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Dipropargyl ethers possessing nitramine units

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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. Elemental analysis was performed on a CHNS/O Analyzer 2400 (Perkin–Elmer instruments Series II). Analytical TLC was performed using commercially pre-coated silica gel plates (Kieselgel 60 F_{254}), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected.

Optimization of the geometry of compounds was carried out using the Gaussian program[S1] at M052X/def2tzvp level of approximation which was succesfully adopted in our erlier calculations.[S2-S4] The AIM theory[S5,S6] was utilized to search for bond critical points of molecular electron density. Correlation of interatomic energy and potential energy density at bond critical point (E=1/2V(r))[S7,S8] was adopted for esimation of the energy of noncovalent intramolecular interactions taking into account its reliability for energetic analysis.[S9-S11]

Materials Most of the reagents and starting materials were purchased from commercial sources and used without additional purification. The starting *N*-(chloromethyl)nitramines **1**, **3-7**[S12] 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.

General Procedure for the Reaction of *N*-(chloromethyl)nitramines with propargyl alcohol. 1-Chloro-2-nitro-2-azapropane **1** (1.24 g, 10.0 mmol) was dissolved in dry propargyl alcohol (5.4 mL, 100.0 mmol) and stirred at 60 °C, passing dry N_2 through the solution for 0.5 h. The excess of propargyl alcohol was removed by vacuum distillation at 30 °C 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 = 0.60) providing **1-(prop-2-yn-1-yloxy)-2-nitro-2-azapropane 2** (73%) as a light yellow liquid; ^{1}H NMR (DMSO-d_6) δ 3.35 (s, 3H, CH_3), 3.49 (t, 1H, J = 2.2 Hz, CH), 4.26 (d, 2H, J = 2.2 Hz, CH_2C), 5.22 (s, 2H, NCH_2O). ^{13}C NMR (DMSO-d_6) δ 37.9, 56.5, 77.5, 79.3, 79.6. ^{14}N NMR (DMSO-d_6) δ -28.2 (NO_2). IR (KBr): 3288, 2955, 2930, 2864, 2119, 1532, 1473, 1435, 1299, 1250, 1080, 1048, 995, 978 cm^{-1}. Anal. calcd. for $C_5H_8N_2O_3$ (144.13): C 41.67, H 5.59, N 19.44. Found: C 41.71, H 5.62, N 19.35.

1,3-Di(prop-2-yn-1-yloxy)-2-nitro-2-azapropane (**8**). Prepared according to the general procedure from 1,3-dichloro-2-nitro-2-azapropane **3** (10.0 mmol). The title compound **8** (58%) is a light yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53 (t, 1H, J = 2.4 Hz, CH), 4.32 (d, 2H, J = 2.4 Hz, OCH2), 5.33 (s, 2H, NCH_2O). ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.9, 75.5, 77.1, 78.4. ^{14}N NMR (21 MHz, $CDCl_3$) δ -32.6 (NO2). IR (KBr): 3288, 2961, 2923, 2867, 2120, 1549, 1443, 1359, 1287, 1179, 1079, 1038, 954 cm^{-1}. Anal. calcd. for $C_8H_{10}N_2O_4$ (198.18): C 48.49, H 5.09, N 14.14; found C 48.53, H 5.13, N 14.07.

1,5-Di(prop-2-yn-1-yloxy)-2,4-dinitro-2,4-diazapentane (**9**). Prepared according to the general procedure from 1,5-dichloro-2,4-dinitro-2,4-diazapentane **4** (10.0 mmol), except that an excess propargyl alcohol (10.8 mL, 200.0 mmol) was used, and after distilling its excess, the residue

was washed with water and purified by crystallization from $CHCl_3$ to give the product **9** (59%); a white solid, mp 60-62°C (from $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 2.55 (t, 1H, *J* = 2.5 Hz, CH), 4.31 (d, 2H, *J* = 2.3 Hz, CH_2C), 5.49 (s, 2H, NCH_2O), 5.58 (s, 2H, NCH_2N). ^{13}C NMR ($CDCl_3$) δ 57.6, 62.1, 75.6, 78.5, 78.7. ^{14}N NMR ($CDCl_3$) δ -33.7 (NO_2). IR (KBr): 3290, 3248, 3038, 3025, 2975, 2924, 2866, 2124, 1578, 1540, 1451, 1425, 1396, 1310, 1289, 1253, 1189, 1083, 1065, 969, 925 cm^{-1}. Anal. calcd. for $C_9H_{12}N_4O_6$ (272.22): C 39.71, H 4.44, N 20.58. Found: C 39.78, H 4.47, N 20. 51.

1,7-Di(prop-2-yn-1-yloxy)-2,4,6-trinitro-2,4,6-triazapentane (**10**). The procedure is the same as for **9**. The title compound **10** (80%) is a white solid, mp 132-134°C; ^{1}H NMR (DMSO-d_6) δ 3.46 (s, 1H, CH), 4.31 (d, 2H, *J* = 1.7 Hz, CH_2C), 5.34 (s, 2H, NCH_2O), 5.83 (s, 2H, NCH_2N). ^{13}C NMR (DMSO-d_6) δ 56.4, 63.9, 77.6, 78.8, 79.4. ^{14}N NMR (DMSO-d_6) δ -32.4 (NO_2). IR (KBr): 3270, 3036, 2114, 1556, 1462, 1429, 1277, 1180, 1063, 929 cm^{-1}. Anal. calcd. for $C_{10}H_{14}N_6O_8$ (346.26): C 34.69, H 4.08, N 24.27. Found: C 34.77, H 4.16, N 24.31.

1,9-Di(prop-2-yn-1-yloxy)-2,4,6,8-tetranitro-2,4,6,8-tetrazapentane (11). The procedure is the same as for **9**. The title compound **11** (81%) is a white solid, mp 159-161°C. ^{1}H NMR (DMSO-d_6) δ 3.53 (d, 1H, *J* = 2.1 Hz, CH), 4.32 (d, 2H, *J* = 2.0 Hz, CH_2C), 5.34 (s, 2H, NCH_2O), 5.82 (s, 2H, $OCH_2NC\underline{H}_2N$), 5.89 (s, 2H, NCH_2N). ^{13}C NMR (DMSO-d_6) δ 56.3, 64.0, 64.9, 77.7, 78.7, 79.4. ^{14}N NMR (DMSO-d_6) δ -30.0, -32.4 (NO_2). IR (KBr): 3283, 3034, 2122, 1556, 1439, 1273, 1192, 1079, 944, 924 cm^{-1}. Anal. calcd. for $C_{11}H_{16}N_8O_{10}$ (420.29): C 31.44, H 3.84, N 26.66. Found: C 31.51, H 3.80, N 26.58.

1,6-Di(prop-2-yn-1-yloxy)-2,5-dinitro-2,5-diazahexane (**12**). The procedure is the same as for **9**. The title compound **11** (85%) is a white solid, mp 83-84°C (from $CHCl_3$). ^{1}H NMR (DMSO-d_6) δ 3.47 (s, 1H, CH), 4.08 (s, 2H, $C\underline{H}_2CH_2$), 4.25 (d, 2H, *J* = 1.9 Hz, CH_2C), 5.21 (s, 2H, NCH_2O). ^{13}C NMR (DMSO-d_6) δ 47.9, 56.5, 77.6, 78.7, 79.5. ^{14}N NMR (DMSO-d_6) δ -29.9 (NO_2). IR (KBr): 3293, 2928, 2120, 1527, 1438, 1290, 1269, 1113, 1069, 1026, 981, 891, 891, 844, 663, 606 cm^{-1}. Anal. calcd. for $C_{10}H_{14}N_4O_6$ (286.24): C 41.96, H 4.93, N 19.57. Found: C 42.04, H 4.97, N 19.62.

