Supporting Information

Chemical Synthesis Enables Biochemical and Antibacterial Evaluation of Streptolydigin Antibiotics

Sergey V. Pronin,[1] Anthony Martinez,[1] Konstantin Kuznedelov,[2] Konstantin Severinov,[2,3]

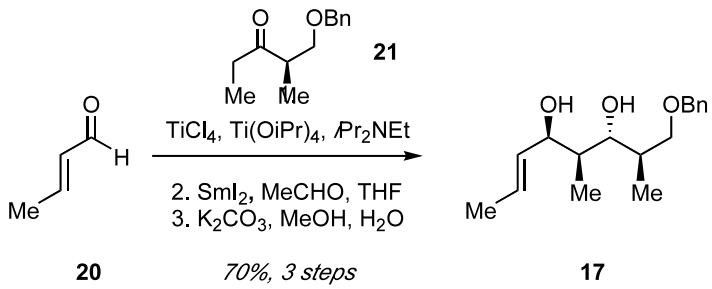
Howard A. Shuman[4] and Sergey A. Kozmin[1]*

[1]Department of Chemistry, University of Chicago, Chicago, Illinois 60607, United States; [2]Department of Molecular Biology and Biochemistry, Rutgers University, Piscataway, New Jersey 08854, United States; [3]Institutes of Gene Biology and Molecular Genetics, Russian Academy of Sciences, Moscow, Russia; [4]Department of Microbiology, University of Chicago, Chicago, Illinois 60607, United States

*Corresponding Author: skozmin@uchicago.edu

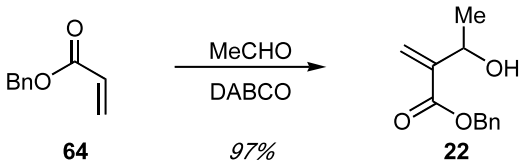
Experimental Procedure

General. All reactions were carried out under positive pressure of nitrogen unless otherwise noted. Ethyl acetate (ACS grade and HPLC grade), hexanes (ACS grade and HPLC grade), diethyl ether (anhydrous grade), toluene (HPLC grade), methanol (HPLC grade), chloroform (HPLC grade), acetone (ACS grade), *N*,*N*-dimethylacetamide (Anhydrous grade), and *tert*-butanol (ACS grade) were purchased from FisherScientific and used without further purification. Tetrahydrofuran was distilled from sodium-benzophenone under positive pressure of nitrogen. Dichloromethane was distilled from calcium hydride under positive pressure of nitrogen. Commercially available reagents were used without further purification unless otherwise noted. Authentic sample of streptolydigin was purchased from ChemCon GmbH (http://www.chemcon.com/). Reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Flash column chromatography was performed over ultra pure silica gel (230-400 mesh) from Silicycle. Preparative TLC was perfomed using Whatman precoated silica gel plates. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DMX-500 and DRX-400 spectrometers using residual solvent peaks as an internal standard. Optical rotations were measured with JASCO DIP-1000 digital polarimeter, using the sodium D line. High-resolution mass spectra were recorded with Waters Q-Top Ultima tandem quadrupole/Time-of-Flight instrument. All cell lines and media were purchased from American Type Culture Collection (ATCC).



Diol 17. Ti(O*i*-Pr)$_4$ (distilled prior to use, 7.66 mL, 0.0259 mol) was added to a stirred solution of $TiCl_4$ (distilled prior to use, 8.5 mL, 0.0776 mol) in dichloromethane (125 mL) at 0 °C. The resulting solution was stirred for 10 min, warmed to room temperature, diluted with dichloromethane (125 mL), and transferred into a stirred solution of (2*R*)-1-(benzyloxy)-2- methylpentan-3-one **21**[1] (19.4 g, 0.094 mol) in dichloromethane (200 mL) at -78 °C (rinsed flask with 30 mL of dichloromethane). Hunig's base (18 mL, 0.103 mol) was then added dropwise, and the resulting solution was stirred for 30 min at -78 °C. Crotonaldehyde (11.8 mL, 0.141 mol) was added dropwise, and stirring was continued for 1 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl and warmed to room temperature. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford a crude aldol product. A stirred solution of crude hydroxyketone and acetaldehyde (21 mL, 0.376 mol) in THF (240 mL) was treated with SmI_2 (0.1 M solution in THF, 188 mL, 0.0188 mol) at -20 °C. The reaction mixture was stirred 3 h at -20 °C and quenched with saturated aqueous $NaHCO_3$. The resulting suspension was warmed to room temperature and extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude acetate was treated with a suspension of

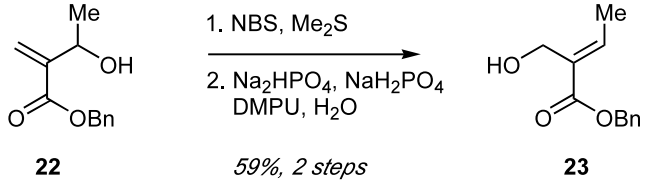
K_2CO_3 (26 g, 0.188 mol) in a mixture of methanol (370 mL) and water (30 mL). After 30 min at room temperature, the reaction mixture was concentrated *in vacuo*. The resulting residue was suspended in diethyl ether (500 mL) and washed with brine. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 18.3 g (70% yield over three steps) of diol **17**. $[\alpha]^{24.1}_D$ = +0.6 (*c* = 3.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 7.0 Hz), 0.97 (d, 3H, *J* = 7.0 Hz), 1.71 (d, 3H, *J* = 6.5 Hz), 1.81 (m, 1H), 2.11 (m, 1H), 3.50 (dd, 1H, *J* = 9.0, 7.0 Hz), 3.57 (m, 1H), 3.69 (dd, 1H, *J* = 9.0, 4.0 Hz), 3.88 (d, 1H, *J* = 3.0 Hz), 4.28 (d, 1H, *J* = 4.0 Hz), 4.40 (m, 1H), 4.53 (m, 2H), 5.54 (ddd, 1H, *J* = 15.5, 6.5, 1.5 Hz), 5.69 (m, 1H), 7.29-7.37 (m, 5H); ^{13}C NMR (125 MHz, CDCl3) δ 11.8, 14.2, 17.8, 35.5, 39.6, 73.3, 73.7, 75.2, 81.3, 126.3, 127.7, 127.9, 128.6, 131.9, 137.4; HRMS (ESI) calculated for $C_{17}H_{27}O_3$ [M+H]+ 279.1960, found 279.1966.



64 *97%* **22**

Alcohol 22. A mixture of benzyl acrylate (50 g, 0.308 mol), acetaldehyde (13.3 mL, 0.237 mol), and DABCO (6.92 g, 0.062 mol) was left at room temperature for 6 days. Purification by flash chromatography on silica gel (elution with hexanes:Et2O 1:1) afforded 47.6 g (97% yield) of known alcohol **22**.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (d, 3H, *J* = 6.5 Hz), 2.69 (d, 1H, *J* = 5.5 Hz), 4.64 (m, 1H), 5.23 (s, 2H), 5.85 (s, 1H), 6.27 (s, 1H), 7.33-7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.1, 66.6, 67.1, 124.5, 128.1,

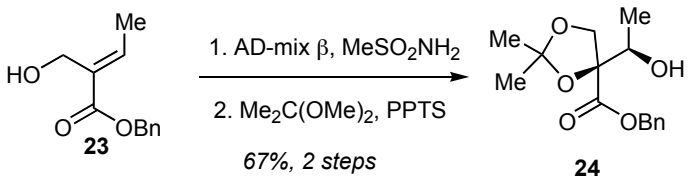
128.4, 128.6, 135.7, 143.5, 166.4.



22 *59%, 2 steps* **23**

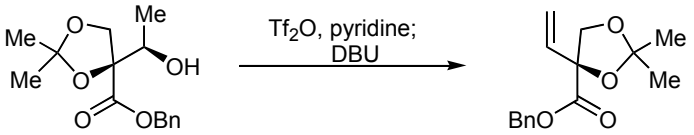
Benzyl enoate 23. Dimethyl sulfide (49 mL, 0.667 mol) was added dropwise to a stirred solution of NBS (59.4 g, 0.334 mol) in 1.1 L of dichloromethane at 0 °C. After 1 h at 0 °C, the solution of alcohol **22** (45.9 g, 0.222 mol, in 220 mL of dichloromethane) was transferred into the reaction mixture. The resulting solution was warmed to room temperature and stirred overnight. The reaction mixture was washed with saturated aqueous solution of $NaHCO_3$, and the aqueous phase was extracted with Et_2O. The combined organic solutions were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude bromide was transferred into a flask containing Na_2HPO_4 (63 g, 0.444 mol), NaH_2PO_4 (53.3 g, 0.444 mol), water (150 mL), and DMPU (300 mL). The resulting mixture was heated to 100 °C for 8 h, cooled to room temperature, and poured into 2.5 L of water. The resulting solution was extracted three times with Et_2O. The combined organic extracts were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:Et2O 1:1) afforded 27 g (59% yield over two steps) of benzyl enoate **23**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.90 (d, 3H, *J* = 7.5 Hz), 2.56 (t, 1H, *J* = 6.0 Hz), 4.37 (d, 2H, *J* = 5.5 Hz), 5.22 (s, 2H), 7.03 (q, 1H, *J* = 7.5 Hz), 7.32-7.40 (m, 5H); ^{13}C NMR (125 MHz, CDCl3) δ 14.2, 56.9, 66.4, 128.1, 128.3, 128.6, 131.7, 135.8,

141.1, 167.2; HRMS (ESI) calculated for $C_{12}H_{15}O_3$ $[M+H]^+$ 207.1021, found 207.1027.



Alcohol 24. Benzyl enoate **23** (15 g, 0.131 mol) was added to a stirred solution of $K_2OsO_2(OH)_4$ (0.107 g, 0.00029 mol), $(DHQD)_2PHAL$ (0.567 g, 0.000727 mol), methanesulfonamide (6.92 g, 0.0727 mol), K_2CO_3 (30.16 g, 0.218 mol), and $K_3[Fe(CN)_6]$ (71.84 g, 0.218 mol) in a mixture of 2-methyl-2-propanol (360 mL) and water (360 mL) at 0 °C. The reaction mixture was stirred overnight at 0 °C, quenched with solid Na_2SO_3 (100g), and stirred 40 min at room temperature. The resulting suspension was filtered, and solids were washed with ethyl acetate. Layers were separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic fractions were dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude triol was dissolved in acetone (360 mL) and treated with 2,2-dimethoxypropane (67 mL, 0.545 mol) and *p*-toluenesulfonic acid hydrate (1.38 g, 0.00727 mol) at room temperature. After 1 h, the reaction was quenched with triethylamine (5 mL, 0.0364 mol), and volatiles were removed *in vacuo*. The residue was dissolved in Et_2O, washed with aqueous HCl (1 M solution) and saturated aqueous solution of $NaHCO_3$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate

4:1) afforded 10.6 g of alcohol **24**. Fractions containing undesired acetonides were combined, concentrated, and treated with *p*-toluenesulfonic acid hydrate (1.38 g, 0.00727 mol) in acetone (360 mL). After 1 h at room temperature, the reaction mixture was worked-up and purified as described above to yield additional 3 g of alcohol **24** (13.6 g overall, 67% yield over two steps, 92% *ee*, determined by chiral HPLC: Daicel Chiralcel OD, hexanes:2-propanol 99:1, 1 mL/min, major enantiomer t_R = 28.1 min, minor enantiomer t_R = 25.3 min). $[\alpha]^{24.9}_D$ = -7.6 (*c* = 2.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (d, 3H, *J* = 6.5 Hz), 1.37 (s, 3H), 1.44 (s, 3H), 2.40 (d, 1H, *J* = 7.0 Hz), 3.98 (m, 1H), 4.07 (d, 1H, *J* = 9.0 Hz), 4.29 (d, 1H, *J* = 9.0 Hz), 5.19 (d, 1H, *J* = 12.0 Hz), 5.27 (d, 1H, *J* = 12.0 Hz), 7.32-7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.3, 25.5, 26.0, 67.3, 68.2, 69.6, 86.8, 111.7, 128.4, 128.5, 128.6, 135.1, 172.5; HRMS (ESI) calculated for $C_{15}H_{21}O_5$ $[M+H]^+$ 281.1389, found 281.1387.

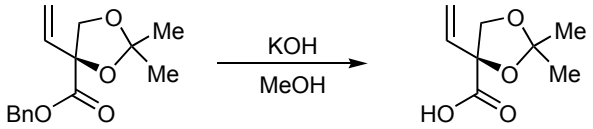


24 **65**

90%

Ester 65. Trifluoromethanesulfonic anhydride (16.7 mL, 0.0991 mol) was added dropwise to a stirred solution of alcohol **24** (22.2 g, 0.0793 mol) and pyridine (16.2 mL, 0.198 mol) in dichloromethane (400 mL) at -78 °C. The reaction mixture was stirred 10 min and then warmed to 0 °C. After 15 min, DBU (59.2 mL, 0.396 mol) was introduced, and the resulting solution was left at room temperature for 2 h before quenching with aqueous HCl (1 L of 1 M solution). Phases were separated, and the organic phase was

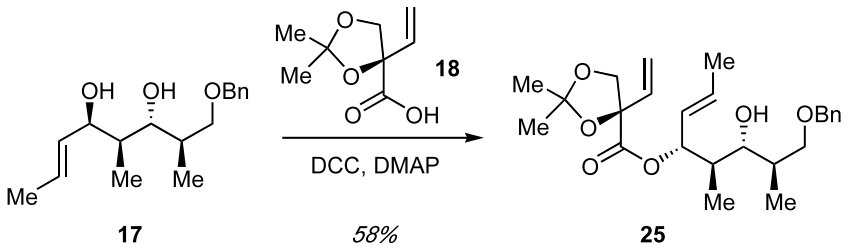
washed with aqueous HCl (1 M solution), water, and saturated aqueous solution of $NaHCO_3$, then dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with dichloromethane) afforded 18.7 g (90% yield) of ester **65**. $[\alpha]^{24.9}_D$ = -68.6 (*c* = 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.47 (s, 3H), 3.87 (d, 1H, *J* = 9.0 Hz), 4.47 (d, 1H, *J* = 9.0 Hz), 5.17 (d, 1H, *J* = 12.5 Hz), 5.25 (d, 1H, *J* = 12.5 Hz), 5.26 (d, 1H, *J* = 10.5 Hz), 5.51 (d, 1H, *J* = 17.5 Hz), 6.03 (dd, 1H, *J* = 17.0, 11.0 Hz), 7.30-7.39 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 26.0, 67.3, 72.8, 84.3, 111.8, 116.6, 128.2, 128.4, 128.5, 134.8, 135.3, 171.7; HRMS (ESI) calculated for $C_{15}H_{18}O_4Na$ $[M+Na]^+$ 285.1103, found 285.1095.



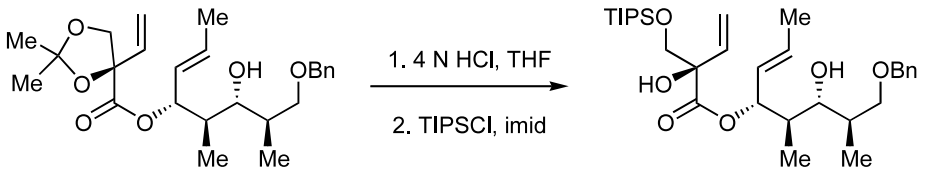
65 *100%* **18**

Acid 18. Ester **65** (6.86 g, 0.0262 mol) was treated with a solution of KOH (7.35 g, 0.13 mol) in methanol (130 mL) at room temperature. After 40 min, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in water (250 mL) and washed twice with diethyl ether. The aqueous solution was cooled to 0 °C and acidified with concentrated aqueous solution of HCl (final pH ~ 5). The resulting solution was saturated with NaCl and extracted twice with ethyl acetate. The combined organic layers were washed twice with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford 4.5 g (100% yield) of acid **18**. $[\alpha]^{25.0}_D$ = -81.0 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.54 (s, 3H), 3.90 (d, 1H, *J* = 9.0 Hz), 4.50 (d, 1H, *J* = 9.0 Hz), 5.30 (d, 1H, *J* = 10.5 Hz), 5.57 (d, 1H, *J* = 17.0 Hz), 6.04 (dd, 1H, *J* = 17.0, 11.0 Hz); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 25.5, 26.1, 72.9, 84.2, 112.3, 117.1, 134.0, 175.9; HRMS (ESI) calculated for $C_8H_{12}O_4Na$ $[M+Na]^+$ 195.0633, found 195.0642.



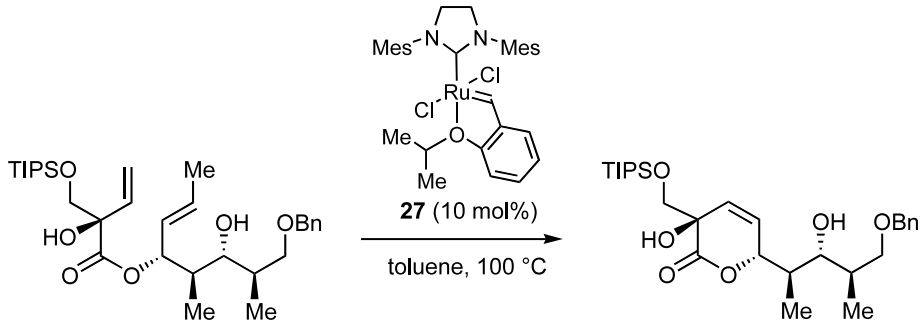
Ester 25. A solution of acid **18** (5.5 g, 0.032 mol), diol **17** (17.4 g, 0.063 mol) and DMAP (0.78 g, 0.0064 mol) in dichloromethane (160 mL) was treated with DCC (7.92 g, 0.0384 mol) at room temperature. After 1 h, the reaction mixture was filtered, solids were washed with dichloromethane, and the resulting solution was concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 8 g (58% yield) of ester **25** (excess diol can be recovered upon elution with hexanes:ethyl acetate 1:1). $[\alpha]^{24.4}_D$ = -23.8 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (d, 3H, *J* = 7.0 Hz), 1.05 (d, 3H, *J* = 7.0 Hz), 1.44 (s, 3H), 1.47 (s, 3H), 1.69 (d, 3H, *J* = 6.0 Hz), 1.84 (m, 1H), 2.00 (m, 1H), 3.16 (d, 1H, *J* = 6.5 Hz), 3.23 (m, 1H), 3.53 (dd, 1H, *J* = 5.0, 1.0 Hz), 3.84 (d, 1H, *J* = 8.5 Hz), 4.48 (m, 3H), 5.24 (d, 2H, *J* = 11.0 Hz), 5.47 (m, 1H), 5.52 (d, 1H, *J* = 17.0), 5.71 (m, 2H), 6.02 (dd, 1H, *J* = 17.0, 10.5 Hz), 7.27-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.9, 15.9, 17.8, 26.00, 26.02, 34.8, 41.4, 72.6, 72.7, 73.4, 75.8, 76.8, 84.5, 111.7, 116.4, 127.57, 127.65, 128.0, 128.4, 128.9, 135.2, 138.1, 171.5; HRMS (ESI) calculated for $C_{25}H_{36}O_6Na$ $[M+Na]^+$ 455.2410, found 455.2408.



25 *57%, 2 steps* **26**

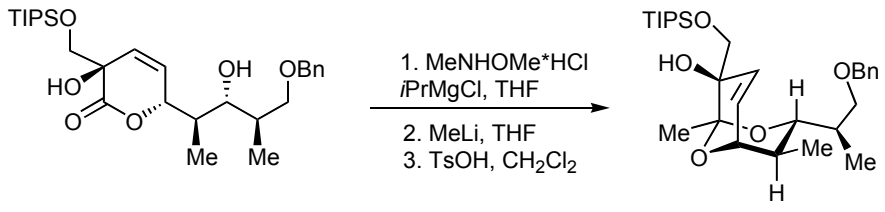
Silyl ether 26. Ester **25** (7.1 g, 0.0164 mol) was treated with a mixture of aqueous HCl (4 M solution, 165 mL) and THF (165 mL). The reaction mixture was stirred 6 h at room temperature and quenched by portionwise addition of solid $NaHCO_3$ (until neutralized). The resulting solution was extracted twice with ethyl acetate. The combined organic layers were washed with saturated aqueous solution of $NaHCO_3$, dryed over $MgSO_4$, and concentrated *in vacuo*. The resulting crude triol, imidazole (2.9 g, 0.0427 mol) and DMAP (0.2 g, 0.00164 mol) were dissolved in dichloromethane (17 mL) and treated dropwise with TIPSCl (4.5 mL, 0.0214 mol) at 0 °C. The reaction mixture was stirred for 2 days at room temperature, diluted with diethyl ether, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 5.2 g (58% yield over two steps) of silyl ether **26**. $[\alpha]^{23.2}_D$ = -10.2 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 7.0 Hz), 1.06 (m, 24H), 1.69 (d, 3H, *J* = 6.5 Hz), 1.86 (m, 1H), 1.98 (m, 1H), 3.04 (d, 1H, *J* = 6.5 Hz), 3.27 (m, 1H), 3.49 (dd, 1H, *J* = 9.0, 6.0 Hz), 3.52 (s, 1H), 3.56 (dd, 1H, *J* = 9.0, 5.0 Hz), 3.61 (d, 1H, *J* = 10.0 Hz), 4.07 (d, 1H, *J* = 9.5 Hz), 4.46 (d, 1H, *J* = 12.0 Hz), 4.49 (d, 1H, *J* = 12.0 Hz), 5.26 (d, 1H, *J* = 10.5 Hz), 5.48 (ddd, 1H, *J* = 16.0, 6.0, 1.0 Hz), 5.60 (d, 1H, *J* = 17.0 Hz), 5.66 (m, 1H), 5.70 (m, 1H), 5.92 (dd, 1H, *J* = 17.0, 11.0 Hz), 7.26-7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.8, 12.0, 16.0, 17.8, 17.89, 17.94, 35.0, 41.6, 69.5, 72.2, 73.4, 76.1, 76.7, 79.2, 117.1, 127.5, 127.6, 128.0, 128.4,

128.9, 134.7, 138.3, 172.9; HRMS (ESI) calculated for $C_{31}H_{52}O_6NaSi$ $[M+Na]^+$ 571.3431, found 571.3427.



26 *80%* **16**

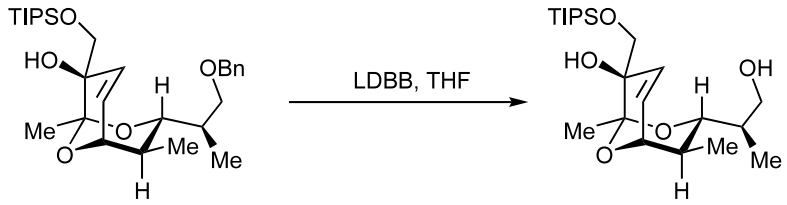
Lactone 16. Silyl ether **26** (5.1 g, 0.0093 mol) and Hoveyda-Grubbs catalyst **27** (0.6 g, 0.00094 mol) were dissolved in toluene (100 mL) and heated at 100 °C for 2 h. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) afforded 3.8 g (80% yield) of lactone **16**. $[\alpha]^{24.7}_D$ = -19.3 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (d, 3H, *J* = 7.0 Hz), 1.04 (d, 18H, *J* = 6.0 Hz), 1.07 (m, 3H), 1.15 (d, 3H, *J* = 7.0 Hz), 1.80 (m, 1H), 1.95 (m, 1H), 2.93 (d, 1H, *J* = 7.5 Hz), 3.39 (s, 1H), 3.53 (dd, 1H, *J* = 9.5, 4.0 Hz), 3.61 (m, 2H), 3.82 (d, 1H, *J* = 9.5 Hz), 3.84 (d, 1H, *J* = 9.5 Hz), 4.47 (d, 1H, *J* = 12.0 Hz), 4.51 (d, 1H, *J* = 12.0 Hz), 5.60 (m, 1H), 5.85 (q, 1H, *J* = 11.0 Hz), 7.28-7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.5, 11.9, 16.1, 17.9, 30.3, 34.5, 42.0, 69.2, 69.4, 71.9, 73.6, 75.5, 80.8, 126.1, 127.7, 127.8, 128.5, 130.1, 137.8, 171.2; HRMS (ESI) calculated for $C_{28}H_{47}O_6Si$ $[M+H]^+$ 507.3142, found 507.3120.



16 *72%, 3 steps* **14**

Bicyclic acetal 14. A stirred mixture of lactone **16** (3.6 g, 0.0071 mol) and *N,O*-dimethylhydroxylamine hydrochloride (2.77 g, 0.0284 mol) in THF (15 mL) was treated dropwise with isopropylmagnesium chloride (28.5 mL of 2 M solution in THF, 0.057 mol) at -15 °C. After 15 min, the resulting solution was warmed to room temperature, stirred for 1.5 h and quenched with saturated aqueous solution of NH_4Cl. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude amide was dissolved in THF (4 mL) and treated dropwise with MeLi (21.5 mL of 1.5 M solution in diethyl ether, 0.032 mol) at -78 °C. After 10 min, the reaction mixture was warmed to 0 °C, stirred for 15 min, and then quenched with saturated aqueous solution of NH_4Cl. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting crude hemiketal was dissolved in dichloromethane (70 mL) and treated with *p*-toluenesulfonic acid hydrate (0.095 g, 0.0005 mol) at room temperature. After 2 h, the reaction was quenched with triethylamine (0.35 mL) and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 2.6 g (72% yield over three steps) of bicyclic acetal **14**. $[\alpha]^{25.0}_{D}$ = +73.9 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (d, 3H, *J* = 7.0 Hz), 1.01 (d, 3H, *J* = 7.0 Hz), 1.08 (d, 18H, *J* =

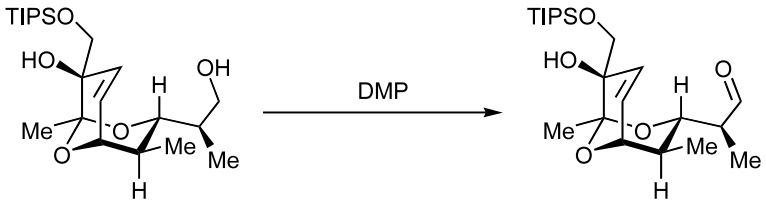
6.0 Hz), 1.12 (m, 3H), 1.41 (s, 3H), 2.00 (m, 1H), 2.24 (m, 1H), 3.11 (s, 1H), 3.27 (dd, 1H, *J* = 9.5, 7.0 Hz), 3.51 (dd, 1H, *J* = 11.5, 1.5 Hz), 3.57 (d, 1H, *J* = 10.0 Hz), 3.71 (dd, 1H, *J* = 9.5, 6.0 Hz), 3.78 (d, 1H, *J* = 10.0 Hz), 4.26 (t, 1H, *J* = 4.5 Hz), 4.47 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 12.0 Hz), 5.99 (dd, 1H, *J* = 10.0, 4.0 Hz), 6.17 (d, 1H, *J* = 10.0 Hz), 7.27 (m, 1H), 7.33 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 12.8, 15.9, 18.0, 24.1, 33.1, 34.2, 65.1, 69.2, 71.3, 71.6, 73.1, 76.8, 99.9, 126.6, 127.4, 128.3, 131.3, 138.7; HRMS (ESI) calculated for $C_{29}H_{49}O_5Si$ $[M+H]^+$ 505.3349, found 505.3350.



14 *99%* **66**

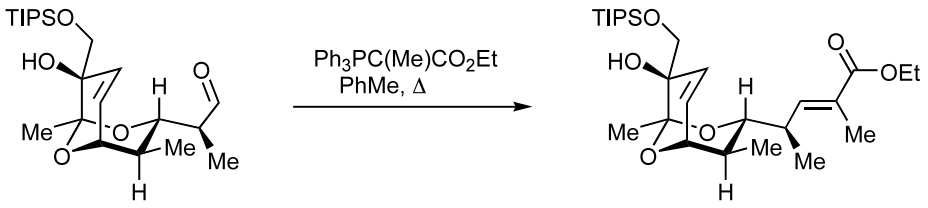
Alcohol 66. Lithium wire (0.03 g, 4.4 mmol) and 4,4'-di-*tert*-butylbiphenyl (1.17 g, 4.4 mmol) were sonicated in THF (22 mL) for 2 h at room temperature under positive pressure of argon. The resulting dark green solution was cooled to -78 °C and cannulated to a cold (-78 °C) solution of bicyclic acetal **14** (0.222 g, 0.44 mmol). The resulting mixture was stirred for 30 min, quenched with saturated aqueous solution of NH_4Cl, and warmed up to room temperature. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:diethyl ether 1:1) afforded 0.18 g (99% yield) of alcohol **66**. $[\alpha]^{25.2}_D$ = +93.8 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, 3H, *J* = 7.0 Hz), 1.10 (d, 18H, *J* = 6.0 Hz), 1.12 (d, 3H, *J* = 7.5 Hz), 1.13 (m, 3H), 1.45 (s, 3H), 1.76 (m, 1H), 2.26 (m, 1H), 2.56 (s, 1H), 3.14 (s, 1H), 3.55 (d, 1H, *J* = 10.0 Hz), 3.58 (d, 1H, *J* =

10.0 Hz), 3.63 (d, 1H, *J* = 10.5 Hz), 3.79 (d, 1H, *J* = 10.0 Hz), 3.94 (dd, 1H, *J* = 11.0, 3.0 Hz), 4.31 (t, 1H, *J* = 4.5 Hz), 6.00 (dd, 1H, *J* = 10.0, 4.0 Hz), 6.18 (d, 1H, *J* = 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8, 12.7, 15.2, 18.0, 24.4, 33.6, 34.3, 63.8, 65.0, 69.0, 71.4, 79.4, 100.4, 126.5, 131.3; HRMS (ESI) calculated for $C_{22}H_{43}O_5Si$ $[M+Na]^+$ 415.2880, found 415.2891.



66 *85%* **67**

Aldehyde 67. A solution of alcohol **66** (0.67 g, 1.62 mmol) in dichloromethane (10 mL) was treated with Dess-Martin periodinane (0.89 g, 2.1 mmol) at room temperature. After 1 h, the reaction was quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$ and stirred for 15 min. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.57 g (85% yield) of aldehyde **67**. $[\alpha]^{25.4}_D$ = +100.6 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (d, 3H, *J* = 7.0 Hz), 1.08 (d, 18H, *J* = 5.5 Hz), 1.13 (m, 3H), 1.17 (d, 3H, *J* = 7.0 Hz), 1.41 (s, 3H), 2.24 (m, 1H), 2.40 (m, 1H), 3.11 (s, 1H), 3.58 (d, 1H, *J* = 10.0 Hz), 3.73 (dd, 1H, *J* = 11.0, 1.5 Hz), 3.81 (d, 1H, *J* = 10.0 Hz), 4.31 (t, 1H, *J* = 4.5 Hz), 6.00 (dd, 1H, *J* = 10.5, 4.0 Hz), 6.19 (d, 1H, *J* = 10.5 Hz), 9.78 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 11.8, 12.6, 18.0, 24.0, 33.7, 46.7, 65.1, 69.0, 71.1, 76.5, 100.3, 126.1, 131.6, 204.2; HRMS (ESI) calculated for $C_{22}H_{41}O_5Si$ $[M+H]^+$ 413.2723, found 413.2718.



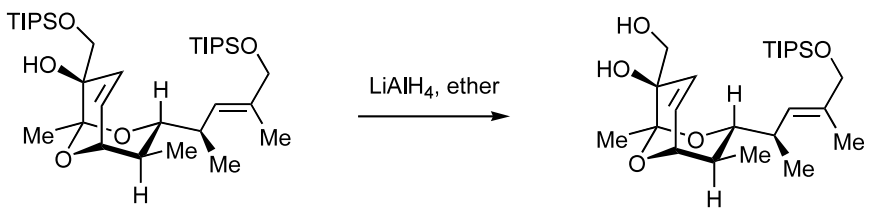
67 *77%* **29**

Ester 29. A solution of aldehyde **67** (0.175 g, 0.423 mmol) and (carbethoxyethylidene)triphenylphosphorane (0.766 g, 2.12 mmol) in toluene (4.5 mL) was heated at 110 °C for 5 h. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 0.162 g (77% yield) of ester **29**. $[\alpha]^{25.7}_{D}$ = +60.4 (*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, 3H, *J* = 7.0 Hz), 1.05 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 18H, *J* = 5.5 Hz), 1.14 (m, 3H), 1.30 (t, 3H, *J* = 7.0 Hz), 1.48 (s, 3H), 1.83 (d, 3H, *J* = 1.5 Hz), 1.86 (m, 1H), 2.65 (m, 1H), 3.12 (s, 1H), 3.51 (d, 1H, *J* = 10.5 Hz), 3.59 (d, 1H, *J* = 10.0 Hz), 3.82 (d, 1H, *J* = 10.0 Hz), 4.20 (m, 2H), 4.23 (t, 1H, *J* = 4.0 Hz), 6.00 (dd, 1H, *J* = 10.5, 4.0 Hz), 6.17 (d, 1H, *J* = 10.0 Hz), 6.89 (d, 1H, *J* = 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9, 12.5, 12.7, 14.3, 16.6, 18.0, 24.0, 34.1, 34.2, 60.5, 65.2, 69.2, 71.2, 76.9, 100.0, 126.6, 127.7, 131.3, 142.0, 168.1; HRMS (ESI) calculated for $C_{27}H_{48}O_6NaSi$ $[M+Na]^+$ 519.3118, found 519.3121.

29 *77%, 2 steps* **30**

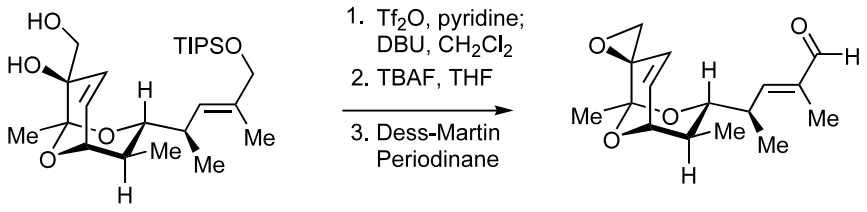
Silyl ether 30. A stirred solution of ester **29** (0.42 g, 0.847 mmol) in dichloromethane (8.5 mL) was treated with DIBAL-H (3.4 mL of 1 M solution in toluene, 3.4 mmol) at -

78 °C. After 1 h, the reaction was quenched with brine (1 mL). The resulting mixture was warmed to room temperature, stirred for 1 h, diluted with diethyl ether and treated with Na_2SO_4. The solution was decanted, and the solids were rinsed with diethyl ether. The combined solutions were dried over $MgSO_4$ and concentrated *in vacuo*. A solution of the resulting crude alcohol, imidazole (0.2 g, 3 mmol) and DMAP (0.018 g, 0.15 mmol) in dichloromethane (1.5 mL) was treated dropwise with TIPSCl (0.32 mL, 1.5 mmol). The reaction mixture was stirred overnight at room temperature, diluted with diethyl ether, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 20:1) afforded 0.39 g (75% yield over two steps) of silyl ether **30**. $[a]^{25.9}_{D}$ = +59.1 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) d 0.66 (d, 3H, *J* = 7.0 Hz), 0.98 (d, 3H, *J* = 7.0 Hz), 1.08 (m, 42H), 1.43 (s, 3H), 1.59 (s, 3H), 1.92 (m, 1H), 2.55 (m, 1H), 3.09 (s, 1H), 3.44 (dd, 1H, *J* = 10.5, 2.0 Hz), 3.59 (d, 1H, *J* = 10.0 Hz), 3.81 (d, 1H, *J* = 10.0 Hz), 4.09 (s, 2H), 4.19 (t, 1H, *J* = 4.5 Hz), 5.58 (d, 1H, *J* = 10.0 Hz), 5.99 (dd, 1H, *J* = 10.5, 4.5 Hz), 6.15 (d, 1H, *J* = 10.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) d 11.8, 12.0, 12.7, 13.4, 17.7, 18.0, 18.1, 23.9, 32.9, 33.7, 65.2, 68.5, 69.3, 71.3, 77.4, 99.8, 124.2, 127.1, 131.0, 134.3; HRMS (ESI) calculated for $C_{34}H_{67}O_5Si_2$ $[M+H]^+$ 611.4527, found 611.4528.



30 *82%* **31**

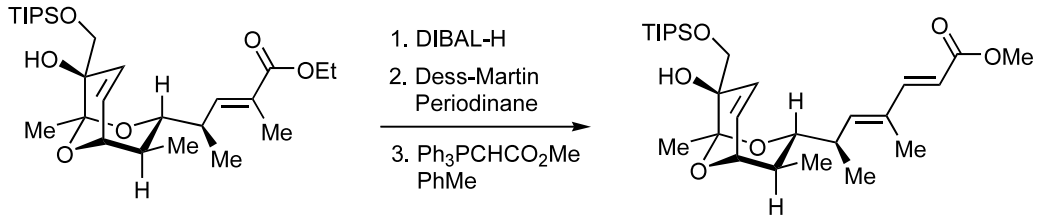
Diol 31. A stirred solution of silyl ether **30** (0.247 g, 0.404 mmol) in THF (3 mL) was treated dropwise with $LiAlH_4$ (0.6 mL of 1 M solution in THF, 0.6 mmol) at 0 °C. After 2 h at room temperature, the reaction was quenched with brine (0.22 mL), stirred 20 min, diluted with diethyl ether and treated with Na_2SO_4. The solution was decanted and solids were rinsed with diethyl ether. The combined solutions were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) afforded 0.15 g (82% yield) of diol **31**. $[a]^{23.7}_D$ = +70.7 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) d 0.67 (d, 3H, *J* = 7.0 Hz), 0.98 (d, 3H, *J* = 7.0 Hz), 1.07 (d, 18H, *J* = 6.0 Hz), 1.10 (m, 3H), 1.42 (s, 3H), 1.59 (s, 3H), 1.94 (m, 1H), 2.21 (s, 1H), 2.23 (m, 1H), 2.55 (m, 1H), 3.52 (m, 2H), 3.72 (dd, 1H, *J* = 12.0, 4.5 Hz), 4.09 (s, 2H), 4.16 (t, 1H, *J* = 4.5 Hz), 5.58 (d, 1H, *J* = 10.0 Hz), 6.01 (dd, 1H, *J* = 10.5, 4.0 Hz), 6.28 (d, 1H, *J* = 10.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.0, 12.7, 13.5, 17.6, 18.1, 23.9, 32.8, 33.8, 64.4, 68.3, 69.6, 71.6, 77.6, 100.3, 123.8, 128.2, 130.8, 134.5; HRMS (ESI) calculated for $C_{25}H_{47}O_5Si$ $[M+H]^+$ 455.3193, found 455.3188.



