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

Amination Catalyzed by Iridium Complexes Using Carbon Monoxide as a Reducing Agent

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Supporting Information

Table of contents

1. General information

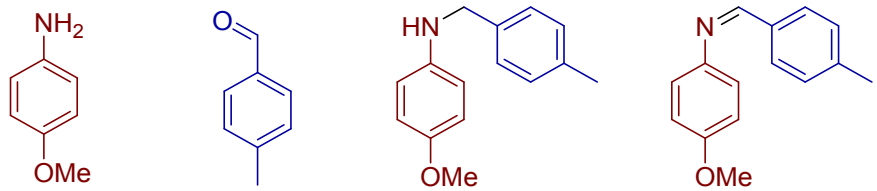
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. THF was distilled over sodium with benzophenone. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Reaction products were purified by column chromatography (Macherey-Nagel, Kieselgel 60, 0.04-0.063 mm) or thin layer chromatography (Macherey Nagel, Kieselgel N/UV_{254}); hexane-ethyl acetate mixture was used as eluent if other is not stated. ^{1}H spectra were recorded in $CDCl_3$ on Bruker Avance 300 and Bruker Avance 400 spectrometers; ^{13}C spectra were recorded in $CDCl_3$ on Bruker Avance 400 spectrometer at 101MHz. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). Chemical shifts δ are reported in ppm relative to the solvent resonance signal as an internal standard. To determine NMR yield DMF was used as internal standard (see page S18 for detailes). Amounts of DMF was evaluated by integrating two peaks of methyl protons (6H). Amounts of the products was evaluated by integrating a signal of a new CH proton, formed in the reaction. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz). Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2 Gas Chromatograph fitted with a flame ionization detector (He carrier gas, 37 mL/min). Injections were made on a Chromatec CR-5 (30 m, 0.2 mm ID, 0.33 µm thickness) capillary column. The injector temperature was 250 °C, the detector temperature was 260 °C, with a split ratio of 23:1. The column oven temperature program was as follows: 140 °C for 3 minutes, 140 °C to 260 °C at 20 °C/min, then 260 °C for 9 minutes. Retention times (tR) and integrated ratios were obtained using Chromatec Analytic Software. Yield of 4-methoxy-N-(4-methylbenzyl)aniline was calculated using GC calibration curve.

GC response factors were established by the following equation using p-anisidine (**1**), p-tolualdehyde (**2**), 4-methoxy-N-(4-methylbenzyl)aniline (**3**) and N-(4-methoxyphenyl)-1-(p-tolyl)methanimine (**4**) with absolute calibration:

$$Response\ factor = \frac{peak\ area}{sample\ concetration\ (mg/ml)}$$

Five samples of different concentration containing a known amount of the desired compound were prepared and dissolved in dichloromethane or toluene. An aliquot of each sample was injected into GC.

GC calibration factors.



a **b** **c** **d**

compound	t_R (min)	response factor
a	4.30	802
b	3.16	1074
c	11.28	846
d	11.46	962

Synthesis of [CpIr(η^3,η^2-C_8H_{11})]PF_6: A solution of CF_3COOAg (60.5 mg, 0.27 mmol) in trifluoroacetic acid (1 ml) was added dropwise to solution of CpIr(cod) (84 mg, 0.23 mmol) in the same solvent (3 ml). The reaction mixture was stirred for 1 h and the solvent was removed *in vacuo*. Saturated solution of KPF_6 in water was added to residue and the suspension obtained was stirred for 24 h. White precipitate was centrifuged off and washed with water. After drying over P_2O_5, the product was reprecipitated from CH_2Cl_2 by ether. Yield 89 mg (76%) of [CpIr(η^3,η^2-C_8H_{11})]PF_6.

^{1}H NMR (acetone-d_6) δ: 6.04 (s, 5H, Cp), 5.76 (m, 1H), 4.92-4.88 (m, 2H), 4.70 (m, 1H), 3.92 (m, 1H), 3.39-3.32 (m, 2H), 2.91 (m, 1H), 2.47-2.79 (m, 2H), 1.62 (m, 1H). Found (%): C, 29.83; H, 3.11. Calc. for $C_{13}H_{16}F_6IrP\cdot 0{,}25CH_2Cl_2$ (%): C, 29.99; H, 3.13.

Synthesis of [(cod)Ir{P(OR)$_3$}$_3$]PF_6 (R = Me, Et): Acetone (3 ml) was added to a mixture of complex [CpIr(cod)Br]PF_6 (67 mg, 0.114 mmol) and $P(OR)_3$ (0.3 ml). The reaction mixture was stirred for 0.5 h (an inert atmosphere is not necessary). The volume of solvent was reduced *in vacuo* to 1 ml and excess of petroleum ether was added. White precipitate formed was centrifuged off and washed with ether.

[(cod)Ir{P(Ome)$_3$}$_3$]PF_6, yield 77 mg (83%). ^{1}H NMR (acetone-d_6) δ:4.02 (br. S, 4H, cod), 3.83 (m, 27H, P(Ome$_3$)$_3$),2.60 (m, 4H, cod),2.33 (m, 4H, cod).^{31}P{^{1}H} NMR (acetone-d_6) δ:89.0 (s, 3P, P(Ome$_3$)$_3$), −144.3 (sept., 1P, PF_6). Found (%):C, 24.74; H, 4.83. Calc. For $C_{17}H_{39}F_6IrO_9P_4$ (%):C, 24.97; H, 4.81.

[(cod)Ir{P(Oet)$_3$}$_3$]PF_6, yield 92.5 mg (86%). ^{1}H NMR (acetone-d_6) δ:4.21 (m, 18H, P(Oet$_3$)$_3$), 3.96 (br. S, 4H, cod), 2.60 (m, 4H, cod), 2.33 (m, 4H, cod), 1.35 (t, 27H, P(Oet$_3$)$_3$).^{31}P{^{1}H} NMR (acetone-d_6) δ:83.1 (s, 3P, P(Oet$_3$)$_3$), −144.3 (sept., 1P, PF_6). Found (%): C, 33.08; H, 6.08. Calc. For $C_{26}H_{57}F_6IrO_9P_4$ (%): C, 33.08; H, 6.10.

Synthesis of [CpIr(2,2′-bipy)Br]PF_6: A solution of [CpIr(cod)Br]PF_6 (134 mg, 0.22 mmol) and 2,2′-bipyridyl (42mg, 0.27mmol) in acetone (3 ml) was stirred for 6 days. The reaction mixture was filtered through layer of Al_2O_3 (5 cm). The solvent was removed *in vacuo* and the residue was reprecipitated from acetone by ether. Yield 118 mg (81%) of [CpIr(2,2′-bipy)Br]PF_6.^{1}H NMR (acetone-d_6) δ:9.62 (d, J = 5.6 Hz, 2H, bipy), 8.78 (d, J = 8.0 Hz, 2H, bipy), 8.38 (t, 2H, bipy), 7.81 (t, 2H, bipy), 6.32 (s, 5H, Cp). Found (%):C, 28.62; H, 2.57;N, 4.58. Calc. for $C_{15}H_{15}N_2BrF_6IrP$ (%): C, 28.13; H, 2.36; N, 4.37.

X-ray crystallography: Crystals of [(cod)Ir{P(Ome)$_3$}$_3$]PF_6 were grown by slow diffusion in two-layer system, petroleum ether and a solution of the complex in CH_2Cl_2.Crystal data:$C_{17}H_{39}F_6IrO_9P_4$, orthorhombic, space group *Pbca*, a = 17.6741(18) Å, b = 16.8387(17) Å, c = 18.4813(19) Å, V = 5500.2(10) Å^3, Z = 8, d_{calc} = 1.975 g cm^{-3}, μ = 5.172 mm^{-1}, crystal size 0.35 × 0.33 × 0.27 mm. X-ray diffraction experiment was carried out with a Bruker SMART APEX2 CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å, $2\theta_{max}$ = 56^o) at 100 K. The absorption correction was applied semi-empirically using SADABS

program (T_{max}/T_{min} = 0.336/0.265). The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were refined in the isotropic approximation in the riding model with U(H) = nUI, where UI is the equivalent temperature factor of the carbon atom to which the H atom is bound, n = 1.2 for the CH and CH_2 groups, and n = 1.5 for the Me groups.The refinement converged to wR_2 = 0.0545 and GOF = 1.014 for all independent reflections (R_1 = 0.0227 was calculated against F for 5886 observed reflections with $I > 2\sigma(I)$).

CCDC 1536381 contains the supplementary crystallographic data, which can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

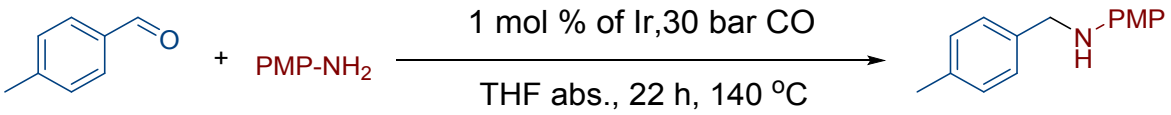
General procedure for reductive amination[1]

Procedure: A glass vial in a 10 mL stainless steel autoclave was charged with 0.5 — 1.0 mol % of the catalyst, THF_{abs}, 150-200 mol % of the amine and 100 mol % of aldehyde/ketone. The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with the 30 bar CO. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. The residue was purified by column chromatography or preparative TLC on silica gel.

[1]O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. S. Perekalin, N. V. Shvydkiy, V. I. Maleev, A. R. Kudinov, D. Chusov, *ACS Catal.,* 2016, **6**, 2043–2046

2. Optimization of reaction conditions

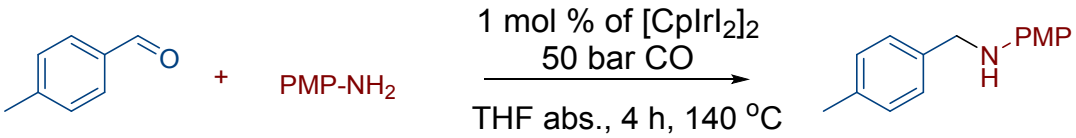
Table S1. Investigation of catalysts



Entry[a]	Catalyst	Yield, %
1	$[CpIrBr_3^-][Cp(COD)IrBr^+]$	21
2	$[CpIr(C_8H_{11})]PF_6$	12
3	$[CpIr(COD)Br]PF_6$	8
4	$[(Ind)IrCp]PF_6$	6
5	Cp^*IrCl_2	28
6	$[(COD)Ir\{POMe_3\}_3]PF_6$	25
7	$[(COE)_2IrCl]_2$	29
8	$[CpIrI_2]_2$	57
9	$[(COD)IrCl]_2$	14
10	$[(Ind)Ir(Mes)](BF4)_2$	8
11	$[(Ind)IrI_2]_2$	39
12	$IrCl_3$	33
13	$IrCl_3$ + 3NaI	47

[a] 0.2 mmol scale, 100 mol % of *p*-tolualdehyde, 100 mol % of *p*-anisidine, see general procedure. Yields were determined by GC. PMP = *p*-methoxyphenyl, Ind = indenyl, COD = cycloocta-1,5-diene, COE = cyclooctene, Cp = cyclopentadienyl, Cp* = 1,2,3,4,5-pentamethyl cyclopentadienyl.

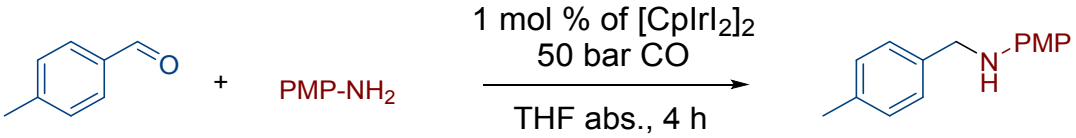
Table S2. Screening of solvents



Entry[a]	Solvent	Temperature, °C	Yield, %
1	THF_{abs}	140	49
2	MeCN	140	22
3	toluene	140	31
4	MeOH	140	32
5	$^{i}PrOH$	140	56
6	1,4-dioxane	140	32
7	Et_2O	140	46
8	solvent free	140	33
9	H_2O	140	22
10	EtOAc	140	15
11	DCM	140	22

[a] 0.2 mmol scale, 100 mol % of *p*-tolualdehyde, 150 mol % of *p*-anisidine, see general procedure. Yields were determined by GC. PMP = *p*-methoxyphenyl. MeCN, Et_2O, $^{i}PrOH$, MeOH, 1,4-dioxane, toluene, EtOAc, DCM were used as received.

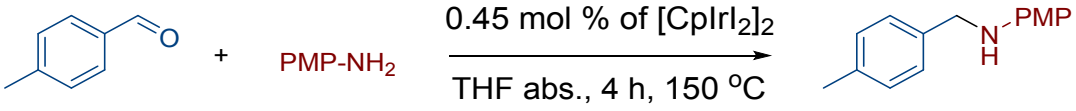
Table S3. Investigation of the effect of temperature



Entry[a]	Temperature, °C	Yield, %
1	140	38
2	150	52
3	160	54
4[b]	130	67
5[b]	140	67
6[b]	150	72

[a] 0.2 mmol scale, 100 mol % of *p*-tolualdehyde, 150 mol % of *p*-anisidine, see general procedure. Yields were determined by GC. PMP = *p*-methoxyphenyl. [b] 100 mol % of *p*-tolualdehyde, 200 mol % of *p*-anisidine. 22 h.

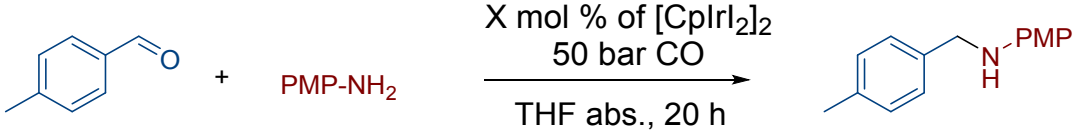
Table S4. Investigation of the effect of pressure



Entry[a]	CO pressure, bar	Yield, %
1	5	2
2	10	9
3	20	11
4	30	34
5	50	37
6	60	39

[a] 0.2 mmol scale, 100 mol % of *p*-tolualdehyde, 150 mol % of *p*-anisidine, see general procedure. Yields were determined by GC. PMP = *p*-methoxyphenyl.

Table S5. Investigation of the catalyst loading



Entry[a]	Catalyst loading, % mol	Yield, %
1	1	46
2	0.5	53
3	0.1	29

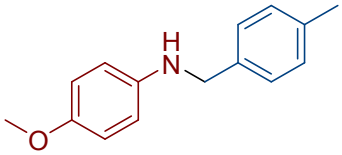
[a] 0.2 mmol scale, 100 mol % of *p*-tolualdehyde, 150 mol % of *p*-anisidine, see general procedure. Yields were determined by GC. PMP = *p*-methoxyphenyl.

Investigation of Schiff base behavior in reaction conditions

$[CpIrI_2]_2$ (1.0 mg, 1 mol %, 0.9 μmol), N-(4-methoxyphenyl)-1-(p-tolyl)methanimine (44.1 mg, 100 mol %, 0.195 mmol) and 300 mg of molecular sieves 3Å were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. NMR analysis revealed 20% of compound **12a** and 75% of initial Schiff base. It might shows that the system contains at least 0.7 μL of water (e.g. walls of glass vial and autoclave). This allows forming hemiaminal from Schiff base and leading to the 20% of the product.

3. Spectroscopic and analytical data

4-methoxy-N-(4-methylbenzyl)aniline (12a)



$[CpIrI_2]_2$ (0.9 mg, 1 mol %, 0.9 μmol), *p*-anisidine (43.3 mg, 200 mol %, 0.352 mmol) and *p*-tolualdehyde (21 μL, 100 mol %, 0.178 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.33 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 150 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 72 % yield by NMR. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 10 : 1; R_f=0.6) to afford 23.4 mg (58 %) of the product as a yellowish solid. mp = 52 — 56 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 4.25 (s, 2H), 3.76 (s, 3H), 2.36 (s, 3H).

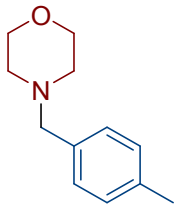
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 142.7, 136.9, 136.8, 129.4, 127.7, 115.0, 114.2, 55.9, 49.1, 21.2.

NMR spectra are in agreement with the literature data.[2]

EI-MS spectrum: calculated [M^+] m/z = 227, found m/z: 227 (38 %), 122 (30), 105 (100), 77 (24).

4-(4-methylbenzyl)morpholine (12b)

[2]P. N. Kolesnikov, N. Z. Yagafarov, D. L. Usanov, V. I. Maleev, D. Chusov, *Org. Lett.*, 2015, **17** (2), 173–175



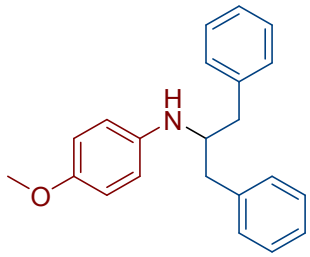
$[CpIrI_2]_2$ (6 mg, 1 mol %, 6 µmol), morpholine (104 µL, 200 mol %, 1.172 mmol) and *p*-tolualdehyde (68 µL, 100 mol %, 0.584 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 130 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 68% yield by NMR. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 5 : 1; R_f=0.6) to afford 123.1 mg (55 %) of the product as a yellowish oil.

^{1}H NMR (300 MHz, CDCl3): δ 7.22 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.75-3.65 (t, *J* = 4.5 Hz, 4H), 3.46 (s, 2H), 2.48-2.37 (t, *J* = 4.5 Hz, 4H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 134.7, 129.3, 129.0, 67.1, 63.3, 53.7, 21.2.

NMR spectra are in agreement with the literature data.[3]

N-(1,3-diphenylpropan-2-yl)-4-methoxyaniline (12c)



$[CpIrI_2]_2$ (5.6 mg, 1 mol %, 5.5 µmol), *p*-anisidine (134.7 mg, 200 mol %, 1.094 mmol) and dibenzyl ketone (108 µL, 100 mol %, 0.547 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.99 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 92 % yield by NMR. The residue was purified by gradient column chromatography (eluent: hexane → hexane:EtOAc 10:1; Rf 0.50 in hexane:EtOAc 5:1) to afford product as a brownish oil. m = 130.9 mg (75%).

[3] X. Cui, X. Dai, Y. Deng, F. Shi, *Chem. Eur. J.*, 2013, **19**, 3665.

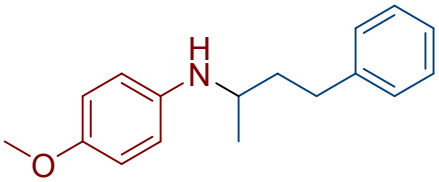
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.11 (m, 10H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 3.90 (quint, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 3.74 – 3.68 (br s, 1H), 2.85 (dd, *J* = 13.9, 6.1 Hz, 2H), 2.78 (dd, *J* = 13.9, 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 141.5, 138.8, 134.1, 129.6, 129.6, 128.9, 128.5, 127.2, 126.4, 115.1, 115.1, 55.9, 55.8, 49.2, 39.8.

EI-MS spectrum: calculated [M^+] m/z = 317, found m/z: 317 (6 %), 227 (15), 226 (100), 122 (34), 91 (28), 65 (10).

HRMS (TOF ESI+): found m/z 318,1851 (M + H^+), calculated for $(C_{22}H_{24}NO)^+$ 318,1852 ($M+H^+$)

4-methoxy-N-(4-phenylbutan-2-yl)aniline (12d)



$[CpIrI_2]_2$ (5.1 mg, 1 mol %, 5.0 µmol), 4-phenylbutan-2-one (74 mg, 100 mol %, 0.5 mmol) and *p*-anisidine (92.3 mg, 150 mol %, 0.75 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.75 mL THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 150 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 92% yield by NMR. The residue was purified by flash chromatography (eluent: hexane:EtOAc:NEt_3 = 30:1:0.2, R_f 0.15) to afford product as a bright yellow oil. m = 117.0 mg (92%).

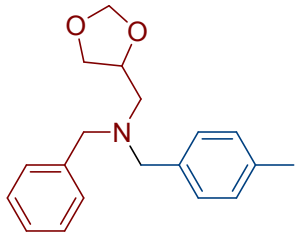
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.13 (m, 5H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.58 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.52 – 3.39 (m, 1H), 3.27 – 3.05 (m, 1H), 2.79 (t, *J* = 7.9 Hz, 2H), 2.02 – 1.72 (m, 2H), 1.26 (d, *J* = 6.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 142.2, 141.8, 128.6, 128.5, 125.9, 115.0, 114.9, 55.9, 49.1, 38.9, 32.6, 21.0.

NMR spectra are in agreement with the literature data.[4]

N-((1,3-dioxolan-4-yl)methyl)-N-benzyl-1-(p-tolyl)methanamine (12e)

[4]P. Yin, T.-P. Loh, *Org. Lett.*, 2009, **11** (17), 3791–3793



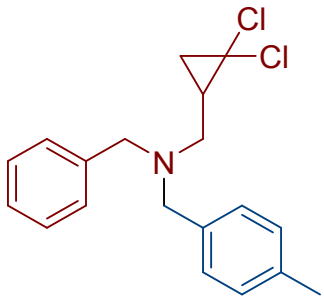
$[CpIrI_2]_2$ (1.5 mg, 1 mol %, 1.46 µmol), N-((1,3-dioxolan-4-yl)methyl)-1-phenylmethanamine (41 µL, 150 mol %, 0.218 mmol) and *p*-tolualdehyde (17.5 µL, 100 mol %, 0.147 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 68 % yield by NMR. The residue was purified by preparative TLC (eluent: toluene:EtOAc:NEt_3 20:1:0.1 mixture, Rf 0.62) to afford product as a yellowish oil. m = 43 mg (30%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 8H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.94 (s, 1H), 4.84 (s, 1H), 4.24 – 4.11 (m, 1H), 3.90 (t, *J* = 7.3 Hz, 1H), 3.82 – 3.68 (m, 2H), 3.62 – 3.50 (m, 2H), 3.48 – 3.41 (m, 1H), 2.76 – 2.66 (m, 1H), 2.66 – 2.56 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 136.7, 136.3, 129.1, 129.0, 128.9, 128.4, 127.1, 95.1, 74.7, 68.8, 59.3, 59.1, 55.6, 21.2.

HRMS (TOF ESI+): found m/z 298,1803 ($M + H^+$), calculated for $(C_{19}H_{24}NO_2)^+$ 298,1802 ($M+H^+$)

N-benzyl-1-(2,2-dichlorocyclopropyl)-N-(4-methylbenzyl)methanamine (12f)

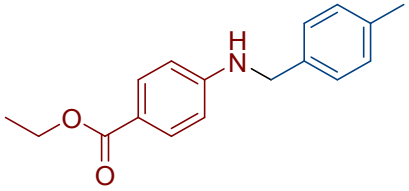


$[CpIrI_2]_2$ (1.5 mg, 1 mol %, 1.46 µmol), *p*-tolualdehyde (17.5 µL, 100 mol %, 0.147) and N-benzyl-1-(2,2-dichlorocyclopropyl)methanamine (51.8 mg, 150 mol %, 0.225 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 130 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 64 % yield by NMR. The residue was purified by column

chromatography (eluent: hexane:EtOAc:NEt_3 10:1:0.1 mixture, Rf 0.3) to afford product as a yellowish oil. m = 24.1 mg (51%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.20 (m, 5H), 7.13 (d, *J* = 7.5 Hz, 2H), 3.82 – 3.64 (m, 2H), 3.62 – 3.49 (m, 2H), 2.79 – 2.56 (m, 2H), 2.33 (s, 3H), 1.89 – 1.70 (m, 1H), 1.57 (dd, *J* = 10.7, 6.9 Hz, 1H), 1.04 (d, *J* = 7.4 Hz, 1H), 1.02 (d, *J* = 7.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 136.7, 136.4, 129.1, 128.9, 128.83, 128.4, 127.1, 61.2, 58.2, 58.0, 53.6, 28.8, 25.8, 21.3.

Ethyl 4-((4-methylbenzyl)amino)benzoate (12g)



$[CpIrI_2]_2$ (5.5 mg, 1 mol %, 5.4 µmol), benzocaine (133.1 mg, 150 mol %, 0.806 mmol) and *p*-tolualdehyde (63 µL, 100 mol %, 0.537 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.74 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 82% yield by NMR. The residue was purified by gradient column chromatography (eluent: hexane → hexane:EtOAc 5:1; Rf 0.34 in hexane:EtOAc 5:1) to afford product as a yellowish solid. m = 107.3 mg (74%). mp = 90 — 92 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.70 – 4.43 (br s, 1H), 4.34 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H).

