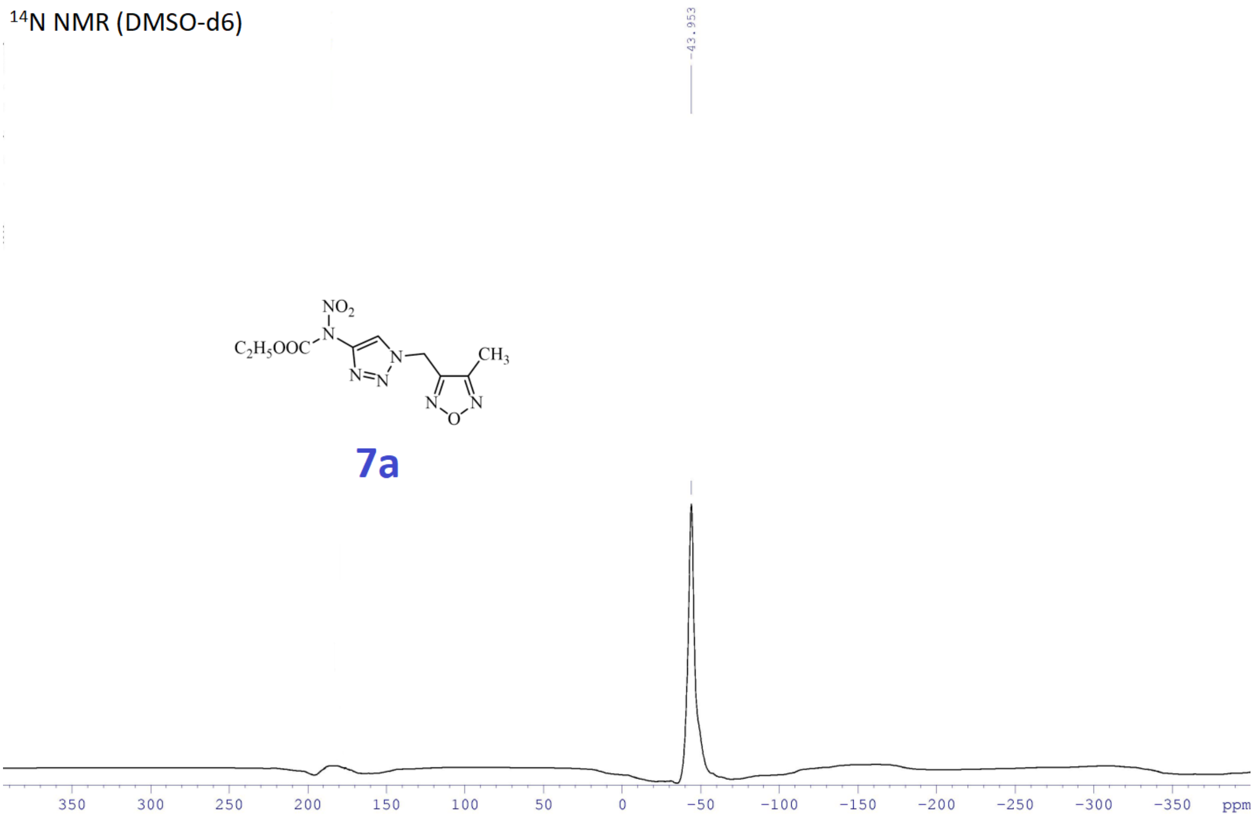


6

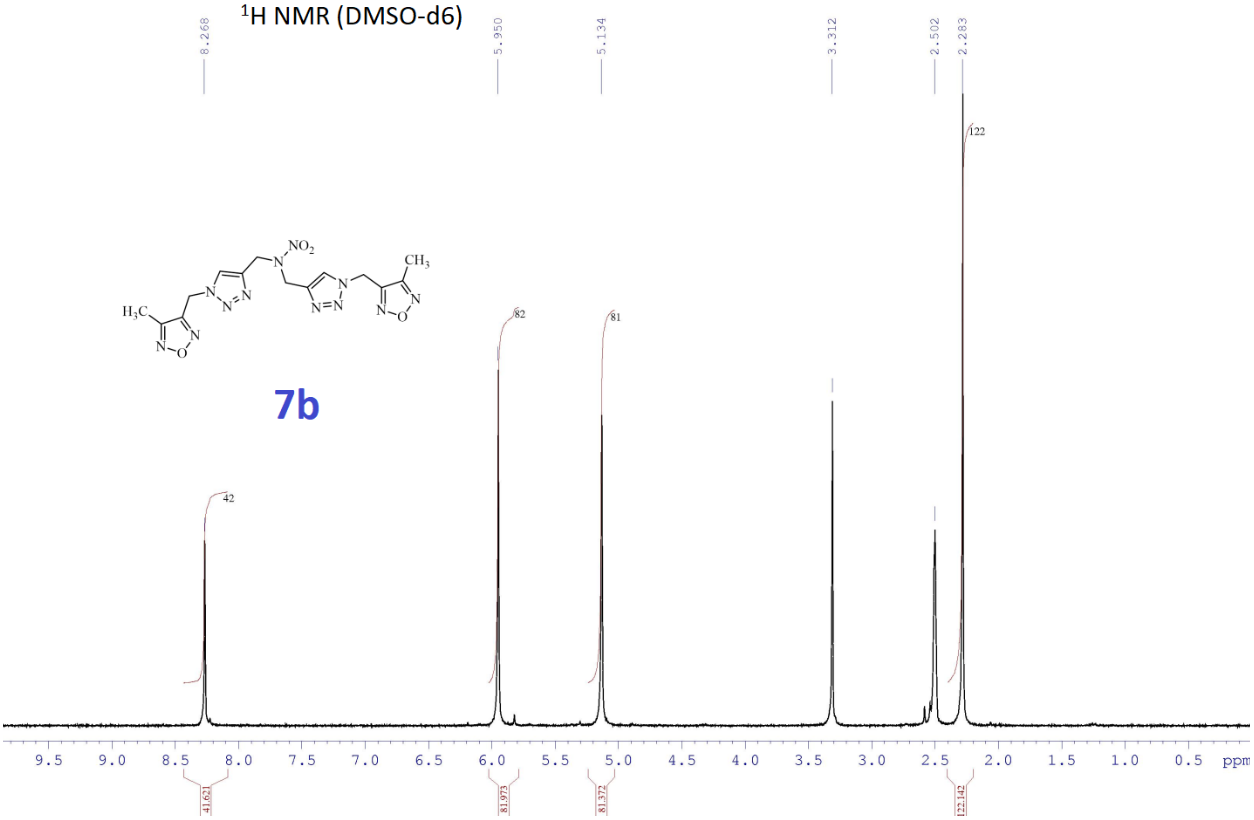

^{1}H NMR (DMSO-d6)
8.291
5.949
5.300
4.332
4.308
3.318
2.510
2.504
2.498
2.493
2.275
1.278
1.254
1.230
39
74
74
74
113
122
NO$_2$
N
C$_2$H$_5$OOC
N
N
N
CH$_3$
N
O
N
7a
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
38.661
74.347
74.403
74.621
113.210
122.129


