Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Divergent reactivity in the syntheses of indolizines and pyrazolo[1,5-a]pyridines via [3+2]-annulation of pyridinium ylides with 1-chloro-2-nitrostyrenes

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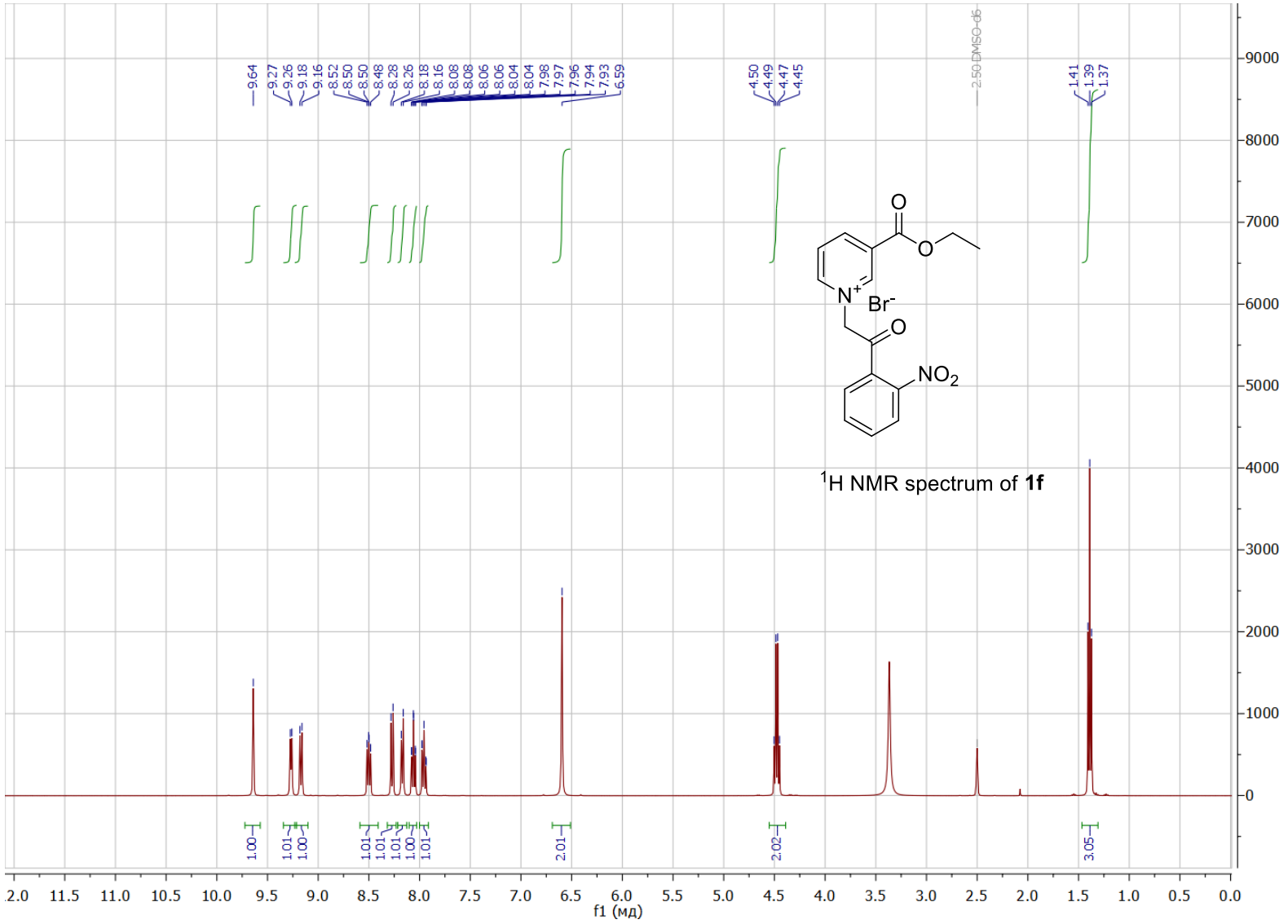
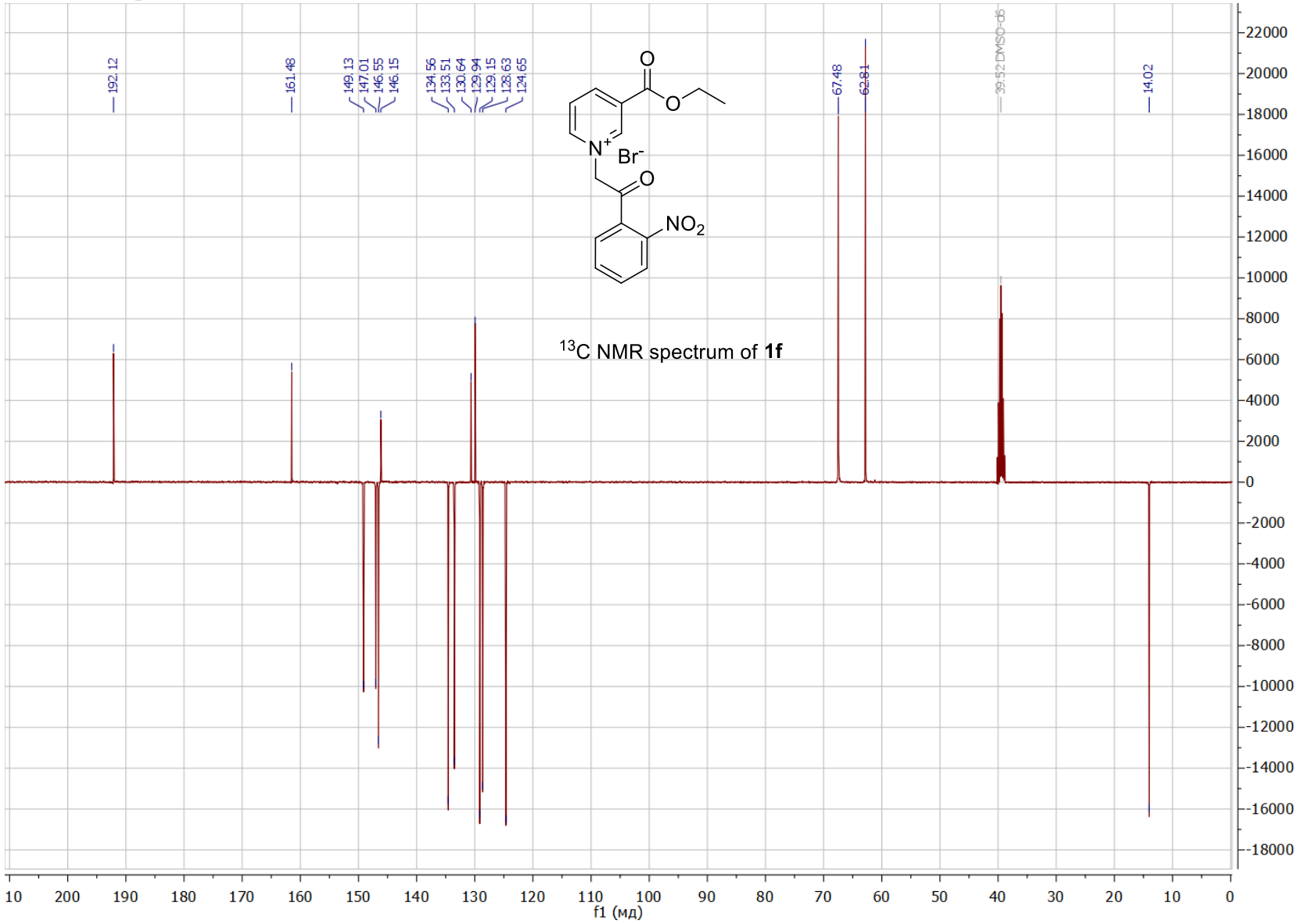
Supporting Information

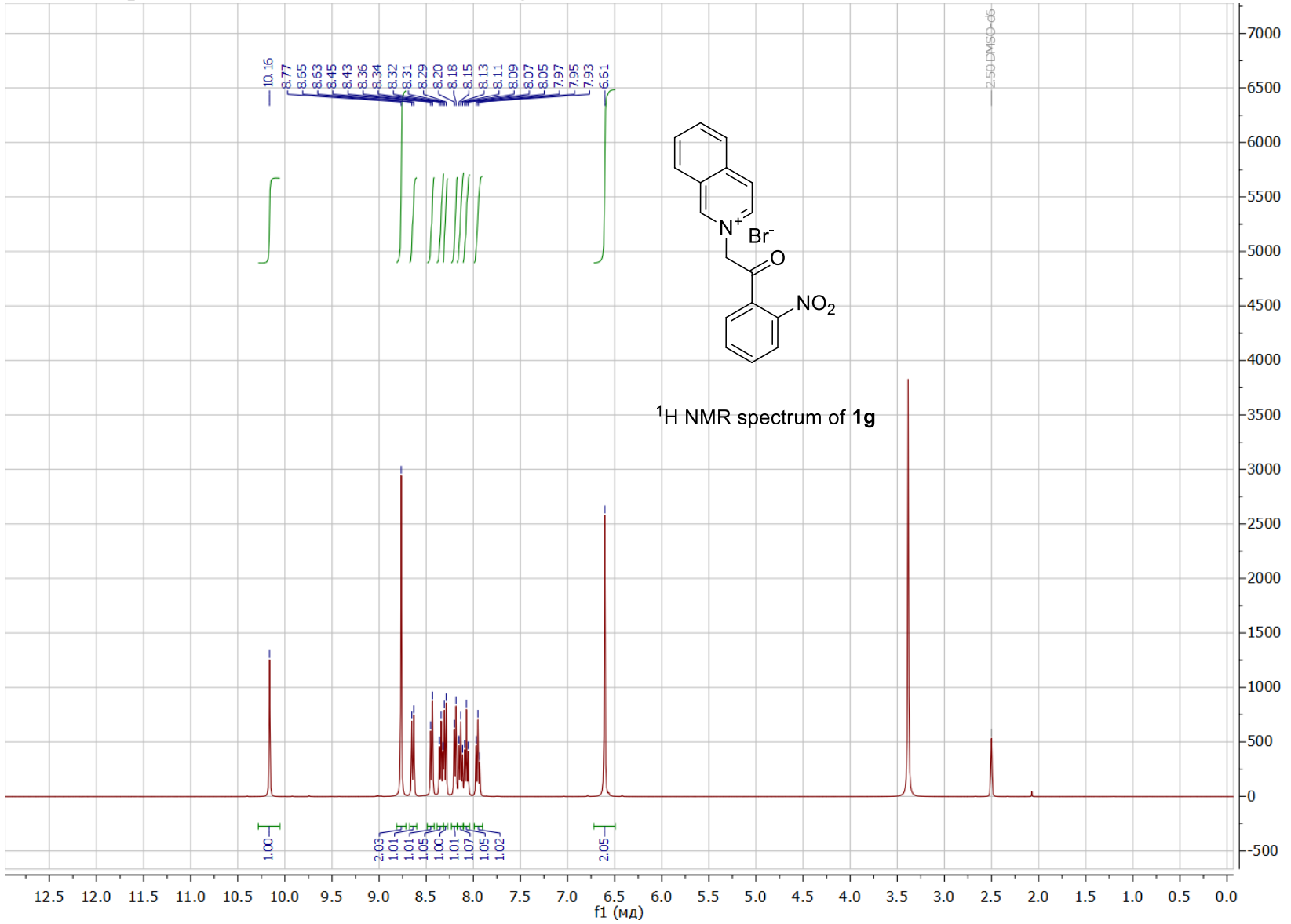
^{1}H and ^{13}C NMR spectral charts for quaternary pyridinium salts. ^{1}H NMR spectrum (400 MHz, DMSO) of **1f**



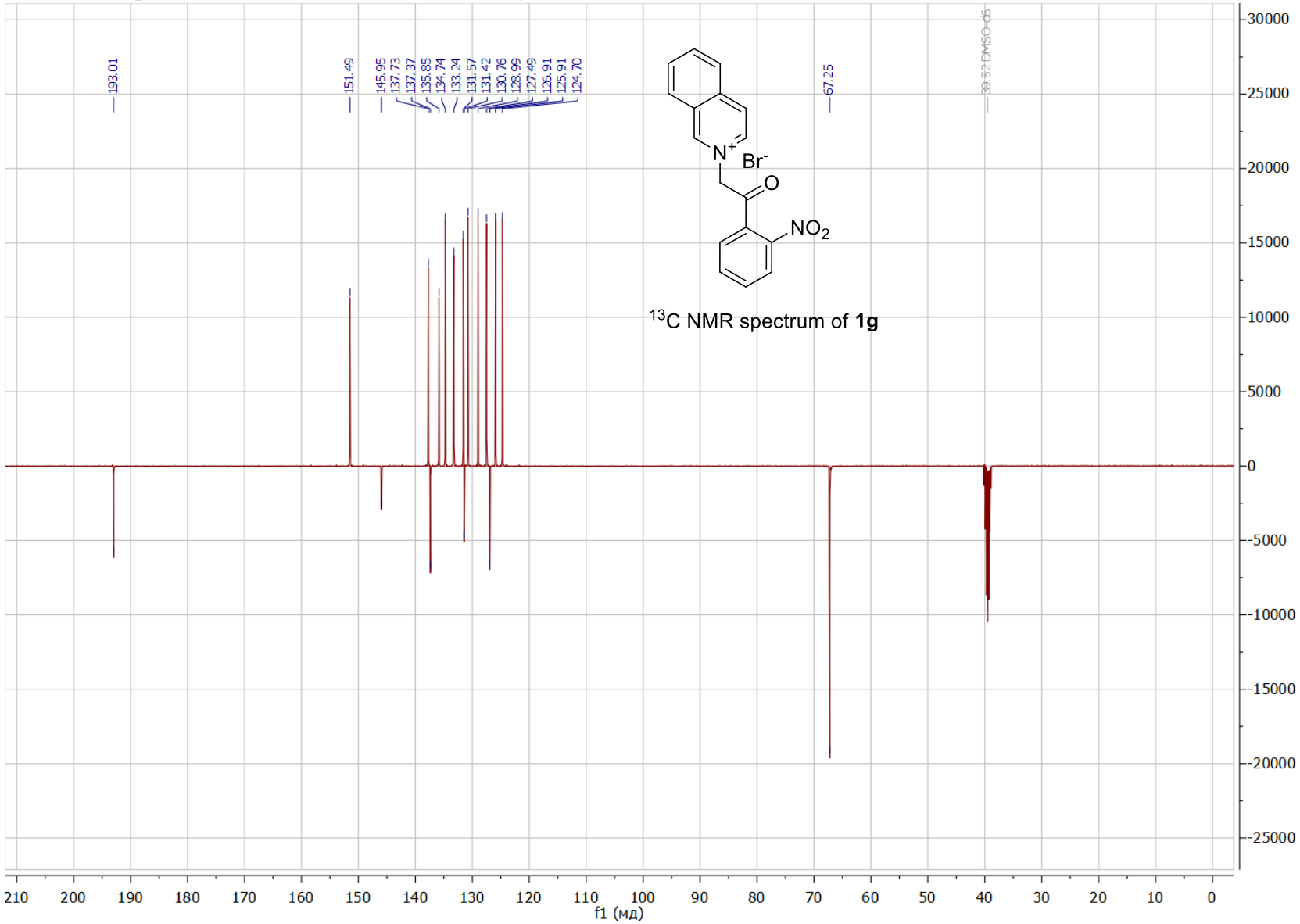
^{13}C NMR spectrum (101MHz, DMSO) of **1f**



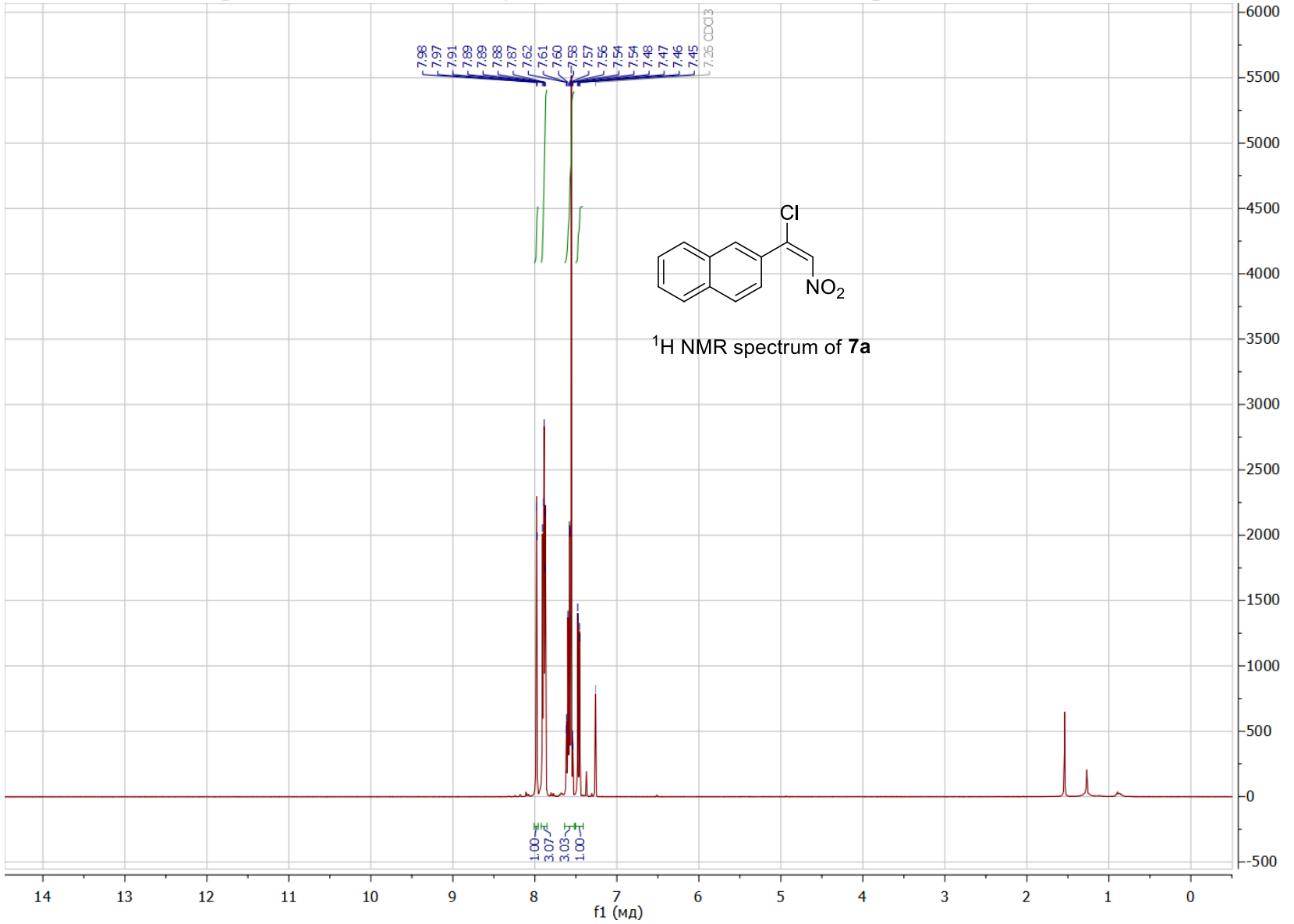
^{1}H NMR spectrum (400 MHz, DMSO) of **1g**



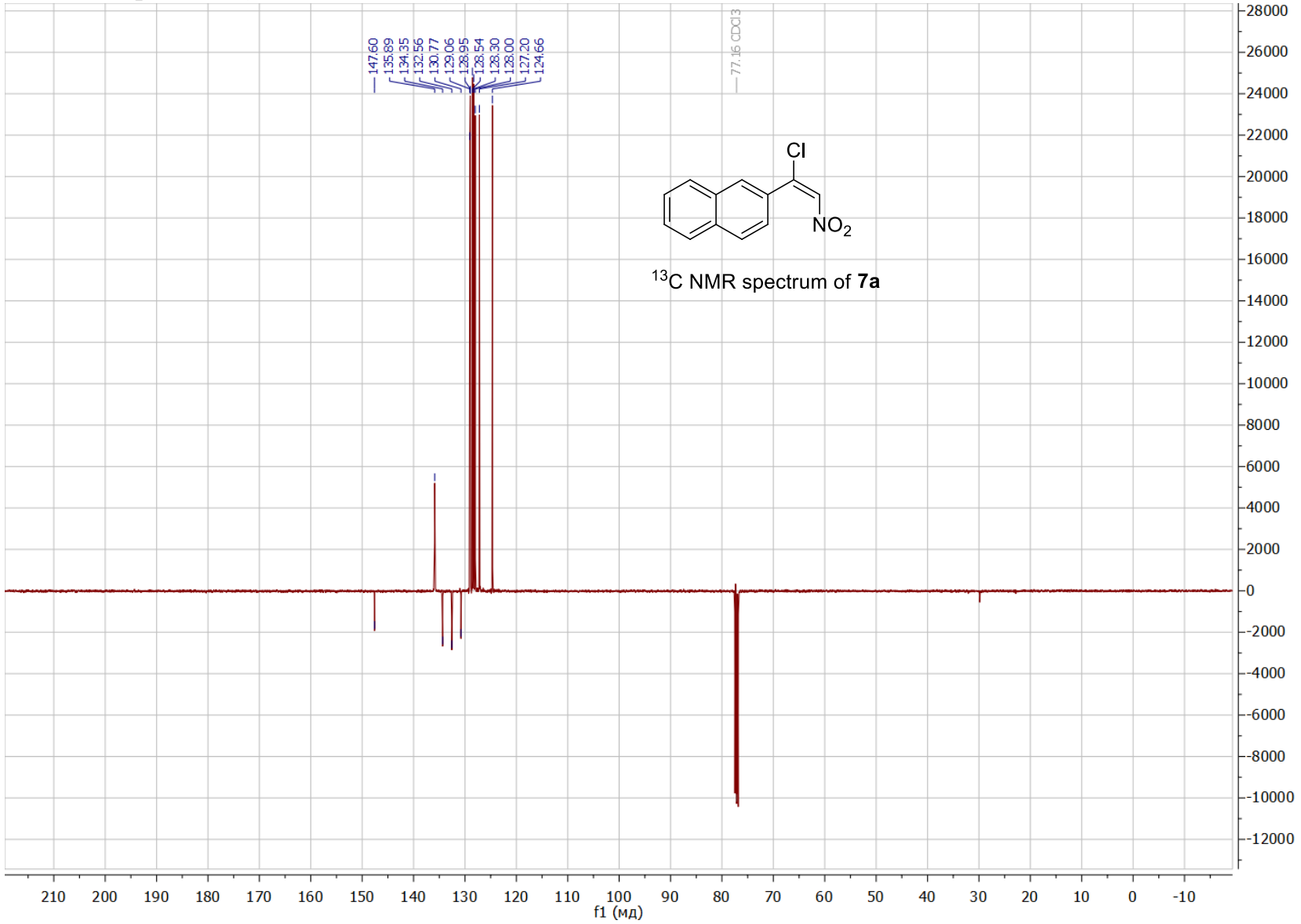
^{13}C NMR spectrum (101MHz, DMSO) of **1g**



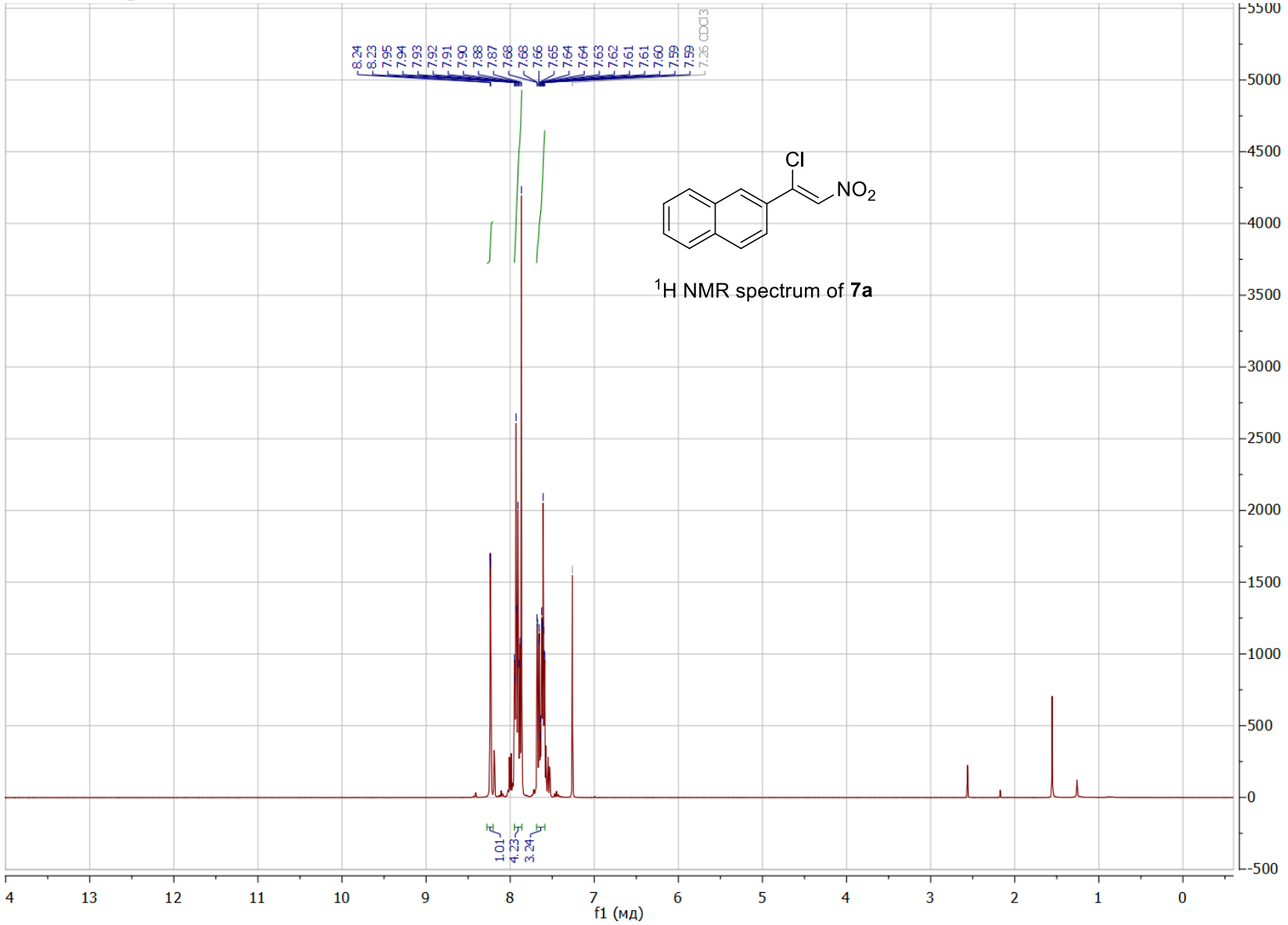
^{1}H and ^{13}C NMR spectral charts for starting nitrochloroalkenes. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a (E)**



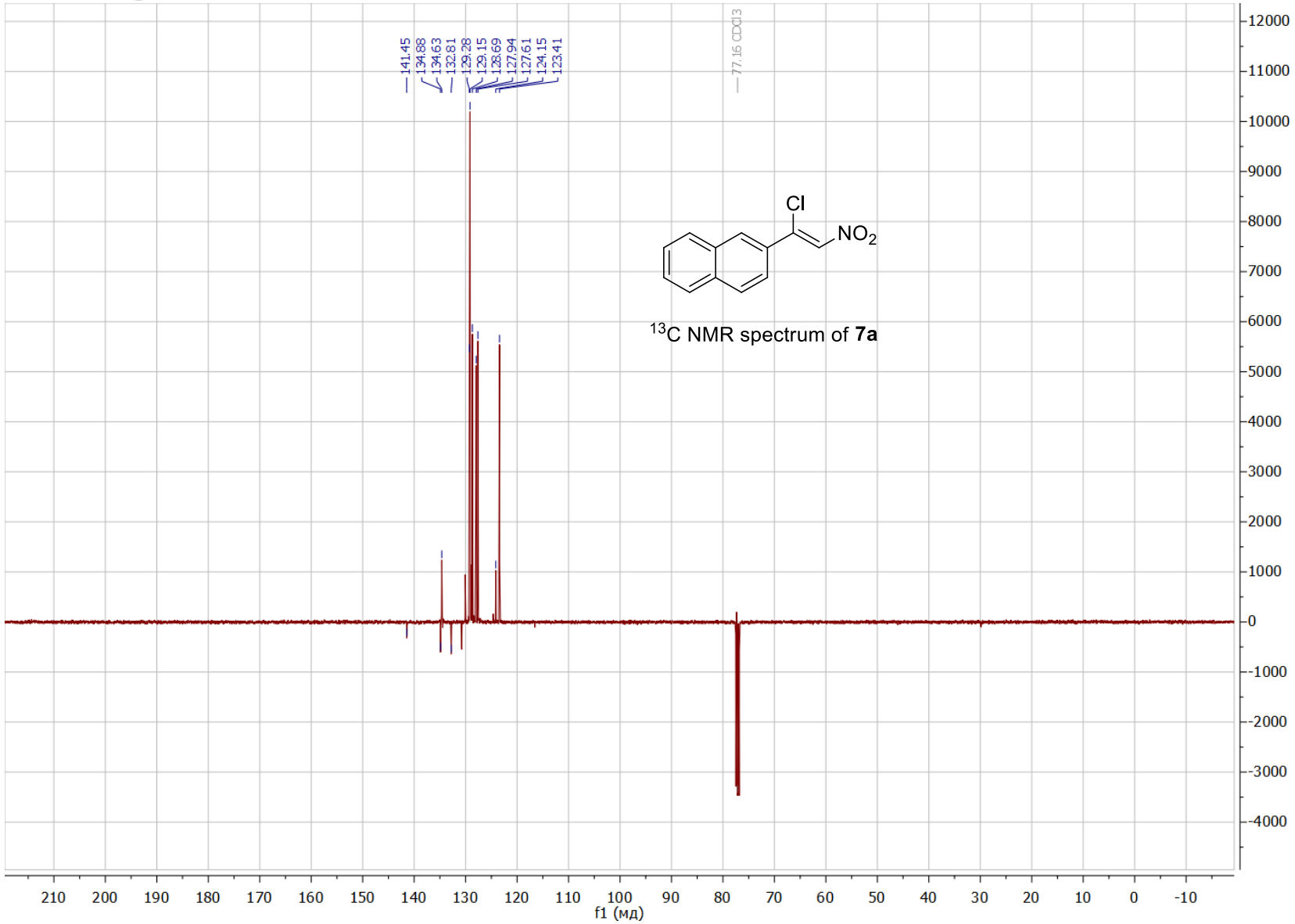
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **7a (E)**



