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

Anthracene rhodium complexes with metal coordination at the central ring – a new class of catalysts for reductive amination.

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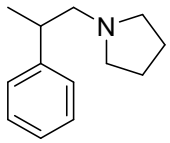
1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Rhodium complexes were synthesized according to published procedure[1,2]. For all reactions, distilled water was used. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Isolation of products was performed by column chromatography (Acros Organics, silica gel 0.06-0.200 mm) or preparative thin-layer chromatography (Macherey-Nagel, Silica gel 60 GF254, fluorescence quenching with UV light at 254 nm). The ^{1}H and ^{13}C NMR spectroscopic data were recorded with Bruker AV-300, AV-400 and Varian Inova400 spectrometers at ambient temperature. 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. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz).

2. Spectroscopic and analytical data

1-(2-phenylpropyl)pyrrolidine (12)



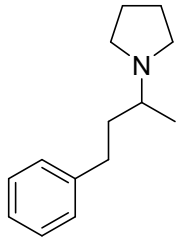
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.72 mg; 1.2 µmol; 1 mol%), tBuOH (113 µl), pyrrolidine (28.3 µl; 24.11 mg; 0.34 mmol; 309 mol%) and 2-phenylpropanal (14.9 µl; 14.93 mg; 0.11 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into a preheated to 60 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. >90% NMR yield. Purification: passed through a short layer of silica gel. Isolated as an yellow oil - 85% (17.6 mg)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.10 (m, 5H), 3.11 – 2.96 (m, 1H), 2.87 – 2.73 (m, 1H), 2.71 – 2.48 (m, 5H), 1.90 – 1.74 (m, 4H), 1.35 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 128.4, 127.2, 126.2, 64.6, 54.6, 39.6, 23.5, 20.4

The obtained NMR data are in agreement with the literature report[3]

1-(4-phenylbutan-2-yl)pyrrolidine (13)



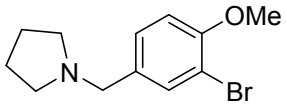
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.98 mg; 1.6 µmol; 1 mol%), tBuOH (163 µl), pyrrolidine (41 µl; 34.93 mg; 0.49 mmol; 307 mol%) and 4-phenylbutan-2-one (24.6 µl; 24.33 mg; 0.16 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into a preheated to 75°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 86% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate/triethylamine 1/1/0.02 (Rf = 0.45). Isolated as an yellow oil - 77% (25.7 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 5H), 2.85 – 2.56 (m, 6H), 2.49 – 2.40 (m, 1H), 2.05 – 1.93 (m, 1H), 1.90 – 1.68 (m, 5H), 1.21 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.5, 128.4, 125.8, 58.7, 51.1, 36.8, 32.2, 23.6, 17.5

The obtained NMR data are in agreement with the literature report[4]

1-(3-bromo-4-methoxybenzyl)pyrrolidine (14)



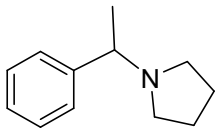
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.87 mg; 1.4 µmol; 1 mol%), tBuOH (140 µl), 3-bromo-4-methoxybenzaldehyde (29.9 mg; 0.14 mmol; 100 mol%) and pyrrolidine (35 µl; 29.82 mg; 0.42 mmol; 300 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 75°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. >90% NMR yield. Purification: flash column chromatography, using eluent hexane/ethyl acetate 1/1 (Rf = 0.6). Isolated as an yellow oil - 75% (28.3 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.22 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 3.87 (s, 3H), 3.52 (s, 2H), 2.58 – 2.39 (m, 4H), 1.93 – 1.63 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 133.8, 133.2, 129.0, 111.7, 111.4, 59.6, 56.4, 54.1, 23.5

HRMS (TOF ESI+): found m/z 270.0477 (M + H^+), calculated for $(C_{12}H_{17}BrNO)^+$ 270.0488 (M + H^+).

1-(1-phenylethyl)pyrrolidine (15)



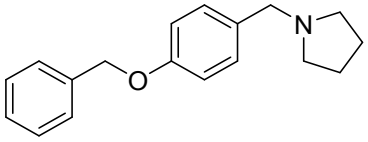
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.63 mg; 2.6 µmol; 1 mol%), tBuOH (262 µl), pyrrolidine (65.5 µl; 55.8 mg; 0.79 mmol; 303 mol%) and acetophenone (30.6 µl; 31.52 mg; 0.26 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 90°C oil bath. After 28 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 87% NMR yield. Purification: flash column chromatography using eluent hexane/ethyl acetate 1/1. Isolated as an transparent oil - 76% (35.1 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 5H), 3.18 (q, J = 6.6 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.44 – 2.31 (m, 2H), 1.82 – 1.69 (m, 4H), 1.41 (d, J = 6.6 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 128.4, 127.3, 126.9, 66.2, 53.1, 23.5, 23.3

The obtained NMR data are in agreement with the literature report[5]

1-(4-(benzyloxy)benzyl)pyrrolidine (16)



Method A: A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.88 mg; 1.4 µmol; 1 mol%), tBuOH (141 µl), 4-(benzyloxy)benzaldehyde (30 mg; 0.14 mmol; 100 mol%) and pyrrolidine (35.4 µl; 30.16 mg; 0.42 mmol; 300 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 74% NMR. Purification: column chromatography, eluent hexane/ethyl acetate/triethylamine 1/1/0.015 (Rf = 0.19). Isolated as an orange oil - 73% (27.6 mg)

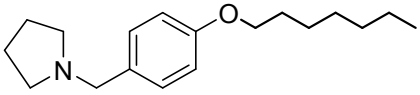
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.35 (m, 5H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.08 (s, 2H), 3.60 (s, 2H), 2.62 – 2.47 (m, 4H), 1.88 – 1.75 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 137.2, 131.7, 130.2, 128.7, 128.0, 127.6, 114.6, 70.1, 60.1, 54.1, 23.5

The obtained NMR data are in agreement with the literature report[6]

Method B: A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.88 mg; 1.4 µmol; 1 mol%), tBuOH (141 µl), 4-(benzyloxy)benzaldehyde (30 mg; 0.14 mmol; 100 mol%) and pyrrolidine (35.4 µl; 30.16 mg; 0.42 mmol; 300 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 90 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 84% NMR yield with 1,4-dinitrobenzene as an internal standard.

1-(4-(heptyloxy)benzyl)pyrrolidine (17)



A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.85 mg; 1.4 µmol; 1 mol%), tBuOH (135 µl), pyrrolidine (33.8 µl; 28.79 mg; 0.40 mmol; 307 mol%) and 4-

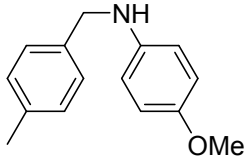
(heptyloxy)benzaldehyde (30 µl; 29.9 mg; 0.13 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 75°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. >90% NMR yield. Purification: preparative thin-layer chromatography, eluent hexane/ethyl acetate/triethylamine 1.5/1/0.1 (Rf = 0.67). Isolated as an yellow oil - 65% (23.6 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 3.59 (s, 2H), 2.61 – 2.47 (m, 4H), 1.89 – 1.69 (m, 6H), 1.51 – 1.39 (m, 2H), 1.38 – 1.23 (m, 6H), 0.94 – 0.84 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 130.6, 130.3, 114.3, 68.1, 60.0, 54.0, 31.9, 29.4, 29.2, 26.1, 23.5, 22.7, 14.2

HRMS (TOF ESI+): found m/z 276.2323 ($M + H^+$), calculated for $(C_{18}H_{30}NO)^+$ 276.2322 ($M + H^+$)

4-methoxy-N-(4-methylbenzyl)aniline (18)



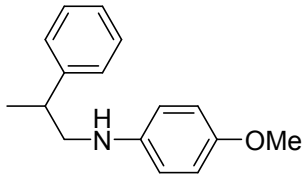
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.81 mg; 1.3 µmol; 0.5 mol%), tBuOH (254 µl), 4-methoxyaniline (31.3 mg; 0.25 mmol; 100 mol%) and 4-methylbenzaldehyde (30 µl; 30.57 mg; 0.25 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into a preheated to 90°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 88% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 20/1 (Rf = 0.18). Isolated as an yellow oil (solidifies after some time) - 82% (47.3 mg)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 4.33 (s, 2H), 3.83 (s, 3H), 2.45 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 142.6, 136.9, 136.7, 129.3, 127.6, 115.0, 114.2, 55.9, 49.0, 21.2

The obtained NMR data are in agreement with the literature report[7]

4-methoxy-N-(2-phenylpropyl)aniline (19)



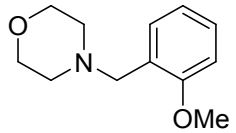
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.39 mg; 2.2 µmol; 1 mol%), tBuOH (224 µl), 4-methoxyaniline (55.3 mg; 0.45 mmol; 204 mol%) and 2-phenylpropanal (30 µl; 30 mg; 0.22 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 90°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 85% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 20/1 (Rf = 0.2). Isolated as an yellow oil - 82% (44.1 mg)

1H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, J = 7.4 Hz, 2H), 7.32 – 7.24 (m, 3H), 6.81 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H), 3.34 (dd, J = 12.1, 6.1 Hz, 1H), 3.23 (dd, J = 12.1, 8.3 Hz, 1H), 3.09 (sext, J = 7.0 Hz, 1H), 1.37 (d, J = 6.9 Hz, 3H)

13C NMR (101 MHz, $CDCl_3$) δ 152.2, 144.7, 142.4, 128.8, 127.4, 126.7, 115.0, 114.5, 55.9, 52.1, 39.3, 19.9

The obtained NMR data are in agreement with the literature report[8]

4-(2-methoxybenzyl)morpholine (20)



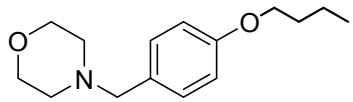
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.50 mg; 2.4 µmol; 0.9 mol%), tBuOH (289 µl), 2-methoxybenzaldehyde (35.4 mg; 0.26 mmol; 100 mol%) and morpholine (72 µl; 71.71 mg; 0.82 mmol; 315 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 90% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate/triethylamine 1/1/0.01 (Rf = 0.38). Isolated as a pale-yellow oil- 70% (37.8 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.7 Hz, 1H), 7.32 – 7.20 (m, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 3.81 – 3.71 (m, 4H), 3.61 (s, 2H), 2.63 – 2.49 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 130.8, 128.4, 125.4, 120.4, 110.6, 67.0, 56.4, 55.5, 53.6

The obtained NMR data are in agreement with the literature report[9]

4-(4-butoxybenzyl)morpholine (21)



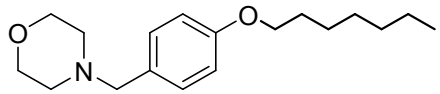
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.17 mg; 1.9 µmol; 0.9 mol%), tBuOH (225 µl), morpholine (56 µl; 55.77 mg; 0.64 mmol; 320 mol%) and 4-bythoxybenzaldehyde (34 µl; 35.0 mg; 0.20 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 80% NMR yield. Purification: preparative thin-layer chromatography, eluent hexane/ethyl acetate/triethylamine 1/1/0.01 (Rf = 0.34). Isolated as a pale-yellow oil - 67% (32.7 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 3.77 – 3.64 (m, 4H), 3.43 (s, 2H), 2.52 – 2.34 (m, 4H), 1.82 – 1.70 (m, 2H), 1.58 – 1.42 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 130.5, 129.6, 114.3, 67.7, 67.1, 63.0, 53.6, 31.5, 19.4, 14.0

HRMS (TOF ESI+): found m/z 250.1801 ($M + H^+$), calculated for $(C_{15}H_{24}NO_2)^+$ 250.1802 ($M + H^+$)

4-(4-(heptyloxy)benzyl)morpholine (22)



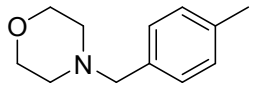
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.24 mg; 2.0 µmol; 0.9 mol%), tBuOH (262 µl), morpholine (59 µl; 58.76 mg; 0.67 mmol; 304 mol%) and 4-heptyloxybenzaldehyde (48.3 µl; 47.8 mg; 0.22 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 90% NMR yield. Purification: flash chromatography, eluent hexane/ethyl acetate/triethylamine 1.2/1/0.01 (Rf = 0.31). Isolated as a pale-yellow oil - 88% (55.66 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.75 – 3.66 (m, 4H), 3.44 (s, 2H), 2.54 – 2.33 (m, 2H), 1.86 – 1.68 (m, 2H), 1.53 – 1.21 (m, 8H), 0.89 (t, *J* = 6.2 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 130.4, 129.2, 114.2, 68.0, 67.0, 62.8, 53.5, 31.8, 29.3, 29.1, 26.0, 22.6, 14.1

HRMS (TOF ESI+): found m/z 292.2273 (M + H^+), calculated for $(C_{18}H_{30}NO_2)^+$ 292.2271 (M + H^+)

4-(4-methylbenzyl)morpholine (23)



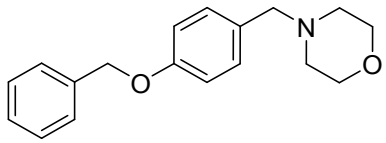
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.40 mg; 2.2 µmol; 1 mol%), tBuOH (230 µl), morpholine (58.2 µl; 57.97 mg; 0.67 mmol; 304 mol%) and 4-methylbenzaldehyde (26.5 µl; 27 mg; 0.22 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 74% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 3/1 (Rf = 0.21). Isolated as a colorless oil - 56% (24.1 mg)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 3.77 – 3.65 (m, 4H), 3.46 (s, 2H), 2.49 – 2.38 (m, 4H), 2.34 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 134.7, 129.3, 129.1, 67.1, 63.3, 53.7, 21.2

The obtained NMR data are in agreement with the literature report[10]

4-(4-(benzyloxy)benzyl)morpholine (24)



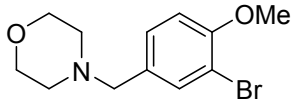
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (2.14 mg; 3.4 µmol; 1 mol%), tBuOH (329 µl), 4-(benzyloxy)benzaldehyde (70 mg; 0.33 mmol; 100 mol%) and morpholine (86 µl; 85.7 mg; 0.98 mmol; 297 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 90°C oil bath. After 48 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 92% NMR yield. Purification: passed through a layer of silica gel. Isolated as a pale-yellow solid - 90% (83.8 mg), m.p. 45-46˚C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.32 (m, 5H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.09 (s, 2H), 3.80 – 3.71 (m, 4H), 3.49 (s, 2H), 2.58 – 2.40 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 137.1, 130.6, 129.8, 128.7, 128.1, 127.6, 114.7, 70.1, 67.0, 62.9, 53.6

The obtained NMR data are in agreement with the literature report[10]

4-(3-bromo-4-methoxybenzyl)morpholine (25)



Method A: A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.80 mg; 1.3 µmol; 1 mol%), tBuOH (130 µl), 3-bromo-4-methoxybenzaldehyde (28 mg; 0.13 mmol; 100 mol%) and morpholine (33.3 µl; 33.2 mg; 0.38 mmol; 292 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 94% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate/triethylamine 1/1/0.015 (Rf = 0.28). Isolated as an light yellow oil that solidifies after some time - 90% (33.6 mg)

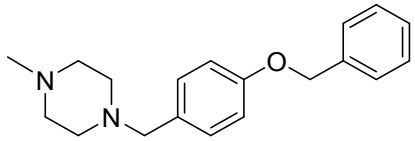
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.20 (d, J = 8.3 Hz, 1H), 6.83 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H), 3.72 – 3.65 (m, 4H), 3.40 (s, 2H), 2.48 – 2.32 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 134.0, 131.6, 129.3, 111.7, 111.5, 67.1, 62.3, 56.4, 53.6

The obtained NMR data are in agreement with the literature report[10]

Method B: A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.85 mg; 1.38 µmol; 1 mol%), tBuOH (137 µl), 3-bromo-4-methoxybenzaldehyde (29 mg; 0.135 mmol; 100 mol%) and morpholine (35.5 µl; 35.4 mg; 0.41 mmol; 304 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 75 °C oil bath. After 21 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 60% NMR yield.

1-(4-(benzyloxy)benzyl)-4-methylpiperazine (26)



A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (0.88 mg; 1.4 µmol; 1 mol%), tBuOH (141 µl), 4-(benzyloxy)benzaldehyde (30 mg; 0.14 mmol; 100 mol%) and 1-methylpiperazine (47 µl; 42.44 mg; 0.42 mmol; 300 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with

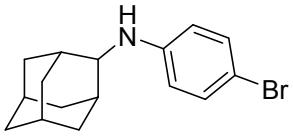
dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 86% NMR yield. Purification: column chromatography, eluent methanol/ethyl acetate/triethylamine 0.1/1/0.01 (Rf = 0.29). Isolated as an yellow oil - 63% (26.5 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 5H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.05 (s, 2H), 3.45 (s, 2H), 2.71 – 2.35 (m, 8H), 2.28 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 137.2, 130.6, 130.5, 128.7, 128.0, 127.6, 114.6, 70.1, 62.5, 55.2, 53.1, 46.1

HRMS (TOF ESI+): found m/z 297.1964 ($M + H^+$), calculated for $(C_{19}H_{25}N_2O)^+$ 297.1961 ($M + H^+$)

N-(4-bromophenyl)adamantan-2-amine (27)



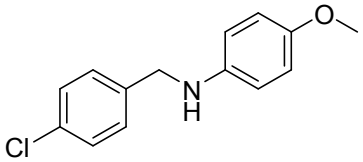
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.60 mg; 2.5 μmol; 2 mol%), tBuOH (165 μl), 2-adamantanone (38.4 mg; 0.25 mmol; 200 mol%) and 4-bromoaniline (22 mg; 0.13 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 120°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 77% NMR yield. Purification: column chromatography, eluent toluene/ethyl acetate 20/1 (Rf = 0.95). Isolated as a slightly beige solid-70% (27.6 mg), m.p. 109˚C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.7 Hz, 2H), 6.47 (d, *J* = 8.7 Hz, 1H), 4.00 (s, 1H), 3.49 (s, 1H), 2.00 (s, 2H), 1.95 – 1.71 (m, 10H), 1.60 (d, *J* = 12.6 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 132.0, 114.7, 108.1, 56.9, 37.8, 37.4, 31.7, 31.5, 27.5, 27.4

The obtained NMR data are in agreement with the literature report[7]

N-(4-chlorobenzyl)-4-methoxyaniline (28)



A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.33 mg; 2.1 μmol; 1 mol%), tBuOH (220 μl), 4-methoxyaniline (53.20 mg; 0.43 mmol; 205 mol%) and 4-chlorobenzaldehyde (30 mg; 0.21 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to

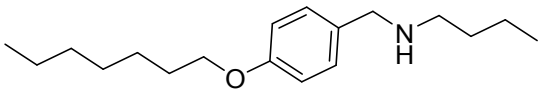
100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. >95% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 20/1 (Rf = 0.16). Isolated as an yellow oil - 95% (50.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 4.27 (s, 2H), 3.75 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 142.2, 138.4, 132.8, 128.8, 128.8, 115.0, 114.2, 55.8, 48.6

The obtained NMR data are in agreement with the literature report[11]

N-(4-(heptyloxy)benzyl)butan-1-amine (29)



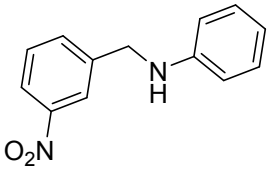
A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (6.7 mg; 10.57 µmol; 1.2 mol%), tBuOH (1220 µl), butylamine (173.6 µl; 128.46 mg; 1.76 mmol; 202 mol%) and 4-heptyloxybenzaldehyde (193 µl; 192.2 mg; 0.87 mmol; 100 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 130°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 78% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 2/1 (Rf = 0.26). Isolated as an yellow oil - 60% (146 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.93 (t, *J* = 6.6 Hz, 2H), 3.71 (s, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.54 – 1.40 (m, 4H), 1.40 – 1.24 (m, 9H), 0.95 – 0.83 (m, 6H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 132.6, 129.3, 114.4, 68.1, 53.6, 49.2, 32.3, 31.9, 29.4, 29.2, 26.1, 22.7, 20.6, 14.2, 14.1

HRMS (TOF ESI+): found m/z 278.2484 (M + H^+), calculated for $(C_{18}H_{32}NO)^+$ 278.2478 (M + H^+)

N-(3-nitrobenzyl)aniline (30)



A glass vial in a 10 mL stainless steel autoclave was charged with the catalyst **9** (1.25 mg; 2.0 μmol; 1.0 mol%), THF (200 μl), 3-nitrobenzaldehyde (30 mg; 0.20 mmol; 100 mol%) and aniline (27.2 μl; 28 mg; 0.30 mmol; 150 mol%). The autoclave was sealed, flushed 2 times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into a preheated to 100°C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were passed through a short layer of silica gel, combined and then concentrated on a rotary evaporator, solvent was removed under reduced pressure and the residue was analyzed by NMR. 32% NMR yield of product and 57% of the corresponding Schiff base.

