

# Ruthenium-Catalysed Reductive Amination without an External Hydrogen Source

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## Supporting information

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## 1. General information

All chemicals were obtained from Sigma-Aldrich and were used without further purification unless otherwise noted. Ruthenium(III) chloride was purchased from AlfaAesar. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia).

All the prepared compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectroscopy.  $^1\text{H}$  spectra were recorded in  $\text{CDCl}_3$  on Bruker Avance 300 or Bruker Avance 400 spectrometers;  $^{13}\text{C}$  spectra were recorded in  $\text{CDCl}_3$  on Bruker Avance 400 spectrometer at 101 MHz and chemical shifts are reported in parts per million relative to  $\text{CHCl}_3$  (7.26 and 77.0 ppm for  $^1\text{H}$  and  $^{13}\text{C}$  respectively).  $^{19}\text{F}$  spectra were recorded in  $\text{CDCl}_3$  on a Bruker Avance 300 spectrometer at 282 MHz and chemical shifts are reported in ppm relative to trifluoroacetic acid. Silica gel was purchased from Merck (60 GF  $_{254}$  for preparative TLC) and Acros Organics (0.06-0.200 mm for column chromatography).

## 2. General methods

**Preparation of the catalyst solution:** ruthenium(III) chloride hydrate (25 mg) was dissolved in 10 ml of acetonitrile. Aliquots of the resulting solution were used for most reactions.

### Procedure A:

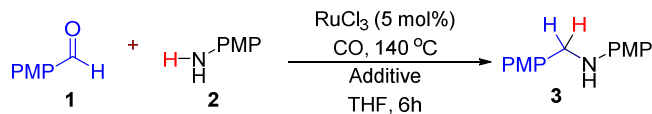
A glass chromatography vial was charged with 0.5 mol% of the catalyst, the corresponding solvent, 100 mol% of the amine and 100 mol% of the carbonyl compound. Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with the indicated pressure of CO. After the indicated time in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. The product was isolated by column chromatography or preparative thin-layer chromatography on silica gel.

### Procedure B:

A 10 ml stainless steel autoclave was charged with 0.5 mol% of the catalyst, the corresponding solvent, 100 mol% of the amine and 100 mol% of the carbonyl compound. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with the indicated pressure of CO and placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel.

### 3. Experimental section

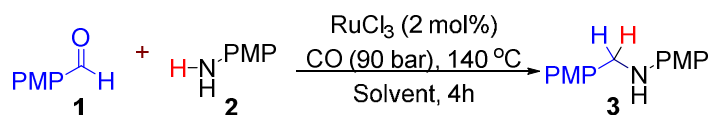
**Table 1.** Screening of ligands and optimization of the reaction pressure.



Entry <sup>a</sup>	Pressure, bar	Additive	Mol% of additive	Yield%, <b>3</b>
1	90	PPh <sub>3</sub>	10	22
2	90	Dppe	10	8
3	90	Dppp	10	6
4	90	PPh <sub>3</sub>	15	2
5	90	PPh <sub>3</sub>	20	1
6	90	PPh <sub>3</sub>	5	60
7	90	-	-	81
8	50	-	-	81
9	20	-	-	72
10	10	-	-	56
10 <sup>b</sup>	10	-	-	89

The experiments were carried out according to Procedure A: <sup>a</sup> 0.2 mmol scale. Yields were determined by NMR with internal standard. <sup>b</sup> reaction time was increased to 24 hours, 1 mol% RuCl<sub>3</sub> was used; PMP = *p*-methoxyphenyl

**Table 2.** Solvent screening

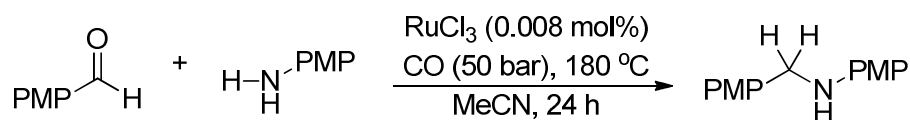


Entry	Solvent	Conditions	Yield %, <b>3</b>
1	Hexane		11
2	Dioxane		13
3	Water		13
4	Ethyl acetate		15
5	Toluene		20
6	Ethanol		20

7	Benzene		21
8	Solvent free		25
9	Methanol		26
10	Chloroform		27
11	Diethyl ether		33
12	Dichloromethane		37
13	Tetrahydrofuran		58
14	Isopropyl alcohol		61
15	Acetonitrile		96
16	Acetonitrile 1.0M	1.0 mol % RuCl <sub>3</sub>	96
17	Acetonitrile 1.0M	0.5% mol % RuCl <sub>3</sub>	95
18	Acetonitrile 1.0M	0.2% mol % RuCl <sub>3</sub>	45
19	Acetonitrile 1.0M	0.1% mol % RuCl <sub>3</sub>	14
20	Acetonitrile 1.0M	135 °C 0.5% mol % RuCl <sub>3</sub>	87
21	Acetonitrile 1.0M	130 °C 0.5% mol % RuCl <sub>3</sub>	67
22	Acetonitrile 1.0M	125 °C 0.5% mol % RuCl <sub>3</sub>	63
23	Acetonitrile 1.0M	125 °C 1% mol % RuCl <sub>3</sub>	94

The experiments were carried out according to Procedure A.

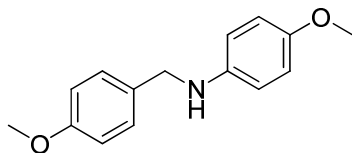
**Figure 1.** Identification of the turnover number using lowered loading of the catalyst.



A stock solution of the catalyst was prepared by dissolving of 1 mg of ruthenium trichloride hydrate in 10 ml of acetonitrile. A 10 ml stainless steel autoclave was charged with 0.008 mol% of the catalyst (1 ml of the stock solution), 0.6 g (4.9 mmol, 120 mol%) of *p*-methoxyaniline and 0.5 ml (4.1 mmol, 100 mol%) of *p*-methoxybenzaldehyde. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with the indicated pressure of CO. The reactor was placed into a preheated oil bath. After 24 h the reactor was cooled to room temperature and depressurized. Then 2 ml of solution reaction was taken from reactor and passed through a short silica gel plug. The solvent was removed under reduced pressure and the residue was analyzed by NMR. 23 % NMR yield (TON = 2465). Eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f = 0.42$ ).

## 4. Spectroscopic and analytical data

### 4-Methoxy-N-(4-methoxybenzyl)aniline (1a)



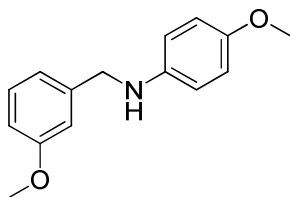
A glass chromatography vial was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (100  $\mu\text{l}$ ) and 4-methoxybenzaldehyde (24  $\mu\text{l}$ ; 26.7 mg; 196  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with the 30 atm of CO. After 22 h at 140  $^{\circ}\text{C}$  in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 95% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f$  = 0.42). Isolated as a yellow solid, 35 mg (73%). mp = 89-91  $^{\circ}\text{C}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J$  = 8.5 Hz, 2H), 6.90 (d,  $J$  = 8.5 Hz, 2H), 6.81 (d,  $J$  = 8.8 Hz, 2H), 6.63 (d,  $J$  = 8.8 Hz, 2H), 4.22 (s, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 3.70 – 3.55 (br s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 152.1, 142.4, 131.6, 128.7, 114.8, 114.0, 113.9, 55.7, 55.2, 48.6.

The obtained NMR data was in agreement with the literature report.<sup>1</sup>

### 4-Methoxy-N-(3-methoxybenzyl)aniline (1b)



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (100  $\mu\text{l}$ ) and 3-methoxybenzaldehyde (24  $\mu\text{l}$ ; 26.7 mg; 196  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 91% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f$  = 0.42). Isolated as a yellow oil, 32 mg (66%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J$  = 7.2 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.73-6.83 (m, 3H), 6.59 (d,  $J$  = 8.8 Hz, 2H), 4.24 (s, 2H), 3.78 (s, 3H), 3.72 (s, 3H), 3.45-3.55 (br s, 1H).

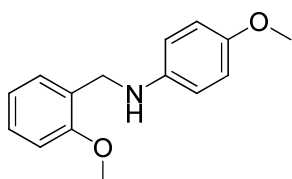
<sup>1</sup> Lei, Q.; Wei, Y.; Talwar, D.; Wang, C.; Xue, D.; Xiao, J. *Chem. Eur. J.* **2013**, *19*, 4021-4029.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.9, 152.2, 142.4, 141.5, 129.6, 119.8, 114.9, 114.2, 113.0, 112.6, 55.8, 55.2, 49.2.

HRMS (TOF ESI<sup>+</sup>): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{15}\text{H}_{18}\text{NO}_2^+$ ) calculated  $m/z$  244.1332, found:  $m/z$  244.1335

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): NH (3397), aromatic C=C (1601; 1585; 1512; 1456; 1437), aromatic C-H (821; 784; 693).

#### **4-Methoxy-N-(2-methoxybenzyl)aniline (1c)**



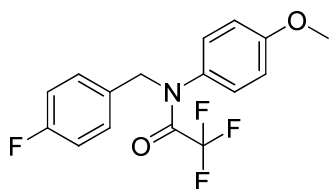
A 10 ml stainless steel autoclave was charged with: 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), 2-methoxybenzaldehyde (26 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%) and acetonitrile (100  $\mu\text{l}$ ). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 91% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.42$ ). Isolated as a yellow oil, 38 mg (80%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 7.4$  Hz, 1H), 7.26 (t,  $J = 7.8$  Hz, 1H), 6.95 – 6.89 (m, 2H), 6.79 (d,  $J = 7.8$  Hz, 2H), 6.64 (d,  $J = 8.9$  Hz, 2H), 4.30 (s, 2H), 3.87 (s, 3H), 3.75 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4, 152.1, 142.7, 129.0, 128.3, 127.6, 120.5, 114.8, 114.5, 110.2, 55.8, 55.3, 44.5.

The obtained NMR data was in agreement with the literature report.<sup>2</sup>

#### **2,2,2-Trifluoro-N-(4-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1d)**



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (48 mg; 393  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ) and 4-fluorobenzaldehyde (42  $\mu\text{l}$ ; 48.6 mg; 393  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 80% NMR yield. The product was dissolved in dichloromethane (0.5

<sup>2</sup> Fleischer, S.; Zhou, S.; Junge, K.; Beller, M. *Chem. Asian J.* **2011**, *6*, 2240-2245.

mL). The solution was cooled down to 0 °C and trifluoroacetic anhydride (200 µl) was added. After 15 minutes the solvent was removed under reduced pressure. Purification: preparative TLC, eluent: hexane/ethyl acetate 5/1 ( $R_f=0.5$ ). Isolated as a greenish oil, 90 mg (70%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.25 (m, 2H), 7.08 (t,  $J = 7.2$  Hz, 1H), 7.00 – 6.90 (m, 3H), 6.79 (d,  $J = 8.0$  Hz, 2H), 4.97 (s, 2H), 3.77 (s, 3H).

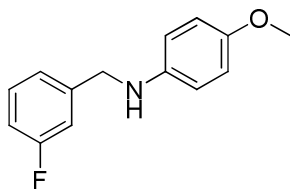
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  10.6, -40.1.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0 (d,  $J = 248.2$  Hz), 159.8, 157.3 (q,  $J = 35.5$  Hz), 131.4 (d,  $J = 3.6$  Hz), 130.9, 130.1 (d,  $J = 8.2$  Hz), 129.6, 124.4 (d,  $J = 3.6$  Hz), 122.3 (d,  $J = 14.7$  Hz), 116.5 (q,  $J = 288.4$  Hz), 115.4 (d,  $J = 21.6$  Hz), 114.2, 55.4, 48.6 (d,  $J = 2.9$  Hz).

HRMS (TOF ESI $^+$ ): for  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{13}\text{F}_4\text{NNaO}_2^+$ ) calculated  $m/z$  350.0780, found  $m/z$  350.0775.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): C=O (1703), aromatic C=C (1600; 1507; 1457; 1418), aromatic C-H (838, 694).

### *N*-(3-fluorobenzyl)-4-methoxyaniline (**1e**)



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (24 mg; 196 µmol; 100 mol%), ruthenium(III) chloride hydrate (100 µl of 2.5 mg/mL solution in acetonitrile; 0.95 µmol; 0.5 mol%), acetonitrile (100 µl) and 3-fluorobenzaldehyde (21 µl; 24.3 mg; 196 µmol; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 80% NMR yield (HMDS was used as internal standard). Purification: Preparative TLC eluent hexane/ethyl acetate/triethylamine 90/30/3 ( $R_f=0.7$ ). Isolated as a yellow oil, 25 mg (54%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.26 (m, 1H), 7.16 – 7.07 (m, 2H), 6.98 – 6.93 (m, 1H), 6.78 (d,  $J = 8.9$  Hz, 2H), 6.58 (d,  $J = 8.9$  Hz, 2H), 4.30 (s, 2H), 3.74 (s, 3H).

$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -35.34.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2 (d,  $J = 246.0$  Hz), 152.4, 142.6 (d,  $J = 6.8$  Hz), 142.1, 130.1 (d,  $J = 8.2$  Hz), 122.9 (d,  $J = 2.8$  Hz), 115.0, 114.4, 114.2 (d,  $J = 22.1$  Hz), 113.9, 55.8, 48.7.

The obtained NMR data was in agreement with the literature report.<sup>2</sup>

As an alternative route, the product was obtained as a trifluoroacetamide derivative. The reductive amination reaction mixture was transferred from the autoclave into a flask and the autoclave was washed with dichloromethane. The solvent was removed under reduced pressure. The product was dissolved in dichloromethane (0.5 mL). The solution was cooled down to 0 °C and trifluoroacetic anhydride (200 µl) was added. After 15 minutes the solvent was removed under reduced pressure. Purification: Preparative

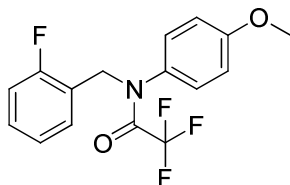
TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.55$ ). Isolated as a greenish oil, 47 mg (74%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.22 (m, 1H), 7.03 – 6.90 (m, 5H), 6.82 (d,  $J = 8.9$  Hz, 2H), 4.84 (s, 2H), 3.80 (s, 3H).

$^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  10.57, -34.80.

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J = 246.8$  Hz), 159.8, 137.8 (d,  $J = 7.1$  Hz), 131.0, 130.2 (d,  $J = 8.2$  Hz), 129.7, 124.9 (d,  $J = 2.7$  Hz), 116.5 (d,  $J = 288.4$  Hz), 116.1 (d,  $J = 21.6$  Hz), 115.2 (d,  $J = 21.1$  Hz), 114.3, 55.4, 55.1.

### ***2,2,2-Trifluoro-N-(2-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1f)***



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (100  $\mu\text{l}$ ) and 2-fluorobenzaldehyde (21  $\mu\text{l}$ ; 24.3 mg; 196  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^\circ\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 85% NMR yield. The product was dissolved in dichloromethane (0.5 mL). The solution was cooled down to 0  $^\circ\text{C}$  and trifluoroacetic anhydride (200  $\mu\text{l}$ ) was added. After 15 minutes the solvent was removed under reduced pressure. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.61$ ). Isolated as a yellow oil, 45 mg (70%).

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.22 (m, 2H), 7.09 (t,  $J = 7.4$  Hz, 1H), 6.98 (d,  $J = 9.9$  Hz, 1H), 6.94 (d,  $J = 8.8$  Hz, 2H), 6.80 (d,  $J = 8.8$  Hz, 2H), 4.97 (s, 2H), 3.78 (s, 3H).

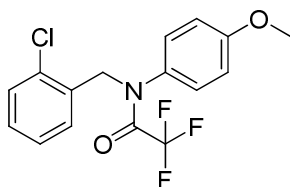
$^{19}\text{F NMR}$  (282 MHz,  $\text{CDCl}_3$ )  $\delta$  10.6, -40.1.

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0 (d,  $J = 248.0$  Hz), 159.8, 157.3 (q,  $J = 35.5$  Hz), 131.4 (d,  $J = 3.6$  Hz), 130.9, 130.1 (d,  $J = 8.1$  Hz), 129.6, 124.4 (d,  $J = 3.6$  Hz), 122.3 (d,  $J = 14.8$  Hz), 116.5 (q,  $J = 288.4$  Hz), 115.4 (d,  $J = 21.6$  Hz), 114.2, 55.4, 48.6 (d,  $J = 3.0$  Hz).

HRMS (TOF ESI $^+$ ): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{16}\text{H}_{14}\text{F}_4\text{NO}_2^+$ ) calculated  $m/z$  328.0955, found  $m/z$  328.0963. For  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{13}\text{F}_4\text{NNaO}_2^+$ ) calculated  $m/z$  350.0775, found  $m/z$  350.0783.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): C=O (1702), aromatic C=C (1608; 1587; 1510; 1457), aromatic C-H (838; 799; 759; 730).

### ***N-(2-chlorobenzyl)-2,2,2-trifluoro-N-(4-methoxyphenyl)acetamide (1g)***



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (100  $\mu\text{l}$ ) and 2-chlorobenzaldehyde (22  $\mu\text{l}$ ; 27.6 mg; 196  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 95% NMR yield (HMDS was used as internal standard). The product was dissolved in dichloromethane (0.5 mL). The solution was cooled down to 0  $^{\circ}\text{C}$  and trifluoroacetic anhydride (200  $\mu\text{l}$ ) was added. After 15 minutes the solvent was removed under reduced pressure. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.47$ ). Isolated as a yellow oil, 48 mg (70%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.16 (m, 4H), 6.94 (d,  $J = 8.6$  Hz, 2H), 6.78 (d,  $J = 8.6$  Hz, 2H), 5.07 (s, 2H), 3.78 (s, 3H).

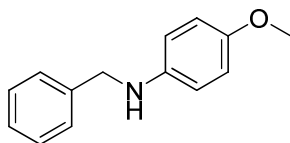
$^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  10.7.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.8, 157.3 (q,  $J = 35.9$  Hz), 134.3, 132.8, 131.0, 130.7, 129.6, 129.6, 129.4, 127.1, 116.5 (q,  $J = 288.4$  Hz), 114.1, 55.4, 52.2.

HRMS (TOF ESI $^+$ ): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{16}\text{H}_{14}\text{ClF}_3\text{NO}_2^+$ ) calculated m/z 344.0665, found m/z 344.0661. For  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{16}\text{H}_{13}\text{ClF}_3\text{NNaO}_2^+$ ) calculated m/z 366.0485, found m/z 366.0477.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): C=O (1701), aromatic C=C (1608; 1585; 1511; 1477).

### *N*-benzyl-4-methoxyaniline (1h)



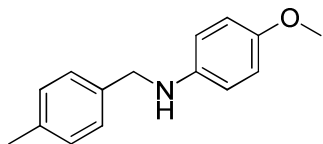
A glass chromatography vial was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 1 mol%), acetonitrile (200  $\mu\text{l}$ ) and benzaldehyde (20  $\mu\text{l}$ ; 21 mg; 196  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm of CO. After 22 h at 140  $^{\circ}\text{C}$  in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 85% NMR yield. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.47$ ). Isolated as a yellow oil, 29 mg (70%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.28 (m, 5H), 6.82 (d,  $J = 8.8$  Hz, 2H), 6.65 (d,  $J = 8.8$  Hz, 2H), 4.33 (s, 2H), 3.78 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.1, 55.8, 49.2.

The obtained NMR data was in agreement with the literature report.<sup>1</sup>

#### **4-Methoxy-N-(4-methylbenzyl)aniline (1i)**



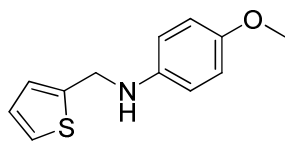
A glass chromatography vial was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 1 mol%), acetonitrile (200  $\mu\text{l}$ ) and 4-methylbenzaldehyde (23  $\mu\text{l}$ ; 23.6 mg; 196  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm of CO. After 22 h at 140  $^{\circ}\text{C}$  in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 81% NMR yield. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.4$ ). Isolated as a yellow oil, 33 mg (73%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (d,  $J = 7.8$  Hz, 2H), 7.17 (d,  $J = 7.8$  Hz, 2H), 6.80 (d,  $J = 8.8$  Hz, 2H), 6.64 (d,  $J = 8.8$  Hz, 2H), 4.25 (s, 2H), 3.76 (s, 3H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 142.2, 136.9, 136.4, 129.3, 127.6, 114.9, 114.4, 55.8, 49.2, 21.1.

The obtained NMR data was in agreement with the literature report.<sup>1</sup>

#### **4-Methoxy-N-(thiophen-2-ylmethyl)aniline (1j)**



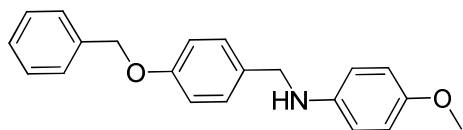
A glass chromatography vial was charged with 4-methoxyaniline (24 mg; 196  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (100  $\mu\text{l}$ ) and 2-thiophenecarboxaldehyde (18  $\mu\text{l}$ ; 22 mg; 196  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm of CO. After 22 h at 140  $^{\circ}\text{C}$  in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 92% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.5$ ). Isolated as a yellow oil, 34 mg (79%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 – 7.19 (m, 1H), 7.03 – 6.95 (m, 2H), 6.80 (d,  $J = 8.9$  Hz, 2H), 6.66 (d,  $J = 8.9$  Hz, 2H), 4.48 (s, 2H), 3.76 (s, 3H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 143.0, 141.5, 126.8, 125.1, 124.6, 115.8, 114.8, 55.7, 44.6

The obtained NMR data was in agreement with the literature report.<sup>3</sup>

### *N*-(4-(benzyloxy)benzyl)-4-methoxyaniline (**1k**)



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (24 mg; 196  $\mu$ mol; 100 mol%), 4-benzyloxybenzaldehyde (41 mg; 196  $\mu$ mol; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu$ l of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu$ mol; 0.5 mol%) and acetonitrile (100  $\mu$ l). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}$ C. After 22 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1 mL). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 81% NMR yield. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.39$ ). Isolated as a yellow solid, 35 mg (56%). mp = 100-102  $^{\circ}$ C.

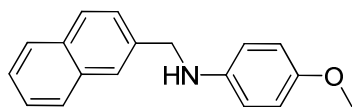
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.26 (m, 7H), 6.98 (d,  $J$  = 8.1 Hz, 2H), 6.81 (d,  $J$  = 8.5 Hz, 2H), 6.64 (d,  $J$  = 8.5 Hz, 2H), 5.08 (s, 2H), 4.23 (s, 2H), 3.76 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.1, 152.3, 142.2, 137.1, 131.8, 129.0, 128.6, 128.0, 127.5, 115.0, 114.9, 114.4, 70.1, 55.8, 48.9.

HRMS (TOF ESI<sup>+</sup>): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{21}\text{H}_{22}\text{NO}_2^+$ ) calculated  $m/z$  320.1645, found  $m/z$  320.1642. For  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{21}\text{H}_{21}\text{NNaO}_2^+$ ) calculated  $m/z$  342.1465, found 342.1469.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): NH (3393), aromatic C=C (1683; 1653; 1558; 1506; 1456), aromatic C-H (821; 757; 738; 698).

### 4-methoxy-*N*-(naphthalen-2-ylmethyl)aniline (**1l**)



A glass chromatography vial was charged with 4-methoxyaniline (24 mg; 196  $\mu$ mol; 100 mol%), 2-naphthaldehyde (30 mg; 196  $\mu$ mol; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu$ l of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu$ mol; 0.5 mol%) and acetonitrile (100  $\mu$ l). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm of CO. After 22 h at 140  $^{\circ}$ C in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 90% NMR yield. Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.37$ ). Isolated as a yellow oil, 42 mg (81%);

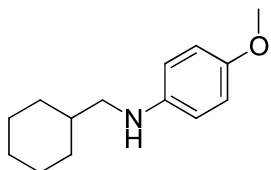
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86-7.81 (m, 4H), 7.53-7.48 (m, 3H), 6.81 (d,  $J$  = 8.8 Hz, 2H), 6.66 (d,  $J$  = 8.8 Hz, 2H), 4.46 (s, 2H), 3.76 (s, 3H).

<sup>3</sup> Deng, J.; Mo, L-P.; Zhao, F-Y.; Hou, L-L.; Yang, L.; Zhang, Z-H. *Green Chem.* **2011**, *13*, 2576–2584.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 142.5, 137.3, 133.5, 132.8, 128.3, 127.8, 127.7, 126.2, 126.0, 125.9, 125.7, 114.9, 114.2, 55.8, 49.4.

The obtained NMR data was in agreement with the literature report.<sup>4</sup>

### *N*-(cyclohexylmethyl)-4-methoxyaniline (**1m**)



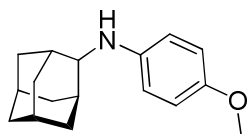
A glass chromatography vial was charged with 4-methoxyaniline (48 mg; 392  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ) and cyclohexanecarboxaldehyde (47.6  $\mu\text{l}$ ; 44.1 mg; 392  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with the 30 atm of CO. After 22 h at 140  $^\circ\text{C}$  in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 70% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.47$ ). Isolated as a yellow oil, 55 mg (64%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (d,  $J = 8.8$  Hz, 2H), 6.59 (d,  $J = 8.8$  Hz, 2H), 3.76 (s, 3H), 3.48 (br s, 1H), 2.92 (d,  $J = 6.6$  Hz, 2H), 1.85-1.69 (m, 5H), 1.68-1.49 (m, 1H), 1.33 – 1.17 (m, 3H), 1.04-0.88 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.9, 142.9, 114.9, 114.0, 55.9, 51.7, 37.6, 31.4, 26.6, 26.0.

The obtained NMR data was in agreement with the literature report.<sup>5</sup>

### *N*-(4-methoxyphenyl)adamantan-2-amine (**1n**)



A 10 ml stainless steel autoclave was charged with *p*-anisidine (30 mg; 240  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (120  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.2  $\mu\text{mol}$ ; 0.5 mol %), acetonitrile (200  $\mu\text{l}$ ) and adamantanone (36 mg; 240  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^\circ\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 93% NMR yield (HMDS was used as internal standard). The product was purified via filtration through thin layer of silica gel in hexane/ethyl acetate/triethylamine (6:1:0.1);  $R_f = 0.46$ ; Isolated as a grey solid, 43 mg (70%); mp = 100-102  $^\circ\text{C}$ .

<sup>4</sup> Fleischer, S.; Zhou, S.; Junge, K.; Beller, M. *Chem. Asian J.* **2011**, *6*, 2240-2245.

<sup>5</sup> Chusov, D.; List, B. *Angew. Chem. Int. Ed.* **2014**, *53*, 5199-5201.

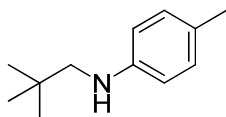
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta$  6.78 (d,  $J$  = 8.8 Hz, 2H), 6.60 (d,  $J$  = 8.8 Hz, 2H), 3.75 (s, 3H), 3.48 (s, 1H), 2.08 – 1.72 (m, 13H), 1.59 (d,  $J$  = 12.6 Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 141.4, 114.9, 114.7, 57.9, 55.8, 37.8, 37.5, 31.6, 31.5, 27.5, 27.4.

HRMS (TOF ESI $^+$ ): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{17}\text{H}_{24}\text{NO}^+$ ) calculated  $m/z$  258.1852, found  $m/z$  258.1853.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): NH (3395), methylene CH (2952; 2922; 2852), aromatic C=C (1615; 1511; 1466), aromatic C-H (814; 747; 654).

#### **4-methyl-N-neopentylaniline (1o)**



A 10 ml stainless steel autoclave was charged with *p*-toluidine (42 mg; 392  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ) and pivalaldehyde (42.7  $\mu\text{l}$ ; 33.8 mg; 392  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 140  $^\circ\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 99% NMR yield (HMDS was used as internal standard). The product was purified by passing through a short silica gel plug in dichloromethane and washed with dichloromethane. The solvent was evaporated under reduced pressure. Isolated as a yellow oil, 69 mg (99%).

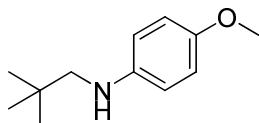
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.00 (d,  $J$  = 8.2 Hz, 2H), 6.57 (d,  $J$  = 8.2 Hz, 2H), 2.89 (s, 2H), 2.25 (s, 3H), 1.01 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 129.7, 126.1, 112.8, 56.3, 31.9, 27.7, 20.4.

HRMS (TOF ESI $^+$ ): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{12}\text{H}_{20}\text{N}^+$ ) calculated  $m/z$  178.1590, found  $m/z$  178.1597.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): NH (3418), methyl CH (2954; 2865), aromatic C=C (1619; 1520; 1476), aromatic C-H (805).

#### **4-Methoxy-N-neopentylaniline (1p)**



A 10 ml stainless steel autoclave was charged with 4-methoxyaniline (48 mg; 392  $\mu\text{mol}$ ; 100 mol%), ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ), and pivalaldehyde (42.7  $\mu\text{l}$ ; 33.8 mg; 392  $\mu\text{mol}$ ; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed

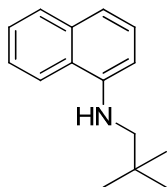
into an oil bath preheated to 140 °C. After 22 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 99% NMR yield (HMDS was used as internal standard). The product was purified by passing through a short silica gel plug in dichloromethane and washed with dichloromethane. The solvent was evaporated under reduced pressure. Isolated as a yellow oil, 75 mg (99%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.80 (d,  $J = 8.8$  Hz, 2H), 6.62 (d,  $J = 8.8$  Hz, 2H), 3.76 (s, 3H), 2.87 (s, 2H), 1.02 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.8, 143.6, 114.9, 113.9, 57.1, 55.9, 31.8, 27.7.

The obtained NMR data was in agreement with the literature report.<sup>6</sup>

### *N*-neopentyl-naphthalen-1-amine (1q)



A glass chromatography vial was charged with 1-naphthylamine (56 mg; 392  $\mu\text{mol}$ ) 100 mol%, ruthenium(III) chloride hydrate (200  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.96  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ) and pivalaldehyde (42.7  $\mu\text{l}$ ; 33.8 mg; 392  $\mu\text{mol}$ ; 100 mol%). Six vials were placed into a cassette inside a 100 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 atm of  $\text{CO}$ , and then charged with the 50 atm of  $\text{CO}$ . After 22 h at 140 °C in the oven, the reactor was cooled to room temperature and depressurized. The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 93% NMR yield (HMDS was used as internal standard). Purification: preparative TLC eluent toluene/ ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.95$ ). Isolated as a yellow oil, 69 mg (81%)

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (t,  $J = 9.8$  Hz, 2H), 7.56 – 7.46 (m, 2H), 7.42 (t,  $J = 7.9$  Hz, 1H), 7.29 (d,  $J = 8.2$  Hz, 1H), 6.70 (d,  $J = 7.5$  Hz, 1H), 4.65 – 4.20 (br s, 1H), 3.12 (s, 2H), 1.18 (s, 9H).

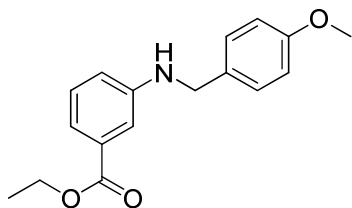
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 134.4, 128.8, 126.8, 125.7, 124.7, 123.5, 119.8, 117.0, 104.2, 55.9, 31.8, 28.0.

The obtained NMR data was in agreement with the literature report.<sup>7</sup>

### *Ethyl 3-(4-methoxybenzylamino)benzoate (1r)*

<sup>6</sup> List, B; Chusov, D. Patent: WO2014/90806 A1, 2014.

<sup>7</sup> Maeda, K.; Horikoshi, Y.; Hayashi, M.; Mori, Y.; Nagano, H. *J. Chem. Soc., Perkin Trans. 1*, 1996, 789-792.



A 10 ml stainless steel autoclave was charged with ethyl 3-aminobenzoate (29  $\mu$ l; 32.4 mg; 196  $\mu$ mol; 100 mol%), ruthenium(III) chloride hydrate (100  $\mu$ l of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu$ mol; 0.5 mol%), acetonitrile (100  $\mu$ l), 4-methoxybenzaldehyde (24  $\mu$ l; 26.7 mg; 196  $\mu$ mol; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}$ C. After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 90% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f$ =0.47). Isolated as a yellow solid, 43 mg (77%). mp = 102-104  $^{\circ}$ C.

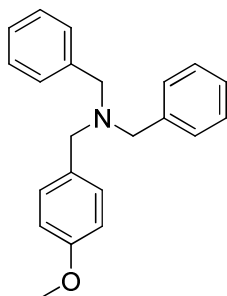
$^1$ H NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40 (d,  $J$  = 7.7 Hz, 1H), 7.34 (s, 1H), 7.29 (d,  $J$  = 8.5 Hz, 2H), 7.22 (t,  $J$  = 7.8 Hz, 1H), 6.89 (d,  $J$  = 8.6 Hz, 2H), 6.79 (dd,  $J$  = 8.0, 1.7 Hz, 1H), 4.35 (q,  $J$  = 7.1 Hz, 2H), 4.29 (s, 2H), 3.81 (s, 3H), 1.38 (t,  $J$  = 7.1 Hz, 3H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  167.0, 159.0, 148.1, 131.4, 130.9, 129.2, 128.9, 118.6, 117.1, 114.1, 113.6, 60.8, 55.3, 47.7, 14.3.

HRMS (TOF ESI $^+$ ): for  $[M+H]^+$  ( $C_{17}H_{20}NO_3^+$ ) calculated m/z 286.1438, found m/z 286.1444. For  $[M+Na]^+$  ( $C_{17}H_{19}NNaO_3^+$ ) calculated 308.1257, found 308.1261

IR ( $\nu_{max}$ ,  $cm^{-1}$ ): NH (3388), CH (2953; 2924; 2853), C=O (1703), aromatic C=C (1608; 1582; 1510; 1464; 1456), aromatic C-H (823; 754; 720).

### *N,N*-dibenzyl-1-(4-methoxyphenyl)methanamine (1s)



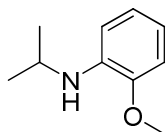
A 10 ml stainless steel autoclave was charged with ruthenium(III) chloride hydrate (100  $\mu$ l of 2.5 mg/mL solution in acetonitrile; 0.95  $\mu$ mol; 0.5 mol%), acetonitrile (100  $\mu$ l), dibenzylamine (37.8  $\mu$ l; 38.7 mg; 196  $\mu$ mol; 100 mol%) and 4-methoxybenzaldehyde (24  $\mu$ l; 26.7 mg; 196  $\mu$ mol; 100 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^{\circ}$ C. After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 93% NMR yield (HMDS was used as internal standard). Purification: preparative TLC, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f$ =0.6). Isolated as yellow oil, 42 mg (68%)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 7.3$  Hz, 4H), 7.39-7.35 (m, 6H), 7.27 (d,  $J = 6.1$  Hz, 2H), 6.90 (d,  $J = 8.3$  Hz, 2H), 3.82 (s, 3H), 3.58 (s, 4H), 3.53 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 131.6, 129.9, 128.8, 128.2, 126.8, 113.6, 57.8, 57.2, 55.3.

The obtained NMR data was in agreement with the literature report.<sup>8</sup>

### *N-isopropyl-2-methoxyaniline (1t)*



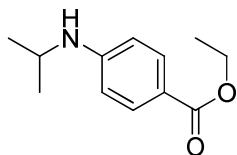
A 10 ml stainless steel autoclave was charged with *o*-anisidine (30 mg; 240  $\mu\text{mol}$ ) 100 mol%, ruthenium(III) chloride hydrate (120  $\mu\text{l}$  of 2.5 mg/mL solution in acetonitrile; 1.2  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (200  $\mu\text{l}$ ) and acetone (22  $\mu\text{l}$ ; 17 mg; 290  $\mu\text{mol}$ ; 120 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^\circ\text{C}$ . After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 99% NMR yield (HMDS was used as internal standard). Purification: filtration through a short silica gel plug;  $R_f = 0.64$ , eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); Isolated as a yellow oil, 39 mg (98%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta$  6.91 (t,  $J = 7.6$  Hz, 1H), 6.80 (d,  $J = 7.8$  Hz, 1H), 6.68 (t,  $J = 7.8$  Hz, 2H), 3.87 (s, 3H), 3.66 (sept,  $J = 6.2$  Hz, 1H), 1.28 (d,  $J = 6.2$  Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.8, 137.4, 121.3, 115.9, 110.3, 109.5, 55.3, 43.8, 23.1

The obtained NMR data was in agreement with the literature report.<sup>9</sup>

### *Ethyl 4-(isopropylamino)benzoate (1u)*



A 10 ml stainless steel autoclave was charged with ethyl 4-aminobenzoate (1 g; 6.0 mmol; 100 mol%), ruthenium(III) chloride hydrate (7.8 mg; 30  $\mu\text{mol}$ ; 0.5 mol%), acetonitrile (0.8 ml) and acetone (0.53 ml; 420 mg; 7.2 mmol; 120 mol%). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140  $^\circ\text{C}$ . After 22 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a

<sup>8</sup> Zhou, S.; Junge, K.; Addis, D.; Das, S.; Beller, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 9507–9510.

<sup>9</sup> Reddy, T.J.; Leclair, M.; Proulx, M. *Synlett* **2005**, 583–586.

flask and the autoclave was washed with dichloromethane (2x1mL). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 98% NMR yield (HMDS was used as internal standard). Purification: column chromatography, eluent: hexane/ethyl acetate/triethylamine (6:1:0.1);  $R_f = 0.31$ . Isolated as a yellow oil, 1.112 g (90%).

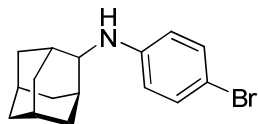
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta$  7.86 (d,  $J = 8.8$  Hz, 2H), 6.52 (d,  $J = 8.8$  Hz, 2H), 4.31 (q,  $J = 7.1$  Hz, 2H), 4.09 (br s, 1H), 3.68 (sept,  $J = 6.3$  Hz, 1H), 1.35 (t,  $J = 7.1$  Hz, 3H), 1.22 (d,  $J = 6.3$  Hz, 6H).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 151.1, 131.5, 118.1, 111.7, 60.1, 43.9, 22.7, 14.5.

HRMS (TOF ESI<sup>+</sup>): for  $[\text{M}+\text{H}]^+$  ( $\text{C}_{12}\text{H}_{18}\text{NO}_2^+$ ) calculated  $m/z$  208.1332, found  $m/z$  208.1329. For  $[\text{M}+\text{Na}]^+$  ( $\text{C}_{12}\text{H}_{17}\text{NNaO}_2^+$ ) calculated  $m/z$  230.1151, found 230.1148.

IR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): NH (3366), CH (2977; 2946; 2904; 2874), C=O (1687), aromatic C=C (1602; 1530; 1456), aromatic C-H (876; 838; 771; 701).

### *N*-(4-bromophenyl)adamantan-2-amine (**1v**)



A 100 ml stainless steel autoclave was charged with 4-bromoaniline (520 mg; 3.03 mmol; 100 mol%), adamantanone (500 mg; 3.33 mmol; 110 mol%), ruthenium(III) chloride hydrate (15.8 mg; 60.5  $\mu\text{mol}$ ; 2 mol%), acetonitrile (3.2 ml) and 4 Å molecular sieves (292 mg). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 30 atm CO. The reactor was placed into an oil bath preheated to 140 °C. After 22 h, 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). The solvent was removed under reduced pressure and the residue was analyzed by NMR. Full conversion, 93% NMR yield (HMDS was used as internal standard). The pure product was obtained after crystallization from acetonitrile; the mother liquor was purified by column chromatography, eluent: toluene/ethyl acetate/triethylamine 20/1/0.1 ( $R_f=0.95$ ). Isolated as a white solid, 836 mg (90%). mp=109 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (d,  $J = 8.6$  Hz, 2H), 6.49 (d,  $J = 8.6$  Hz, 2H), 3.50 (s, 1H), 2.01 (s, 2H), 1.93 – 1.75 (m, 10H), 1.61 (d,  $J = 12.6$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.2, 131.9, 114.7, 108.2, 56.9, 37.6, 37.3, 31.5, 31.4, 27.4, 27.3.