31 *78%, 3 steps* **11**

Streptal (11). Trifluoromethanesulfonic anhydride (0.067 mL, 0.4 mmol) was added dropwise to a stirred solution of diol **31** (0.14 g, 0.308 mmol) and pyridine (0.065 mL, 0.8 mmol) in dichloromethane (3 mL) at -78 °C. The mixture was warmed up to 0 °C,

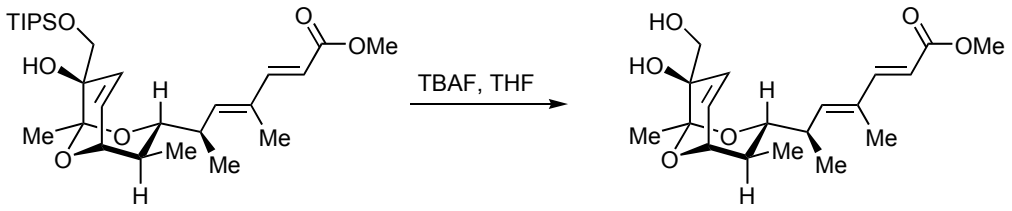
stirred for 15 min, and treated with DBU (0.24 mL, 1.6 mmol). The resulting solution was stirred for 1 h, diluted with diethyl ether, and washed with aqueous HCl (1 M solution), water, and saturated aqueous solution of $NaHCO_3$. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. A solution of the resulting crude epoxide in THF (2 mL) was treated with TBAF (0.6 mL of 1 M solution in THF, 0.6 mmol) at 0°C. After 2 h, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting crude alcohol was dissolved in dichloromethane (3 mL) and treated with solid $NaHCO_3$ (0.144 g, 1.72 mmol). The resulting suspension was treated with Dess-Martin periodinane (0.182 g, 0.43 mmol), stirred for 1 h at room temperature, and quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$. After 15 min, the reaction mixture was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 5:1) afforded 0.067 g (78% yield over three steps) of streptal (**11**). $[a]^{24.3}_D$ = +196.1 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) d 0.70 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 3H, *J* = 7.0 Hz), 1.23 (s, 3H), 1.74 (s, 3H), 1.90 (m, 1H), 2.82 (d, 1H, *J* = 5.0 Hz), 2.88 (m, 1H), 2.98 (d, 1H, *J* = 5.0 Hz), 3.68 (dd, 1H, *J* = 10.5, 2 Hz), 4.36 (t, 1H, *J* = 4.5 Hz), 5.63 (d, 1H, *J* = 10.0 Hz), 6.34 (dd, 1H, *J* = 10.5, 4.5 Hz), 6.66 (d, 1H, *J* = 10.0 Hz), 9.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 9.2, 12.5, 16.6, 22.2, 33.9, 35.2, 50.5, 54.9, 71.3, 75.8, 98.9, 130.6, 133.6, 139.1, 154.1, 195.4; HRMS (ESI) calculated for $C_{16}H_{23}O_4$ $[M+H]^+$ 279.1596, found 279.1602.



29 *100%* **32**

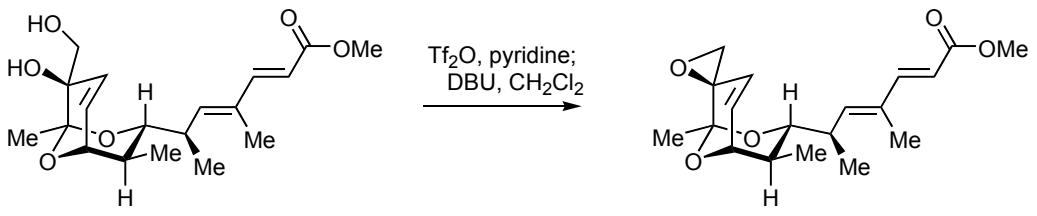
Ester 32. A stirred solution of ester **29** (0.063 g, 0.127 mmol) in dichloromethane (2 mL) was treated with DIBAL-H (0.6 mL of 1 M solution in toluene, 0.6 mmol) at -78°C. After 1 hr reaction was quenched with ethyl acetate (0.2 mL) followed by brine (0.15 mL). The resulting mixture was warmed up to room temperature, stirred 30 min and diluted with diethyl ether. Solution was decanted, and solids were rinsed with diethyl ether. Combined solutions were dried over $MgSO_4$, concentrated *in vacuo* and azeotroped with toluene. A stirred mixture of the resulting alcohol and solid $NaHCO_3$ (0.027 g, 0.32 mmol) in dichloromethane (1.5 mL) was treated with Dess-Martin periodinane (0.068 g, 0.16 mmol). After 30 min at room temperature (carboxymethylidene)triphenylphosphorane (0.2 g, 0.605 mmol) was added, and reaction mixture was left overnight and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.065 g (100% over two steps) of ester **32**. $[a]^{24.1}_{D}$ = +40.6 (*c* = 0.45, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) d 0.66 (d, 3H, *J* = 7.0 Hz), 1.03 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 18H, *J* = 6.0 Hz), 1.14 (m, 3H), 1.46 (s, 3H), 1.76 (s, 3H), 1.83 (m, 1H), 2.68 (m, 1H), 3.10 (s, 1H), 3.50 (d, 1H, *J* = 10.0 Hz), 3.58 (d, 1H, *J* = 10.0 Hz), 3.75 (s, 3H), 3.81 (d, 1H, *J* = 10.0 Hz), 4.20 (t, 1H, *J* = 4.5 Hz), 5.78 (d, 1H, *J* = 15.5 Hz), 5.98 (dd, 1H, *J* = 10.5, 4.5 Hz), 6.06 (d, 1H, *J* = 10.0 Hz), 6.15 (d, 1H, *J* = 10.5 Hz), 7.33 (d, 1H, *J* = 15.5 Hz); ^{13}C NMR (125

MHz, $CDCl_3$) d 11.9, 12.3, 12.7, 17.2, 18.0, 24.1, 34.06, 34.08, 51.5, 65.2, 69.2, 71.1, 77.1, 100.0, 115.5, 126.7, 131.2, 132.4, 142.3, 149.9, 167.8; HRMS (ESI) calculated for $C_{28}H_{49}O_6Si$ $[M+H]^+$ 509.3298, found 509.3310.



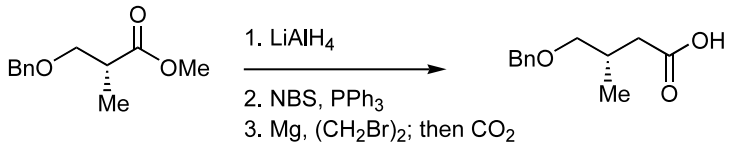
32 *100%* **68**

Diol 68. A stirred solution of ester **32** (0.065 g, 0.128 mmol) in THF (1.5 mL) was treated with TBAF (0.14 mL of 1 M solution in THF, 0.14 mmol) at 0 °C. After 15 min reaction was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. Organic layer was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) afforded 0.045 g (100% yield) of diol **68**. $[\alpha]^{23.8}_D$ = +61.9 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (d, 3H, *J* = 7.0 Hz), 1.03 (d, 3H, *J* = 6.5 Hz), 1.45 (s, 3H), 1.76 (s, 3H), 1.83 (m, 1H), 2.30 (s, 1H), 2.47 (s, 1H), 2.68 (m, 1H), 3.48 (d, 1H, *J* = 12.0 Hz), 3.55 (dd, 1H, *J* = 10.5, 1.5 Hz), 3.61 (dd, 1H, *J* = 10.5, 1.5 Hz), 3.75 (s, 3H), 4.17 (t, 1H, *J* = 4.5 Hz), 5.79 (d, 1H, *J* = 16.0 Hz), 6.00-6.06 (m, 2H), 6.30 (d, 1H, *J* = 10.5 Hz), 7.34 (d, 1H, *J* = 15.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.3, 12.7, 17.0, 24.0, 34.0, 34.2, 51.5, 64.2, 69.6, 71.4, 77.2, 100.5, 115.6, 127.7, 130.9, 132.5, 142.1, 149.9, 167.9; HRMS (ESI) calculated for $C_{19}H_{29}O_6$ $[M+H]^+$ 353.1964, found 353.1960.



68 *75%* Methyl Streptolate (**33**)

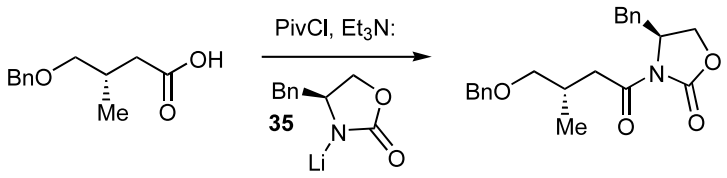
Methyl streptolate 33. Trifluoromethanesulfonic anhydride (0.017 mL, 0.102 mmol) was added dropwise to a stirred solution of diol **68** (0.03 g, 0.085 mmol) and pyridine (0.017 mL, 0.204 mmol) in dichloromethane (1 mL) at -78 °C. Reaction mixture was stirred 10 min and then warmed up to 0 °C. After 15 min DBU (0.06 mL, 0.408 mmol) was introduced, the resulting solution was left at room temperature for 1 hour and diluted with diethyl ether. The s olution was washed with aqueous HCl (1 N solution), water and saturated aqueous $NaHCO_3$, then dried over $MgSO_4$ and concentrated *in vacuo*. Purification by preparative TLC (development with hexanes:ethyl acetate 4:1) afforded 0.021 g (75% yield) of methyl streptolate **33**. $[\alpha]^{26.0}_{D}$ = +130.9 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (d, 3H, *J* = 7.0 Hz), 1.02 (d, 3H, *J* = 7.0 Hz), 1.22 (s, 3H), 1.77 (s, 3H), 1.93 (m, 1H), 2.72 (m, 1H), 2.80 (d, 1H, *J* = 5.0 Hz), 2.97 (d, 1H, *J* = 5.0 Hz), 3.61 (dd, 1H, *J* = 10.5, 2 Hz), 3.75 (s, 3H), 4.34 (t, 1H, *J* = 4.5 Hz), 5.61 (d, 1H, *J* = 10.5 Hz), 5.79 (d, 1H, *J* = 15.5 Hz), 6.06 (d, 1H, *J* = 10.0 Hz), 6.34 (dd, 1H, *J* = 10.0, 5.0 Hz), 7.35 (d, 1H, *J* = 15.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.2, 12.5, 17.2, 22.2, 33.7, 35.0, 50.6, 51.5, 55.0, 71.4, 76.2, 98.8, 115.6, 130.5, 132.5, 133.9, 142.1, 149.9, 167.9; HRMS (ESI) calculated for $C_{19}H_{27}O_5$ $[M+H]^+$ 335.1858, found 335.1861.



69 *77%, 3 steps* **34**

Acid 34. A stirred solution of known ester **69**[3] (5.1 g, 0.0245 mol) in diethyl ether (36 mL) was treated dropwise with $LiAlH_4$ (12 mL of 2 M solution in THF, 0.024 mol) at 0 °C. After 30 min at room temperature, the reaction was quenched with brine (9 mL) and treated with anhydrous Na_2SO_4. The resulting mixture was diluted with diethyl ether, the solution was decanted, and the solids were washed with diethyl ether. The combined solutions were dried over $MgSO_4$ and concentrated *in vacuo*. A mixture of the resulting crude alcohol and triphenylphosphine (8.39 g, 0.032 mol) was dissolved in dichloromethane (50 mL) and treated with NBS (5.7 g, 0.032 mol) at 0 °C. The reaction mixture was stirred overnight at room temperature, quenched with saturated aqueous $NaHCO_3$, and extracted twice with hexanes. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was suspended in hexanes, filtered, and the solids were rinsed with additional portion of hexanes. The combined solutions were concentrated *in vacuo* to afford crude bromide. A solution of the product and 1,2-dibromoethane (0.1 mL) in THF (25 mL) was added slowly to a stirred suspension of magnesium powder (1.2 g, 0.05 mol) in THF (5 mL). The resulting suspension was refluxed for 30 min, cooled to room temperature, and poured into a slurry of dry ice in diethyl ether (~100 mL). The resulting suspension was warmed up to room temperature and diluted with hexanes. The solution was decanted, the solids were treated with

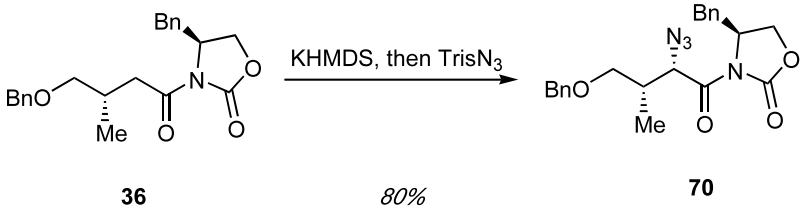
aqueous HCl (200 mL of 1 M solution), and the resulting solution was extracted twice with ethyl acetate. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford 3.93 g (77% yield over three steps) of known acid **34**.[9] $[\alpha]^{25.2}_D$ = -4.4 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (d, 3H, *J* = 7.0 Hz), 2.22 (dd, 1H, *J* = 15.0, 7.5 Hz), 2.34 (m, 1H), 2.57 (dd, 1H, *J* = 15.0, 6.0 Hz), 3.32 (dd, 1H, *J* = 9.0, 7.0 Hz), 3.42 (dd, 1H, *J* = 9.0, 5.0 Hz), 4.51 (d, 1H, *J* = 12.0 Hz), 4.54 (d, 1H, *J* = 12.0 Hz), 7.27-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8, 30.6, 38.5, 72.9, 74.6, 127.5, 128.3, 138.3, 179.2.



34 *78%* **36**

Imide 36. A stirred solution of acid **34** (3.85 g, 0.0185 mol) in THF (150 mL) was treated with triethylamine (3.35 mL, 0.024 ml) and pivaloyl chloride (2.5 mL, 0.0203 mol) at -78 °C. After 15 min, the reaction was warmed to 0 °C, stirred for 45 min, and the resulting solution of mixed anhydride was cooled to -78 °C. In a separate flask, a stirred solution of (4*S*)-4-benzyl-1,3-oxazolidin-2-one (5.9 g, 0.0333 mol) in THF (70 mL) was treated with butyllithium (13 mL of 2.56 M solution in hexanes, 0.0333 mol) at -78 °C, and the resulting mixture was cannulated to the solution of mixed anhydride. After 15 min, the reaction was warmed up to room temperature over 1.5 h and quenched with aqueous $NaHSO_4$ (150 mL of 1 M solution). Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were

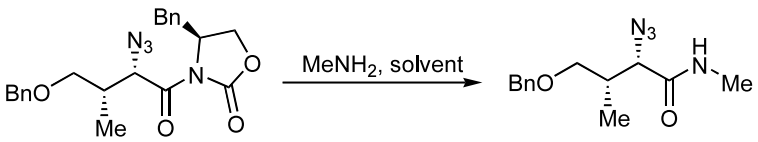
washed with brine, saturated aqueous solution of $NaHCO_3$, brine, then dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 5.3 g (78% yield) of imide **36**. $[\alpha]^{26.1}_D$ = +42.4 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (d, 3H, *J* = 7.0 Hz), 2.51 (m, 1H), 2.70 (dd, 1H, *J* = 13.0, 10.0 Hz), 2.76 (dd, 1H, *J* = 16.0, 6.5 Hz), 3.21 (dd, 1H, *J* = 16.0, 7.0 Hz), 3.26 (dd, 1H, *J* = 13.5, 3.0 Hz), 3.38 (dd, 1H, *J* = 9.0, 8.0 Hz), 3.45 (dd, 1H, *J* = 9.0, 5.5 Hz), 3.91 (t, 1H, *J* = 8.0 Hz), 4.04 (dd, 1H, *J* = 9.0, 3.0 Hz), 4.47 (d, H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 12.0 Hz), 4.54 (m, 1H), 7.18 (d, 2H, *J* = 7.0 Hz), 7.23-7.34 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.2, 30.6, 37.9, 39.4, 55.0, 65.9, 72.9, 75.1, 127.2, 127.4, 127.5, 128.2, 128.8, 129.3, 135.3, 138.5, 153.5, 172.6; HRMS (ESI) calculated for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1862, found 368.1865.



36 *80%* **70**

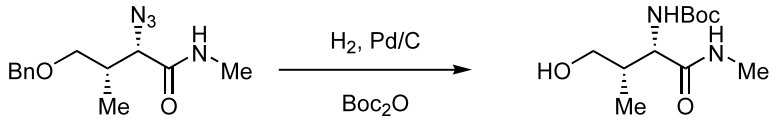
Imide 70. A cold (-78 °C) solution of imide **36** (5 g, 0.0137 mol) was cannulated to a stirred mixture of KHMDS (29 mL of 0.54 M solution in toluene, 0.0151 mol) and THF (50 mL) at -78 °C. After 30 min, the resulting enolate solution was treated with a cold (-78 °C) solution of trisyl azide[i] (5.3 g, 0.0172 mol) in THF (50 mL). After 5 min, acetic acid (3.6 mL, 0.063 mol) was introduced, and the reaction was left overnight at room temperature. The resulting suspension was washed with saturated aqueous solution of $NaHCO_3$, brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash

chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 4.48 g (80% yield) of imide **70**. $[a]^{26.1}_{D}$ = +129.2 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) d 1.00 (d, 3H, *J* = 7.0 Hz), 2.67 (m, 1H), 2.72 (dd, 1H, *J* = 14.0, 10.0 Hz), 3.21 (dd, 1H, *J* = 14.0, 4.0 Hz), 3.40 (t, 1H, *J* = 9.0 Hz), 3.50 (t, 1H, *J* = 10.0 Hz), 3.55 (dd, 1H, *J* = 10.0, 5.0 Hz), 3.87 (dd, 1H, *J* = 9.0, 4.0 Hz), 4.21 (m, 1H), 4.34 (d, 1H, *J* = 11.0 Hz), 4.48 (d, 1H, *J* = 11.0 Hz), 5.08 (d, 1H, *J* = 9.0 Hz), 7.11 (d, 2H, *J* = 7.0 Hz), 7.21-7.35 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) d 13.3, 35.7, 37.7, 54.8, 62.1, 66.0, 72.9, 73.2, 127.2, 127.5, 127.7, 128.2, 128.8, 129.3, 134.9, 138.0, 153.3, 170.8; HRMS (ESI) calculated for $C_{22}H_{25}N_4O_4$ $[M+H]^+$ 409.1876, found 409.1865.



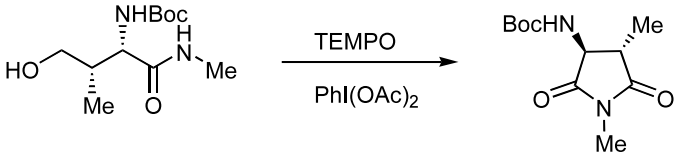
70 *88%* **19**

Amide 19. Imide **70** (4.44 g, 0.0109 mol) was dissolved in a cold (0 °C) solution of methylamine (54 mL of 2 M solution in THF, 0.108 mol), left for 1 h, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 2:1) afforded 2.5 g (88% yield) of amide **19**. $[\alpha]^{26.1}_{D}$ = -8.2 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, 3H, *J* = 7.0 Hz), 2.65 (m, 1H), 2.82 (d, 3H, *J* = 5.0 Hz), 3.37 (t, 1H, *J* = 9.5 Hz), 3.48 (dd, 1H, *J* = 9.5, 5.0 Hz), 4.76 (d, 1H, *J* = 3.5 Hz), 4.53 (m, 2H), 6.50 (m, 1H), 7.27-7.36 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.7, 26.1, 36.4, 65.7, 71.6, 73.0, 127.7, 127.8, 128.4, 138.0, 169.8; HRMS (ESI) calculated for $C_{13}H_{19}N_4O_2$ $[M+H]^+$ 263.1508, found 263.1516.



19 *87%* **37**

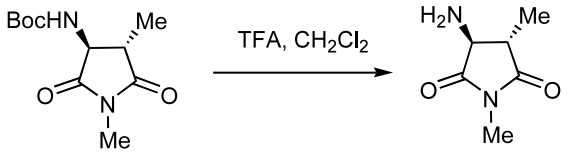
Alcohol 37. A mixture of amide **19** (2.45 g, 9.34 mmol), Boc anhydride (2.45 g, 11.2 mmol), and palladium on carbon (2.5 g, 10% w/w) in THF (45 mL) was vigorously stirred under hydrogen atmosphere for 2 days at room temperature. The reaction was sparged with nitrogen, filtered though Celite, and concentrated *in vacuo*. The residue was washed with hexanes and dried *in vacuo* to afford 2 g (87%) of alcohol **37**. $[\alpha]^{26.1}_{D}$ = +53.9 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69 (d, 3H, *J* = 5.5 Hz), 1.43 (s, 9H), 2.09 (m, 1H), 2.81 (d, 3H, *J* = 3.0 Hz), 3.27 (m, 1H), 3.46 (m, 1H), 4.46 (d, 1H, *J* = 4.0 Hz), 4.70 (m, 1H), 5.78 (d, 1H, *J* = 4.0 Hz), 7.10 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.1, 26.3, 28.2, 39.8, 53.4, 64.0, 80.3, 157.3, 171.7; HRMS (ESI) calculated for $C_{11}H_{23}N_2O_4$ $[M+H]^+$ 247.1658, found 247.1666.



37 *80%* **38**

Carbamate 38. A solution of alcohol **37** (0.96 g, 3.9 mmol), iodobenzene diacetate (10 g, 31.2 mmol), and TEMPO (0.183 g, 1.17 mmol) in dichloromethane (40 mL) was left

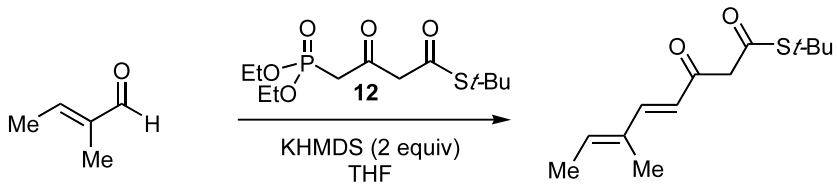
for 3 days at room temperature. The reaction was quenched with saturated aqueous solution of $NaHCO_3$ (20 mL) followed by saturated aqueous solution of $Na_2S_2O_3$ (40 mL) and stirred for 1 h. The resulting mixture was extracted twice with ethyl acetate, and the combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The bulk of iodobenzene was removed under vacuum (35 °C, 0.5 torr), and the residue was purified by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) to afford 0.75 g (80% yield) of carbamate **38**. $[\alpha]^{26.3}_D$ = -73.0 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (d, 3H, *J* = 7.5 Hz), 1.42 (s, 9H), 2.91 (m, 1H), 3.00 (s, 3H), 3.85 (m, 1H), 5.30 (d, 1H, *J* = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 25.0, 28.2, 42.2, 57.9, 80.8, 155.3, 175.0, 177.4; HRMS (ESI) calculated for $C_{11}H_{18}N_2O_4Na$ $[M+Na]^+$ 265.1164, found 265.1167.



38 *100%* **13**

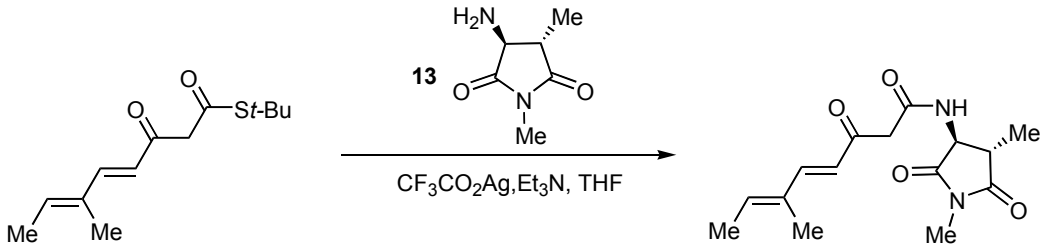
Amine 13. Carbamate **38** (0.96 g, 3.97 mmol) was dissolved in a mixture of TFA (10 mL) and dichloromethane (30 mL), left for 1.5 h at room temperature, and concentrated *in vacuo*. The residue was azeotroped three times with chloroform until crystallization occurred, dissolved in ethyl acetate, and passed through a plug of basic alumina to afford 0.56 g (quantitative yield) of amine **13**. $[\alpha]^{26.6}_D$ = -152.7 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (d, 3H, *J* = 7.0 Hz), 1.68 (s, 2H), 2.52 (m, 1H), 2.99 (s, 3H), 3.45 (d,

1H, *J* = 6.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 24.9, 44.6, 58.5, 177.8, 178.6; HRMS (ESI) calculated for $C_6H_{11}N_2O_2$ $[M+H]^+$ 143.0821, found 143.0823.

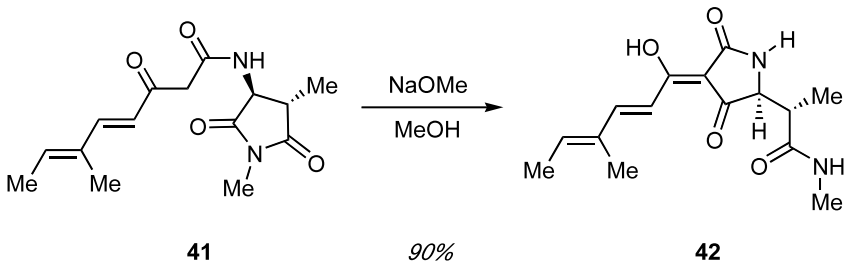


39 *93%* **40**

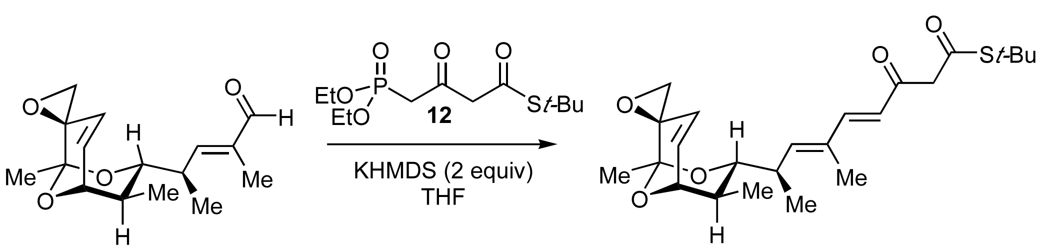
Thioester 40. A stirred solution of phosphonate **12** (0.2 g, 0.64 mmol) in THF (6 mL) was treated dropwise with KHMDS (2.4 mL of 0.54 M solution in toluene, 1.28 mmol) at -78 °C. The reaction mixture was stirred 15 min and treated with tiglic aldehyde **39** (0.06 mL, 0.6 mmol). After 45 min, reaction was warmed up to room temperature, stirred 30 min, and quenched with saturated aqueous NH_4Cl. The resulting solution was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 0.134 g (93% yield) of thioester **40**. ^{1}H NMR (ketone and enol forms, 500 MHz, $CDCl_3$) d 1.46 (s, 4.5H), 1.51 (s, 9H), 1.75 (s, 3H), 1.77 (s, 1.5H), 1.78 (d, 3H, *J* = 7.0 Hz), 1.82 (d, 1.5H, *J* = 7.0 Hz), 3.72 (s, 1H), 5.38 (s, 1H), 5.65 (d, 1H, *J* = 15.5 Hz), 5.90 (q, 1H, *J* = 7.0 Hz), 6.09 (q, 0.5H, *J* = 7.0 Hz), 6.13 (d, 0.5H, *J* = 16.0 Hz), 7.10 (d, 1H, *J* = 15.5 Hz), 7.22 (d, 0.5H, *J* = 15.5 Hz); ^{13}C NMR (ketone and enol forms, 125 MHz, $CDCl_3$) d 11.69, 11.74, 14.5, 14.8, 29.6, 30.1, 48.2, 48.9, 56.6, 101.0, 118.6, 122.9, 134.13, 134.15, 134.6, 139.1, 143.1, 150.0, 167.5, 191.9, 192.8, 195.9; HRMS (ESI) calculated for $C_{13}H_{20}O_2NaS$ $[M+Na]^+$ 263.1082, found 263.1082.



Ketoamide 41. A stirred solution of thioester **40** (26.0 mg, 0.108 mmol) and amine **51** (23.0 mg, 0.162 mmol) in THF (1.6 mL) was treated with triethylamine (0.06 mL, 0.432 mmol) at 0 °C, followed by addition of silver (I) trifluoroacetate (48.0 mg, 0.216 mmol) in one portion. After 1 h, the reaction mixture was concentrated *in vacuo*. Purification by preparative TLC on silica gel (developed in AcOEt) afforded 27.0 mg (86% yield) of ketoamide **41**. $[\alpha]^{23.2}_{D}$ = -64.9 (*c* = 2.7, $CHCl_3$); ^{1}H NMR (ketone form, 500 MHz, $CDCl_3$) d 1.38 (d, 3H, *J* = 7.0 Hz), 1.77 (s, 3H), 1.84 (d, 3H, *J* = 7.0 Hz), 2.92 (m, 1H), 3.00 (s, 3H), 3.61 (s, 2H), 4.09 (t, 1H, *J* = 7.0 Hz), 6.07 (d, 1H, *J* = 15.5 Hz), 6.13 (q, 1H, *J* = 7.0 Hz) 7.26 (d, 1H, *J* = 16.0 Hz), 8.20 (d, 1H, *J* = 7.0 Hz); ^{13}C NMR (ketone form, 125 MHz, $CDCl_3$) d 11.7, 14.0, 14.9, 25.0, 41.8, 45.7, 56.9, 123.0, 134.0, 140.6, 150.8, 167.0, 174.3, 177.3, 195.6; HRMS (ESI) calculated for $C_{15}H_{20}N_2O_4Na$ $[M+Na]^+$ 315.1321, found 315.1322.



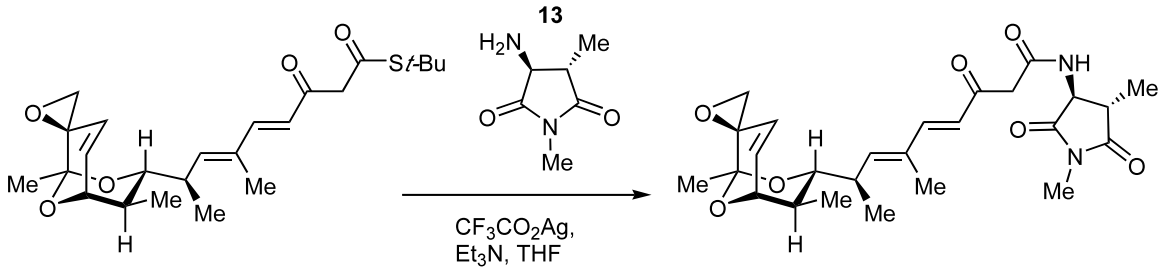
Truncated aglycone 42. A stirred solution of ketoamide **41** (0.053 g, 0.182 mmol) in methanol (1.1 mL) was treated with sodium methoxide (1.1 mL of 0.5 M solution in methanol, 0.55 mmol) at 0 °C. Reaction mixture was stirred overnight at room temperature and concentrated *in vacuo*. The residue was treated with aqueous HCl (0.7 mL of 1 N solution) and extracted twice with ethyl acetate. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to afford 0.048 g (90% yield) of truncated aglycone **42**. $[\alpha]^{24.3}_D$ = -2.9 (*c* = 2.4, $CHCl_3$); ^{1}H NMR (ketone forms, 500 MHz, $CDCl_3$) d 1.02 (d, 3H, *J* = 7.0 Hz), 1.86 (m, 6H) 2.80 (d, 3H, *J* = 2.5 Hz), 2.90 (m, 1H), 4.10 (s, 1H), 6.17 (m, 2H), 6.84 (s, 1H), 7.04 (d, 1H, *J* = 15.5 Hz) 7.51 (d, 1H, *J* = 15.5 Hz); ^{13}C NMR (ketone form, 125 MHz, $CDCl_3$) d 11.26, 11.72, 15.1, 26.3, 40.8, 63.0, 100.1, 115.5, 135.1, 140.8, 150.3, 175.0, 175.76, 175.84, 194.3; HRMS (ESI) calculated for $C_{15}H_{20}N_2O_4Na$ $[M+Na]^+$ 315.1321, found 315.1319.



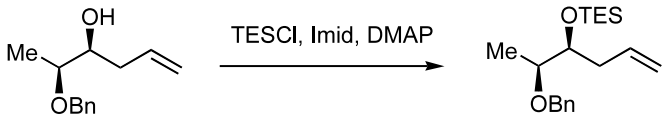
11 *100%* **43**

Thioester 43. A stirred solution of phosphonate **12** (0.045 g, 0.144 mmol) in THF (1.2 mL) was treated dropwise with KHMDS (0.53 mL of 0.54 M solution in toluene, 0.288 mmol) at -78 °C. After 15 min reaction mixture was transferred *via* cannula into the cold (-78 °C) solution of streptal (**11**) (0.022 g, 0.079 mmol) in THF (0.4 mL). After 45 min

reaction was warmed up to room temperature, stirred 30 min and quenched with saturated aqueous NH_4Cl. The resulting solution was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 0.035 g (100% yield) of thioester **43**. $[\alpha]^{23.7}_D$ = +89.4 (*c* = 0.7, $CHCl_3$); ^1H NMR (ketone and enol forms, 500 MHz, $CDCl_3$) δ 0.67 (m, 3H), 1.02 (m, 3H), 1.21 (m, 3H), 1.47 (s, 3H), 1.51 (s, 6H), 1.77 (m, 3H), 1.93 (m, 1H), 2.70 (m, 1H), 2.80 (m, 1H), 2.97 (m, 1H), 3.62 (m, 1H), 3.74 (d, 0.6H, *J* = 2.0 Hz), 4.33 (m, 1H), 5.39 (s, 0.6H), 5.61 (m, 1H), 5.68 (d, 0.75H, *J* = 15.5 Hz), 5.99 (d, 0.7H, *J* = 10.5 Hz), 6.15 (d, 0.5H, *J* = 15.5 Hz), 6.33 (dd, 1H, *J* = 10.0, 5.0 Hz), 7.15 (d, 0.7H, *J* = 15.5 Hz), 7.26 (d, 0.4H, *J* = 15.5 Hz); ^{13}C NMR (data for ketone form only, 125 MHz, $CDCl_3$) δ 12.2, 12.48, 12.49, 17.1, 17.2, 22.2, 29.6, 30.2, 33.7, 33.9, 35.0, 35.1, 48.2, 49.0, 50.50, 50.51, 54.97, 55.02, 56.2, 71.38, 71.43, 76.1, 76.2, 98.77, 98.83, 101.1, 119.3, 123.8, 130.48, 130.53, 132.91, 132.95, 133.8, 133.9, 140.3, 143.3, 144.5, 150.1, 167.3, 192.0, 192.9, 195.9; HRMS (ESI) calculated for $C_{24}H_{35}O_5S$ $[M+H]^+$ 435.2205, found 435.2203.



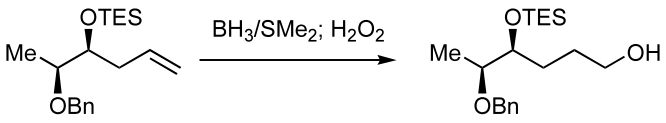
Ketoamide 44. A stirred solution of thioester **43** (16.0 mg, 0.036 mmol) and amine **13** (8.0 mg, 0.054 mmol) in THF (0.5 mL) was treated with triethylamine (0.02 mL, 0.144 mmol) at 0 °C, followed by addition of silver (I) trifluoroacetate (16.0 mg, 0.072 mmol) in one portion. After 15 min reaction mixture was concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:3) afforded 17.0 mg (100% yield) of ketoamide **44**. $[\alpha]^{24.3}_{D}$ = +30.3 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (ketone form, 500 MHz, $CDCl_3$) δ 0.69 (d, 3H, *J* = 7.0 Hz), 1.04 (d, 3H, *J* = 7.0 Hz), 1.40 (d, 3H, *J* = 7.5 Hz), 1.80 (s, 3H), 1.92 (m, 1H), 2.75 (m, 1H), 2.81 (d, 1H, *J* = 5.5 Hz), 2.94 (m, 1H), 2.97 (d, 1H, *J* = 5.5 Hz), 3.02 (s, 3H), 3.63 (m, 3H), 4.09 (m, 1H), 4.34 (t, 1H, *J* = 4.5 Hz), 5.62 (d, 1H, *J* = 10.0 Hz), 6.12 (d, 1H, *J* = 15.5 Hz), 6.22 (d, 1H, *J* = 10.0 Hz), 6.33 (dd, 1H, *J* = 10.0, 4.5 Hz), 7.31 (d, 1H, *J* = 16.0 Hz), 8.16 (d, 1H, *J* = 7.0 Hz); ^{13}C NMR (ketone form, 125 MHz, $CDCl_3$) δ 12.2, 12.5, 14.0, 17.0, 22.2, 25.1, 34.0, 35.1, 41.8, 45.6, 50.5, 54.9, 57.0, 71.3, 76.0, 98.8, 123.7, 130.5, 132.8, 133.7, 145.9, 150.9, 166.8, 174.3, 177.3, 195.5; HRMS (ESI) calculated for $C_{26}H_{35}N_2O_7$ $[M+H]^+$ 487.2444, found 487.2438.



45 *100%* **71**

Silyl ether 71. A stirred solution of known (2*S*,3*S*)-2-(benzyloxy)hex-5-en-3-ol **45**[4] (4 g, 0.0194 mol), imidazole (3 g, 0.044 mol), and DMAP (0.244 g, 0.002 mol) in dichloromethane (20 mL) was treated with chlorotriethylsilane (4.9 mL, 0.029 mol). The reaction was left overnight at room temperature then diluted with hexanes, washed with

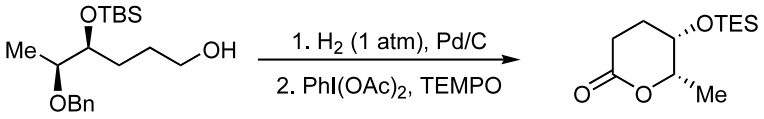
brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was heated at 60 °C under vacuum (0.5 torr) for 1 h to yield silyl ether **71**. $[\alpha]^{27.9}_D$ = -0.2 (*c* = 2.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.56 (q, 6H, *J* = 7.5 Hz), 0.94 (t, 9H, *J* = 7.5 Hz), 1.15 (d, 3H, *J* = 6.5 Hz), 2.17 (m, 1H), 2.40 (m, 1H), 3.50 (m, 1H), 3.75 (m, 1H), 4.51 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 12.0 Hz), 5.00-5.10 (m, 2H), 5.83 (m, 1H), 7.28 (m, 1H), 7.35 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.0, 6.9, 14.1, 36.5, 71.0, 74.0, 77.2, 116.5, 127.4, 127.6, 128.2, 136.9, 139.0; HRMS (ESI) calculated for $C_{19}H_{33}O_2Si$ $[M+H]^+$ 321.2250, found 321.2253.



71 *81%* **46**

Alcohol 46. A stirred solution of the silyl ether **71** in THF (19 mL) was treated dropwise with borane-dimethylsulfide complex (37.7 mL of 2 M solution in THF, 0.0755 mol) at 0 °C. The reaction was left overnight at room temperature then cooled to 0 °C and treated dropwise with aqueous NaOH (110 mL of 3 M solution) followed by aqueous H_2O_2 (50 mL of 30% w/w solution). After 2 h at room temperature, the mixture was extracted twice with diethyl ether. The combined organic extracts were washed with saturated aqueous solution of $Na_2S_2O_3$ and brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 5.16 g (81% yield over two steps) of alcohol **46**. $[\alpha]^{27.9}_D$ = -2.5 (*c* = 1.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.58 (q, 6H, *J* = 8.0 Hz), 0.93 (t, 9H, *J* = 8.0 Hz),

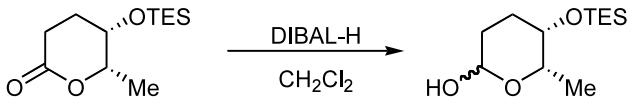
1.13 (d, 3H, *J* = 6.5 Hz), 1.41-1.59 (m, 2H), 1.68 (m, 2H), 1.90 (m, 1H), 3.51 (m, 1H), 3.62 (m, 1H), 3.73 (m, 1H), 4.49 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 12.0 Hz), 7.28 (m, 1H), 7.33 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 5.0, 6.9, 13.8, 27.9, 29.1, 63.1, 71.0, 74.0, 77.2, 127.4, 127.6, 128.2, 138.8; HRMS (ESI) calculated for $C_{19}H_{35}O_3Si$ $[M+H]^+$ 339.2355, found 339.2361.