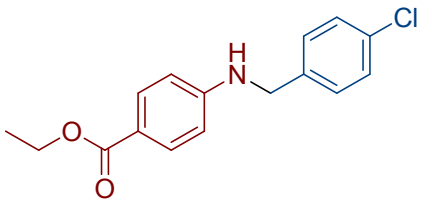
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 151.8, 137.3, 135.4, 131.6, 129.5, 127.5, 119.0, 111.7, 60.3, 47.5, 21.2, 14.6.

NMR spectra are in agreement with the literature data.[5]

EI-MS spectrum: calculated [M^+] m/z = 269, found m/z: 269 (34 %), 105 (100), 79 (12).

Ethyl 4-((4-chlorobenzyl)amino)benzoate (12h)

[5]S. D. Nielsen, G. Smith, M. Begtrup, J. L. Kristensen, *Eur. J. Org. Chem*., 2010, ***19***, 3704–3710.



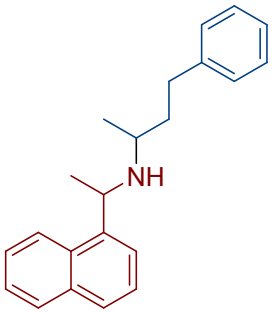
$[CpIrI_2]_2$ (5.1 mg, 1 mol %, 5.0 µmol), benzocaine (164.5 mg, 200 mol %, 0.996 mmol) and *p*-chlorobenzaldehyde (70.0 mg, 100 mol %, 0.498 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 1.00 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 70 % yield by NMR. The residue was purified by column chromatography (eluent: hexane:EtOAc 5:1; Rf 0.30) to afford product as a yellowish solid. m = 77.9 mg (54%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.27 (m, 4H), 6.59 (d, *J* = 8.6 Hz, 2H), 4.55 (s, 1H), 4.40 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 151.5, 137.1, 133.3, 131.6, 129.0, 128.7, 119.5, 111.8, 60.4, 47.1, 14.6.

HRMS (TOF ESI+): found m/z 290,0944 (M + H^+), calculated for $(C_{16}H_{17}ClNO_2)^+$ 290,0942 ($M+H^+$)

N-(1-(naphthalen-1-yl)ethyl)-4-phenylbutan-2-amine (12i)

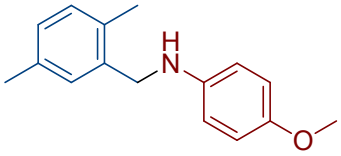


$[CpIrI_2]_2$ (4 mg, 1 mol %, 7.8 µmol), (R)-(+)-1-(1-Naphthyl)ethylamine (125.0 µL, 200 mol %, 0.782 mmol) and 4-phenyl-2-butanone (57 µL, 100 mol %, 0.391 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (4x1mL); combined solvents were removed on a rotary evaporator. 96 % yield by NMR. d.r. = 1.5:1. The residue was purified by column chromatography (eluent: hexane:EtOAc 4:1; Rf 0.3) to afford 99 mg (84%) of product as a yellowish oil (mixture of diastereomers).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz) and 8.32 (d, *J* = 8.1 Hz) – 1H, 8.02 – 7.94 (m, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.74 (t, *J* = 7.3 Hz, 1H), 7.67 – 7.52 (m, 3H), 7.39 – 7.31 (m, 2H), 7.30 – 7.17 (m, 3H), 4.94 (q, *J* = 6.6 Hz) and 4.89 (q, *J* = 6.6 Hz) – 1H, 2.90 – 2.56 (m, 3H), 2.06 – 1.67 (m, 2H), 1.60 (d, *J* = 6.6 Hz) and 1.57 (d, *J* = 6.6 Hz) – 3H, 1.22 (d, *J* = 5.9 Hz) and 1.21 (d, *J* = 5.8 Hz) – 1H.

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 142.2, 141.7, 134.1, 131.5, 131.3, 129.1, 128.4, 127.2, 127.1, 125.9, 125.9, 125.8, 125.7, 125.4, 123.2, 123.0, 122.9, 50.3, 50.1, 49.9, 40.0, 38.5, 32.6, 32.3, 24.9, 24.1, 21.3, 20.6.

N-(2,5-dimethylbenzyl)-4-methoxyaniline (12j)



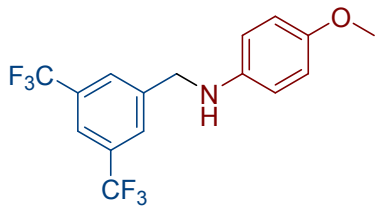
$[CpIrI_2]_2$ (4.0 mg, 1 mol % 3.911 µmol), *p*-anisidine (72.3 mg, 150 mol %, 0.587 mmol) and 2,5-dimethylbenzaldehyde (55 µL, 100 mol %, 0.391 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 69 % yield by NMR. The residue was purified by column chromatography (eluent: hexane:EtOAc 30:1 mixture, Rf 0.13) to afford product as a yellowish oil. m = 58.5 mg (62%)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.20 (s, 2H), 3.77 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.9, 137.2, 135.7, 133.3, 130.4, 129.2, 128.1, 115.0, 114.0, 56.0, 47.5, 21.1, 18.6.

HRMS (TOF ESI+): found m/z 242,1548 (M + H^+), calculated for $(C_{16}H_{20}NO)^+$ 242,1539 ($M+H^+$)

N-(3,5-bis(trifluoromethyl)benzyl)-4-methoxyaniline (12k)



$[CpIrI_2]_2$ (3.0 mg, 1 mol %, 2.92 µmol), *p*-anisidine (53.8 mg, 150 mol %, 0.436 mmol) and 3,5-bis(trifluoromethyl)benzaldehyde (48 µL, 100 mol %, 0.292 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.4 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 45 % yield by NMR. The residue was purified by column chromatography (eluent: hexane:EtOAc 30:1, Rf 0.15) to afford product as an orange oil. m = 30 mg (30%).

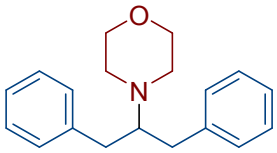
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.78 (s, 1H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 4.43 (s, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 142.9, 141.6, 132.0 (q, *J* = 33.3 Hz), 127.5 (q, *J* = 2.6 Hz), 123.5 (q, *J* = 272.7 Hz), 121.3 (q, *J* = 2.5 Hz), 115.1, 114.4, 55.9, 48.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.

HRMS (TOF ESI+): found m/z 350.0972 (M + H^+), calculated for $(C_{16}H_{14}NO)^+$ 350,0974 ($M+H^+$)

4-(1,3-diphenylpropan-2-yl)morpholine (12l)



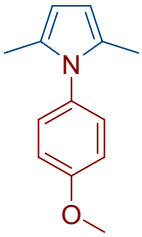
$[CpIrI_2]_2$ (1.9 mg, 1 mol %, 1.85 µmol), morpholine (34 µL, 200 mol %, 0.389 mmol) and dibenzyl ketone (38 µL, 100 mol %, 0.188 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.4 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 60 % yield by NMR. The residue was purified by column chromatography (eluent: hexane:EtOAc 10:1 mixture, Rf 0.18) to afford product as a white solid. m = 22.5 mg (41%). mp = 80 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 – 7.07 (m, 10H), 3.61 (t, *J* = 4.5, 4H), 2.95 (quint, *J* = 6.7 Hz, 1H), 2.86 (dd, *J* = 13.4, 6.5 Hz, 2H), 2.63 (t, *J* = 4.5, 4H), 2.51 (dd, *J* = 13.4, 6.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 129.3, 128.3, 125.9, 68.7, 67.6, 49.1, 35.9.

NMR spectra are in agreement with the literature data.[6]

1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole (12m)

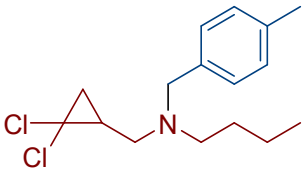


$[CpIrI_2]_2$ (1.5 mg, 1 mol %, 1.46 µmol), *p*-anisidine (18.0 mg, 100 mol %, 0.146 mmol) and hexane-2,5-dione (17 µL, 100 mol %, 0.145 µmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 96 % yield by NMR. Compound was isolated as brown oil by means of flash chromatography (eluent: hexane:EtOAc 10:1 mixture, Rf 0.56). m = 28.0 mg (96%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.90 (s, 2H), 3.87 (s, 3H), 2.03 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 131.8, 129.3, 129.2, 114.3, 105.3, 55.6, 13.1.

NMR spectra are in agreement with the literature data.[7]

N-((2,2-dichlorocyclopropyl)methyl)-N-(4-methylbenzyl)butan-1-amine (12n)



$[CpIrI_2]_2$ (4.0 mg, 1 mol %, 3.911 µmol), N-((2,2-dichlorocyclopropyl)methyl)butan-1-amine (107.6 µL, 150 mol %, 0.587 mmol) and *p*-tolualdehyde (46.1 µL, 100 mol %, 0.391 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL of THF_{abs} was added

[6]K. D. Hesp, M. Stradiotto, *J. Am. Chem. Soc.*, 2010, **132** (51), 18026–18029

[7] S. J. Pridmore, P. A. Slatford, J. E. Taylor, M. K. Whittlesey, J. M. J. Jonathan, *Tetrahedron,* 2009, ***65****(44)*, 8981–8986

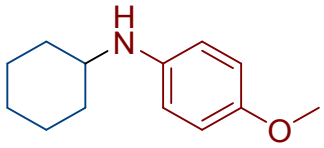
and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 4 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL), combined solvents were removed on a rotary evaporator. 62 % yield by NMR. The residue was purified by preparative TLC (eluent: toluene:EtOAc:NEt_3 20:1:0.1 mixture, Rf 0.59) to afford product as a yellowish oil. m = 62 mg (53%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.68 – 2.45 (m, 4H), 2.35 (s, 3H), 1.83 – 1.71 (m, 1H), 1.66 – 1.55 (m, 1H), 1.55 – 1.44 (m, 2H), 1.42 – 1.26 (m, 2H), 1.15 – 1.01 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 136.5, 129.0, 128.8, 61.3, 58.2, 53.7, 53.4, 29.4, 28.8, 25.8, 21.2, 20.6, 14.2.

HRMS (TOF ESI+): found m/z 300.1282 (M + H^+), calculated for $(C_{16}H_{24}Cl_2N)^+$ 350,1280 ($M+H^+$)

N-cyclohexyl-4-methoxyaniline (12o)



$[CpIrI_2]_2$ (1.5 mg, 1 mol %, 1.46 µmol), cyclohexanone (14.7 mg, 100 mol %, 0.15 mmol) and *p*-anisidine (27.7 mg, 150 mol %, 0.225 mmol) were charged into a glass vial in a 10 mL stainless steel autoclave. 0.2 mL THF_{abs} was added and the autoclave was sealed, flushed three times with 10 bar of CO, and then charged with 30 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 24 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. 93 % yield by NMR (average of two experiments – 96 and 91 %). The residue was purified by column chromatography (eluent: hexane:EtOAc:NEt_3 10:1:0.1 mixture, Rf 0.3) to afford product as a yellowish oil. m = 23.9 mg (78%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.57 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 2H), 3.31 – 3.06 (m, 1H), 2.10 – 1.95 (m, 2H), 1.86 – 1.57 (m, 3H), 1.47 – 1.03 (m, 5H).

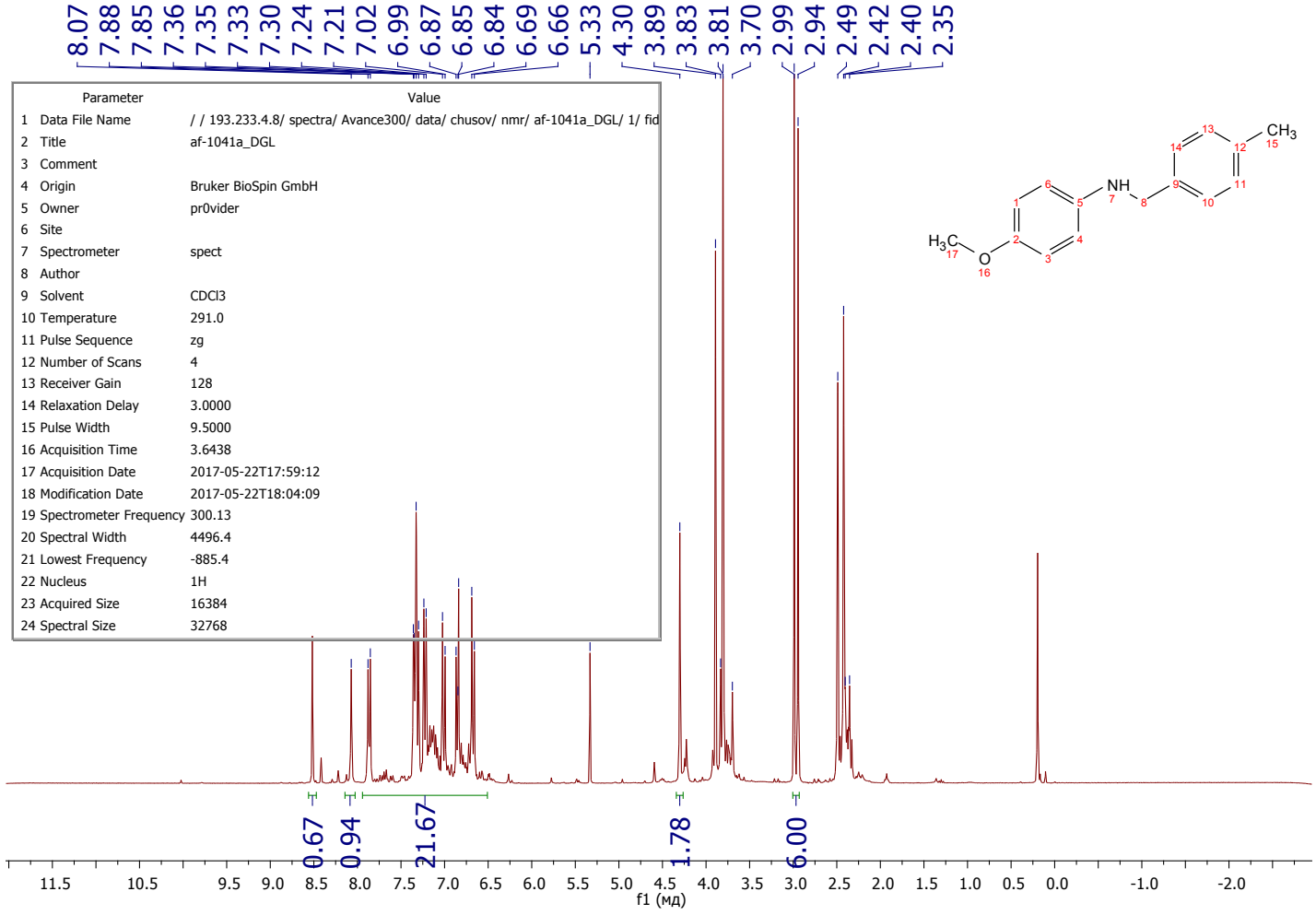
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 141.7, 115.0, 115.0, 56.0, 53.0, 33.8, 26.1, 25.2.

NMR spectra are in agreement with the literature data.[8]

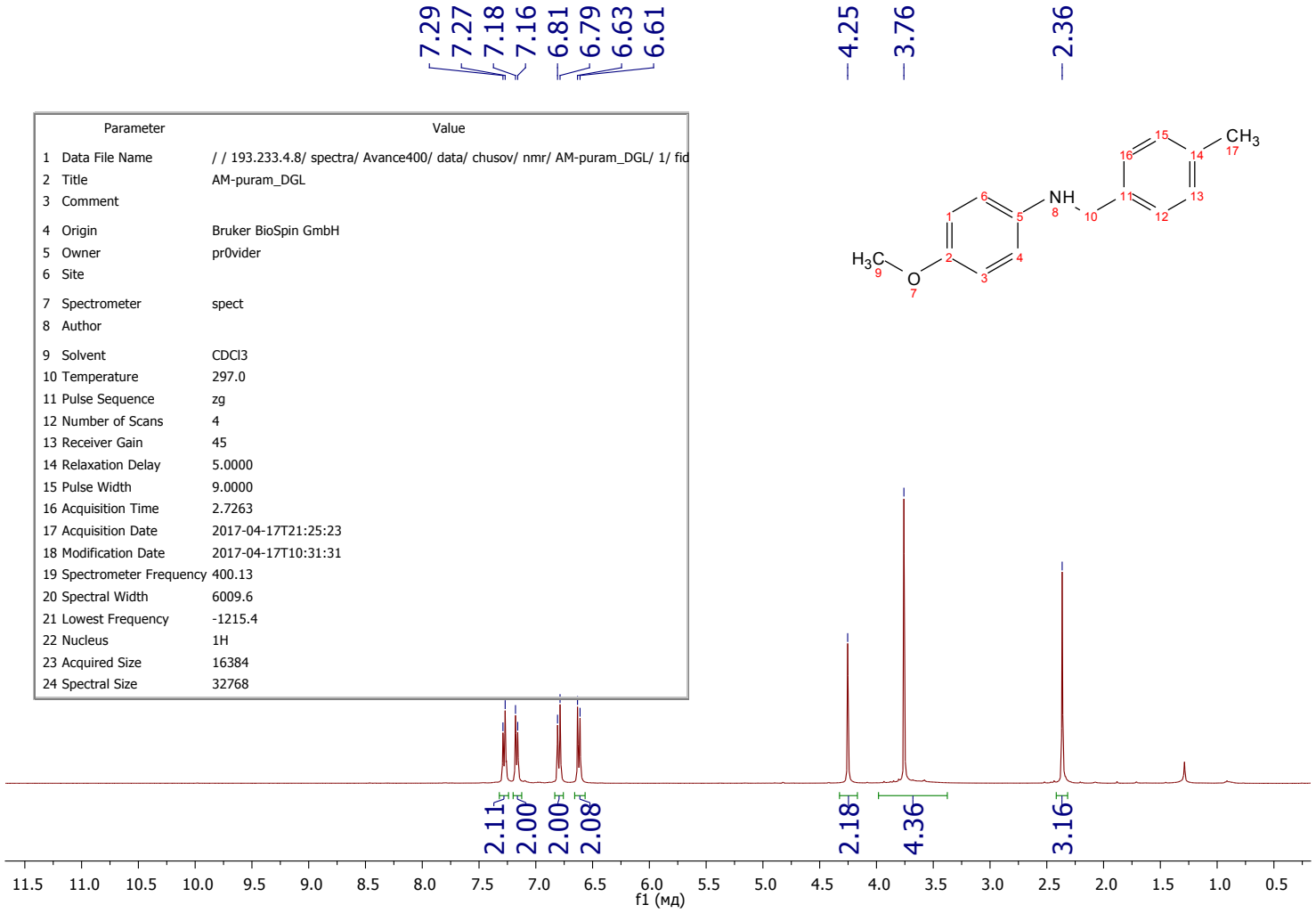
[8]B. P. Fors, N. R. Davis, S. L. Buchwald, *J. Am. Chem. Soc.*, 2009, **131** (16), 5766–5768

4. ^{1}H, ^{13}C NMR and mass spectra of obtained compounds

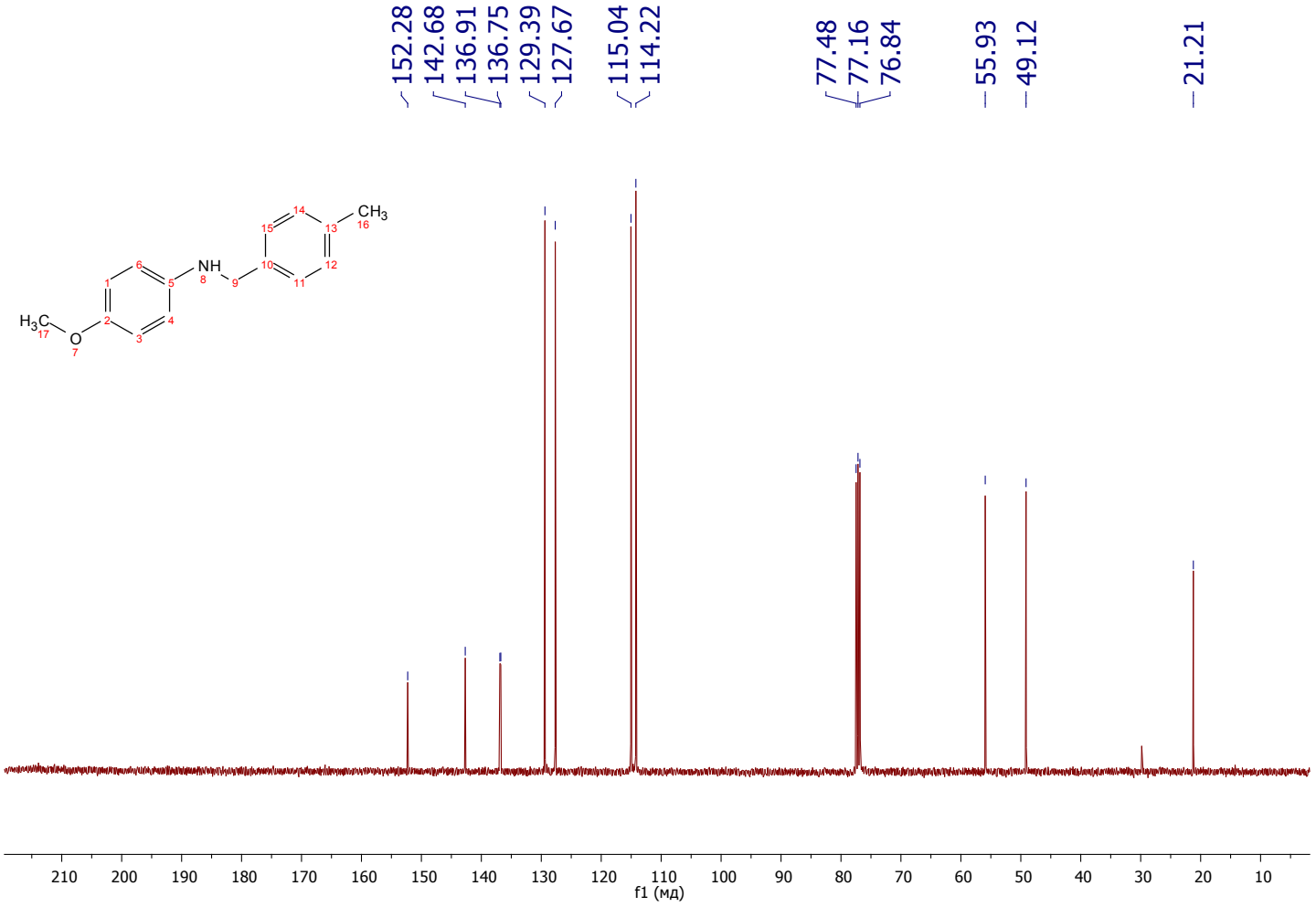
Example of integration of reaction mixture with DMF as internal standard (table 1, entry 12).