Calorimetric measurements

The main method for determining the enthalpy of formation (ΔH^o_f) 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).[S13] Basic design features of the calorimeter used in this study: 1) small heat equivalent (~500 cal K^{-1}) with a large volume of bomb (200 cm^3); 2) easy maintenance of the calorimeter bomb; 3) continuously thermostated 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 ($-\Delta U'_B$) 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. Samples of test compounds, 1,7-di(prop-2-yn-1-yloxy)-2,4,6-trinitro-2,4,6-triazapentane (**10**) and 1,6-di(prop-2-yn-1-yloxy)-2,5-dinitro-2,5-diazahexane (**12**), were burned in a platinum crucible. Pressed tablets of **10** and **12** were weighed on Bunge microanalytic scales with an error of $2\cdot10^{-6}$ g. The suspended 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, distilled water (1 mL) 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 ($-\Delta U'_B$) 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.[S14]

For thermochemical experiments several samples of compounds **10** and **12** have been obtained and purified by different methods. The purity of the samples was at least 99.5% (HPLC).

The combustion energies ($-\Delta U'_B$, cal·g^{-1}) under calorimetric bomb conditions for the compound **10** and **12** are given in Table S1 and S2.

Table S1. Determination of the combustion energy ($-\Delta U'_B$) of compound **10**.

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	0.090239	2.33954	1257.71	863.46	7.19	2.07	8.75	4169.4
2	0.087977	2.57305	1383.25	997.42	7.25	2.04	8.77	4175.6
3	0.088052	2.34586	1261.11	875.79	7.18	2.00	8.64	4173.7
4	0.075319	2.22891	1198.24	866.35	7.23	1.71	9.01	4168.1
5	0.071028	2.22952	1198.57	884.36	7.22	1.69	8.71	4175.7
-ΔU'в = 4172.5 ± 4.1 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}.

Table S2. Determination of the combustion energy ($-\Delta U'_B$) of compound **12**.

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	0.082127	2.47093	1328.35	900.66	7.18	1.66	6.93	5015.6
2	0.079911	2.43754	1310.40	892.39	7.26	1.62	8.80	5009.7
3	0.071469	2.34820	1262.37	887.16	7.28	1.45	8.41	5010.1
4	0.075032	2.36189	1269.73	876.47	7.29	1.62	8.14	5014.0
5	0.070648	2.36721	1272.59	901.09	7.36	1.43	8.47	5014.1
-ΔU'в = 5012.7 ± 3.0 кал·г$^{-1}$								

Reactions of combustion of compounds **10** and **12** proceeds in accordance with the stoichiometry presented by equations (I) and (II):

$$C_{10}H_{14}N_4O_{6(cr)} + 10.5O_{2(g)} = 10CO_{2(g)} + 7H_2O_{(l)} + 2N_{2(g)} \quad (I),$$

$$C_{10}H_{14}N_6O_{8(cr)} + 9.5O_{2(g)} = 10CO_{2(g)} + 7H_2O_{(l)} + 3N_{2(g)} \quad (II)$$

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

The enthalpies of formation (ΔH^o_f) of compound **10** and **12** for the standard state were calculated from the corresponding enthalpies of combustion (ΔH^o_c) in accordance with the stoichiometry of the reaction (I) and (II):

$$\Delta H^o_f[C_{10}H_{14}N_4O_6]_{(cr)} = 10\Delta H^o_f[CO_2]_{(g)} + 7\Delta H^o_f[H_2O]_{(ж)} - \Delta H^o_c \qquad \text{(III)}$$

$$\Delta H^o_f[C_{10}H_{14}N_6O_8]_{(cr)} = 10\Delta H^o_f[CO_2]_{(g)} + 7\Delta H^o_f[H_2O]_{(ж)} - \Delta H^o_c \qquad \text{(IV)}$$

where ΔH°_c – the standard enthalpies of combustion of the compounds **10** and **12**, kcal·mol^{-1}, and ΔH°_f – the standard enthalpies of their formations, kcal·mol^{-1}.

When calculating the standard enthalpy of formation of the compounds **10** and **12**, the reference values of the enthalpies of formation of combustion products were used:[S15]

$$\Delta H^\circ_f[CO_2]_{(g)} = -94.051 \pm 0.031 \text{ kcal·mol}^{-1}$$

$$\Delta H^\circ_f[H_2O]_{(l)} = -68.315 \pm 0.009 \text{ kcal·mol}^{-1}$$

With the above data, the standard enthalpy of formation in the solid state was calculated. As shown in Table S3, the enthalpy of formation is positive for both compounds. When normalized on a per gram basis, the values of 0.321 and 0.126 kJ g^{-1} are realized for compound **10** and **12**, respectively.

Table S3. Thermochemical data in the standard state for the compounds of this study.

Compound	Formula (Mw)	$-U'_B$ cal g^{-1}	ΔH^o_c kcal·mol^{-1}	ΔH^o_f	
				kcal·mol^{-1}	kJ·mol^{-1}
10	$C_{10}H_{14}N_6O_{8(cr)}$ (286.24)	4172.5 ± 4.1	-1440.7 ± 1.4	22.0 ± 1.4	92.0 ± 5.8
12	$C_{10}H_{14}N_4O_{6(cr)}$ (346.26)	5012.7 ± 3.0	-1429.1 ± 0.9	10.4 ± 0.9	43.5 ± 3.7

X-ray diffraction study

Single crystal X-ray diffraction experiments for compounds **9** and **10** 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.[S16] 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.[S17]