The obtained NMR data was in agreement with the literature report.<sup>10</sup>

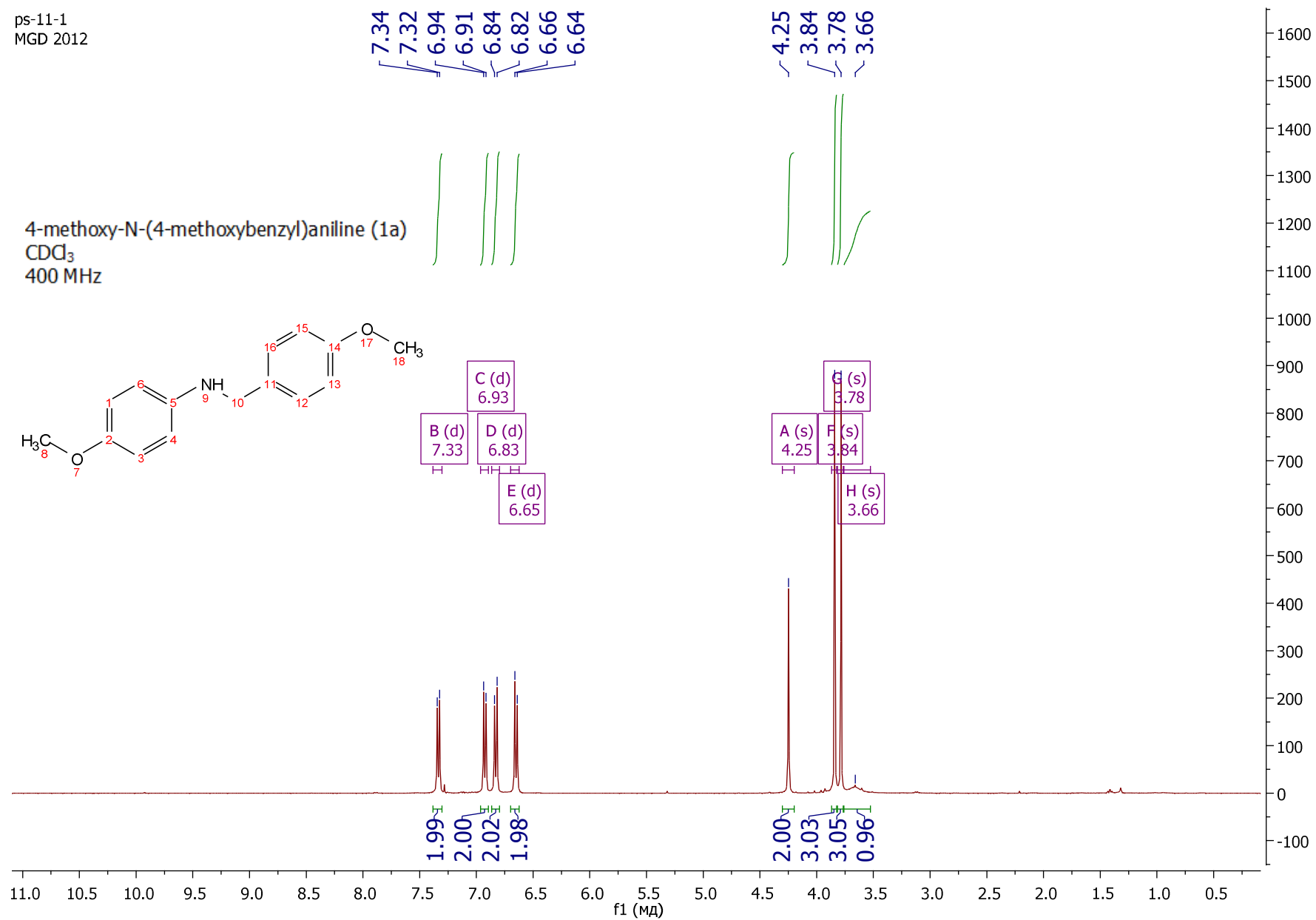
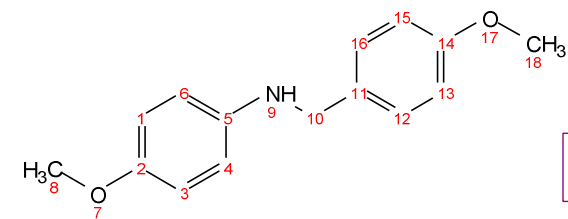
<sup>10</sup> Averin, A.D.; Ulanovskaya M.A.; Kovalev V.V.; Buryak, A.K.; Orlinson, B.S.; Novakov, I.A.; Beletskaya, I.P. *Russ. J. Org. Chem.* **2010**, *46*, 64–72.

***$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR, IR and high-resolution  
mass spectra of obtained compounds***

# 4-methoxy-N-(4-methoxybenzyl)aniline (1a)

ps-11-1  
MGD 2012

4-methoxy-N-(4-methoxybenzyl)aniline (1a)  
CDCl<sub>3</sub>  
400 MHz

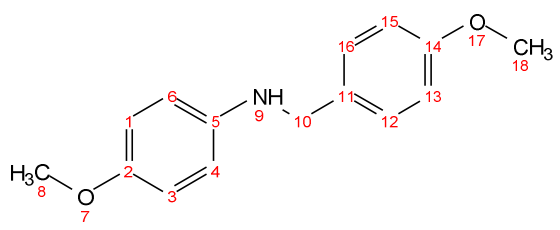


ps 11 1 c

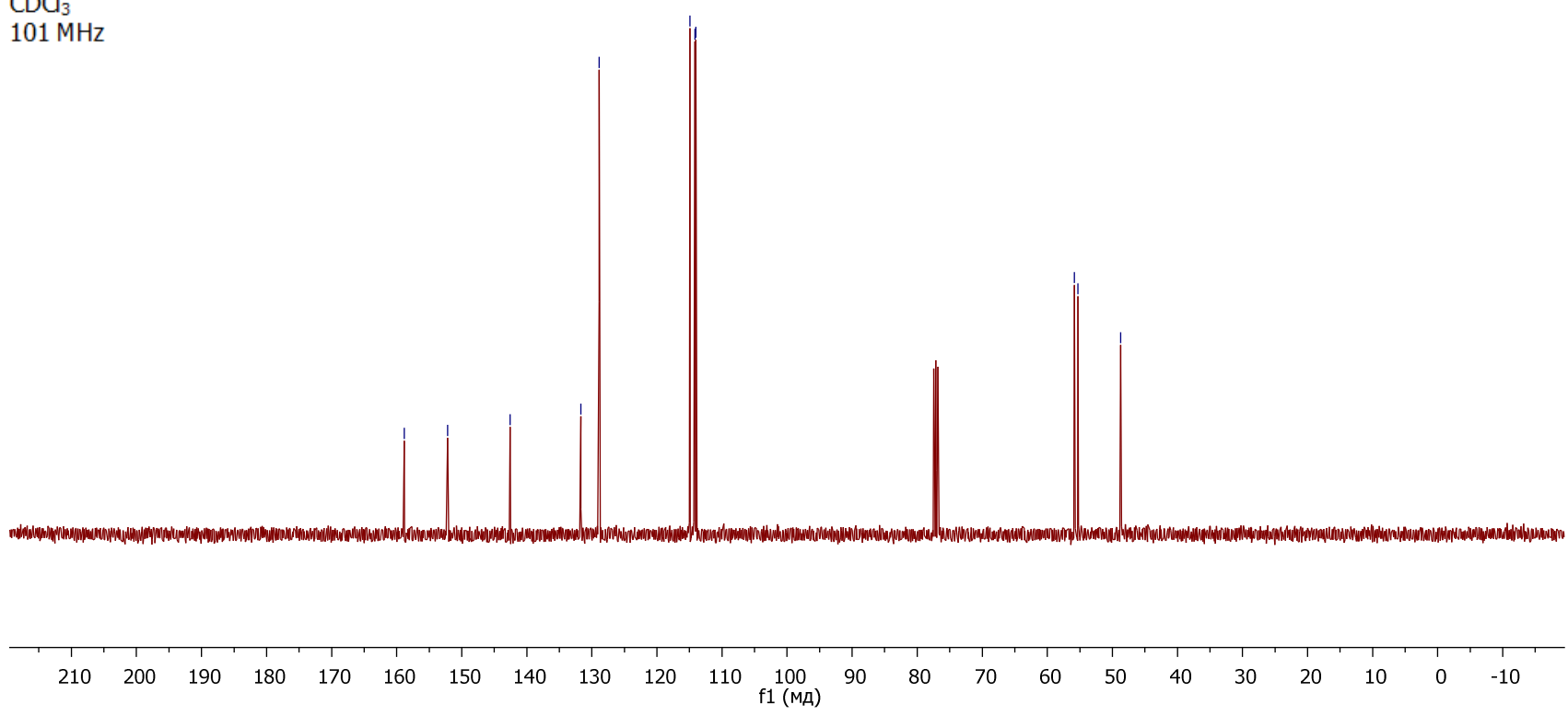
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142.56  
131.71  
128.87  
114.92  
114.16  
114.01

55.82  
55.31  
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7000  
6000  
5000  
4000  
3000  
2000  
1000  
0  
-1000

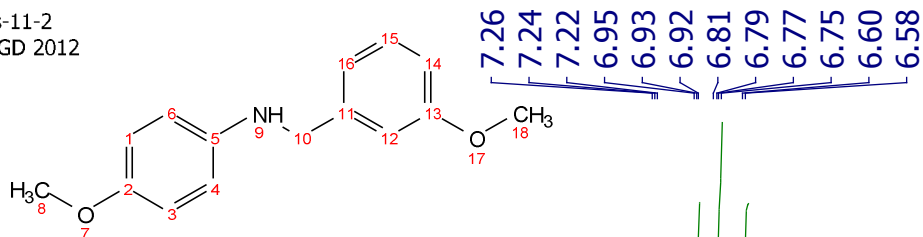


4-methoxy-N-(4-methoxybenzyl)aniline (1a)  
CDCl<sub>3</sub>  
101 MHz

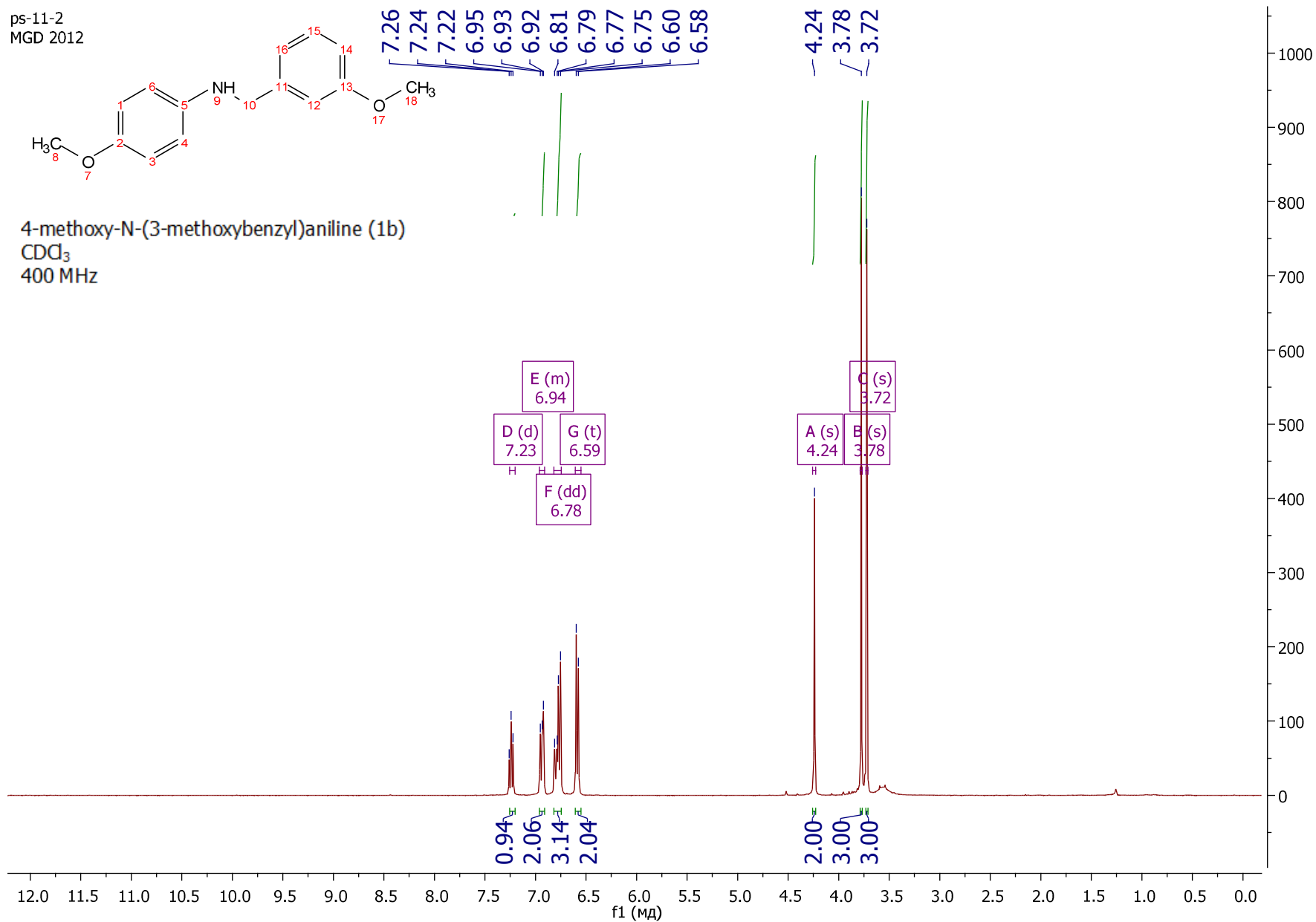


# 4-methoxy-N-(3-methoxybenzyl)aniline (1b)

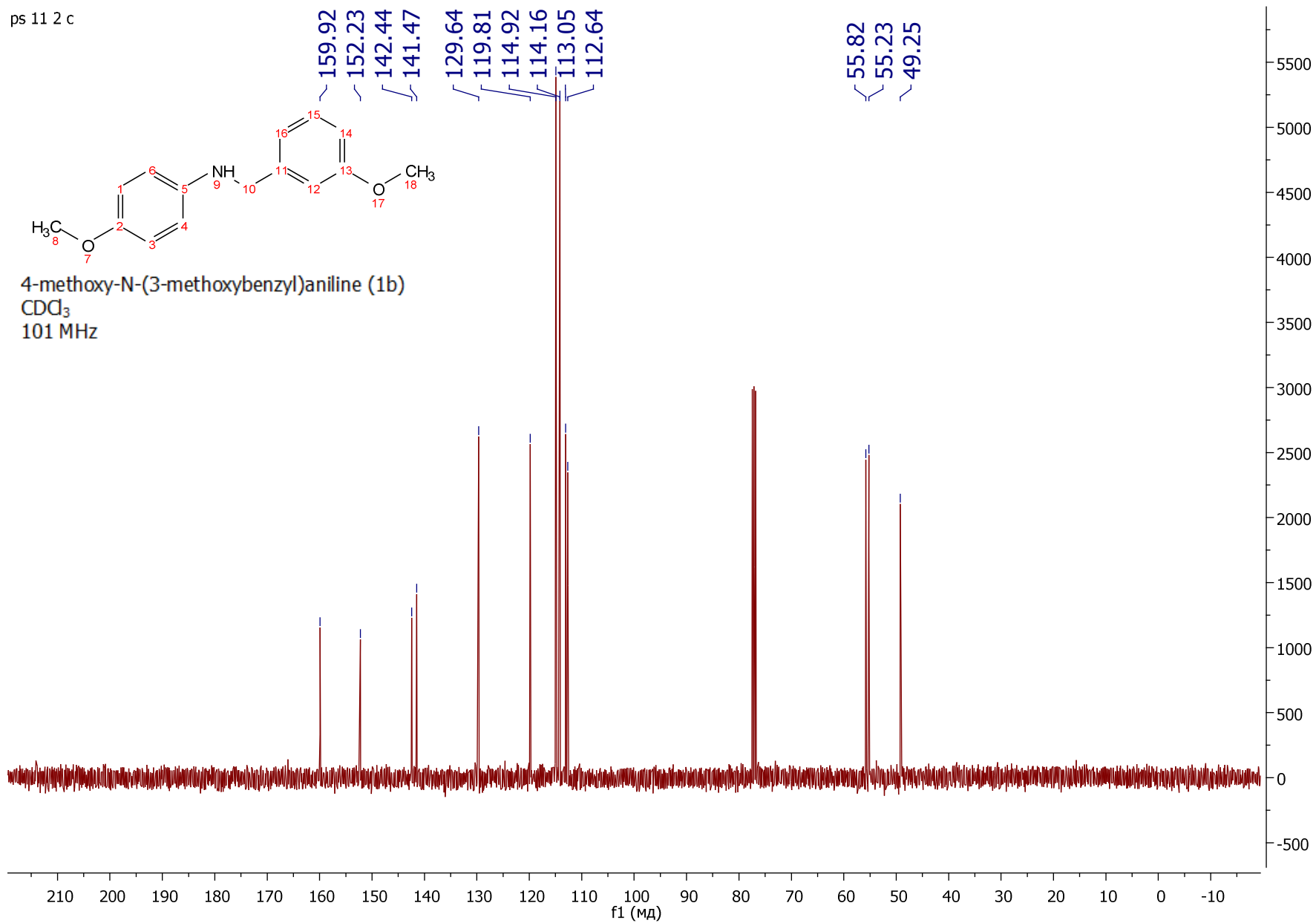
ps-11-2  
MGD 2012



4-methoxy-N-(3-methoxybenzyl)aniline (1b)  
CDCl<sub>3</sub>  
400 MHz



ps 11 2 c



# Display Report

## Analysis Info

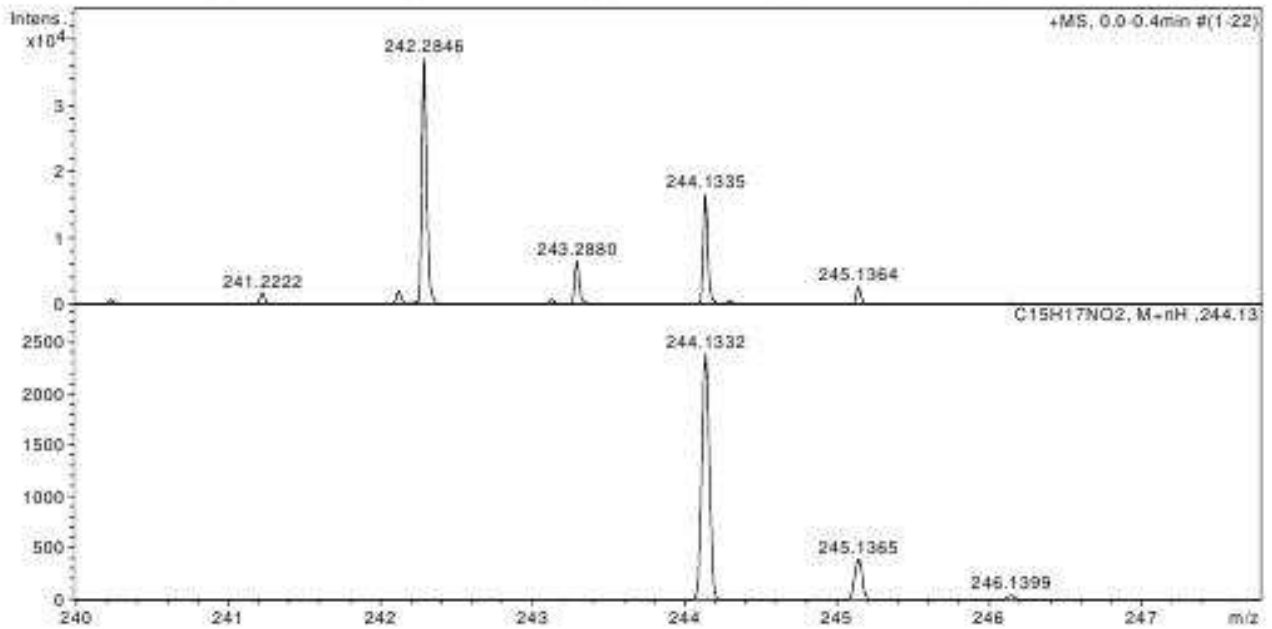
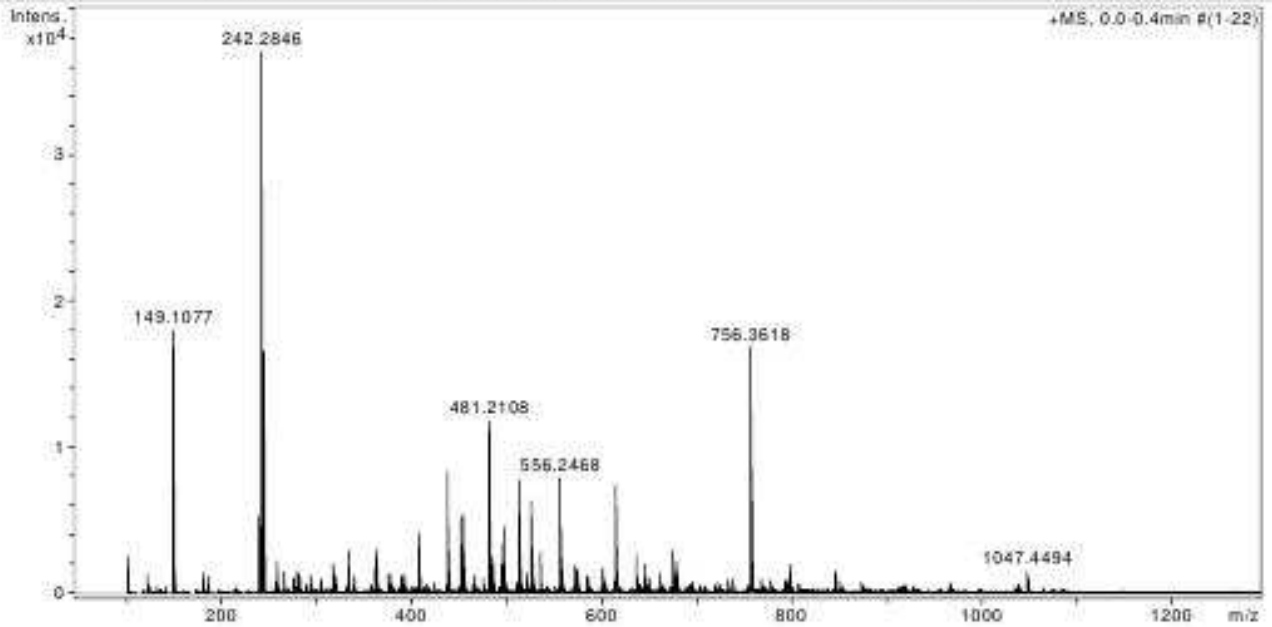
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Method tune\_low.m  
Sample Name /LEVH DEN-1blow  
Comment CH3CN 100 %

Acquisition Date 25.11.2014 15:53:37

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

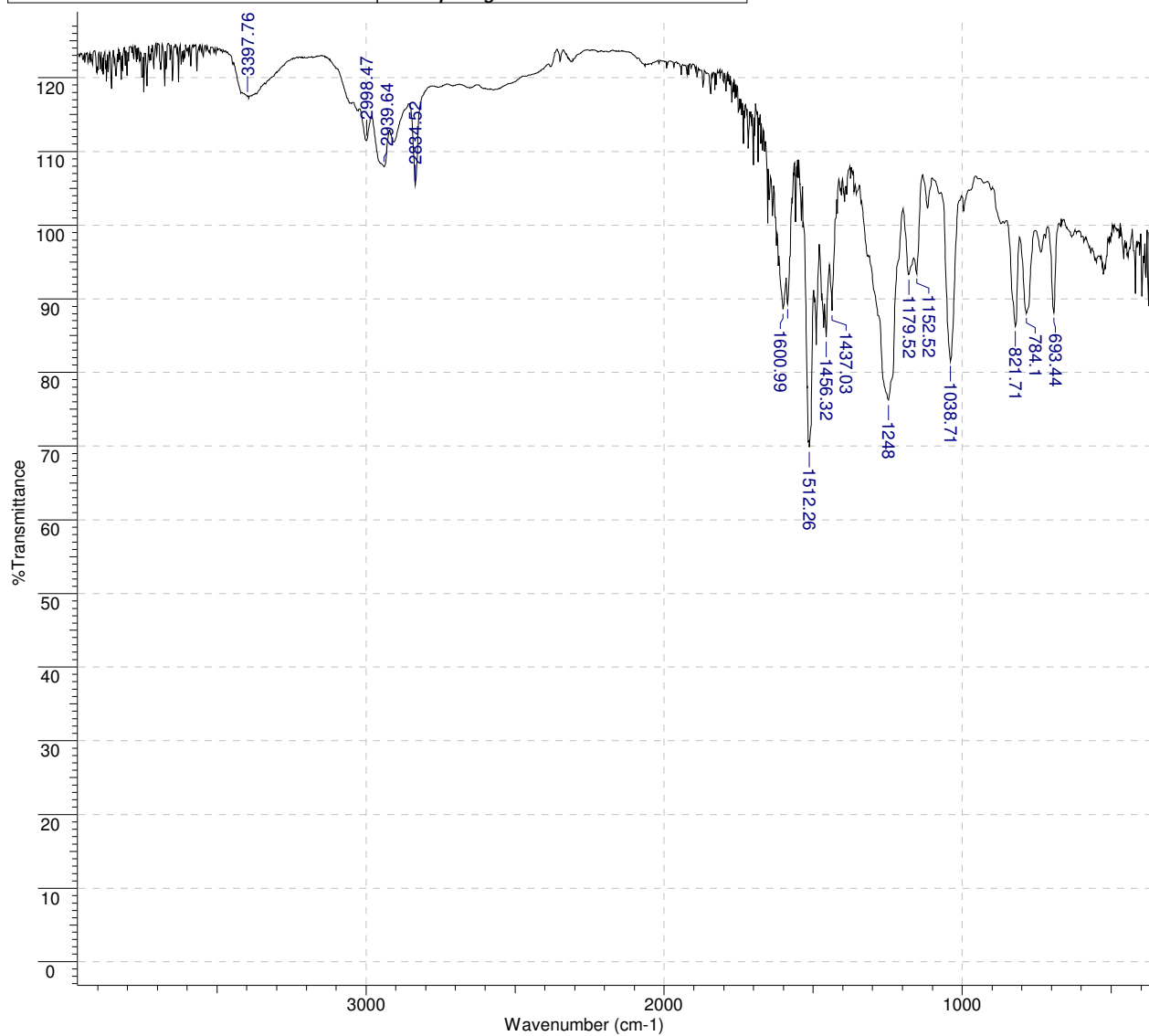
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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



# 1b

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<b>Date</b>	03 Dec 2014 13:42:46	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
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		<b>Spectrum Range</b>	349.1309 - 5000.6699

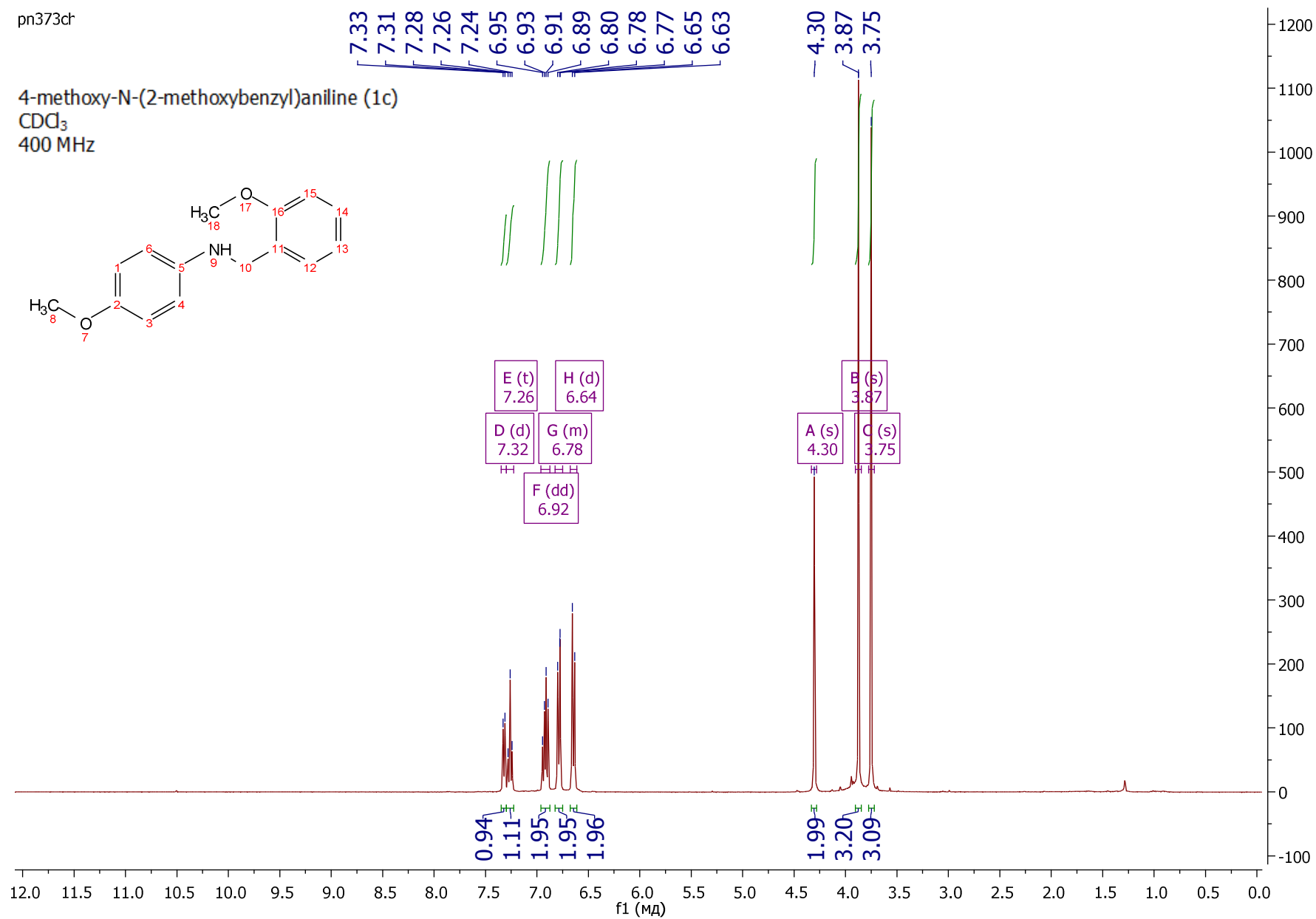
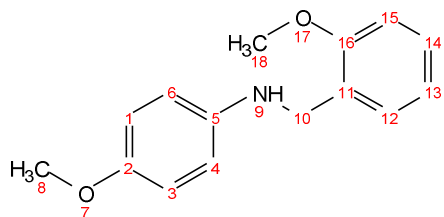


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6	1179.52	93.232	M
7	1248.00	76.224	S
8	1437.03	88.368	S
9	1456.32	84.803	S
10	1512.26	69.862	VS
11	1585.55	89.288	S
12	1600.99	88.576	S
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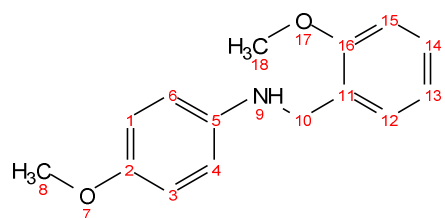
# 4-methoxy-N-(2-methoxybenzyl)aniline (1c)

pn373cr

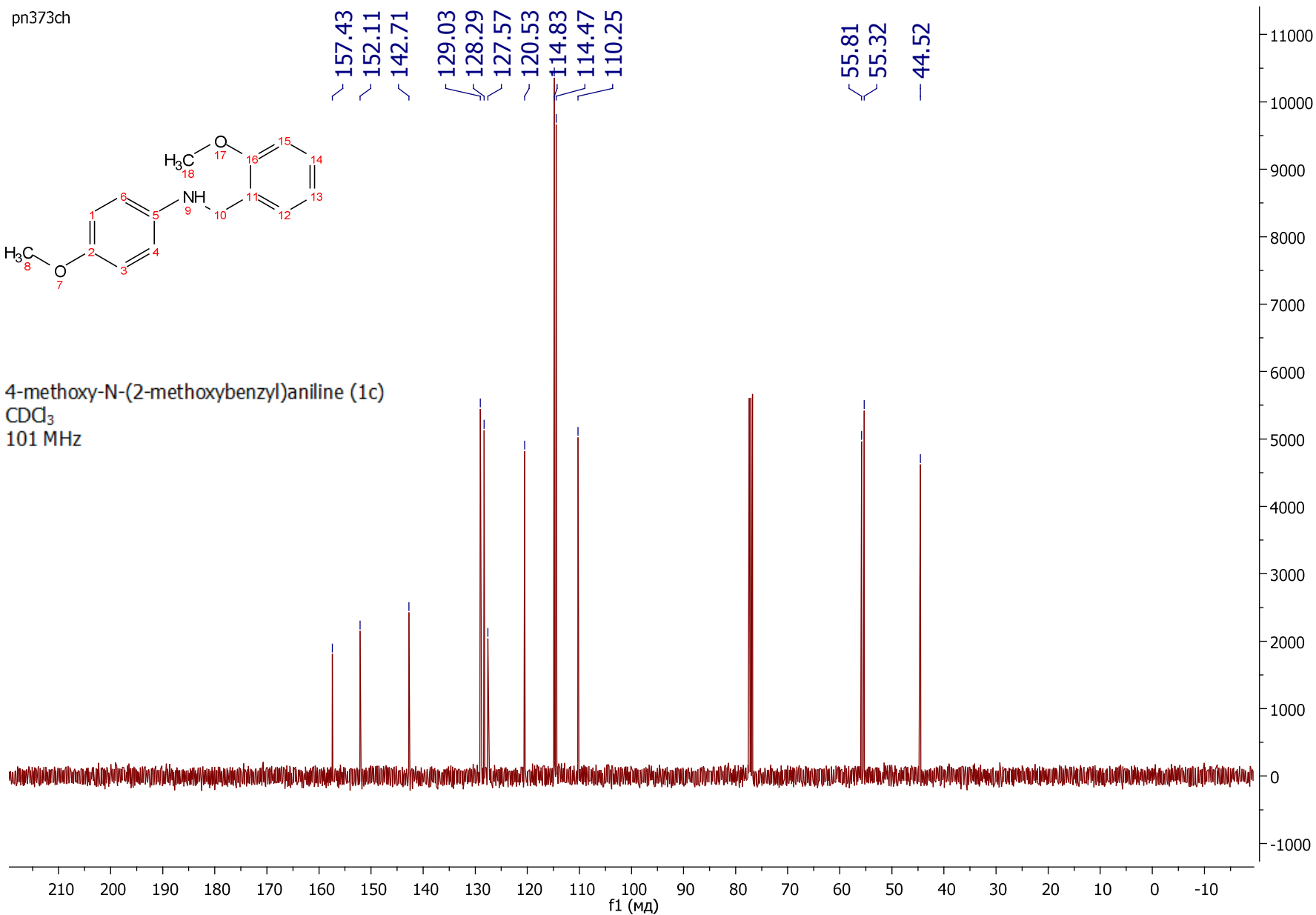
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CDCl<sub>3</sub>  
400 MHz



pn373ch

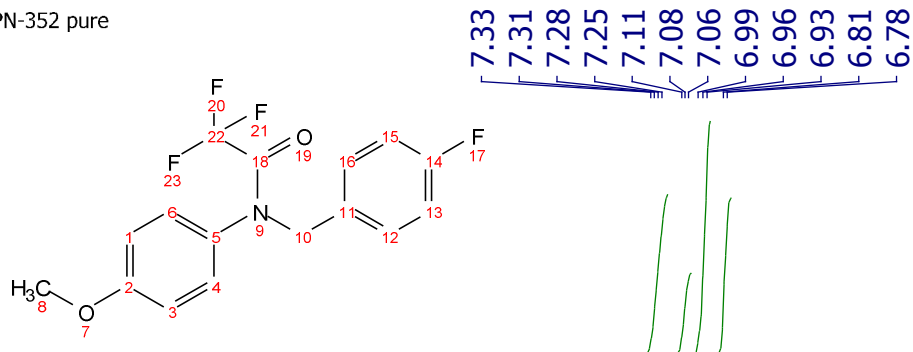


4-methoxy-N-(2-methoxybenzyl)aniline (1c)  
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# 2,2,2-trifluoro-N-(4-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1d)

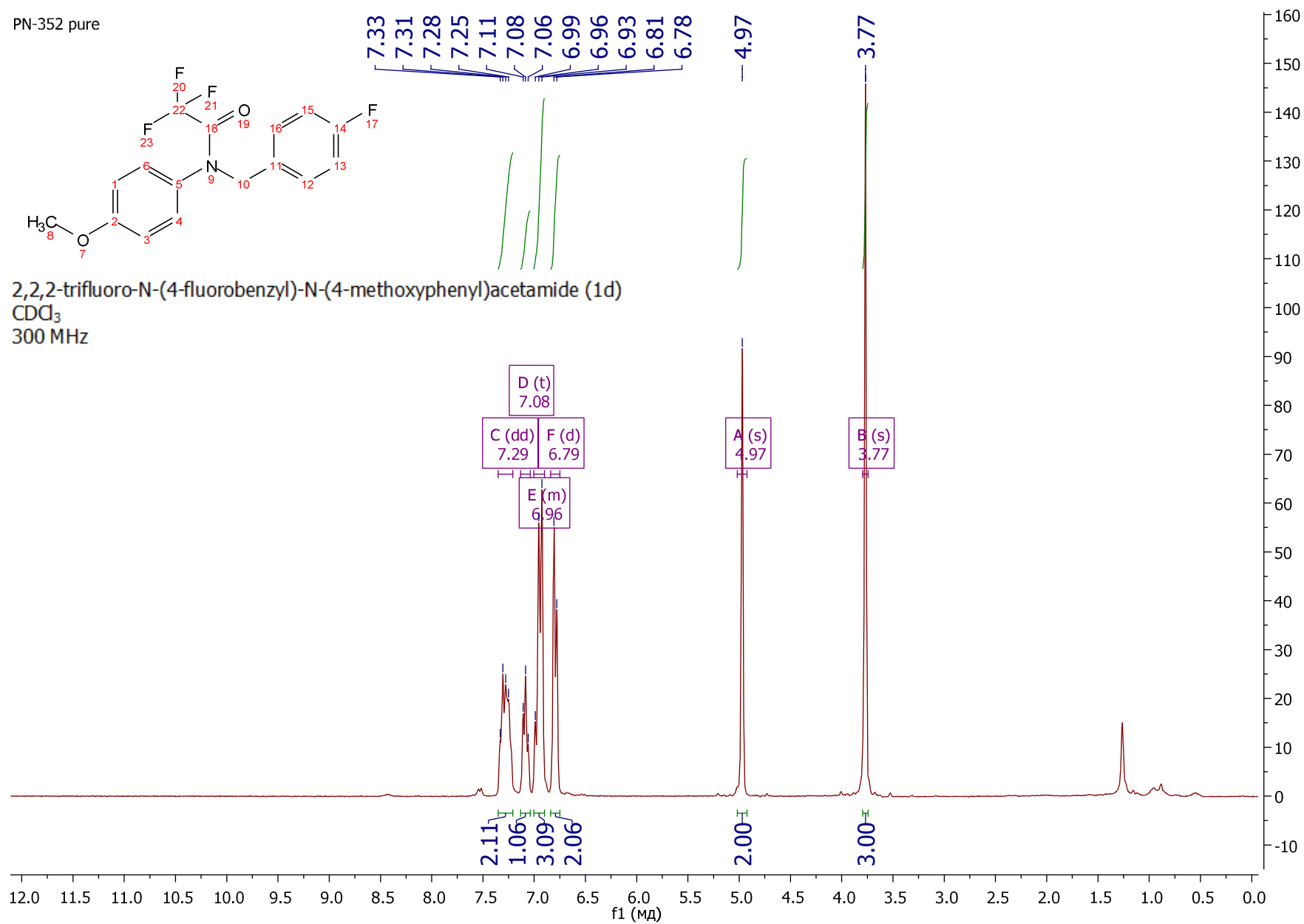
PN-352 pure



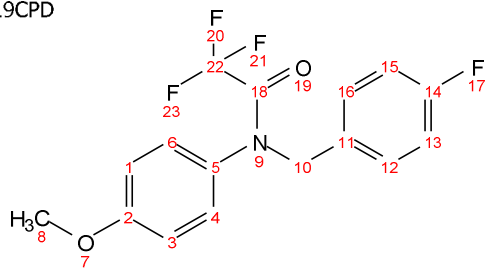
2,2,2-trifluoro-N-(4-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1d)

CDCl<sub>3</sub>

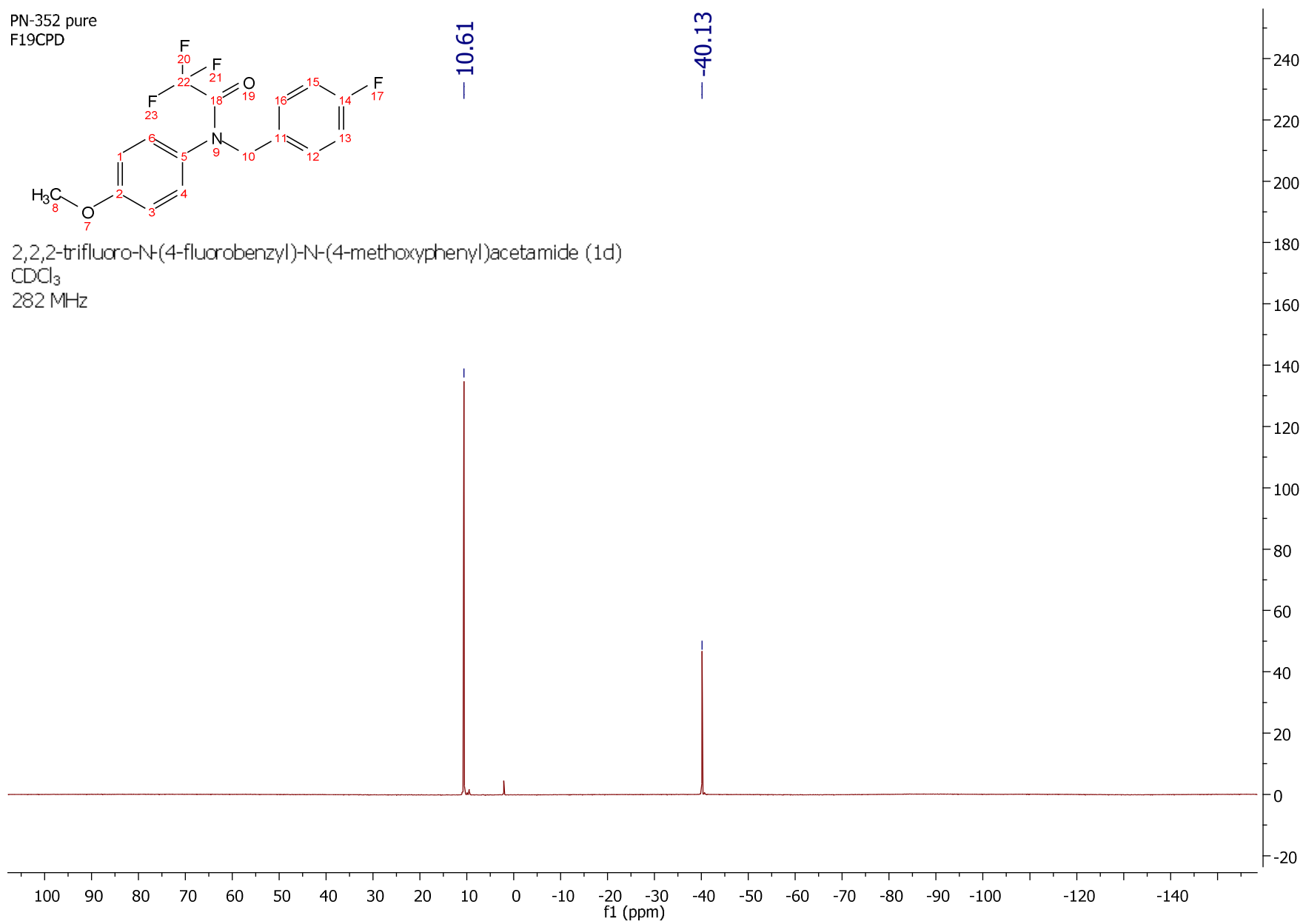
300 MHz



PN-352 pure  
F19CPD



2,2,2-trifluoro-N-(4-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1d)  
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282 MHz



