Synthesis of Sterically Hindered Amines by Direct Reductive Amination of Ketones

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Supporting Information

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1. General information

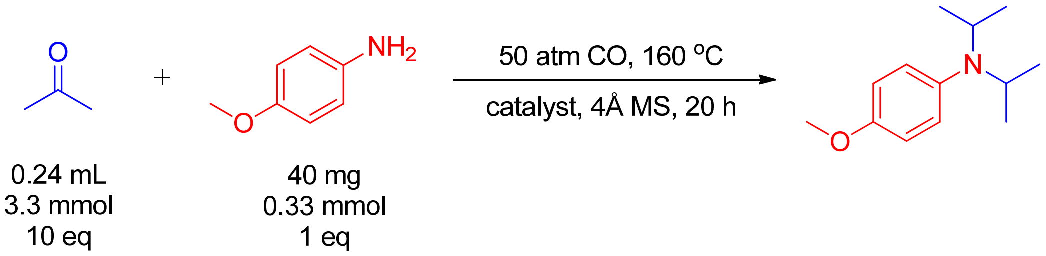
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification (THF was distilled over sodium/benzophenone, methanol was distilled over Mg). Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Isolation of products on less than 200 mg scales was performed by preparative TLC (Macherey-Nagel, Silica gel 60 GF_{254}, fluorescence quenching with UV light at 254 nm); reaction products prepared on scales exceeding 200 mg were purified by column chromatography (Acros Organics, silica gel 0.06-0.200 mm), hexane-ethyl acetate-triethylamine system was used as eluent. ^1H and ^{13}C NMR spectra were recorded on Bruker AV-300, AV-400 and AV-600 spectrometers at ambient temperature. Chemical shifts δ are reported in ppm using the solvent resonance signal as an internal standard. ^{19}F spectra were recorded on Bruker Avance 300 spectrometer at 282 MHz; chemical shifts are reported in ppm relative to trichlorofluoromethane. NMR yields were calculated with HMDS (hexamethyldisiloxane) as an internal standard (unless otherwise noted). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz). HRMS (ESI-MS): spectra were recorded on Bruker micrOTOF II and Maxis instruments under electrospray ionization (ESI) conditions in a positive ion mode (interface capillary voltage: 4500 V) with a mass range m/z 50–3000 Da; external and internal calibrations were performed with Electrospray Calibrant Solution. All samples for ESI-MS were prepared in MeCN; syringe injections were used (flow rate: 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 ^{o}C. The spectra were processed with DataAnalysis software package. IR spectra (Nujol mull) were recorded on FTIR Shimadzu IR Prestige-21 spectrometer.

2. General procedure

Procedure: A 10 mL stainless steel autoclave was charged with 2 mol% of rhodium trichloride (method A) or 5 mol% of ruthenium trichloride (method B), the corresponding solvent, 1 eq. of the amine and 1-10 eq. of the ketone. 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 the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with dichloromethane (2x1mL); combined solvents were removed on a rotary evaporator. The residue was purified by flash chromatography on silica gel.

3. Experimental section

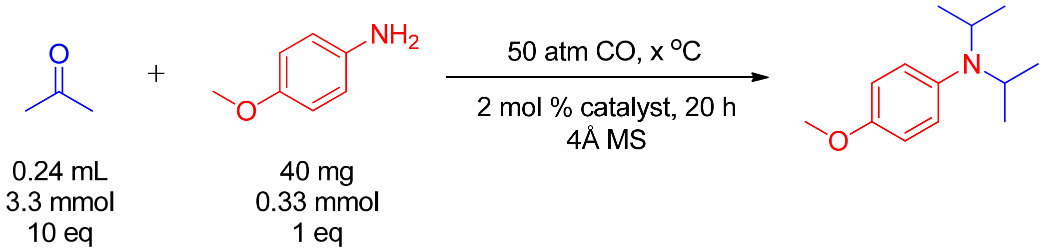
Table 1. Screening of Rh catalysts.



catalyst	catalyst loading, mg (mol %)	yield*, %
-	-	0
CpRh(CO)I_2	3.0 (2.0 mol %)	49
[(COD)RhCl]$_2$	1.6 (1.0 mol %)	76
[Rh(CO)$_2$Cl$_2$]$_2$	1.3 (1.0 mol %)	81
Rh$_2$(OAc)$_4$	1.5 (1.0 mol %)	83
(Rh(CF$_3$COO)$_2$)$_2$	2.2 (1.0 mol %)	85
RhCl$_3$·4H$_2$O	**1.9 (2.0 mol %)**	**85**

*Determined by ^{1}H NMR spectroscopy.

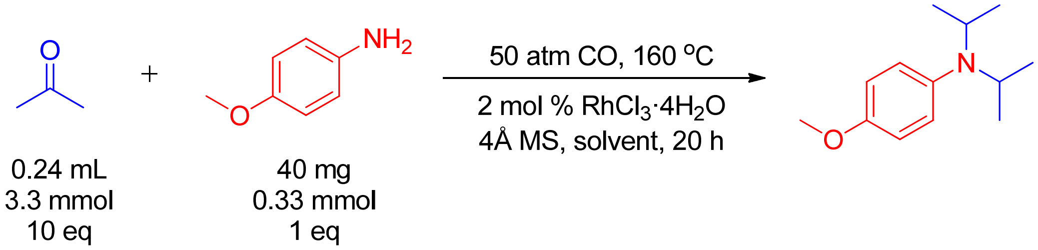
Table 2. Temperature screening



catalyst	temperature, °C	yield*, %
RhCl$_3$·4H$_2$O	140	65
RhCl$_3$·4H$_2$O	150	69
RhCl$_3$·4H$_2$O	**160**	**85**

*Determined by ^{1}H NMR spectroscopy.

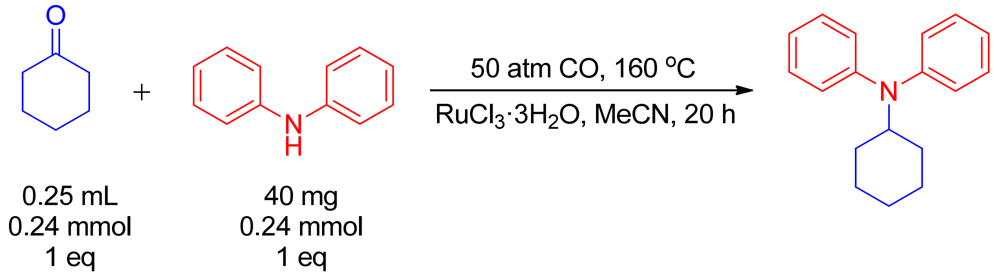
Table 3. Solvent screening



solvent	yield*, %
dichloromethane	0
diethyl ether	0
acetonitrile	10
toluene	13
tetrahydrofuran	18
ethyl acetate	35
1,4-dioxane	45
ethanol	59
acetone[a]	**85**

*Determined by ^{1}H NMR spectroscopy. [a] 10 eq of acetone was used.

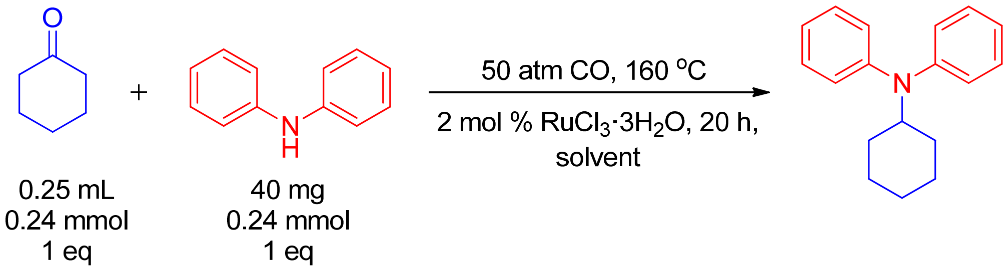
Table 4. Screening of Ru catalyst loading



catalyst	catalyst loading, mg (mol %)	yield*, %
$RuCl_3 \cdot 3H_2O$	0.3 (0.5 mol %)	56
$RuCl_3 \cdot 3H_2O$	0.6 (1.0 mol %)	58
$RuCl_3 \cdot 3H_2O$	1.3 (2.0 mol %)	83
$RuCl_3 \cdot 3H_2O$	**3.1 (5.0 mol %)**	**91**

*Determined by ^{1}H NMR spectroscopy.

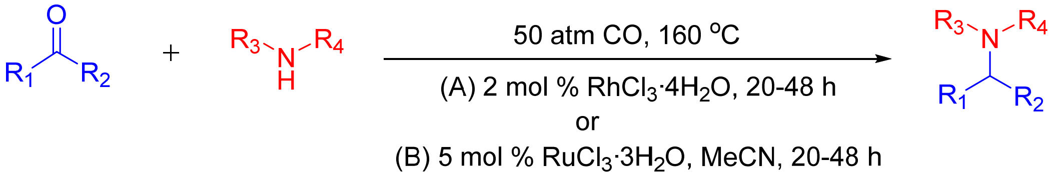
Table 5. Solvent screening

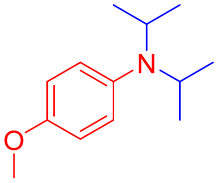


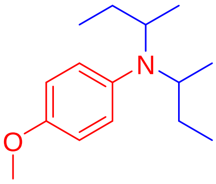
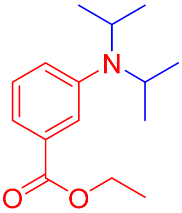
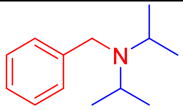
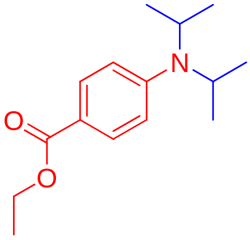
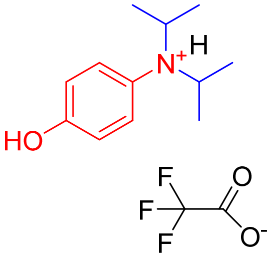
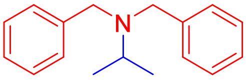
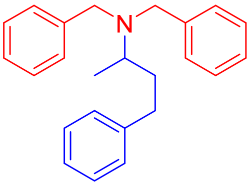
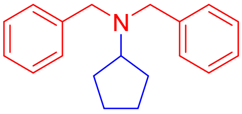
solvent	yield*, %
ethanol (2 mol% $RhCl_3$)	40
-	0
ethyl acetate	4
methanol	44
toluene	73
ethanol	80
tetrahydrofuran	81
acetonitrile	**83**

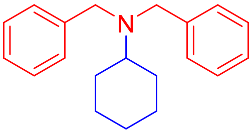
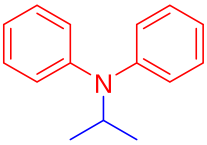
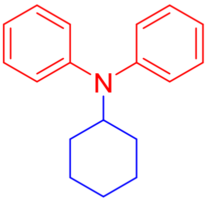
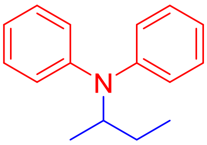
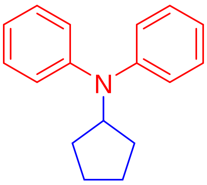
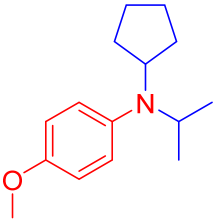
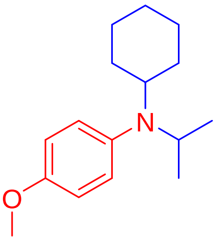
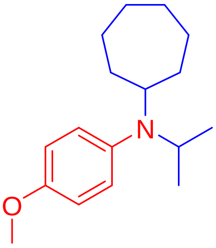
*Determined by ^{1}H NMR spectroscopy.

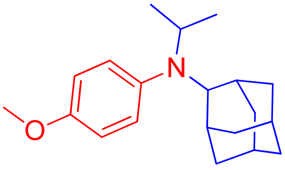
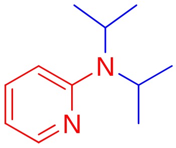
Table 6. Difference in yield between Rh and Ru catalysis



substrate/catalyst	yield, %^{a}	yield, %^{a}
	$RhCl_3$·$4H_2O$ (Method A)	**$RuCl_3$·$3H_2O$ (Method B)**
 **1a**	85^b	72^b

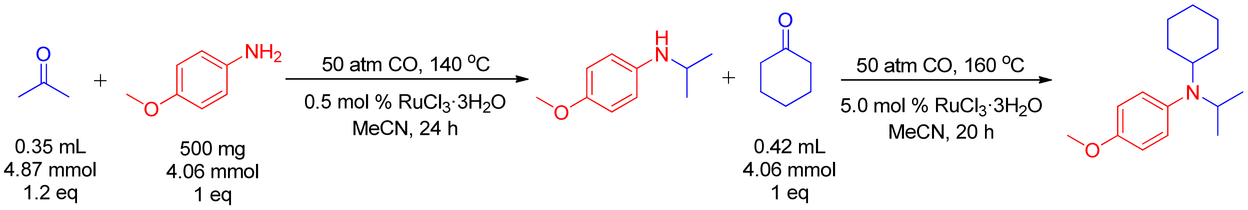
 **1b**	60	65
 **1c**	31	75
 **1d**	63[b]	43[b]
 **1e**	27 %	42 %
 **1f**	53[b]	43[b]
 **1g**	89	80
 **1h**	77	55
 **1i**	87	27

 **1j**	90	51
 **1k**	40	93
 **1l**	40	91
 **1m**	-	74
 **1n**	-	70
 **1o**	30	42
 **1p**	40 %	66 %
 **1q**	16 %	36 %

 **1r**	40 %	35 %
	3 %	0 %

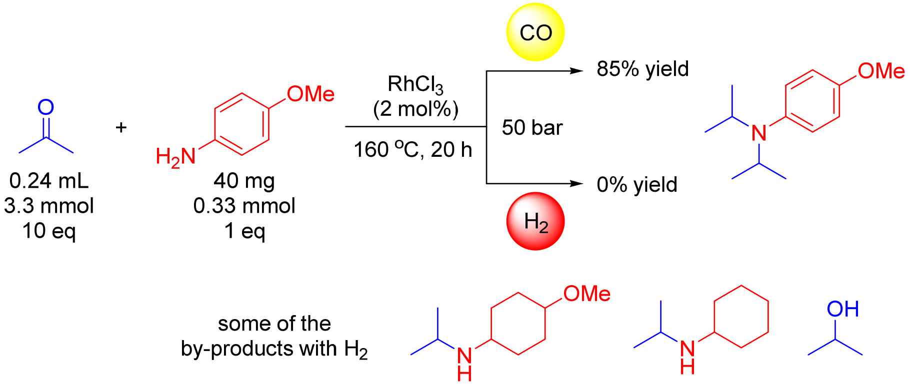
[a] Yield determined by ^{1}H NMR spectroscopy. [b] Prepared in the presence of 4Å molecular sieves.

Figure 1. One-pot synthesis of unsymmetrical tertiary amines.



A 10 mL stainless steel autoclave was charged with ruthenium(III) chloride hydrate (5.3 mg, 0.5 mol%, 0.02 mmol), acetonitrile (0.5 mL), 4-methoxyaniline (500 mg, 1 eq, 4.06 mmol) and acetone (0.35 mL, 1.2 eq, 4.87 mmol). 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 24 h, the reactor was cooled to room temperature, depressurized and placed under vacuum for 30 min. The second stage reagents were charged through the valve: ruthenium(III) chloride hydrate (53 mg, 5 mol%, 0.2 mmol), acetonitrile (0.5 mL) and cyclohexanone (0.42 mL, 1 eq, 4.06 mmol). 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 160 °C. After 20 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. 60% NMR yield (HMDS was used as internal standard). The residue was purified by preparative thin-layer chromatography (eluent: toluene/ethyl acetate (6:1); R_f=0.48) to afford 296.4 mg (30 %) of the product as a yellow oil.

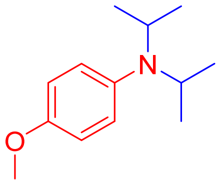
Figure 2. Comparison of the reaction outcomes in the atmospheres of carbon monoxide and dihydrogen.



$RhCl_3{\cdot}4H_2O$ (1.9 mg, 2 mol %, 0.0066 mmol) and *p*-anisidine (40 mg, 1 eq, 0.33 mmol) were dissolved in acetone (0.24 mL, 10 eq, 3.3 mmol) with 4Å molecular sieves (12 mg). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. No desired tertiary amine was detected when hydrogen was used as a reductant. Some of the by-products were detected by NMR and GC-MS.

4. Spectroscopic and analytical data

***N,N*-diisopropyl-4-methoxyaniline (1a)**



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3 \cdot 4H_2O$ (1.9 mg, 2 mol %, 0.0066 mmol) and *p*-anisidine (40 mg, 1 eq, 0.33 mmol) were dissolved in acetone (0.24 mL, 10 eq, 3.3 mmol) with 4Å molecular sieves (12 mg). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 85 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.61) to afford 42.6 mg (61 %) of the product as a dark yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 3.56 (sept, *J* = 6.4 Hz, 2H), 1.03 (d, *J* = 6.4 Hz, 12H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 155.4, 140.4, 127.4, 113.3, 55.4, 48.6, 21.2;

HRMS calculated for $[M+H]^+$ 208.1696, found 208.1702;

IR (ν_{max}, cm^{-1}): CH (913), CN (1377).

NMR data was in agreement with the literature report[1].

(Method B) $RuCl_3 \cdot 3H_2O$ (4.3 mg, 5 mol %, 0.0165 mmol) and *p*-anisidine (40 mg, 1 eq, 0.33 mmol) were dissolved in acetone (0.24 mL, 10 eq, 3.3 mmol) and acetonitrile (0.1 mL) with 4Å molecular sieves (12 mg). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 72 % yield by NMR.

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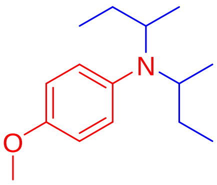
[1] R.P. Rucker, M.A. Whittaker, H. Dang, G. Lalic. *Angew. Chem. Int. Ed.* 2012, **51**, 3953–3956.

N,*N*-di-sec-butyl-4-methoxyaniline (1b)



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3{\cdot}4H_2O$ (4.8 mg, 2 mol %, 0.017 mmol) and *p*-anisidine (110 mg, 1 eq, 0.89 mmol) were dissolved in butanone-2 (0.4 mL, 5 eq, 4.5 mmol). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 60 % yield by NMR. The product was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (5:1); R_f=0.80) to afford 104.0 mg (50 %) of the product as a dark yellow oil (dr = 1:1, determined by ^{1}H NMR).

^{1}H NMR of diastereomeric mixture ($CDCl_3$, 400 MHz, 25 °C) δ 6.98 – 6.94 (m, 2H), 6.83 – 6.80 (m, 2H), 3.79 (s, 3H), 3.33 – 3.26 (m, 2H), 1.68 – 1.60 (m, 2H), 1.47 – 1.36 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 7.3, 3H), 0.93 (t, *J* = 7.3, 3H);

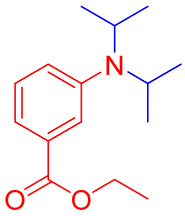
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.7, 141.9, 124.6, 124.3, 113.5, 55.3, 29.2, 28.4, 19.1, 18.3, 11.5, 11.4;

HRMS calculated for $[M+H]^+$ 236.2009, found 236.2011;

IR (ν_{max}, cm^{-1}): CH (2964), CN (1509).

(Method B) $RuCl_3{\cdot}3H_2O$ (4.3 mg, 5 mol %, 0.0165 mmol), *p*-anisidine (40 mg, 1 eq, 0.33 mmol) and butanone-2 (0.15 mL, 5 eq, 1.65 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 65 % yield by NMR.

Ethyl 3-(diisopropylamino)benzoate (1c)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (7.8 mg, 5 mol %, 0.03 mmol), ethyl 3-aminobenzoate (0.085 mL, 1 eq, 0.6 mmol) and acetone (0.44 mL, 10 eq, 6.0 mmol) were dissolved in acetonitrile (0.1 mL). 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 180 °C. After 48 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); combined solvents were removed on a rotary evaporator. 75 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.67) to afford 90.0 mg (60 %) of the product as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.57 (s, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.82 (sept, *J* = 6.7 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 6.7 Hz, 12H);

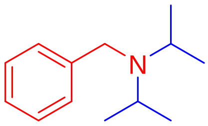
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 167.2, 148.0, 130.6, 128.2, 122.6, 119.1, 118.6, 60.6, 47.5, 21.1, 14.2;

HRMS calculated for $[M+H]^+$ 250.1802, found 250.1799;

IR (ν_{max}, cm^{-1}): CH (2932), CN (1307), C=O (1717).

(Method A) $RhCl_3 \cdot 4H_2O$ (3.4 mg, 2 mol %, 0.012 mmol), ethyl 3-aminobenzoate (0.085 mL, 1 eq, 0.6 mmol) and acetone (0.44 mL, 10 eq, 6.0 mmol) were dissolved in ethanol (0.1 mL). 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 180 °C. After 48 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); combined solvents were removed on a rotary evaporator. 31 % yield by NMR.

N-benzyl-*N*-isopropylpropan-2-amine (1d)



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3{\cdot}4H_2O$ (2.1 mg, 2 mol %, 0.0074 mmol) and benzylamine (0.041 mL, 1 eq, 0.37 mmol) were dissolved in acetone (0.27 mL, 10 eq, 3.7 mmol) with 4Å molecular sieves (12 mg). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 63 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.85) to afford 36.5 mg (51 %) of the product as a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 2H), 3.10 (sept, *J* = 6.6 Hz, 2H), 1.11 (d, *J* = 6.6 Hz, 12H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 143.2, 127.9, 127.8, 126.1, 48.9, 47.7, 20.7;

HRMS calculated for $[M+H]^+$ 192.1747, found 192.1756;

IR (ν_{max}, cm^{-1}): CH (2945), CN (1464).

NMR data was in agreement with the literature report[2].

(Method B) $RuCl_3{\cdot}3H_2O$ (4.8 mg, 5 mol %, 0.0185 mmol), benzylamine (0.041 mL, 1 eq, 0.37 mmol) and acetone (0.27 mL, 10 eq, 3.7 mmol) were dissolved in acetonitrile (0.1 mL) with 4Å molecular sieves (12 mg). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 43 % yield by NMR.

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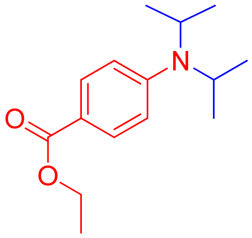
[2] S-H. Xiang, J. Xu, H-Q. Yuan, P-Q. Huang, *Synlett* 2010, **12**, 1829–1832.



ethyl 4-(diisopropylamino)benzoate (1e)

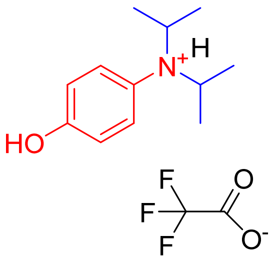
(B) $RuCl_3*3H_2O$ (11.8 mg, 5 mol %, 0.045 mmol), ethyl 4-aminobenzoate (150 mg, 1 eq, 0.9 mmol) and acetone (0.66 mL, 10 eq, 9.0 mmol) were dissolved in acetonitrile (0.1 mL). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 42 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.53) to afford 67.0 mg (30 %) of the colorless oil product.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.86 (d, *J* = 9.1 Hz, 2H), 6.78 (d, *J* = 9.1 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.98-3.88 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 6.6 Hz, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 166.9, 151.6, 130.6, 116.9, 113.9, 59.9, 47.3, 20.8, 14.4;

(A) $RhCl_3*4H_2O$ (5.1 mg, 2 mol %, 0.018 mmol), ethyl 4-aminobenzoate (150 mg, 1 eq, 0.9 mmol) were dissolved in acetone (0.66 mL, 10 eq, 9.0 mmol). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 27 % yield by NMR.

4-hydroxy-*N*,*N*-diisopropylbenzenaminium 2,2,2-trifluoroacetate (1f)



$RhCl_3 \cdot 4H_2O$ (10.1 mg, 2 mol %, 0.036 mmol) and *p*-aminophenol (200 mg, 1 eq, 1.8 mmol) were dissolved in acetone (1.32 mL, 10 eq, 18.0 mmol) with 4Å molecular sieves (12 mg). 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 160 °C. After 48 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), combined solvents were removed on a rotary evaporator. 53 % yield by NMR. The residue was dissolved in 1 mL of dichloromethane and the solution was cooled using an ice bath; trifluoroacetic acid anhydride (0.45 mL, 2 eq, 3.6 mmol) was added to the mixture. After 60 min, the solvent was removed on a rotary evaporator. Then alcohol alkaline solution (15 mL, 50 % KOH in ethanol) was added until pH 6. After 60 min, the solvent was removed on a rotary evaporator. $CHCl_3$ (10 mL) and water (10 mL) were added. The aqueous layer was extracted with $CHCl_3$ (2x10mL), the aqueous layers were combined and saturated with NaCl (500 mg). After 60 min of stirring, the aqueous layer was extracted twice with EtOAc (2x10mL). The organic layers were combined, dried over anhydrous calcined $MgSO_4$ (500 mg) and concentrated in vacuum to afford 130 mg (23 %) of slightly brown crystals (R_f=0.34 in dichloromethane/methanol 10:1). The product has a substantially lower solubility in $CDCl_3$ than in $(CD_3)_2CO$.

^{1}H NMR ($(CD_3)_2CO$, 400 MHz, 25 °C) δ 12.8-12.0 (br s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 4.20 (sept, *J* = 6.3 Hz, 2H), 1.35-1.26 (m, 12H);

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 11.6-11.4 (br s, 1H), 7.48-7.29 (m, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.97 (sept, *J* = 6.3 Hz, 2H), 1.36 (d, *J* = 6.3 Hz, 6H), 1.22 (d, *J* = 6.3 Hz, 6H);

^{13}C NMR ($(CD_3)_2CO$, 150 MHz, 25 °C) δ 160.9 (q, *J* = 33.4 Hz), 159.3, 127.0, 126.6, 117.7 (q, *J* = 294.1 Hz), 116.8, 55.9, 18.6, 17.0;

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 161.4, 159.1, 125.3, 126.6, 116.8, 115.9, 115.0, 55.8, 18.9, 17.1;

^{19}F NMR ($CDCl_3$, 282 MHz, 25 °C) δ -76.6;

mp = 119 – 121 °C.

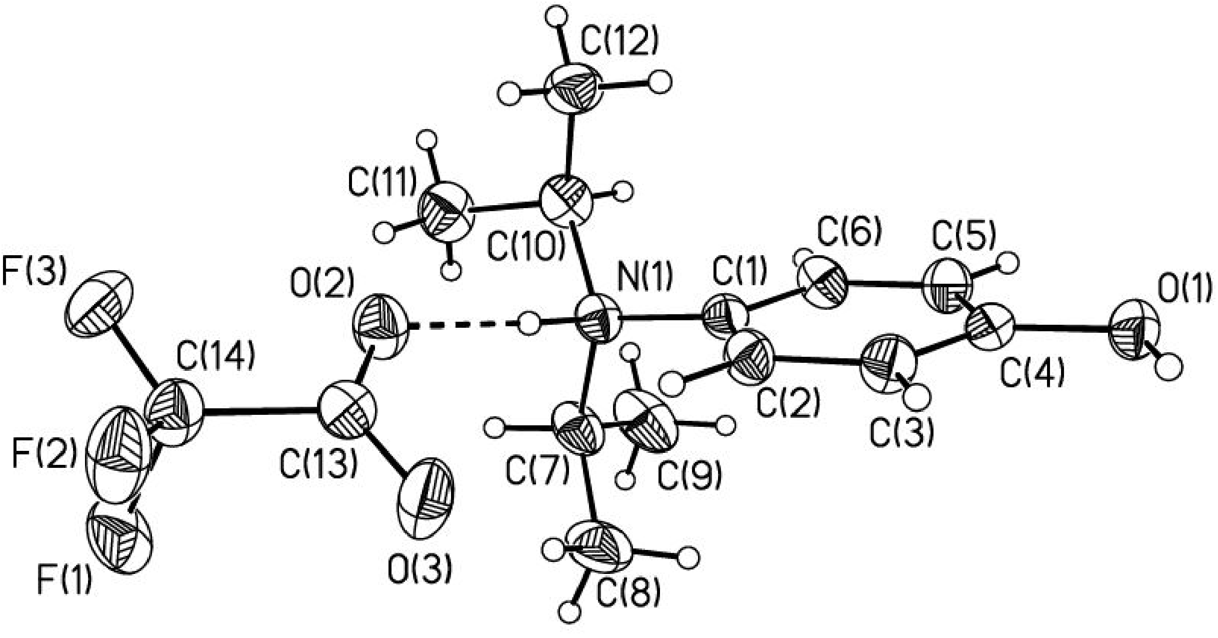
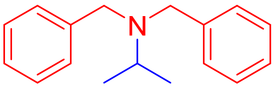


Figure 3. General view for the salt of **1f** with CF_3COO^- in representation of atoms *via* thermal ellipsoids at 50% probability level; only one component of the disordered CF_3 group of the trifluoroacetate anion is shown.

Crystallographic data for the salt of **1f** with CF_3COO^- ($C_{14}H_{20}F_3NO_3$, M = 307.31) at 120 K: Crystals are orthorhombic, space group Pbca, a = 7.7764(12), b = 15.755(2), c = 25.521(4) Å, V = 3126.7(8) $Å^3$, Z = 8 (Z' = 1), d_{calc} = 1.306 gcm^{-3}, $\mu(MoK\alpha)$ = 1.14 cm^{-1}, F(000) = 1296. Intensities of 31077 reflections were measured on Bruker APEX2 DUO CCD diffractometer [$\lambda(MoK\alpha)$ = 0.71072Å, ω-scans, $2\theta<54°$], and 3402 independent reflections [R_{int} = 0.0401] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atoms of NH and OH groups were located from the Fourier density synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in the isotropic approximation within the riding model. The refinement converged to wR2 = 0.1850 and GOF = 1.376 for all the independent reflections (R1 = 0.0734 was calculated against F for 2467 observed reflections with $I>2\sigma(I)$)**.** All calculations were performed using SHELXTL PLUS 5.0 [G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112-122].

N,N-dibenzylpropan-2-amine (1g)



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3•4H_2O$ (1.1 mg, 2 mol %, 0.004 mmol) and dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) were dissolved in acetone (0.15 mL, 10 eq, 2.0 mmol). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 89 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.70) to afford 30.4 mg (65 %) of the product as a dark yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.43 (d, *J* = 7.4 Hz, 4H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.24 (t, *J* = 7.4 Hz, 2H), 3.60 (s, 4H), 2.98 (sept, *J* = 6.6 Hz, 1H), 1.10 (d, *J* = 6.6 Hz, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 141.0, 128.5, 128.1, 126.5, 53.2, 48.1, 17.5;

HRMS calculated for $[M+H]^+$ 240.1747, found 240.1752;

IR (ν_{max}, cm^{-1}): CH (2854), CN (1494).

NMR data was in agreement with the literature report[3].

(Method B) $RuCl_3•3H_2O$ (2.6 mg, 5 mol %, 0.01 mmol) and dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) were dissolved in acetone (0.15 mL, 10 eq, 2.0 mmol) and acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 80 % yield by NMR.

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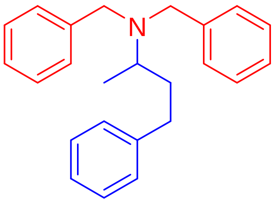
[3] M. Tokizane, K. Sato, Y. Sakami, Y. Imori, C. Matsuo, T. Ohta, Y. Ito, *Synthesis* 2010, **1**, 36-42.

***N,N*-dibenzyl-4-phenylbutan-2-amine (1h)**



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3 \cdot 4H_2O$ (0.6 mg, 2 mol %, 0.002 mmol), dibenzylamine (0.019 mL, 1eq, 0.1 mmol) and 4-phenylbutan-2-one (0.015 mL, 1 eq, 0.1 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 77 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (8:1); R_f=0.79) to afford 20.0 mg (61 %) of the product as a light yellow oil.

^1H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.41 (d, *J* = 7.3 Hz, 4H), 7.32 (t, *J* = 7.3 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 4H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 3.76 (d, *J* = 13.8 Hz, 2H), 3.46 (d, *J* = 13.8 Hz, 2H), 2.90 – 2.74 (m, 2H), 2.55 – 2.48 (m, 1H), 2.03 – 1.86 (m, 1H), 1.64 – 1.50 (m, 2H), 1.07 (d, *J* = 6.6 Hz, 3H);

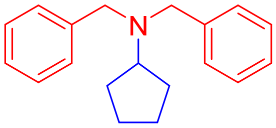
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 143.0, 140.7, 128.6, 128.3, 128.2, 128.1, 126.7, 125.5, 53.3, 52.4, 36.1, 33.3, 13.4;

HRMS calculated for $[M+H]^+$ 330.2216, found 330.2211;

IR (ν_{max}, cm^{-1}): CH (2923), CN (1506).

(Method B) $RuCl_3 \cdot 3H_2O$ (2.6 mg, 5 mol %, 0.01 mmol), dibenzylamine (0.039 mL, 1eq, 0.2 mmol) and 4-phenylbutan-2-one (0.034 mL, 1 eq, 0.2 mmol) were dissolved in 0.1 mL (acetonitrile). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 55 % yield by NMR.

N,*N*-dibenzylcyclopentanamine (1i)



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3{\cdot}4H_2O$ (1.1 mg, 2 mol %, 0.004 mmol), dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) and cyclopentanone (0.018 mL, 1 eq, 0.2 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 87 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.79) to afford 37.2 mg (70 %) of the product as a dark yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.44-7.21 (m, 10H), 3.64 (s, 4H), 3.25 – 3.17 (m, 1H), 1.7-1.76 (m, 2H), 1.64-1.48 (m, 6H);

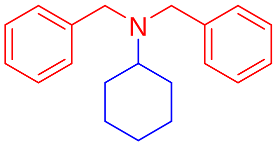
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 140.6, 128.7, 128.0, 126.5, 62.1, 55.2, 28.1, 24.5;

HRMS calculated for $[M+H]^+$ 266.1903, found 266.1899;

IR (ν_{max}, cm^{-1}): CH (2889), CN (1528).

(Method B) $RuCl_3{\cdot}3H_2O$ (2.6 mg, 5 mol %, 0.01 mmol), dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) and cyclohexanone (0.018 mL, 1 eq, 0.2 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 27 % yield by NMR.

***N,N*-dibenzylcyclohexanamine (1j)**



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3{\cdot}4H_2O$ (1.1 mg, 2 mol %, 0.004 mmol), dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) and cyclohexanone (0.021 mL, 1 eq, 0.2 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 90 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.86) to afford 36.3 mg (65 %) of the product as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.61 (d, *J* = 7.4 Hz, 4H), 7.49 (t, *J* = 7.4 Hz, 4H), 7.40 (t, *J* = 7.2 Hz, 2H), 3.85 (s, 4H), 2.75-2.67 (m, 1H), 2.10-2.14 (m, 2H), 1.99-1.96 (m, 2H), 1.82-1.79 (m, 1H), 1.59-1.47 (m, 2H), 1.41-1.25 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 141.2, 128.3, 128.0, 126.4, 57.6, 53.7, 28.6, 26.5, 26.1;

HRMS calculated for $[M+H]^+$ 280.2060, found 280.2053;

IR (ν_{max}, cm^{-1}): CH (2924), CN (1464);

mp = 56 – 58 °C.

NMR data was in agreement with the literature report[4].

(Method B) $RuCl_3{\cdot}3H_2O$ (2.6 mg, 5 mol %, 0.01 mmol), dibenzylamine (0.039 mL, 1 eq, 0.2 mmol) and cyclohexanone (0.021 mL, 1 eq, 0.2 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 51 % yield by NMR.

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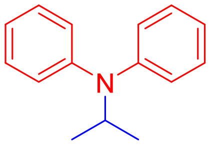
[4] C. Guerin, V. Bellosta, G. Guillamot, J. Cossy, *Org. Lett.* 2011, **13**, 3534–3537.

N-isopropyl-N-phenylaniline (1k)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (3.1 mg, 5 mol %, 0.012 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) and acetone (0.088 mL, 5 eq, 1.2 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 93 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.75) to afford 38.7 mg (75 %) of the product as a dark colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.28–7.26 (m, 4H), 7.00 (t, J = 7.3 Hz, 2H), 6.87 (d, J = 7.7 Hz, 4H), 4.34 (sept, J = 6.6 Hz, 1H), 1.17 (d, J = 6.6 Hz, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 146.1, 129.1, 122.8, 121.6, 47.9, 20.9;

HRMS calculated for $[M+H]^+$ 212.1434, found 212.1442;

IR (ν_{max}, cm^{-1}): CH (2972), CN (1495).

NMR data was in agreement with the literature report[5].

(Method A) $RhCl_3 \cdot 4H_2O$ (1.4 mg, 2 mol %, 0.0048 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) was dissolved in acetone (0.088 mL, 5 eq, 1.2 mmol). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 40 % yield by NMR.

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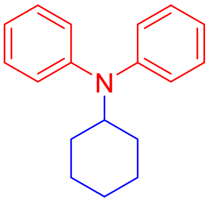
[5] T.J. Reddy, M. Leclair, M. Proulx, *Synlett* 2005, **4**, 583–586.

N-cyclohexyl-*N*-phenylaniline (1l)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (3.1 mg, 5 mol %, 0.012 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) and cyclohexanone (0.025 mL, 1 eq, 0.24 mmol) were solved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 91 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.79) to afford 42.2 mg (70 %) of the product as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.29-7.25 (m, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 7.7 Hz, 4H), 3.88 – 3.80 (m, 1H), 2.03 (d, *J* = 11.7 Hz, 2H), 1.80 (d, *J* = 13.6 Hz, 2H), 1.64 (d, *J* = 13.1 Hz, 1H), 1.46 – 1.34 (m, 2H), 1.25 – 0.97 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 146.3, 129.1, 122.7, 121.5, 56.7, 31.7, 26.2, 25.7;

HRMS calculated for $[M+H]^+$ 252.1747, found 252.1755;

IR (ν_{max}, cm^{-1}): CH (2972), CN (1497).

NMR data was in agreement with the literature report[6].

(Method A) $RhCl_3 \cdot 4H_2O$ (1.4 mg, 2 mol %, 0.0048 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) and cyclohexanone (0.025 mL, 1 eq, 0.24 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 40 % yield by NMR.

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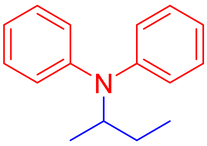
[6] Y-H. Lee, Y-C. Chen, J-C. Hsieh, *Eur. J. Org. Chem.* 2012, **2**, 247–250.

N-(sec-butyl)-*N*-phenylaniline (1m)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (3.1 mg, 5 mol %, 0.012 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) and butanone-2 (0.21 mL, 10 eq, 2.4 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 74 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.68) to afford 29.2 mg (54 %) of the product as a yellow oil.

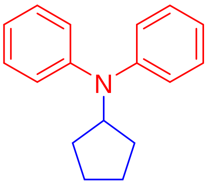
^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.29 (t, J = 7.8 Hz, 4H), 7.00 (t, J = 7.3 Hz, 2H), 6.89 (d, J = 8.1 Hz, 4H), 4.12 – 3.97 (m, 1H), 1.83 – 1.67 (m, 1H), 1.45-1.36 (m, 1H), 1.18 (d, J = 6.6 Hz, 3H), 1.01 (t, J = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 146.6, 129.1, 122.8, 121.5, 54.6, 28.2, 18.4, 11.7;

HRMS calculated for $[M+H]^+$ 226.1590, found 226.1585;

IR (ν_{max}, cm^{-1}): CH (2932), CN (1404).

N-cyclopentyl-*N*-phenylaniline (1n)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (3.1 mg, 5 mol %, 0.012 mmol), diphenylamine (40 mg, 1 eq, 0.24 mmol) and cyclopentanone (0.022 mL, 1 eq, 0.24 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 70 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.75) to afford 34.1 mg (60 %) of the product as a yellow oil.

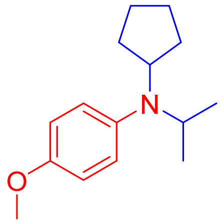
^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 7.32 – 7.27 (t, *J* = 7.8 Hz, 4H), 7.01 (t, *J* = 7.3 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 4H), 4.33 – 4.23 (m, 1H), 2.04 – 1.96 (m, 2H), 1.63 – 1.52 (m, 4H), 1.48 – 1.37 (m, 2H);

^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C) δ 147.2, 129.1, 123.0, 121.6, 59.8, 30.3, 23.0;

HRMS calculated for $[M+H]^+$ 238.1590, found 238.1589;

IR (ν_{max}, cm^{-1}): CH (2958), CN (1496).