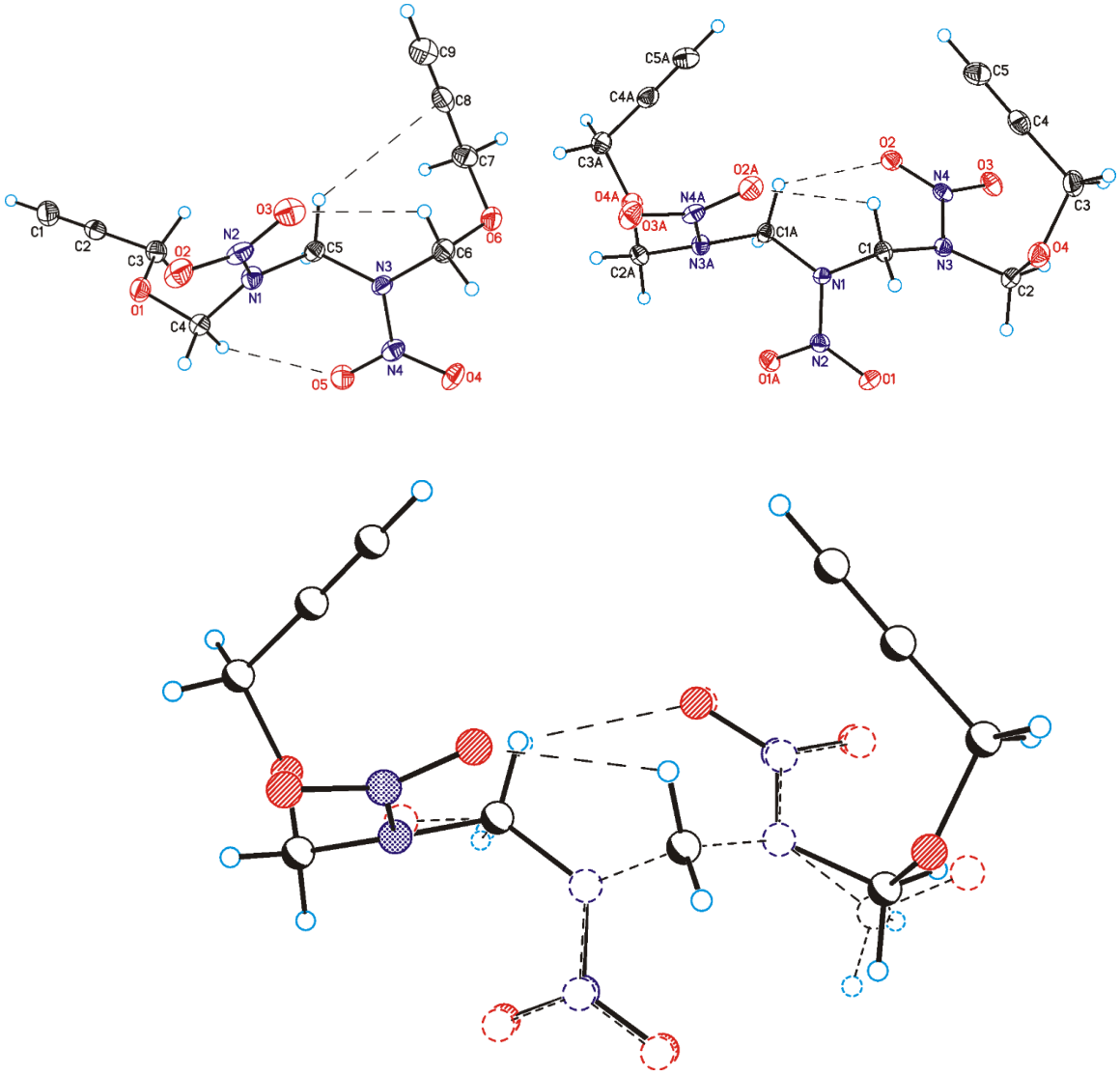

Figure S1. Top-left: general view of molecule **9**; top-right: general view of molecule **10**; bottom: superimposition of the central fragment of molecule **9** onto molecule **10**.

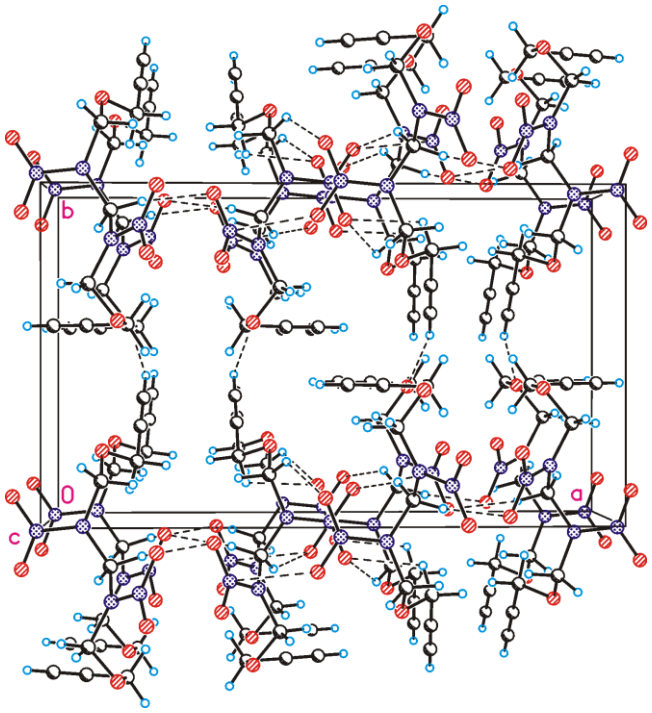

Figure S2. Crystal packing fragment of compound **9**. The propargyl groups participate in C-H…π and ≡C-H…O interactions. The nitramino groups form O(N)…O(N) and O…H-C contacts

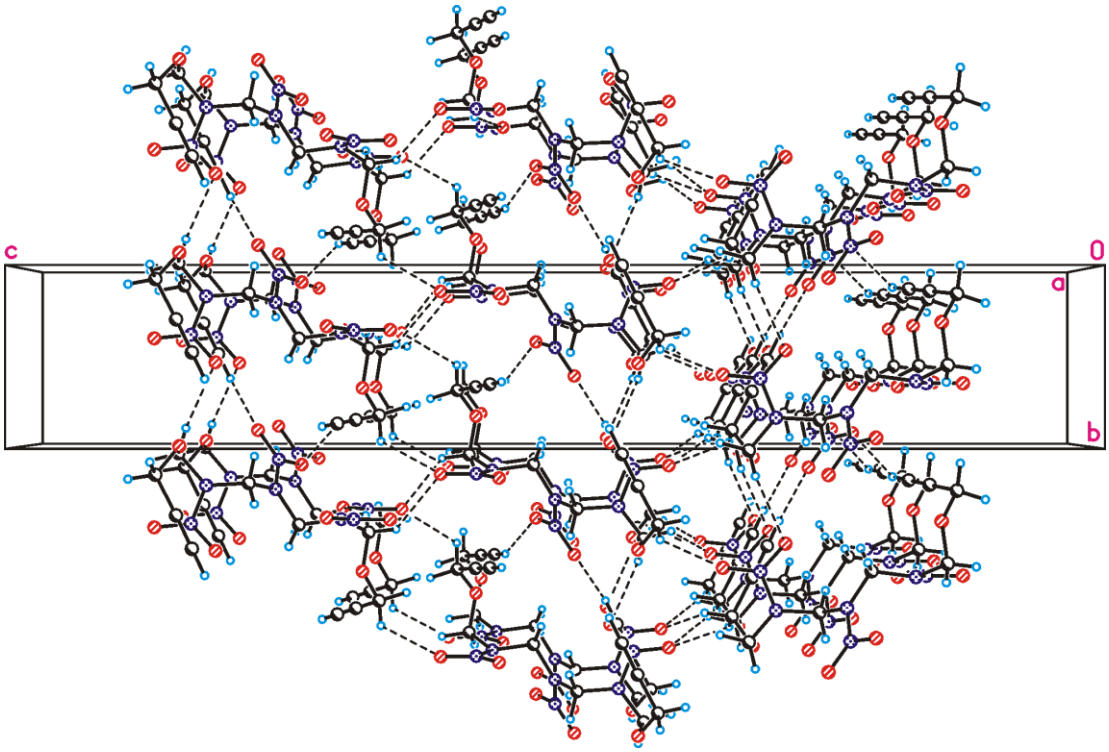

Figure S3. Crystal packing fragment of compound **10**. The propargyl moieties participate in weak π…π stacking interaction with the nitramino group and ≡C-H…O interactions. The nitramino groups form O…O and O…H-C contacts and participate in π…π stacking interaction with the propargyl groups.