^{13}C NMR (DMSO-d6)
151.268
151.156
149.805
141.325
124.612
64.613
44.406
42.107
40.321
40.080
40.045
39.800
39.767
39.522
39.491
39.243
39.212
38.938
38.694
13.732
7.478
NO$_2$
N
C$_2$H$_5$OOC
N
N
N
CH$_3$
N
O
N
7a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

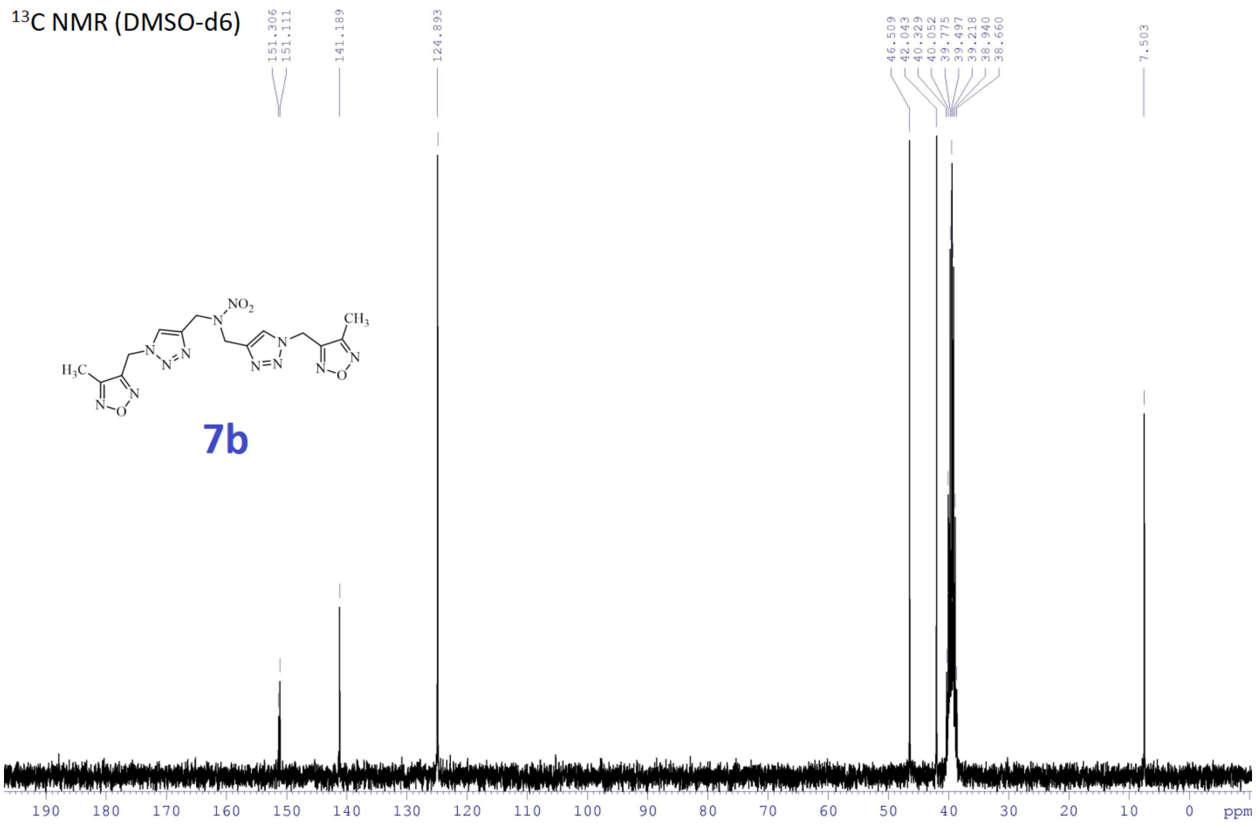
^{14}N NMR (DMSO-d6)



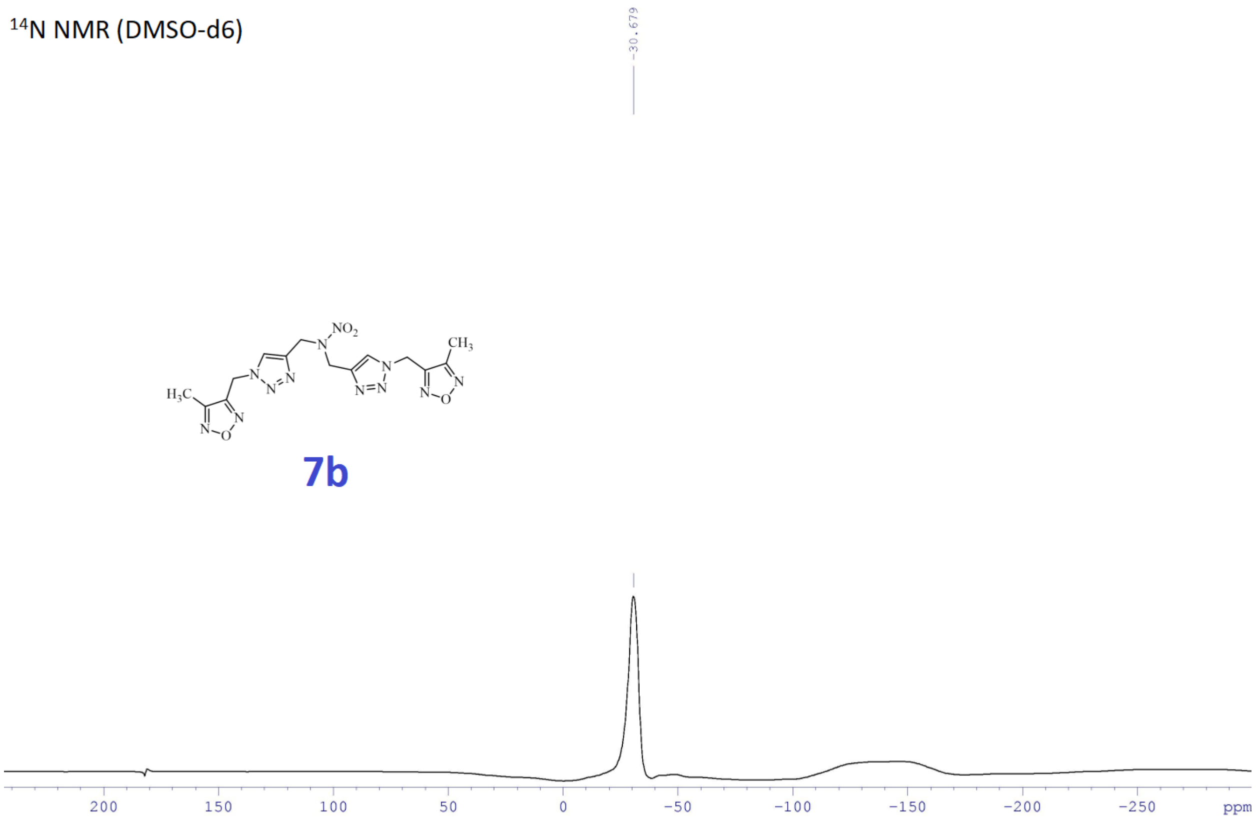
^{1}H NMR (DMSO-d6)

