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Supporting Information

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Supporting Information for:

Synthesis of Octalactin A by a Strategic Vanadium-Catalyzed Oxidative Kinetic Resolution

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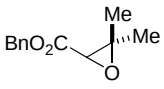
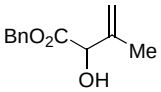
I. Materials and Methods. All commercially available reagents were purchased from suppliers and used without purification unless otherwise noted. Diethyl ether (Et_2O), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), and toluene were dried according to the method of Grubbs[1] as modified by Bergman.[2] Dimethylsulfoxide (DMSO) and pyridine were purchased from Aldrich in Sure-Seal bottles. Acetone for the vanadium-catalyzed asymmetric oxidation reactions was used as received from EMD Chemicals. Chiral ligand (S)- and (R)-**1** were prepared by condensation of the corresponding aldehydes and amino alcohols in methanol.[3] Iodosobenzene was prepared from $PhI(OAc)_2$ by basic hydrolysis.[4] Pd/C(en) was prepared according to the method of Hirota.[5] Diisopropenylzinc was prepared by the method described by Soai.[6] Oxygen and nitrogen atmospheres were maintained via a Tygon gas line vented through an oil bubbler. Argon and hydrogen atmospheres were maintained via balloon pressure. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F_{254} TLC plates. Flash column chromatography was carried out on Merck 60 silica gel (32-63 μm). ^1H and ^{13}C NMR spectra were recorded with Bruker AVB-400, AVQ-400, and AV-300 spectrometers and referenced to $CHCl_3$ (7.26 ppm) unless otherwise noted. Analytical chiral HPLC was performed with a Shimadzu VP Series Chiral HPLC with detection at 210, 254, and 280 nm using Chiralcel OJ and OD columns. Analytical GC was carried out with a Hewlett Packard HP 6850 GC equipped with an Agilent DB-WAX (30.0 m x 0.25 mm) column for achiral separation and a Chiraldex G-TA (30.0 m x 0.25 mm) column for chiral separation. $[\alpha]^{T°C}_D$ (c = g/mL, in $CHCl_3$) were measured on Perkin-Elmer 241 polarimeter using a quartz cell (l = 10 cm), with high-pressure sodium lamp (λ = 589 nm). Mass spectral and microanalysis data were obtained from the Micro-Mass Facility operated by the College of Chemistry, University of California, Berkeley.

II. Procedures and Analytical Data



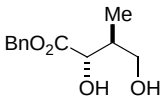
S1

Darzens condensation. In a flame-dried, nitrogen-purged 1-L three-neck flask, benzyl chloroformate (19.0 mL; 125 mmol) and freshly distilled acetone (11.0 mL; 150 mmol) were dissolved in anhydrous THF (425 mL). The solution was cooled to -78 ºC. A -78 ºC solution of potassium *tert*-butoxide (15.7 g; 140 mmol) in dry THF (200 mL) was added dropwise via cannula over 1.5 h. The reaction was maintained at -78 ºC for an additional 1.5 h with stirring. The reaction was quenched by the addition of 3.0 mL of acetic acid at -78 ºC and warmed to room temperature. The reaction mixture was diluted with half-saturated aqueous $NaHCO_3$ solution, transferred to a separatory funnel and partitioned. The aqueous layer was extracted with EtOAc (3 x 100 mL), then the combined organic layers were washed with brine (250 mL), dried ($MgSO_4$), filtered and concentrated. The residue was chromatographed on silica (3:1 Hex:Et_2O) to afford **S1** as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.32 (m, 5H), 5.23 (d, J = 21.2 Hz, 1H), 5.19 (d, J = 21.2 Hz, 1H), 3.38 (s, 1H), 1.41 (s, 3H), 1.36 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.4, 135.2, 128.6, 128.5, 67.0, 60.4, 59.3, 24.3, 18.2 ppm; IR (thin film) 2968, 1749, 1726, 1186, 1118, 748, 679 cm $^{-1}$; Anal. Calc'd, C: 69.88, H: 6.84; Found, C: 69.81, H: 6.74.



7

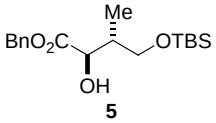
Acid catalyzed rearrangement. Glycidyl ester **S1** (3.38 g, 16.4 mmol) and 10-camphorsulfonic acid (0.76 g, 3.3 mmol) were dissolved in dry toluene (30 mL) and the mixture was heated to reflux for 2.5 h. The mixture was then cooled to 0 ºC to induce crystallization of camphorsulfonic acid, then filtered over a glass frit. The filtrate was diluted with EtOAc (250 mL) and washed with sat. $NaHCO_{3(aq)}$ (2 x 100 mL). The combined aqueous washes were back extracted with EtOAc (1 x 100 mL) and the combined organic layers were washed with brine (150 mL), dried ($MgSO_4$), filtered and concentrated. The crude product was purified by Kugelrohr bulb-to-bulb distillation to afford **7** as a colorless oil (2.76 g, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.33 (m, 5H), 5.13 (app s, 2H), 5.03 (t, J = 1.4 Hz, 1H), 4.92 (app s, 1H); 4.62 (app s, 1H), 1.71 (t, J = 1.4 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.7, 142.0, 135.4, 128.9, 128.8, 128.5, 115.6, 75.2, 67.9, 18.0 ppm; IR (thin film) 3503, 3035, 2949, 1734, 1190, 1082 cm $^{-1}$; HRMS (FAB) calc'd for $[C_{12}H_{14}O_3 + H]^+$: 207.1023; found: 207.1012.



S2

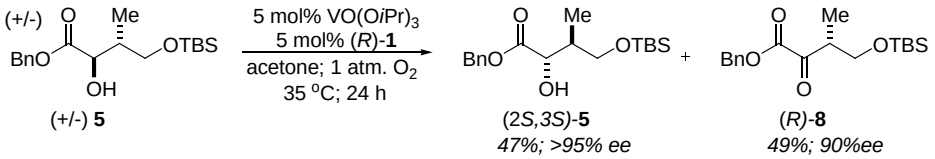
Hydroboration. A solution of 9-BBN (350 mL, 0.5M, 175 mmol) was added via canula to a flame-dried, nitrogen-purged 1-L three-neck flask and diluted with a 200 mL portion of dry THF. To this solution, allylic alcohol **7** (16.27 g, 78.8 mmol) in dry THF (200 mL) was added dropwise via canula

over 30 min during which time gas evolution was observed. The resulting mixture was stirred at room temperature for 5 h, then cooled to 0 ºC and a solution of mCBPA (140 g, 77% wt. reagent, 615 mmol) in 150 mL of THF was added dropwise over 1 h. The resulting mixture was warmed to room temperature and stirred for 20 h. A 750 mL portion of aqueous sodium potassium tartrate solution (0.5 M) was added and the mixture stirred for 3 h. The mixture was transferred to a separatory funnel and partitioned. The aqueous layer was extracted with EtOAc (4 x 150 mL) and the combined organics were washed sequentially with sat. Na_2SO_3 (2 x 250 mL) and sat. $NaHCO_3$ (2 x 250 mL). The combined aqueous washes were back extracted with EtOAc (2 x 150 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (1:1 Hex:EtOAc) to yield the unstable diol **S2**, a colorless oil, as a 10:1 mixture of diastereomers (68 %), which was typically silylated immediately to prevent unwanted decomposition. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.32 (m, 5H), 5.22 (app s, 2H), 4.18 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.65-3.56 (m, 2H), 3.05 (d, *J* = 6.4 Hz, 1H), 2.24 (m, 1H), 0.99 (d, *J* = 7.2 Hz, 3H) ppm.



5

Silylation. Diol **S2** (9.88 g, 44 mmol) was dissolved in dry methylene chloride (450 mL) and cooled to 0 ºC under nitrogen atmosphere. To this solution, imidazole (6.13 g, 90 mmol) and *tert*-butyldimethylsilyl chloride (6.78 g, 45 mmol) were added sequentially. The reaction mixture was warmed to room temperature with stirring overnight. The resulting white suspension was diluted with water (200 mL), and transferred to a separatory funnel. The layers were partitioned and the aqueous phase was extracted with methylene chloride (3 x 100 mL). The combined organic extracts were washed sequentially with 0.5 M aqueous HCl solution (100 mL), saturated aqueous sodium bicarbonate (100 mL), and brine (100 mL), then dried ($MgSO_4$) and concentrated. The residue was purified by silica gel chromatography (5:1 Hex:EtOAc) to yield the title compound as a colorless oil (9.17 g, 62 %), followed by the minor *syn* diastereomer. Characterization data for the major diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.33 (m, 5H), 5.20 (m, 2H), 4.15 (d, *J* = 3.6 Hz, 1H), 3.62-3.55 (m, 2H), 2.22 (m, 1H), 1.00 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.5, 135.5, 128.6, 128.5, 128.4, 73.8, 67.0, 64.8, 38.8, 25.9, 18.4, 13.9, -5.6 (2) ppm; IR (thin film) 3513, 2954, 2929, 2882, 2857, 1734, 1461, 1254, 1094, 837 cm $^{-1}$; HRMS (FAB) calc'd for $[C_{18}H_{30}O_4Si + H]^+$: 339.1992; found: 339.2007. Characterization for the minor diastereomer: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.33 (m, 5H), 5.2 (m, 2H), 4.48 (m, 1H), 3.62-3.55 (m, 2H), 2.17 (m, 1H), 0.89 (s, 9H), 0.75 (d, *J* = 7.2 Hz, 3H), 0.06 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.9, 135.4, 128.6, 128.5, 128.4, 71.2, 67.2, 65.3, 39.0, 25.9, 18.3, 9.9, -5.5 (2) ppm; IR (thin film) 3528, 2955, 2930, 2882, 2857, 1732, 1462, 1253, 1133, 1098, 837 cm $^{-1}$.



Asymmetric Aerobic Oxidation with Ligand (R)-1. To a yellow solution of ligand (R)-**1** (123 mg, 0.37 mmol) in acetone (25 mL) was added $VO(OiPr)_3$ (87 μL, 0.37 mmol) via syringe, at which time the mixture darkened immediately. The reaction vessel was sealed with a rubber septum and fitted with an oxygen gas line vented through an oil bubbler. **CAUTION: Organic solvents under oxygen atmosphere are extremely flammable. Although we have never experienced an accident, caution should always be exhibited to avoid ignition.** The mixture was stirred at room temperature under oxygen for 15 min, then racemic substrate (±)-**5** (2.49 g, 7.36 mmol) was added via syringe as a solution in acetone (5 mL, 2 x 2.5 mL washes). The resulting mixture was warmed to 35 ºC with stirring for 24 h, at which time ^{1}H NMR analysis of an aliquot indicated roughly 50% conversion of starting material. The crude reaction mixture was concentrated by rotary evaporation, and the dark red residue was applied to a silica gel column and chromatographed (20:1 →10:1 hexanes:ethyl ether) to afford to the ketone (R)-**8** (1.22 g, 49 %) followed by (2S,3S)-**5** (1.17 g, 47 %) as lightly colored oils. The alcohol (2S,3S)-**7** thus obtained was found to have an optical rotation: $[\alpha]_D^{23}$ = +7.4 (c = 0.6, $CHCl_3$); the absolute stereochemistry was assigned by analysis of the Mosher's esters as depicted in Figure S1.

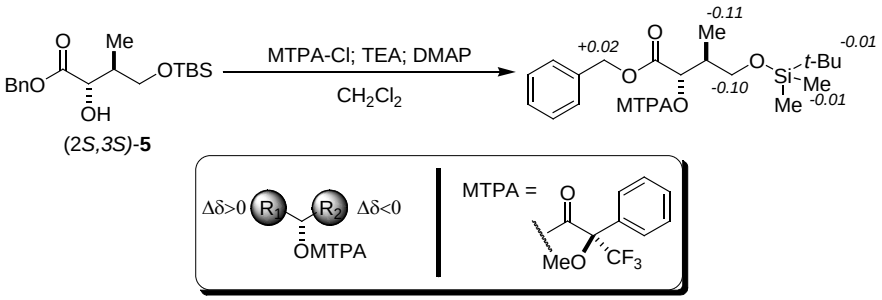
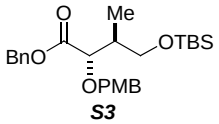


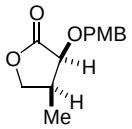
Figure S1. Analysis of Mosher's Ester Derivatives of (2S,3S)-**5**.[7]

Characterization data for ketone (R)-**11**: $[\alpha]_D^{23}$ = -18.7 (c = 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.34 (m, 5H), 5.27 (m, 2H), 3.83-3.75 (m, 2H), 3.50-3.45 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.82 (s, 9H), -0.01 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.8, 161.3, 134.7, 128.7, 128.6, 67.7, 64.8, 45.0, 25.8, 18.2, 12.2, -5.7 ppm + 1 carbon unresolved; IR (thin film) 2953, 2930, 2882, 2857, 1729, 1462, 1255, 1105, 1019, 837 cm $^{-1}$; HRMS (ESI) calc'd for $[C_{18}H_{28}O_4Si + Na]^+$: 359.1655; found: 359.1650.



S3

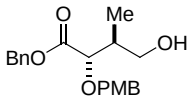
***p*-Methoxybenzyl ether formation**. To a suspension of sodium hydride (60 % wt in mineral oil, 132 mg, 3.3 mmol) in diethyl ether (65 mL) at room temperature was added dropwise via syringe *p*-methoxybenzyl alcohol (4.10 mL, 33.0 mmol). The resulting solution was stirred for 45 min, then cooled to 0 c Trichloroacetonitrile (3.3 mL, 33.0 mmol) was then added dropwise via syringe, and the resulting yellow solution was warmed to room temperature with stirring for 4 h. The crude mixture was concentrated by rotary evaporation to an orange syrup, which was triturated with 65 mL of pentane containing 0.13 mL of methanol for 30 min. The suspension was filtered and the filtrate concentrated to yield the *p*-methoxybenzyl tricholoracetimidate as a colorless oil. This reagent was dried azeotropically with toluene by rotary evaporation (3 x 5 mL) and then dissolved in 40 mL of anhydrous ethyl ether. Alcohol (*2S,3S*)-**5** (4.46 g, 13.2 mmol) was added as a solution in 40 mL of ethyl ether. The resulting solution was cooled to 0 ºC, and trityl tetrafluoroborate (43 mg, 0.13 mmol) was added. The resulting suspension was warmed to room temperature with stirring over 8 hours, then concentrated by rotary evaporation. The residue was triturated with 100 mL of pentane for 2 h. After filtration over celite, the filtrate was concentrated and the residue purified by column chromatography (silica gel, 20:1→10:1 hexanes/ethyl ether) to yield the desired PMB ether **S3** as a colorless oil (4.55 g, 75 %). $[\alpha]_D^{23}$ = -42.2 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.33 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.18 (m, 2H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.32 (d, *J* = 11.5 Hz, 1H), 3.91 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.62-3.57 (m, 2H), 2.10 (m, 1H), 0.88 (d, *J* = 6.0 Hz, 3H), 0.86 (s, 9H), 0.003 (s, 3H), -0.005 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.4, 159.3, 135.8, 129.7, 128.6, 128.5, 128.3, 113.7, 79.3, 72.3, 66.3, 63.8, 55.3, 39.2, 26.0, 18.4, 13.3, -5.5 (2) ppm; IR (thin film) 2952, 2928, 2855, 1754, 1613, 1513, 1462, 1248, 1171, 1093, 833 cm $^{-1}$; HRMS (FAB) calc'd for $[C_{26}H_{38}O_5Si + Li]^+$: 465.2649; found: 465.2644.



S4

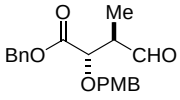
Desilylation/Lactonization. Compound **S3** (575 mg, 1.25 mmol) was dissolved in 6.25 mL of tetrahydrofuran and the solution cooled to 0 ºC. Tetrabutylammonium fluoride (1.5 mL, 1.50 mmol, 1.0 M in THF) was added dropwise via syringe over 5 min, and the mixture was stirred at 0 ºC for 30 min then poured into half-saturated brine in a separatory funnel. The aqueous mixture was extracted with ethyl acetate (3 x 10 mL) and the combined organic layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. Column chromatography (3:1 hexanes:ethyl acetate) gave the lactone **S4** as a colorless oil (63 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, *J* = 8.1 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 4.79 (d, *J* = 7.0 Hz, 1H), 4.65 (d, *J* = 7.0 Hz, 2H), 4.27 (dd, *J* = 7.4, 6.8 Hz, 1H), 4.06 (d, *J* = 7.4 Hz, 1H), 4.01 (m, 1H), 3.80 (s, 3H), 2.59 (m, 1H), 1.10 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$,

100 MHz) δ 175.0, 159.5, 129.7, 129.0, 113.9, 74.6, 71.9, 71.8, 55.3, 34.6, 11.3 ppm; IR (thin film) 1775, 1611, 1513, 1246, 1124, 1055, 818, 519 cm^{-1}, Relative stereochemistry determined by NOESY, see spectral appendix.



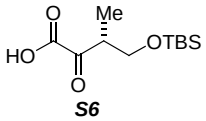
S5

Desilylation without lactonization. Compound **S3** (1.39 g, 3.0 mmol) was dissolved in 6 mL of tetrahydrofuran and 6 mL of water at room temperature. Acetic acid (18 mL) was then added, and the homogeneous mixture was stirred at room temperature for 14 h. The mixture was transferred to a separatory funnel and diluted with 75 mL of water. This aqueous phases was extracted with ethyl acetate (3 x 30 mL) and the combine organics were washed with brine (25 mL), dried (Na_2SO_4), filtered and concentrated. The residue was chromatographed (silica gel, 3:1 hexanes/ethyl acetate) to yield the alcohol **S5** as a colorless oil (1.00 g, 97 %). $[\alpha]_D^{23}$ = -67.7 (c = 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.34 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.20 (m, 2H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.31 (d, *J* = 11.5 Hz, 1H), 3.91 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.60-3.57 (m, 2H), 2.20 (m, 1H), 0.92 (d, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.1, 159.5, 135.4, 129.8, 129.0, 128.6, 128.5, 113.8, 81.2, 72.4, 66.7, 65.1, 55.2, 38.5, 13.6, ppm; IR (thin film) 3436, 2937, 2880, 1740, 1613, 1513, 1455, 1247, 1173, 1093, 1032 cm^{-1}; HRMS (ESI) calc'd for $[C_{20}H_{24}O_5 + Na]^+$: 367.1521; found: 367.1538.



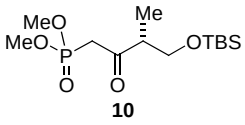
9

Alcohol oxidation. Alcohol **S5** (2.52 g, 7.33 mmol) was dissolved in dry methylene chloride (75 mL) at room temperature and the Dess-Martin periodinane[8] (4.66 g, 11.0 mmol) was added in a single portion. The reaction mixture was stirred at room temperature for 2 h, then quenched by the addition of half-saturated $NaHCO_3$ (25 mL) and half-saturated $NaSO_3$ (25 mL) solutions. The resulting biphasic mixture was stirred vigorously for 30 min, then transferred to a separatory funnel and partitioned. The aqueous phases was extracted with methylene chloride (3 x 25 mL) and the combined methylene chloride layers were washed with saturated $NaHCO_3$ solution (25 mL) and brine, then dried (Na_2SO_4), filtered and concentrated. Column chromatography (silica gel, 5:1 hexanes/ethyl acetate) afforded the desired aldehyde **9** as a colorless oil (2.29 g, 91 %). $[\alpha]_D^{23}$ = -63.7 (c = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.66 (s, 1H), 7.38-7.34 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.21 (m, 2H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.18 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 2.82 (m, 1H), 1.06 (d, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.4, 170.8, 159.6, 135.2, 130.0, 128.8, 128.7, 128.6, 113.9, 77.9, 72.6, 67.1, 55.3, 48.8, 10.2 ppm; IR (thin film) 2958, 2937, 1746, 1731, 1612, 1515, 1456, 1251, 1176, 1119, 1034 cm^{-1}; Anal. Calc'd, C: 70.16, H: 6.48; Found, C: 69.82, H: 6.15.



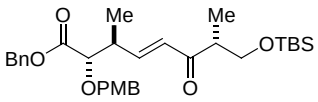
S6

Hydrogenolysis. Ketoester (*R*)-**8** (5.02 g, 14.9 mmol) was dissolved in ethyl acetate (75 mL) and palladium on carbon (400 mg, 10 wt% reagent) was added. The reaction vessel was capped with a septum and the atmosphere was exchanged for H_2 by three successive evacuation/backfill cycles. The heterogeneous mixture was stirred under balloon H_2 pressure for 2 h. The mixture was filtered over celite, and the filter cake was washed with additional ethyl acetate. The filtrate was concentrated, yielding the desired ketoacid **S6** as a colorless oil (3.25 g, quantitative). $[\alpha]_D^{23}$ = -14.9 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.40-9.17 (br s, 1H), 3.94 (m, 1H), 3.80 (m, 1H), 3.59 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H), 0.84 (s, 9H), 0.02 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 160.6, 65.4, 43.9, 26.0, 18.4, 12.5, -5.4 (2) ppm; IR (thin film) 2954, 2930, 2858, 1724, 1471, 1253, 1007, 835 cm $^{-1}$; HRMS (ESI) calc'd for $[C_{11}H_{21}O_4Si + 2\ Li]^+$: 259.1529; found: 259.1541.



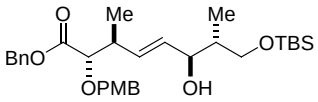
10

Oxidative decarboxylation. The ketoacid **S6** was dissolved in anhydrous tetrahydrofuran and iodosobenzene was added in a single portion. The resulting mixture was stirred at room temperature for 6 h, at which time triethylamine was added, followed by freshly distilled ethyl chloroformate. The mixture was stirred for an addition 2 h, then diluted with pentane. The suspension was filtered over celite, and the filter cake washed with pentane. The filtrate was concentrated, and dried in vacuo for 1 h. The residue was redissolved in dry tetrahydrofuran and cooled to -78 °C under nitrogen atmosphere. In a separate flask, dimethyl methanephosphonate was dissolved in dry tetrahydrofuran and cooled to -78 °C. *n*-Butyllithium was added via syringe, and the resulting mixture stirred for 1 h, then transferred dropwise via cannula to the flask containing the mixed anhydride over 1 h. After an additional hour of stirring at -78 °C, the reaction was quenched by the addition of saturated ammonium chloride solution and warmed to room temperature. The resulting biphasic mixture was transferred to a separatory funnel and partitioned and the aqueous phase was extracted with ethyl acetate. The combined organics were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (silica gel, 10:10:1 hexanes/ethyl acetate/methanol) to give the product as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.79 (d, *J* = 2.0 Hz, 3H), 3.76 (d, *J* = 2.0 Hz, 3H), 3.67 (d, *J* = 6.4 Hz, 2H), 3.33 (m, 1H), 3.09 (m, 1H), 3.01 (m, 1H), 1.02 (d, *J* = 8.4 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 65.8, 53.0 (2), 52.9, 49.3, 41.5 (d, *J* = 520 Hz), 25.8, 18.2, 12.7, -5.6 (2) ppm + 1 carbon unresolved; ^{31}P NMR ($CDCl_3$, 161.97 MHz) δ 23.2 ppm; HRMS (FAB) calc'd for $[C_{13}H_{29}O_5SiP + H]^+$: 325.1600; found: 325.1599.



11

Horner-Wadsworth-Emmons reaction (Modification of Paterson's conditions). Phosphonate **10** (2.51 mg, 7.74 mmol) was dissolved in dry diethyl ether (50 mL) and the solution was cooled to 0 ºC. Barium oxide (647 mg, 4.22 mmol) was added, followed by water (0.15 mL, 8.44 mmol)and the mixture was stirred for 15 min. Aldehyde **9** (2.40 g, 7.04 mmol) was added dropwise as a solution in ether (10 mL, then 2 x 5 mL wash), . The resulting turbid reaction mixture was stirred at 0 ºC for 1 h, then quenched with 100 mL of 0.1M HCl solution. The mixture was transferred to a separatory funnel, partitioned, and the aqueous layer was extracted with ethyl ether (3 x 35 mL). The combined organics were washed with brine, dried ($MgSO_4$), filtered and concentrated. Column chromatography (silica gel, 10:1 hexanes/ethyl acetate) yield the desired enone **11** as a colorless oil (3.11 g, 82 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.34 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.78 (dd, *J* = 16.0, 7.6 Hz, 1H), 6.08 (dd, *J* = 16.0, 0.8 Hz, 1H), 5.17 (m, 2H), 4.63 (d, *J* = 11.2 Hz, 1H), 4.31 (d, *J* = 11.2 Hz, 1H), 3.86 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.55 (m, 1H), 2.97 (m, 1H), 2.80 (m, 1H), 1.06 (d, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.85 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 171.2, 159.5, 146.6, 135.4, 130.1, 129.9, 129.1, 128.7, 128.6 (2), 113.8, 80.8, 72.3, 66.7, 65.4, 55.3, 46.2, 39.9, 25.9, 18.3, 15.8, 13.7, -5.4 (2) ppm; IR (thin film) 2954, 2931, 2856, 1747, 1515, 1456, 1249, 1097, 835 cm $^{-1}$; Anal. Calc'd, C: 68.85, H: 8.20; Found, C: 68.77, H: 8.57; HRMS (ESI) calc'd for $[C_{31}H_{44}O_6Si + Na]^+$: 563.2805; found: 563.2820; HRMS (FAB) calc'd for $[C_{31}H_{44}O_6Si + H]^+$: 541.2985; found: 541.2985.



12

DIP-Cl reduction. In an inert atmosphere glovebox, (+)-DIP-Cl (2.03 g, 6.33 mmol) added to a 25 mL round bottom flask. The charged flask was stoppered with a rubber septum and removed from the box and cooled to -20 ºC. Enone **11** (3.10 g, 5.75 mmol) was added dropwise as a solution in dry diethyl ether (3.0 mL, then 2 x 1.5 mL washes) and the reaction was stirred at -20 ºC for 18 h. The reaction was quenched by the addition acetaldehyde and stirred to room temperature for 1 h. The mixture was diluted with 50 mL of diethyl ether and 50 mL of sat. $NaHCO_3$, transferred to a separatory funnel and partitioned. The aqueous layer was extracted with diethyl ether (3 x 30 mL), and the combined aqueous layers were washed with brine, dried ($MgSO_4$), filtered and concentrated. The crude residue was purified by column chromatography (silica gel, 5:1 hexanes:ethyl acetate) to give an inseparable mixture of diastereomers (2.50 g, 80%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.34 (m, 5H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.60 (m, 1H), 5.40 (m, 1H), 5.15 (m, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 3.89 (m, 1H), 3.82 (m, 1H), 3.79 (s, 3H), 3.73 (m, 1H), 3.53 (m, 2H), 2.67 (m, 1H), 1.65 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.73 (d, *J* = 7.0 Hz, 3H), 0.07 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ

171.7, 159.2, 135.6, 132.9, 132.7, 129.7, 129.5, 128.5 (2), 128.3, 113.6, 81.7, 78.1, 72.2, 68.2, 66.4, 55.2, 40.2, 39.8, 25.8, 18.0, 17.0, 13.4, -5.6, -5.7 ppm; HRMS (ESI) calc'd for $[C_{31}H_{46}O_6Si + Na]^+$: 565.2961; found: 565.2967. The configuration of the major diastereomer was confirmed by analysis of the Mosher's ester derivatives as depicted in Figure S2.

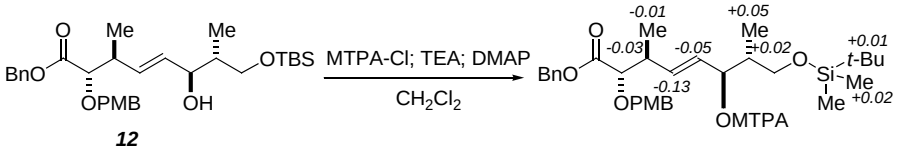
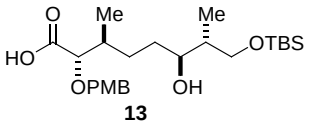
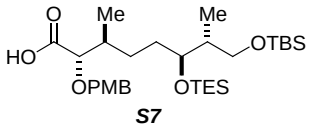


Figure S2. Analysis of Mosher's Ester Derivatives of Alcohol **12**.

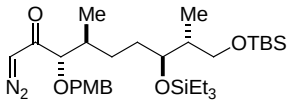


Catalytic Hydrogenation. Allylic alcohol **12** (2.50 g, 4.61 mmol) was dissolved in 45 mL of methanol and 250 mg of palladium on carbon-ethylenediamine complex[5] was added. The reaction vessel was capped with a rubber septum and the atmosphere was exchanged for H_2 by three successive evacuation/backfill cycles. The heterogeneous reaction mixture was stirred under balloon H_2 pressure for 2 h, then filtered over celite and the cake washed with methanol. The filtrate was concentrated to give a quantitative yield of a diastereomeric mixture. The diastereomeric products thus formed were separated by column chromatography (silica gel, 100:1 -> 20:1 methylene chloride/acetic acid) to afford essentially pure hydroxy acid **13** as a colorless oil (1.52 g, 73 %). $[\alpha]_D^{23}$ = -38.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (MeOH-d_4, 500 MHz) δ 7.28 (d, J = 6.4 Hz, 2H), 6.88 (d, J = 6.4 Hz, 2H), 4.60 (d, J = 9.2 Hz, 2H), 4.29 (d, J = 9.2 Hz, 2H), 3.78 (s, 3H), 3.73 (m, 1H), 3.67 (m, 1H), 3.57 (m, 1H), 3.46 (m, 1H), 1.90 (m, 1H), 1.68 (m, 1H), 1.46 (m, 3H), 0.94 (d, J = 5.2 Hz, 3H), 0.90 (s, 9H), 0.86 (d, J = 5.6 Hz, 3H), 0.05 (s, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 136.6, 129.6, 129.5, 113.2, 82.0, 73.2, 71.7, 65.5, 54.2, 41.0, 36.2, 30.8, 27.9, 24.9, 17.6, 15.0, 12.0, -7.8 ppm; HRMS (ESI) calc'd for $[C_{24}H_{42}O_6Si + Na]^+$: 477.2648; found: 477.2632.



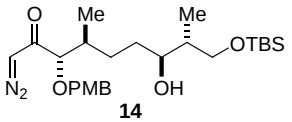
TES protection. The hydroxy acid **13** (1.52 mg, 3.35 mmol) was dissolved in dry methylene chloride (35 mL) at room temperature. Triethylamine (1.60 mL, 11.73 mmol), 4-dimethylaminopyridine (40 mg, 0.34 mmol) and chlorotriethylsilane (1.40 mL, 8.37 mmol) were then added sequentially and the reaction mixture was stirred at room temperature for 4 h. Methanol (5 mL) was then added and the mixture was stirred for an additional hour. The mixture was then diluted with saturated $NaHSO_4$ and the biphasic mixture transferred to a separatory funnel and partitioned. The aqueous layer was extracted with methylene chloride (3 x 25 mL) and the combined methylene chloride layers were washed with brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by column chromatography (silica gel, 1:1 hexanes/ethyl acetate) to give the silyl

ether **S7** (1.60 mg, 84 %). $[\alpha]_D^{23}$ = -16.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.64 (d, *J* = 11.0 Hz, 1H), 4.41 (d, *J* = 11.0 Hz, 1H), 3.81 (s, 3H), 3.70 (m, 1H), 3.51 (m, 1H), 3.42 (m, 1H), 1.94 (m, 1H), 1.78 (m, 1H), 1.51-1.25 (m, 6H), 0.96 (m, 12H), 0.88 (s, 9H), 0.83 (d, *J* = 12.5 Hz, 3H), 0.58 (m, 6H), 0.02 (s, 6H) ppm, ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.2, 159.5, 129.8, 129.7, 129.0, 113.8, 82.0, 73.1, 72.7, 65.2, 55.2, 41.2, 36.6, 30.0, 27.5, 25.9, 18.2, 15.6, 12.1, 7.0, 5.2, -5.4 (2) ppm; HRMS (ESI) calc'd for $[C_{30}H_{56}O_6Si_2\text{-}H^+]^-$ (negative mode): 567.3537; found: 567.3510.



S8

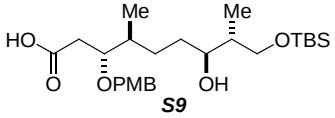
Diazoketone formation. The substrate (1.60 g, 2.81 mmol) was dissolved in tetrahydrofuran (15 mL) and cooled to 0 ºC. Triethylamine (0.47 mL, 3.37 mmol) was added, followed by dropwise addition of freshly distilled ethyl chloroformate (0.30 mL, 3.10 mmol). The resulting mixture was stirred at 0 ºC for 30 min, then the mixture was dilute with pentane (15 mL) and filtered over celite. The filtrate was concentrated to a colorless oil and dried in vacuo for 1 h. The residue thus obtained was treated with an ethereal solution of excess diazomethane and the yellow solution was stirred at room temperature for 16 h. The reaction mixture was quenched with acetic acid and the volatile components were removed by rotary evaporation. The residue was then chromatographed (silica gel, 10:1 hexanes/ethyl acetate) to give the desired diazoketone **S8** as a light yellow oil (1.23 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 5.72 (s, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.35 (d, *J* = 11.0 Hz, 1H), 3.81 (s, 3H), 3.69 (m, 1H), 3.59 (d, *J* = 5.5 Hz, 1H), 3.51 (m, 1H), 3.41 (m, 1H), 1.77 (m, 2H), 1.54-1.25 (m, 3H), 0.93 (m, 9H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.58 (m, 6H), 0.02 (s, 3H), 0.02 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 159.3, 129.4, 113.8, 88.2, 73.2, 72.6, 65.2, 55.2, 52.9, 41.3, 37.1, 29.8, 27.4, 25.9, 18.2, 15.6, 12.1, 7.0, 5.2, -5.4, -5.5 ppm; HRMS (ESI) calc'd for $[C_{31}H_{56}N_2O_5Si_2 + Na]^+$: 615.3625; found: 615.3617.



