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An unexpected product of the reaction between *N*-hydroxy-6-methyluracil-5-carboximidoyl chloride and thioureas

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EXPERIMENTAL SECTION

^{1}H and ^{13}C spectra were recorded on a Bruker Avance-III 500 MHz pulsed spectrometer with working frequencies of 500.13 MHz (^{1}H), 125.76 MHz (^{13}C) and 50.68 MHz (^{15}N) using a 5 mm probe with PABBO Z-gradient at a constant sample temperature of 298K in DMSO-d_6. Chemical shifts in the NMR spectra of ^{1}H, ^{13}C are given in ppm relative to the solvent signal (δ_H 2.50 and δ_C 39.52). Chemical shifts for ^{15}N nuclei are obtained from the $^{15}N\{^{1}H\}$ spectrum with reverse discontinuous decoupling from protons and $^{15}N\{^{1}H\}$ INEPT spectrum, and are confirmed by correlations in $\{^{1}H, ^{15}N\}$ HSQC and HMBC spectra, values are given in the ammonia scale. For ^{15}N nuclei, the calibration procedure was used according to the χ-standard [S1,S2]. The mass-spectra were recorded on a high-resolution Agilent LC/QTOF 6530 time-of-flight liquid chromatomass spectrometer, electrospray ionization (IER) and chromatographic separation (eluent acetonitrile/water = 1:1 and 0.1% formic acid, flow rate 0.25 ml min^{-1}, chromatographic column C18 Zorbax Extend-C18, 2.1 mm, 1.8 μm) the capillary potential is 4 kV (the speed and temperature of the drying gas (nitrogen) is 10 dm^3 min^{-1} and 325 ºC, the pressure of the spraying gas is 4.2 atm). IR spectra of substances were taken on the device Shimadzu IR Prestige-21 in Nujol in the range of 400-4000 cm^{-1}. The elemental analysis was performed on the EURO-3000 device. The melting point is determined in a glass capillary.

The general method. To a homogeneous mixture of compound **1** (0.10 g, 0.50 mmol) and **2a-f** (1.00 mmol) in MeOH (2.0 ml), one portion of Et_3N (0.14 ml, 1.00 mmol) was added, and this was stirred at room temperature or at 0 °C for 1 hour. The precipitate was filtered, washed with MeOH, distilled water, dried (Table 1 of this article).

5-Isothiocyanato-6-methylpyrimidine-2,4(1*H*,3*H*)-dione 3. White needles, m.p. >300 °C (MeOH), decomp. ^{1}H NMR , δ, ppm: 2.12 s (3H, H^7), 11.28 s (1H, H^1), 11.56 s (1H, H^3). $^{13}C\{^{1}H\}$ NMR , δ, ppm: 15.92 (C^7), 105.19 (C^5), 144.94 (N=C=S), 148.11 (C^6), 149.47 (C^2), 160.29 (C^4). $^{15}N\{^{1}H\}$ NMR, δ, ppm: 95.53 (N=C=S), 137.73 (N^1), 154.91 (N^3). Mass-spectrum, m/z (%):182.0022 (100) $[M-H]^-$ $C_6H_4N_3O_2S$. IR spectrum, ν, $см^{-1}$ (in vaseline oil) 1686-1737 (C=O), 1633-1653 (C=N). The data of the elemental analysis correspond to the formula $C_6H_5N_3O_2S$.

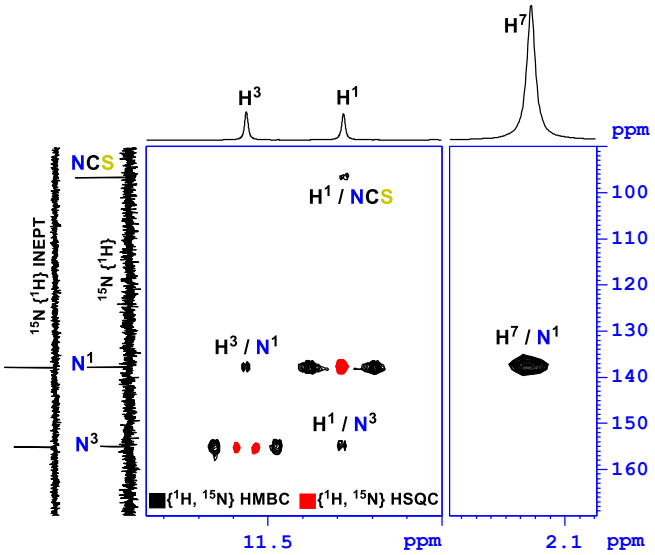


Figure S1 Superposition of the {^{1}H, ^{15}N} HSQC and {^{1}H, ^{15}N} HMBC spectra of compound **3** in DMSO-d_6 solution.

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

Empirical formula	$C_6H_5N_3O_2S$
Formula weight	183.19
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	4.7912(2)
b/Å	7.2561(4)
c/Å	12.1180(6)
α/°	98.484(5)
β/°	90.493(4)
γ/°	106.926(5)
Volume/Å^3	398.04(4)
Z	2
ρ_{calc}g/cm^3	1.528
μ/mm^{-1}	0.366
F(000)	188.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.942 to 69.702
Index ranges	-7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	15221
Independent reflections	3283 [R_{int} = 0.0408]
Data/restraints/parameters	3283/0/111
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0488, wR_2 = 0.1306
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1484
Largest diff. peak/hole / e Å^{-3}	0.45/-0.48

Table S2. Bond Lengths for compound **3.**

Bond	Length/Å	Bond	Length/Å
S1–C9	1.5666(15)	N3–C4	1.3758(15)
O2–C4	1.2329(14)	N8–C5	1.3807(16)
O1–C2	1.2282(14)	N8–C9	1.1853(18)
N1–C2	1.3652(15)	C4–C5	1.4452(17)
N1–C6	1.3711(16)	C6–C5	1.3632(17)
N3–C2	1.3681(14)	C6–C7	1.4885(18)

Table S3. Bond Angles for compound **3.**

Bond Angle	Angle/°	Bond Angle	Angle/°
C2–N1–C6	124.12(10)	N3–C4–C5	115.01(10)
C2–N3–C4	125.84(10)	N1–C6–C7	116.46(11)
C9–N8–C5	141.66(13)	C5–C6–N1	118.83(11)
O1–C2–N1	122.77(10)	C5–C6–C7	124.69(12)
O1–C2–N3	121.82(11)	N8–C5–C4	117.87(11)
N1–C2–N3	115.40(10)	C6–C5–N8	121.44(11)
O2–C4–N3	121.35(11)	C6–C5–C4	120.64(11)
O2–C4–C5	123.59(11)	N8–C9–S1	173.51(13)

Table S4. Torsion Angles for compound **3.**

Torsion Angle	Angle/°	Torsion Angle	Angle/°
O2–C4–C5–N8	2.95(19)	C2–N3–C4–C5	0.45(18)
O2–C4–C5–C6	-174.46(12)	C4–N3–C2–O1	178.25(12)
N1–C6–C5–N8	178.53(12)	C4–N3–C2–N1	-2.97(18)
N1–C6–C5–C4	-4.16(19)	C6–N1–C2–O1	-179.22(12)
N3–C4–C5–N8	-179.36(11)	C6–N1–C2–N3	2.01(17)
N3–C4–C5–C6	3.24(18)	C9–N8–C5–C4	10.7(3)
C2–N1–C6–C5	1.46(19)	C9–N8–C5–C6	-171.9(2)
C2–N1–C6–C7	-177.01(12)	C7–C6–C5–N8	-3.1(2)
C2–N3–C4–O2	178.20(12)	C7–C6–C5–C4	174.18(13)

