Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Total Synthesis, Configuration and Biological Evaluation of Anguinomycin C

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Experimental Part

General Methods

Unless otherwise stated, chemicals were purchased from Fluka, ABCR or Acros and used without further purification. $MeB(OH)_2$ was purchased from Lancaster. Solvents for work-up and chromatography were distilled from technical quality. Solvents used for chemical transformations were either puriss quality or dried by filtration through activated aluminium oxide under argon (H_2O content < 30 ppm, *Karl-Fischer* titration). All non-aqueous reactions were run under Ar or N_2 in dry glassware. Concentration under reduced pressure was performed by rotary evaporation at 40 °C (unless otherwise specified). Yields are based on purified, dried and spectroscopically pure compounds.

Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates (0.25 mm thickness) precoated with fluorescent indicator. The developed plates were examined under UV light and stained with ceric ammonium molybdate followed by heating.

Flash chromatography was performed using silica gel 60 (230-240 mesh) from Fluka using a forced flow eluant at 0.3-0.5 bar pressure.

All ^{1}H and ^{13}C NMR spectra were recorded using either Varian Gemini 300 MHz (^{1}H) or 75 MHz (^{13}C), Varian Mercury 300 MHz (^{1}H) or 75 MHz (^{13}C), Bruker DRX 500 MHz (^{1}H) or 125 MHz (^{13}C), Bruker DPX 400 MHz (^{1}H) or 100 MHz (^{13}C), Bruker DRX 600 MHz (^{1}H) or 150 MHz (^{13}C) FT spectrometers at room temperature, chemical shift δ given in ppm and coupling constant *J* in Hz.

Analytical gas chromatography (GC) was performed on *Hewelett Packard, HP6810. Column*: supelco β dex 120, 30 m x 0.25 mm x 0.25 μm. *Carrier gas*: H_2. *Temperature*: 120 °C isothermal. *Flow*: 2 mL/min. *Split ratio*: 40:1. *Detector*: FID.

Analytical high-performance liquid chromatography (HPLC) was performed on a *Dionex Chromatography System* (Interface Chromeleon, UV detector 170U, Pump P680, degaser). The *flow rate* was 1 ml / min and the detector wavelength was fixed at λ = 241 nm. *Column*:

Phenomenex Gemini (5 µm) (C18 (150 x 4.6 mm)), solvent A: H_2O, solvent B: MeOH).
Semi-preparative reversed-phase high-performance liquid chromatography (SP-HPLC) was performed on a *Dionex Chromatography System* (Interface Chromeleon, UV detector 170U, Pump P680, degaser). The *flow rate* was 5 ml / min and the detector wavelength was fixed at λ = 241 nm. *Column*: Phenomenex Gemini (5 µm) (C18 110A (150 x 10 mm)), solvent A: H_2O, solvent B: MeOH). All separations were performed at ambient temperature.

IR spectra were recorded as $CHCl_3$ solution using a *Varian 2000 FT-IR ATR Spectrometer* or *Varian 800 FT-IR ATR Spectrometer*. The absorptions are reported in cm^{-1} and the IR bands were assigned as *s* (strong), *m* (medium) or *w* (weak).

Optical rotations $[\alpha]^T_D$ were measured at the sodium D line using a 1 mL cell with a 1 dm path length on a Jasco DIP 1000 digital polarimeter, Jasco P-1020 digital polarimeter, Jasco P-2000 digital polarimeter and the concentration *c* is given in g/100mL and the used solvent is $CHCl_3$.

Elemental analysis were performed by Mikroanalyse Labor of the Laboratorium für Organische Chemie der ETH Zürich or by Mr. Euro Solari in the Laboratory of Supramolecular Chemistry at the EPF Lausanne.

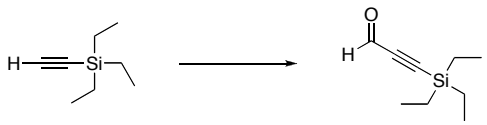
All mass spectra were recorded by the Mass spectroscopy Service of Laboratorium für Organische Chemie der ETH Zürich on VG-TRIBRID (EI-MS) spectrometer and spectra measured at 70 eV, on TSQ 7000 ESI or by the Mass spectroscopy Service of EPF Lausanne on MICROMASS (ESI) Q-TOF Ultima API. Fragment ions are given in *m/z* with relative intensities (%) in parentheses.

UV spectra were measured on a *Varian Cary 1 Bio* UV-Visible spectrophotometer in a *Starna* quartz cell (10 mm path length).

Lyophilisations were performed using a *Christ Freeze Dryer Alpha 1-2 LD plus.*

Melting points were determined using a Büchi B-545 apparatus in open capillaries and are uncorrected.

3-(Triethylsilyl)propionaldehyde (2) [1]



To a suspension of Mg (0.50 g, 20.0 mmol, 1.00 eq.) in dry THF (80 mL) was added EtBr (1.50 mL, 20.0 mmol, 1.00 eq.) and the mixture was stirred at rt until all Mg was consumed. The resultant solution was added dropwise to a solution of trimethylsilylacetylene (3.58 mL, 20.0 mmol, 1.00 eq.). The mixture was heated at reflux for 5 minutes and slowly added via canula to a solution of DMF (9.52 mL, 122 mmol, 6.10 eq.) in THF (80 mL) forming a white precipitate. The reaction was heated at reflux for 5 minutes, acidified to pH~7 with dilute HCl solution, diluted with water (200 mL) and extracted with Et_2O (3 x 100 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was diluted in Et_2O and washed with dilute $CuSO_4$ solution (pH ≈ 5) and saturated $NaHCO_3$. The organic layer was dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography on SiO_2 (cyclohexane/AcOEt 100:0 → 98:2) to give 3-(triethylsilyl)propionaldehyde **(2)** (2.98 g, 13.5 mmol, 67%) as a pale yellow oil.

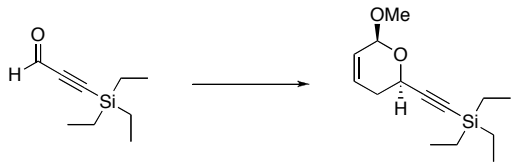
$\mathbf{R_f}$ = 0.46 (cyclohexane/AcOEt 9.5:0.5).

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.18 (s, 1 H), 1.01 (t, *J* = 7.8 Hz, 9 H), 0.68 (q, *J* = 7.8 Hz, 6 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 176.4, 103.4, 101.3, 7.3, 3.8.

IR Spectroscopy ν 2959*m*, 2915*w*, 2879*m*, 2175*w*, 1689*s*, 1670*s*, 1461*w*, 1405*w*, 1262*m*, 1236*m*, 1002*m*, 913*w* cm^{-1}.

Triethyl(((2*R*,6*S*)-6-methoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane (3)



In a 10 mL flask under Ar was added 4Å molecular sieves (1.26 g), **4** (0.30 g, 0.29 mmol, 0.02 eq., 2.3 mol%), 3-(triethylsilyl)propionaldehyde **(2)** (2.12 g, 12.6 mmol, 1.00 eq.) and 1-methoxy-1,3-butadiene (1.28 mL, 12.6 mmol, 1.00 eq.) and the mixture was stirred at rt for 18 hours. The reaction was diluted with pentane, filtered through Celite and concentrated. The residue was purified by flash chromatography on SiO_2 (pentane/Et_2O 100:0 → 98:2) to give triethyl(((2*R*,6*S*)-6-methoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane **(3)** (2.73 g, 10.8 mmol, 86%) as a colorless oil.

R_f = 0.37 (pentane/Et_2O 9.5:0.5).

Optical rotation $[\alpha]^{27.9}_D$ (*c* 0.92, $CHCl_3$) = +105.8°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.96-5.90 (m, 1 H), 5.66 (dq, J_1 = 10.3 Hz, J_2 = 1.9 Hz, 1 H), 5.01-4.98 (m, 1 H), 4.54 (dd, J_1 = 7.3 Hz, J_2 = 4.9 Hz, 1 H), 3.46 (s, 3 H), 2.42-2.20 (m, 2 H), 0,96 (t, *J* = 7.9 Hz, 9 H), 0.56 (q, *J* = 7.9 Hz, 6 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 127.5, 126.6, 105.5, 97.2, 86.1, 61.5, 55.2, 31.3, 7.5, 4.3.

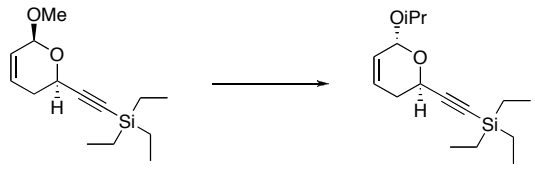
GC (β-dex chiral column) (T = 120°C): $t_{R1(minor)}$ = 42.08 minutes, $t_{R2\ (major)}$ = 43.00 minutes and *ee* = 96.2.

Elemental analysis calcd. for $C_{14}H_{24}O_2Si$: [C] 66.61 %, [H] 9.58 %, [O] 12.68 %, [Si] 11.13 %; found [C] 66.61 %, [H] 9.67 %.

ESI 275.3 (100, $[M+Na]^+$).

IR Spectroscopy ν 2956*m*, 2879*m*, 1982*w*, 1735*w*, 1336*w*, 1036*m*, 763*s*, 740*s* cm^{-1}.

Triethyl(((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane



To a solution of *p*-TsOH (76.0 mg, 0.40 mmol, 1.00 eq.) in ^{i}PrOH (1.00 mL, 0.4M) was added triethyl(((2*R*,6*S*)-6-methoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane (**3**) (100 mg, 0.40 mmol, 1.00 eq.) and the solution was stirred at rt for 2 hours. The reaction was quenched with dilute $NaHCO_3$ and extracted with Et_2O (3 x 20 mL). The organic layer was dried ($MgSO_4$), filtered and concentrated to afford triethyl(((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane (96.0 mg, 0.34 mmol, 86%) as a colorless oil which was used without further purification.

Optical rotation $[\alpha]^{28.7}_{D}$ (*c* 0.795, $CHCl_3$) = +33.7°.

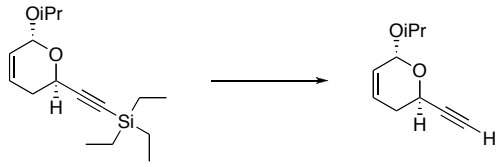
^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.96 (dd, J_1 = 10.0 Hz, J_2 = 5.4 Hz, 1 H), 5.71 (dd, J_1 = 10.1 Hz, J_2 = 1.1 Hz, 1 H), 5.14 (br. s, 1 H), 4.71 (dd, J_1 = 11.1 Hz, J_2 = 3.7 Hz, 1 H), 4.07 (sept., J = 6.2 Hz, 1 H), 2.41 (dd, J_1 = 17.7 Hz, J_2 = 11.2 Hz, 1 H), 2.23 (dd, J_1 = 17.7 Hz, J_2 = 4.1 Hz, 1 H), 1.29 (d, J = 6.2 Hz, 3 H), 1.19 (d, J = 6.1 Hz, 3 H), 1.00 (t, J = 7.8 Hz, 9 H), 0.63 (q, J = 7.8 Hz, 6 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 128.2, 126.3, 106.1, 93.4, 87.0, 70.3, 58.0, 32.1, 24.2, 24.4, 7.8, 4.7.

ESI 303.2 (100, $[M+Na]^+$).

IR Spectroscopy ν 2957*m*, 2012*m*, 2877*m*, 2186*w*, 1697*w*, 1461*w*, 1380*w*, 1317*w*, 1182*w*, 1098*w*, 1059*w*, 1024*s*, 1000*s*, 799*w*, 726*s* cm^{-1}.

(2*R*,6*R*)-2-Ethynyl-6-isopropoxy-3,6-dihydro-2*H*-pyran (5)



To a solution of triethyl(((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)ethynyl)silane (2.97 g, 10.6 mmol, 1.00 eq.) in THF (26.0 mL) was was dropwise added at 0 °C TBAF (10.6 mL, 10.6 mmol, 1.0 eq., 1.0 M in THF). The reaction was stirred for 15 minutes, warmed to rt, stirred for 1 h and quenched with water (50 mL). The mixture was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with brine (1 x 60 mL), dried ($MgSO_4$), filtered and carefully concentrated in vacuo at 0 °C. The residue was purified by flash chromatography on SiO_2 (pentane/Et_2O 100:0 → 95:5) to give (2*R*,6*R*)-2-ethynyl-6-isopropoxy-3,6-dihydro-2*H*-pyran **(5)** (1.68 g, 10.1 mmol, 95%) as a colorless volatile oil.

The analytical data matched those reported in reference [2]

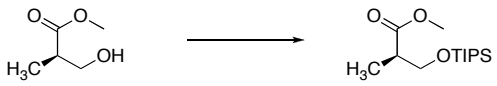
R_f = 0.45 (cyclohexane/AcOEt 9:1).

Optical rotation $[\alpha]^{26.9}_{D}$ (*c* 0.58, $CHCl_3$) = +80.6°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.93 (dd, J_1 = 10.1 Hz, J_2 = 5.7 Hz 1 H), 5.68 (ddd, J_1 = 10.2 Hz, J_2 = 2.9 Hz, J_3 = 1.3 Hz, 1H), 5.10 (br. s, 1 H), 4.67 (dddd, J_1 = 11.2 Hz, J_2 = 3.7 Hz, J_3 = 2.2 Hz, J_4 = 0.6 Hz, 1 H), 4.03 (sept., *J* = 6.3 Hz, 1 H), 2.44 (d, *J* = 2.2 Hz, 1 H), 2.37 (ddd, J_1 = 11.2 Hz, J_2 = 4.3 Hz, J_3 = 2.1 Hz, J_4 = 0.6 Hz, 1H), 2.19 (dddd, J_1 = 17.8 Hz, J_2 = 5.2 Hz, J_3 = 3.8 Hz, J_4 = 1.3 Hz, 1 H), 1.25 (d, *J* = 6.2 Hz, 3 H), 1.16 (d, *J* = 6.2 Hz, 3 H).

IR Spectroscopy ν 3306*m*, 2971*m*, 2928*m*, 2053*w*, 1736*w*, 1380*w*, 1184*w*, 1023*m*, 1002*w*, 784*s* cm^{-1}.

(*R*)-methyl 2-methyl-3-(triisopropylsilyloxy)propanoate



To a cooled (0 °C) solution of (*R*)-methyl-3-hydroxy-2-methyl propionate (1.50 mL, 13.6 mmol, 1.00 eq.) in CH_2Cl_2 (13.6 mL) were added imidazole (2.04 g, 30.0 mmol, 2.20 eq.), TIPSCl (4.10 mL, 19.0 mmol, 1.40 eq.), DMAP (cat.). The reaction was allowed to return to RT and stirred overnight. The reaction was diluted with CH_2Cl_2, washed with diluted HCl (pH = 3) (3x), H_2O (2x), dried ($MgSO_4$). Purification by flash chromatography on SiO_2 (cyclohexane/EtOAc 9.5:0.5) afford (*R*)-methyl 2-methyl-3-(triisopropylsilyloxy)propanoate (3.73 g, 13.6 mmol, quant.) as a colorless oil.

R_f = 0.53 (cyclohexane/AcOEt 9:1).

Optical rotation $[\alpha]^{24.1}{}_D$ (*c* 1.00, $CHCl_3$) = -19.6°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.85 (dd, J_1 = 9.4 Hz, J_2 = 6.7 Hz, 1 H), 3.75 (dd, J_1 = 9.4 Hz, J_2 = 6.0 Hz, 1 H), 3.66 (s, 3 H), 2.72-2.60 (m, 1 H), 1.15 (d, *J* = 7.0 Hz, 3 H), 1.05-1.00 (m, 21 H).

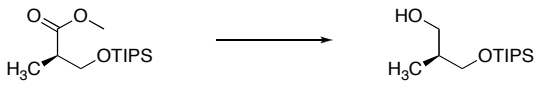
^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.7, 65.8, 51.6, 42.8, 18.1, 13.6, 12.1.

Elemental analysis calcd. for $C_{14}H_{30}O_3Si$: [C] 61.26 %, [H] 11.02 %, [O] 17.49 %, [Si] 10.23 %; found [C] 61.53 %, [H] 10.78 %.

MS EI calcd. for $C_{11}H_{23}O_3Si$: $[M\text{-}C_3H_7]^+$ 231.1411; found 231.1410.

IR Spectroscopy ν 2943*s*, 2867*s*, 1743*s*, 1463*m*, 1435*w*, 1389*w*, 1250*m*, 1198*m*, 1176*m*, 1105*s*, 1068*m*, 1027*w*, 882*m*, 797*w*, 682*m* cm^{-1}.

(*S*)-2-methyl-3-(triisopropylsilyloxy)propan-1-ol



To a cooled (-78 °C) solution of (*R*)-methyl 2-methyl-3-(triisopropylsilyloxy)propanoate (12.35 g, 45.0 mmol, 1.00 eq.) in CH_2Cl_2 (230 mL), DIBAL-H (78.0 mL, 78.0 mmol, 2.00 eq, 1.0 M in hexanes) was added dropwise. The mixture was stirred for 1 hour at -78 °C, then between -20 °C and -15 °C for 30 minutes. The reaction was quenched by addition of MeOH and saturated Rochelle's salt. The mixture was vigorously stirred at RT for 1 hour. The aqueous phase was extracted with CH_2Cl_2 (3x) and the combined organic layers washed with brine (1x), dried ($MgSO_4$) and concentrated. Purification by flash chromatography on SiO_2 (cyclohexane/EtOAc 9.5:0.5 → 7:3) afford (*S*)-2-methyl-3-(triisopropylsilyloxy)propan-1-ol (9.30 g, 37.7 mmol, 84%) and (*R*)-2-methyl-3-(triisopropylsilyloxy)propanal (1.78 g, 7.3 mmol, 16%) as a colorless oils.

R_f = 0.56 (hexane/AcOEt 8:2).

Optical rotation $[\alpha]^{25.0}_{D}$ (*c* 0.25, $CHCl_3$) = -6.8°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.87 (dd, J_1 = 9.7 Hz, J_2 = 4.3 Hz, 1 H), 3.69-3.62 (m, 3 H), 3.03 (br. s, 1 H), 2.07-1.96 (m, 1 H), 1.17-1.03 (m, 21 H), 0.86 (d, *J* = 7.0 Hz, 3 H).

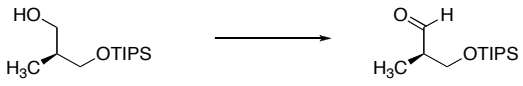
^{13}C-NMR (100 MHz, $CDCl_3$) δ 69.9, 69.0, 37.5, 18.3, 13.4, 12.1.

Elemental analysis calcd. for $C_{13}H_{30}O_2Si$: [C] 63.35 %, [H] 12.27 %, [O] 12.98 %, [Si] 11.40 %; found [C] 63.55 %, [H] 12.13 %.

MS EI calcd. for $C_{10}H_{23}O_2Si$: $[M\text{-}C_3H_7]^+$ 203.1462; found 203.1464.

IR Spectroscopy ν 3368*m*, 2943*s*, 2866*s*, 1463*m*, 1384*w*, 1247*w*, 1096*s*, 1035*s*, 995*m*, 881*s*, 791*m*, 680*s*, 668*s*, 659*m* cm^{-1}.

(*R*)-2-methyl-3-(triisopropylsilyloxy)propanal



To a cooled (15 °C) solution of (*S*)-2-methyl-3-(triisopropylsilyloxy)propan-1-ol (10.1 g, 40.9 mmol, 1.00 eq.) in DMSO (225 mL) was sequentially added Et_3N (13.7 mL, 98.2 mmol, 2.40 eq) and pyridine sulfur trioxide (13.0 g, 81.8 mmol, 2.00 eq.). The solution was stirred for 5 minutes at 15 °C, then allowed to return to RT and stirred for 1.5 hours. The solution was cooled with an ice bath, quenched by addition of water (300 mL), diluted with hexane (750 mL) and stirred for 2 hours at RT. The aqueous layer was extracted with hexane (3x) and the combined organic layer washed with water (1x) and brine (1x), dried ($MgSO_4$) and concentrated. Purification by chromatography on SiO_2 (cyclohexane/EtOAc 97:3) afford (*R*)-2-methyl-3-(triisopropylsilyloxy)propanal (10.0 g, 40.9 mmol, quant.) as a colorless oil.

R_f = 0.83 (hexane/AcOEt 8:2).

Optical rotation $[\alpha]^{25.0}_{D}$ (*c* 0.45, $CHCl_3$) = -35.6°.

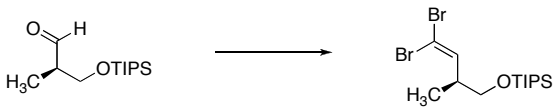
^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.80 (d, *J* = 1.5 Hz, 1 H), 4.00 (dd, J_1 = 10.0 Hz, J_2 = 5.1 Hz, , 1 H), 3.92 (dd, J_1 = 9.9 Hz, J_2 = 6.4 Hz, 1 H), 2.61-2.53 (m, 1 H), 1.13 (d, *J* = 7.0 Hz, 3 H), 1.10-1.05 (m, 21 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.2, 64.4, 49.5, 18.4, 12.3, 10.7.

MS EI calcd. for $C_{13}H_{28}O_2NaSi$: $[M\text{-}Na]^+$ 267.1756; found 267.1762.

IR Spectroscopy ν 2961*m*, 2930*m*, 2858*m*, 1782*m*, 1696*m*, 1461*w*, 1384*m*, 1251*w*, 1204*m*, 1100*w*, 1054*w*, 835*w*, 773*w* cm^{-1}.

(*S*)-(4,4-dibromo-2-methylbut-3-enyloxy)triisopropylsilane (6)



To a cooled (0 °C) solution of CBr_4 (16.0 g, 48.2 mmol, 2.20 eq.) in CH_2Cl_2 (87 mL), PPh_3 (25.3 g, 96.3 mmol, 4.40 eq.) was added in portion over 2 minutes. The solution turn from clear to brown and after 15 minutes at 0 °C, a solution of (*R*)-2-methyl-3-(triisopropylsilyloxy)propanal (5.35 g, 21.9 mmol, 1.00 eq.) and 2,6-lutidine (5.61 mL, 48.2 mmol, 2.20 eq.) in CH_2Cl_2 (87 mL) was added by canula over 20 minutes. The resulting dark-brown mixture was stirred at 0 °C for 2.5 hours. The reaction was quenched by addition of saturated NH_4Cl and stirred for 30 minutes at RT. The aqueous layer was extracted with CH_2Cl_2 (2x) and the combined organic layer washed with saturated $NaHCO_3$ (1x) and brine (1x), dried ($MgSO_4$) and concentrated. The residue was triturated in hexane and the filtered concentrated. Purification by flash chromatography on SiO_2 (hexane 100%) afford (*S*)-(4,4-dibromo-2-methylbut-3-enyloxy)triisopropylsilane **(6)** (5.58 g, 14.0 mmol, 64%) as a colorless oil.

The analytical data matched those reported in reference [3]

R_f = 0.47 (hexane 100%).

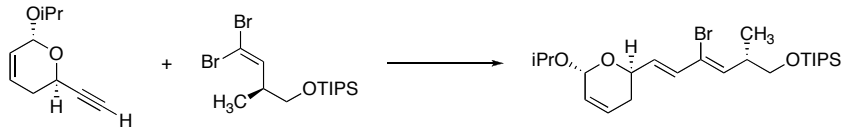
Optical rotation $[\alpha]^{27.6}_{D}$ (*c* 0.90, $CHCl_3$) = +12.9°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.31 (d, J = 9.2 Hz, 1 H), 3.62 (dd, J_1 = 9.5 Hz, J_2 = 5.8 Hz, 1 H), 3.58 (dd, J_1 = 9.5 Hz, J_2 = 5.8 Hz, 1 H), 2.71-2.58 (m, 1 H), 1.06-1.05 (m, 24 H).

Elemental analysis calcd. for $C_{17}H_{31}Br_2OSi$: [C] 42.01 %, [H] 7.05 %, [O] 4.00 %, [Si] 7.02 %, [Br] 39.93 %; found [C] 42.06 %, [H] 7.07 %, [Br] 40.02 %.

MS EI calcd. for $C_{14}H_{28}Br_2OSi$: $[M\text{-}C_3H_7]^+$ 354.9723; found 354.9720.

((*S*,3*Z*,5*E*)-4-bromo-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2-methylhexa-3,5-dienyloxy)triisopropylsilane (7)



To a cooled (0 °C) solution of (2*R*,6*R*)-2-ethynyl-6-isopropoxy-3,6-dihydro-2*H*-pyran **(5)** (200 mg , 1.20 mmol, 1.00 eq.) in THF (6.00 mL, 0.2 M vs **5**) was added Cp_2ZrHCl (374 mg, 1.44 mmol, 1.20 eq.). The flask was covered with an aluminium foil, stirred for 5 min at 0 °C and 45 minutes at rt. In a separate flask $ZnCl_2$ (229 mg, 1.68 mmol, 1.40 eq.) was fused and dissolved in THF (8.40 mL) and the solution was added to the solution of alkenylzirconocene at 0°C and the reaction was stirred at rt for 30 minutes. In a separate flask, to a mixture of $Pd(PPh_3)_4$ (70.0 mg, 0.06 mmol, 0.05 eq., 5 mol %) in THF (6.00 mL, 0.2 M vs **6**) was added DIBAL-H (10% in hexane) (120 µL, 0.12 mmol, 0.10 eq., 10 %) and the mixture was stirred 30 minutes at rt and then (*S*)-(4,4-dibromo-2-methylbut-3-enyloxy)triisopropylsilane **(6)** (481 mg , 1.20 mmol, 1.00 eq.) was added. The dibromoolefin solution was stirred for 5 minutes at rt and then was added to the organozinc solution. The mixture was stirred 5 minutes at rt and then 10 hours at 40 °C. The reaction was quenched with water (30 mL) and extracted with Et_2O (3 x 40 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography on SiO_2 (cyclohexane/EtOAc 97.5:2.5) to give ((*S*,3*Z*,5*E*)-4-bromo-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2-methylhexa-3,5-dienyloxy)triisopropylsilane (**7**) (472 mg, 0.97 mmol, 81%) as a colorless oil.

R_f = 0.39 (CH_2Cl_2/cyclohexane 7:3).

Optical rotation $[\alpha]^{25.0}_D$ (*c* 0.97, $CHCl_3$) = +50.0°.

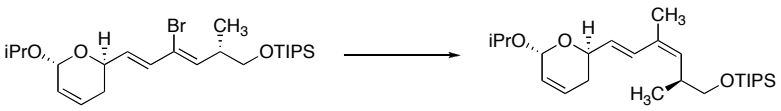
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.28 (dd, J_1 = 14.8 Hz, J_2 = 1.2 Hz, 1 H), 6.07 (dd, J_1 = 14.8 Hz, J_2 = 5.3 Hz, 1 H), 6.02-5.97 (m, 1 H), 5.88 (d, J = 8.9 Hz, 1 H), 5.72 (ddd, J_1 = 10.0 Hz, J_2 = 4.3 Hz, J_3 = 2.6 Hz, 1 H), 5.12 (d, J = 2.8 Hz, 1 H), 4.58-4.51 (m, 1 H), 4.00 (sept., J = 6.2 Hz, 1 H), 3.61 (ddd, J_1 = 15.8 Hz, J_2 = 9.4 Hz, J_3 = 5.8 Hz, 2 H), 2.99-2.86 (m, 1 H), 2.10-2.05 (m, 2 H), 1.22 (d, J = 6.2 Hz, 3 H), 1.17 (d, J = 6.1 Hz, 3 H), 1.05 (s, 24 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 137.3, 133.4, 129.3, 128.2, 126.0, 124.0, 93.1, 69.6, 66.8, 65.7, 39.5, 30.9, 24.0, 22.1, 18.1, 16.2, 12.1.

MS EI calcd. for $C_{44}H_{43}BrO_3Si$: $[M\text{-}C_3H_7]^+$ 443.1612; found 443.1610.

IR Spectroscopy ν 2942*m*, 2893*m*, 2866*m*, 1463*w*, 1383*w*, 1180*w*, 1102*m*, 1028*s*, 1000*m*, 952*w*, 883*w*, 787*m*, 684*m* cm^{-1}.

((*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dienyloxy)triisopropylsilane (8)



To a solution of ((*S*,3*Z*,5*E*)-4-bromo-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2-methylhexa-3,5-dienyloxy)triisopropylsilane **(7)** (100 mg , 0.23 mmol, 1.00 eq.) in THF (1.00 mL, 0.23 M vs 16) was added $Pd(PPh_3)_4$ (24.0 mg, 0.02 mmol, 0.10 eq,). The solution was stirred for 10 minutes at rt, treated with Me_2Zn (0.21 mL, 0.42 mmol, 2.00 eq., 2.0 M in toluene) and the reaction was stirred at 45 °C for 24 hours. An additional portion of Me_2Zn (0.10 mL, 0.21 mmol, 1.00 eq.) was added and the solution was stirred at 45 °C for 14 hours. The reaction was quenched with dilute NH_4Cl and extracted with Et_2O (3 x 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography on SiO_2 (CH_2Cl_2/cyclohexane 7:3) to afford ((*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dienyloxy)triisopropylsilane **(8)** (66.3 mg, 0.16 mmol, 68%) as a colorless oil.

R_f = 0.21 (CH_2Cl_2/cyclohexane 7:3).

Optical rotation $[\alpha]^{28.2}_D$ (*c* 0.62, $CHCl_3$) = +37.9°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.69 (d, J = 15.7 Hz, 1 H), 6.01 (dddd, J_1 = 7.7 Hz, J_2 = 5.3 Hz, J_3 = 1.9 Hz, J_4 = 0.9 Hz, 1 H), 5.77-5.67 (m, 2 H), 5.19 (d, J = 9.6 Hz, 1 H), 5.13-5.12 (m, 1 H),

4.54-5.47 (m, 1 H), 4.02 (sept., J = 6.2 Hz, 1 H), 3.50 (ddd, J_1 = 16.9 Hz, J_2 = 9.4 Hz, J_3 = 6.5 Hz, 2 H), 2.87-2.74 (m, 1 H), 2.20-2.00 (m, 2 H), 1.82 (d, J = 1.2 Hz, 3 H), 1.24 (d, J = 6.2 Hz, 3 H), 1.18 (d, J = 6.1 Hz, 3 H), 1.05-1.04 (m, 24 H).

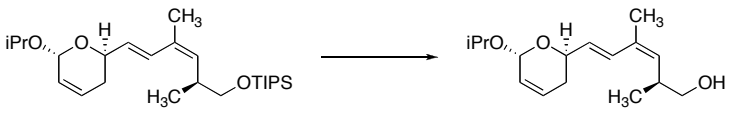
^{13}C-NMR (75 MHz, $CDCl_3$) δ 134.2, 131.3, 129.3, 128.4, 128.1, 126.0, 93.0, 69.4, 68.0, 66.9, 34.9, 30.7, 23.8, 21.9, 20.4, 17.9, 17.5, 11.9.

Elemental analysis calcd. for $C_{25}H_{46}O_3Si$: [C] 71.03, [H] 10.97, [O] 11.35, [Si] 6.64; found [C] 71.11, [H] 10.99.

MS EI calcd. for $C_{25}H_{46}O_3Si$: $[M]^+$ 422,3211; found 422.3219.

IR Spectroscopy ν 2942*m*, 2867*m*, 1462*w*, 1382*w*, 1182*w*, 1122*w*, 1101*w*, 1029*m*, 1000*w*, 780*s*, 683*m* cm^{-1}.

(*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dien-1-ol



To a cooled (0 °C) solution of ((*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dienyloxy)triisopropylsilane **(8)** (13.8 mg , 0.03 mmol, 1.00 eq.) in THF (160 μL) was added TBAF (1.0 M in THF) (64 μL, 0.06 mmol, 2.00 eq.). The reaction was stirred 1 hour at 0 °C and then 1 hour at RT. The reaction was quenched with water and extracted with Et_2O (3x). The combined organic layers were dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography on SiO_2 (hexane/AcOEt 8:2) to give (*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dien-1-ol (8.4 mg, 0.03 mmol, 99%) as a colorless oil.

R_f = 0.19 (CH_2Cl_2/AcOEt 9:1).

Optical rotation $[\alpha]^{28.9}_{D}$ (*c* 0.49, $CHCl_3$) = +29.2°.

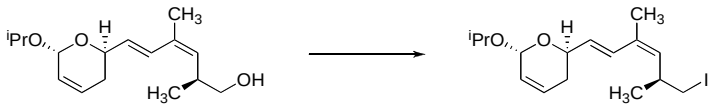
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.69 (d, *J* = 15.7 Hz, 1 H), 6.01 (ddd, J_1 = 10.0 Hz, J_2 = 4.7 Hz, J_3 = 2.1 Hz, 1 H), 5.77 (dd, J_1 = 15.8 Hz, J_2 = 6.0 Hz, 1 H), 5.76-5.70 (m, 1 H), 5.17-5.12 (m, 2 H), 4.52 (dt, J_1 = 10.3 Hz, J_2 = 5.3 Hz, 1 H), 4.01 (sept., *J* = 6.2 Hz, 1 H), 3.54-3.35 (m, 2 H), 2.94-2.79 (m, 1 H), 2.19-2.00 (m, 2 H), 1.86 (s, 3 H), 1.24 (d, *J* = 6.2 Hz, 3 H), 1.18 (d, *J* = 6.2Hz, 3 H), 0.97 (d, *J* = 6.7 Hz, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 133.6, 130.5, 128.5, 127.9, 127.8, 126.3, 93.3, 69.8, 67.9, 66.9, 34.9, 30.9, 24.0, 22.2, 20.8, 17.3.

MS EI calcd. for $C_{16}H_{26}O_3$: $[M]^+$ 266.1877; found 266.1869.

IR Spectroscopy ν 3416*m*, 2970*m*, 2925*m*, 1455*w*, 1379*w*, 1317*w*, 1126*w*, 1100*m*, 1027*s*, 999*s*, 774*m*, 670*m* cm^{-1}.

(2*R*,6*R*)-2-((*S*,1*E*,3*Z*)-6-iodo-3,5-dimethylhexa-1,3-dienyl)-6-isopropoxy-3,6-dihydro-2*H*-pyran (9)



To a cooled (0 °C) solution of (*S*,3*Z*,5*E*)-6-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-2,4-dimethylhexa-3,5-dien-1-ol (4.0 mg , 0.015 mmol, 1.00 eq.) in a mixture toluene/Et_2O (375 μL/100μL), imidazole (14.4 mg, 0.21 mmol, 14.1 eq.) and PPh_3 (21.2 mg, 0.08 mmol, 5.4 eq.) were added and the resulting mixture stirred at 0 °C for 15 minutes. A solution of I_2 (19.8 mg, 0.078 mmol, 5.2 eq.) in Et_2O (375 μL) was added dropwise and the resulting mixture covered by an aluminium foil, stirred 10 minutes at 0 °C and then 2 hours at RT. The mixture was directly filtered over cotton and concentrated. The residue was diluted in pentane, the precipitate filtered and the filtrated concentrated. Purification by chromatography on SiO_2 (hexane/EtOAc 100:0 → 99:1) afford (2*R*,6*R*)-2-((*S*,1*E*,3*Z*)-6-iodo-3,5-dimethylhexa-1,3-dienyl)-6-isopropoxy-3,6-dihydro-2*H*-pyran **(9)** (4.2 mg, 0.011 mmol, 75%) as a colorless oil.

R_f = 0.48 (hexane/AcOEt 8.5:1.5).

Optical rotation $[\alpha]^{25.0}_{D}$ (*c* 0.11 , $CHCl_3$) = +6.4°.

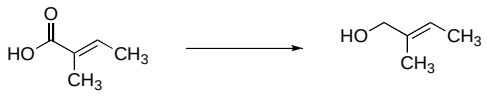
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 15.7 Hz, 1 H), 6.05-6.02 (m, 1 H), 5.80 (dd, J_1 = 15.7 Hz, J_2 = 5.8 Hz, 1 H), 5.77-5.75 (m, 1 H), 5.17 (d, *J* = 9.5 Hz, 1 H), 5.16 (s, 1 H), 4.58-4.53 (m, 1 H), 4.05 (sept., *J* = 6.2 Hz, 1 H), 3.17 (dd, J_1 = 9.4 Hz, J_2 = 5.7 Hz, 1 H), 3.09 (dd, J_1 = 9.4 Hz, J_2 = 7.3 Hz, 1 H), 2.92-2.82 (m, 1 H), 2.20-2.03 (m, 2 H), 1.87 (s, 3 H), 1.29 (d, *J* = 6.1 Hz, 3 H), 1.22 (d, *J* = 6.1 Hz, 3 H), 1.13 (d, *J* = 6.6 Hz, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.3, 132.7, 131.1, 128.6, 128.0, 126.7, 93.7, 70.1, 67.2, 34.4, 31.2, 24.3, 22.5, 21.9, 20.7, 15.2.

MS EI calcd. for $C_{16}H_{25}O_2NaI$: $[M + Na]^+$ 399.0797; found 399.0801.

IR Spectroscopy ν 3322*w*, 2968*w*, 2924*w*, 1659*w*, 1377*w*, 1454*w*, 1377*w*, 1180*w*, 1099*w*, 1028*m*, 1000*m*, 785*s* cm^{-1}.

(*E*)-2-methylbut-2-en-1-ol

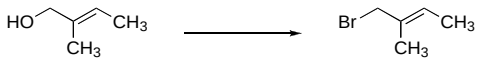


In a 1L three-necked round bottom flask condenser equipped a suspension of $LiAlH_4$ (19.2 g, 510 mmol, 2.05 eq.) in Et_2O (100 mL) was cooled to 0 °C and a solution of tiglic acid (24.7 g, 246 mmol, 1.00 eq.) was slowly added over a period of 1 hours. The resulting solution was stirred 15 minutes at 0 °C and then 3 hours at RT. The reaction was cooled to 0 °C and quenched by carefully addition of H_2O (18 mL), NaOH (15 %) (18 mL) and H_2O (54 mL). The white granular aluminum salts were filtered over celite and washed with Et_2O (3x). The combined organic layers were washed with HCl (1N) (1x), $NaHCO_3$ (sat.) (1x) and brine (1x), dried ($MgSO_4$) and concentrated to afford (*E*)-2-methylbut-2-en-1-ol (18.2 g, 211 mmol, 86%) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.51-5.44 (m, 1 H), 3.98 (m, 2 H), 1.65 (s, 3 H), 1.62-1.59 (m, 3 H).

IR Spectroscopy ν 3335*s*, 2919*m*, 2863*m*, 1674*w*, 1447*w*, 1381*w*, 1003*s*, 829*w*, 774*w*, 668*m* cm^{-1}.

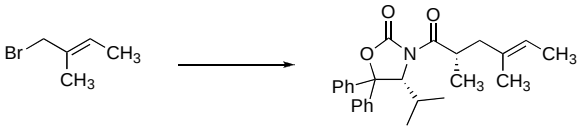
(*E*)-1-bromo-2-methylbut-2-ene



A solution of (*E*)-2-methylbut-2-en-1-ol (1.00 g, 11.6 mmol, 1.00 eq.) in Et_2O (23.0 mL, 0.5 M) was cooled to 0 °C and PBr_3 (0.55 mL, 5.80 mmol, 0.50 eq.) was added dropwise. The resulting solution was stirred at 0 °C for 30 minutes and then at RT for 3 hours. The reaction was quenched and washed with an aqueous K_2CO_3 solution (1x) and brine (1x), dried ($MgSO_4$) and carefully concentrated under reduce pressure to afford (*E*)-1-bromo-2-methylbut-2-ene (1.25 g, 8.41 mmol, 73%) as a colorless oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.73-5.65 (m, 1 H), 3.98 (m, 2 H), 1.76-1.75 (m, 3 H), 1.63 (ddd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, J_3 = 0.8 Hz, 3 H).

(*R*)-3-((*S*,*E*)-2,4-dimethylhex-4-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one (11)



In a 1L double-necked round bottom flask a solution of DIPA (11.7 mL, 89.0 mmol, 1.25 eq.) in THF (200 mL) was cooled to 0 °C and n-BuLi (1.6 M in hexane) (55.7 mL, 89.0 mmol, 1.25 eq.) was slowly added. The resulting solution was stirred at 0 °C for 30 minutes and then cooled to -78 °C. A precooled solution of **10** (24.0 g, 71.0 mmol, 1.00 eq.) in THF (130 mL) was slowly added and the resulting mixture stirred at -78 °C for 30 minutes followed by the slowly addition of a precooled solution of (*E*)-1-bromo-2-methylbut-2-ene (22.2 g, 149 mmol, 2.10 eq.) in THF

(60 mL). The reaction was stirred at -78 °C was continued for 5 minutes and then allowed to warm up to -10 °C where stirring was continued for 26 hours. The reaction was quenched by addition of saturated NH_4Cl solution and extracted with Et_2O (3x). The combined organic layers were dried ($MgSO_4$) and concentrated. The crude pale yellow solid was washed with a small amount of ice-cold pentane to afford (*R*)-3-((*S*,*E*)-2,4-dimethylhex-4-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one **(11)** (26.4 g, 65.0 mmol, 92%, dr > 97:3) as a white crystalline solid.

R_f = 0.50 (cyclohexane/EtOAc 9:1)

M.p. = 101-103 °C

Optical rotation $[\alpha]^{28.3}_{D}$ (*c* 1.00, $CHCl_3$) = +177.0°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2 H), 7.42-7.26 (m, 8 H), 5.40 (d, *J* = 3.2 Hz, 1H), 5.30-5.22 (m, 1 H), 3.90 (sext., *J* = 7.2 Hz, 1 H), 2.54 (dd, J_1 = 13.4 Hz, J_1 = 7.2 Hz, 1 H), 2.01-1.89 (m, 2 H), 1.64 (m, 3 H), 1.55 (dd, J_1 = 6.7 Hz, J_2 = 1.0 Hz, 3 H), 0.85 (d, *J* = 7.0 Hz, 3 H), 0.79 (d, *J* = 6.8 Hz, 3 H), 0.74 (d, *J* = 6.7 Hz, 3 H).

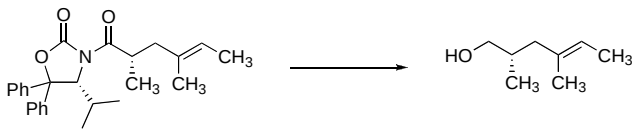
^{13}C-NMR (75 MHz, $CDCl_3$) δ 176.7, 152.7, 142.2, 138.0, 132.8, 128.6, 128.4, 128.2, 127.7, 125.7, 125.5, 120.9, 89.0, 64.2, 43.6, 35.3, 29.6, 21.5, 16.1, 16.0, 15.3, 13.2.

Elemental analysis calcd. for $C_{26}H_{31}NO_3$: [C] 77.01 %, [H] 7.70 %, [N] 3.45 %; found: [C] 76.79 %, [H] 7.67 %, [N] 3.52 %.

HRMS EI calcd. for $[C_{26}H_{31}NO_3]^+$ $[M]^+$: 405.2299; found 405.2301.

IR Spectroscopy ν 2968*w*, 2934*w*, 2888*w*, 1776*s*, 1698*s*, 1495*w*, 1450*m*, 1385*m*, 1371*m*, 1348*m*, 1312*m*, 1246*m*, 1207*s*, 1174*s*, 1149*m*, 1123*m*, 1094*m*, 1056*m*, 1035*w*, 986*s*, 949*m*, 764*s*, 750*s*, 703*s*, 694*s*, 668*s*, 636*m* cm^{-1}.

(*S*,*E*)-2,4-dimethylhex-4-en-1-ol



To a cooled (0 °C) suspension of $LiAlH_4$ (1.56 g, 41.2 mmol, 8 eq.) in Et_2O (20 mL), a solution of (*R*)-3-((*S*,*E*)-2,4-dimethylhex-4-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one **(11)** (2.09 g, 5.15 mmol, 1 eq.) in Et_2O (48 mL) was slowly added. The resulting solution was stirred 30 minutes at 0 °C and then 3 hours at RT. The reaction was cooled to 0 °C and quenched by addition of H_2O (3 mL), NaOH (15 %) (3 mL) and H_2O (9 mL). The white granular aluminum salts were filtered over celite and washed with Et_2O (3x). The combined organic layers were dried ($MgSO_4$) and concentrated to afford (*S*,*E*)-2,4-dimethylhex-4-en-1-ol (0.66 g, 5.15 mmol, 100%) as a colorless oil.

The analytical data matched those reported in reference [4]

R_f = 0.19 (cyclohexane/EtOAc 8.5:1.5)

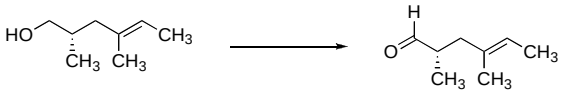
Optical rotation $[\alpha]^{24.6}_{D}$ (*c* 0.55, $CHCl_3$) = -4.7°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.24 (qd, J_1 = 6.6 Hz, J_2 = 1.2 Hz, 1 H), 3.52-3.39 (m, 2 H), 2.11-2.02 (m, 1 H), 1.89-1.77 (m, 2 H), 1.61-1.57 (m, 6 H), 0.86 (d, *J* = 6.5 Hz, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 134.3, 120.1, 68.5, 44.3, 33.7, 16.8, 15.7, 13.5.

IR Spectroscopy ν 3320*m*, 2917*m*, 1456*w*, 1037*m*, 786*s*, 668*w* cm^{-1}.

(*S*,*E*)-2,4-dimethylhex-4-enal (12)



To a cooled (-78 °C) solution of $(COCl)_2$ (867 µL, 9.94 mmol, 2.00 eq.) in CH_2Cl_2 (10.5 mL) a solution of DMSO (1.41 mL, 20.0 mmol, 4.00 eq.) in CH_2Cl_2 (10.5 mL) was added dropwise. After 5 minutes a solution of (*S*,*E*)-2,4-dimethylhex-4-en-1-ol (637 mg, 4.97 mmol, 1.00 eq.) in CH_2Cl_2 (10.0 mL) was slowly added. Stirring at -78 °C was continued 15 minutes, followed by addition of a solution of NEt_3 (4.16 mL, 29.8 mmol, 6 eq.) in CH_2Cl_2 (10.5 mL). The resulting solution was stirred at -78 °C for 20 minutes and then at 0 °C for 30 minutes. The reaction was quenched by addition of buffer phosphate (pH = 7) (32 mL) and the solution stirred at RT for further 15 minutes. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3x). The combined organic layers were washed with water (2x) and brine (1x), dried ($MgSO_4$) and concentrated. Purification by chromatography on SiO_2 (CH_2Cl_2/cyclohexane 7:3) afford (*S*,*E*)-2,4-dimethylhex-4-enal **(12)** (619 mg, 4.91 mmol, 99%) as a colorless oil.

The analytical data matched those reported in reference [4]

R_f = 0.42 (pentane/Et_2O 9.5:0.5)

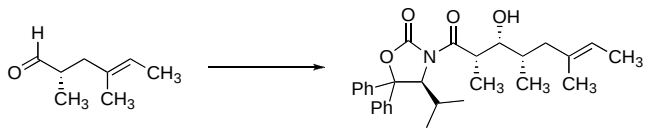
Optical rotation $[\alpha]^{22.0}_D$ (*c* 0.93, $CHCl_3$) = +9.9°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 9.61 (d, *J* = 2.1 Hz, 1 H), 5.29-5.23 (m, 1 H), 2.57-2.45 (m, 1 H), 2.41 (dd, J_1 = 13.4 Hz, J_2 = 6.6, Hz, 1 H), 1.98 (dd, J_1 = 13.7 Hz, J_2 = 7.7 Hz, 1 H), 1.59 (s, 3 H), 1.58 (d, *J* = 7.0 Hz, 3 H), 1.03 (d, *J* = 6.8 Hz, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 205.5, 132.2, 121.6, 44.5, 40.9, 15.7, 13.5, 13.3.

IR Spectroscopy ν 2922*m*, 1708*w*, 1442*w*, 1378*w*, 777*s* cm^{-1}.

(*S*)-3-((2*S*,3*R*,4*S*,*E*)-3-hydroxy-2,4,6-trimethyloct-6-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one (13)



To a cooled (-5°C) solution of *ent*-**10** (84.4 mg, 0.25 mmol, 1.00 eq.) in CH_2Cl_2 (0.30 mL), Bu_2BOTf (1M) (263 µL, 0.26 mmol, 1.05 eq.) was slowly added and the solution turn from colorless to pale green colored. NEt_3 (42 µL, 0.30 mmol, 1.20 eq.) was slowly added over a period of 5 minutes and the solution turn to pale yellow. Stirring at 0 °C was continued for 1 hours. The resulting solution was cooled to -78 °C and (*S*,*E*)-2,4-dimethylhex-4-enal **(12)** (63 mg, 0.50 mmol, 2.00 eq.) in CH_2Cl_2 (0.20 mL) was slowly added and the mixture stirred for 1 hour at -78 °C and finally for 1 further hour at 0 °C. The reaction was quenched at 0 °C by sequentially addition of buffer phosphate (pH = 7) (0.3 mL), MeOH (0.9 mL) and MeOH/H_2O_2 (2:1) (0.9 mL). The mixture was stirred for 1.5 hours at RT before to be diluted with Et_2O, washed with HCl (0.5 M) (1x), saturated $NaHCO_3$ solution (1x) and brine (1x), dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (Et_2O/pentane 8:2) to afford (*S*)-3-((2*S*,3*R*,4*S*,*E*)-3-hydroxy-2,4,6-trimethyloct-6-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one **(13)** (89.2 mg, 0.19 mmol, 77%, dr > 87:13) as a colorless crystalline solid. An analytical sample was obtained by chromatography on SiO_2 (Et_2O/pentane 8.5:1.5 → 8:2) as a pure diastereoisomer.

R_f = 0.33 (pentane/Et_2O 7:3)

M.p. = 98-99 °C

Optical rotation $[\alpha]^{24.5}_D$ (*c* = 1.00 , $CHCl_3$) = -103.6°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2 H), 7.43-7.28 (m, 8 H), 5.37 (d, *J* = 3.6 Hz, 1 H), 5.18-5.11 (m, 1 H), 3.83-3.74 (m, 1 H), 3.43 (td, J_1 = 6.7 Hz, J_2 = 4.9 Hz, 1 H), 2.06-1.90 (m, 2 H), 1.86 (d, *J* = 5.1 Hz, 1 H), 1.66-1.57 (m, 2 H), 1.56 (d, *J* = 6.6 Hz, 3 H), 1.51 (s, 3 H), 1.31 (d, *J* = 6.9 Hz, 3 H), 0.86 (d, *J* = 6.9 Hz, 3 H), 0.78 (d, *J* = 6.8 Hz, 3 H), 0.41 (d, *J* = 6.7 Hz, 3 H).

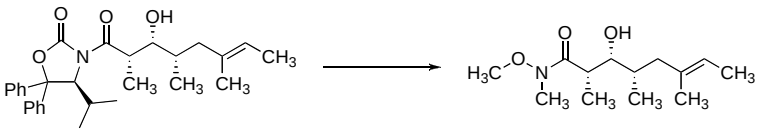
^{13}C-NMR (75 MHz, $CDCl_3$) δ 176.1, 152.4, 142.2, 137.6, 133.6, 128.7, 128.4, 128.3, 127.8, 125.6, 125.2, 120.3, 89.4, 64.6, 44.0, 40.4, 33.0, 29.8, 21.7, 16.5, 15.4, 13.9, 13.5, 13.4.

Elemental analysis calcd. for $C_{29}H_{37}NO_4$: [C] 74.57 %, [H] 8.19 %, [N] 2.91 %; found: [C] 74.68 %, [H] 8.03 %, [N] 2.91 %.

HRMS EI calcd. for $[C_{29}H_{35}NO_3]^+$ $[M\text{-}H_2O]^+$: 445.2611; found 445.2611.

IR Spectroscopy ν 3475*m*, 2965*m*, 2931*m*, 1781*s*, 1697*m*, 1494*w*, 1450*m*, 1374*m*, 1316*w*, 1254*w*, 1208*s*, 1176*s*, 1050*m*, 987*m*, 954*w*, 760*m*, 704*m*, 668*m* cm^{-1}.

(2*S*,3*R*,4*S*,*E*)-3-hydroxy-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide



To a cooled (0 °C) suspension of MeONHMe·HCl (503 mg, 5.16 mmol, 6.00 eq.) in CH_2Cl_2 (5.2 mL) was added $AlMe_3$ (2 M in toluene) (2.10 mL, 5.16 mmol, 6.00 eq). The resulting solution was stirred at 0 °C for 5 minutes, then at RT for 1 hour. The clear solution was cooled to 0 °C and (*S*)-3-((2*S*,3*R*,4*S*,*E*)-3-hydroxy-2,4,6-trimethyloct-6-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one (**13**) (400 mg, 0.86 mmol, 1.00 eq.) in CH_2Cl_2 (1.0 mL) was transferred by canula. Stirring at 0 °C was continued for 5 minutes, then at RT for 15 hours. The reaction mixture was slowly transferred in a diluted HCl (27.0 mL, 0.5 M) solution, diluted with more CH_2Cl_2 and stirred at RT for 1hour. The aqueous layer was separated and extracted with CH_2Cl_2 (3x). The combined organic phases were washed with saturated $NaHCO_3$ (1x) and brine(1x), dried ($MgSO_4$) and concentrated. The residue was diluted in ice-cold Et_2O, the precipitated cleaved auxiliary was filtered and the filtrate was concentrated. Purification by chromatography on SiO_2 (pentane/Et_2O 4:6) afford (2*S*,3*R*,4*S*,*E*)-3-hydroxy-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide (179 mg, 0.74 mmol, 86%) as white crystalline solid.

R_f = 0.21 (pentane/Et_2O 4:6)

M.p. = 54-55 °C

Optical rotation $[\alpha]^{22.4}_{D}$ (*c* = 0.50, $CHCl_3$) = +6.7°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.23 (q, *J* = 6.2 Hz, 1 H), 3.70 (s, 3 H), 3.57-3.53 (m, 1 H), 3.33 (d, *J* = 2.5 Hz, 1 H), 3.19 (s, 3 H), 3.12 (br. s, 1 H), 2.08 (d, *J* = 8.5 Hz, 1 H), 1.82-1.68 (m, 2 H), 1.60-1.58 (m, 6 H), 1.19 (d, *J* = 7.0 Hz, 3 H), 0.90 (d, *J* = 6.3 Hz, 3 H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 178.0, 133.8, 120.4, 75.3, 61.4, 43.7, 36.3, 33.0, 31.9, 15.2, 14.7, 13.2, 11.2.

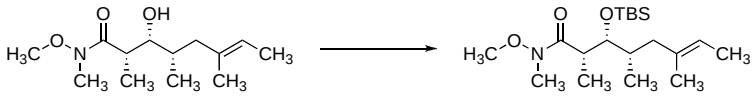
Elemental analysis calcd. for $C_{13}H_{25}NO_3$: [C] 64.17 %, [H] 10.35 %, [N] 5.76 %, [O] 19.72 %; found: [C] 64.23 %, [H] 10.46 %, [N] 5.67 %.

ESI 266.2 (100, $[M + Na]^+$).

IR Spectroscopy ν 3452*m*, 2965*s*, 2934*s*, 1640*s*, 1513*w*, 1457*s*, 1382*s*, 1300*m*, 1249*m*, 1176*m*, 1122*m*, 993*s*, 826*w* cm^{-1}.

Crystallographic data is given at the end of the supporting information.

(2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide



To a cooled (-20 °C) solution of (2*S*,3*R*,4*S*,*E*)-3-hydroxy-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide (467 mg, 1.92 mmol, 1.00 eq.) in CH_2Cl_2 (4.0 mL) was sequentially added 2,6-lutidine (257 µL, 2.21 mmol, 1.15 eq.) and TBSOTf (354 µL, 2.02 mmol, 1.05 eq.). The resulting solution was stirred for 15 min at -20 °C; then at 0 °C for 45 min. The reaction mixture was diluted in more CH_2Cl_2 and washed with diluted citric acid (pH = 4) (1x), saturated $NaHCO_3$ (1x), brine (1x), dried ($MgSO_4$) and concentrated. Purification by chromatography on SiO_2 (pentane/Et_2O 9:1) afford (2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide (680 mg, 1.90 mmol, 99%) as a clear oil.

R_f = 0.38 (hexane/EtOAc 9:1)

Optical rotation $[\alpha]^{24.3}_D$ (*c* = 1.00 , $CHCl_3$) = +6.8°.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.17 (q, *J* = 6.6 Hz, 1 H), 3.85 (dd, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1 H), 3.69 (s, 3 H), 3.16 (s, 3 H), 3.06 (br. s, 1 H), 2.14 (d, *J* = 12.4 Hz, 1 H), 1.86-1.78 (m, 1 H), 1.71-1.61 (m, 1 H), 1.56 (d, *J* = 6.6 Hz, 3 H), 1.52 (s, 3 H), 1.14 (d, *J* = 7.0 Hz, 3 H), 0.92 (s, 9 H), 0.73 (d, *J* = 6.8 Hz, 3 H), 0.08 (s, 6 H).

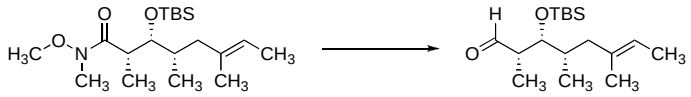
^{13}C-NMR (75 MHz, $CDCl_3$) δ 176.9, 134.3, 119.7, 77.3, 61.4, 44.2, 39.0, 35.9, 32.4, 26.3, 18.6, 15.9, 15.4, 13.4, 13.3, -3.4, -3.5.

Elemental analysis calcd. for $C_{19}H_{39}NO_3Si$: [C] 63.82 %, [H] 10.99 %, [N] 3.92 %, [O] 13.42 %, [Si] 7.85 %; found [C] 63.79 %, [H] 11.00 %, [N] 4.10 %.

ESI 380.2 (100, $[M + Na]^+$).

IR Spectroscopy ν 3369*s*, 2959*m*, 2931*m*, 2857*m*, 1662*s*, 1461*m*, 1382*m*, 1252*m*, 1176*w*, 1108*m*, 1049*s*, 997*s*, 869*m*, 833*s*, 773*s*, 668*s* cm^{-1}.

(2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-2,4,6-trimethyloct-6-enal



To a cooled (-78 °C) solution of (2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide (663 mg, 1.85 mmol, 1.00 eq.) in THF (13.2 mL) was added DIBAL-H (1M) (3.60 mL, 3.60 mmol, 2.00 eq.). The resulting solution was stirred at -78 °C for 1 hour; then quenched by addition of saturated Rochelle's salt, diluted in Et_2O and vigorously stirred at RT for 1h. The aqueous layer was extracted with Et_2O (3x) and the combined organic phase dried ($MgSO_4$) and concentrated (bath T < 20 °C). Purification by chromatography on SiO_2 (hexane/EtOAc 9.5:0.5) afford (2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-2,4,6-trimethyloct-6-enal (551 mg, 1.85 mmol, 100%) as a clear oil.

R_f = 0.70 (cyclohexane/EtOAc 9:1)

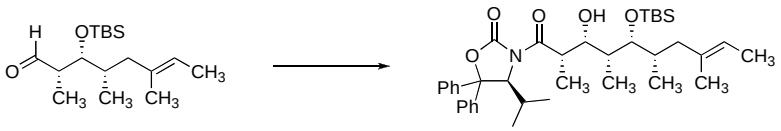
Optical rotation $[\alpha]^{25.0}_{D}$ (*c* = 0.20, $CHCl_3$) = +53.5°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1 H), 5.22 (q, *J* = 6.5 Hz, 1 H), 4.00-3.98 (m, 1 H), 2.59-2.53 (m, 1 H), 2.16-2.09 (m, 1 H), 1.85-1.78 (m, 2 H), 1.60 (d, *J* = 6.7 Hz, 3 H), 1.57 (s, 3 H), 1.10 (d, *J* = 7.0 Hz, 3 H), 0.92 (s, 9 H), 0.78 (d, *J* = 6.1 Hz, 3 H), 0.11 (s, 3 H), 0.06 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 205.7, 134.2, 120.9, 75.9, 51.4, 44.7, 35.1, 26.3, 18.7, 15.8, 14.7, 13.7, 9.7, -3.5, -3.7.

HRMS ESI calcd. for $[C_{17}H_{35}O_2Si]^+$ $[M + H]^+$: 299.2406, found 299.2419.

(*S*)-3-((2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one (14)



To a cooled (-5°C) solution of *ent*-**10** (81.0 mg, 0.24 mmol, 1.20 eq.) in CH_2Cl_2 (0.48 mL) was sequentially added Bu_2BOTf (1 M) (240 µL, 0.24 mmol, 1.20 eq.) and NEt_3 (39 µL, 0.28 mmol, 1.40 eq.). Stirring at 0 °C was continued for 45 minutes; then the resulting solution was cooled to -78 °C and (2*S*,3*R*,4*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-2,4,6-trimethyloct-6-enal (59 mg, 0.20 mmol, 1.00 eq.) in CH_2Cl_2 (0.45 mL) was slowly transferred by canula. The reaction was stirred for 45 minutes at -78 °C, then allowed to return to 0 °C over 3 hour. The reaction was quenched at 0 °C by sequentially addition of buffer phosphate (pH = 7) (0.24 mL), MeOH (0.72 mL) and MeOH/H_2O_2 (2:1) (0.72 mL). The mixture was stirred at RT for 30 minutes before to be diluted with Et_2O, washed with HCl (0.5 M) (1x), saturated $NaHCO_3$ (1x) and brine (1x), dried ($MgSO_4$) and concentrated. The residue was purified by chromatography on SiO_2 (hexane/EtOAc 9.5:0.5) to afford (*S*)-3-((2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one **(14)** (77.0 mg, 0.12 mmol, 61%, dr > 97:3) as a white crystalline solid.

R_f = 0.60 (pentane/Et_2O 7:3)

M.p. = 105-107 °C

Optical rotation $[\alpha]^{25.0}_D$ (*c* = 0.29, $CHCl_3$) = -118.6°.

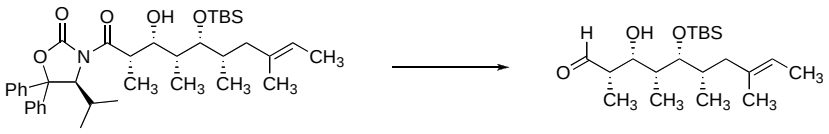
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.52-7.51 (m, 2 H arom.), 7.43-7.41 (m, 2 H arom.), 7.37-7.26 (m, 6 H), 5.44 (d, *J* = 3.5 Hz, 1 H), 5.24 (q, *J* = 6.3 Hz, 1 H), 3.79-3.78 (m, 2 H), 3.50 (t, *J* = 3.8 Hz, 1 H), 2.49 (br. s, 1 H), 2.12 (d, *J* = 12.3 Hz, 1 H), 2.05-1.98 (m, 1 H), 1.82-1.76 (m, 1 H), 1.73-1.68 (m, 1 H), 1.62 (d, *J* = 6.6 Hz, 3 H), 1.58 (s, 3 H), 1.53-1.49 (m, 1 H), 1.36 (d, *J* = 6.4 Hz, 3 H), 0.89 (d, *J* = 7.1 Hz, 3 H), 0.87 (s, 9 H), 0.80 (d, *J* = 6.8 Hz, 3 H), 0.76 (d, *J* = 6.6 Hz, 3 H), 0.67 (d, *J* = 6.9 Hz, 3 H), 0.01 (s, 3 H), -0.24 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.3, 152.7, 142.6, 138.3, 134.8, 129.3, 129.0, 128.8, 128.4, 126.2, 125.8, 120.4, 89.7, 77.1, 74.0, 64.3, 44.2, 40.9, 38.4, 35.9, 30.3, 26.5, 22.1, 18.8, 16.7, 15.9, 15.3, 13.9, 13.8, 9.4, -3.0, -3.9.

HRMS ESI calcd. for $[C_{38}H_{57}NO_5NaSi]^+$ $[M + Na]^+$: 658.3904, found 658.3911.

IR Spectroscopy ν 3360*w*, 2928*m*, 2857*m*, 1786*m*, 1693*w*, 1458*w*, 1374*w*, 1253*w*, 1210*w*, 1044*w*, 892*w*, 766*w*, 689*w* cm^{-1}.

(2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enal (15)



To a cooled (-17 °C) solution of (*S*)-3-((2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enoyl)-4-isopropyl-5,5-diphenyloxazolidin-2-one (**14**) (320 mg, 0.50 mmol, 1.00 eq.) in toluene (10 mL) a solution of $LiAlH_4$ (1M in Et_2O) (1.00 mL, 1.00 mmol, 2.00 eq.) was slowly added. The resulting solution was stirred for 20 minutes, then quenched at -17 °C by dropwise addition of saturated Rochelle's salt and diluted in Et_2O. The mixture was vigorously stirred at RT for 2 hours, then extracted with Et_2O (3x) and the combined organic phase dried ($MgSO_4$) and concentrated (bath T < 20 °C). The residue was diluted in Et_2O and the precipitated cleaved auxiliary recovered. The filtered was concentrated and the residue purified by chromatography on SiO_2 (pentane/Et_2O 9:1) to afford (2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enal **(15)** (149 mg, 0.42 mmol, 83%) as a colorless oil.

R_f = 0.28 (pentane/Et_2O 7:3)

Optical rotation $[\alpha]^{25.0}_D$ (*c* = 0.08, $CHCl_3$) = -23.8°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.2 Hz, 1 H), 5.21 (q, *J* = 6.4 Hz, 1 H), 4.03 (q, *J* = 5.2 Hz, 1 H), 3.58 (dd, J_1 = 4.2 Hz, J_2 = 2.9 Hz, 1 H), 2.68-2.62 (m, 1 H), 2.20 (d, *J* = 12.3 Hz, 1

H), 1.97 (d, *J* = 4.4 Hz, 1 H), 1.89-1.77 (m, 2 H), 1.76-1.67 (m, 1 H), 1.60 (d, *J* = 6.8 Hz, 3 H), 1.57 (s, 3 H), 1.17 (d, *J* = 7.1 Hz, 3 H), 1.00 (d, *J* = 6.9 Hz, 3 H), 0.94 (s, 9 H), 0.81 (d, *J* = 6.7 Hz, 3 H), 0.11 (s, 3 H), 0.09 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.8, 134.5, 120.7, 78.2, 73.2, 50.1, 44.3, 39.3, 36.1, 26.5, 18.8, 15.8, 13.7, 10.0, 8.8, -2.8, -3.5.

HRMS ESI calcd. for $[C_{20}H_{40}O_3NaSi]^+$ $[M + Na]^+$: 379.2644, found 379.2639.

IR Spectroscopy ν 2957*m*, 2931*m*, 2859*m*, 1727*w*, 1462*w*, 1384*w*, 1255*w*, 1096*w*, 1032*w*, 837*w*, 775*w* cm^{-1}.

(2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-ethyl 7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienoate

To a solution of (2*S*,3*R*,4*R*,5*R*,6*S*,*E*)-5-(*tert*-butyldimethylsilyloxy)-3-hydroxy-2,4,6,8-tetramethyldec-8-enal **(15)** (61.1 mg, 0.17 mmol, 1.00 eq.) in toluene (1.7 mL) was added 1-carbethoxyethylidentriphenylphosphorane (123.2 mg, 0.34 mmol, 2.00 eq.) and the mixture was stirred at 35 °C for 5 hours. The reaction was diluted in pentane, filtered over cotton and concentrated. The residue was purified by chromatography on SiO_2 (pentane/Et_2O 9:1) to afford (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-ethyl 7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienoate (73.8 mg, 0.17 mmol, 99%, dr > 97:3).

R_f = 0.39 (pentane/Et_2O 8:2)

Optical rotation $[\alpha]^{25.0}_D$ (*c* = 0.09, $CHCl_3$) = +24.7°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.53 (dd, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1 H), 5.21 (q, *J* = 6.2 Hz, 1 H), 4.27-4.15 (m, 2 H), 3.65 (t, *J* = 3.9 Hz, 1 H), 3.53-3.49 (m, 1 H), 2.70-2.60 (m, 1 H), 2.17 (d, *J* = 12.6 Hz, 1 H), 1.93 (d, *J* = 4.3 Hz, 1 H), 1.89 (d, *J* = 1.1 Hz, 3 H), 1.87-1.82 (m, 1 H), 1.80-

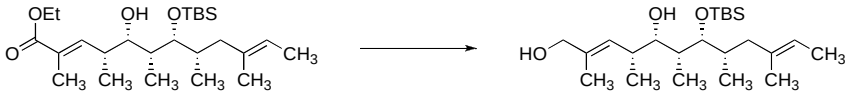
1.74 (m, 1 H), 1.72-1.66 (m, 1 H), 1.59 (d, *J* = 6.6 Hz, 3 H), 1.57 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.10 (d, *J* = 6.6 Hz, 3 H), 0.94 (s, 9 H), 0.87 (d, *J* = 7.0 Hz, 3 H), 0.77 (d, *J* = 6.7 Hz, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 168.5, 144.0, 134.7, 127.7, 120.5, 79.9, 78.6, 60.9, 44.1, 39.0, 38.0, 35.7, 26.5, 18.7, 16.9, 15.9, 15.0, 14.6, 13.7, 13.0, 8.8, -2.8, -3.7.

HRMS ESI calcd. for $[C_{25}H_{49}O_4Si]^+$ $[M + H]^+$: 441.3400, found 441.3404.

IR Spectroscopy ν 3519*w*, 2959*m*, 2923*m*, 2858*m*, 1712*m*, 1650*w*, 1462*w*, 1369*w*, 1252*m*, 1094*m*, 1038*m*, 835*m*, 773*m*, 675*m* cm^{-1}.

(2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-2,4,6,8,10-pentamethyldodeca-2,10-diene-1,5-diol



To a cooled (-78 °C) solution of (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-ethyl 7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienoate (67.0 mg, 0.15 mmol, 1.00 eq.) in THF (1.6 mL) was slowly added DIBAL-H (1M) (800 µL, 0.80 mmol, 5.30 eq.). The resulting solution was stirred for 5 minutes at -78 °C, then between at -15 and -5 °C for 1.5 hours. The reaction was quenched by the addition of MeOH, diluted in saturated Rochelle's salt and Et_2O and vigorously stirred at RT for 1 hour. The aqueous layer was extracted with Et_2O (3x) and the combined organic phase dried ($MgSO_4$) and concentrated (bath T < 25 °C). Purification by chromatography on SiO_2 (pentane/Et_2O 9:1 → 7:3) afford (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-2,4,6,8,10-pentamethyldodeca-2,10-diene-1,5-diol (56.3 mg, 0.14 mmol, 93%) as a colorless oil.

R_f = 0.15 (pentane/Et_2O 7:3)

Optical rotation $[\alpha]^{22.5}_D$ (*c* = 0.0041 , $CHCl_3$) = - 1.0°.

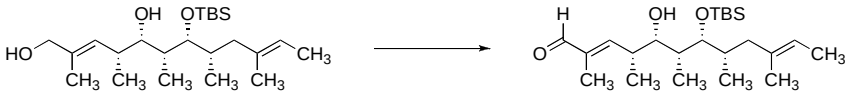
^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.23-5.17 (m, 2 H), 4.01 (s, 2 H), 3.63-3.60 (m, 1 H), 3.39 (d, *J* = 8.8 Hz, 1 H), 2.59-2.49 (m, 1 H), 2.16 (d, *J* = 12.2 Hz, 1 H), 1.91-1.75 (m, 4 H), 1.71 (d, *J* = 0.5 Hz, 3 H), 1.59 (d, *J* = 7.0 Hz, 3 H), 1.57 (s, 3 H), 1.41 (s, 1 H), 1.04 (d, *J* = 6.6 Hz, 3 H), 0.93 (s, 9 H), 0.88 (d, *J* = 7.0 Hz, 3 H), 0.76 (d, *J* = 6.6 Hz, 3 H), 0.11 (s, 3 H), 0.10 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.0, 134.8, 129.1, 120.4, 79.9, 78.9, 69.2, 44.3, 38.5, 36.8, 35.6, 26.5, 18.8, 17.8, 15.9, 14.9, 14.3, 13.8, 9.0, -2.8, -3.6.

HRMS ESI calcd. for $[C_{23}H_{46}O_3NaSi]^+$ $[M + Na]^+$: 421.3114, found 421.3116.

IR Spectroscopy ν 3349*m*, 2956*m*, 2930*m*, 2860*m*, 1459*w*, 1383*w*, 1253*m*, 1070*m*, 1035*m*, 1011*m*, 836*m*, 775*m*, 676*m* cm^{-1}.

(2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16)



To a solution of (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-2,4,6,8,10-pentamethyldodeca-2,10-diene-1,5-diol (121 mg, 0.30 mmol, 1.00 eq.) in CH_2Cl_2 (3.0 mL), MnO_2 (396 mg, 4.50 mmol, 15.0 eq.) was added. The mixture was stirred at RT for 2.5 hours; then filtered over celite, rinsed with CH_2Cl_2 and concentrated (bath T < 25 °C). The product (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal **(16)** (103 mg, 0.26 mmol, 86%) crystallize under high vacuum. An analytical sample was recrystallized (hexane) for X-ray analysis and the rest directly used in the next step without further purification.

R_f = 0.37 (pentane/Et_2O 7:3)

M.p. = 75-77 °C

Optical rotation $[\alpha]^{22.5}_{D}$ (*c* = 0.0082 , $CHCl_3$) = -10.9°.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1 H), 6.27 (dd, J_1 = 10.3 Hz, J_2 = 1.0 Hz, 1 H), 5.21 (q, *J* = 6.3 Hz, 1 H), 3.65 (t, *J* = 3.8 Hz, 1 H), 3.59-3.56 (m, 1 H), 2.92-2.82 (m, 1 H), 2.18 (d, *J* = 12.8 Hz, 1 H), 2.00 (d, *J* = 4.2 Hz, 1 H), 1.92-1.83 (m, 1 H), 1.81 (d, *J* = 0.9 Hz, 3 H), 1.79-1.73 (m, 1 H), 1.66-1.63 (m, 1 H), 1.60 (d, *J* = 7.1 Hz, 3 H), 1.57 (s, 3 H), 1.16 (d, *J* = 6.6 Hz, 3 H), 0.94 (s, 9 H), 0.90 (d, *J* = 7.0 Hz, 3 H), 0.77 (d, *J* = 6.8 Hz, 3 H), 0.13 (s, 3 H), 0.11 (s, 3 H).

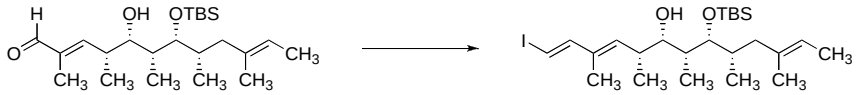
^{13}C-NMR (100 MHz, $CDCl_3$) δ 195.6, 156.4, 139.1, 134.5, 120.6, 79.8, 78.1, 44.1, 39.3, 38.3, 35.7, 26.5, 18.7, 16.7, 15.9, 15.2, 13.8, 9.9, 8.9, -2.8, -3.7.

HRMS ESI calcd. for $[C_{23}H_{44}O_3NaSi]^+$ $[M + Na]^+$: 419.2957, found 419.2960.

IR Spectroscopy ν 3520*w*, 2961*m*, 2928*m*, 2889*m*, 2885*m*, 1667*m*, 1635*w*, 1459*w*, 1378*w*, 1251*w*, 1096*w*, 1073*w*, 1040*w*, 1011*m*, 974*w*, 883*m*, 772*m*, 681*m* cm^{-1}.

Crystallographic data is given at the end of the supporting information.

(1*E*,3*E*,5*R*,6*S*,7*R*,8*R*,9*S*,11*E*)-8-(*tert*-butyldimethylsilyloxy)-1-iodo-3,5,7,9,11-pentamethyltrideca-1,3,11-trien-6-ol (17)



To a cooled (-5 °C) suspension of $CrCl_2$ (446 mg, 3.63 mmol, 24.00 eq.) in dry THF (4.4 mL), a solution of (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal **(16)** (60.0 mg, 0.15 mmol, 1.00 eq.) and CHI_3 (358 mg, 0.91 mmol, 6.00 eq.) in THF (4.4 mL) was slowly added. The dark brown mixture was covered with an aluminium foil and stirred between -5 and 0 °C for 2.5 hours. The mixture was quenched by addition of water and extracted with Et_2O (3x). The combined organic layer was washed with saturated sodium thiosulfate (1x), water (1x), dried ($MgSO_4$) and concentrated (bath T < 20 °C). Purification by chromatography on SiO_2 (pentane/Et_2O 9:1) afford (1*E*,3*E*,5*R*,6*S*,7*R*,8*R*,9*S*,11*E*)-

8-(*tert*-butyldimethylsilyloxy)-1-iodo-3,5,7,9,11-pentamethyltrideca-1,3,11-trien-6-ol **(17)** (78.4 mg, 0.15 mmol, quant., dr > 97:3) as a colorless oil.

R_f = 0.68 (pentane/Et_2O 7:3)

Optical rotation $[\alpha]^{22.4}_D$ (*c* = 0.006 , $CHCl_3$) = + 25.4°.

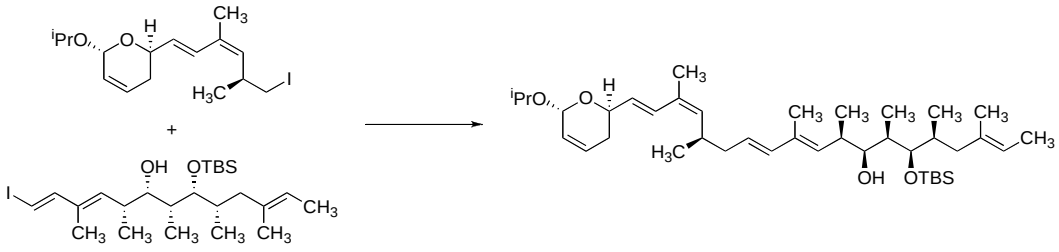
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 14.6 Hz, 1 H), 6.20 (d, *J* = 14.6 Hz, 1 H), 5.24-5.19 (m, 2 H), 3.63 (t, *J* = 3.9 Hz, 1 H), 3.43-3.40 (m, 1 H), 2.65-2.56 (m, 1 H), 2.17 (d, *J* = 12.3 Hz, 1 H), 1.87 (d, *J* = 4.3 Hz, 1 H), 1.86-1.82 (m, 1 H), 1.77 (d, *J* = 0.7 Hz, 3 H), 1.76-1.70 (m, 2 H), 1.60 (d, *J* = 6.9 Hz, 3 H), 1.58 (s, 3 H), 1.06 (d, *J* = 6.6 Hz, 3 H), 0.94 (s, 9 H), 0.86 (d, *J* = 7.0 Hz, 3 H), 0.77 (d, *J* = 6.6 Hz, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.0, 137.0, 134.7, 134.3, 120.5, 80.0, 78.8, 74.1, 44.2, 38.8, 37.4, 35.7, 26.5, 18.8, 17.6, 15.9, 15.0, 13.8, 12.6, 8.8, -2.7, -3.6.

HRMS ESI calcd. for $[C_{24}H_{45}O_2NaSiI]^+$ $[M + Na]^+$: 543.2131, found 543.2133.

IR Spectroscopy ν 3482*w*, 2958*m*, 2929*m*, 2858*m*, 1461*w*, 1387*w*, 1254*w*, 1091*w*, 1039*w*, 980*w*, 950*w*, 836*w*, 774*w*, 678*w* cm^{-1}.