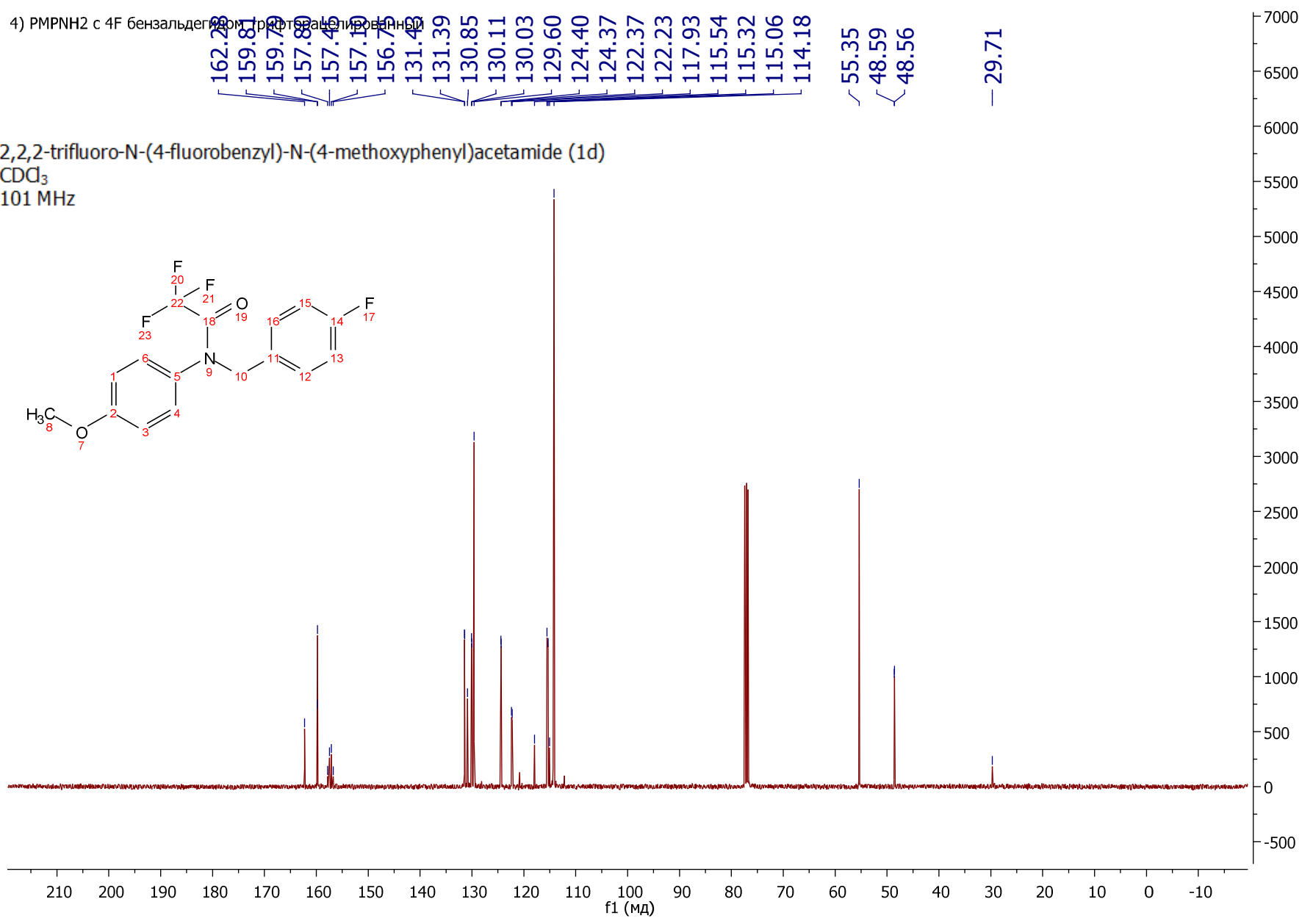
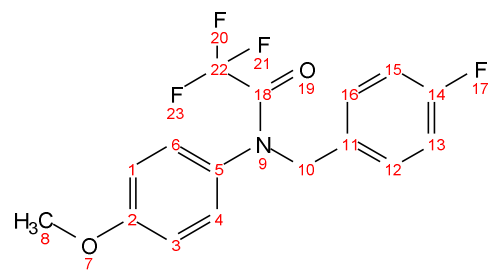
4) PMPNH2 с 4F бензальдегидом трифторацелированной

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130.11  
130.03  
129.60  
124.40  
124.37  
122.37  
122.23  
117.93  
115.54  
115.32  
115.06  
114.18

55.35  
48.59  
48.56

29.71

2,2,2-trifluoro-N-(4-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1d)  
CDCl<sub>3</sub>  
101 MHz



# Display Report

## Analysis Info

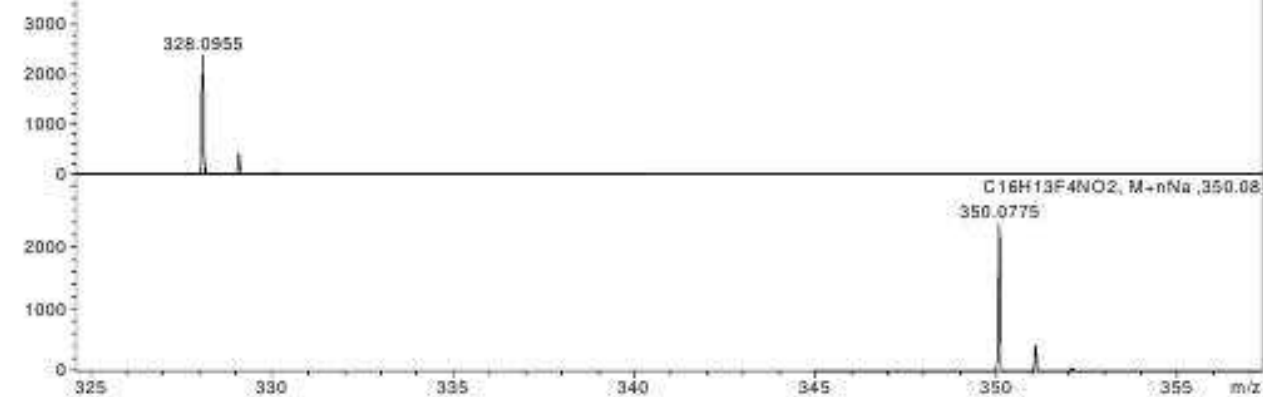
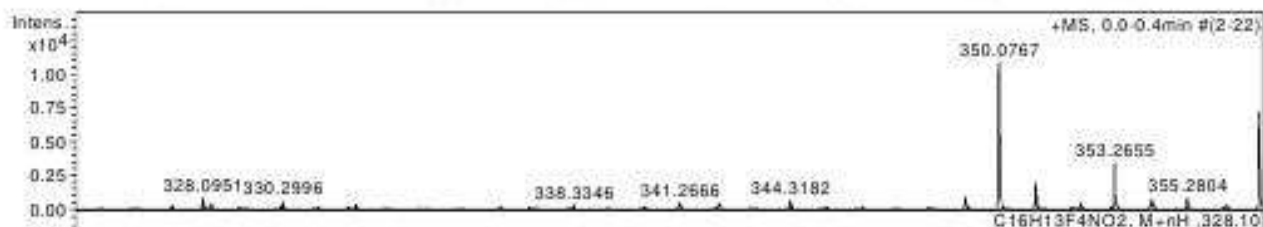
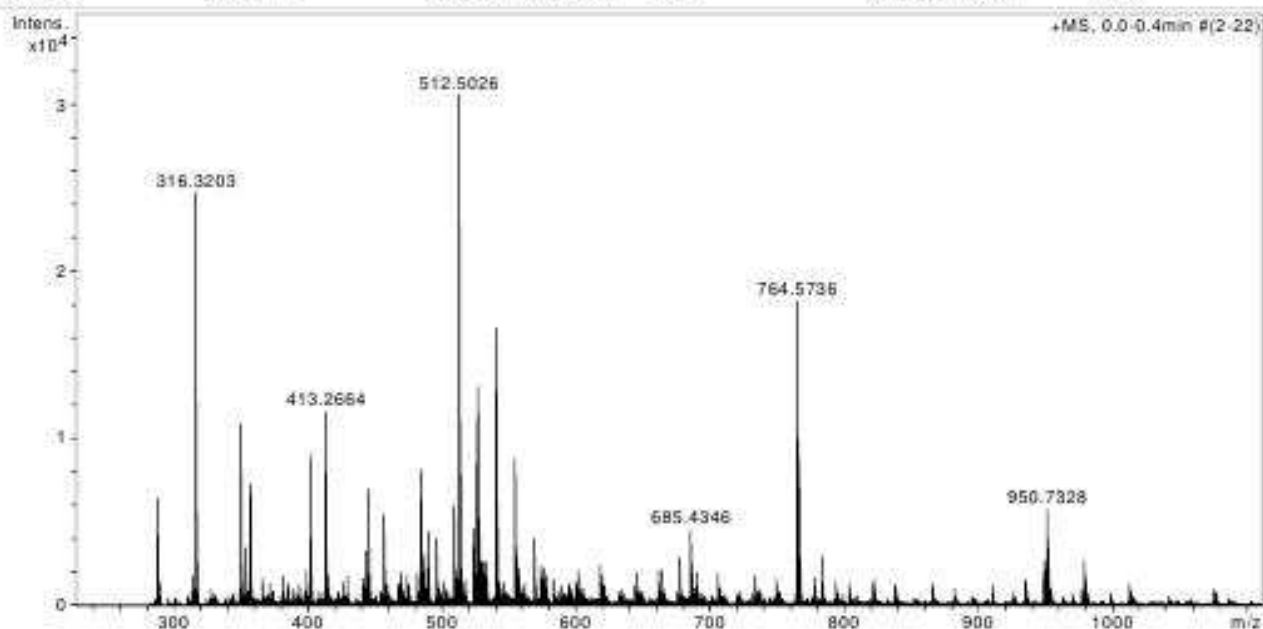
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Operator BDAL@DE  
Instrument / Ser# micrOTOF 10248

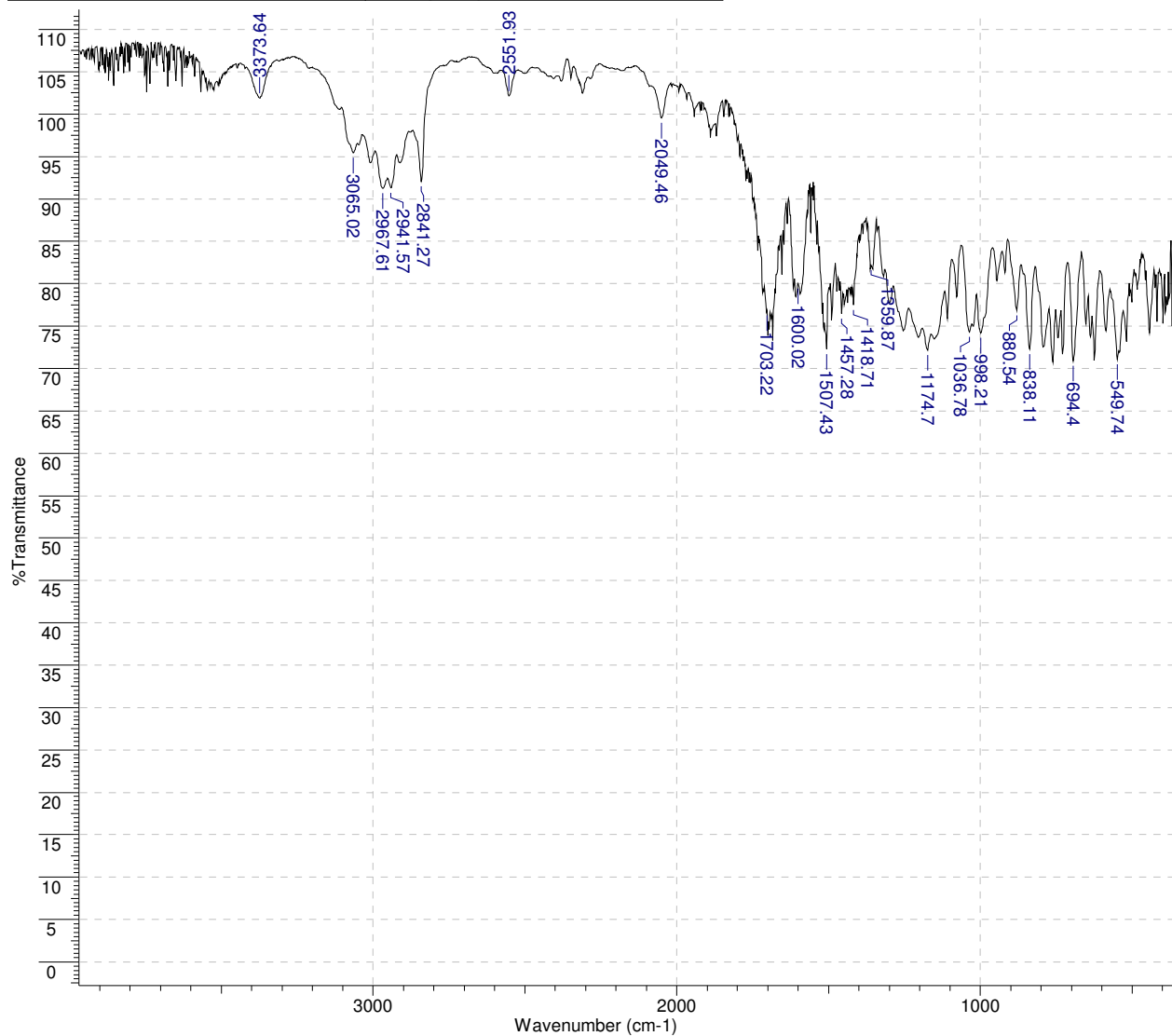
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# 1d

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<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699

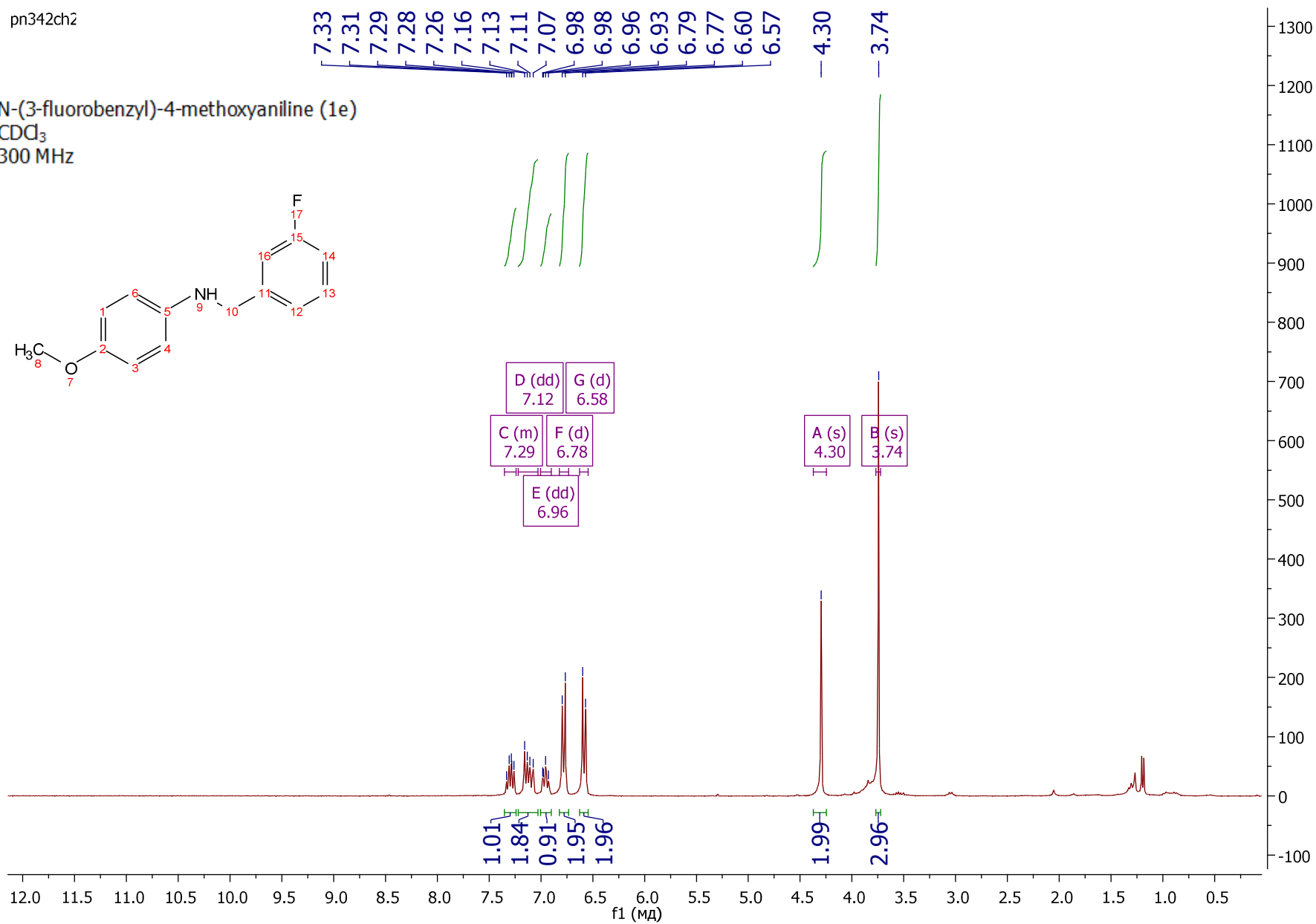
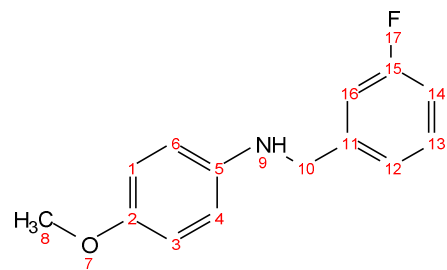


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4	880.54	76.854	S	14	2049.46	99.549	W
5	998.21	74.185	S	15	2551.93	102.134	W
6	1036.78	74.338	S	16	2841.27	92.090	M
7	1174.70	72.150	S	17	2941.57	91.284	M
8	1359.87	82.193	S	18	2967.61	91.227	M
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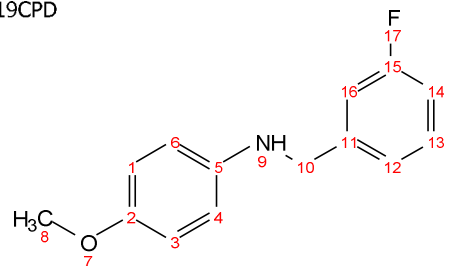
# *N*-(3-fluorobenzyl)-4-methoxyaniline (1e)

pn342ch2

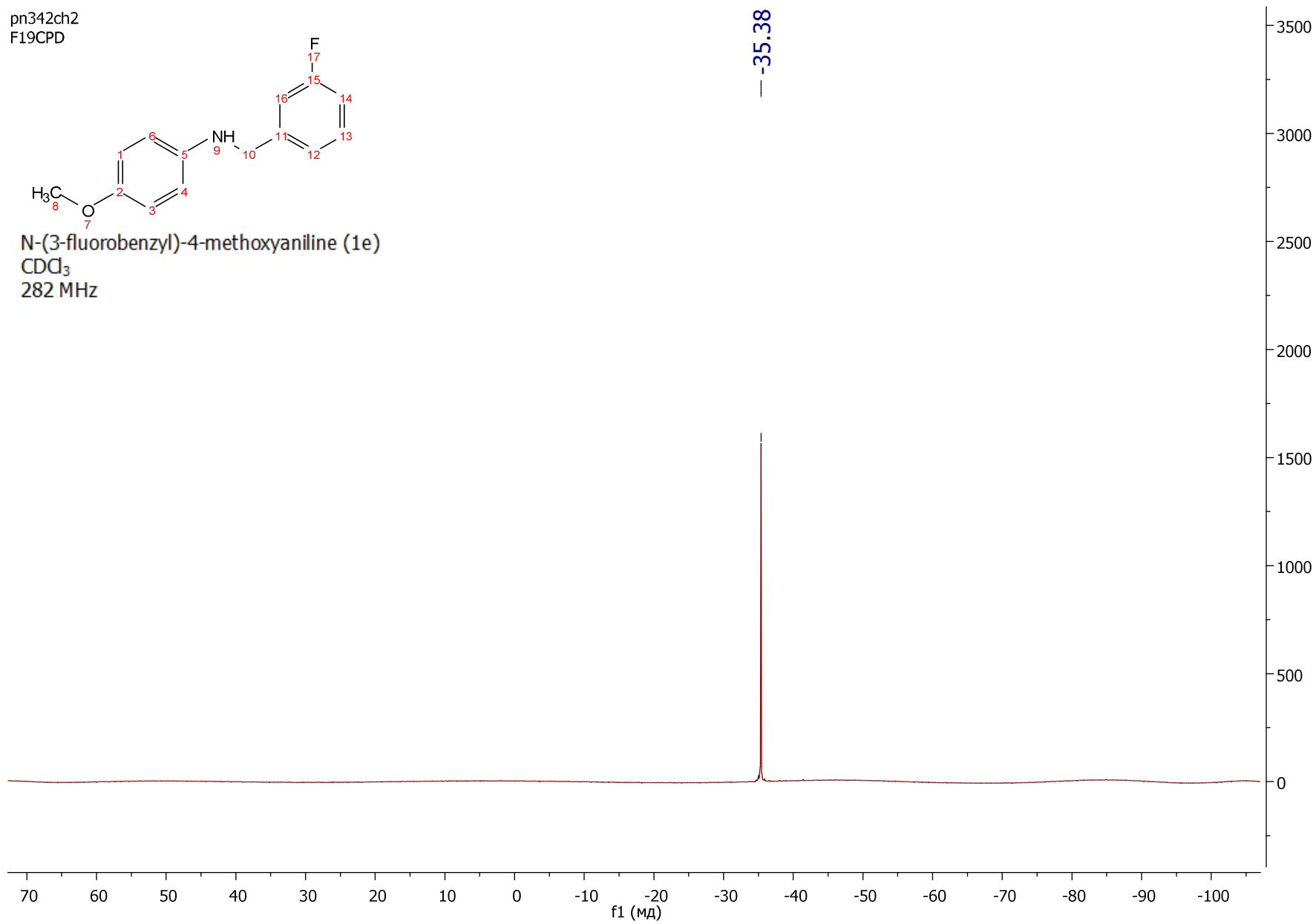
*N*-(3-fluorobenzyl)-4-methoxyaniline (1e)  
CDCl<sub>3</sub>  
300 MHz



pn342ch2  
F19CPD



N-(3-fluorobenzyl)-4-methoxyaniline (1e)  
CDCl<sub>3</sub>  
282 MHz

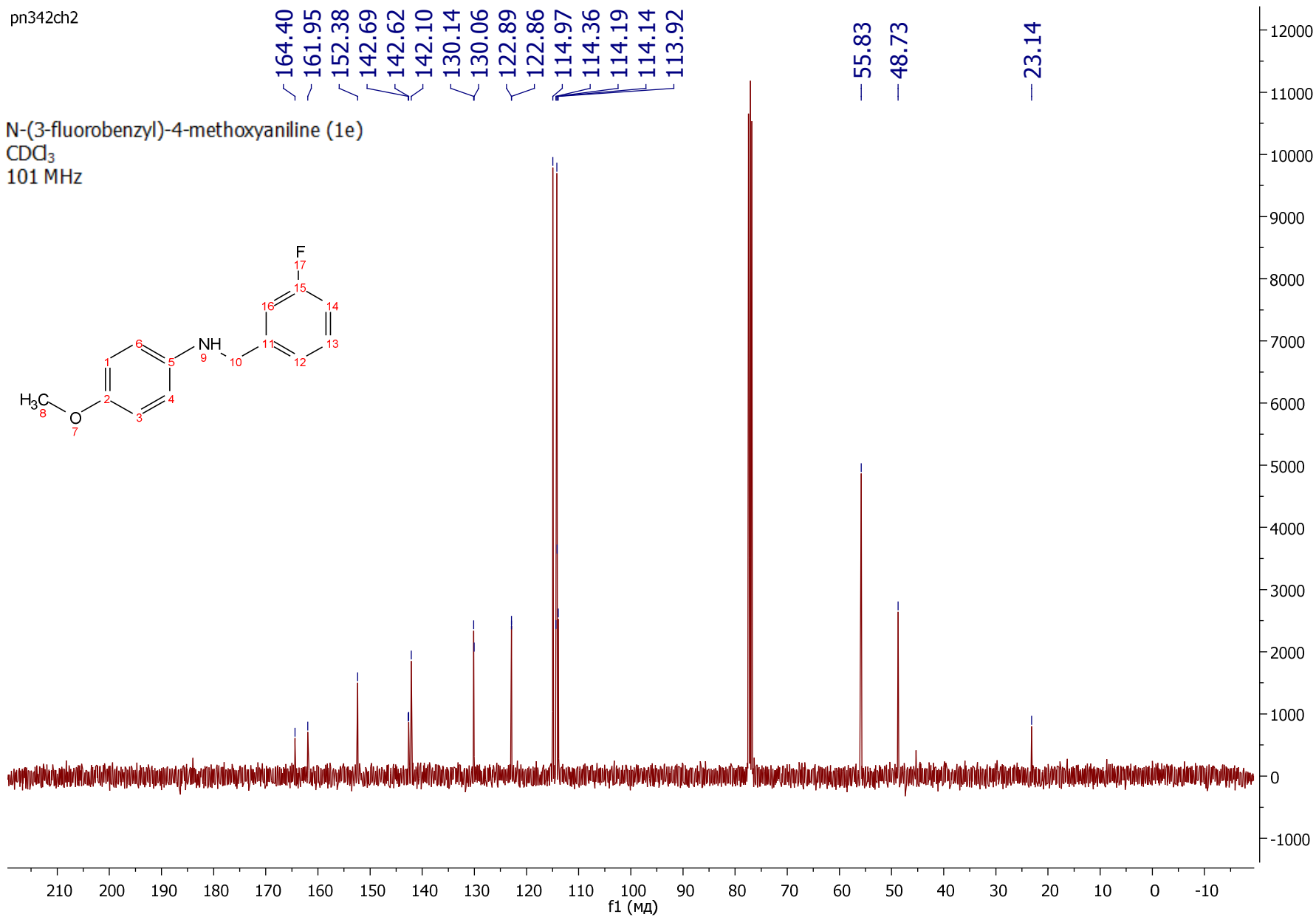
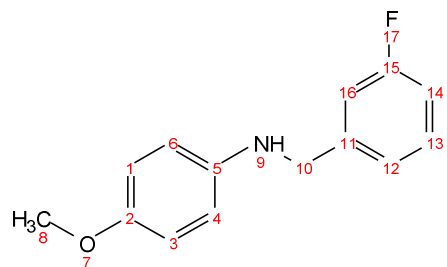


pn342ch2

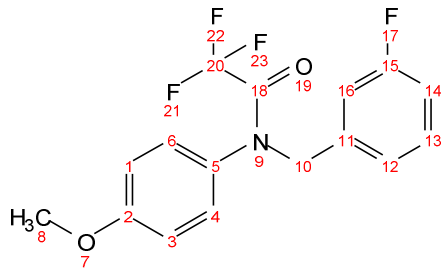
164.40  
161.95  
152.38  
142.69  
142.62  
142.10  
130.14  
130.06  
122.89  
122.86  
114.97  
114.36  
114.19  
114.14  
113.92

55.83  
48.73  
23.14

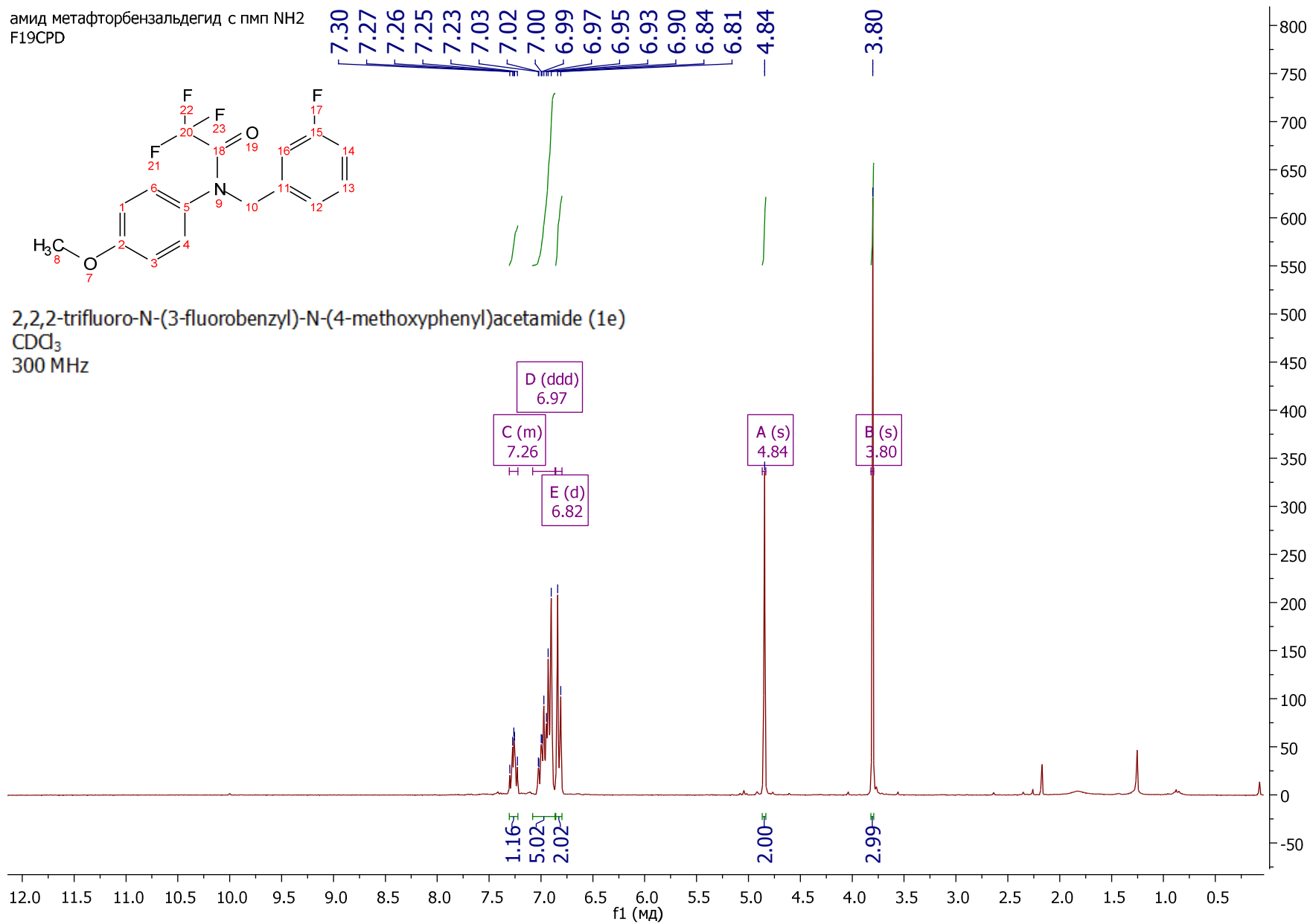
N-(3-fluorobenzyl)-4-methoxyaniline (1e)  
CDCl<sub>3</sub>  
101 MHz



амид метафторбензальдегид с пмп NH2  
F19CPD

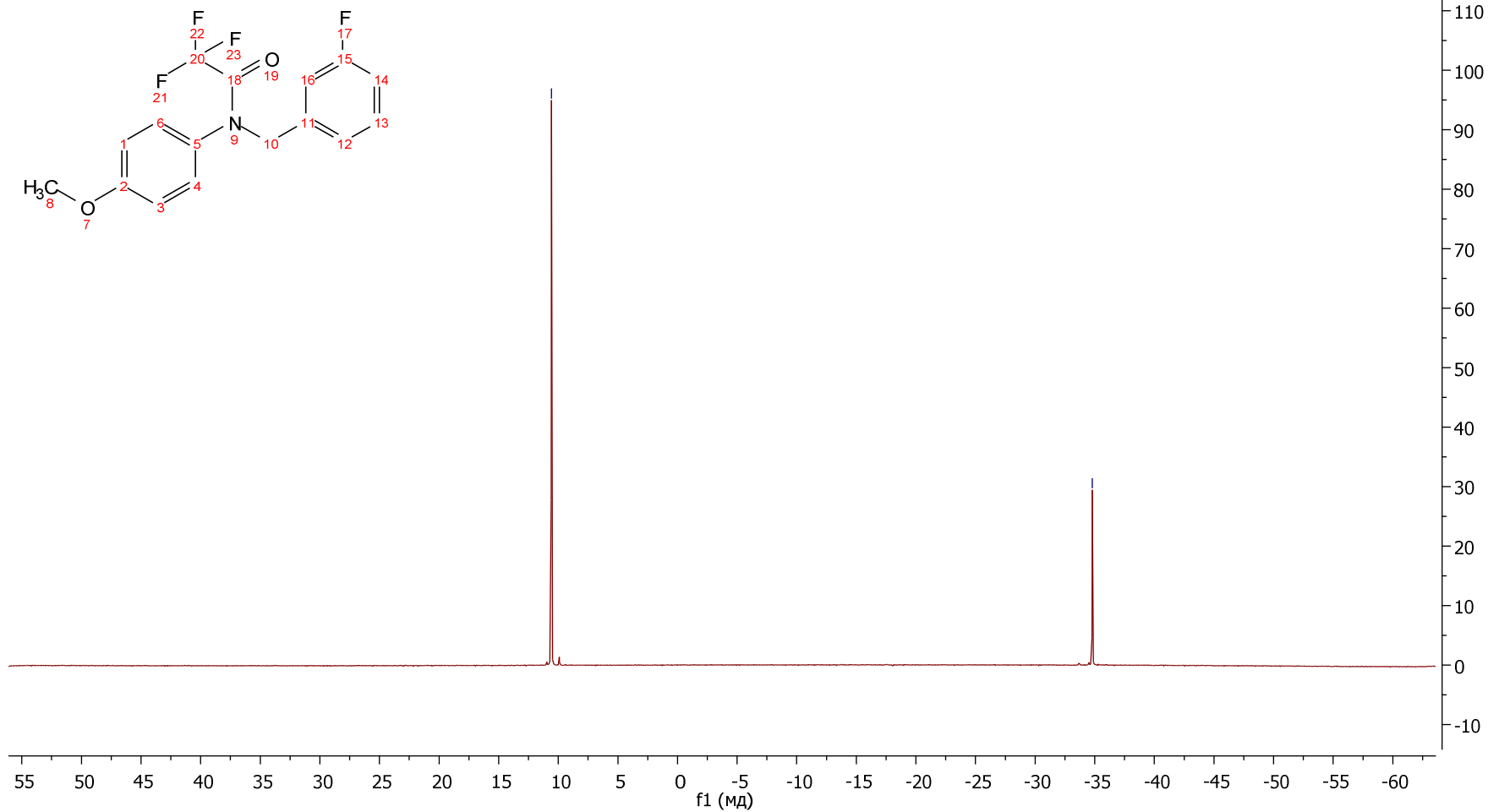


2,2,2-trifluoro-N-(3-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1e)  
CDCl<sub>3</sub>  
300 MHz



амид метафторбензальдегид с пмп NH2  
F19CPD

2,2,2-trifluoro-N-(3-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1e)  
CDCl<sub>3</sub>  
282 MHz



амид метафторбензальдегида дип NH2  
F19CPD

164.37  
161.10  
159.82

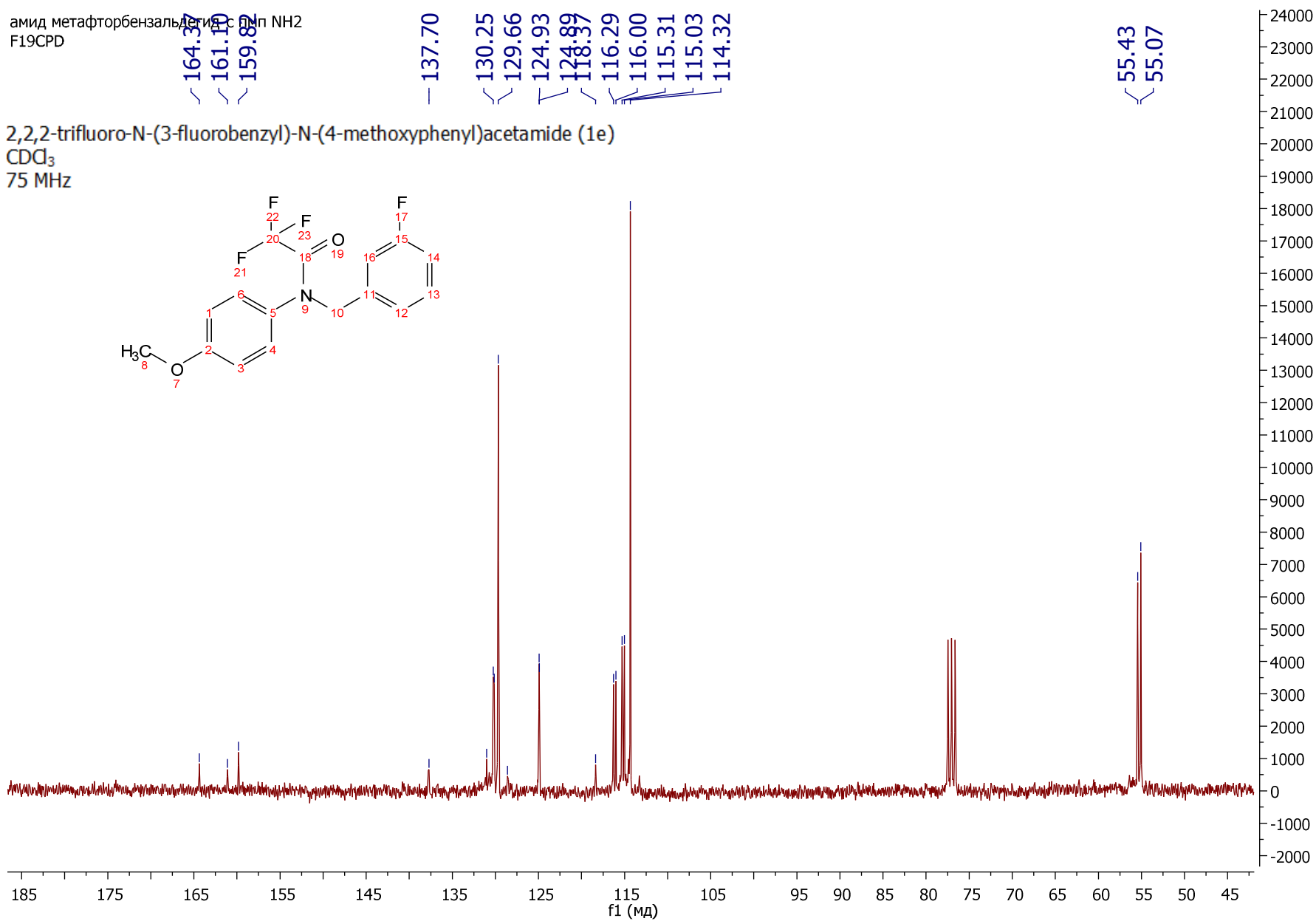
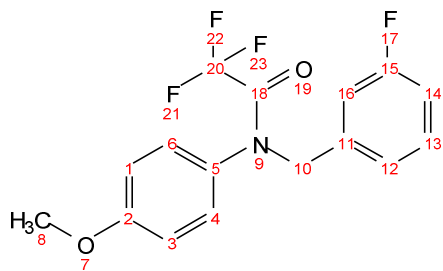
137.70

130.25  
129.66  
124.93  
124.89  
118.97  
116.29  
116.00  
115.31  
115.03  
114.32