N-cyclopentyl-*N*-isopropyl-4-methoxyaniline (1o)



The product was isolated in a pure form using Method B.

(Method B) RuCl$_3$•3H$_2$O (4.7 mg, 5 mol %, 0.018 mmol), *N*-isopropyl-4-methoxyaniline (0.06 mL, 1 eq, 0.36 mmol) and cyclopentanone (0.032 mL, 1 eq, 0.36 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 42 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: toluene/ethyl acetate/triethylamine (6:1:0.1); R_f = 0.45) to afford 15.0 mg (18 %) of the product as a yellow oil.

^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C) δ 7.03 (d, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 3.66 (d, *J* = 8.0 Hz, 1H), 3.49-3.42 (m, 1H), 1.76-1.66 (m, 2H), 1.57 – 1.46 (m, 4H), 1.40 – 1.27 (m, 2H), 0.96 (d, *J* = 6.0 Hz, 6H);

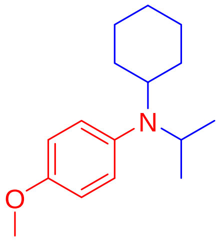
^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C) δ 129.1, 113.0, 55.3, 32.0, 30.3, 23.8, 23.2, 19.7;

HRMS calculated for $[M+H]^+$ 234.1852, found 234.1858;

IR (ν_{max}, cm^{-1}): CH (2981), CN (1507).

(Method A) RhCl$_3$•4H$_2$O (1.0 mg, 2 mol %, 0.0036 mmol), *N*-isopropyl-4-methoxyaniline (0.03 mL, 1 eq, 0.18 mmol) and cyclopentanone (0.016 mL, 1 eq, 0.18 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 30 % yield by NMR.

***N*-cyclohexyl-*N*-isopropyl-4-methoxyaniline (1p)**



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (4.7 mg, 5 mol %, 0.018 mmol), *N*-isopropyl-4-methoxyaniline (0.06 mL, 1 eq, 0.36 mmol) and cyclohexanone (0.037 mL, 1 eq, 0.36 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 66 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: toluene/ethyl acetate (6:1); R_f=0.48) to afford 15.3 mg (17 %) of the product as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 6.95 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 3.76 (s, 3H), 3.62 – 3.54 (m, 1H), 3.11 – 3.03 (m, 1H), 1.79 – 1.69 (m, 5H), 1.56 – 1.53 (m, 1H), 1.24 – 1.14 (m, 4H), 1.00 (d, *J* = 6.3 Hz, 6H);

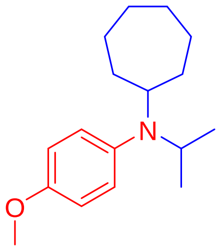
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 155.4, 140.7, 127.9, 113.2, 57.7, 55.4, 48.0, 31.7, 26.1, 25.9, 21.4;

HRMS calculated for $[M+H]^+$ 248.2009, found 248.2019;

IR (ν_{max}, cm^{-1}): CH (2924), CN (1457).

(Method A) $RhCl_3 \cdot 4H_2O$ (1.0 mg, 2 mol %, 0.0036 mmol), *N*-isopropyl-4-methoxyaniline (0.03 mL, 1 eq, 0.18 mmol) and cyclohexanone (0.019 mL, 1 eq, 0.18 mmol) was dissolved in ethanol (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 40 % yield by NMR.

N-cycloheptyl-*N*-isopropyl-4-methoxyaniline (1q)



The product was isolated in a pure form using Method B.

(Method B) $RuCl_3 \cdot 3H_2O$ (4.7 mg, 5 mol %, 0.018 mmol), *N*-isopropyl-4-methoxyaniline (0.06 mL, 1 eq, 0.36 mmol) and cycloheptanone (0.042 mL, 1 eq, 0.36 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 36 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: toluene/ethyl acetate (6:1); R_f=0.48) to afford 20.4 mg (22 %) of the product as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 6.86 (d, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.70 – 3.61 (m, 1H), 3.40 - 3.30 (m, 1H), 1.94 - 1.80 (m, 1H), 1.70 – 1.38 (m, 11H), 1.11 (d, *J* = 5.6 Hz, 6H);

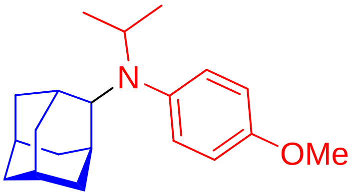
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 153.3, 141.9, 123.0, 113.7, 58.5, 55.5, 49.0, 33.6, 27.8, 25.8, 21.6;

HRMS calculated for $[M+H]^+$ 262.2165, found 262.2167;

IR (ν_{max}, cm^{-1}): CH (2929), CN (1181).

(Method A) $RhCl_3 \cdot 4H_2O$ (1.0 mg, 2 mol %, 0.0036 mmol), *N*-isopropyl-4-methoxyaniline (0.03 mL, 1 eq, 0.18 mmol) and cycloheptanone (0.021 mL, 1 eq, 0.18 mmol) were dissolved in ethanol (0.1 mL). 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 160 °C. After 20 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); combined solvents were removed on a rotary evaporator. 16 % yield by NMR.

(*N*-isopropyl-*N*-(4-methoxyphenyl)adamantan-2-amine (1r)



The product was isolated in a pure form using Method A.

(Method A) $RhCl_3\cdot 4H_2O$ (1.3 mg, 2 mol %, 0.0046 mmol), *N*-(4-methoxyphenyl)adamantan-2-amine (60 mg, 1 eq, 0.23 mmol) were dissolved in acetone (0.17 mL, 10 eq, 2.3 mmol). 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 180 °C. After 48 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); combined solvents were removed on a rotary evaporator. 40 % yield by NMR. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate/triethylamine (6:1:0.1); R_f=0.69) to afford 21.0 mg (31 %) of the product as a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C) δ 7.07 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.44 (sept, *J* = 6.6 Hz, 1H), 3.35 – 3.25 (m, 1H), 2.18 – 2.12 (m, 2H), 1.80 – 1.74 (m, 6H), 1.71 – 1.64 (m, 3H), 1.33 – 1.23 (m, 3H), 0.87 (d, *J* = 6.6 Hz, 6H).

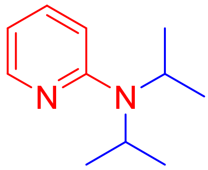
^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C) δ 156.6, 138.6, 131.3, 112.8, 61.3, 55.2, 45.4, 37.8, 37.2, 30.9, 29.8, 27.6, 19.2;

HRMS calculated for $[M+H]^+$ 300.2323, found 300.2322;

IR (ν_{max}, cm^{-1}): CH (2879), CN (1456).

(Method B) $RuCl_3\cdot 3H_2O$ (3.0 mg, 5 mol %, 0.0115 mmol), *N*-(4-methoxyphenyl)adamantan-2-amine (60 mg, 1 eq, 0.23 mmol) and acetone (0.17 mL, 10 eq, 2.3 mmol) were dissolved in acetonitrile (0.1 mL). 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 180 °C. After 48 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); combined solvents were removed on a rotary evaporator. 35 % yield by NMR.

N,N-diisopropylpyridin-2-amine

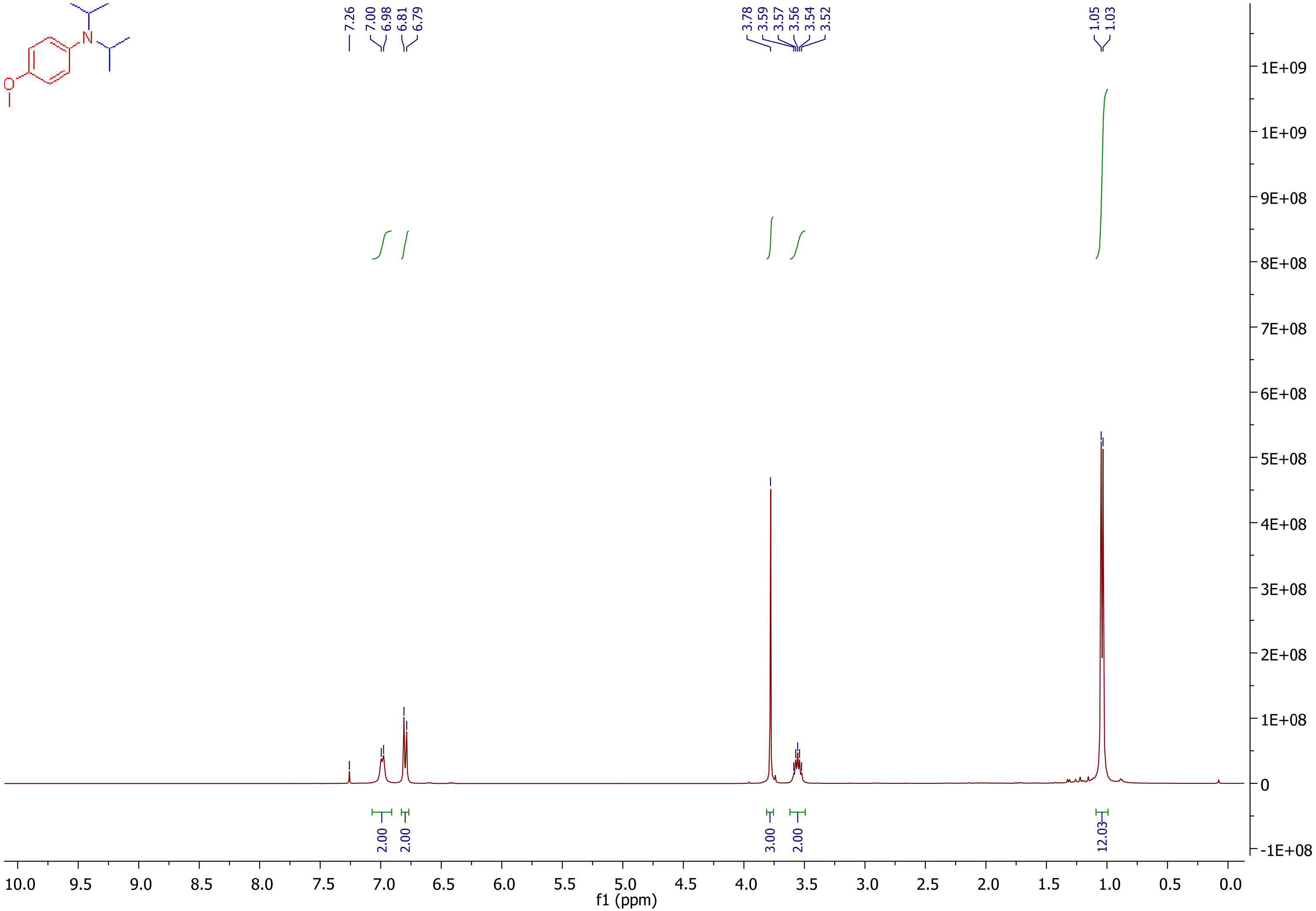


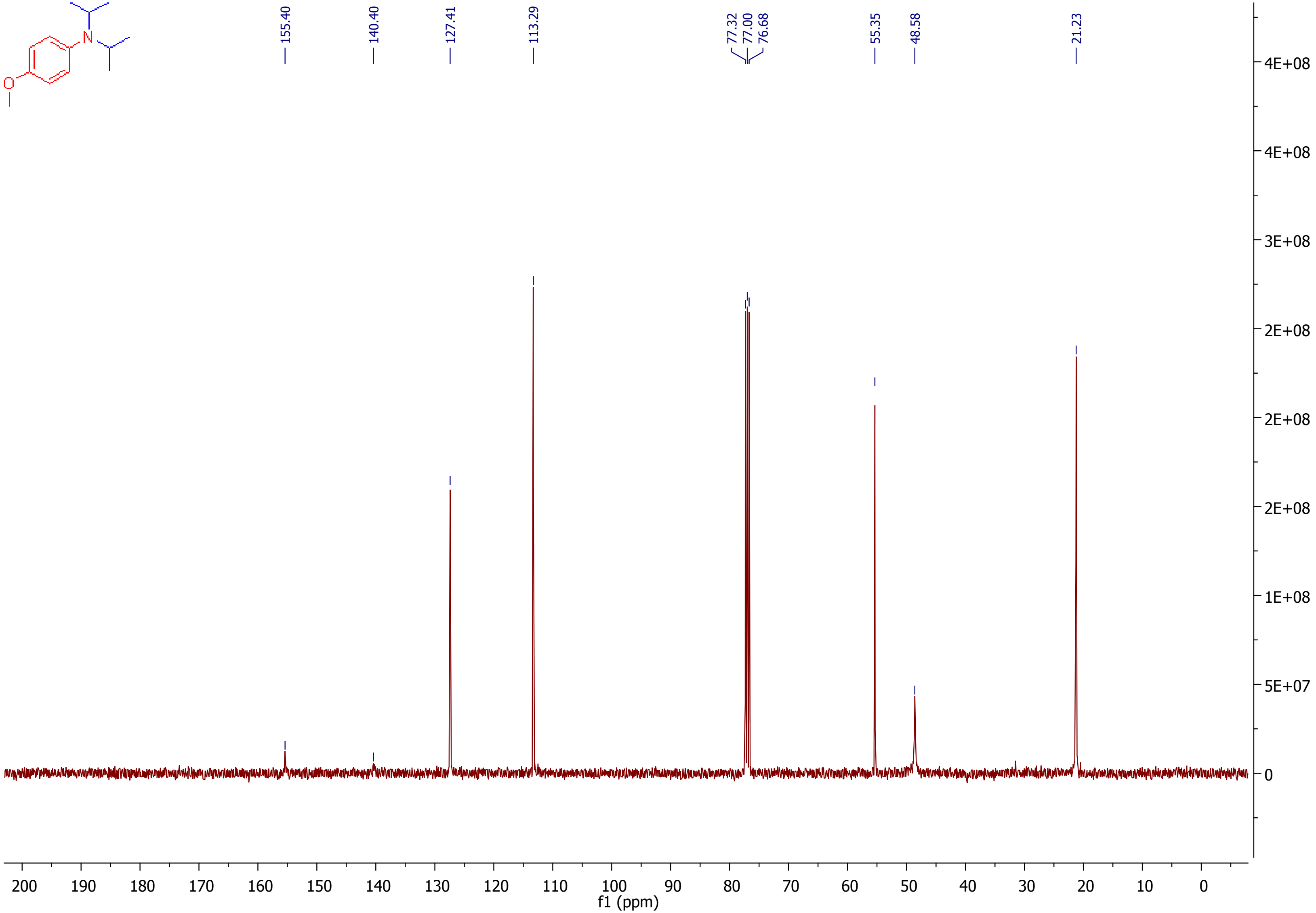
(Method A) $RhCl_3 \cdot 4H_2O$ (11.8 mg, 2 mol %, 0.042 mmol), 2-aminopyridine (200 mg, 1 eq, 2.1 mmol) were dissolved in acetone (1.54 mL, 10 eq, 21.0 mmol). The autoclave was sealed, flushed three times with 10 atm of CO, and then charged with 50 atm CO. The reactor was placed into an oil bath preheated to 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 3 % yield by NMR and 29 % yield of secondary amine by NMR.

(Method B) $RuCl_3 \cdot 3H_2O$ (6.9 mg, 5 mol %, 0.027 mmol), 2-aminopyridine (50 mg, 1 eq, 0.53 mmol) and acetone (0.39 mL, 10 eq, 5.3 mmol) were dissolved in acetonitrile (0.1 mL). 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 160 °C. After 48 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); combined solvents were removed on a rotary evaporator. 0 % yield by NMR and 0 % yield of secondary amine by NMR.

5. ^{1}H, ^{13}C, ^{19}F NMR, mass, and IR spectra of obtained compounds

***N*,*N*-diisopropyl-4-methoxyaniline (1a)**

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f1 (ppm)

Display Report

Analysis Info

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Sample Name	/LB58 NY-270-2	Instrument / Ser#	micrOTOF 10248
Comment	C13H21NO mw 207 calibrant added		

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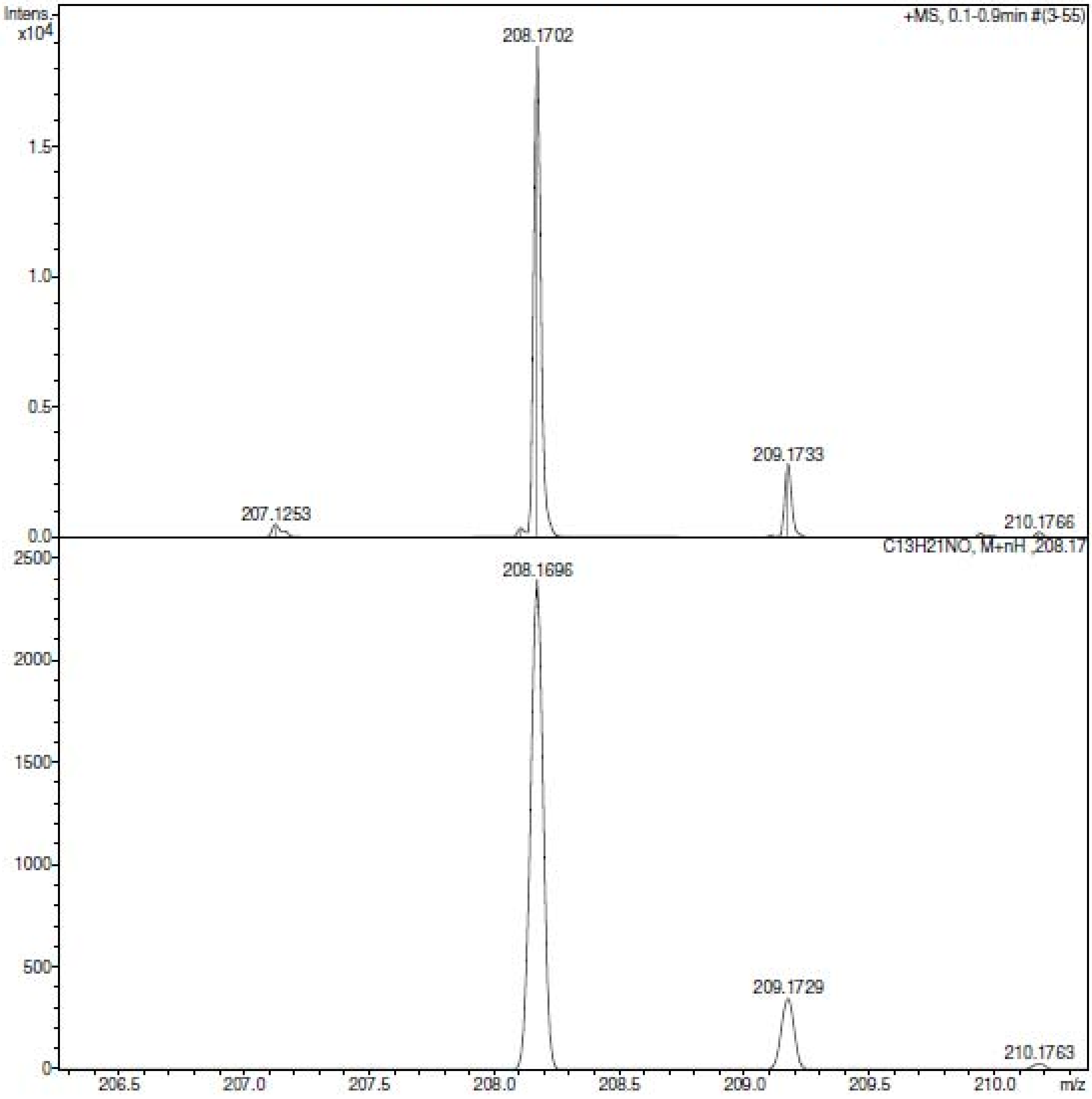
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste		



29 Jul 2015

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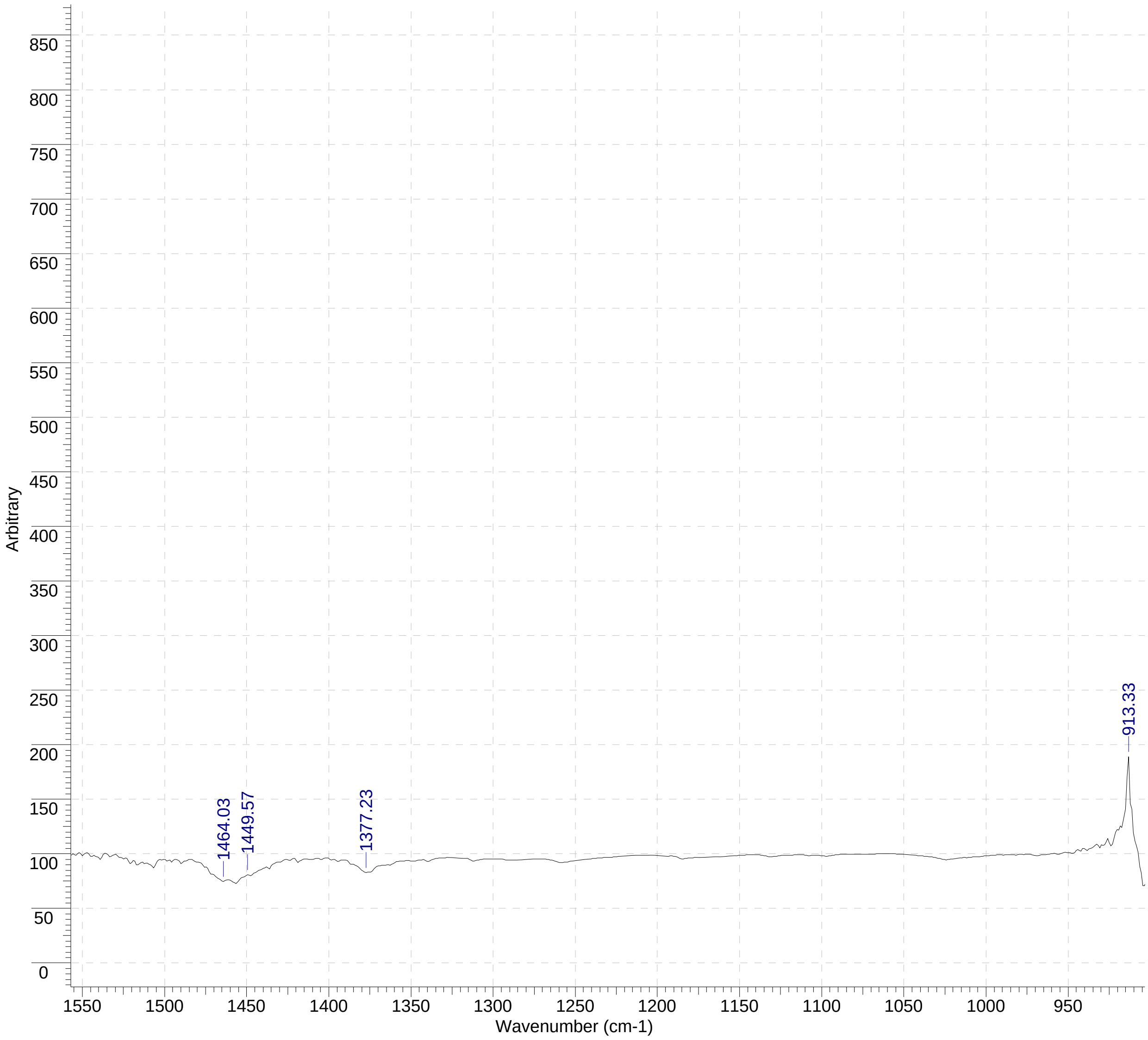

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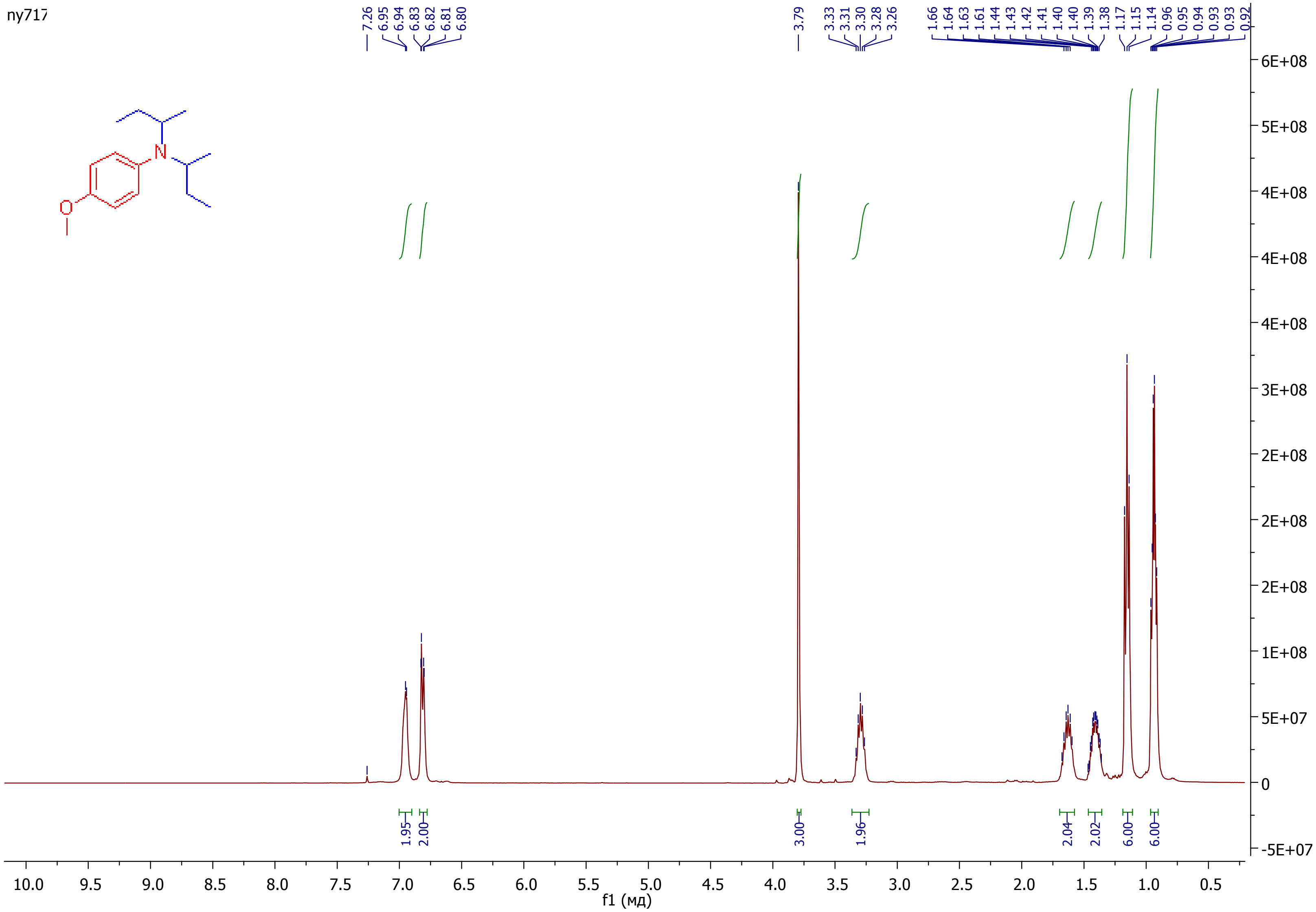
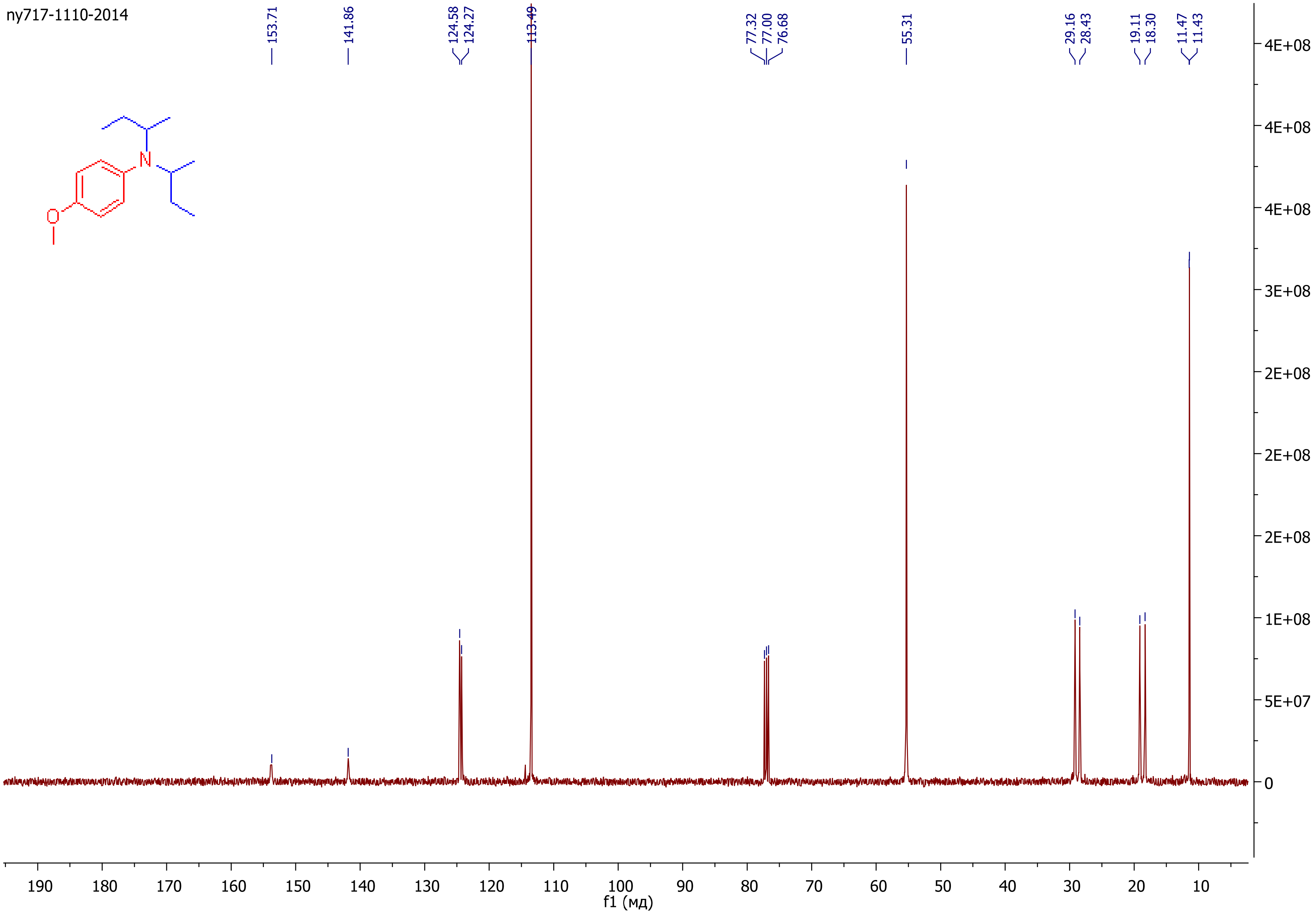
4	1464.03	74.797	VW
5	2853.81	59.493	VW
6	2923.25	51.127	VW
7	2945.43	62.416	VW
8	2953.14	61.078	VW

N,N-di-sec-butyl-4-methoxyaniline (1b)

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f1 (мд)

Display Report

Analysis Info

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Method	tune_low.m	Operator	BDAL@DE
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Comment	C15H25NO mw 235 calibrant added		

Acquisition Parameter

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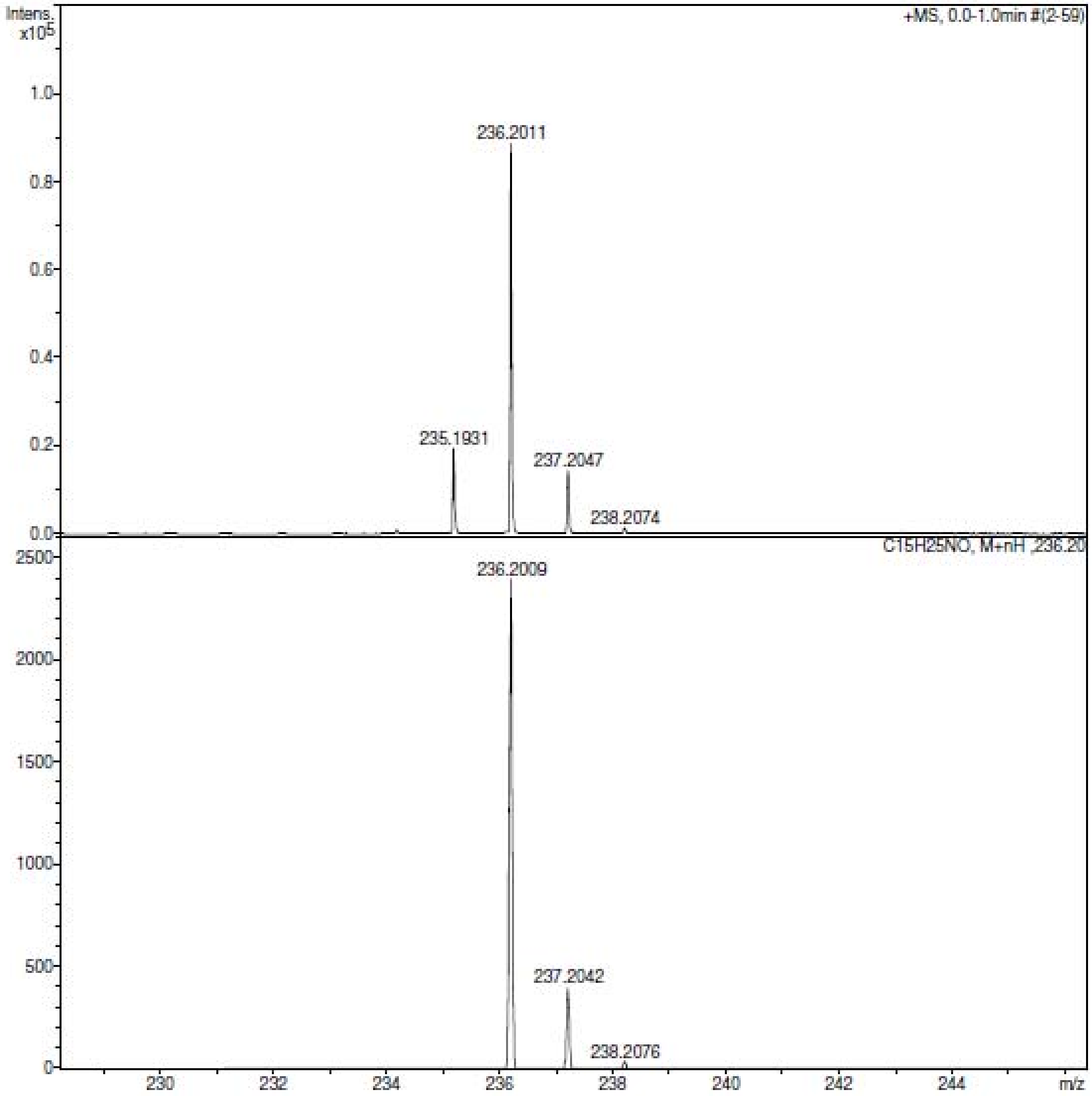

Bruker Compass DataAnalysis 4.0 printed: 13.11.2014 13:23:07 Page 1 of 1

29 Jul 2015

File Name	G:\IR SPECTRA\717.TXT			***Date***	11 Dec 2014 16:05:50
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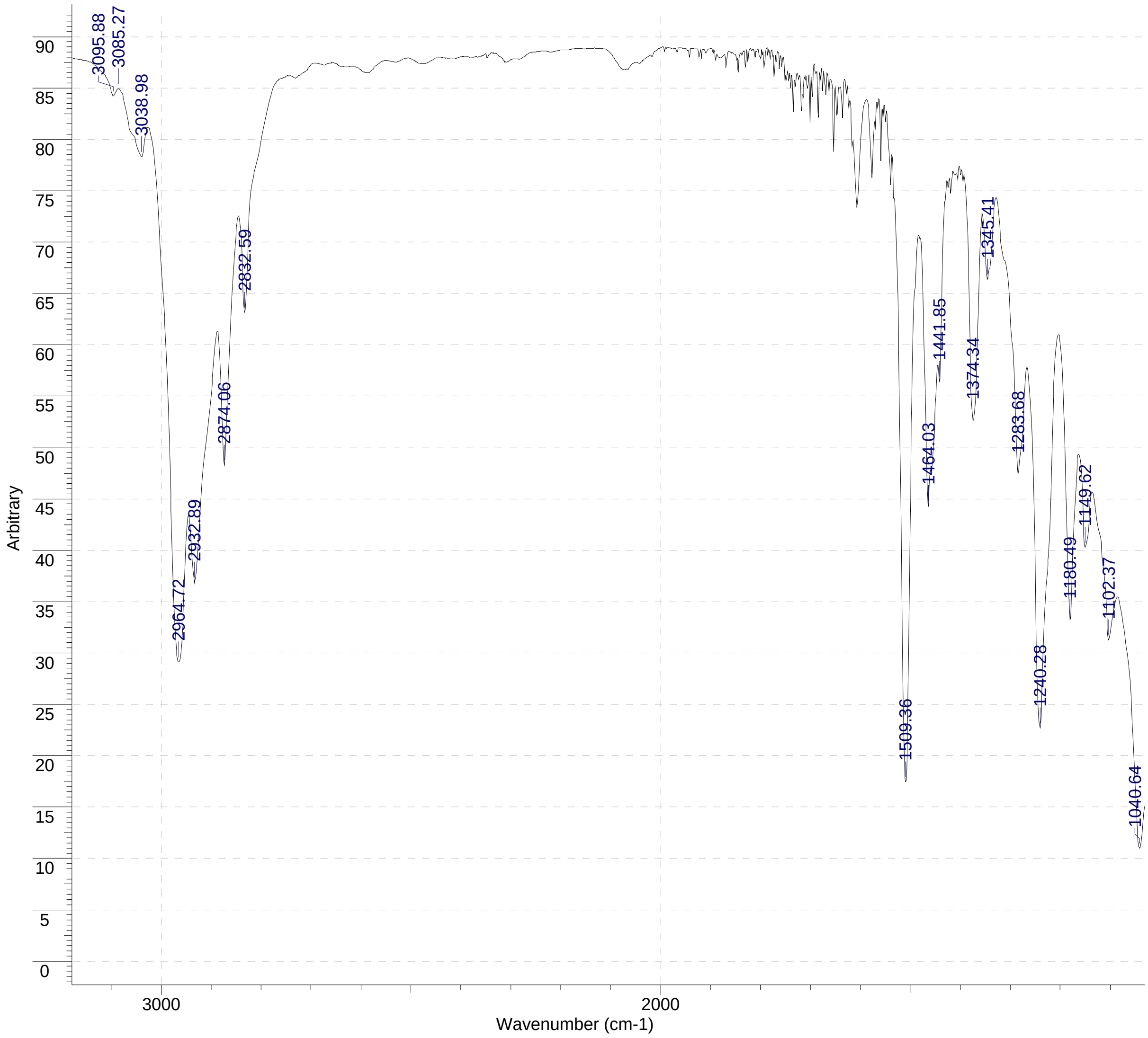