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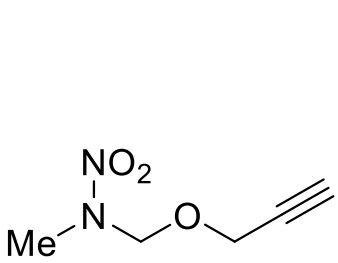
^{1}H NMR in DMSO-d6



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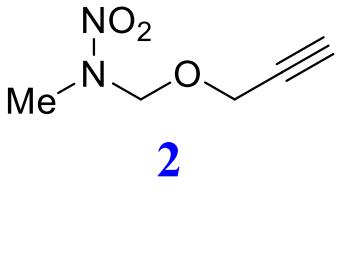

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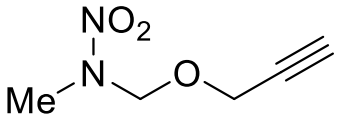

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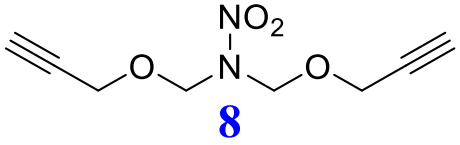

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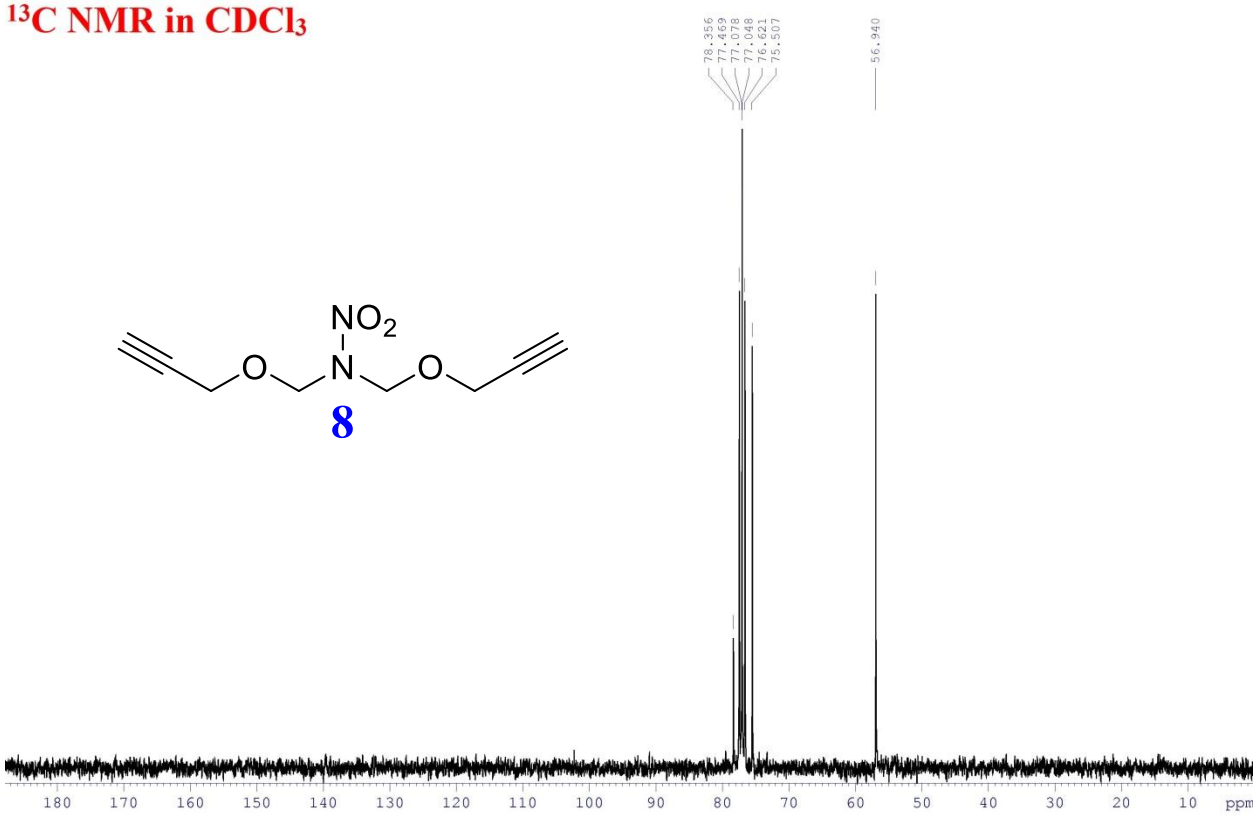

