Electronic Supplementary Material (ESI) for RSC Advances.

Electrophilic Alkylation of Arenes with 5-Bromopyrimidine en route to 4-Aryl-5-alkynylpyrimidines

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Supporting Information

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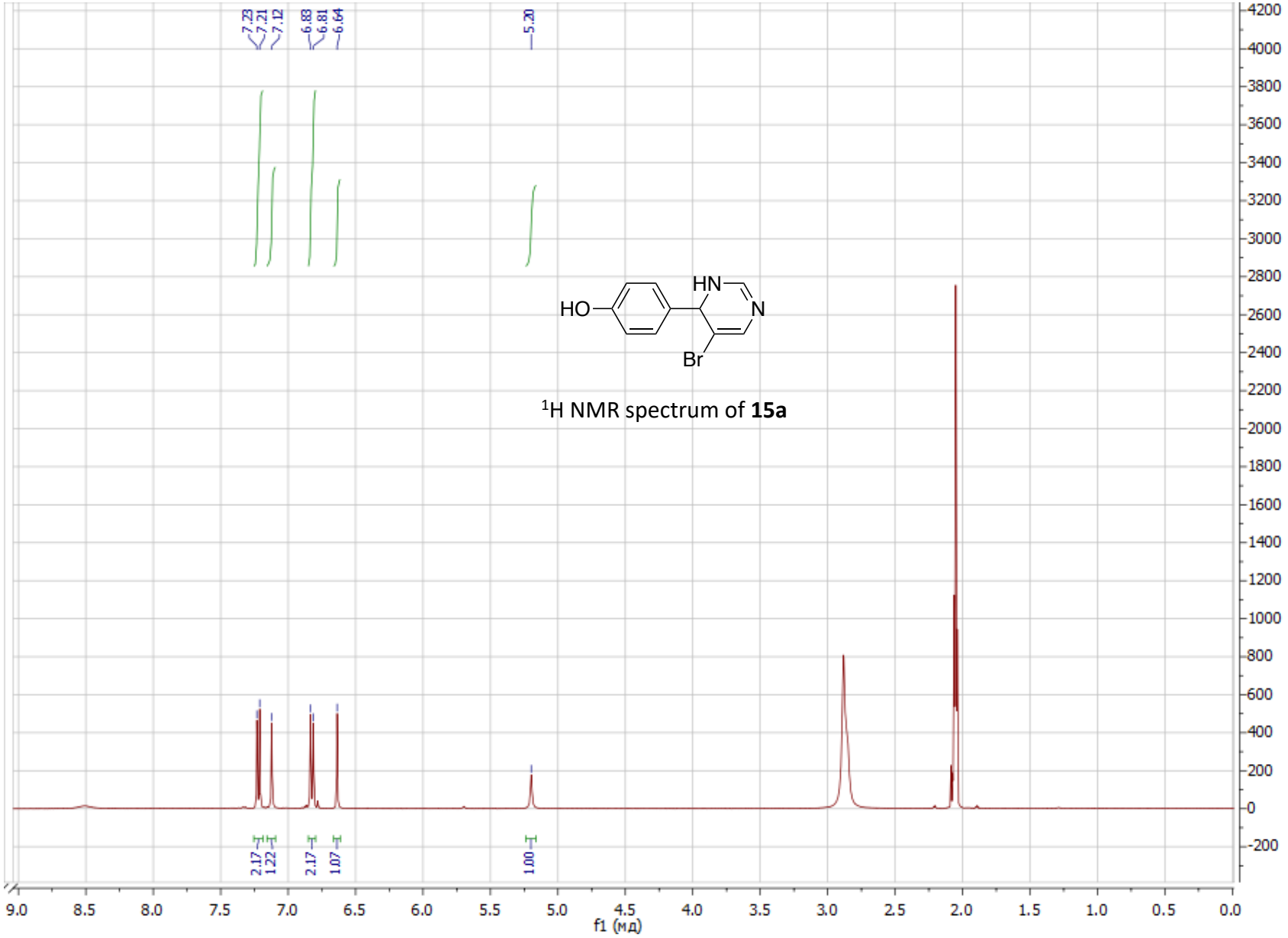
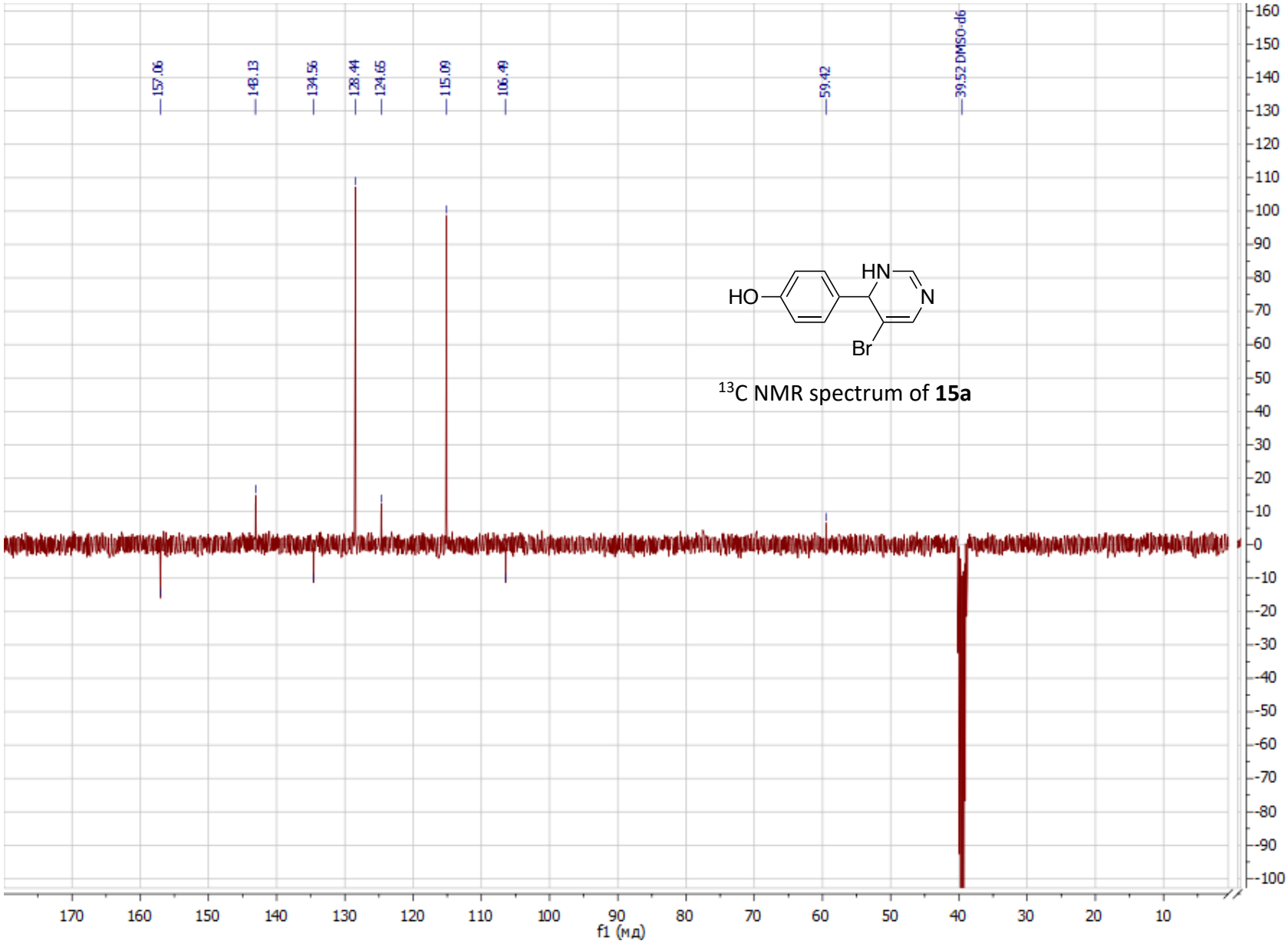
Spectral Data



^{1}H NMR spectrum of **15a**



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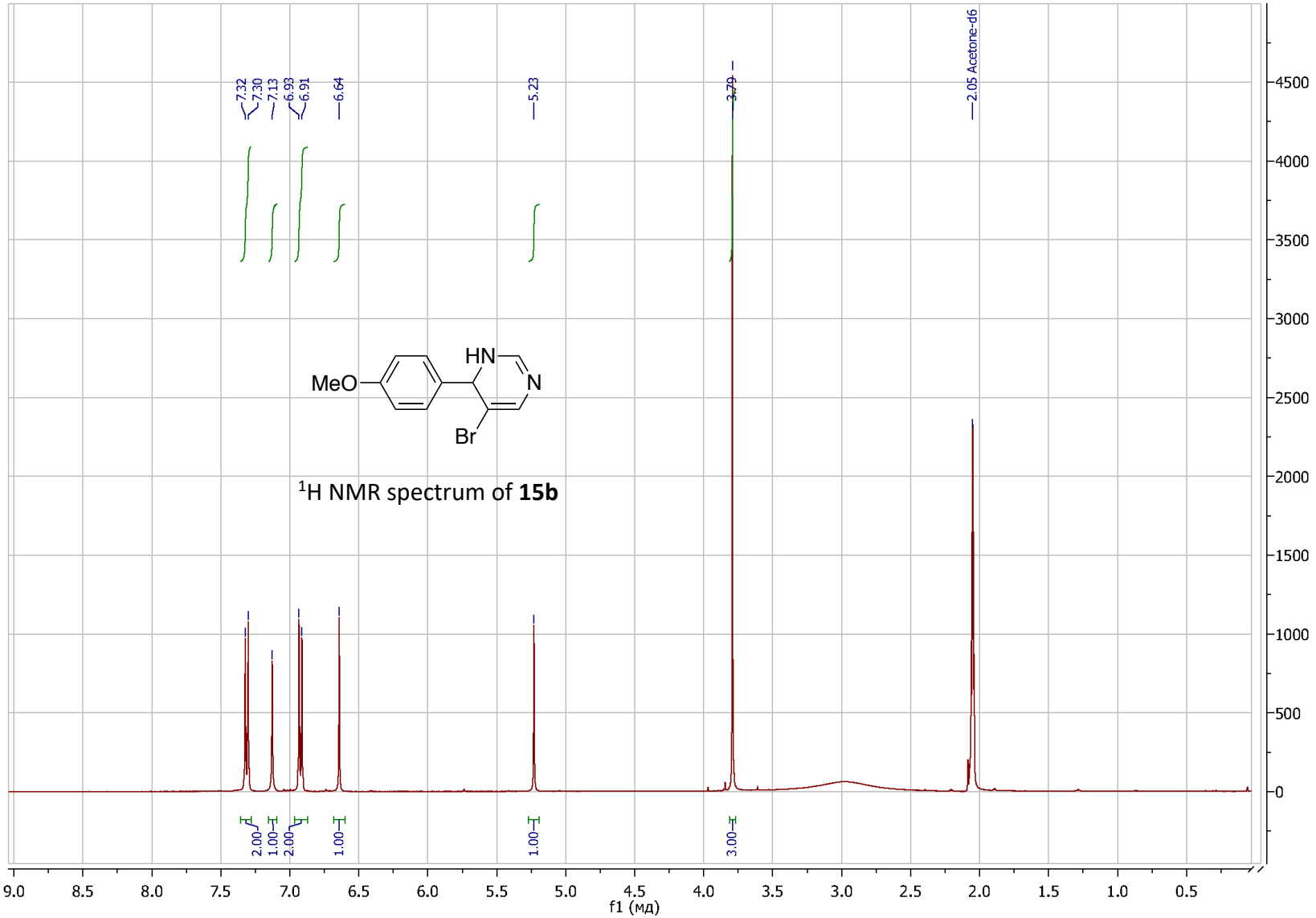

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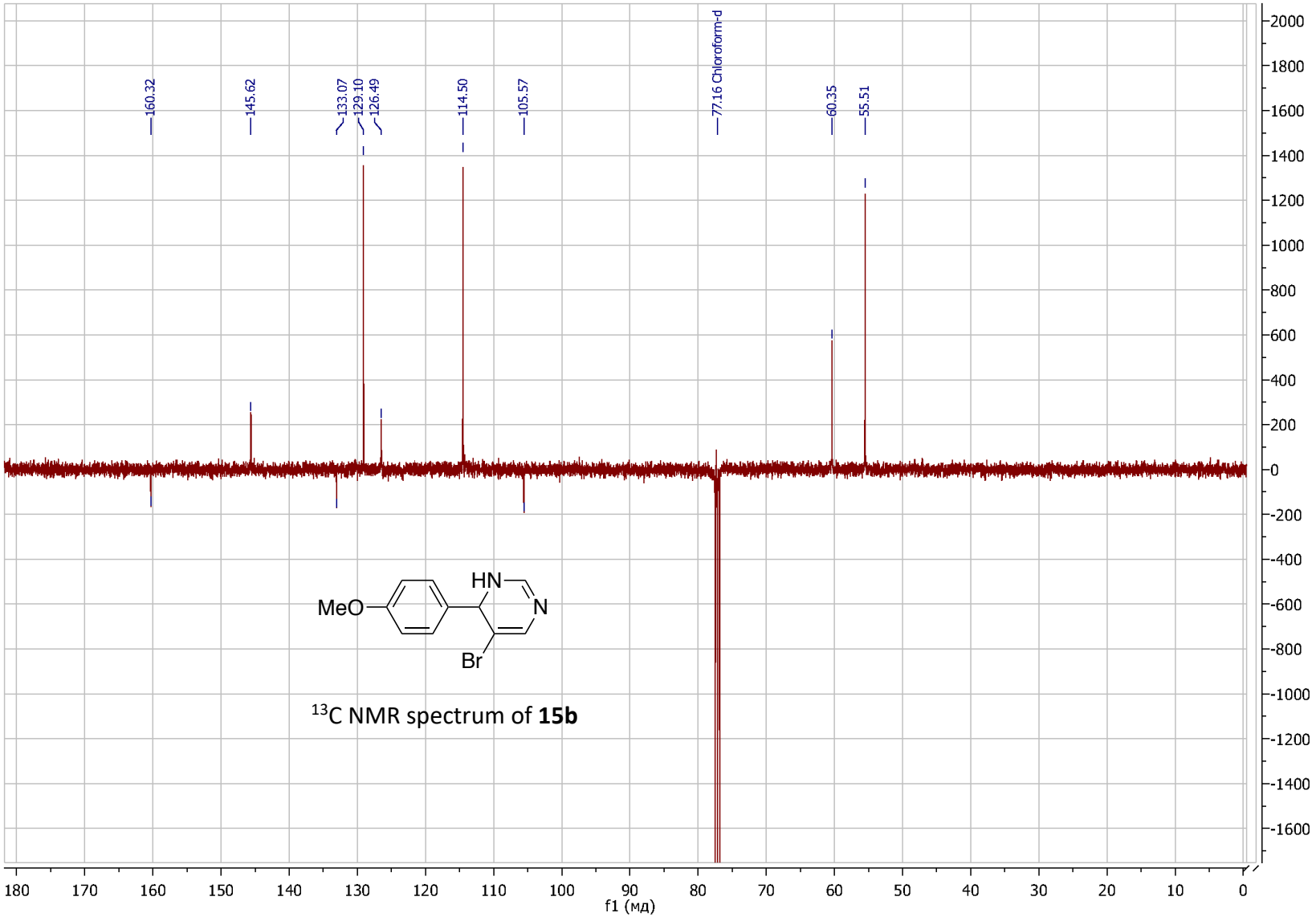

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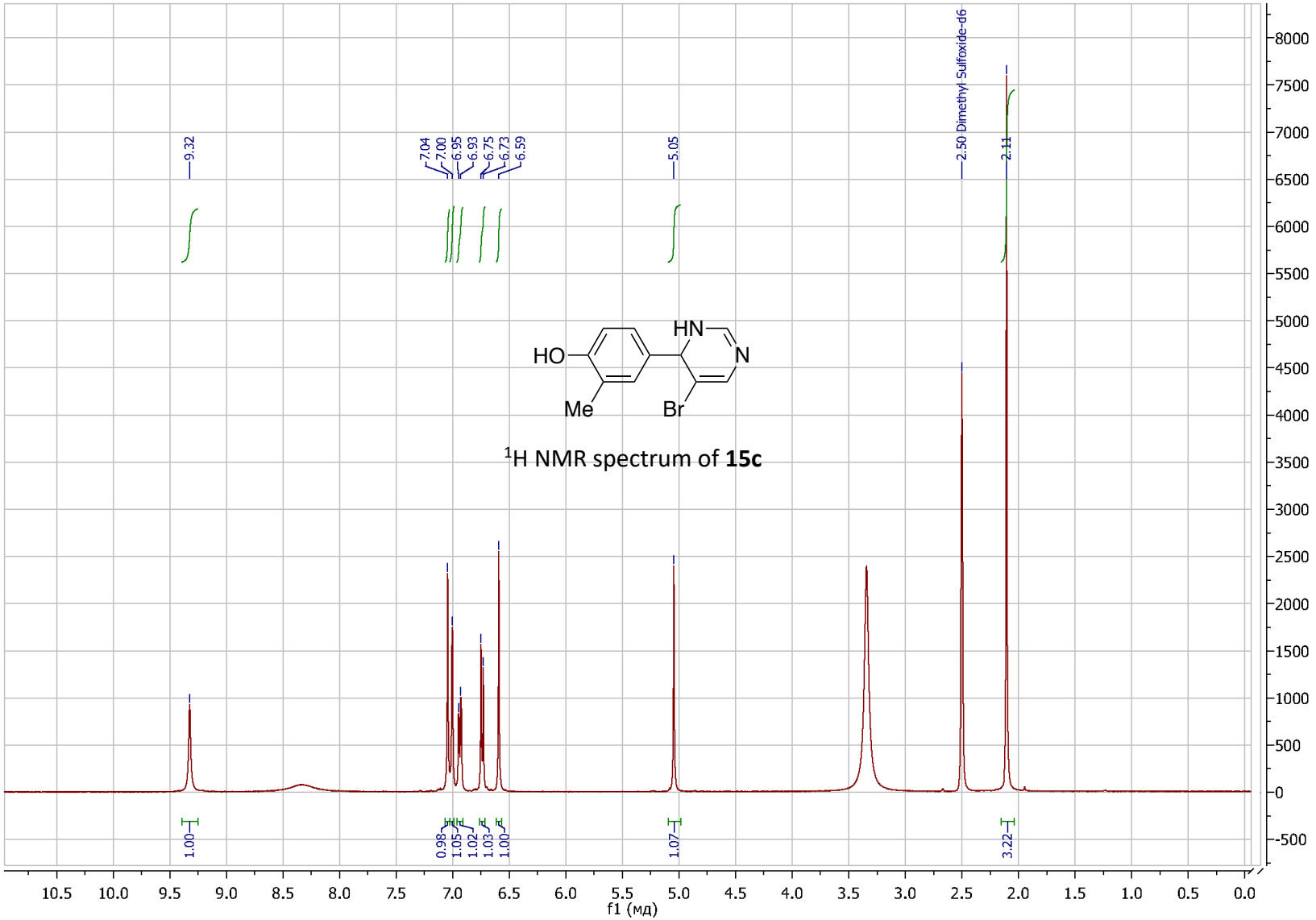

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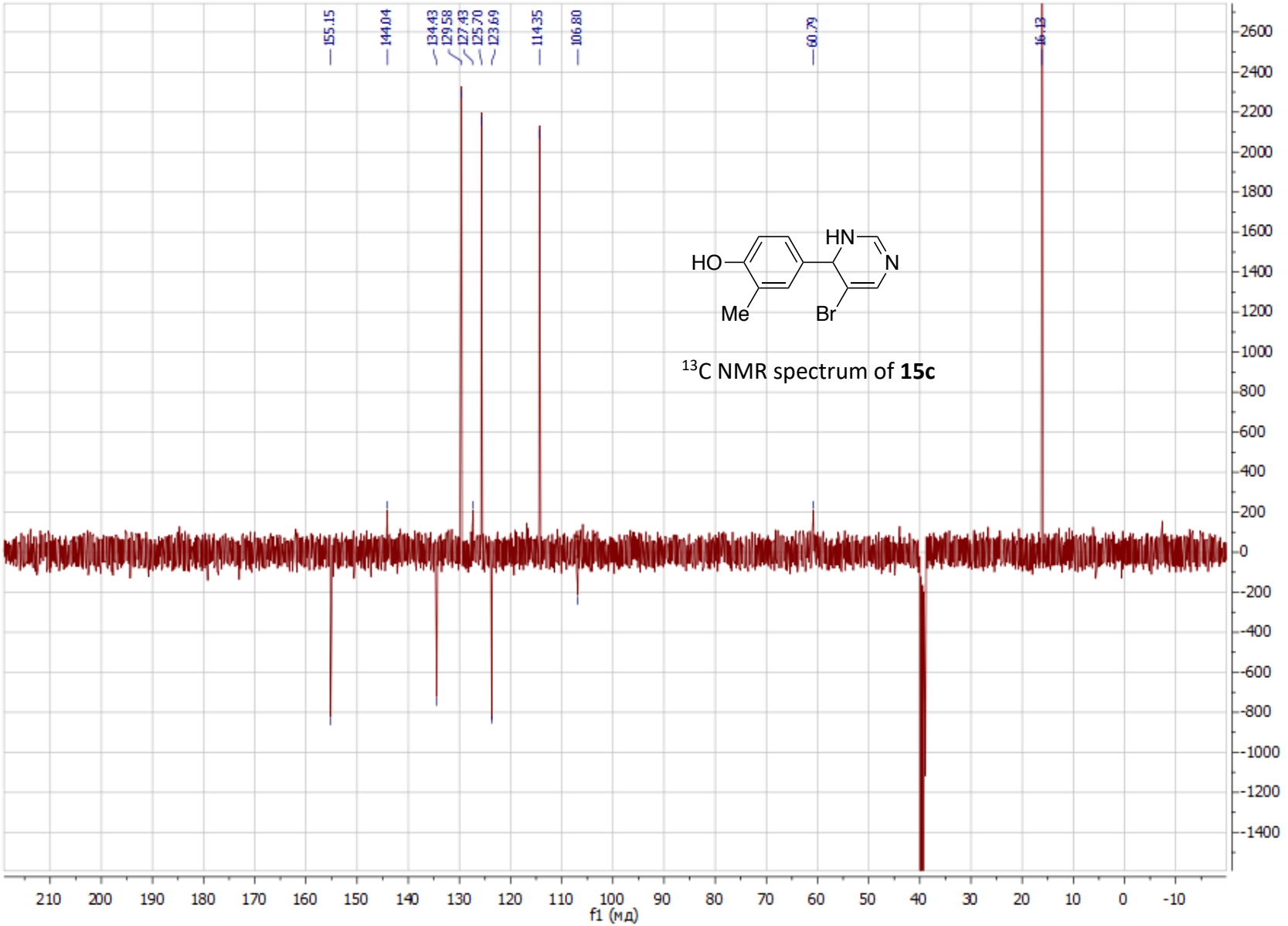