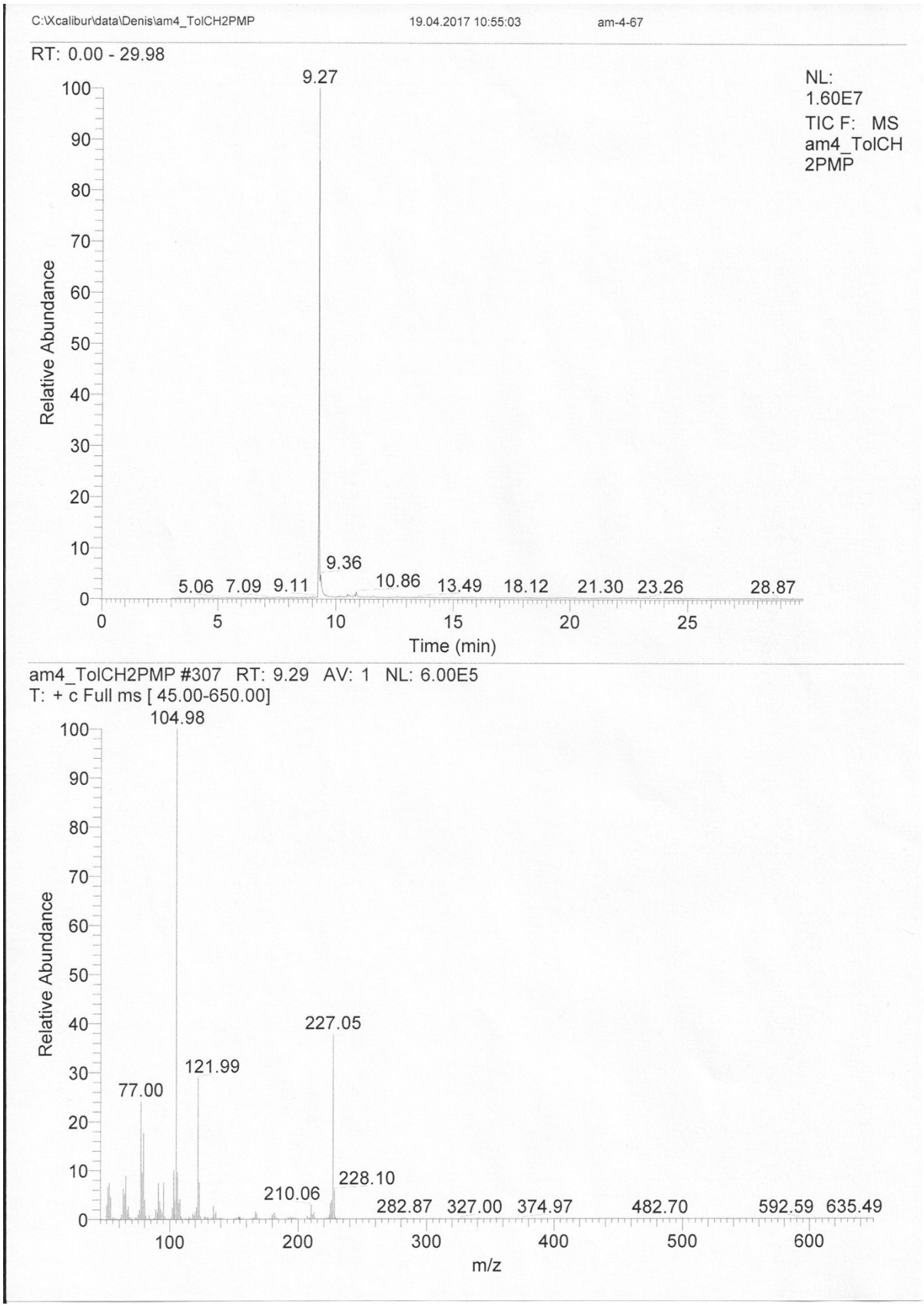
4-methoxy-N-(4-methylbenzyl)aniline (12a), ^{1}H NMR, $CDCl_3$, 400 MHz



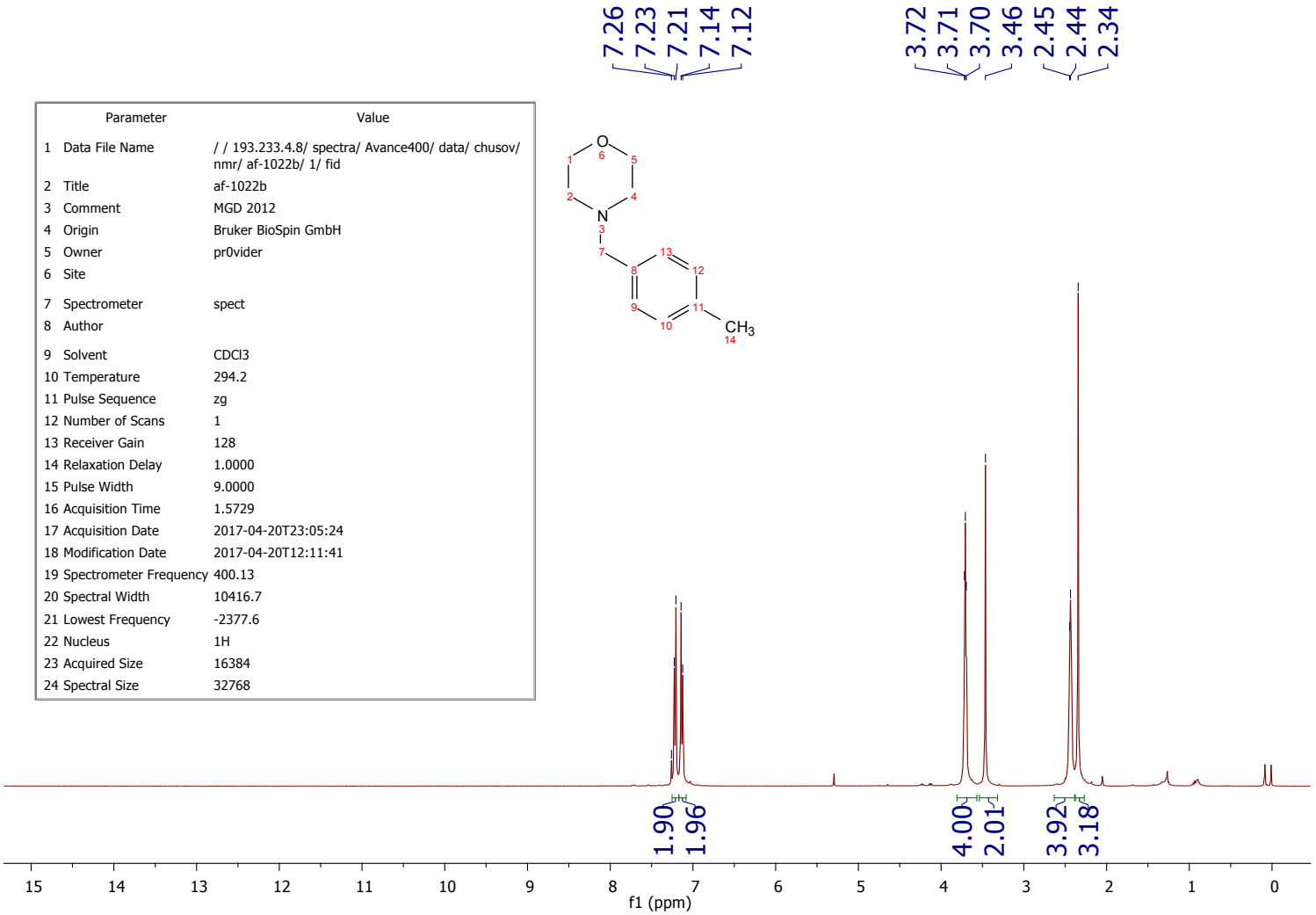
4-methoxy-N-(4-methylbenzyl)aniline (12a), ^{13}C NMR, $CDCl_3$, 101 MHz



EI-MS spectrum of **12a**



4-(4-methylbenzyl)morpholine (12b), ^{1}H NMR, $CDCl_3$, 400 MHz



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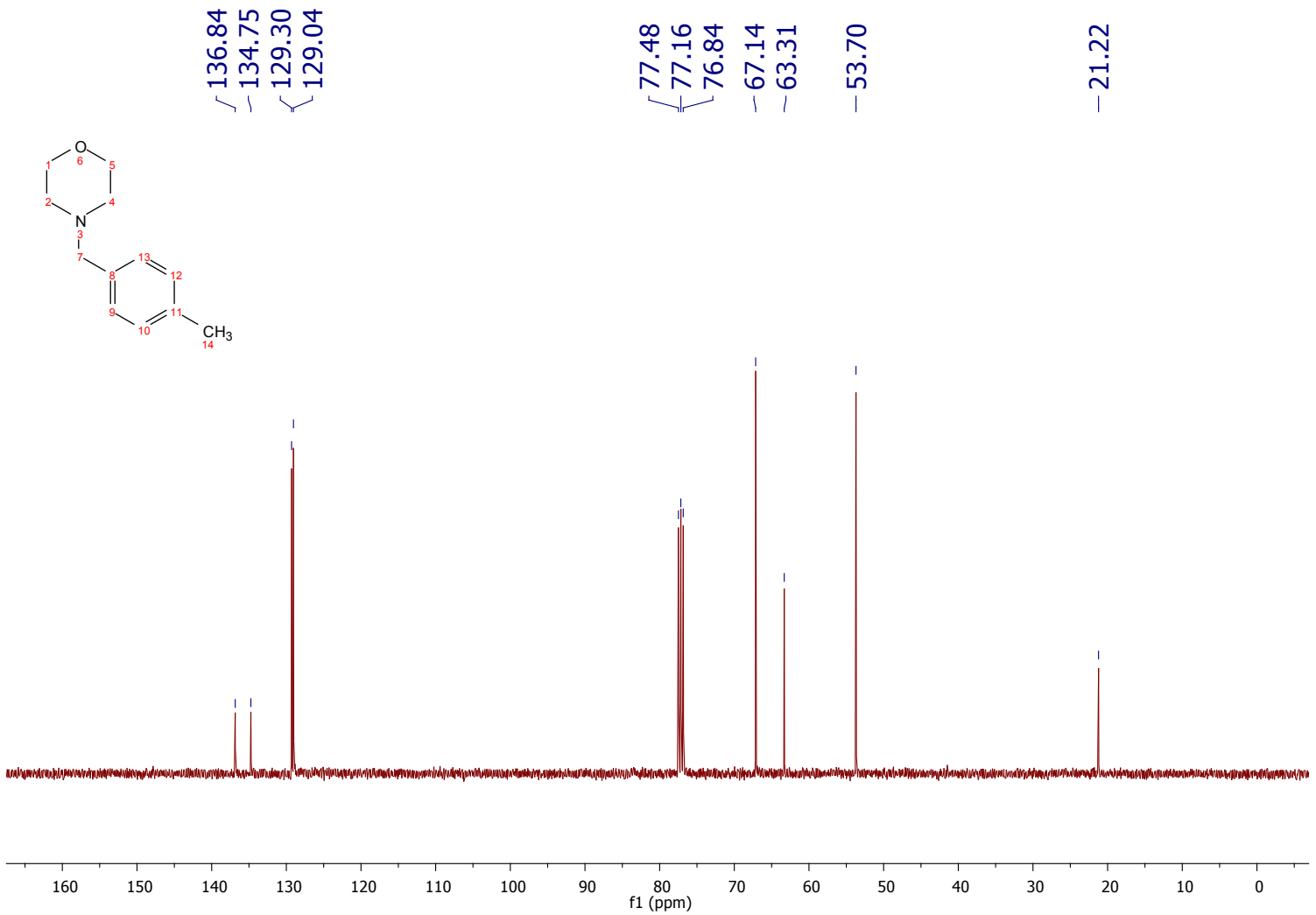
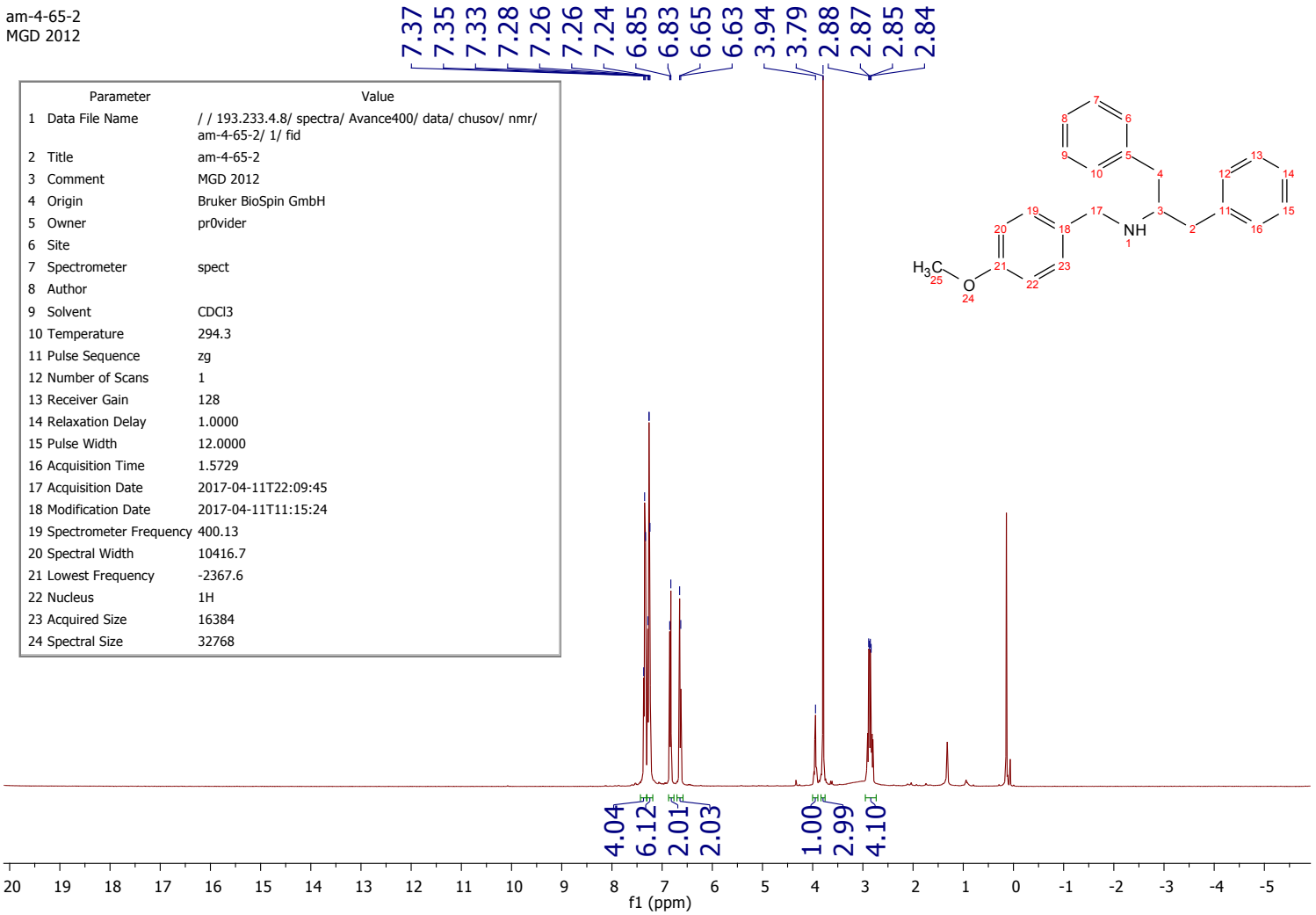
2	Title	af-1022b
3	Comment	MGD 2012
4	Origin	Bruker BioSpin GmbH
5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.2
11	Pulse Sequence	zg
12	Number of Scans	1
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.0000
16	Acquisition Time	1.5729
17	Acquisition Date	2017-04-20T23:05:24
18	Modification Date	2017-04-20T12:11:41
19	Spectrometer Frequency	400.13
20	Spectral Width	10416.7
21	Lowest Frequency	-2377.6
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	32768

4-(4-methylbenzyl)morpholine (12b), ^{13}C NMR, $CDCl_3$, 101 MHz



N-(1,3-diphenylpropan-2-yl)-4-methoxyaniline (12c), ^{1}H NMR, $CDCl_3$, 400 MHz



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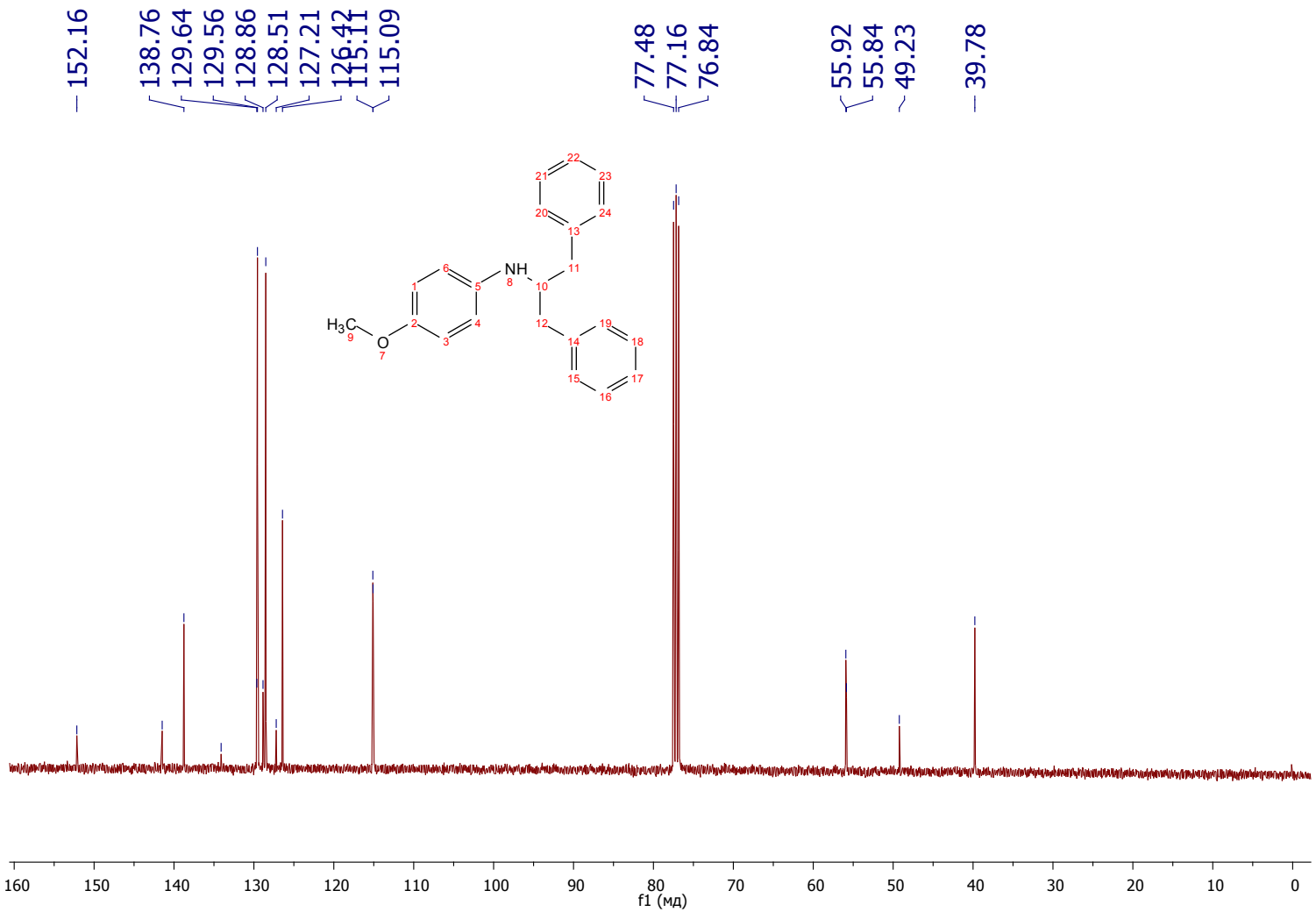
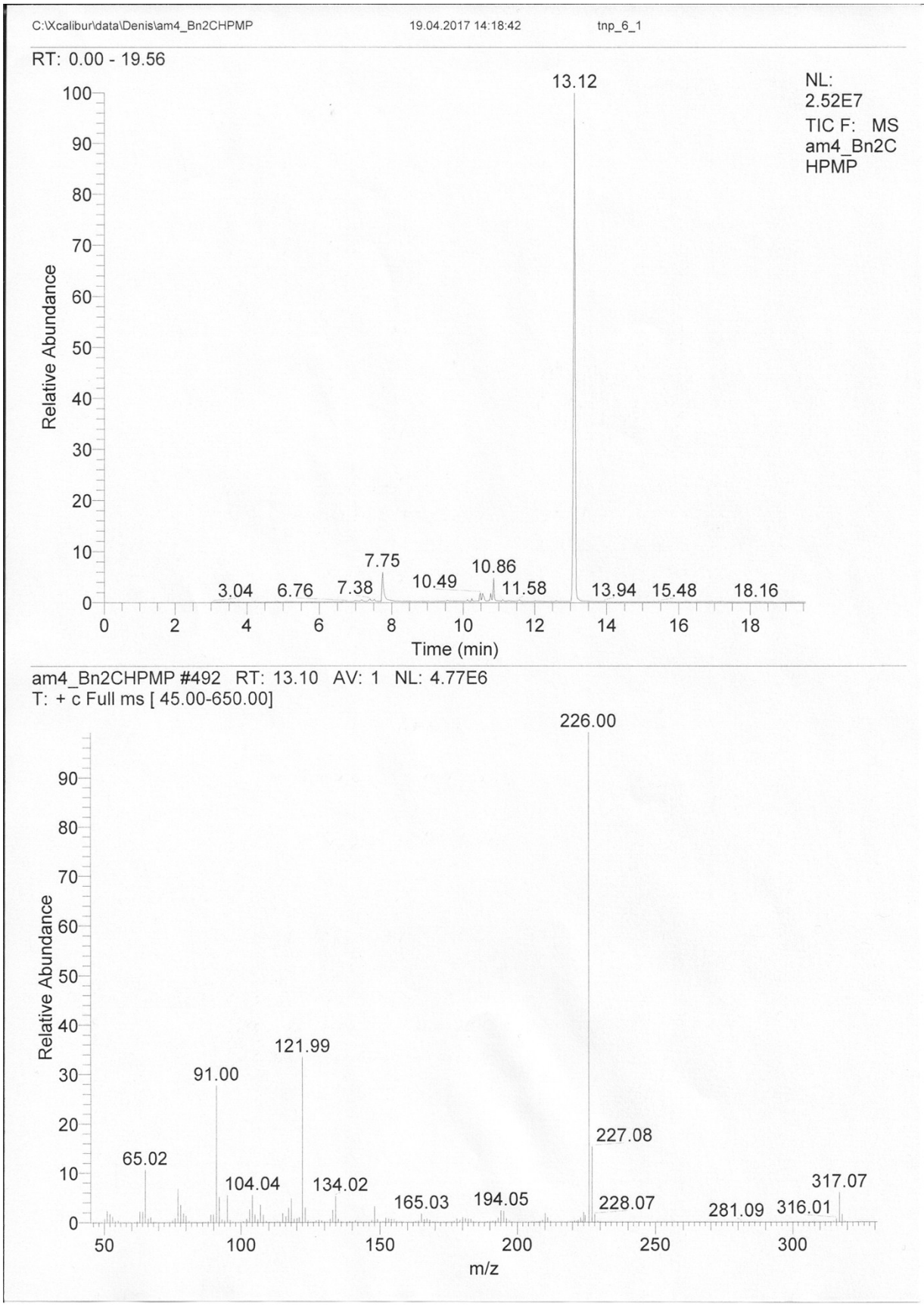
4	Origin	Bruker BioSpin GmbH
5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.3
11	Pulse Sequence	zg
12	Number of Scans	1
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	12.0000
16	Acquisition Time	1.5729
17	Acquisition Date	2017-04-11T22:09:45
18	Modification Date	2017-04-11T11:15:24
19	Spectrometer Frequency	400.13
20	Spectral Width	10416.7
21	Lowest Frequency	-2367.6
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	32768

N-(1,3-diphenylpropan-2-yl)-4-methoxyaniline (12c), ^{13}C NMR, $CDCl_3$, 101 MHz



