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

Hydrogen-Free Reductive Amination Using Iron Pentacarbonyl as a Reducing Agent

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Supporting Information

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1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and were used without further purification. Reaction products were purified by column chromatography (Acros Organics, silica gel 0.06-0.200 mm). ^{1}H spectra were recorded in $CDCl_3$ on Bruker Avance 300, Bruker Avance 400 spectrometers; ^{13}C spectra were recorded in $CDCl_3$ on Bruker Avance 400 and Bruker Avance 600 spectrometers. 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). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz). ESI-HRMS experiments: high resolution mass spectra were recorded on Bruker microTOF II instrument equipped with electrospray ionization (ESI) ion source.[1,2] Measurements were performed in positive (MS^+) ion mode (interface capillary voltage: 4500 V) with scan range m/z: 50-3000. External calibration of the mass spectrometer was performed with sodium formate solution in MeCN. Direct syringe injection was used for all the analyzed solutions in MeCN (flow rate: 3 µL/min). Nitrogen was used as a nebulizer gas (0.4 bar) and as a dry gas (4.0 L/min); interface temperature was set at 180 ºC. Recorded spectra were processed using Bruker DataAnalysis 4.0 software package. Reactions with heating were carried out in high pressure Schlenk tubes, made from borosilicate glass (Rettberg, articular no.134029514, fig. 1). Reactions without heating were carried out in regular Schlenk tubes.

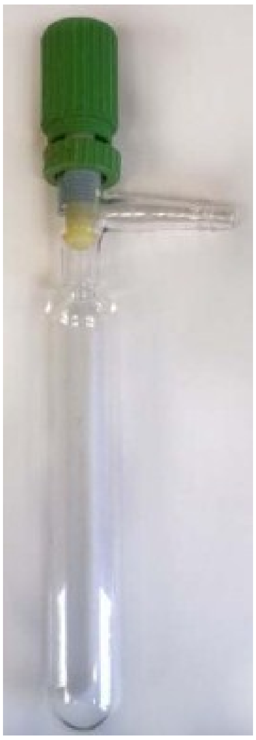

Fig. 1. High pressure Schlenk tube used for reductive amination reaction.

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[1] Belyakov, P. A.; Kadentsev, V. I.; Chizhov, A. O.; Kolotyrkina, N. G.; Shashkov, A. S.; Ananikov, V. P. *Mendeleev Commun.* **2010**, *20*, 125-131.

[2] Kachala, V. V.; Khemchyan, L. L.; Kashin, A. S.; Orlov, N. V.; Grachev, A. A.; Zalesskiy, S. S.; Ananikov, V. P. *Russ. Chem. Rev*. **2013**, *82*, 648-685.

General procedure for reductive amination

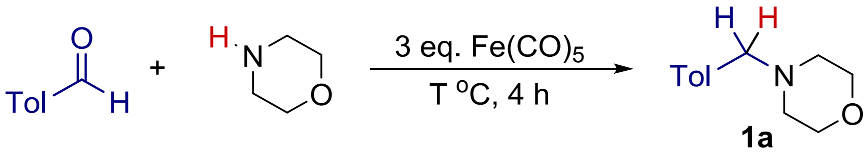
Procedure: A dry Schlenk tube with a magnetic stirrer was flashed with argon three times. The indicated amounts of the amine and the carbonyl compound were added, followed by dropwise addition of iron carbonyl (note 1). The Schlenk tube was sealed and placed into a preheated oil bath. After the indicated time (note 2) the Schlenk tube was opened to air, and the reaction mixture was transferred to a round bottom flask. Volatile components were evaporated in vacuum. In order to break the iron complex of the desired product, an excess of triethylamine was added and the reaction mixture was dried in vacuum. After this workup it is possible to purify the products via column chromatography on silica gel. Iron complexes with target amines can also be broken with sodium hydroxide. For this purpose, after removal of the volatile components the reaction mixture was dissolved in methanol, and excess amount of sodium hydroxide solution in water was added. This mixture was evaporated to dryness on a rotary evaporator. The resulting black residue was suspended in DCM, filtered via a celite pad and concentrated. The resulting oil can be distilled or purified via column chromatography.

Note 1: In case of active amines (e.g. pyrrolidine) cooling is necessary during the addition of $Fe(CO)_5$.

Note 2: Four hours are usually sufficient for this reaction. Active amines react in 2 hours.

2. Optimization of the reaction conditions

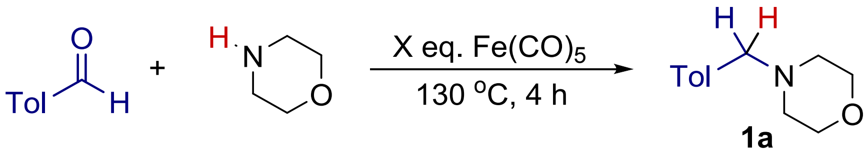
Investigation of the temperature influence



Entry[a]	Temperature	yield, %
1	90°C	14%
2	110 °C	26%
3	130 °C	41%
4	150 °C	40%
5	160 °C	41%
6	180 °C	44%

[a] 1.5 eq. of amine and 1 eq. of aldehyde were used. Yields were determined via GC with internal standard. Tol = *p*-methylphenyl.

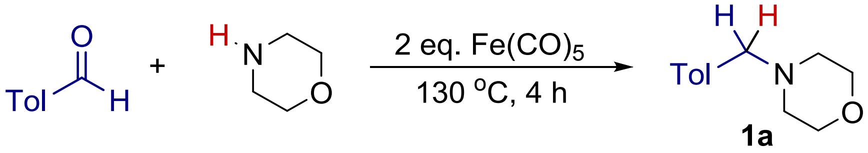
Screening of various amounts of iron carbonyl



Entry[a]	Number of $Fe(CO)_5$ equivalents	yield, %
1	5	51%
2	3	41%
3	2	45%
4	1	24%
5	0.5	15%
6	0.2	11%

[a] 1.5 eq. of amine and 1 eq. of aldehyde were used. Yields were determined via GC with internal standard. Tol = *p*-methylphenyl.

Screening of various amounts of the amine

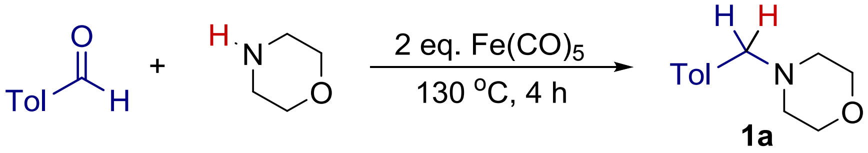


Entry[a]	Number of morpholine equivalents	yield, %
1	1	18%
2	1.2	27%
3	2	52%
4	3	73%
5[b]	3	86%

[a] x eq. of amine and 1 eq. of aldehyde were used. Yields were determined via GC with internal standard. Tol = *p*-methylphenyl.

[b] 3 equivalents of iron carbonyl were used.

Investigation of the influence of reaction atmosphere

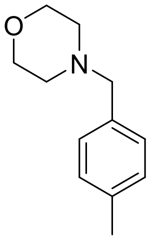


Entry[a]	Headspace fill gas	yield, %
1	Ar	73%
2	CO	61%
3	N_2	74%

[a] 3 eq. of amine and 1 eq. of aldehyde were used. Yields were determined via GC with internal standard. Tol = *p*-methylphenyl.

3. Spectroscopic and analytical data

4-(4-methylbenzyl)morpholine (1a)



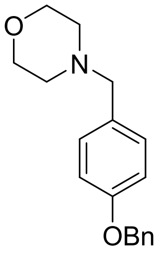
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 µL, 300 mol %, 3.44 mmol), *p*-tolylaldehyde (135 µL, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 µL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 5 : 1; Rf=0.6) to afford 189 mg (86 %) of the product as a yellowish oil, solidified at room temperature (mp 54-55°C)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.78 (t, *J* = 4.5 Hz, 4H), 3.56 (s, 2H), 2.53 (t, *J* = 4.5 Hz, 4H), 2.41 (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.[3,4]

4-(4-(benzyloxy)benzyl)morpholine (1b)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 µL, 300 mol %, 3.44 mmol), *p*-benzyloxybenzaldehyde (243.6 mg, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 µL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 1 : 1; Rf=0.3) to afford 227 mg (70 %) of the product as a white solid (mp 45-46°C).

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

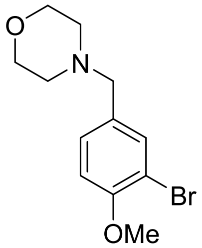
[4] Moskovets, A. P.; Usanov, D. L.; Afanasyev, O. I.; Fastovskiy, V. A.; Molotkov, A. P.; Muratov, K. M.; Denisov, G. L.; Zlotskii, S. S.; Smolyakov, A. F.; Loginov, D. A.; Chusov, D. *Org. Biomol. Chem.*, **2017**, *30*, 6384.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.33 (m, 5H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.10 (s, 2H), 3.75 (t, *J* = 4.5 Hz, 4H), 3.49 (s, 2H), 2.53 – 2.40 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 158.1, 137.1, 130.4, 130.1, 128.6, 127.9, 127.5, 114.6, 70.0, 67.1, 62.8, 53.6.

HRMS: Calculated for $C_{18}H_{22}NO_2$ $(M+H)^+$: 284.1645: found: 284.1646

4-(3-bromo-4-methoxybenzyl)morpholine (1c)



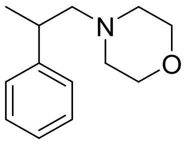
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 μL, 300 mol %, 3.44 mmol), *3*-bromo-4-methoxybenzaldehyde (246.8 mg, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 μL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 4 : 1; Rf=0.1) to afford 253 mg (77 %) of the product as a white solid (mp 92-93^{o}C).

1H NMR (400 MHz, CDCl$_3$) δ 7.51 (s, 1H), 7.20 (d, J = 8.2 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 3.87 (s, 3H), 3.75 – 3.59 (m, 4H), 3.39 (s, 2H), 2.50 – 2.28 (m, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.1, 134.0, 131.5, 129.3, 111.7, 111.5, 67.1, 62.3, 56.4, 53.6 .

HRMS: Calculated for $C_{12}H_{17}{}^{79}BrNO_2$ $(M+H)^+$: 286.0437: found: 286.0433
Calculated for $C_{12}H_{17}{}^{81}BrNO_2$ $(M+H)^+$: 288.0417: found: 288.0420

4-(2-phenylpropyl)morpholine (1d)



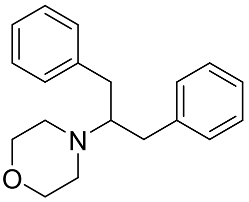
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (328 μL, 300 mol %, 3.80 mmol), 2-phenylpropanal (170 μL, 100 mol %, 1.27 mmol) and iron pentacarbonyl (512 μL, 300 mol %, 3.80 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 4 : 1; Rf=0.4) to afford 239 mg (92 %) of the product as a colorless oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.46 – 7.23 (m, 5H), 3.82 – 3.70 (m, 4H), 3.05 – 2.84 (m, 1H), 2.62 – 2.50 (m, 4H), 2.50 – 2.40 (m, 2H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 146.0, 128.4, 127.2, 126.2, 67.1, 66.6, 54.0, 37.1, 19.9.

NMR spectra is in accordance with the literature data [5,6]

4-(1,3-diphenylpropan-2-yl)morpholine (1e)



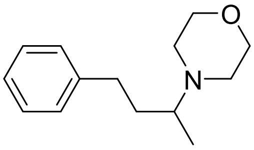
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 μL, 300 mol %, 3.44 mmol), 1,3-diphenylpropan-2-one (226 μL, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 μL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 4 : 1; Rf=0.5) to afford 242 mg (75 %) of the product as a colorless oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.40 – 7.17 (m, 10H), 3.70 (t, *J* = 4.5, 4H), 3.03 (quint, *J* = 6.6 Hz, 1H), 2.94 (dd, *J* = 13.4, 6.6 Hz, 2H), 2.71 (t, *J* = 4.5, 4H), 2.61 (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.[7,4]

4-(4-phenylbutan-2-yl)morpholine (1f)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 μL, 300 mol %, 3.44 mmol), 4-phenylbutan-2-one (172 μL, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 μL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 2 : 1; Rf=0.4) to afford 190 mg (75 %) of the product as a yellowish oil.

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[5] Andrews, K. G.; Summers, D. M.; Donnelly, L. J.; Denton, R. M.; *Chem. Commun.*, **2016**, *52*, 1855

[6] Dutta, B.; Schwarz, R.; Omar, S.; Natour, S.; Abu-Reziq, R. *Eur. J. Org. Chem.*, **2015,** 1961

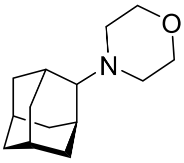
[7] K. D. Hesp, M. Stradiotto, *J. Am. Chem. Soc.*, **2010**, *132*, 18026–18029

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.02 (m, 5H), 3.84 – 3.60 (m, 4H), 2.79 – 2.36 (m, 7H), 1.95 – 1.81 (m, 1H), 1.67 – 1.54 (m, 1H), 1.05 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.7, 128.5, 128.4, 125.7, 67.6, 58.5, 48.8, 35.3, 32.9, 13.9.

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

4-(adamantan-2-yl)morpholine (1g)



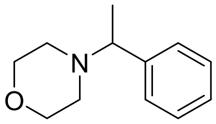
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 µL, 300 mol %, 3.44 mmol), adamantanone (172.4 mg, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 µL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 4 : 1; Rf=0.7; visualizing of the TLC spot with iodine) to afford 215 mg (85 %) of the product as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.70 (t, *J* = 4.6 Hz, 4H), 2.39 (s, 4H), 2.11 – 1.94 (m, 5H), 1.88 – 1.73 (m, 4H), 1.71 – 1.57 (m, 4H), 1.36 (d, *J* = 11.8 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 68.0, 67.4, 50.3, 37.9, 37.3, 31.4, 28.6, 27.6, 27.5.

NMR spectra are in agreement with the literature data. [9]

4-(1-phenylethyl)morpholine (1h)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. Morpholine (297 µL, 300 mol %, 3.44 mmol), acetophenone (134 µL, 100 mol %, 1.15 mmol) and iron pentacarbonyl (464 µL, 300 mol %, 3.44 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 130 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 4 : 1; Rf=0.3) to afford 193 mg (88 %) of the product as a yellowish oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.48 – 7.24 (m, 5H), 3.75 (t, *J* = 4.5 Hz, 4H), 3.36 (q, *J* = 6.6 Hz, 1H), 2.63 – 2.35 (m, 4H), 1.42 (d, *J* = 6.6 Hz, 3H).

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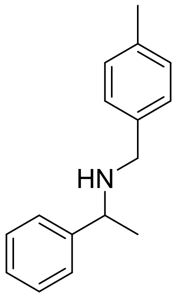
[8] Kyasa, S.; Fisher, T. J.; Dussault, P. H. *Synthesis* **2011**, 3475.

[9] Tankabekyan, N.A.; Mokhov, V.M.; Popov, Yu.V. *Zh. Org. Khim.,* **2014**, *50*, 1071.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 128.3, 127.6, 126.9, 67.2, 65.4, 51.3, 19.9.

NMR spectra are in agreement with the literature data. [10]

N-(4-methylbenzyl)-1-phenylethan-1-amine (1i)



A dry Schlenk tube with a magnetic stirrer was flashed with argon benzylethylamine (312 µL, 200 mol %, 2.50 mmol), *p*-tolylaldehyde (147 µL, 100 mol %, 1.25 mmol) and iron pentacarbonyl (336 µL, 200 mol %, 2.50 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 140 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 10 : 1; Rf=0.4) to afford 220 mg (78 %) of the product as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 5H), 7.21 (d, J = 7.7 Hz, 2H), 7.16 (d, J = 7.7 Hz, 2H), 3.88 - 3.79 (m, 1H), 3.66 (d, J = 13.0 Hz, 2H), 3.59 (d, J = 13.0 Hz, 1H), 2.37 (s, 3H), 1.57 (br. s, 1H), 1.39 (d, J = 4.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 137.7, 136.5, 129.2, 128.6, 128.2, 127.0, 126.8, 57.5, 51.5, 24.7, 21.2.

NMR spectra are in agreement with the literature data. [11,12]

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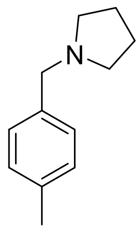
[10] Varjosaari, S. E.; Skrypai, V.; Suating, P.; Hurley, J. J. M.; Lio, A. M. D.; Gilbert, T. M.; Adler, M. J. *Adv. Synth. Catal.*, **2017**, *359*, 1872.

[11] Nişancı, B.; Ganjehyan, K.; Metin, Ö.; Daştan, A.; Török, B *J. Mol. Catal. A Chem.* **2015**, *409*, 191.

[12] Saidi, O.; Blacker, A. J.; Farah, M. M.; Marsden, S. P.; Williams, J. M. J. *Chem. Commun.* **2010**, *46*, 1541.

1-(4-methylbenzyl)pyrrolidine (1j)



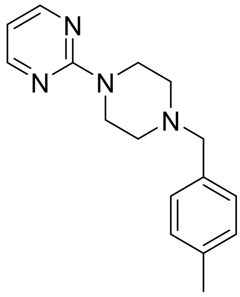
A dry Schlenk tube with a magnetic stirrer was flashed with argon Pyrrolidine (346 µL, 300 mol %, 4.22 mmol) and *p*-tolylaldehyde (166 µL, 100 mol %, 1.41 mmol) were added, the reaction flask was placed into an ice bath and iron pentacarbonyl (568 µL, 300 mol %, 4.22 mmol) was added dropwise. CAUTION: addition of $Fe(CO)_5$ initiates exothermic reaction! Schlenk tube was allowed to warm to room temperature, and stirring was continued overnight (actually, 2-3 hours should be enough). The Schlenk tube was opened to air, and reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 1 : 1; Rf=0.3) to afford 209 mg (85 %) of the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.7 Hz, 2H), 7.13 (d, J = 7.7 Hz, 2H), 3.59 (s, 2H), 2.56 – 2.44 (m, 4H), 2.35 (s, 3H), 1.85 – 1.71 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 136.4, 128.9, 60.6, 54.2, 23.5, 21.2.

NMR spectra are in agreement with the literature data [13,14]

2-(4-(4-methylbenzyl)piperazin-1-yl)pyrimidine (1k)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. 2-(Piperazin-1-yl)pyrimidine (300 mg, 200 mol %, 1.83 mmol), *p*-tolylaldehyde (72 µL, 100 mol %, 0.61 mmol) and iron pentacarbonyl (246 µL, 300 mol %, 1.83 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 140 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 1 : 1; Rf=0.4) to afford 142 mg (87 %) of the product as an off-white solid (mp 71-72°C) .

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[13] Varjosaari, S.E.; Skrypai, V.; Suating, P.; Hurley, J. J. M.; De Lio, A. M.; Gilbert, T. M.; Adler, M. J. *Adv. Synth. Catal.* **2017**, *359*, 1872.

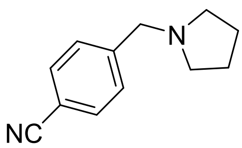
[14] Kovalenko, O. O.; Volkov, A.; Adolfsson, H. *Org. Lett.* **2015**, *17,* 446.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 4.7 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.45 (t, J = 4.7 Hz, 1H), 3.83 (t, J = 5.0 Hz, 4H), 3.51 (s, 2H), 2.50 (t, J = 5.0 Hz, 4H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 157.8, 136.8, 134.9, 129.3, 129.1, 109.8, 62.9, 53.0, 43.8, 21.2.

HRMS: Calculated for $C_{16}H_{21}N_4$ $(M+H)^+$: 269.1761: found: 269.1764

4-(pyrrolidin-1-ylmethyl)benzonitrile (1l)



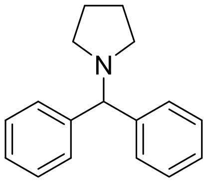
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Pyrrolidine (346 µL, 300 mol %, 4.22 mmol) and *p*-cyanobenzaldehyde (184 mg, 100 mol %, 1.41 mmol) were added, reaction flask was placed into the ice bath and iron pentacarbonyl (568 µL, 300 mol %, 4.22 mmol) was added drop wise. Caution: addition of $Fe(CO)_5$ initiates exothermic reaction! Schlenk tube was allowed to warm to room temperature, and stirring was continued overnight (actually, 2-3 hours should be enough). Schlenk tube was opened to air, and reaction mixture was transferred to the round bottom flask. Volatile components were evaporated in the vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 2 : 1; Rf=0.3) to afford 187 mg (72 %) of the product as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.7 Hz, 2H), 7.43 (d, J = 7.7 Hz, 2H), 3.64 (s, 2H), 2.54 – 2.39 (m, 4H), 1.84 – 1.69 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 132.1, 129.4, 119.1, 110.7, 60.3, 54.3, 23.6.

NMR spectra are in agreement with the literature data.[15]

1-benzhydrylpyrrolidine (1m)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. Pyrrolidine (346 µL, 300 mol %, 4.22 mmol), benzophenone (256 mg, 100 mol %, 1.41 mmol) and iron pentacarbonyl (569 µL, 300 mol %, 4.22 mmol) were added, the Schlenk tube was sealed and placed into an oil bath preheated to 90 °C. After 4 hours of heating, the Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate 9 : 1; Rf=0.4) to afford 230 mg (69 %) of the product as a white solid. Melting point 75-76°C is in agreement with the literature data (76-78°C).[16]

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[15] Chusov, D.; List, B.; *Angew. Chemie Int. Ed.* **2014**, *53,* 5199.