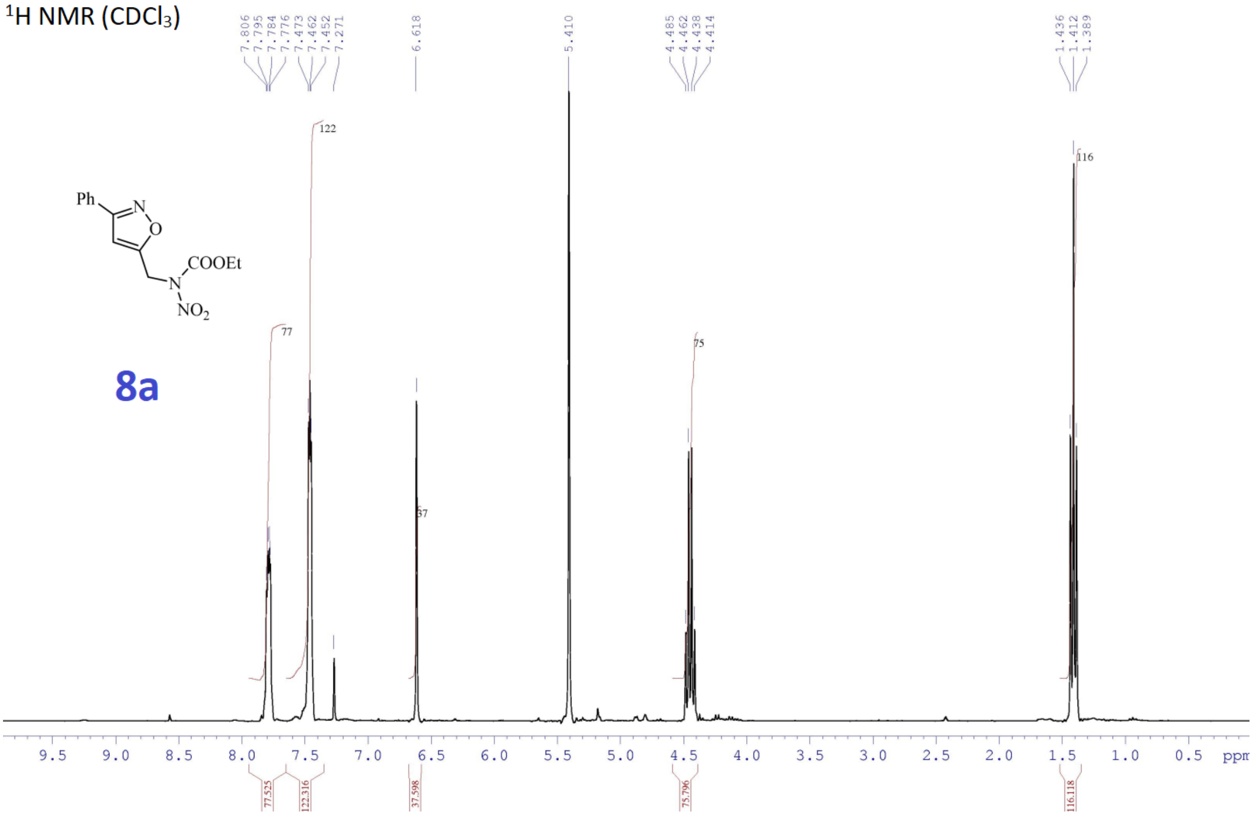


^{13}C NMR (DMSO-d6)



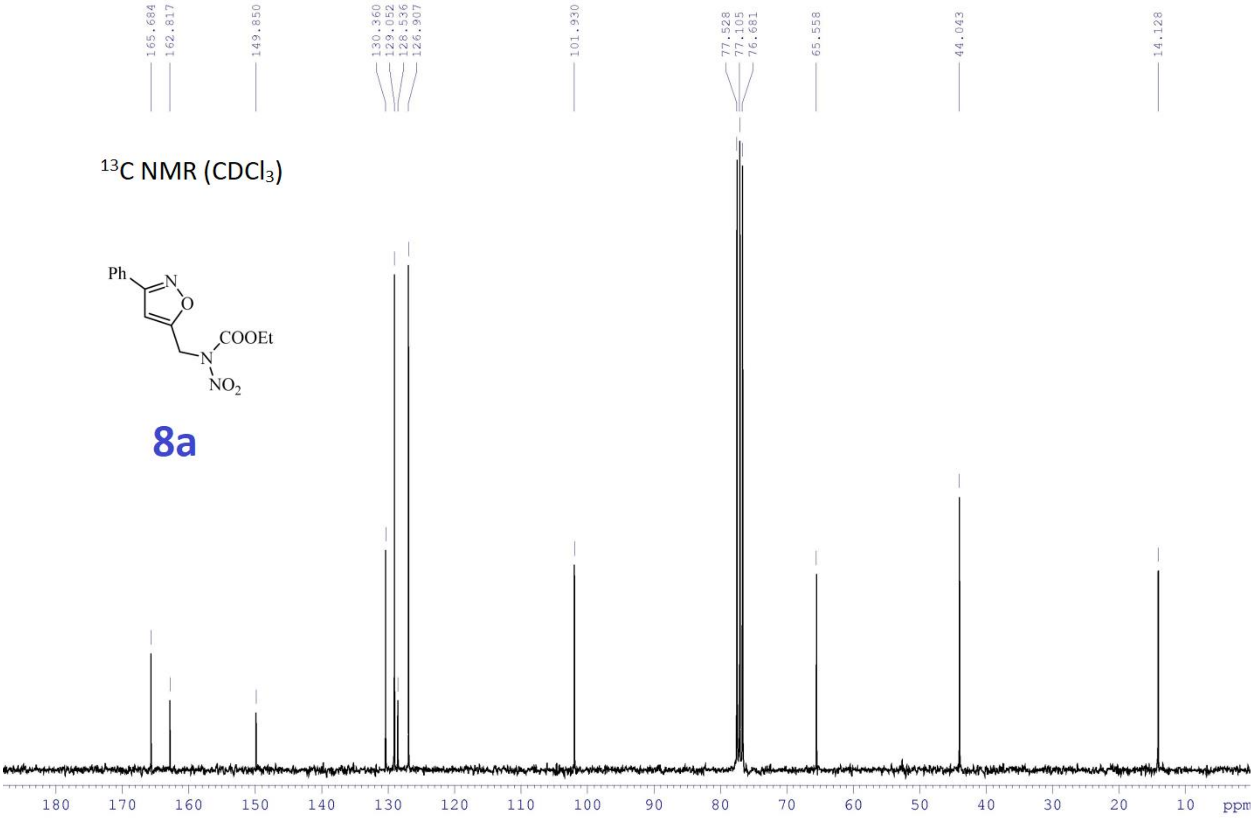
^{14}N NMR (DMSO-d6)