14

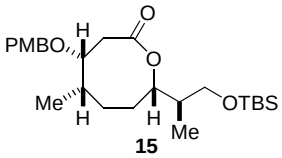
Desilylation. Silyl ether **S8** (1.23 g, 2.08 mmol) was dissolved in methanol (20 mL) and acetic acid (0.5 mL) was added. The resulting solution was stirred at room temperature for 16 h, at which time TLC analysis indicated that the reaction had completed. The reaction mixture was concentrated by rotary evaopration and the residue chromatographed (silica gel, 4:1 hexanes/ethyl acetate) to give the desired compound **14** as a light yellow oil (870 mg, 87 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 5.75 (s, 1H), 4.53 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 11.0 Hz, 1H), 3.80 (s, 3H), 3.77 (m, 1H), 3.63 (m, 1H), 3.55 (m, 1H), 3.48 (m, 1H), 1.85 (m, 1H), 1.67-1.41 (m, 4H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.06 (s, 6H) ppm; ^{13}C

NMR ($CDCl_3$, 100 MHz) δ 197.6, 159.3, 129.5, 113.8, 88.1, 76.7, 72.7, 68.5, 55.2, 53.1, 39.5, 37.0, 32.5, 27.6, 25.8, 20.5, 18.0, 15.7, 13.6, -5.7 (2) ppm; HRMS (ESI) calc'd for $[C_{25}H_{42}N_2O_5Si + Na]^+$: 501.2761; found: 501.2707.



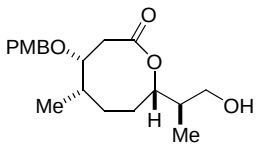
S9

Photolytic Wolff rearrangement. Diazoketone **14** (680 mg, 1.42 mmol) was dissolved in tetrahydrofuran (5.8 mL) and water (1.4 mL). The solution was sparged with argon for 10 min, then photolyzed for 5 h at 254 nm. The reaction mixture was diluted with ethyl acetate (20 mL) and brine (20 mL), and transferred to a separatory funnel and partitioned. The aqueous phase was extracted with ethyl acetate (4 x 10 mL) and the combined organics were dried (Na_2SO_4), filtered and concentrated. The residue was loaded onto a silica gel column and chromatographed (1:1 hexanes/ethyl acetate → 100% ethyl acetate) to give the hydroxy acid **S9**. This material was taken directly on to the ensuing lactonization.



15

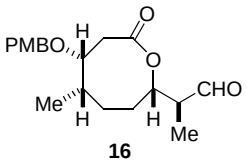
Lactonization. The desired lactone was prepared by a slight modification of the literature procedure.[9] Hydroxy acid **S9** from above was dissolved in dry methylene chloride (550 mL), and benzoic acid (480 mg, 2.13 mmol) and 4-dimethylaminpyridine (607 mg, 4.97 mmol) were added via syringe as a solution in dry methylene chloride (20 mL). The resulting mixture was stirred at room temperature for 12 h, then concentrated by rotary evaporation. The residue was applied to a silica gel column and chromatographed (10:1 hexanes/ethyl acetate) to yield lactone **15**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.83 (d, *J* = 11.2 Hz, 2H), 4.43 (m, 1H), 4.39 (d, *J* = 11.2 Hz, 2H), 3.80 (s, 3H), 3.77 (d, *J* = 4.4 Hz, 1H), 3.60 (m, 2H), 3.01 (m, 1H), 2.68 (d, *J* = 12.8 Hz, 1H), 1.90-1.50 (m 5H), 1.05 (d, J = 7.2 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H), 0.91 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.9, 159.1, 130.5, 129.7, 78.1, 77.8, 70.4, 64.2, 55.27, 40.2, 37.9, 34.8, 31.7, 25.9, 24.0, 21.9, 18.3, 13.5, -5.4, -5.5 ppm; IR (thin film) 2956, 2929, 2860, 1730, 1514, 1251, 1084, 846 cm^{-1}; HRMS (ESI) calc'd for $[C_{25}H_{42}O_5Si + Na]^+$: 473.2699; found: 473.2707.



S10

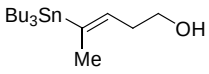
Desilylation. Lactone **15** (5 mg, 0.01 mmol) was dissolved in tetrahydrofuran (0.1 mL) at room temperature. Acetic acid (3.0 μL, 0.05 mmol) and tetrabutylammonium fluoride (30 μl, 0.03 mmol, 1.0M in THF) were added sequentially. The resulting mixture was stirred at room temperature for 8 h. The reaction mixture was concentrated and the residue applied to a silica gel column. Chromatography (1:1 hexanes/ethyl acetate) affords the product **S10** which exhibits spectroscopic characteristics that match literature reported values.[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.83 (d, *J* = 11.2 Hz,

2H), 4.43 (m, 1H), 4.39 (d, *J* = 11.2 Hz, 2H), 3.80 (s, 3H), 3.77 (d, *J* = 4.4 Hz, 1H), 3.60 (m, 2H), 3.01 (m, 1H), 2.68 (d, *J* = 12.8 Hz, 1H), 1.90-1.50 (m 5H), 1.05 (d, J = 7.2 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 159.1, 130.3, 129.6, 113.6, 79.2, 78.1, 70.4, 64.2, 55.2, 39.9, 37.5, 34.9, 31.8, 24.1, 13.5 ppm; HRMS (ESI) calc'd for $[C_{19}H_{28}O_5 + Na]^+$: 359.1834; found: 359.1826.



16

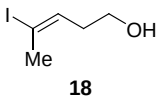
Alcohol oxidation to aldehyde. Primary alcohol **S10** (13.6 mg, 0.0404 mmol) was dissolved in anhydrous methylene chloride (3 mL). To the stirred solution was added Dess-Martin periodinane (37.7 mg, 0.0889 mmol) in a single portion. The mixture was stirred for 30 min at rt and then concentrated. The resulting oil was immediately purified by column chromatography (55:45 hexanes/ethyl acetate) to afford a quantitative yield of the desired aldehyde (13.5 mg) which was promptly used in the Nozaki-Hiyama-Kishi coupling described below. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.40 (s, H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.35–4.27 (m, 2H), 3.37 (s, 3H), 3.35–3.31 (m, 1H), 3.25 (d, *J* = 6.3 Hz, 1H), 2.89 (dd, *J* = 13.4, 6.6, Hz, 1H), 2.33 (d, *J* = 13.2 Hz, 1H), 2.24–2.20 (m, 1H), 2.09–2.04 (m, 1H), 1.22 (m, 3H), 1.06 (d, *J* = 13.8 Hz, 3H), 0.67 (d, *J* = 7.5 Hz, 3H).



17

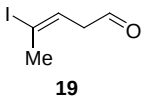
Dyotropic rearrangement. Alcohol **17** was prepared by a slight modification of the literature procedure.[11] 2,3-Dihydrofuran (1.7 mL, 20 mmol) was dissolved in anhydrous tetrahydrofuran (20 mL) at -78 ºC and *tert*-butyllithium (14 mL, 1.7 M in pentane, 24 mmol) was added dropwise over 15 min. The resulting mixture was warmed to 0 ºC and stirred for 1 h. During this time, in a separate flask copper(I) cyanide (1.8 g, 20 mmol) was suspended in ethyl ether (40 mL) and tetrahydrofuran (24 mL) at – 40 ºC. *n*-Butyllithium (16 mL, 40 mmol, 2.5 M in hexanes) was added dropwise via syringe over 10 min, and the mixture was warmed to -10 ºC with stirring for 15 min. The mixture was then recooled to – 40 ºC and tri-*n*-butylstannane (11 mL, 40 mmol) was added dropwise. To this mixture, the prepared 2-lithiodihydrofuran (see above) at – 40 ºC was added dropwise via cannula. The resulting mixture was warmed to 0 ºC for 1.5 h, then cooled to – 40 ºC and iodomethane (8.8 mL, 140 mmol) was added via syringe, and the reaction mixture was warmed to room temperature with stirring for 3 h. The reaction was quenched with a 4:1 mixture of sat. NH_4Cl/sat. NH_4OH solution (150 mL) and stirred for 1 h. The resulting blue biphasic mixture was transferred to a separatory funnel, partitioned and the aqueous phase extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated. Column chromatography (silica gel, 5:1 hexanes/ethyl ether + 1 % triethylamine) gave the title compound as a colorless oil (5.16 g, 69 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (m,

1H), 3.65 (q, J = 6.4 Hz, 2H), 2.42 (q, J = 6.4 Hz, 2H), 1.87 (m, 3H), 1.58-1.41 (m, 6H), 1.38-1.25 (m ,6H), 0.96-0.79 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.5, 135.7, 62.3, 31.7, 29.2, 27.4, 19.4, 13.7, 9.12 ppm; IR (thin film) 2957, 2921, 2872, 2850, 2020, 1930, 1463, 1048 cm $^{-1}$; HRMS (EI) calc'd for $[C_{17}H_{36}O^{119}Sn]^+$: 375.1799; found: 375.1705.



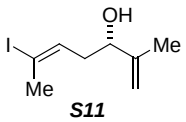
18

Iododestannylation. Stannane **17** (4.2 g, 11.20) was dissolved in anhydrous ethyl ether (80 mL) at 0 °C and iodine (3.4 g, 13.44 mmol) was added dropwise as a solution in ether (20 mL) until a light yellow color persisted in solution. The reaction was stirred at 0 °C for an addition 30 min, then was diluted with 20 mL of acetone. Potassium fluoride (2.11 g, 22.4 mmol) was added as a solution in 20 mL of water and the resulting biphasic mixture was stirred vigorously for 3 h. After filtration over celite, the filtrate was transferred to a separatory funnel and partitioned. The aqueous phase was extracted with ethyl ether (3 x 30 mL) and the combined organic layers were washed with sat. sodium thiosulfate solution (30 mL), dried ($MgSO_4$), filtered and concentrated. The residue was chromatographed (silica gel:potassium fluoride, methylene chloride)[12] to give the vinyl iodide **18** as a colorless oil (2.28 g, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (td, J = 8.0, 2.0 Hz, 1H), 3.65 (t, J = 8.4 Hz, 2H), 2.40 (t, J = 0.8 Hz, 3H), 2.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4, 96.5, 61.7, 34.2, 28.0 ppm; IR (thin film) 3345, 2958, 2914, 2877, 1428, 1055 cm $^{-1}$.



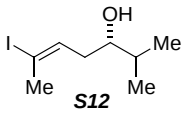
19

Alcohol oxidation. Vinyl iodide **18** (1.0 g, 4.72 mmol) was dissolved in methylene chloride (100 mL) and the Dess-Martin periodinane[8] (3.0 g, 7.07 mmol) was added in a single portion. The resulting solution was stirred at room temperature for 2.5 h, then quenched by the addition of a solution of NaS_2O_3 and $NaHCO_3$. The resulting biphasic mixture was stirred vigorously for 30 min, then transferred to a separatory funnel and partitioned. The aqueous phase was extracted with methylene chloride (2 x 25 mL) and the combined methylene chloride layers were washed with sat. $NaHCO_3$ (25 mL) and brine (25 mL), then dried ($MgSO_4$), filtered and concentrated. The resulting unstable aldehyde was found to be > 95 % pure and suitable for direct use in subsequent reactions (931 mg, 94 %). Spectral data consistent with literature values.[13]



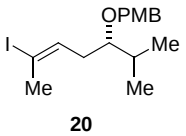
S11

Asymmetric isopropenylation. Diisopropenylzinc[6] (30 mg, 0.20 mmol) was dissolved in toluene (0.3 mL), and diethylzinc (0.2 mL, 0.20 mmol, 1.0M in hexanes) followed by ligand **21**[14] (7.3 mg, 0.02 mmol) in 0.2 mL of toluene were added. The resulting mixture was stirred at room temperature for 30 min, then cooled to -40 ºC. To this solution, aldehyde **19** (20 mg, 0.10 mmol) was added as a solution in toluene (0.5 mL). The resulting mixture was stirred at -40 ºC for 4 h, then quenched with half-saturated ammonium chloride solution (2.0 mL). The biphasic mixture was transferred to a separatory funnel and partitioned. The aqueous phase was extracted with ethyl ether (3 x 3 mL) and the combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated. Column chromatography gave the product **S11** as a light yellow oil (17 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (td, *J* = 6.0, 1.2 Hz, 1H), 4.99 (s, 1H), 4.89 (s, 1H), 4.11 (t *J* = 1.2 Hz, 1H), 2.40 (t, *J* = 0.8 Hz, 3H), 2.31 (m, 2H), 1.74 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.3, 136.7, 111.6, 95.9, 74.4, 36.2, 27.8, 17.9 ppm. The product *ee* was determined to be 83% by chiral GC analysis of the trifluoroacetate derivative (Chiraldex G-TA; 90 °C hold 0 min, then 0.5 °C/min to 100 °C; 2.0 mL/min He carrier gas), t_R 15.61 min (minor), 15.89 min (major).



S12

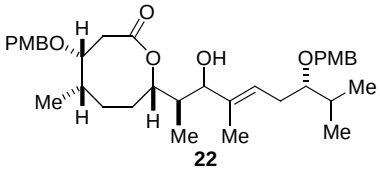
Alkene Hydrogenation. Substrate **S11** (100 mg, 0.40 mmol) was dissolved in 4 mL of toluene and loaded into a stainless steel Parr pressure vessel. Wilkinson's complex (37 mg, 0.04 mmol) was added and the vessel sealed and pressurized with hydrogen (500 psi). The mixture was stirred at room temperature for 4 h, then concentrated. The residue was chromatographed (silica gel, 5:1 hexanes/diethyl ether) to give the product **S12** as a colorless oil (75%). $[\alpha]_D^{23}$ –24.1º (c 0.66, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (t, *J* = 8.0 Hz, 1H), 3.41 (dt, *J* = 7.5, 5.0 Hz, 1H), 2.40 (s, 3H), 2.17 (m, 2H), 1.69 (m, 1H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.7, 95.7, 75.6, 35.4, 33.0, 27.8, 18.8, 17.3 ppm.



20

PMB protection of vinyl iodide. A stirred suspension of NaH (3.3 mg, 0.14 mmol) in dry Et_2O (3 mL) was cooled to 0 ºC under an N_2 atmosphere. A solution of *p*-methoxybenzyl alcohol (191 mg, 1.39 mmol) in anhydrous ether (3 mL) was added dropwise to the stirred solution. After stirring for 30 min at 0 ºC, trichloroacetonitrile (200 mg, 1.39 mmol) was added to the reaction. The solution was gradually warmed to rt over a period of 2 h. The reaction was then quenched with 5 drops of methanol and diluted with hexanes (5 mL). The resulting suspension was filtered through Celite and the filtrate was then concentrated to afford the *p*-methoxybenzyl trichloroacetimidate. The PMB trichloroacetimidate was then redissolved in anhydrous methylene chloride (3 mL). 10-

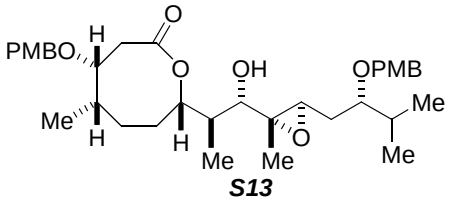
Camphorsulfonic acid (25 mg, 0.11 mmol) was added to the stirred solution, followed by homoallylic alcohol **S12** (176 mg, 0.693 mmol) as a solution in CH_2Cl_2 (2 mL). The reaction was stirred under N_2 for 14 h, then quenched with aqueous saturated $NaHCO_3$ (5 mL). The suspension was extracted with CH_2Cl_2 (4 x 5 mL), and the combined organic layers were dried over sodium sulfate, filtered and concentrated. Purification of the crude material (silica gel; 60:40 benzene/hexanes) afforded the title compound **20** as a colorless oil (181 mg, 70% yield). $[\alpha]_D^{23}$ –19.2º (c 1.19, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.18 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.13 (t, *J* = 7.5 Hz, 1H), 4.39–4.33 (m, 2H), 3.71 (s, 3H), 3.06 (q, *J* = 7.0 Hz, 1H), 2.28 (s, 3H), 2.13 (dd, *J* = 7.3 Hz, 2H), 1.76 (septet, *J* = 6.5 Hz, 1H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.1, 138.1, 130.8, 129.3, 113.7, 94.6, 82.7, 71.8, 55.2, 31.9, 31.1, 27.7, 18.3, 18.2 ppm.



22

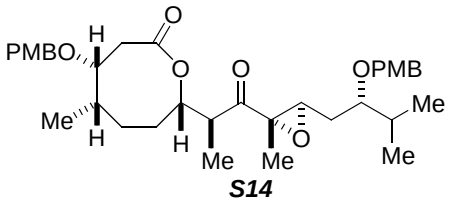
Nozaki-Hiyama-Kishi coupling. The pure aldehyde **16** (13.5 mg, 0.0404 mmol) was mixed with vinyl iodide **20** (60.4 mg, 0.162 mmol) and the compounds were dried azeotropically with benzene (2 x 2 mL). The compounds were then dissolved in anhydrous DMSO (1.3 mL) and added to a mixture of 1% (w/w) $NiCl_2$ in $CrCl_2$ (49.6 mg) under N_2. The mixture was stirred with the exclusion of light for 13 h at rt, then diluted with aqueous saturated NH_4Cl (5 mL). The aqueous phase was extracted with CH_2Cl_2 (6 x 5 mL) and the combined organic layers were then washed once with aq. sat. NH_4Cl (5 mL), dried over sodium sulfate, filtered and concentrated. The resulting residue was purified by column chromatography (70:30 hexanes/ethyl acetate). The desired diastereomer (major: R_f 0.21, 70:30 hexanes/ethyl acetate) was isolated as a white solid (8.4 mg, 36% yield), while the minor diastereomer (R_f 0.12, 70:30 hexanes/ethyl acetate) was recovered as a colorless oil (8.0 mg, 34% yield). Major diastereomer (α-**22**)**:** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.27–7.25 (m, 2H+$CHCl_3$), 6.88 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.48 (t, *J* = 6.8 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.49–4.43 (m, 2H), 4.39 (d, *J* = 11.0 Hz, 1H), 4.27 (s, 1H), 3.81 (s, 6H), 3.61 (d, *J* = 6.0 Hz, 1H), 3.19 (q, *J* = 5.5 Hz, 1H), 3.03 (dd, *J* =13.5, 6.5 Hz, 1H), 2.75 (d, *J* = 13.0 Hz, 1H), 2.28 (m, 2H), 2.01–1.80 (m, 3H), 1.74–1.62 (m, 3H), 1.57 (s, 3H), 1.42 (m, 1H), 1.26 (s, 1H), 1.19 (d, *J* = 15.0 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.2, 159.1. 159.0, 137.1, 131.2, 130.4, 129.6, 129.3, 120.7,

113.6 (d), 83.8, 79.2, 74.1, 71.5, 70.4, 55.3, 55.2, 40.1, 37.7, 34.8, 32.5, 31.0, 29.7, 28.8, 24.2, 21.5, 18.6, 18.1, 14.0, 8.9 ppm.



S13

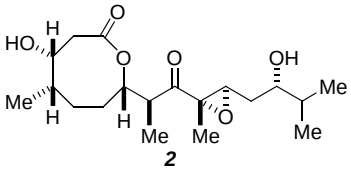
Directed epoxidation. To a stirred solution of the allylic alcohol α-**22** (8.4 mg, 0.014 mmol) in benzene (1.5 mL) was added $VO(acac)_2$ (1.0 mg, 0.0039 mmol). *t*-BuOOH (5.5 M in decane) was syringed into the solution (7.9 μL, 0.043 mmol) and the mixture was stirred at room temperature for 1 h. The crude reaction solution was concentrated and the resulting residue was purified by column chromatography (70:30 hexanes/ethyl acetate). The desired epoxide (7.2 mg, 84% yield) was isolated as a single diastereomer as observed by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.28–7.27 (m, 2H + $CHCl_3$), 7.87 (d, *J* = 8.5 Hz, 4H), 4.87 (d, *J* = 11.5 Hz, 1H), 4.49–4.38 (m, 3H), 4.06 (s, 1H), 3.81 (s, 6H), 3.61 (d, *J* = 5.5 Hz, 1H), 3.33–3.29 (m, 2H), 3.04 (dd, *J* = 13.3, 6.3 Hz, 1H), 2.77 (d, *J* = 13 Hz, 1H), 2.05–1.96 (m, 3H), 1.80–1.76 (m, 3H), 1.26–1.18 (m, 4H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.0, 159.1 (d), 130.8, 130.4 129.7, 129.2, 113.7, 113.6, 82.1, 78.5, 77.6, 71.0, 70.3, 70.2, 61.3, 56.2, 55.3, 55.2, 39.3, 37.8, 34.6, 32.7, 30.6, 28.8, 24.0, 18.6, 17.9, 14.7, 9.4 ppm.



S14

Alcohol oxidation to ketone. Epoxide **S13** (6.5 mg, 0.011 mmol) was dissolved in anhydrous CH_2Cl_2 (1.2 mL). To the stirred mixture was added Dess-Martin periodinane (10.1 mg, 0.024 mmol). After stirring for 1 h at rt, the reaction solution was concentrated and the resulting white residue was purified by column chromatography (4:1 hexanes/ethyl acetate). The epoxy ketone **S14** was isolated as a colorless residue (4.5 mg, 69% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.56–4.48 (m, 2H), 4.35 (d, *J* = 11.0 Hz, 1H), 3.79 (d, 6H), 3.62 (d, *J* = 5.5 Hz, 1H), 3.38 (m, 1H), 3.27–3.25 (m, 1H), 3.03 (dd, *J* = 13.8, 6.3 Hz, 1H), 1.99–1.88 (m, 2H), 1.85 (m, 1H), 1.72–1.69 (m, 3H), 1.44–1.39 (m, 4H), 1.28–1.26 (m, 4H), 1.07 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.2, 170.9, 159.1, 159.0, 130.9, 130.4, 129.7, 129.6,

113.7, 113.6, 81.7, 77.6, 77.5, 71.4, 70.4, 62.3, 58.2, 55.2, 43.3, 37.8, 34.6, 31.6, 31.0, 29.4, 23.4, 22.2, 18.4, 17.9, 17.8, 13.5, 13.1 ppm.



2

PMB deprotection. To a vigorously stirred solution of epoxy ketone **S14** (3.9 mg, 0.0065 mmol) in aqueous methylene chloride (9:1 CH_2Cl_2:H_2O, 0.75 mL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (5.9 mg, 0.026 mmol) in a single portion. The mixture was stirred for 45 min at room temperature. The suspension was diluted with H_2O (2 mL) and then extracted with CH_2Cl_2 (5 x 3 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified by column chromatography (1:1 hexanes/ethyl acetate) to furnish 2.3 mg (quantitative yield) of octalactin A (**2**). $[\alpha]_D^{23}$ –147.4º (c 0.19, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.60 (t, *J* = 10.5 Hz, 1H), 4.03 (br s, 1H), 3.55 (t, *J* = 6.3 Hz, 1H), 3.50 (br m, 1H), 2.99–2.85 (m, 2H), 2.75 (br s, 1H, OH), 2.73 (dd, *J* = 13.3, 6.3 Hz, 1H). 1.96 (br s, 1H, OH), 1.79–1.63 (m, 8H), 1.44 (s, 3H), 1.21–1.19 (m, 1H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.5, 172.5, 79.3, 74.5, 71.2, 62.4, 58.9, 42.4, 39.2, 37.9, 34.0, 32.1, 31.9, 22.4, 22.1, 18.4, 17.6, 13.5, 12.6 ppm.

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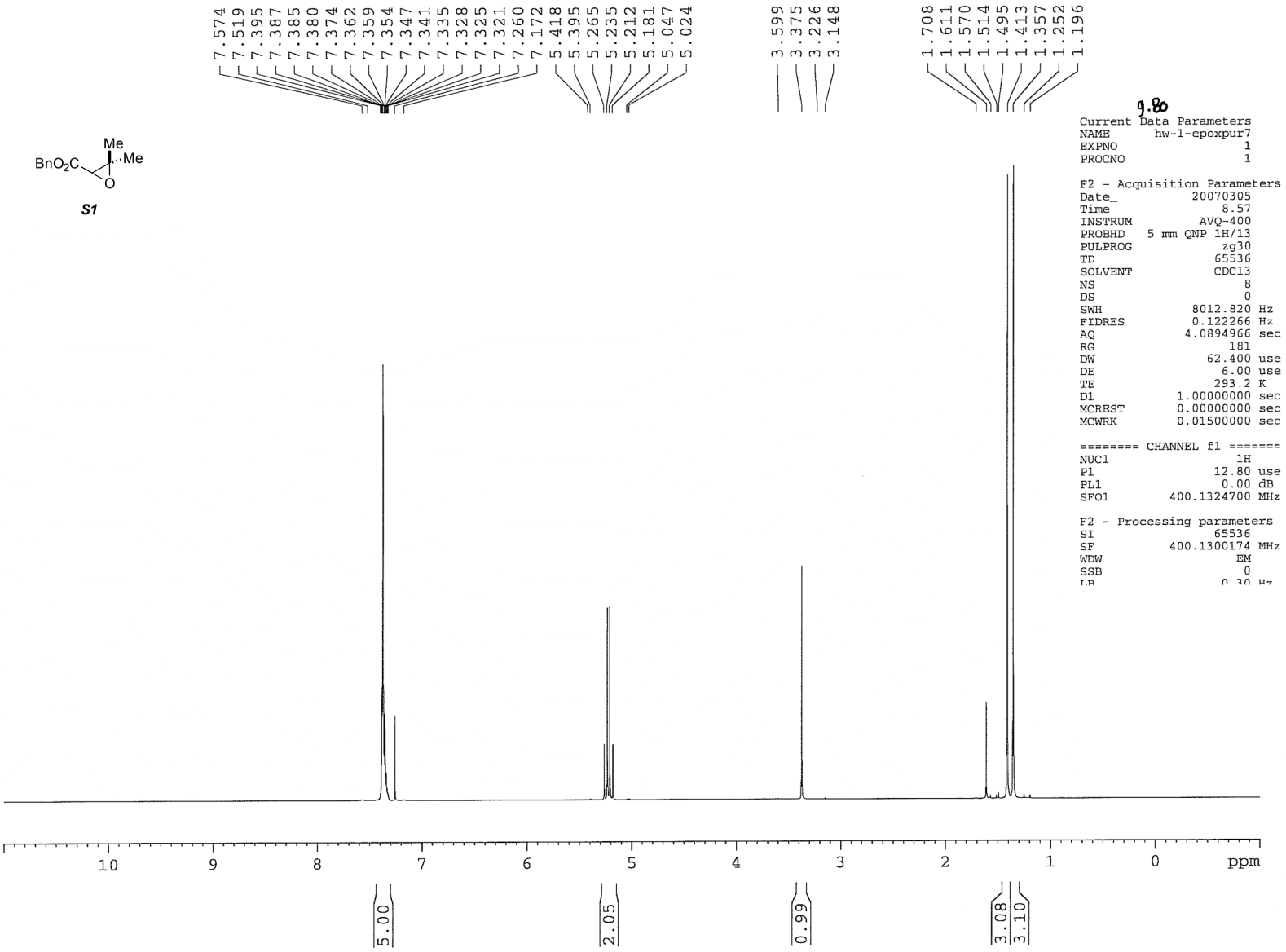

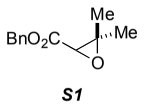

S1

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60.38
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18.21

9.80

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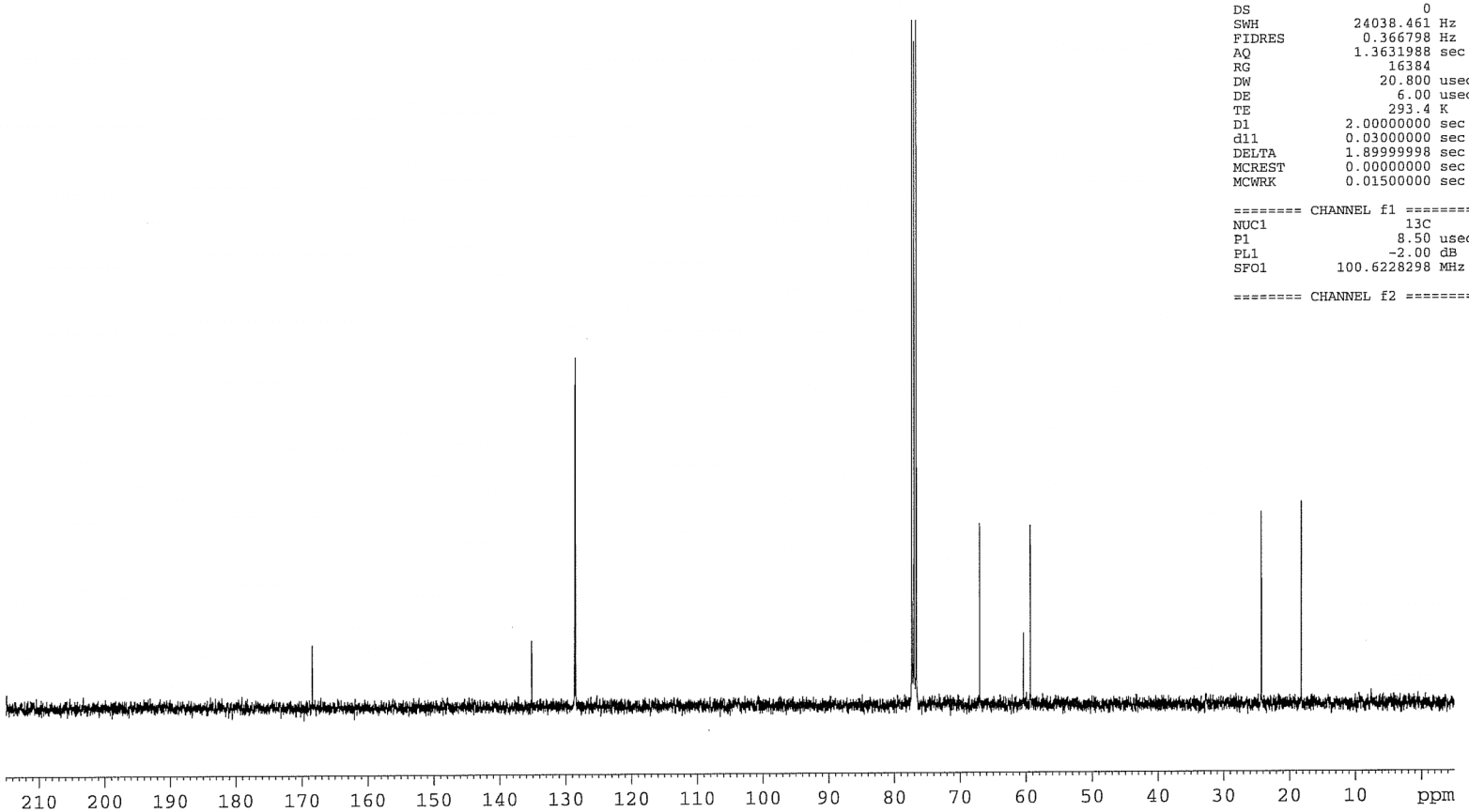
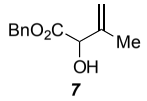
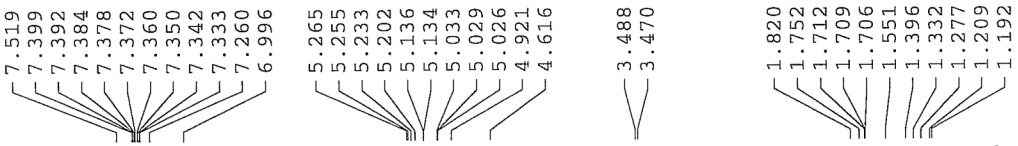