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6	1283.68	47.413	M
7	1345.41	66.379	S
8	1374.34	52.648	M
9	1441.85	56.442	S
10	1464.03	44.346	M
11	1509.36	17.446	W
12	2832.59	63.188	S
13	2874.06	48.288	M
14	2932.89	36.860	M
15	2964.72	29.110	M
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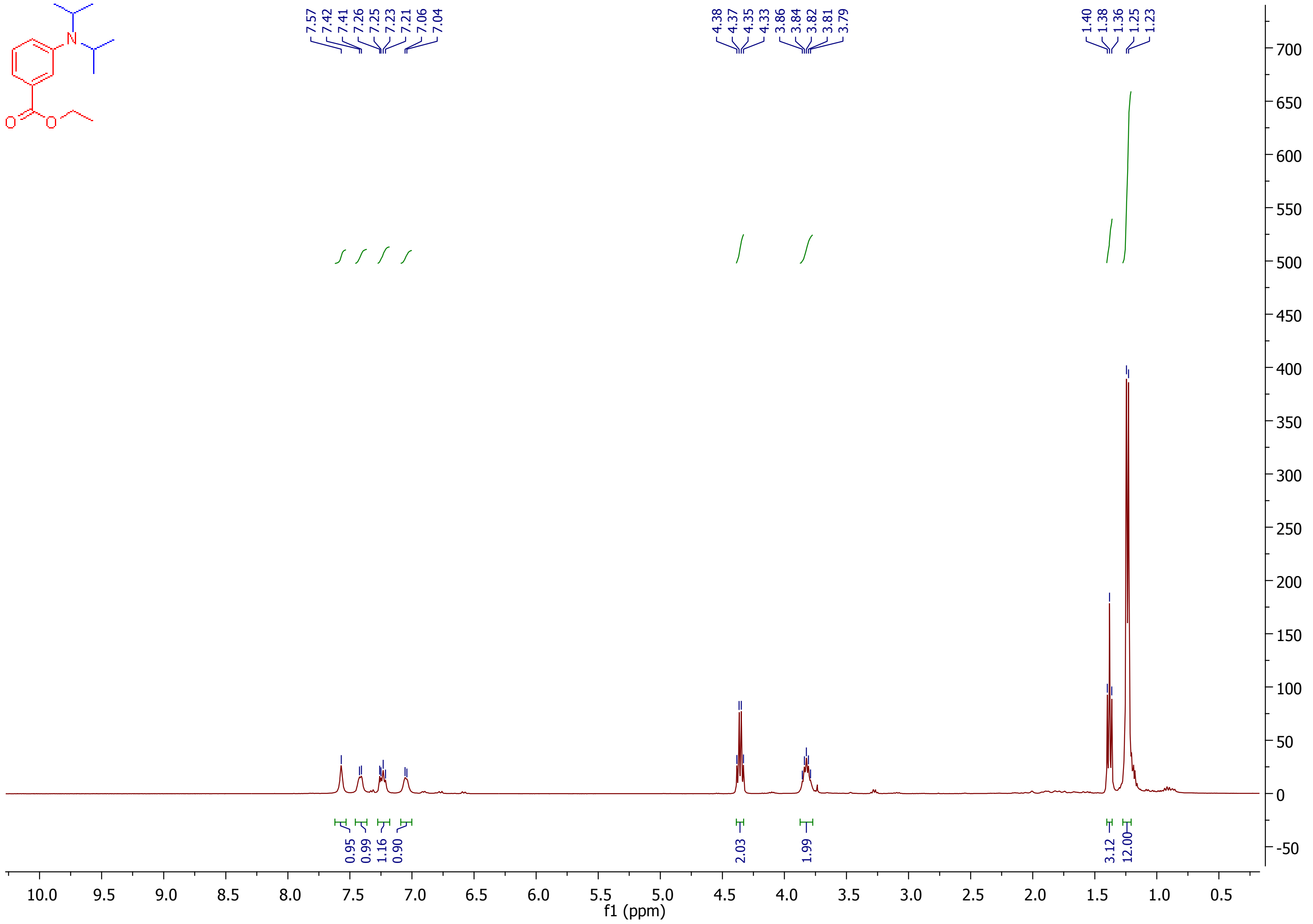
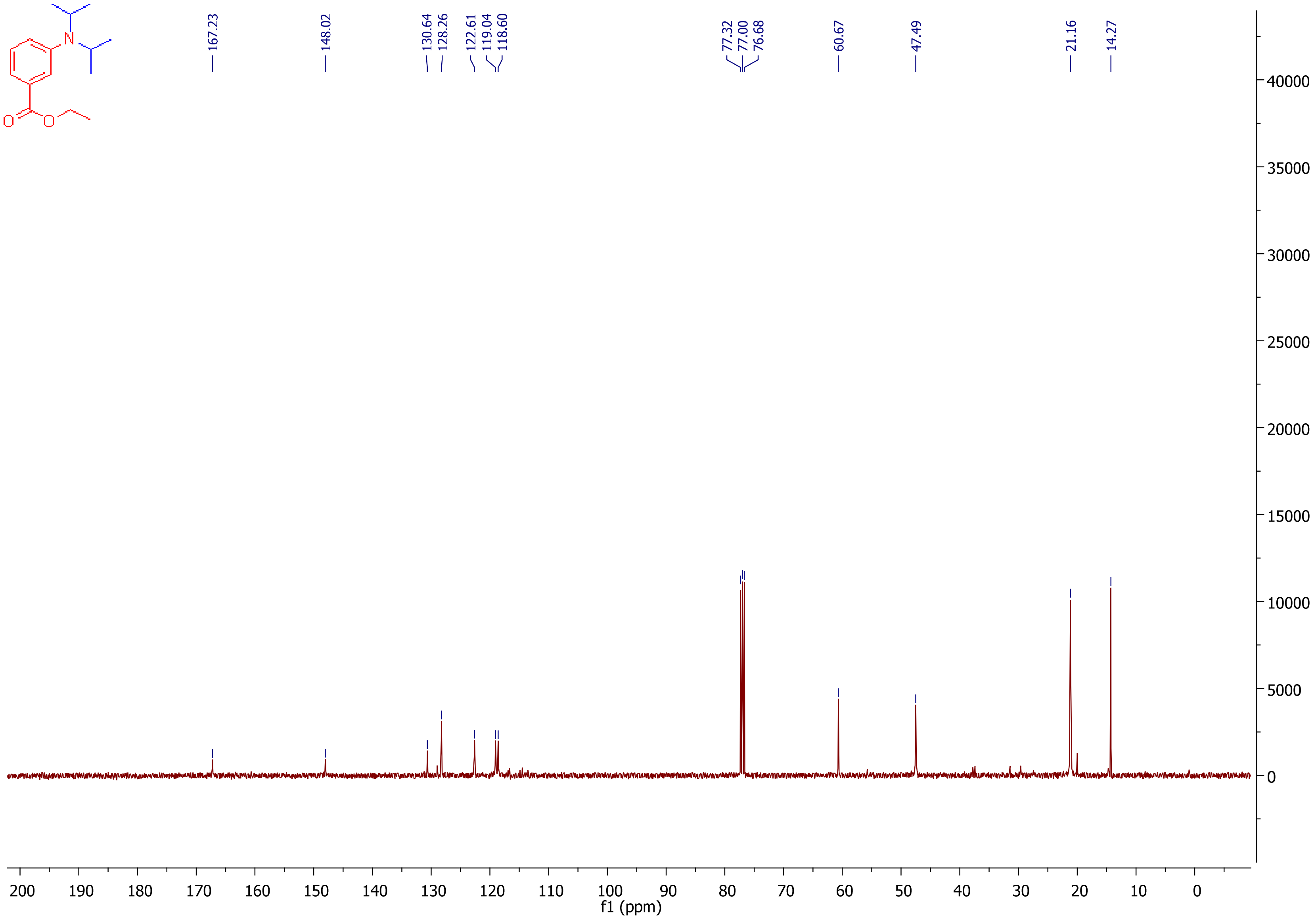
Ethyl 3-(diisopropylamino)benzoate (1c)

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f1 (ppm)

Display Report

Analysis Info

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Sample Name	/LB58 NY-598	Instrument / Ser#	micrOTOF 10248
Comment	C15H23NO2 mw 249 calibrant added		

Acquisition Parameter

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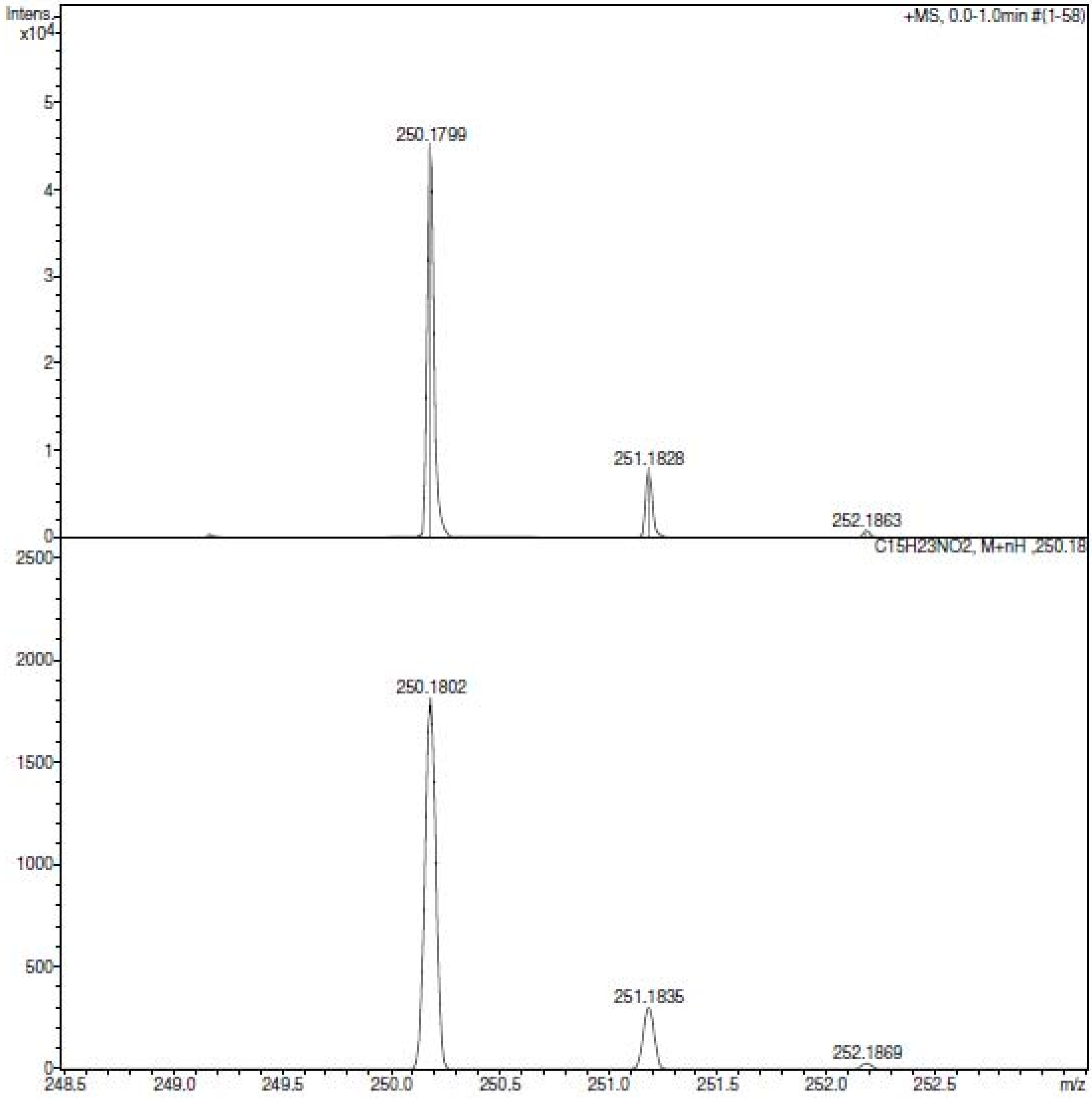
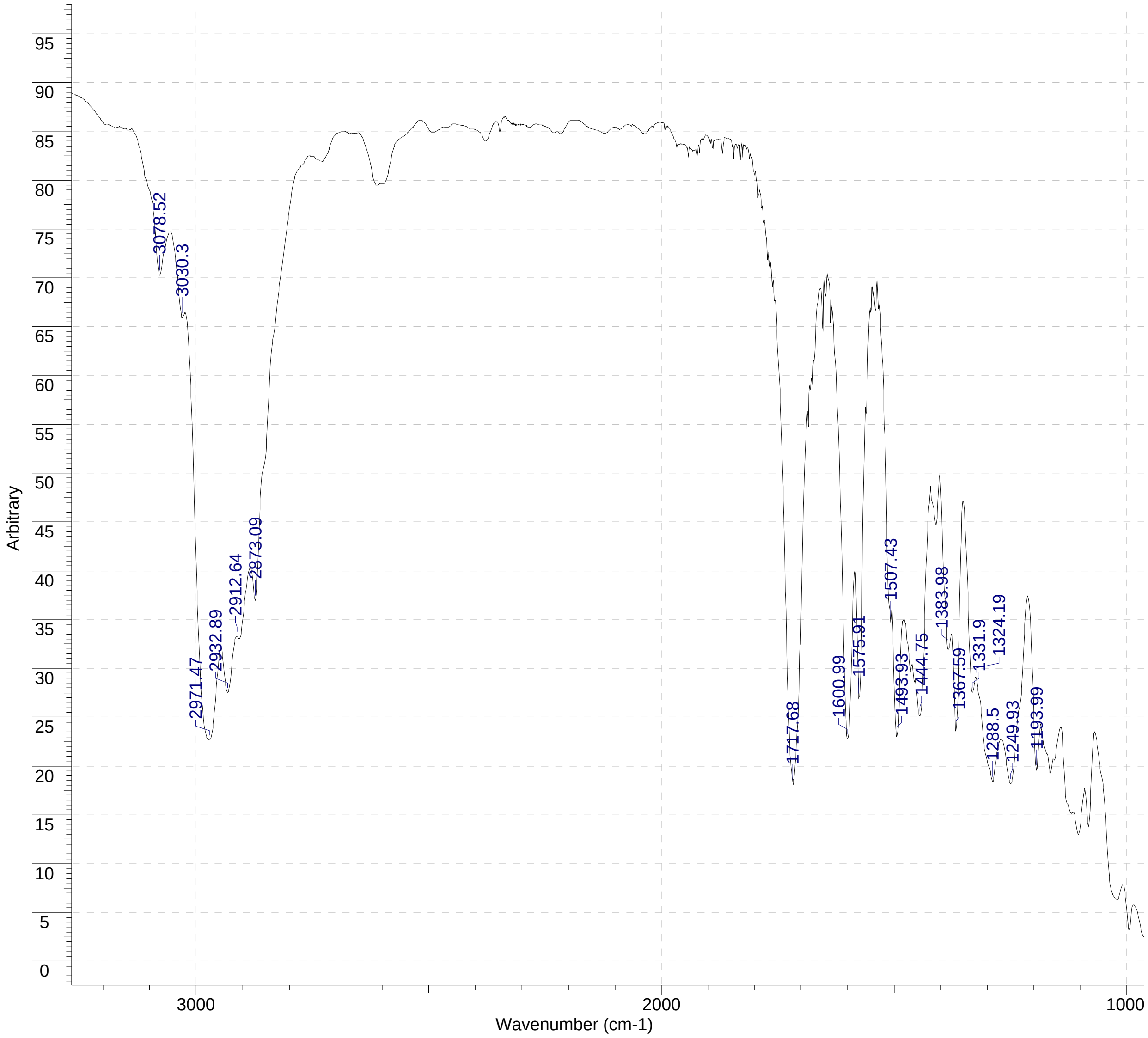
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



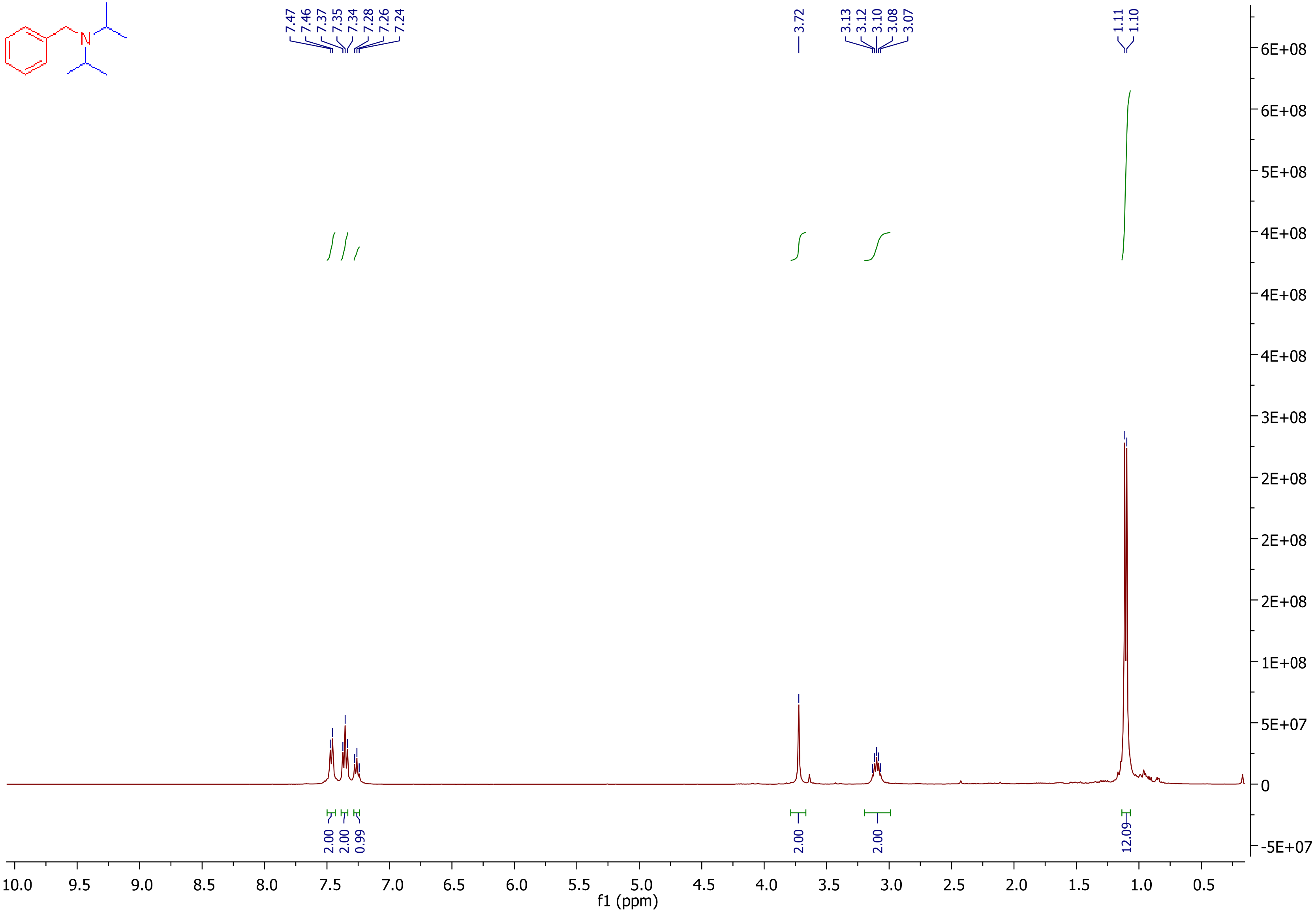
29 Jul 2015

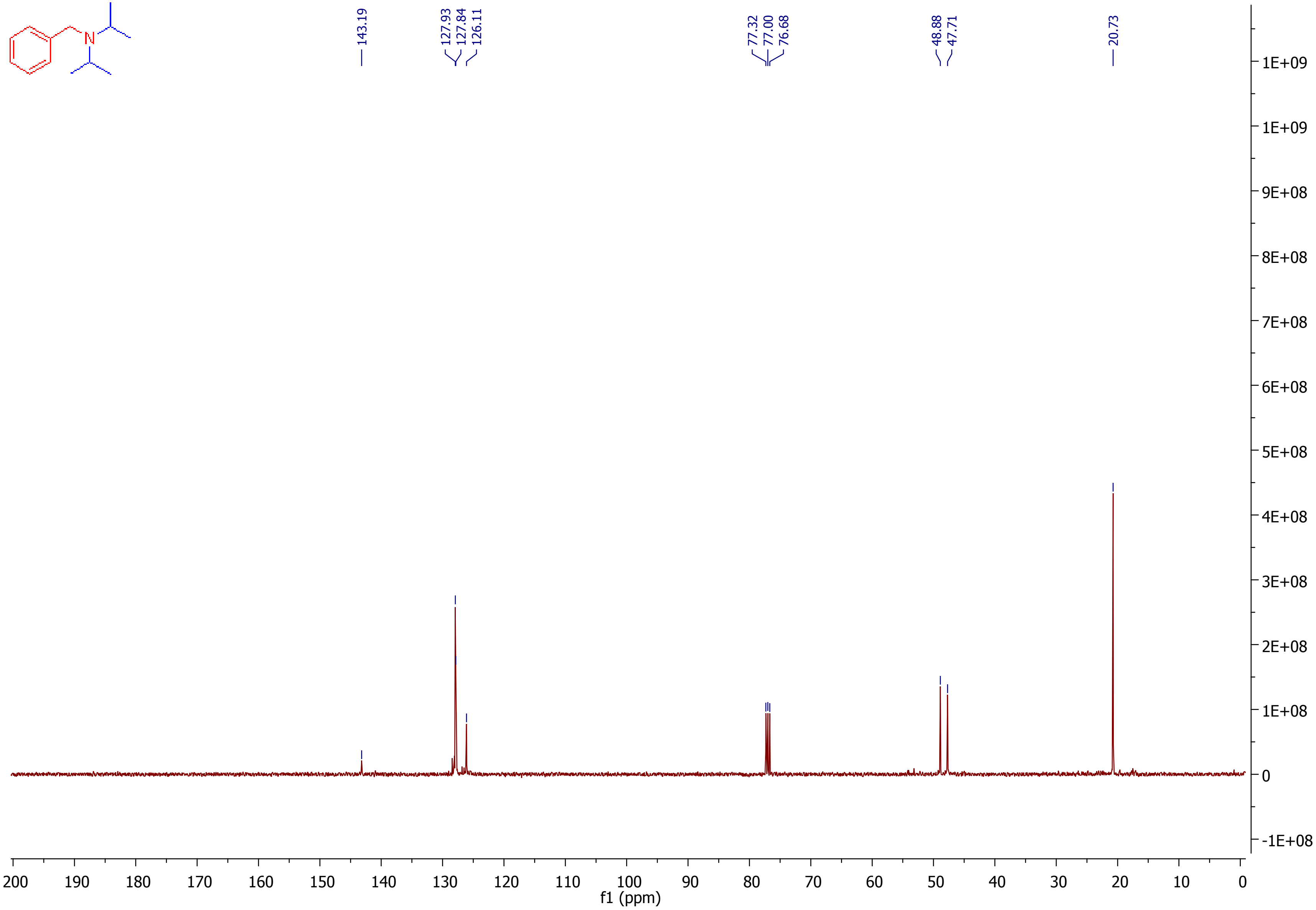
File Name	G:\IR SPECTRA\598.TXT		***Date***	11 Dec 2014 16:05:26	
Technique	Infrared	***Spectral Region*** NIR-IR	***X Axis***	Wavenumber (cm-1)	
Y Axis	Arbitrary	***Spectrum Range*** 349.1309 - 5000.6699		***Points Count***	4824
Data Spacing	0.9644				



No	cm-1	Arbitrary	Intensity
1	1193.99	19.617	W
2	1249.93	18.201	W
3	1288.50	18.415	W
4	1324.19	29.088	M
5	1331.90	27.546	W
6	1367.59	23.601	W
7	1383.98	31.910	M
8	1444.75	25.137	W
9	1493.93	23.049	W
10	1507.43	34.822	M
11	1575.91	26.945	W
12	1600.99	22.797	W
13	1717.68	18.112	W
14	2873.09	36.999	M
15	2912.64	33.288	M
16	2932.89	27.562	W
17	2971.47	22.642	W
18	3030.30	65.926	S
19	3078.52	70.259	S

N-benzyl-N-isopropylpropan-2-amine (1d)





143.19
127.93
127.84
126.11
77.32
77.00
76.68
48.88
47.71
20.73
N
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

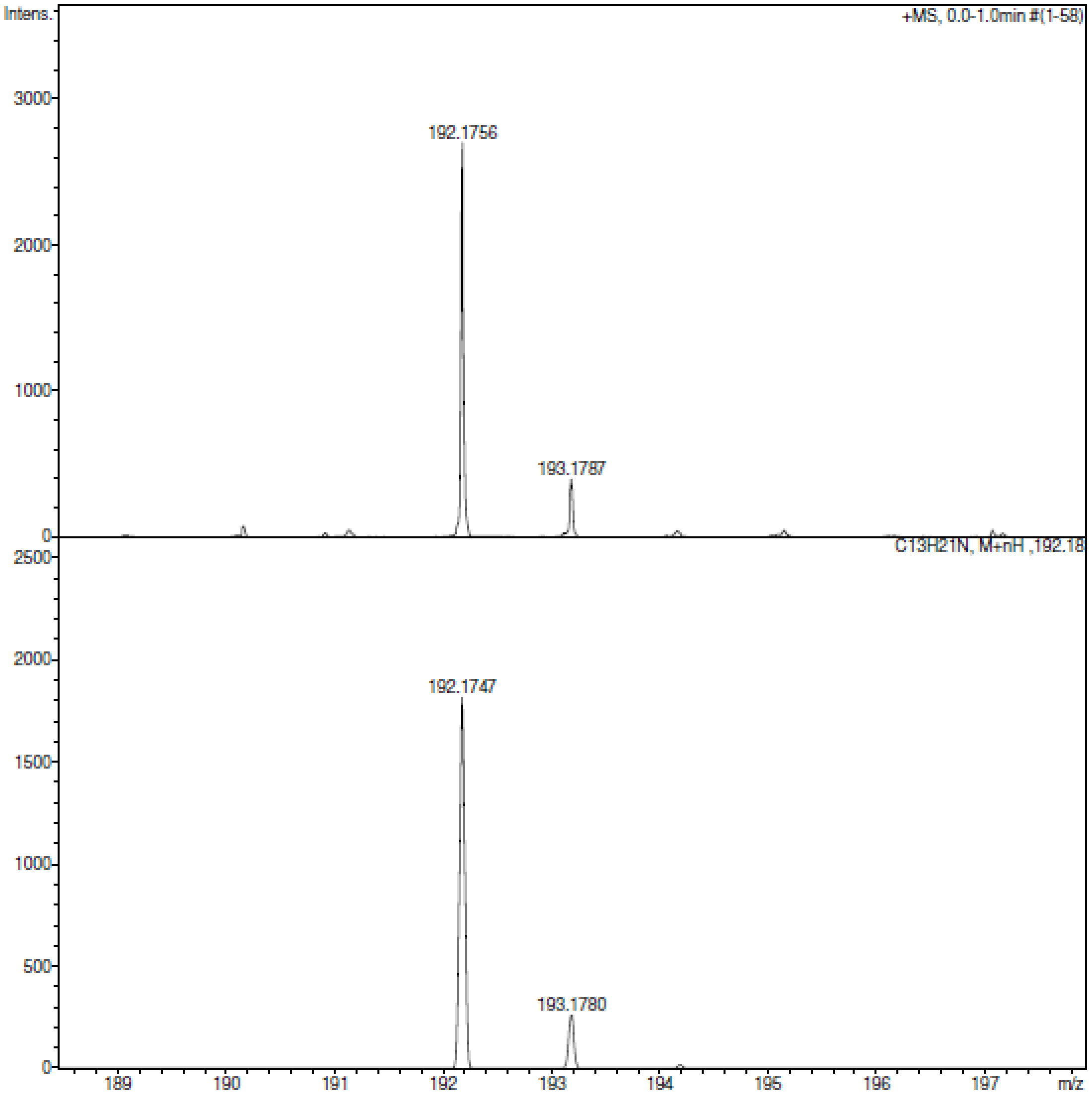
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113010.d	Acquisition Date	13.11.2014 12:37:26
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-344	Instrument / Ser#	micrOTOF 10248
Comment	C13H21N mw 191 calibrant added		

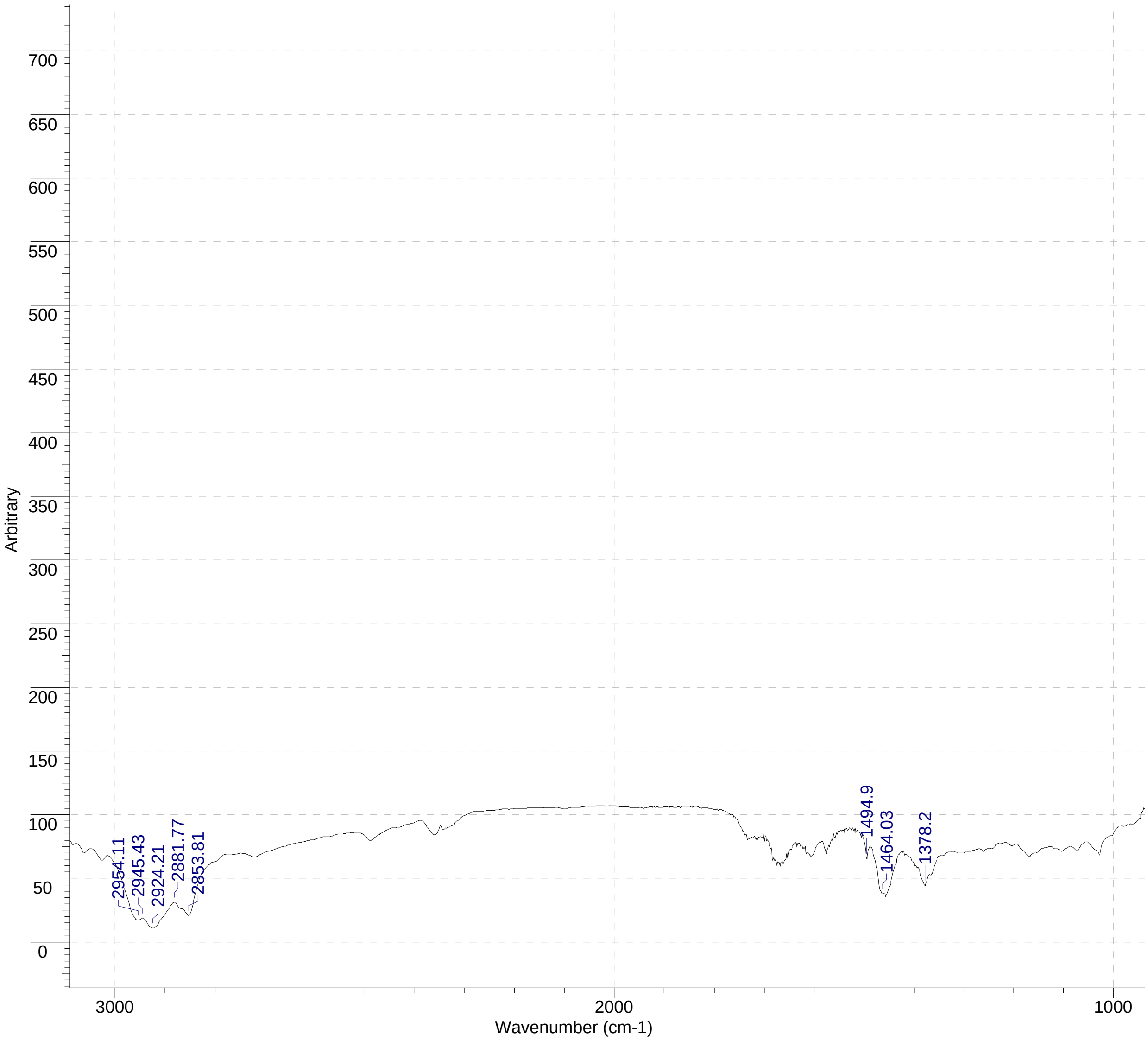
Acquisition Parameter

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



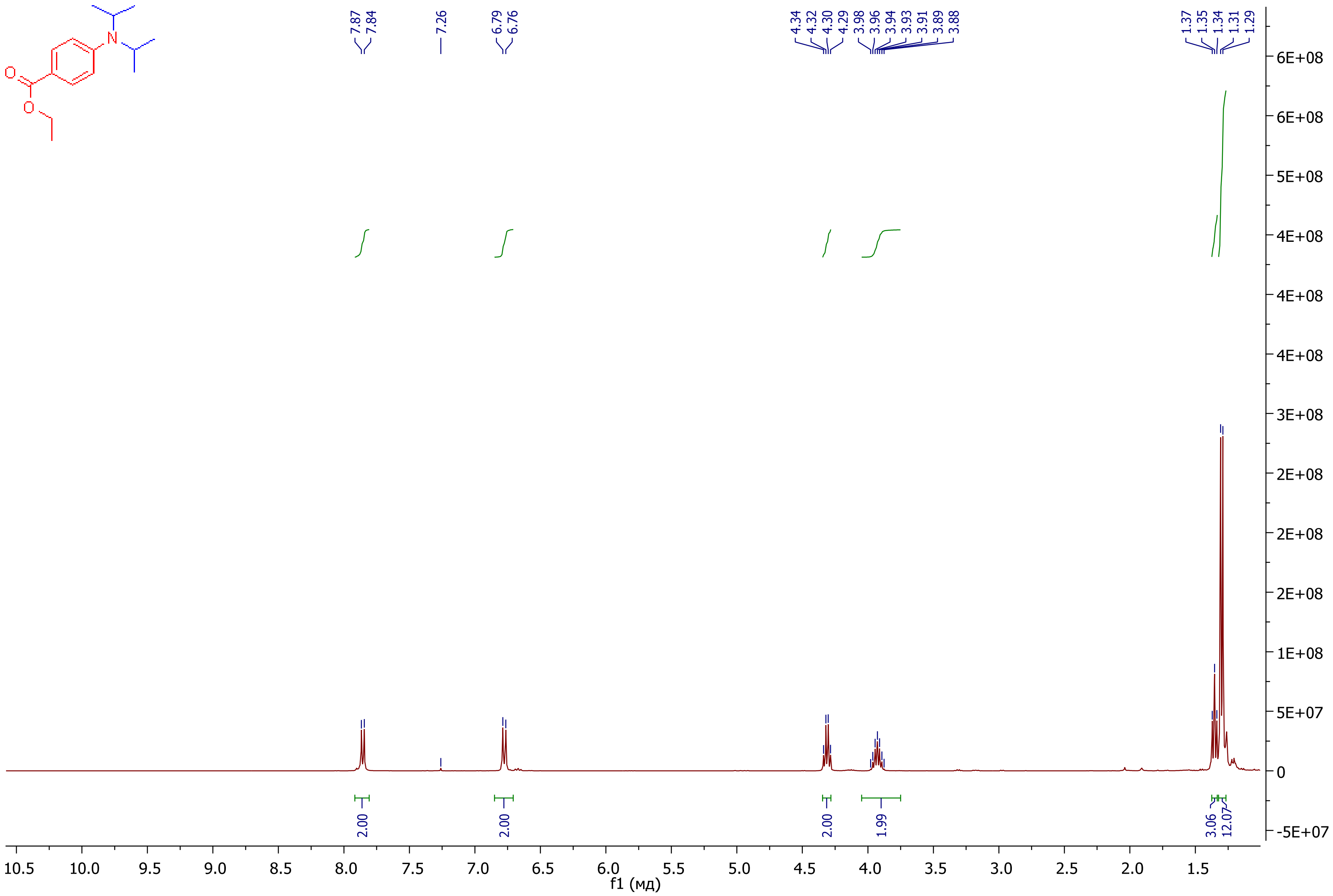
29 Jul 2015

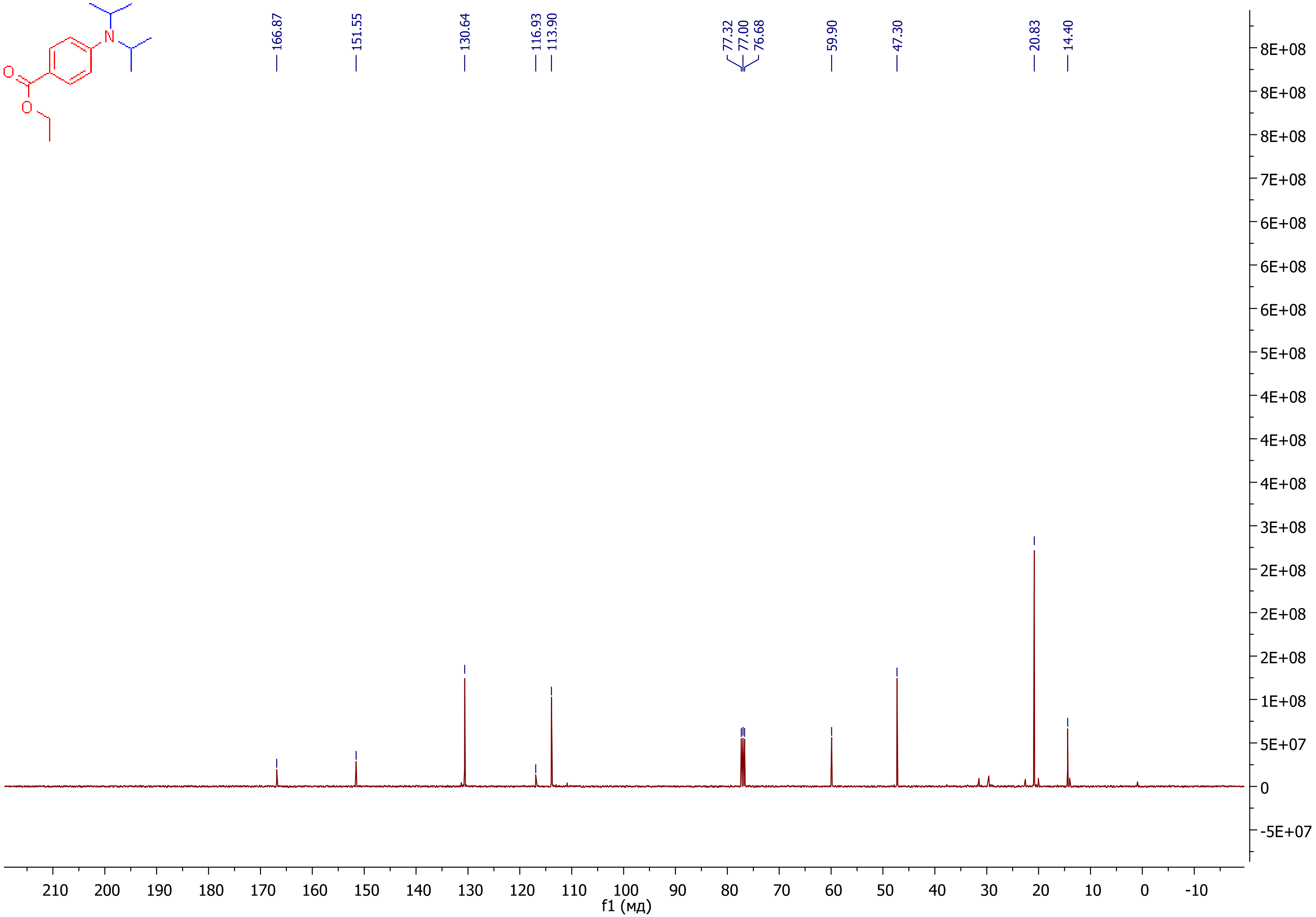
File Name	G:\IR SPECTRA\1\NY-344.TXT			***Date***	16 Dec 2014 12:59:06
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



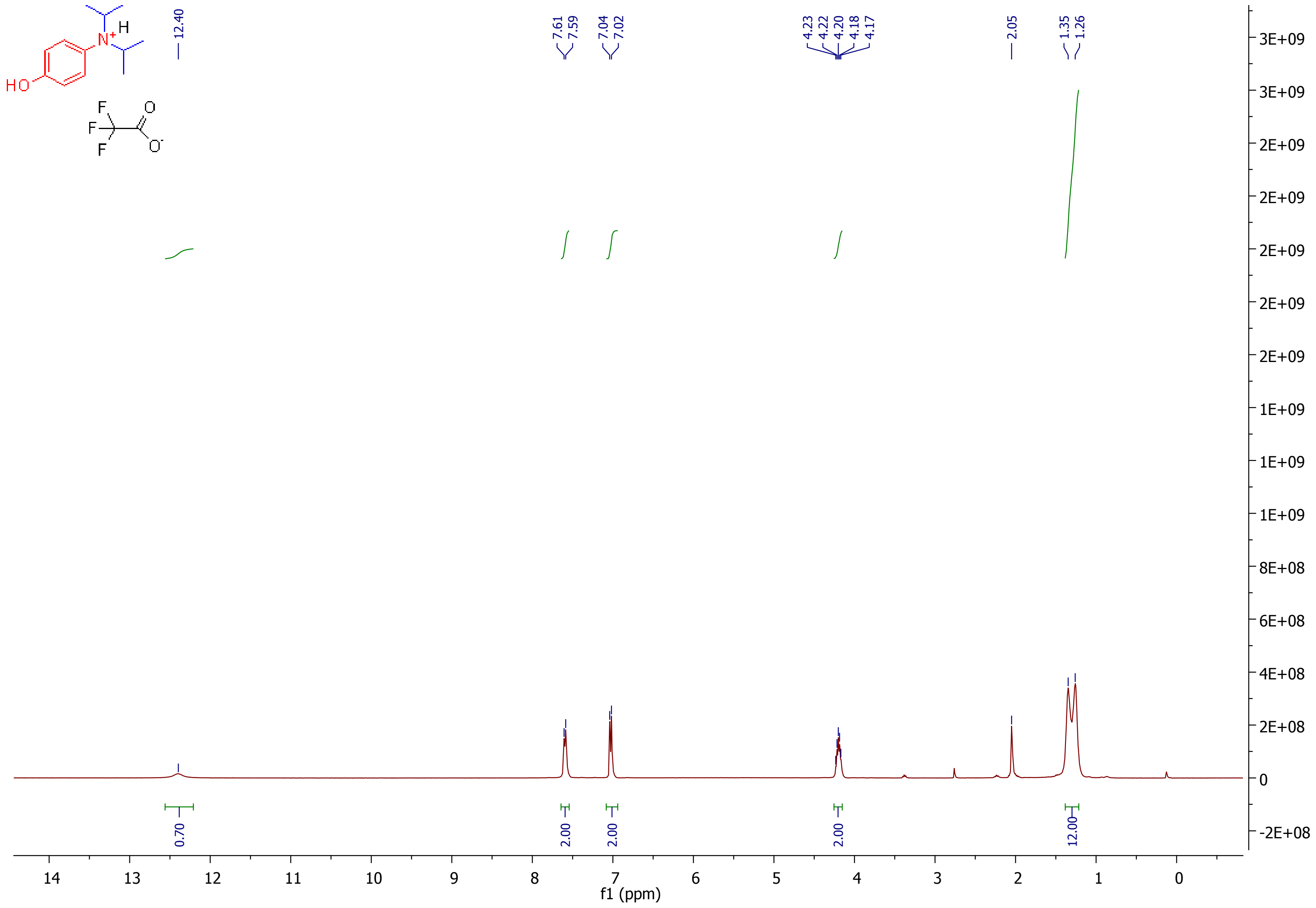
No	cm-1	Arbitrary	Intensity
1	1378.20	44.253	VW
2	1464.03	37.944	VW
3	1494.90	65.278	VW
4	2853.81	20.967	VW
5	2881.77	31.252	VW
6	2924.21	11.052	VW
7	2945.43	18.686	VW
8	2954.11	17.243	VW