55.43  
55.07

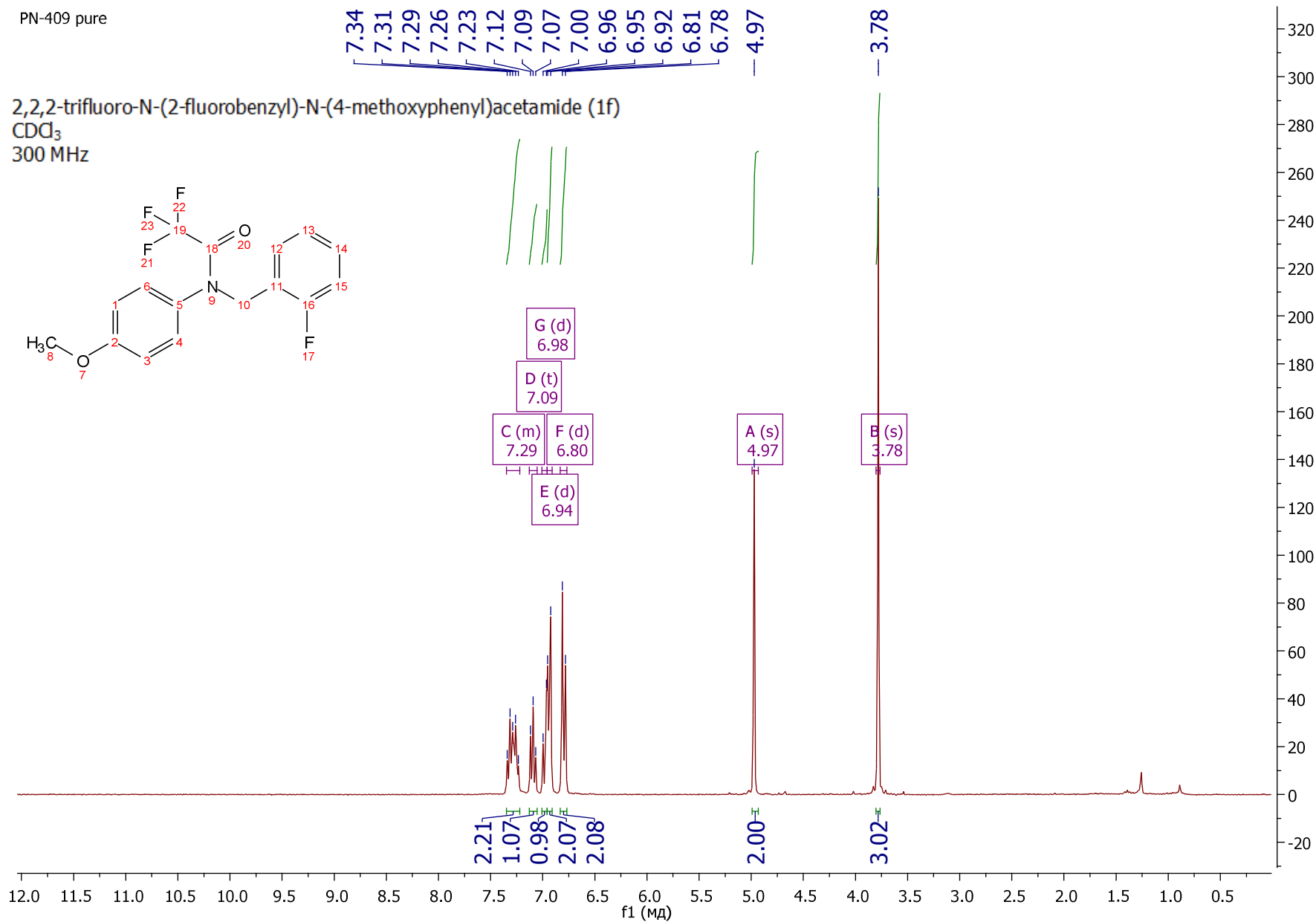
2,2,2-trifluoro-N-(3-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1e)

CDCl<sub>3</sub>  
75 MHz

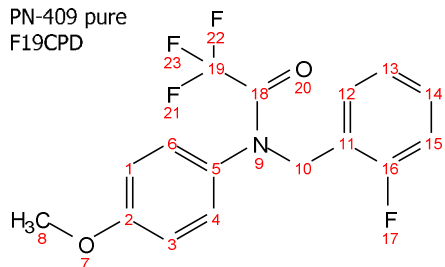


# 2,2,2-trifluoro-N-(2-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1f)

PN-409 pure



PN-409 pure  
F19CPD



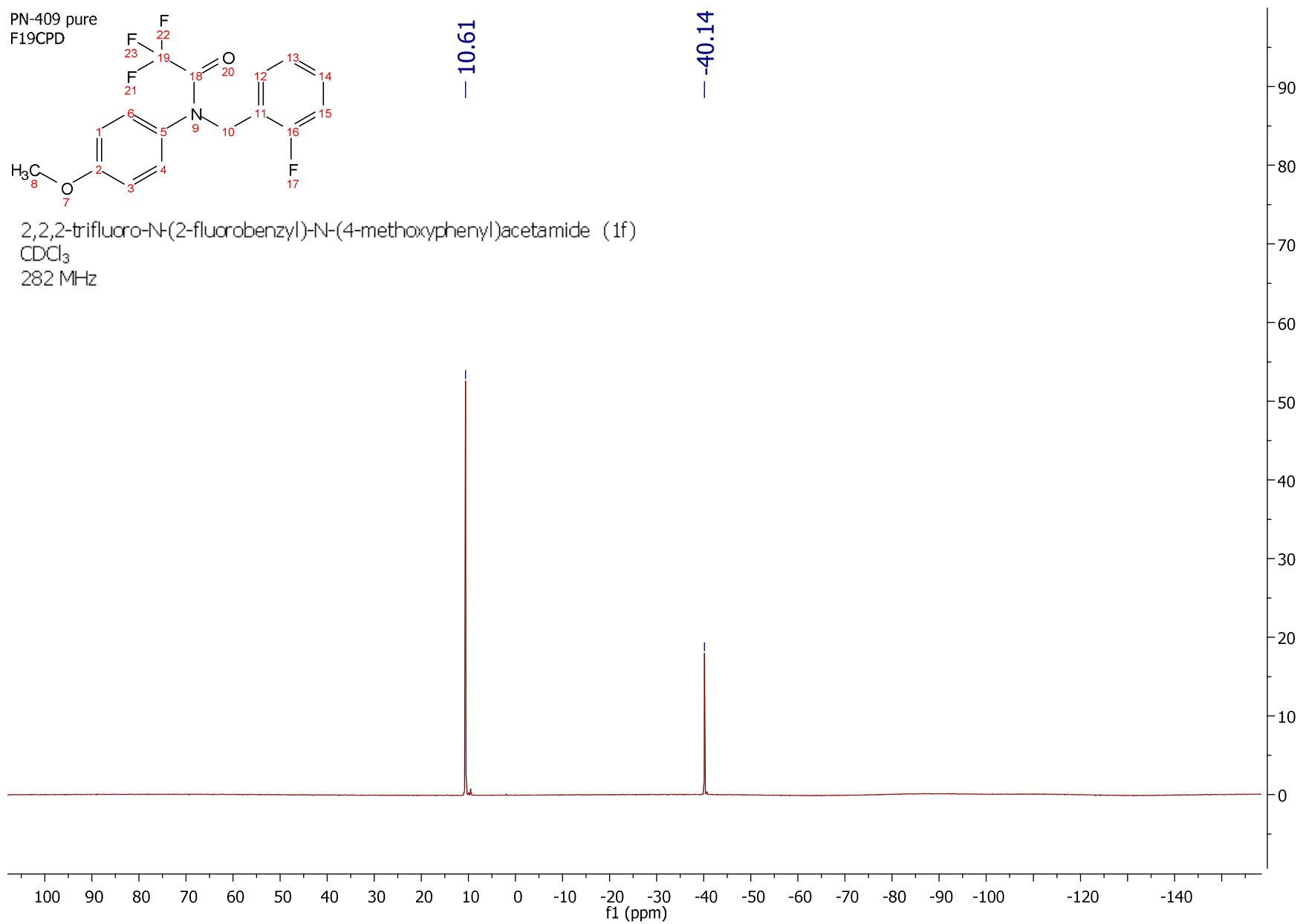
2,2,2-trifluoro-N-(2-fluorobenzyl)-N-(4-methoxyphenyl)acetamide (1f)

CDCl<sub>3</sub>

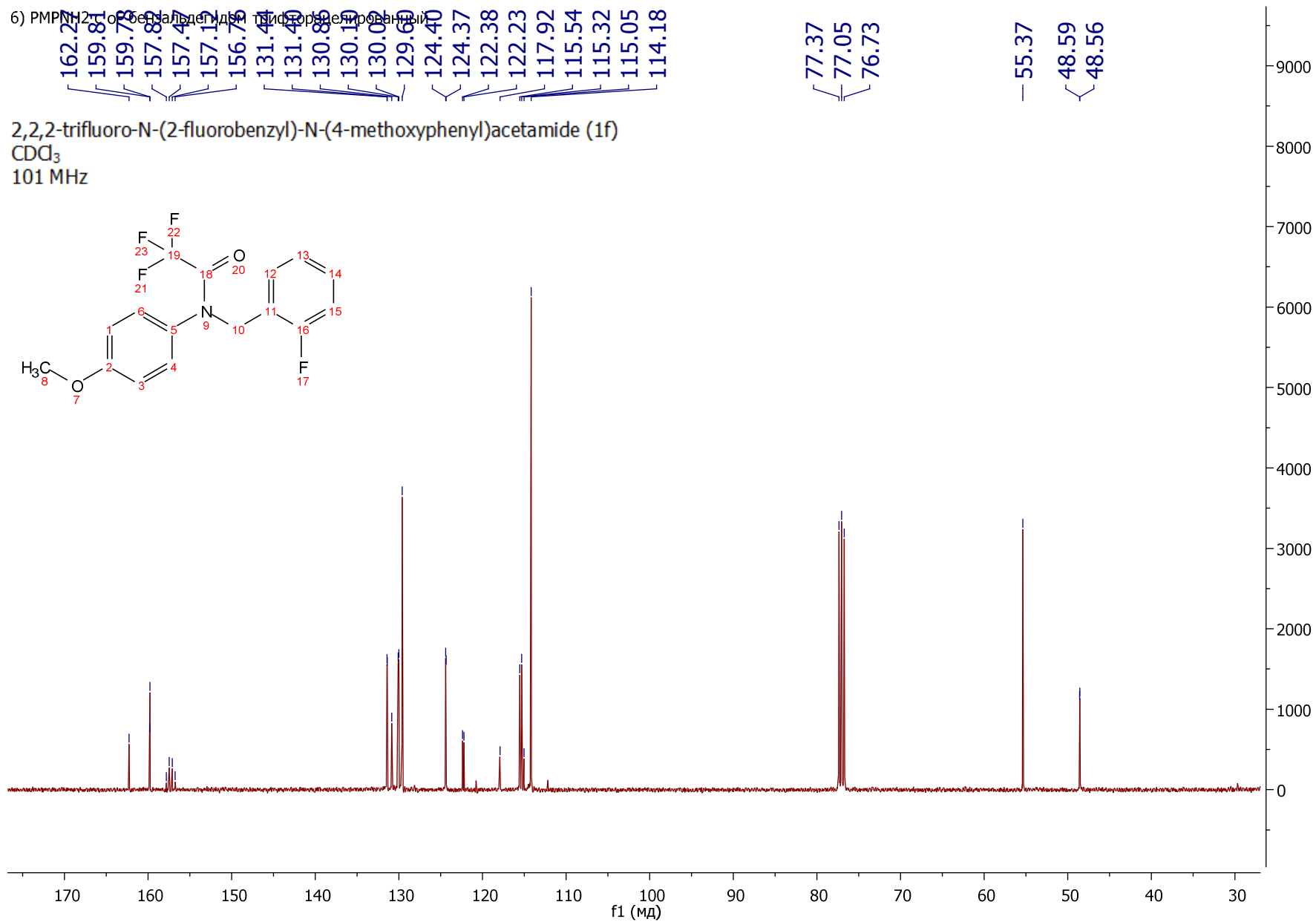
282 MHz

— 10.61

— 40.14



6) PMR N2, 13C бензальдегид, трифтороацетонитрил



# Display Report

## Analysis Info

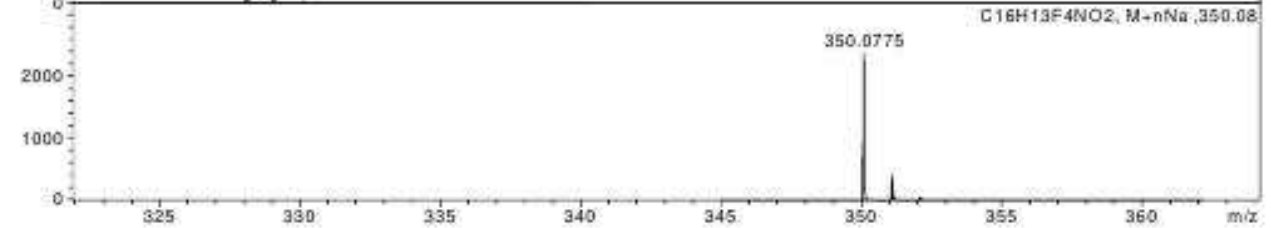
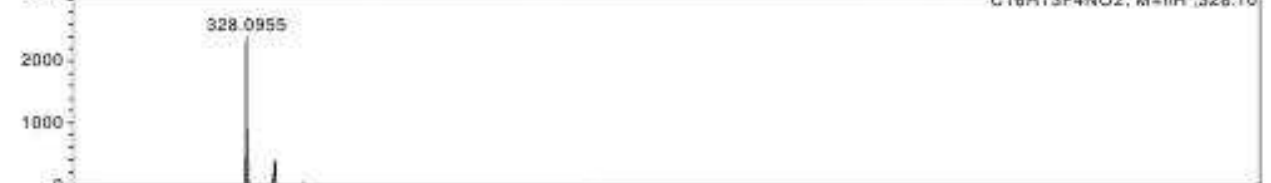
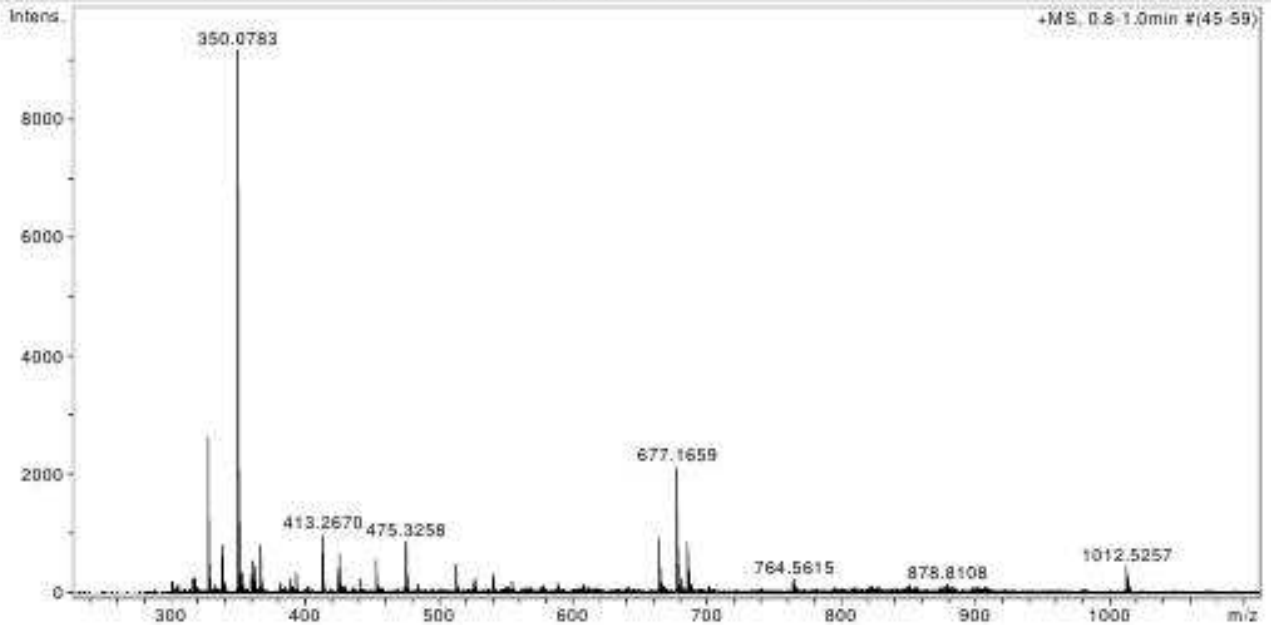
Analysis Name D:\Data\Ivanova\DEN-1flow.d  
Method tune\_wide.m  
Sample Name /LEVH DEN-1flow  
Comment CH3CN 100 %, dil 200

Acquisition Date 25.11.2014 16:22:01

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

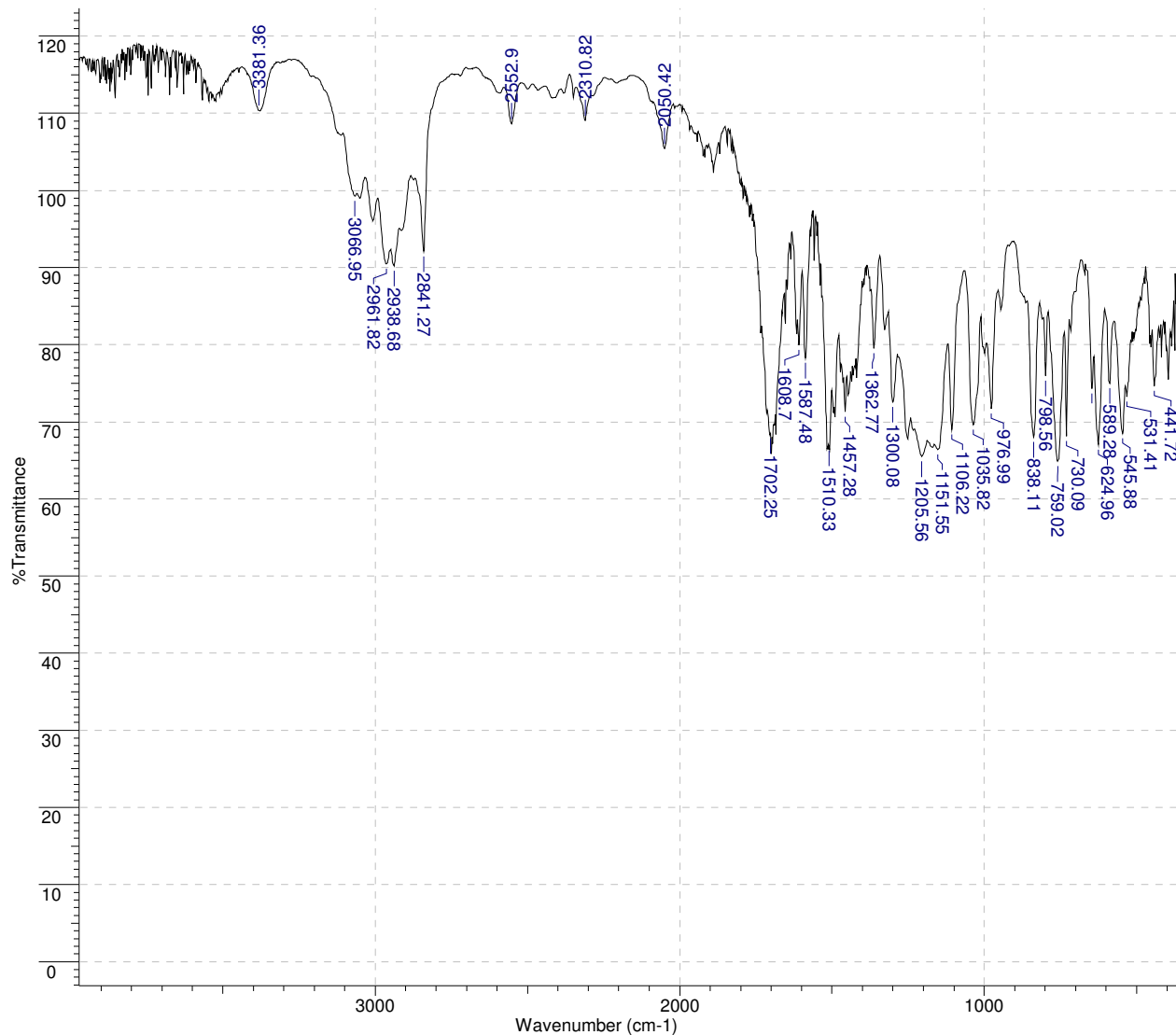
## Acquisition Parameter

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



1f

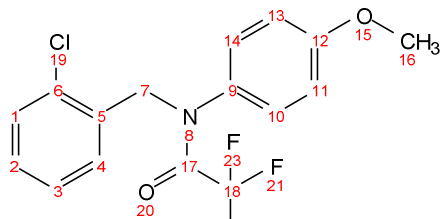
<b>Title</b>	1f		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚĀĀĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1F.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:43:06	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699



No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	441.72	74.660	S	16	1300.08	72.521	S
2	531.41	73.258	S	17	1362.77	79.547	S
3	545.88	68.495	VS	18	1457.28	71.315	S
4	589.28	74.960	S	19	1510.33	66.904	VS
5	624.96	67.036	VS	20	1587.48	78.301	S
6	646.18	74.274	S	21	1608.70	79.918	S
7	730.09	68.123	VS	22	1702.25	68.474	VS
8	759.02	64.893	VS	23	2050.42	105.441	W
9	798.56	75.943	S	24	2310.82	109.042	W
10	838.11	68.050	VS	25	2552.90	108.646	W
11	976.99	71.709	S	26	2841.27	92.086	M
12	1035.82	69.587	VS	27	2938.68	90.239	M
13	1106.22	68.963	VS	28	2961.82	90.467	M
14	1151.55	66.427	VS	29	3066.95	99.245	M
15	1205.56	65.537	VS	30	3381.36	110.343	W

# *N*-(2-chlorobenzyl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (**1g**)

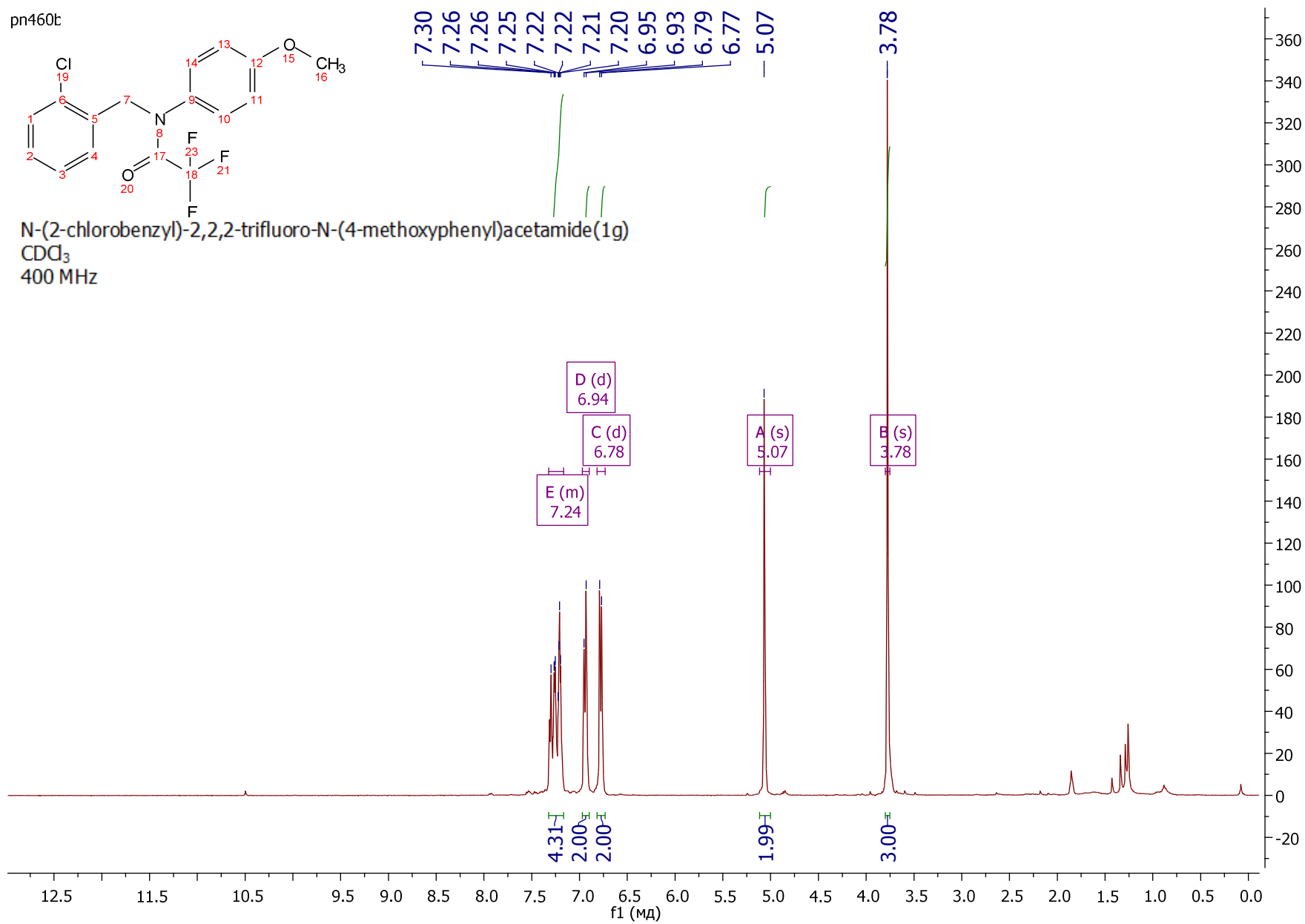
pn460t



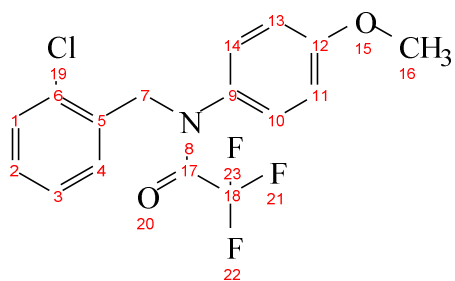
*N*-(2-chlorobenzyl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (**1g**)

CDCl<sub>3</sub>

400 MHz

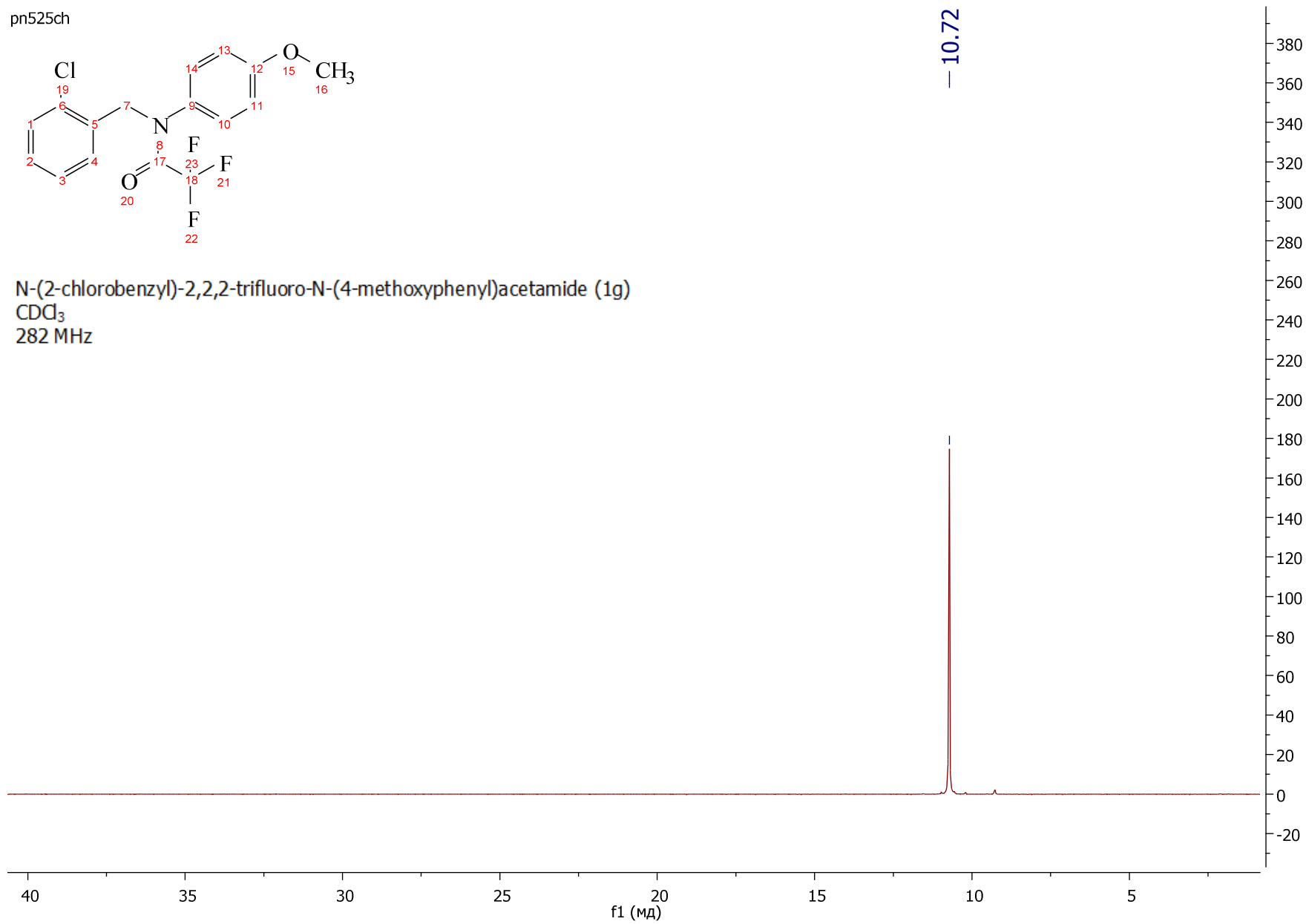


pn525ch



N-(2-chlorobenzyl)-2,2,2-trifluoro-N-(4-methoxyphenyl)acetamide (1g)

CDCl<sub>3</sub>  
282 MHz

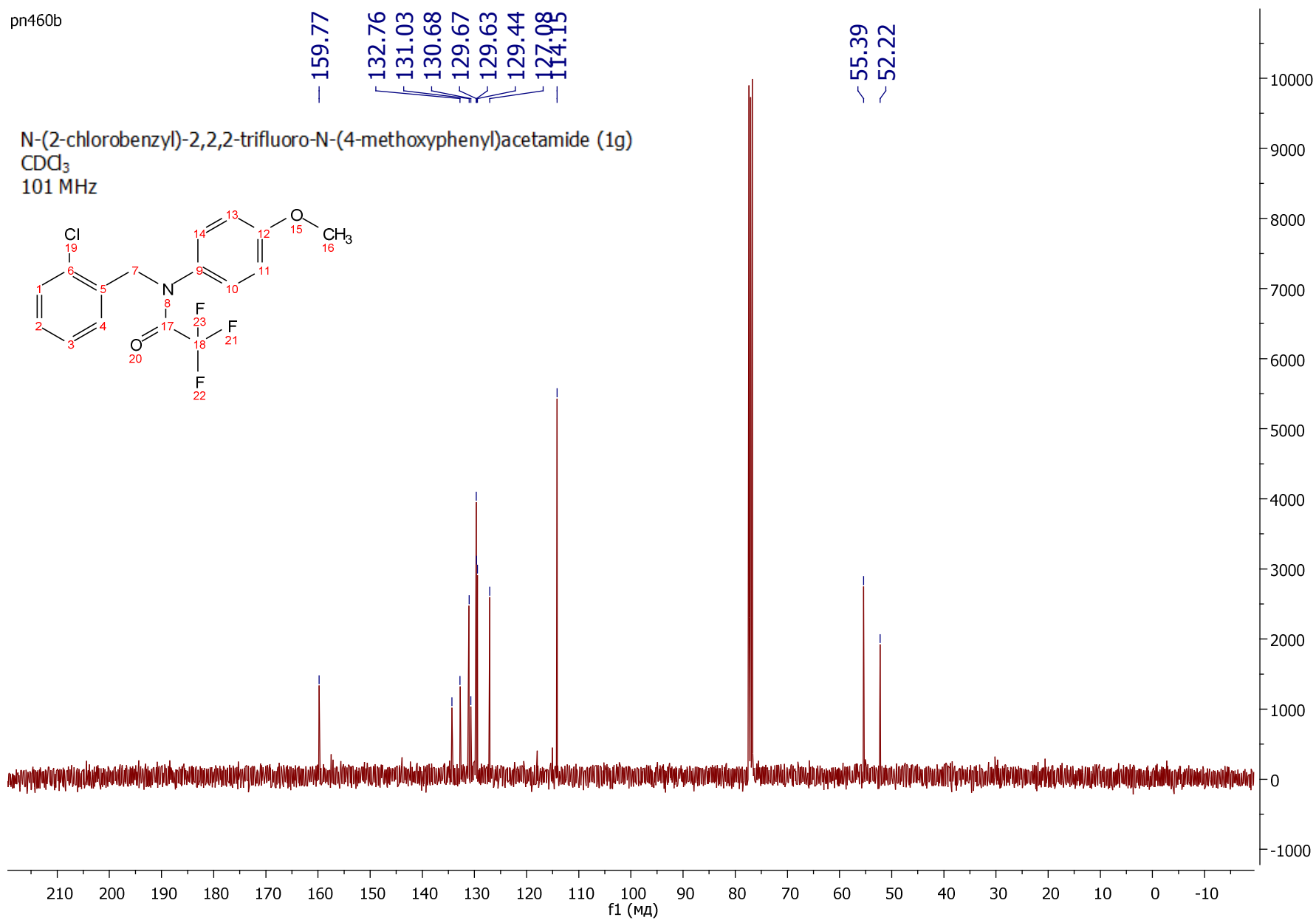
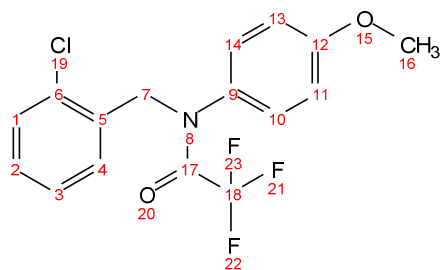


pn460b

159.77  
132.76  
131.03  
130.68  
129.67  
129.63  
129.44  
127.08  
114.15

55.39  
52.22

N-(2-chlorobenzyl)-2,2,2-trifluoro-N-(4-methoxyphenyl)acetamide (1g)  
CDCl<sub>3</sub>  
101 MHz



# Display Report

## Analysis Info

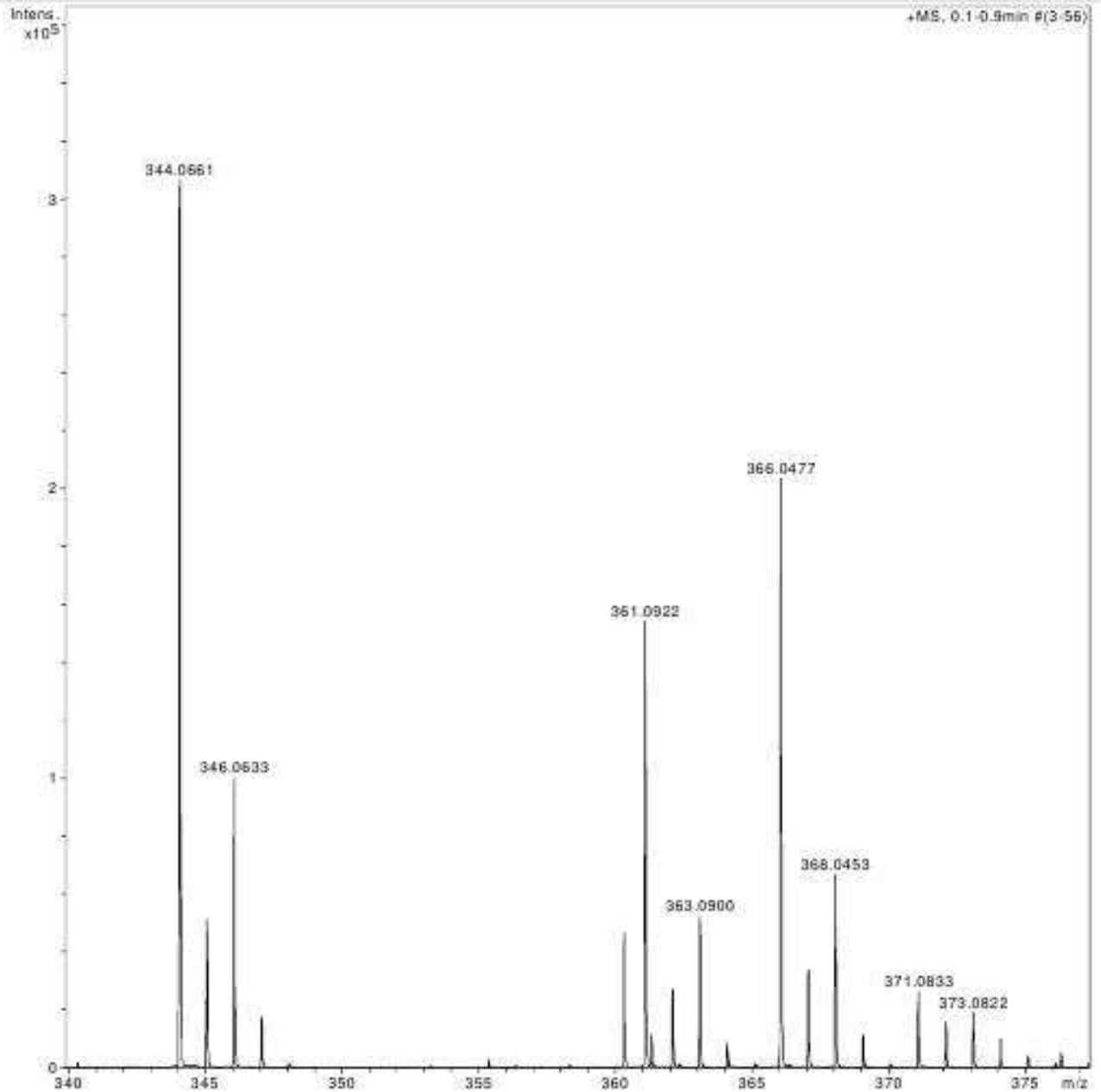
Analysis Name D:\Data\Kolotyrkina\2014\Titov\1203023.d  
Method tune\_low.m  
Sample Name /LB58 PN-525ch  
Comment C14H14ClNO mw.247 calibrant added

Acquisition Date 03.12.2014 18:33:12

Operator BDAL@DE  
Instrument / Ser# micrOTOF 10248

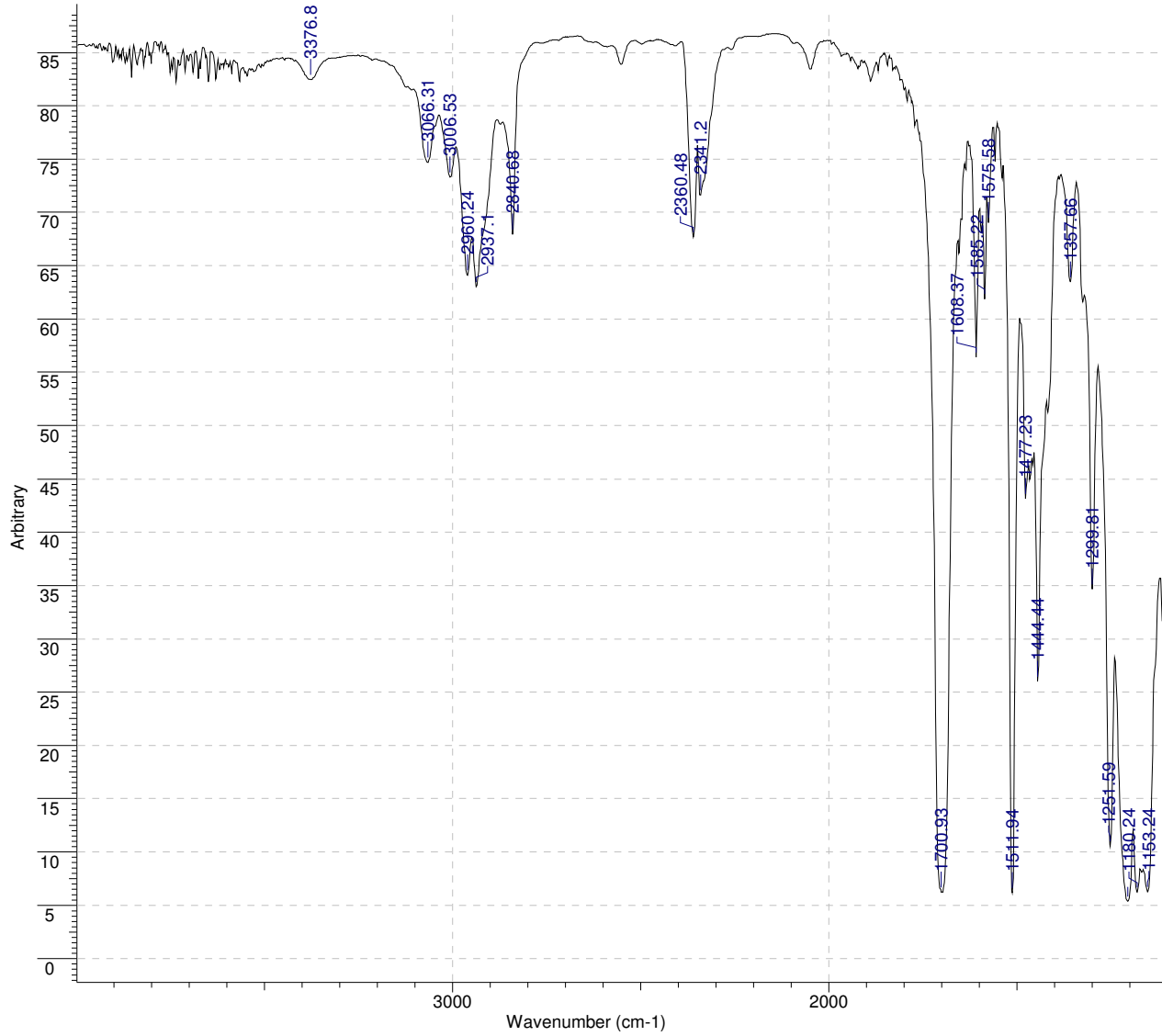
## Acquisition Parameter

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



# 1g

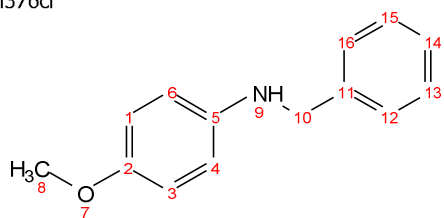
<b>Title</b>	1g	<b>File Name</b>	H:\KOLESNIKOV\PN-525OH.CSV		<b>Date</b>	05 Dec 2014 15:57:12
<b>Technique</b>	Infrared	<b>Spectral Region</b>	IR	<b>X Axis</b>	Wavenumber (cm-1)	
<b>Y Axis</b>	Arbitrary	<b>Spectrum Range</b>	399.1990 - 4001.6321		<b>Points Count</b>	1869
<b>Data Spacing</b>	1.9285					



No	cm-1	Arbitrary	Intensity	No	cm-1	Arbitrary	Intensity
1	1153.24	6.279	VW	12	1608.37	56.423	S
2	1180.24	6.214	VW	13	1700.93	6.205	VW
3	1205.31	5.358	VW	14	2341.20	71.632	S
4	1251.59	10.549	W	15	2360.48	67.666	S
5	1299.81	34.666	M	16	2840.68	67.943	S
6	1357.66	63.452	S	17	2937.10	63.036	S
7	1444.44	25.980	W	18	2960.24	64.084	S
8	1477.23	43.118	M	19	3006.53	73.296	S
9	1511.94	6.172	VW	20	3066.31	74.676	S
10	1575.58	69.024	S	21	3376.80	82.441	VS
11	1585.22	61.868	S				