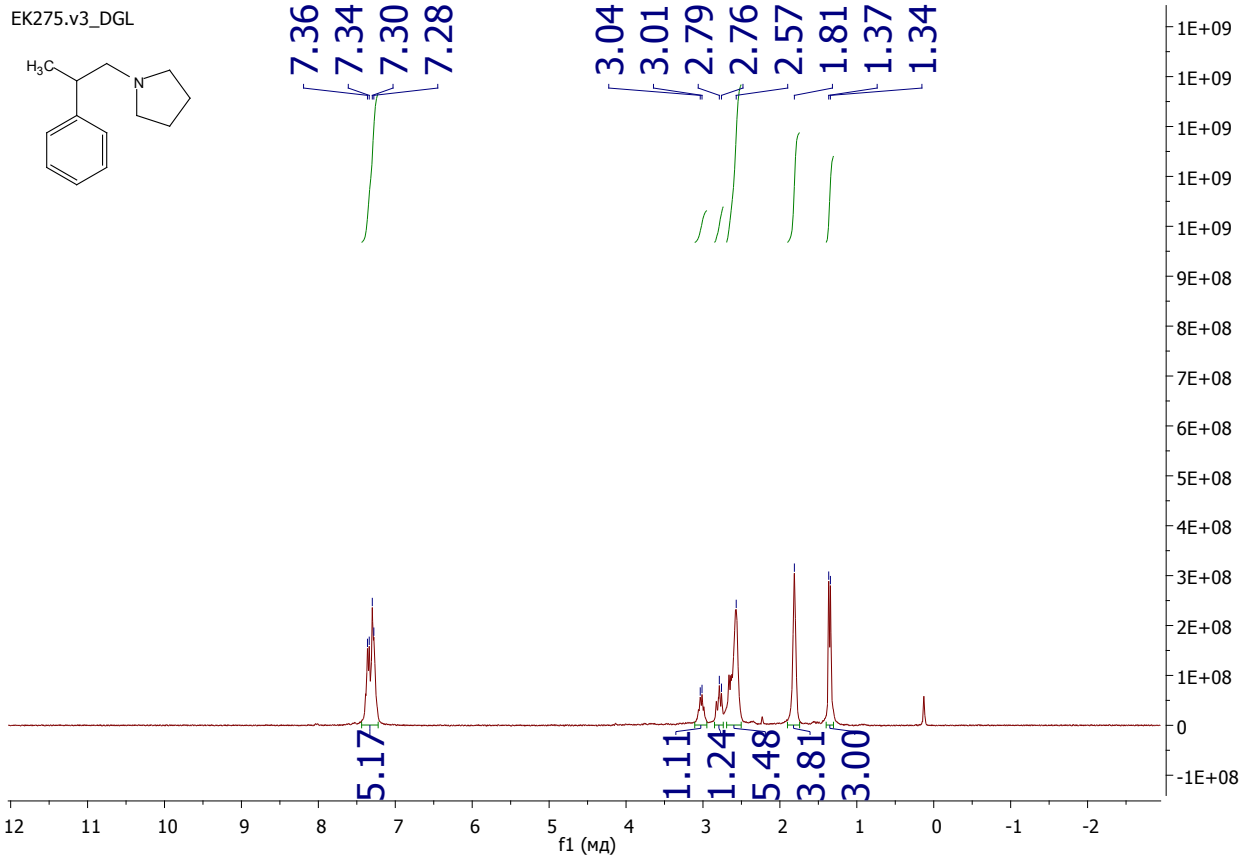
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.18 (t, J = 7.9 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 4.47 (d, J = 4.5 Hz, 2H), 4.25 (br s, 1H)

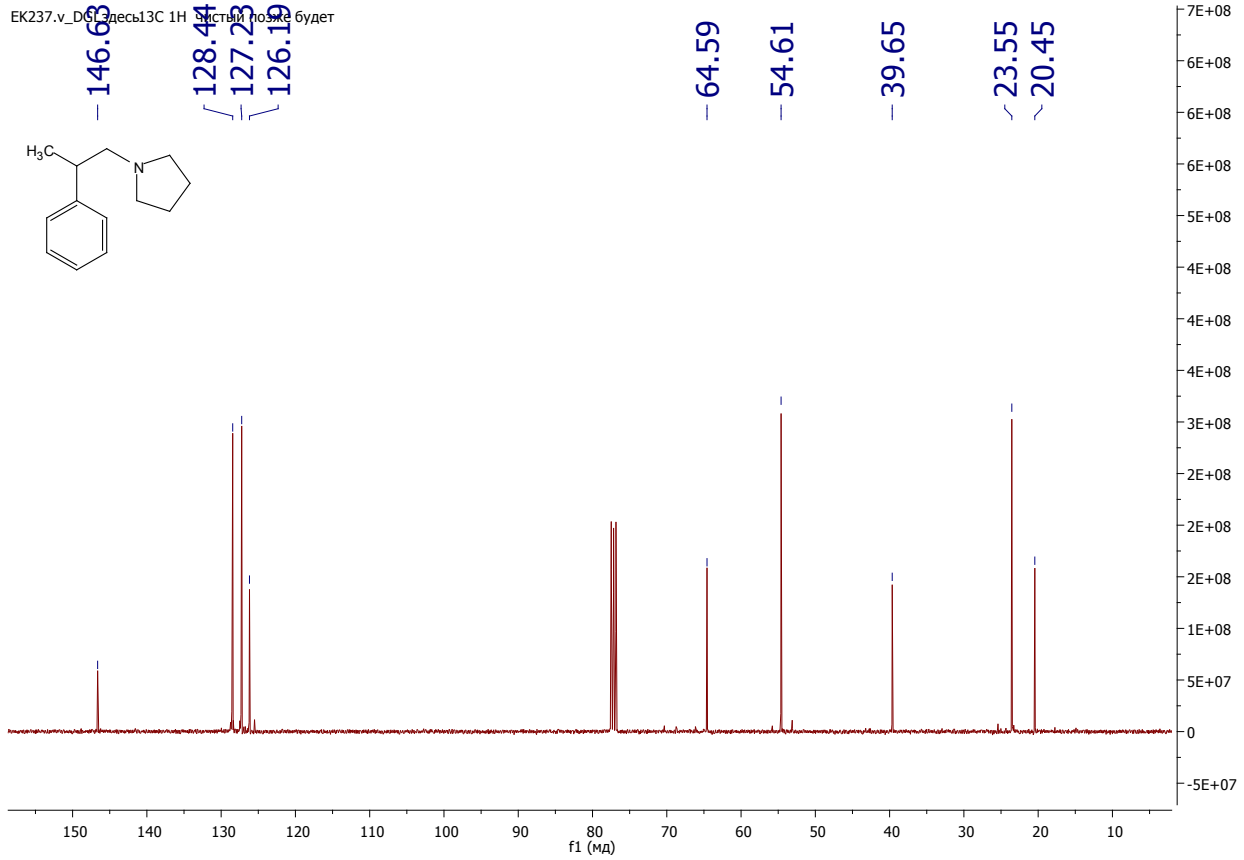
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 147.4, 142.1, 133.3, 129.7, 129.5, 122.4, 122.2, 118.3, 113.1, 47.6

The obtained NMR data are in agreement with the literature report[11]

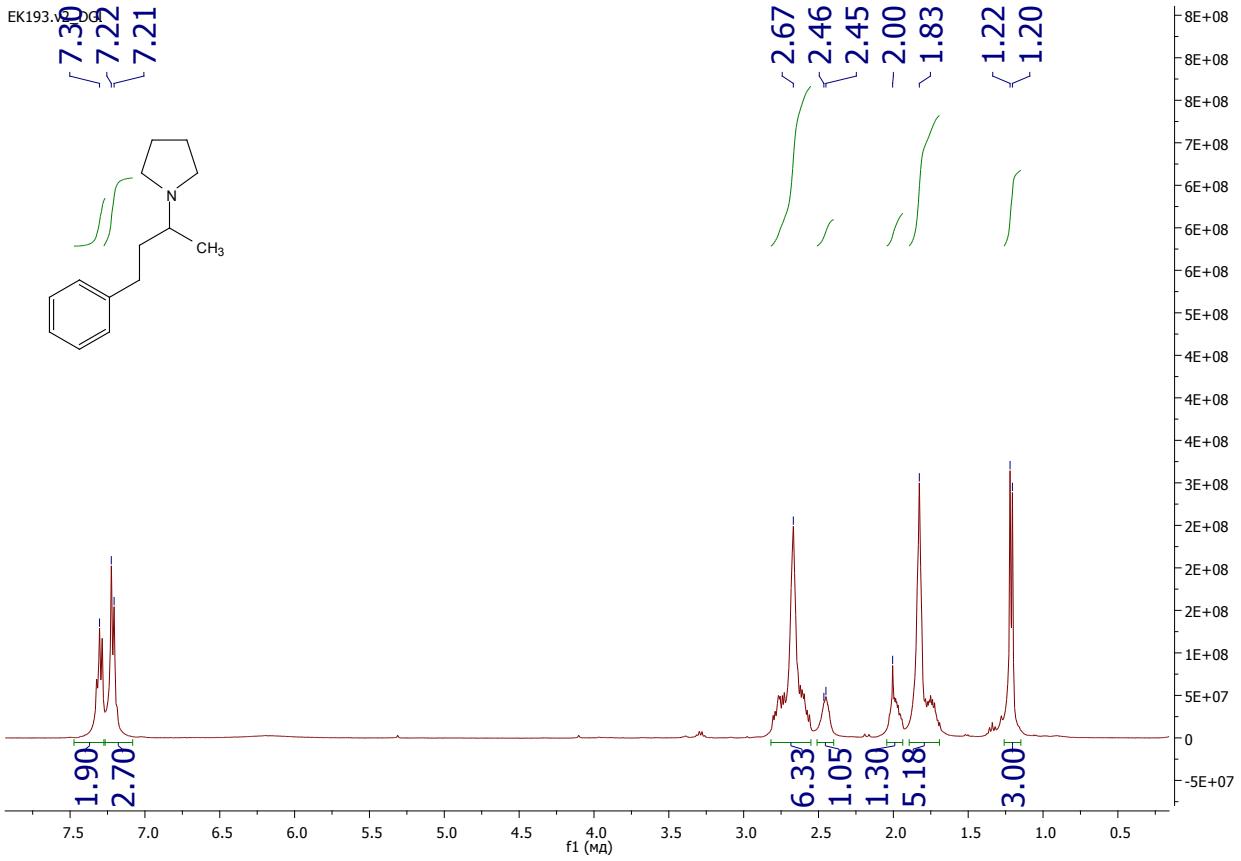
3. 1H and 13C NMR spectra of obtained compounds

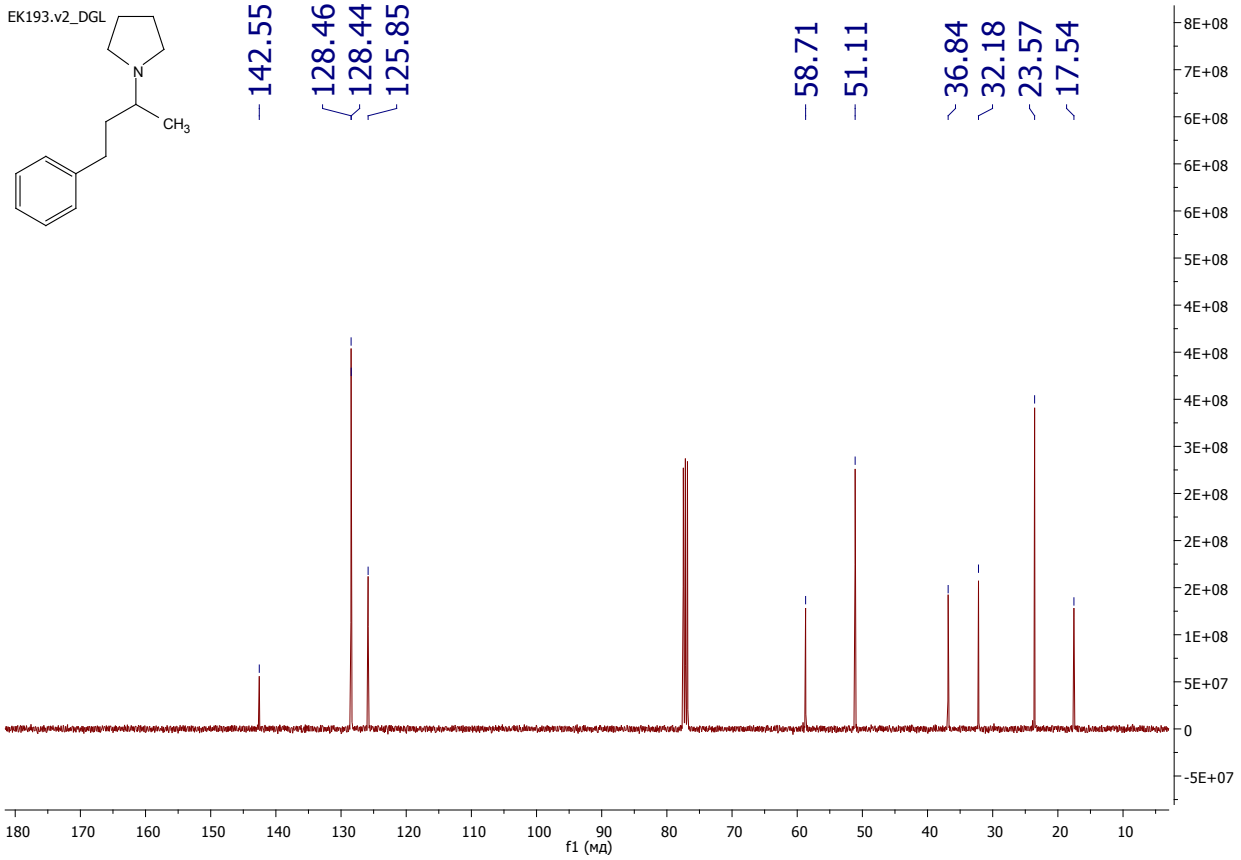
1-(2-phenylpropyl)pyrrolidine (12)



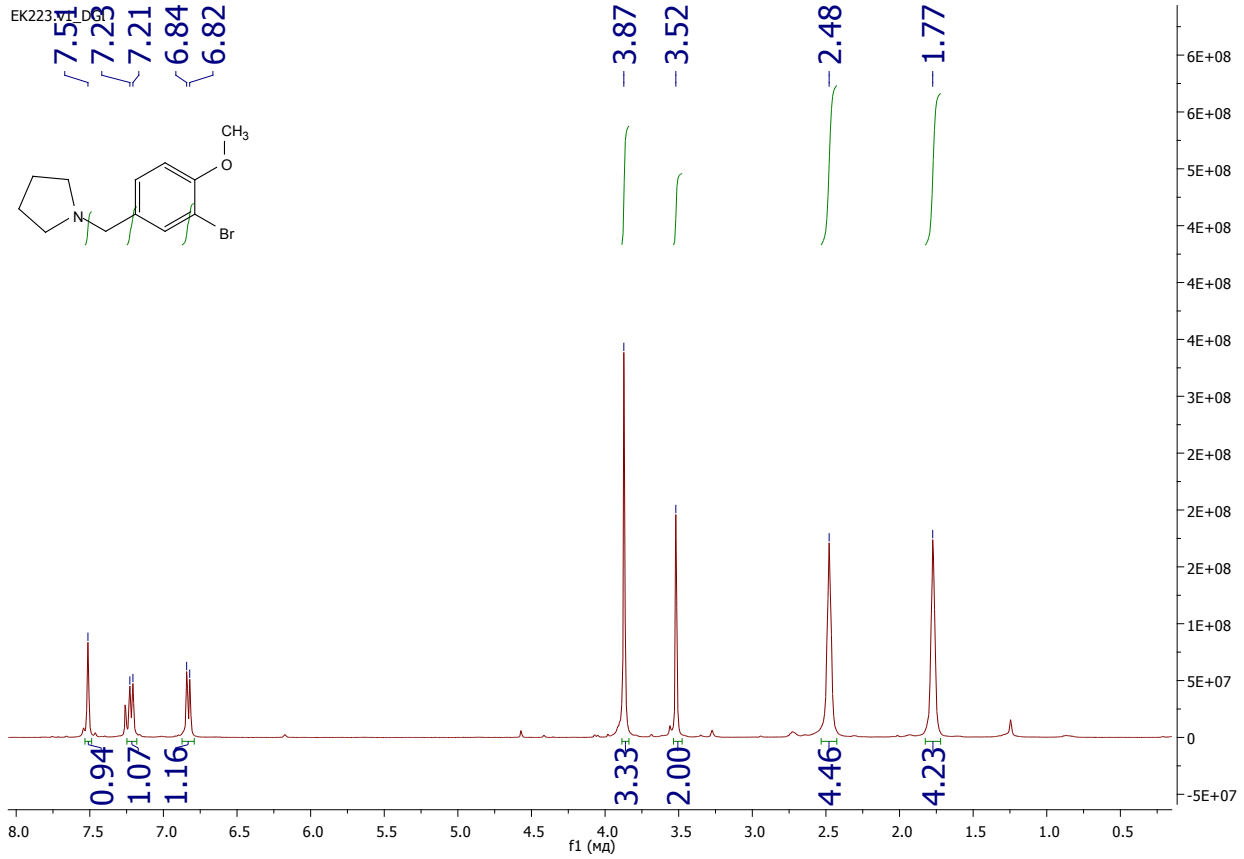


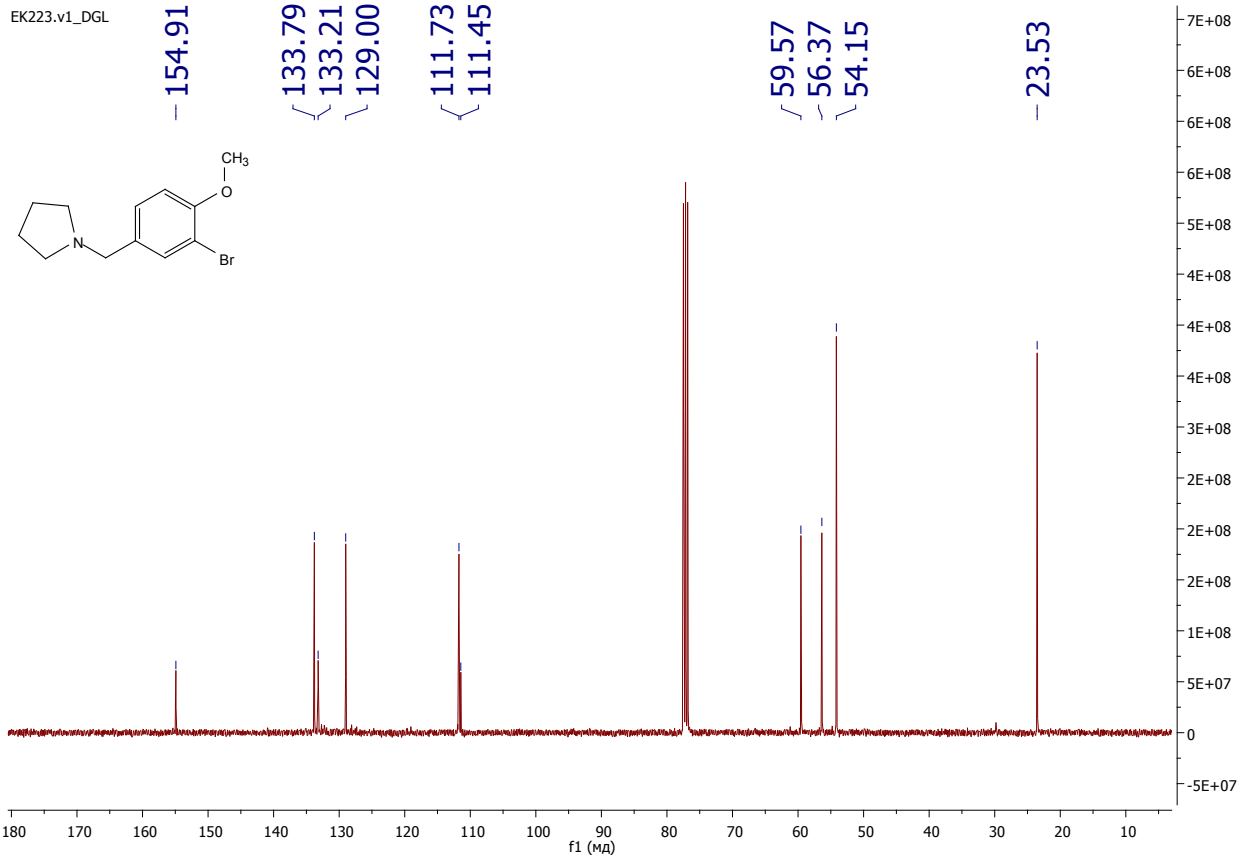
1-(4-phenylbutan-2-yl)pyrrolidine (13)