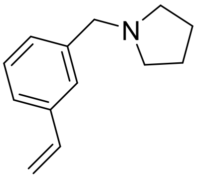
[16] Le Gall, E.; Haurena, C.; Sengmany, S.; Martens, T.; Troupel, M. *J. Org. Chem.* **2009**, *74*, 7970.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.23 – 7.16 (m, 2H), 4.19 (s, 1H), 2.50 – 2.40 (m, 4H), 1.83 – 1.77 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 128.5, 127.6, 126.9, 76.7, 53.8, 23.7.

NMR spectra are in agreement with the literature data.[18]

1-(3-vinylbenzyl)pyrrolidine (1n)



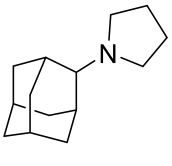
A dry Schlenk tube with a magnetic stirrer was flashed with argon. Pyrrolidine (346 µL, 300 mol %, 4.22 mmol) and 3-vinylbenzaldehyde (179 µL, 100 mol %, 1.41 mmol) were added, the reaction flask was placed into an ice bath and iron pentacarbonyl (568 µL, 300 mol %, 4.22 mmol) was added dropwise. CAUTION: addition of $Fe(CO)_5$ initiates exothermic reaction! The Schlenk tube was allowed to warm to room temperature, and stirring was continued overnight (actually, 2-3 hours should be enough). The Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. 3 ml of triethylamine were added, and the volatile components were removed again. The residue was purified by column chromatography (eluent: hexane : ethyl acetate : triethylamine 3 : 1 : 0.1; Rf=0.3) to afford 184 mg (70 %) of the product as a colorless oil. Usage of triethylamine in eluent composition is very important, it prevents decomposition of the product on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.35 – 7.20 (m, 3H), 6.72 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.77 (d, *J* = 17.5 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 3.62 (s, 2H), 2.58 – 2.44 (m, 4H), 1.85 – 1.74 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 137.6, 136.9, 128.6, 128.5, 126.9, 124.8, 113.8, 60.8, 54.3, 23.5.

HRMS: Calculated for $C_{13}H_{18}N^+$ $(M+H)^+$: 188.1434: found: 188.1437

1-(adamantan-2-yl)pyrrolidine (1o)



A dry Schlenk tube with a magnetic stirrer was flashed with argon. Pyrrolydine (2.31 ml, 300 mol %, 28.12 mmol), adamantanone (1.41 g, 100 mol %, 9.37 mmol) were added, the reaction flask was placed into an ice bath and iron pentacarbonyl (3.80 ml, 300 mol %, 28.12 mmol) was added dropwise. CAUTION: addition of $Fe(CO)_5$ initiates exothermic reaction! The Schlenk tube was allowed to warm to room temperature, and stirring was continued for two hours. The Schlenk tube was opened to air, and the reaction mixture was transferred to a round-bottom flask. Volatile components were evaporated in vacuum. The residue was dissolved in 10 ml of methanol, and concentrated solution of 4 g of NaOH in water was added. The solvents were removed in vacuum. The residue was suspended in DCM, sonicated for 5 minutes and filtered via a celite pad. The resulting solution was concentrated, and the crude product was purified by short distillation in vacuum. The target amine was isolated as colorless oil, 1.71 g, 89%.

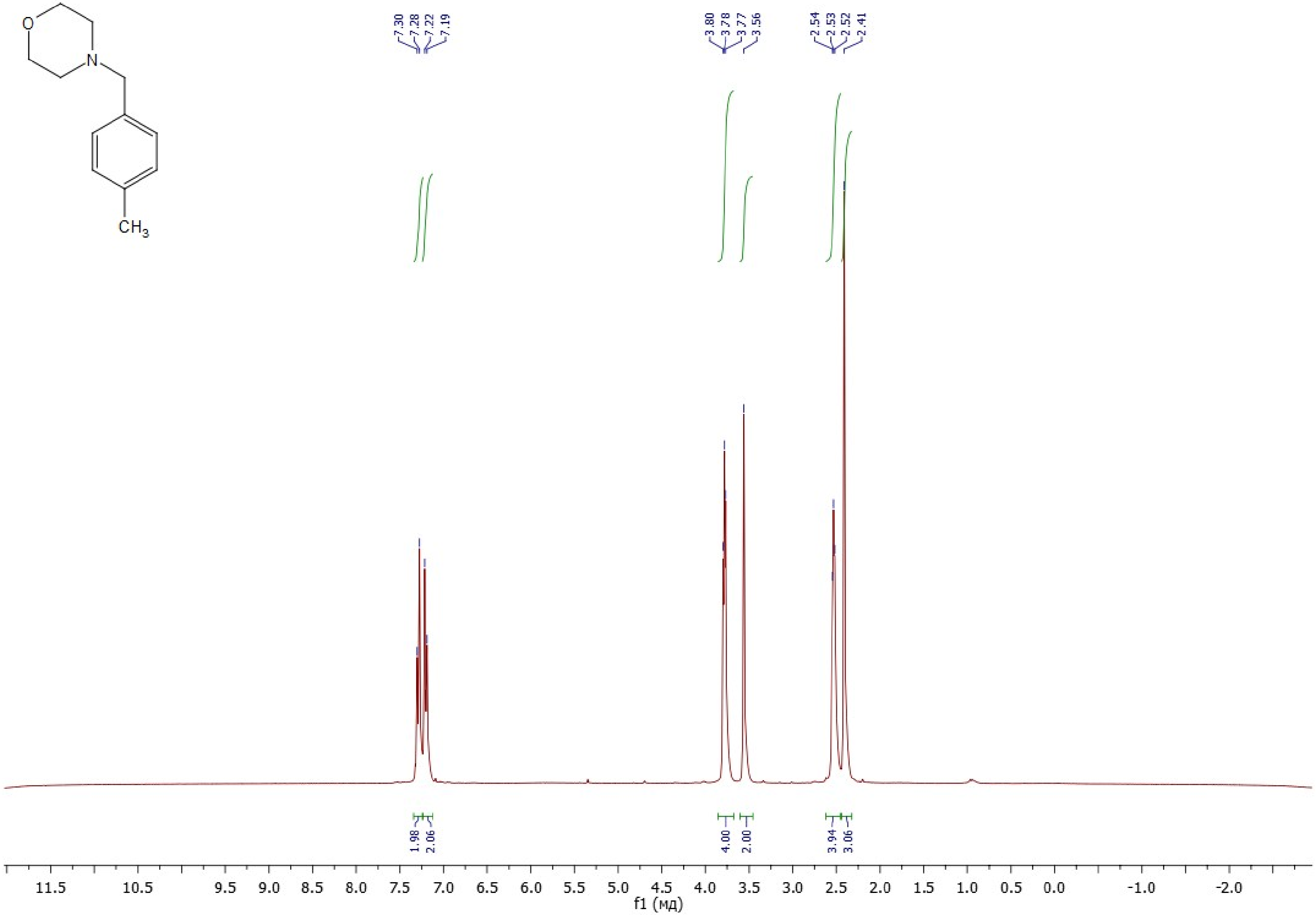
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 – 2.40 (m, 4H), 2.14 – 2.01 (m, 3H), 1.96 – 1.89 (m, 2H), 1.84 – 1.63 (m, 12H), 1.42 (d, J = 12.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 70.5, 51.6, 38.2, 37.4, 31.7, 31.7, 27.8, 27.7, 23.5.

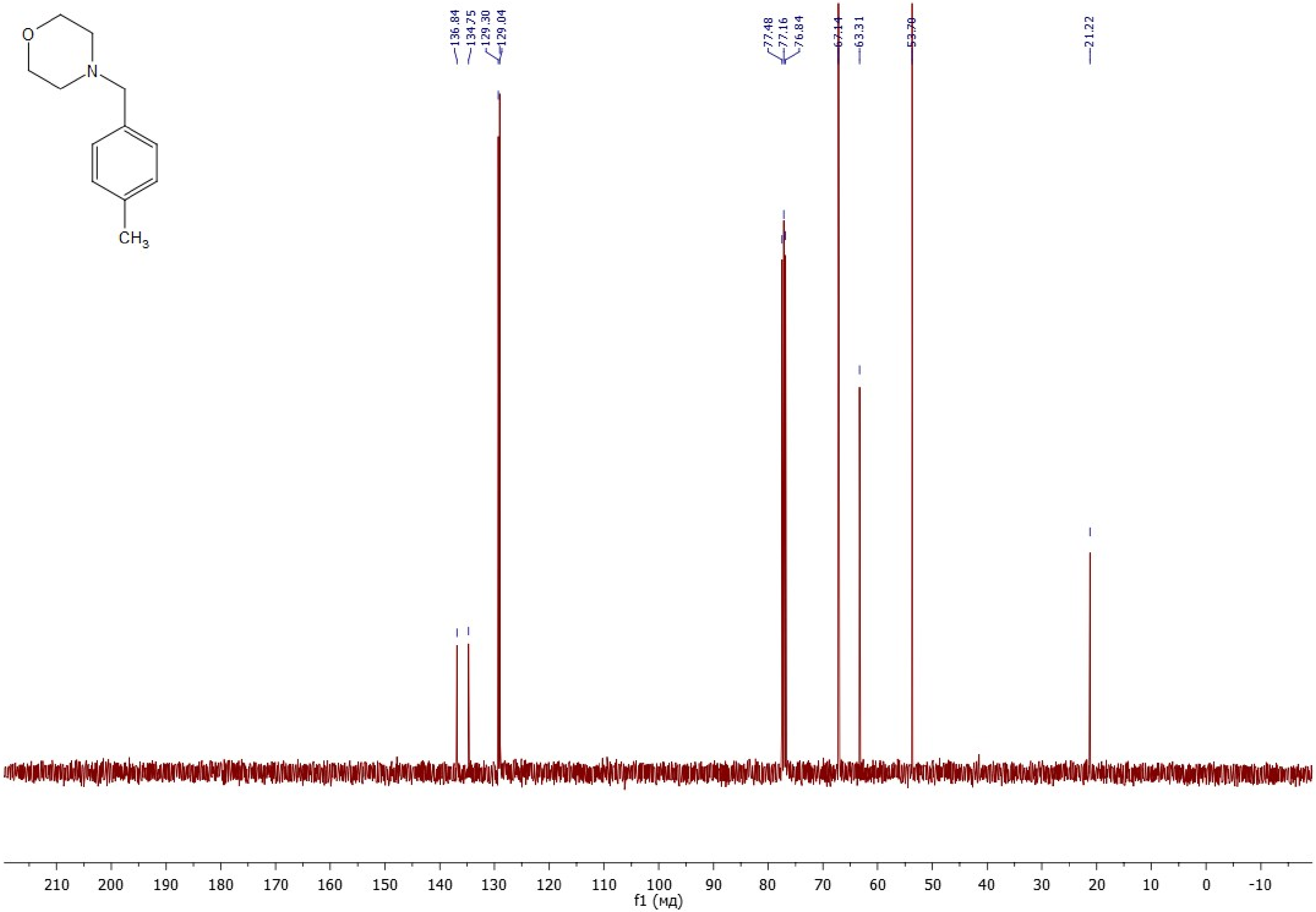
HRMS: Calculated for $C_{14}H_{24}N^+$ $(M+H)^+$: 206.1903: found: 206.1903

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

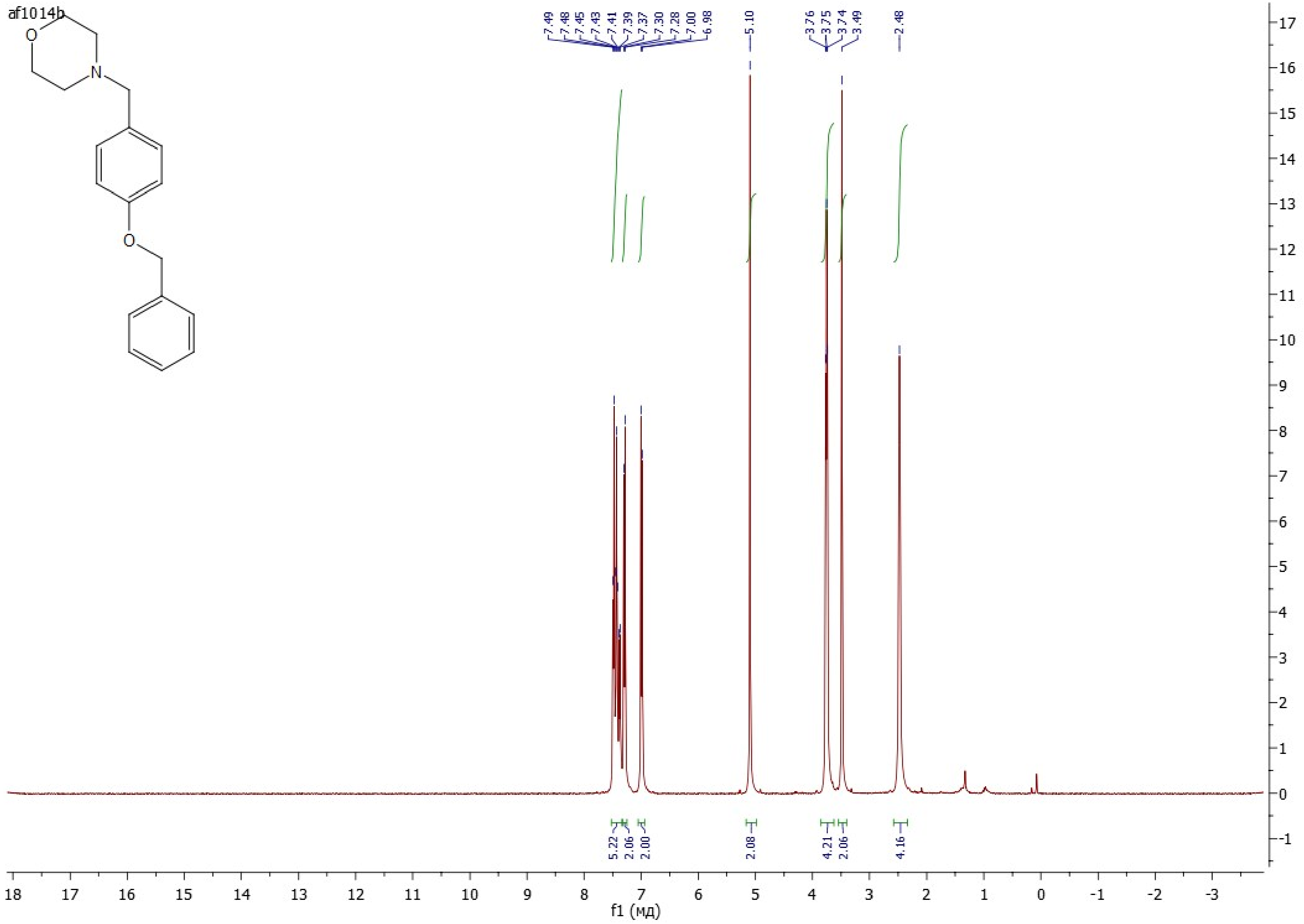
4-(4-methylbenzyl)morpholine (1a) ^{1}H NMR, $CDCl_3$, 300 MHz



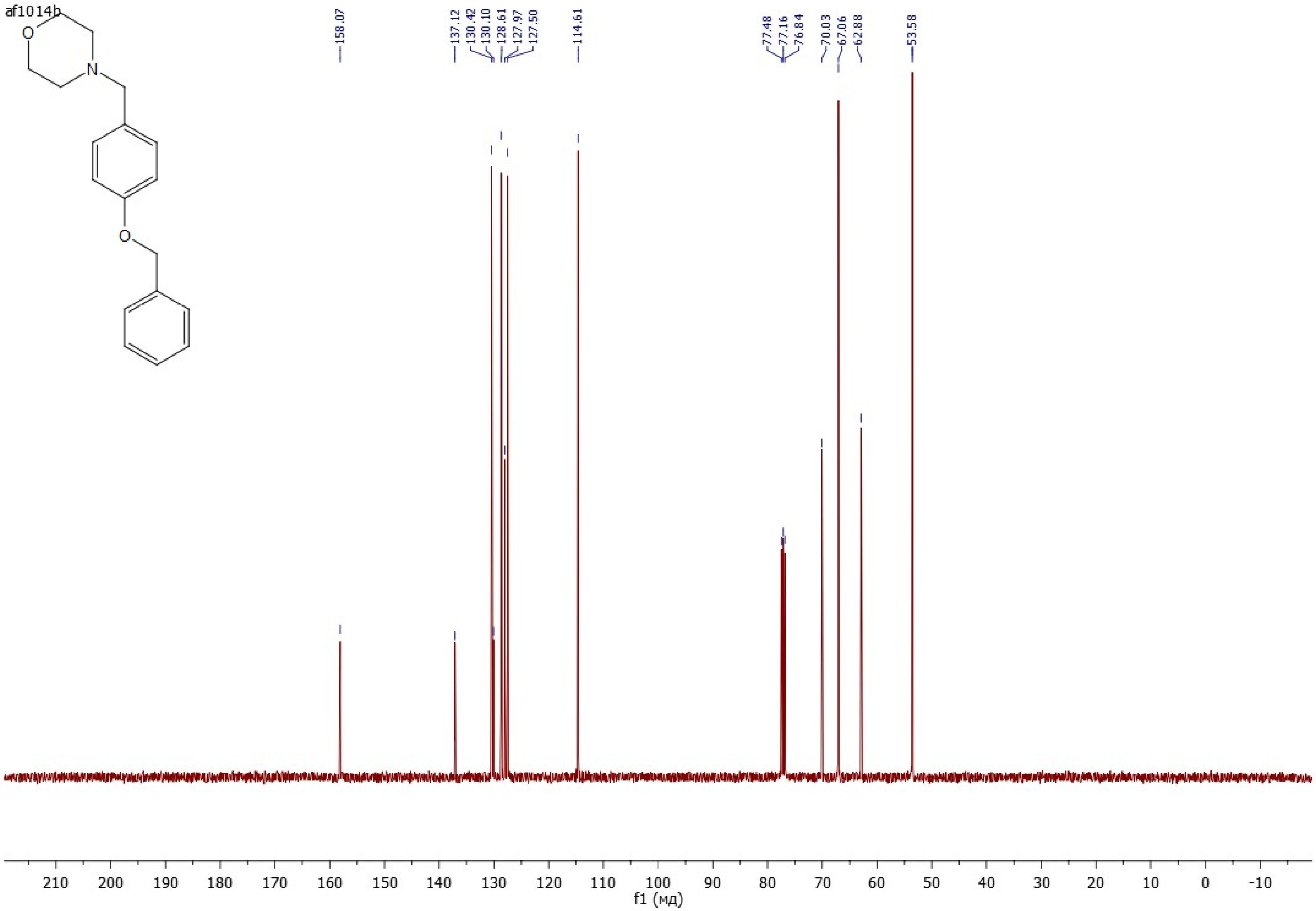
4-(4-methylbenzyl)morpholine (1a) ^{13}C NMR, CDCl$_3$, 101 MHz



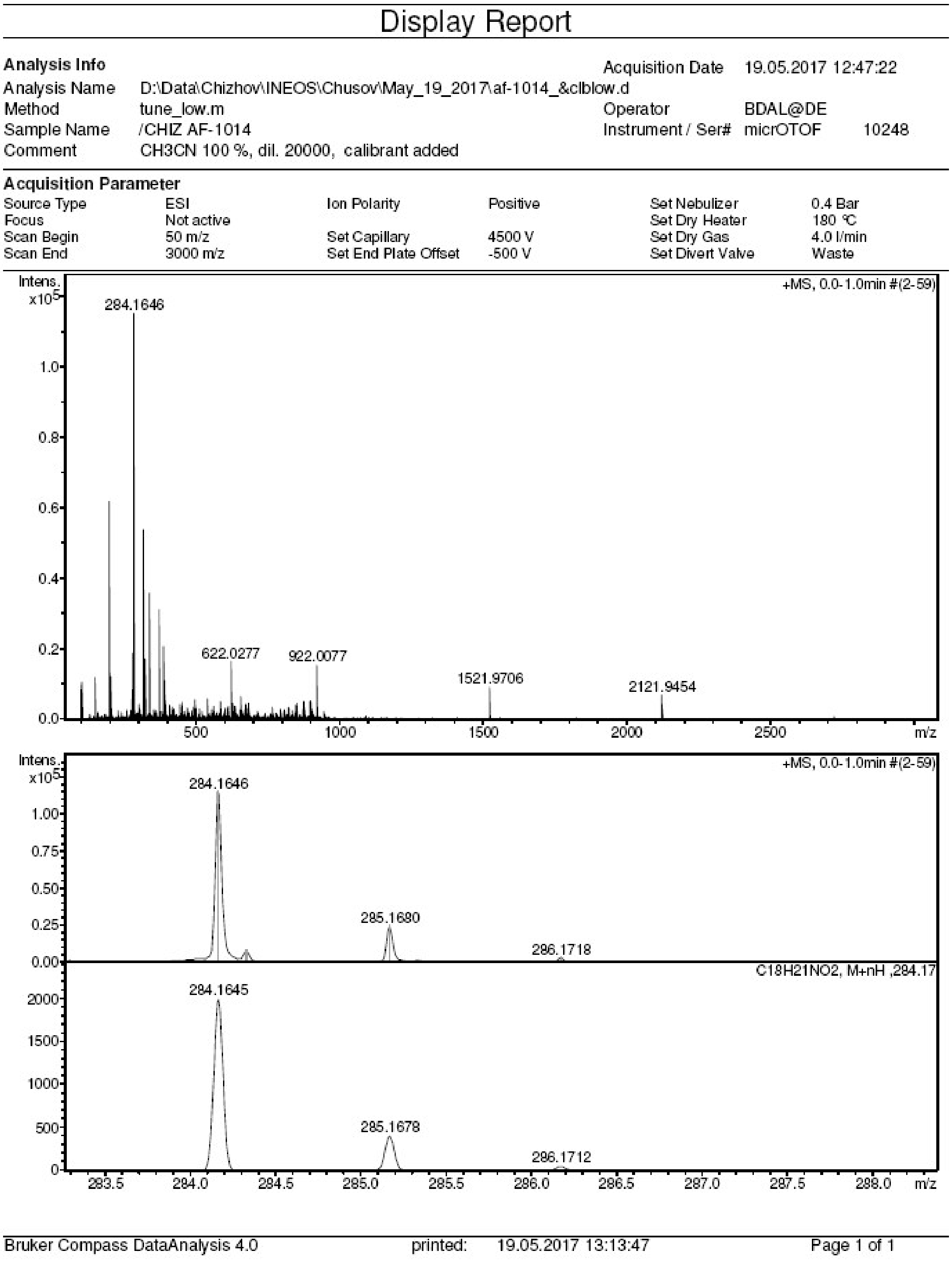
4-(4-(benzyloxy)benzyl)morpholine (1b) ^{1}H NMR, CDCl$_3$, 400 MHz