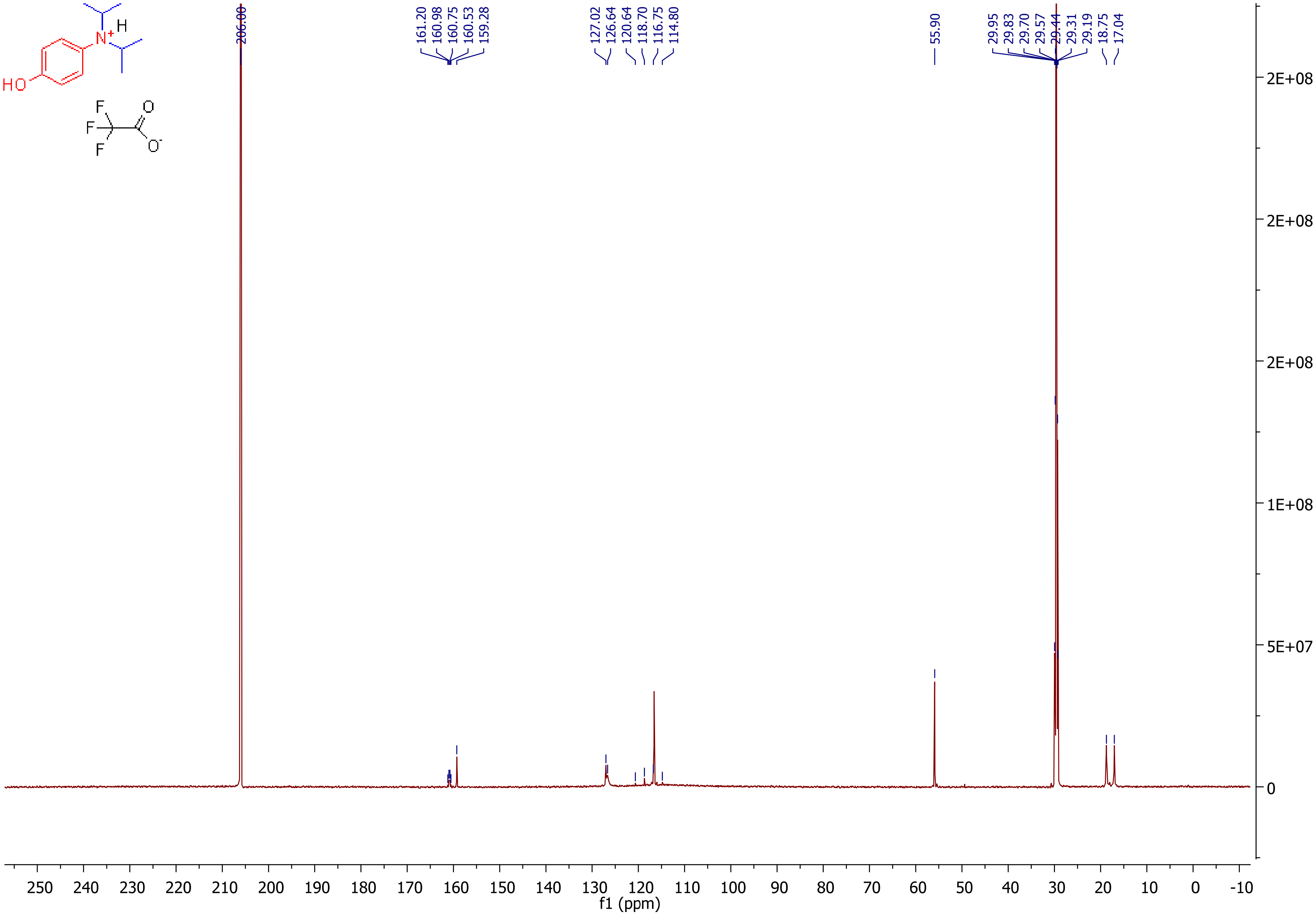
ethyl 4-(diisopropylamino)benzoate (1e)

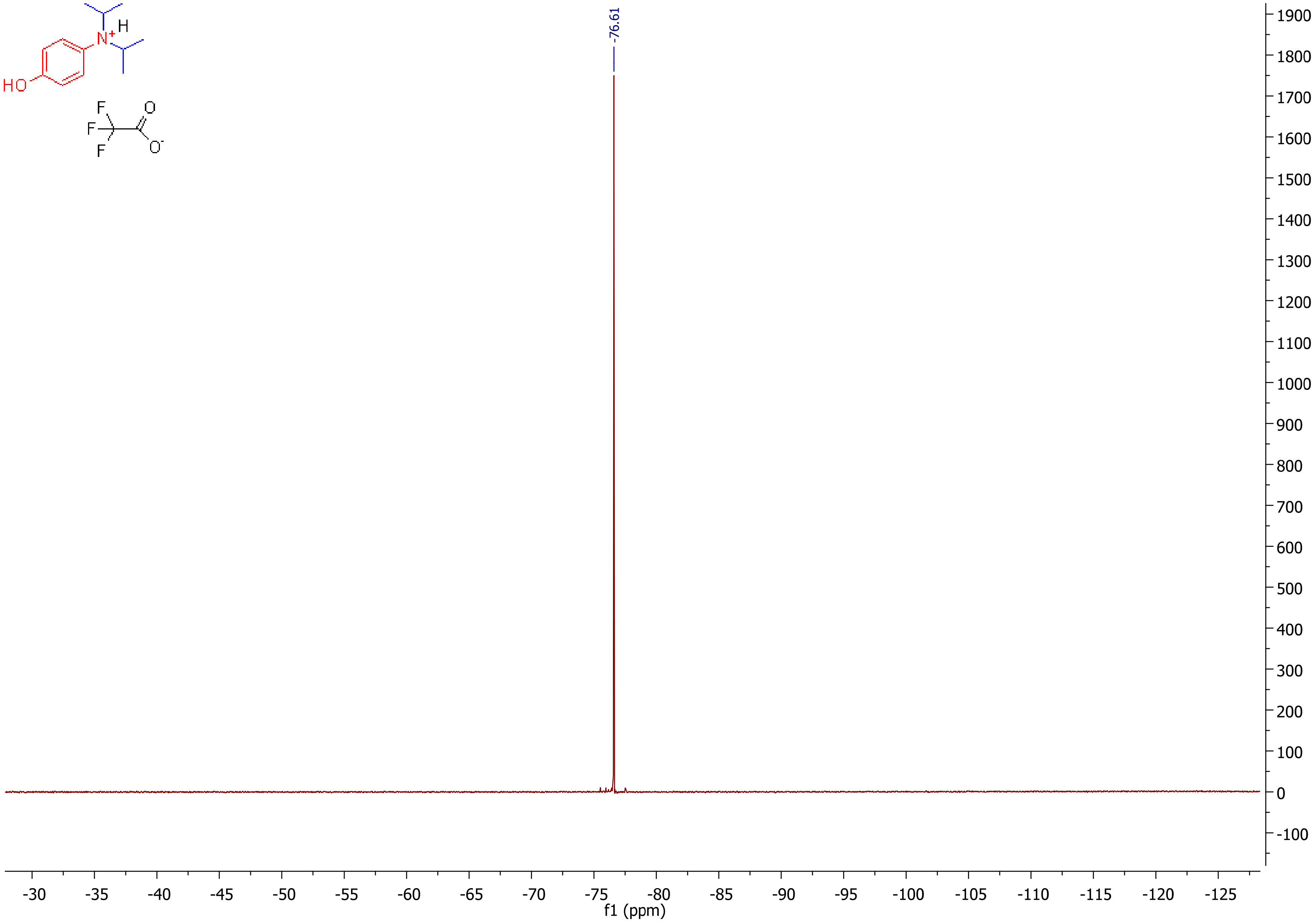



166.87
151.55
130.64
116.93
113.90
77.32
77.00
76.68
59.90
47.30
20.83
14.40
O
O
N
8E+08
8E+08
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (мд)

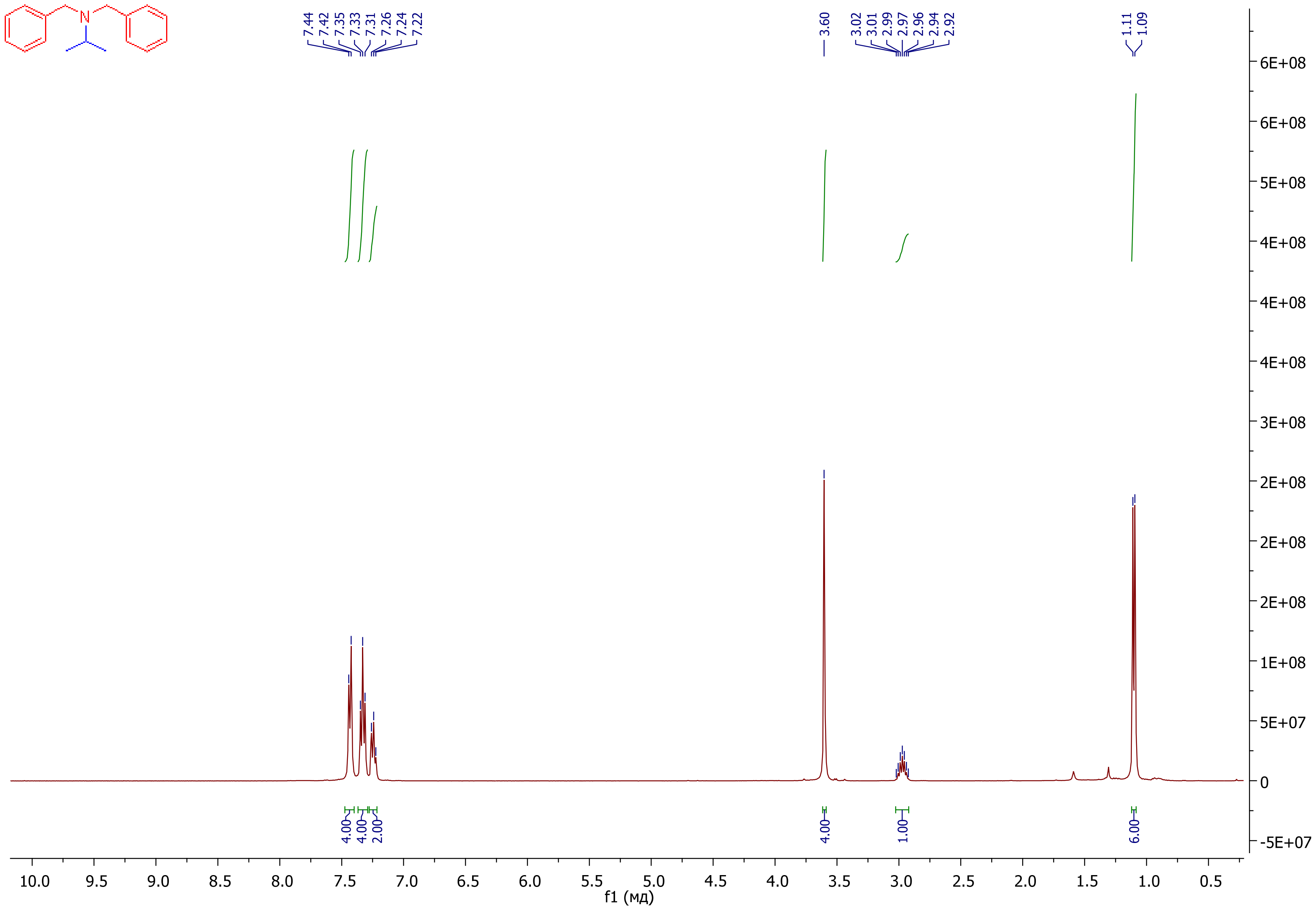
4-hydroxy-*N*,*N*-diisopropylbenzenaminium 2,2,2-trifluoroacetate (1f).

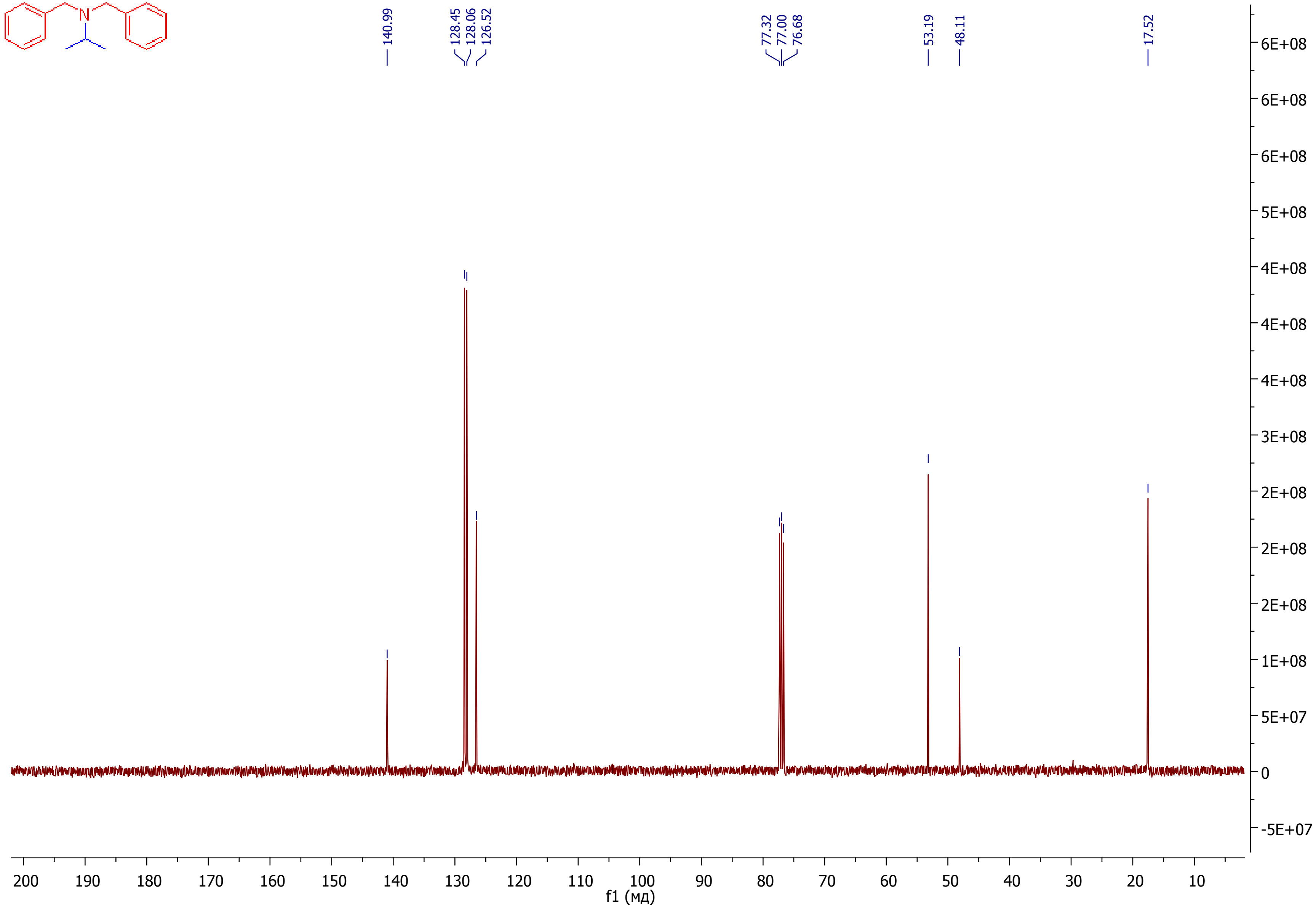



HO
N+
H
F
F
F
O
O-
206.00
161.20
160.98
160.75
160.53
159.28
127.02
126.64
120.64
118.70
116.75
114.80
55.90
29.95
29.83
29.70
29.57
29.44
29.31
29.19
18.75
17.04
2E+08
2E+08
2E+08
1E+08
5E+07
0
250
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
N+
H
F
F
F
O
O-
-76.61
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
f1 (ppm)

N,*N*-dibenzylpropan-2-amine (1g)




N
140.99
128.45
128.06
126.52
77.32
77.00
76.68
53.19
48.11
17.52
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)

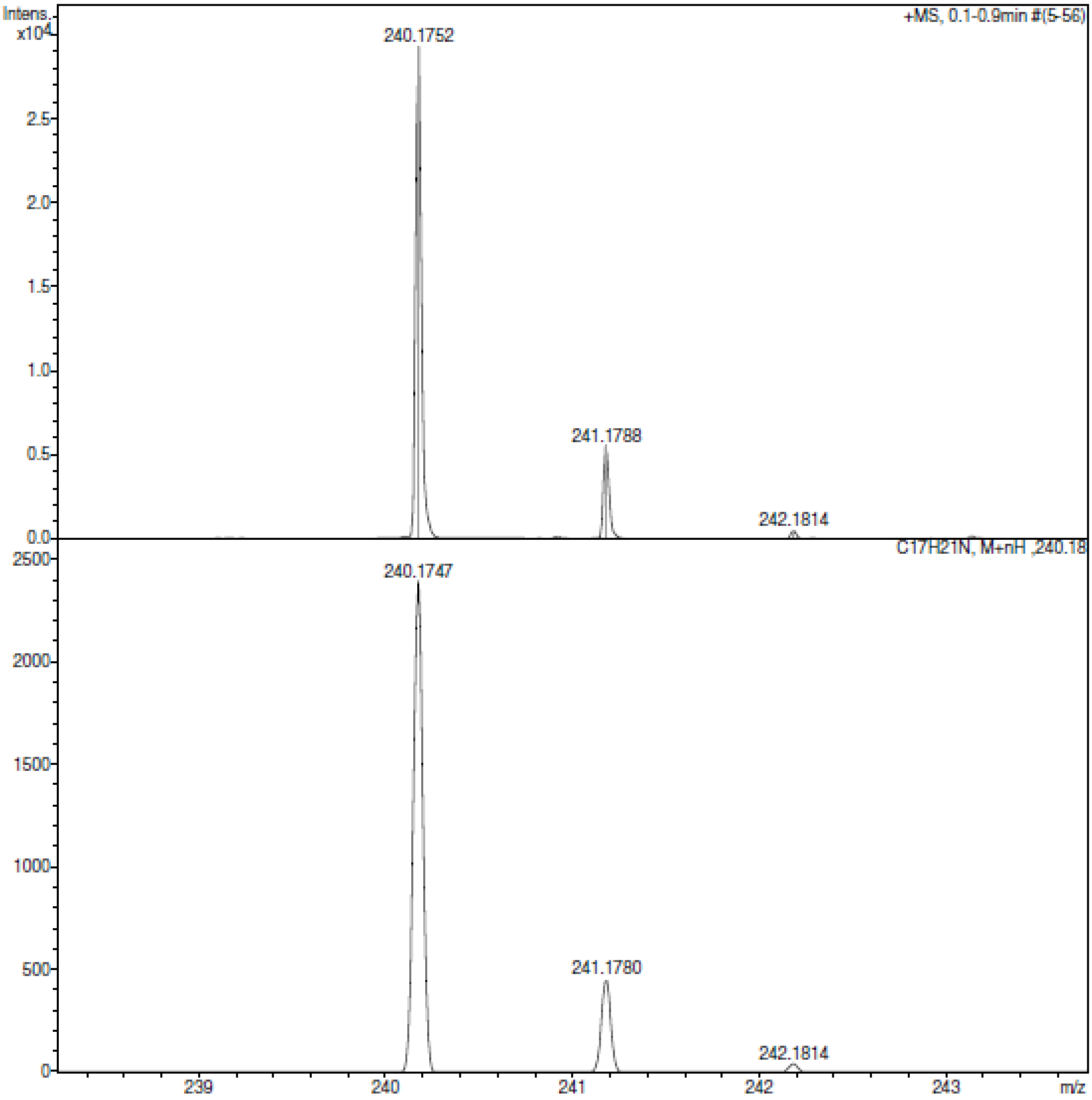
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1112028.d	Acquisition Date	12.11.2014 17:45:35
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-313	Instrument / Ser#	micrOTOF 10248
Comment	C17H21N mw 239 calibrant added		

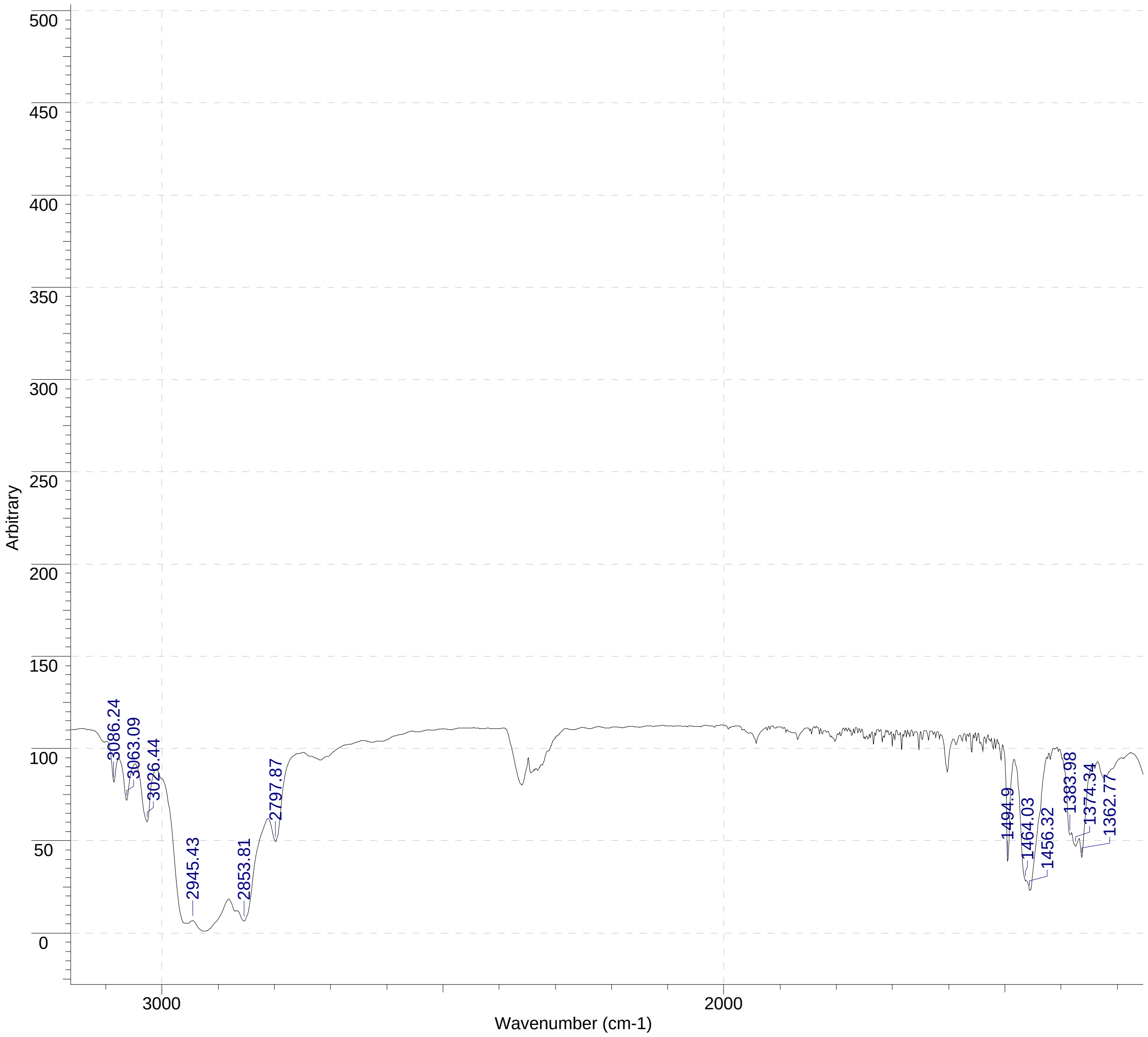
Acquisition Parameter

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



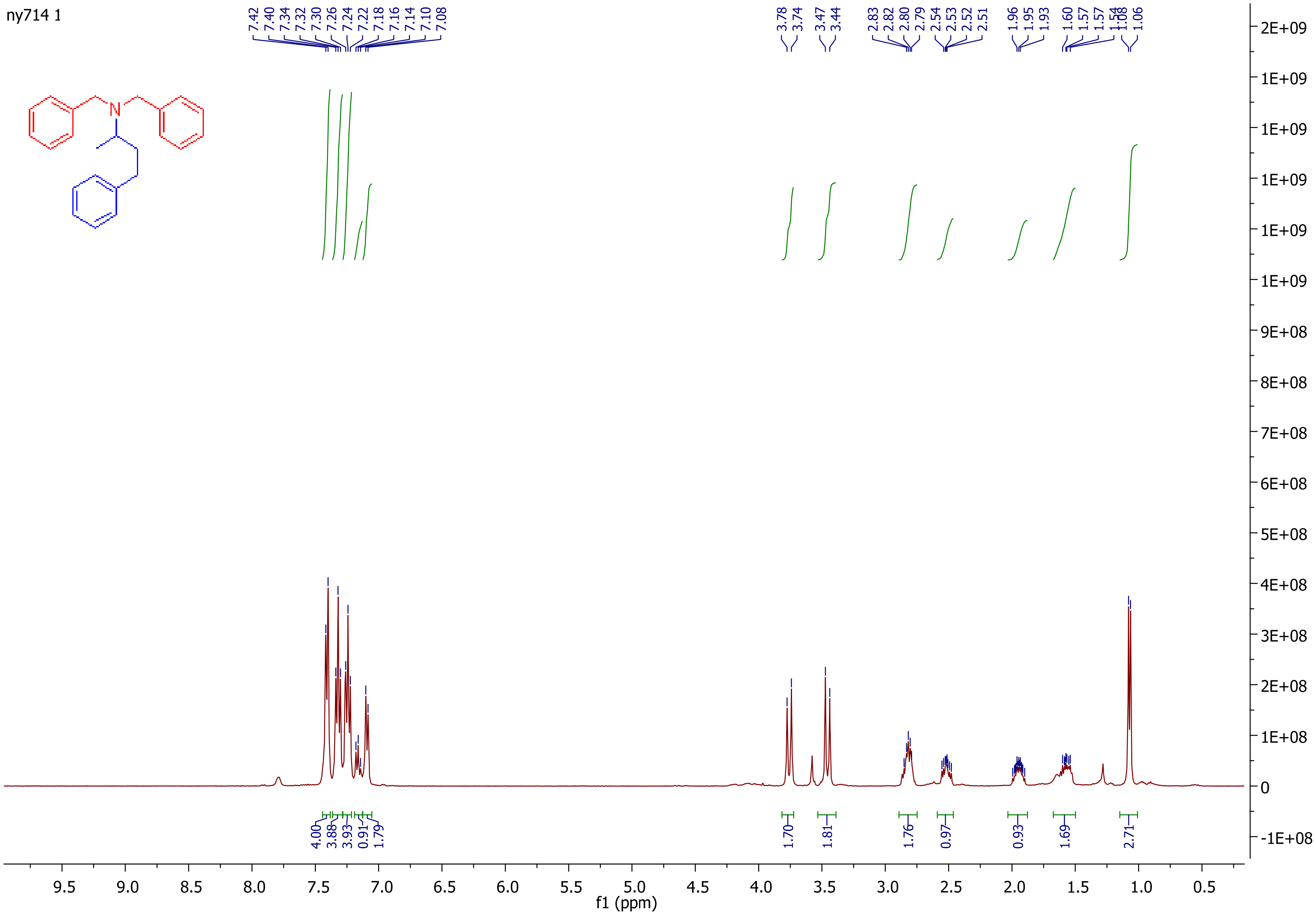
29 Jul 2015

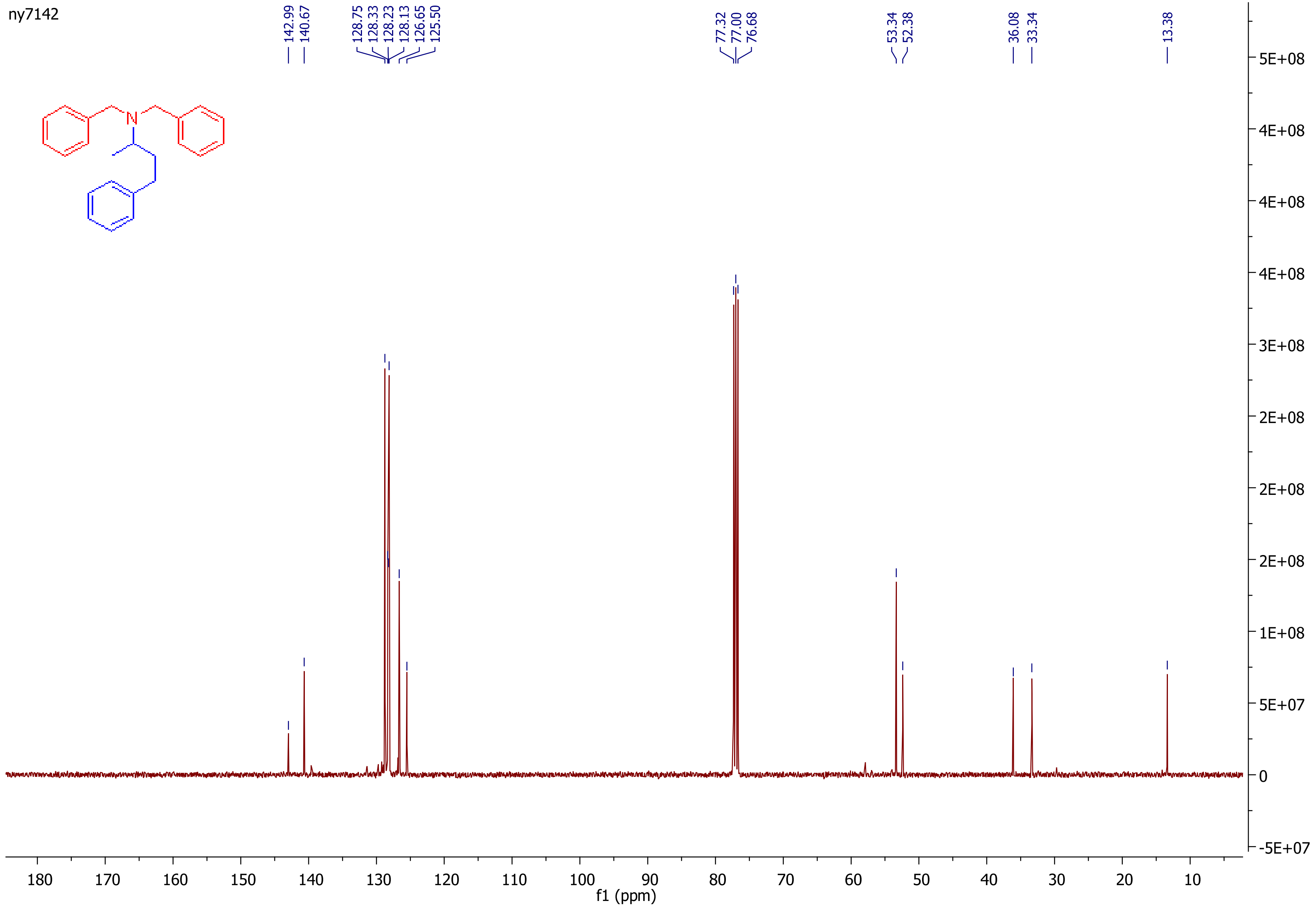
File Name	G:\IR SPECTRA\1\NY-313.TXT			***Date***	16 Dec 2014 12:58:08
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1362.77	40.946	VW
2	1374.34	47.154	VW
3	1383.98	53.176	VW
4	1456.32	23.267	VW
5	1464.03	28.315	VW
6	1494.90	39.213	VW
7	2797.87	49.450	VW
8	2853.81	6.503	VW
9	2945.43	6.670	VW
10	3026.44	60.319	VW
11	3063.09	71.942	VW
12	3086.24	81.931	VW

N,*N*-dibenzyl-4-phenylbutan-2-amine (1h)




ny7142
142.99
140.67
128.75
128.33
128.23
128.13
126.65
125.50
77.32
77.00
76.68
53.34
52.38
36.08
33.34
13.38
N
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

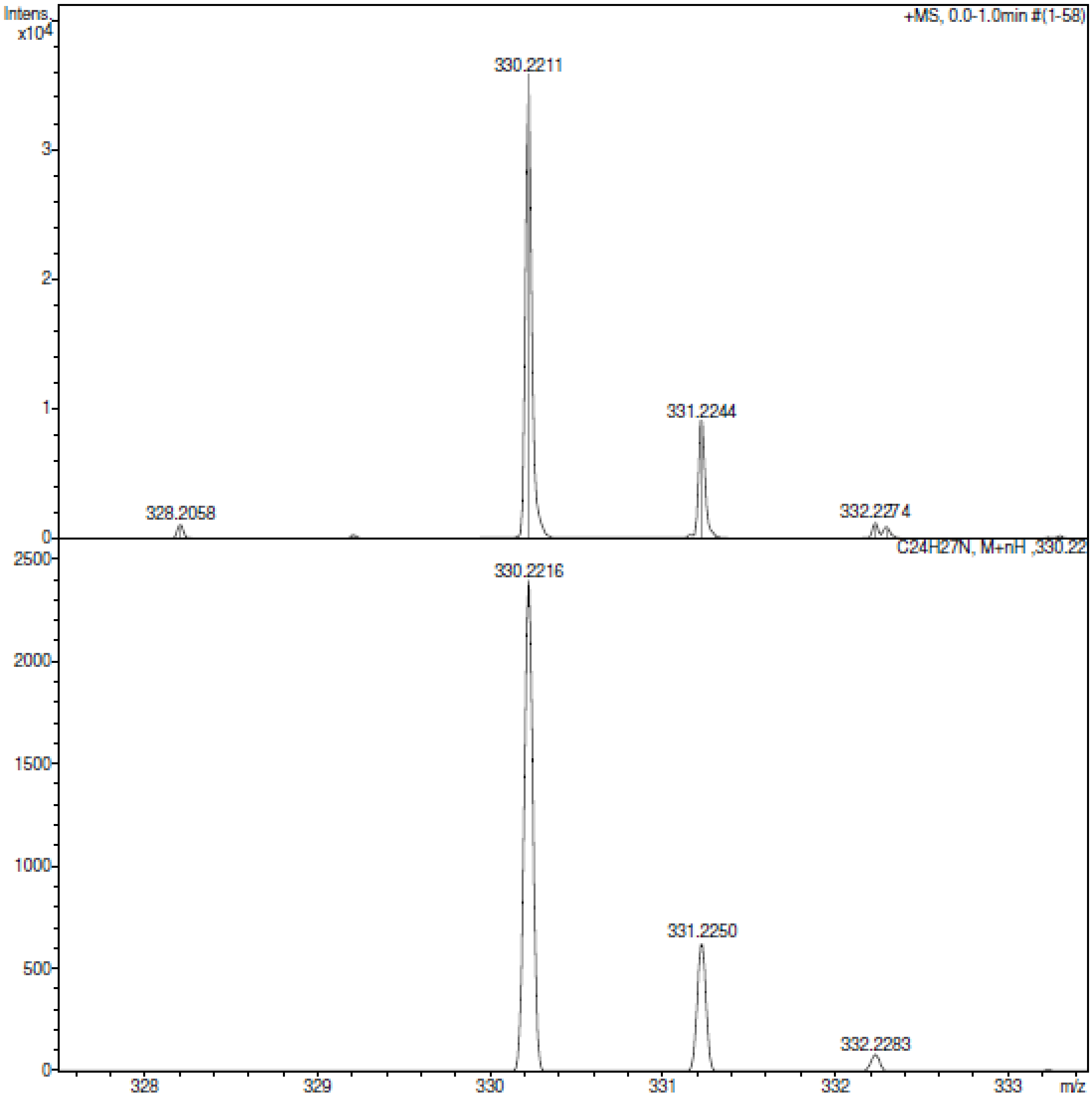
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113014.d	Acquisition Date	13.11.2014 13:13:07
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-714	Instrument / Ser#	micrOTOF 10248
Comment	C24H27N mw 329 calibrant added		