(2*E*,5*S*,6*R*,7*R*,8*S*,9*R*,10*E*,12*E*,15*R*,16*Z*,18*E*)-6-(*tert*-butyldimethylsilyloxy)-19-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-3,5,7,9,11,15,17-heptamethylnonadeca-2,10,12,16,18-pentaen-8-ol



To a solution of (2*R*,6*R*)-2-((*S*,1*E*,3*Z*)-6-iodo-3,5-dimethylhexa-1,3-dienyl)-6-isopropoxy-3,6-dihydro-2*H*-pyran **(9)** (29.0 mg, 0.077 mmol, 1.30 eq.) in Et_2O (850 µL), 9-MeO-9-BBN (1M in

hexane) (202 μL, 0.202 mmol, 3.42 eq.) was added. The resulting solution was cooled to -78 °C and treated with ^{t}BuLi (1.5 M in pentane) (118 μL, 0.177 mmol, 3.00 eq.). After 5 minutes THF (850 μL) was added and the solution allowed to return to RT; stirring was continued for 1 hour. Separately in another flask (1*E*,3*E*,5*R*,6*S*,7*R*,8*R*,9*S*,11*E*)-8-(*tert*-butyldimethylsilyloxy)-1-iodo-3,5,7,9,11-pentamethyltrideca-1,3,11-trien-6-ol **(17)** (30.7 mg, 0.059 mmol, 1.00 eq.) was taken up in DMF (850 μL) to which Pd(dppf)Cl_2 (2.2 mg, 0.003 mmol, 0.05 eq.), $AsPh_3$ (2.8 mg, 0.009, 0.15 eq.), $CsCO_3$ (77.0 mg, 0.236 mmol, 4.0 eq.) and H_2O (26 μL, 1.416 mmol, 24 eq.) were sequentially added. The alkyl boronate solution was transferred in the DMF solution and the resulting red-brown mixture stirred at RT overnight. The reaction was diluted with water and extracted with Et_2O (3x). The combined organic layer was washed with water (1x) and brine (1x), dried ($MgSO_4$) and concentrated. Purification by chromatography on SiO_2 (pentane/Et_2O 92.5:7.5) afford (2*E*,5*S*,6*R*,7*R*,8*S*,9*R*,10*E*,12*E*,15*R*,16*Z*,18*E*)-6-(*tert*-butyldimethylsilyloxy)-19-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-3,5,7,9,11,15,17-heptamethylnonadeca-2,10,12,16,18-pentaen-8-ol **(19)** (30.2 mg, 0.047 mmol, 80%) as a pale yellow oil.

R_f = 0.13 (pentane/Et_2O 9:1)

Optical rotation $[\alpha]^{22.0}_{D}$ (*c* = 0.0034 , $CHCl_3$) = + 52.1°.

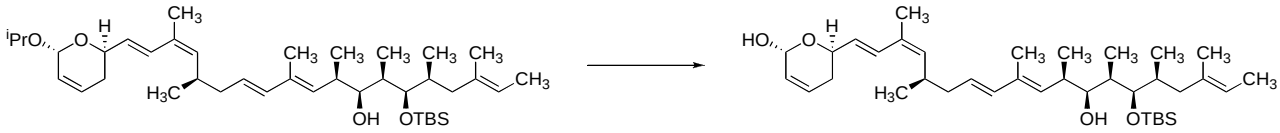
^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.70 (d, *J* = 15.7 Hz, 1 H), 6.06-6.02 (m, 1 H), 6.02 (d, *J* = 15.5 Hz, 1 H), 5.77-5.70 (m, 2 H), 5.53 (dt, J_1 = 15.5 Hz, J_2 = 7.2 Hz, 1 H), 5.24-5.18 (m, 2 H), 5.15 (s, 1 H), 5.09 (d, *J* = 9.9 Hz, 1 H), 4.57-4.51 (m, 1 H), 4.05 (sept., *J* = 6.2 Hz 1 H), 3.63-3.61 (m, 1H), 3.39 (dd, J_1 = 8.86, J_2 = 2.57 Hz, 1H), 2.75-2.68 (m, 1H), 2.65-2.55 (m, 1H), 2.20-2.02 (m, 5H), 1.90-1.86 (m, 1H), 1.84 (s, 3H), 1.81-1.78. (m, 3H), 1.75 (s, 3H), 1.59 (d, *J* = 5.5 Hz, 3H), 1.57 (s, 3H), 1.27 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.94 (s, 9H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.9, 136.5, 134.8, 133.5, 133.4, 130.4, 129.6, 128.9, 128.6, 126.5, 126.3, 120.3, 93.7, 79.9, 79.1, 70.0, 67.4, 44.3, 41.2, 38.6, 37.3, 35.6, 32.5, 31.2, 26.6, 24.3, 22.5, 20.9, 20.8, 18.8, 18.0, 15.9, 14.9, 13.8, 13.2, 8.9, -2.8, -3.6.

HRMS ESI calcd. for $[C_{40}H_{70}O_4NaSi]^+$ $[M + Na]^+$: 665.4941, found 665.4946.

IR Spectroscopy ν 3503*w*, 2962*m*, 2928*m*, 2859*m*, 1459*w*, 1381*w*, 1317*w*, 1253*w*, 1181*w*, 1099*m*, 1029*m*, 1001*m*, 964*m*, 836*w*, 774*w*, 718*w*, 678*w* cm^{-1}.

(2*R*,6*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,12*S*,13*R*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-12-hydroxy-3,5,9,11,13,15,17-heptamethylnonadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-ol



To a solution of (2*E*,5*S*,6*R*,7*R*,8*S*,9*R*,10*E*,12*E*,15*R*,16*Z*,18*E*)-6-(*tert*-butyldimethylsilyloxy)-19-((2*R*,6*R*)-6-isopropoxy-3,6-dihydro-2*H*-pyran-2-yl)-3,5,7,9,11,15,17-heptamethylnonadeca-2,10,12,16,18-pentaen-8-ol **(19)** (6.8 mg, 0.011 mmol, 1.00 eq.) in a mixture of acetone/water (3/1) (220 µL), PPTS (1.3 mg, 0.005 mmol, 0.5 eq.) was added and the resulting solution stirred at RT for 22 hours. The reaction was diluted with water, extracted with Et_2O (3x) and the combined organic layer dried ($MgSO_4$) and concentrated. Purification by chromatography on SiO_2 (pentane/Et_2O 9:1 → 7:3) afforded (2*R*,6*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,12*S*,13*R*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-12-hydroxy-3,5,9,11,13,15,17-heptamethylnonadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-ol (6.3 mg, 0.010 mmol, 95%) as a pale yellow oil.

R_f = 0.20 (pentane/Et_2O 7:3)

Optical rotation $[\alpha]^{22.8}_D$ (*c* = 0.001, $CHCl_3$) = + 53.1°.

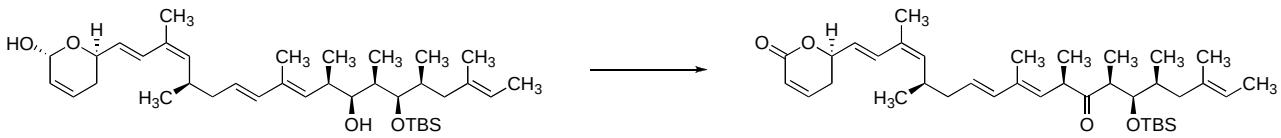
^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.73 (d, *J* = 15.7 Hz, 1H), 6.11-6.07 (m, 1H), 6.02 (d, *J* = 15.5 Hz, 1H), 5.85 (dd, J_1 = 10.1 Hz, J_2 = 0.8 Hz, 1H), 5.73 (dd, J_1 = 15.7 Hz, J_2 = 6.5 Hz, 1H), 5.53 (dt, J_1 = 15.5 Hz, J_2 = 7.3 Hz, 1H), 5.48 (br. s, 1H), 5.24 (d, *J* = 9.7 Hz, 1H), 5.23-5.18 (m, 1H), 5.10 (d, *J* = 9.9 Hz, 1H), 4.61-4.56 (m, 1H), 3.63-3.61 (m, 1H), 3.42-3.39 (m, 1H), 2.79-2.69 (m, 2H), 2.66-2.56 (m, 1H), 2.21-2.01 (m, 5H), 1.91-1.86 (m, 1H), 1.84 (s, 3H), 1.82-1.78 (m, 3H), 1.75 (s, 3H), 1.59-1.57 (m, 6H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.94 (s, 9H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$) δ 138.2, 136.5, 134.9, 133.6, 133.4, 130.2, 129.2, 129.1, 126.4, 126.3, 120.3, 89.7, 79.9, 79.1, 67.8, 44.3, 41.2, 38.6, 37.3, 35.6, 32.5, 31.2, 26.6, 21.0, 20.8, 18.8, 17.9, 15.9, 14.9, 13.8, 13.3, 9.0, -2.8, -3.6.

HRMS ESI calcd. for $[C_{37}H_{64}O_4NaSi]^+$ $[M + Na]^+$: 623.4472, found 623.4475.

IR Spectroscopy ν 3396*w*, 2959*m*, 2928*m*, 2859*w*, 1684*w*, 1457*w*, 1382*w*, 1253*w*, 1094*w*, 1033*w*, 964*w*, 835*w*, 772*w*, 680*m* cm^{-1}.

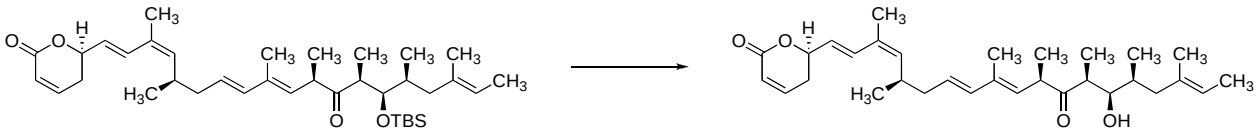
(*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,13*S*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-3,5,9,11,13,15, 17-heptamethyl-12-oxononadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-one



To a solution of (2*R*,6*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,12*S*,13*R*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-12-hydroxy-3,5,9,11,13,15,17-heptamethylnonadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-ol (3.2 mg, 0.005 mmol, 1.00 eq.) in CH_2Cl_2 (100 µL), DMP (5.6 mg, 0.013 mmol, 1.00 eq.) was added and the resulting mixture stirred at RT for 4 hours. The mixture was directly loaded over a pipette column of silica and eluted with pentane/Et_2O 9.5/0.5 → 7/3. The reaction mixture was concentrated and directly treated with MnO_2 (7.0 mg, 0.080 mmol, 15.0 eq.) in CH_2Cl_2 (300 µL) at RT for 14 hours. The mixture was filtered over celite, washed with CH_2Cl_2 and concentrated to afford (*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,13*S*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-3,5,9,11,13,15,17-heptamethyl-12-oxononadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-one (1.5 mg, 0.003 mmol, 47%) as a pale yellow oil, which was directly used in the next step without further purification.

R_f = 0.19 (pentane/Et_2O 7:3)

(*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,13*S*,14*R*,15*S*,17*E*)-14-hydroxy-3,5,9,11,13,15,17-heptamethyl-12-oxononadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-one (20)



In a 10 ml plastic vial under Ar, a solution of (*R*)-6-((1*E*,3*Z*,5*R*,7*E*,9*E*,11*R*,13*S*,14*R*,15*S*,17*E*)-14-(*tert*-butyldimethylsilyloxy)-3,5,9,11,13,15,17-heptamethyl-12-oxononadeca-1,3,7,9,17-pentaenyl)-5,6-dihydro-2*H*-pyran-2-one (1.4 mg, 0.002 mmol, 1.00 eq.) in THF (300 µL) was cooled to 0 °C and treated dropwise with a solution of HF·pyridine (120 µL) and pyridine (60 µL) in THF (200 µL). After addition the resulting pale yellow solution was allowed to return to RT and stirred for 4.5 days. The reaction mixture was diluted in Et_2O and transferred by canula in a saturated $NaHCO_3$ solution and extracted with Et_2O (3x). The combined organic layers were washed with saturated NH_4Cl (1x), dried ($MgSO_4$) and concentrated. The crude mixture was directly purified by HPLC to afford anguinomycin C (**20**) (0.9 mg, 0.0019 mmol, 82%) as a colorless oil.

Optical rotation $[\alpha]^{23.1}_D$ (*c* = 0.00012, $CHCl_3$) = - 116.7°.

Optical rotation $[\alpha]^{22.5}_D$ (*c* = 0.0000642, MeOH) = - 101.2°.

^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.93 (dt, J_1 = 9.8 Hz, J_2 = 4.3 Hz, 1 H), 6.76 (d, J = 15.6 Hz, 1 H), 6.09 (td, J_1 = 9.7 Hz, J_2 = 1.8 Hz, 1 H), 6.04 (d, J = 15.6 Hz, 1 H), 5.75 (dd, J_1 = 15.6 Hz, J_2 = 6.9 Hz, 1 H), 5.61 (dt, J_1 = 15.5 Hz, J_2 = 7.4 Hz, 1 H), 5.30 (d, J = 9.8 Hz, 1 H), 5.22 (qd, J_1 = 6.6 Hz, J_2 = 1.1 Hz, 1 H), 5.15 (d, J = 10.1 Hz, 1 H), 5.01 (dt, J_1 = 7.3 Hz, J_2 = 7.1 Hz, 1 H), 3.69 (dq, J_1 = 10.1 Hz, J_2 = 6.7 Hz, 1 H), 3.59 (ddd, J_1 = 5.5 Hz, J_2 = 5.5 Hz, J_3 = 4.0 Hz, 1 H), 2.88 (qd, J_1 = 7.1 Hz, J_2 = 5.7 Hz, 1 H), 2.74-2.67 (m, 1 H), 2.51-2.49 (m, 2 H), 2.40 (d, J = 4.0 Hz, 1 H), 2.15-2.06 (m, 2 H), 2.02 (dd, J_1 = 13.0 Hz, J_2 = 6.1 Hz, 1 H), 1.85 (d, J = 1.1 Hz, 3 H), 1.84 (d, J = 1.1 Hz, 3 H), 1.74 (dd, J_1 = 13.0 Hz, J_2 = 8.8 Hz, 1 H), 1.69-1.64 (m, 1 H), 1.60 (dd, J_1 = 6.8 Hz, J_2 = 0.5 Hz, 3 H), 1.58 (s, 3 H), 1.17 (d, J = 7.1 Hz, 3 H), 1.16 (d, J = 6.6 Hz, 3 H), 0.99 (d, J = 6.7 Hz, 3 H), 0.80 (d, J = 6.6 Hz, 3 H).

^{13}C-NMR (150 MHz, $CDCl_3$) δ 215.4, 163.7, 144.3, 138.7, 135.8, 135.1, 133.6, 130.4, 129.1, 128.1, 127.3, 125.0, 121.3, 120.1, 78.3, 74.0, 46.1, 45.3, 43.7, 40.4, 32.8, 31.9, 29.7, 20.3, 20.0, 15.8, 14.9, 13.8, 13.0, 12.7, 11.8.

HRMS ESI calcd. for $[C_{31}H_{46}O_4Na]^+$ $[M + Na]^+$: 505.3294, found 505.3281.

IR Spectroscopy ν 3440*m*, 2963*m*, 2927*m*, 2856*w*, 1709*m*, 1454*w*, 1381*w*, 1248*w*, 891*m* cm^{-1}.

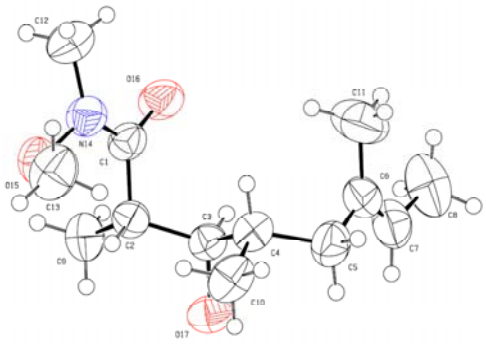
UV spectrum: λ_{max} = 241nm in MeOH

Analytical HPLC: R_t = 32.35 minutes (C_{18}, 60%-100% MeOH in 50 minutes).

Semi-preparative HPLC: R_t = 38.82 minutes (C_{18}, 60%-80% MeOH in 50 minutes, 80%-100% MeOH in 10 minutes).

Crystallographic Data

Crystal and molecular structure of (2*S*,3*R*,4*S*,*E*)-3-hydroxy-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide



Abstract

We present the crystal and molecular structure of (2*S*,3*R*,4*S*,*E*)-3-hydroxy-*N*-methoxy-*N*,2,4,6-tetramethyloct-6-enamide

Comment [5]

The study of the title structure was undertaken to establish its three dimensional structure. Geometries are tabulated below. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

Experimental

Crystal data

$C_{13}H_{25}NO_3$	Z = 2
$C_{13}H_{25}NO_3$	D_x = 1.083 Mg m^{-3}
M_r = 243.347	Density measured by: not measured
Monoclinic $P2_1$	fine-focus sealed tube
a = 8.5218 (3)Å	Mo *K*α radiation λ = 0.71073
b = 9.5856 (4)Å	Cell parameters from 4731 refl.
c = 9.8281 (4)Å	θ = 0.998—27.485 °
α = 90.00°	μ = 0.076 mm^{-1}
β = 111.648 (2)°	T = 298 K
γ = 90.00°	Cube
	0.7 x 0.5 x 0.24 mm
	Colourless
V = 746.20 (5)$Å^3$	Crystal source: Seeberger laboratory

Data collection

KappaCCD CCD diffractometer	R_{int} = 0.031
Absorption correction: none	θ_{max} = 27.50 °
3267 measured reflections	h = -11 →11
3253 independent reflections	k = -12 →12
2636 observed reflections	l = -12 →12
Criterion: >2sigma(I)	

Refinement

	fullmatrix least squares refinement
Refinement on F^2	R(all) = 0.0658

R(gt) = 0.0513
wR(ref) = 0.1627
wR(gt)= 0.1464
S(ref) = 1.089
3253 reflections
154 parameters
1 restraints
H positions constr

Δ/σ_{max} = 0.001
$\Delta\rho_{max}$ = 0.118eÅ^3
$\Delta\rho_{min}$ = -0.133eÅ^3
Extinction correction: none
Atomic scattering factors from International Tables Vol C Tables 4.2.6.8 and 6.1.1.4
Flack parameter = 0.8 (12)
Flack H D (1983), *Acta Cryst.* A39, 876-881

Calculated weights $1/[\sigma^2(I_o)+(I_o+I_c)^2/900]$

Data collection: KappaCCD
Cell refinement: HKL Scalepack (Otwinowski & Minor 1997)
Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997)
Program(s) used to solve structure: *SIR*97(Cascarano al.,*Acta Cryst.*,1996,A52,C-79)
Program(s) used to refine structure: *SHELXL*-97 (Sheldrick, 1997)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)*
$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i.\boldsymbol{a}_j$.

	x	y	z	U_{eq}	Occ
O15	0.4624 (2)	0.13136 (19)	0.09136 (15)	0.0734 (5)	1
O16	0.5725 (2)	0.16592 (17)	0.46659 (15)	0.0756 (5)	1
O17	0.6126 (2)	0.58537 (14)	0.35834 (16)	0.0644 (4)	1
N14	0.5317 (3)	0.0979 (2)	0.23996 (19)	0.0644 (5)	1
C1	0.5406 (3)	0.1991 (2)	0.3379 (2)	0.0555 (4)	1
C2	0.5139 (2)	0.3488 (2)	0.28732 (18)	0.0532 (4)	1
C3	0.6496 (2)	0.44252 (19)	0.39736 (19)	0.0504 (4)	1
C4	0.8276 (3)	0.4111 (2)	0.4034 (2)	0.0580 (5)	1
C5	0.9593 (3)	0.4908 (3)	0.5312 (2)	0.0719 (6)	1
C6	0.9636 (3)	0.4592 (3)	0.6812 (2)	0.0690 (5)	1
C7	0.9432 (3)	0.5587 (3)	0.7665 (3)	0.0785 (7)	1
C8	0.9499 (4)	0.5465 (5)	0.9203 (3)	0.1116 (12)	1
C9	0.3350 (3)	0.3917 (3)	0.2720 (3)	0.0742 (6)	1
C10	0.8514 (3)	0.4454 (3)	0.2610 (3)	0.0749 (6)	1
C11	0.9960 (6)	0.3108 (4)	0.7273 (4)	0.1168 (14)	1
C12	0.5262 (4)	-0.0497 (3)	0.2723 (3)	0.0842 (7)	1
C13	0.5851 (4)	0.1171 (4)	0.0259 (3)	0.0938 (8)	1
H17	0.5523	0.6165	0.3997	0.097	1
H2	0.5227	0.3564	0.1930	0.064	1
H3	0.6461	0.4257	0.4925	0.060	1
H4	0.8451	0.3127	0.4198	0.070	1
H5A	1.0703	0.4715	0.5294	0.086	1
H5B	0.9388	0.5900	0.5137	0.086	1
H7	0.9207	0.6524	0.7302	0.094	1
H8A	0.8393	0.5616	0.9219	0.167	1
H8B	1.0263	0.6150	0.9804	0.167	1
H8C	0.9885	0.4549	0.9572	0.167	1
H9A	0.3160	0.4867	0.2392	0.089	1
H9B	0.3230	0.3836	0.3651	0.089	1

H9C	0.2540	0.3324	0.2021	0.089	1
H10A	0.9653	0.4244	0.2711	0.090	1
H10B	0.8294	0.5427	0.2391	0.090	1
H10C	0.7746	0.3905	0.1831	0.090	1
H11A	0.9955	0.3000	0.8242	0.140	1
H11B	1.1035	0.2823	0.7263	0.140	1
H11C	0.9086	0.2540	0.6603	0.140	1
H12A	0.5777	-0.0647	0.3759	0.101	1
H12B	0.5852	-0.1028	0.2233	0.101	1
H12C	0.4103	-0.0790	0.2384	0.101	1
H13A	0.5358	0.1397	-0.0763	0.113	1
H13B	0.6241	0.0222	0.0371	0.113	1
H13C	0.6785	0.1783	0.0733	0.113	1

Table 2. *Anisotropic displacement parameters (Å^2)*

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
O15	0.0763 (10)	-0.0070 (8)	0.0195 (6)	0.0857 (11)	-0.0122 (7)	0.0543 (7)
O16	0.1066 (13)	-0.0215 (9)	0.0340 (8)	0.0687 (9)	0.0038 (6)	0.0551 (7)
O17	0.0802 (9)	0.0025 (7)	0.0364 (7)	0.0513 (8)	-0.0005 (6)	0.0693 (8)
N14	0.0763 (11)	-0.0042 (8)	0.0233 (8)	0.0579 (10)	-0.0064 (7)	0.0579 (8)
C1	0.0603 (10)	-0.0103 (8)	0.0258 (8)	0.0561 (10)	-0.0013 (8)	0.0542 (9)
C2	0.0586 (10)	-0.0052 (9)	0.0223 (8)	0.0574 (10)	0.0007 (8)	0.0461 (8)
C3	0.0572 (9)	-0.0021 (8)	0.0245 (7)	0.0495 (9)	-0.0006 (7)	0.0489 (8)
C4	0.0596 (11)	-0.0029 (8)	0.0296 (9)	0.0542 (10)	-0.0047 (8)	0.0656 (10)
C5	0.0577 (12)	-0.0091 (10)	0.0209 (10)	0.0746 (15)	-0.0037 (11)	0.0797 (14)
C6	0.0612 (11)	0.0057 (11)	0.0102 (9)	0.0665 (12)	0.0032 (10)	0.0679 (11)
C7	0.0649 (13)	0.0066 (12)	0.0091 (10)	0.0846 (17)	-0.0080 (12)	0.0721 (13)
C8	0.090 (2)	0.015 (2)	0.0152 (14)	0.155 (4)	-0.0147 (18)	0.0768 (16)
C9	0.0579 (12)	-0.0028 (11)	0.0171 (10)	0.0852 (16)	-0.0042 (11)	0.0734 (13)
C10	0.0778 (14)	-0.0166 (13)	0.0496 (11)	0.0814 (15)	-0.0135 (12)	0.0826 (14)
C11	0.166 (4)	0.032 (2)	0.023 (2)	0.079 (2)	0.0135 (15)	0.0860 (19)
C12	0.0972 (18)	-0.0073 (13)	0.0340 (15)	0.0575 (12)	-0.0065 (13)	0.0966 (17)
C13	0.110 (2)	-0.0175 (17)	0.0480 (14)	0.103 (2)	-0.0279 (15)	0.0788 (15)

Table 3 . *Geometric parameters (Å, °)*

O15—N14	1.396 (2)	C4—C5	1.544 (3)
O15—C13	1.422 (3)	C5—C6	1.492 (3)
O16—C1	1.233 (2)	C6—C7	1.323 (4)
O17—C3	1.426 (2)	C6—C11	1.488 (4)
N14—C1	1.349 (3)	C7—C8	1.495 (4)
N14—C12	1.455 (3)	O17—H17	0.8200
C1—C2	1.508 (3)	C2—H2	0.9600
C2—C9	1.532 (3)	C3—H3	0.9600
C2—C3	1.546 (2)	C4—H4	0.9600
C3—C4	1.526 (3)	C5—H5A	0.9700
C4—C10	1.522 (3)	C5—H5B	0.9700

C7—H7	0.9601	C11—H11A	0.9600
C8—H8A	0.9600	C11—H11B	0.9600
C8—H8B	0.9600	C11—H11C	0.9600
C8—H8C	0.9600	C12—H12A	0.9600
C9—H9A	0.9600	C12—H12B	0.9600
C9—H9B	0.9599	C12—H12C	0.9600
C9—H9C	0.9600	C13—H13A	0.9600
C10—H10A	0.9600	C13—H13B	0.9600
C10—H10B	0.9600	C13—H13C	0.9600
C10—H10C	0.9601		

N14—O15—C13	110.6 (2)	C8—C7—H7	112.2
C1—N14—O15	118.18 (18)	C7—C8—H8A	109.5
C1—N14—C12	122.8 (2)	C7—C8—H8B	109.5
O15—N14—C12	114.60 (18)	H8A—C8—H8B	109.5
O16—C1—N14	118.6 (2)	C7—C8—H8C	109.5
O16—C1—C2	122.23 (18)	H8A—C8—H8C	109.5
N14—C1—C2	119.13 (16)	H8B—C8—H8C	109.5
C1—C2—C9	108.13 (18)	C2—C9—H9A	109.0
C1—C2—C3	109.85 (15)	C2—C9—H9B	109.7
C9—C2—C3	111.87 (17)	H9A—C9—H9B	109.5
O17—C3—C4	108.52 (16)	C2—C9—H9C	109.7
O17—C3—C2	109.65 (15)	H9A—C9—H9C	109.5
C4—C3—C2	112.85 (15)	H9B—C9—H9C	109.5
C10—C4—C3	112.94 (18)	C4—C10—H10A	109.4
C10—C4—C5	109.76 (18)	C4—C10—H10B	109.6
C3—C4—C5	110.36 (17)	H10A—C10—H10B	109.5
C6—C5—C4	116.7 (2)	C4—C10—H10C	109.4
C7—C6—C11	123.3 (3)	H10A—C10—H10C	109.5
C7—C6—C5	121.3 (2)	H10B—C10—H10C	109.5
C11—C6—C5	115.4 (2)	C6—C11—H11A	109.7
C6—C7—C8	128.3 (3)	C6—C11—H11B	109.8
C3—O17—H17	109.5	H11A—C11—H11B	109.5
C1—C2—H2	109.6	C6—C11—H11C	108.9
C9—C2—H2	108.3	H11A—C11—H11C	109.5
C3—C2—H2	109.1	H11B—C11—H11C	109.5
O17—C3—H3	109.9	N14—C12—H12A	109.8
C4—C3—H3	108.5	N14—C12—H12B	109.9
C2—C3—H3	107.5	H12A—C12—H12B	109.5
C10—C4—H4	107.6	N14—C12—H12C	108.7
C3—C4—H4	106.9	H12A—C12—H12C	109.5
C5—C4—H4	109.2	H12B—C12—H12C	109.5
C6—C5—H5A	108.1	O15—C13—H13A	109.9
C4—C5—H5A	108.1	O15—C13—H13B	108.7
C6—C5—H5B	108.1	H13A—C13—H13B	109.5
C4—C5—H5B	108.1	O15—C13—H13C	109.8
H5A—C5—H5B	107.3	H13A—C13—H13C	109.5
C6—C7—H7	119.5	H13B—C13—H13C	109.5

C13—O15—N14—C1	116.5 (2)	C13—O15—N14—C12	-86.4 (3)

O15—N14—C1—O16	167.07 (19)	C9—C2—C3—C4	-174.36 (18)
C12—N14—C1—O16	12.0 (4)	O17—C3—C4—C10	-56.1 (2)
O15—N14—C1—C2	-13.9 (3)	C2—C3—C4—C10	65.6 (2)
C12—N14—C1—C2	-168.9 (2)	O17—C3—C4—C5	67.2 (2)
O16—C1—C2—C9	-78.4 (2)	C2—C3—C4—C5	-171.09 (16)
N14—C1—C2—C9	102.5 (2)	C10—C4—C5—C6	-174.7 (2)
O16—C1—C2—C3	43.9 (3)	C3—C4—C5—C6	60.2 (3)
N14—C1—C2—C3	-135.14 (19)	C4—C5—C6—C7	-122.8 (3)
C1—C2—C3—O17	-173.36 (15)	C4—C5—C6—C11	58.6 (4)
C9—C2—C3—O17	-53.3 (2)	C11—C6—C7—C8	0.9 (5)
C1—C2—C3—C4	65.5 (2)	C5—C6—C7—C8	-177.6 (2)

Crystal and molecular structure of (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16)

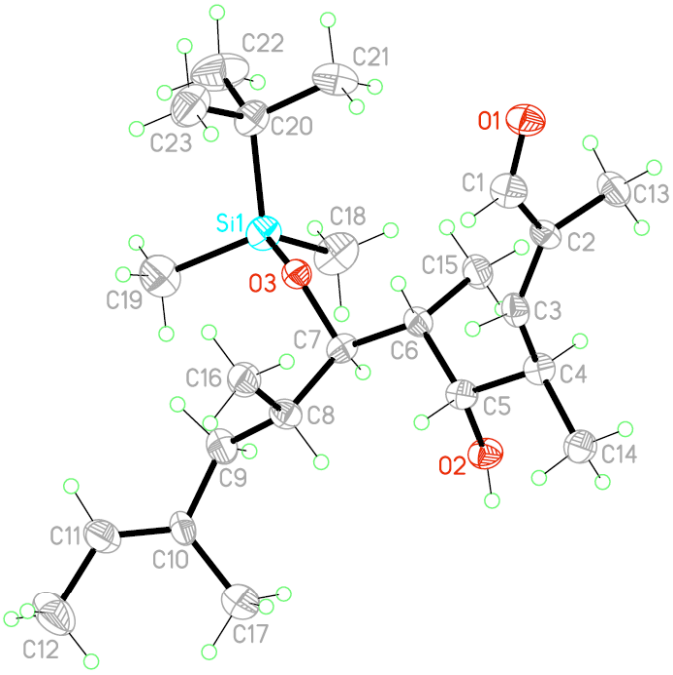


Table 1. Crystal data and structure refinement for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16).

Identification code	sb373	
Empirical formula	C23 H44 O3 Si	
Formula weight	396.67	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.404(5) Å	α= 90°.
	b = 14.93(3) Å	β= 90°.
	c = 20.26(5) Å	γ = 90°.
Volume	2541(8) $Å^3$	
Z	4	
Density (calculated)	1.037 Mg/m^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	880	
Crystal size	0.42 x 0.17 x 0.06 mm^3	
Theta range for data collection	3.31 to 23.20°.	

Index ranges	-9<=h<=9, -16<=k<=16, -22<=l<=22
Reflections collected	27234
Independent reflections	3591 [R(int) = 0.1531]
Completeness to theta = 23.20°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.1855
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3591 / 0 / 246
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0670, wR2 = 0.1138
R indices (all data)	R1 = 0.1170, wR2 = 0.1332
Absolute structure parameter	0.1(3)
Extinction coefficient	0.0030(11)
Largest diff. peak and hole	0.229 and -0.216 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	5210(2)	7809(1)	8474(1)	38(1)
O(1)	11173(4)	8462(2)	5235(2)	42(1)
O(2)	3118(4)	9390(2)	6184(2)	36(1)
O(3)	5240(3)	7747(2)	7669(1)	30(1)
C(1)	9727(6)	8398(3)	5199(2)	40(1)
C(2)	8573(5)	9082(3)	5414(2)	30(1)
C(3)	7030(6)	8868(3)	5370(2)	32(1)
C(4)	5600(5)	9403(3)	5546(2)	32(1)
C(5)	4518(5)	8875(3)	6035(2)	30(1)
C(6)	5334(5)	8629(3)	6682(2)	30(1)
C(7)	4244(5)	8111(3)	7159(2)	31(1)
C(8)	3206(5)	7374(3)	6845(2)	32(1)
C(9)	1974(5)	7029(3)	7341(3)	40(1)
C(10)	565(5)	6557(3)	7056(2)	34(1)
C(11)	238(6)	5712(4)	7195(3)	51(2)
C(12)	-1180(6)	5174(4)	6987(3)	69(2)
C(13)	9261(5)	9957(3)	5659(3)	43(2)

C(14)	4672(6)	9637(3)	4913(2)	41(1)
C(15)	6001(6)	9461(3)	7034(2)	40(1)
C(16)	4230(6)	6615(3)	6567(3)	41(1)
C(17)	-523(6)	7125(4)	6634(3)	56(2)
C(18)	4465(7)	8915(3)	8762(3)	55(2)
C(19)	3902(6)	6921(4)	8836(3)	54(2)
C(20)	7329(6)	7586(4)	8741(2)	40(1)
C(21)	8463(6)	8300(4)	8460(3)	57(2)
C(22)	7460(7)	7618(5)	9500(3)	77(2)
C(23)	7857(7)	6664(4)	8498(3)	61(2)

Table 3. Bond lengths [Å] and angles [°] for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16).

Si(1)-O(3)	1.633(5)
Si(1)-C(18)	1.859(6)
Si(1)-C(19)	1.873(6)
Si(1)-C(20)	1.890(5)
O(1)-C(1)	1.221(5)
O(2)-C(5)	1.438(5)
O(2)-H(2)	0.8400
O(3)-C(7)	1.437(5)
C(1)-C(2)	1.474(7)
C(1)-H(1)	0.9500
C(2)-C(3)	1.338(6)
C(2)-C(13)	1.513(7)
C(3)-C(4)	1.486(6)
C(3)-H(3)	0.9500
C(4)-C(14)	1.541(7)
C(4)-C(5)	1.559(6)
C(4)-H(4)	1.0000
C(5)-C(6)	1.524(7)
C(5)-H(5)	1.0000
C(6)-C(15)	1.537(6)
C(6)-C(7)	1.540(6)
C(6)-H(6)	1.0000
C(7)-C(8)	1.541(6)

C(7)-H(7)	1.0000
C(8)-C(16)	1.531(6)
C(8)-C(9)	1.532(6)
C(8)-H(8)	1.0000
C(9)-C(10)	1.495(6)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.321(7)
C(10)-C(17)	1.511(7)
C(11)-C(12)	1.497(7)
C(11)-H(11)	0.9500
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(23)	1.527(7)
C(20)-C(21)	1.539(7)
C(20)-C(22)	1.543(8)
C(21)-H(21A)	0.9800

C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

O(3)-Si(1)-C(18)	111.7(2)
O(3)-Si(1)-C(19)	111.0(2)
C(18)-Si(1)-C(19)	108.0(3)
O(3)-Si(1)-C(20)	105.1(2)
C(18)-Si(1)-C(20)	112.6(3)
C(19)-Si(1)-C(20)	108.4(3)
C(5)-O(2)-H(2)	109.5
C(7)-O(3)-Si(1)	133.4(3)
O(1)-C(1)-C(2)	125.7(5)
O(1)-C(1)-H(1)	117.2
C(2)-C(1)-H(1)	117.2
C(3)-C(2)-C(1)	116.9(5)
C(3)-C(2)-C(13)	126.7(5)
C(1)-C(2)-C(13)	116.4(4)
C(2)-C(3)-C(4)	129.7(5)
C(2)-C(3)-H(3)	115.1
C(4)-C(3)-H(3)	115.1
C(3)-C(4)-C(14)	109.4(4)
C(3)-C(4)-C(5)	110.6(4)
C(14)-C(4)-C(5)	110.4(4)
C(3)-C(4)-H(4)	108.8
C(14)-C(4)-H(4)	108.8
C(5)-C(4)-H(4)	108.8
O(2)-C(5)-C(6)	108.5(4)
O(2)-C(5)-C(4)	109.9(4)
C(6)-C(5)-C(4)	113.9(4)
O(2)-C(5)-H(5)	108.1
C(6)-C(5)-H(5)	108.1
C(4)-C(5)-H(5)	108.1
C(5)-C(6)-C(15)	111.7(4)

C(5)-C(6)-C(7)	113.1(4)
C(15)-C(6)-C(7)	109.4(4)
C(5)-C(6)-H(6)	107.5
C(15)-C(6)-H(6)	107.5
C(7)-C(6)-H(6)	107.5
O(3)-C(7)-C(6)	107.1(4)
O(3)-C(7)-C(8)	110.9(4)
C(6)-C(7)-C(8)	115.9(4)
O(3)-C(7)-H(7)	107.5
C(6)-C(7)-H(7)	107.5
C(8)-C(7)-H(7)	107.5
C(16)-C(8)-C(9)	111.8(4)
C(16)-C(8)-C(7)	111.2(4)
C(9)-C(8)-C(7)	110.6(4)
C(16)-C(8)-H(8)	107.7
C(9)-C(8)-H(8)	107.7
C(7)-C(8)-H(8)	107.7
C(10)-C(9)-C(8)	116.1(4)
C(10)-C(9)-H(9A)	108.3
C(8)-C(9)-H(9A)	108.3
C(10)-C(9)-H(9B)	108.3
C(8)-C(9)-H(9B)	108.3
H(9A)-C(9)-H(9B)	107.4
C(11)-C(10)-C(9)	122.2(5)
C(11)-C(10)-C(17)	122.1(5)
C(9)-C(10)-C(17)	115.7(4)
C(10)-C(11)-C(12)	128.1(5)
C(10)-C(11)-H(11)	116.0
C(12)-C(11)-H(11)	116.0
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(2)-C(13)-H(13A)	109.5
C(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(2)-C(13)-H(13C)	109.5

H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(4)-C(14)-H(14A)	109.5
C(4)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(4)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(6)-C(15)-H(15A)	109.5
C(6)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(6)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(8)-C(16)-H(16A)	109.5
C(8)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(8)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(10)-C(17)-H(17A)	109.5
C(10)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(10)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
Si(1)-C(18)-H(18A)	109.5
Si(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(23)-C(20)-C(21)	109.0(5)

C(23)-C(20)-C(22)	109.1(5)
C(21)-C(20)-C(22)	107.7(5)
C(23)-C(20)-Si(1)	109.9(4)
C(21)-C(20)-Si(1)	110.8(4)
C(22)-C(20)-Si(1)	110.3(4)
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(20)-C(23)-H(23A)	109.5
C(20)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(20)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for sb373. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	43(1)	41(1)	30(1)	-3(1)	0(1)	2(1)
O(1)	28(2)	49(2)	48(3)	-6(2)	2(2)	4(2)
O(2)	28(2)	38(2)	42(2)	-3(2)	2(2)	7(2)
O(3)	28(2)	32(2)	31(2)	1(2)	1(2)	-1(2)
C(1)	42(3)	42(3)	36(3)	-8(3)	0(3)	0(3)
C(2)	29(3)	34(3)	28(3)	-4(3)	-1(2)	-6(2)
C(3)	45(3)	27(3)	23(3)	-3(2)	-2(2)	-9(3)

C(4)	34(3)	33(3)	28(3)	-4(2)	2(2)	1(2)
C(5)	29(3)	27(3)	33(3)	-9(2)	0(2)	4(2)
C(6)	30(2)	28(3)	32(3)	-2(2)	0(2)	-3(2)
C(7)	31(3)	34(3)	28(3)	1(2)	-1(2)	4(2)
C(8)	34(3)	36(3)	28(3)	-4(3)	-2(2)	-3(2)
C(9)	40(3)	35(4)	45(3)	1(3)	3(3)	-6(3)
C(10)	35(3)	27(3)	40(3)	4(3)	5(3)	-7(2)
C(11)	35(3)	45(4)	71(4)	0(3)	-5(3)	-6(3)
C(12)	40(3)	51(4)	115(6)	-9(4)	16(4)	-5(3)
C(13)	31(3)	30(3)	67(4)	-6(3)	6(3)	-3(2)
C(14)	40(3)	49(3)	33(3)	10(3)	-2(3)	-6(3)
C(15)	46(3)	38(3)	36(3)	5(3)	-5(3)	-12(3)
C(16)	45(3)	37(3)	41(3)	-2(3)	-4(3)	-3(3)
C(17)	43(3)	58(4)	66(4)	10(3)	-4(3)	-8(3)
C(18)	69(4)	57(4)	39(3)	-12(3)	-3(3)	16(3)
C(19)	60(4)	63(5)	39(4)	-3(3)	6(3)	-9(3)
C(20)	47(3)	42(4)	30(3)	0(3)	0(3)	5(3)
C(21)	42(3)	71(4)	58(4)	-7(4)	-13(3)	-6(3)
C(22)	64(4)	124(7)	43(4)	-2(4)	-15(3)	11(4)
C(23)	59(4)	60(4)	62(4)	14(4)	3(4)	13(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16).

	x	y	z	U(eq)
H(2)	2479	9360	5865	54
H(1)	9309	7860	5018	48
H(3)	6817	8286	5202	38
H(4)	5952	9972	5762	38
H(5)	4176	8308	5814	36
H(6)	6255	8232	6573	36
H(7)	3512	8555	7370	37
H(8)	2615	7650	6467	39
H(9A)	2516	6615	7649	48
H(9B)	1586	7545	7603	48

H(11)	997	5408	7461	61
H(12A)	-1905	5554	6732	103
H(12B)	-1731	4947	7380	103
H(12C)	-830	4670	6714	103
H(13A)	8409	10402	5698	64
H(13B)	10063	10172	5345	64
H(13C)	9756	9865	6091	64
H(14A)	5394	9915	4592	61
H(14B)	3812	10056	5020	61
H(14C)	4220	9090	4723	61
H(15A)	5139	9891	7111	60
H(15B)	6822	9738	6758	60
H(15C)	6466	9283	7458	60
H(16A)	4828	6333	6927	61
H(16B)	4974	6857	6240	61
H(16C)	3543	6167	6357	61
H(17A)	-129	7131	6179	83
H(17B)	-544	7738	6807	83
H(17C)	-1600	6873	6643	83
H(18A)	5153	9391	8590	82
H(18B)	4471	8931	9245	82
H(18C)	3376	9006	8602	82
H(19A)	2785	7068	8749	81
H(19B)	4079	6887	9313	81
H(19C)	4156	6341	8634	81
H(21A)	9551	8175	8607	85
H(21B)	8138	8893	8617	85
H(21C)	8421	8287	7976	85
H(22A)	6812	7138	9692	115
H(22B)	7077	8199	9660	115
H(22C)	8573	7537	9631	115
H(23A)	8956	6553	8638	91
H(23B)	7795	6644	8015	91
H(23C)	7159	6204	8686	91

Table 6. Torsion angles [°] for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16).

C(18)-Si(1)-O(3)-C(7)	-33.9(5)
C(19)-Si(1)-O(3)-C(7)	86.7(4)
C(20)-Si(1)-O(3)-C(7)	-156.3(4)
O(1)-C(1)-C(2)-C(3)	-176.3(5)
O(1)-C(1)-C(2)-C(13)	4.0(8)
C(1)-C(2)-C(3)-C(4)	179.9(5)
C(13)-C(2)-C(3)-C(4)	-0.4(9)
C(2)-C(3)-C(4)-C(14)	112.6(6)
C(2)-C(3)-C(4)-C(5)	-125.6(6)
C(3)-C(4)-C(5)-O(2)	-178.2(4)
C(14)-C(4)-C(5)-O(2)	-57.0(5)
C(3)-C(4)-C(5)-C(6)	59.8(5)
C(14)-C(4)-C(5)-C(6)	-179.0(4)
O(2)-C(5)-C(6)-C(15)	-66.8(5)
C(4)-C(5)-C(6)-C(15)	55.9(5)
O(2)-C(5)-C(6)-C(7)	57.1(5)
C(4)-C(5)-C(6)-C(7)	179.8(4)
Si(1)-O(3)-C(7)-C(6)	125.6(4)
Si(1)-O(3)-C(7)-C(8)	-107.1(4)
C(5)-C(6)-C(7)-O(3)	166.9(4)
C(15)-C(6)-C(7)-O(3)	-67.9(5)
C(5)-C(6)-C(7)-C(8)	42.5(5)
C(15)-C(6)-C(7)-C(8)	167.7(4)
O(3)-C(7)-C(8)-C(16)	-57.1(5)
C(6)-C(7)-C(8)-C(16)	65.3(5)
O(3)-C(7)-C(8)-C(9)	67.8(5)
C(6)-C(7)-C(8)-C(9)	-169.8(4)
C(16)-C(8)-C(9)-C(10)	-75.4(5)
C(7)-C(8)-C(9)-C(10)	160.1(4)
C(8)-C(9)-C(10)-C(11)	118.9(6)
C(8)-C(9)-C(10)-C(17)	-65.0(6)
C(9)-C(10)-C(11)-C(12)	175.3(5)
C(17)-C(10)-C(11)-C(12)	-0.5(9)
O(3)-Si(1)-C(20)-C(23)	-59.1(4)
C(18)-Si(1)-C(20)-C(23)	179.1(4)
C(19)-Si(1)-C(20)-C(23)	59.7(4)
O(3)-Si(1)-C(20)-C(21)	61.4(4)
C(18)-Si(1)-C(20)-C(21)	-60.3(5)

C(19)-Si(1)-C(20)-C(21)	-179.7(4)
O(3)-Si(1)-C(20)-C(22)	-179.5(4)
C(18)-Si(1)-C(20)-C(22)	58.8(5)
C(19)-Si(1)-C(20)-C(22)	-60.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for (2*E*,4*R*,5*S*,6*R*,7*R*,8*S*,10*E*)-7-(*tert*-butyldimethylsilyloxy)-5-hydroxy-2,4,6,8,10-pentamethyldodeca-2,10-dienal (16). [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)#1	0.84	2.15	2.879(6)	144.6

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

Cell culture techniques, antibodies and indirect immunofluorescence.

HeLa cells were cultured at 37°C in Dulbecco's modified eagle's medium (DMEM), supplemented with 10% fetal calf serum, 100 units/ml penicillin and 100 μg/ml streptomycin.

For studying the inhibition of CRM1-mediated nuclear export, HeLa cells were grown on coverslips for 24 h to about 75% confluency. Cells were then incubated with different concentrations of LMB (LC laboratories, USA) or Anguinomycin C for 90 min at 37°C. For detection of Rio2, cells were fixed in 4% paraformaldehyde for 15 min and permeabilized for 5 min in 1 x detergent (0.1% Triton-X, 0.02% SDS in 1xPBS). Incubation with α-Rio2 antibody (polyclonal antibody, raised against recombinant full-length human Rio2 in rabbit, affinity-purified) and fluorescently labelled secondary antibody (α-rabbit, Alexa 488-labeled, Invitrogen). Pictures were acquired using a Leica TCS NT1 laser-scanning confocal microscope.

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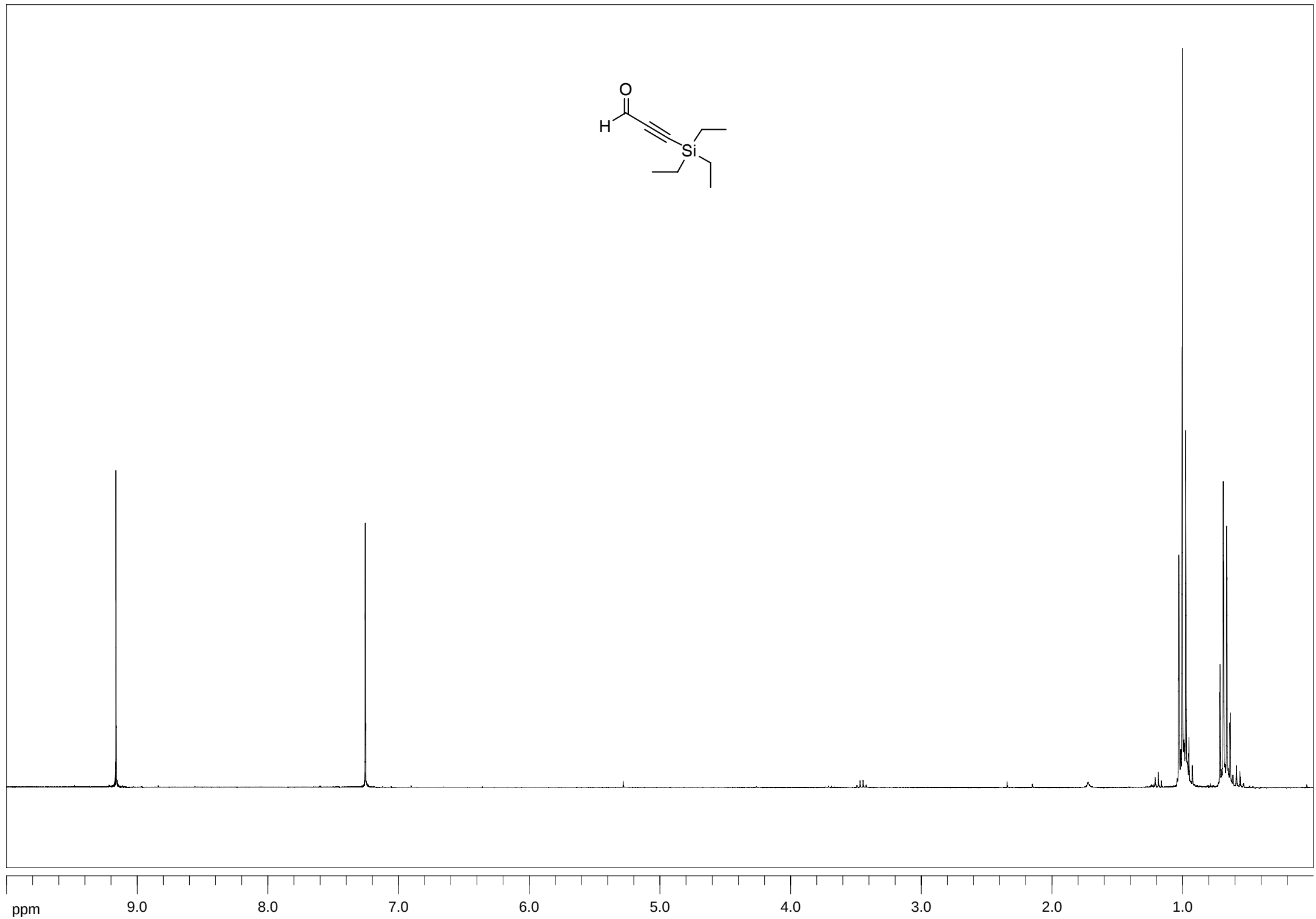
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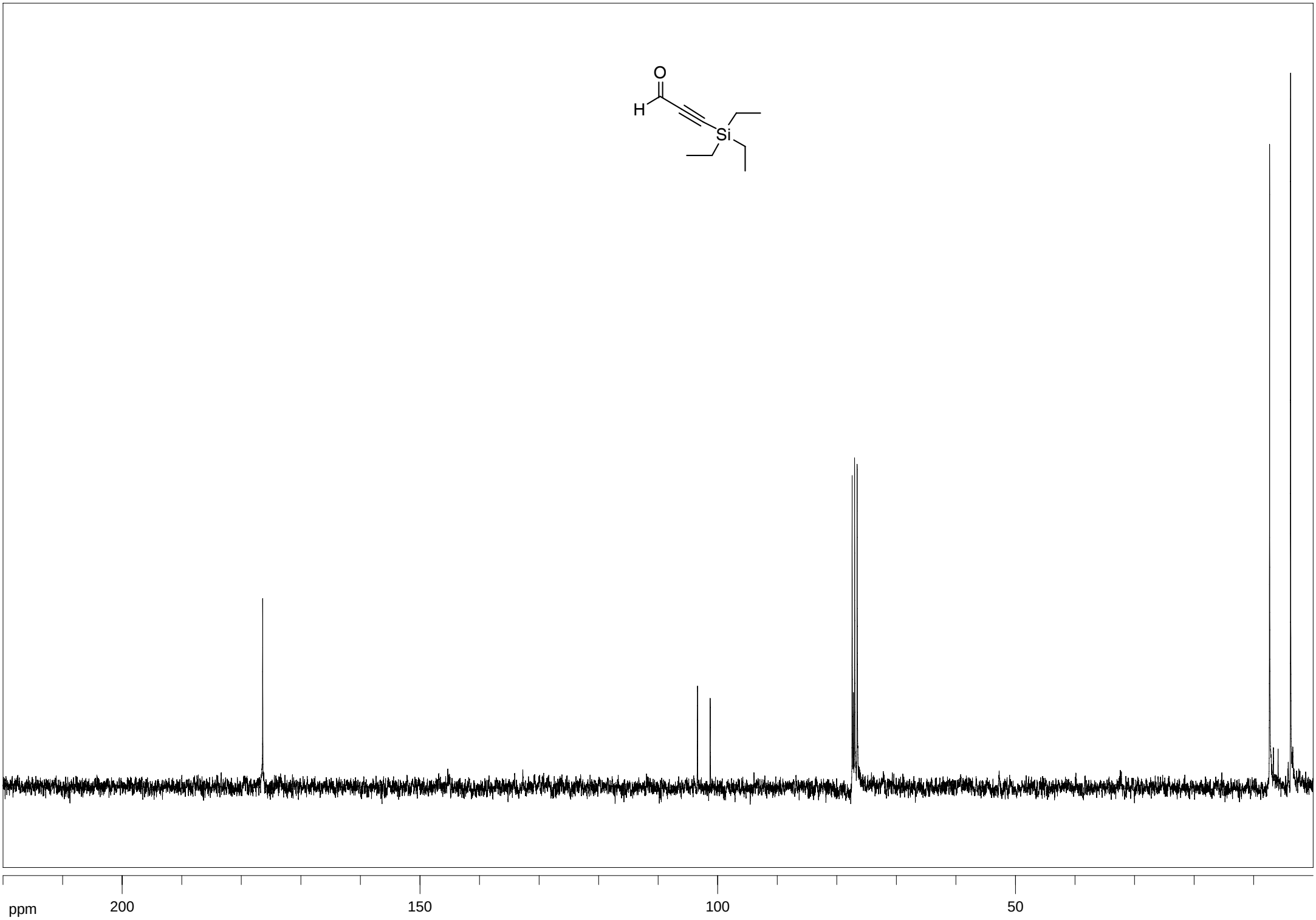
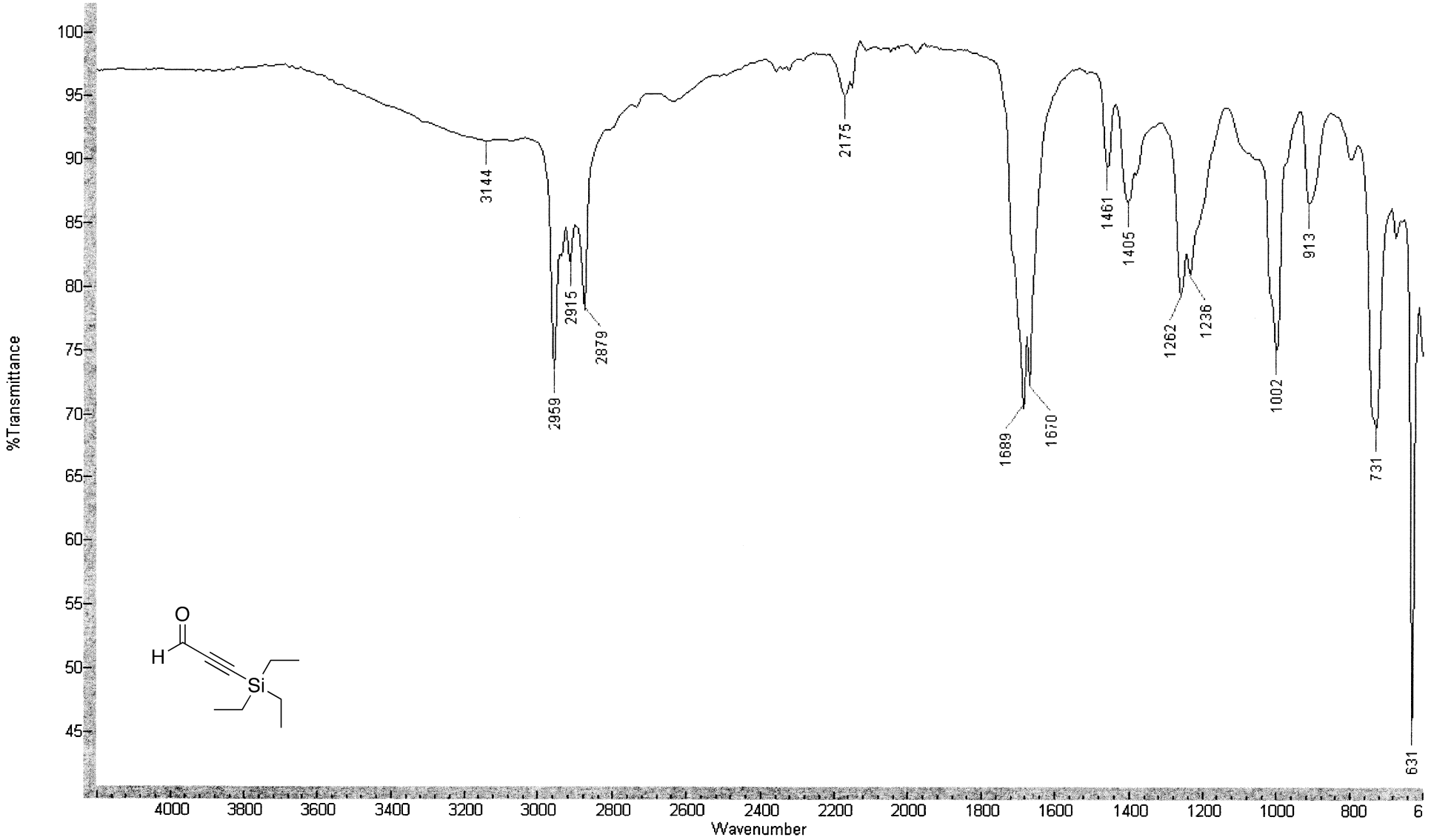
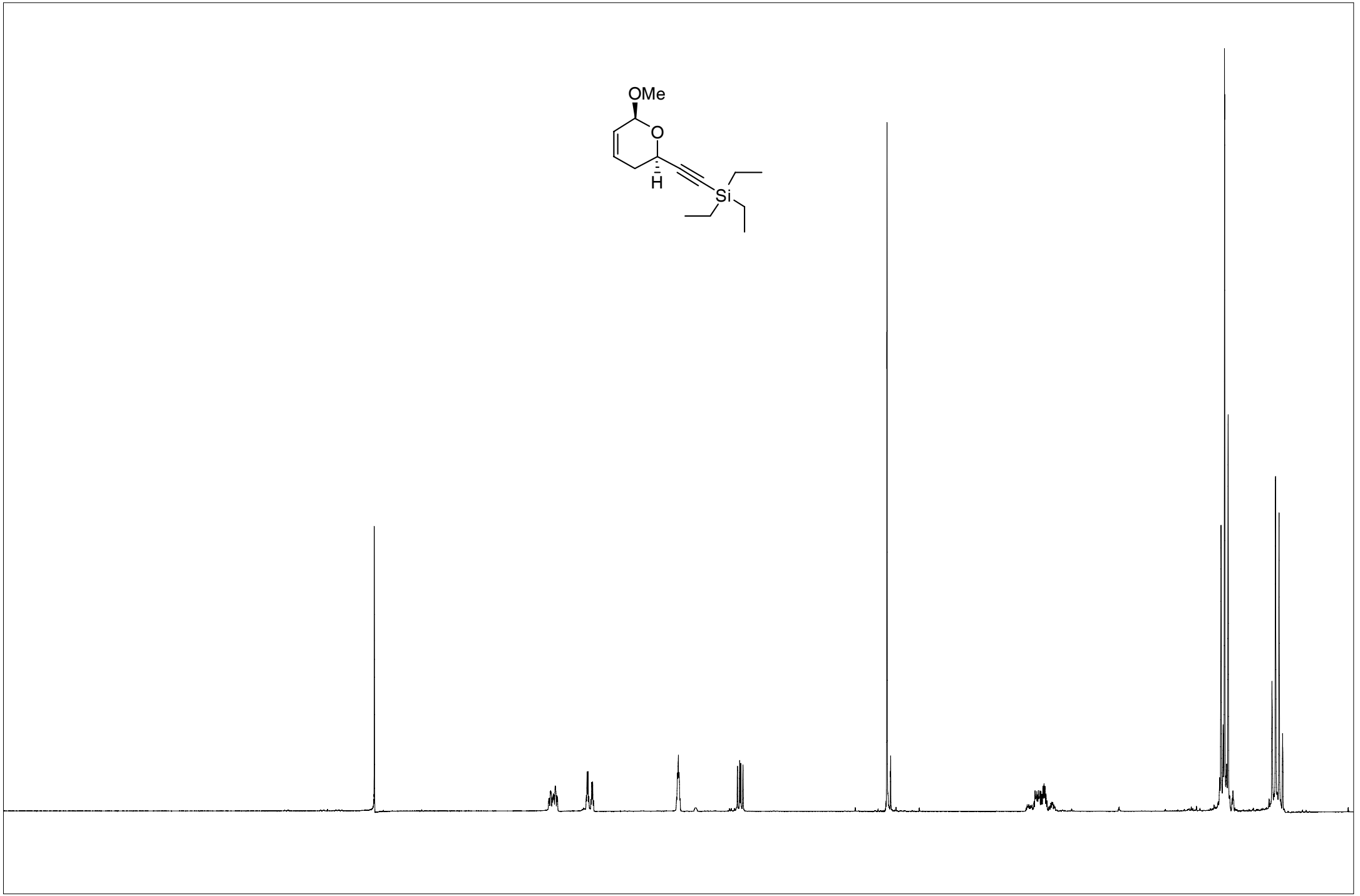
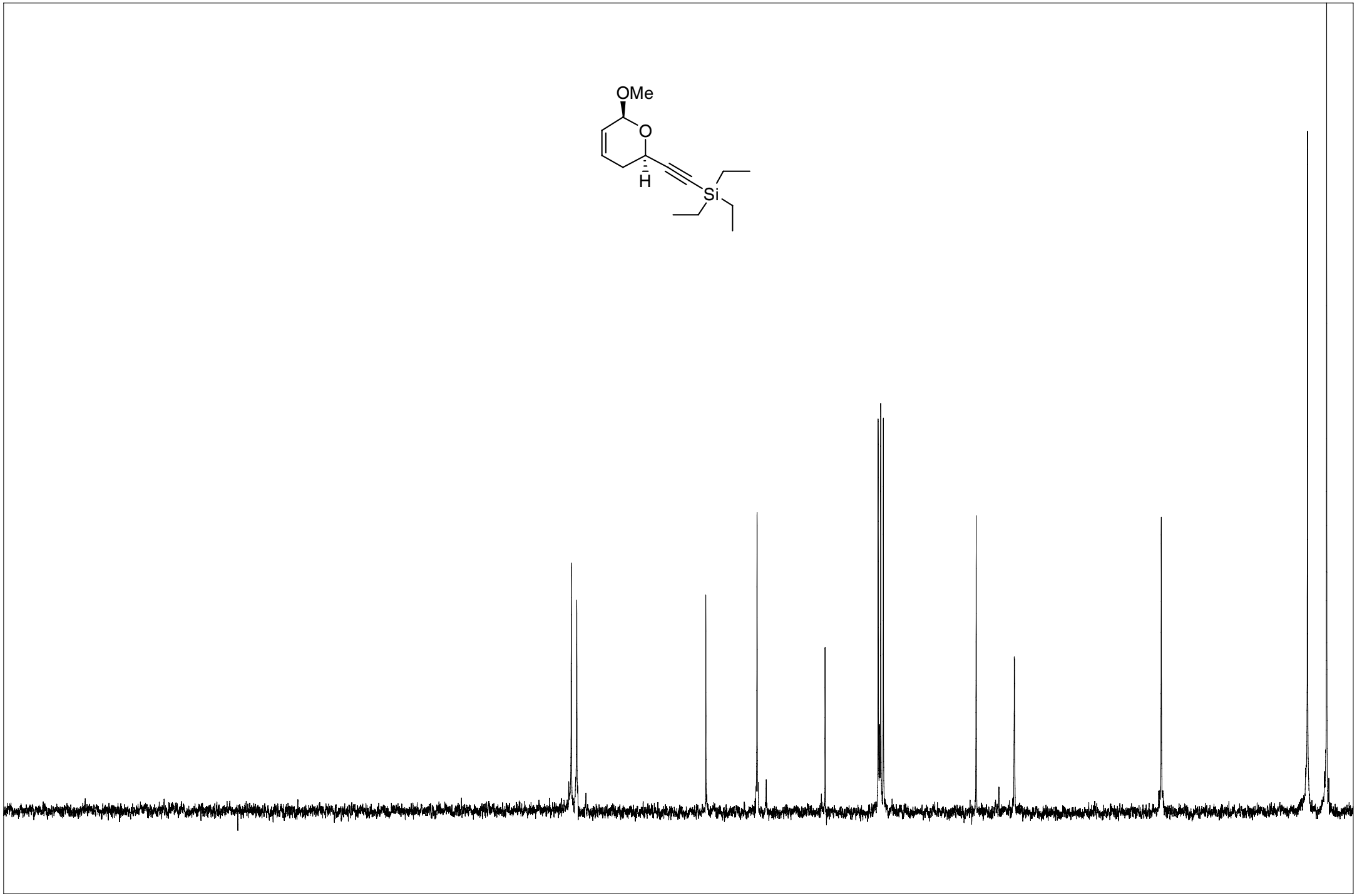
2.0
1.0

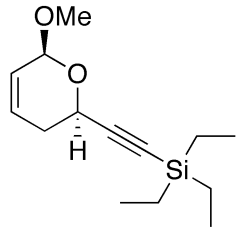

O
H
Si
ppm
200
150
100
50


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
3144
2959
2915
2879
2175
1689
1670
1461
1405
1262
1236
1002
913
731
631
O
H
Si
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber


OMe
O
H
Si
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


OMe
O
H
Si
ppm
200
150
100
50

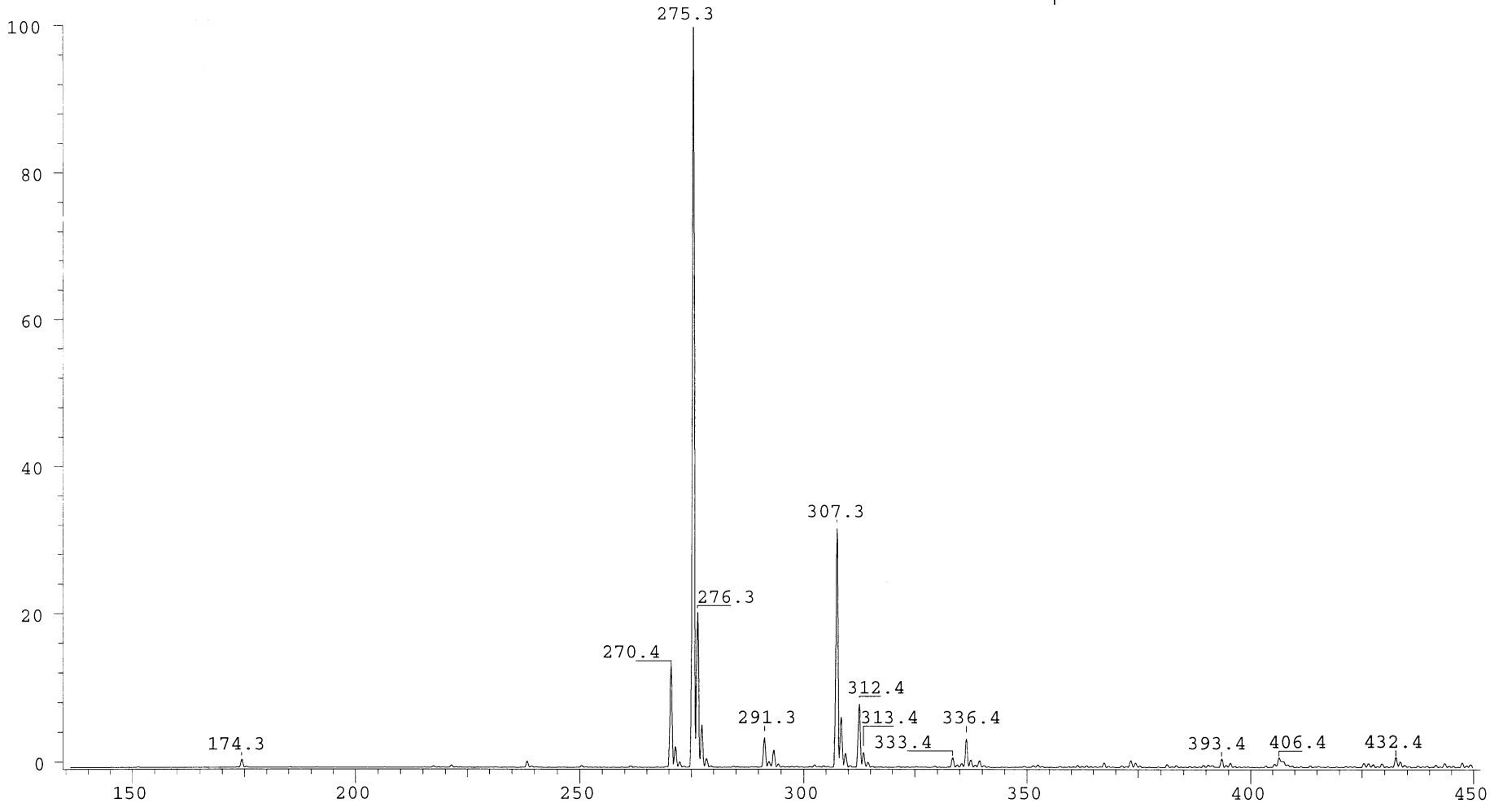
SPEC: esi5286_1.dat (15-DEC-05 17:27:18)
Samp: S.Bonazzi/Carreira - SB56
Comm: LM: CH3OH
Oper: o.s. Study:
Base: 275.32 Masses: 10.00 > 450.02
Peak: 1000.0 mmu Intensity: 1315687
Scan 1 @ 0.05 min (ESI +Q1MS LMR AVER UP PROF) (SM 5)



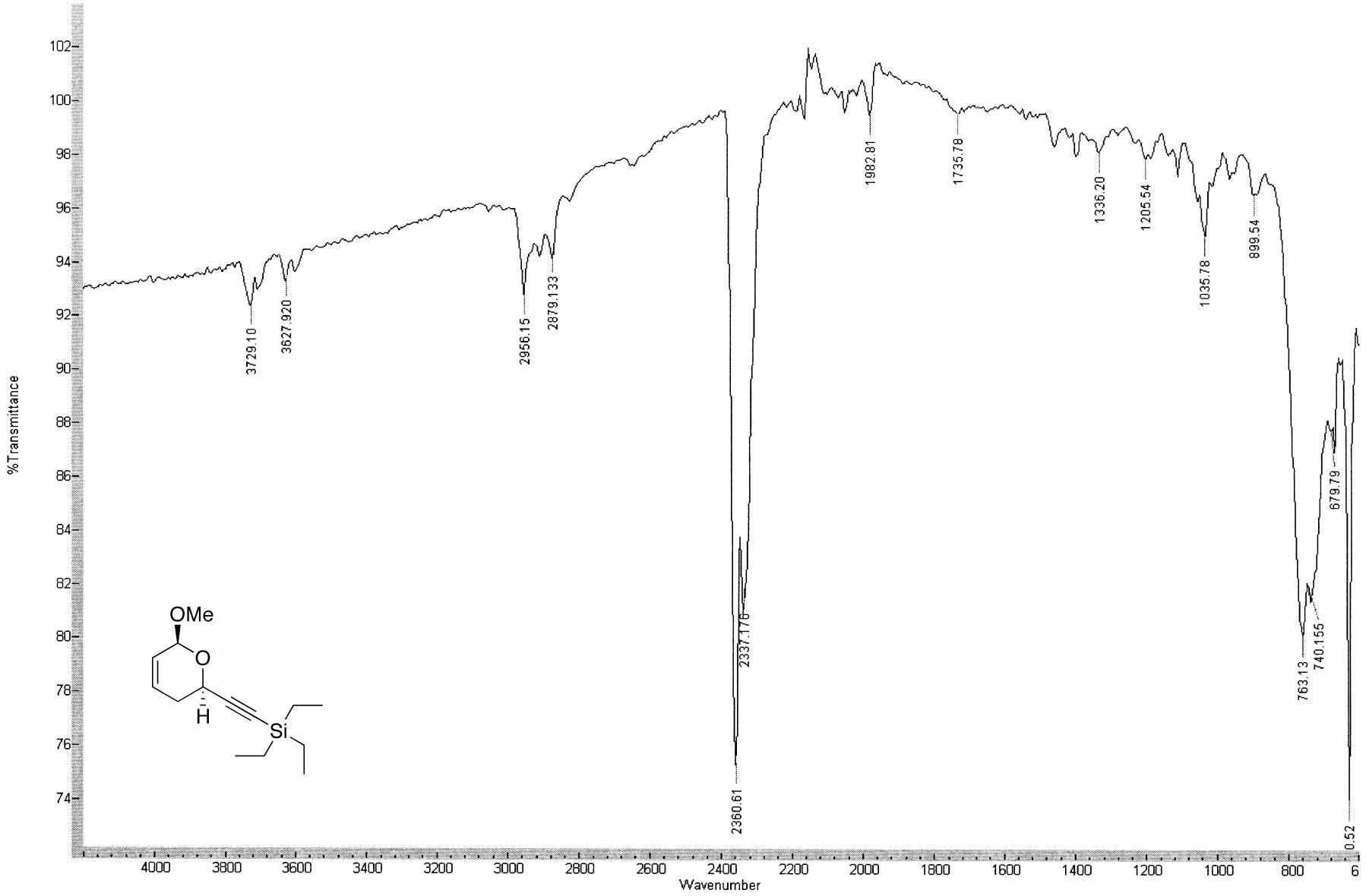
Scans: 1 > 3

Client:
#Peaks: 4399
RIC: 1545668

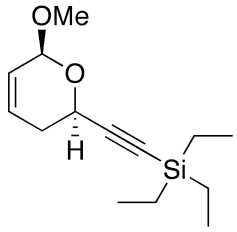
1.1E+06



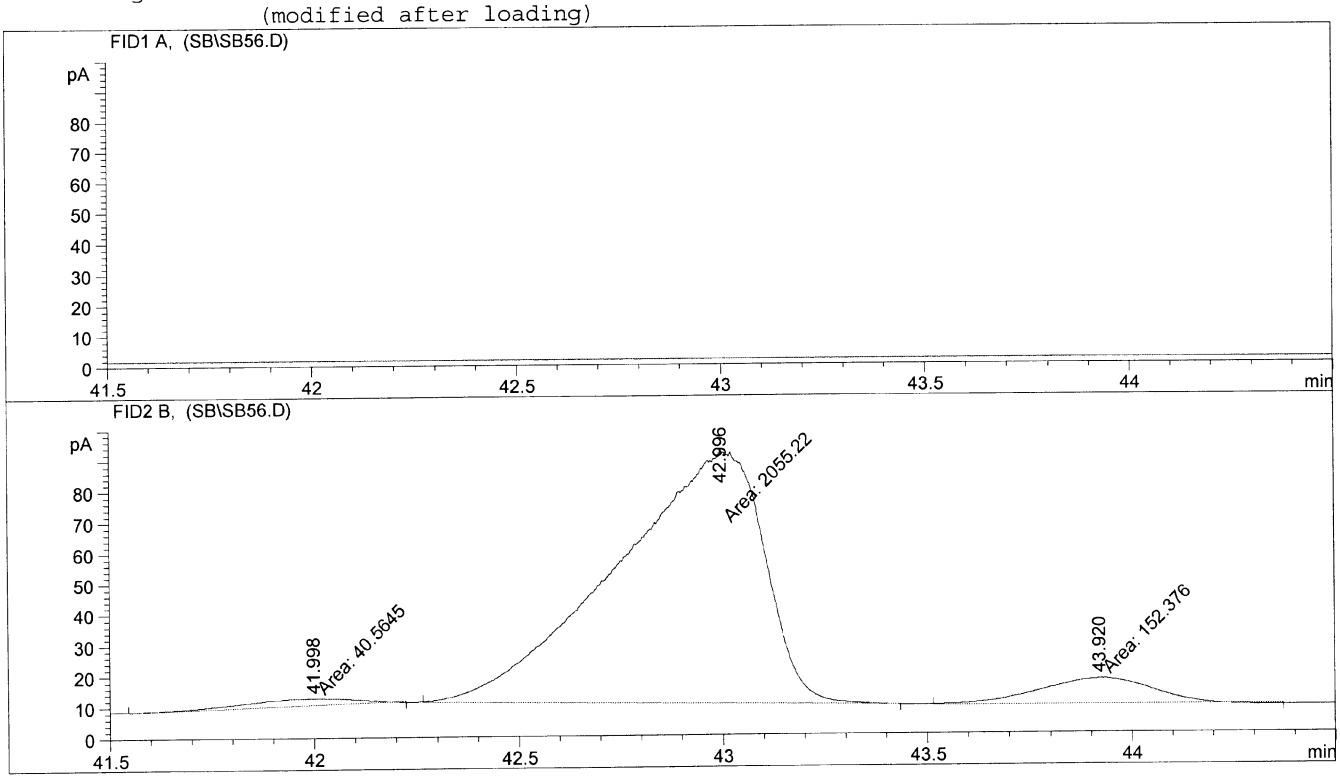
Date: Fri Dec 16 13:01:08 2005 ICIS: 8.3.0 SP2 for OSF1 (V4.0) build 98-238 from 26-Aug-98


%Transmittance
Wavenumber
3729.10
3627.920
2956.15
2879.133
2360.61
2337.176
1982.81
1735.78
1336.20
1205.54
1035.78
899.54
763.13
740.155
679.79
0.52
OMe
O
H
Si

Data File D:\HPCHEM\1\DATA\SB\SB56.D

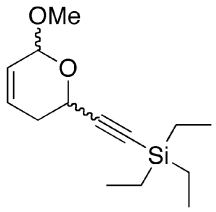



```
==========================================================================
Injection Date  : 15.12.2005 13:11:11
Sample Name     :                                   Location : Vial 2
Acq. Operator   : simone                               Inj :   1
Acq. Instrument : GC 6890                       Inj Volume : Manually
Acq. Method     : C:\HPCHEM\1\METHODS\BETA1.M
Last changed    : 15.12.2005 13:09:46  by simone
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\BETA1.M
Last changed    : 15.12.2005 14:52:58  by simone
                  (modified after loading)
```