1-(3-bromo-4-methoxybenzyl)pyrrolidine (14)





Display Report

Analysis Info

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Sample Name	/CHIZ 4	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 20000, calibrant added		

Acquisition Parameter

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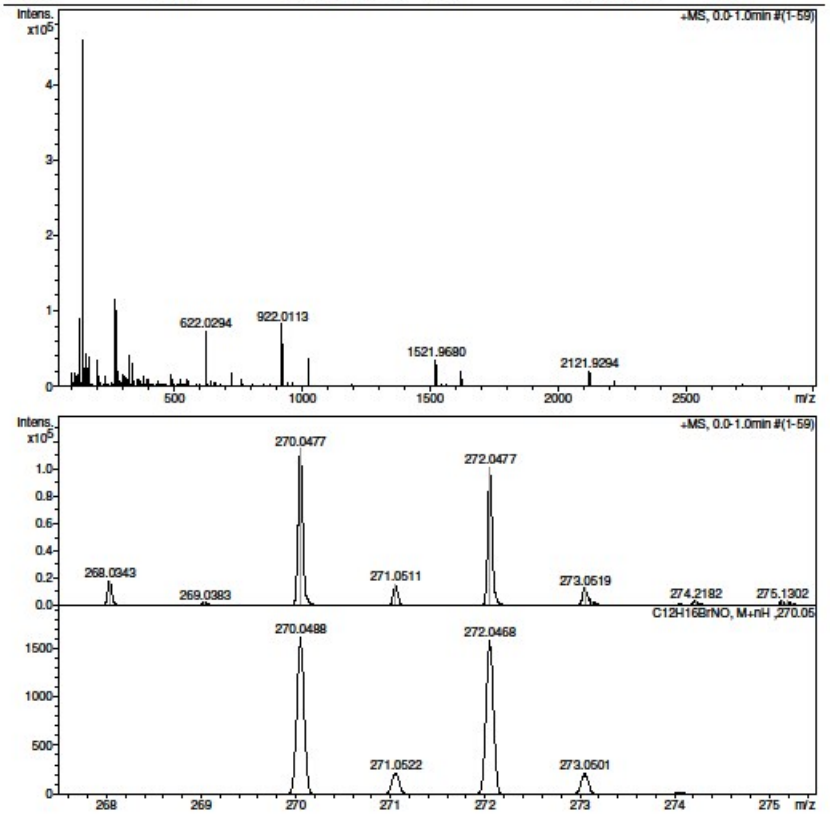
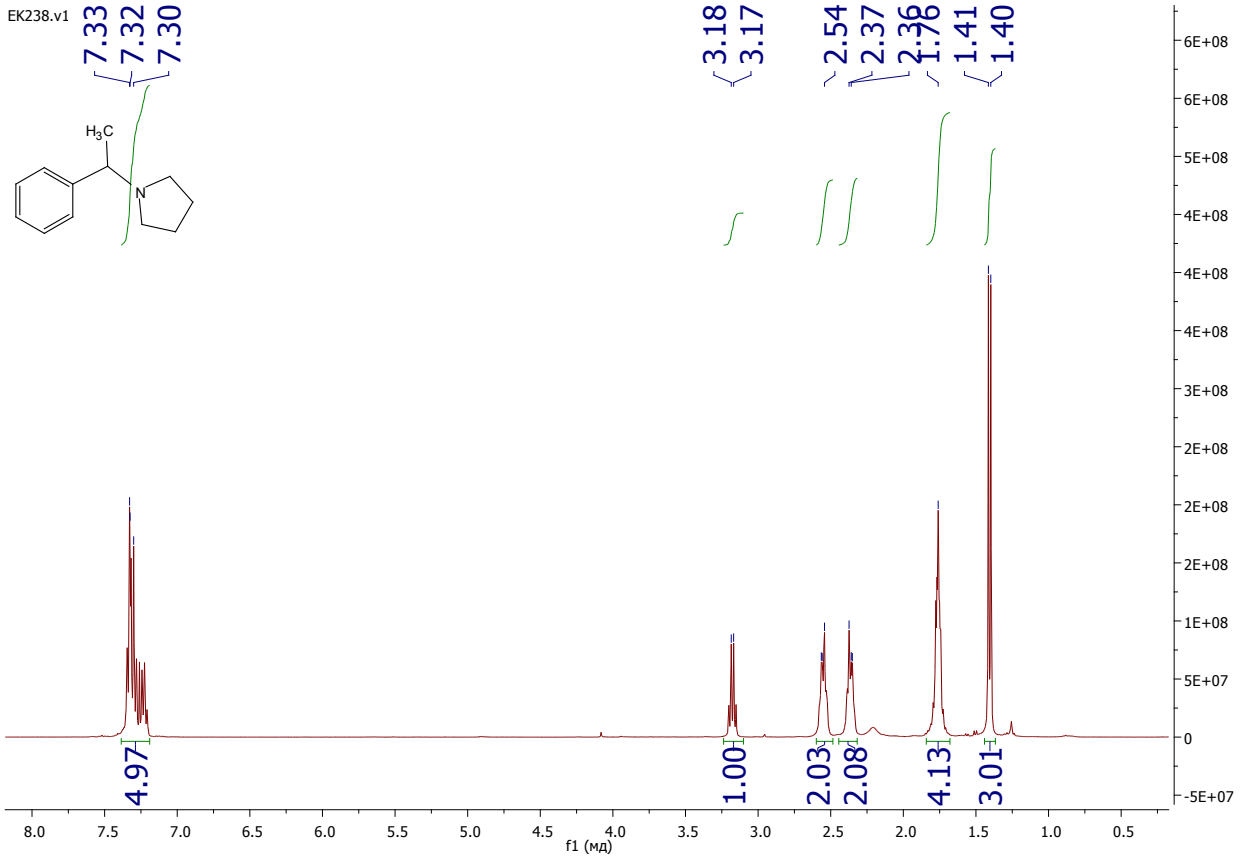
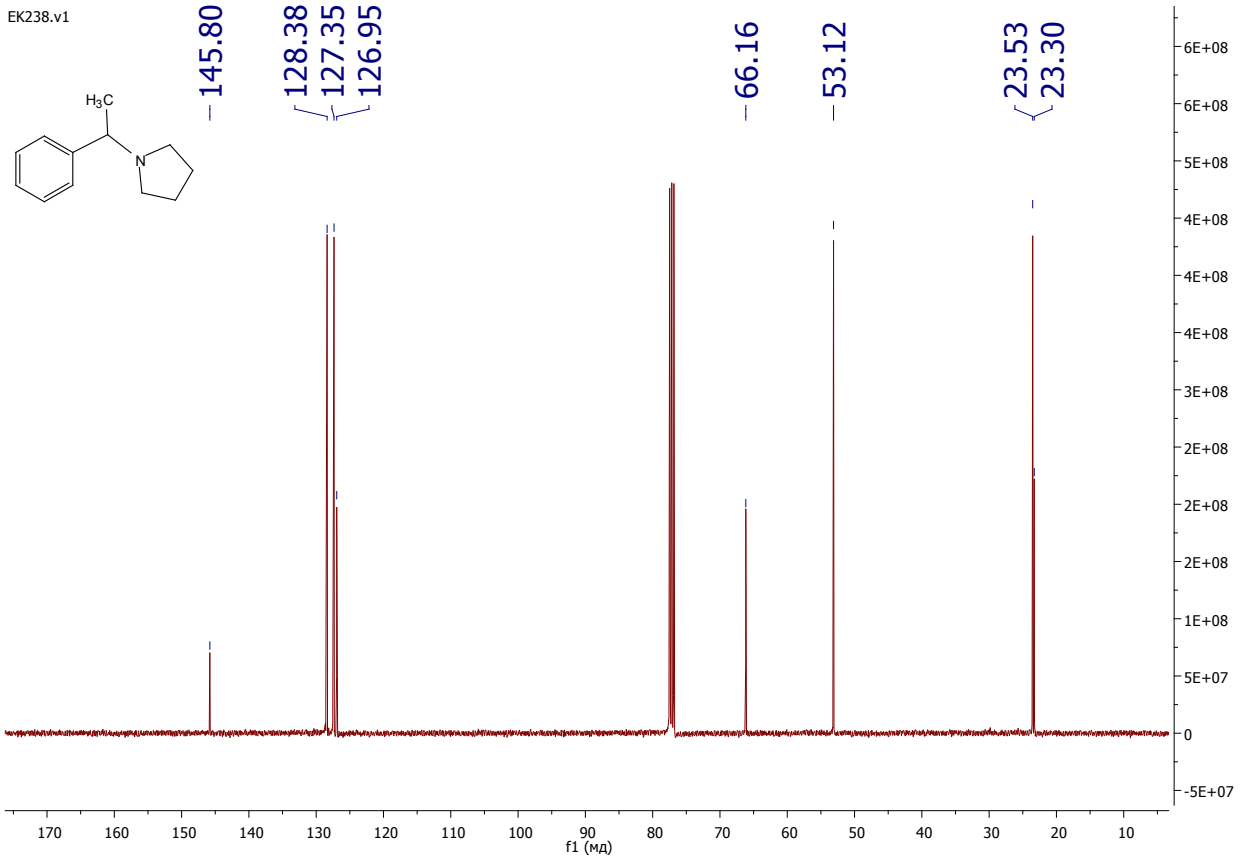
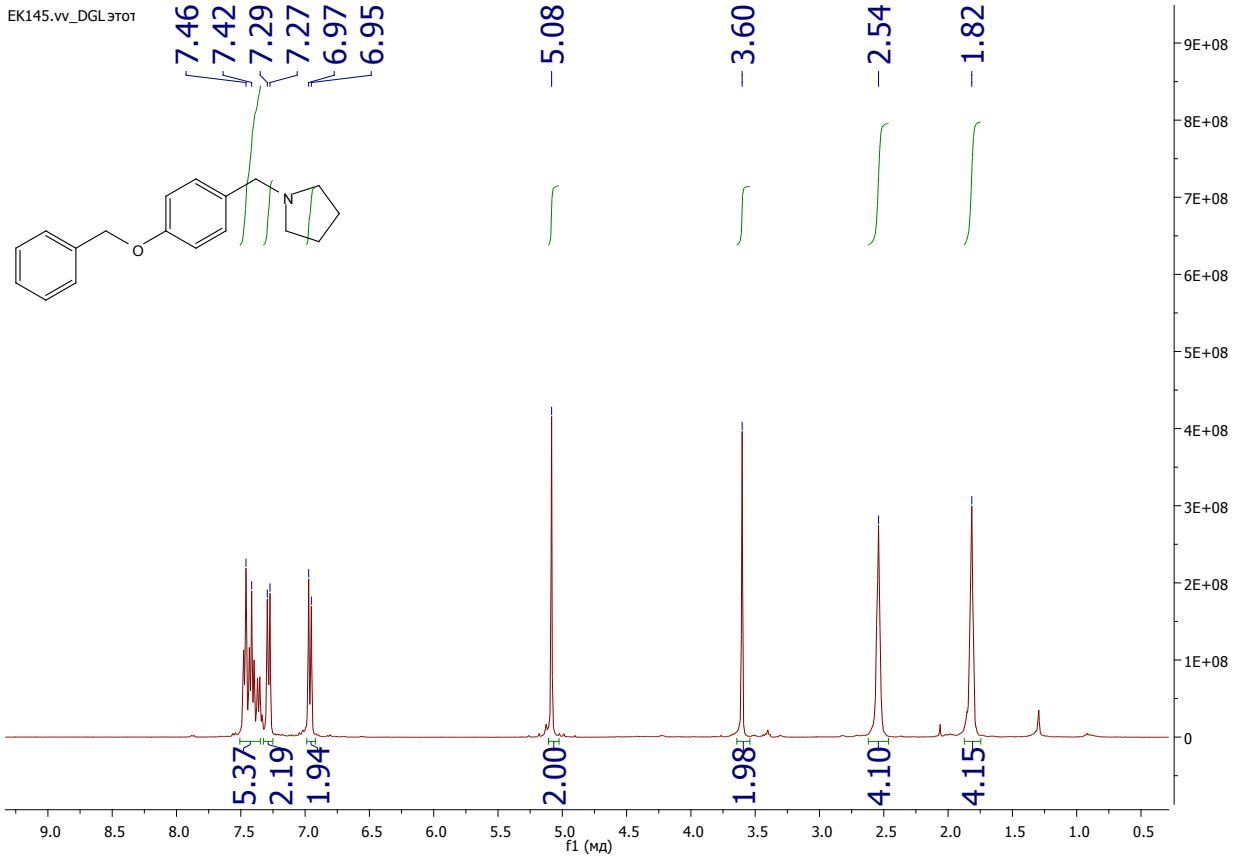


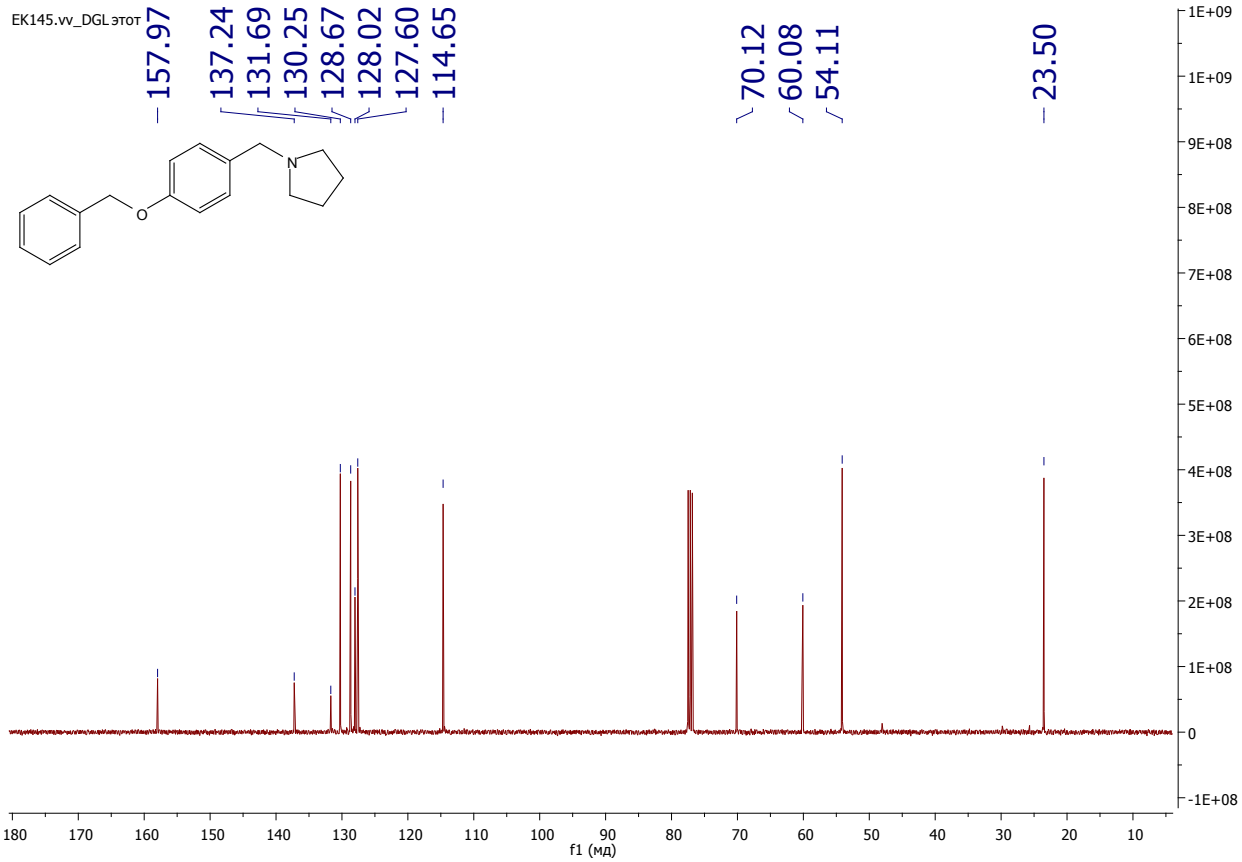
1-(1-phenylethyl)pyrrolidine (15)



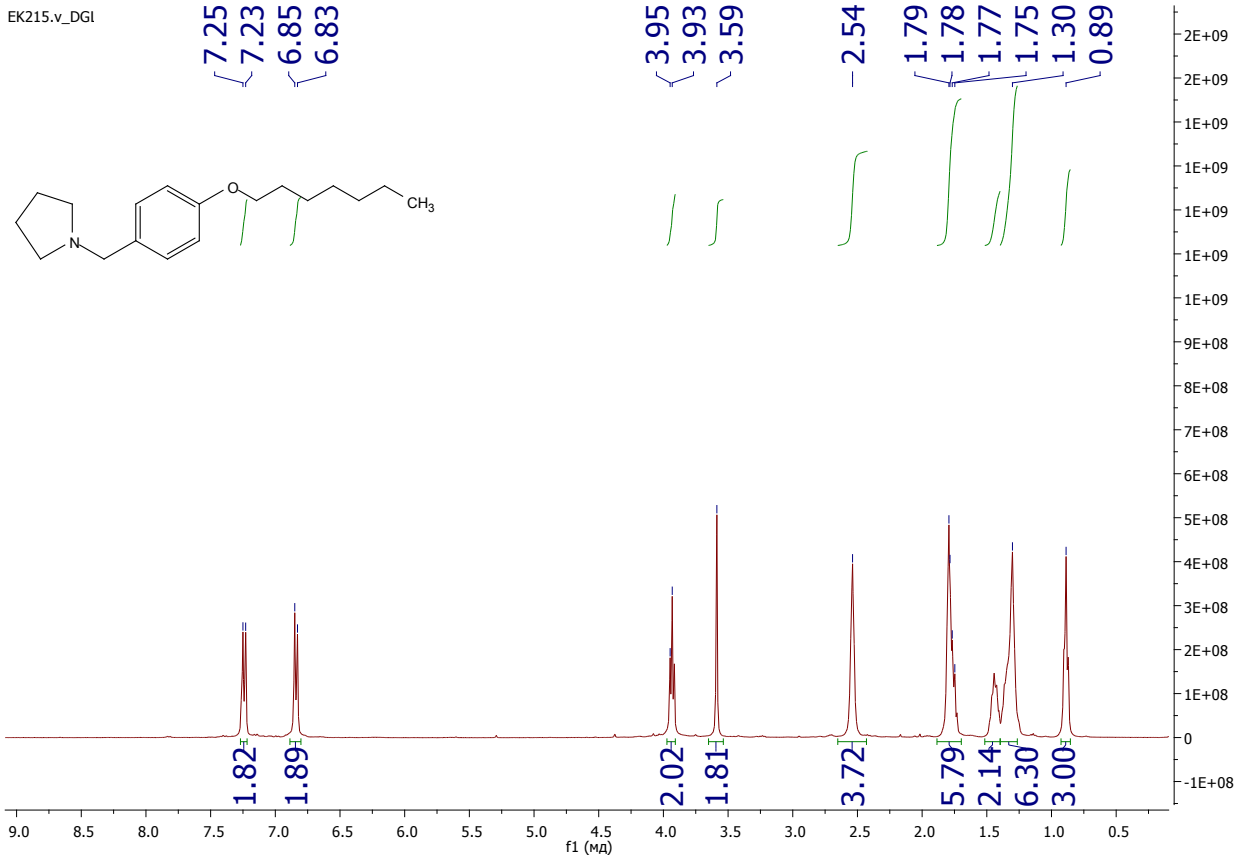


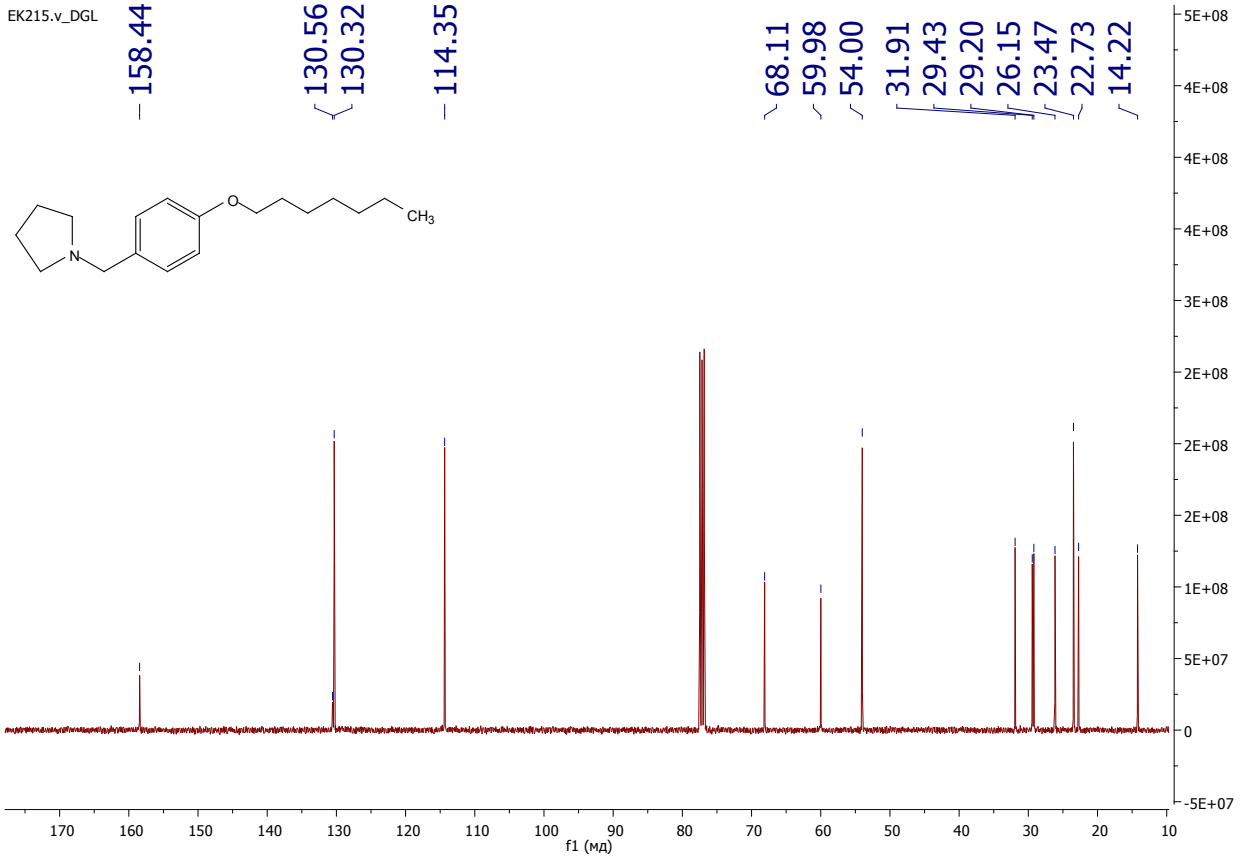
1-(4-(benzyloxy)benzyl)pyrrolidine (16)





