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Novel energetic oxadiazole assemblies

Alexander A. Larin, Alexander V. Shaferov, Konstantin A. Monogarov, Dmitry B. Meerov, Alla N. Pivkina and Leonid L. Fershtat

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S1. Experimental Section

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300 and 75.5 MHz, respectively) spectrometer and referenced to residual solvent peak. ^{14}N NMR spectra were measured on a Bruker AM-300 (21.7 MHz) spectrometer using $MeNO_2$ (δ_{14N} = 0.0 ppm) as an external standard. The chemical shifts are reported in ppm (δ). The IR spectra were recorded on a Bruker "Alpha" spectrometer in the range 400-4000 cm^{-1} (resolution 2 cm^{-1}). Analytical thin-layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminum sheets. The visualization of the TLC plates was accomplished with a UV light. Column chromatography was performed on silica gel 60 A (0.060-0.200 mm, Acros Organics). All solvents were purified and dried using standard methods prior to use. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification.

4-[(Dimethylaminomethylidene)amino]-4'-nitro-[3,3'-bi(1,2,5-oxadiazole)] 2,5'-dioxide ***1***. A solution of the corresponding chloroxime **5** (2.80 g, 12.0 mmol) in dry DMF (25 mL) was added dropwise to a magnetically stirred and ice-cooled solution of $NaCH(NO_2)_2$ (3.37 g, 26.4 mmol) in DMF (25 mL). The resulting mixture was stirred at 0–5 °C for 30 min and left to stand in a refrigerator for 72 h. Then, anhydrous AcONa (4.30 g, 54 mmol) was added in one portion with stirring at 0–5 °C and stirred for additional 30 min. Acetic acid (50 mL) was added dropwise at 0–5 °C followed by the addition of $NaNO_2$ (4.90 g, 54 mmol) in one portion. The reaction mixture was stirred for 15 min at 0–5 °C, then allowed to warm to room temperature and stirred for additional 4 h. The reaction mixture was then poured into cold water (100 mL), stirred for 1 h, the solid formed was collected by filtration, washed with water and dried in air. Yield 1.88 g (55%). Yellow powder. IR (KBr): 2931, 2821, 1666, 1626, 1545, 1527, 1434, 1395, 1355, 1331, 1114, 941, 856, 830, 793, 728 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.93 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 8.41 (s, 1H, CH). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 34.6, 40.9, 103.1, 126.7, 138.8, 157.1, 160.5. ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -38.9 (NO_2). Elemental analysis calcd (%) for $C_7H_7N_7O_6$ (285.18): C 29.48, H 2.47, N 34.38; found: C 29.30, H 2.52, N 34.02.

4-[(Dimethylamino)methylidene)amino]-4'-nitro-[3,3'-bi(1,2,5-oxadiazole)] 2,2'-dioxide ***2***. A solution of compound **1** (0.50 g, 1.75 mmol) in CCl_4 (15 mL) was refluxed for 5 h. Then the solvent was evaporated under reduced pressure and dried in air. Yield 0.46 g (90%). Yellow crystals. IR (KBr): 2927, 2817, 1666, 1632, 1577, 1555, 1522, 1480, 1430, 1403, 1370, 1339,

1111, 946, 833, 798 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.91 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 8.40 (s, 1H, CH). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 34.5, 40.8, 100.1, 100.3, 155.8, 156.9, 160.3. ^{14}N NMR (21.7 MHz, DMSO-d_6) δ: -35.0 (NO_2). Elemental analysis calcd (%) for $C_7H_7N_7O_6$ (285.18): C 29.48, H 2.47, N 34.38; found: C 29.69, H 2.62, N 34.06.

*4-Amino-3'-nitro-3,4'-bifuroxan **3***. To a magnetically stirred solution of compound **1** (0.29 g, 1 mmol) in MeCN (3 mL) was added water (5 mL) and then methanesulfonic acid (1 mL). The reaction mixture was stirred at room temperature for 2 h. The resulted solution was extracted with CH_2Cl_2 (2x10 mL) and dried over $MgSO_4$. The solvent was then evaporated, and the residue was purified by column chromatography (eluent: $CHCl_3$-EtOAc, 15:1) to afford the title compound. Yield 0.05 g (21%). Light yellow crystals. IR (KBr): 3490, 3385, 1638, 1617, 1561, 1541, 1468, 1355, 1291, 1256, 1176, 1019, 941 cm^{-1}. ^{1}H NMR (300 MHz, CD_3CN) δ: 5.33 (s, 2H, NH_2). ^{13}C NMR (75.5 MHz, acetone-d_6) δ: 99.9, 126.3, 138.7, 155.7. ^{14}N NMR (21.7 MHz, acetone-d_6) δ: -39.7 (NO_2). Elemental analysis calcd (%) for $C_4H_2N_6O_5$ (230.10): C 20.88, H 0.88, N 36.52; found: C 20.62, H 1.05, N 36.28.

*3,4-Bis(5-amino-1,2,4-oxadiazolyl)furoxan **4***. To a magnetically stirred solution of $KHCO_3$ (1.85 g, 18.5 mmol) in water (15 mL) was added bis(amidoxime) **6** (1.50 g, 7.4 mmol) in EtOH (50 mL) in one portion. Then BrCN (1.96 g, 18.5 mmol) was added in portions. The reaction mixture was stirred for 10 h at 20 °C. The reaction mixture was quenched with 1 N HCl (60 mL), the precipitate formed was filtered off, washed with water (2x30mL) and dried in air. Yield 1.43 g (76%). Light brown solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.37 (s, 4H, NH_2). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ: 106.7, 147.0, 156.4, 158.8, 172.9, 173.0. Elemental analysis calcd (%) for $C_6H_4N_8O_4$ (252.15): C 28.58, H 1.60, N 44.44; found: C 28.39, H 1.69, N 44.18.

S2. Crystallographic Data

Table S1 Crystal data and structure refinement for **3**.

Empirical formula	C4 H2 N6 O6	
Formula weight	230.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.2485(4) Å	α= 90°.
	b = 11.9618(5) Å	β= 102.808(2)°.
	c = 9.3932(5) Å	γ = 90°.
Volume	794.18(7) $Å^3$	
Z	4	
Density (calculated)	1.925 g/cm^3	
Absorption coefficient	0.181 mm^{-1}	
F(000)	464	
Crystal size	0.220 x 0.130 x 0.110 mm^3	
Theta range for data collection	2.801 to 32.492°.	
Index ranges	-10<=h<=10, -17<=k<=18, -11<=l<=14	
Reflections collected	9947	
Independent reflections	2862 [R(int) = 0.0546]	
Observed reflections	1933	
Completeness to theta = 25.242°	100.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2862 / 0 / 153	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.0892	
R indices (all data)	R1 = 0.0824, wR2 = 0.1097	
Largest diff. peak and hole	0.468 and -0.349 $e.Å^{-3}$	

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1041(2)	5062(1)	6733(1)	17(1)
C(1)	4165(2)	5243(1)	7527(2)	14(1)
O(1)	1653(2)	4332(1)	7860(1)	20(1)
N(2)	3672(2)	4443(1)	8336(1)	17(1)
C(2)	2522(2)	5618(1)	6531(2)	12(1)
O(2)	4480(2)	3853(1)	9342(1)	24(1)
N(3)	6077(2)	5637(1)	7795(2)	18(1)
C(3)	2264(2)	6465(1)	5409(2)	12(1)
O(3)	6279(2)	6623(1)	7515(1)	21(1)
N(4)	3502(2)	6648(1)	4590(1)	14(1)
C(4)	665(2)	7164(1)	4858(2)	15(1)
O(4)	7330(2)	4975(1)	8298(2)	32(1)
O(5)	2734(2)	7465(1)	3543(1)	18(1)
N(5)	943(2)	7770(1)	3762(2)	18(1)
O(6)	5059(2)	6261(1)	4555(1)	19(1)
N(6)	-950(2)	7163(1)	5331(2)	20(1)

Table S3 Bond lengths [Å] and angles [°] for **3**.

