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Electronic Supplementary Information

Novel Trinitroethanol Derivatives: High Energetic 2-(2,2,2-Trinitroethoxy)-1,3,5-triazines

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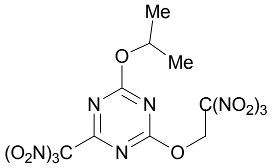
Experimental Section

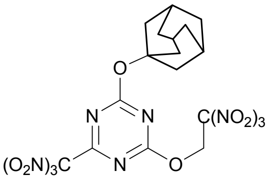
Caution! All prepared compounds are highly energetic materials and sensitive to various stimuli. Although none of the compounds described herein has exploded or detonated in the course of this research, safety precautions, such as face shields, a leather apron, gloves, and hearing protection should be employed. These compounds should only be prepared by an experienced synthetic chemist and should be handled with great care.

General: All the reagents were of analytical grade, purchased from commercial sources, and used as received. Infrared spectra were determined in KBr pellets on a Perkin–Elmer Model 577 spectrometer. Mass-spectra were recorded on a Varian MAT-311 A instrument. The ^{1}H, ^{13}C, ^{15}N, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument at 300.13, 75.47, 50.7, and 21.68 MHz, respectively. The chemical shift values (δ) are expressed relative to the chemical shift of the [D]solvent or to external standard (nitromethane for ^{14}N and ^{15}N NMR) without correction. Analytical TLC was performed using commercially pre-coated silica gel plates (Silufol UV$_{254}$), and visualization was effected with short-wavelength UV-light. Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected. The decomposition points were recorded on a thermogravimetric analyzer (TGA) at a scan rate of 5°C min^{-1} or 10°C min^{-1}. Elemental analyses were obtained by using a CHNS/O Analyzer 2400 (Perkin–Elmer instruments Series II).

2-Isopropoxy-4-(2,2,2-trinitroethoxy)-6-(trinitromethyl)-1,3,5-triazine (**15a**). A mixture consisting trinitroethanol (7.24 g, 40 mmol), 2-isopropoxy-4,6-bis(trinitromethyl)-1,3,5-triazine **14a** (4.37 g, 10 mmol), potassium trinitromethanide (1.89 g, 10 mmol), and absolute acetone (25 mL) was stirred at room temperature for *ca*. 44 h (TLC monitoring). The mixture was filtered and then concentrated (50%) in *vacuo*. The filtrate was diluted by water (70 mL) to give a suspension that was neutralized to pH 7 with $NaHCO_3$. The precipitate was filtered off, washed with water (4×20 mL), and dried to give a bright yellow solid **15a**. Recrystallization from isopropanol gave a colorless solid (2.48 g, 50 %), mp 104-105°C. ^{1}H NMR ($CDCl_3$): δ = 1.47 (d, 6H, Me, *J* = 6 Hz), 5.37 (s, 1H, OCH), 5.73 ppm (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ = 21.3 (Me), 64.5 (OCH_2), 76.9 (OCH), 122.1 (bs, $C(NO_2)_3$), 164.7 (N=$\underline{C}$-$C(NO_2)_3$), 170.7 (N=$\underline{C}$-OCHMe$_2$), 171.4 ppm (N=$\underline{C}$-OCH_2); ^{14}N NMR (aceton-d$_6$): δ = -36.7, -39.2 ppm. IR: ν = 2995, 2939, 2924, 2881, 1635, 1595, 1524, 1506, 1444, 1423, 1379, 1327, 1304, 1254, 1173, 1128, 1095, 989, 910, 894, 843, 824, 800, 783, 748, 658, 604, 571 cm^{-1}; elemental analysis calcd (%) for $C_9H_9N_9O_{14}$ (467.22): C 23.44, H 1.94, N 26.98; found: C 23.11, H 2.03, N 27.04.



2-(Adamantan-1-oxy)-4-(2,2,2-trinitroethoxy)-6-(trinitromethyl)- 1,3,5-triazine (**15b**). A mixture of trinitroethanol (7.24 g, 40 mmol), 2-(adamantan-1-oxy)-4,6-bis(trinitromethyl)-1,3,5-triazine **14b** (5.29 g, 10 mmol), and potassium trinitromethanide (1.89 g, 10 mmol) in absolute acetone (25 mL) was stirred at room temperature for *ca*. 48 h (TLC monitoring). The mixture was worked up as described above, giving 3.35 g (60%) product **15b**, mp 149-150°C (dec.). ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 6H, Ad), 2.24 (s, 6H, Ad), 2.31 (s, 3H, Ad), 5.72 ppm (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$): δ = 31.3 (Ad), 35.8 (Ad), 41.0 (Ad), 64.5 (OCH_2), 90.2 (Ad), 122.3 (bs, $C(NO_2)_3$), 164.2 (N=$\underline{C}$-$C(NO_2)_3$), 170.5 (N=$\underline{C}$-OAd), 171.2 ppm (N=$\underline{C}$-OCH_2); IR: ν = 3023, 2925, 2854, 1581, 1515, 1442, 1411, 1369, 1330, 1297, 1240, 1126, 1083, 1039, 960, 865, 829, 815, 796 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{17}N_9O_{14}$ (559.37): C 34.36, H 3.06, N 22.54; found: C 34.39, H 3.11, N 22.59.

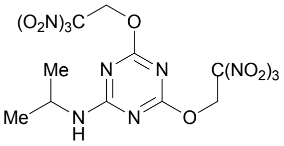


General synthesis of 2-amino-substituted 4,6-*bis*(2,2,2-trinitroethoxy)-1,3,5-triazines (22a-c).

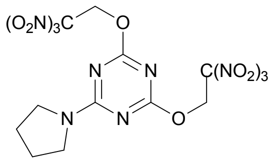
An amine (3 mmol) was added dropwise to a solution of compound **16** (0.618 g, 1 mmol) in DCE (3 mL) at 10-15° C for *ca*. 1 h. The mixture was stirred at room temperature until the completion (TLC monitoring; *iso*-propylamine – 72 h, pyrrolidine – 24 h, morpholine – 24 h).

The reaction mixture was filtered and the filtrate was evaporated in *vacuo* to dryness. The residue was stirred with cold water (2x40 mL) for 40 min and then with hot water (2x40 mL) for 40 min. The solid was filtered off and dried in air.

2-*iso*-Propylamino-4,6-*bis*(2,2,2-trinitroethoxy)-1,3,5-triazine (**22a**). The yield is 43%, mp 126-127°C (dec.). ^{1}H NMR (DMSO-d6) δ = 1.14-1.18 (m, 6H CH_3), 4.10-4.118 (m, 1H, CH), 6.10-6.18 (m, 4H, OCH_2), 8.53-8.59 ppm (m, 1H, NH). ^{13}C NMR (DMSO-d6) δ = 21.9, (CH_3), 42.6 ($N\underline{C}H(CH_3)_2$), 63.31 (OCH_2), 124.2 ($C(NO_2)_3$), 165.96 (C-N), 169.34, 169.93 ppm ($\underline{C}$-$OCH_2C(NO_2)_3$). ^{14}N NMR (DMSO-d6) δ = -36,34 ppm. IR: ν = 3423, 3275, 3198, 3155, 2980, 2941, 2893, 1597, 1549, 1468, 1450, 1431, 1412, 1371, 1335, 1298, 1244, 1178, 1146, 1132, 1090, 982, 881, 856, 804, 783, 723, 644, 548 cm^{-1}; elemental analysis calcd (%) for $C_{10}H_{12}N_{10}O_{14}$ (497.27): C 24.20; H 2.44; N 28.22; found: C 24.25; H 2.38; N 28.26.



2-Pyrrolidino-4,6-*bis*(2,2,2-trinitroethoxy)-1,3,5-triazine (**22b**). The yield is 65%, mp 150-151 °C (dec.). ^{1}H NMR (DMSO-d6) δ = 1.98 (s, 4H, CH_2CH_2); 3.6 (s, 4H, CH_2NCH_2); 6.2 ppm (s, 4H, OCH_2). ^{13}C NMR (DMSO-d6) δ = 24.48 (CH_2CH_2), 46.74 (CH_2NCH_2), 63.3 (OCH_2), 124.54 ($C(NO_2)_3$), 163.61 (C-N), 169.31 ppm ($\underline{C}$-$OCH_2C(NO_2)_3$). ^{14}N NMR (DMSO-d6) δ = -32,39 ppm. IR: ν = 3192, 3014, 2972, 2929, 2889, 2669, 2591, 2503, 1603, 1531, 1475, 1458, 1414, 1373, 1335, 1302, 1248, 1196, 1182, 1136, 1090, 1041, 968, 914, 879, 856, 839, 806, 785, 746, 654, 559 cm^{-1}; elemental analysis calcd (%) for $C_{11}H_{12}N_{10}O_{14}$ (508.28): C 25.99; H 2.38; N 27.56; found: C 26.01; H 2.30; N 27.51.



2-Morpholino-4,6-*bis*(2,2,2-trinitroethoxy)-1,3,5-triazine (**22c**).The yield is 80%, mp 175 °C (dec.). ^{1}H NMR (DMSO-d6) δ = 3.68 (s, 4H, CH_2NCH_2); 3.82 (s, 4H, CH_2OCH_2); 6.2 ppm (s, 4H, OCH_2). ^{13}C NMR ($CDCl_3$) δ = 44.08 (CH_2NCH_2) 63.36 ($O\underline{C}H_2C(NO_2)_3$), 65.69 ($CH_2OCH_2$), 122.06 ($C(NO_2)_3$), 165.32 (C-N), 169.79 ppm ($\underline{C}$-$OCH_2C(NO_2)_3$). .). IR: ν = 3423, 3005, 2964, 2926, 2874, 1618, 1599, 1527, 1450, 1414, 1369, 1335, 1304, 1282, 1267, 1250, 1200, 1138, 1115, 1086, 1072, 1022, 889, 875, 856, 835, 804, 785, 748, 669, 650, 553, 540 cm^{-1}. elemental analysis calcd (%) for $C_{11}H_{12}N_{10}O_{15}$ (524.28), %: C 25.20; H 2.31; N 26.72; found: C 25.22; H 2.21; N 26.77.

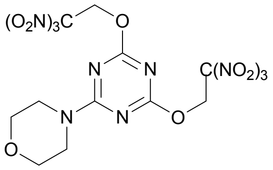


Table 1S. Selected torsion angles (°) in symmetrically independent molecules A, A', A'' of compound **16**, as well as compounds **21** and **20**.

Torsion angle	**16**			**21**	**20**
	A	A'	A''		
N1-C1-O1-C4	178.8(6)	-173.2(6)	-171.3(6)	-175.1(2)	-178.8(2)
C1-O1-C4-C5	129.9(6)	117.5(7)	113.7(7)	158.7(2)	-144.1(2)
O1-C4-C5-N4	40.4(7)	36.5(8)	41.6(8)	49.2(2)	-44.2(2)
O1-C4-C5-N5	-80.2(7)	-83.2(7)	-80.3(7)	-73.5(2)	75.8(2)
O1-C4-C5-N6	159.8(5)	155.9(6)	161.3(6)	168.6(2)	-163.6(2)
C4-C5-N4-O2	-131.3(7)	-127.4(7)	-121.1(7)	-141.0(2)	107.0(2)
C4-C5-N5-O5	-139.5(7)	-141.9(9)	-151.5(7)	-136.9(2)	169.6(2)
C4-C5-N6-O6	-141.6(7)	-142.2(7)	-140.6(7)	-145.8(2)	150.8(2)
N2-C2-O8-C6	172.7(6)	179.2(6)	-179.8(6)	177.9(2)	
C2-O8-C6-C7	160.7(7)	161.4(6)	162.7(6)	167.6(2)	
O8-C6-C7-N7	46.8(9)	-50.0(7)	-50.2(7)	54.6(2)	
O8-C6-C7-N8	-78.5(8)	73.6(7)	70.6(7)	-68.0(2)	
O8-C6-C7-N9	166.1(6)	-167.2(5)	-168.5(5)	174.2(2)	
C6-C7-N7-O9	-114.3(10)	140.8(7)	143.7(7)	111.7(2)	
C6-C7-N8-O12	-127.1(8)	137.6(7)	123.3(7)	150.6(2)	
C6-C7-N9-O13	-157.7(8)	137.8(7)	144.5(7)	143.6(2)	
N3-C3-O15-C8	176.3(6)	179.7(6)	178.8(6)		
C3-O15-C8-C9	-131.8(7)	-145.6(6)	-143.2(6)		
O15-C8-C9-N10	-45.8(8)	-42.2(8)	-42.6(8)		
O15-C8-C9-N11	77.0(8)	80.5(7)	78.0(8)		
C8-C9-N10-O17	137.1(8)	130.0(7)	127.9(7)		
C8-C9-N11-O19	126.3(7)	146.2(7)	145.3(7)		
C8-C9-N12-O20	133.4(7)	130.6(7)	133.4(7)		

Estimation of of pair intermolecular interaction energies was carried out as follows.

1. The closest molecular surroundings was chosen based on consideration of shortened intermolecular contacts. Molecule is considered to be the closest neighbour if at least one intermolecular contact is equal to or less than van-der-Waals radius + 0.1Å.
2. So chosen pairs were taken for quantum chemical calculation using X-ray geometry without further optimization
3. Calculation was carried out within M052X/6-311G(df,pd) level of theory using the Gaussian program [Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, ReVision E.01*; Gaussian, Inc.: Wallingford, CT, 2004.]
4. Pair intermolecular energy was estimated as the difference between the energy of dimer and twice the energy of isolated molecule including BSSE.

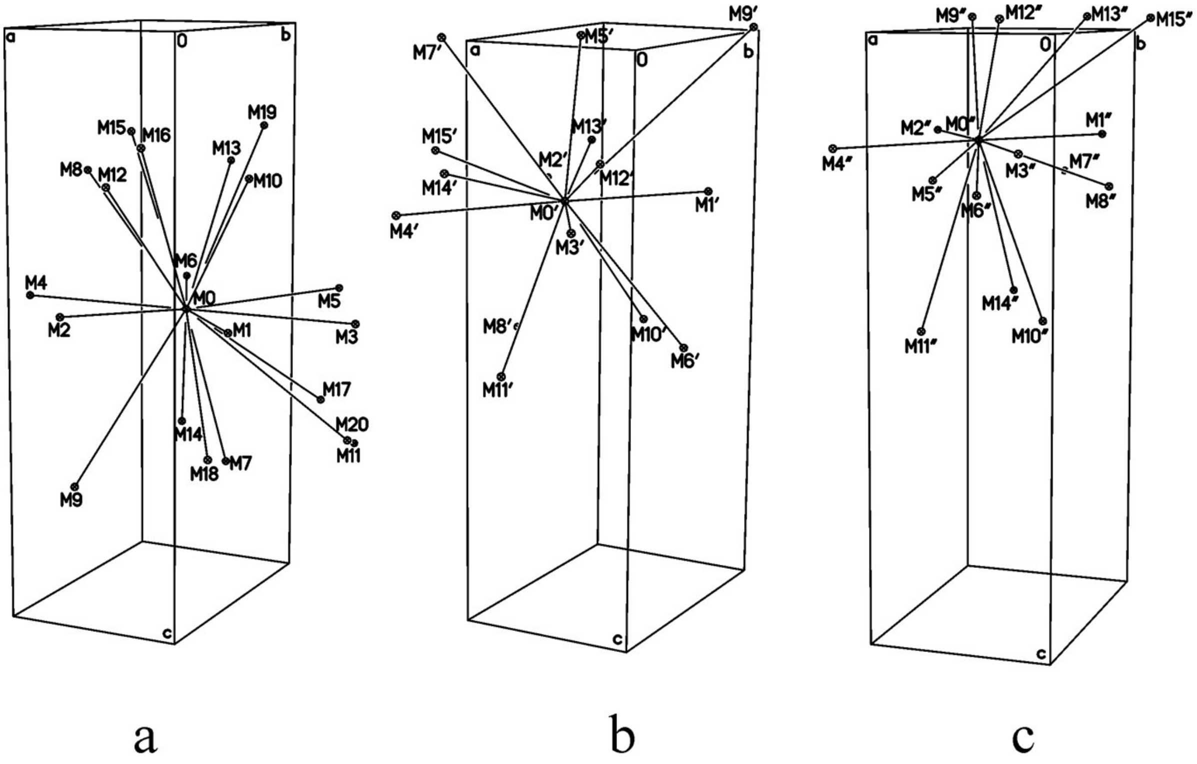


Figure 1S. Intermolecular interaction pattern of molecules A (a), A' (b) and A" (c) in the crystal structure of compound **16**. Central molecule and its environment are represented as small circles; central molecules are denoted as M0, M0', M0". Numbering of the environment corresponds to Tables 2S-4S.

Molecules in the crystal of compound **16** are connected to each other by peak/hole interactions of the nitrogen and oxygen atoms of the nitro groups as well as by stacking interactions between π-density of the triazine rings, and C-H…O contacts. Atoms of the nitro groups are involved in nearly all close contacts observed (Tables 2S-4S). For the molecule A, the strongest interaction is observed between molecules of the same type (A…A, M0…M1, M0…M2), however relatively strong interactions are also observed for A…A' and A…A" pairs (M0…M7, M0…M14, M0…M15). At the same time, molecules A' and A" strongly interact to each other; the strongest attraction is provided by the triazine…triazine stacking interaction and by the nitro group…nitro group peak/hole interaction. A number of A'…A' and A"…A" interacting pairs is relatively low and their energies are smaller.

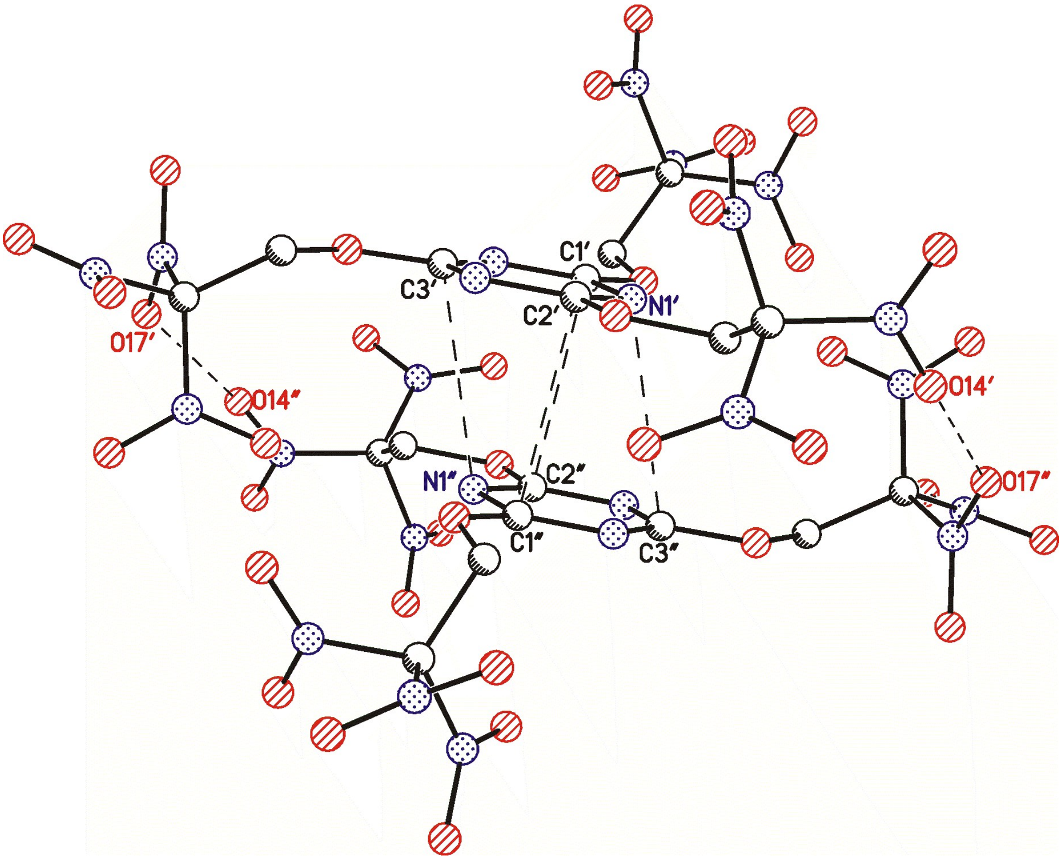


Figure 2S. Stacking-connected dimer for molecular pair A'…A" (M0'…M12', Entry 12). The shortest atom…atom contacts are given by dashed lines.