4-(4-(benzyloxy)benzyl)morpholine (1b) ^{13}C NMR, CDCl$_3$, 101 MHz



4-(4-(benzyloxy)benzyl)morpholine (1b), HRMS spectrum



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Sample Name	/CHIZ AF-1014	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 20000, calibrant added		

Acquisition Parameter

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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

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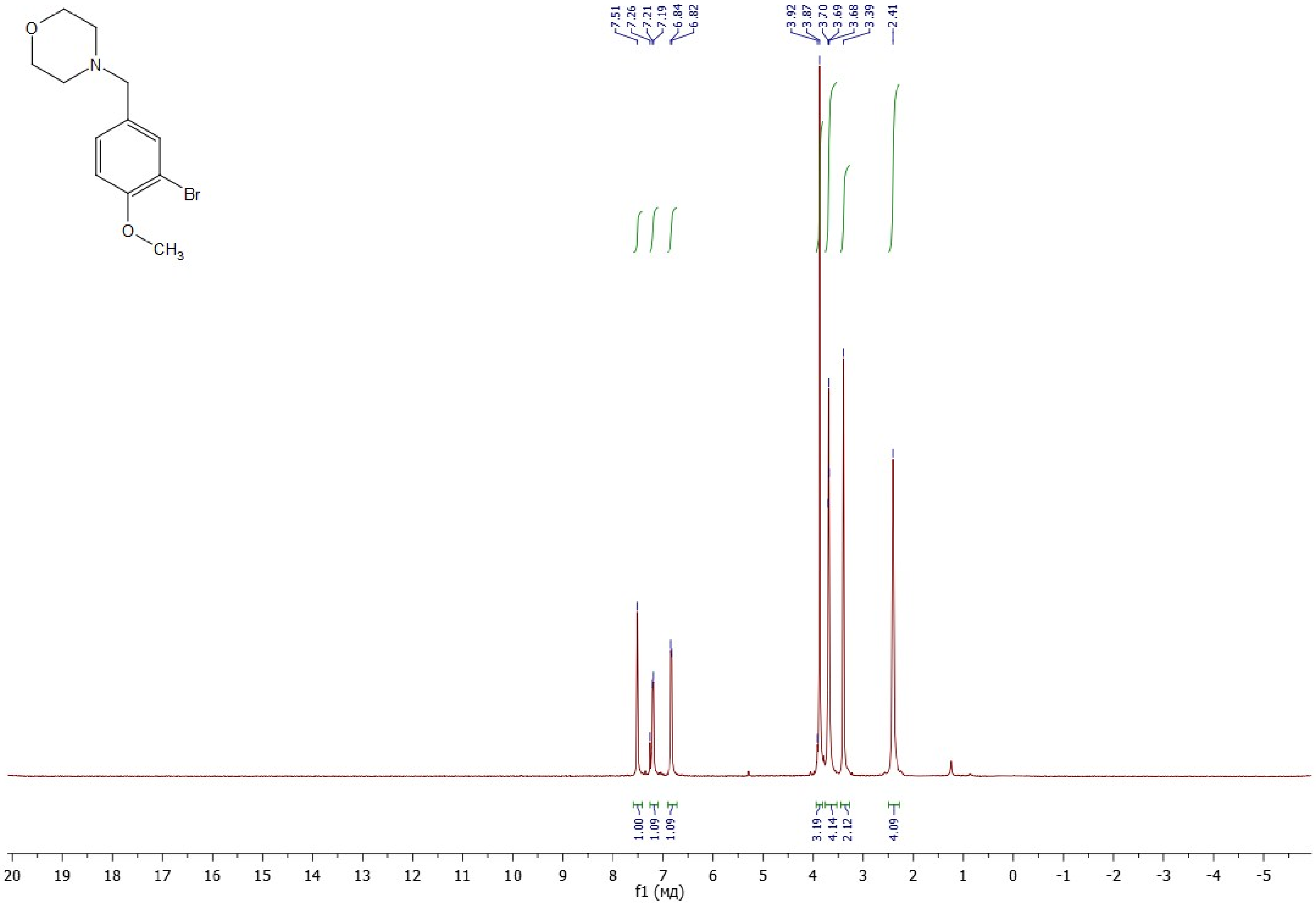
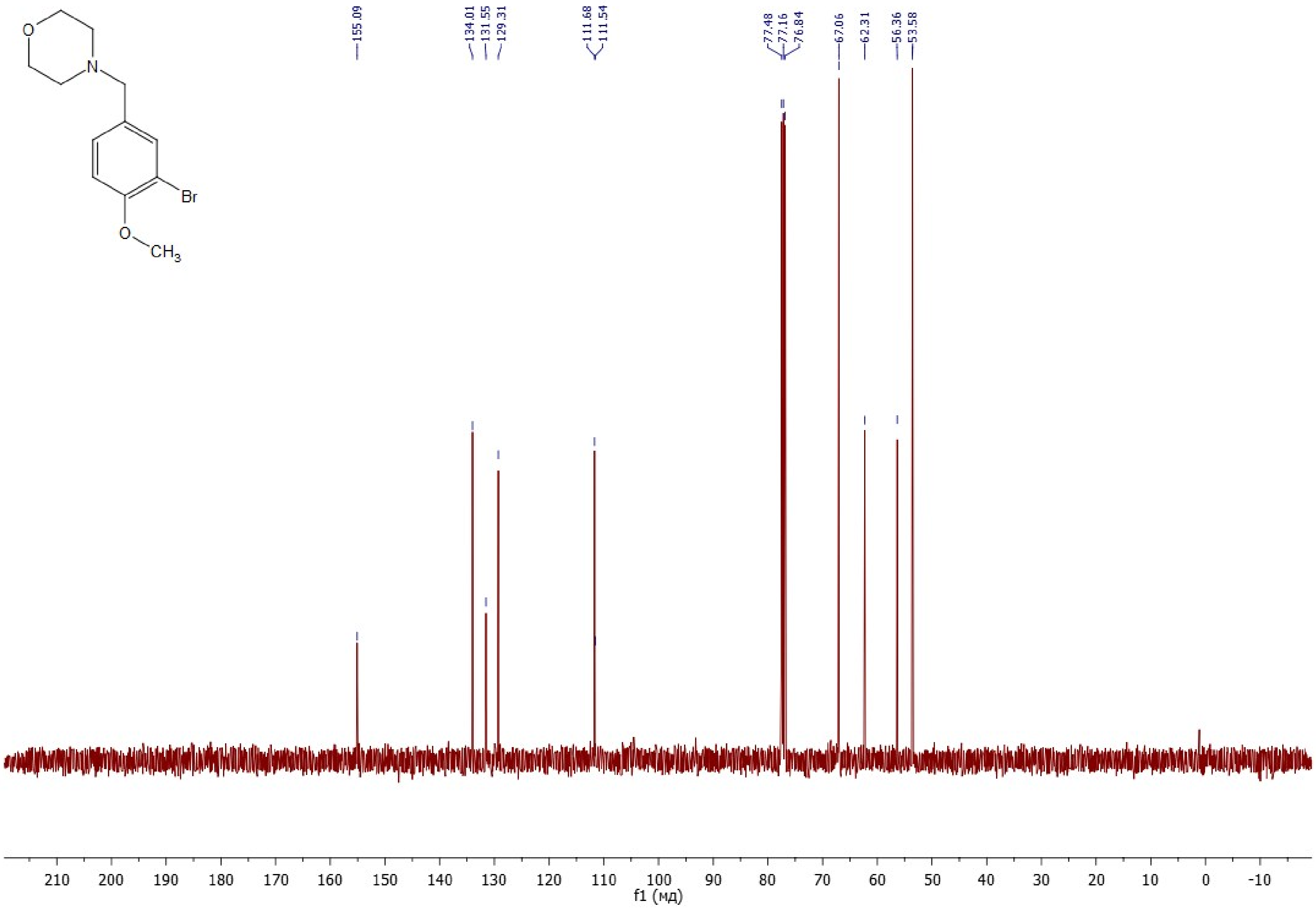
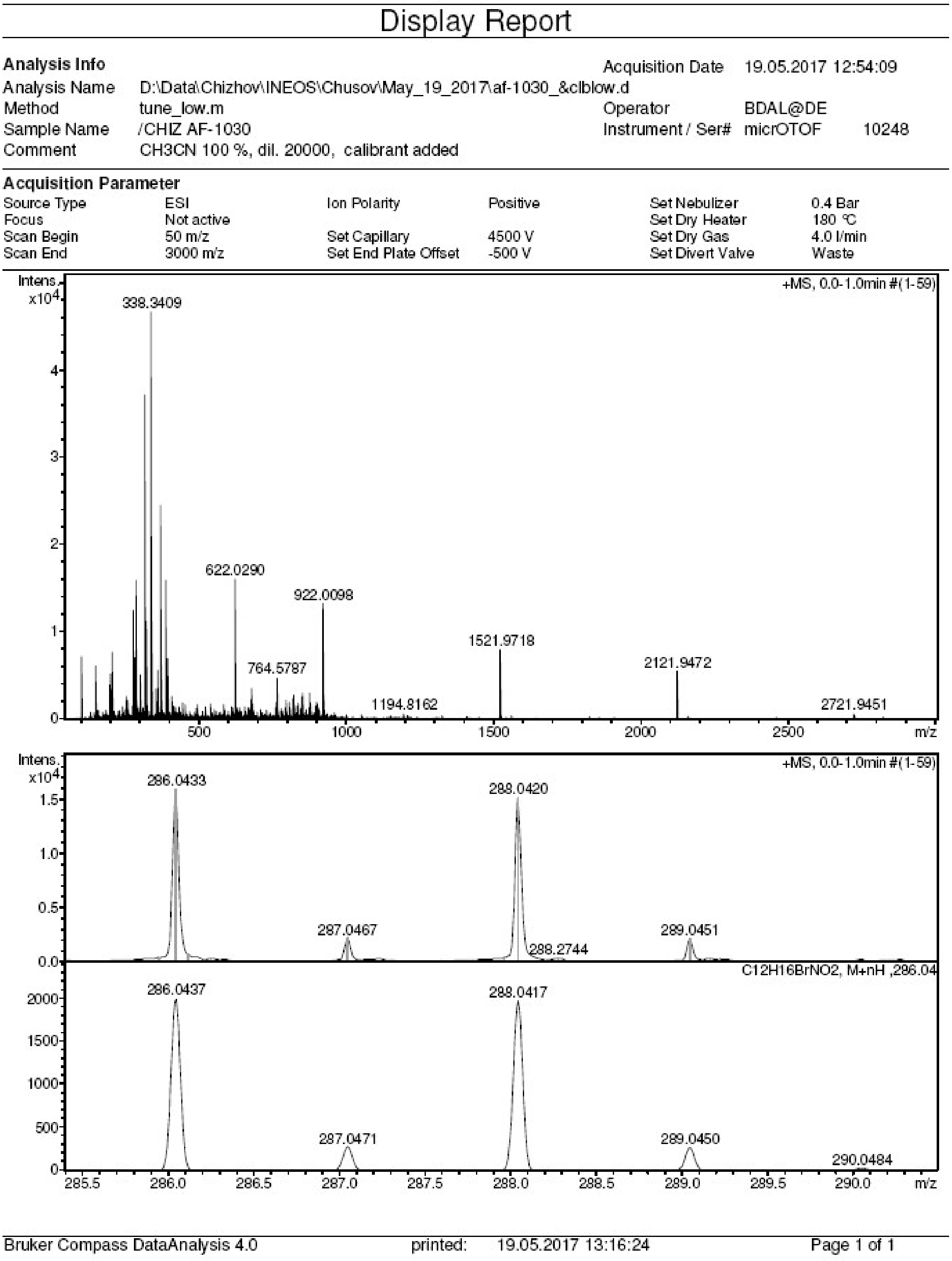
4-(3-bromo-4-methoxybenzyl)morpholine (1c) ^{1}H NMR, CDCl$_3$, 400 MHz



4-(3-bromo-4-methoxybenzyl)morpholine (1c) ^{13}C NMR, $CDCl_3$, 101 MHz



4-(3-bromo-4-methoxybenzyl)morpholine (1c), HRMS spectrum



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Analysis Info

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Sample Name	/CHIZ AF-1030	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 20000, 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

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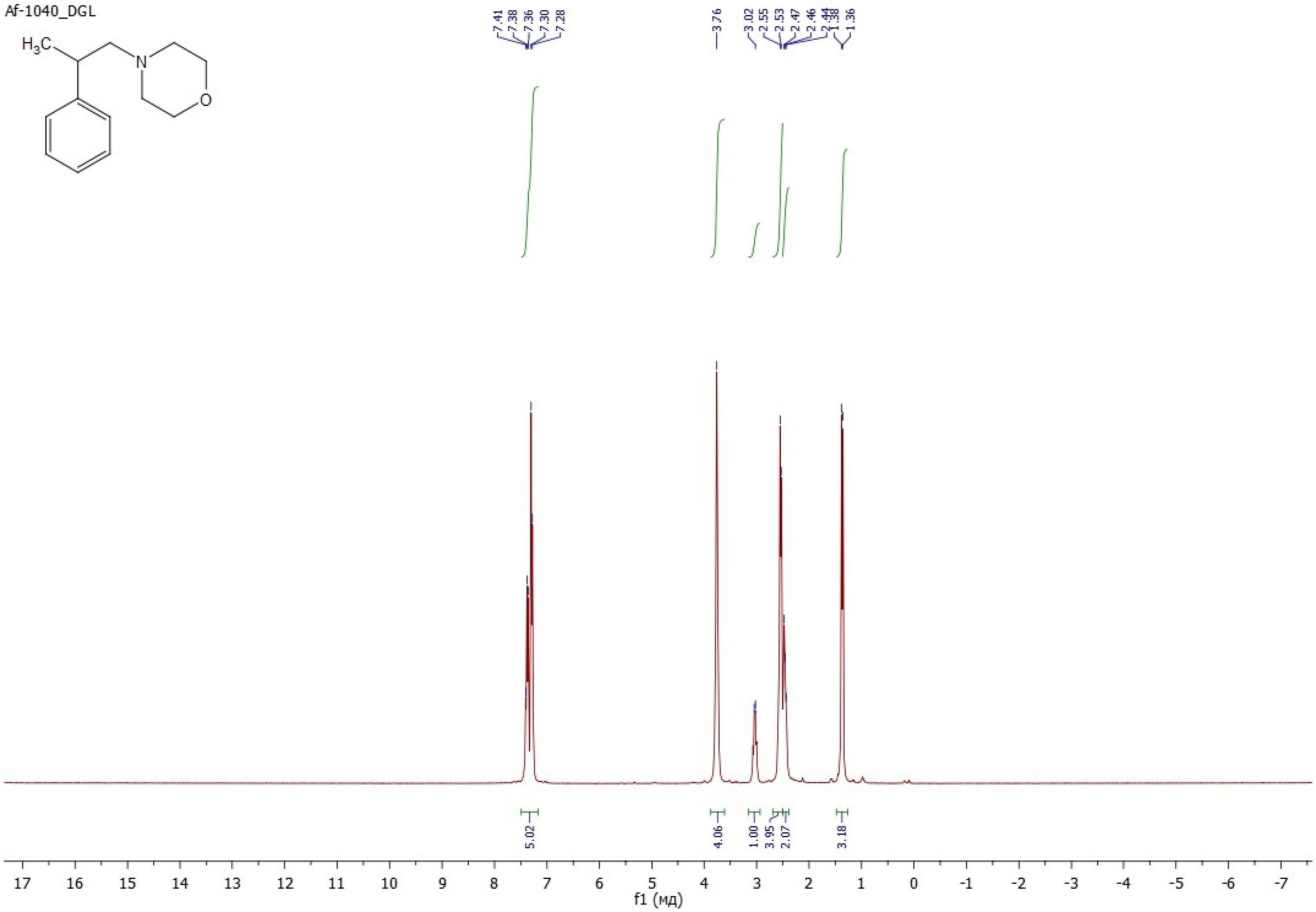
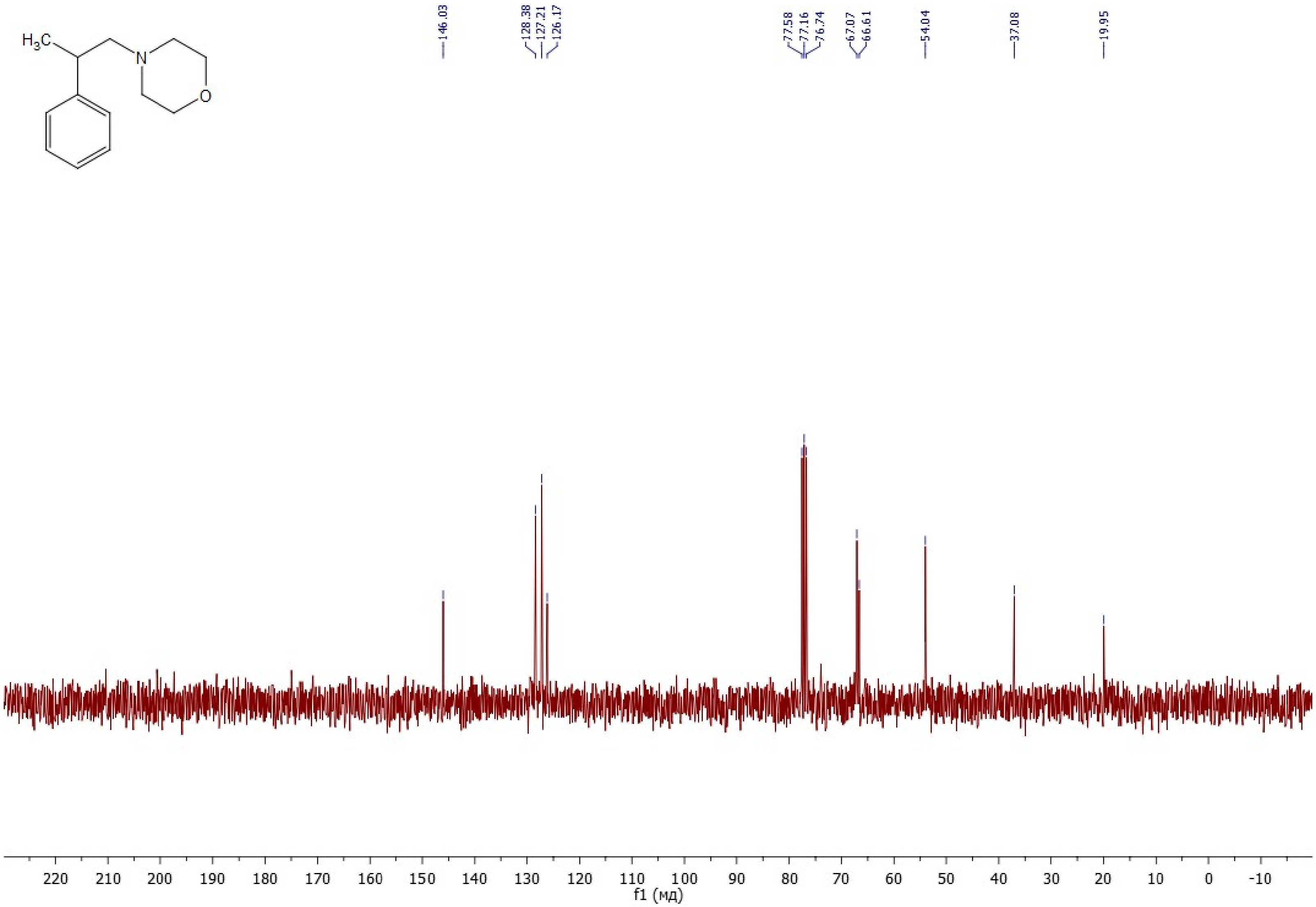
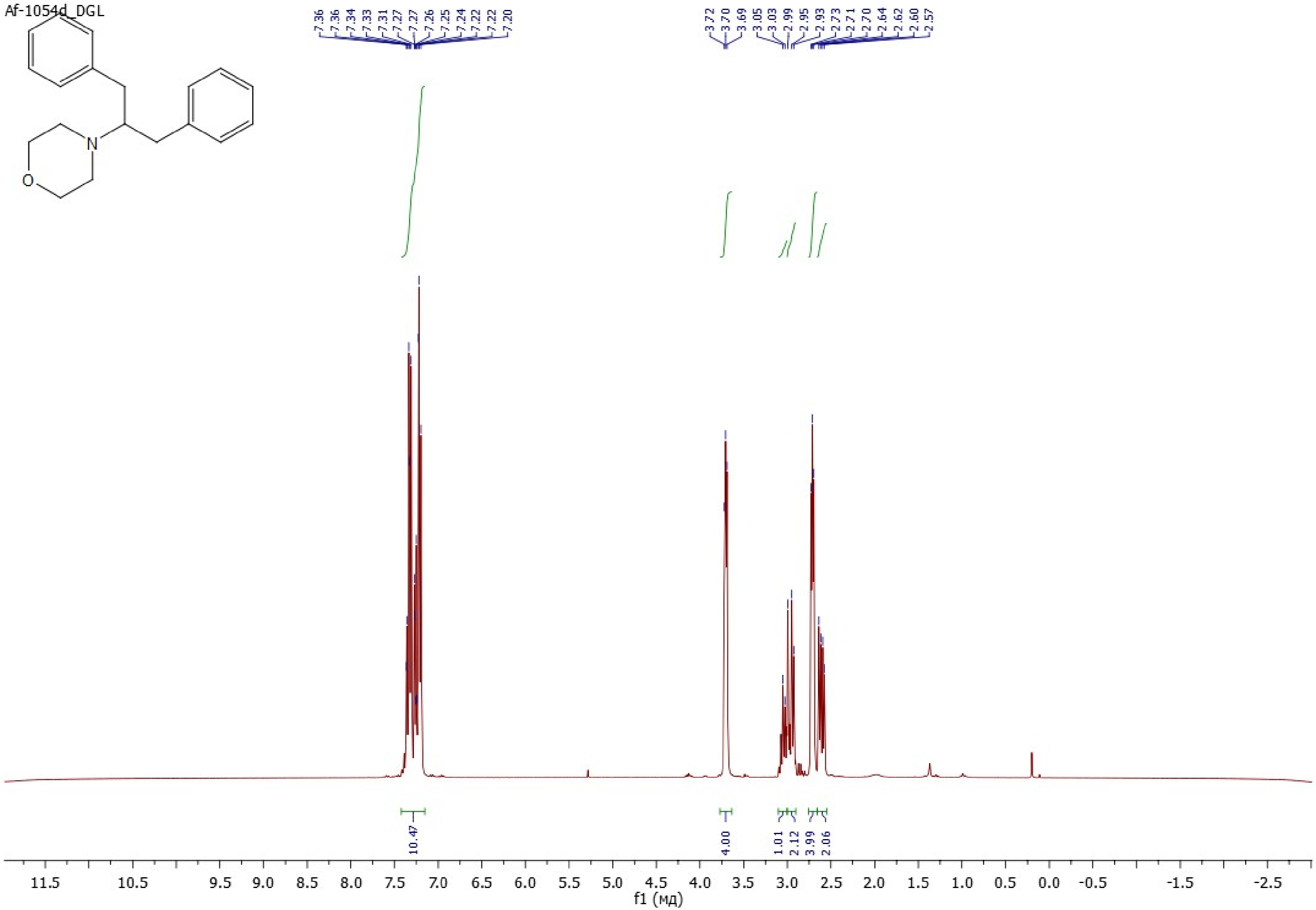
4-(2-phenylpropyl)morpholine (1d) ^{1}H NMR, $CDCl_3$, 300 MHz