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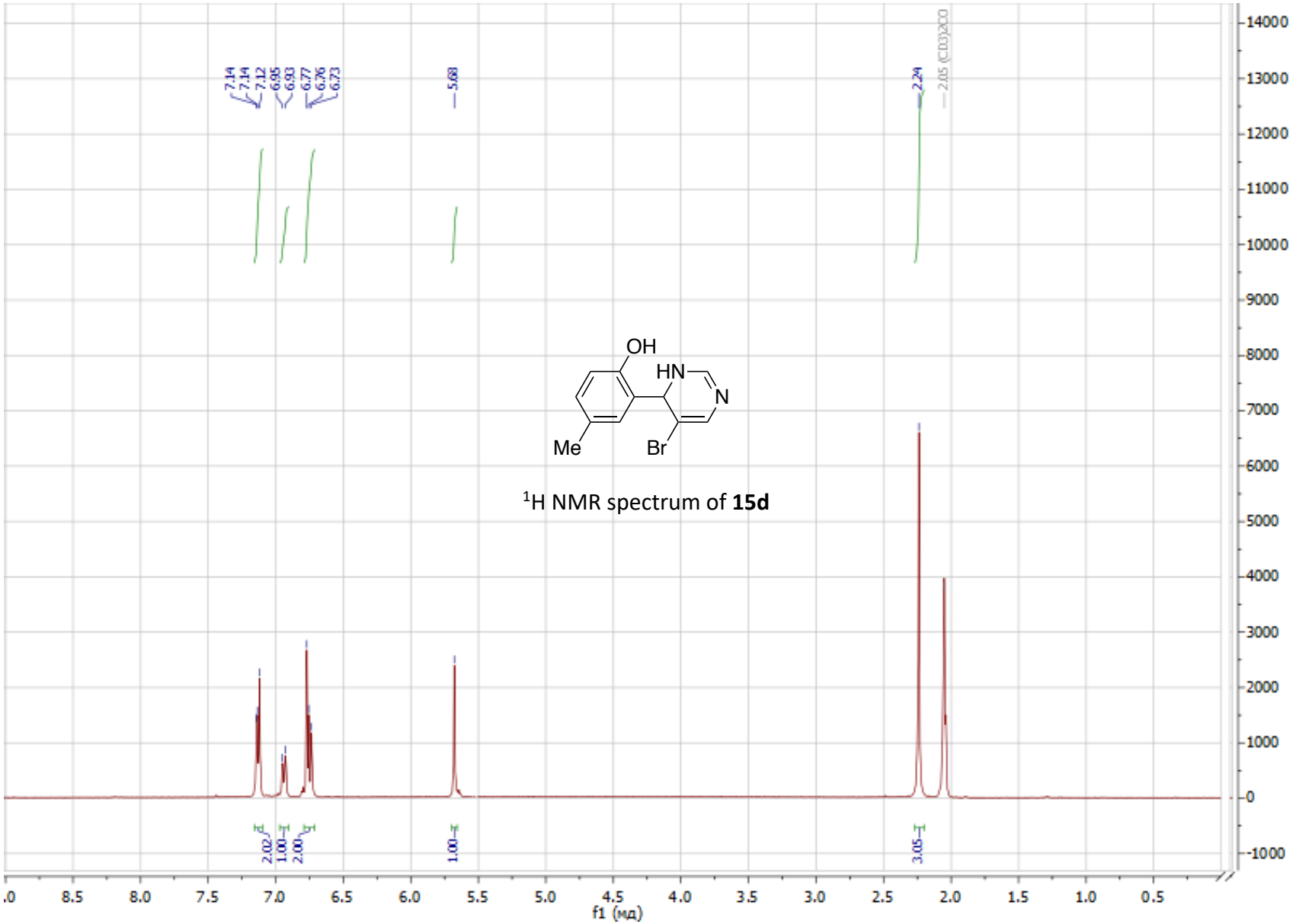

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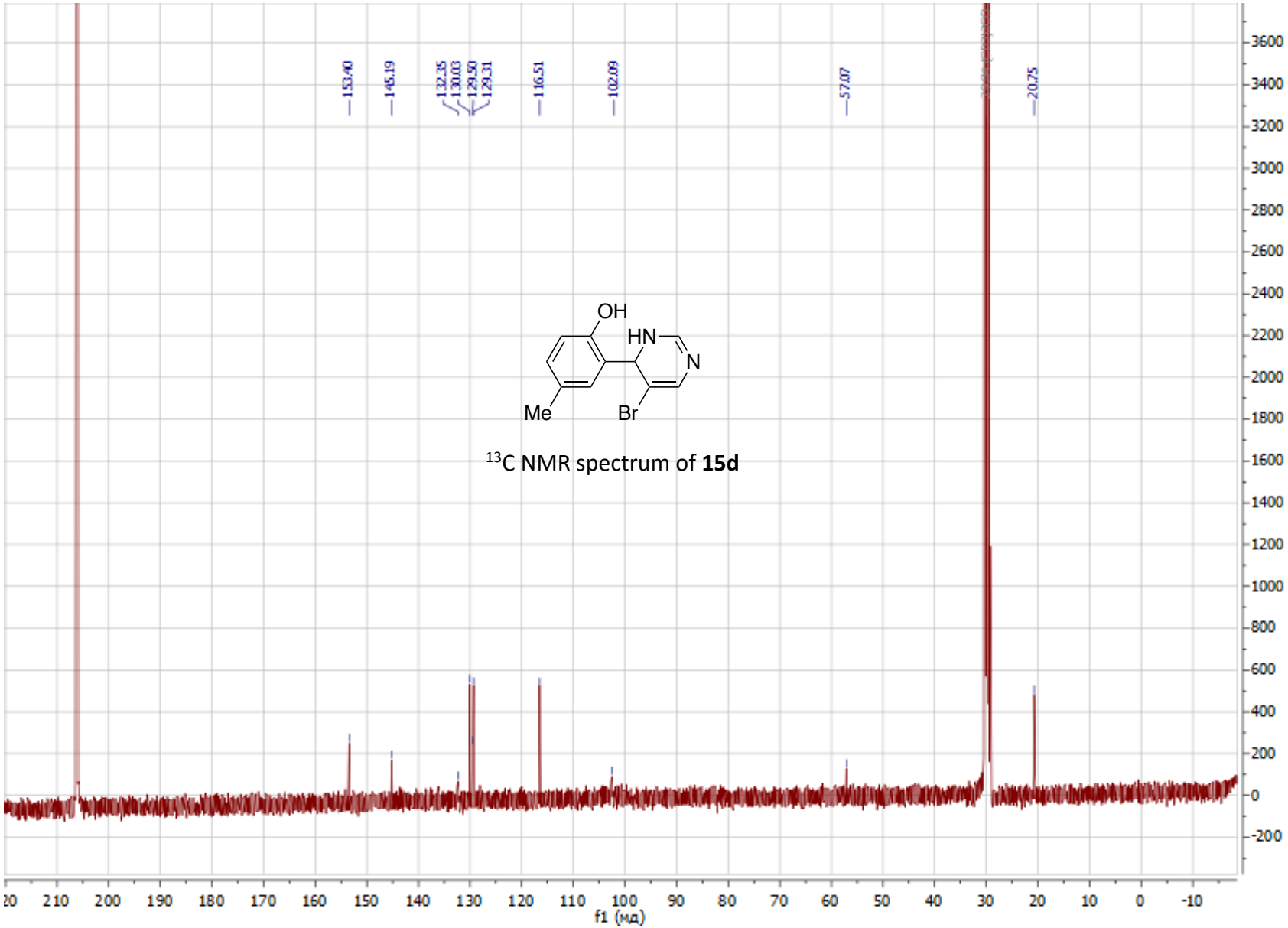

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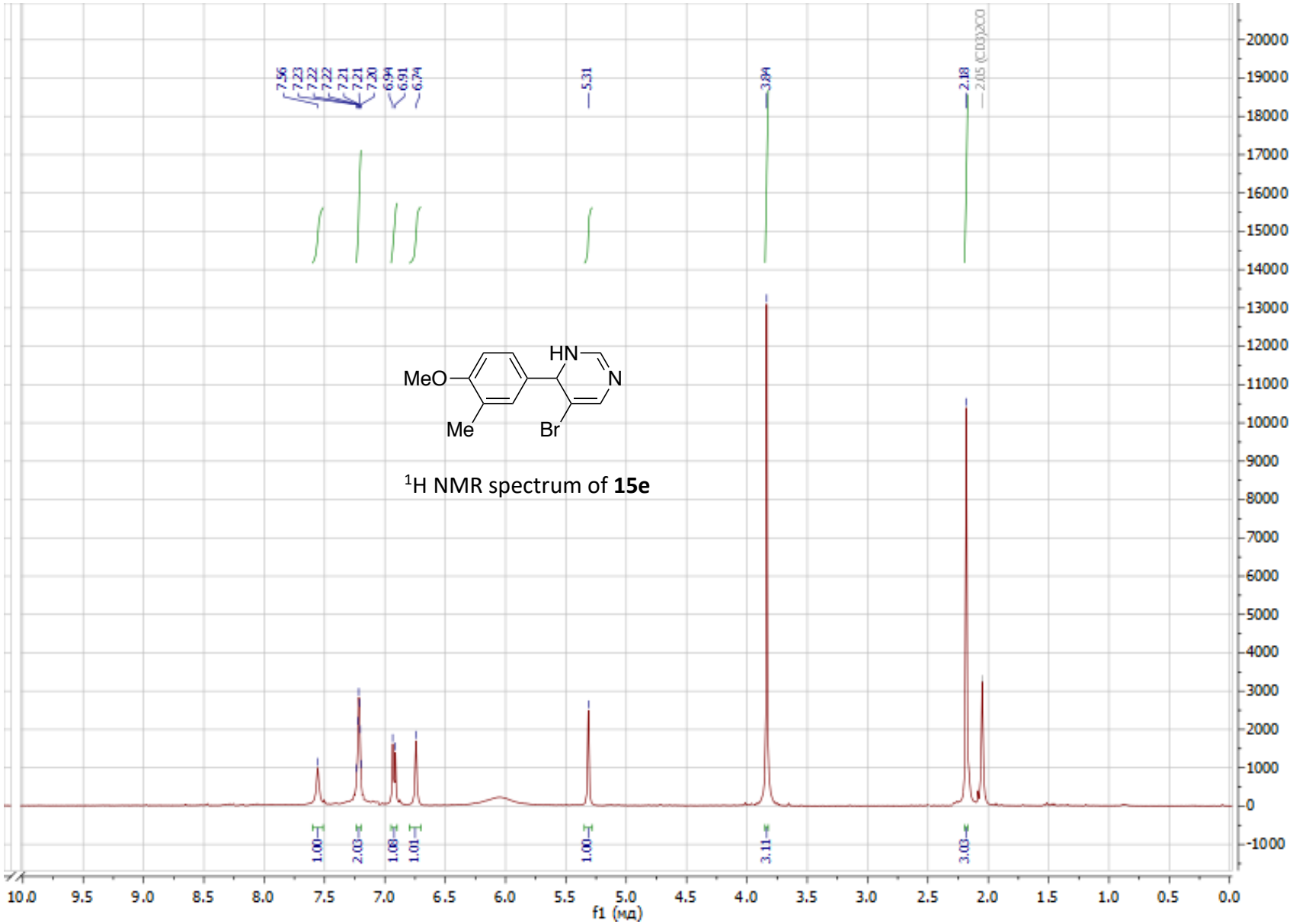

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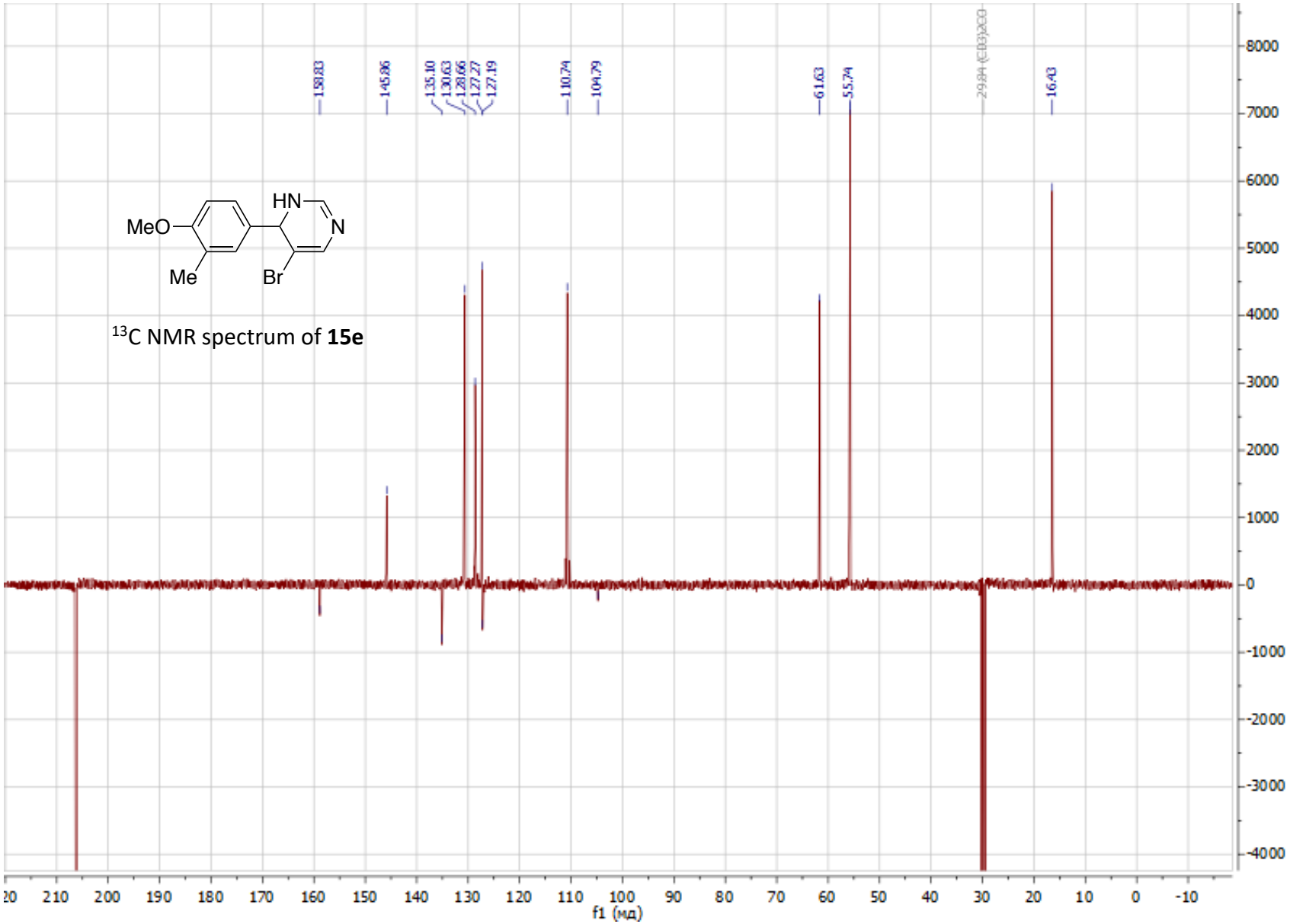

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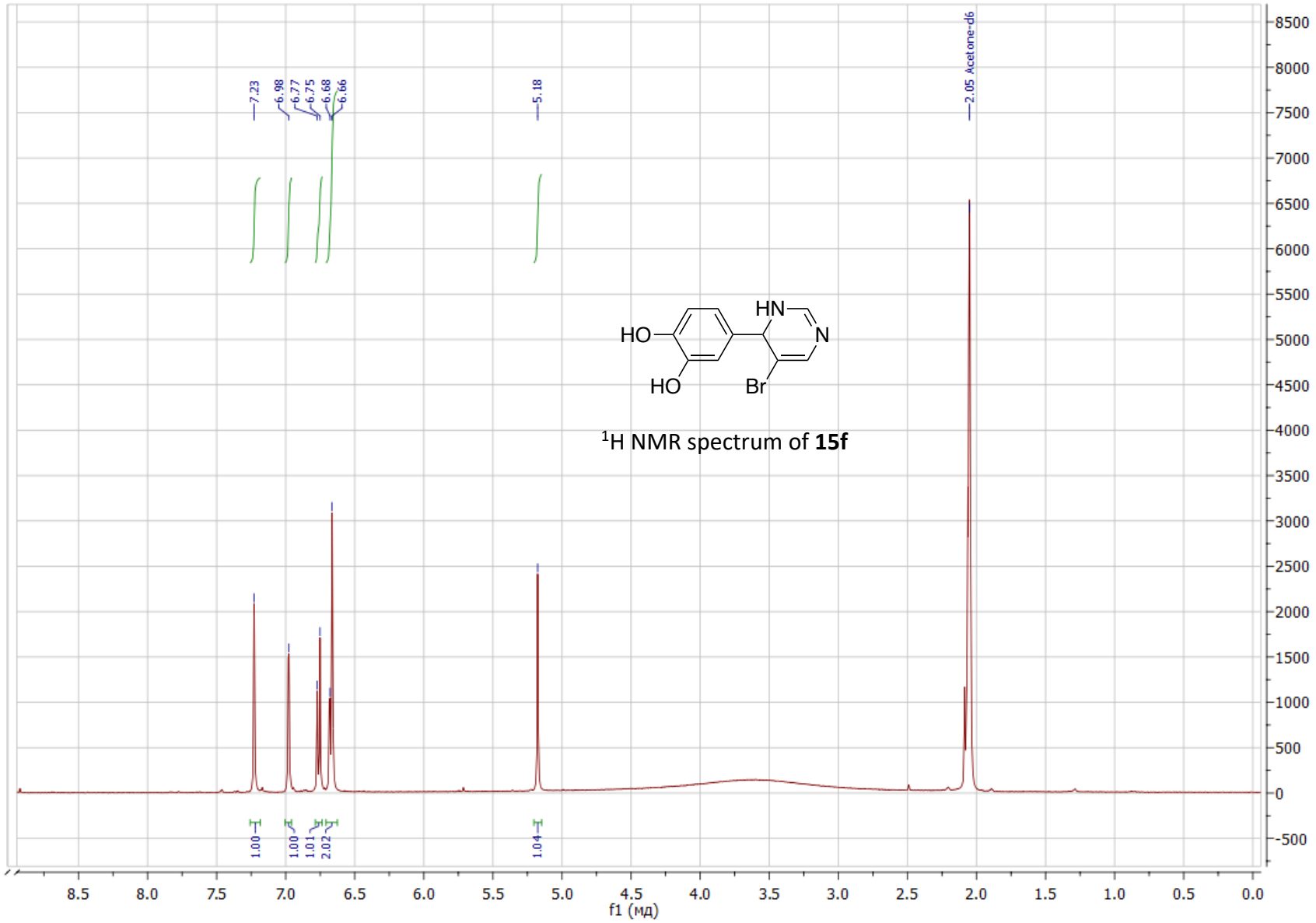