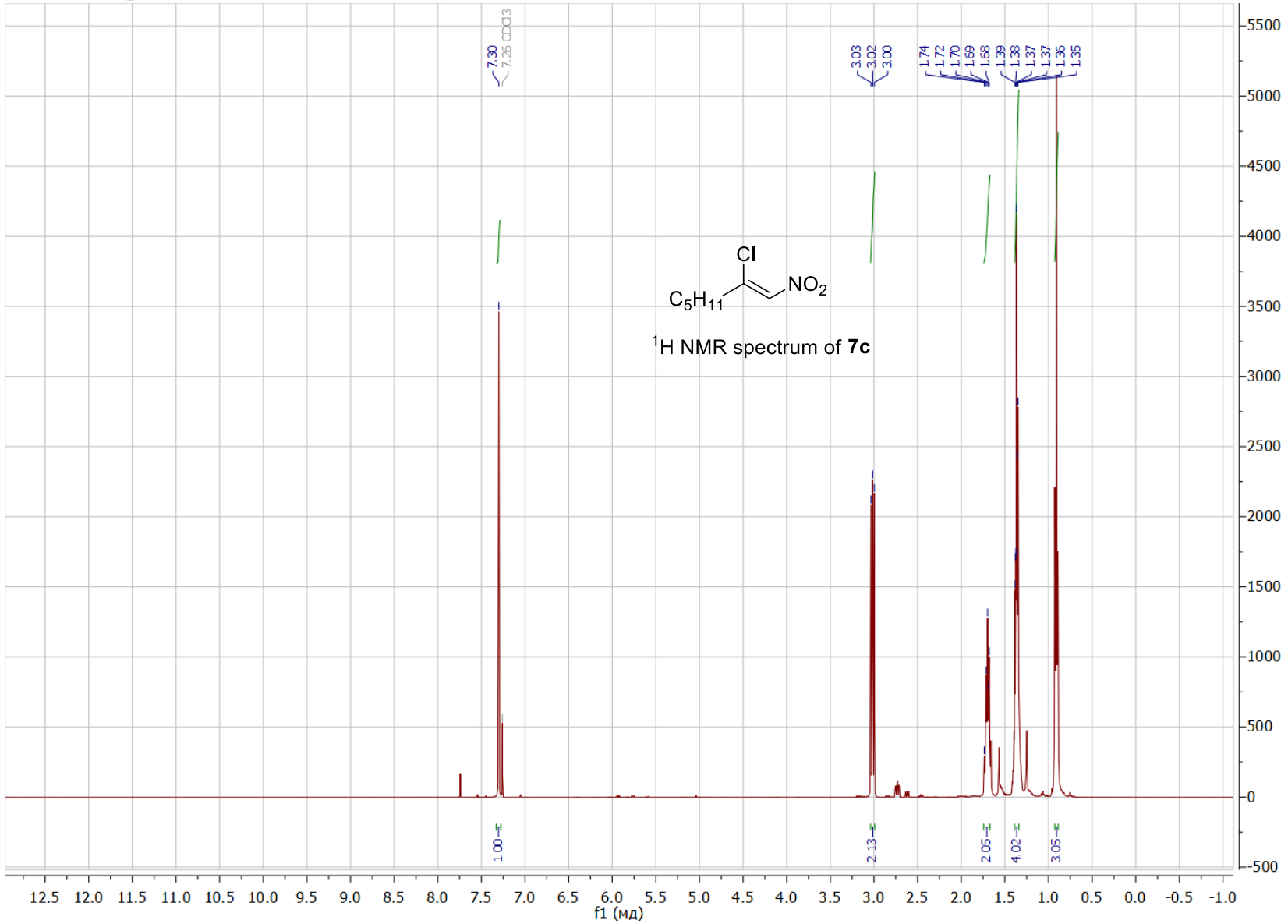
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7a (Z)**



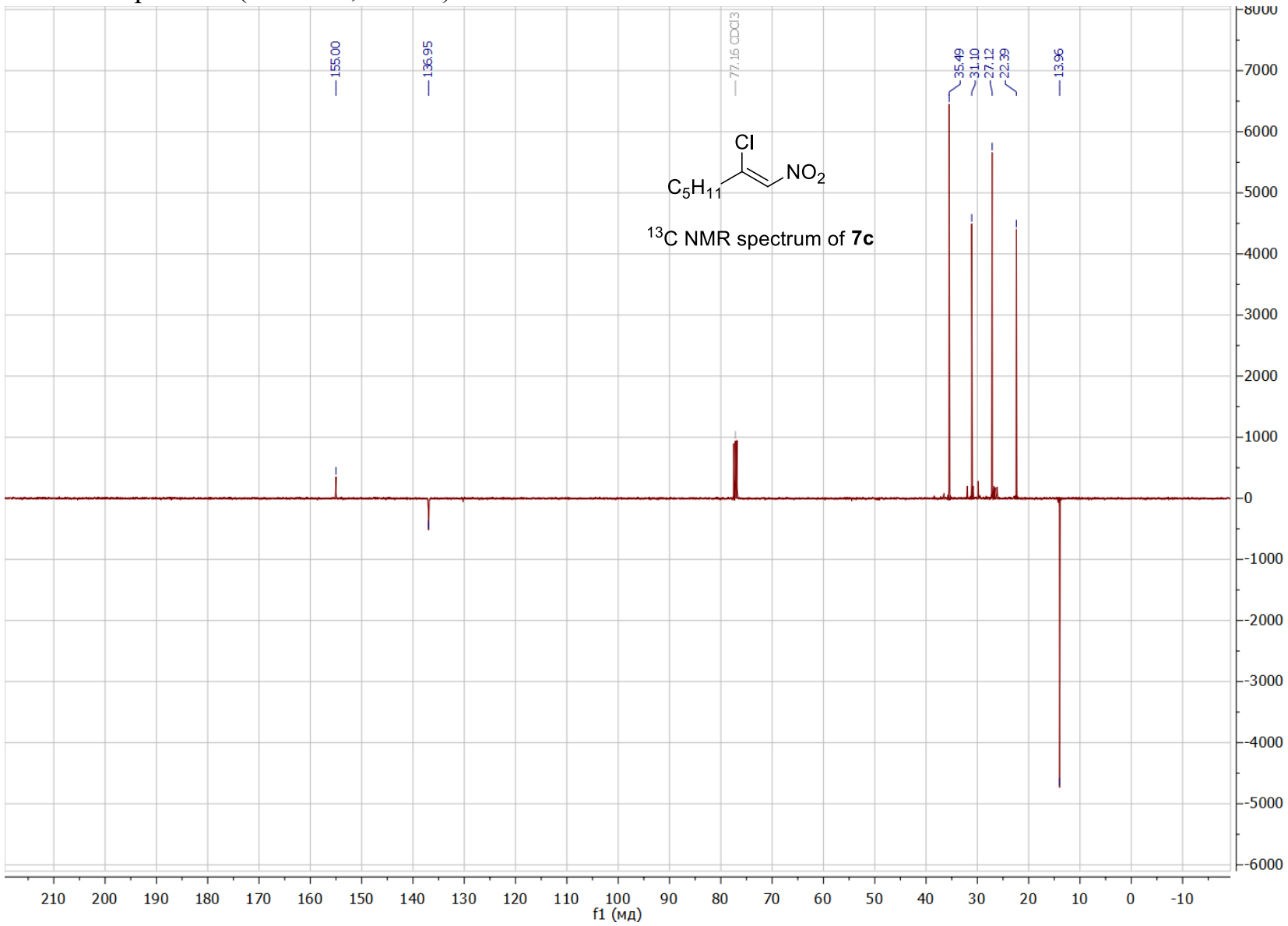
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **7a (Z)**



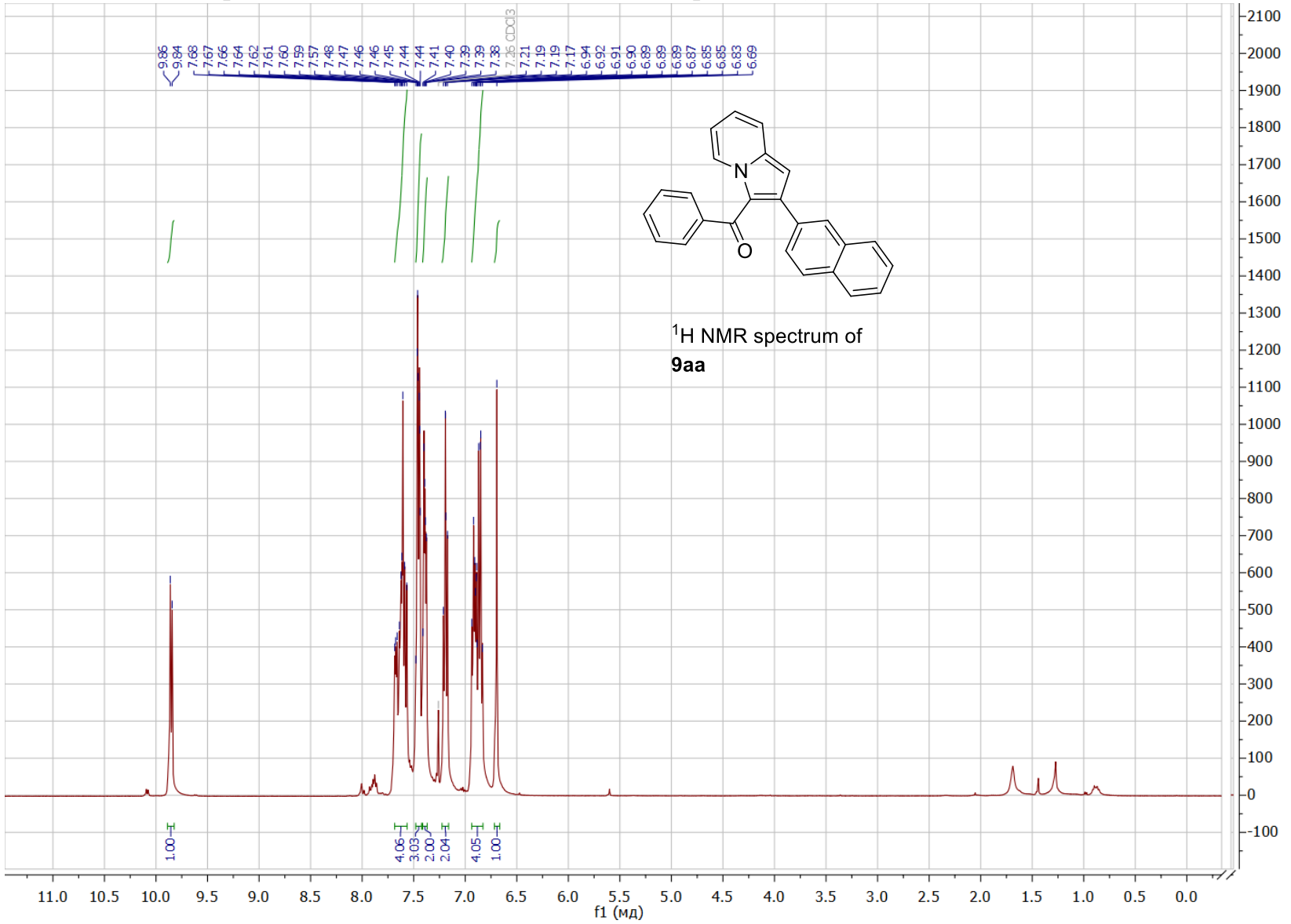
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7c**



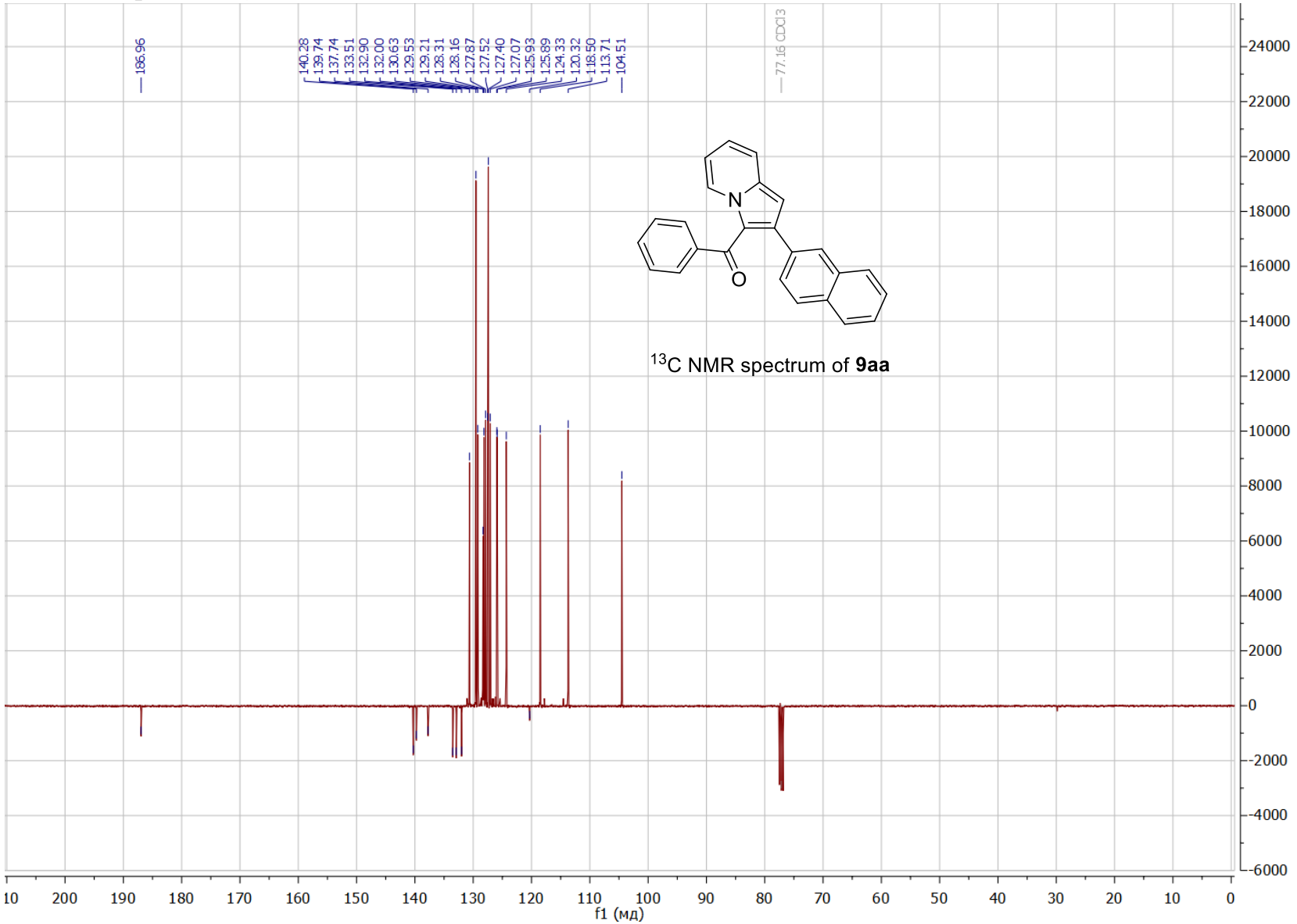
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **7c**



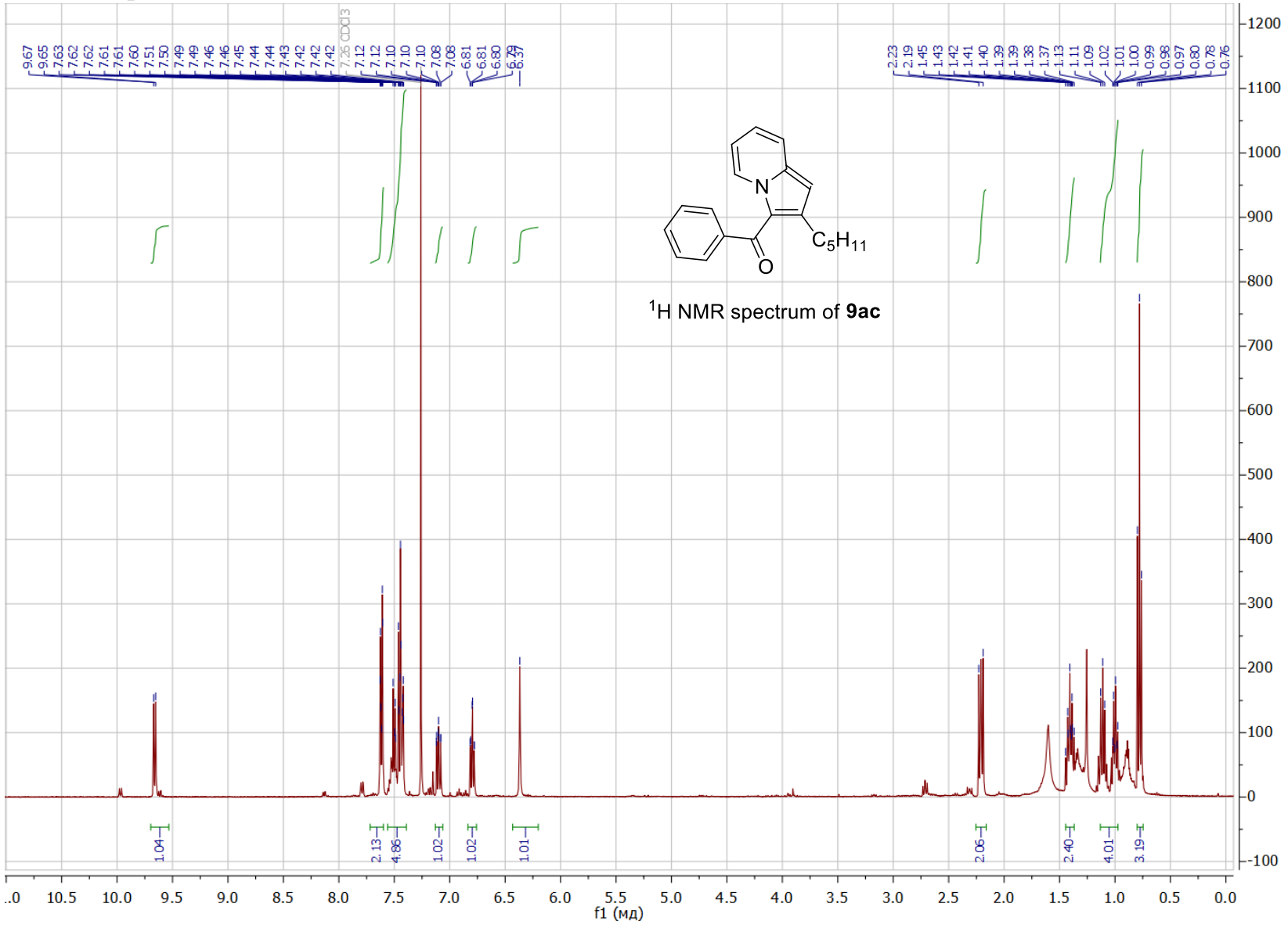
^{1}H and ^{13}C NMR spectral charts for indolizines. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9aa**



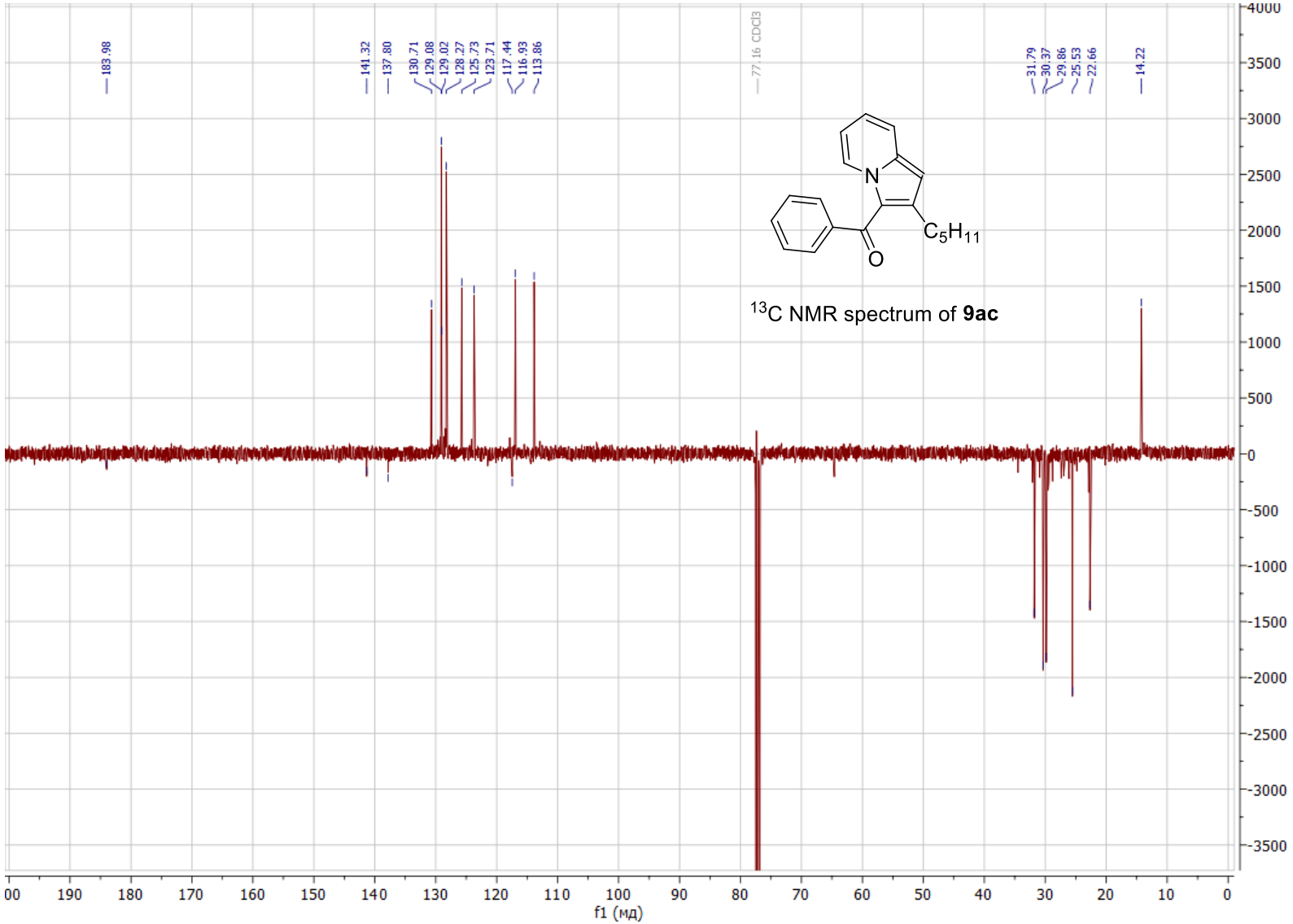
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9aa**



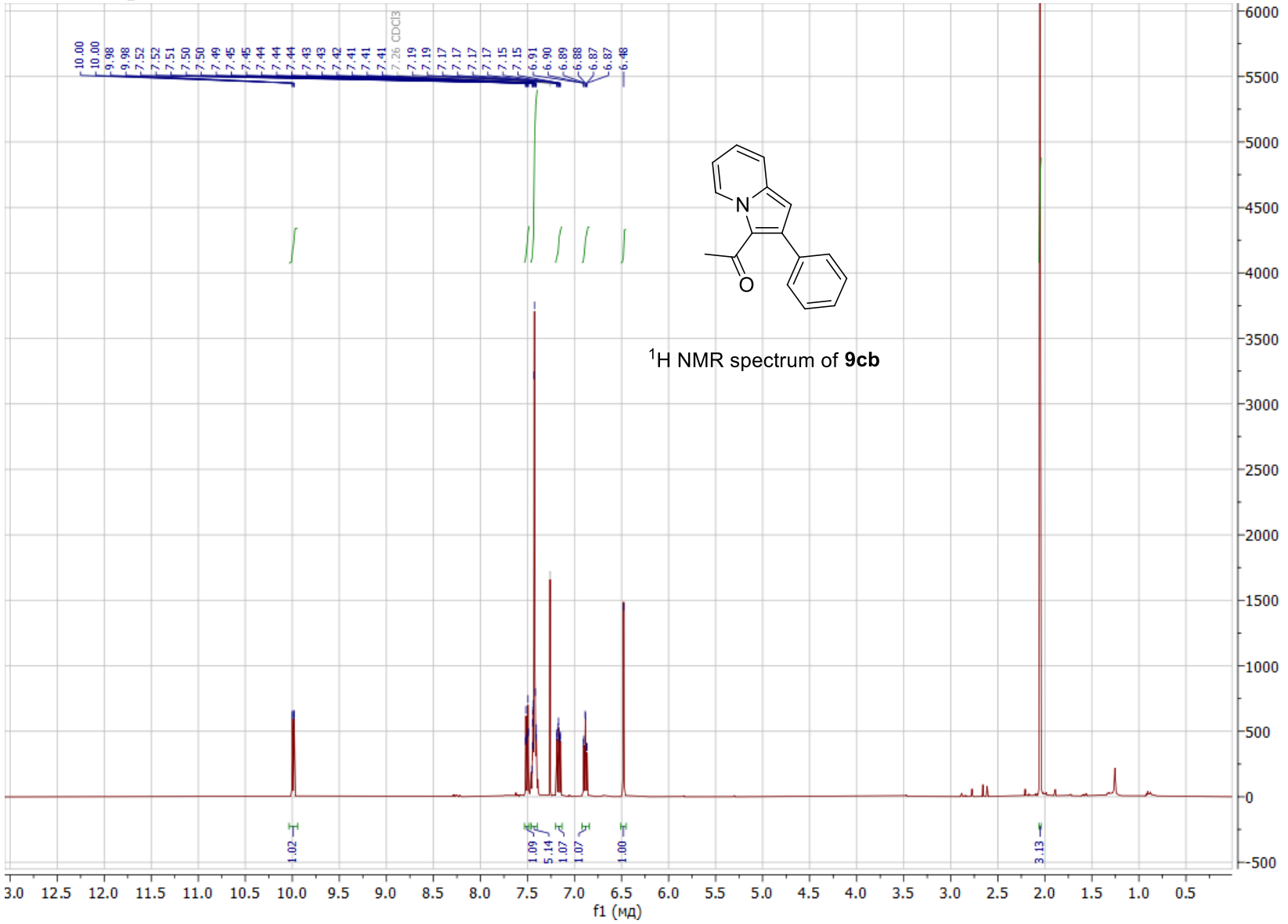
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9ac**



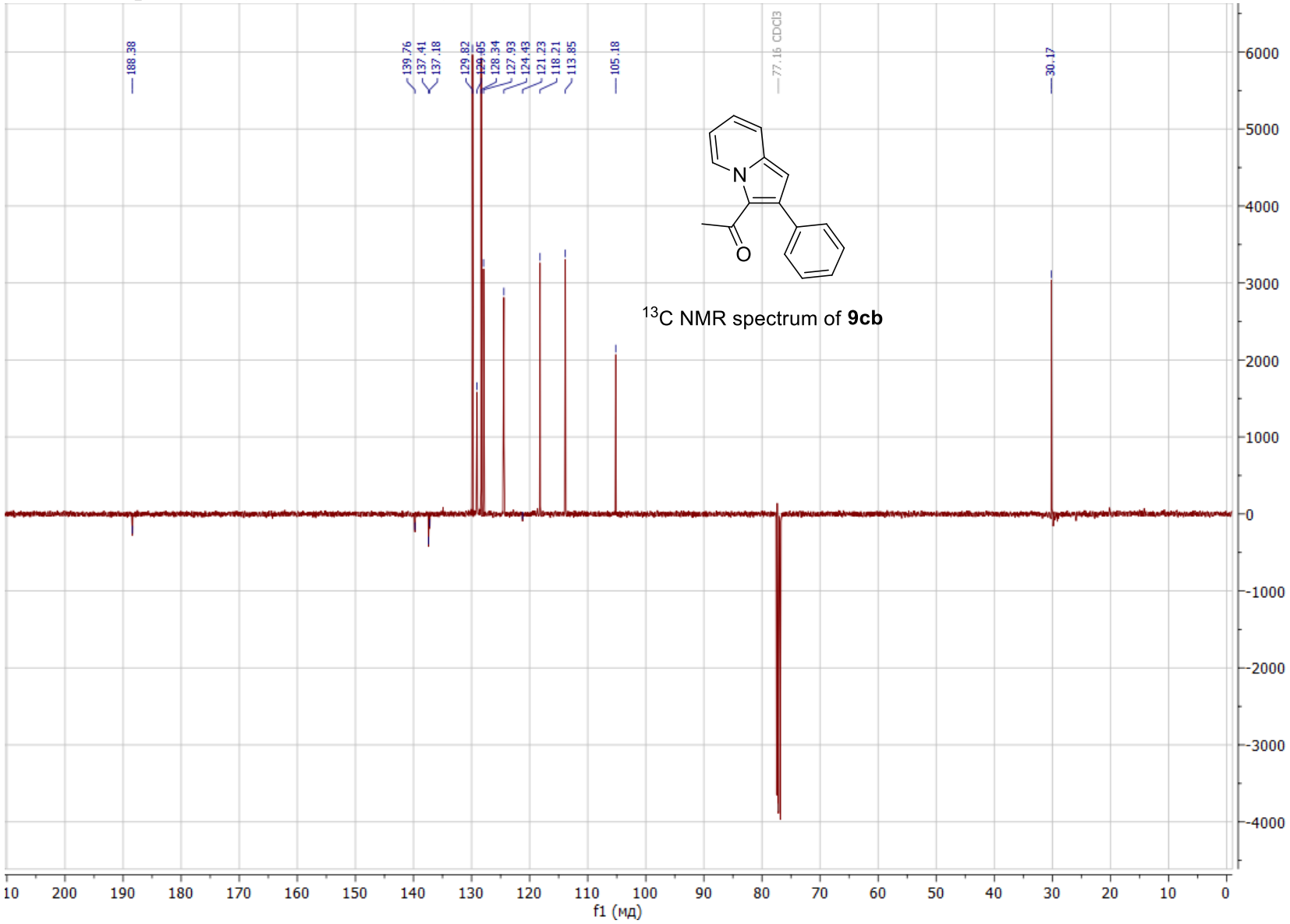
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9ac**