Table 2S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A of compound **16** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation

Entry*	No**	Type of pair interaction	Shortened contact	Symmetry code	Distance	Energy
1	–	A…A	H4A…O3	-1/2+x,1/2-y,z	2.505	-6.7
2	–	A…A	O3…H4A	1/2+x,1/2-y,z	2.505	-6.7
3	–	A…A	H8A…O13	-1+x,y,z	2.641	-4.4
4	–	A…A	O13…H8A	1+x,y,z	2.641	-4.4
5	–	A…A	O21…O8 O21…O10	-1/2+x,1.5-y,z	3.011 2.810	-3.9
6	–	A…A	O8…O21 O10…O21	1/2+x,1.5-y,z	3.011 2.810	-3.9
7	(5')	A…A'	O17…O21'	1/2-x,1/2+y,1/2+z	2.852	-4.1
8	(6')	A…A'	O14…O3'	1/2+x,1/2-y,z	2.822	-3.3
9	(7')	A…A'	H4B…O20'	1-x,-y,1/2+z	2.440	-3.1
10	(8')	A…A'	C3…O6'	-1/2+x,1/2-y,z	2.855	-2.4
11	(9')	A…A'	O17…O12' O19…O12'	-x,1-y,1/2+z	2.872 2.974	-0.6
12	(10')	A…A'	O2…O3'	x,y,z	3.083	-0.4
13	(11')	A…A'	O9…O7'	x,1+y,z	2.924	-0.1
14	(9")	A…A"	N1…O6" N3…O3" C1…O3" C2…O6"	1-x,1-y,1/2+z	2.842 3.064 3.158 2.920	-5.4
15	(10")	A…A"	O11…O21" N8…O21"	x,y,z	2.969 2.966	-4.0
16	(11")	A…A"	O5…O21"	-1/2+x,1/2-y,z	2.860	-1.3
17	(12")	A…A"	O19…O7" O21…O7"	1/2-x,1/2+y,1/2+z	2.836 2.941	-1.1
18	(13")	A…A"	O7…O2"	1/2-x,-1/2+y,1/2+z	2.875	-1.0
19	(14")	A…A"	O11…O12"	-1/2+x,1.5-y,z	2.989	-0.8
20	(15")	A…A"	O17…O5"	-x,1-y,1/2+z	3.038	-0.5
Sum of all interaction energies of molecule A						-58.1

* Numbers of entries correspond to numbers of neighbouring molecules in Figure 1S

** Numbers of entries given in the second column in parentheses correspond to the equivalent interactions from Tables 3S and 4S

Table 3S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A' of compound **16** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation

Entry*	No**	Type of pair interaction	Shortened contact	Symmetry code	Distance	Energy
1'	–	A'…A'	O12'…N2' O14'…O10' O14'…C2' H6'B…O10'	-1/2+x,1/2-y,z	2.991 3.001 2.971 2.426	-6.8
2'	–	A'…A'	O10'…O14' O10'…H6'B N2'…O12' C2'…O14'	1/2+x,1/2-y,z	3.001 2.426 2.991 2.971	-6.8
3'	–	A'…A'	O19'…O20'	-1/2+x,-1/2-y,z	3.014	-0.3
4'	–	A'…A'	O20'…O19'	1/2+x,-1/2-y,z	3.014	-0.3
5'	(7)	A'…A	O21'…O17	1/2-x,-1/2+y,-1/2+z	2.852	-4.1
6'	(8)	A'…A	O3'…O14	-1/2+x,1/2-y,z	2.822	-3.3
7'	(9)	A'…A	O20'…H4B	1-x,-y,-1/2+z	2.440	-3.1
8'	(10)	A'…A	O6'…C3	1/2+x,1/2-y,z	2.855	-2.4
9'	(11)	A'…A	O12'…O17 O12'…O19	-x,1-y,-1/2+z	2.872 2.974	-0.6
10'	(12)	A'…A	O3'…O2	x,y,z	3.083	-0.4
11'	(13)	A'…A	O7'…O9	x,-1+y,z	2.924	-0.1
12'	(5")	A'…A"	O11'…C4" O14'…O17" O17'…O14" O18'…N1" N1'…O18" N1'…C3" C1'…C2" C2'…C1" C3'…N1" C4'…O11"	-1/2+x,1/2-y,z	3.124 2.818 2.827 2.997 2.991 3.225 3.129 3.125 3.217 3.152	-10.4
13'	(6")	A'…A"	O2'…O17" O2'…O19" O9'…O7" O14'…O16" N9'…O16"	x,y,z	2.952 2.987 2.934 3.015 2.958	-8.4
14'	(7")	A'…A"	O7'…O9" O17'…O2" O19'…O2"	x,-1+y,z	3.034 2.963 2.982	-7.1
15'	(8")	A'…A"	O5'…O21" O5'…N12" O20'…O5" N12'…O5"	1/2+x,1/2-y,z	2.975 2.955 2.946 2.931	-4.5
Sum of all interaction energies of molecule A						-58.6

* Numbers of entries correspond to numbers of neighbouring molecules in Figure 1S

** Numbers of entries given in the second column in parentheses correspond to the equivalent interactions from Tables 2S and 4S

Table 4S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule A" of compound **16** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation

Entry*	No**	Type of pair interaction	Shortened contact	Symmetry code	Distance	Energy
1"	–	A"…A"	O10"… O14" C2"…O14"	-1/2+x,1.5-y,z	3.000 2.998	-7.5
2"	–	A"…A"	O14"…O10" O14"…C2"	½+x,1.5-y,z	3.000 2.998	-7.5
3"	–	A"…A"	O20"…O19"	-1/2+x,1/2-y,z	3.049	-0.4
4"	–	A"…A"	O19"…O20"	½+x,1/2-y,z	3.049	-0.4
5"	(12')	A"…A'	O11"…C4' O14"…O17' O17"…O14' O18"…N1' N1"…O18' N1"…C3' C1"…C2' C2"…C1' C3"…N1' C4"…O11'	½+x,1/2-y,z	3.152 2.827 2.818 2.991 2.997 3.217 3.125 3.129 3.225 3.124	-10.4
6"	(13')	A"…A'	O17"…O2' O19"…O2' O7"…O9' O16"…O14' O16"…N9'	x,y,z	2.952 2.987 2.934 3.015 2.958	-8.4
7"	(14')	A"…A'	O9"…O7' O2"…O17' O2"…O19'	x,1+y,z	3.034 2.963 2.982	-7.1
8"	(15')	A"…A'	O5"…O20' O5"…N12' O21"…O5' N12"…O5'	-1/2+x,1/2-y,z	2.946 2.931 2.975 2.955	-4.5
9"	(14)	A"…A	O3"…N3 O3"…C1 O6"…N1 O6"…C2	1-x,1-y,-1/2+z	3.064 3.158 2.842 2.920	-5.4
10"	(15)	A"…A	O21"…O11 O21"…N8	x,y,z	2.969 2.966	-4.0
11"	(16)	A"…A	O21"…O5	1/2+x,1/2-y,z	2.860	-1.3
12"	(17)	A"…A	O7"…O19 O7"…O21	1/2-x,-1/2+y,-1/2+z	2.836 2.941	-1.1
13"	(18)	A"…A	O2"…O7	1/2-x,1/2+y,-1/2+z	2.875	-1.0
14"	(19)	A"…A	O12"…O11	½+x,1.5-y,z	2.989	-0.8
15"	(20)	A"…A	O5"…O17	-x,1-y,-1/2+z	3.038	-0.5
Sum of all interaction energies of molecule A						-58.3

* Numbers of entries correspond to numbers of neighbouring molecules in Figure 1S

** Numbers of entries given in the second column in parentheses correspond to the equivalent interactions from Tables 2S and 3S

Table 5S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **21** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation

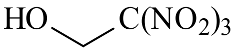
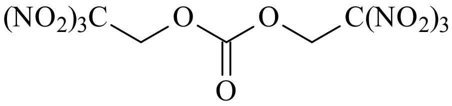
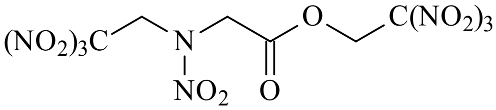
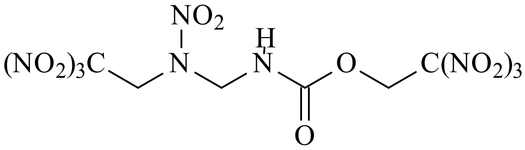
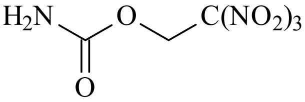
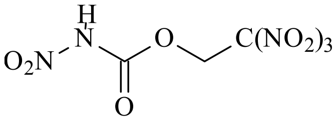
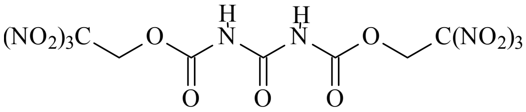
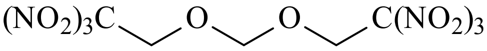
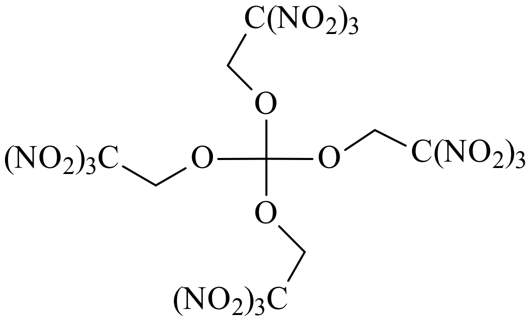
Entry	Shortened contact	Symmetry Code	Distance	Energy
1	N2…N10	3-x,2-y,1-z	2.956	-16.6
	N2…H2		2.107	
	N10…N2		2.956	
	H2…N2		2.107	
2	O10…N3	2-x,2-y,1-z	3.135	-11.2
	N3…O10		3.135	
	O9…N10		3.109	
	N10…O9		3.109	
3	O4…O2	1-x,2-y,-z	2.941	-7.4
	O2…O4'		2.761	
	N4…O4'		3.094	
	O6…O11		3.106	
	O11…O6		3.106	
	O2…N1		3.061	
	N1…O2		3.061	
4	O4…C1	2-x,2-y,-z	3.240	-6.6
	O4…O4'		3.079	
	O5…N2		3.113	
	O5…C2		3.053	
	O5…C3		3.319	
	N2…O5		3.113	
	C2…O5		3.053	
	C3…O5		3.319	
	O7…O11		3.014	
	O11…O7		3.014	
5	O3…H4A	-1+x,y,z	2.491	-3.8
	O14…O8		3.076	
	O14…O11		2.987	
	O14…O12		3.076	
	O14…N8		2.933	
6	O8…O14	1+x,y,z	3.076	-3.8
	O11…O14		2.987	
	O12…O14		3.076	
	N8…O14		2.933	
	H4A…O3		2.491	
7	O11…O6	x,-1+y,z	3.106	-2.9
	O13…O3		2.980	
8	O3…O13	x,1+y,z	2.980	-2.9
	O6…O11		3.106	
9	O13…O7	-1+x,-1+y,z	3.083	-2.3
10	O7…O13	1+x,1+y,z	3.083	-2.3
11	O6…O7	2-x,3-y,-z	3.050	-0.4
	O7…O6		3.050	
	O7…O7		3.064	
12	O9…O9	1-x,1-y,1-z	2.811	-0.1
	O9…O13		3.043	
	O13…O9		3.043	
13	O10…O12	2-x,1-y,1-z	3.144	-0.1
	O12…O10		3.144	

Table 6S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of molecule of compound **20** with its closest environment in the crystal obtained at M052X/6-311G(df,pd) and M052X/aug-cc-pvdz levels of approximation[a].

Entry	Shortened contact	Symmetry Code	Distance	Energy[b]	Energy[c]	Comment
1	O8…N2 O8…H2 N2…O8 H2…O8	1-x,1-y,-z	2.822 1.963 2.822 1.963	-10.5	-10.3	Inside the layer
2	O8…O3 N2…O3 C2…O3 O9…N1 O9…H1	x,1/2-y,-1/2+z	3.138 3.141 2.862 2.763 1.912	-9.3	-9.2	Inside the layer
3	O3…O8 O3…N2 O3…C2 N1…O9 H1…O9	x,1/2-y,1/2+z	3.138 3.141 2.862 2.763 1.912	-9.3	-9.2	Inside the layer
4	O4…O6 O9…C4 O9…H4A N3…O3	x,-1/2-y,-1/2+z	3.090 3.314 2.344 3.149	-8.1	-7.9	Inside the layer
5	O3…N3 O6…O4 C4…O9 H4A…O9	x,-1/2-y,1/2+z	3.149 3.090 3.314 2.344	-8.1	-7.9	Inside the layer
6	O9…C3 C3…O9 C3…C3	1-x,-y,-z	3.247 3.247 3.488	-5.9	-5.9	Inside the layer
7	O1…O8 N1…O8 C1…O8	1-x,-1/2+y,1/2-z	3.041 2.959 2.966	-3.7	-3.7	Inside the layer
8	O8…O1 O8…N1 O8…C1	1-x,1/2+y,1/2-z	3.041 2.959 2.966	-3.7	-3.7	Inside the layer
9	O2…O5 O5…O2 O5…O6 O5…N4 O6…O5 N4…O5	-x,-y,1-z	2.904 2.904 3.092 3.117 3.092 3.117	-2.1	-2.0	Between layers
10	O5…O4 O7…O5	-x,-1/2+y,1/2-z	3.118 2.956	-1.8	-1.9	Between layers
11	O4…O5 O5…O7	-x,1/2+y,1/2-z	3.118 2.956	-1.8	-1.9	Between layers
12	O7…O2	x,-1+y,z	3.095	-0.1	-0.3	Inside the layer
13	O2…O7	x,1+y,z	3.095	-0.1	-0.3	Inside the layer
14	O6…O6	-x,-1-y,1-z	3.139	-0.1	-0.2	Between layers

[a] in columns 5 and 6, energy obtained at M052X/6-311G(df,pd) and M052X/aug-cc-pvdz levels, respectively; it is seen that differences in energies do not exceed 0.2 kcal/mol

Table 7S. List of selected energetic aliphatic trinitroethoxy compounds studied by X-ray crystallography.

Entry	Compound	Density/T[a]	Density[b]
1		1.839/100	1.777
2		1.975/100	1.908
3		1.922/173	1.881
4		1.815/173	1.776
5		1.839/173	1.799
6		1.729/243	1.712
7		1.899/173	1.858
8		1.844[b]	1.813
9		1.938[b]	1.905

[a] Density (g/cm^3) calculated from X-ray data at experimental temperature.

[b] Density (g/cm^3) recalculated at room temperature for easily comparison; recalculation was carried out based on data from Tables 10s and 11S, and our recent X-ray studies on polynitro compounds and high nitrogen heterocycles at 100K and room temperature [Refs. 2c, 2p from main text, and Sheremetev, A. B.; Aleksandrova, N. S.; Suponitsky, K. Yu.; Antipin M. Yu.; Tartakovsky, V. A. *Mendeleev Commun.*, **2010**, *20*, 249-252; Vatsadze, I. A.; Serushkina, O. V.; Dutov, M. D.; Shkineva, T. K.; Suponitsky, K. Yu.; Ugrak, B. I.; Dalinger, I. L. *Chem. Heterocycl. Comp.*, **2015**, *51*, 695-703]. It appears that decrease of density from 100 to 298K

vary in narrow range (3-4%). Densities were recalculated using 3.5% as average value in assumption of linear dependence of density *vs*. temperature ($d_T = -kT+b$).

[c] There are two polymorphs. Only the densest polymorph is taken into consideration. For entry 8, density of the second polymorph is 1.778 g/cm^3 at 200K. For entry 9, density of the second polymorph is 1.808 g/cm^3 at 258K.

A replacement at the carbonyl core of one trinitroethoxy moiety with amino group or substituted amino group leads to a reduction in density (compare entry 2 with entries 4-7). Compound from entry 7 which form strongly H-bonded dimers (as in the case of compound **21**) have greatest density among these amides and contain four independent molecules in the asymmetric unit cell. Dramatic changes in density is also observed for ethers bearing four or two trinitroethoxy moieties at the one-carbon core, respectively (compare entries 8 and 9).

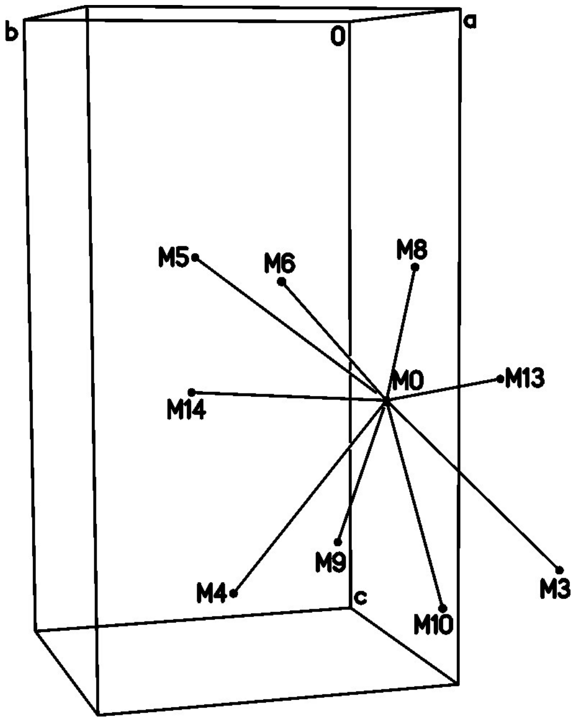


Figure 3S. Intermolecular interaction pattern of the central molecule of *bis*(2,2,2-trinitroethyl) carbonate (see, table 1, entry 2). Environment is presented as small circles; the central molecule is denoted as M0; numbering of the environment corresponds to numbering in Table 8S; only neighbours with interaction energy higher than 2 kcal/mol are shown.

Table 8S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of *bis*(2,2,2-trinitroethyl) carbonate molecule with its closest environment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Shortened contact	Symmetry Code	Distance	Energy
1	O5…N6 O5…O14 O5…O15 O8…O13	1/2-x,-y,-1/2+z	2.994 2.863 2.942 2.942	-1.2
2	N6…O5 O13…O8 O14…O5 O15…O5	1/2-x,-y,1/2+z	2.994 2.942 2.863 2.942	-1.2
3	O12…O15	1-x,-1/2+y,1.5-z	2.993	-4.4
4	O15…O12	1-x,1/2+y,1.5-z	2.993	-4.4
5	O8…C2 O8…O1	-1/2+x,1/2-y,1-z	3.079 3.046	-2.2
6	C2…O8 O1…O8	1/2+x,1/2-y,1-z	3.079 3.046	-2.2
7	O5…O6 O6…O5 O6…O6	-x,-y,1-z	2.957 2.957 3.070	-0.9
8	H2…O1 C2…O1 N1…O1 O1…H2 O1…C2 O1…N1 O1…O5 O5…O1	1-x,-y,1-z	2.447 3.260 3.000 2.447 3.260 3.000 3.068 3.068	-10.6
9	O2…O11 O3…O11 O7…O11 O14…N4 O14…O12	-1/2+x,y,1.5-z	3.027 2.985 3.072 3.104 2.838	-4.7
10	N4…O14 O11…O2 O11…O3 O11…O7 O12…O14	1/2+x,y,1.5-z	3.104 3.027 2.985 3.072 2.838	-4.7
11	O9…O15	x,1/2-y,-1/2+z	3.075	-0.1
12	O15…O9	x,1/2-y,1/2+z	3.075	-0.1
13	O4…N3 O4…O7 O4…O8	1/2-x,-1/2+y,z	3.012 2.832 3.093	-5.3
14	N3…O4 O7…O4 O8…O4	1/2-x,1/2+y,z	3.012 2.832 3.093	-5.3

Description of the crystal packing of cyanuric acid

In order to find the reasons for lower density of the crystal structure of cyanuric acid in comparison to 1,3,5-triazines **16**, **20**, **21**, we have investigated crystal structure of cyanuric acid in the same way as done for the triazines (using combination of geometrical and energetic approaches). In the case of cyanuric acid, visual analysis coincides with a description based on pair intermolecular energies (Table 9S).

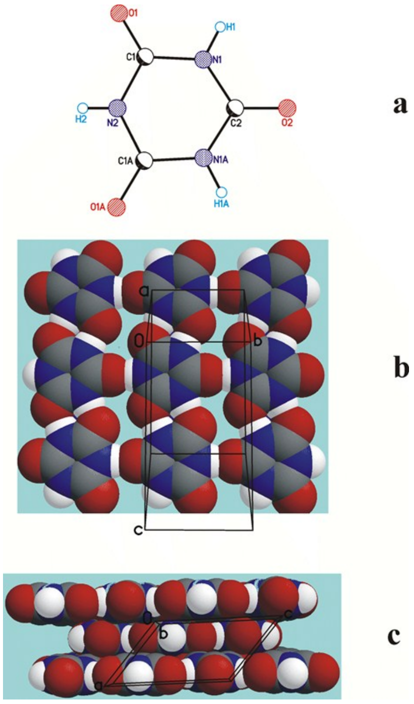


Figure 4S. General view of the molecule (a), and crystal packing fragments of cyanuric acid. Atoms are presented as spheres of van-der-Waals radius (C: 1.75; N: 1.61; O: 1.58; H: 1.2 Å; Rowland, R.S.; Taylor, R. *J. Phys. Chem.*, **1996**, *100*, 7384-7391). b) H-bonded layers, projection onto *bc* crystallographic plane; c) projection onto *ac* crystallographic plane.

By means of strong H-bonds, molecules are assembled into the layers parallel to the *bc* crystallografic plane (Fig. 4Sb) while connection between layers is provided by $\pi \ldots \pi$ stacking interactions (Fig. 4Sc). The former interactions are stronger than the latter ones, therefore energy inside the layer is higher (37.4 kcal/mol, M1, M2, M3, M4, M13, M14) than that between the layers (-19.4 kcal/mol, M5-M12). Nevertheless the stacking interactions are still significantly stronger than nitro…nitro interactions observed in trinitroethoxy triazines. Therefore crystal structure of cyanuric acid is stabilized by strong interactions in all three directions. Why its density is lower than that of trinitroethoxy triazines? An answer to this question can be obtained by a quick glance at Figure 4S. Due to strong H-bonding interactions and their directionality, molecules in H-bonded layer (Figure 4Sb) are arranged so that layers contain voids (strong intermolecular bonding restricts molecular freedom of movement). In perpendicular direction, as stated above, intermolecular interactions are weaker, and molecules are packed more densely (no voids observed in Figure 4Sc). However intralayer voids cannot be filled with atoms of the adjacent layers that leads to lower density of cyanuric acid in comparison to trinitroethoxy triazines.

Table 9S. Pair intermolecular interaction energies (kcal/mol) and shortened contacts (Å) of cyanuric acid with its closest enviroment in the crystal obtained at M052X/6-311G(df,pd) level of approximation.

Entry	Shortened contact	Symmetry Code	Distance	Energy	Comment
1	N1…O1 O1…N1 O1…H1 H1…O1	1/2-x,1/2-y,-z	2.814 2.814 1.806 1.806	-12.2	Inside the layer
2	N1B…O1B H1B…O1B O1B…N1B O1B…H1B	1/2-x,1/2-y,1-z	2.814 1.806 2.814 1.806	-12.2	Inside the layer
3	N2…O2 H2…O2	x,-1+y,z	2.780 1.770	-6.4	Inside the layer
4	O2…N2 O2…H2	x,1+y,z	2.780 1.770	-6.4	Inside the layer
5	C1…C1 C1…O1 N2…O1 O1…C1 O1…N2 O1…O1	-x,-y,-z	3.367 2.978 3.125 2.978 3.125 3.065	-4.1	Between layers
6	N2…O1B C1B…C1B C1B…O1B O1B…N2 O1B…C1B O1B…O1B	1-x,-y,1-z	3.125 3.367 2.978 3.125 2.978 3.065	-4.1	Between layers
7	C1B…O2 O1B…C2 O1B…O2	-1/2+x,-1/2+y,z	3.243 3.059 3.046	-2.6	Between layers
8	C2…O1 O2…C1 O2…O1	-1/2+x,1/2+y,z	3.059 3.243 3.046	-2.6	Between layers
9	C1…O2 O1…C2 O1…O2	1/2+x,-1/2+y,z	3.243 3.059 3.046	-2.6	Between layers
10	C2…O1B O2…C1B O2…O1B	1/2+x,1/2+y,z	3.059 3.243 3.046	-2.6	Between layers
11	no close contacts	-x,1-y,-z	–	-0.4	Between layers
12	no close contacts	1-x,1-y,1-z	–	-0.4	Between layers
13	no close contacts	1/2-x,-1/2-y,-z	–	-0.1	Inside the layer
14	no close contacts	1/2-x,-1/2-y,1-z	–	-0.1	Inside the layer

X-ray crystallography.