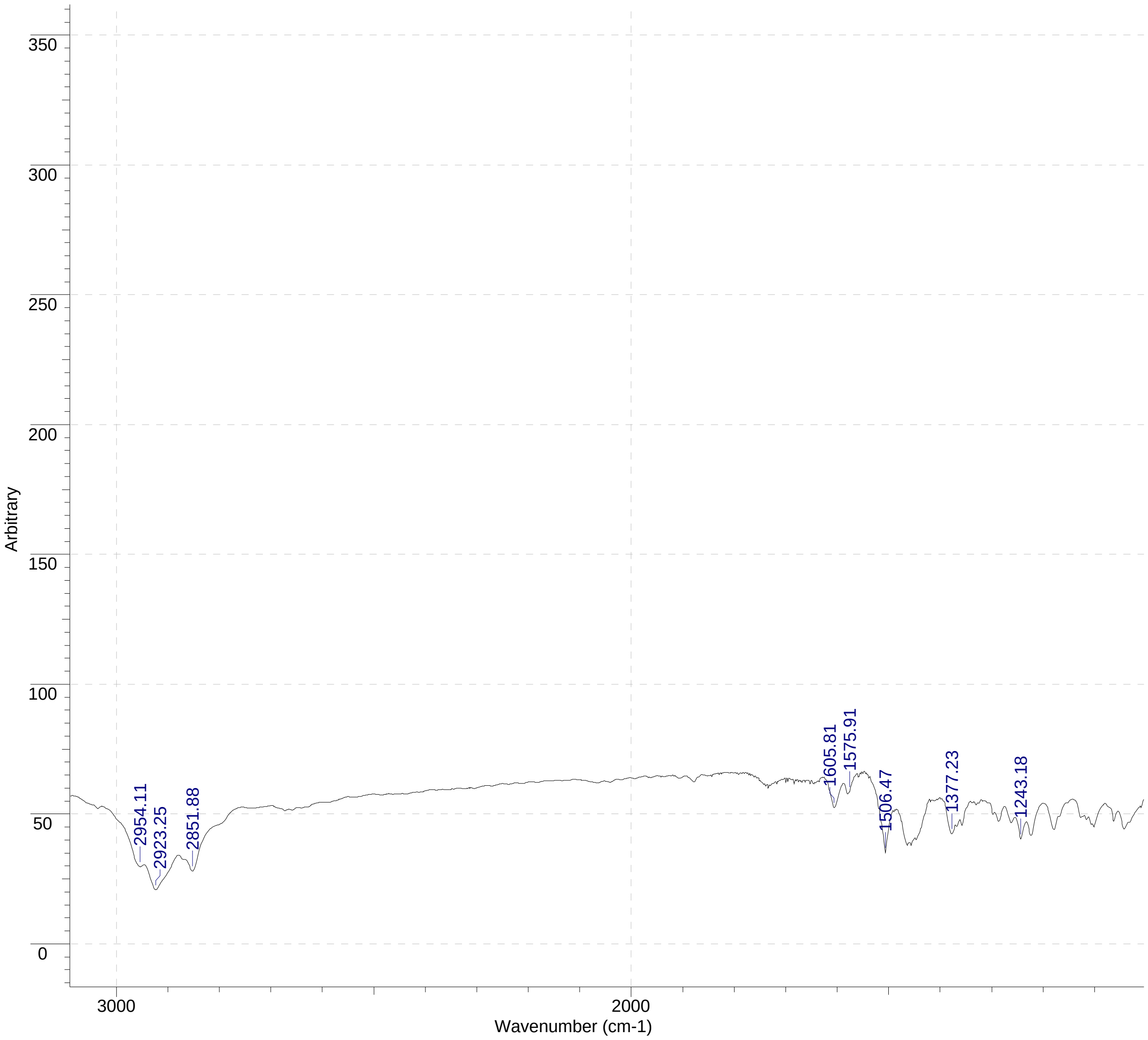
Acquisition Parameter

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



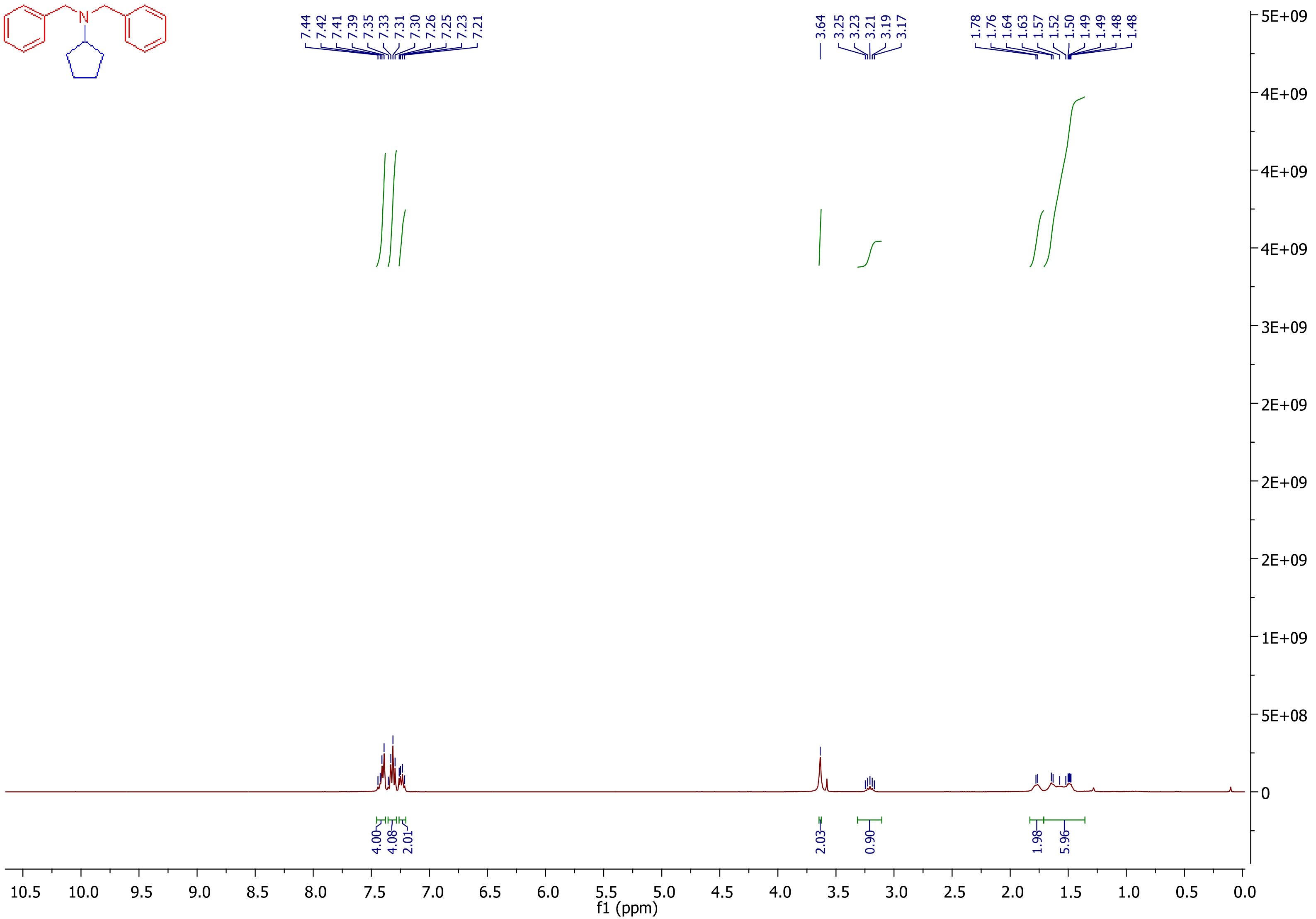
29 Jul 2015

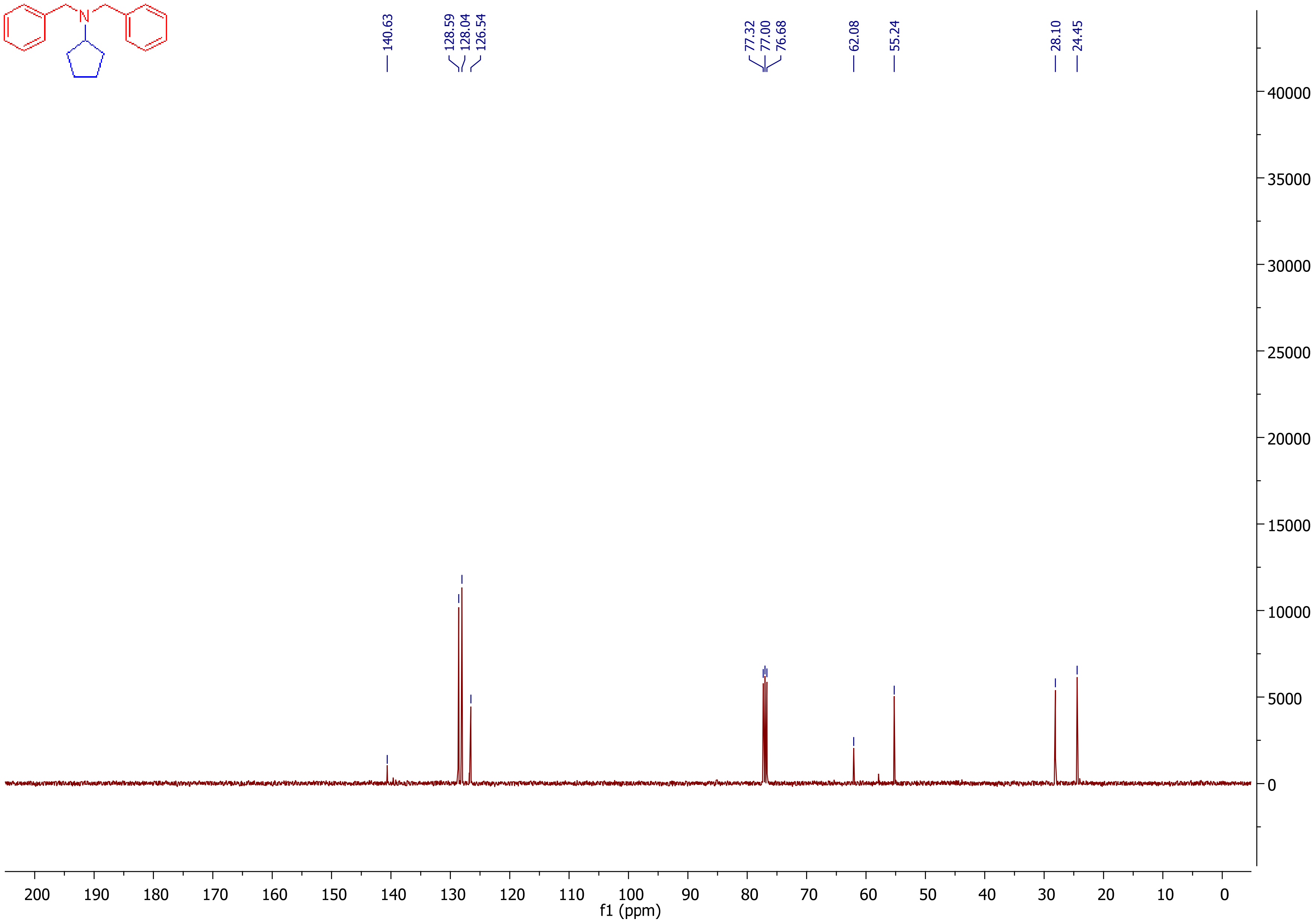
File Name	G:\IR SPECTRA\1\NY-714.TXT			***Date***	16 Dec 2014 12:59:38
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1243.18	40.425	VW
2	1377.23	42.342	VW
3	1506.47	35.142	VW
4	1575.91	58.506	VW
5	1605.81	52.500	VW
6	2851.88	28.046	VW
7	2923.25	20.883	VW
8	2954.11	29.721	VW

N,N-dibenzylcyclopentanamine (1i)




140.63
128.59
128.04
126.54
77.32
77.00
76.68
62.08
55.24
28.10
24.45
N
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

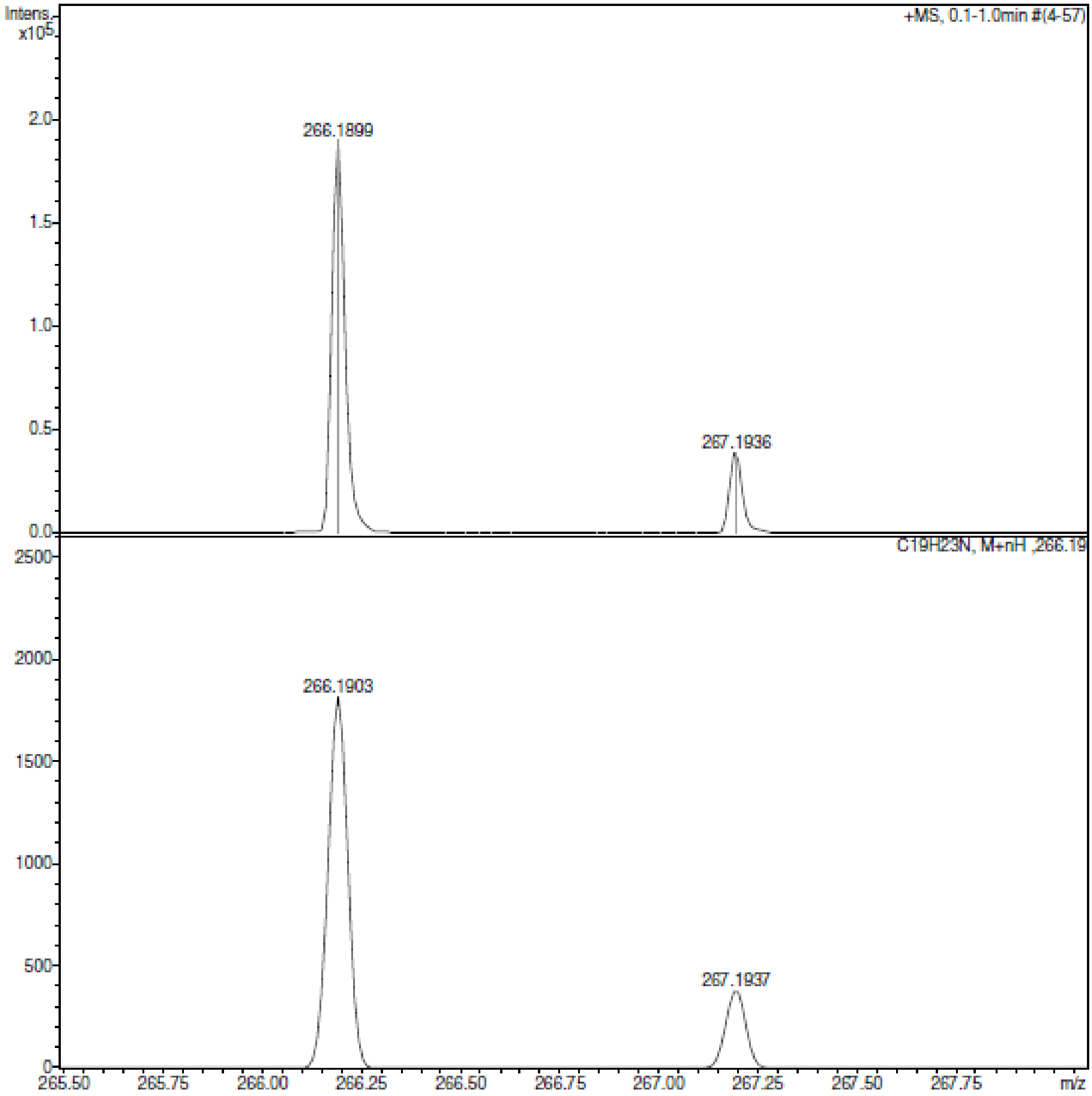
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113005.d	Acquisition Date	13.11.2014 10:06:06
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-325-1	Instrument / Ser#	micrOTOF 10248
Comment	C19H23N mw 265 calibrant added		

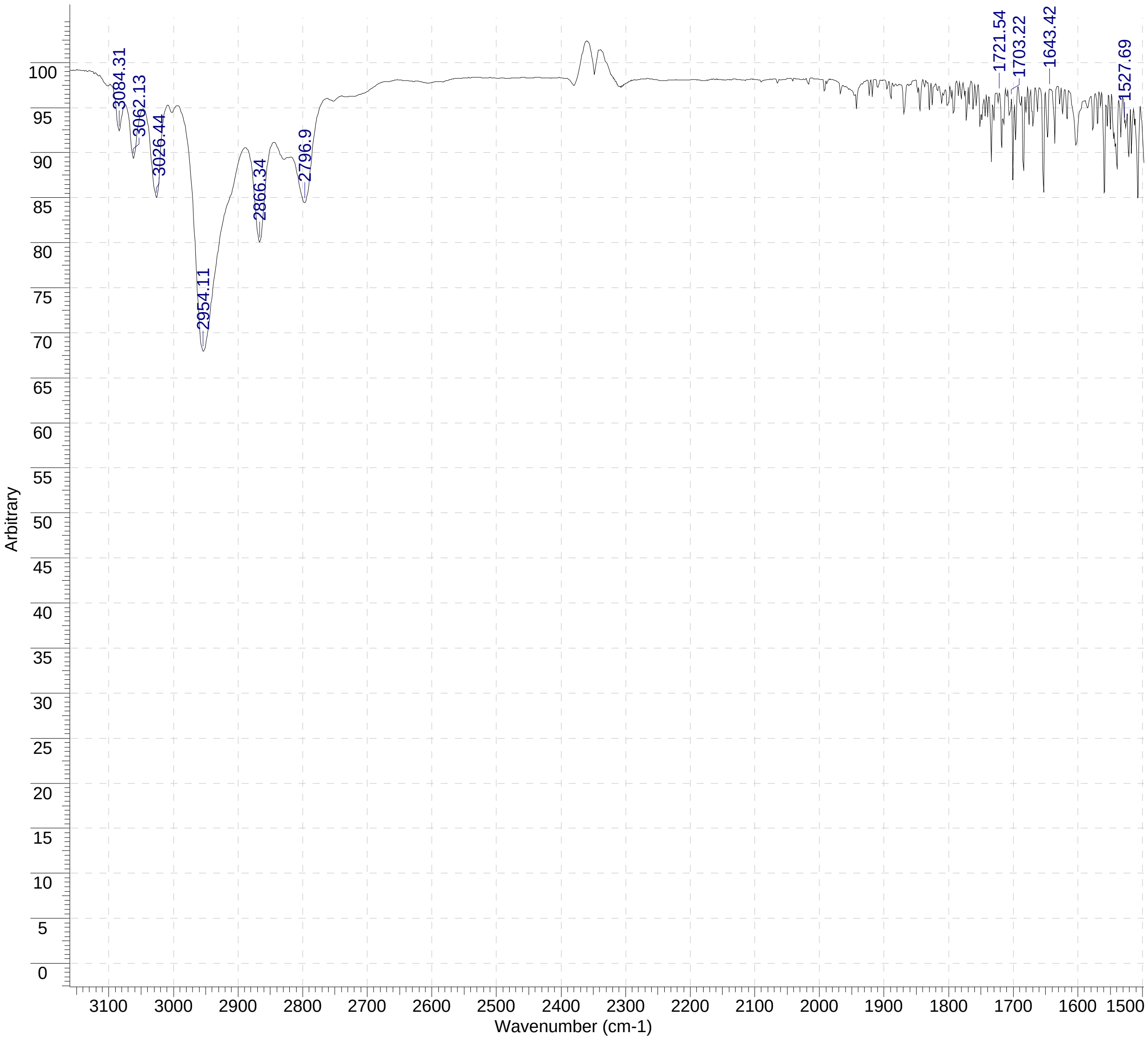
Acquisition Parameter

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



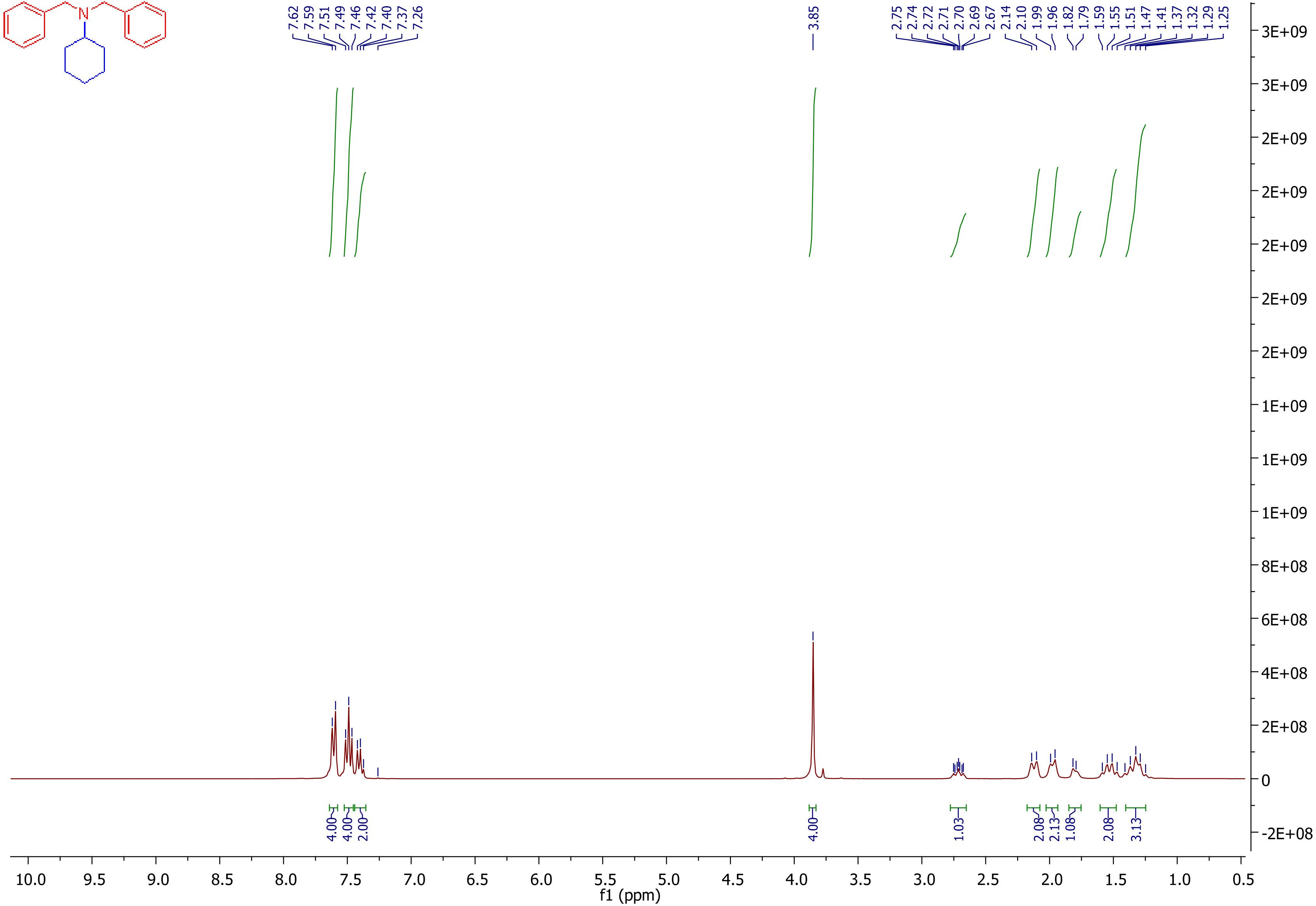
29 Jul 2015

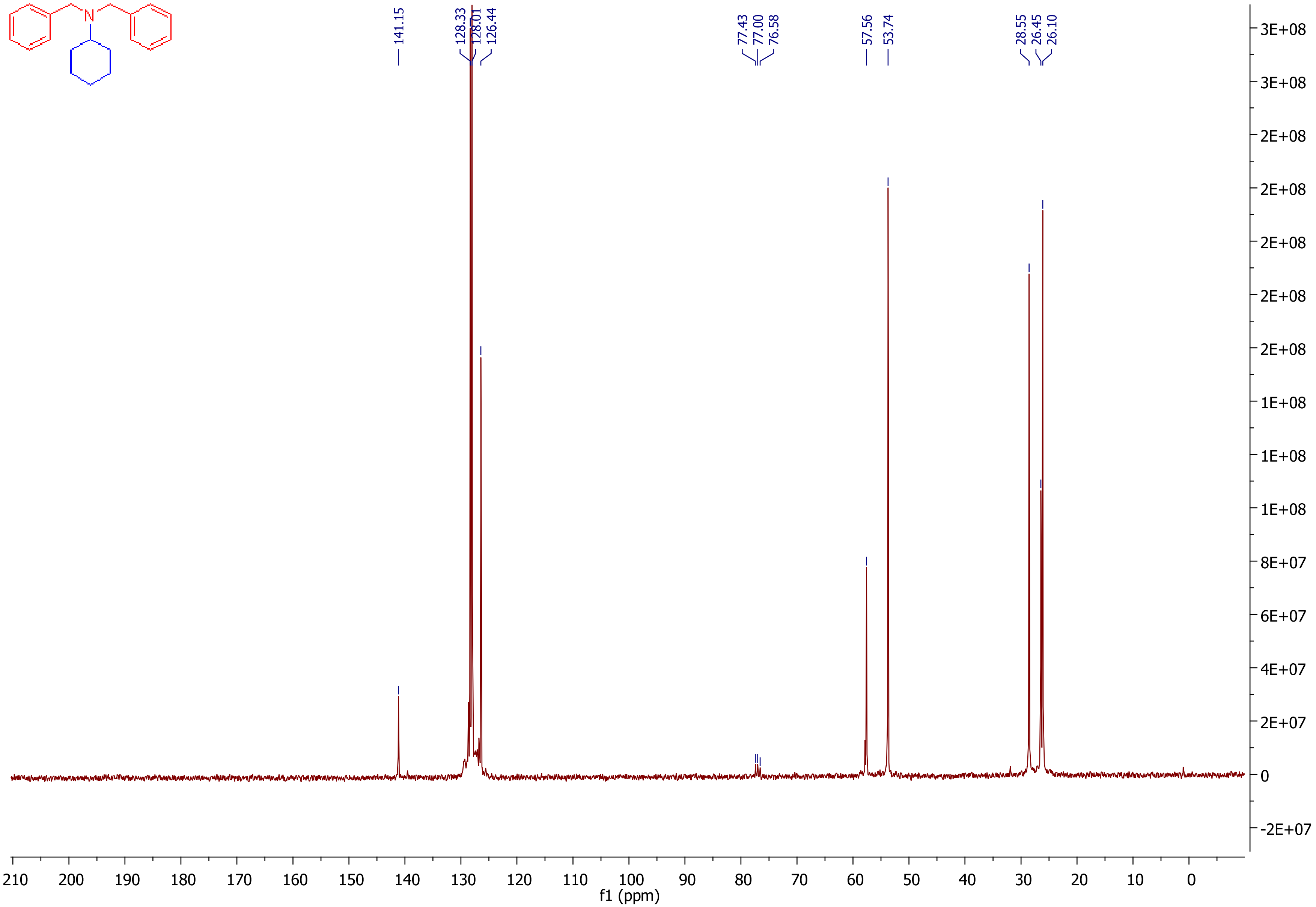
File Name	G:\IR SPECTRA\NY-325-1.TXT			***Date***	11 Dec 2014 16:06:24
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1527.69	93.349	VS
2	1643.42	97.089	VS
3	1703.22	95.986	VS
4	1721.54	96.612	VS
5	2796.90	84.448	S
6	2866.34	80.086	S
7	2954.11	67.940	S
8	3026.44	85.044	S
9	3062.13	89.401	S
10	3084.31	92.434	VS

***N*,*N*-dibenzylcyclohexanamine (1j)**




N
141.15
128.33
128.01
126.44
77.43
77.00
76.58
57.56
53.74
28.55
26.45
26.10
3E+08
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

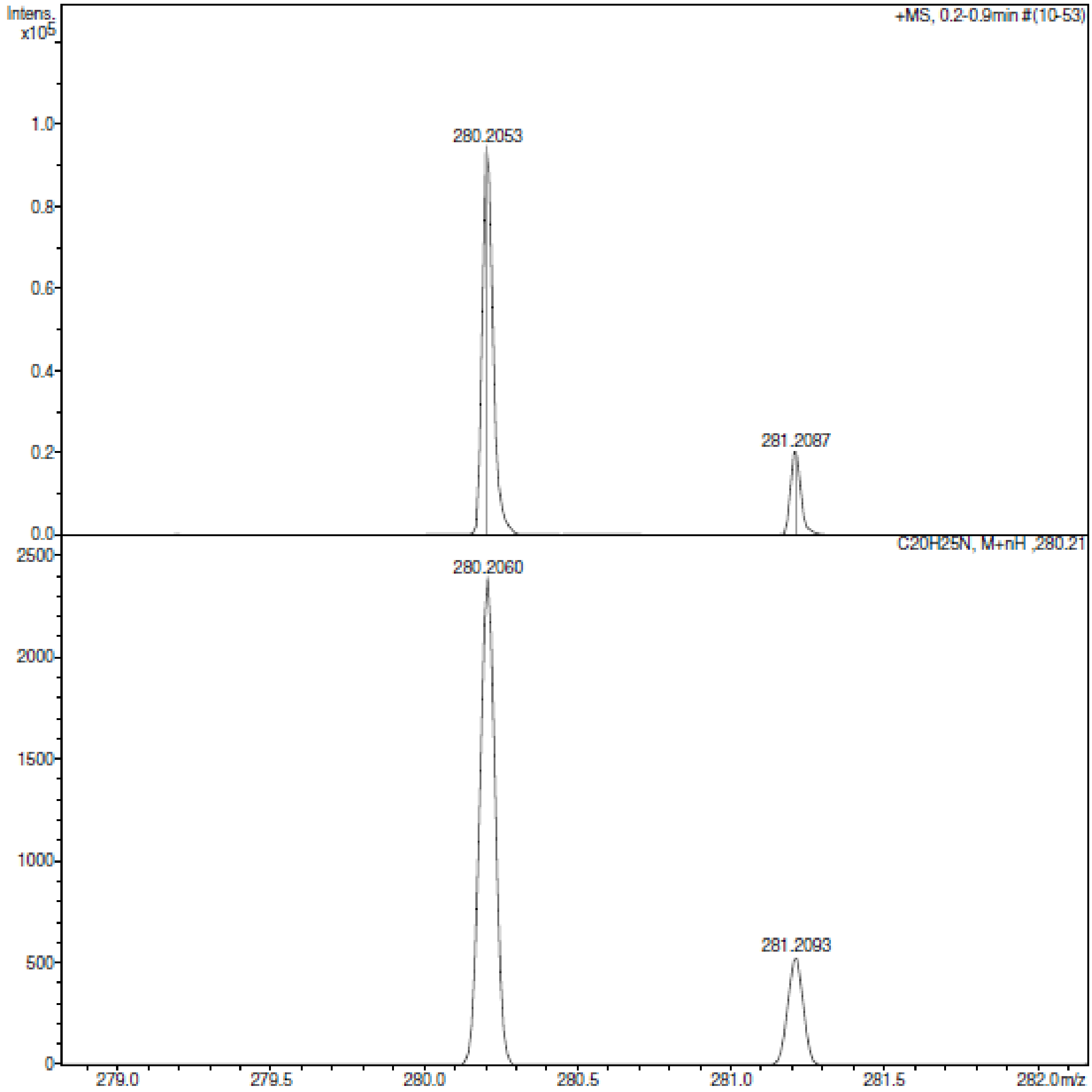
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113003.d	Acquisition Date	13.11.2014 9:50:16
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-324-1	Instrument / Ser#	micrOTOF 10248
Comment	C20H25N mw 279 calibrant added		

Acquisition Parameter

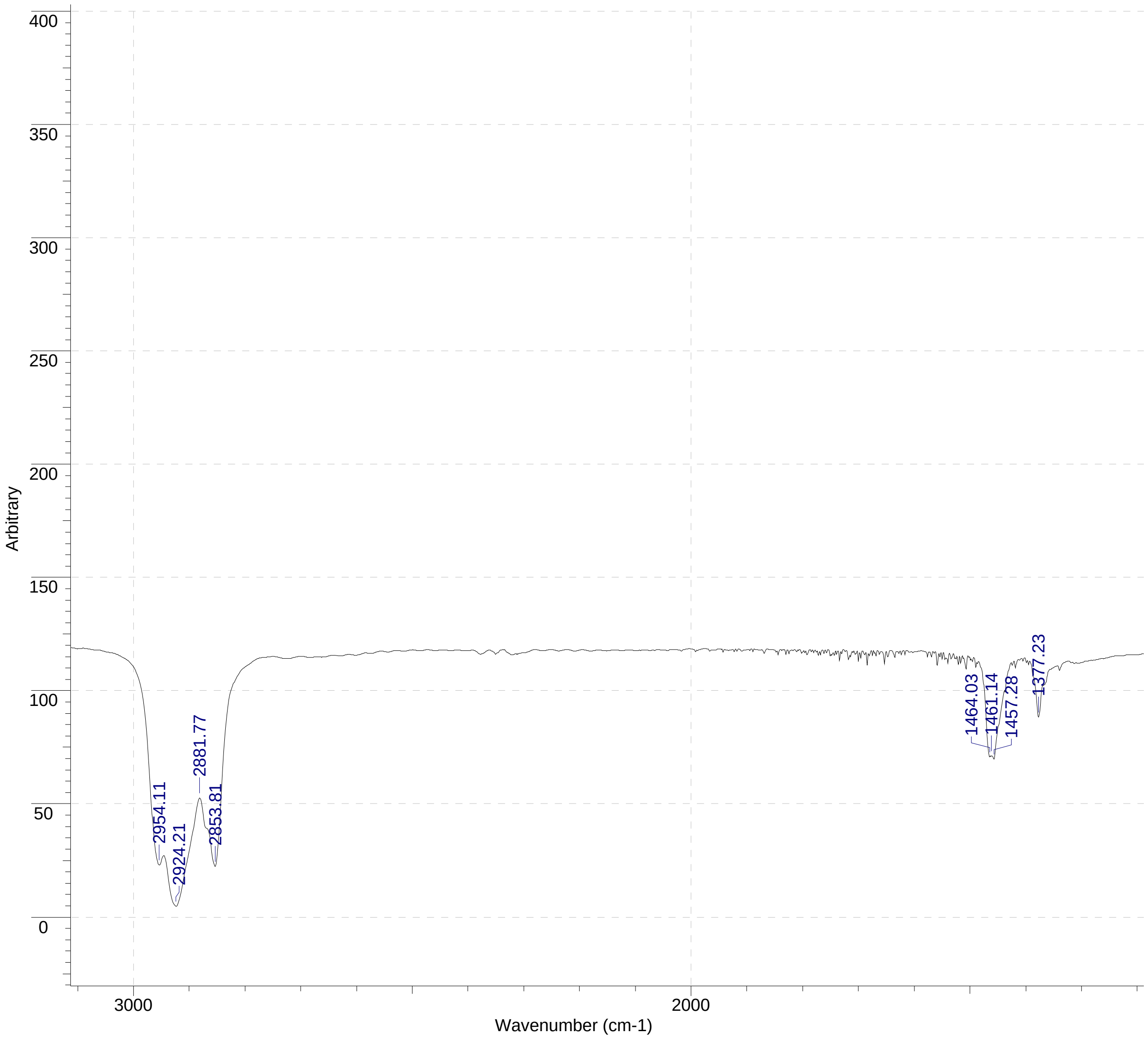
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 13.11.2014 9:53:49 Page 1 of 1

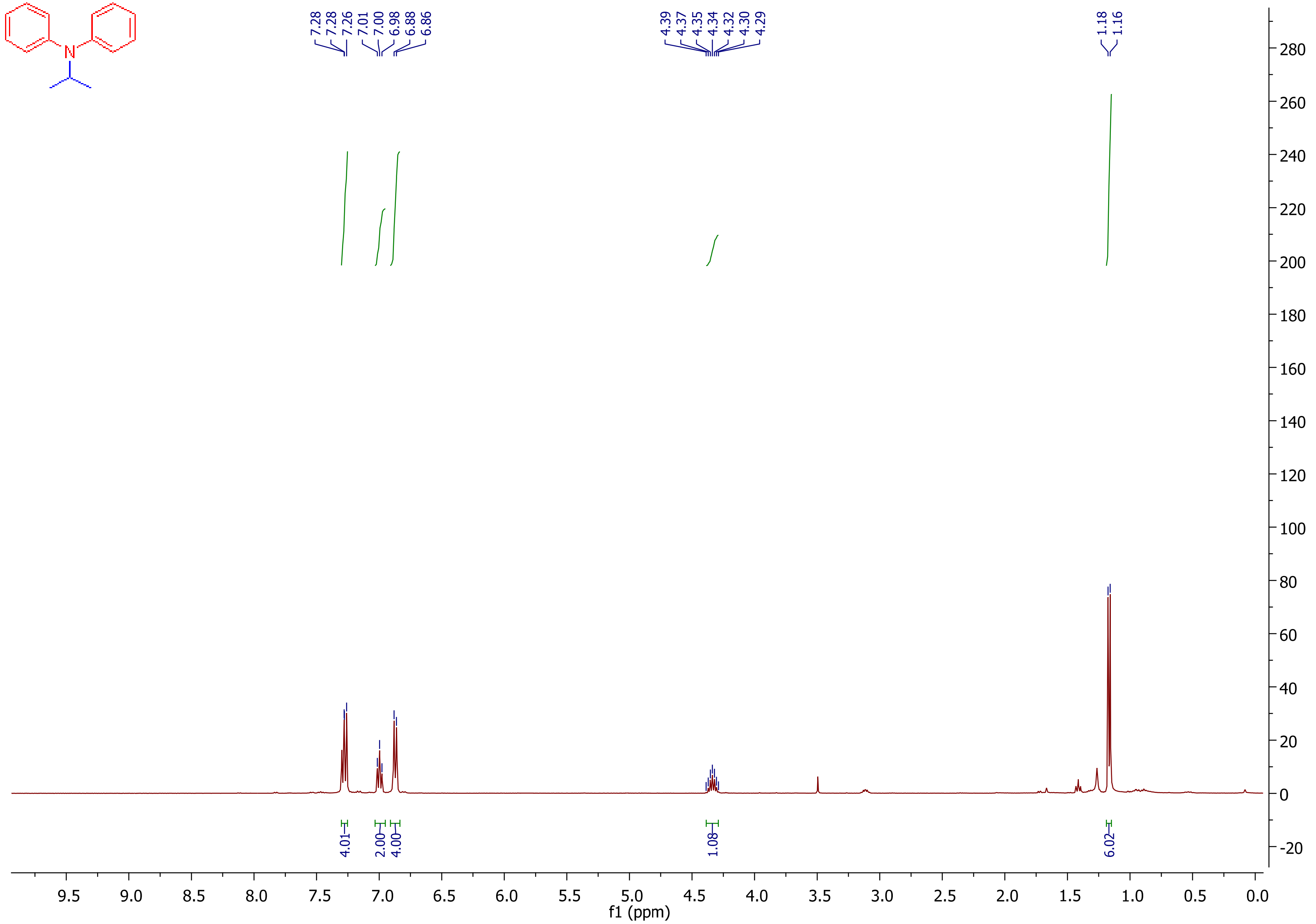
29 Jul 2015

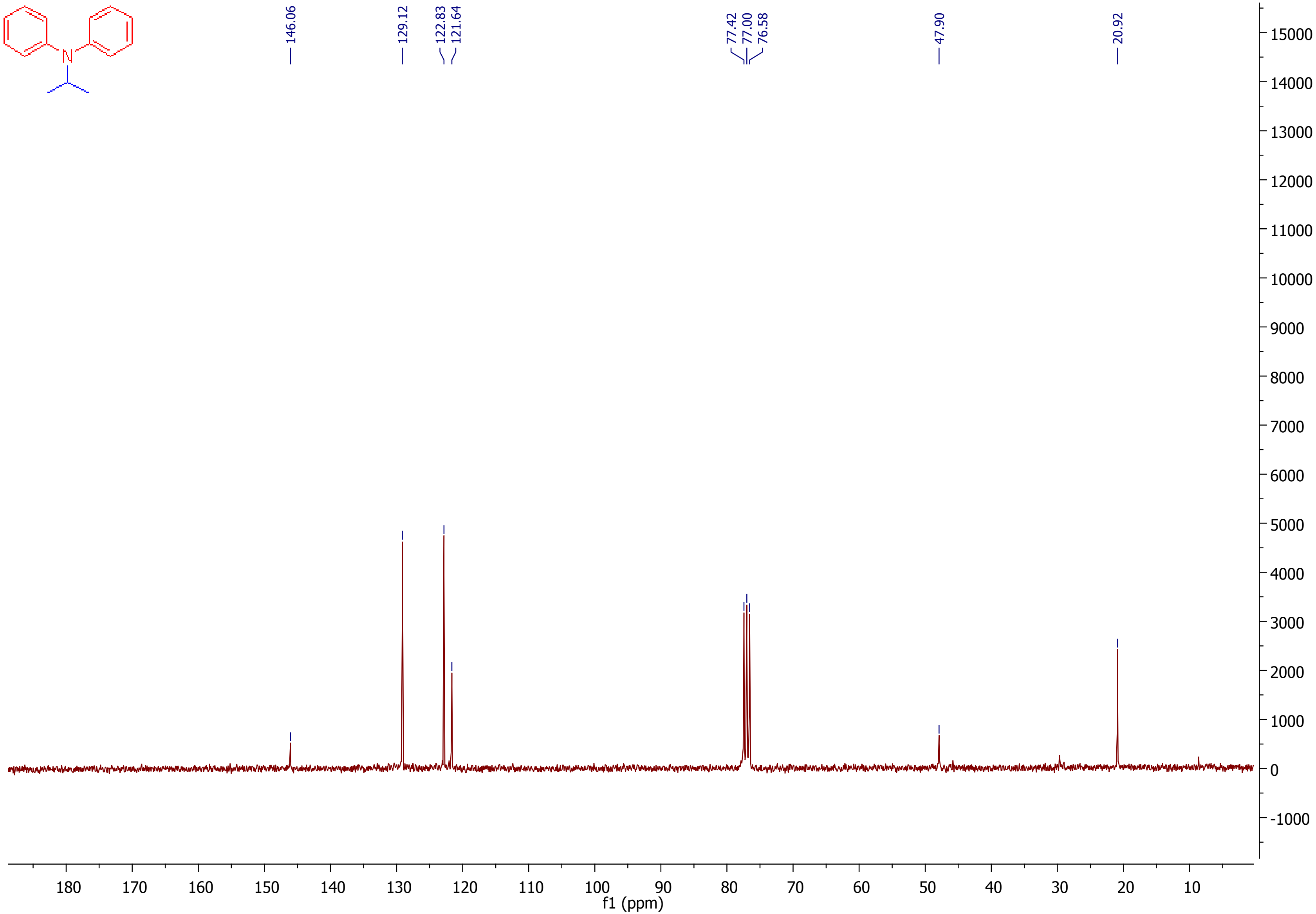
File Name	G:\IR SPECTRA\1\NY-324-1.TXT			***Date***	16 Dec 2014 12:58:32
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	FWHH	Asym	Intensity
1	1377.23	88.292	-	-	VW
2	1457.28	69.811	-	-	VW
3	1461.14	71.089	-	-	VW
4	1464.03	70.602	-	-	VW
5	2853.81	22.361	-	-	VW
6	2881.77	52.566	44.38	-0.16	VW
7	2924.21	4.826	-	-	VW
8	2954.11	22.952	-	-	VW

N-isopropyl-*N*-phenylaniline (1k)




N
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129.12
122.83
121.64
77.42
77.00
76.58
47.90
20.92
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