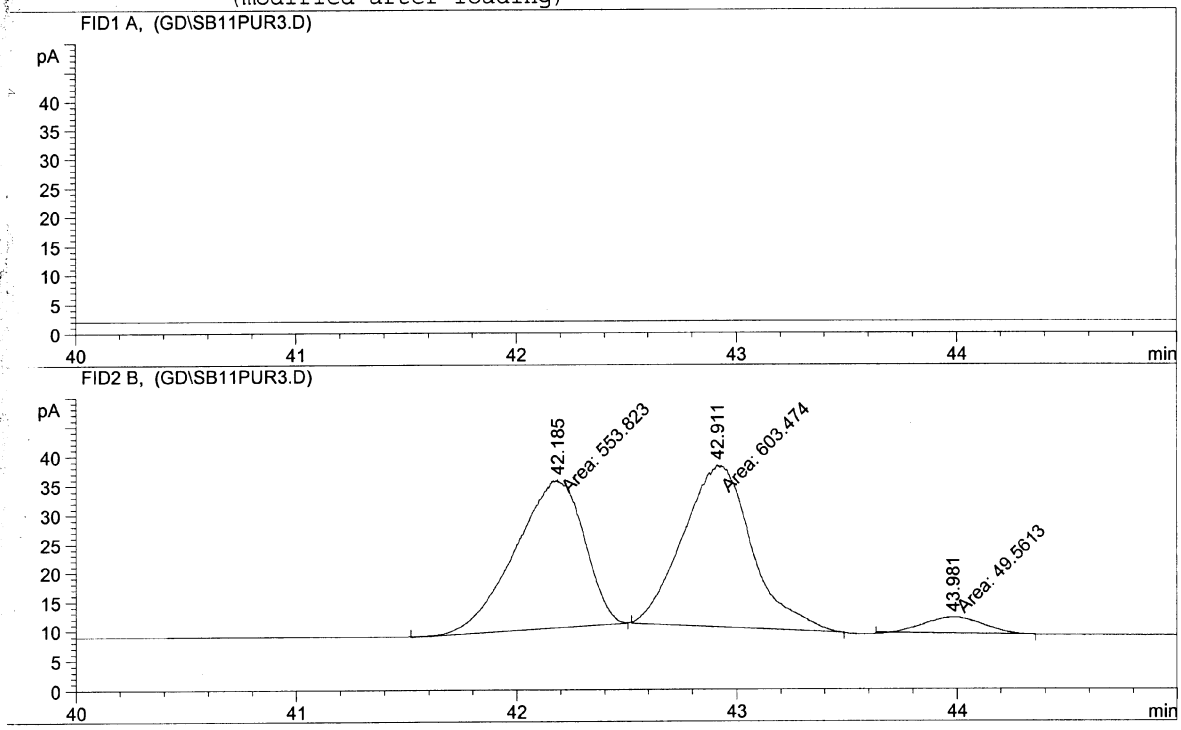



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,


Signal 2: FID2 B,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  41.998 MM    0.3174   40.56447    2.12978  1.80434
   2  42.996 MM    0.4170 2055.21826   82.14944 91.41783
   3  43.920 MM    0.3104  152.37637    8.18065  6.77783

Totals :                  2248.15910   92.45986

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

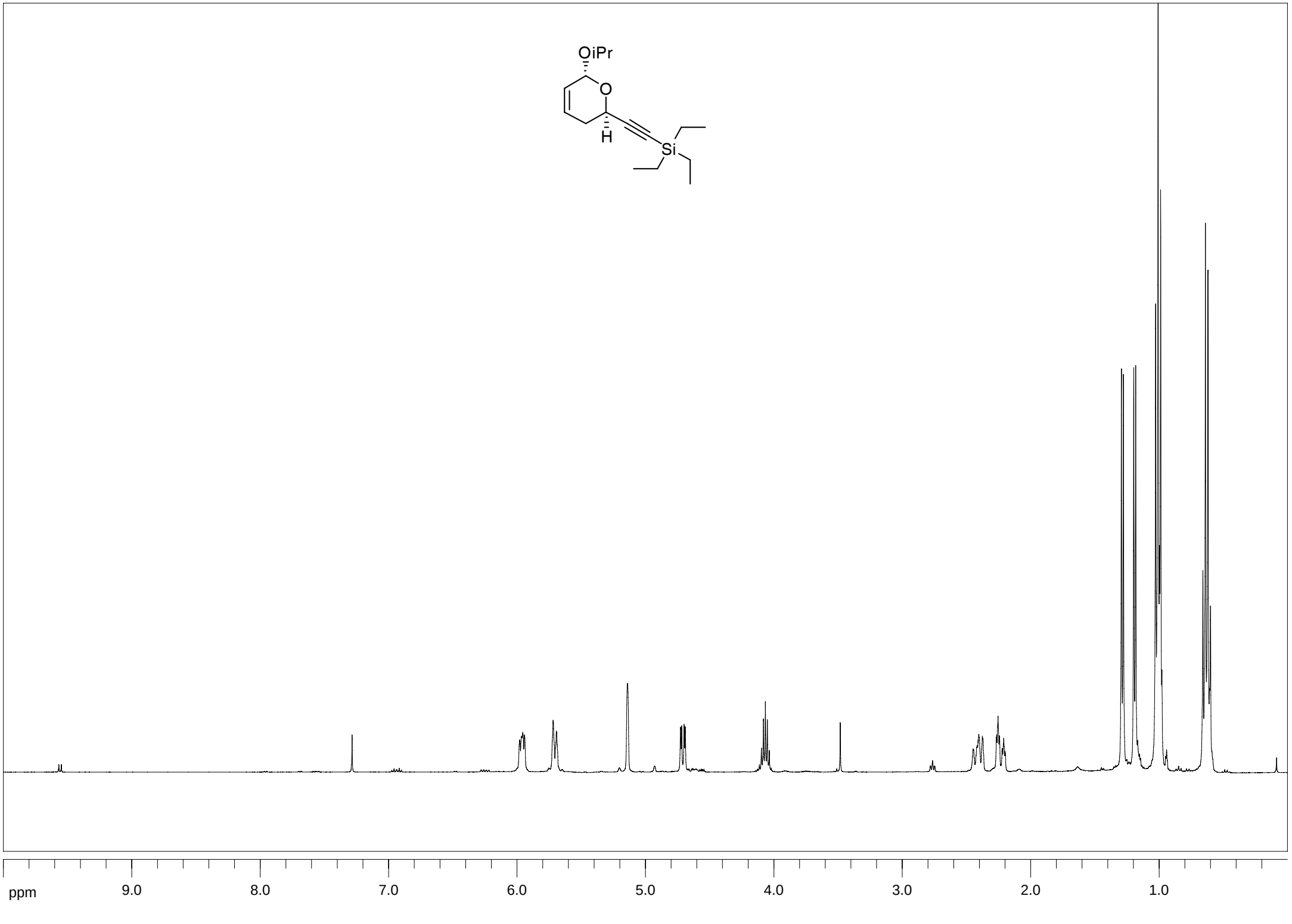
ile D:\HPCHEM\1\DATA\GD\SB11PUR3.D

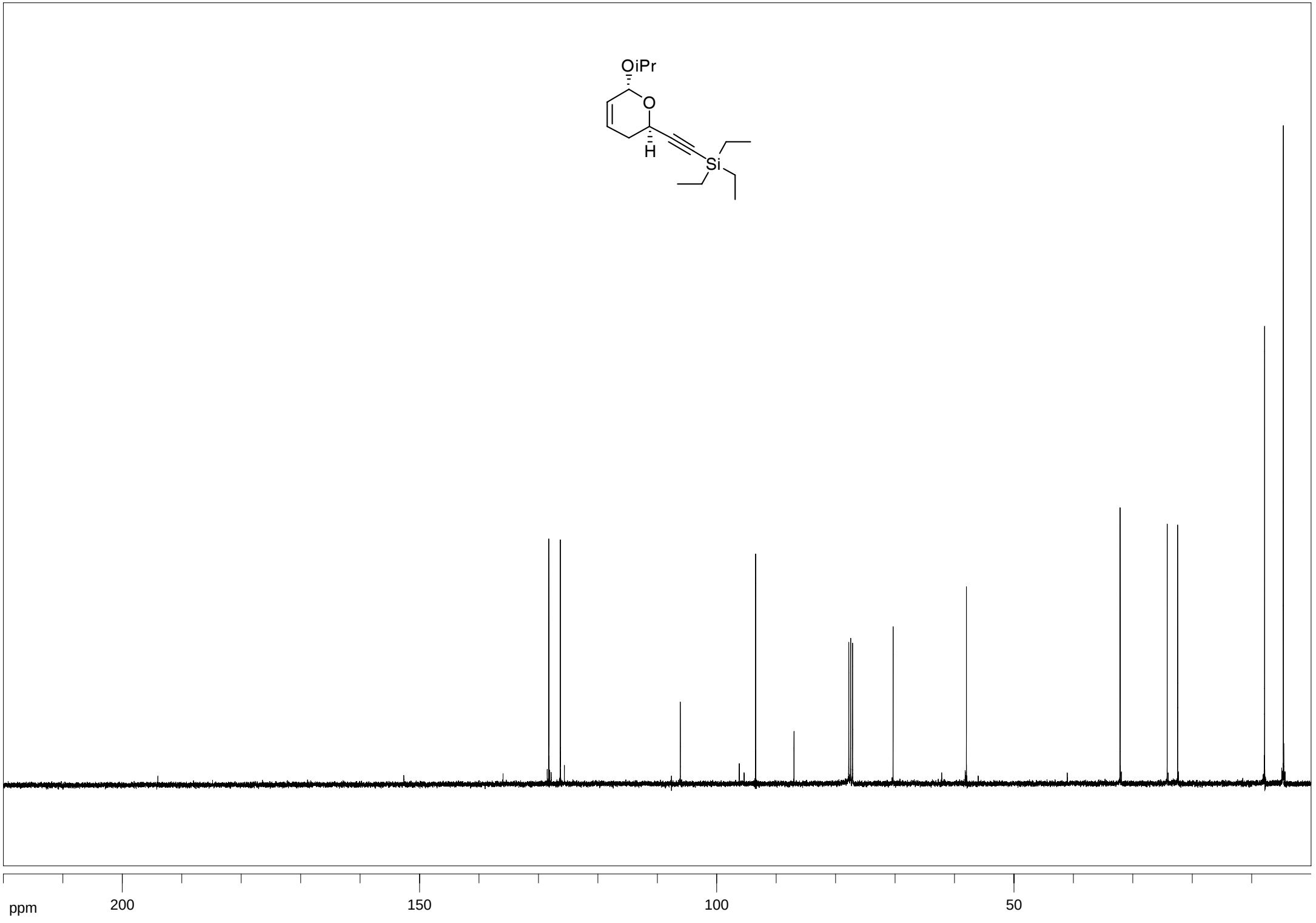



```
==========================================================================
ection Date  : 21.10.2005 16:19:54
ple Name     :                                    Location : Vial 2
 Operator    : Jerome                                Inj :   1
 Instrument  : GC 6890                          Inj Volume : Manually
 Method      : C:\HPCHEM\1\METHODS\BETA1.M
 changed     : 21.10.2005 16:58:05  by Jerome
               (modified after loading)
ysis Method  : C:\HPCHEM\1\METHODS\SLEEP2.M
t changed    : 24.10.2005 13:27:06  by Jerome
               (modified after loading)
```

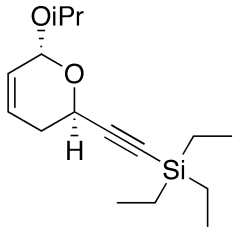



```
==========================================================================
                        Area Percent Report
==========================================================================

d By              :      Signal
plier             :      1.0000
ion               :      1.0000
Multiplier & Dilution Factor with ISTDs


al 1: FID1 A,


nal 2: FID2 B,

k RetTime Type  Width     Area      Height     Area
   [min]        [min]    [pA*s]      [pA]       %
--|-------|----|-------|----------|----------|--------|
1  42.185 MM    0.3646  553.82330   25.31449 45.88967
2  42.911 MM    0.3621  603.47382   27.77560 50.00370
3  43.981 MM    0.3045   49.56127    2.71250  4.10664

ls :                   1206.85839   55.80259

lts obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```


OiPr
O
H
Si
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


OiPr
O
H
Si
ppm
200
150
100
50

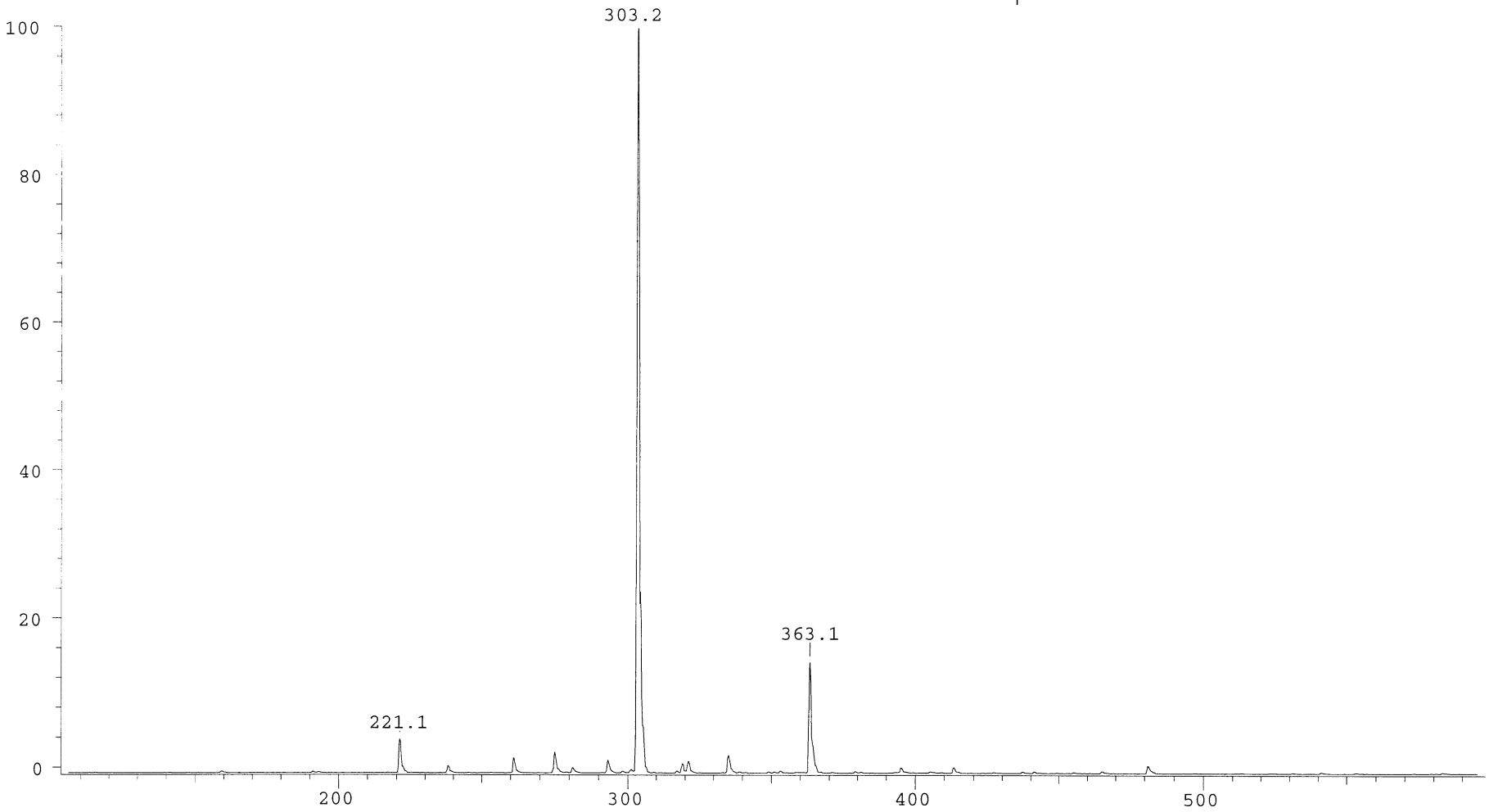
SPEC: esi5178_1.dat (22-NOV-05 15:21:28)
Samp: S.Bonazzi/Carreira - SB36
Comm: LM:CH3OH
Oper: o.s. Study:
Base: 303.16 Masses: 10.00 > 999.98
Peak: 1000.0 mmu Intensity: 11336928
Scan 1 @ 0.05 min (ESI +Q1MS LMR AVER UP PROF)



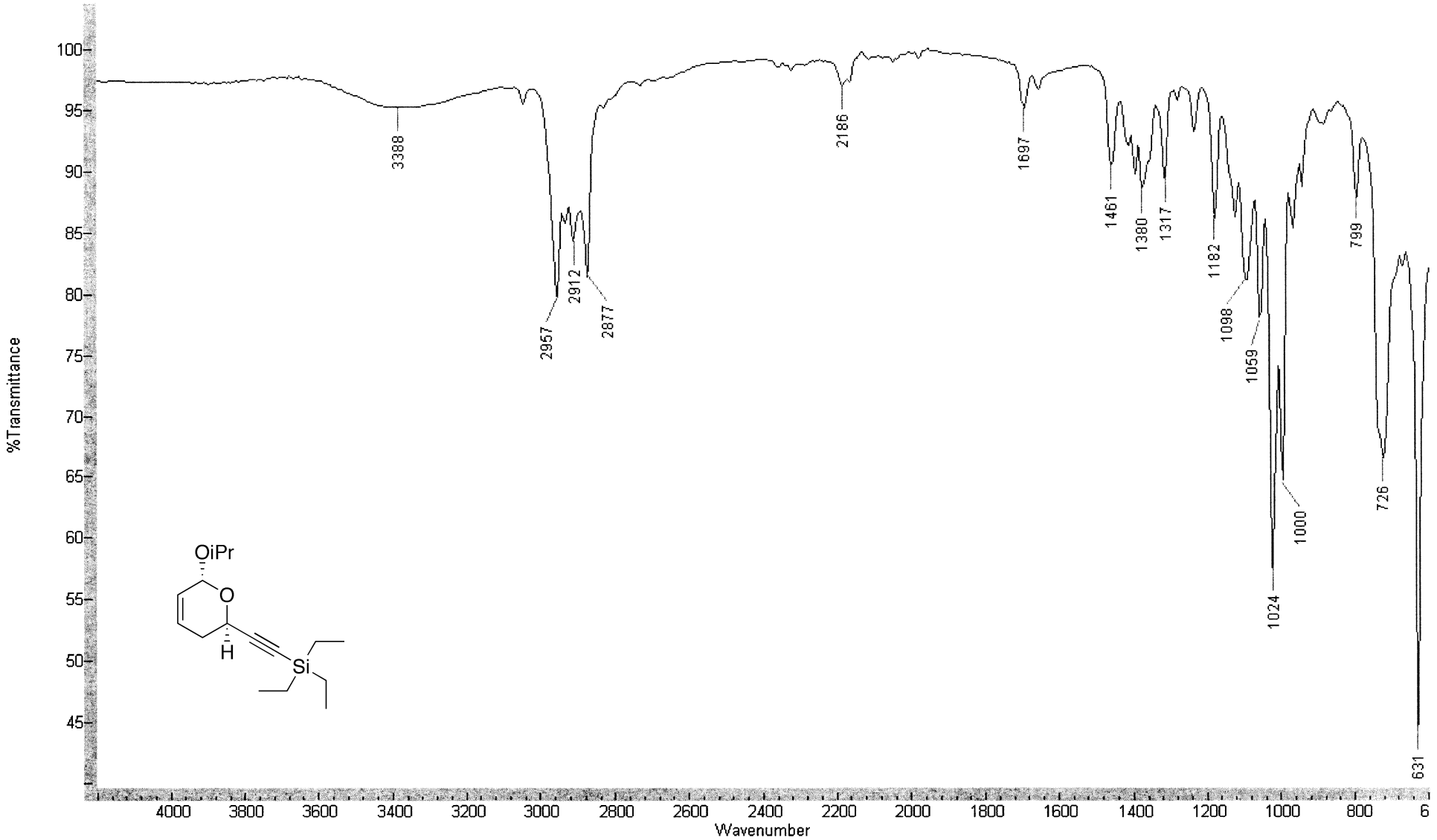
Scans: 1 > 3

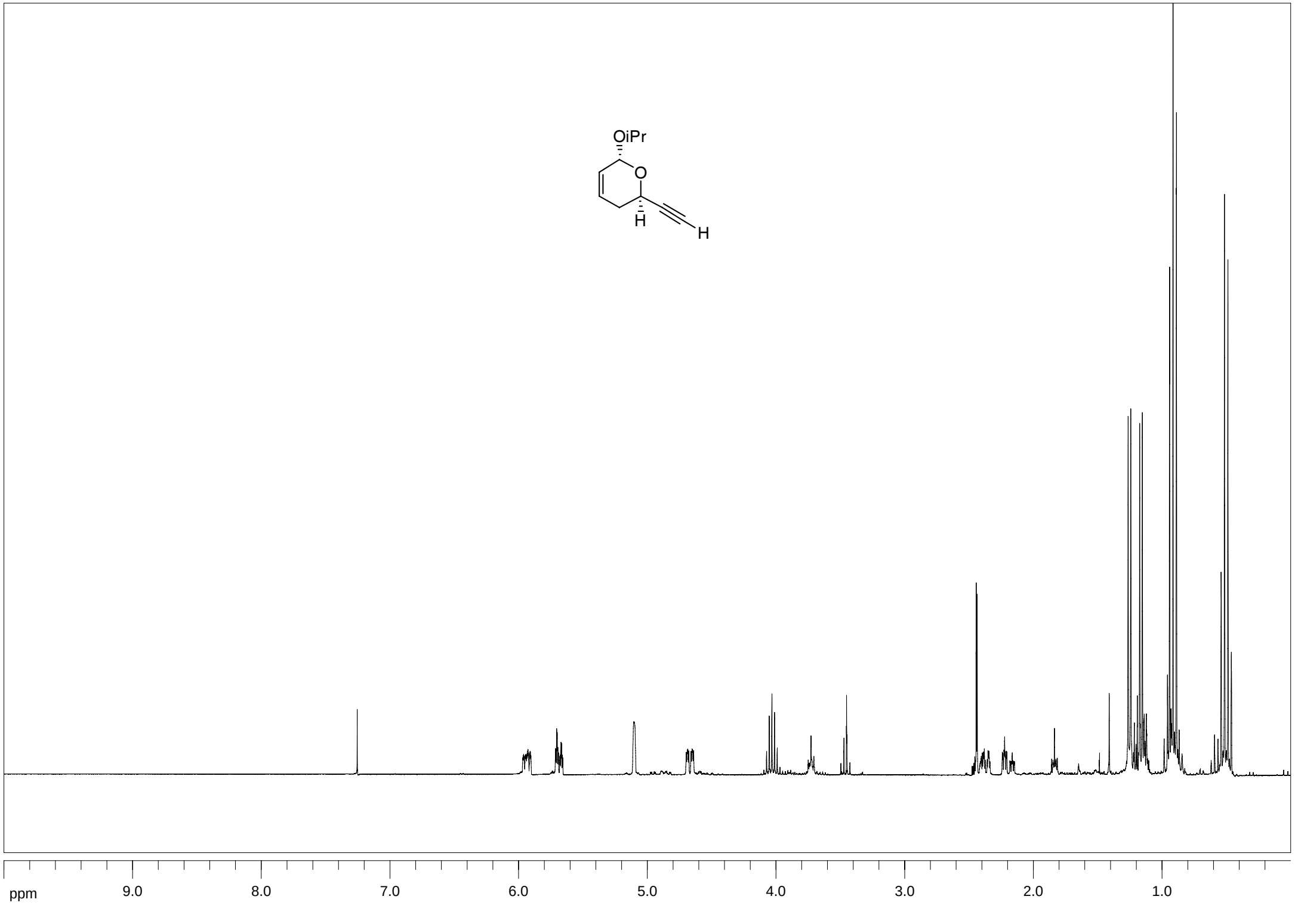
Client:
#Peaks: 9901
RIC: 20138871

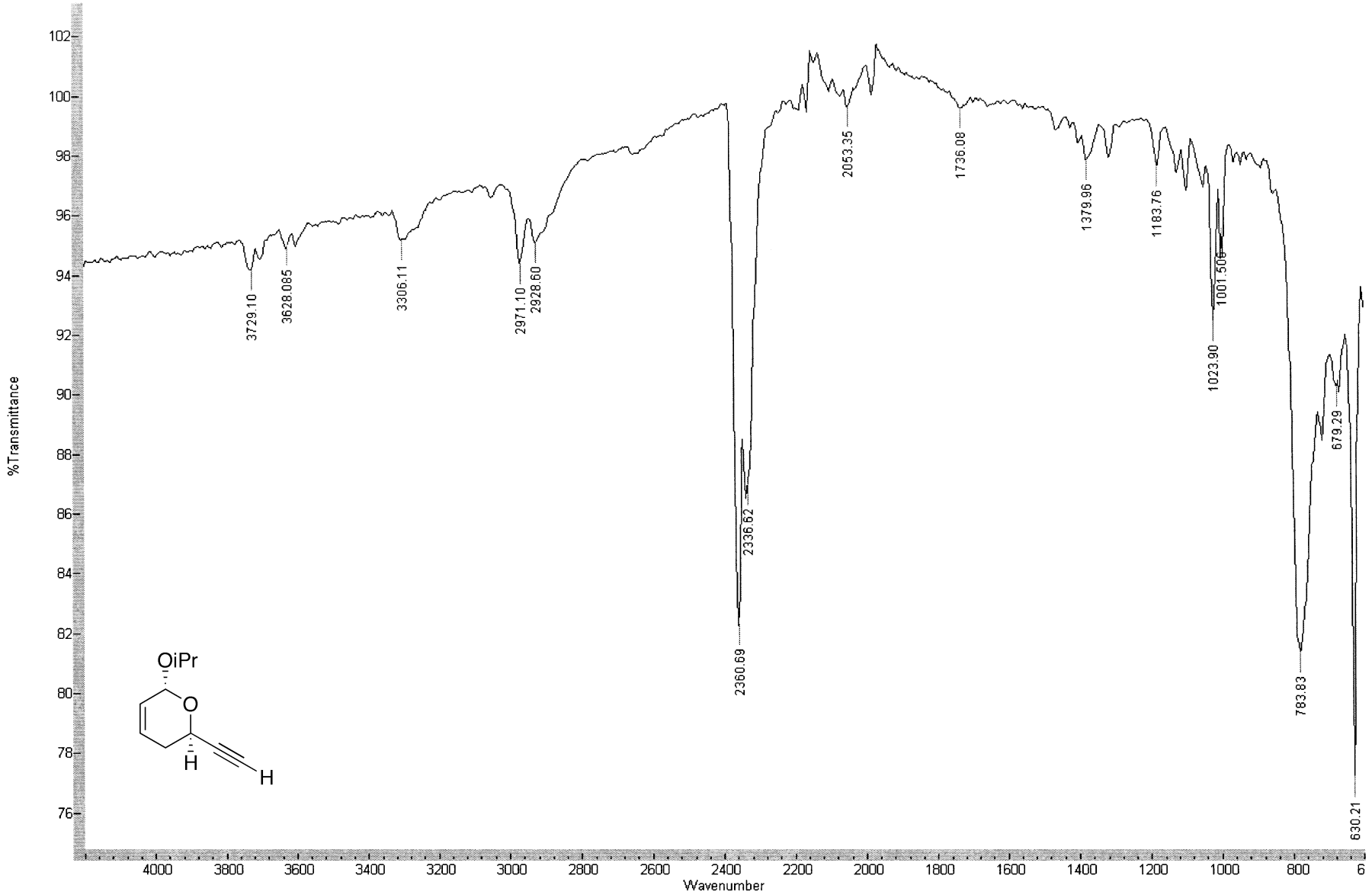
1.1E+07

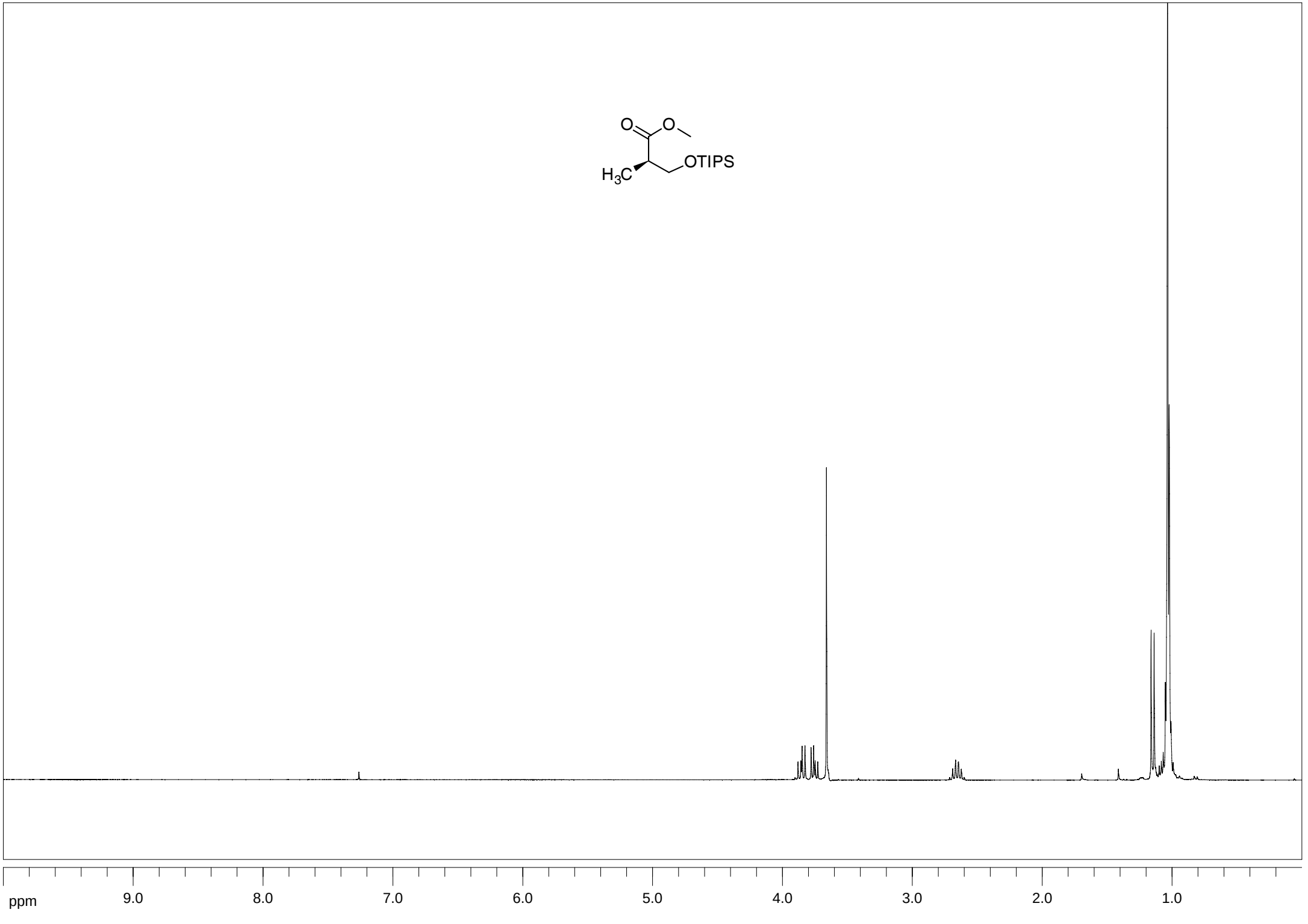


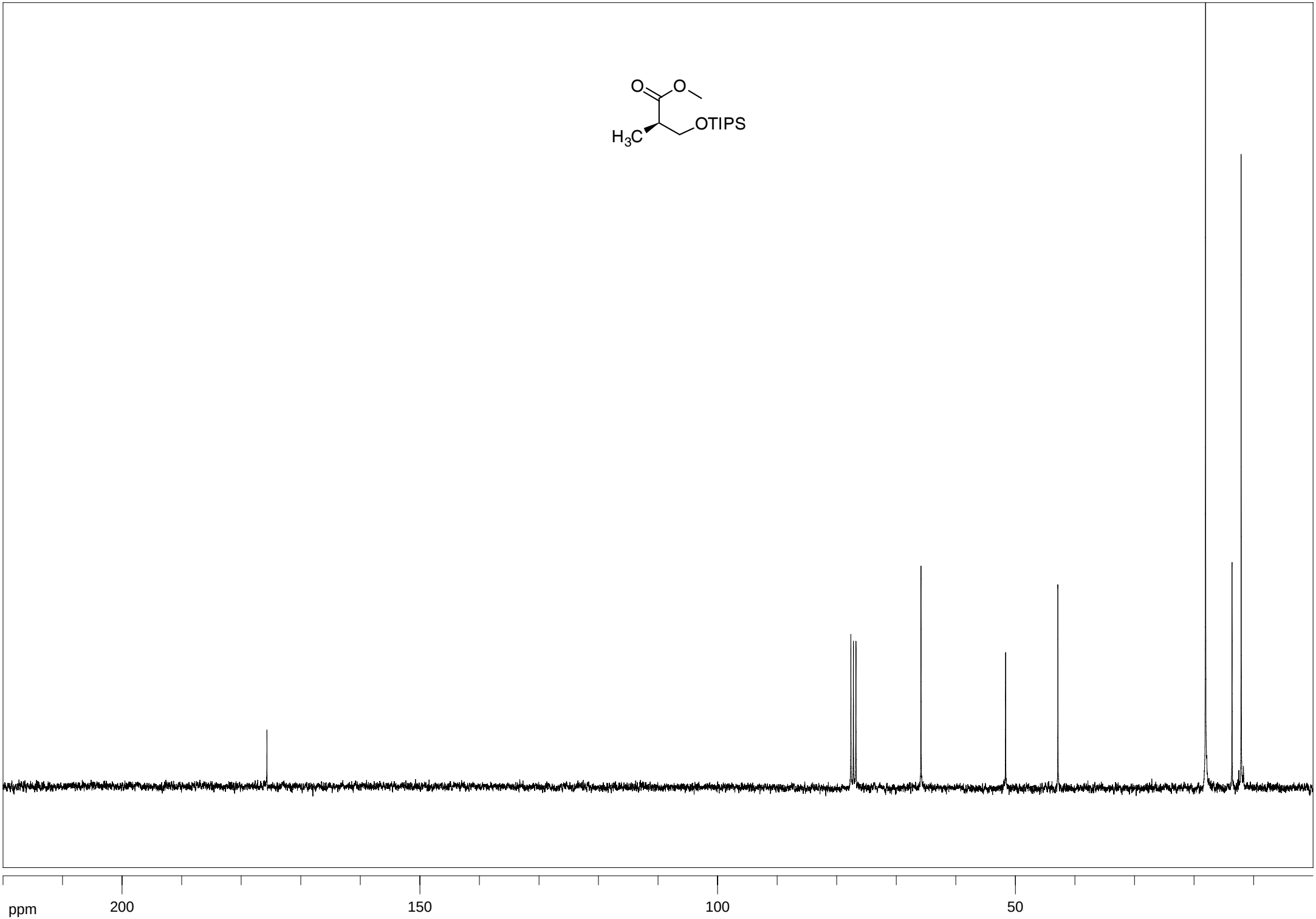
Date: Tue Nov 22 16:12:41 2005 ICIS: 8.3.0 SP2 for OSF1 (V4.0) build 98-238 from 26-Aug-98


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
3388
2957
2912
2877
2186
1697
1461
1380
1317
1182
1098
1059
1024
1000
799
726
631
OiPr
O
H
Si
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber


OiPr
O
H
H
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


%Transmittance
Wavenumber
3729.10
3628.085
3306.11
2971.10
2928.60
2360.69
2336.62
2053.35
1736.08
1379.96
1183.76
1023.90
1001.506
783.83
679.29
630.21
OiPr
O
H
H


O
O
OTIPS
H3C
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

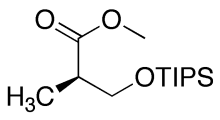

O
O
OTIPS
H3C
ppm
200
150
100
50

S. Bonazzi/Carreira;

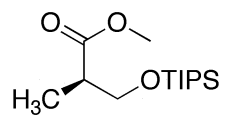
29-Jun-2006
13:54:49

EI3003 5 (0.544) Cm (5-28:37)

Magnet EI+
1.90e4



ETHZ



date: 15.08.2006

SB158.005 - 15.08.2006 - SB158

analyst: Student

last transform history: AutoSmooth "E:\pel_data\spectra\Student\SB158.004", 4000, 600, "E:\pel_data\spectra\Student\SB158.~0" 'Student, Tue Aug 15 17:51:16 2006

spectrum pathname: E:\pel_data\spectra\Student\SB158.005

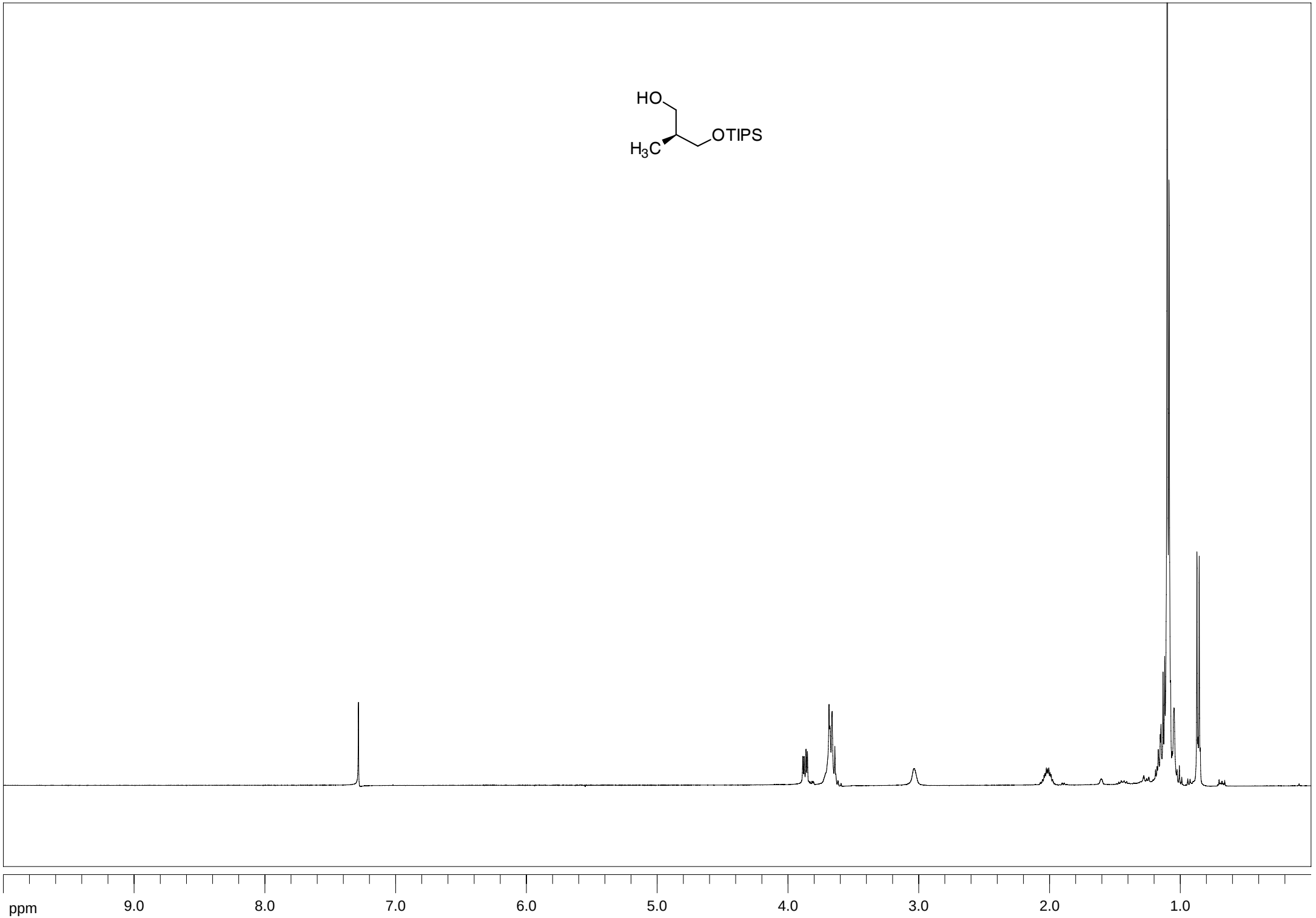
instrument model: Spectrum BX Series

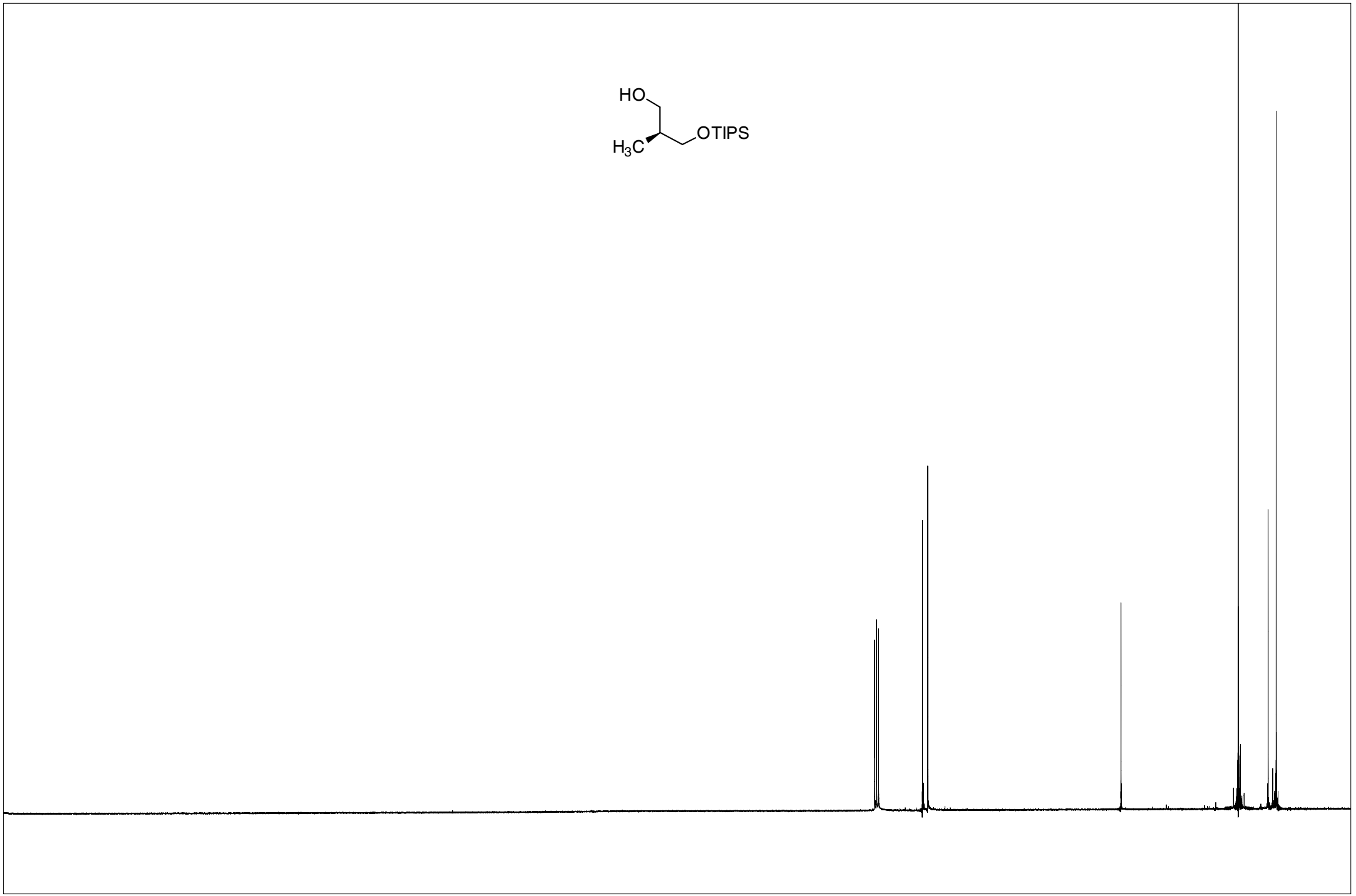
instrument serial number: 67273

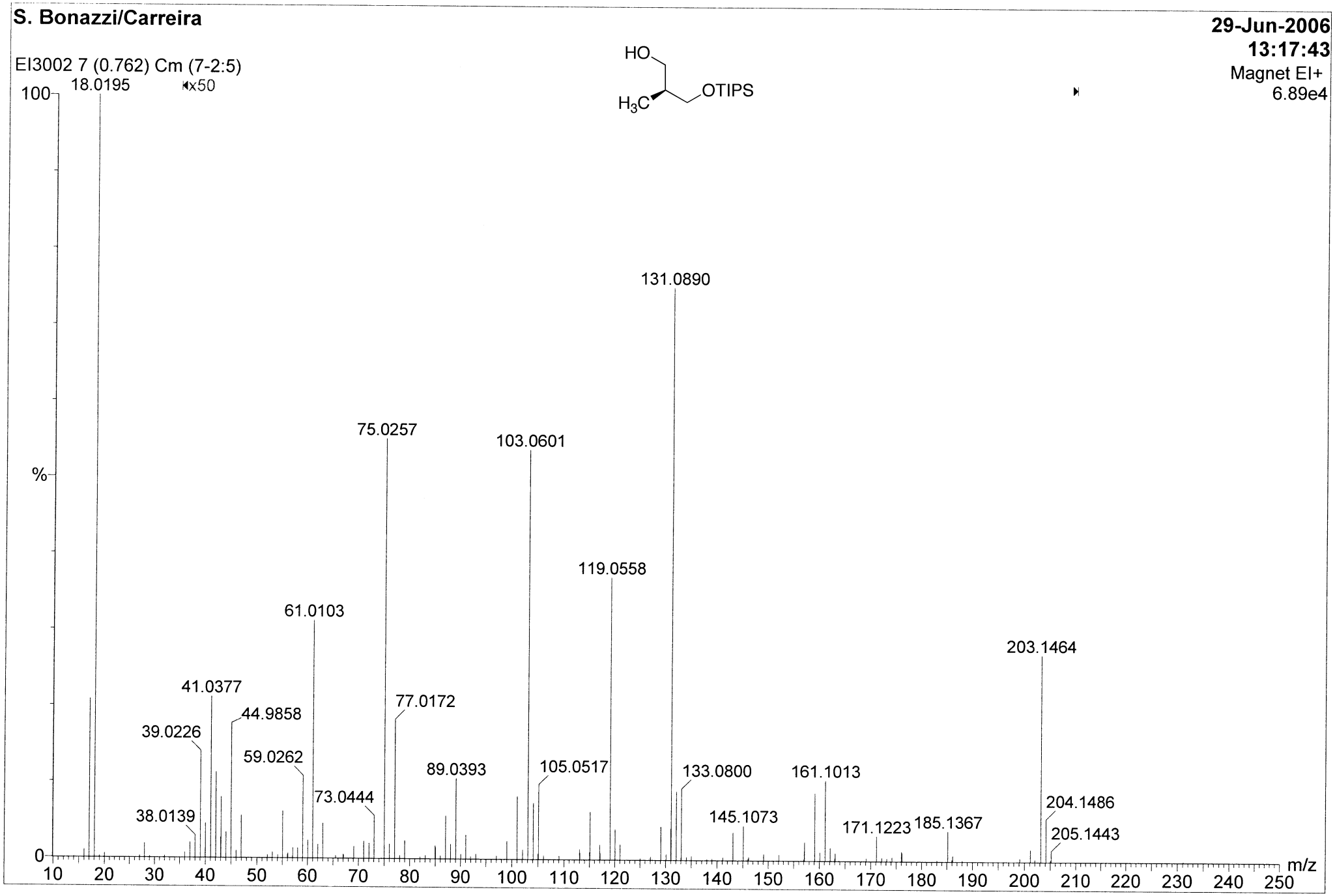
accumulations: 4

resolution: 4 cm-1

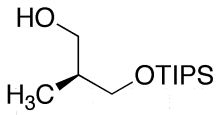
apodization: Strong


HO
OTIPS
H3C
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

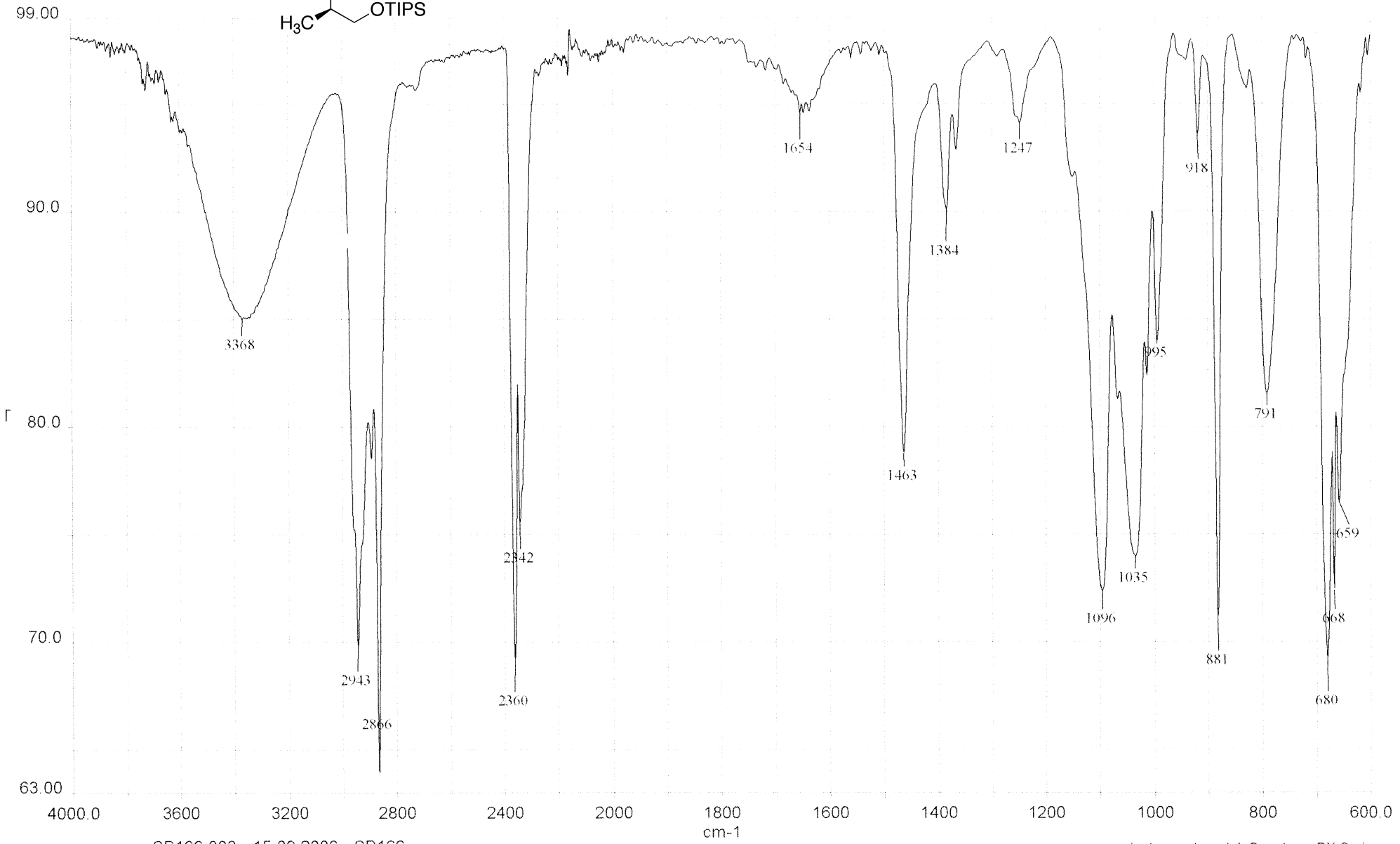

HO
OTIPS
H3C
ppm
200
150
100
50


S. Bonazzi/Carreira
29-Jun-2006
13:17:43
Magnet EI+
6.89e4
EI3002 7 (0.762) Cm (7-2:5)
x50
HO
OTIPS
H3C
100
%
0
18.0195
131.0890
75.0257
103.0601
119.0558
61.0103
203.1464
41.0377
77.0172
44.9858
39.0226
59.0262
89.0393
105.0517
133.0800
161.1013
73.0444
204.1486
38.0139
145.1073
171.1223
185.1367
205.1443
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250
m/z

ETHZ



date: 15.09.2006



SB166.003 - 15.09.2006 - SB166

analyst: Student

last transform history: AutoFlat_2 "E:\pel_data\spectra\Student\SB166.sp", 4000, 600, "E:\pel_data\spectra\Student\SB166.~0" 'Student, Fri Sep 15 15:52:27 2006

spectrum pathname: E:\pel_data\spectra\Student\SB166.003

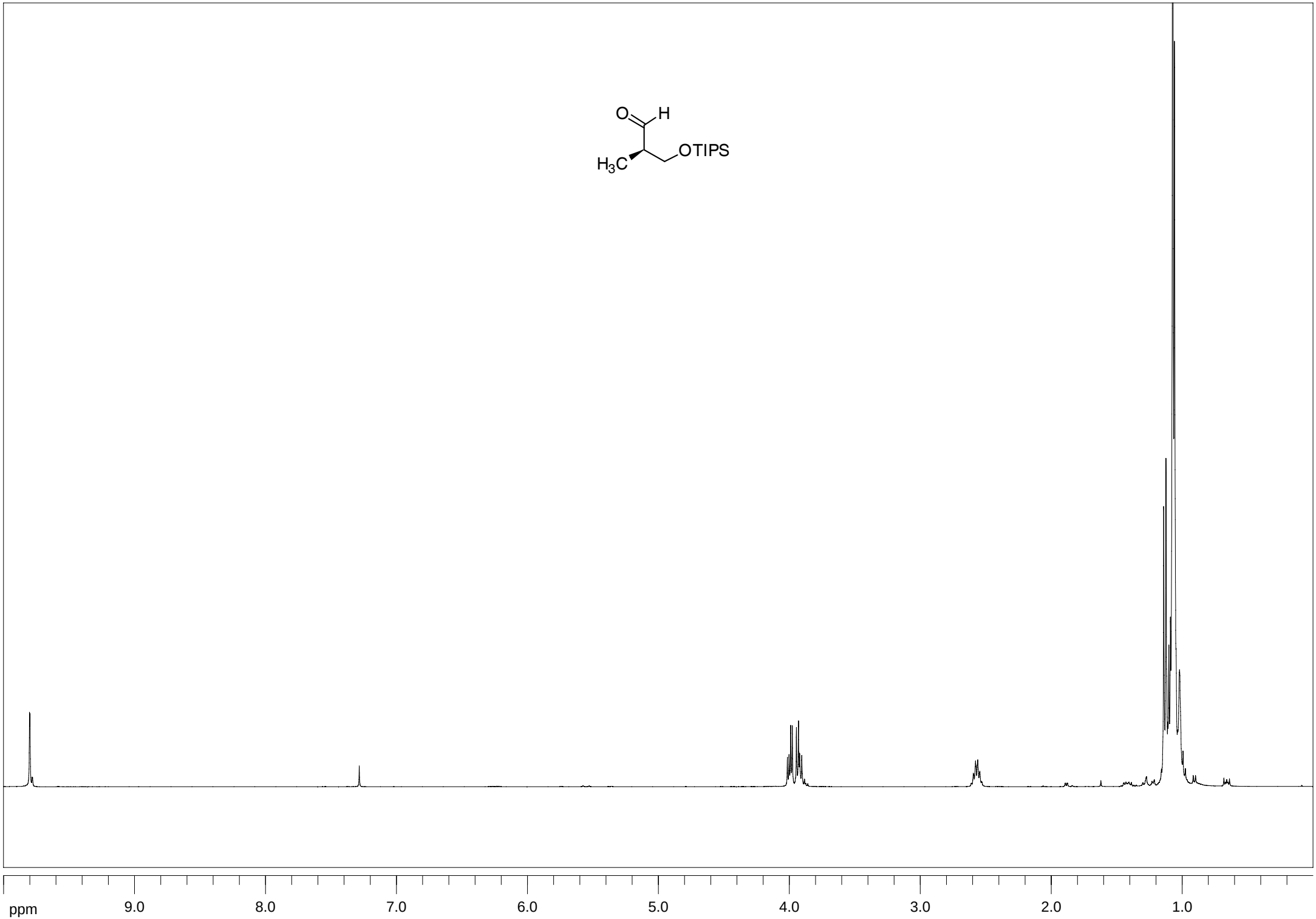
instrument model: Spectrum BX Series

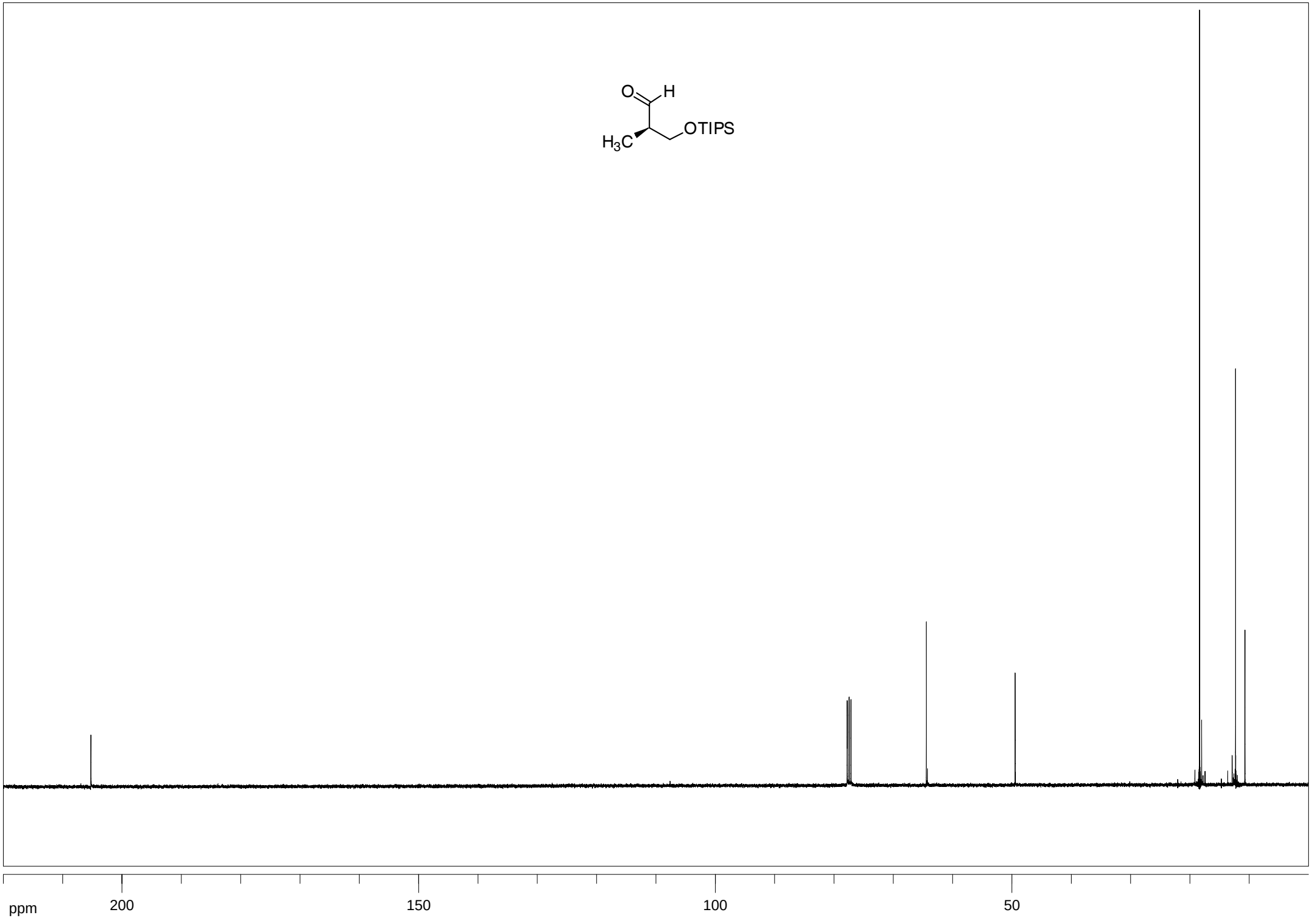
instrument serial number: 67273

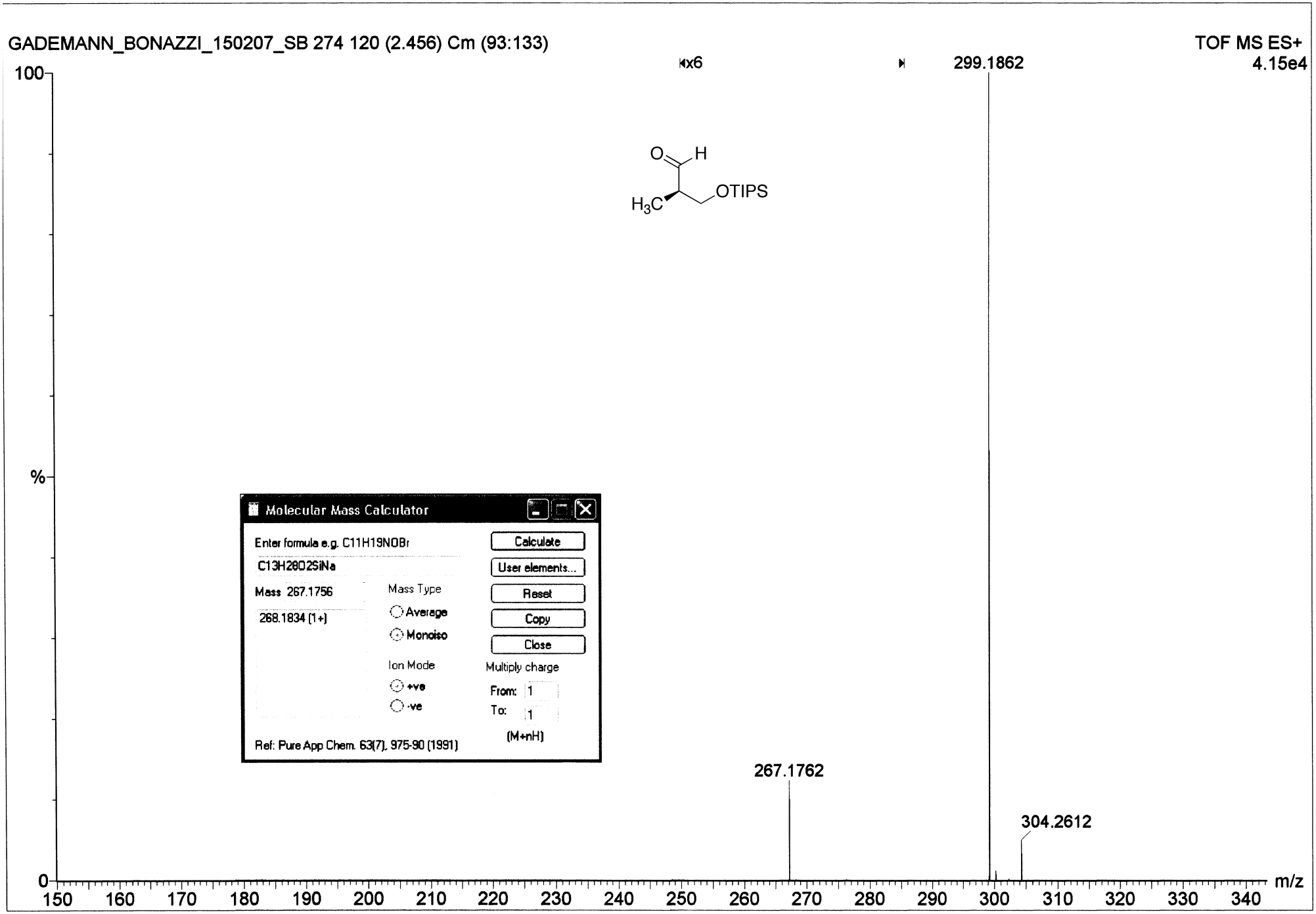
accumulations: 4

resolution: 4 cm-1

apodization: Strong


O
H
OTIPS
H3C
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


O
H
OTIPS
H3C
ppm
200
150
100
50

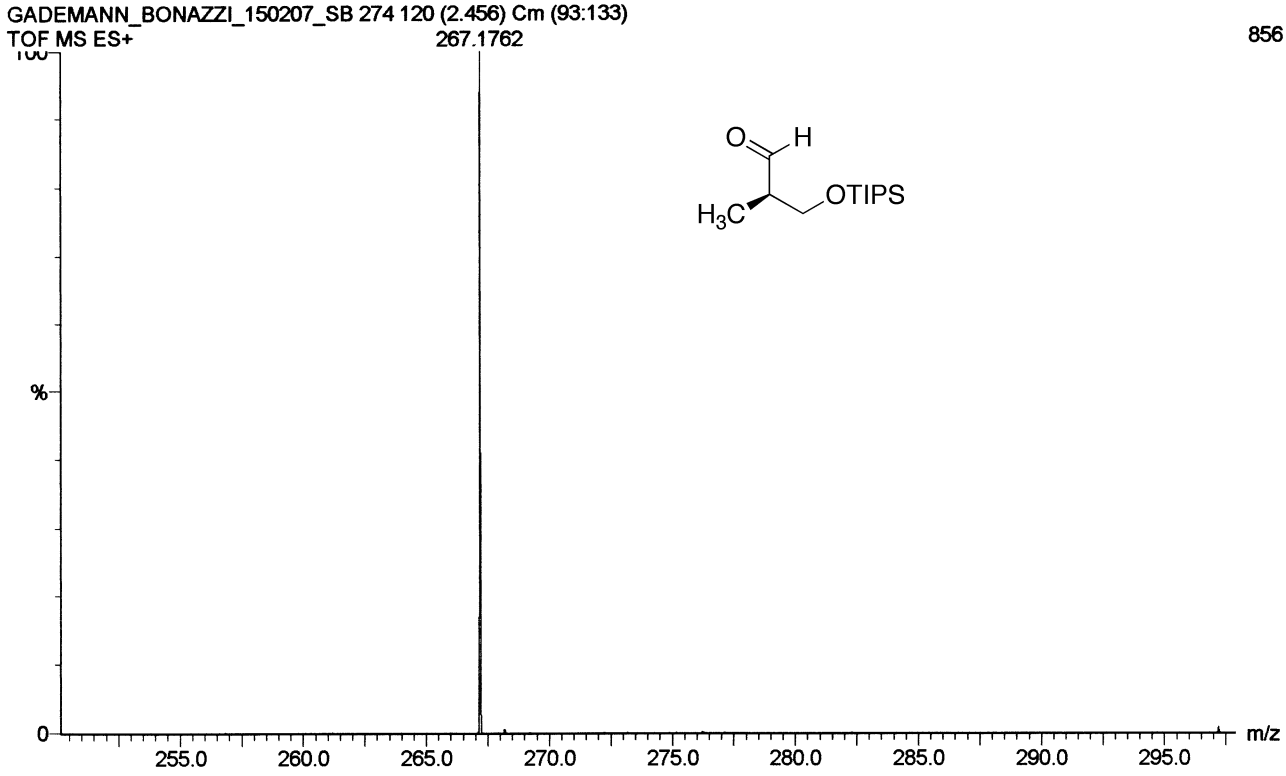

GADEMANN_BONAZZI_150207_SB 274 120 (2.456) Cm (93:133)
TOF MS ES+
4.15e4
x6
299.1862
100
%
0
O
H
H3C
OTIPS
Molecular Mass Calculator
Enter formula e.g. C11H19NOBr
C13H28O2SiNa
Mass 267.1756
268.1834 (1+)
Mass Type
Average
Monoiso
Ion Mode
+ve
-ve
Calculate
User elements...
Reset
Copy
Close
Multiply charge
From: 1
To: 1
(M+nH)
Ref: Pure App Chem. 63(7), 975-90 (1991)
267.1762
304.2612
150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340
m/z

Elemental Composition Report

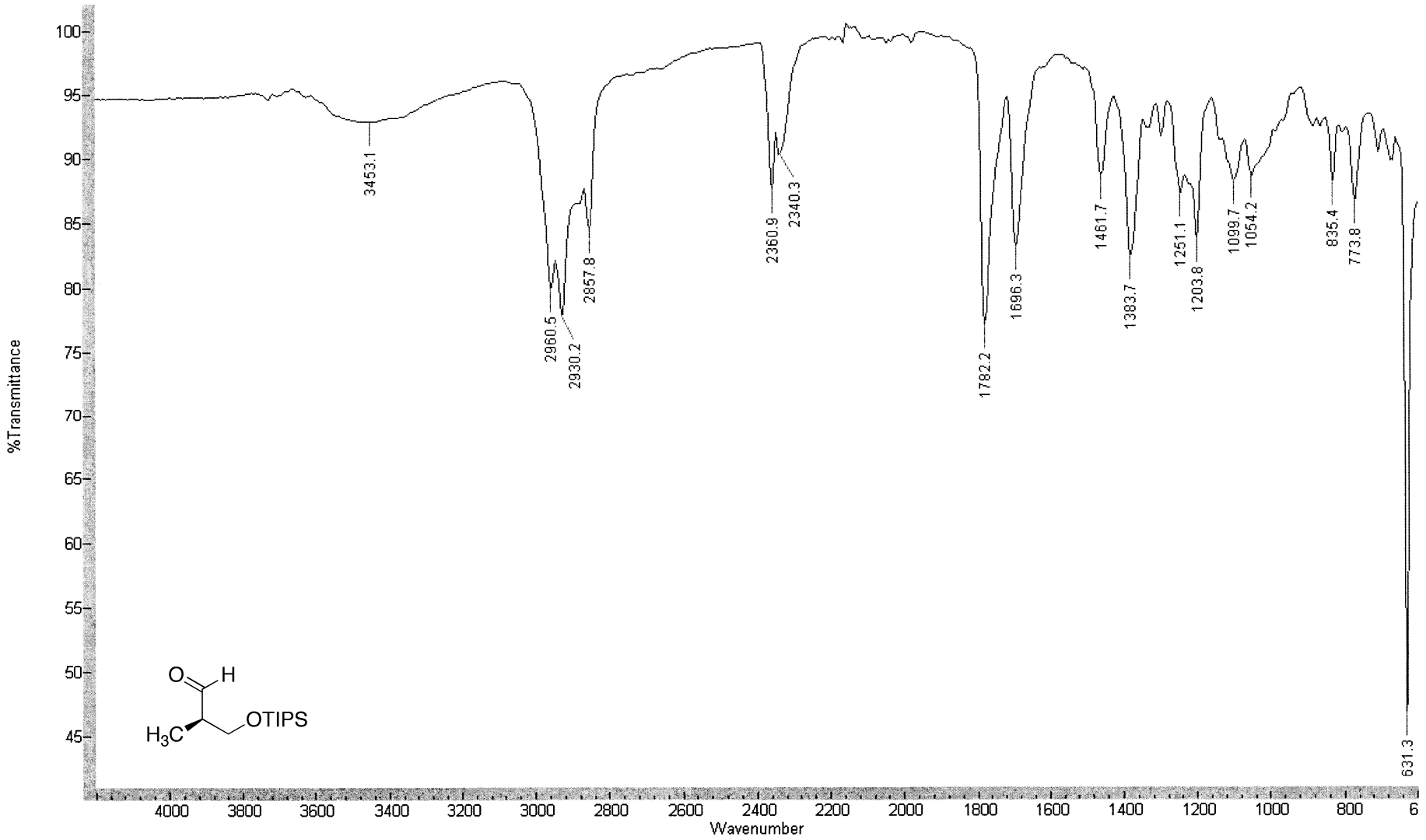
Single Mass Analysis

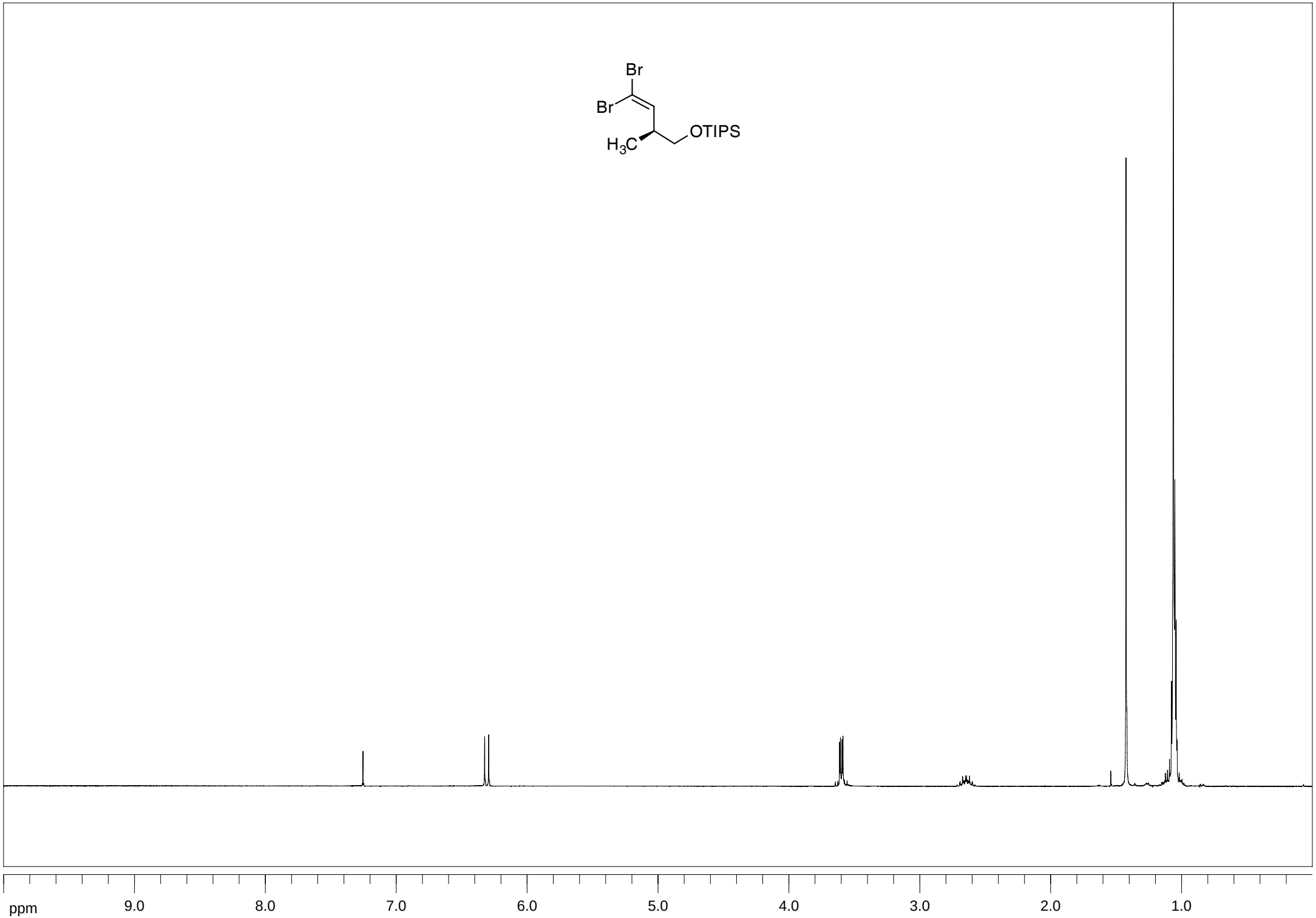
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

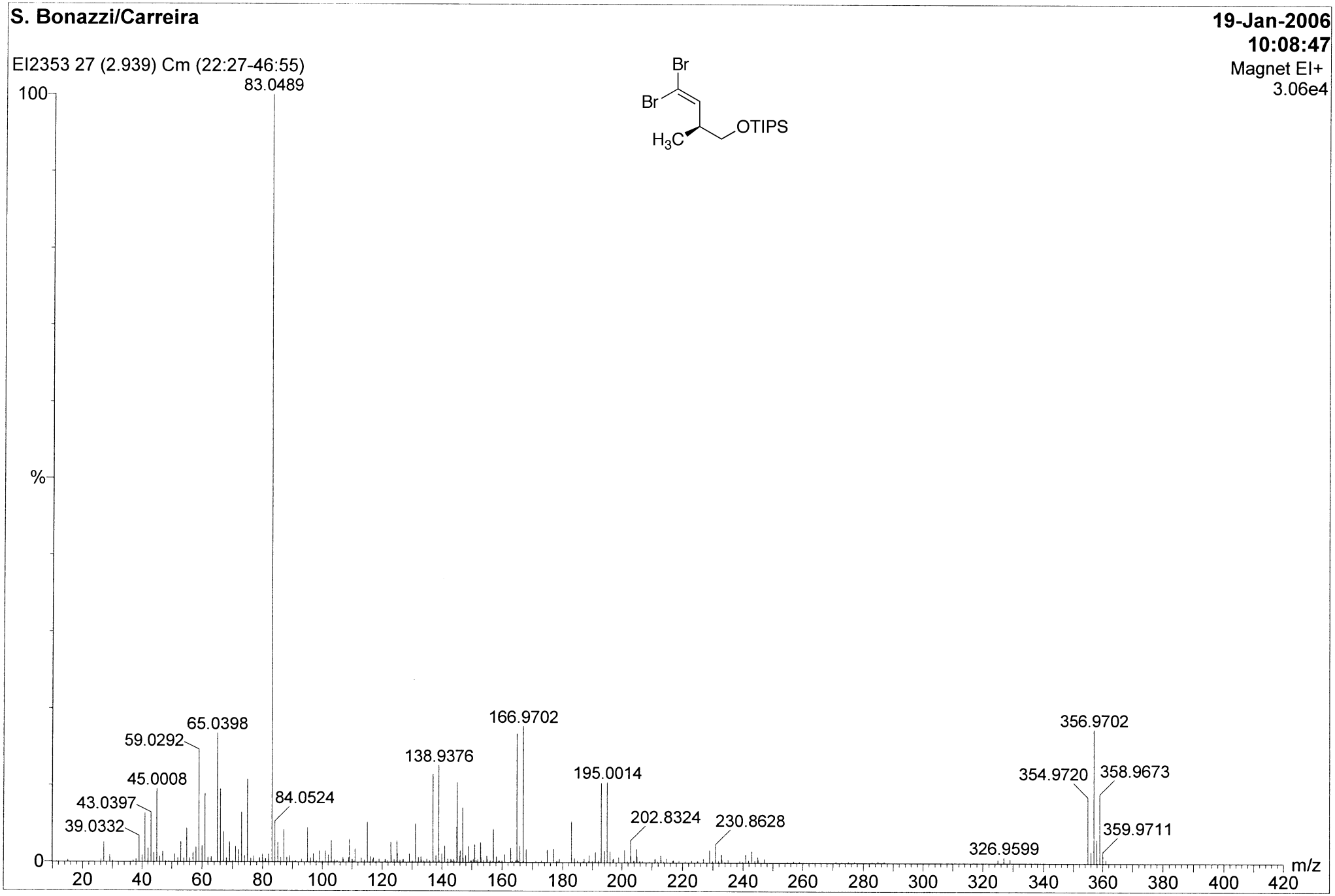
Monoisotopic Mass, Odd and Even Electron Ions
868 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

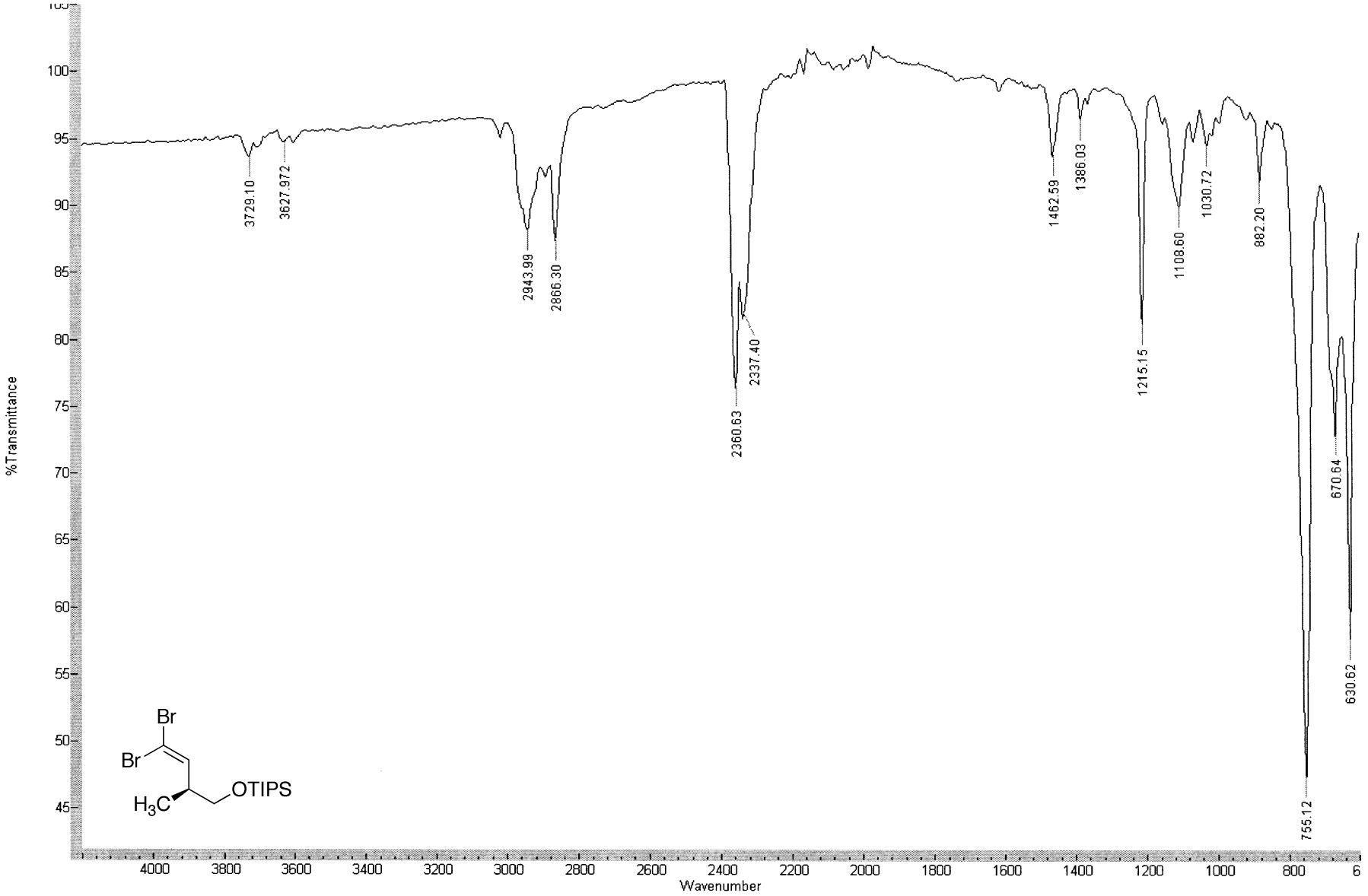


Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
267.1762	267.1767	-0.5	-1.8	4.0	C13 H25 N3 O Si
	→267.1756	0.6	2.2	0.5	C13 H28 O2 Na Si
	267.1753	0.9	3.2	4.5	C11 H23 N6 Si
	267.1749	1.3	4.9	8.5	C19 H23 O

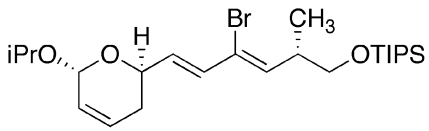

%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
3453.1
2960.5
2930.2
2857.8
2360.9
2340.3
1782.2
1696.3
1461.7
1383.7
1251.1
1203.8
1099.7
1054.2
835.4
773.8
631.3
O
H
H3C
OTIPS
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber


Br
Br
OTIPS
H3C
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


S. Bonazzi/Carreira
19-Jan-2006
10:08:47
EI2353 27 (2.939) Cm (22:27-46:55)
Magnet EI+
3.06e4
Br
Br
H3C
OTIPS
100
%
0
83.0489
65.0398
59.0292
45.0008
43.0397
39.0332
84.0524
138.9376
166.9702
195.0014
202.8324
230.8628
326.9599
354.9720
356.9702
358.9673
359.9711
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420
m/z


%Transmittance
Wavenumber
3729.10
3627.972
2943.99
2866.30
2360.63
2337.40
1462.59
1386.03
1215.15
1108.60
1030.72
882.20
755.12
670.64
630.62
Br
Br
H3C
OTIPS

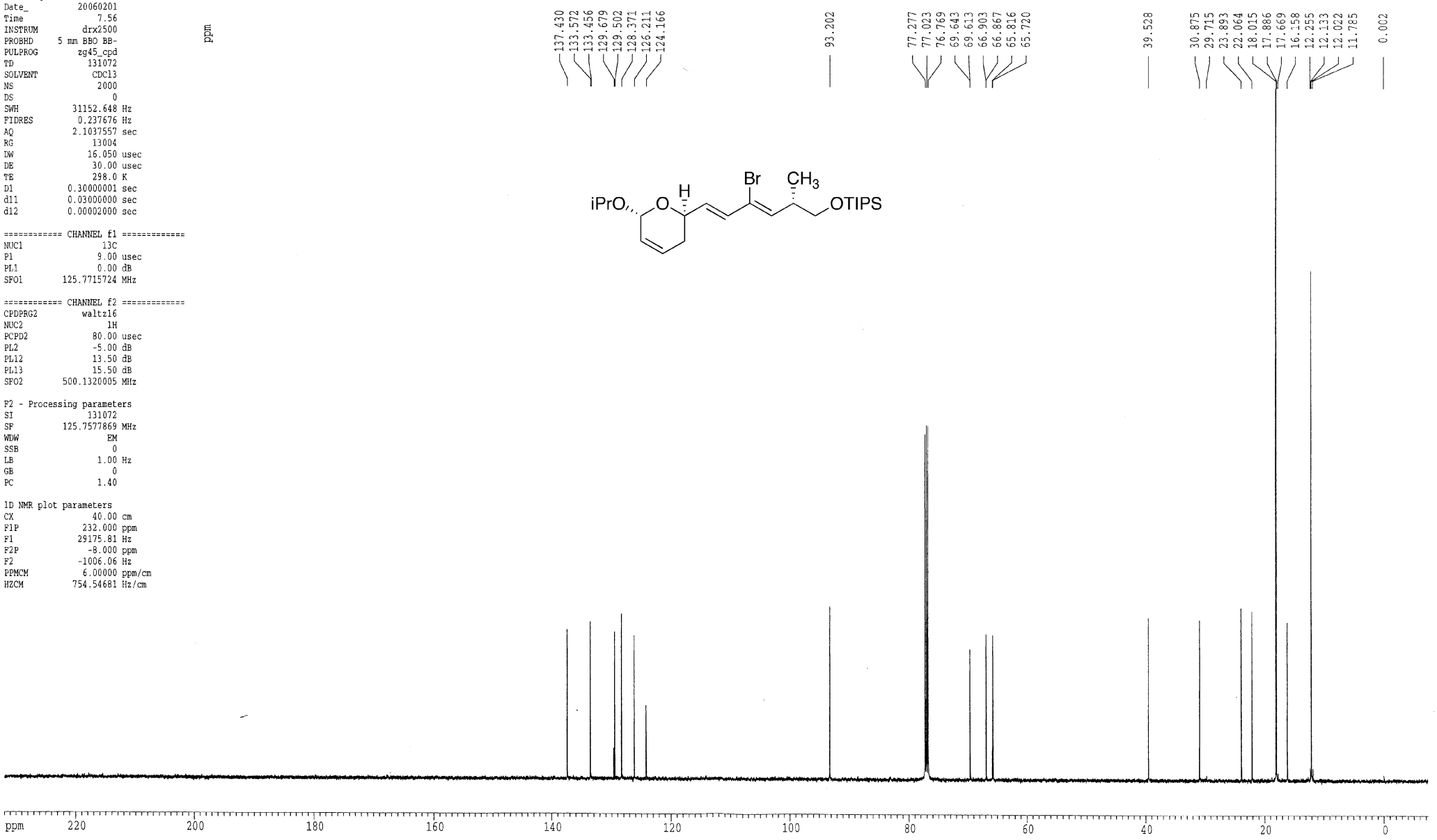
S.Bonazzi/Carreira SB 77 Opr:Br
500MHz 1H-NMR



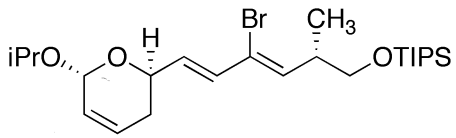