Collected data were analyzed by the SAINT и SADABS programs incorporated into APEX2 program package [*APEX2 and SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, **2009**]. All structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. Hydrogen atoms were located in the difference Fourier maps and refined in isotropic approximation. The refinement was carried out with the SHELXTL program [Sheldrick, G. M. *Acta Crystallogr.*, **2008**, *A64*, 112-122]. The details of data collection and crystal structures refinement for low-temperature experiments are summarized in Table 10S while those for room-temperature experiments are presented in Table 11S. CCDC (numbers 1434738, 1434739 and 1434740 for compounds **16**, **20**, and **21**, respectively at 100K, and 1436944, 1436945 for compounds **21**, **20** at 298K, respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table 10S. Crystallographic data for low-temperature experiment (298K) for compounds **16**, **21**, and **20**.

	16	**21**	**20**
Empirical formula	$C_9H_6N_{12}O_{21}$	$C_7H_6N_{10}O_{14}$	$C_5H_4N_6O_9$
Fw	618.26	454.22	292.14
Temperature, K	100	100	100
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pna2_1$	P-1	$P2_1/c$
a, Å	10.9186(15)	6.0315(5)	13.2903(13)
b, Å	17.007(2)	11.7427(10)	6.6865(7)
c, Å	35.300(5)	11.9923(10)	11.6787(12)
α, deg	90.00	101.500(2)	90.00
β, deg	90.00	101.738(2)	93.175(2)
γ, deg	90.00	97.607(2)	90.00
V, Å^3	6555.0(15)	801.56(12)	1036.24(18)
Z	12	2	4
ρ_{calc}, g·cm^{-3} (at 100K)	1.879	1.882	1.873
ρ_{calc}, g·cm^{-3} (at 298K)	1.809	1.808	1.797
F(000)	3744	460	592
μ, mm^{-1}	0.188	0.183	0.181
θ range, deg.	2.10 – 30.20	1.78 – 28.00	1.53 – 26.99
Reflections collected	80248	14710	15138
Independent reflections / R_{int}	9824/0.1717	3862/0.0456	2234/0.0482
Completeness to theta θ, %	99.4	100.0	99.0
Refined parameters	1134	298	189
GOF (F^2)	1.041	1.058	1.141
Reflections with $I>2\sigma(I)$	6038	2834	1803
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0792	0.0513	0.0467
$wR_2(F^2)$ (all data)[b]	0.2113	0.1240	0.0944
Largest dif. peak/hole, e·Å^{-3}	0.553 / -0.487	0.473 / -0.443	0.313 / -0.264

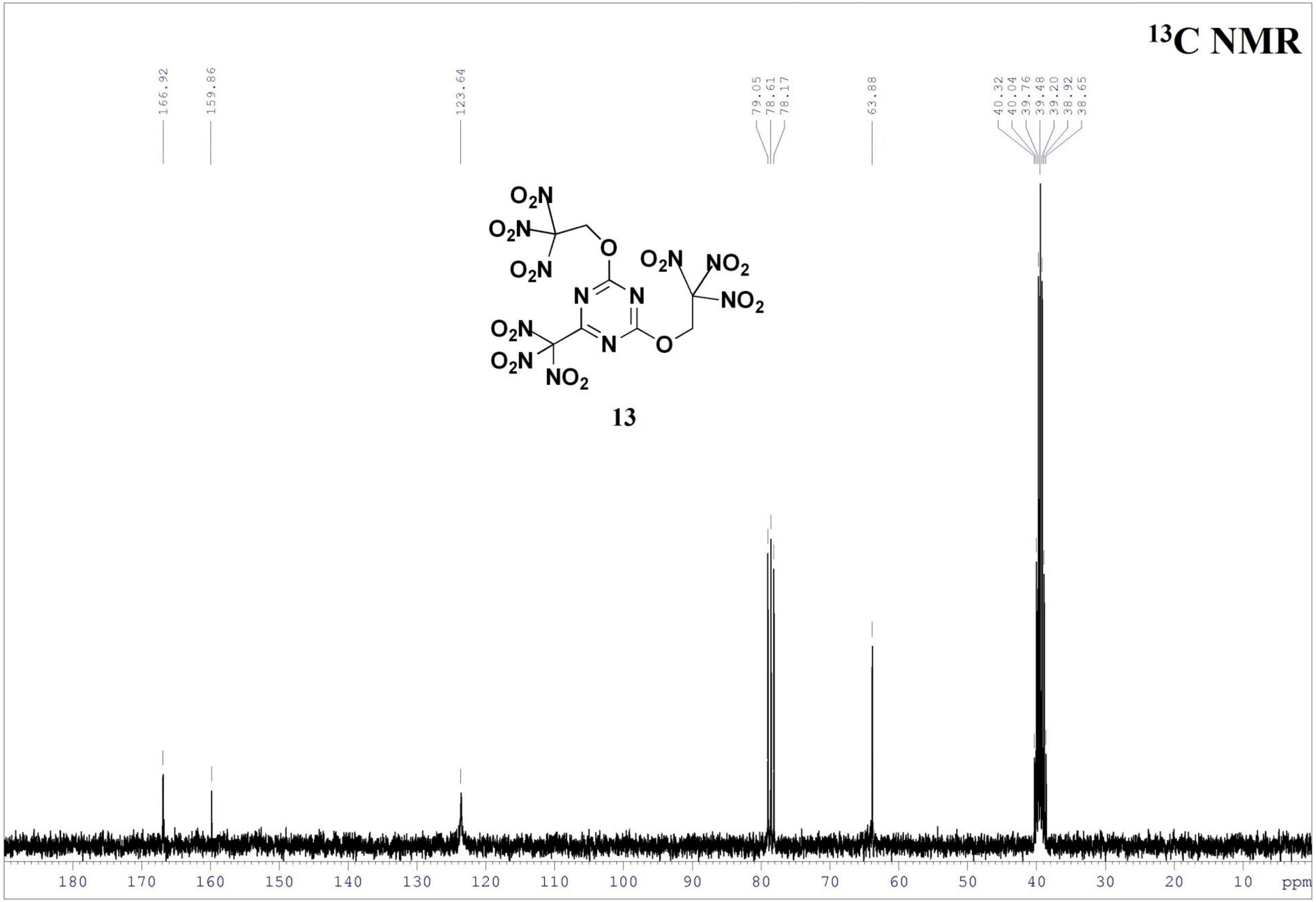
[a] $R_1 = \sum|F_o - |F_c||/\sum(F_o)$. [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{½}$

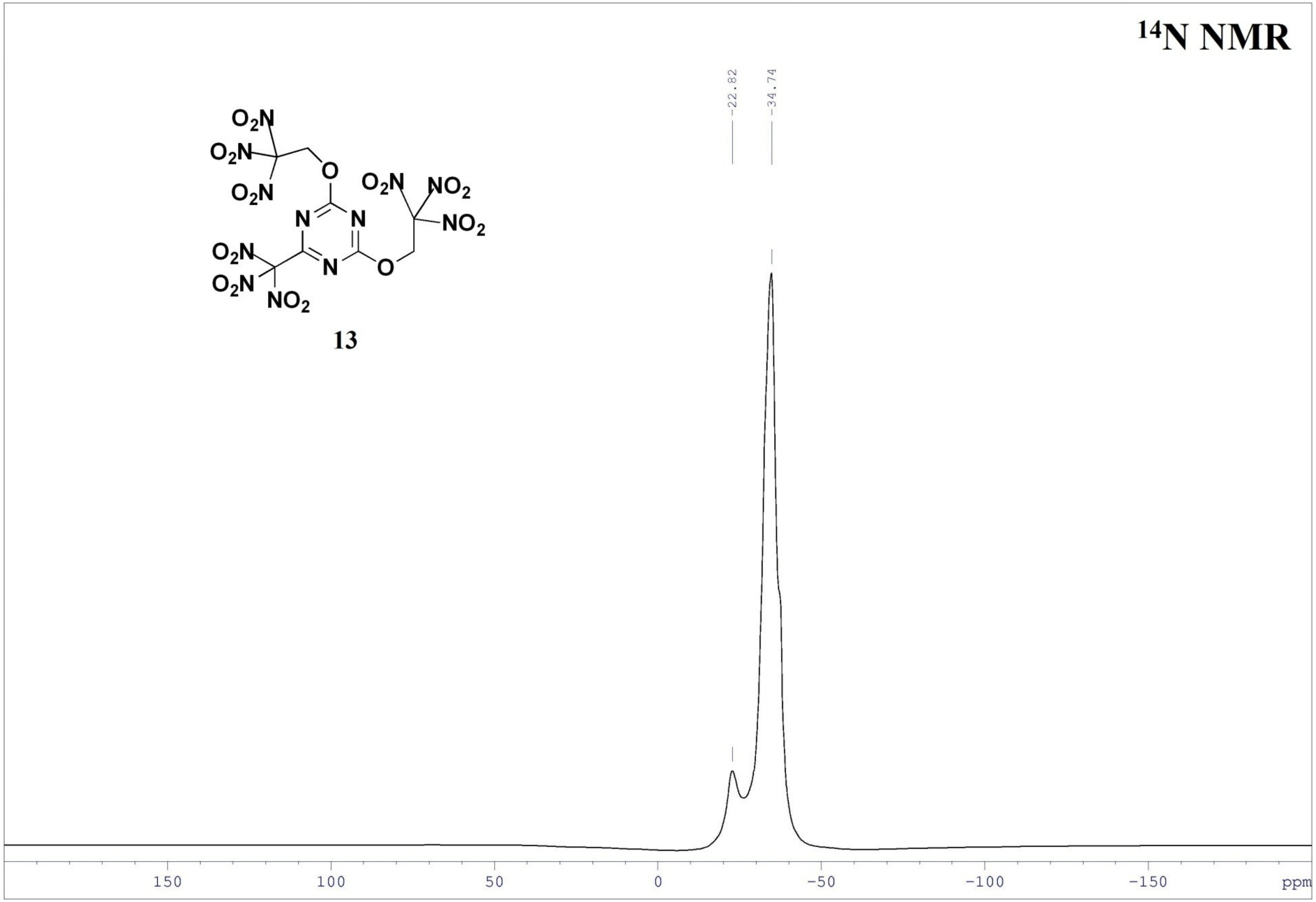
Table 11S. Crystallographic data of room-temperature experiment (298K) for compounds **16**, **21**, and **20**.

	16*	**21**	**20**
Formula	$C_9H_6N_{12}O_{21}$	$C_7H_6N_{10}O_{14}$	$C_5H_4N_6O_9$
Fw	618.26	454.22	292.14
Temperature, K	298	298	298
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$Pna2_1$	P-1	$P2_1/c$
a, Å	11.13(2)	6.1667(12)	13.6640(13)
b, Å	17.05(3)	11.796(2)	6.7290(6)
c, Å	35.85(7)	12.164(2)	11.7479(11)
α, deg.	90.00	101.234(4)	90.00
β, deg.	90.00	102.649(4)	91.804(2)
γ, deg.	90.00	97.005(4)	90.00
V, Å^3	6805(9)	834.2(3)	1079.63(17)
Z	12	2	4
ρ_{calc}, g·cm^{-3} (at 298K)	1.809	1.808	1.797
F(000)	3744	460	592
μ, mm^{-1}		0.176	0.174
θ range, deg.		1.76 – 28.00	1.49 – 27.00
Reflections collected		15317	16874
Independent reflections / R_{int}		4024/0.0551	2369/0.0550
Completeness to theta θ, %		99.9	100.0
Refined parameters		298	189
GOF (F^2)		1.003	1.141
Reflections with $I>2\sigma(I)$		2143	1490
$R_1(F)$ ($I>2\sigma(I)$)[a]		0.0584	0.0501
$wR_2(F^2)$ (all data)[b]		0.1521	0.1477
Largest diff. peak/hole, e·Å^{-3}		0.250 / -0.239	0.267 / -0.271

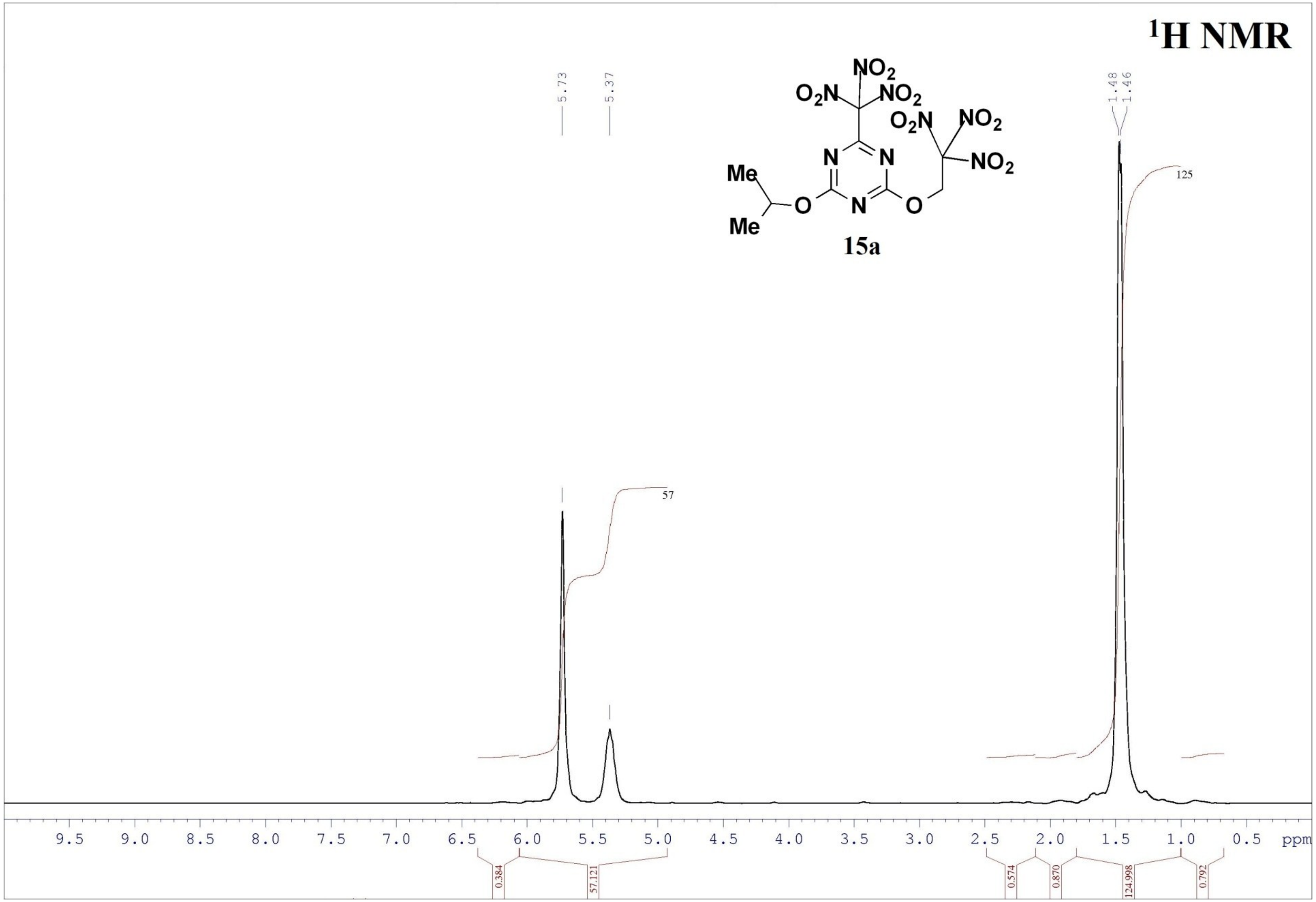
[a] $R_1 = \sum|F_o - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{½}$

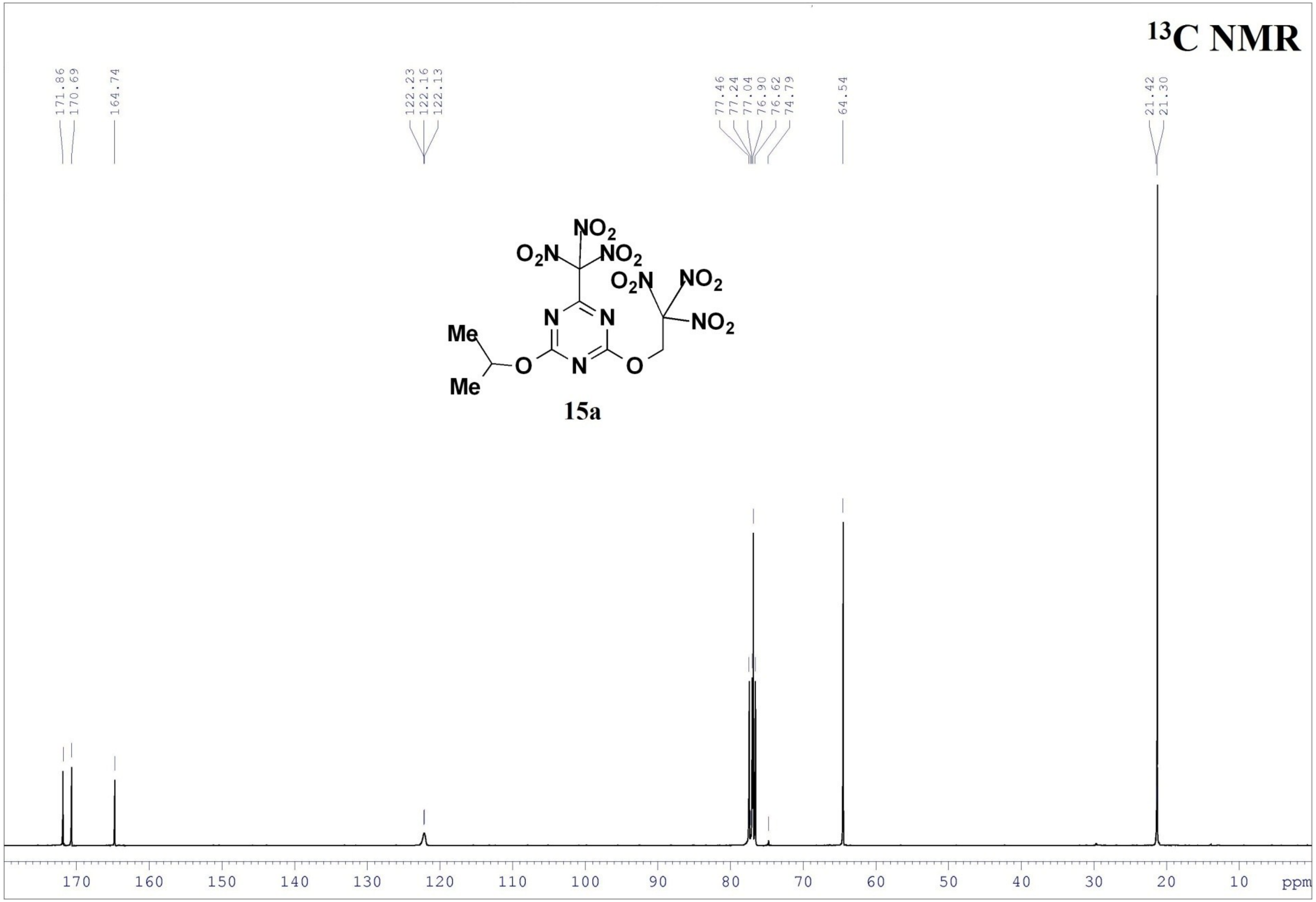
* quality of the room-temperature X-ray experiment for compound **16** is very low due probably to significant thermal motion and possible disorder of the nitro groups. We have determined only unit cell parameters that allow us to estimate room-temperature crystal packing density

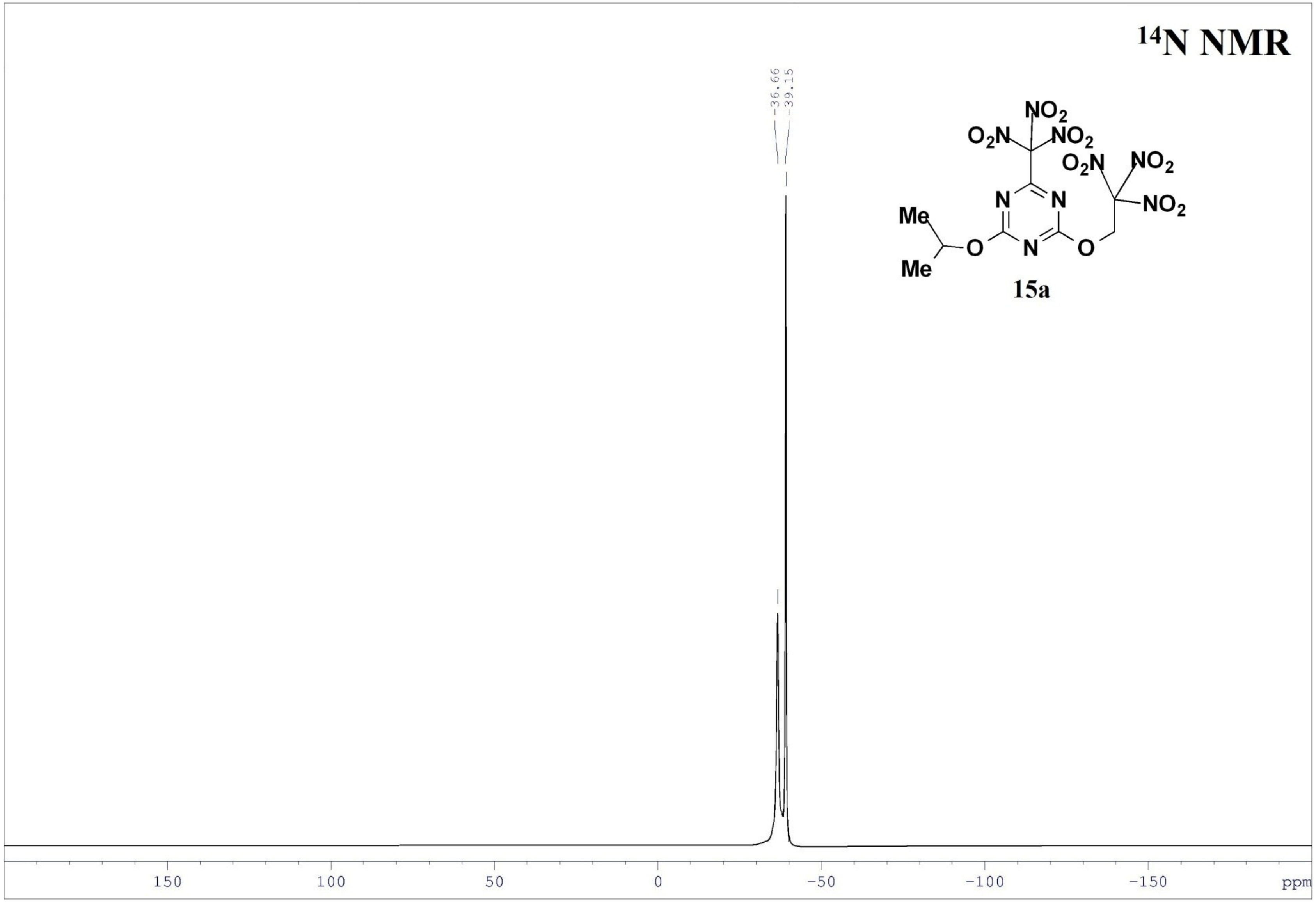

^{13}C NMR
166.92
159.86
123.64
79.05
78.61
78.17
63.88
40.32
40.04
39.76
39.48
39.20
38.92
38.65
O_2N
NO_2
N
O
13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