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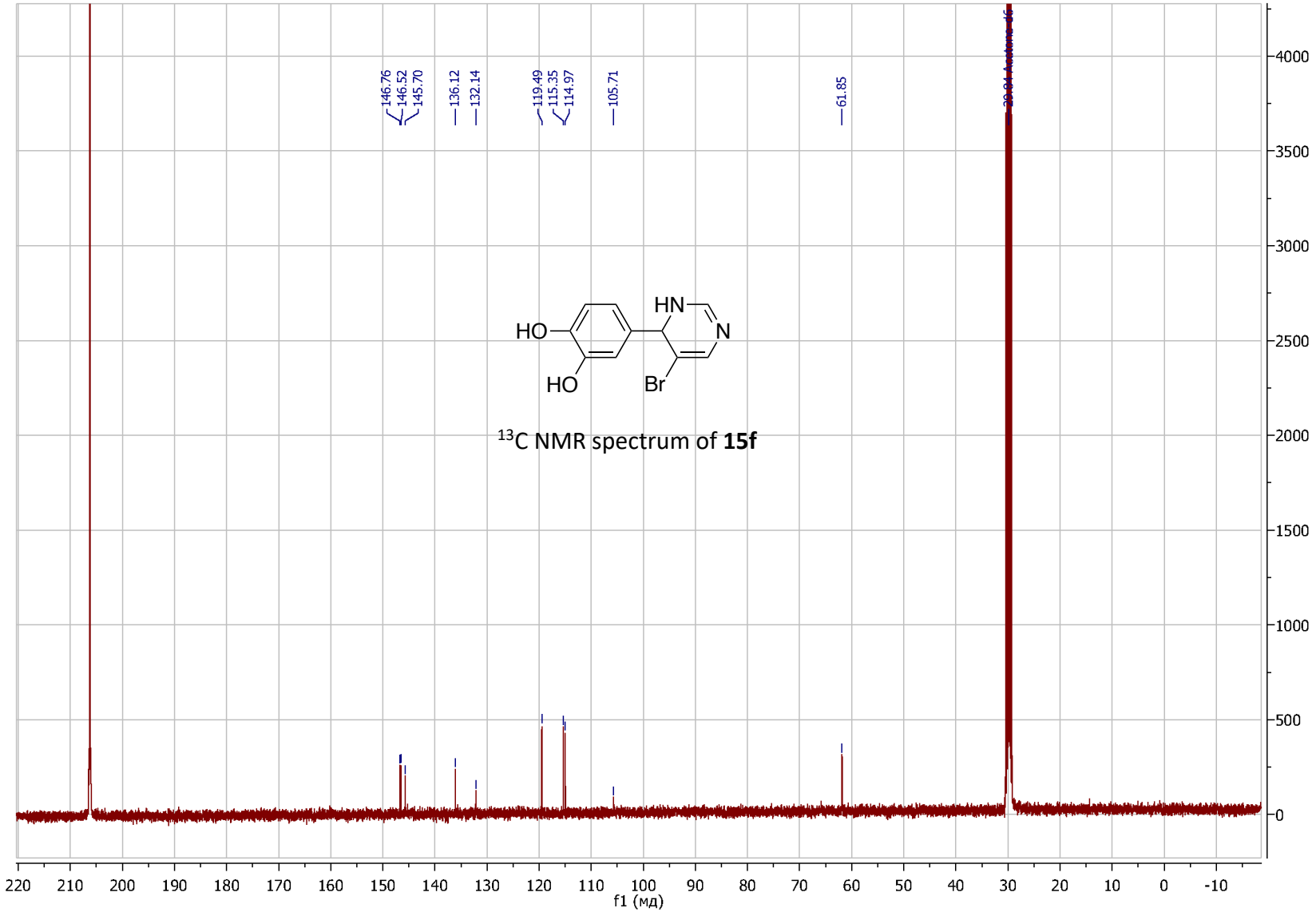

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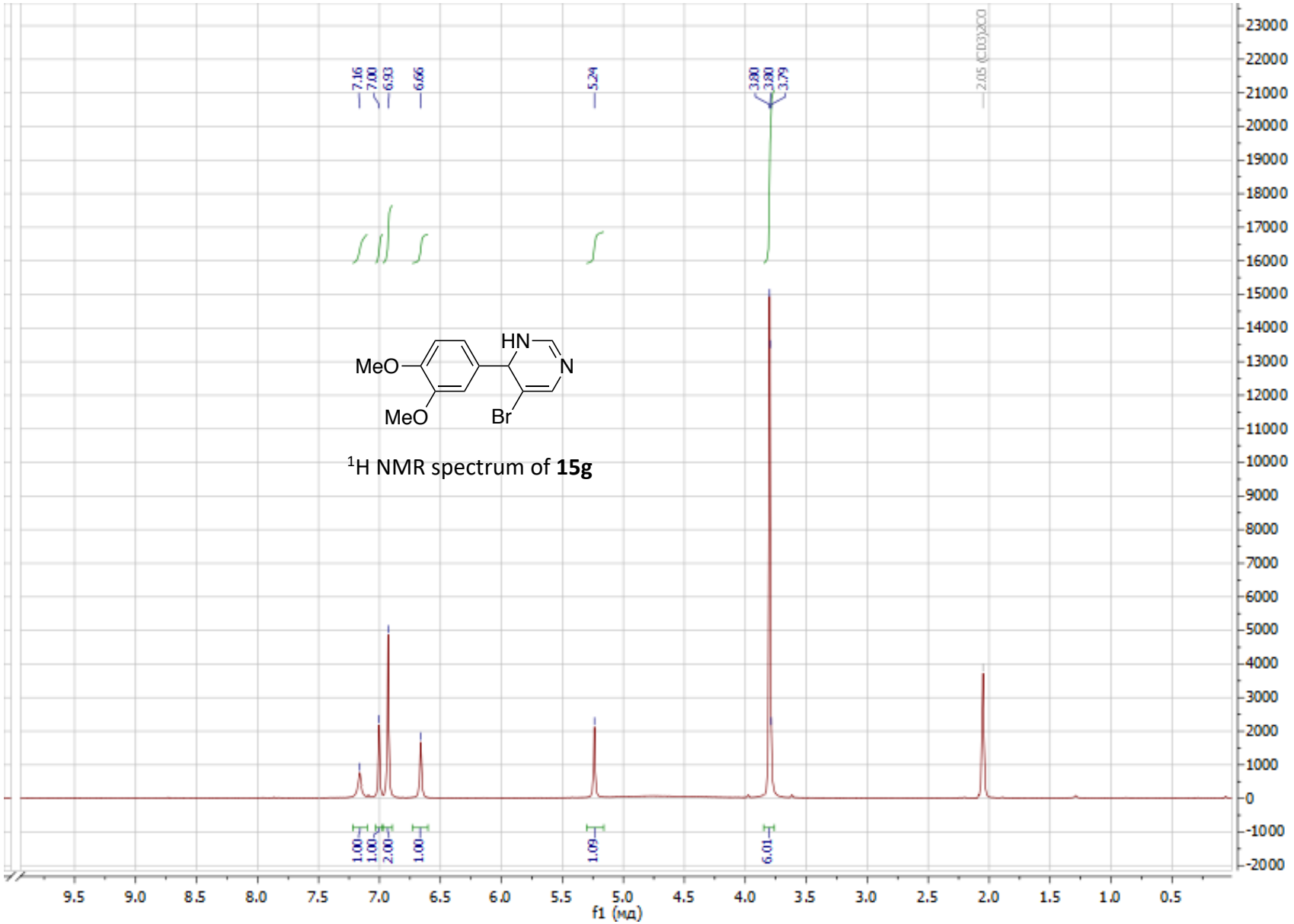

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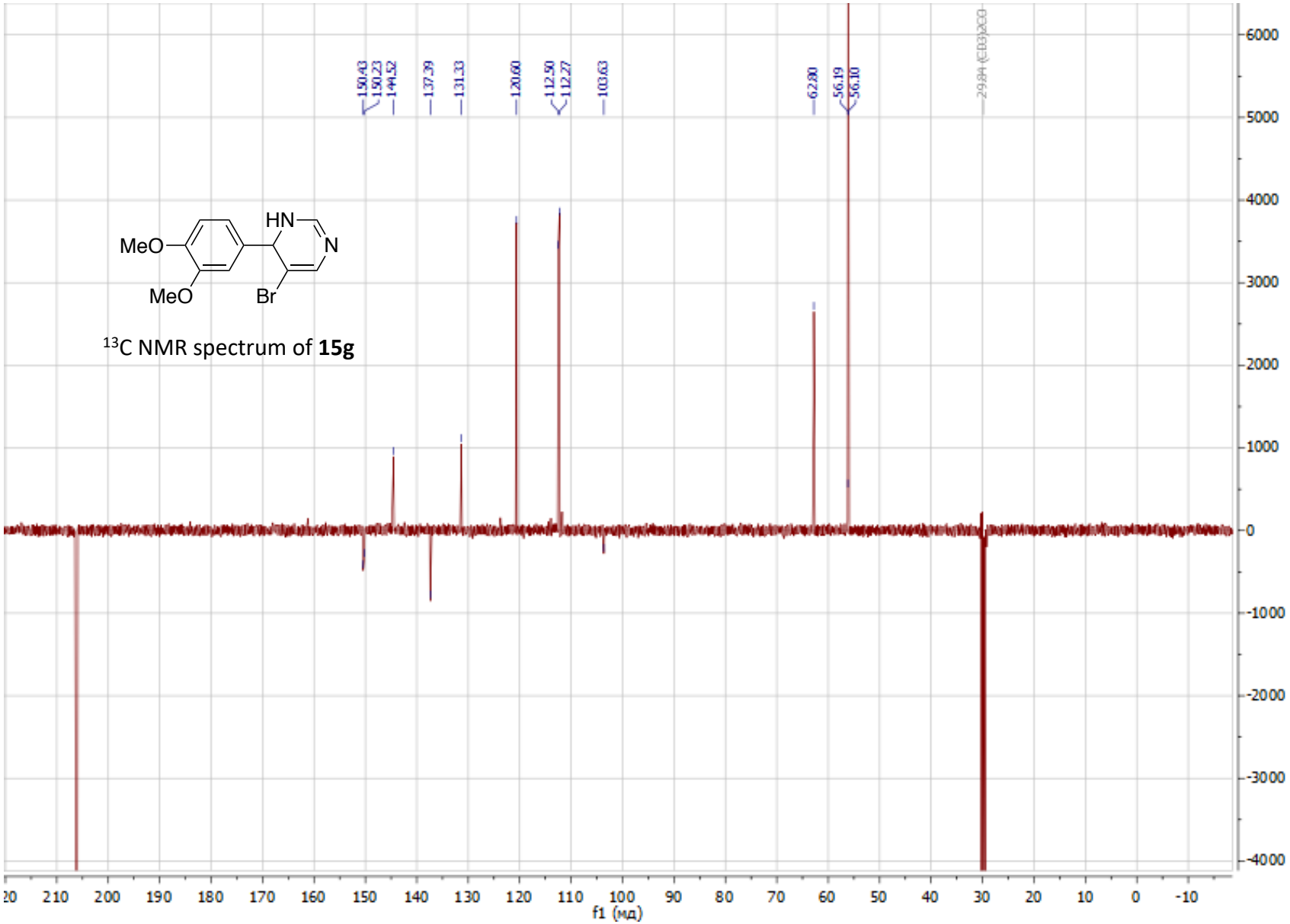

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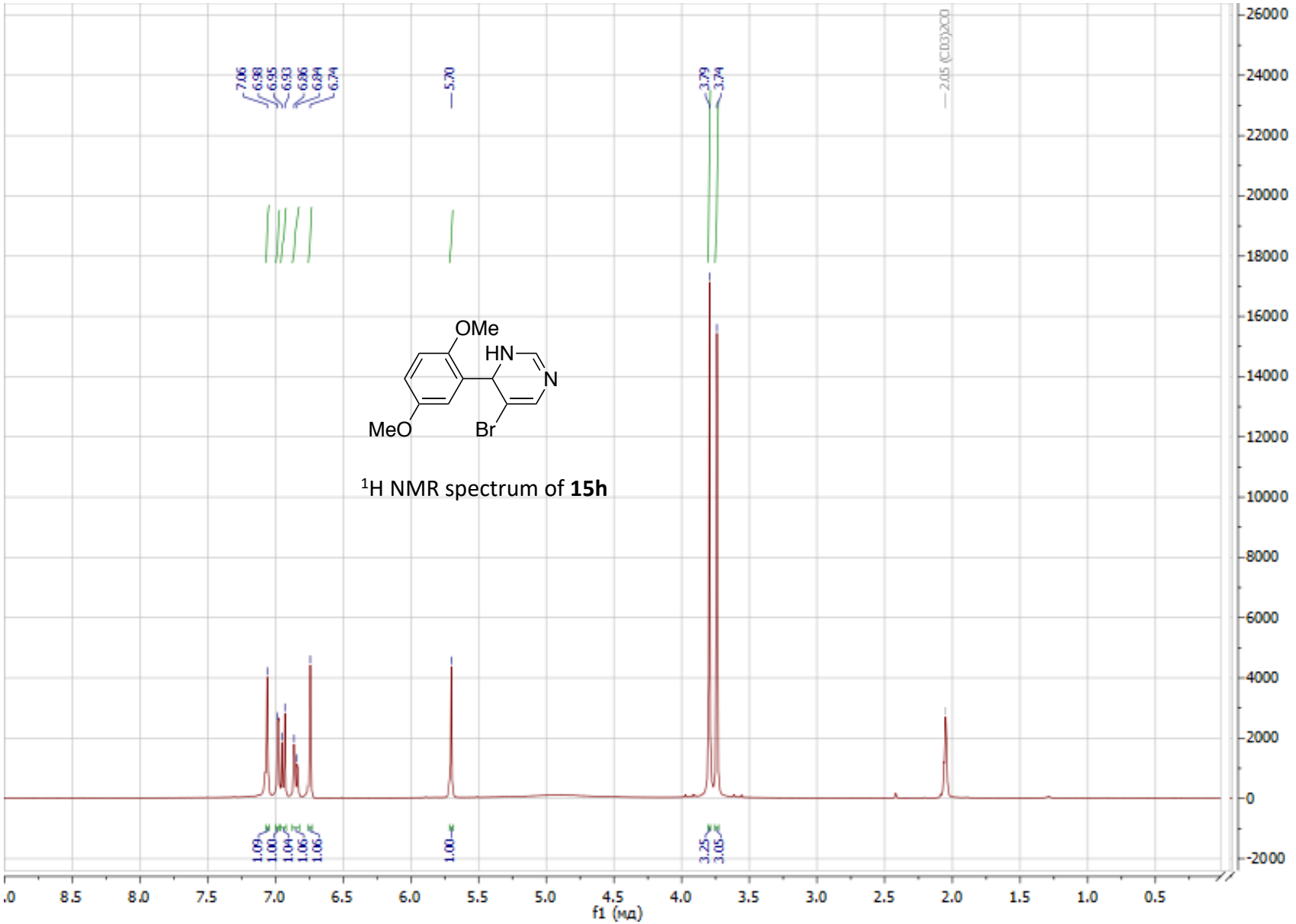

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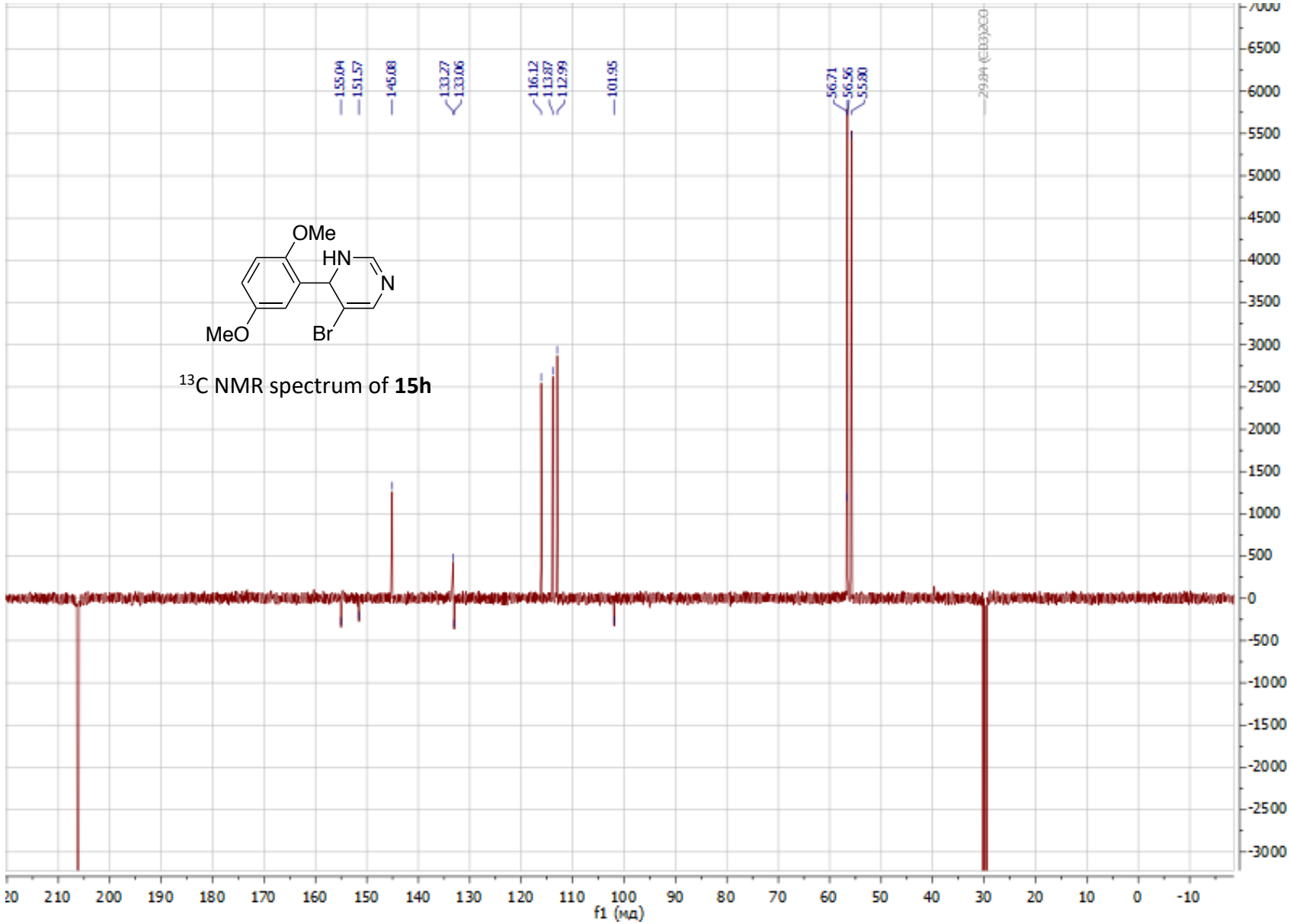

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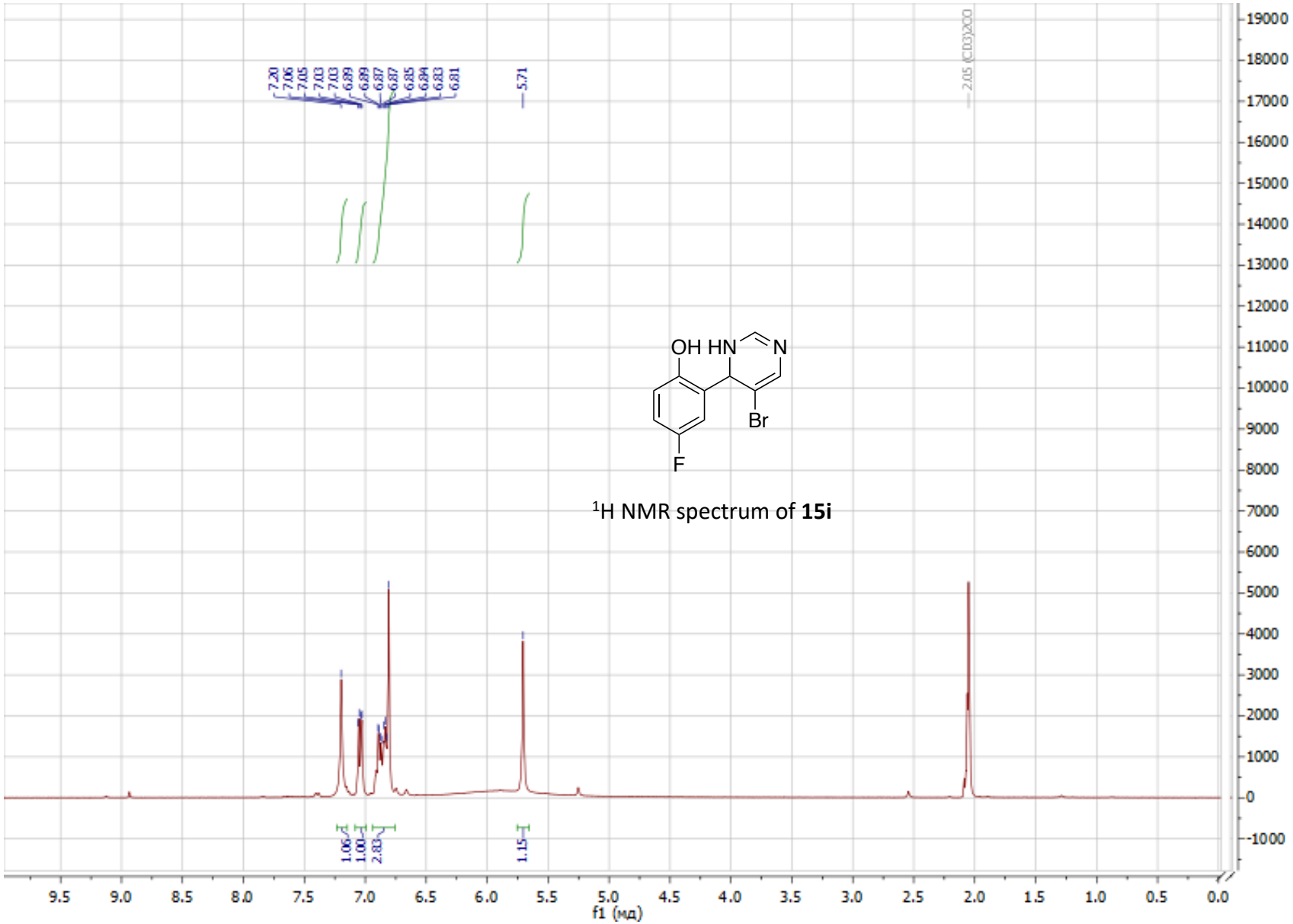