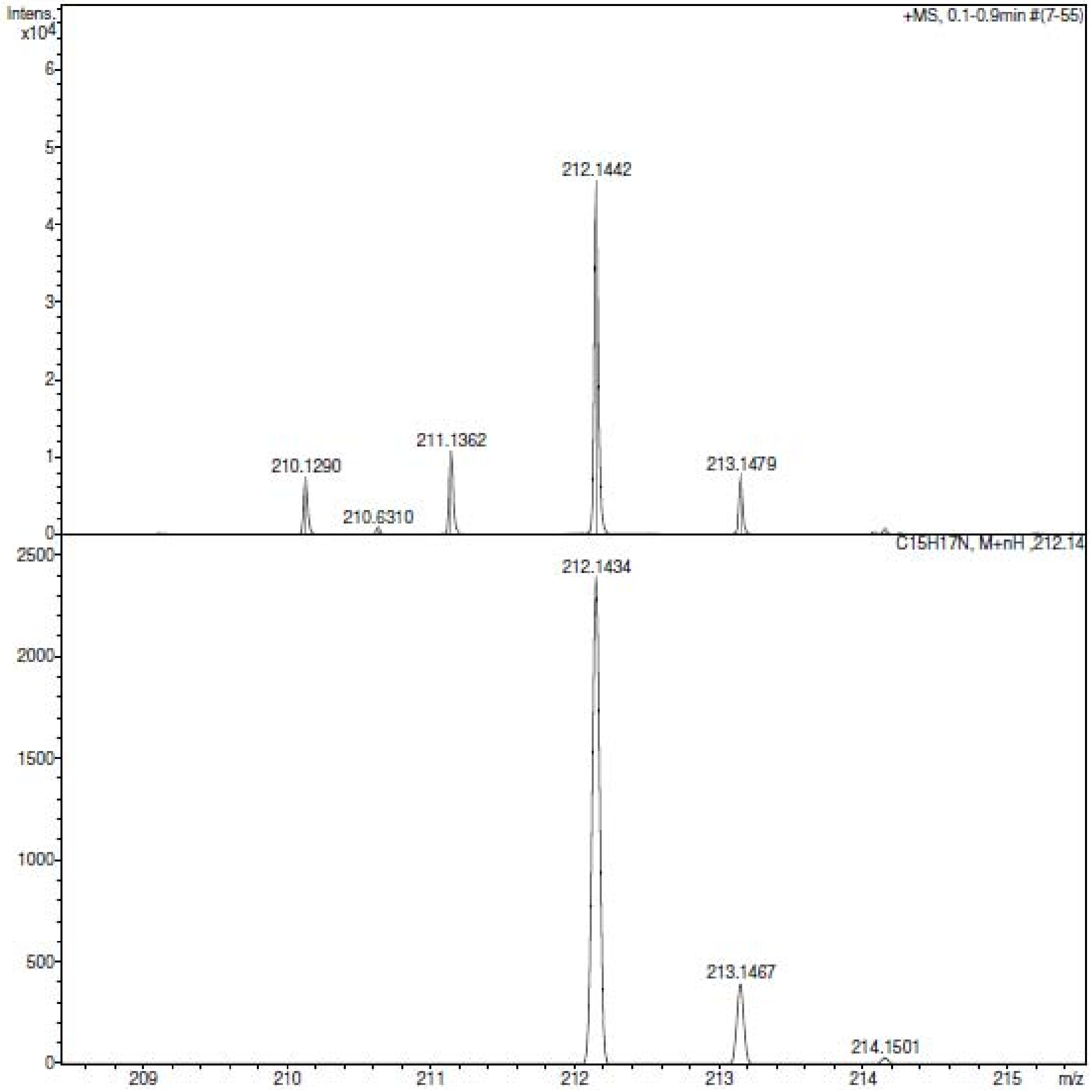
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1203022.d	Acquisition Date	03.12.2014 18:14:42
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 PN-526ch	Instrument / Ser#	micrOTOF 10248
Comment	C15H17N mw 211 calibrant added		

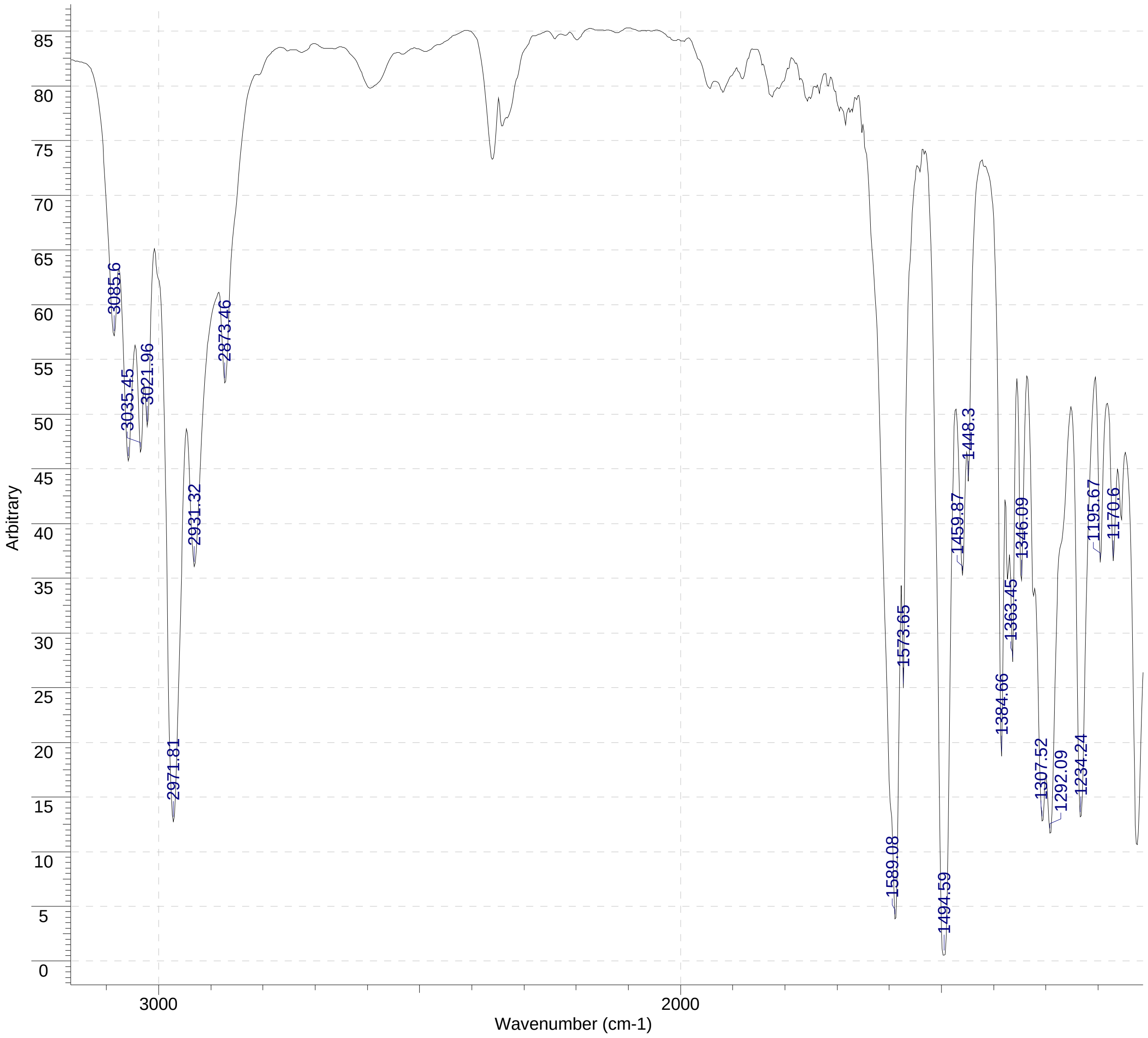
Acquisition Parameter

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



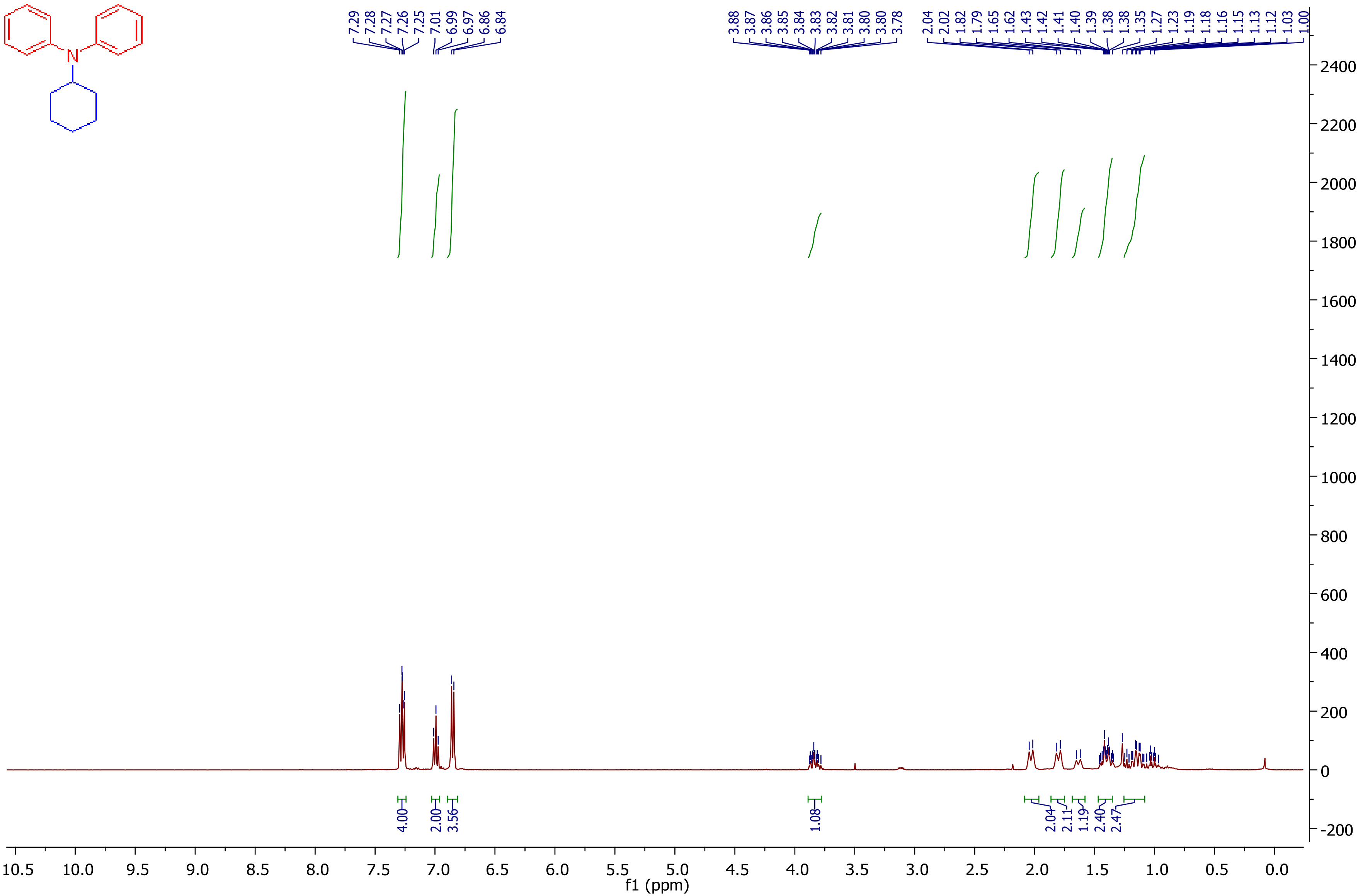
Bruker Compass DataAnalysis 4.0 printed: 03.12.2014 18:19:11 Page 1 of 1

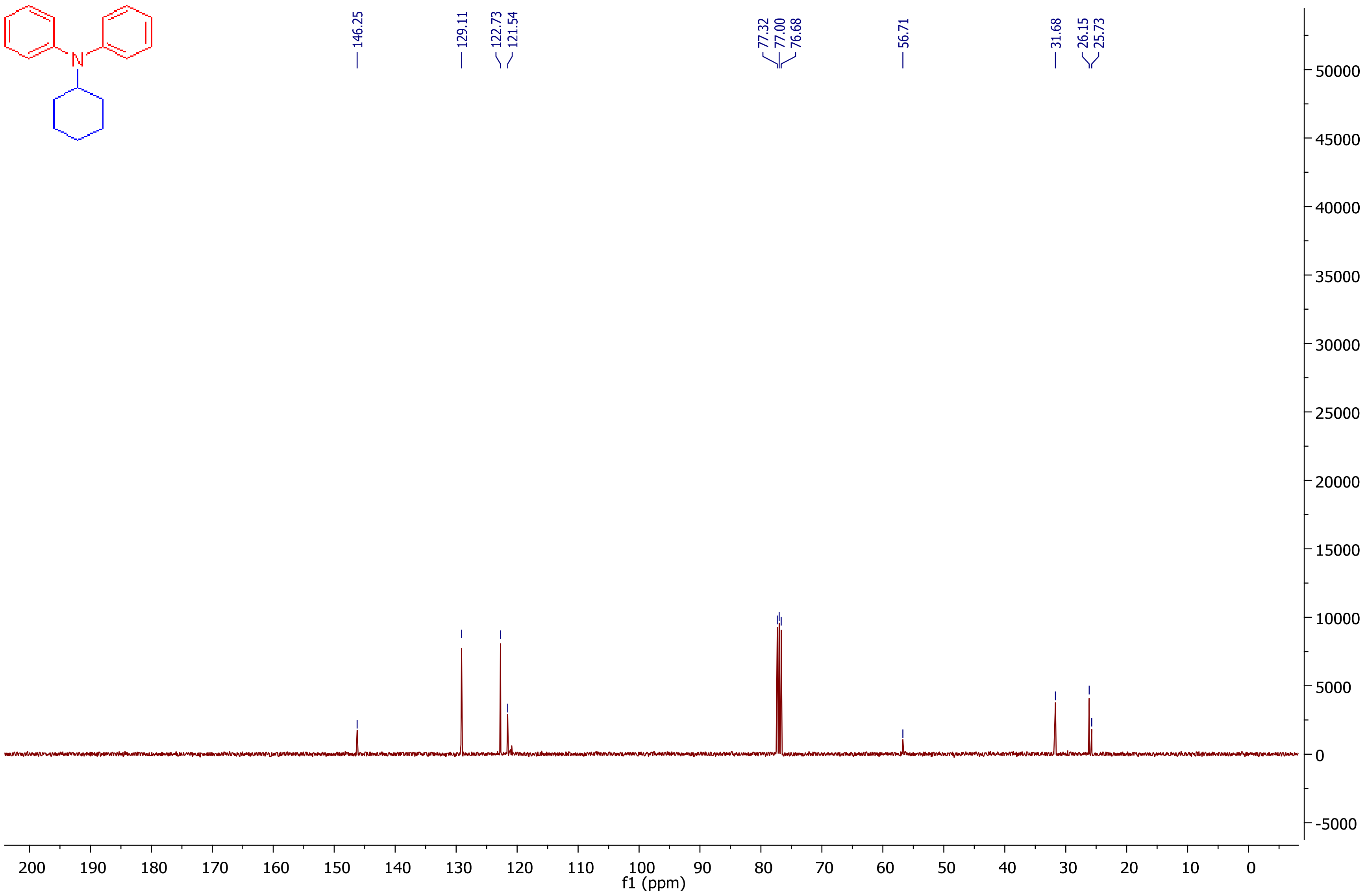
File Name	G:\IR SPECTRA\èêí èÿçó\èêí èÿçó\PN-526CH.CSV			***Date***	05 Dec 2014 16:57:28
Technique	Infrared	***Spectral Region***	IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	399.1990 - 4001.6321		
Points Count	1869	***Data Spacing***	1.9285		



No	cm-1	Arbitrary	Intensity	No	cm-1	Arbitrary	Intensity
1	1170.60	36.601	M	11	1494.59	0.555	VW
2	1195.67	36.437	M	12	1573.65	24.939	W
3	1234.24	13.205	W	13	1589.08	3.851	VW
4	1292.09	11.706	W	14	2873.46	52.855	S
5	1307.52	12.821	W	15	2931.32	36.048	M
6	1346.09	34.800	M	16	2971.81	12.731	W
7	1363.45	27.336	M	17	3021.96	48.899	M
8	1384.66	18.751	W	18	3035.45	46.547	M
9	1448.30	43.833	M	19	3058.60	45.709	M
10	1459.87	35.256	M	20	3085.60	57.139	S

N-cyclohexyl-*N*-phenylaniline (1l)




N
146.25
129.11
122.73
121.54
77.32
77.00
76.68
56.71
31.68
26.15
25.73
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

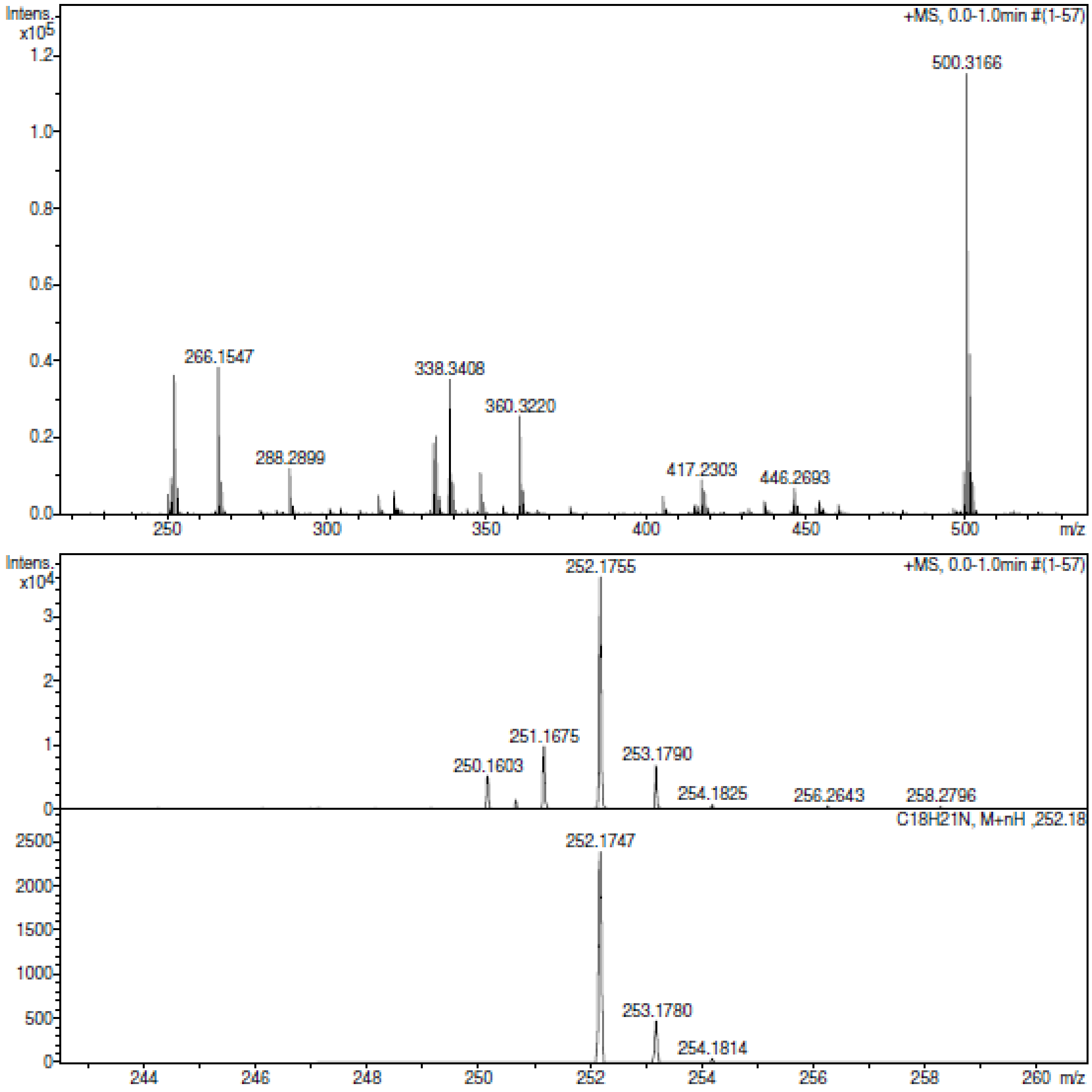
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1203024.d	Acquisition Date	03.12.2014 18:42:40
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NU-749	Instrument / Ser#	micrOTOF 10248
Comment	C18H21N mw 251 calibrant added		

Acquisition Parameter

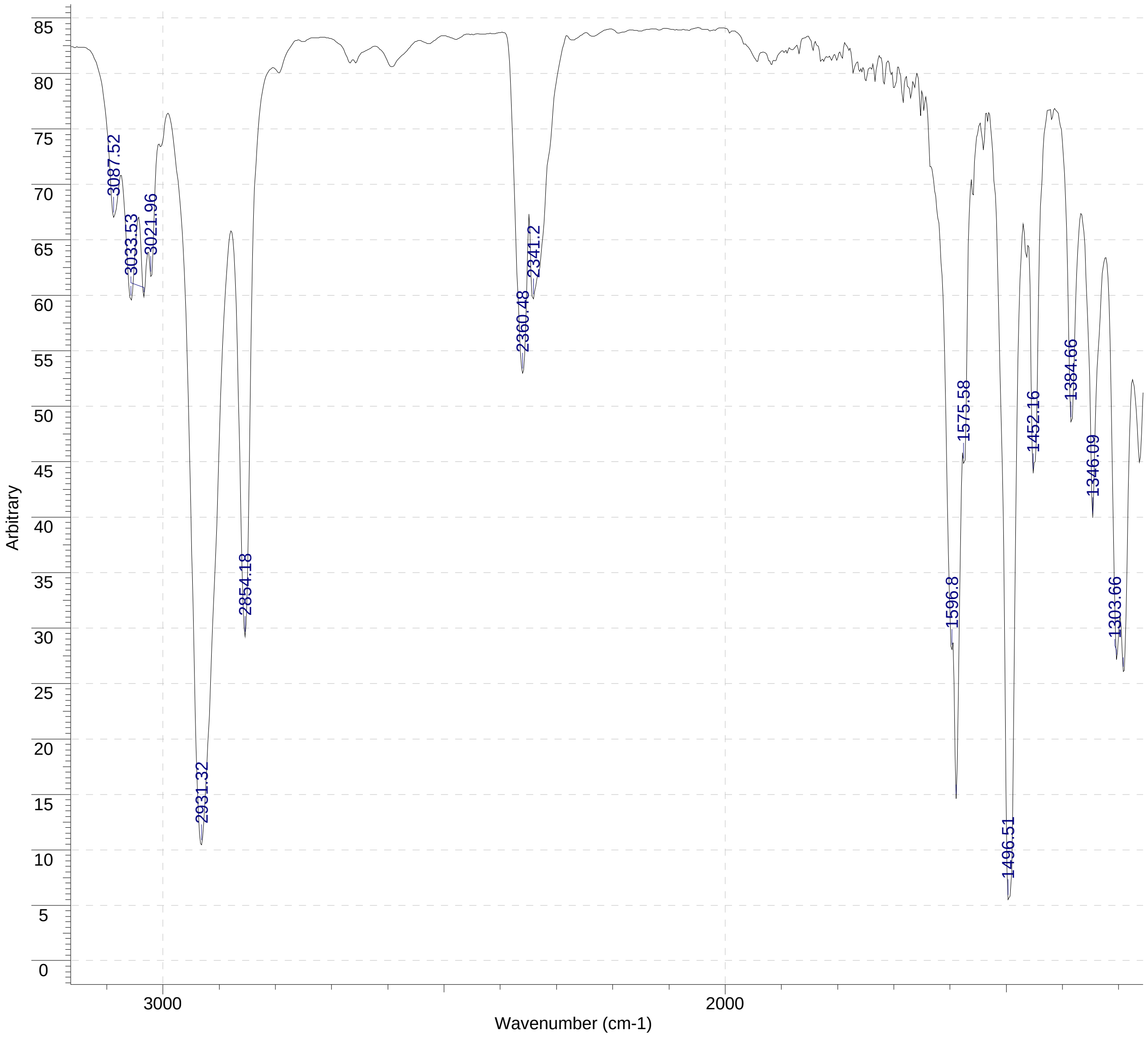
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 03.12.2014 18:47:26 Page 1 of 1

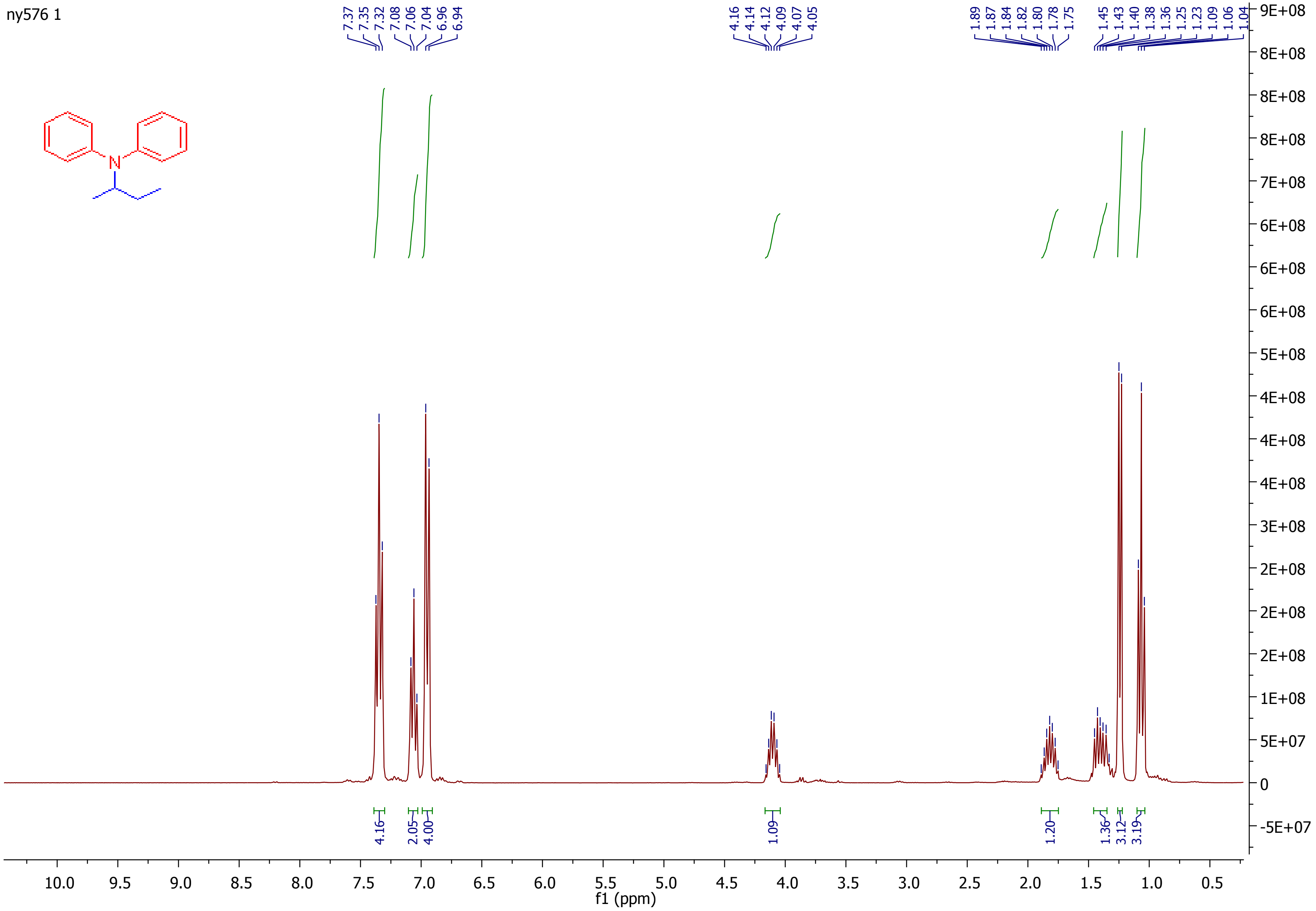
29 Jul 2015

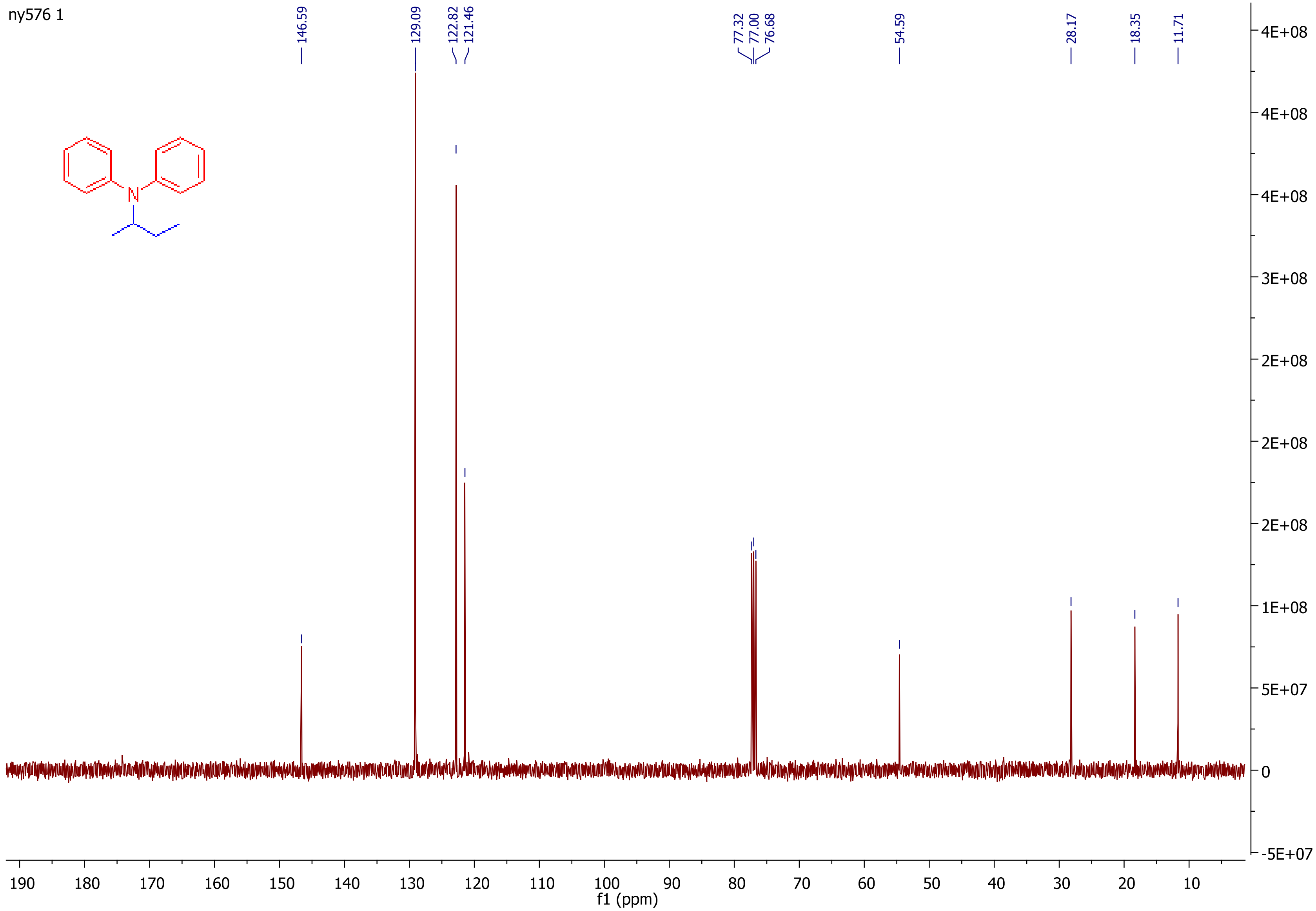
File Name	G:\IR SPECTRA\èê í èÿçó\èê í èÿçó\NY-749.CSV			***Date***	05 Dec 2014 16:57:20
Technique	Infrared	***Spectral Region***	IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	399.1990 - 4001.6321		
Points Count	1869	***Data Spacing***	1.9285		



No	cm-1	Arbitrary	Intensity
1	1292.09	26.051	M
2	1303.66	27.172	M
3	1346.09	39.932	M
4	1384.66	48.592	M
5	1452.16	43.934	M
6	1496.51	5.489	VW
7	1575.58	44.835	M
8	1589.08	14.583	W
9	1596.80	28.056	M
10	2341.20	59.687	S
11	2360.48	52.954	S
12	2854.18	29.255	M
13	2931.32	10.472	W
14	3021.96	61.686	S
15	3033.53	59.840	S
16	3056.67	59.575	S
17	3087.52	67.017	S

N-(sec-butyl)-*N*-phenylaniline (1m)




ny576 1
146.59
129.09
122.82
121.46
77.32
77.00
76.68
54.59
28.17
18.35
11.71
N
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

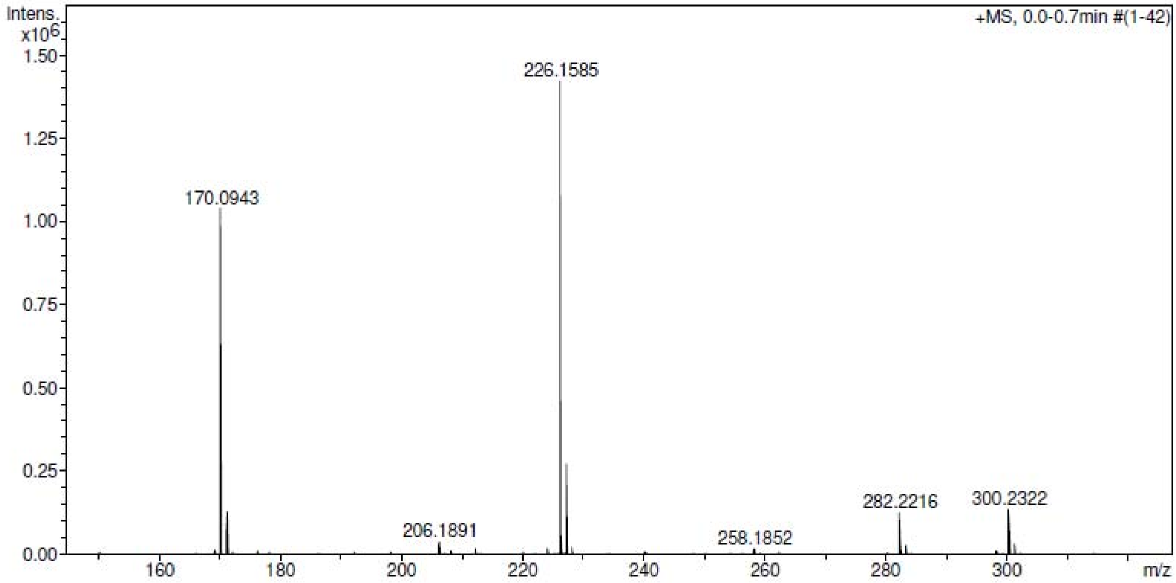
Display Report

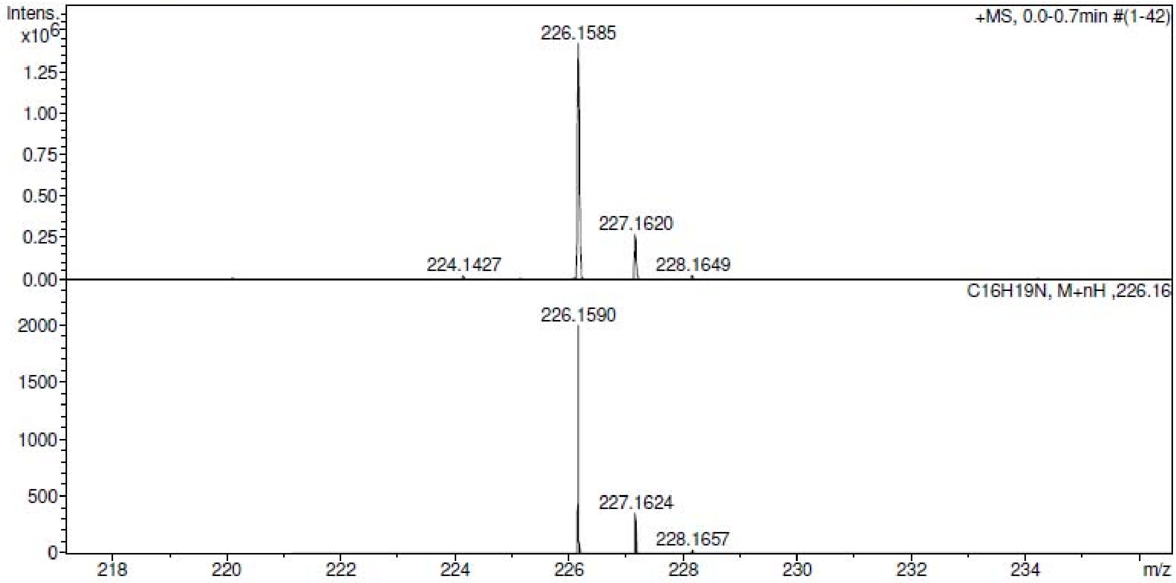
Analysis Info

		Acquisition Date	21.01.2015 11:56:35
Analysis Name	D:\Data\Kolotyrkina\2015\Titov\0121009.d		
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 5904	Instrument / Ser#	micrOTOF 10248
Comment	C16H19N mw 225 calibrant and FA added		

Acquisition Parameter

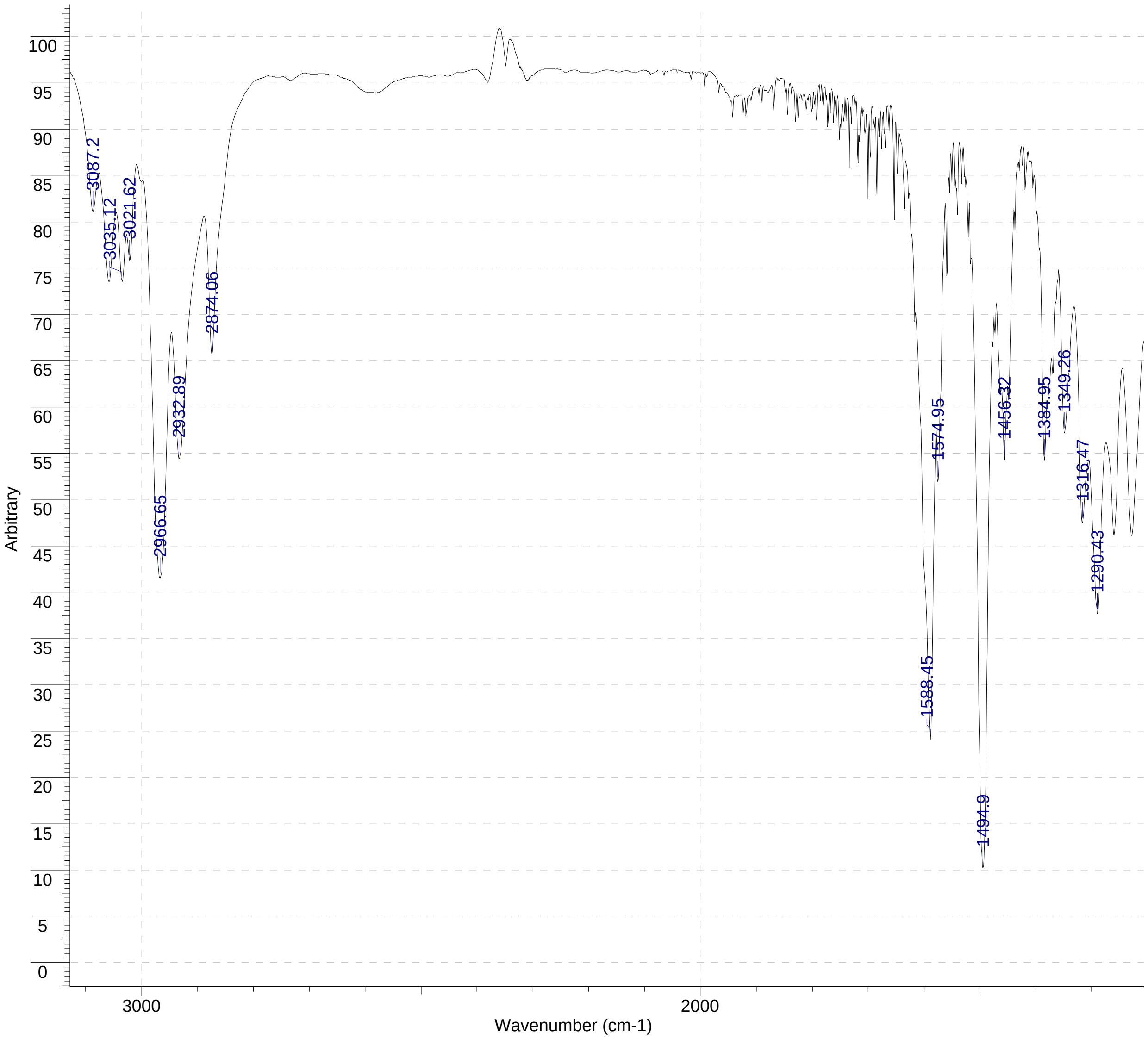
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