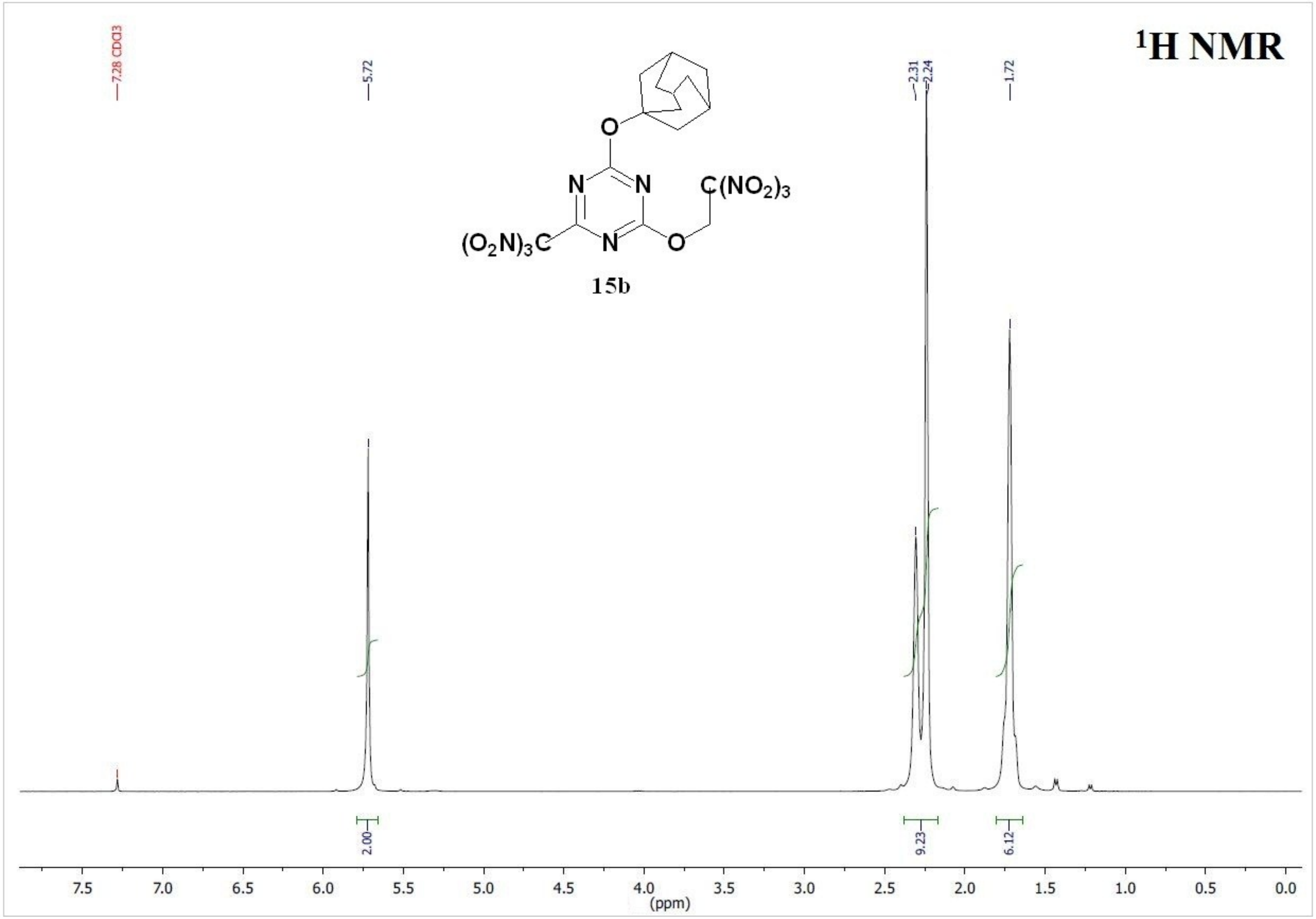

^{14}N NMR
-22.82
-34.74
O_2N
O_2N
O_2N
O
O_2N
NO_2
N
N
NO_2
O_2N
N
O
O_2N
O_2N
NO_2
150
100
50
0
-50
-100
-150
ppm

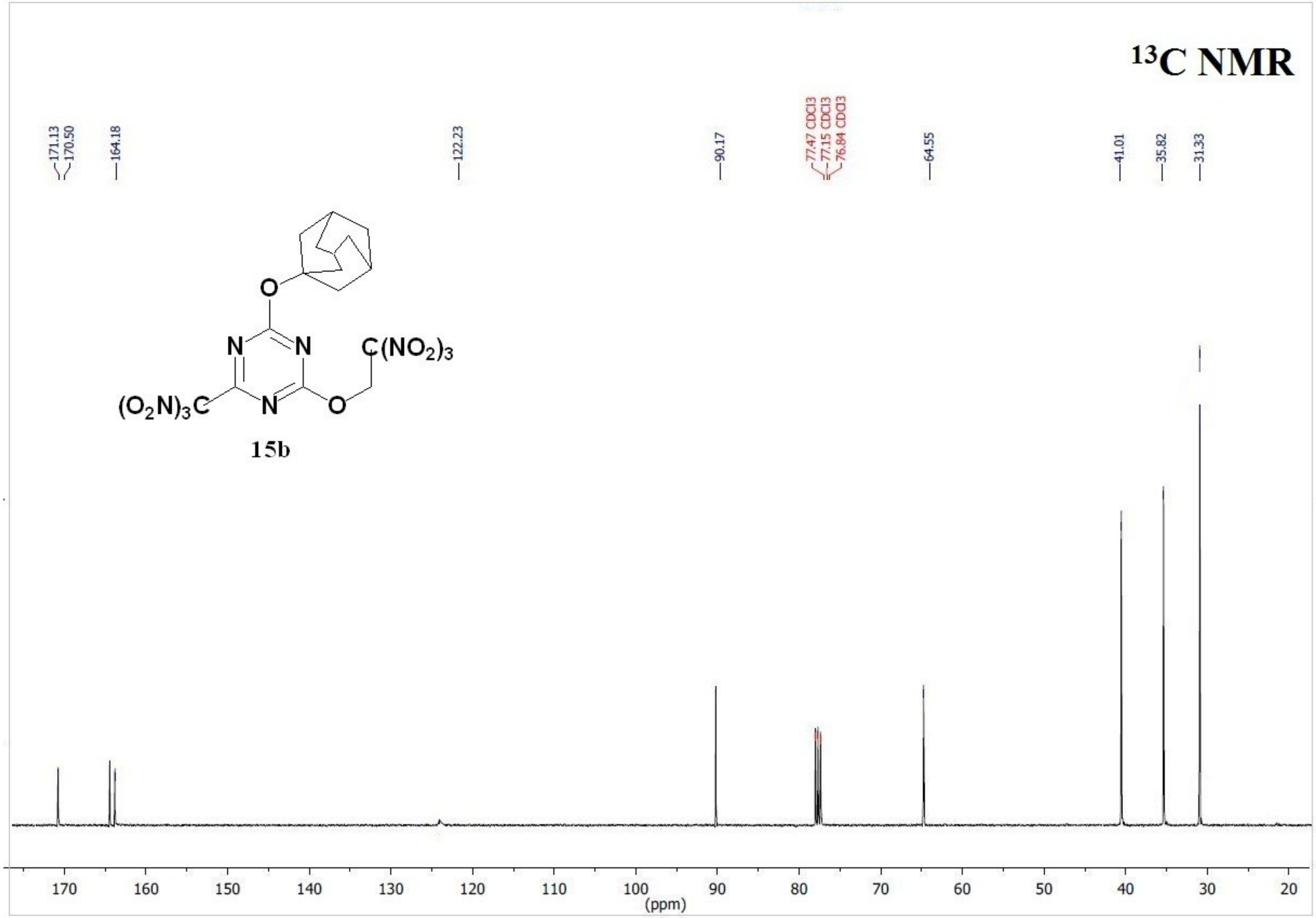
13

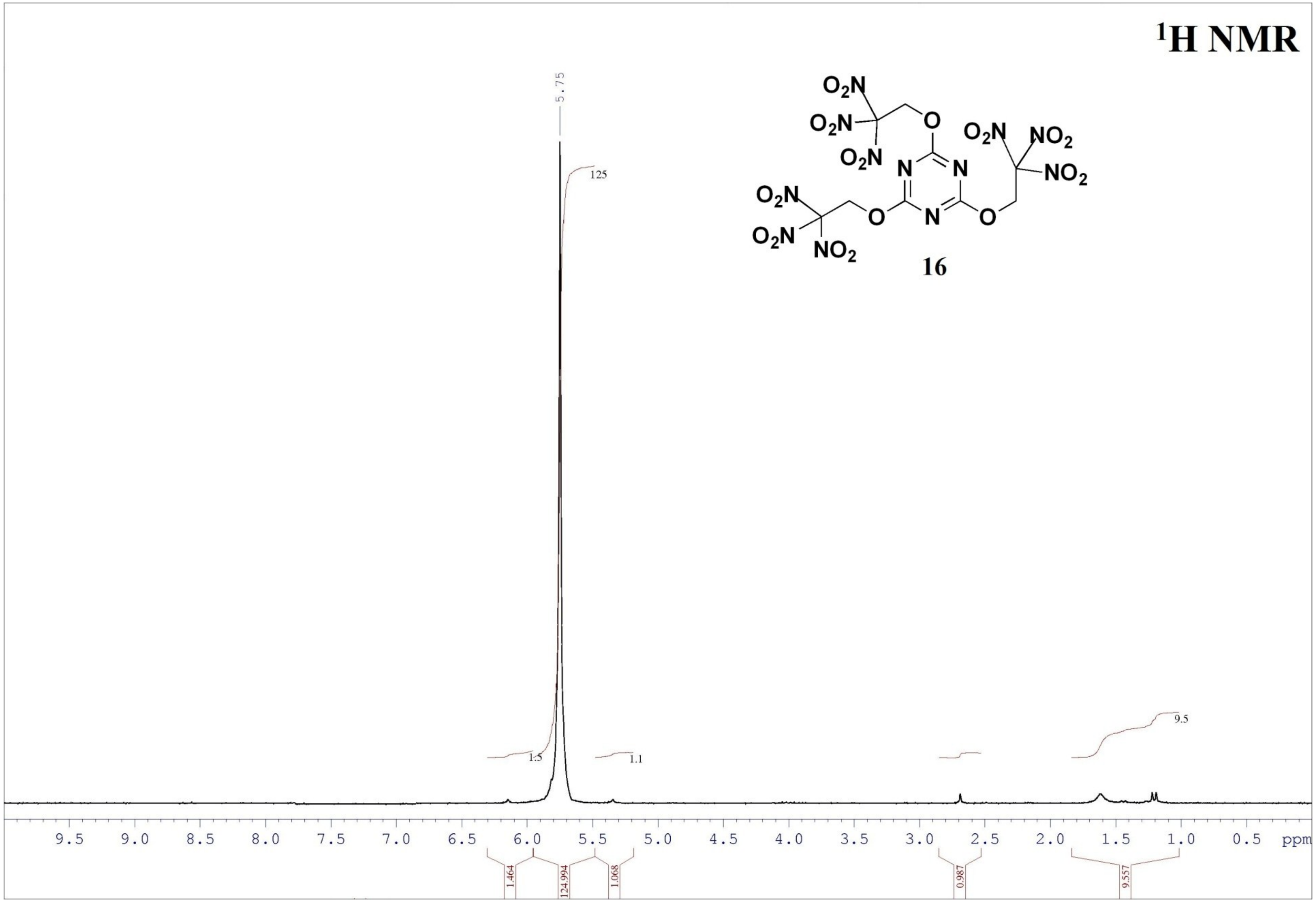

1H NMR
5.73
5.37
1.48
1.46
57
125
15a
Me
Me
O
N
NO2
O2N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.384
57.121
0.574
0.870
124.998
0.792

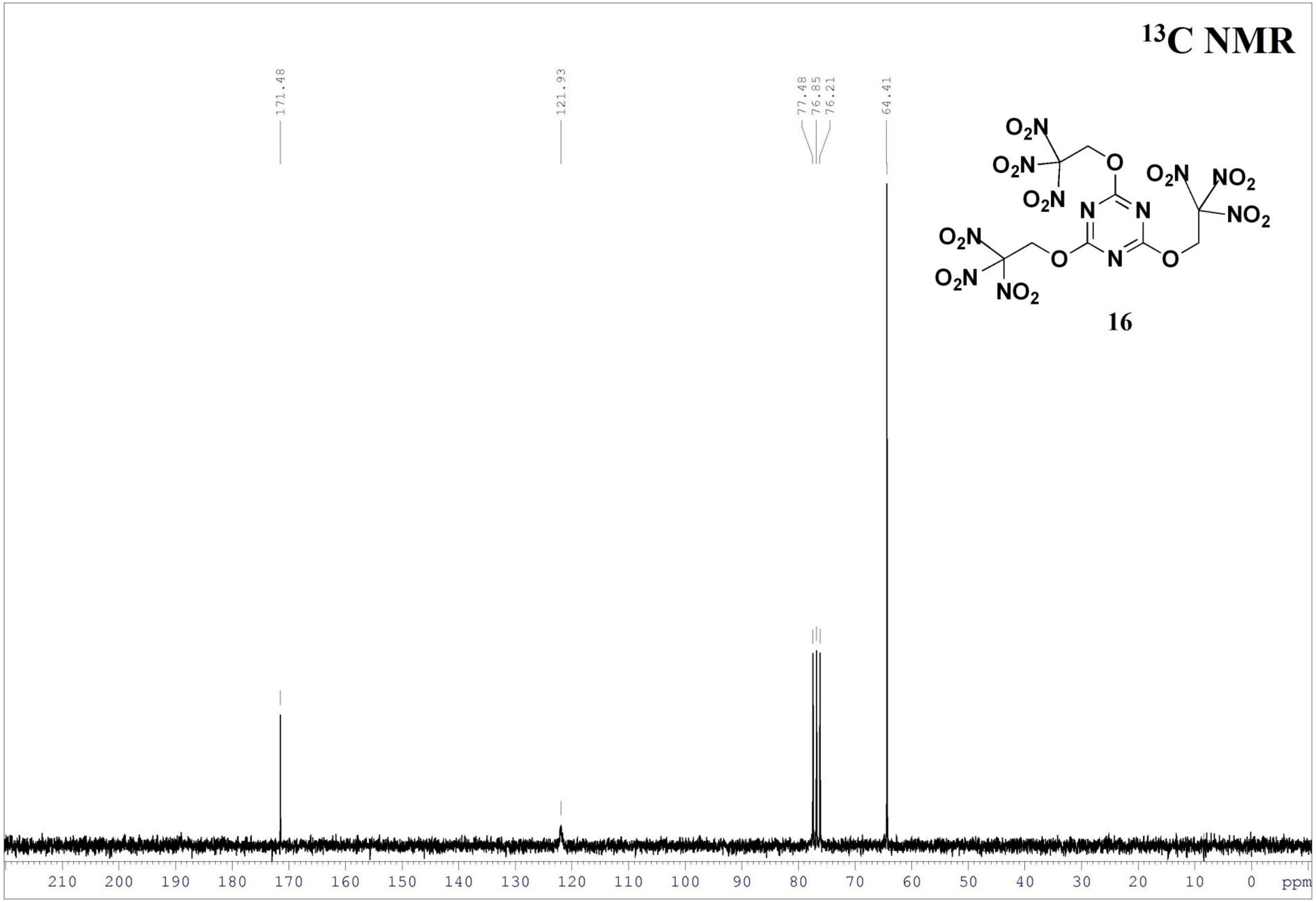

^{13}C NMR
171.86
170.69
164.74
122.23
122.16
122.13
77.46
77.24
77.04
76.90
76.62
74.79
64.54
21.42
21.30
NO_2
O_2N
NO_2
O_2N
NO_2
NO_2
N
N
N
Me
Me
O
O
15a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

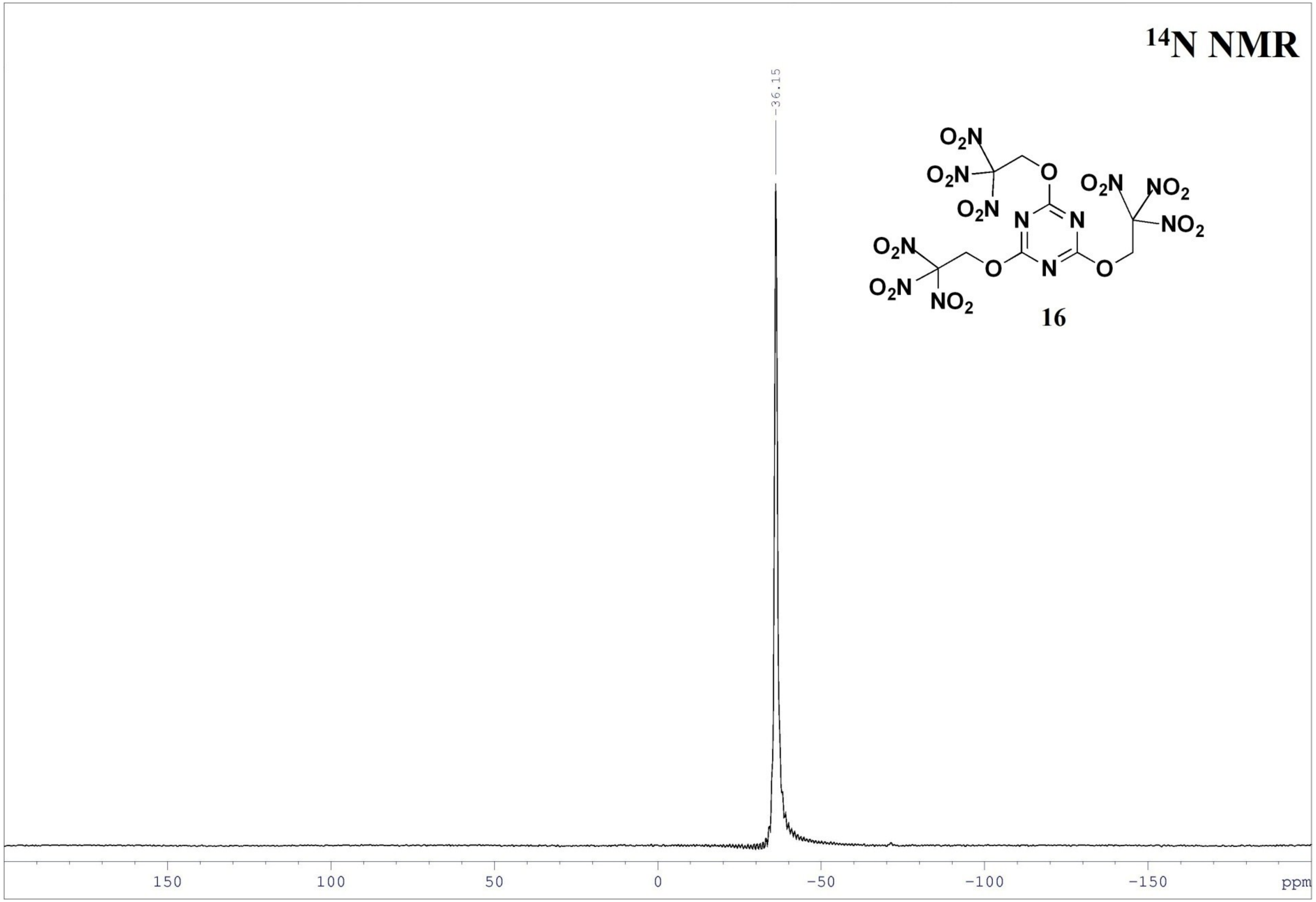

^{14}N NMR
-36.66
-39.15
NO_2
O_2N
NO_2
O_2N
NO_2
NO_2
N
N
N
O
O
Me
Me
15a
150
100
50
0
−50
−100
−150
ppm