```
Current Data Parameters
NAME                  F0385
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060131
Time                  9.05
INSTRUM             DRX500
PROBHD     5 mm BBI 1H-
PULPROG                zg30
TD                    90112
SOLVENT               CDCl3
NS                       32
DS                        0
SWH                8090.615 Hz
FIDRES             0.089784 Hz
AQ                5.5689716 sec
RG                     80.6
DW                   61.800 usec
DE                    6.00 usec
TE                   300.0 K
D1              0.01000000 sec

============ CHANNEL f1 =============
NUC1                      1H
P1                     7.10 usec
PL1                   -4.00 dB
SFO1           500.0332000 MHz

F2 - Processing parameters
SI                    65536
SF              500.0300108 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.80

1D NMR plot parameters
CX                    40.00 cm
F1P                    9.500 ppm
F1                  4750.29 Hz
F2P                   -0.500 ppm
F2                  -250.01 Hz
PPMCM               0.25000 ppm/cm
HZCM              125.00750 Hz/cm
```

S.Bonazzi/Carreira SB 77 Opr:Br
125 MHz BB 13C NMR

```
Current Data Parameters
NAME                 F0385
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060201
Time                 7.56
INSTRUM             drx2500
PROBHD     5 mm BBO BB-
PULPROG           zg45_cpd
TD                  131072
SOLVENT               CDCl3
NS                     2000
DS                        0
SWH              31152.648 Hz
FIDRES            0.237676 Hz
AQ                2.1037557 sec
RG                    13004
DW                  16.050 usec
DE                  30.00 usec
TE                  298.0 K
D1              0.30000001 sec
d11             0.03000000 sec
d12             0.00002000 sec

============ CHANNEL f1 =============
NUC1                   13C
P1                   9.00 usec
PL1                  0.00 dB
SFO1           125.7715724 MHz

============ CHANNEL f2 =============
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -5.00 dB
PL12                13.50 dB
PL13                15.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                  131072
SF             125.7577869 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  40.00 cm
F1P                232.000 ppm
F1               29175.81 Hz
F2P                 -8.000 ppm
F2               -1006.06 Hz
PPMCM               6.00000 ppm/cm
HZCM             754.54681 Hz/cm
```

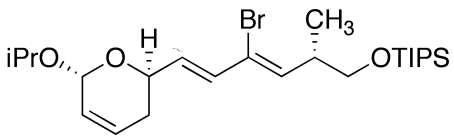


S.Bonazzi/Carreira SB 77 Opr:Br
125 MHz 13C DEPT 90+135 NMR



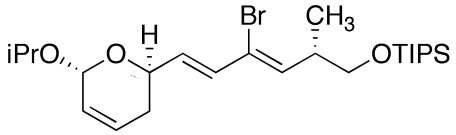

```
Current Data Parameters
NAME              F0385
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20060201
Time               9.43
INSTRUM         drx2500
PROBHD     5 mm BBO BB-
PULPROG        dept1eth
TD               131072
SOLVENT            CDCl3
NS                   400
DS                     0
SWH            31152.648 Hz
FIDRES         0.237676 Hz
AQ             2.1037557 sec
RG                 13004
DW                16.050 usec
DE                30.00 usec
TE                298.0 K
CNST2         145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001146 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 9.00 usec
p2                18.00 usec
PL1                0.00 dB
SFO1         125.7715724 MHz

============ CHANNEL f2 =============
CPDPRG2          waltz16
NUC2                1H
P0                11.00 usec
P3                11.00 usec
p4                22.00 usec
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              13.50 dB
SFO2         500.1320005 MHz

F2 - Processing parameters
SI                 65536
SF           125.7577869 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                40.00 cm
F1P              232.000 ppm
F1             29175.80 Hz
F2P               -8.000 ppm
F2             -1006.06 Hz
PPMCM           6.00000 ppm/cm
HZCM          754.54675 Hz/cm
```

S.Bonazzi/Carreira SB 77 Opr:Br
500 MHz 1H NOE difference spectrum



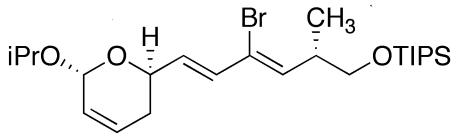

```
Current Data Parameters
NAME                 F0385
EXPNO                   32
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060131
Time                 16.27
INSTRUM             DRX500
PROBHD     5 mm BBI 1H-
PULPROG              noemul
TD                    90112
SOLVENT               CDCl3
NS                      320
DS                        4
SWH                8090.615 Hz
FIDRES             0.089784 Hz
AQ                 5.5689716 sec
RG                       80
DW                    61.800 usec
DE                     6.00 usec
TE                    300.0 K
D1              0.10000000 sec
d11             0.03000000 sec
d12             0.00002000 sec
D20             0.07000000 sec
L4                       30
NUC1                     1H
P1                     7.10 usec
PL1                   -4.00 dB
SFO1          500.0332000 MHz
FQ2LIST          f2list.4
NUC2                     1H
PL2                  120.00 dB
PL14                  76.00 dB
SFO2          500.0332000 MHz

F2 - Processing parameters
SI                    65536
SF            500.0300108 MHz
WDW                      EM
SSB                       0
LB                     0.60 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                    40.00 cm
F1P                    9.500 ppm
F1                  4750.29 Hz
F2P                   -0.500 ppm
F2                  -250.01 Hz
PPMCM                 0.25000 ppm/cm
HZCM                125.00750 Hz/cm
```

S.Bonazzi/Carreira SB 77 Opr:Br
500 MHz 1H NOE difference spectrum




```
Current Data Parameters
NAME                  F0385
EXPNO                    31
PROCNO                    1

F2 - Acquisition Parameters
Date_              20060131
Time                  16.25
INSTRUM              DRX500
PROBHD     5 mm BBI 1H-
PULPROG               noemul
TD                     90112
SOLVENT                CDCl3
NS                       320
DS                         4
SWH                 8090.615 Hz
FIDRES              0.089784 Hz
AQ                  5.5689716 sec
RG                        80
DW                    61.800 usec
DE                     6.00 usec
TE                     300.0 K
D1                0.10000000 sec
d11               0.03000000 sec
d12               0.00002000 sec
D20               0.07000000 sec
L4                        30
NUC1                      1H
P1                     7.10 usec
PL1                   -4.00 dB
SFO1           500.0332000 MHz
FQ2LIST             f2list.3
NUC2                      1H
PL2                  120.00 dB
PL14                  76.00 dB
SFO2           500.0332000 MHz

F2 - Processing parameters
SI                     65536
SF              500.0300108 MHz
WDW                       EM
SSB                        0
LB                      0.60 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     40.00 cm
F1P                     9.500 ppm
F1                   4750.29 Hz
F2P                    -0.500 ppm
F2                   -250.01 Hz
PPMCM                0.25000 ppm/cm
HZCM               125.00750 Hz/cm
```

S.Bonazzi/Carreira SB 77 Opr:Br
500 MHz 1H NOE difference spectrum



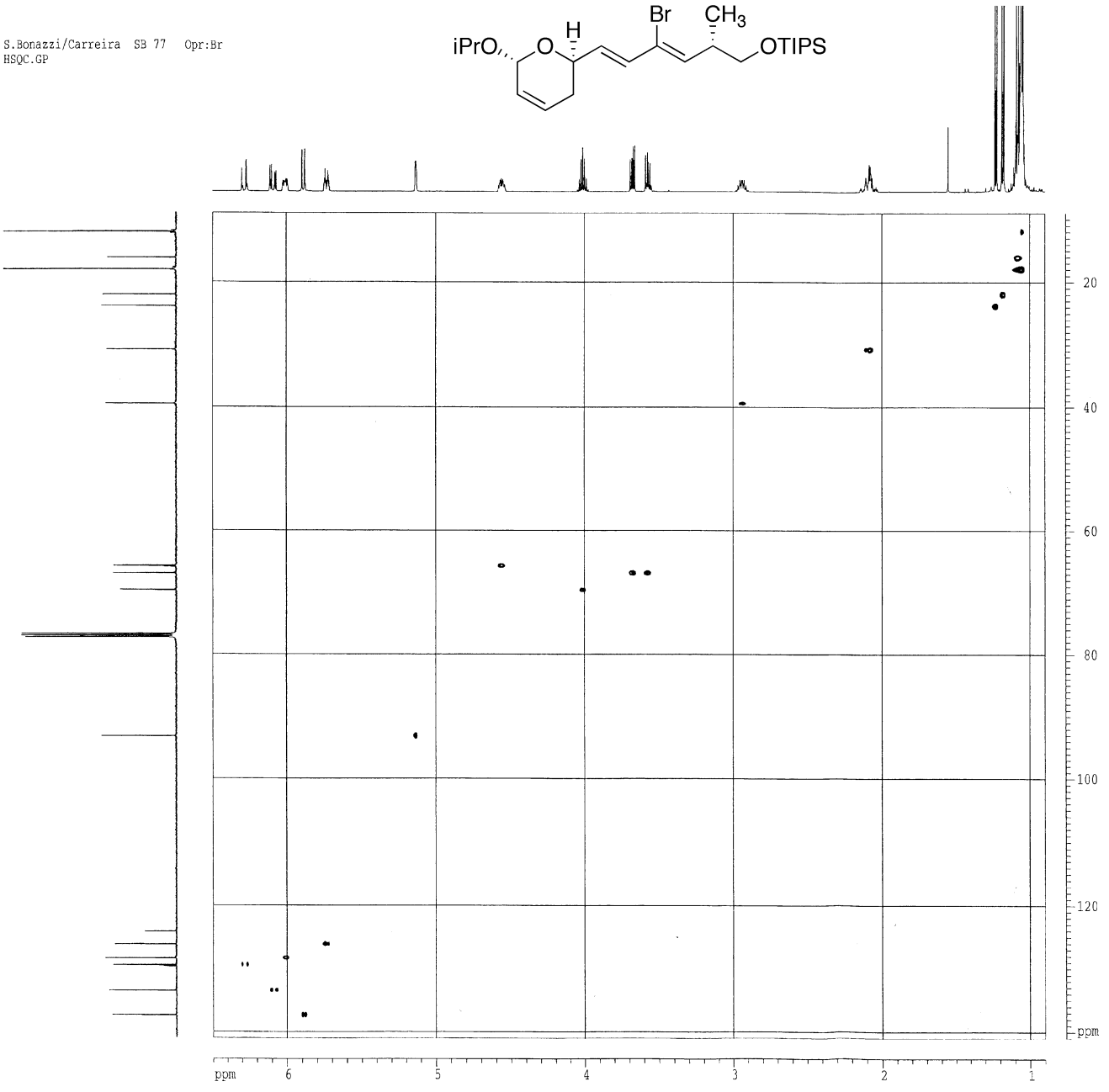
Current Data Parameters
NAME F0385
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060131
Time 16.22
INSTRUM DRX500
PROBHD 5 mm BBI 1H-
PULPROG noemul
TD 90112
SOLVENT CDCl3
NS 320
DS 4
SWH 8090.615 Hz
FIDRES 0.089784 Hz
AQ 5.5689716 sec
RG 80
DW 61.800 usec
DE 6.00 usec
TE 300.0 K
D1 0.10000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
D20 0.07000000 sec
L4 30
NUC1 1H
P1 7.10 usec
PL1 -4.00 dB
SFO1 500.0332000 MHz
FQ2LIST f2list.2
NUC2 1H
PL2 120.00 dB
PL14 76.00 dB
SFO2 500.0332000 MHz

F2 - Processing parameters
SI 65536
SF 500.0300108 MHz
WDW EM
SSB 0
LB 0.60 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 40.00 cm
F1P 9.500 ppm
F1 4750.29 Hz
F2P -0.500 ppm
F2 -250.01 Hz
PPMCM 0.25000 ppm/cm
HZCM 125.00750 Hz/cm

S.Bonazzi/Carreira SB 77 Opr:Br
HSQC.GP



Current Data Parameters

NAME	FO385
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20060131
Time	10.31
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	invigptp
TD	2048
SOLVENT	CDCl3
NS	4
DS	16
SWH	4496.403 Hz
FIDRES	2.195509 Hz
AQ	0.2277876 sec
RG	8192
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
CNST2	145.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d4	0.00172414 sec
d11	0.03000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
d20	0.00110000 sec
d21	0.00061714 sec
IN0	0.00001030 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	7.10 usec
p2	14.20 usec
PL1	-4.00 dB
SFO1	500.0315318 MHz

========== CHANNEL f2 ==========

CPDPRG2	garp
NUC2	13C
P3	12.50 usec
p4	25.00 usec
PCPD2	76.00 usec
PL2	-3.00 dB
PL12	13.00 dB
SFO2	125.7431995 MHz

========== GRADIENT CHANNEL ========

GPNAM1	sine.100
GPNAM2	sine.100
GPNAM3	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPX3	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPY3	0.00 %
GPZ1	80.00 %
GPZ2	30.00 %
GPZ3	20.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	4
TD	512
SFO1	125.7432 MHz
FIDRES	47.405945 Hz
SW	193.027 ppm

F2 - Processing parameters

SI	1024
SF	500.0300108 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

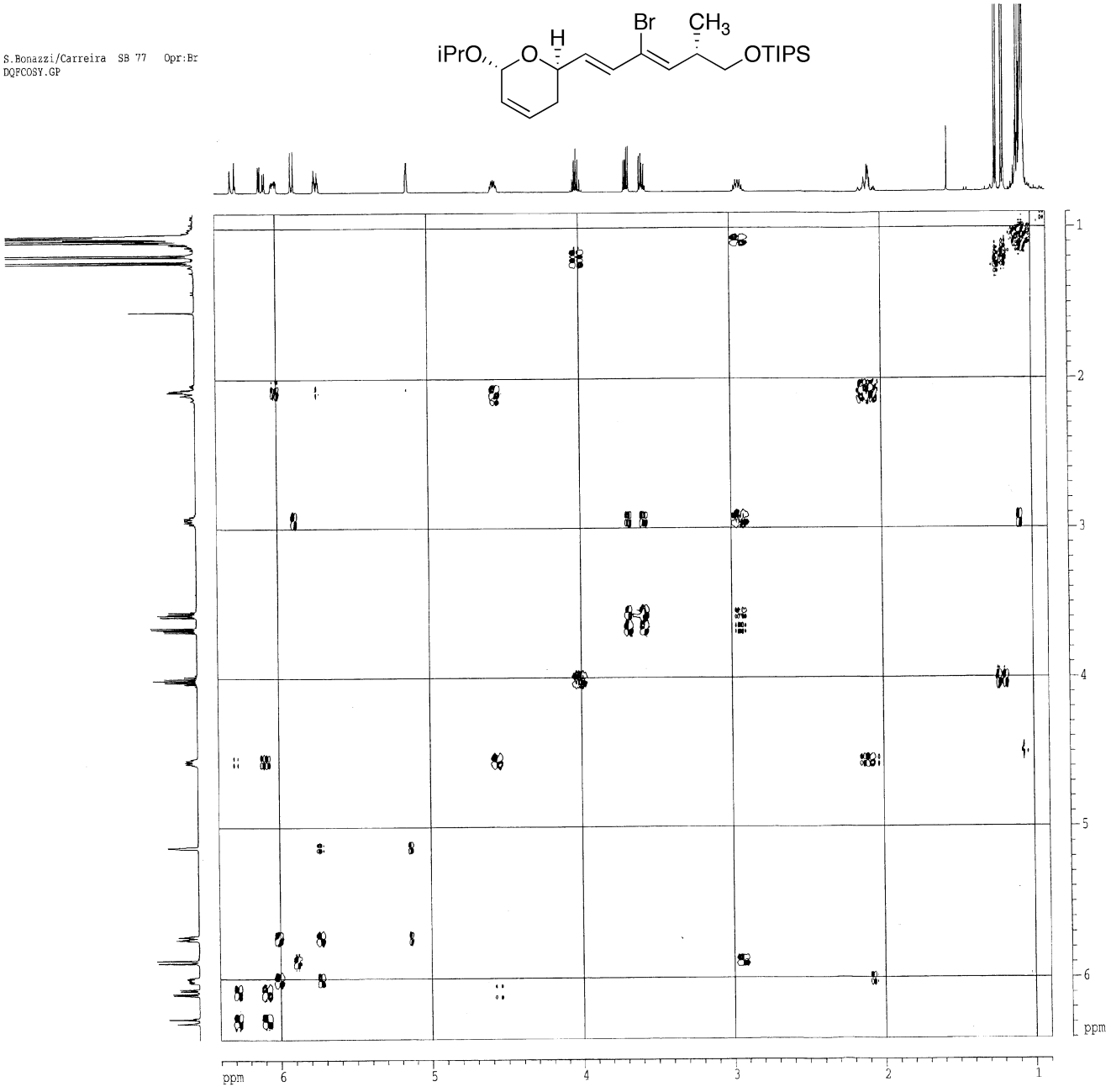
F1 - Processing parameters

SI	1024
MC2	TPPI
SF	125.7326514 MHz
WDW	SINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	6.500 ppm
F2LO	3250.20 Hz
F2PHI	0.900 ppm
F2HI	450.03 Hz
F1PLO	141.000 ppm
F1LO	17728.30 Hz
F1PHI	9.000 ppm
F1HI	1131.59 Hz
F2PPMCM	0.28000 ppm/cm
F2HZCM	140.00839 Hz/cm
F1PPMCM	6.60000 ppm/cm

S.Bonazzi/Carreira SB 77 Opr:Br
DQFCOSY.GP



Current Data Parameters

NAME	P0385
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20060131
Time	9.11
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	cosydfgptp
TD	2048
SOLVENT	CDCl3
NS	4
DS	16
SWH	4496.403 Hz
FIDRES	2.195509 Hz
AQ	0.2277876 sec
RG	4096
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
d0	0.00000300 sec
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
d13	0.00000300 sec
D16	0.00015000 sec
d20	0.00215300 sec
IN0	0.00011120 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	7.10 usec
p2	14.20 usec
PL1	-4.00 dB
PL12	8.00 dB
SFO1	500.0319318 MHz

========== GRADIENT CHANNEL ========

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	15.00 %
GPZ2	30.00 %
P16	2000.00 usec

F1 - Acquisition parameters

ND0	2
TD	512
SFO1	500.0319 MHz
FIDRES	8.782037 Hz
SW	8.992 ppm

F2 - Processing parameters

SI	1024
SF	500.0300108 MHz
WDW	QSINE
SSB	3
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	1024
MC2	TPPI
SF	500.0300108 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

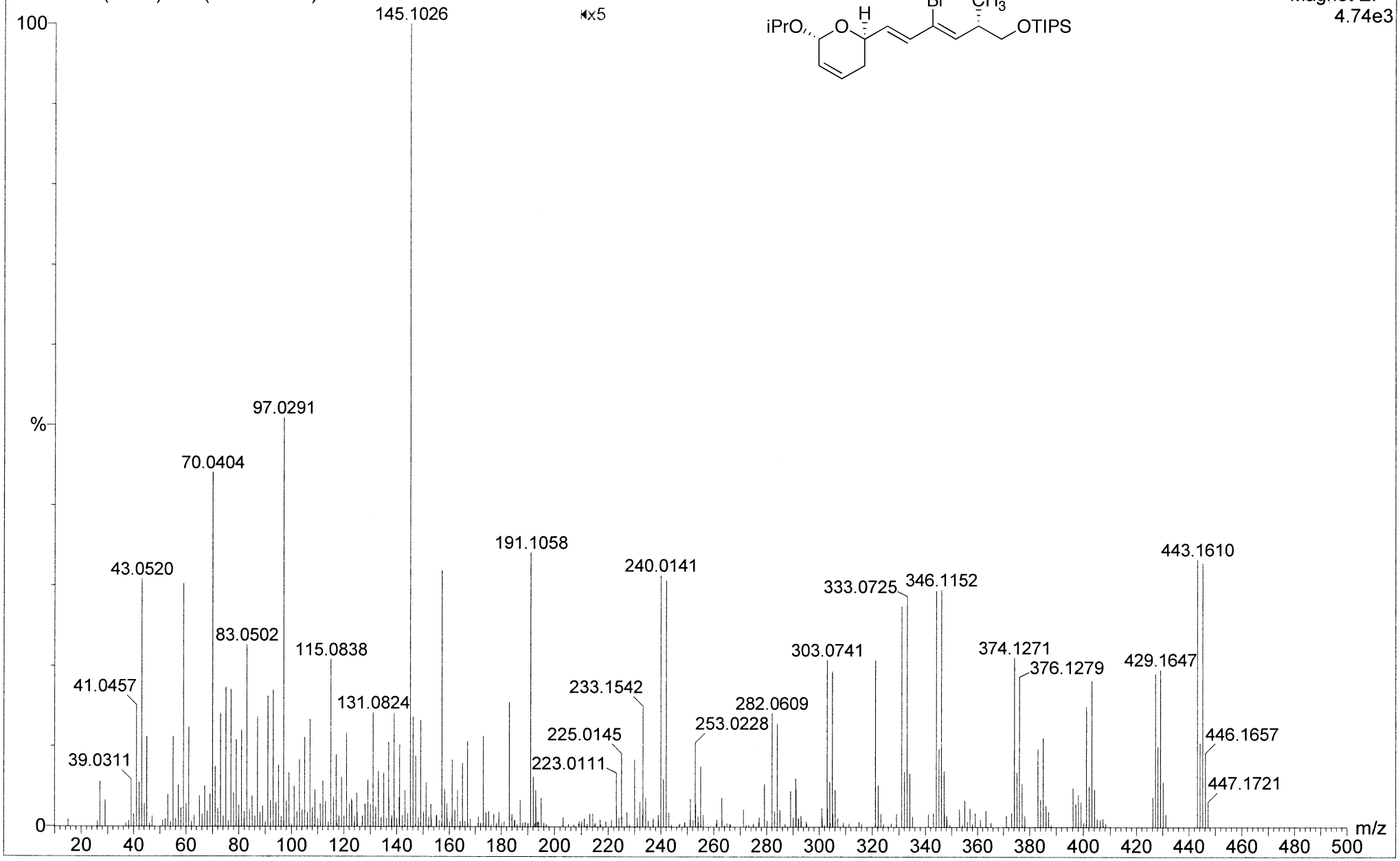
CX2	20.00 cm
CX1	20.00 cm
F2PLO	6.406 ppm
F2LO	3203.18 Hz
F2PHI	0.900 ppm
F2HI	450.01 Hz
F1PLO	6.406 ppm
F1LO	3203.18 Hz
F1PHI	0.900 ppm
F1HI	450.01 Hz
F2PPMCM	0.27530 ppm/cm
F2HZCM	137.65843 Hz/cm
F1PPMCM	0.27530 ppm/cm

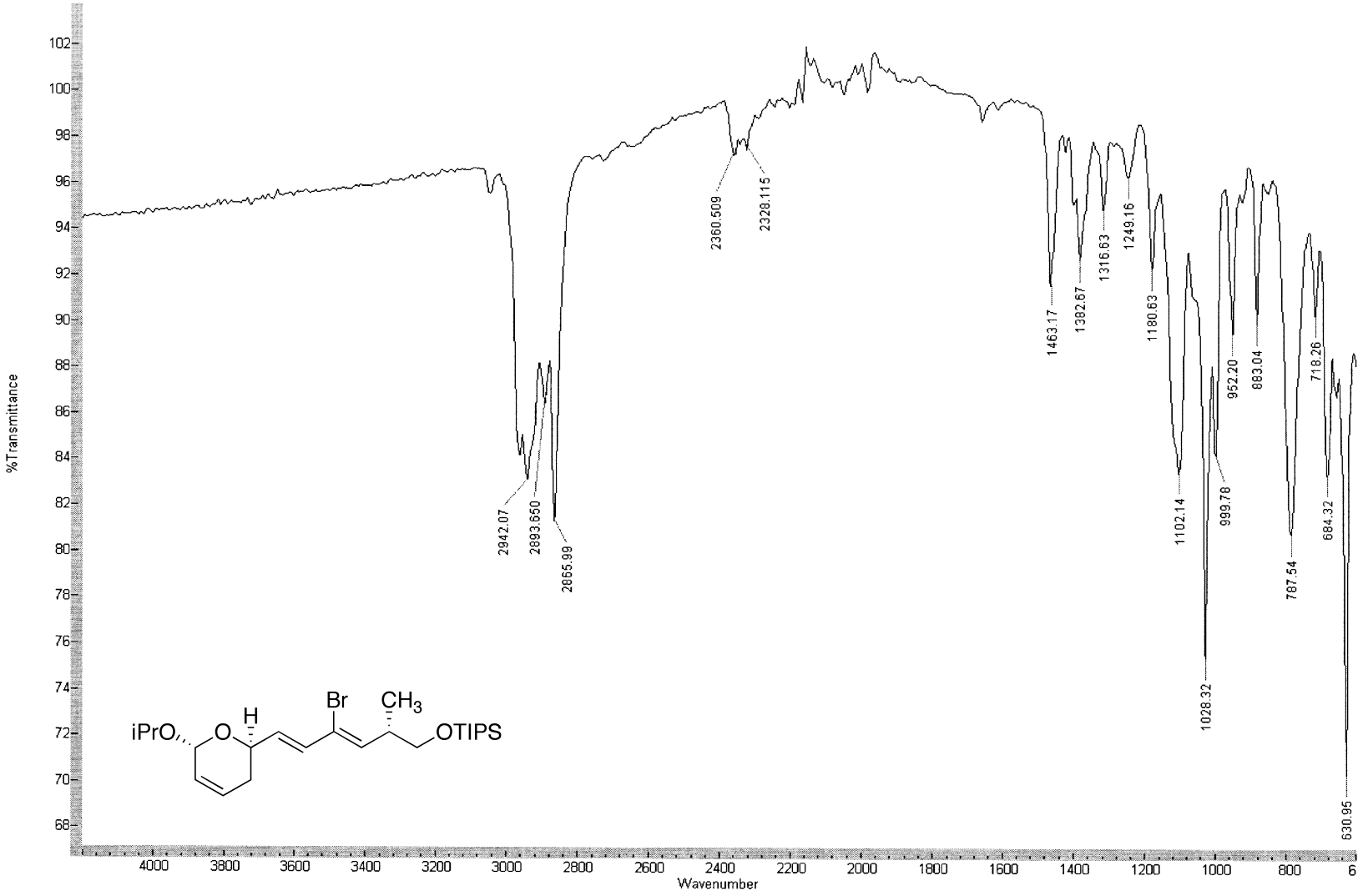
S. Bonazzi/Carreira

04-Sep-2006
13:49:36

EI3351 15 (1.633) Cm (15:19-42:50)

Magnet EI+
4.74e3




%Transmittance
Wavenumber
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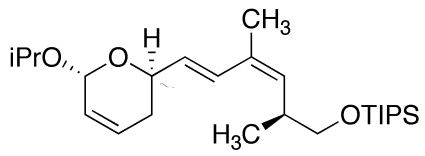
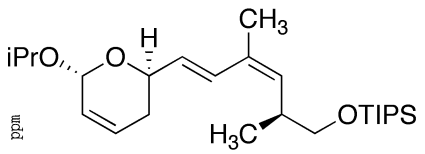
2893.650
2865.99
2360.509
2328.115
1463.17
1382.67
1316.63
1249.16
1180.63
1102.14
1028.32
999.78
952.20
883.04
787.54
718.26
684.32
630.95
iPrO
O
H
Br
CH3
OTIPS

S.Bonazzi/Carreira SB 79 Opr:Br
500MHz 1H-NMR

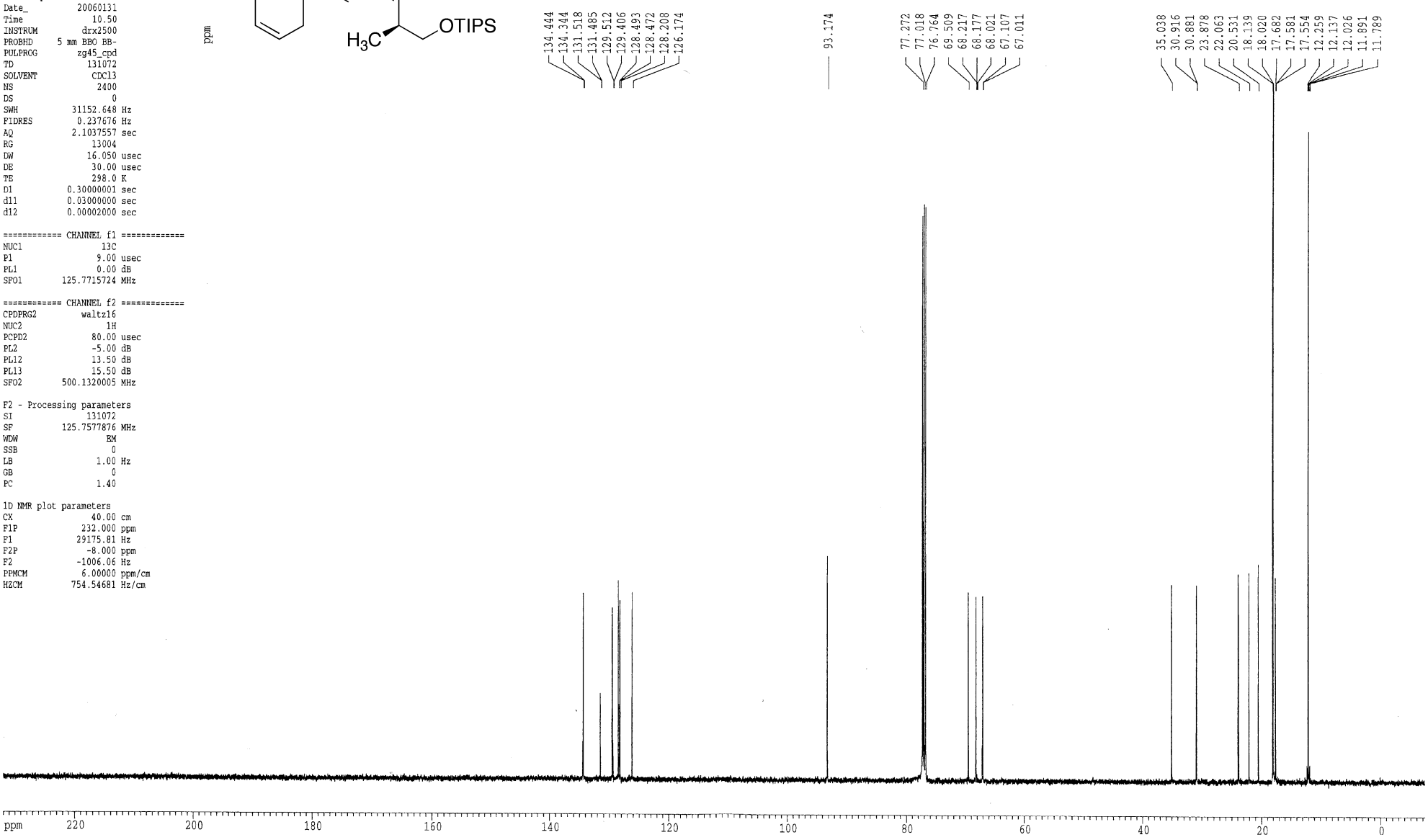



```
Current Data Parameters
NAME                 F0384
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060130
Time                 8.14
INSTRUM            DRX500
PROBHD     5 mm BBI 1H-
PULPROG              zg30
TD                  90112
SOLVENT              CDCl3
NS                      32
DS                       0
SWH              8090.615 Hz
FIDRES           0.089784 Hz
AQ               5.5689716 sec
RG                      90
DW                 61.800 usec
DE                  6.00 usec
TE                 300.0 K
D1            0.01000000 sec

============ CHANNEL f1 =============
NUC1                    1H
P1                   7.10 usec
PL1                 -4.00 dB
SFO1          500.0332000 MHz

F2 - Processing parameters
SI                   65536
SF            500.0300108 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.80

1D NMR plot parameters
CX                   40.00 cm
F1P                  9.500 ppm
F1                4750.29 Hz
F2P                 -0.500 ppm
F2                -250.01 Hz
PPMCM             0.25000 ppm/cm
HZCM            125.00750 Hz/cm
```

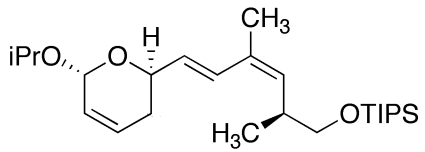
S.Bonazzi/Carreira SB 79 Opr:Br
125 MHz BB 13C NMR




```
Current Data Parameters
NAME                 F0384
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060131
Time                 10.50
INSTRUM              drx2500
PROBHD     5 mm BBO BB-
PULPROG              zg45_cpd
TD                   131072
SOLVENT              CDCl3
NS                   2400
DS                      0
SWH              31152.648 Hz
FIDRES           0.237676 Hz
AQ               2.1037557 sec
RG                   13004
DW                  16.050 usec
DE                  30.00 usec
TE                  298.0 K
D1              0.30000001 sec
d11             0.03000000 sec
d12             0.00002000 sec

============ CHANNEL f1 =============
NUC1                   13C
P1                    9.00 usec
PL1                   0.00 dB
SFO1           125.7715724 MHz

============ CHANNEL f2 =============
CPDPRG2            waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                  -5.00 dB
PL12                 13.50 dB
PL13                 15.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                   131072
SF             125.7577876 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   40.00 cm
F1P                232.000 ppm
F1                29175.81 Hz
F2P                 -8.000 ppm
F2                -1006.06 Hz
PPMCM              6.00000 ppm/cm
HZCM             754.54681 Hz/cm
```

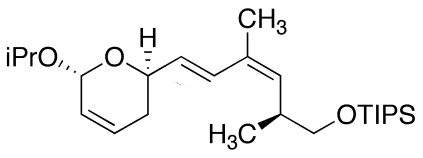


S.Bonazzi/Carreira SB 79 Opr:Br
125 MHz 13C DEPT 90+135 NMR




```
Current Data Parameters
NAME                 F0384
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20060131
Time                 11.25
INSTRUM           drx2500
PROBHD      5 mm BBO BB-
PULPROG          dept1eth
TD                 131072
SOLVENT             CDCl3
NS                     512
DS                       0
SWH              31152.648 Hz
FIDRES           0.237676 Hz
AQ               2.1037557 sec
RG                   13004
DW                 16.050 usec
DE                 30.00 usec
TE                 298.0 K
CNST2          145.0000000
D1              2.00000000 sec
d2              0.00344828 sec
d12             0.00002000 sec
DELTA           0.00001146 sec

============ CHANNEL f1 =============
NUC1                   13C
P1                    9.00 usec
p2                   18.00 usec
PL1                   0.00 dB
SFO1           125.7715724 MHz

============ CHANNEL f2 =============
CPDPRG2           waltz16
NUC2                   1H
P0                   11.00 usec
P3                   11.00 usec
p4                   22.00 usec
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 13.50 dB
SFO2           500.1320005 MHz

F2 - Processing parameters
SI                    65536
SF             125.7577876 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                   40.00 cm
F1P                232.000 ppm
F1                29175.80 Hz
F2P                 -8.000 ppm
F2                -1006.06 Hz
PPMCM              6.00000 ppm/cm
HZCM             754.54675 Hz/cm
```

S.Bonazzi/Carreira SB 79 Opr:Br
500 MHz 1H NOE difference spectrum



Current Data Parameters

NAME	F0384
EXPNO	31
PROCNO	1

F2 - Acquisition Parameters

Date_	20060130
Time	14.28
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	noemul
TD	90112
SOLVENT	CDCl3
NS	320
DS	4
SWH	8090.615 Hz
FIDRES	0.089784 Hz
AQ	5.5689716 sec
RG	90
DW	61.800 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
D20	0.07000000 sec
L4	30
NUC1	1H
P1	7.10 usec
PL1	-4.00 dB
SFO1	500.0332000 MHz
FQ2LIST	f2list.3
NUC2	1H
PL2	120.00 dB
PL14	74.00 dB
SFO2	500.0332000 MHz

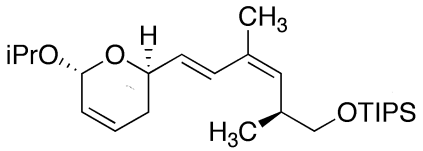
F2 - Processing parameters

SI	65536
SF	500.0300108 MHz
WDW	EM
SSB	0
LB	0.60 Hz
GB	0
PC	1.00

1D NMR plot parameters

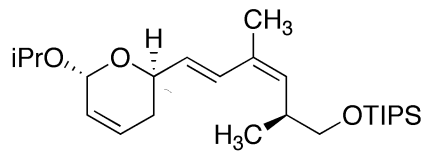
CX	40.00 cm
F1P	9.500 ppm
F1	4750.29 Hz
F2P	-0.500 ppm
F2	-250.01 Hz
PPMCM	0.25000 ppm/cm
HZCM	125.00750 Hz/cm

S.Bonazzi/Carreira SB 79 Opr:Br
500 MHz 1H NOE difference spectrum




```
Current Data Parameters
NAME              F0384
EXPNO                32
PROCNO                1

F2 - Acquisition Parameters
Date_          20060130
Time              14.31
INSTRUM          DRX500
PROBHD     5 mm BBI 1H-
PULPROG           noemul
TD                90112
SOLVENT           CDCl3
NS                  320
DS                    4
SWH            8090.615 Hz
FIDRES         0.089784 Hz
AQ             5.5689716 sec
RG                   90
DW                61.800 usec
DE                 6.00 usec
TE                300.0 K
D1           0.10000000 sec
d11          0.03000000 sec
d12          0.00002000 sec
D20          0.07000000 sec
L4                   30
NUC1                 1H
P1                 7.10 usec
PL1                -4.00 dB
SFO1         500.0332000 MHz
FQ2LIST        f2list.4
NUC2                 1H
PL2               120.00 dB
PL14               74.00 dB
SFO2         500.0332000 MHz