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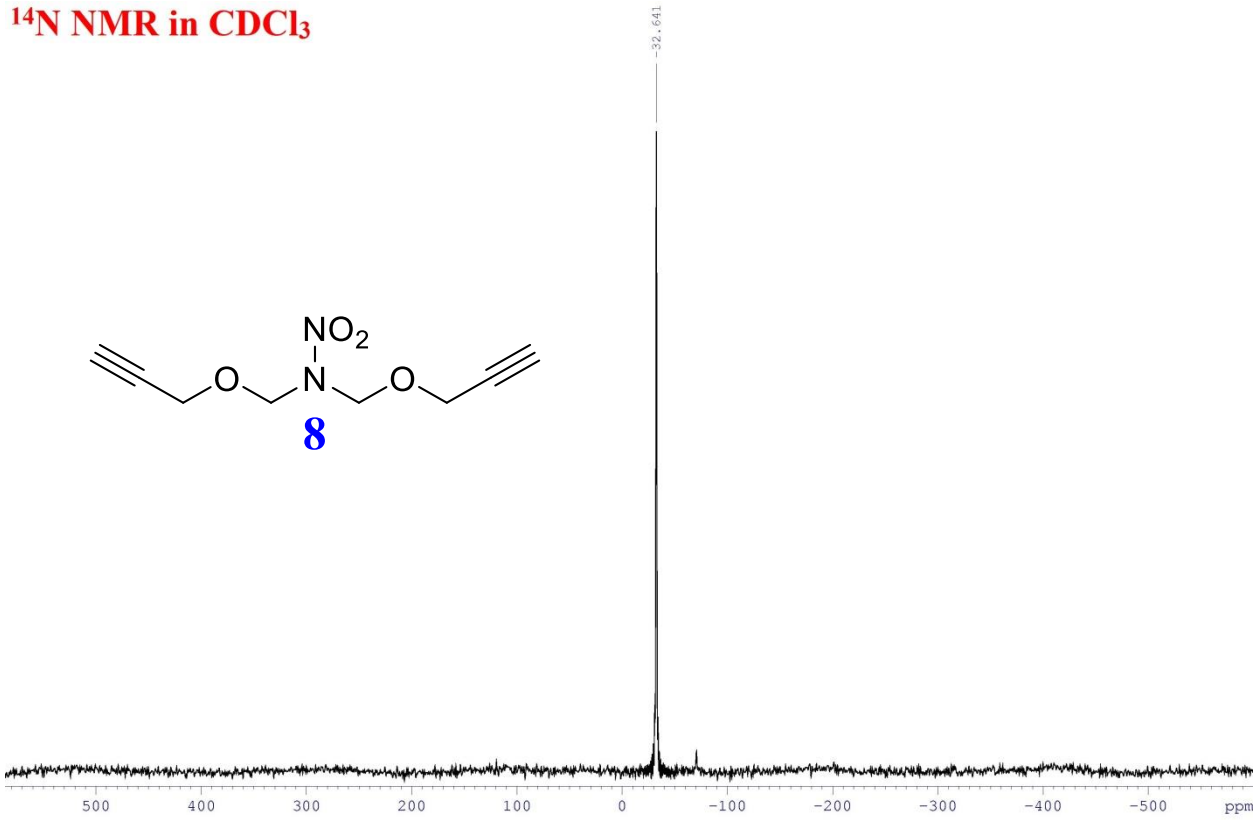
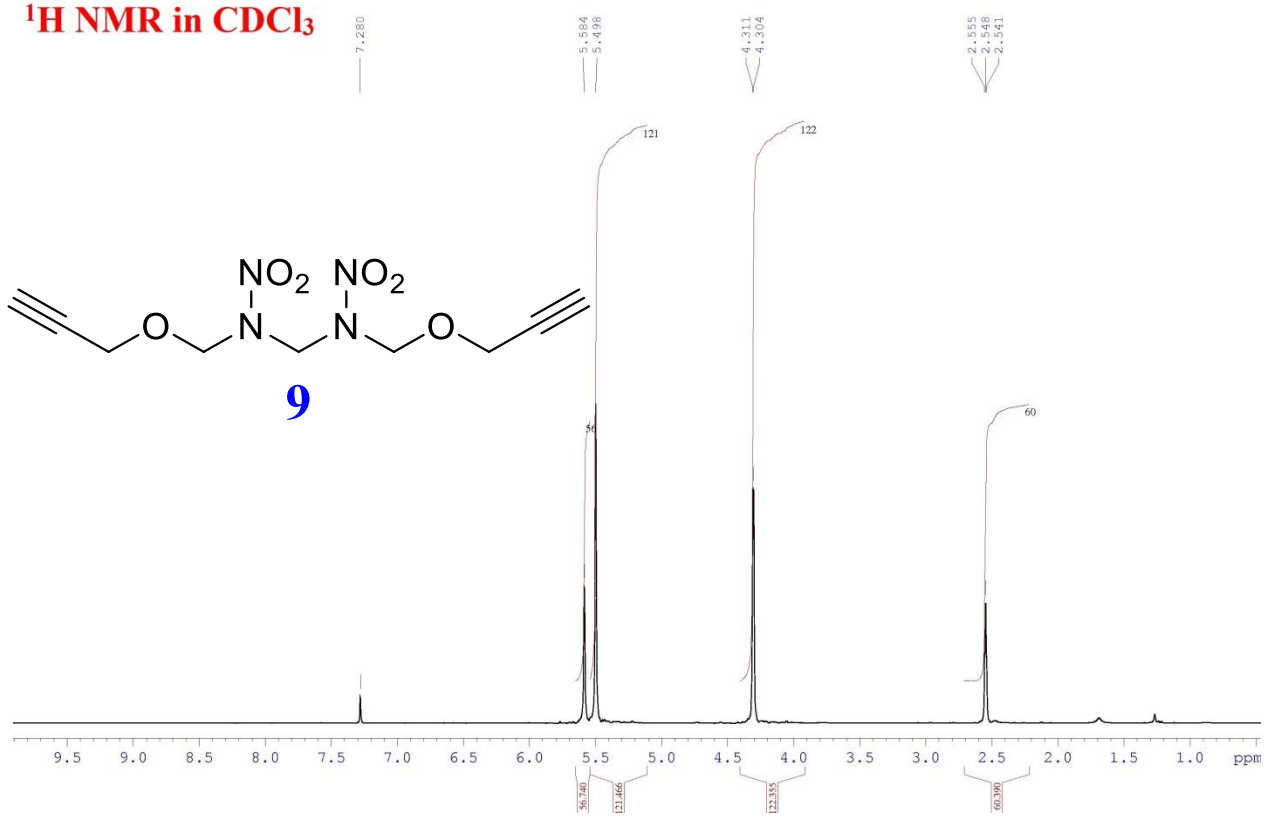