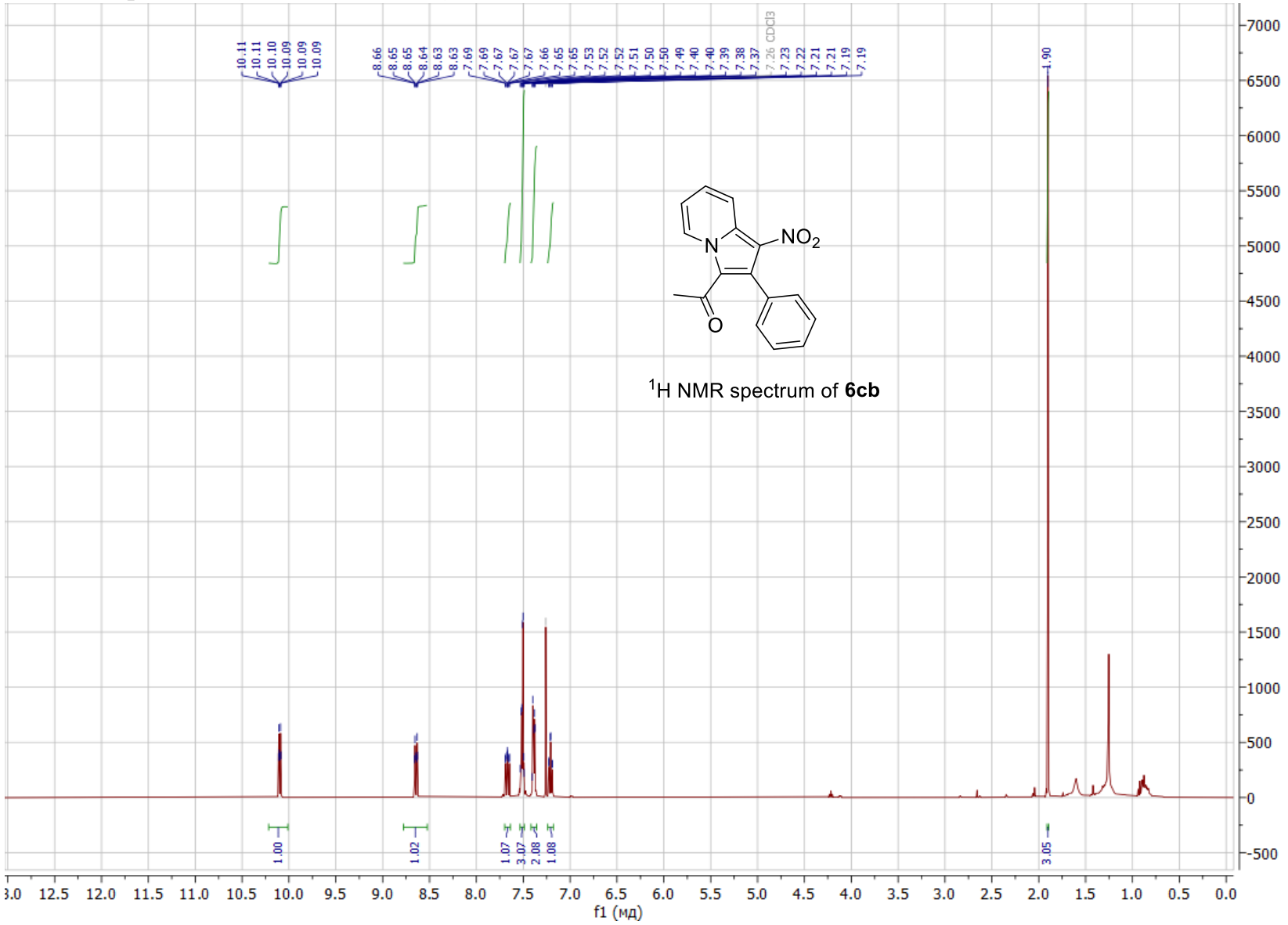
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9cb**



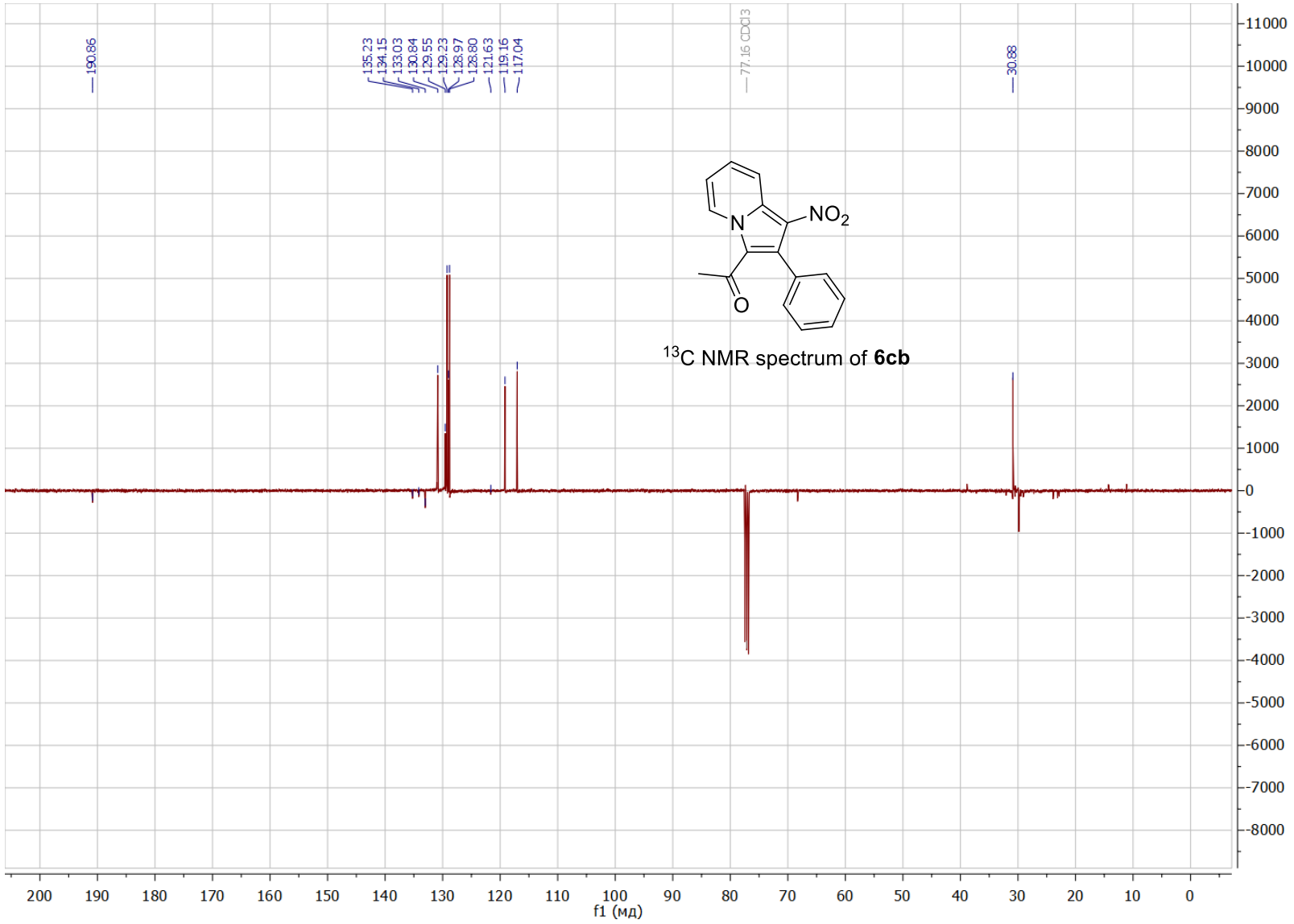
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9cb**



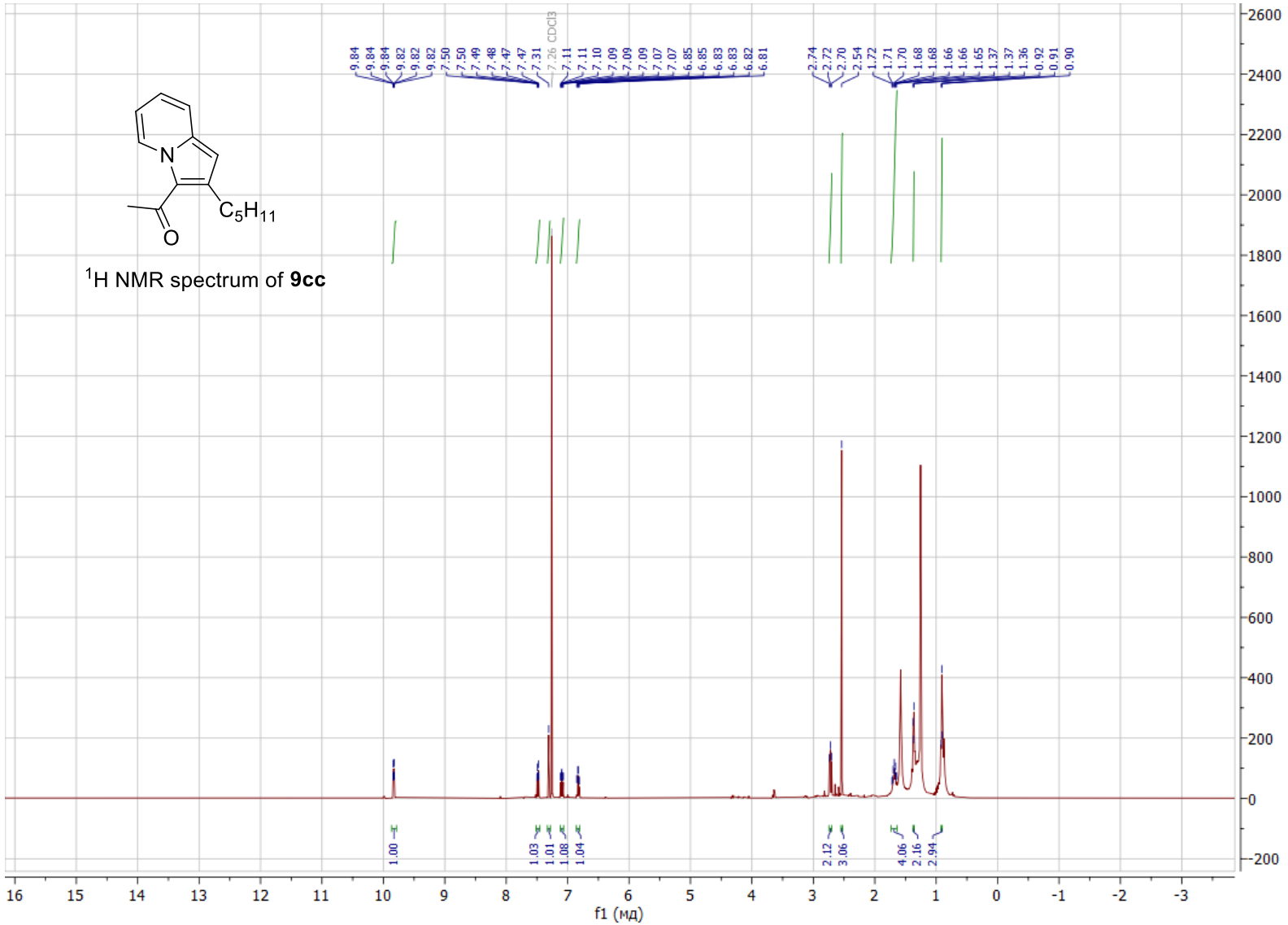
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6cb**



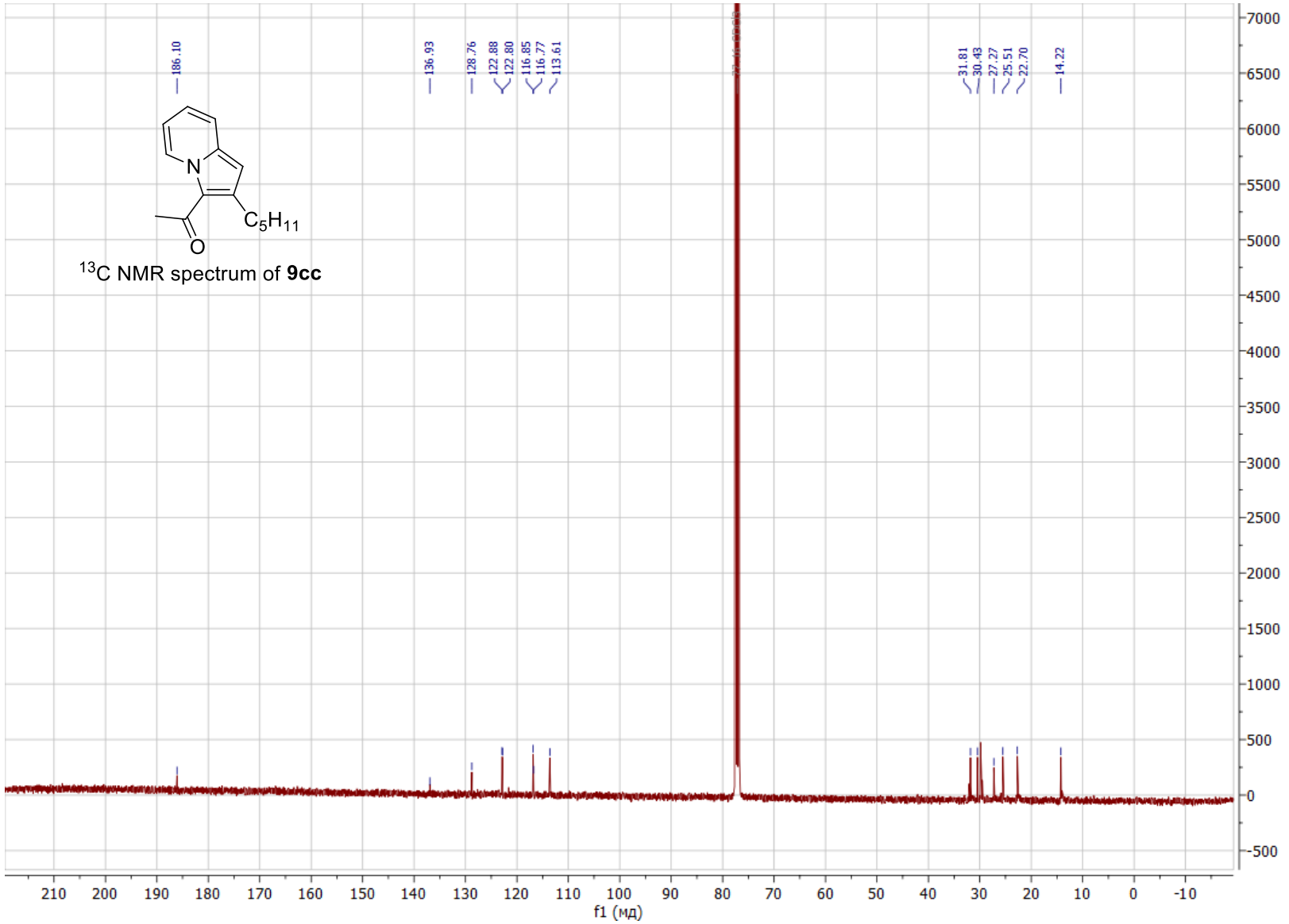
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **6cb**



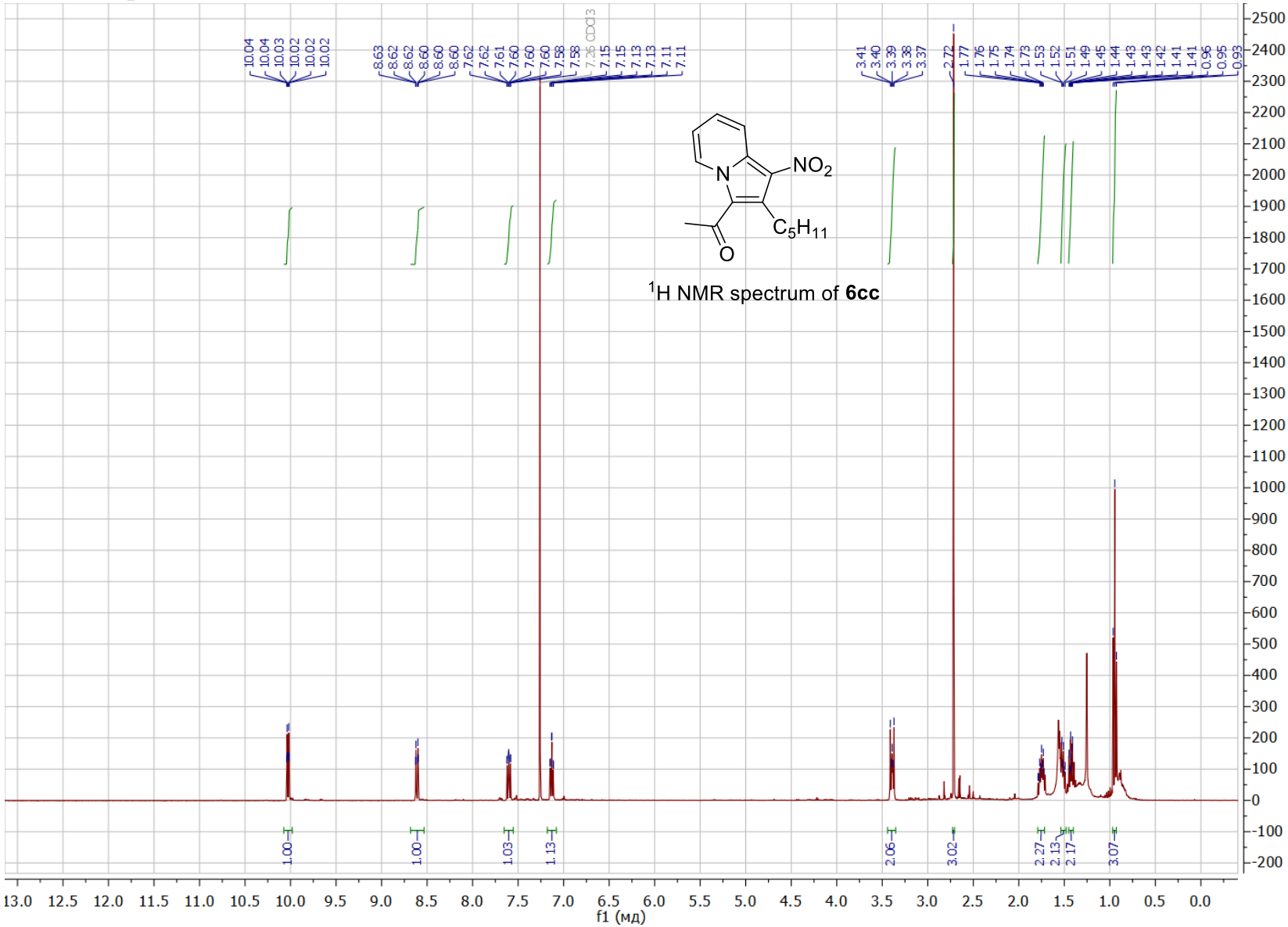
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9cc**



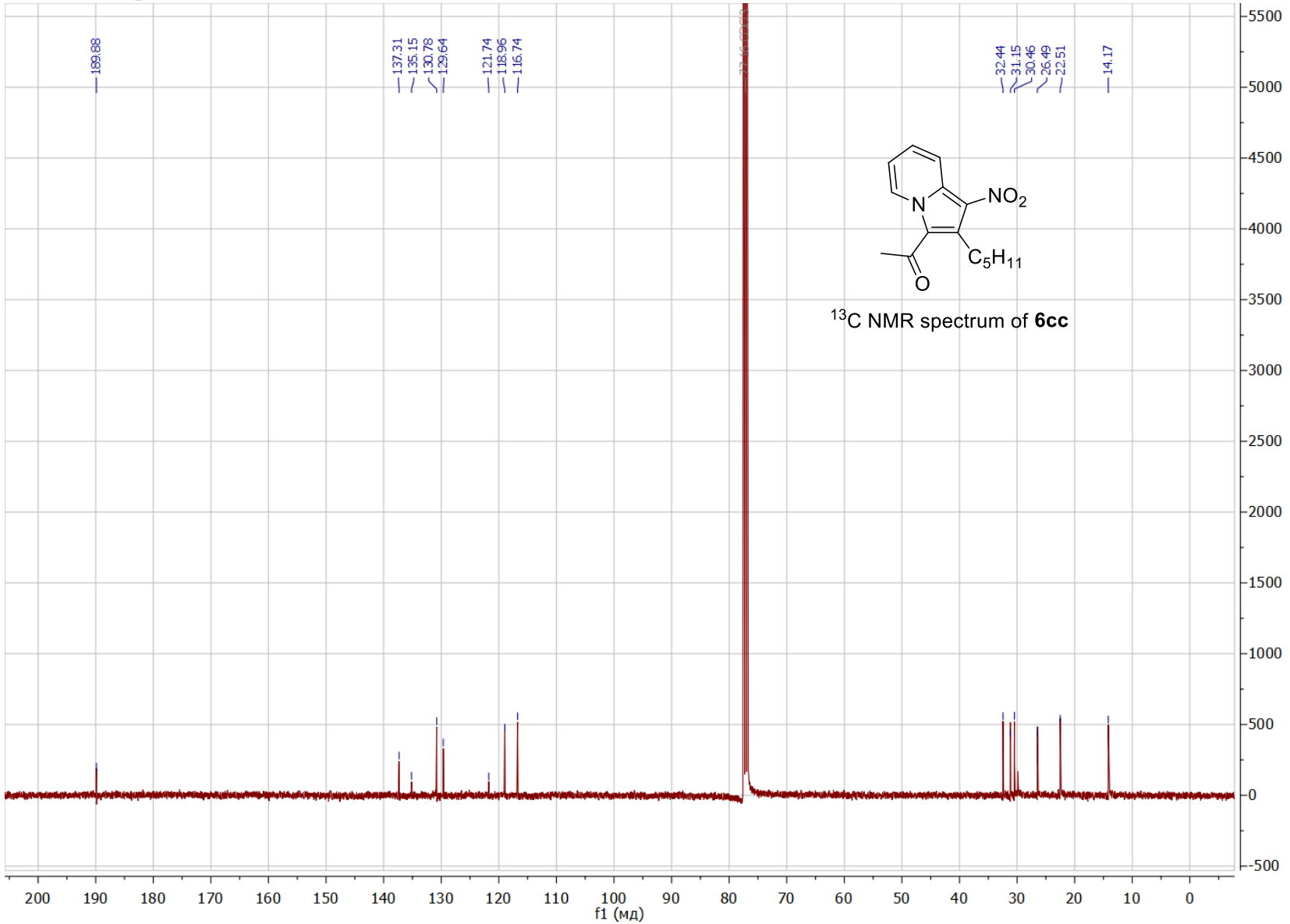
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9cc**



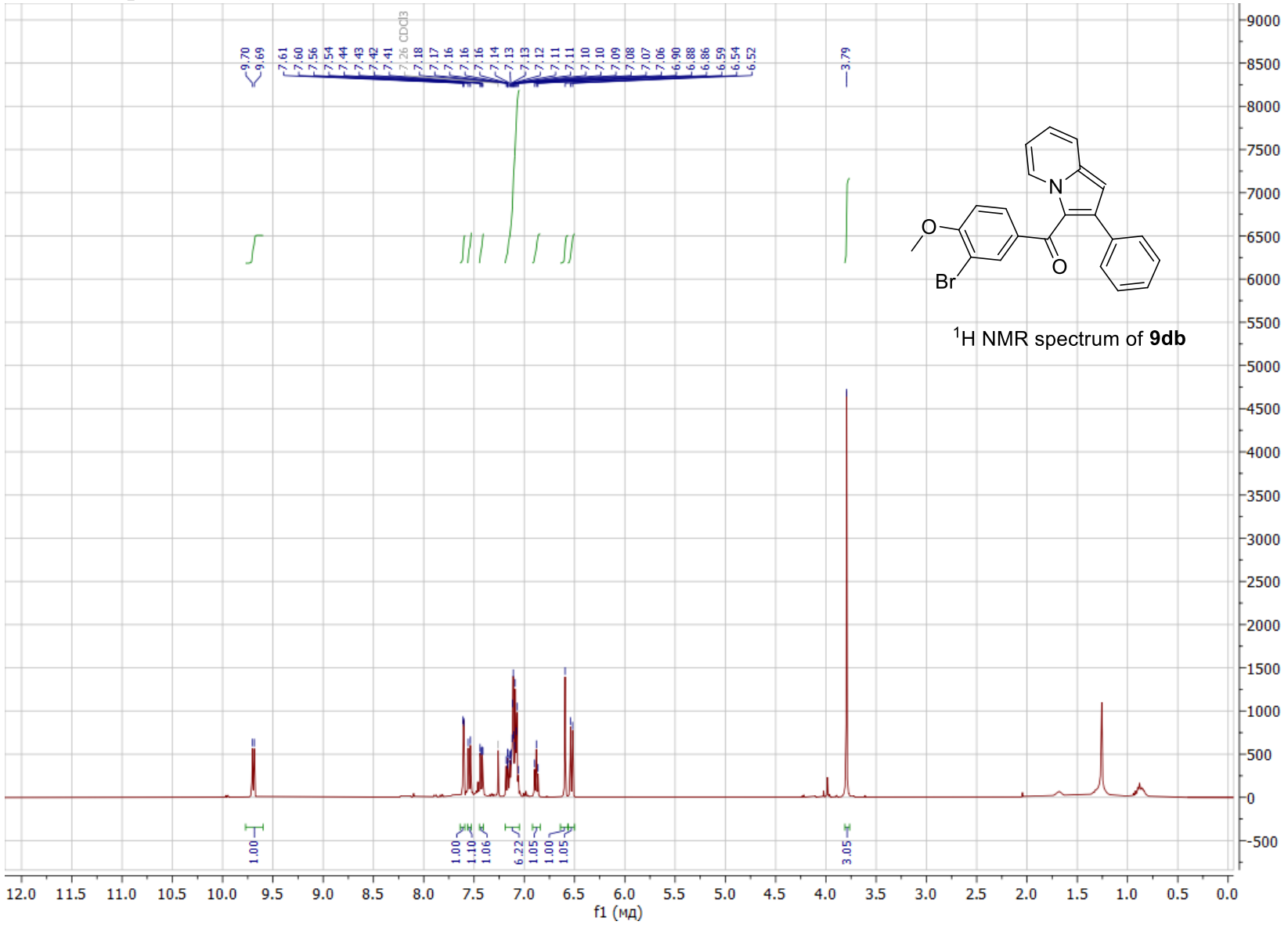
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6cc**