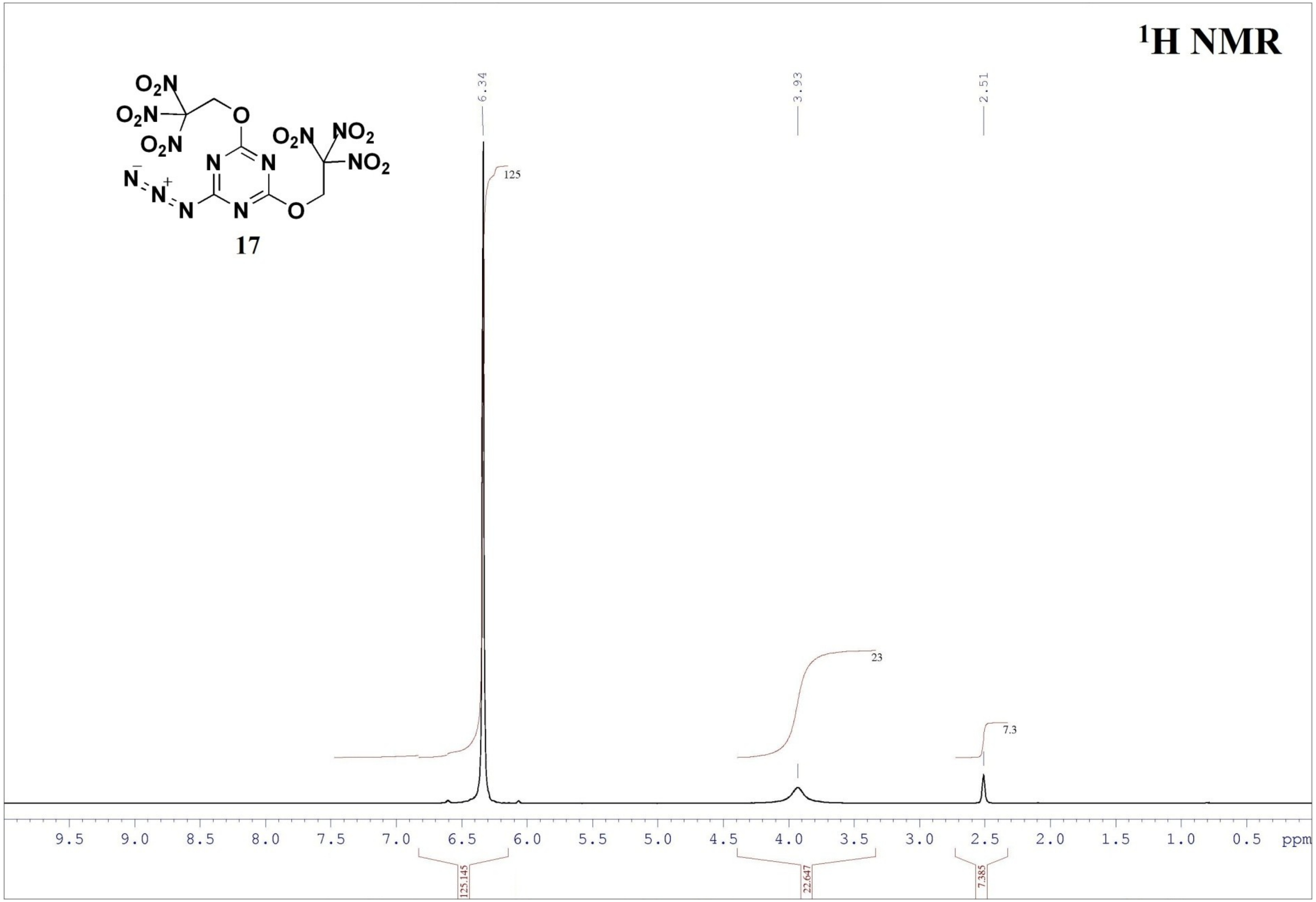

^{1}H NMR
7.28 CDCl3
5.72
2.31
2.24
1.72
$(O_2N)_3C$
$C(NO_2)_3$
N
O
15b
2.00
9.23
6.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

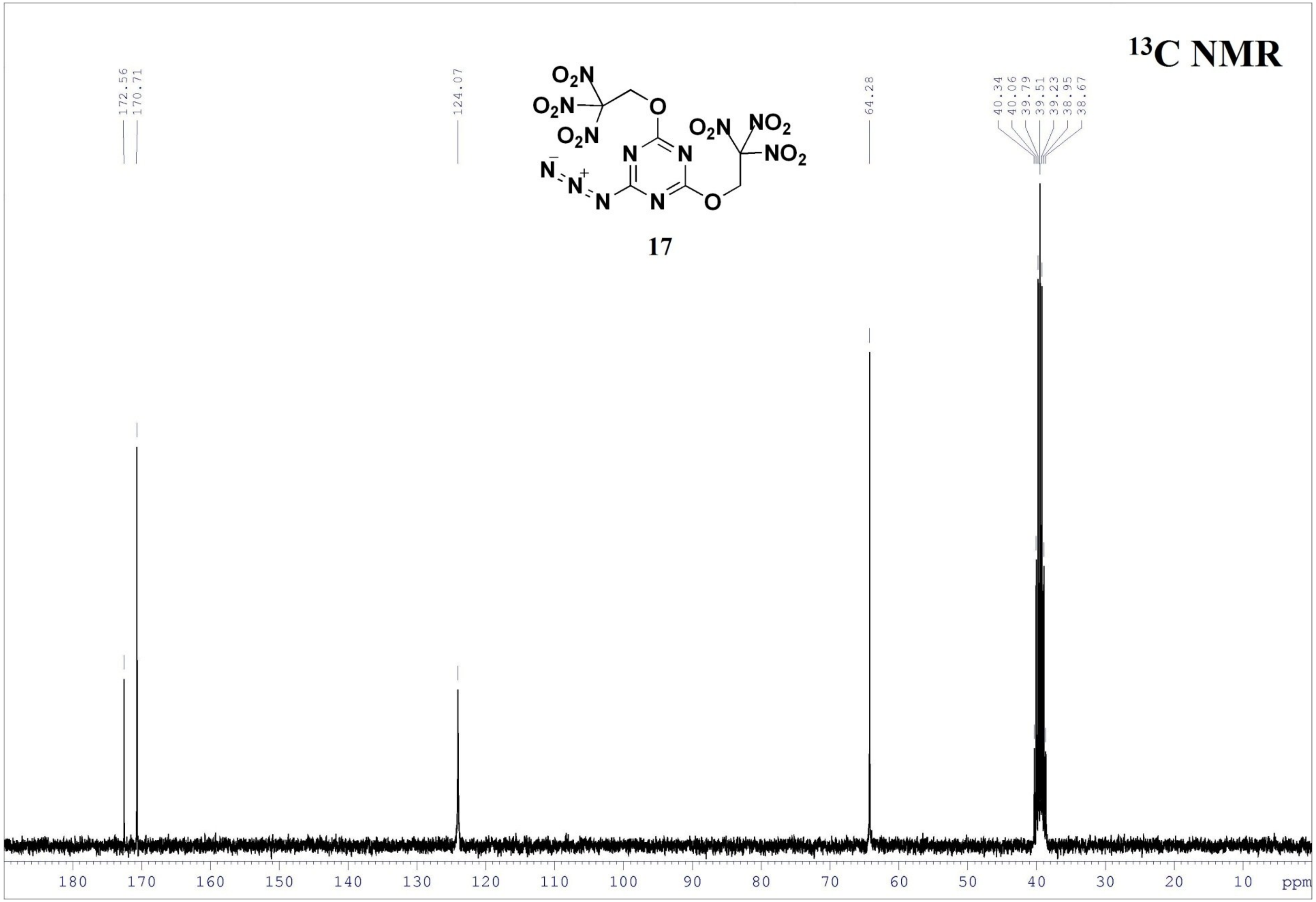

13C NMR
171.13
170.50
164.18
122.23
90.17
77.47 CDCl3
77.15 CDCl3
76.84 CDCl3
64.55
41.01
35.82
31.33
O
N
N
N
C(NO2)3
(O2N)3C
O
15b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

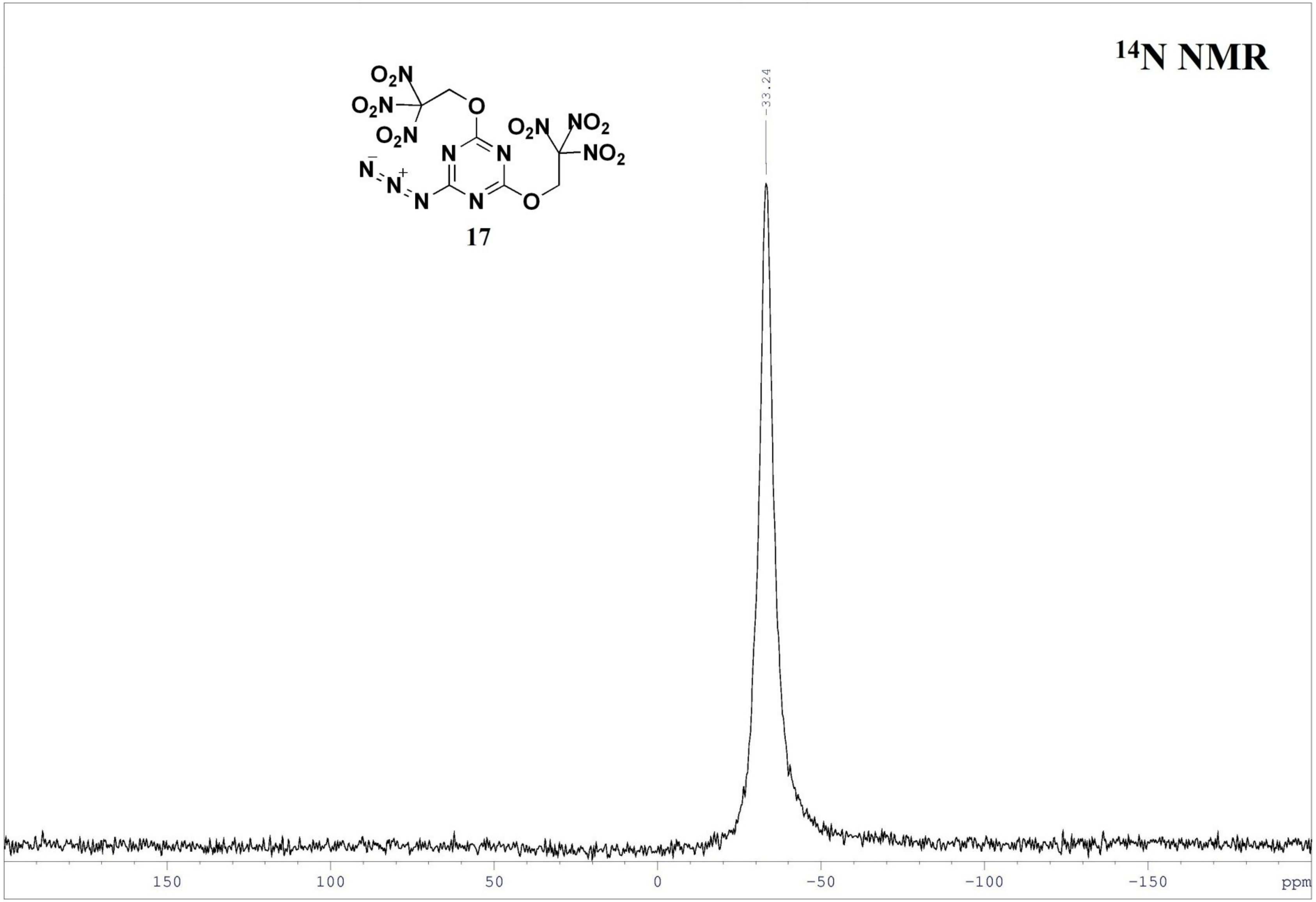

^{1}H NMR
O_2N
NO_2
N
O
16
5.75
125
1.5
1.1
9.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.464
124.994
1.068
0.987
9.557

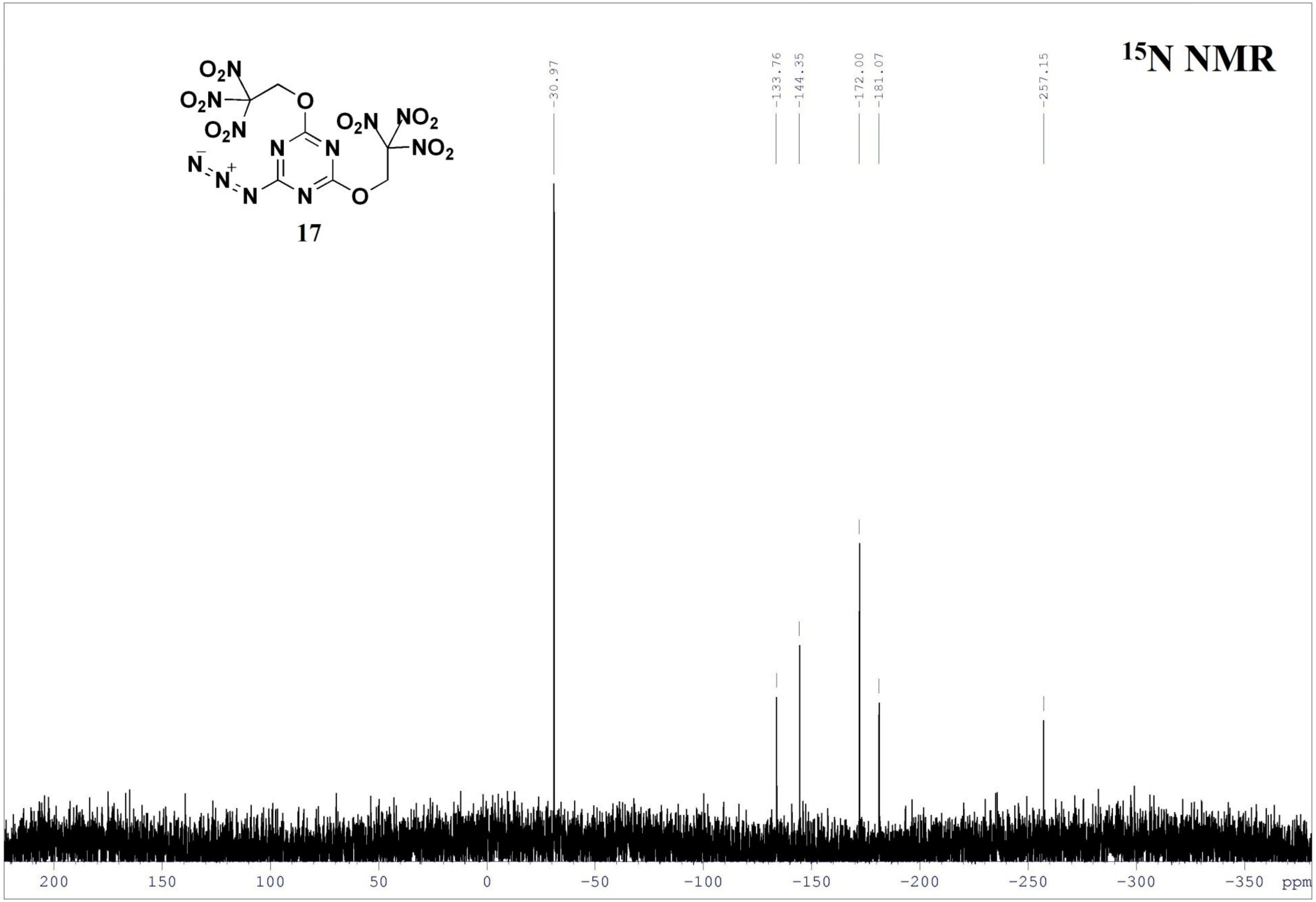

^{13}C NMR
171.48
121.93
77.48
76.85
76.21
64.41
O_2N
O_2N
O_2N
O
O_2N
NO_2
N
N
NO_2
O_2N
O
N
O
O_2N
NO_2
16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

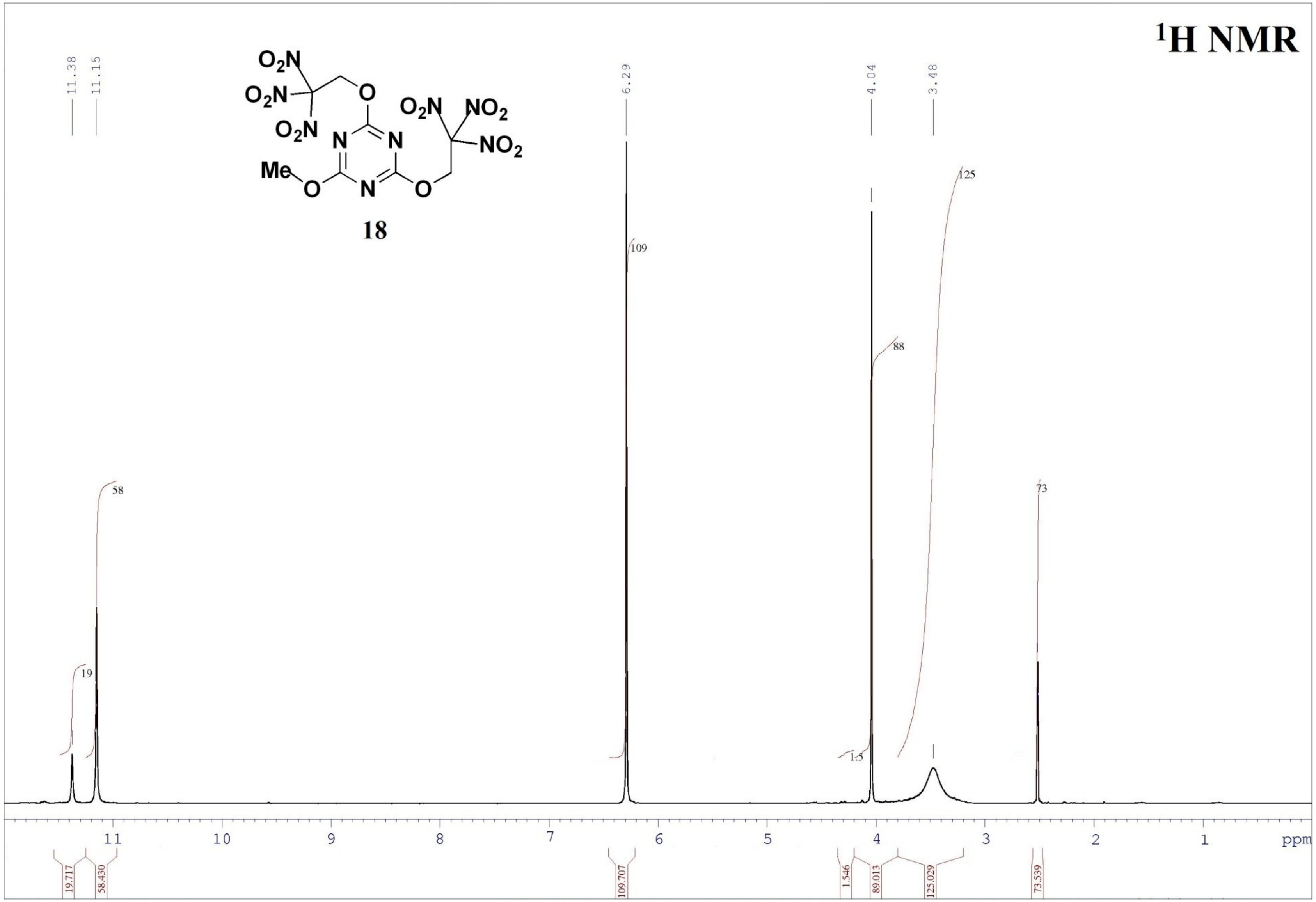

^{14}N NMR
-36.15
16
150
100
50
0
-50
-100
-150
ppm

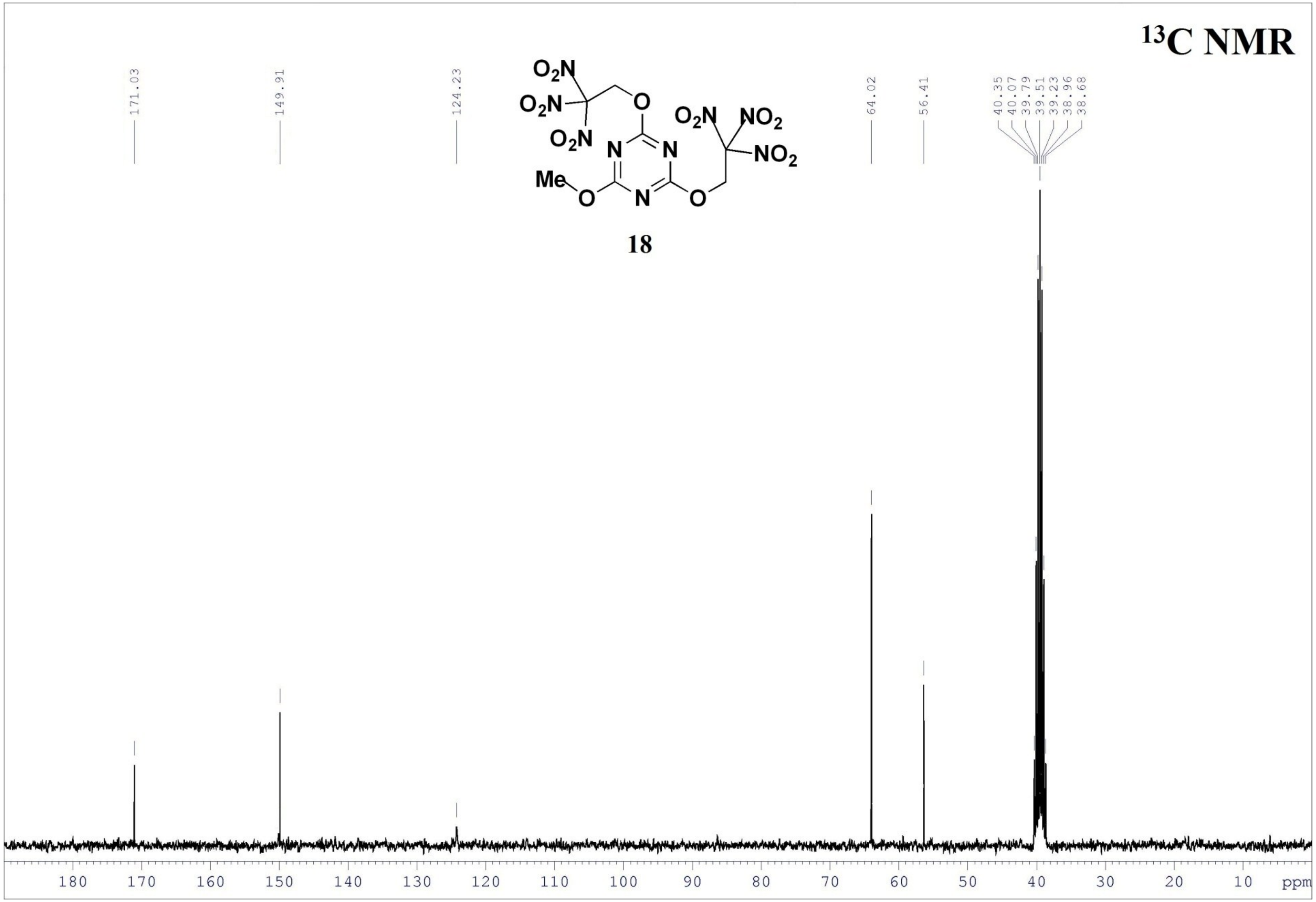

1H NMR
17
6.34
3.93
2.51
125
23
7.3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
125.145
22.647
7.385