AVQ-400 QNP Proton starting parameters. 7/16/03. Revised 7/22/03 RN



7



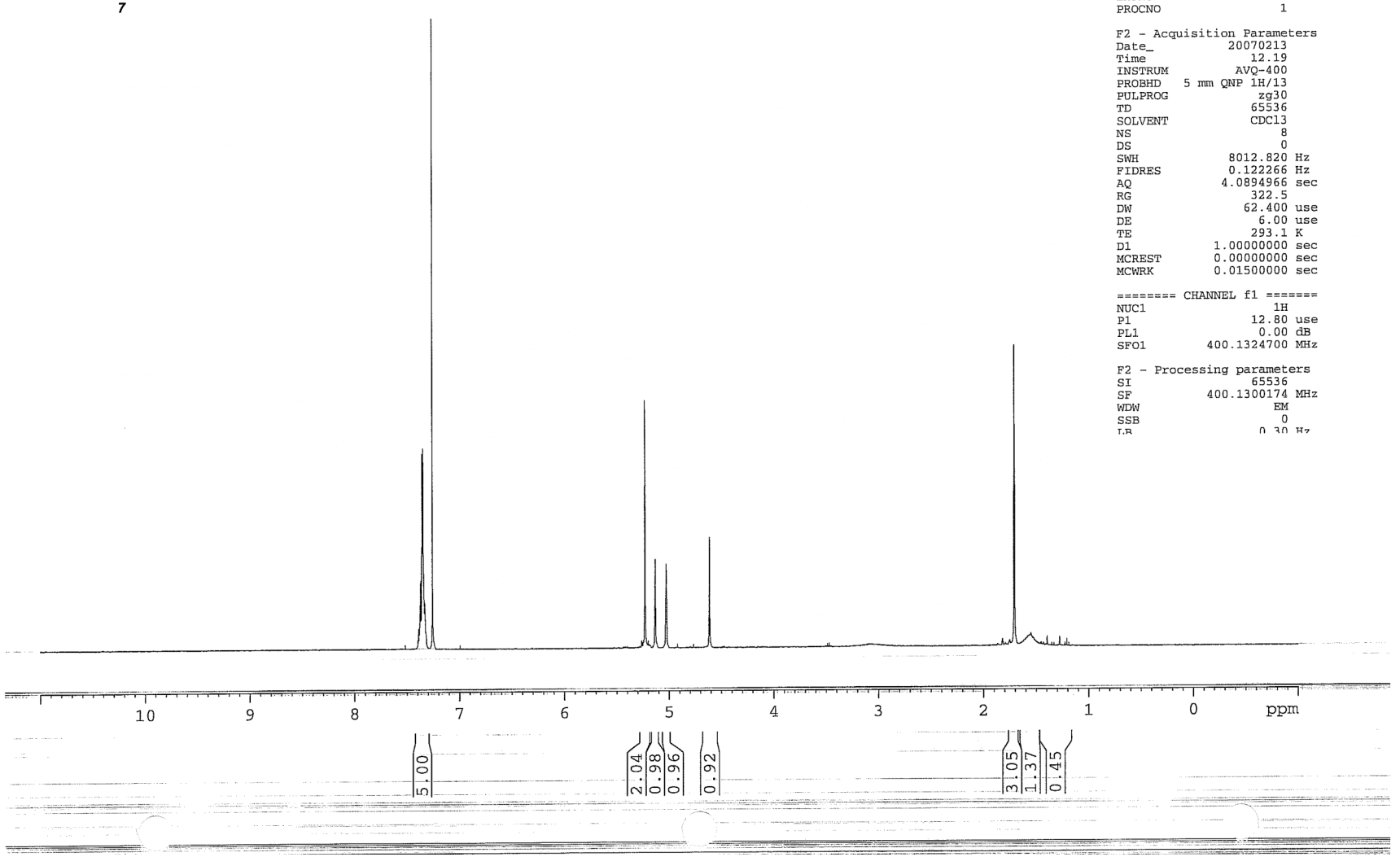
1.81

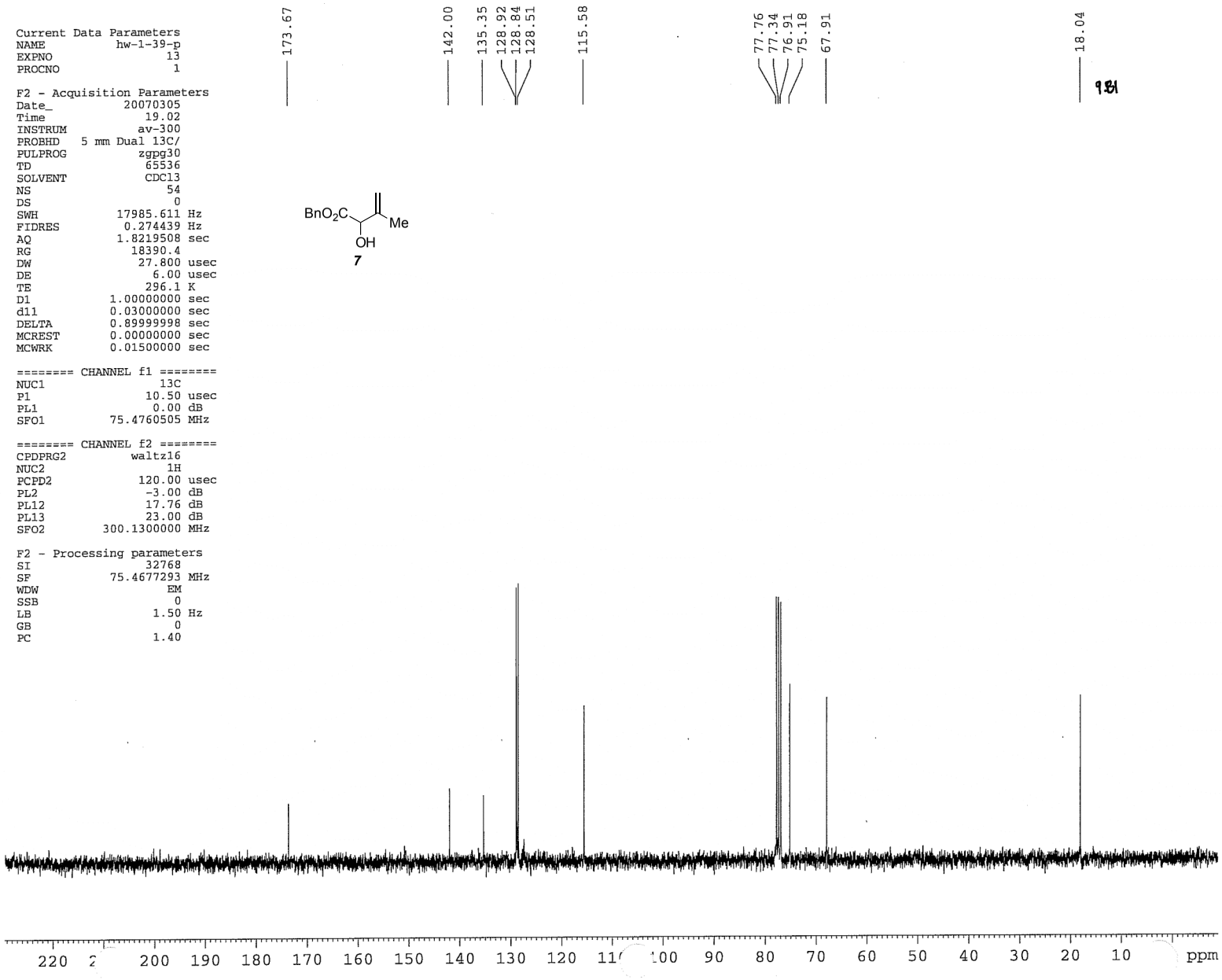
Current Data Parameters
NAME hw-1-32-p2
EXPNO 1
PROCNO 1

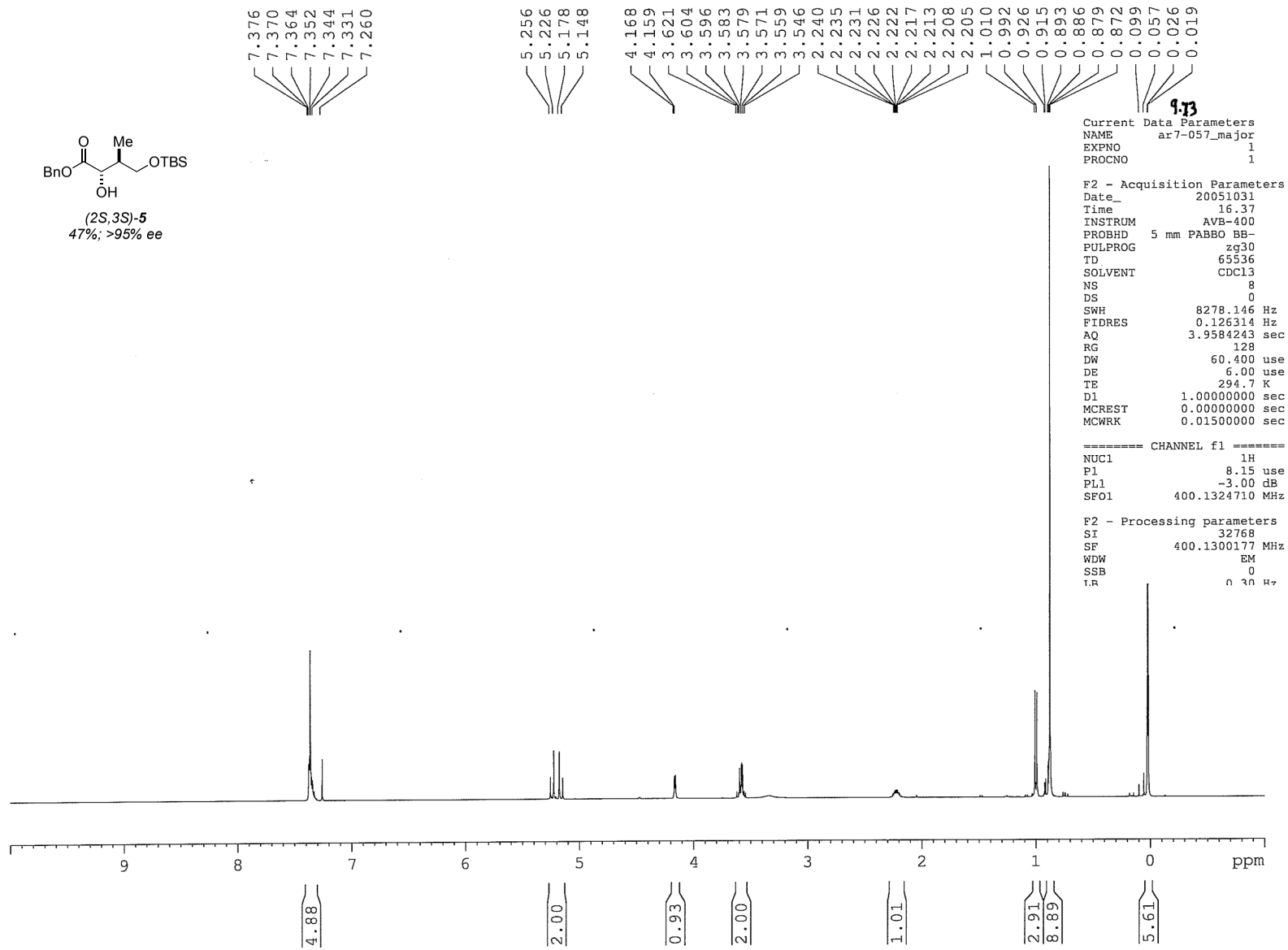
F2 - Acquisition Parameters
Date_ 20070213
Time 12.19
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 322.5
DW 62.400 use
DE 6.00 use
TE 293.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

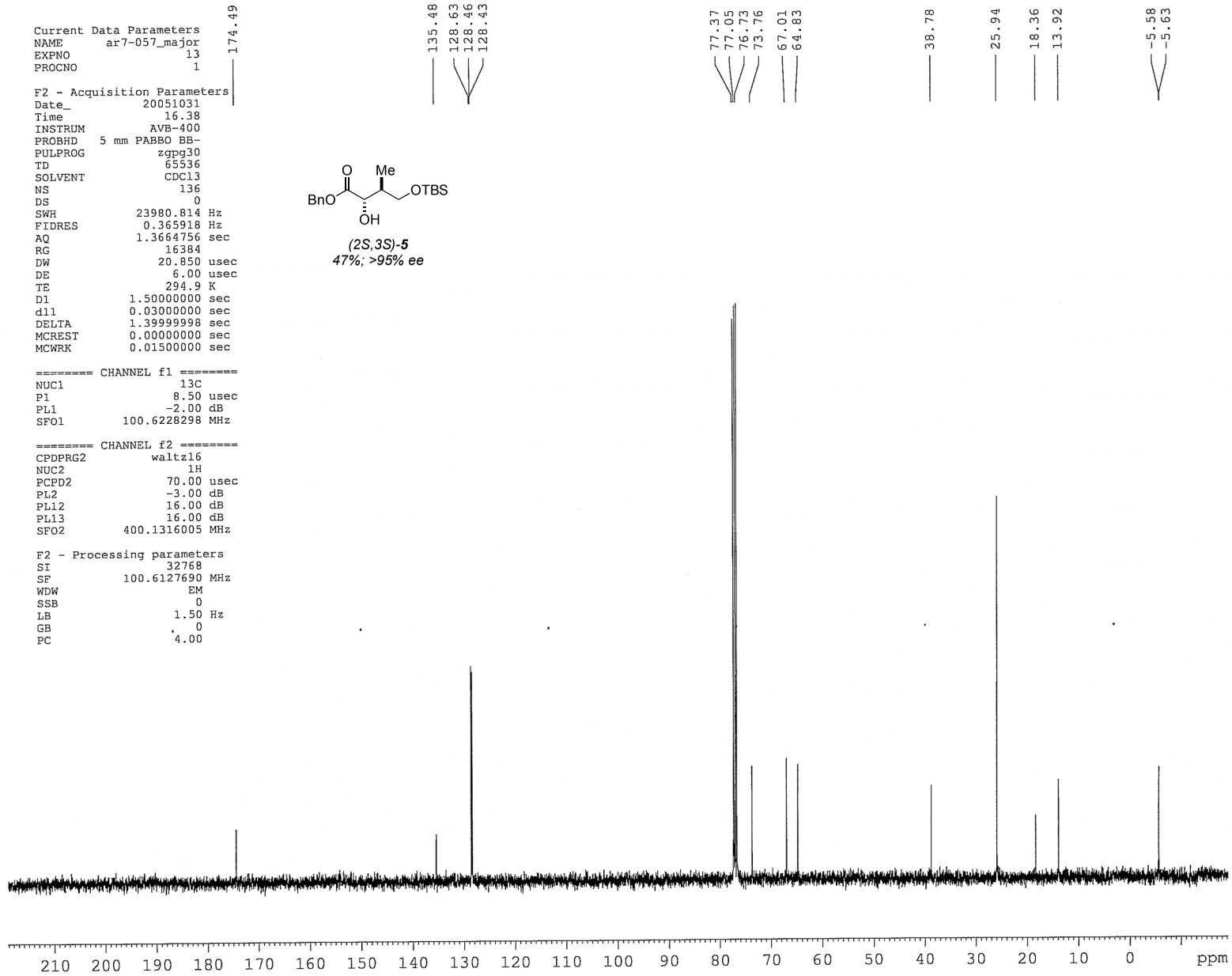
======== CHANNEL f1 =======
NUC1 1H
P1 12.80 use
PL1 0.00 dB
SFO1 400.1324700 MHz

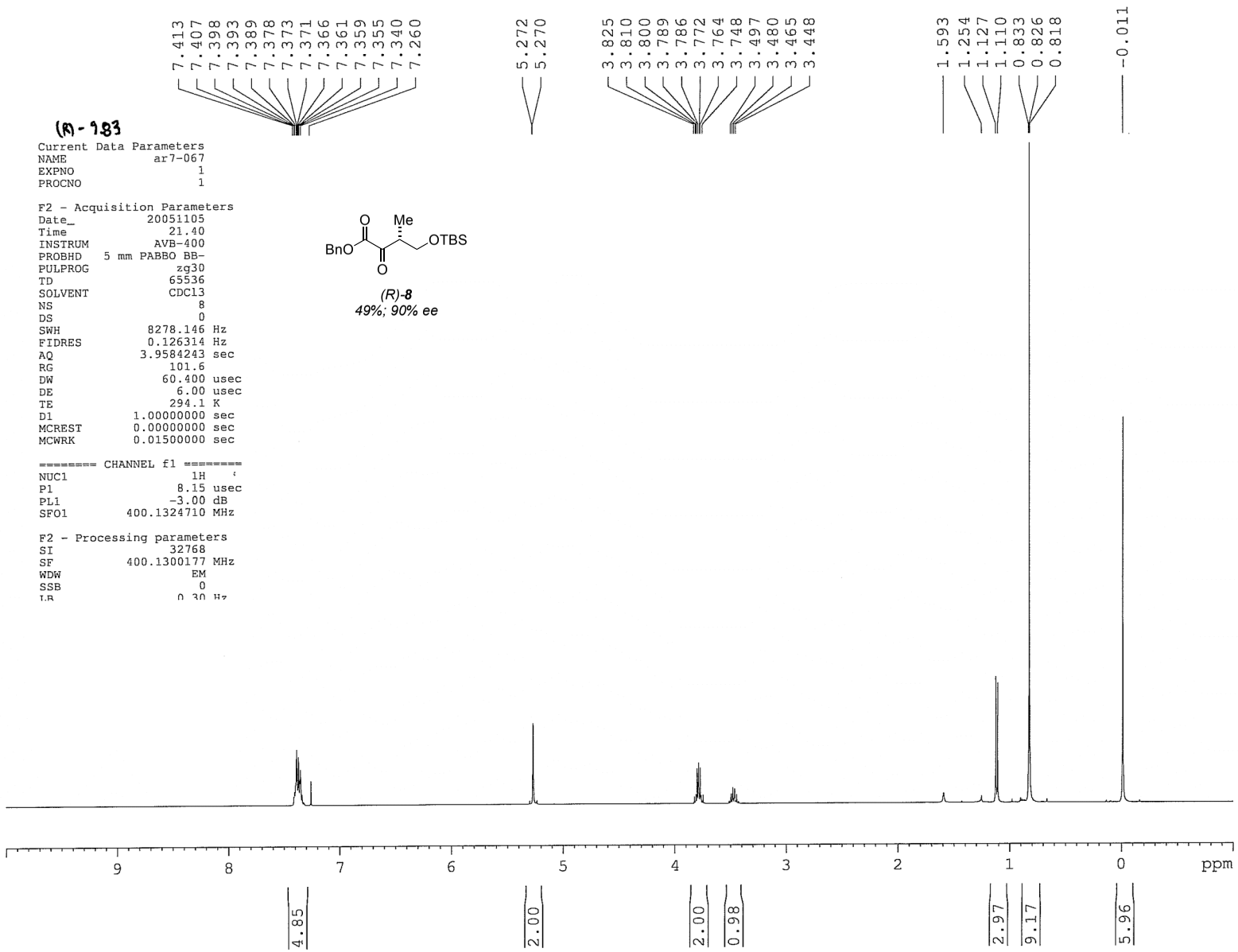
F2 - Processing parameters
SI 65536
SF 400.1300174 MHz
WDW EM
SSB 0
LB 0.30 Hz

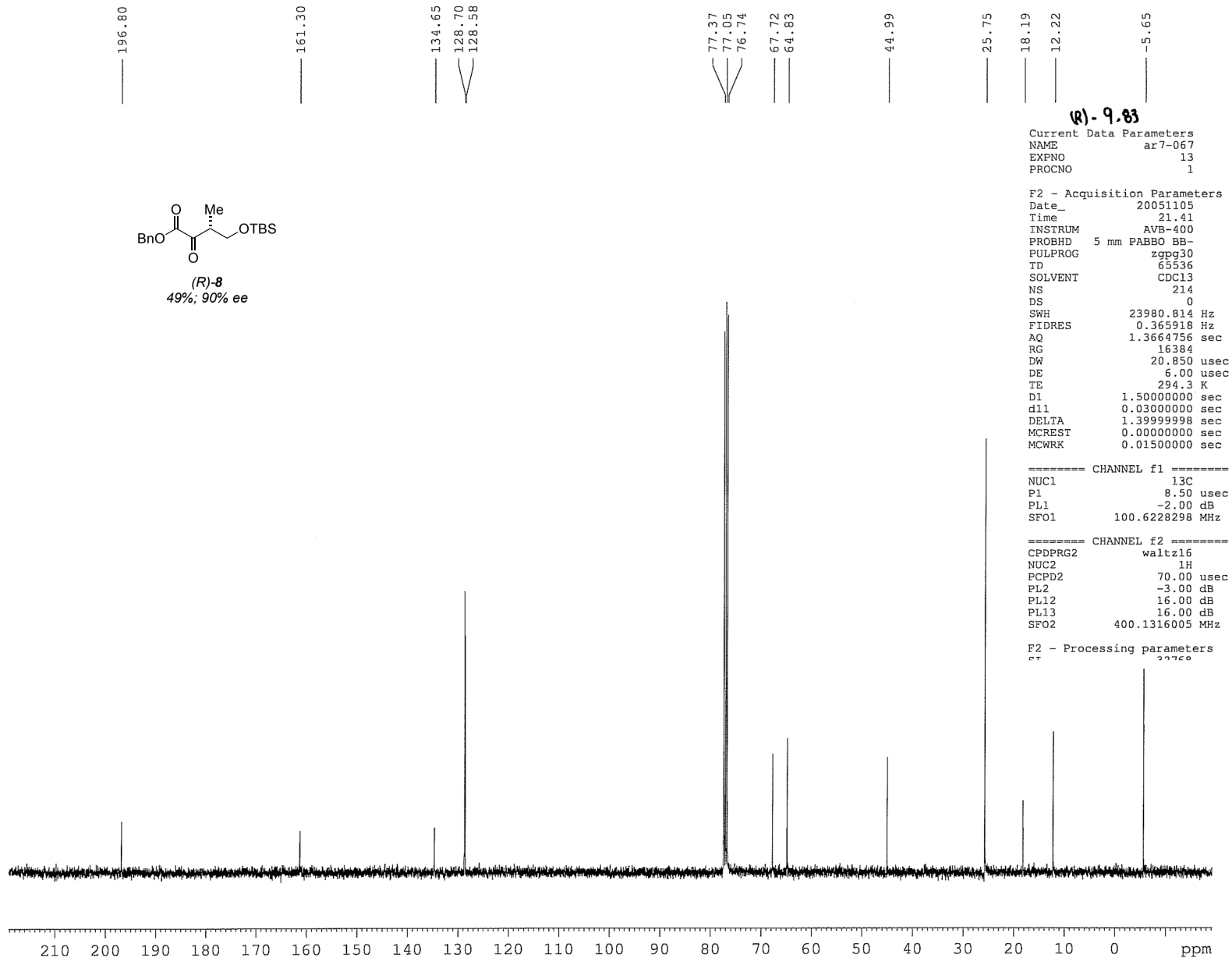


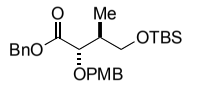

Current Data Parameters
NAME hw-1-39-p
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070305
Time 19.02
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 54
DS 0
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 18390.4
DW 27.800 usec
DE 6.00 usec
TE 296.1 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 0.00 dB
SFO1 75.4760505 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 120.00 usec
PL2 -3.00 dB
PL12 17.76 dB
PL13 23.00 dB
SFO2 300.1300000 MHz
F2 - Processing parameters
SI 32768
SF 75.4677293 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
173.67
142.00
135.35
128.92
128.84
128.51
115.58
77.76
77.34
76.91
75.18
67.91
18.04
9.81
BnO2C
Me
OH
7
220
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.376
7.370
7.364
7.352
7.344
7.331
7.260
5.256
5.226
5.178
5.148
4.168
4.159
3.621
3.604
3.596
3.583
3.579
3.571
3.559
3.546
2.240
2.235
2.231
2.226
2.222
2.217
2.213
2.208
2.205
1.010
0.992
0.926
0.915
0.893
0.886
0.879
0.872
0.099
0.057
0.026
0.019
9.73
O
Me
BnO
OTBS
OH
(2S,3S)-5
47%; >95% ee
Current Data Parameters
NAME ar7-057_major
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051031
Time 16.37
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 128
DW 60.400 use
DE 6.00 use
TE 294.7 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 =======
NUC1 1H
P1 8.15 use
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300177 MHz
WDW EM
SSB 0
9 8 7 6 5 4 3 2 1 0 ppm
4.88
2.00
0.93
2.00
1.01
2.91
8.89
5.61


Current Data Parameters
NAME ar7-057_major
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051031
Time 16.38
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 136
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 294.9 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB
PL13 16.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 4.00
174.49
135.48
128.63
128.46
128.43
77.37
77.05
76.73
73.76
67.01
64.83
38.78
25.94
18.36
13.92
-5.58
-5.63
O
Me
BnO
OTBS
OH
(2S,3S)-5
47%; >95% ee
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


(R)-983
Current Data Parameters
NAME ar7-067
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051105
Time 21.40
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 101.6
DW 60.400 usec
DE 6.00 usec
TE 294.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.15 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300177 MHz
WDW EM
SSB 0
LB 0.30 Hz
7.413
7.407
7.398
7.393
7.389
7.378
7.373
7.371
7.366
7.361
7.359
7.355
7.340
7.260
5.272
5.270
3.825
3.810
3.800
3.789
3.786
3.772
3.764
3.748
3.497
3.480
3.465
3.448
1.593
1.254
1.127
1.110
0.833
0.826
0.818
-0.011
BnO
O
Me
OTBS
(R)-8
49%; 90% ee
9
8
7
6
5
4
3
2
1
0
ppm
4.85
2.00
2.00
0.98
2.97
9.17
5.96

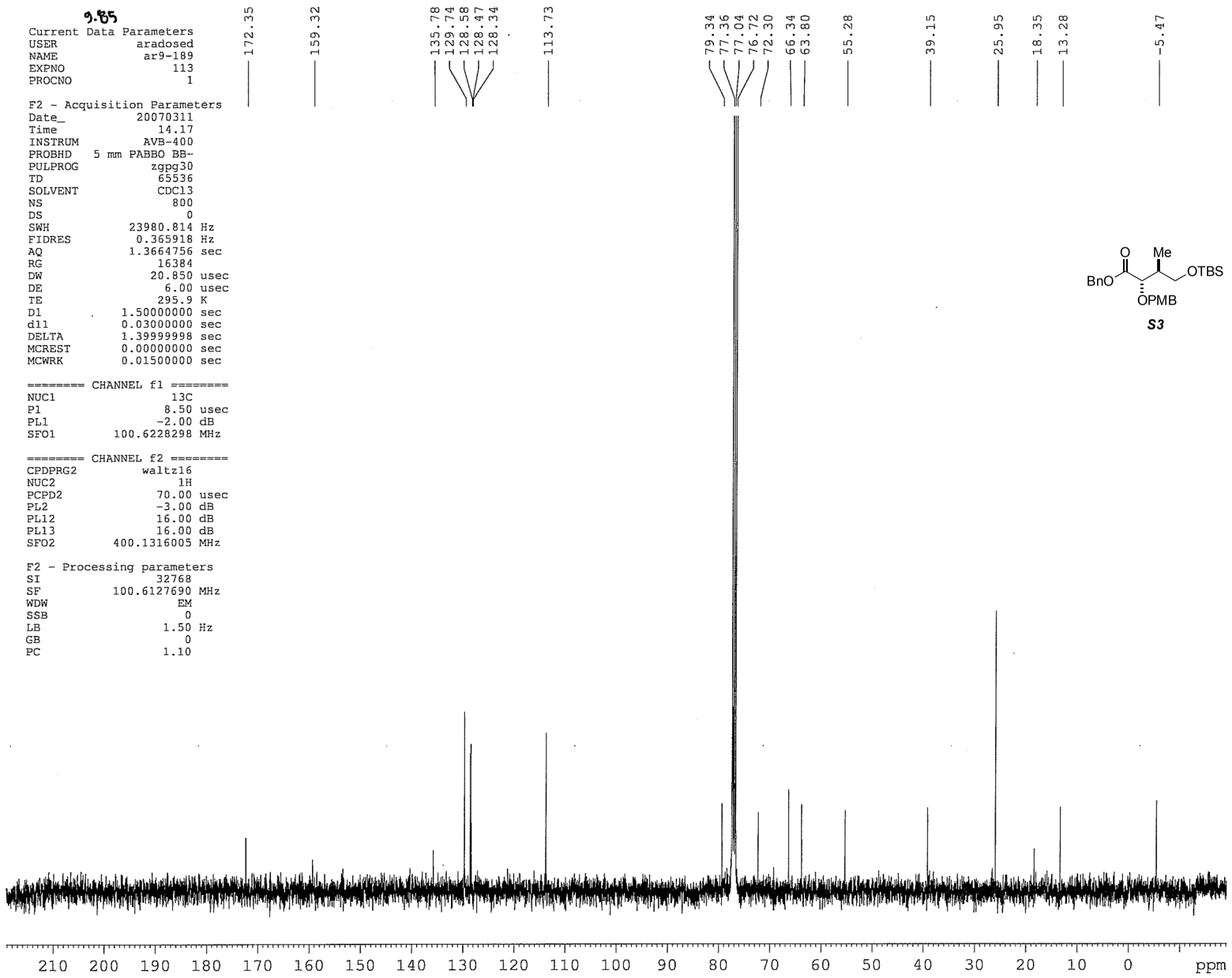

196.80
161.30
134.65
128.70
128.58
77.37
77.05
76.74
67.72
64.83
44.99
25.75
18.19
12.22
-5.65
(R)-9.83
Current Data Parameters
NAME ar7-067
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051105
Time 21.41
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 214
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 294.3 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB
PL13 16.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
O
Me
BnO
OTBS
O
(R)-8
49%; 90% ee
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

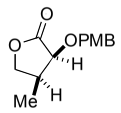


S3

9.85

```
Current Data Parameters
USER            aradosed
NAME            ar9-189c
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070309
Time               11.57
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     2
DS                     0
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ             3.2768500 sec
RG                 456.1
DW                50.000 usec
DE                 7.11 usec
TE                293.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 12.20 usec
PL1                -5.00 dB
SFO1         500.1330883 MHz

F1 - Acquisition parameters
ND0                    2
TD                    64
SFO1            500.1321 MHz
FIDRES         65.540741 Hz
```

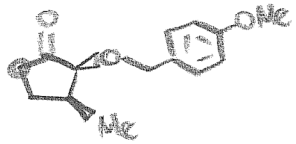

9.85
Current Data Parameters
USER aradosed
NAME ar9-189
EXPNO 113
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070311
Time 14.17
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 800
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 295.9 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB
PL13 16.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.10
172.35
159.32
135.78
129.74
128.58
128.47
128.34
113.73
79.34
77.36
77.04
76.72
72.30
66.34
63.80
55.28
39.15
25.95
18.35
13.28
-5.47
O
Me
BnO
OTBS
OPMB
S3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



S4

7.519 7.335 7.313 7.260 6.996 6.915 6.908 6.903 6.891 6.886

4.995 4.967 4.717 4.689 4.416 4.397 4.394 4.375 3.991 3.813 3.775 3.762 3.751 3.727 3.631 2.610 2.591 2.587 2.574 2.570 2.551 2.547 2.528 1.555 1.251 1.111 1.094 0.973 0.951 0.933



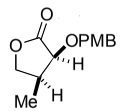
1.88

```
Current Data Parameters
NAME                  ar7-097
EXPNO                       1
PROCNO                      1
DU                         /u
USER                aradosed

F2 - Acquisition Parameters
Date_              20051214
Time                  23.43
INSTRUM            AVB-400
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                    456.1
DW                   60.400 use
DE                    6.00 use
TE                   294.4 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 =======
NUC1                     1H
P1                    8.15 use
PL1                  -3.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF             400.1300180 MHz
WDW                      EM
```

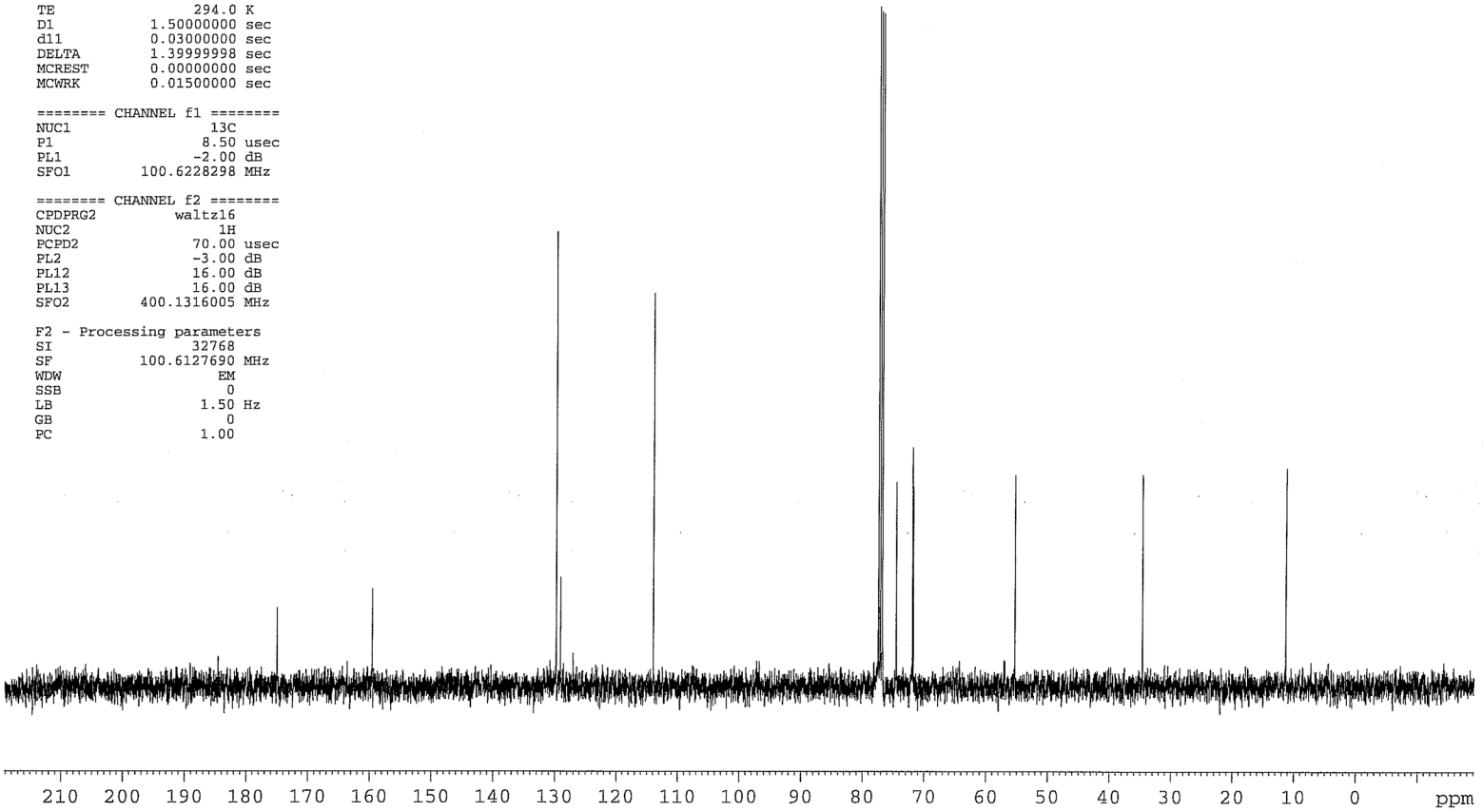
9.08

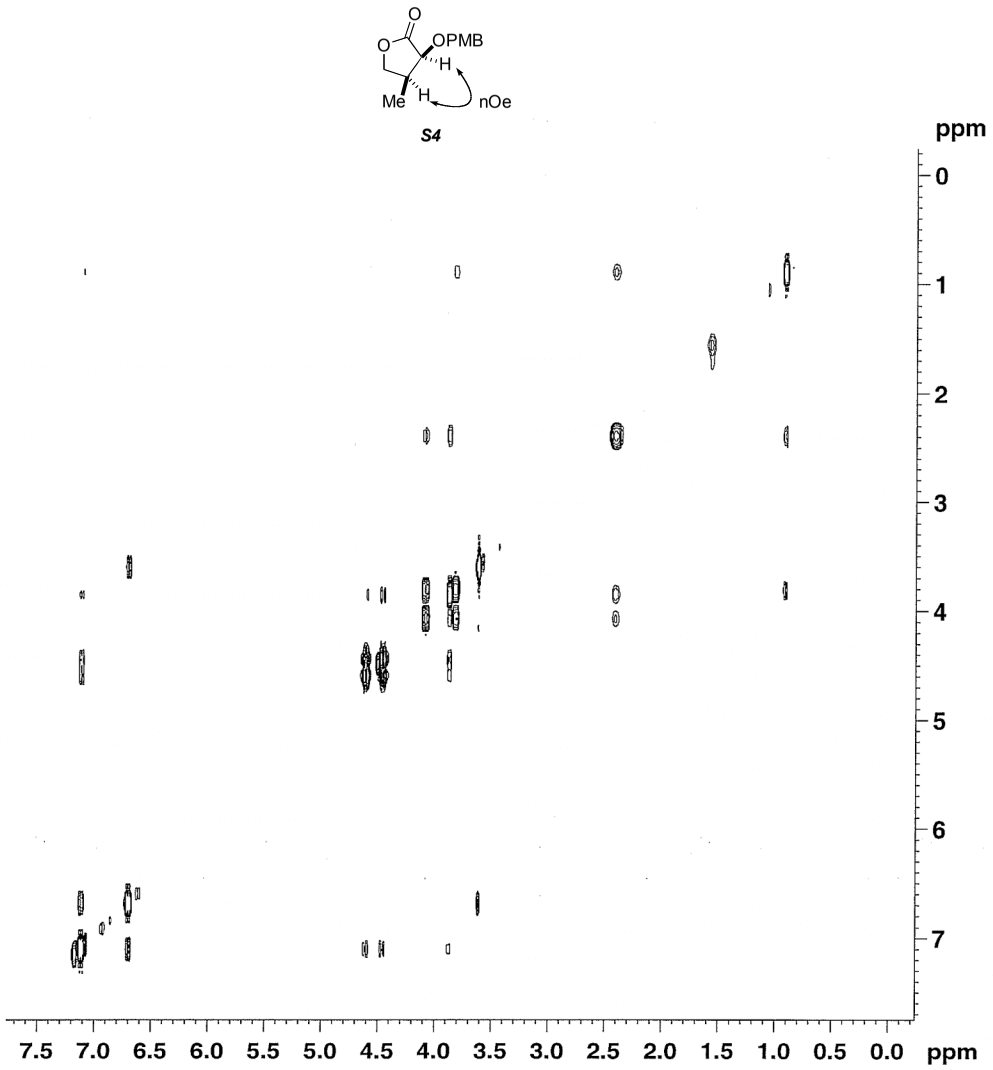
```
Current Data Parameters
NAME        ar10-lactone
EXPNO                 13
PROCNO                 1
DU                    /u
USER           aradosed

F2 - Acquisition Parameters
Date_           20070426
Time               20.00
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   21
DS                    0
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                16384
DW               20.850 usec
DE                6.00 usec
TE                294.0 K
D1           1.50000000 sec
d11          0.03000000 sec
DELTA        1.39999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              70.00 usec
PL2                -3.00 dB
PL12               16.00 dB
PL13               16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  1.00
```