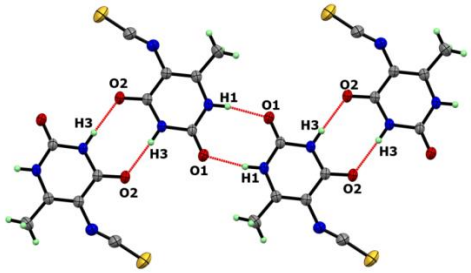
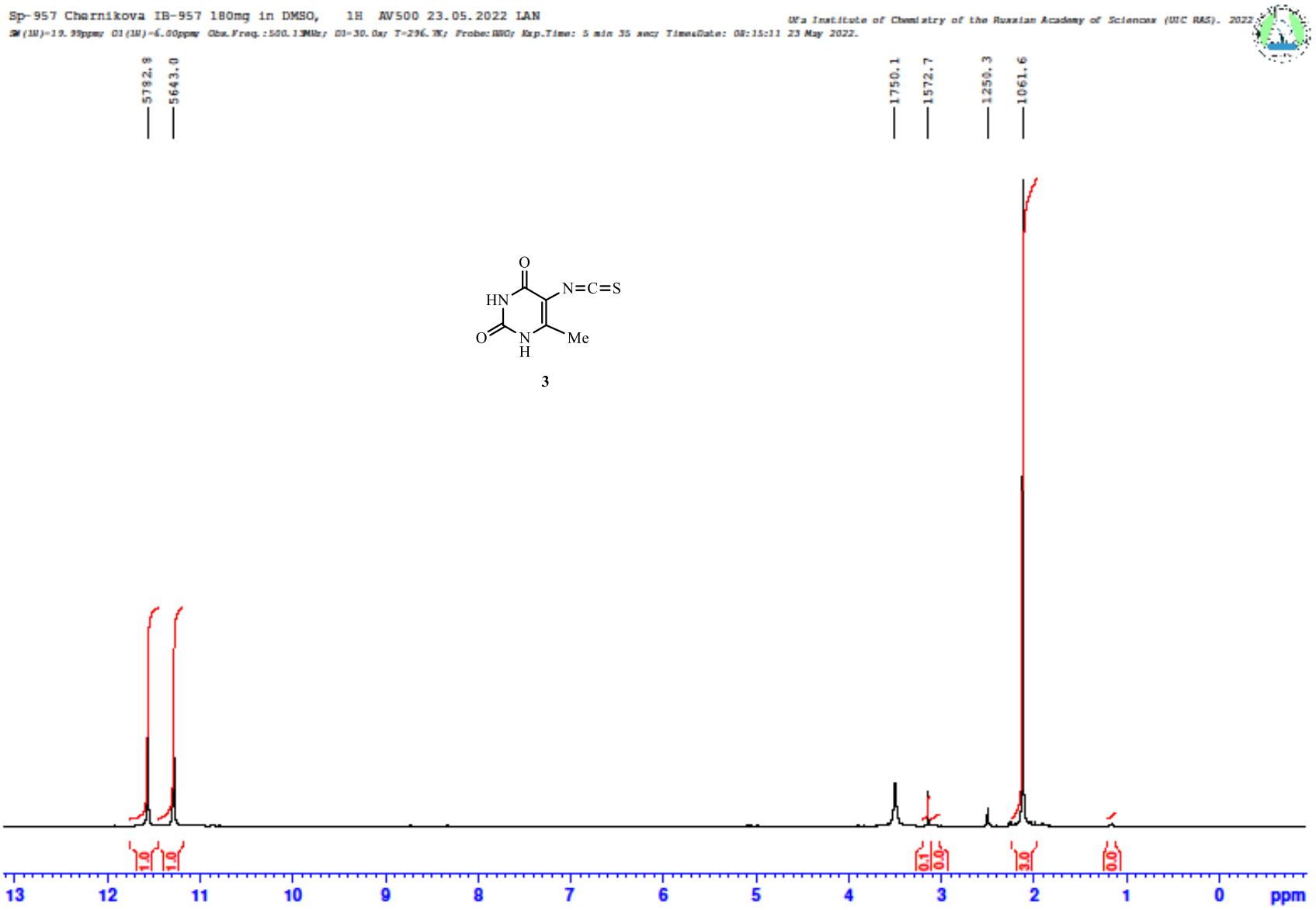


Figure S2 Fragment of the crystal packaging of compound **3**.

[S1] R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem*., 2001, **73**, 1795.

[S2] R. K.Harris, E. D. Becker, S. M. Cabral De Menezes, P. Granger, R. E. Hoffman, K. W. Zilm, *Pure Appl. Chem*., 2008, **80**, 59.



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

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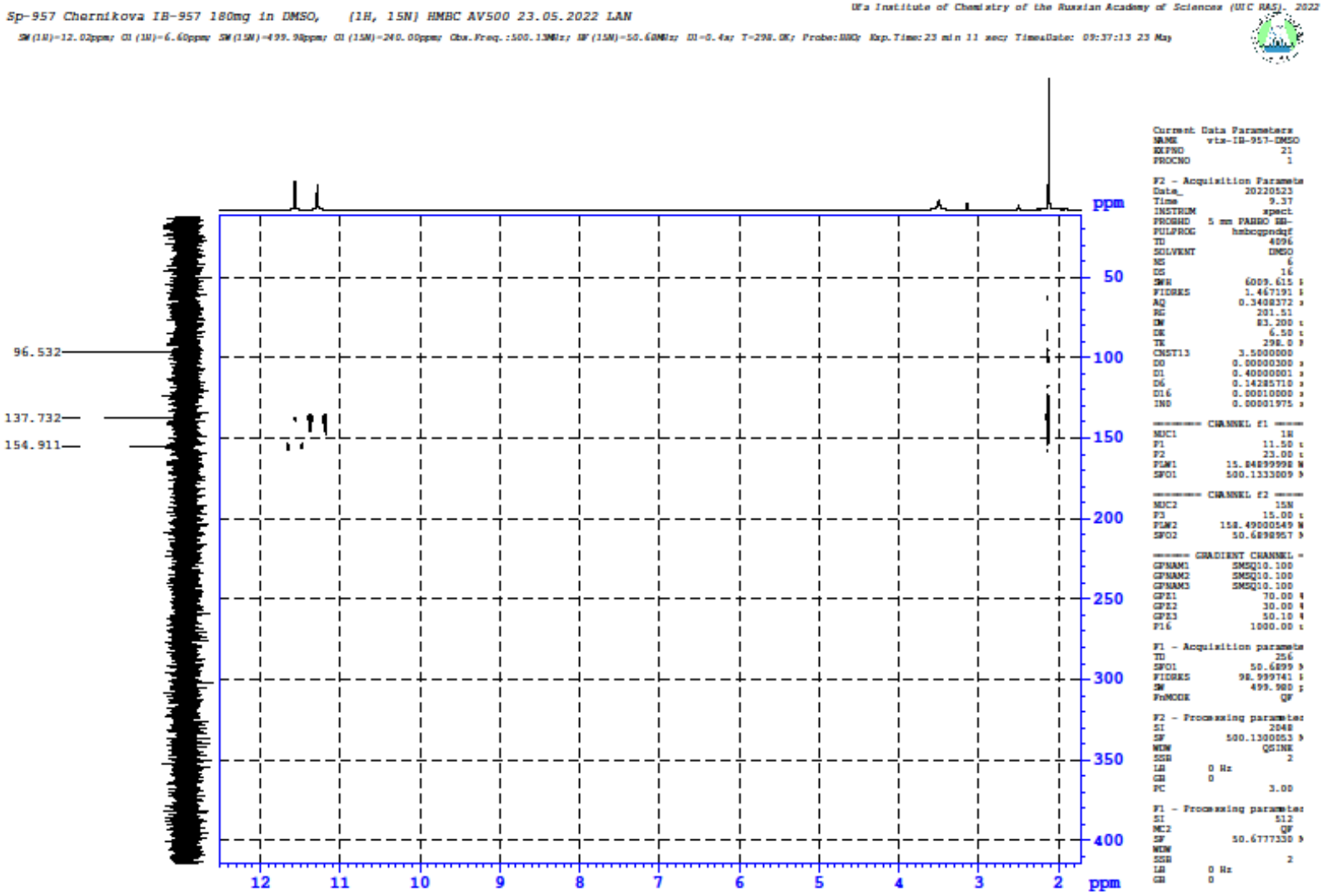