F2 - Processing parameters
SI                65536
SF         500.0300108 MHz
WDW                  EM
SSB                   0
LB                 0.60 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                40.00 cm
F1P               9.500 ppm
F1             4750.29 Hz
F2P              -0.500 ppm
F2             -250.01 Hz
PPMCM          0.25000 ppm/cm
HZCM         125.00750 Hz/cm
```

S.Bonazzi/Carreira SB 79 Opr:Br
500 MHz 1H NOE difference spectrum



Current Data Parameters

NAME	F0384
EXPNO	30
PROCNO	1

F2 - Acquisition Parameters

Date_	20060130
Time	14.26
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	noemul
TD	90112
SOLVENT	CDCl3
NS	320
DS	4
SWH	8090.615 Hz
FIDRES	0.089784 Hz
AQ	5.5689716 sec
RG	90
DW	61.800 usec
DE	6.00 usec
TE	300.0 K
D1	0.10000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
D20	0.07000000 sec
L4	30
NUC1	1H
P1	7.10 usec
PL1	-4.00 dB
SFO1	500.0332000 MHz
FQ2LIST	f2list.2
NUC2	1H
PL2	120.00 dB
PL14	74.00 dB
SFO2	500.0332000 MHz

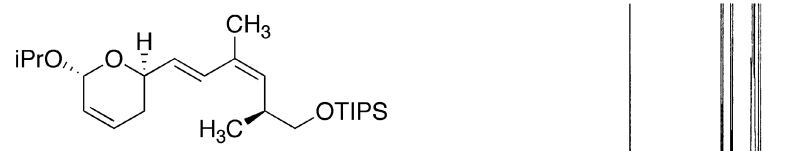
F2 - Processing parameters

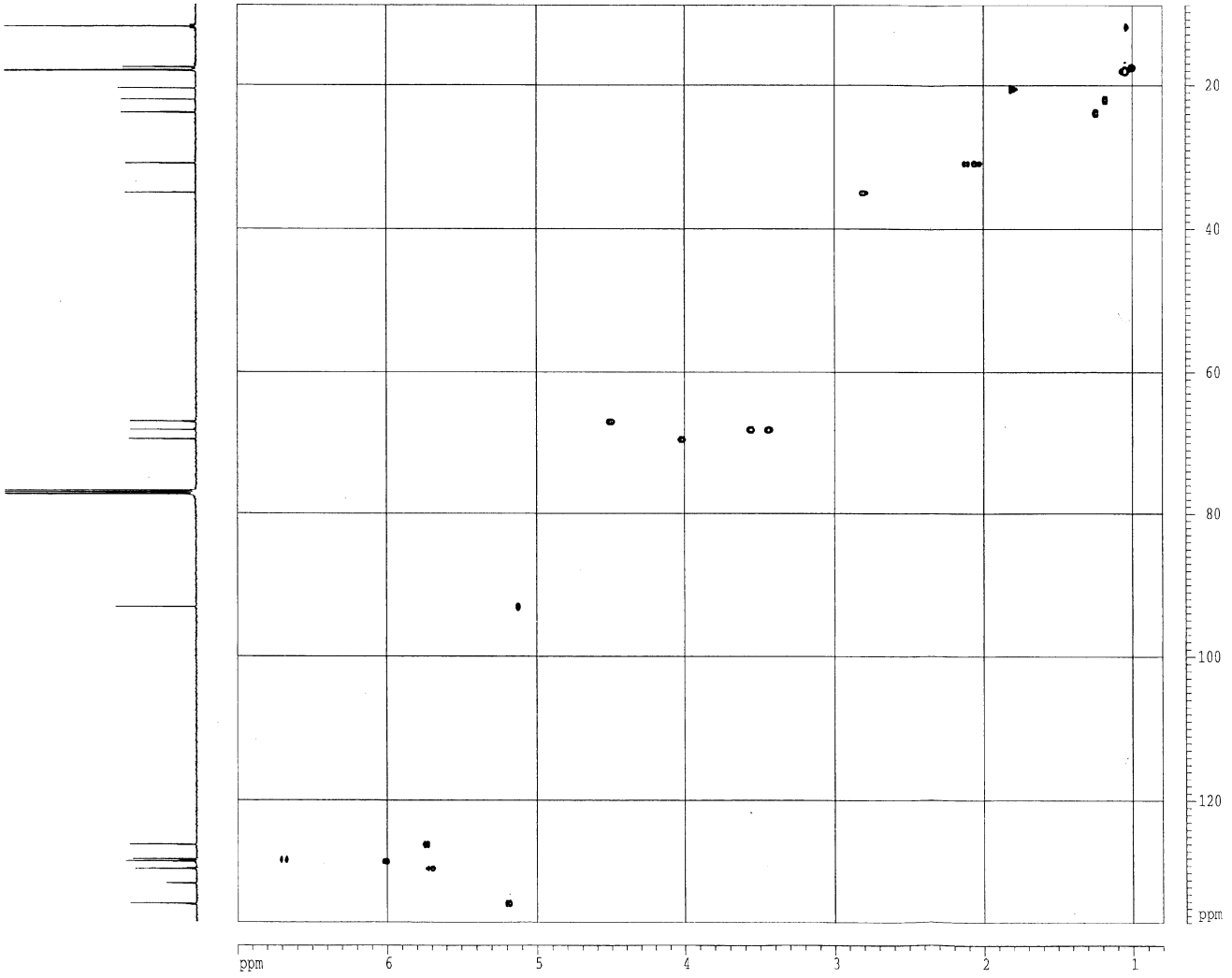
SI	65536
SF	500.0300108 MHz
WDW	EM
SSB	0
LB	0.60 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	40.00 cm
F1P	9.500 ppm
F1	4750.29 Hz
F2P	-0.500 ppm
F2	-250.01 Hz
PPMCM	0.25000 ppm/cm
HZCM	125.00750 Hz/cm

S.Bonazzi/Carreira SB 79 Opr:Br
HSQC.GP





Current Data Parameters

NAME	F0384
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20060130
Time	9.44
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	invigptp
TD	2048
SOLVENT	CDCl3
NS	4
DS	16
SWH	4496.403 Hz
FIDRES	2.195509 Hz
AQ	0.2277876 sec
RG	8192
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
CNST2	145.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d4	0.00172414 sec
d11	0.03000000 sec
d13	0.00000300 sec
d16	0.00010000 sec
d20	0.00110000 sec
d21	0.00061714 sec
IN0	0.00001030 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	7.10 usec
p2	14.20 usec
PL1	-4.00 dB
SFO1	500.0319318 MHz

========== CHANNEL f2 ==========

CPDPRG2	garp
NUC2	13C
P3	12.50 usec
p4	25.00 usec
PCPD2	76.00 usec
PL2	-3.00 dB
PL12	13.00 dB
SFO2	125.7431995 MHz

========== GRADIENT CHANNEL =======

GPNAM1	sine.100
GPNAM2	sine.100
GPNAM3	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPX3	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPY3	0.00 %
GPZ1	80.00 %
GPZ2	30.00 %
GPZ3	20.00 %
P16	1000.00 usec

F1 - Acquisition parameters

NDO	4
TD	461
SFO1	125.7432 MHz
FIDRES	52.650421 Hz
SW	193.027 ppm

F2 - Processing parameters

SI	1024
SF	500.0300108 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

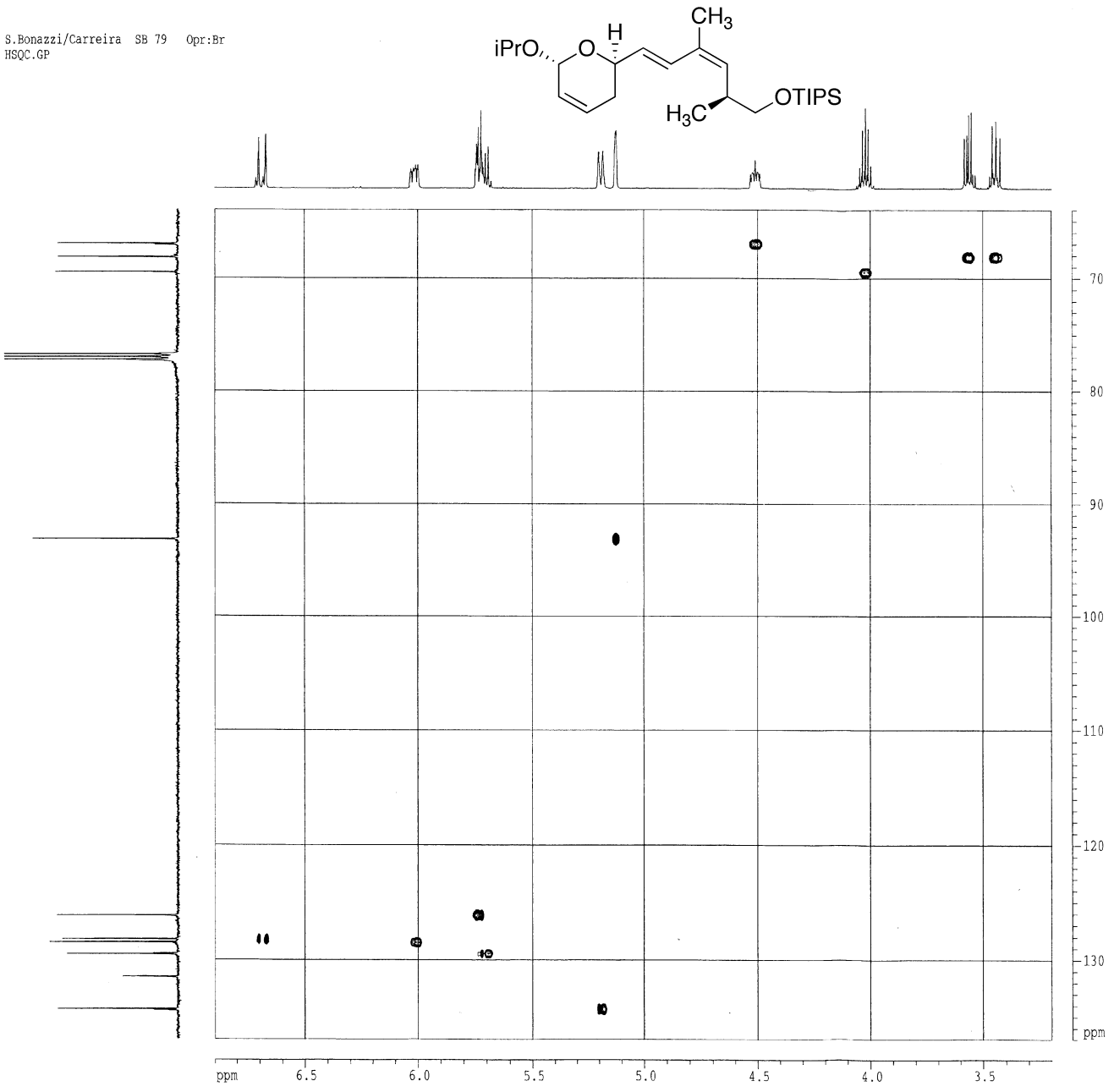
F1 - Processing parameters

SI	1024
MC2	TPPI
SF	125.7326423 MHz
WDW	SINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	7.000 ppm
F2LO	3500.21 Hz
F2PHI	0.800 ppm
F2HI	400.02 Hz
F1PLO	137.000 ppm
F1LO	17225.37 Hz
F1PHI	9.000 ppm
F1HI	1131.59 Hz
F2PPMCM	0.31000 ppm/cm
F2HZCM	155.00929 Hz/cm
F1PPMCM	6.40000 ppm/cm

S.Bonazzi/Carreira SB 79 Opr:Br
HSQC.GP



Current Data Parameters

NAME	F0384
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20060130
Time	9.44
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	invigptp
TD	2048
SOLVENT	CDCl3
NS	4
DS	16
SWH	4496.403 Hz
FIDRES	2.195509 Hz
AQ	0.2277676 sec
RG	8192
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
CNST2	145.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d4	0.00172414 sec
d11	0.03000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
d20	0.00110000 sec
d21	0.00061714 sec
IN0	0.00001030 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	7.10 usec
p2	14.20 usec
PL1	-4.00 dB
SFO1	500.0319318 MHz

========== CHANNEL f2 ==========

CPDPRG2	garp
NUC2	13C
P3	12.50 usec
p4	25.00 usec
PCPD2	76.00 usec
PL2	-3.00 dB
PL12	13.00 dB
SFO2	125.7431995 MHz

========== GRADIENT CHANNEL ========

GPNAM1	sine.100
GPNAM2	sine.100
GPNAM3	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPX3	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPY3	0.00 %
GPZ1	80.00 %
GPZ2	30.00 %
GPZ3	20.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	4
TD	461
SFO1	125.7432 MHz
FIDRES	52.650421 Hz
SW	193.027 ppm

F2 - Processing parameters

SI	1024
SF	500.0300108 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

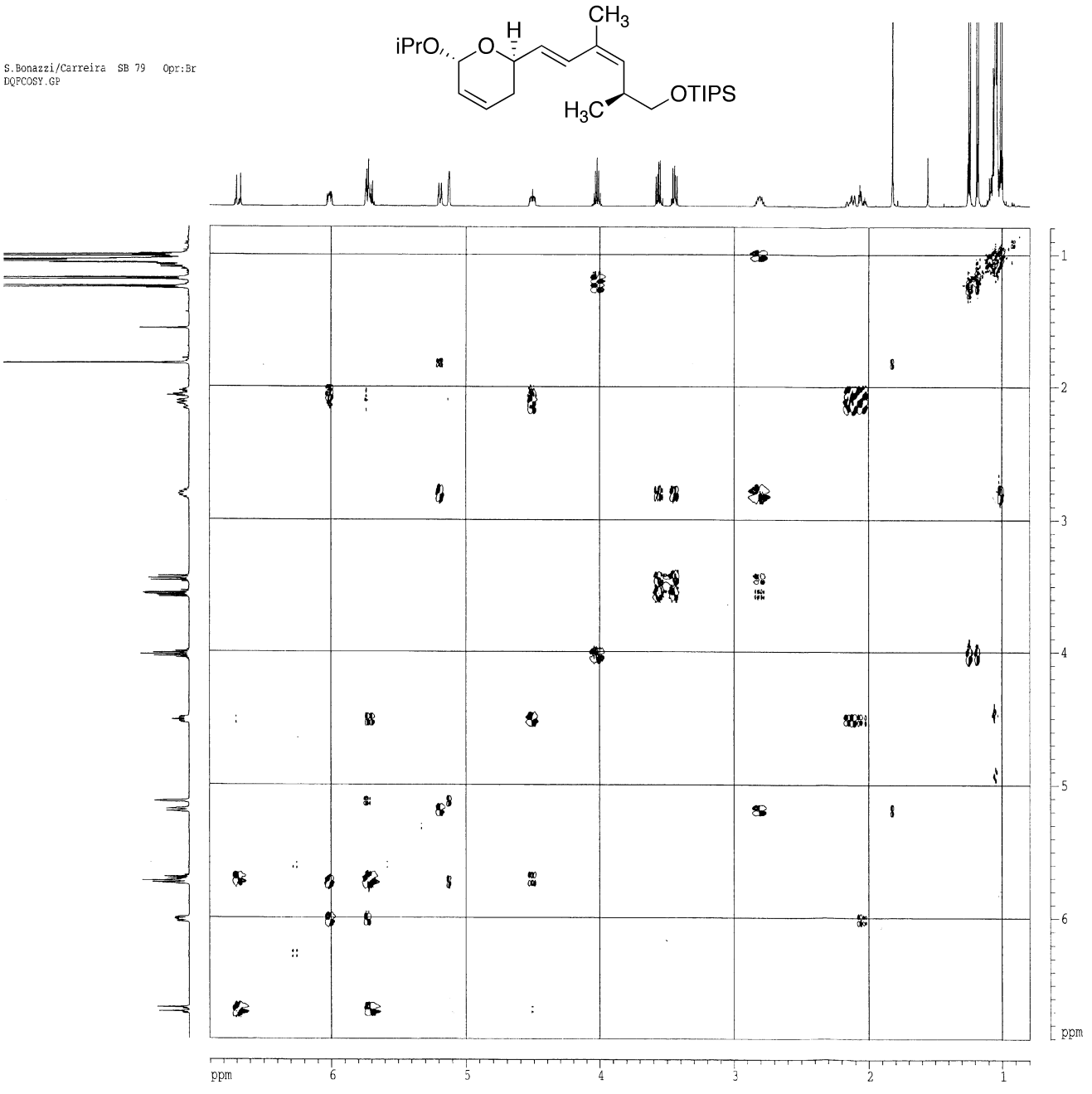
F1 - Processing parameters

SI	1024
MC2	TPPI
SF	125.7726423 MHz
WDW	STNE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	6.900 ppm
F2LO	3450.21 Hz
F2PHI	3.200 ppm
F2HI	1600.10 Hz
F1PLO	137.000 ppm
F1LO	17225.37 Hz
F1PHI	64.000 ppm
F1HI	8046.89 Hz
F2PPMCM	0.18500 ppm/cm
F2HZCM	92.50555 Hz/cm
F1PPMCM	3.65000 ppm/cm

S.Bonazzi/Carreira SB 79 Opr:Br
DQFCOSY.GP



Current Data Parameters

NAME	F0384
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20060130
Time	8.25
INSTRUM	DRX500
PROBHD	5 mm BBI 1H-
PULPROG	cosydfqptp
TD	2048
SOLVENT	CDCl3
NS	4
DS	16
SWH	4496.403 Hz
FIDRES	2.195509 Hz
AQ	0.2277876 sec
RG	4096
DW	111.200 usec
DE	6.00 usec
TE	300.0 K
d0	0.00000300 sec
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec
d13	0.00000300 sec
D16	0.00015000 sec
d20	0.00215300 sec
IN0	0.00011120 sec

========== CHANNEL f1 ==========

NUC1	1H
P1	7.10 usec
p2	14.20 usec
PL1	-4.00 dB
PL12	8.00 dB
SFO1	500.0319318 MHz

========== GRADIENT CHANNEL ========

GPNAM1	sine.100
GPNAM2	sine.100
GPX1	0.00 %
GPX2	0.00 %
GPY1	0.00 %
GPY2	0.00 %
GPZ1	15.00 %
GPZ2	30.00 %
P16	2000.00 usec

F1 - Acquisition parameters

ND0	2
TD	512
SFO1	500.0319 MHz
FIDRES	8.782037 Hz
SW	8.992 ppm

F2 - Processing parameters

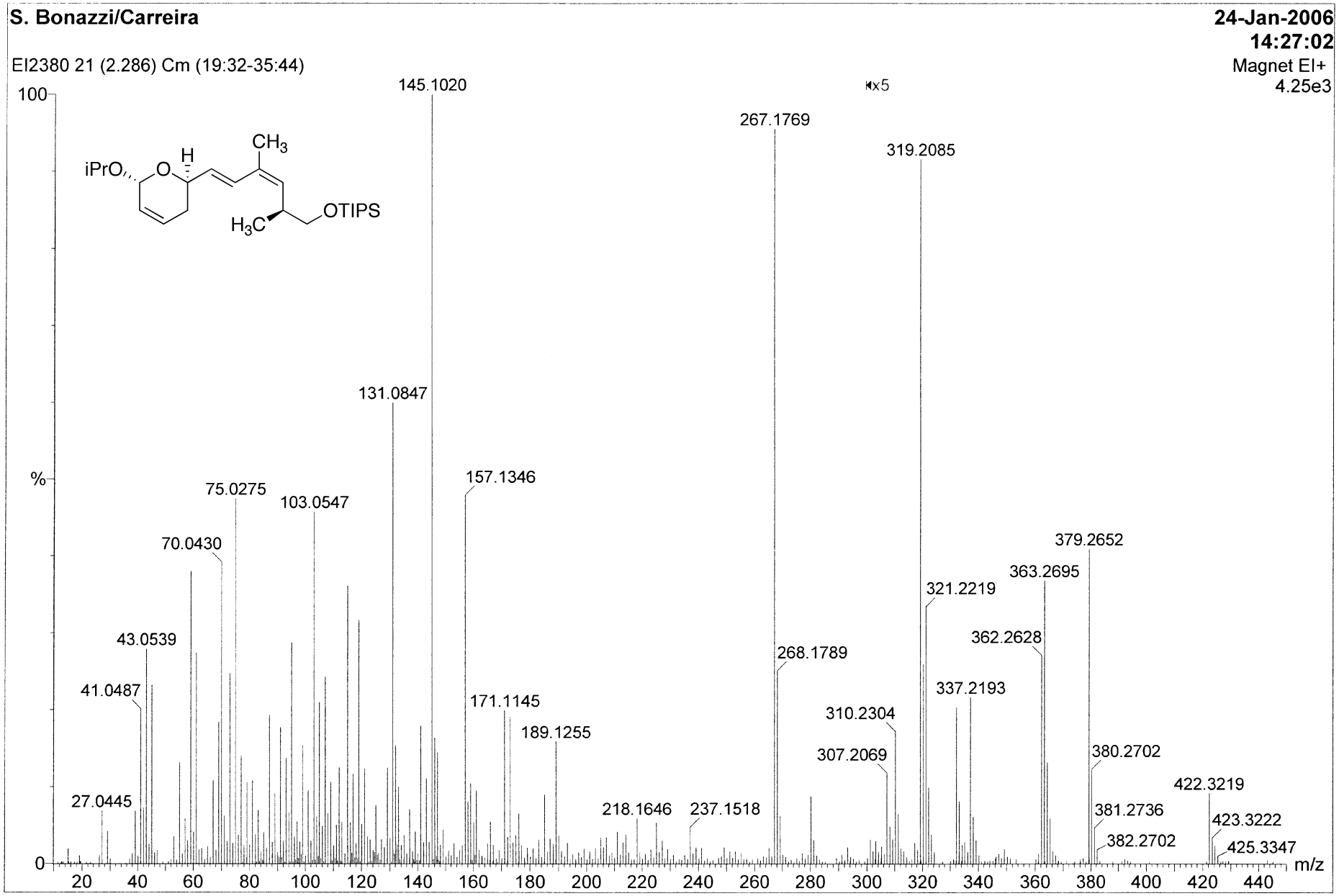
SI	1024
SF	500.0300108 MHz
WDW	QSINE
SSB	3
LB	0.00 Hz
GB	0
PC	1.00

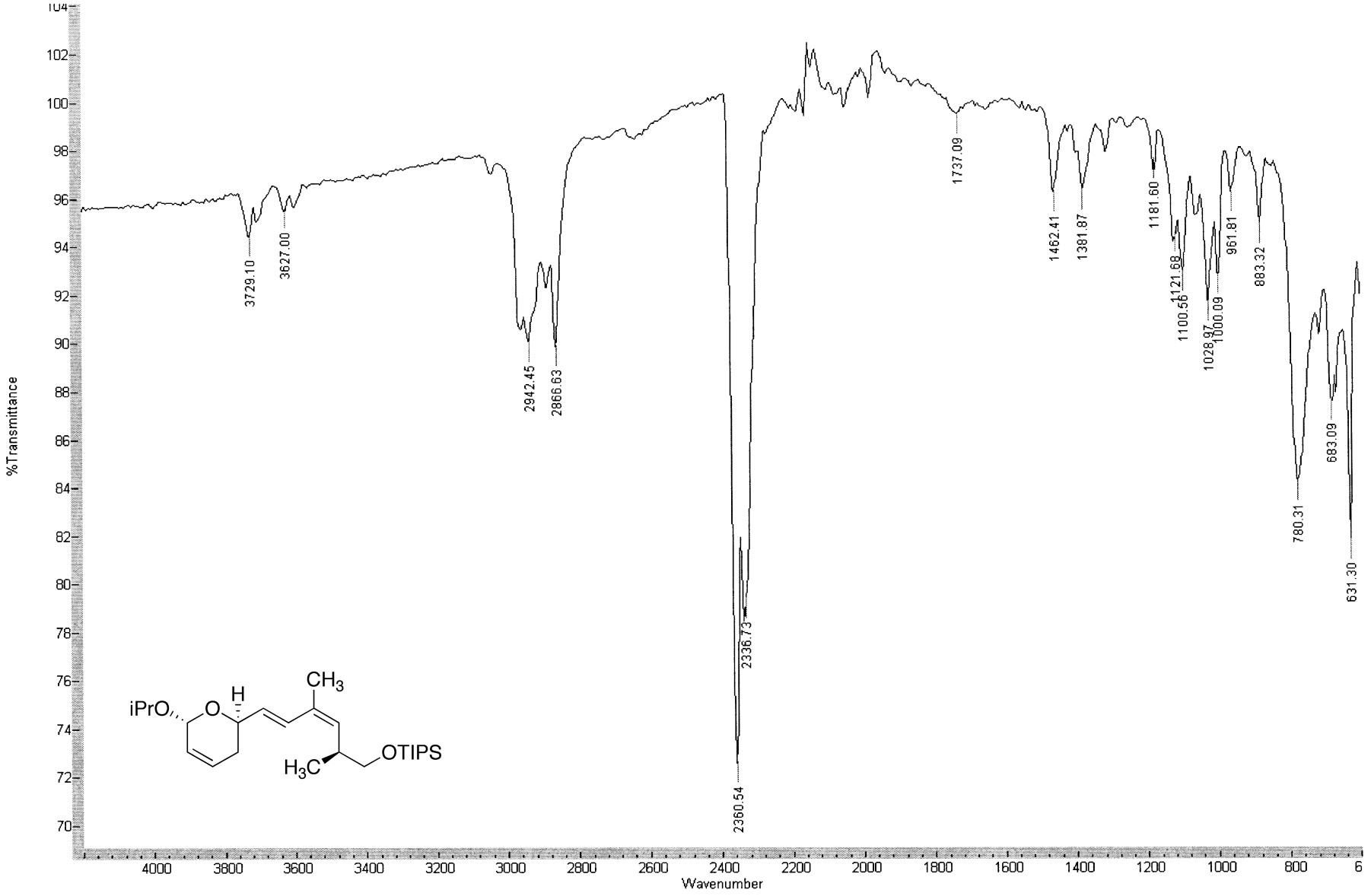
F1 - Processing parameters

SI	1024
MC2	TPPI
SF	500.0300108 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	6.907 ppm
F2LO	3453.47 Hz
F2PHI	0.795 ppm
F2HI	397.32 Hz
F1PLO	6.907 ppm
F1LO	3453.47 Hz
F1PHI	0.795 ppm
F1HI	397.32 Hz
F2PPMCM	0.30560 ppm/cm
F2HZCM	152.80743 Hz/cm
F1PPMCM	0.30560 ppm/cm


S. Bonazzi/Carreira
24-Jan-2006
14:27:02
EI2380 21 (2.286) Cm (19:32-35:44)
Magnet EI+
4.25e3
x5
iPrO
O
H
CH3
H3C
OTIPS
145.1020
267.1769
319.2085
131.0847
157.1346
75.0275
103.0547
70.0430
379.2652
363.2695
321.2219
43.0539
362.2628
268.1789
41.0487
337.2193
171.1145
310.2304
189.1255
307.2069
380.2702
422.3219
27.0445
218.1646
237.1518
381.2736
423.3222
382.2702
425.3347
100
%
0
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440


%Transmittance
Wavenumber
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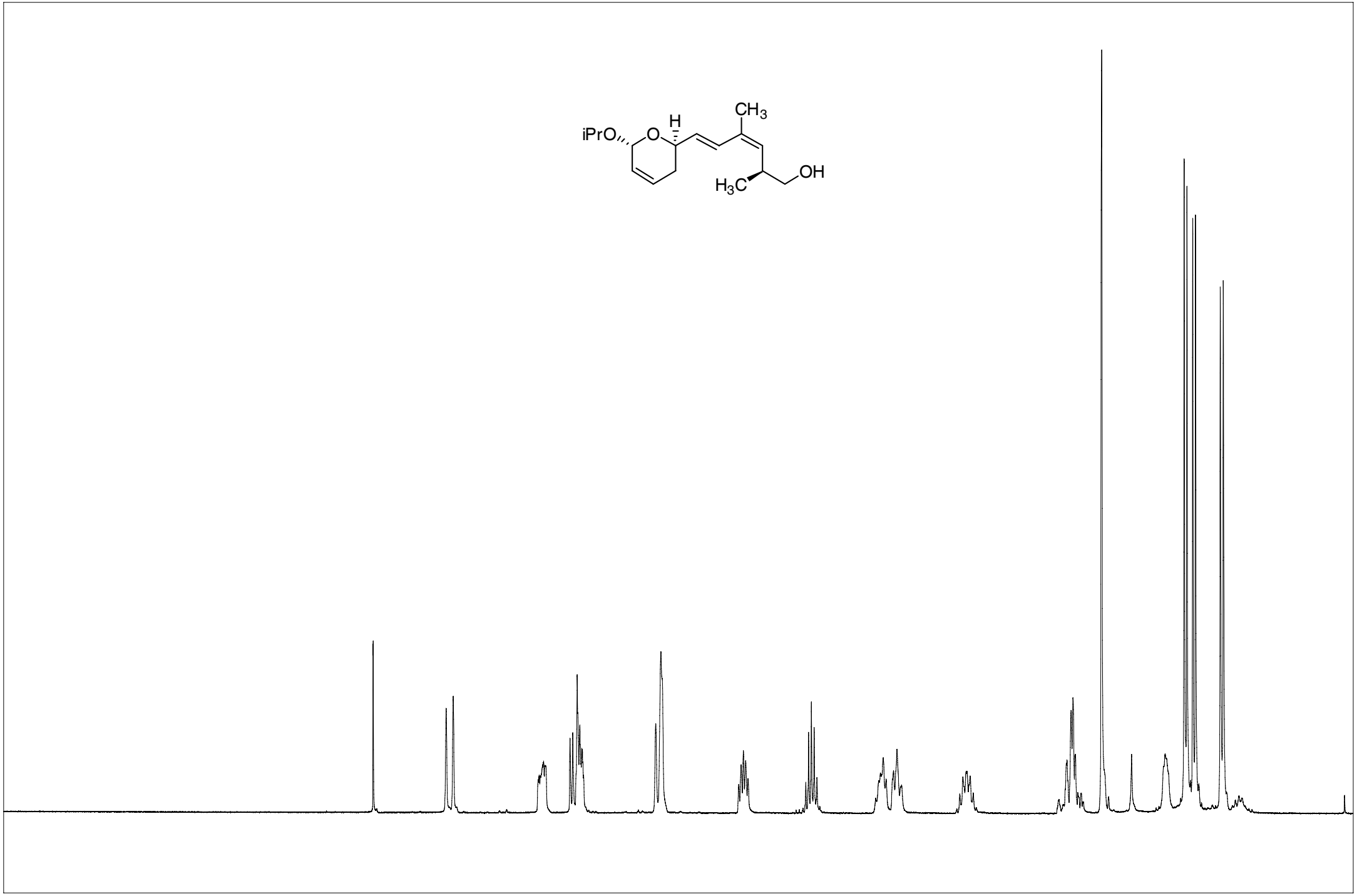
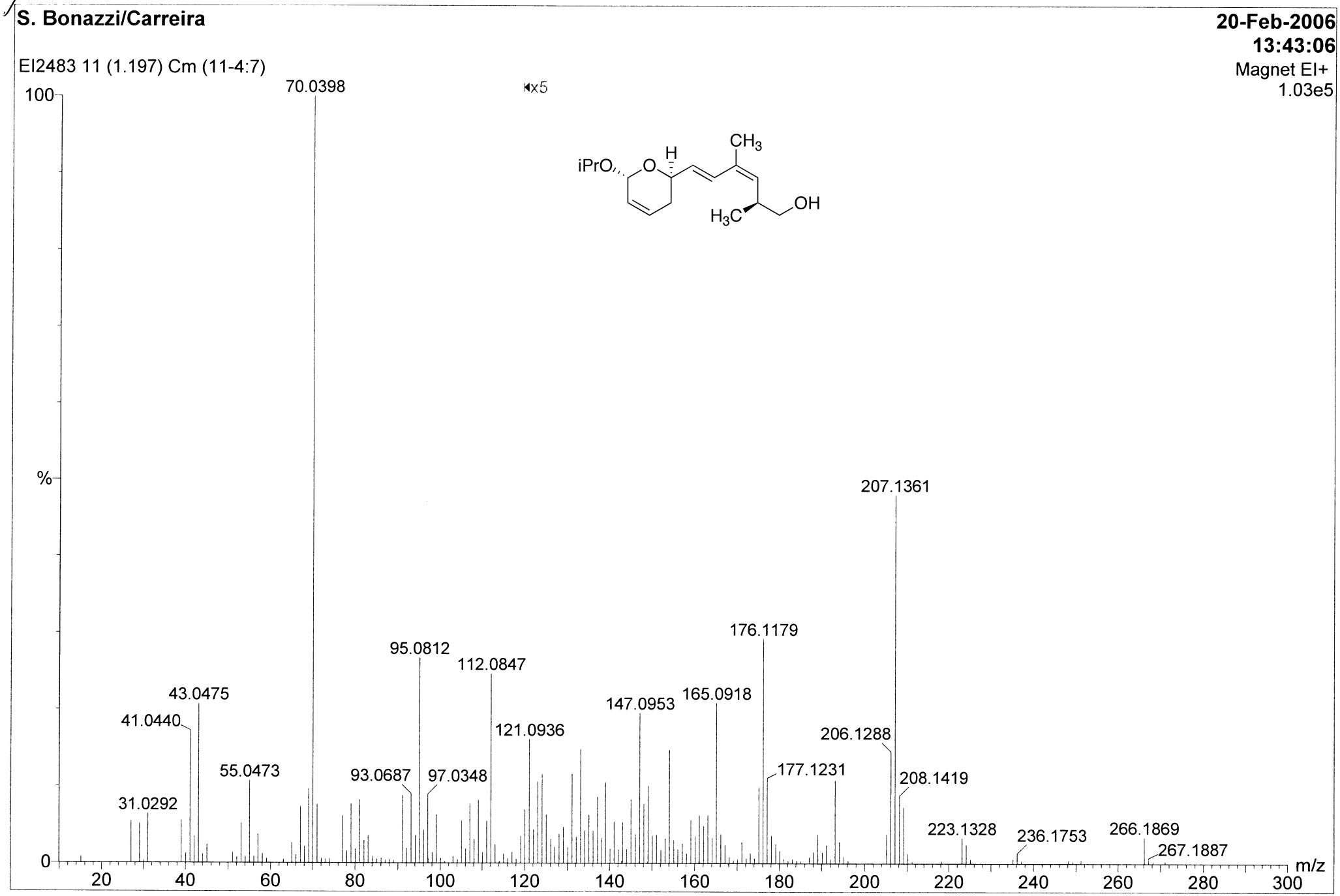
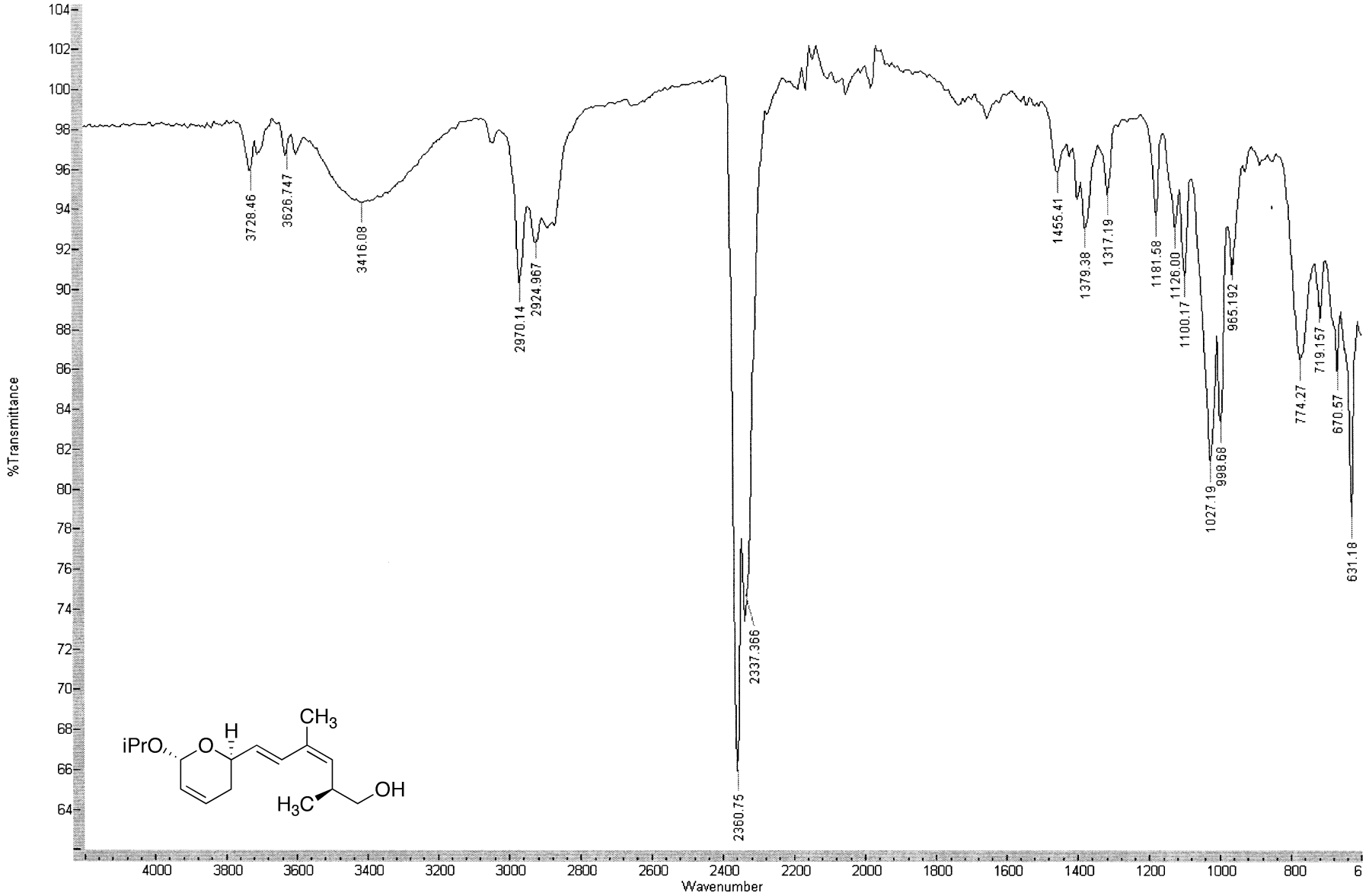
3627.00
2942.45
2866.63
2360.54
2336.73
1737.09
1462.41
1381.87
1181.60
1121.68
1100.56
1028.97
1000.09
961.81
883.32
780.31
683.09
631.30
iPrO
O
H
CH3
H3C
OTIPS


iPrO
O
H
CH3
OH
H3C
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


iPrO
O
H
CH3
H3C
OH
ppm
200
150
100
50


S. Bonazzi/Carreira
20-Feb-2006
13:43:06
EI2483 11 (1.197) Cm (11-4:7)
Magnet EI+
1.03e5
x5
iPrO
O
H
CH3
OH
H3C
100
%
0
70.0398
207.1361
176.1179
95.0812
112.0847
43.0475
41.0440
147.0953
165.0918
121.0936
206.1288
55.0473
93.0687
97.0348
177.1231
208.1419
31.0292
223.1328
236.1753
266.1869
267.1887
m/z
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300


%Transmittance
Wavenumber
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3626.747
3416.08
2970.14
2924.967
2360.75
2337.366
1455.41
1379.38
1317.19
1181.58
1126.00
1100.17
1027.19
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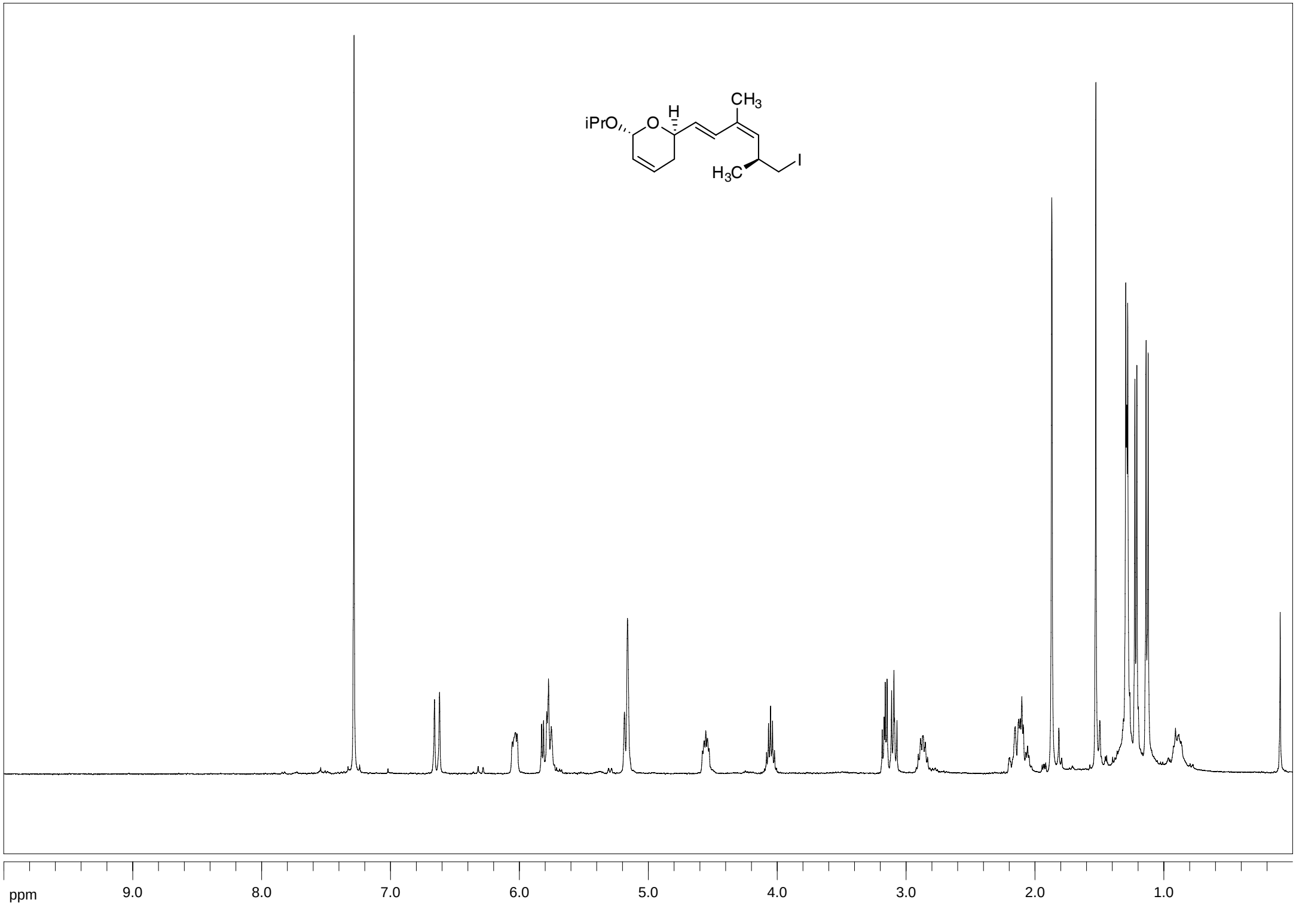
774.27
719.157
670.57
631.18
iPrO
O
H
CH3
H3C
OH


iPrO
O
H
CH3
H3C
I
ppm
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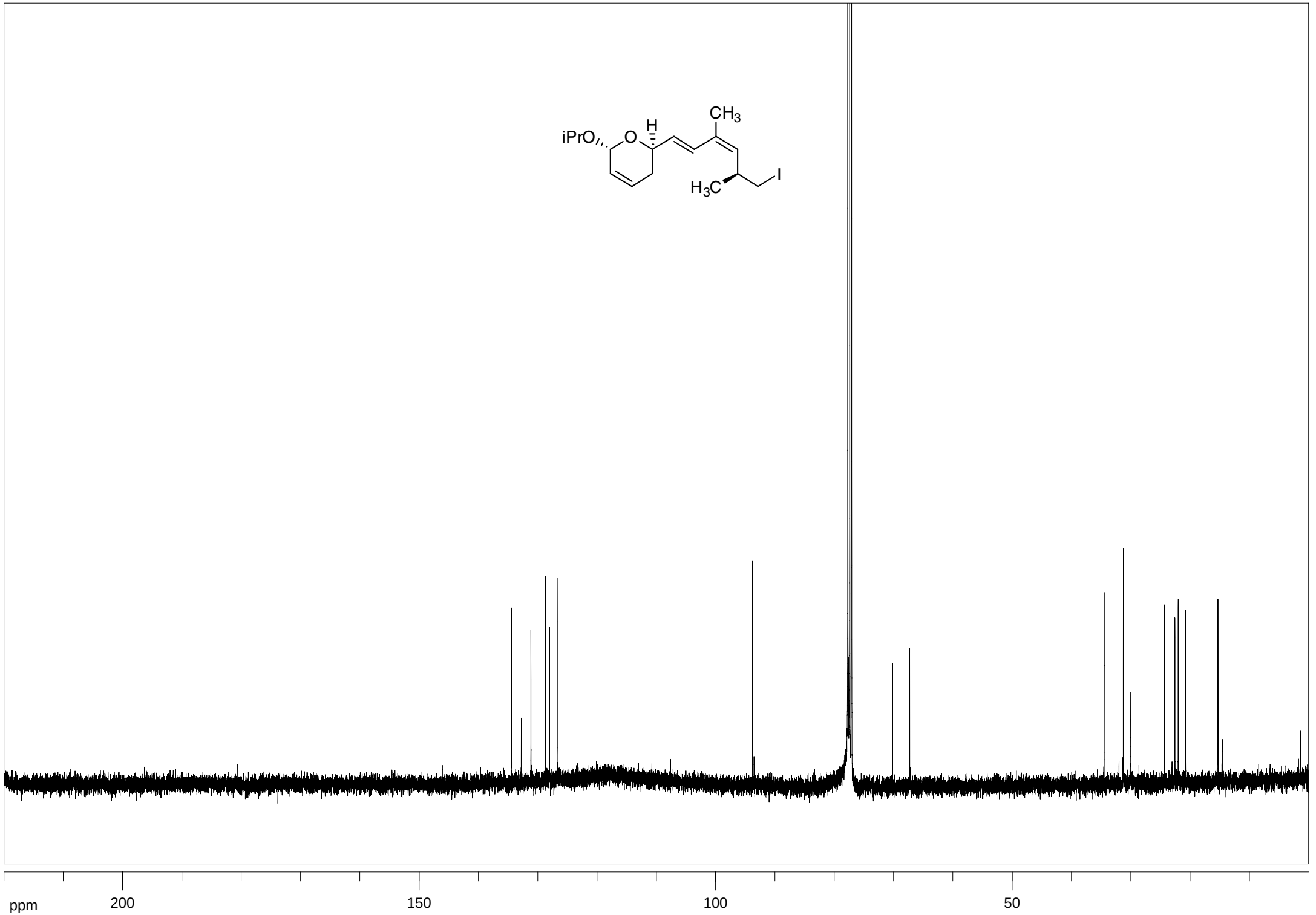
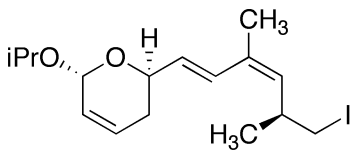
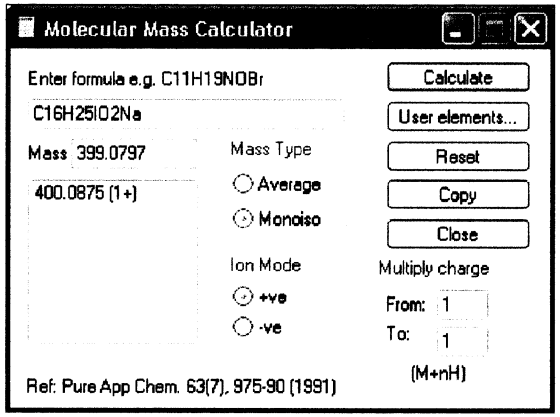
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


iPrO
O
H
CH3
H3C
I
ppm
200
150
100
50

GADEMANN_BONAZZI_040407_SB 325 3 (0.068) Cm (1:9)

TOF MS ES+
4.23e3



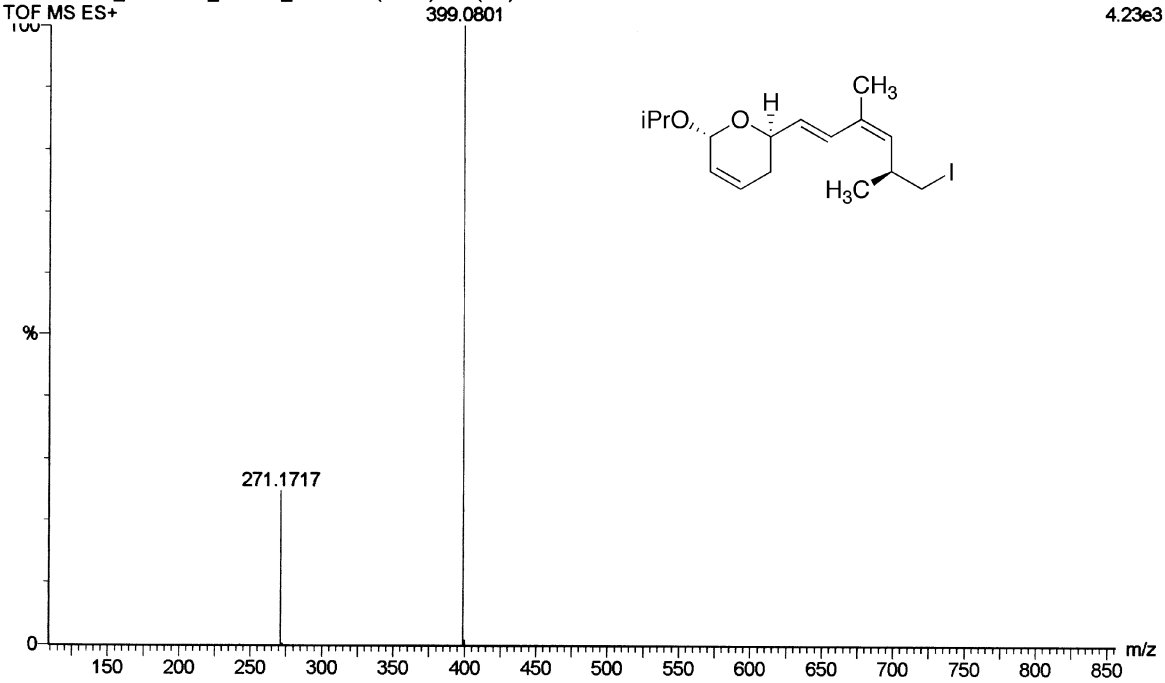


Single Mass Analysis (displaying only valid results)

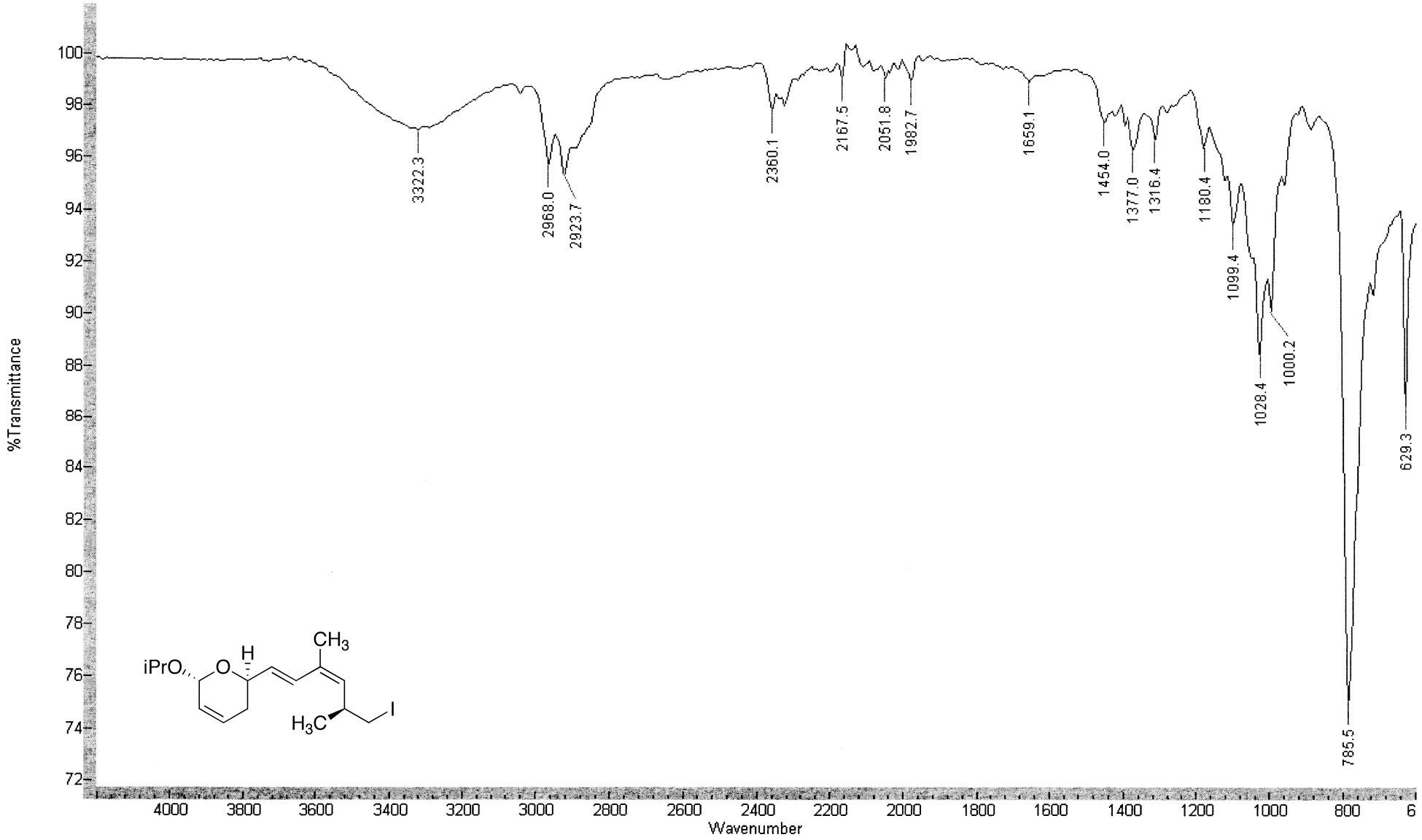
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

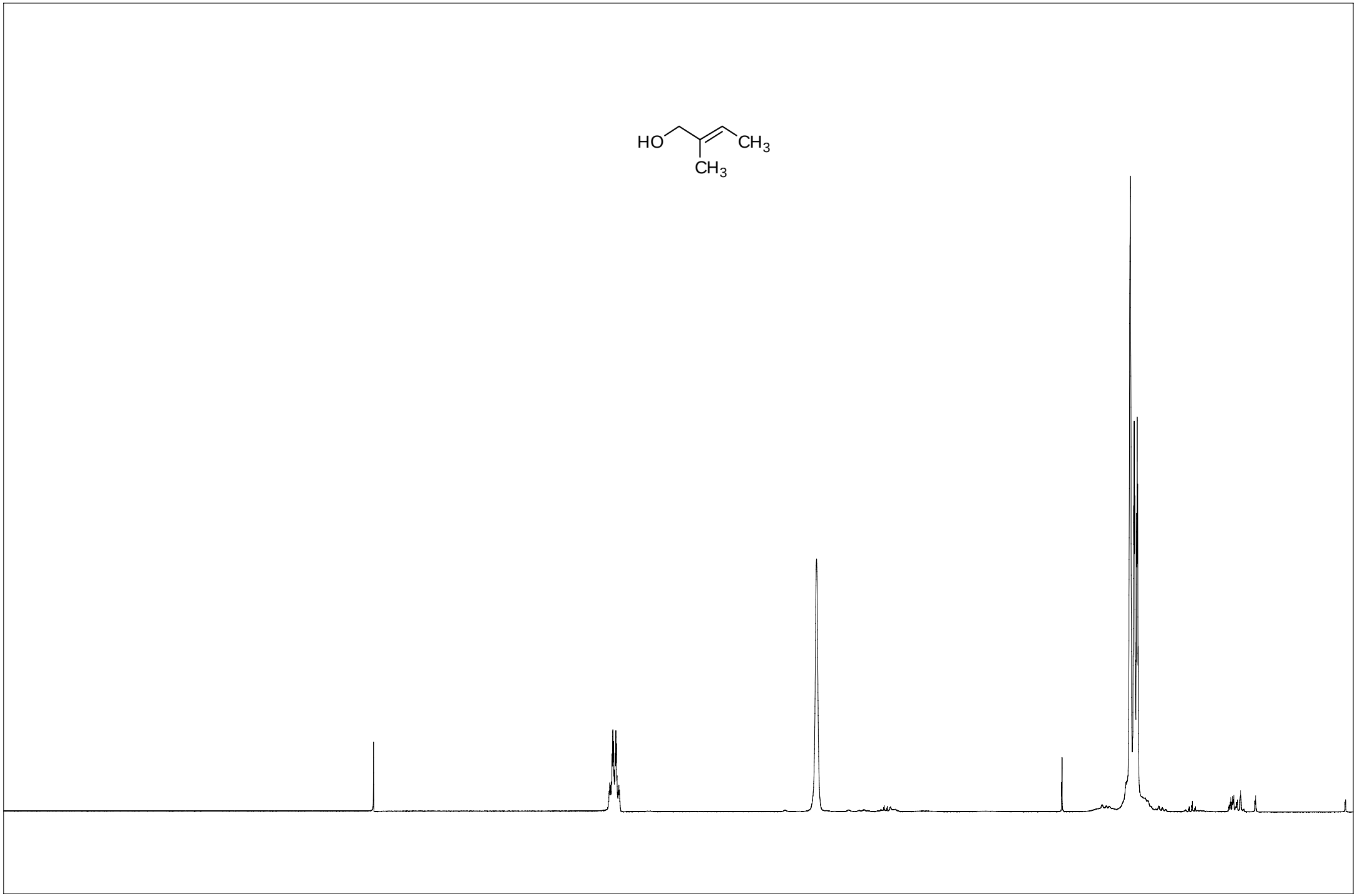
Monoisotopic Mass, Odd and Even Electron Ions
668 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

GADEMANN_BONAZZI_040407_SB 325 3 (0.068) Cm (1:9)
TOF MS ES+ 399.0801 4.23e3



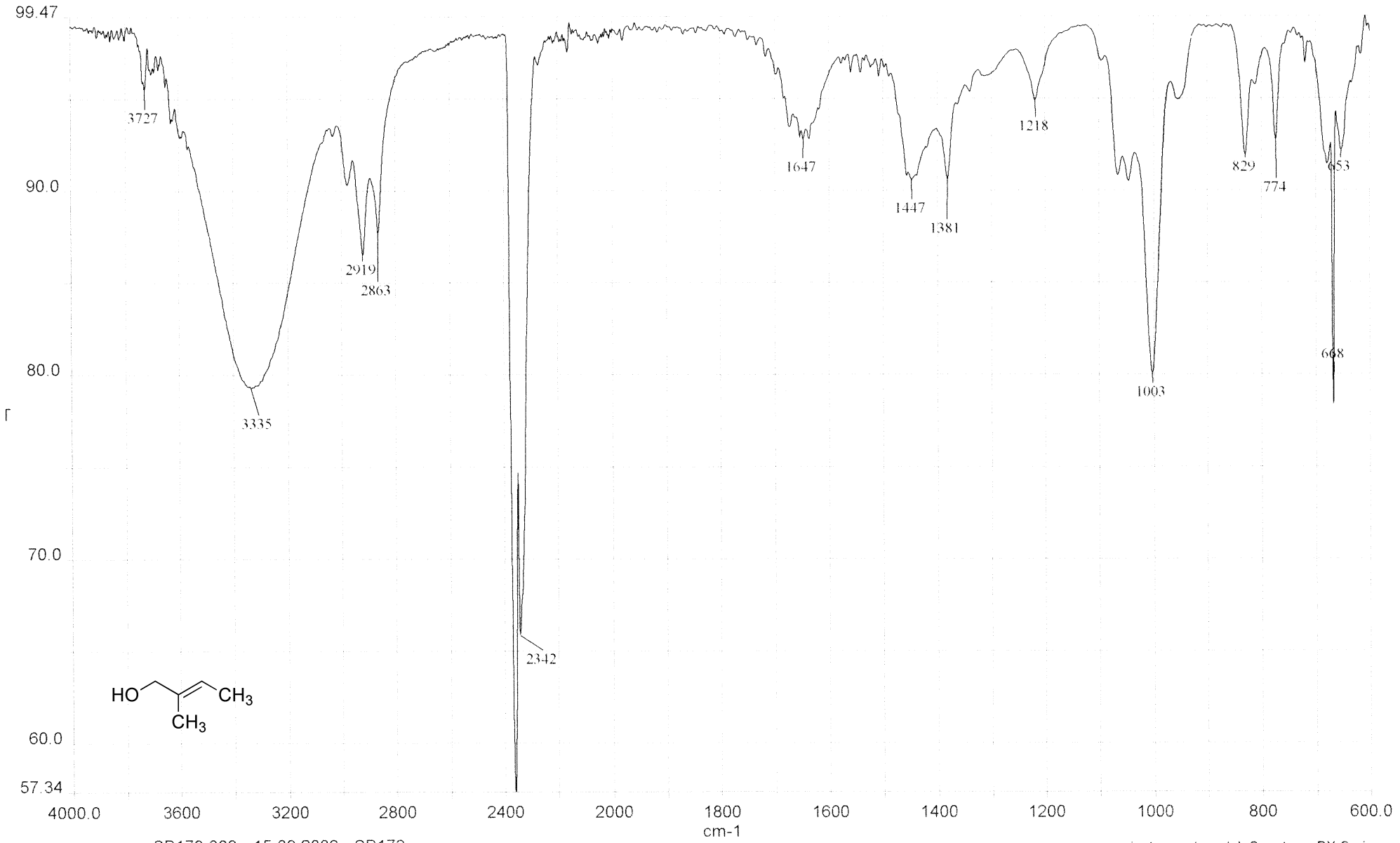
Minimum:				-1.5	