^{13}C NMR spectrum (101MHz, $CDCl_3$) of **6cc**

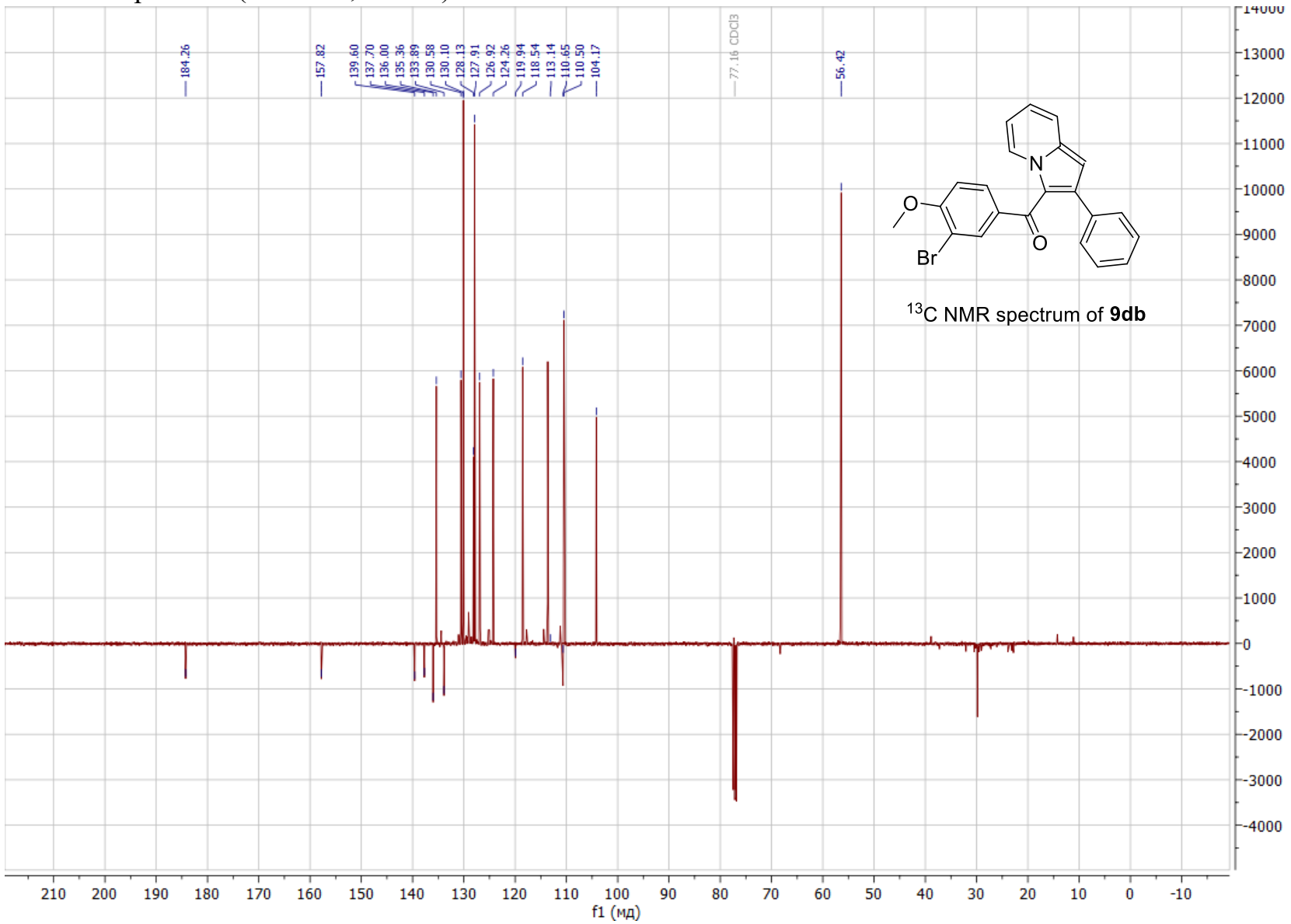


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9db**

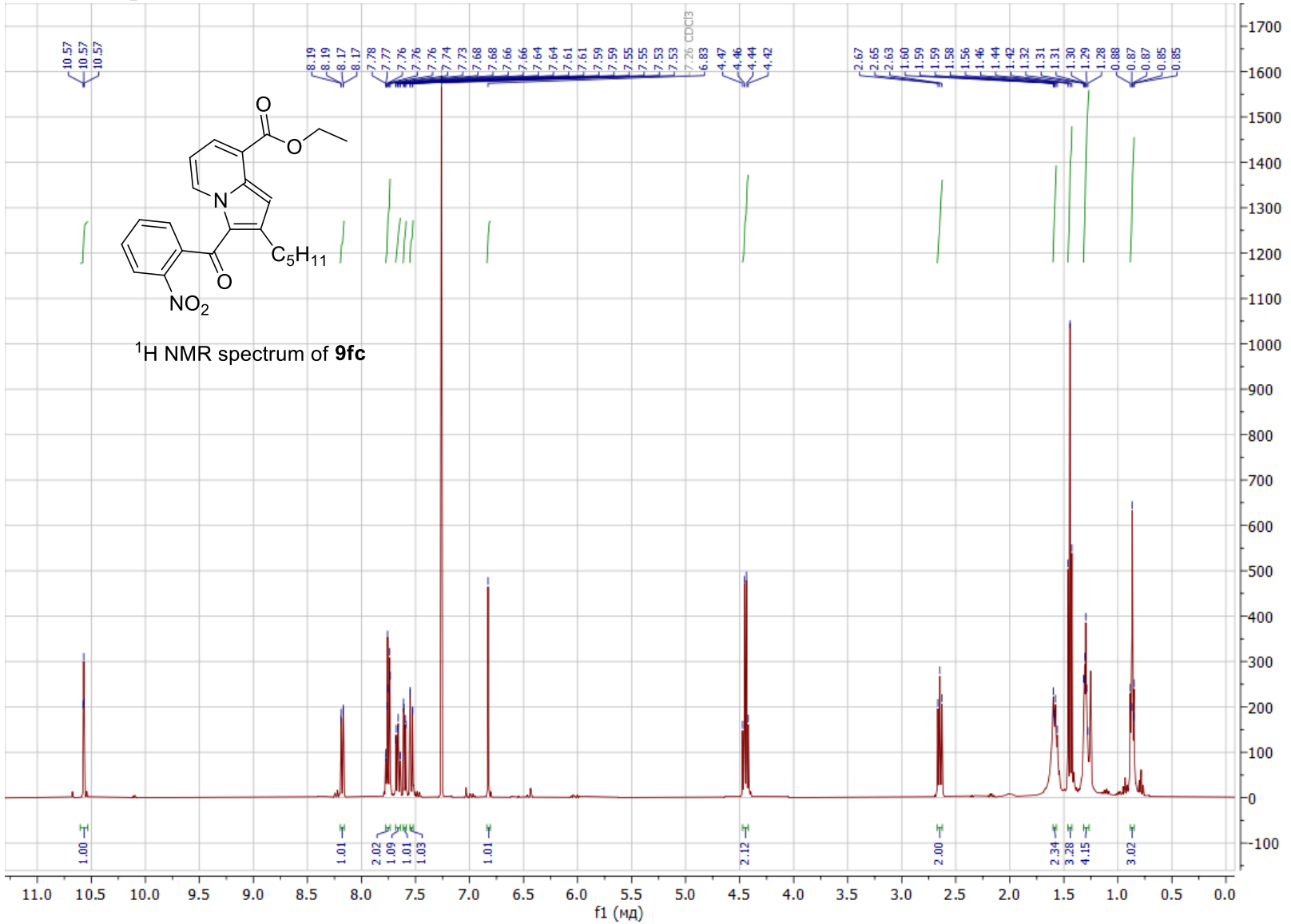


^{1}H NMR spectrum of **9db**

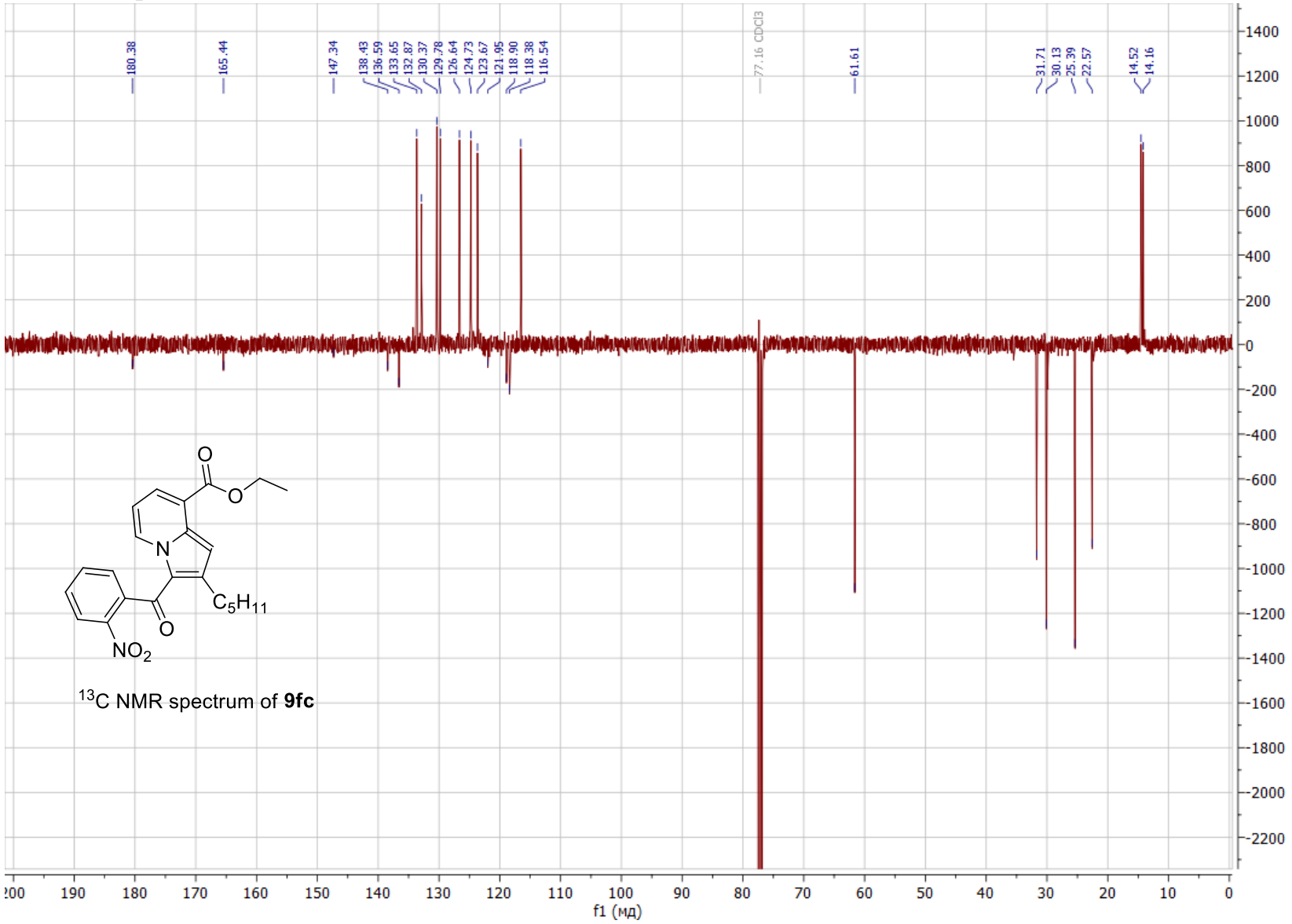
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9db**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9fc**

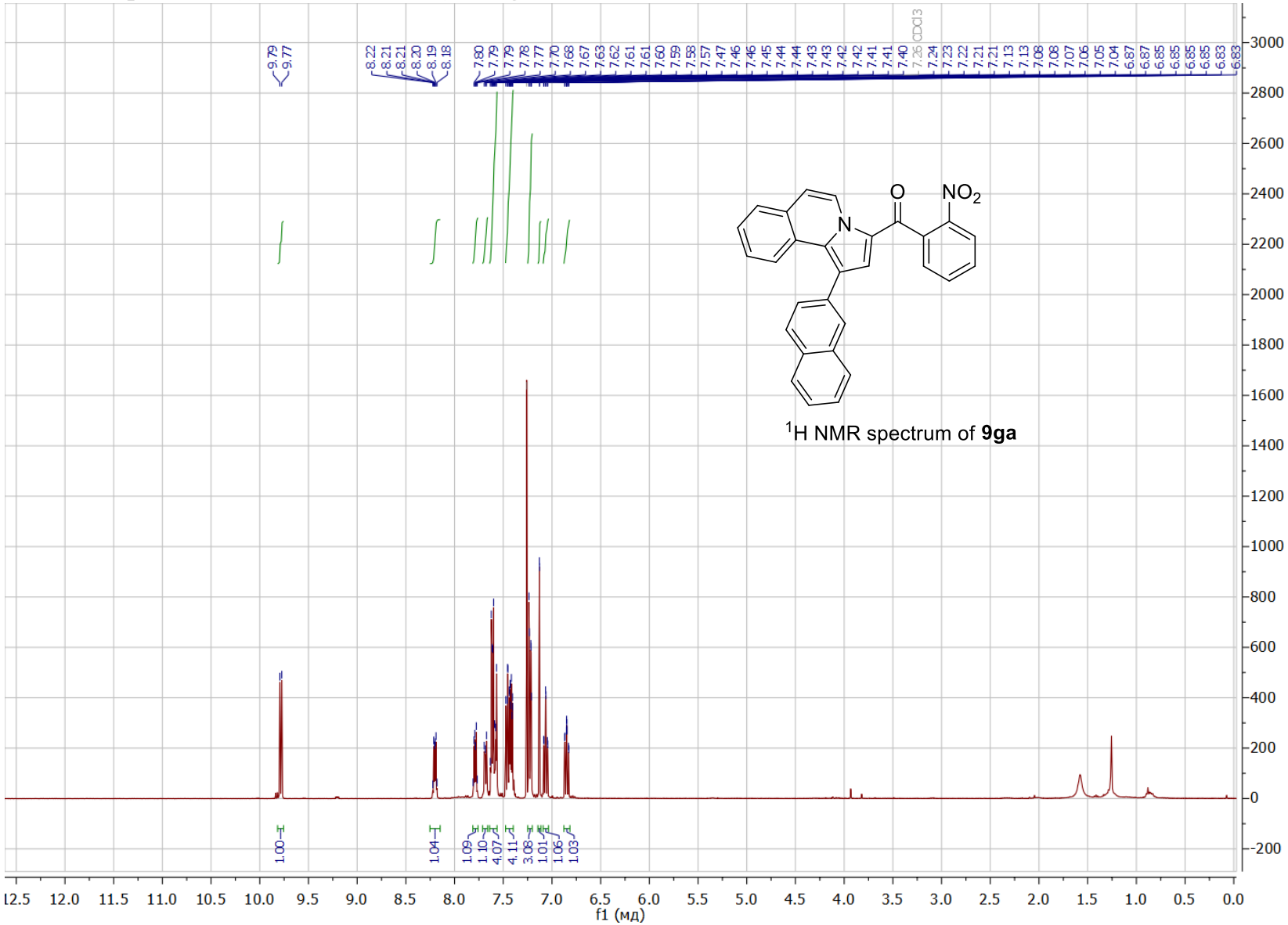


^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9fc**

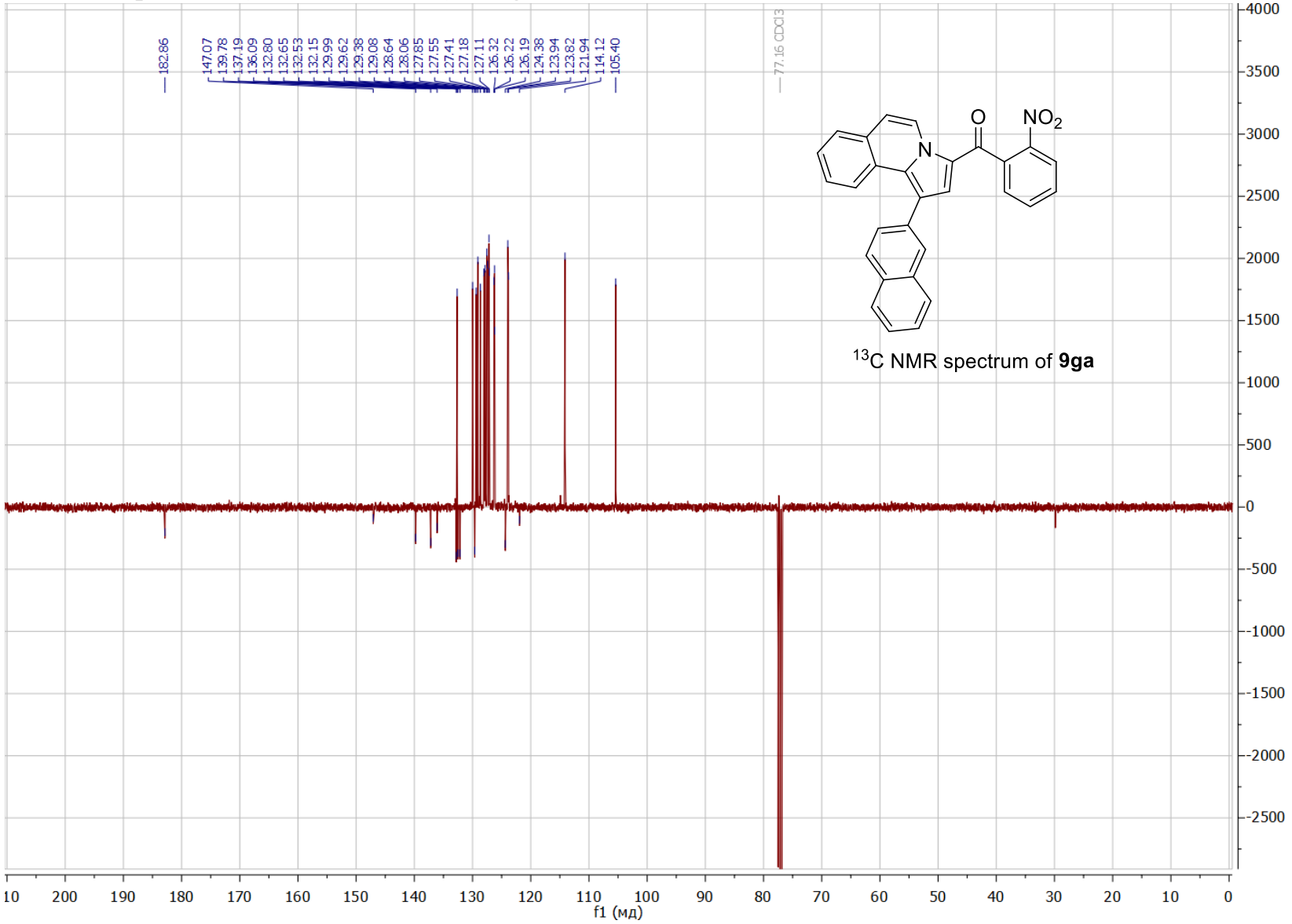


^{13}C NMR spectrum of **9fc**

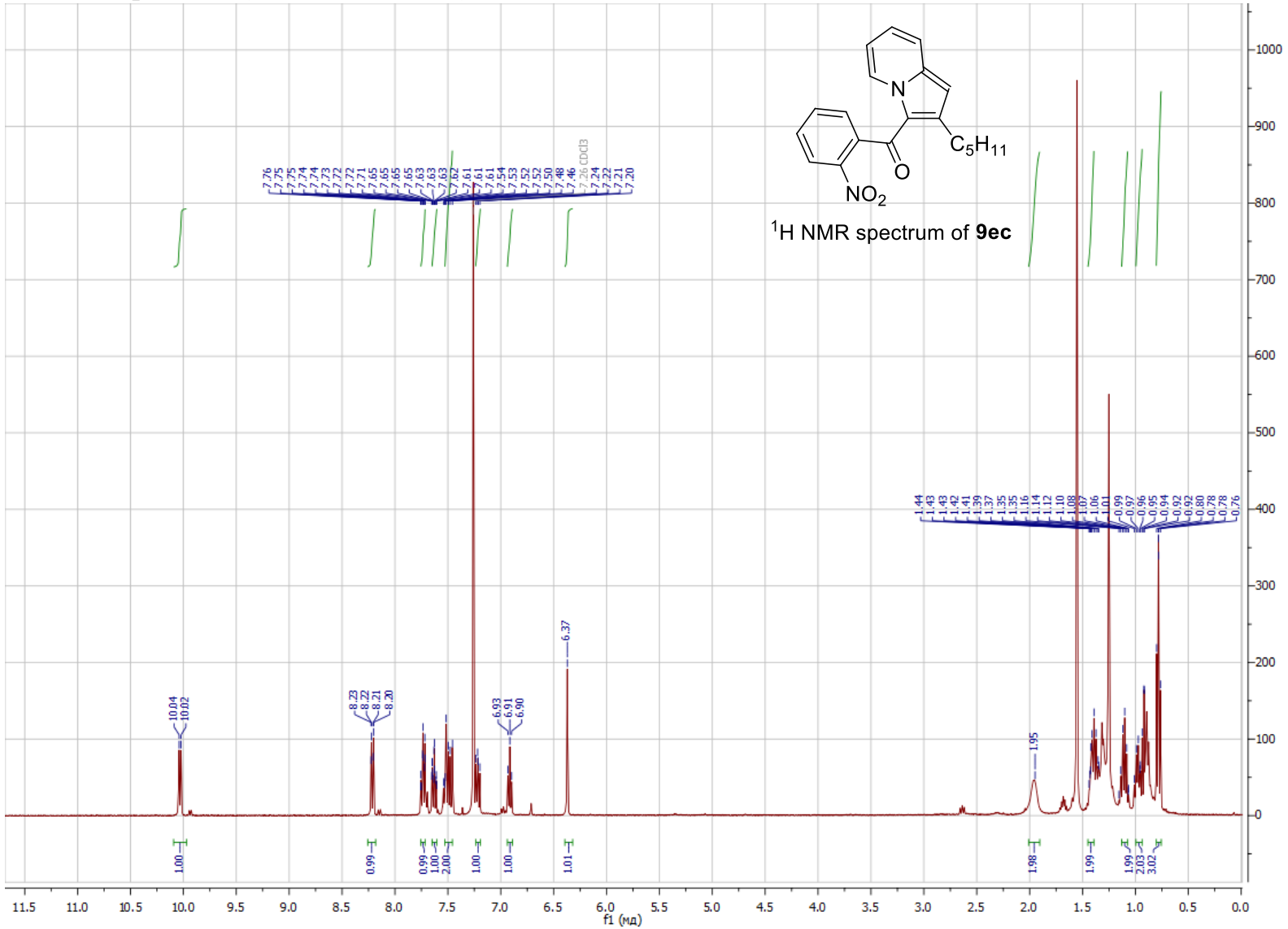
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9ga**



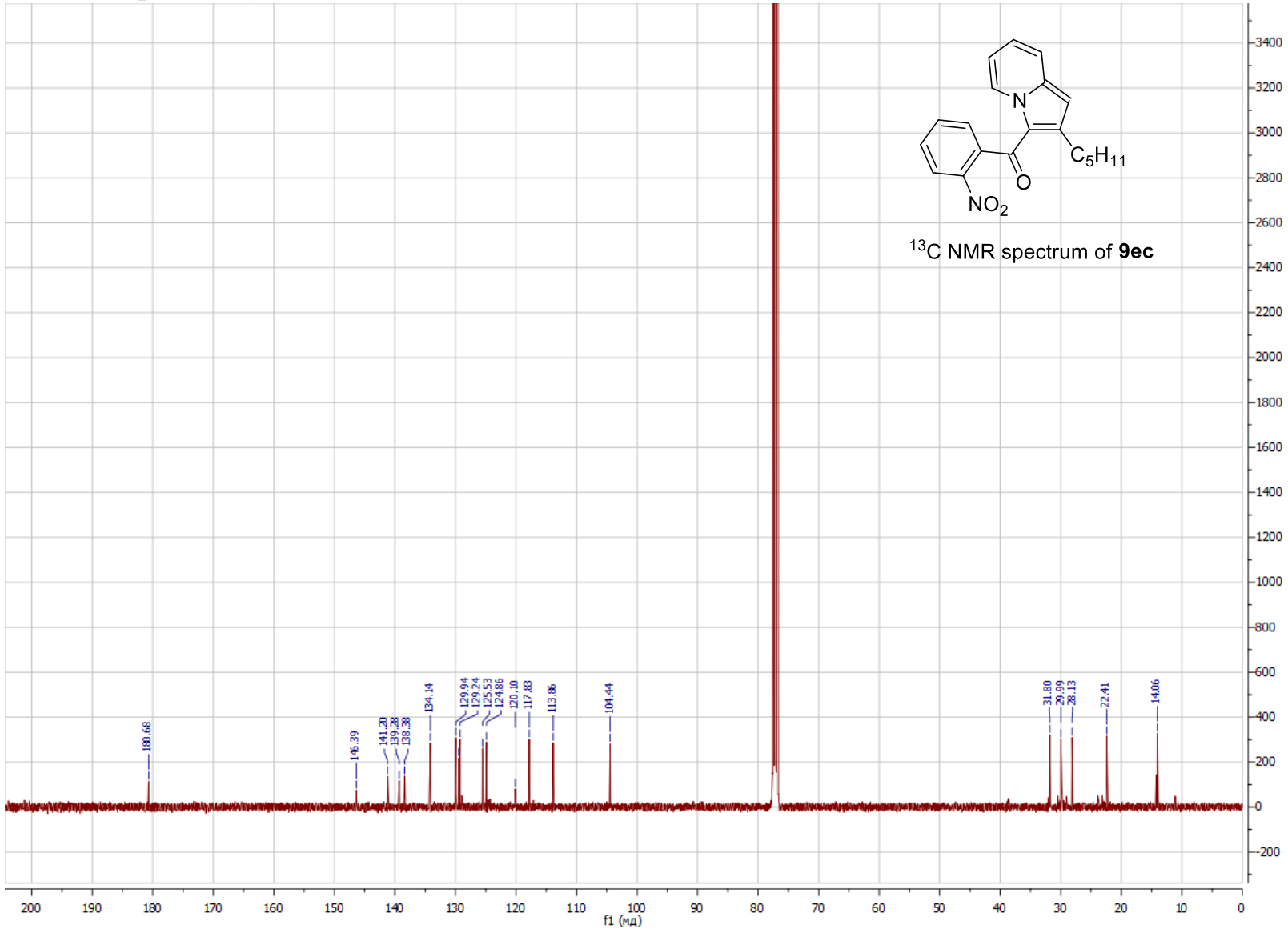
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9ga**



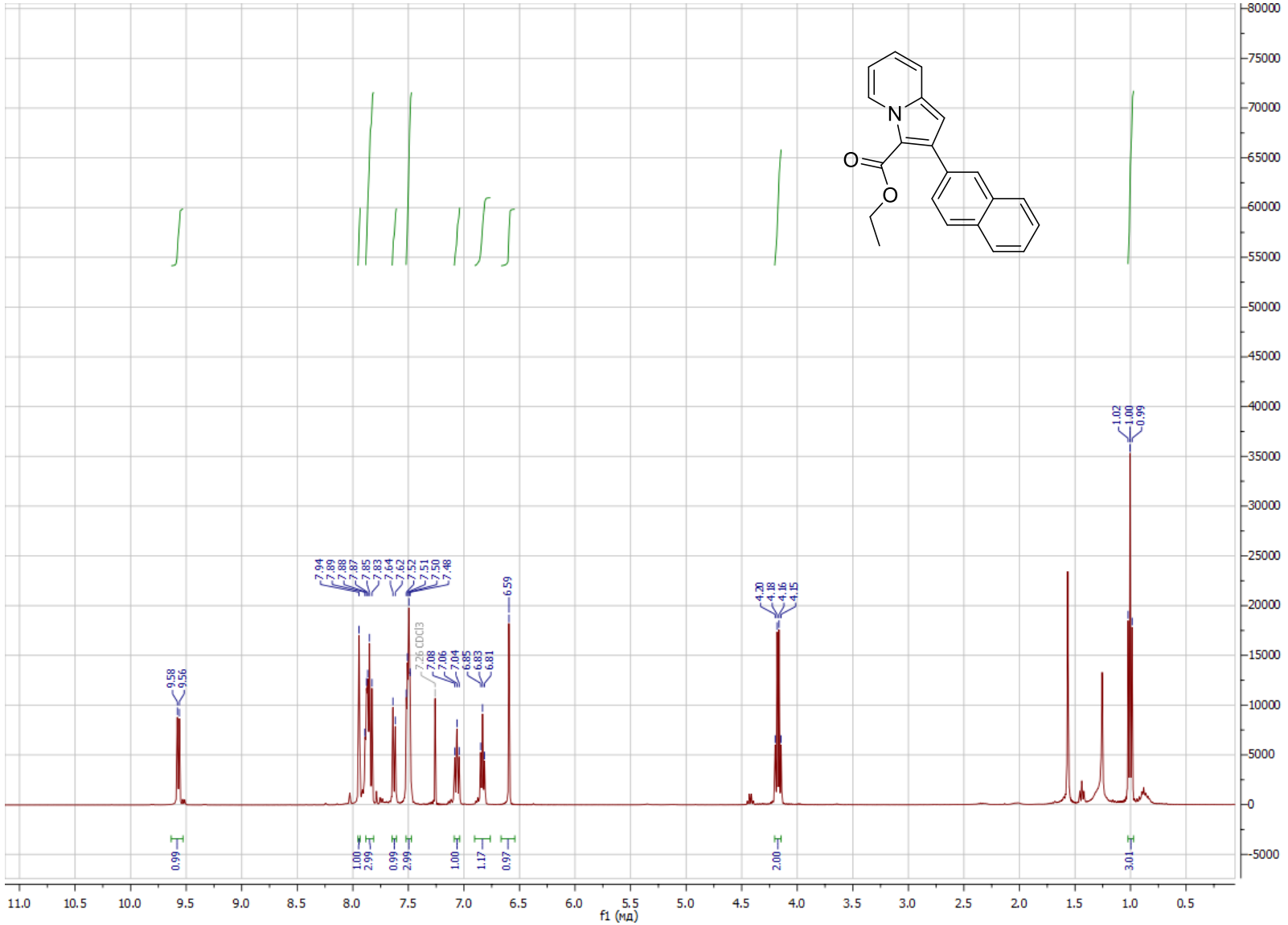
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9ec**



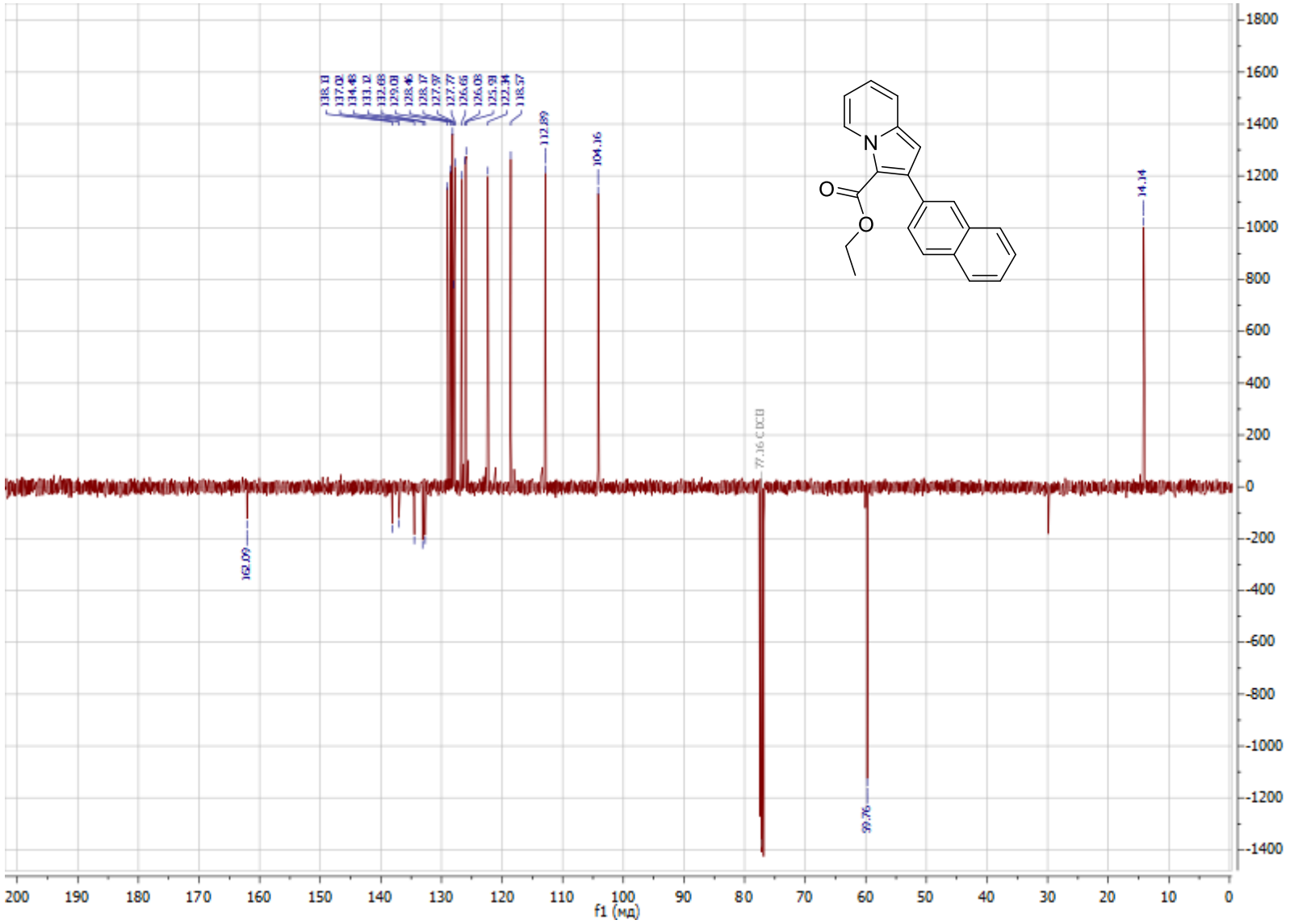
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9ec**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **9ha**