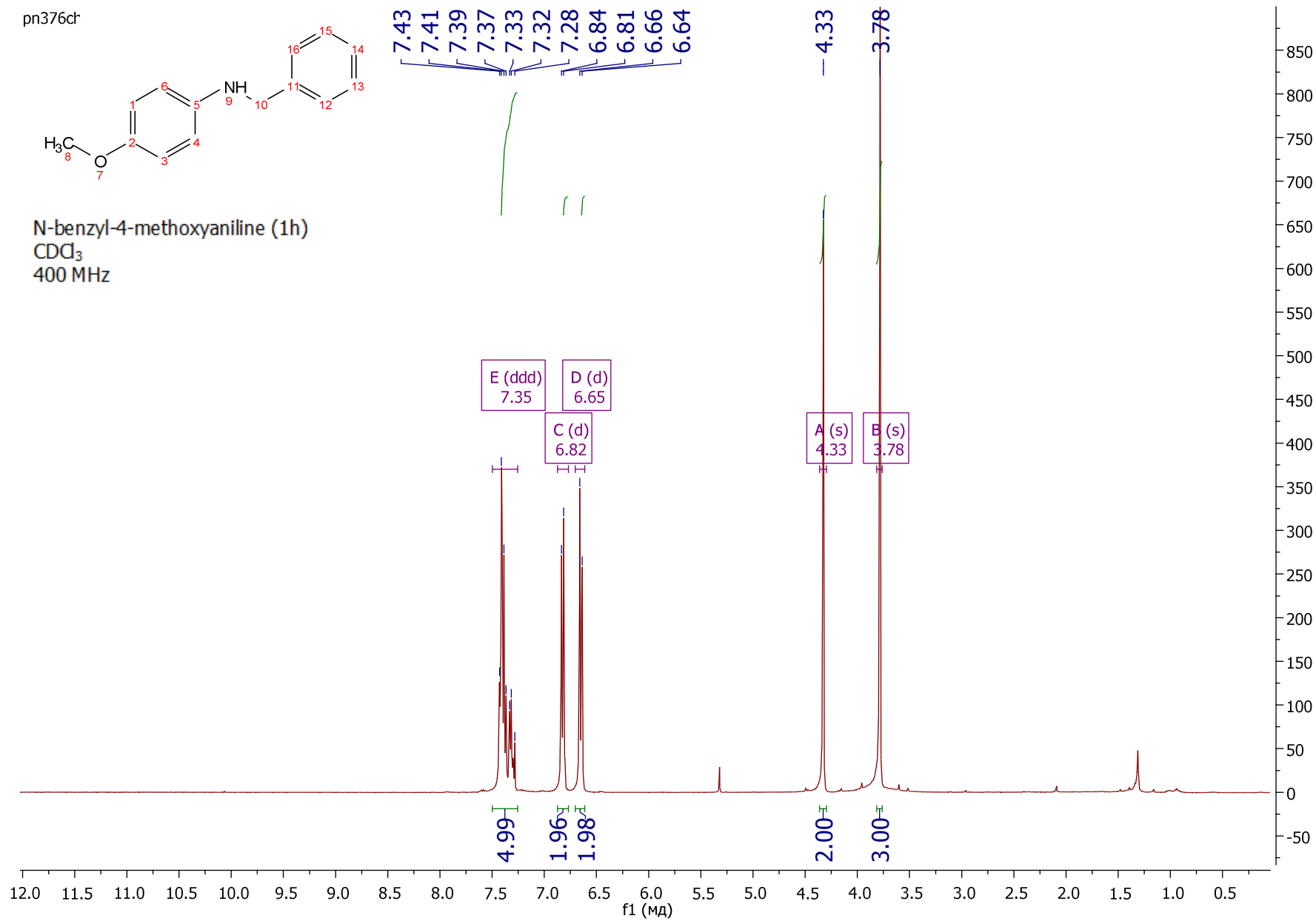
# *N*-benzyl-4-methoxyaniline (1h)

pn376ct



*N*-benzyl-4-methoxyaniline (1h)

CDCl<sub>3</sub>  
400 MHz

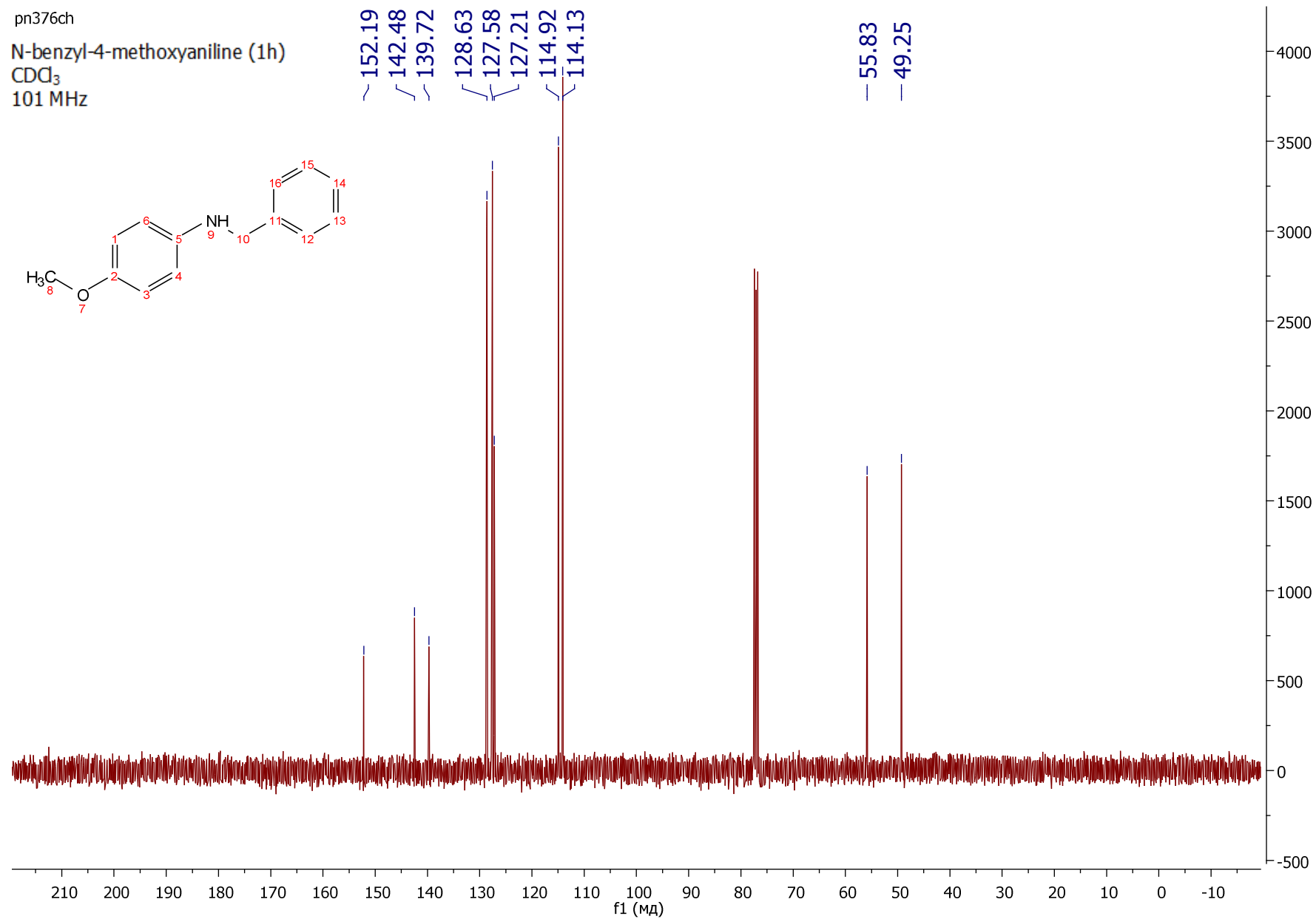
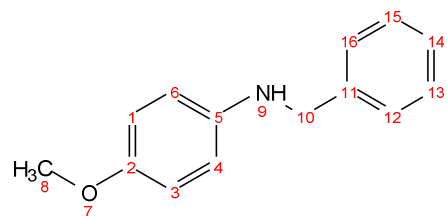


pn376ch

N-benzyl-4-methoxyaniline (1h)

CDCl<sub>3</sub>

101 MHz



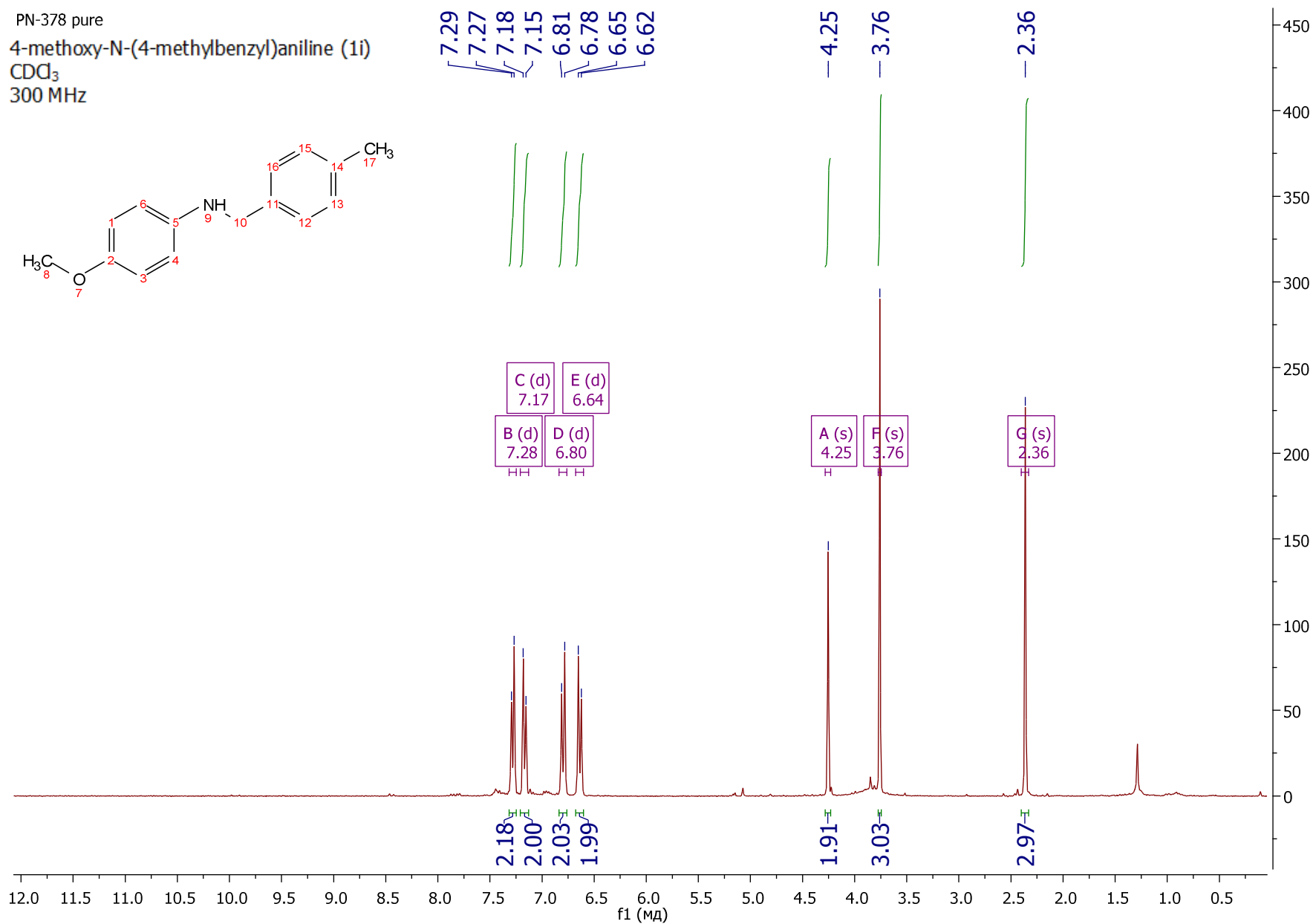
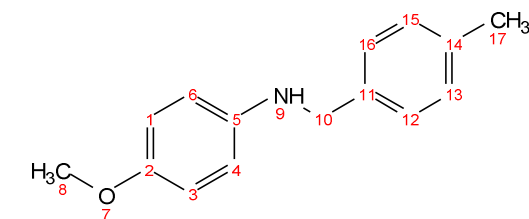
# 4-methoxy-N-(4-methylbenzyl)aniline (1i)

PN-378 pure

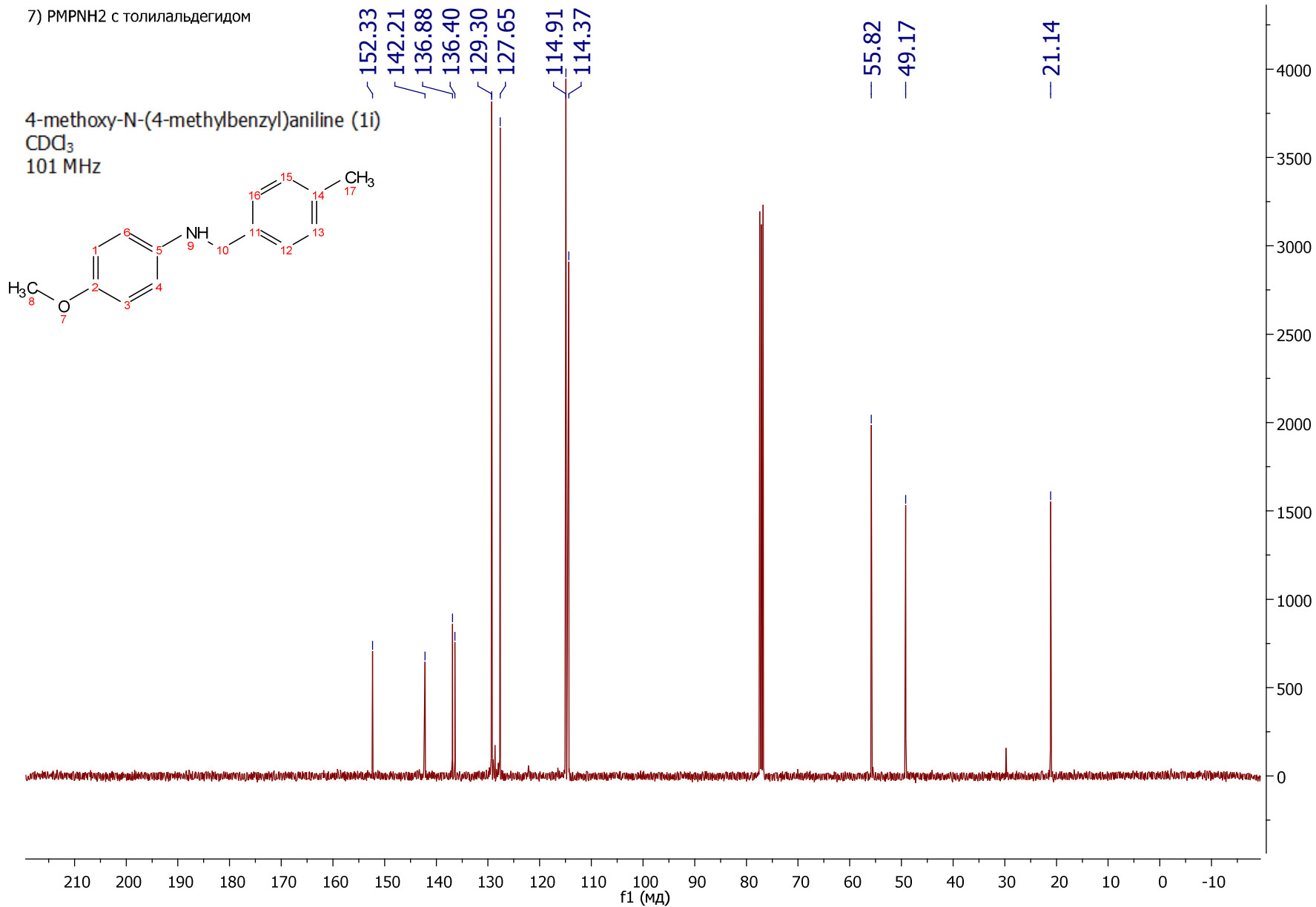
4-methoxy-N-(4-methylbenzyl)aniline (1i)

CDCl<sub>3</sub>

300 MHz



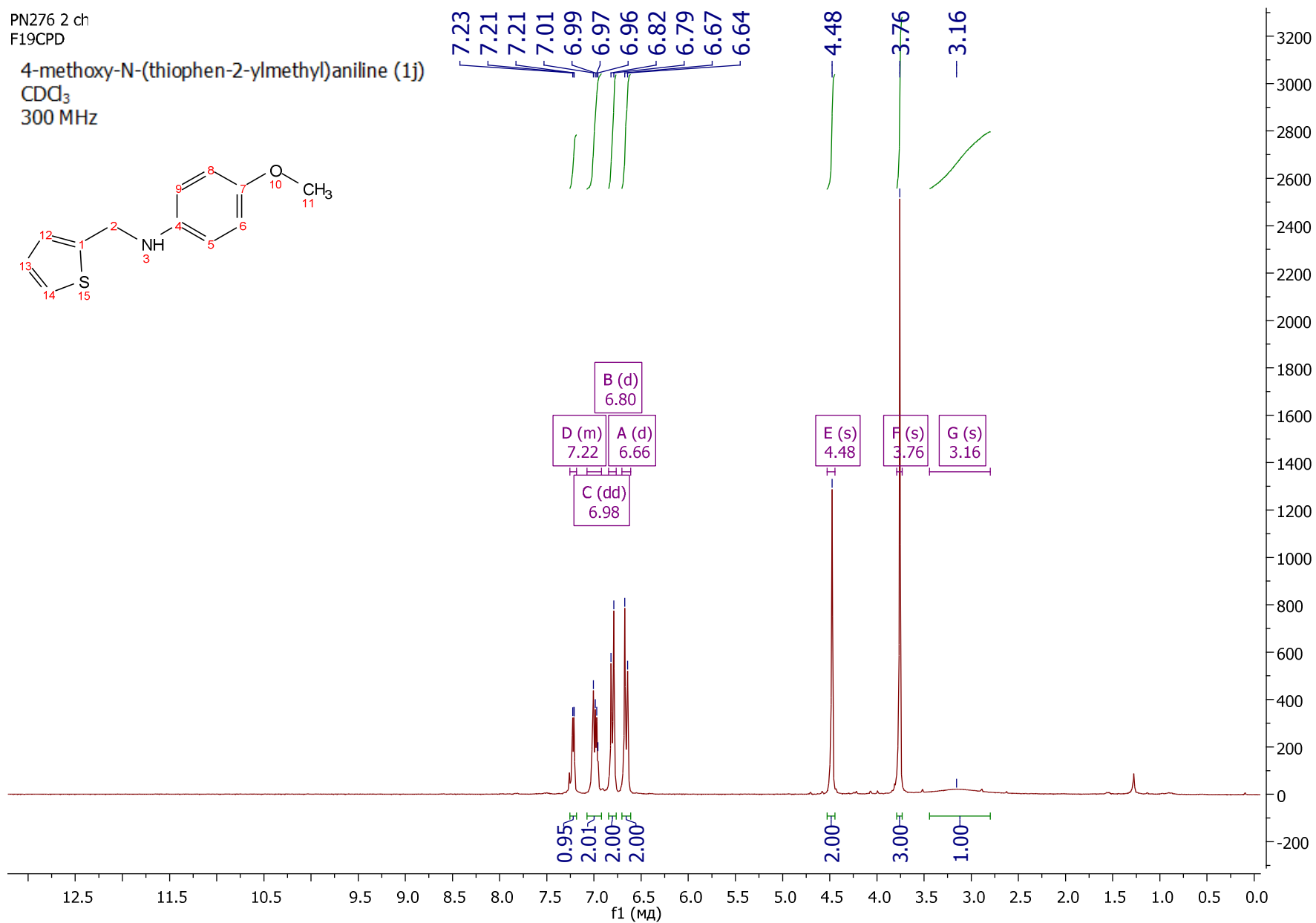
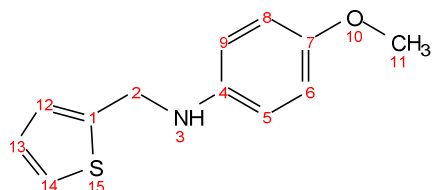
7) PMPNH2 с толилальдегидом



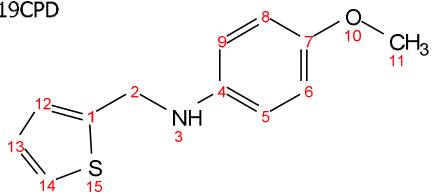
# 4-methoxy-N-(thiophen-2-ylmethyl)aniline (1j)

PN276 2 ch  
F19CPD

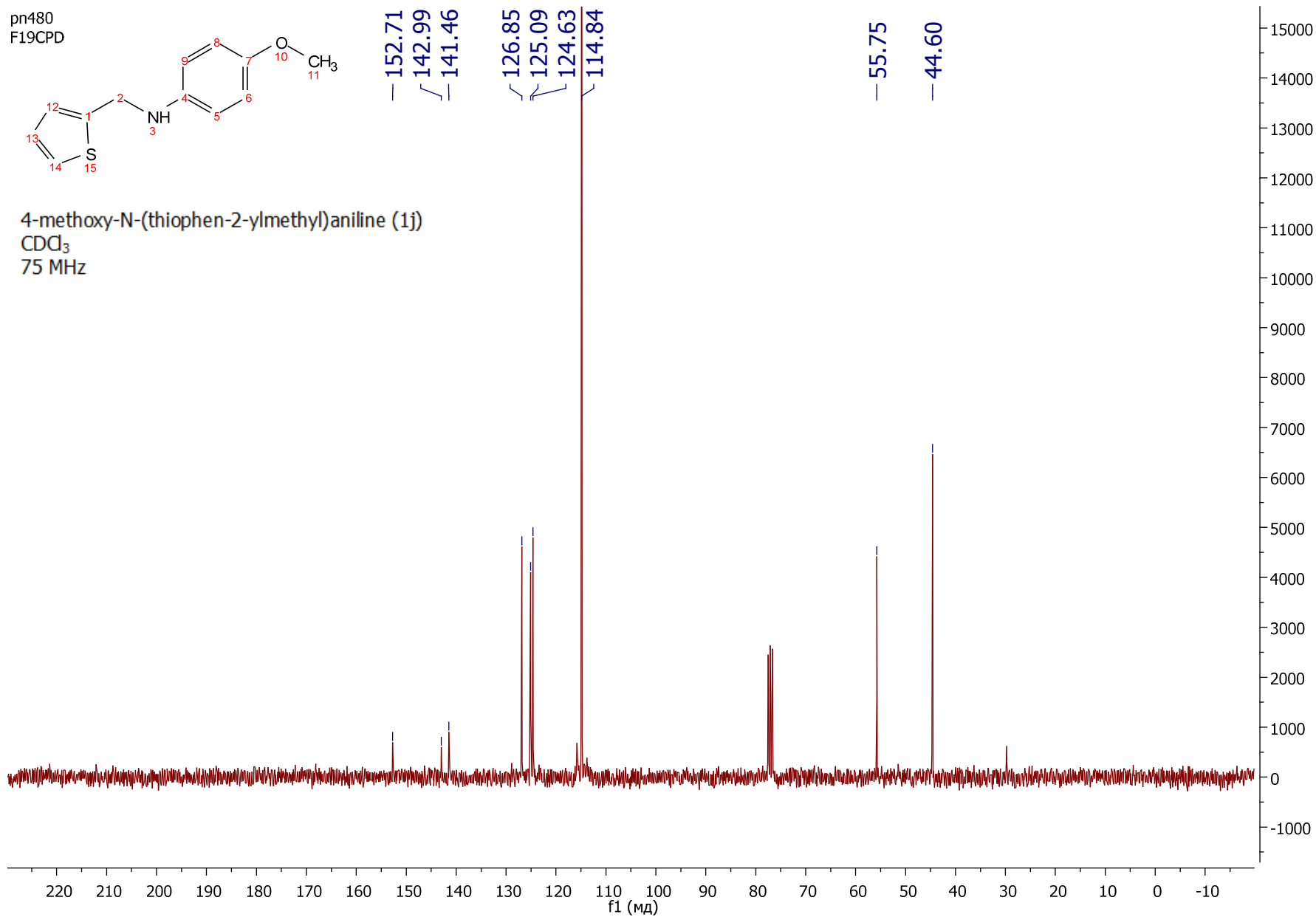
4-methoxy-N-(thiophen-2-ylmethyl)aniline (1j)  
CDCl<sub>3</sub>  
300 MHz



pn480  
F19CPD



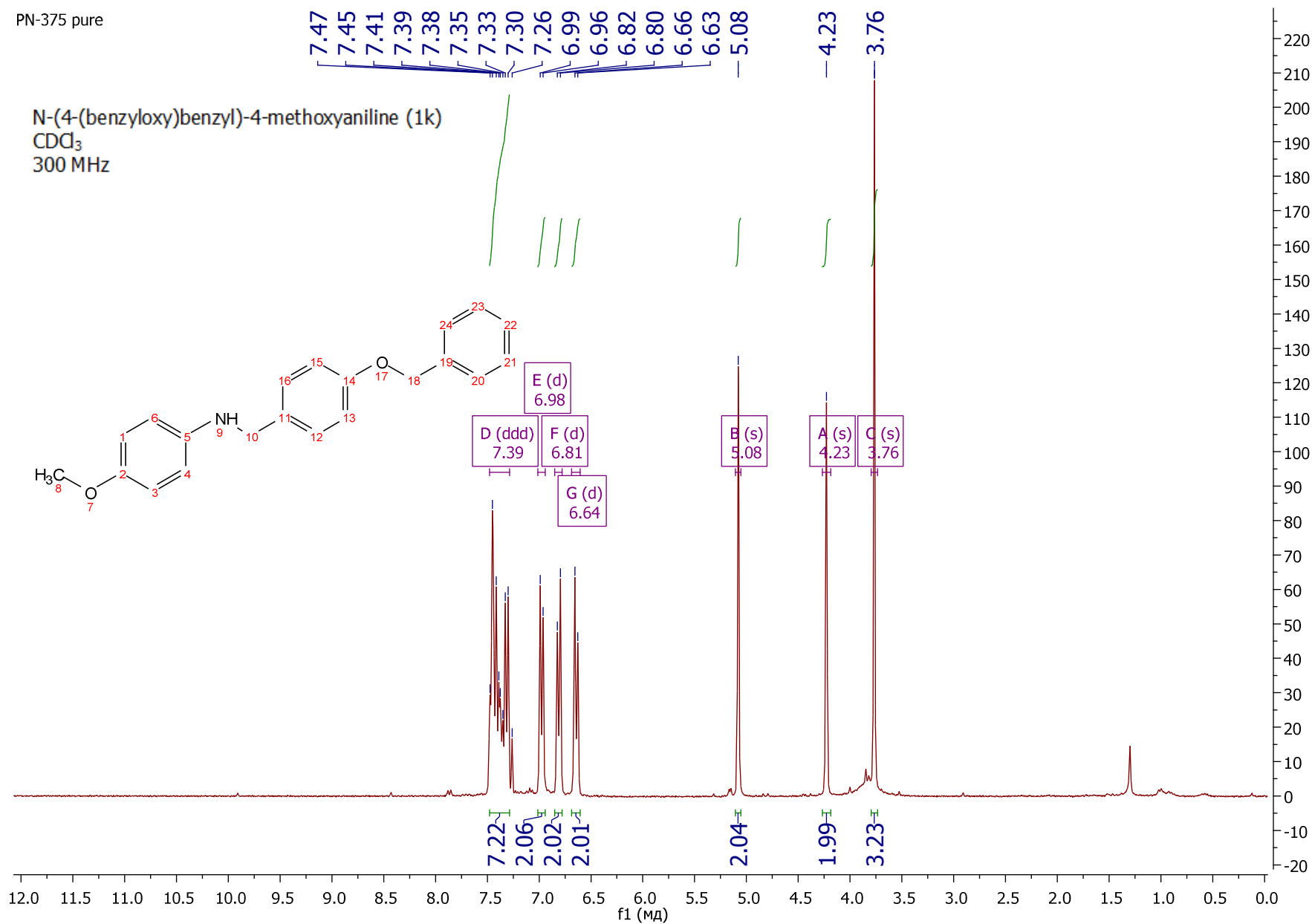
4-methoxy-N-(thiophen-2-ylmethyl)aniline (1j)  
CDCl<sub>3</sub>  
75 MHz



# *N*-(4-(benzyloxy)benzyl)-4-methoxyaniline (1k)

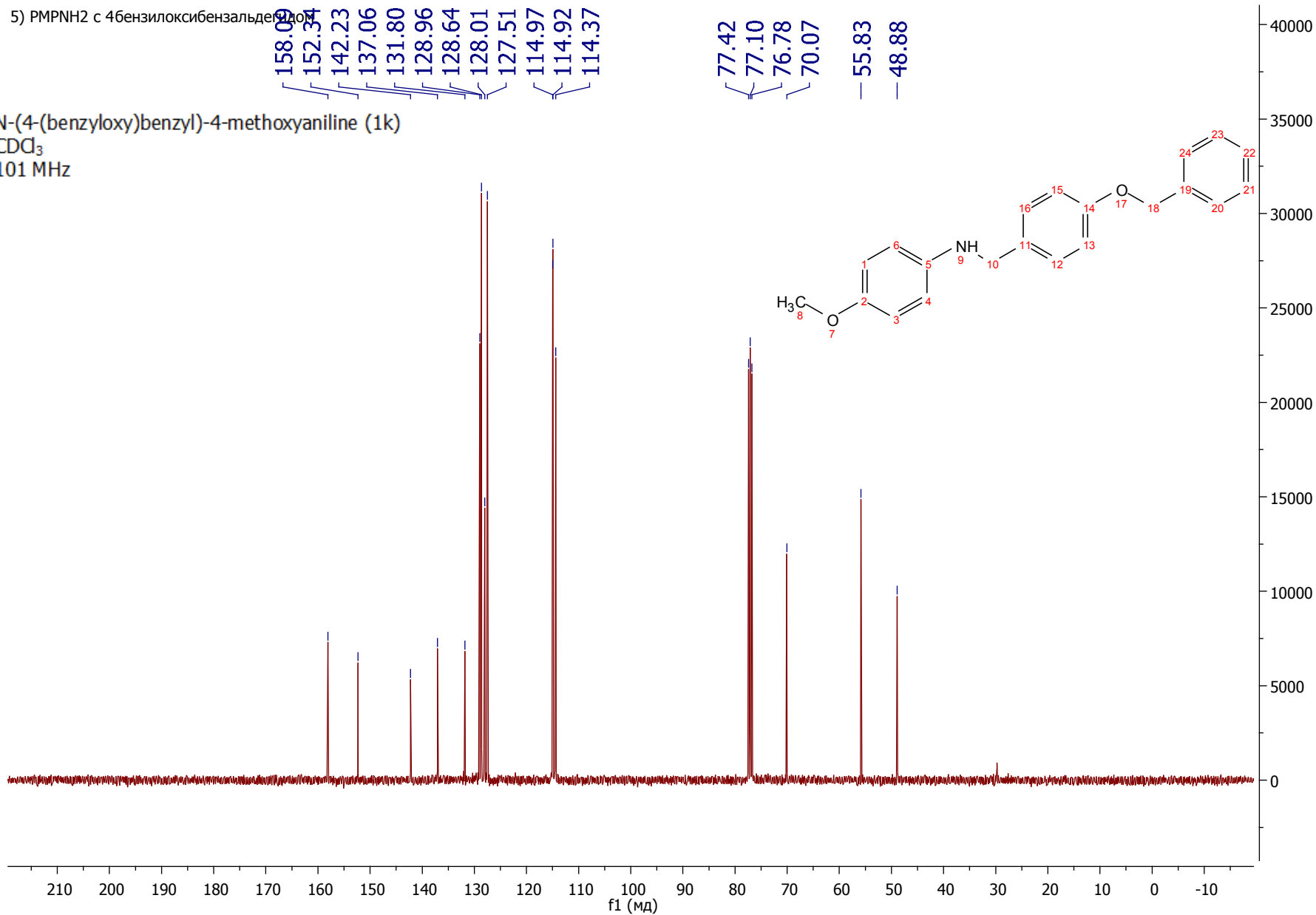
PN-375 pure

*N*-(4-(benzyloxy)benzyl)-4-methoxyaniline (1k)  
CDCl<sub>3</sub>  
300 MHz



5) PMPNH2 с 4бензилоксибензальдегидом

N-(4-(benzyloxy)benzyl)-4-methoxyaniline (1k)  
CDCl<sub>3</sub>  
101 MHz



# Display Report

## Analysis Info

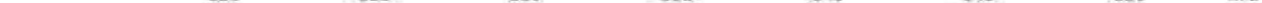
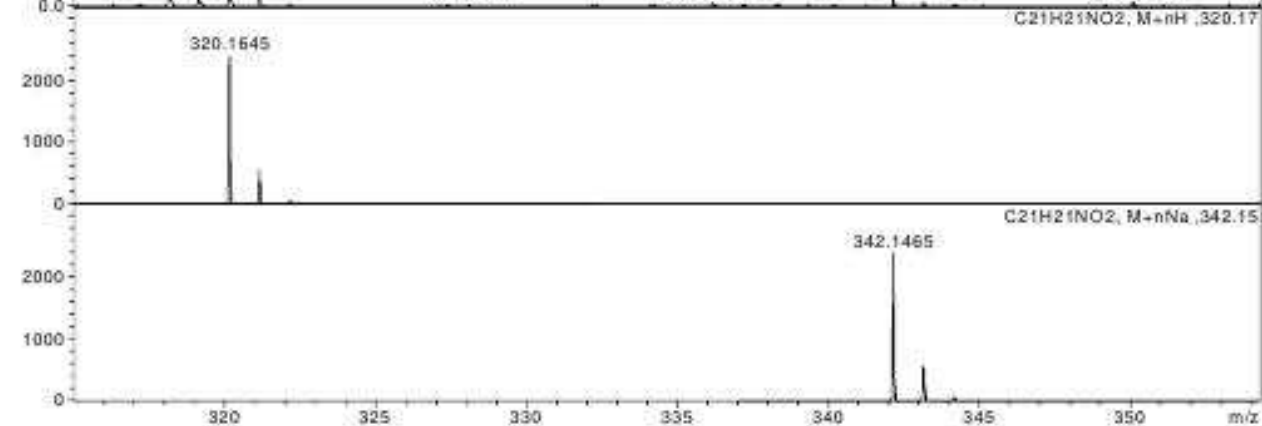
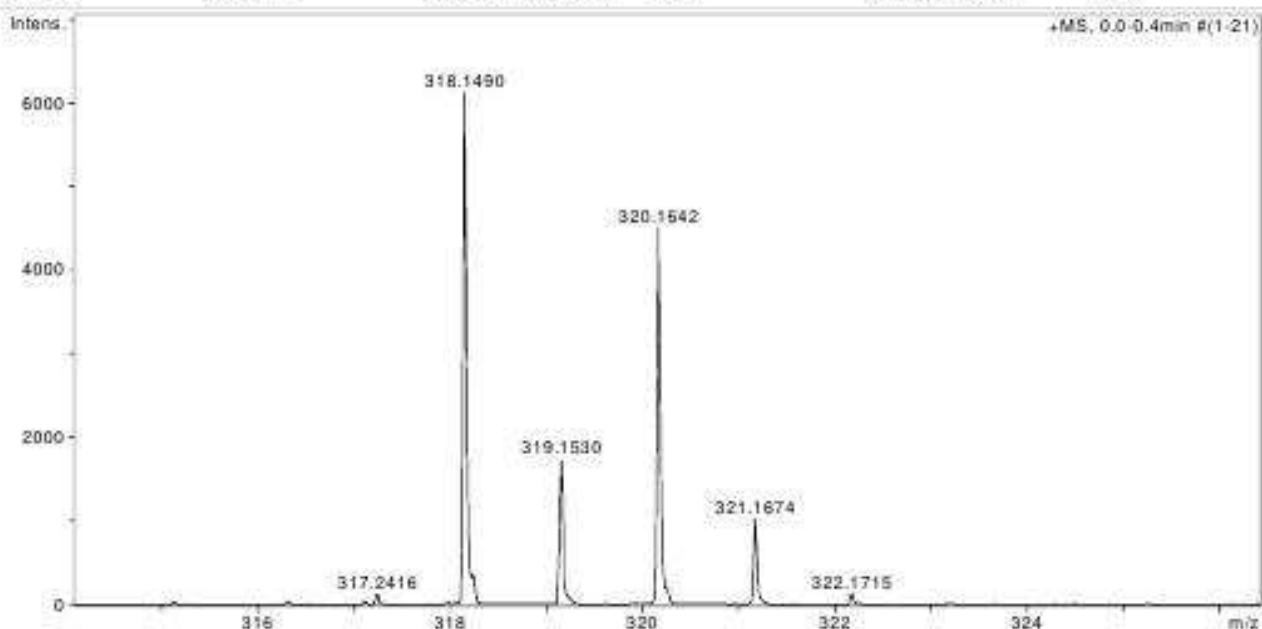
Analysis Name D:\Data\Ivanova\DenisChusov\DEN-1k.d  
Method tune\_low.m  
Sample Name /LEVH DEN-1k  
Comment CH3CN 100 %, dil 200

Acquisition Date 25.11.2014 17:08:01

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

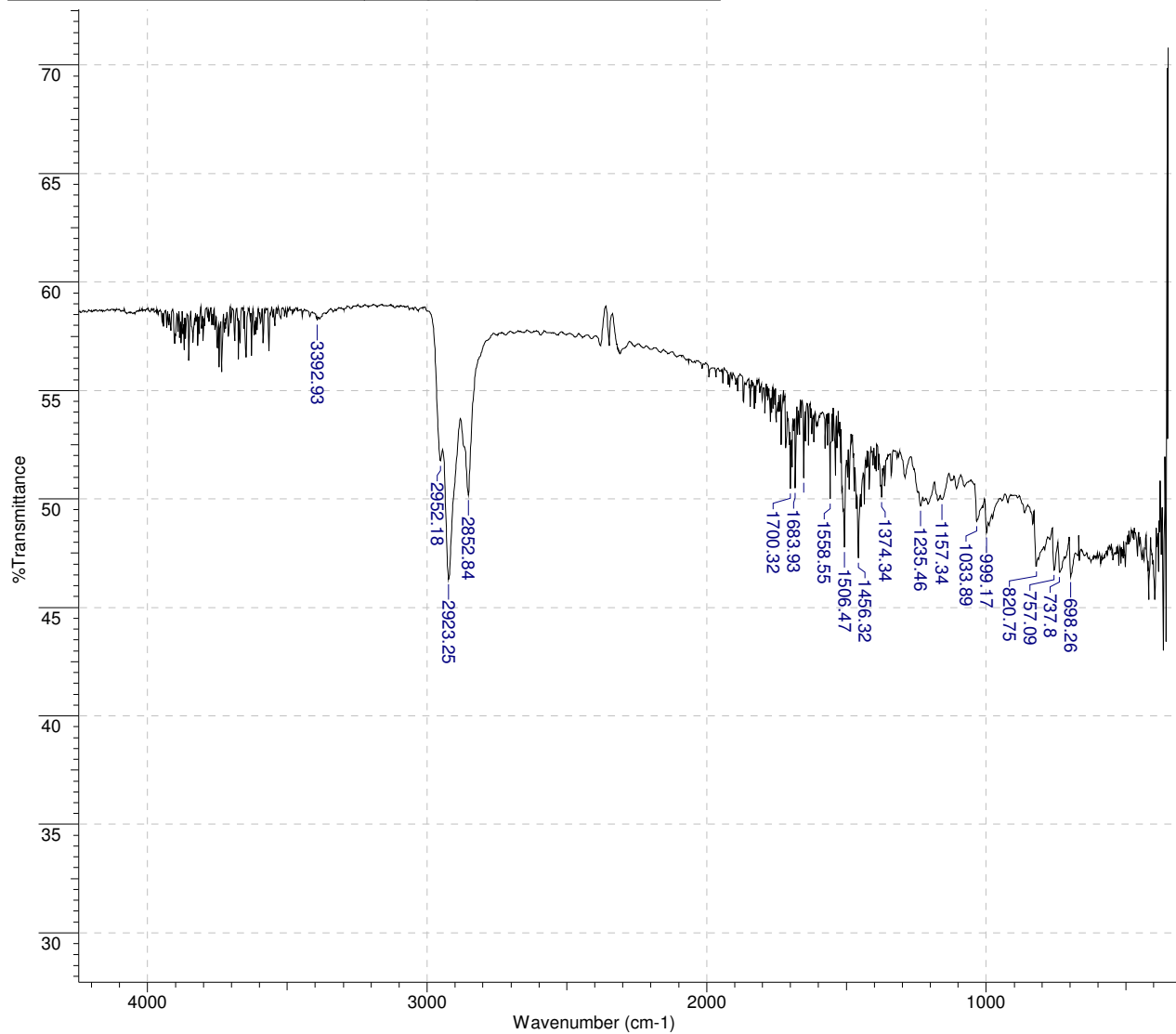
## Acquisition Parameter

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



# 1k

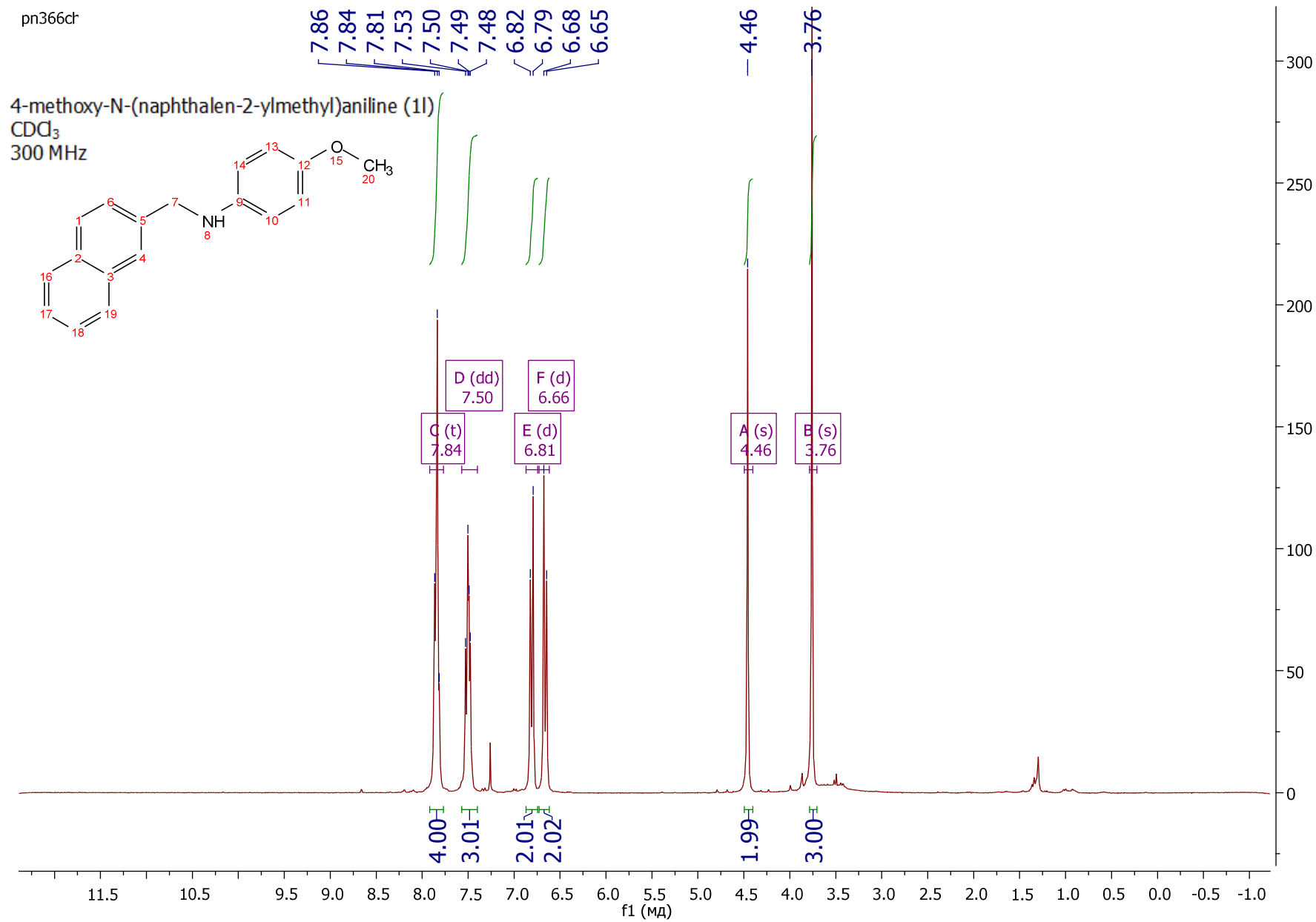
<b>Title</b>	1k		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚÁĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1K.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:43:22	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699