^{1}H NMR ($CDCl_3$)

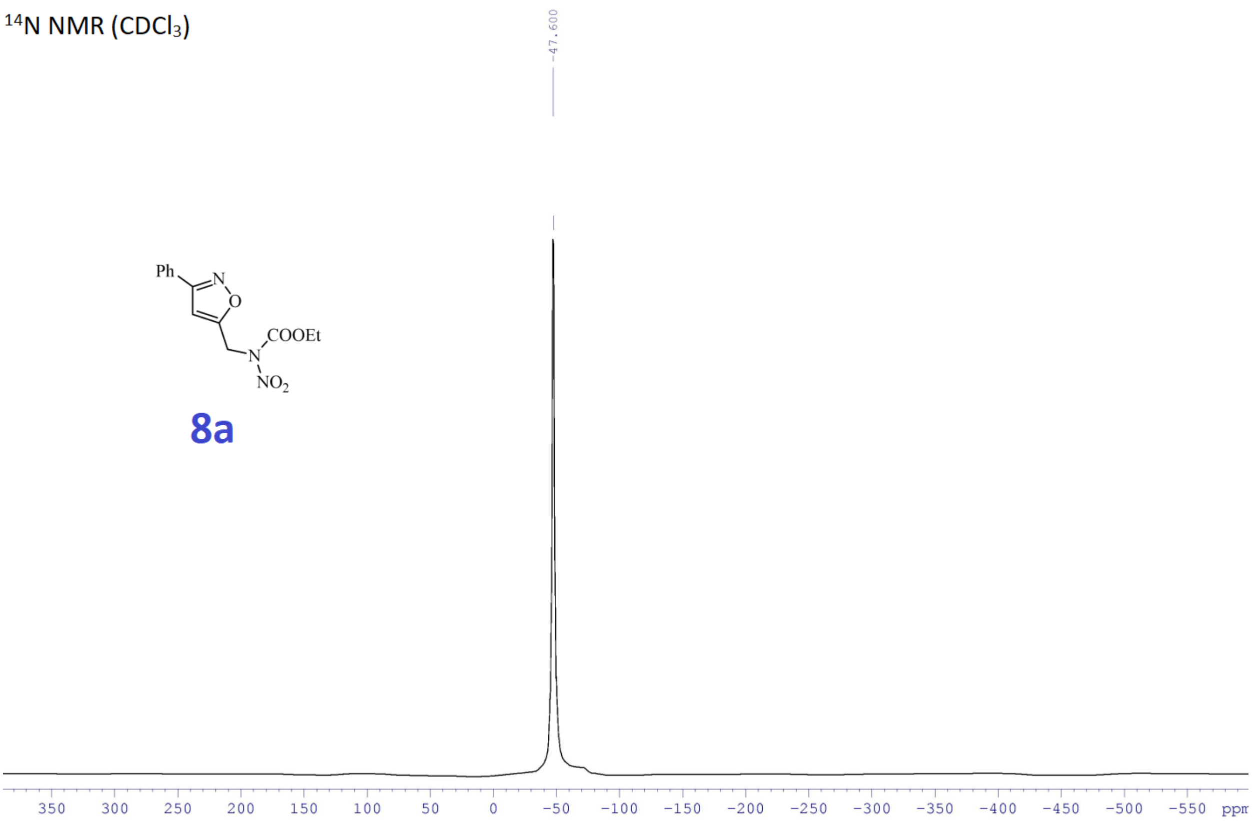
8a



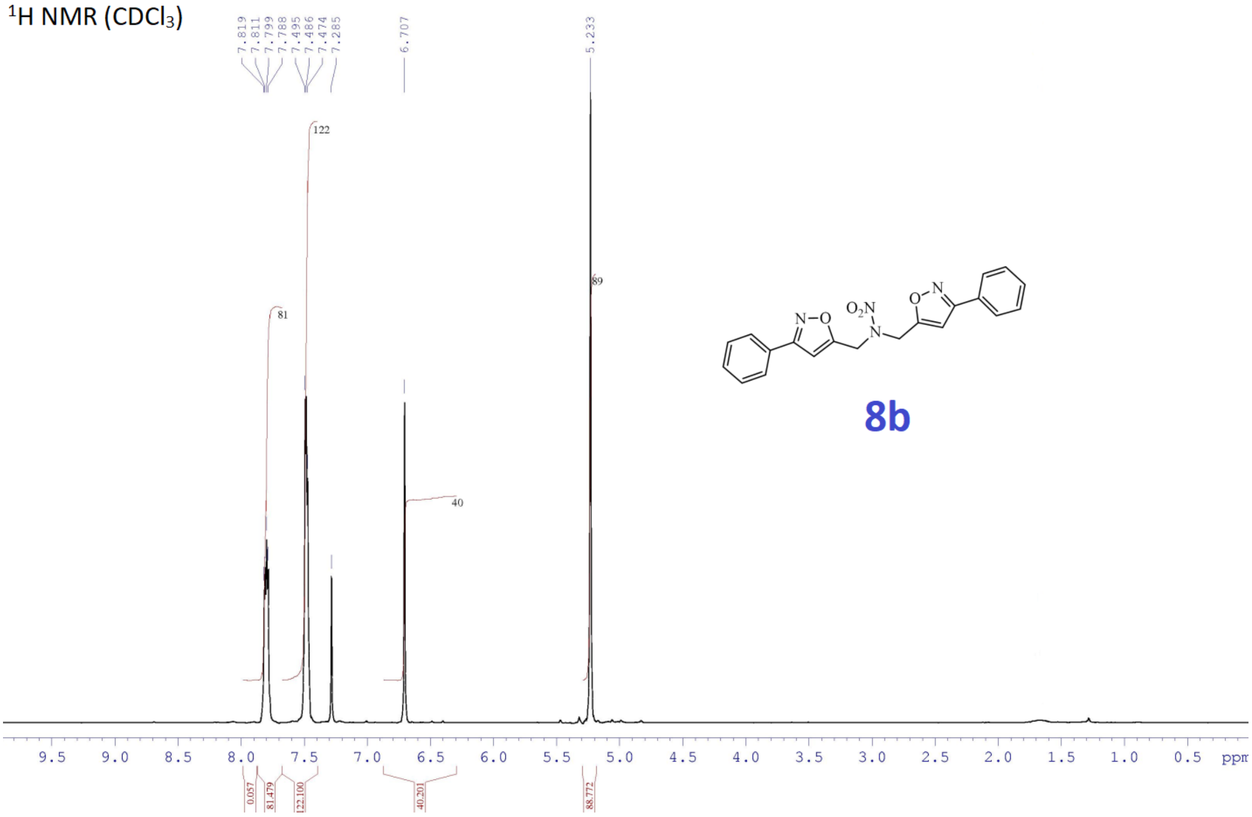
^{13}C NMR ($CDCl_3$)