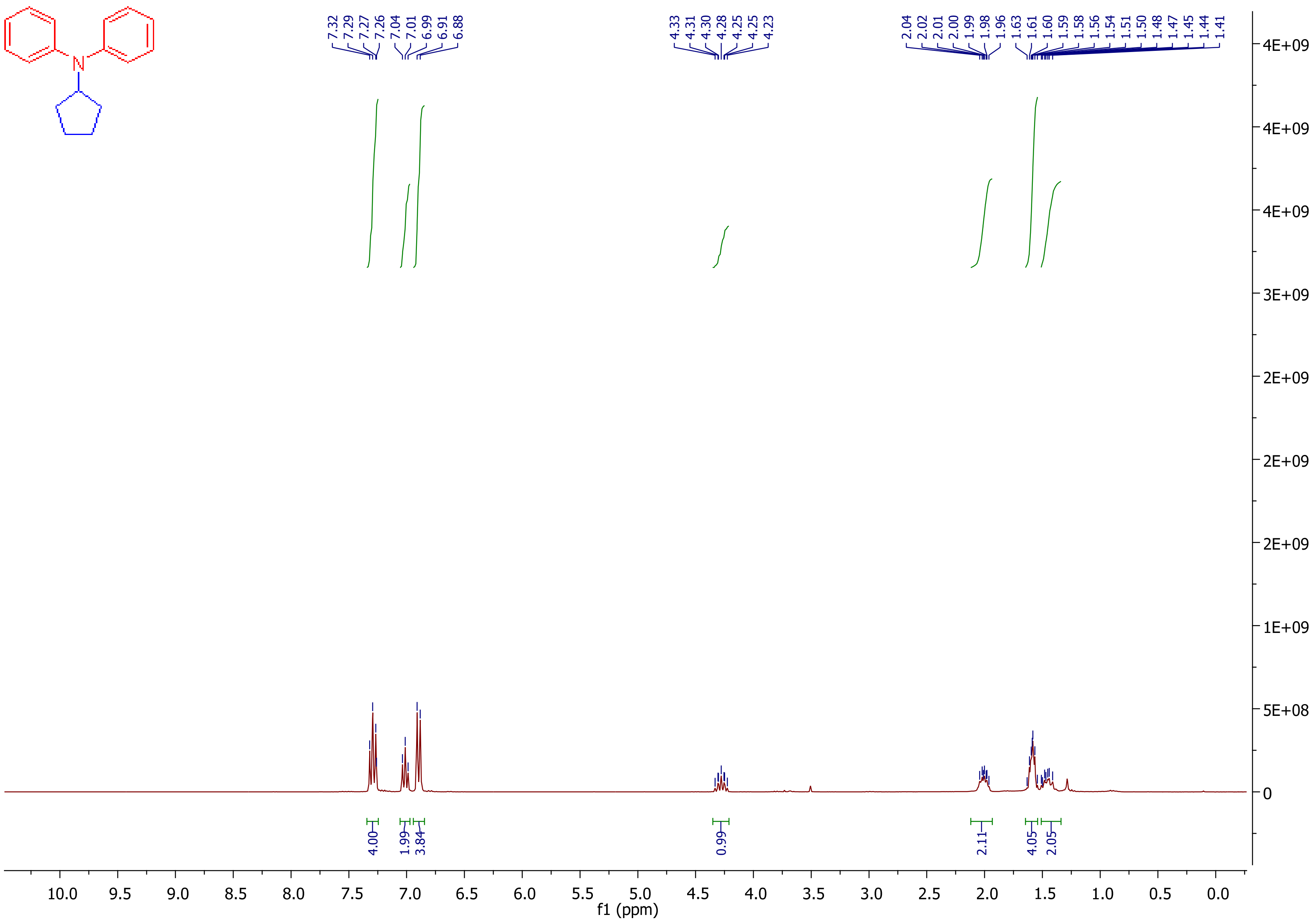
29 Jul 2015

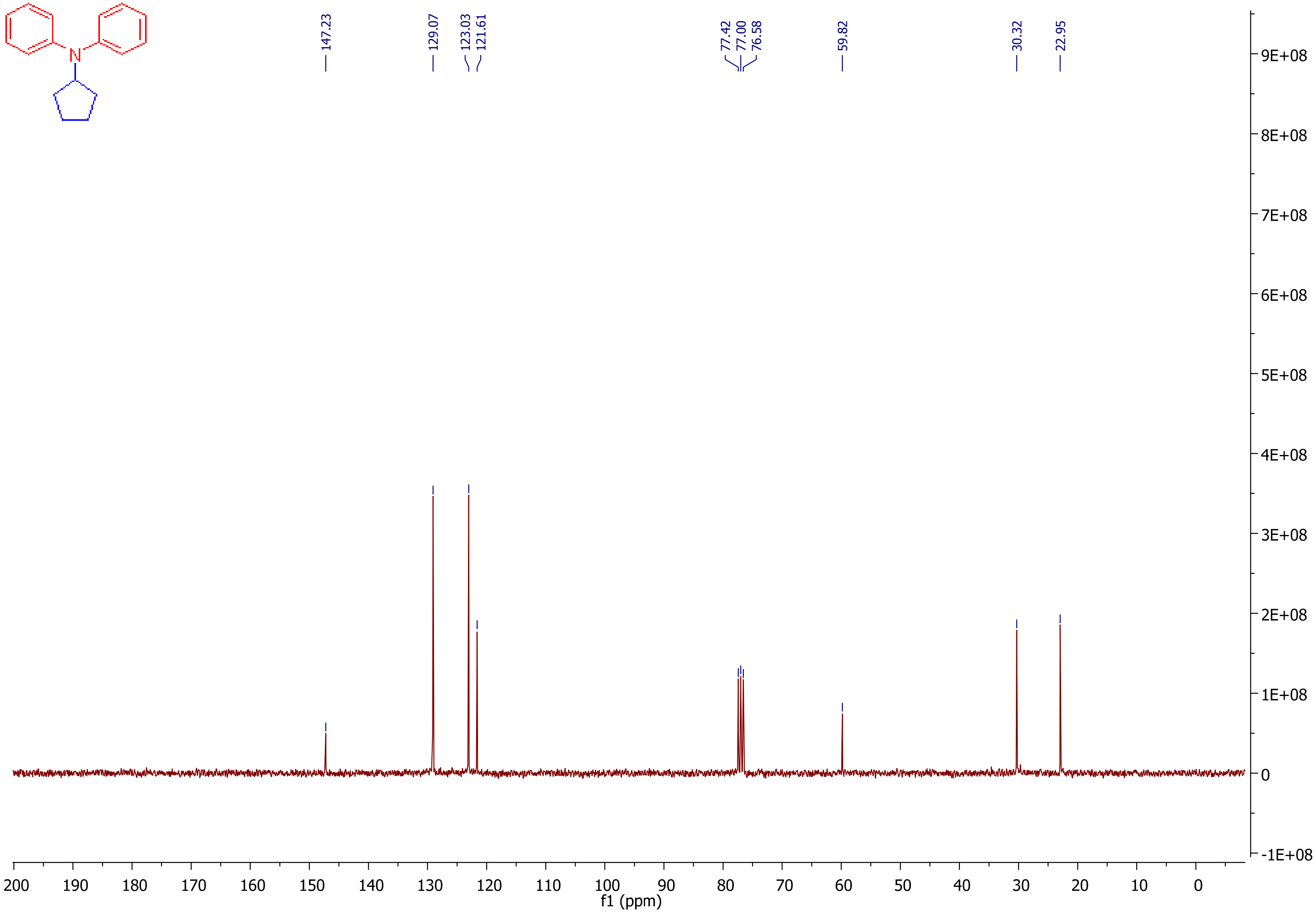
File Name	G:\IR SPECTRA\590_4.TXT			***Date***	11 Dec 2014 16:05:14
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699	***Points Count***	4824
Data Spacing	0.9644				



No	cm-1	Arbitrary	Intensity
1	1290.43	37.701	M
2	1316.47	47.509	M
3	1349.26	57.202	M
4	1384.95	54.343	M
5	1456.32	54.246	M
6	1494.90	10.239	W
7	1574.95	51.923	M
8	1588.45	24.146	W
9	2874.06	65.675	S
10	2932.89	54.388	M
11	2966.65	41.522	M
12	3021.62	75.833	S
13	3035.12	73.557	S
14	3058.27	73.505	S
15	3087.20	81.118	S

N-cyclopentyl-*N*-phenylaniline (1n)




N
147.23
129.07
123.03
121.61
77.42
77.00
76.58
59.82
30.32
22.95
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

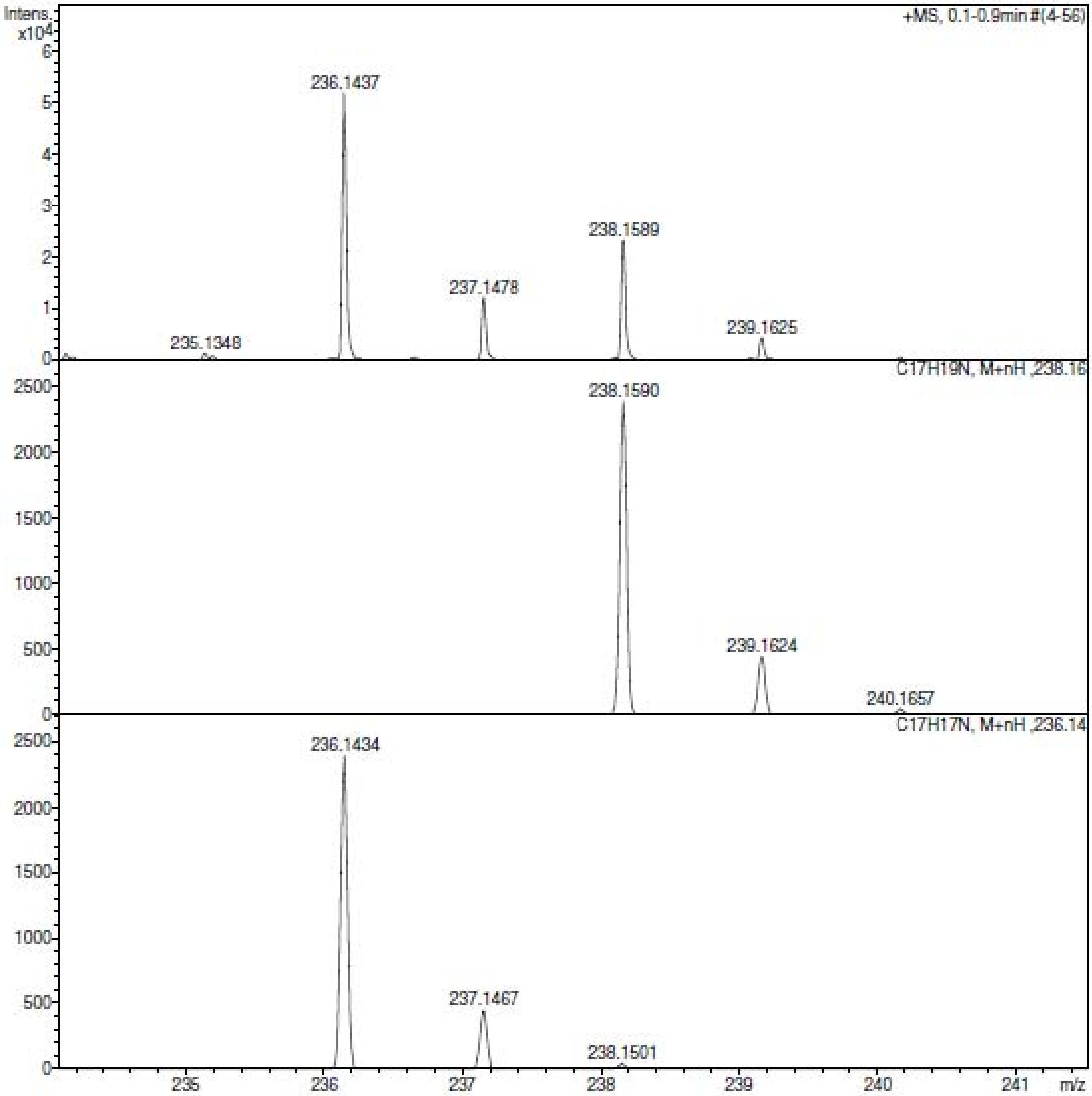
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113016.d	Acquisition Date	13.11.2014 13:29:20
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-427-1	Instrument / Ser#	micrOTOF 10248
Comment	C17H19N mw 237 calibrant added		

Acquisition Parameter

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



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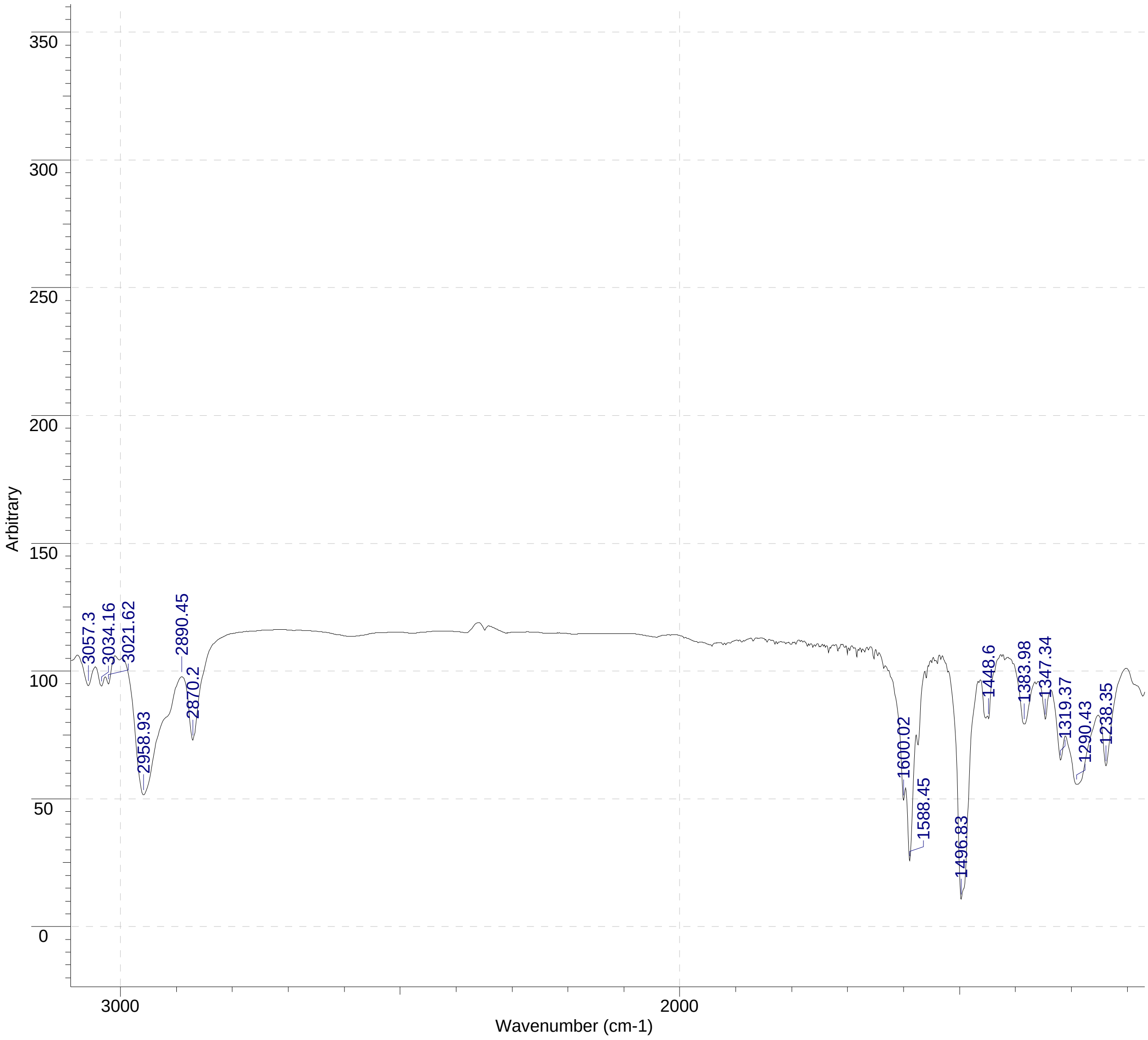
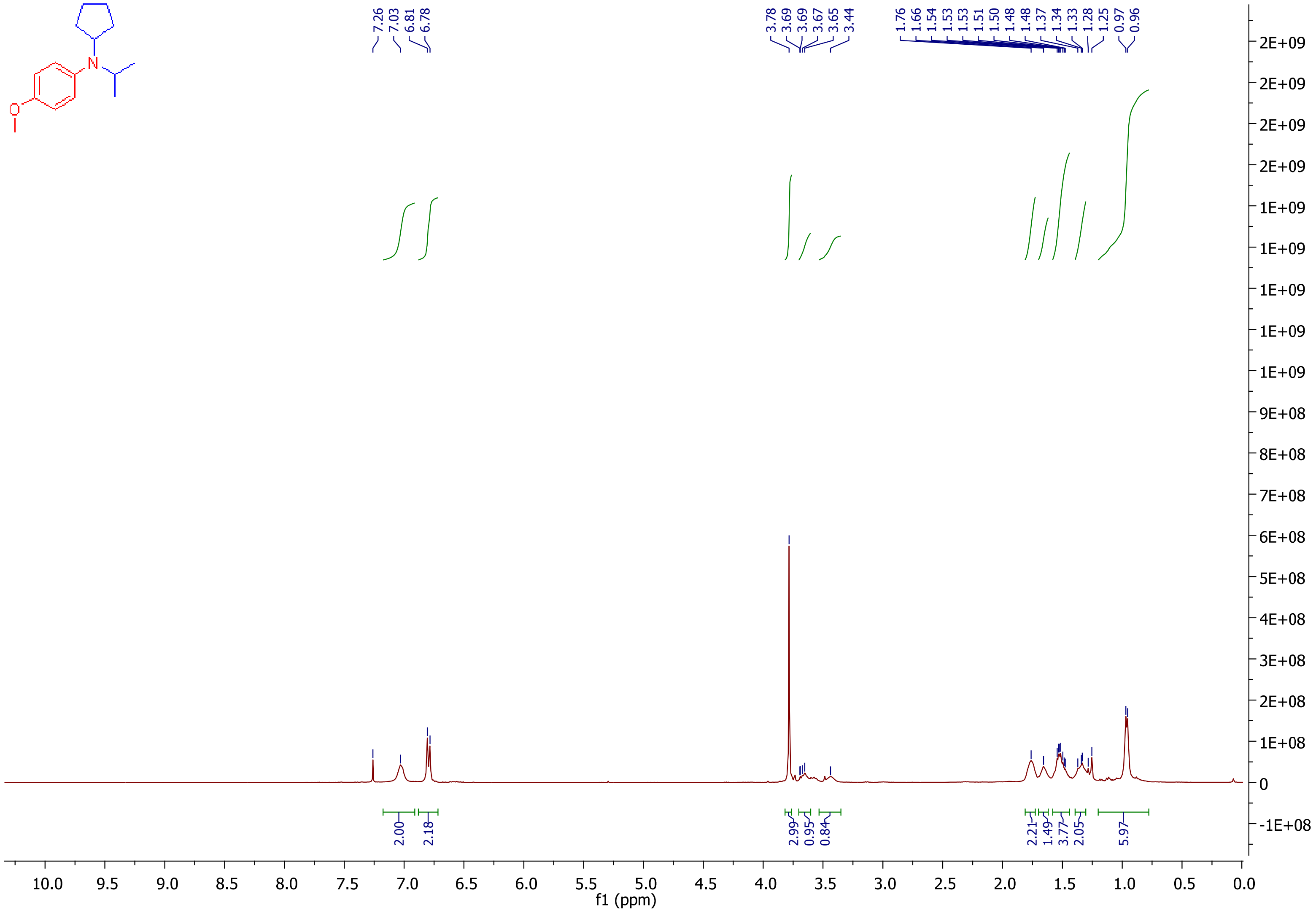
29 Jul 2015

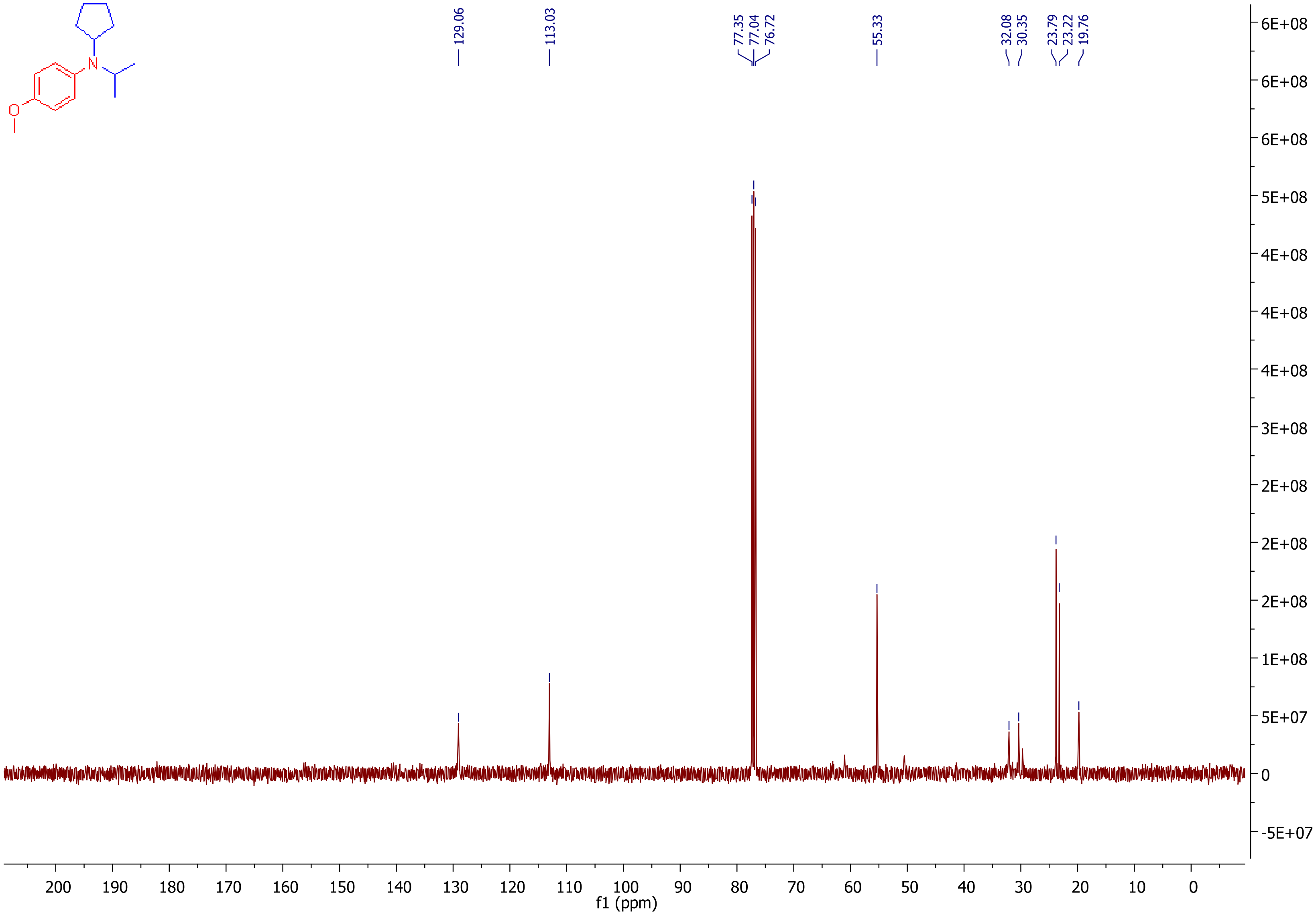
File Name	G:\IR SPECTRA\2015.02.11\NY-427-1_T.SMF.TXT			***Date***	11 Feb 2015 15:32:00
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	499.5850 - 5000.6699		
Points Count	4668	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1238.35	62.848	VW
2	1290.43	55.697	VW
3	1319.37	65.211	VW
4	1347.34	81.231	VW
5	1383.98	79.206	VW
6	1448.60	81.276	VW
7	1496.83	10.777	VW
8	1588.45	25.643	VW
9	1600.02	49.492	VW
10	2870.20	73.021	VW
11	2890.45	97.800	VW
12	2958.93	51.591	VW
13	3021.62	94.964	VW
14	3034.16	94.100	VW
15	3057.30	94.233	VW

N-cyclopentyl-*N*-isopropyl-4-methoxyaniline (1o)




N
O
129.06
113.03
77.35
77.04
76.72
55.33
32.08
30.35
23.79
23.22
19.76
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

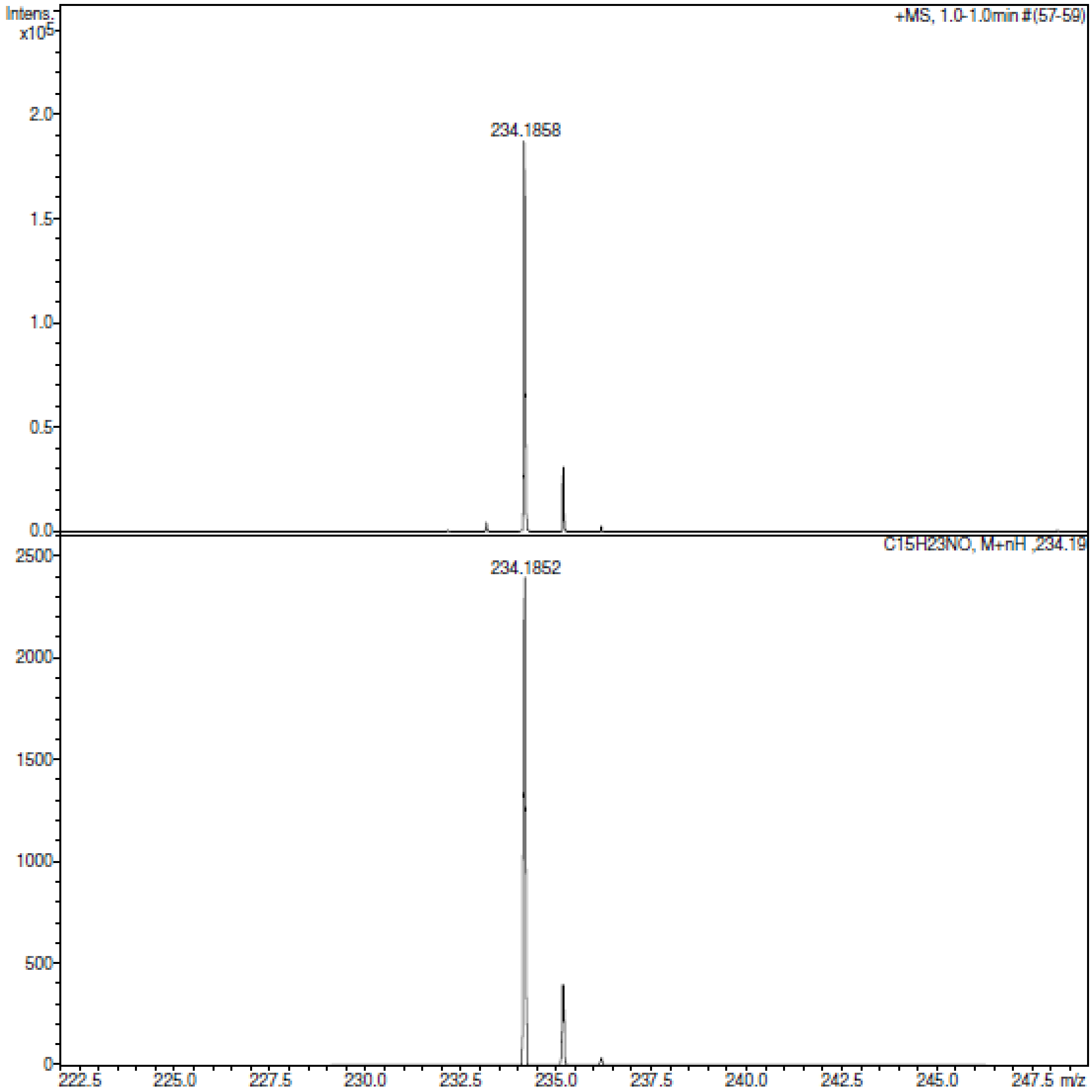
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1112029.d	Acquisition Date	12.11.2014 17:50:20
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-578-1	Instrument / Ser#	micrOTOF 10248
Comment	C15H23NO mw 233 calibrant added		

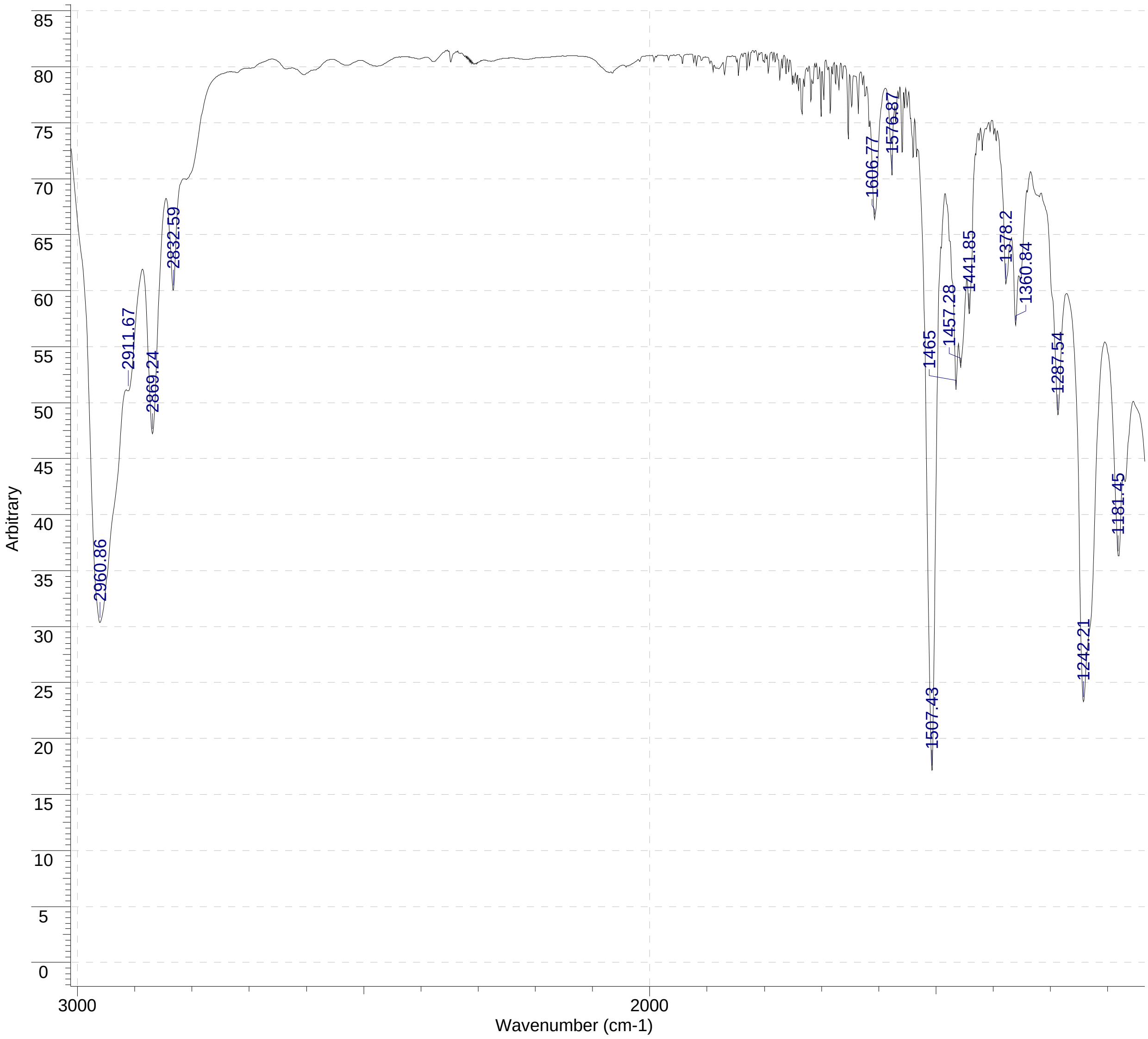
Acquisition Parameter

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



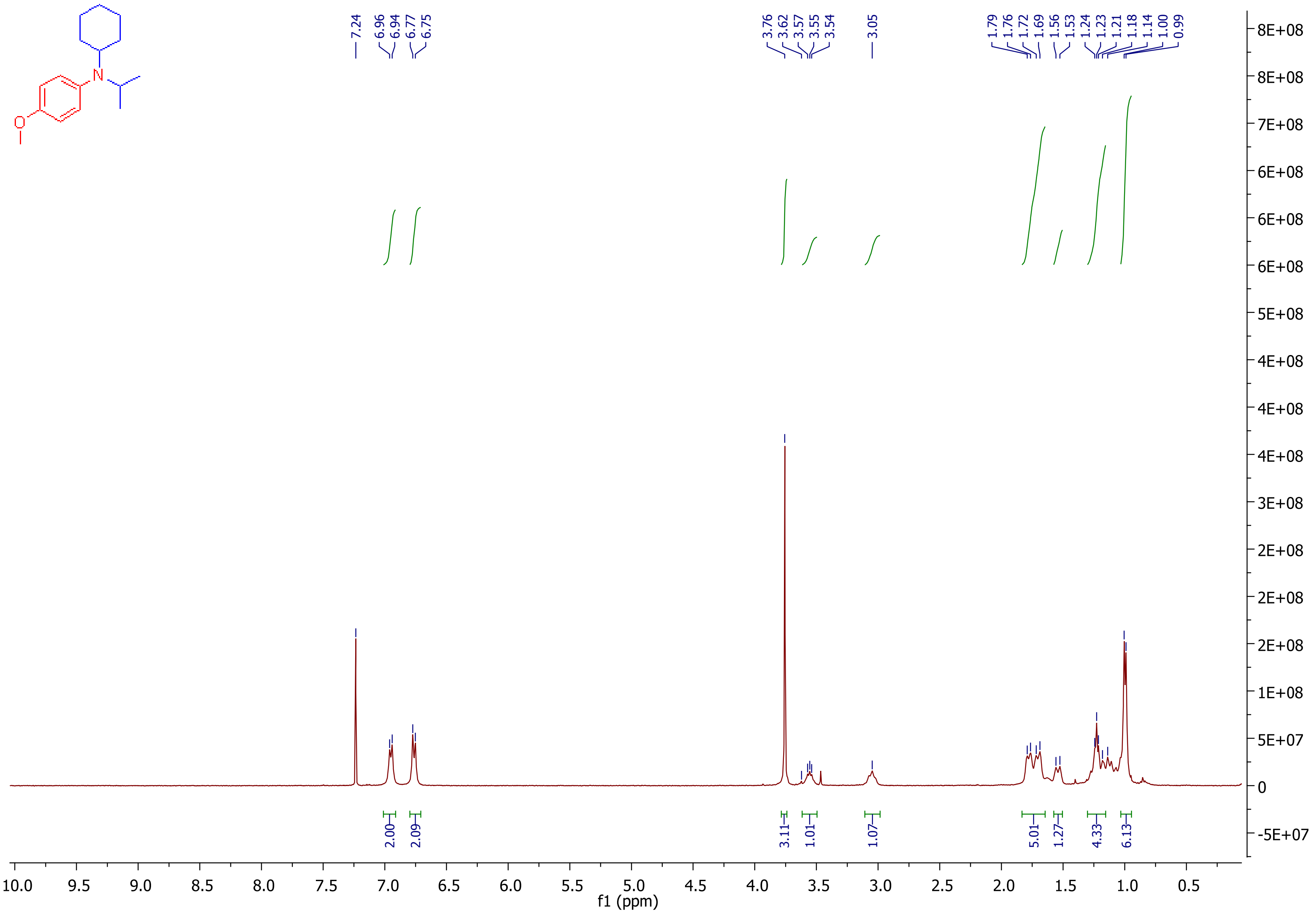
29 Jul 2015

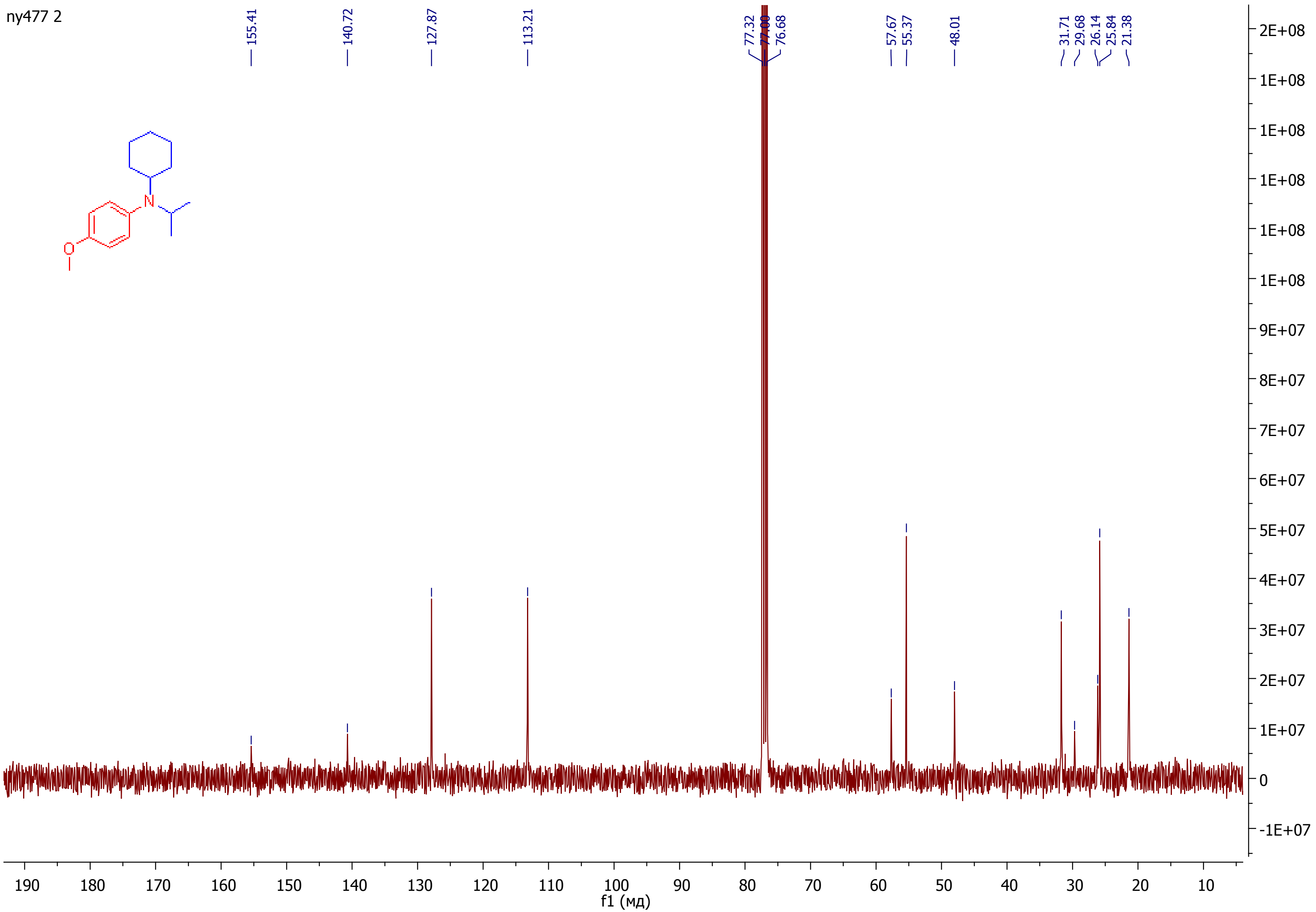
File Name	G:\IR SPECTRA\578-1.SMF.TXT			***Date***	11 Dec 2014 16:05:02
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1181.45	36.317	M
2	1242.21	23.280	W
3	1287.54	48.905	M
4	1360.84	56.911	S
5	1378.20	60.615	S
6	1441.85	57.938	S
7	1457.28	53.118	S
8	1465.00	51.145	S
9	1507.43	17.133	W
10	1576.87	70.288	S
11	1606.77	66.392	S
12	2832.59	60.045	S
13	2869.24	47.202	M
14	2911.67	51.043	S
15	2960.86	30.359	M

N-cyclohexyl-*N*-isopropyl-4-methoxyaniline (1p)




ny477 2
155.41
140.72
127.87
113.21
77.32
77.00
76.68
57.67
55.37
48.01
31.71
29.68
26.14
25.84
21.38
N
O
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (мд)