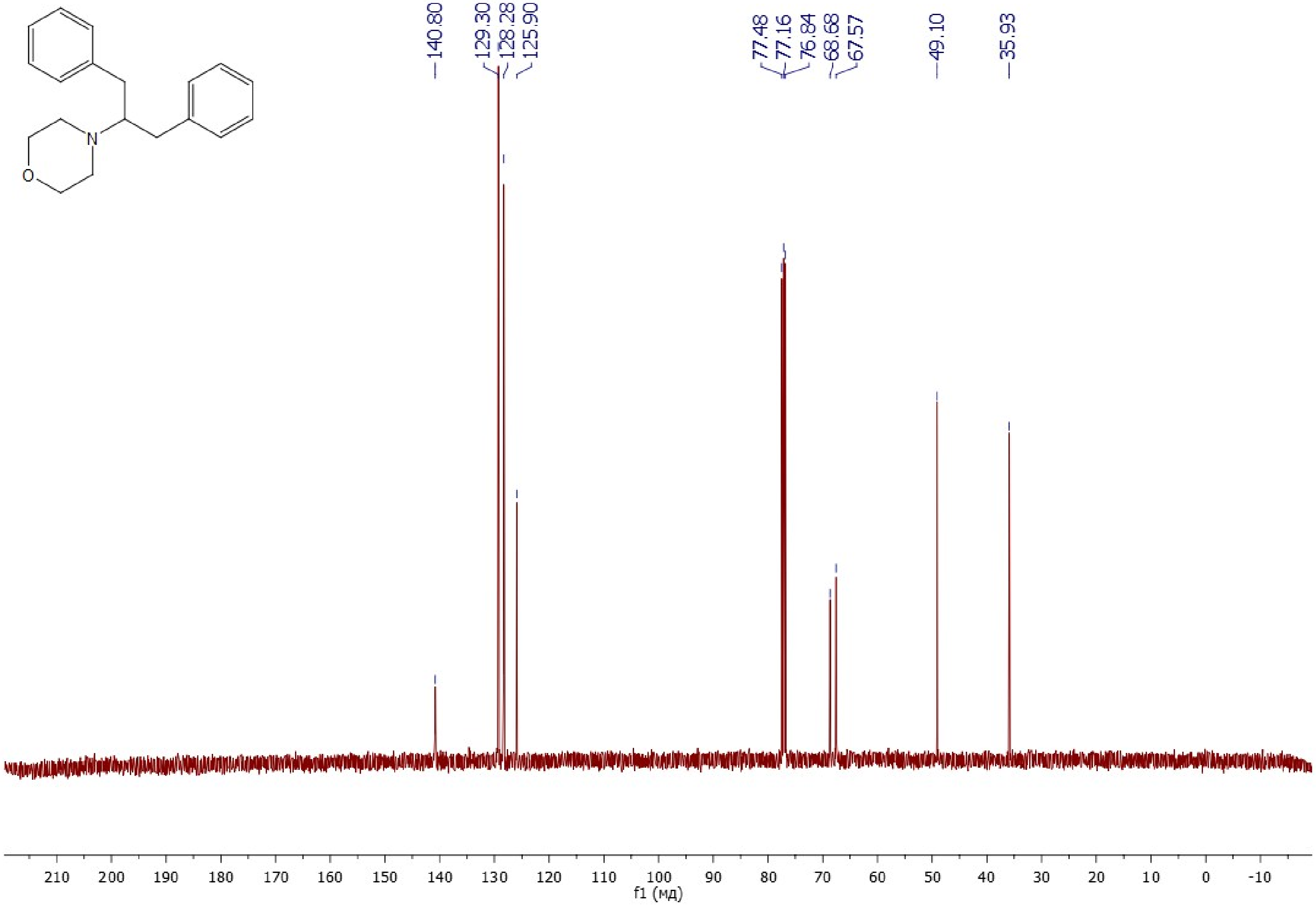
4-(2-phenylpropyl)morpholine (1d) ^{13}C NMR, CDCl$_3$, 101 MHz



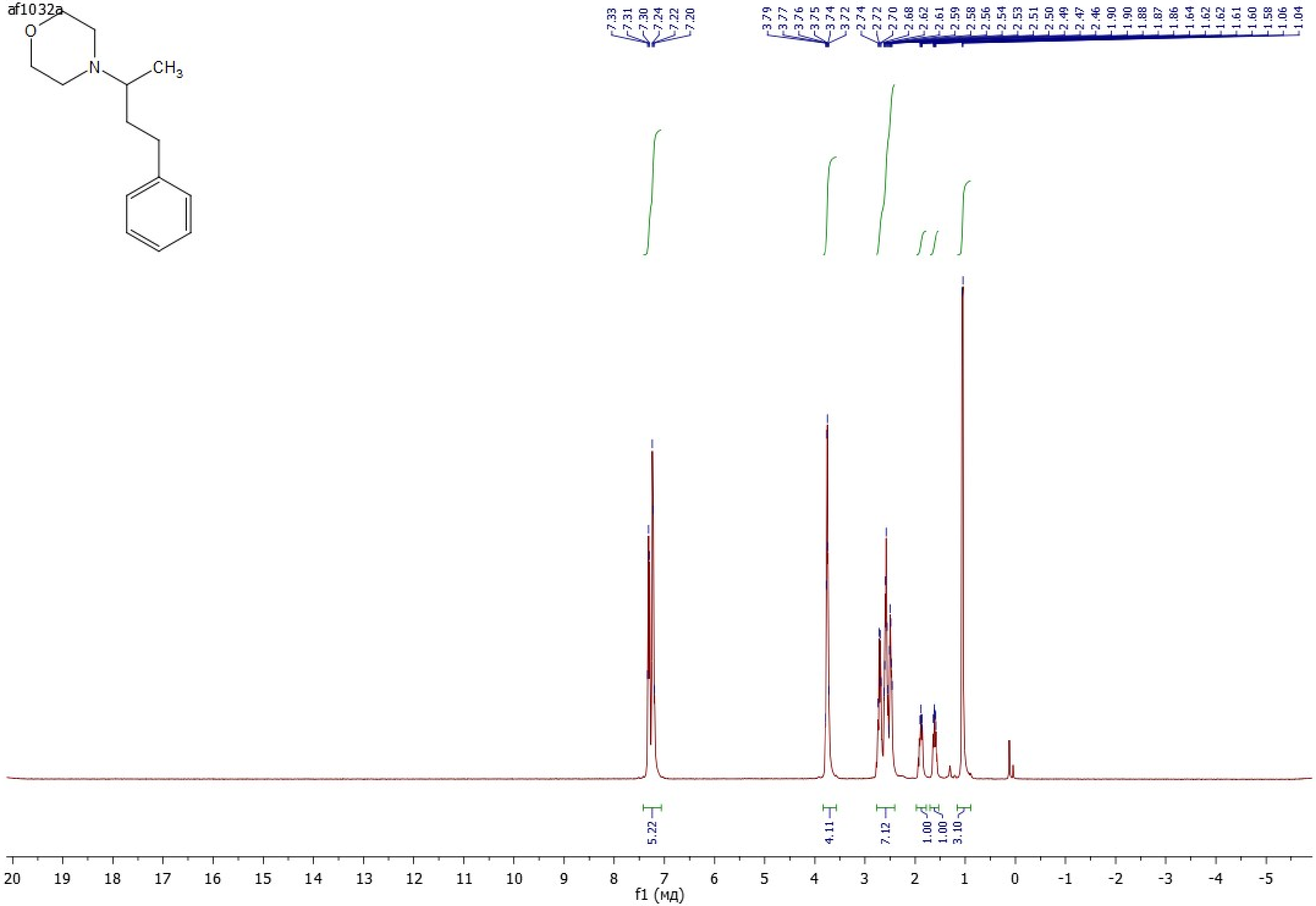
4-(1,3-diphenylpropan-2-yl)morpholine (1e) ^{1}H NMR, CDCl$_3$, 300 MHz



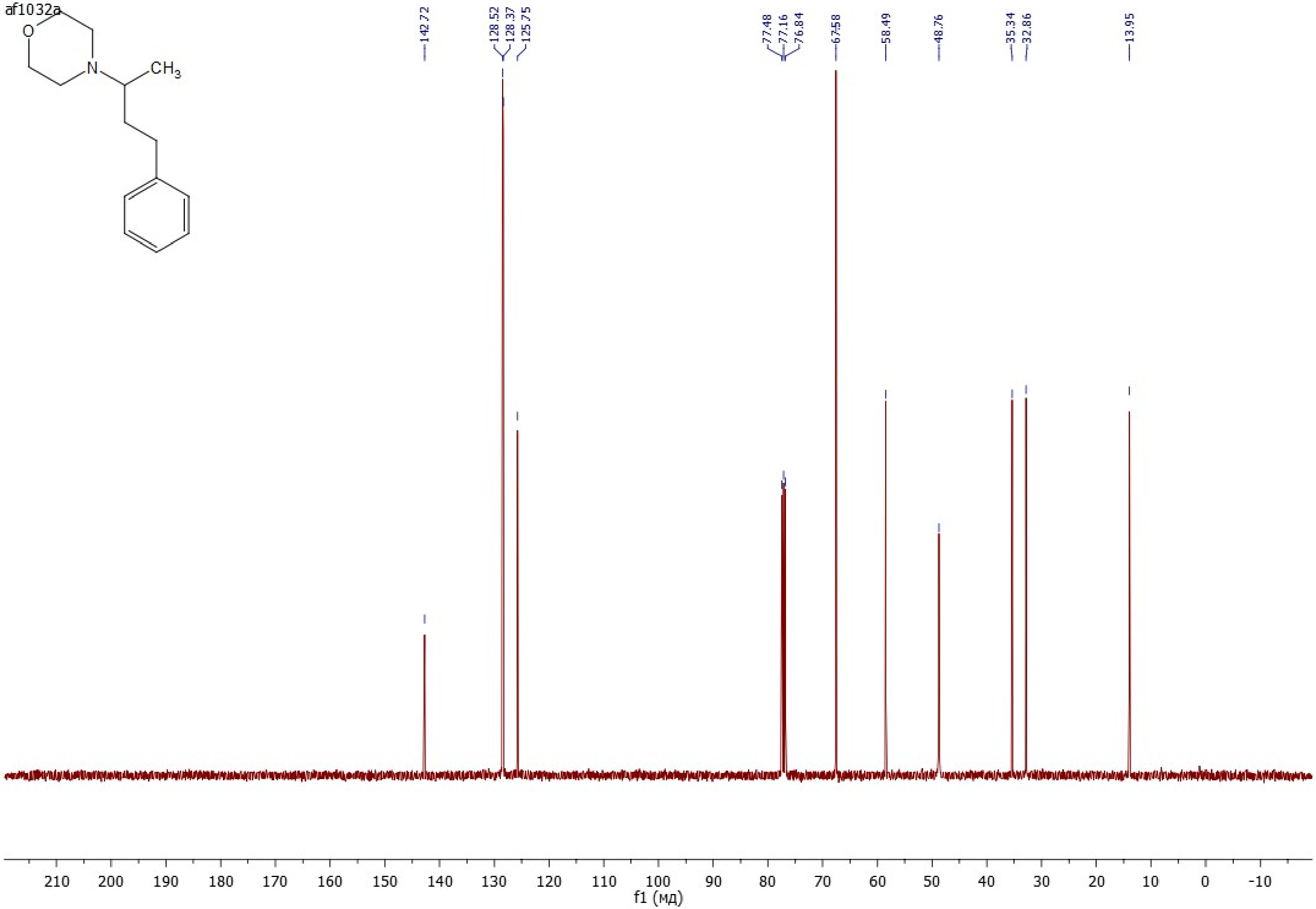
4-(1,3-diphenylpropan-2-yl)morpholine (1e) ^{13}C NMR, $CDCl_3$, 101 MHz



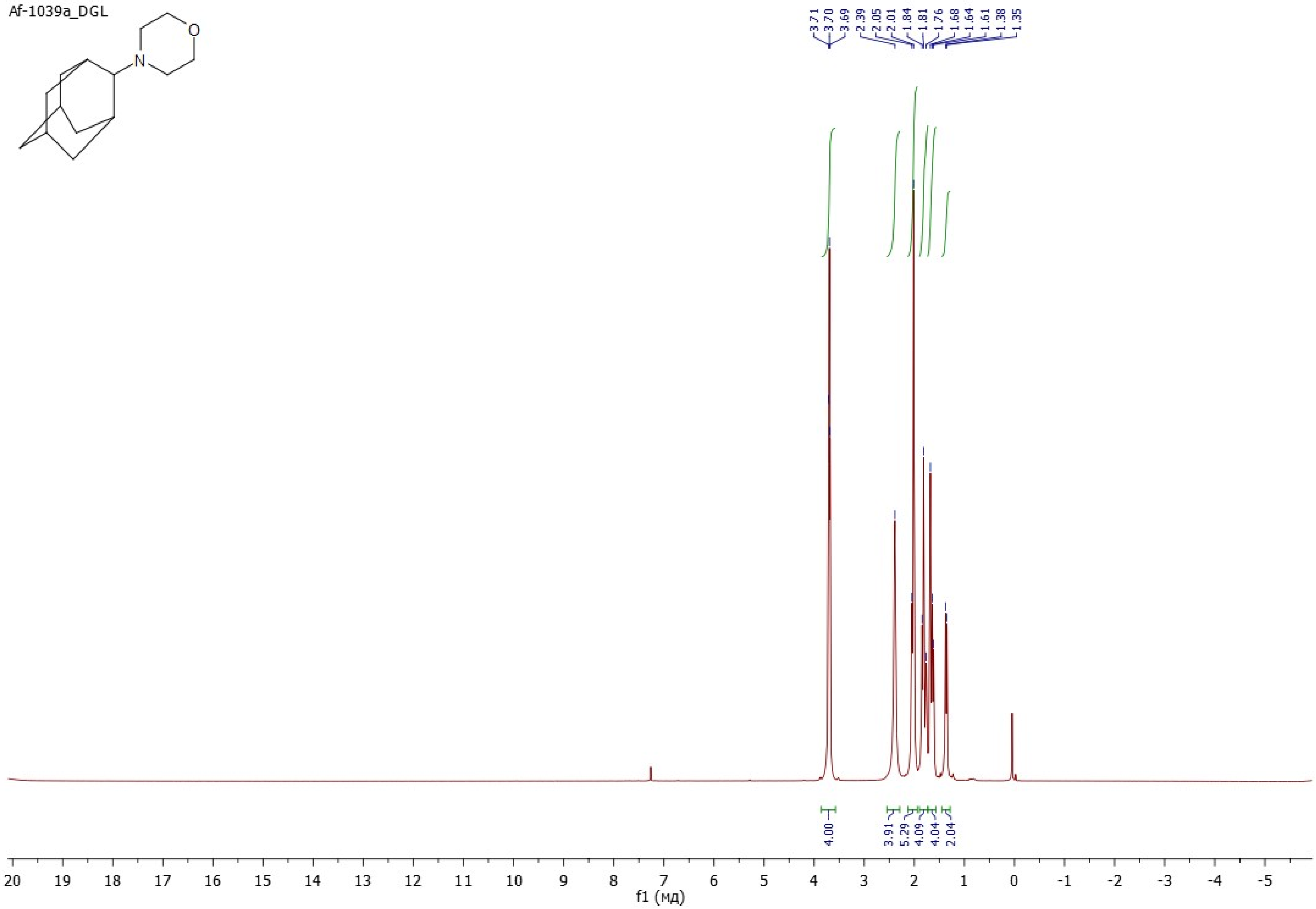
4-(4-phenylbutan-2-yl)morpholine (1f) ^{1}H NMR, CDCl$_3$, 400 MHz



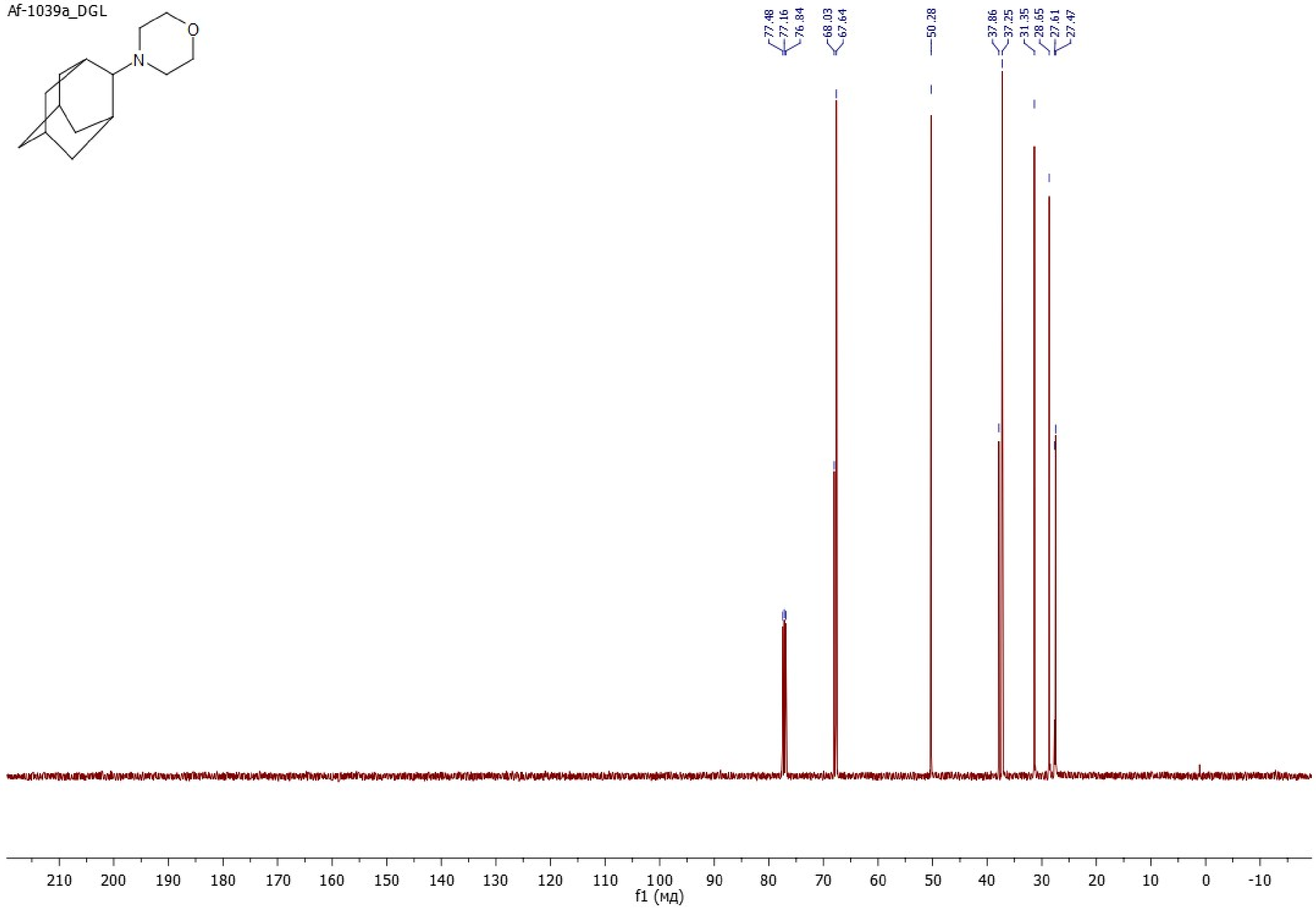
4-(4-phenylbutan-2-yl)morpholine (1f) ^{13}C NMR, CDCl$_3$, 101 MHz