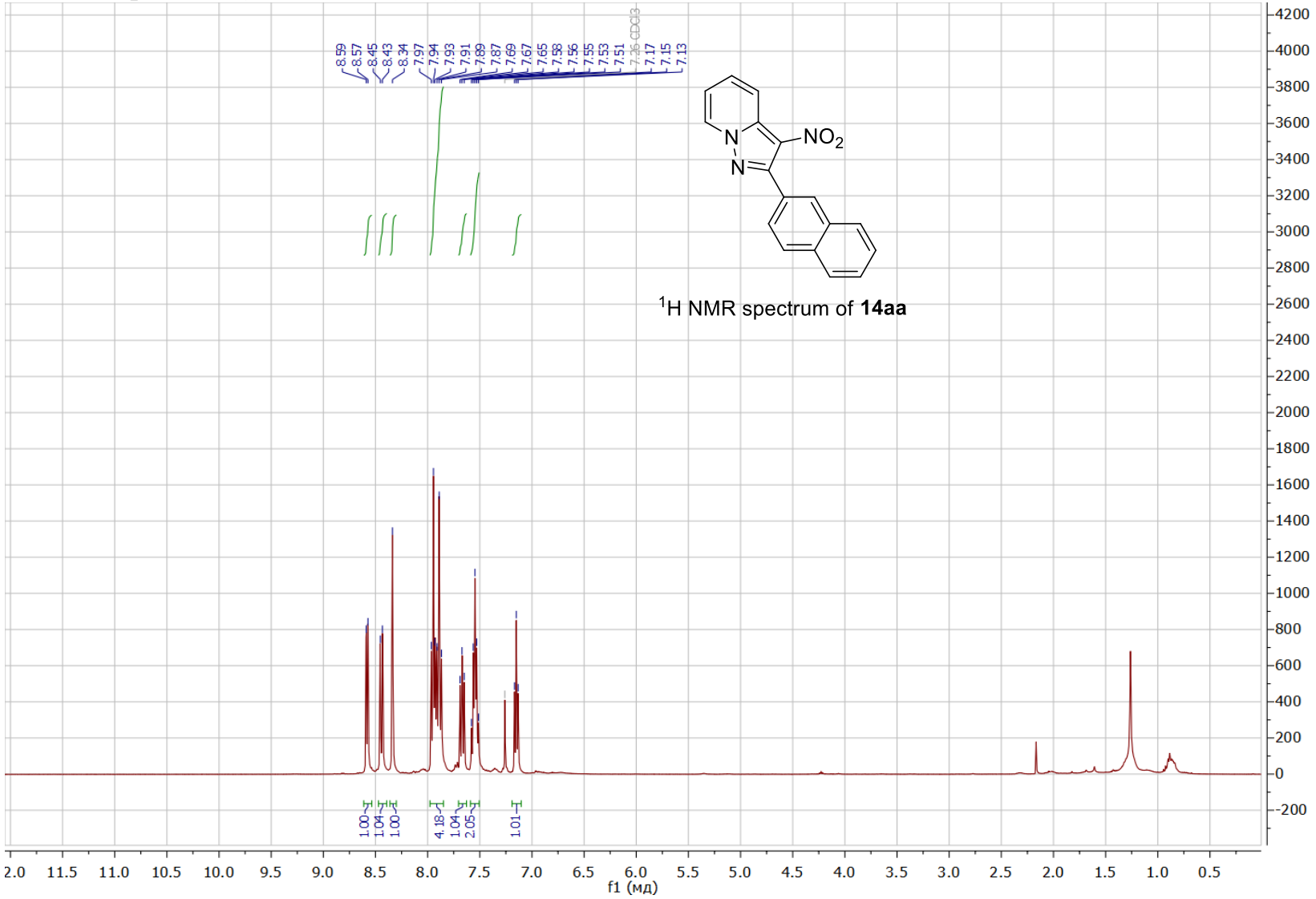


^{13}C NMR spectrum (101MHz, $CDCl_3$) of **9ha**

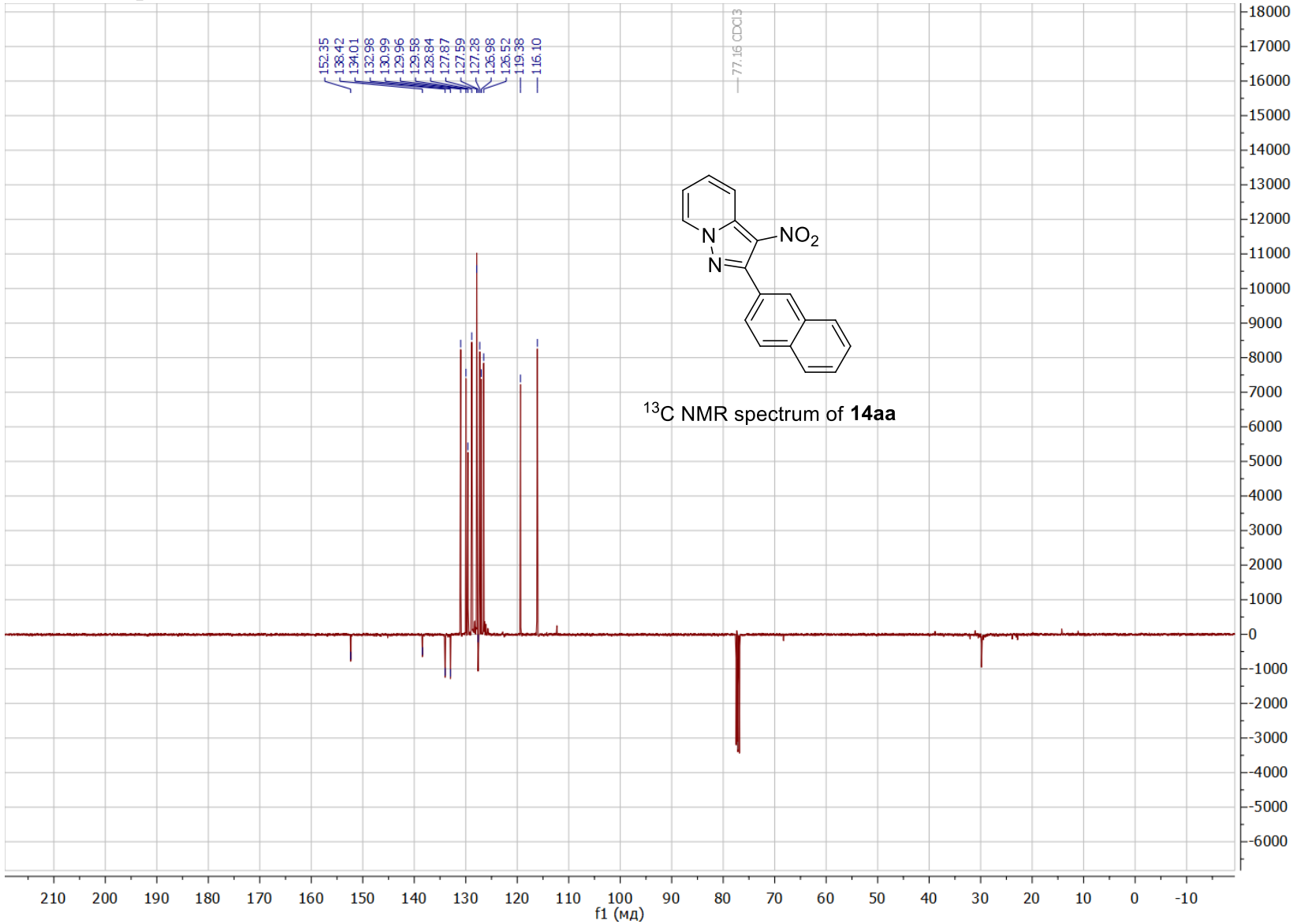


^{1}H and ^{13}C NMR spectral charts for pyrazolo[1,5-*a*]pyridines.

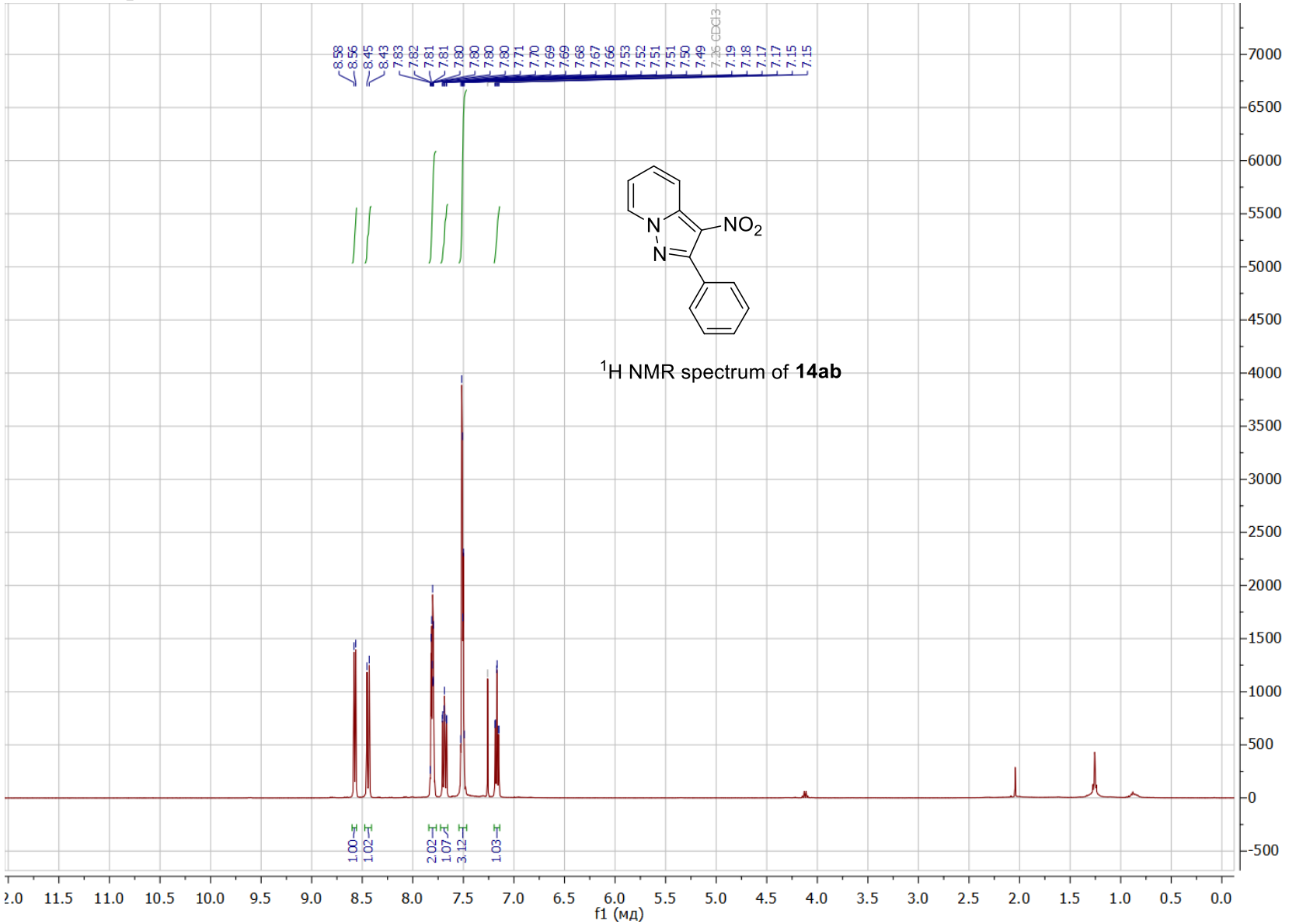
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14aa**



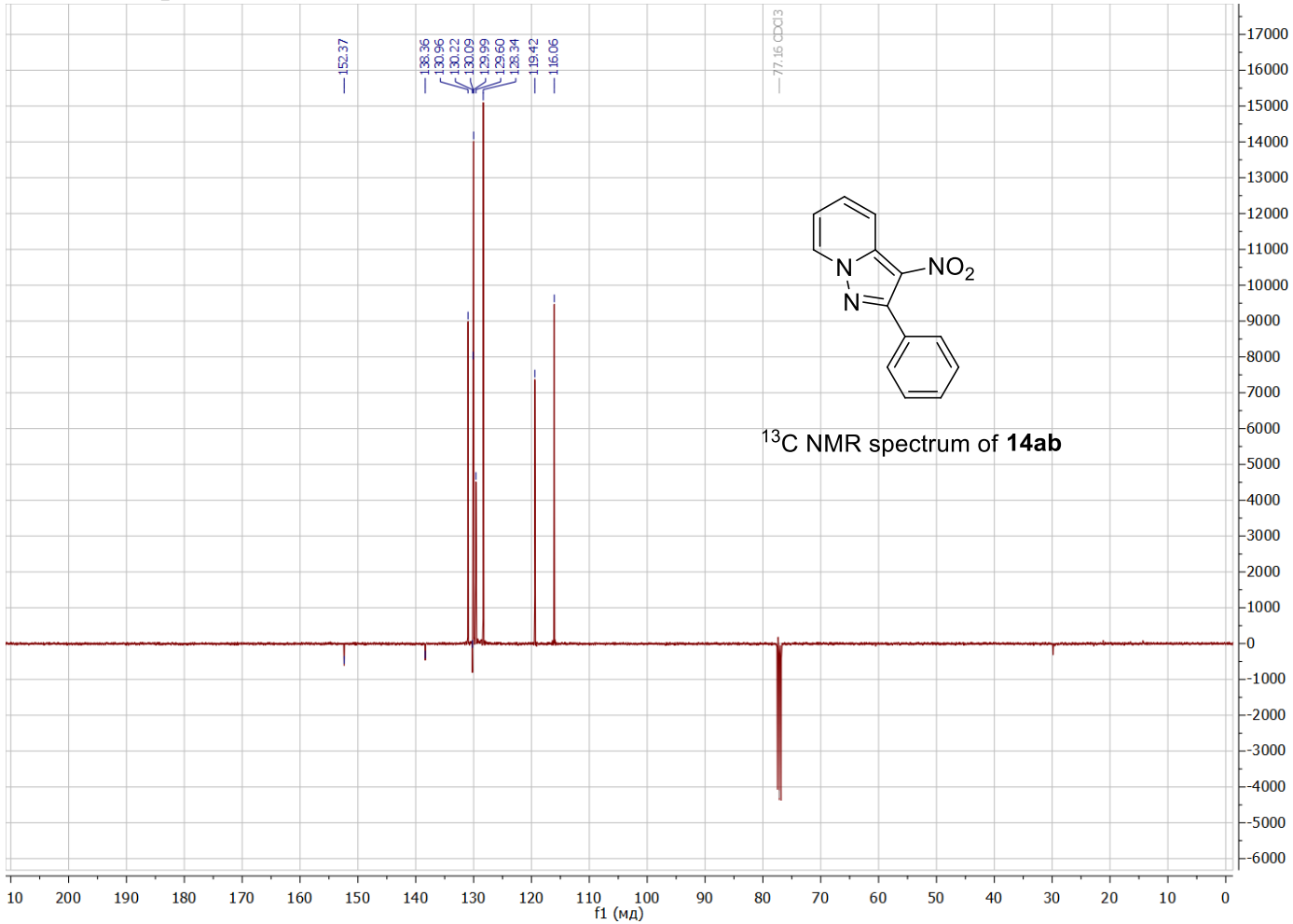
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14aa**



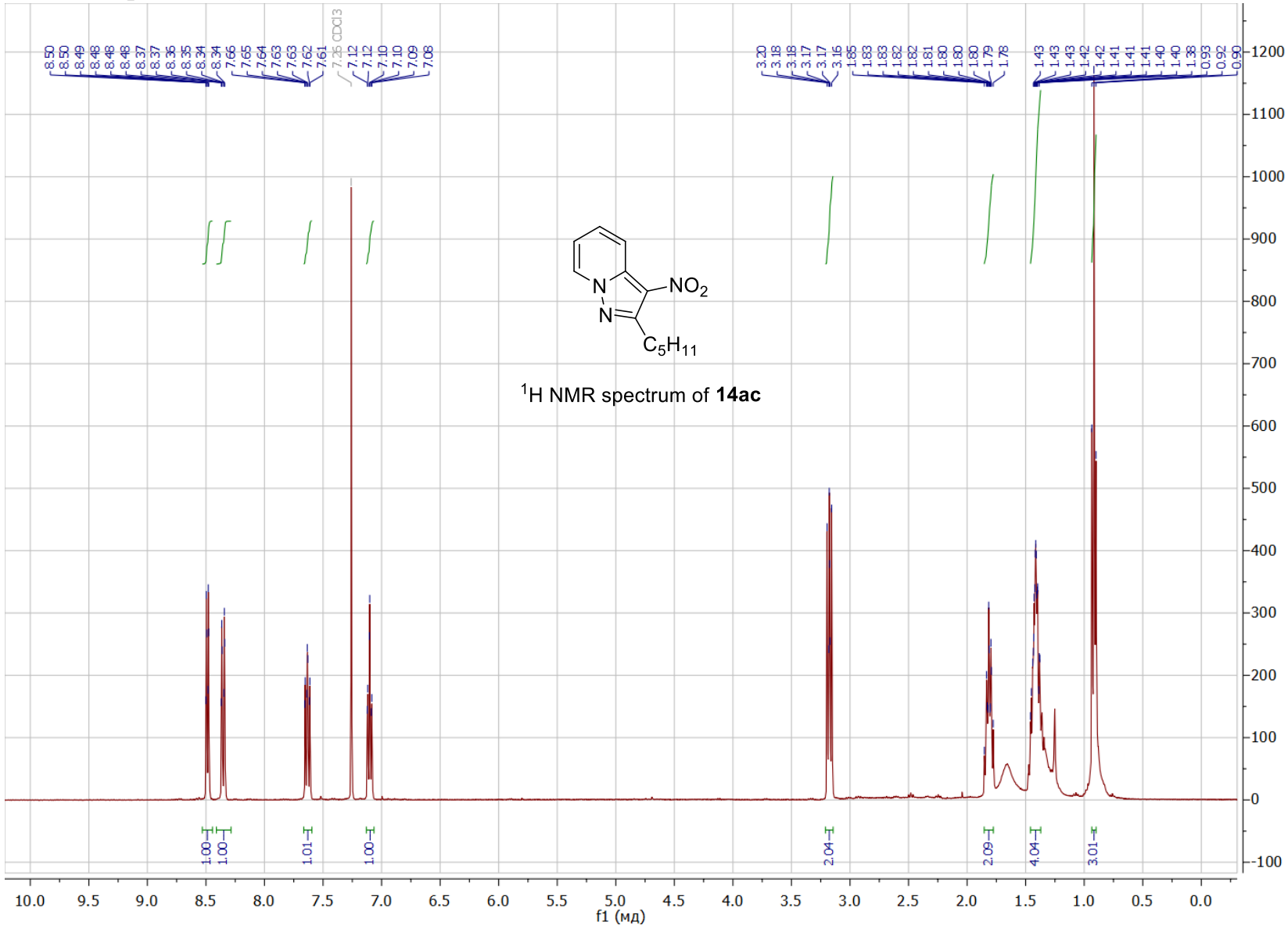
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14ab**



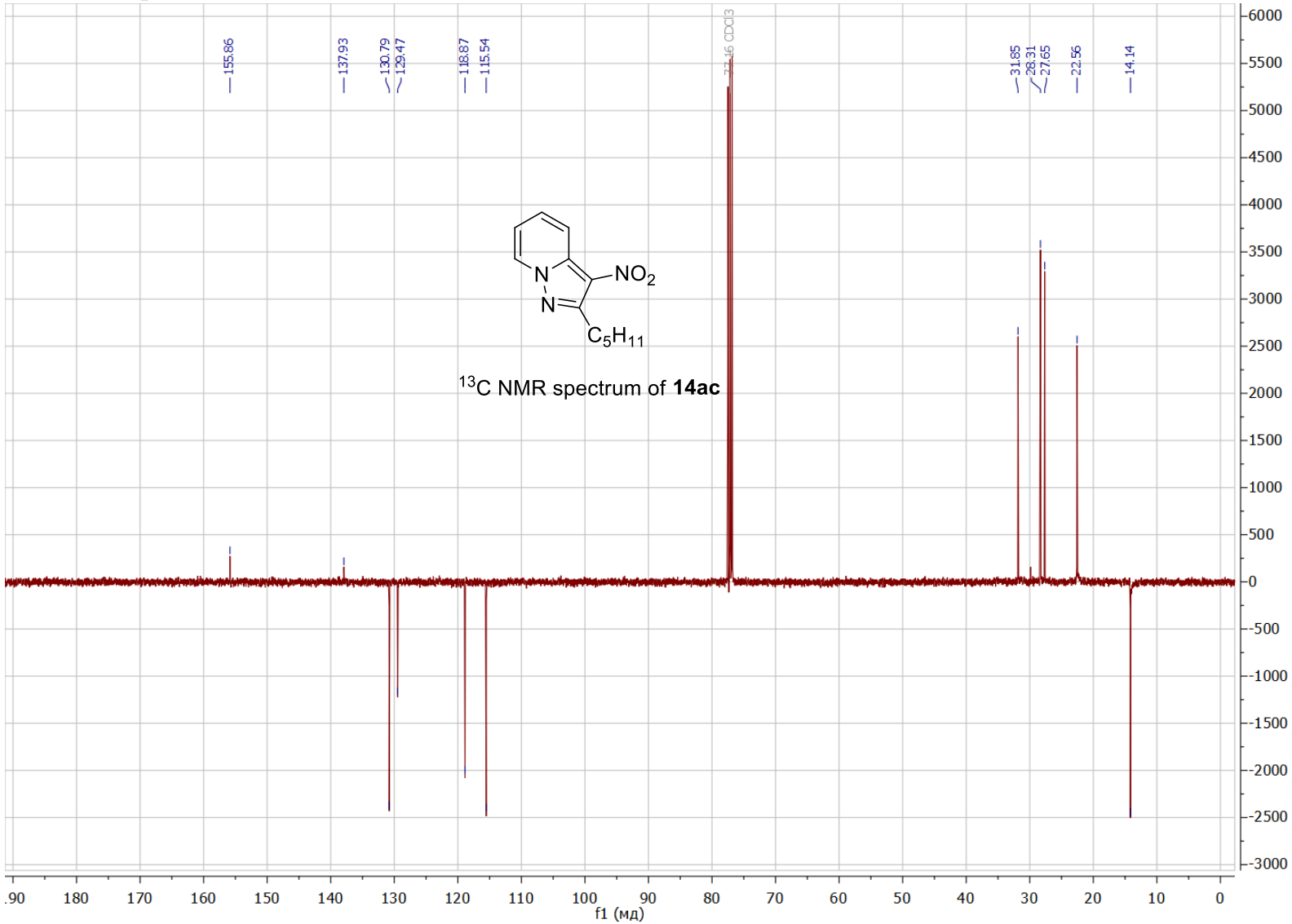
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14ab**



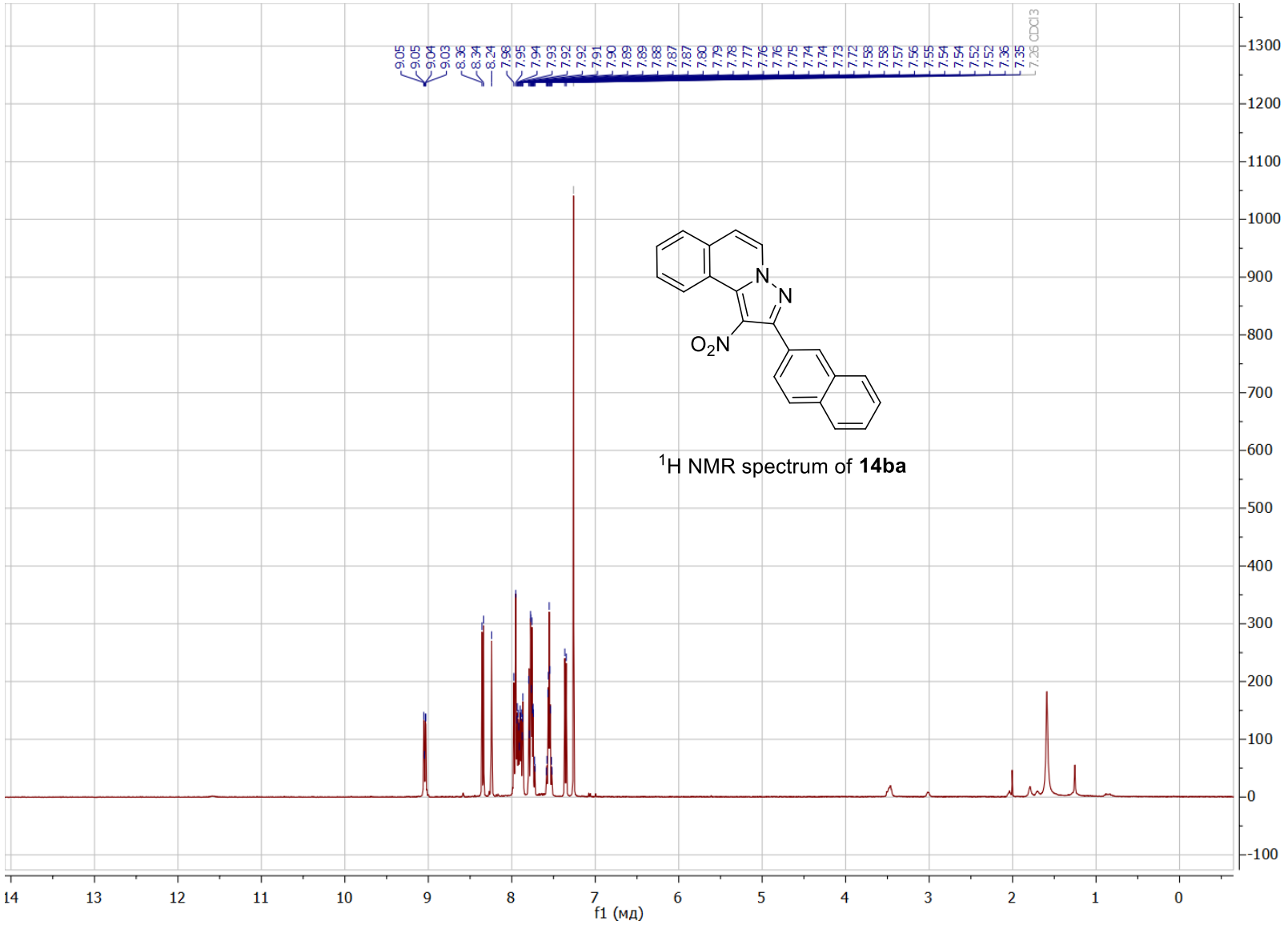
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14ac**



^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14ac**

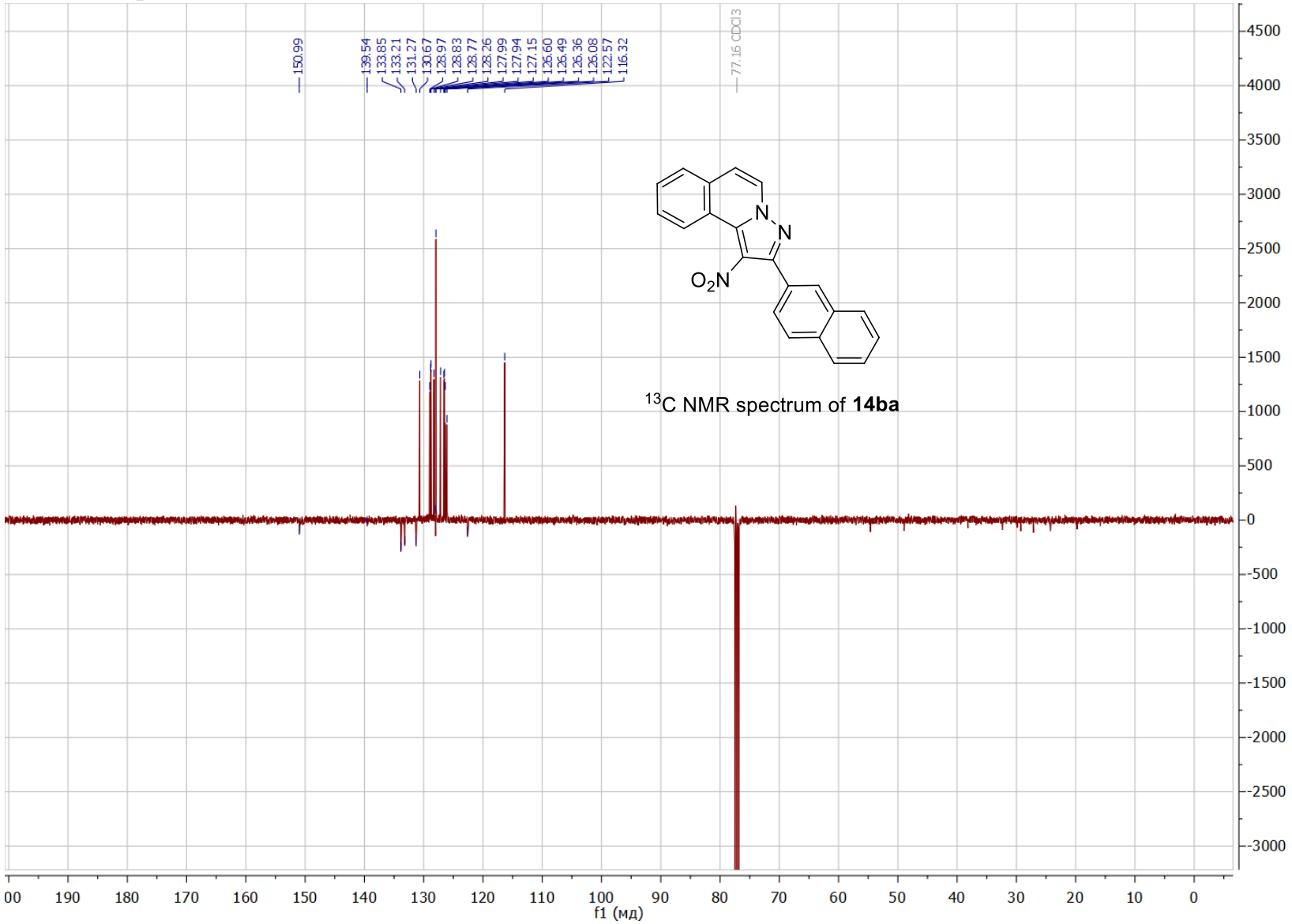


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14ba**

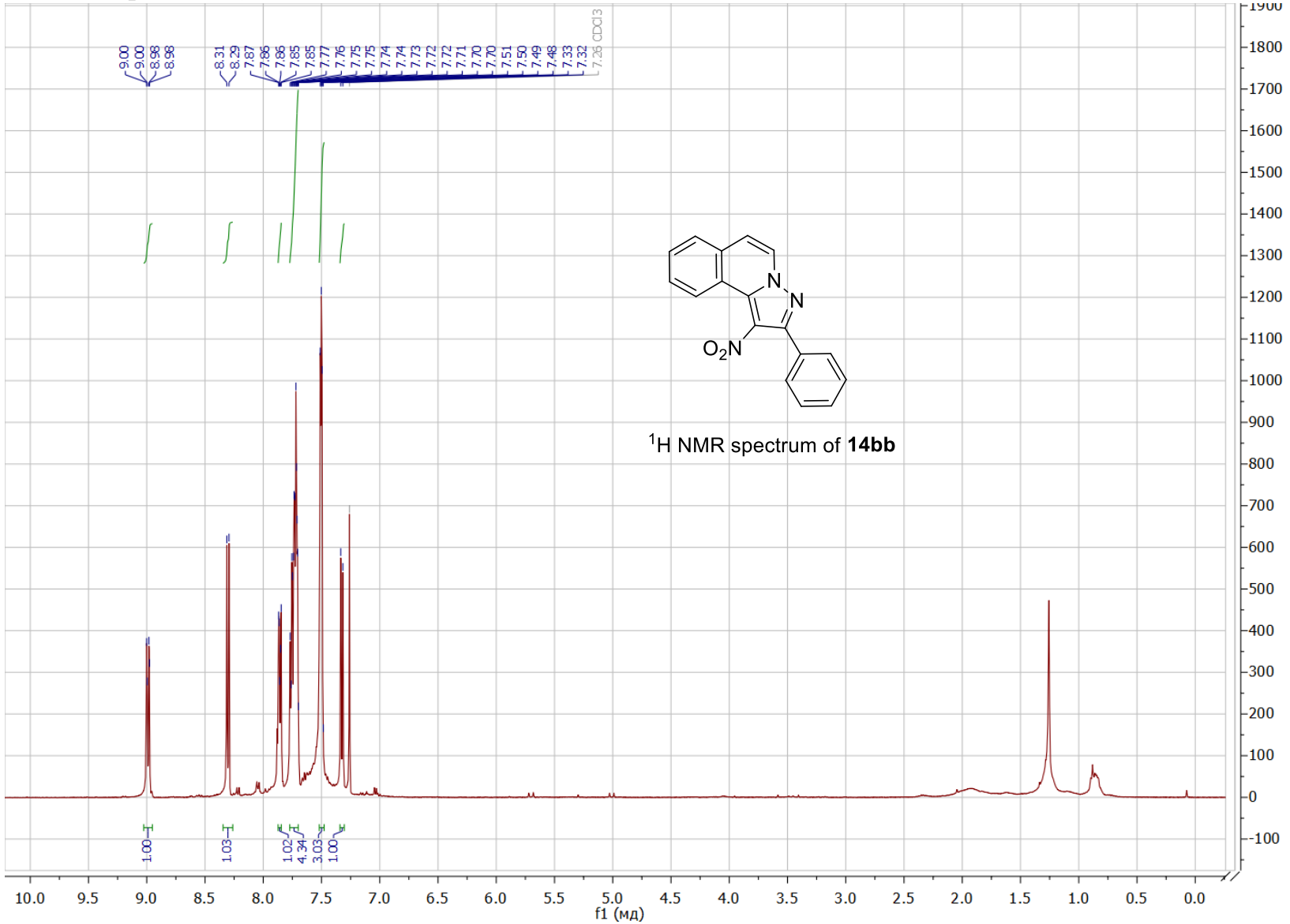


^{1}H NMR spectrum of **14ba**

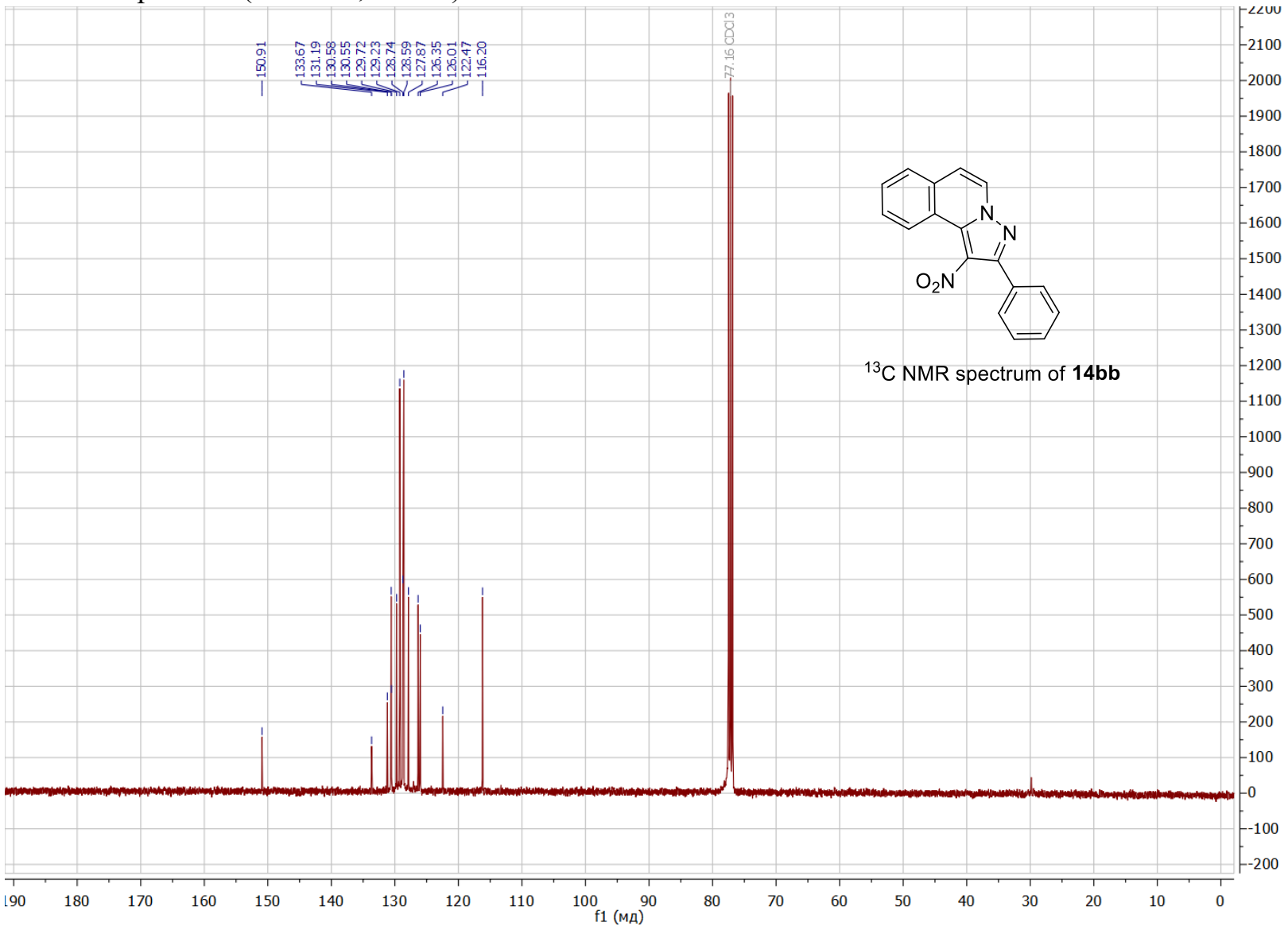
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14ba**