1-(4-(heptyloxy)benzyl)pyrrolidine (17)





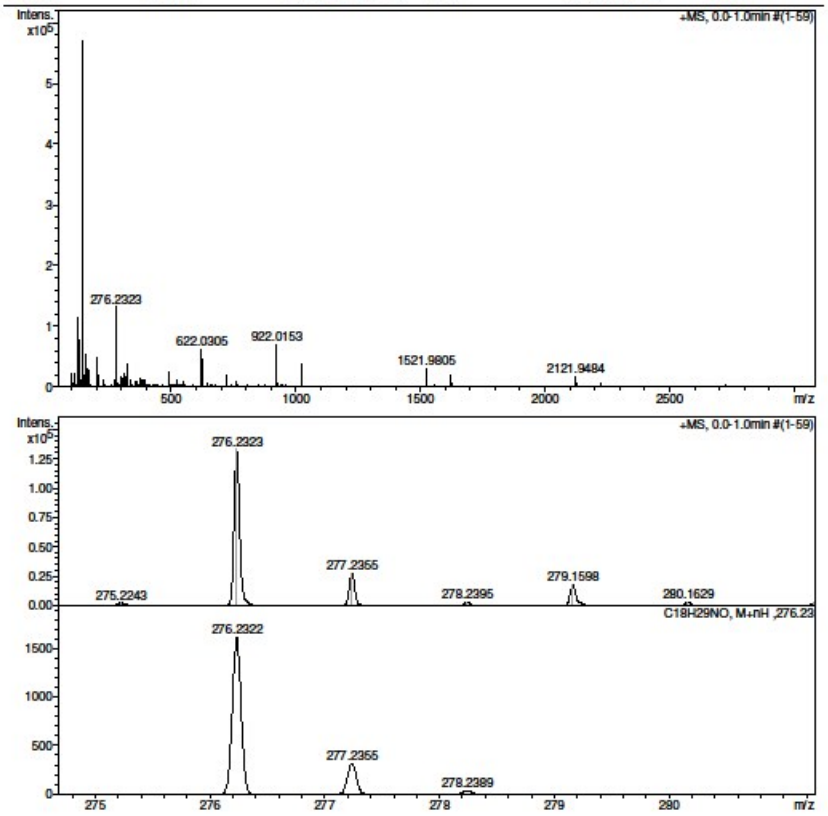
Display Report

Analysis Info

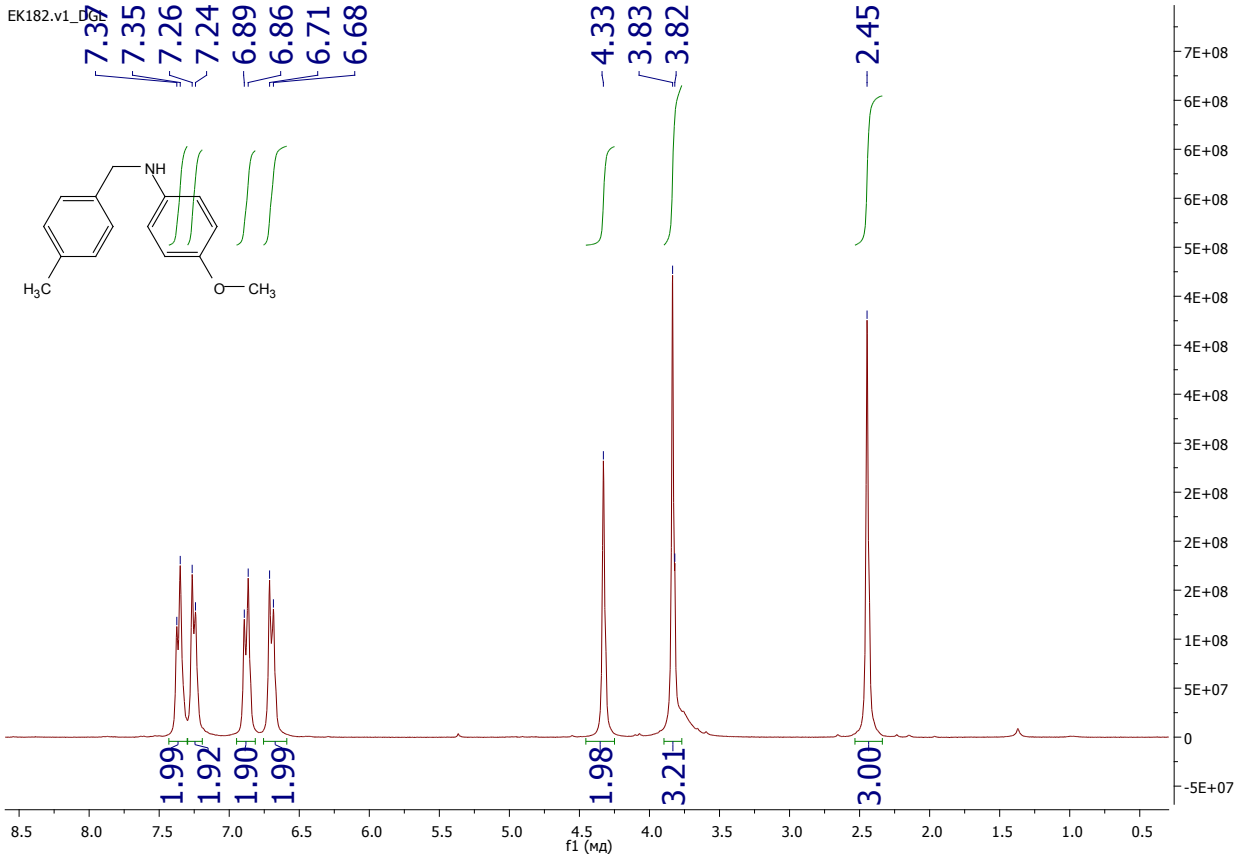
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\Oct_19_2018\3_&clblow.d	Acquisition Date	19.10.2018 13:54:49
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ 3	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 20000, calibrant added		

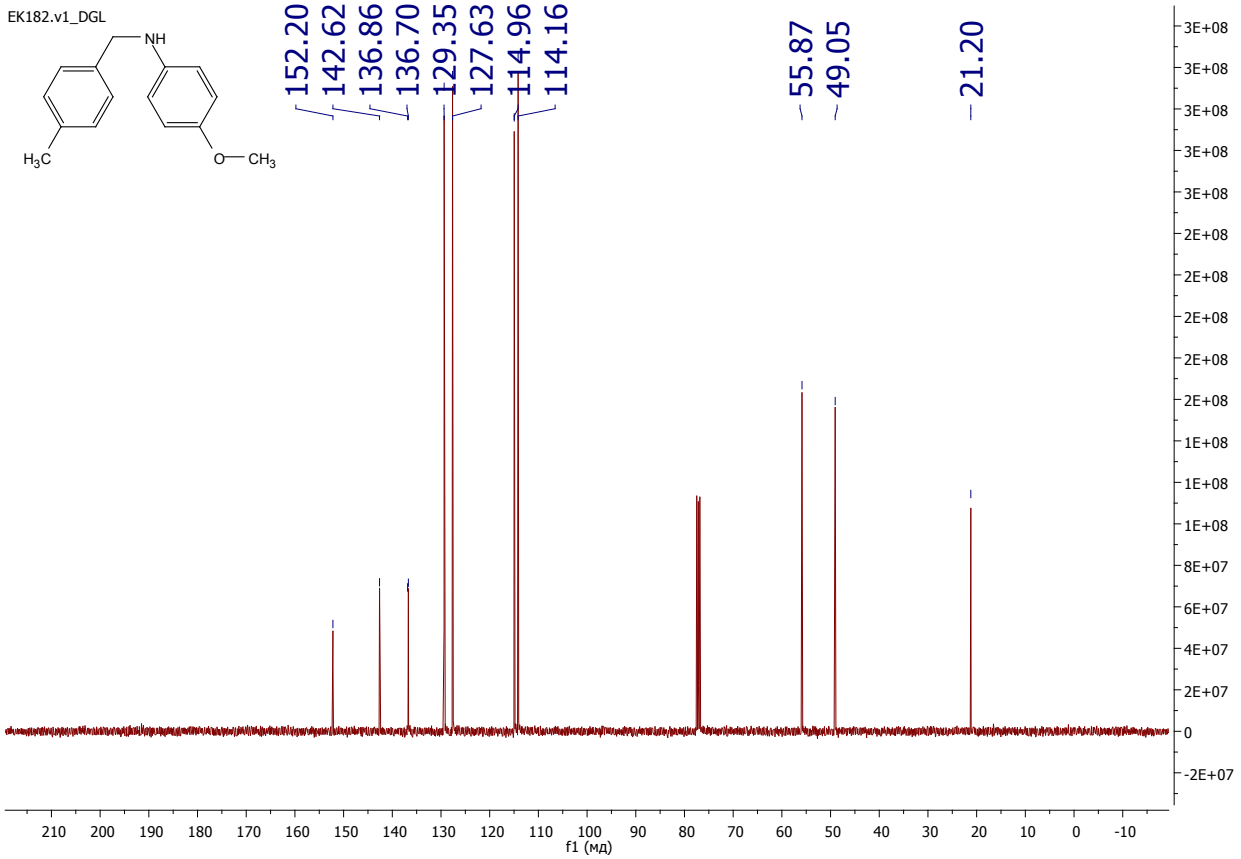
Acquisition Parameter

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

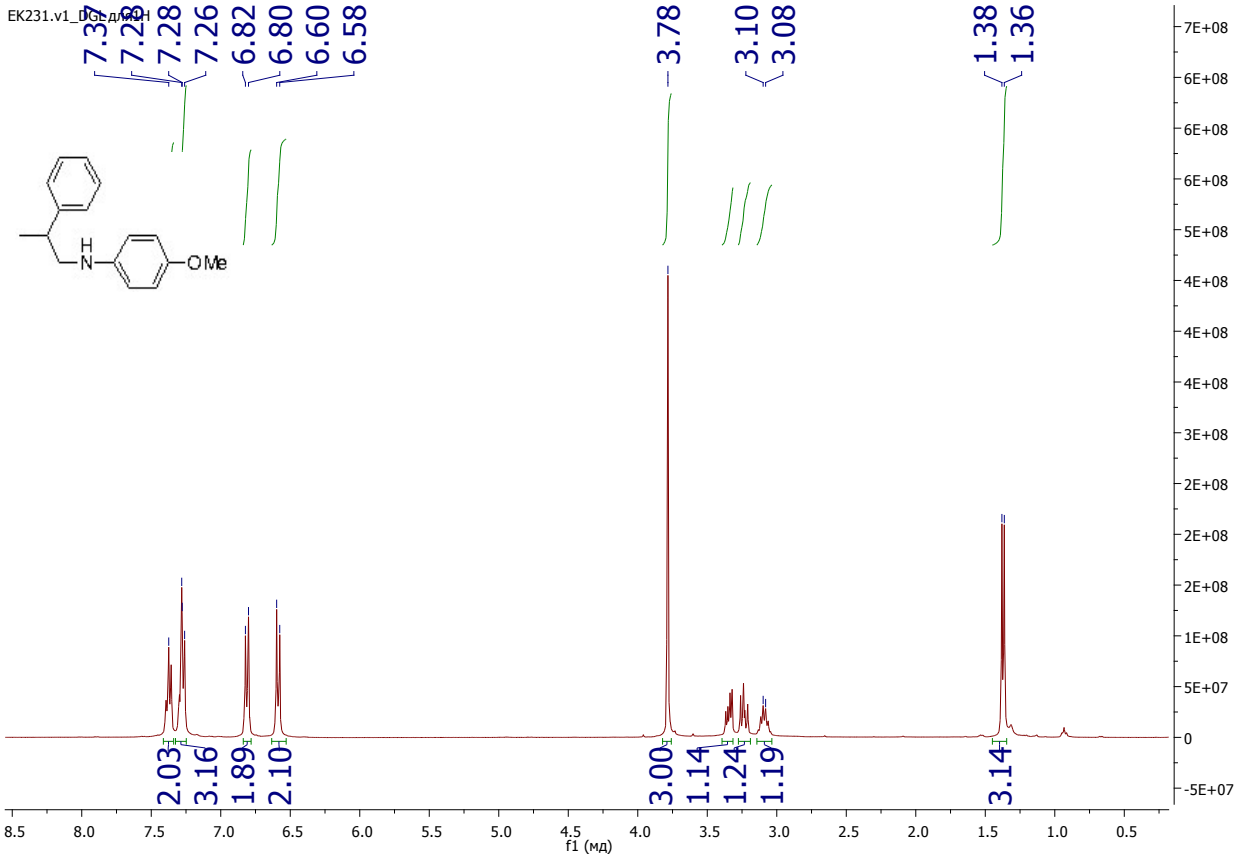


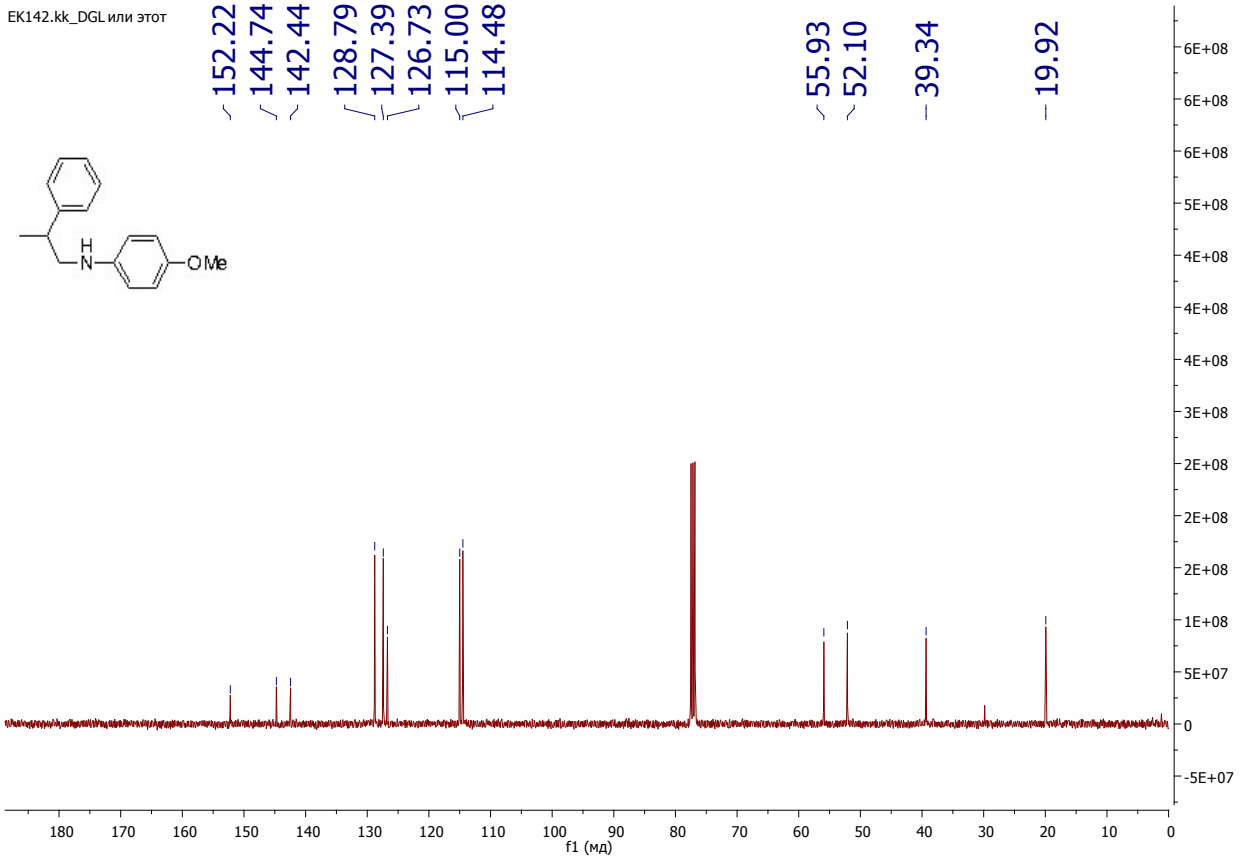
4-methoxy-N-(4-methylbenzyl)aniline (18)