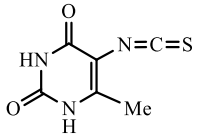

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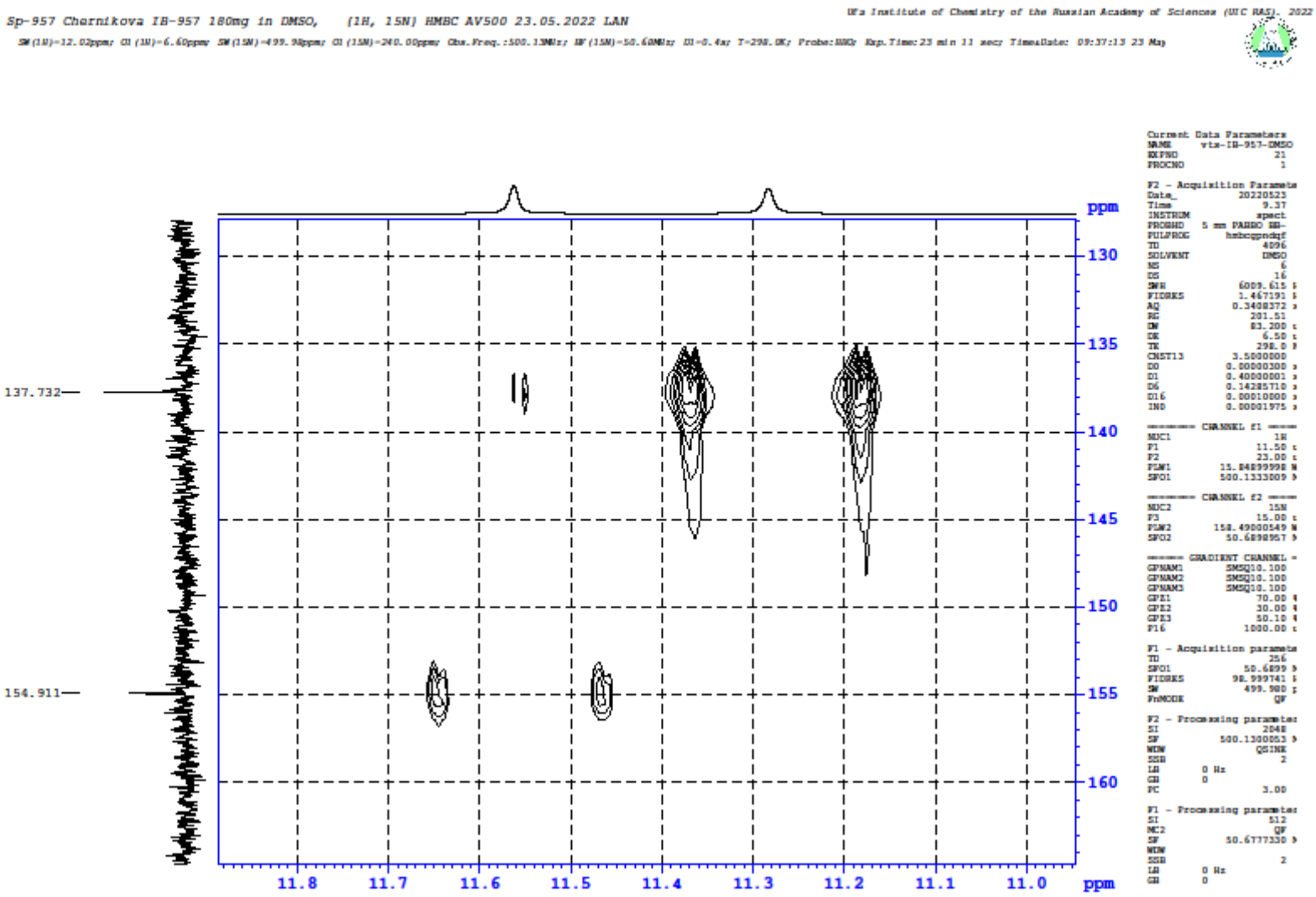
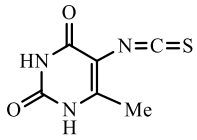
^{1}H-^{15}N HMBC NMR spectrum compound **3**





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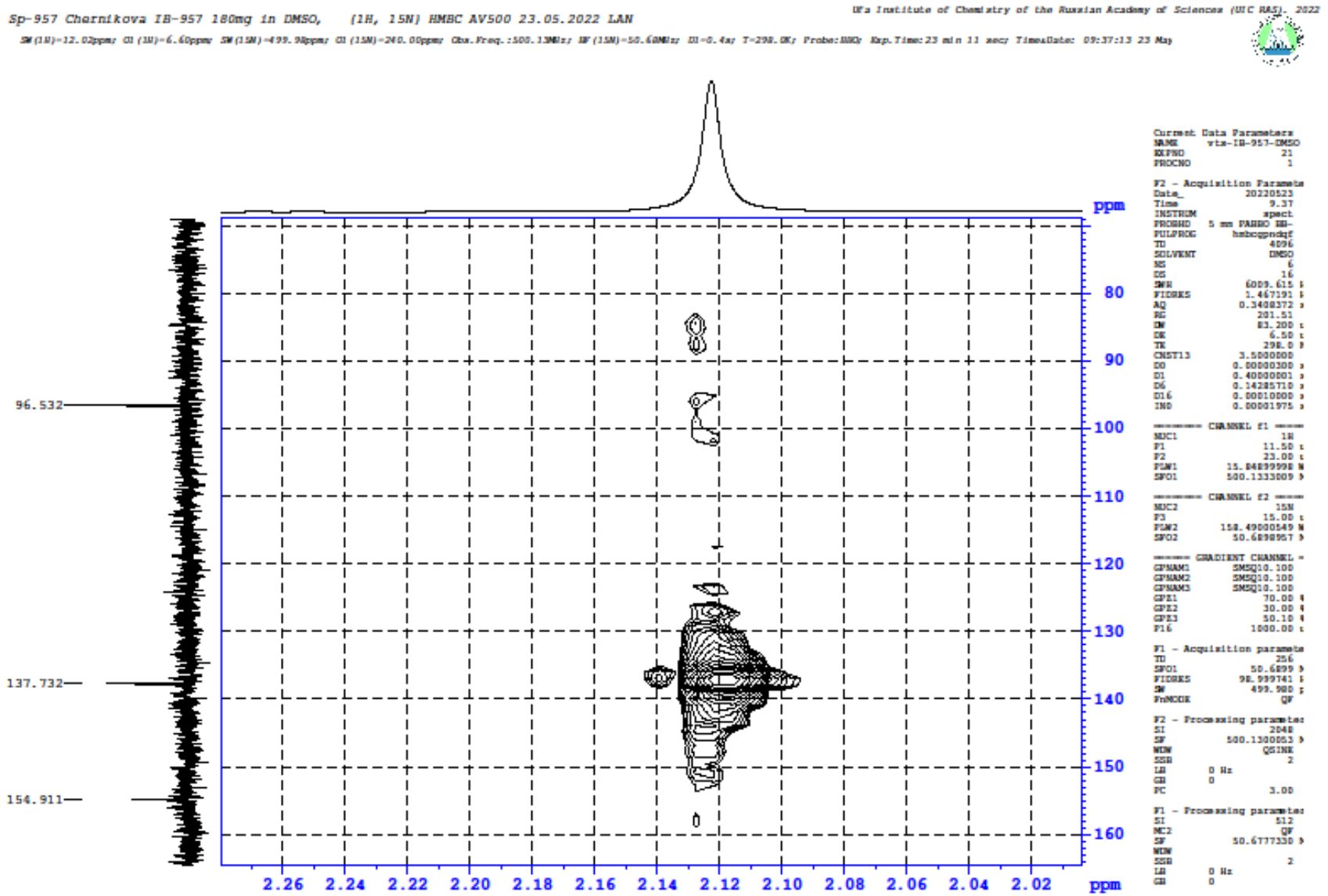
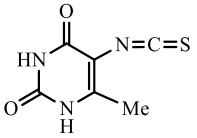
^{1}H-^{15}N HMBC NMR spectrum 1 of compound **3**





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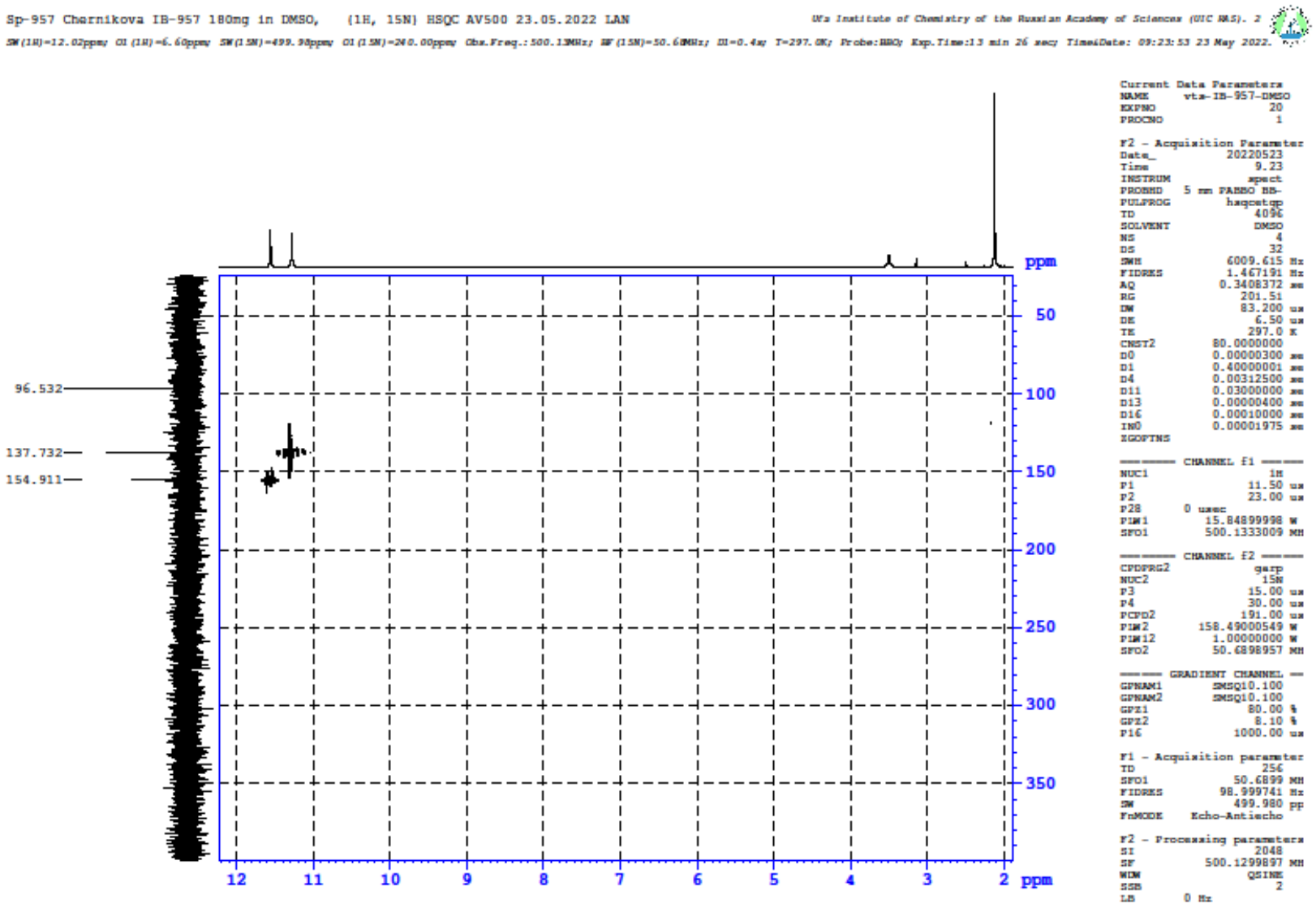
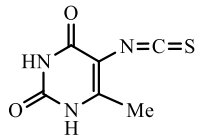
^{1}H-^{15}N HMBC NMR spectrum 2 of compound **3**