N(1)-C(2)	1.311(2)
N(1)-O(1)	1.3689(17)
C(1)-N(2)	1.320(2)
C(1)-C(2)	1.414(2)
C(1)-N(3)	1.433(2)
O(1)-N(2)	1.4391(17)
N(2)-O(2)	1.2195(17)
C(2)-C(3)	1.443(2)
N(3)-O(4)	1.2185(18)
N(3)-O(3)	1.2240(19)
C(3)-N(4)	1.323(2)
C(3)-C(4)	1.430(2)
N(4)-O(6)	1.2272(17)
N(4)-O(5)	1.4108(17)
C(4)-N(5)	1.311(2)
C(4)-N(6)	1.342(2)
O(5)-N(5)	1.4066(18)
N(6)-H(6A)	0.88(3)
N(6)-H(6B)	0.82(2)
C(2)-N(1)-O(1)	107.50(12)
N(2)-C(1)-C(2)	108.40(13)
N(2)-C(1)-N(3)	120.76(13)
C(2)-C(1)-N(3)	130.72(14)
N(1)-O(1)-N(2)	108.31(11)
O(2)-N(2)-C(1)	136.15(15)
O(2)-N(2)-O(1)	117.90(13)
C(1)-N(2)-O(1)	105.90(12)
N(1)-C(2)-C(1)	109.85(14)
N(1)-C(2)-C(3)	118.91(13)
C(1)-C(2)-C(3)	131.24(14)
O(4)-N(3)-O(3)	126.53(15)
O(4)-N(3)-C(1)	117.63(15)
O(3)-N(3)-C(1)	115.82(13)

N(4)-C(3)-C(4)	106.97(14)
N(4)-C(3)-C(2)	123.07(14)
C(4)-C(3)-C(2)	129.68(14)
O(6)-N(4)-C(3)	134.38(14)
O(6)-N(4)-O(5)	117.74(12)
C(3)-N(4)-O(5)	107.86(12)
N(5)-C(4)-N(6)	123.93(15)
N(5)-C(4)-C(3)	110.78(15)
N(6)-C(4)-C(3)	125.19(15)
N(5)-O(5)-N(4)	108.16(11)
C(4)-N(5)-O(5)	106.20(13)
C(4)-N(6)-H(6A)	117.0(17)
C(4)-N(6)-H(6B)	116.7(17)
H(6A)-N(6)-H(6B)	122(2)

Table S4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	18(1)	16(1)	14(1)	2(1)	2(1)	-2(1)
C(1)	16(1)	13(1)	14(1)	-1(1)	2(1)	1(1)
O(1)	23(1)	18(1)	17(1)	4(1)	2(1)	-6(1)
N(2)	21(1)	14(1)	13(1)	-1(1)	1(1)	-1(1)
C(2)	15(1)	11(1)	11(1)	-2(1)	3(1)	0(1)
O(2)	35(1)	16(1)	16(1)	5(1)	-1(1)	3(1)
N(3)	16(1)	22(1)	16(1)	-1(1)	1(1)	1(1)
C(3)	13(1)	13(1)	12(1)	0(1)	2(1)	-1(1)
O(3)	20(1)	22(1)	21(1)	0(1)	5(1)	-6(1)
N(4)	17(1)	13(1)	12(1)	0(1)	3(1)	0(1)
C(4)	16(1)	14(1)	14(1)	-1(1)	1(1)	1(1)
O(4)	19(1)	34(1)	40(1)	5(1)	-2(1)	8(1)
O(5)	19(1)	18(1)	17(1)	6(1)	6(1)	1(1)
N(5)	18(1)	18(1)	19(1)	3(1)	4(1)	2(1)
O(6)	16(1)	22(1)	20(1)	0(1)	8(1)	2(1)
N(6)	16(1)	26(1)	18(1)	3(1)	5(1)	6(1)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **3**.

	x	y	z	U(eq)
H(6A)	-1860(40)	7620(20)	4890(30)	44(7)
H(6B)	-890(30)	6930(20)	6160(30)	35(7)

Table S6 Torsion angles [°] for **3**.

C(2)-N(1)-O(1)-N(2)	-1.78(16)
C(2)-C(1)-N(2)-O(2)	-178.91(18)
N(3)-C(1)-N(2)-O(2)	-2.6(3)
C(2)-C(1)-N(2)-O(1)	-1.51(17)
N(3)-C(1)-N(2)-O(1)	174.82(13)
N(1)-O(1)-N(2)-O(2)	-179.98(13)
N(1)-O(1)-N(2)-C(1)	2.06(16)
O(1)-N(1)-C(2)-C(1)	0.85(17)
O(1)-N(1)-C(2)-C(3)	-179.02(13)
N(2)-C(1)-C(2)-N(1)	0.47(18)
N(3)-C(1)-C(2)-N(1)	-175.37(16)
N(2)-C(1)-C(2)-C(3)	-179.67(15)
N(3)-C(1)-C(2)-C(3)	4.5(3)
N(2)-C(1)-N(3)-O(4)	30.2(2)
C(2)-C(1)-N(3)-O(4)	-154.43(17)
N(2)-C(1)-N(3)-O(3)	-148.60(15)
C(2)-C(1)-N(3)-O(3)	26.8(2)
N(1)-C(2)-C(3)-N(4)	-143.09(15)
C(1)-C(2)-C(3)-N(4)	37.1(3)
N(1)-C(2)-C(3)-C(4)	30.1(2)
C(1)-C(2)-C(3)-C(4)	-149.79(17)
C(4)-C(3)-N(4)-O(6)	-177.73(16)
C(2)-C(3)-N(4)-O(6)	-3.2(3)
C(4)-C(3)-N(4)-O(5)	0.97(16)

C(2)-C(3)-N(4)-O(5)	175.46(13)
N(4)-C(3)-C(4)-N(5)	-1.38(18)
C(2)-C(3)-C(4)-N(5)	-175.38(15)
N(4)-C(3)-C(4)-N(6)	175.08(15)
C(2)-C(3)-C(4)-N(6)	1.1(3)
O(6)-N(4)-O(5)-N(5)	178.64(13)
C(3)-N(4)-O(5)-N(5)	-0.31(15)
N(6)-C(4)-N(5)-O(5)	-175.36(15)
C(3)-C(4)-N(5)-O(5)	1.15(17)
N(4)-O(5)-N(5)-C(4)	-0.54(16)

Table S7 Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(2)#1	0.88(3)	2.63(3)	3.328(2)	136(2)
N(6)-H(6A)...O(3)#2	0.88(3)	2.51(3)	3.2841(19)	147(2)
N(6)-H(6B)...N(1)	0.82(2)	2.63(2)	3.048(2)	113(2)
N(6)-H(6B)...N(5)#3	0.82(2)	2.53(2)	3.211(2)	141(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y+1/2,-z+3/2 #2 x-1,-y+3/2,z-1/2 #3 x,-y+3/2,z+1/2

S3. DSC Curves

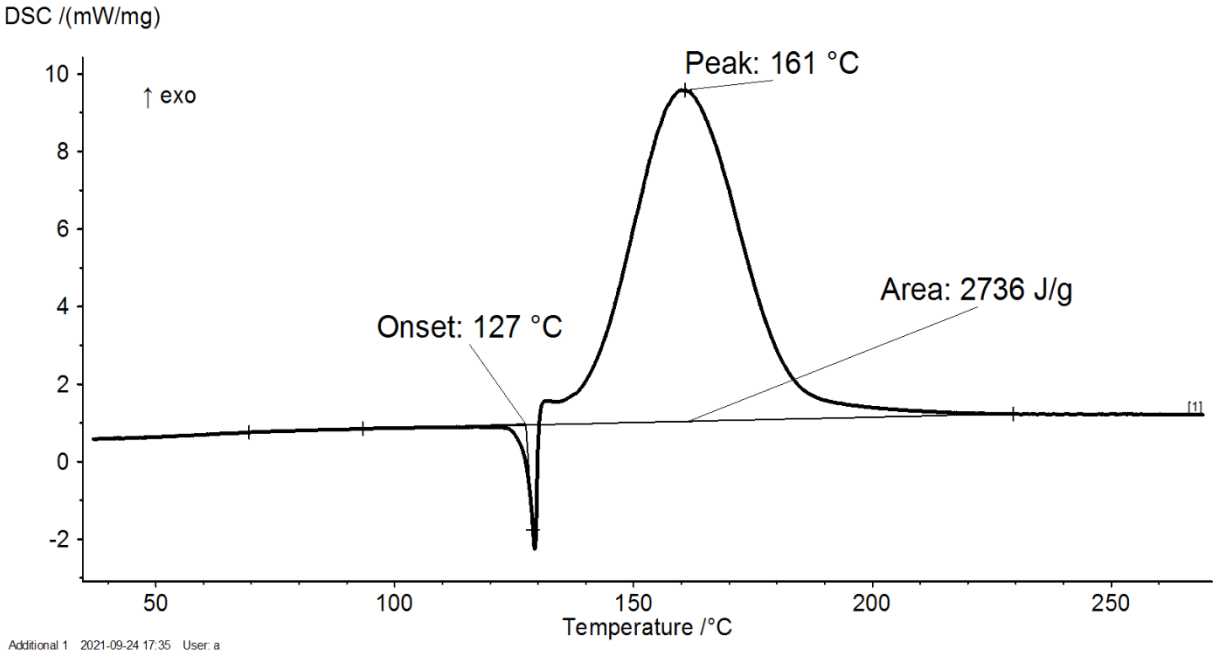


Figure S1 DSC data for compound **1**.

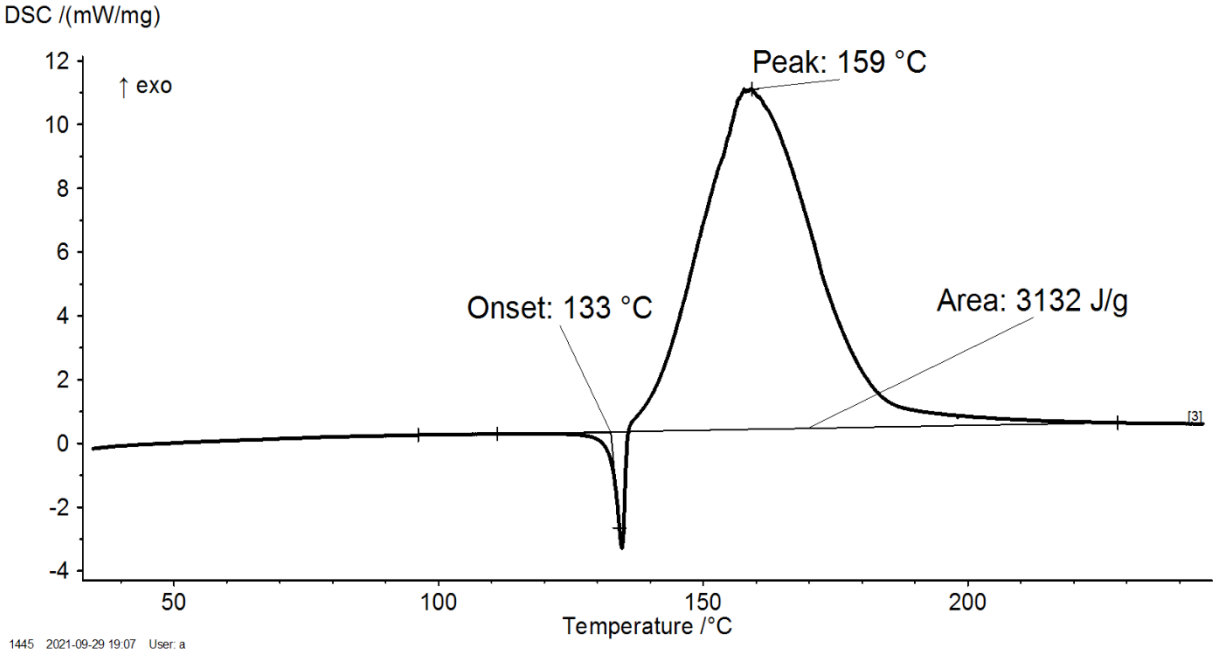


Figure S2 DSC data for compound **2**.

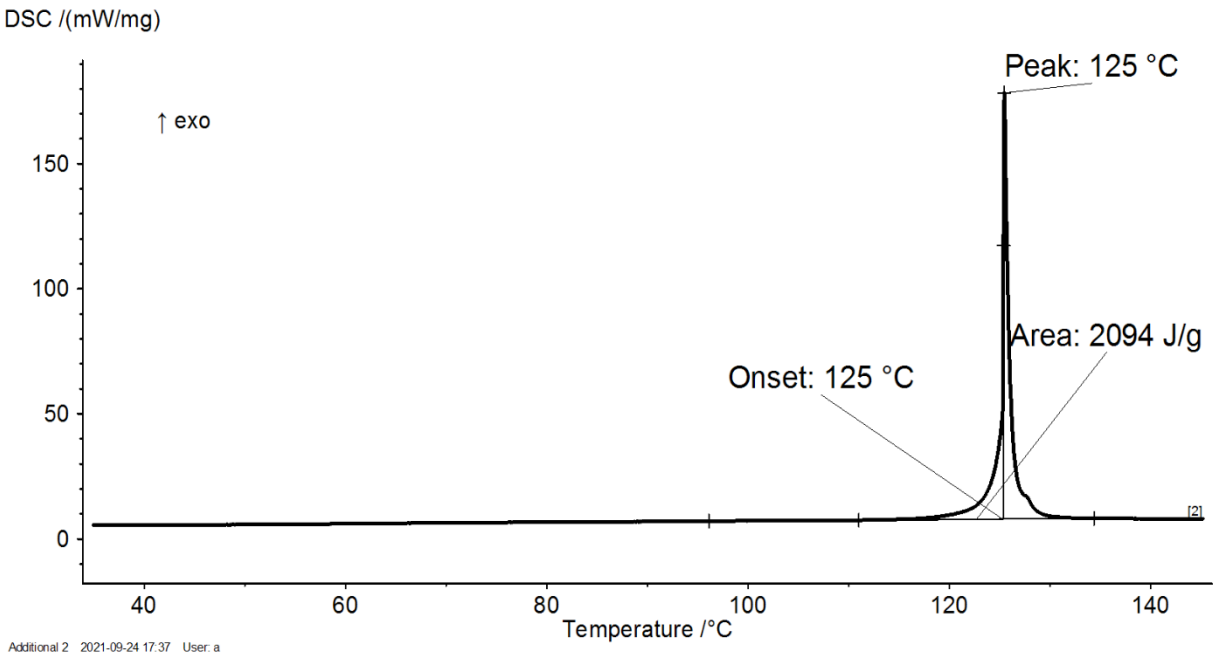


Figure S3 DSC data for compound **3**.

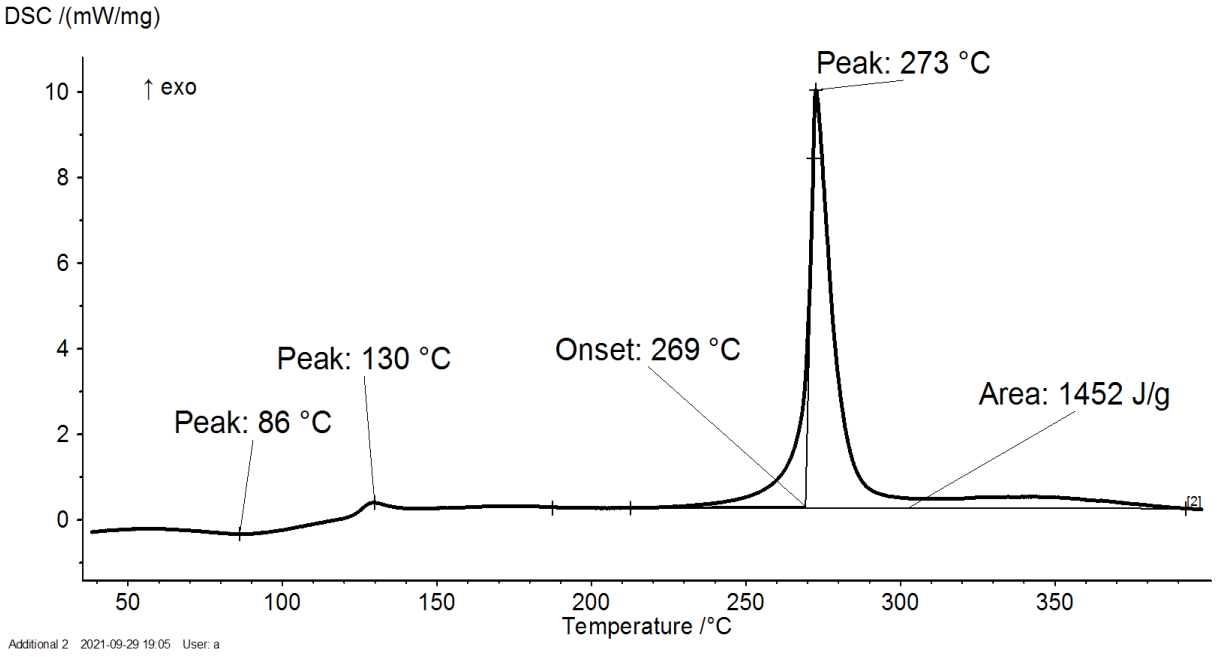
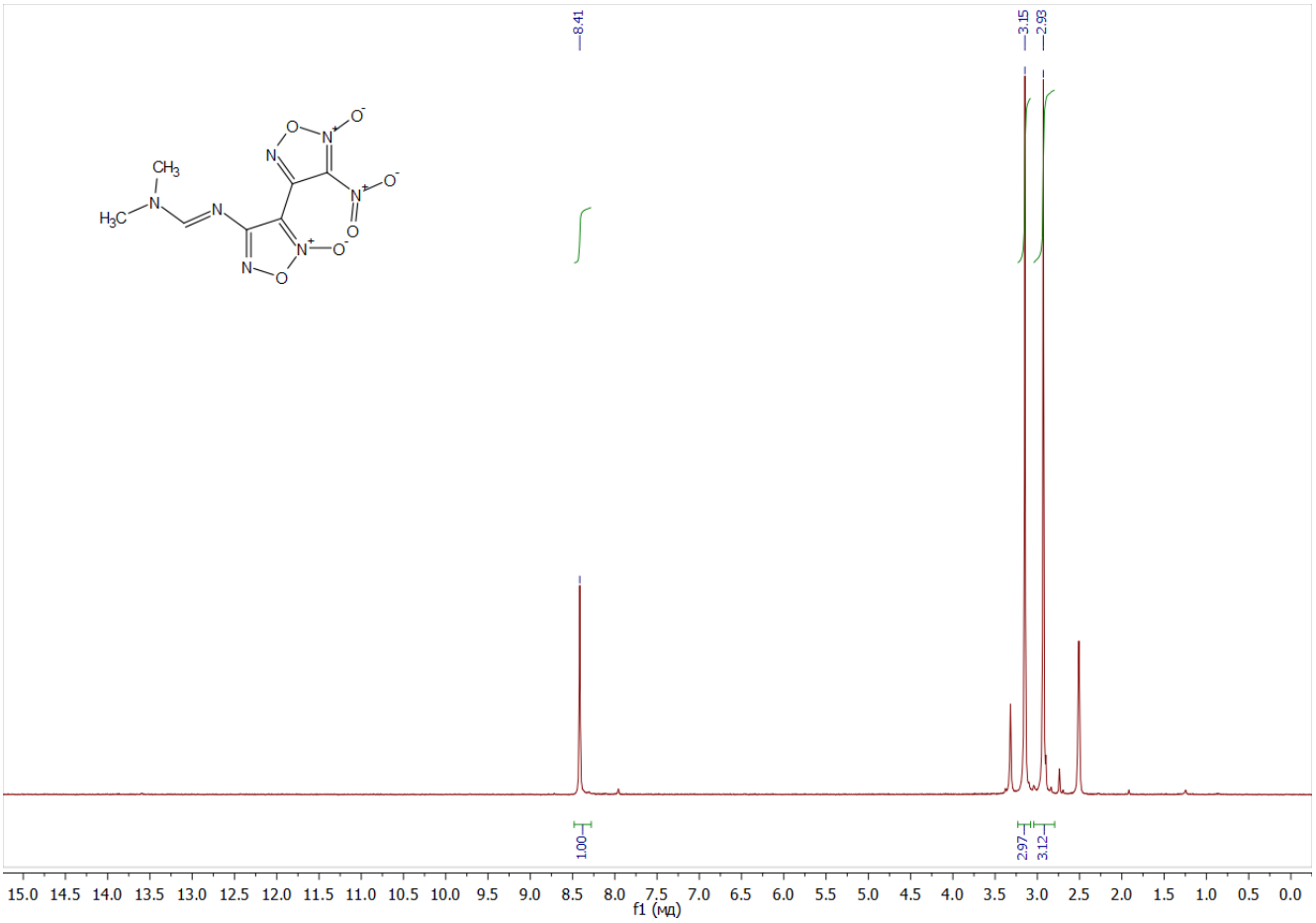
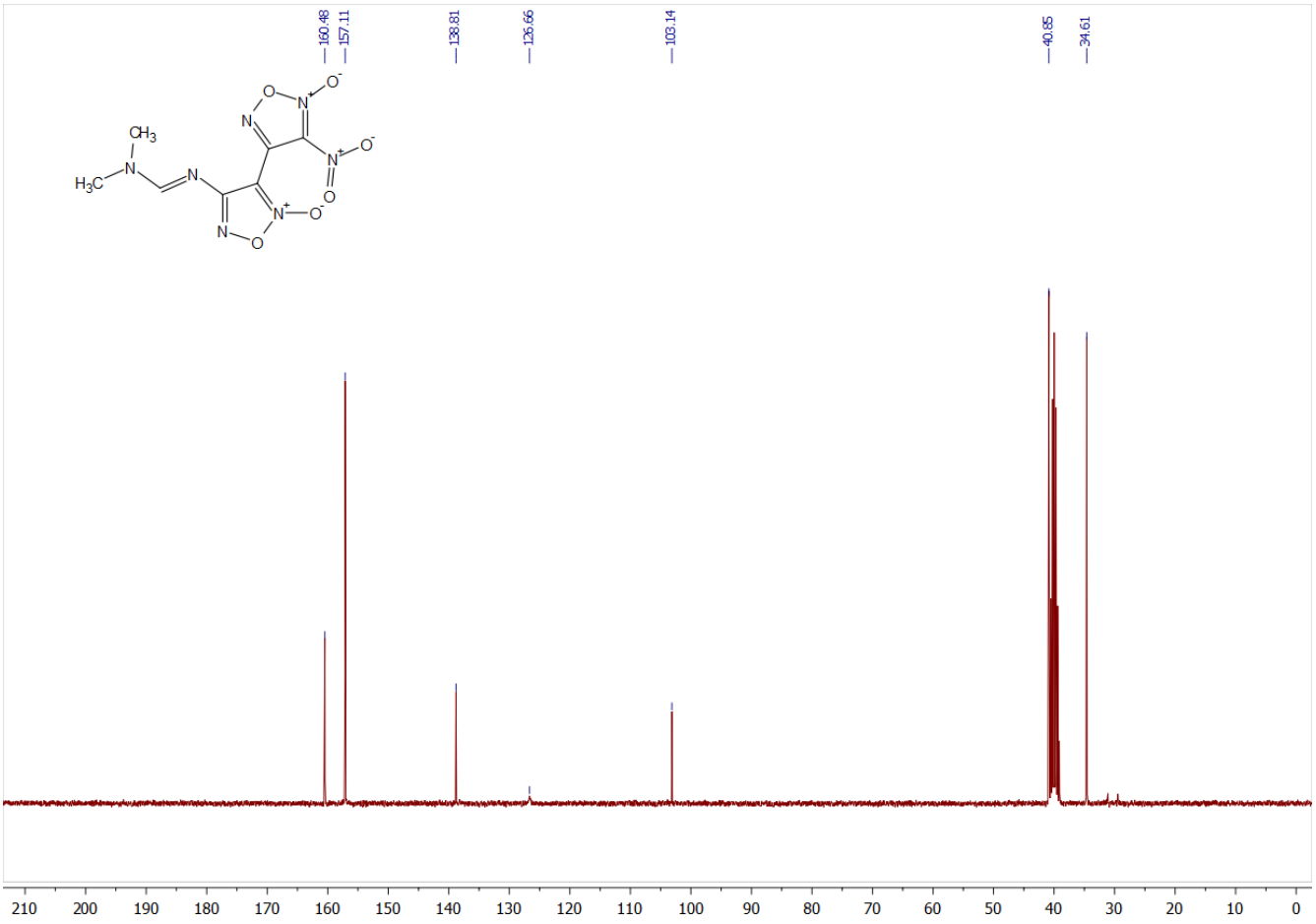


Figure S4 DSC data for compound **4**.

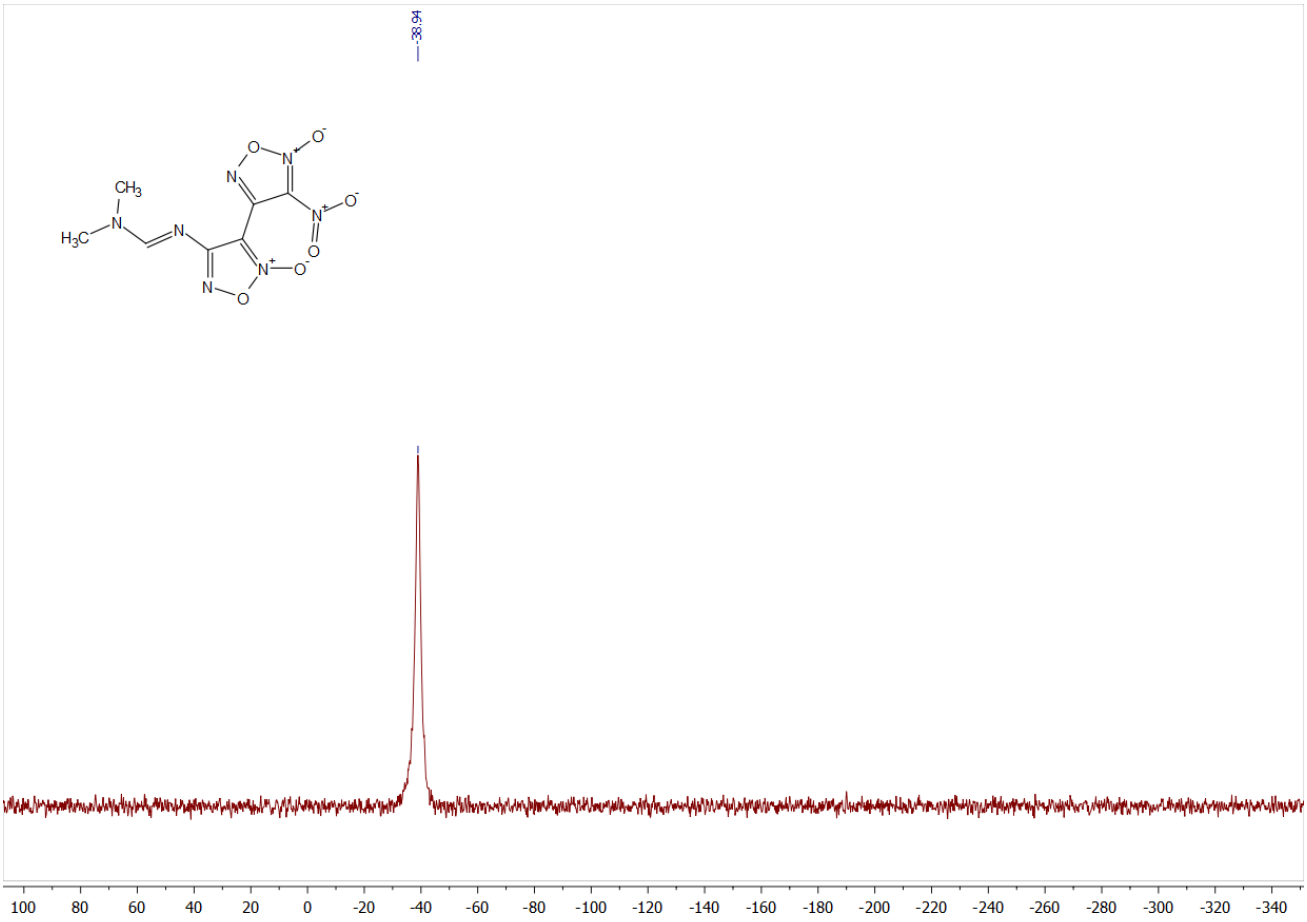
S4. Copies of NMR Spectra



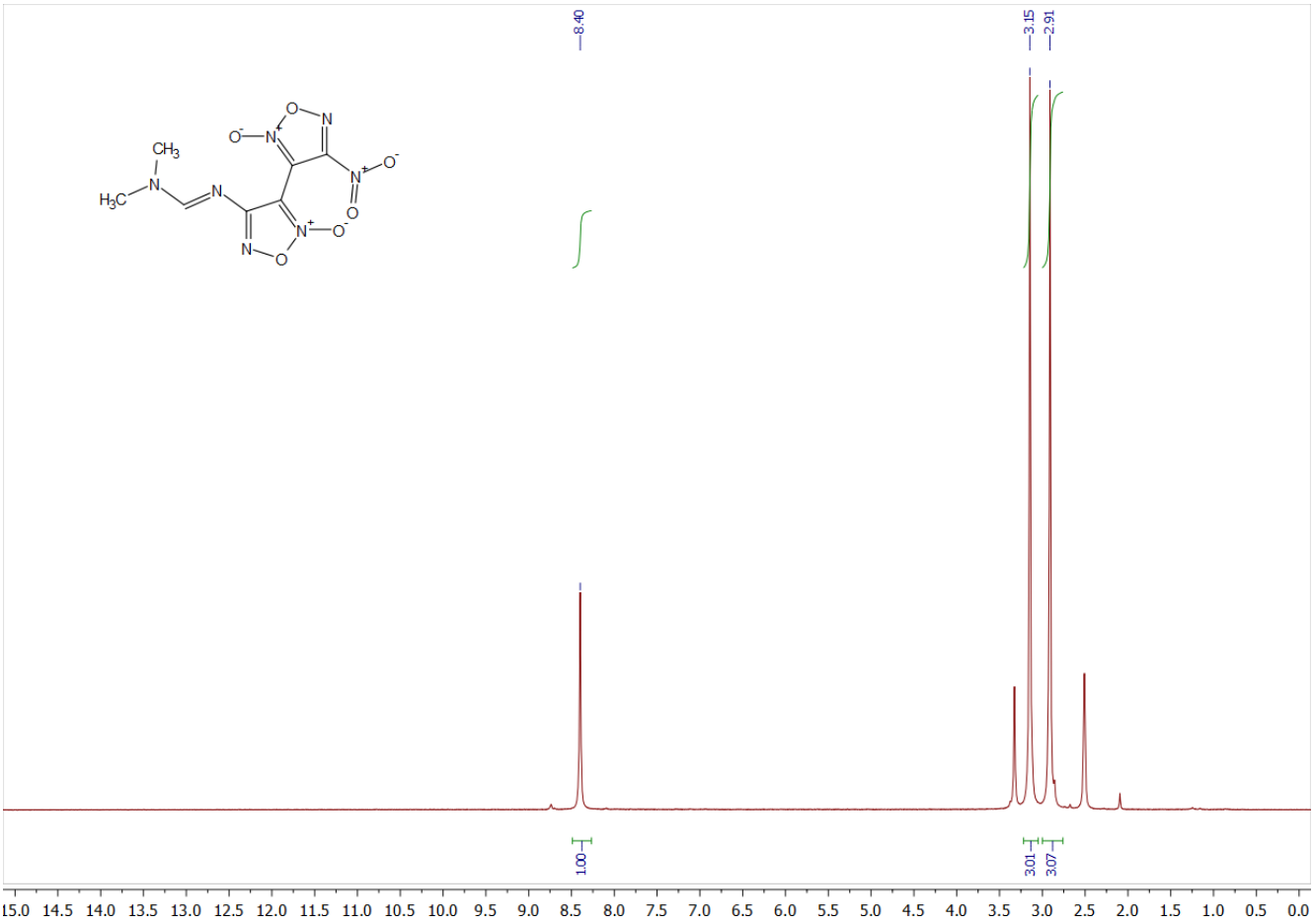
^{1}H NMR spectrum of compound **1**



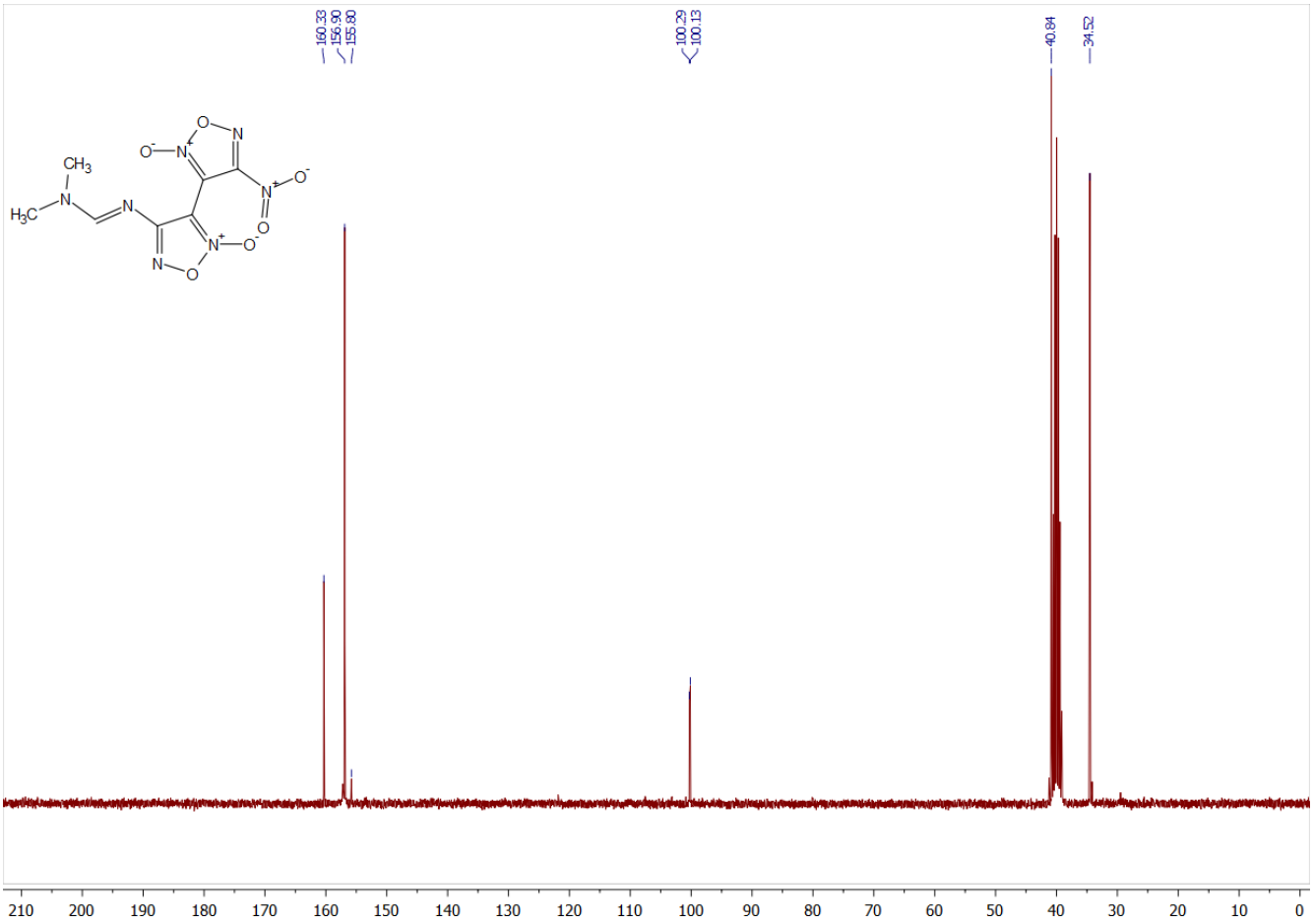
^{13}C NMR spectrum of compound **1**



^{14}N NMR spectrum of compound **1**



^{1}H NMR spectrum of compound **2**



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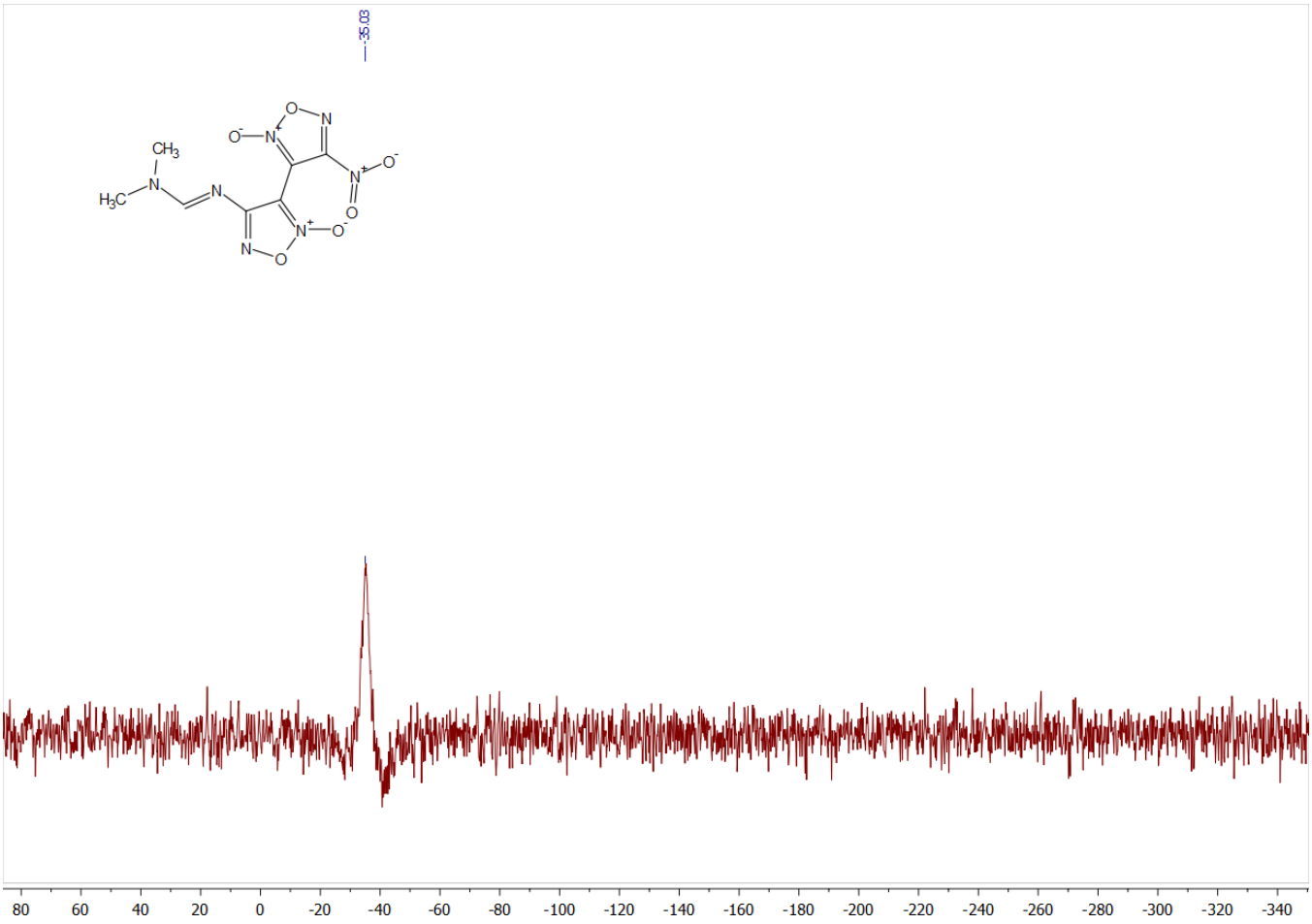
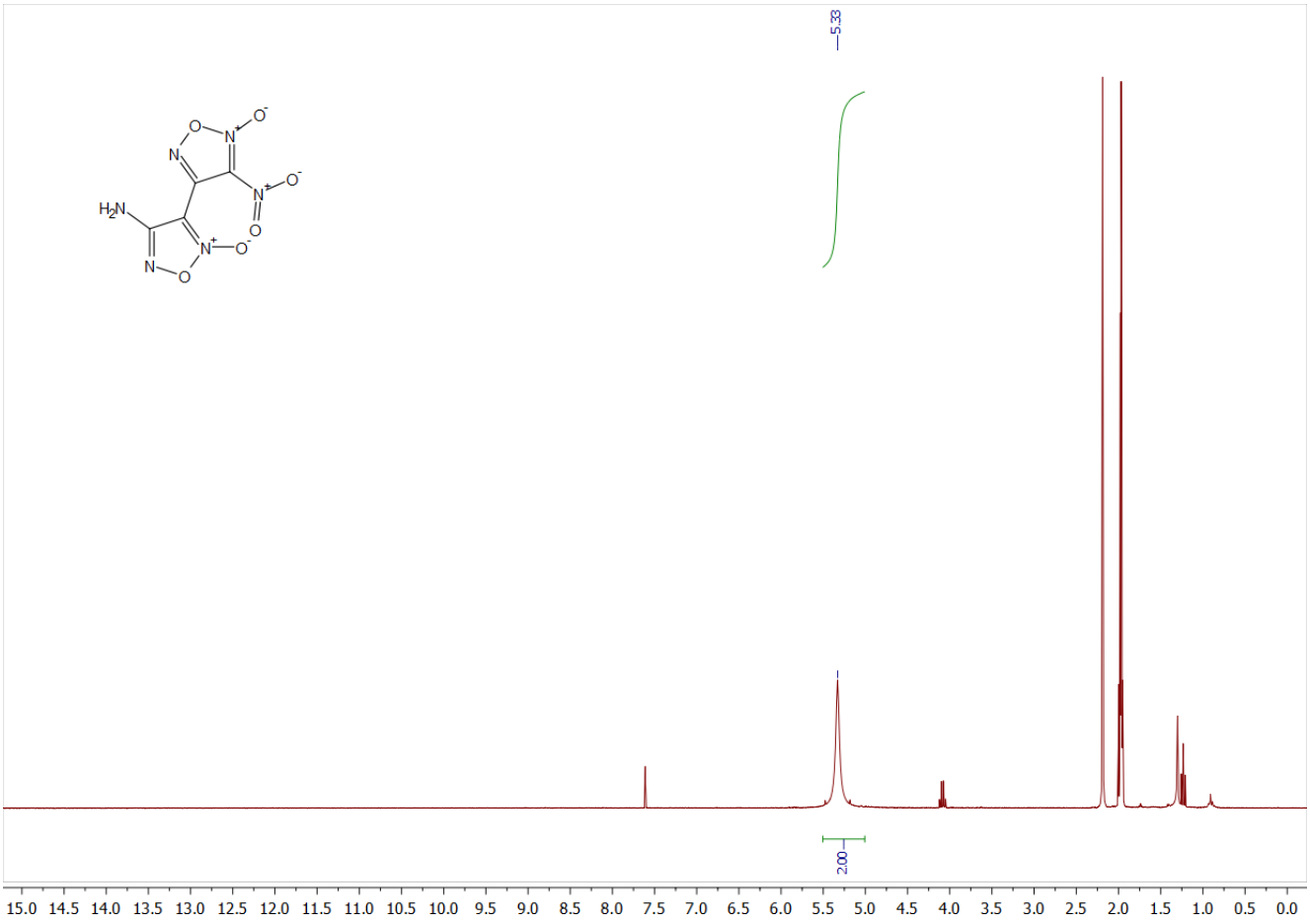
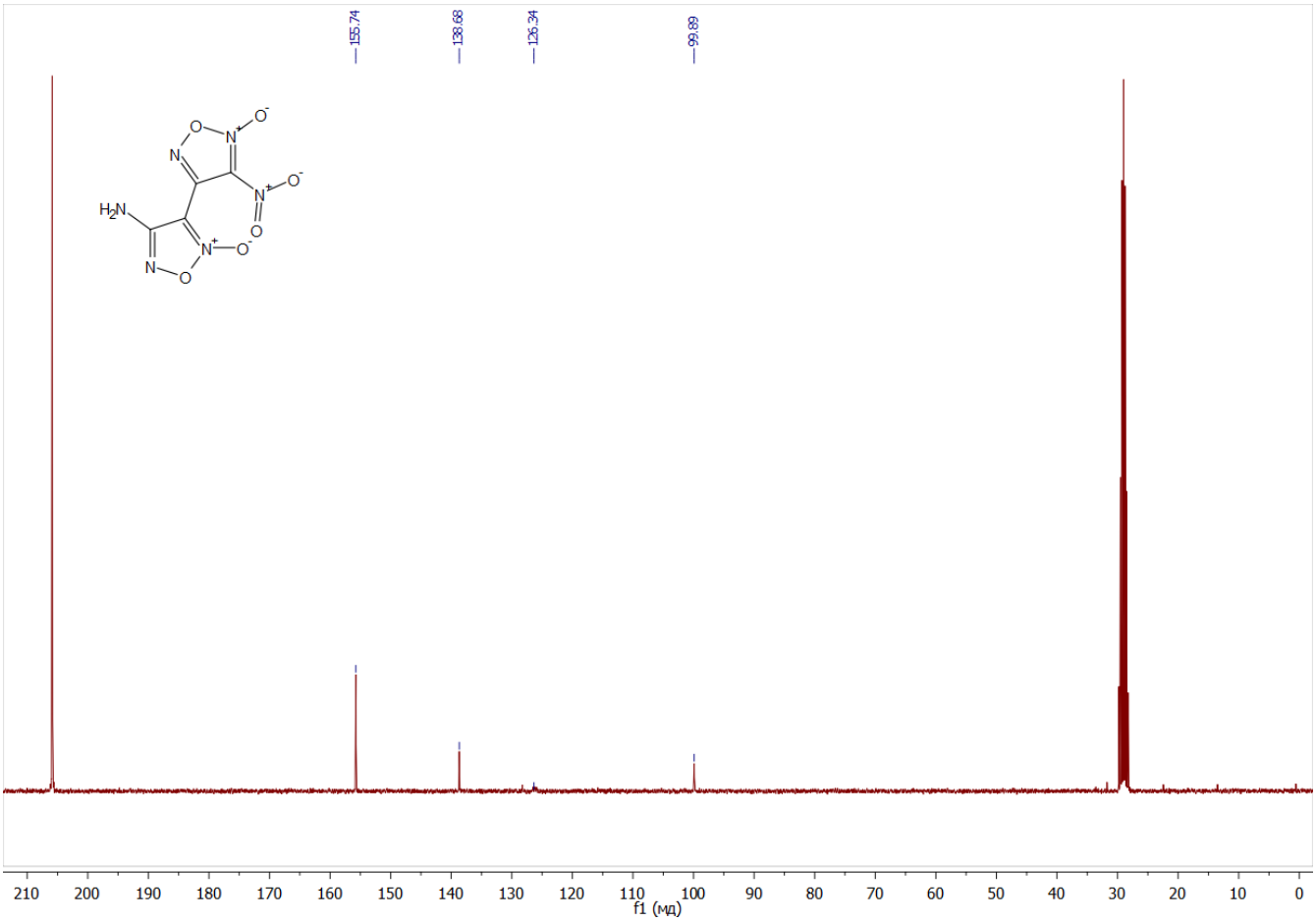


^{14}N NMR spectrum of compound **2**



^{1}H NMR spectrum of compound **3**



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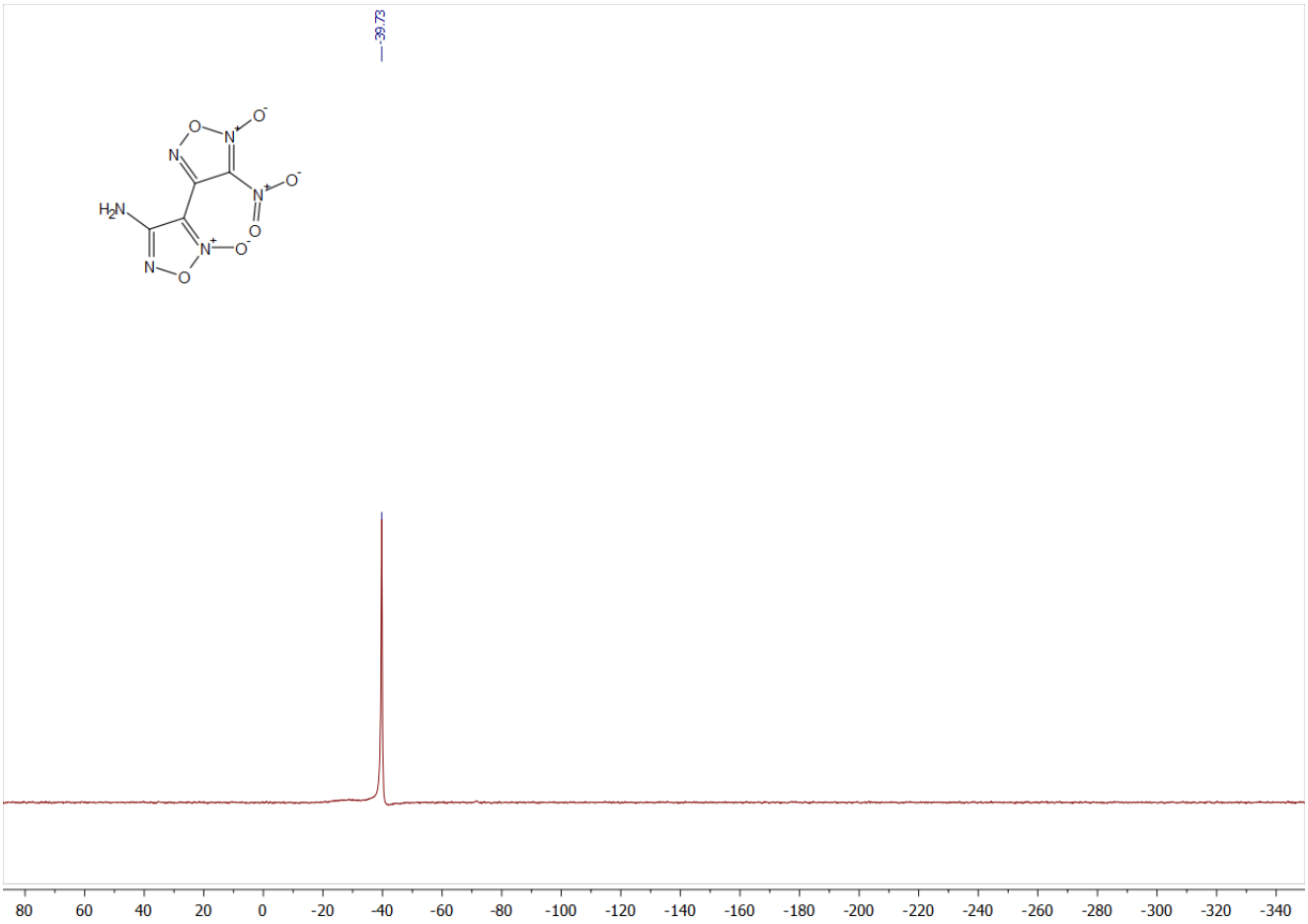
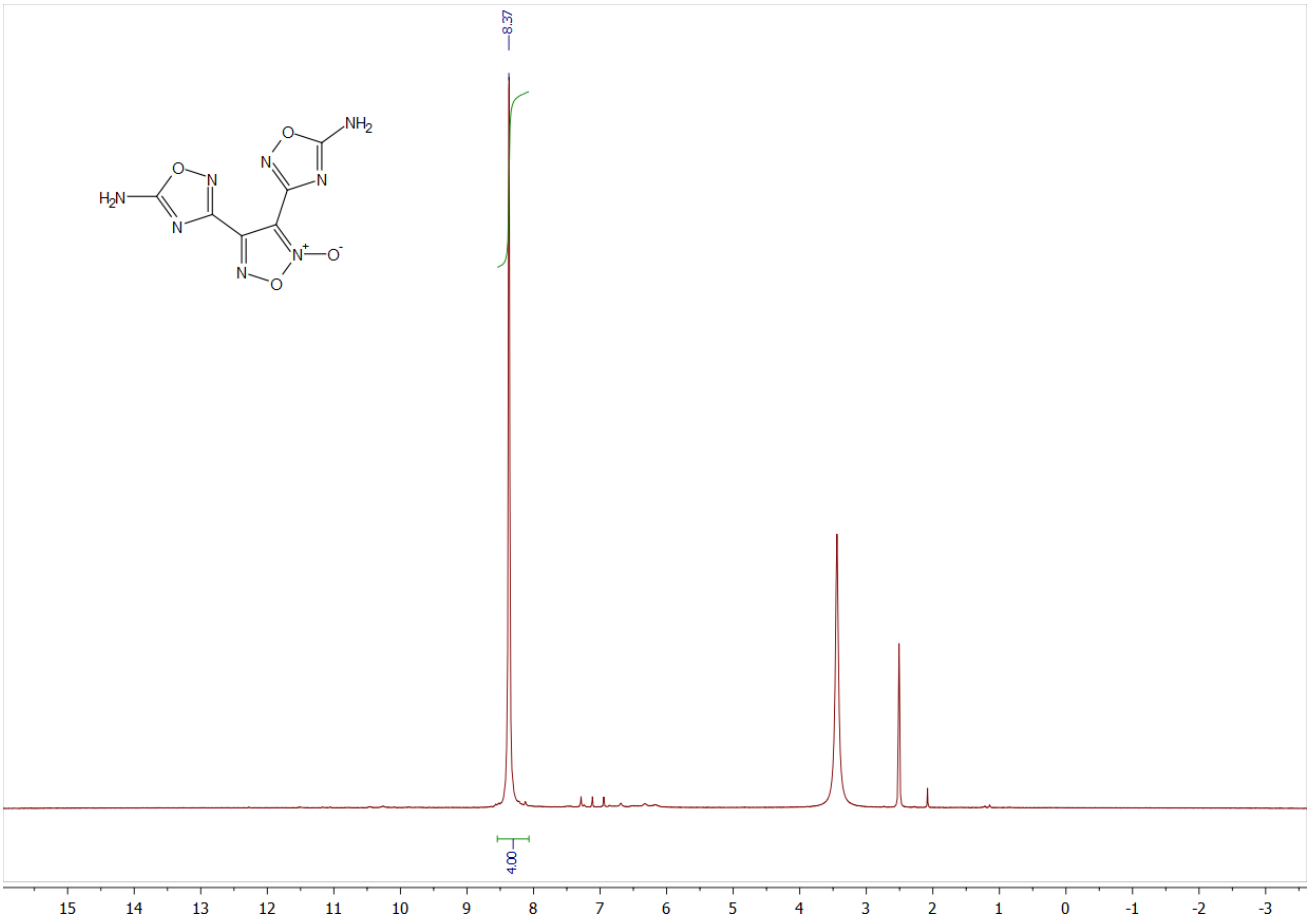
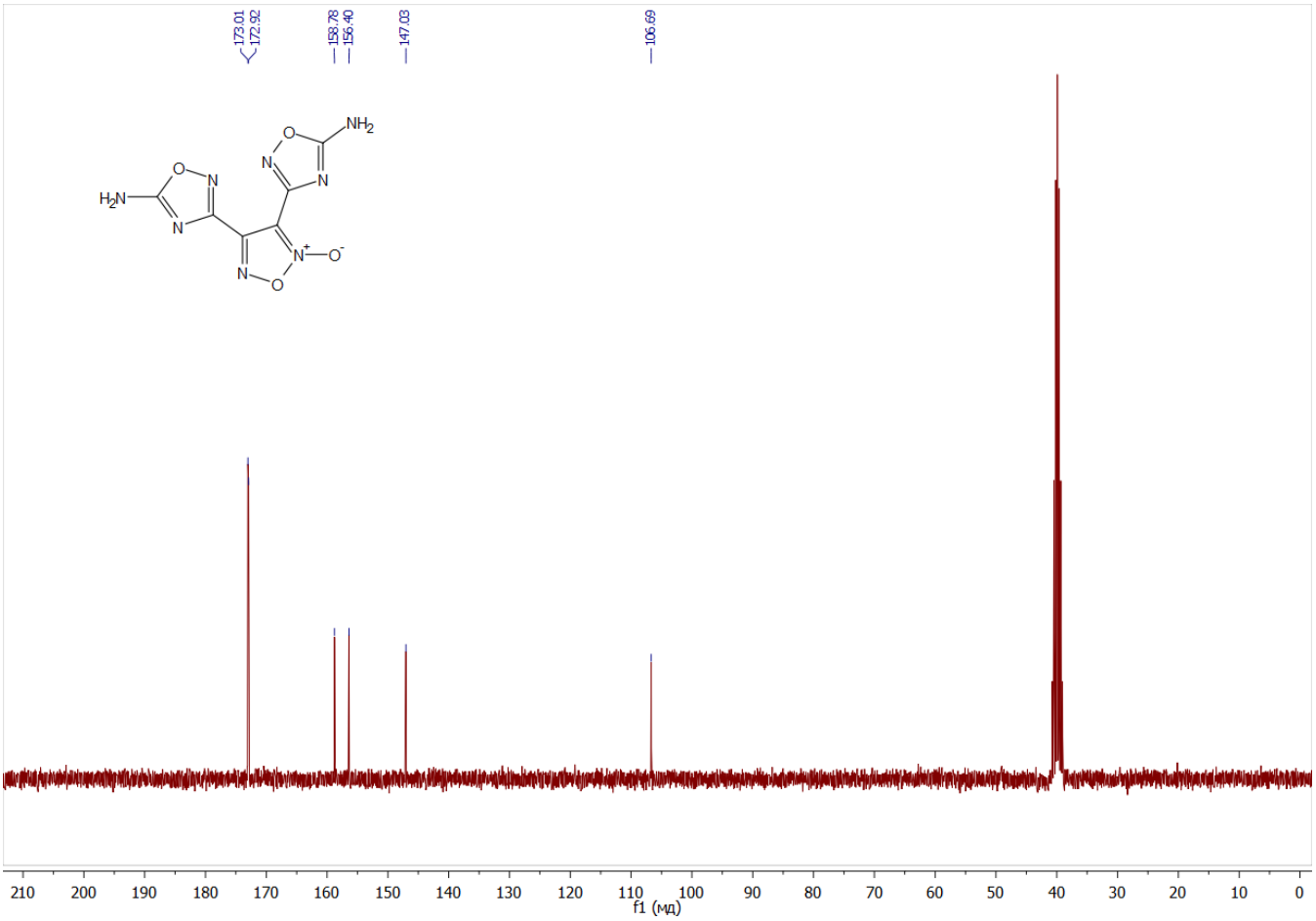


^{14}N NMR spectrum of compound **3**



^{1}H NMR spectrum of compound **4**



^{13}C NMR spectrum of compound **4**