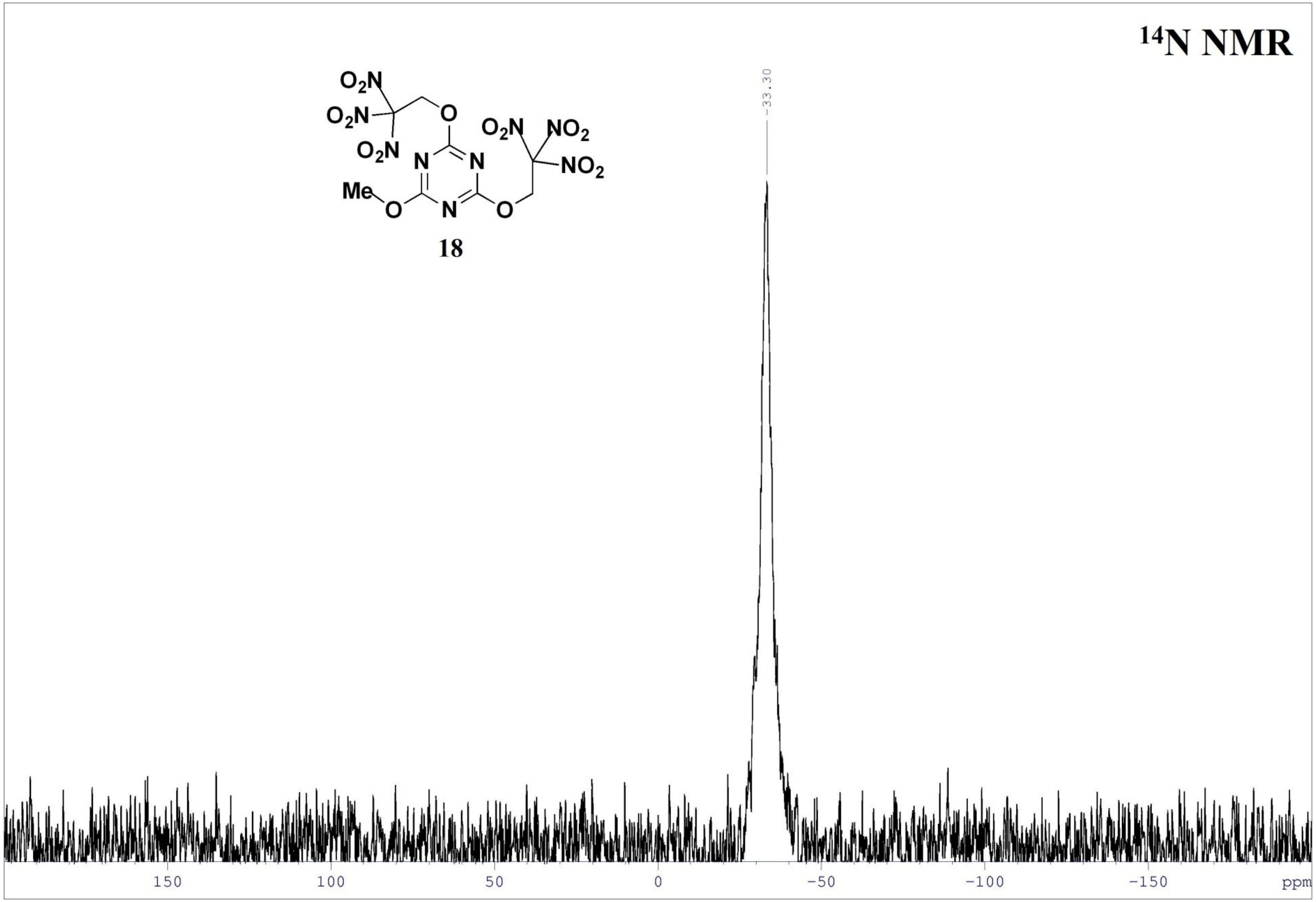

13C NMR
17
172.56
170.71
124.07
64.28
40.34
40.06
39.79
39.51
39.23
38.95
38.67
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


^{14}N NMR
O_2N
O_2N
O_2N
O
N
N
O_2N
NO_2
NO_2
N
N
N
N
O
17
-33.24
150
100
50
0
-50
-100
-150
ppm

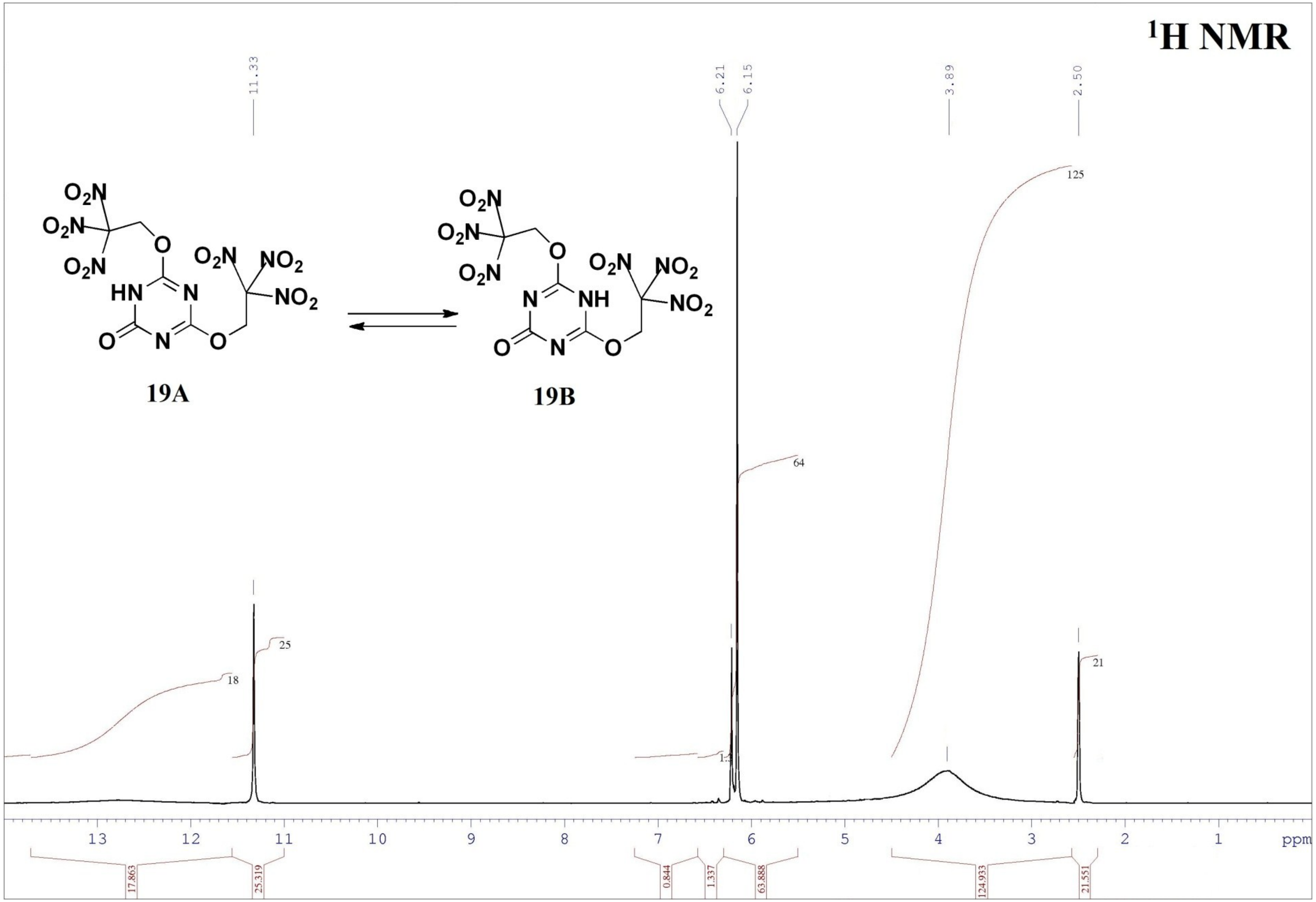

15N NMR
17
-30.97
-133.76
-144.35
-172.00
-181.07
-257.15
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

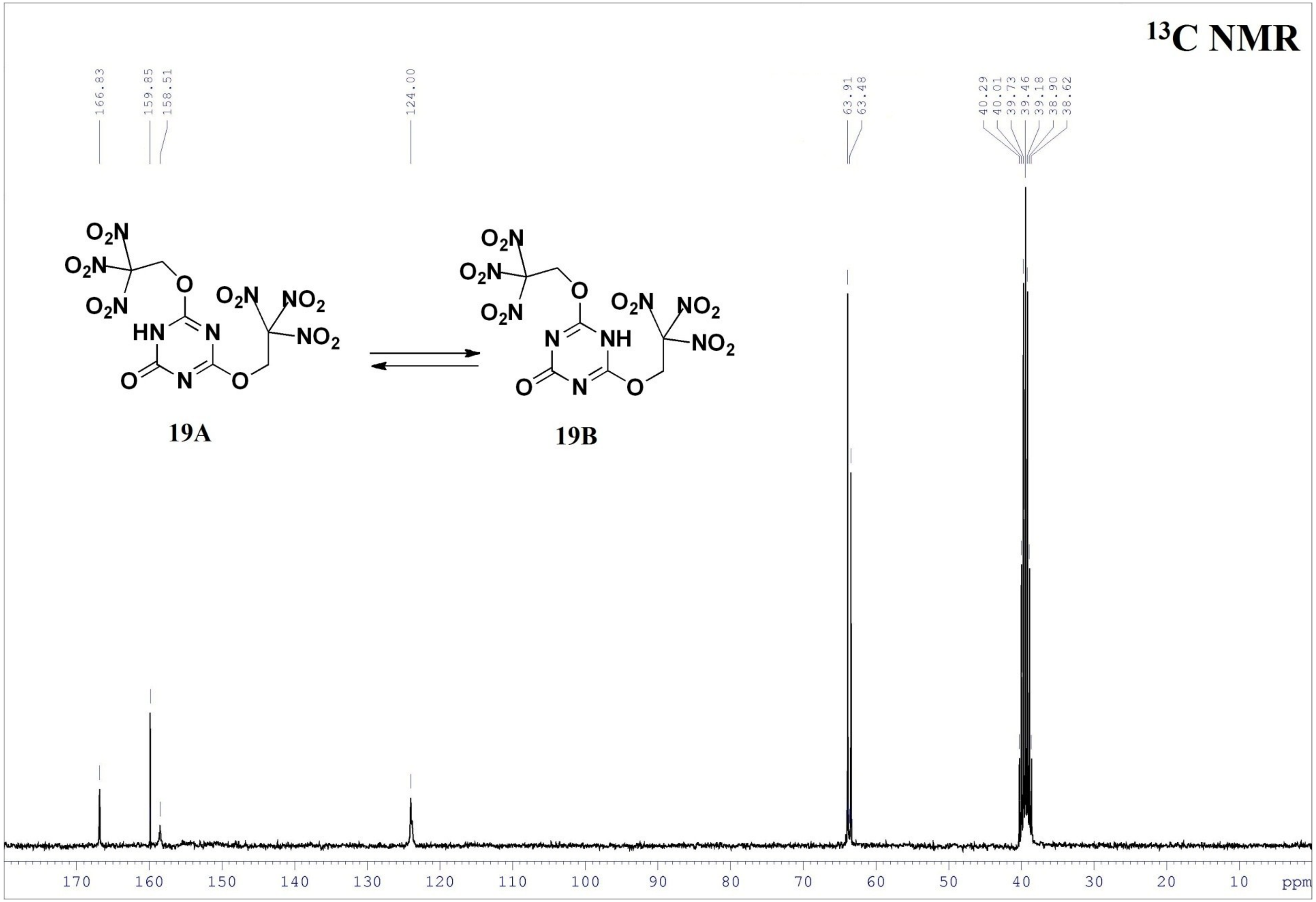

1H NMR
18
11.38
11.15
6.29
4.04
3.48
19
58
109
1.5
88
125
73
11
10
9
8
7
6
5
4
3
2
1
ppm
19.717
58.430
109.707
1.546
89.013
125.029
73.539

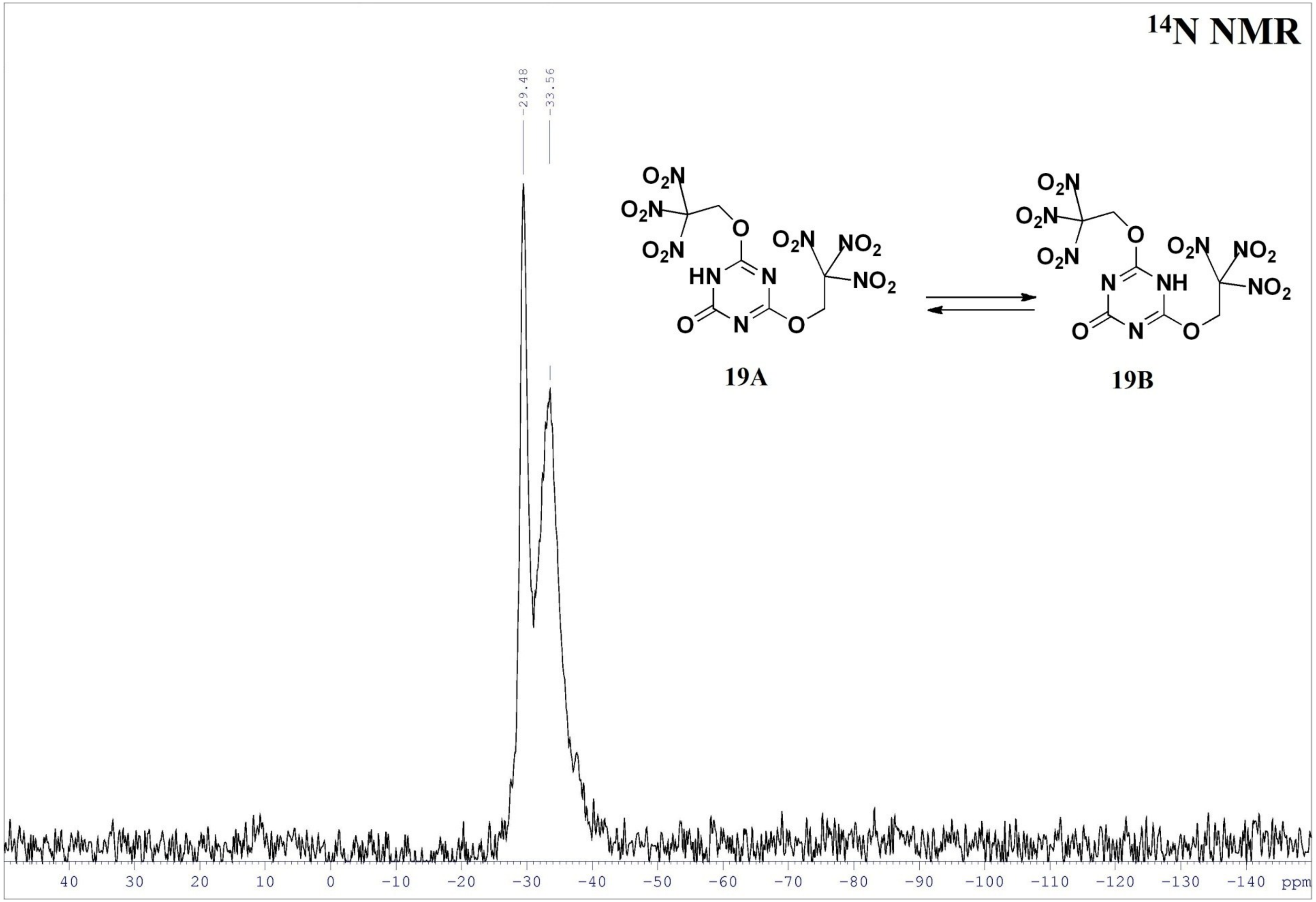

^{13}C NMR
171.03
149.91
124.23
64.02
56.41
40.35
40.07
39.79
39.51
39.23
38.96
38.68
O_2N
NO_2
N
O
Me
18
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