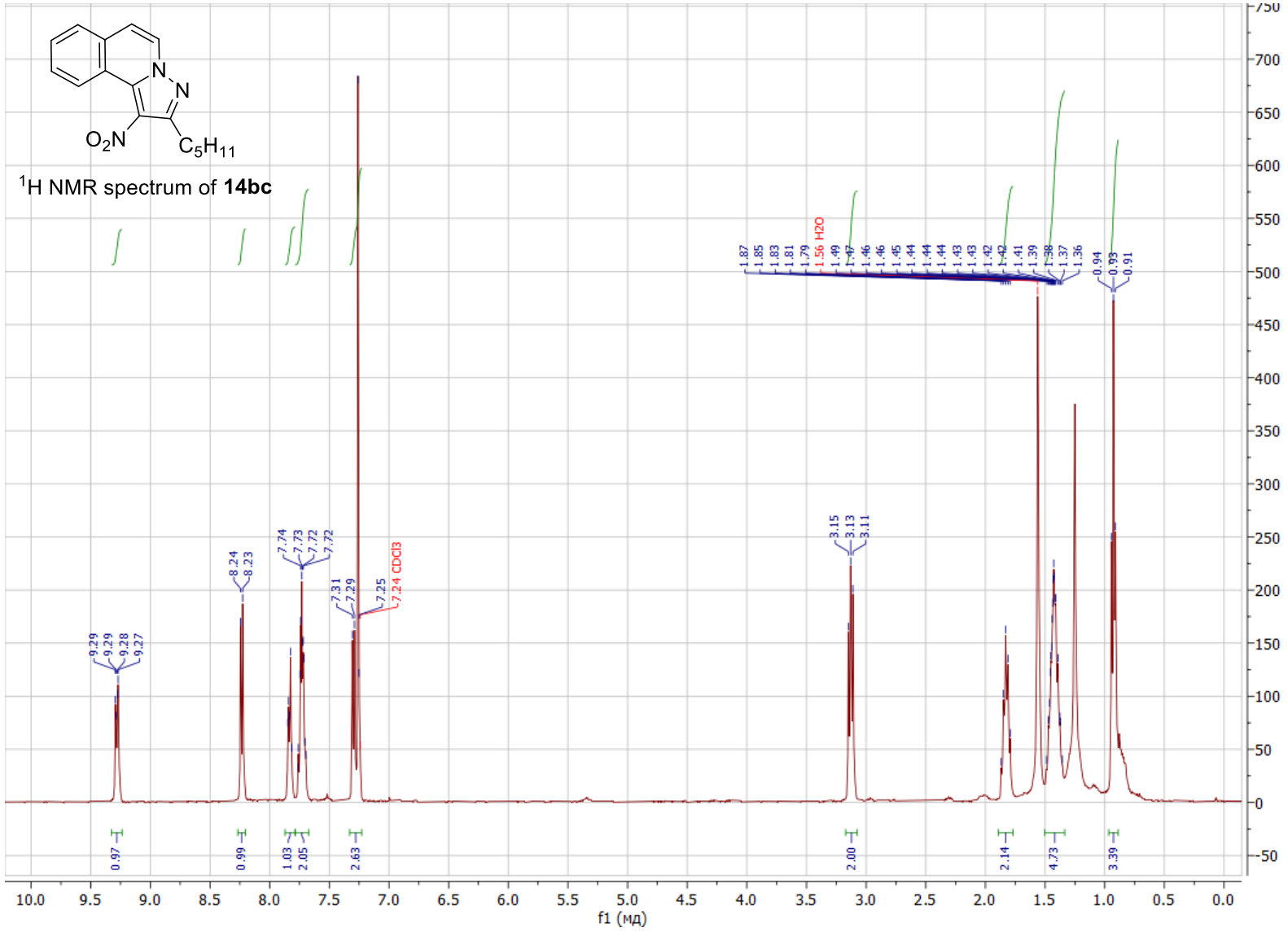
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14bb**



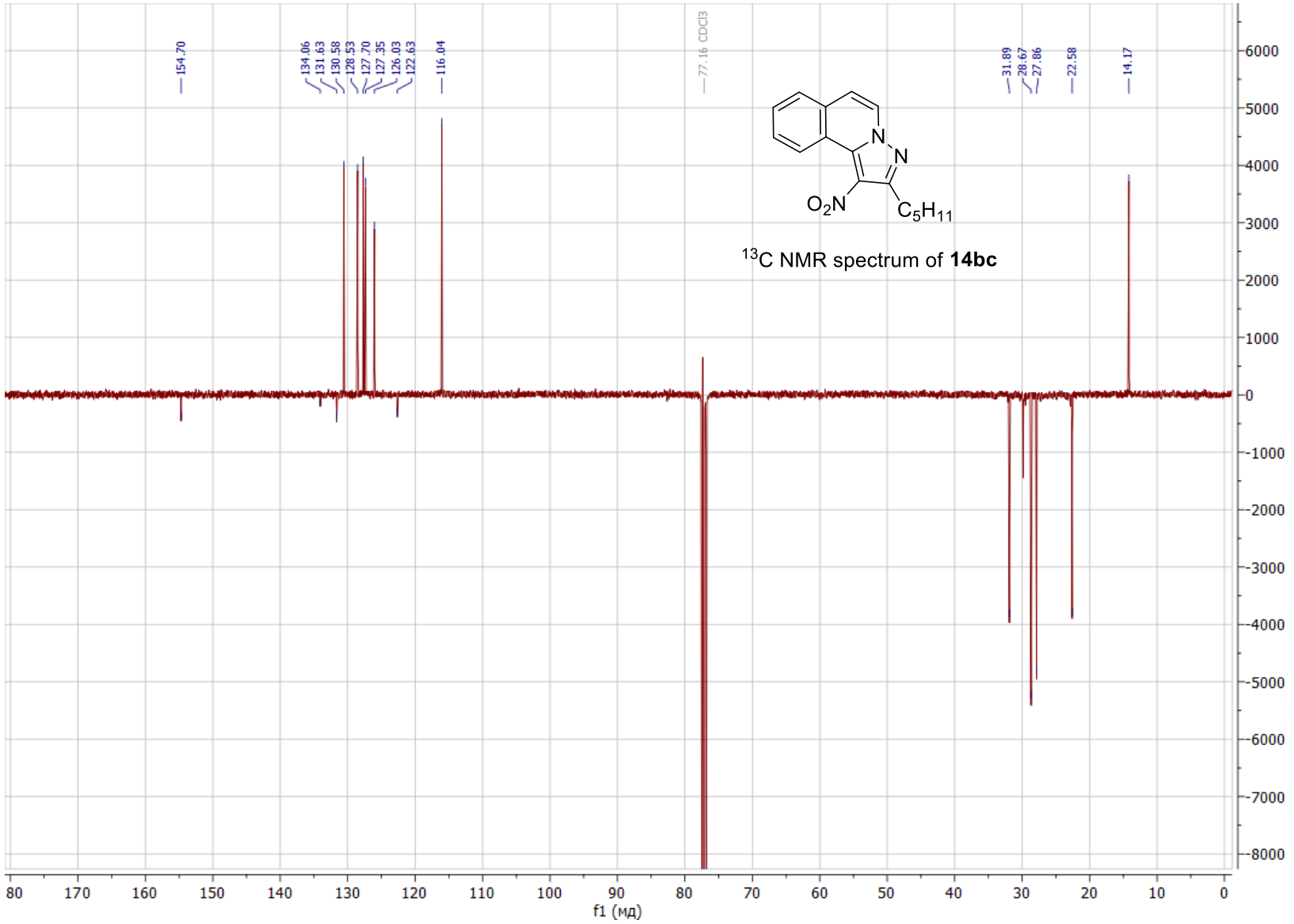
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14bb**



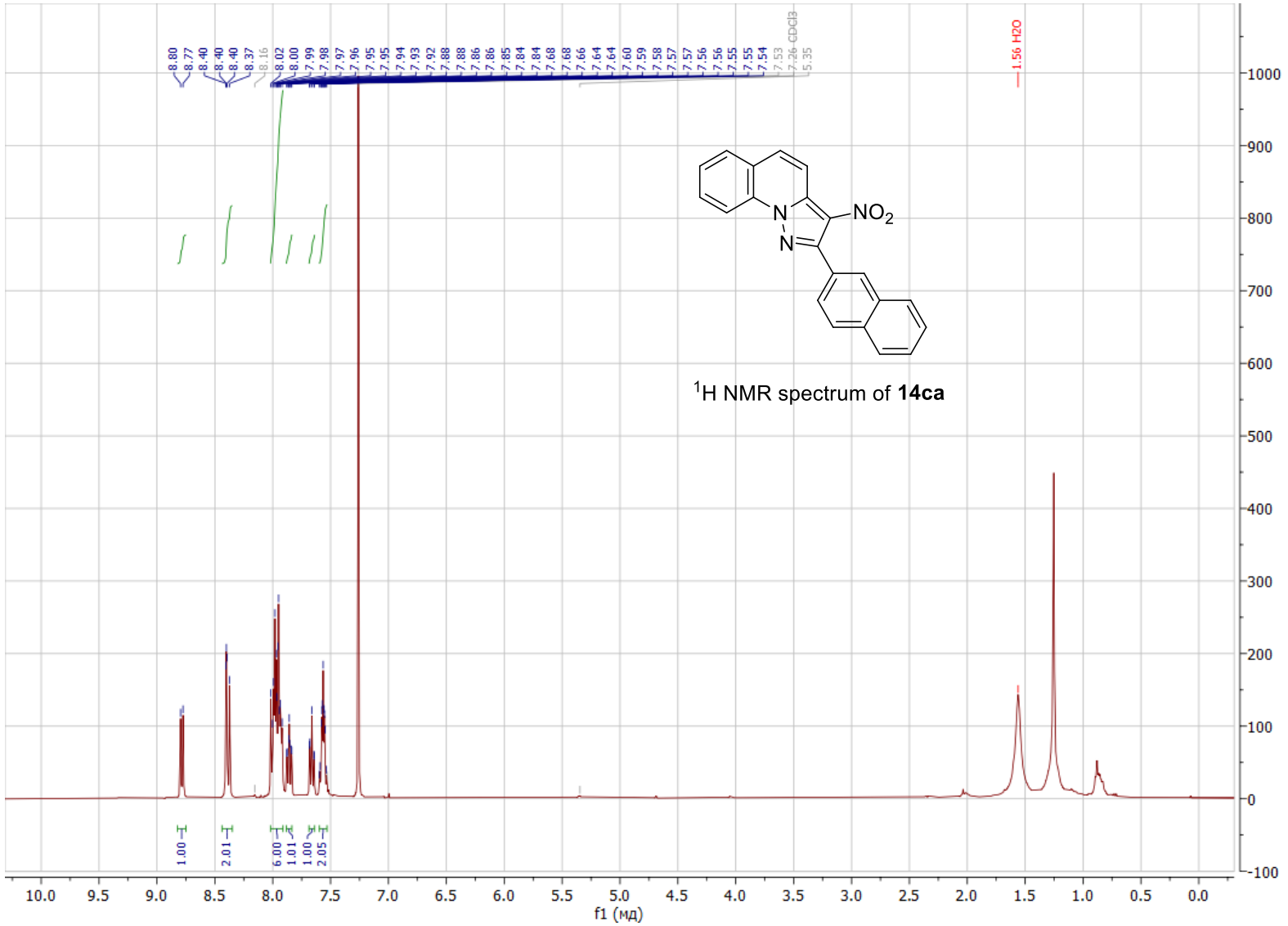
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14bc**



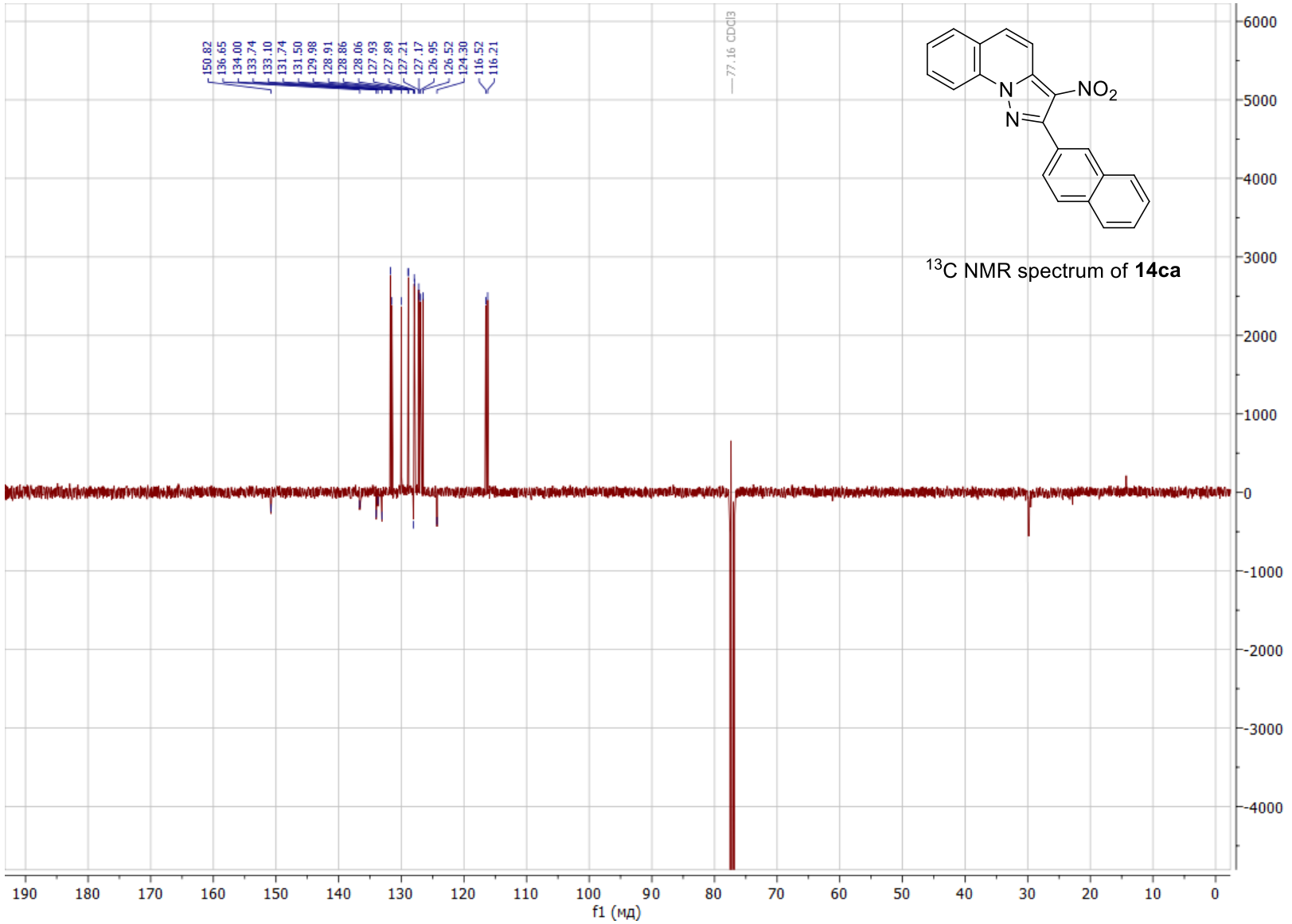
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14bc**



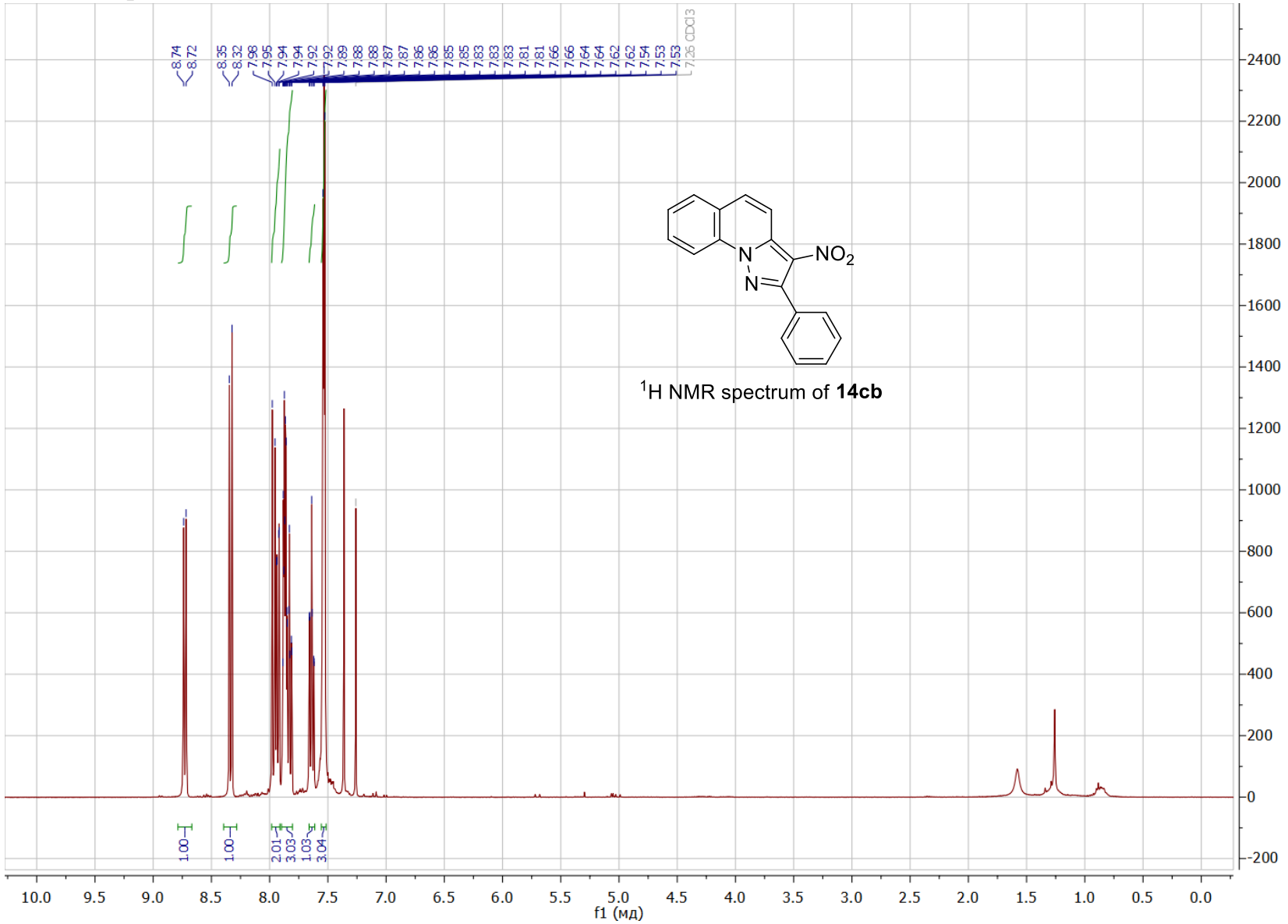
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14ca**



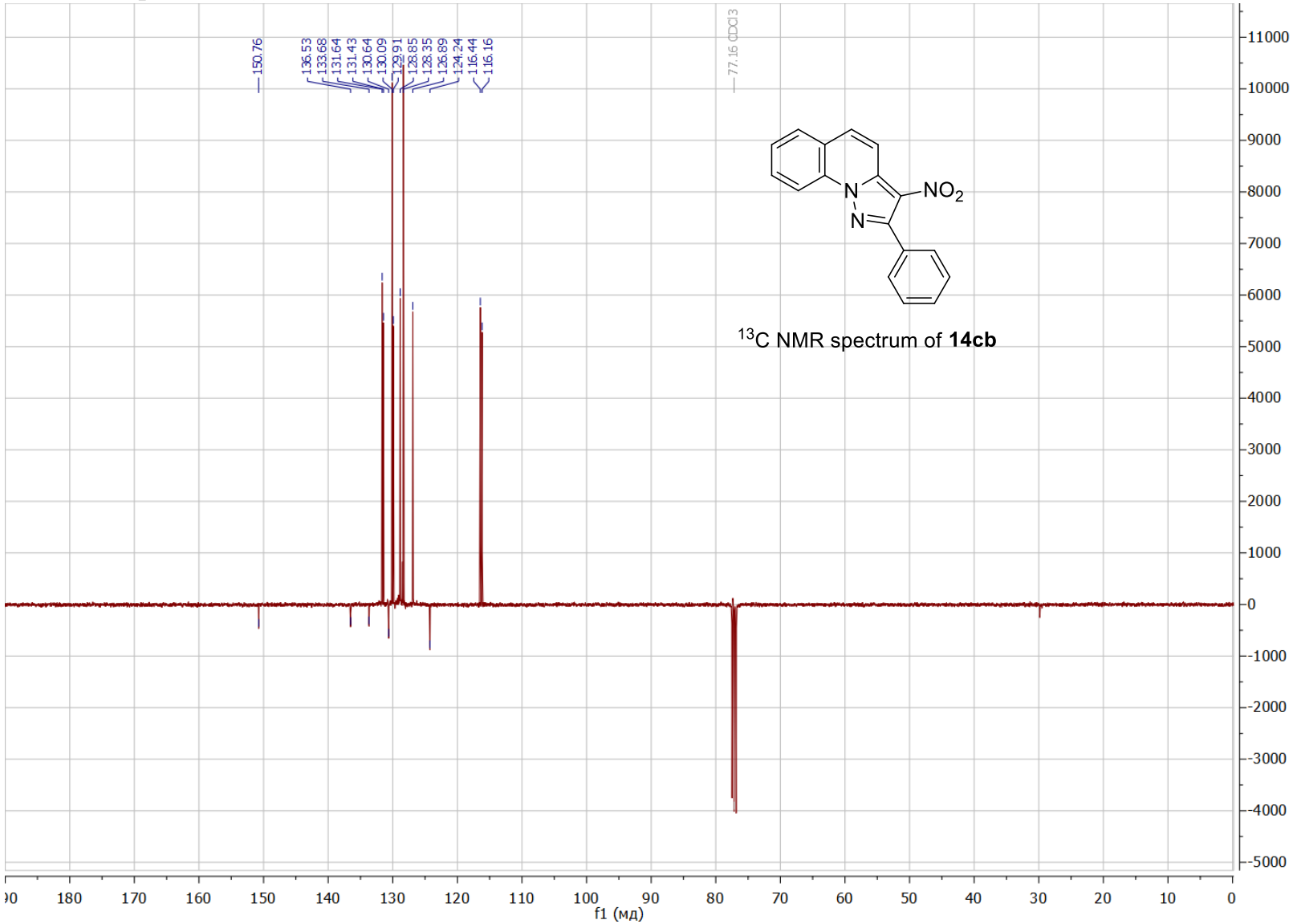
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14ca**



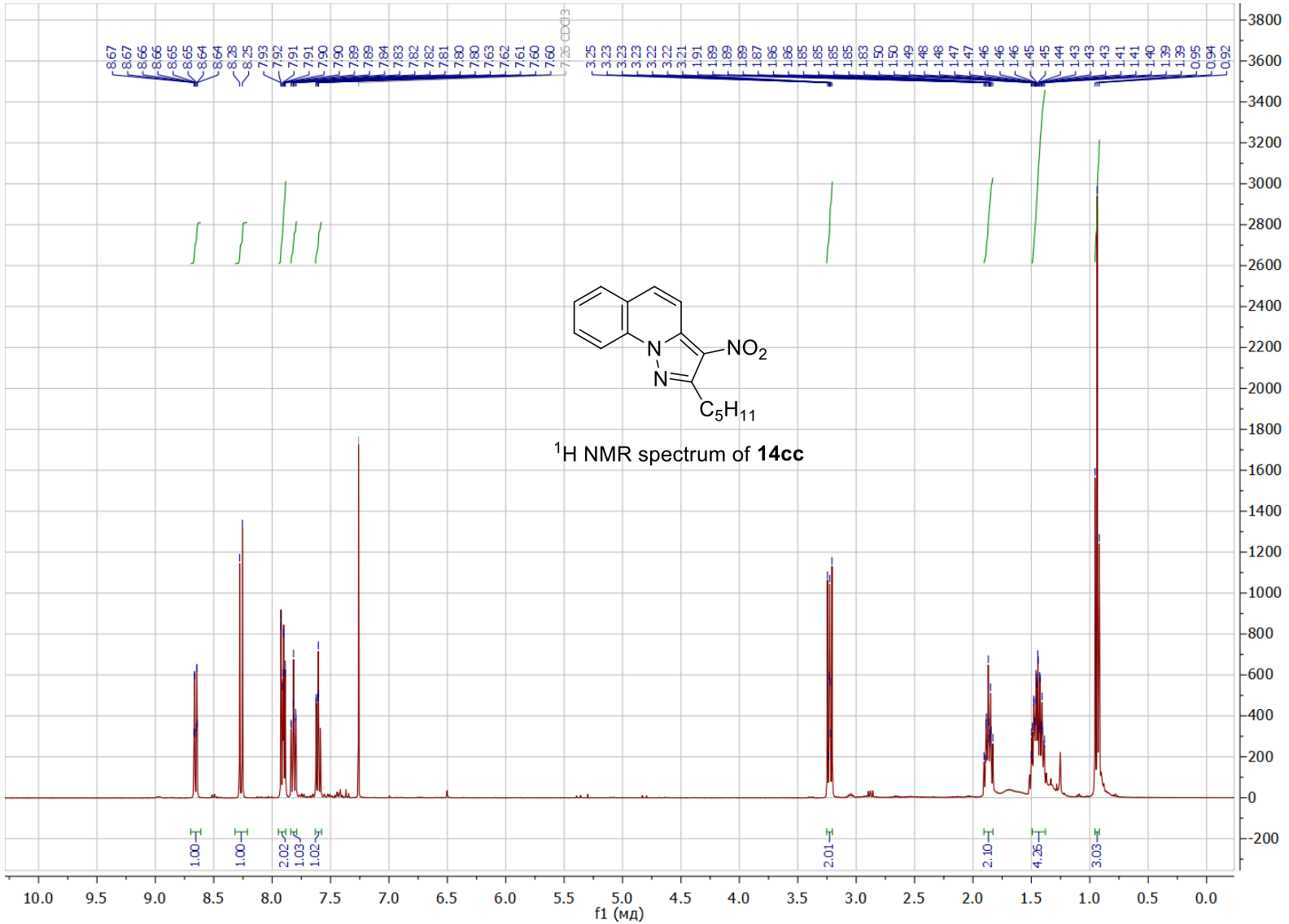
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14cb**