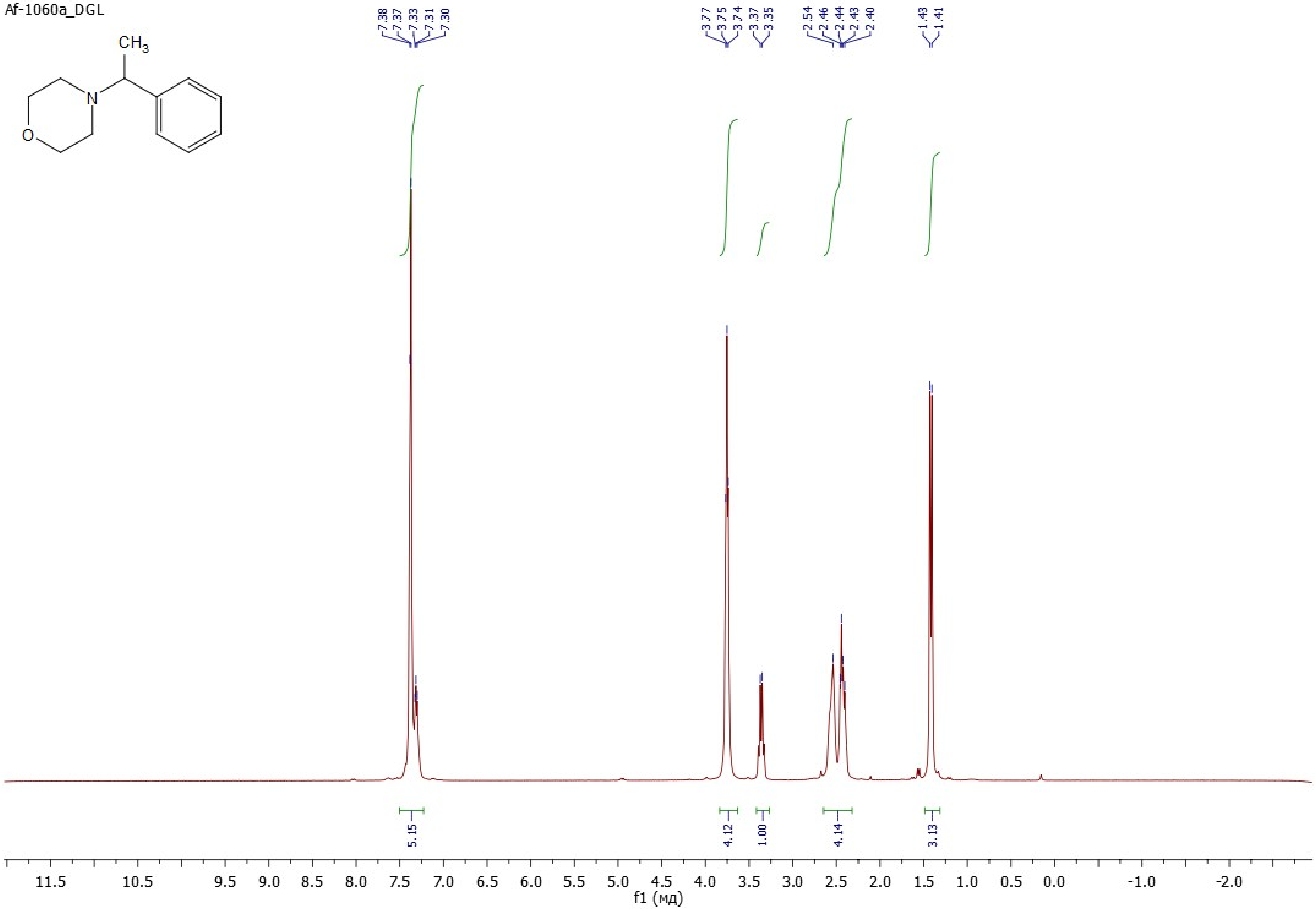
4-(adamantan-2-yl)morpholine (1g) ^{1}H NMR, $CDCl_3$, 400 MHz



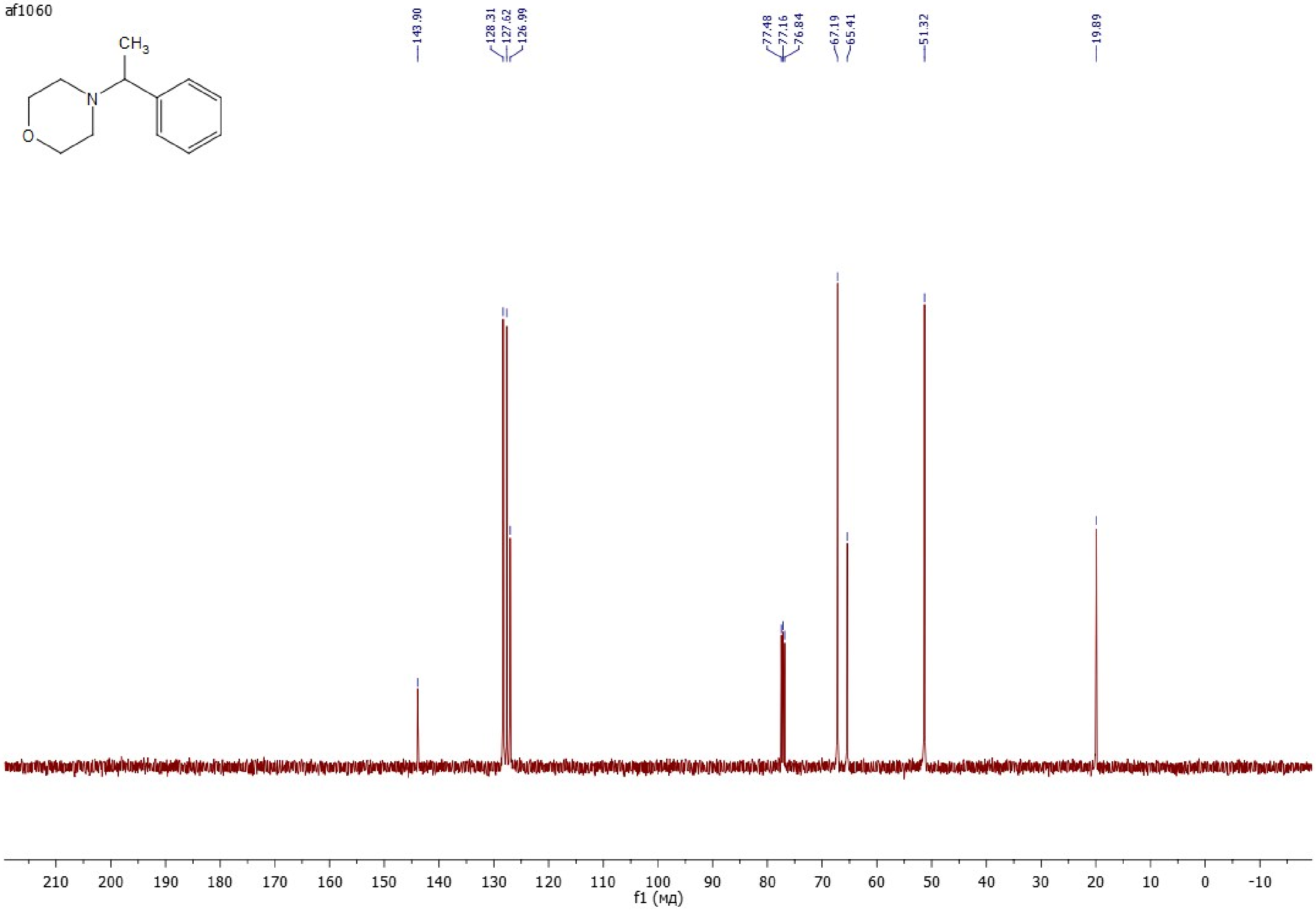
4-(adamantan-2-yl)morpholine (1g) ^{13}C NMR, $CDCl_3$, 101 MHz



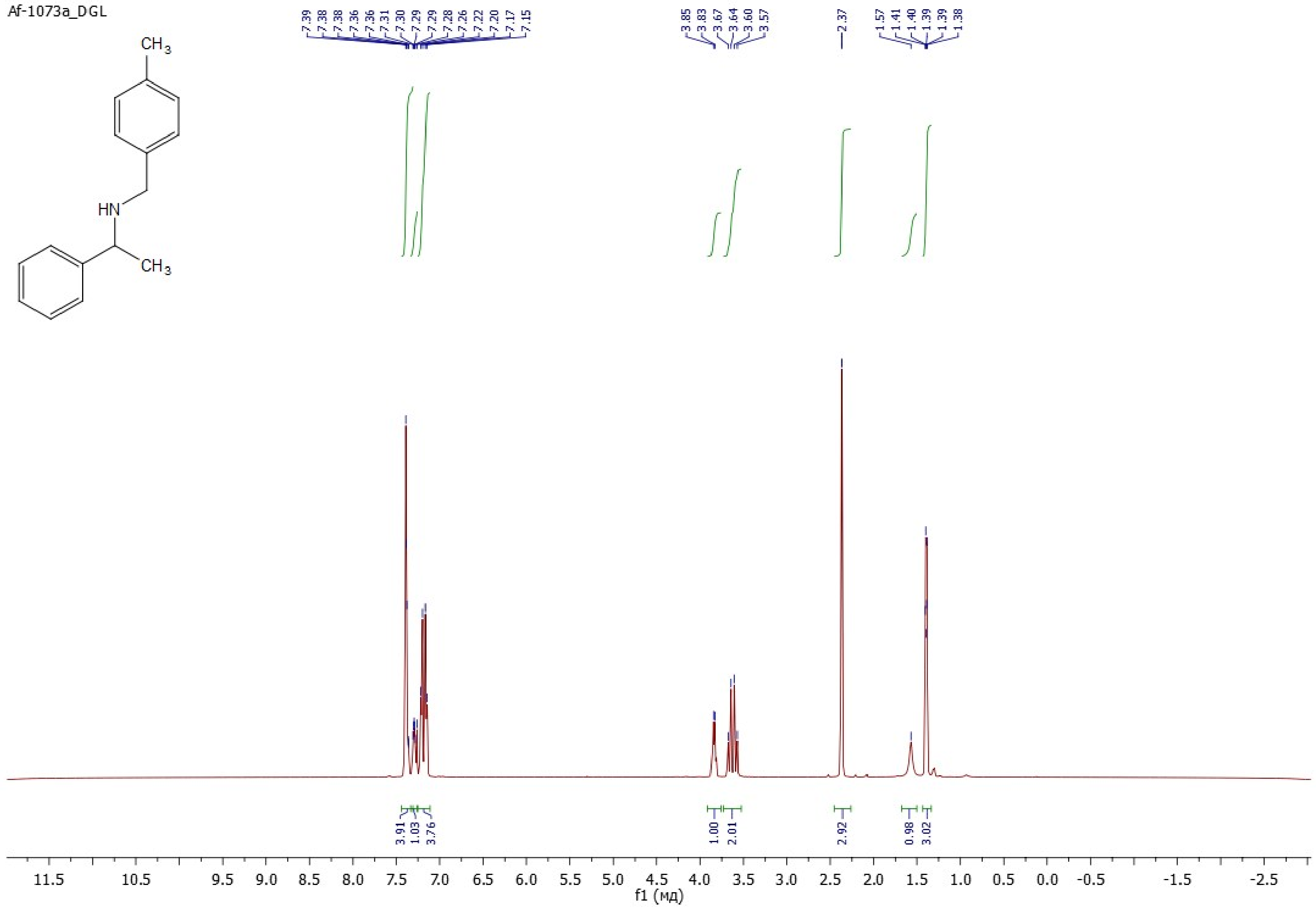
4-(1-phenylethyl)morpholine (1h) ^{1}H NMR, $CDCl_3$, 400 MHz



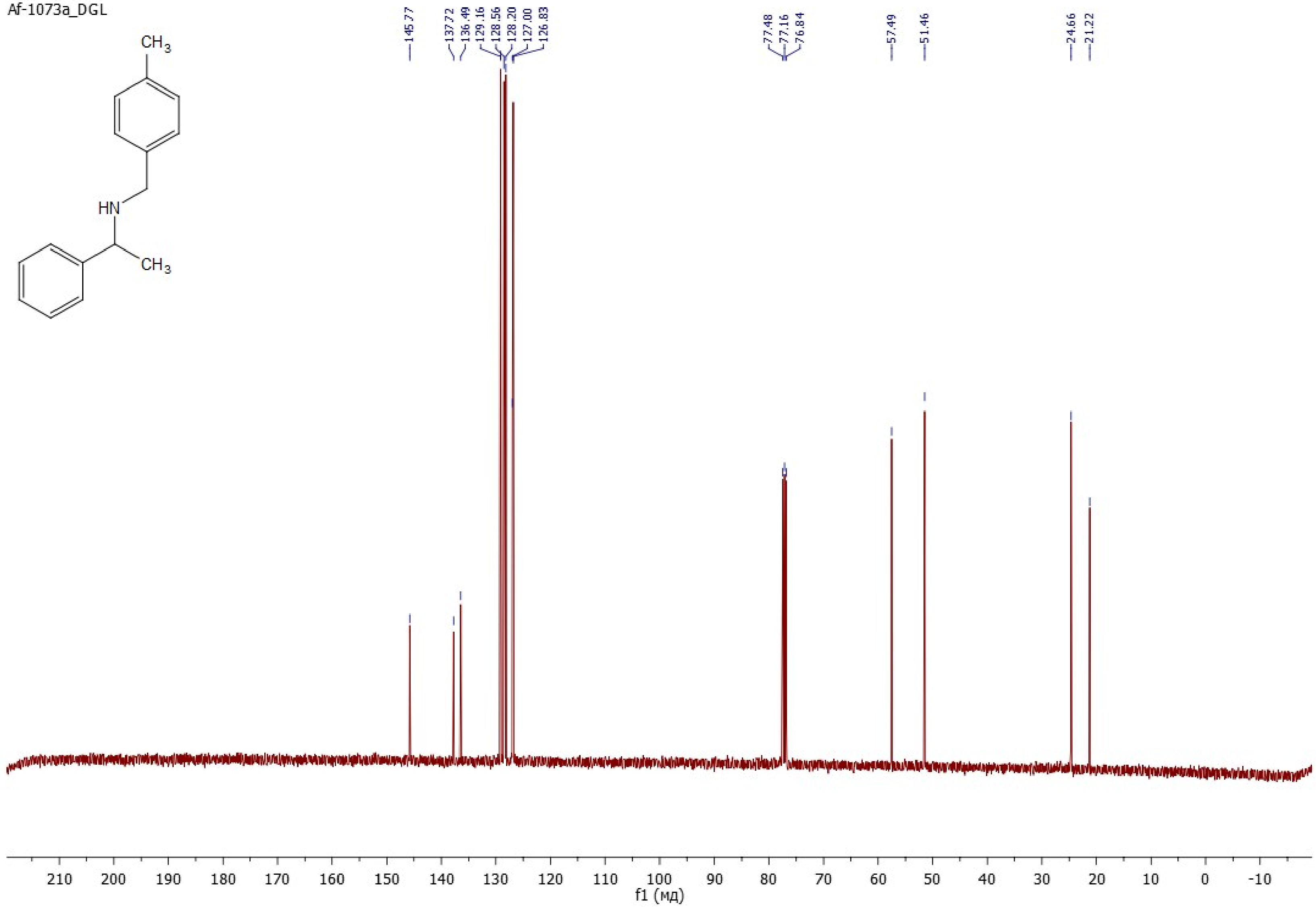
4-(1-phenylethyl)morpholine (1h) ^{13}C NMR, CDCl$_3$, 101 MHz



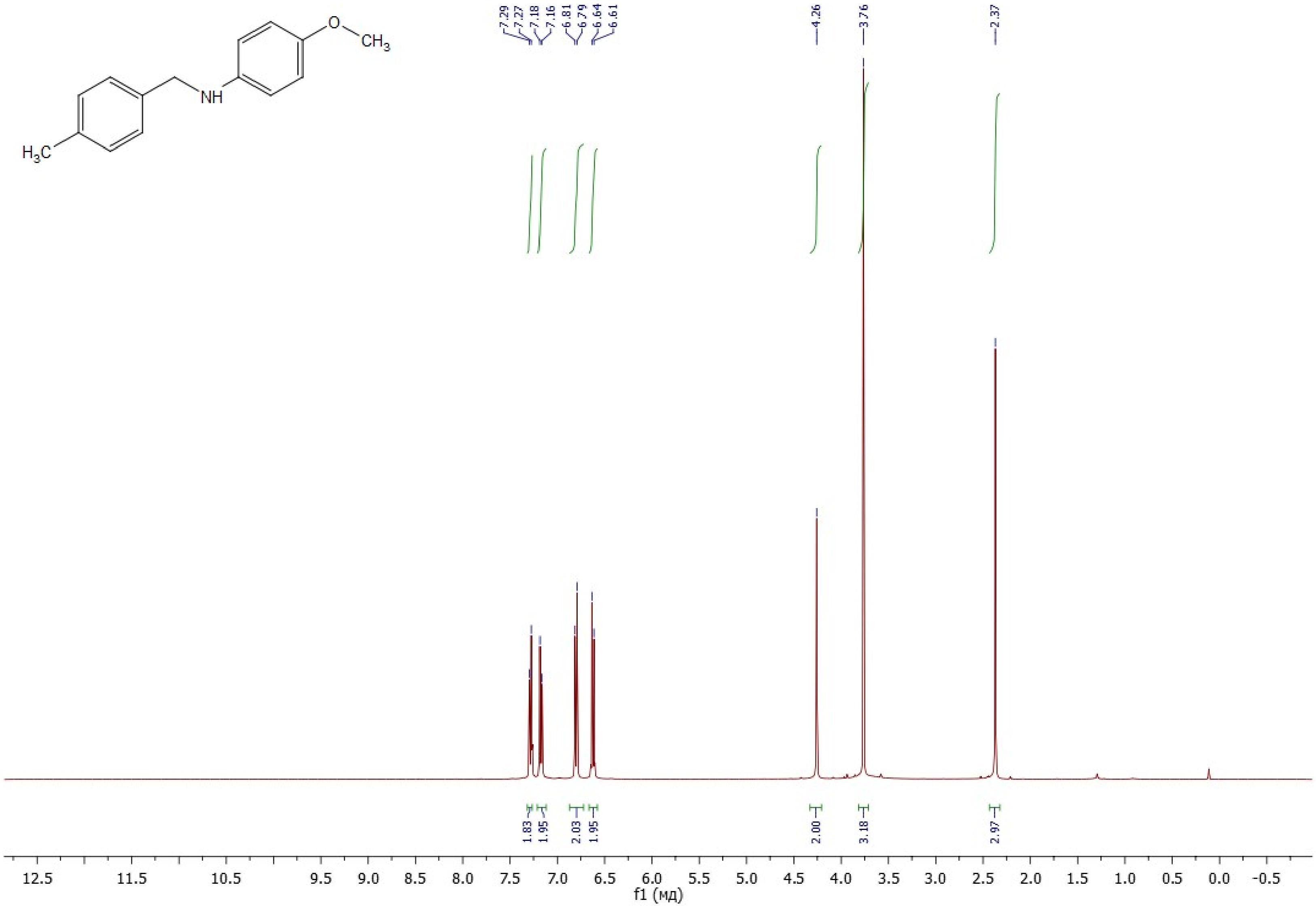
N-(4-methylbenzyl)-1-phenylethan-1-amine (1i) ^{1}H NMR, $CDCl_3$, 400 MHz