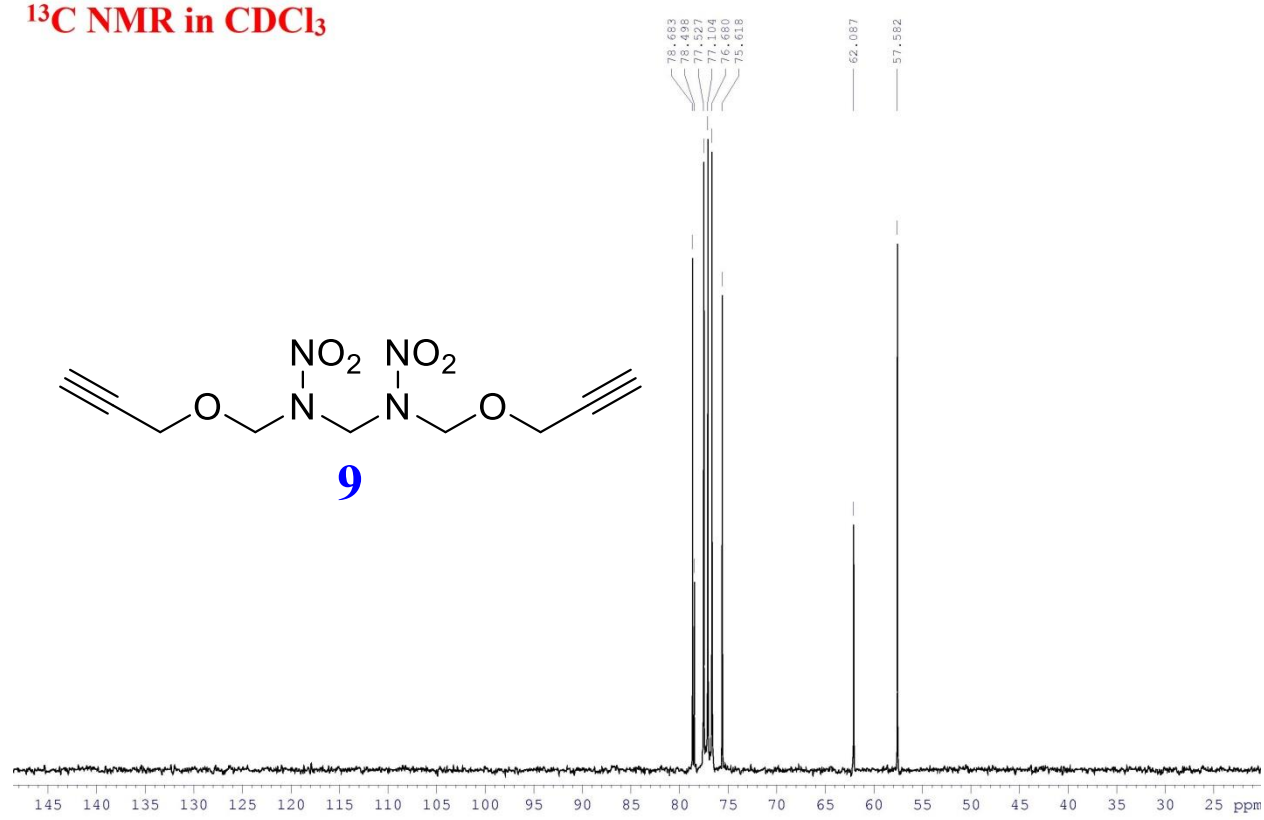
8

^{1}H NMR in $CDCl_3$



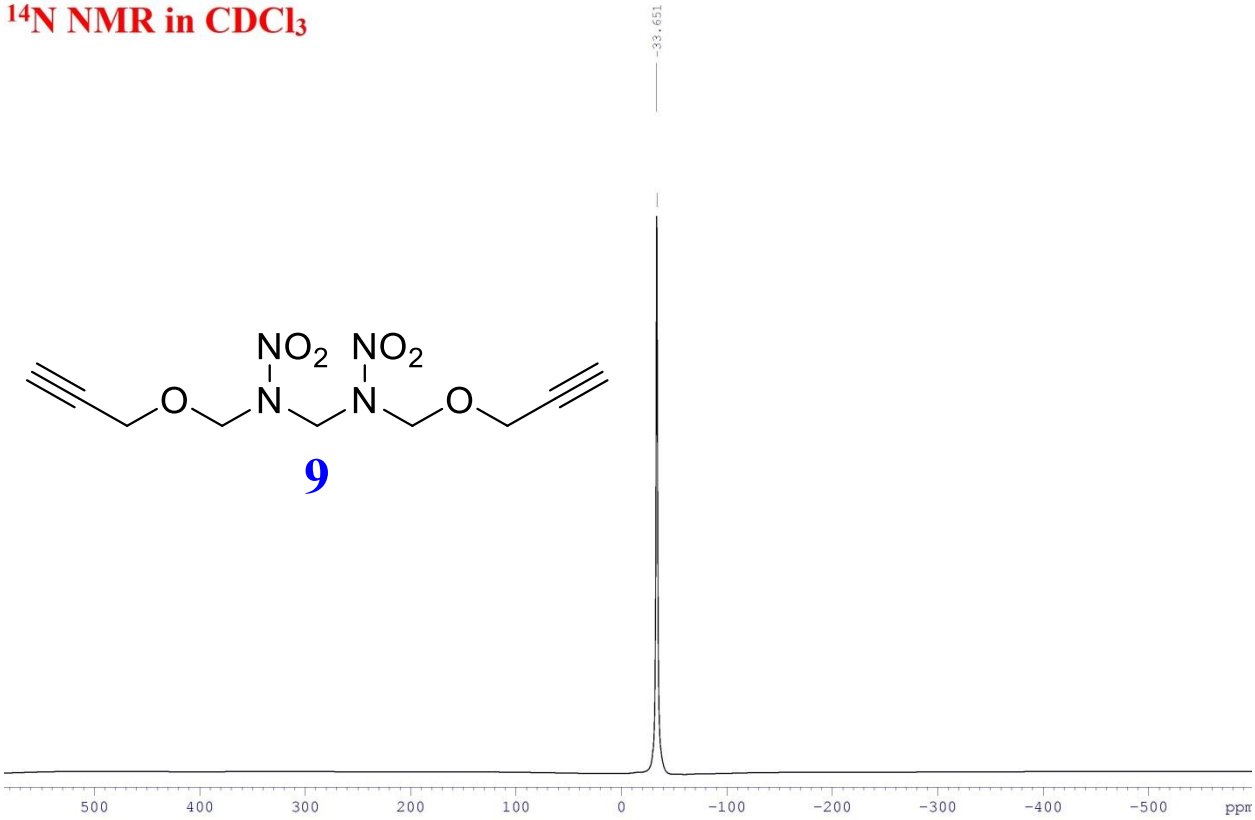
9

^{13}C NMR in $CDCl_3$



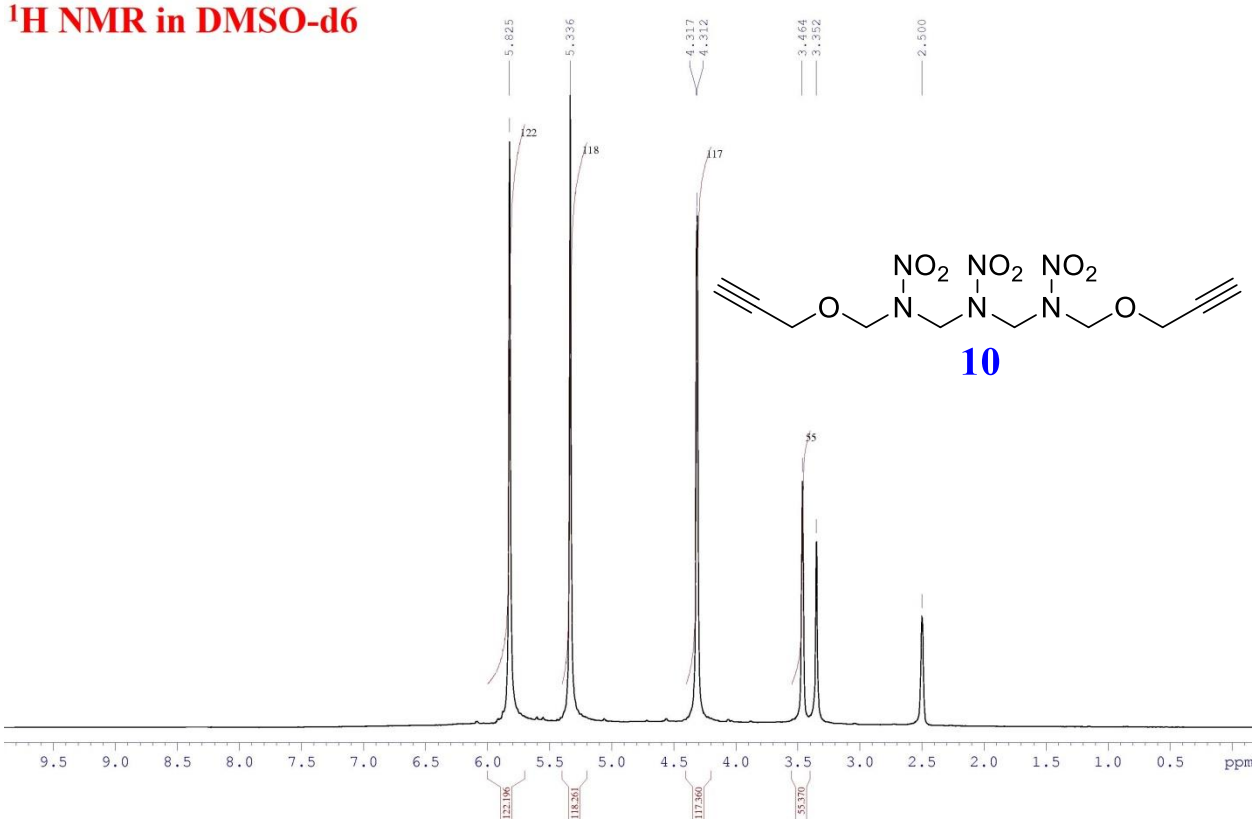
9

^{14}N NMR in $CDCl_3$



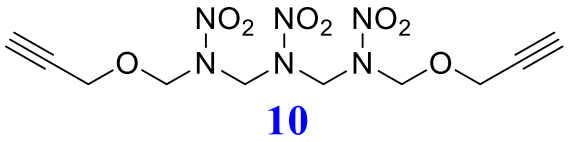
9

^{1}H NMR in DMSO-d6