Maximum:		200.0	2.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
399.0801	399.0797	0.4	1.1	3.5	C16 H25 O2 Na I
	399.0806	-0.5	-1.2	-0.5	C9 H23 O15 Si


%Transmittance
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
3322.3
2968.0
2923.7
2360.1
2167.5
2051.8
1982.7
1659.1
1454.0
1377.0
1316.4
1180.4
1099.4
1028.4
1000.2
785.5
629.3
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber
iPrO
O
H
CH3
H3C
I


HO
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

ETHZ

date: 15.09.2006



SB173.003 - 15.09.2006 - SB173

analyst: Student

last transform history: AutoFlat_2 "E:\pel_data\spectra\Student\SB173.sp", 4000, 600, "E:\pel_data\spectra\Student\SB173.~0" 'Student, Fri Sep 15 14:34:10 2006

spectrum pathname: E:\pel_data\spectra\Student\SB173.003

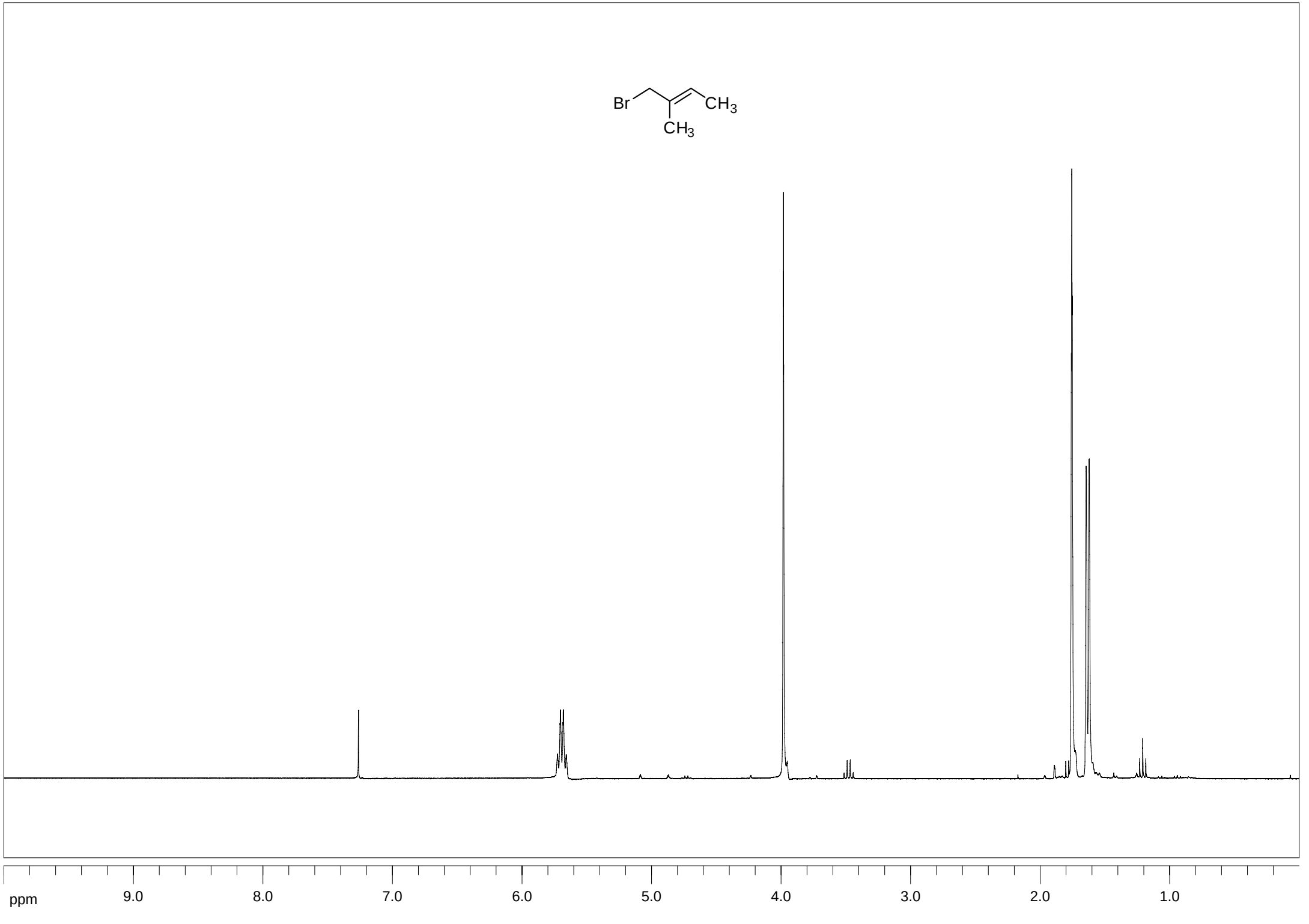
instrument model: Spectrum BX Series

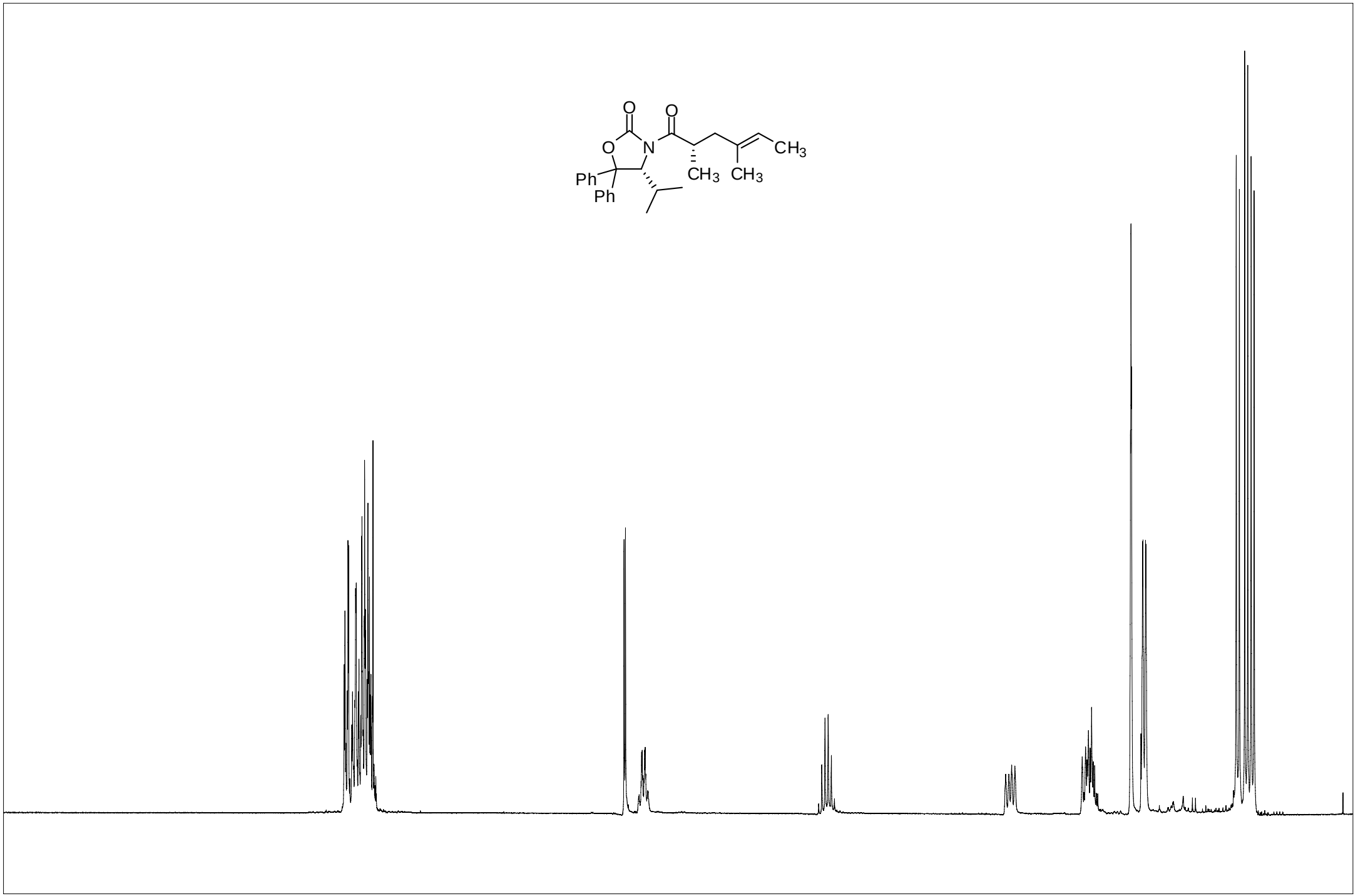
instrument serial number: 67273

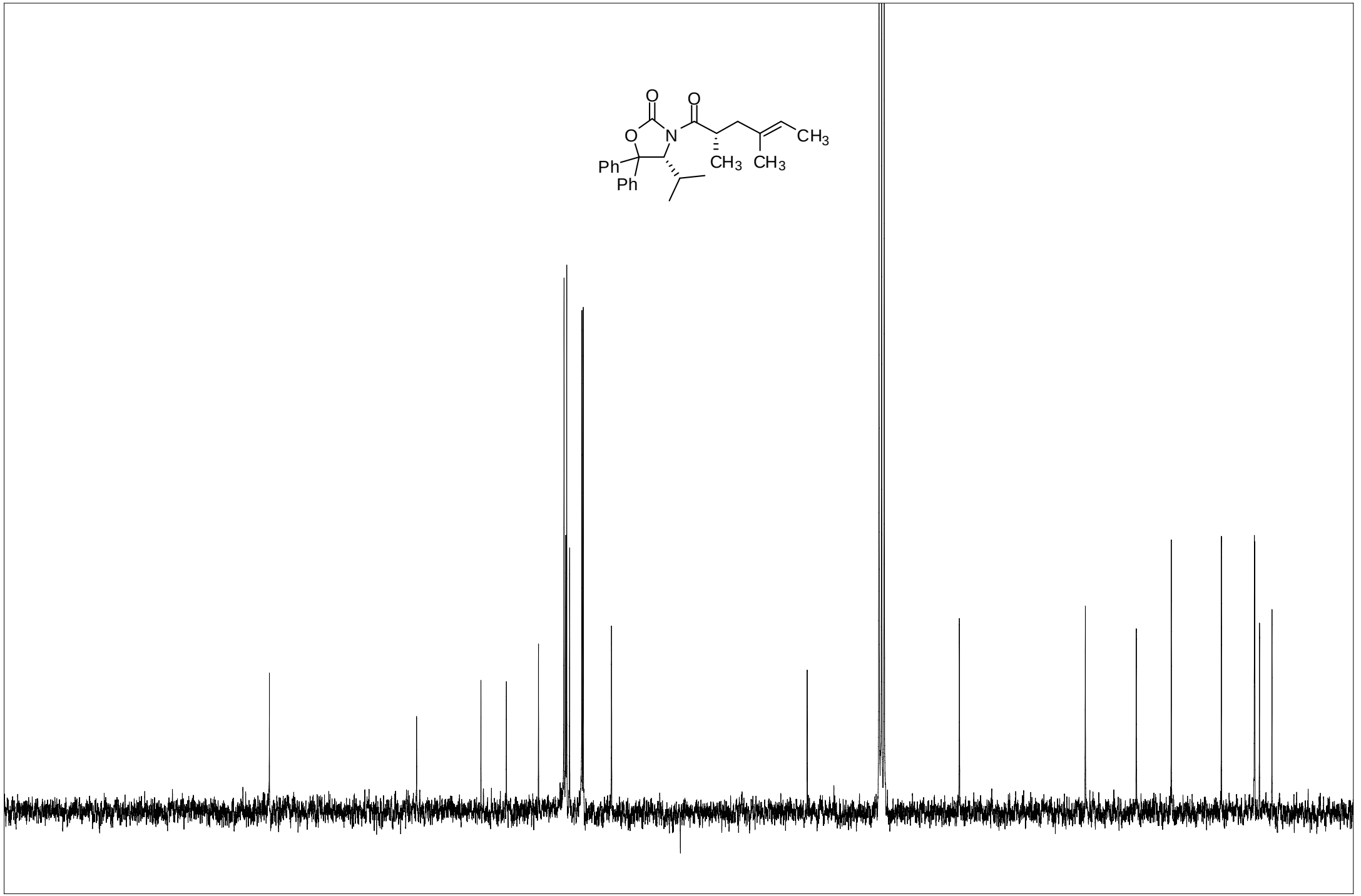
accumulations: 4

resolution: 4 cm-1

apodization: Strong


Br
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


O
O
O
N
CH3
CH3
CH3
Ph
Ph
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

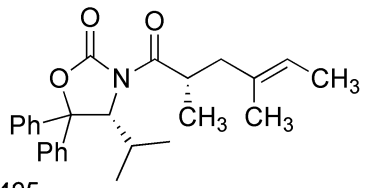

O
O
O
N
CH3
CH3
CH3
Ph
Ph
ppm
200
150
100
50

S. Bonazzi/Carreira

08-Jun-2006
13:26:36

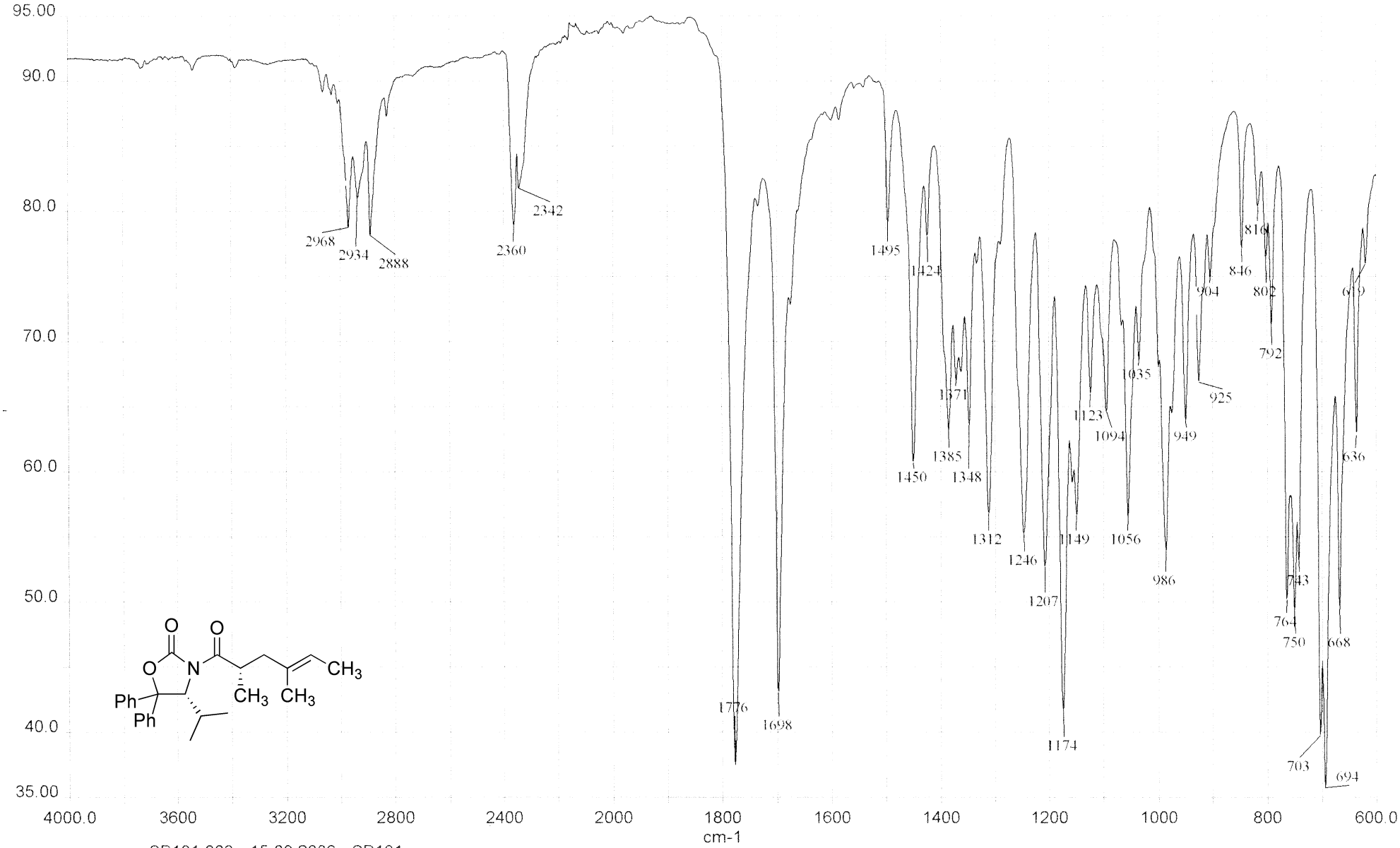
EI2924 23 (2.502) Cm (19:23-37:45)

Magnet EI+
1.44e4



ETHZ

date: 15.08.2006



SB181.003 - 15.08.2006 - SB181

analyst: Student

last transform history: AutoSmooth "E:\pel_data\spectra\Student\SB181.sp", 4000, 600, "E:\pel_data\spectra\Student\SB181.~0" 'Student, Tue Aug 15 17:56:17 2006

spectrum pathname: E:\pel_data\spectra\Student\SB181.003

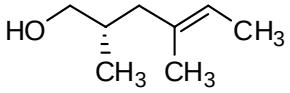
instrument model: Spectrum BX Series

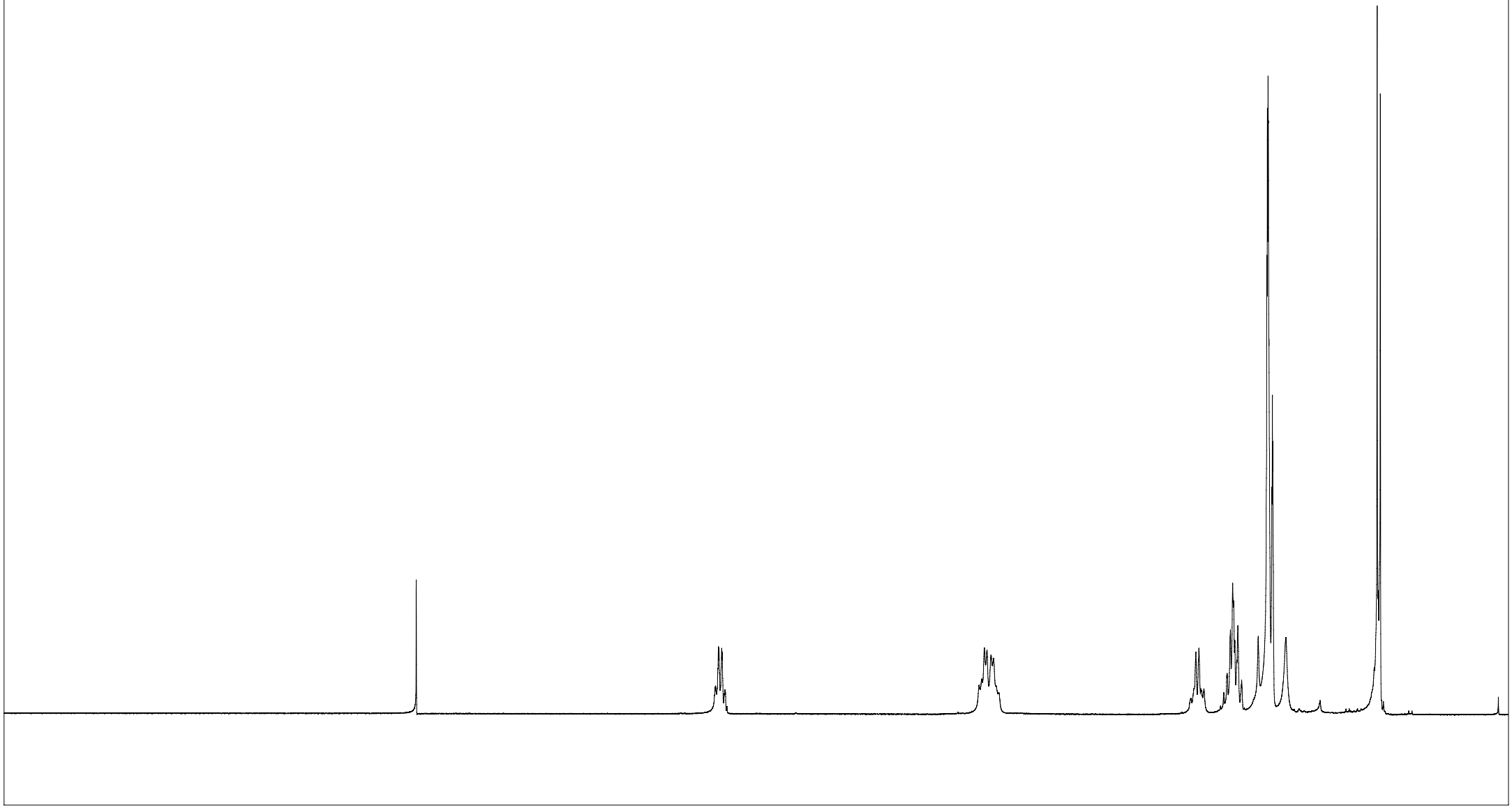
instrument serial number: 67273

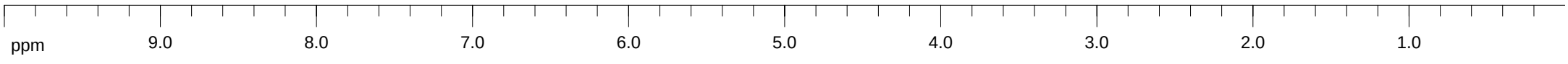
accumulations: 4

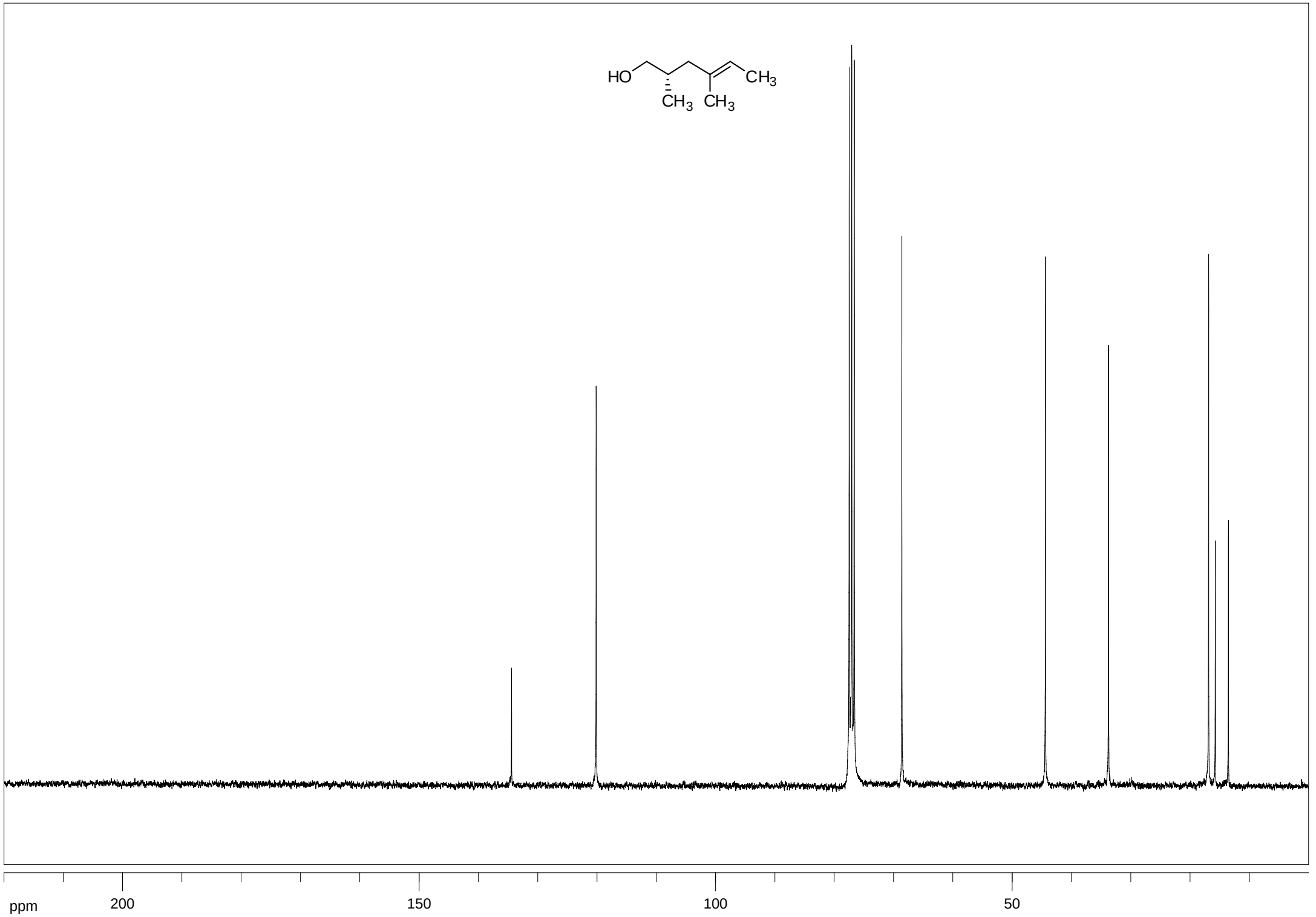
resolution: 4 cm-1

apodization: Strong


HO
CH3
CH3
CH3

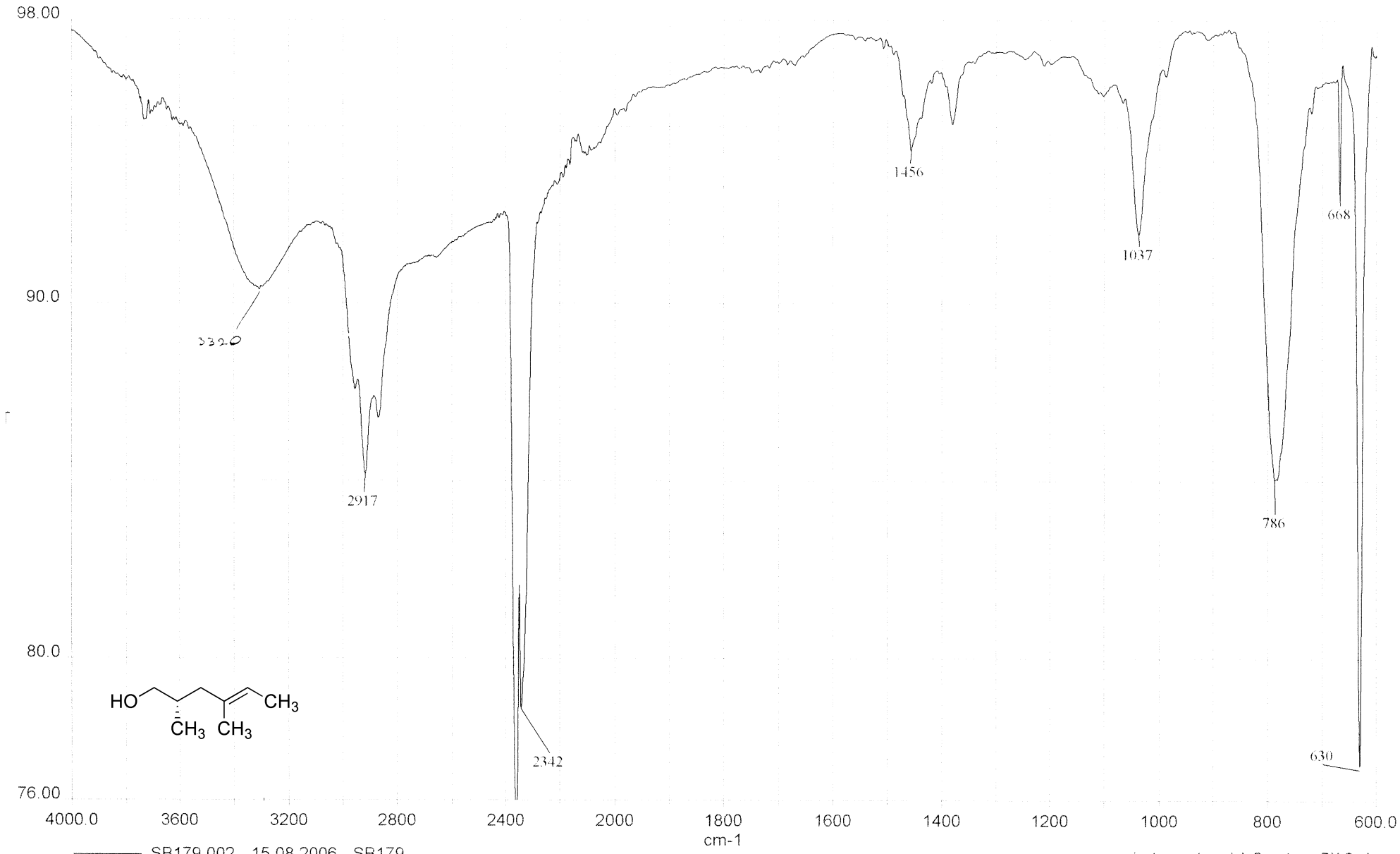



ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


HO
CH3
CH3
CH3
ppm
200
150
100
50

ETHZ

date: 15.08.2006



SB179.002 - 15.08.2006 - SB179

analyst: Student

last transform history: AutoSmooth "E:\pel_data\spectra\Student\SB179.001", 4000, 600, "E:\pel_data\spectra\Student\SB179.~0" 'Student, Tue Aug 15 17:53:36 2006

spectrum pathname: E:\pel_data\spectra\Student\SB179.002

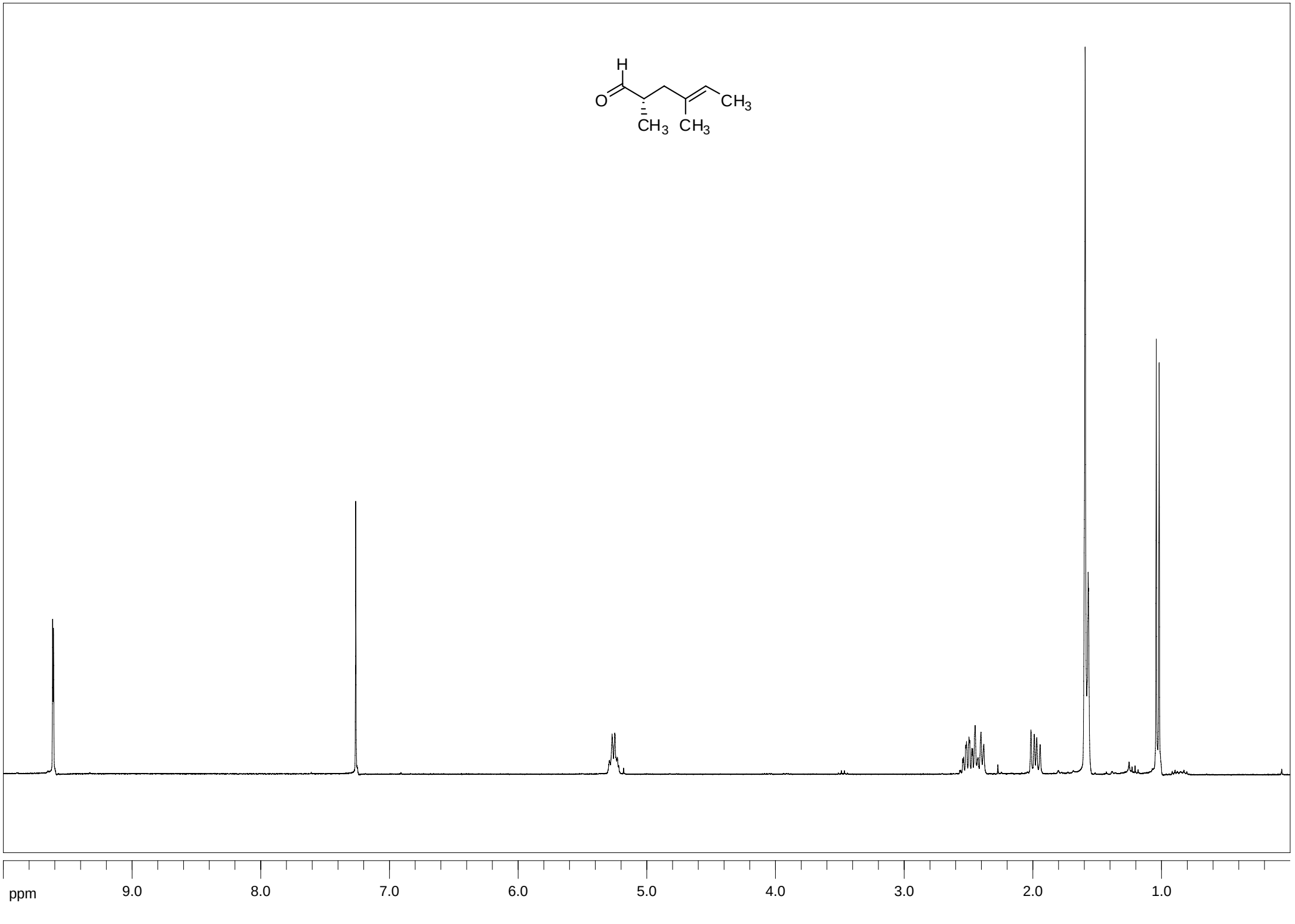
instrument model: Spectrum BX Series

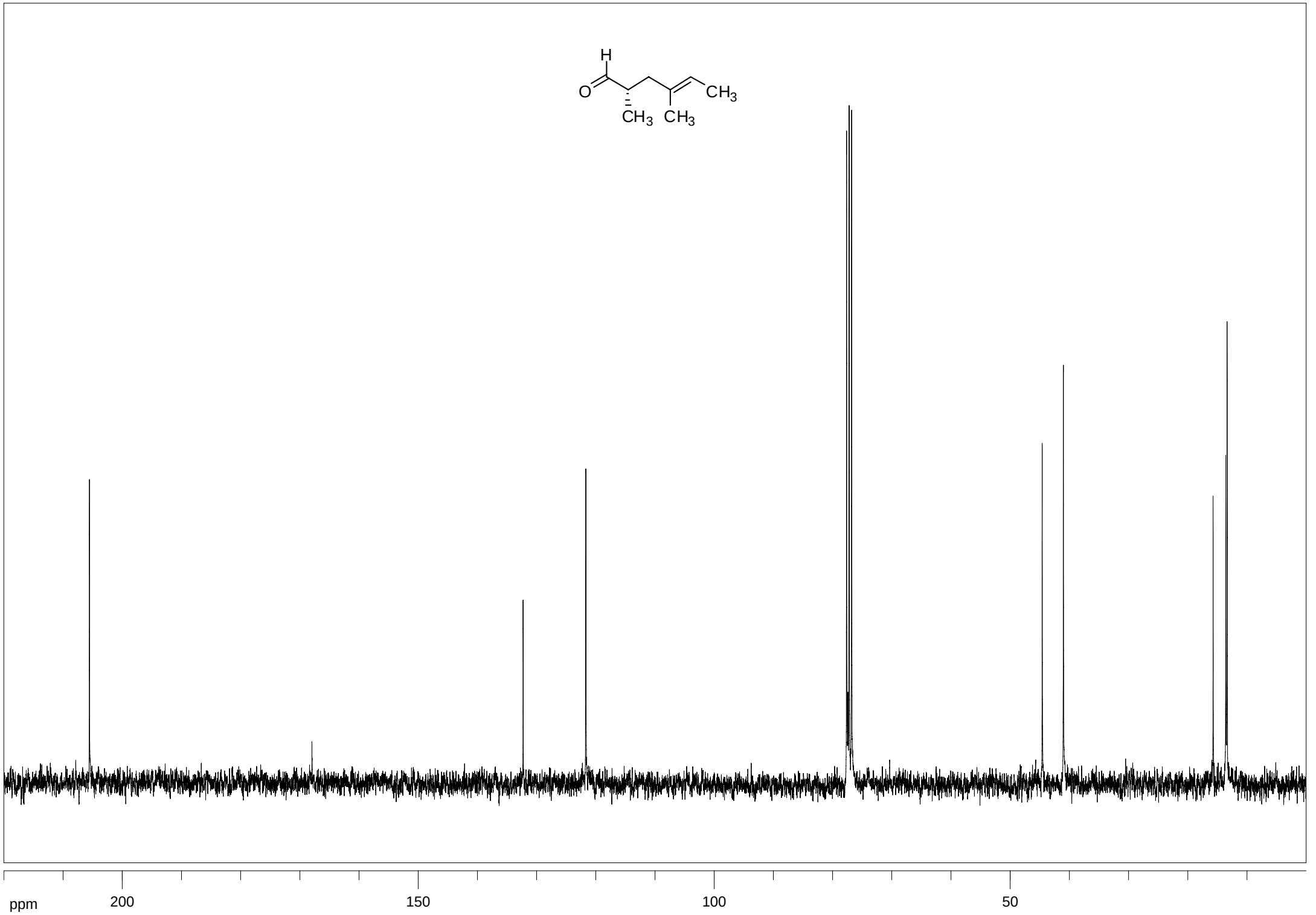
instrument serial number: 67273

accumulations: 4

resolution: 4 cm-1

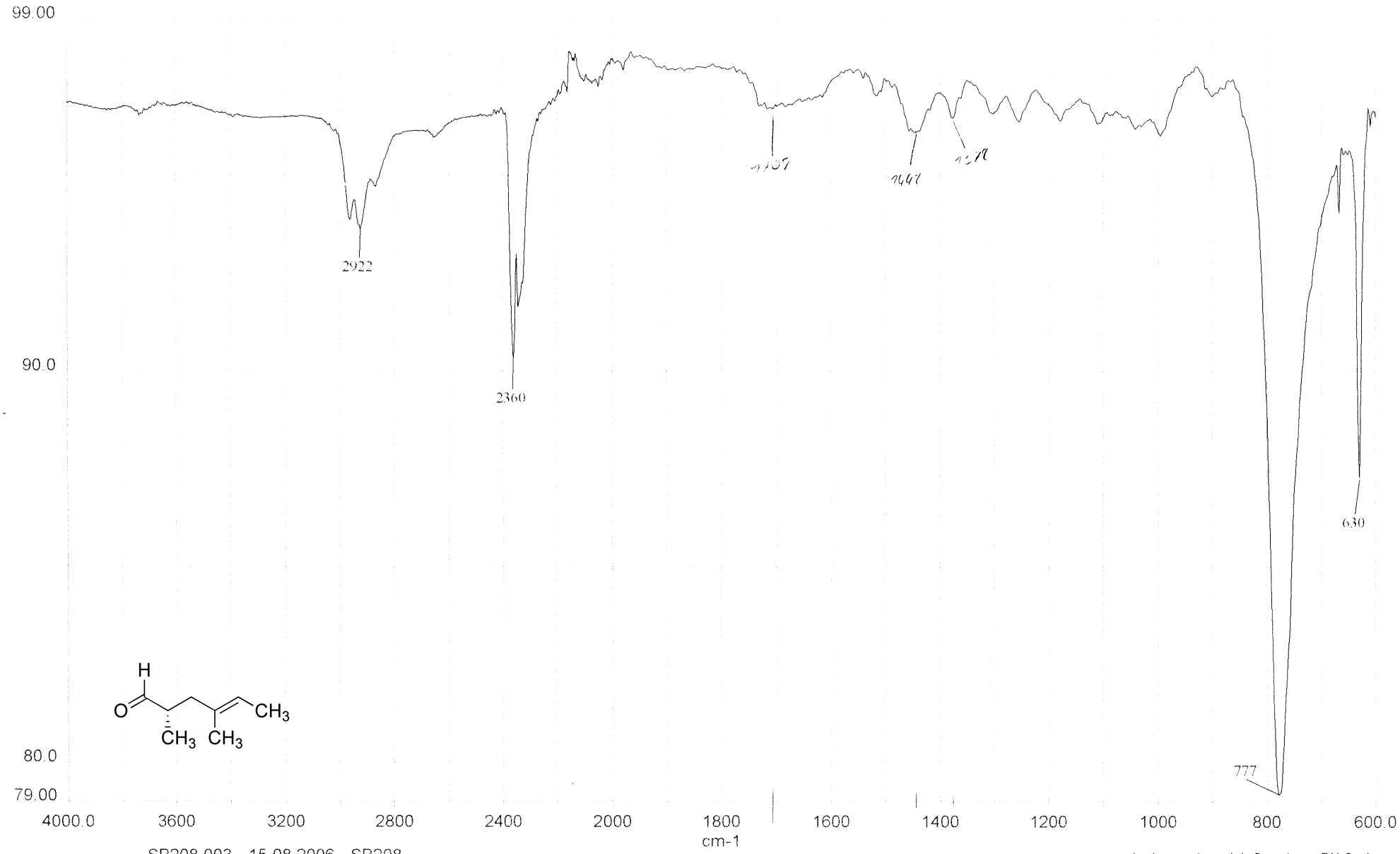
apodization: Strong


H
O
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


H
O
CH3
CH3
CH3
ppm
200
150
100
50

ETHZ

date: 15.08.2006



SB208.003 - 15.08.2006 - SB208

analyst: Student

last transform history: AutoSmooth "E:\pel_data\spectra\Student\SB208.sp", 4000, 600, "E:\pel_data\spectra\Student\SB208.~0" 'Student, Tue Aug 15 17:48:40 2006

spectrum pathname: E:\pel_data\spectra\Student\SB208.003

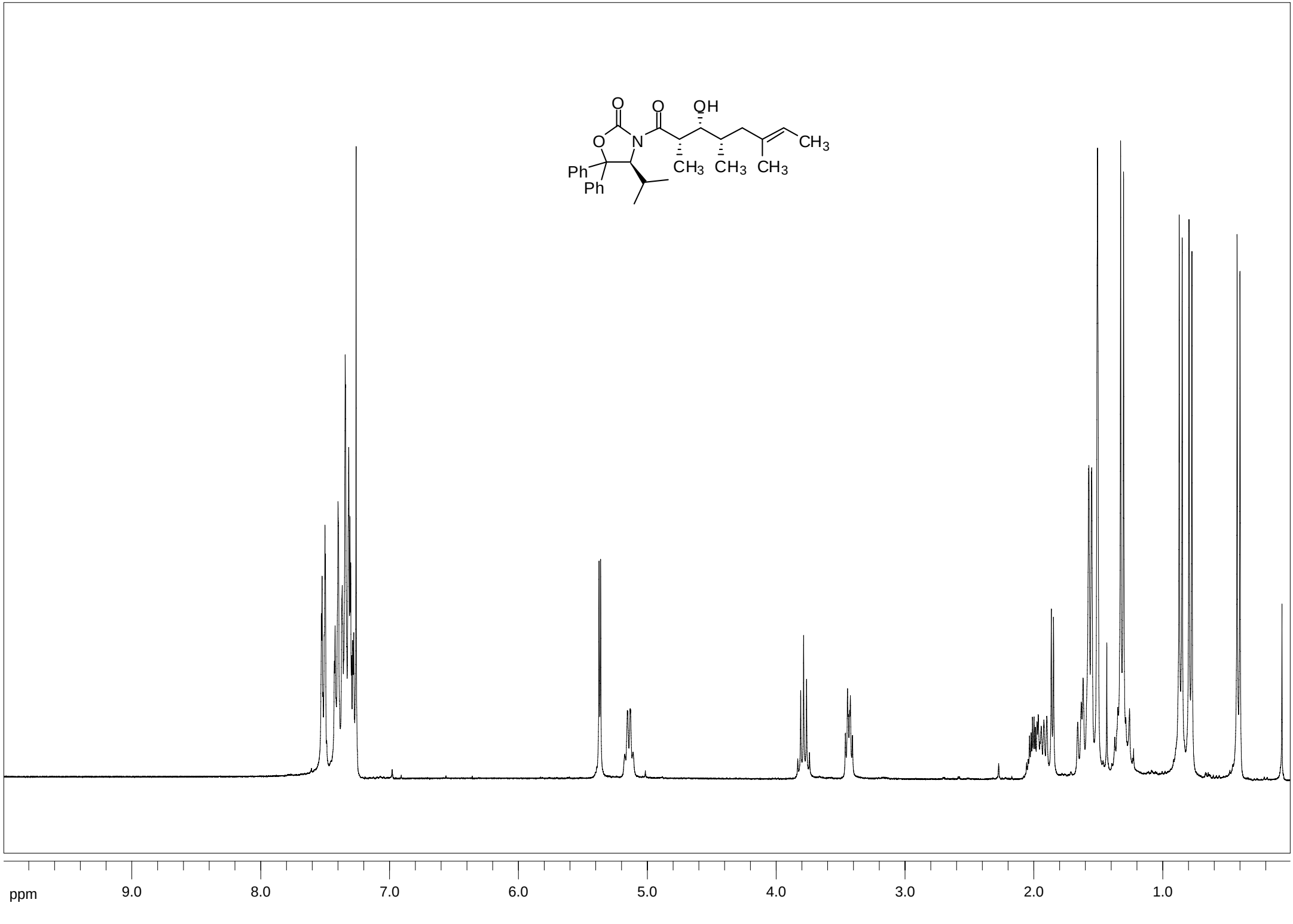
instrument model: Spectrum BX Series

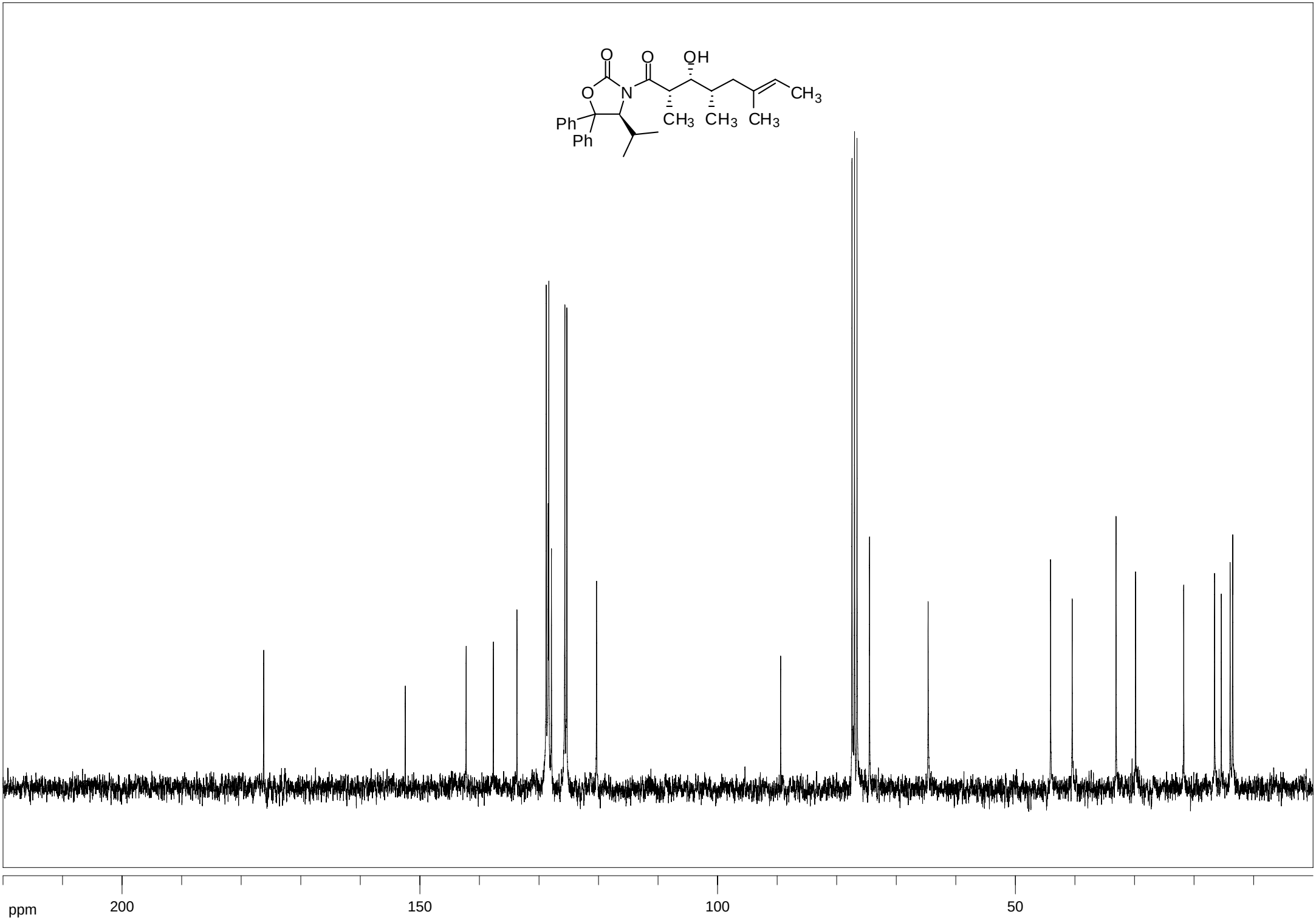
instrument serial number: 67273

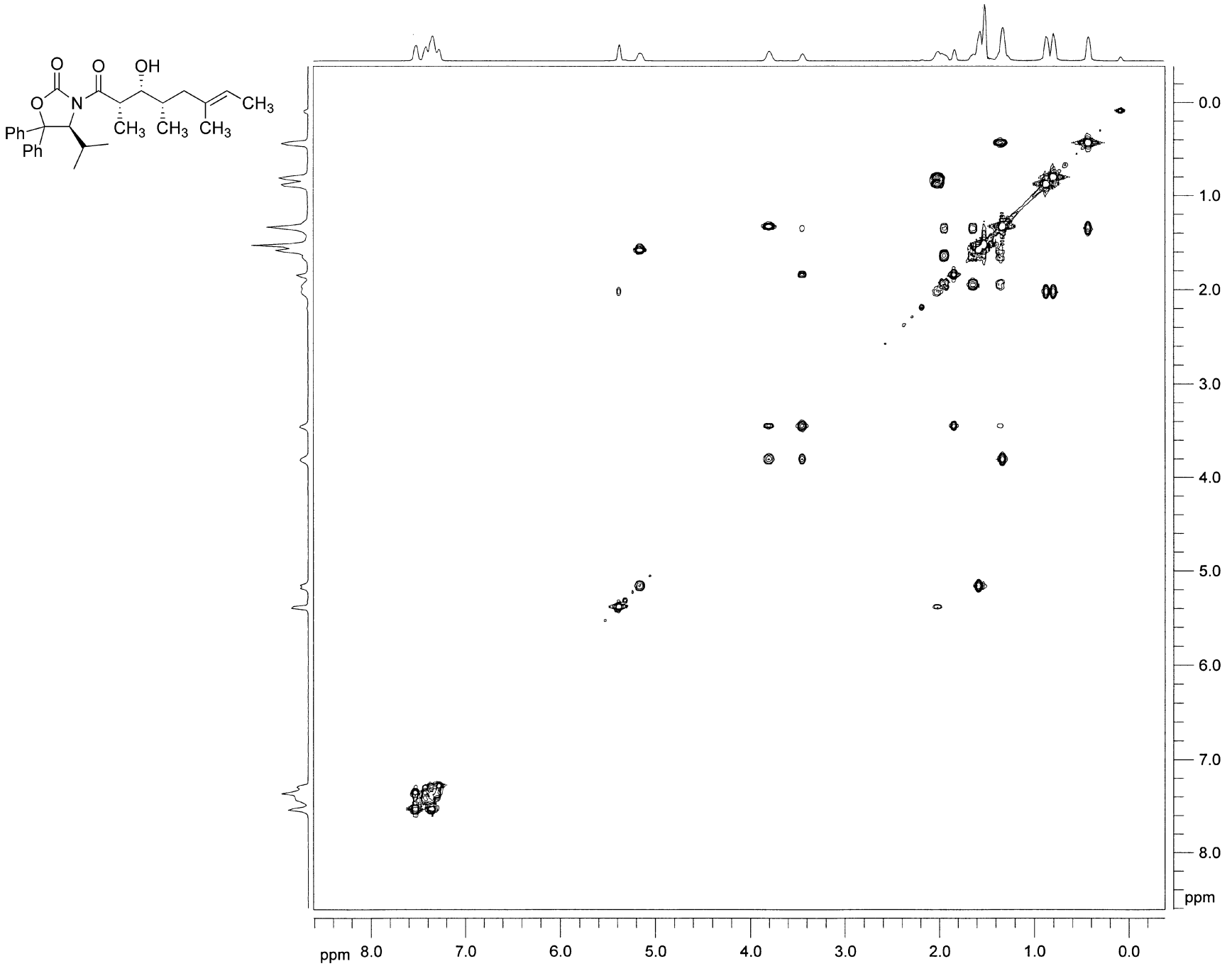
accumulations: 4

resolution: 4 cm-1

apodization: Strong


O
O
OH
O
N
CH3
CH3
CH3
CH3
Ph
Ph
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


O
O
OH
O
N
CH3
CH3
CH3
CH3
Ph
Ph
ppm
200
150
100
50

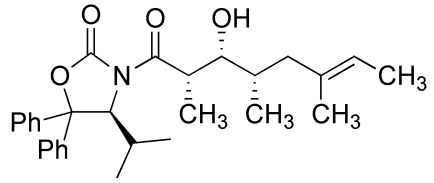

O
O
OH
O
N
CH3
CH3
CH3
CH3
Ph
Ph
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm
ppm
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

S. Bonazzi/Carreira

27-Jul-2006
14:44:37

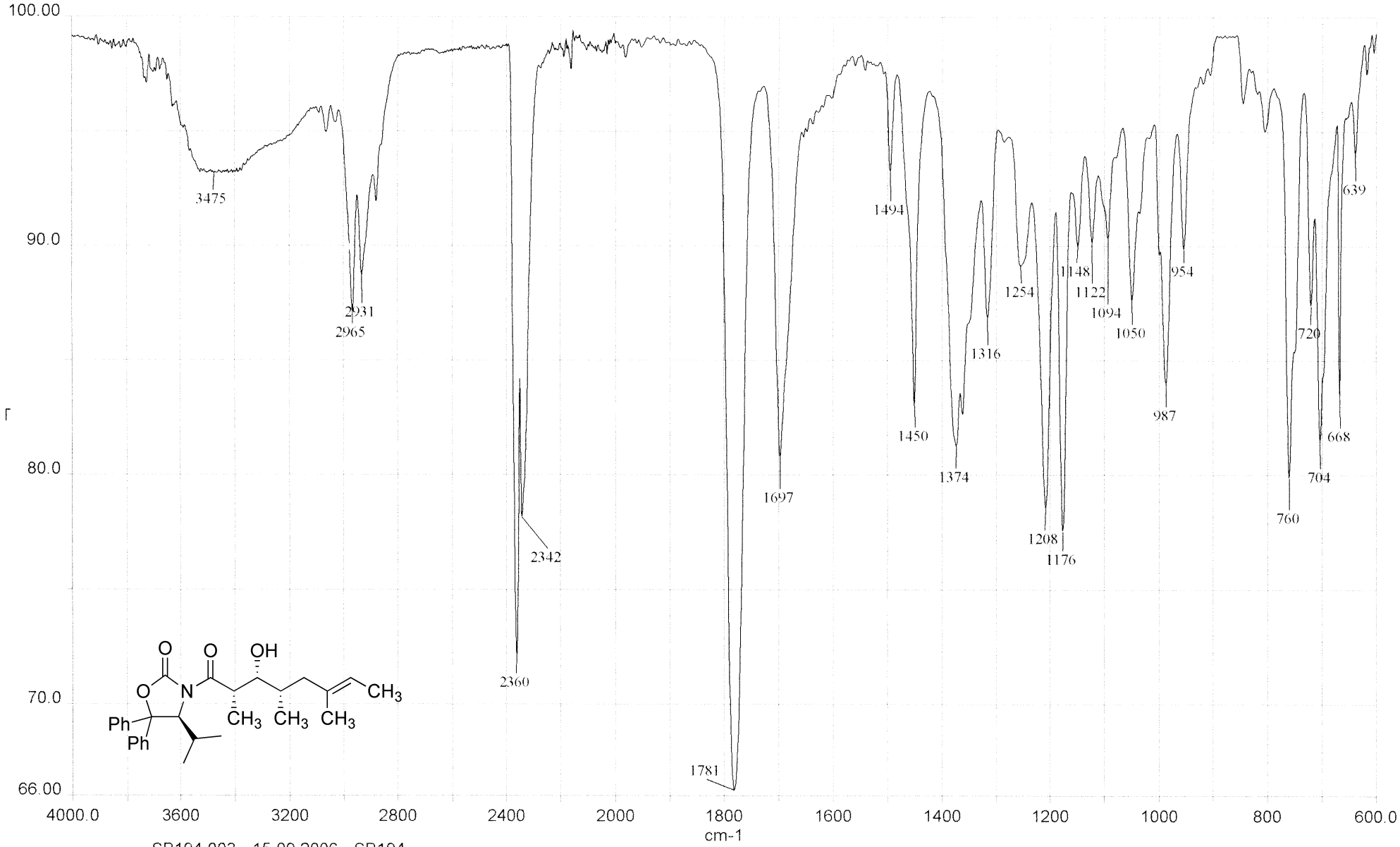
EI3149 35 (3.918) Cm (32:36-46:49)

Magnet EI+
2.02e3



ETHZ

date: 15.09.2006



SB194.003 - 15.09.2006 - SB194

analyst: Student

last transform history: AutoFlat_2 "E:\pel_data\spectra\Student\SB194.sp", 4000, 600, "E:\pel_data\spectra\Student\SB194.~0" 'Student, Fri Sep 15 14:30:48 2006

spectrum pathname: E:\pel_data\spectra\Student\SB194.003

instrument model: Spectrum BX Series

instrument serial number: 67273

accumulations: 4

resolution: 4 cm-1

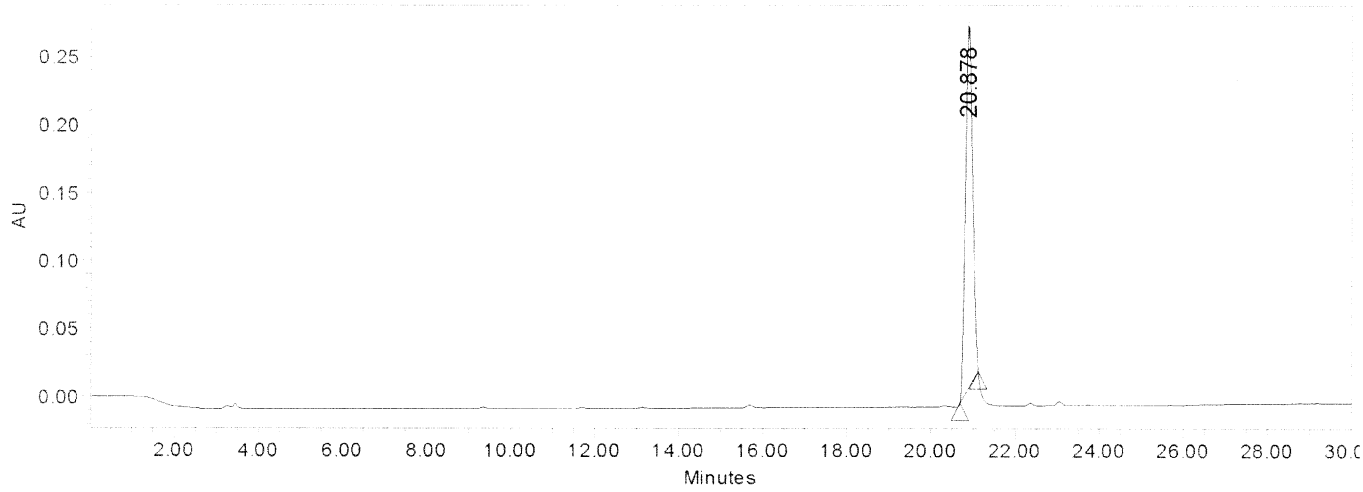
apodization: Strong

HPLC Sonia
Colonne C18

SampleName jb-test simone

Date Acquired 08.11.2006 09:52:00

Auto-Scaled Chromatogram



Processed Channel: 254 nm

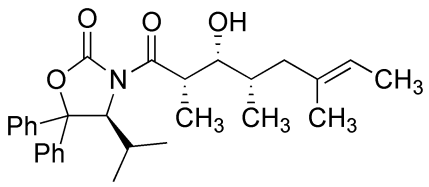
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	254 nm	20.878	3175641	100.00	268688

Instrument Method: SDS_50_100_30_RT

Stored: 06.06.2006 13:56:24

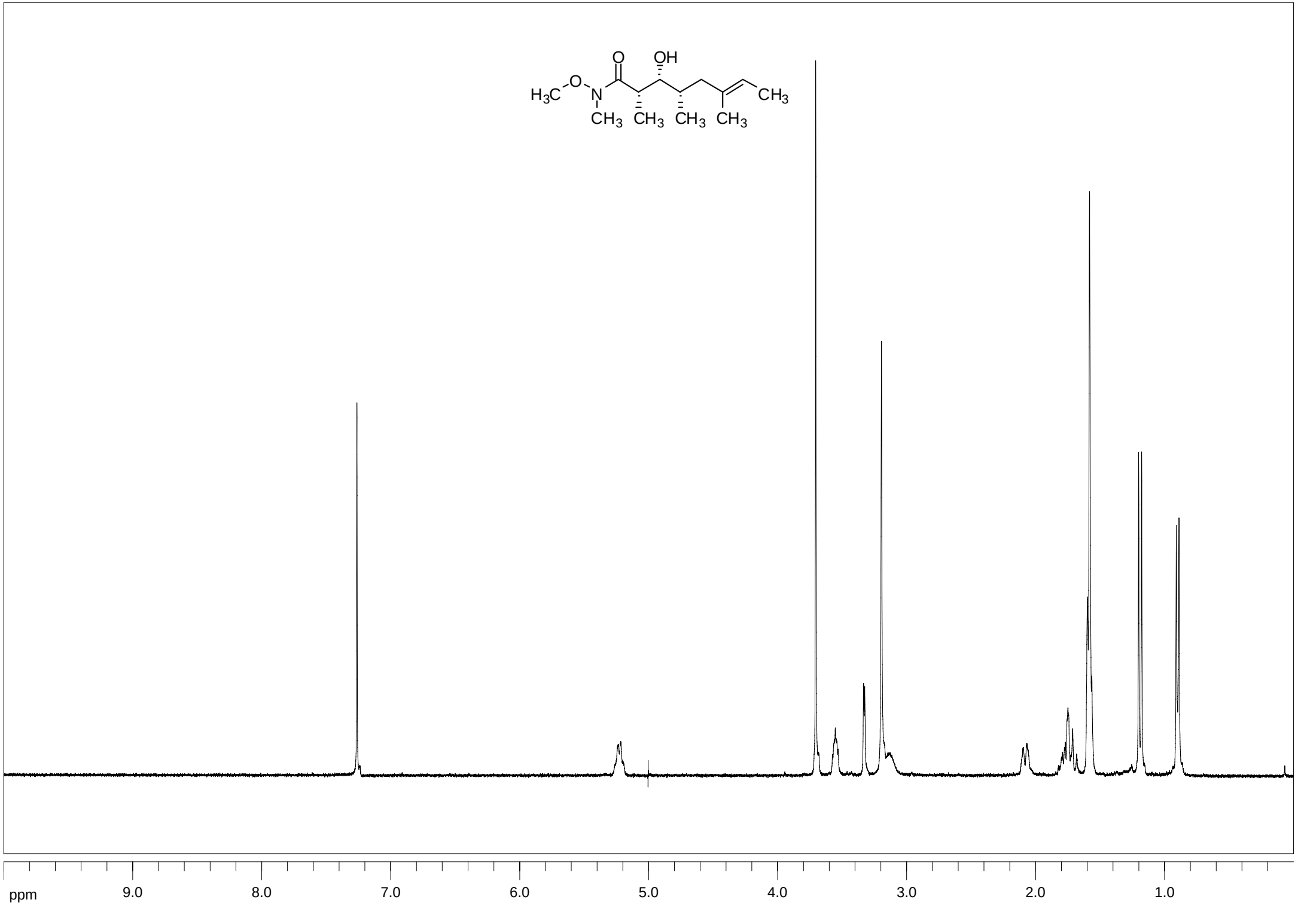
Method Information

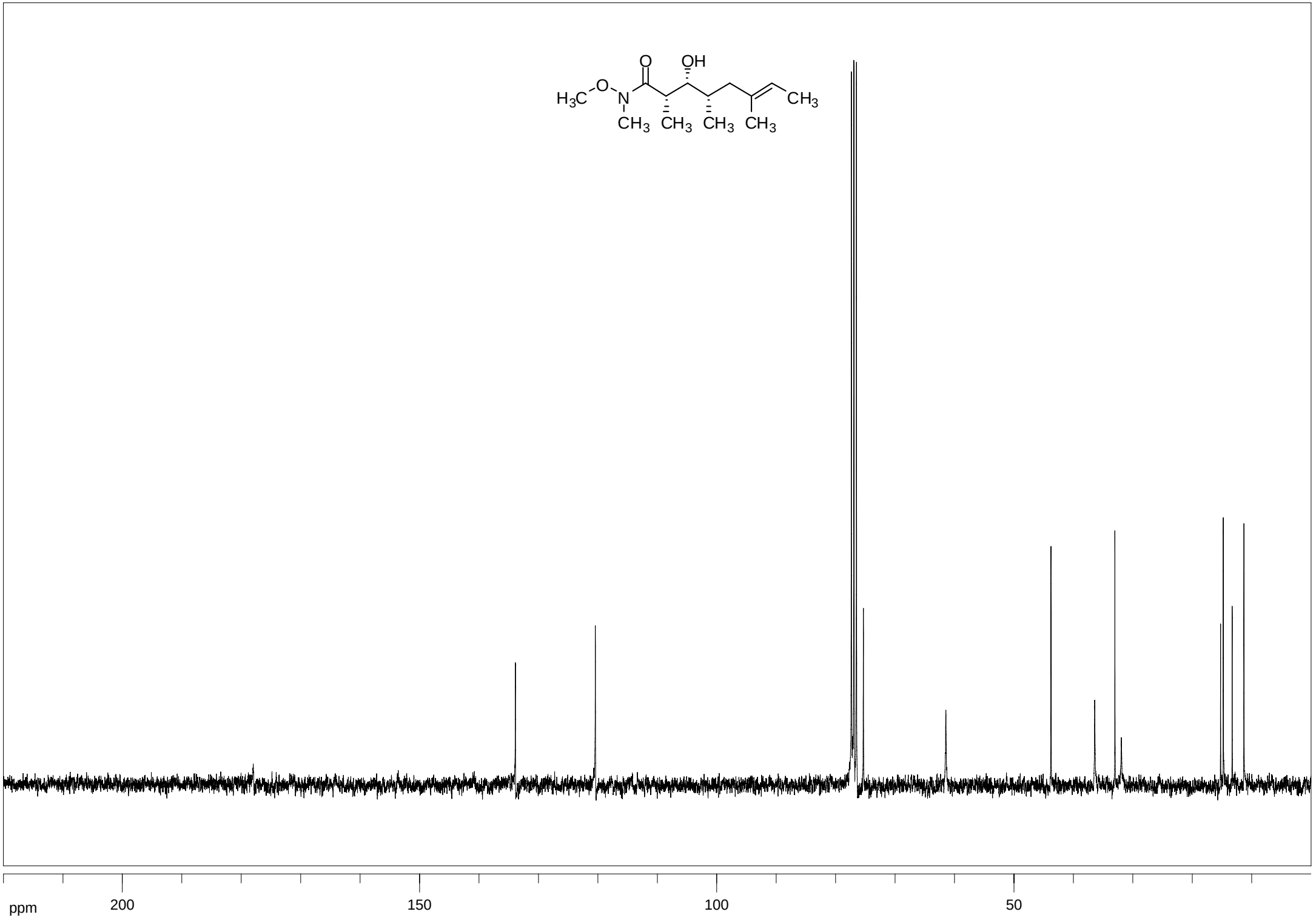
Comments	de 50 à 100% ACN en 30 min a RT
Modified User	System
Locked	No
Method Id	1666
Method Version	2
Edit User	



Revision History

This method contains 3 items in the revision history.


O
OH
H3C
O
N
CH3
CH3
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


O
OH
H3C
O
N
CH3
CH3
CH3
CH3
CH3
ppm
200
150
100
50

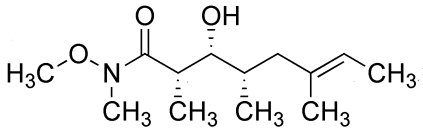
SPEC: esi5831_1.dat (17-AUG-06 09:41:12)
Samp: Bonazzi/Carreira
Comm: LM: CH3OH
Oper: L.B.
Base: 266.16
Peak: 1000.0 mmu

Study: Identify Project
Masses: 10.00 > 999.98
Intensity: 4125750

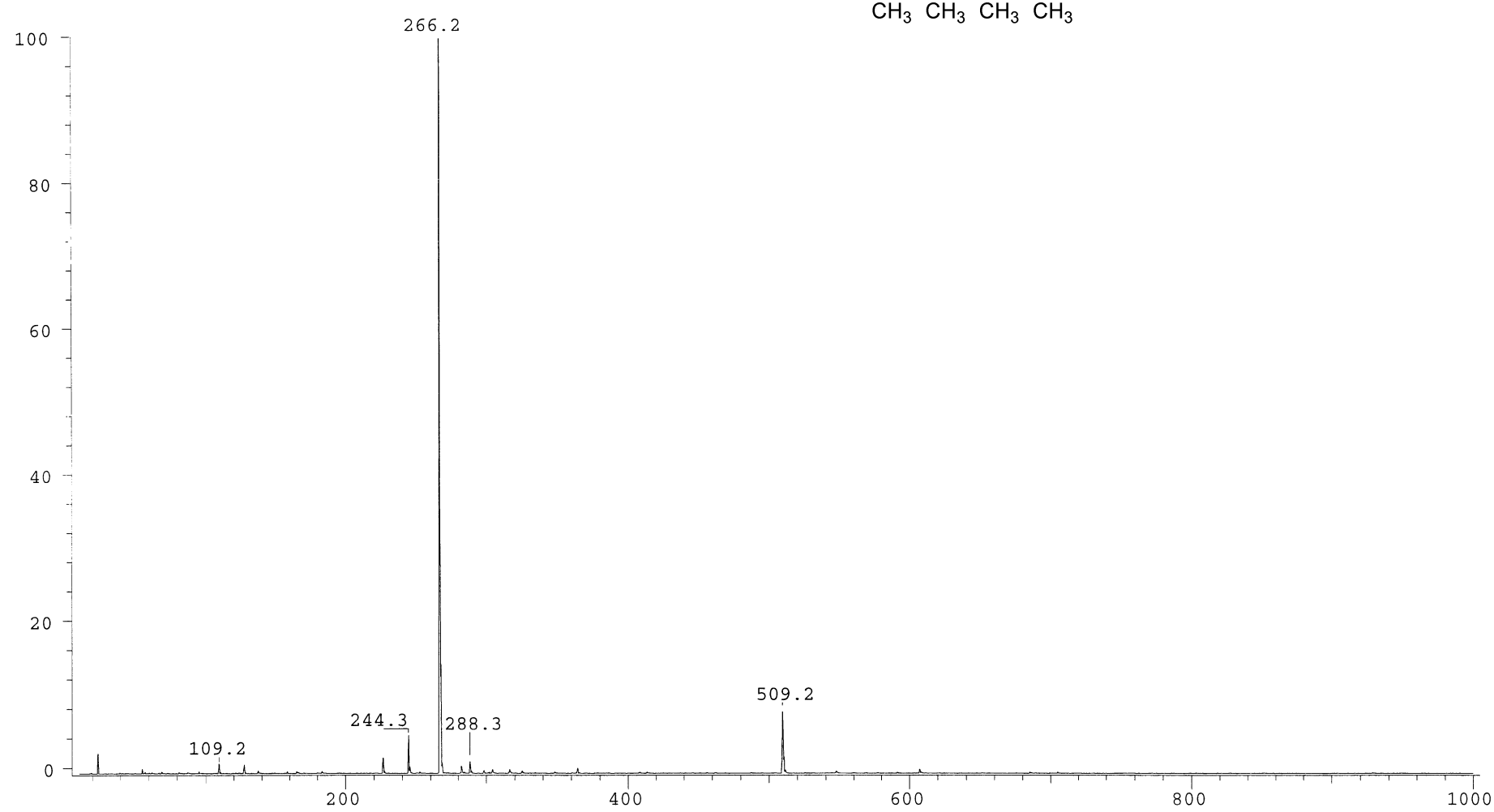
Scans: 1 > 3

Client: Identify Customers
#Peaks: 9901
RIC: 4451376

Scan 1 @ 0.06 min (ESI +Q1MS APICID LMR AVER UP PROF)



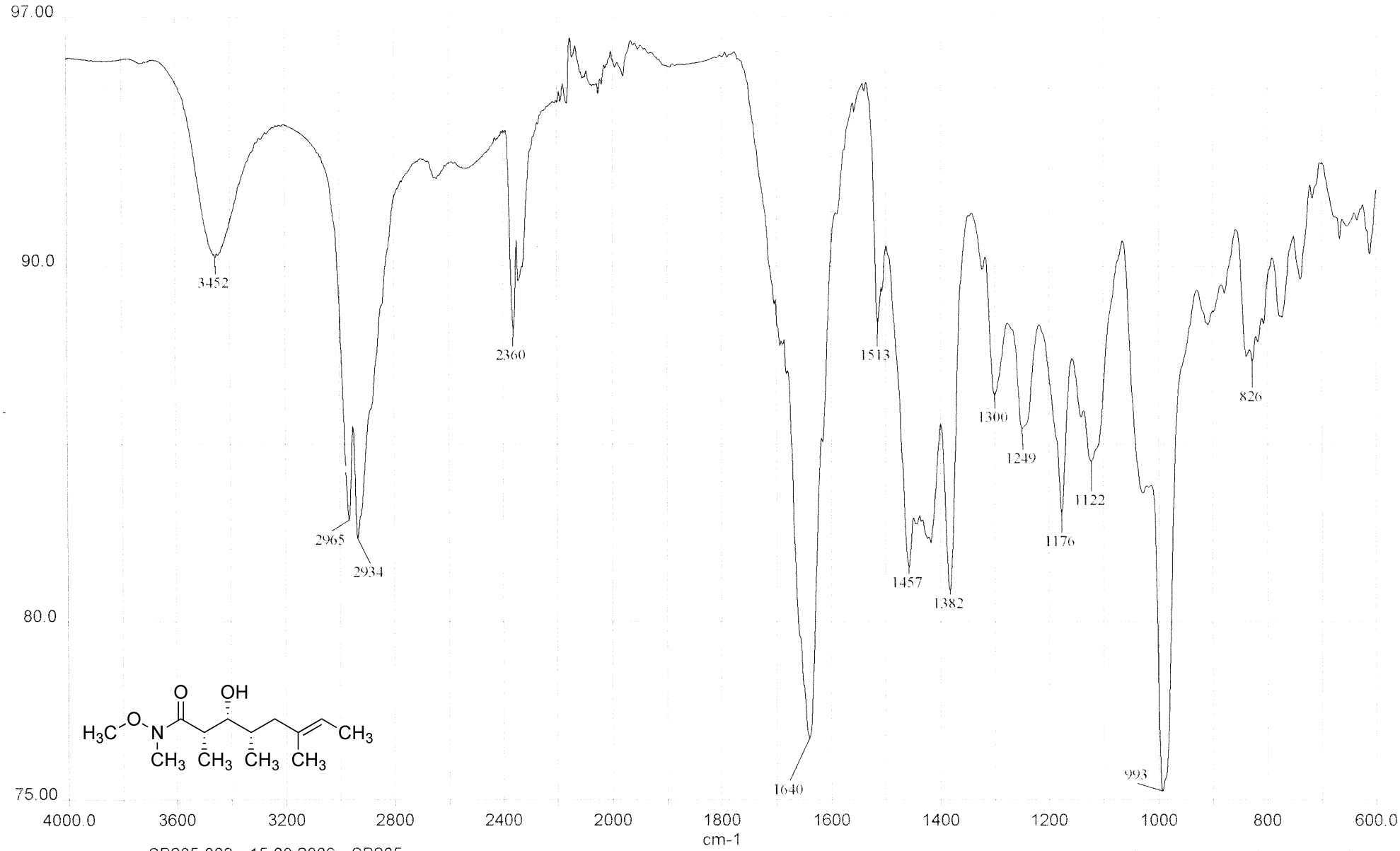
4.1E+06



Date: Thu Aug 17 10:46:45 2006 ICIS: 8.3.0 SP2 for OSF1 (V4.0) build 98-238 from 26-Aug-98

ETHZ

date: 15.08.2006



SB205.003 - 15.08.2006 - SB205

analyst: Student

last transform history: AutoSmooth "E:\pel_data\spectra\Student\SB205.sp", 4000, 600, "E:\pel_data\spectra\Student\SB205.~0" 'Student, Tue Aug 15 17:45:53 2006

spectrum pathname: E:\pel_data\spectra\Student\SB205.003

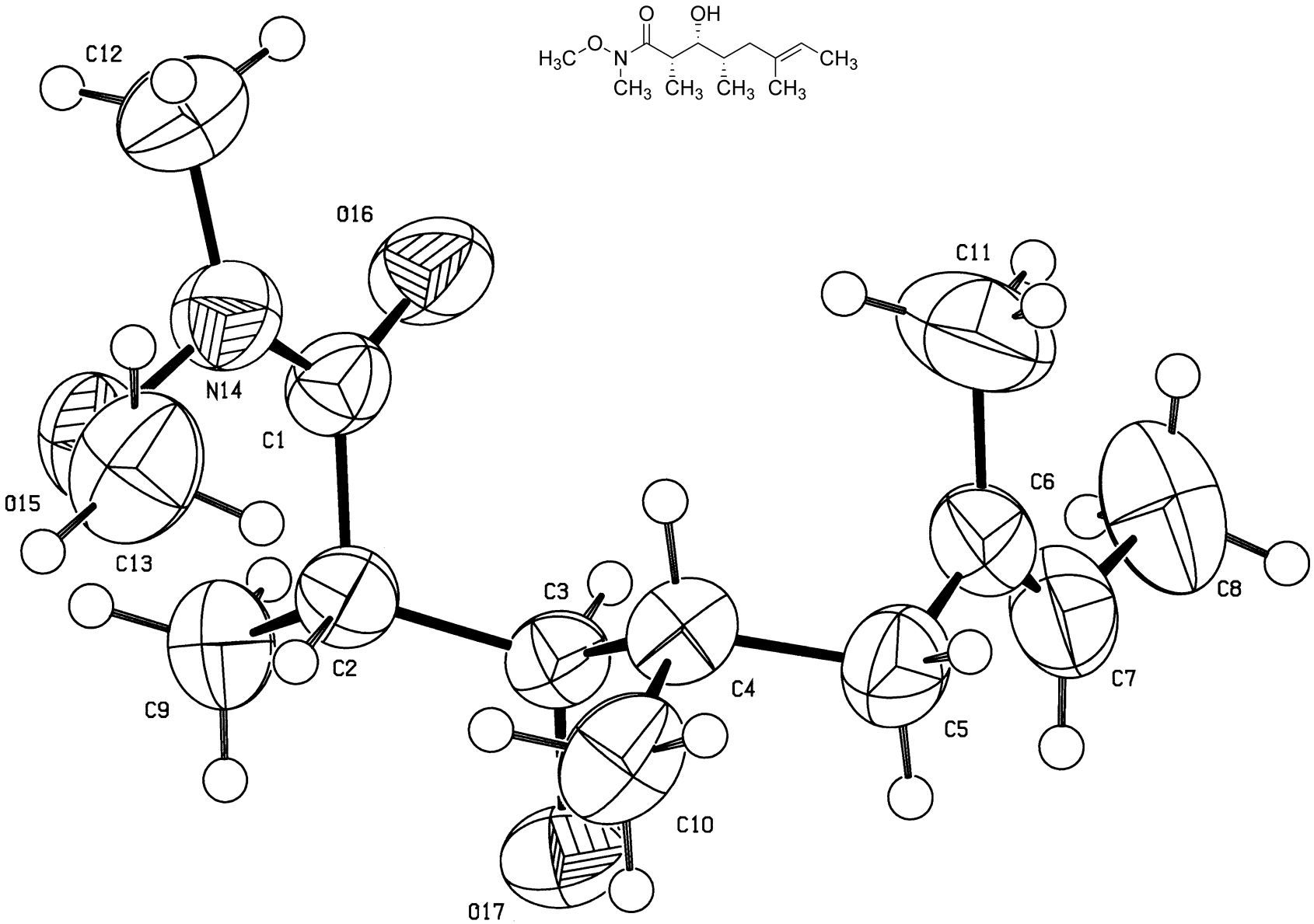
instrument model: Spectrum BX Series

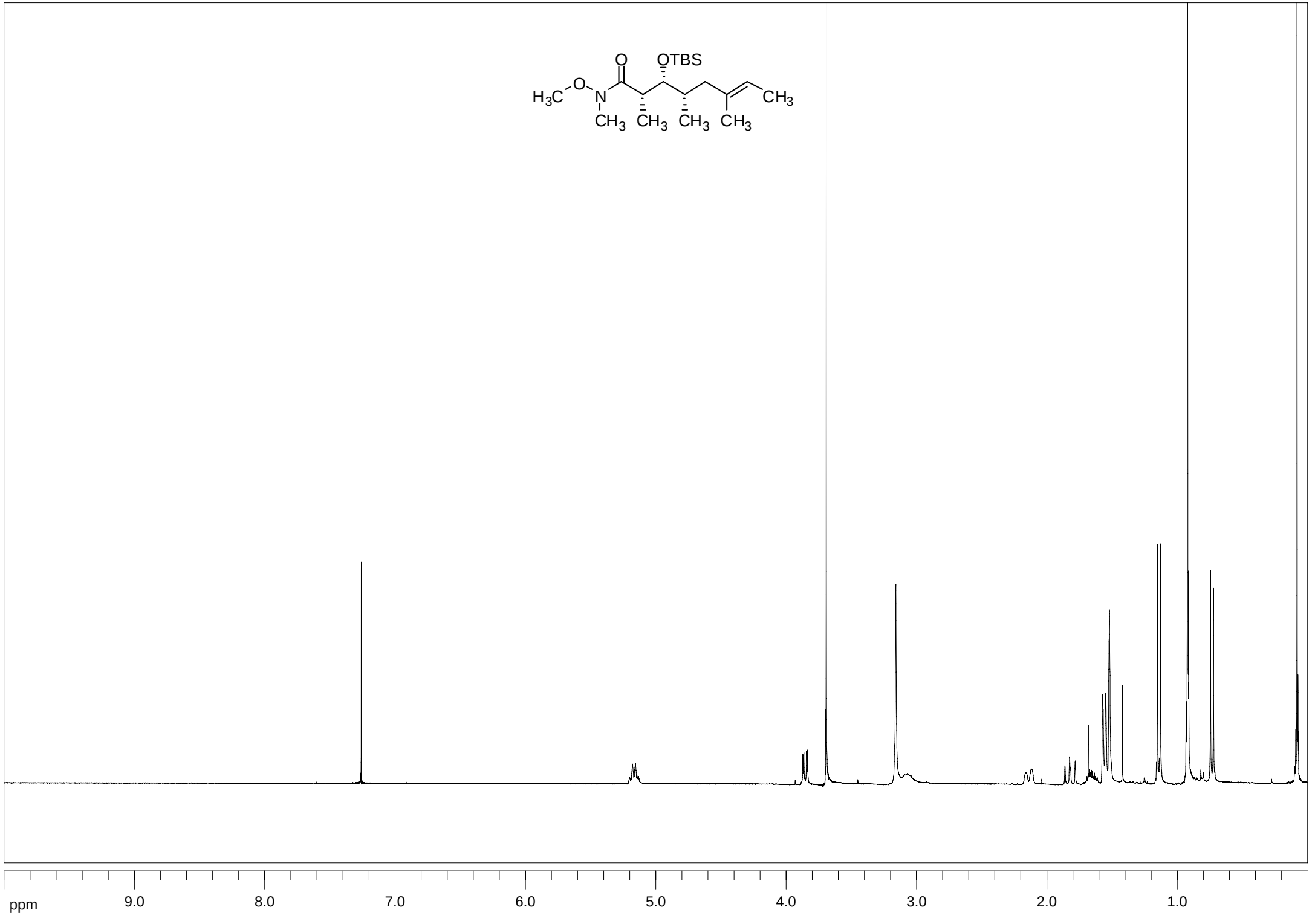
instrument serial number: 67273

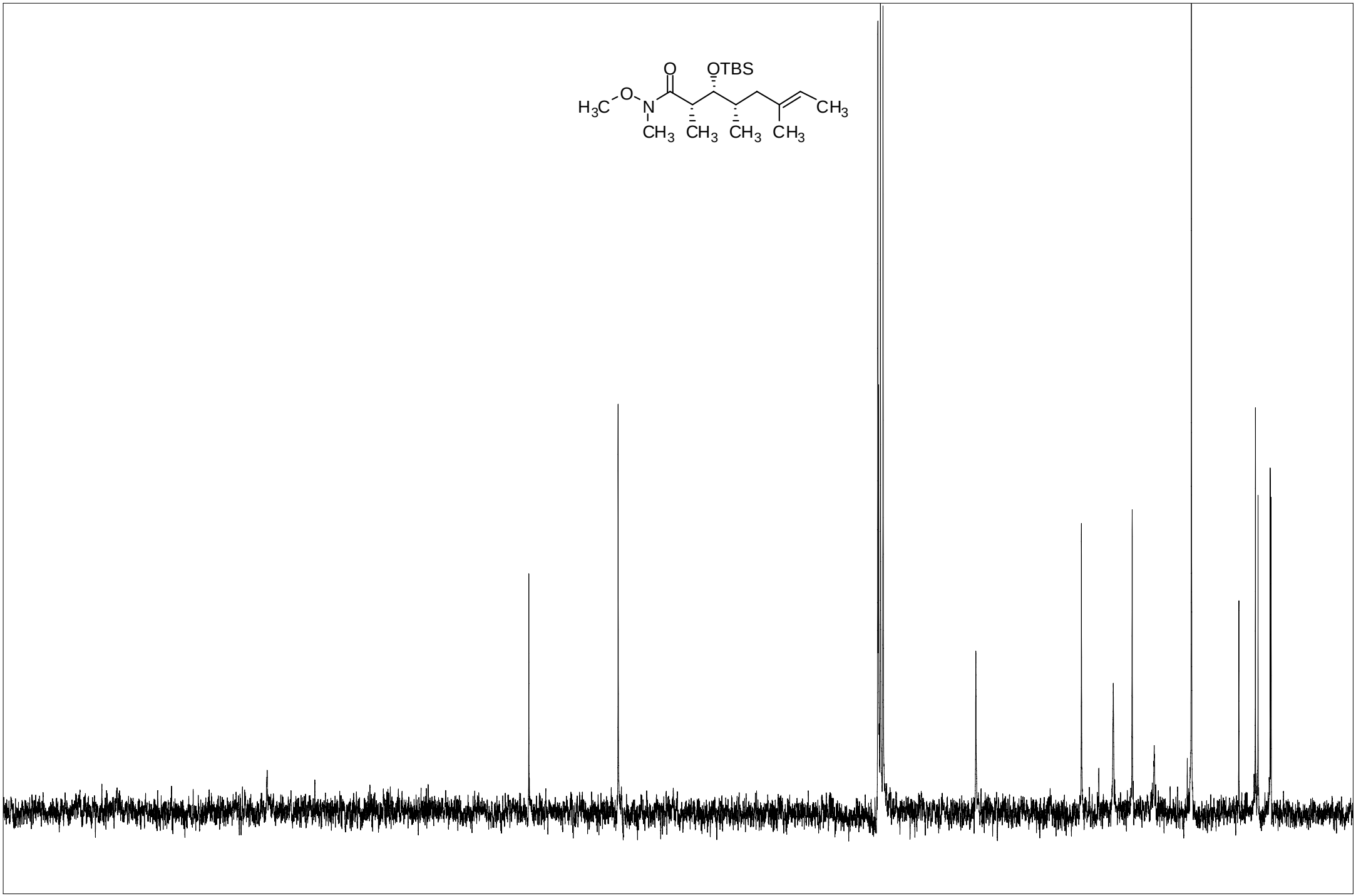
accumulations: 4

resolution: 4 cm-1

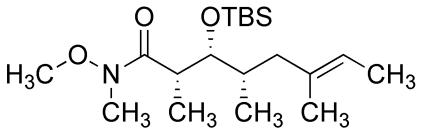
apodization: Strong


O
OH
H3C
O
N
CH3
CH3
CH3
CH3
CH3
C12
O16
C11
N14
C1
O15
C13
C6
C8
C3
C2
C4
C7
C9
C5
C10
O17


O
OTBS
H3C
O
N
CH3
CH3
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


O
OTBS
H3C
O
N
CH3
CH3
CH3
CH3
CH3
ppm
200
150
100
50

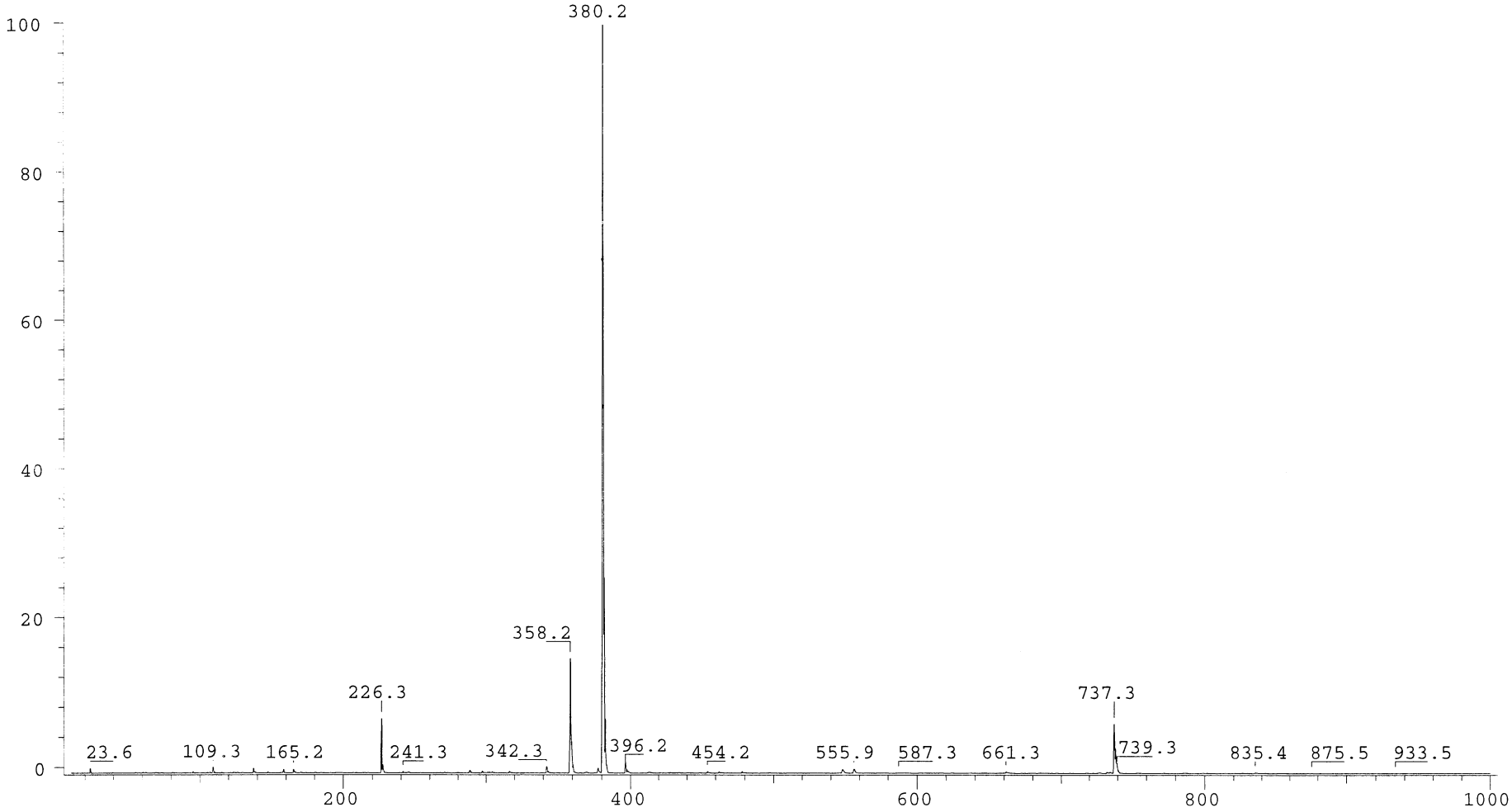
SPEC: esi5868_1.dat (12-SEP-06 14:55:43)
Samp: Bonazzi/Carreira
Comm: LM: MeOH
Oper: L.B. Study: Identify Project
Base: 380.25 Masses: 10.00 > 999.98
Peak: 1000.0 mmu Intensity: 18287091
Scan 1 @ 0.06 min (ESI +Q1MS APICID LMR AVER UP PROF)



Scans: 1 > 3

Client: Identify Customers
#Peaks: 9901
RIC: 23153249

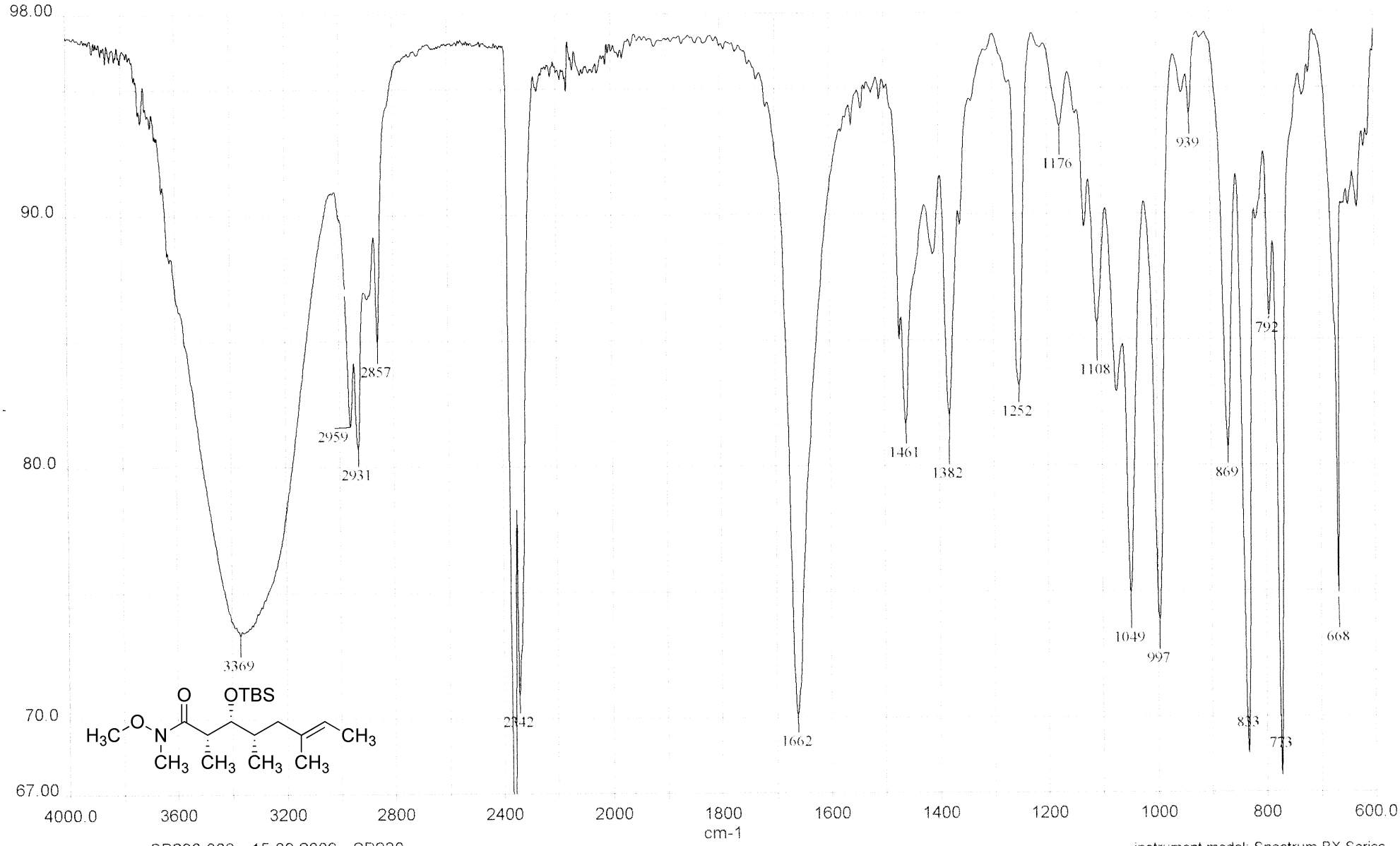
1.8E+07



Date: Tue Sep 12 15:08:25 2006 ICIS: 8.3.0 SP2 for OSF1 (V4.0) build 98-238 from 26-Aug-98

ETHZ

date: 15.09.2006



SB230.003 - 15.09.2006 - SB230

analyst: Student

last transform history: AutoFlat_2 "E:\pel_data\spectra\Student\SB230.sp", 4000, 600, "E:\pel_data\spectra\Student\SB230.~0" 'Student, Fri Sep 15 15:54:43 2006

spectrum pathname: E:\pel_data\spectra\Student\SB230.003

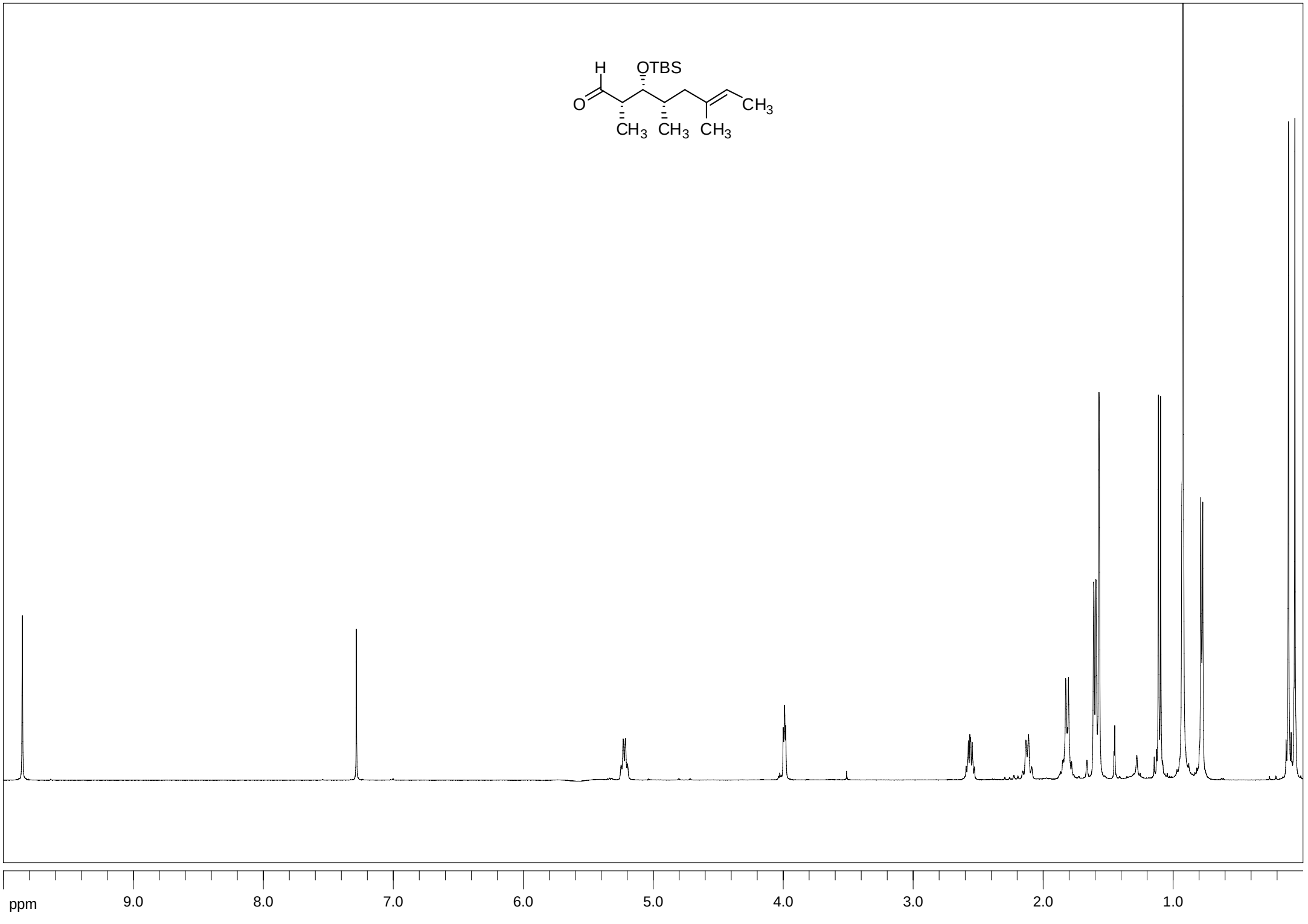
instrument model: Spectrum BX Series

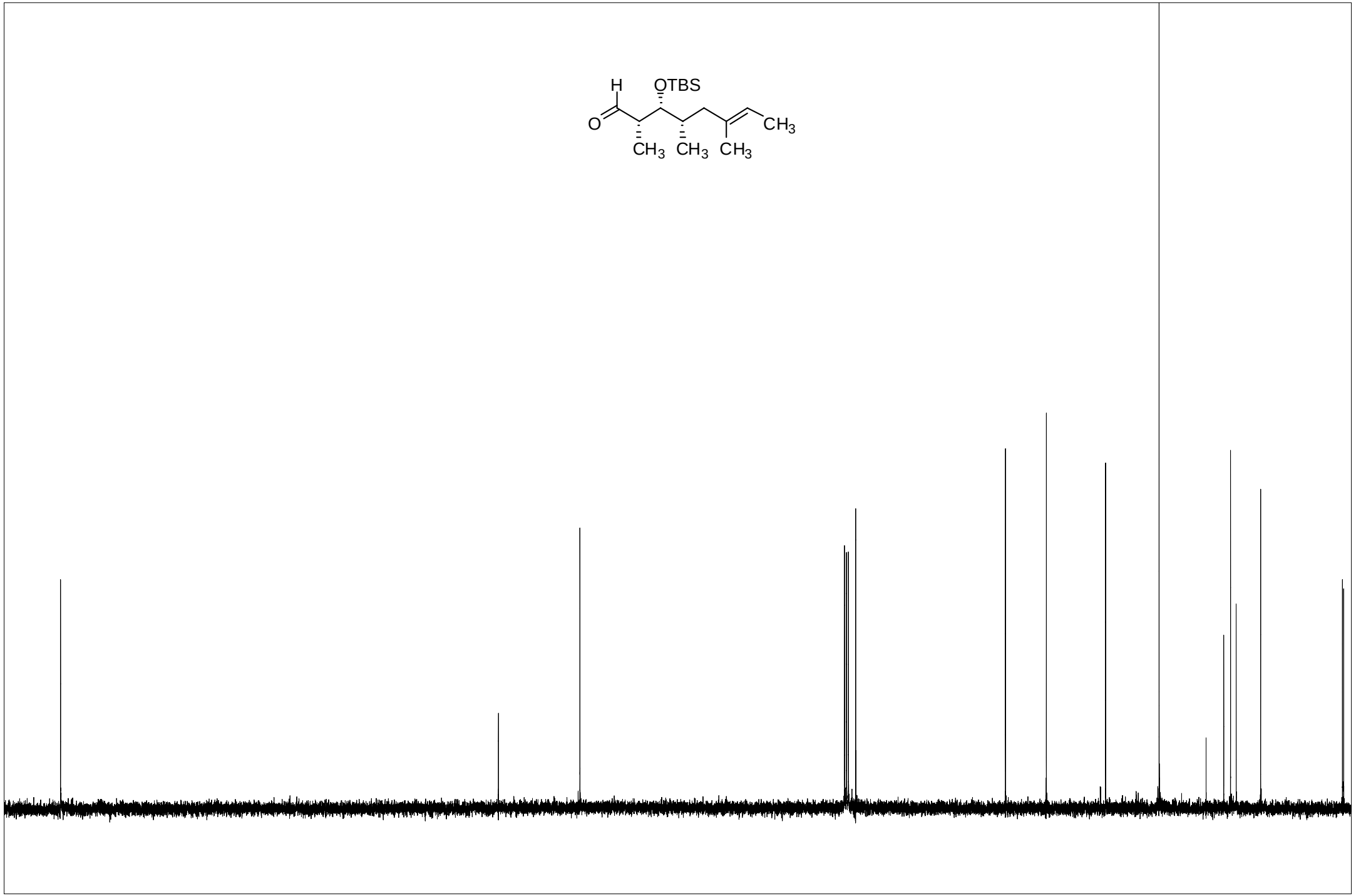
instrument serial number: 67273

accumulations: 4

resolution: 4 cm-1

apodization: Strong


H
OTBS
O
CH3
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


H
OTBS
O
CH3
CH3
CH3
CH3
ppm
200
150
100
50
0

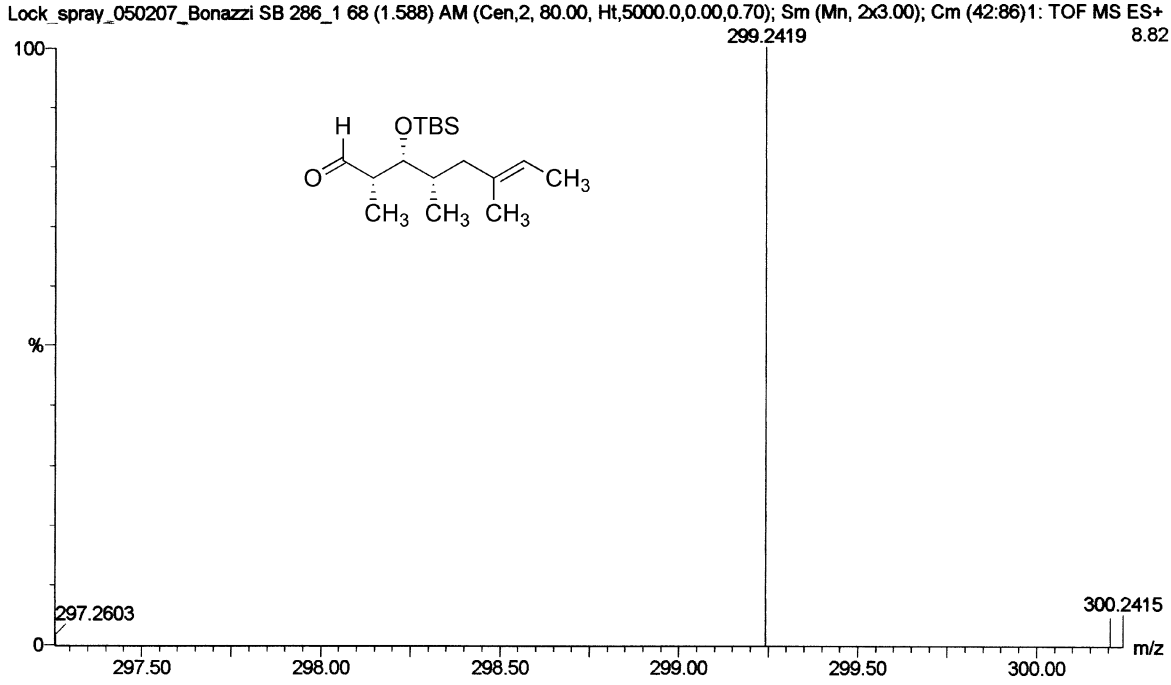
Elemental Composition Report

Single Mass Analysis

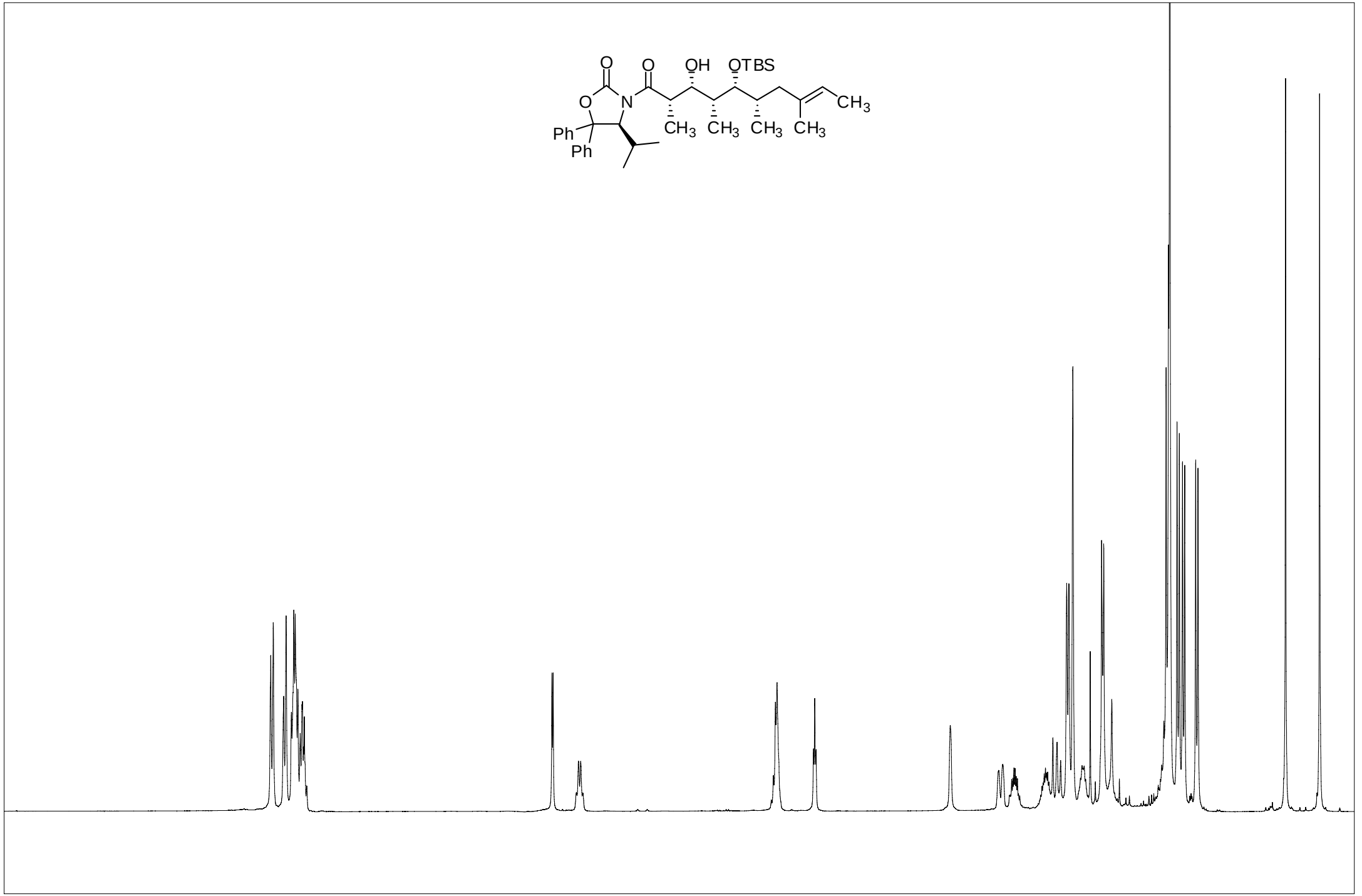
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
155 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

test lock
Lock_spray_050207_Bonazzi SB 286_1 68 (1.588) AM (Cen,2, 80.00, Ht,5000.0,0.00,0.70); Sm (Mn, 2x3.00); Cm (42:86)1: TOF MS ES+



Minimum:				-1.5		
Maximum:		200.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
299.2419	299.2406	1.3	4.3	1.5	1	C17 H35 O2 Si


O
O
OH
OTBS
O
N
CH3
CH3
CH3
CH3
CH3
Ph
Ph
ppm
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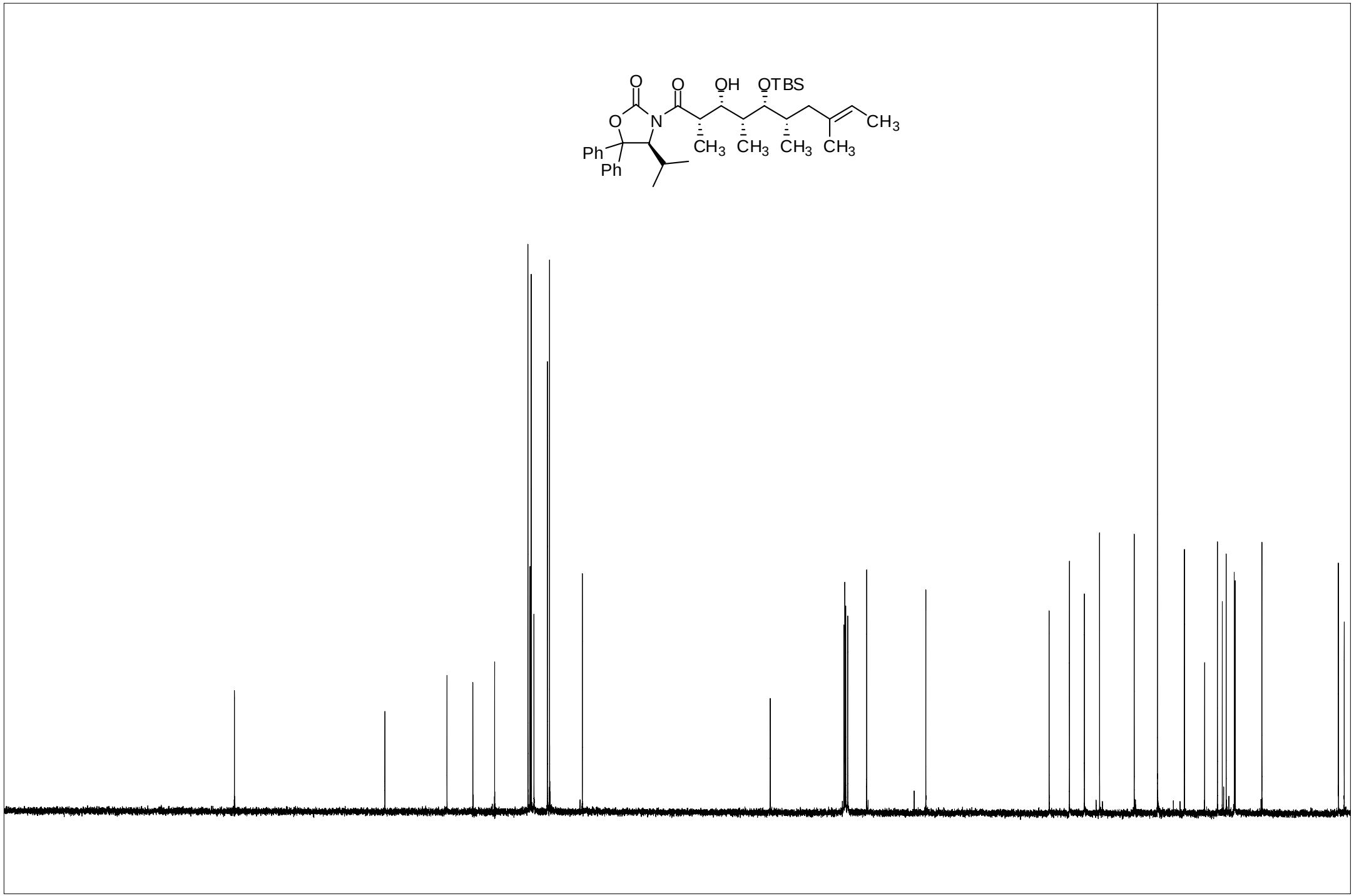
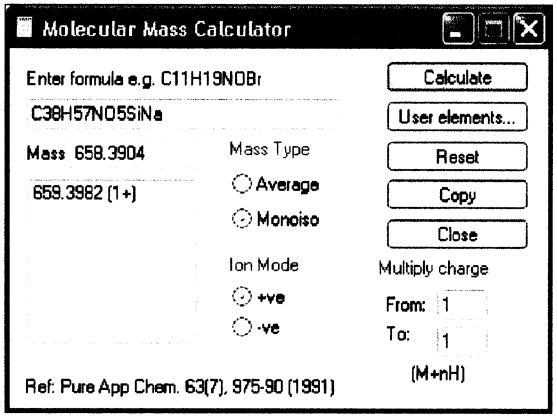
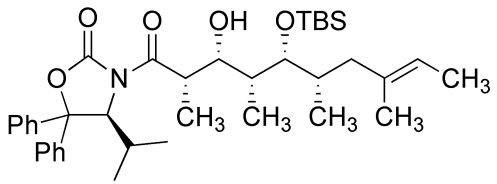
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


O
O
OH
OTBS
O
N
CH3
CH3
CH3
CH3
Ph
Ph
ppm
200
150
100
50
0

GADEMANN_BONAZZI_150207_SB 289 136 (2.791) Cm (136:145)