174.98 159.54 129.77 129.07 113.92 77.43 77.11 76.79 74.56 71.93 71.80 55.32 34.64 11.29



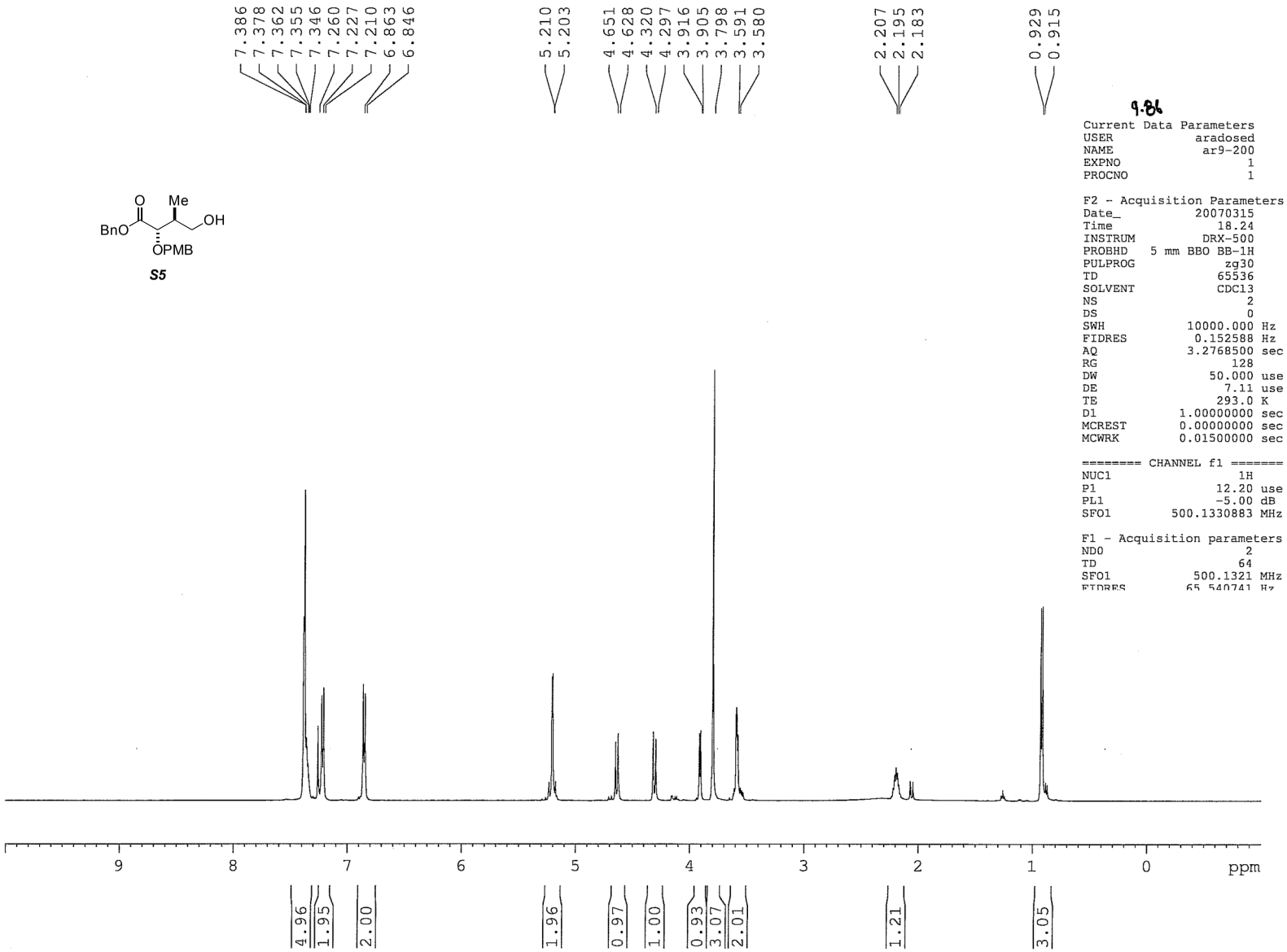
S4

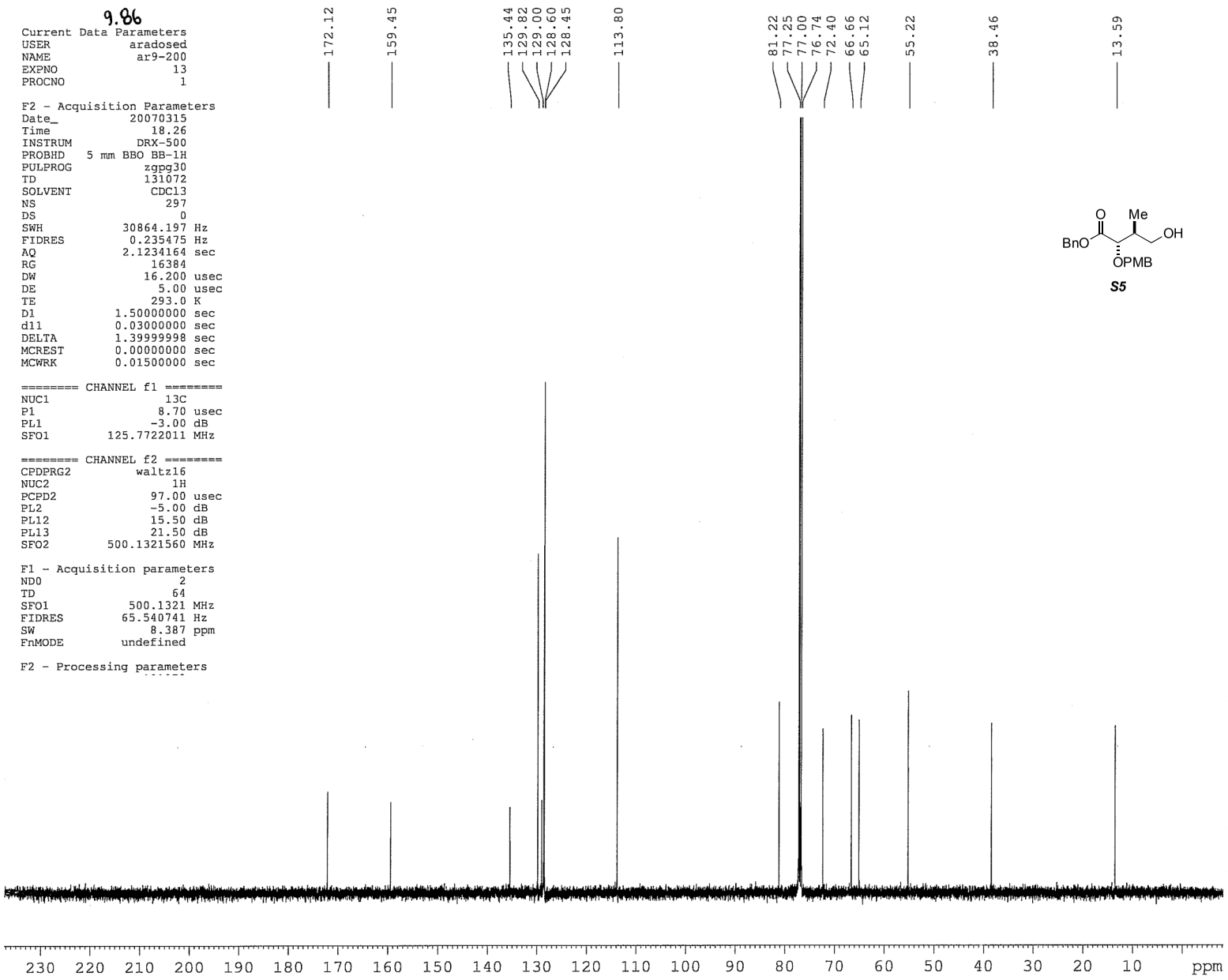


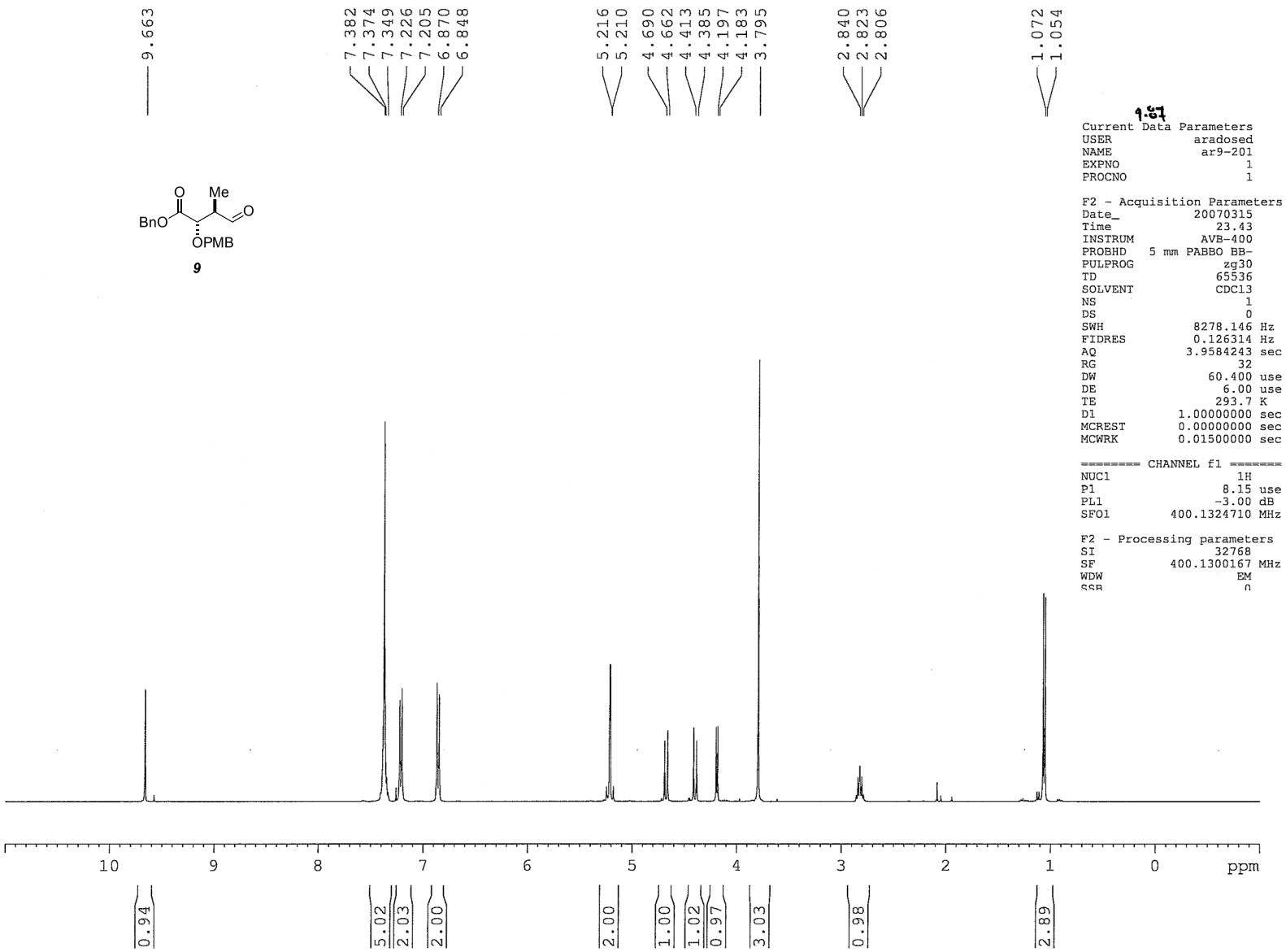


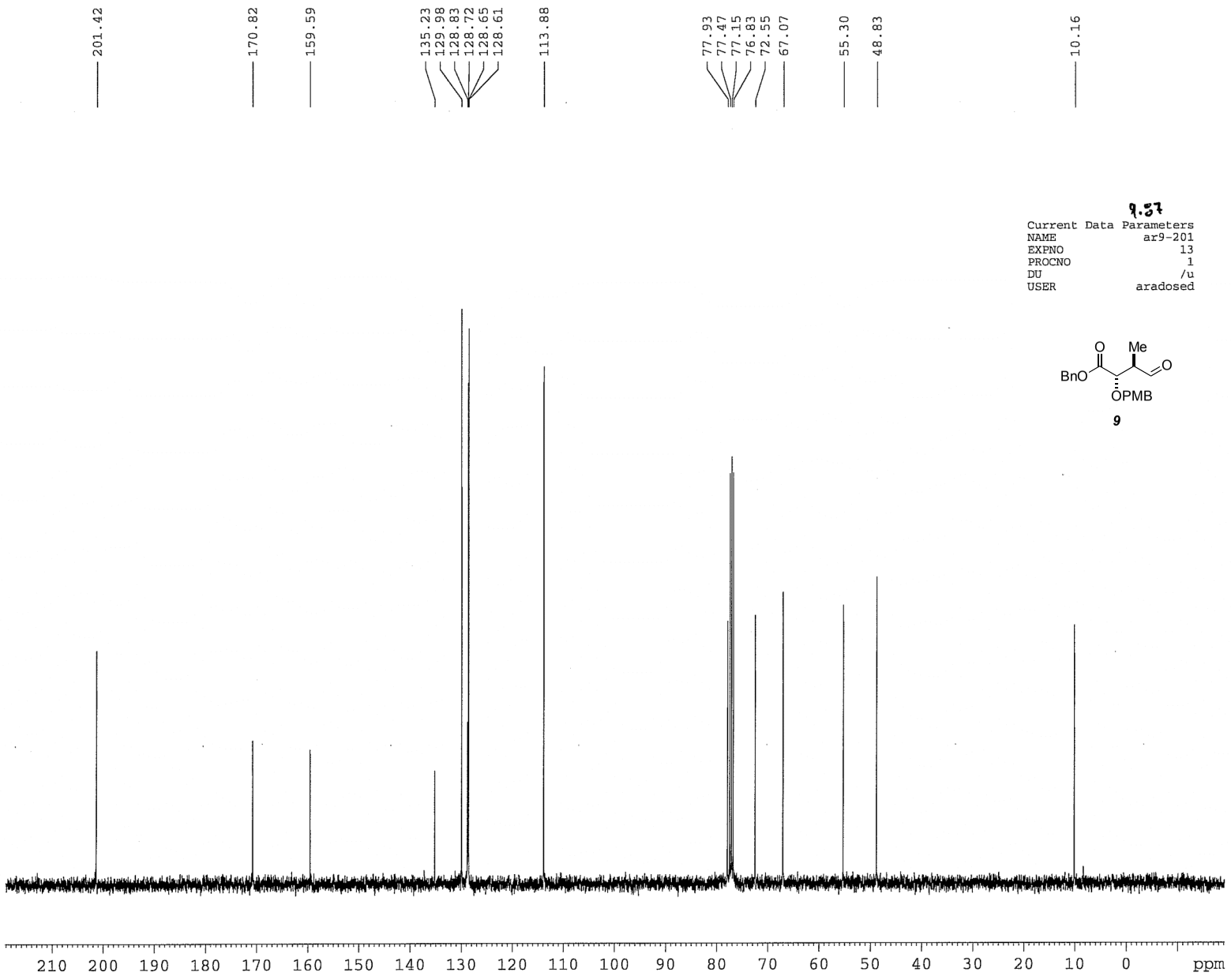
9.88

```
Current Data Parameters
NAME         ar10-lactone
EXPNO                   8
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070426
Time                23.33
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG         noesygpph
TD                   2048
SOLVENT              CDCl3
NS                      8
DS                     16
SWH              3205.128 Hz
FIDRES           1.565004 Hz
AQ               0.3195380 sec
RG                    50.8
DW                156.000 usec
DE                  7.11 usec
TE                 293.5 K
d0             0.00014576 sec
D1             2.00000000 sec
D8             3.00000000 sec
D16            0.00020000 sec
IN0            0.00031240 sec
MCREST         0.00000000 sec
MCWRK          2.00000000 sec
TAU            1.49880004 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.20 usec
P2                  16.40 usec
PL1                 -3.00 dB
SFO1         400.1316005 MHz

====== GRADIENT CHANNEL ====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1                 0.00 %
GPX2                 0.00 %
GPY1                 0.00 %
GPY2                 0.00 %
GPZ1                40.00 %
GPZ2               -40.00 %
P16                1000.00 usec

F1 - Acquisition parameters
ND0                     1
TD                    128
SFO1           400.1316 MHz
FIDRES          25.008003 Hz
SW                 8.000 ppm
FnMODE              TPPI

F2 - Processing parameters
SI                   2048
SF           400.1300942 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   4.00

F1 - Processing parameters
SI                   1024
MC2                  TPPI
SF           400.1300998 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```


7.386
7.378
7.362
7.355
7.346
7.260
7.227
7.210
6.863
6.846
5.210
5.203
4.651
4.628
4.320
4.297
3.916
3.905
3.798
3.591
3.580
2.207
2.195
2.183
0.929
0.915
O
Me
BnO
OH
OPMB
S5
9.86
Current Data Parameters
USER aradosed
NAME ar9-200
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070315
Time 18.24
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 128
DW 50.000 use
DE 7.11 use
TE 293.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 =======
NUC1 1H
P1 12.20 use
PL1 -5.00 dB
SFO1 500.1330883 MHz
F1 - Acquisition parameters
ND0 2
TD 64
SFO1 500.1321 MHz
FIDRES 65.540741 Hz
9
8
7
6
5
4
3
2
1
0
ppm
4.96
1.95
2.00
1.96
0.97
1.00
0.93
3.07
2.01
1.21
3.05

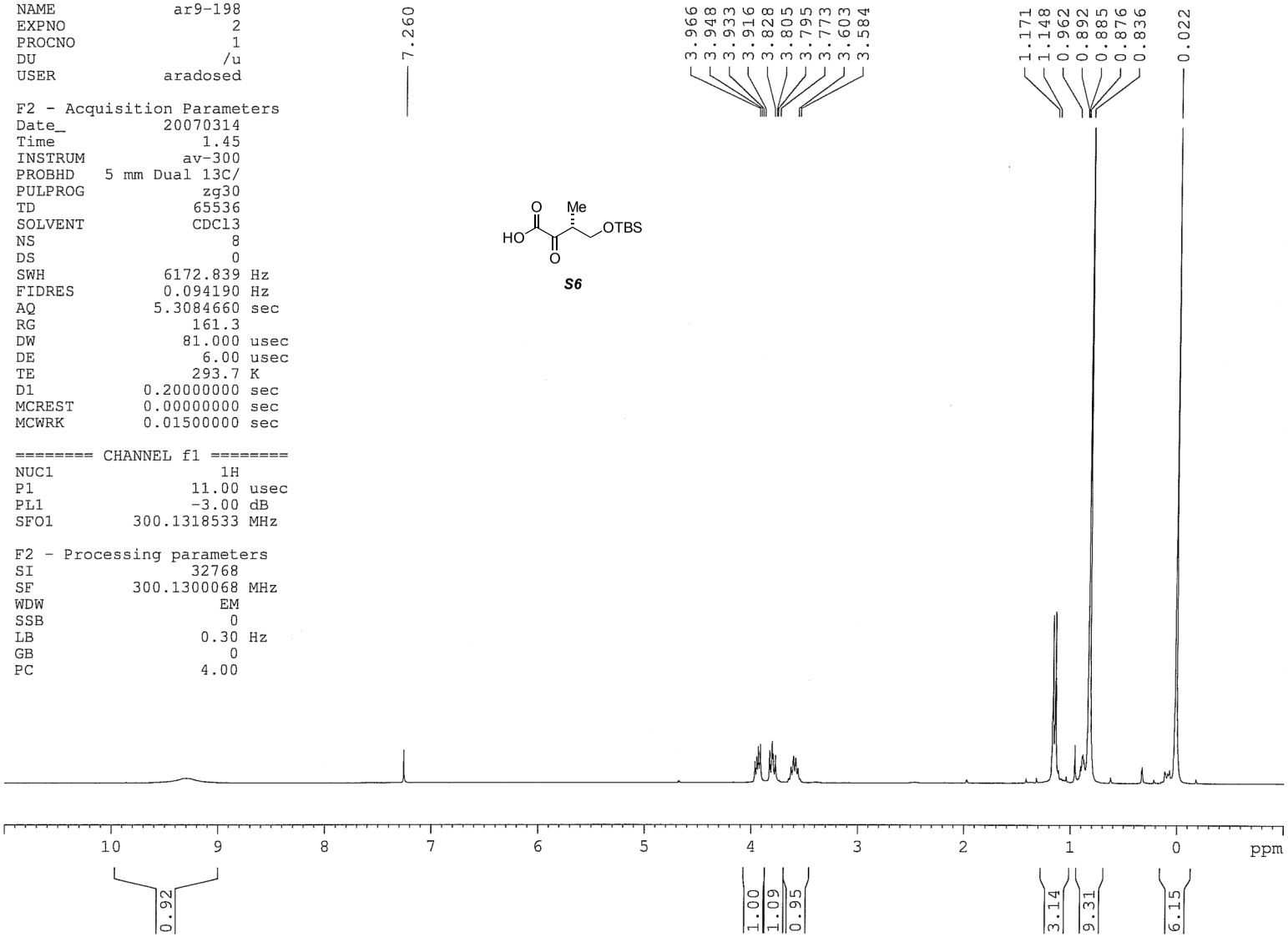

9.86
Current Data Parameters
USER aradosed
NAME ar9-200
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070315
Time 18.26
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 297
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F1 - Acquisition parameters
ND0 2
TD 64
SFO1 500.1321 MHz
FIDRES 65.540741 Hz
SW 8.387 ppm
FnMODE undefined
F2 - Processing parameters
172.12
159.45
135.44
129.82
129.00
128.60
128.45
113.80
81.22
77.25
77.00
76.74
72.40
66.66
65.12
55.22
38.46
13.59
O
Me
BnO
OH
OPMB
S5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


9.663
7.382
7.374
7.349
7.226
7.205
6.870
6.848
5.216
5.210
4.690
4.662
4.413
4.385
4.197
4.183
3.795
2.840
2.823
2.806
1.072
1.054
BnO
O
Me
O
OPMB
9
9.67
Current Data Parameters
USER aradosed
NAME ar9-201
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070315
Time 23.43
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 1
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 32
DW 60.400 use
DE 6.00 use
TE 293.7 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 =======
NUC1 1H
P1 8.15 use
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300167 MHz
WDW EM
SSB 0
10
9
8
7
6
5
4
3
2
1
0
ppm
0.94
5.02
2.03
2.00
2.00
1.00
1.02
0.97
3.03
0.98
2.89


201.42
170.82
159.59
135.23
129.98
128.83
128.72
128.65
128.61
113.88
77.93
77.47
77.15
76.83
72.55
67.07
55.30
48.83
10.16
9.57
Current Data Parameters
NAME ar9-201
EXPNO 13
PROCNO 1
DU /u
USER aradosed
O
Me
BnO
O
OPMB
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

9.89

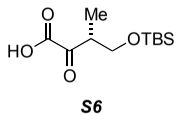
```
Current Data Parameters
NAME              ar9-198
EXPNO                   2
PROCNO                  1
DU                     /u
USER              aradosed

F2 - Acquisition Parameters
Date_            20070314
Time                 1.45
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                 161.3
DW                81.000 usec
DE                 6.00 usec
TE                293.7 K
D1           0.20000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.00 usec
PL1                -3.00 dB
SFO1         300.1318533 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00
```



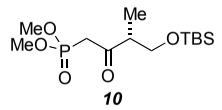
S6

9.89

```
Current Data Parameters
NAME                ar9-198
EXPNO                    13
PROCNO                    1
F2 - Acquisition Parameters
Date_              20070314
Time                   0.29
INSTRUM              av-300
PROBHD    5 mm Dual 13C/
PULPROG              zgpg30
TD                    65536
SOLVENT                CDC13
NS                        70
DS                         0
SWH               17985.611 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                     32768
DW                    27.800 usec
DE                     6.00 usec
TE                    293.9 K
D1                1.00000000 sec
D11               0.03000000 sec
DELTA             0.89999998 sec
TCREST            0.00000000 sec
TCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.50 usec
PL1                     0.00 dB
SFO1              75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                120.00 usec
PL2                   -3.00 dB
PL12                  17.76 dB
PL13                  23.00 dB
SFO2             300.1300000 MHz

F2 - Processing parameters
SI                     32768
SF                75.4677293 MHz
WDW                       EM
SSB                        0
LB                      1.50 Hz
GB                         0
PC                      4.00
```



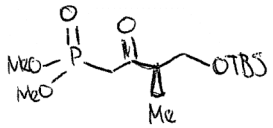
S6



10

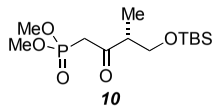
9.90

```
Current Data Parameters
NAME                 ar7-066
EXPNO                      1
PROCNO                     1
DU                        /u
USER                aradosed

F2 - Acquisition Parameters
Date_              20051104
Time                 21.20
INSTRUM            AVB-400
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                   228.1
DW                  60.400 usec
DE                   6.00 usec
TE                  294.2 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.15 usec
PL1                  -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300177 MHz
WDW                     EM
```



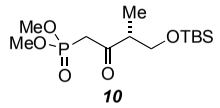
9.90