No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	698.26	46.387	S	11	1506.47	47.769	S
2	737.80	46.616	S	12	1558.55	50.012	S
3	757.09	46.719	S	13	1653.07	50.960	S
4	820.75	46.884	S	14	1683.93	50.506	S
5	999.17	48.440	S	15	1700.32	50.483	S
6	1033.89	48.961	S	16	2852.84	50.169	S
7	1157.34	49.976	S	17	2923.25	46.300	S
8	1235.46	49.686	S	18	2952.18	51.759	S
9	1374.34	50.069	S	19	3392.93	58.256	M
10	1456.32	47.285	S				

# 4-methoxy-N-(naphthalen-2-ylmethyl)aniline (11)

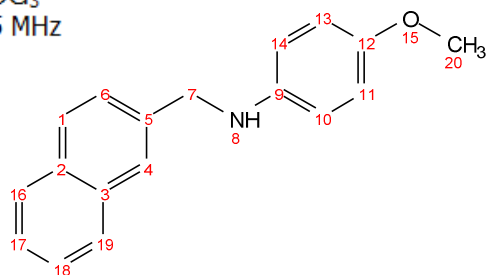
pn366ct



pn366ch

4-methoxy-N-(naphthalen-2-ylmethyl)aniline (1)

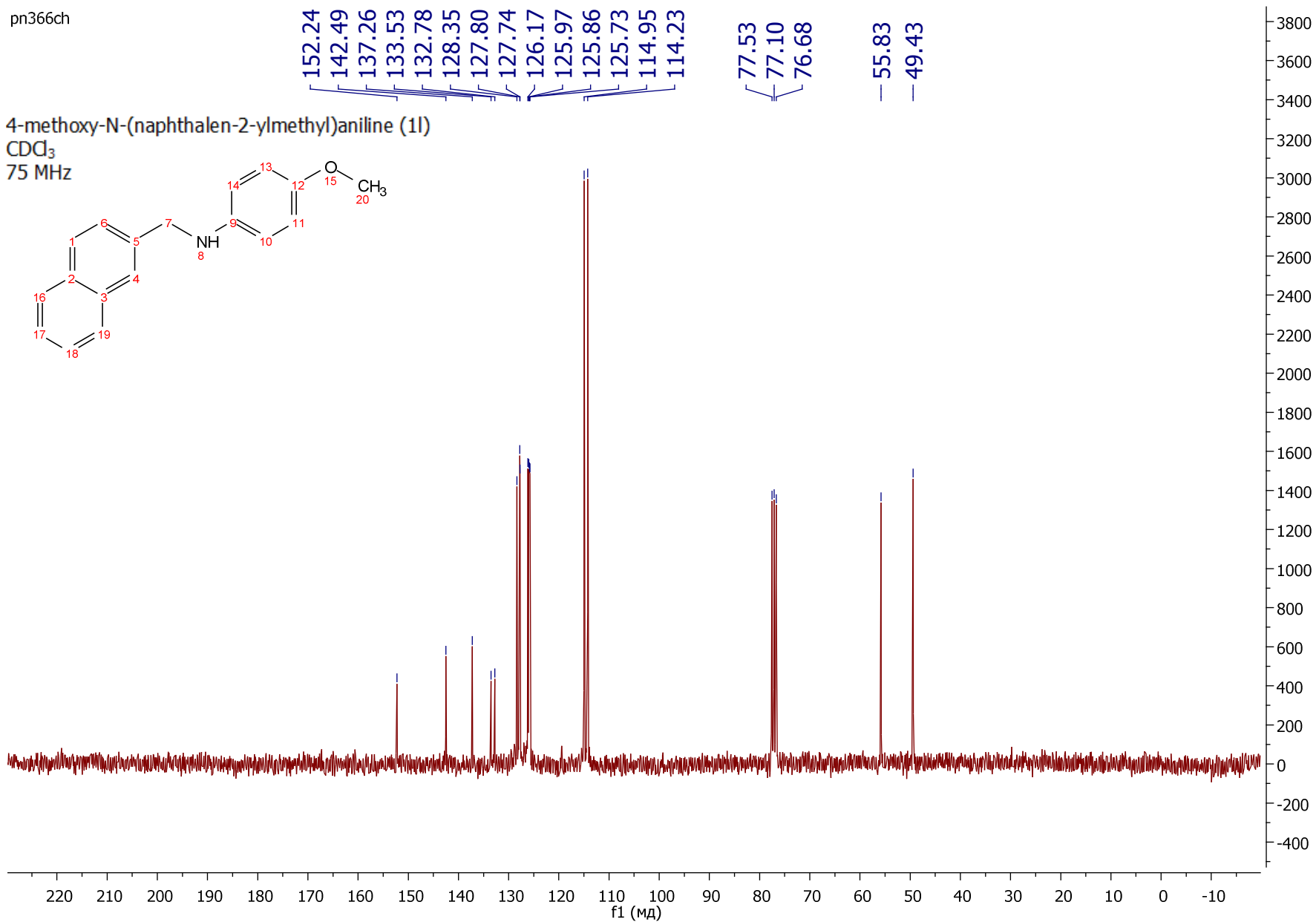
CDCl<sub>3</sub>  
75 MHz



152.24  
142.49  
137.26  
133.53  
132.78  
128.35  
127.80  
127.74  
126.17  
125.97  
125.86  
125.73  
114.95  
114.23

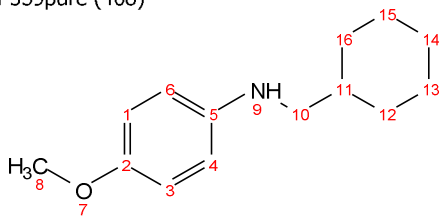
77.53  
77.10  
76.68

55.83  
49.43

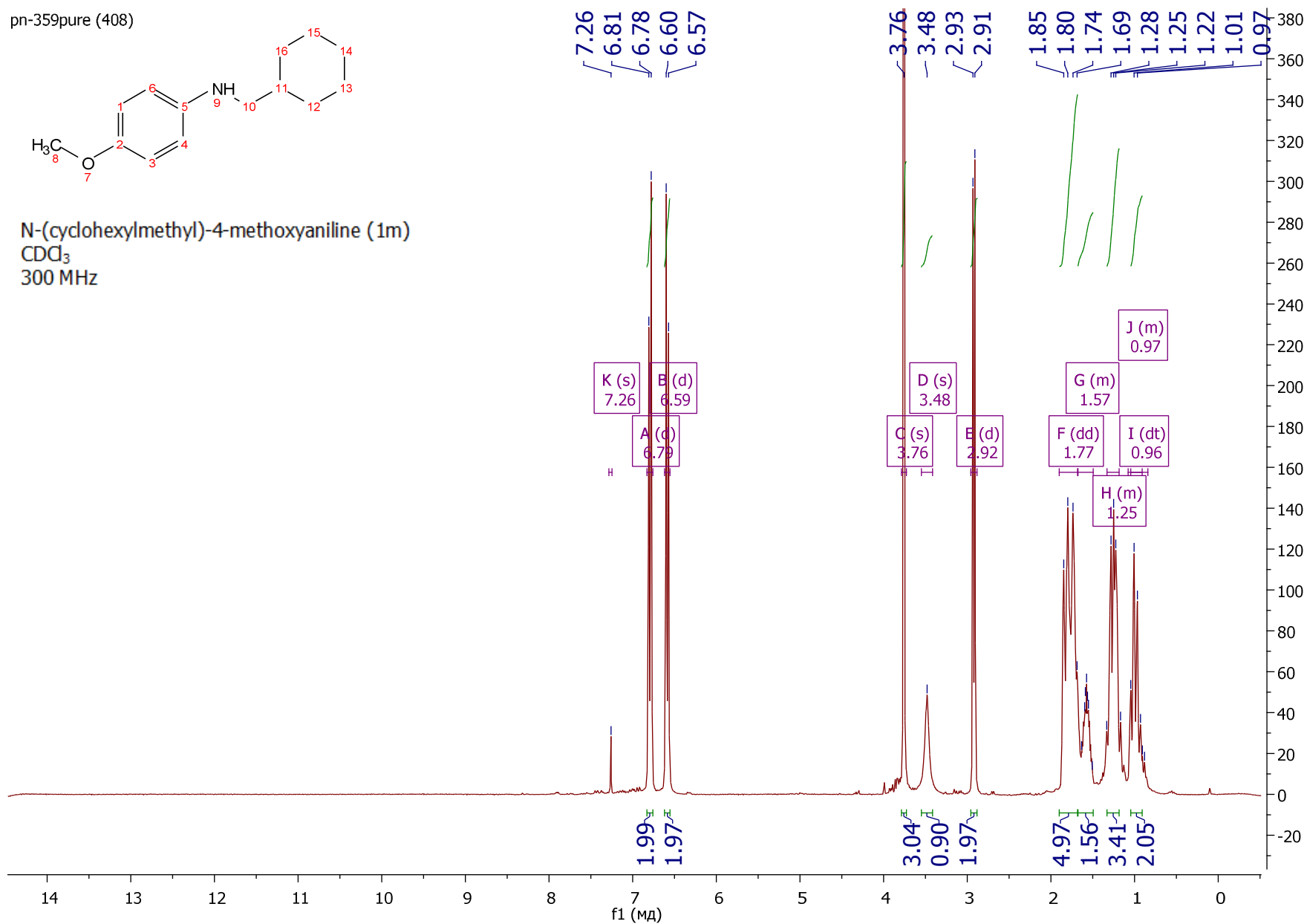


# *N*-(cyclohexylmethyl)-4-methoxyaniline (1m)

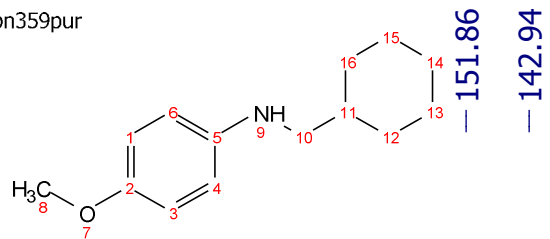
pn-359pure (408)



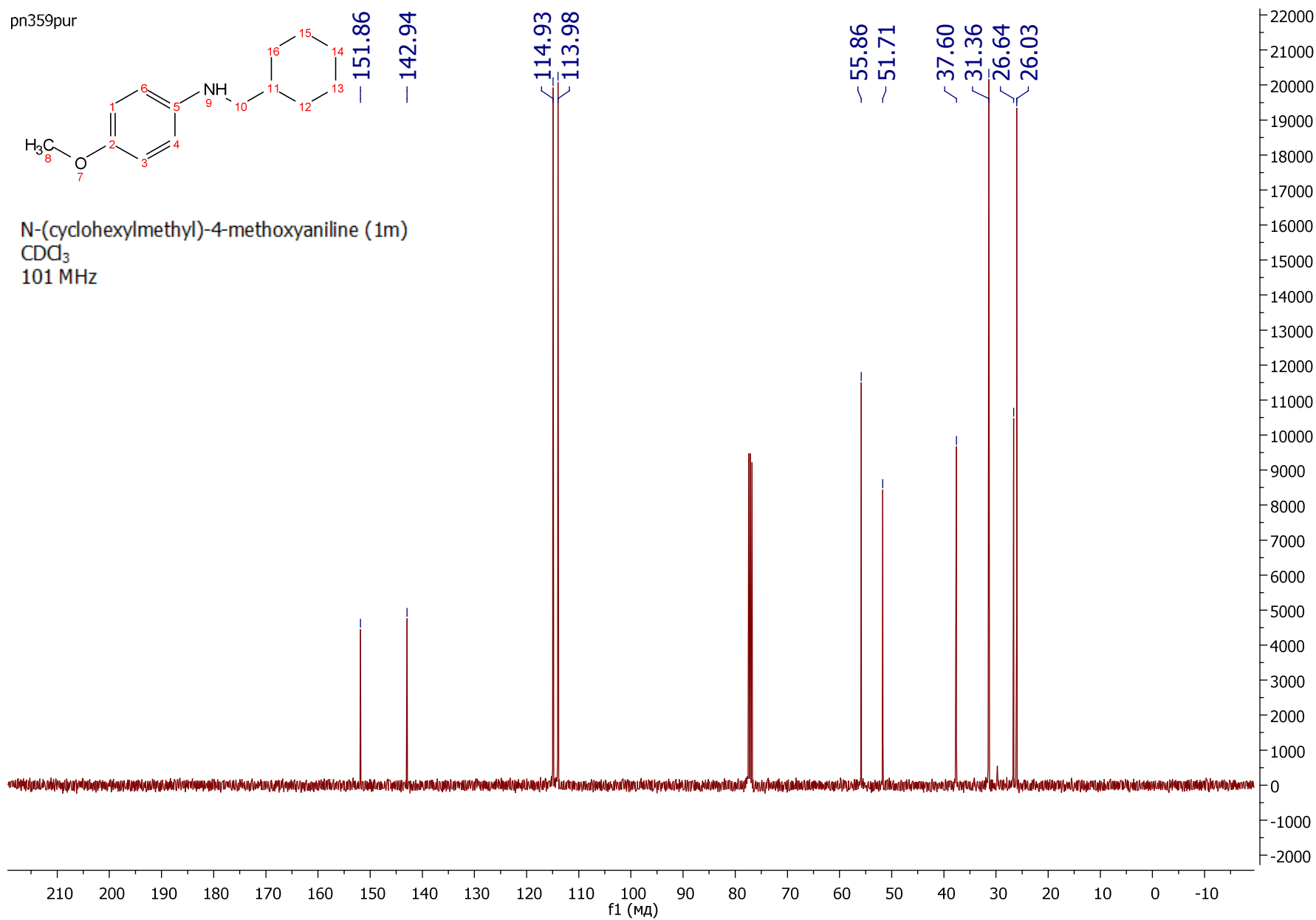
*N*-(cyclohexylmethyl)-4-methoxyaniline (1m)  
CDCl<sub>3</sub>  
300 MHz



pn359pur

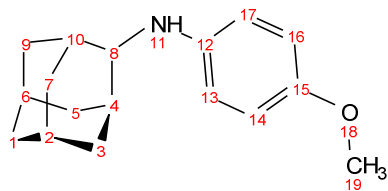


N-(cyclohexylmethyl)-4-methoxyaniline (1m)  
CDCl<sub>3</sub>  
101 MHz

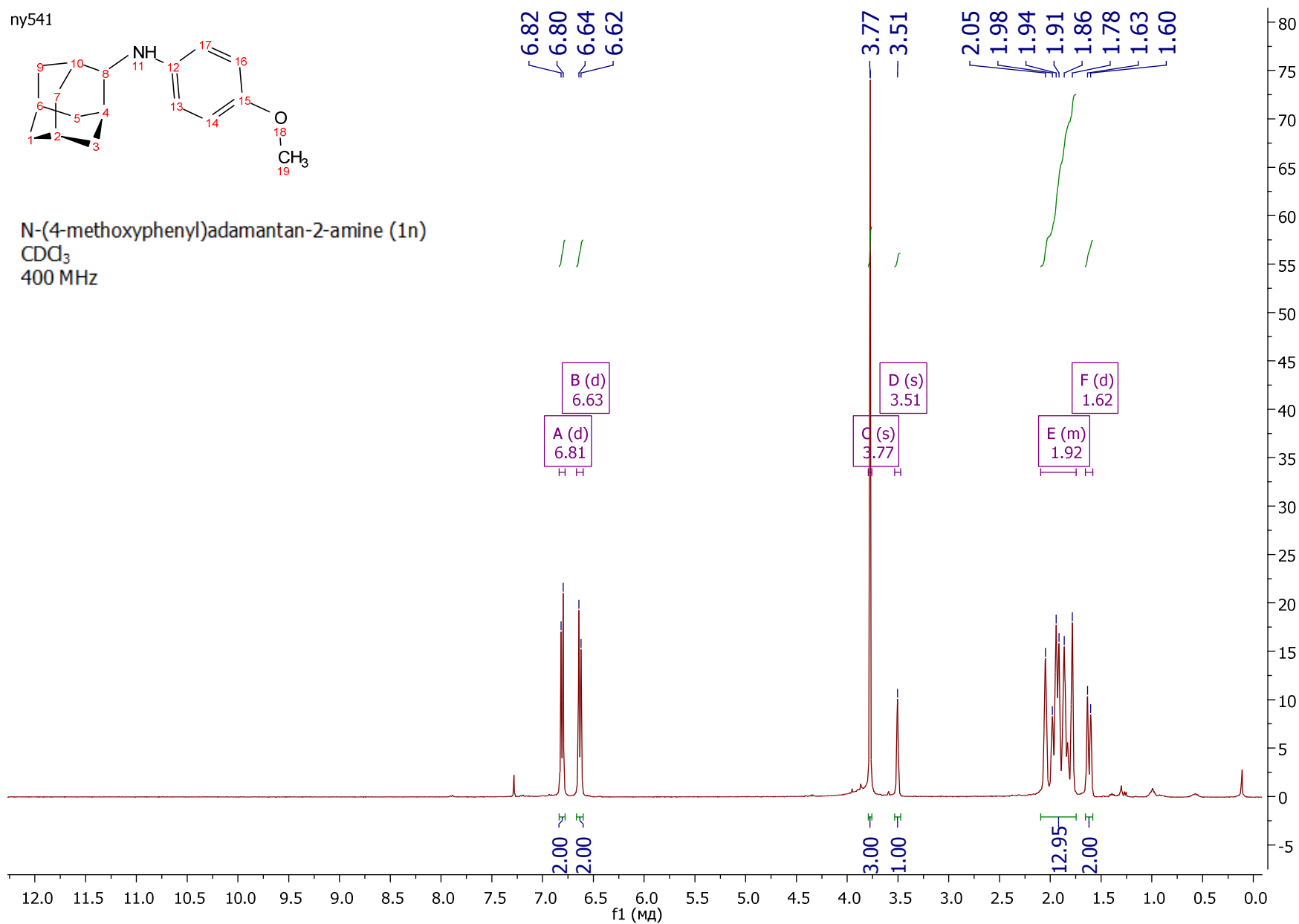


# *N*-(4-methoxyphenyl)adamantan-2-amine (1n)

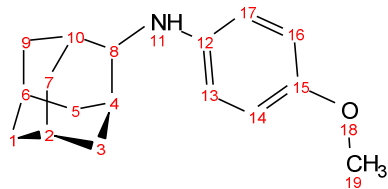
ny541



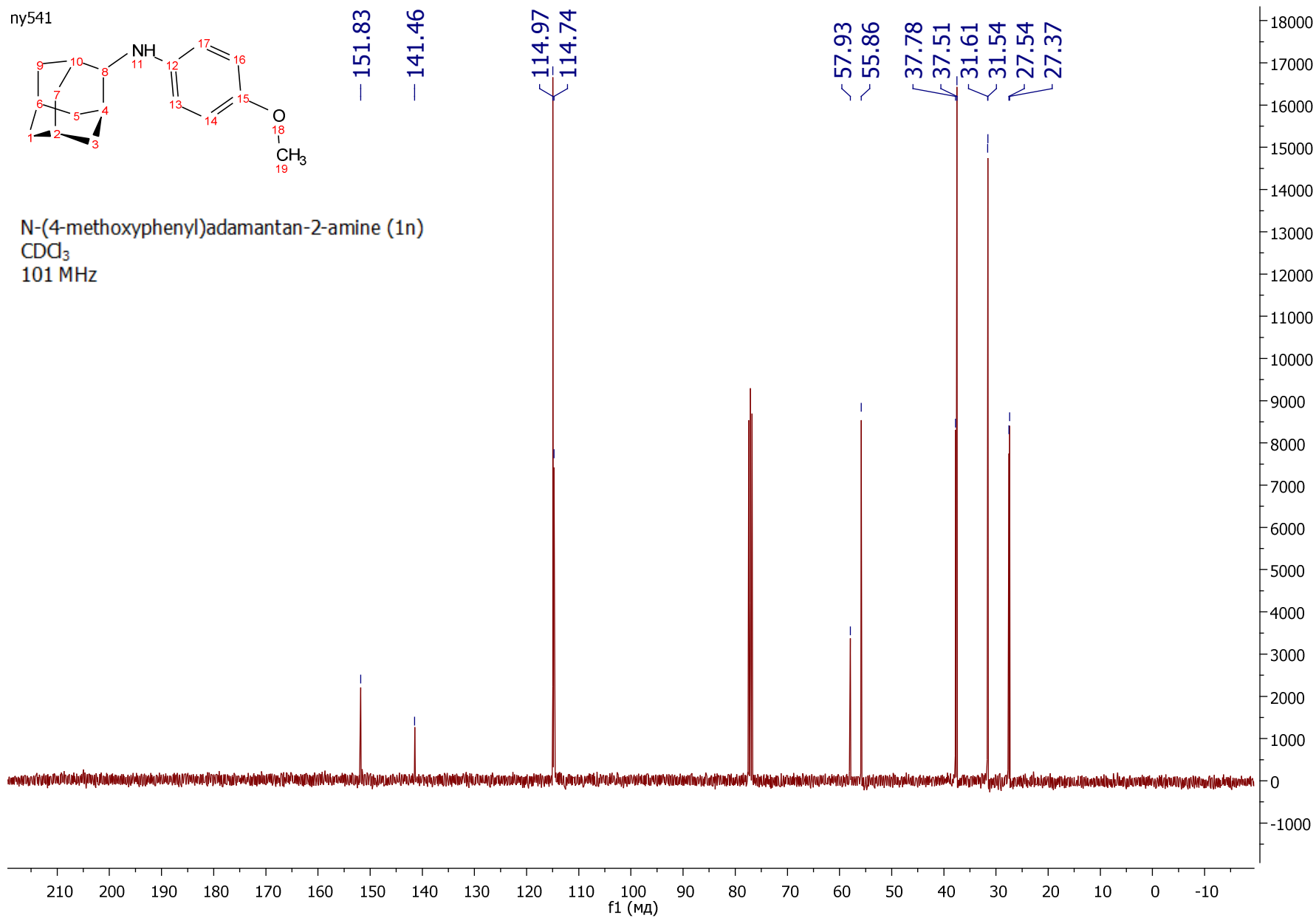
*N*-(4-methoxyphenyl)adamantan-2-amine (1n)  
CDCl<sub>3</sub>  
400 MHz



ny541



N-(4-methoxyphenyl)adamantan-2-amine (1n)  
CDCl<sub>3</sub>  
101 MHz



# Display Report

## Analysis Info

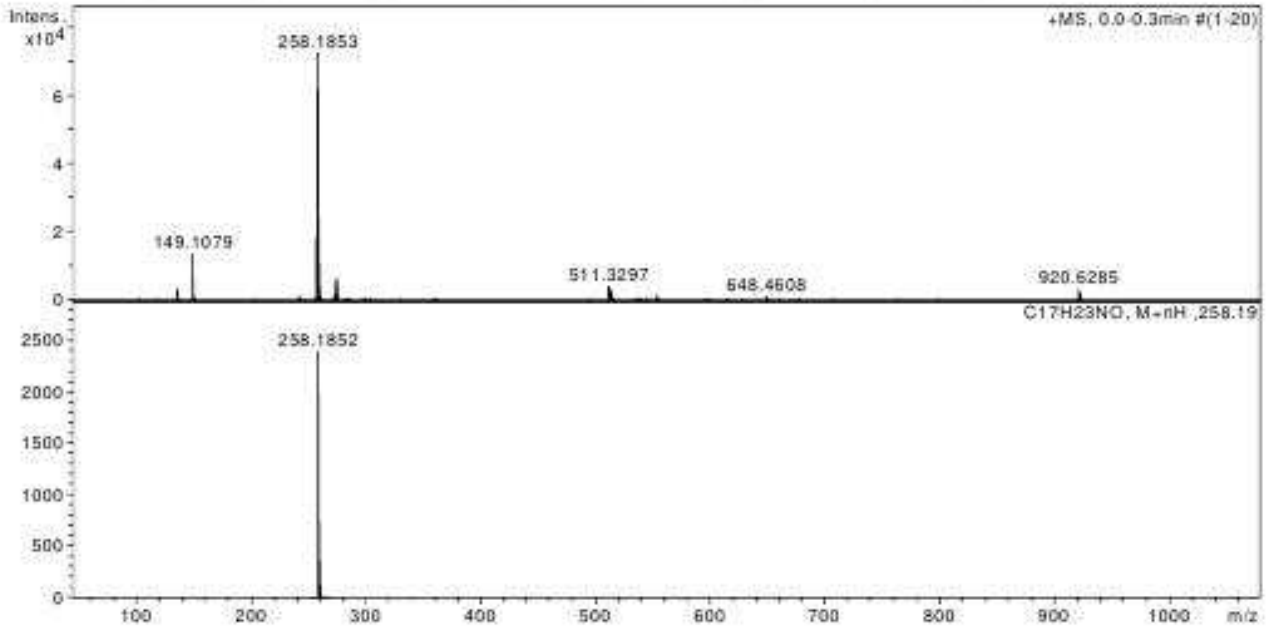
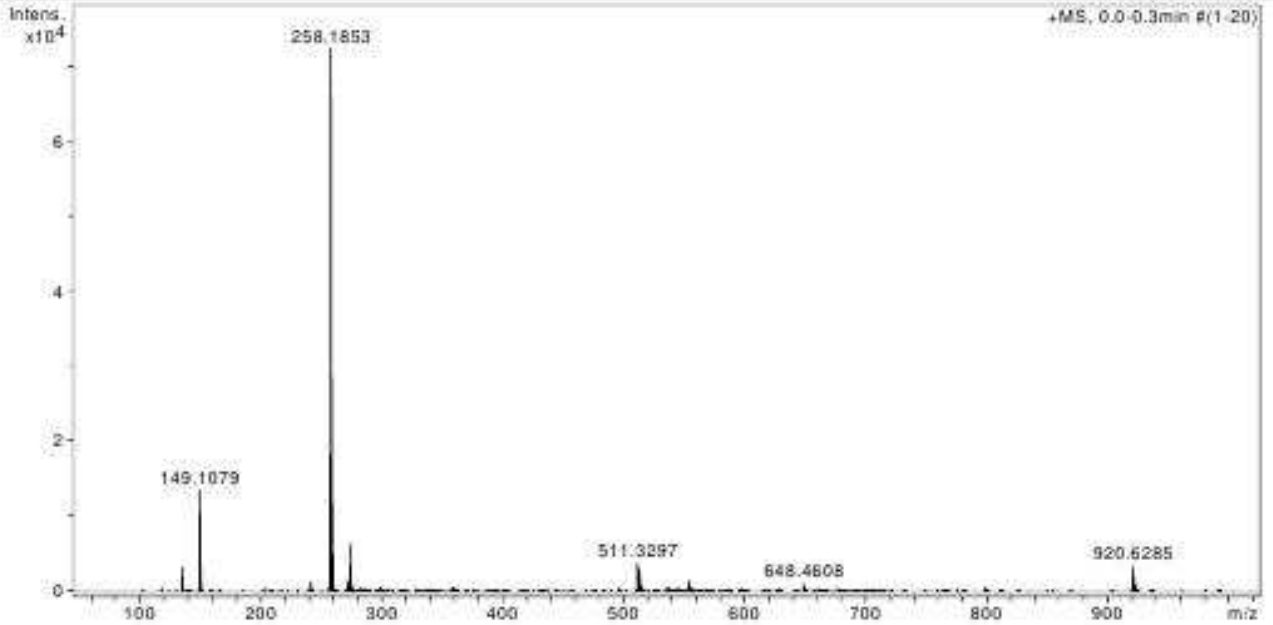
Analysis Name D:\Data\Ivanova\DEN-1n.d  
Method tune\_low.m  
Sample Name /LEVH DEN-1n  
Comment CH3CN 100 %, dil 200

Acquisition Date 25.11.2014 17:39:38

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

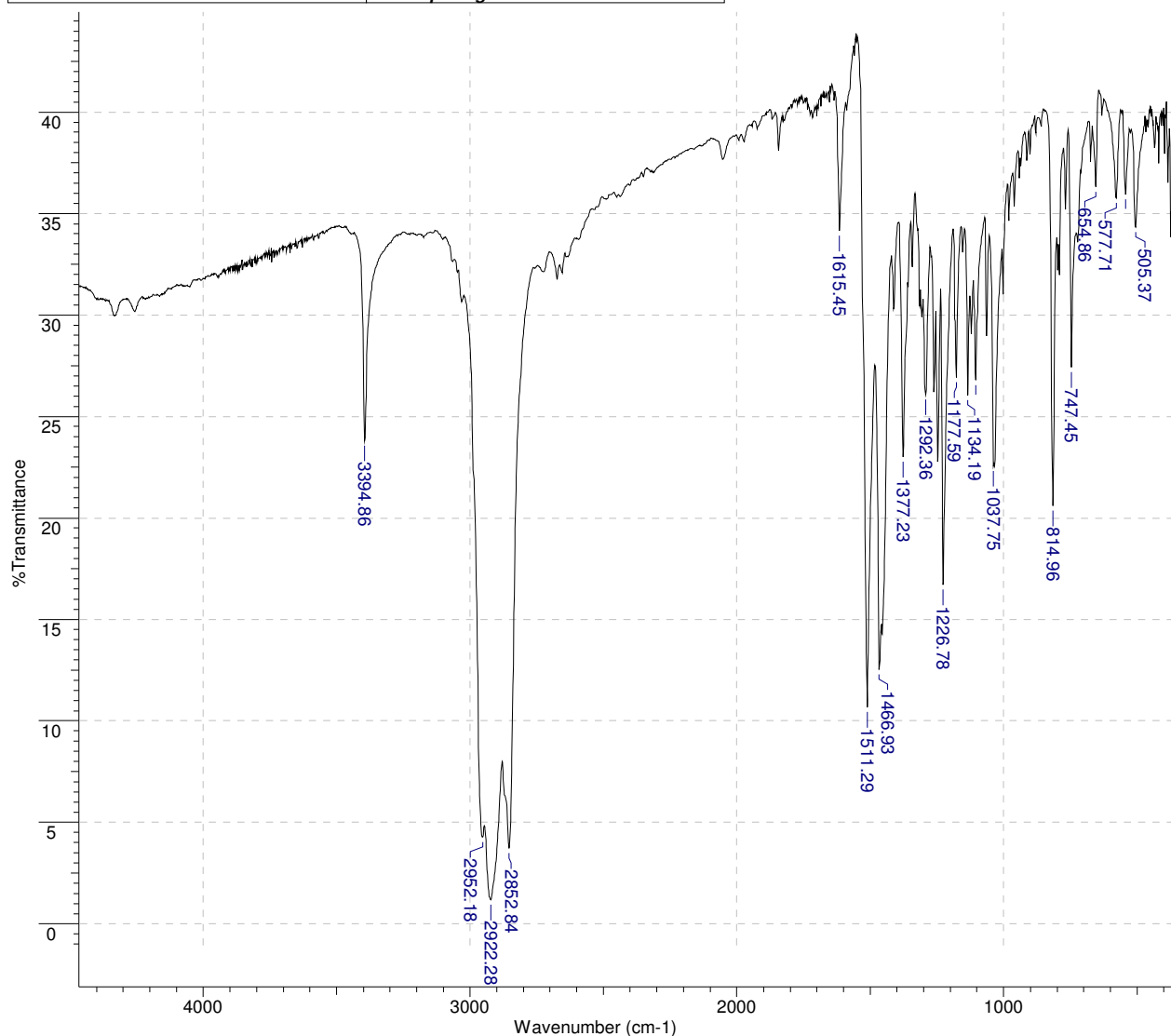
## Acquisition Parameter

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



# 1n

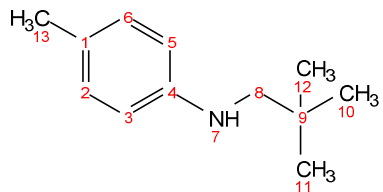
<b>Title</b>	1n		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚÁÁĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1N1.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:43:48	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699



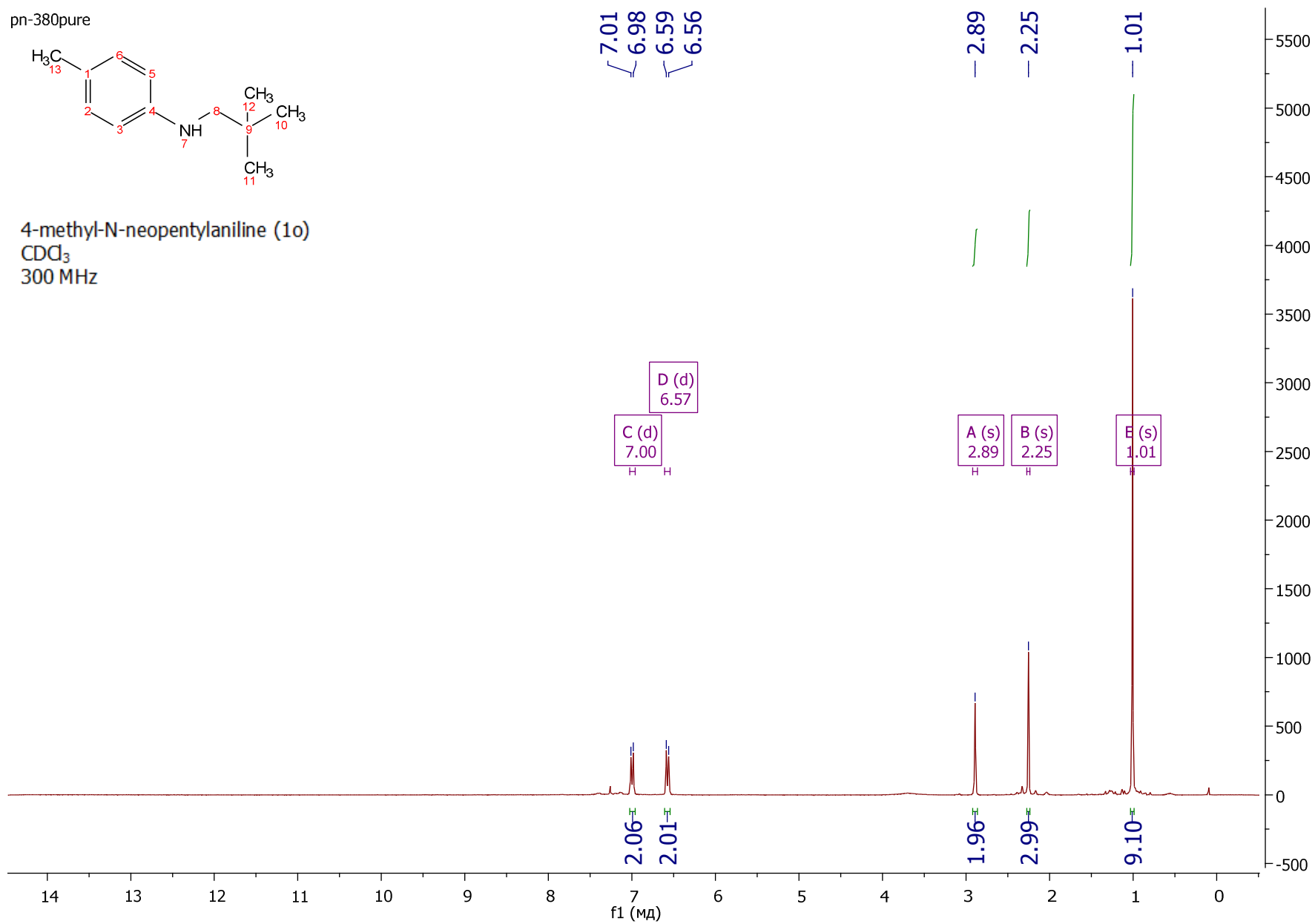
No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	505.37	34.320	W	11	1226.78	16.717	S
2	543.95	35.934	W	12	1292.36	26.077	M
3	577.71	35.757	W	13	1377.23	23.006	M
4	654.86	36.322	W	14	1466.93	12.524	S
5	747.45	27.421	M	15	1511.29	10.684	S
6	814.96	20.606	M	16	1615.45	34.149	W
7	1037.75	22.545	M	17	2852.84	3.718	VS
8	1105.26	26.792	M	18	2922.28	1.177	VS
9	1134.19	26.052	M	19	2952.18	4.266	VS
10	1177.59	26.918	M	20	3394.86	23.794	M