TOF MS ES+
1.75e3





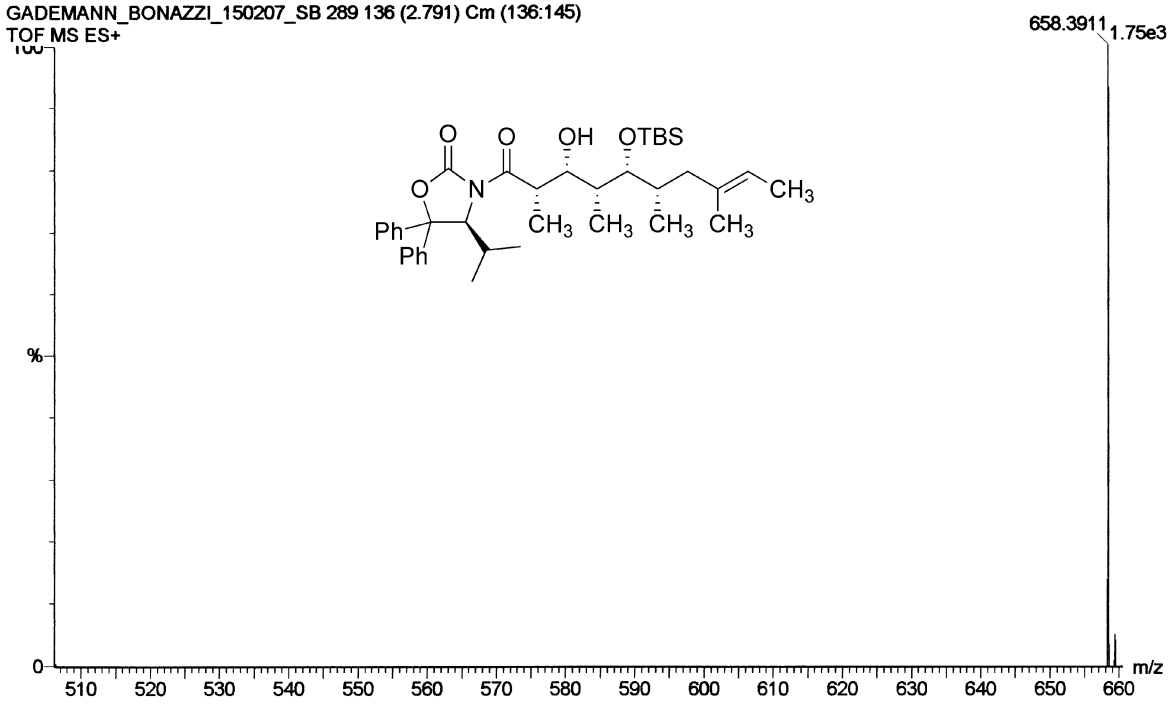
Elemental Composition Report

Single Mass Analysis

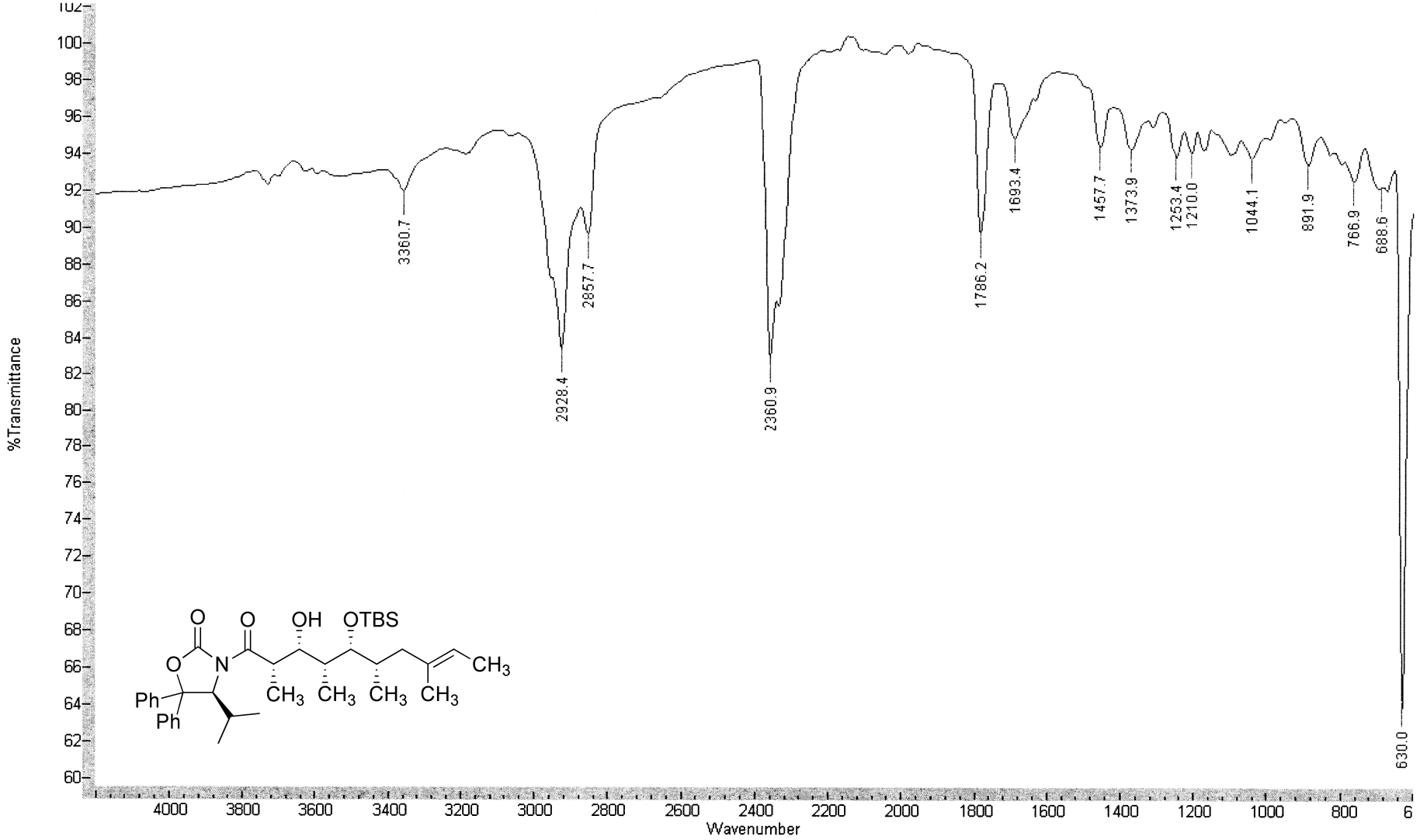
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

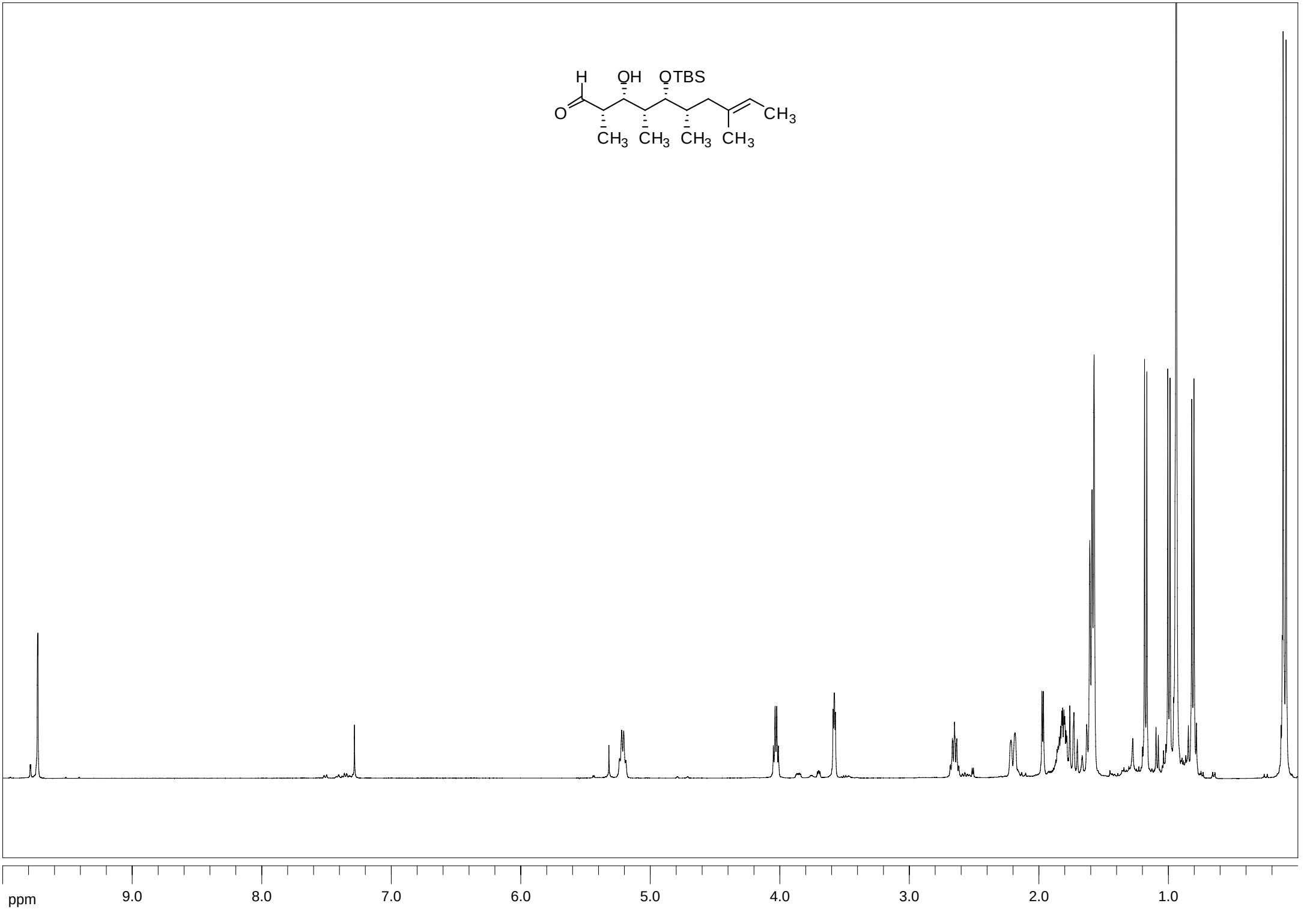
Monoisotopic Mass, Odd and Even Electron Ions
2245 formula(e) evaluated with 17 results within limits (up to 50 closest results for each mass)

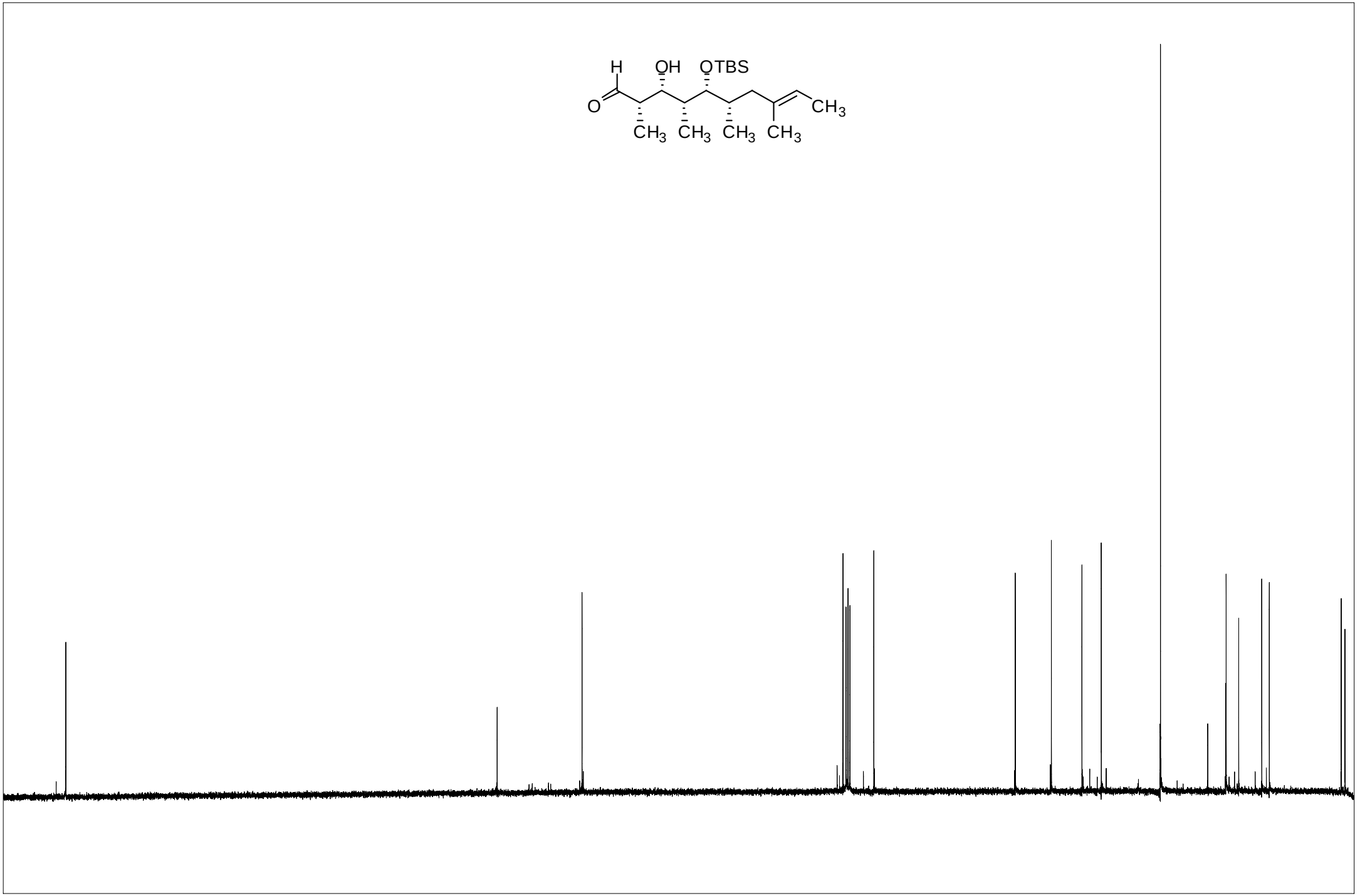
GADEMANN_BONAZZI_150207_SB 289 136 (2.791) Cm (136:145)
TOF MS ES+



Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
658.3911	658.3910	0.1	0.2	24.5	C45 H48 N5
	658.3914	-0.3	-0.5	15.0	C38 H54 N4 O4 Si
	658.3917	-0.6	-0.9	16.5	C39 H53 N5 O Na Si
→	658.3904	0.7	1.1	11.5	C38 H57 N O5 Na Si
	658.3922	-1.1	-1.6	7.0	C32 H59 N4 O5 Na Si2
	658.3900	1.1	1.6	18.5	C43 H56 N O Si2
	658.3923	-1.2	-1.8	24.0	C47 H50 N2 O
	658.3899	1.2	1.8	21.0	C45 H51 N2 O Na
	658.3896	1.5	2.2	19.5	C44 H52 N O4
	658.3928	-1.7	-2.5	14.5	C40 H56 N O5 Si
	658.3931	-1.9	-2.9	16.0	C41 H55 N2 O2 Na Si
	658.3890	2.1	3.2	12.0	C36 H55 N4 O4 Na Si
	658.3935	-2.4	-3.6	6.5	C34 H61 N O6 Na Si2
	658.3887	2.4	3.7	19.0	C41 H54 N4 Si2
	658.3886	2.5	3.9	21.5	C43 H49 N5 Na
	658.3883	2.8	4.3	20.0	C42 H50 N4 O3
	658.3941	-3.0	-4.6	19.5	C41 H52 N5 O Si

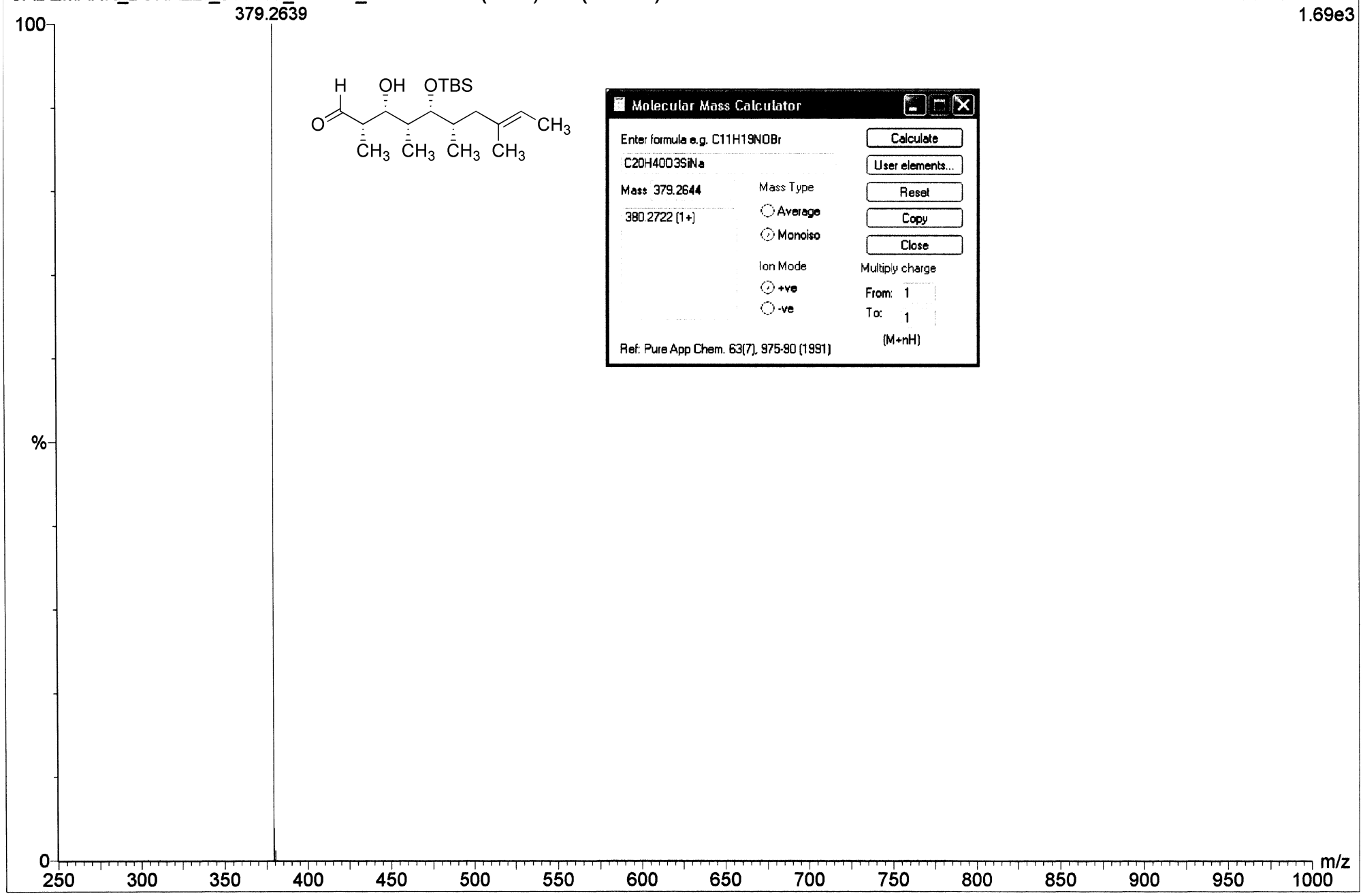

%Transmittance
Wavenumber
3360.7
2928.4
2857.7
2360.9
1786.2
1693.4
1457.7
1373.9
1253.4
1210.0
1044.1
891.9
766.9
688.6
630.0
OH
OTBS
Ph
Ph
CH3


H
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


H
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
ppm
200
150
100
50
0

GADEMANN_BONAZZI_090307_SB 305_FR2 BIS 212 (4.329) Cm (174:213)

TOF MS ES+
1.69e3



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C20H40O3SiNa

Mass 379.2644

380.2722 (1+)

Mass Type
- Average
- Monoiso

Ion Mode
- +ve
- -ve

Calculate

User elements...

Reset

Copy

Close

Multiply charge
From: 1
To: 1
(M+nH)

Ref: Pure App Chem. 63(7), 975-90 (1991)

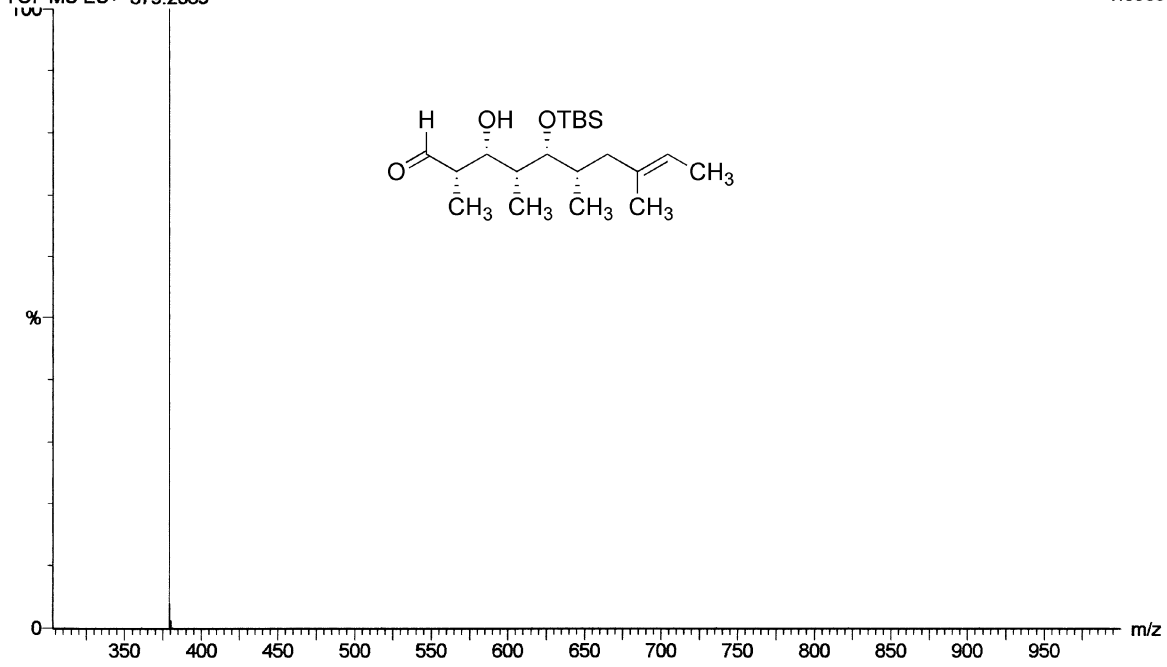
Elemental Composition Report

Single Mass Analysis (displaying only valid results)

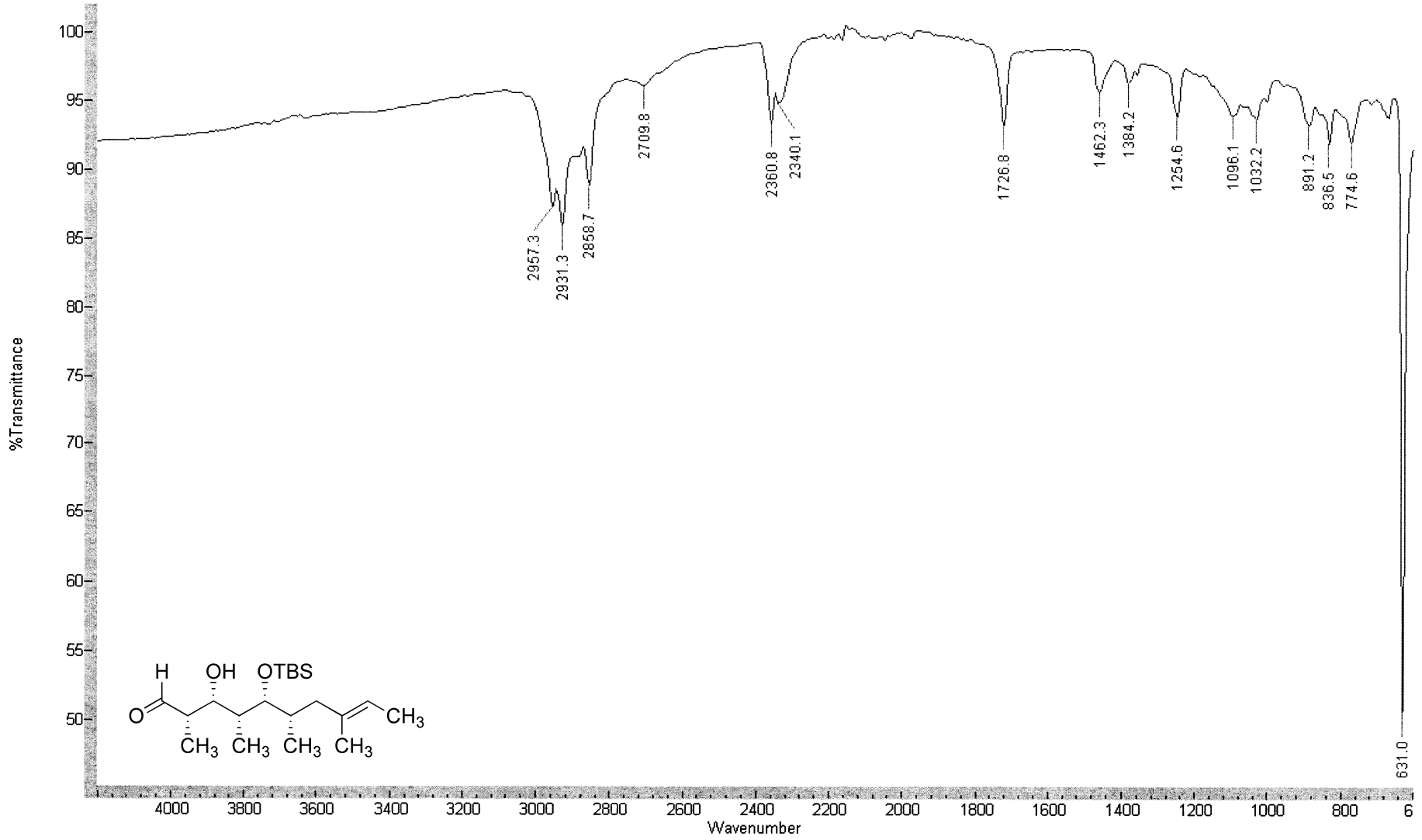
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
415 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)

GADEMANN_BONAZZI_090307_SB 305_FR2 BIS 212 (4.329) Cm (174:213)
TOF MS ES+ 379.2639 1.69e3



Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
379.2639	379.2637	0.2	0.5	9.5	C26 H35 O2
	379.2644	-0.6	-1.5	1.5	C20 H40 O3 Na Si


%Transmittance
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90
85
80
75
70
65
60
55
50
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2931.3
2858.7
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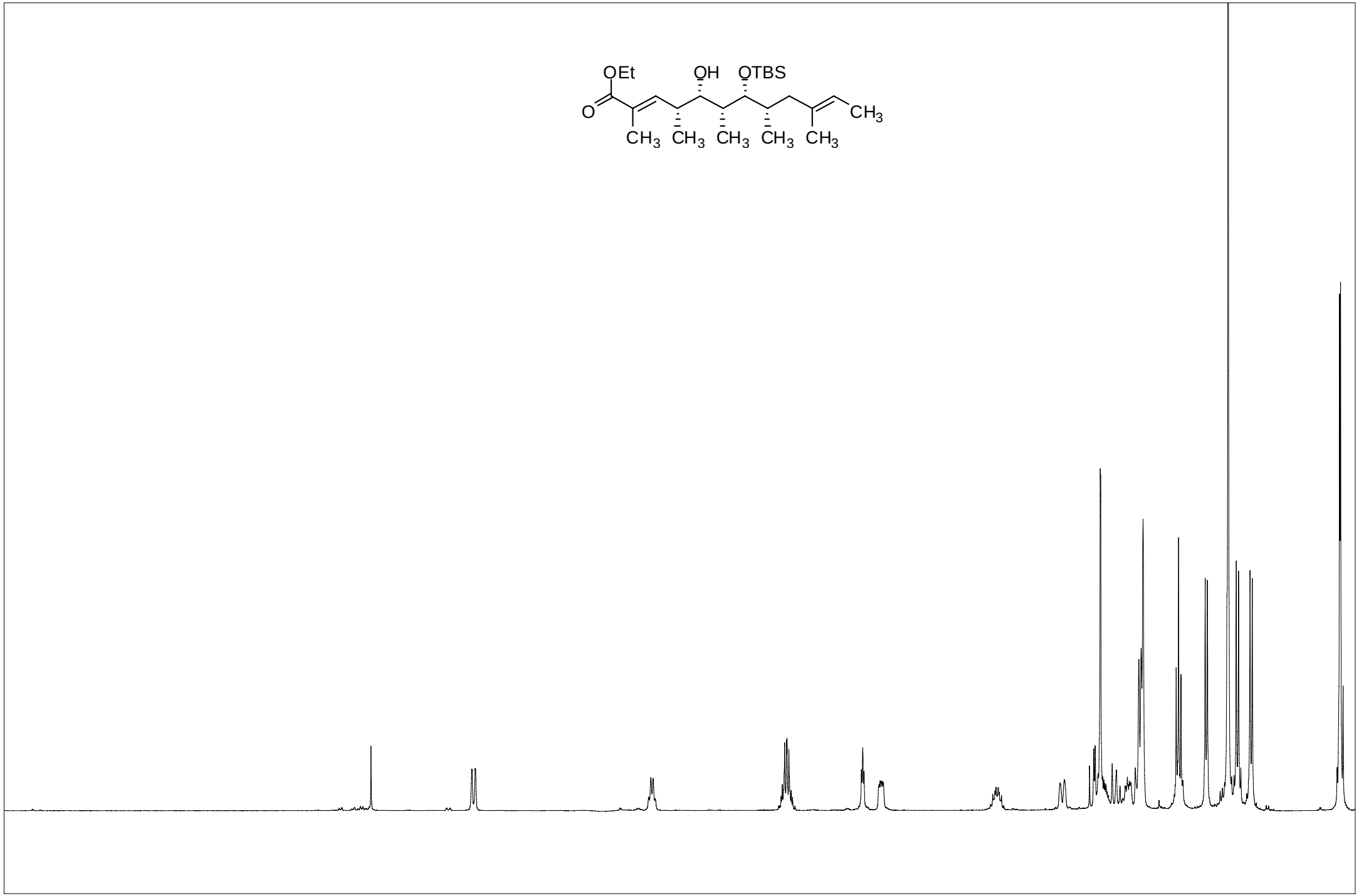
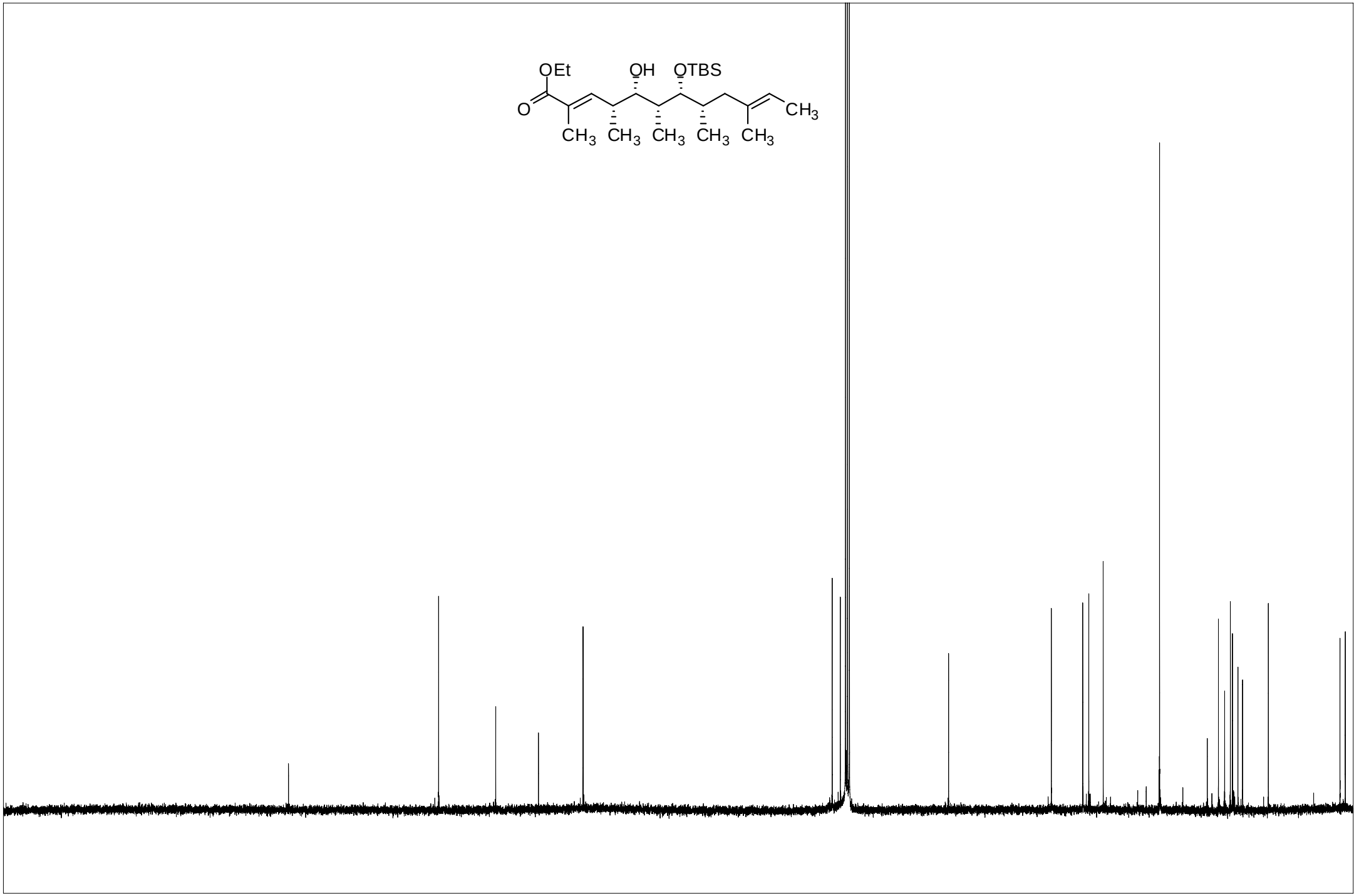
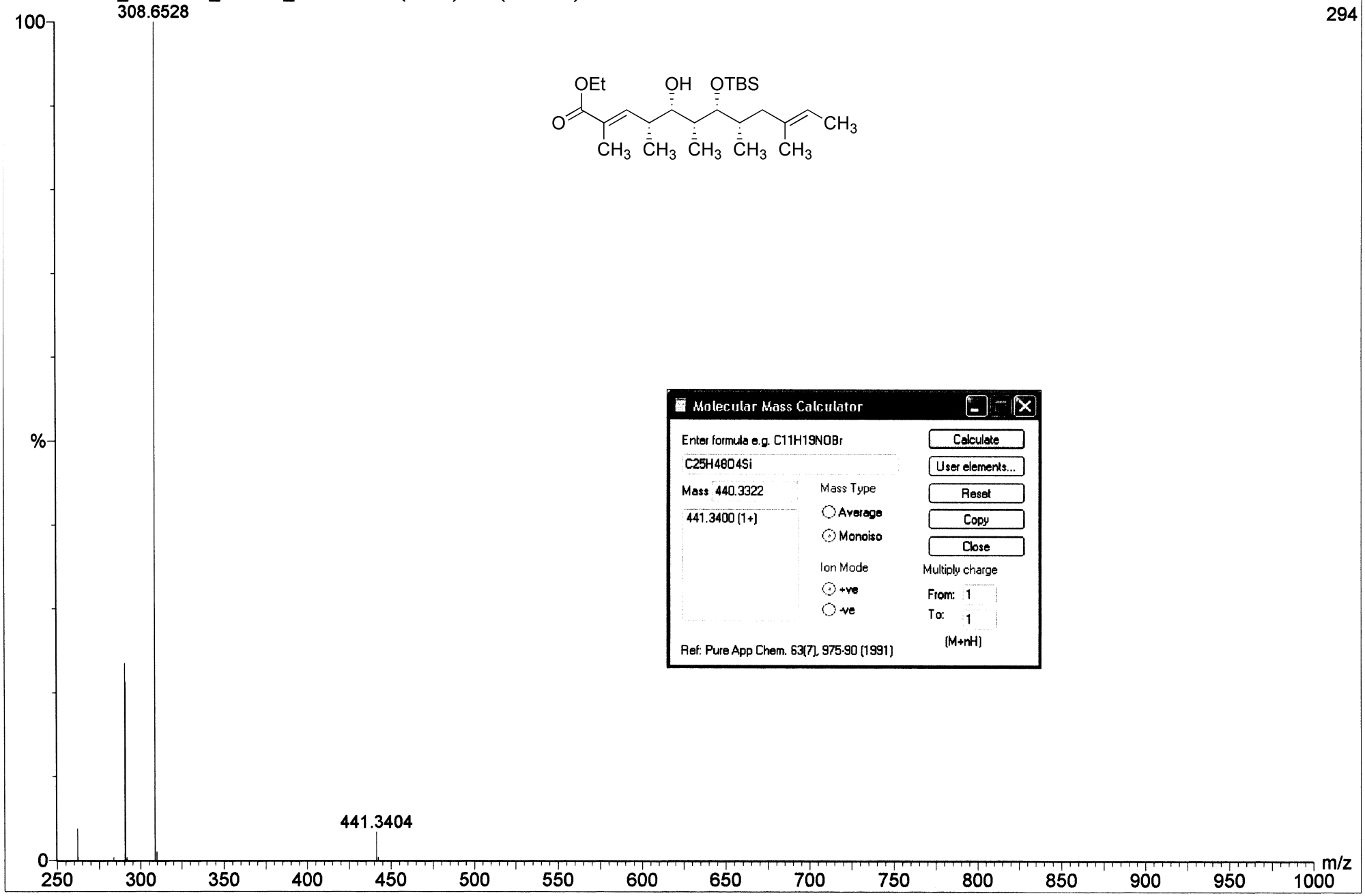
2360.8
2340.1
1726.8
1462.3
1384.2
1254.6
1096.1
1032.2
891.2
836.5
774.6
631.0
H
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber


OEt
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
CH3
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


OEt
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
CH3
ppm
200
150
100
50
0

GADEMANN_BONAZZI_090307_SB 301 165 (3.369) Cm (156:165)

TOF MS ES+
294

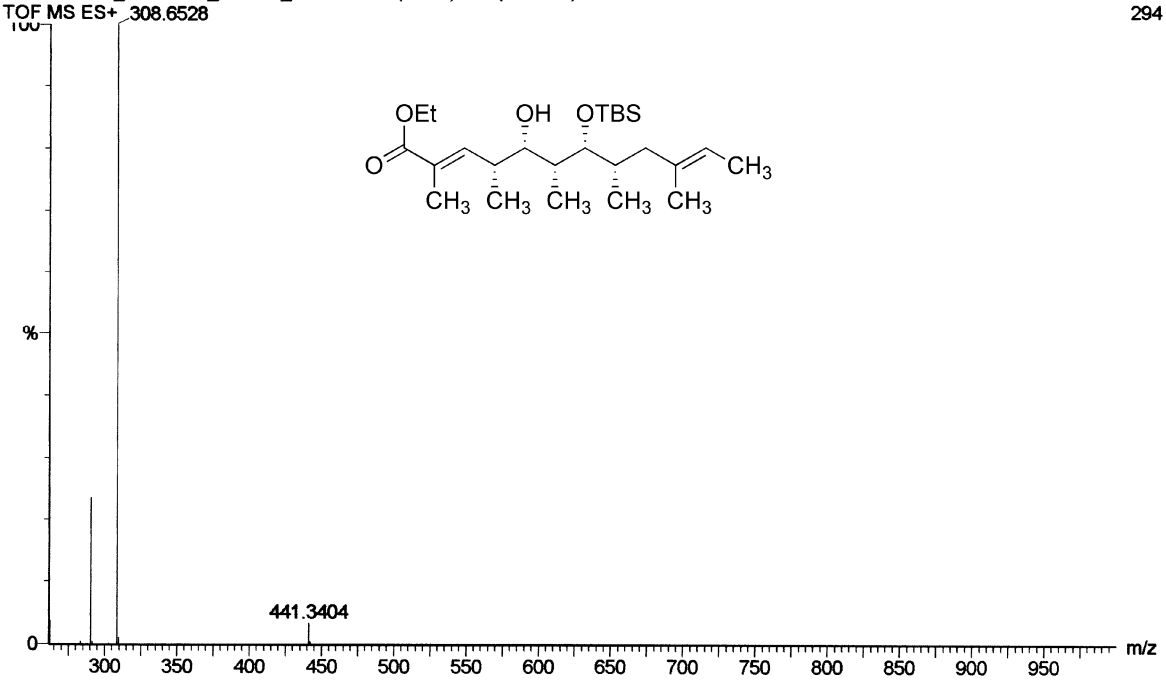


Single Mass Analysis (displaying only valid results)

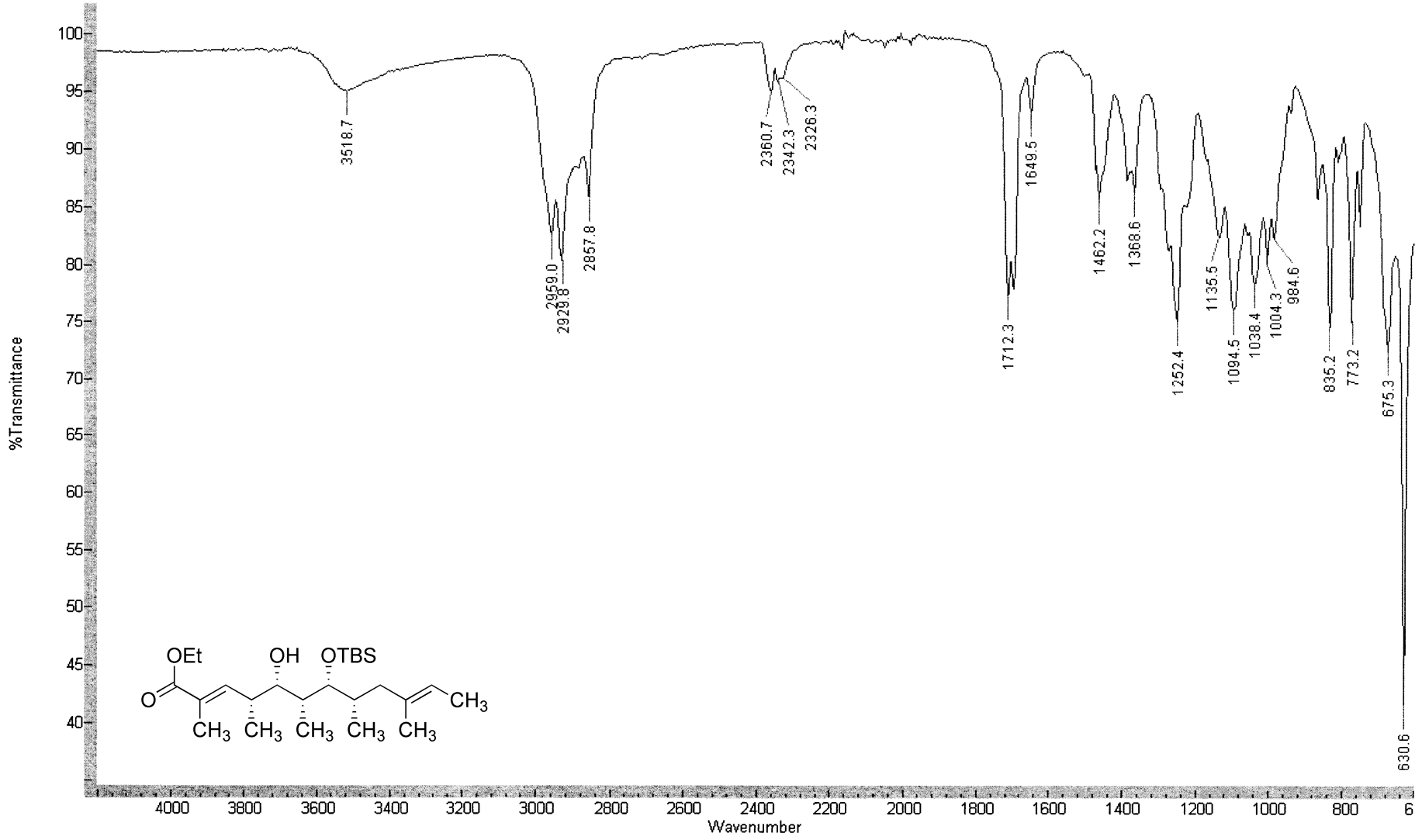
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
7029 formula(e) evaluated with 21 results within limits (up to 50 closest results for each mass)

GADEMANN_BONAZZI_090307_SB 301 165 (3.369) Cm (156:165)
TOF MS ES+ 308.6528 294



Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
441.3404	441.3403	0.0	0.1	1.0	C19 H44 N7 O3 Na
	441.3403	0.1	0.2	4.0	C26 H48 N O Na Si
	441.3405	-0.1	-0.2	-1.5	C17 H49 N6 O3 Si2
	441.3405	-0.1	-0.3	1.0	C9 H39 N19 Si
	441.3401	0.3	0.7	-0.5	C18 H45 N6 O6
	441.3401	0.3	0.7	5.0	C17 H39 N13 O
→	441.3400	0.3	0.8	2.5	C25 H49 O4 Si
	441.3407	-0.4	-0.9	0.0	C18 H48 N7 Na Si2
	441.3396	0.8	1.8	12.0	C32 H43 N
	441.3414	-1.0	-2.2	7.5	C26 H45 N4 Si
	441.3414	-1.0	-2.3	4.5	C19 H41 N10 O2
	441.3414	-1.0	-2.4	-1.0	C20 H47 N3 O7
	441.3391	1.2	2.8	-1.0	C15 H47 N9 O2 Si2
	441.3417	-1.3	-3.0	0.5	C21 H46 N4 O4 Na
	441.3390	1.4	3.1	1.5	C17 H42 N10 O2 Na
	441.3389	1.4	3.2	4.5	C24 H46 N4 Na Si
	441.3419	-1.5	-3.4	0.5	C11 H41 N16 O Si
	441.3387	1.6	3.7	0.0	C16 H43 N9 O5
	441.3387	1.7	3.7	5.5	C15 H37 N16
	441.3387	1.7	3.8	3.0	C23 H47 N3 O3 Si
	441.3421	-1.7	-3.9	-0.5	C20 H50 N4 O Na Si2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85
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75
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65
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55
50
45
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2929.8
2857.8
2360.7
2342.3
2326.3
1712.3
1649.5
1462.2
1368.6
1252.4
1135.5
1094.5
1038.4
1004.3
984.6
835.2
773.2
675.3
630.6
OEt
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
CH3
4000
3800
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3000
2800
2600
2400
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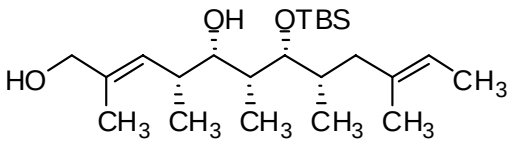
1600
1400
1200
1000
800
6
Wavenumber


OH
OTBS
HO
CH3
CH3
CH3
CH3
CH3
CH3

ppm
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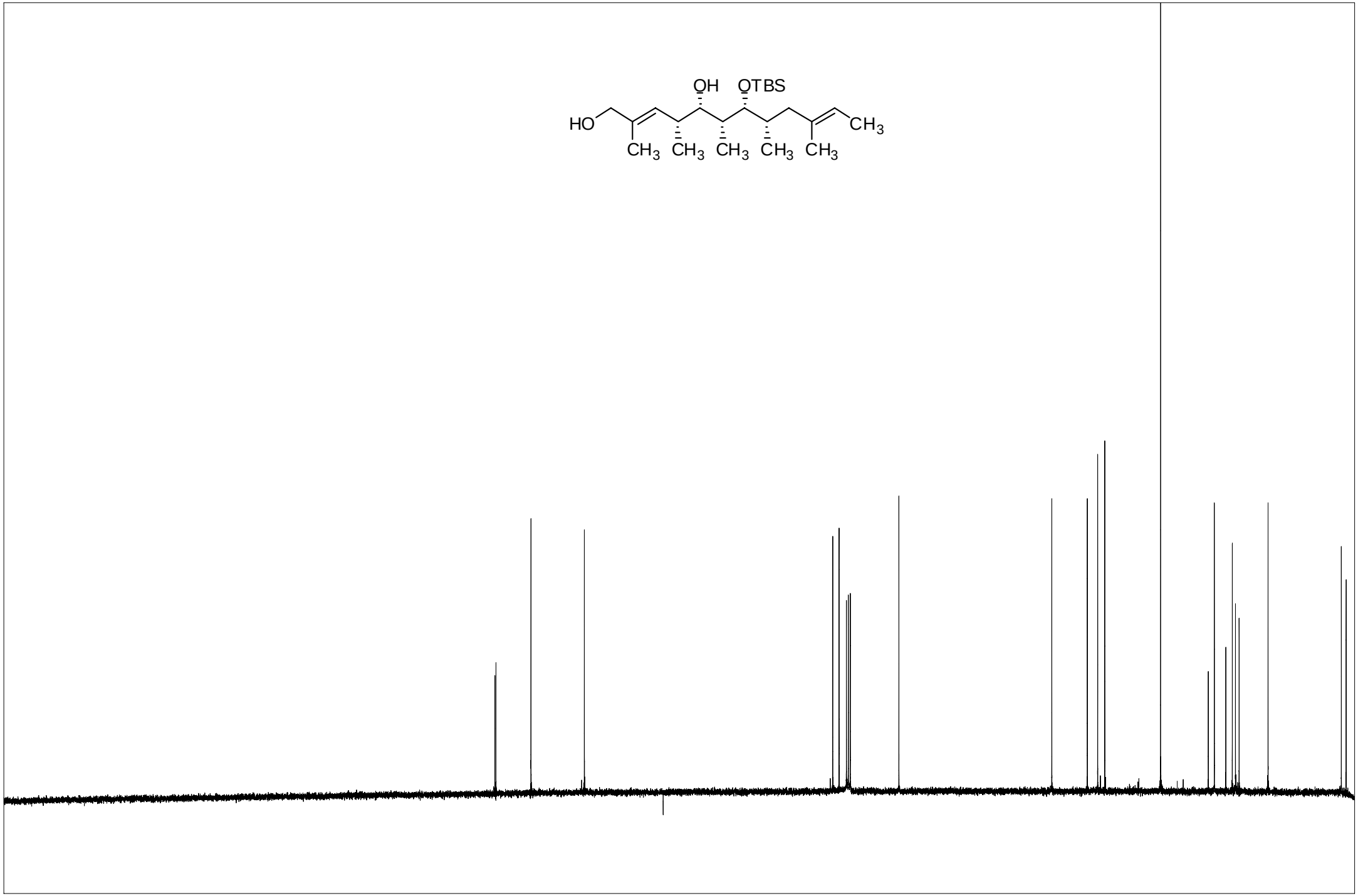
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


OH
OTBS
HO
CH3
CH3
CH3
CH3
CH3
CH3
ppm
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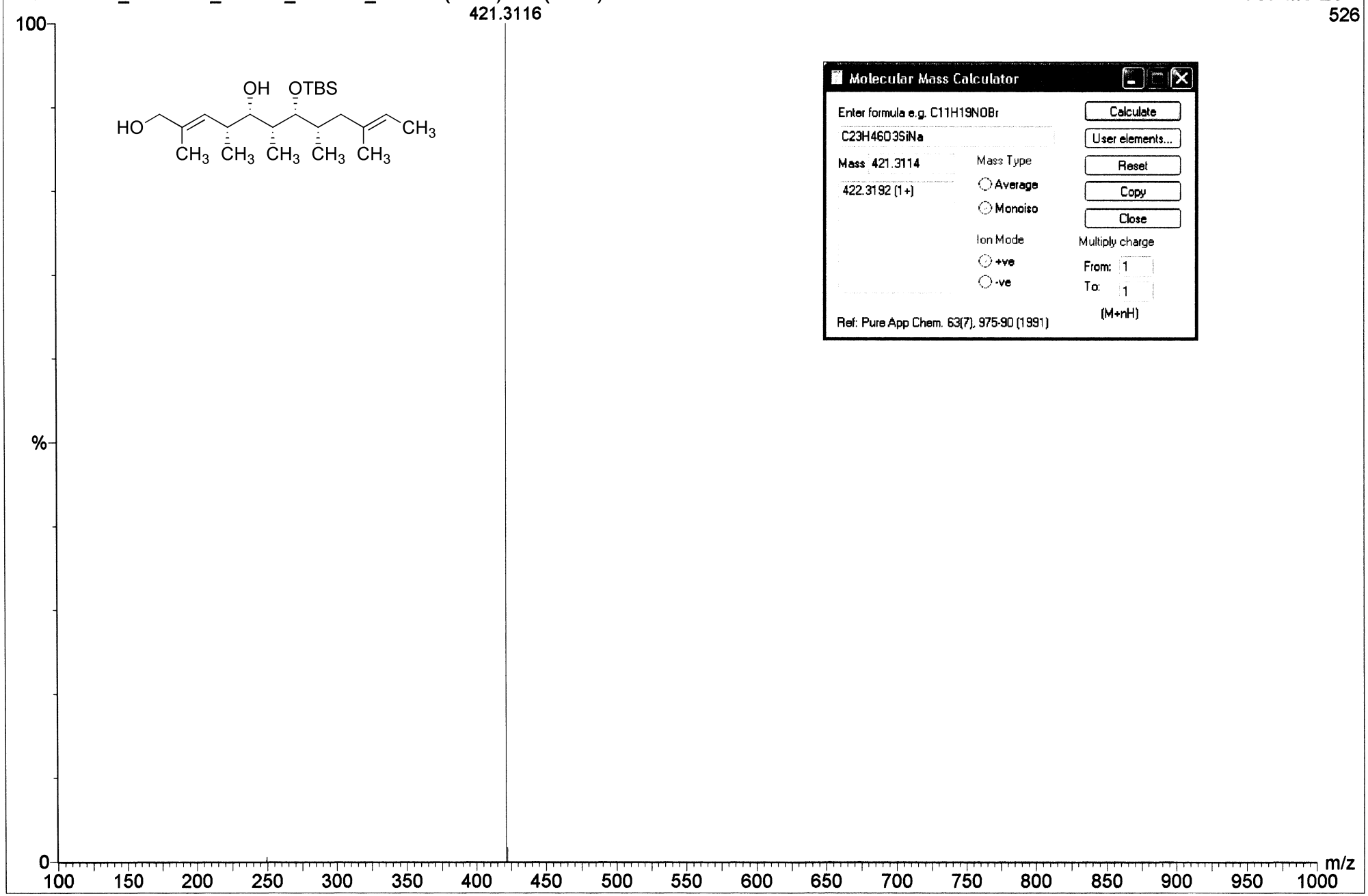
150
100
50
0

GADEMANN_BONAZZI_220507_SB272B_FR1 12 (0.251) Cm (11:13)

TOF MS ES+

526

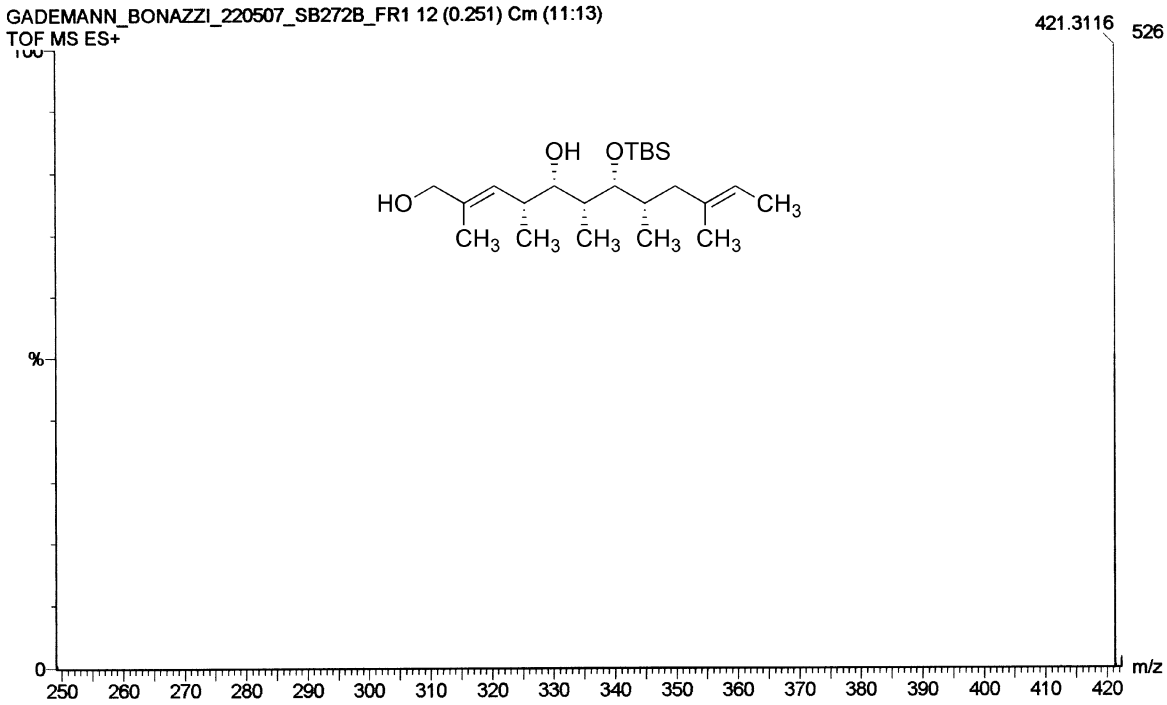


Elemental Composition Report

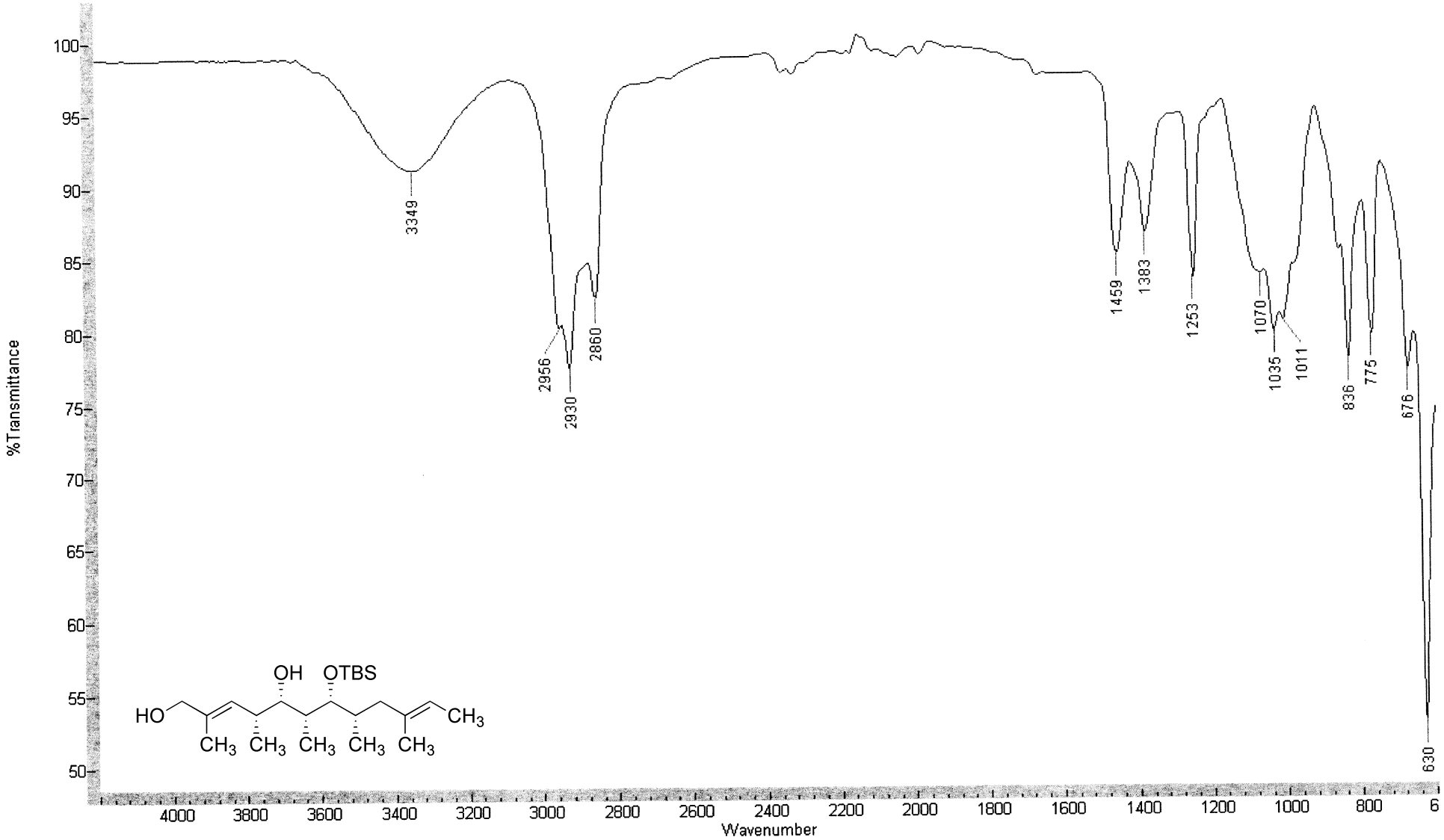
Single Mass Analysis (displaying only valid results)

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
718 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)



Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
421.3116	421.3114	0.3	0.6	1.5	C23 H46 O3 Na Si
	421.3107	1.0	2.3	9.5	C29 H41 O2


%Transmittance
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95
90
85
80
75
70
65
60
55
50
3349
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2860
1459
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2200
2000
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800
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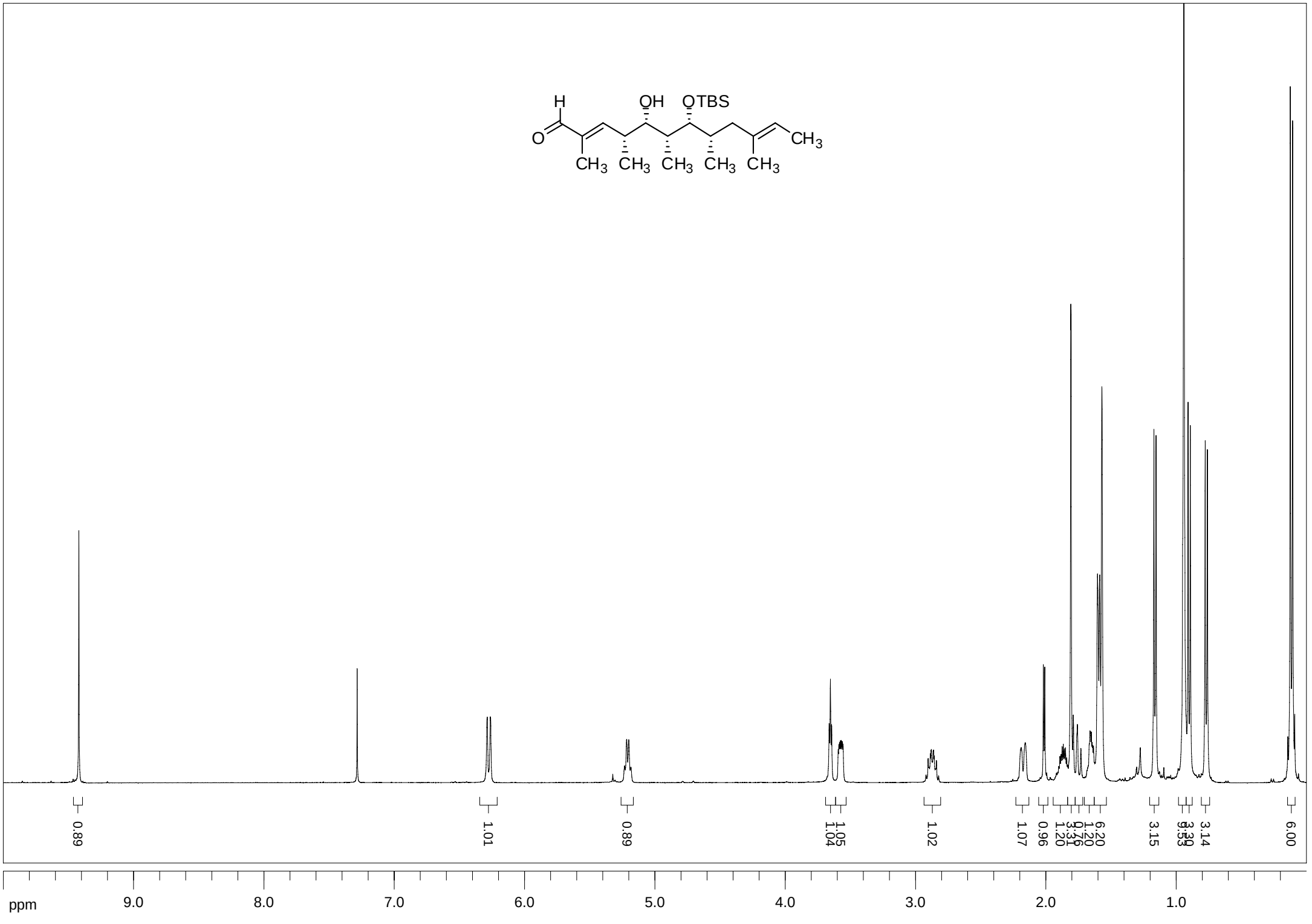
Wavenumber
OH
OTBS
HO
CH3
CH3
CH3
CH3
CH3
CH3


H
O
OH
OTBS
CH3
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CH3
CH3
CH3
CH3
0.89
1.01
0.89
1.05
1.04
1.02
1.07
0.96
1.20
3.31
0.76
1.20
6.20
3.15
3.39
3.14
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ppm
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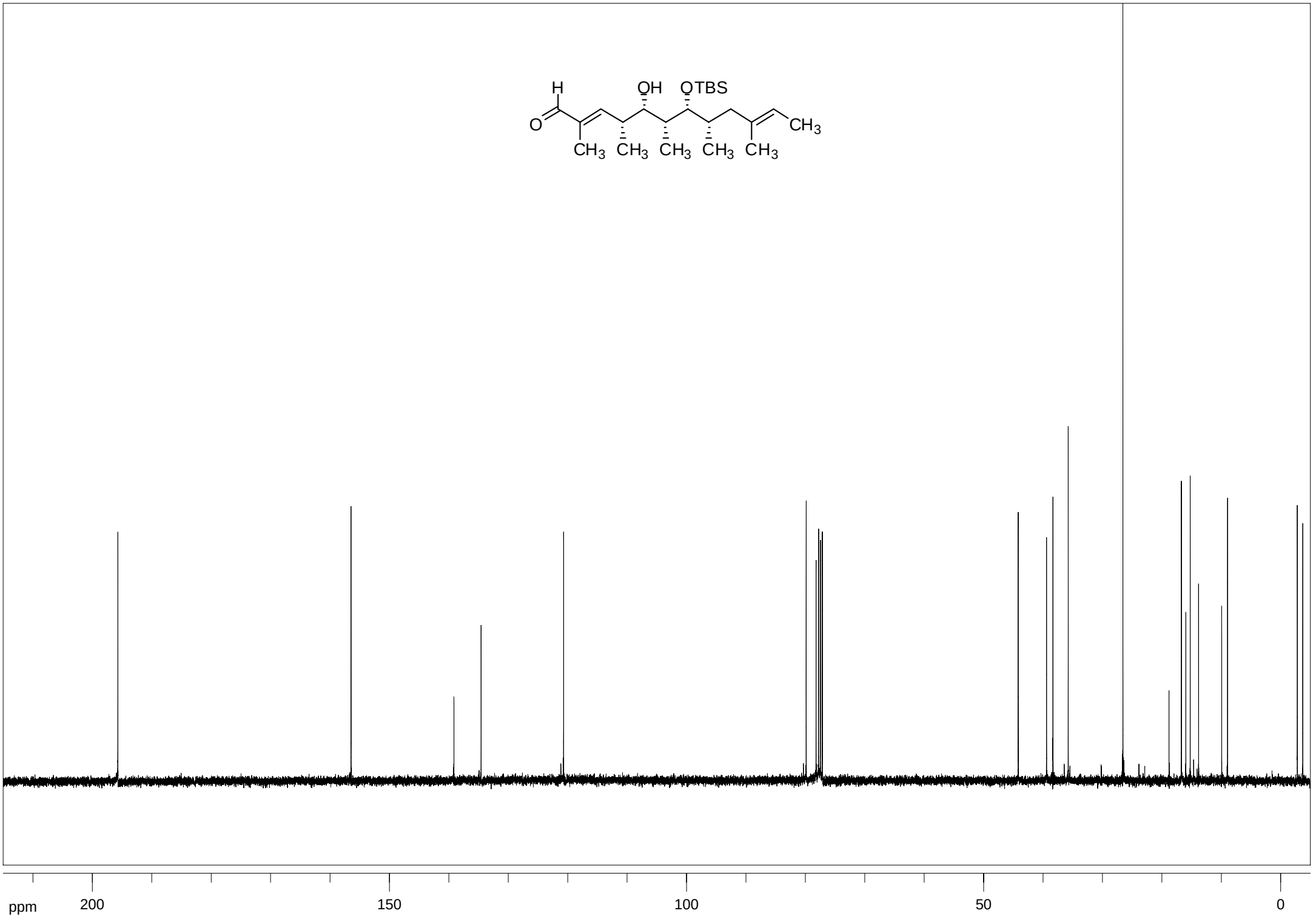
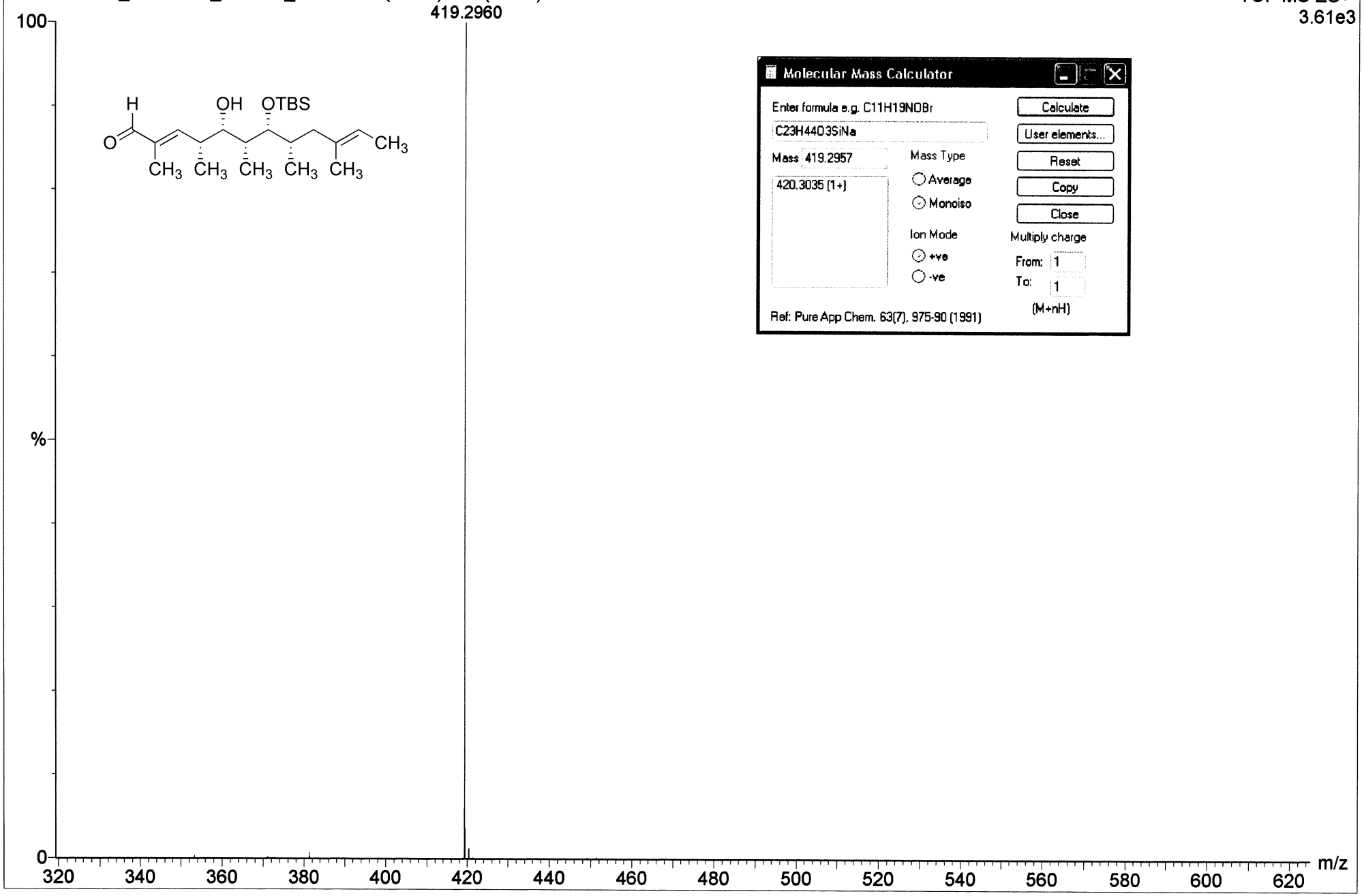
7.0
6.0
5.0
4.0
3.0
2.0
1.0


H
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
CH3
ppm
200
150
100
50
0

GADEMANN_BONAZZI_240507_SB373 32 (0.661) Cm (31:35)

TOF MS ES+
3.61e3



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C23H44O3SiNa

Calculate

User elements...

Reset

Copy

Close

Mass 419.2957

420.3035 (1+)

Mass Type

Average

Monoiso

Ion Mode

+ve

-ve

Multiply charge

From: 1

To: 1

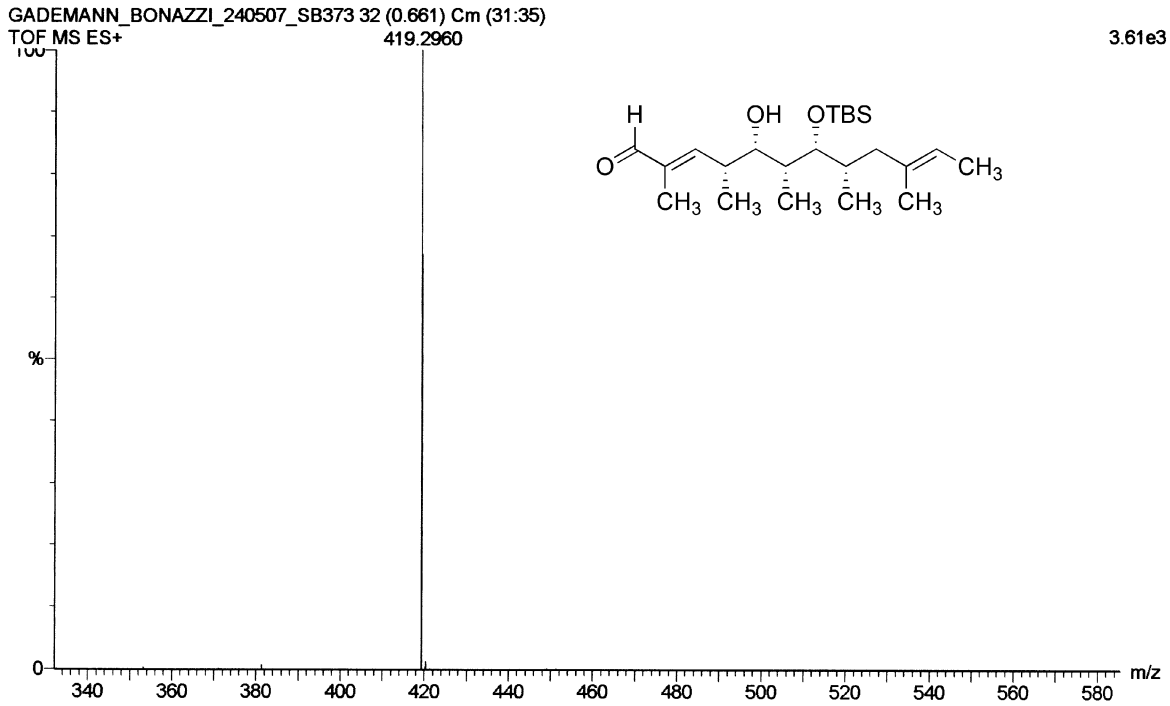
(M+nH)

Ref: Pure App Chem. 63(7), 975-90 (1991)

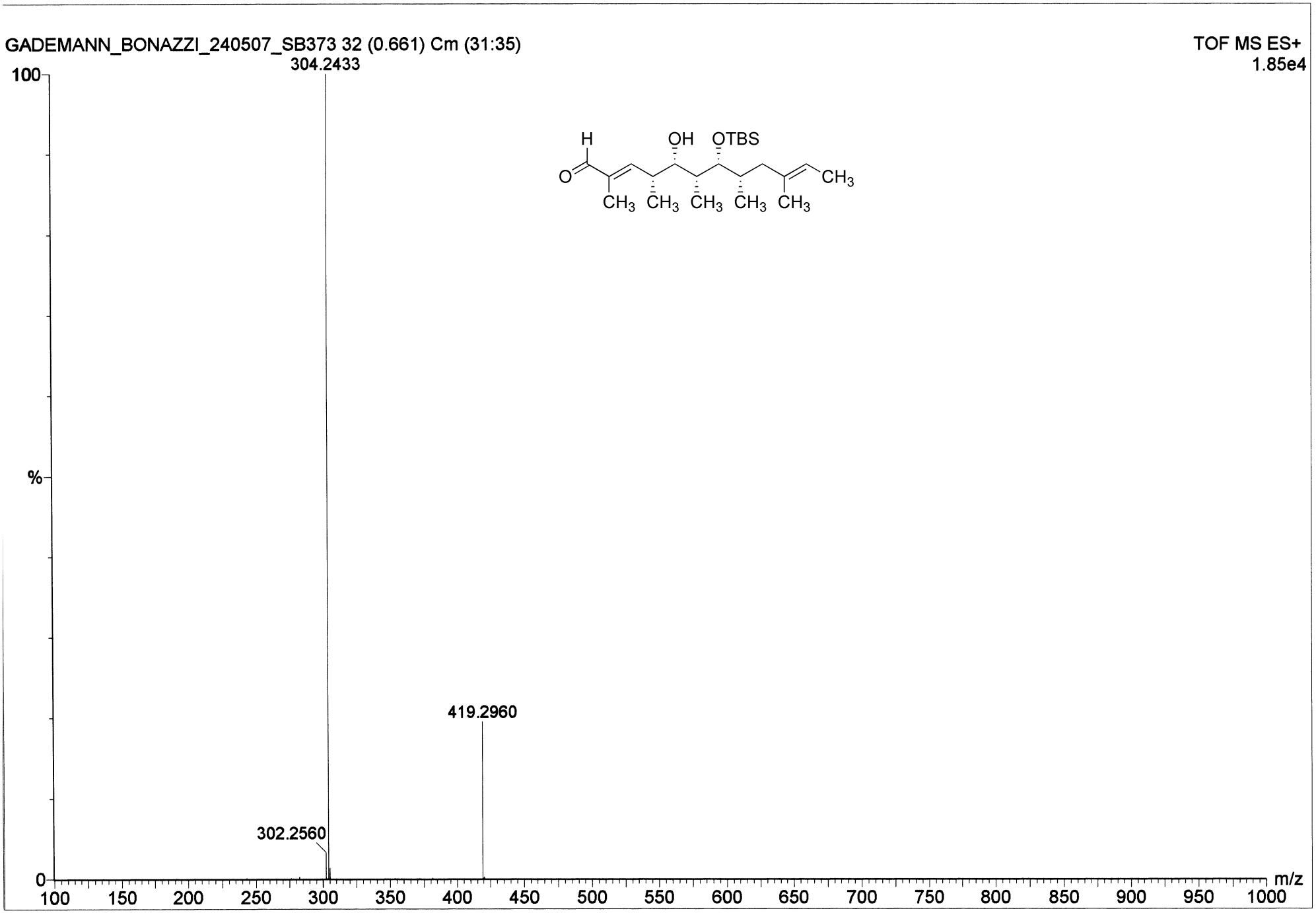
Single Mass Analysis (displaying only valid results)

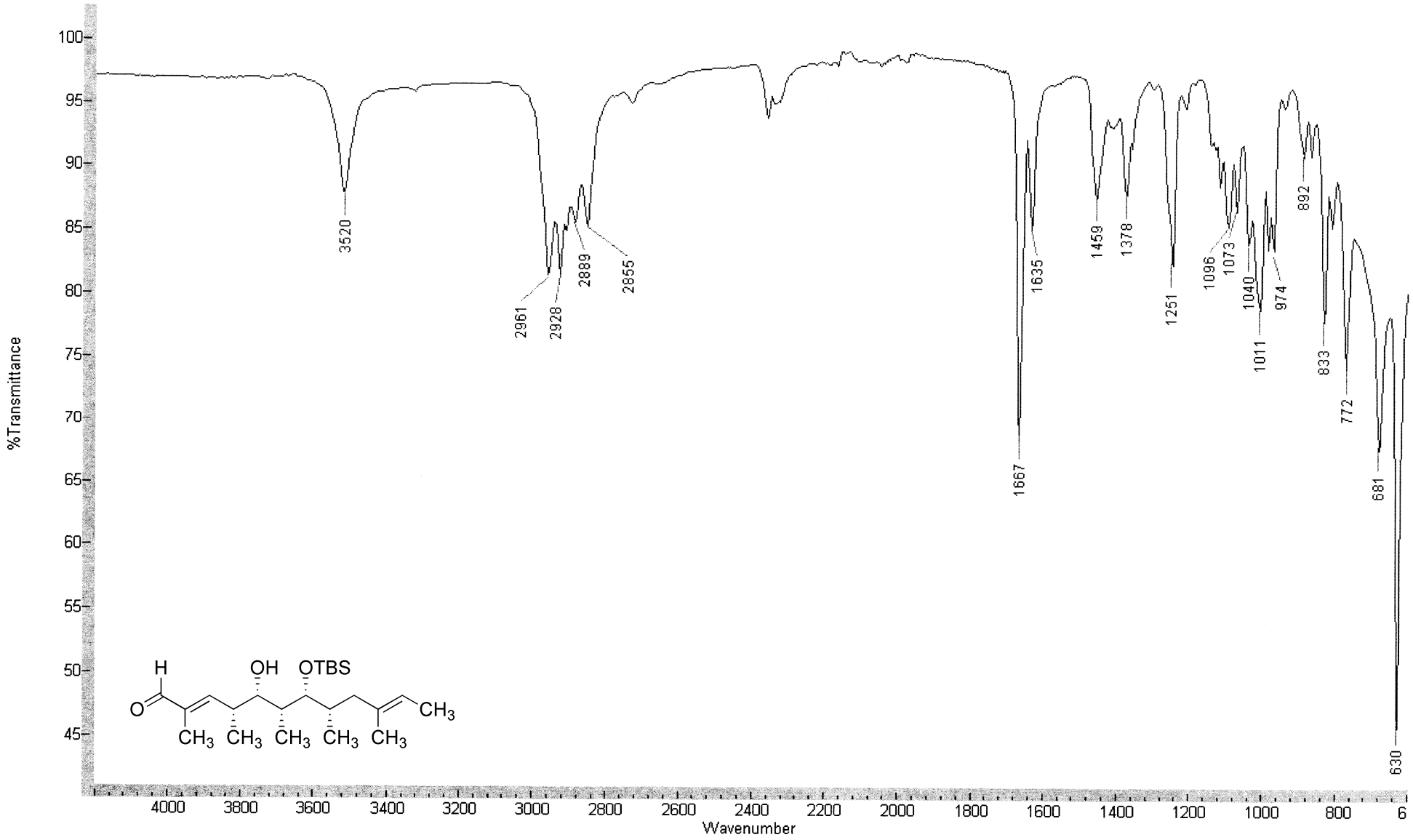
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
730 formula(e) evaluated with 2 results within limits (up to 50 closest results for each mass)



Minimum:				-1.5	
Maximum:		200.0	5.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
419.2960	419.2957	0.2	0.6	2.5	C23 H44 O3 Na Si
	419.2950	1.0	2.3	10.5	C29 H39 O2


GADEMANN_BONAZZI_240507_SB373 32 (0.661) Cm (31:35)
TOF MS ES+
1.85e4
304.2433
100
%
0
419.2960
302.2560
m/z
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
H
O
OH
OTBS
CH3
CH3
CH3
CH3
CH3
CH3


%Transmittance
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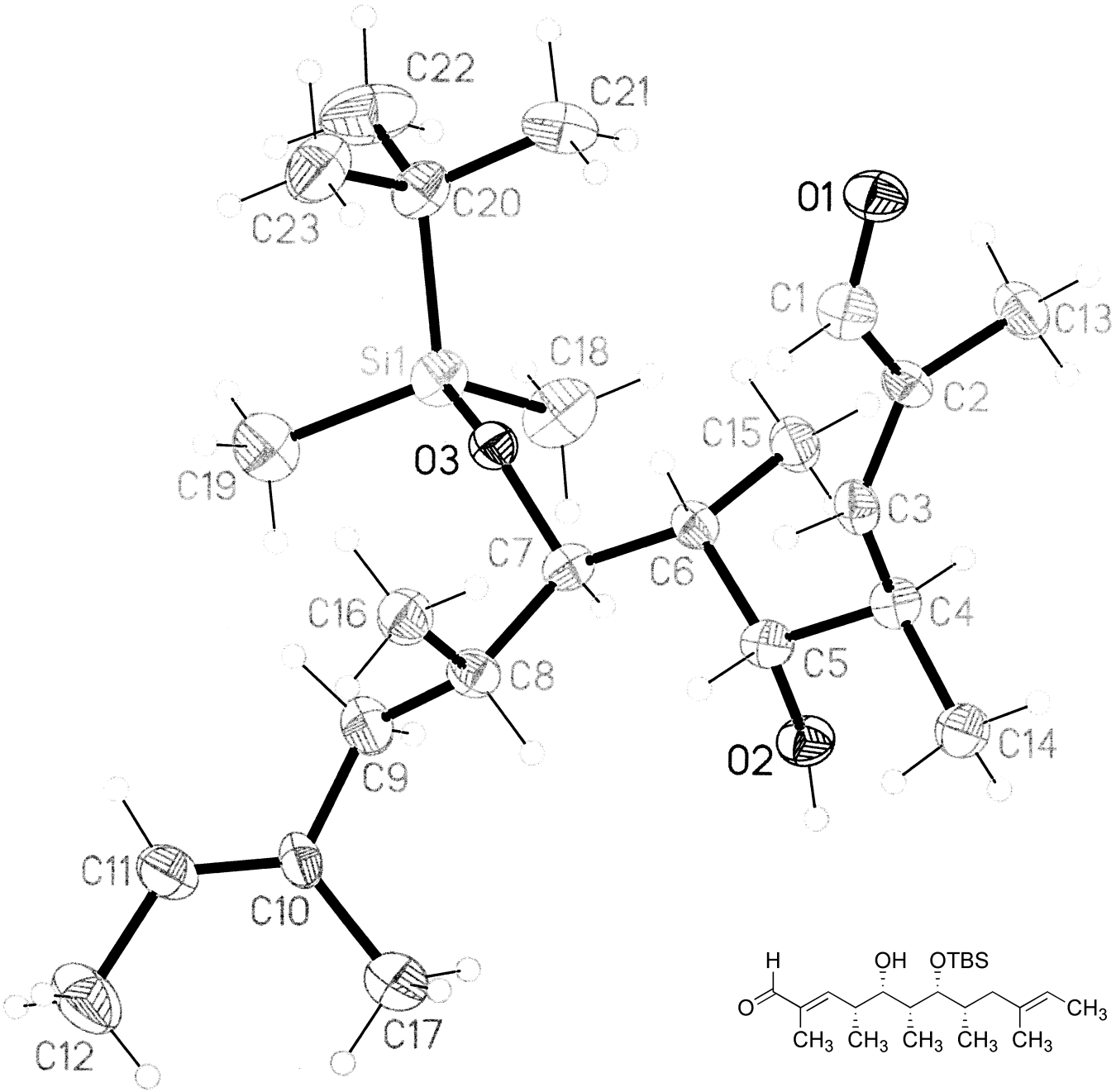
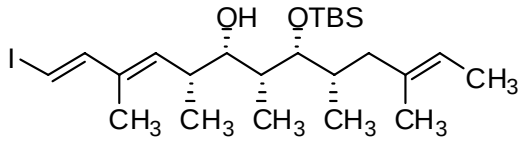
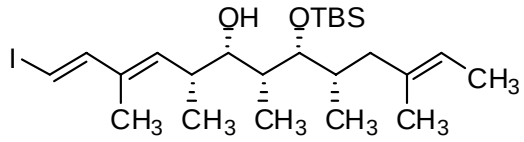
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber
H
O
OH
OTBS
CH3
CH3
CH3
CH3
CH3
CH3

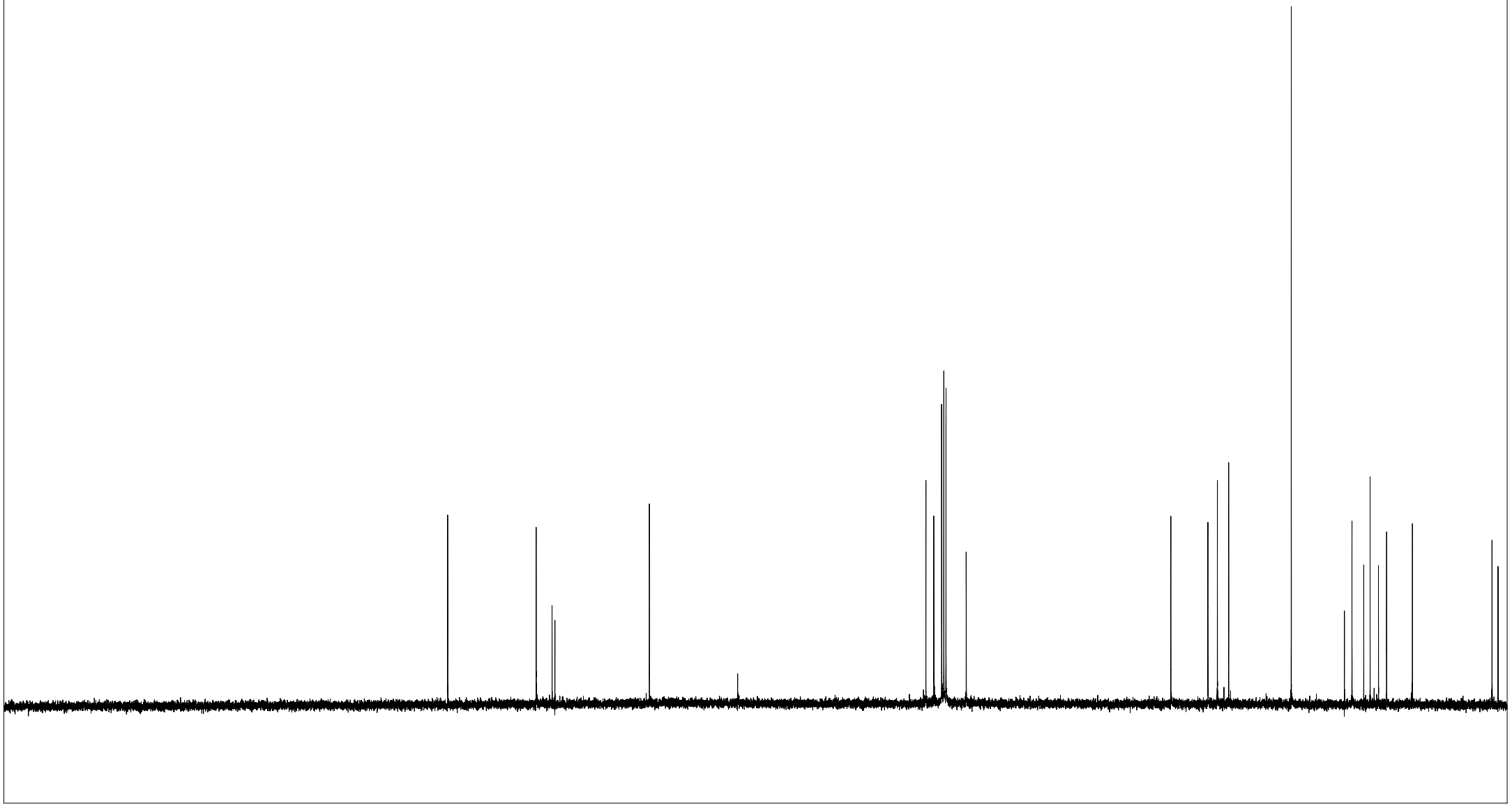

C22
C21
C23
C20
O1
C1
C13
Si1
C18
C2
C15
O3
C19
C3
C7
C6
C16
C4
C8
C5
O2
C14
C9
C11
C10
C12
C17
H
OH
OTBS
O
CH3
CH3
CH3
CH3
CH3
CH3