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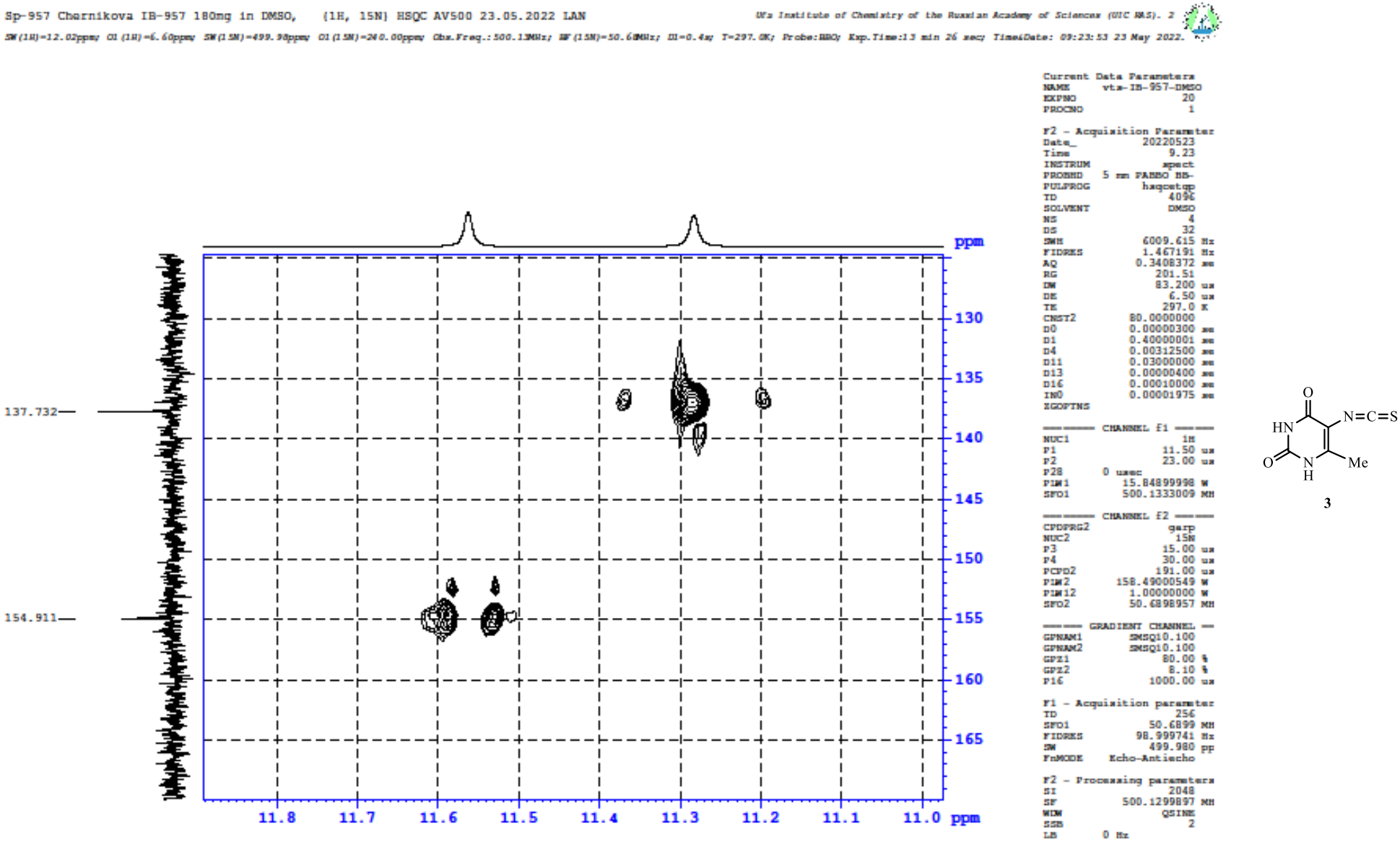
^{1}H-^{15}N HSQC NMR spectrum of compound **3**



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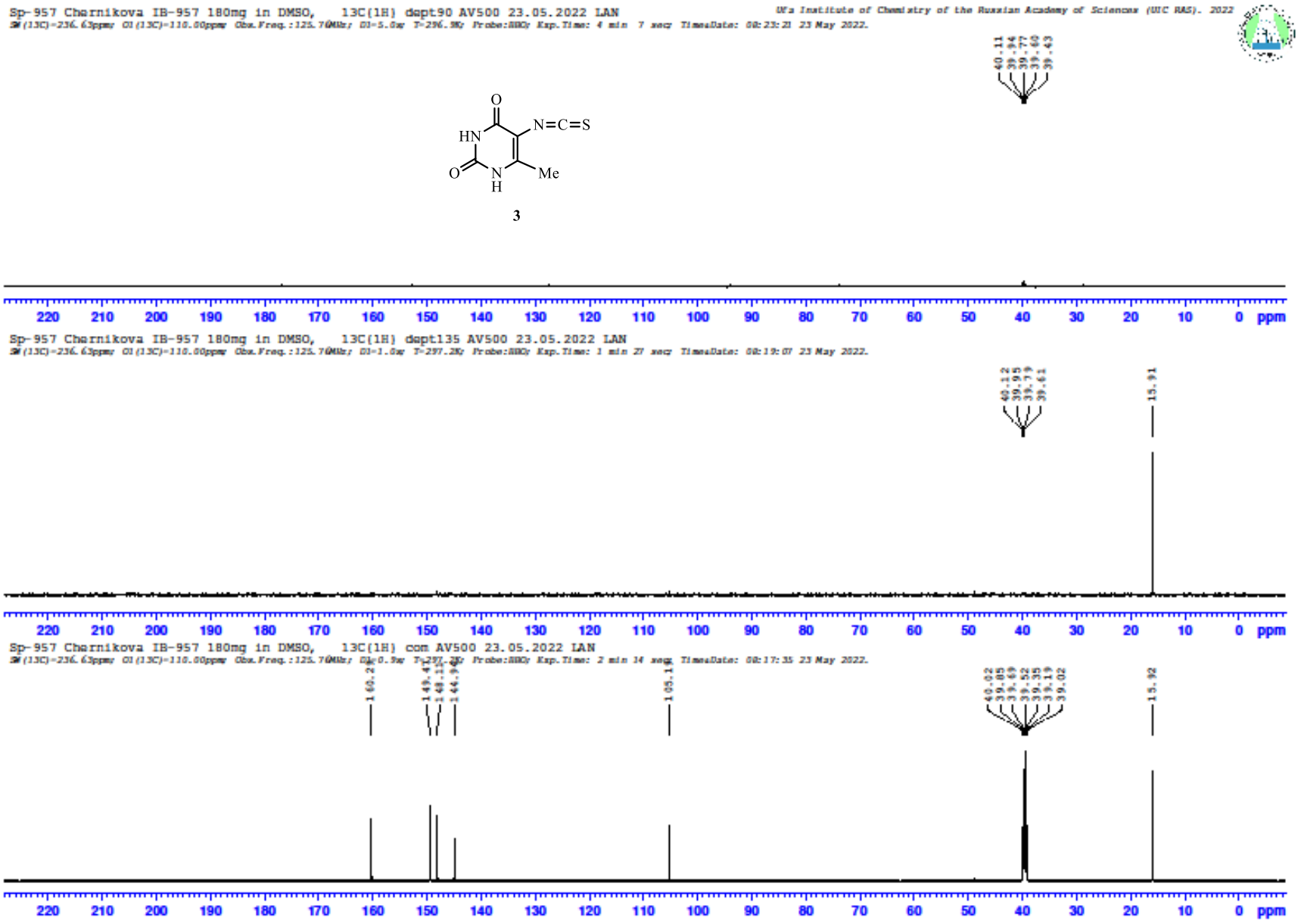
^{1}H-^{15}N HSQC NMR spectrum1 of compound **3**