8a

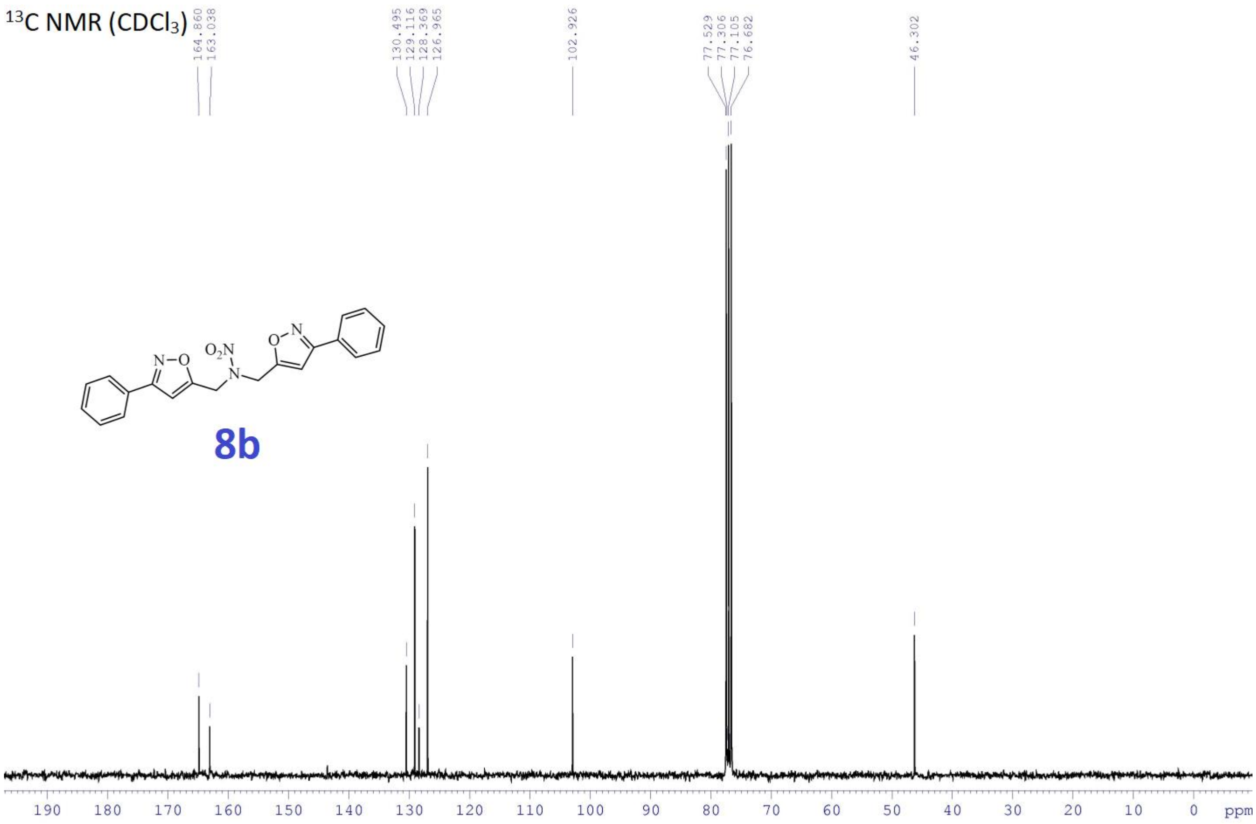
^{14}N NMR ($CDCl_3$)



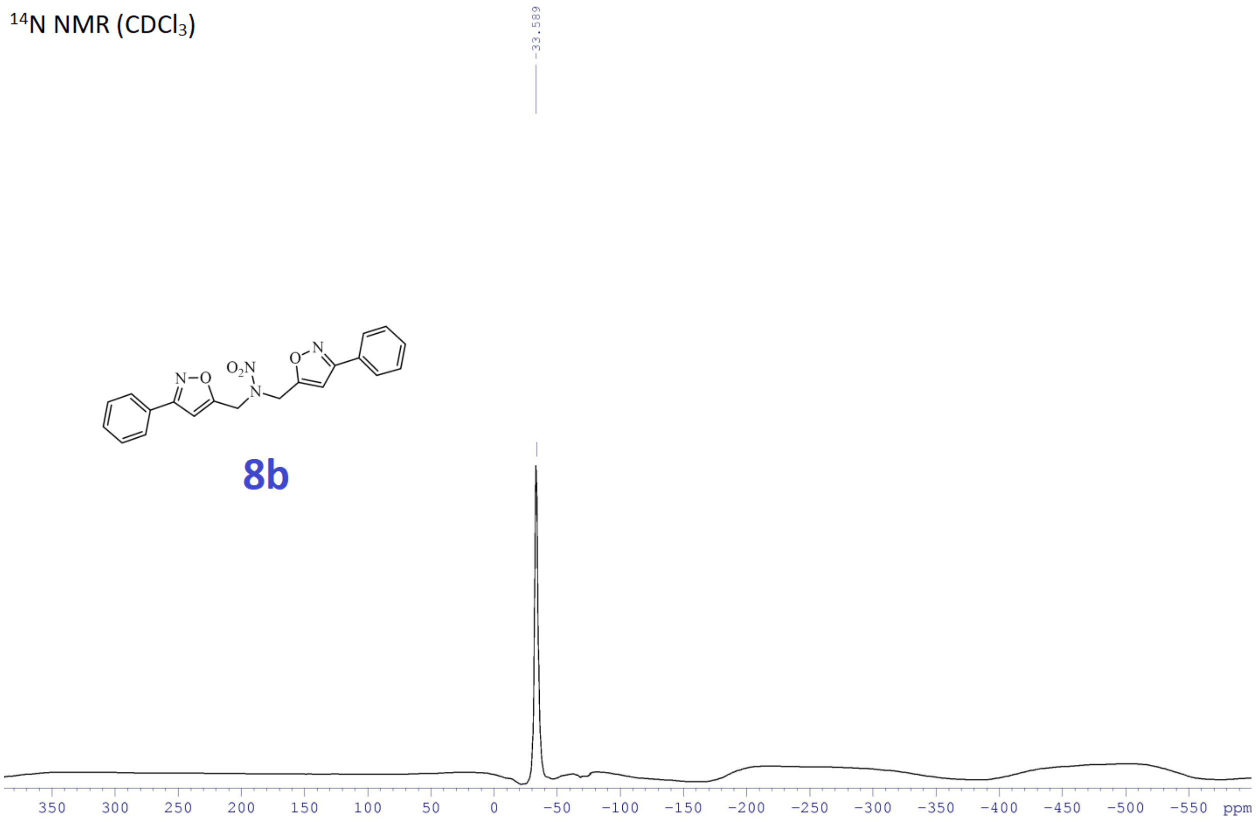
^{1}H NMR ($CDCl_3$)