EI-MS spectrum of **12c**



HRMS (TOF ESI+) spectrum of **12c**

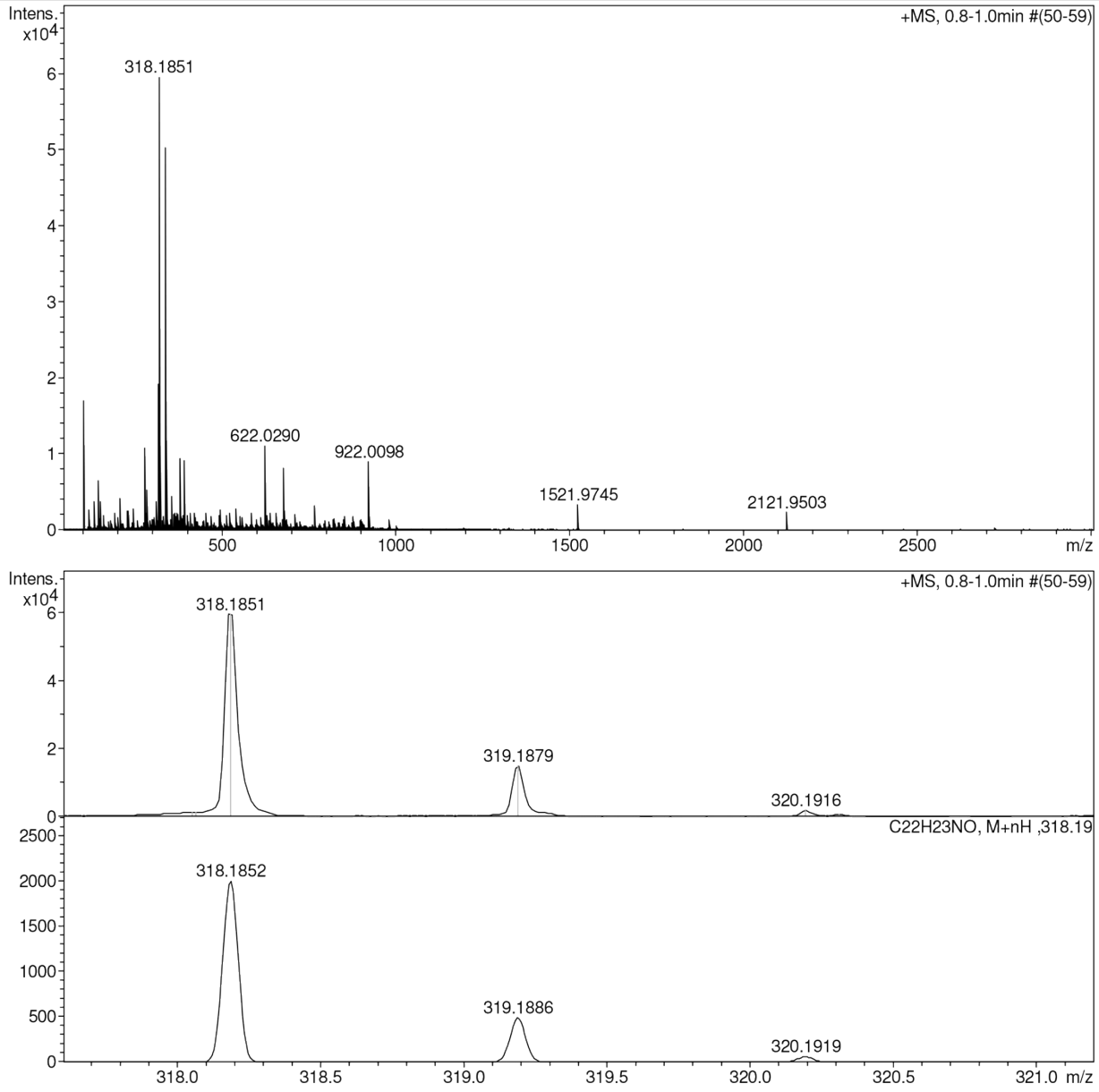
Display Report

Analysis Info

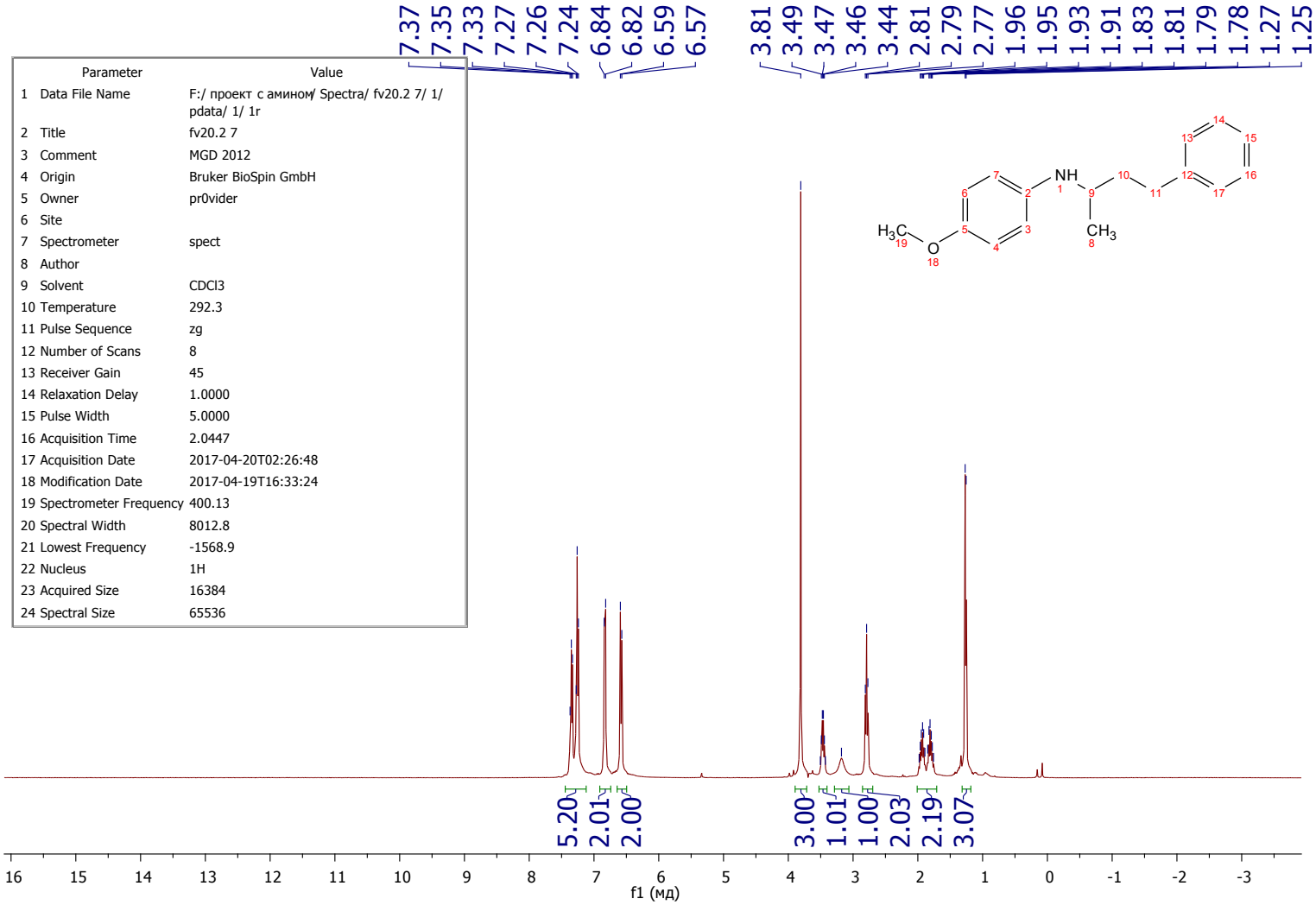
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\May_19_2017\am-4-65-2_&clblow.d	Acquisition Date	19.05.2017 13:30:38
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AM-4-65-2	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



4-methoxy-N-(4-phenylbutan-2-yl)aniline (12d), ^{1}H NMR, $CDCl_3$, 400 MHz



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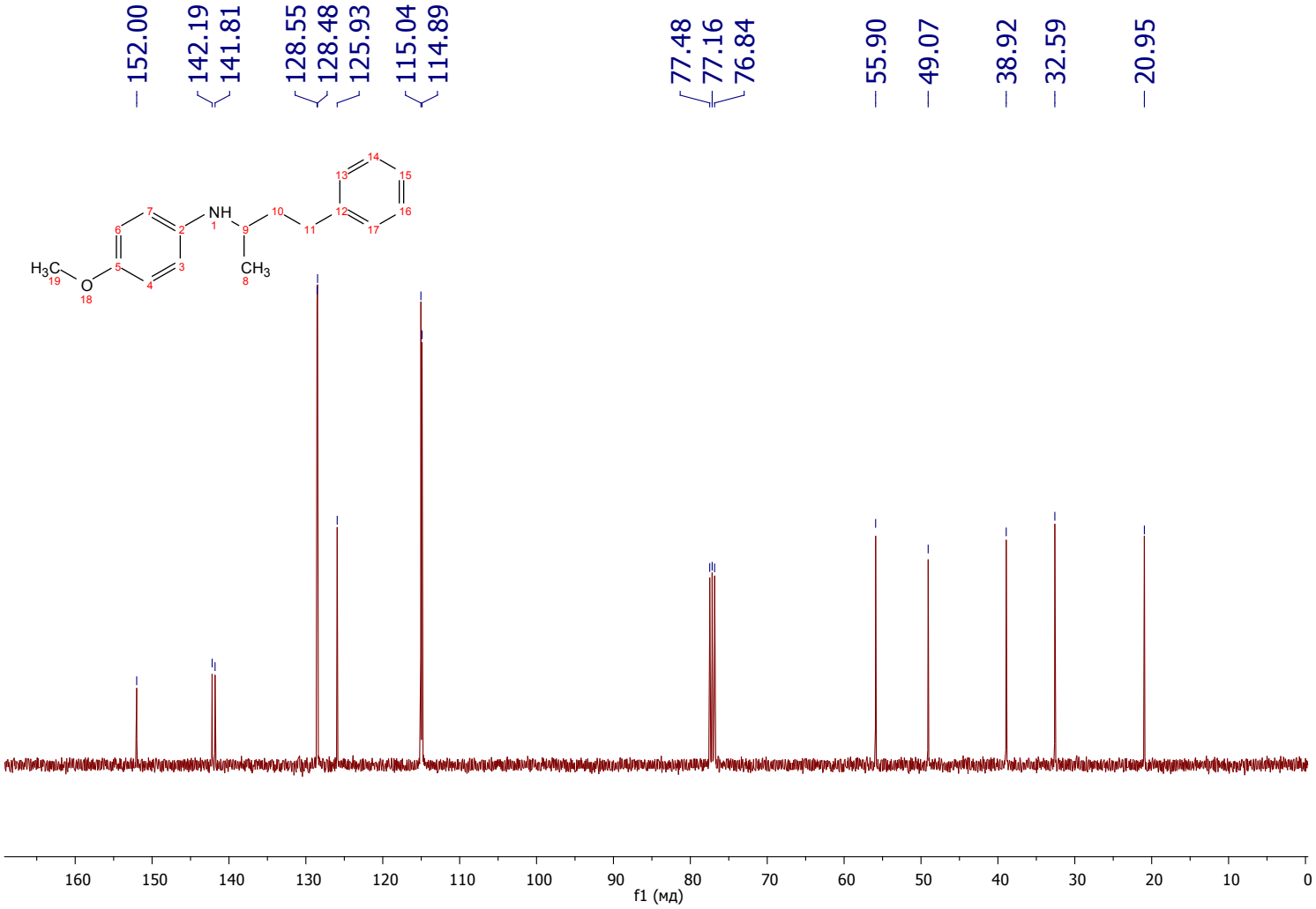
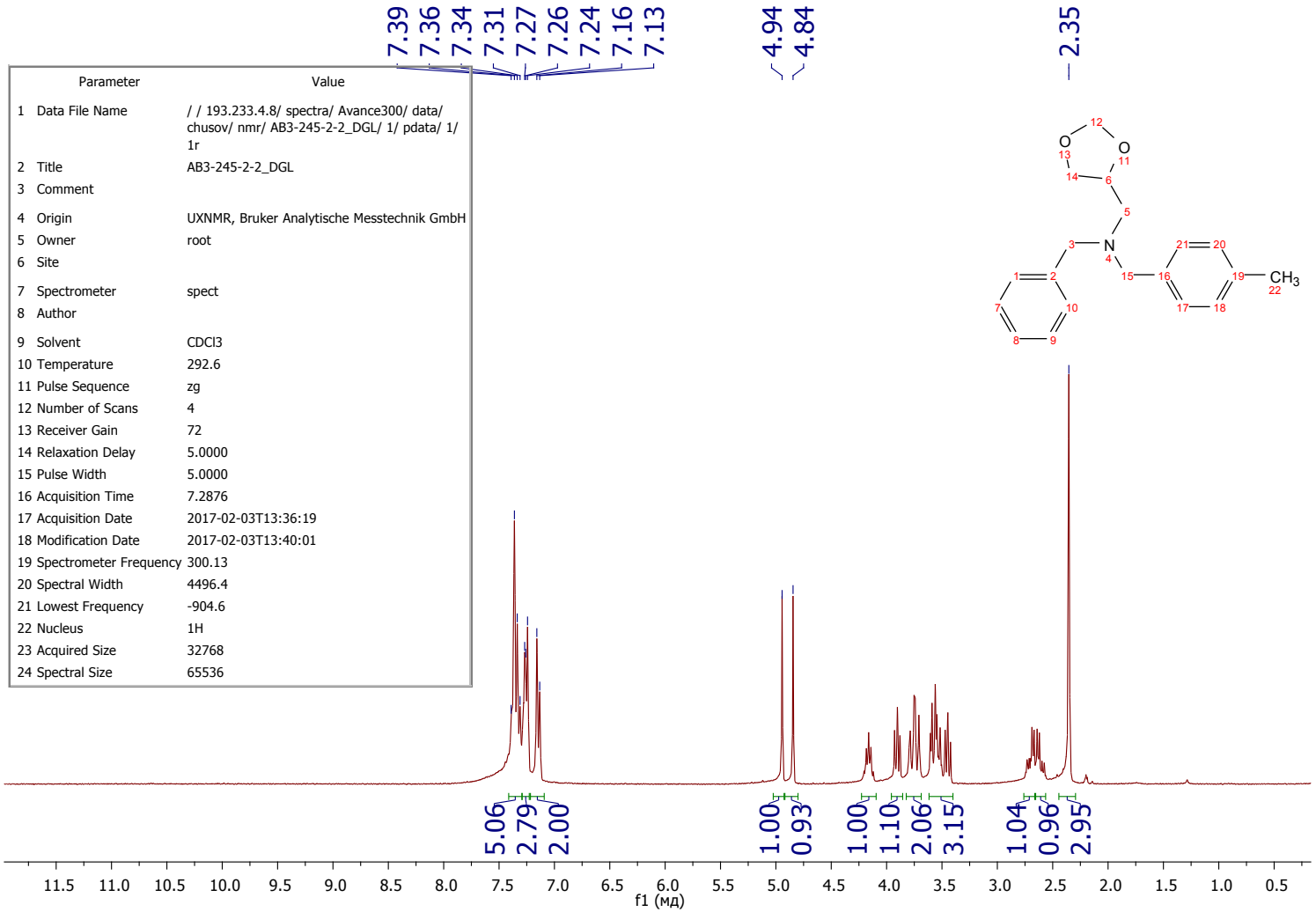
5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.3
11	Pulse Sequence	zg
12	Number of Scans	8
13	Receiver Gain	45
14	Relaxation Delay	1.0000
15	Pulse Width	5.0000
16	Acquisition Time	2.0447
17	Acquisition Date	2017-04-20T02:26:48
18	Modification Date	2017-04-19T16:33:24
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1568.9
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	65536

4-methoxy-N-(4-phenylbutan-2-yl)aniline (12d), ^{13}C NMR, $CDCl_3$, 101 MHz



N-((1,3-dioxolan-4-yl)methyl)-N-benzyl-1-(p-tolyl)methanamine (12e), ^{1}H NMR, $CDCl_3$, 300 MHz



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3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.6
11	Pulse Sequence	zg
12	Number of Scans	4
13	Receiver Gain	72
14	Relaxation Delay	5.0000
15	Pulse Width	5.0000
16	Acquisition Time	7.2876
17	Acquisition Date	2017-02-03T13:36:19
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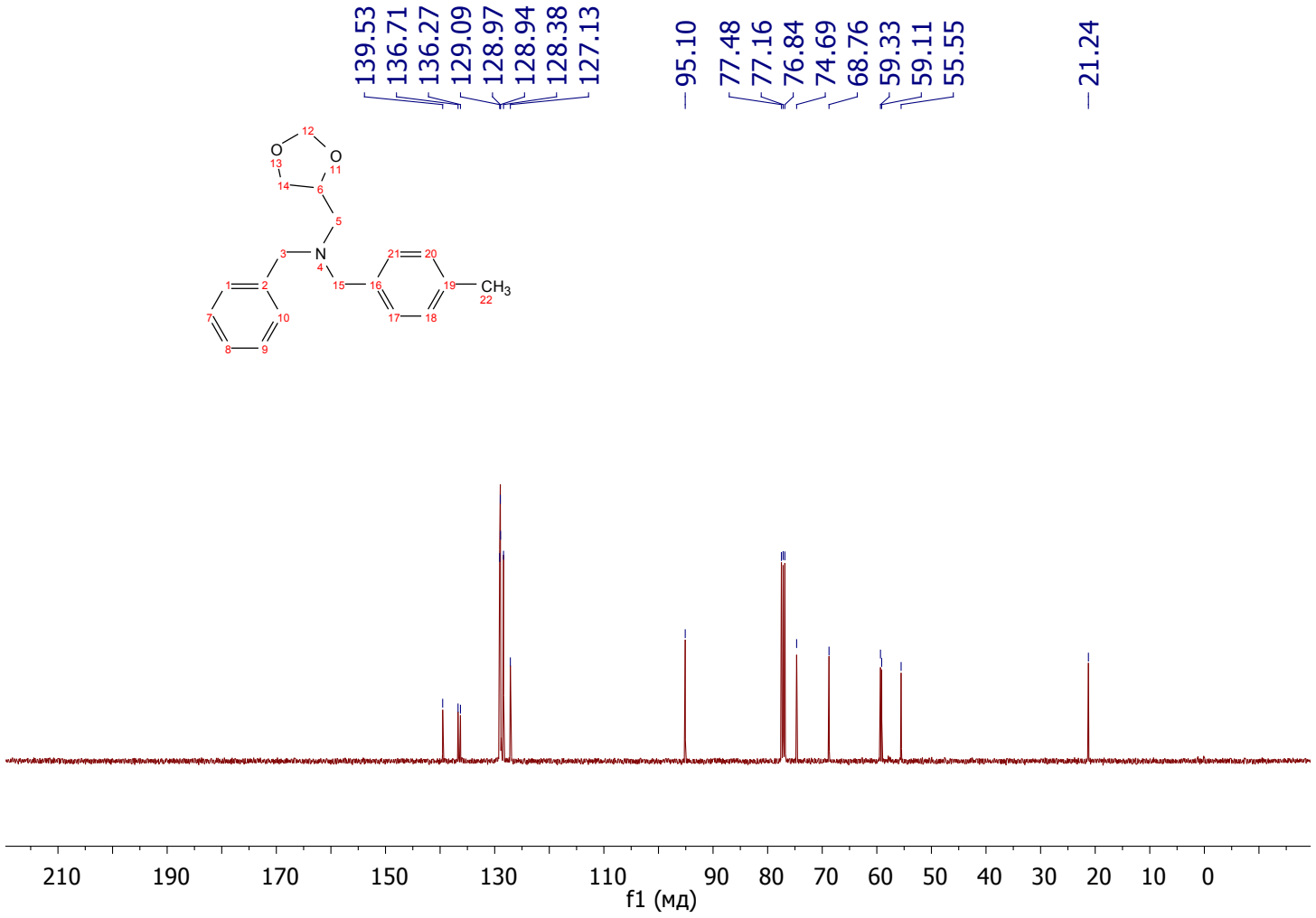
19	Spectrometer Frequency	300.13
20	Spectral Width	4496.4
21	Lowest Frequency	-904.6
22	Nucleus	1H
23	Acquired Size	32768
24	Spectral Size	65536

N-((1,3-dioxolan-4-yl)methyl)-N-benzyl-1-(p-tolyl)methanamine (12e), ^{13}C NMR, $CDCl_3$, 101 MHz



HRMS (ESI-TOF) of **12e**

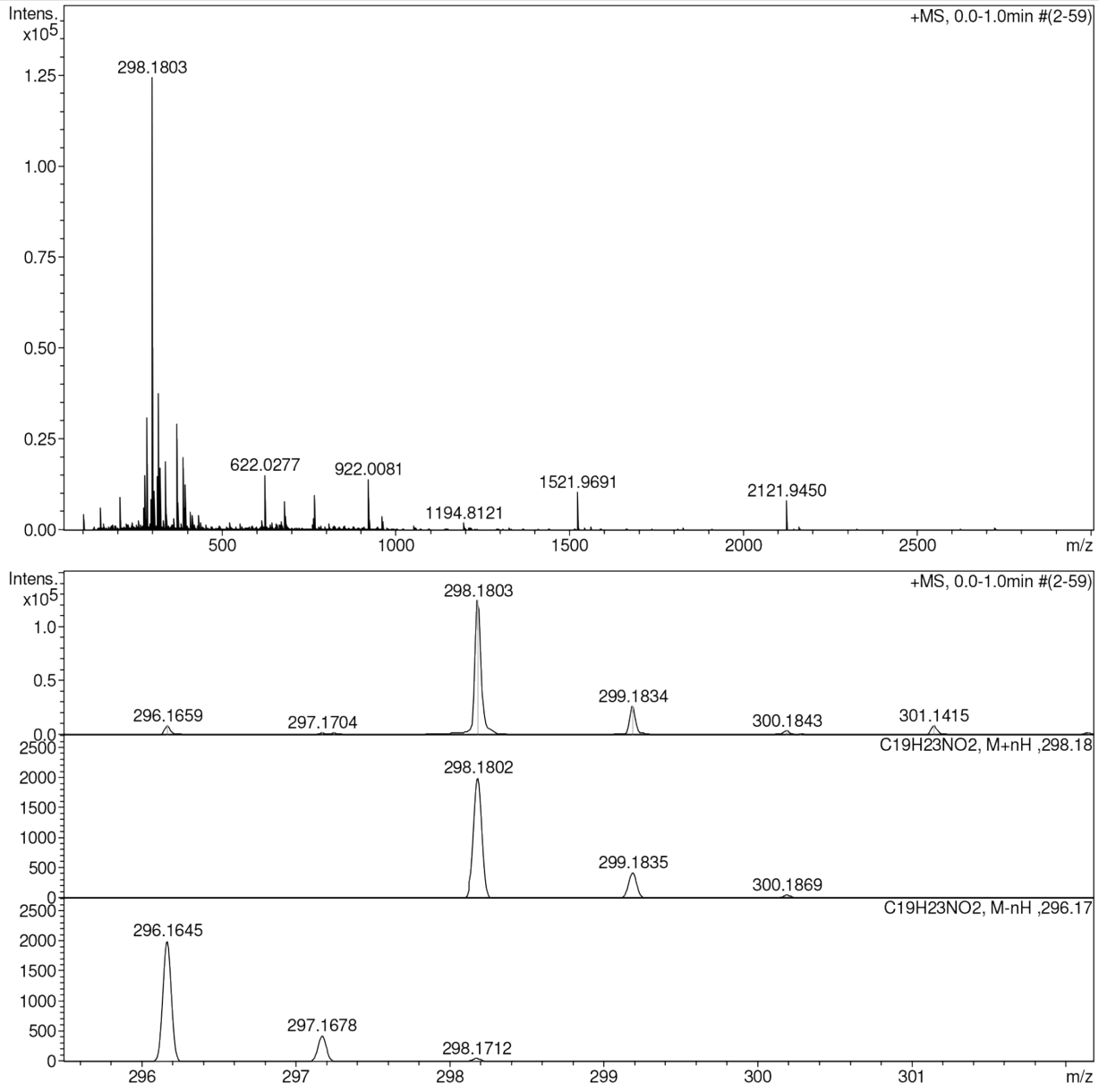
Display Report

Analysis Info

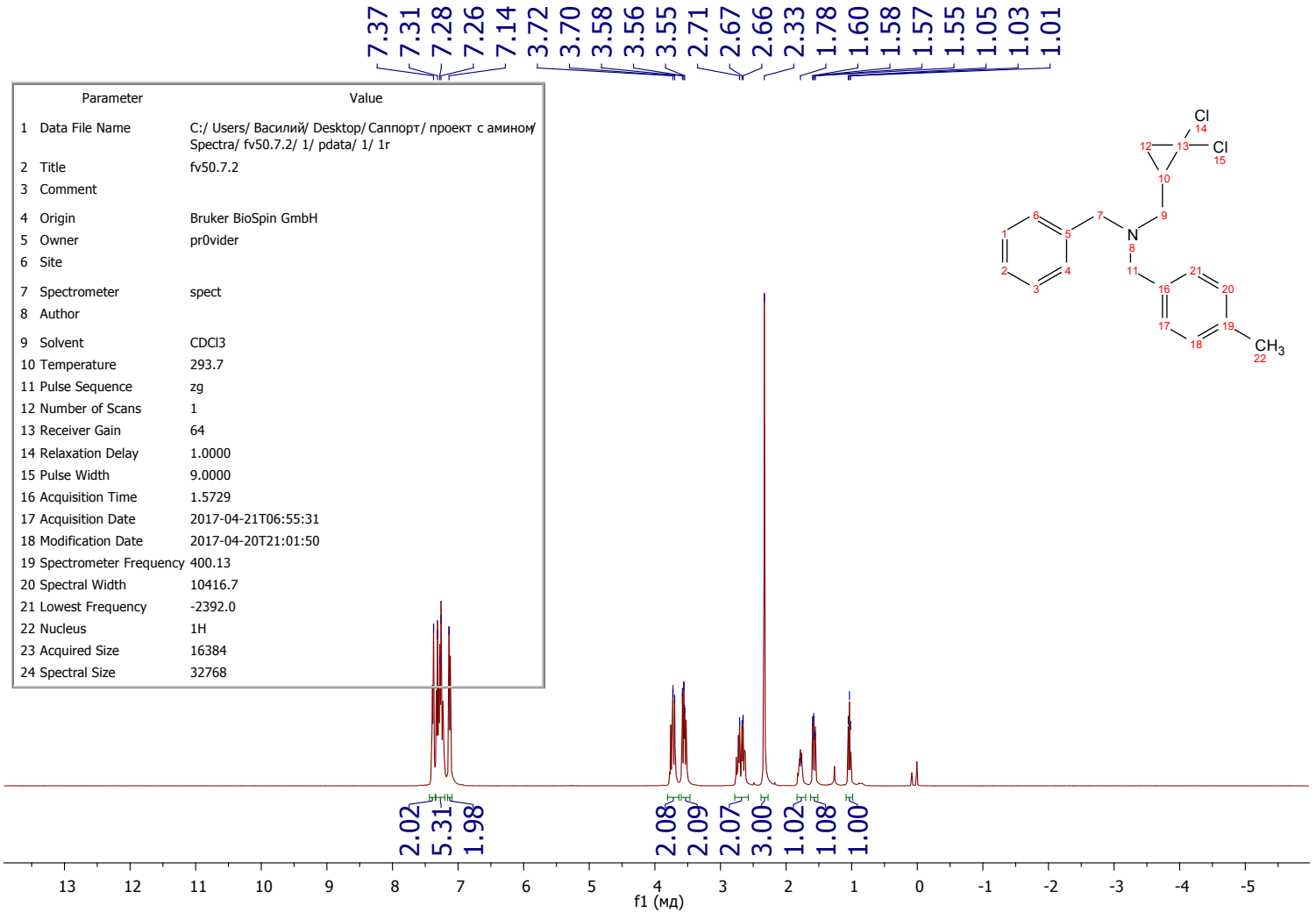
Acquisition Date	19.05.2017 14:22:21		
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\May_19_2017\ab-uf3_&clblow.d		
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AB-Uf3	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