```
Current Data Parameters
NAME                  ar7-066
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_               20051104
Time                   21.23
INSTRUM              AVB-400
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                       312
DS                         0
SWH                23980.814 Hz
FIDRES             0.365918 Hz
AQ                 1.3664756 sec
RG                     16384
DW                    20.850 usec
DE                     6.00 usec
TE                    294.3 K
D1               1.50000000 sec
d11              0.03000000 sec
DELTA            1.39999998 sec
MCREST           0.00000000 sec
MCWRK            0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                      8.50 usec
PL1                    -2.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 70.00 usec
PL2                    -3.00 dB
PL12                   16.00 dB
PL13                   16.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                       32768
SF              100.6127690 MHz
WDW                         EM
SSB                          0
LB                        1.50 Hz
GB                           0
PC                        4.00
```



10

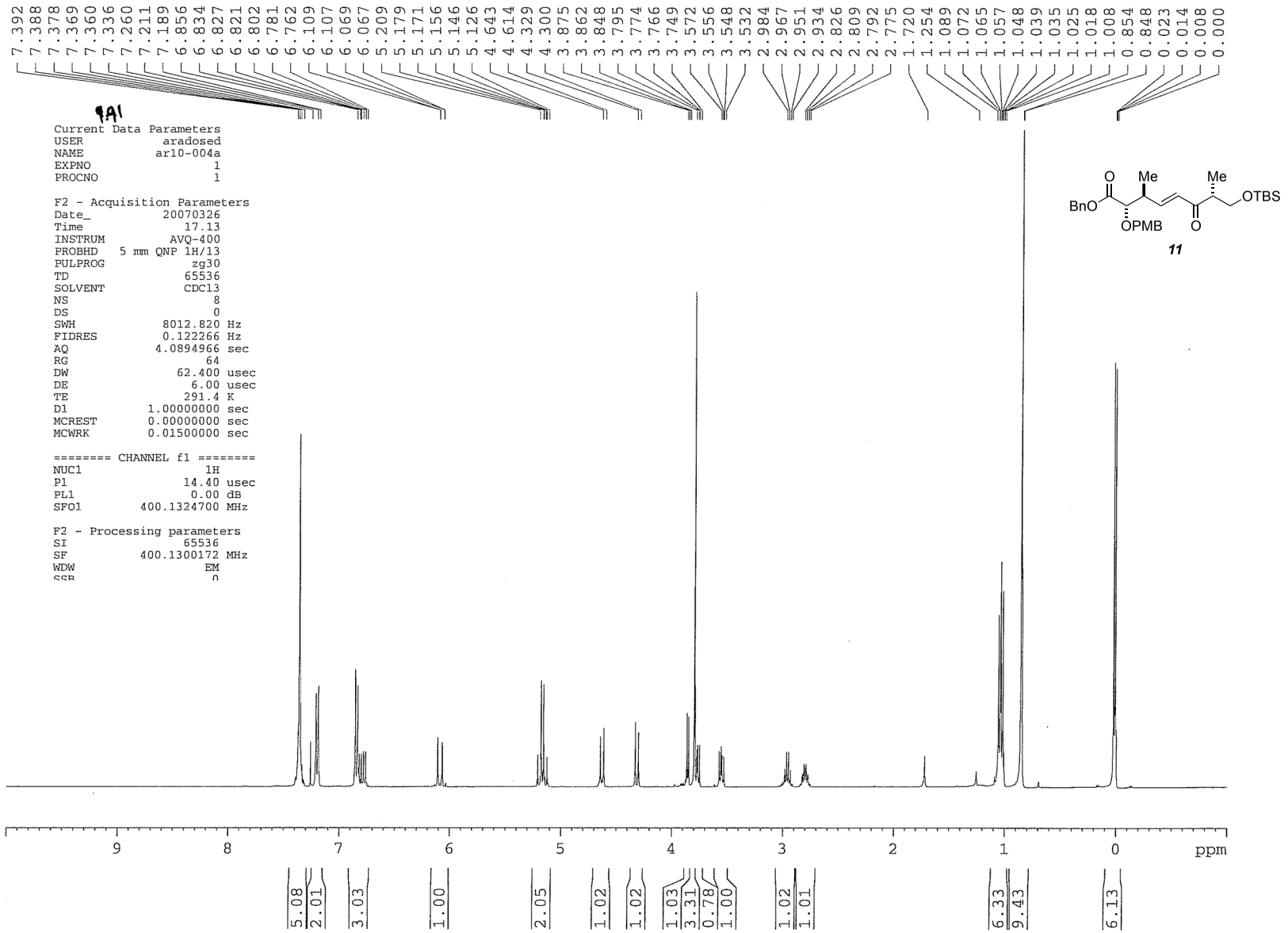
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN

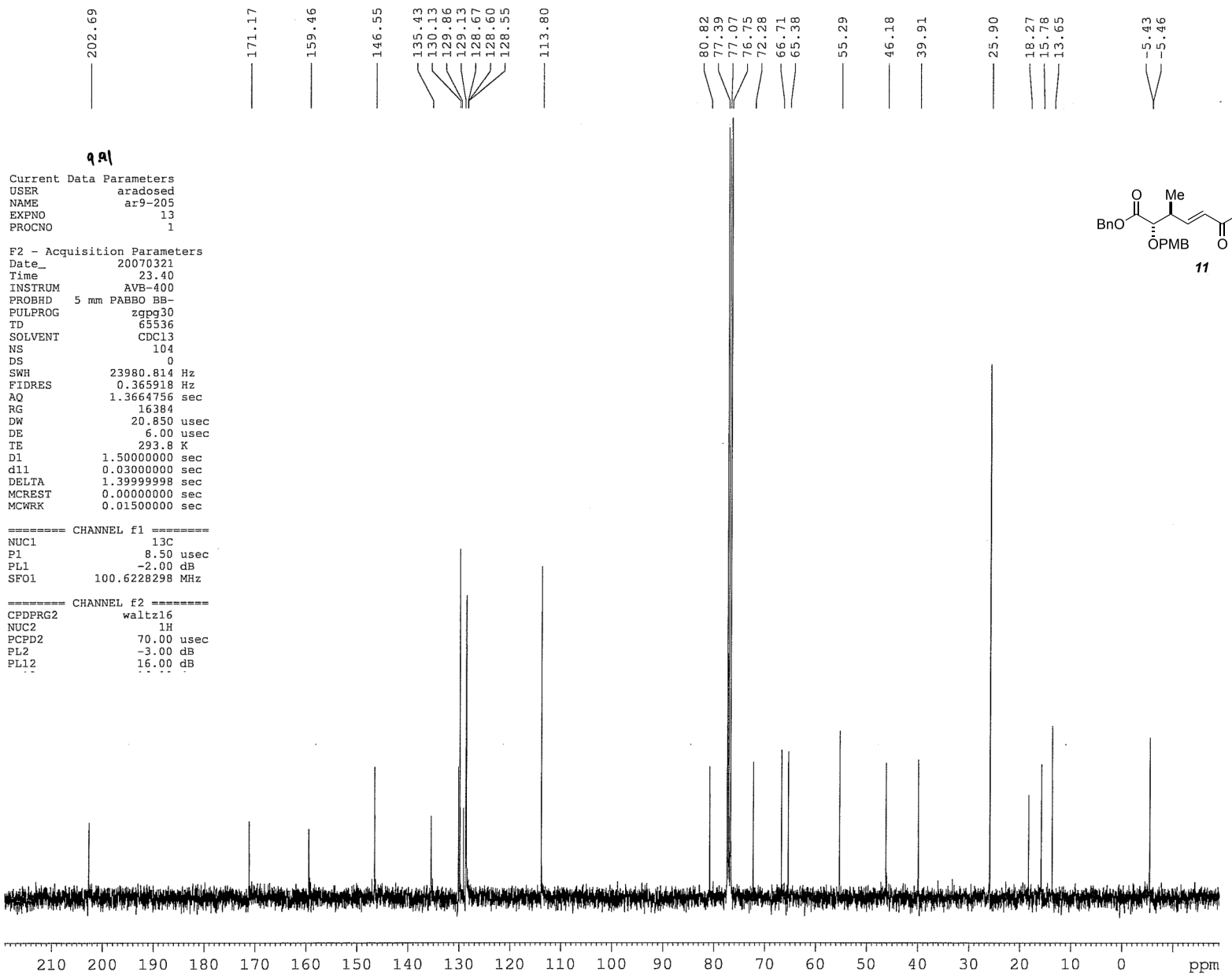


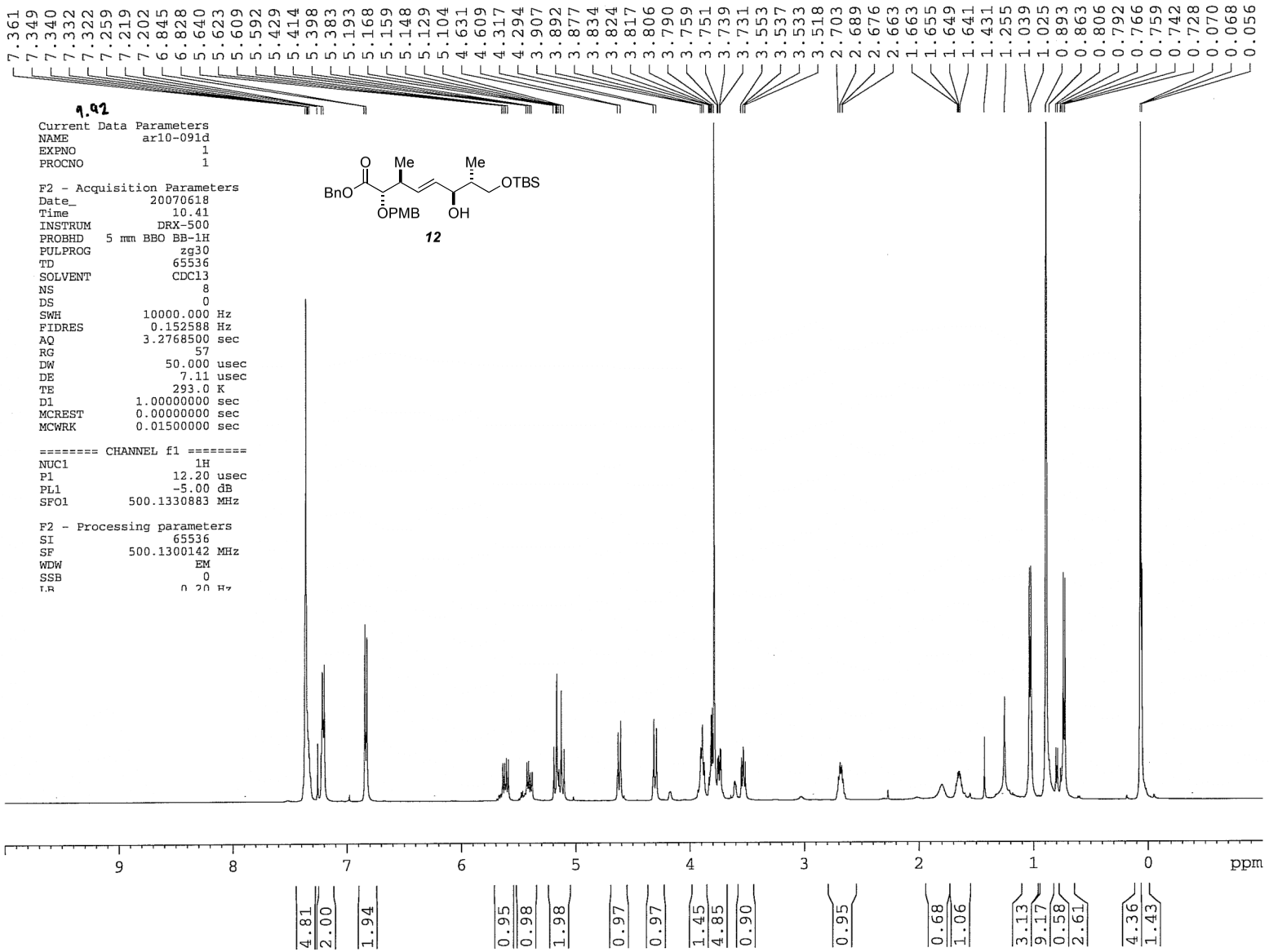
10

9.50

```
Current Data Parameters
USER              aradosed
NAME              ar7-066
EXPNO                   31
PROCNO                   1

F2 - Acquisition Parameters
Date_           20051104
Time               19.37
INSTRUM          AVQ-400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   21
DS                    0
SWH           64724.918 Hz
FIDRES         0.987624 Hz
AQ            0.5063156 sec
RG                 8192
DW                7.725 usec
DE                6.00 usec
TE                293.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 31P
P1                  7.70 usec
PL1                -2.00 dB
SFO1        161.9674750 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              70.00 usec
PL2                 0.00 dB
PL12               15.00 dB
PL13               17.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF          161.9755989 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  4.00
```

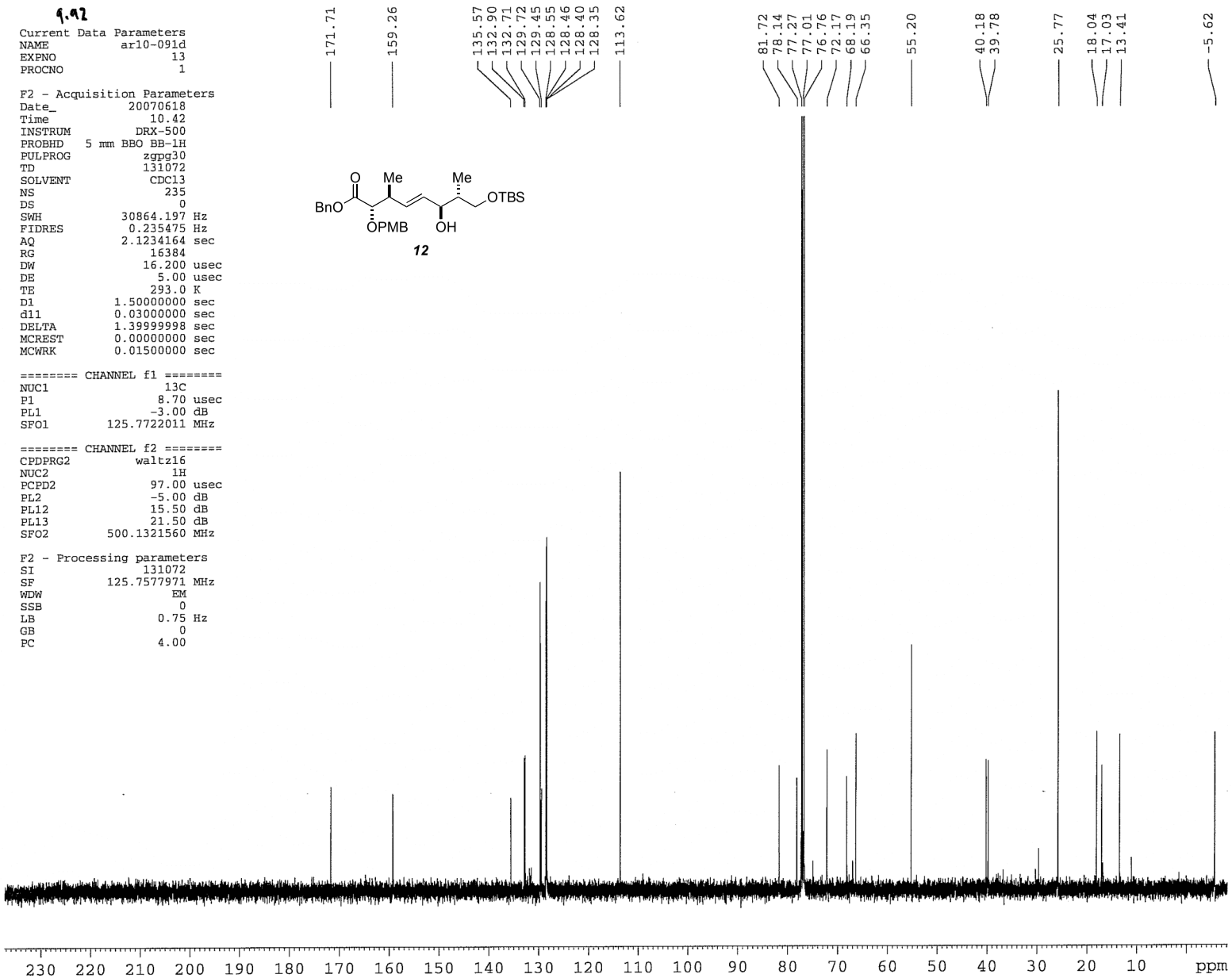

7.392 7.388 7.378 7.369 7.360 7.336 7.260 7.211 7.189 6.856 6.834 6.827 6.821 6.802 6.781 6.762 6.109 6.107 6.069 6.067 5.209 5.179 5.171 5.156 5.146 5.126 4.643 4.614 4.329 4.300 3.875 3.862 3.848 3.795 3.774 3.766 3.749 3.572 3.556 3.548 3.532 2.984 2.967 2.951 2.934 2.826 2.809 2.792 2.775 1.720 1.254 1.089 1.072 1.065 1.057 1.048 1.039 1.035 1.025 1.018 1.008 0.854 0.848 0.023 0.014 0.008 0.000
9A1
Current Data Parameters
USER aradosed
NAME ar10-004a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070326
Time 17.13
INSTRUM AVQ-400
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 64
DW 62.400 usec
DE 6.00 usec
TE 291.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 14.40 usec
PL1 0.00 dB
SFO1 400.1324700 MHz
F2 - Processing parameters
SI 65536
SF 400.1300172 MHz
WDW EM
BnO
OPMB
Me
Me
OTBS
11
9 8 7 6 5 4 3 2 1 0 ppm
5.08 2.01 3.03 1.00 2.05 1.02 1.02 1.03 3.31 0.78 1.00 1.02 1.01 6.33 9.43 6.13

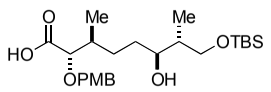

202.69
171.17
159.46
146.55
135.43
130.13
129.86
129.13
128.67
128.60
128.55
113.80
80.82
77.39
77.07
76.75
72.28
66.71
65.38
55.29
46.18
39.91
25.90
18.27
15.78
13.65
-5.43
-5.46
9 A1
Current Data Parameters
USER aradosed
NAME ar9-205
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070321
Time 23.40
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 104
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 293.8 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 16.00 dB
O
Me
Me
BnO
OTBS
OPMB
O
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.361 7.349 7.340 7.332 7.322 7.259 7.219 7.202 6.845 6.828 5.640 5.623 5.609 5.592 5.429 5.414 5.398 5.383 5.193 5.168 5.159 5.148 5.129 5.104 4.631 4.609 4.317 4.294 3.907 3.892 3.877 3.834 3.824 3.817 3.806 3.790 3.759 3.751 3.739 3.731 3.553 3.537 3.533 3.518 2.703 2.689 2.676 2.663 1.663 1.655 1.649 1.641 1.431 1.255 1.039 1.025 0.893 0.863 0.806 0.792 0.766 0.759 0.742 0.728 0.070 0.068 0.056
9.92
Current Data Parameters
NAME ar10-091d
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070618
Time 10.41
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 57
DW 50.000 usec
DE 7.11 usec
TE 293.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
PL1 -5.00 dB
SFO1 500.1330883 MHz
F2 - Processing parameters
SI 65536
SF 500.1300142 MHz
WDW EM
SSB 0
LB 0.20 Hz
O
Me
Me
BnO
OTBS
OPMB
OH
12
9
8
7
6
5
4
3
2
1
0
ppm
4.81
2.00
1.94
0.95
0.98
1.98
0.97
0.97
1.45
4.85
0.90
0.95
0.68
1.06
3.13
9.17
0.58
2.61
4.36
1.43

9.92

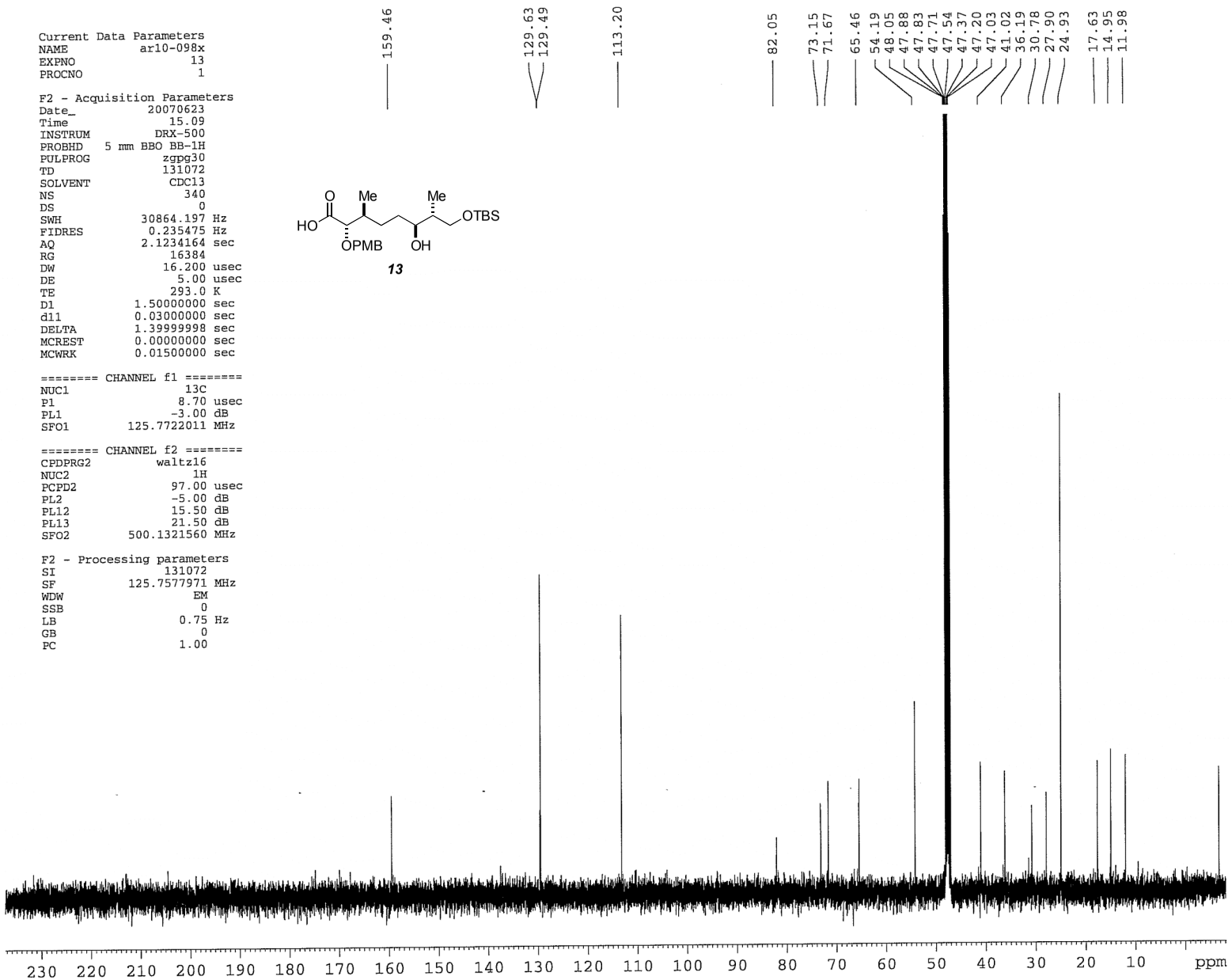
```
Current Data Parameters
NAME          ar10-091d
EXPNO                13
PROCNO                1

F2 - Acquisition Parameters
Date_          20070618
Time              10.42
INSTRUM         DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD               131072
SOLVENT            CDCl3
NS                   235
DS                     0
SWH            30864.197 Hz
FIDRES             0.235475 Hz
AQ             2.1234164 sec
RG                 16384
DW                16.200 usec
DE                 5.00 usec
TE                293.0 K
D1            1.50000000 sec
d11           0.03000000 sec
DELTA         1.39999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.70 usec
PL1                -3.00 dB
SFO1        125.7722011 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              97.00 usec
PL2                -5.00 dB
PL12               15.50 dB
PL13               21.50 dB
SFO2        500.1321560 MHz

F2 - Processing parameters
SI                131072
SF          125.7577971 MHz
WDW                 EM
SSB                  0
LB                0.75 Hz
GB                   0
PC                4.00
```

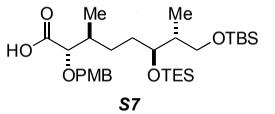




13

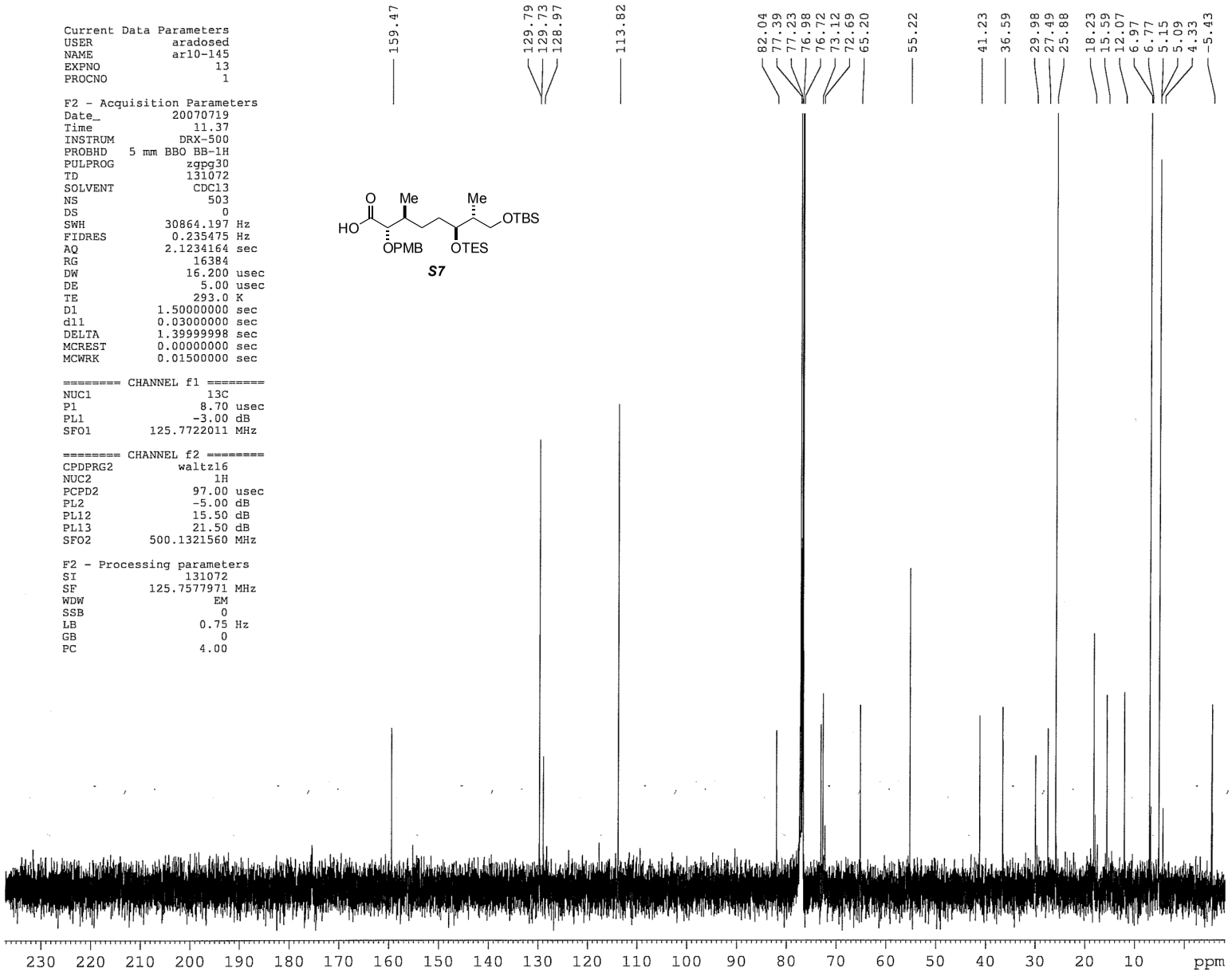

```
Current Data Parameters
NAME                  ar10-098x
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070623
Time                      15.08
INSTRUM                DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG                   zg30
TD                       65536
SOLVENT                   MeOD
NS                            1
DS                            0
SWH                10000.000 Hz
FIDRES                 0.152588 Hz
AQ                 3.2768500 sec
RG                        161.3
DW                     50.000 usec
DE                      7.11 usec
TE                      293.0 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                       12.20 usec
PL1                      -5.00 dB
SFO1               500.1330883 MHz

F2 - Processing parameters
SI                           65536
SF                 500.1300127 MHz
WDW                          EM
SSB                           0
LB                            0.20 Hz
```


Current Data Parameters
NAME ar10-098x
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070623
Time 15.09
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 340
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577971 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 1.00
159.46
129.63
129.49
113.20
82.05
73.15
71.67
65.46
54.19
48.05
47.88
47.83
47.71
47.54
47.37
47.20
47.03
41.02
36.19
30.78
27.90
24.93
17.63
14.95
11.98
O
Me
Me
HO
OTBS
OPMB
OH
13
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

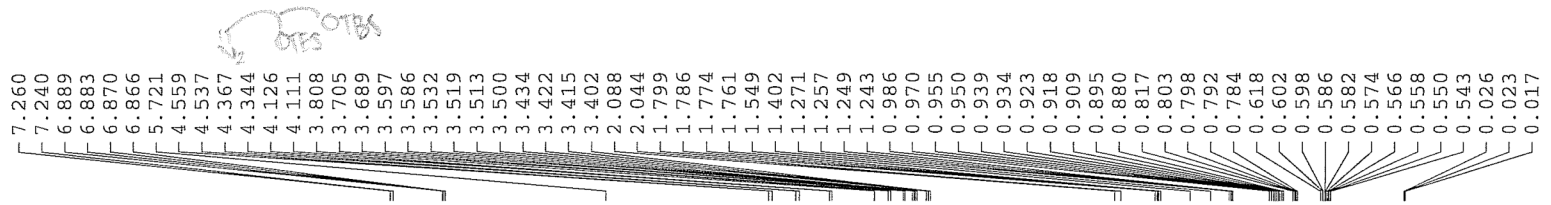


S7

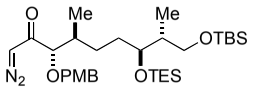
```
Current Data Parameters
USER            aradosed
NAME            ar10-145
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070719
Time               11.36
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ             3.2768500 sec
RG                   114
DW                50.000 usec
DE                 7.11 usec
TE                293.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.20 usec
PL1                -5.00 dB
SFO1         500.1330883 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300145 MHz
WDW                   EM
SSB                    0
```



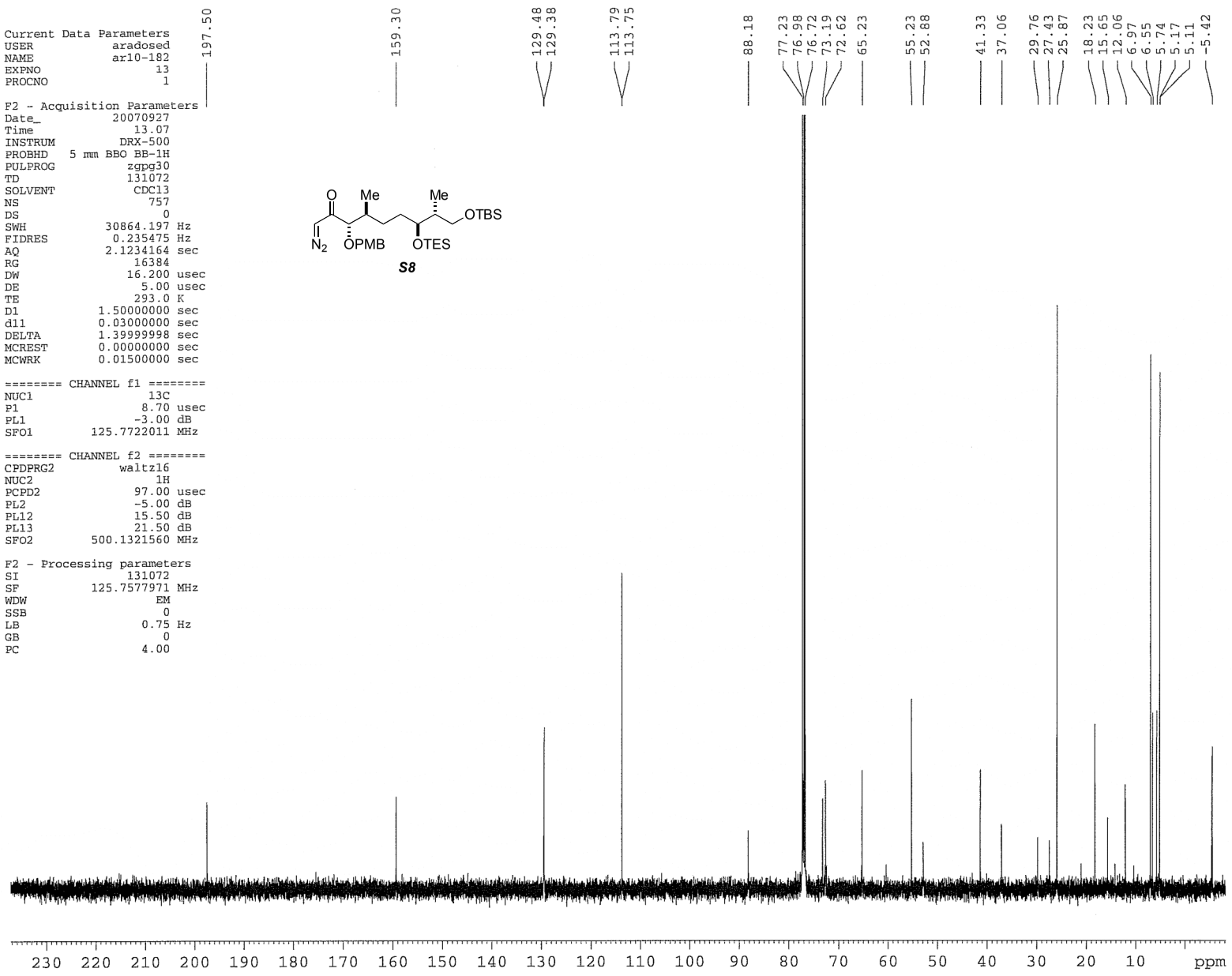

```
Current Data Parameters
USER            aradosed
NAME            ar10-145
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070719
Time                11.37
INSTRUM          DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                131072
SOLVENT             CDCl3
NS                    503
DS                      0
SWH             30864.197 Hz
FIDRES          0.235475 Hz
AQ              2.1234164 sec
RG                  16384
DW                16.200 usec
DE                 5.00 usec
TE                293.0 K
D1             1.50000000 sec
d11            0.03000000 sec
DELTA          1.39999998 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 8.70 usec
PL1               -3.00 dB
SFO1         125.7722011 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             97.00 usec
PL2               -5.00 dB
PL12              15.50 dB
PL13              21.50 dB
SFO2         500.1321560 MHz

F2 - Processing parameters
SI                131072
SF           125.7577971 MHz
WDW                 EM
SSB                  0
LB                0.75 Hz
GB                   0
PC                4.00
```

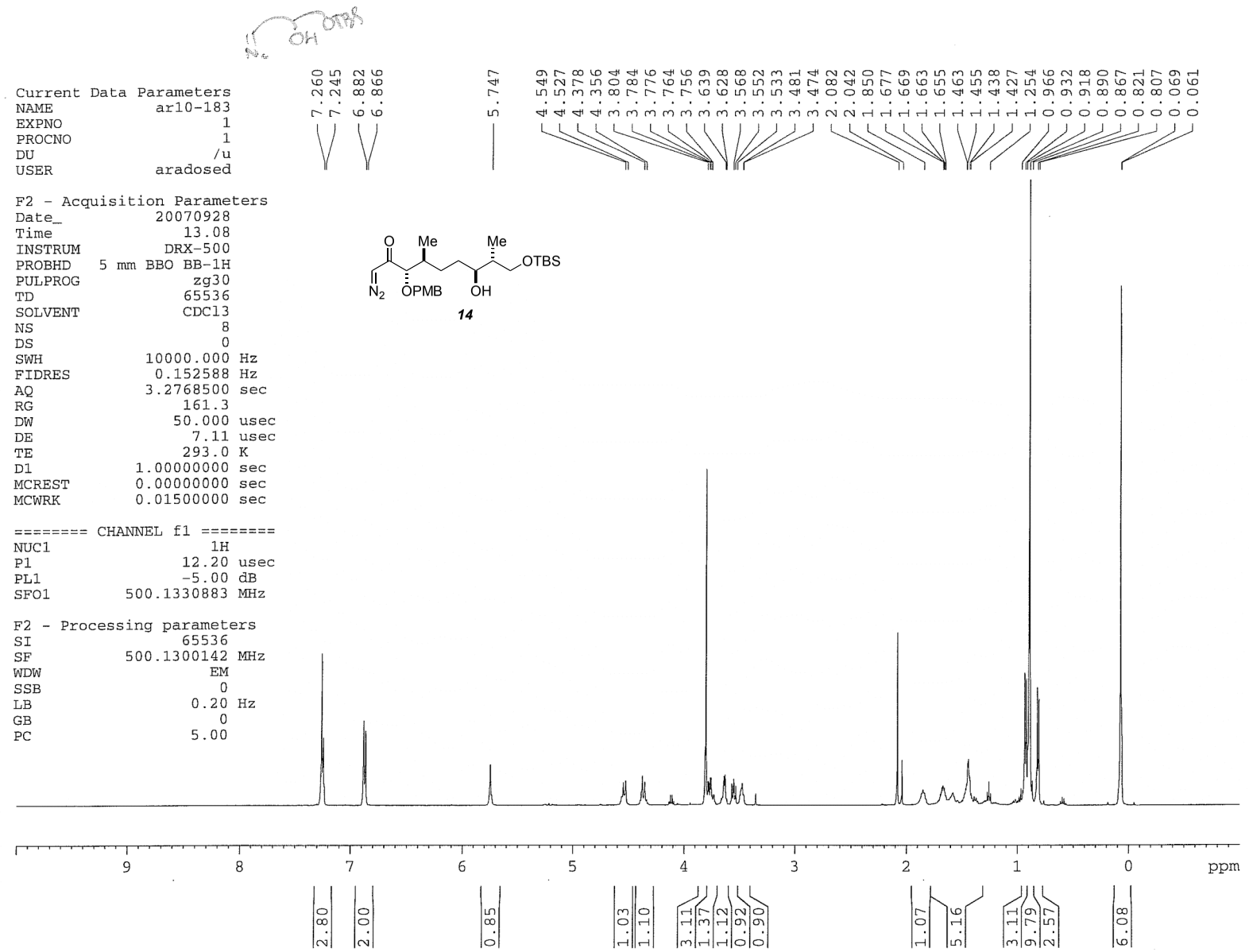


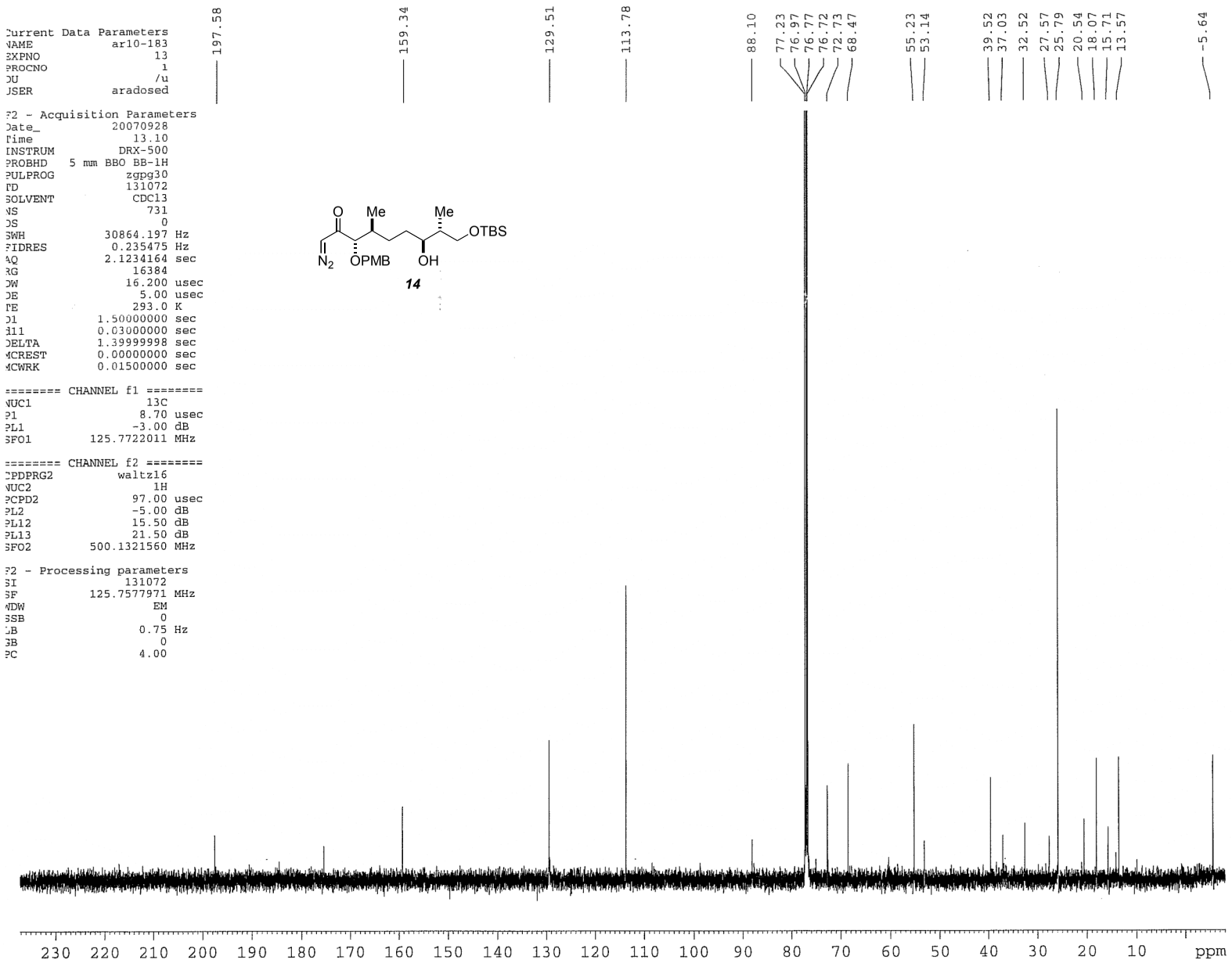