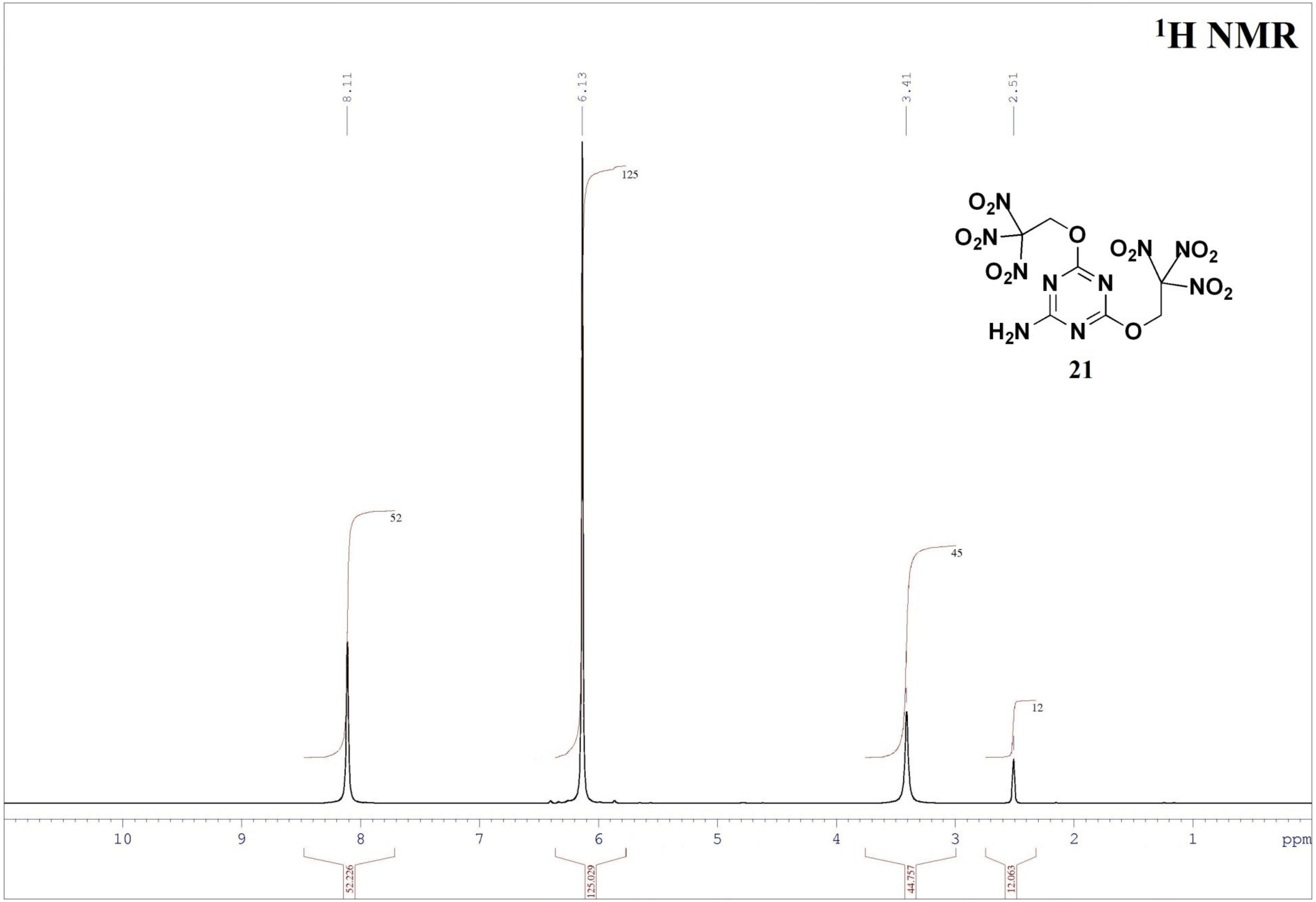

^{14}N NMR
O_2N
O_2N
O_2N
O_2N
NO_2
NO_2
O
N
N
Me
O
N
O
-33.30
150
100
50
0
-50
-100
-150
ppm

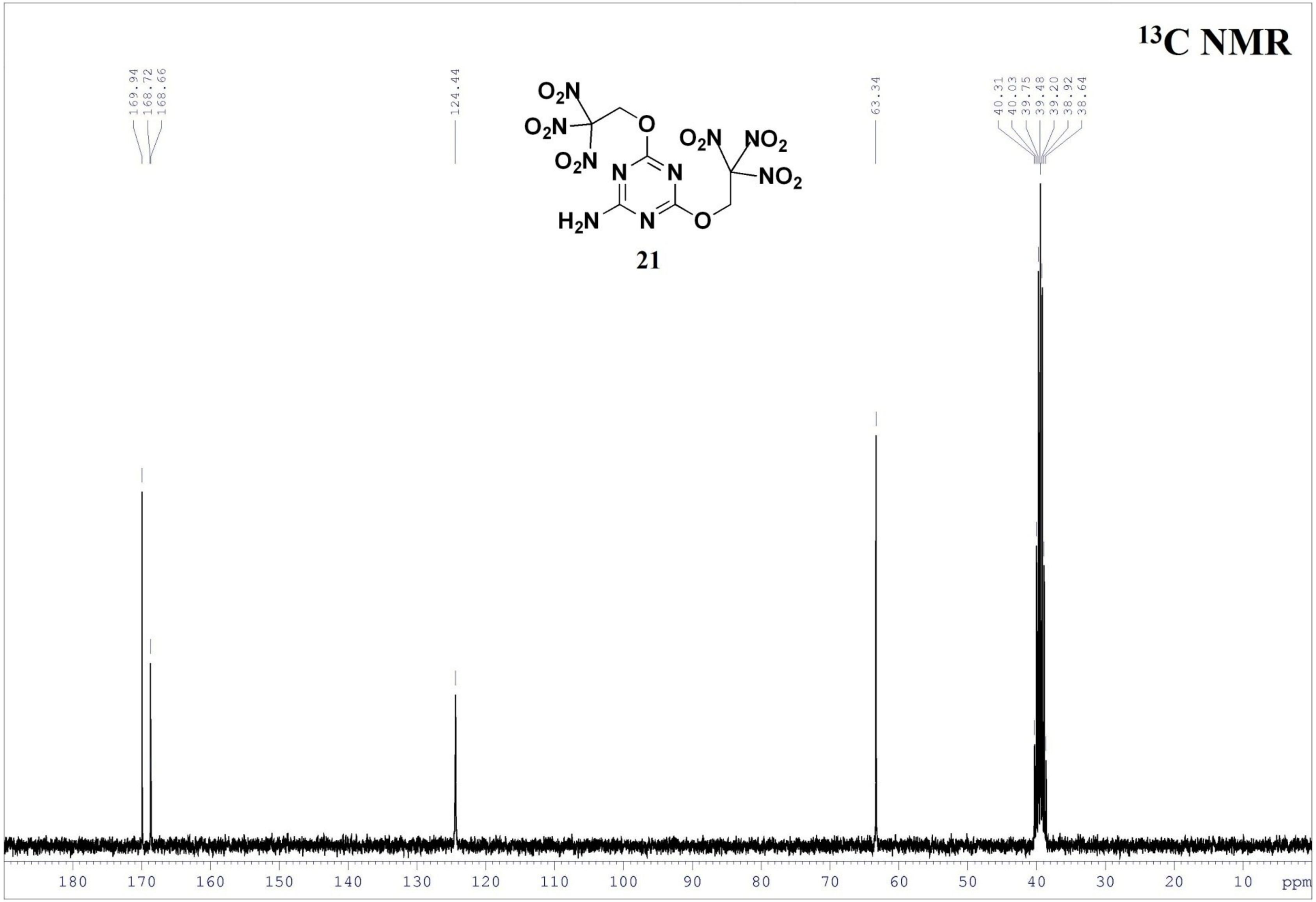
18

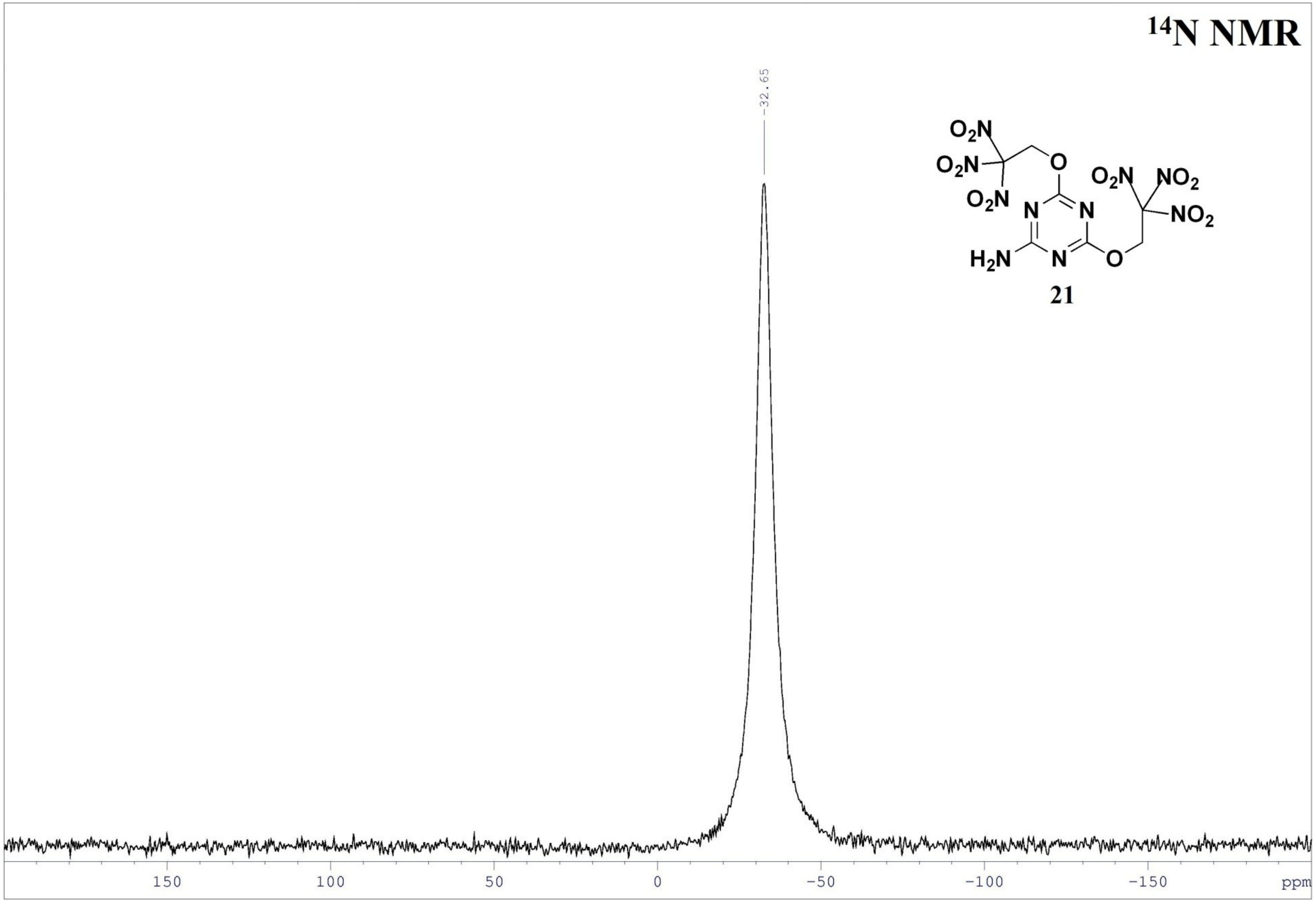

^{1}H NMR
11.33
6.21
6.15
3.89
2.50
19A
19B
125
64
25
18
21
1.3
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
17.863
25.319
0.844
1.337
63.888
124.933
21.551

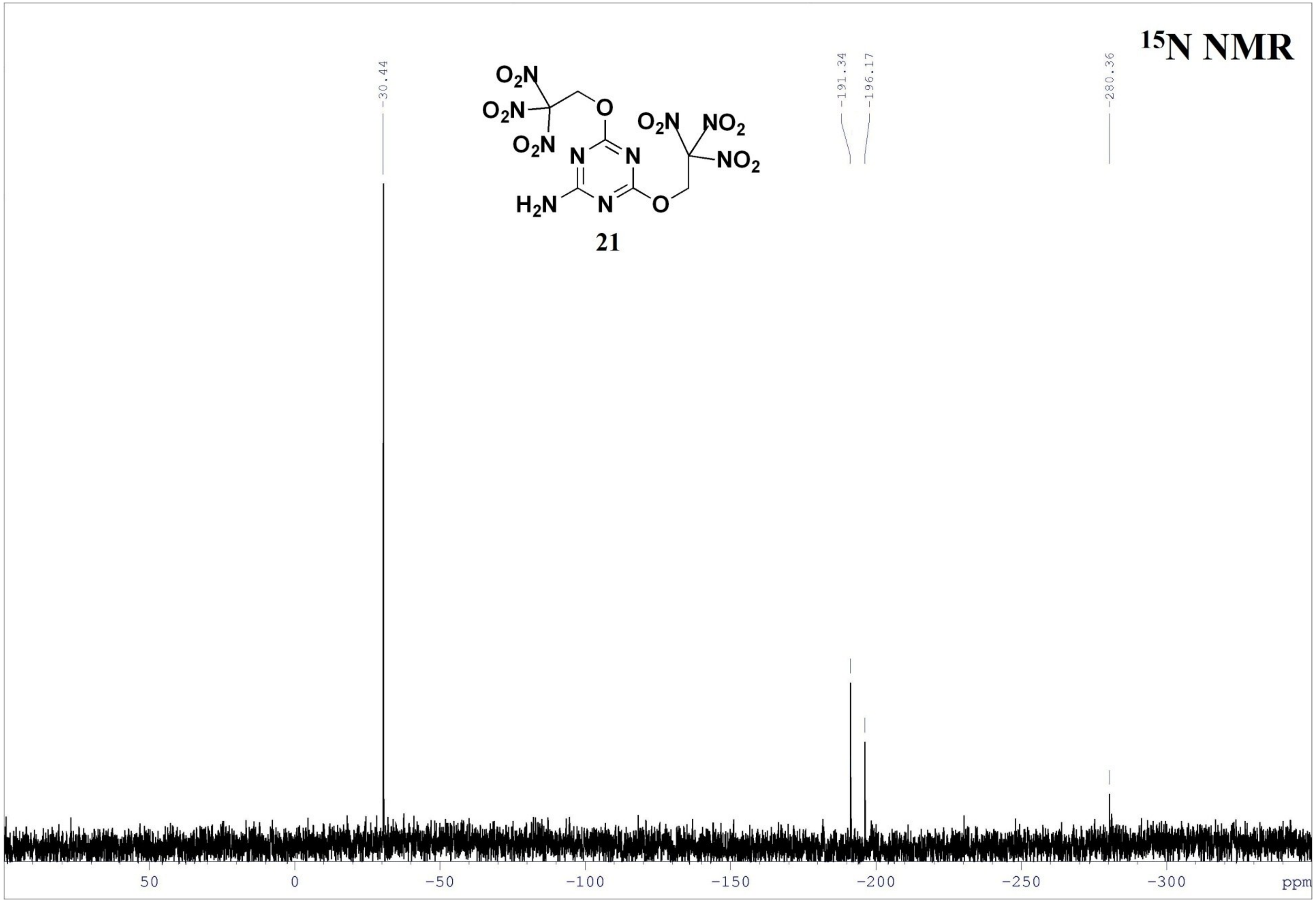

^{13}C NMR
166.83
159.85
158.51
124.00
63.91
63.48
40.29
40.01
39.73
39.46
39.18
38.90
38.62
O_2N
NO_2
HN
NH
N
O
19A
19B
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


^{14}N NMR
-29.48
-33.56
19A
19B
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
ppm

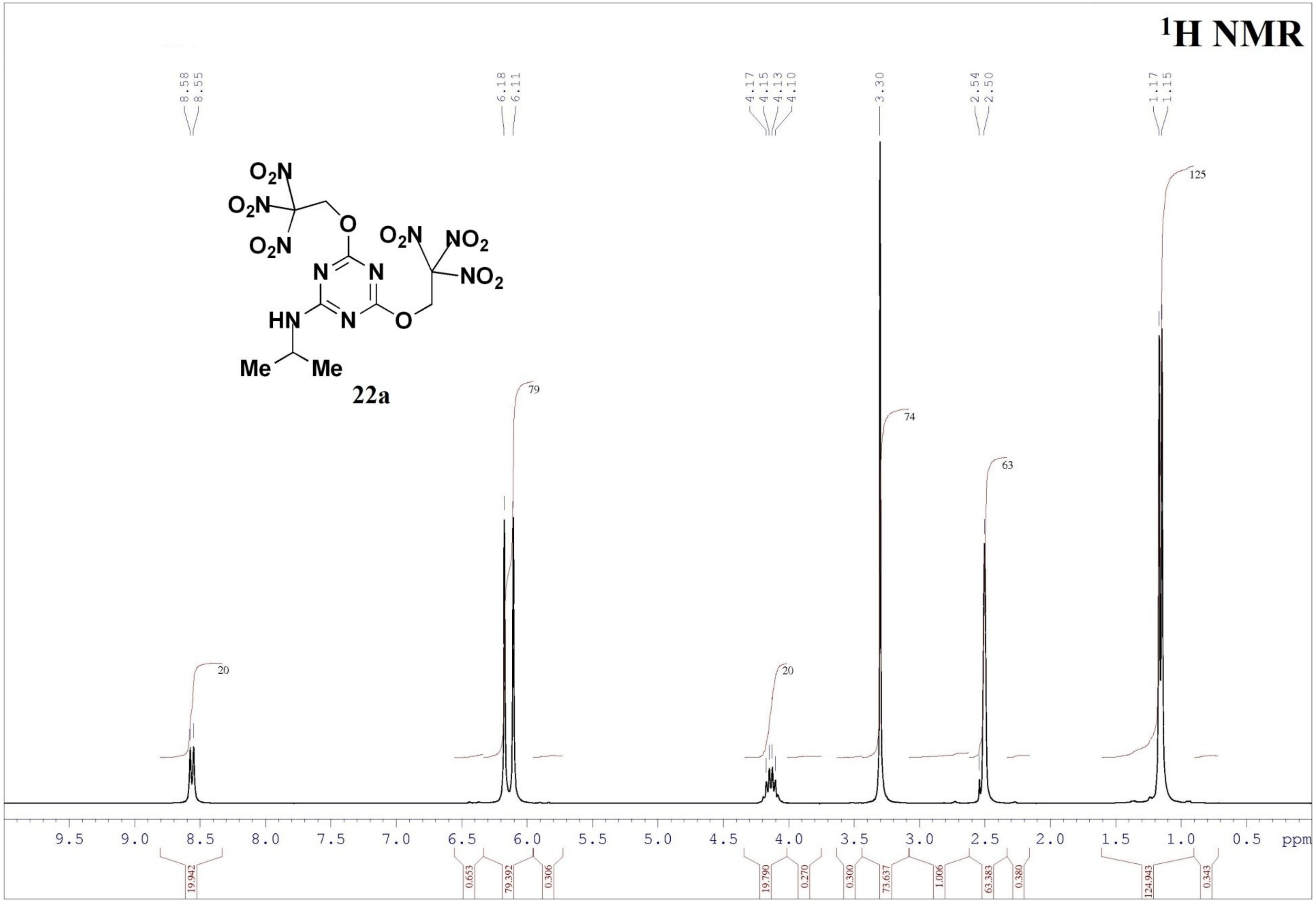

^{1}H NMR
8.11
6.13
3.41
2.51
125
52
45
12
10
9
8
7
6
5
4
3
2
1
ppm
52.226
125.029
44.757
12.063
O_2N
O_2N
O_2N
O
O_2N
NO_2
N
N
NO_2
H_2N
N
O
21

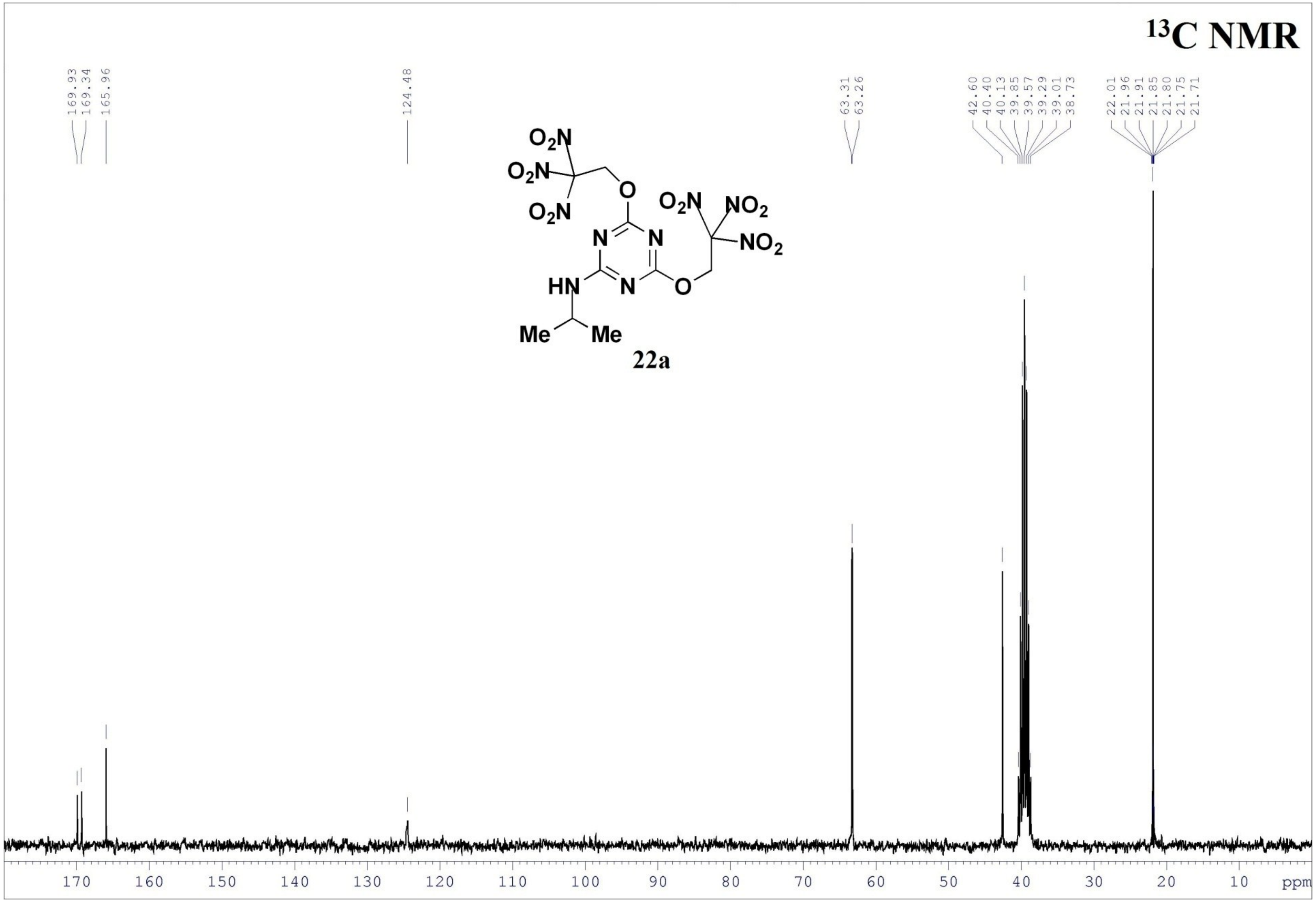

^{13}C NMR
169.94
168.72
168.66
124.44
63.34
40.31
40.03
39.75
39.48
39.20
38.92
38.64
O_2N
O_2N
O_2N
O
O_2N
NO_2
NO_2
N
N
N
H_2N
O
21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