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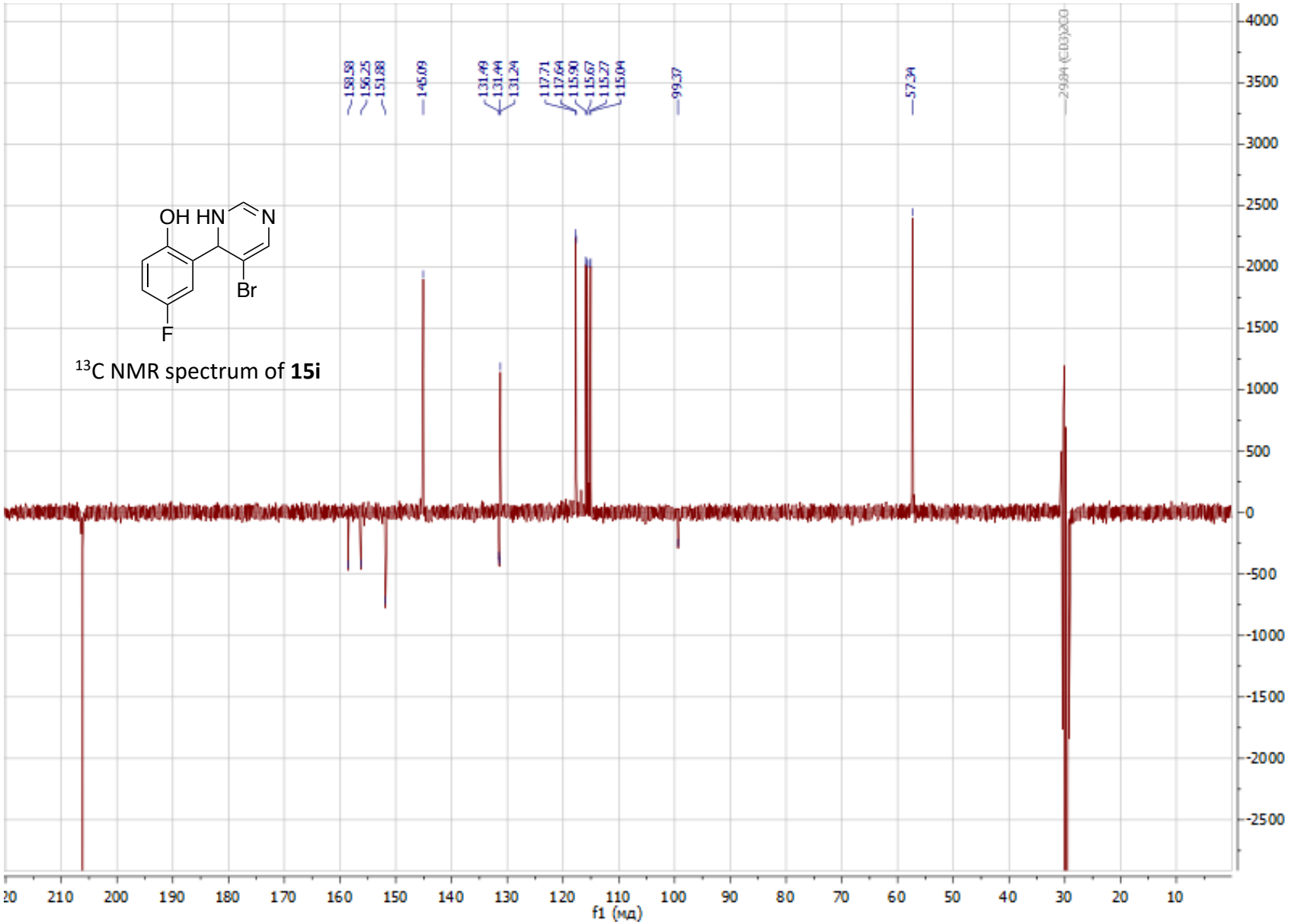

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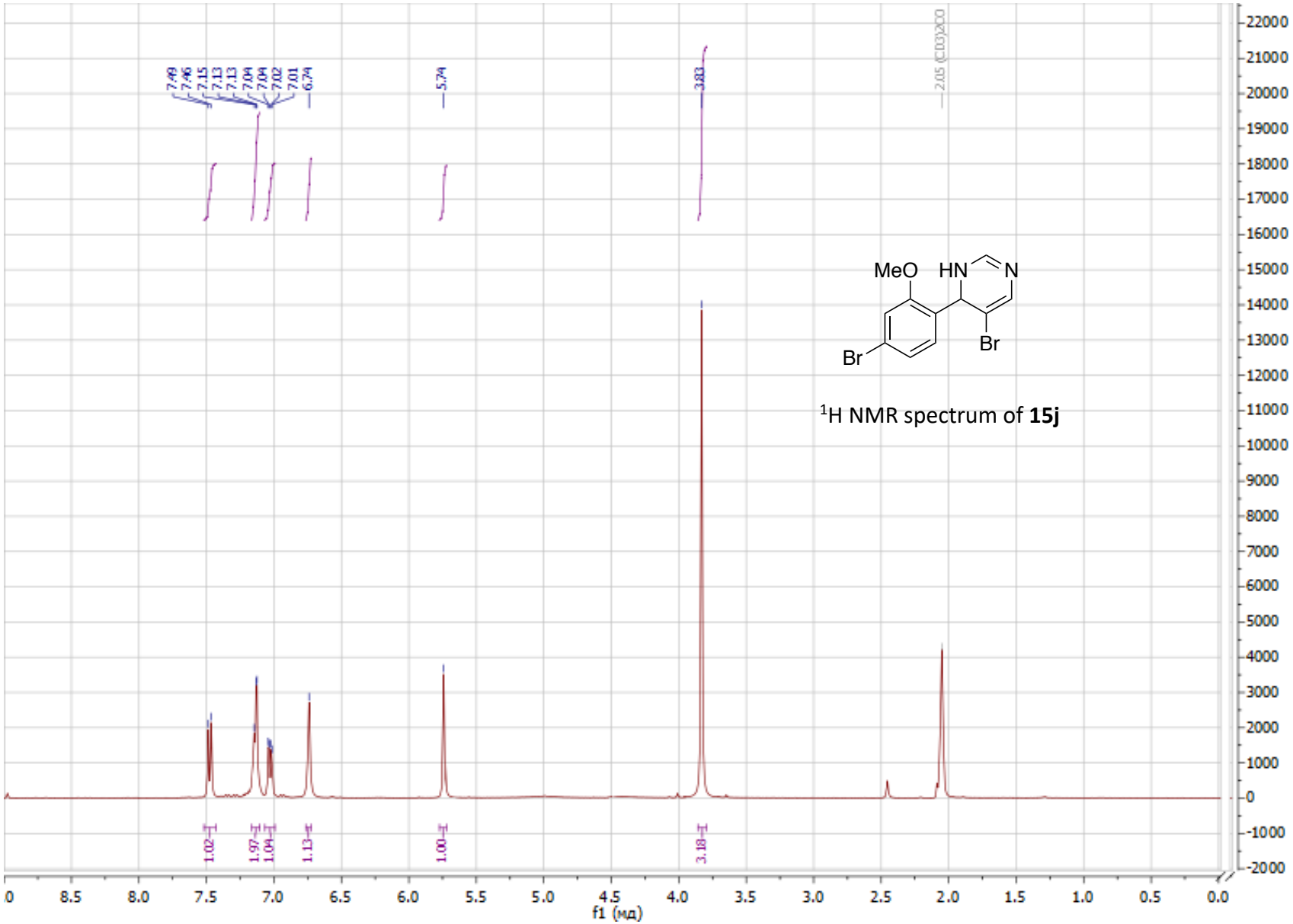

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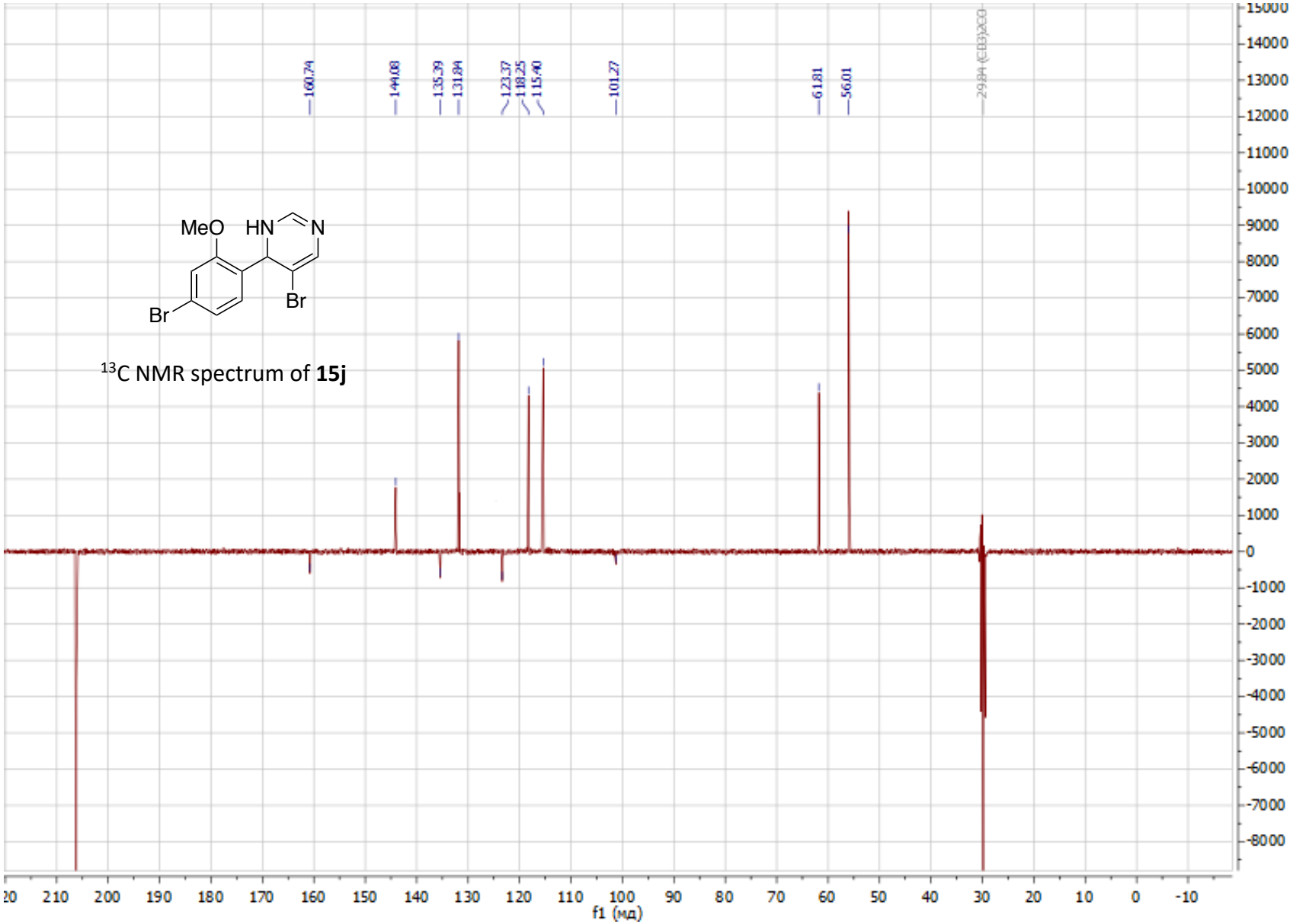

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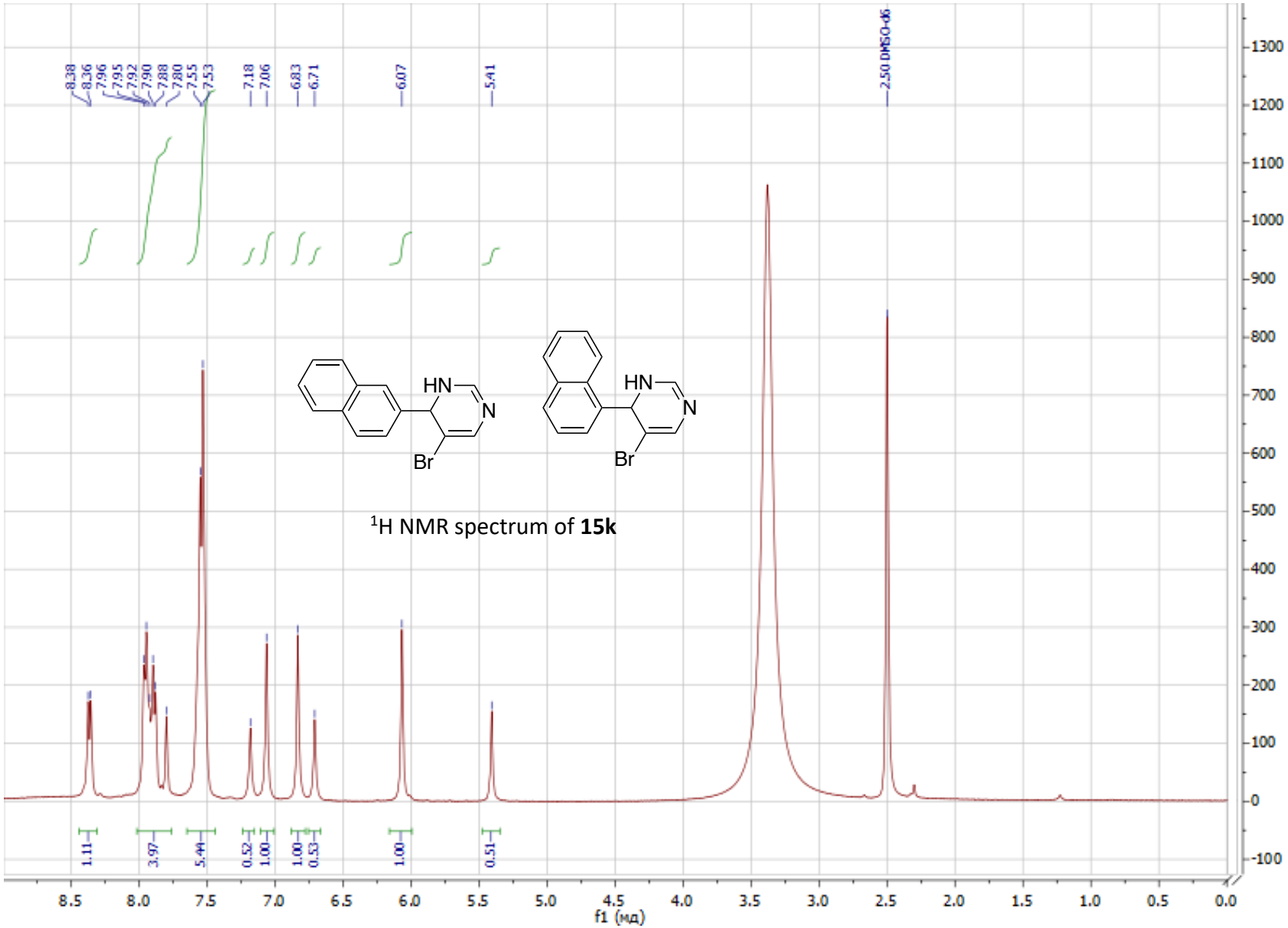

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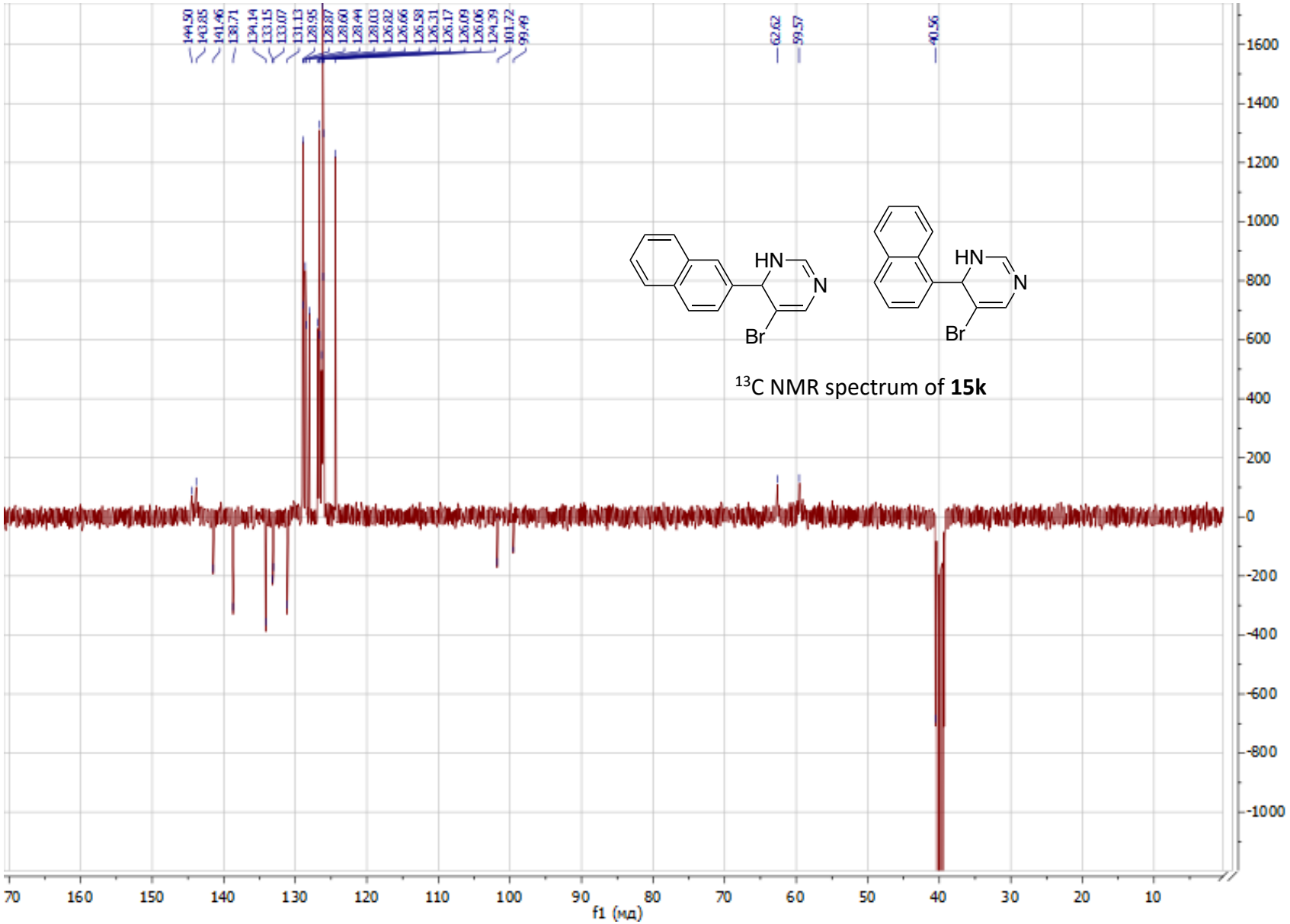

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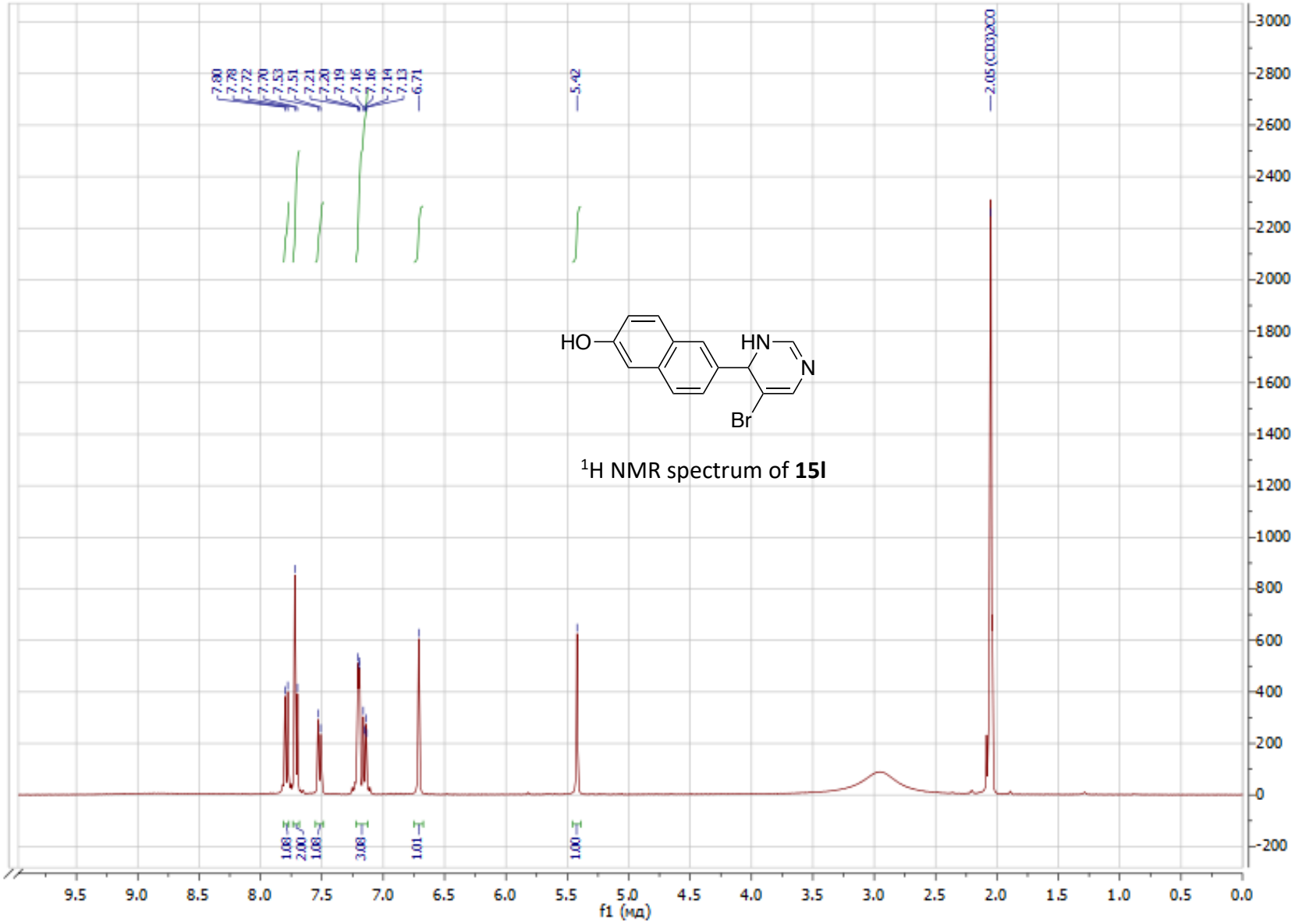