46 *73%, 2 steps* **47**

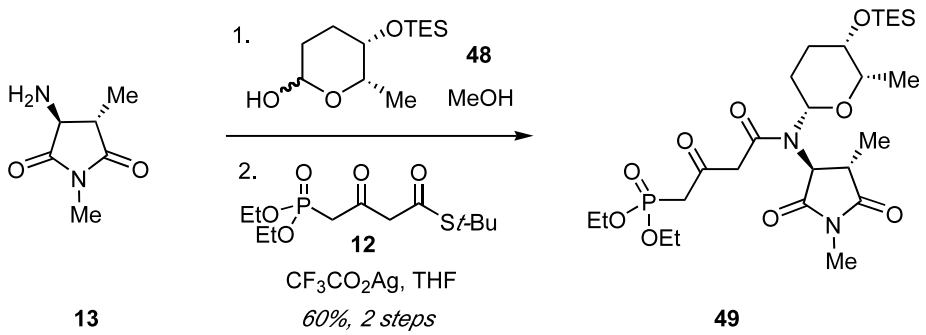
Lactone 47. A mixture of alcohol **46** (0.76 g, 2.25 mmol) and palladium on carbon (0.38 g, 10% w/w) in THF (11 mL) was vigorously stirred under hydrogen atmosphere for 2 days at room temperature. The reaction was sparged with nitrogen, filtered though Celite, and concentrated *in vacuo*. The residue was dissolved in dichloromethane (30 mL), and iodobenzene diacetate (3.62 g, 11.25 mmol) and TEMPO (0.07 g, 0.45 mmol) were added. The reaction was left overnight at room temperature, quenched with saturated aqueous solution of $Na_2S_2O_3$, and stirred for 1 h. Phases were separated, and the organic phase was washed with saturated aqueous solution of $NaHCO_3$, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) afforded 0.4 g (73% yield over two steps) of lactone **47**. $[\alpha]^{27.9}_D$ = -9.9 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.61 (q, 6H, *J* = 8.0 Hz), 0.95 (t, 9H, *J* = 8.0 Hz), 1.32 (d, 3H, *J* = 6.5 Hz), 1.94 (m, 2H), 2.47 (m, 1H), 2.69 (m, 1H), 3.89 (m, 1H), 4.38 (q, 1H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.7,

6.7, 17.5, 24.9, 27.8, 65.7, 79.5, 170.8; HRMS (ESI) calculated for $C_{12}H_{25}O_3Si$ $[M+H]^+$ 245.1573, found 245.1582.



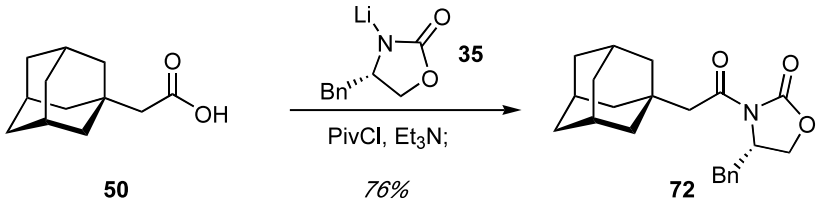
47 *98%* **48**

Rhodinose 48. A stirred solution of lactone **47** (0.37 g, 1.51 mmol) in dichloromethane (14 mL) was treated dropwise with DIBAL-H (1.8 mL of 1 M solution in toluene, 1.8 mmol) at -78 °C. After 1 h, the reaction was quenched with brine (0.5 mL) and warmed to room temperature. Sodium sulfate was added, and the resulting suspension was stirred overnight. The liquids were decanted and the solids were rinsed with diethyl ether. The combined solutions were dried over $MgSO_4$ and concentrated *in vacuo* to afford 0.366 g (98% yield) of known rhodinose **48**.[5] $[\alpha]^{28.0}_D$ = -22.5 (*c* = 1.6, $CHCl_3$); ^{1}H NMR (a-pyranose and b-pyranose forms, 500 MHz, $CDCl_3$) δ 0.63 (m, 6H), 0.96 (m, 9H), 1.13 (d, 1.8H, *J* = 6.5 Hz), 1.20 (d, 1.3H, *J* = 6.5 Hz), 1.46-2.13 (m, 4H), 3.23 (s, 0.6H), 3.50 (s, 0.4H), 3.58 (q, 0.4H, *J* = 6.5 Hz), 3.61 (s, 0.6H), 3.75 (d, 0.4H, *J* = 8.0 Hz), 4.11 (q, 0.6H, *J* = 6.5 Hz), 4.70 (t, 0.4H, *J* = 7.5 Hz), 5.31 (s, 0.6H); ^{13}C NMR (α-pyranose and β-pyranose forms, 125 MHz, $CDCl_3$) δ 4.9, 6.9, 17.3, 17.6, 23.8, 25.7, 27.5, 30.5, 66.7, 67.1, 67.8, 74.6, 91.6, 96.3.



Phosphonate 49. Protected rhodinose **48** (0.2 g, 0.812 mmol) and amine **13** (0.115 g, 0.812 mmol) were dissolved in methanol (3 mL). The solution was left overnight and concentrated *in vacuo* to afford crude *N*-glycosyl imide. Molecular sieves (5Å, 0.8 g, activated under vacuum) were added to the solution of crude *N*-glycosyl imide and thioate **12**[6] (0.31 g, 1 mmol) in THF (7 mL). The resulting slurry was treated with the solution of silver (I) trifluoroacetate (0.29 g, 1.3 mmol) in THF (3 mL), and the reaction was stirred for 1.5 h at room temperature. Diethyl ether was added and the resulting suspension was washed twice with saturated aqueous solution of $NaHCO_3$. The organic layers were dried over $MgSO_4$, filtered through Celite, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with ethyl acetate) afforded 0.29 g (60% yield over two steps) of phosphonate **49**. $[a]^{23.0}_D$ = -36.0 (*c* = 3.0, $CHCl_3$); ^{1}H NMR (ketone and enol forms, 500 MHz, $CDCl_3$) d 0.56 (m, 6H), 0.92 (m, 9H), 1.13 (m, 3H), 1.32 (m, 9H), 1.60 (m, 1H), 1.74 (s, 1H), 1.89 (m, 1H), 2.02 (m, 1H), 2.75 (d, 1H, *J* = 22.5 Hz), 2.93 (m, 1H), 2.99 (m, 3H), 3.18 (d, 1H, *J* = 22.5 Hz), 3.52 (s, 1H), 3.60 (q, 1H, *J* = 6.0 Hz), 3.74 (dd, 2H, *J* = 20.0, 15.5 Hz), 3.85 (d, 1H, *J* = 5.5 Hz), 4.12 (m, 4H), 4.94 (dd, 0.7H, *J* = 11.0, 3.0 Hz), 5.00 (dd, 0.2H, *J* = 11.0, 3.0 Hz), 5.31 (d, 0.2H, *J* = 3.0 Hz), 13.96 (s, 0.2H); ^{13}C NMR (data for ketone form only, 125 MHz, $CDCl_3$) d 4.8, 6.8,

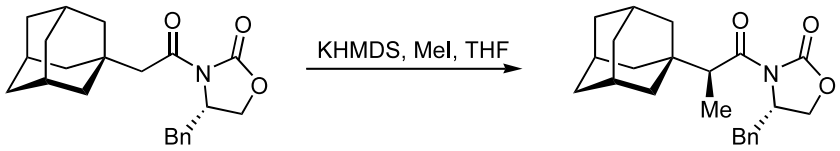
13.9, 16.19, 16.24, 17.7, 23.2, 24.9, 30.5, 40.5, 41.5, 42.5, 49.7, 59.1, 62.7, 62.8, 65.9, 75.9, 84.6, 165.8, 174.2, 178.2, 195.1; HRMS (ESI) calculated for $C_{26}H_{48}N_2O_9SiP$ $[M+H]^+$ 591.2867, found 591.2871.



50 *76%* **72**

Imide 72. Triethyl amine (2.0 mL, 0.01435 mol) was added drop-wise to a stirred solution of 1-adamantane acetic acid (**50**) (2.2106 g, 0.01138 mol) in 80 mL of THF at -78 °C. To this solution, 1.5 mL of pivaloyl chloride was added drop-wise, and stirred at -78°C for 15 minutes. The solution was subsequently warmed to 0°C for 45 minutes and returned to -78°C. A separate flask was charged with 3.2219 g of (4*S*)-4-benzyl-1,3-oxazolidin-2-one (**35**) (0.01818 mol) and equipped with a stir bar. Lithium Oxazolidinone **35** was dissolved in 40 mL of THF and cooled to -78°C. This solution was treated drop wise with 9.0 mL of n-butyllithium (2.59M in hexanes) and stirred for 5 minutes. This solution was added to the reaction mixture via cannula, and stirred at -78°C for 15 minutes. The solution was warmed to room temperature and stirred for 1 hour. The reaction was quenched with 82 mL of 1 M potassium bisulfate. The resulting solution was extracted three times with Et_2O. The combined organic extracts were washed with saturated aqueous sodium bicarbonate and brine, and dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with 100% CH_2Cl_2)

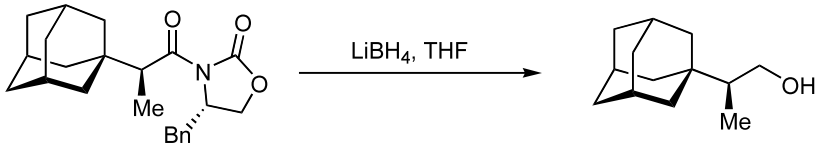
afforded 3.0354 g (76% yield) of imide **72**. $[\alpha]^{23.1}_{D}$ = -1.7 (c = 0.53, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 12H), δ 1.97 (s, 3H), δ 2.69 (t, 1H, *J* = 11.65 Hz), δ 2.82 (q, 2H, *J* = 13.88 Hz), δ 3.35 (d, 1H, *J* = 13.20 Hz), δ 4.13 (s, 1H), δ 7.13 – 7.42 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.88, 34.14, 36.98, 38.34, 42.47, 47.09, 55.67, 65.96, 127.51, 129.16, 129.63, 135.71, 153.75, 171.53; HRMS (ESI) calculated for $C_{22}H_{28}NO_3$ $[M+H]^+$ 354.2069, found 354.2045.



72 *76%* **51**

Imide 51. A round bottom flask was charged with 17.5 mL of NaHMDS solution (0.6M in toluene). The flask was equipped with a magnetic stir bar and 25.75 mL of THF was added. The resulting solution was cooled to -78°C. A separate flask was charged with 3.0354 g of imide **72** (0.00859 mol). This flask was equipped with a stir bar and 57.25 mL of THF was added. The resulting solution was cooled to -78°C and added to the NaHMDS solution via cannula. After 1 hour, 1.60 mL of iodomethane (0.02576 mol) was added drop-wise to the stirred reaction mixture. The solution was warmed to room temperature, and quenched with saturated aqueous solution of NH_4Cl. The pH of the aqueous layer was adjusted to 2 with 1 M HCl. The resulting mixture was extracted three times with ethyl acetate. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, saturated aqueous $Na_2S_2O_3$, and brine, and dried over $MgSO_4$, and concentrated *in vacuo.* Purification by flash chromatography on silica gel (elution with

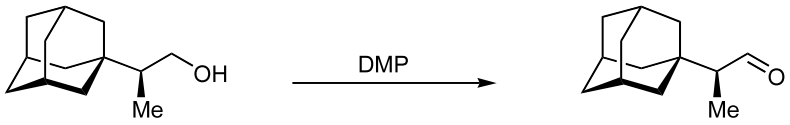
hexanes:ethyl acetate 9:1) afforded 2.3896 g of imide **51**. $[\alpha]^{24.9}_{D}$ = +40.1 (c = 5.0, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (d, 3H, *J* = 7.01 Hz), 1.51 – 1.85 (m, 12H), 2.01 (s, 3H), 2.79 (dd, 1H, *J* = 9.70, 13.31 Hz), 3.31 (dd, 1H, *J* = 3.12, 13.32) 3.83 (q, 1H, *J* = 6.99 Hz), 4.69 – 4.78 (m, 1H), 7.22 – 7.42 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.61, 28.93, 35.90, 37.28, 38.21, 39.67, 45.88, 55.89, 66.02, 127.63, 129.25, 129.81, 135.80, 153.81, 176.59. HRMS (ESI) calculated for $C_{23}H_{30}NO_3$ $[M+H]^+$ 368.2226, found 368.2202.



51 *38%* **52**

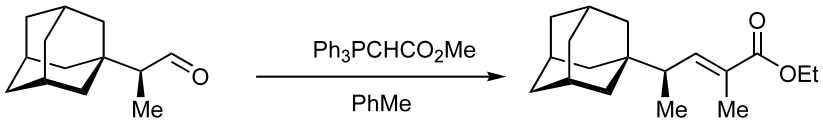
Alcohol 52. A stirred solution of imide **51** (1.1948 g, 0.00327 mol, in 30 mL of THF) was cooled to 0°C. To this solution, 0.20 mL of MeOH was added, followed by 3.50 mL of $LiBH_4$ solution (2M in THF, 0.00700 mol). After stirring for 2 hours at 0°C, the solution was warmed to room temperature, and stirred for an additional 4 hours. The reaction mixture was washed with 20 mL of aqueous 2M NaOH, and stirred until both phases were clear. The organic phase was separated and the aqueous layer was extracted three times with Et_2O. The combined organic extracts were washed with H_2O and brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution using 30% Et_2O in pentanes) afforded 0.2379 g (37.5% yield) of pure alcohol **52**. $[\alpha]^{25.2}_{D}$ = +110.16 (c = 0.64, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (d, 3H, *J* = 6.9 Hz), 1.12-1.26 (m, 2H), 1.58 (ddt, 12H, *J* = 7.08, 7.08, 12.12, 32.82 Hz), 1.95

(s, 3H), 3.36 (dd, 1H, *J* = 8.46, 10.38 Hz), 3.84 (dd, 1H, *J* = 3.91, 10.42 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.03, 28.81, 34.24, 37.43, 40.01, 46.21, 64.56; HRMS (ESI) calculated for $C_{13}H_{22}O$ $[M]^+$ 194.16707, found 194.16516.



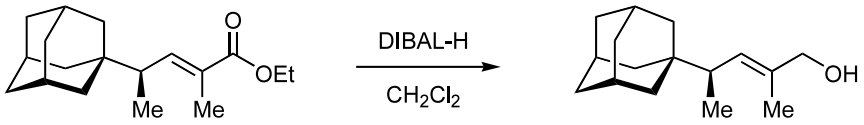
52 *71%* **73**

Aldehyde 73. A round bottom flask was charged with 0.0404 g of alcohol **52** (0.208 mmol), and equipped with a magnetic stir bar. Dichloromethane (1.0 mL) was added to the flask, and the resulting solution was cooled to 0°C. This solution was then treated with 0.1406 g of dess martin periodinane (0.3315 mmol). After 5 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ solution, washed with saturated aqueous $Na_2S_2O_3$, and extracted three times with Et_2O. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (elution with hexanes:ethyl acetate 4:1) afforded 0.0282 g (70.5% yield) of pure aldehyde **73**. $[\alpha]^{24.7}_D$ = +36.86 (c = 0.64, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (d, 3H, *J* = 7.02 Hz), 1.60 – 1.78 (m, 12H), 2.01 (s, 4H), 9.82 (dd, 1H, *J* = 0.93, 3.46 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.45, 28.40, 35.18, 36.84, 39.99, 56.21, 206.76; HRMS (ESI) calculated for $C_{13}H_{20}O$ $[M]^+$ 192.15142, found 192.15038.



73 *56%* **53**

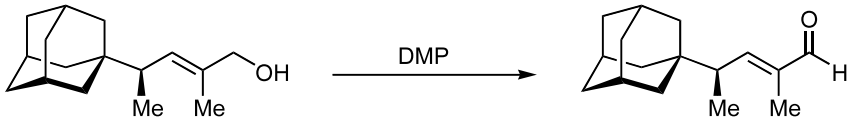
Ester 53. (Carbethoxyethylidene)triphenylphosphorane (0.2000 g, 0.5519 mmol) was added to a stirred solution of aldehyde **73** (0.0233 g, 0.121 mmol) in toluene (1.5 mL). The flask was equipped with a water condenser, and the mixture was stirred at reflux overnight. Ice-cold Et_2O was added, and the mixture was filtered. The filtrate was collected and concentrated *in vacuo*. Purification by flash chromatography (elution with 5% ethyl acetate in hexanes) afforded 0.0187 g (55.9% yield) of pure ester **53**. $[\alpha]^{24.9}_{D}$ = +23.47 (c = 0.85, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89 (d, 3H, *J* = 6.88 Hz), 1.30 (t, 3H, *J* = 7.12 Hz), 1.45 – 1.72 (m, 12H), 1.82 (d, 3H, *J* = 1.43 Hz), 1.95 (s, 3H), 2.13 (dd, 1H, *J* = 6.87, 10.99 Hz), 4.19 (qd, 2H, *J* = 1.04, 7.11, 7.08, 7.08 Hz), 6.73 (dd, 1H, *J* = 1.44, 10.99 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.81, 13.13, 14.47, 28.81, 35.70, 37.36, 39.84, 43.71, 60.52, 126.95, 145.44, 168.68; HRMS (ESI) calculated for $C_{18}H_{29}O_2$ $[M+H]^+$ 277.2168, found 277.2168.



53 *100%* **54**

Alcohol 54. A stirred solution of ester **53** (0.0152 g, 0.0550 mmol) in CH_2Cl_2 (0.55 mL) was cooled to -78°C and 0.165 mL of DIBAL solution (1 M in toluene, 0.165 mmol) was added drop wise. After stirring for 1 hour, the reaction was quenched with 0.10 mL of methanol, and stirred for 5 minutes. Then, 0.10 mL of brine solution was added, and the resulting mixture was warmed to room temperature. Sodium sulfate was added to the flask, and the solution was diluted with 3.0 mL of Et_2O. The resulting solution was stirred

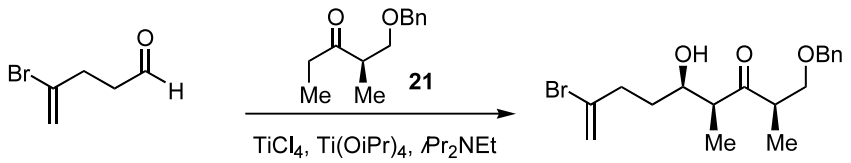
for 30 minutes, filtered, and washed with Et_2O. The solution was dried over $MgSO_4$ and concentrated *in vacuo* to afford 0.0128 g (quantitative yield) of alcohol **54**. $[\alpha]^{24.7}_D$ = +10.08 (c = 1.82, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (d, 3H, *J* = 6.78 Hz), 1.29 (s, 1H), 1.43 – 1.54 (m, 6H), 1.55 – 1.71 (m, 9H), 1.94 (s, 3H), 2.01 (dq, 1H, *J* = 10.4, 6.9 Hz), 4.02 (s, 2H), 5.33 (dd, 1H, *J* = 1.25, 10.44 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.02, 14.19, 28.88, 35.41, 37.49, 39.78, 42.35, 69.60, 129.56, 133.84; HRMS (ESI) calculated for $C_{16}H_{26}O$ $[M]^+$ 234.19837, found 234.19706.



54 *67%* **55**

Aldehyde 55. A stirred solution of alcohol **55** (0.0170 g, 0.0730 mmol) in CH_2Cl_2 (0.50 mL) was cooled to 0°C, and 0.0462 g of Dess-Martin periodinane (0.109 mmol) was added. After stirring for 5 hours, the reaction was quenched with the addition of saturated aqueous $NaHCO_3$ solution and washed with saturated aqueous Na_2S_2O3 solution. The organic layer was separated, and the aqueous layer was extracted three times with Et_2O. The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with 10% ethyl acetate in hexanes) afforded 0.0114 g (67.2% yield) of aldehyde **55**. $[\alpha]^{25.6}_D$ = +6.17 (c = 0.34, acetone); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (d, 1H, *J* = 6.9 Hz), 1.45 - 1.73 (m, 1H), 1.74 (d, 3H, *J* = 1.3 Hz), 1.98 (s, 3H), 2.34 (dq, 1H, *J* = 10.9, 6.9 Hz), 6.46 (dd, 1H, *J* = 10.8, 1.3 Hz), 9.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.73, 13.03, 28.75, 35.84,

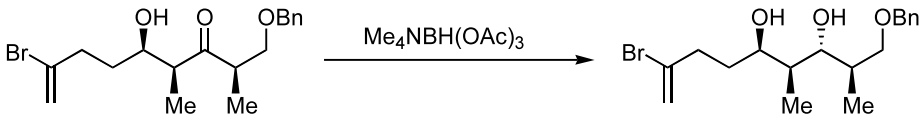
37.28, 39.87, 44.01, 138.56, 158.40, 195.79; HRMS (ESI) calculated for $C_{16}H_{24}ONa$ $[M+Na]^+$ 255.1725, found 255.1725



57 *100%* **74**

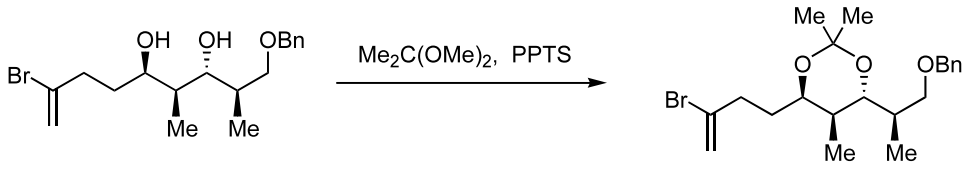
Ketone 74. $Ti(OiPr)_4$ (distilled prior to use, 0.415 mL, 1.408 mmol) was added to a stirred solution of $TiCl_4$ (distilled prior to use, 0.46 mL, 4.224 mmol) in dichloromethane (4 mL) at 0 °C. The resulting solution was stirred for 10 min, warmed to room temperature, diluted with dichloromethane (4 mL), and transferred into a stirred solution of (2*R*)-1-(benzyloxy)-2-methylpentan-3-one **21** (1.06 g, 5.12 mmol) in dichloromethane (8 mL) at -78 °C. Hunig's base (0.99 mL, 5.7 mmol) was then added dropwise, and the resulting solution was stirred for 30 min at -78 °C. A solution of aldehyde **57**[8] (1 mL, 6.14 mmol) in dichloromethane (3 mL) was added dropwise, and stirring was continued for 1 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl and warmed to room temperature. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was heated to 30 °C under vacuum (0.5 torr) for 1 hr to afford 1.89 g (quantitative yield) of ketone **74**. $[\alpha]^{23.0}_D$ = -0.3 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) d 0.76 (d, 3H, *J* = 6.5 Hz), 1.00 (d, 3H, *J* = 7.5 Hz), 1.50-1.58 (m, 1H), 1.61-1.70 (m, 1H), 2.36-2.42 (m, 2H), 2.54-2.61 (m, 1H), 2.76-2.81 (m, 1H), 2.86 (dd, 1H, *J* = 4.5, 1.5 Hz), 3.05 (dd, 1H, *J* = 8.5, 5.0 Hz), 3.45 (t, 1H, *J*

= 9.0 Hz), 3.97-4.01 (m, 1H), 4.07 (d, 1H, *J* = 12.0 Hz), 4.12 (d, 1H, *J* = 12.0 Hz) 5.29 (s, 2H), 7.07-7.20 (m, 5H); ^{13}C NMR (125 MHz, C_6D_6) d 9.2, 13.5, 32.6, 38.5, 44.7, 51.6, 69.2, 73.5, 117.0, 127.9, 128.3, 128.7, 134.9, 138.0, 216.5; HRMS (ESI) calculated for $C_{18}H_{25}O_3NaBr$ $[M+Na]^+$ 391.0885, found 391.0879.



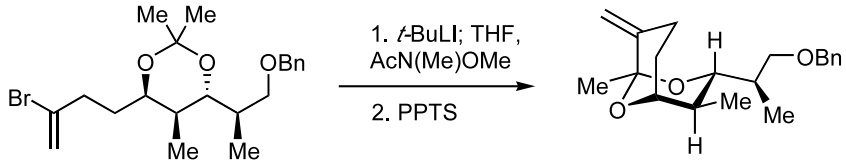
74 *73%* **75**

Diol 75. A solution of $Me_4NBH(OAc)_3$ (2.922 g, 11.12 mmol) in a mixture of MeCN (10 mL) and AcOH (10 mL) was stirred 30 min at room temperature, cooled to -40 °C, and treated with a solution of ketone **74** (0.821 g, 2.224 mmol) in MeCN (7 mL). The resulting solution was stirred 22 hrs at -25 °C, warmed up to room temperature, and stirred additional 1 hr. The reaction mixture was quenched with saturated aqueous potassium sodium tartrate and extracted twice with diethyl ether. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, brine, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.603 g (73% yield) of diol **75**. $[\alpha]^{24.0}_D$ = +6.1 (*c* = 1.4, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.84 (d, 3H, *J* = 7.0 Hz), 1.02 (d, 3H, *J* = 7.0 Hz), 1.56-1.80 (m, 3H), 2.09-2.17 (m, 1H), 2.45-2.53 (m, 1H), 2.59-2.65 (m, 1H), 3.46 (t, 1H, *J* = 9.0 Hz), 3.57 (m, 1H), 3.67 (dd, 1H, *J* = 9.0, 4.0 Hz), 3.90 (s, 1H), 3.95 (m, 1H), 4.43 (d, 1H, *J* = 2.0 Hz), 4.52 (s, 2H), 5.40 (s, 1H), 5.62 (s, 1H), 7.29-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) d 11.4, 13.7, 32.8, 35.5, 38.1, 38.3, 69.9, 73.6, 75.9, 82.4, 116.7, 127.7, 127.9, 128.5, 134.5, 137.1; HRMS (ESI) calculated for $C_{18}H_{27}O_3NaBr$ $[M+Na]^+$ 393.1041, found 393.1032.



75 *95%* **58**

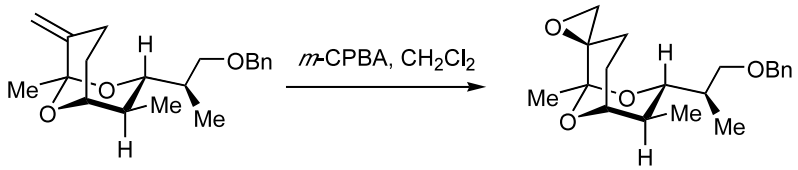
Acetonide 58. A solution of diol **75** (0.05 g, 0.1347 mmol) and 2,2-dimethoxypropane (0.08 mL, 0.674 mmol) in dichloromethane (1 mL) was treated with PPTS (several crystals). The reaction mixture was stirred 3 hrs at room temperature and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 0.052 g (95% yield) of acetonide **58**. $[\alpha]^{24.0}_{D}$ = -6.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.87 (d, 3H, *J* = 6.5 Hz), 1.03 (d, 3H, *J* = 7.0 Hz), 1.28 (s, 3H), 1.31 (s, 3H), 1.60-1.66 (m, 2H), 1.85 (m, 1H), 1.96 (m, 1H), 2.41 (m, 1H), 2.55 (m, 1H), 3.25 (dd, 1H, *J* = 7.0, 5.5 Hz), 3.35 (dd, 1H, *J* = 9.0, 7.0 Hz), 3.58 (dd, 1H, *J* = 9.0, 5.0 Hz), 3.74 (m, 1H), 4.47 (d, 1H, *J* = 12.0 Hz), 4.51 (d, 1H, *J* = 12.0 Hz), 5.42 (s, 1H), 5.60 (s, 1H), 7.25-7.39 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.6, 14.4, 23.5, 25.6, 29.1, 36.9, 37.7, 38.0, 68.0, 72.2, 73.1, 76.5, 100.4, 116.9, 127.4, 127.6, 128.3, 134.4, 138.8; ; HRMS (ESI) calculated for $C_{21}H_{31}O_3NaBr$ $[M+Na]^+$ 433.1354, found 433.1356.



58 *56%, 2 steps* **59**

Alkene 59. A solution of acetonide **58** (0.023 g, 0.056 mmol) in THF (1 mL) was treated dropwise with a solution of *tert*-BuLi (0.065 mL, 0.112 mmol, 1.7 M in pentane) at -78

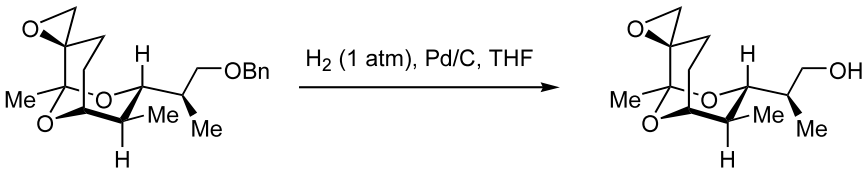
°C. The reaction mixture was stirred 5 min and treated with *N*-methoxy-*N*-methylacetamide (0.012 mL, 0.112 mmol). The resulting solution was stirred 10 min, quenched with aqueous HCl (1 N solution) and warmed up to room temperature. The resulting solution was extracted with Et_2O, and the organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting ketone was dissolved in MeOH (1 mL) and treated with PPTS (several crystals). The reaction mixture was stirred overnight and evaporated. Purification by preparative TLC on silica gel (development with Hexanes:AcOEt 4:1) afforded 0.01 g (56% yield over two steps) of alkene **59**. $[\alpha]^{24.0}_{D}$ = +10.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.71 (d, 3H, *J* = 7.0 Hz), 1.02 (d, 3H, *J* = 7.0 Hz), 1.38 (s, 3H), 1.54 (m, 1H), 1.93-2.05 (m, 2H), 2.15-2.24 (m, 2H), 2.26-2.34 (m, 1H), 3.30 (dd, 1H, *J* = 9.0, 7.5 Hz), 3.56 (dd, 1H, *J* = 11.0, 2.0 Hz), 3.73 (dd, 1H, *J* = 9.0, 5.5 Hz), 4.06 (m, 1H), 4.48 (d, 1H, *J* = 11.5 Hz), 4.52 (d, 1H, *J* = 11.5 Hz), 4.93 (s, 1H), 5.01 (s, 1H), 7.26-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.0, 15.6, 21.4, 27.3, 28.0, 34.1, 34.9, 70.7, 71.5, 73.1, 74.6, 98.6, 110.0, 127.3, 127.4, 128.3, 138.9, 150.6; HRMS (ESI) calculated for $C_{20}H_{28}O_3Na$ $[M+Na]^+$ 339.1936, found 339.1938.



59 *53%* **60**

Epoxide 60. A solution of alkene **59** (0.127 g, 0.4 mmol) in dichloromethane (2 mL) was treated with *m*-CPBA (0.184 g, 0.8 mmol, 75% purity). The reaction mixture was stirred

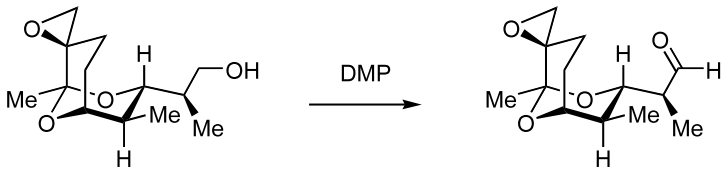
overnight and diluted with Et_2O. The resulting suspension was washed with aqueous NaOH (1 N solution), saturated aqueous Na_2SO_3, and brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 9:1) afforded 0.07 g (53% yield) of epoxide **60**. $[\alpha]^{23.0}_D$ = +52.5 (*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.80 (d, 3H, *J* = 7.0 Hz), 1.03 (d, 3H, *J* = 7.0 Hz), 1.18 (s, 3H), 1.67-1.89 (m, 3H), 2.04-2.14 (m, 2H), 2.30 (m, 1H), 2.64 (d, 1H, *J* = 5.5 Hz), 2.78 (d, 1H, *J* = 5.0 Hz), 3.27 (dd, 1H, *J* = 9.0, 7.5 Hz), 3.70 (dd, 1H, *J* = 9.0, 5.5 Hz), 3.78 (d, 1H, *J* = 11.0 Hz), 4.02 (m, 1H), 4.47 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, *J* = 12.0 Hz), 7.25-7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.8, 15.9, 20.7, 22.7, 27.1, 34.2, 35.0, 51.6, 58.9, 70.5, 71.3, 73.1, 76.4, 98.2, 127.42, 127.43, 128.3, 138.7; HRMS (ESI) calculated for $C_{20}H_{28}O_4Na$ $[M+Na]^+$ 355.1885, found 355.1882.



60 *93%* **76**

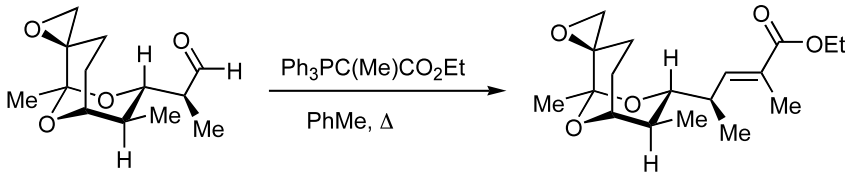
Alcohol 76. A mixture of epoxide **60** (0.06 g, 0.18 mmol) and palladium on carbon (0.05 g, 10% w/w) in THF (1.8 mL) was vigorously stirred under hydrogen atmosphere overnight. The resulting suspension was filtered through Celite and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 1:1) afforded 0.04 g (93% yield) of alcohol **74**. $[a]^{24.3}_D$ = + 67.9 (*c* = 2.0, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.77 (d, 3H, *J* = 7.0 Hz), 1.09 (d, 3H, *J* = 7.0 Hz), 1.18 (s, 3H),

1.63-1.68 (m, 1H), 1.72-1.87 (m, 3H), 2.10 (m, 1H), 2.31 (m, 1H), 2.64 (d, 1H, *J* = 5.0 Hz), 2.76 (d, 1H, *J* = 5.0 Hz), 3.50 (dd, 1H, *J* = 11.5, 4.5 Hz), 3.85-3.90 (m, 2H), 4.06 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.5, 15.2, 20.5, 22.8, 26.7, 34.6, 35.0, 51.4, 58.5, 63.3, 70.2, 78.6, 98.5; HRMS (ESI) calculated for $C_{13}H_{22}O_4Na$ $[M+Na]^+$ 265.1416, found 265.1418.



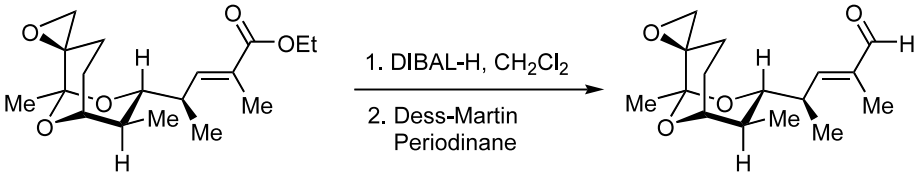
76 *46%* **61**

Aldehyde 61. A mixture of alcohol **76** (0.035 g, 0.157 mmol) and $NaHCO_3$ (0.2 g, 2.4 mmol) in dichloromethane (1.5 mL) was treated with Dess-Martin periodinane (0.1 g, 0.24 mmol) at room temperature. After 2 hrs, the reaction was quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$ and stirred for 15 min. Phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.016 g (46% yield) of aldehyde **61**. $[a]^{23.4}_D$ = + 88.5 (*c* = 1.5, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.82 (d, 3H, *J* = 7.0 Hz), 1.18 (s, 3H), 1.20 (d, 3H, *J* = 7.0 Hz), 1.75-1.85 (m, 1H), 2.15 (m, 1H), 2.23 (m, 1H), 2.45 (m, 1H), 2.64 (d, 1H, *J* = 5.0 Hz), 2.80 (d, 1H, *J* = 5.0 Hz), 4.06 (m, 2H), 9.77 (d, 1H, *J* = 2.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) d 11.4, 12.7, 20.8, 22.4, 27.4, 34.6, 47.9, 51.2, 58.1, 70.2, 76.3, 98.4, 204.3; HRMS (ESI) calculated for $C_{13}H_{20}O_4Na$ $[M+Na]^+$ 263.1259, found 263.1255.



61 *84%* **77**

Ester 77. A solution of aldehyde **61** (0.015 g, 0.0625 mmol) and (carbethoxyethylidene)triphenylphosphorane (0.113 g, 0.313 mmol) in toluene (0.6 mL) was heated at 110 °C for 2 hrs. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.017 g (84% yield) of ester **77**. $[a]^{24.1}_{D}$ = + 41.2 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.74 (d, 3H, *J* = 7.0 Hz), 1.05 (d, 3H, *J* = 7.0 Hz), 1.20 (s, 3H), 1.28 (m, 3H), 1.71-1.97 (m, 7H), 2.09 (m, 1H), 2.63 (d, 1H, *J* = 5.0 Hz), 2.71 (m, 1H), 2.80 (d, 1H, *J* = 5.0 Hz), 3.80 (d, 1H, *J* = 11.0 Hz), 3.98 (m, 1H), 4.19 (m, 2H), 6.85 (d, 1H, *J* = 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) d 12.5, 12.7, 14.2, 16.7, 20.9, 22.5, 27.4, 34.9, 35.0, 51.3, 58.5, 60.5, 70.3, 77.0, 98.1, 128.0, 141.9, 168.1; HRMS (ESI) calculated for $C_{18}H_{28}O_5Na$ $[M+Na]^+$ 347.1834, found 347.1835.



77 77% **62**

Aldehyde 62. A stirred solution of ester **77** (0.015 g, 0.046 mmol) in dichloromethane (0.5 mL) was treated with DIBAL-H (0.11 mL of 1 M solution in toluene, 0.11 mmol) at -78 °C. After 1 h, the reaction was quenched with MeOH (0.1 mL), then treated with brine (0.1 mL). The resulting mixture diluted with diethyl ether, dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The resulting crude alcohol was dissolved in

dichloromethane (0.5 mL) and treated with solid $NaHCO_3$ (0.077 g, 0.91 mmol). The resulting suspension was treated with Dess-Martin periodinane (0.039 g, 0.092 mmol), stirred for 30 min at room temperature, and quenched with saturated aqueous solution of $Na_2S_2O_3$ and saturated aqueous solution of $NaHCO_3$. After 15 min, the reaction mixture was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography on silica gel (elution with hexanes:ethyl acetate 4:1) afforded 0.01 g (77% yield over two steps) of aldehyde **62**. $[a]^{22.8}_D$ = + 39.8 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (500 MHz,) d 0.77 (d, 3H, *J* = 7.0 Hz), 1.12 (d, 3H, *J* = 7.0 Hz), 1.24 (s, 3H), 1.71-1.85 (m, 6H), 1.89 (m, 1H), 2.14 (m, 1H), 2.65 (d, 1H, *J* = 5.0 Hz), 2.82 (d, 1H, *J* = 5.0 Hz), 2.93 (m, 1H), 3.87 (dd, 1H, *J* = 11.0, 2.0 Hz), 4.00 (m, 1H), 6.66 (d, 1H, *J* = 10.0 Hz), 9.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) d 9.3, 12.6, 16.7, 21.0, 22.5, 27.2, 35.1, 35.2, 51.3, 58.4, 70.2, 77.0, 98.3, 139.4, 154.2, 195.4; HRMS (ESI) calculated for $C_{16}H_{24}O_4Na$ $[M+Na]^+$ 303.1572, found 303.1573.