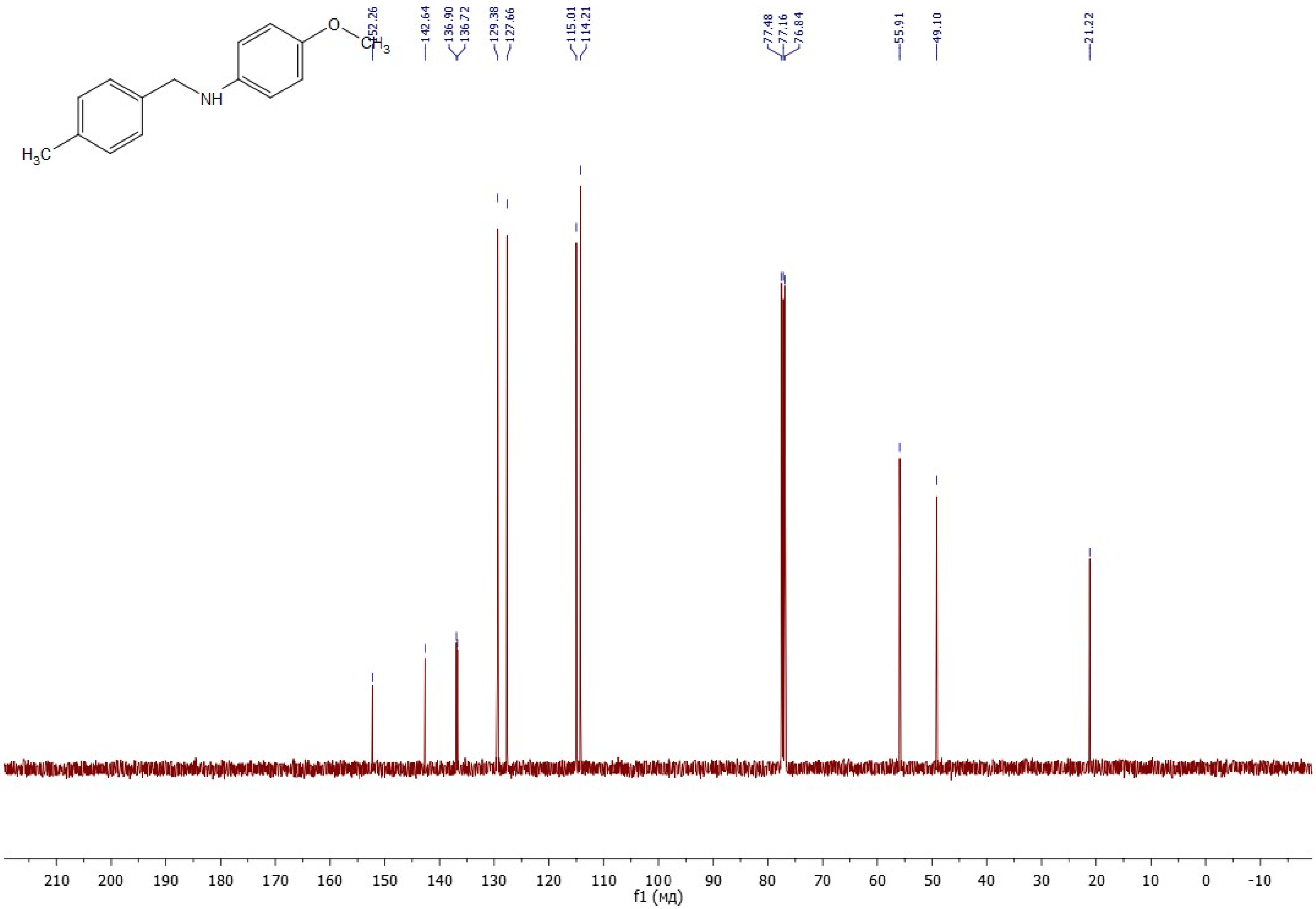
N-(4-methylbenzyl)-1-phenylethan-1-amine (1i) ^{13}C NMR, $CDCl_3$, 101 MHz



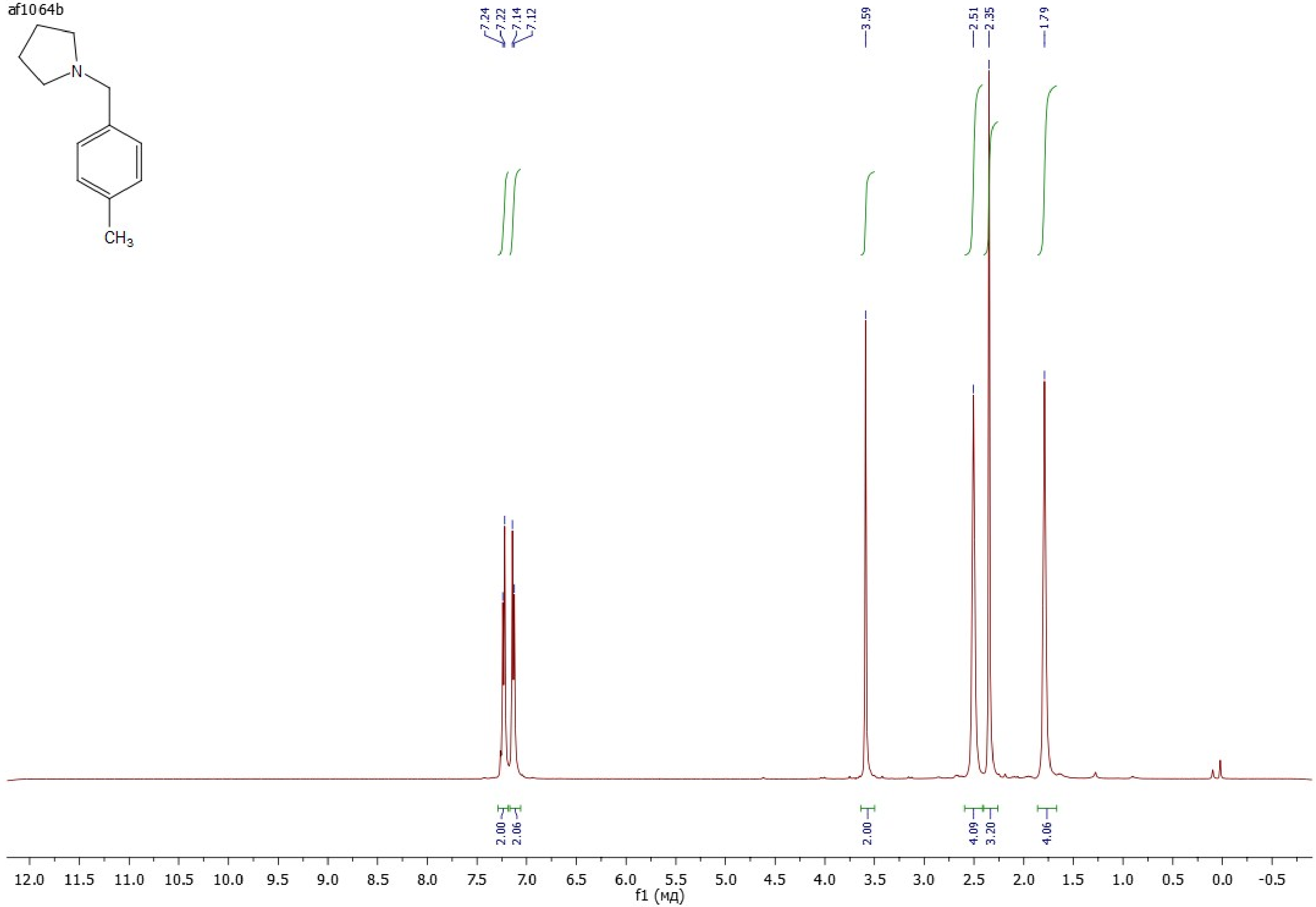
4-methoxy-N-(4-methylbenzyl)aniline (1j) ^{1}H NMR, CDCl$_3$, 400 MHz



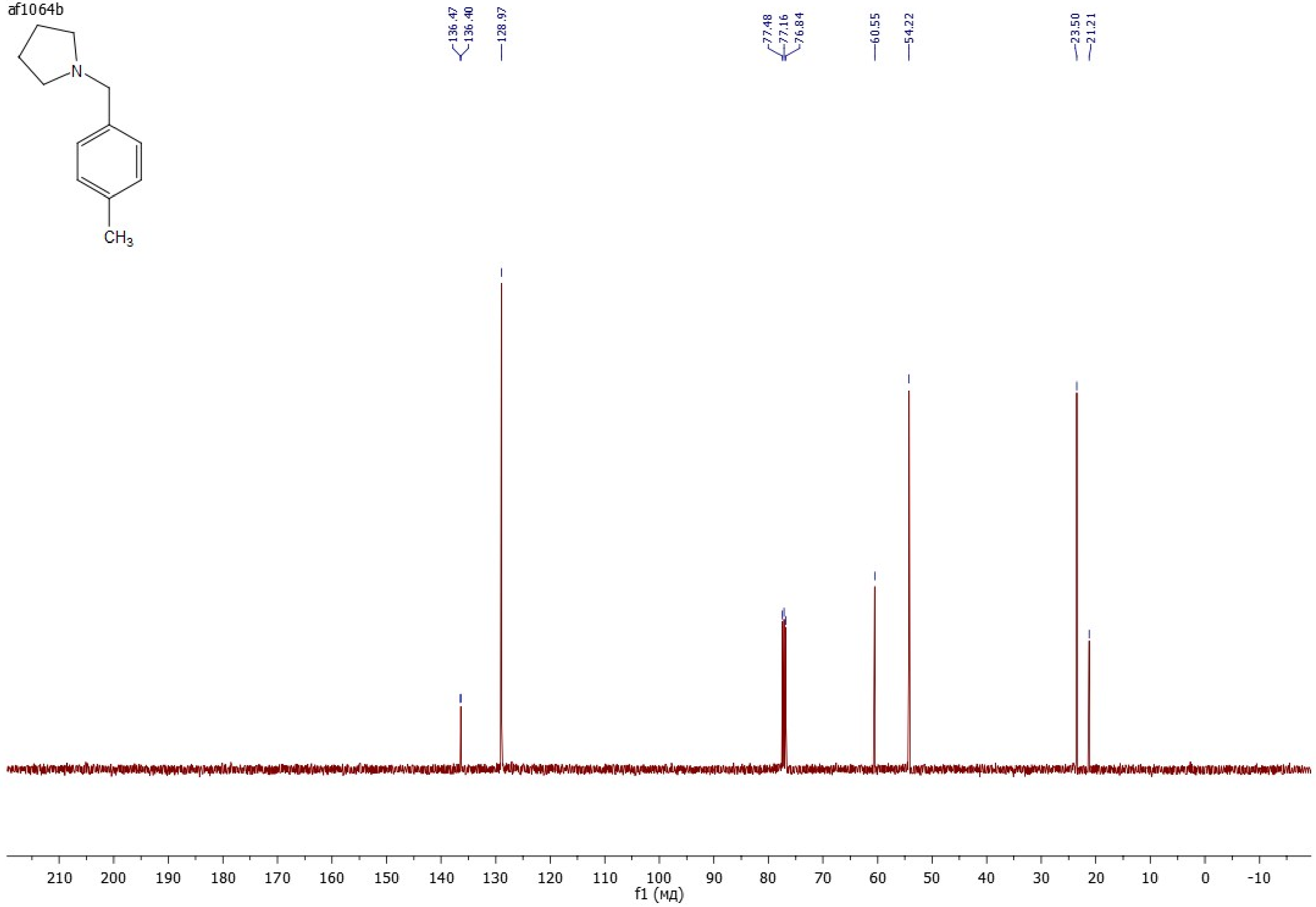
4-methoxy-N-(4-methylbenzyl)aniline (1j) ^{13}C NMR, CDCl$_3$, 101 MHz



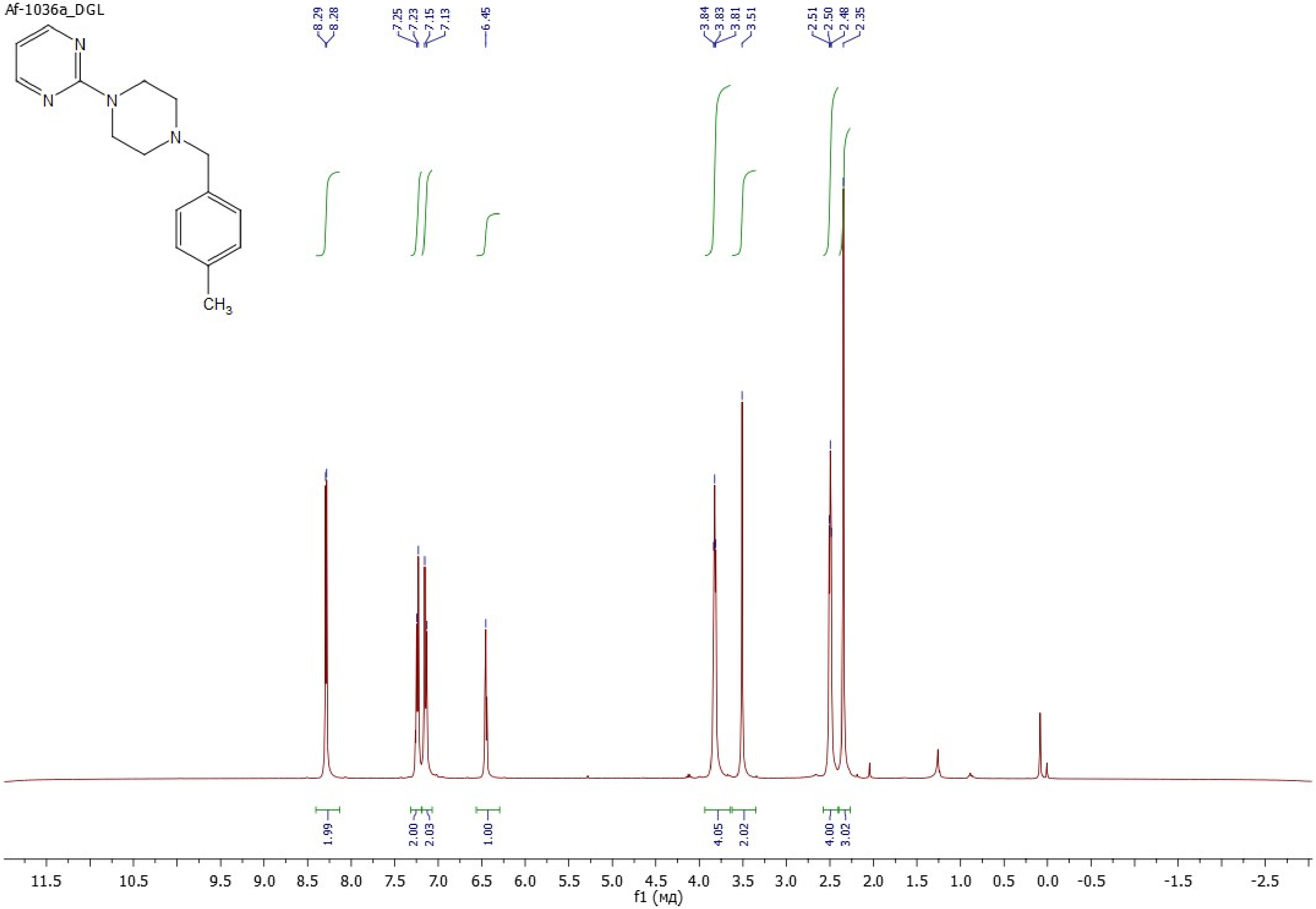
1-(4-methylbenzyl)pyrrolidine (1j) ^{1}H NMR, CDCl$_3$, 400 MHz



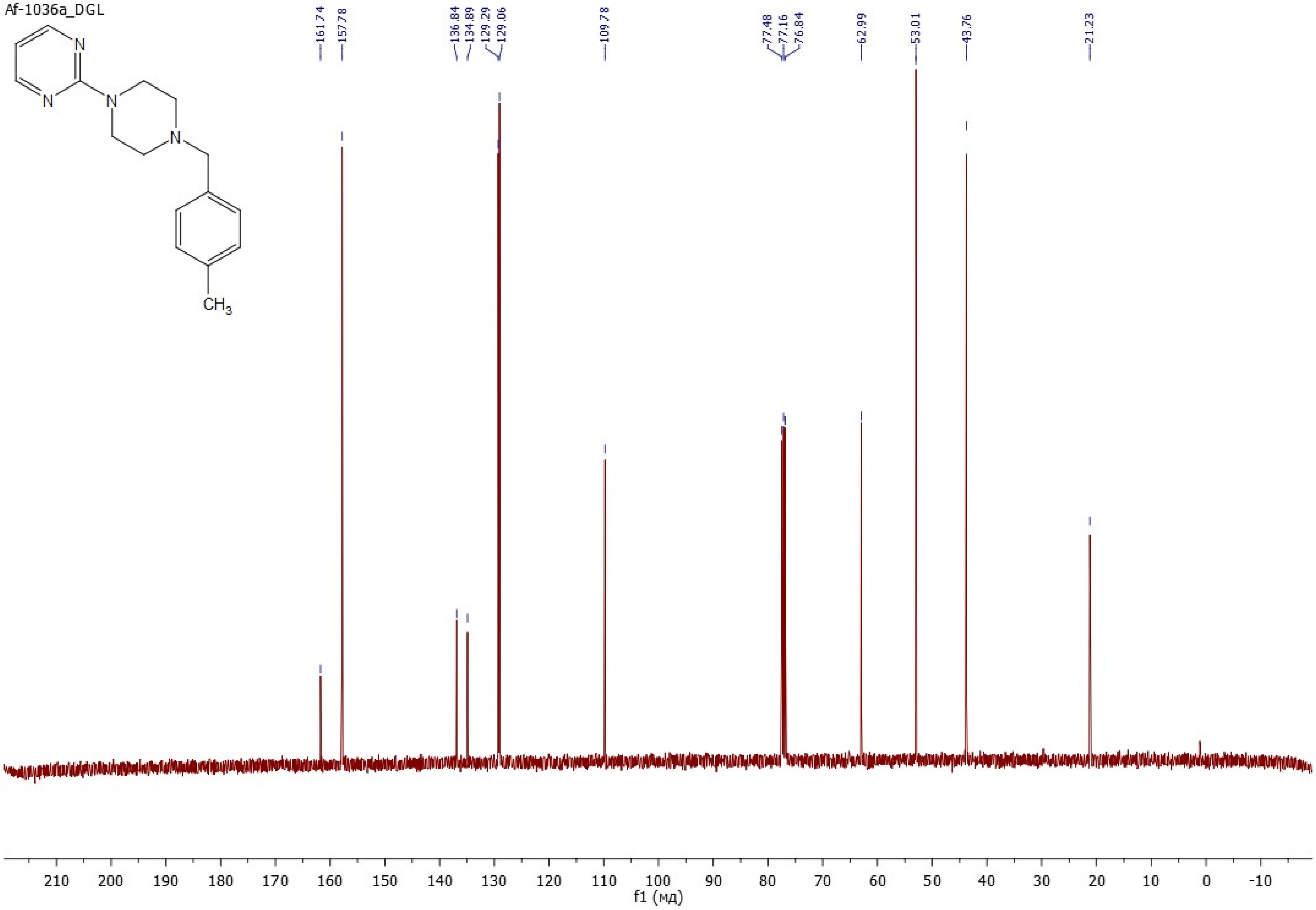
1-(4-methylbenzyl)pyrrolidine (1j) ^{13}C NMR, CDCl$_3$, 101 MHz



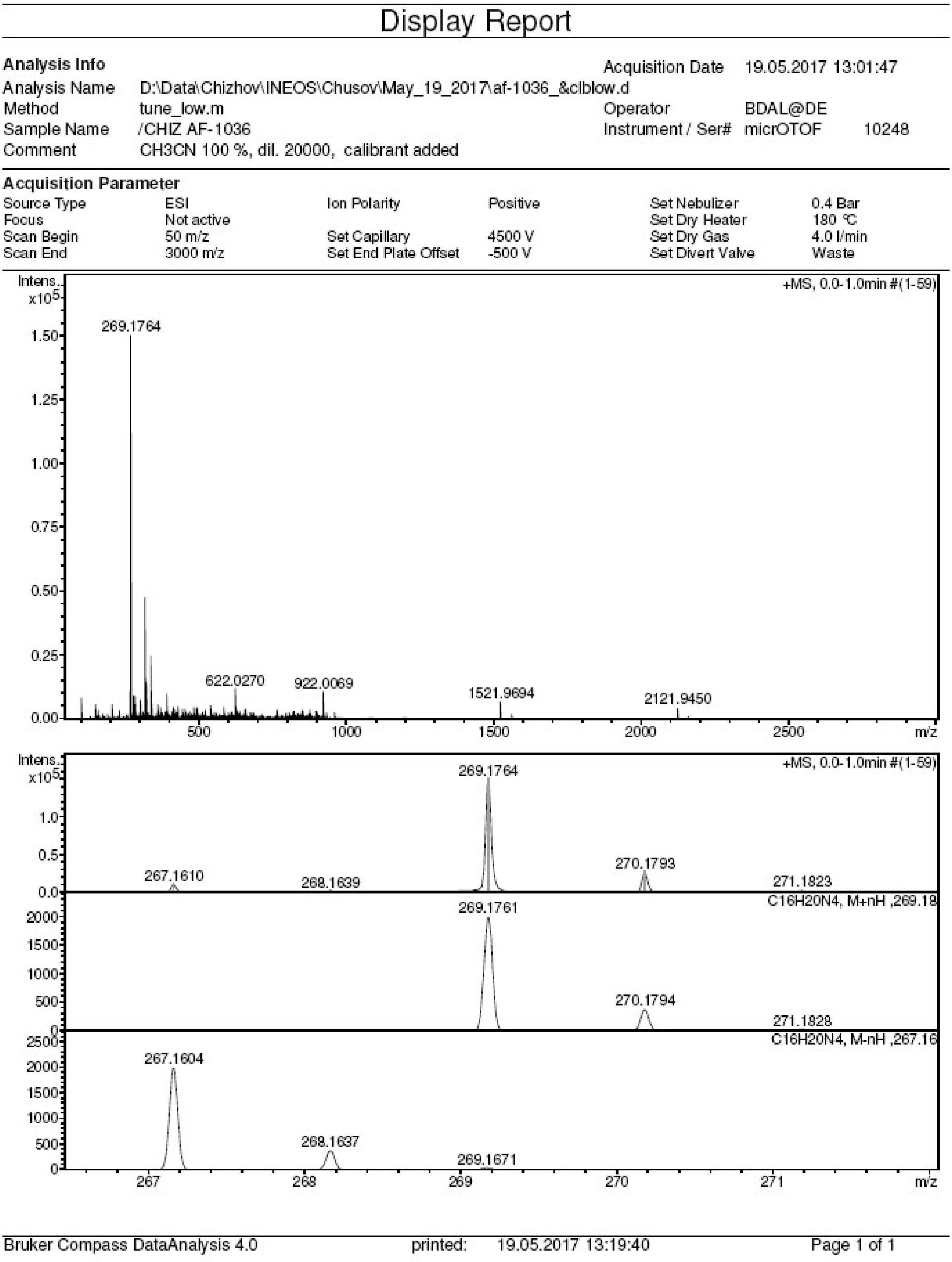
2-(4-(4-methylbenzyl)piperazin-1-yl)pyrimidine (1k) ^{1}H NMR, CDCl$_3$, 400 MHz