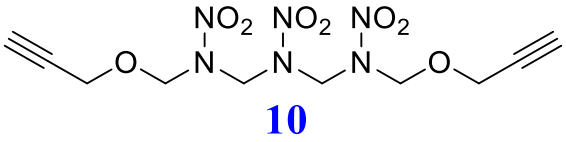
10

^{13}C NMR in DMSO-d6



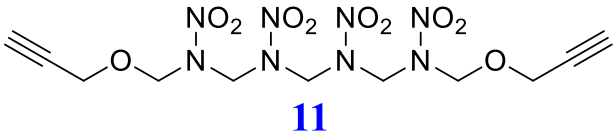
10

^{14}N NMR in DMSO-d6



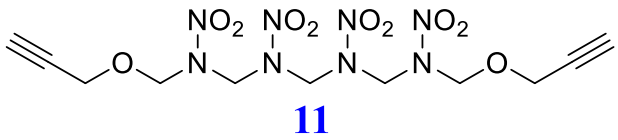
10

^{1}H NMR in DMSO-d6



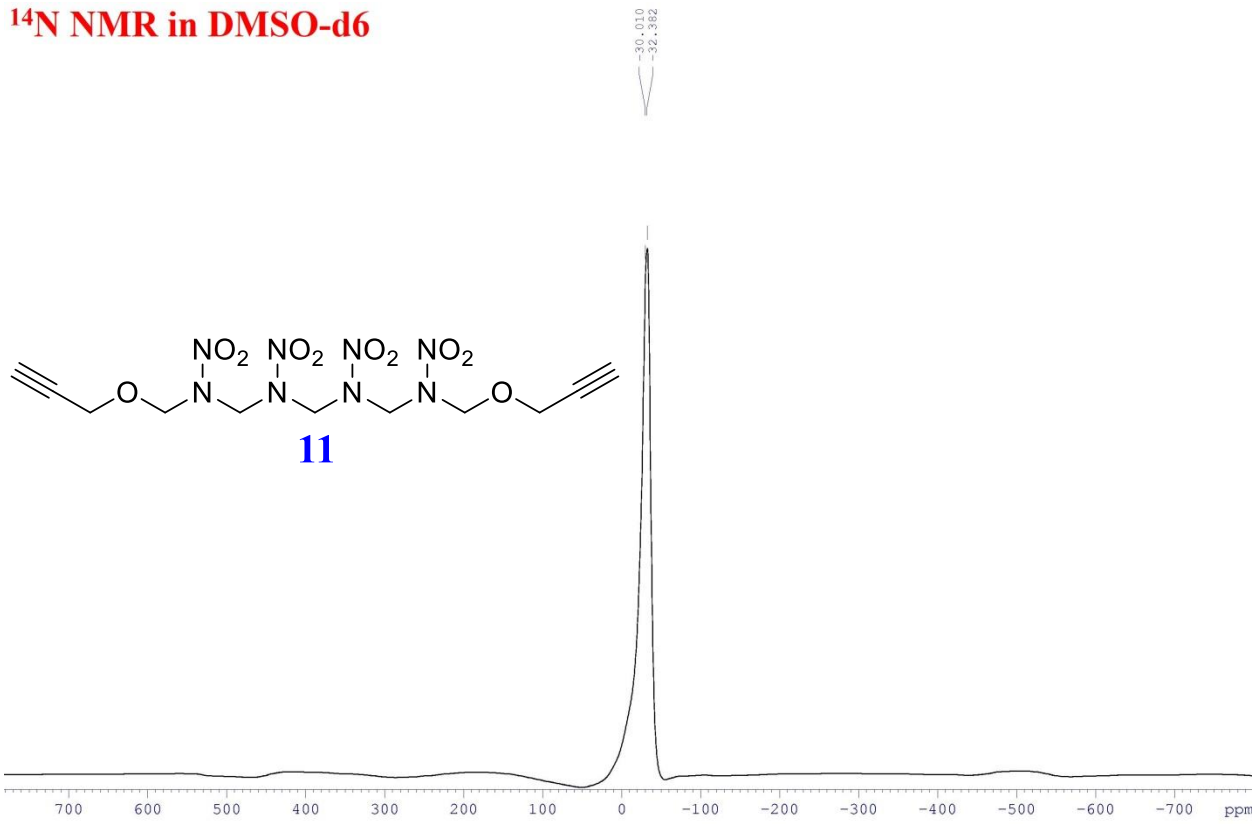
11