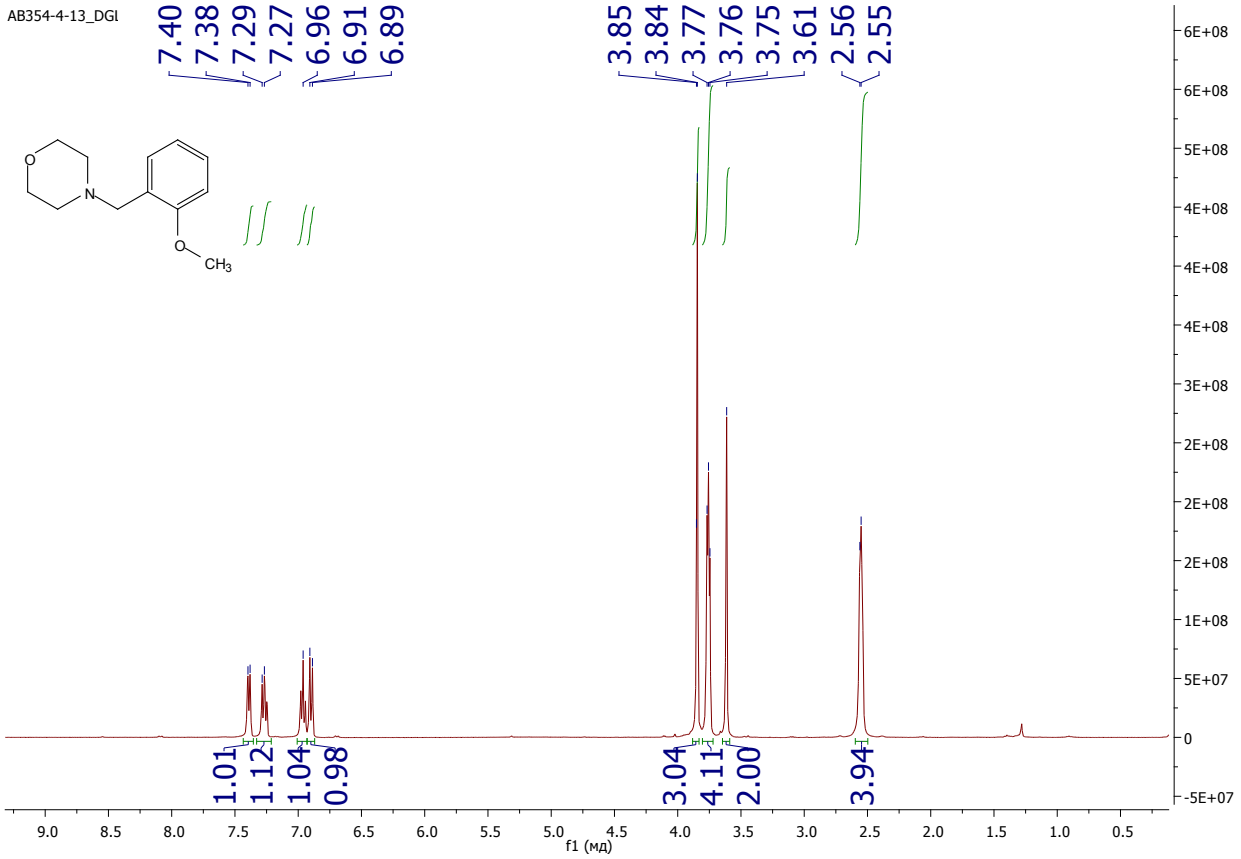


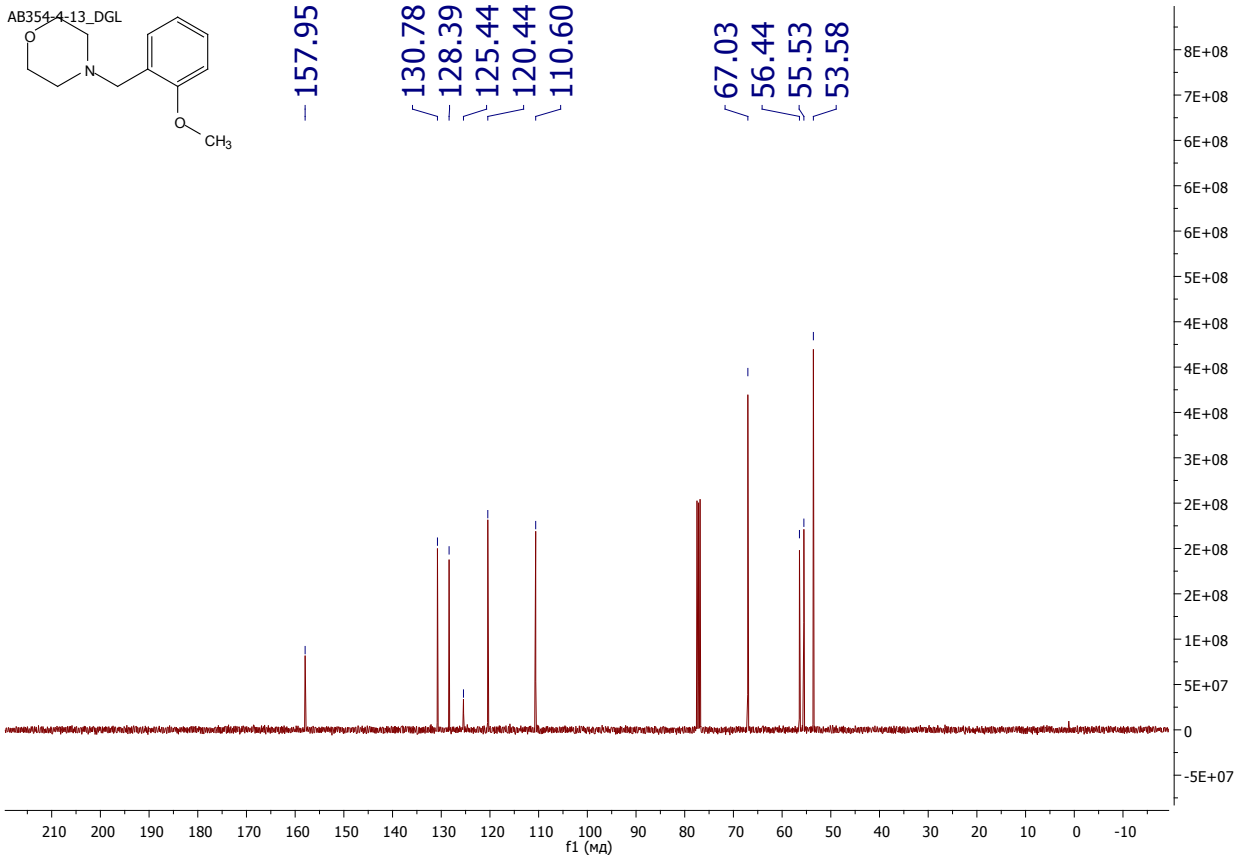
4-methoxy-N-(2-phenylpropyl)aniline (19)



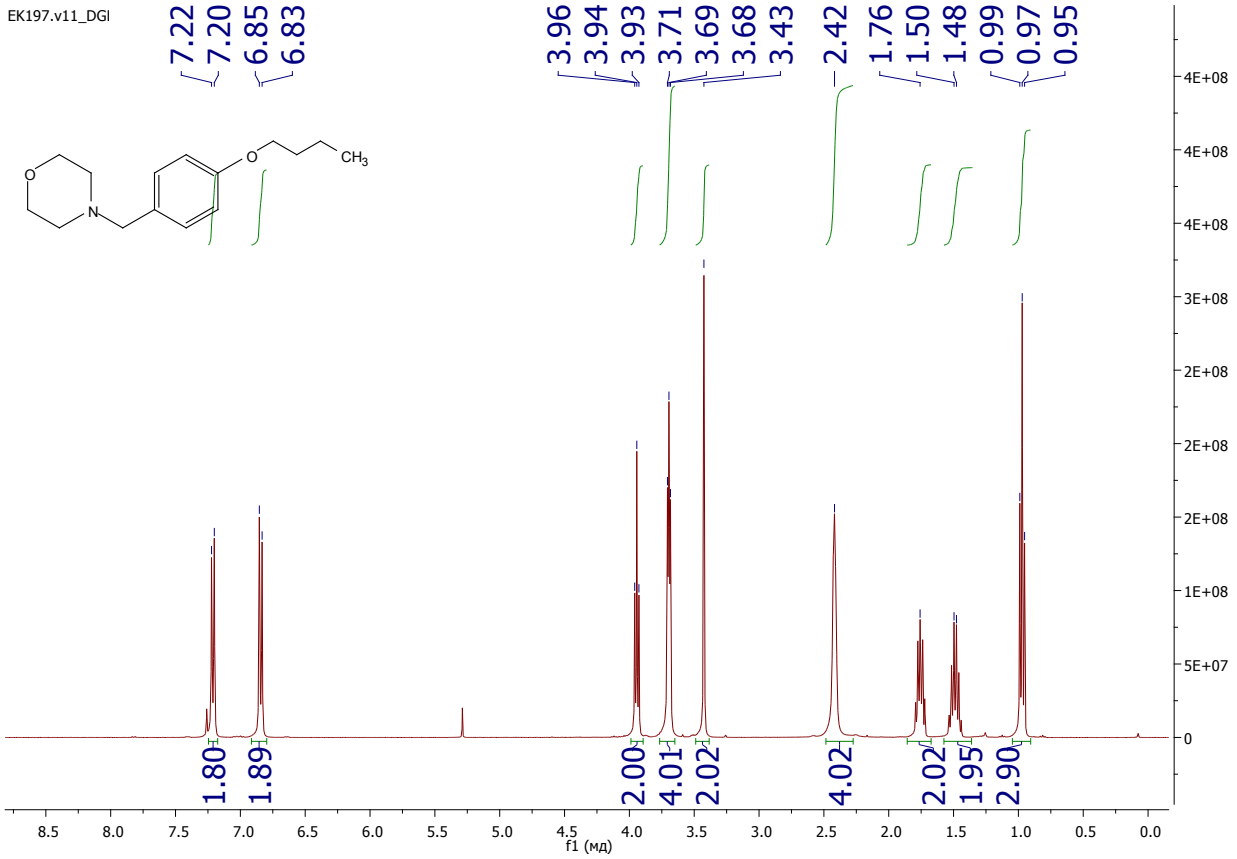


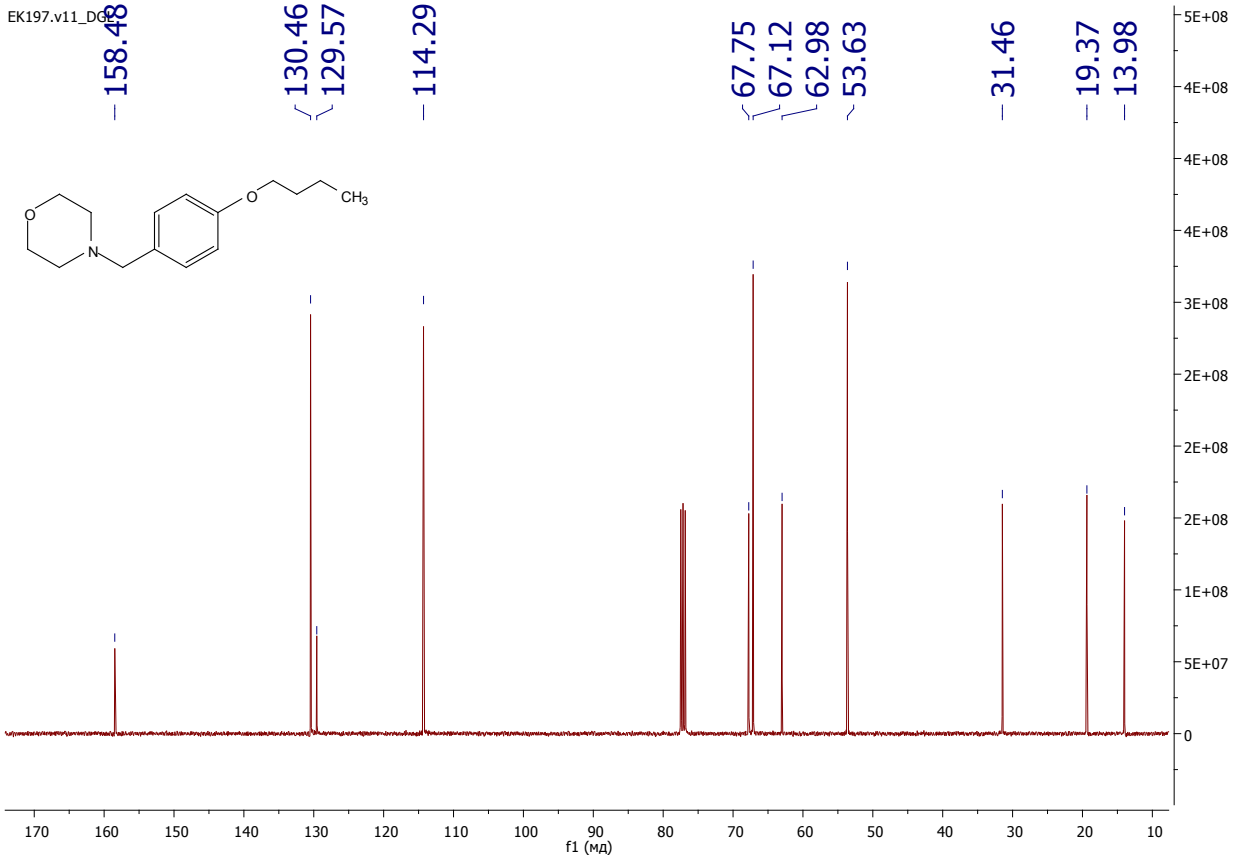
4-(2-methoxybenzyl)morpholine (20)





4-(4-butoxybenzyl)morpholine (21)





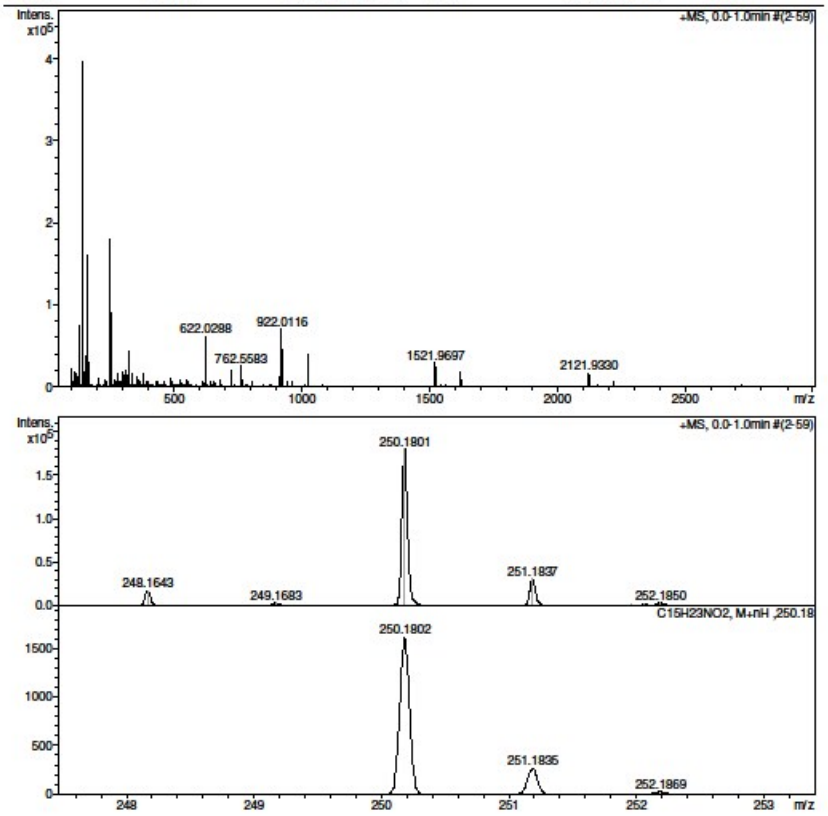
Display Report

Analysis Info

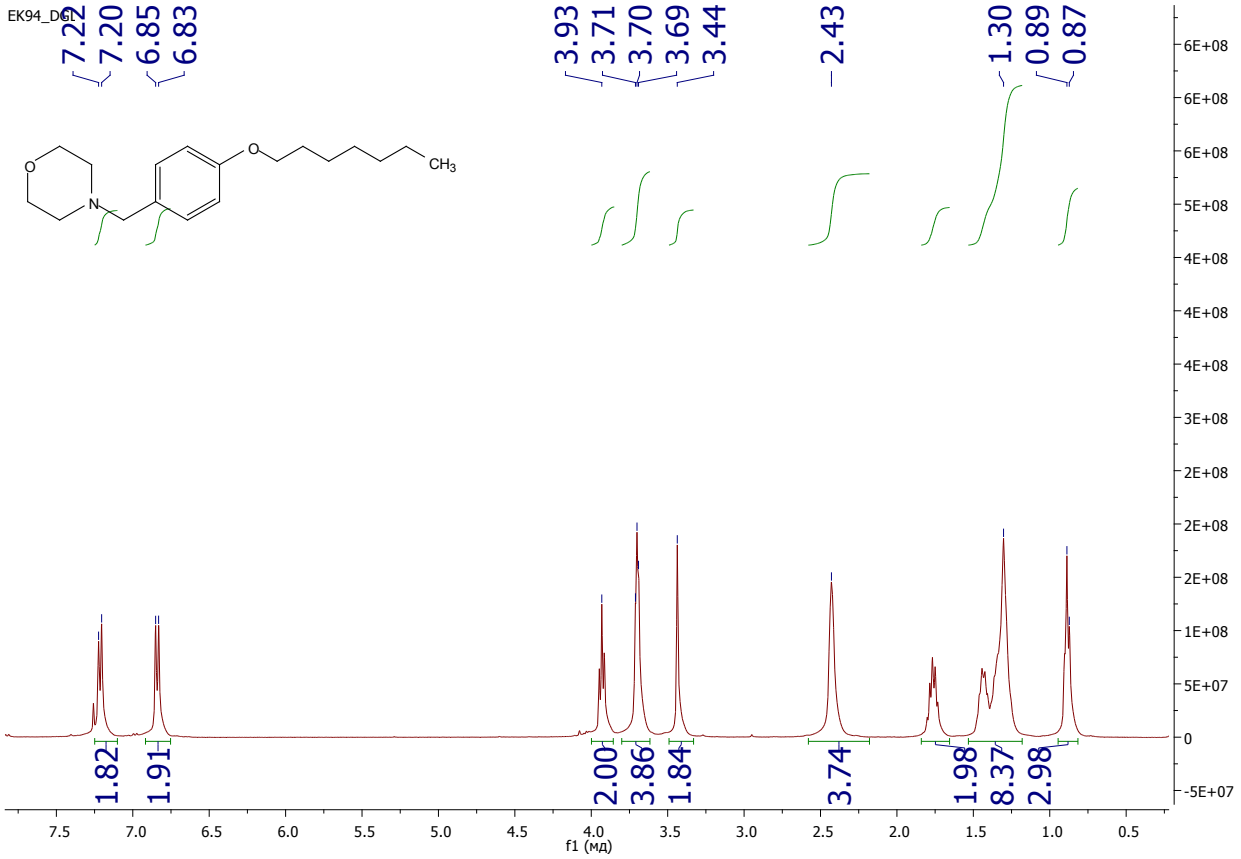
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\Oct_19_2018\11_&dblow.d	Acquisition Date	19.10.2018 14:04:56
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ 11	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

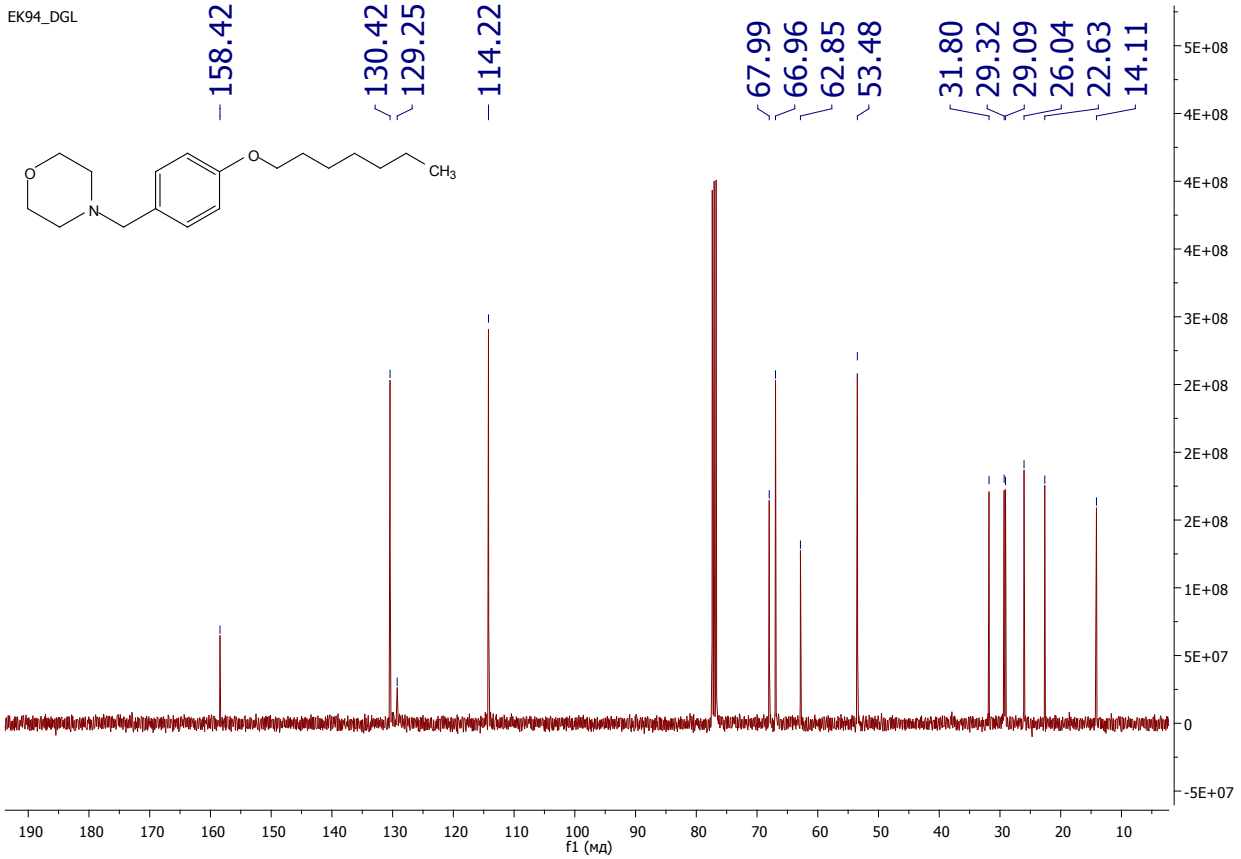
Acquisition Parameter

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-(4-(heptyloxy)benzyl)morpholine (22)