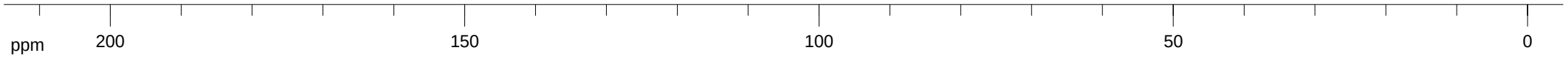

OH
OTBS
I
CH3
CH3
CH3
CH3
CH3
CH3

0.89
0.83
1.89
1.00
1.02
1.02
1.03
2.74
3.53
6.27
3.01
9.33
3.06
3.03
6.01

ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

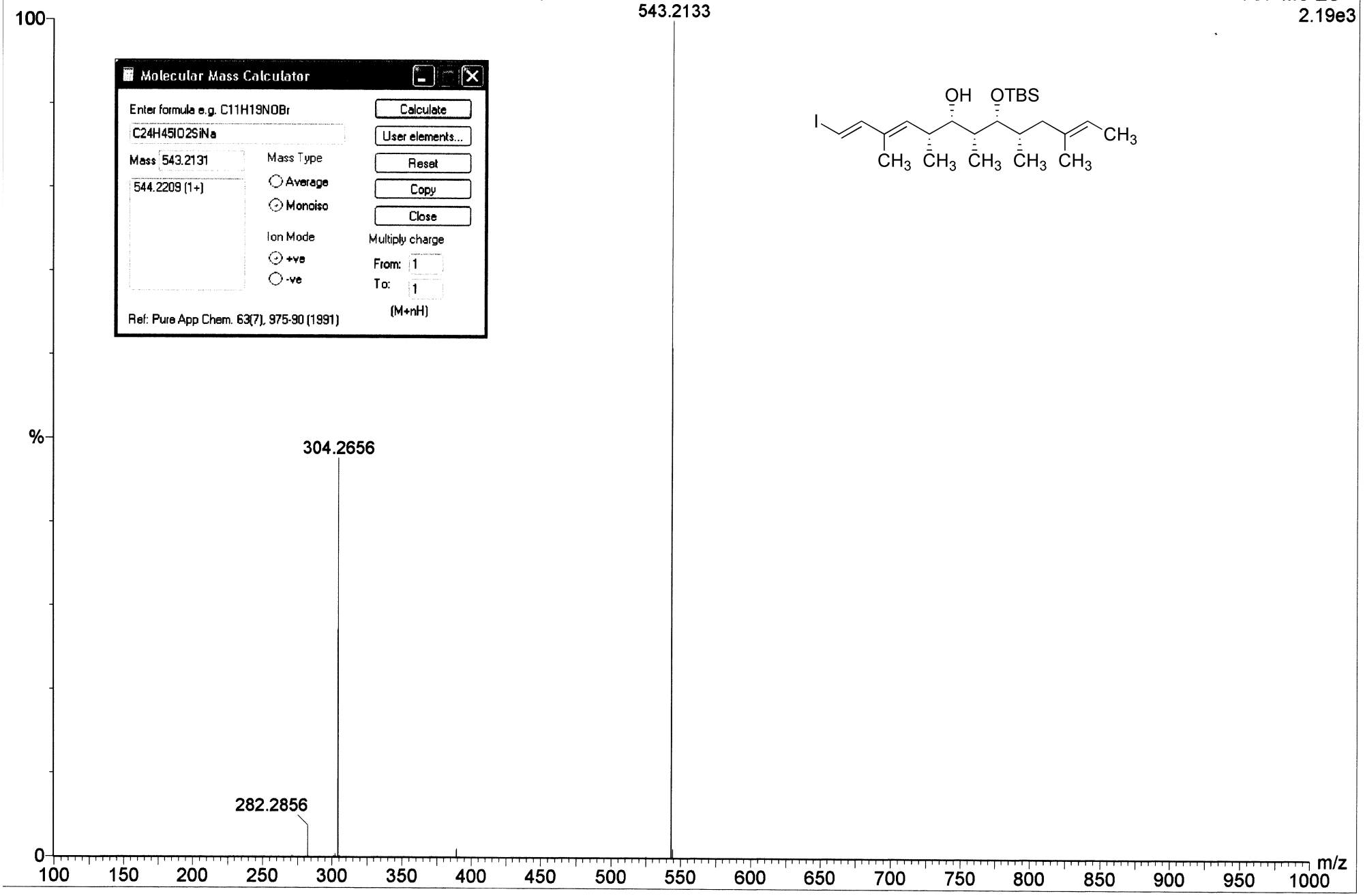

OH
OTBS
I
CH3
CH3
CH3
CH3
CH3
CH3




ppm
200
150
100
50
0

GADEMANN_BONAZZI_300507_SB 374 16 (0.332) Cm (15:20)

TOF MS ES+
2.19e3



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C24H45IO2SiNa

Mass 543.2131

544.2209 (1+)

Mass Type
- Average
- Monoiso

Ion Mode
- +ve
- -ve

Multiply charge
From: 1
To: 1
(M+nH)

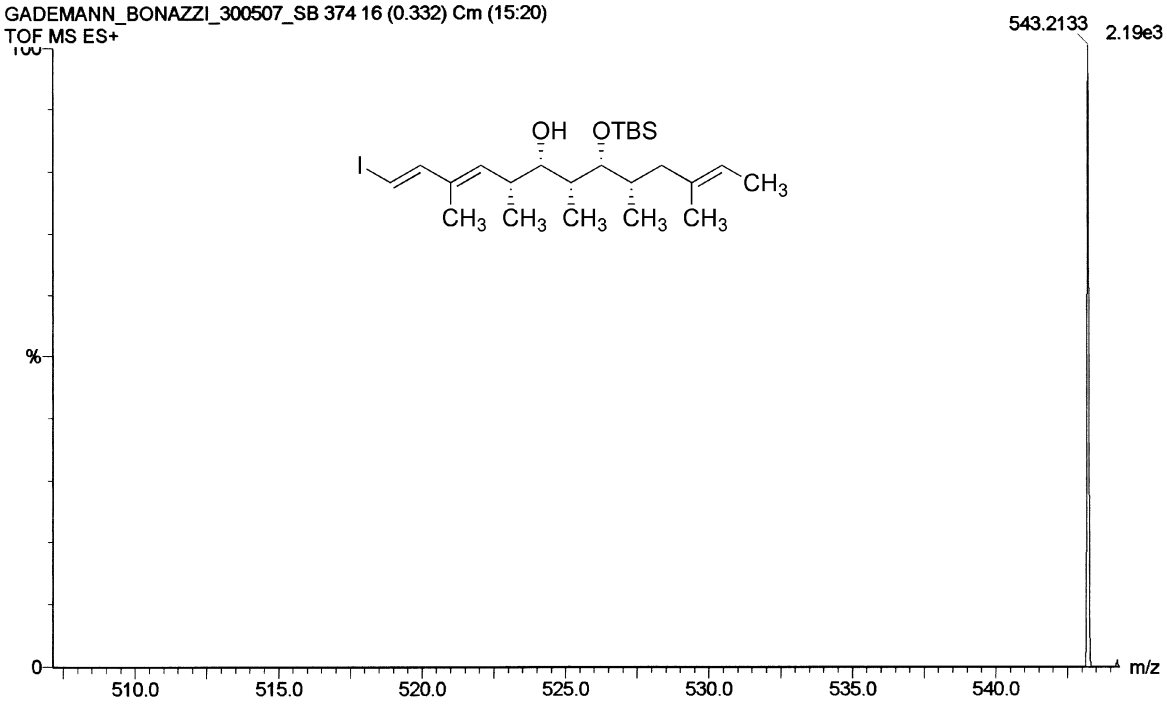
Calculate
User elements...
Reset
Copy
Close

Ref: Pure App Chem. 63(7), 975-90 (1991)

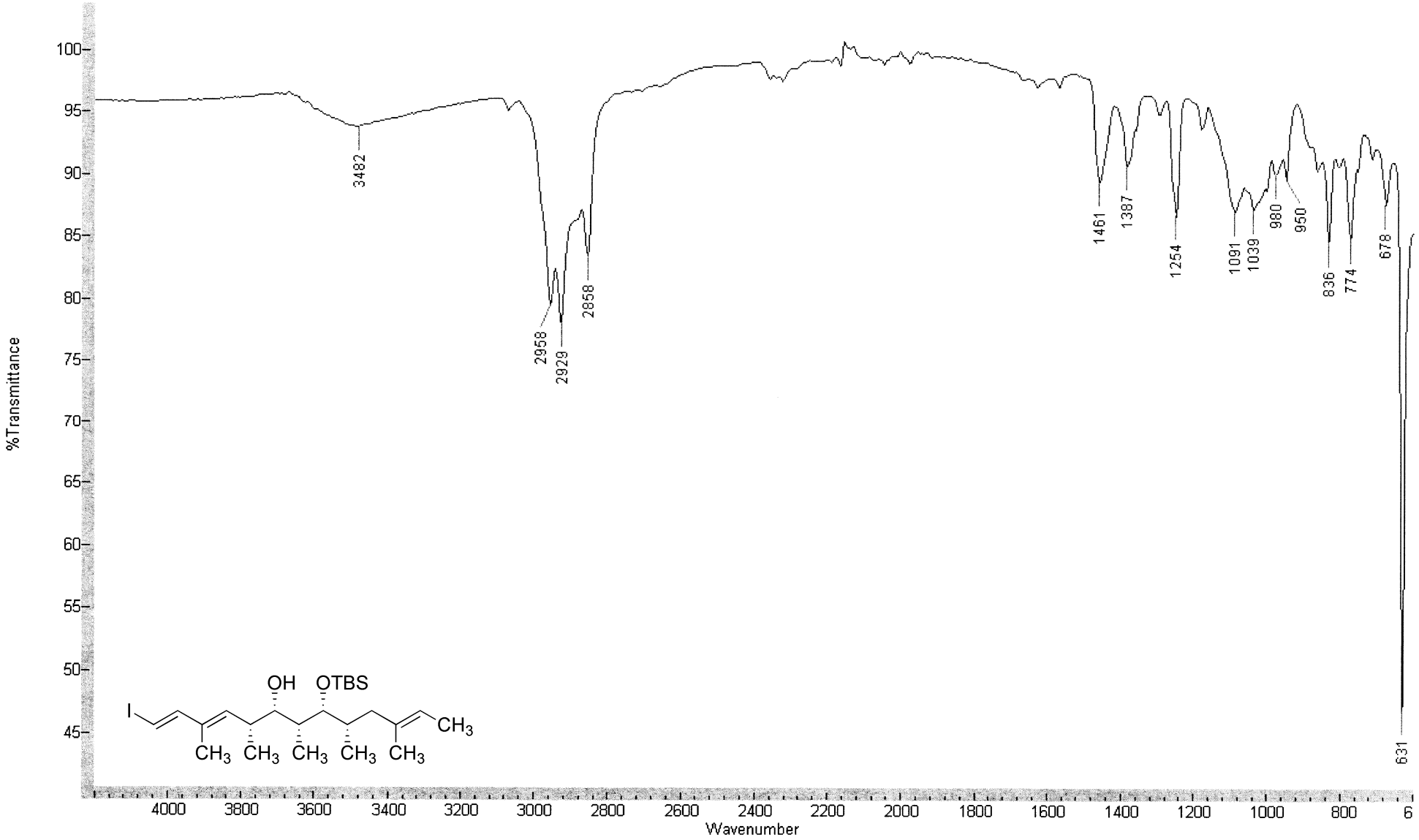
Elemental Composition Report

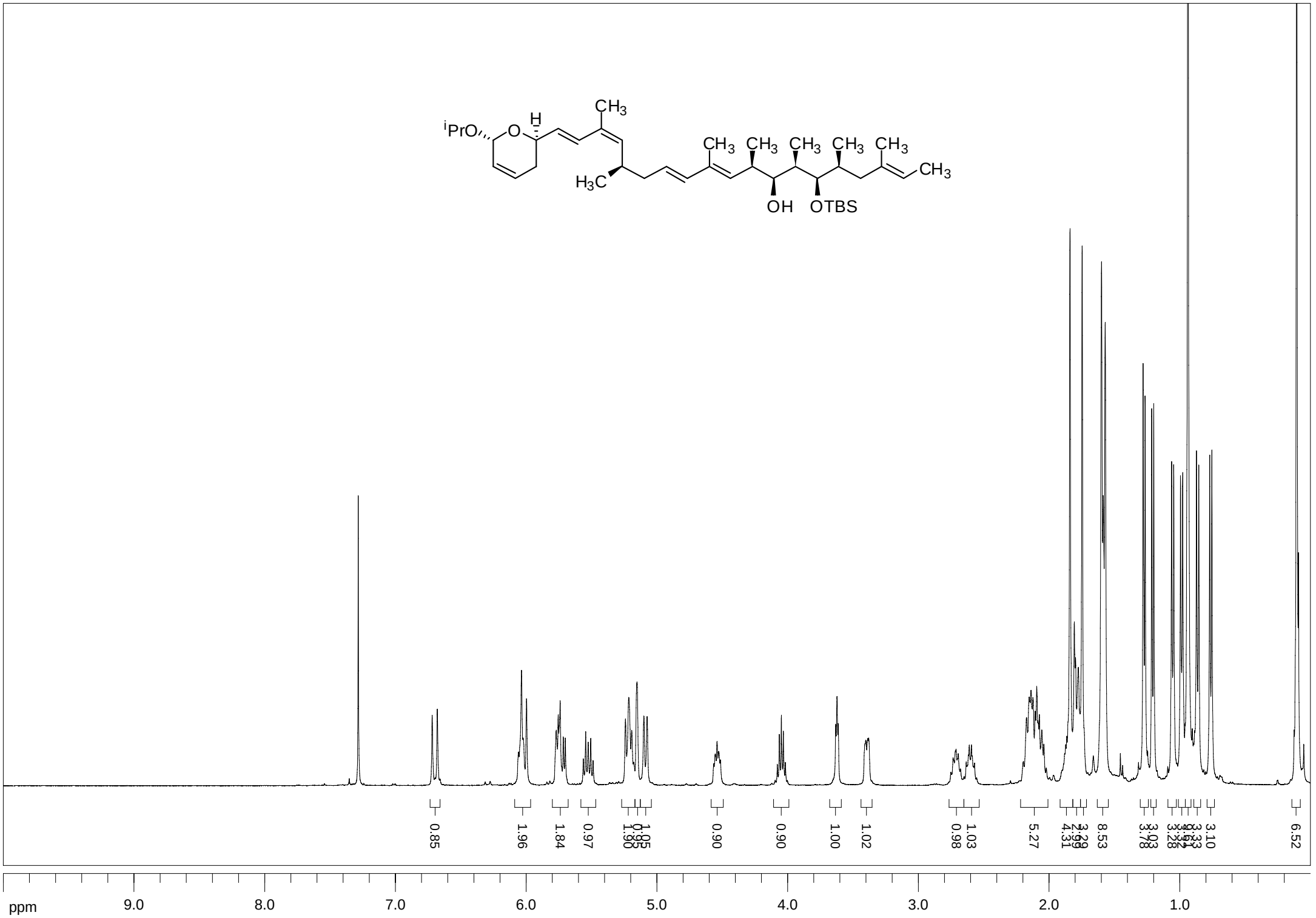
Single Mass Analysis (displaying only valid results)
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
1116 formula(e) evaluated with 5 results within limits (up to 50 closest results for each mass)



Minimum:				-1.5	
Maximum:		200.0	2.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
543.2133	543.2131	0.2	0.3	2.5	C24 H45 O2 Na Si I
	543.2136	-0.3	-0.6	-0.5	C18 H39 O18
	543.2141	-0.7	-1.4	-1.5	C17 H43 O15 Si2
	543.2124	0.9	1.7	10.5	C30 H40 O I


%Transmittance
100
95
90
85
80
75
70
65
60
55
50
45
3482
2958
2929
2858
1461
1387
1254
1091
1039
980
950
836
774
678
631
OH
OTBS
I
CH3
CH3
CH3
CH3
CH3
CH3
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber


iPrO
O
H
CH3
H3C
CH3 CH3 CH3 CH3 CH3
CH3
OH
OTBS
0.85
1.96
1.84
0.97
1.90
0.90
0.90
1.00
1.02
0.98
1.03
5.27
4.31
8.53
3.78
3.10
6.52
ppm
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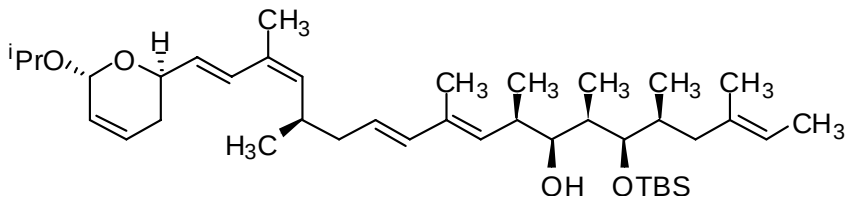
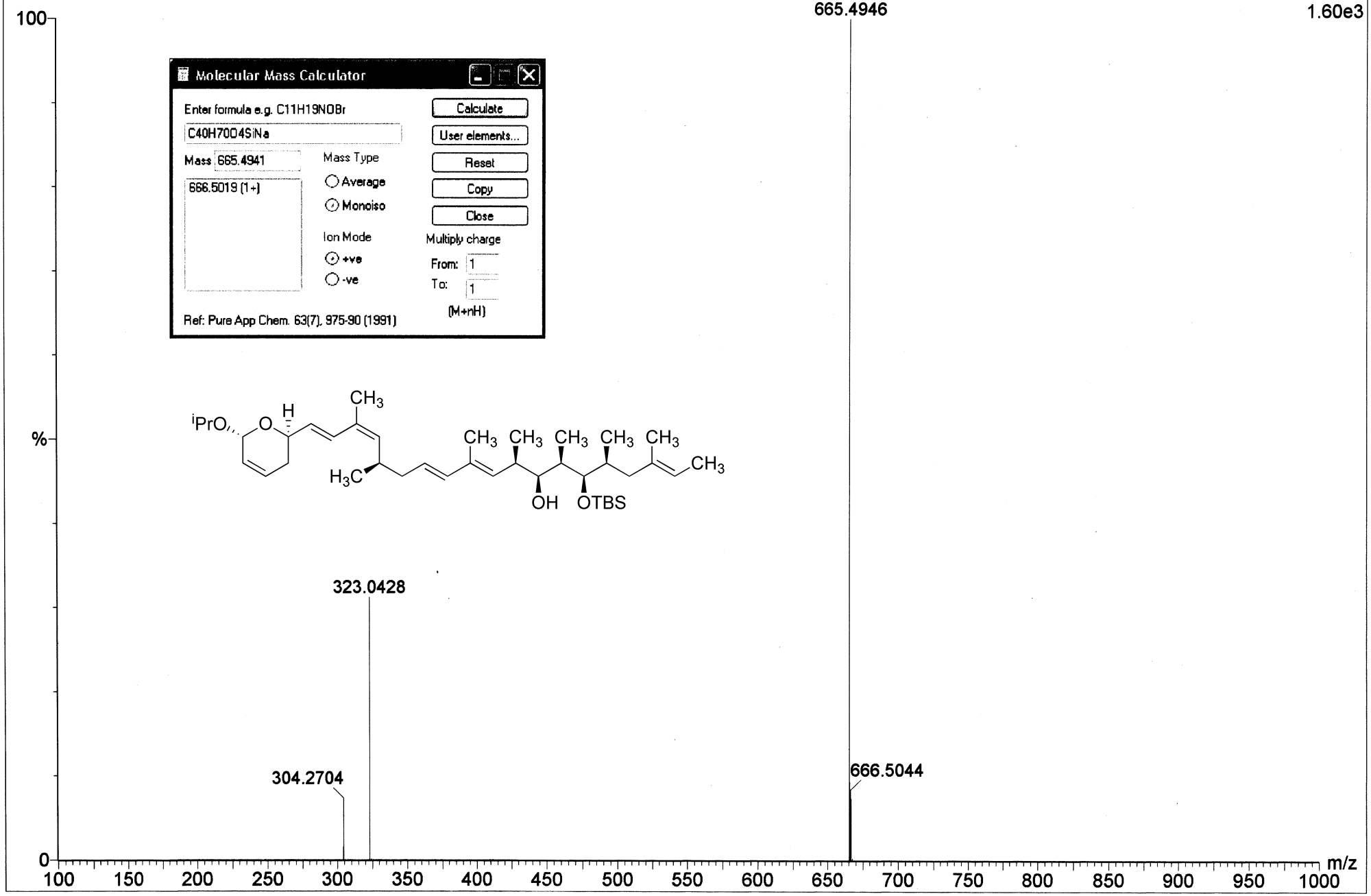
5.0
4.0
3.0
2.0
1.0


iPrO
O
H
CH3
H3C
CH3 CH3 CH3 CH3 CH3
CH3
OH
OTBS

ppm
200
150
100
50
0

GADEMANN_BONAZZI_010607_SB 375 2 (0.048) Cm (1:6)

TOF MS ES+
1.60e3



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C40H70O4SiNa

Mass 665.4941

666.5019 (1+)

Mass Type
- Average
- Monoiso

Ion Mode
- +ve
- -ve

Multiply charge
From: 1
To: 1
(M+nH)

Calculate | User elements... | Reset | Copy | Close

Ref: Pure App Chem. 63(7), 975-90 (1991)

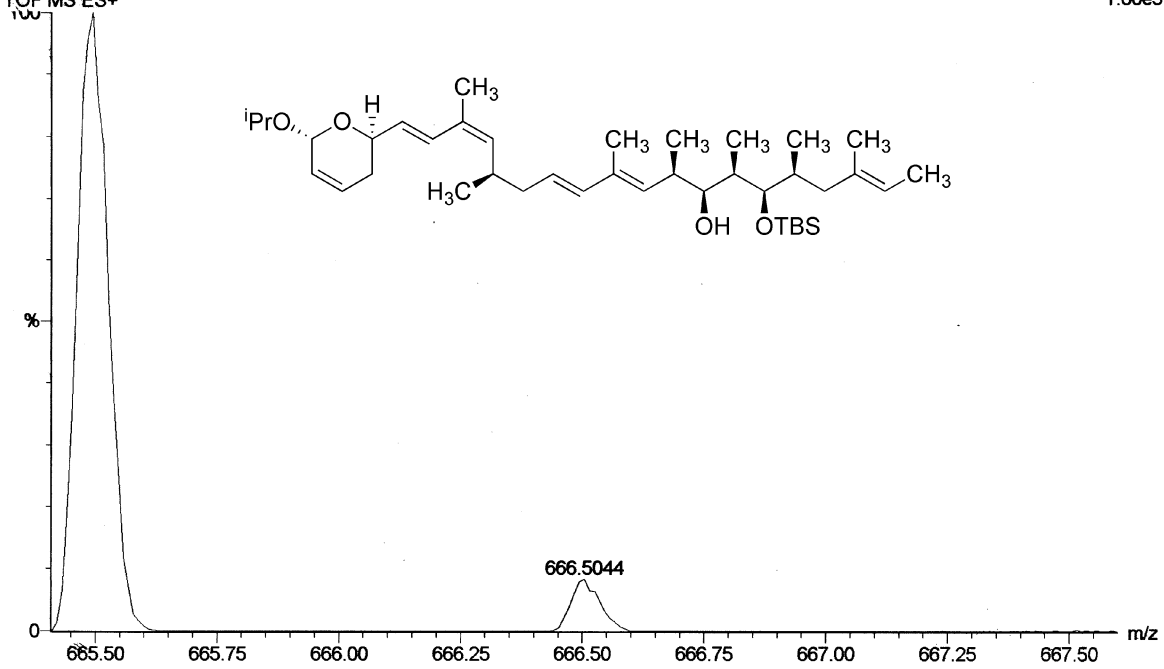
Elemental Composition Report

Single Mass Analysis (displaying only valid results)

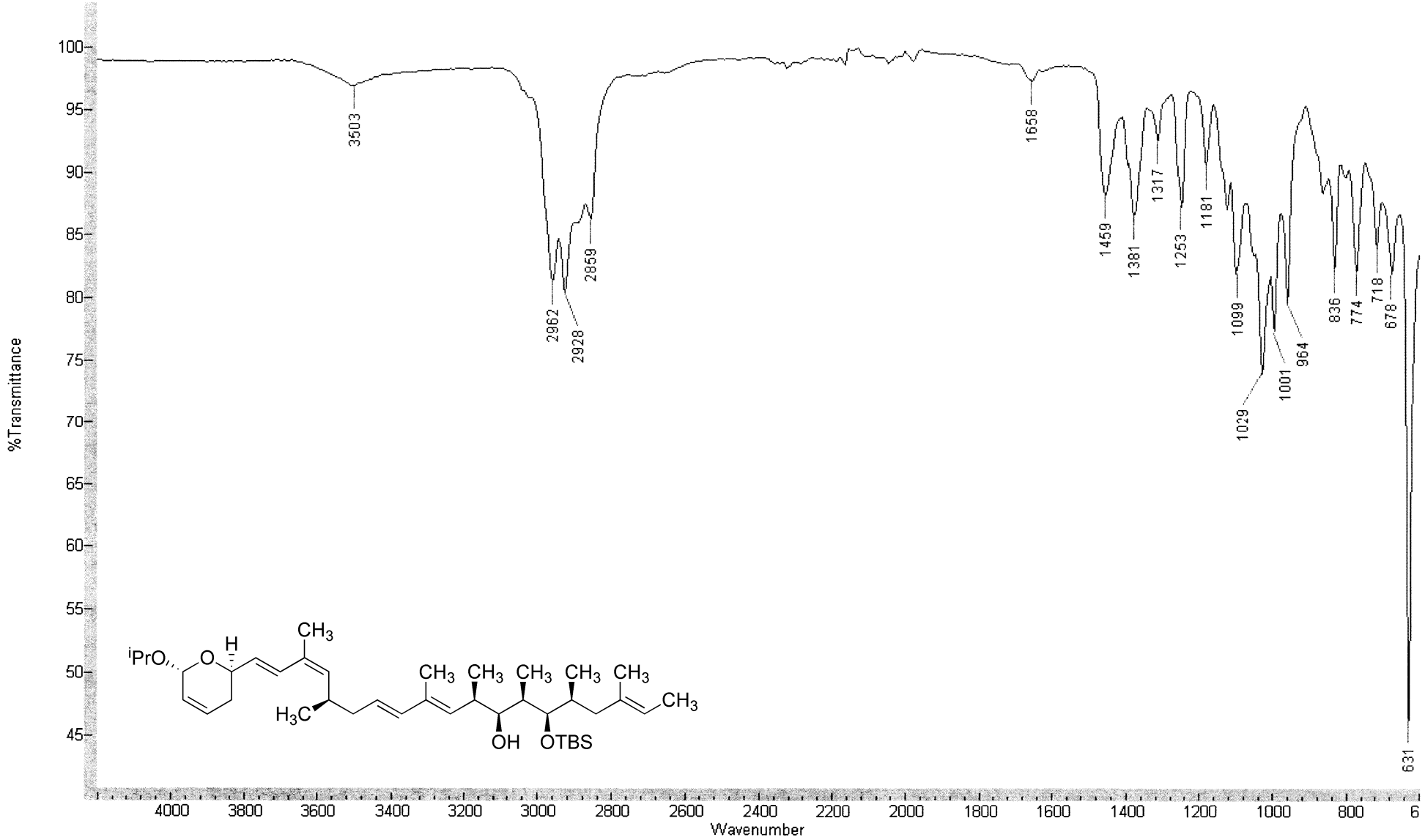
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
1503 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

GADEMANN_BONAZZI_010607_SB 375 2 (0.048) Cm (1:6)
TOF MS ES+ 1.60e3



Minimum:				-1.5	
Maximum:		200.0	2.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
665.4946	665.4941	0.5	0.7	6.5	C40 H70 O4 Na Si
	665.4938	0.8	1.2	13.5	C45 H69 Si2
	665.4934	1.2	1.8	14.5	C46 H65 O3


%Transmittance
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95
90
85
80
75
70
65
60
55
50
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2962
2928
2859
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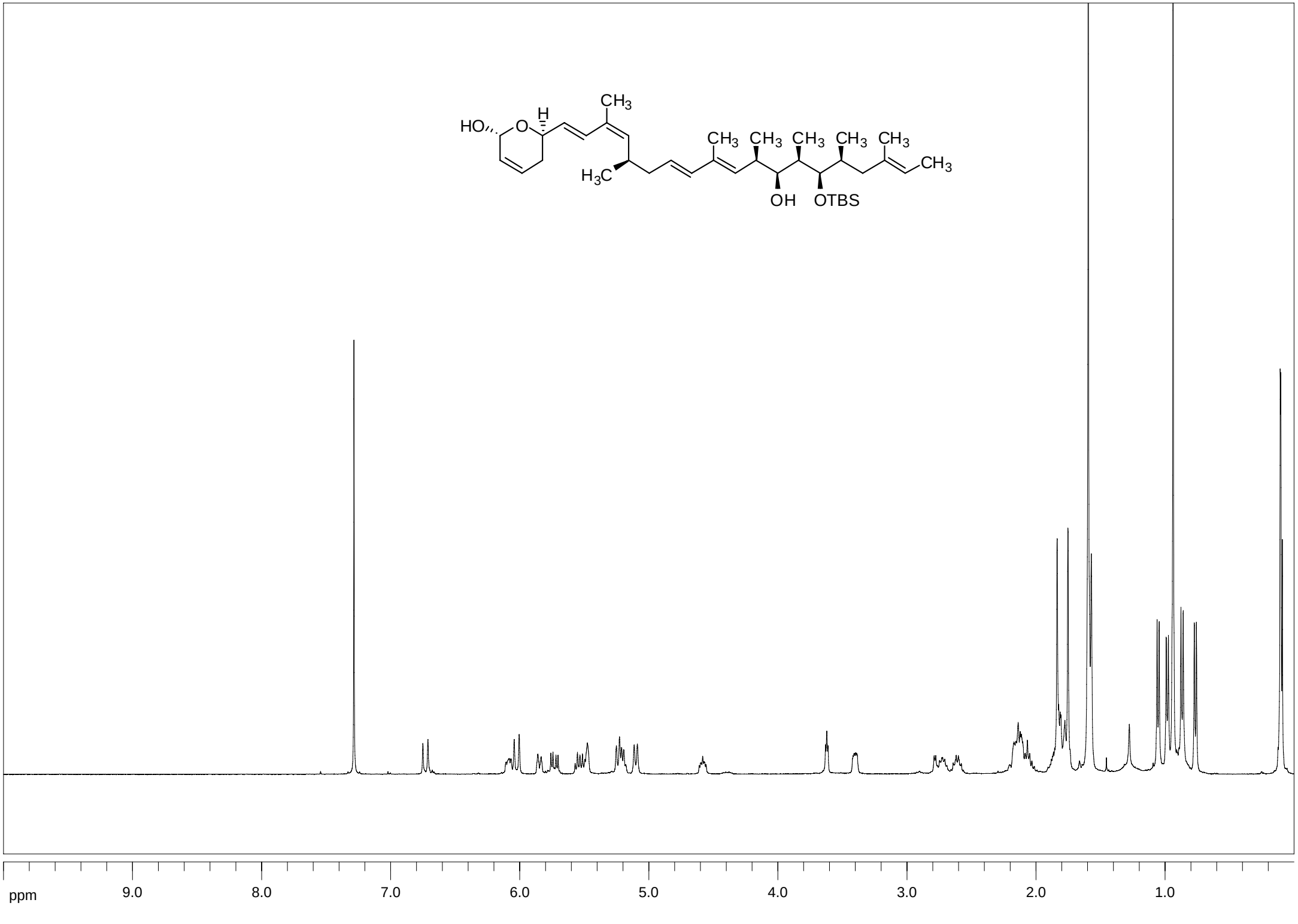
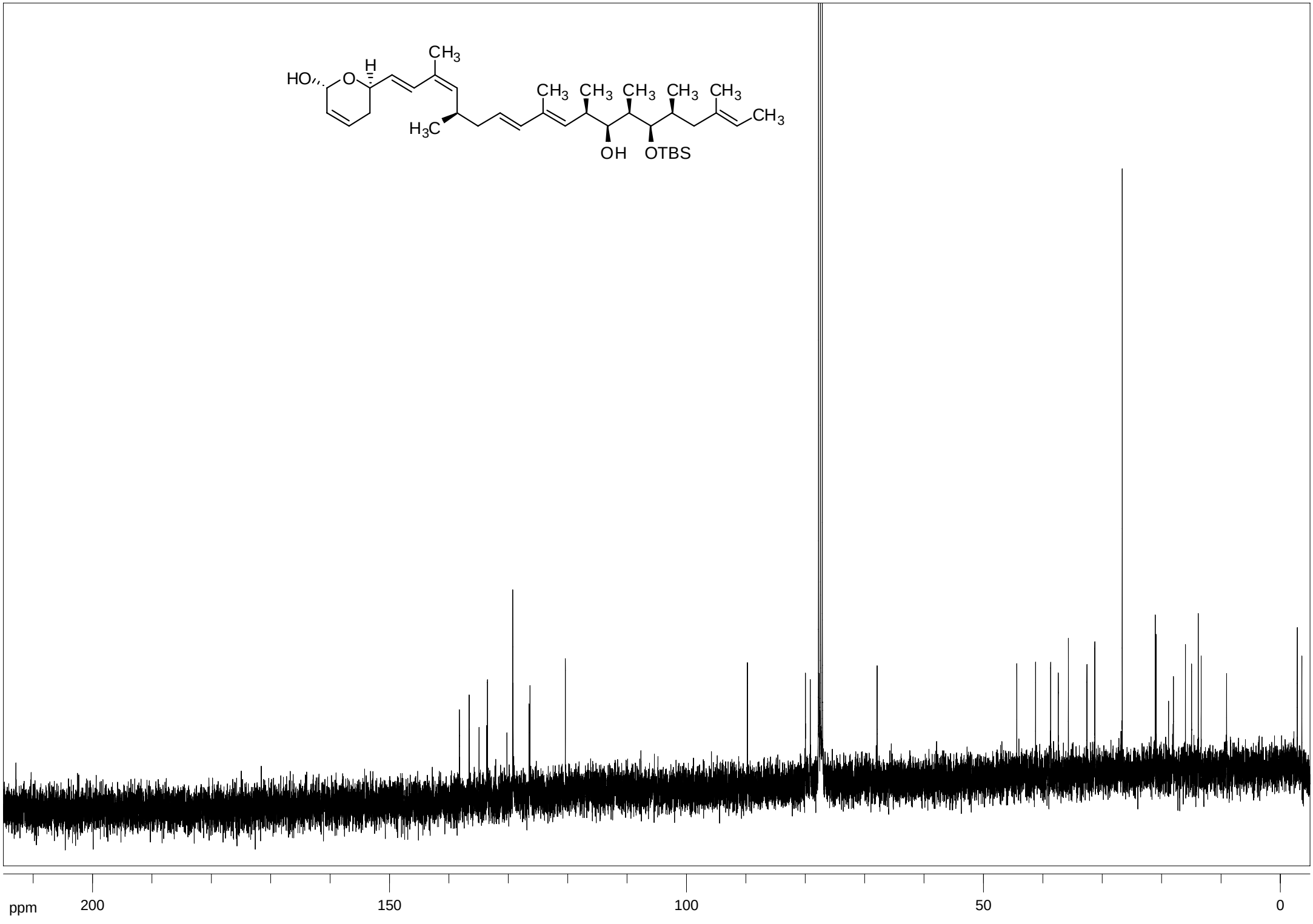
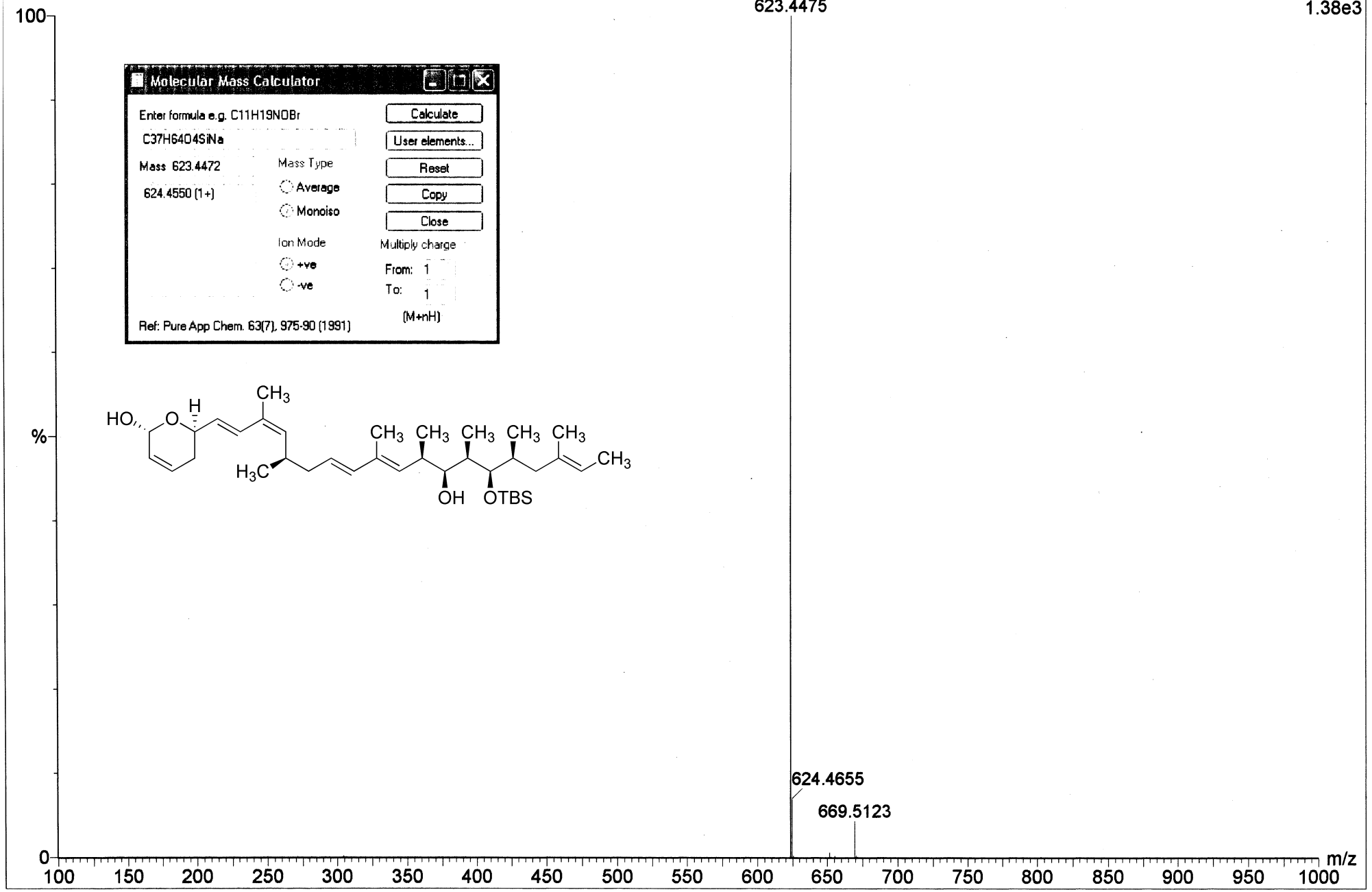
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber
iPrO
O
H
CH3
H3C
CH3
CH3
CH3
CH3
CH3
CH3
OH
OTBS


HO
O
H
CH3
H3C
CH3 CH3 CH3 CH3 CH3
CH3
OH
OTBS
ppm
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


HO
O
H
CH3
H3C
CH3
CH3
CH3
CH3
CH3
CH3
OH
OTBS
ppm
200
150
100
50
0

GADEMANN_BONAZZI_040607_SB376_FR4 3 (0.068) Cm (3:9)

TOF MS ES+
1.38e3



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C37H64O4SiNa

Mass 623.4472

624.4550 (1+)

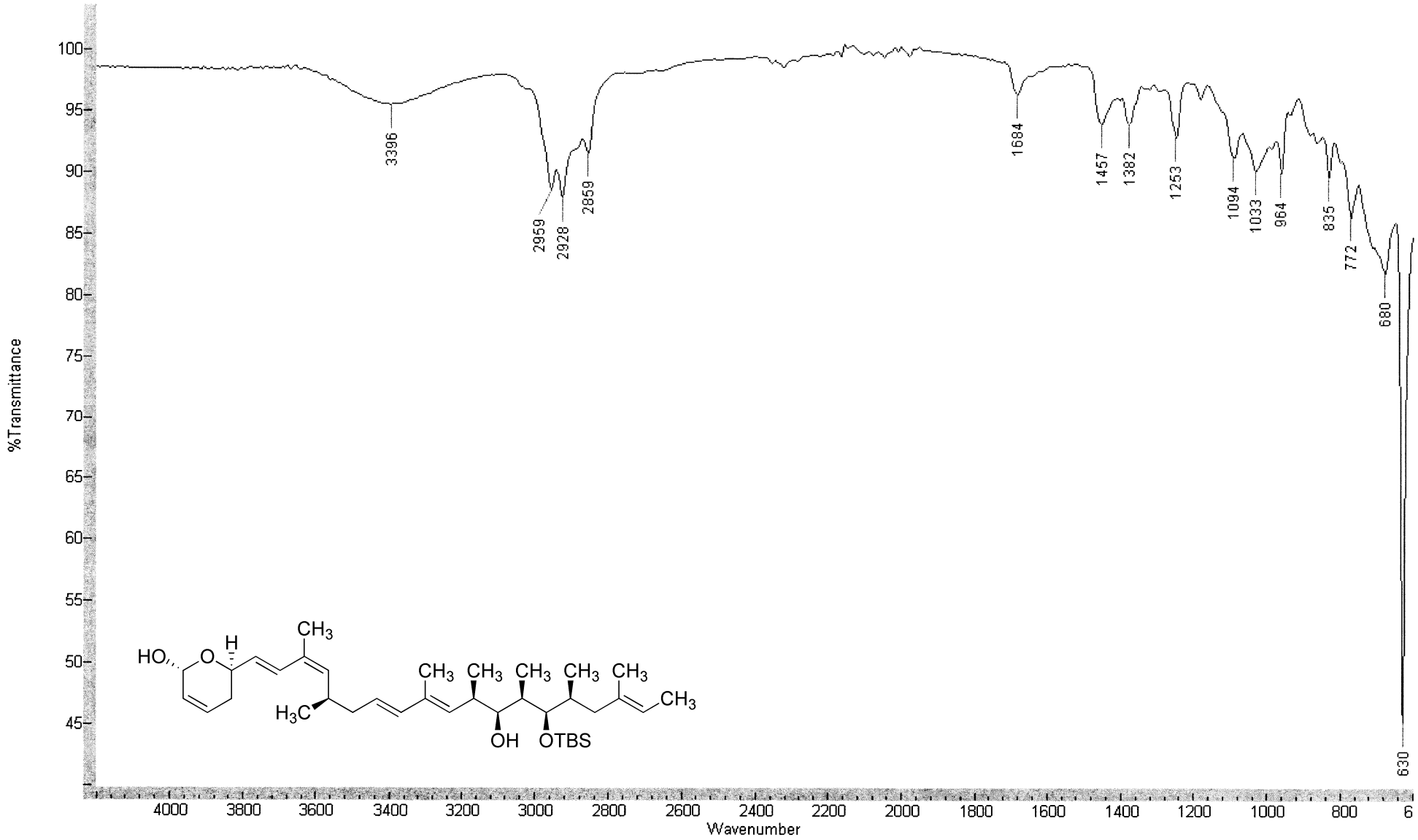
Mass Type
Average
Monoiso

Ion Mode
+ve
-ve

Multiply charge
From: 1
To: 1
(M+nH)

Calculate
User elements...
Reset
Copy
Close

Ref: Pure App Chem. 63(7), 975-90 (1991)


%Transmittance
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90
85
80
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70
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50
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3396
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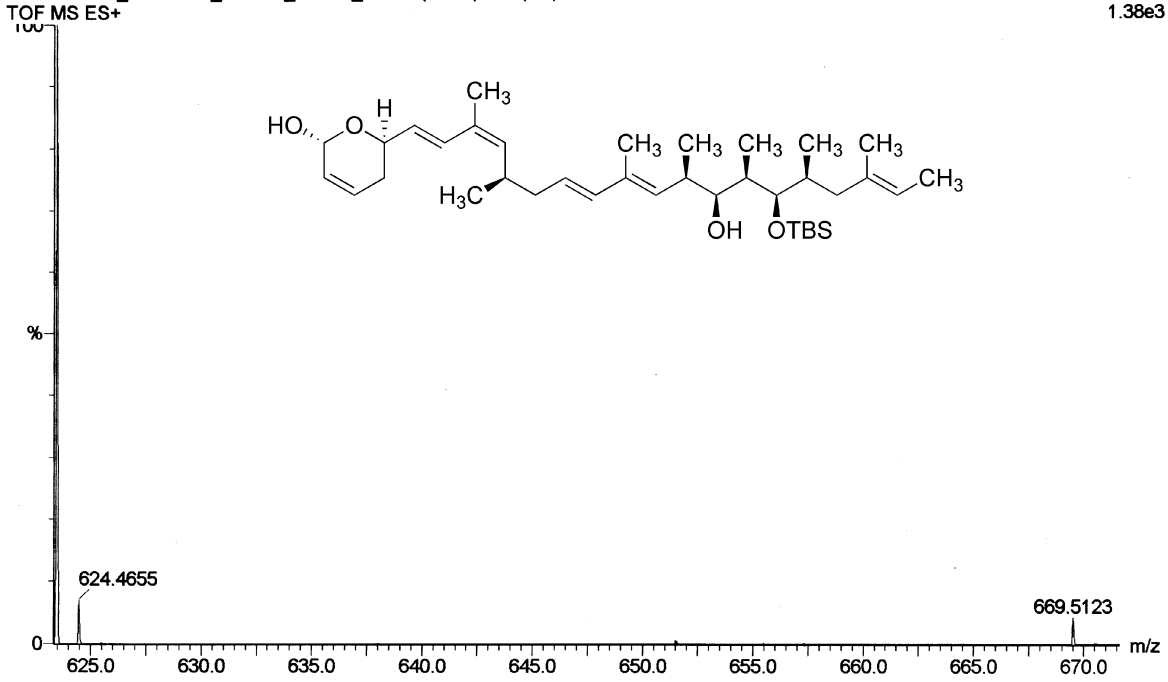
2928
2859
1684
1457
1382
1253
1094
1033
964
835
772
680
630
HO
O
H
CH3
H3C
CH3
CH3
CH3
CH3
CH3
CH3
OH
OTBS
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber

Single Mass Analysis (displaying only valid results)
Tolerance = 2.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
1356 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)

GADEMANN_BONAZZI_040607_SB376_FR4 3 (0.068) Cm (3:9)
TOF MS ES+ 1.38e3



Minimum:				-1.5	
Maximum:		200.0	2.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
623.4475	623.4472	0.4	0.6	6.5	C37 H64 O4 Na Si
	623.4468	0.7	1.1	13.5	C42 H63 Si2
	623.4464	1.1	1.7	14.5	C43 H59 O3


O
O
H
CH3
CH3
CH3
CH3
CH3
CH3
CH3
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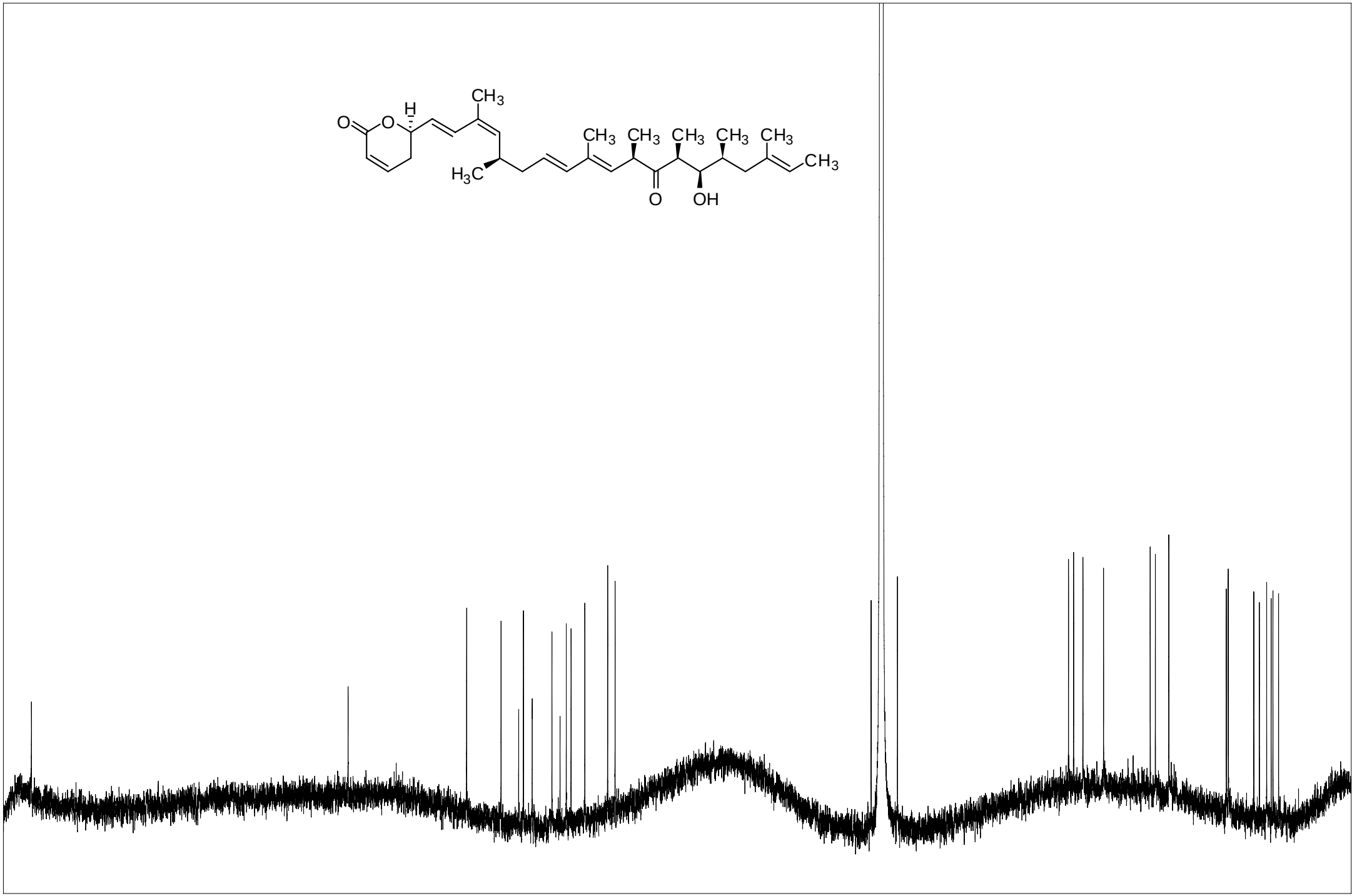
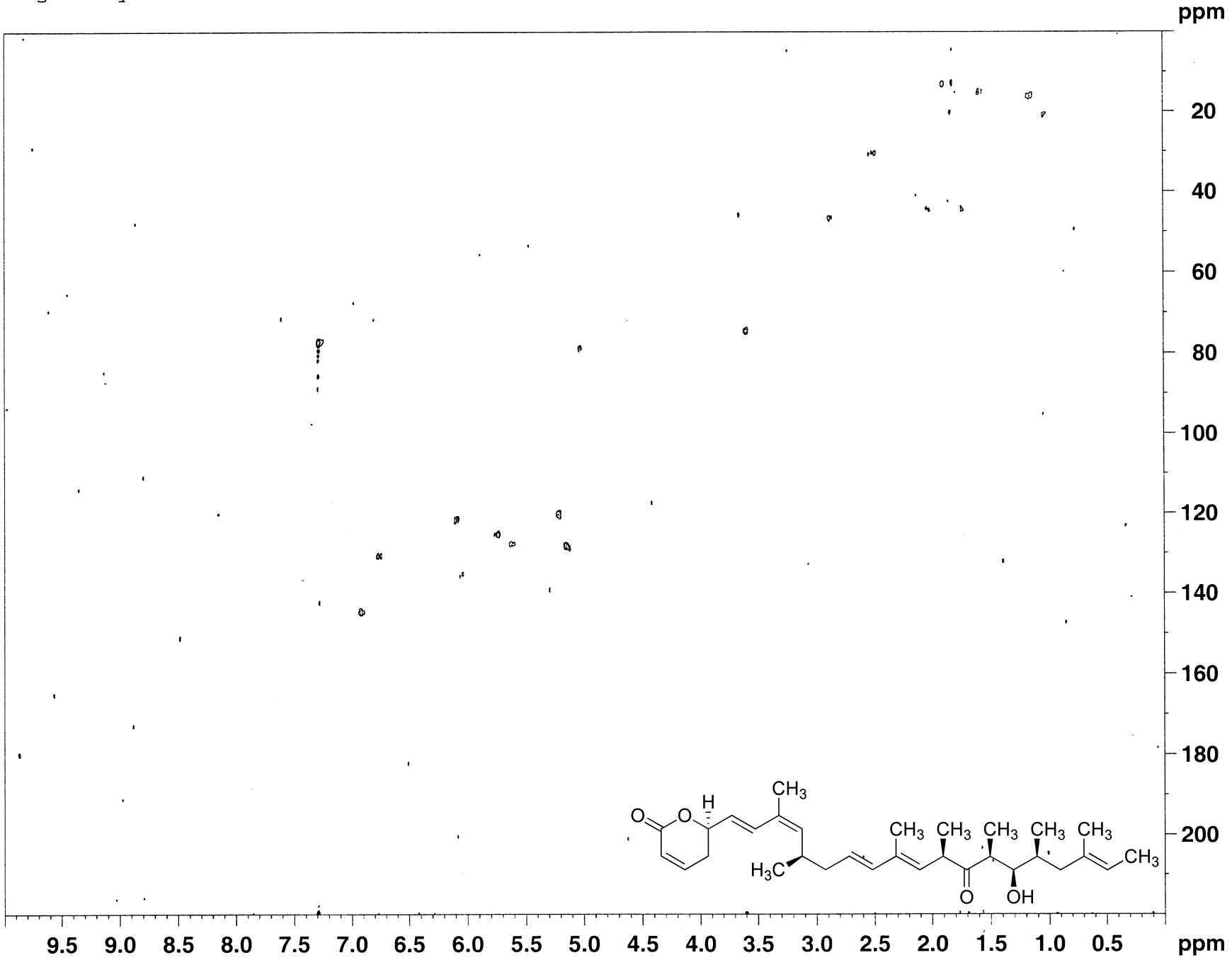
6.0
5.0
4.0
3.0
2.0
1.0


O
O
H
CH3
H3C
CH3
CH3
CH3
CH3
CH3
CH3
O
OH
ppm
200
150
100
50

Anguinomycin C



Current Data Pa
NAME
EXPNO
PROCNO

F2 - Acquisitio
Date_
Time
INSTRUM
PROBHD 5 mm C
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ 0
RG
DW
DE
TE
CNST2 145
d0 0.
D1 3.
d4 0.
d11 0.
d13 0.
D16 0.
DELTA 0.
DELTA1 0.
DELTA2 0.
IN0 0.
MCREST 0.
MCWRK 3.

======== CHANNE
NUC1
P1
p2
PL1
SFO1 600

======== CHANNE
CPDPRG2
NUC2
P3
p4
PCPD2
PL2
PL12
SFO2 150

====== GRADIENT
GPNAM1
GPNAM2
GPNAM3
GPX1
GPX2
GPX3
GPY1
GPY2
GPY3
GPZ1
GPZ2
GPZ3
P16

F1 - Acquisitic
ND0
TD
SFO1
FIDRES 1
SW
FnMODE

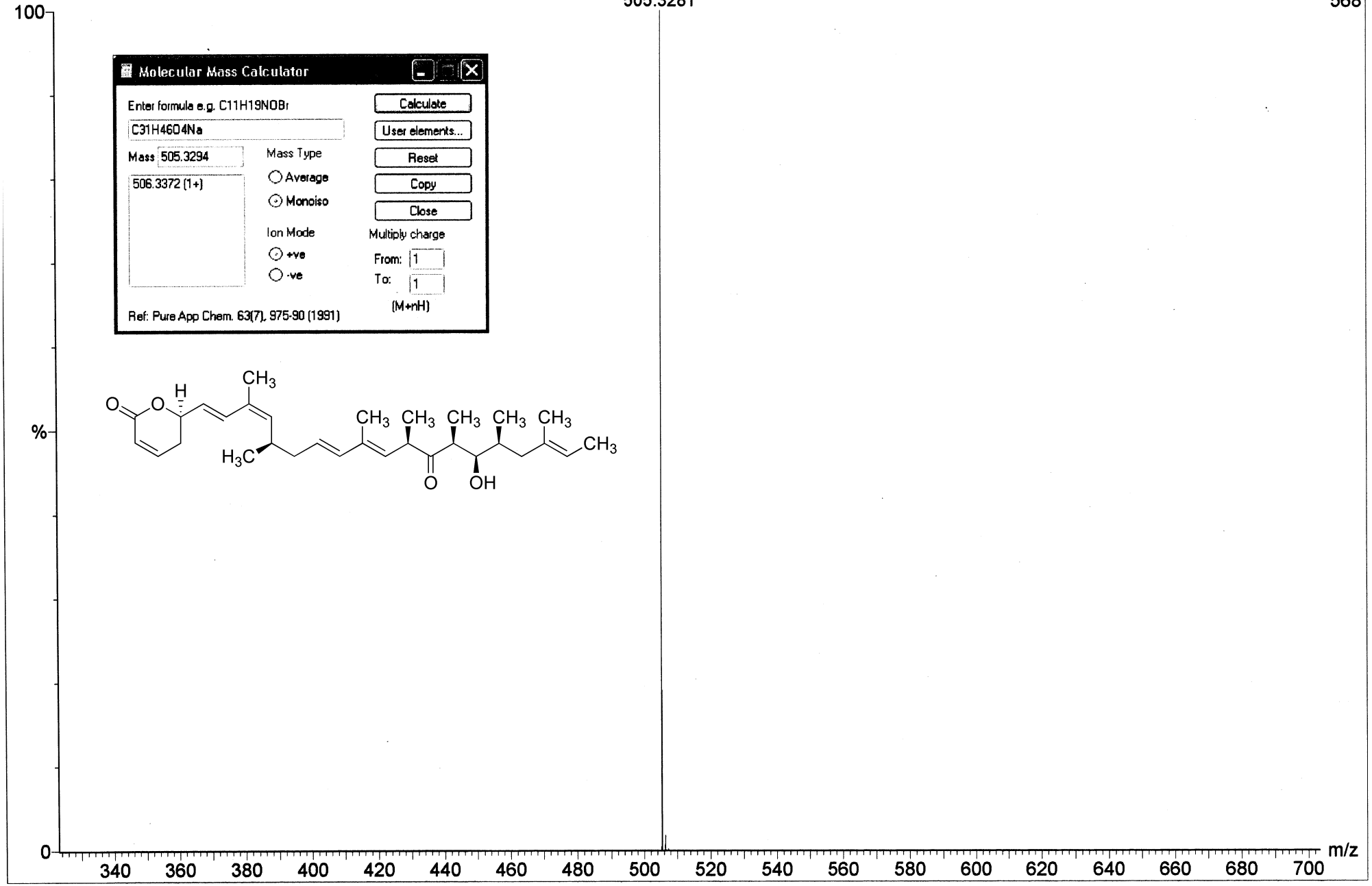
F2 - Processing
SI
SF 600
WDW
SSB
LB
GB
PC

F1 - Processing
SI
MC2
SF 150
WDW
SSB
LB
GB

GADEMANN_BONAZZI_180607_SB 381 146 (2.989) Cm (142:147)

TOF MS ES+
568

505.3281



Molecular Mass Calculator

Enter formula e.g. C11H19NOBr

C31H46O4Na

Mass 505.3294

506.3372 (1+)

Mass Type
Average
Monoiso

Ion Mode
+ve
-ve

Calculate
User elements...
Reset
Copy
Close

Multiply charge
From: 1
To: 1
(M+nH)

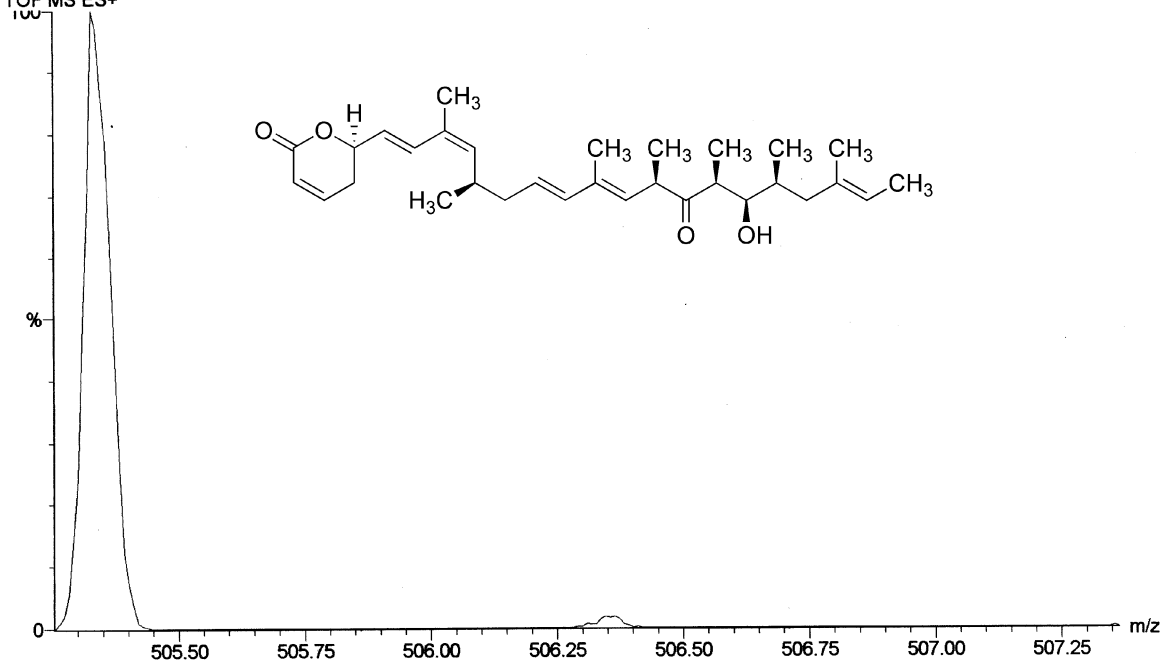
Ref: Pure App Chem. 63(7), 975-90 (1991)

Elemental Composition Report

Single Mass Analysis (displaying only valid results)
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Isotope matching not enabled

Monoisotopic Mass, Odd and Even Electron Ions
991 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

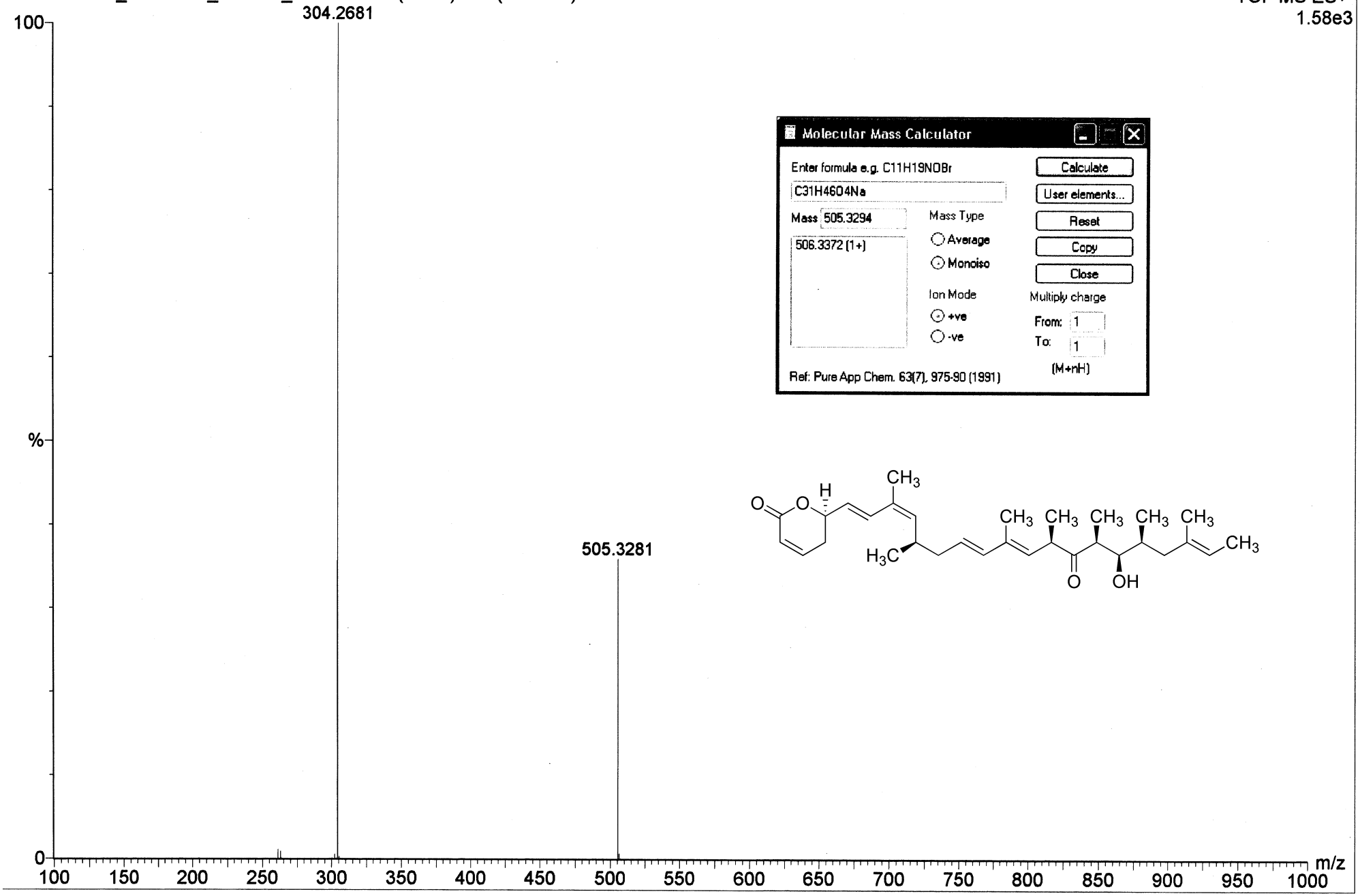
GADEMANN_BONAZZI_180607_SB 381 146 (2.989) Cm (142:147)
TOF MS ES+

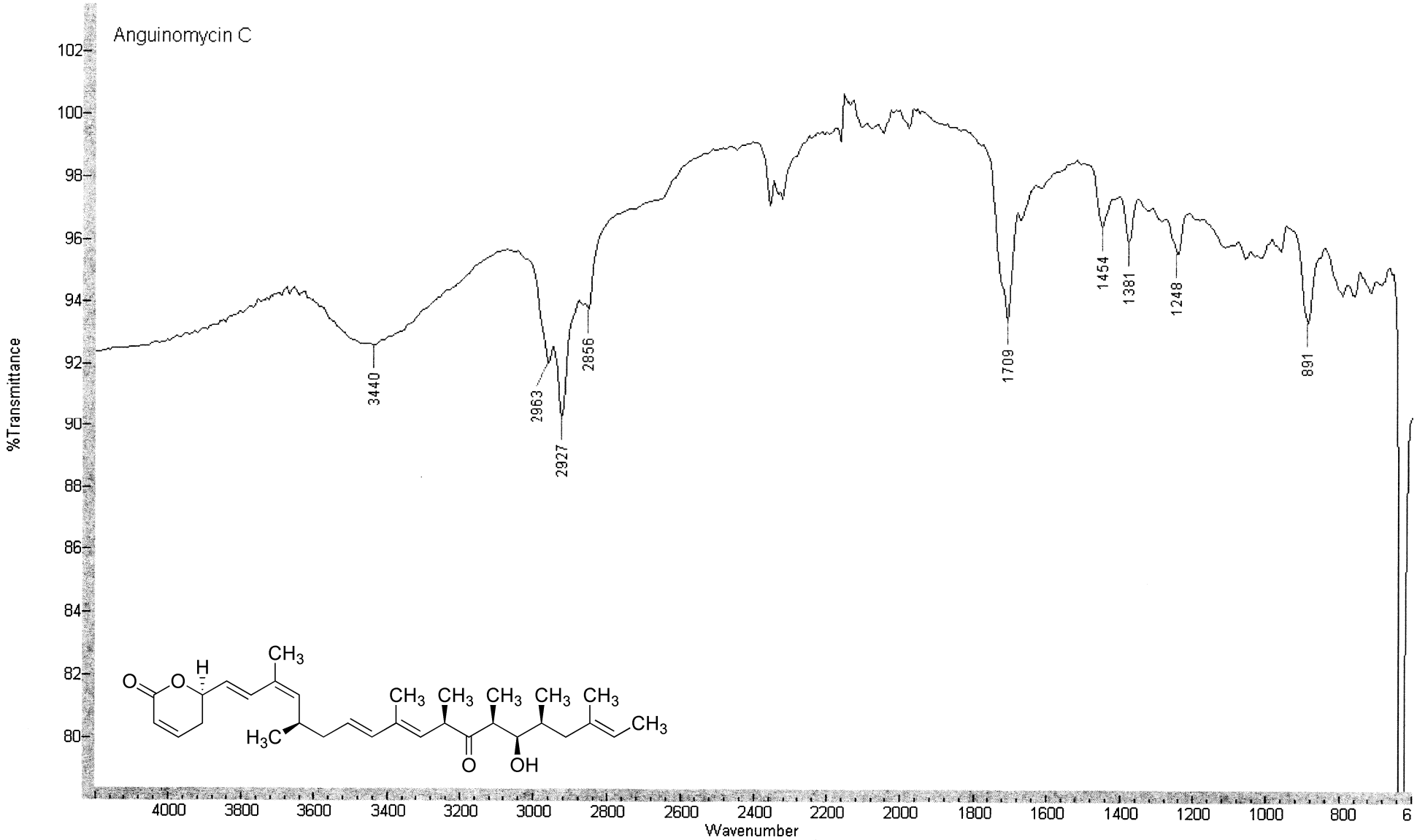


Minimum:				-1.5	
Maximum:		200.0	3.0	50.0	
Mass	Calc. Mass	mDa	PPM	DBE	Formula
505.3281	505.3291	-1.0	-2.0	15.5	C36 H45 Si
	505.3270	1.0	2.0	0.5	C27 H54 I
→	505.3294	-1.3	-2.6	8.5	C31 H46 O4 Na
	505.3266	1.4	2.8	12.5	C34 H46 Na Si

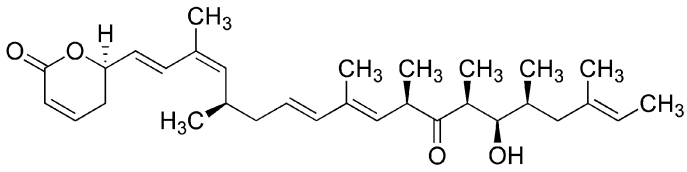
GADEMANN_BONAZZI_180607_SB 381 146 (2.989) Cm (142:147)

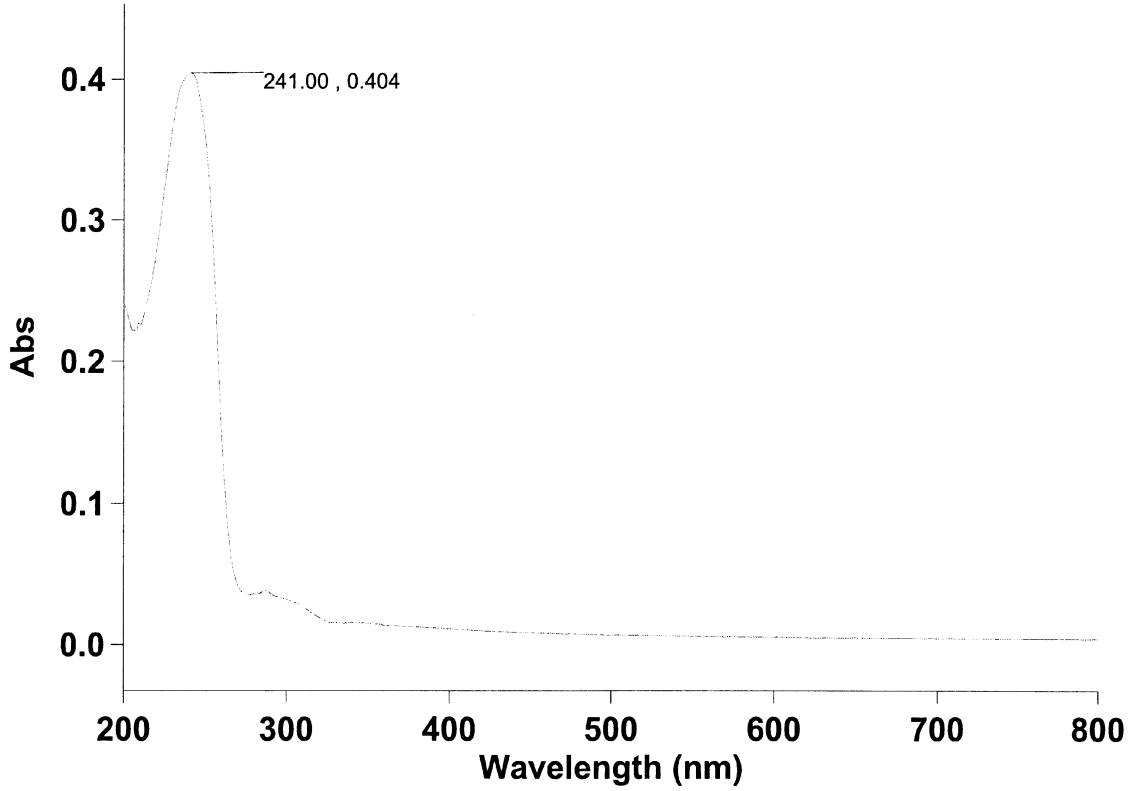
TOF MS ES+
1.58e3




Anguinomycin C
%Transmittance
102
100
98
96
94
92
90
88
86
84
82
80
3440
2963
2927
2856
1709
1454
1381
1248
891
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
6
Wavenumber
O
O
H
CH3
H3C
CH3
CH3
CH3
CH3
CH3
CH3
O
OH

EPFL BCH
Instrument Serial Number EL96053143





Scan Analysis Report

Report Time : lun. 09 juil. 07:06:17 PM 2007
Batch: D:\Gademann group\LSYNC\Simone\Anguinomycin C.BSW
Software version: 3.00(182)
Operator: Simone

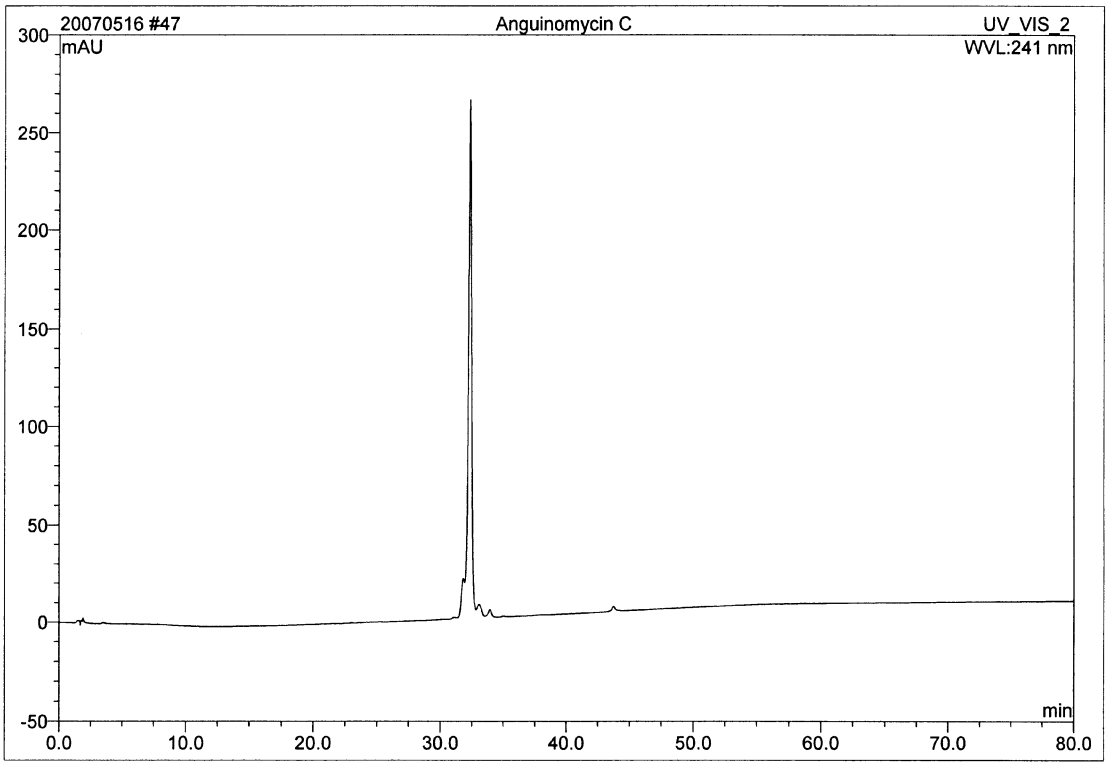
Sample Name: Anguinomycin_2

Collection Time	09.07.2007 11:17:42
Peak Table	
Peak Style	Peaks
Peak Threshold	0.0100
Range	800.00nm to 200.00nm

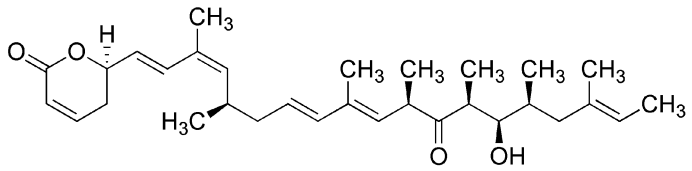
Wavelength (nm)	Abs
241.00	0.404

47 Anguinomycin C

Sample Name:	**Anguinomycin C**	*Injection Volume:*	**25.0**
Vial Number:	**GA13**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**241**
Control Program:	**simone3**	*Bandwidth:*	**1**
Quantif. Method:	**delay ms**	*Dilution Factor:*	**1.0000**
Recording Time:	**7/10/2007 8:45**	*Sample Weight:*	**1.0000**
Run Time (min):	**80.00**	*Sample Amount:*	**1.0000**



Analytical HPLC: Rt = 32.35 minutes (C18, 60%-100% MeOH in 50 minutes)



47 Anguinomycin C

Sample Name:	**Anguinomycin C**	*Injection Volume:*	**25.0**
Vial Number:	**GA13**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Mass Range:*	**n.a.**
Control Program:	**simone3**	*Polarity:*	**n.a.**
Quantif. Method:	**delay ms**	*Dilution Factor:*	**1.0000**
Recording Time:	**7/10/2007 8:45**	*Sample Weight:*	**1.0000**
Run Time (min):	**80.00**	*Sample Amount:*	**1.0000**