# 4-methyl-N-neopentylaniline (1o)

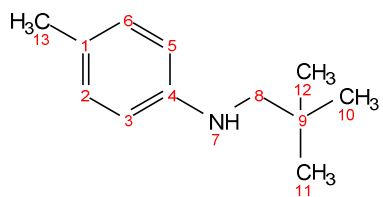
pn-380pure



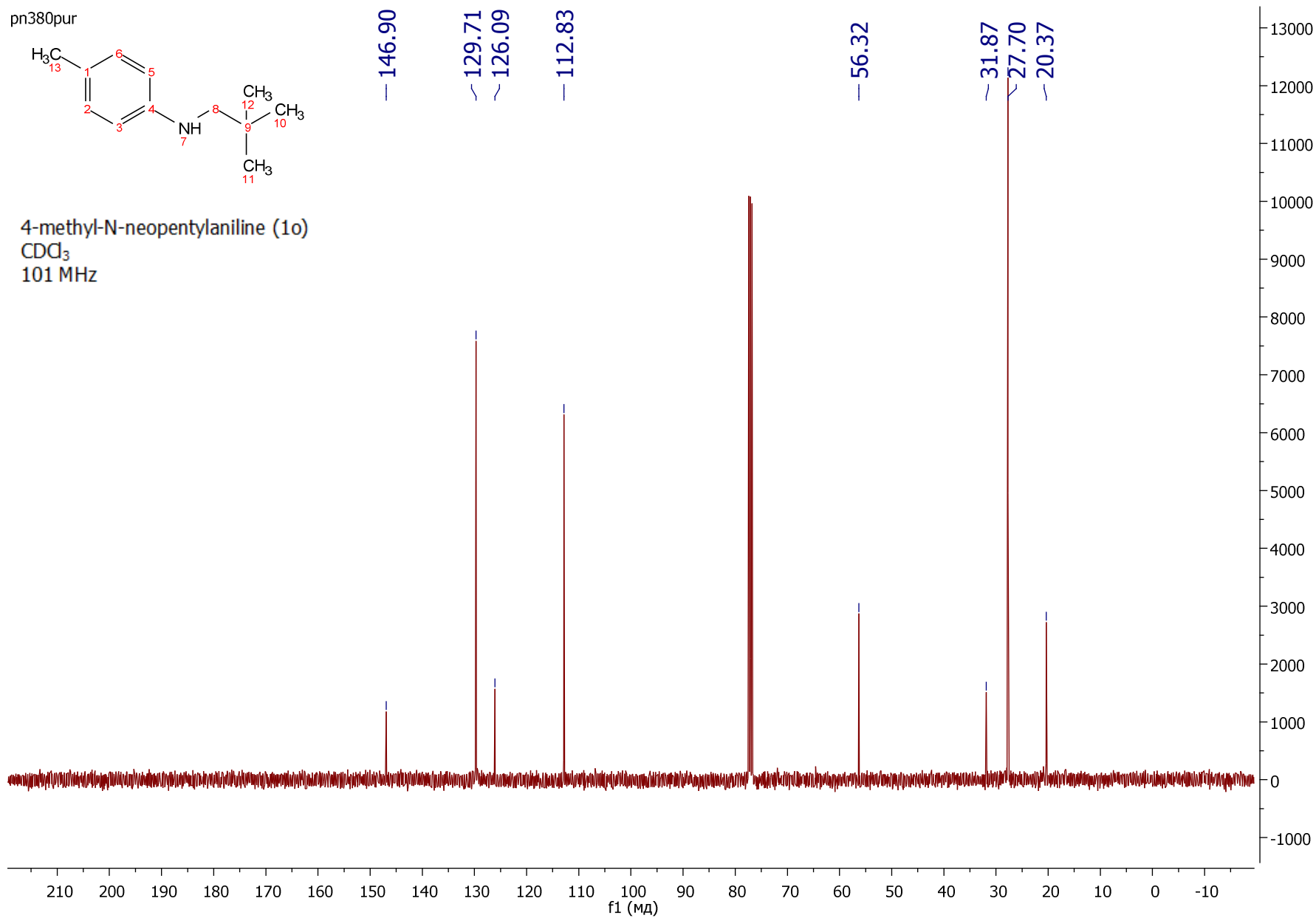
4-methyl-N-neopentylaniline (1o)  
CDCl<sub>3</sub>  
300 MHz



pn380pur



4-methyl-N-neopentylaniline (1o)  
CDCl<sub>3</sub>  
101 MHz



# Display Report

## Analysis Info

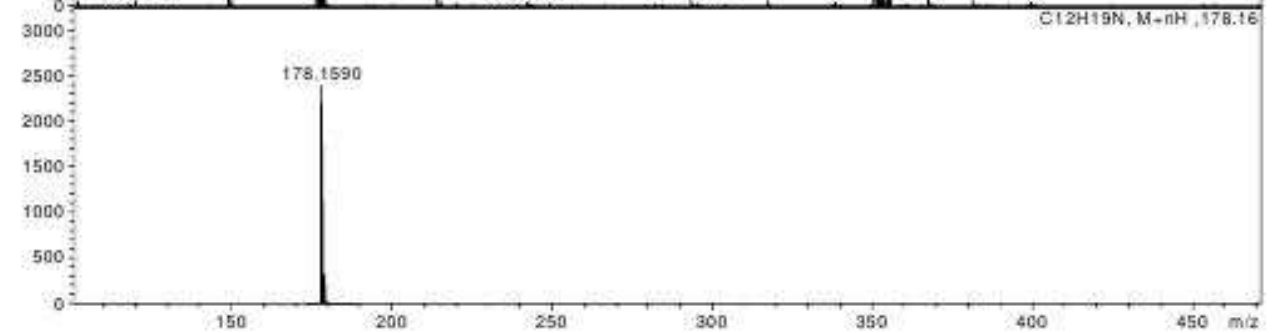
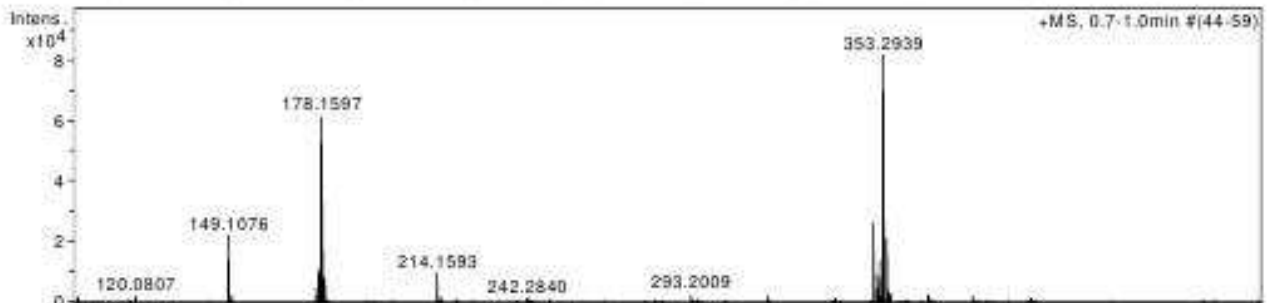
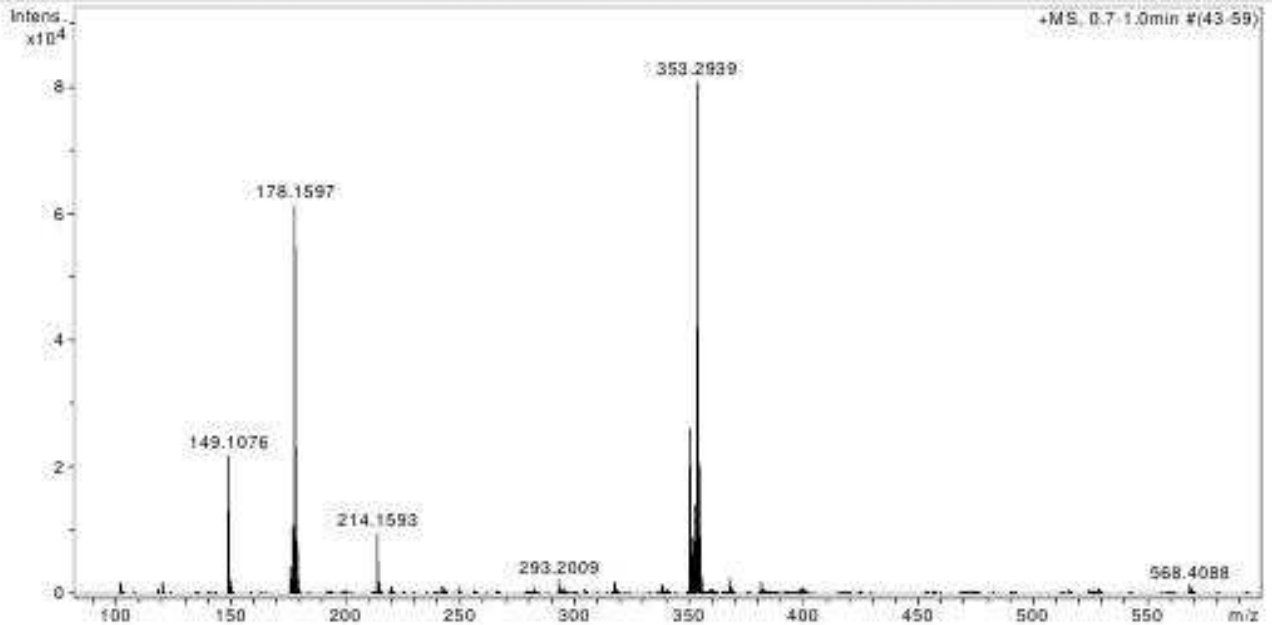
Analysis Name D:\Data\Ivanova\DEN-1olow.d  
Method tune\_low.m  
Sample Name /LEVH DEN-1olow  
Comment CH3CN 100 %

Acquisition Date 25.11.2014 16:10:11

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

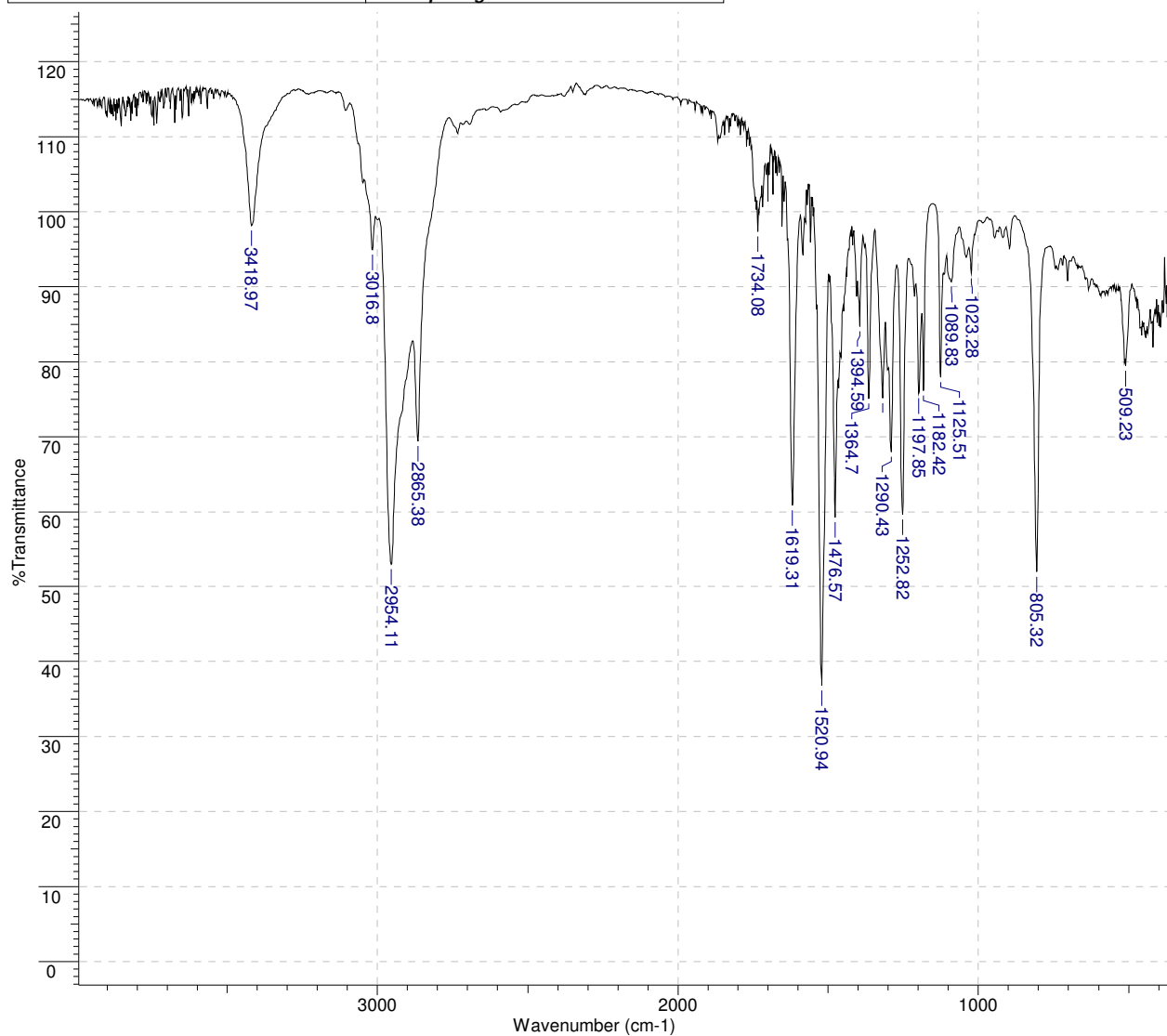
## Acquisition Parameter

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



## 10

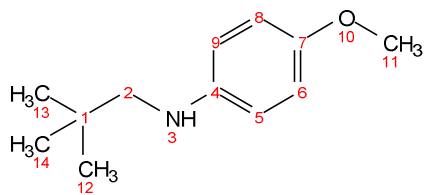
<b>Title</b>	1o		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚĀĀĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1O1.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:44:04	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699



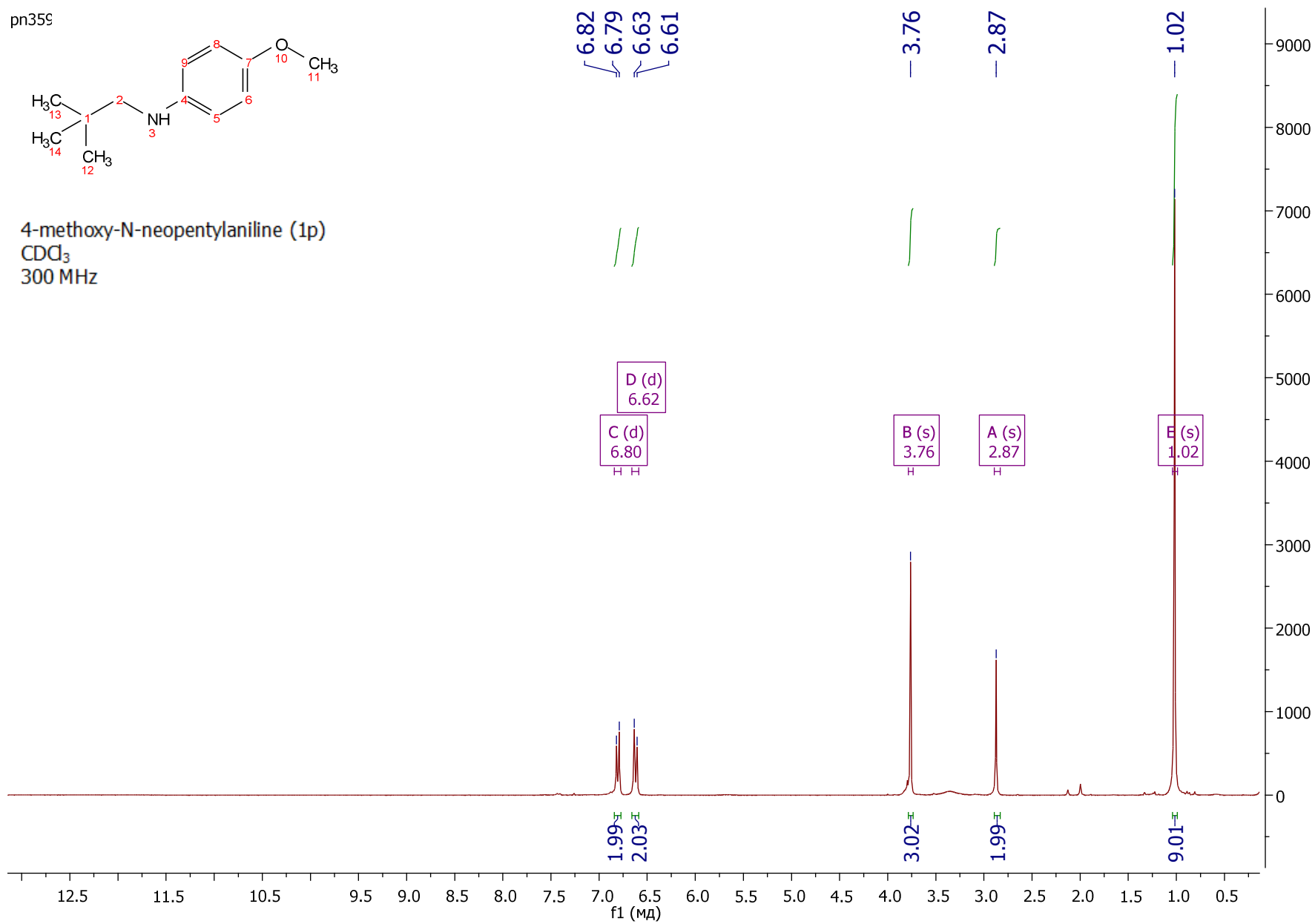
No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	509.23	79.433	M	11	1364.70	75.050	M
2	805.32	51.971	S	12	1394.59	84.708	M
3	1023.28	91.788	M	13	1476.57	59.281	S
4	1089.83	90.654	M	14	1520.94	36.831	VS
5	1125.51	77.933	M	15	1619.31	60.849	S
6	1182.42	76.152	M	16	1734.08	97.374	M
7	1197.85	75.759	M	17	2865.38	69.370	S
8	1252.82	59.591	S	18	2954.11	52.967	S
9	1290.43	67.985	S	19	3016.80	94.916	M
10	1318.40	75.147	M	20	3418.97	98.170	W

# 4-methoxy-N-neopentylaniline (1p)

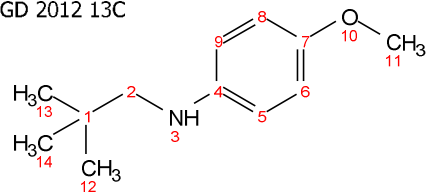
pn359



4-methoxy-N-neopentylaniline (1p)  
CDCl<sub>3</sub>  
300 MHz



pn-359  
MGD 2012 13C



— 151.80  
— 143.57

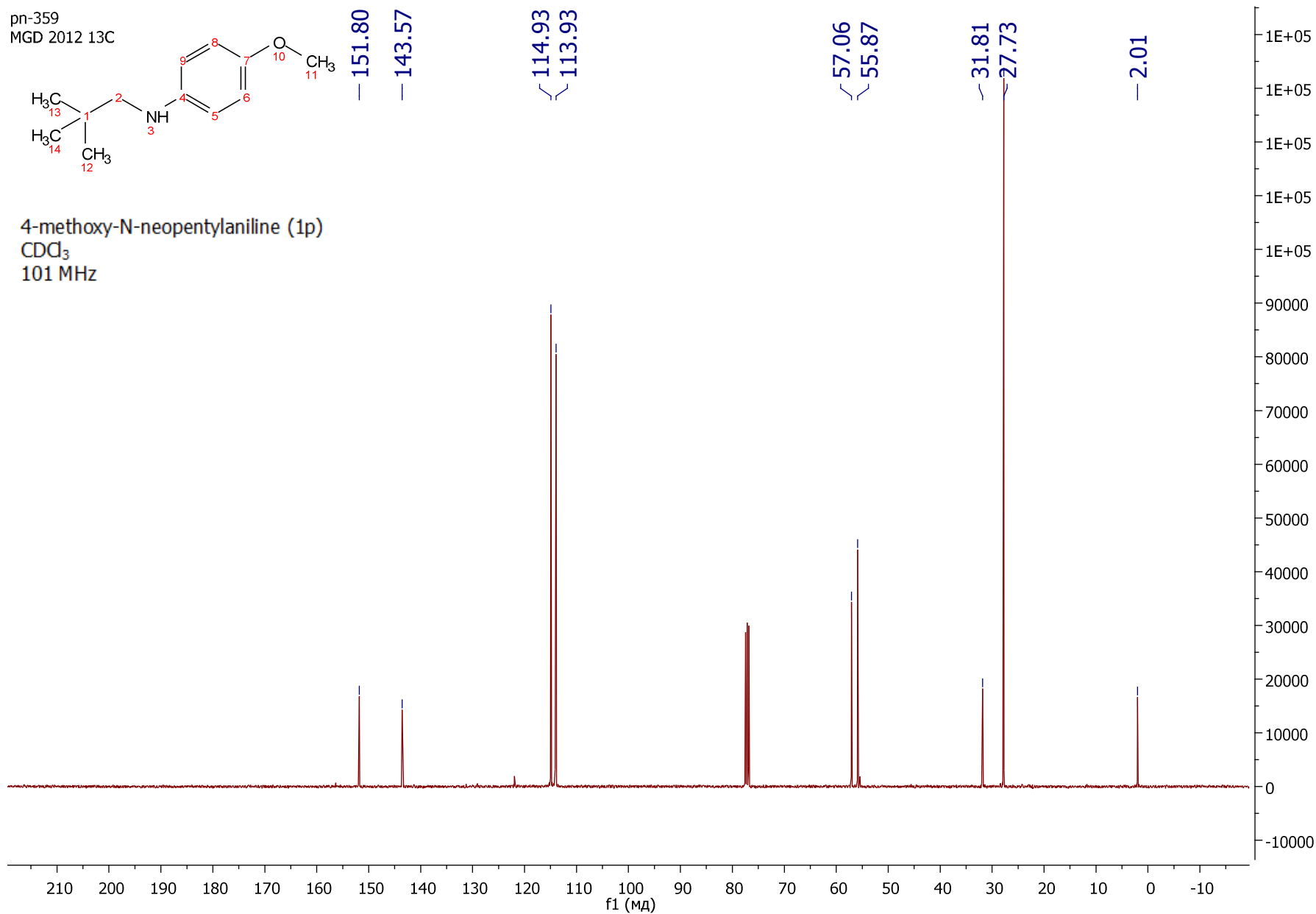
— 114.93  
— 113.93

— 57.06  
— 55.87

— 31.81  
— 27.73

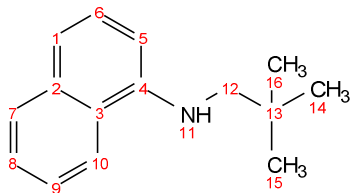
— 2.01

4-methoxy-N-neopentylaniline (1p)  
CDCl<sub>3</sub>  
101 MHz



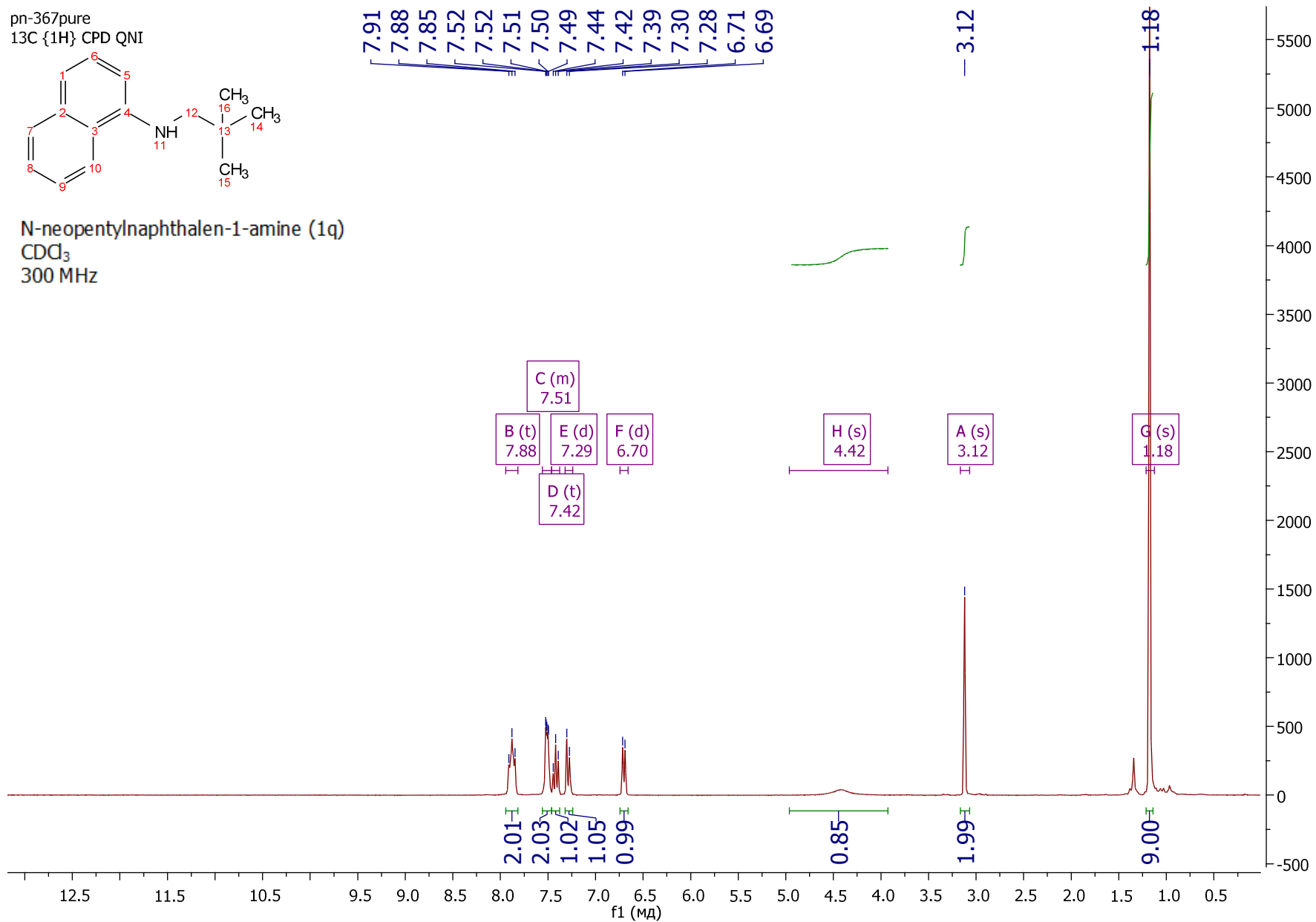
# *N*-neopentyl-naphthalen-1-amine (1q)

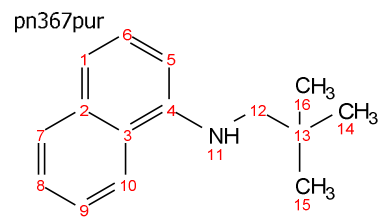
pn-367pure  
13C {1H} CPD QNI



*N*-neopentyl-naphthalen-1-amine (1q)

CDCl<sub>3</sub>  
300 MHz



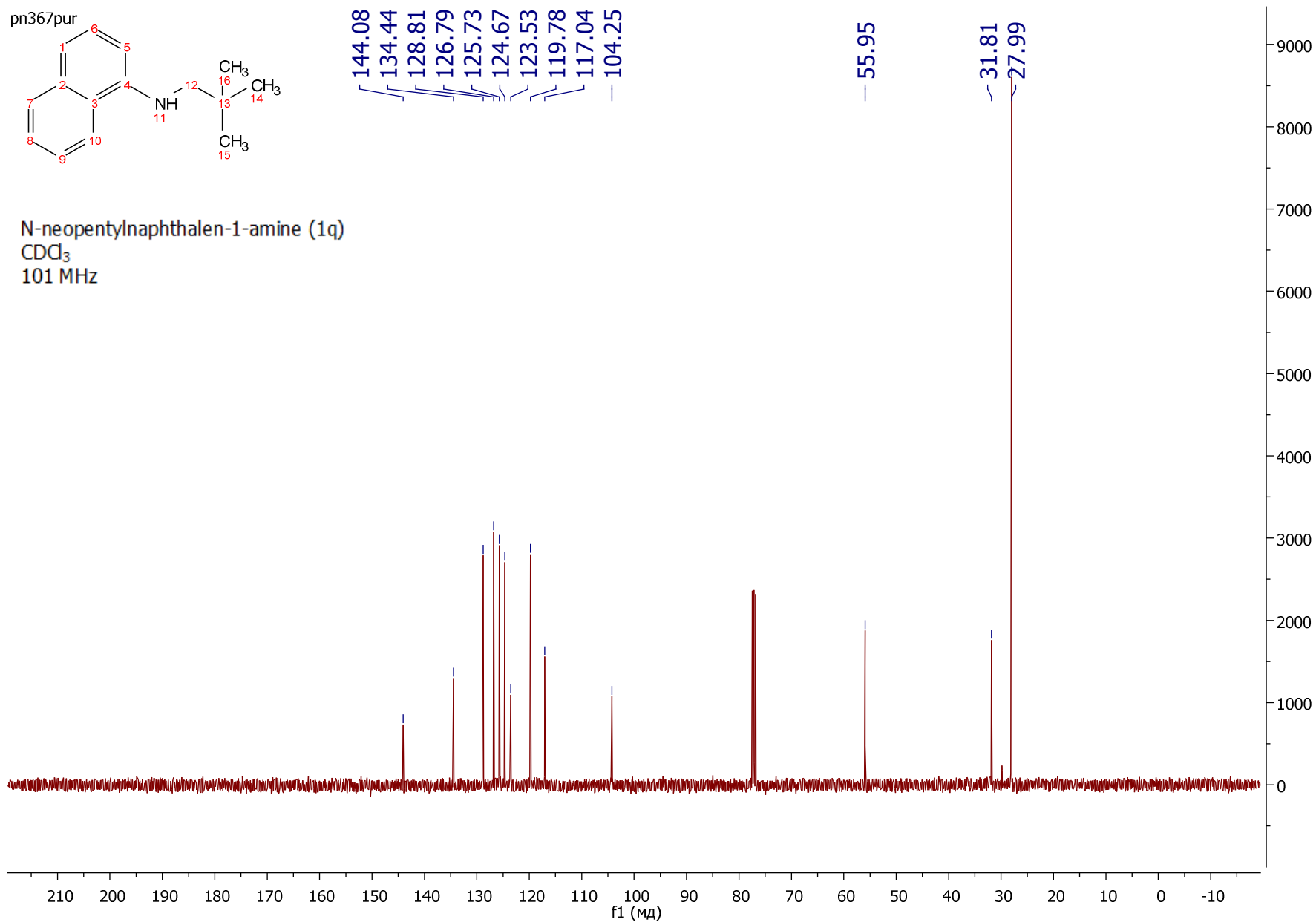


N-neopentylphthalen-1-amine (1q)  
CDCl<sub>3</sub>  
101 MHz

144.08  
134.44  
128.81  
126.79  
125.73  
124.67  
123.53  
119.78  
117.04  
104.25

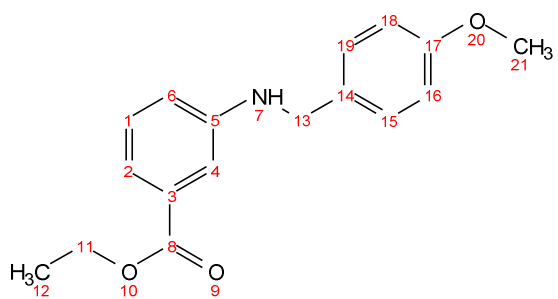
55.95

31.81  
27.99

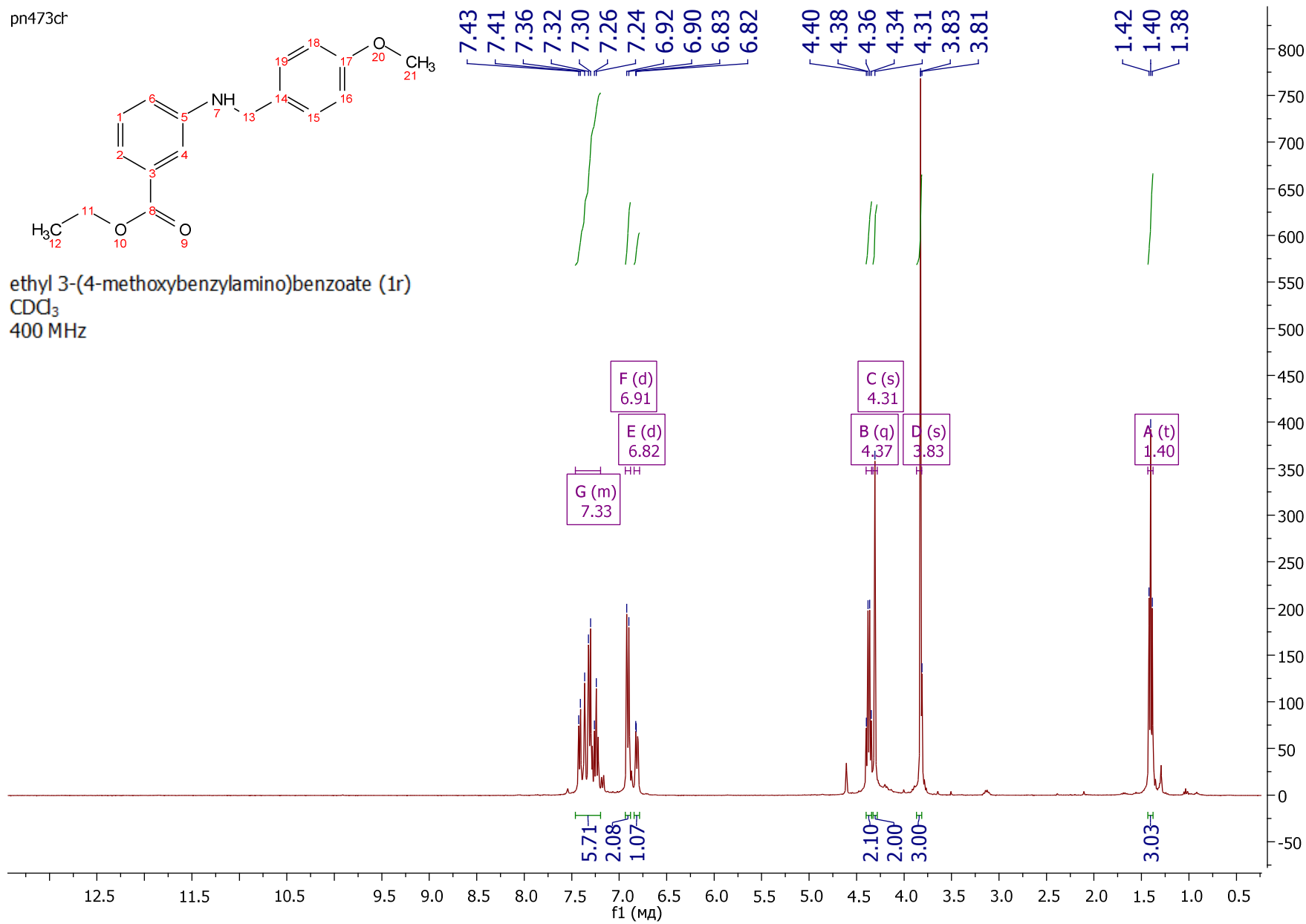


**ethyl 3-(4-methoxybenzylamino)benzoate (1r)**

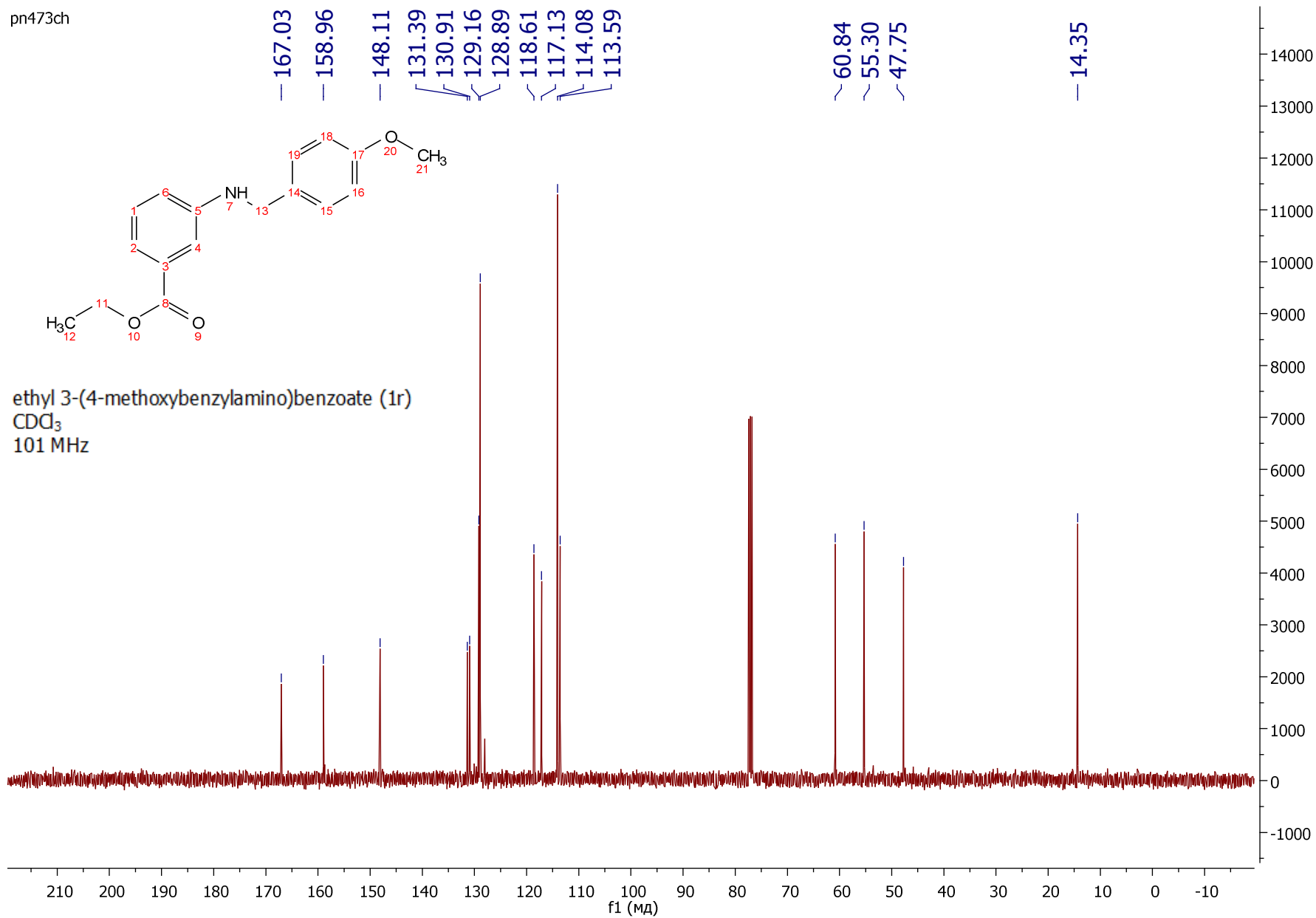
pn473ct



ethyl 3-(4-methoxybenzylamino)benzoate (1r)  
CDCl<sub>3</sub>  
400 MHz



pn473ch



# Display Report

## Analysis Info

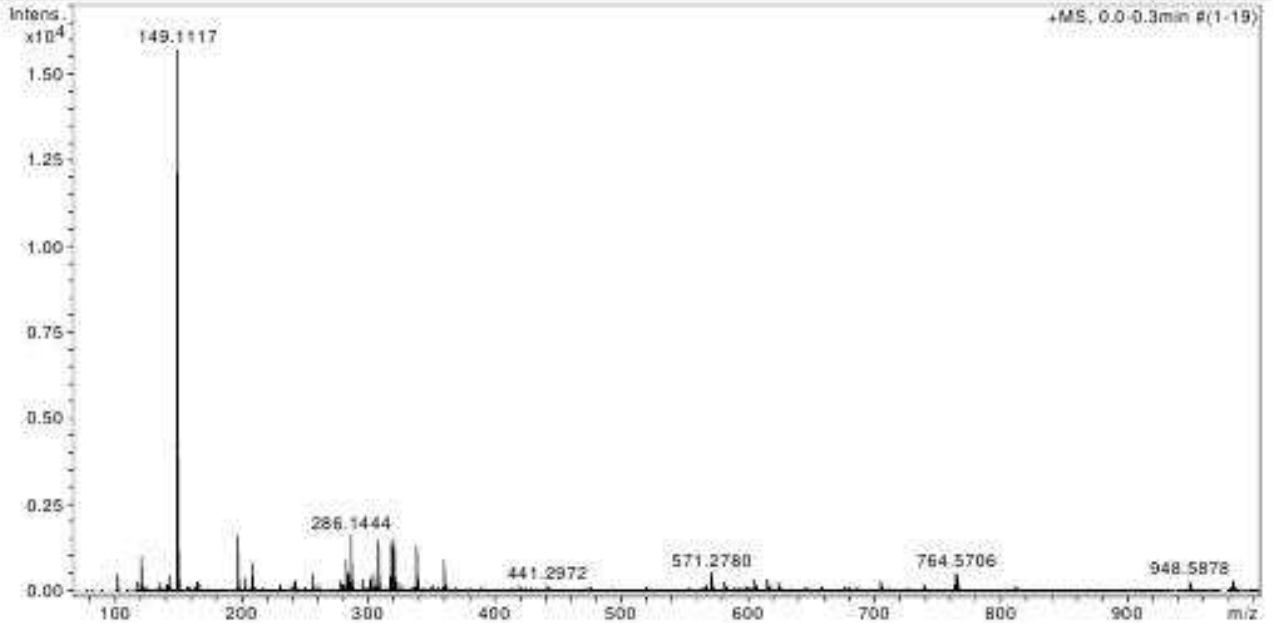
Analysis Name D:\Data\Ivanova\DEN-1r.d  
Method tune\_low.m  
Sample Name /LEVH DEN-1r  
Comment CH3CN 100 %, dil 200

Acquisition Date 25.11.2014 17:28:47

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

## 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

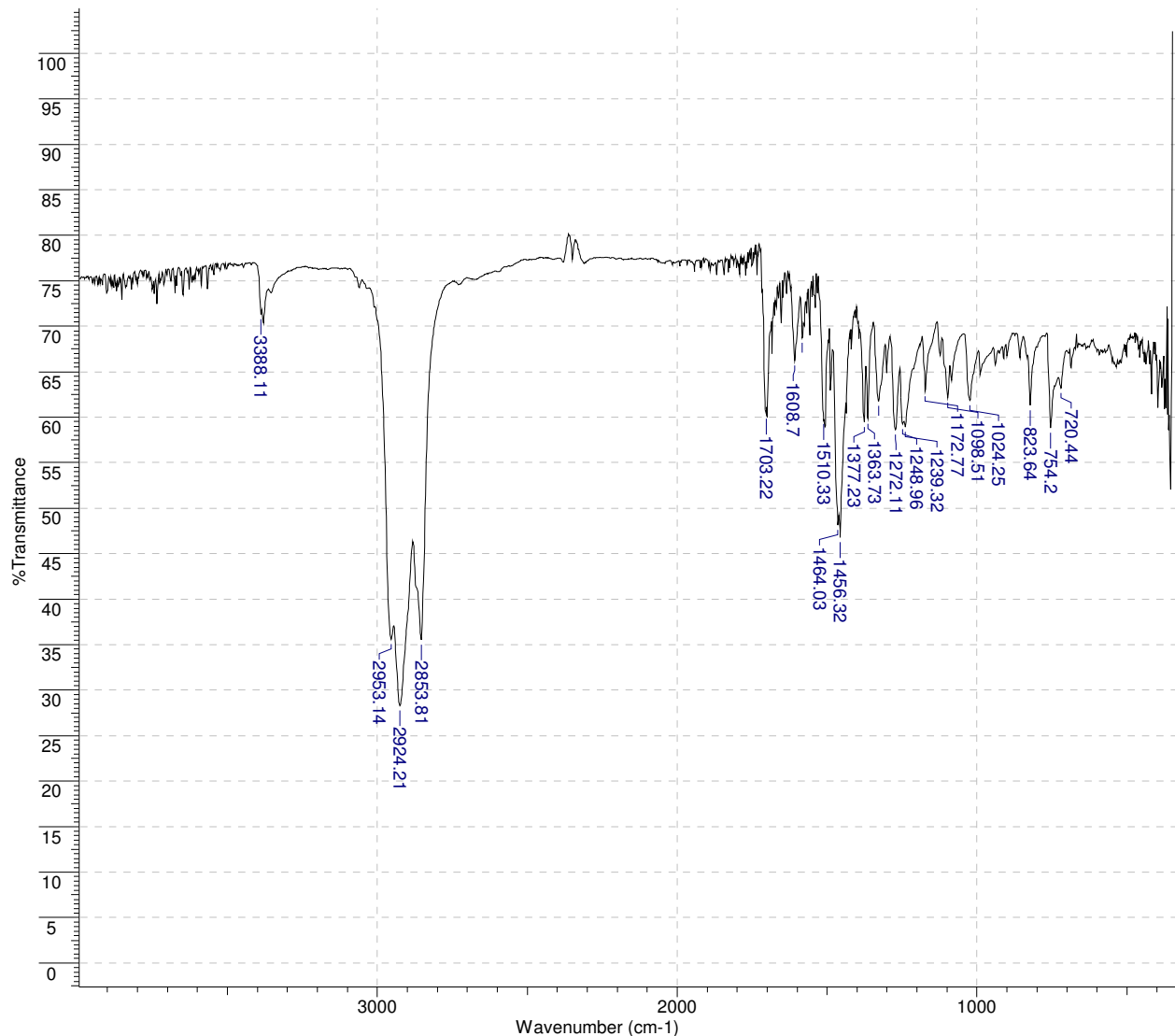


C<sub>9</sub>H<sub>13</sub>N<sub>2</sub>, 149.11



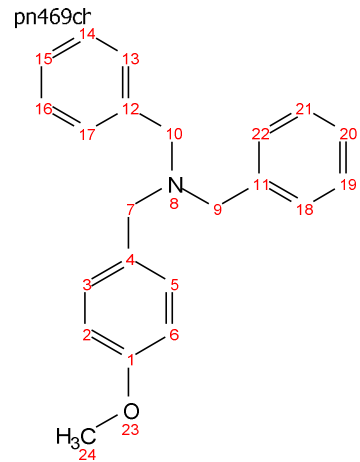
1r

<b>Title</b>	1r		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚÁÁĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1R.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:44:16	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699