Display Report

Analysis Info

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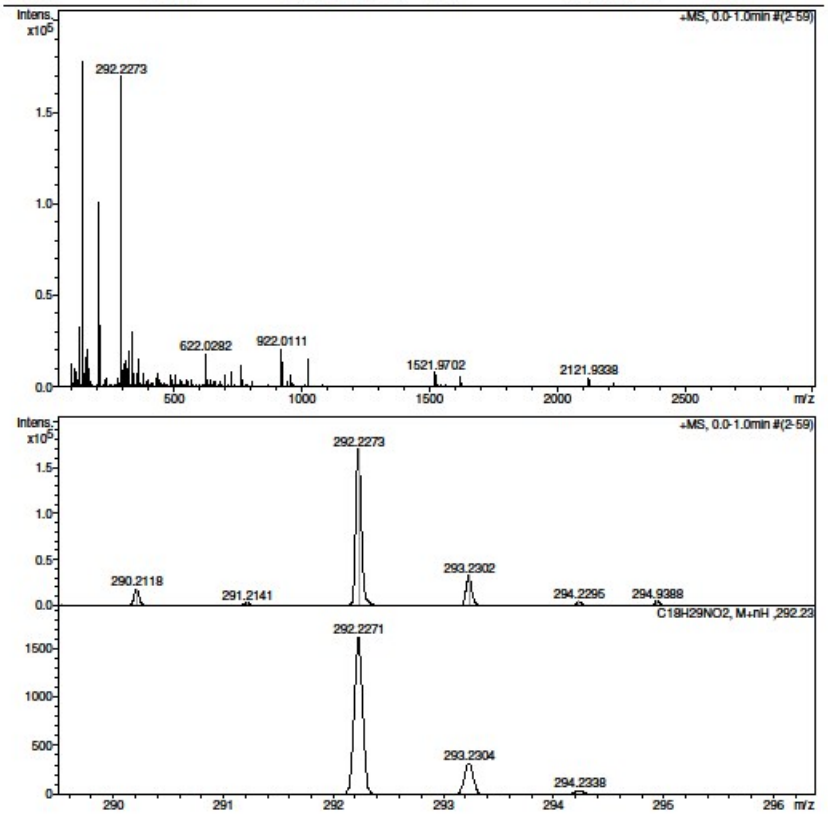
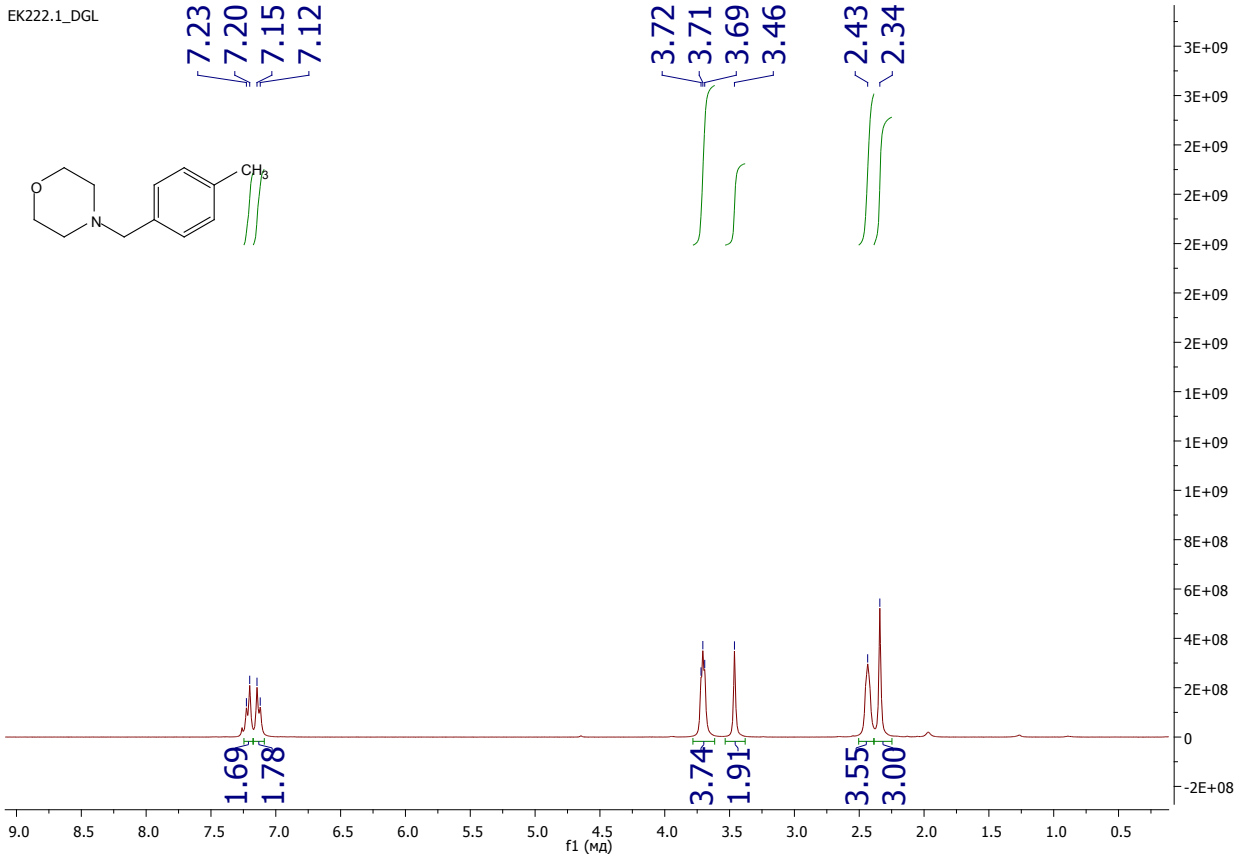
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ 12	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

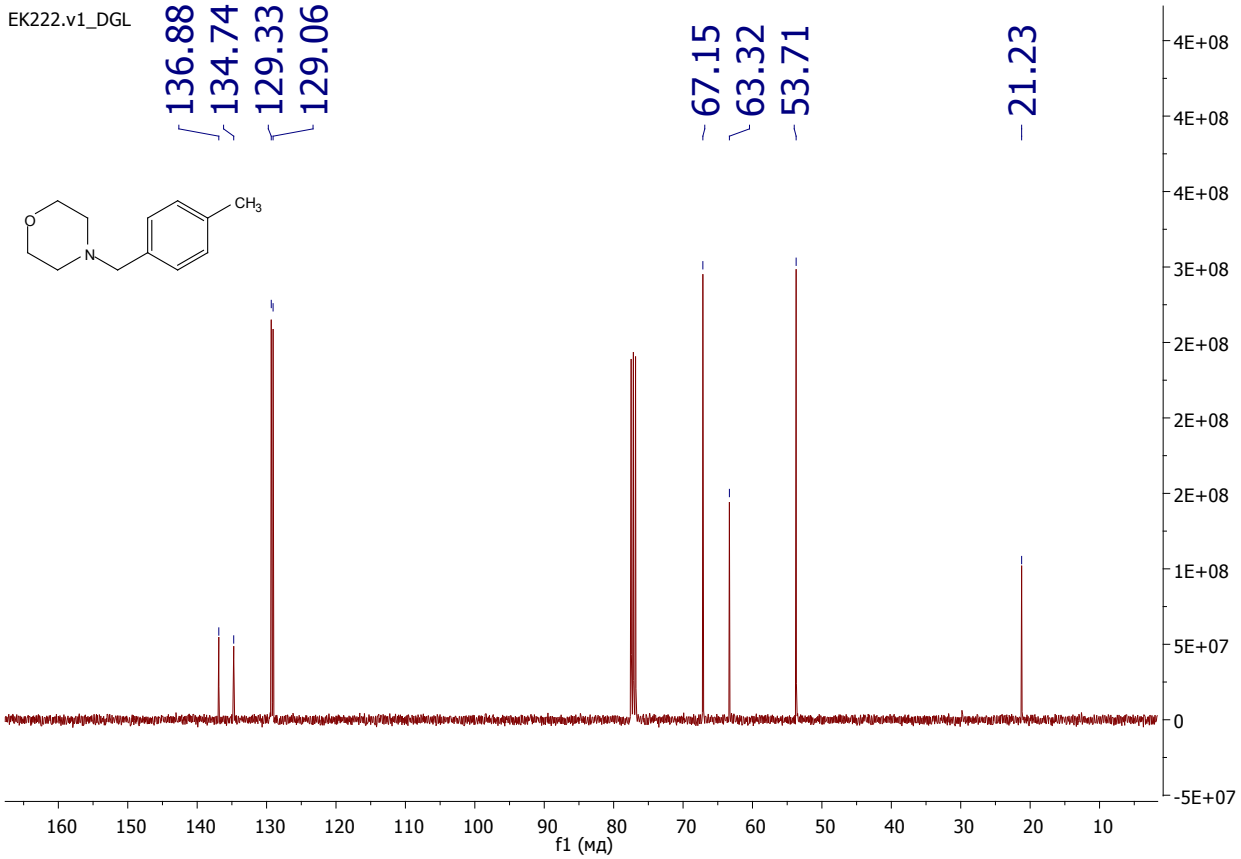
Acquisition Parameter

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

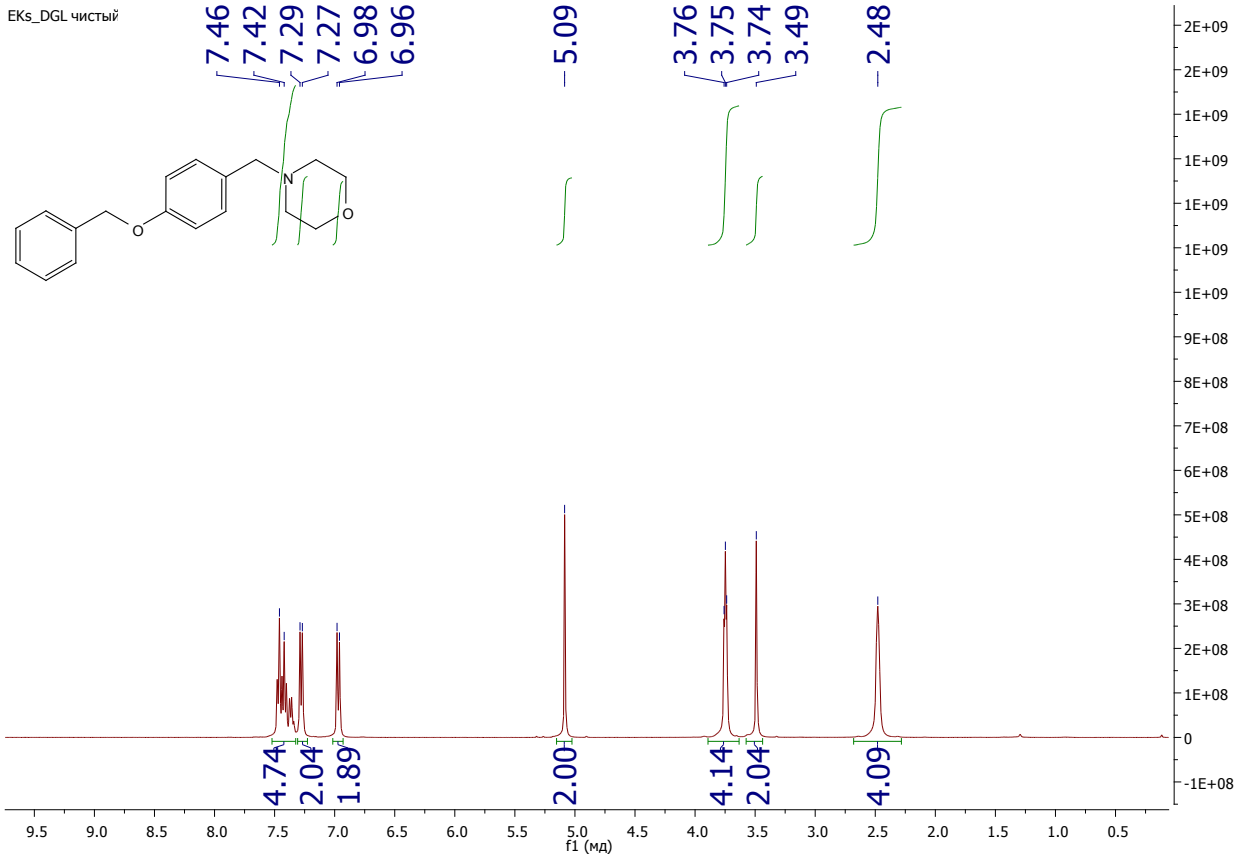


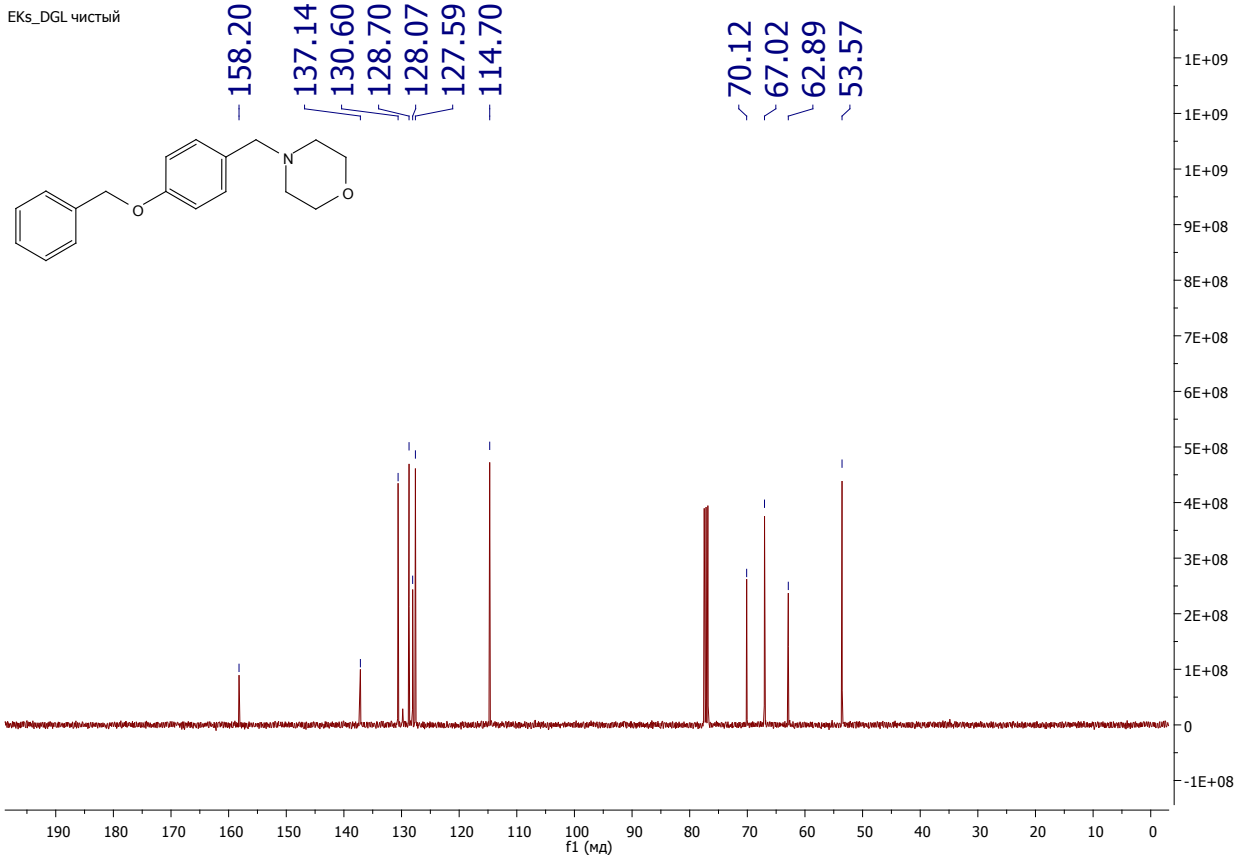
4-(4-methylbenzyl)morpholine (23)



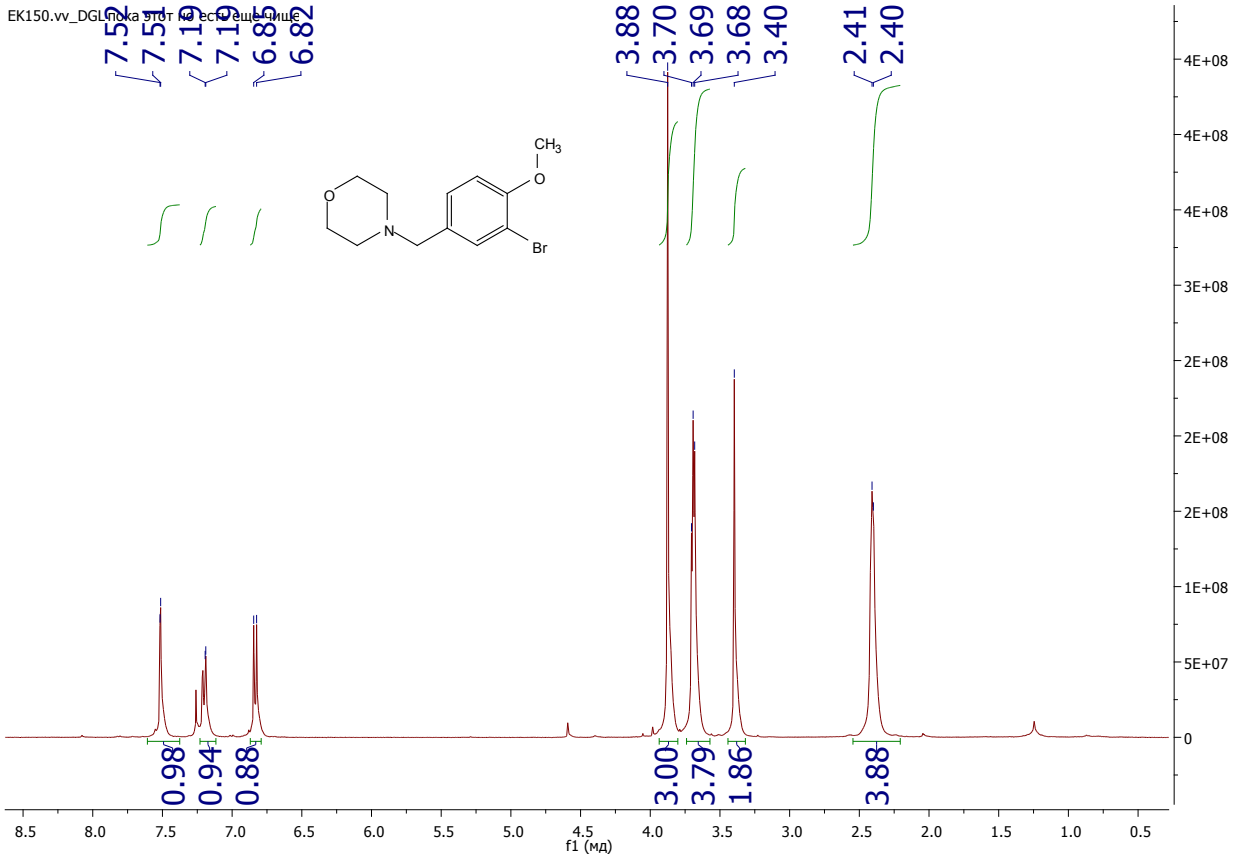


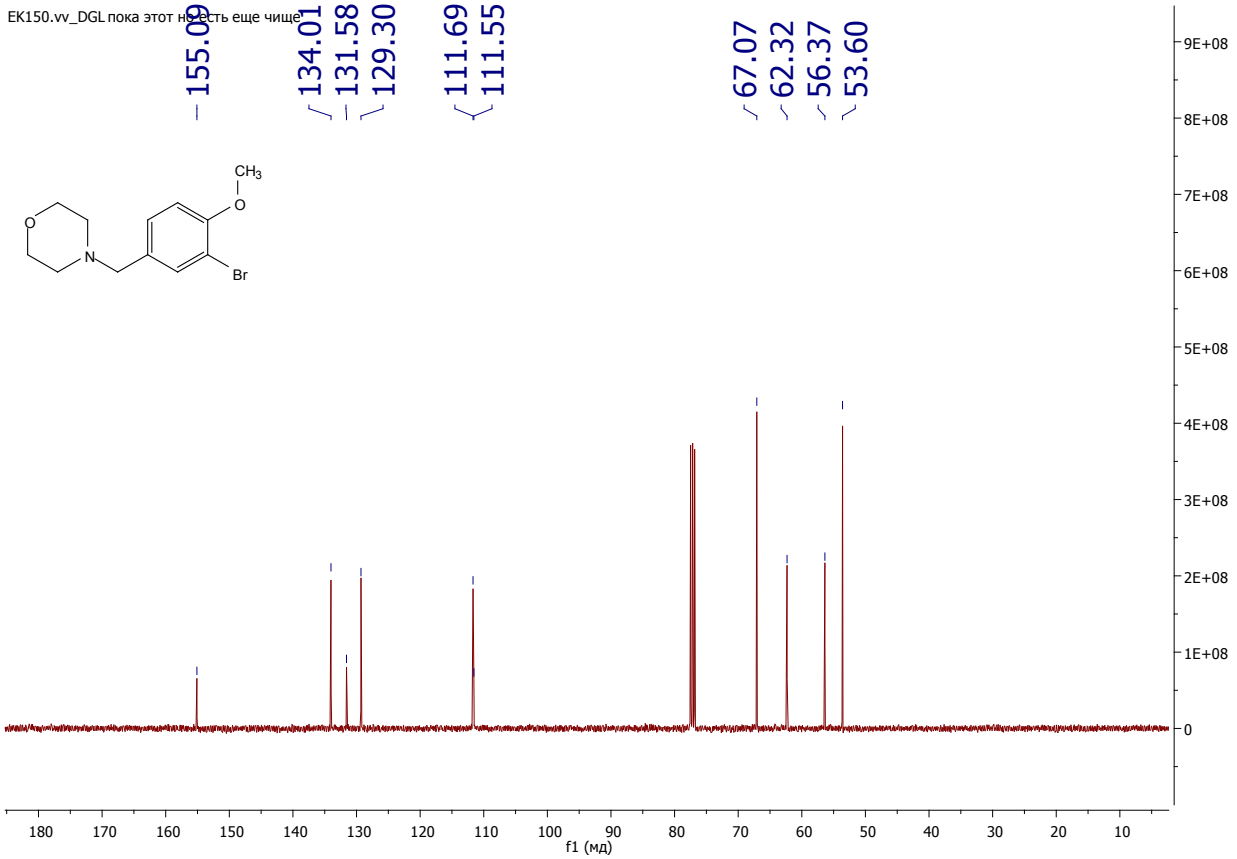
4-(4-(benzyloxy)benzyl)morpholine (24)