^{13}C NMR in DMSO-d6



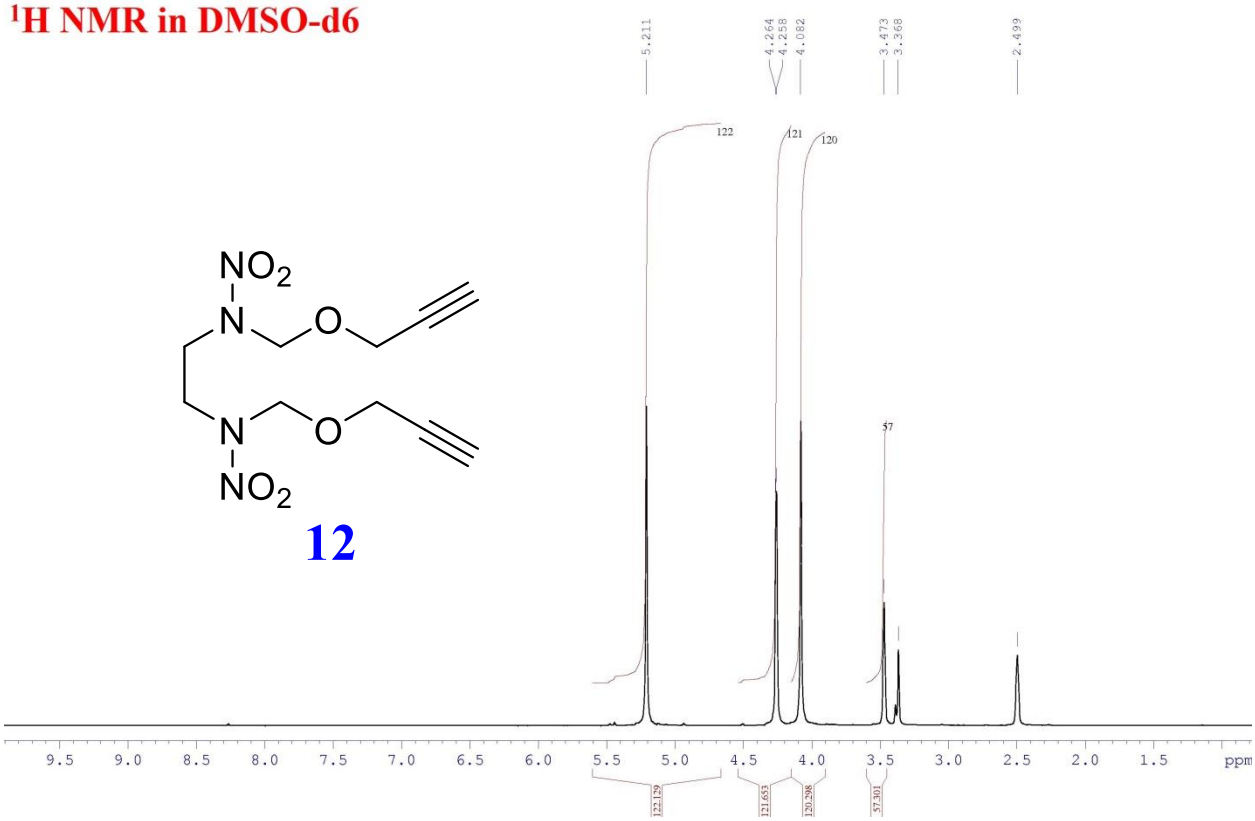
11

^{14}N NMR in DMSO-d6



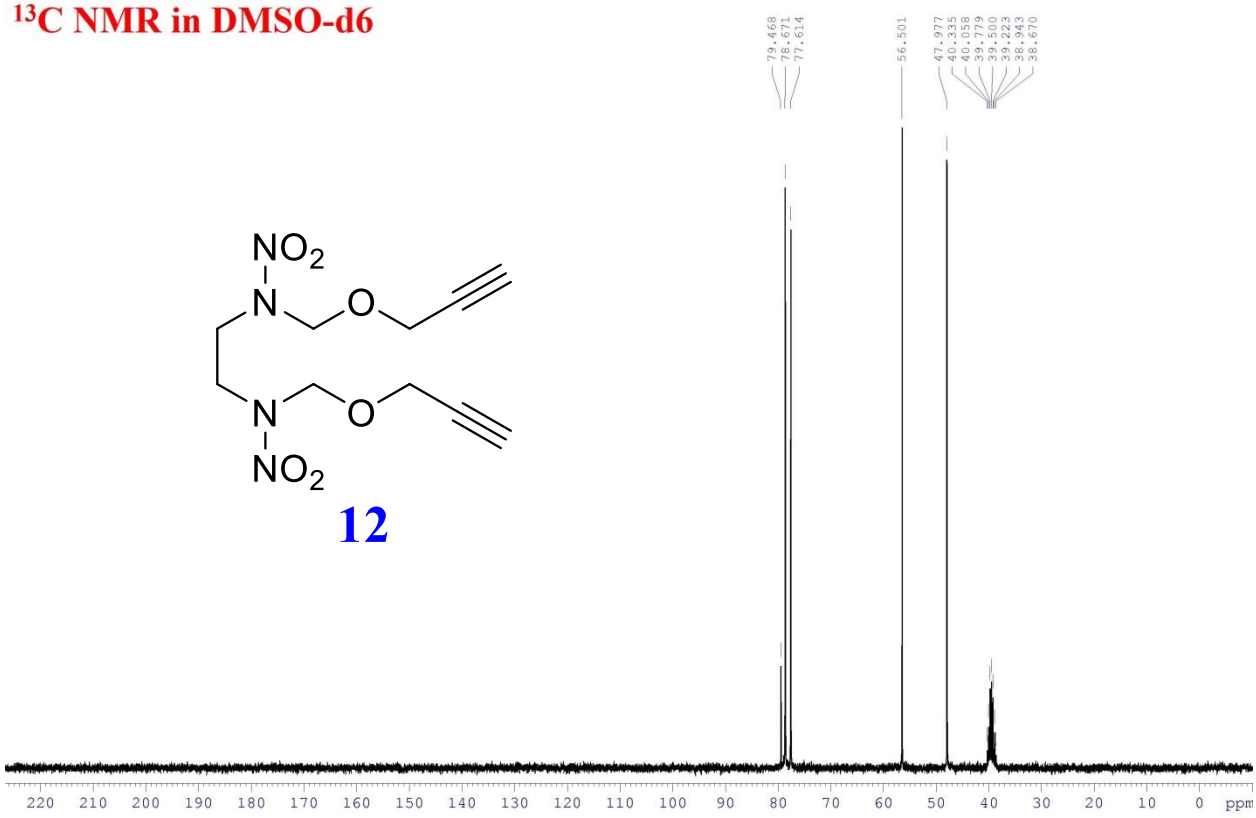
11

^{1}H NMR in DMSO-d6



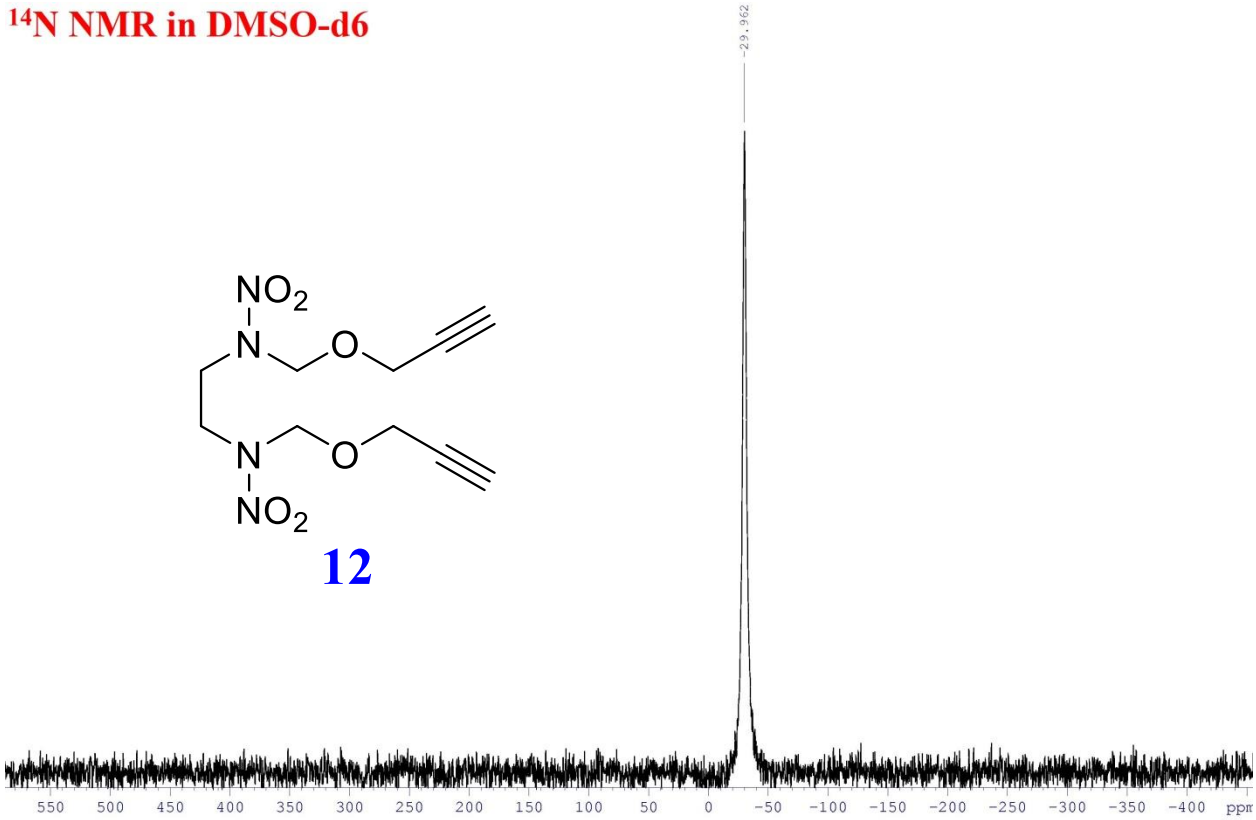
12

^{13}C NMR in DMSO-d6



12

^{14}N NMR in DMSO-d6



12