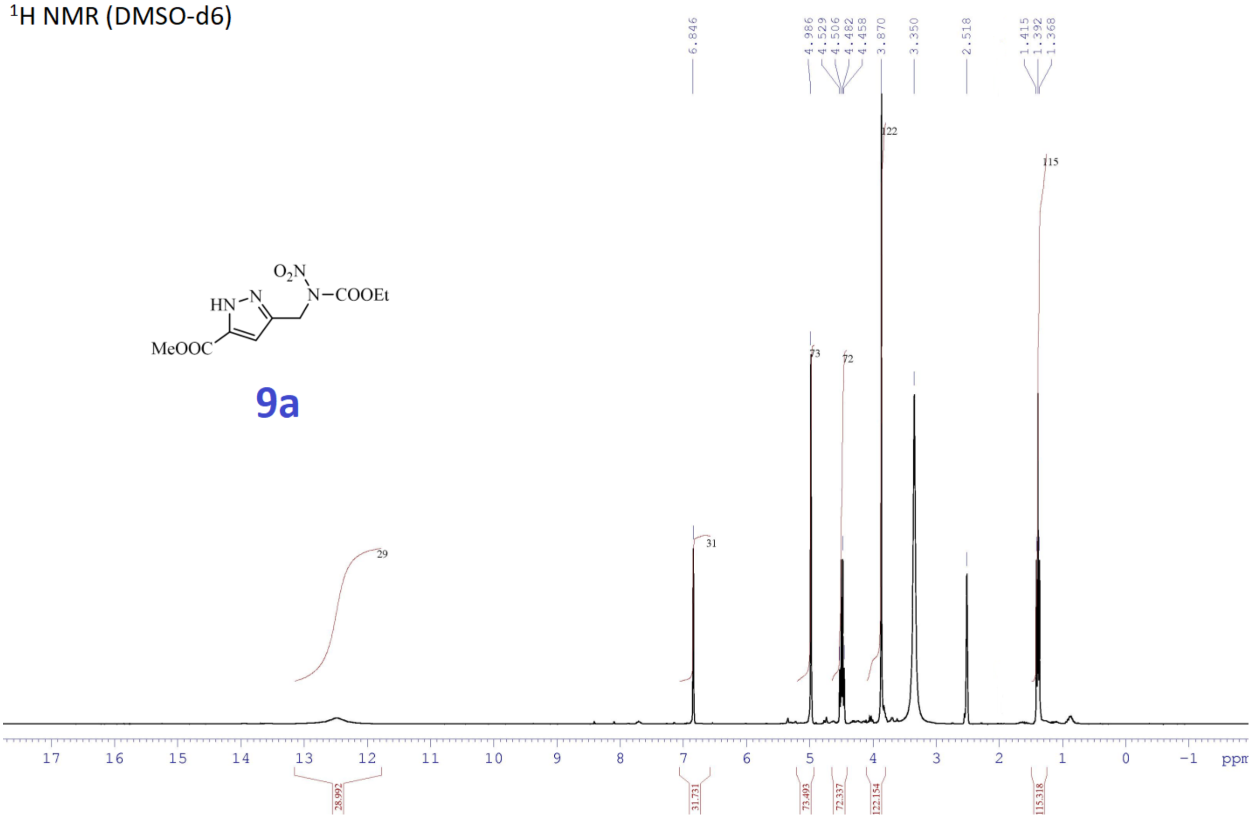
^{13}C NMR ($CDCl_3$)



^{14}N NMR ($CDCl_3$)

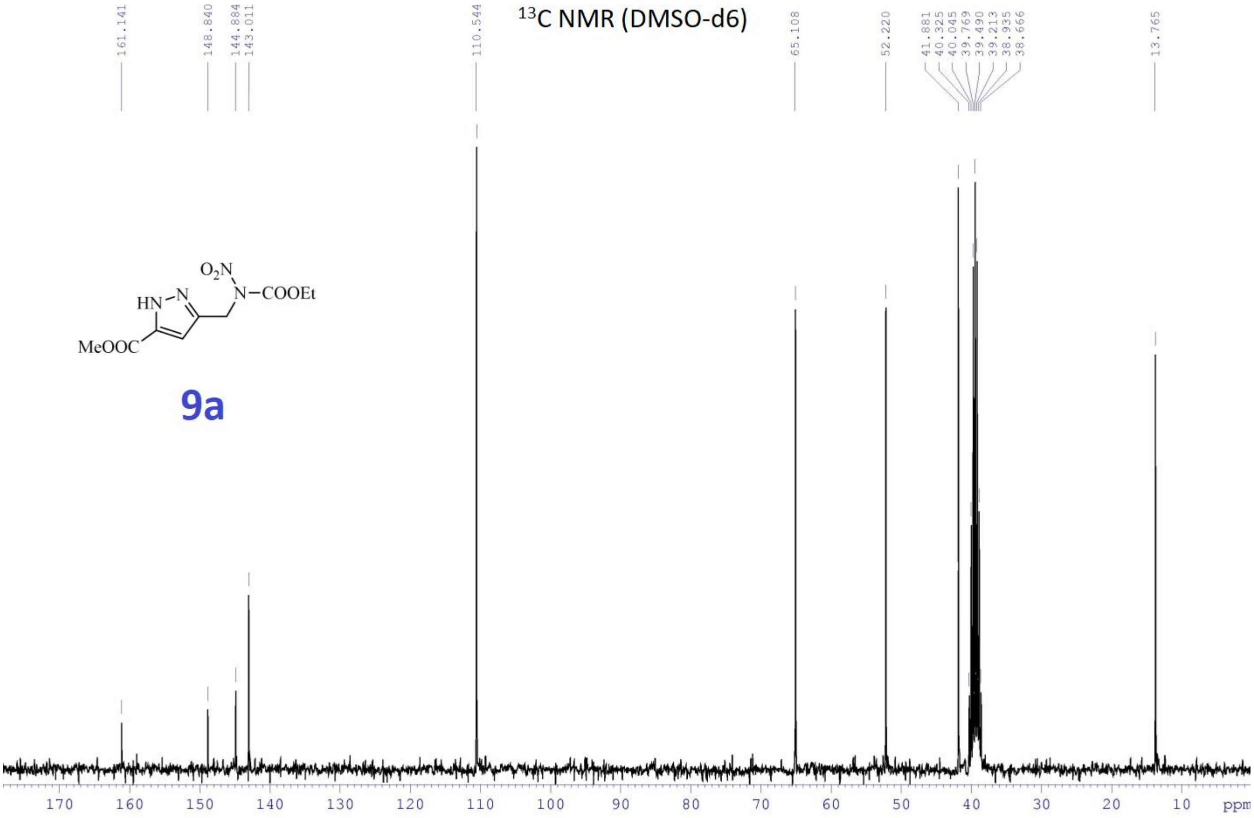


^{1}H NMR (DMSO-d6)