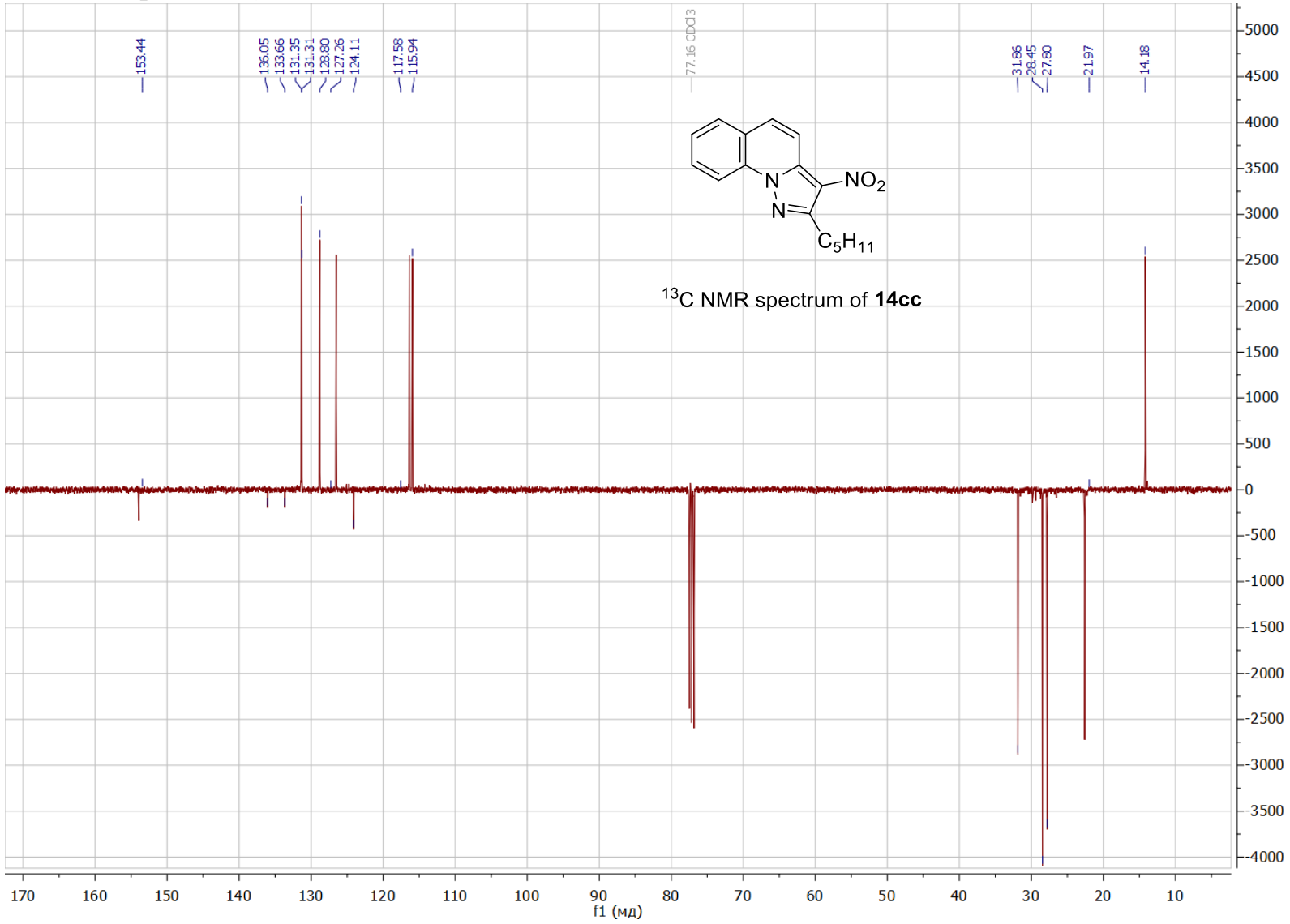
^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14cb**



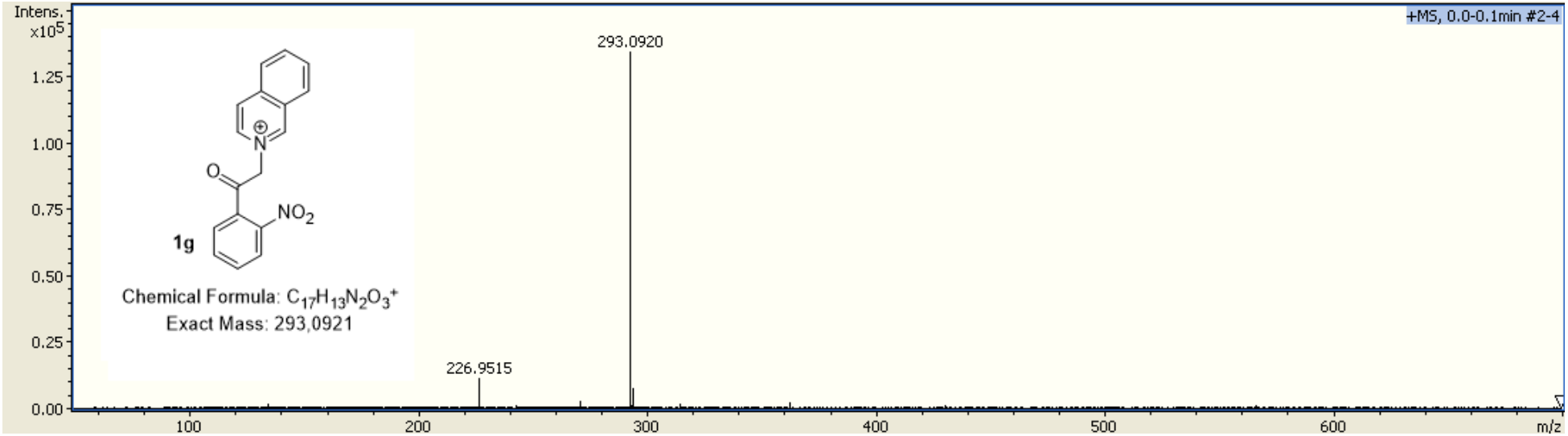
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **14cc**

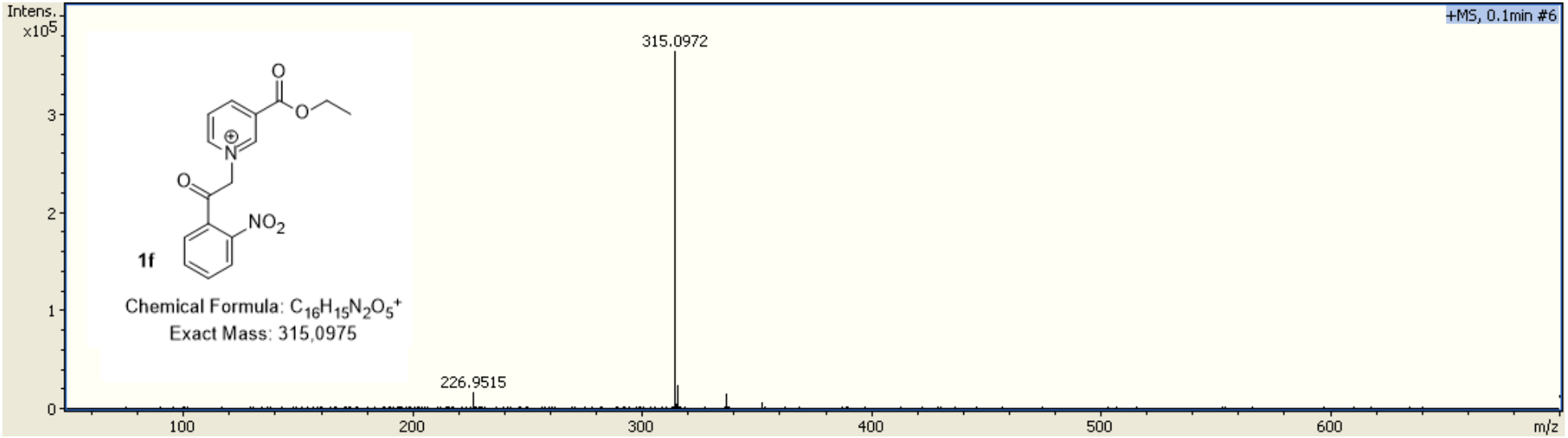


^{13}C NMR spectrum (101MHz, $CDCl_3$) of **14cc**

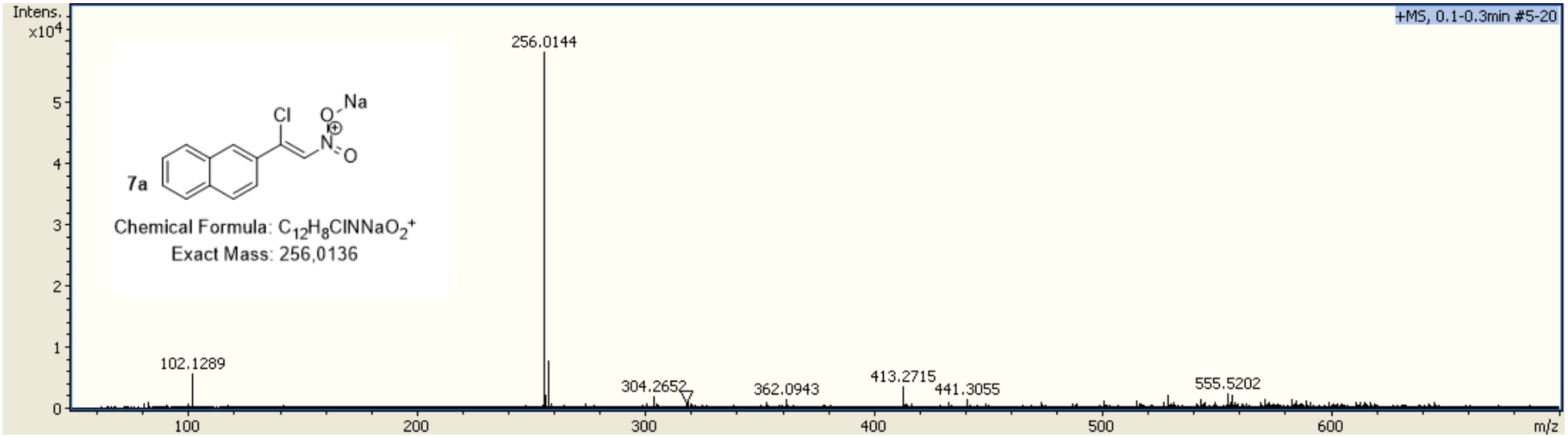


HRMS charts for quaternary pyridinium salts

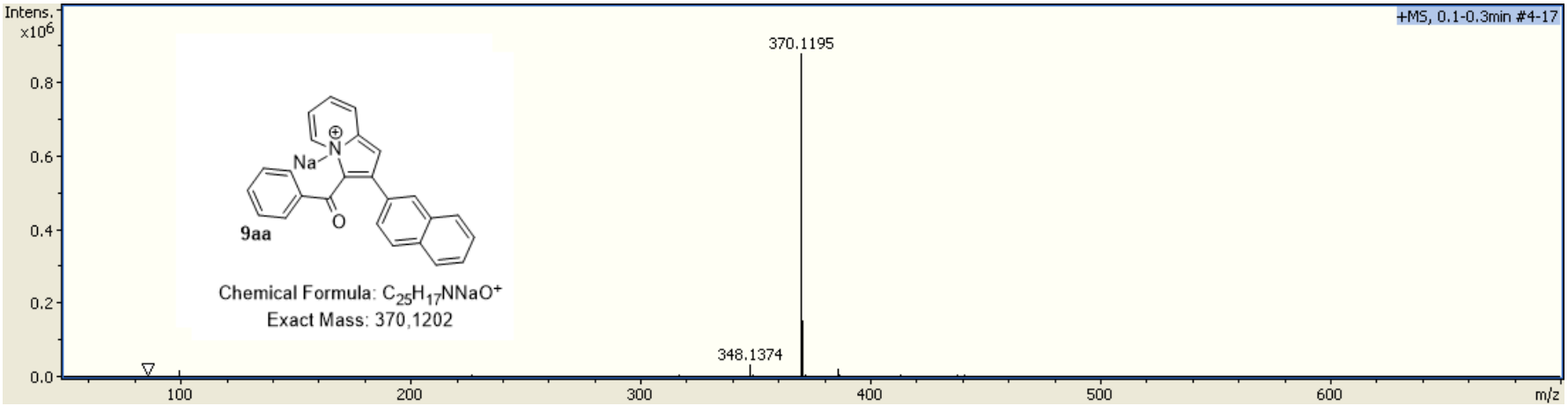


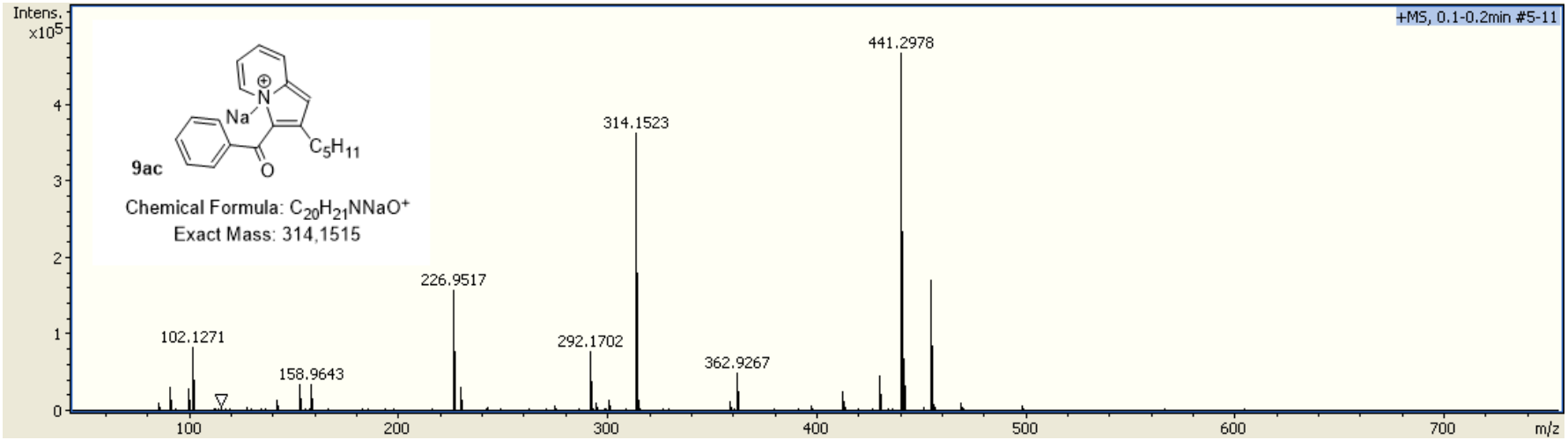


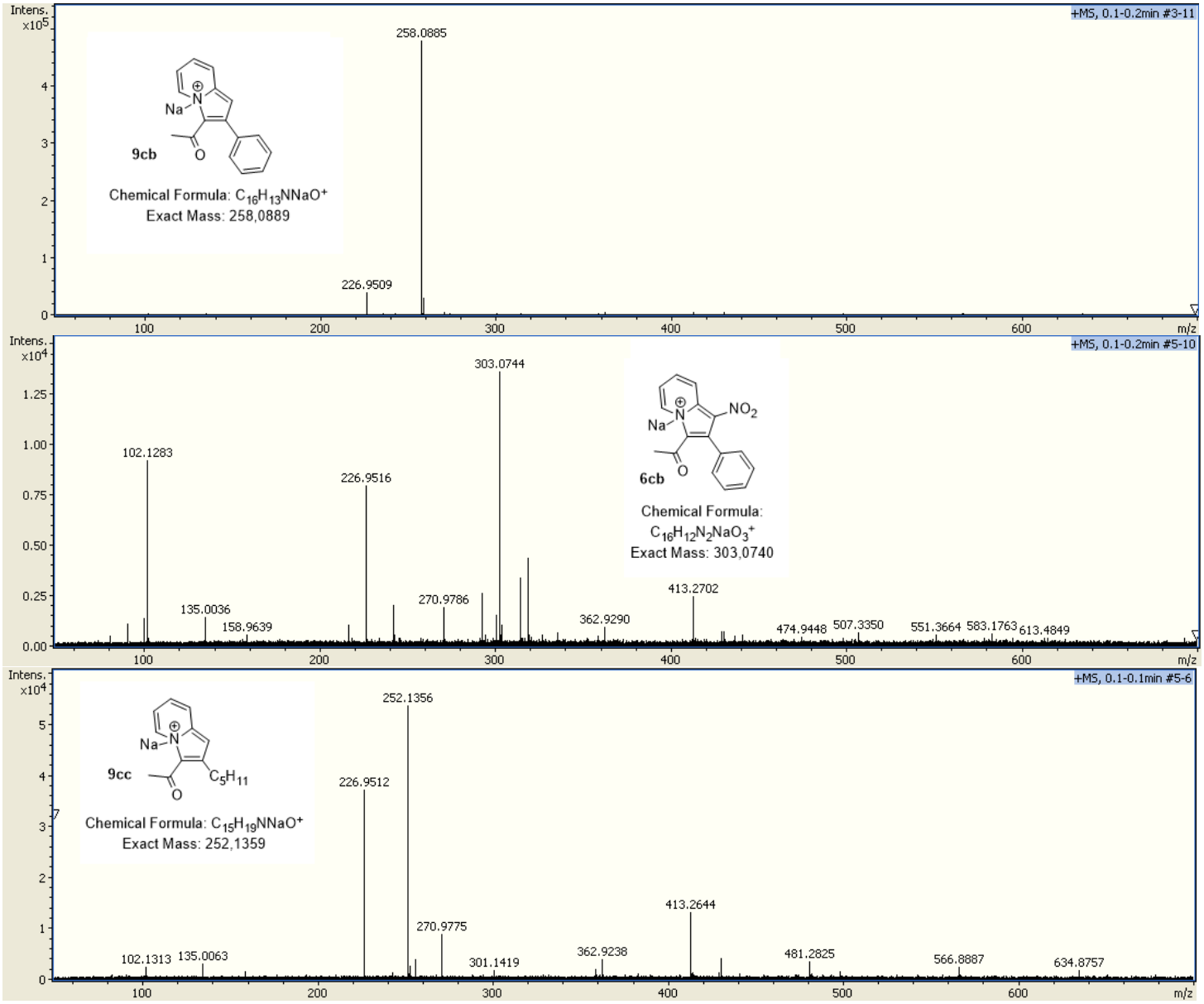
HRMS charts for nitrochloroalkenes

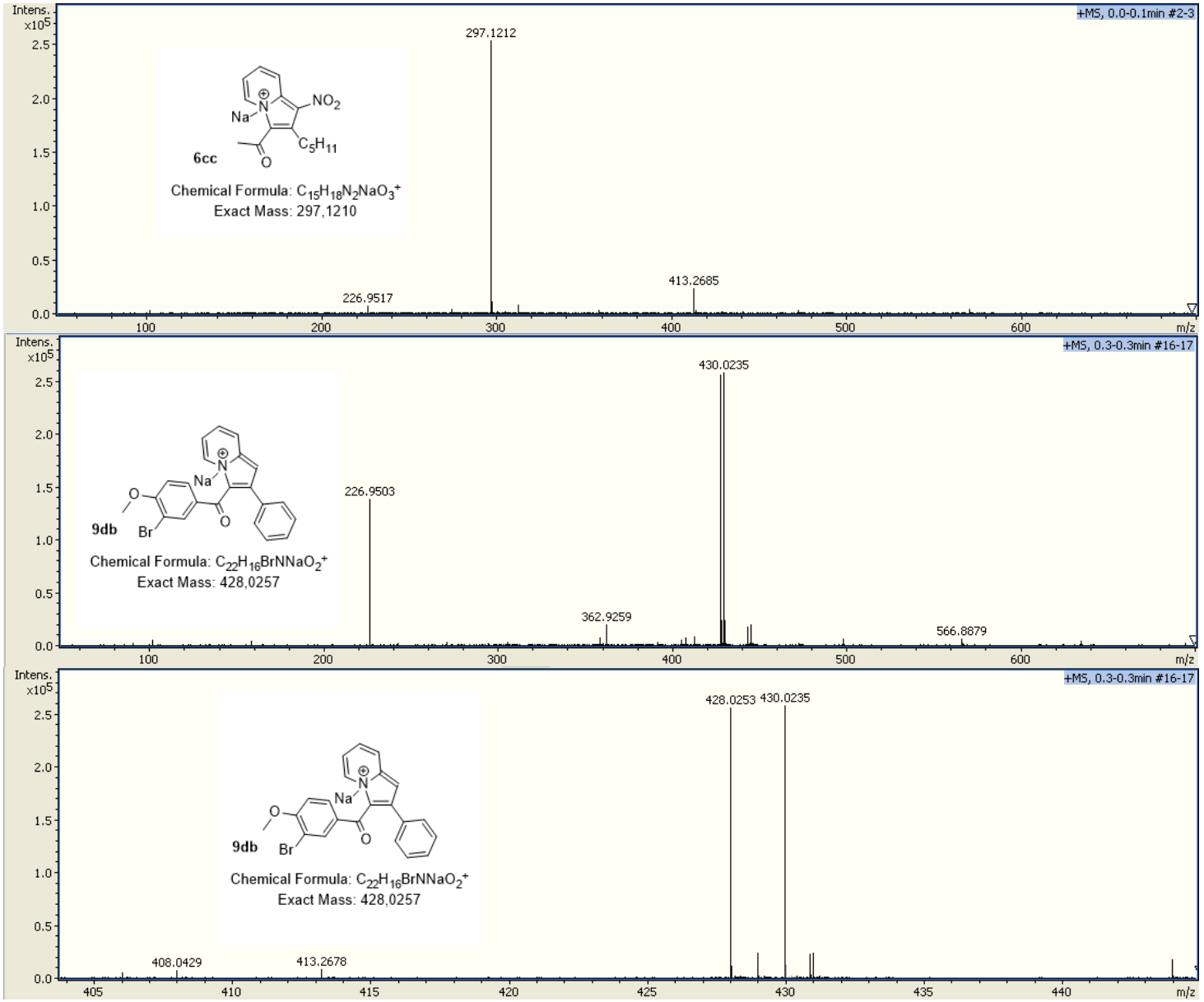


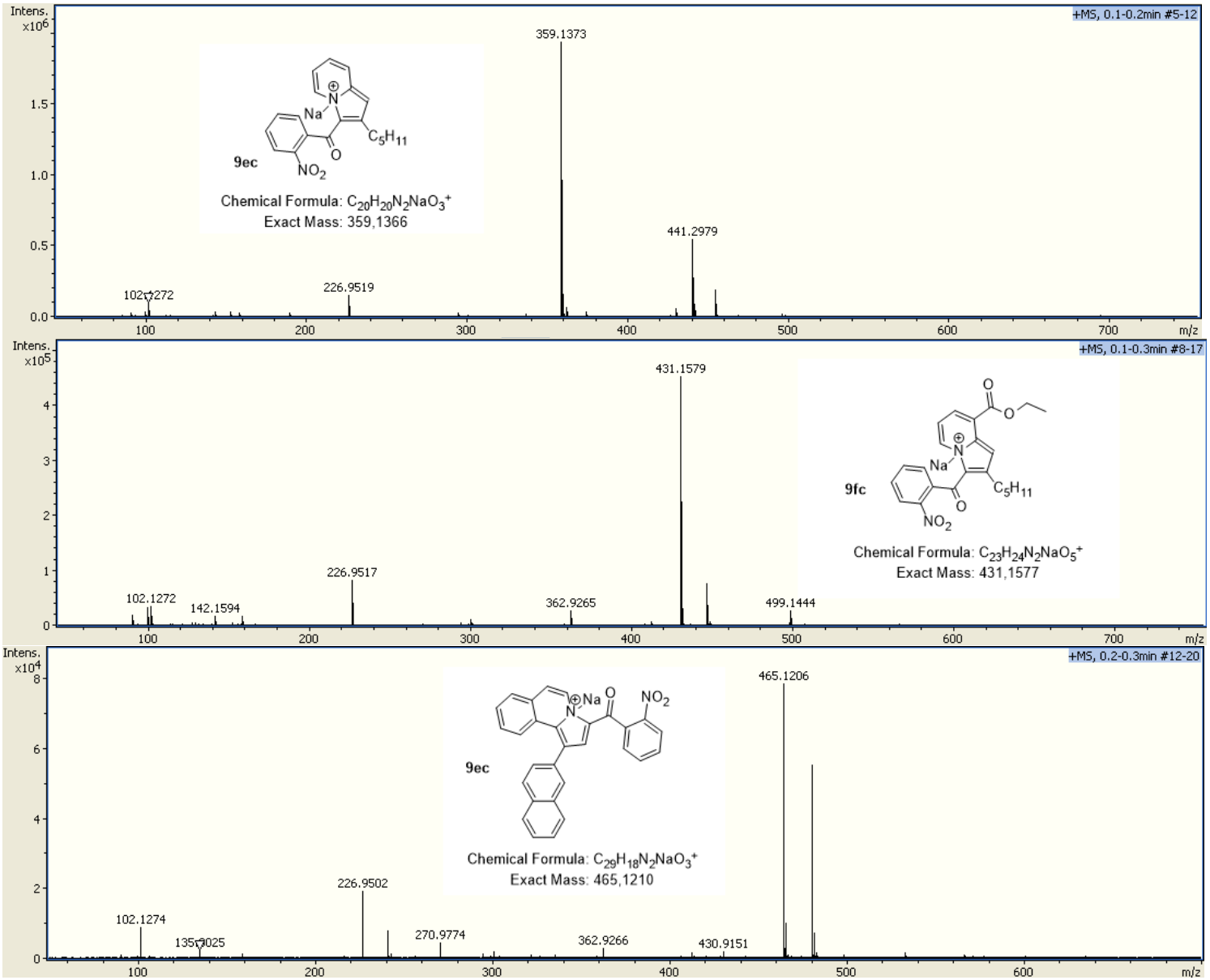
HRMS charts for indolizines



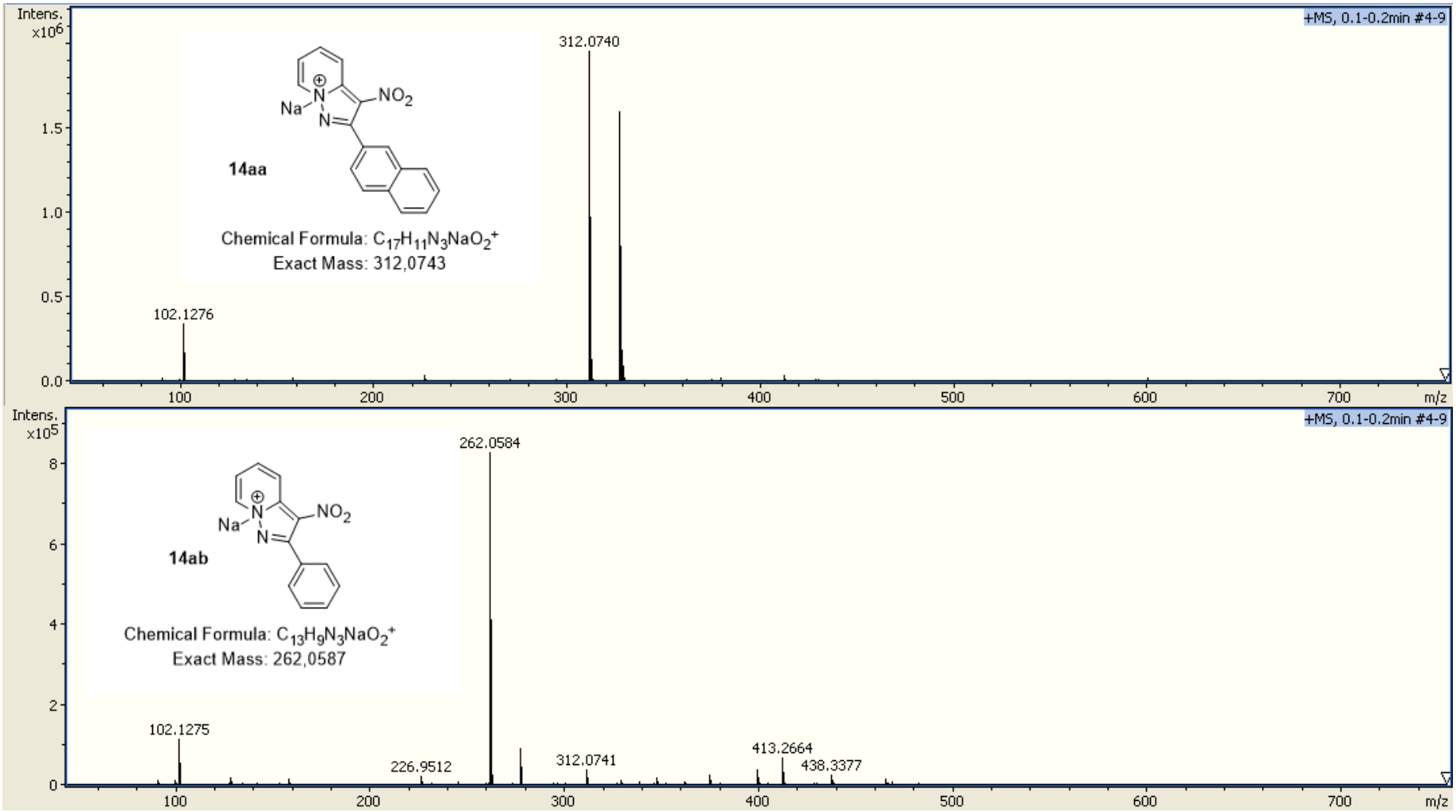


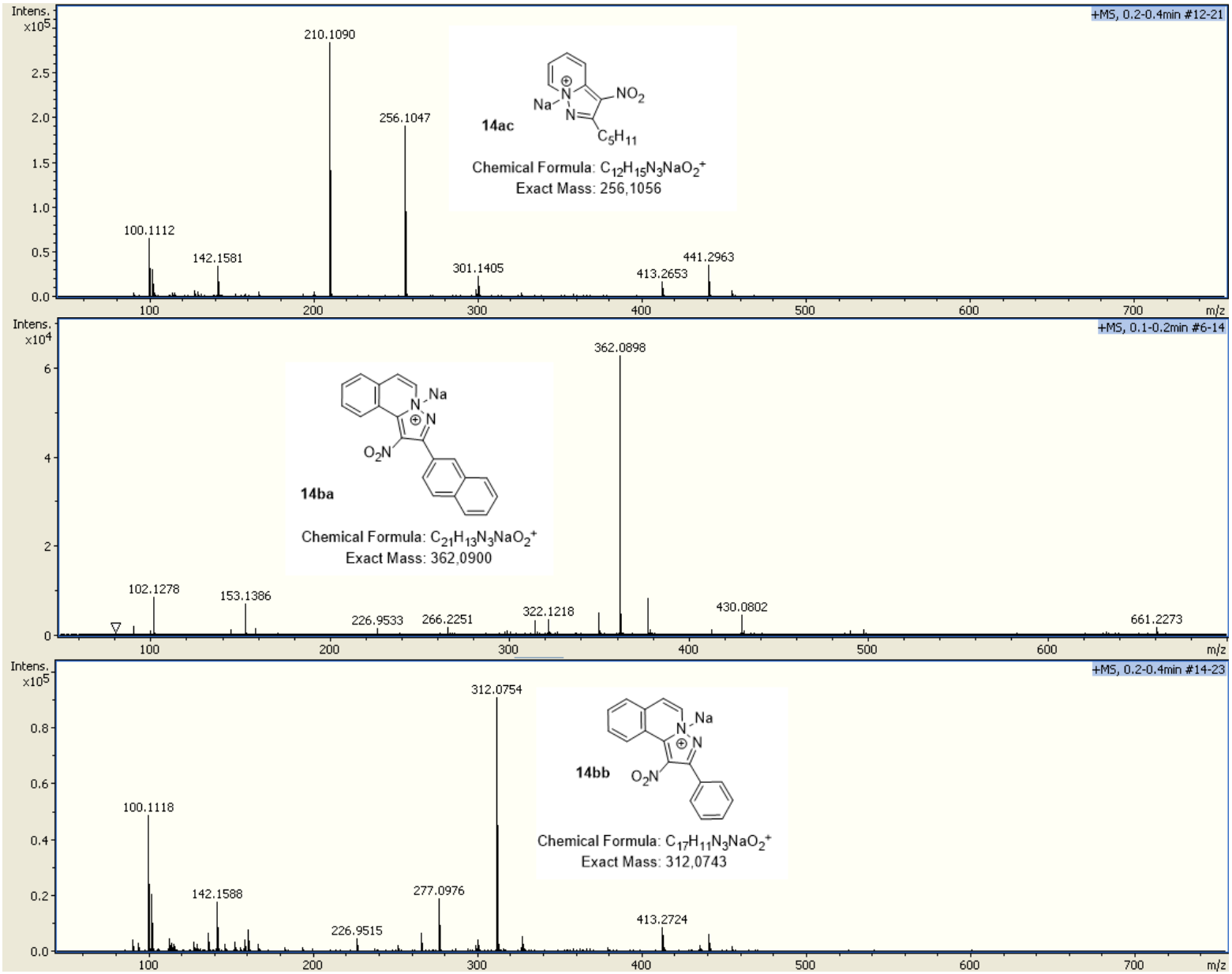

Intens.
x10^5
+MS, 0.1-0.2min #3-11
258.0885
226.9509
9cb
Chemical Formula: C16H13NNaO+
Exact Mass: 258,0889
m/z
Intens.
x10^4
+MS, 0.1-0.2min #5-10
303.0744
102.1283
226.9516
6cb
Chemical Formula:
C16H12N2NaO3+
Exact Mass: 303,0740
135.0036
158.9639
270.9786
362.9290
413.2702
474.9448
507.3350
551.3664
583.1763
613.4849
m/z
Intens.
x10^4
+MS, 0.1-0.1min #5-6
252.1356
226.9512
9cc
Chemical Formula: C15H19NNaO+
Exact Mass: 252,1359
102.1313
135.0063
270.9775
301.1419
362.9238
413.2644
481.2825
566.8887
634.8757
m/z