2-(4-(4-methylbenzyl)piperazin-1-yl)pyrimidine (1k) ^{13}C NMR, CDCl$_3$, 101 MHz



2-(4-(4-methylbenzyl)piperazin-1-yl)pyrimidine (1k), HRMS spectrum



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Comment	CH3CN 100 %, dil. 20000, calibrant added		

Acquisition Parameter

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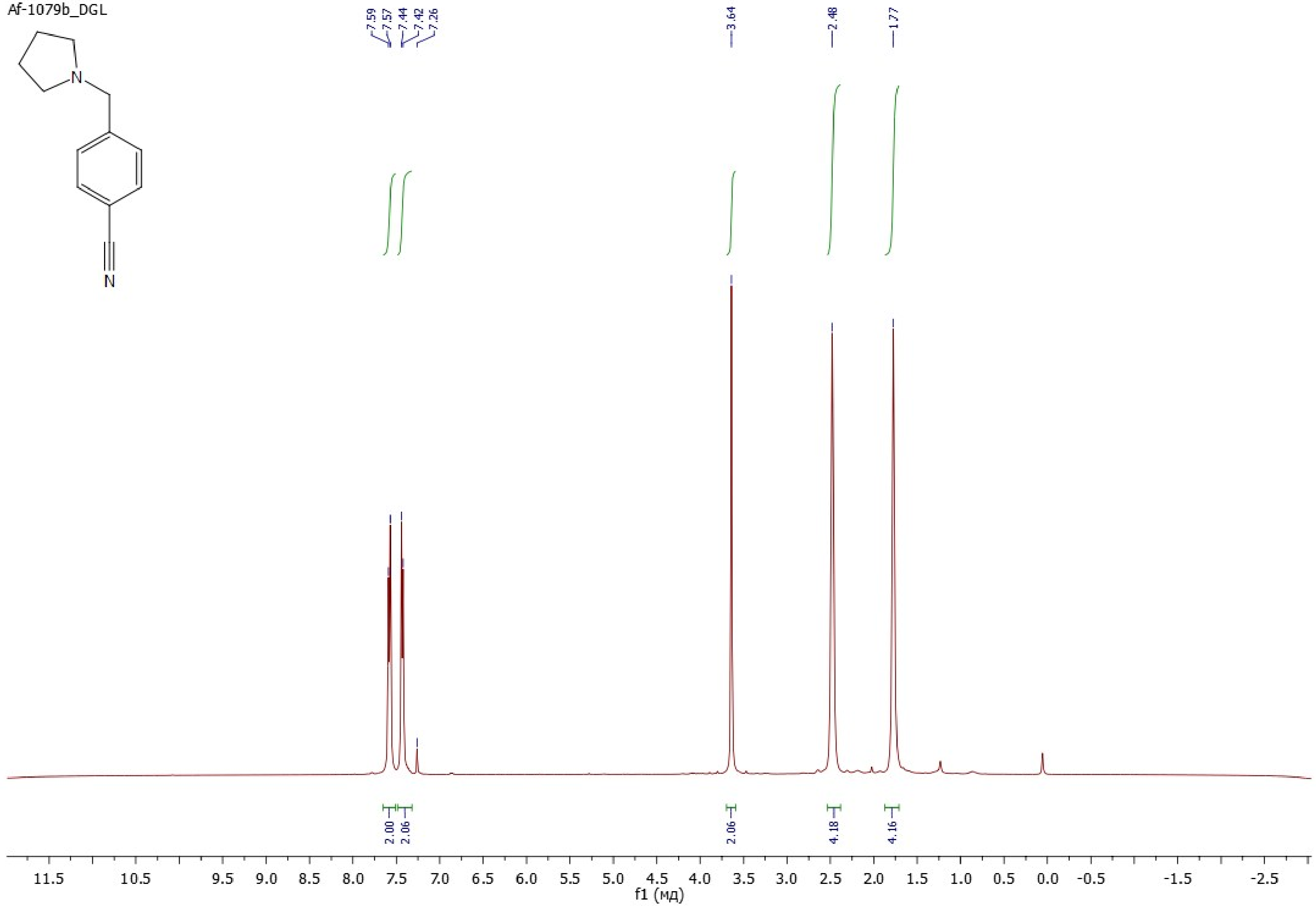
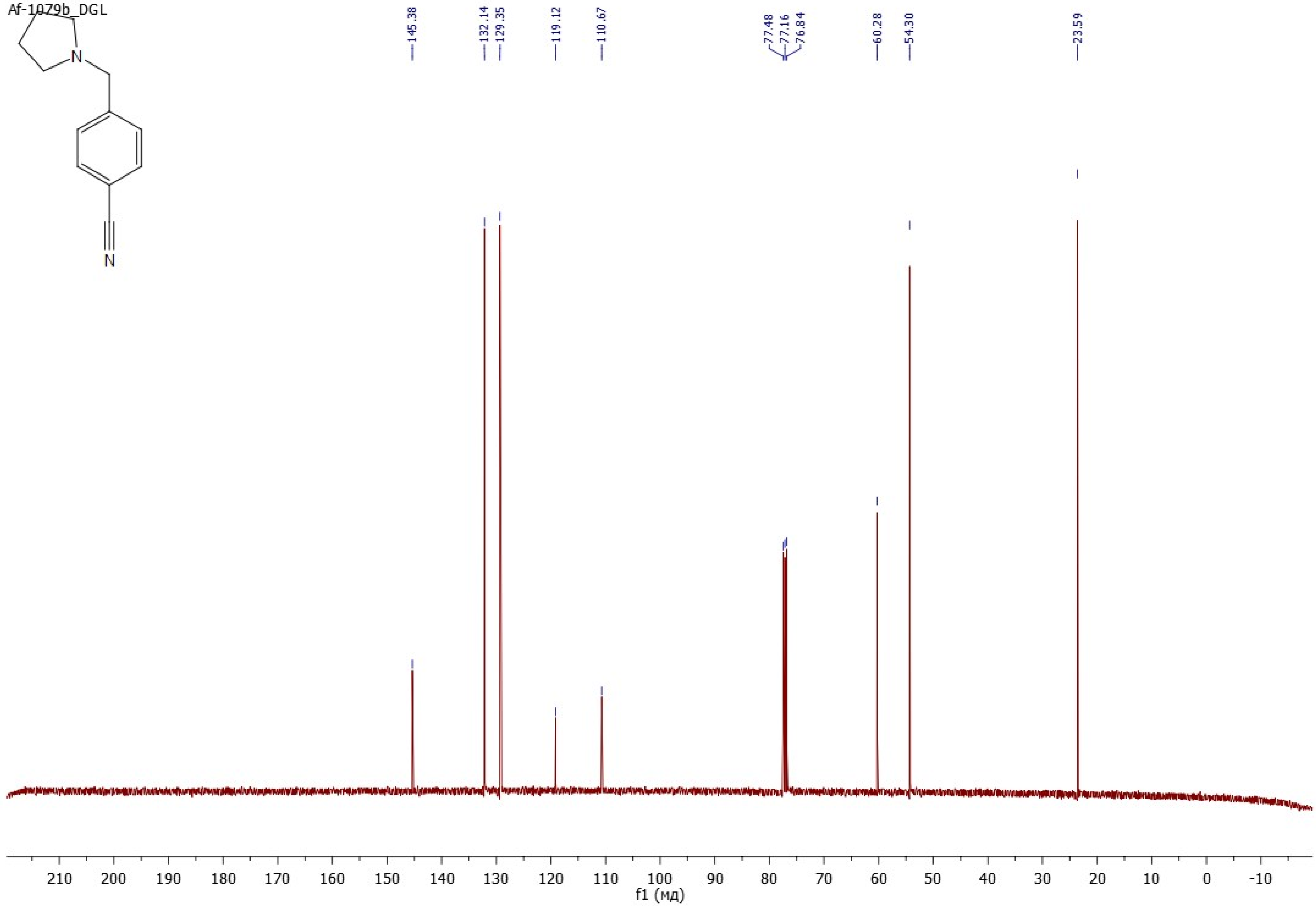
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Bruker Compass DataAnalysis 4.0 printed: 19.05.2017 13:19:40 Page 1 of 1

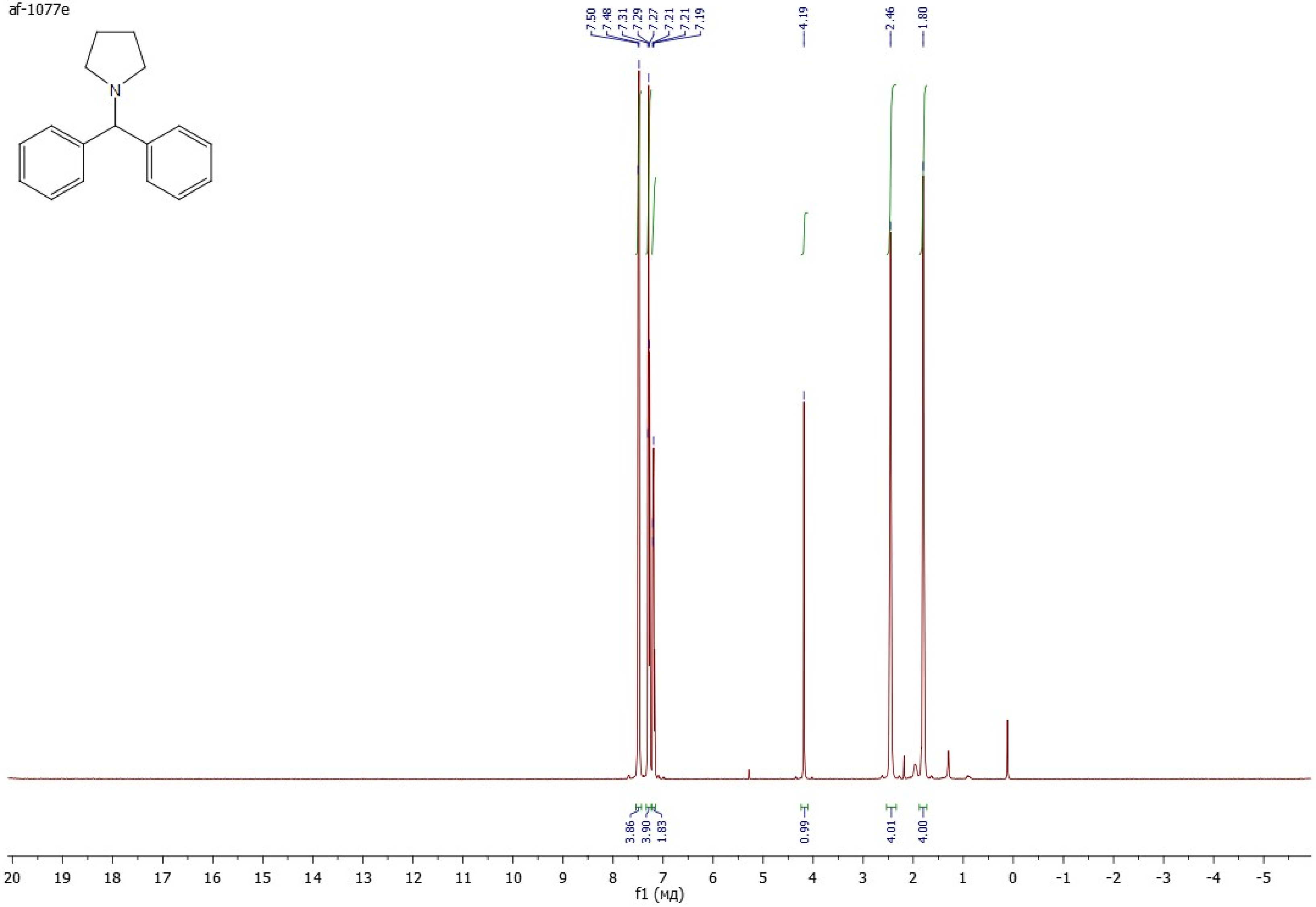
4-(pyrrolidin-1-ylmethyl)benzonitrile (1l) ^{1}H NMR, CDCl$_3$, 400 MHz



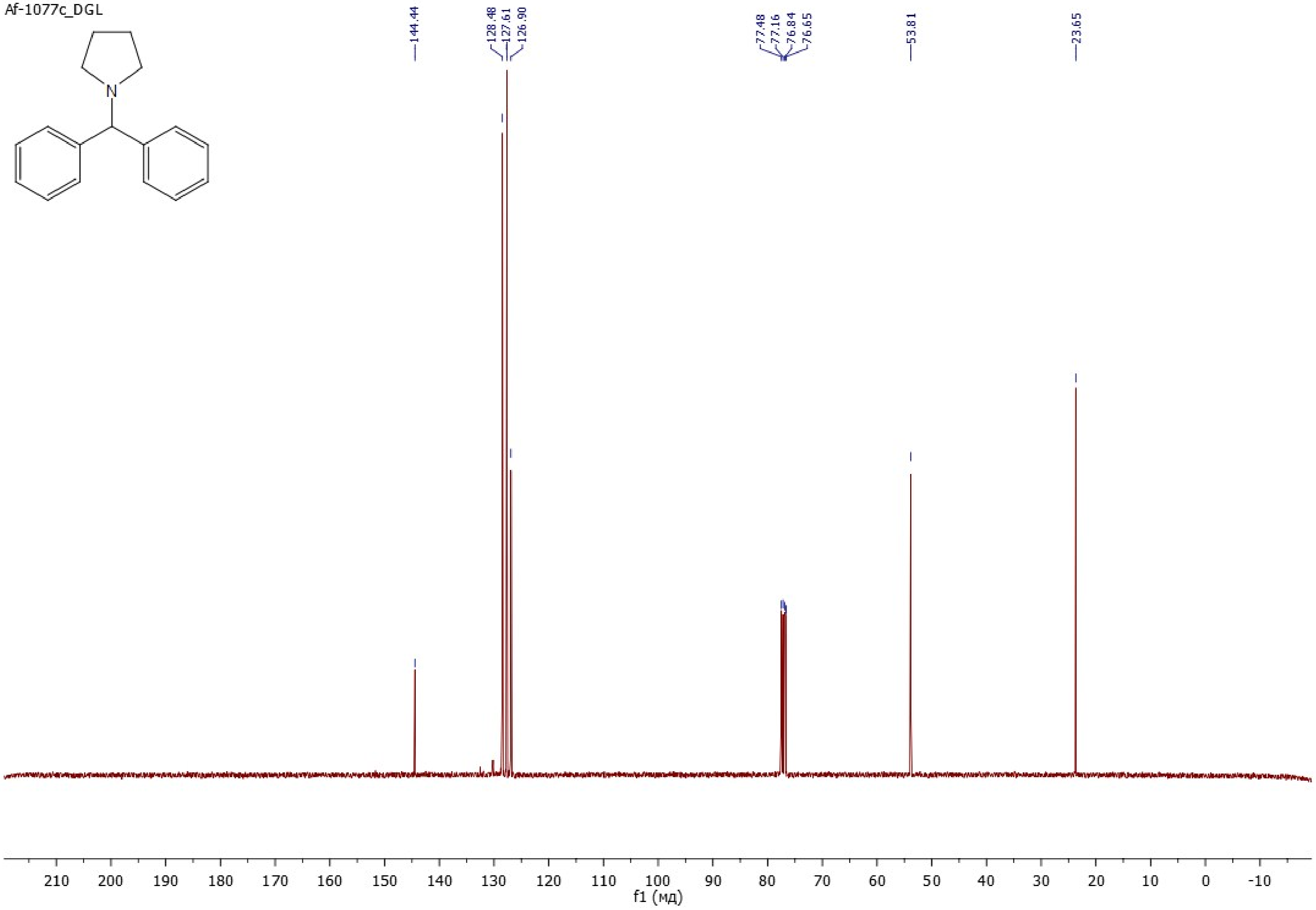
4-(pyrrolidin-1-ylmethyl)benzonitrile (1l) ^{13}C NMR, $CDCl_3$, 101 MHz



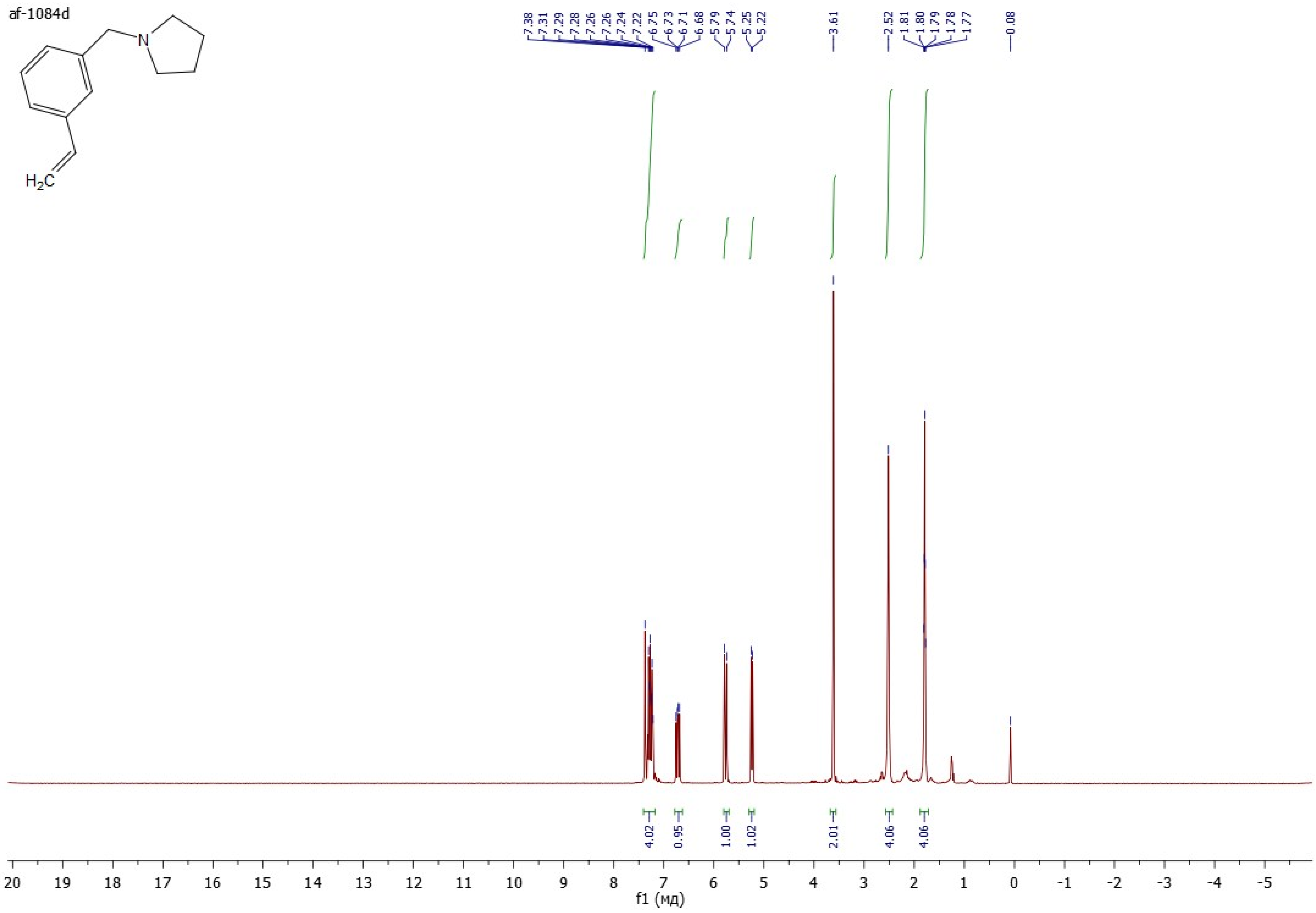
1-benzhydrylpyrrolidine (1m) ^{1}H NMR, $CDCl_3$, 400 MHz