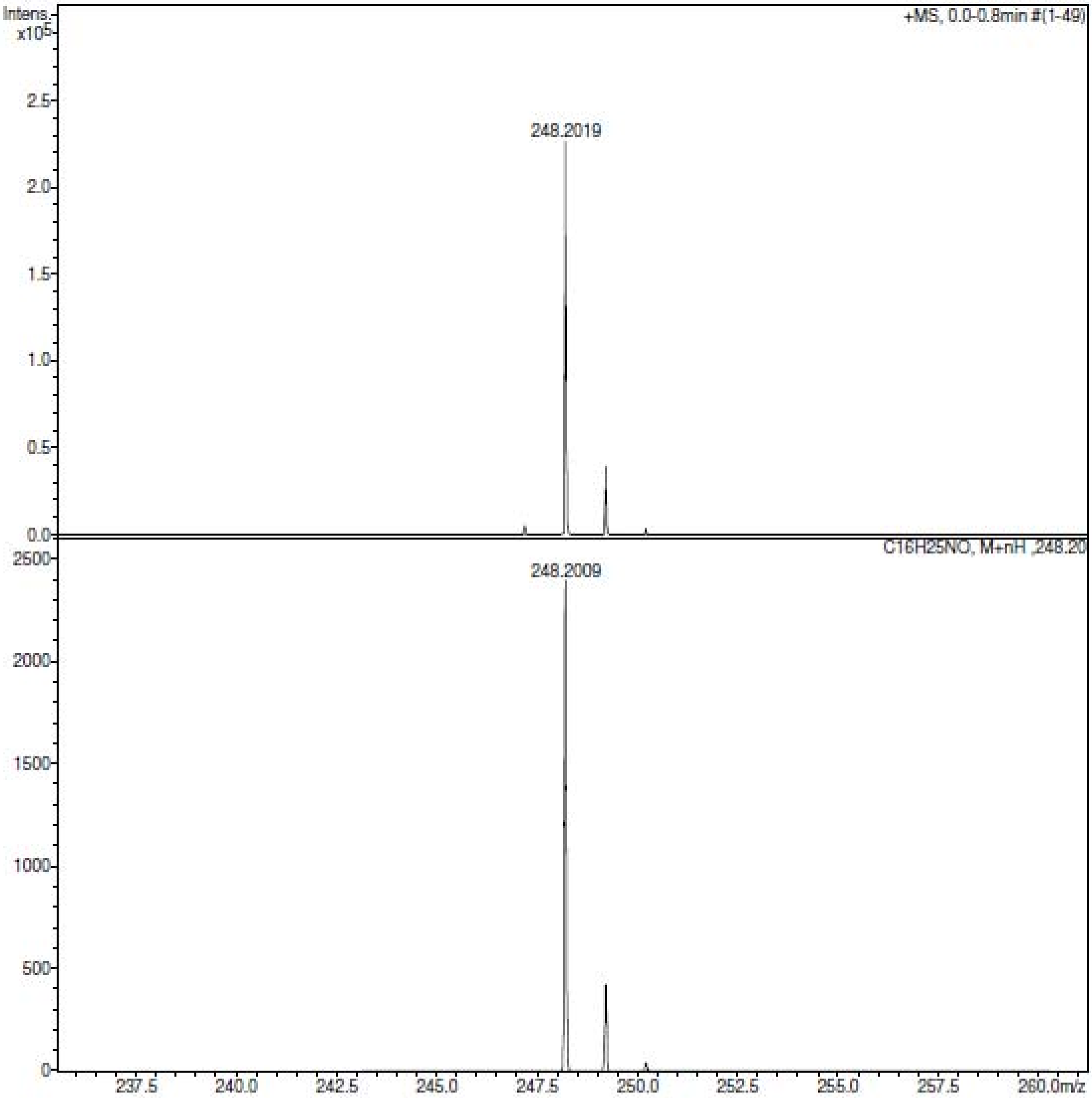
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1112025.d	Acquisition Date	12.11.2014 17:17:50
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-477-2	Instrument / Ser#	micrOTOF 10248
Comment	C16H25NO mw 247 calibrant added		

Acquisition Parameter

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



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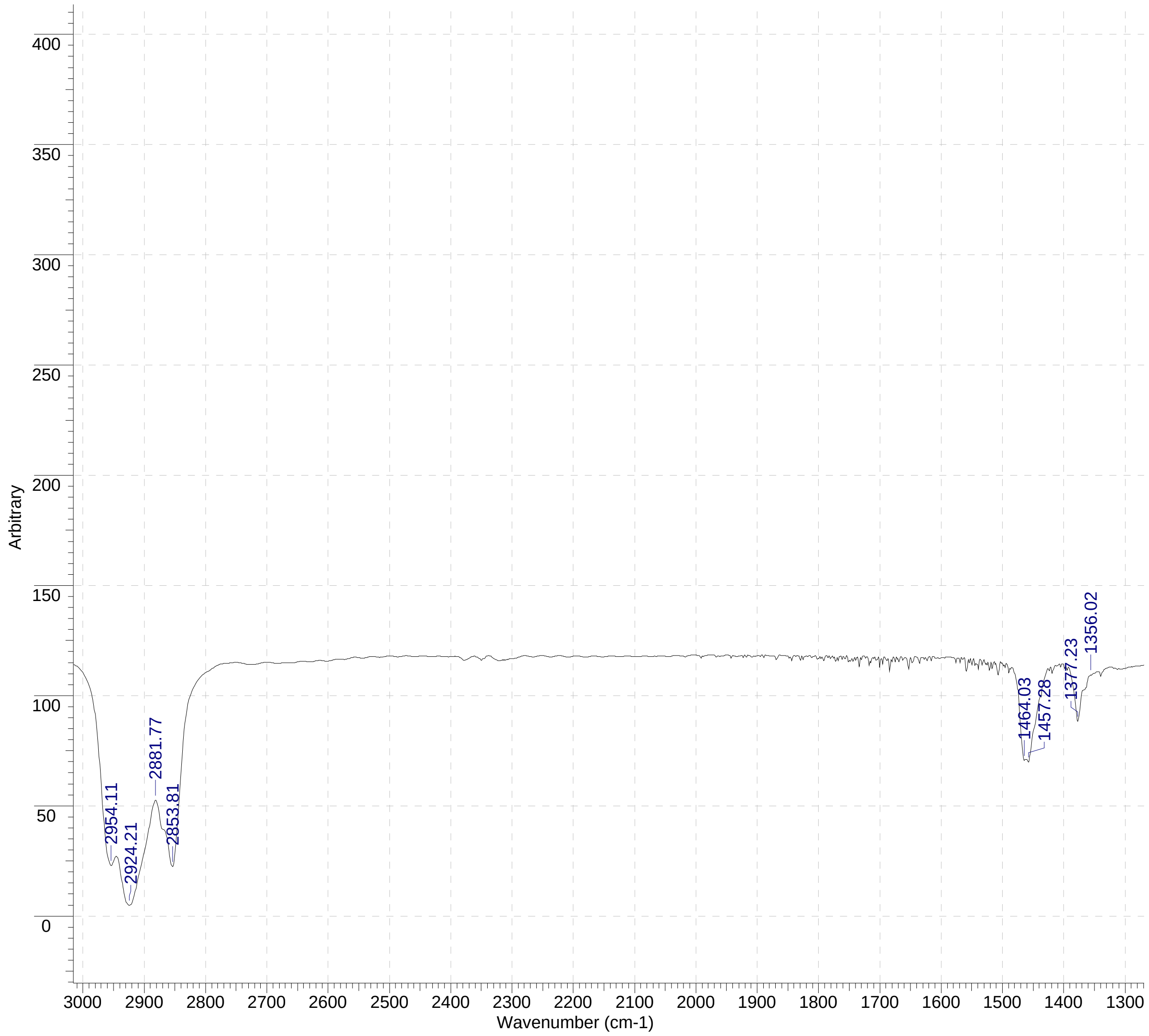
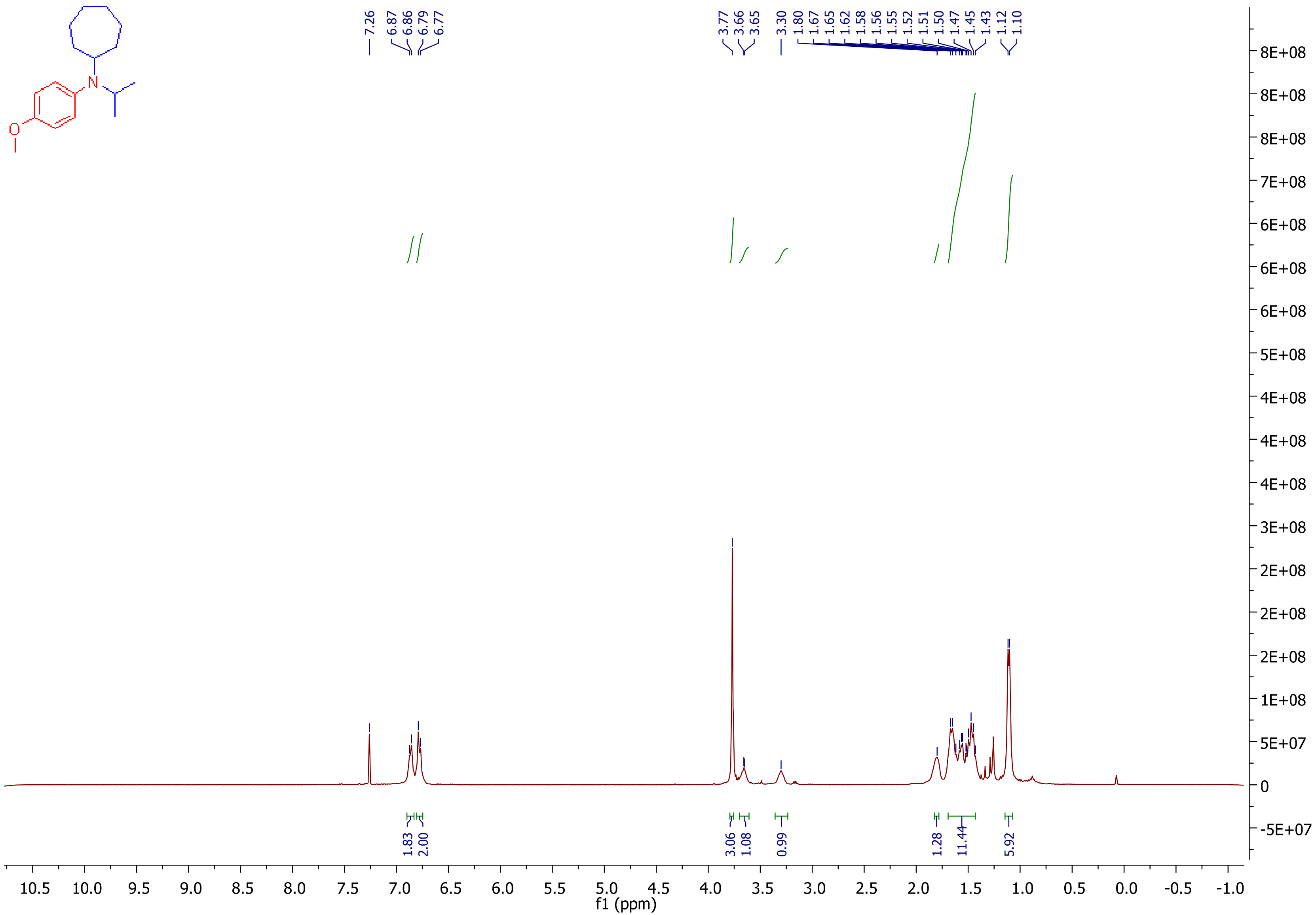
29 Jul 2015

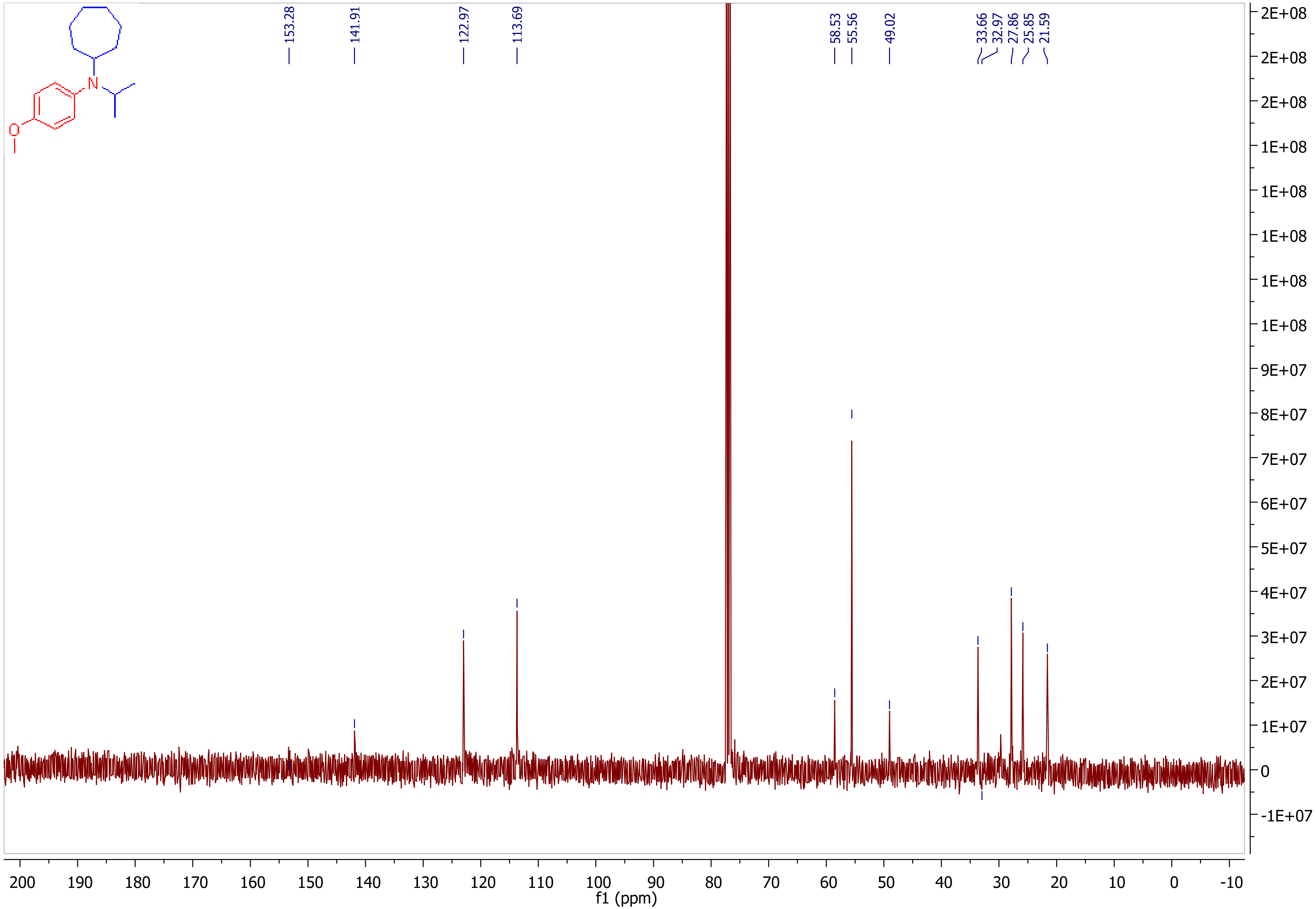
File Name	G:\IR SPECTRA\1\NUJOL.TXT			***Date***	16 Dec 2014 12:58:22
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	FWHH	Asym	Intensity
1	1356.02	109.414	-	-	VW
2	1377.23	88.292	-	-	VW
3	1457.28	69.811	-	-	VW
4	1464.03	70.602	-	-	VW
5	2853.81	22.361	-	-	VW
6	2881.77	52.566	44.38	-0.16	VW
7	2924.21	4.826	-	-	VW
8	2954.11	22.952	-	-	VW

N-cycloheptyl-*N*-isopropyl-4-methoxyaniline (1q)




153.28
141.91
122.97
113.69
58.53
55.56
49.02
33.66
32.97
27.86
25.85
21.59
N
O
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

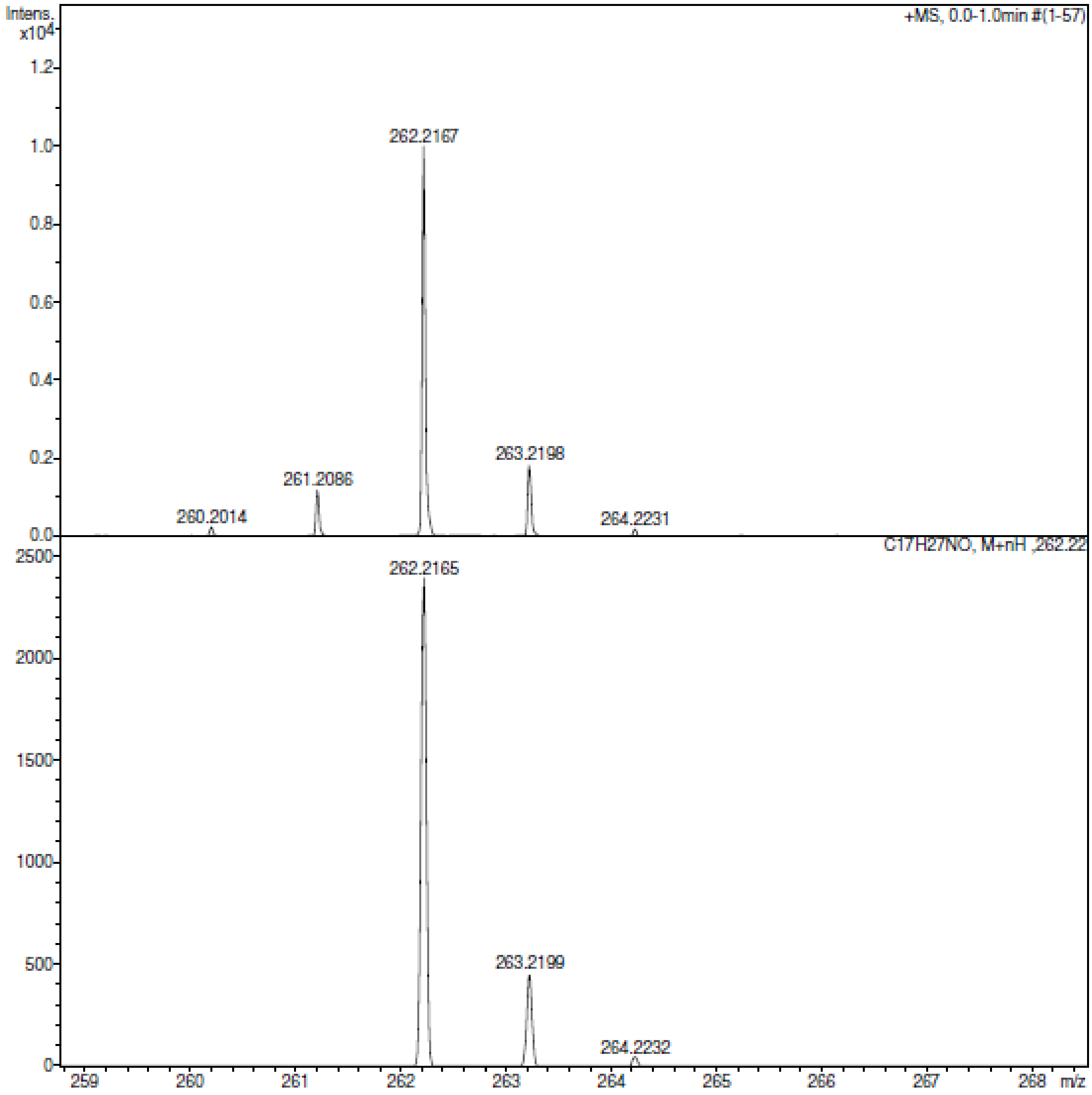
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113002.d	Acquisition Date	13.11.2014 9:40:11
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-479-1	Instrument / Ser#	micrOTOF 10248
Comment	C17H27NO mw 261 calibrant added		

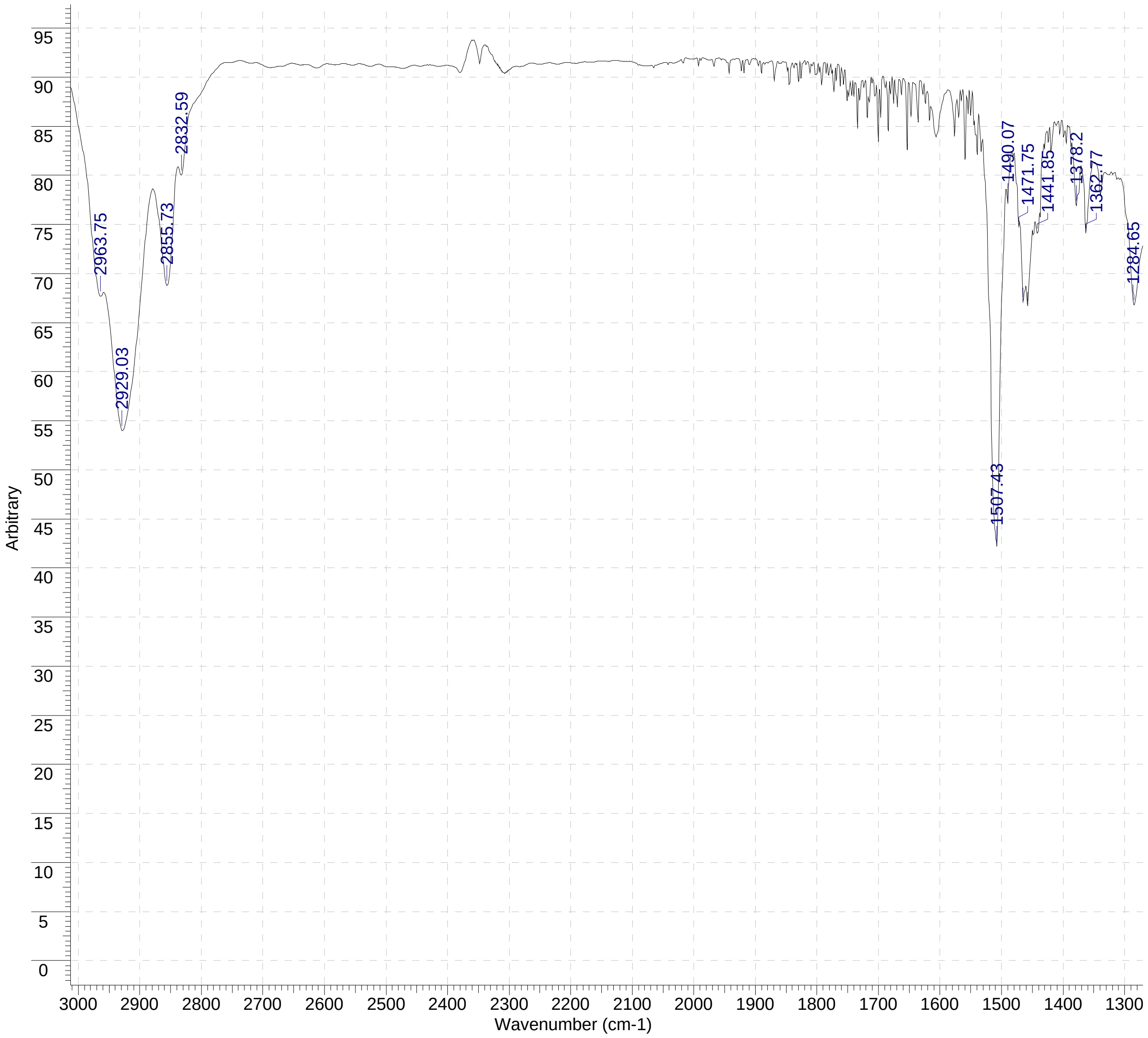
Acquisition Parameter

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



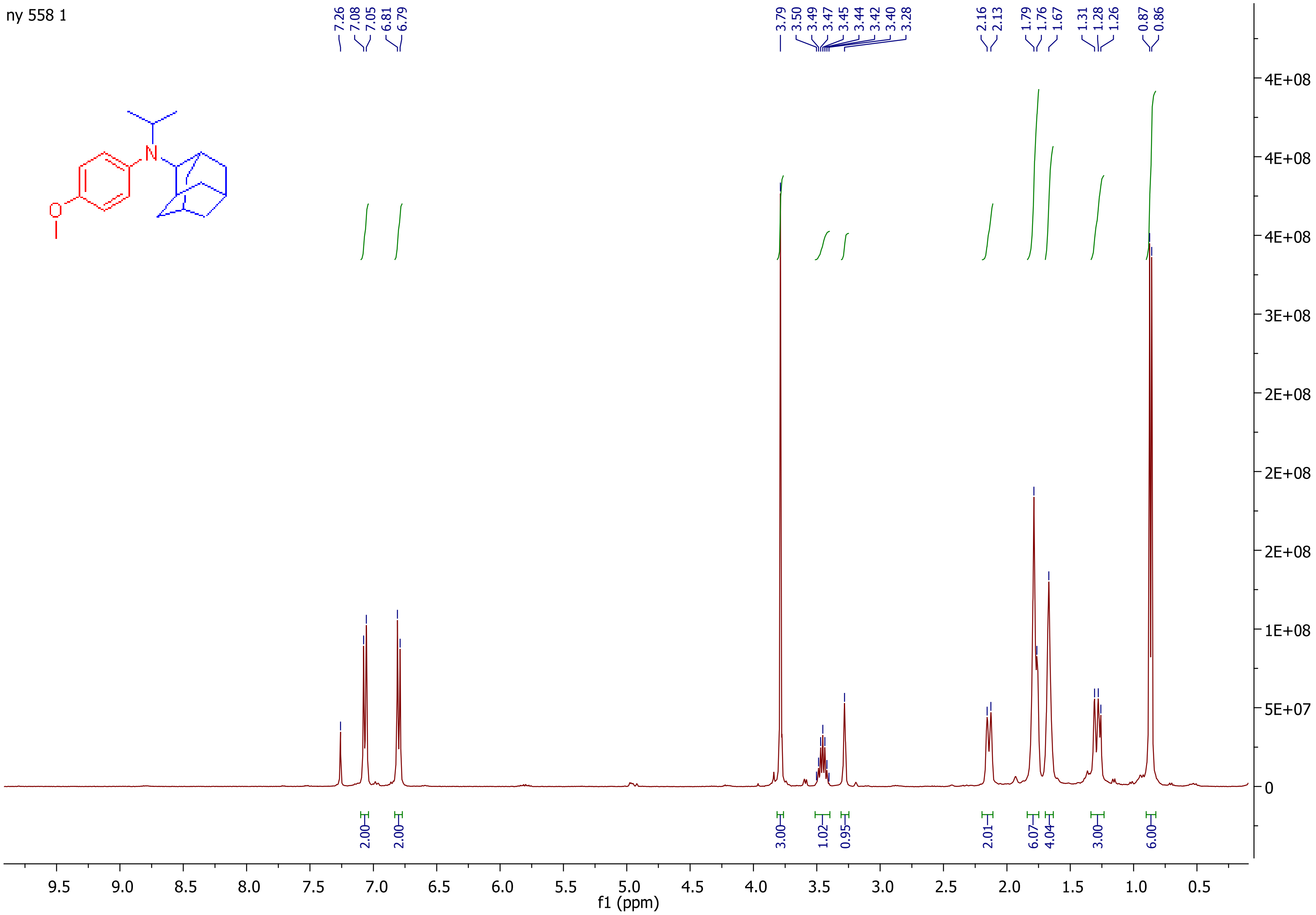
29 Jul 2015

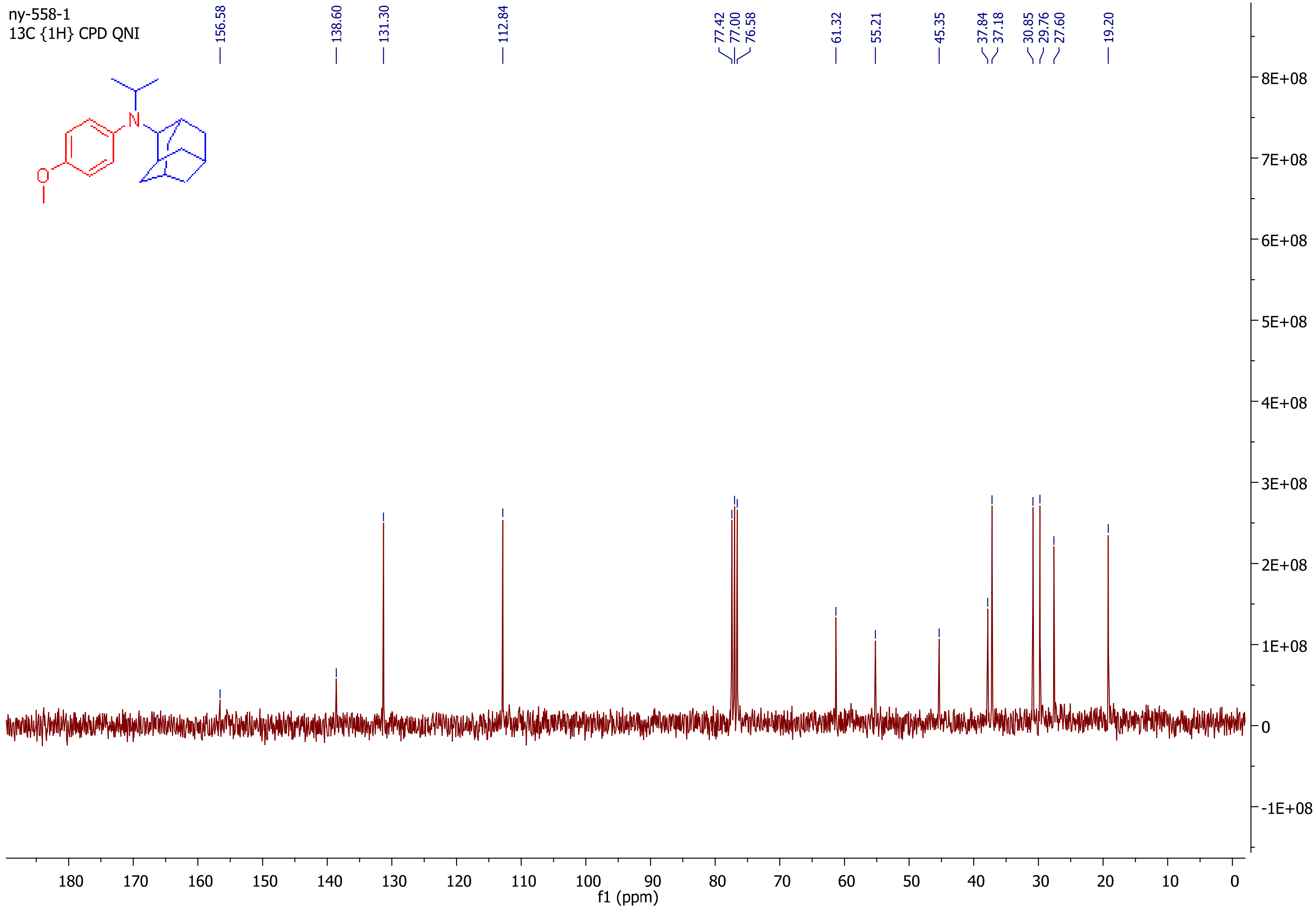
File Name	G:\IR SPECTRA\NY-479-1.TXT			***Date***	11 Dec 2014 16:07:18
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1284.65	66.776	S
2	1362.77	74.094	S
3	1378.20	76.937	S
4	1441.85	74.095	S
5	1457.28	66.698	S
6	1465.00	67.115	S
7	1471.75	74.804	S
8	1490.07	77.153	S
9	1507.43	42.229	M
10	2832.59	80.036	S
11	2855.73	68.789	S
12	2929.03	54.000	M
13	2963.75	67.681	S

(*N*-isopropyl-*N*-(4-methoxyphenyl)adamantan-2-amine (1r)




ny-558-1
13C {1H} CPD QNI
156.58
138.60
131.30
112.84
77.42
77.00
76.58
61.32
55.21
45.35
37.84
37.18
30.85
29.76
27.60
19.20
N
O
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

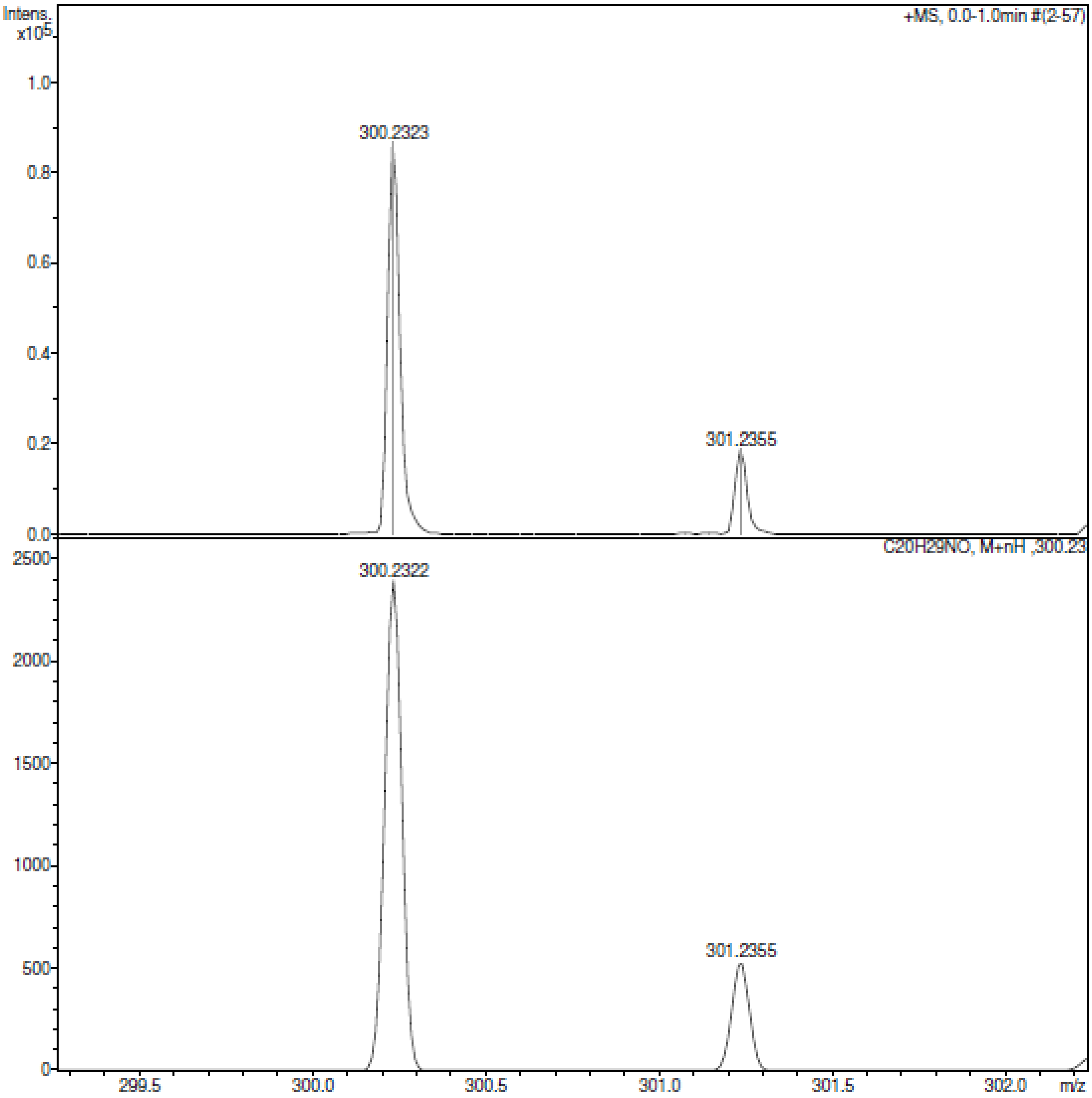
Display Report

Analysis Info

Analysis Name	D:\Data\Kolotyrkina\2014\Titov\1113004.d	Acquisition Date	13.11.2014 9:57:14
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/LB58 NY-558-1	Instrument / Ser#	micrOTOF 10248
Comment	C20H29NO mw 299 calibrant added		

Acquisition Parameter

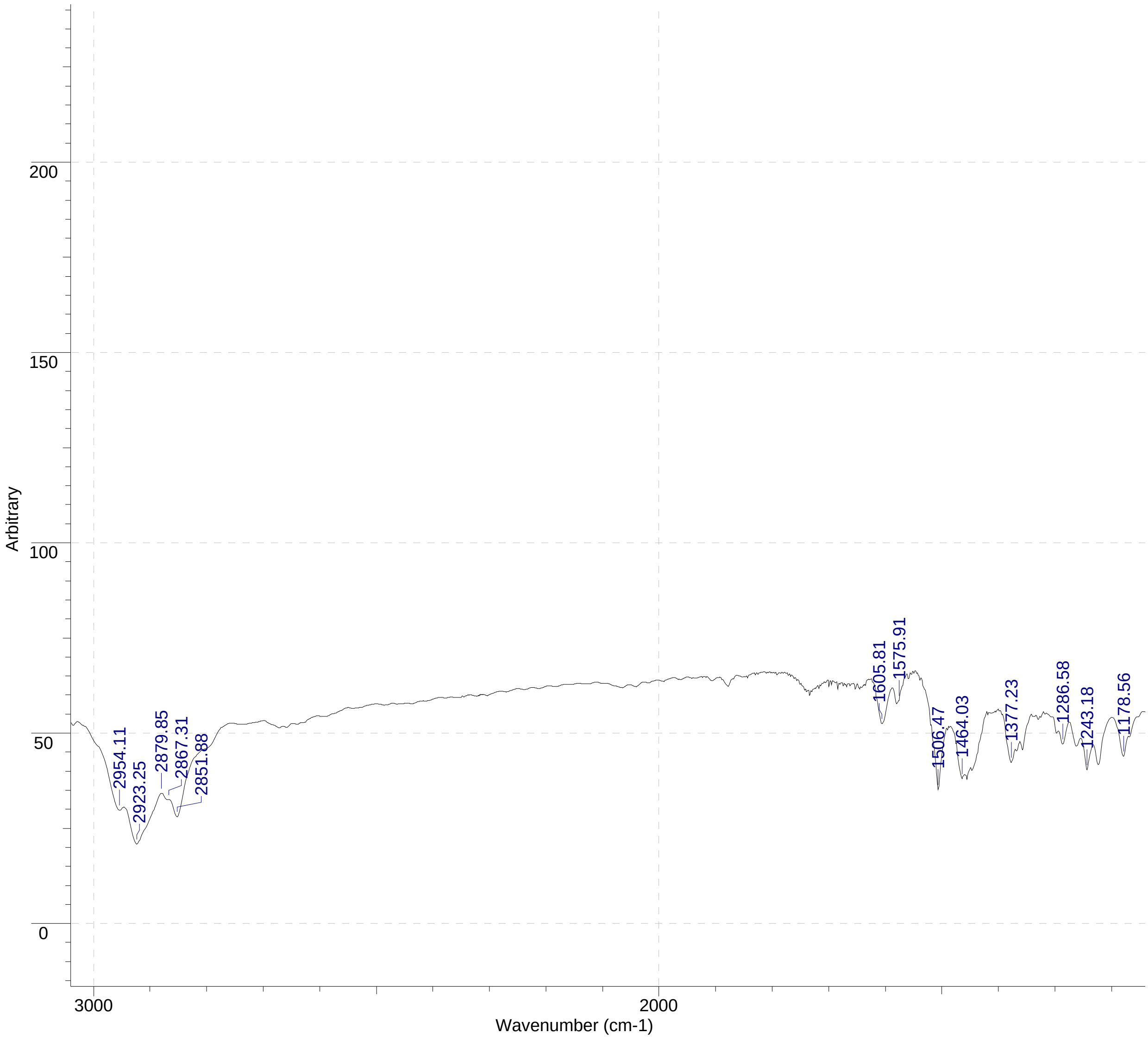
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 13.11.2014 10:02:10 Page 1 of 1

29 Jul 2015

File Name	G:\IR SPECTRA\1\NY-558-1.TXT			***Date***	16 Dec 2014 12:59:26
Technique	Infrared	***Spectral Region***	NIR-IR	***X Axis***	Wavenumber (cm-1)
Y Axis	Arbitrary	***Spectrum Range***	349.1309 - 5000.6699		
Points Count	4824	***Data Spacing***	0.9644		



No	cm-1	Arbitrary	Intensity
1	1178.56	43.927	VW
2	1243.18	40.425	VW
3	1286.58	47.167	VW
4	1377.23	42.342	VW
5	1464.03	38.014	VW
6	1506.47	35.142	VW
7	1575.91	58.506	VW
8	1605.81	52.500	VW
9	2851.88	28.046	VW
10	2867.31	32.582	VW
11	2879.85	34.220	VW
12	2923.25	20.883	VW
13	2954.11	29.721	VW