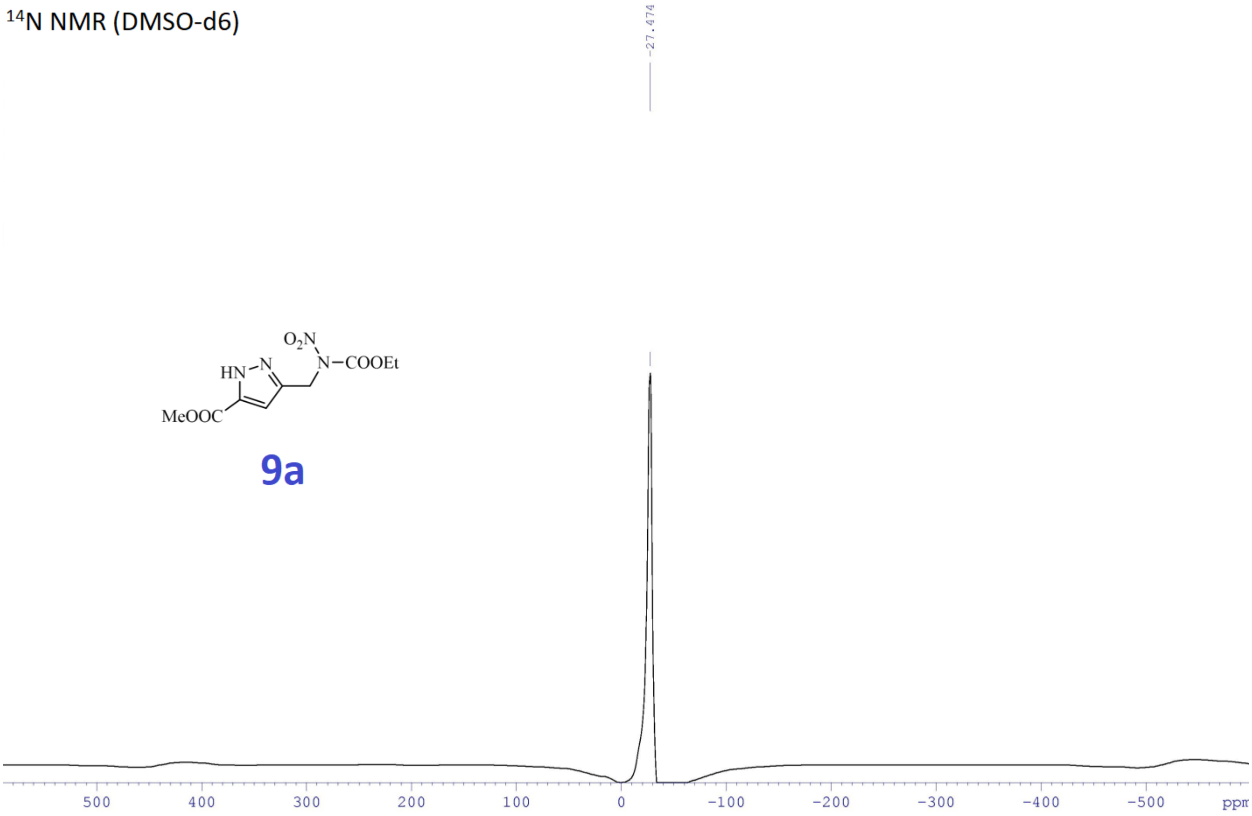
9a

^{13}C NMR (DMSO-d6)