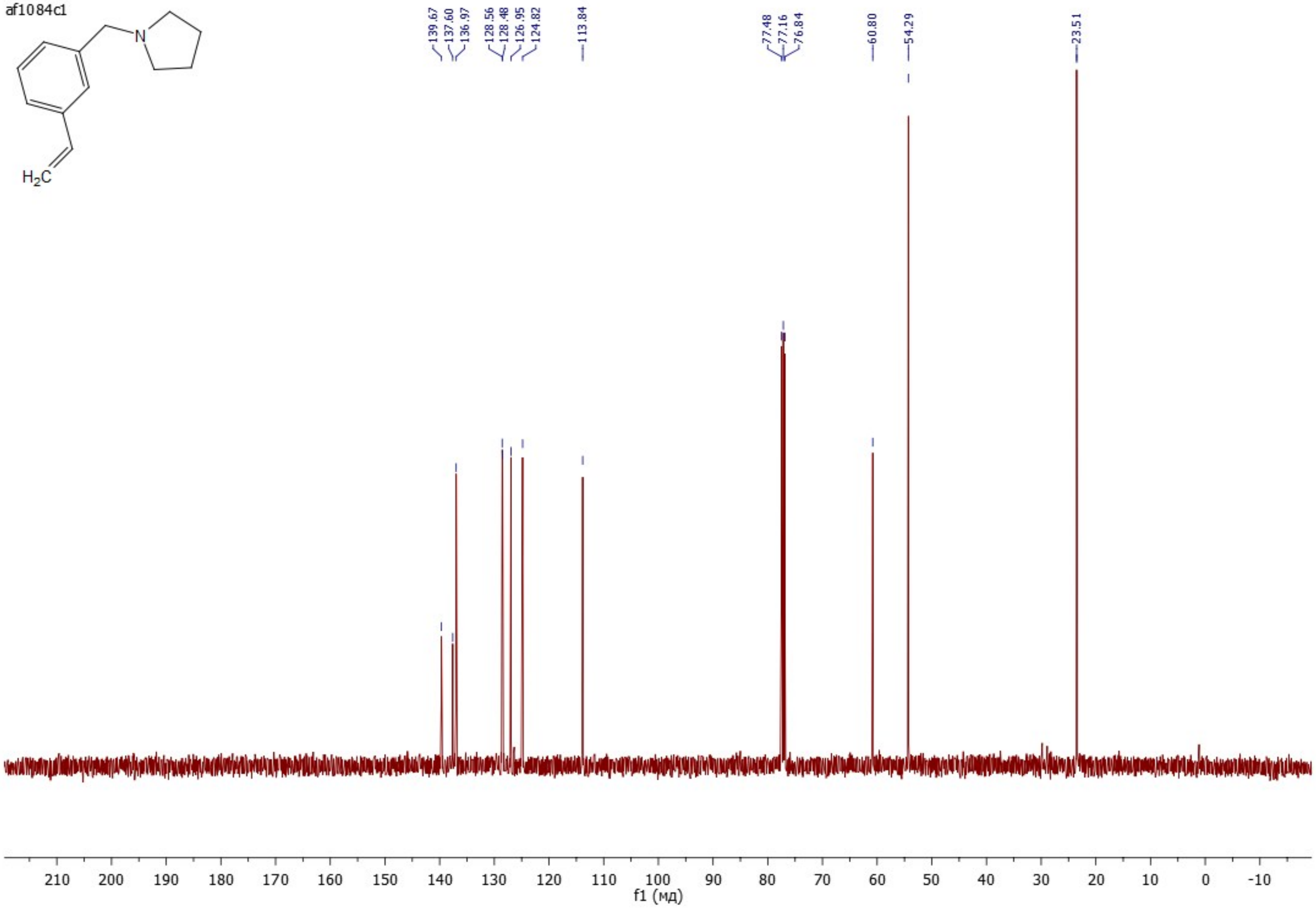
1-benzhydrylpyrrolidine (1m) ^{13}C NMR, CDCl$_3$, 101 MHz



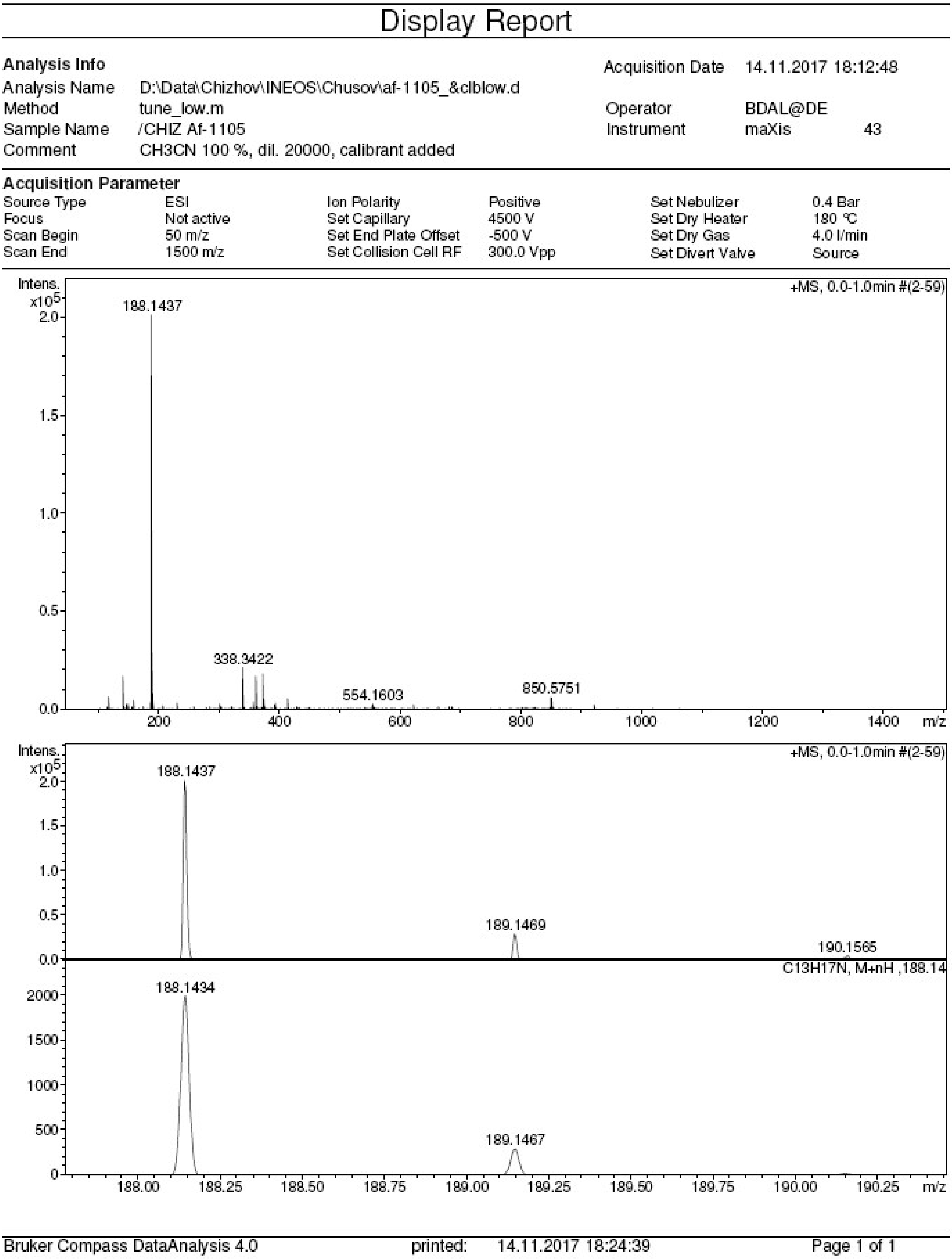
1-(3-vinylbenzyl)pyrrolidine (1n) ^{1}H NMR, CDCl$_3$, 400 MHz



1-(3-vinylbenzyl)pyrrolidine (1n) ^{13}C NMR, CDCl$_3$, 101 MHz



1-(3-vinylbenzyl)pyrrolidine (1n) HRMS spectrum



Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\INEOS\Chusov\af-1105_&clblow.d	Acquisition Date	14.11.2017 18:12:48
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ Af-1105	Instrument	maXis 43
Comment	CH3CN 100 %, dil. 20000, calibrant added		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source

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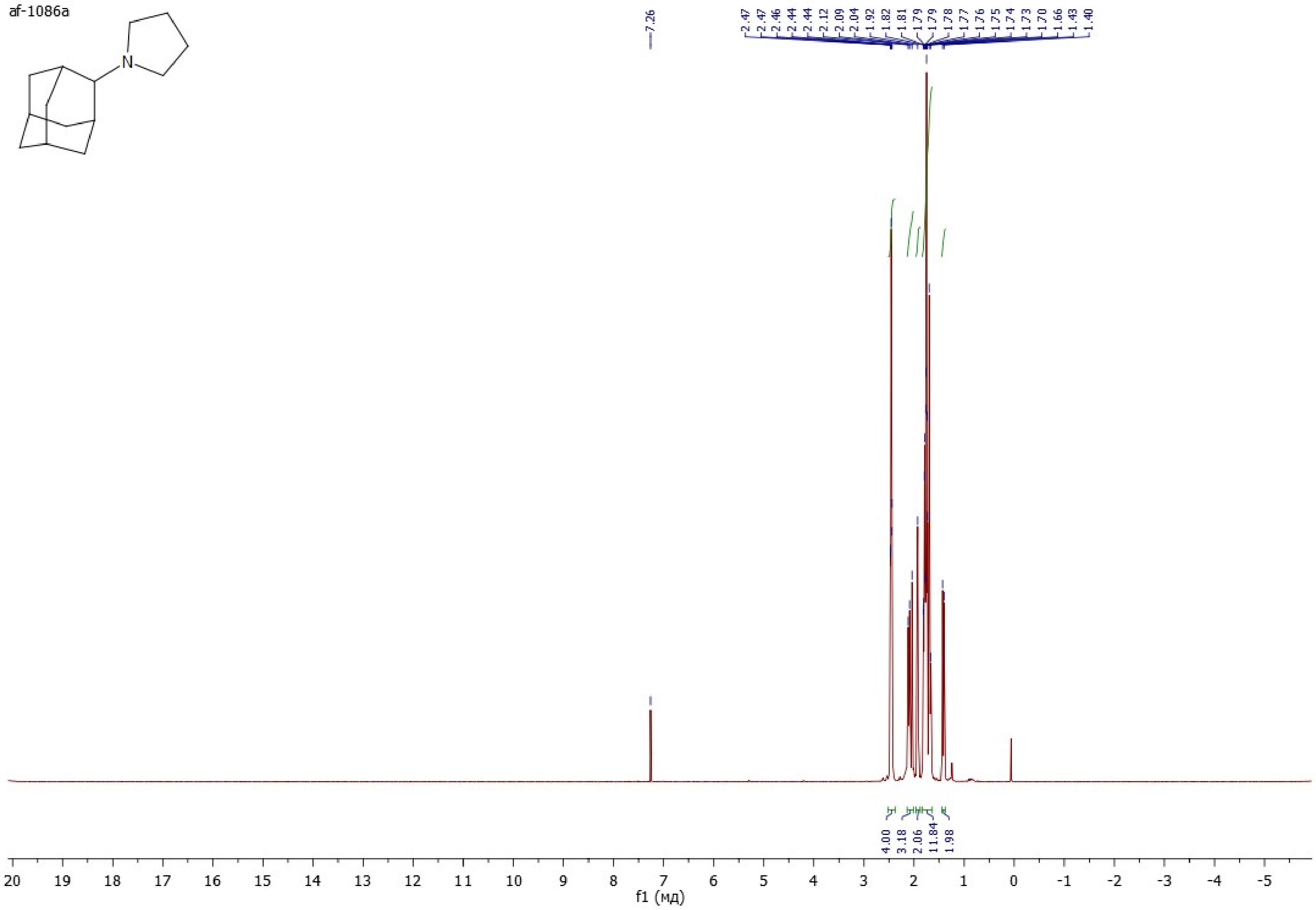
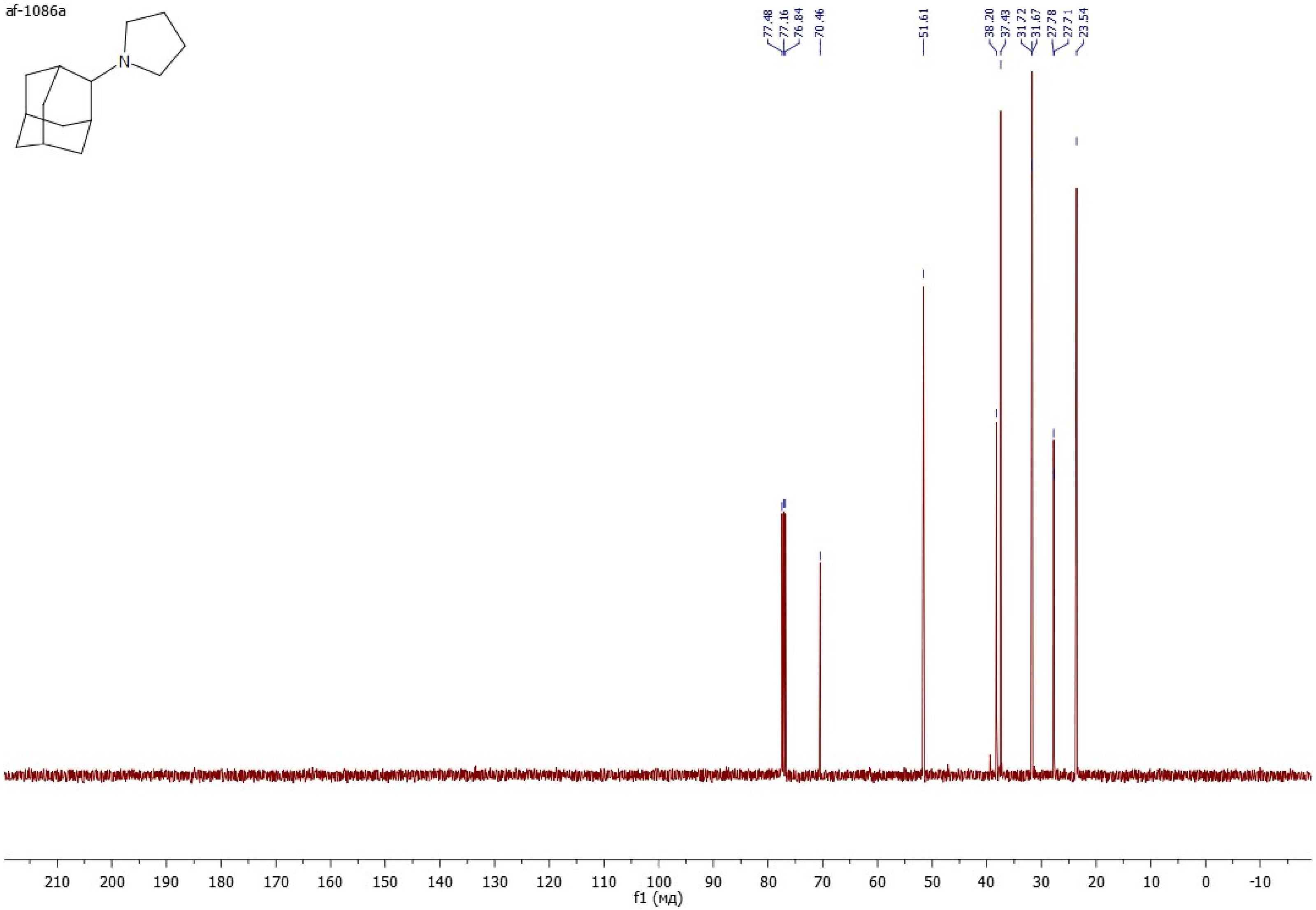
1-(adamantan-2-yl)pyrrolidine (1o) ^{1}H NMR, CDCl$_3$, 400 MHz



1-(adamantan-2-yl)pyrrolidine (1o) ^{13}C NMR, CDCl$_3$, 101 MHz



1-(adamantan-2-yl)pyrrolidine (1o) HRMS spectrum

Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\INEOS\Chusov\af-1086_&clblow.d	Acquisition Date	14.11.2017 18:06:41
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ Af-1086	Instrument	maXis 43
Comment	CH3CN 100 %, dil. 2000, calibrant added		

Acquisition Parameter

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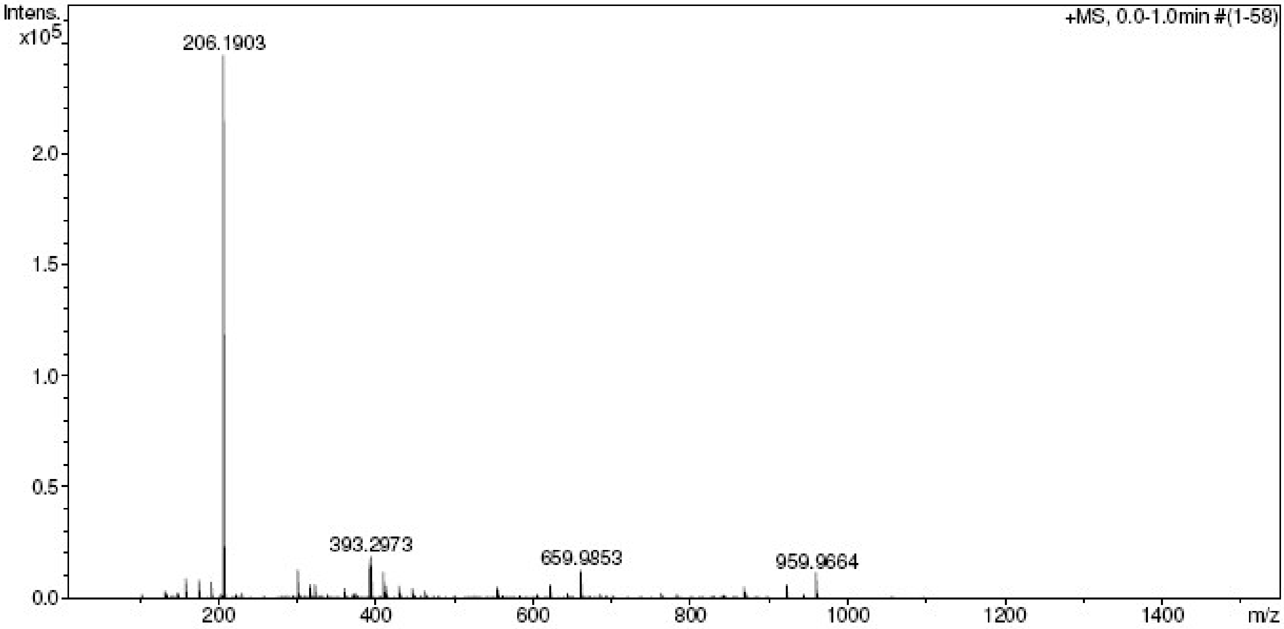
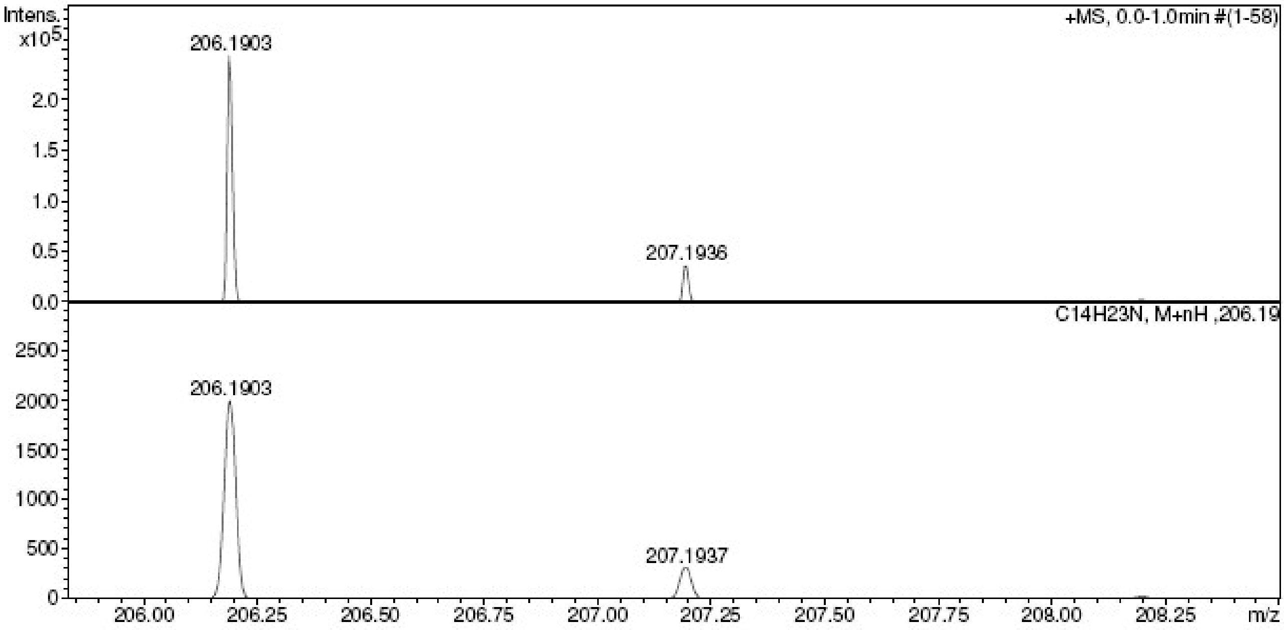
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	300.0 Vpp	Set Divert Valve	Source





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