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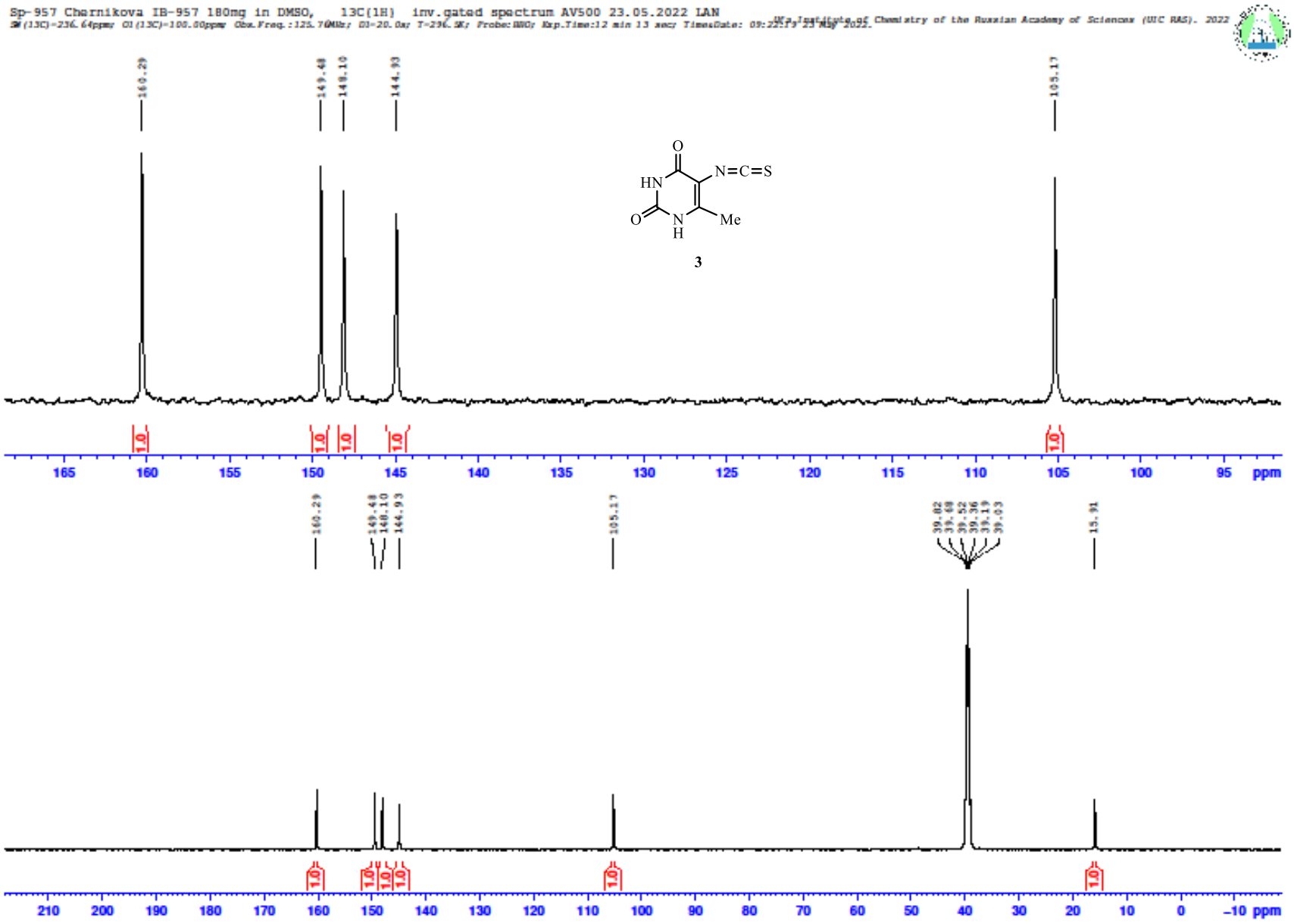
^{13}C NMR spectrum of compound **3**



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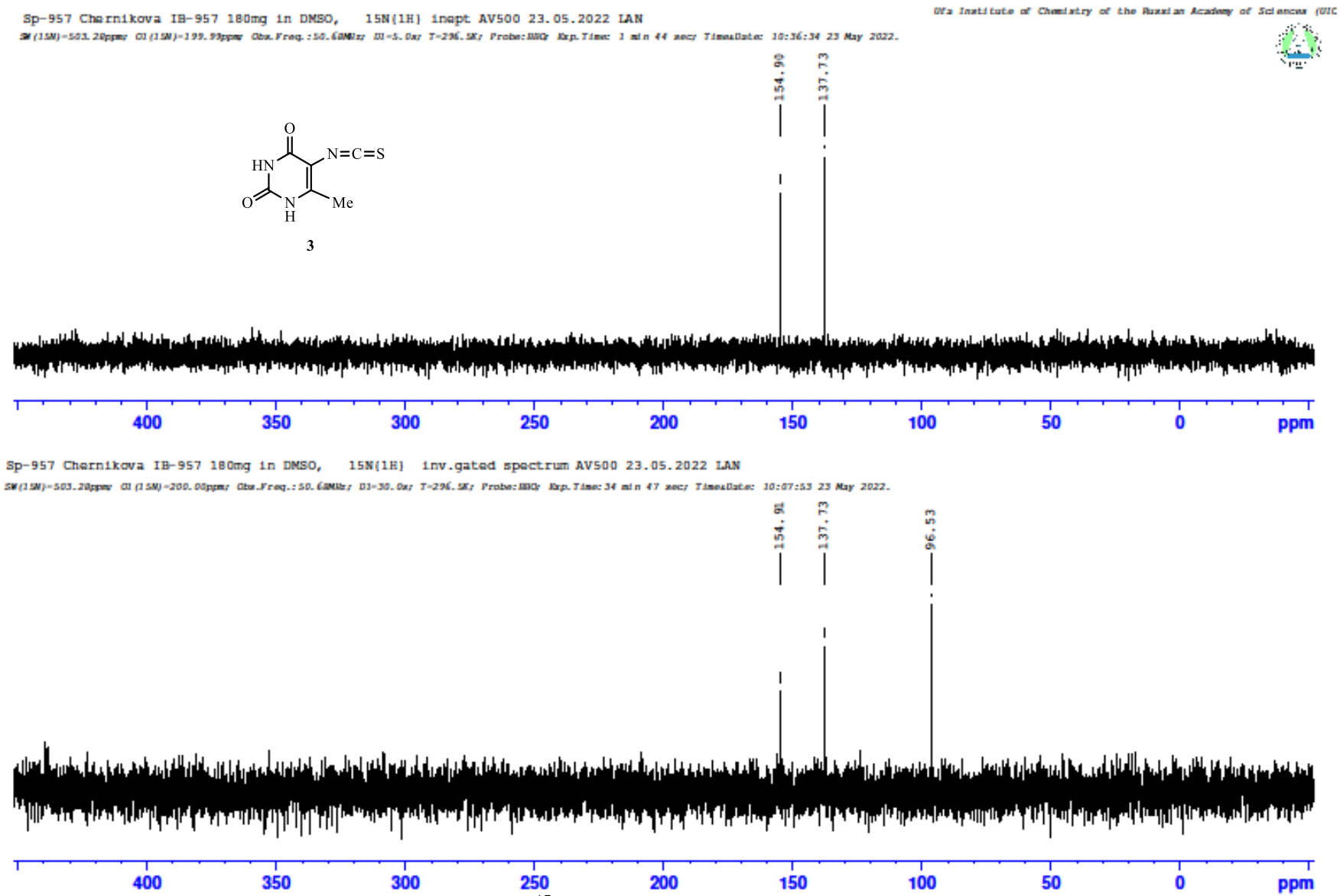
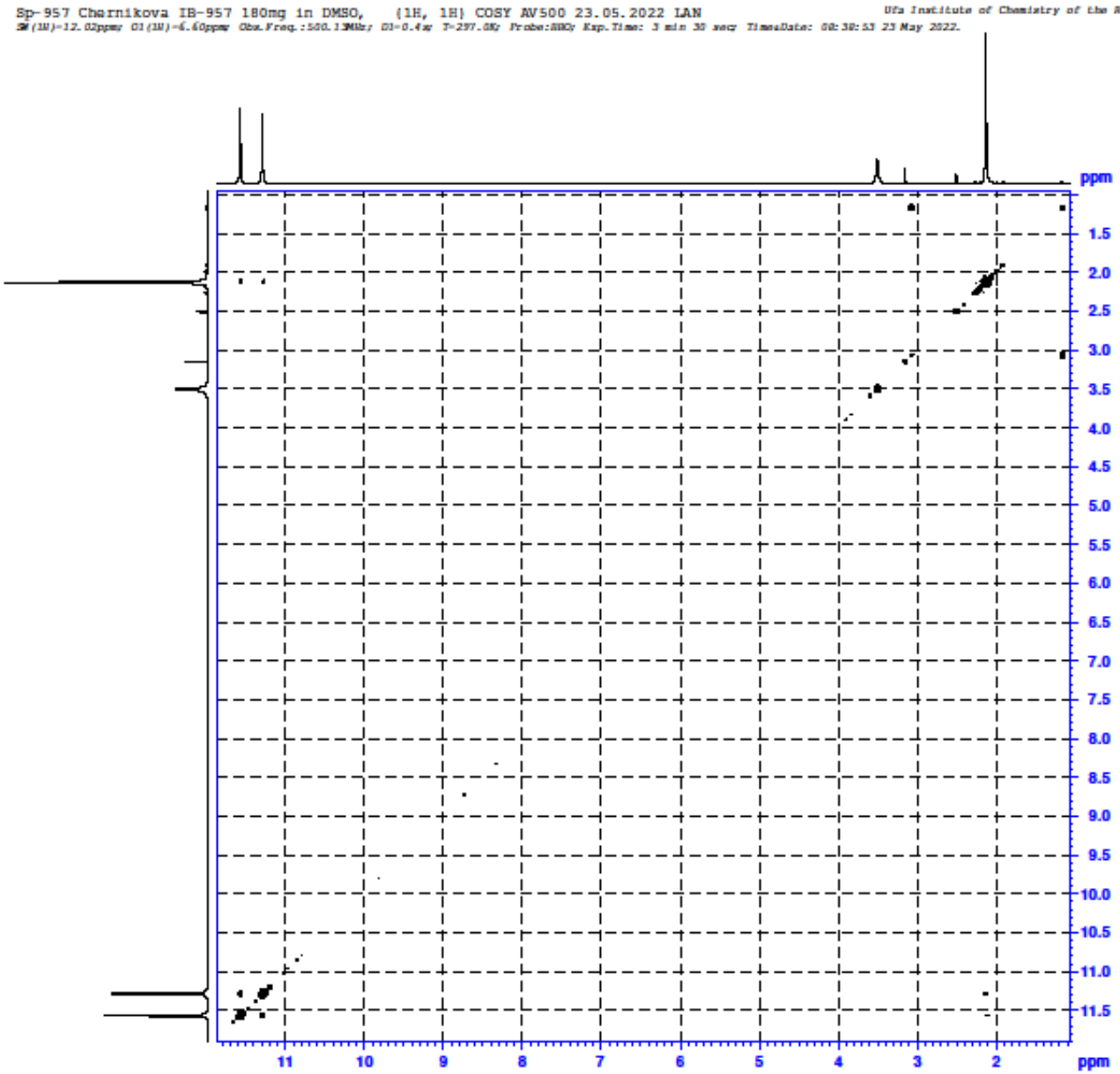
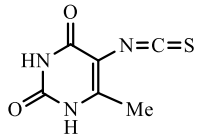
^{13}C NMR spectrum integrals for compound **3**