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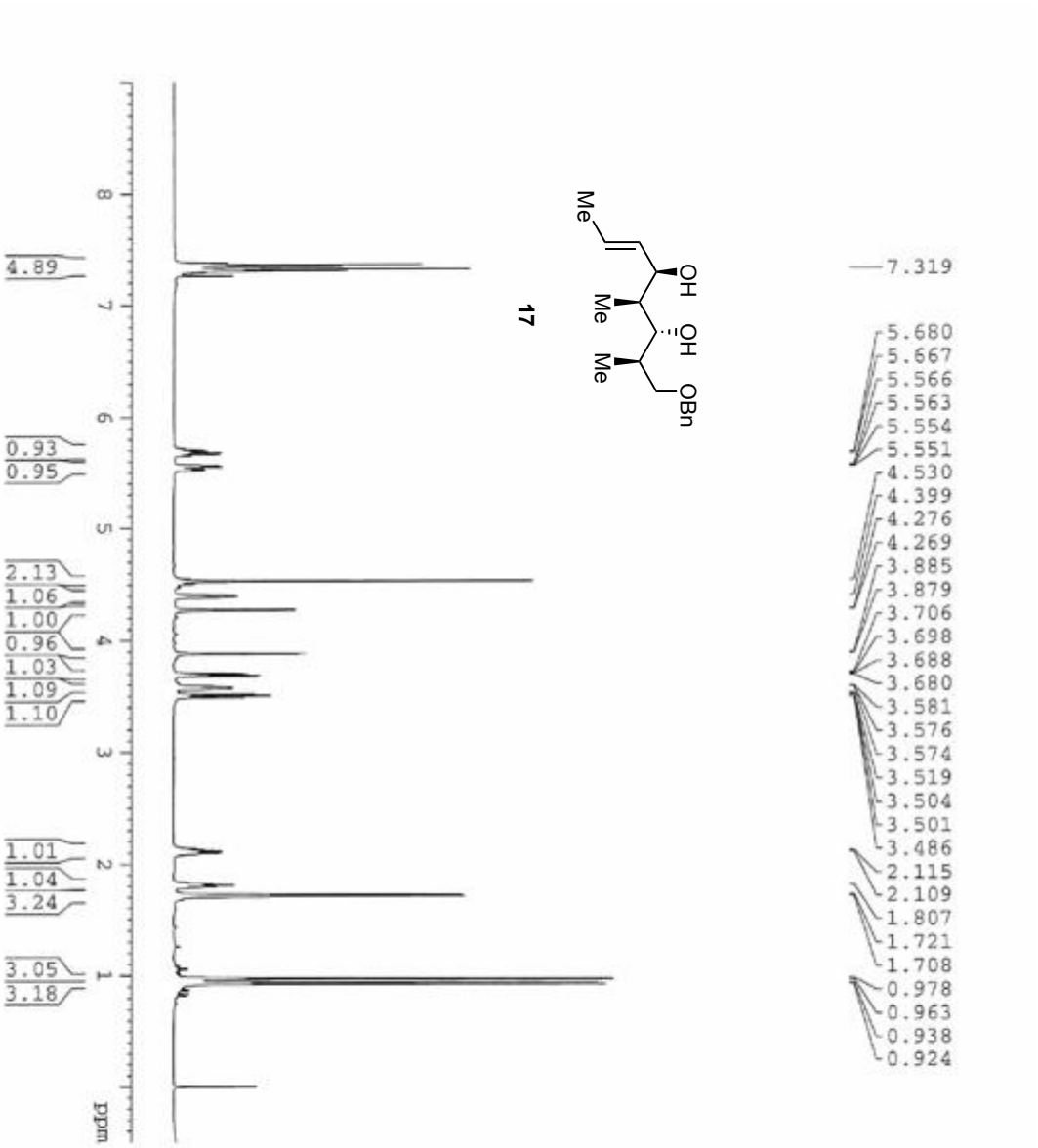
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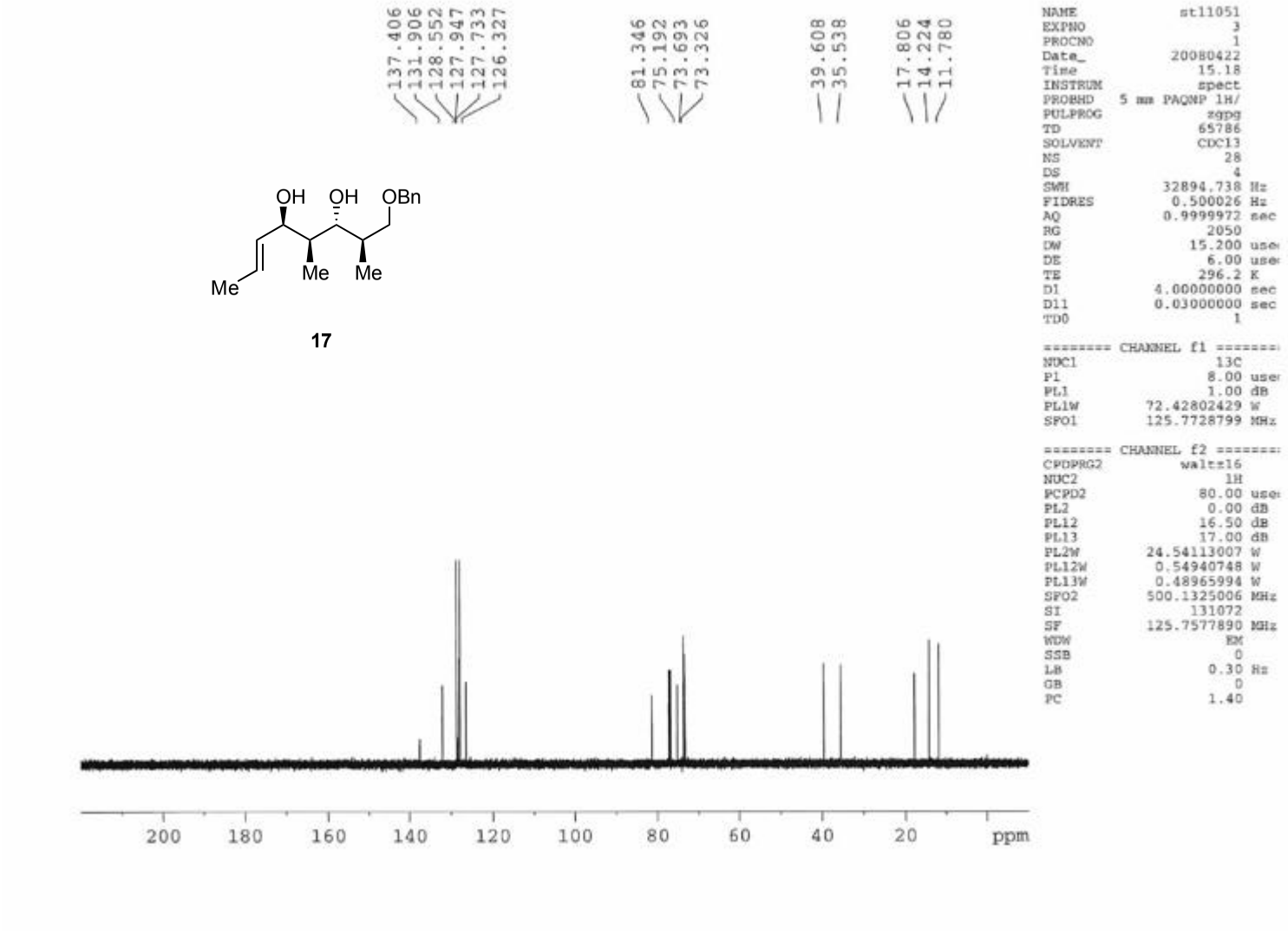
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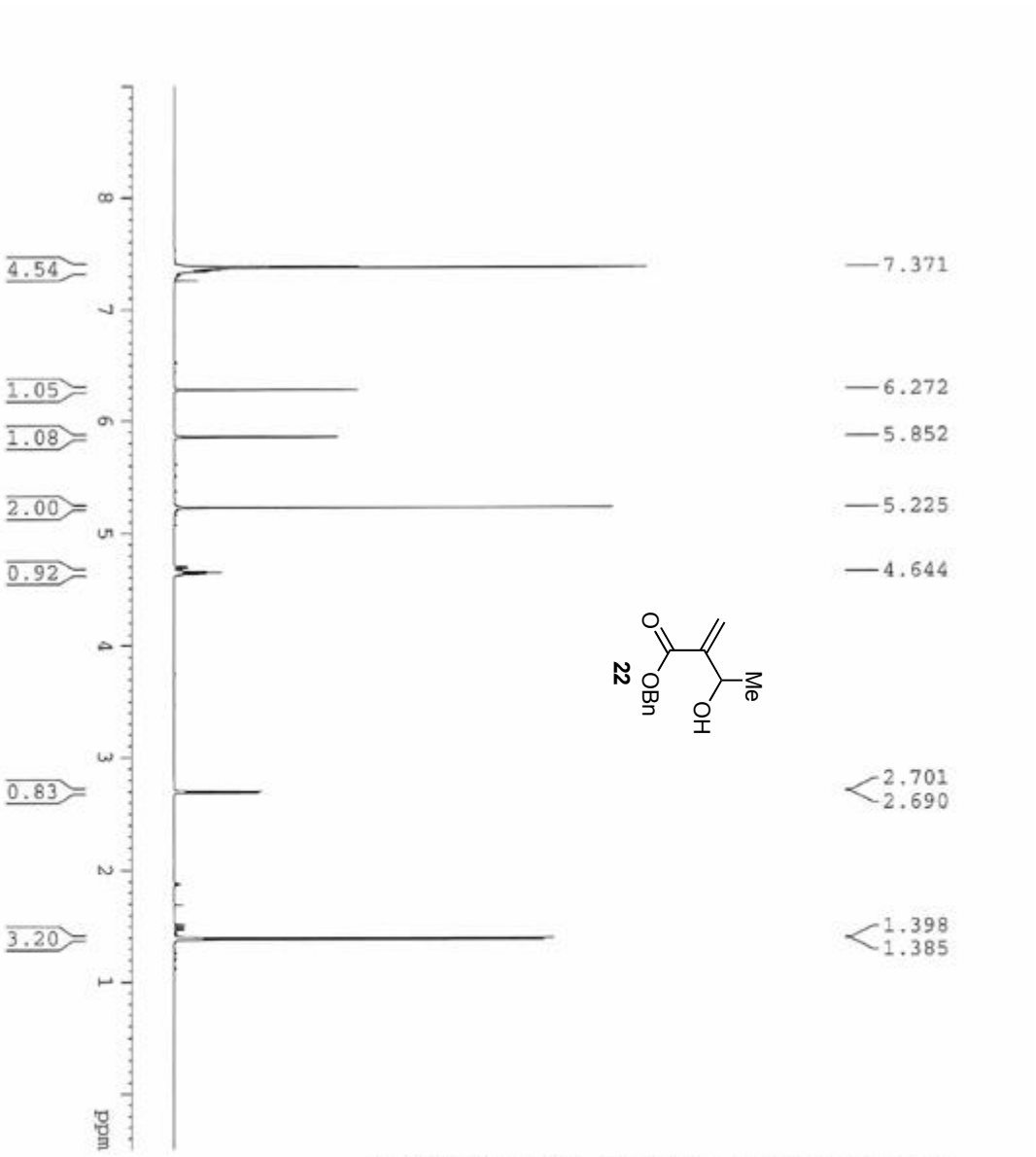
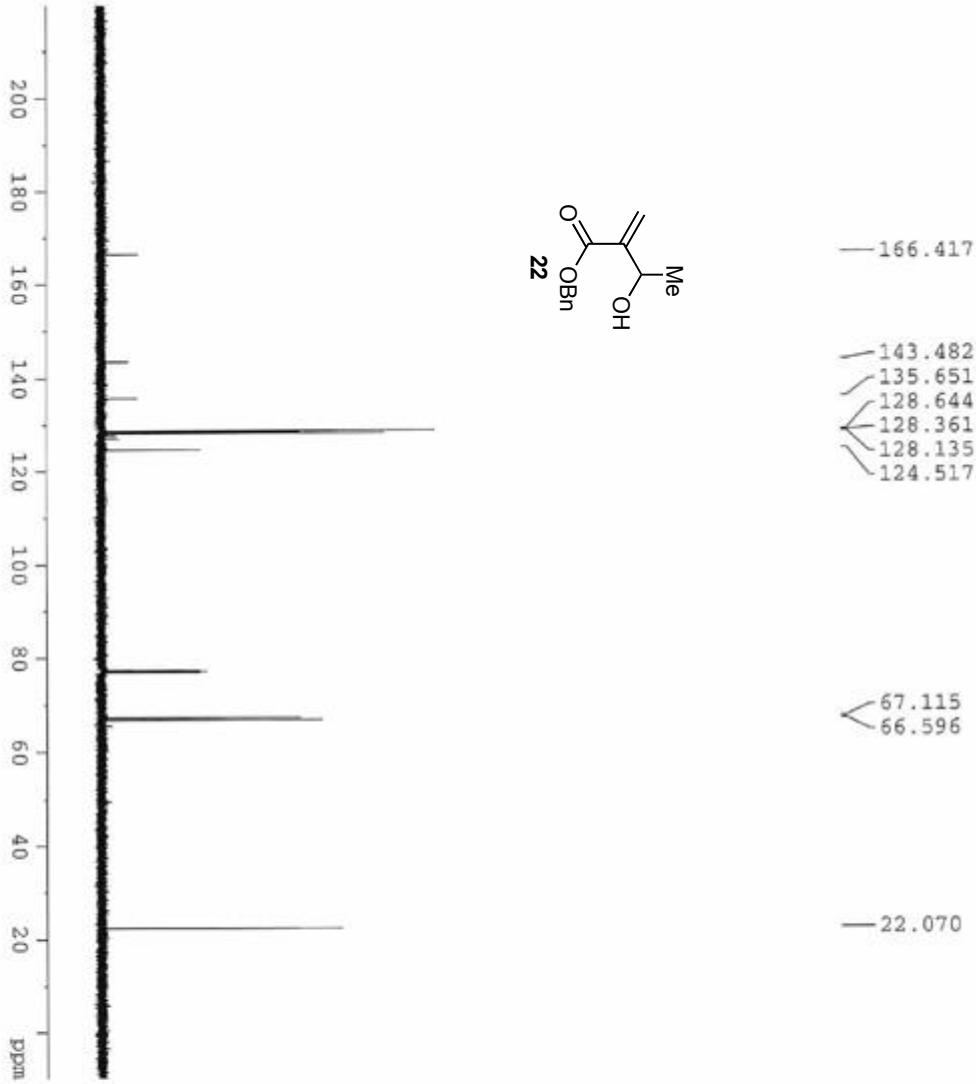
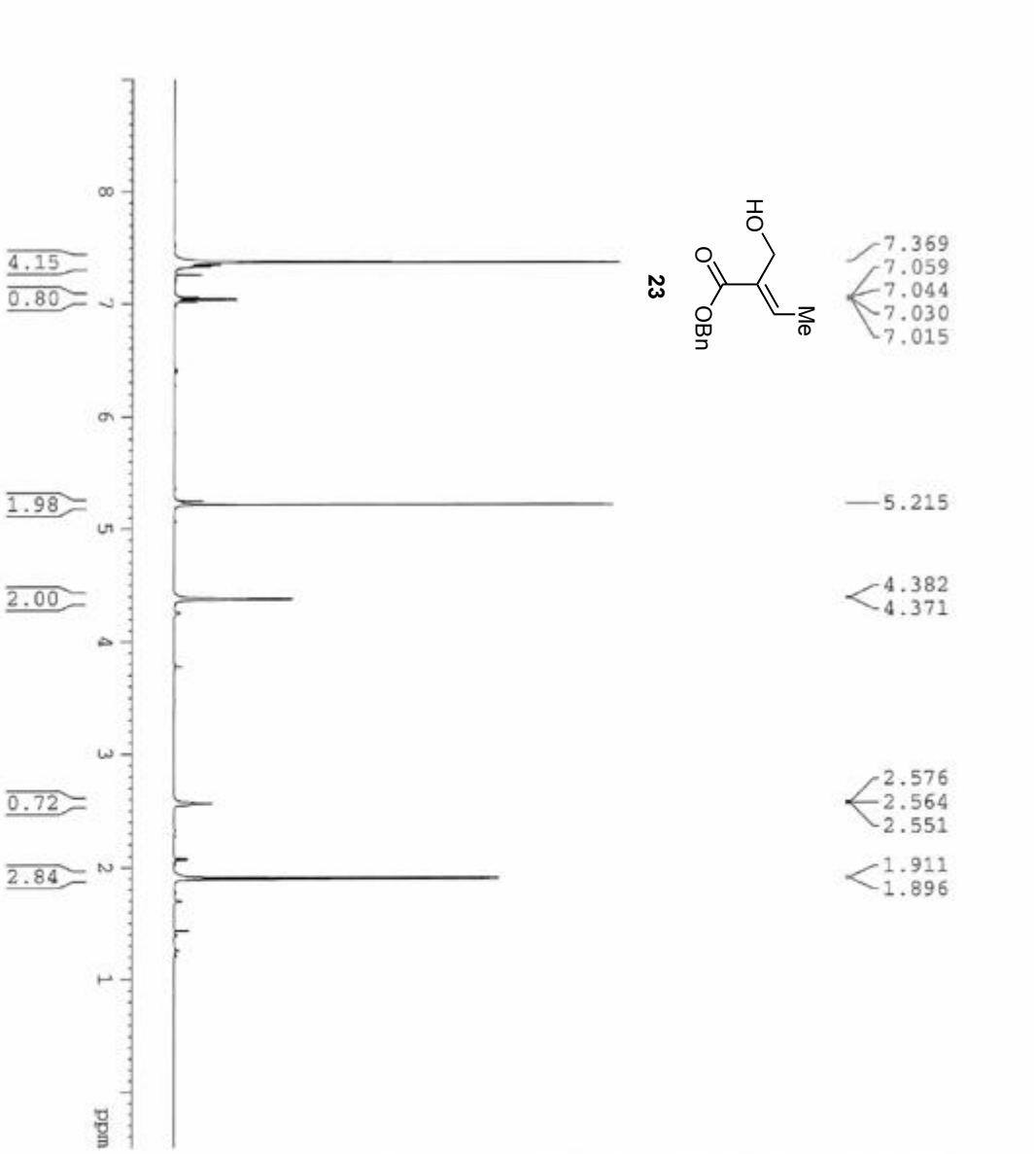
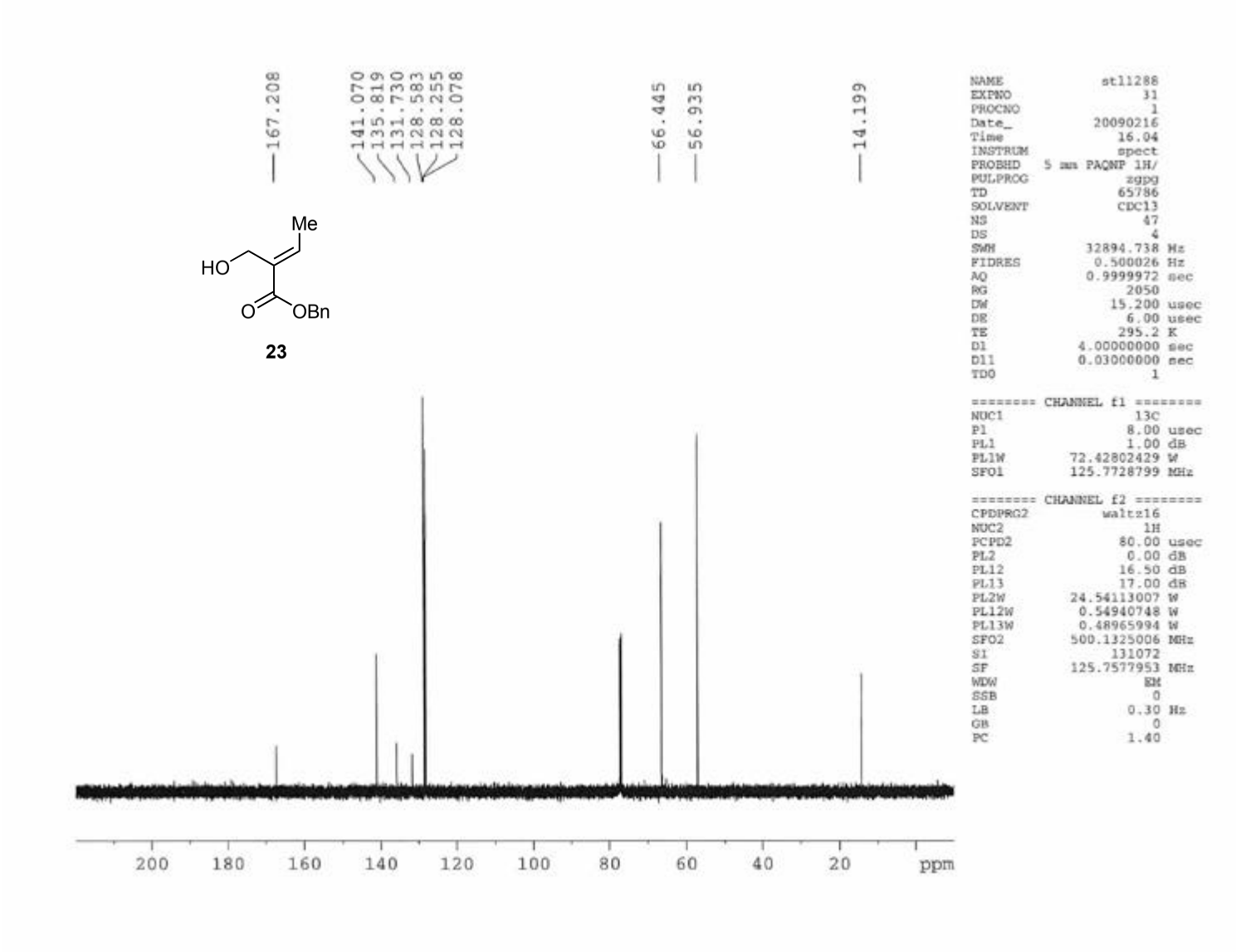
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm


7.371
6.272
5.852
5.225
4.644
2.701
2.690
1.398
1.385
4.54
1.05
1.08
2.00
0.92
0.83
3.20
ppm
OBn
Me
OH
22

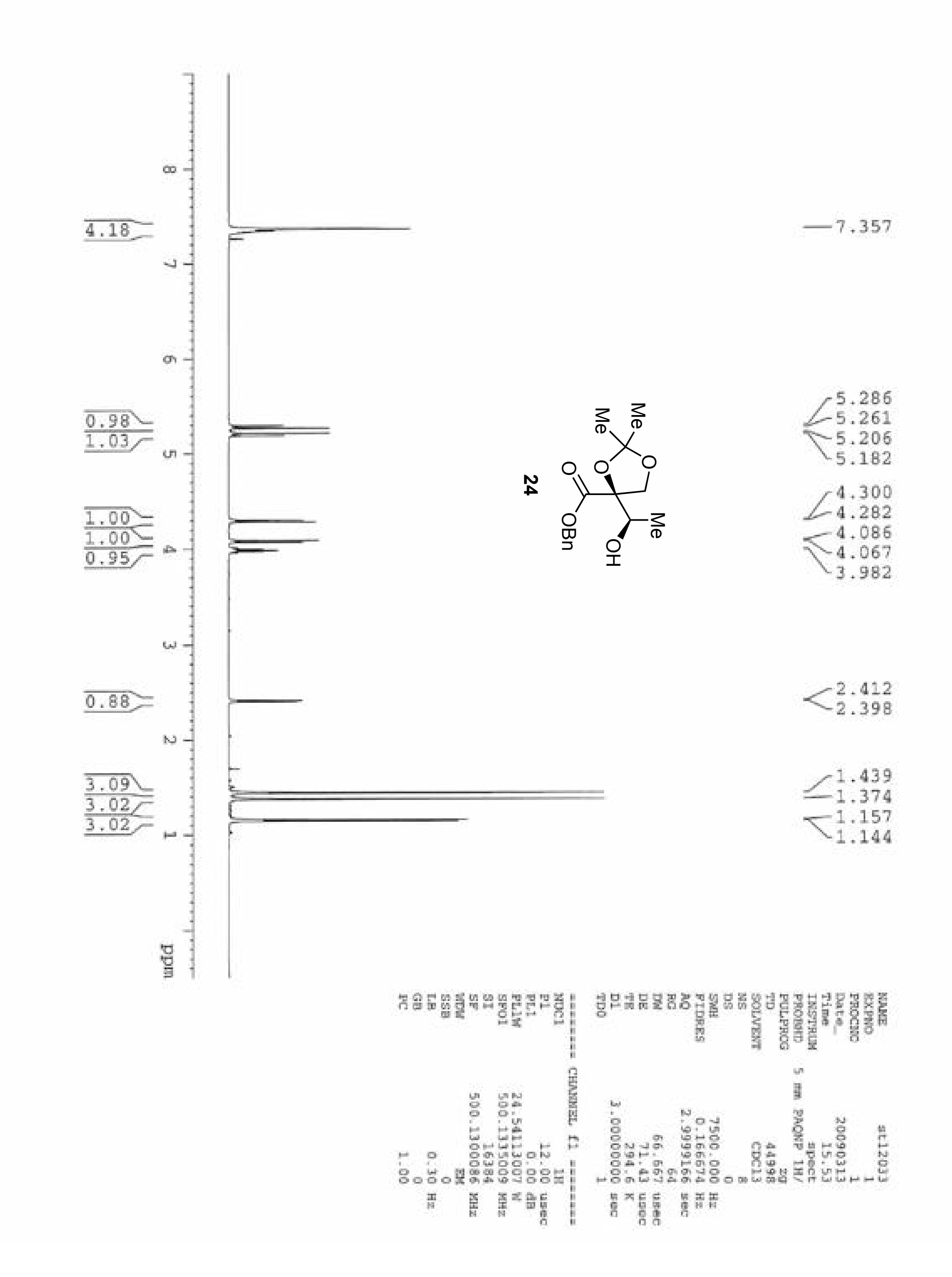


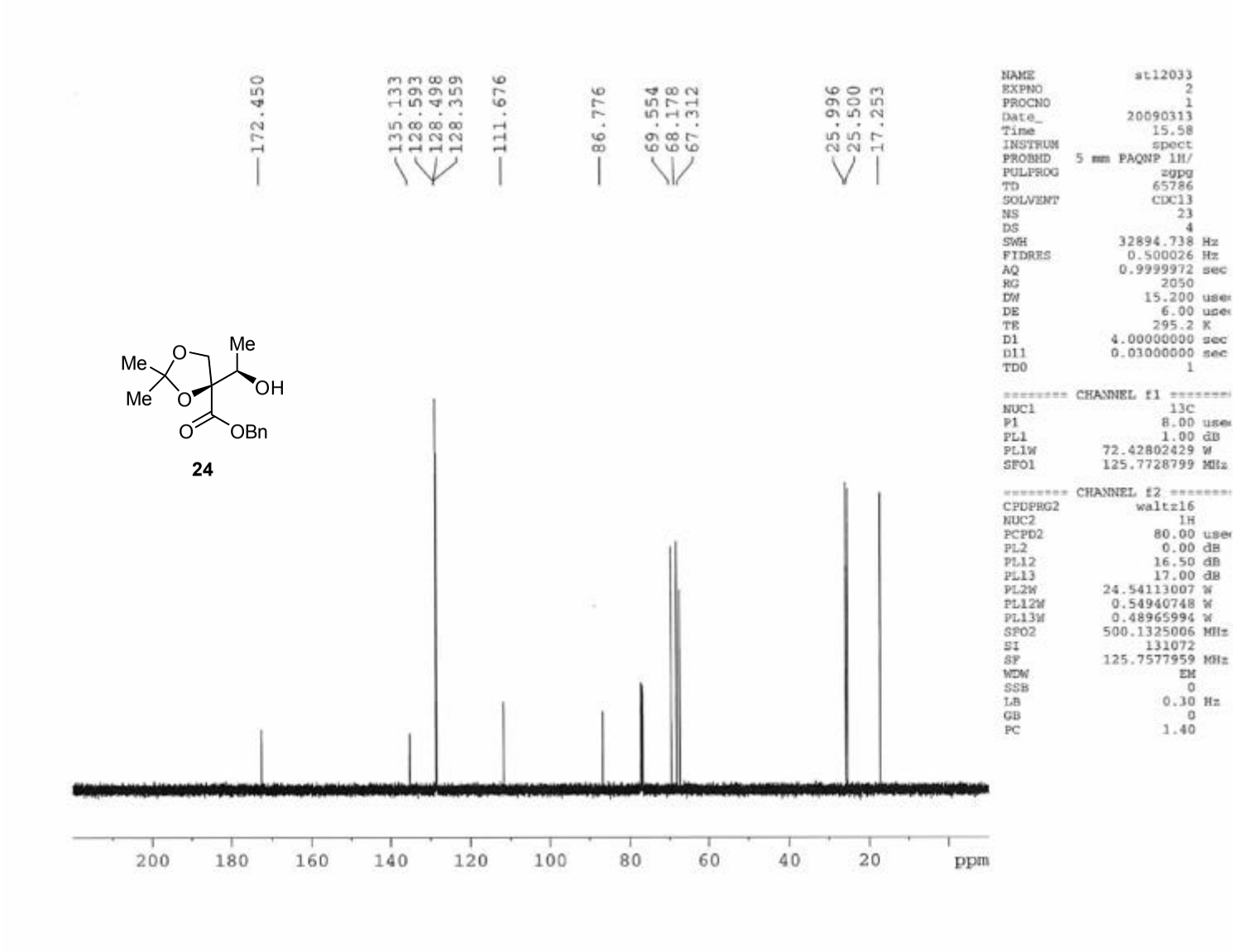

```
NAME                                    st12009
EXPNO                                        21
PROCNO                                        1
Date_                               20090224
Time                                    11.01
INSTRUM                                   spect
PROBHD                  5 mm PAQNP 1H/
PULPROG                                   zgpg
TD                                       65786
SOLVENT                                  CDCl3
NS                                          31
DS                                           4
SWH                                  32894.738 Hz
FIDRES                                0.500026 Hz
AQ                                    0.9999972 sec
RG                                         2050
DW                                       15.200 usec
DE                                        6.00 usec
TE                                       295.1 K
D1                                    4.00000000 sec
D11                                   0.03000000 sec
TD0                                           1

======== CHANNEL f1 ========
NUC1                                        13C
P1                                        8.00 usec
PL1                                       1.00 dB
PL1W                                 72.42802429 W
SFO1                                 125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                                   waltz16
NUC2                                         1H
PCPD2                                    80.00 usec
PL2                                       0.00 dB
PL12                                     16.50 dB
PL13                                     17.00 dB
PL2W                                 24.54113007 W
PL12W                                 0.54940748 W
PL13W                                 0.48965994 W
SFO2                                 500.1325006 MHz
SI                                         131072
SF                                   125.7577890 MHz
WDW                                          EM
SSB                                           0
LB                                         0.30 Hz
GB                                            0
PC                                         1.40
```

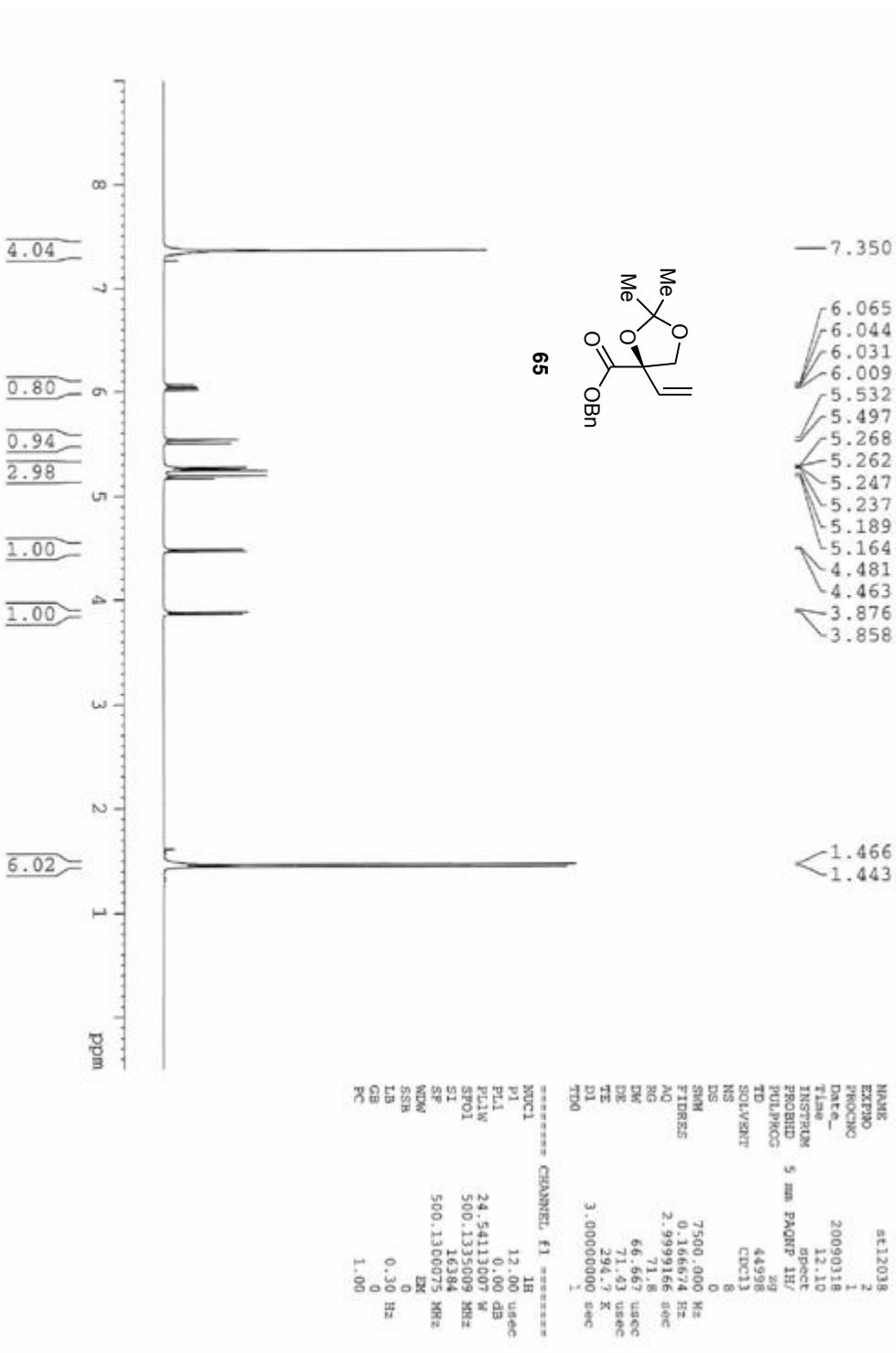

HO
O
OBn
Me
23
7.369
7.059
7.044
7.030
7.015
5.215
4.382
4.371
2.576
2.564
2.551
1.911
1.896
4.15
0.80
1.98
2.00
0.72
2.84
ppm

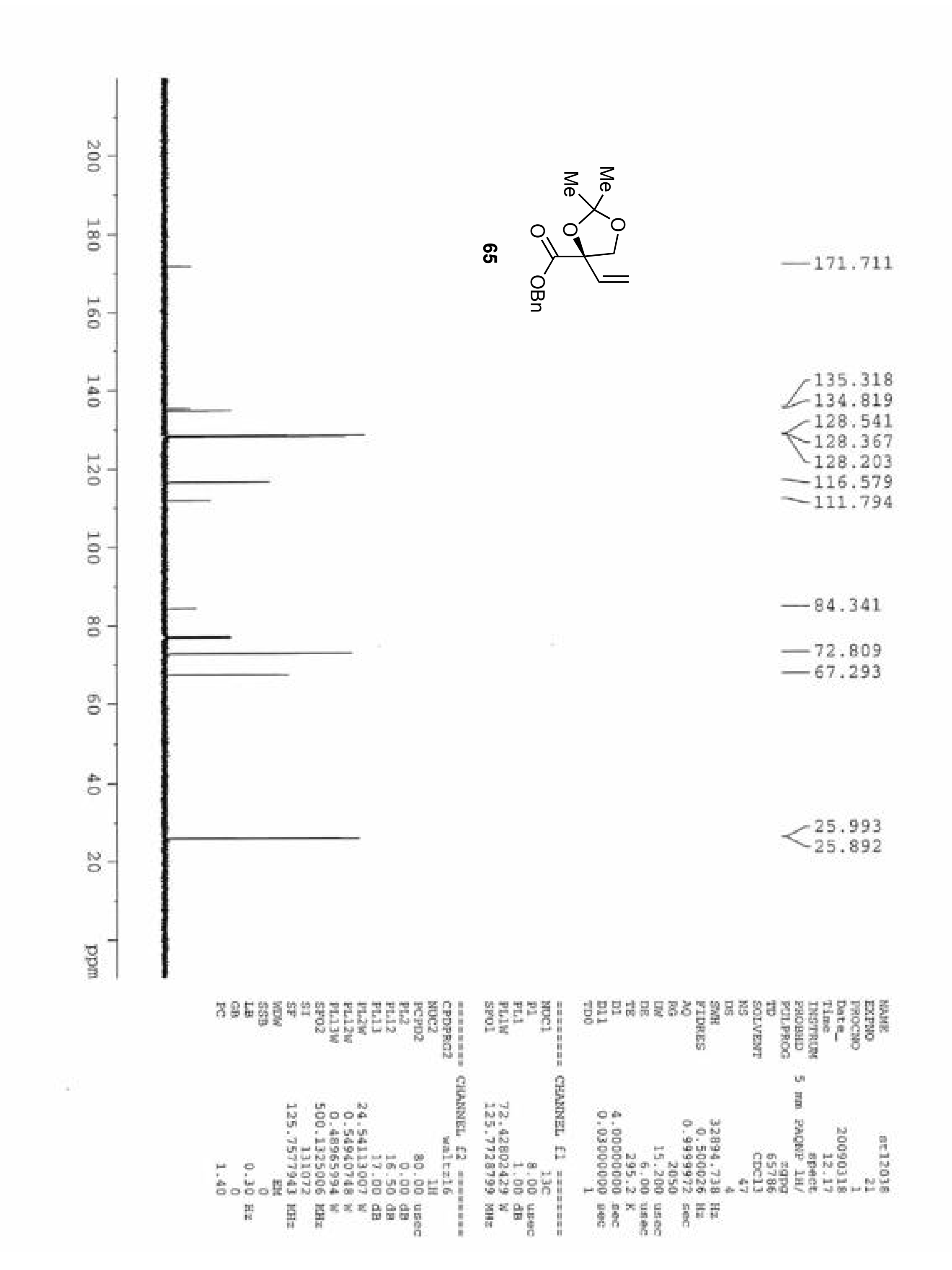


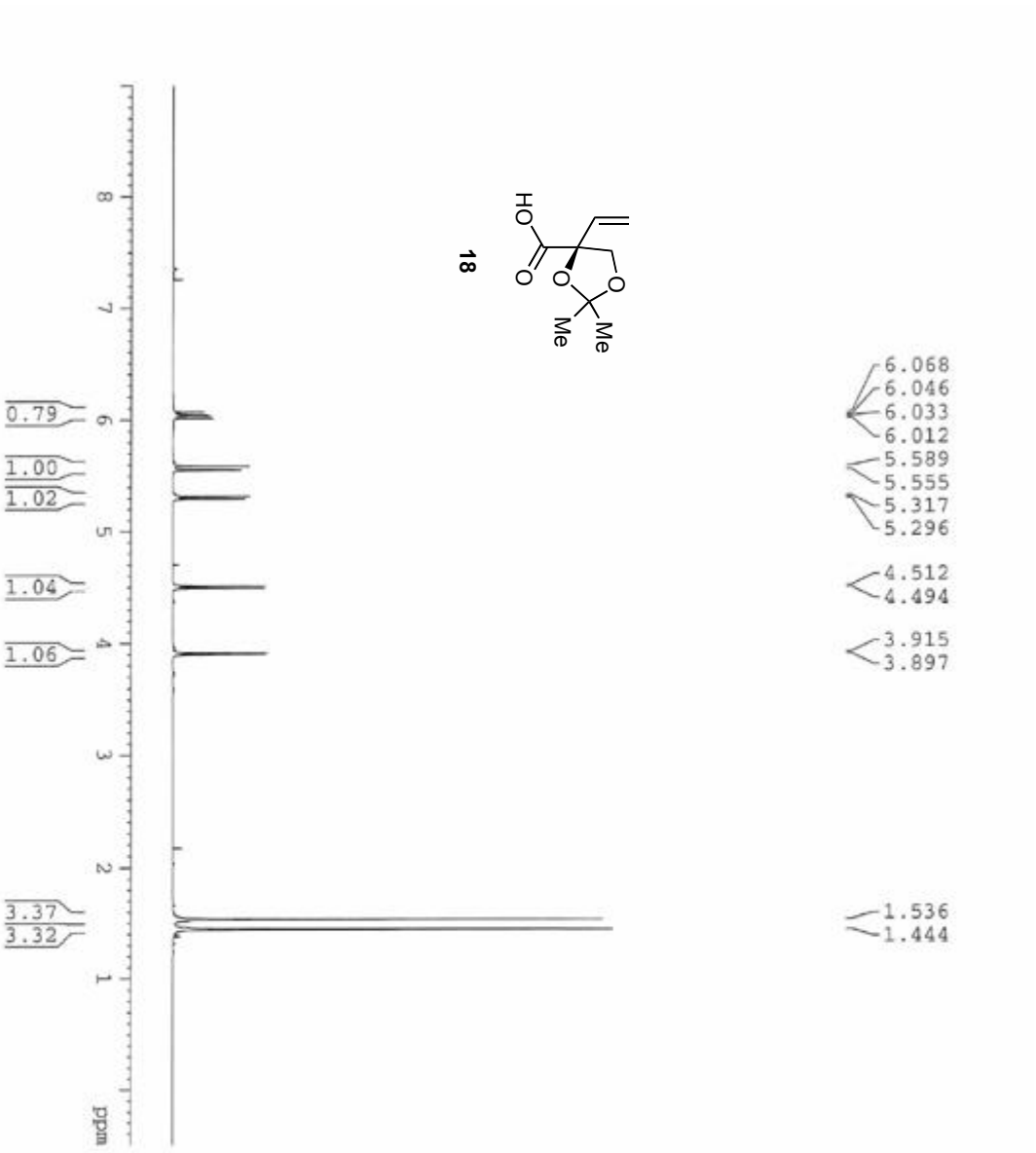
NAME	stl1288
EXPNO	31
PROCNO	1
Date_	20090216
Time	16.04
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg
TD	65786
SOLVENT	CDCl3
NS	47
DS	4
SWH	32894.738 Hz
FIDRES	0.500026 Hz
AQ	0.9999972 sec
RG	2050
DW	15.200 usec
DE	6.00 usec
TE	295.2 K
D1	4.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	1.00 dB
PL1W	72.42802429 W
SFO1	125.7728799 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	24.54113007 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325006 MHz
SI	131072
SF	125.7577953 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

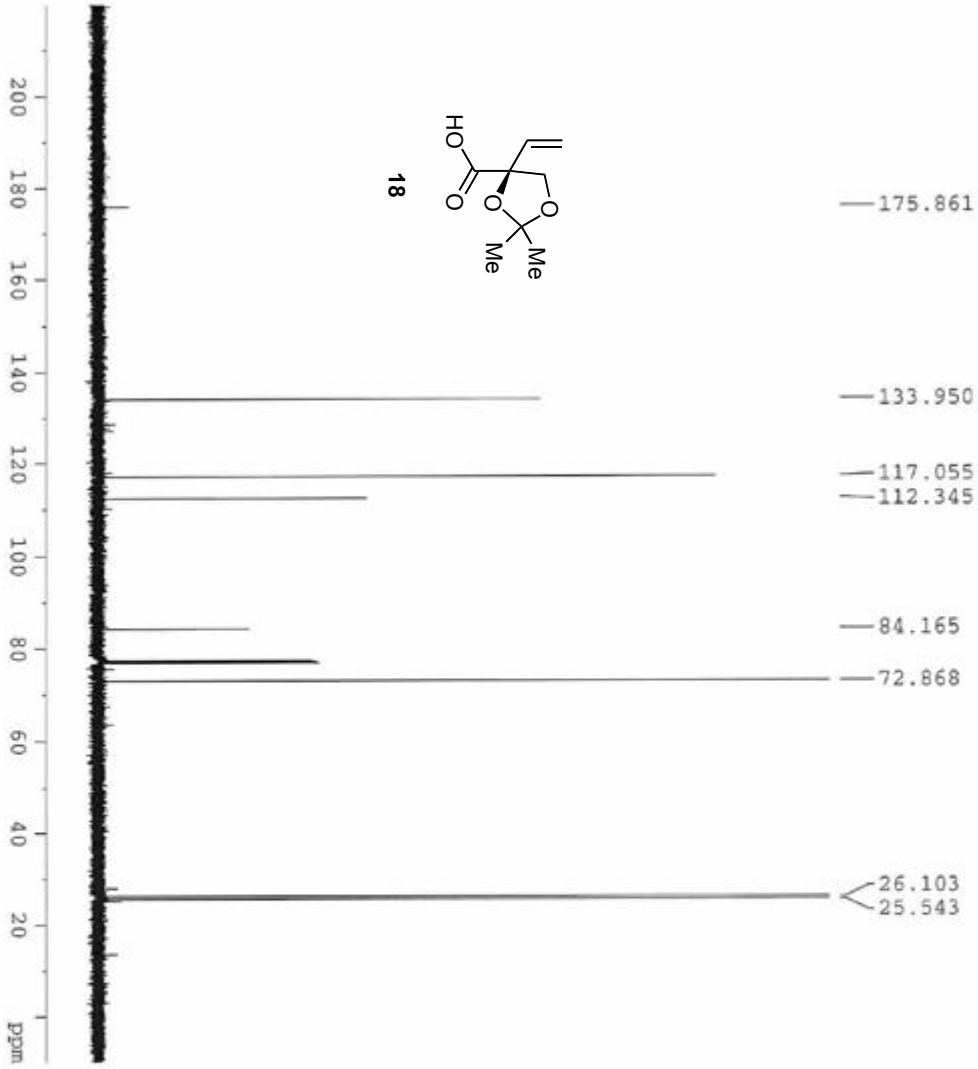

7.357
5.286
5.261
5.206
5.182
4.300
4.282
4.086
4.067
3.982
2.412
2.398
1.439
1.374
1.157
1.144
4.18
0.98
1.03
1.00
1.00
0.95
0.88
3.09
3.02
3.02
ppm
24
Me
Me
O
O
OH
Me
O
OBn


172.450
135.133
128.593
128.498
128.359
111.676
86.776
69.554
68.178
67.312
25.996
25.500
17.253
Me
Me
O
Me
O
OH
O
OBn
24
200
180
160
140
120
100
80
60
40
20
ppm
NAME st12033
EXPNO 2
PROCNO 1
Date_ 20090313
Time 15.58
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 23
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 use
DE 6.00 use
TE 295.2 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 use
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577959 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40


7.350
6.065
6.044
6.031
6.009
5.532
5.497
5.268
5.262
5.247
5.237
5.189
5.164
4.481
4.463
3.876
3.858
1.466
1.443
Me
Me
O
O
O
OBn
65
4.04
0.80
0.94
2.98
1.00
1.00
6.02
ppm
NAME st12038
EXPNO 2
PROCNO 1
Date_ 20090318
Time 12.10
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 71.8
DW 66.667 usec
DE 71.43 usec
TE 294.7 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

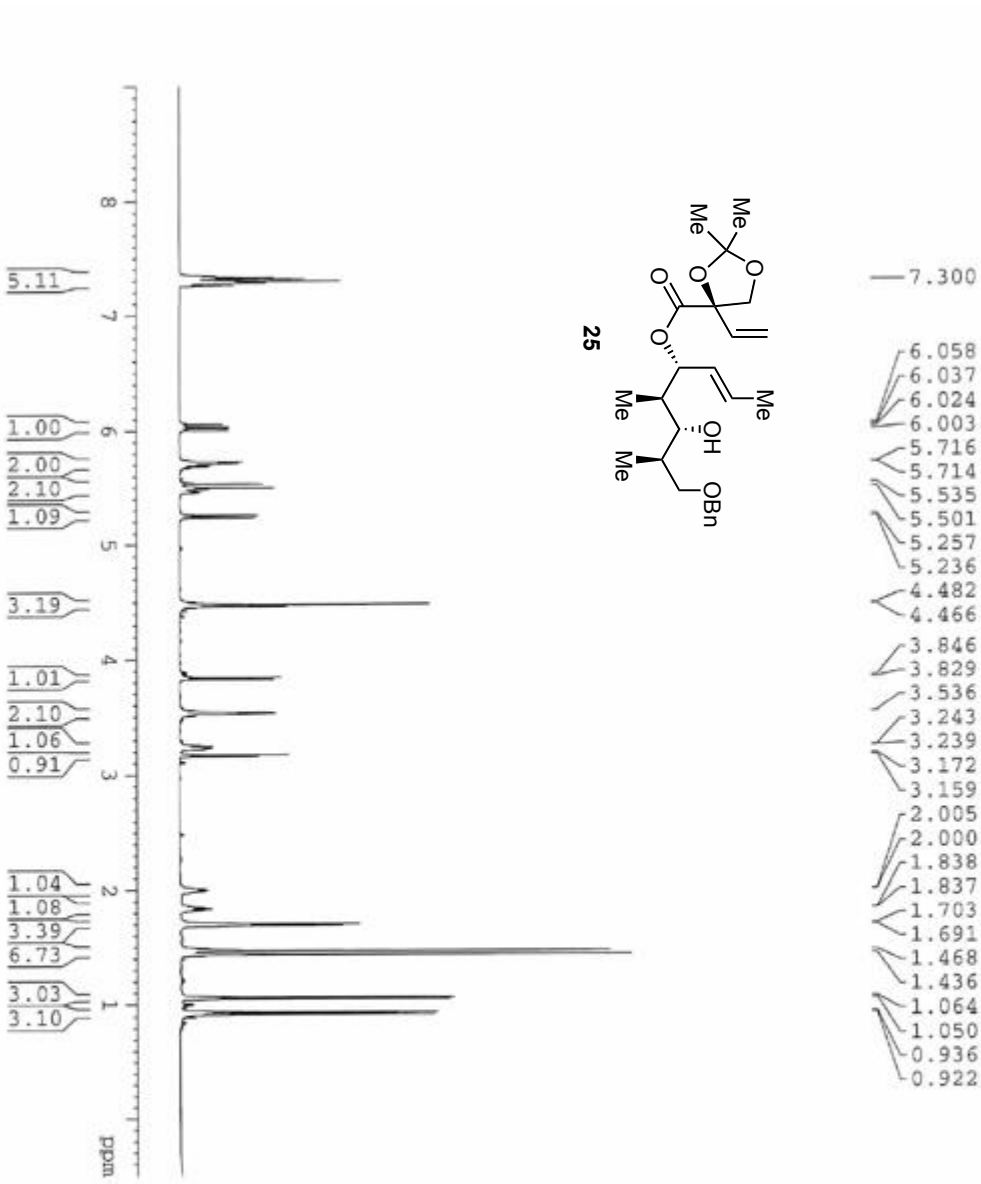

65
OBn
Me
Me
171.711
135.318
134.819
128.541
128.367
128.203
116.579
111.794
84.341
72.809
67.293
25.993
25.892
200
180
160
140
120
100
80
60
40
20
ppm


HO
O
O
O
Me
Me
18
6.068
6.046
6.033
6.012
5.589
5.555
5.317
5.296
4.512
4.494
3.915
3.897
1.536
1.444
0.79
1.00
1.02
1.04
1.06
3.37
3.32
ppm
NAME st12108
EXPNO 1
PROCNO 1
Date_ 20090520
Time 10.55
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 71.8
DW 66.667 usec
DE 71.43 usec
TE 295.0 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300090 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



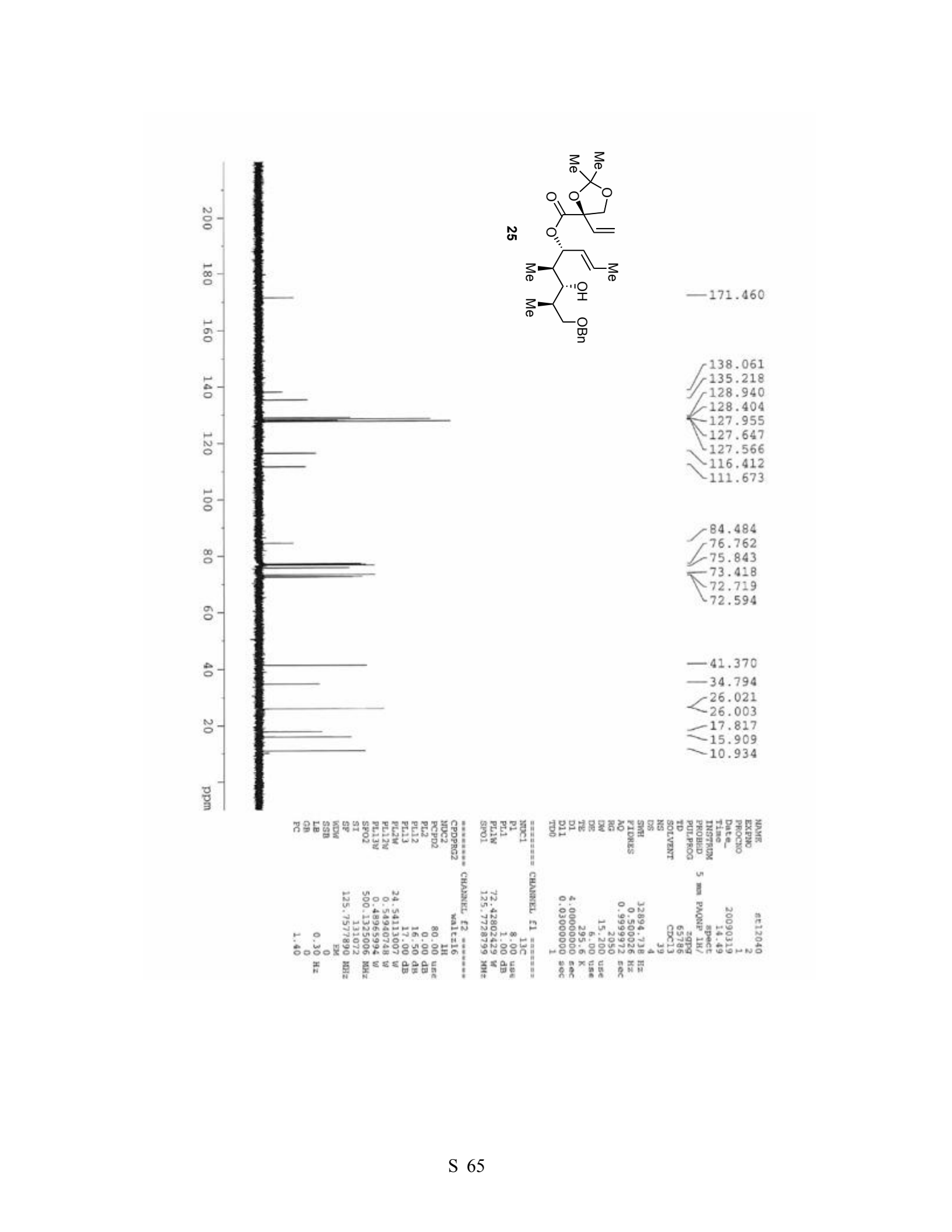
18

```
NAME                                    st12108
EXPNO                                         2
PROCNO                                        1
Date_                               20090520
Time                                      11.01
INSTRUM                                   spect
PROBHD                 5 mm PABBO BB/
PULPROG                                   zgpg
TD                                       65786
SOLVENT                                  CDCl3
NS                                          111
DS                                            4
SWH                                 32894.738 Hz
FIDRES                                  0.500026 Hz
AQ                                      0.9999972 sec
RG                                         2050
DW                                       15.200 usec
DE                                        6.00 usec
TE                                       295.6 K
D1                                      4.00000000 sec
D11                                     0.03000000 sec
TD0                                           1

======== CHANNEL f1 ========
NUC1                                        13C
P1                                        8.00 usec
PL1                                       1.00 dB
PL1W                                72.62802429 W
SFO1                                125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                                 waltz16
NUC2                                        1H
PCPD2                                    80.00 usec
PL2                                       0.00 dB
PL12                                     16.50 dB
PL13                                     17.00 dB
PL2W                                24.56113007 W
PL12W                                0.54940748 W
PL13W                                0.48965994 W
SFO2                                500.1325006 MHz
SI                                         131072
SF                                  125.7577914 MHz
WDW                                          EM
SSB                                           0
LB                                         0.30 Hz
GB                                            0
PC                                         1.40
```



NAME st12040
EXPNO 1
PROCNO 1
Date_ 20090319
Time 14.41
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 64
DW 66.667 usec
DE 71.43 usec
TE 295.0 K
D1 3.00000000 sec
TD0 1

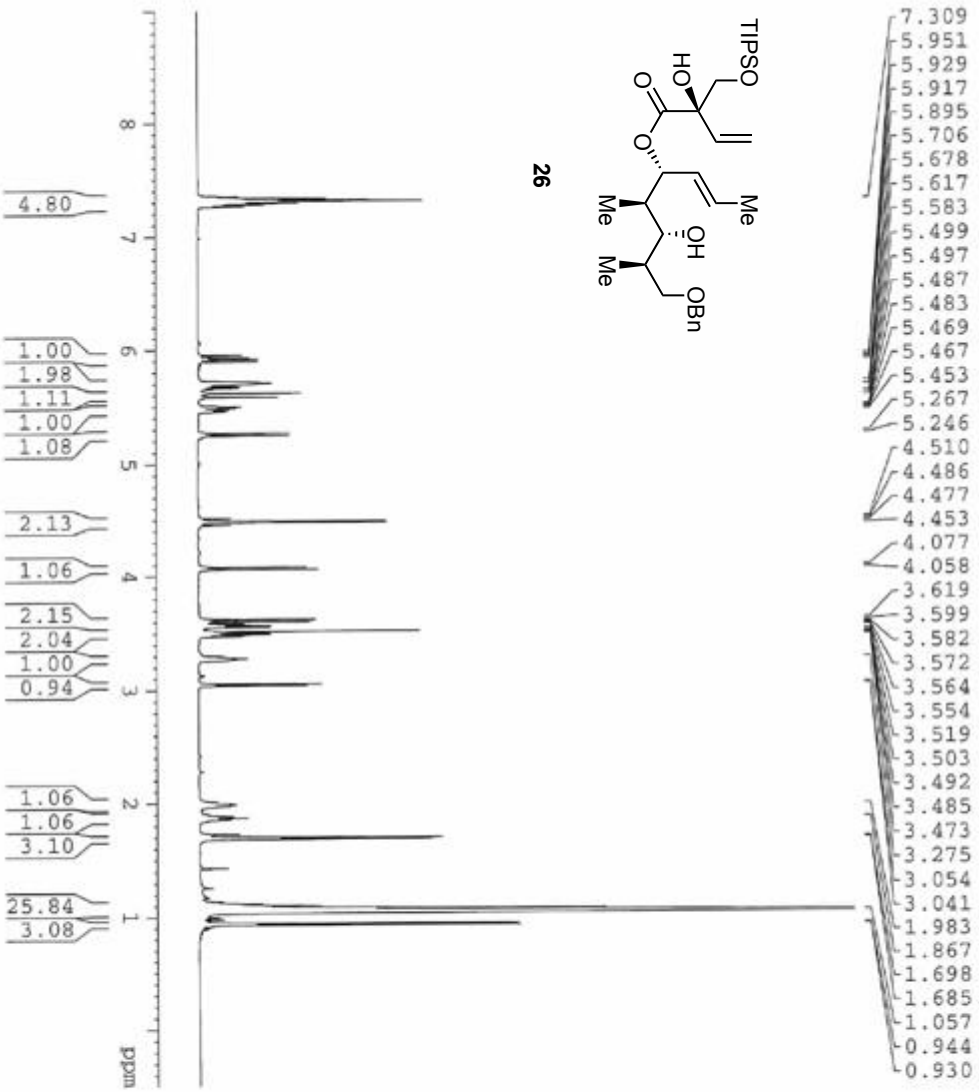
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

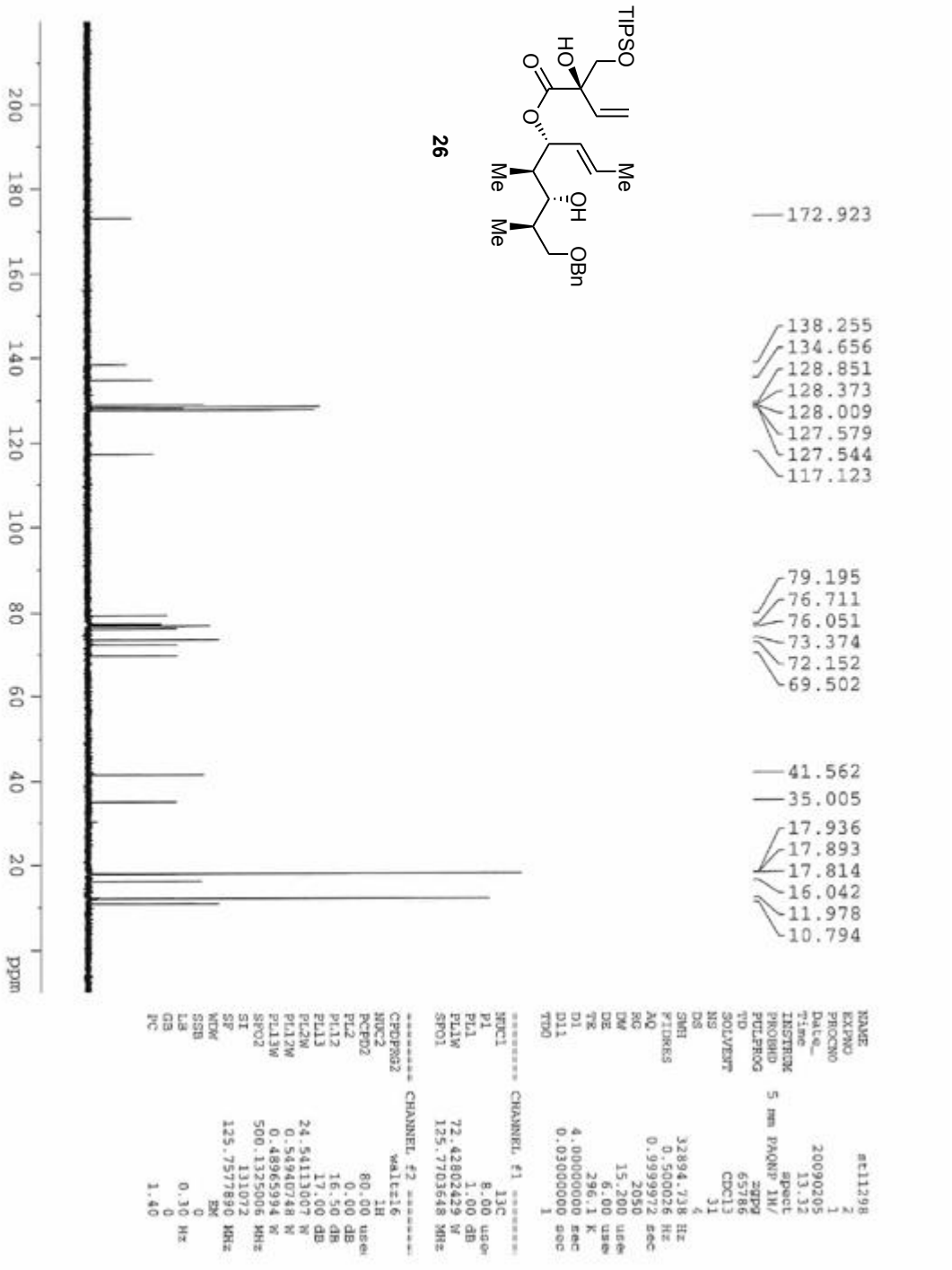


NAME et12040
EXPNO 2
PROCNO 1
Date_ 20090319
Time 14.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 39
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 295.6 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40


TIPSO
HO
O
O
Me
Me
Me
OH
OBn
26
7.309
5.951
5.929
5.917
5.895
5.706
5.678
5.617
5.583
5.499
5.497
5.487
5.483
5.469
5.467
5.453
5.267
5.246
4.510
4.486
4.477
4.453
4.077
4.058
3.619
3.599
3.582
3.572
3.564
3.554
3.519
3.503
3.492
3.485
3.473
3.275
3.054
3.041
1.983
1.867
1.698
1.685
1.057
0.944
0.930
4.80
1.00
1.98
1.11
1.00
1.08
2.13
1.06
2.15
2.04
1.00
0.94
1.06
1.06
3.10
25.84
3.08
ppm
NAME et11298
EXPNO 1
PROCNO 1
Date_ 20090205
Time 13.24
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.999166 sec
RG 32
DW 66.667 usec
DE 71.43 usec
TE 295.5 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113607 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300083 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


TIPSO
HO
O
O
Me
OH
OBn
Me
Me
26
172.923
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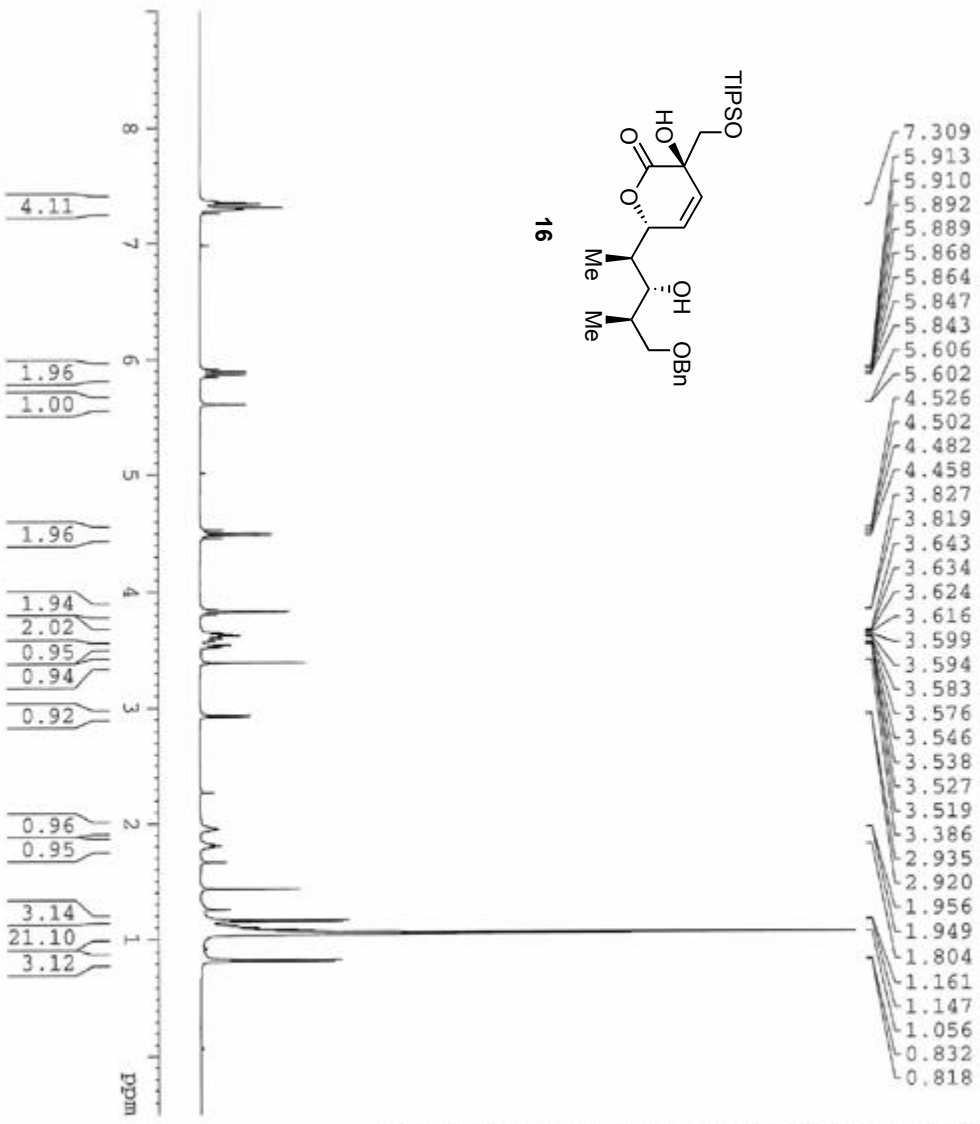
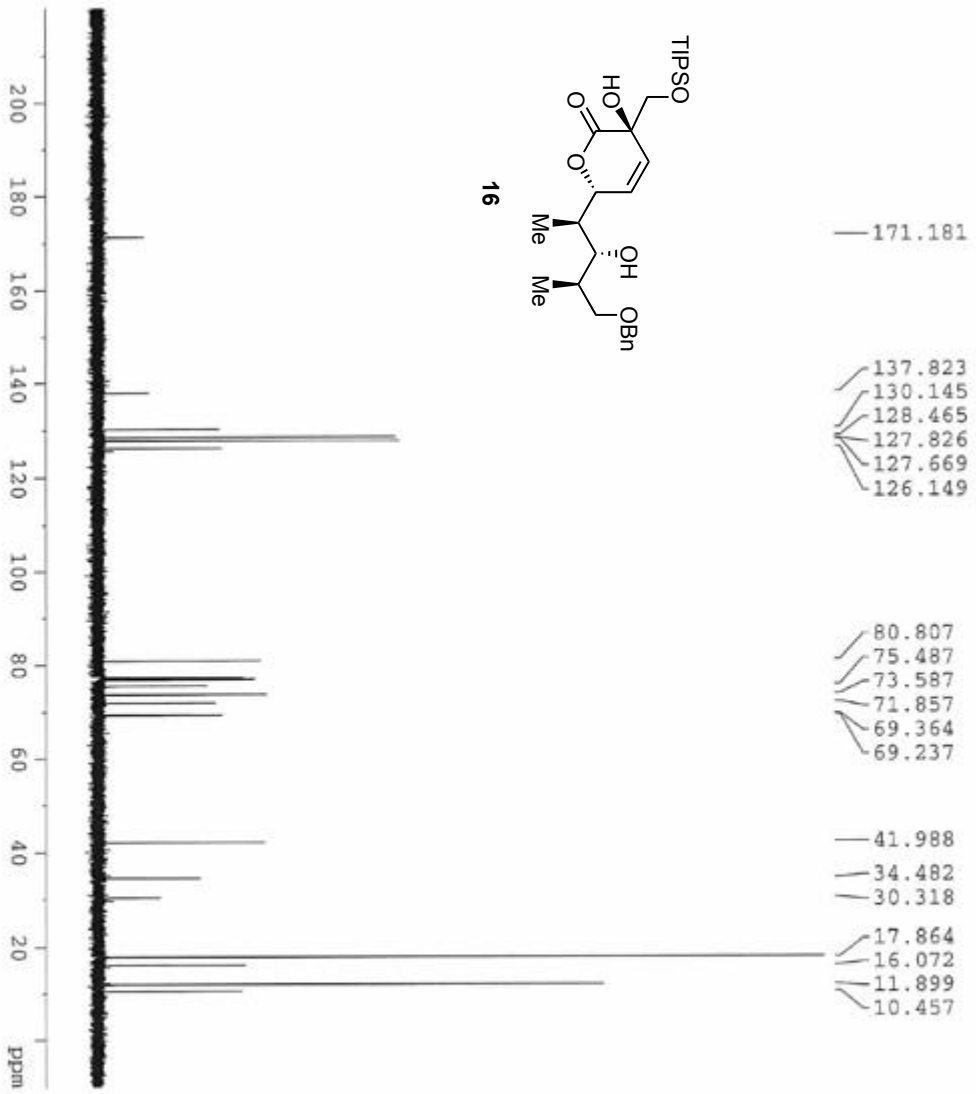
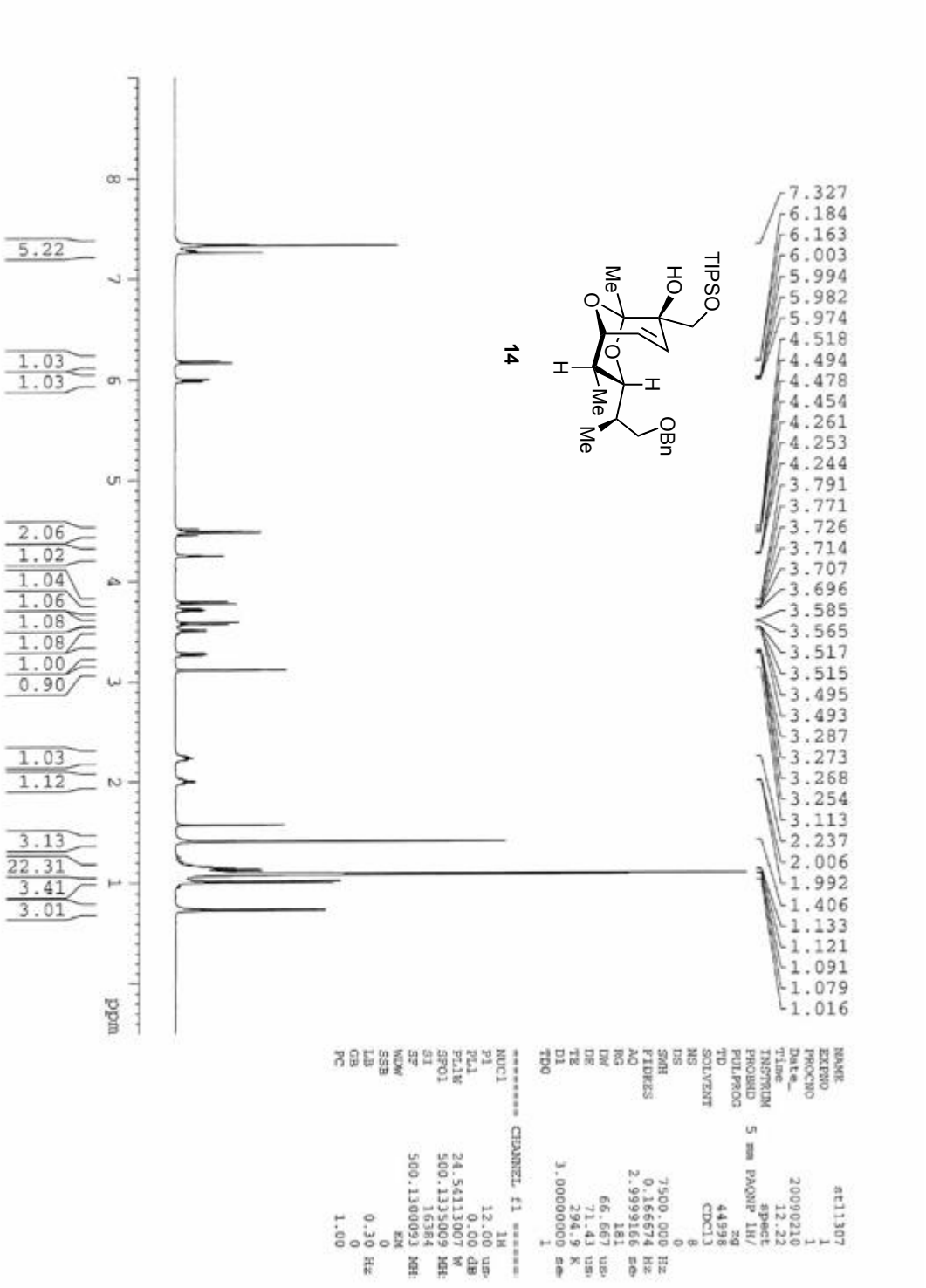
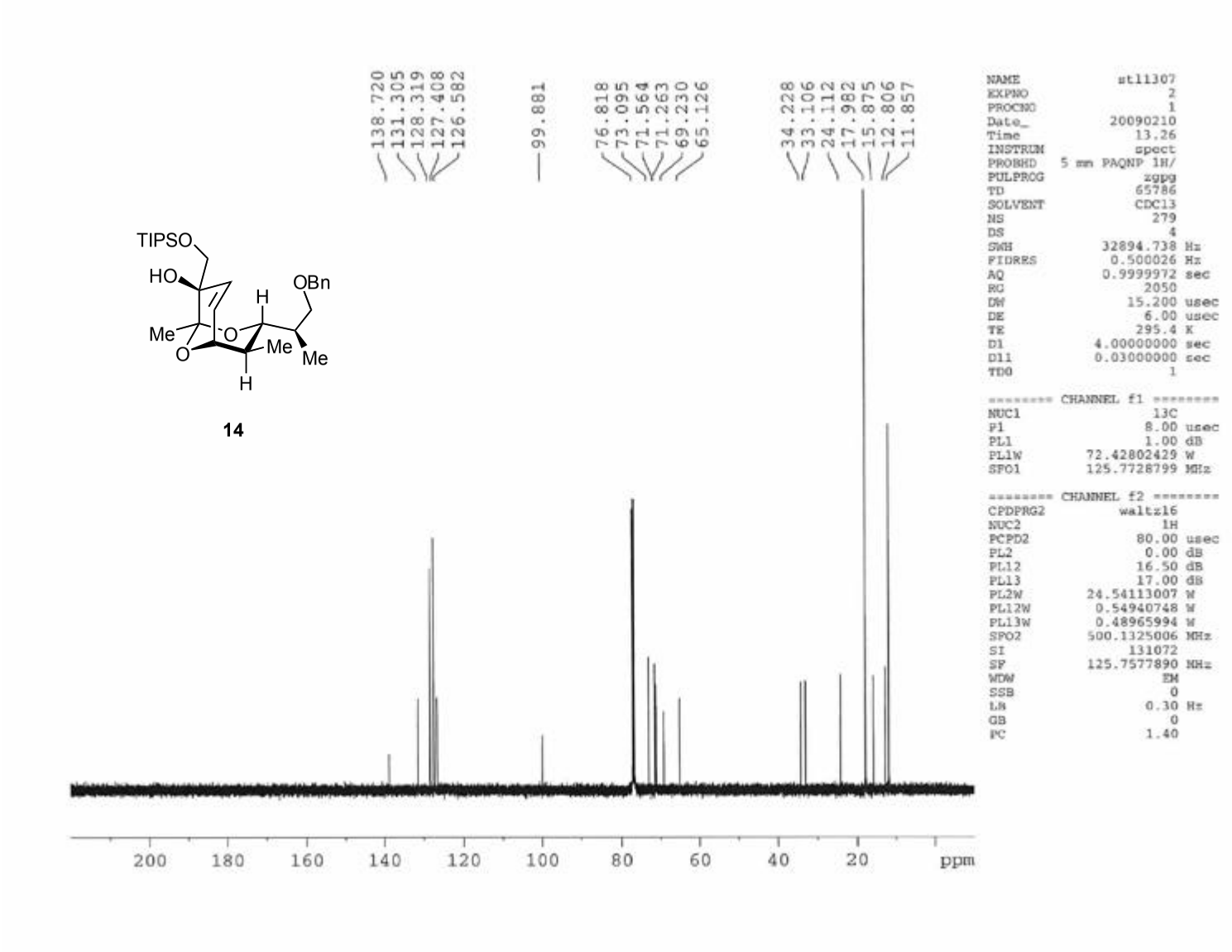
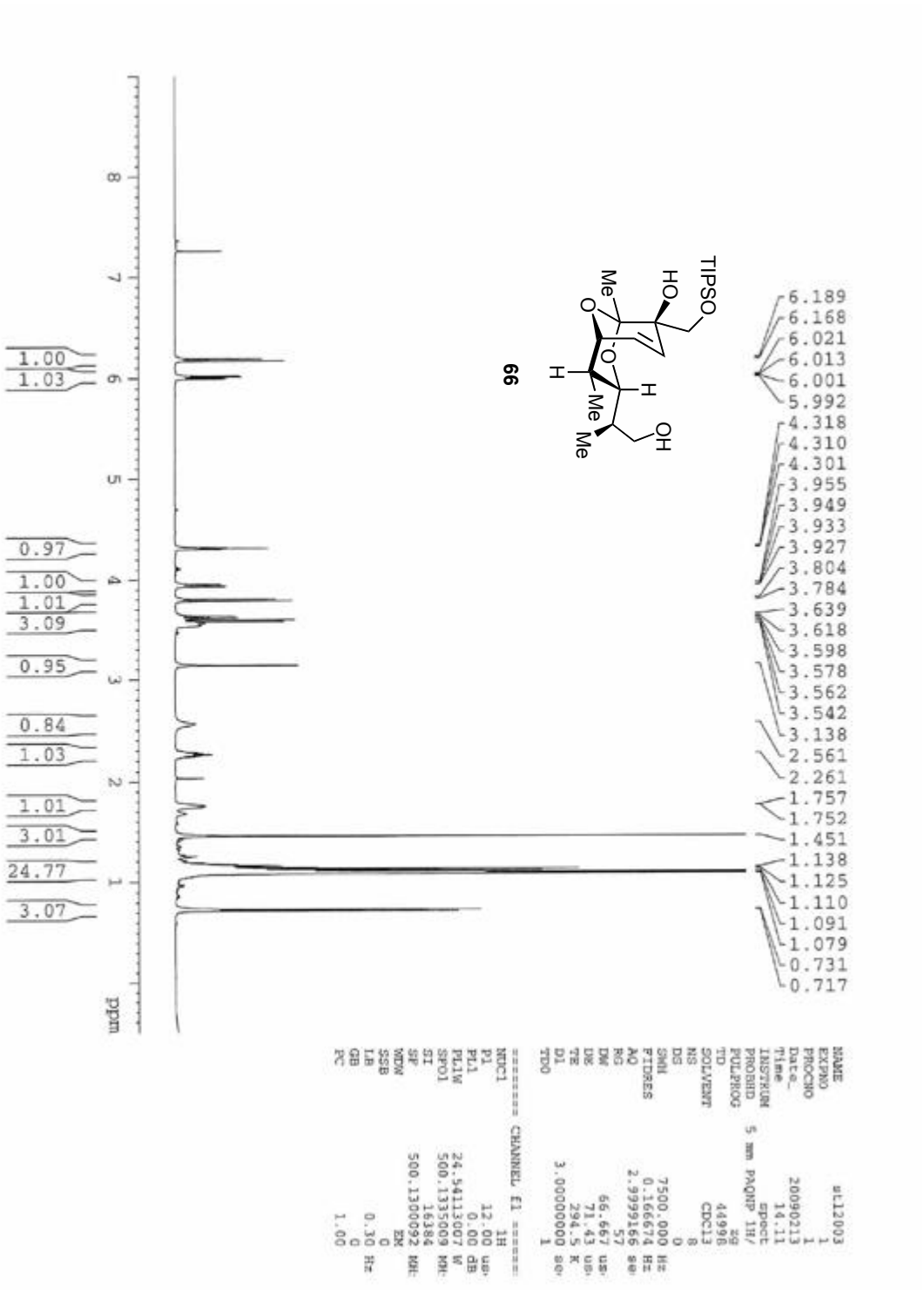
134.656
128.851
128.373
128.009
127.579
127.544
117.123
79.195
76.711
76.051
73.374
72.152
69.502
41.562
35.005
17.936
17.893
17.814
16.042
11.978
10.794
200
180
160
140
120
100
80
60
40
20
ppm

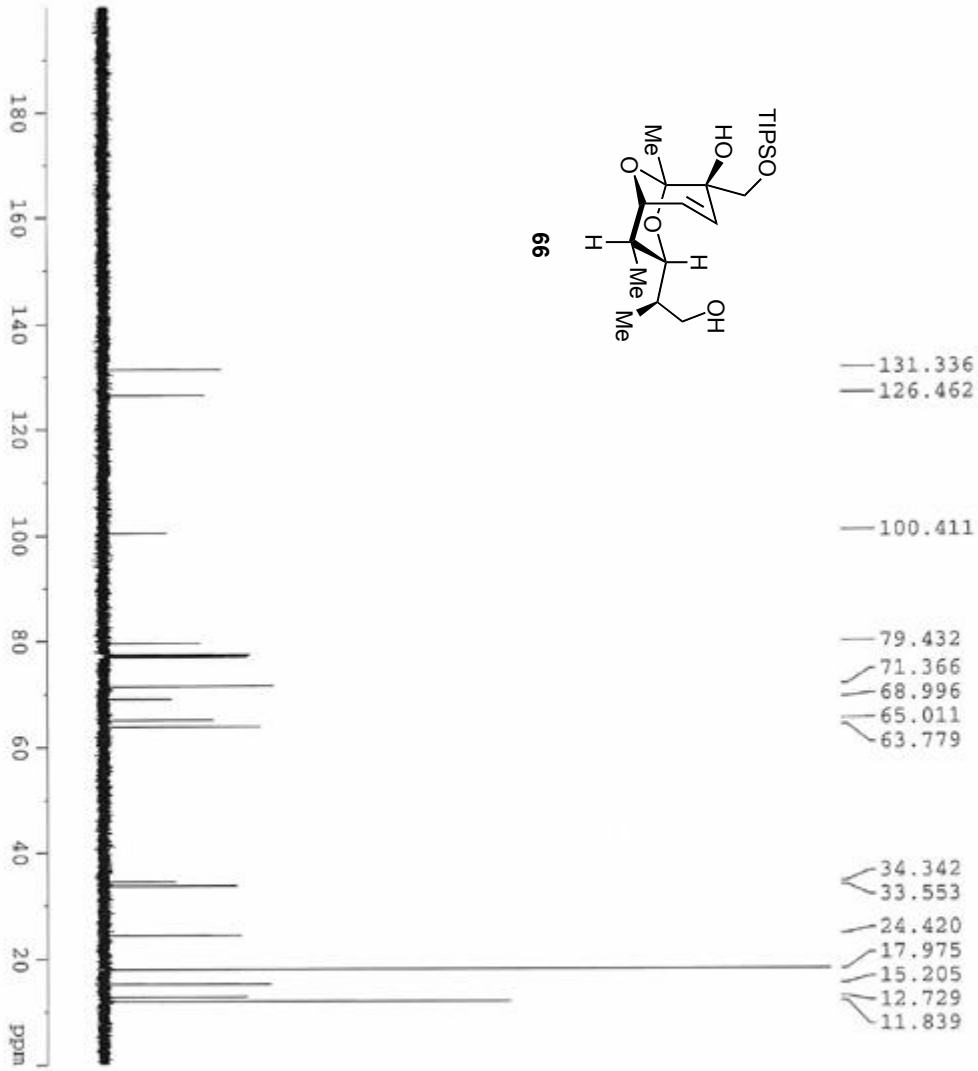

TIPSO
HO
O
O
Me
Me
OH
OBn
16
7.309
5.913
5.910
5.892
5.889
5.868
5.864
5.847
5.843
5.606
5.602
4.526
4.502
4.482
4.458
3.827
3.819
3.643
3.634
3.624
3.616
3.599
3.594
3.583
3.576
3.546
3.538
3.527
3.519
3.386
2.935
2.920
1.956
1.949
1.804
1.161
1.147
1.056
0.832
0.818
4.11
1.96
1.00
1.96
1.94
2.02
0.95
0.94
0.92
0.96
0.95
3.14
21.10
3.12
8
7
6
5
4
3
2
1
ppm

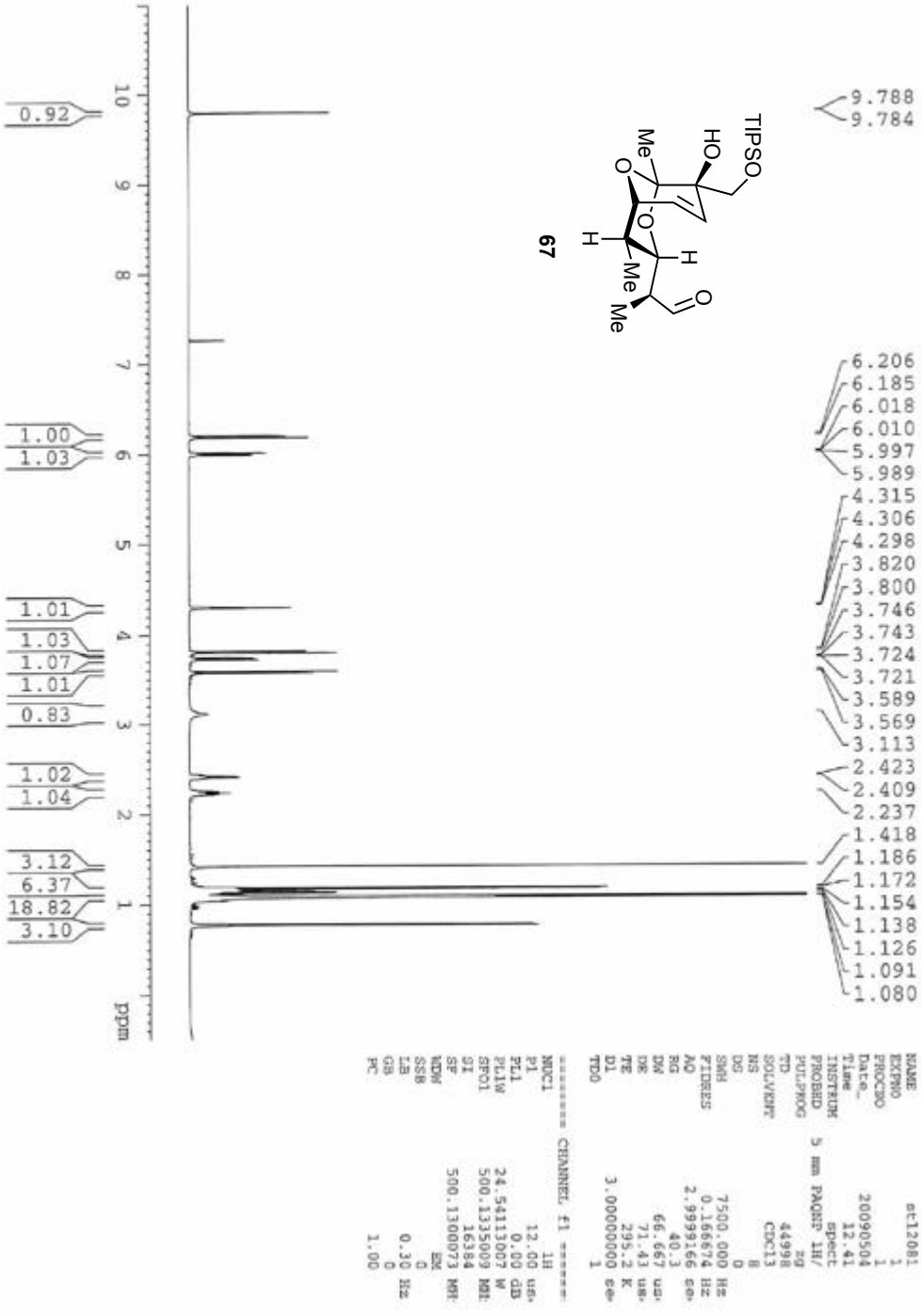

TIPSO
HO
O
O
Me
Me
OH
OBn
16
171.181
137.823
130.145
128.465
127.826
127.669
126.149
80.807
75.487
73.587
71.857
69.364
69.237
41.988
34.482
30.318
17.864
16.072
11.899
10.457
200
180
160
140
120
100
80
60
40
20
ppm

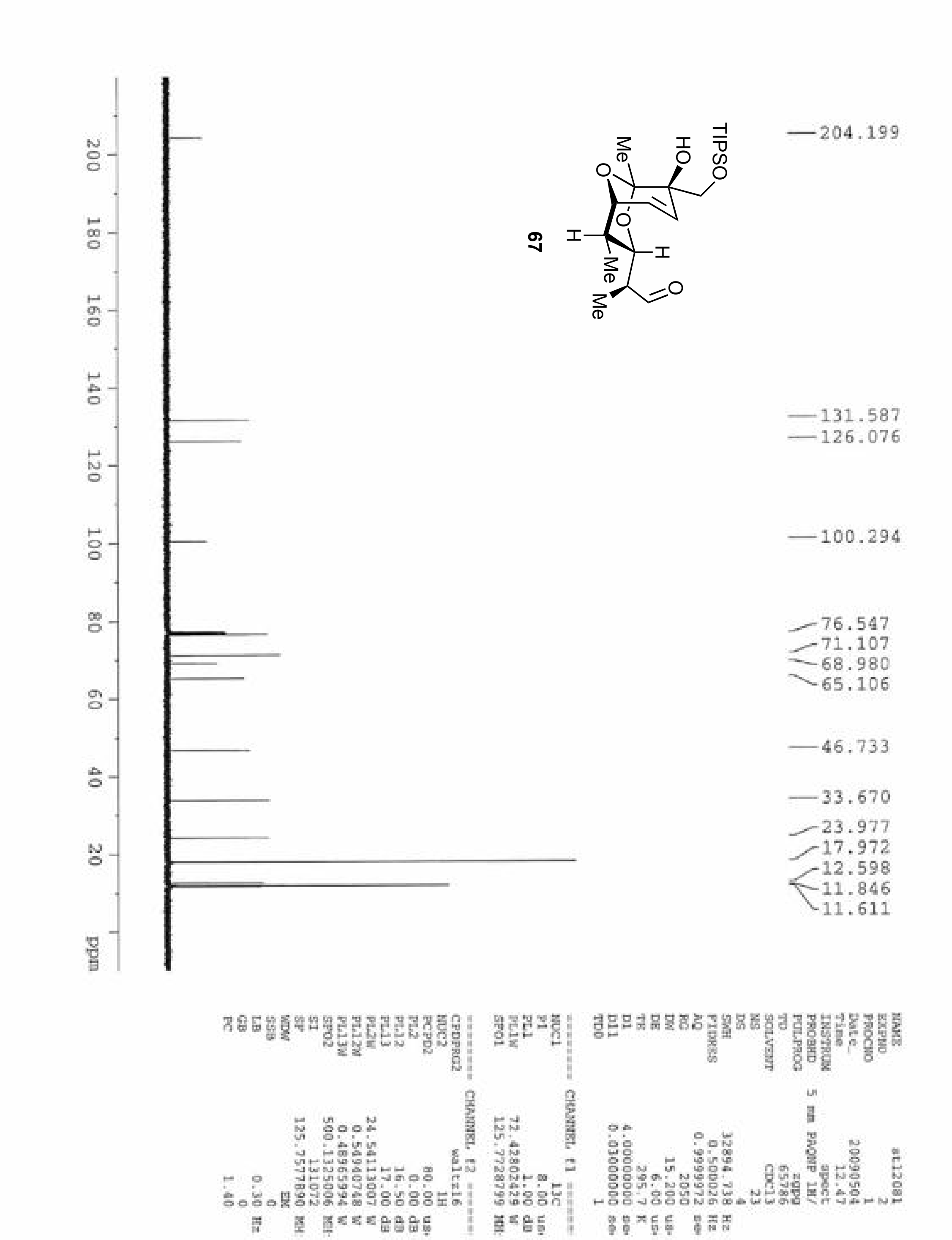

14
TIPSO
HO
Me
O
O
H
H
Me
Me
OBn
7.327
6.184
6.163
6.003
5.994
5.982
5.974
4.518
4.494
4.478
4.454
4.261
4.253
4.244
3.791
3.771
3.726
3.714
3.707
3.696
3.585
3.565
3.517
3.515
3.495
3.493
3.287
3.273
3.268
3.254
3.113
2.237
2.006
1.992
1.406
1.133
1.121
1.091
1.079
1.016
5.22
1.03
1.03
2.06
1.02
1.04
1.06
1.08
1.08
1.00
0.90
1.03
1.12
3.13
22.31
3.41
3.01
ppm


138.720
131.305
128.319
127.408
126.582
99.881
76.818
73.095
71.564
71.263
69.230
65.126
34.228
33.106
24.112
17.982
15.875
12.806
11.857
TIPSO
HO
OBn
H
Me
O
O
Me
Me
H
14
200
180
160
140
120
100
80
60
40
20
ppm
NAME st11307
EXPNO 2
PROCNO 1
Date_ 20090210
Time 13.26
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 279
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 295.4 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

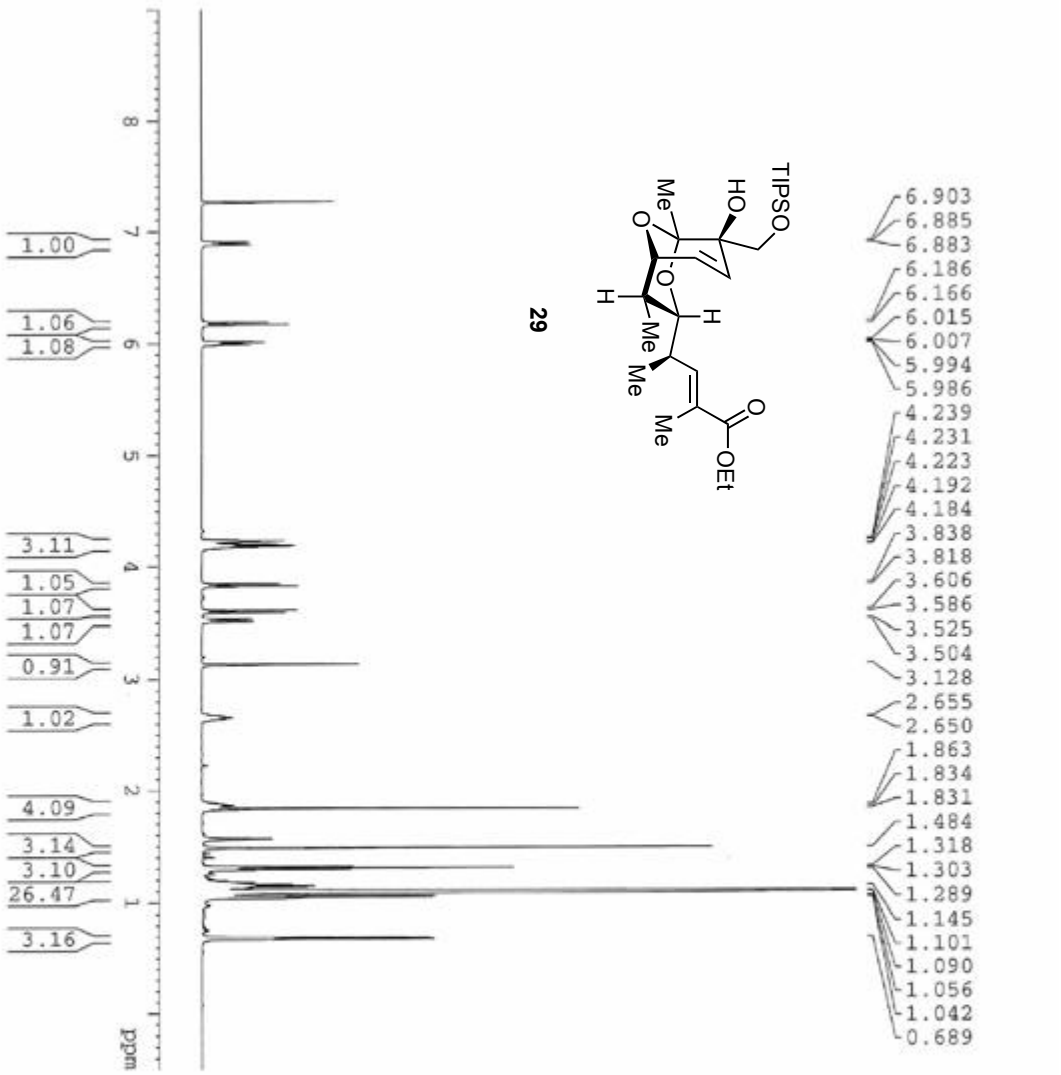

TIPSO
HO
Me
O
O
H
H
Me
Me
OH
66
6.189
6.168
6.021
6.013
6.001
5.992
4.318
4.310
4.301
3.955
3.949
3.933
3.927
3.804
3.784
3.639
3.618
3.598
3.578
3.562
3.542
3.138
2.561
2.261
1.757
1.752
1.451
1.138
1.125
1.110
1.091
1.079
0.731
0.717
1.00
1.03
0.97
1.00
1.01
3.09
0.95
0.84
1.03
1.01
3.01
24.77
3.07
ppm
NAME st12003
EXPNO 1
PROCNO 1
Date_ 20090213
Time 14.11
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999165 se
RG 57
DW 66.667 us
DE 71.43 us
TE 294.5 K
D1 3.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 12.00 us
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MH
SI 16384
SF 500.1300092 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

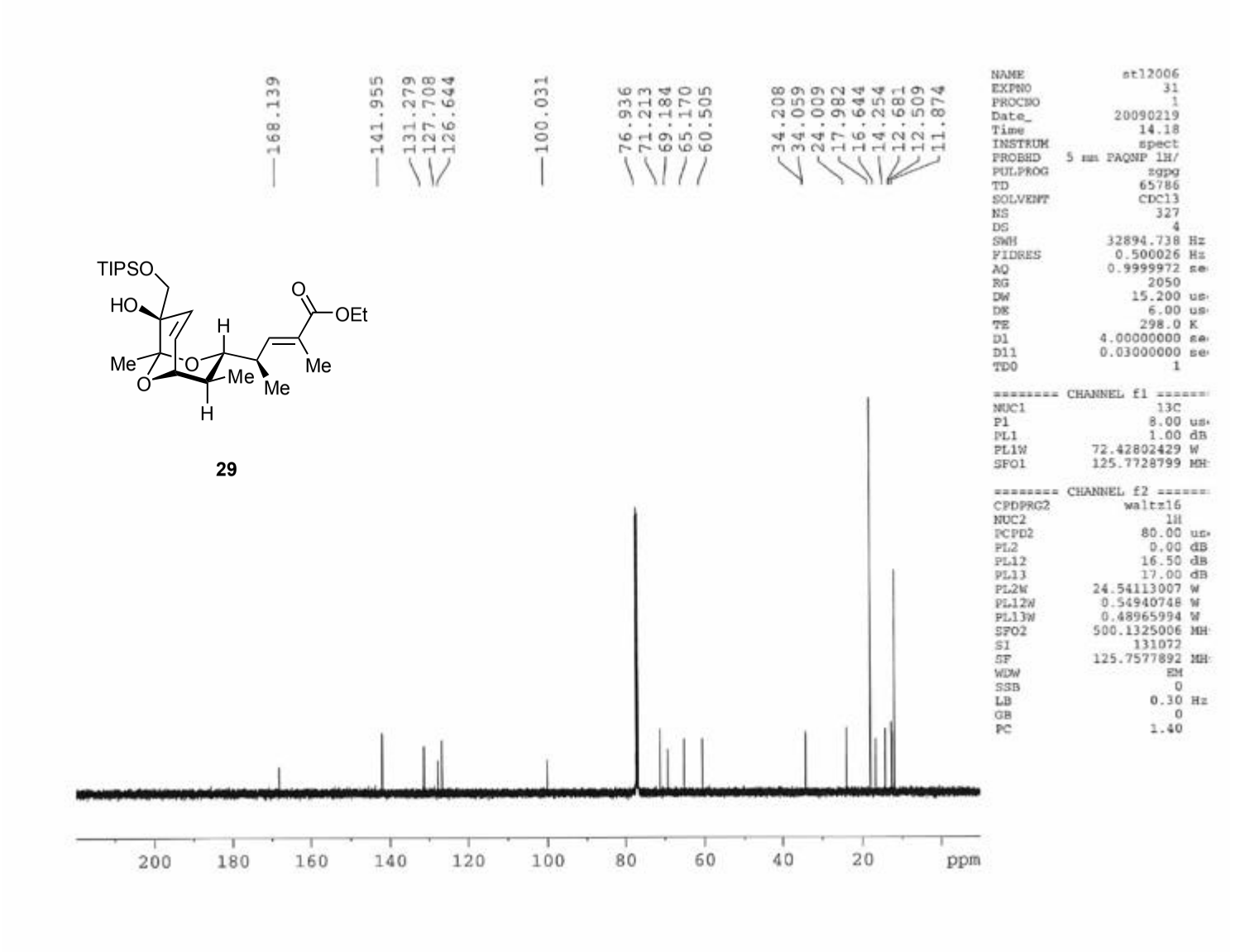

TIPSO
HO
Me
O
O
H
Me
Me
H
OH
66
131.336
126.462
100.411
79.432
71.366
68.996
65.011
63.779
34.342
33.553
24.420
17.975
15.205
12.729
11.839
180
160
140
120
100
80
60
40
20
ppm

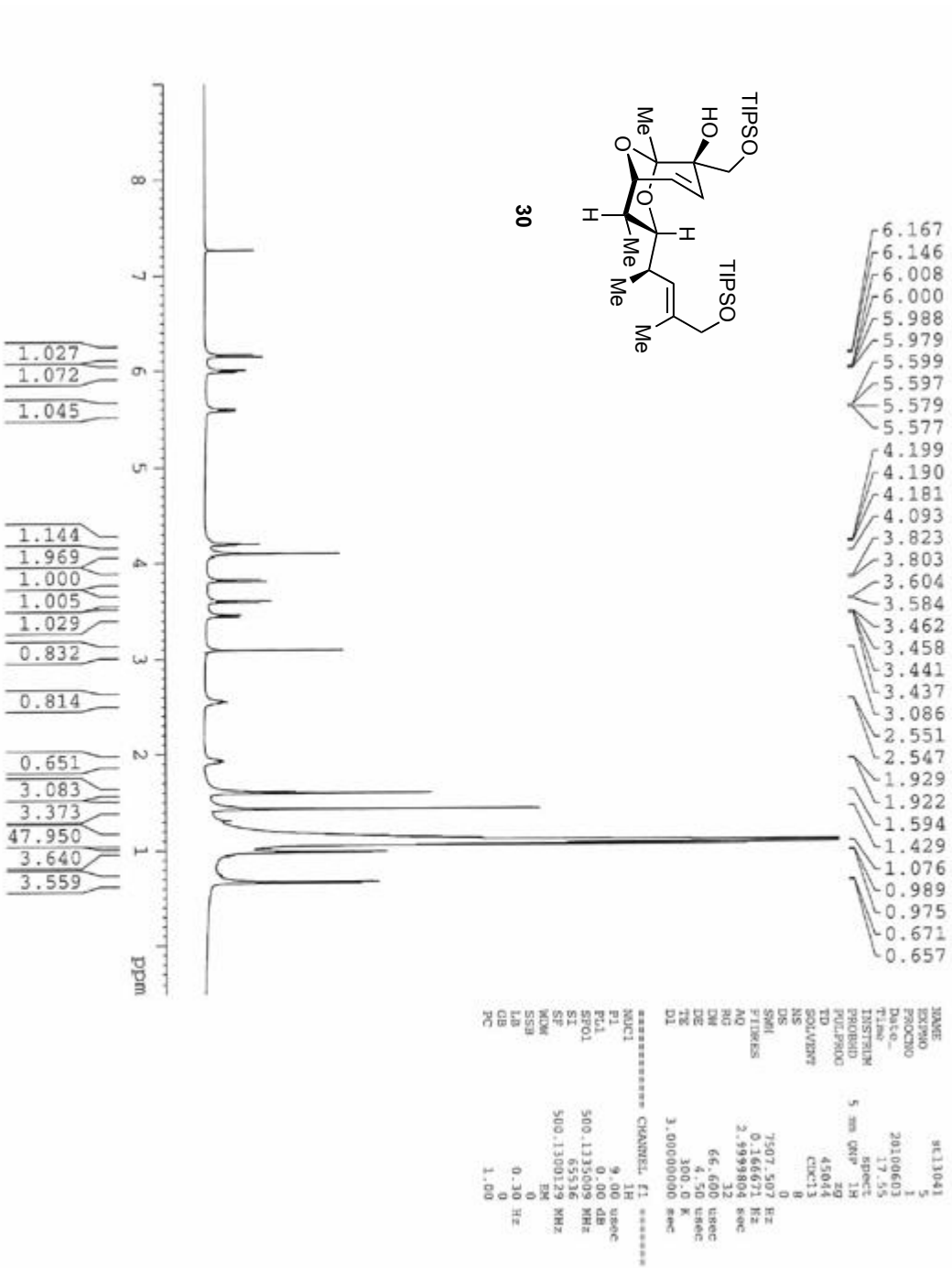

9.788
9.784
6.206
6.185
6.018
6.010
5.997
5.989
4.315
4.306
4.298
3.820
3.800
3.746
3.743
3.724
3.721
3.589
3.569
3.113
2.423
2.409
2.237
1.418
1.186
1.172
1.154
1.138
1.126
1.091
1.080
0.92
1.00
1.03
1.01
1.03
1.07
1.01
0.83
1.02
1.04
3.12
6.37
18.82
3.10
ppm
TIPSO
HO
Me
O
O
H
H
O
Me
Me
67

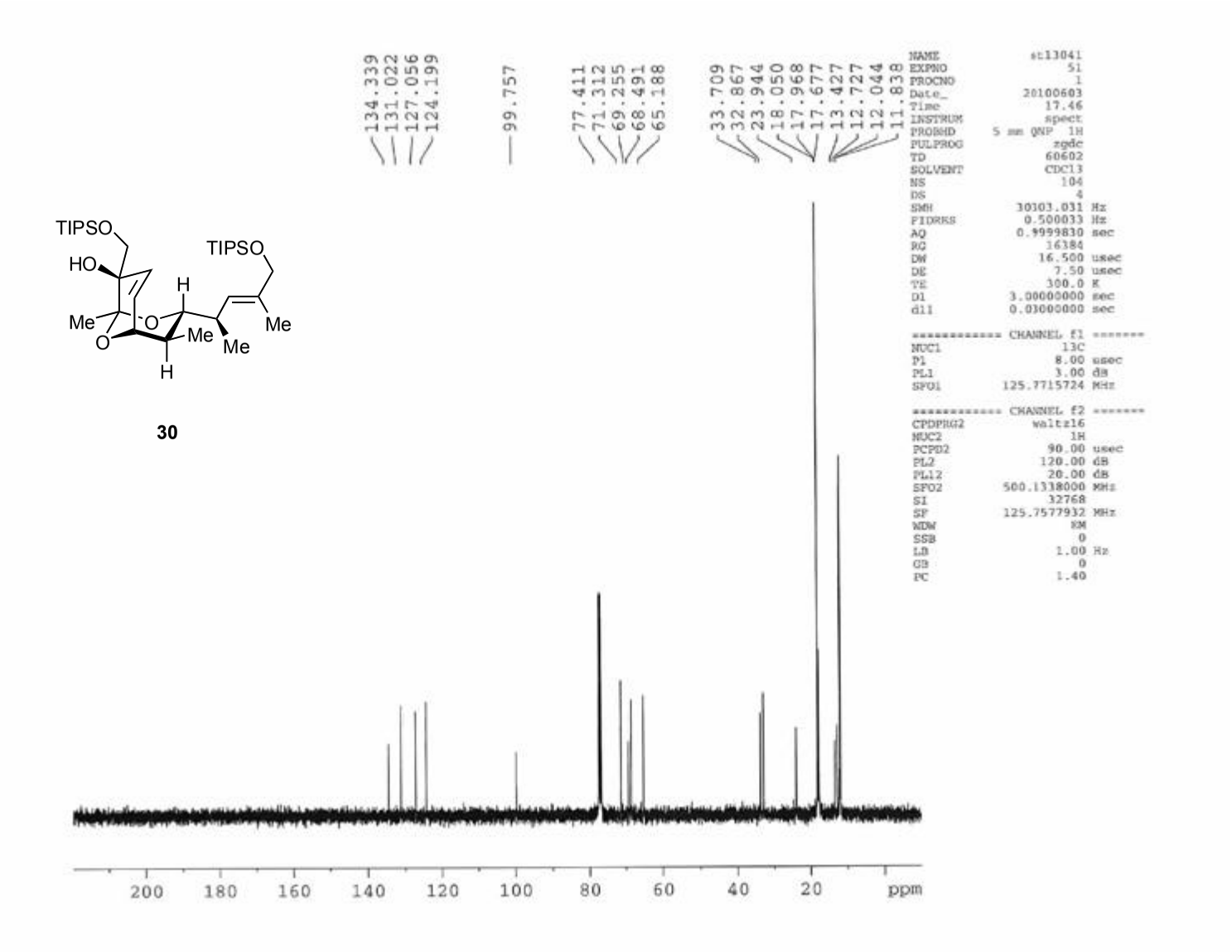


TIPSO
HO
Me
O
O
H
O
Me
Me
H
67
204.199
131.587
126.076
100.294
76.547
71.107
68.980
65.106
46.733
33.670
23.977
17.972
12.598
11.846
11.611
200
180
160
140
120
100
80
60
40
20
ppm
NAME st12081
EXPNO 2
PROCNO 1
Date_ 20090504
Time 12.47
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 23
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 295.7 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40


TIPSO
HO
Me
O
O
H
Me
Me
H
Me
O
OEt
29
6.903
6.885
6.883
6.186
6.166
6.015
6.007
5.994
5.986
4.239
4.231
4.223
4.192
4.184
3.838
3.818
3.606
3.586
3.525
3.504
3.128
2.655
2.650
1.863
1.834
1.831
1.484
1.318
1.303
1.289
1.145
1.101
1.090
1.056
1.042
0.689
1.00
1.06
1.08
3.11
1.05
1.07
1.07
0.91
1.02
4.09
3.14
3.10
26.47
3.16
ppm
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
TD0
======== CHANNEL f1 ========
NUC1
P1
PL1
PL1W
SFO1
SI
SF
WDW
SSB
LB
GB
PC

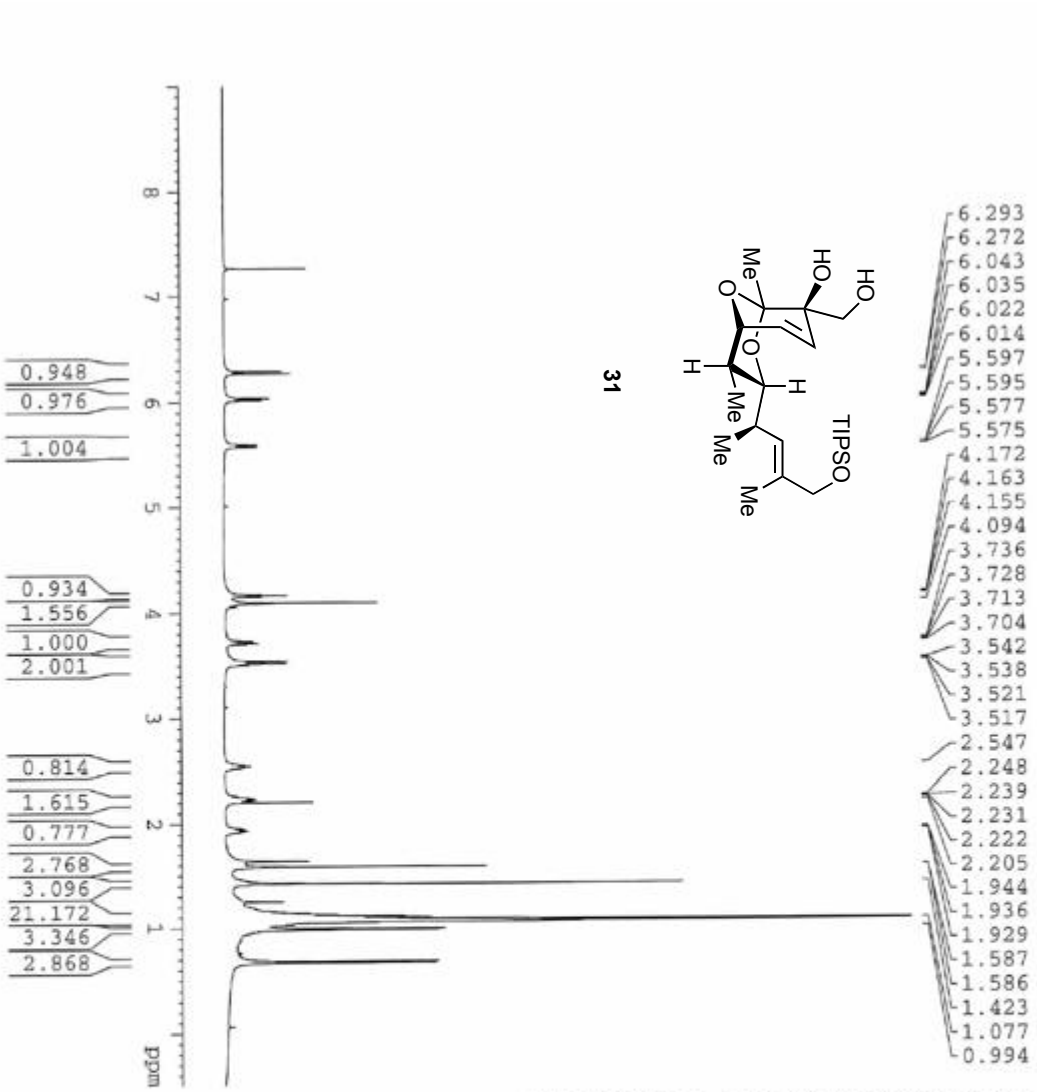

168.139
141.955
131.279
127.708
126.644
100.031
76.936
71.213
69.184
65.170
60.505
34.208
34.059
24.009
17.982
16.644
14.254
12.681
12.509
11.874
TIPSO
HO
O
OEt
H
Me
O
Me
Me
O
H
29
200
180
160
140
120
100
80
60
40
20
ppm
NAME st12006
EXPNO 31
PROCNO 1
Date_ 20090219
Time 14.18
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 327
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 se
RG 2050
DW 15.200 us
DE 6.00 us
TE 298.0 K
D1 4.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.00 us
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MH
SI 131072
SF 125.7577892 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

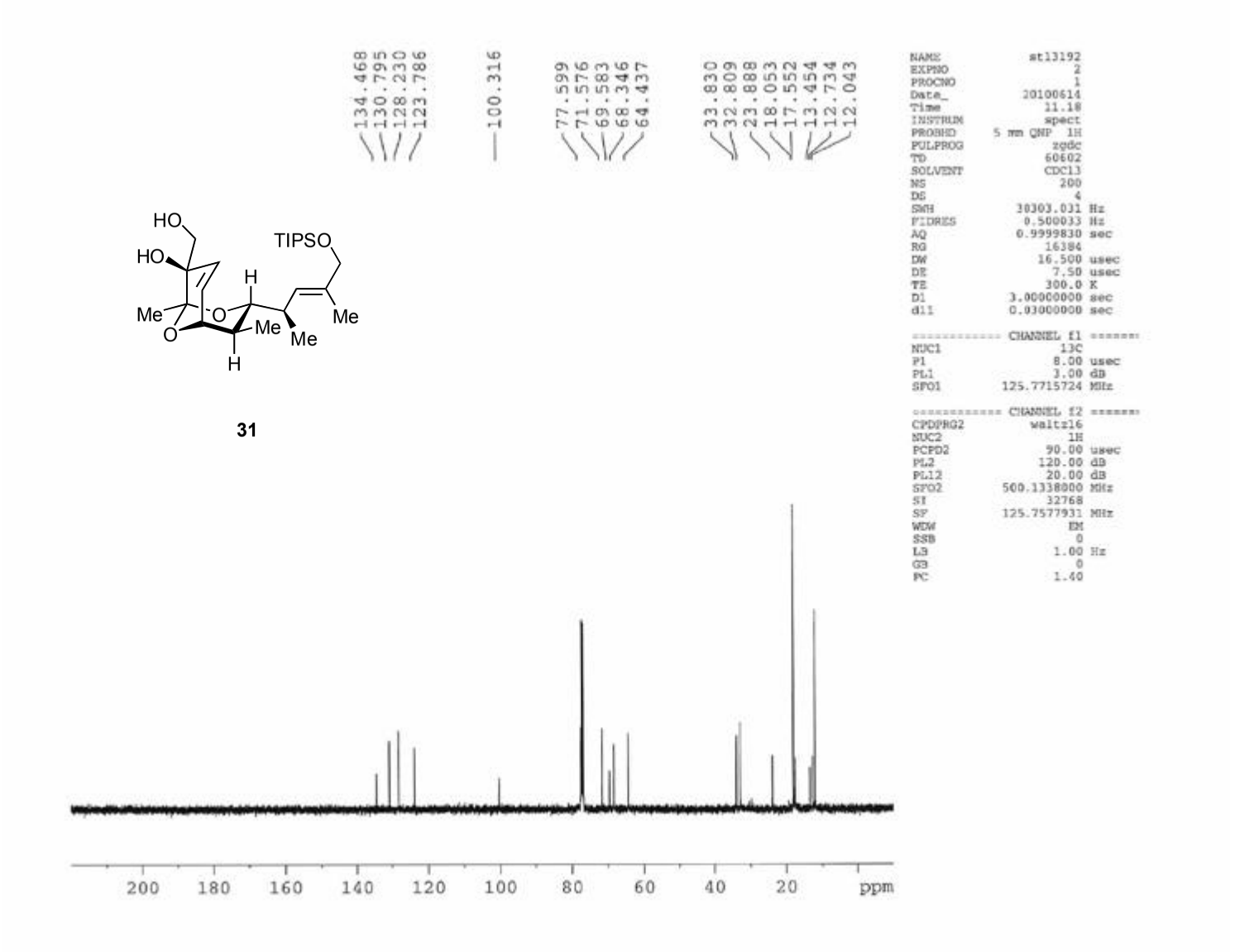

TIPSO
HO
Me
O
O
H
H
Me
Me
Me
TIPSO
30
6.167
6.146
6.008
6.000
5.988
5.979
5.599
5.597
5.579
5.577
4.199
4.190
4.181
4.093
3.823
3.803
3.604
3.584
3.462
3.458
3.441
3.437
3.086
2.551
2.547
1.929
1.922
1.594
1.429
1.076
0.989
0.975
0.671
0.657
1.027
1.072
1.045
1.144
1.969
1.000
1.005
1.029
0.832
0.814
0.651
3.083
3.373
47.950
3.640
3.559
ppm

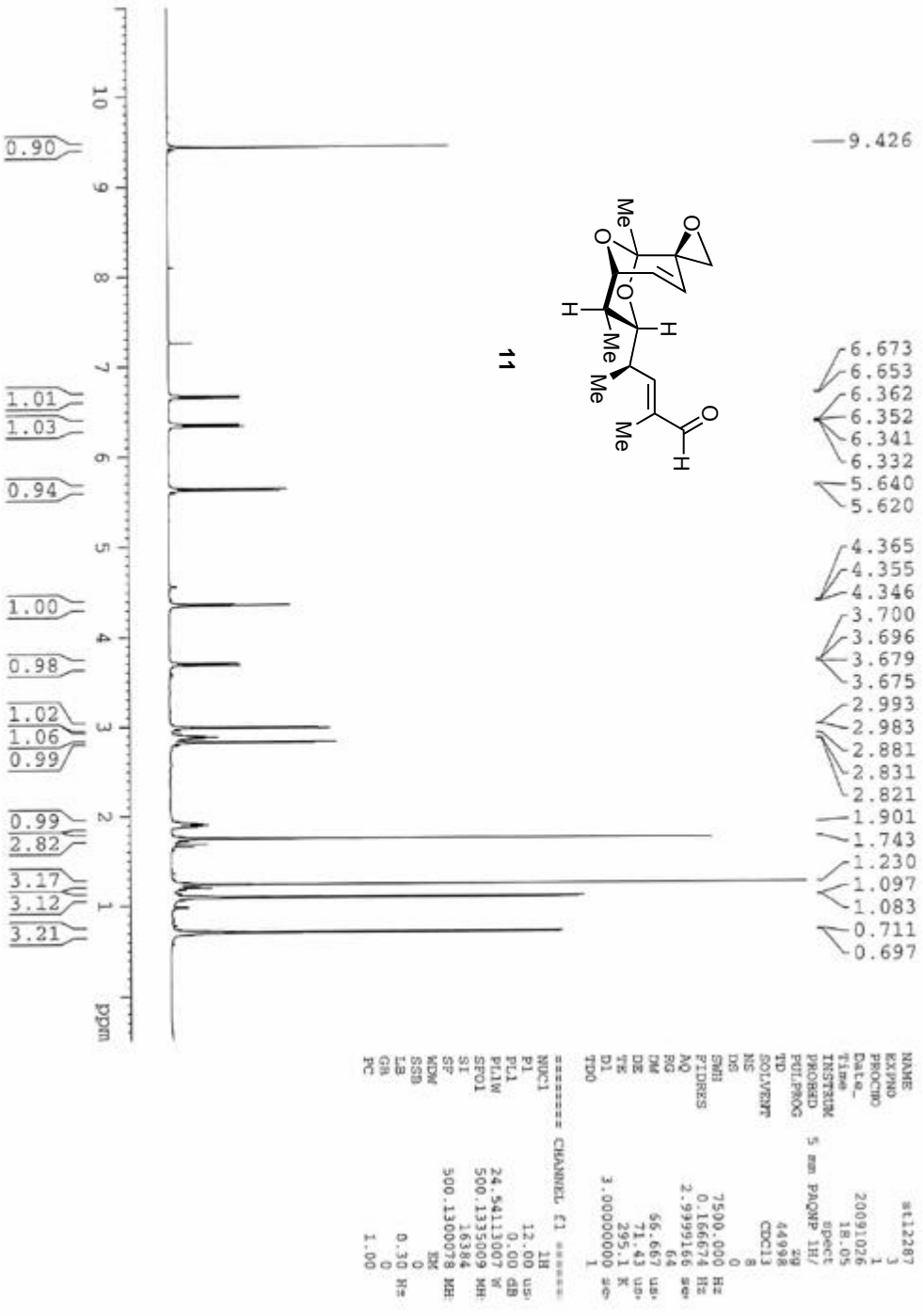


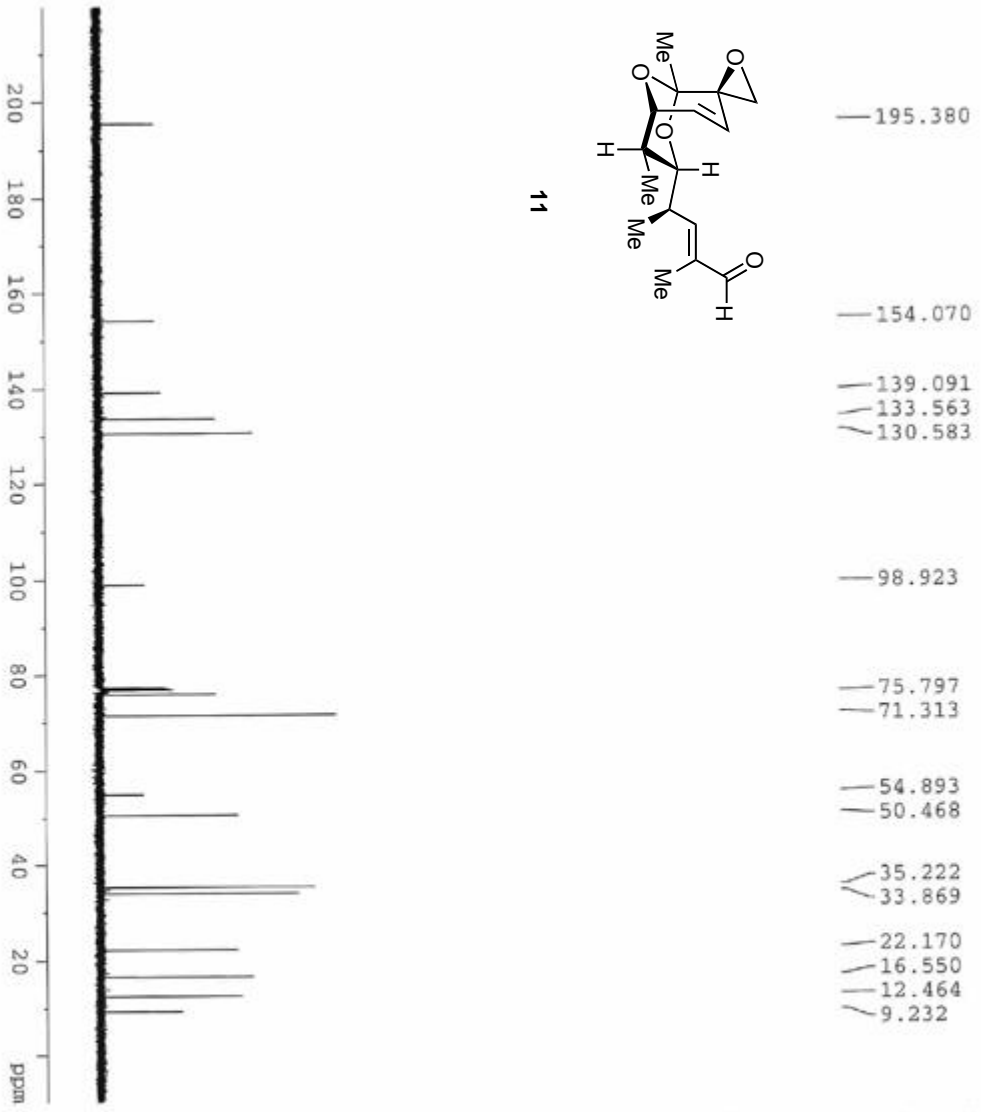
30

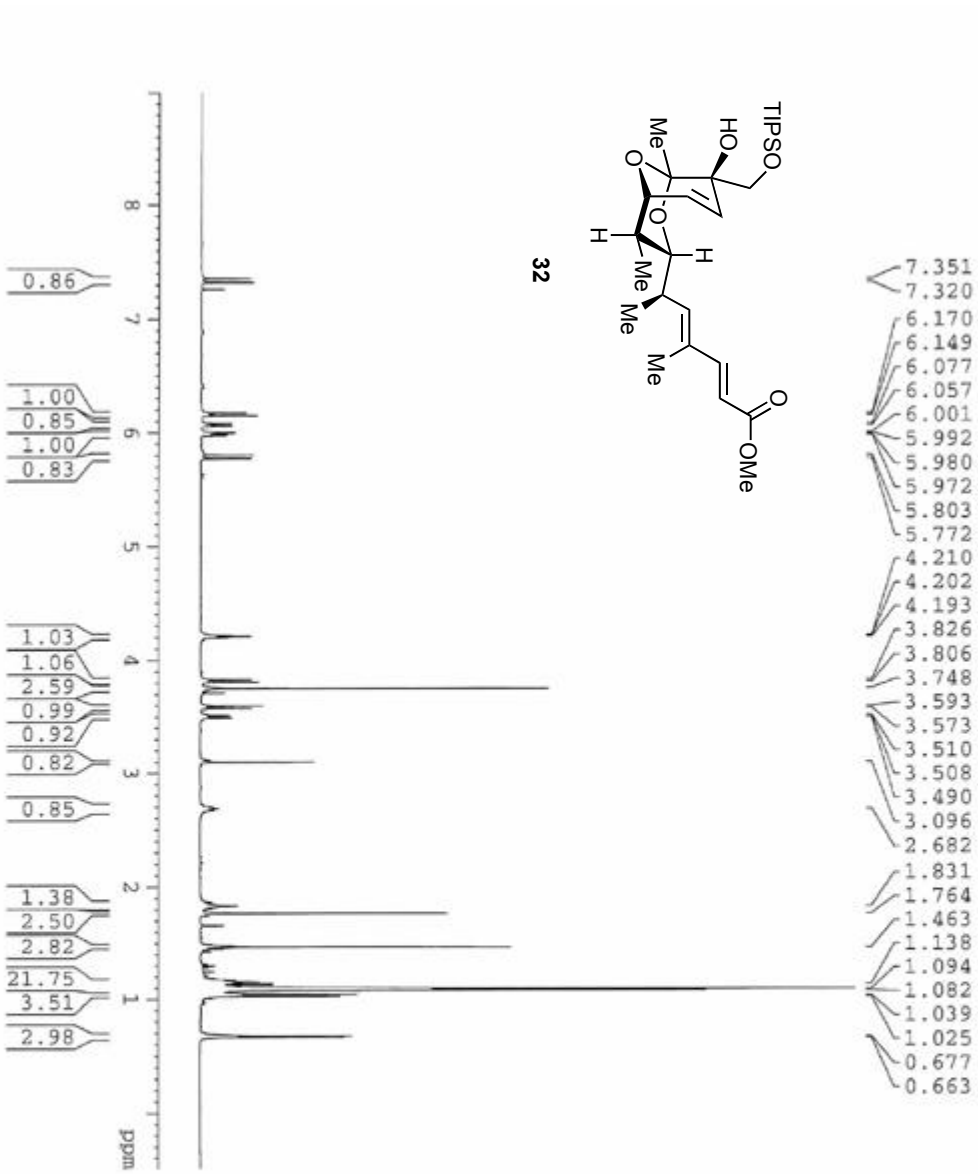
NAME	st13041
EXPNO	51
PROCNO	1
Date_	20100603
Time	17.46
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	104
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	16384
DW	16.500 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
========== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
========== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1318000 MHz
SI	32768
SF	125.7577932 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

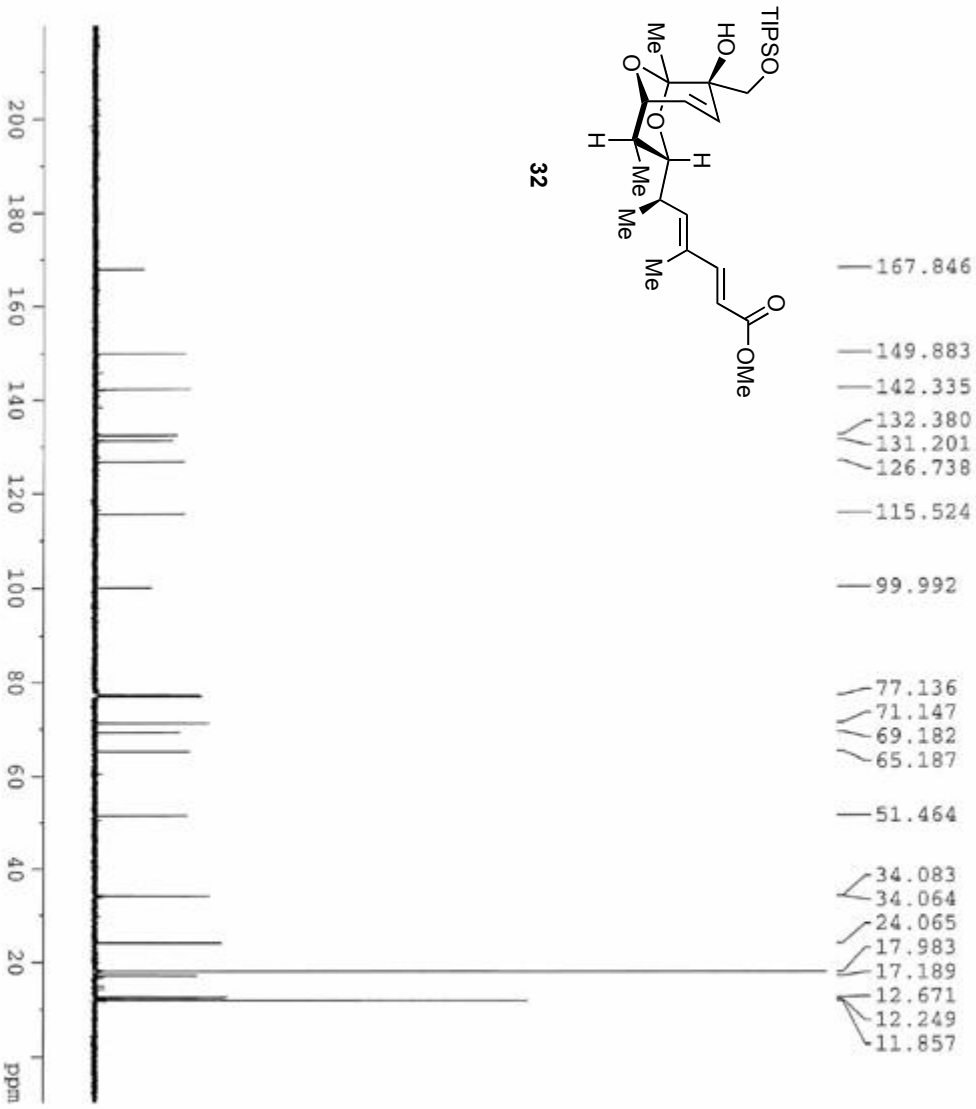

31
HO
HO
Me
O
O
H
H
Me
Me
Me
TIPSO
6.293
6.272
6.043
6.035
6.022
6.014
5.597
5.595
5.577
5.575
4.172
4.163
4.155
4.094
3.736
3.728
3.713
3.704
3.542
3.538
3.521
3.517
2.547
2.248
2.239
2.231
2.222
2.205
1.944
1.936
1.929
1.587
1.586
1.423
1.077
0.994
0.948
0.976
1.004
0.934
1.556
1.000
2.001
0.814
1.615
0.777
2.768
3.096
21.172
3.346
2.868
ppm
NAME st13192
EXPNO 1
PROCNO 1
Date_ 20100614
Time 11.15
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT CDCl3
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166631 Hz
AQ 2.9999804 sec
RG 64
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz
SI 65536
SF 500.1300133 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

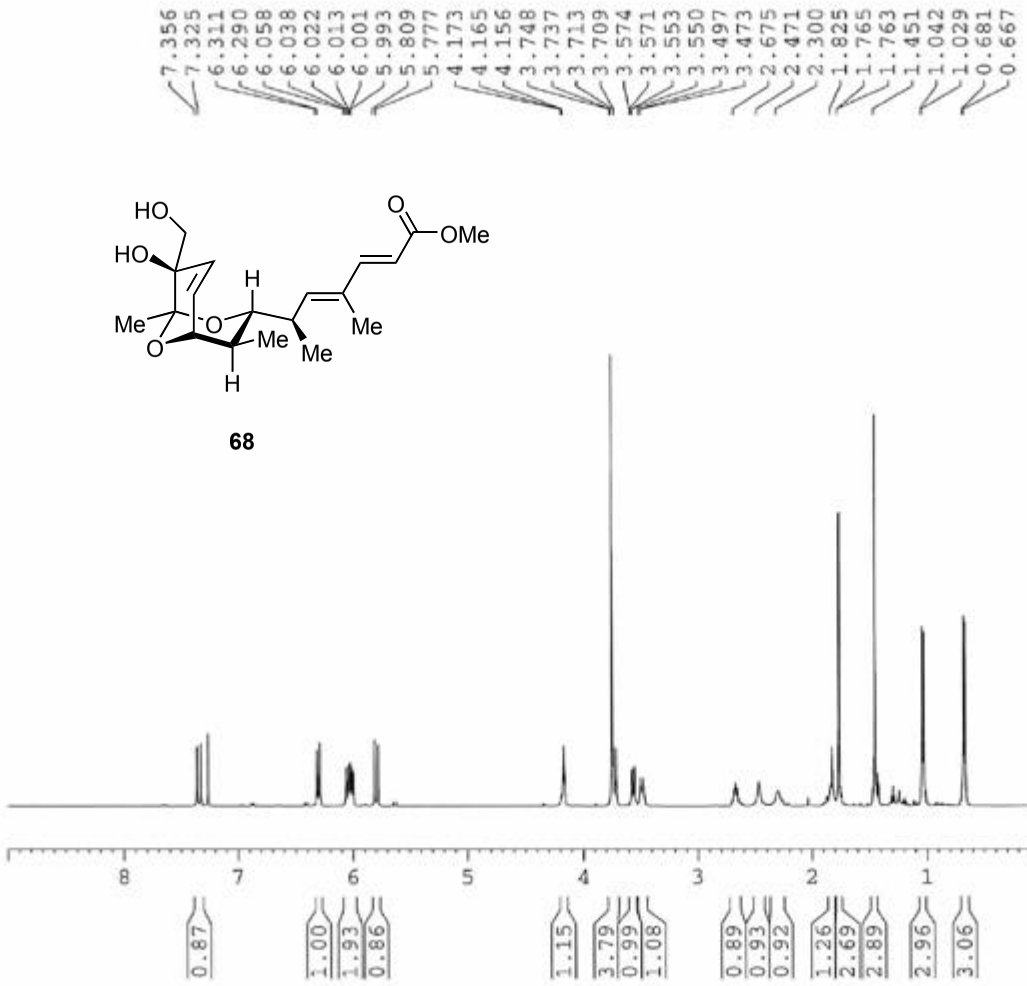

134.468
130.795
128.230
123.786
100.316
77.599
71.576
69.583
68.346
64.437
33.830
32.809
23.888
18.053
17.552
13.454
12.734
12.043
HO
HO
TIPSO
H
Me
O
O
Me
Me
Me
H
31
NAME st13192
EXPNO 2
PROCNO 1
Date_ 20100614
Time 11.18
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 60602
SOLVENT CDCl3
NS 200
DS 4
SWH 30303.031 Hz
FIDRES 0.500033 Hz
AQ 0.9999830 sec
RG 16384
DW 16.500 usec
DE 7.50 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7715724 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 500.1338000 MHz
SI 32768
SF 125.7577931 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm


9.426
6.673
6.653
6.362
6.352
6.341
6.332
5.640
5.620
4.365
4.355
4.346
3.700
3.696
3.679
3.675
2.993
2.983
2.881
2.831
2.821
1.901
1.743
1.230
1.097
1.083
0.711
0.697
11
0.90
1.01
1.03
0.94
1.00
0.98
1.02
1.06
0.99
0.99
2.82
3.17
3.12
3.21
ppm

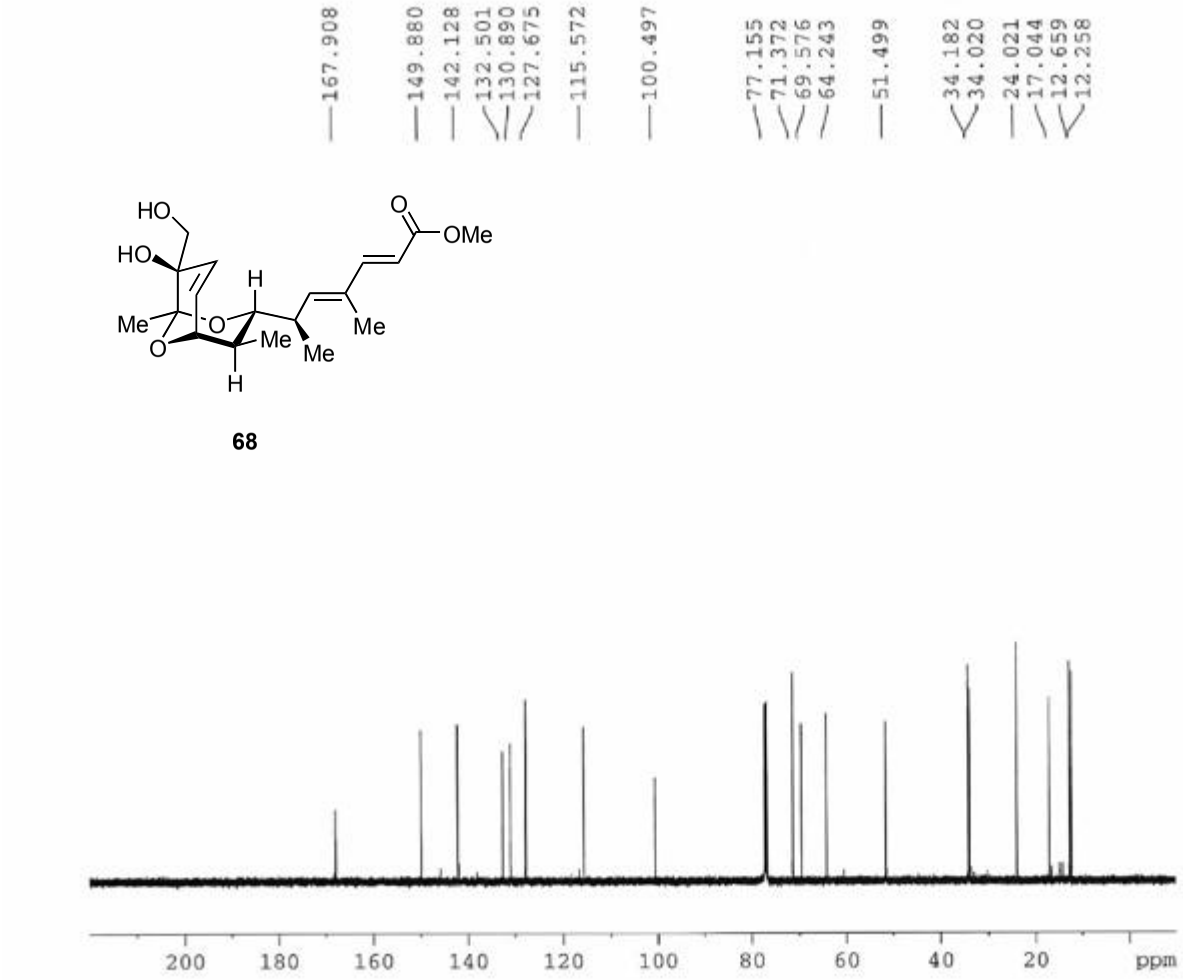

11
195.380
154.070
139.091
133.563
130.583
98.923
75.797
71.313
54.893
50.468
35.222
33.869
22.170
16.550
12.464
9.232
200
180
160
140
120
100
80
60
40
20
ppm


32
TIPSO
HO
Me
O
O
H
H
Me
Me
Me
O
OMe
7.351
7.320
6.170
6.149
6.077
6.057
6.001
5.992
5.980
5.972
5.803
5.772
4.210
4.202
4.193
3.826
3.806
3.748
3.593
3.573
3.510
3.508
3.490
3.096
2.682
1.831
1.764
1.463
1.138
1.094
1.082
1.039
1.025
0.677
0.663
0.86
1.00
0.85
1.00
0.83
1.03
1.06
2.59
0.99
0.92
0.82
0.85
1.38
2.50
2.82
21.75
3.51
2.98
ppm
NAME sc12053
EXPNO 1
PROCNO 1
Date_ 20090407
Time 11.22
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 45.2
DW 66.667 usec
DE 71.43 usec
TE 295.0 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


TIPSO
HO
Me
O
O
H
H
Me
Me
Me
O
OMe
32
167.846
149.883
142.335
132.380
131.201
126.738
115.524
99.992
77.136
71.147
69.182
65.187
51.464
34.083
34.064
24.065
17.983
17.189
12.671
12.249
11.857
200
180
160
140
120
100
80
60
40
20
ppm