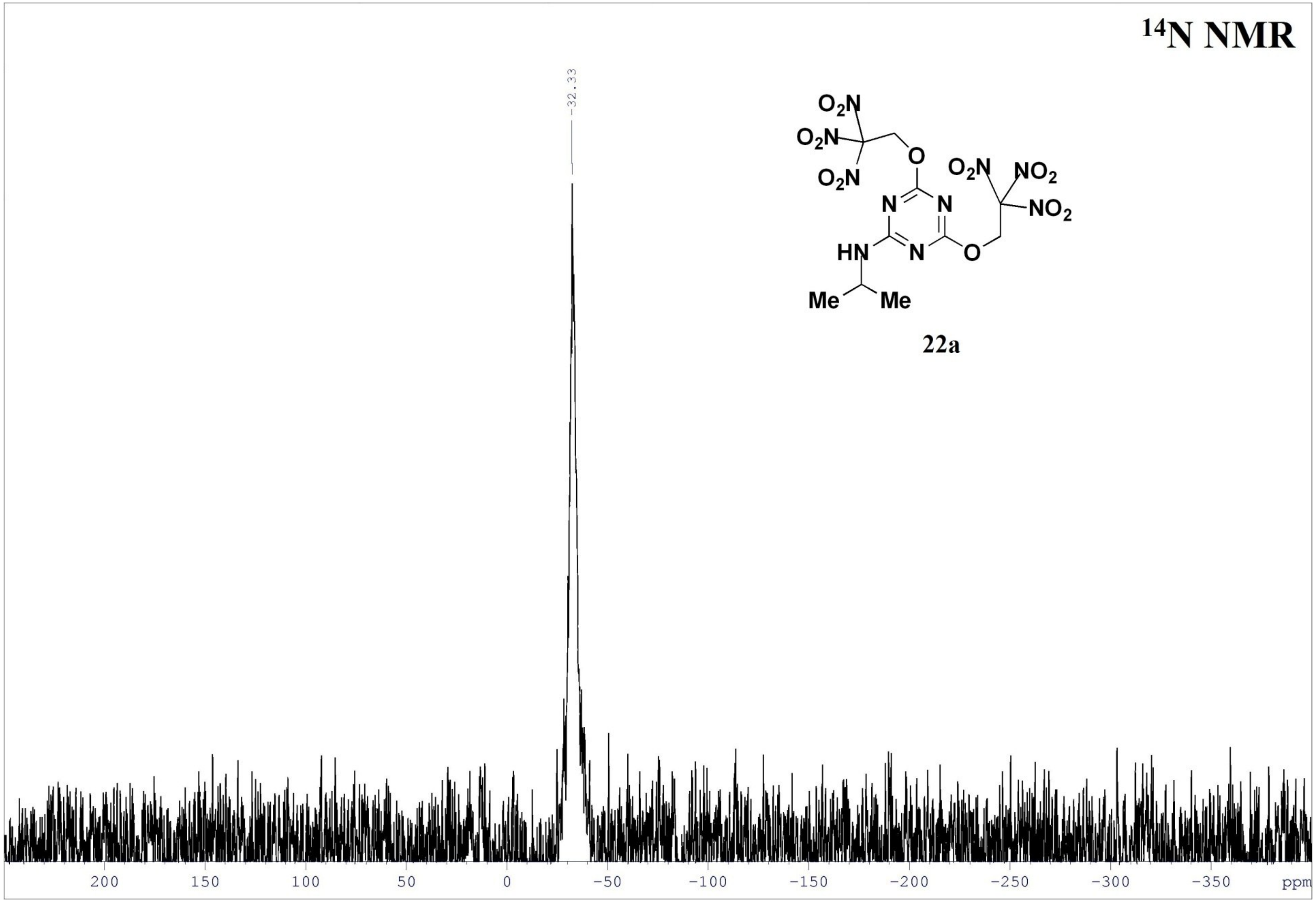

^{14}N NMR
-32.65
O_2N
O_2N
O_2N
O
N
N
H_2N
N
O
O_2N
NO_2
NO_2
21
150
100
50
0
-50
-100
-150
ppm

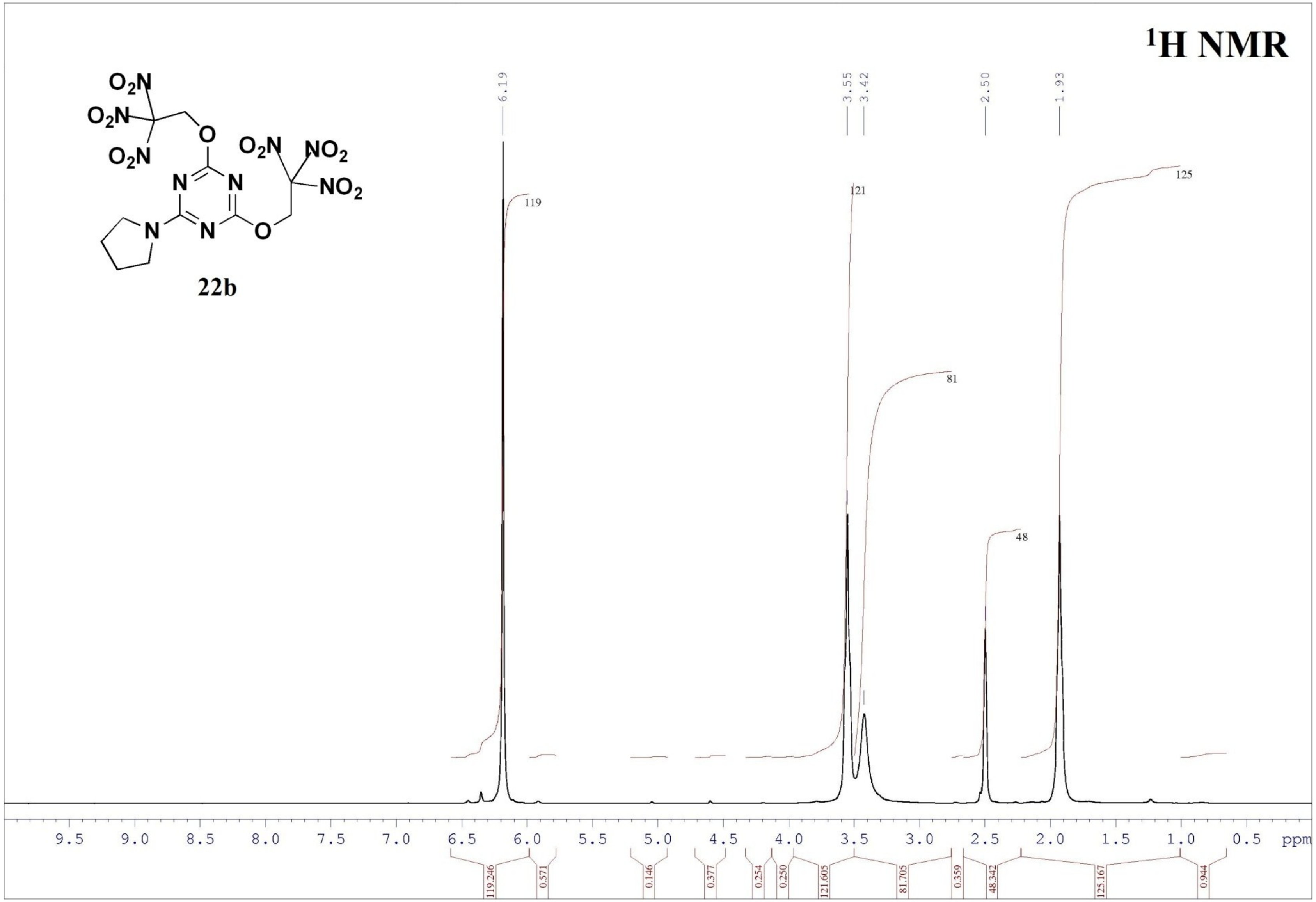

15N NMR
-30.44
-191.34
-196.17
-280.36
O2N
O2N
O2N
O
N
N
N
H2N
O
O2N
NO2
NO2
21
50
0
-50
-100
-150
-200
-250
-300
ppm

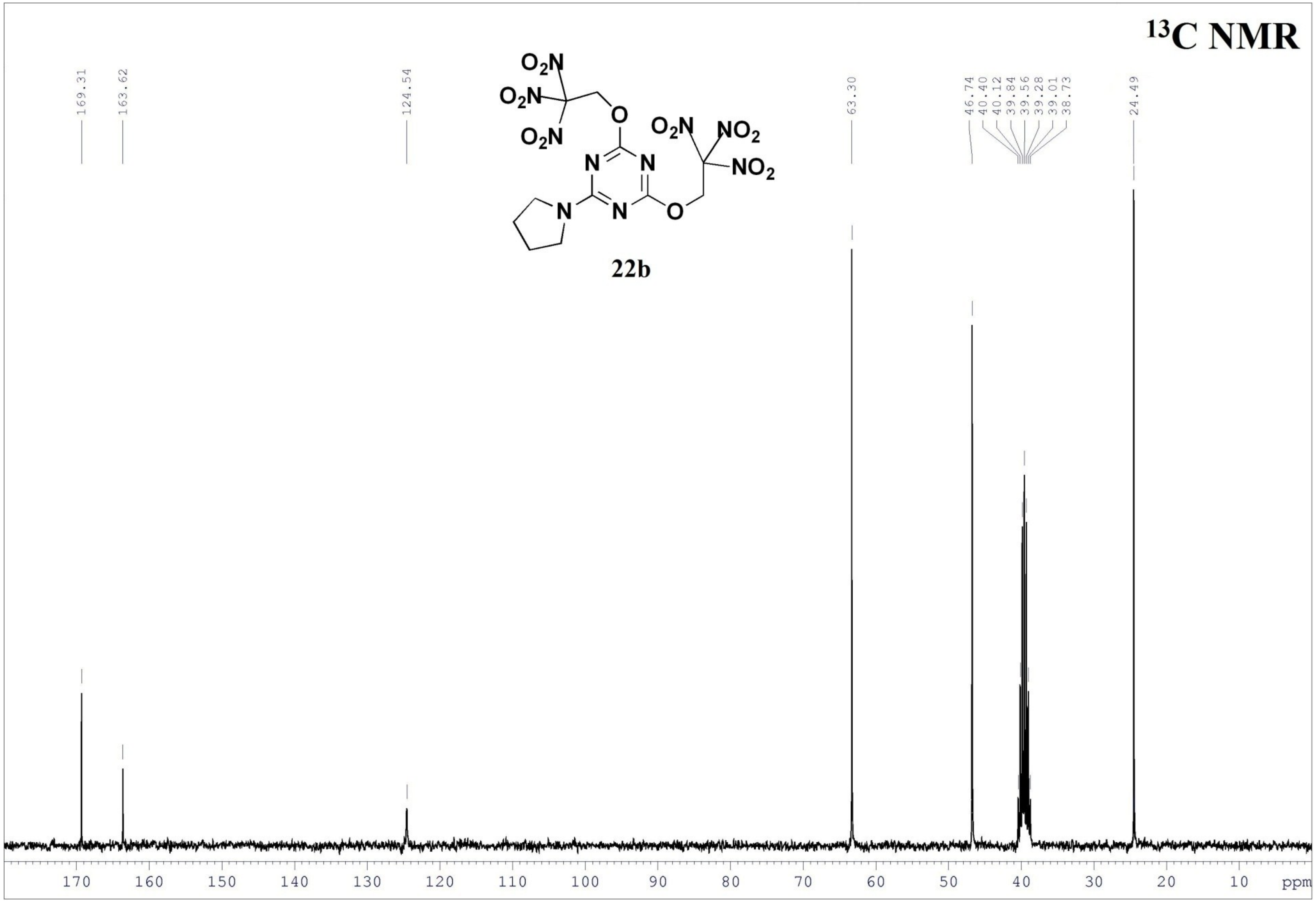
Electronic Supplementary Material (ESI) for RSC Advances




13C NMR
169.93
169.34
165.96
124.48
63.31
63.26
42.60
40.40
40.13
39.85
39.57
39.29
39.01
38.73
22.01
21.96
21.91
21.85
21.80
21.75
21.71
O2N
O2N
O2N
O
O2N
NO2
NO2
N
N
HN
N
O
Me
Me
22a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

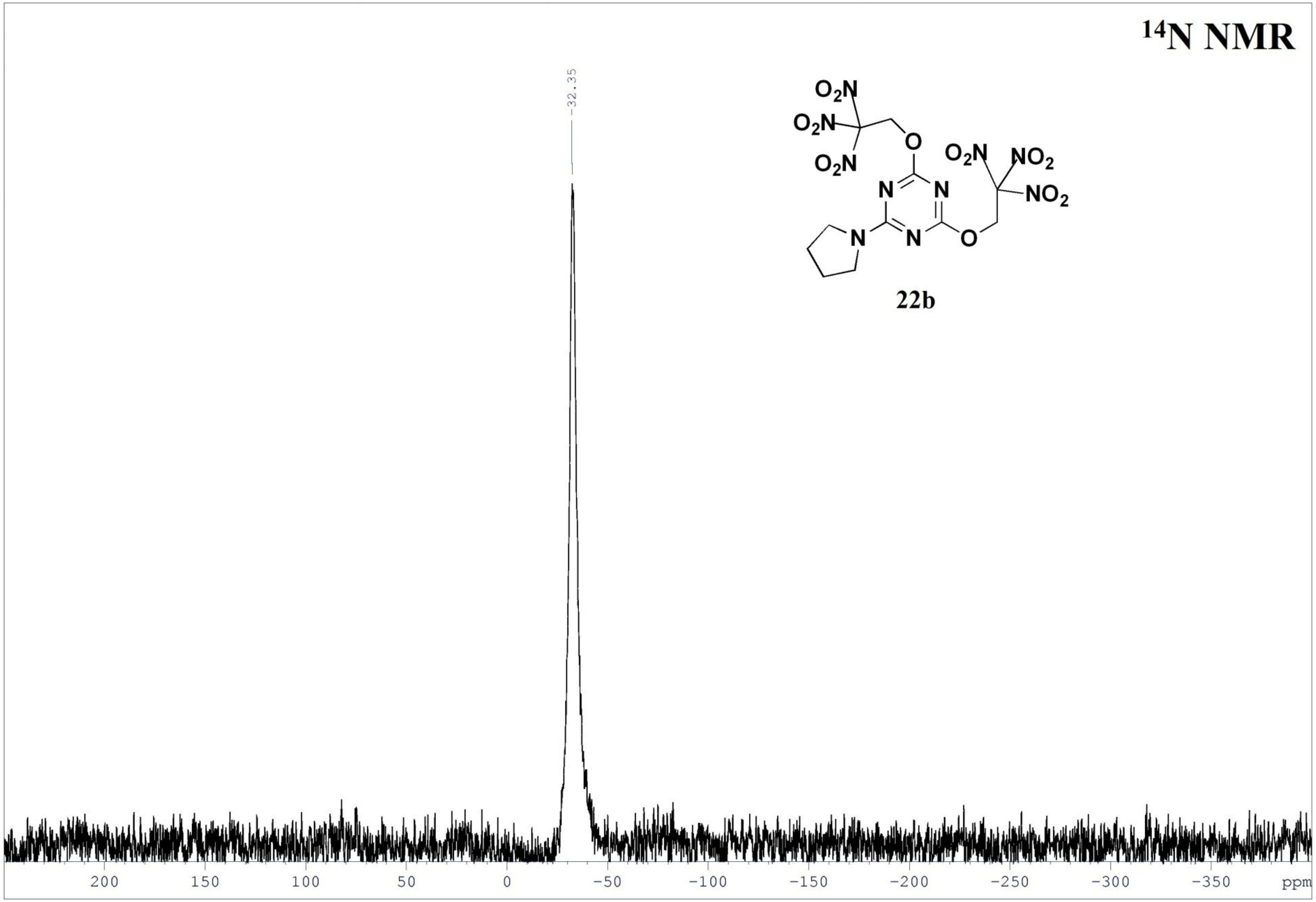

^{14}N NMR
-32.33
O_2N
O_2N
O_2N
O
O_2N
NO_2
NO_2
N
N
HN
N
O
Me
Me
22a
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

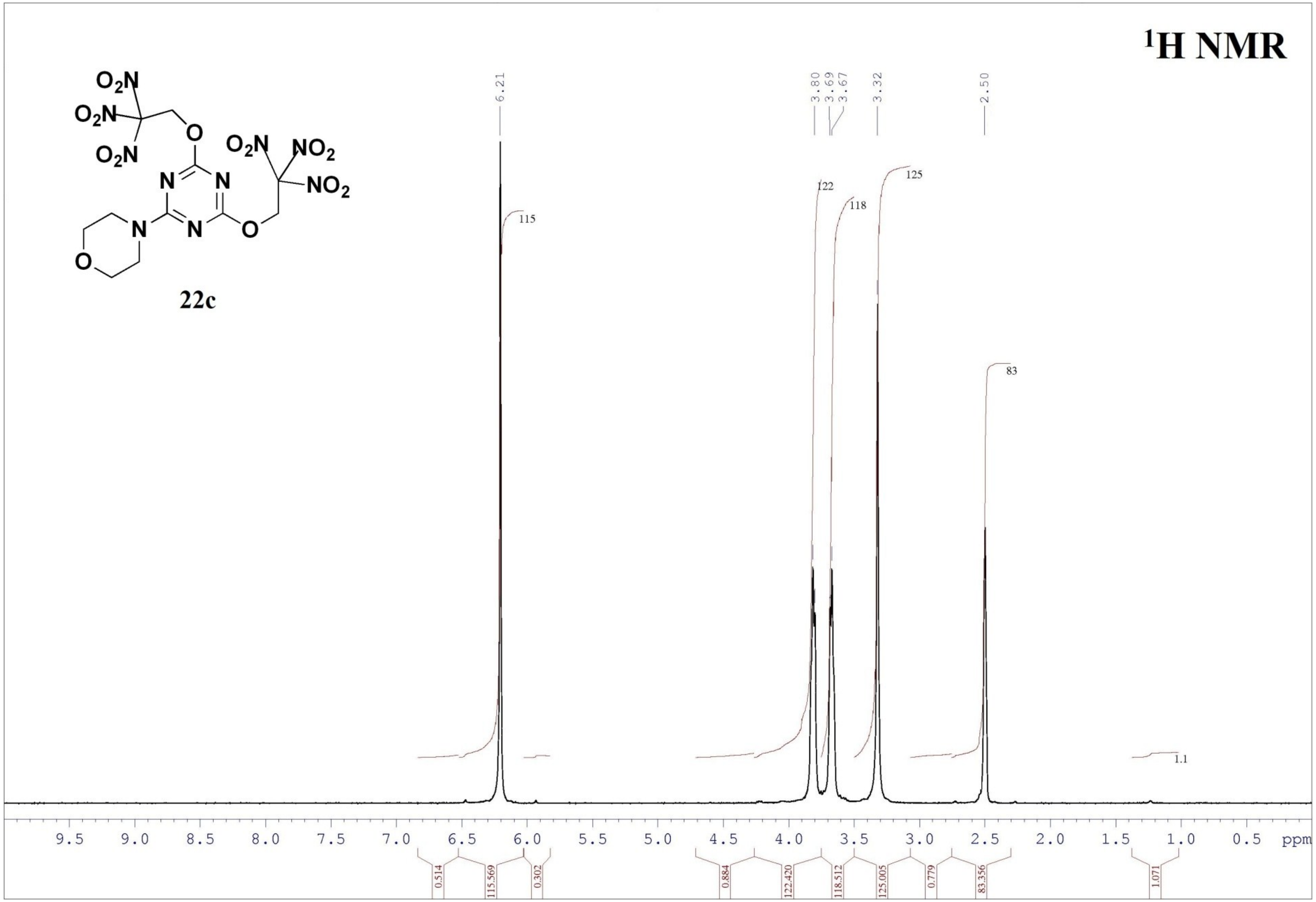

¹H NMR
O₂N
O₂N
O₂N
NO₂
NO₂
O
O
N
N
N
N
22b
6.19
3.55
3.42
2.50
1.93
119
121
81
48
125
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
119.246
0.571
0.146
0.377
0.254
0.250
121.605
81.705
0.359
48.342
125.167
0.944

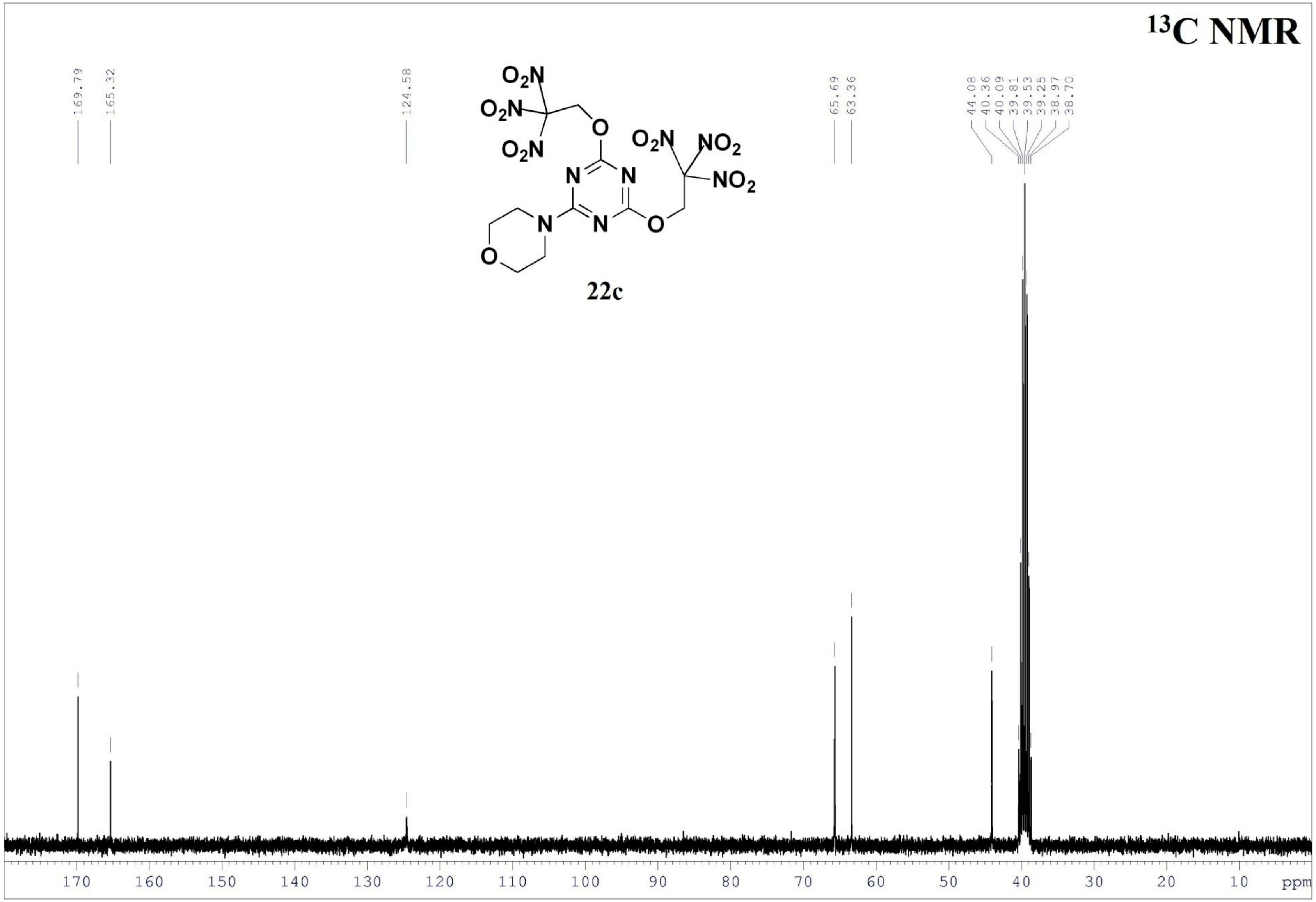


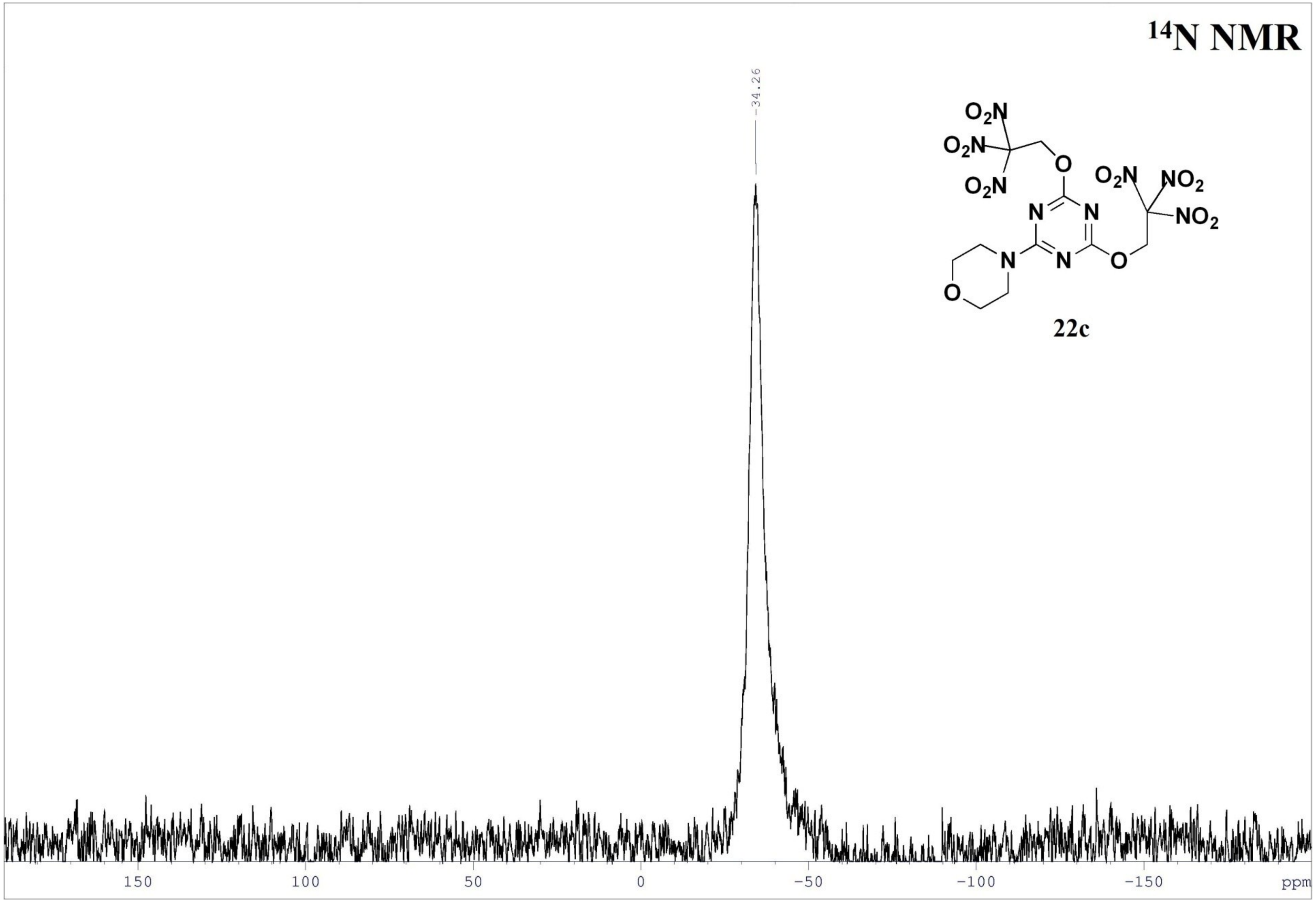
13C NMR
169.31
163.62
124.54
63.30
46.74
40.40
40.12
39.84
39.56
39.28
39.01
38.73
24.49
O2N
O2N
O2N
O
O2N
NO2
NO2
N
N
N
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

22b


^{14}N NMR
-32.35
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm
O₂N
O₂N
O₂N
O
N
N
N
N
O
O₂N
NO₂
NO₂
22b


^{1}H NMR
22c
6.21
3.80
3.69
3.67
3.32
2.50
115
122
118
125
83
1.1
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
0.514
115.569
0.302
0.884
122.420
118.512
125.005
0.779
83.356
1.071


13C NMR
169.79
165.32
124.58
65.69
63.36
44.08
40.36
40.09
39.81
39.53
39.25
38.97
38.70
O2N
O2N
O2N
O
O2N
NO2
NO2
N
N
N
N
O
O
22c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



22c