^{15}N NMR spectrum of compound **3**





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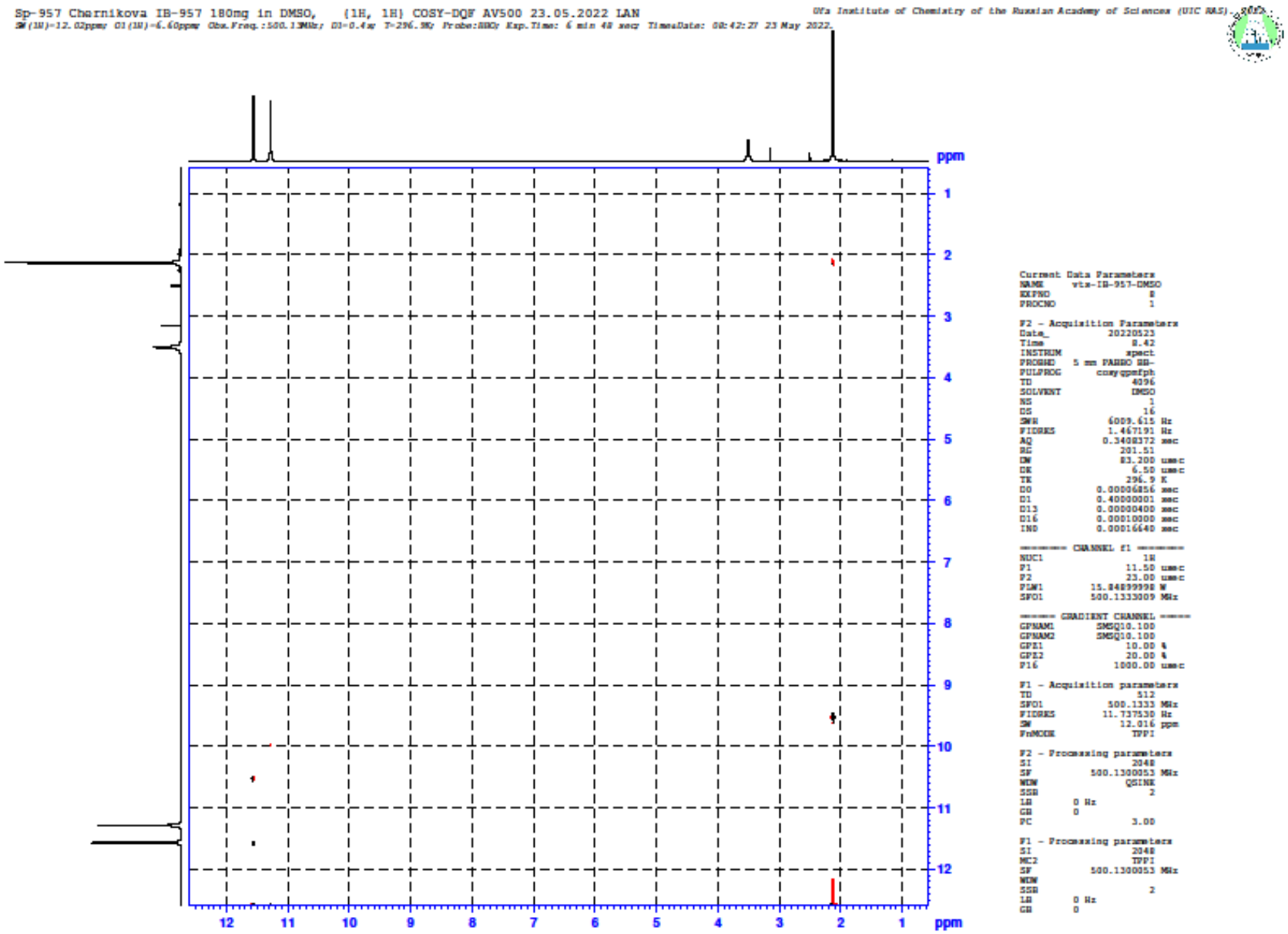
COSY NMR spectrum of compound **3**

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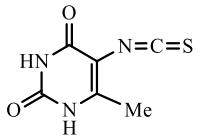

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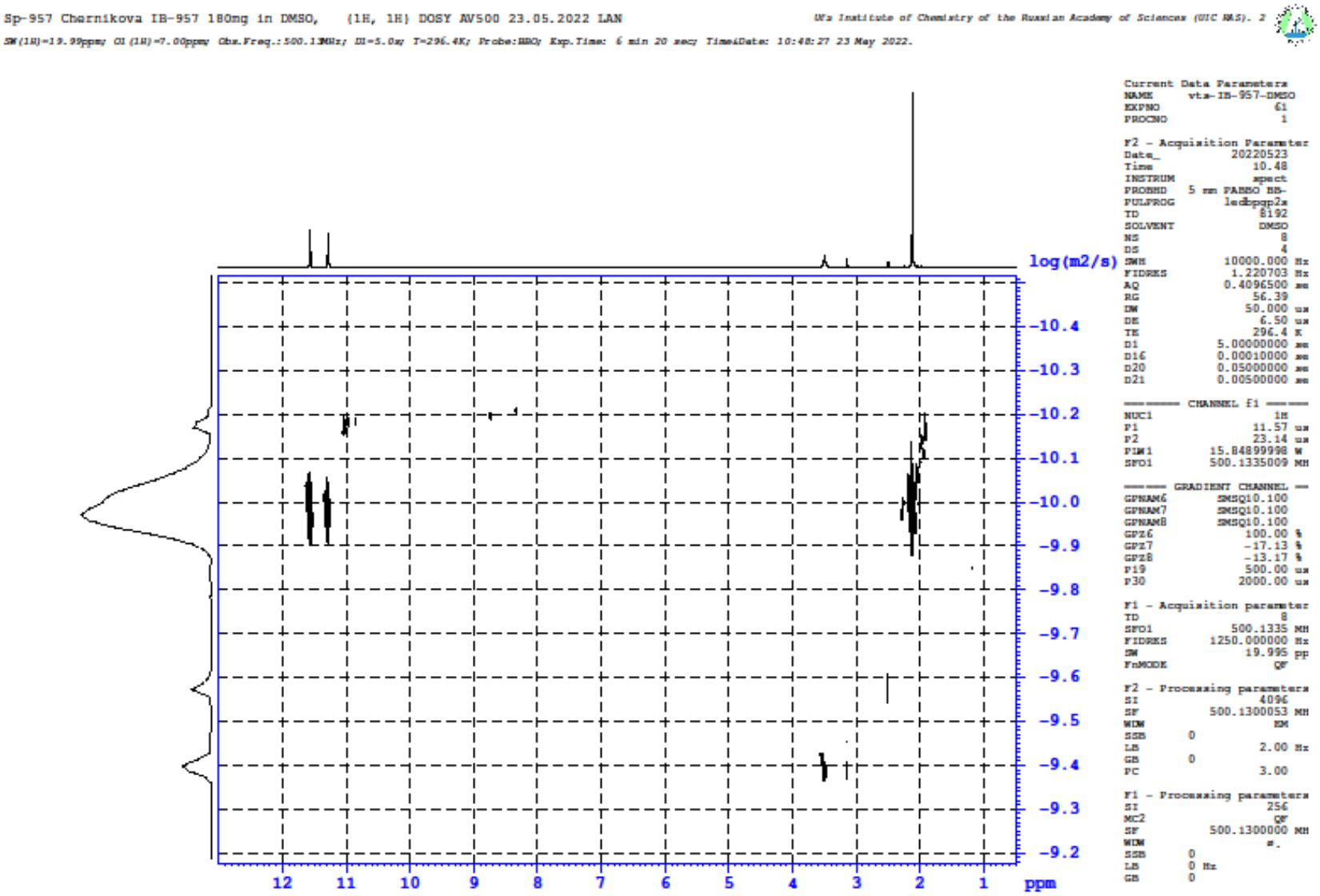
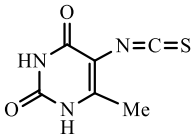
COSY DQF NMR spectrum of compound **3**