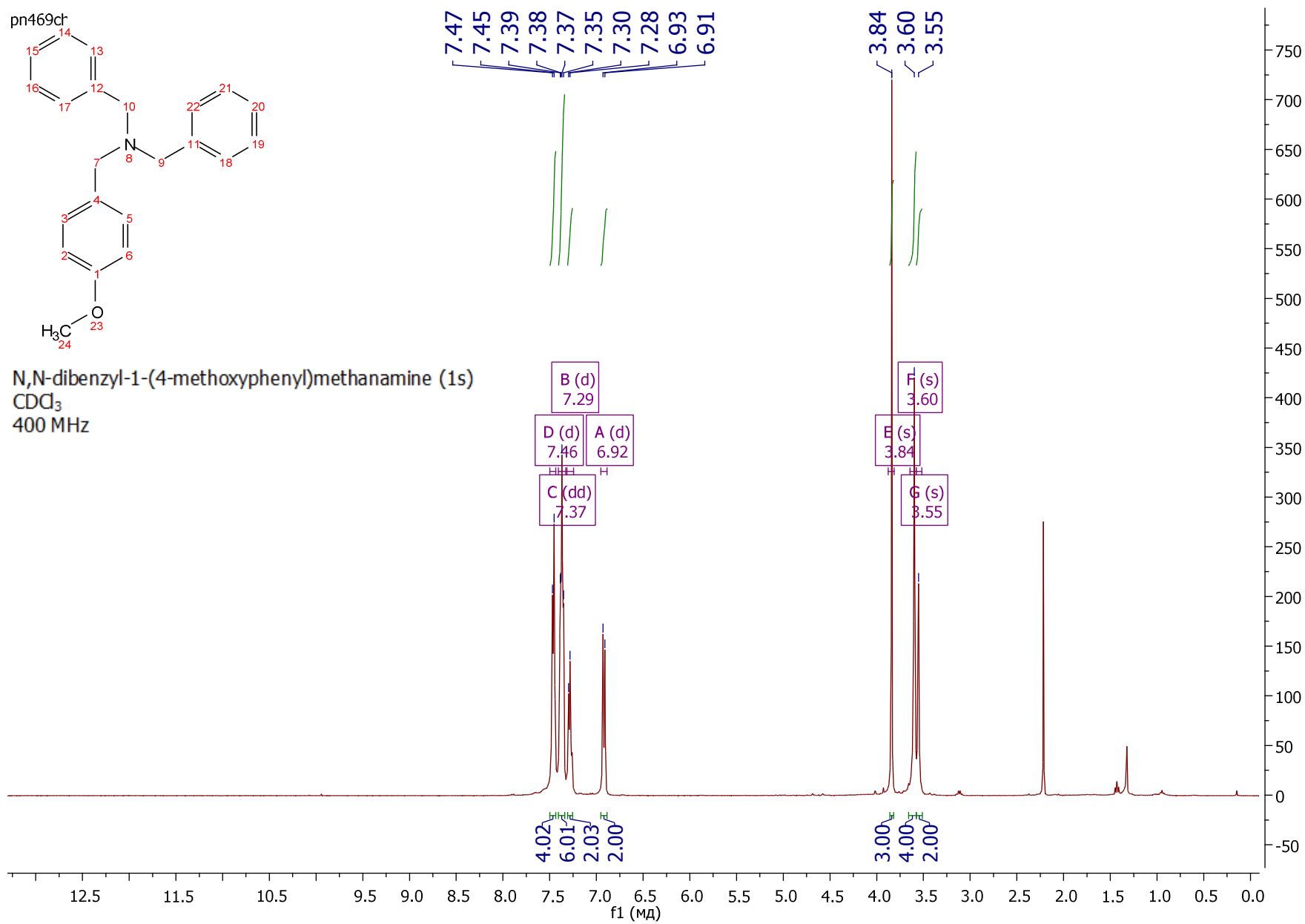


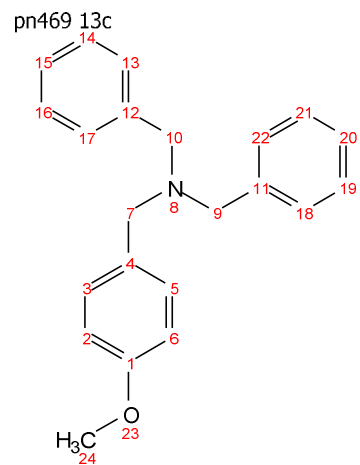
No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	720.44	63.211	M	12	1377.23	59.451	M
2	754.20	58.831	M	13	1456.32	46.819	S
3	823.64	61.284	M	14	1464.03	48.129	S
4	1024.25	61.858	M	15	1510.33	59.739	M
5	1098.51	62.156	M	16	1582.66	68.705	M
6	1172.77	62.825	M	17	1608.70	66.240	M
7	1239.32	58.918	M	18	1703.22	60.383	M
8	1248.96	59.218	M	19	2853.81	35.563	VS
9	1272.11	58.639	M	20	2924.21	28.317	VS
10	1328.05	61.770	M	21	2953.14	35.611	VS
11	1363.73	59.829	M	22	3388.11	71.340	M

*N,N*-dibenzyl-1-(4-methoxyphenyl)methanamine (1s)

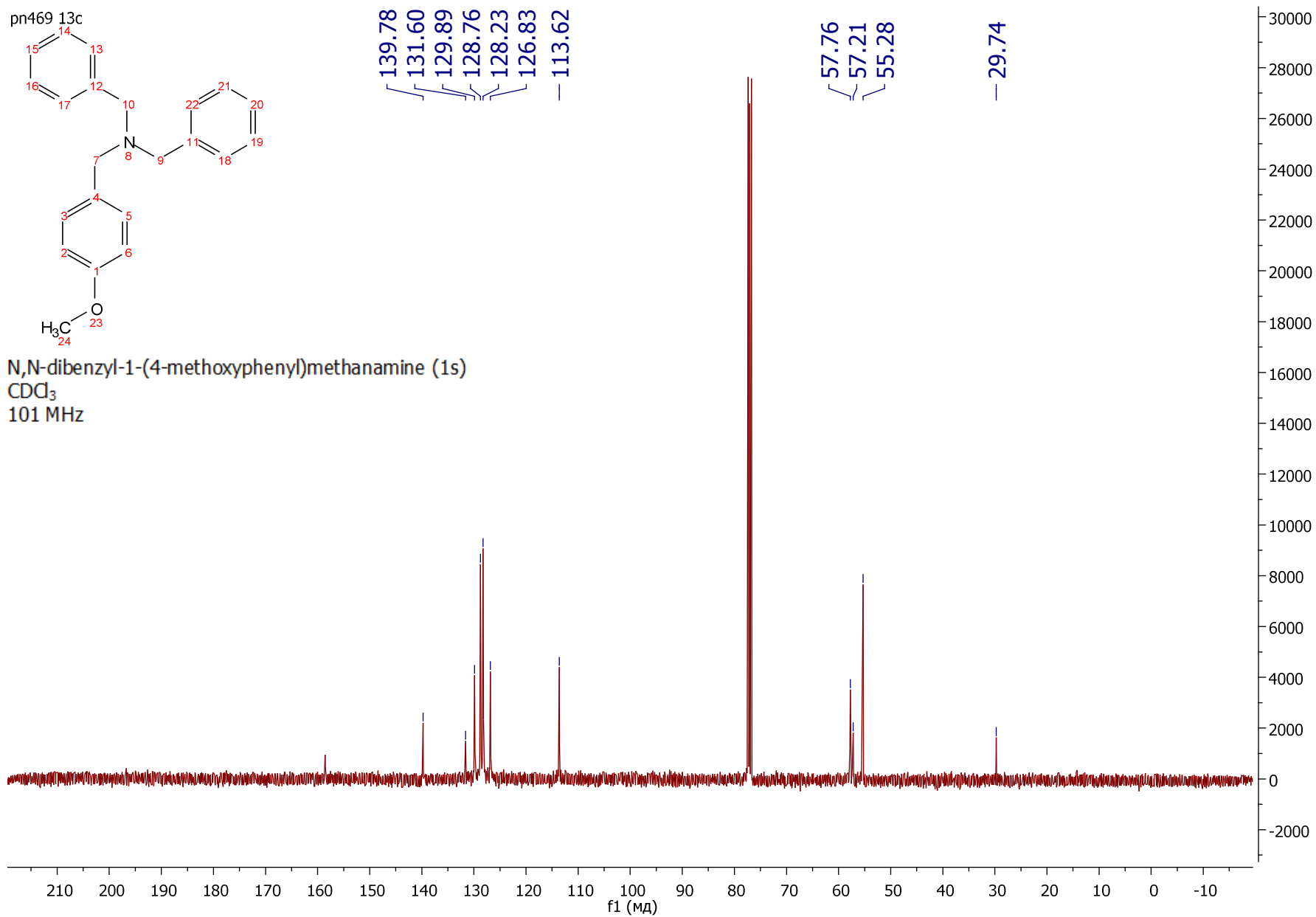


*N,N*-dibenzyl-1-(4-methoxyphenyl)methanamine (1s)  
CDCl<sub>3</sub>  
400 MHz



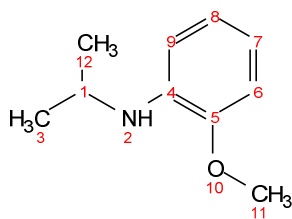


**N,N-dibenzyl-1-(4-methoxyphenyl)methanamine (1s)**  
CDCl<sub>3</sub>  
101 MHz



# *N*-isopropyl-2-methoxyaniline (1t)

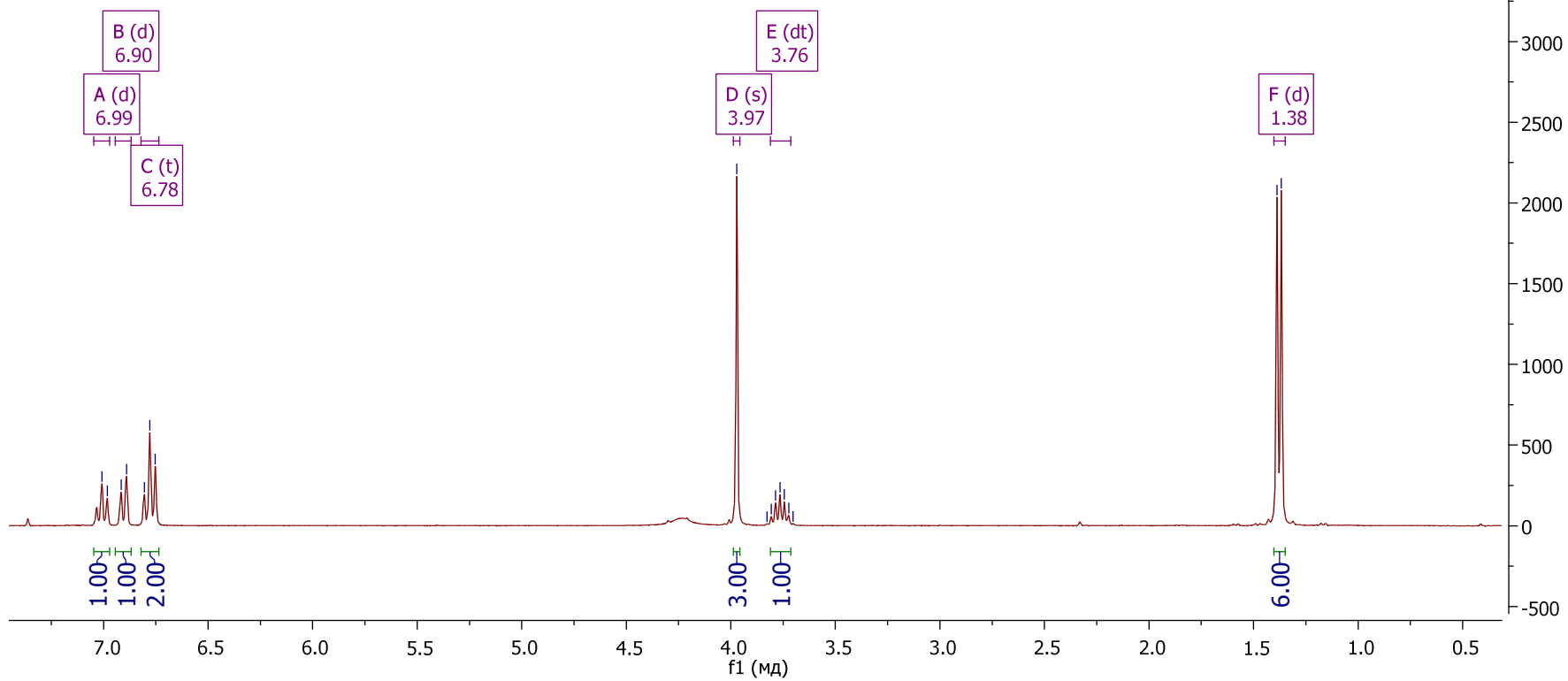
7.03  
6.98  
6.92  
6.89  
6.80  
6.78  
6.75



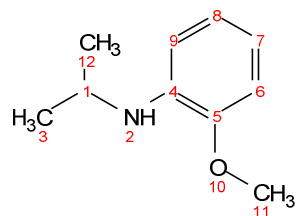
3.97  
3.83  
3.81  
3.79  
3.76  
3.74  
3.72  
3.70

1.39  
1.37

*N*-isopropyl-2-methoxyaniline (1t)  
CDCl<sub>3</sub>  
400 MHz



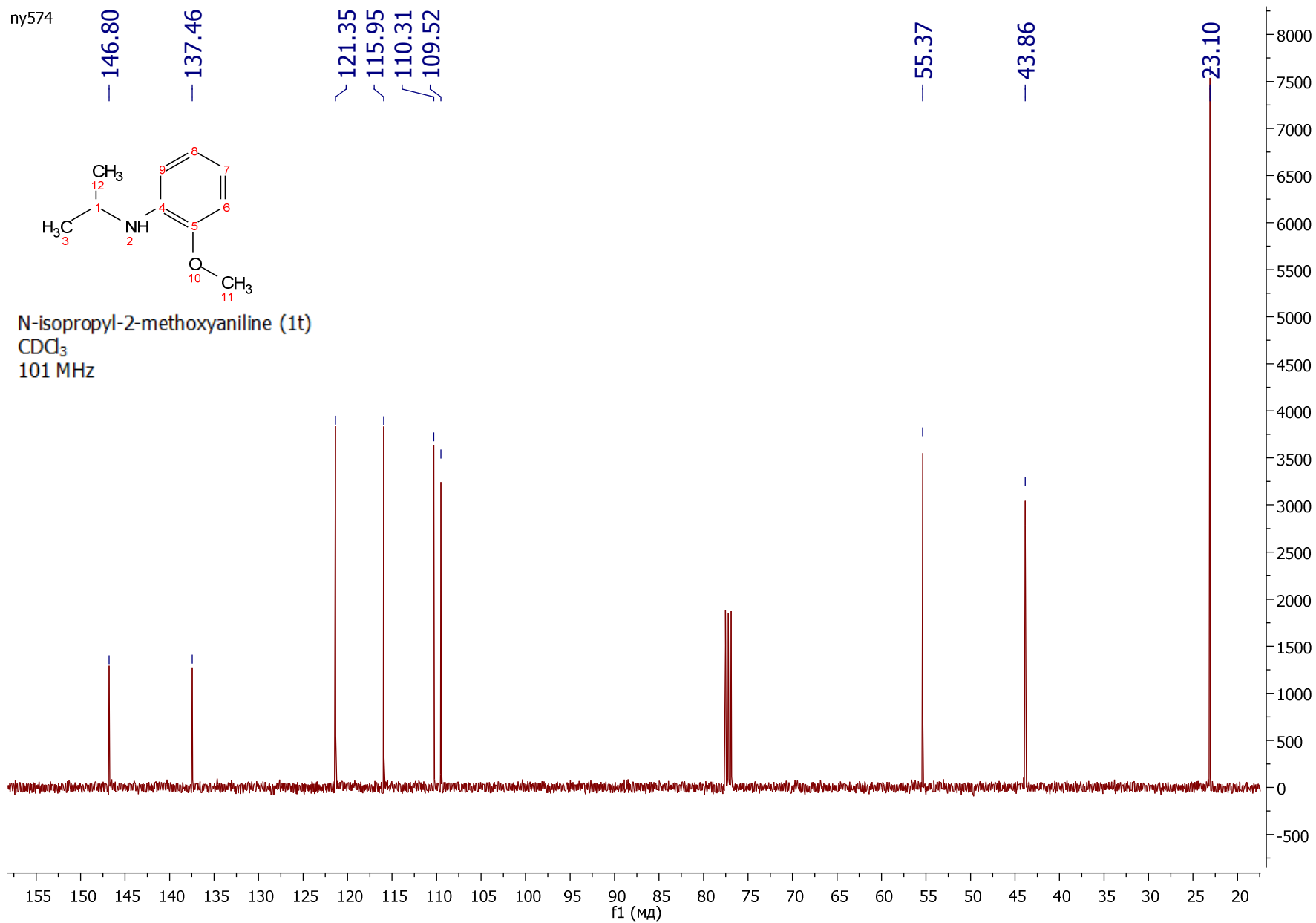
ny574



N-isopropyl-2-methoxyaniline (1t)

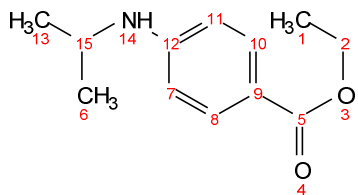
CDCl<sub>3</sub>

101 MHz

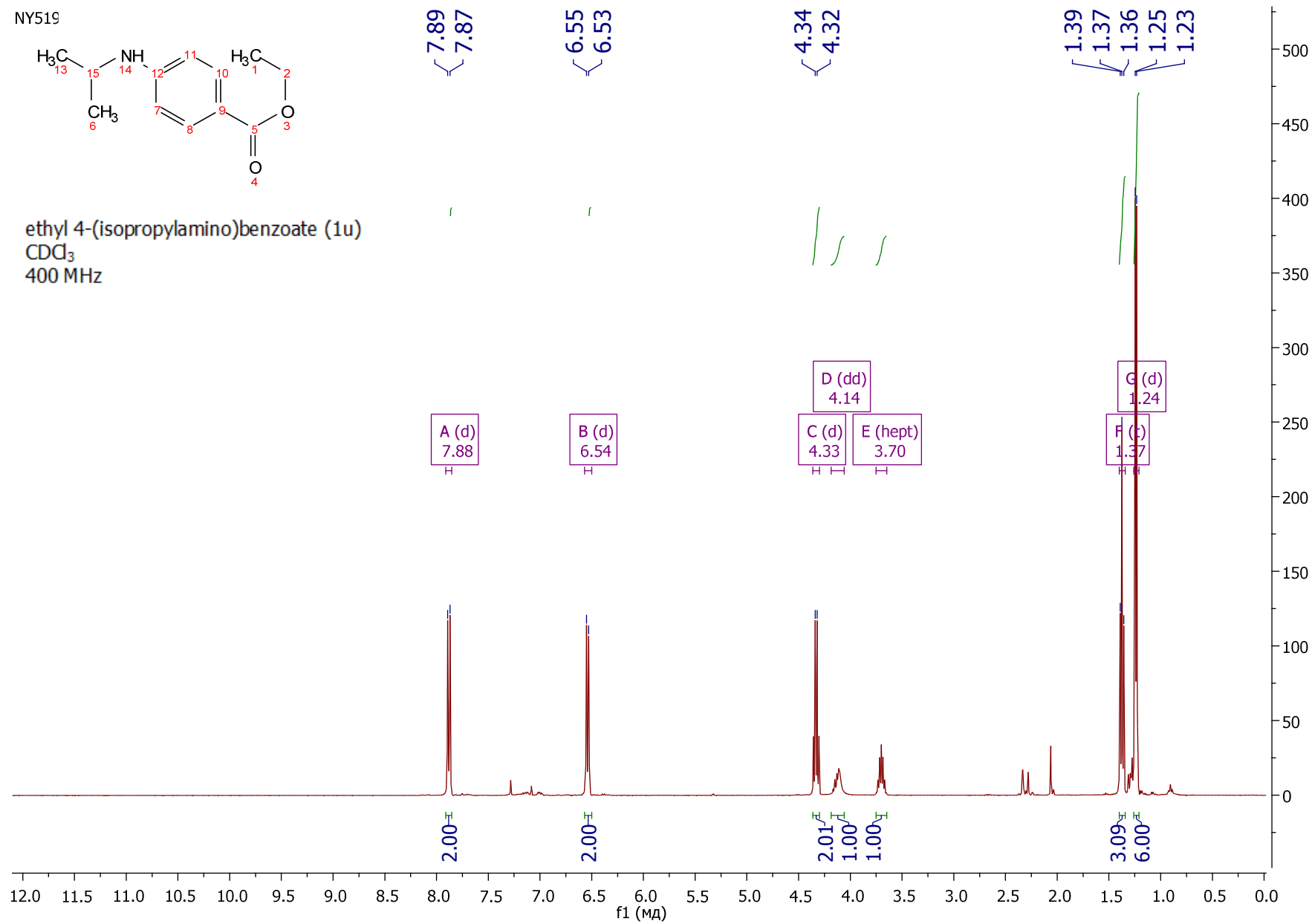


*ethyl 4-(isopropylamino)benzoate (1u)*

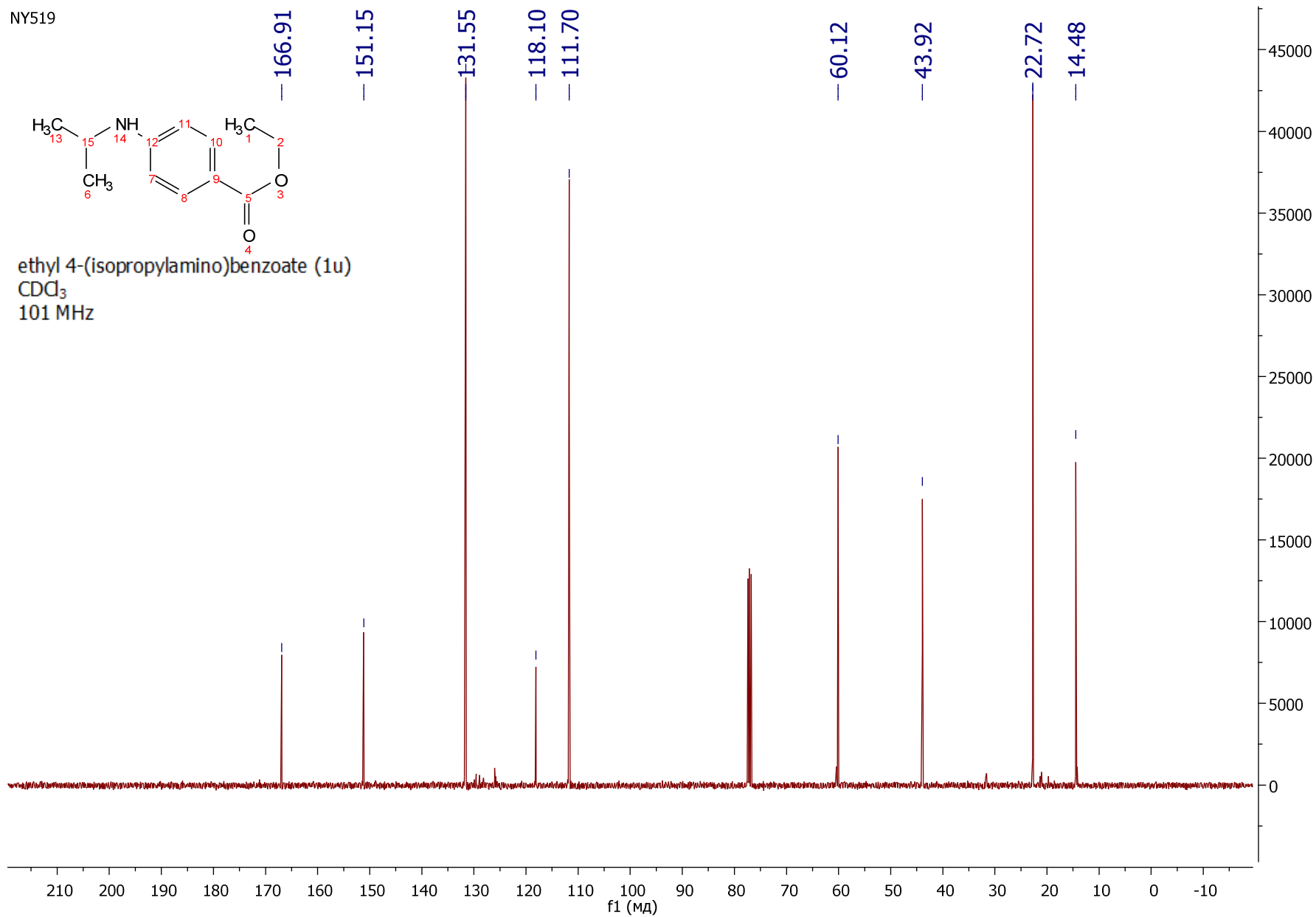
NY519



ethyl 4-(isopropylamino)benzoate (1u)  
CDCl<sub>3</sub>  
400 MHz



NY519



# Display Report

## Analysis Info

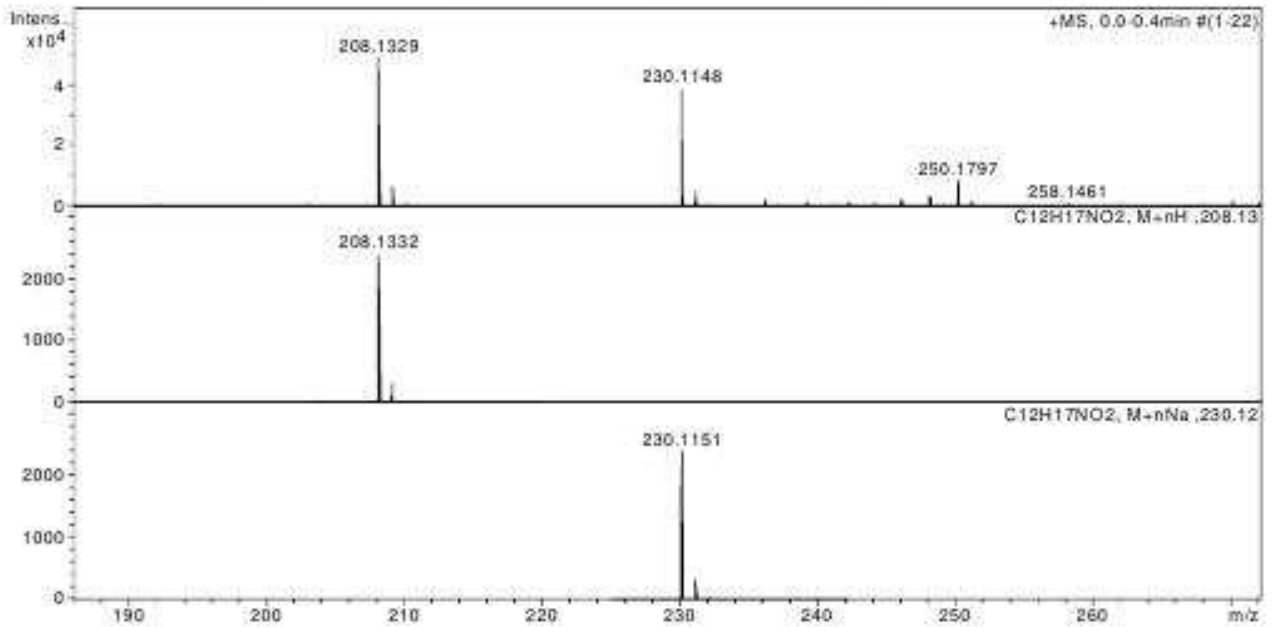
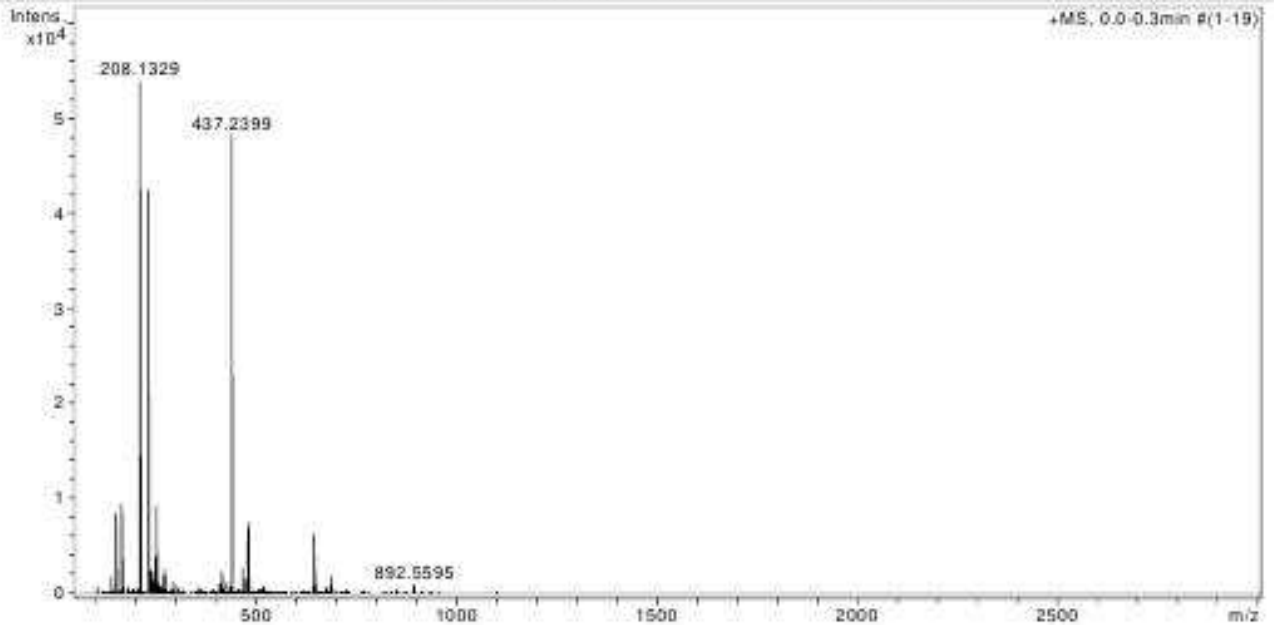
Analysis Name D:\Data\Ivanova\DEN-1u.d  
Method tune\_low.m  
Sample Name /LEVH DEN-1u  
Comment CH3CN 100 %, dil 200

Acquisition Date 25.11.2014 17:19:01

Operator BDAL@DE  
Instrument / Ser# microTOF 10248

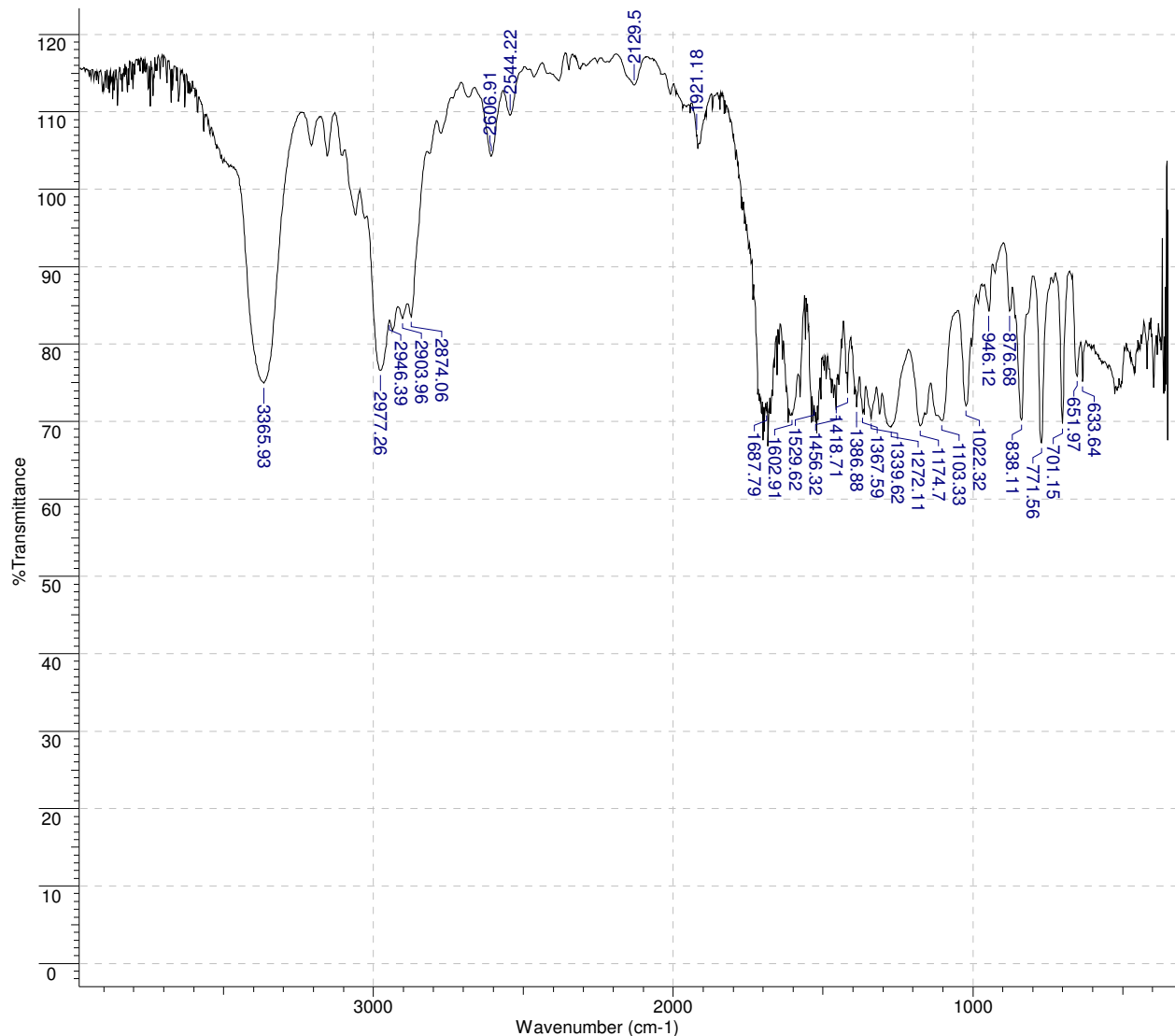
## Acquisition Parameter

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



# 1u

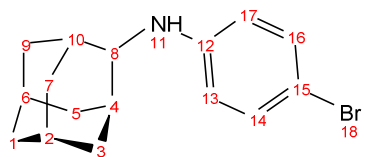
<b>Title</b>	1u		
<b>File Name</b>	C:\USERS\LENOVO\DESKTOP\ĚÁÁĪ ĚĚ\REDUCTIVE AMINATION PURE\IR\2014.12.02\1U.SMF.TXT		
<b>Date</b>	03 Dec 2014 13:44:32	<b>Technique</b>	Infrared
<b>X Axis</b>	Wavenumber (cm-1)	<b>Y Axis</b>	%Transmittance
<b>Points Count</b>	4824	<b>Data Spacing</b>	0.9644
		<b>Spectral Region</b>	NIR-IR
		<b>Spectrum Range</b>	349.1309 - 5000.6699



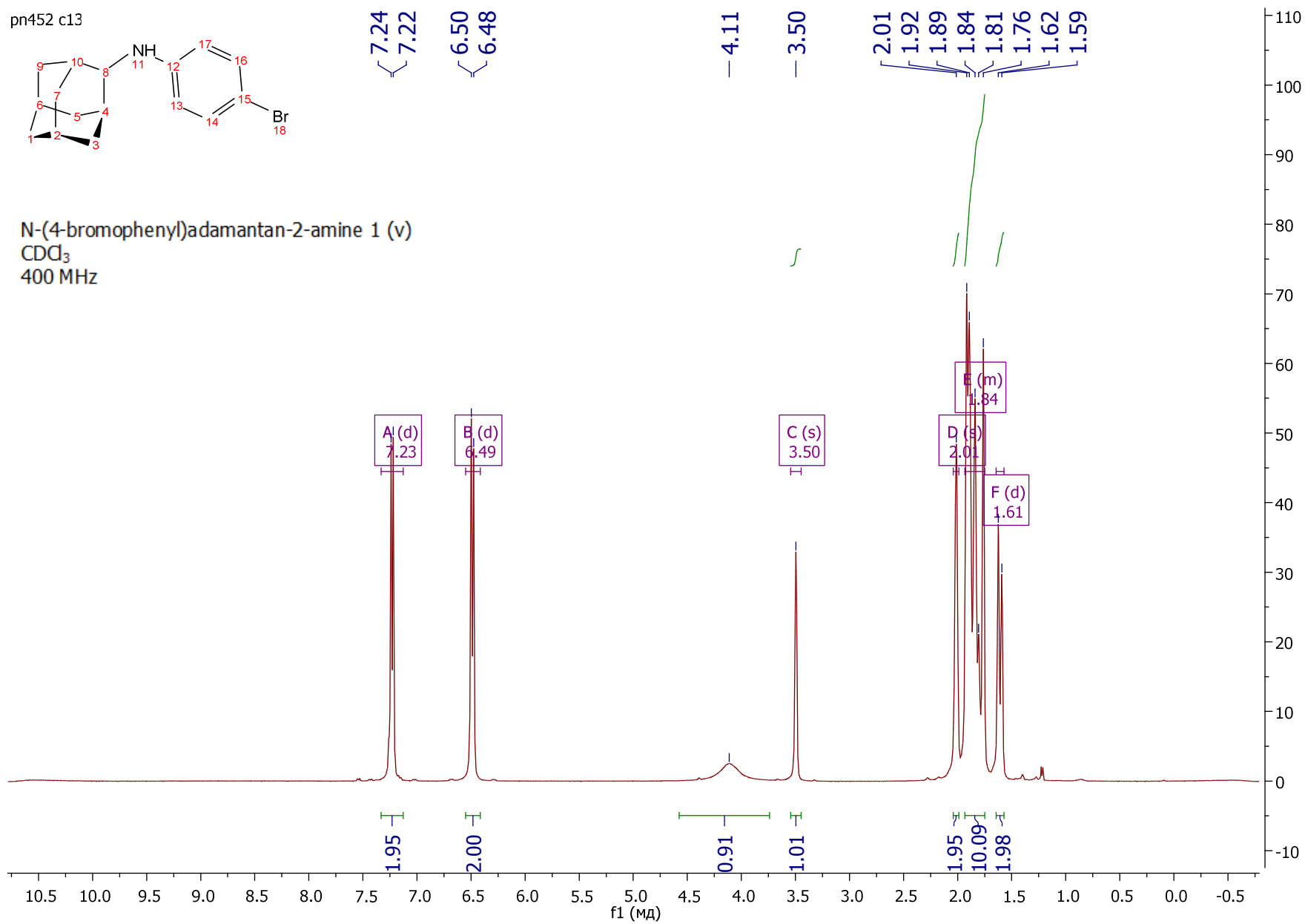
No	cm-1	%T	Intensity	No	cm-1	%T	Intensity
1	633.64	75.188	S	15	1418.71	73.730	S
2	651.97	75.872	S	16	1456.32	71.478	VS
3	701.15	69.751	VS	17	1529.62	72.061	S
4	771.56	67.237	VS	18	1602.91	70.848	VS
5	838.11	70.216	VS	19	1687.79	71.422	VS
6	876.68	84.269	S	20	1921.18	107.065	W
7	946.13	84.248	S	21	2129.50	113.467	VW
8	1022.32	72.030	S	22	2544.22	109.570	W
9	1103.33	70.150	VS	23	2606.91	104.243	W
10	1174.70	69.430	VS	24	2874.06	83.486	S
11	1272.11	69.340	VS	25	2903.96	83.319	S
12	1339.62	70.321	VS	26	2946.39	83.071	S
13	1367.59	71.135	VS	27	2977.26	76.608	S
14	1386.88	71.903	S	28	3365.93	74.973	S

# *N*-(4-bromophenyl)adamantan-2-amine (1v)

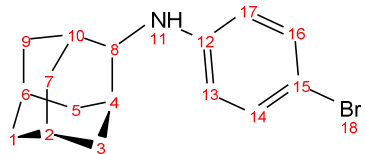
pn452 c13



*N*-(4-bromophenyl)adamantan-2-amine 1 (v)  
CDCl<sub>3</sub>  
400 MHz



pn452 c13



N-(4-bromophenyl)adamantan-2-amine 1(v)  
CDCl<sub>3</sub>  
101 MHz