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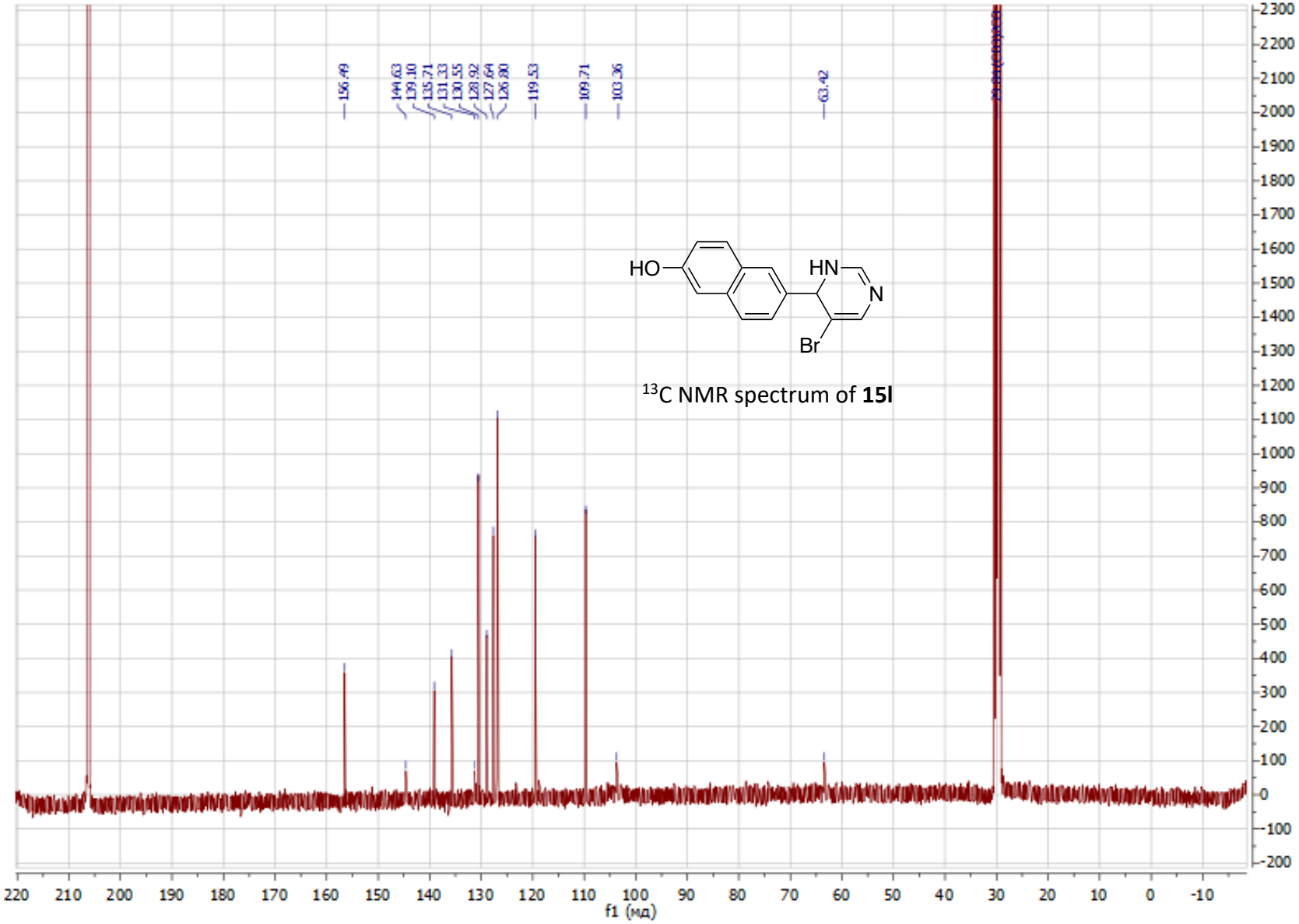

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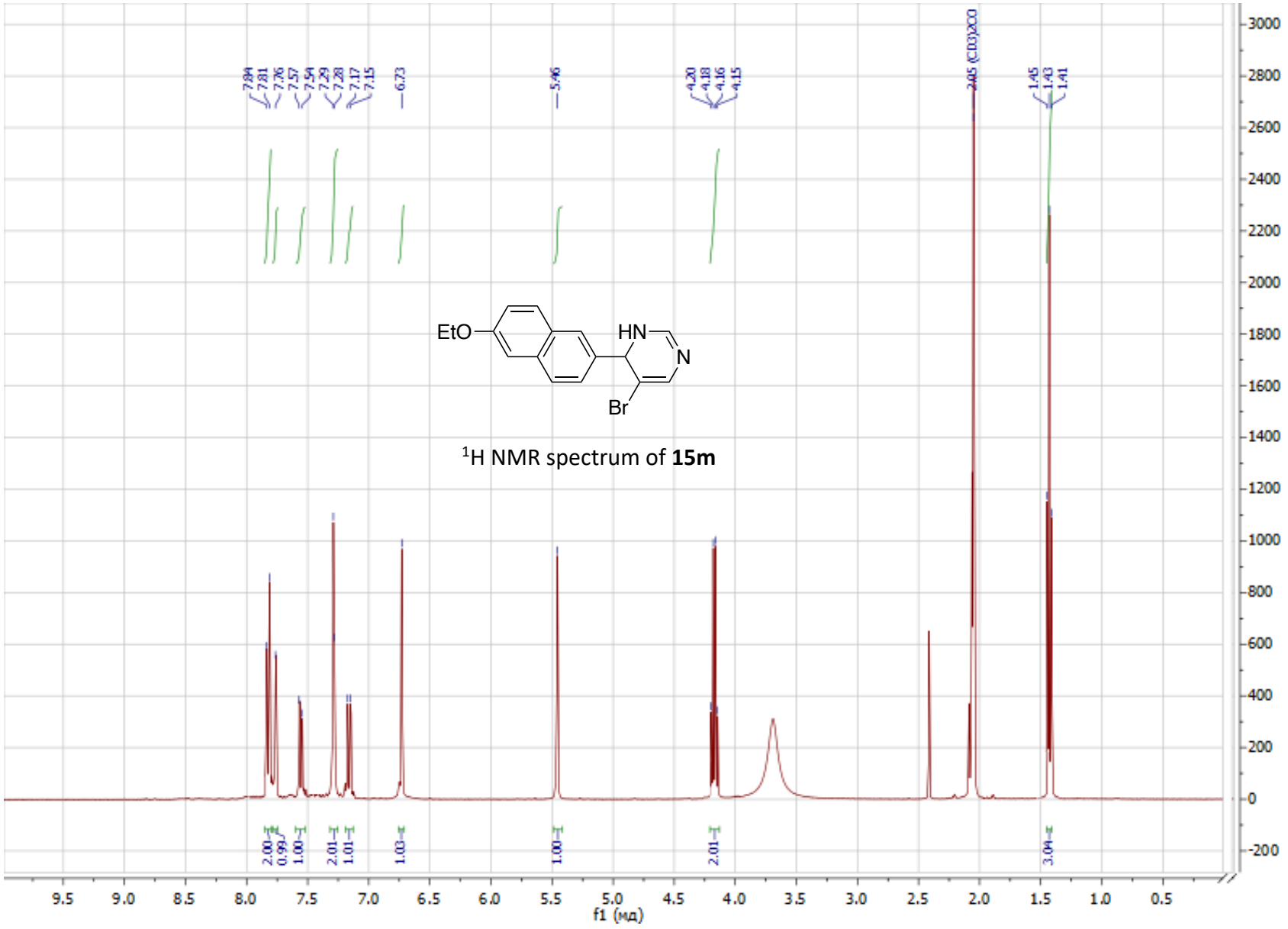

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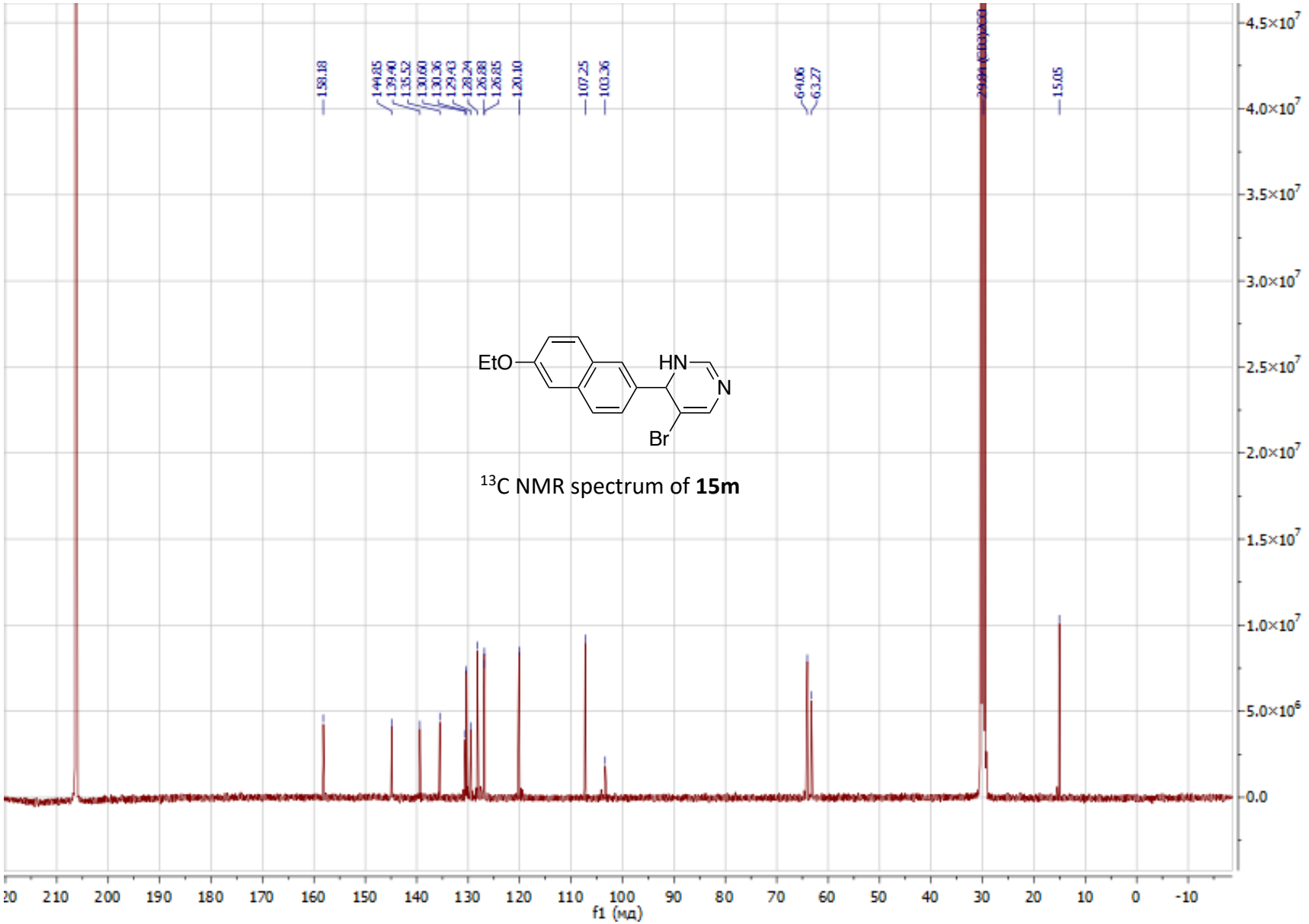
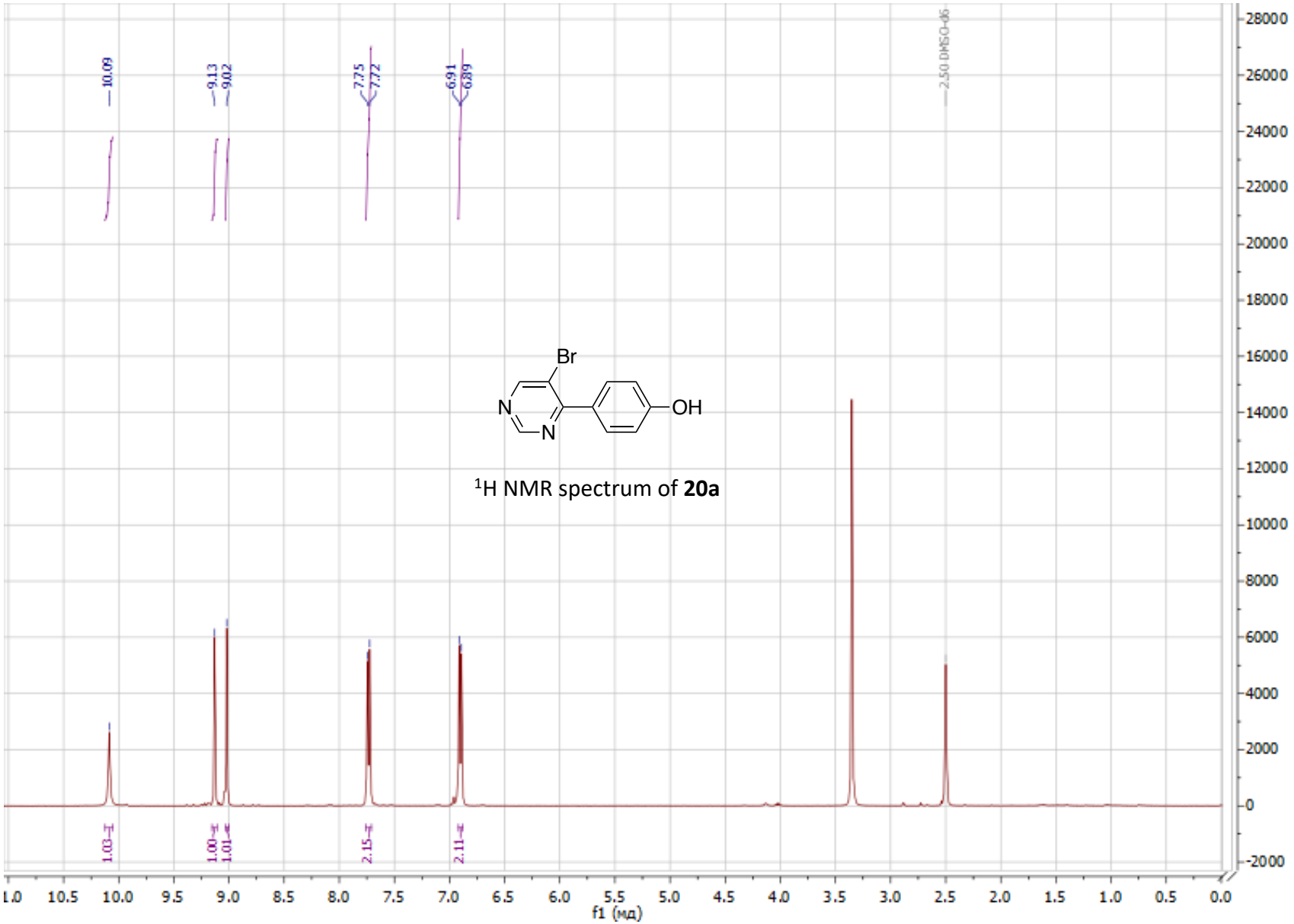


^{13}C NMR spectrum of **15m**



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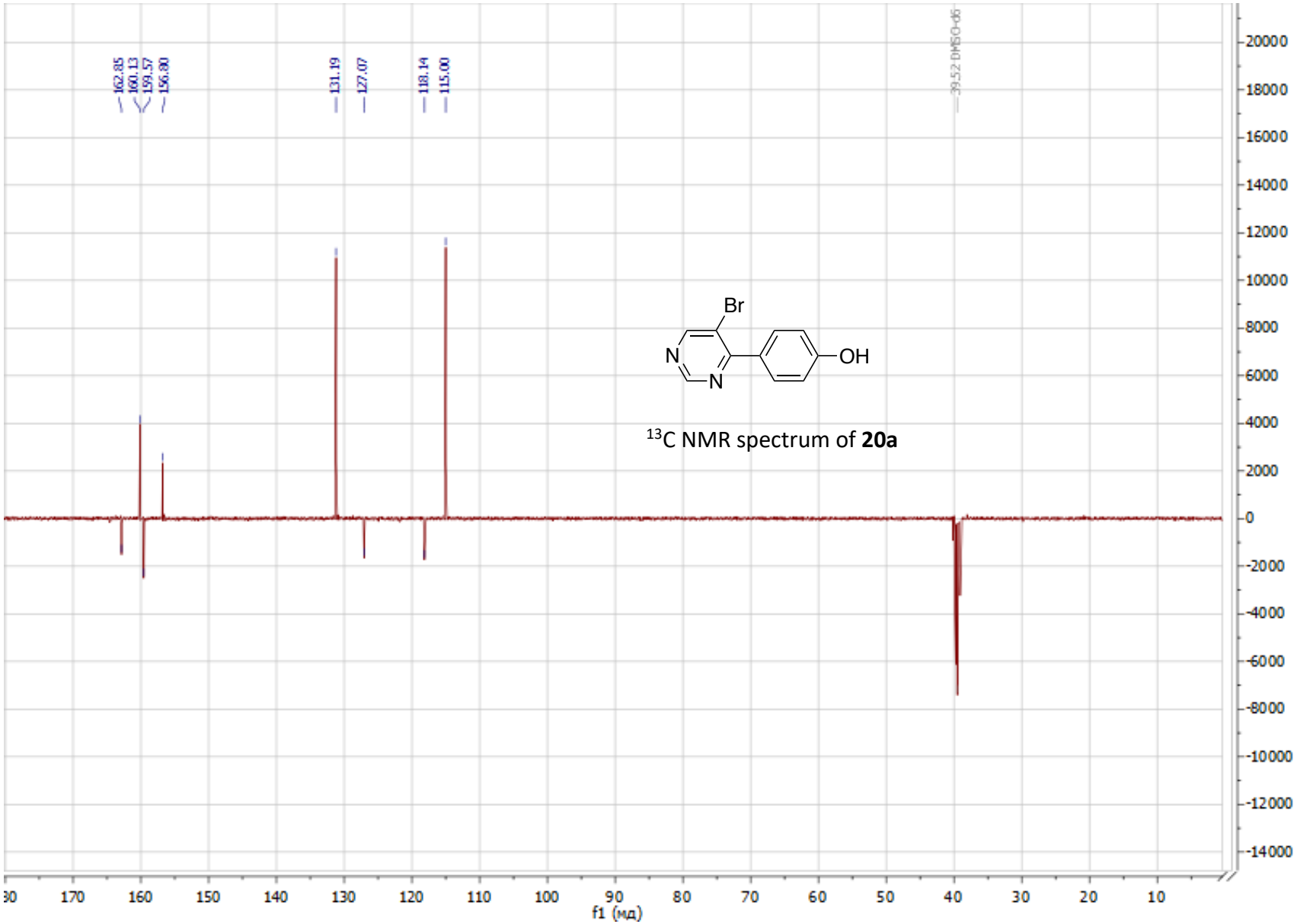
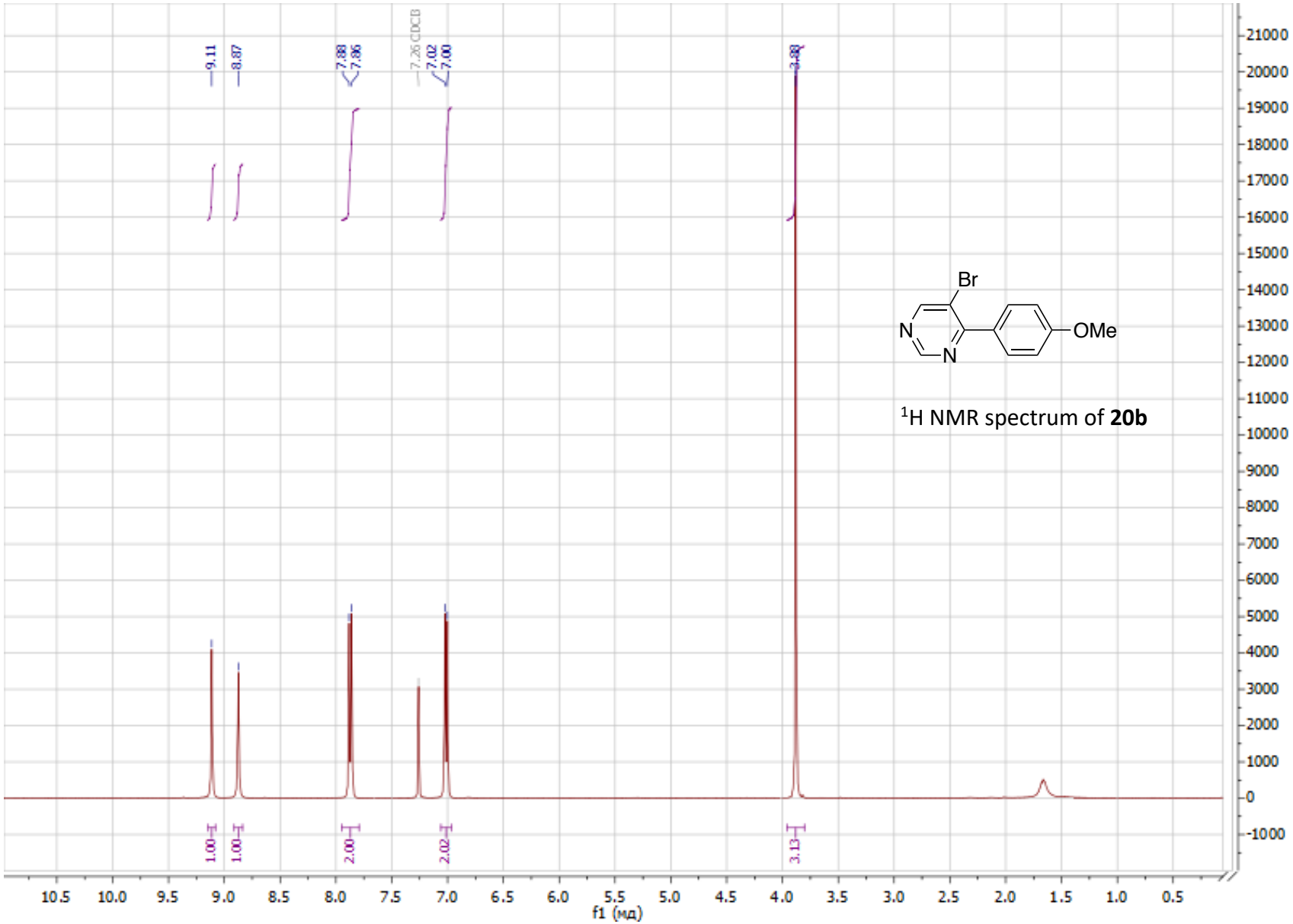


^{13}C NMR spectrum of **20a**



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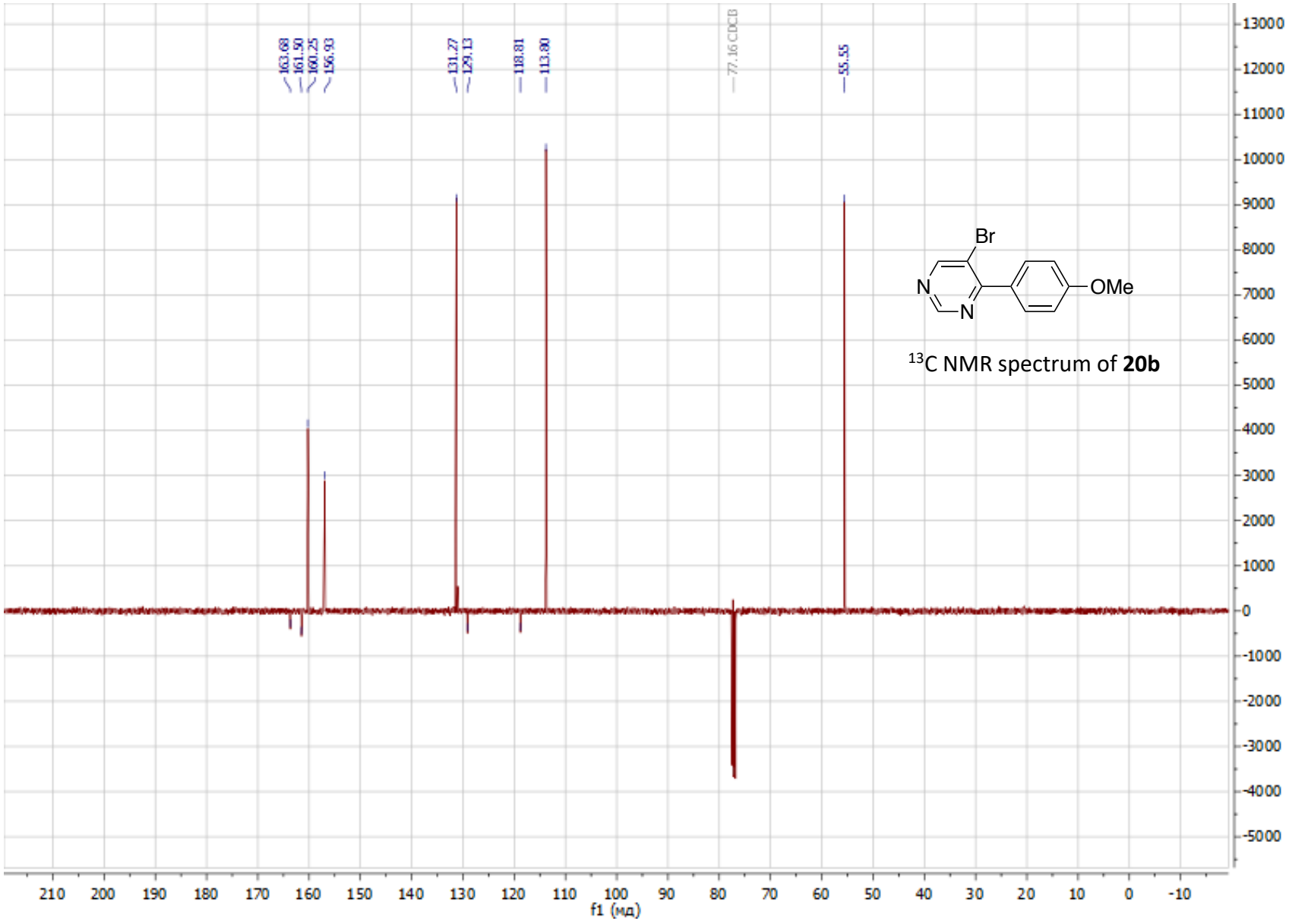

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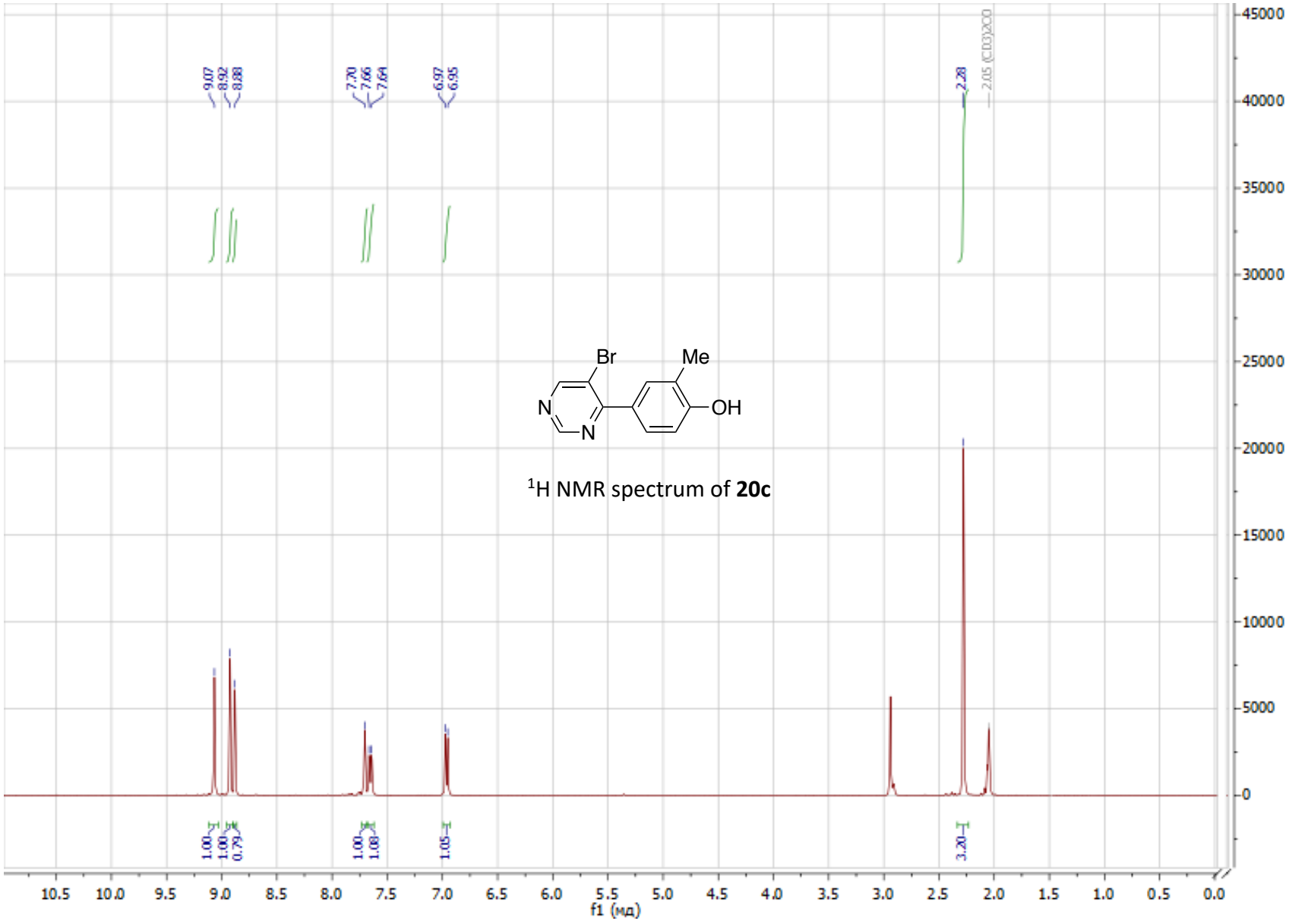

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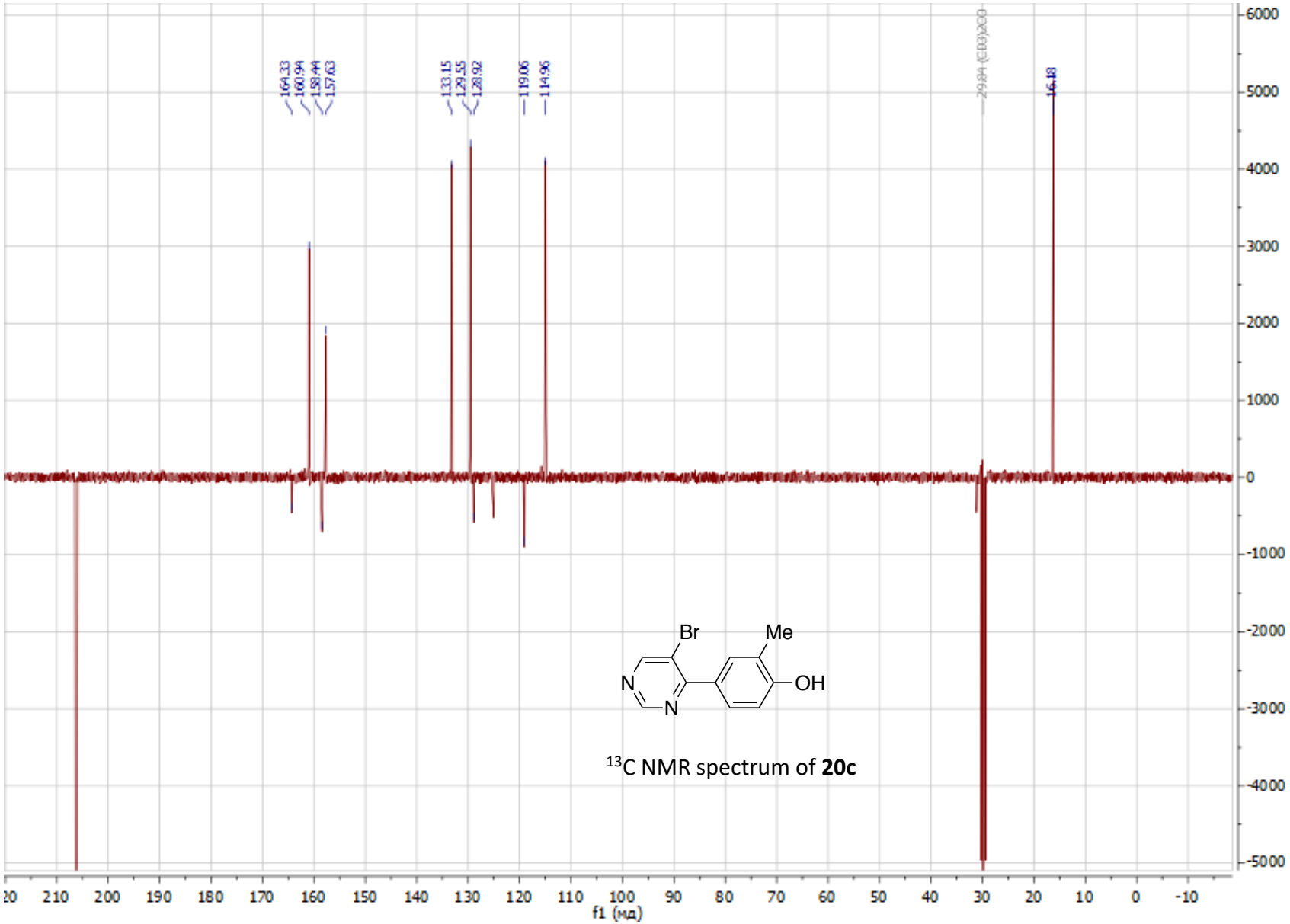

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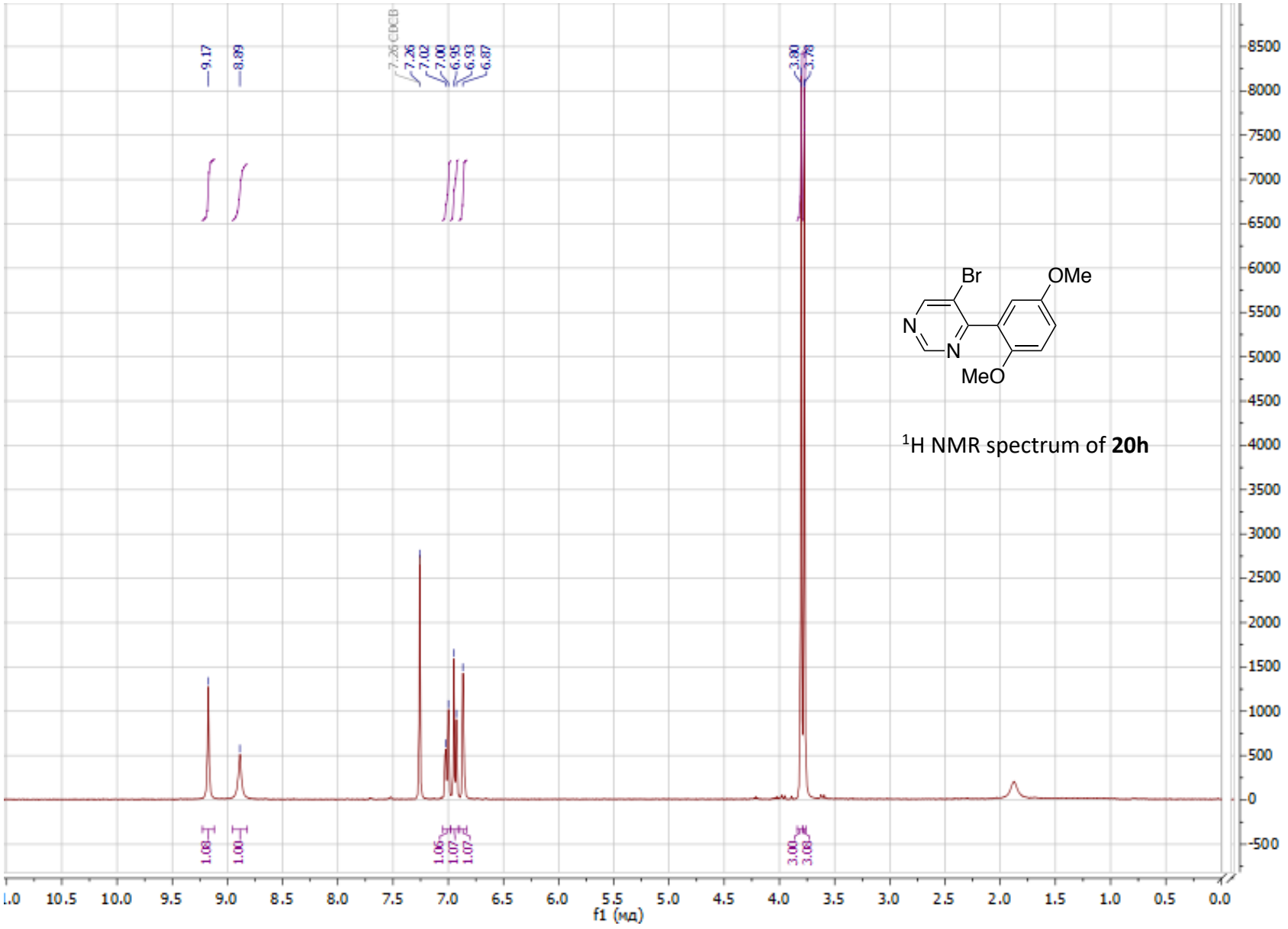

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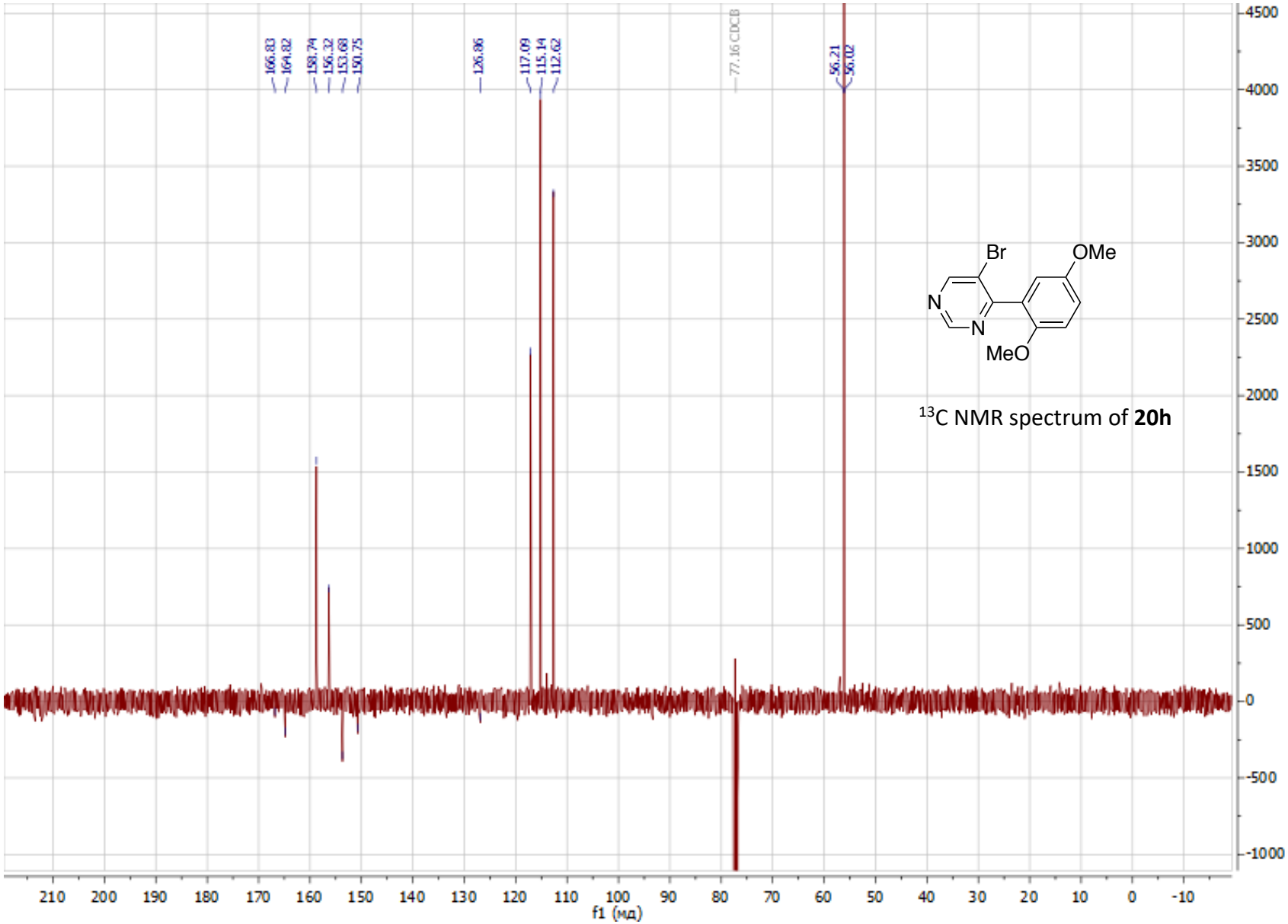

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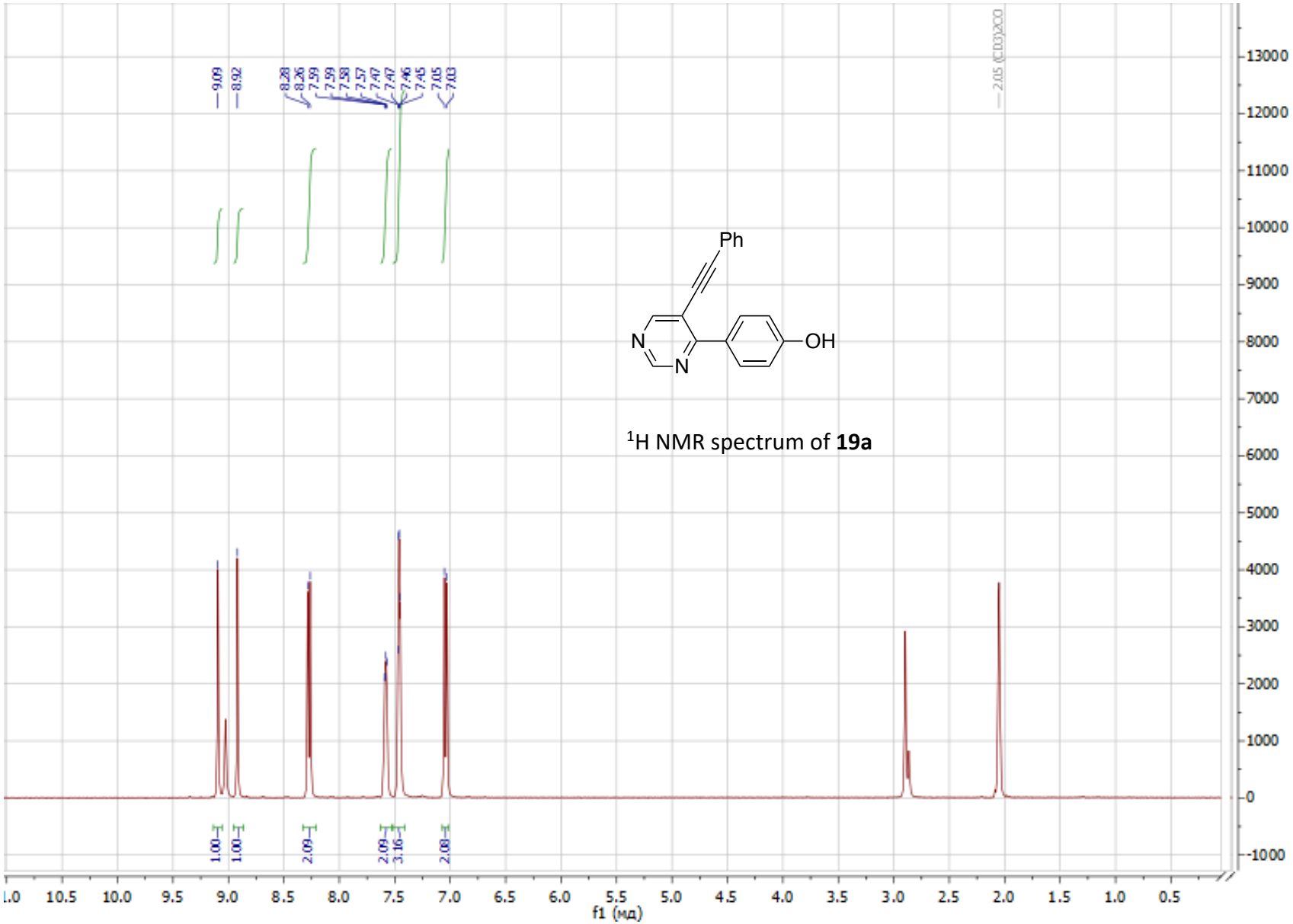

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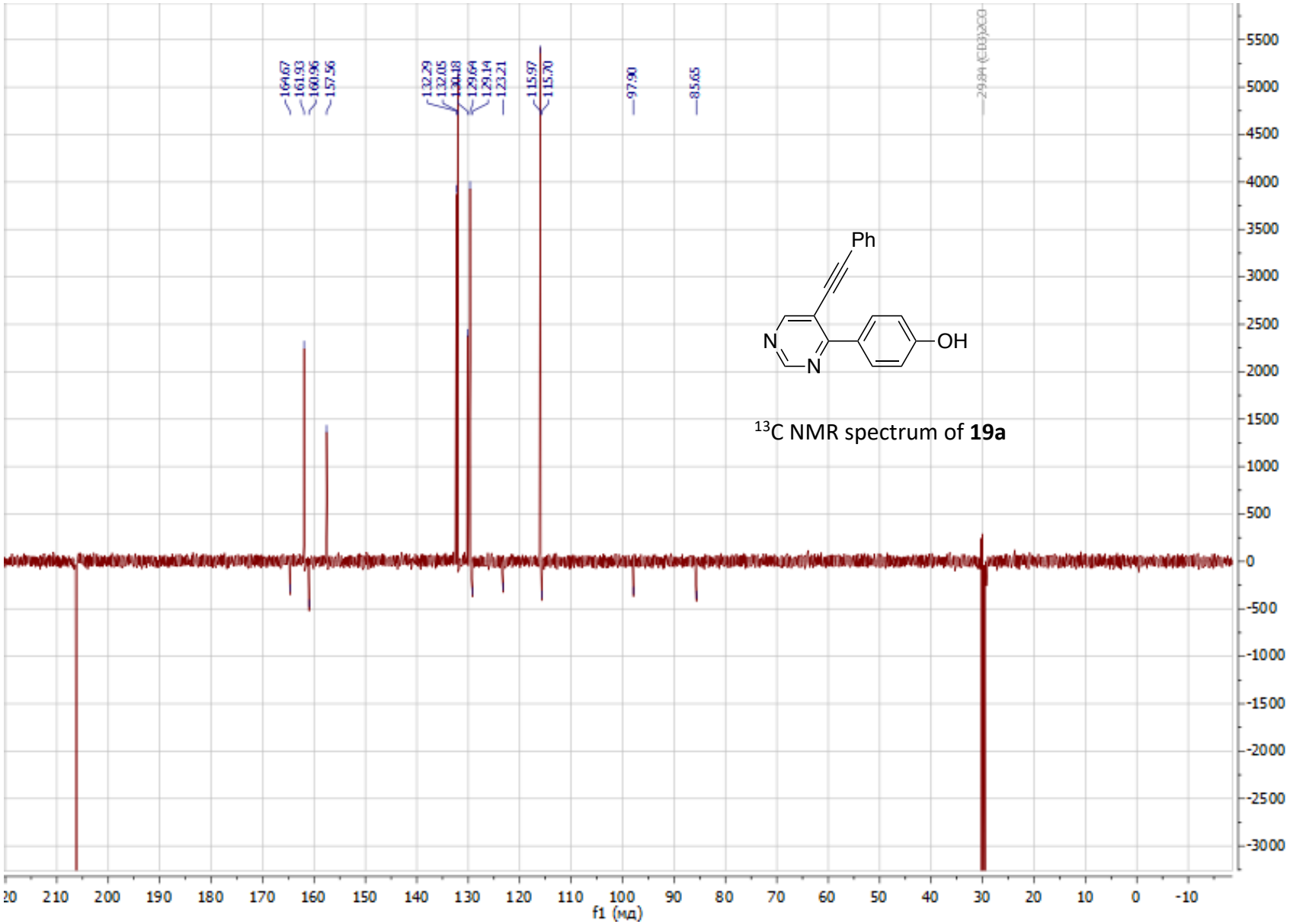

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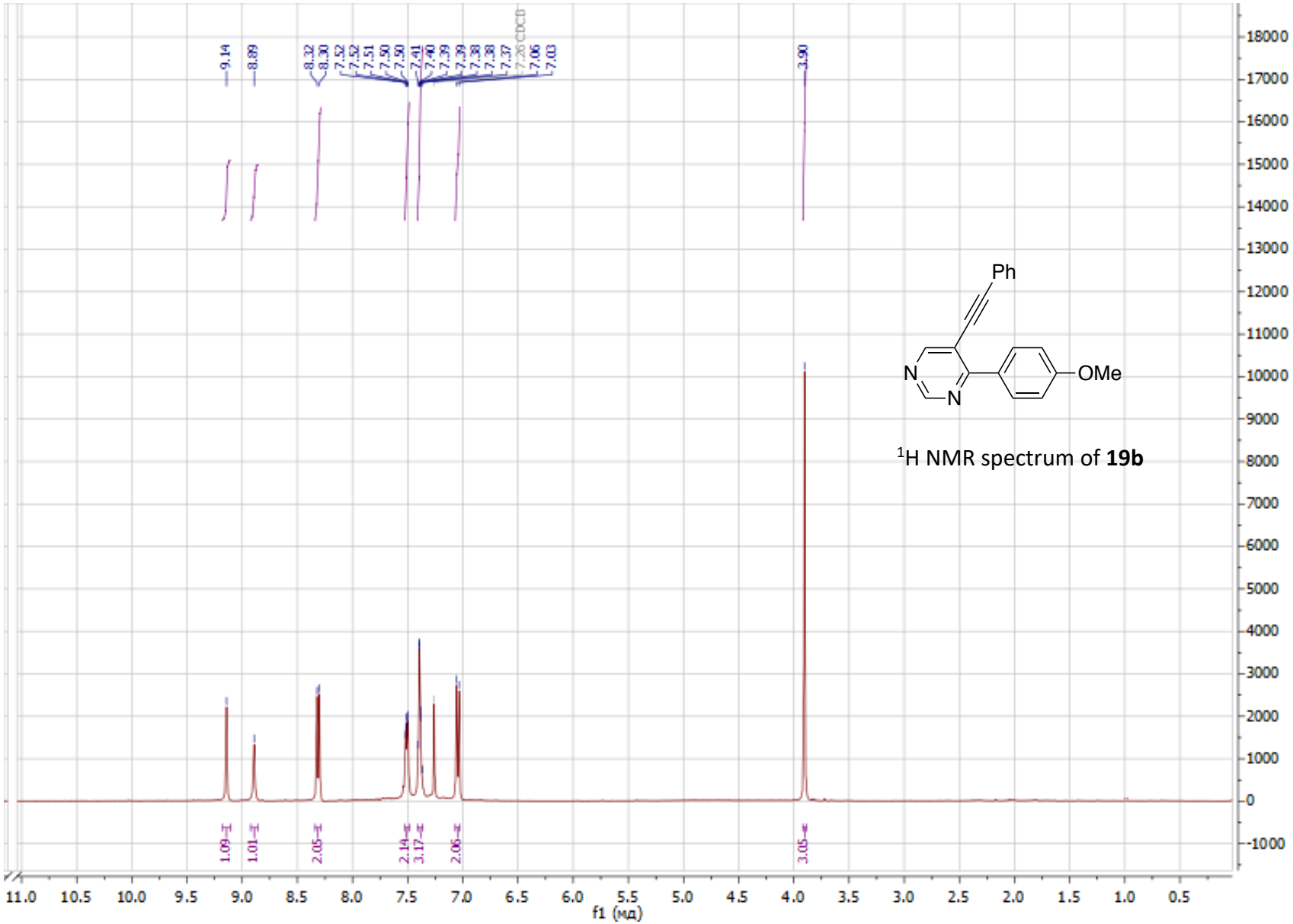

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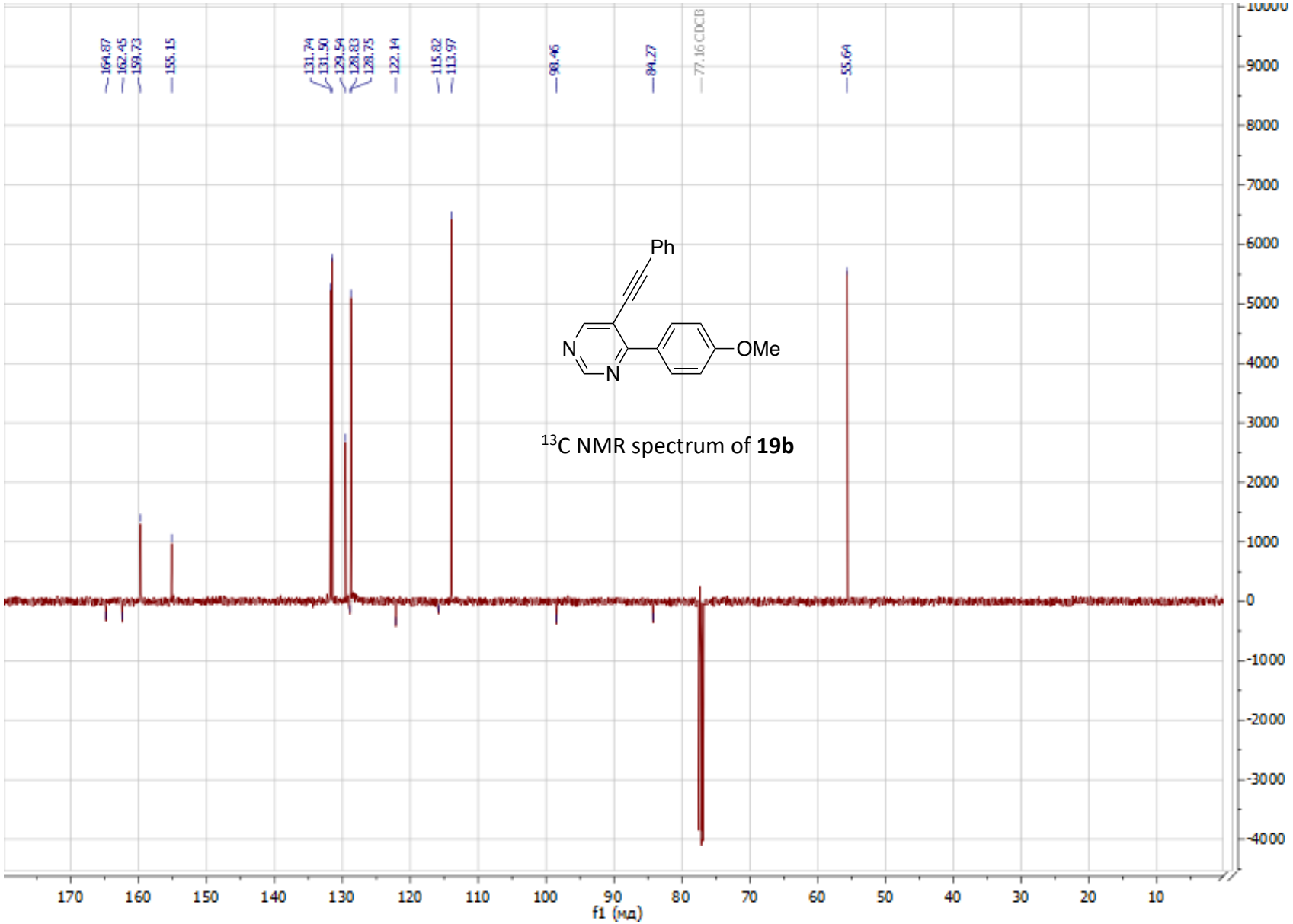

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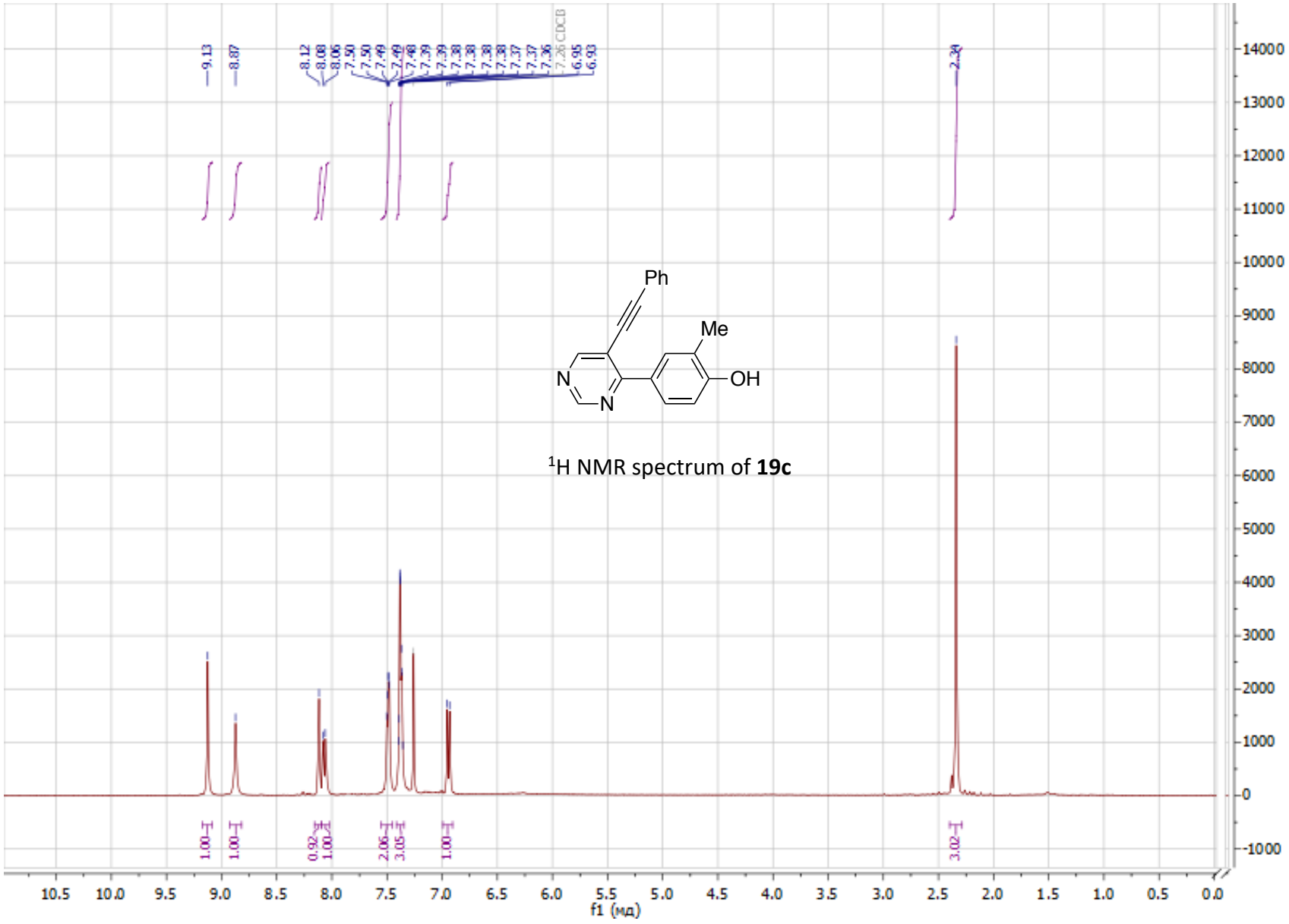

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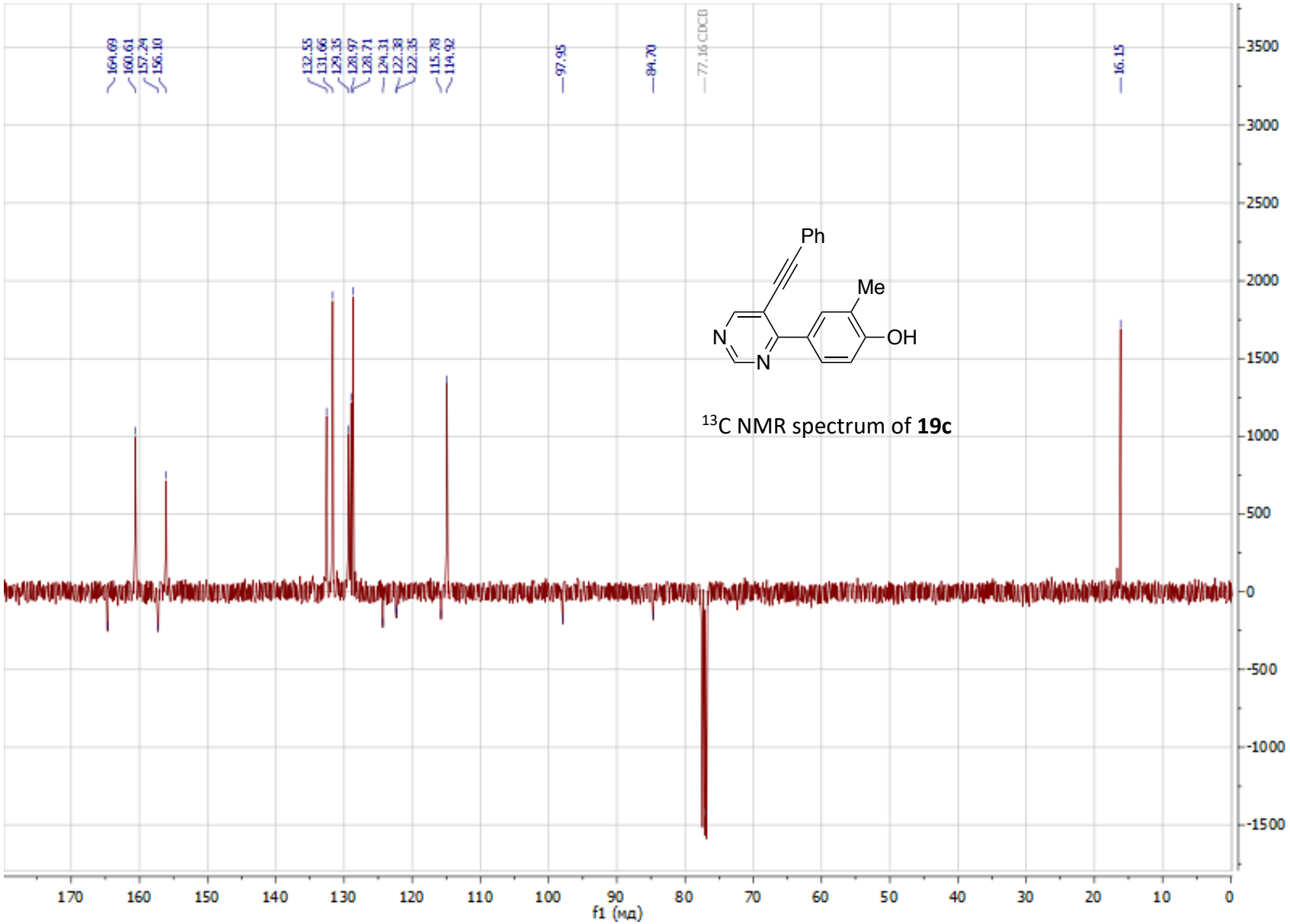

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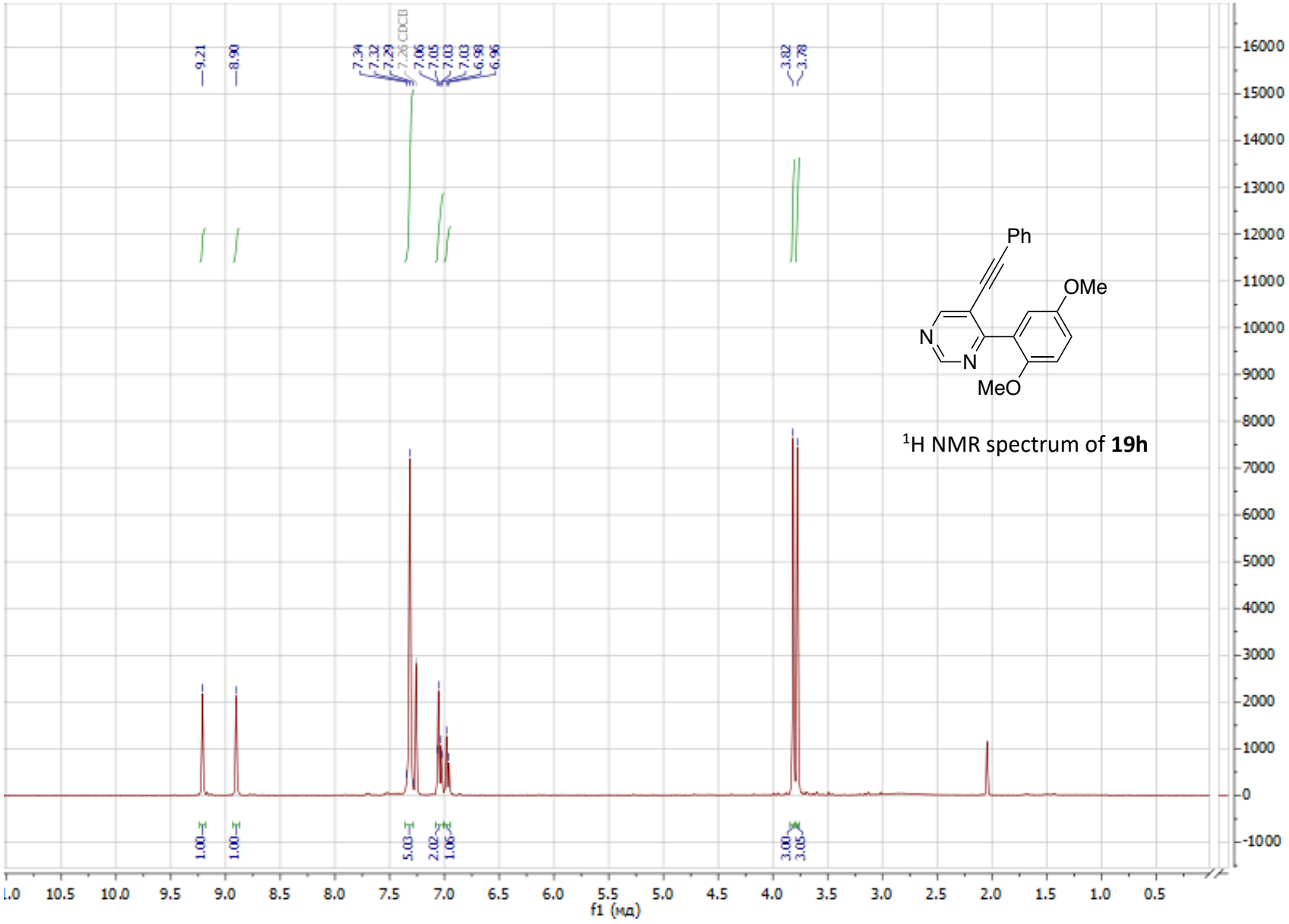

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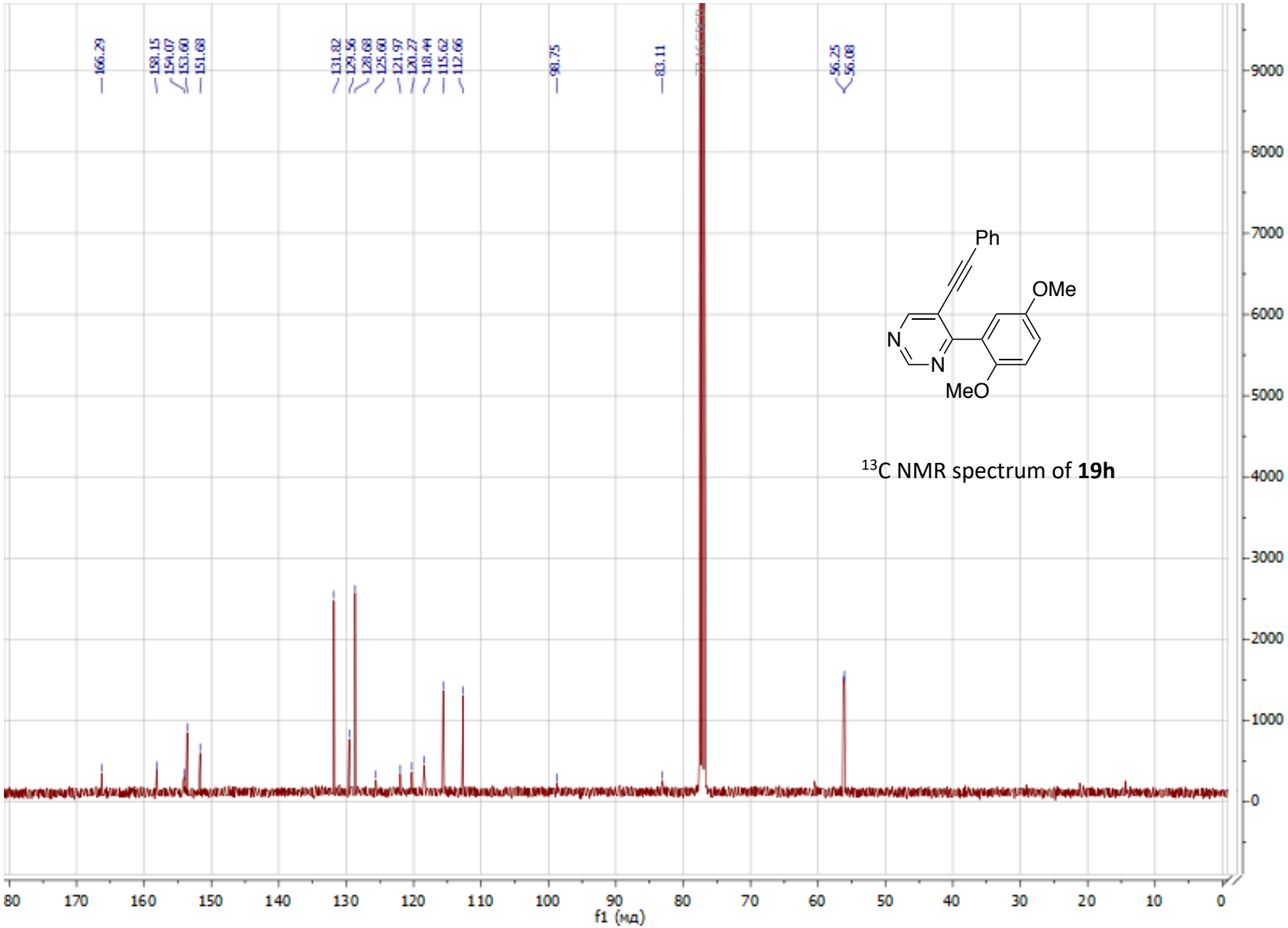
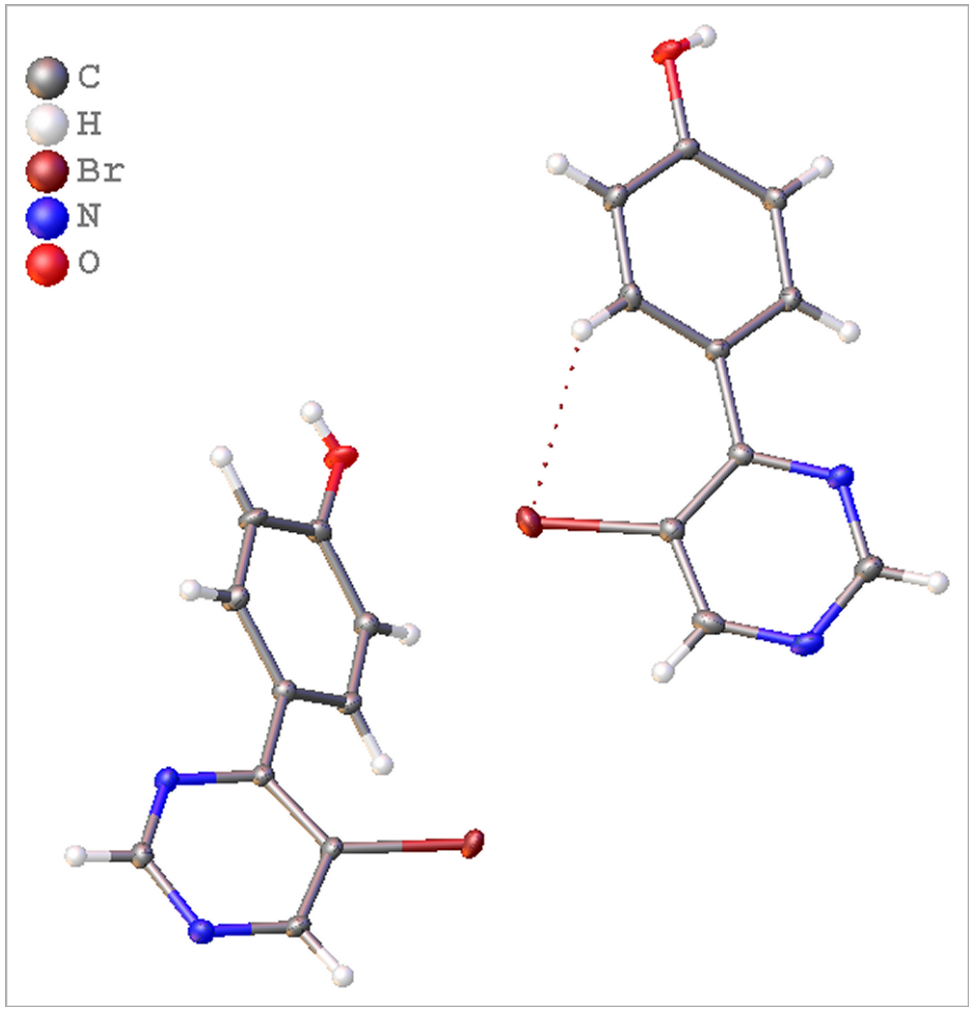


^{13}C NMR spectrum of **19h**

X-Ray Crystallography Data



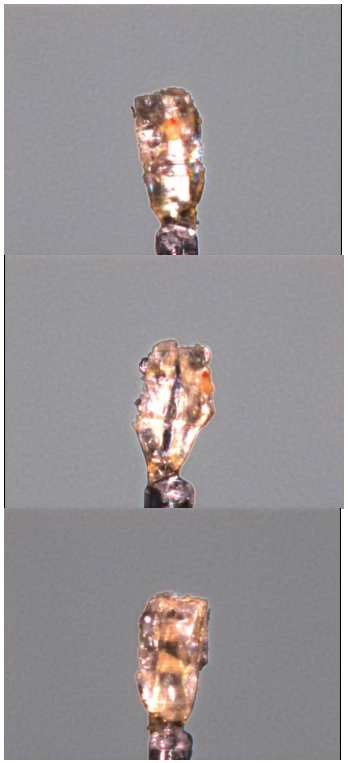


Figure S1. ORTEP drawing of compound **20a** (left, CCDC 1983237) showing 50% thermal ellipsoids. Microphotography of the cry
right.

Table S1. Crystal data and structure refinement for **20a**.

Identification code	ANNA_STAS99604_5
Empirical formula	$C_{10}H_7BrN_2O$
Formula weight	251.09
Temperature/K	100.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0376(2)
b/Å	9.5049(2)
c/Å	11.5608(2)
α/°	77.439(2)
β/°	76.725(2)
γ/°	87.542(2)
Volume/Å^3	943.39(3)
Z	4
ρ_{calc}g/cm^3	1.768
μ/mm^{-1}	5.662
F(000)	496.0
Crystal size/mm^3	0.426 × 0.227 × 0.214
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.044 to 152.36
Index ranges	$-11 \leq h \leq 10$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$
Reflections collected	19731
Independent reflections	3943 [R_{int} = 0.0426, R_{sigma} = 0.0228]
Data/restraints/parameters	3943/0/262
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0762
Final R indexes [all data]	R_1 = 0.0311, wR_2 = 0.0780
Largest diff. peak/hole / e Å^{-3}	0.69/-0.65

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **20a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*
Br2	5699.7(2)	568.0(2)	1734.0(2)
Br1	6859.3(3)	1631.2(3)	4926.8(2)
O1	9701(2)	2857.1(18)	9509.9(16)
O2	8735(2)	5533.8(19)	3597.9(17)
N4	3365(2)	4423(2)	1226.5(17)
N2	9046(2)	-1891(2)	6621.5(18)
N3	2314(2)	2781(2)	332.9(17)
N1	7982(2)	-2583(2)	5122.5(18)
C17	8148(3)	4166(2)	2302(2)
C18	7670(3)	5082(2)	3111(2)
C16	7108(2)	3626(2)	1798.9(19)
C5	8791(2)	399(2)	7179(2)
C12	3356(3)	1817(2)	629(2)
C3	8462(2)	-552(2)	6411.3(19)
C14	4458(2)	3480(2)	1499.2(19)
C11	2357(2)	4031(2)	683(2)
C8	9443(2)	2033(2)	8758.4(19)
C15	5571(2)	3993(2)	2071.7(19)
C13	4430(2)	2113(2)	1228(2)
C4	7619(3)	-207(2)	5502(2)
C6	10063(2)	89(2)	7696(2)
C19	6140(3)	5469(2)	3387(2)
C7	10390(2)	902(2)	8469(2)
C1	7402(3)	-1265(3)	4900(2)
C10	7842(2)	1530(2)	7493(2)
C20	5105(3)	4941(2)	2858(2)
C2	8807(3)	-2819(3)	5974(2)
C9	8154(3)	2329(2)	8278(2)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **20a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br2	17.32(14)	12.65(14)	23.15(15)	-8.12(9)	-9.44(10)	5.77(9)
Br1	28.10(16)	18.58(15)	18.80(15)	-1.47(10)	-12.72(10)	4.85(10)
O1	15.9(8)	19.6(8)	24.3(9)	-14.9(7)	-11.4(7)	6.4(6)
O2	19.5(8)	21.1(9)	26.2(9)	-14.8(7)	-12.5(7)	2.8(7)
N4	14.3(9)	12.3(9)	15.7(9)	-5.1(7)	-5.9(7)	3.0(7)
N2	17.1(9)	14.9(9)	17.5(9)	-7.6(7)	-7.1(7)	2.5(7)
N3	15.9(9)	15.4(9)	15.6(9)	-5.7(7)	-7.7(7)	2.4(7)
N1	17.1(9)	20.8(10)	18.8(9)	-11.5(8)	-6.1(8)	0.5(8)
C17	14.0(10)	14.7(10)	15.4(10)	-4.5(8)	-5.3(8)	2.0(8)
C18	16.4(10)	13.3(10)	15.1(10)	-3.8(8)	-8.1(8)	-0.6(8)
C16	14.5(10)	11.9(10)	11.6(9)	-4.6(8)	-2.4(8)	1.2(8)
C5	13.4(10)	12.6(10)	13.7(10)	-5.0(8)	-5.1(8)	0.4(8)
C12	16.7(10)	12.9(10)	13.8(10)	-6.4(8)	-4.6(8)	2.1(8)
C3	11.3(9)	15.1(10)	12.0(10)	-4.4(8)	-3.2(8)	1.0(8)
C14	13.3(10)	12.1(10)	11.1(9)	-4.4(8)	-3.7(8)	2.5(8)
C11	13.9(10)	12.9(10)	14.8(10)	-3.4(8)	-5.3(8)	2.9(8)
C8	14.1(10)	12.7(10)	13.2(10)	-5.4(8)	-4.1(8)	-0.6(8)
C15	12.1(10)	11.9(10)	12.4(9)	-3.2(8)	-3.6(8)	0.2(8)
C13	13.2(10)	12.3(10)	13.8(10)	-5.5(8)	-4.2(8)	4.1(8)
C4	14.7(10)	15.4(10)	14.2(10)	-4.0(8)	-5.6(8)	1.8(8)
C6	12.9(10)	12.6(10)	14.8(10)	-4.7(8)	-4.3(8)	3.5(8)
C19	20.6(11)	16.6(11)	17.7(11)	-11.3(9)	-6.5(9)	3.3(9)
C7	13.3(10)	16.9(11)	16.4(10)	-5.9(8)	-7.9(8)	3.7(8)
C1	15.9(10)	23.8(12)	13.8(10)	-6.1(9)	-5.3(8)	-0.9(9)
C10	13.6(10)	13.2(10)	20.1(11)	-4.2(8)	-8.9(8)	2.9(8)
C20	13.6(10)	16.4(11)	18.5(11)	-8.0(9)	-5.5(8)	2.9(8)
C2	19.4(11)	16.4(11)	20.9(11)	-9.4(9)	-7.0(9)	3.7(9)
C9	14.5(10)	12.6(10)	20.5(11)	-7.0(8)	-6.7(9)	3.3(8)

Table S4. Bond Lengths for **20a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br2	C13	1.899(2)	C16	C15	1.398(3)
Br1	C4	1.889(2)	C5	C3	1.479(3)
O1	C8	1.352(3)	C5	C6	1.406(3)
O2	C18	1.348(3)	C5	C10	1.403(3)
N4	C14	1.350(3)	C12	C13	1.385(3)
N4	C11	1.325(3)	C3	C4	1.410(3)
N2	C3	1.351(3)	C14	C15	1.475(3)
N2	C2	1.327(3)	C14	C13	1.403(3)
N3	C12	1.335(3)	C8	C7	1.395(3)
N3	C11	1.341(3)	C8	C9	1.395(3)
N1	C1	1.332(3)	C15	C20	1.402(3)
N1	C2	1.343(3)	C4	C1	1.385(3)
C17	C18	1.399(3)	C6	C7	1.387(3)
C17	C16	1.381(3)	C19	C20	1.392(3)
C18	C19	1.397(3)	C10	C9	1.385(3)

Table S5. Hydrogen Bonds for **20a**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	N31	0.75(4)	2.03(4)	2.734(3)	159(4)
O2	H2	N12	0.74(4)	2.02(4)	2.737(3)	166(4)

Table S6. Bond Angles for **20a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	N4	C14	118.59(19)	O1	C8	C7	122.8(2)
C2	N2	C3	119.2(2)	O1	C8	C9	117.6(2)
C12	N3	C11	115.44(19)	C9	C8	C7	119.6(2)
C1	N1	C2	115.2(2)	C16	C15	C14	121.81(19)
C16	C17	C18	120.1(2)	C16	C15	C20	118.5(2)
O2	C18	C17	117.0(2)	C20	C15	C14	119.58(19)
O2	C18	C19	123.4(2)	C12	C13	Br2	116.76(16)
C19	C18	C17	119.6(2)	C12	C13	C14	119.3(2)
C17	C16	C15	121.1(2)	C14	C13	Br2	123.80(16)
C6	C5	C3	118.22(19)	C3	C4	Br1	125.92(17)
C10	C5	C3	123.59(19)	C1	C4	Br1	115.44(17)
C10	C5	C6	118.0(2)	C1	C4	C3	118.5(2)
N3	C12	C13	121.8(2)	C7	C6	C5	120.9(2)
N2	C3	C5	115.09(19)	C20	C19	C18	119.9(2)
N2	C3	C4	117.8(2)	C6	C7	C8	120.2(2)
C4	C3	C5	127.1(2)	N1	C1	C4	123.0(2)
N4	C14	C15	116.05(19)	C9	C10	C5	121.2(2)
N4	C14	C13	117.9(2)	C19	C20	C15	120.7(2)
C13	C14	C15	126.08(19)	N2	C2	N1	126.3(2)
N4	C11	N3	126.8(2)	C10	C9	C8	120.1(2)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **20a**

Atom	*x*	*y*	*z*	U(eq)
H17	9168.24	3919.87	2102.57	17
H16	7435.11	3008.82	1269.59	15
H12	3361.83	920.73	427.42	17
H11	1600.66	4692.86	528.34	16
H6	10694	-670.49	7517.54	16
H19	5814.6	6078.53	3923.6	20
H7	11243.32	691.53	8796.24	17
H1A	6825.48	-1045.76	4314.34	21
H10	6989.12	1746.29	7166.98	18
H20	4093.46	5220.57	3028.94	18
H2A	9255.35	-3719.39	6124.49	21
H9	7502.85	3064.09	8486.13	18
H1	10470(40)	2690(40)	9630(30)	33(10)
H2	8390(40)	6030(40)	4000(40)	34(10)

Experimental

Single crystals of $C_{10}H_7BrN_2O$ (**20a**) were re-crystallized from benzene/hexane mixture. A suitable crystal was selected and mounted on the glass stick with acrylic glue. The diffraction spectrum was registered on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2,[S1] the structure was solved with the ShelXT [S2] structure solution program using Intrinsic Phasing and refined with the ShelXL [S3] refinement package using Least Squares minimization.

Crystal structure determination of 20a

Crystal Data for $C_{10}H_7BrN_2O$ (M =251.09 g/mol): triclinic, space group P-1 (no. 2), a = 9.0376(2) Å, b = 9.5049(2) Å, c = 11.5608(2) Å, α = 77.439(2)°, β = 76.725(2)°, γ = 87.542(2)°, V = 943.39(3) Å^3, Z = 4, T = 100.0(2) K, μ(CuKα) = 5.662 mm^{-1}, *Dcalc* = 1.768 g/cm^3, 19731 reflections measured (8.044° ≤ 2Θ ≤ 152.36°), 3943 unique (R_{int} = 0.0426, R_{sigma} = 0.0228) which were used in all calculations. The final R_1 was 0.0295 (I > 2σ(I)) and wR_2 was 0.0780 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C17(H17), C16(H16), C12(H12), C11(H11), C6(H6), C19(H19), C7(H7), C1(H1A),
 C10(H10), C20(H20), C2(H2A), C9(H9)
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(S1) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. *J. Appl. Cryst*. **2009**, *42*, 339-341.

(S2) Sheldrick, G.M. *Acta Cryst*. **2015**, *A71*, 3-8.

(S3) Sheldrick, G.M. *Acta Cryst*. **2015**, *C71*, 3-8.