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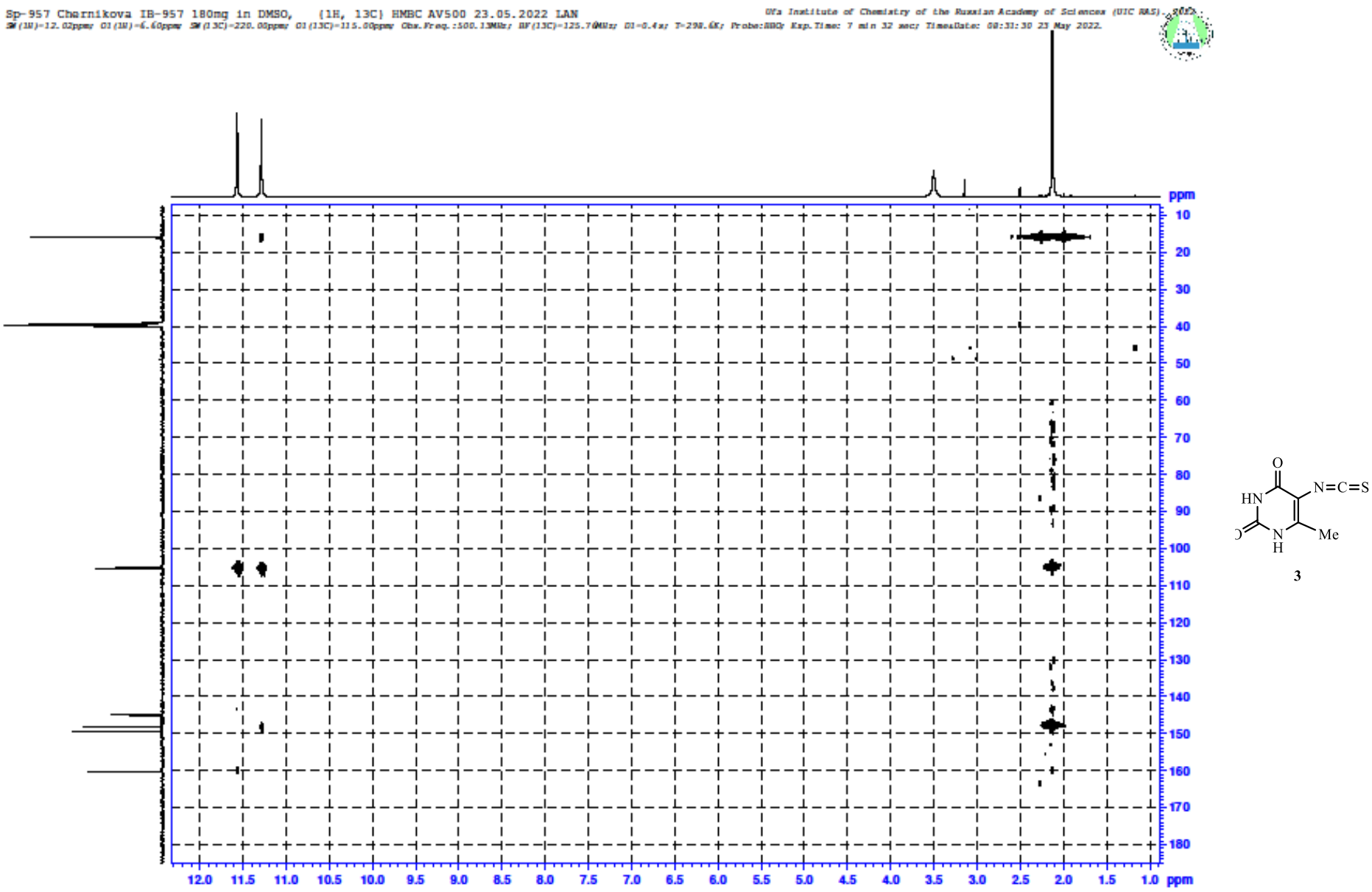
DOSY NMR spectrum of compound **3**



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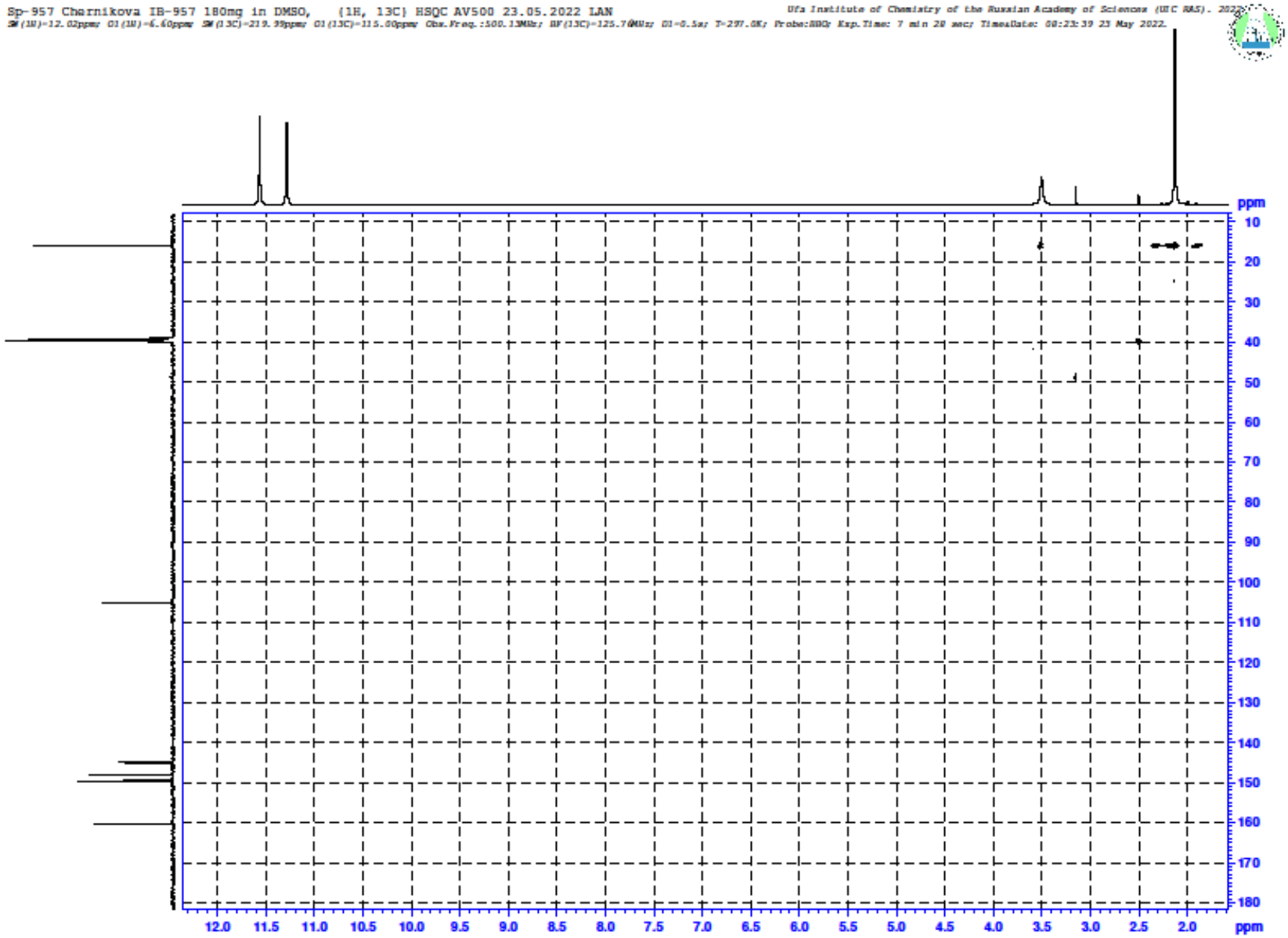
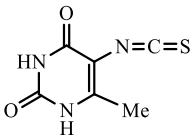
HMBC NMR spectrum of compound **3**