```
Current Data Parameters
USER            aradosed
NAME            ar10-182
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070927
Time              13.05
INSTRUM         DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2768500 sec
RG                   128
DW              50.000 usec
DE               7.11 usec
TE               293.0 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1              12.20 usec
PL1             -5.00 dB
SFO1        500.1330883 MHz

F2 - Processing parameters
SI                 65536
SF          500.1300142 MHz
WDW                   EM
SSB                    0
```

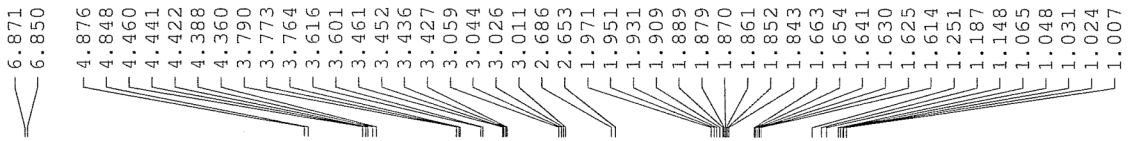


S8

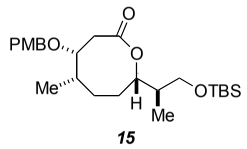

197.50
159.30
129.48
129.38
113.79
113.75
88.18
77.23
76.98
76.72
73.19
72.62
65.23
55.23
52.88
41.33
37.06
29.76
27.43
25.87
18.23
15.65
12.06
6.97
6.55
5.74
5.17
5.11
-5.42
Current Data Parameters
USER aradosed
NAME ar10-182
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070927
Time 13.07
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 757
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577971 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 4.00
O
Me
Me
OTBS
N2
OPMB
OTES
S8
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Current Data Parameters
NAME ar10-183
EXPNO 1
PROCNO 1
DU /u
USER aradosed
F2 - Acquisition Parameters
Date_ 20070928
Time 13.08
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 161.3
DW 50.000 usec
DE 7.11 usec
TE 293.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
PL1 -5.00 dB
SFO1 500.1330883 MHz
F2 - Processing parameters
SI 65536
SF 500.1300142 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 5.00
7.260
7.245
6.882
6.866
5.747
4.549
4.527
4.378
4.356
3.804
3.784
3.776
3.764
3.756
3.639
3.628
3.568
3.552
3.533
3.481
3.474
2.082
2.042
1.850
1.677
1.669
1.663
1.655
1.463
1.455
1.438
1.427
1.254
0.966
0.932
0.918
0.890
0.867
0.821
0.807
0.069
0.061
O
Me
Me
OTBS
N2
OPMB
OH
14
9
8
7
6
5
4
3
2
1
0
ppm
2.80
2.00
0.85
1.03
1.10
3.11
1.37
1.12
0.92
0.90
1.07
5.16
3.11
9.79
2.57
6.08

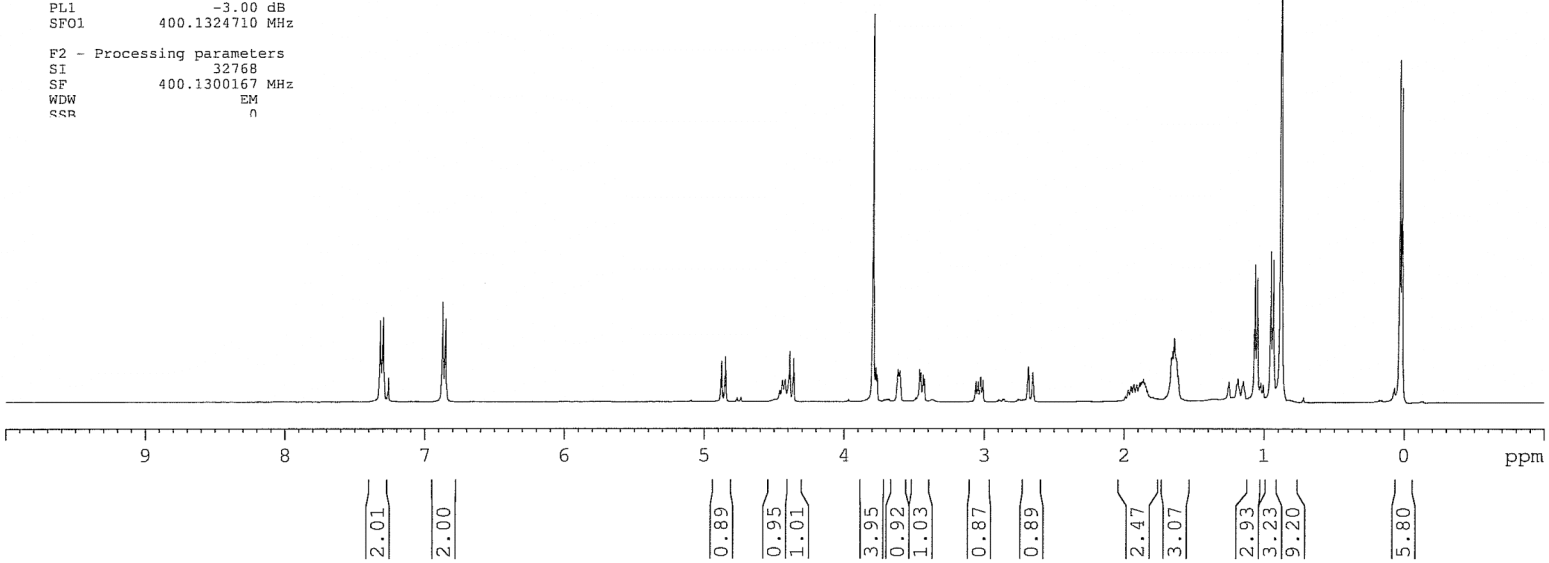

Current Data Parameters
NAME ar10-183
EXPNO 13
PROCNO 1
DU /u
USER aradosed
F2 - Acquisition Parameters
Date_ 20070928
Time 13.10
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 731
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577971 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 4.00
197.58
159.34
129.51
113.78
88.10
77.23
76.97
76.77
76.72
72.73
68.47
55.23
53.14
39.52
37.03
32.52
27.57
25.79
20.54
18.07
15.71
13.57
-5.64
O
Me
Me
OTBS
N2
OPMB
OH
14
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

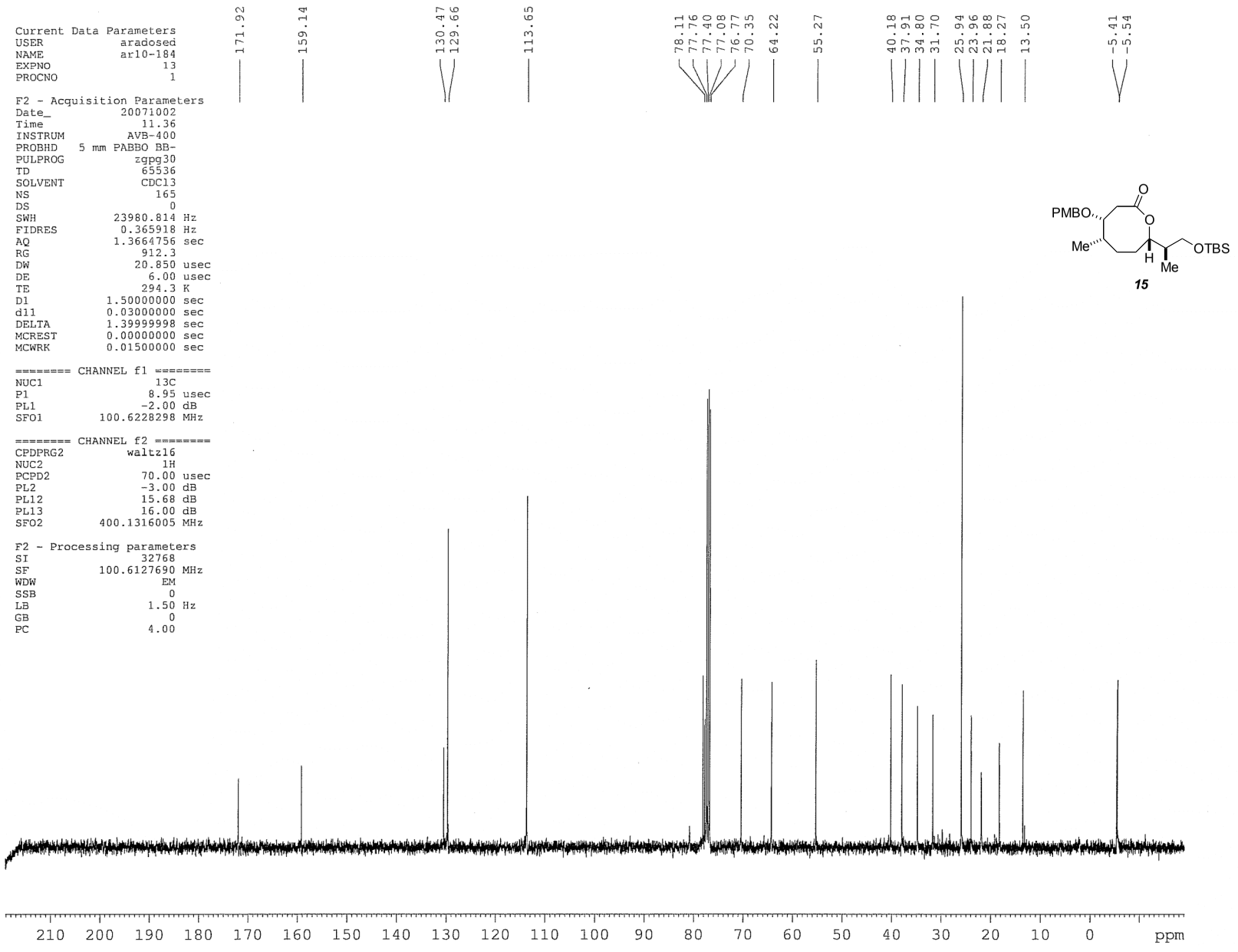


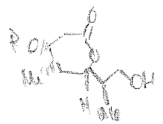

```
Current Data Parameters
USER              aradosed
NAME              ar10-184
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_            20071002
Time                 9.58
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       4
DS                       0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    35.9
DW                  60.400 usec
DE                   6.00 usec
TE                  294.1 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.15 usec
PL1                 -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF           400.1300167 MHz
WDW                     EM
SSB                      0
```



15




171.92
159.14
130.47
129.66
113.65
78.11
77.76
77.40
77.08
76.77
70.35
64.22
55.27
40.18
37.91
34.80
31.70
25.94
23.96
21.88
18.27
13.50
-5.41
-5.54
Current Data Parameters
USER aradosed
NAME ar10-184
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071002
Time 11.36
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 165
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 912.3
DW 20.850 usec
DE 6.00 usec
TE 294.3 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.95 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -3.00 dB
PL12 15.68 dB
PL13 16.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 4.00
O
PMBO
O
Me
H
Me
OTBS
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



Current Data Parameters
NAME ar10-188
EXPNO 1
PROCNO 1
DU /u
USER aradosed

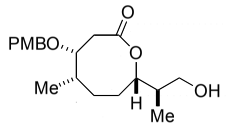
F2 - Acquisition Parameters
Date_ 20071009
Time 19.15
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 1
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 293.7 K
D1 0.20000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -3.00 dB
SFO1 300.1318533 MHz

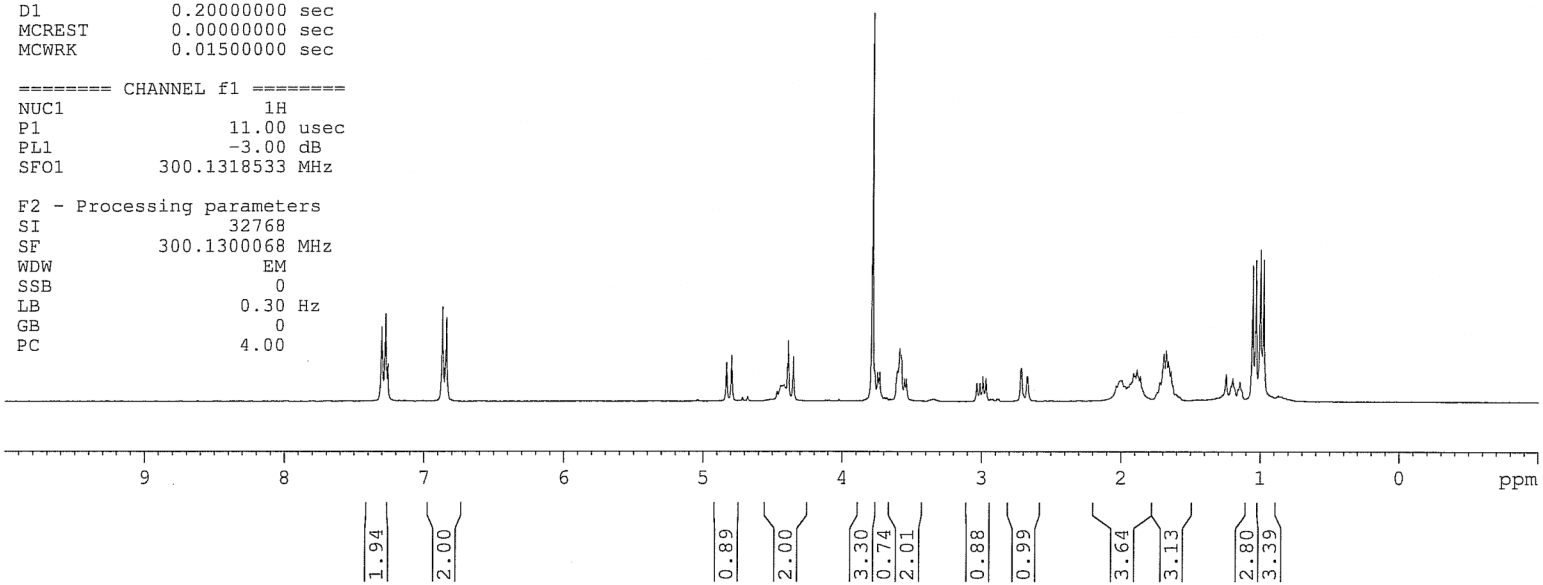
F2 - Processing parameters
SI 32768
SF 300.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 4.00

7.306 7.277 7.260 6.870 6.841

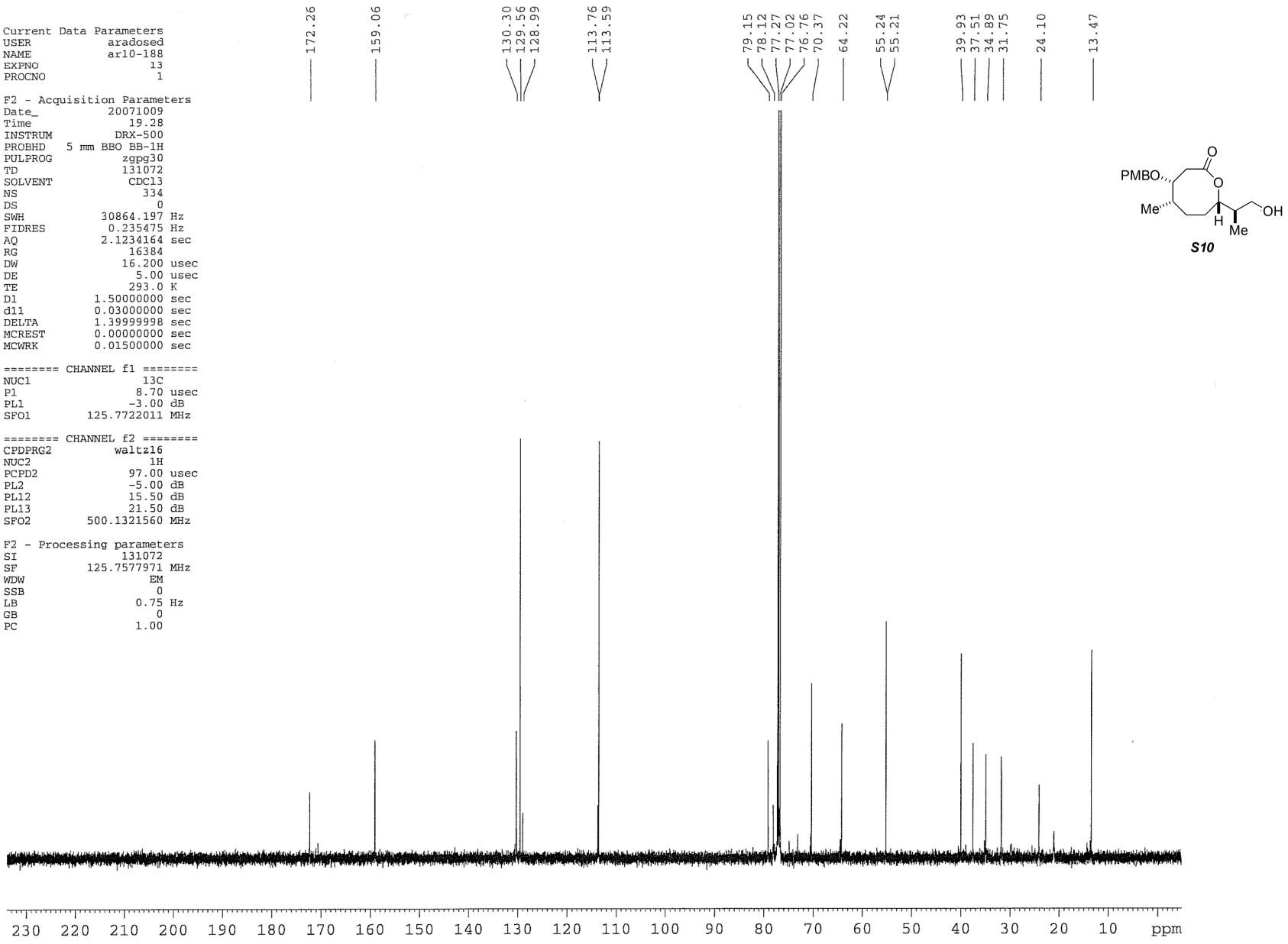
4.834 4.796 4.417 4.388 4.351 3.787 3.746 3.732 3.606 3.590 3.578 3.555 3.542 3.036 3.014 2.992 2.970 2.718 2.674 2.037 1.996 1.913 1.902 1.888 1.864 1.723 1.696 1.678 1.663 1.643 1.246 1.198 1.146 1.058 1.035 1.004 0.981

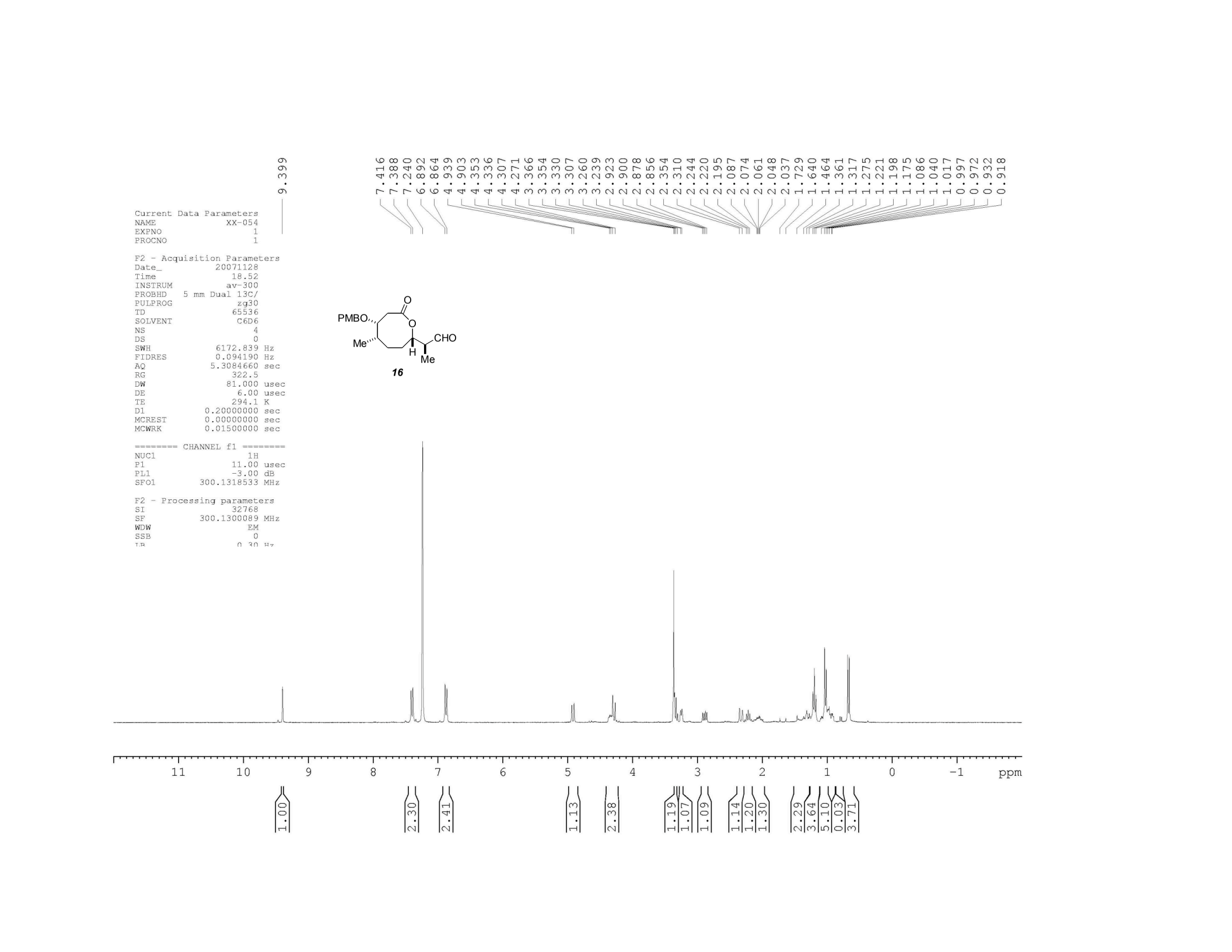


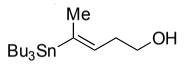
S10



1.94 2.00 0.89 2.00 3.30 0.74 2.01 0.88 0.99 3.64 3.13 2.80 3.39


Current Data Parameters
USER aradosed
NAME ar10-188
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071009
Time 19.28
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 334
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577971 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 1.00
172.26
159.06
130.30
129.56
128.99
113.76
113.59
79.15
78.12
77.27
77.02
76.76
70.37
64.22
55.24
55.21
39.93
37.51
34.89
31.75
24.10
13.47
PMBO
Me
O
O
H
Me
OH
S10
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

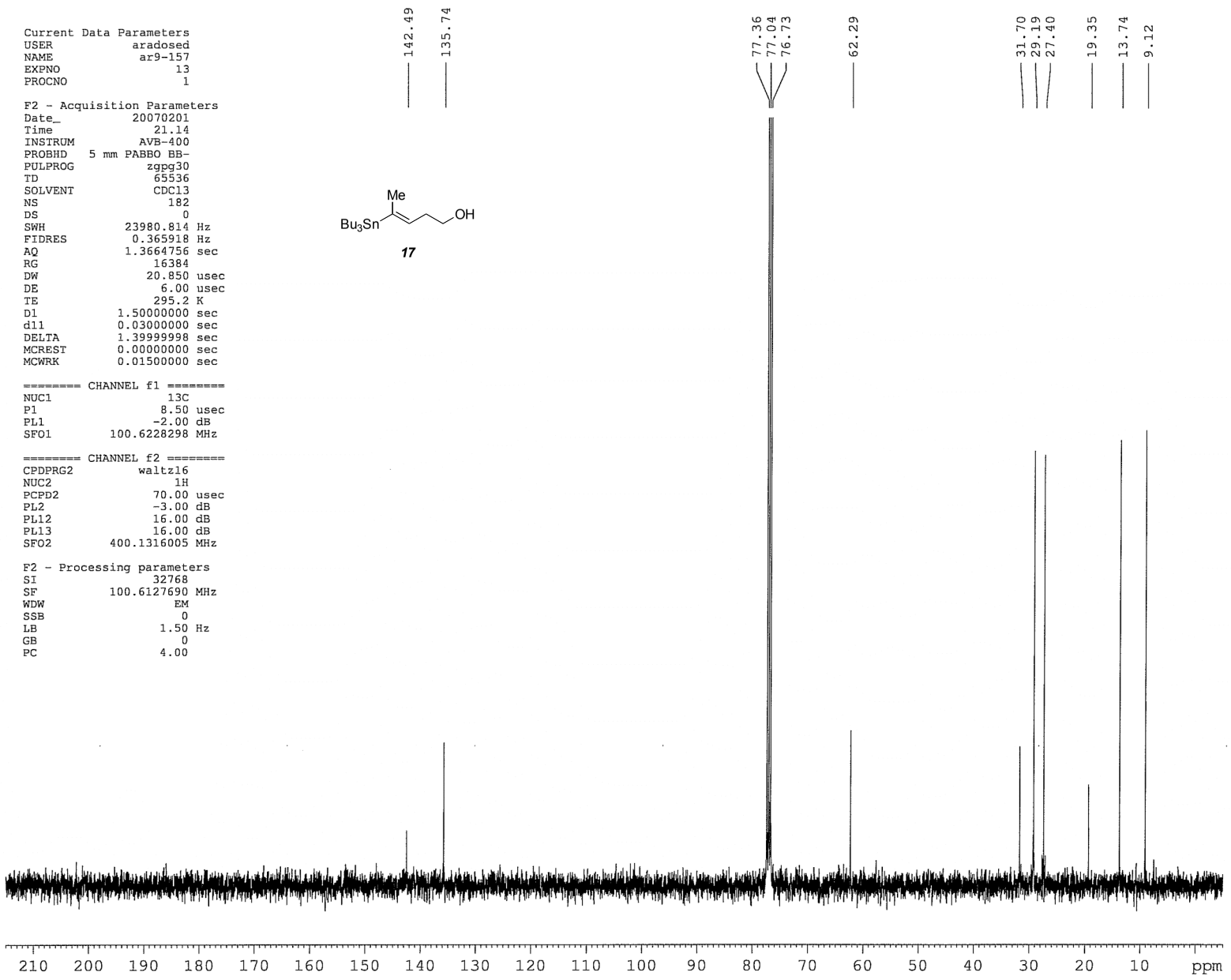

9.399
7.416
7.388
7.240
6.892
6.864
4.939
4.903
4.353
4.336
4.307
4.271
3.366
3.354
3.330
3.307
3.260
3.239
2.923
2.900
2.878
2.856
2.354
2.310
2.244
2.220
2.195
2.087
2.074
2.061
2.048
2.037
1.729
1.640
1.464
1.361
1.317
1.275
1.221
1.198
1.175
1.086
1.040
1.017
0.997
0.972
0.932
0.918
Current Data Parameters
NAME XX-054
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20071128
Time 18.52
INSTRUM av-300
PROBHD 5 mm Dual 13C/
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 4
DS 0
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 322.5
DW 81.000 usec
DE 6.00 usec
TE 294.1 K
D1 0.20000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 11.00 usec
PL1 -3.00 dB
SFO1 300.1318533 MHz
F2 - Processing parameters
SI 32768
SF 300.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
PMBO
Me
CHO
H
Me
16
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
2.30
2.41
1.13
2.38
1.19
1.07
1.09
1.14
1.20
1.30
2.29
3.64
5.10
0.03
3.71



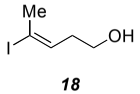
17

9.116

```
Current Data Parameters
USER              aradosed
NAME               ar9-157
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20070201
Time                21.09
INSTRUM           AVB-400
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ               3.9584243 sec
RG                    128
DW                 60.400 usec
DE                  6.00 usec
TE                 295.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.15 usec
PL1                -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300167 MHz
WDW                    EM
SSB                     0
```