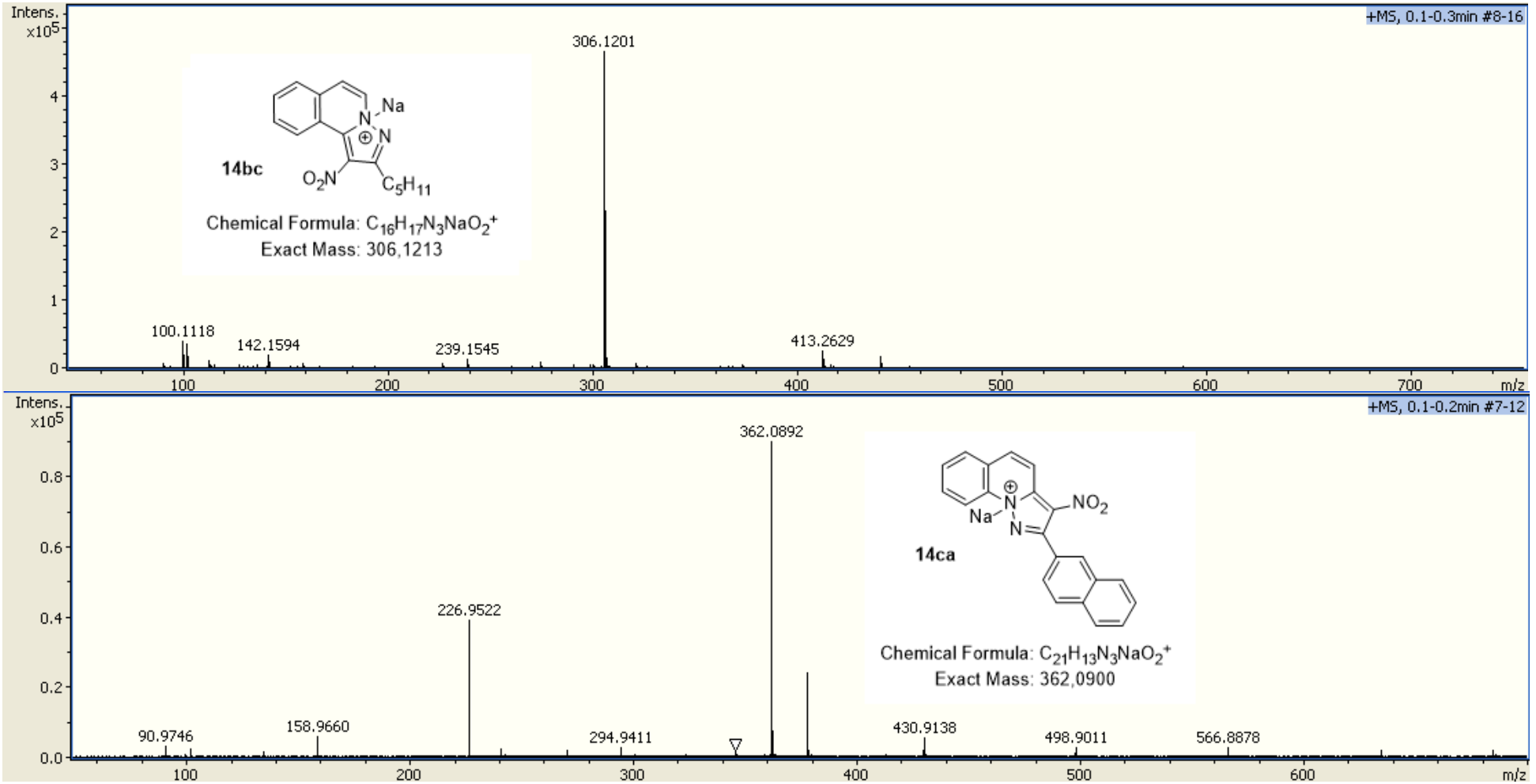

Intens.
x10^5
+MS, 0.0-0.1min #2-3
297.1212
226.9517
413.2685
6cc
Chemical Formula: C15H18N2NaO3+
Exact Mass: 297,1210
+MS, 0.3-0.3min #16-17
430.0235
226.9503
362.9259
566.8879
9db
Chemical Formula: C22H16BrNNaO2+
Exact Mass: 428,0257
+MS, 0.3-0.3min #16-17
428.0253
430.0235
408.0429
413.2678
9db
Chemical Formula: C22H16BrNNaO2+
Exact Mass: 428,0257
m/z

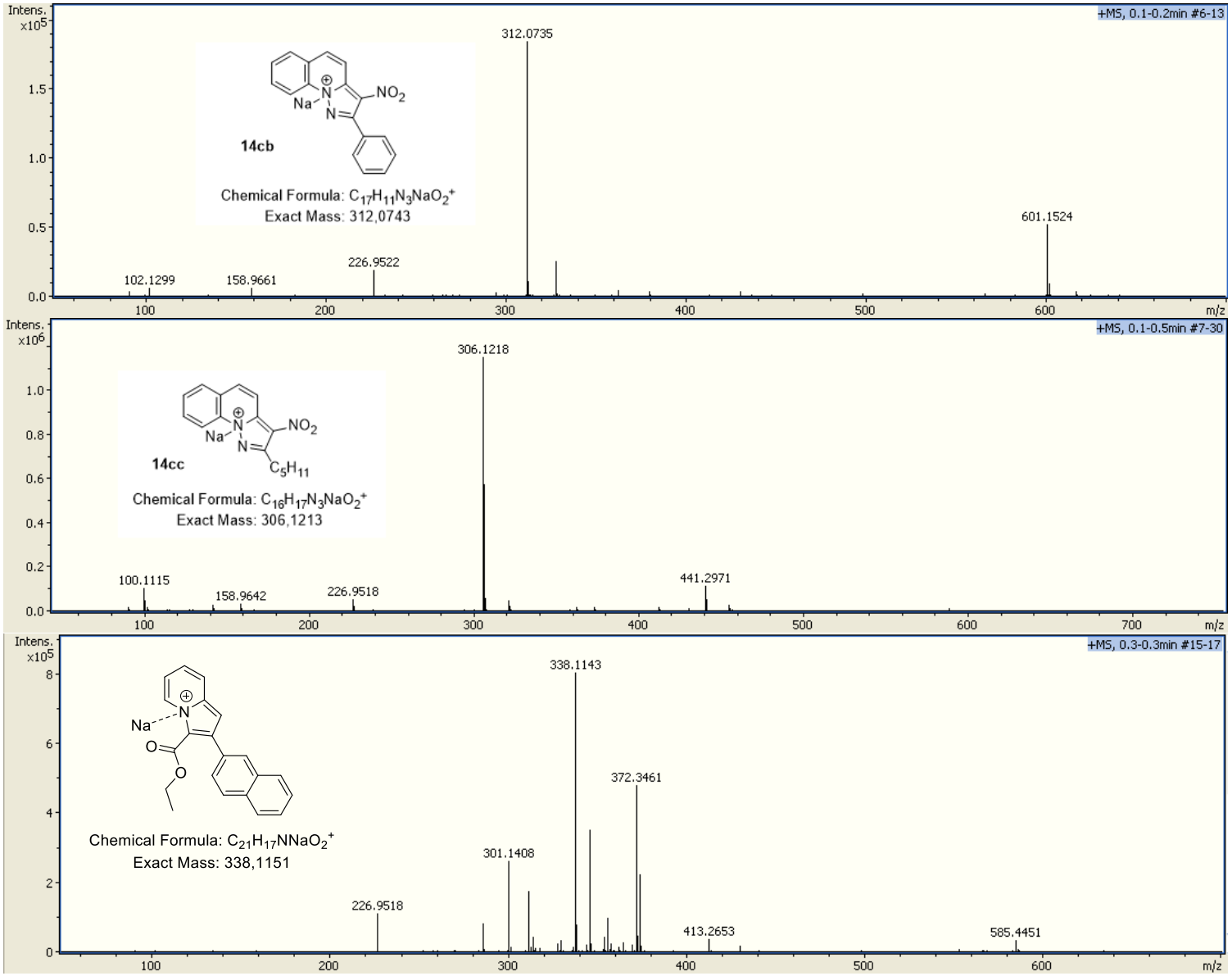

Intens.
x10^6
+MS, 0.1-0.2min #5-12
359.1373
441.2979
226.9519
102.1272
9ec
Chemical Formula: C20H20N2NaO3+
Exact Mass: 359,1366
m/z
Intens.
x10^5
+MS, 0.1-0.3min #8-17
431.1579
226.9517
102.1272
142.1594
362.9265
499.1444
9fc
Chemical Formula: C23H24N2NaO5+
Exact Mass: 431,1577
m/z
Intens.
x10^4
+MS, 0.2-0.3min #12-20
465.1206
226.9502
102.1274
135.0025
270.9774
362.9266
430.9151
9ec
Chemical Formula: C29H18N2NaO3+
Exact Mass: 465,1210
m/z

HRMS charts for pyrazolo[1,5-*a*]pyridines




+MS, 0.2-0.4min #12-21
Intens.
x10^5
210.1090
256.1047
100.1112
142.1581
301.1405
413.2653
441.2963
14ac
Chemical Formula: C12H15N3NaO2+
Exact Mass: 256,1056
+MS, 0.1-0.2min #6-14
Intens.
x10^4
362.0898
102.1278
153.1386
226.9533
266.2251
322.1218
430.0802
661.2273
14ba
Chemical Formula: C21H13N3NaO2+
Exact Mass: 362,0900
+MS, 0.2-0.4min #14-23
Intens.
x10^5
312.0754
100.1118
142.1588
226.9515
277.0976
413.2724
14bb
Chemical Formula: C17H11N3NaO2+
Exact Mass: 312,0743
m/z


Intens.
x10^5
+MS, 0.1-0.3min #8-16
306.1201
100.1118
142.1594
239.1545
413.2629
14bc
Chemical Formula: C16H17N3NaO2+
Exact Mass: 306,1213
m/z
Intens.
x10^5
+MS, 0.1-0.2min #7-12
362.0892
226.9522
90.9746
158.9660
294.9411
430.9138
498.9011
566.8878
14ca
Chemical Formula: C21H13N3NaO2+
Exact Mass: 362,0900
m/z


Intens.
x10^5
+MS, 0.1-0.2min #6-13
312.0735
601.1524
226.9522
102.1299
158.9661
14cb
Chemical Formula: C17H11N3NaO2+
Exact Mass: 312,0743
m/z
Intens.
x10^6
+MS, 0.1-0.5min #7-30
306.1218
441.2971
100.1115
158.9642
226.9518
14cc
Chemical Formula: C16H17N3NaO2+
Exact Mass: 306,1213
m/z
Intens.
x10^5
+MS, 0.3-0.3min #15-17
338.1143
372.3461
301.1408
226.9518
413.2653
585.4451
Chemical Formula: C21H17NNaO2+
Exact Mass: 338,1151
m/z

X-Ray crystallography data

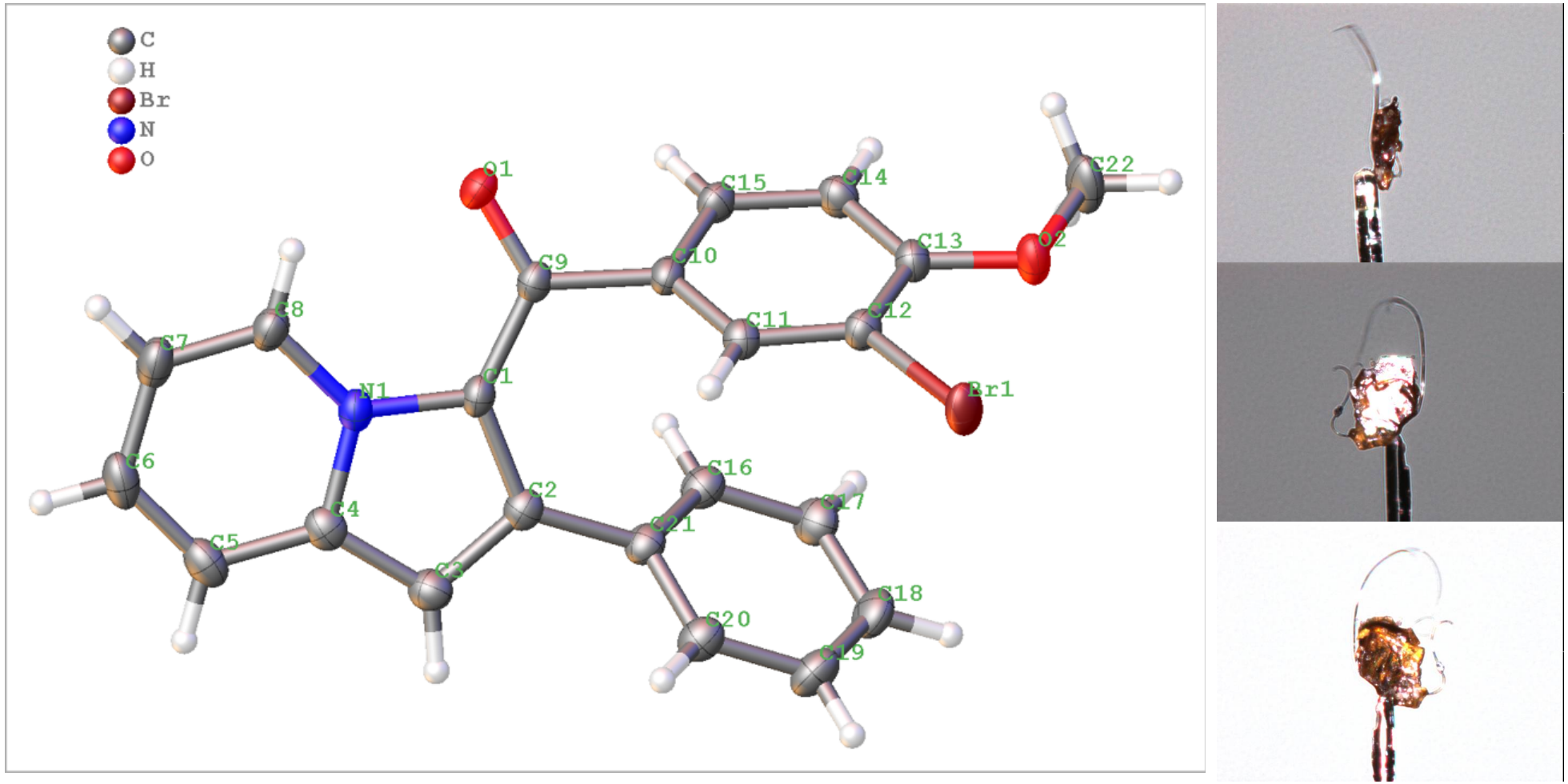


Figure S1. ORTEP drawing of the crystal structure (left) and microphotography of the single crystal of compound **9db** used for X-Ray diffraction analysis (right)

Table S1 Crystal data and structure refinement for 9db

Identification code	ANNA_ARK480_4
Empirical formula	$C_{22}H_{16}BrNO_2$
Formula weight	406.27
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.7634(2)
b/Å	10.22041(19)
c/Å	10.3147(2)
α/°	83.8073(16)
β/°	70.137(2)
γ/°	83.8485(17)
Volume/Å^3	861.35(3)
Z	2
ρ_{calc}g/cm^3	1.566
μ/mm^{-1}	3.383
F(000)	412.0
Crystal size/mm^3	0.329 × 0.22 × 0.102
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.728 to 152.788
Index ranges	$-11 \leq h \leq 10$, $-11 \leq k \leq 12$, $-12 \leq l \leq 12$
Reflections collected	18049
Independent reflections	3583 [R_{int} = 0.0395, R_{sigma} = 0.0219]
Data/restraints/parameters	3583/0/236
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0834
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0845
Largest diff. peak/hole / e Å^{-3}	1.15/-0.66

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 9db. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	-1075.4(3)	7875.2(2)	9559.7(2)	30.83(10)
O1	3116.1(19)	2893.6(14)	6925.0(17)	26.7(3)
O2	-1244(2)	8221.3(16)	6714.7(17)	29.6(3)
N1	5849(2)	3298.3(17)	7728.1(18)	22.1(4)
C9	3313(2)	4004(2)	7189(2)	20.6(4)
C2	5258(3)	5505(2)	7686(2)	22.1(4)
C1	4703(2)	4300(2)	7522(2)	21.0(4)
C13	-142(3)	7194(2)	6768(2)	23.5(4)
C11	1249(2)	5884(2)	8193(2)	21.7(4)
C12	137(3)	6895(2)	8029(2)	23.3(4)
C15	1745(3)	5366(2)	5859(2)	23.2(4)
C4	7063(3)	3863(2)	8017(2)	24.6(4)
C21	4606(3)	6878(2)	7459(2)	23.1(4)
C3	6678(3)	5226(2)	8015(2)	25.9(4)
C14	671(3)	6413(2)	5684(2)	24.7(4)
C10	2073(2)	5113(2)	7100(2)	21.4(4)
C8	5878(3)	1951(2)	7709(2)	26.5(4)
C5	8385(3)	3043(2)	8206(2)	29.7(5)
C17	3765(3)	8622(2)	6017(2)	29.1(5)
C16	4356(3)	7331(2)	6215(2)	25.8(4)
C20	4310(3)	7763(2)	8473(2)	28.1(5)
C18	3414(3)	9484(2)	7048(3)	31.6(5)
C6	8425(3)	1710(3)	8155(2)	32.3(5)
C7	7138(3)	1163(2)	7922(3)	31.5(5)
C19	3704(3)	9055(2)	8268(3)	32.7(5)
C22	-1600(3)	8490(3)	5451(3)	38.0(6)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 9db. 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}
Br1	31.65(14)	34.60(15)	25.89(14)	-11.32(10)	-11.17(10)	13.55(10)
O1	30.5(8)	18.3(7)	33.9(8)	-6.4(6)	-14.2(7)	2.8(6)
O2	32.5(8)	29.9(8)	28.6(8)	-6.1(6)	-16.2(7)	12.3(7)
N1	22.0(8)	20.9(9)	22.7(9)	-2.6(7)	-7.7(7)	3.4(7)
C9	22.4(10)	18.5(9)	19.3(9)	-2.9(7)	-5.3(8)	2.2(8)
C2	24.5(10)	21.0(10)	19.5(10)	-1.2(7)	-6.0(8)	-1.0(8)
C1	21.7(10)	18.4(9)	21.7(10)	-2.4(7)	-6.7(8)	3.5(8)
C13	22.0(10)	22.2(10)	26.5(11)	-2.3(8)	-9.4(8)	2.5(8)
C11	21.6(10)	21.3(10)	21.9(10)	-0.9(8)	-7.3(8)	-0.4(8)
C12	23.1(10)	22.3(10)	23.9(10)	-4.4(8)	-7.1(8)	1.1(8)
C15	24.2(10)	22.1(10)	23.2(10)	-5.8(8)	-7.5(8)	1.4(8)
C4	24.0(10)	29.1(11)	20.2(10)	-1.1(8)	-7.0(8)	-1.3(8)
C21	23.8(10)	19.0(10)	24.7(10)	-0.3(8)	-5.8(8)	-3.4(8)
C3	26.9(11)	25.9(11)	25.7(11)	0.4(8)	-9.9(9)	-4.3(8)
C14	25.8(10)	27.4(11)	22.4(10)	-2.1(8)	-10.6(8)	0.2(8)
C10	20.0(9)	17.4(9)	26.5(10)	-2.5(8)	-7.5(8)	0.2(7)
C8	31.1(11)	20.6(10)	28.8(11)	-5.7(8)	-12.1(9)	4.3(8)
C5	24.9(11)	38.8(13)	26.2(11)	0.0(9)	-11.3(9)	0.9(9)
C17	33.4(12)	24.6(11)	29.5(12)	4.5(9)	-12.0(9)	-3.9(9)
C16	28.7(11)	22.3(10)	25.1(11)	-1.1(8)	-6.9(9)	-3.7(8)
C20	33.9(12)	24.3(11)	25.2(11)	-1.9(8)	-8.4(9)	-3.3(9)
C18	35.8(12)	18.1(10)	39.5(13)	0.6(9)	-11.7(10)	-0.7(9)
C6	29.1(11)	38.8(13)	27.6(12)	-3.4(10)	-11.5(9)	12.4(10)
C7	38.6(13)	25.3(11)	31.6(12)	-6.5(9)	-15.4(10)	10.3(9)
C19	42.2(13)	22.5(11)	31.5(12)	-6.6(9)	-8.4(10)	-2.0(10)
C22	45.6(15)	39.1(14)	33.9(13)	-5.7(10)	-24.4(11)	17.4(11)

Table S4 Bond Lengths for 9db.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C12	1.897(2)	C11	C10	1.390(3)
O1	C9	1.238(3)	C15	C14	1.386(3)
O2	C13	1.358(3)	C15	C10	1.396(3)
O2	C22	1.433(3)	C4	C3	1.397(3)
N1	C1	1.407(3)	C4	C5	1.411(3)
N1	C4	1.392(3)	C21	C16	1.396(3)
N1	C8	1.377(3)	C21	C20	1.395(3)
C9	C1	1.441(3)	C8	C7	1.361(3)
C9	C10	1.502(3)	C5	C6	1.366(4)
C2	C1	1.419(3)	C17	C16	1.385(3)
C2	C21	1.483(3)	C17	C18	1.388(3)
C2	C3	1.391(3)	C20	C19	1.391(3)
C13	C12	1.399(3)	C18	C19	1.383(4)
C13	C14	1.387(3)	C6	C7	1.410(4)
C11	C12	1.380(3)			

Table S5 Bond Angles for 9db.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	O2	C22	116.98(18)	N1	C4	C3	107.70(19)
C4	N1	C1	109.26(17)	N1	C4	C5	119.1(2)
C8	N1	C1	130.01(18)	C3	C4	C5	133.2(2)
C8	N1	C4	120.72(18)	C16	C21	C2	121.27(19)
O1	C9	C1	123.47(19)	C20	C21	C2	119.9(2)
O1	C9	C10	118.19(18)	C20	C21	C16	118.8(2)
C1	C9	C10	118.29(18)	C2	C3	C4	108.35(19)
C1	C2	C21	129.24(19)	C15	C14	C13	119.9(2)
C3	C2	C1	108.57(19)	C11	C10	C9	122.77(19)
C3	C2	C21	122.02(19)	C11	C10	C15	119.33(19)
N1	C1	C9	121.53(18)	C15	C10	C9	117.90(19)
N1	C1	C2	106.10(18)	C7	C8	N1	119.8(2)
C2	C1	C9	132.36(19)	C6	C5	C4	119.8(2)
O2	C13	C12	116.62(19)	C16	C17	C18	120.6(2)
O2	C13	C14	124.58(19)	C17	C16	C21	120.4(2)
C14	C13	C12	118.76(19)	C19	C20	C21	120.4(2)
C12	C11	C10	119.46(19)	C19	C18	C17	119.4(2)
C13	C12	Br1	119.29(16)	C5	C6	C7	119.7(2)
C11	C12	Br1	119.19(16)	C8	C7	C6	120.8(2)
C11	C12	C13	121.50(19)	C18	C19	C20	120.4(2)
C14	C15	C10	120.9(2)				

Table S6 Torsion Angles for 9db.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C9	C1	N1	-7.6(3)	C21	C2	C3	C4	−173.79(19)
O1	C9	C1	C2	171.1(2)	C21	C20	C19	C18	-1.1(4)
O1	C9	C10	C11	124.6(2)	C3	C2	C1	N1	-1.4(2)
O1	C9	C10	C15	-55.3(3)	C3	C2	C1	C9	179.8(2)
O2	C13	C12	Br1	2.5(3)	C3	C2	C21	C16	122.1(2)
O2	C13	C12	C11	−179.03(19)	C3	C2	C21	C20	-54.6(3)
O2	C13	C14	C15	-178.5(2)	C3	C4	C5	C6	179.8(2)
N1	C4	C3	C2	-1.7(2)	C14	C13	C12	Br1	−175.66(16)
N1	C4	C5	C6	-2.4(3)	C14	C13	C12	C11	2.9(3)
N1	C8	C7	C6	-0.4(4)	C14	C15	C10	C9	−177.00(19)
C2	C21	C16	C17	-179.2(2)	C14	C15	C10	C11	3.1(3)
C2	C21	C20	C19	179.7(2)	C10	C9	C1	N1	175.05(18)
C1	N1	C4	C3	0.8(2)	C10	C9	C1	C2	-6.3(3)
C1	N1	C4	C5	−177.44(19)	C10	C11	C12	Br1	176.31(15)
C1	N1	C8	C7	179.2(2)	C10	C11	C12	C13	-2.2(3)
C1	C9	C10	C11	-57.9(3)	C10	C15	C14	C13	-2.5(3)
C1	C9	C10	C15	122.2(2)	C8	N1	C1	C9	-2.2(3)
C1	C2	C21	C16	-52.7(3)	C8	N1	C1	C2	178.8(2)
C1	C2	C21	C20	130.7(2)	C8	N1	C4	C3	−177.79(19)
C1	C2	C3	C4	1.9(2)	C8	N1	C4	C5	4.0(3)
C12	C13	C14	C15	-0.5(3)	C5	C4	C3	C2	176.2(2)
C12	C11	C10	C9	179.34(19)	C5	C6	C7	C8	1.9(4)
C12	C11	C10	C15	-0.8(3)	C17	C18	C19	C20	-1.3(4)
C4	N1	C1	C9	179.32(18)	C16	C21	C20	C19	3.0(3)

Table S6 Torsion Angles for 9db.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	N1	C1	C2	0.3(2)	C16	C17	C18	C19	1.8(4)
C4	N1	C8	C7	-2.5(3)	C20	C21	C16	C17	-2.5(3)
C4	C5	C6	C7	-0.4(3)	C18	C17	C16	C21	0.1(3)
C21	C2	C1	N1	173.9(2)	C22	O2	C13	C12	-176.8(2)
C21	C2	C1	C9	-4.9(4)	C22	O2	C13	C14	1.2(3)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 9db.

Atom	*x*	*y*	*Z*	U(eq)
H11	1445.21	5719.43	9029.59	26
H15	2254.84	4825.77	5140.55	28
H3	7270.1	5840.57	8200.72	31
H14	495.02	6591.4	4840.71	30
H8	5039.81	1580.21	7550.36	32
H5	9225.72	3409.05	8365.2	36
H17	3601.02	8912.99	5184.73	35
H16	4588.97	6762.86	5515.36	31
H20	4518.17	7487.44	9289.29	34
H18	2987.78	10342.55	6921.21	38
H6	9296.02	1164.92	8272.13	39
H7	7149.87	252.58	7915.08	38
H19	3492.91	9633.94	8955.29	39
H22A	-659.19	8800.59	4730.49	57
H22B	-2490.77	9152.6	5574.13	57
H22C	-1889.53	7696.82	5200.5	57

Experimental

Single crystals of $C_{22}H_{16}BrNO_2$ **9db** were prepared by slow evaporation of EtOAc solution. A suitable crystal was selected and mounted on the glass stick by acrylic glue on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

Crystal structure determination of 9db

Crystal Data for $C_{22}H_{16}BrNO_2$ (M =406.27 g/mol): triclinic, space group P-1 (no. 2), a = 8.7634(2) Å, b = 10.22041(19) Å, c = 10.3147(2) Å, α = 83.8073(16)°, β = 70.137(2)°, γ = 83.8485(17)°, V = 861.35(3) Å^3, Z = 2, T = 100.00(10) K, μ(Cu Kα) = 3.383 mm^{-1}, *Dcalc* = 1.566 g/cm^3, 18049 reflections measured (8.728° ≤ 2Θ ≤ 152.788°), 3583 unique (R_{int} = 0.0395, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0345 (I > 2σ(I)) and wR_2 was 0.0845 (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
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C11(H11), C15(H15), C3(H3), C14(H14), C8(H8), C5(H5), C17(H17), C16(H16),
 C20(H20), C18(H18), C6(H6), C7(H7), C19(H19)
2.b Idealised Me refined as rotating group:
 C22(H22A,H22B,H22C)
```


References

(S1) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX 2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst*. **2009**, 42, 339-341.

(S2) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst*. **2015**, A71, 3-8.

(S3) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst*. **2015**, C71, 3-8