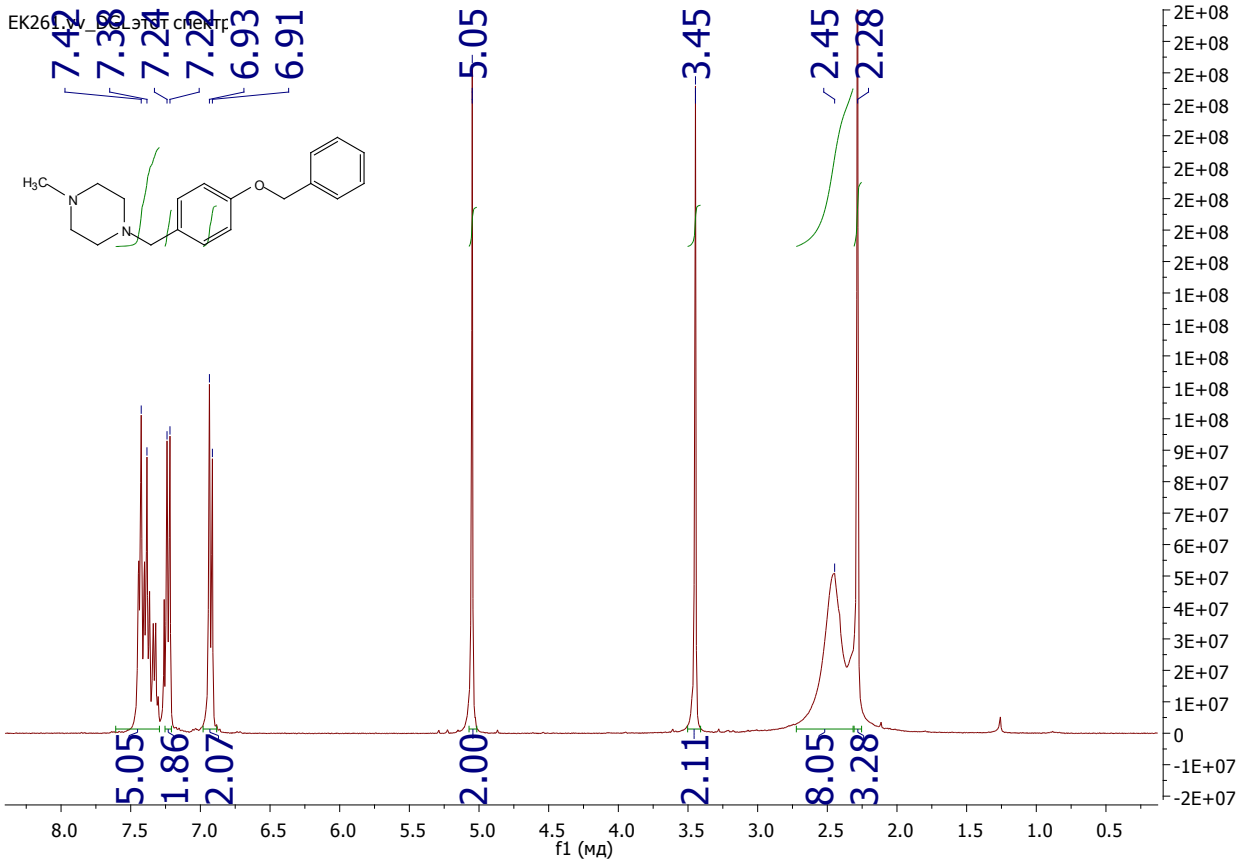


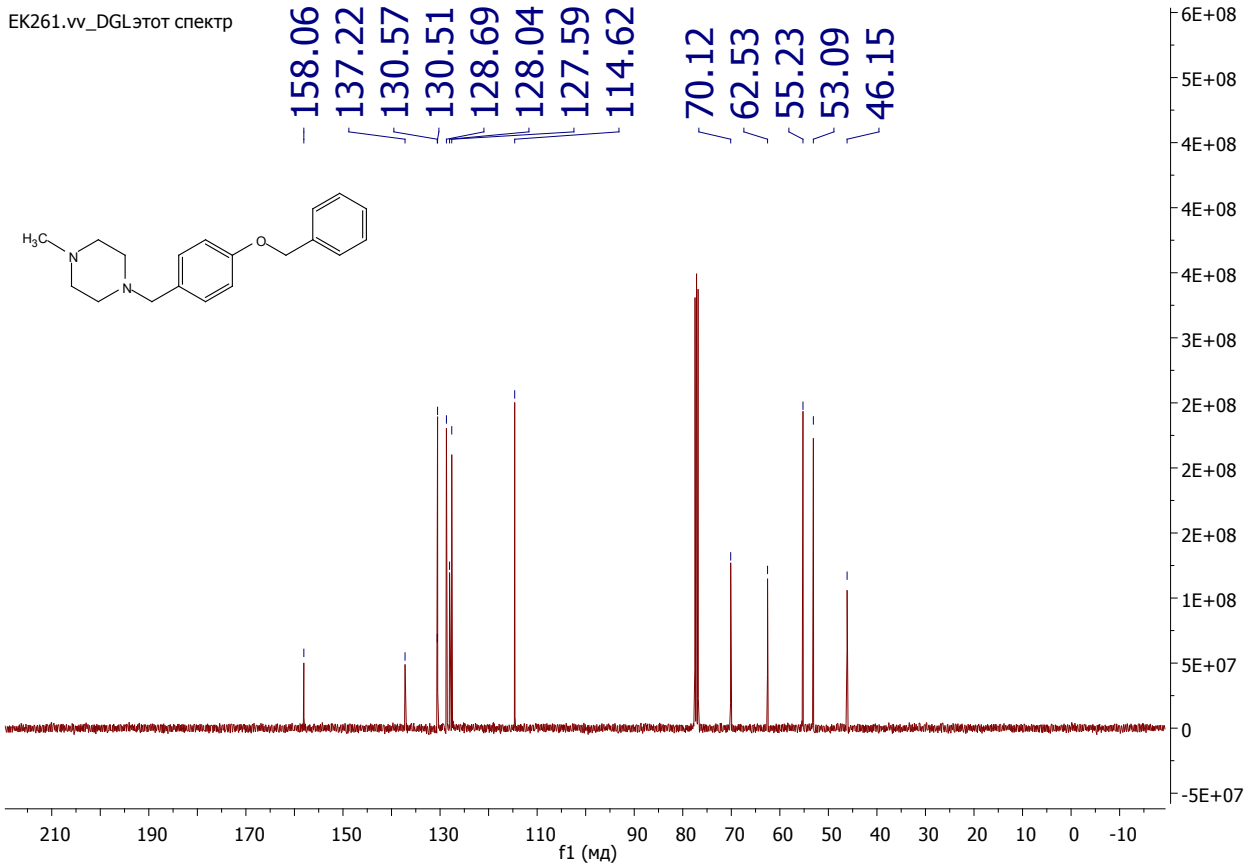
4-(3-bromo-4-methoxybenzyl)morpholine (25)





1-(4-(benzyloxy)benzyl)-4-methylpiperazine (26)





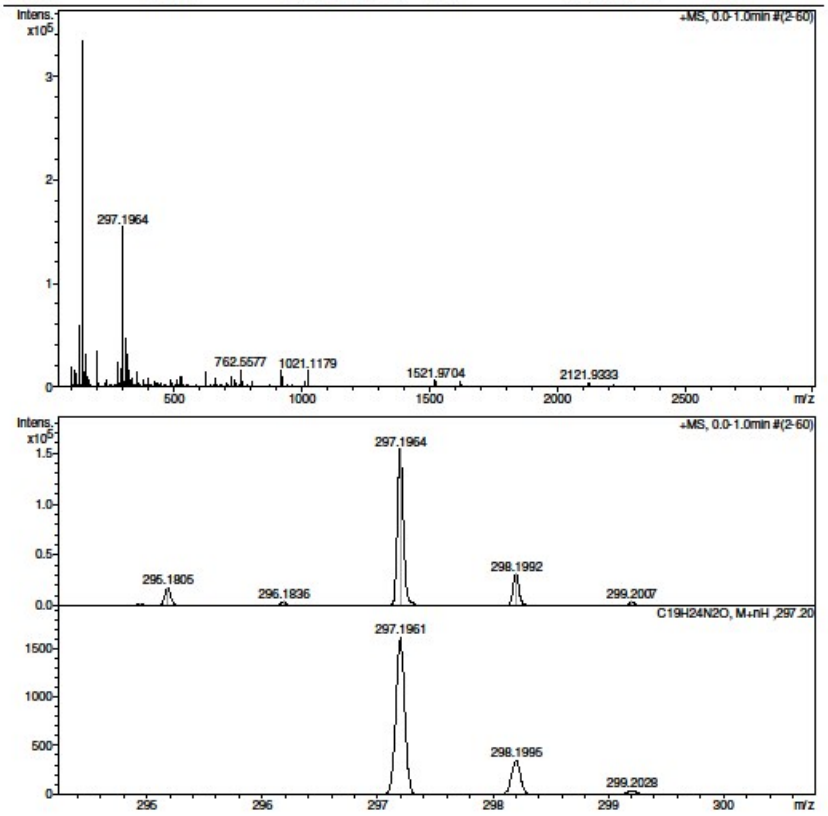
Display Report

Analysis Info

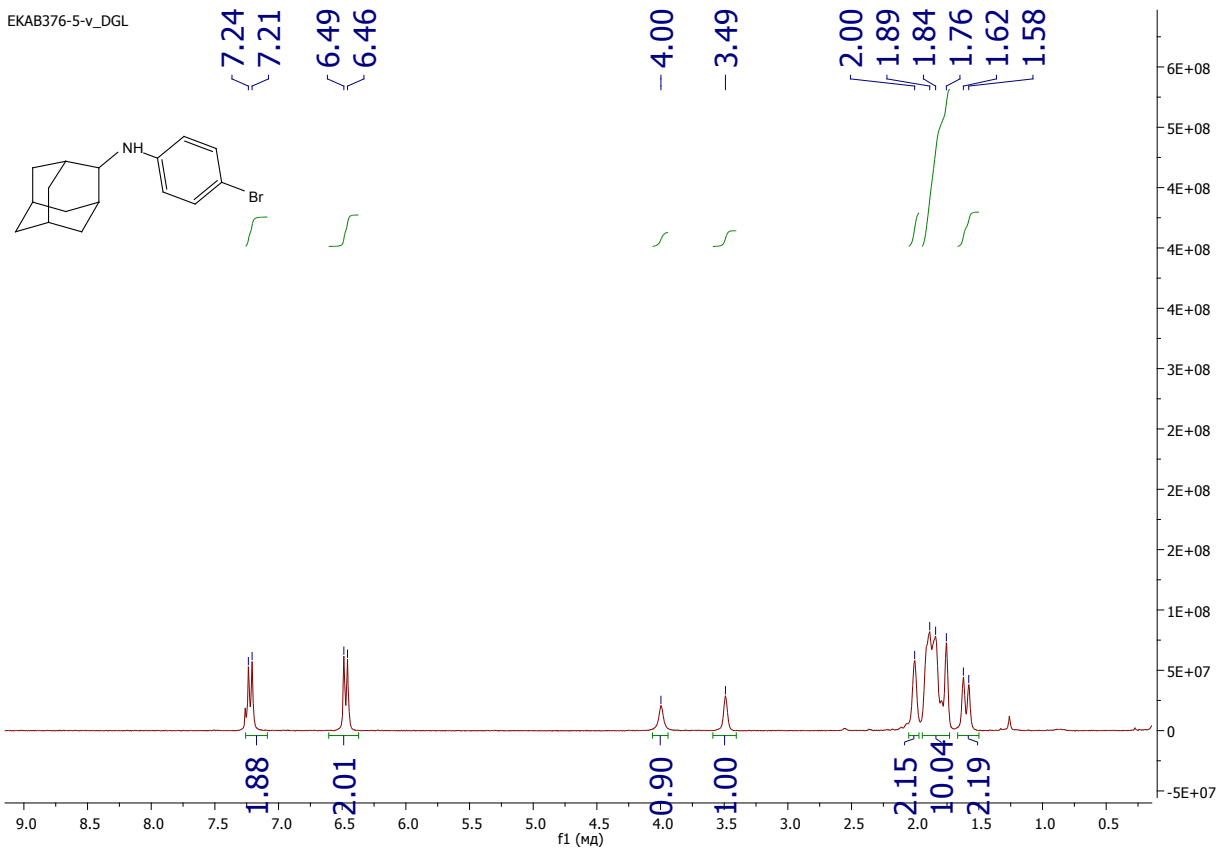
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\Oct_19_2018\15_&dblow.d	Acquisition Date	19.10.2018 14:14:05
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ 15	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