```
Current Data Parameters
USER            aradosed
NAME             ar9-157
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070201
Time               21.14
INSTRUM          AVB-400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  182
DS                    0
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                16384
DW               20.850 usec
DE                6.00 usec
TE               295.2 K
D1           1.50000000 sec
d11          0.03000000 sec
DELTA        1.39999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.50 usec
PL1               -2.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              16.00 dB
PL13              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.50 Hz
GB                    0
PC                 4.00
```



18

7.260

6.210
6.205
6.184
6.179
6.175
6.159
6.154

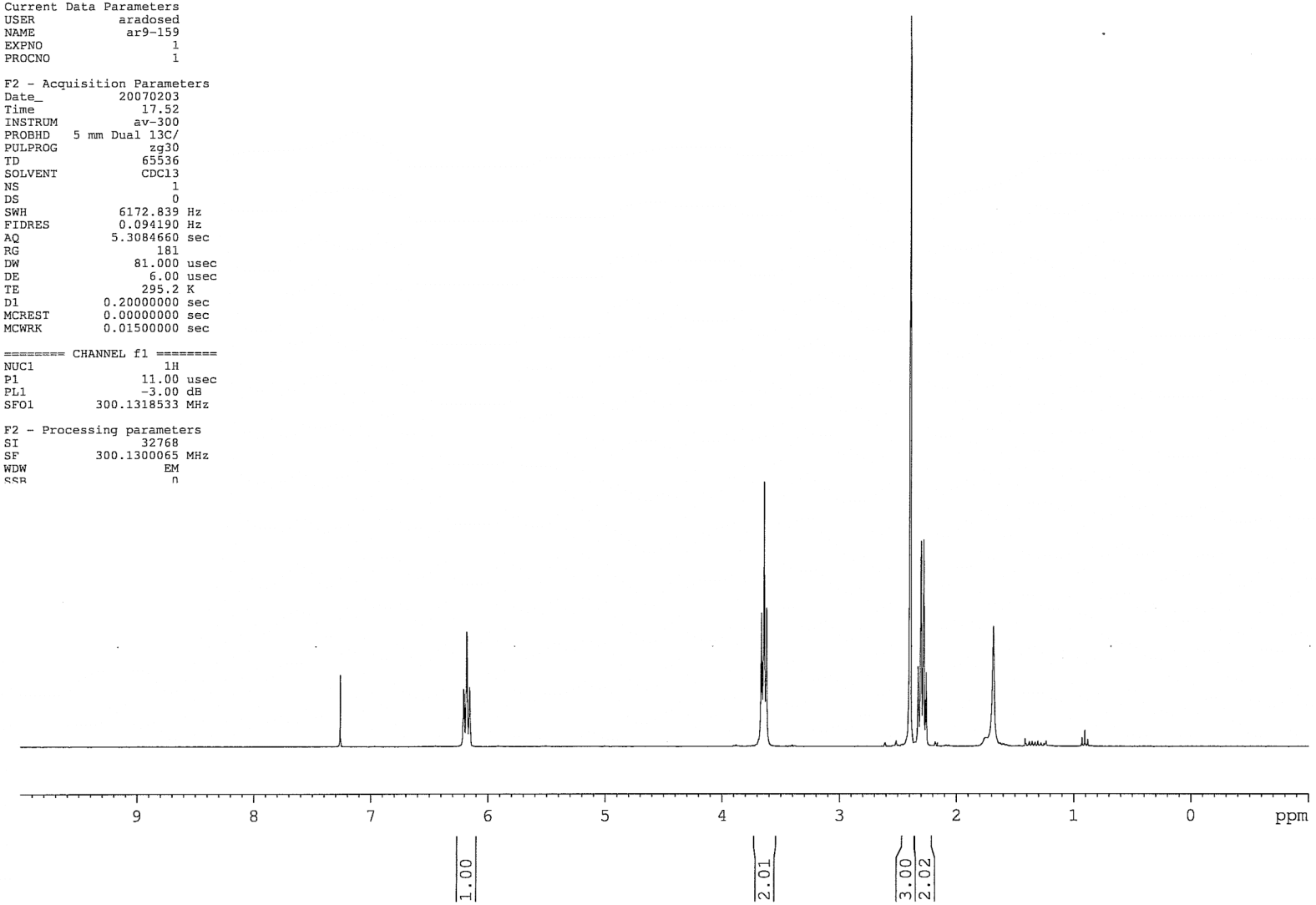
3.666
3.645
3.624

2.400
2.397
2.395
2.329
2.326
2.307
2.304
2.282
2.280
2.261
2.258

1.687

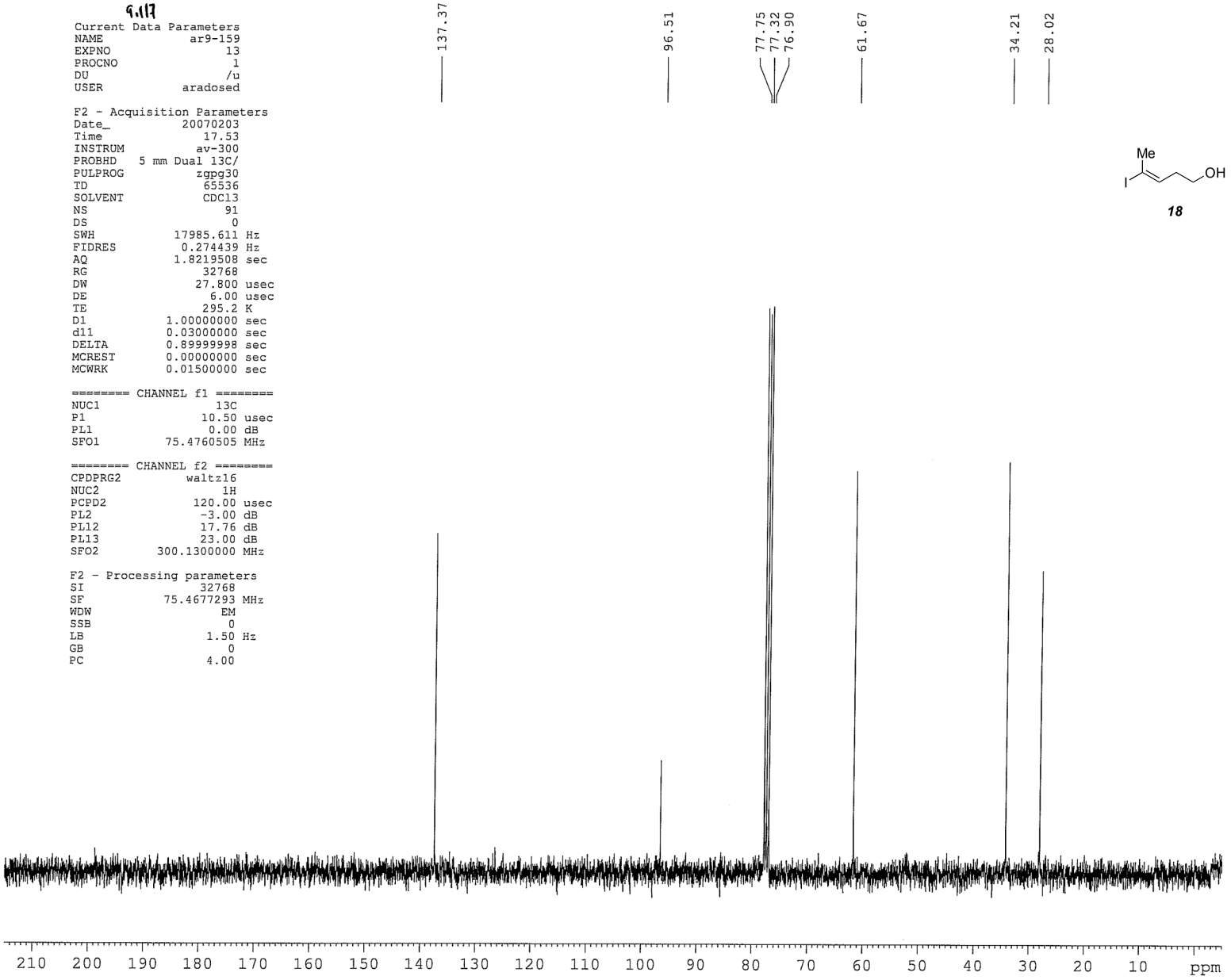
6.117

```
Current Data Parameters
USER            aradosed
NAME             ar9-159
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20070203
Time               17.52
INSTRUM          av-300
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     1
DS                     0
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                295.2 K
D1            0.20000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PL1                -3.00 dB
SFO1         300.1318533 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300065 MHz
WDW                   EM
SSB                    0
```



9.117

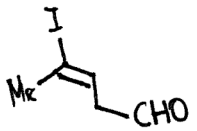
```
Current Data Parameters
NAME              ar9-159
EXPNO                  13
PROCNO                  1
DU                     /u
USER             aradosed

F2 - Acquisition Parameters
Date_            20070203
Time                17.53
INSTRUM           av-300
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT             CDCl3
NS                     91
DS                      0
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 32768
DW                27.800 usec
DE                 6.00 usec
TE                295.2 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.50 usec
PL1                 0.00 dB
SFO1          75.4760505 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             120.00 usec
PL2                -3.00 dB
PL12               17.76 dB
PL13               23.00 dB
SFO2         300.1300000 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677293 MHz
WDW                   EM
SSB                    0
LB                  1.50 Hz
GB                     0
PC                  4.00
```

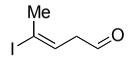


AVB-400 ZBO Proton starting parameters. 6/11/03 RN

8.032 8.028 8.010 7.720 7.700 7.374 7.353 7.151 7.043 6.976 6.958 6.941 6.937 6.836 6.818 6.799 6.478 6.460 6.440 6.124 6.120 6.106 6.102 6.088 6.084 6.048 6.045 6.041 6.034 6.030 6.026 6.023 6.016 6.012 6.008 6.004 5.867 5.657 2.648 2.629 2.453 2.451 2.435 2.433 2.177 2.175 2.174 2.159 2.157 2.104 2.101 2.063 2.036 2.000 1.981 1.929 1.844 1.841 1.821 1.818 1.768 1.728 1.725 1.691 1.626

1.118





19

Current Data Parameters

NAME	ar10-120
EXPNO	1
PROCNO	1
DU	/u
USER	aradosed

F2 - Acquisition Parameters

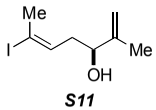
Date_	20070703
Time	16.10
INSTRUM	AVB-400
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	C6D6
NS	1
DS	0
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	181
DW	60.400 use
DE	6.00 use
TE	673.2 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	1H
P1	8.20 use
PL1	-3.00 dB
SFO1	400.1324710 MHz

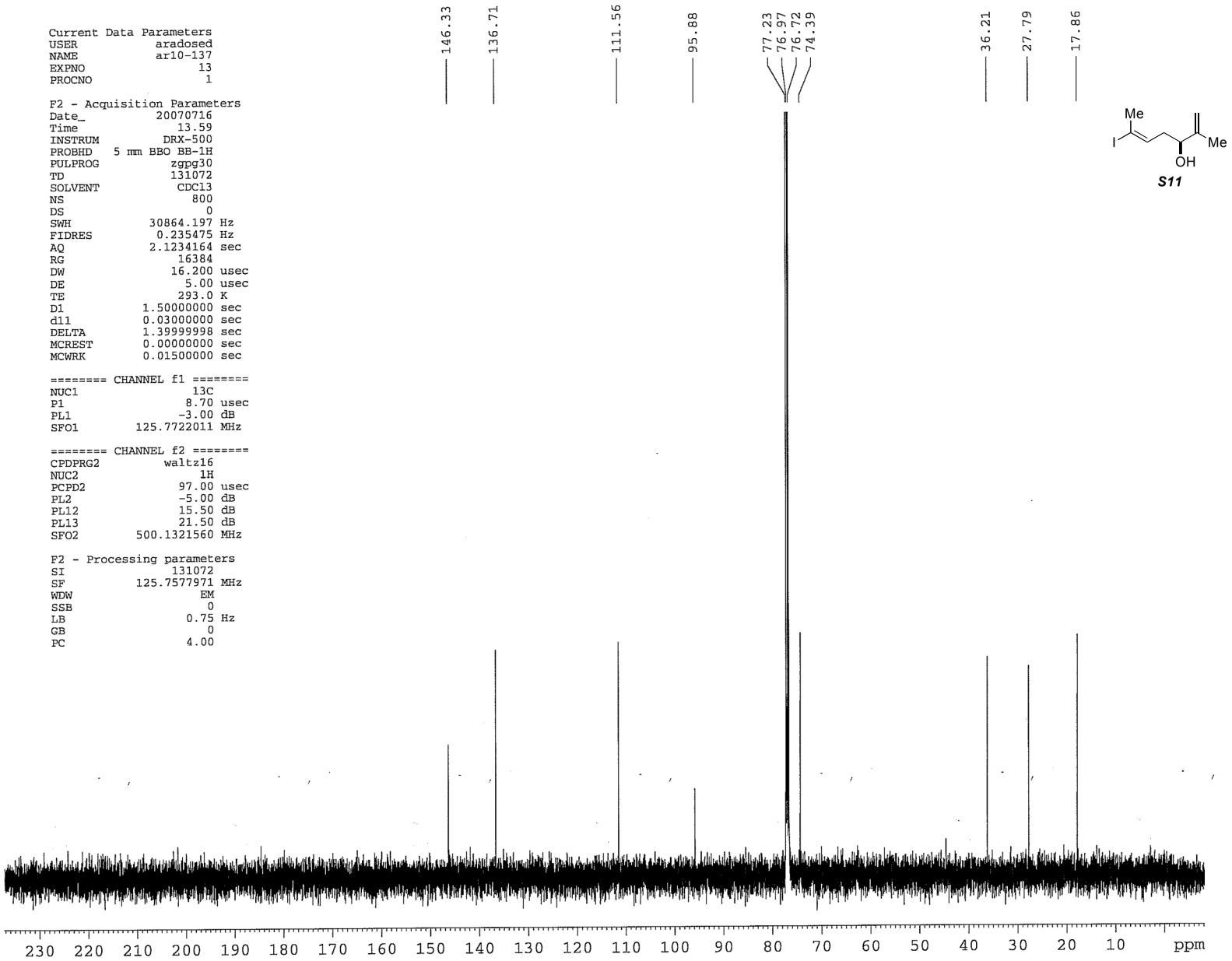
F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM

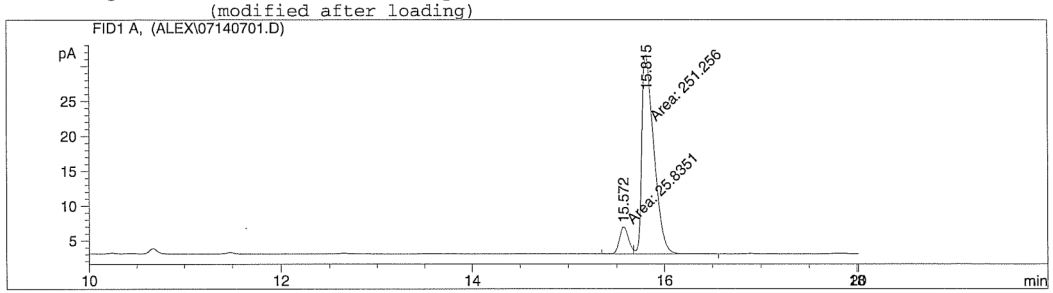


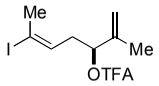
S11


```
Current Data Parameters
USER                aradosed
NAME                ar10-137
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20070716
Time                  13.58
INSTRUM             DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH           10000.000 Hz
FIDRES            0.152588 Hz
AQ                3.2768500 sec
RG                    456.1
DW                 50.000 use
DE                  7.11 use
TE                  293.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 =======
NUC1                      1H
P1                     12.20 use
PL1                    -5.00 dB
SFO1          500.1330883 MHz

F2 - Processing parameters
SI                        65536
SF            500.1300138 MHz
WDW                       EM
SSB                        0
```


Current Data Parameters
USER aradosed
NAME ar10-137
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070716
Time 13.59
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 800
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 16384
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.70 usec
PL1 -3.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 15.50 dB
PL13 21.50 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577971 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 4.00
146.33
136.71
111.56
95.88
77.23
76.97
76.72
74.39
36.21
27.79
17.86
Me
I
Me
OH
S11
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Injection Date	: 7/14/07 9:59:48 PM	Seq. Line :	1
Sample Name	: ar10-137	Vial :	8
Acq. Operator	: Alex	Inj :	1
		Inj Volume :	1 µl
Acq. Method	: D:\HPCHEM\1\METHODS\IODIDE.M		
Last changed	: 7/12/07 2:46:19 PM by Cole		
Analysis Method	: D:\HPCHEM\1\METHODS\IODIDE.M		
Last changed	: 8/16/07 10:42:08 PM by Cole (modified after loading)		





S11-TFA

Area Percent Report

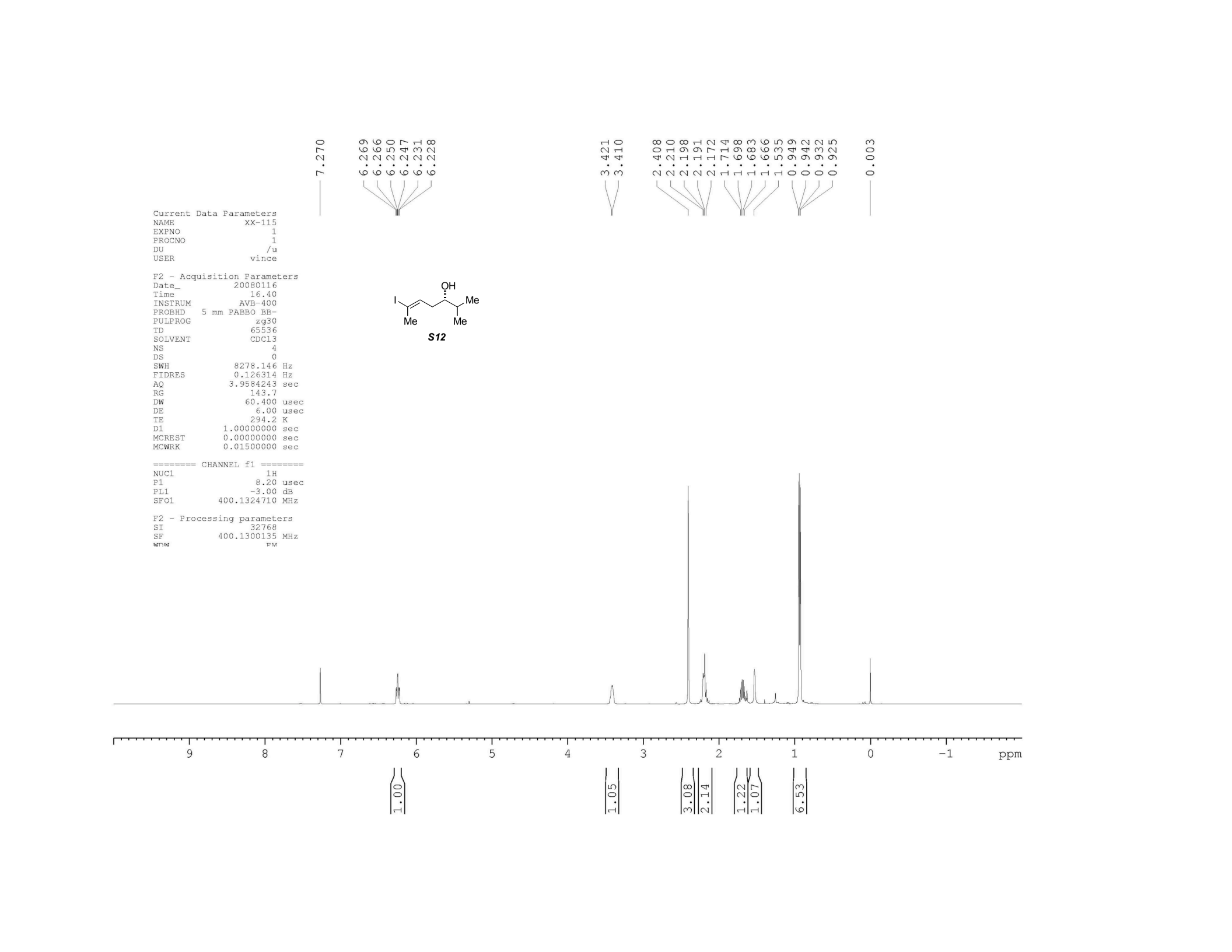
Sorted By	:	Signal
Multiplier	:	1.0000
Dilution	:	1.0000

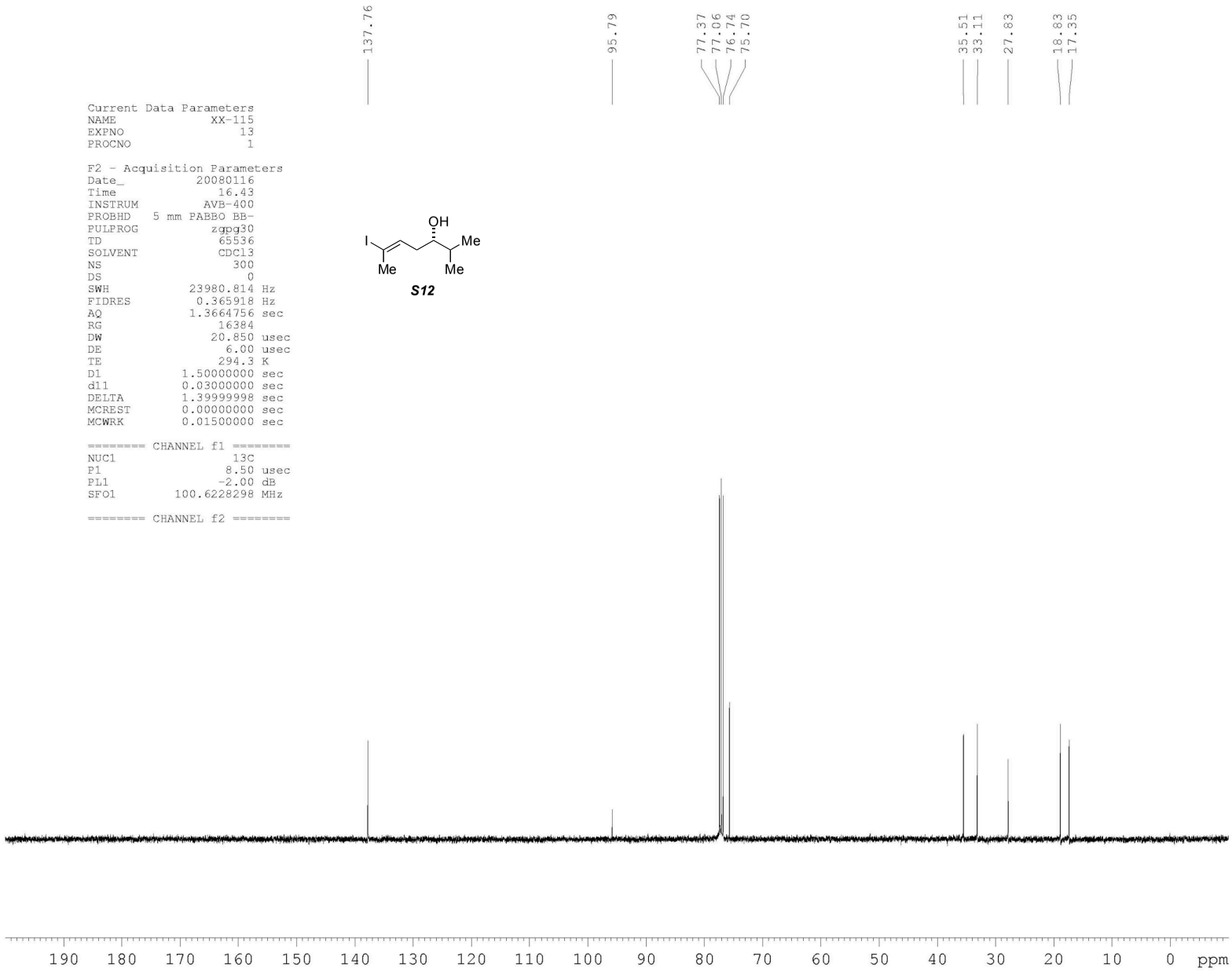
Signal 1: FID1 A,

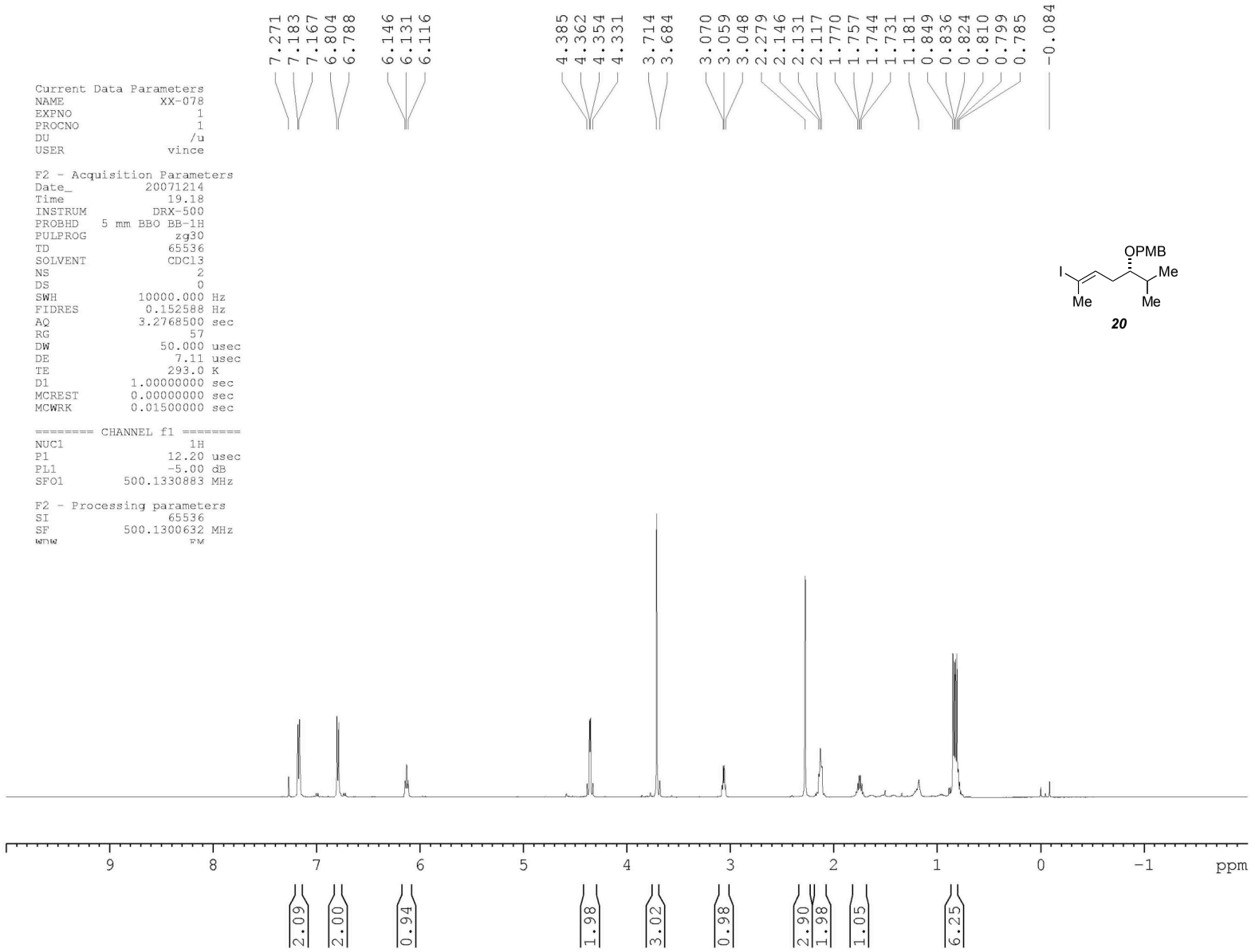
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.572	MF	0.1100	25.83508	3.91282	9.32367
2	15.815	FM	0.1463	251.25633	28.62295	90.67633
Totals :				277.09142	32.53577	

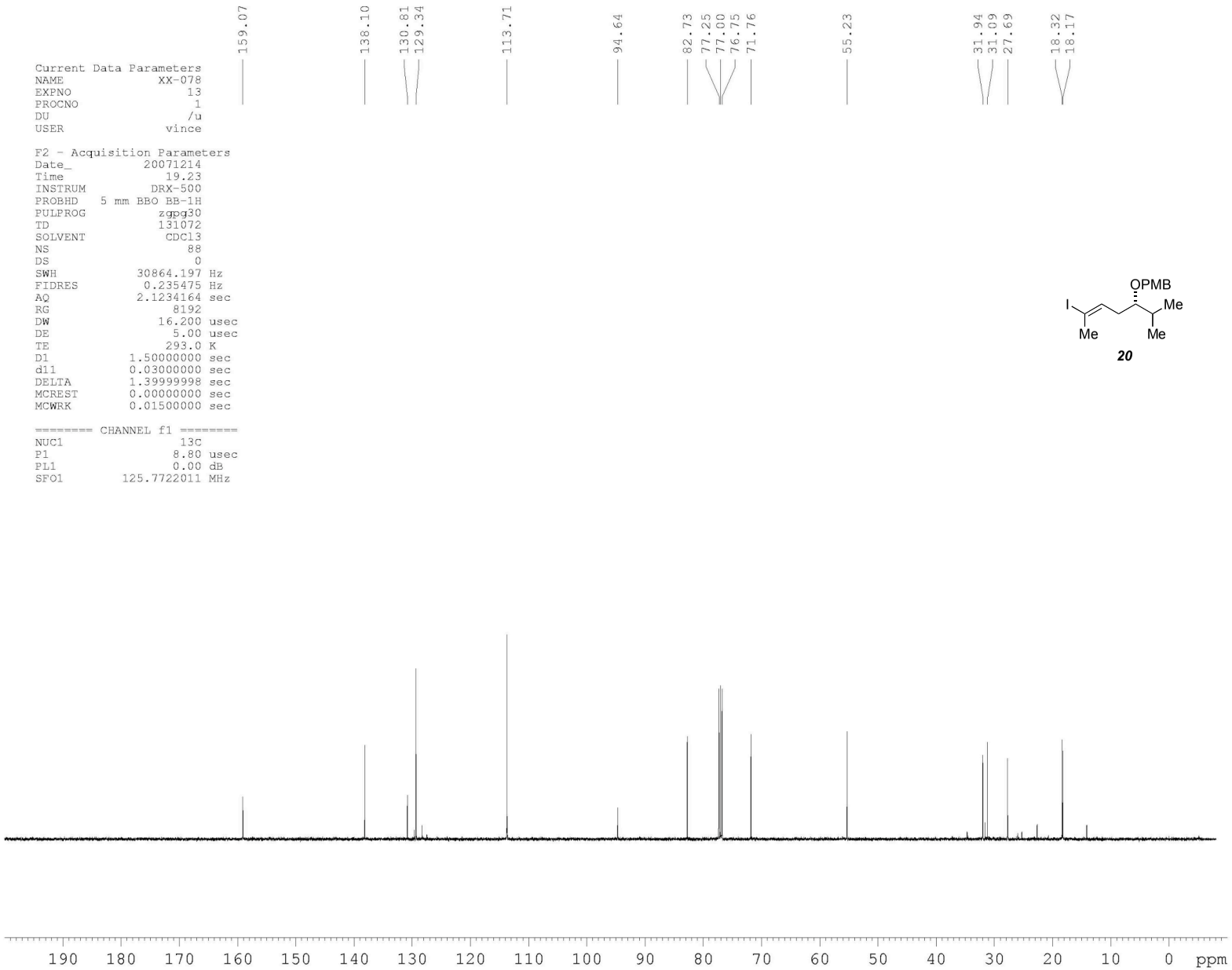
Results obtained with enhanced integrator!

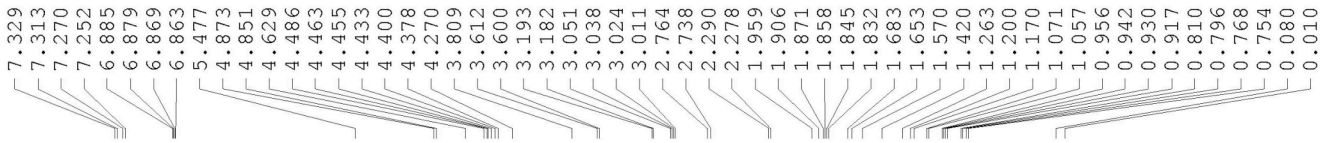
*** End of Report ***


7.270
6.269
6.266
6.250
6.247
6.231
6.228
3.421
3.410
2.408
2.210
2.198
2.191
2.172
1.714
1.698
1.683
1.666
1.535
0.949
0.942
0.932
0.925
0.003
Current Data Parameters
NAME XX-115
EXPNO 1
PROCNO 1
DU /u
USER vince
F2 - Acquisition Parameters
Date_ 20080116
Time 16.40
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 4
DS 0
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 143.7
DW 60.400 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.20 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300135 MHz
WDW EM
OH
I
Me
Me
Me
S12
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
1.05
3.08
2.14
1.22
1.07
6.53

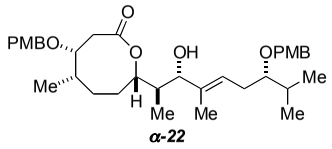

137.76
95.79
77.37
77.06
76.74
75.70
35.51
33.11
27.83
18.83
17.35
Current Data Parameters
NAME XX-115
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080116
Time 16.43
INSTRUM AVB-400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 300
DS 0
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 16384
DW 20.850 usec
DE 6.00 usec
TE 294.3 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
OH
I
Me
Me
Me
S12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.271
7.183
7.167
6.804
6.788
6.146
6.131
6.116
4.385
4.362
4.354
4.331
3.714
3.684
3.070
3.059
3.048
2.279
2.146
2.131
2.117
1.770
1.757
1.744
1.731
1.181
0.849
0.836
0.824
0.810
0.799
0.785
-0.084
Current Data Parameters
NAME XX-078
EXPNO 1
PROCNO 1
DU /u
USER vince
F2 - Acquisition Parameters
Date_ 20071214
Time 19.18
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 57
DW 50.000 usec
DE 7.11 usec
TE 293.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
PL1 -5.00 dB
SFO1 500.1330883 MHz
F2 - Processing parameters
SI 65536
SF 500.1300632 MHz
WDW EM
OPMB
I
Me
Me
Me
20
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.09
2.00
0.94
1.98
3.02
0.98
2.90
1.98
1.05
6.25

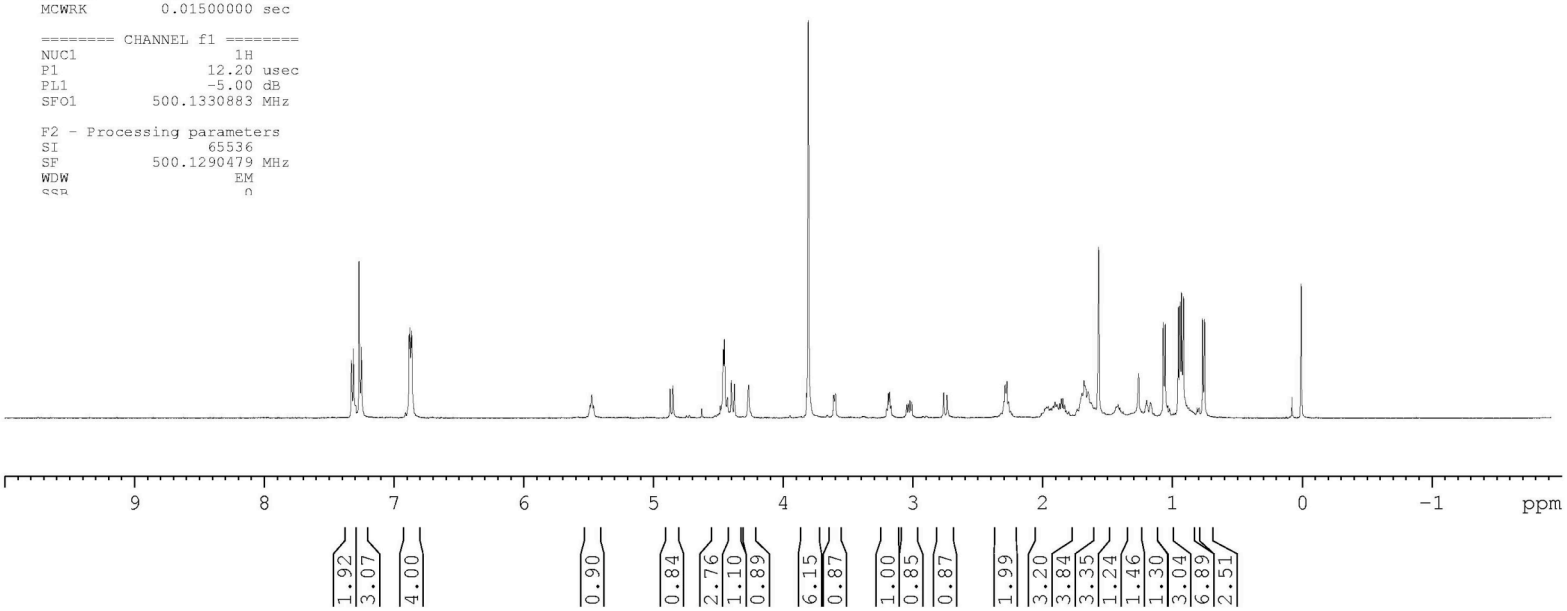

159.07
138.10
130.81
129.34
113.71
94.64
82.73
77.25
77.00
76.75
71.76
55.23
31.94
31.09
27.69
18.32
18.17
Current Data Parameters
NAME XX-078
EXPNO 13
PROCNO 1
DU /u
USER vince
F2 - Acquisition Parameters
Date_ 20071214
Time 19.23
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 88
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 8192
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 0.00 dB
SFO1 125.7722011 MHz
OPMB
I
Me
Me
Me
20
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

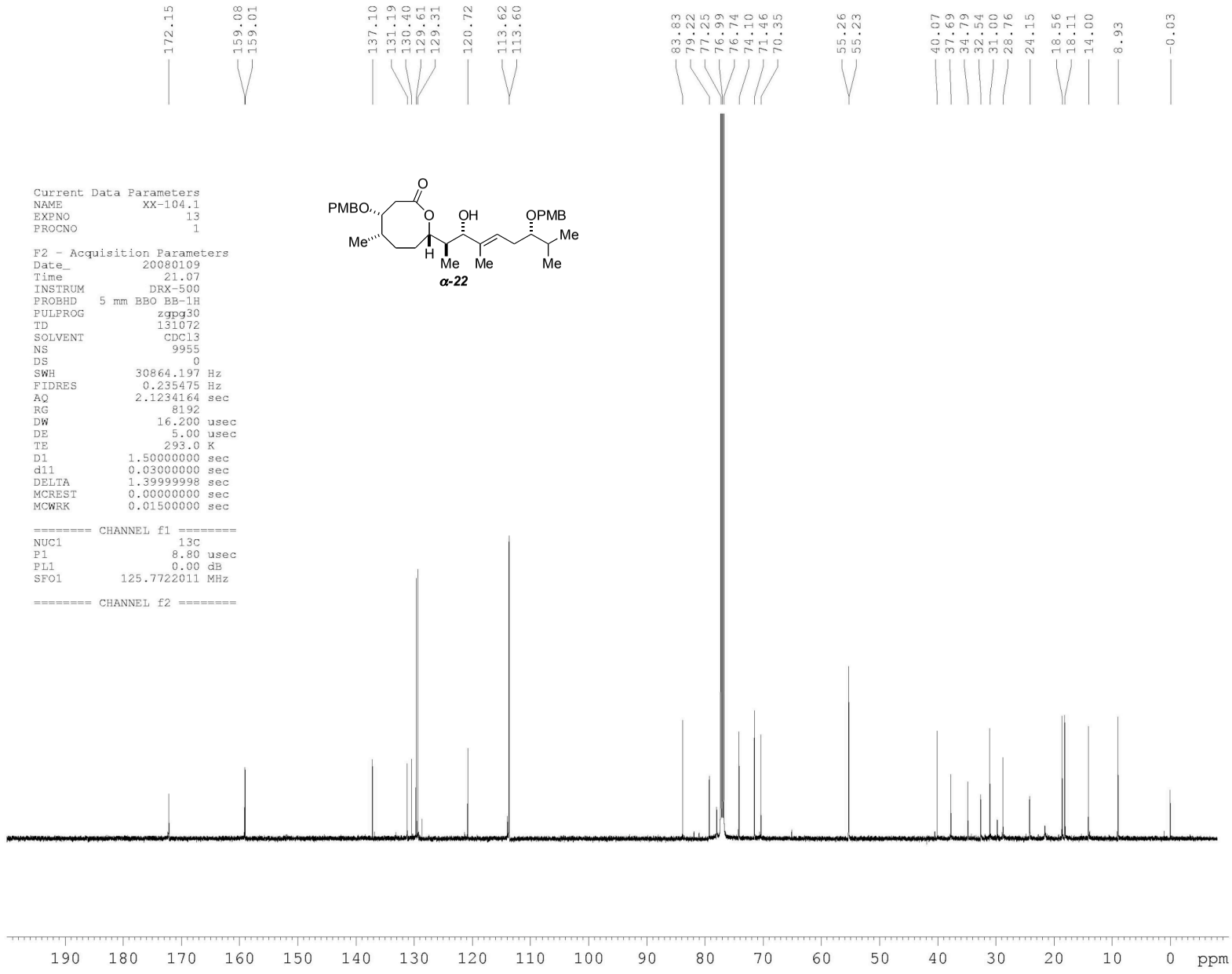


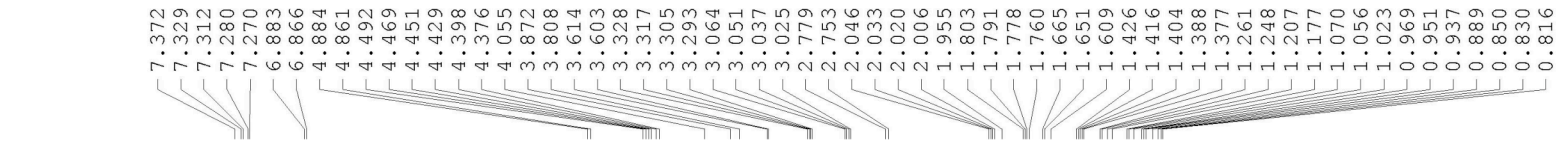