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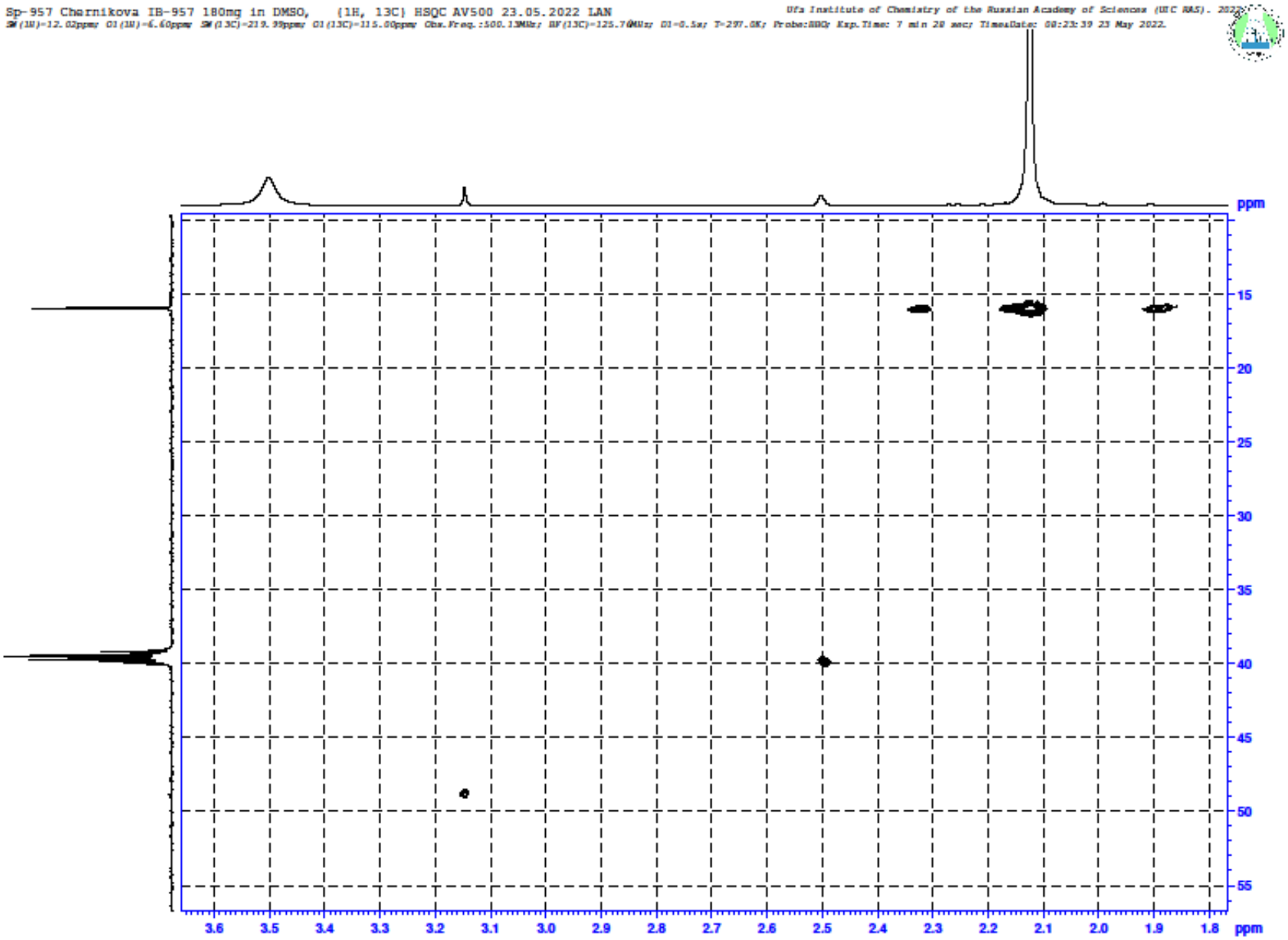
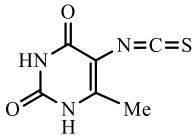
HSQC NMR spectrum of compound **3**





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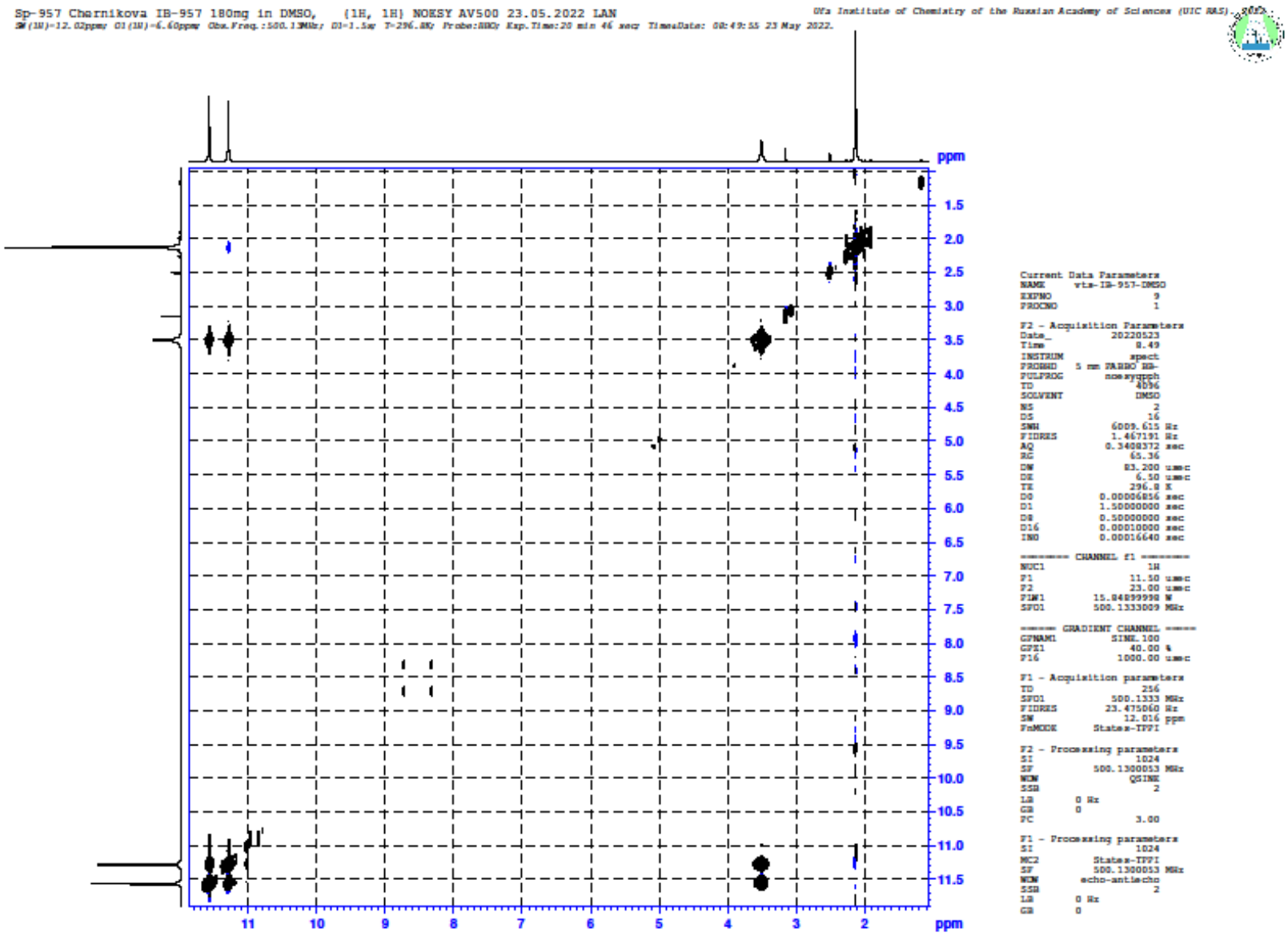
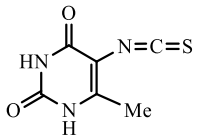
HSQC NMR spectrum1 of compound **3**





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NOESY NMR spectrum of compound **3**