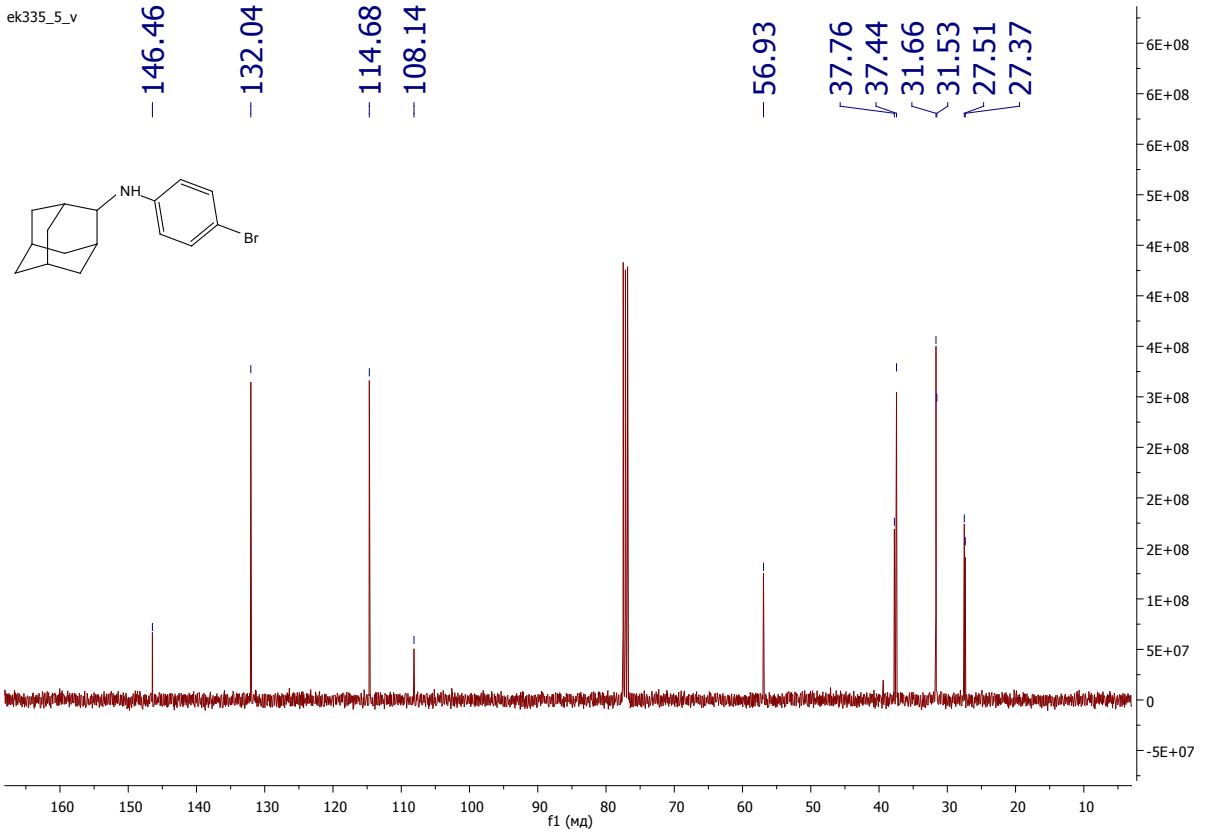
Acquisition Parameter

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

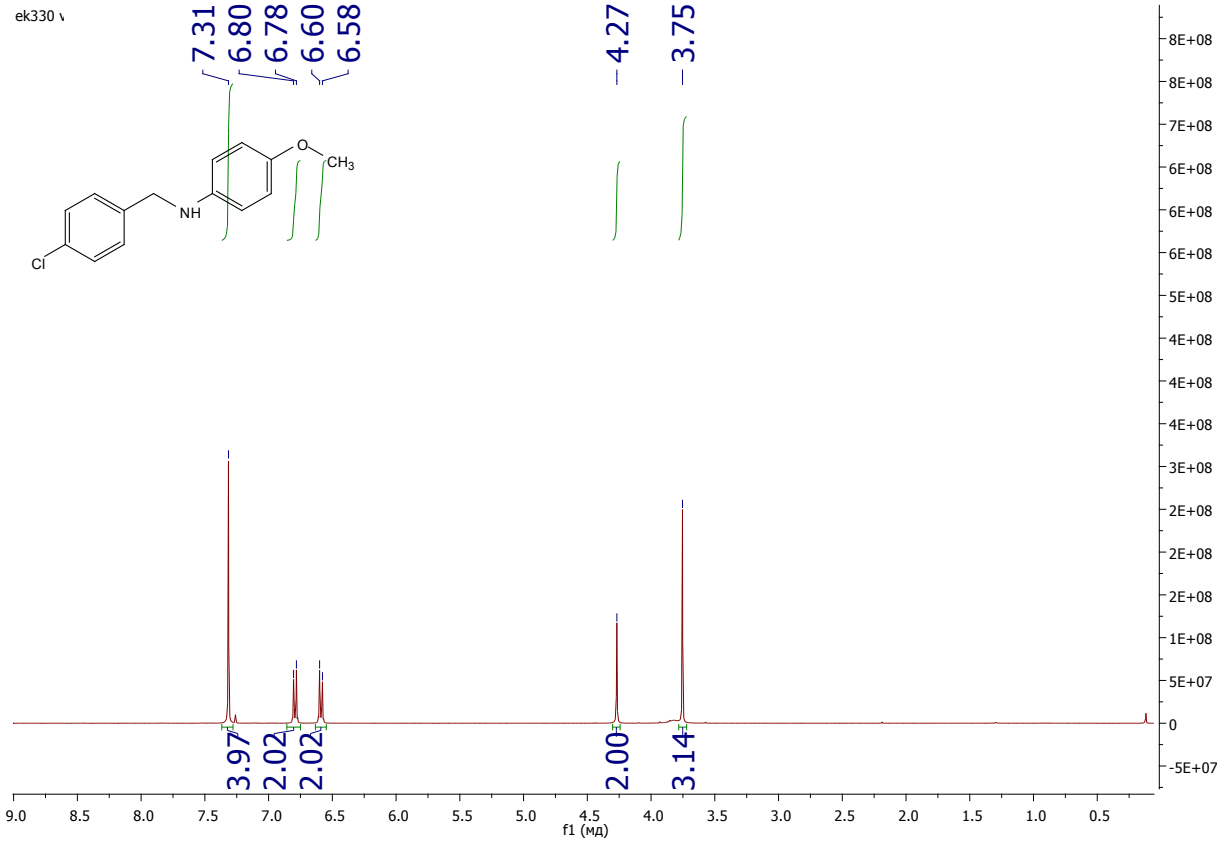


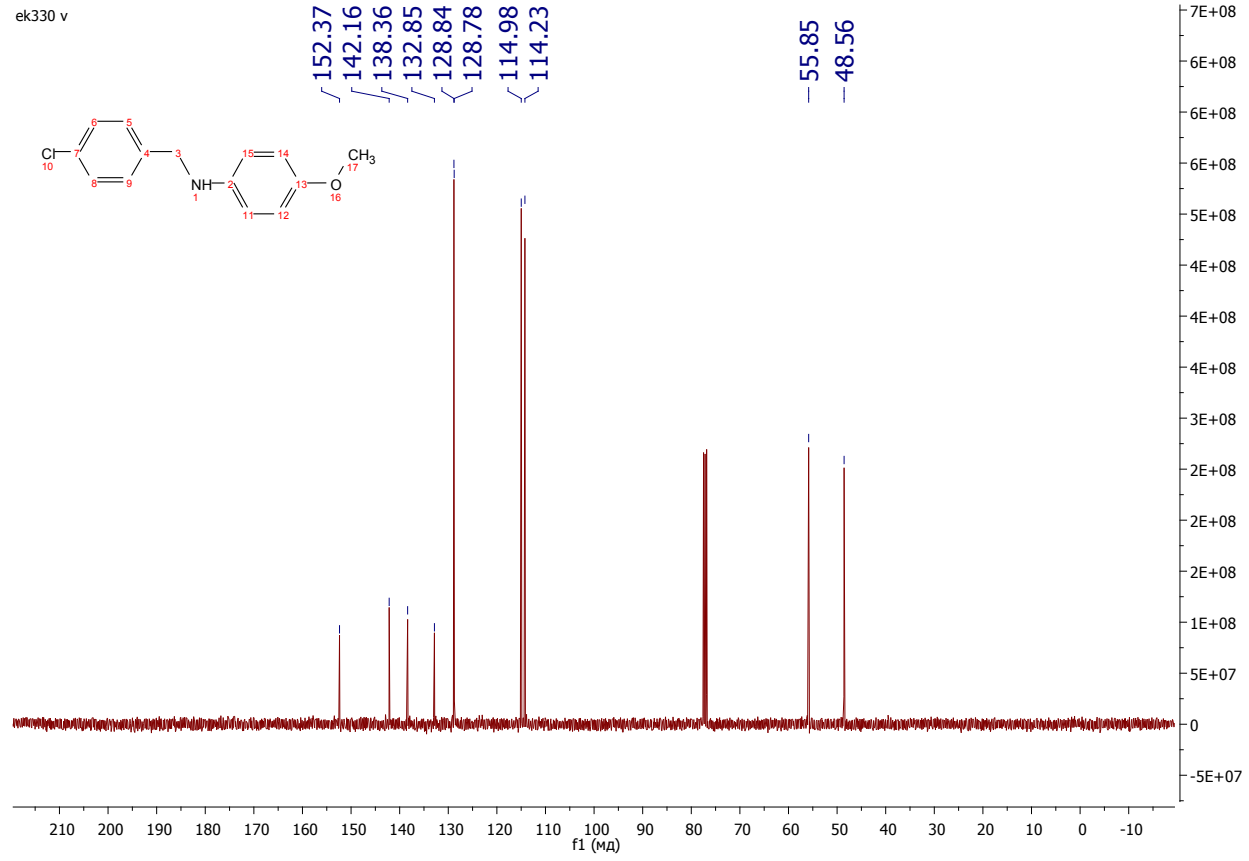
N-(4-bromophenyl)adamantan-2-amine (27)



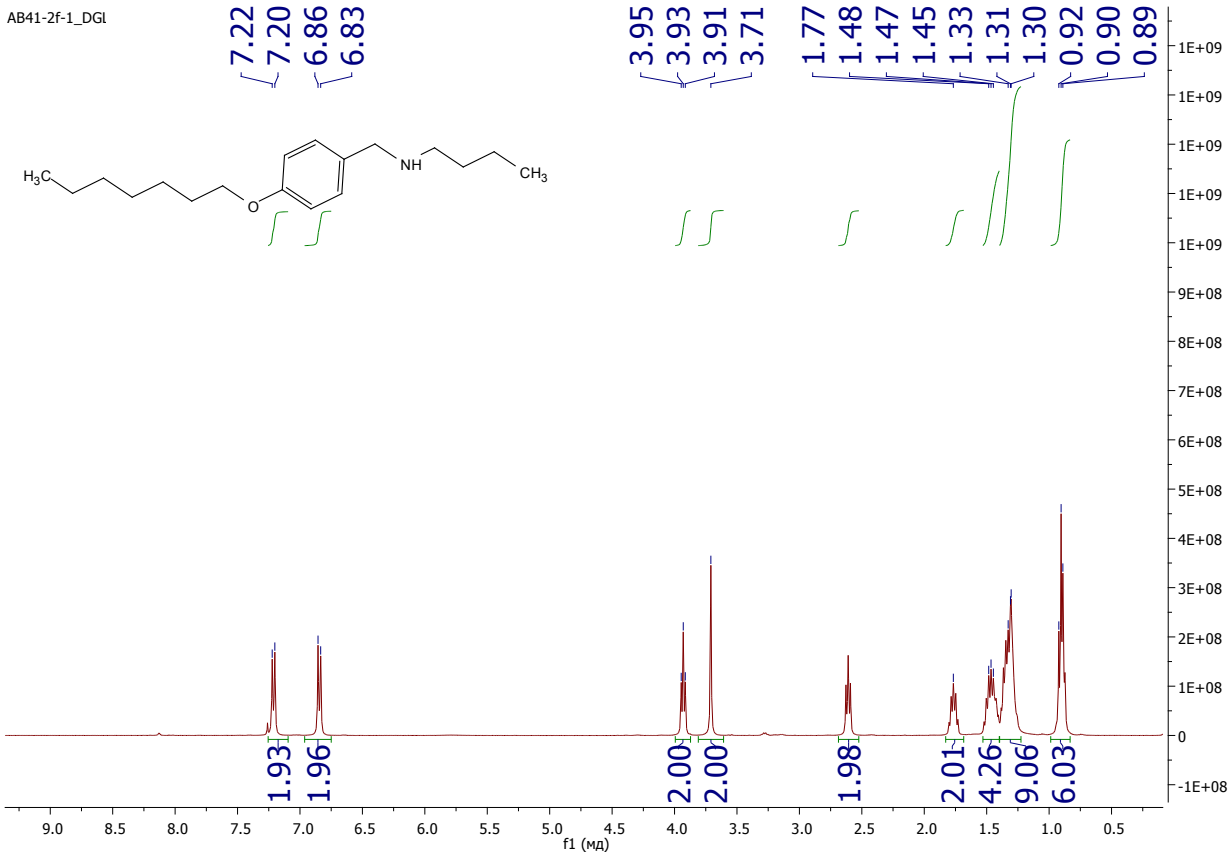


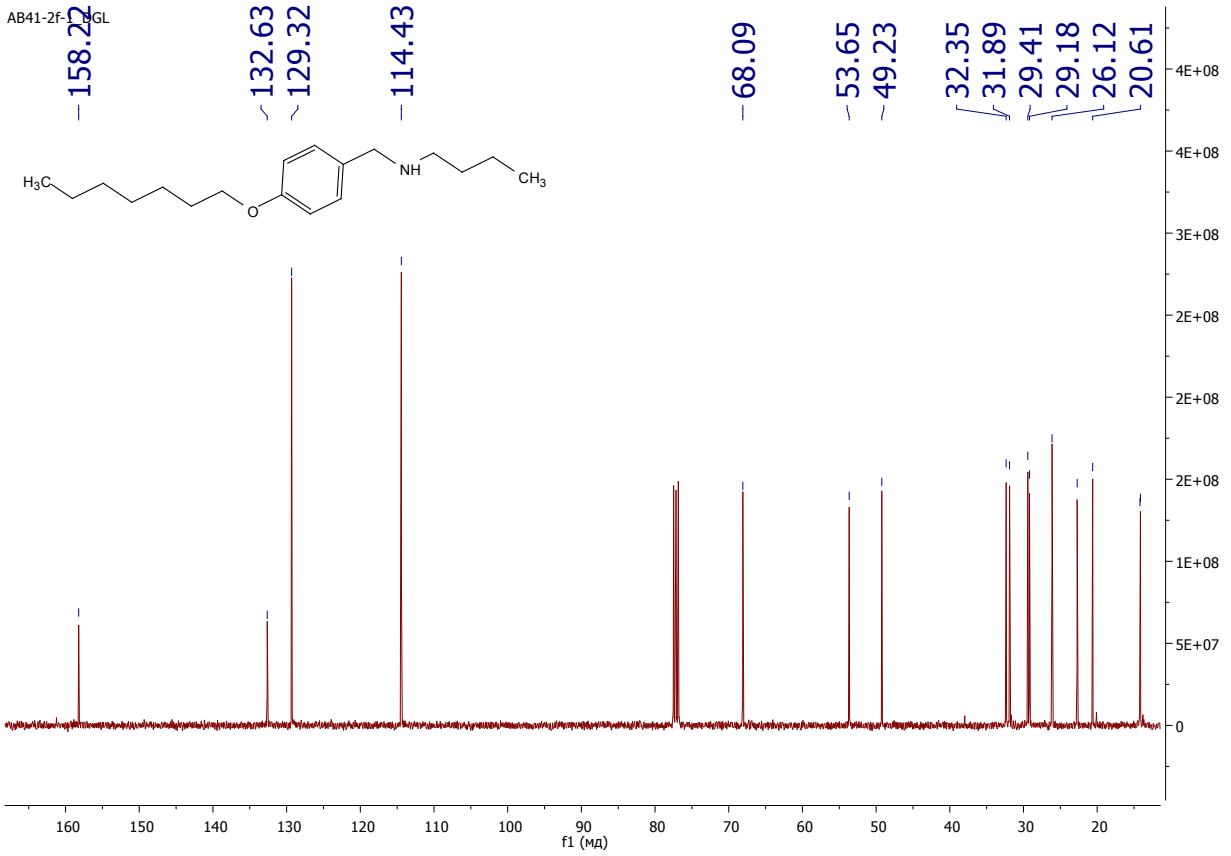
N-(4-chlorobenzyl)-4-methoxyaniline (28)





N-(4-(heptyloxy)benzyl)butan-1-amine (29)





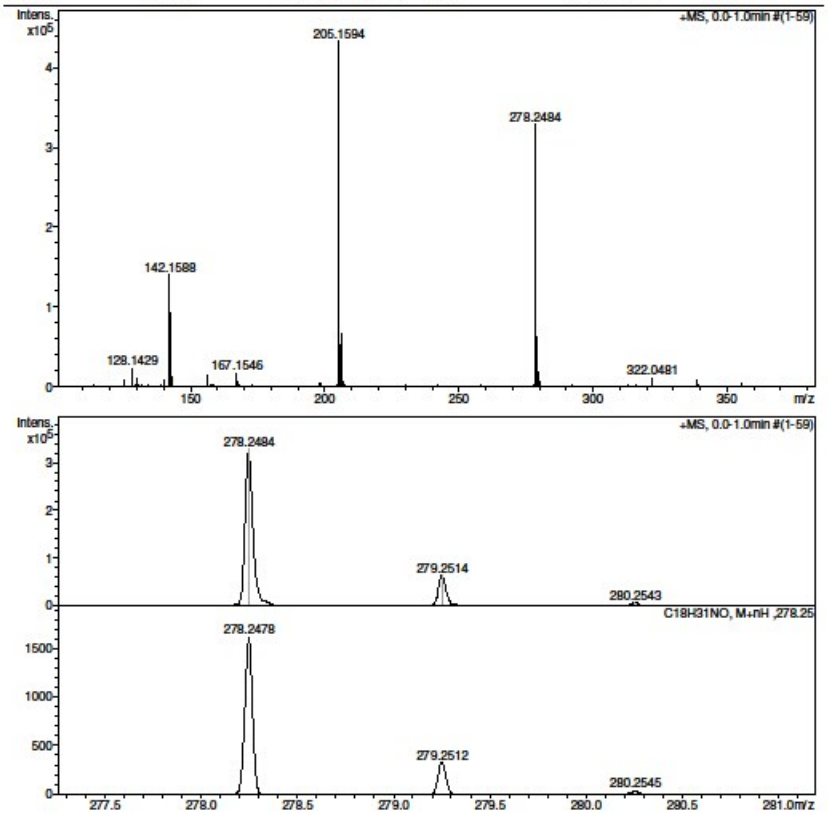
Display Report

Analysis Info

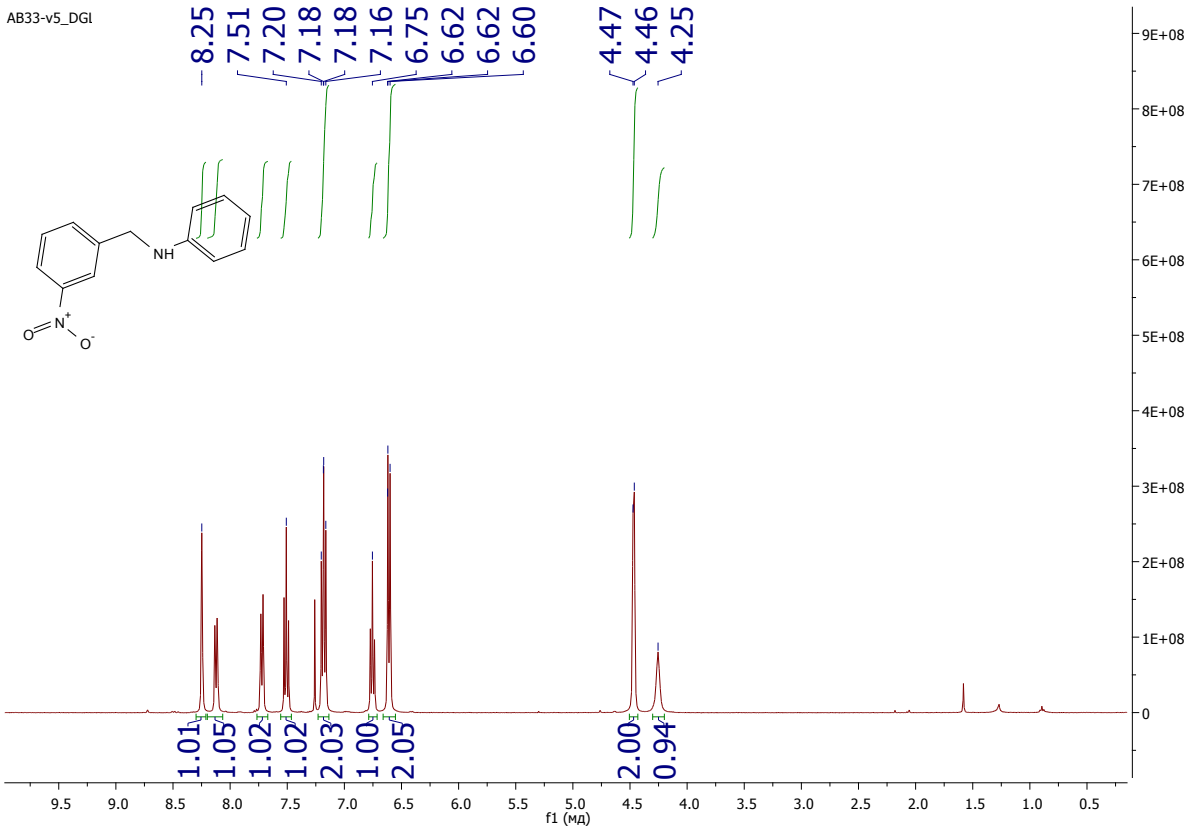
Analysis Name	D:\Data\Chizhov\INEOS\Chusov\abhep_&clblow.d	Acquisition Date	26.11.2018 13:37:56
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/CHIZ AB-Hep	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added.		

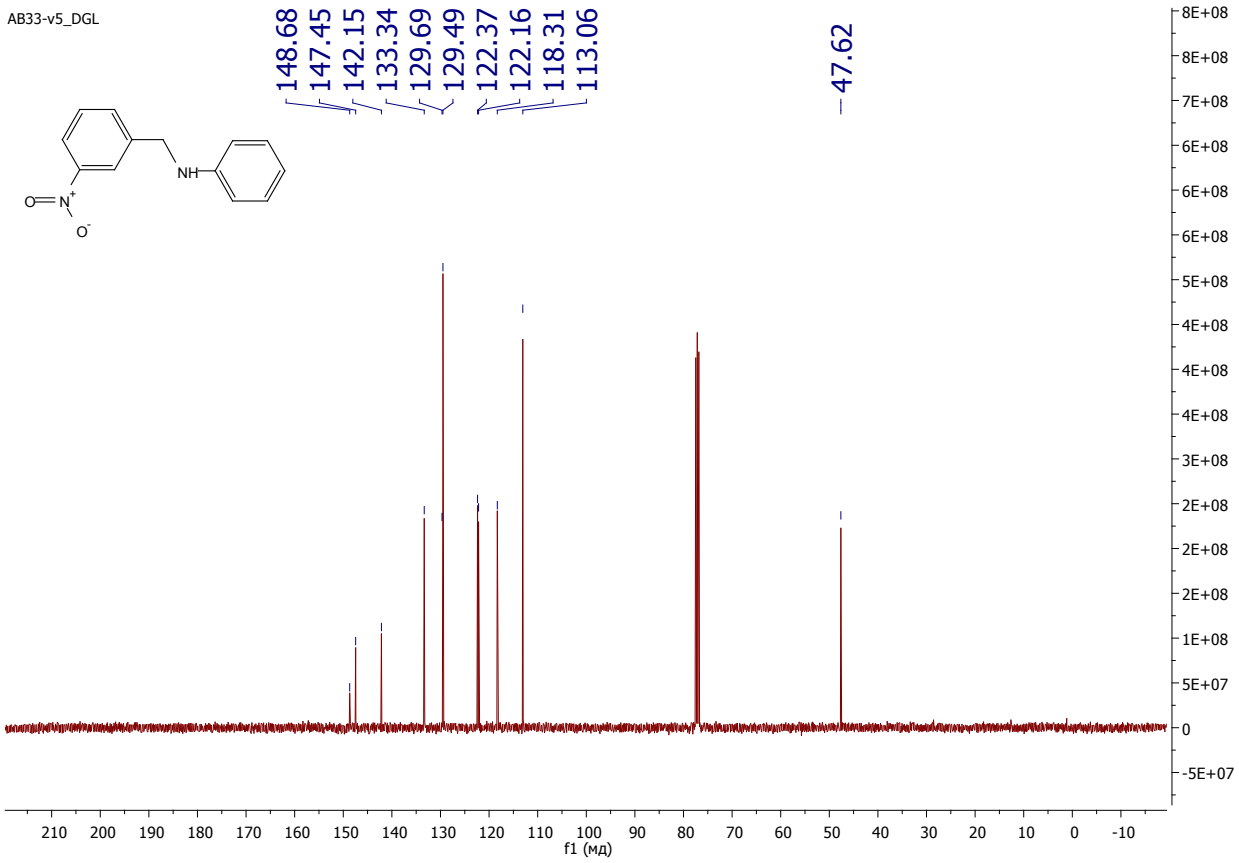
Acquisition Parameter

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-nitrobenzyl)aniline (30)





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