N-benzyl-1-(2,2-dichlorocyclopropyl)-N-(4-methylbenzyl)methanamine (12f), ^{1}H NMR, $CDCl_3$, 400 MHz



Parameter	Value
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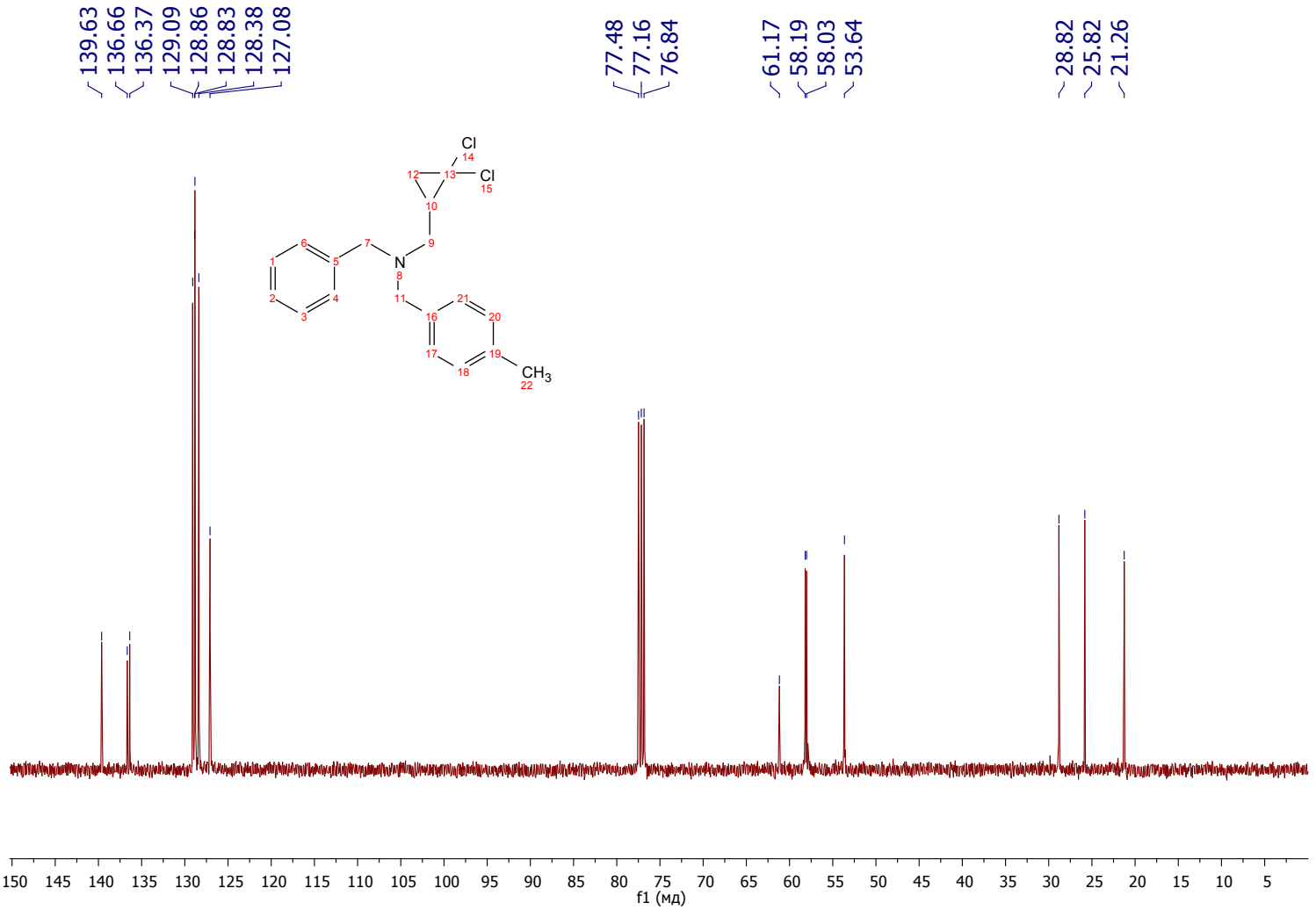
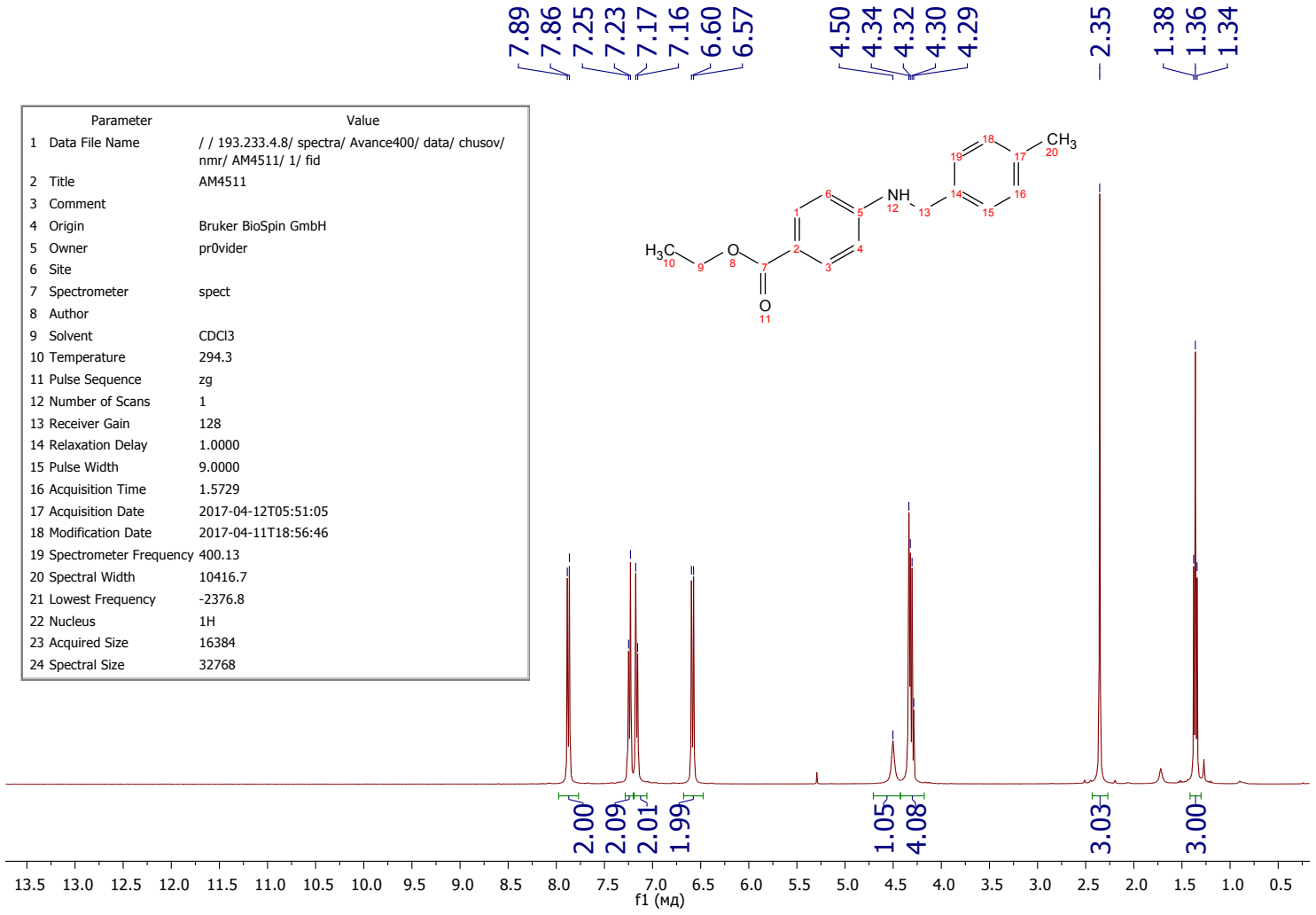
2 Title	fv50.7.2
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	pr0vider
6 Site	
7 Spectrometer	spect
8 Author	
9 Solvent	CDCl3
10 Temperature	293.7
11 Pulse Sequence	zg
12 Number of Scans	1
13 Receiver Gain	64
14 Relaxation Delay	1.0000
15 Pulse Width	9.0000
16 Acquisition Time	1.5729
17 Acquisition Date	2017-04-21T06:55:31
18 Modification Date	2017-04-20T21:01:50
19 Spectrometer Frequency	400.13
20 Spectral Width	10416.7
21 Lowest Frequency	-2392.0
22 Nucleus	1H
23 Acquired Size	16384
24 Spectral Size	32768

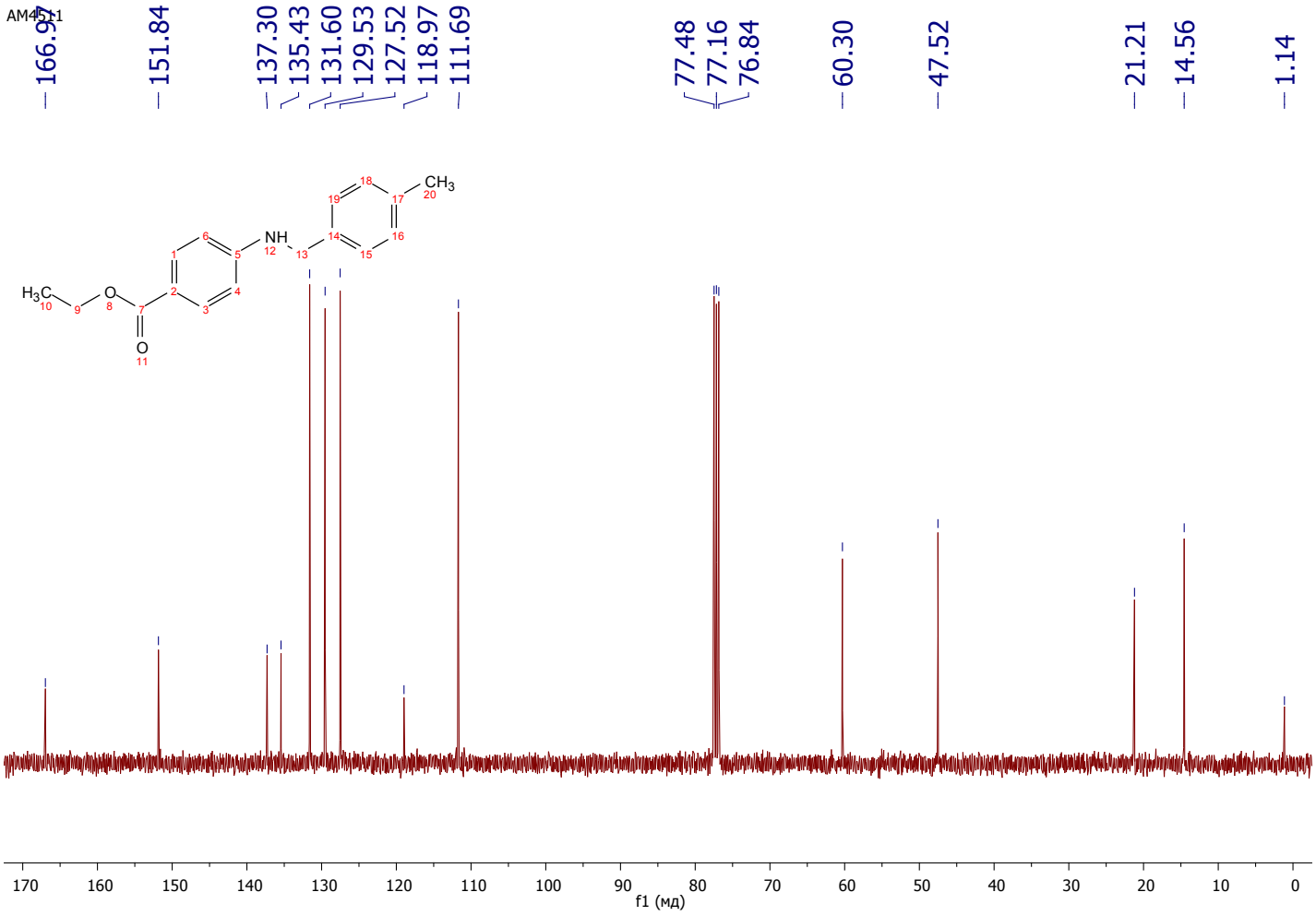
N-benzyl-1-(2,2-dichlorocyclopropyl)-N-(4-methylbenzyl)methanamine (12f), ^{13}C NMR, $CDCl_3$, 101 MHz



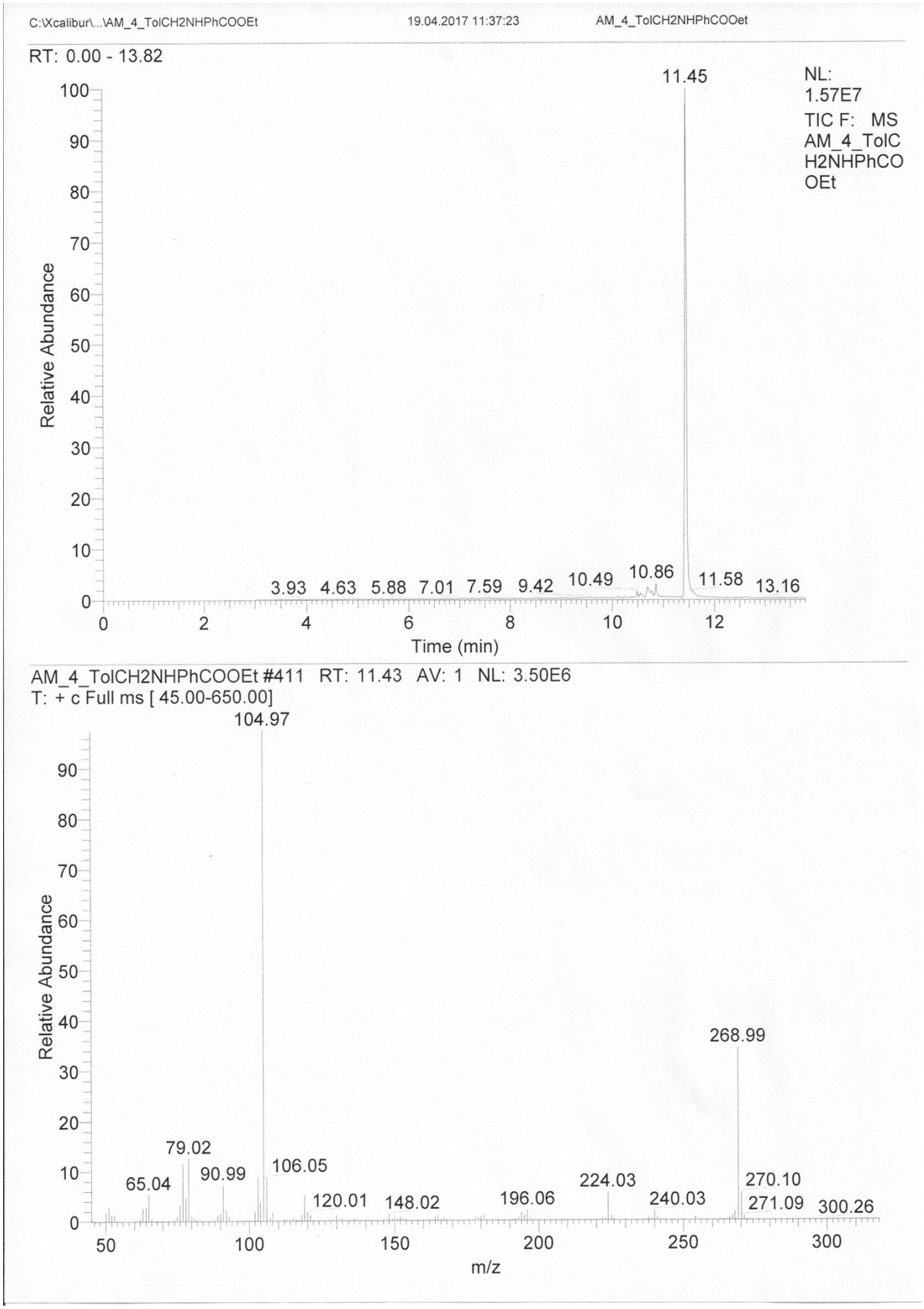
ethyl 4-((4-methylbenzyl)amino)benzoate (12g), ^{1}H NMR, $CDCl_3$, 400 MHz



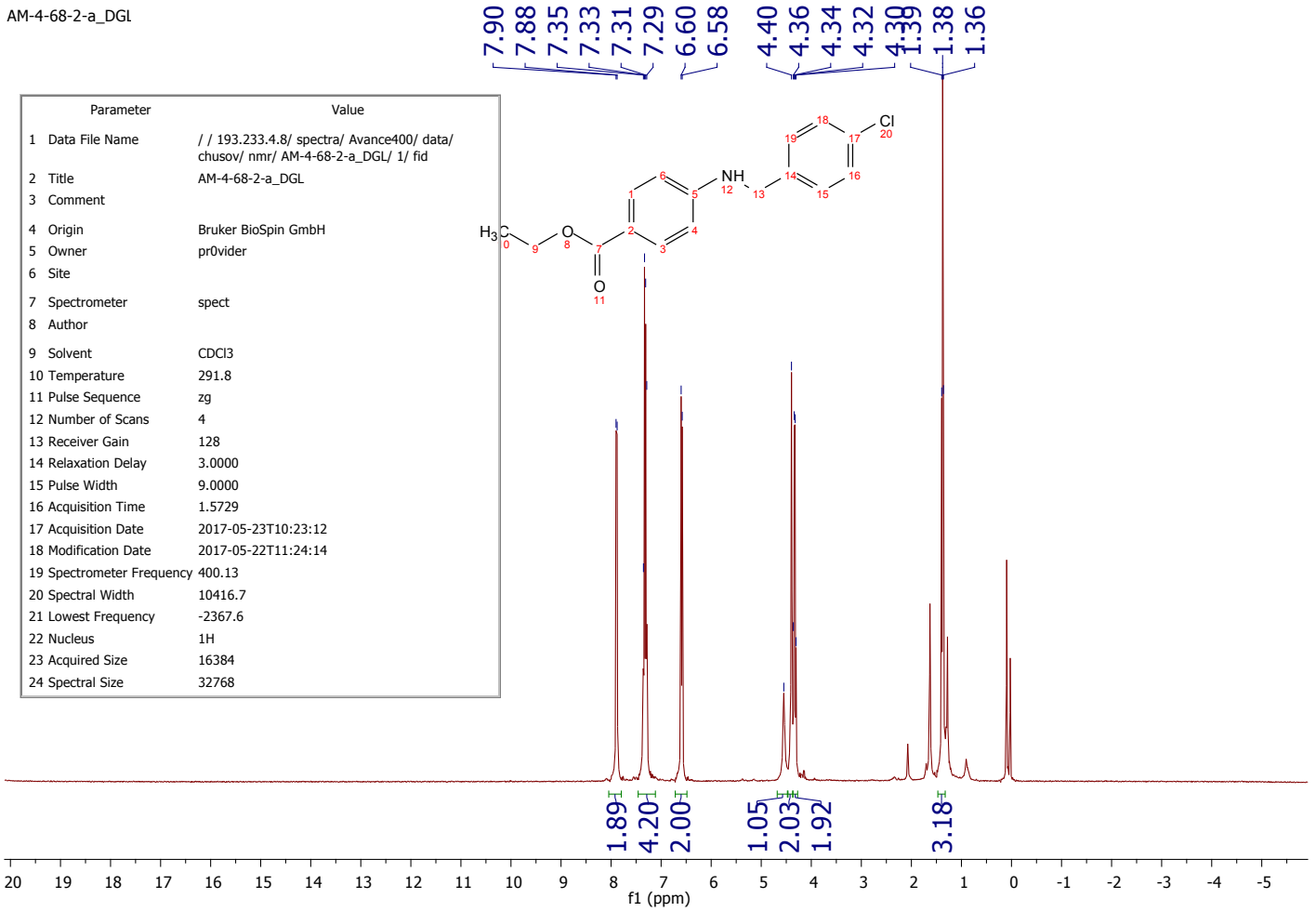
ethyl 4-((4-methylbenzyl)amino)benzoate (12g), ^{13}C NMR, $CDCl_3$, 101 MHz



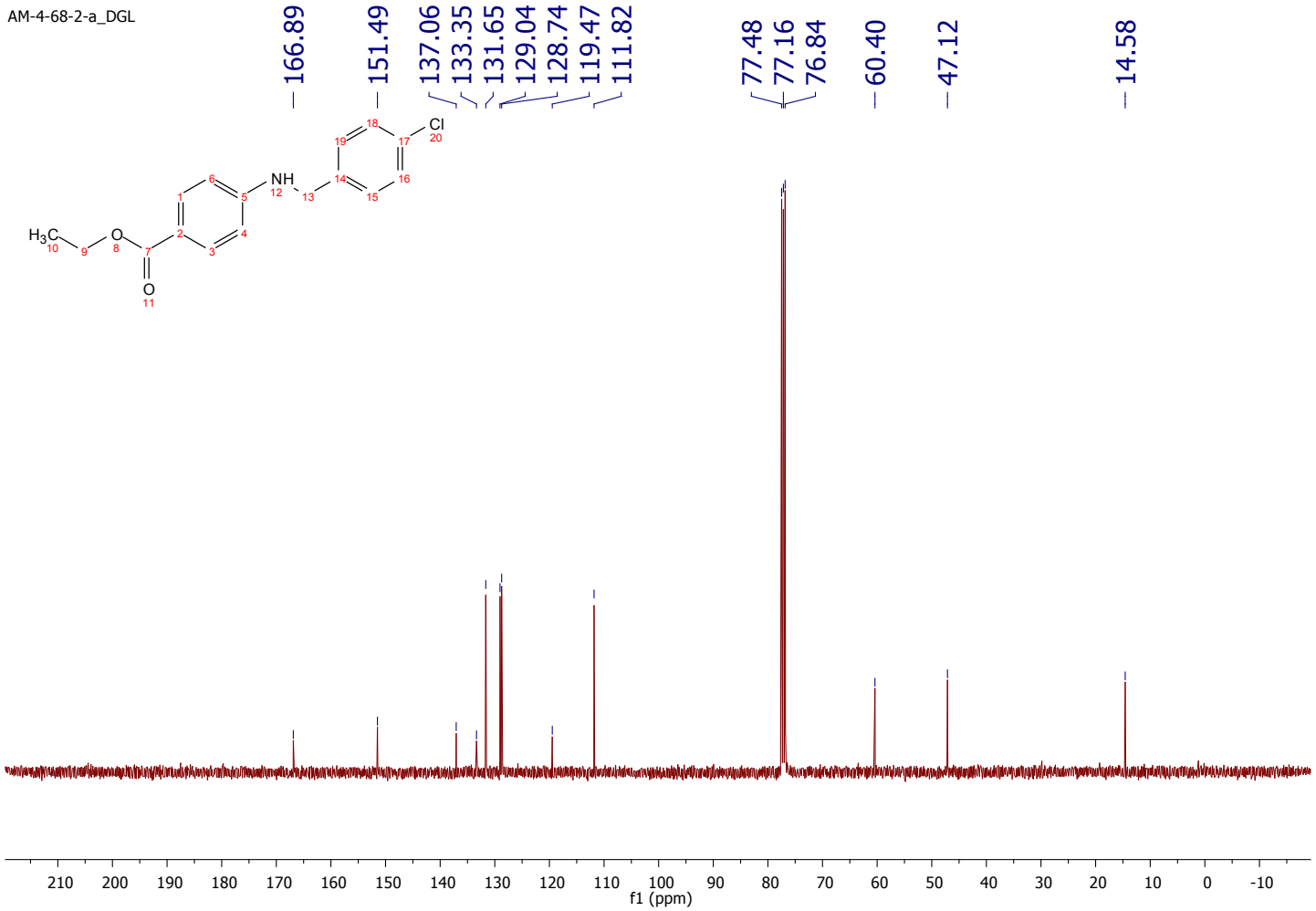
EI-MS spectrum of **12g**



Ethyl 4-((4-chlorobenzyl)amino)benzoate (12h), ^{1}H NMR, $CDCl_3$, 400 MHz



Ethyl 4-((4-chlorobenzyl)amino)benzoate (12h), ^{13}C NMR, $CDCl_3$, 101 MHz



HRMS (ESI-TOF) of **12h**

Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\INEOS\Chusov\May_19_2017\am-4-68-1_&clblow.d	Acquisition Date	19.05.2017 13:55:24
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AM-4-68-1	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
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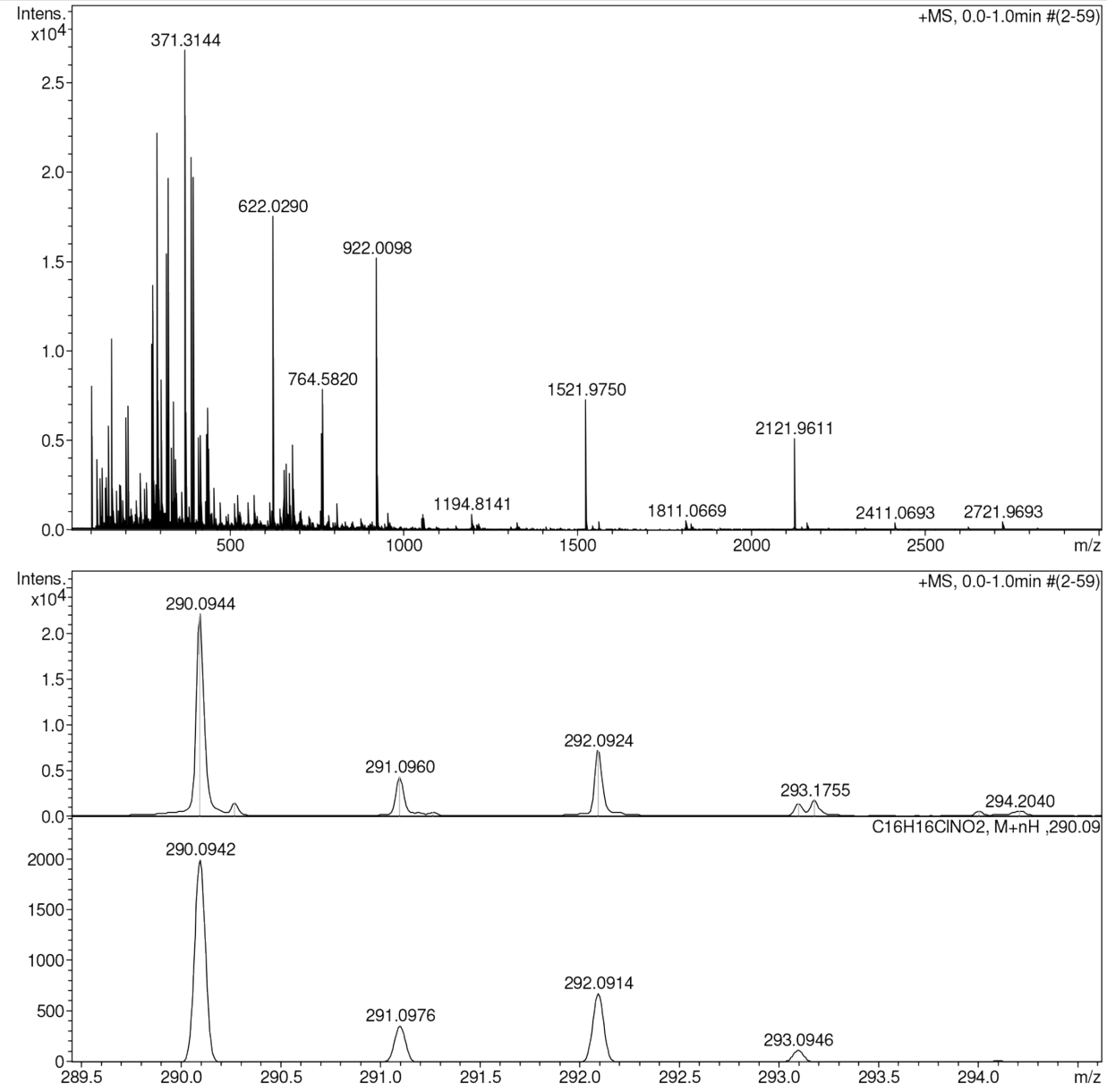
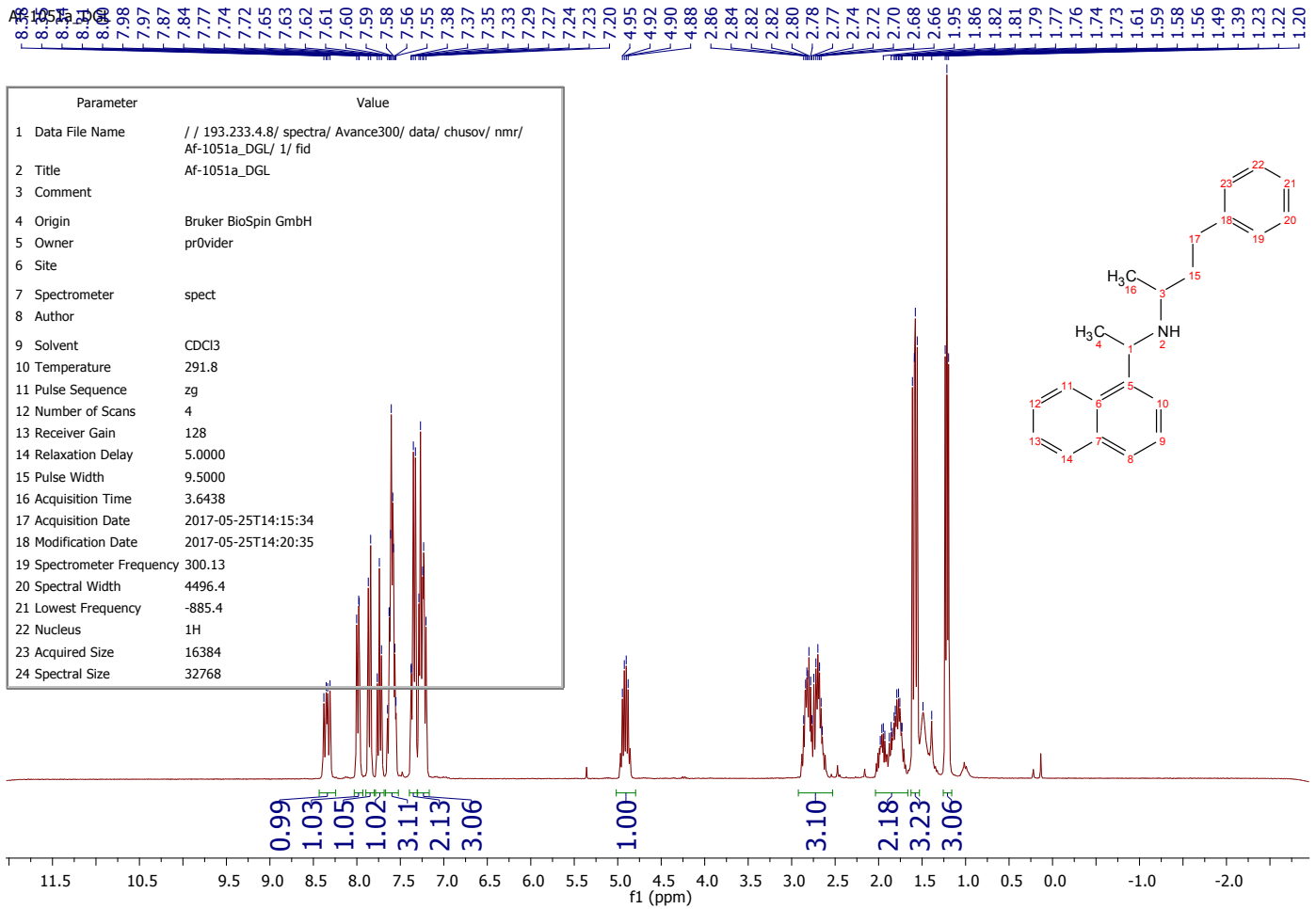
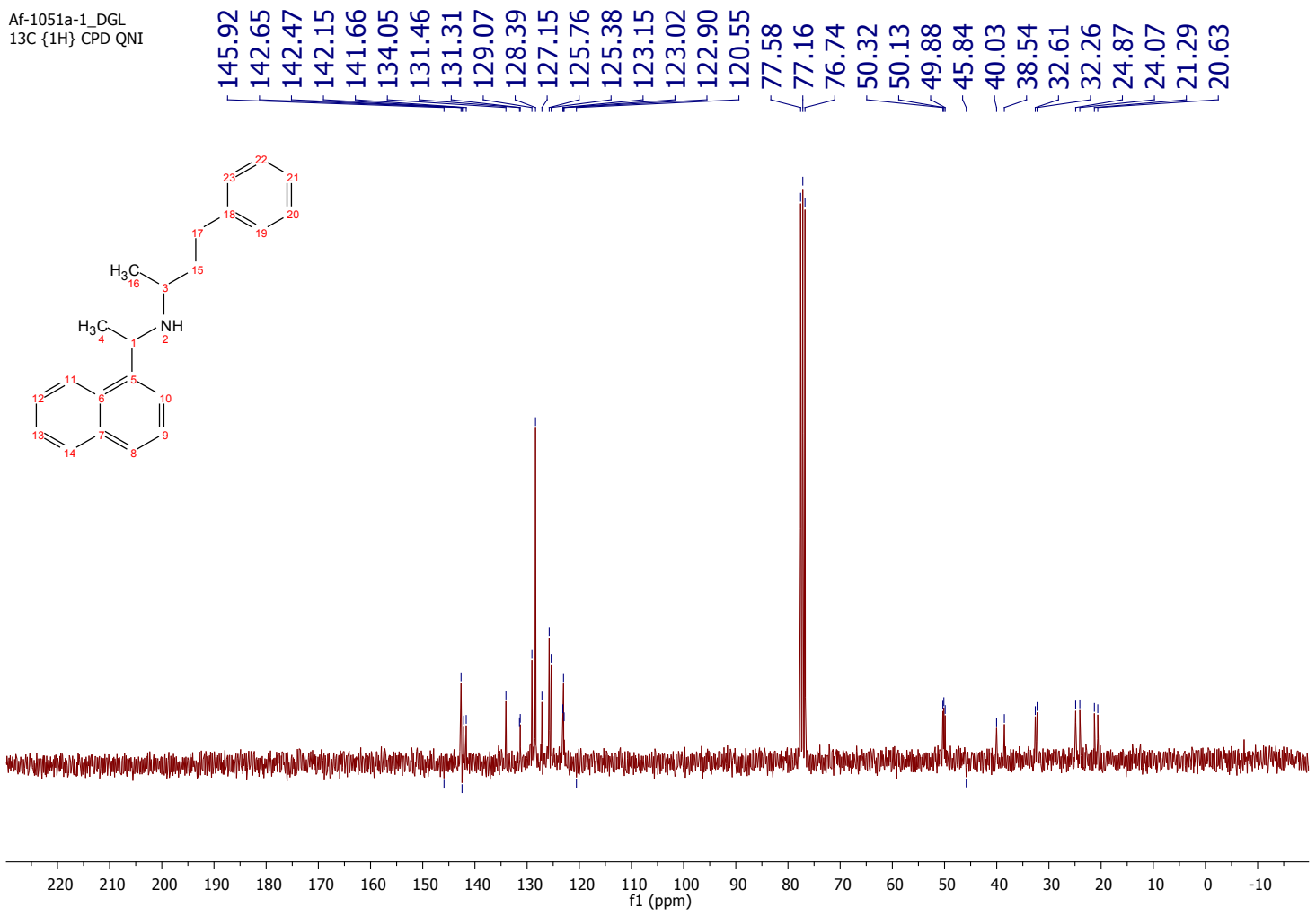
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



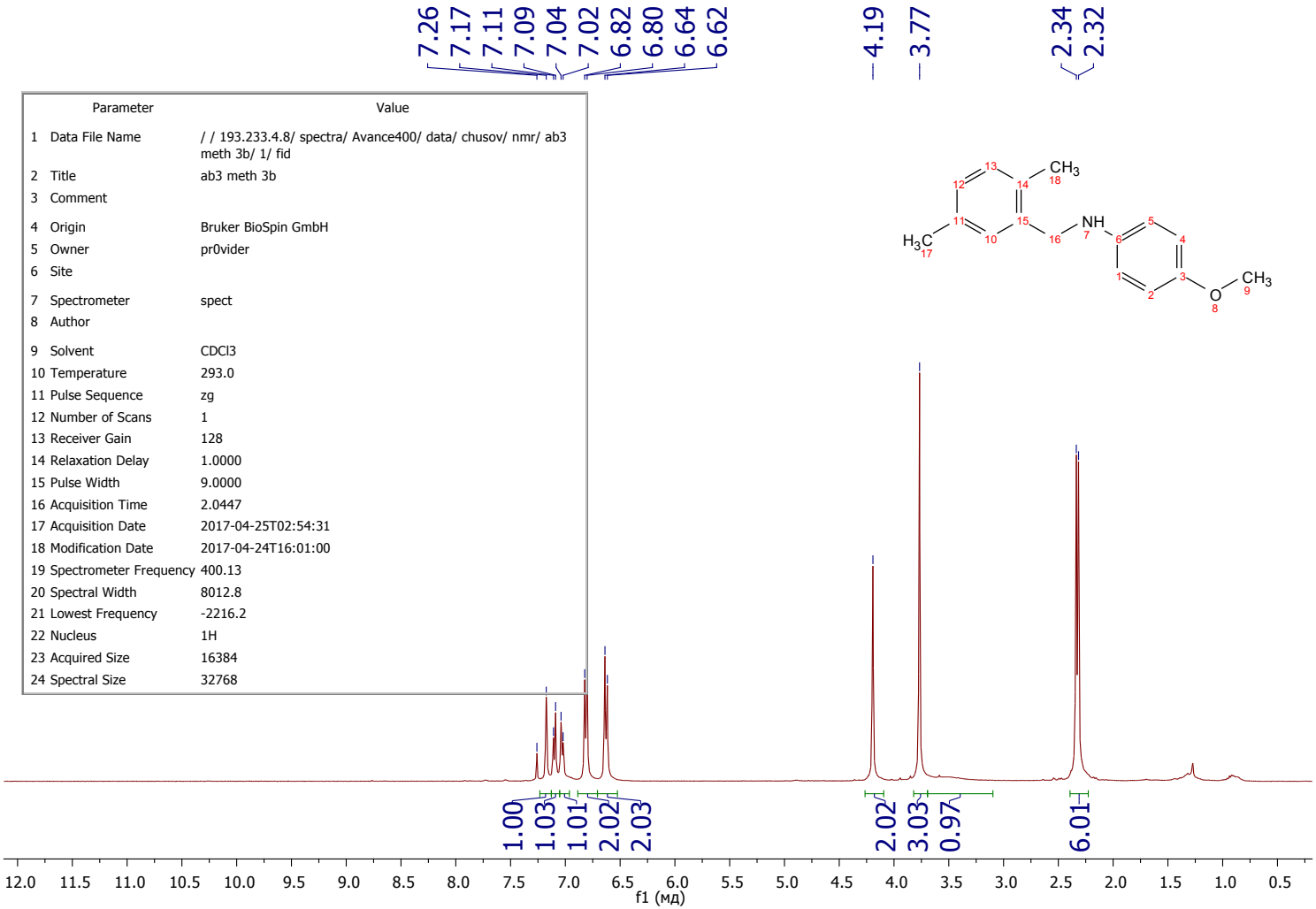
N-(1-(naphthalen-1-yl)ethyl)-4-phenylbutan-2-amine (12i), ^{1}H NMR, $CDCl_3$, 300 MHz



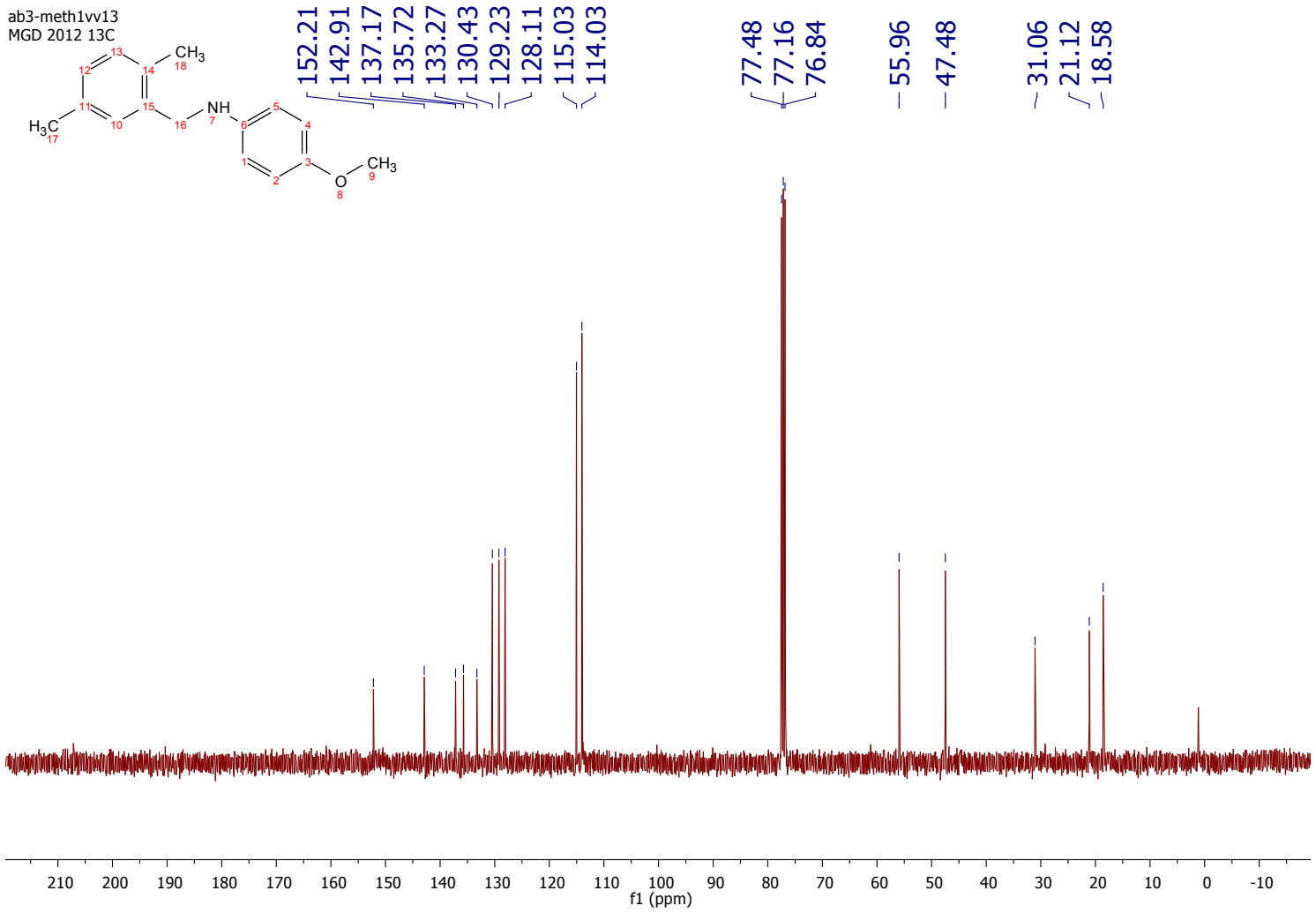
N-(1-(naphthalen-1-yl)ethyl)-4-phenylbutan-2-amine (12i), ^{13}C NMR, $CDCl_3$, 101 MHz



N-(2,5-dimethylbenzyl)-4-methoxyaniline (12j), ^{1}H NMR, $CDCl_3$, 400 MHz



N-(2,5-dimethylbenzyl)-4-methoxyaniline (12j), ^{13}C NMR, $CDCl_3$, 101 MHz



HRMS (ESI-TOF) of **12j**

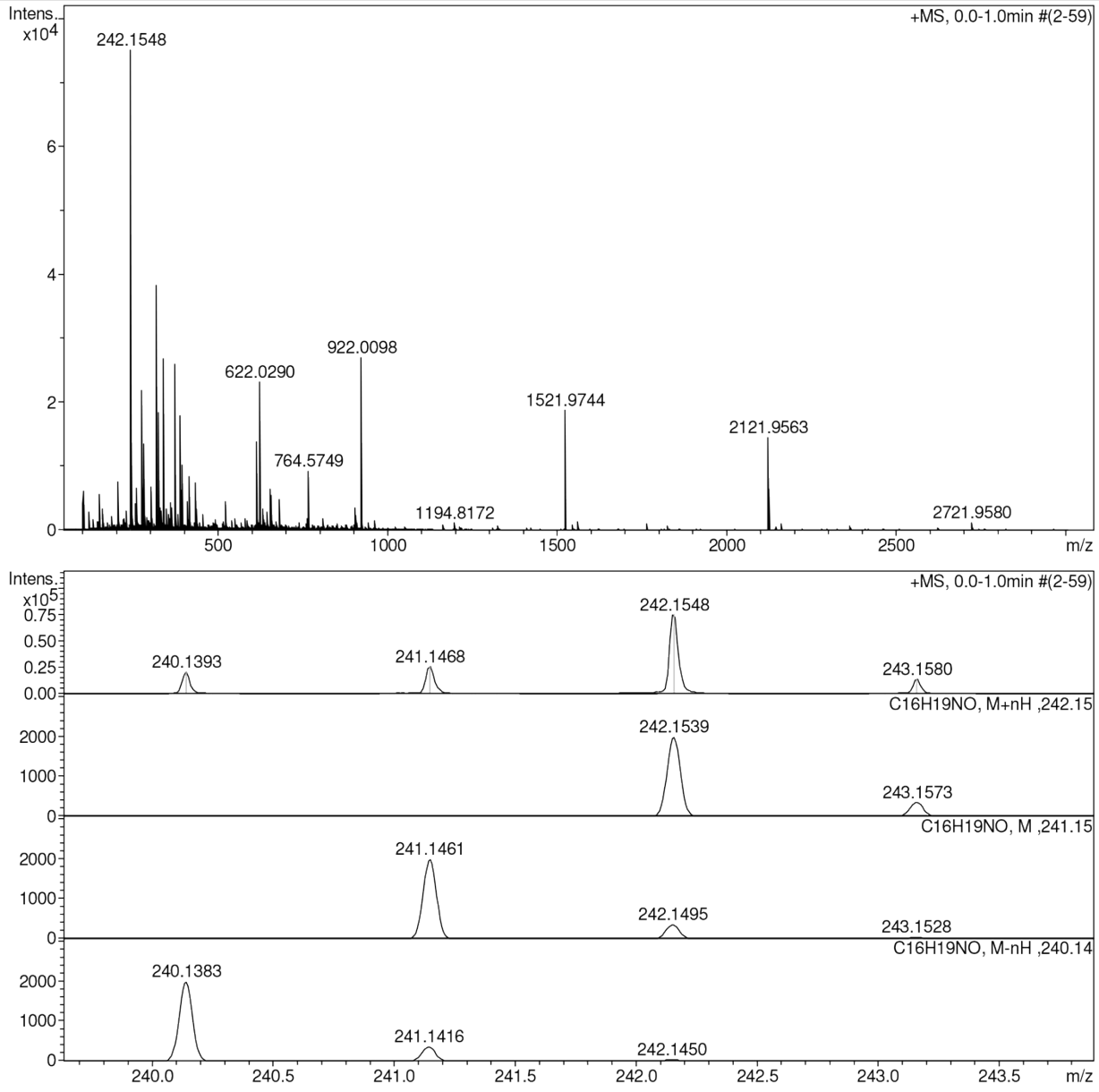
Display Report

Analysis Info

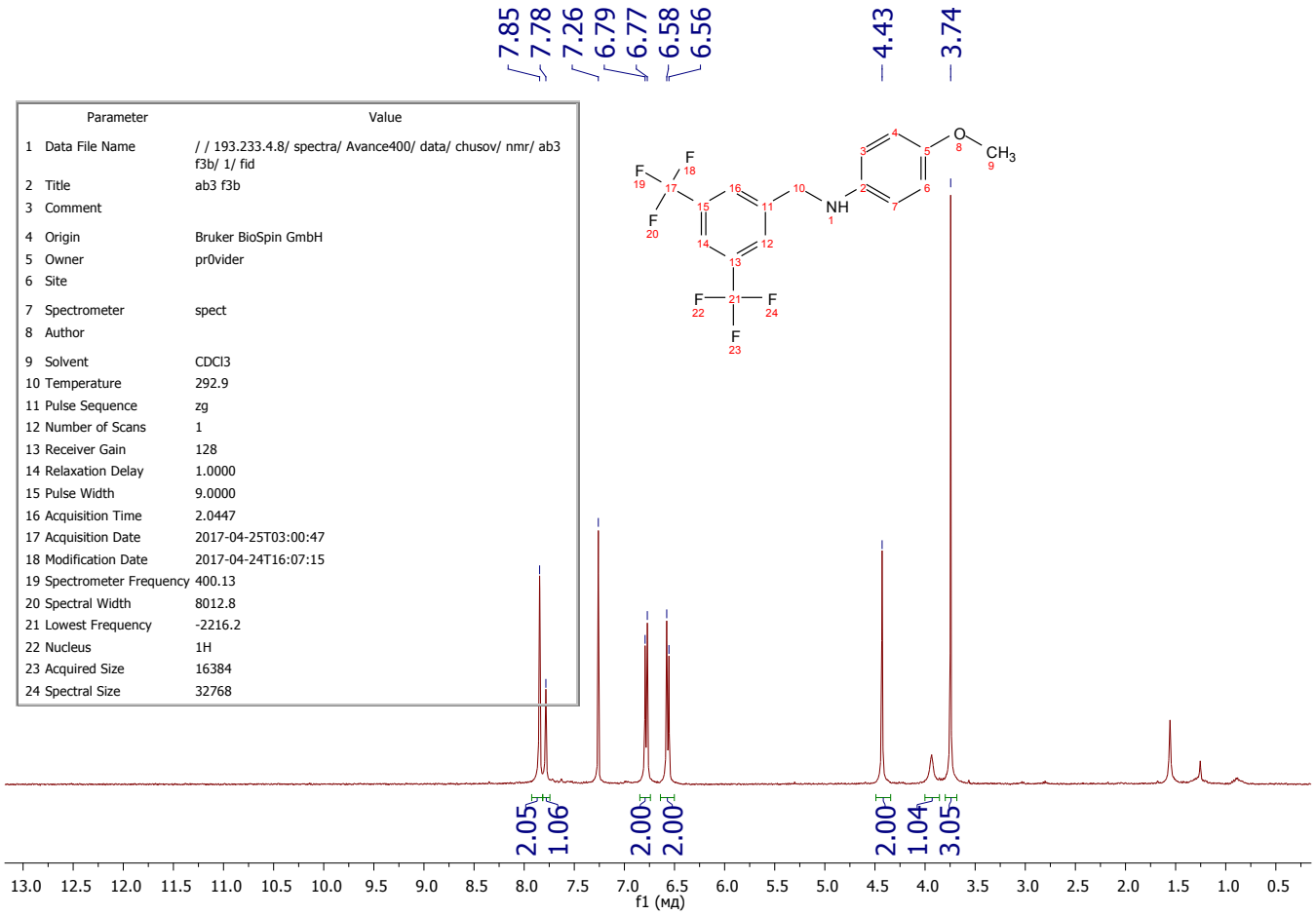
Acquisition Date	19.05.2017 14:09:05		
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\May_19_2017\ab-1me_&clblow.d		
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AB-1Me	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



N-(3,5-bis(trifluoromethyl)benzyl)-4-methoxyaniline (12k), ^{1}H NMR, $CDCl_3$, 400 MHz



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3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.9
11	Pulse Sequence	zg
12	Number of Scans	1
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.0000
16	Acquisition Time	2.0447
17	Acquisition Date	2017-04-25T03:00:47
18	Modification Date	2017-04-24T16:07:15
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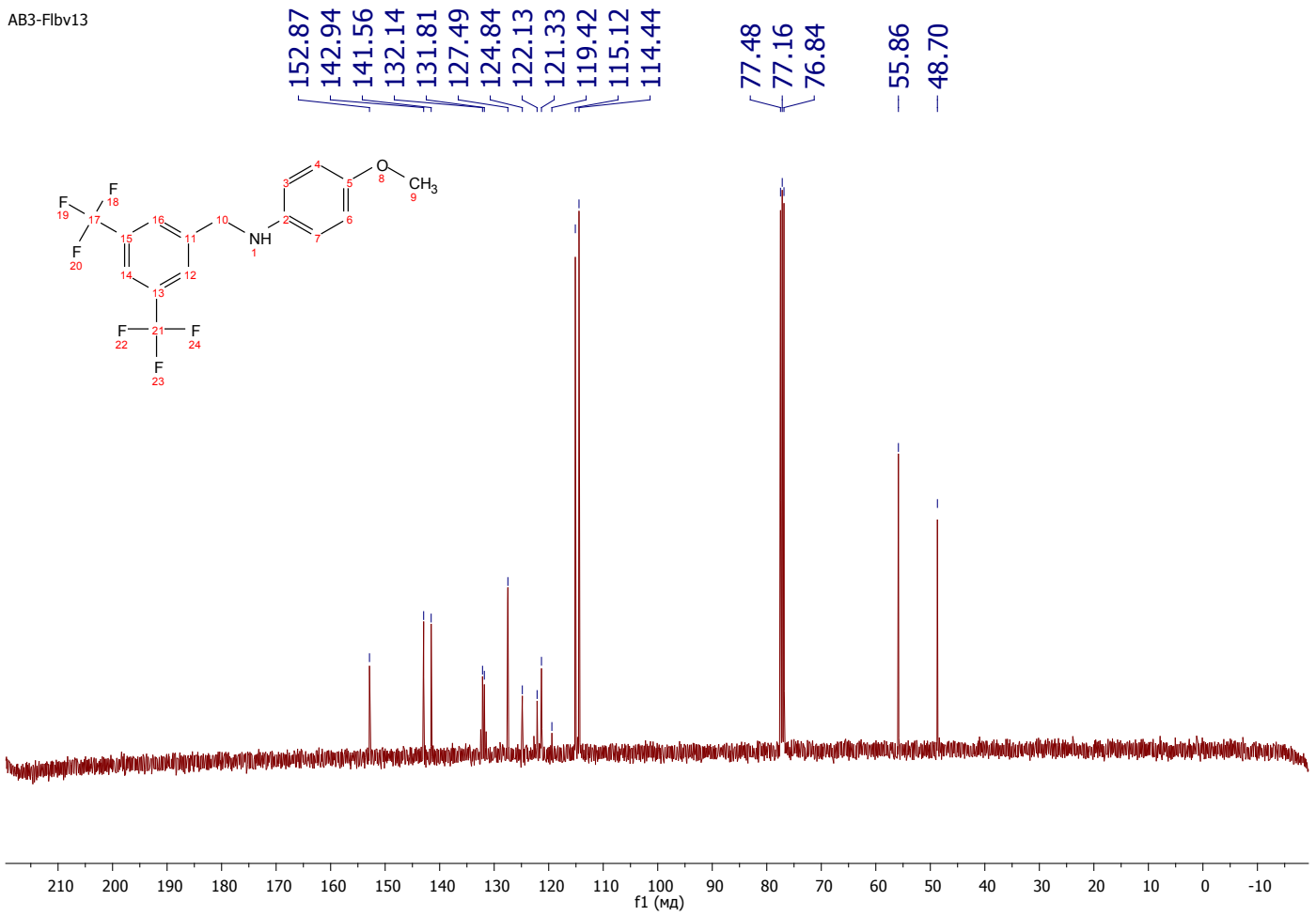
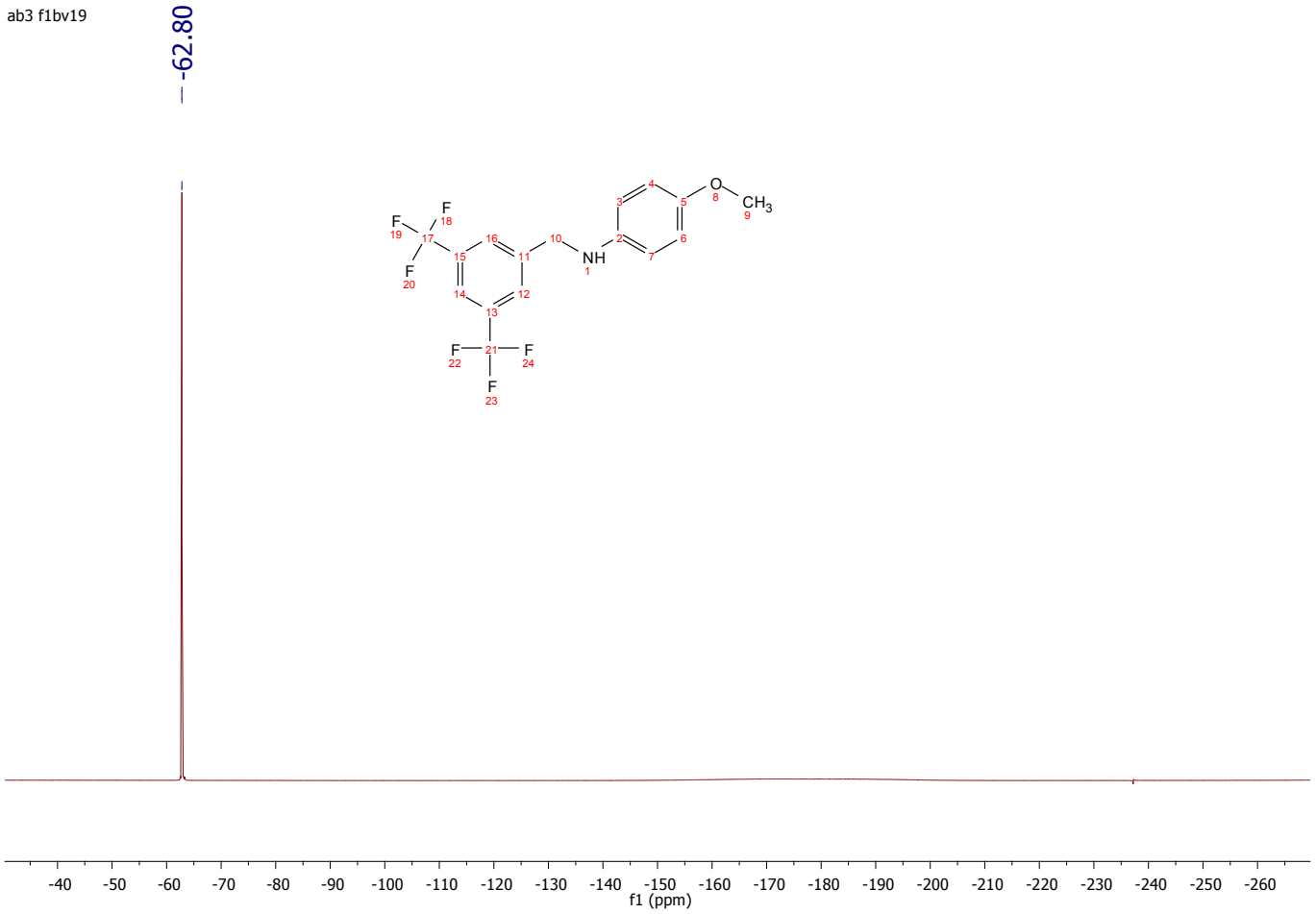
20	Spectral Width	8012.8
21	Lowest Frequency	-2216.2
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	32768

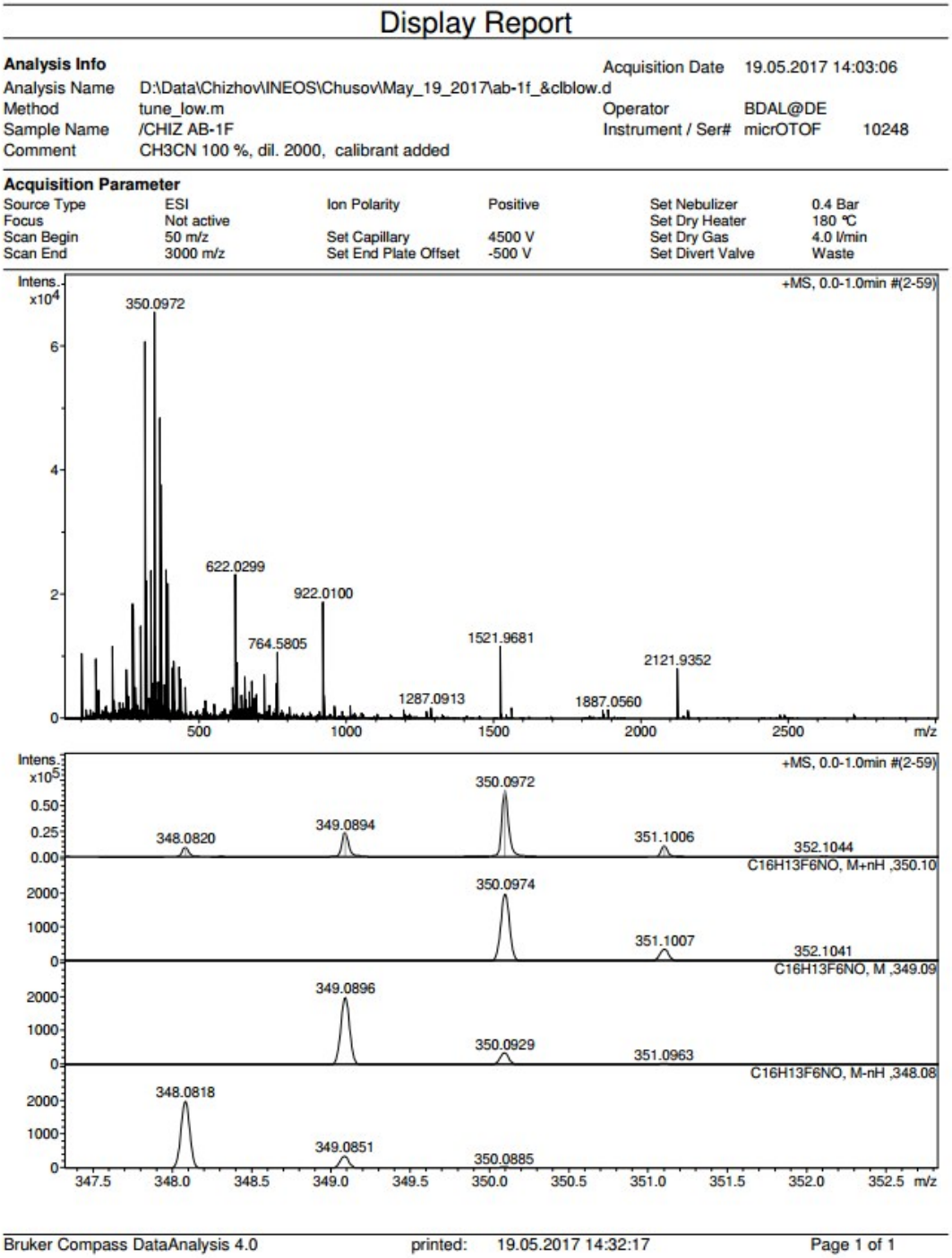
N-(3,5-bis(trifluoromethyl)benzyl)-4-methoxyaniline (12k), ^{13}C NMR, $CDCl_3$, 101 MHz



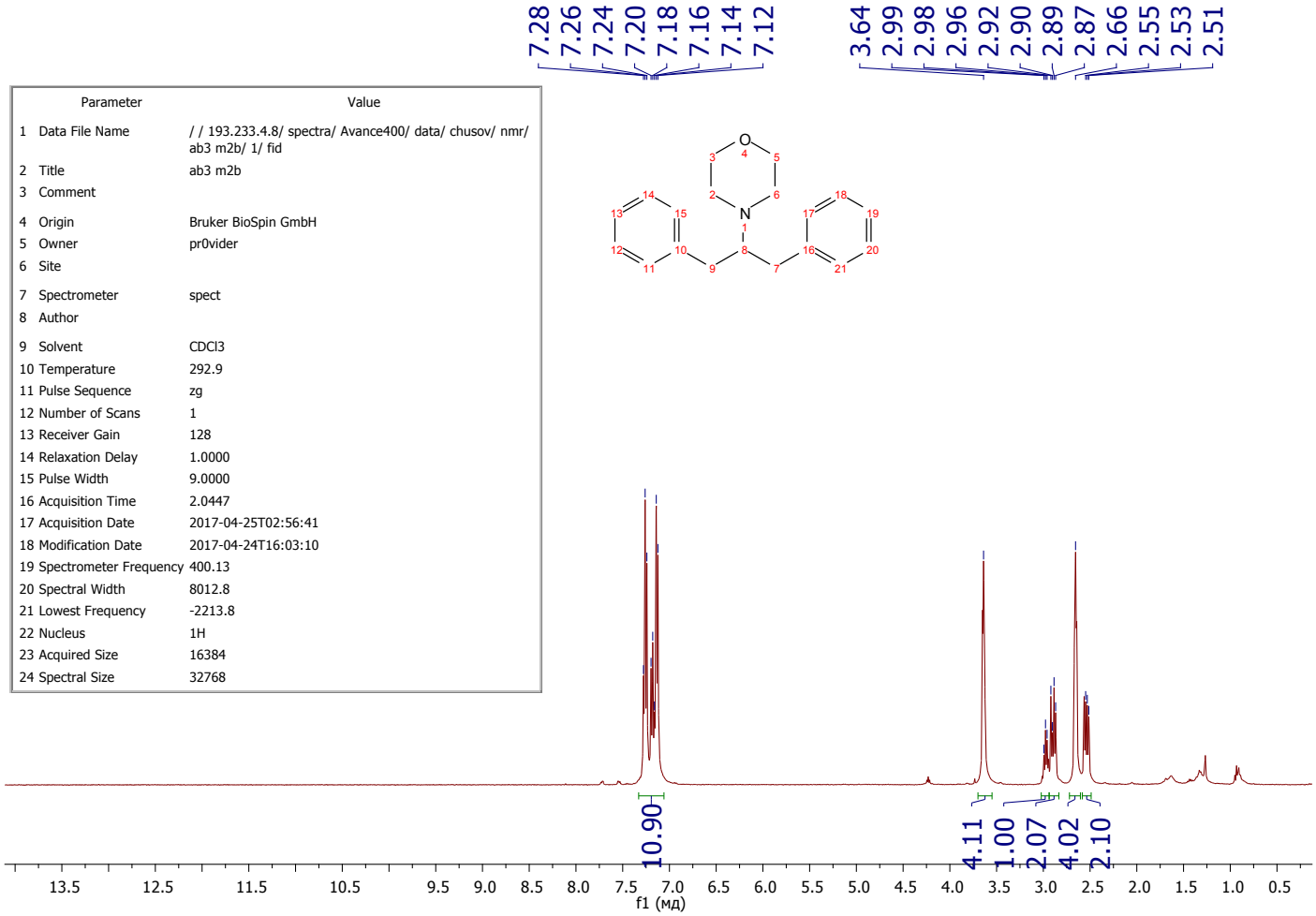
N-(3,5-bis(trifluoromethyl)benzyl)-4-methoxyaniline (12k), ^{19}F NMR, $CDCl_3$, 376 MHz



HRMS (TOF ESI+) spectrum of **12k**



4-(1,3-diphenylpropan-2-yl)morpholine (12l) , ^{1}H NMR, $CDCl_3$, 400 MHz



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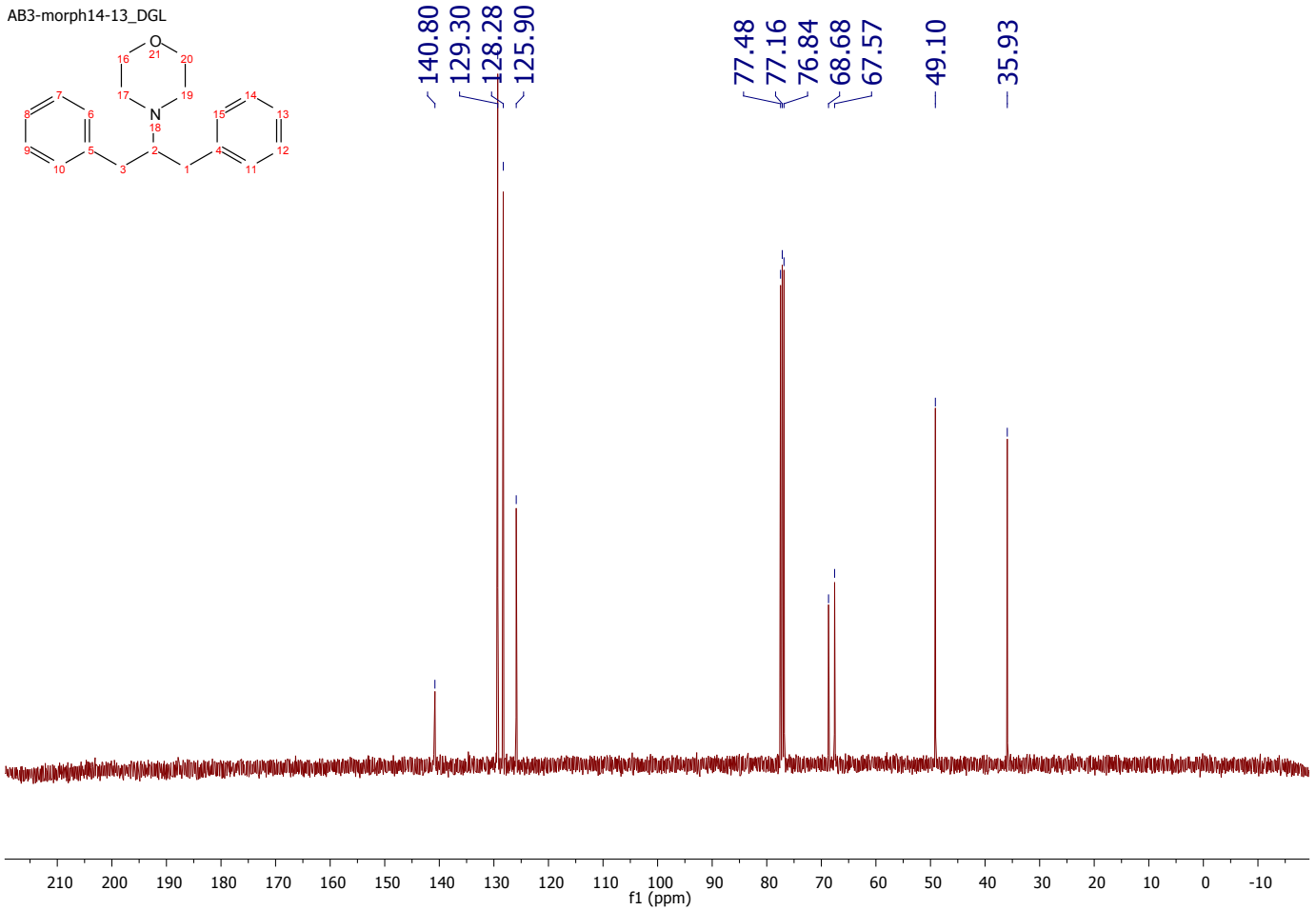
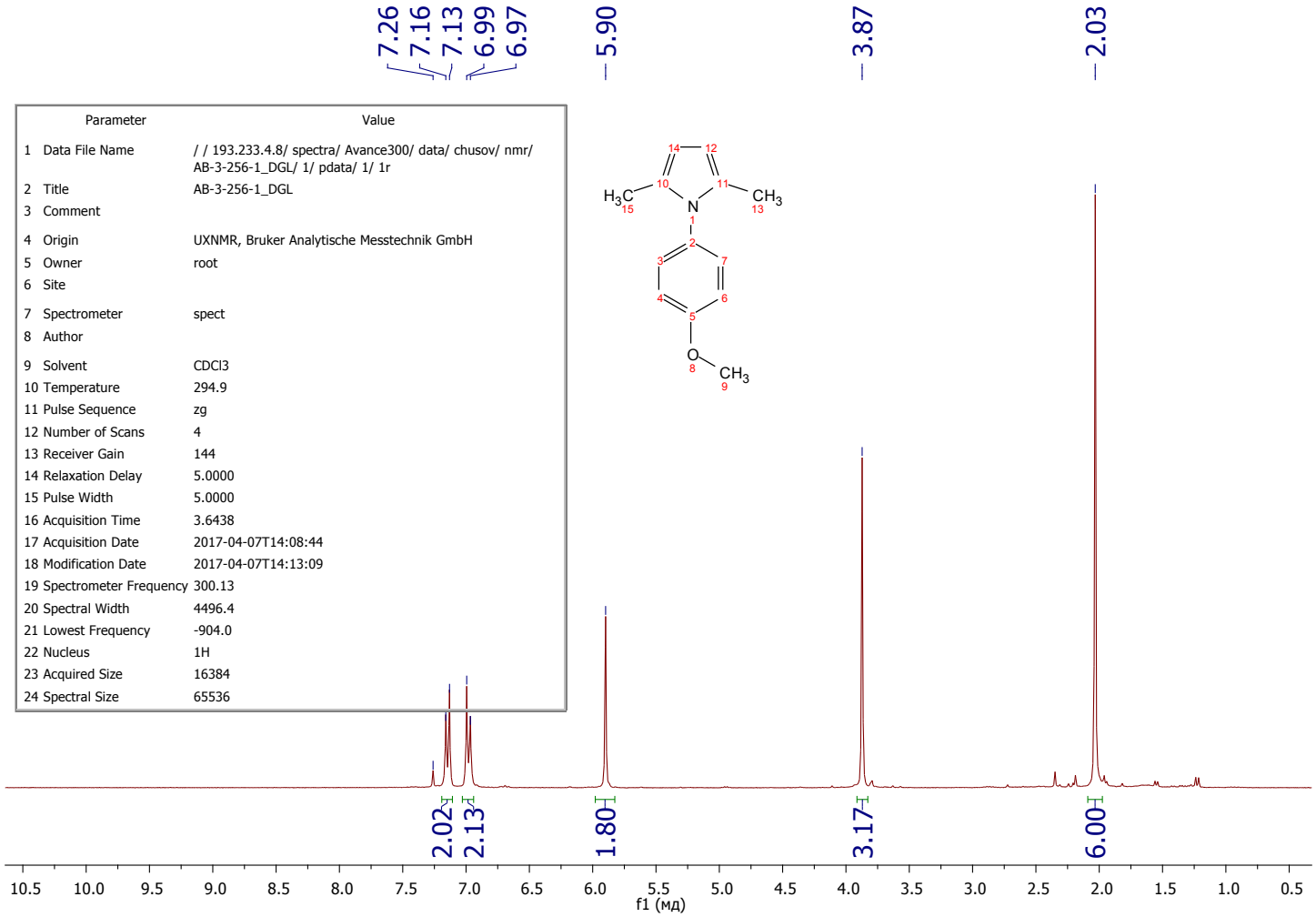
3	Comment	
4	Origin	Bruker BioSpin GmbH
5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	292.9
11	Pulse Sequence	zg
12	Number of Scans	1
13	Receiver Gain	128
14	Relaxation Delay	1.0000
15	Pulse Width	9.0000
16	Acquisition Time	2.0447
17	Acquisition Date	2017-04-25T02:56:41
18	Modification Date	2017-04-24T16:03:10
19	Spectrometer Frequency	400.13
20	Spectral Width	8012.8
21	Lowest Frequency	-2213.8
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	32768

4-(1,3-diphenylpropan-2-yl)morpholine (12l) , ^{13}C NMR, $CDCl_3$, 101 MHz



1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole (12m) – reaction mixture, ^{1}H NMR, $CDCl_3$, 300 MHz



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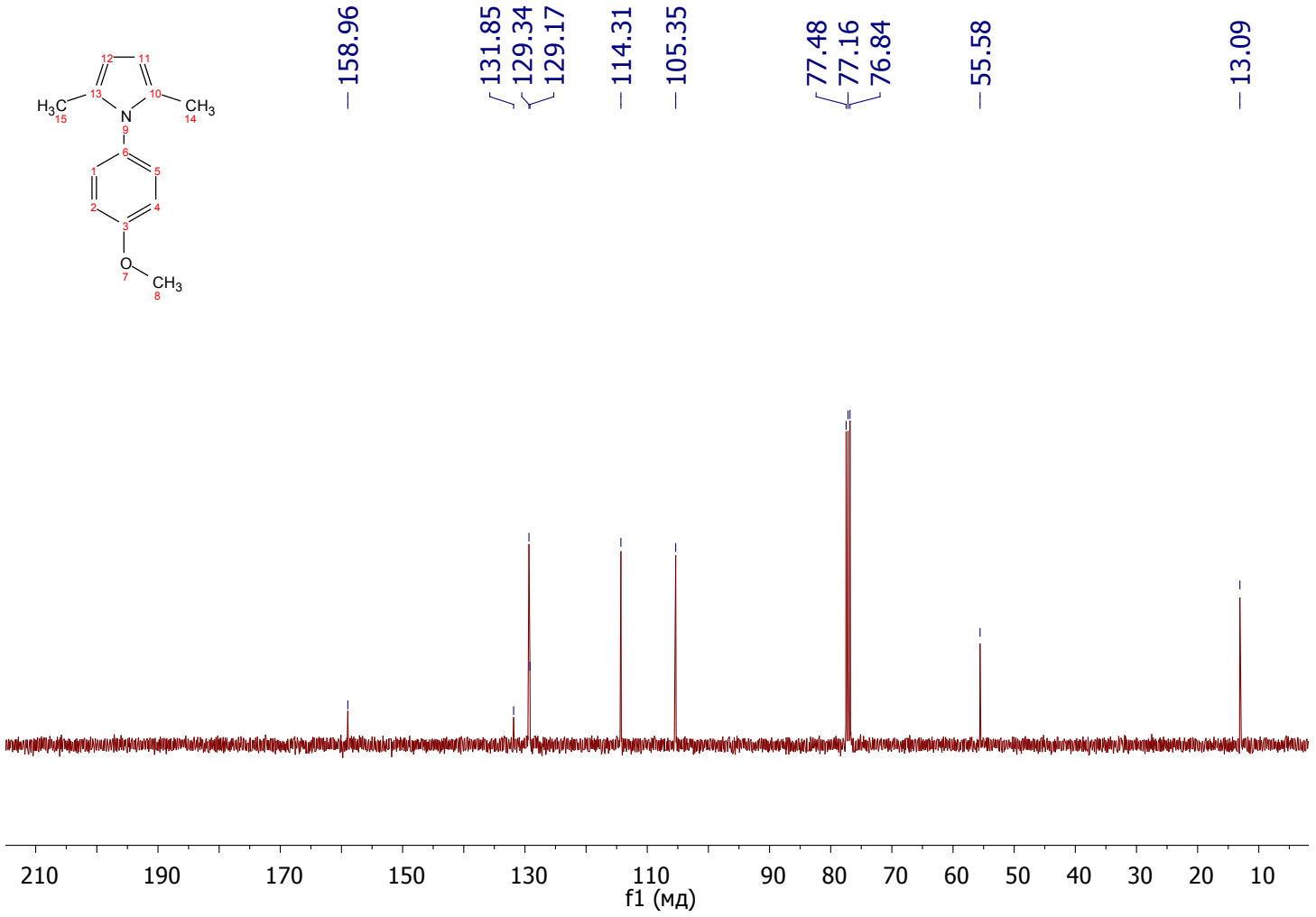
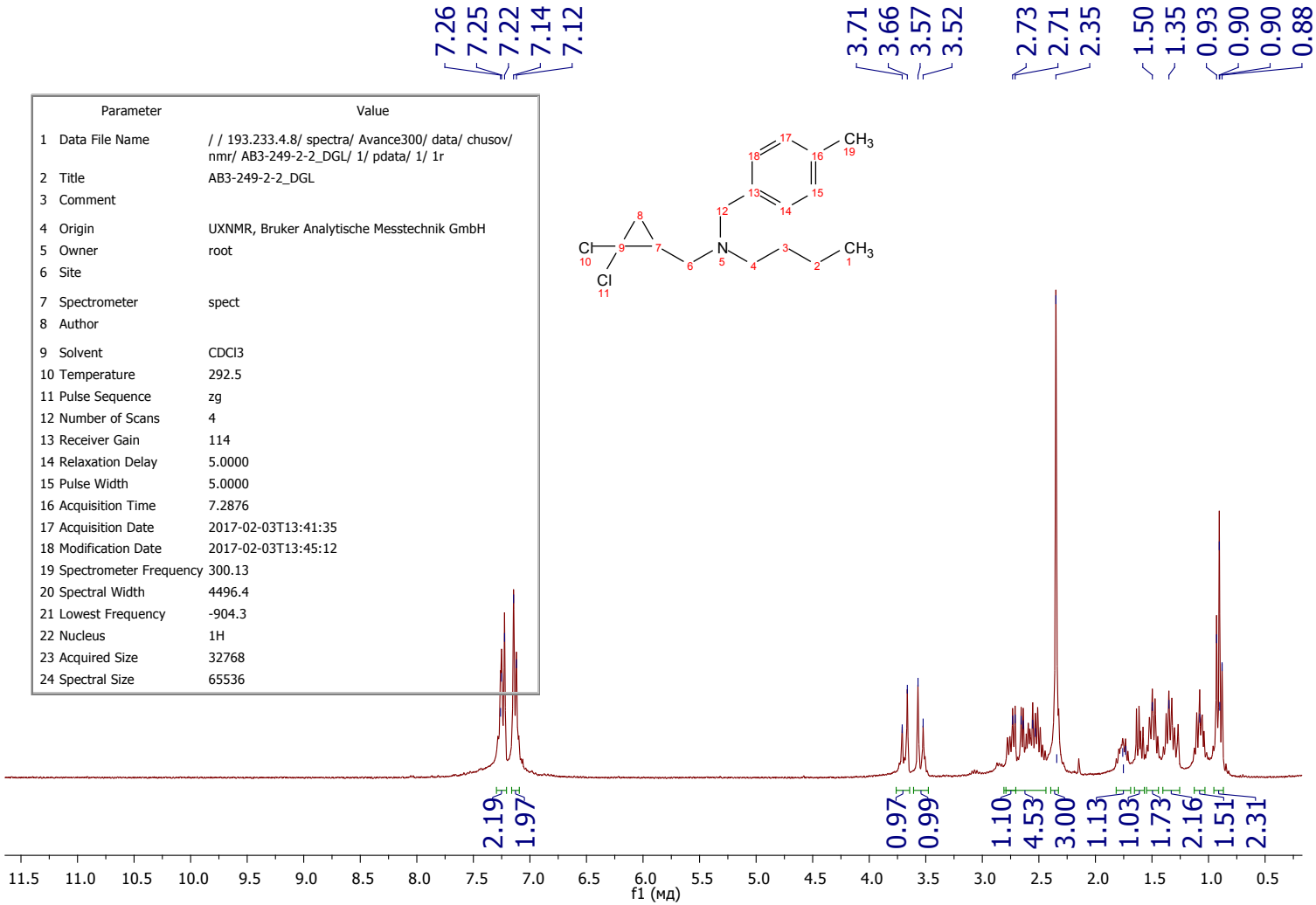
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	zg
12	Number of Scans	4
13	Receiver Gain	144
14	Relaxation Delay	5.0000
15	Pulse Width	5.0000
16	Acquisition Time	3.6438
17	Acquisition Date	2017-04-07T14:08:44
18	Modification Date	2017-04-07T14:13:09
19	Spectrometer Frequency	300.13
20	Spectral Width	4496.4
21	Lowest Frequency	-904.0
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	65536

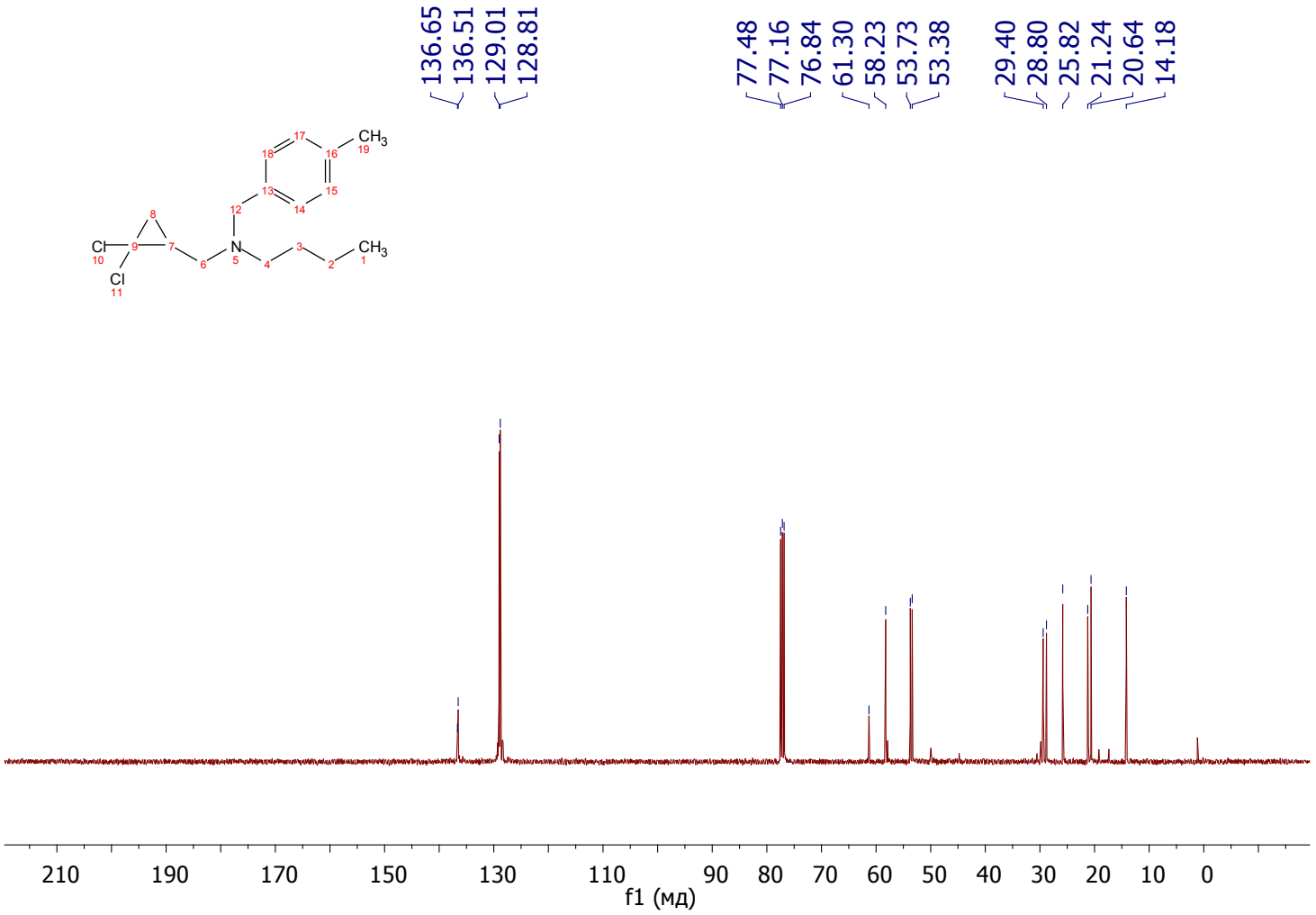
1-(4-methoxyphenyl)-2,5-dimethyl-1H-pyrrole (12m), ^{13}C NMR, $CDCl_3$, 101 MHz



N-((2,2-dichlorocyclopropyl)methyl)-N-(4-methylbenzyl)butan-1-amine (12n), ^{1}H NMR, $CDCl_3$, 300 MHz



N-((2,2-dichlorocyclopropyl)methyl)-N-(4-methylbenzyl)butan-1-amine (12n), ^{13}C NMR, $CDCl_3$, 101 MHz



HRMS (ESI-TOF) of **12n**

Display Report

Analysis Info

Acquisition Date	19.05.2017 14:17:59		
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\May_19_2017\ab-uf1_&clblow.d		
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AB-Uf1	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
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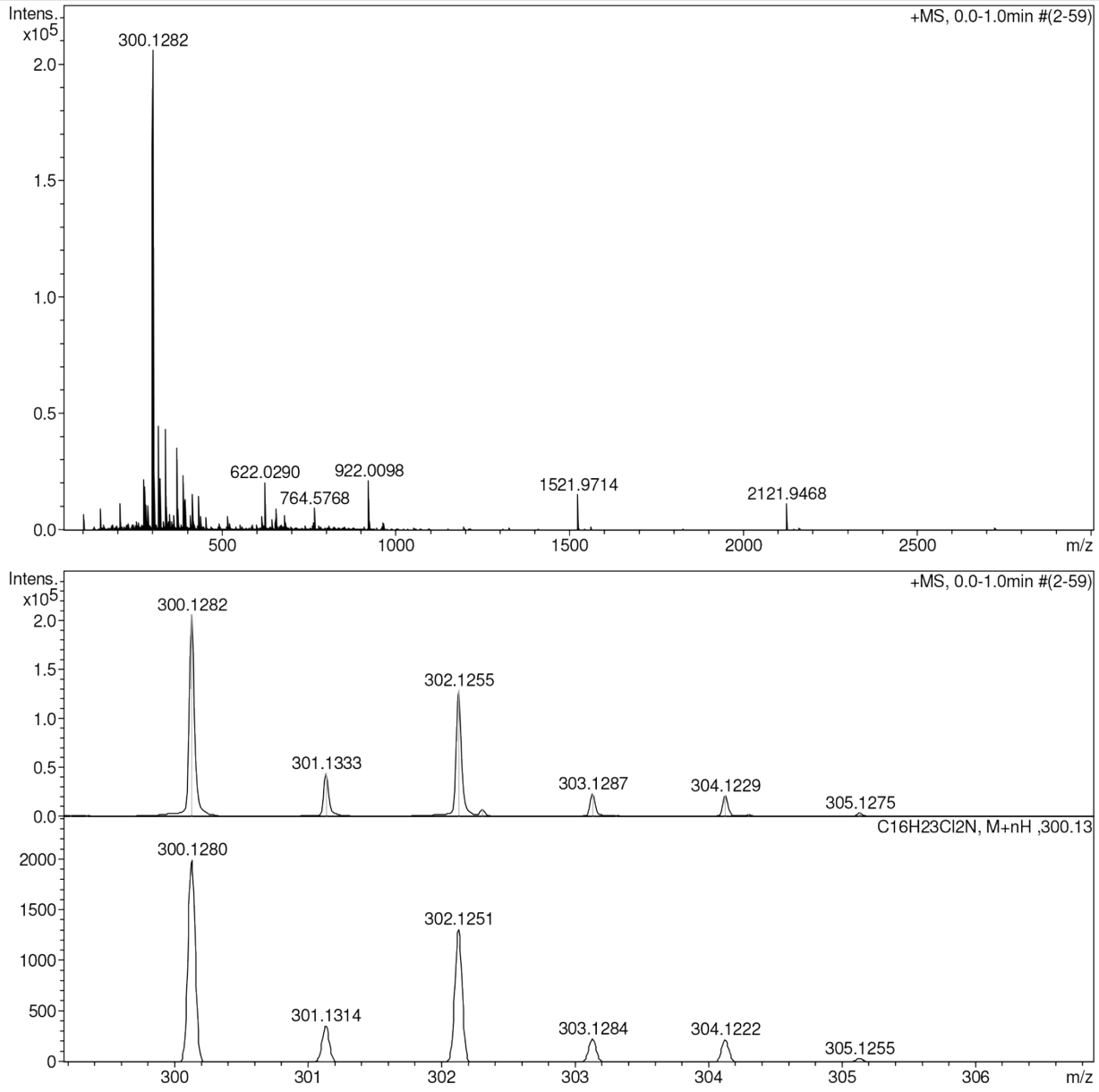
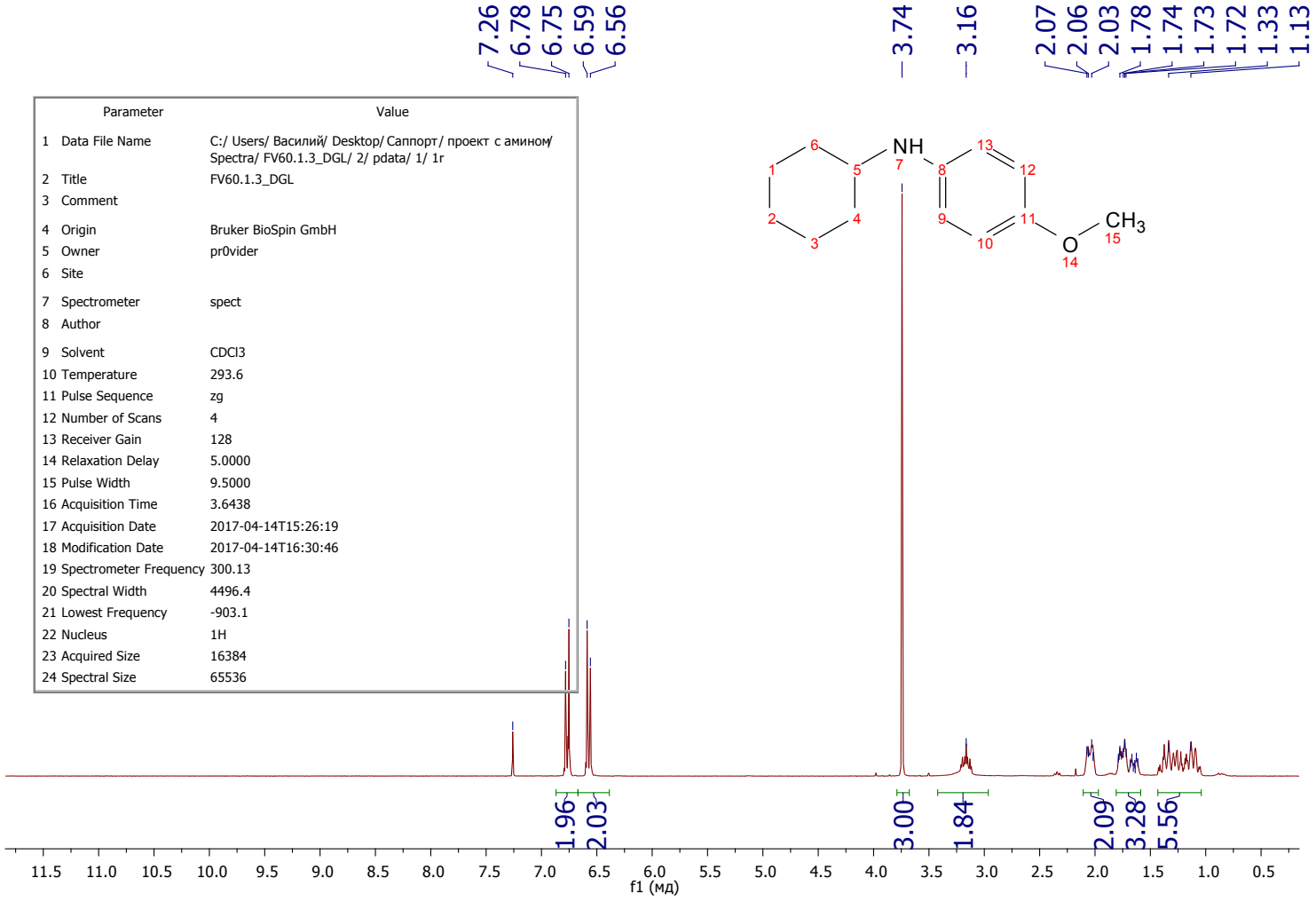
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 19.05.2017 14:42:31 Page 1 of 1

N-cyclohexyl-4-methoxyaniline (12o), ^{1}H NMR, $CDCl_3$, 300 MHz



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5	Owner	pr0vider
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	293.6
11	Pulse Sequence	zg
12	Number of Scans	4
13	Receiver Gain	128
14	Relaxation Delay	5.0000
15	Pulse Width	9.5000
16	Acquisition Time	3.6438
17	Acquisition Date	2017-04-14T15:26:19
18	Modification Date	2017-04-14T16:30:46
19	Spectrometer Frequency	300.13
20	Spectral Width	4496.4
21	Lowest Frequency	-903.1
22	Nucleus	1H
23	Acquired Size	16384
24	Spectral Size	65536

N-cyclohexyl-4-methoxyaniline (12o), ^{13}C NMR, $CDCl_3$, 101 MHz