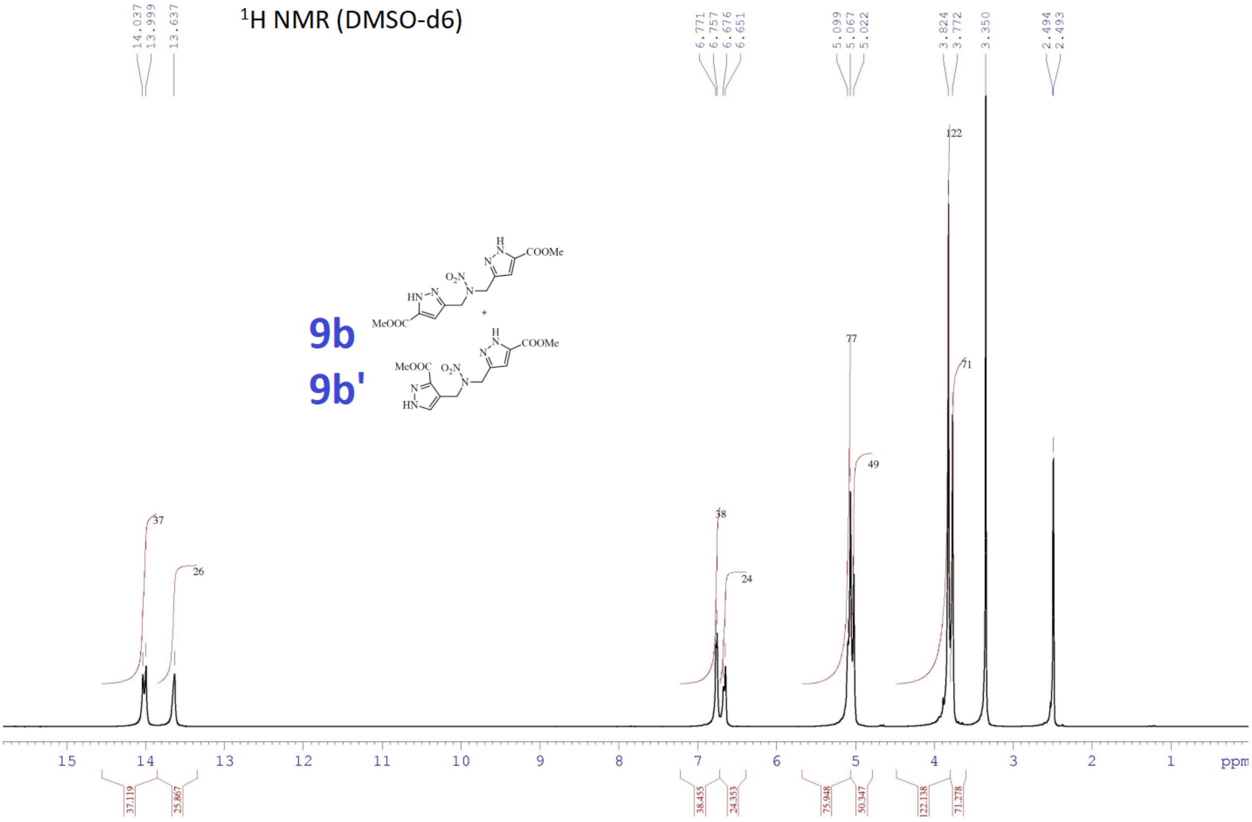


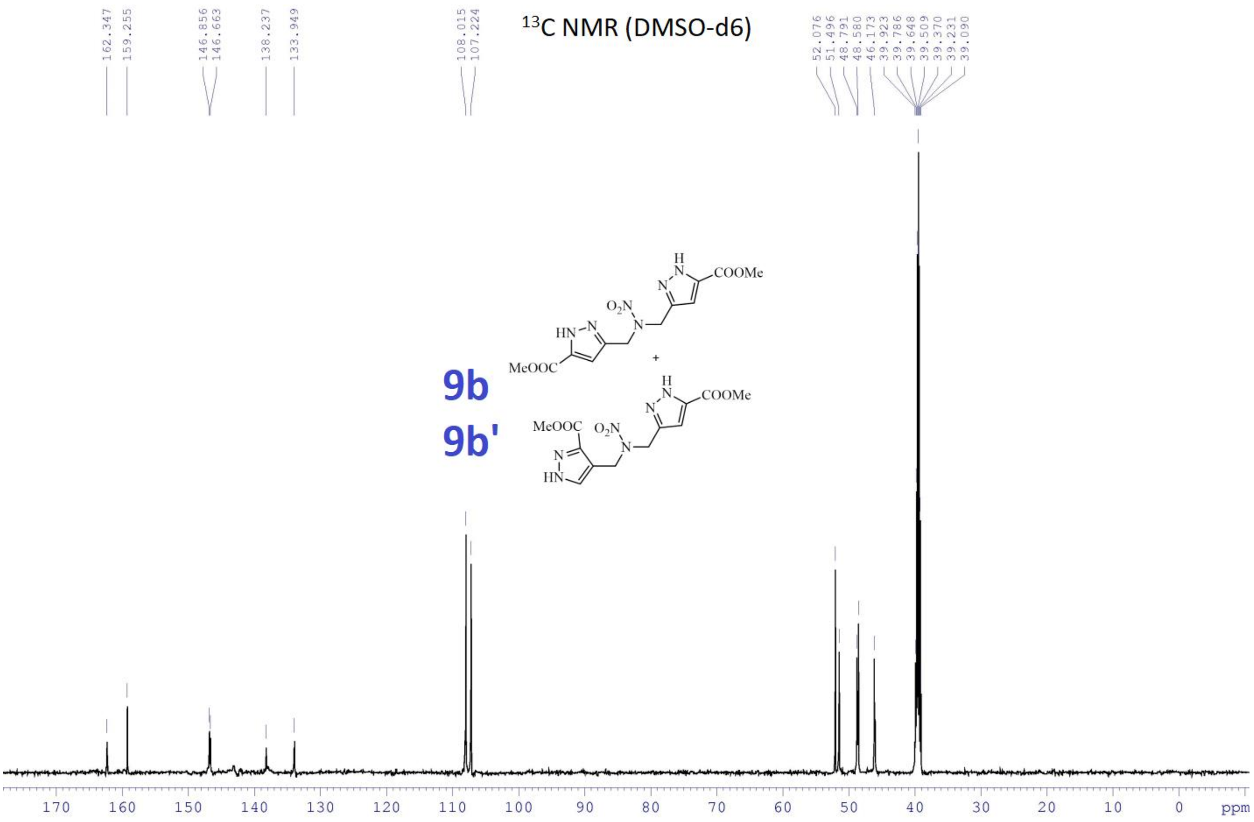
9a

^{14}N NMR (DMSO-d6)



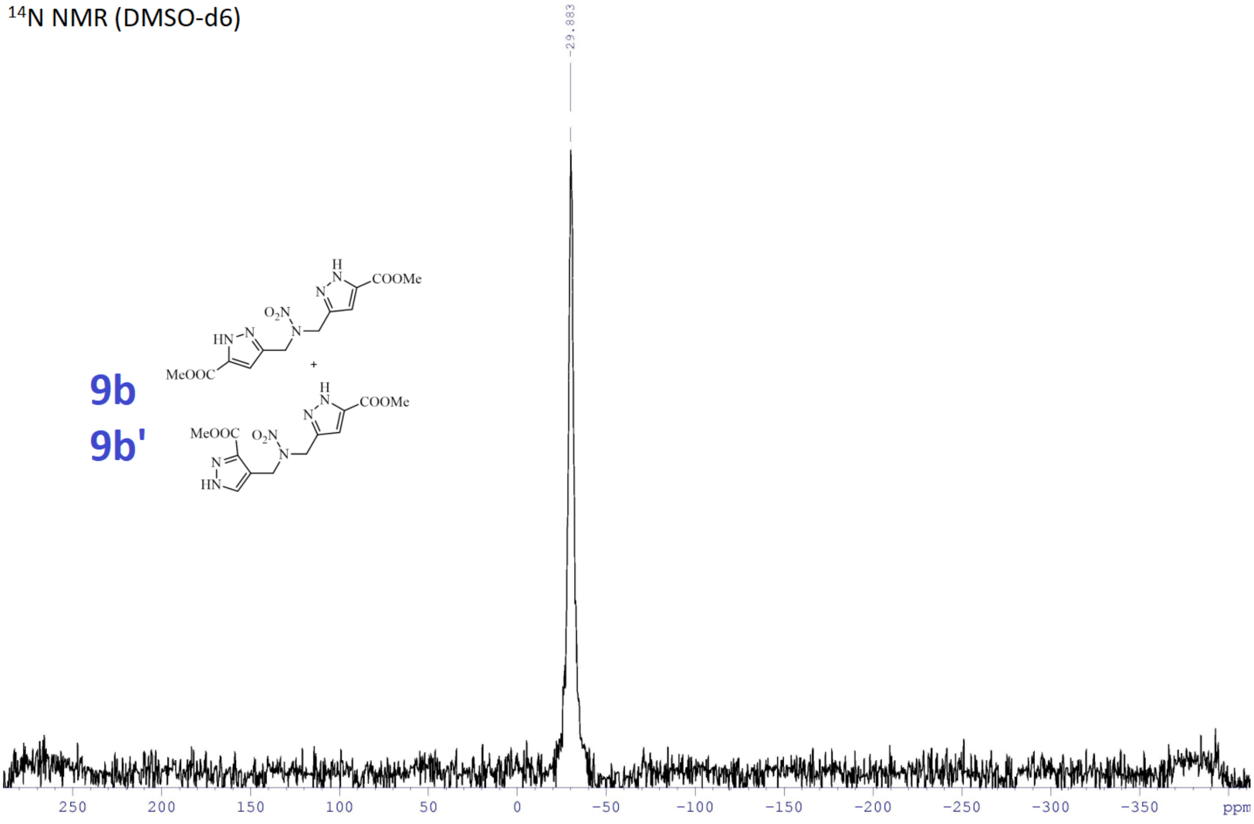
^{1}H NMR (DMSO-d6)




^{13}C NMR (DMSO-d6)

9b

9b'


^{14}N NMR (DMSO-d6)

9b

9b'