```
Current Data Parameters
USER                vince
NAME             XX-104.1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080109
Time                17.32
INSTRUM           DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       4
DS                       0
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ               3.2768500 sec
RG                     203.2
DW                  50.000 usec
DE                    7.11 usec
TE                   293.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   12.20 usec
PL1                  -5.00 dB
SFO1           500.1330883 MHz

F2 - Processing parameters
SI                   65536
SF             500.1290479 MHz
WDW                     EM
SSB                      0
```



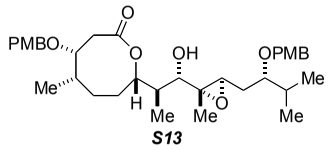
α-22



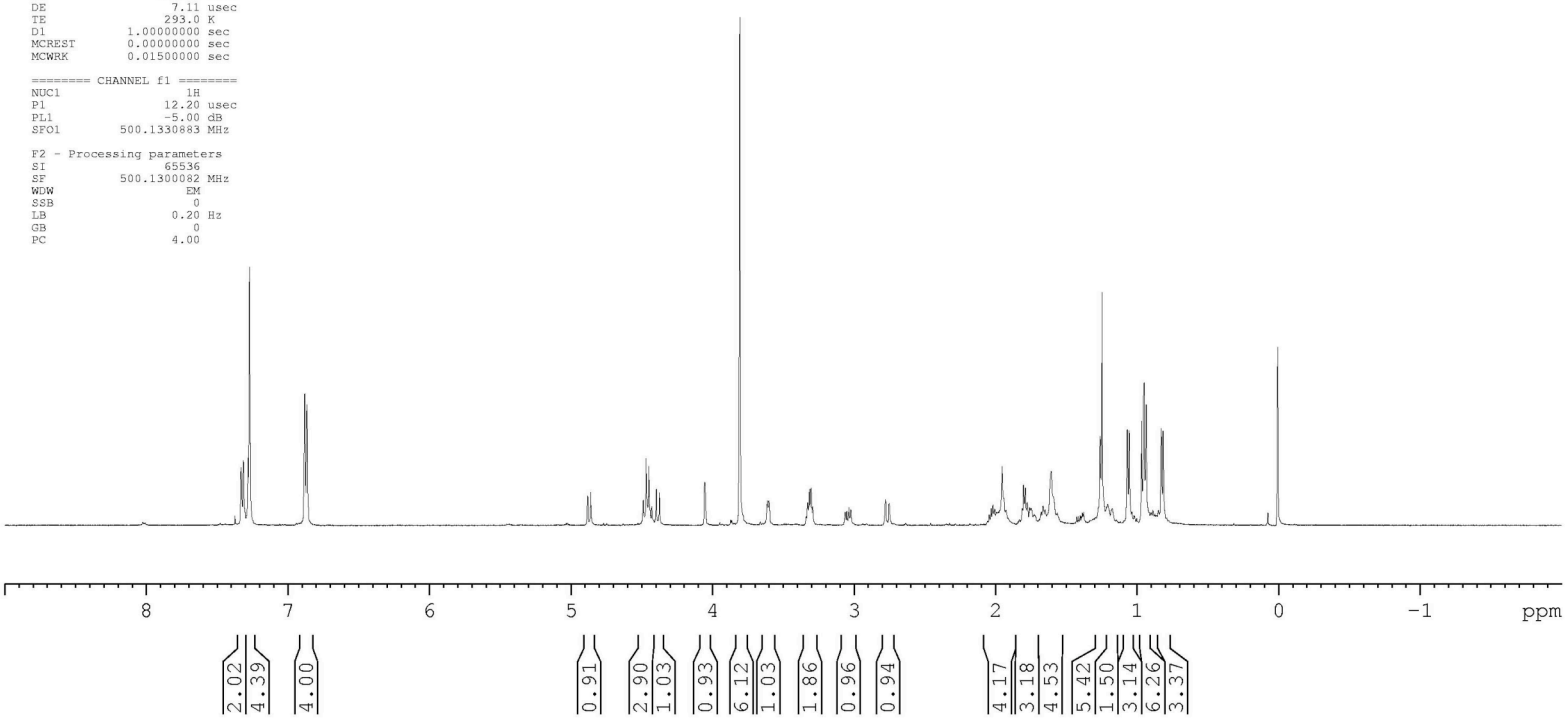

172.15
159.08
159.01
137.10
131.19
130.40
129.61
129.31
120.72
113.62
113.60
83.83
79.22
77.25
76.99
76.74
74.10
71.46
70.35
55.26
55.23
40.07
37.69
34.79
32.54
31.00
28.76
24.15
18.56
18.11
14.00
8.93
-0.03
Current Data Parameters
NAME XX-104.1
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080109
Time 21.07
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 9955
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 8192
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 0.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
PMBO
O
O
OH
OPMB
Me
Me
H
Me
Me
Me
α-22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

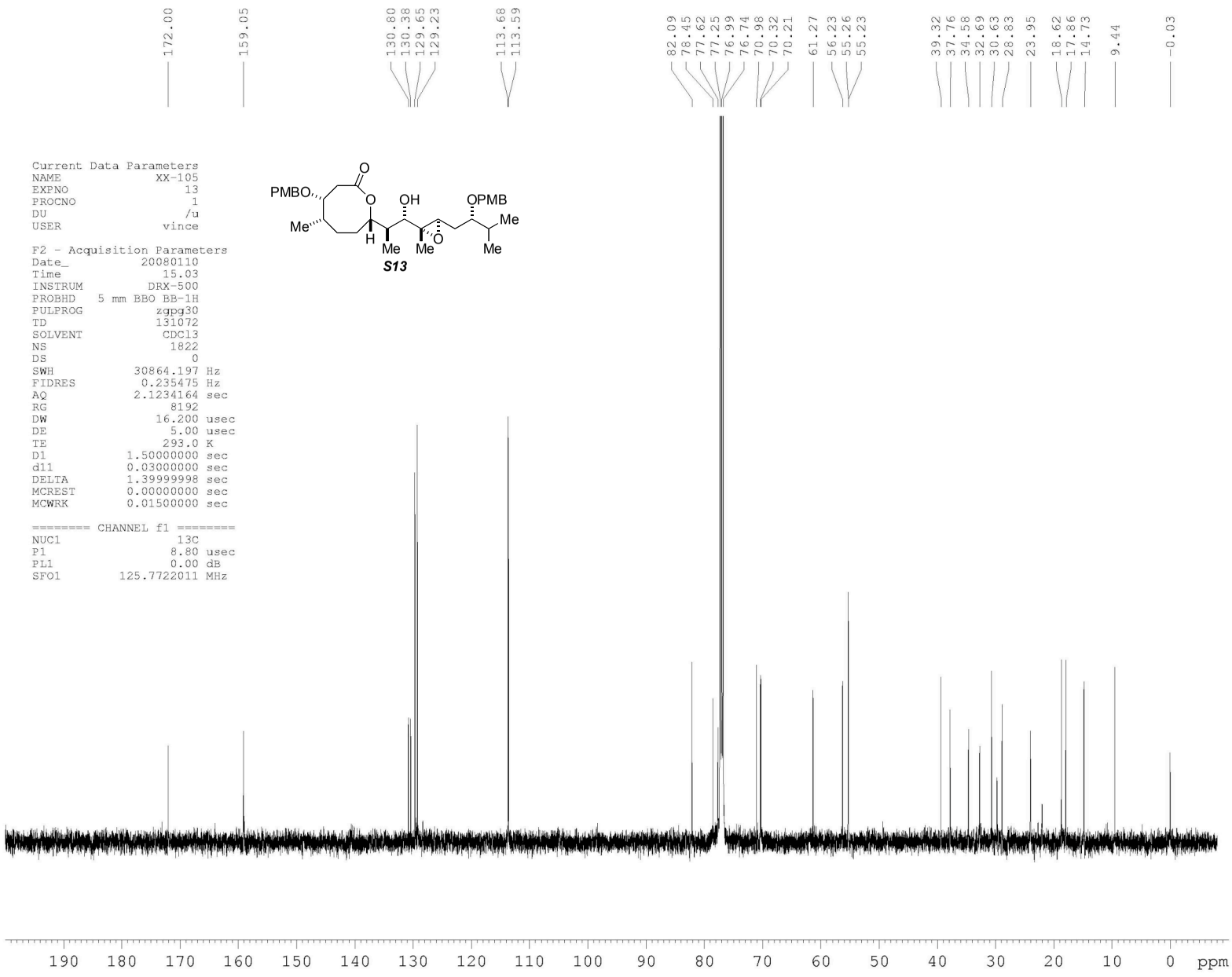


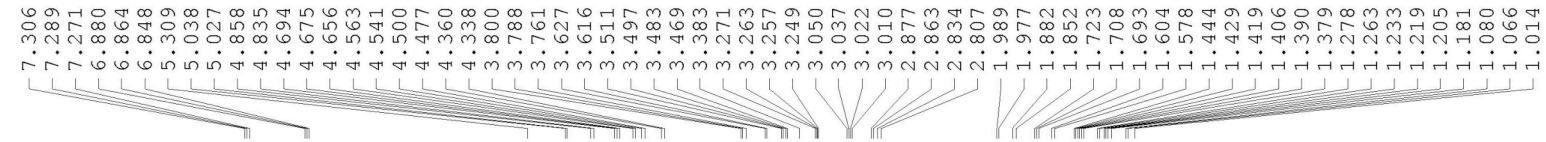

```
Current Data Parameters
USER                vince
NAME               XX-105
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080110
Time                12.54
INSTRUM           DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             10000.000 Hz
FIDRES              0.152588 Hz
AQ                3.2768500 sec
RG                     256
DW                  50.000 usec
DE                   7.11 usec
TE                  293.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  12.20 usec
PL1                 -5.00 dB
SFO1           500.1330883 MHz

F2 - Processing parameters
SI                   65536
SF             500.1300082 MHz
WDW                     EM
SSB                      0
LB                    0.20 Hz
GB                       0
PC                    4.00
```

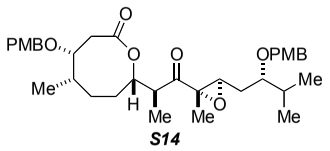


S13



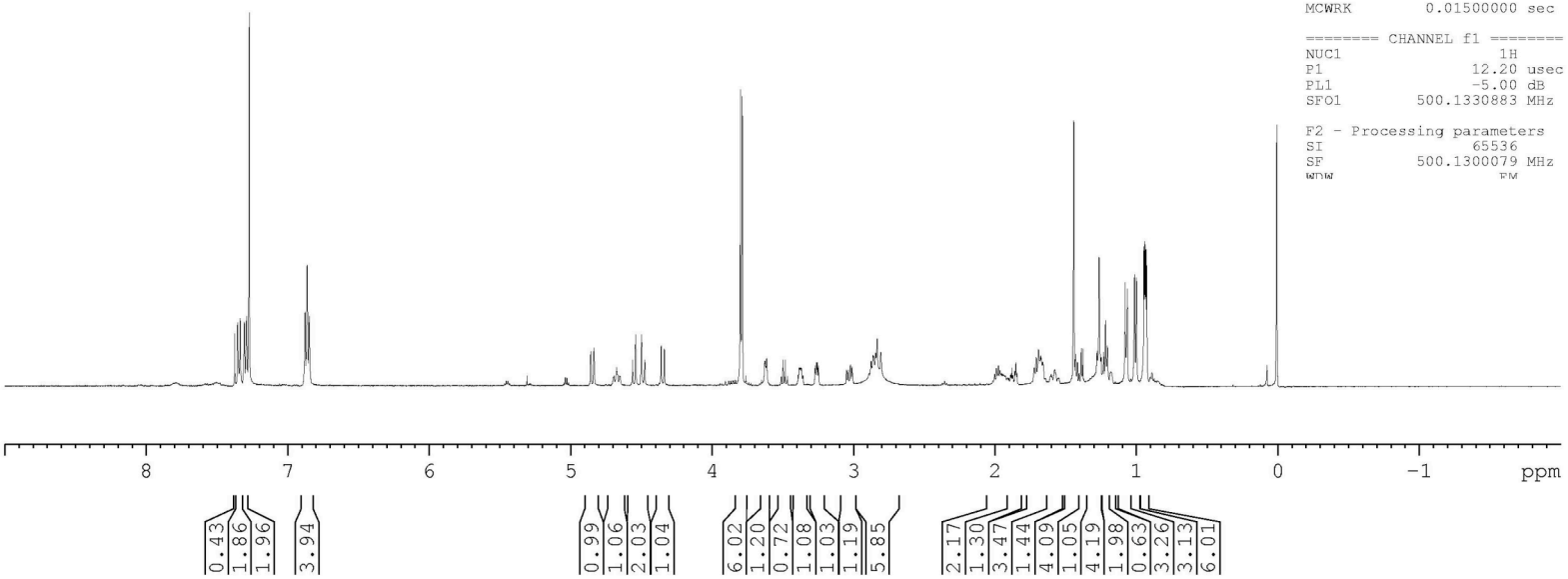

172.00
159.05
130.80
130.38
129.65
129.23
113.68
113.59
82.09
78.45
77.62
77.25
76.99
76.74
70.98
70.32
70.21
61.27
56.23
55.26
55.23
39.32
37.76
34.58
32.69
30.63
28.83
23.95
18.62
17.86
14.73
9.44
-0.03
Current Data Parameters
NAME XX-105
EXPNO 13
PROCNO 1
DU /u
USER vince
F2 - Acquisition Parameters
Date_ 20080110
Time 15.03
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 1822
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 8192
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 0.00 dB
SFO1 125.7722011 MHz
PMBO
OH
OPMB
Me
Me
H
Me
Me
Me
S13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

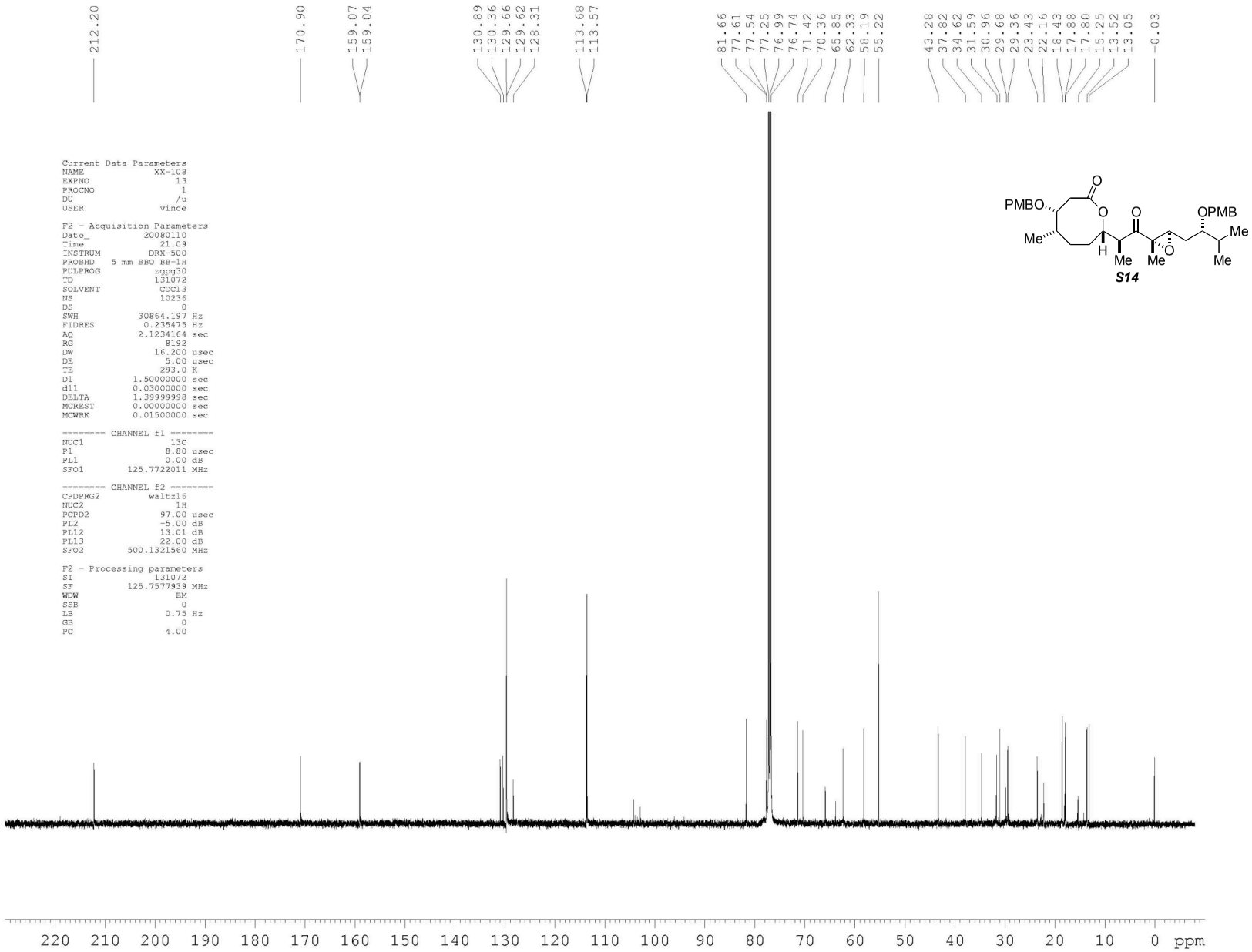


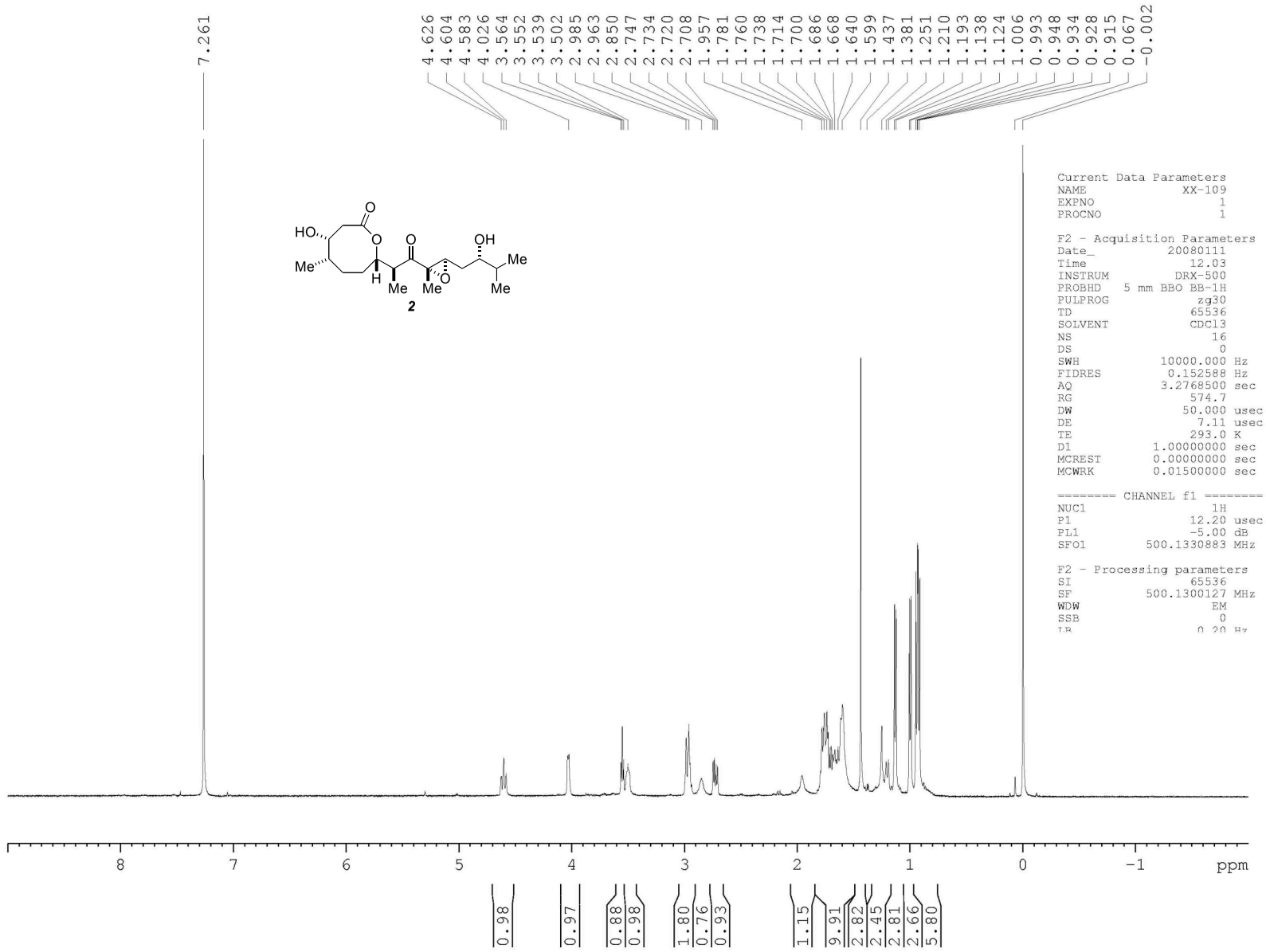


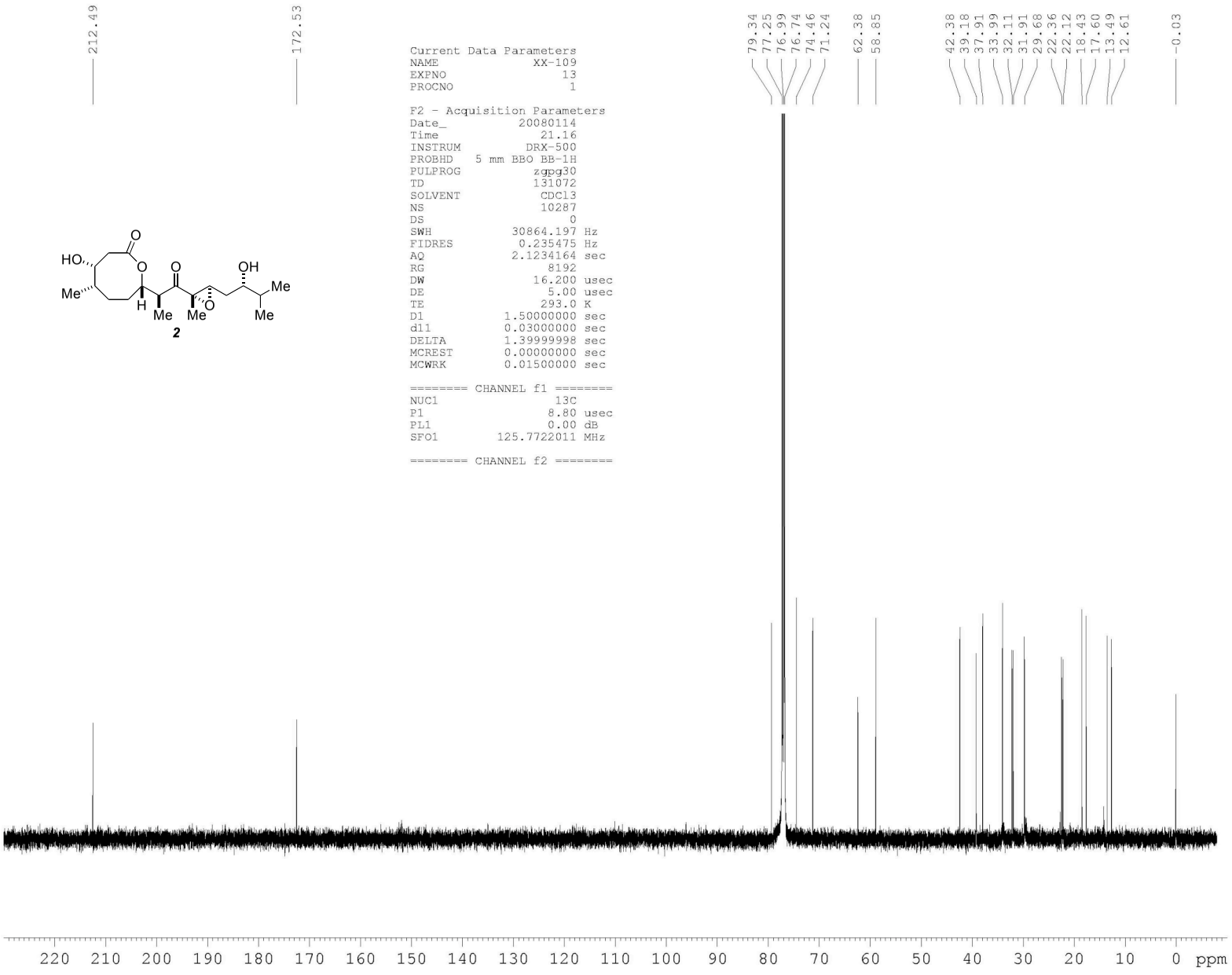
S14

```
Current Data Parameters
NAME                 XX-108
EXPNO                     1
PROCNO                    1
DU                       /u
USER                  vince

F2 - Acquisition Parameters
Date_              20080110
Time                 21.04
INSTRUM            DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2768500 sec
RG                    322.5
DW                 50.000 usec
DE                  7.11 usec
TE                  293.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                  12.20 usec
PL1                 -5.00 dB
SFO1           500.1330883 MHz

F2 - Processing parameters
SI                    65536
SF             500.1300079 MHz
WDW                     EM
```




212.20
170.90
159.07
159.04
130.89
130.36
129.66
129.62
128.31
113.68
113.57
81.66
77.61
77.54
77.25
76.99
76.74
71.42
70.36
65.85
62.33
58.19
55.22
43.28
37.82
34.62
31.59
30.96
29.68
29.36
23.43
22.16
18.43
17.88
17.80
15.25
13.52
13.05
-0.03
Current Data Parameters
NAME XX-108
EXPNO 13
PROCNO 1
DU /u
USER vince
F2 - Acquisition Parameters
Date_ 20080110
Time 21.09
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 10236
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 8192
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 0.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 97.00 usec
PL2 -5.00 dB
PL12 13.01 dB
PL13 22.00 dB
SFO2 500.1321560 MHz
F2 - Processing parameters
SI 131072
SF 125.7577939 MHz
WDW EM
SSB 0
LB 0.75 Hz
GB 0
PC 4.00
PMBO
OPMB
Me
Me
Me
Me
Me
H
O
O
O
O
S14
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.261
4.626
4.604
4.583
4.026
3.564
3.552
3.539
3.502
2.985
2.963
2.850
2.747
2.734
2.720
2.708
1.957
1.781
1.760
1.738
1.714
1.700
1.686
1.668
1.640
1.599
1.437
1.381
1.251
1.210
1.193
1.138
1.124
1.006
0.993
0.948
0.934
0.928
0.915
0.067
-0.002
HO
O
O
O
OH
Me
Me
H
Me
Me
O
Me
2
Current Data Parameters
NAME XX-109
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080111
Time 12.03
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2768500 sec
RG 574.7
DW 50.000 usec
DE 7.11 usec
TE 293.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.20 usec
PL1 -5.00 dB
SFO1 500.1330883 MHz
F2 - Processing parameters
SI 65536
SF 500.1300127 MHz
WDW EM
SSB 0
8
7
6
5
4
3
2
1
0
-1
ppm
0.98
0.97
0.88
0.98
1.80
0.76
0.93
1.15
9.91
2.82
2.45
2.81
2.66
5.80


212.49
172.53
79.34
77.25
76.99
76.74
74.46
71.24
62.38
58.85
42.38
39.18
37.91
33.99
32.11
31.91
29.68
22.36
22.12
18.43
17.60
13.49
12.61
-0.03
Current Data Parameters
NAME XX-109
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080114
Time 21.16
INSTRUM DRX-500
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 10287
DS 0
SWH 30864.197 Hz
FIDRES 0.235475 Hz
AQ 2.1234164 sec
RG 8192
DW 16.200 usec
DE 5.00 usec
TE 293.0 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PL1 0.00 dB
SFO1 125.7722011 MHz
======== CHANNEL f2 ========
HO
O
O
O
OH
Me
Me
H
Me
Me
O
Me
2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm