Supporting Information for

New thermally stable and friction-insensitive nitrogen-rich salts: a synergy of 1,2,4-triazole, furoxan and hydroxytetrazole motifs

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S1. Crystallographic data

X-ray diffraction data were collected at 100K on a Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω-scan technique), using monochromatized Cu K_α-radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program[1]. The structure was solved by direct methods using SHELXT[2] and refined on F^2 using SHELXL-2018[3] in the OLEX2 program.[4] Positions of all atoms were found from the electron density-difference map. Atoms were refined with individual anisotropic (non-hydrogen atoms) or isotropic (hydrogen atoms) displacement parameters.

Table S1. Crystal data and structure refinement for synthesized compounds

Compound	**4**	**5**	**7**	**11**
Empirical formula	C7 H9 N9 O4 S	C5 H3 N9 O3	C5 H5 K2 N9 O5	C6 H8 N12 O3
Formula weight	315.29	237.16	349.38	296.24
Temperature	100.00(10) K	100.00(10) K	99.99(10) K	100.00(10) K
Wavelength (Radiation)	1.54184 Å (Cu Kα)	1.54184 Å (Cu Kα)	1.54184 Å (Cu Kα)	1.54184 Å (Cu Kα)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P $2_1/c$	C $2/c$	P $\bar{1}$	Cc
a [Å] b [Å] c [Å]	18.0728(2) 9.94200(10 7.11510(10)	18.3967(3) 7.17590(10) 13.5983(2)	6.9975(2) 8.9440(2) 11.0111(3)	3.83694(5) 17.9329(2) 16.51337(18)
Angles [α, β, γ]	α = 90° β = 93.4250(10)° γ = 90°	α = 90° β = 110.355(2)° γ = 90°	α = 66.363(3)° β = 86.447(2)° γ = 75.934(2)°°	α = 90° β = 94.2871(11)° γ = 90°
Volume	1276.16(3) $Å^3$	1683.05(5) $Å^3$	611.90(3) $Å^3$	1133.06(2) $Å^3$
Z	4	8	2	4
Density (calculated)	1.641 g/cm^3	1.872 g/cm^3	1.896 g/cm^3	1.737 g/cm^3
F(000)	648	960	352	608
Theta range for data collection	2.449 to 80.152°	5.129 to 79.832°	4.387 to 80.176°	4.932 to 79.895°.
Reflections collected	17412	9651	30583	12386
Independent reflections	2756 [R(int) = 0.0504]	1837 [R(int) = 0.0285]	2641 [R(int) = 0.0630]	2351 [R(int) = 0.0331]
Observed reflections	2699	1690	2544	2328
Absorption correction	Analytical	Gaussian	Gaussian	Gaussian
Max. and min. transmission	0.840 and 0.441	1.000 and 0.735	1.000 and 0.524	1.000 and 0.629
Data / restraints / parameters	2756 / 0 / 226	1837 / 0 / 166	2641 / 0 / 210	2351 / 2 / 215

Goodness-of-fit on F^2	1.067	1.072	1.106	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1079	R1 = 0.0320, wR2 = 0.0873	R1 = 0.0458, wR2 = 0.1293	R1 = 0.0250, wR2 = 0.0655
R indices (all data)	R1 = 0.0397, wR2 = 0.1085	R1 = 0.0341, wR2 = 0.0889	0.0464, wR2 = 0.1302	R1 = 0.0252, wR2 = 0.0657
Largest diff. peak and hole	0.322 and -0.487 e. $Å^{-3}$	0.269 and -0.243 e.$Å^{-3}$	0.795 and -0.733 e. $Å^{-3}$	0.213 and -0.170 e.$Å^{-3}$
CCDC	2492505	2492510	2492506	2492507

S2. Computational details

The enthalpies of formation in solid state ($\Delta H^0_{f,solid}$) of compound **5** was estimated by the equation using empirical relationship of enthalpy of sublimation and temperature of melting point[5]:

$$\Delta H^0_{f,\,solid} = \Delta H^0_{f,gas} - 188T_m$$

Calculations of enthalpies by CBS-4M method were carried out in Gaussian G09 program package[6]. The gas-phase enthalpies of formation ($\Delta H^0_{f,gas}$) were calculated by atomization energy method. Empirical and calculated by CBS-4M method values of enthalpies of formation for atoms H, C, O, N were used in the following relation:

$$\Delta H^0_{f,gas} = \Sigma H_{atom} - \Sigma \Delta_f H_{atom} - \Sigma D_0$$

where

$$\Delta_f H_{atom} = \Delta_f H_{0K} - \Delta\Delta H$$

$$\Sigma D_0 = \Sigma H_{atom,\,CBS4M} - H_{molecule,\,CBS4M}$$

Empirical enthalpies of formaton at 0K for atoms ($\Delta_f H_{0K}$), changes of enthalpy from state at 0K to standard state ($\Delta\Delta H$) and enthalpies of formaton calculated by CBS-4M method ($H_{atom,\,CBS4M}$) are presented in the Table S2.

Table S2.

	$\Delta_f H_{0K}$, kcal mol^{-1}	$\Delta\Delta H$, kcal mol^{-1}	$H_{atom,\,CBS4M}$, *hartree*
H	51.63	1.01	-0.500991
C	169.98	0.25	-37.786156
N	112.53	1.04	-54.522462
O	58.99	1.04	-74.991202

Solid-state enthalpies of formation of salts **6-9, 11-13** were calculated using procedure described in [7] by following equation:

$$\Delta H^0_{f,\,solid} = \Delta H^0_{f,\,cation,\,gas,\,CBS4M} + \Delta H^0_{f,\,anion,\,gas,\,CBS4M} - \Delta H_{lattice}$$

Gas-phase enthalpies of formation $\Delta H^0_{f,\,gas}$ for deprotonated hydroxytetrazole and organic cations were calculated by atomization method described above. Lattice enthalpies were evaluated using following equation:

$$\Delta H_{lattice} = U_{lattice} + \left(n_{cation}\left(\frac{a_{cation}}{2} - 2\right) + n_{anion}\left(\frac{a_{anion}}{2} - 2\right)\right)$$

where n_i equals number of cations or anions in structure and a_i equals 3 for monoatomic ions, 5 for linear polyatomic ions and 6 for nonlinear polyatomic ions.

Lattice energy $U_{lattice}$ of salts was estimated by its relation to a sum of ionic volumes using equation and coefficients listed in[8]:

$$U_{lattice} = 2I\left(\alpha/\sqrt[3]{V} + \beta\right)$$

where $I = 1$, $\alpha = 117.3$ kJ nm mol^{-1}, $\beta = 51.9$ kJ mol^{-1} for 1:1 salts and V is the corrected sum of volumes of cation and anion.

Ionic volumes were calculated for optimized structures at B3LYP/6-311G+(d,p) level of theory inside of a surface corresponding to 0.001 electron Bohr^{-3} density using Gaussian G09 program package[5]. Corrections to the sum of volumes V were applied in a manner described by Rice et. al.[9].

Calculated volumes and gas-phase enthalpies of formation of ions presented in Table S3. Corrected sum of volumes, lattice energies, lattice enthalpies and solid-state enthalpies of formation are presented in Table S4.

Table S3.

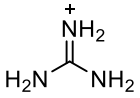
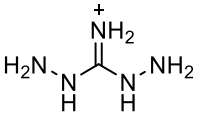
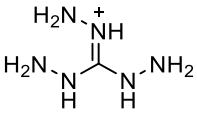
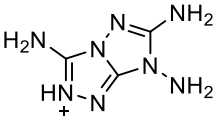
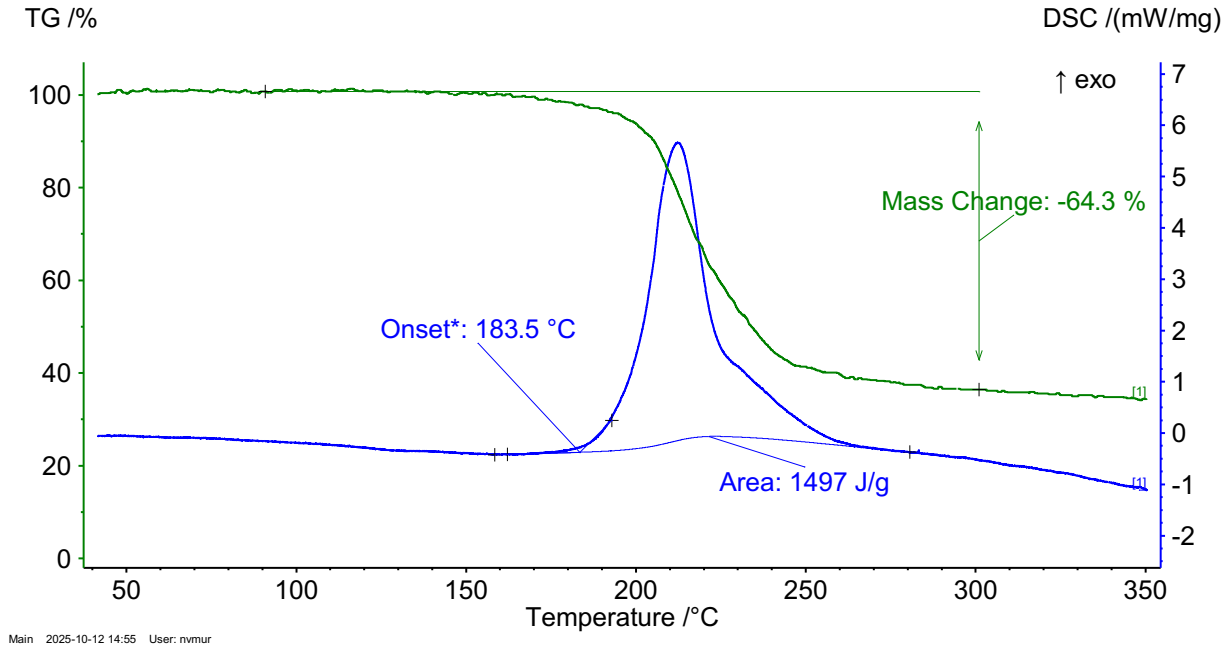
	Volume, nm^3	$\Delta H^0_{f,\,gas,\,CBS4M}$, kcal mol^{-1}
Hydroxytetrazole anion	0.236540	101.032
	0.076206	121.613
	0.112857	204.098
	0.123365	261.198
	0.147070	224.930
NH_4^+	0.028362	142.066
Na^+	0.008701	118.308
K^+	0.014360	99.904

Table S4.

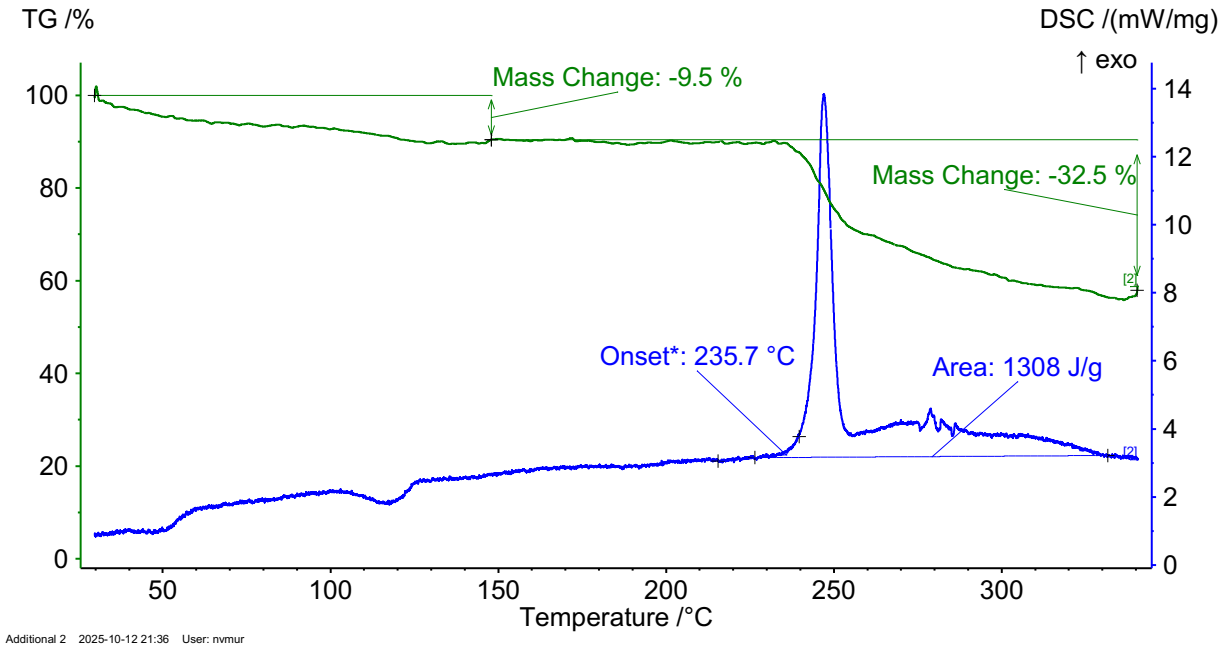
	$V_{cation}+V_{anion}$, nm^3	$V_{corrected}$, nm^3	$U_{lattice}$, kcal mol^{-1}	$H_{lattice}$ kcal mol^{-1}	$\Delta H^0_{f,\,solid}$, kcal mol^{-1}
6	0.24524	0.24268	114.702	114.998	104.34
7	0.25090	0.24834	114.014	114.310	86.63
8	0.26490	0.25858	112.821	114.005	129.09
9	0.38361	0.37446	102.601	103.785	222.18

11	0.34940	0.33930	105.200	106.384	198.75
12	0.35991	0.34887	104.458	105.643	256.58
13	0.29854	0.29033	109.487	110.672	99.90

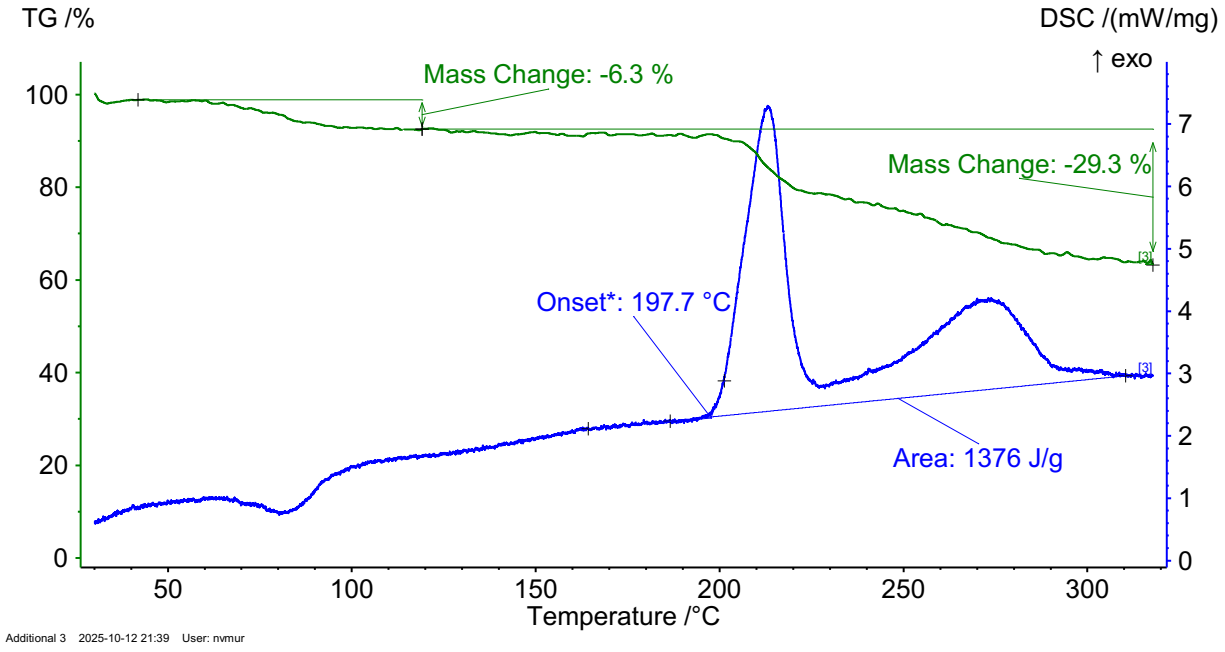
S3. Thermal behavior



DSC/TGA signals for linearly heated **5.**



DSC/TGA signals for linearly heated **6.**



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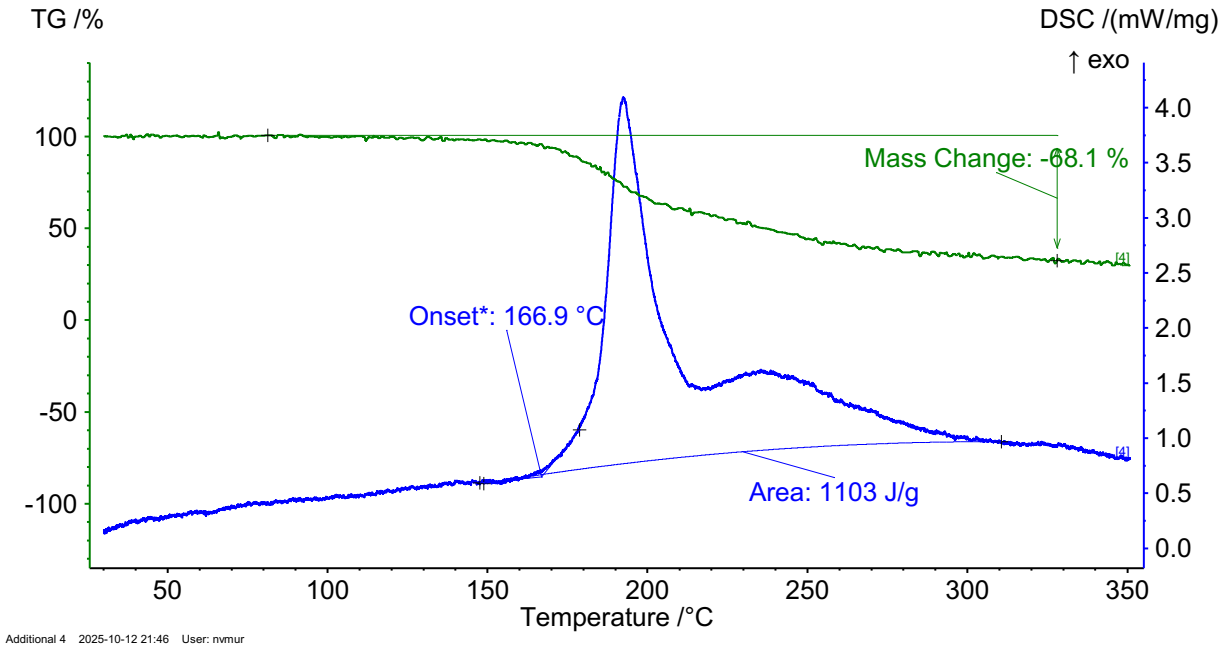
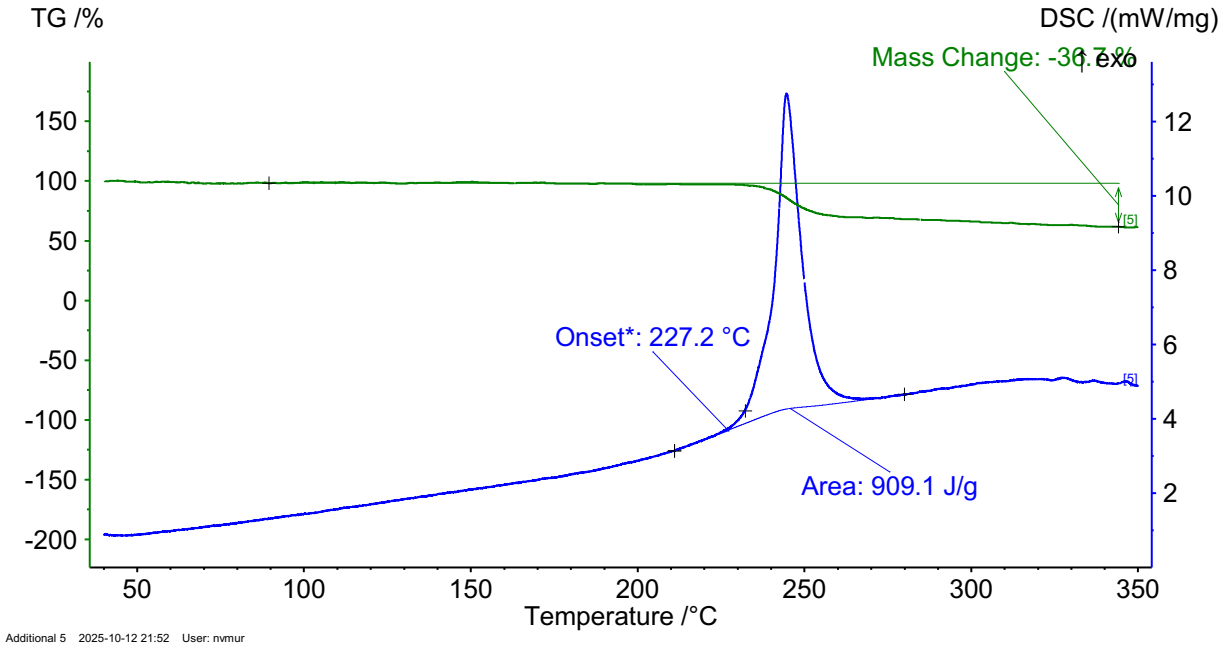
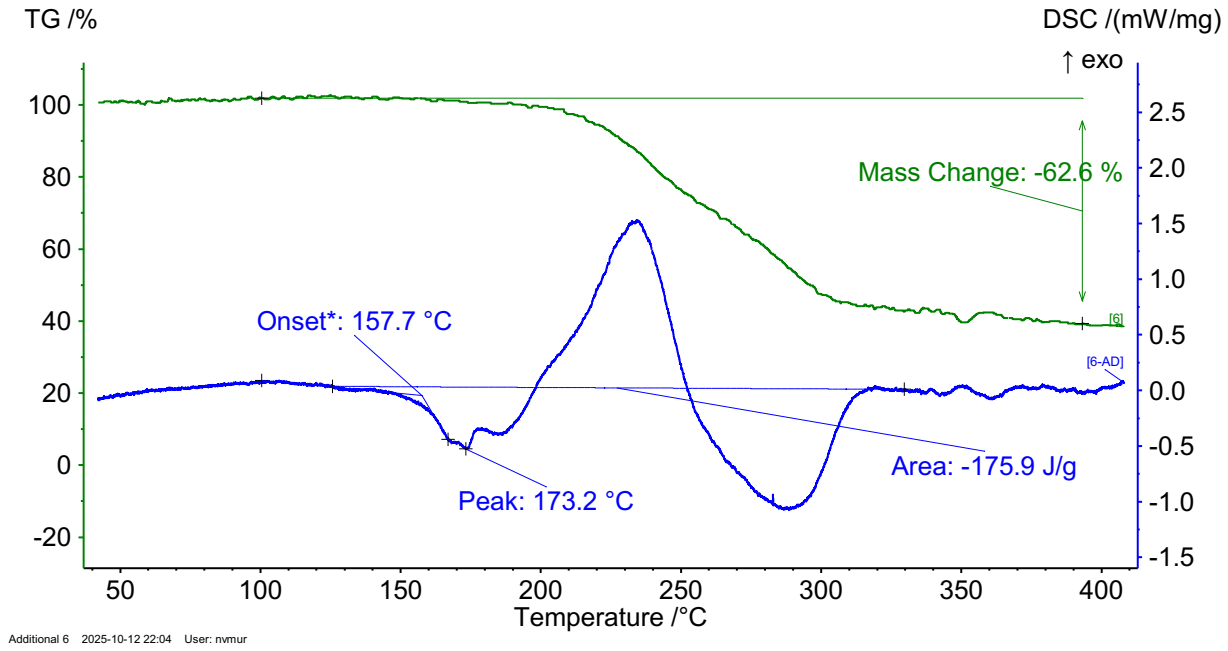


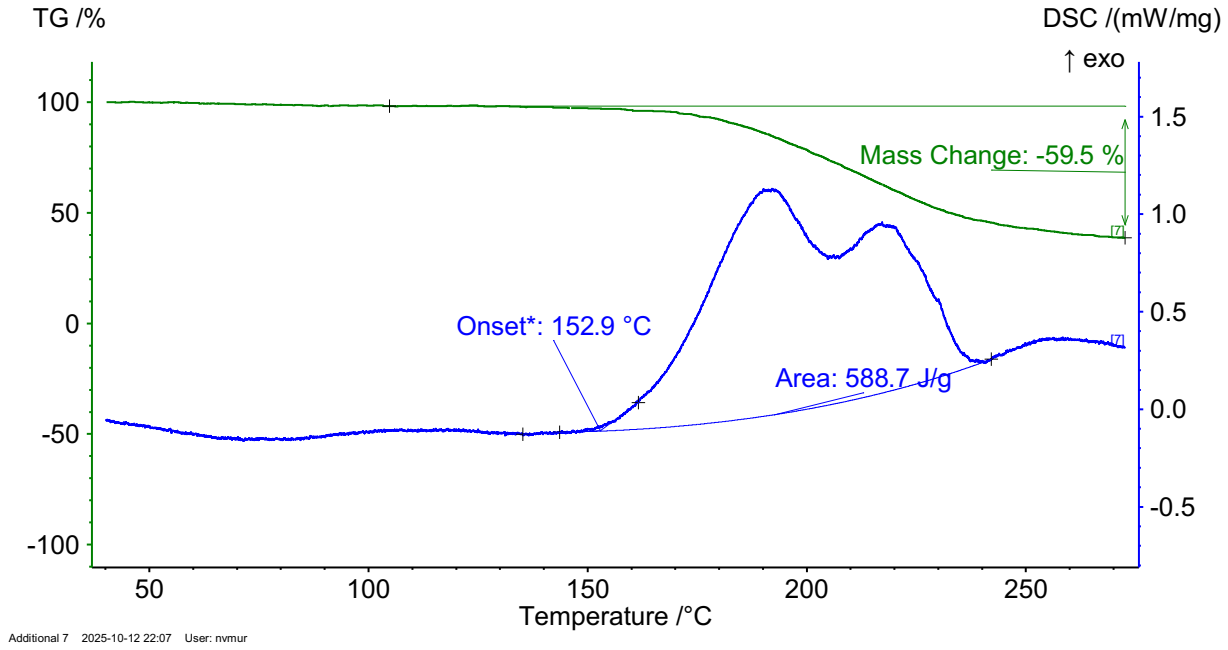
DSC/TGA signals for linearly heated **8.**



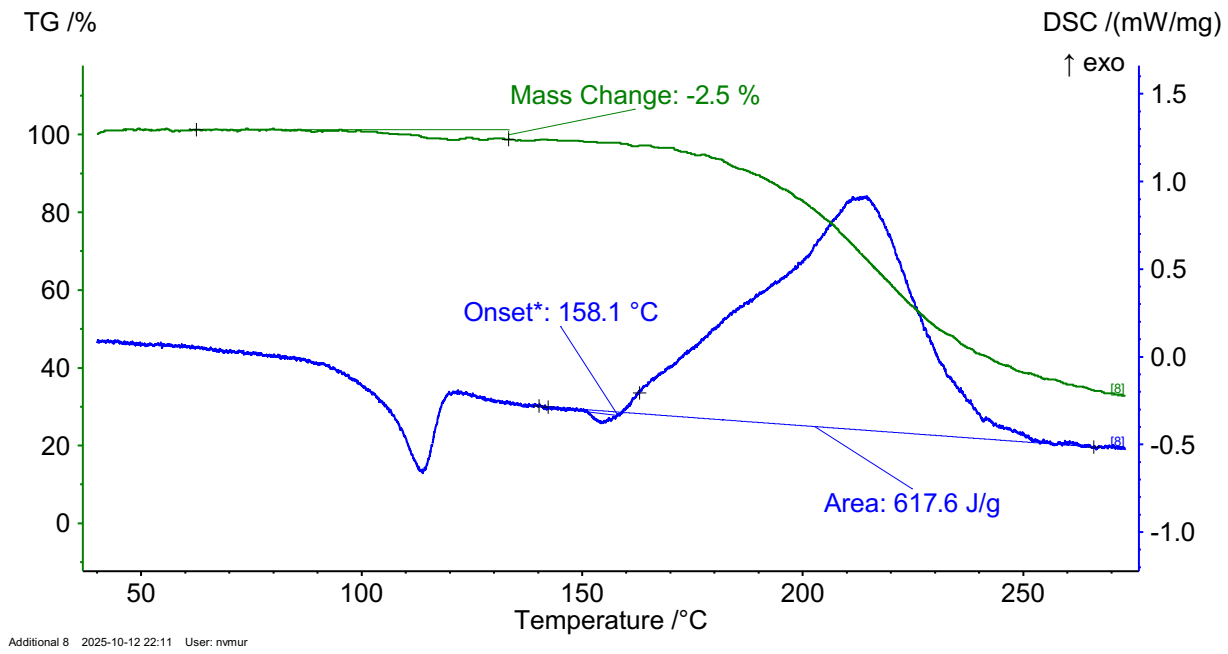
DSC/TGA signals for linearly heated **9.**



DSC/TGA signals for linearly heated **11.**

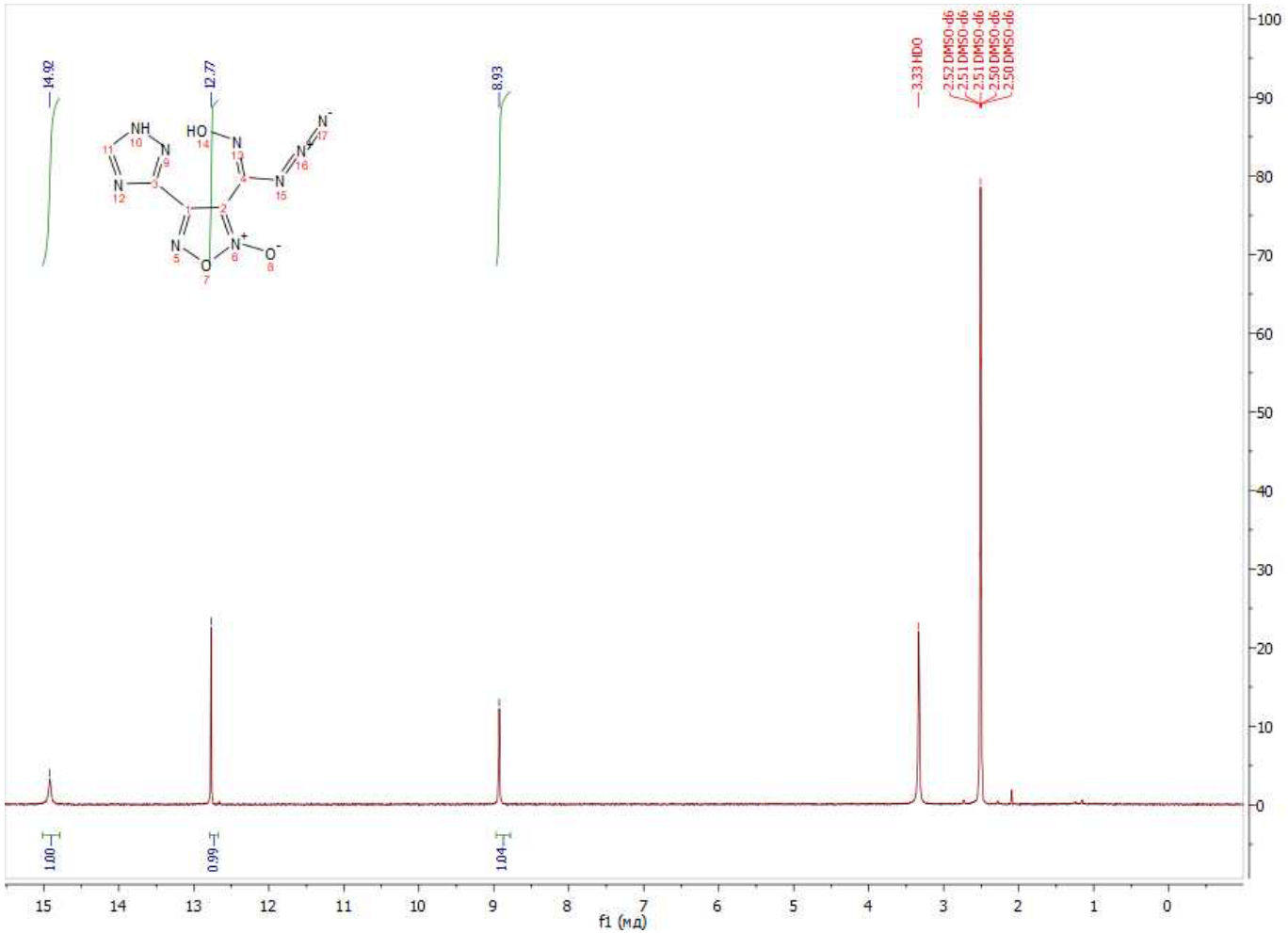


DSC/TGA signals for linearly heated **12.**

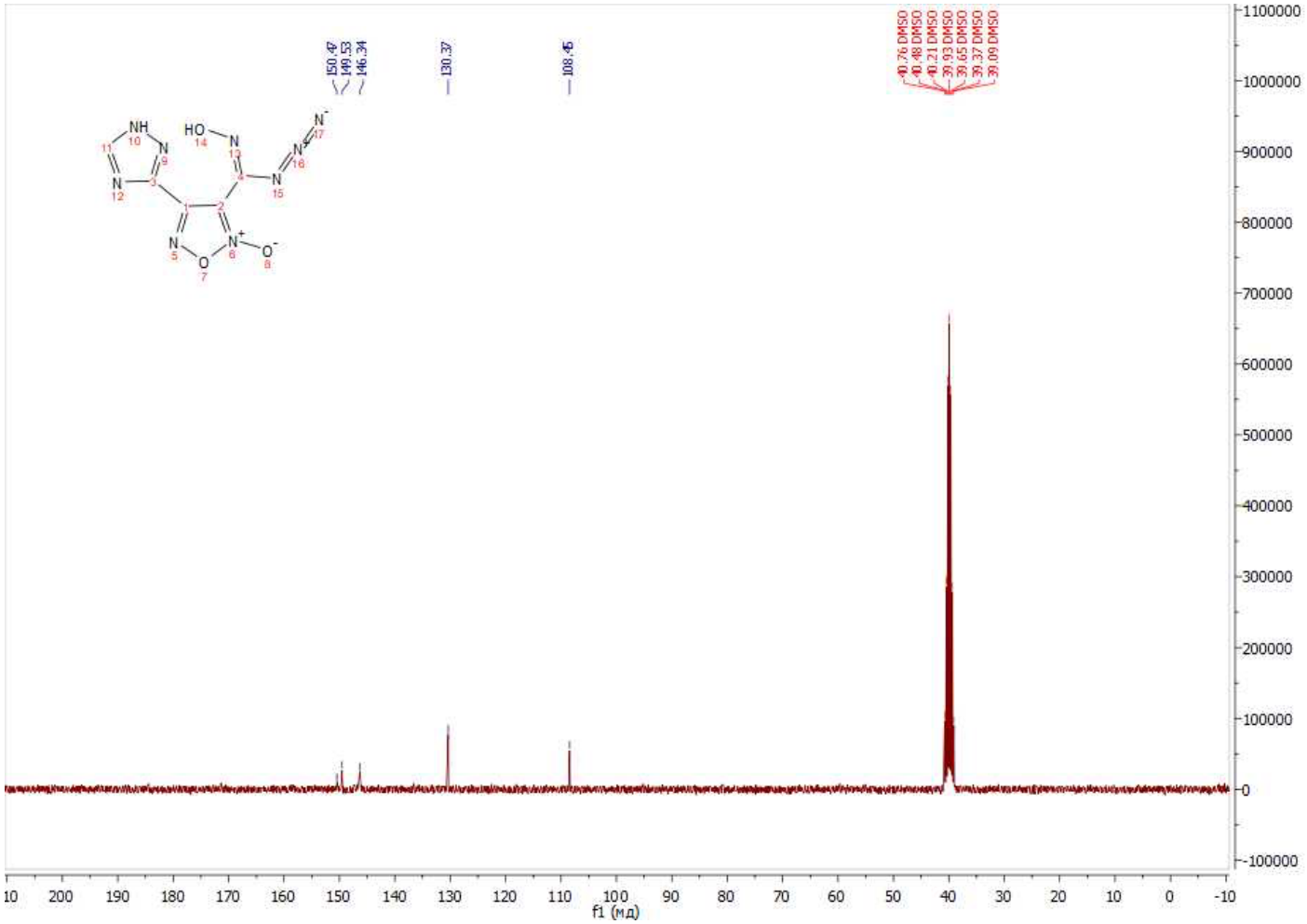


DSC/TGA signals for linearly heated **13.**

S4. Copies of NMR spectra



^{1}H NMR spectrum of **4**, DMSO-[d_6]



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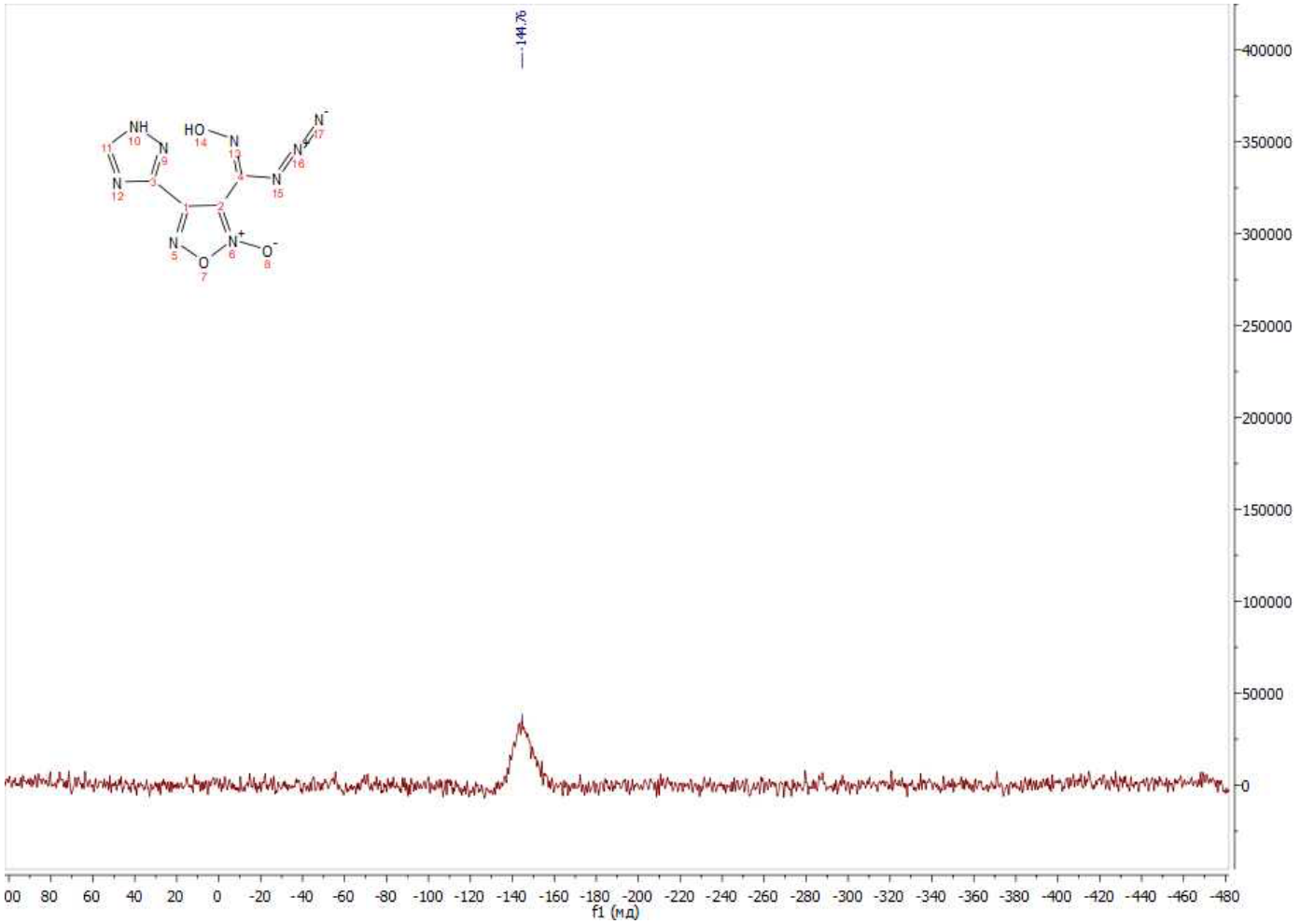

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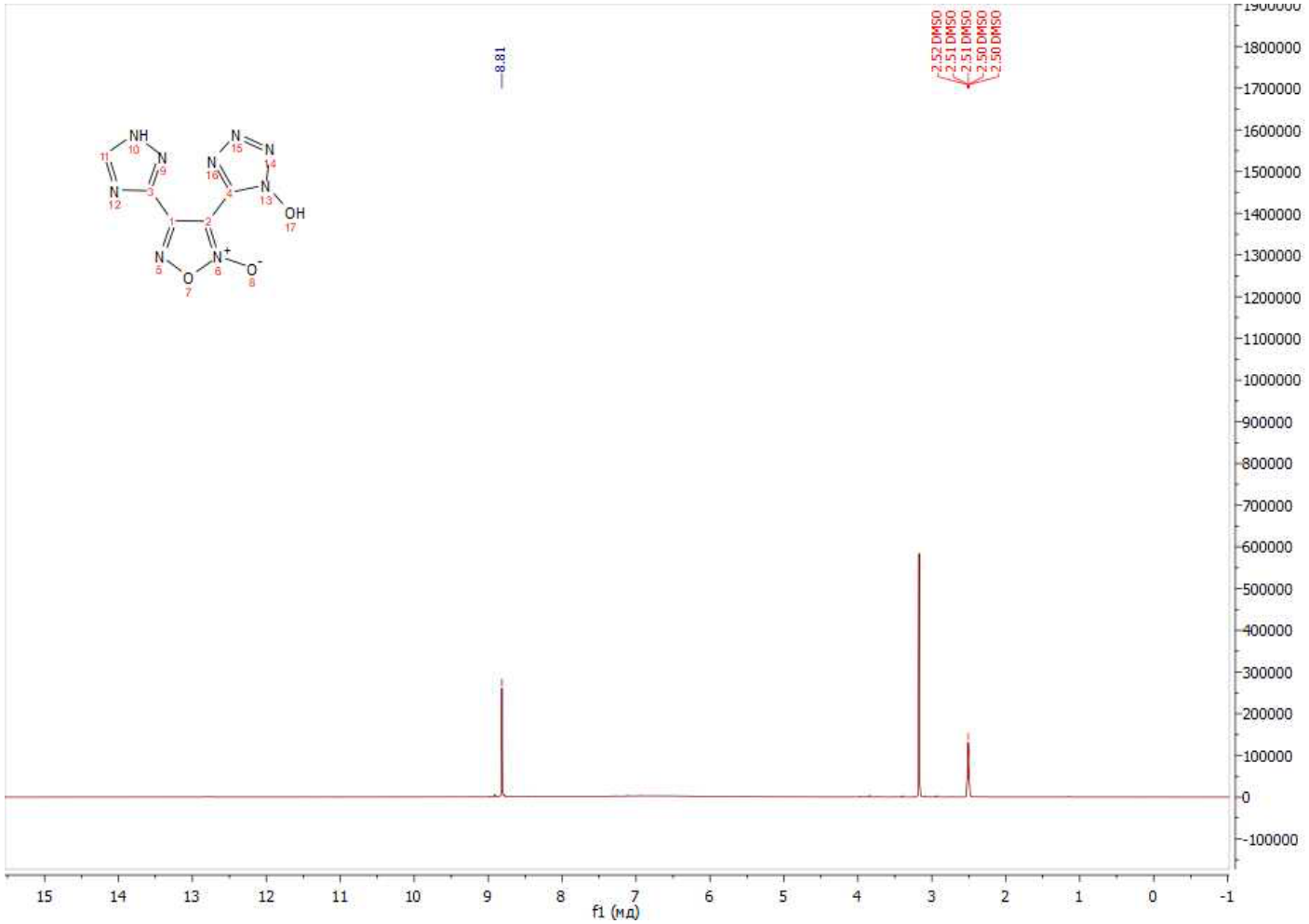
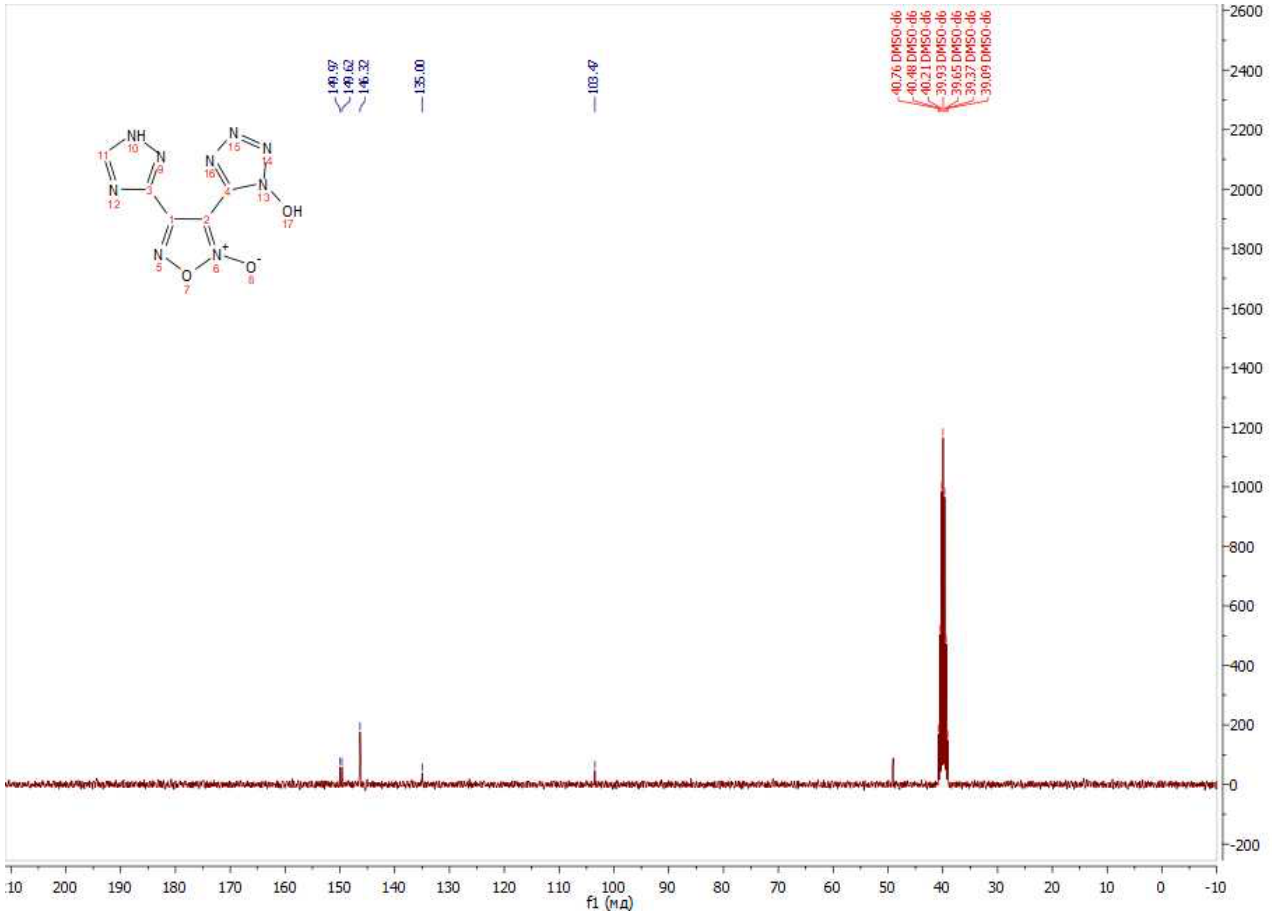


^{1}H NMR spectrum of **5**, DMSO-[d_6]



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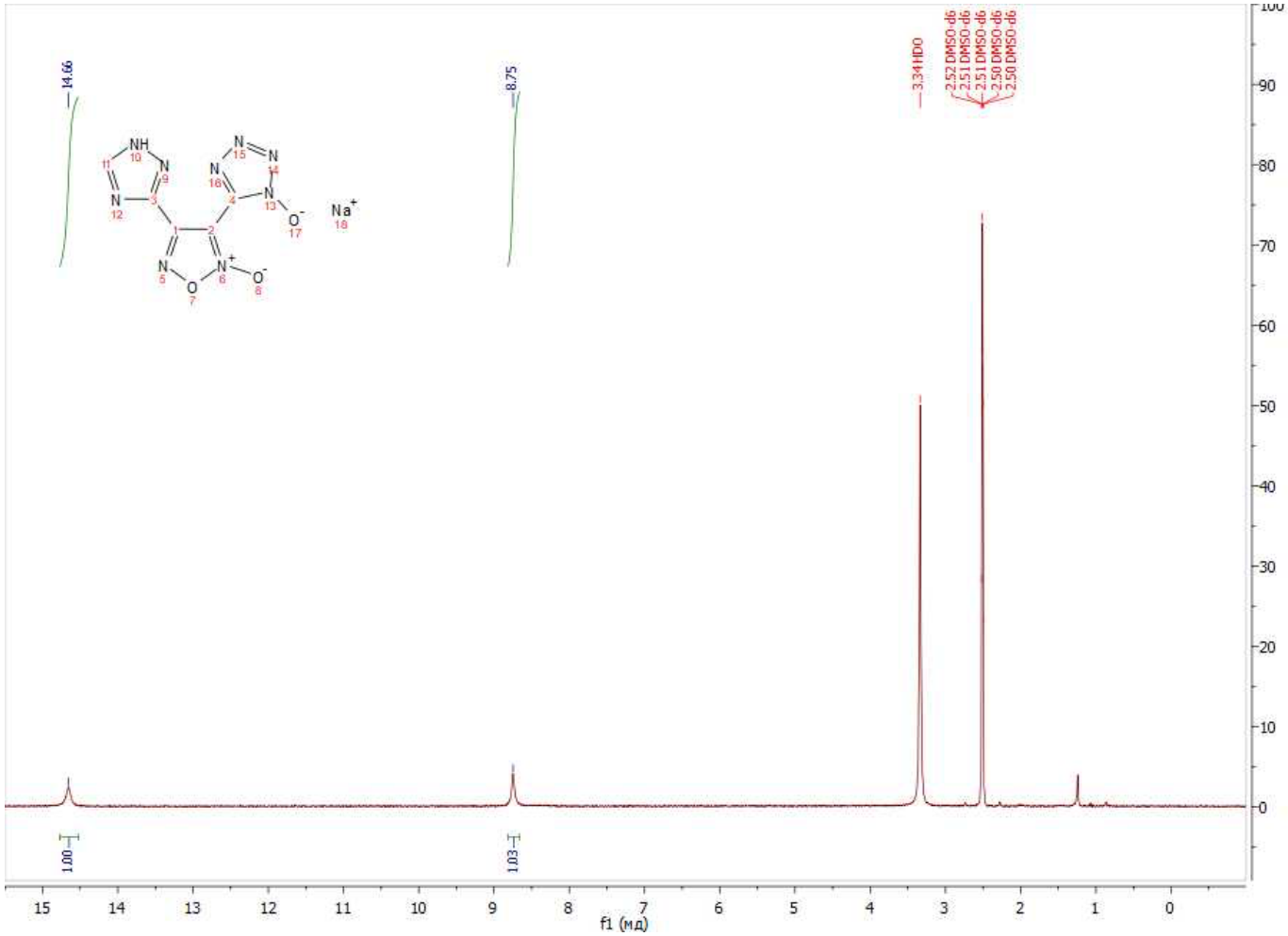

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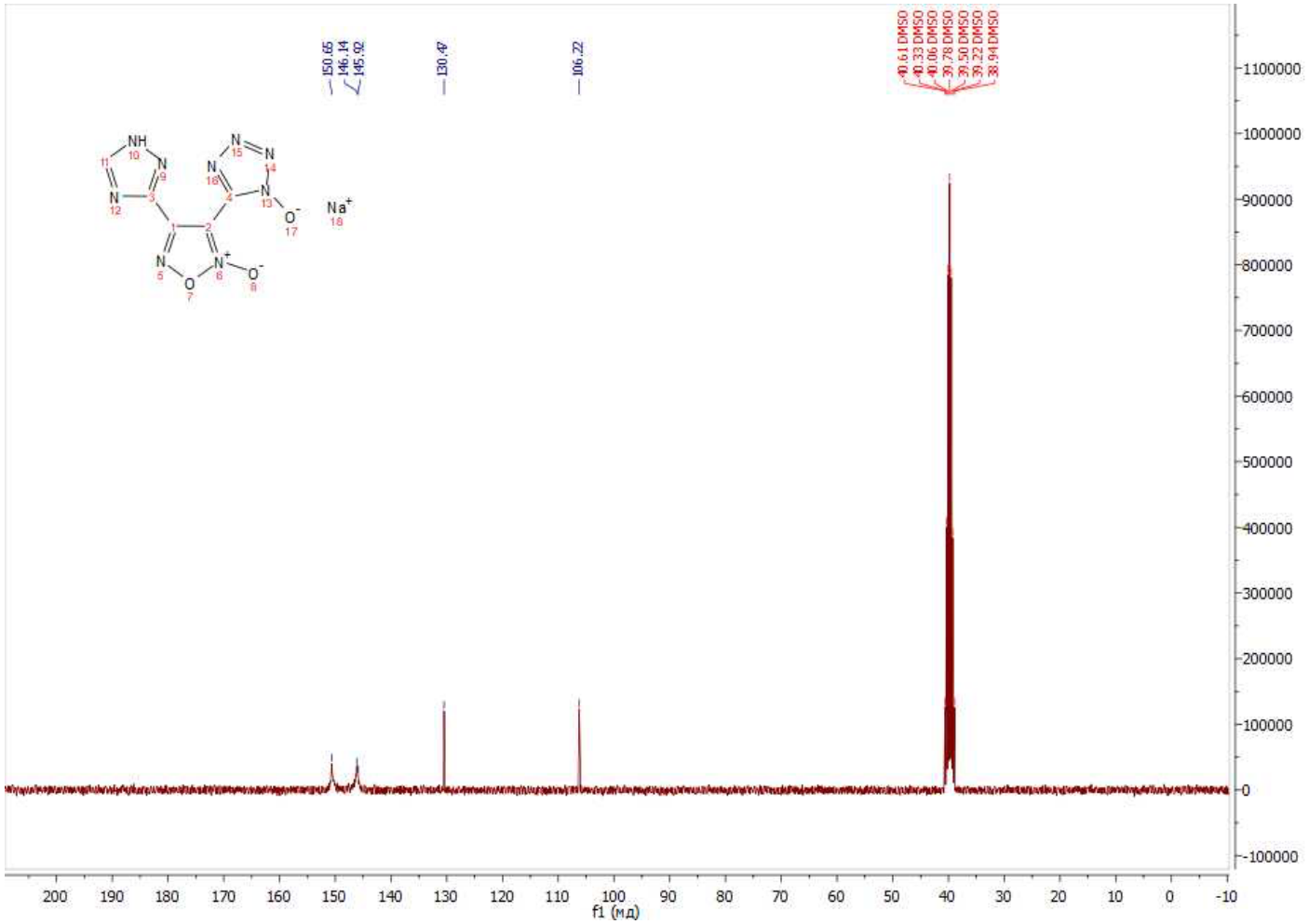

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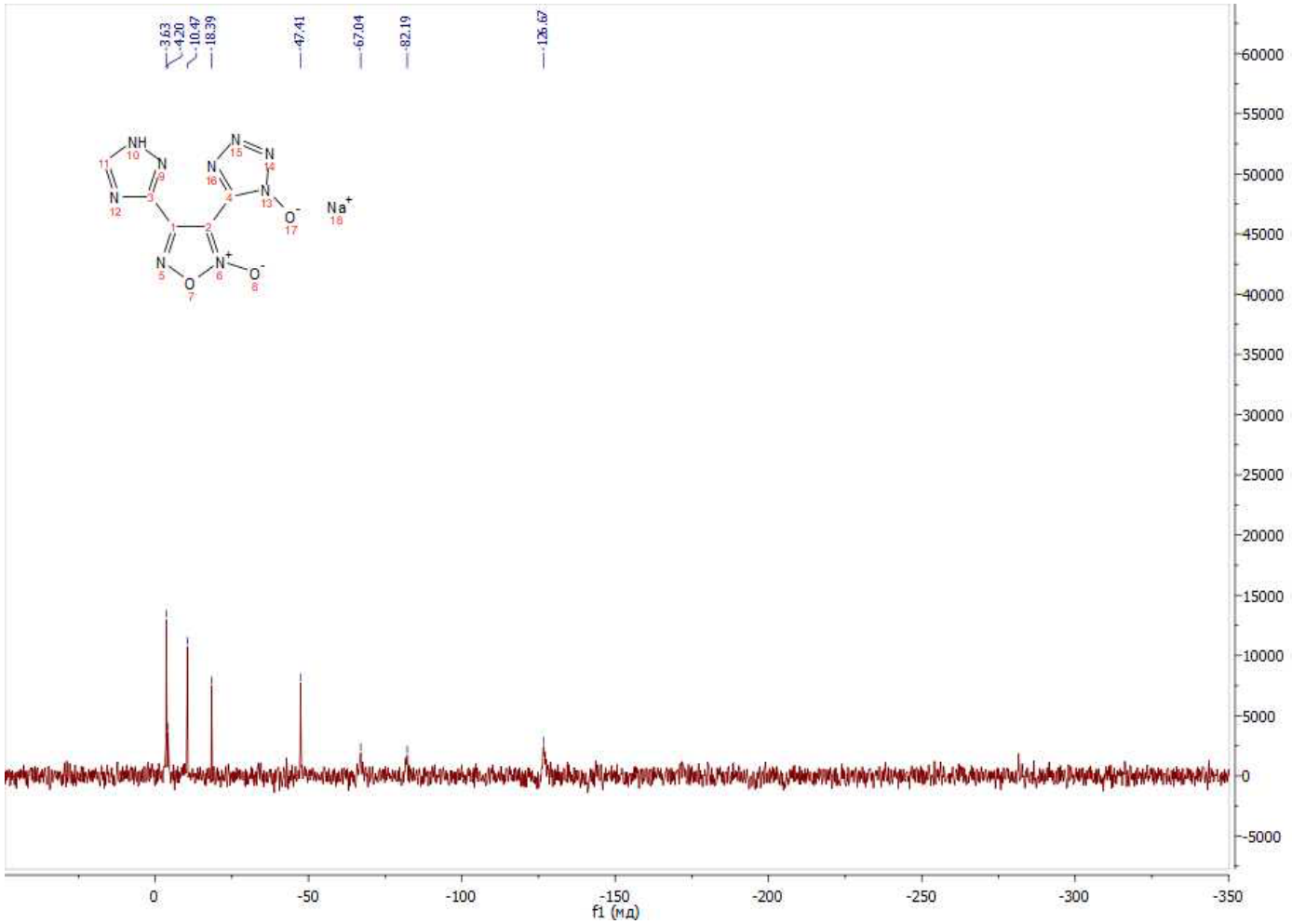
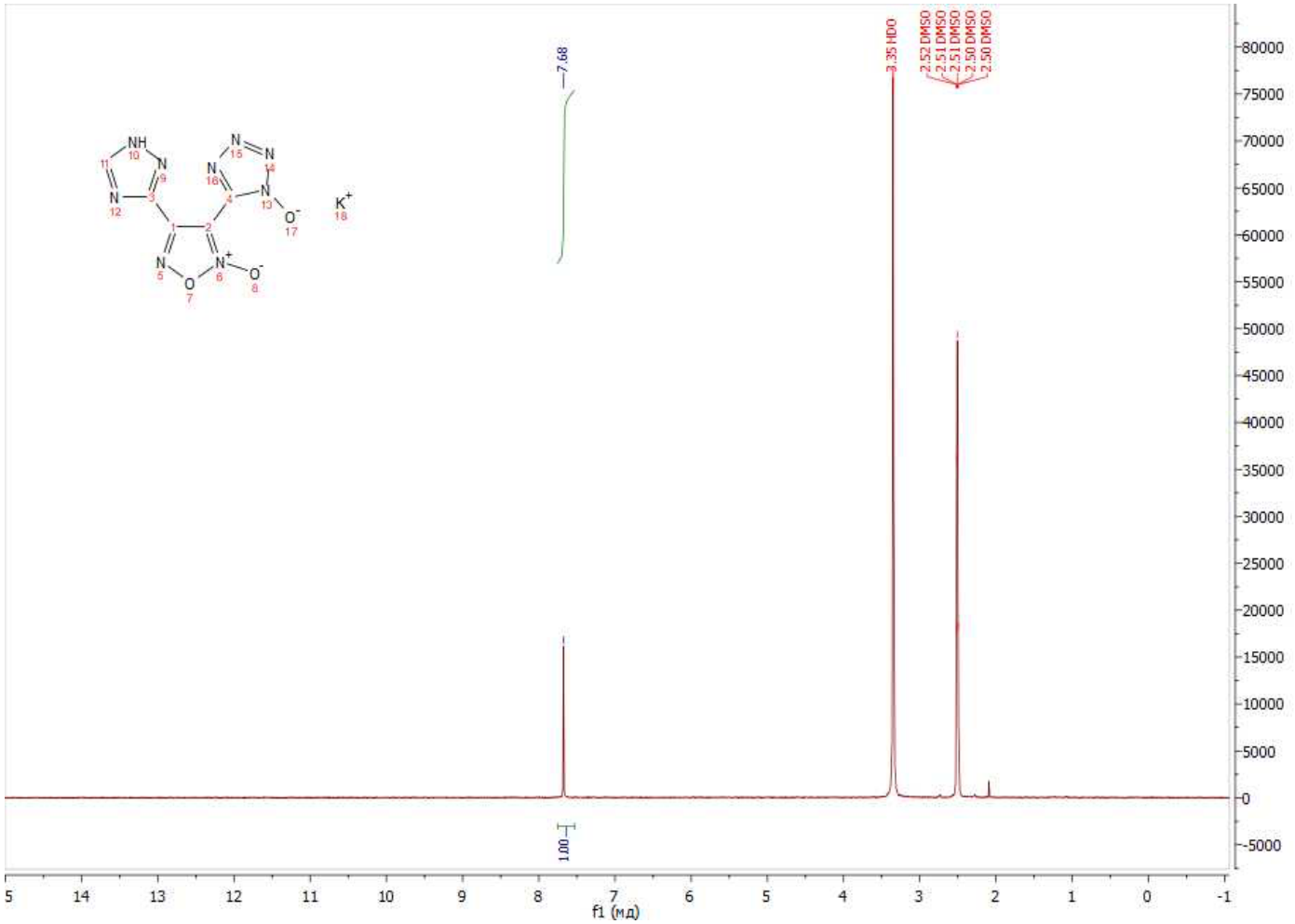


^{15}N NMR spectrum of **6**, DMSO-[d_6]



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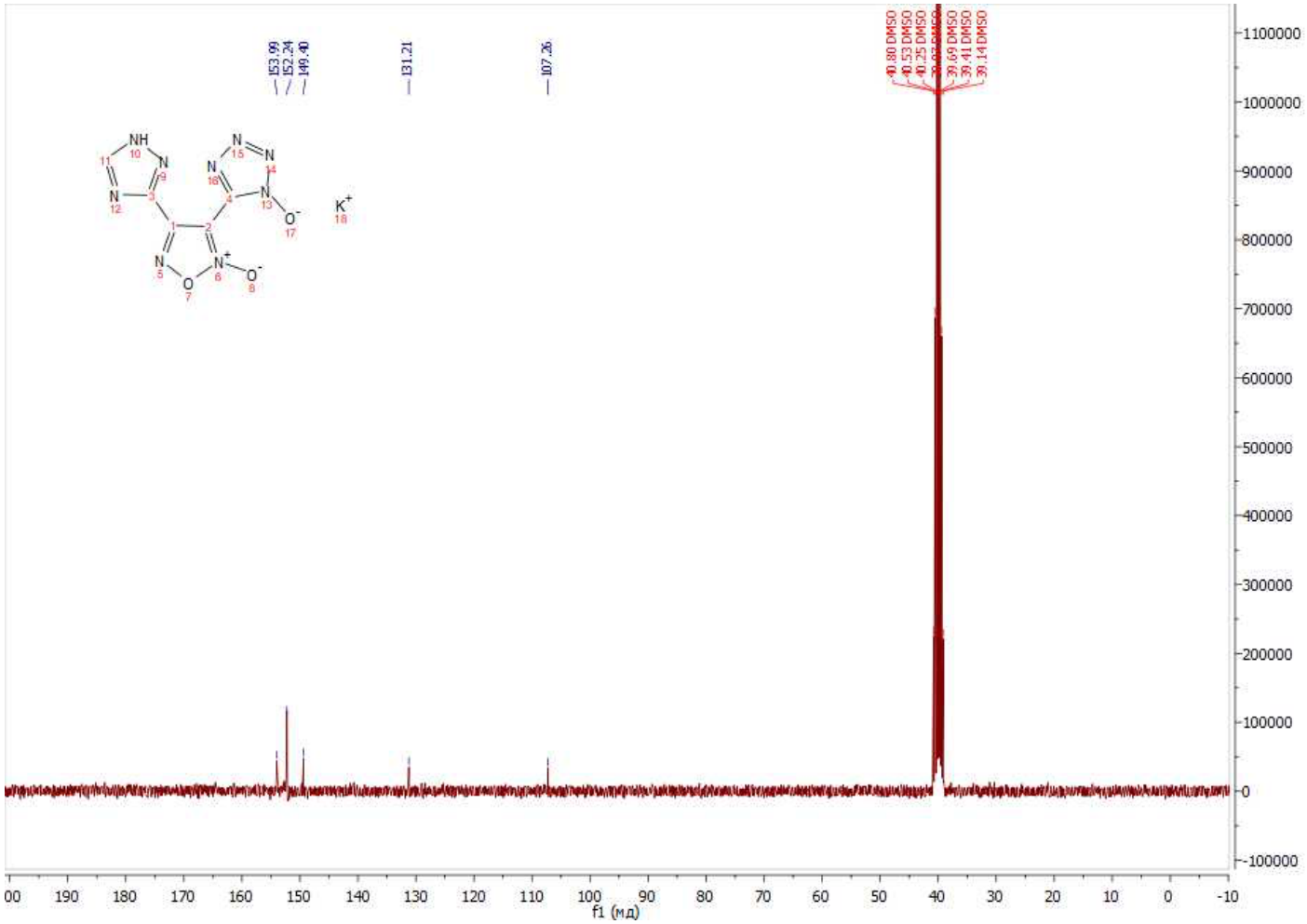

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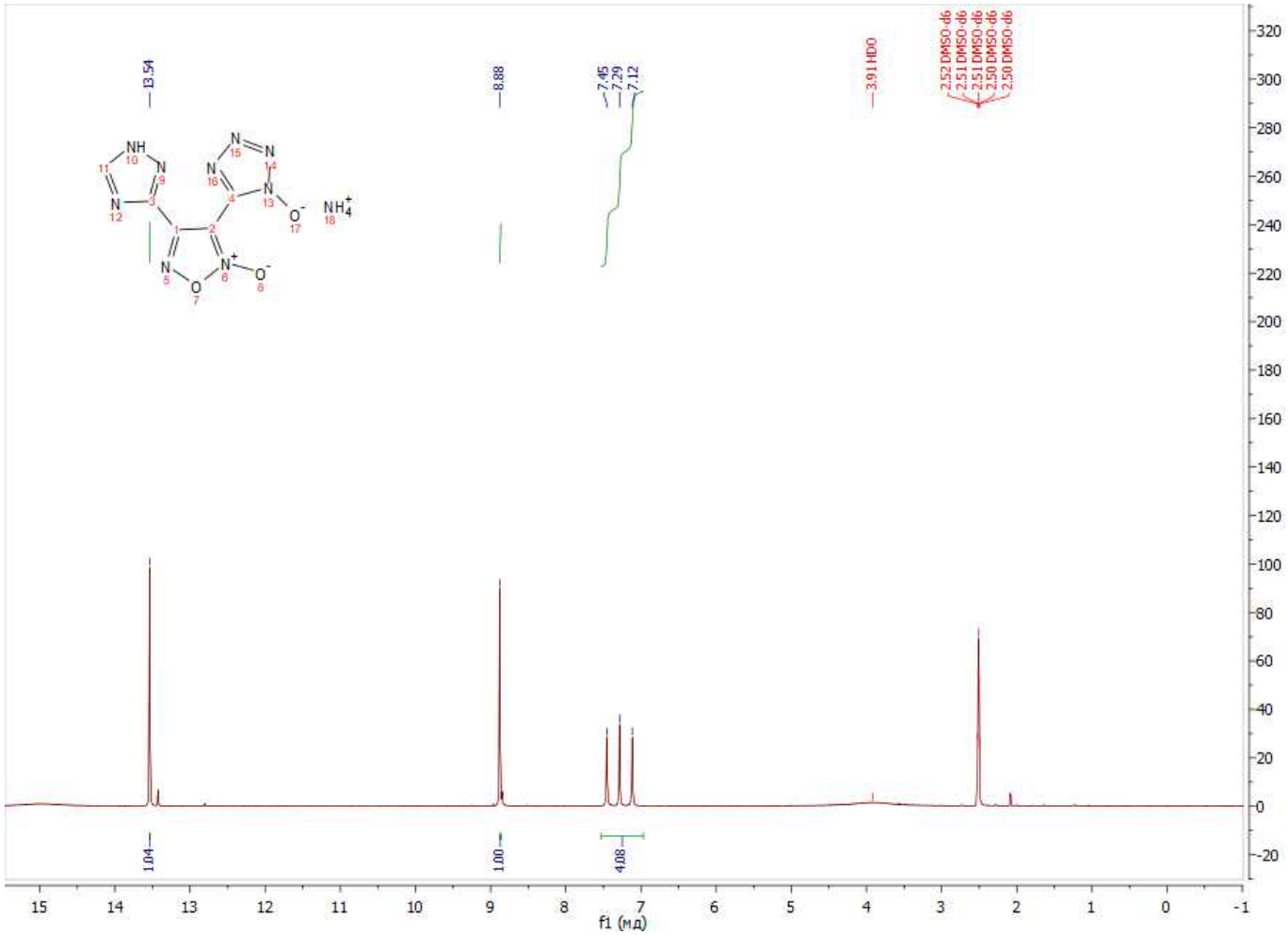

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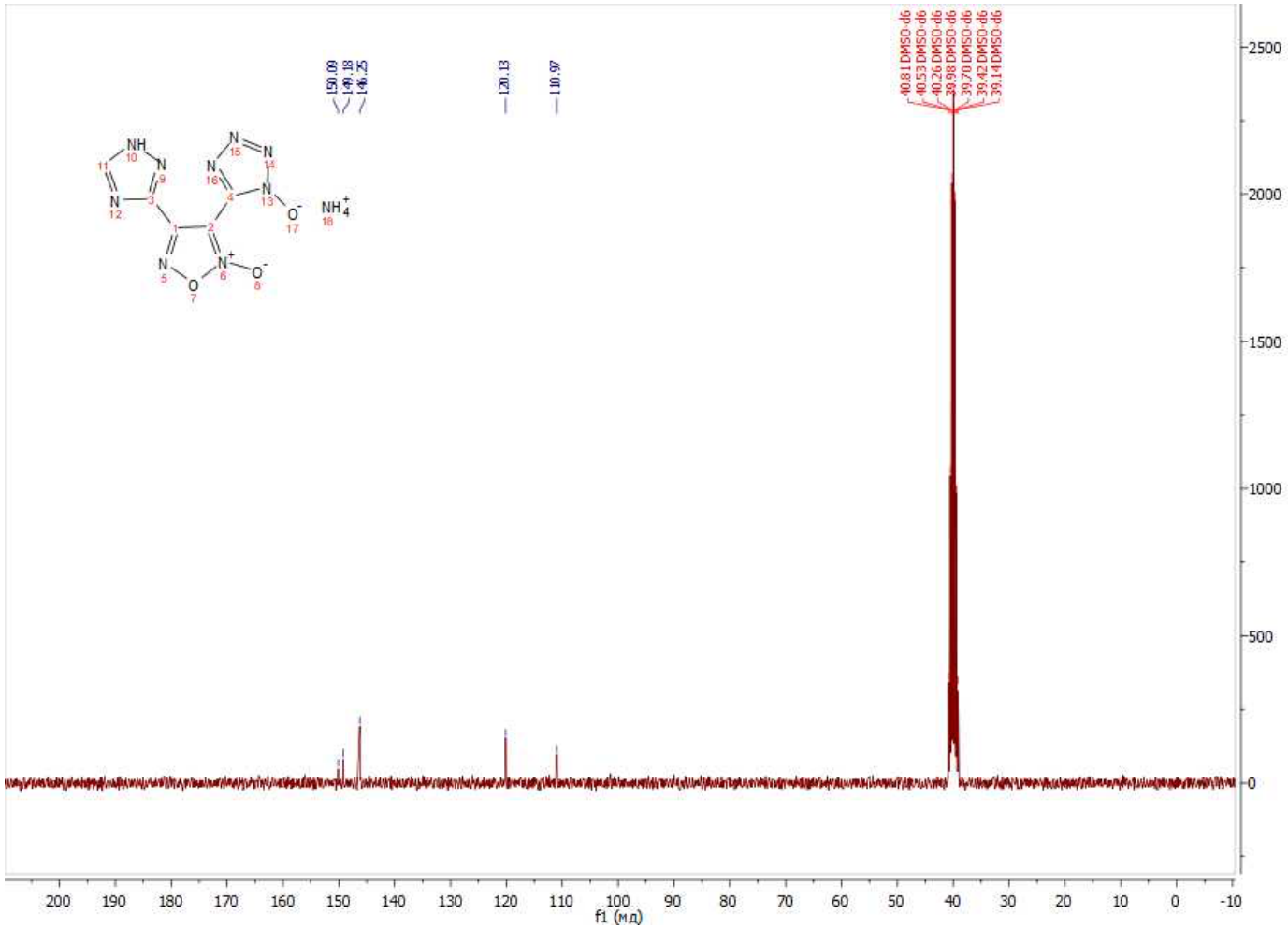
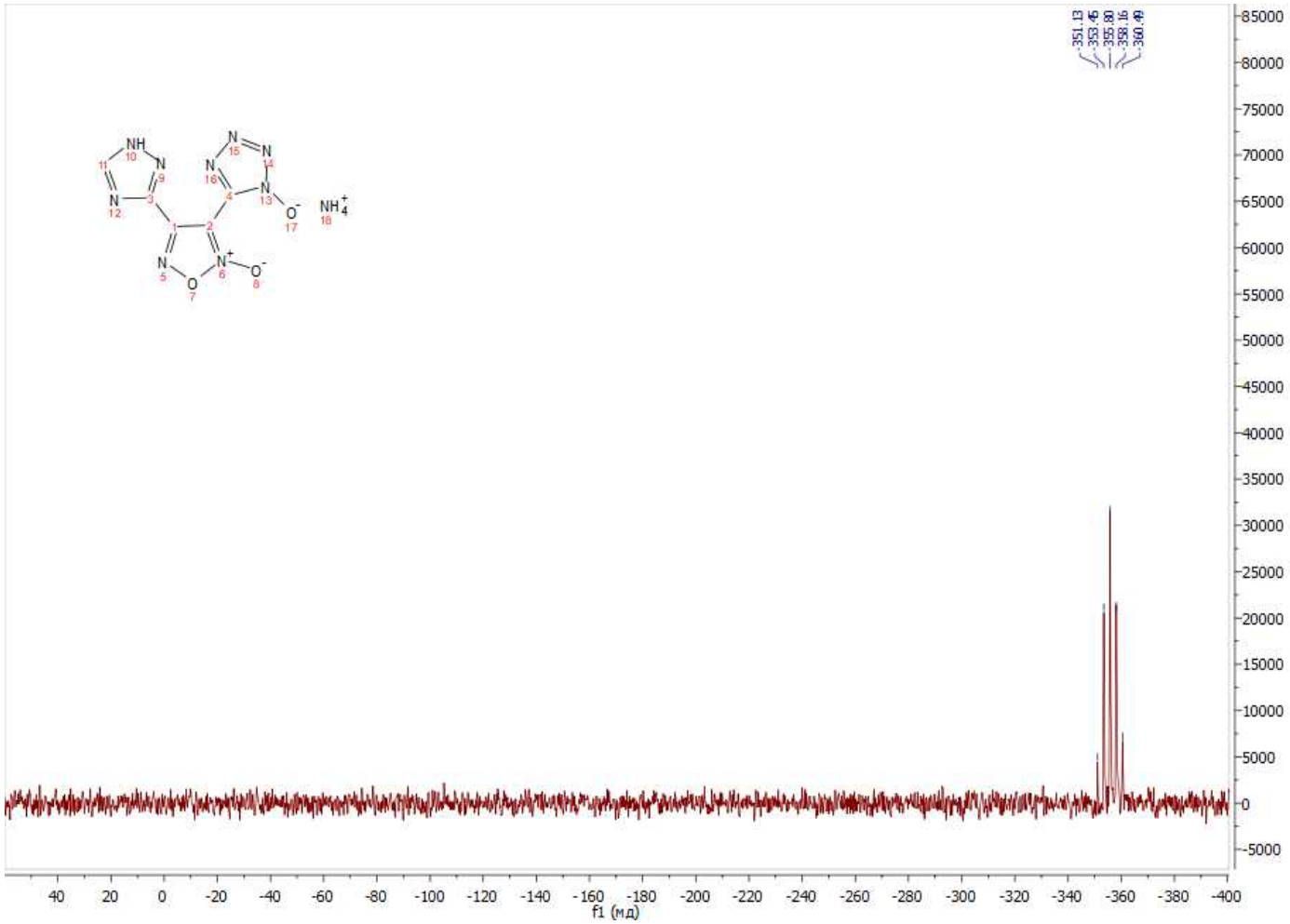


^{13}C NMR spectrum of **8**, DMSO-[d_6]



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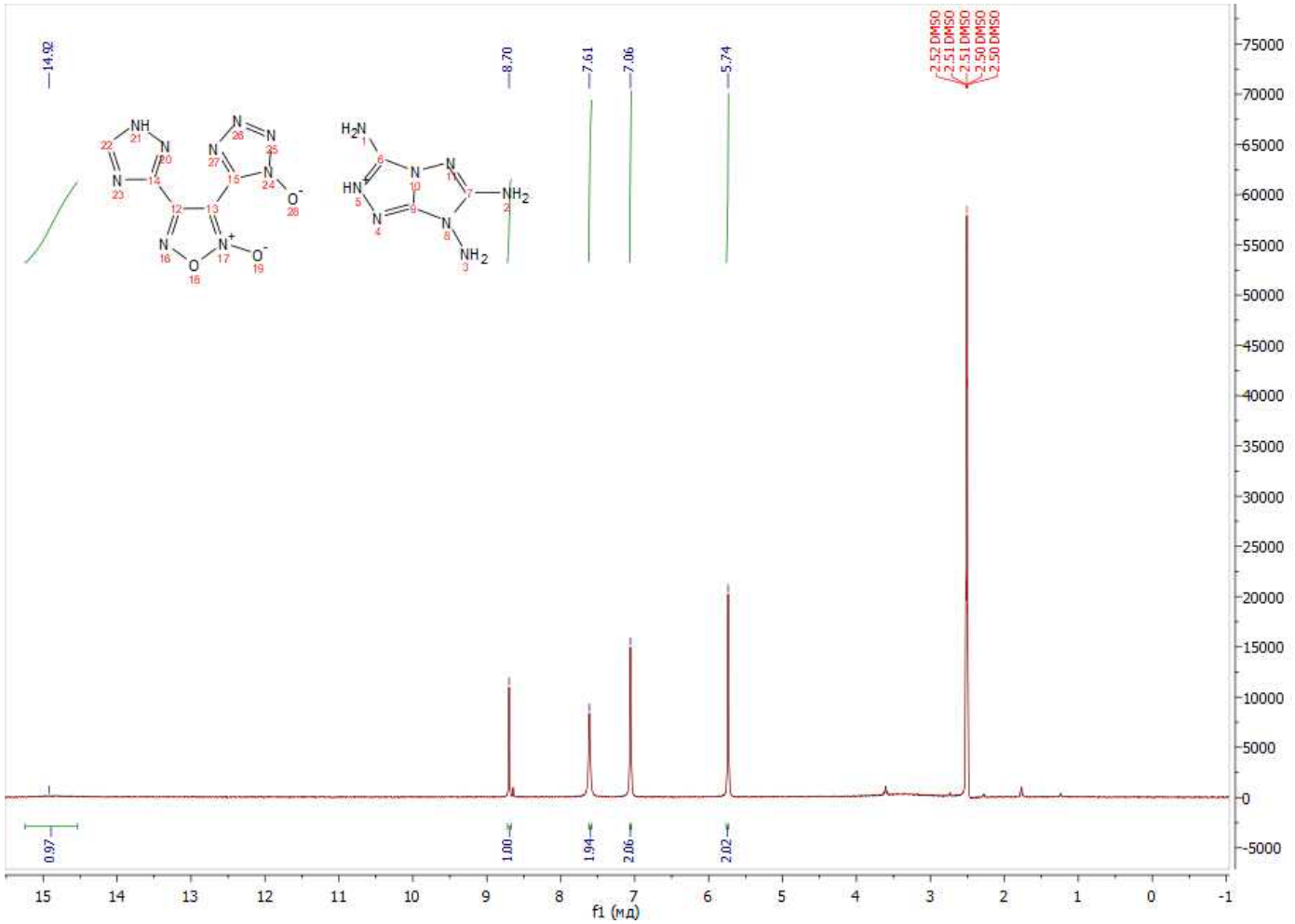

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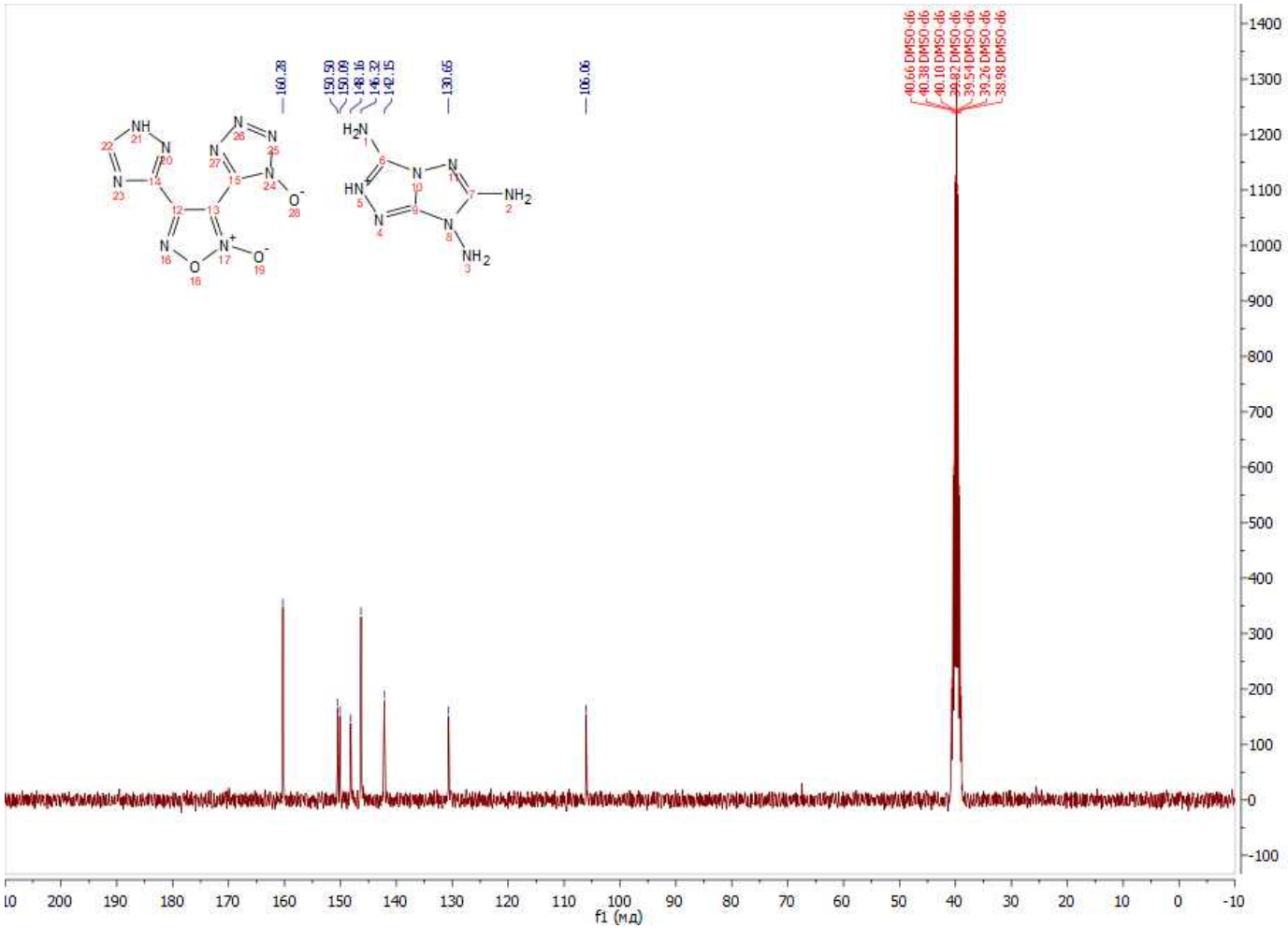
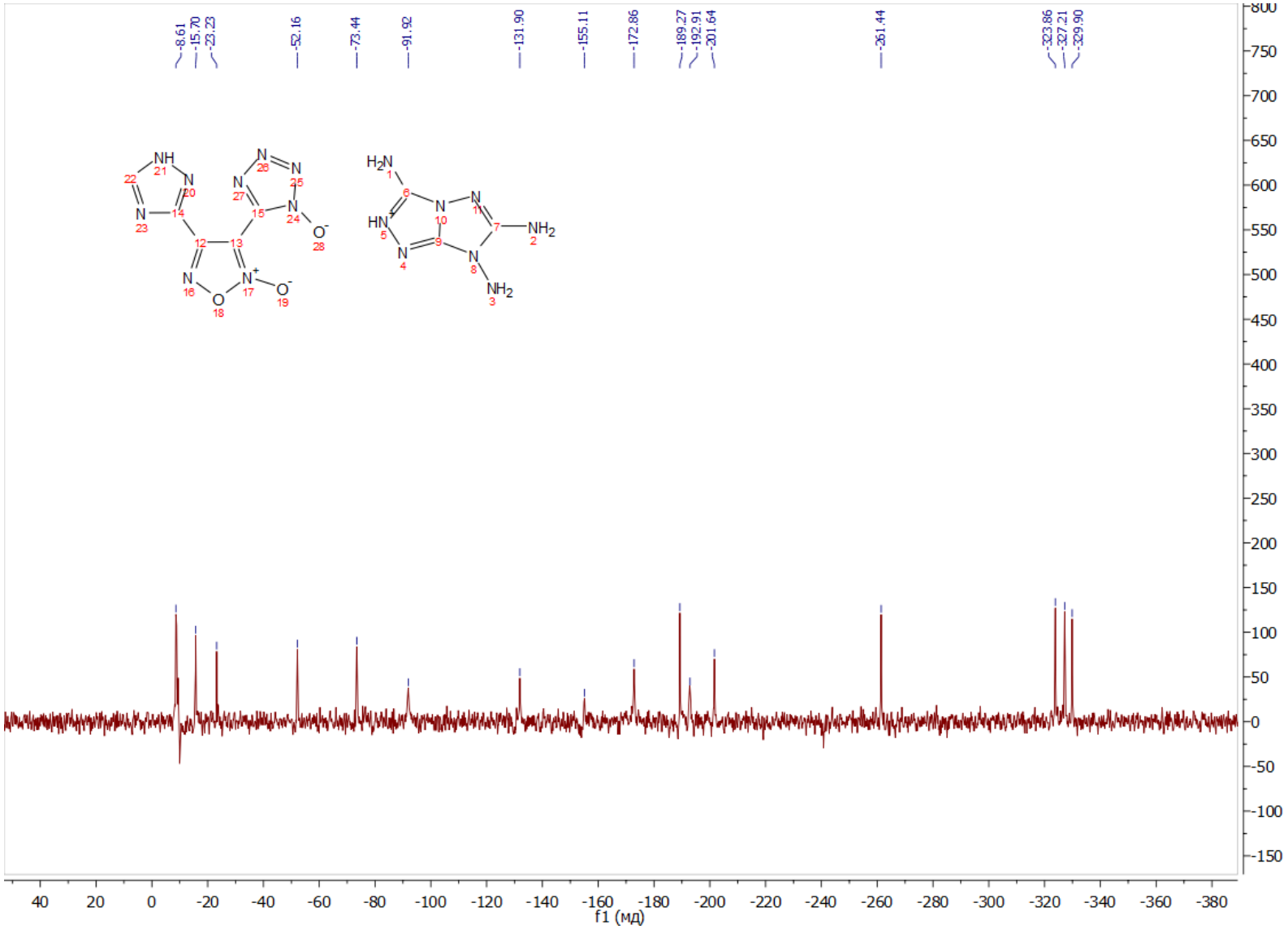
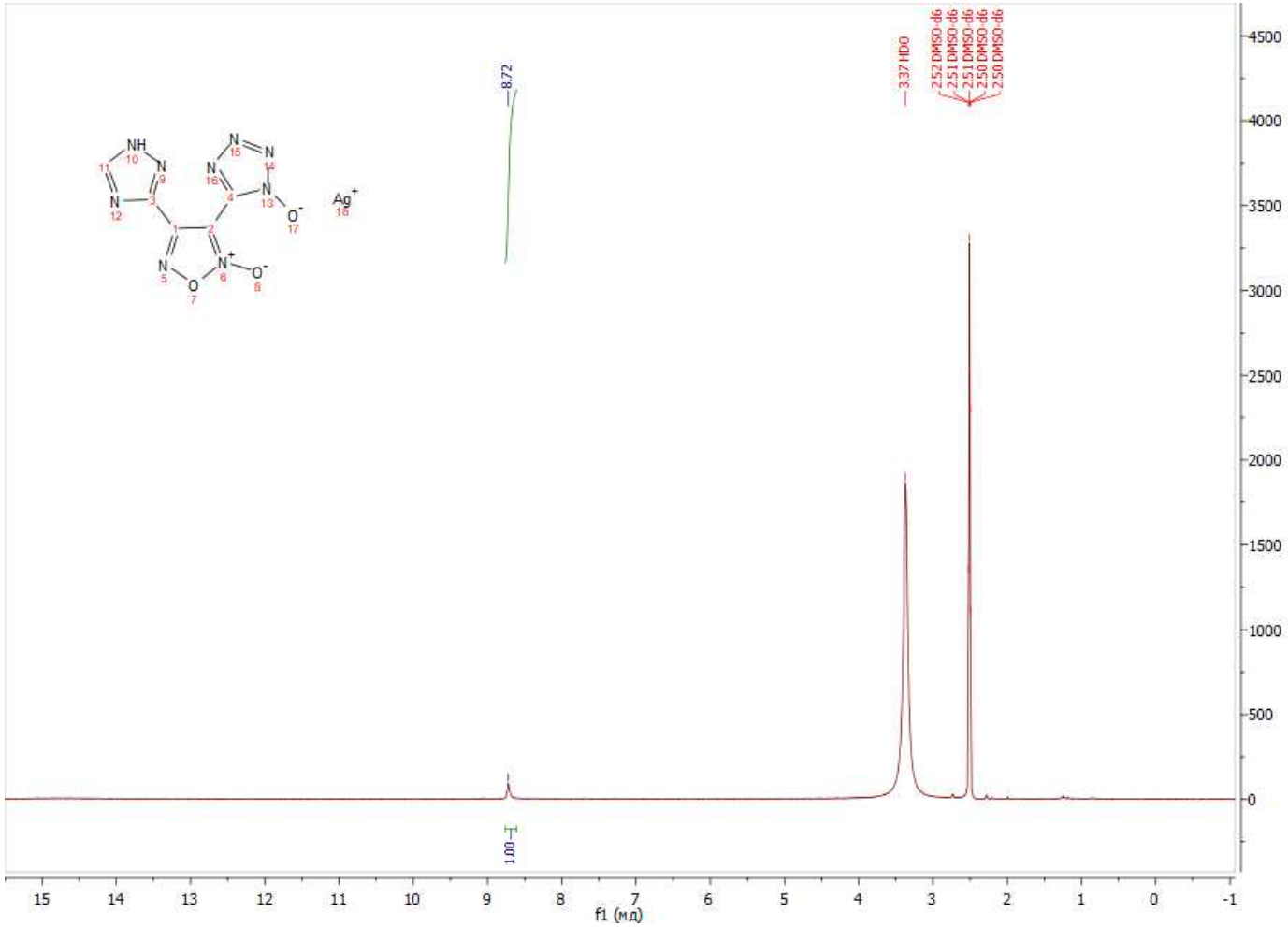


^{13}C NMR spectrum of **9**, DMSO-[d_6]



^{15}N NMR spectrum of **9**, DMSO-[d_6]



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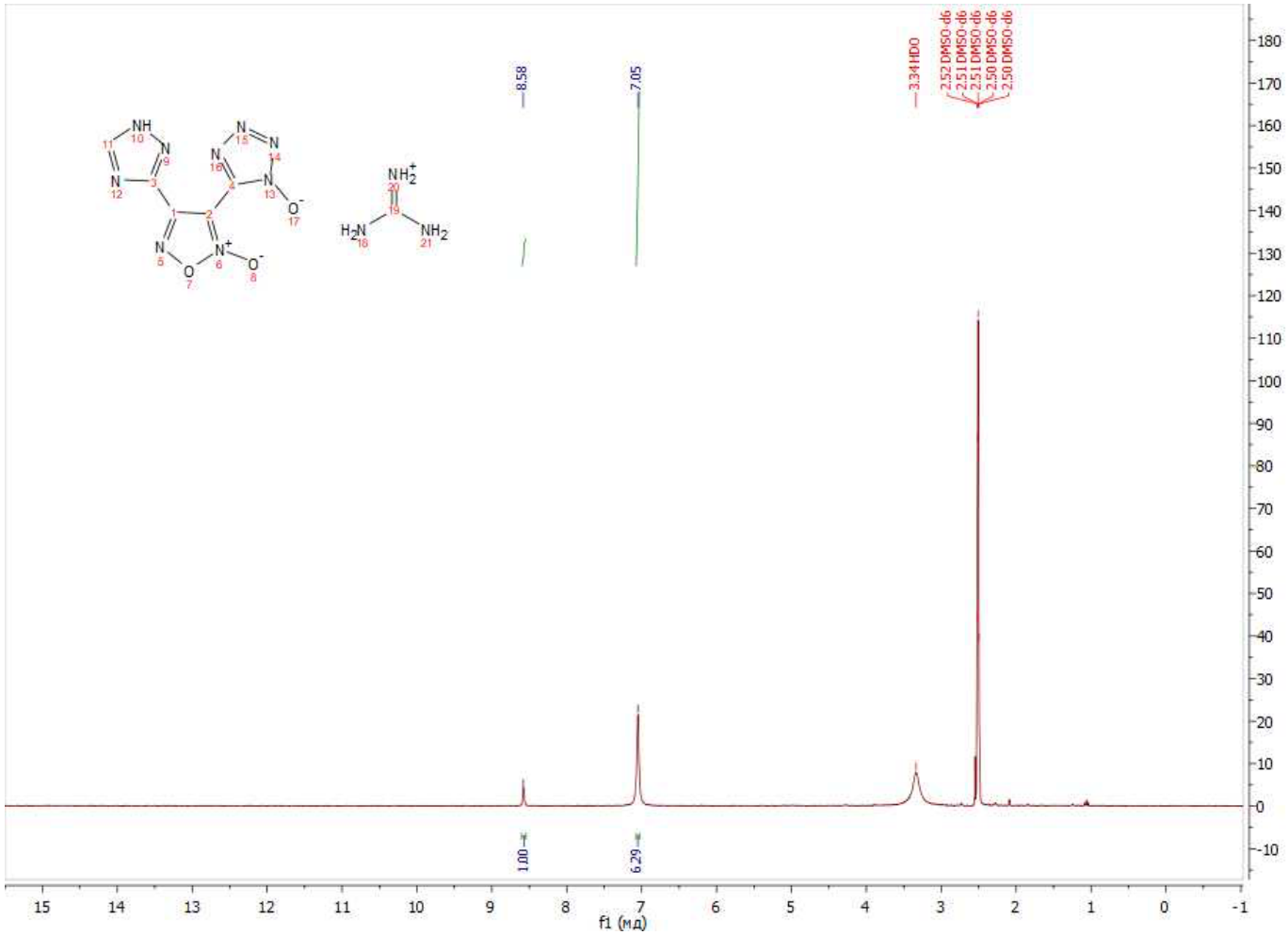

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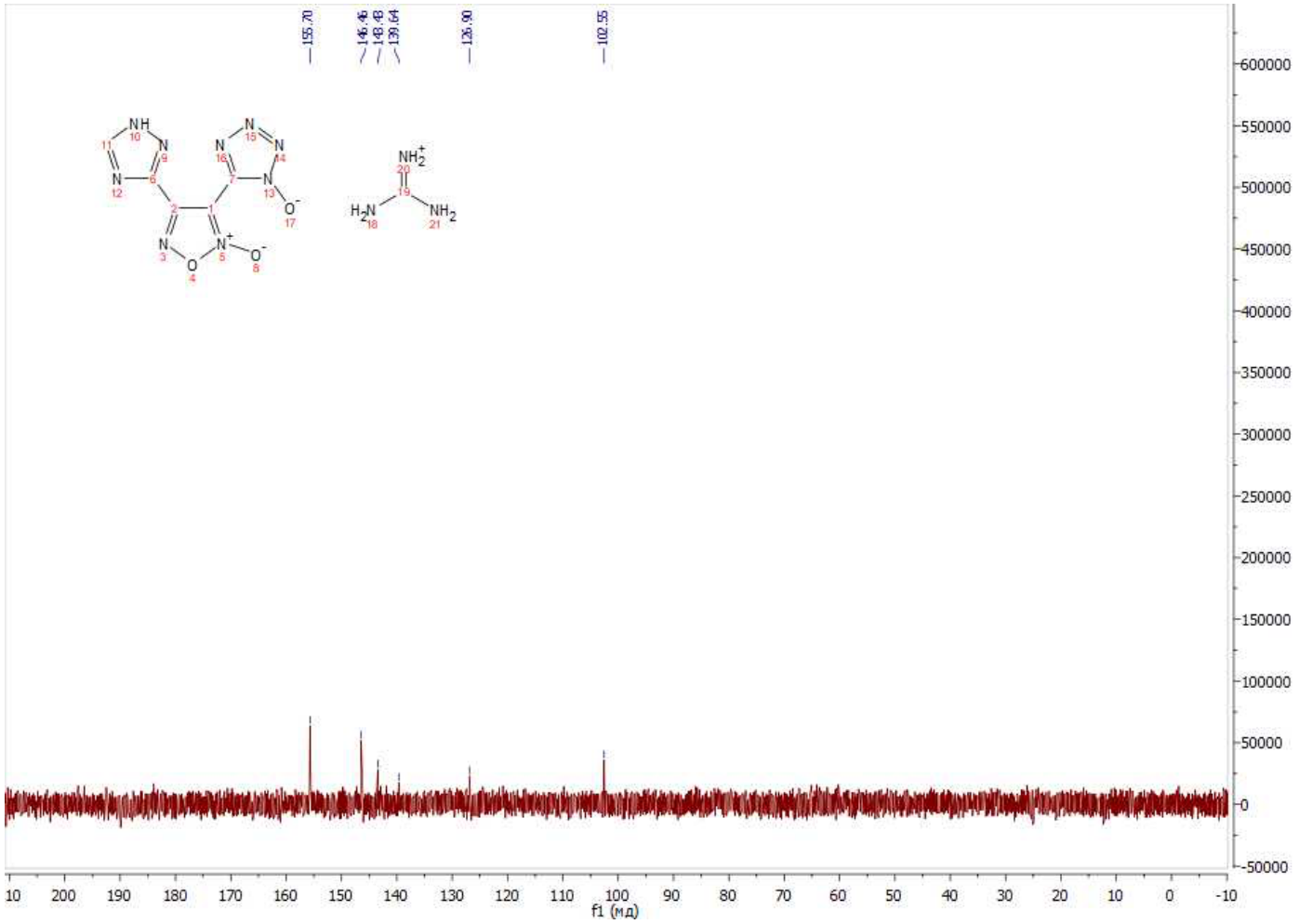

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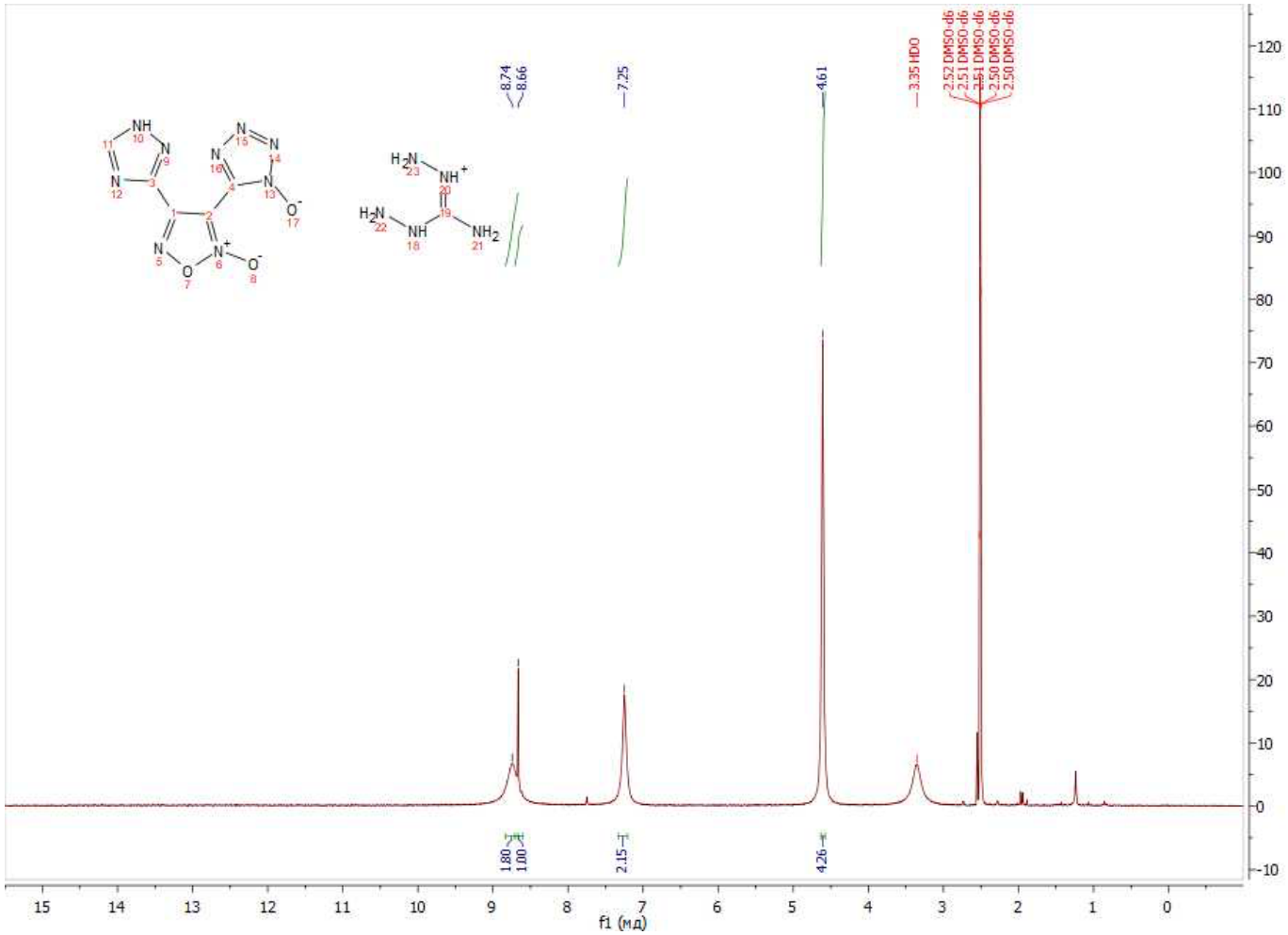

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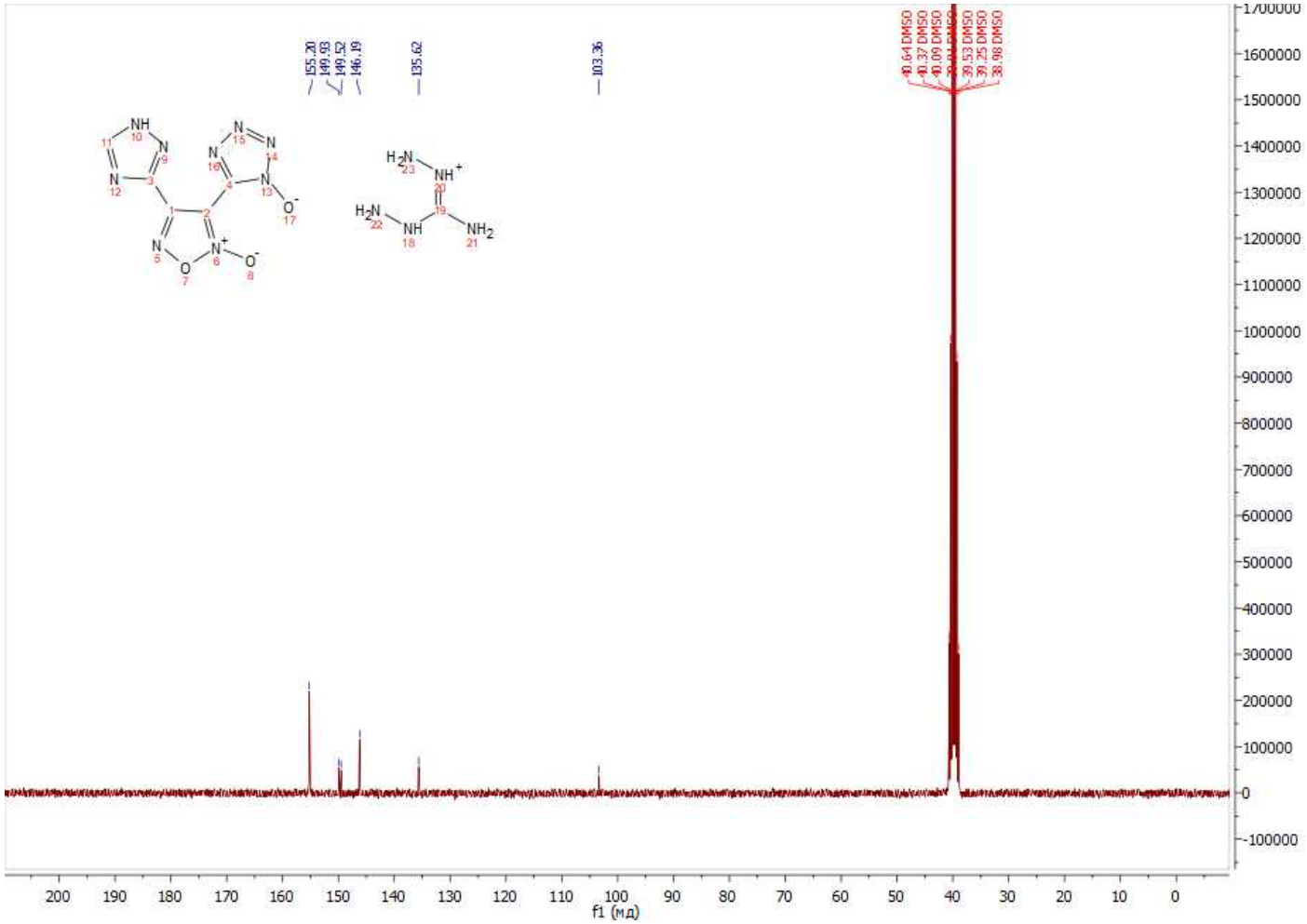

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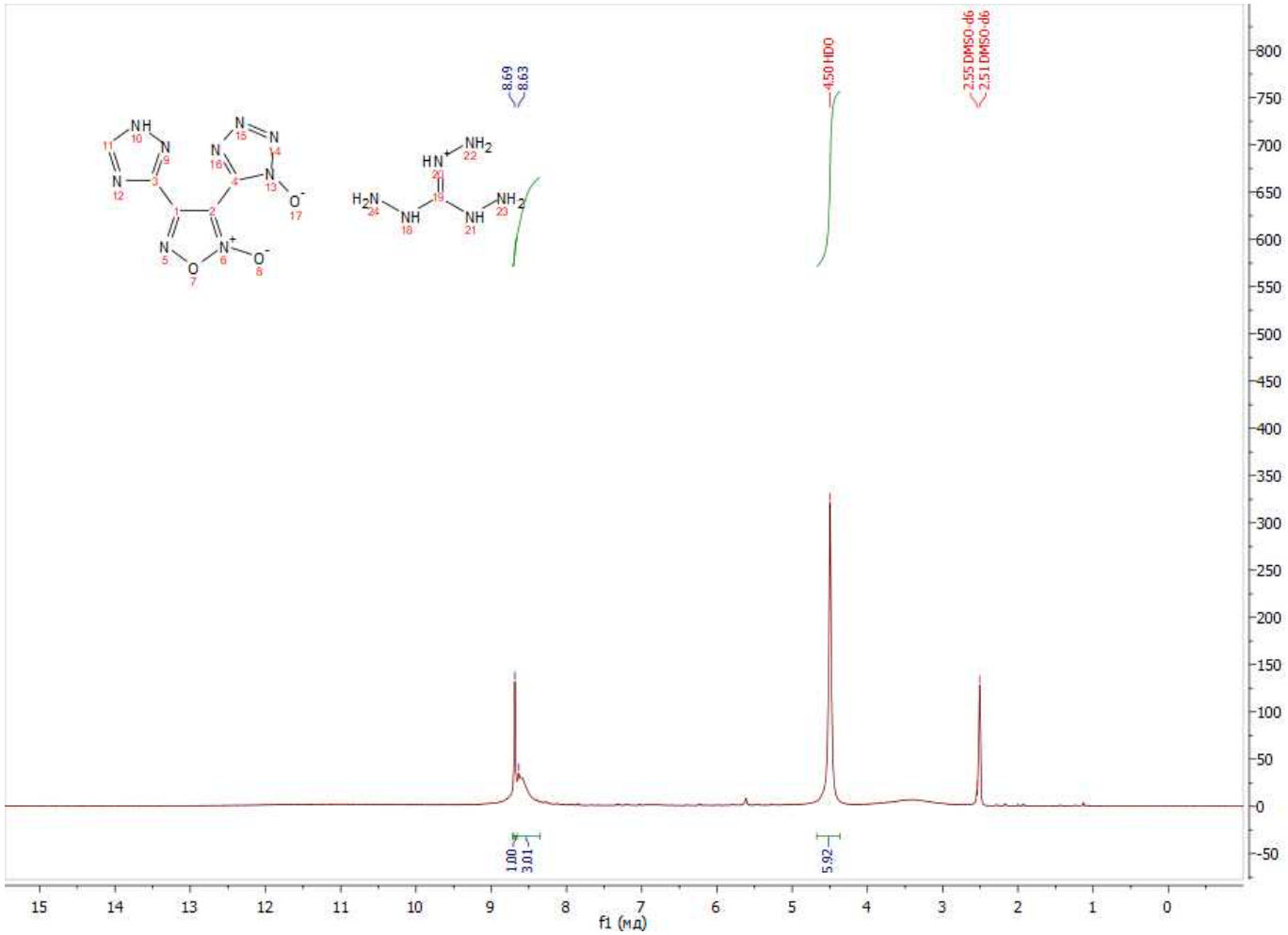

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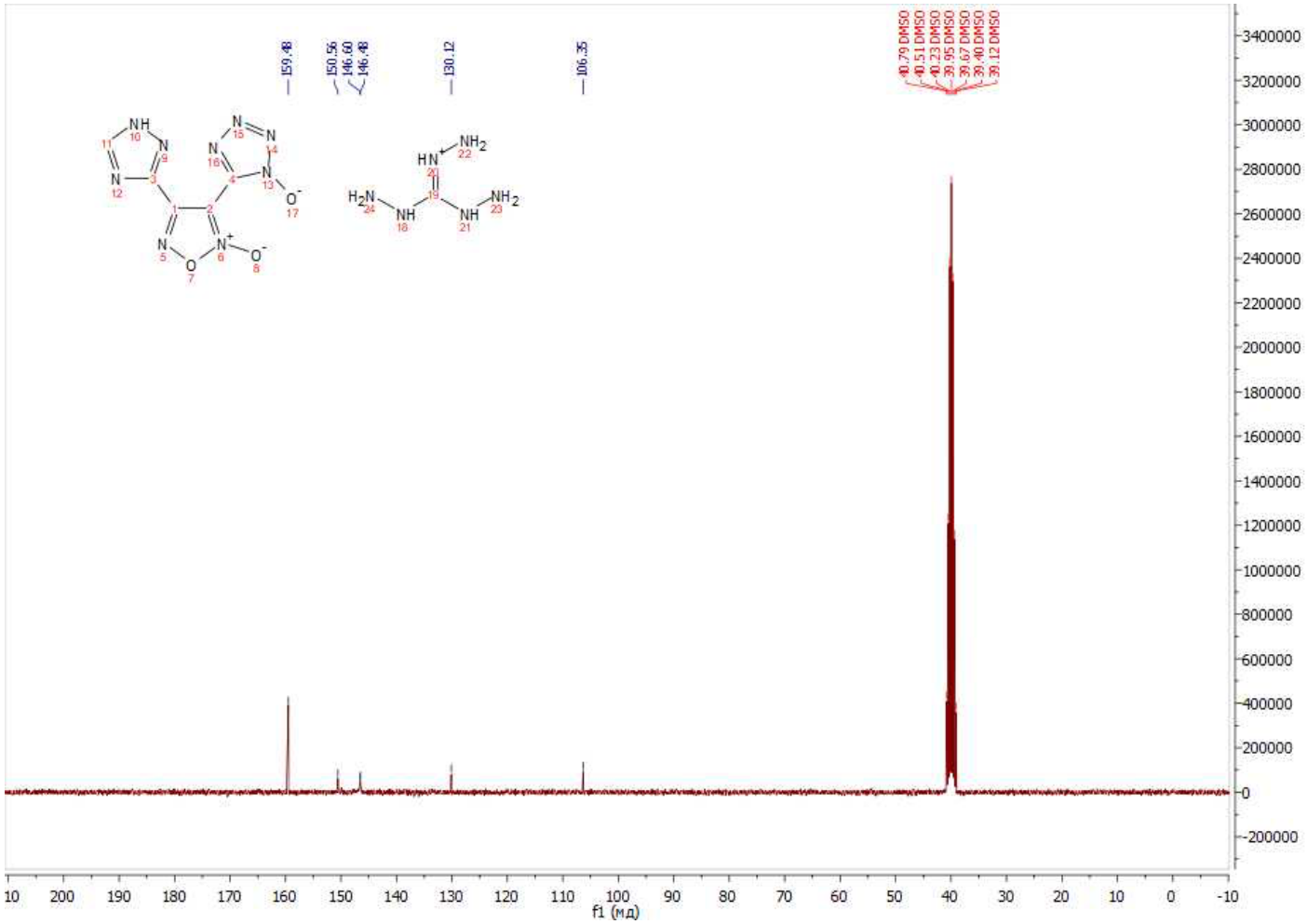

^{13}C NMR spectrum of **13**, DMSO-[d_6]

S5. References

1. CrysAlisPro. Version 1.171.42. *Rigaku Oxford Diffraction*, **2022**.
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