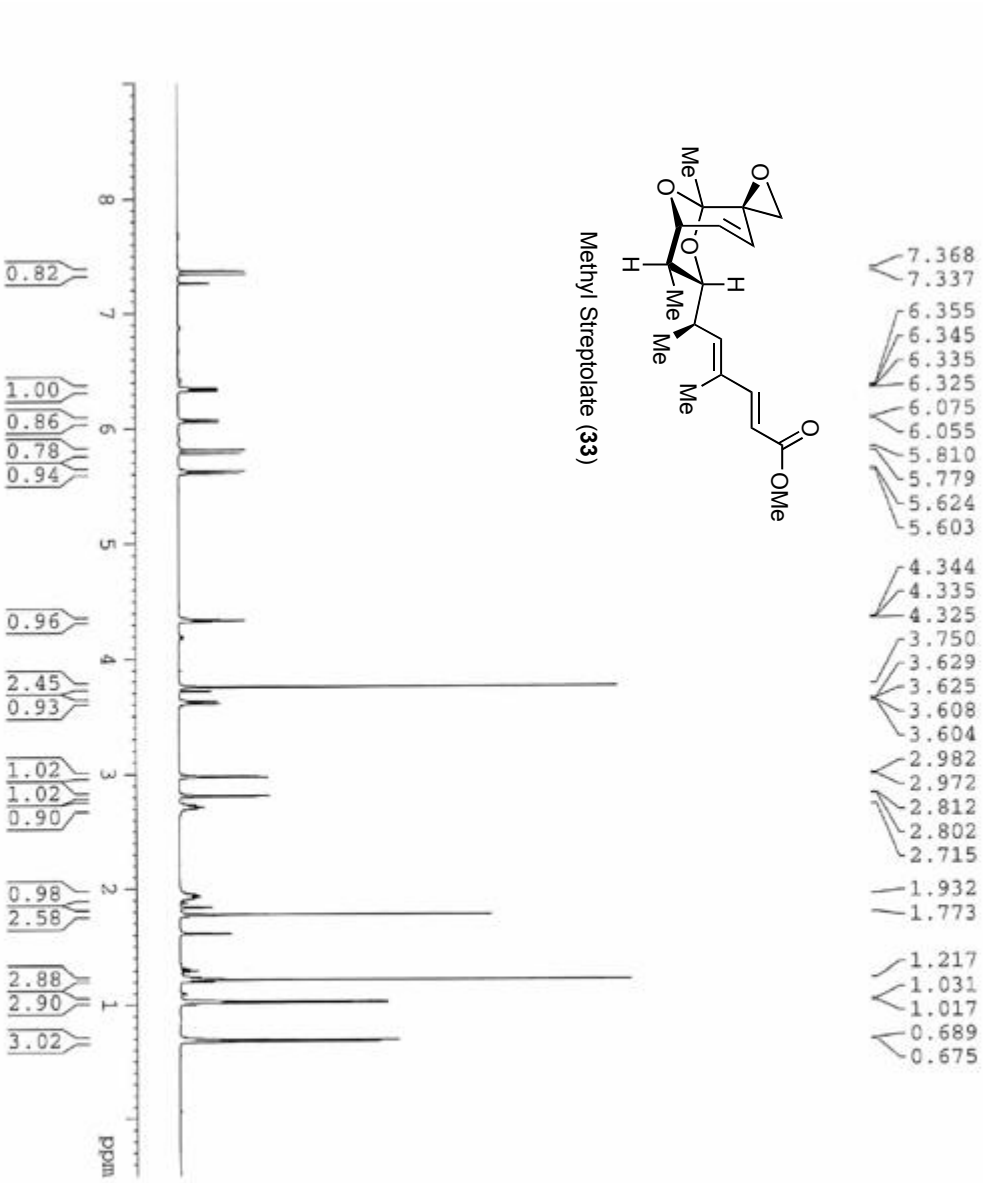


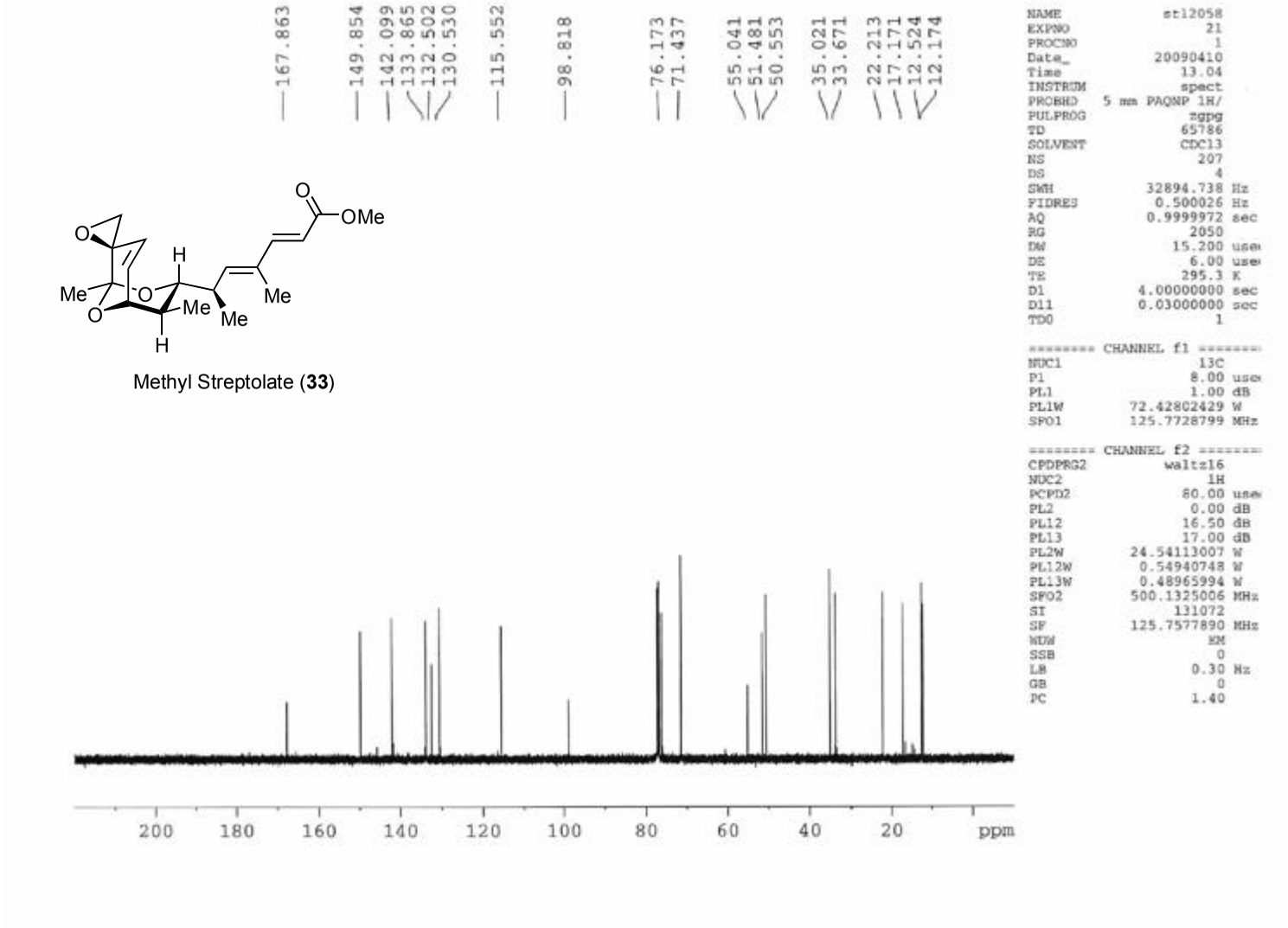

```
NAME              st12056
EXPNO                   1
PROCNO                  1
Date_            20090409
Time                14.37
INSTRUM             spect
PROBND   5 mm PAQNP 1H/
PULPROG                 zg
TD                  44998
SOLVENT             CDC13
NS                      8
DS                      0
SWH           7500.000 Hz
FIDRES        0.166674 Hz
AQ            2.9999166 sec
RG                     64
DW              66.667 use
DE               71.43 use
TE               295.3 K
D1           3.00000000 sec
TD0                     1

======== CHANNEL f1 =======
NUC1                   1H
P1                 12.00 use
PL1                 0.00 dB
PL1W        24.54113007 W
SFO1        500.1335009 MHz
SI                  16384
SF          500.1300078 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



68

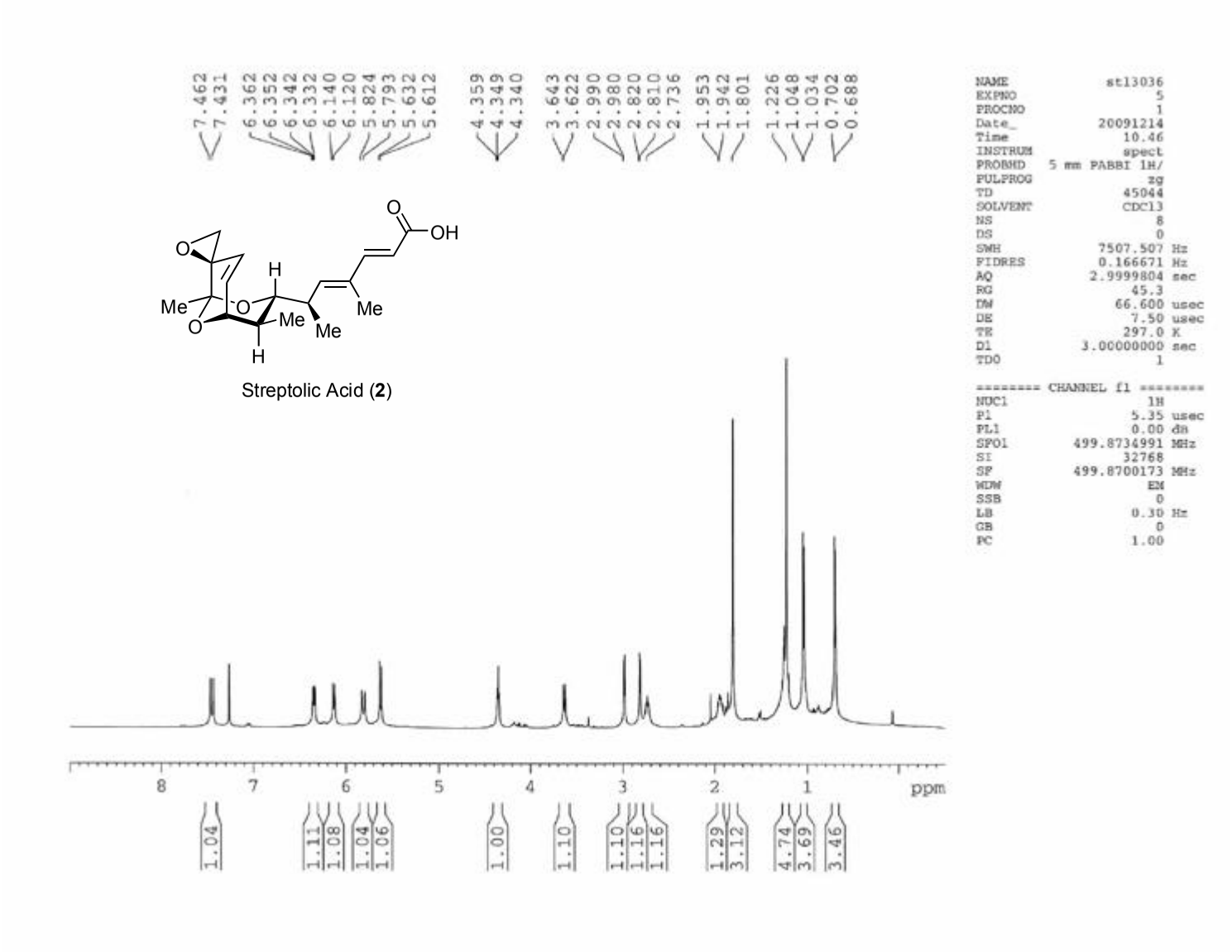
NAME	st12056
EXPNO	2
PROCNO	1
Date_	20090409
Time	14.44
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg
TD	65786
SOLVENT	CDCl3
NS	175
DS	4
SWH	32894.738 Hz
FIDRES	0.500026 Hz
AQ	0.9999972 sec
RG	2050
DW	15.200 use
DE	6.00 use
TE	296.0 K
D1	4.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
NUC1	13C
P1	8.00 use
PL1	1.00 dB
PL1W	72.42802429 W
SFO1	125.7728799 MHz
========	CHANNEL f2 ========
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 use
PL2	0.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	24.54113007 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325006 MHz
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

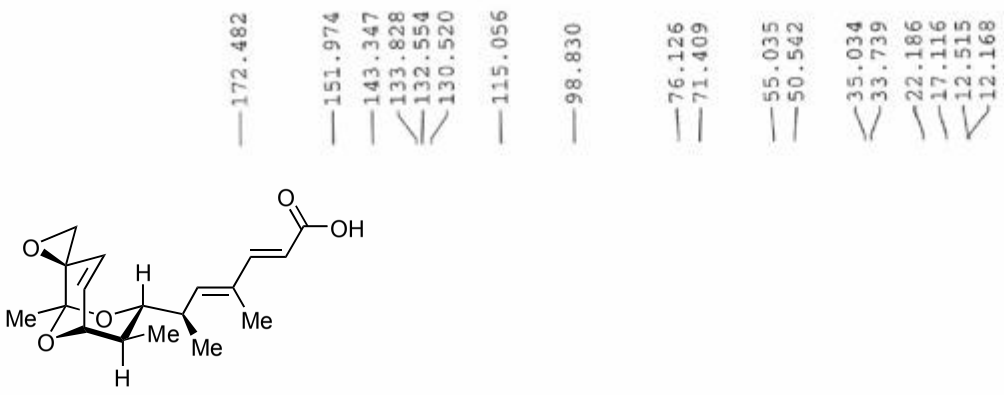

Methyl Streptolate (33)
7.368
7.337
6.355
6.345
6.335
6.325
6.075
6.055
5.810
5.779
5.624
5.603
4.344
4.335
4.325
3.750
3.629
3.625
3.608
3.604
2.982
2.972
2.812
2.802
2.715
1.932
1.773
1.217
1.031
1.017
0.689
0.675
0.82
1.00
0.86
0.78
0.94
0.96
2.45
0.93
1.02
1.02
0.90
0.98
2.58
2.88
2.90
3.02
ppm



Methyl Streptolate (**33**)

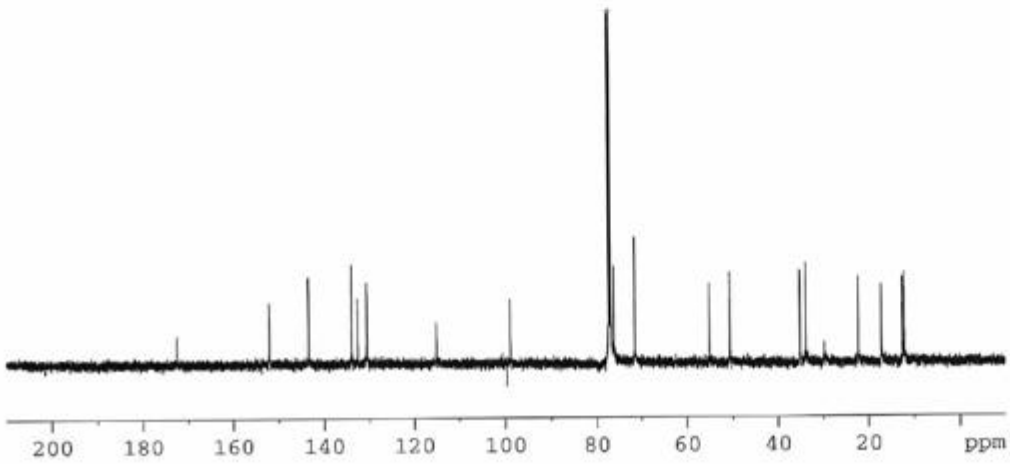
NAME	st12058	
EXPNO	21	
PROCNO	1	
Date_	20090410	
Time	13.04	
INSTRUM	spect	
PROBHD	5 mm PAQNP 1H/	
PULPROG	zgpg	
TD	65786	
SOLVENT	CDCl3	
NS	207	
DS	4	
SWH	32894.738	Hz
FIDRES	0.500026	Hz
AQ	0.9999972	sec
RG	2050	
DW	15.200	use
DE	6.00	use
TE	295.3	K
D1	4.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	8.00	use
PL1	1.00	dB
PL1W	72.42802429	W
SFO1	125.7728799	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	use
PL2	0.00	dB
PL12	16.50	dB
PL13	17.00	dB
PL2W	24.54113007	W
PL12W	0.54940748	W
PL13W	0.48965994	W
SFO2	500.1325006	MHz
SI	131072	
SF	125.7577890	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.40	

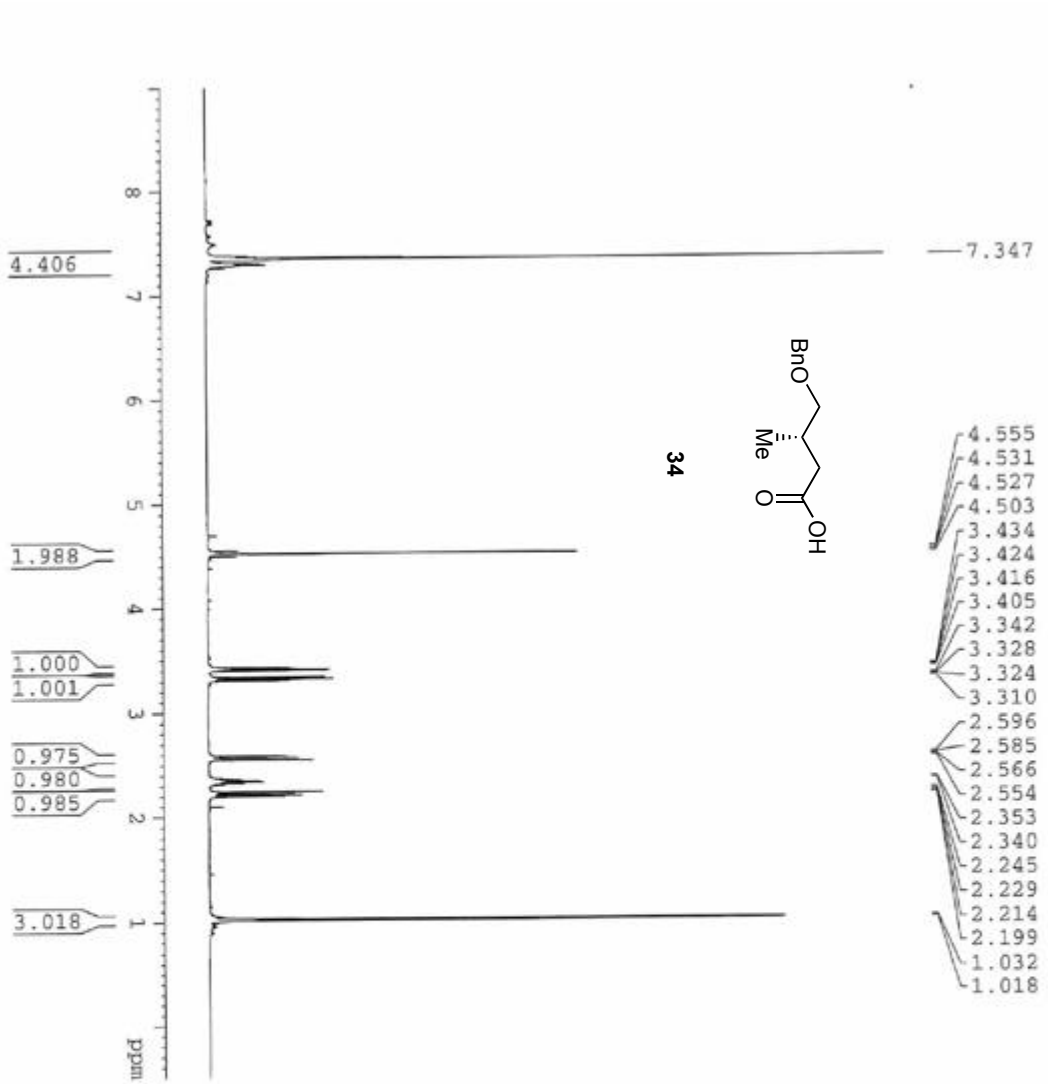

7.462
7.431
6.362
6.352
6.342
6.332
6.140
6.120
5.824
5.793
5.632
5.612
4.359
4.349
4.340
3.643
3.622
2.990
2.980
2.820
2.810
2.736
1.953
1.942
1.801
1.226
1.048
1.034
0.702
0.688
O
OH
O
H
Me
O
Me
Me
O
Me
H
Streptolic Acid (2)
NAME st13036
EXPNO 5
PROCNO 1
Date_ 20091214
Time 10.46
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg
TD 45044
SOLVENT CDCl3
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 45.3
DW 66.600 usec
DE 7.50 usec
TE 297.0 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.35 usec
PL1 0.00 dB
SFO1 499.8734991 MHz
SI 32768
SF 499.8700173 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8
7
6
5
4
3
2
1
ppm
1.04
1.11
1.08
1.04
1.06
1.00
1.10
1.10
1.16
1.16
1.29
3.12
4.74
3.69
3.46

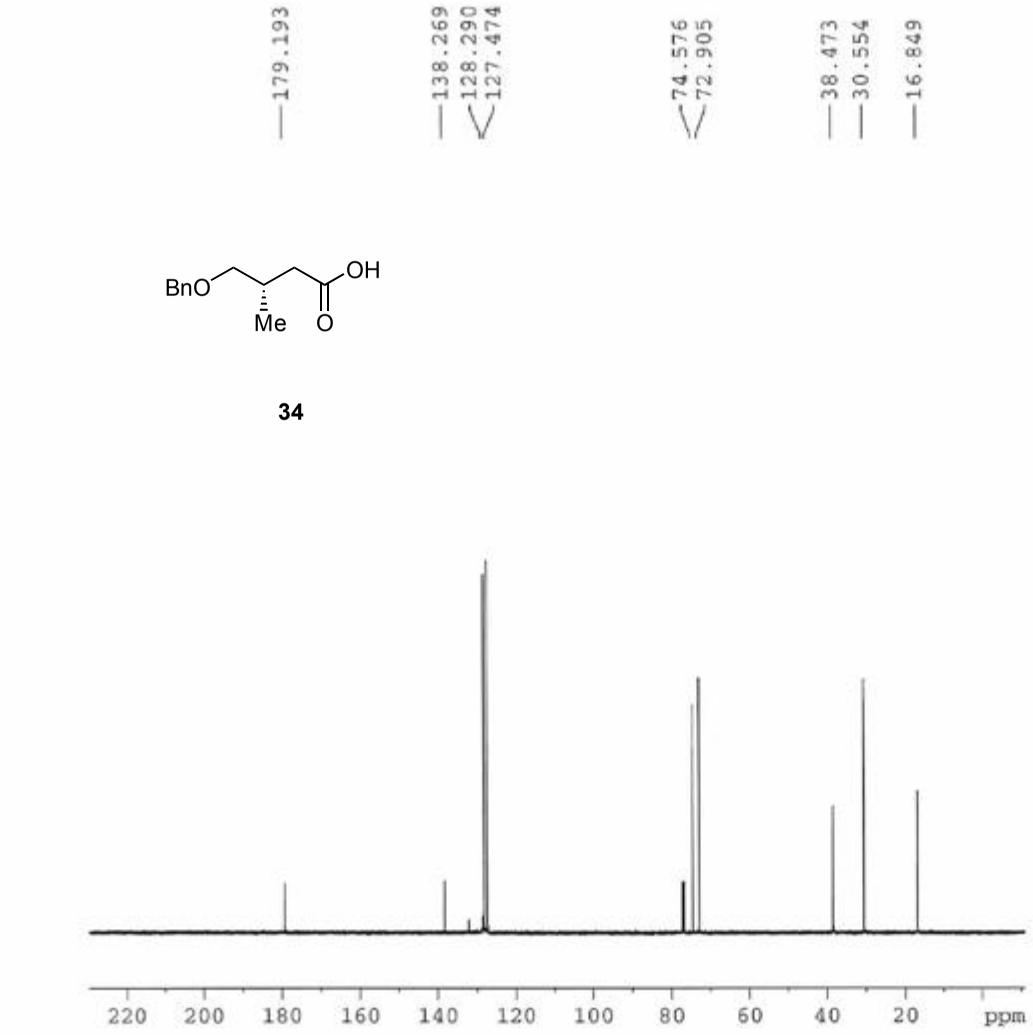


Streptolic Acid (**2**)

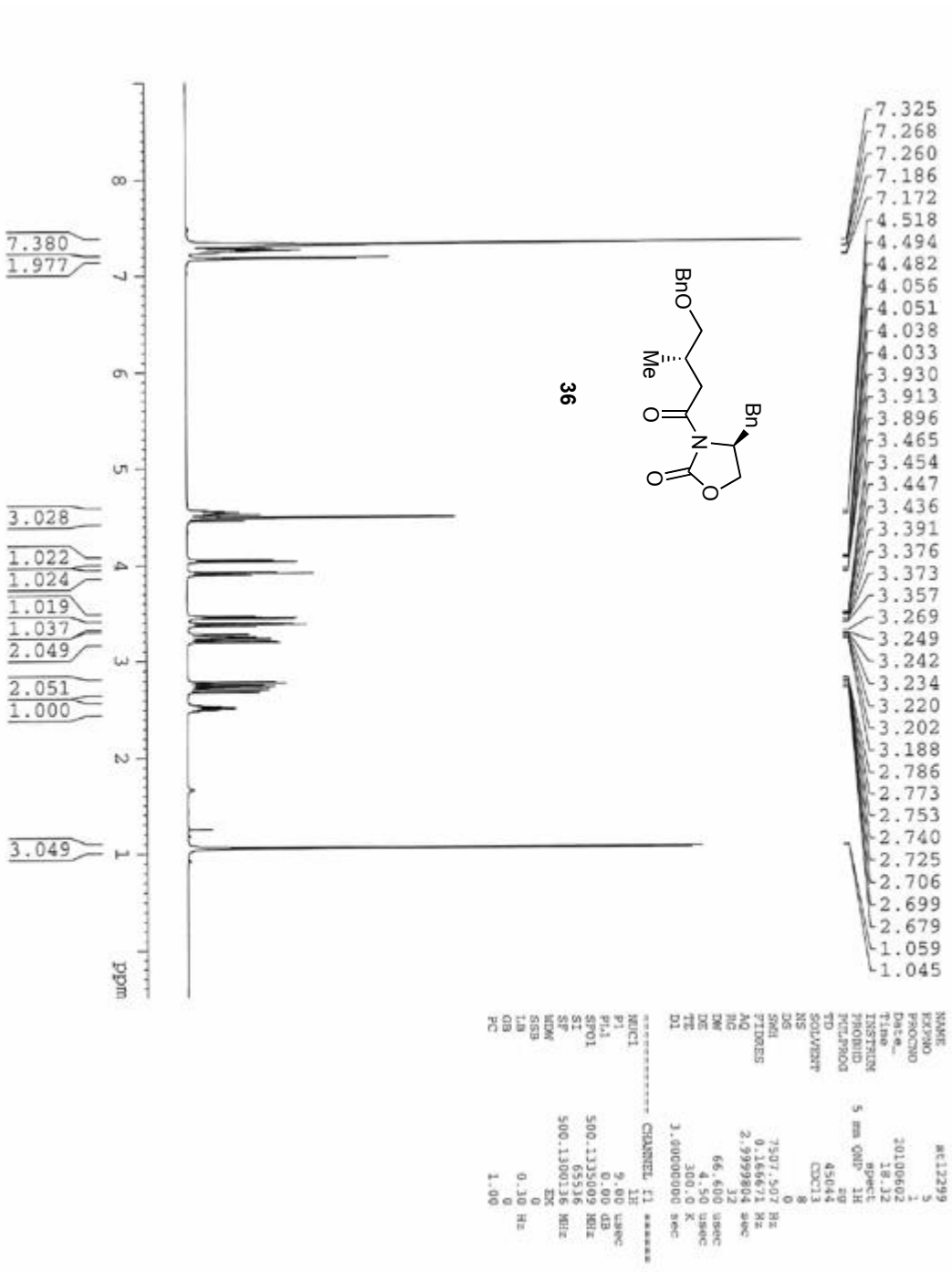
NAME	st13036
EXPNO	51
PROCNO	1
Date_	20091215
Time	11.01
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	55552
SOLVENT	CDCl3
NS	641
DS	4
SWH	27777.777 Hz
FIDRES	0.500032 Hz
AQ	0.9999860 sec
RG	16384
DW	18.000 usec
DE	7.50 usec
TE	300.0 K
D1	4.00000000 sec
d11	0.03000000 sec
======	CHANNEL f1 ======
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7703148 MHz
======	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7577924 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

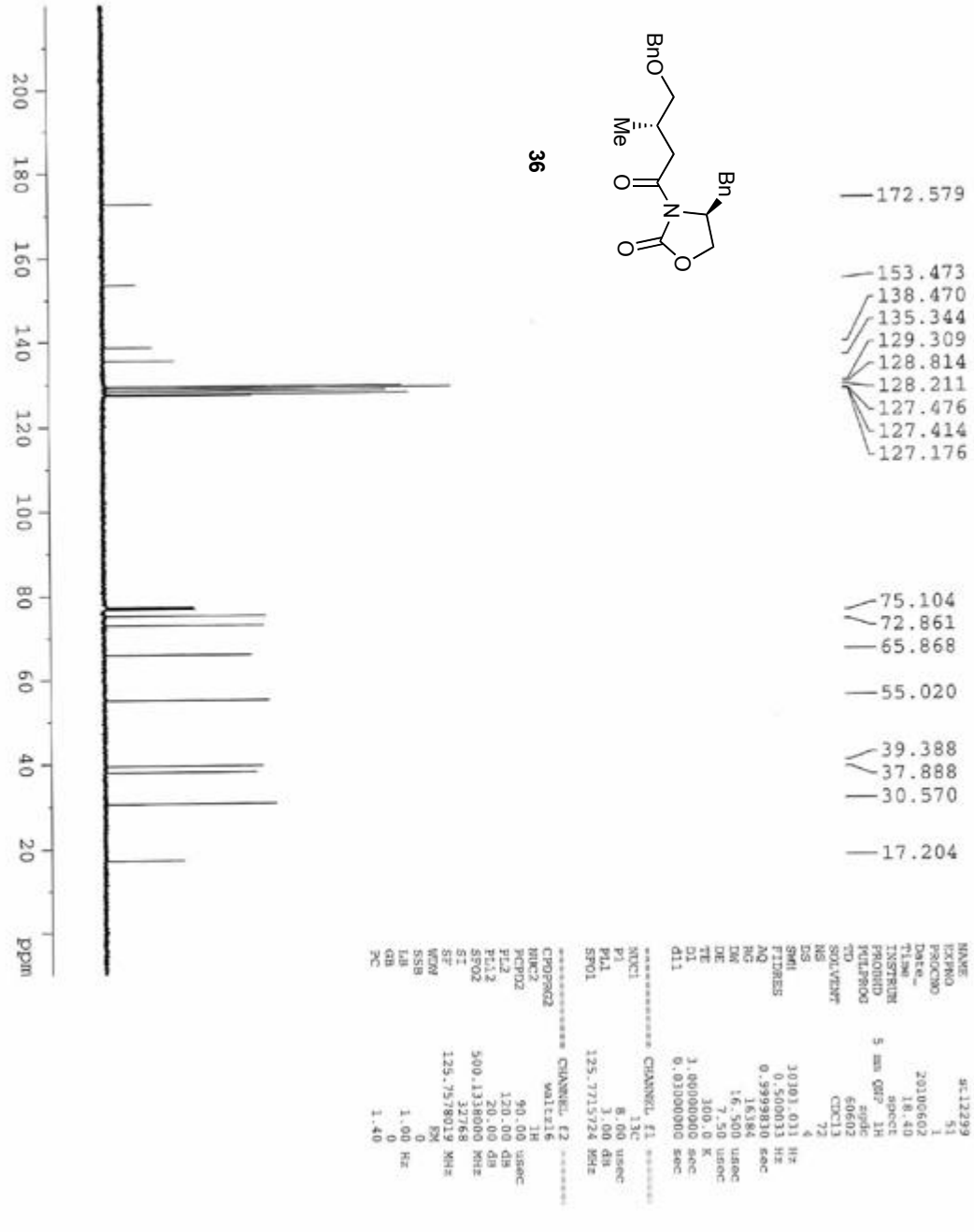


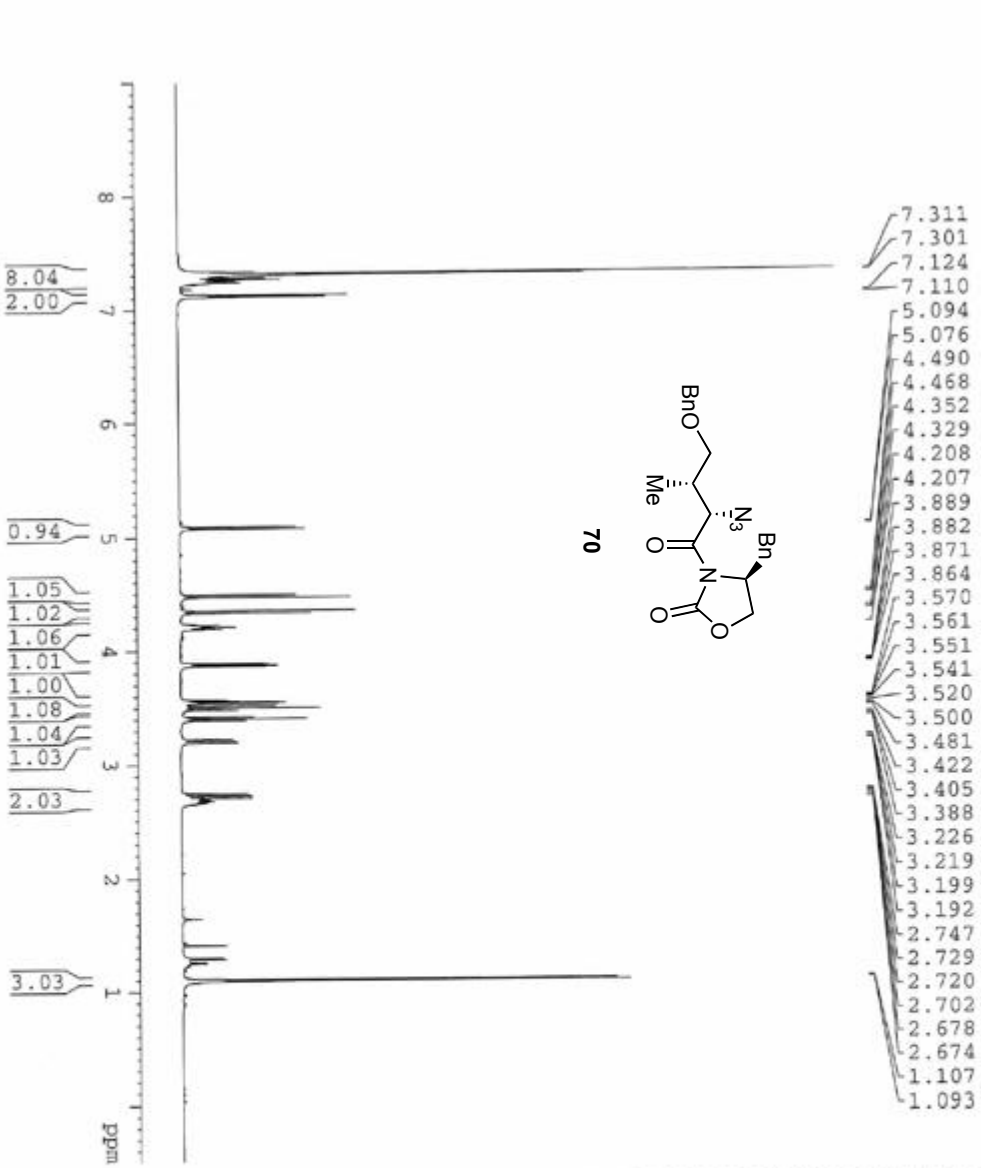

7.347
4.555
4.531
4.527
4.503
3.434
3.424
3.416
3.405
3.342
3.328
3.324
3.310
2.596
2.585
2.566
2.554
2.353
2.340
2.245
2.229
2.214
2.199
1.032
1.018
BnO
Me
O
OH
34
4.406
1.988
1.000
1.001
0.975
0.980
0.985
3.018
ppm

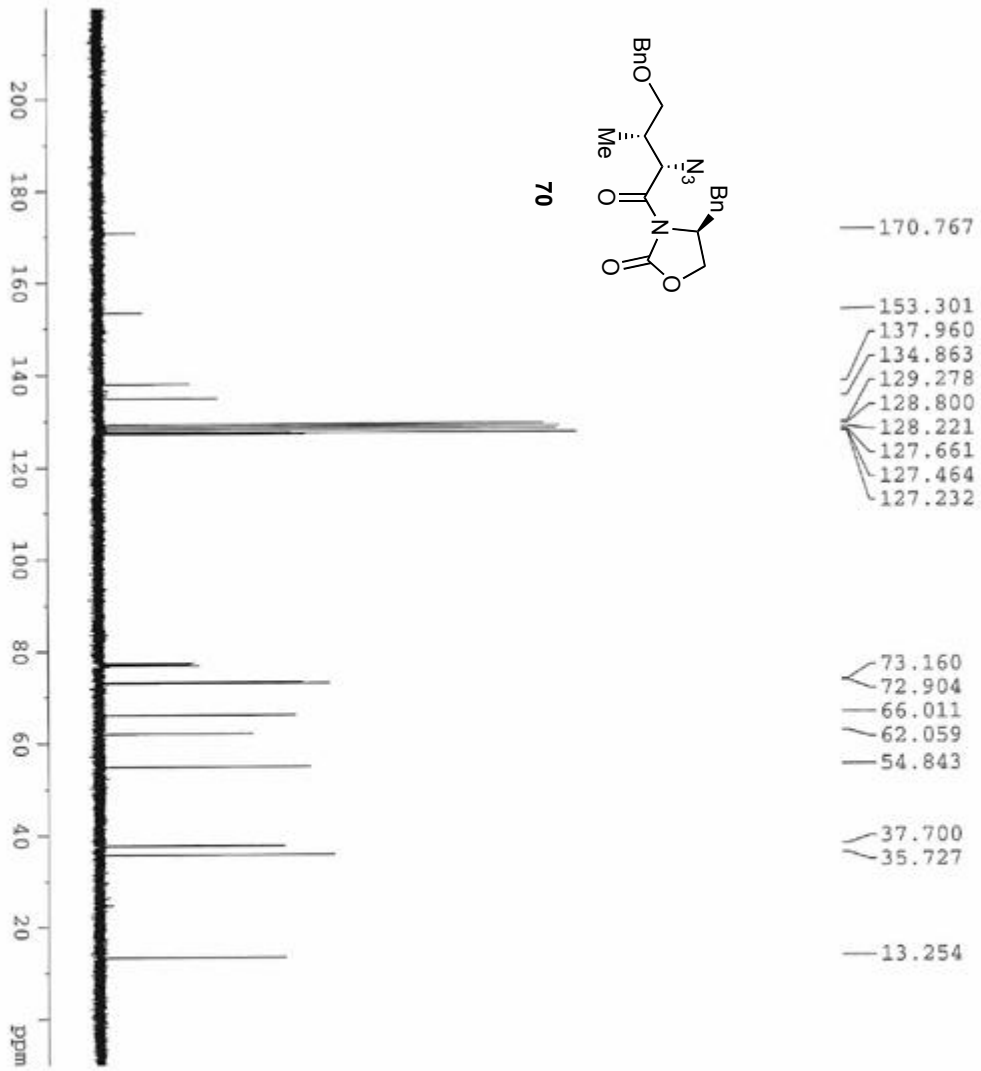


NAME	at12270
EXPNO	51
PROCNO	1
Date_	20100602
Time	18.24
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	40
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	8192
DW	16.560 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
========== CHANNEL f1 ======	
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
========== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7578019 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

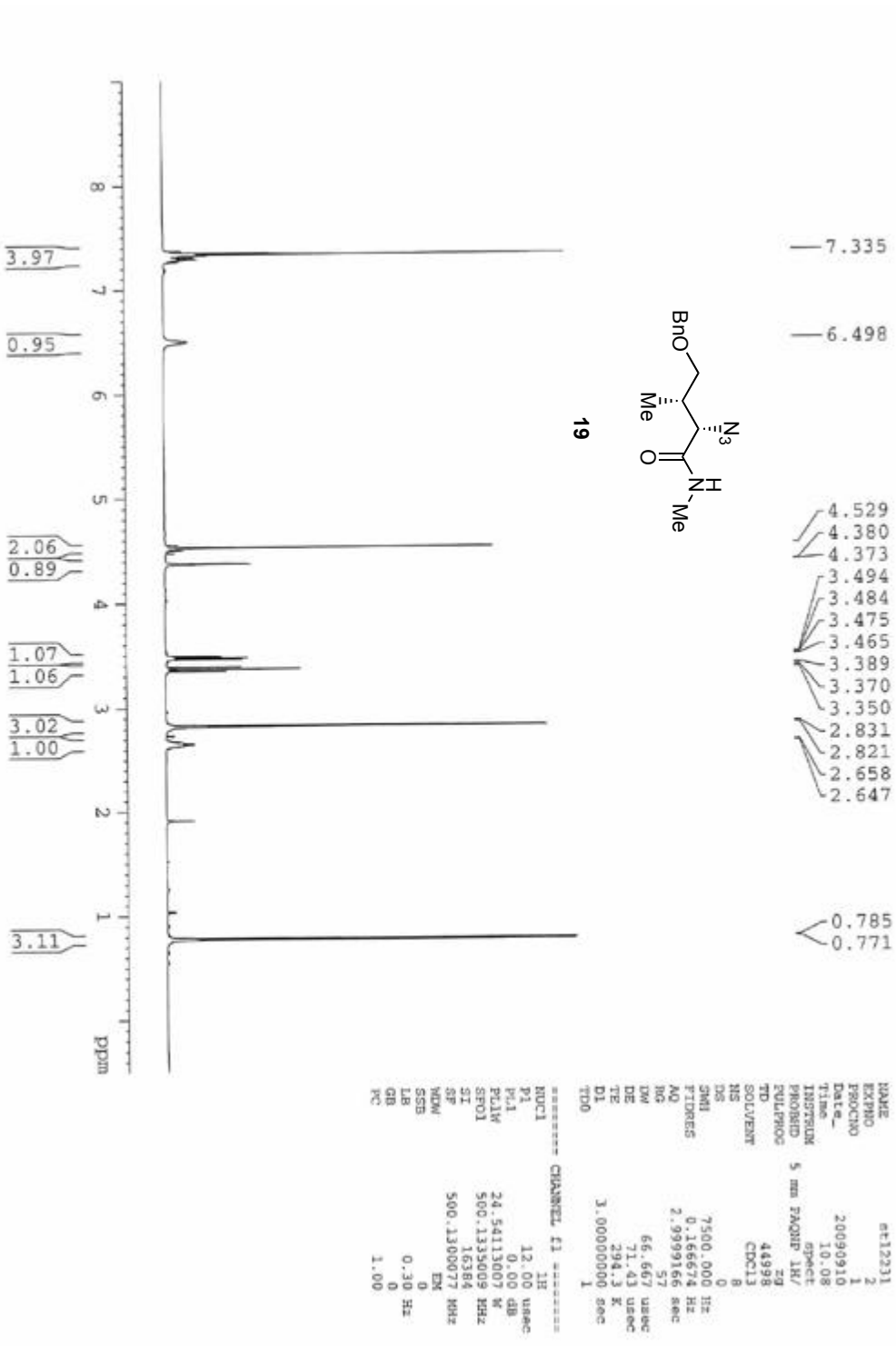

7.380
1.977
3.028
1.022
1.024
1.019
1.037
2.049
2.051
1.000
3.049
ppm
36
BnO
Me
Bn
7.325
7.268
7.260
7.186
7.172
4.518
4.494
4.482
4.056
4.051
4.038
4.033
3.930
3.913
3.896
3.465
3.454
3.447
3.436
3.391
3.376
3.373
3.357
3.269
3.249
3.242
3.234
3.220
3.202
3.188
2.786
2.773
2.753
2.740
2.725
2.706
2.699
2.679
1.059
1.045

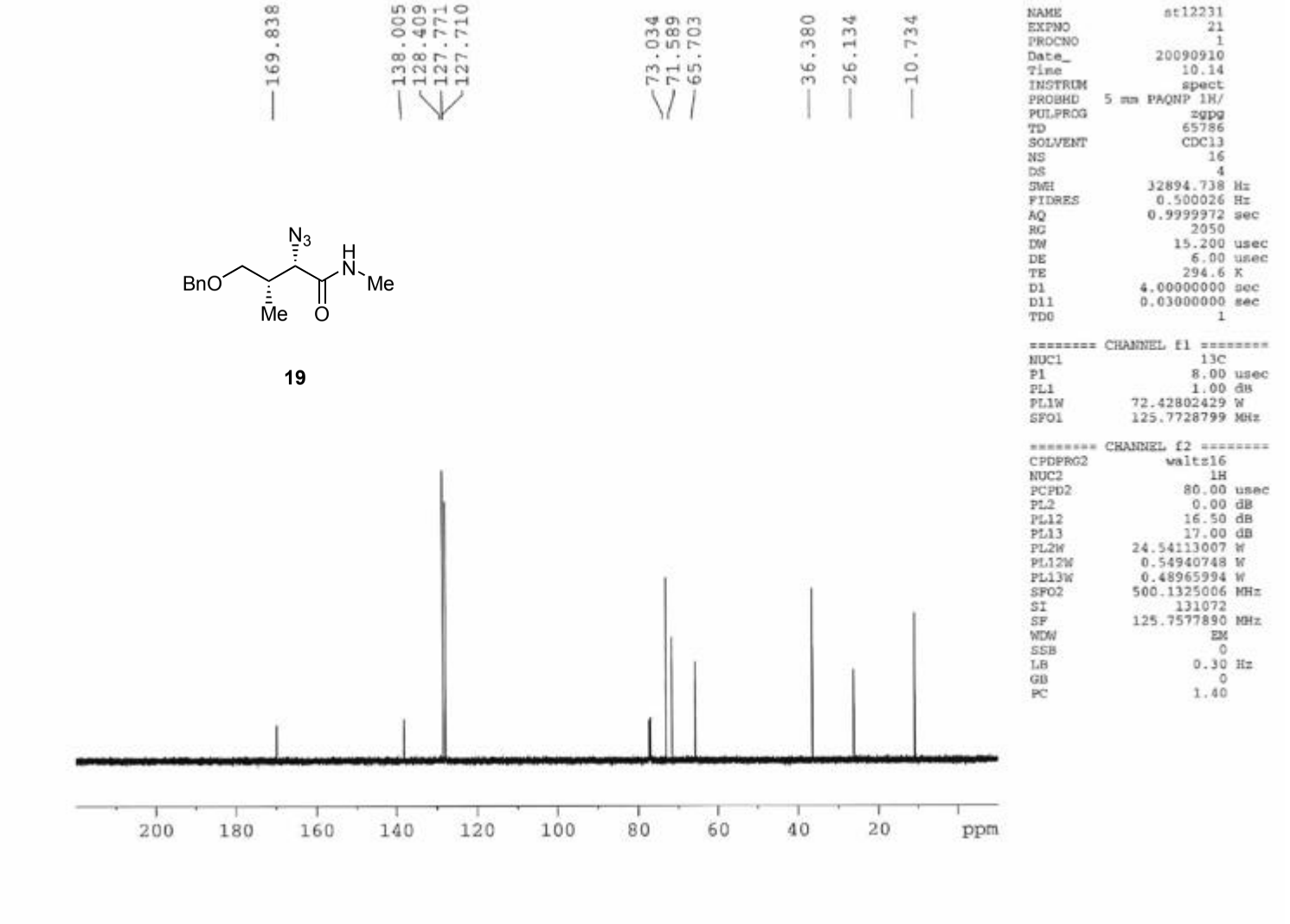

36
BnO
Me
O
N
Bn
O
O
172.579
153.473
138.470
135.344
129.309
128.814
128.211
127.476
127.414
127.176
75.104
72.861
65.868
55.020
39.388
37.888
30.570
17.204
200
180
160
140
120
100
80
60
40
20
ppm

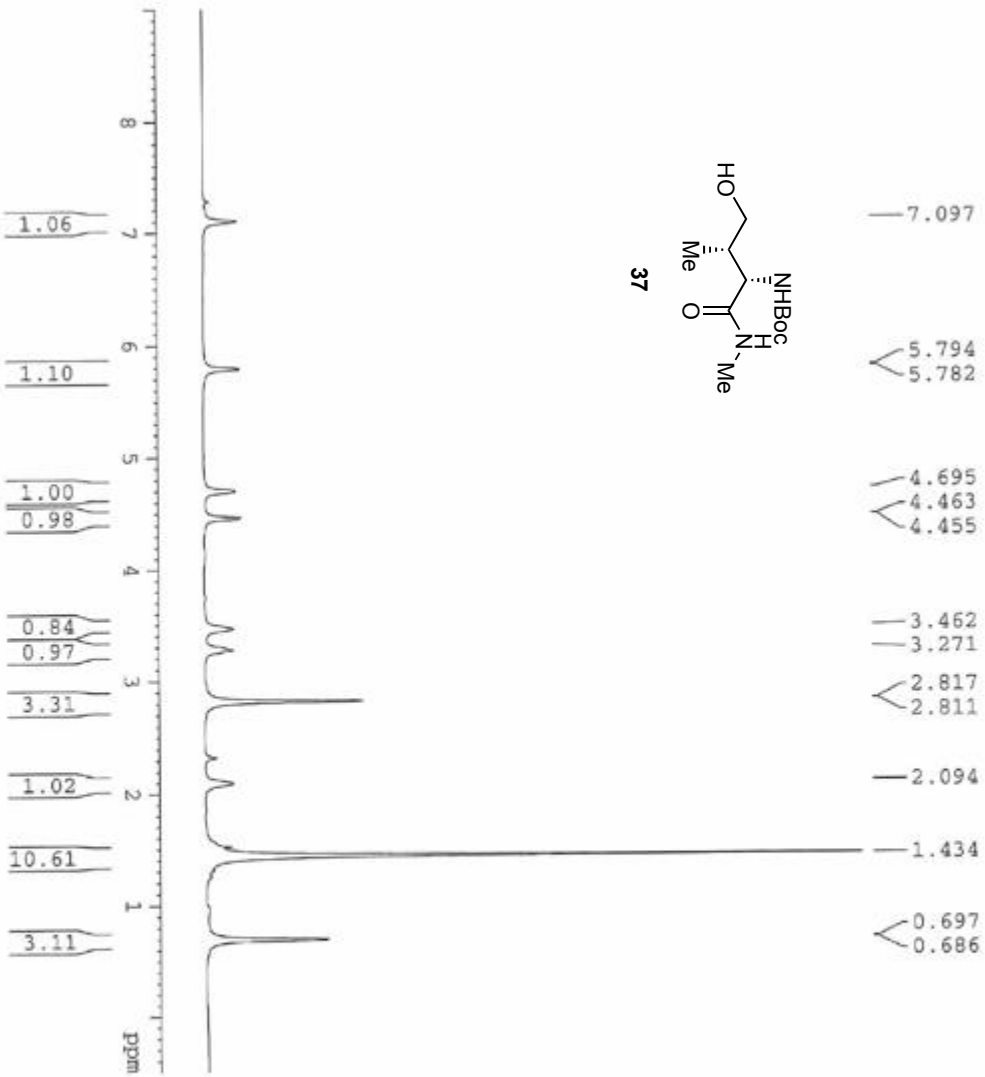

7.311
7.301
7.124
7.110
5.094
5.076
4.490
4.468
4.352
4.329
4.208
4.207
3.889
3.882
3.871
3.864
3.570
3.561
3.551
3.541
3.520
3.500
3.481
3.422
3.405
3.388
3.226
3.219
3.199
3.192
2.747
2.729
2.720
2.702
2.678
2.674
1.107
1.093
BnO
Me
N3
Bn
O
N
O
O
70
8.04
2.00
0.94
1.05
1.02
1.06
1.01
1.00
1.08
1.04
1.03
2.03
3.03
8
7
6
5
4
3
2
1
ppm
NAME st12230
EXPNO 1
PROCNO 1
Date_ 20090909
Time 15.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 50.8
DW 66.667 usec
DE 71.43 usec
TE 294.1 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1325009 MHz
SI 16384
SF 500.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00




```
NAME                                    st12230
EXPNO                                         2
PROCNO                                        1
Date_                               20090909
Time                                    15.18
INSTRUM                                 spect
PROBHD                 5 mm PABBO 1H/
PULPROG                                 zgpg
TD                                     65786
SOLVENT                                CDCl3
NS                                        16
DS                                         4
SWH                                 32894.738 Hz
FIDRES                                0.500026 Hz
AQ                                    0.9999972 sec
RG                                         2050
DW                                    15.200 usec
DE                                     6.00 usec
TE                                     294.5 K
D1                                    4.00000000 sec
D11                                   0.03000000 sec
TD0                                           1

======== CHANNEL f1 ========
NUC1                                        13C
P1                                     8.00 usec
PL1                                    1.00 dB
PL1W                                72.42802429 W
SFO1                                125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                                 waltz16
NUC2                                        1H
PCPD2                                 80.00 usec
PL2                                    0.00 dB
PL12                                  16.50 dB
PL13                                  17.00 dB
PL2W                                24.54113007 W
PL12W                                0.54940748 W
PL13W                                0.48965994 W
SFO2                                500.1325006 MHz
SI                                      131072
SF                                  125.7578005 MHz
WDW                                       EM
SSB                                        0
LB                                      0.30 Hz
GB                                         0
PC                                      1.40
```

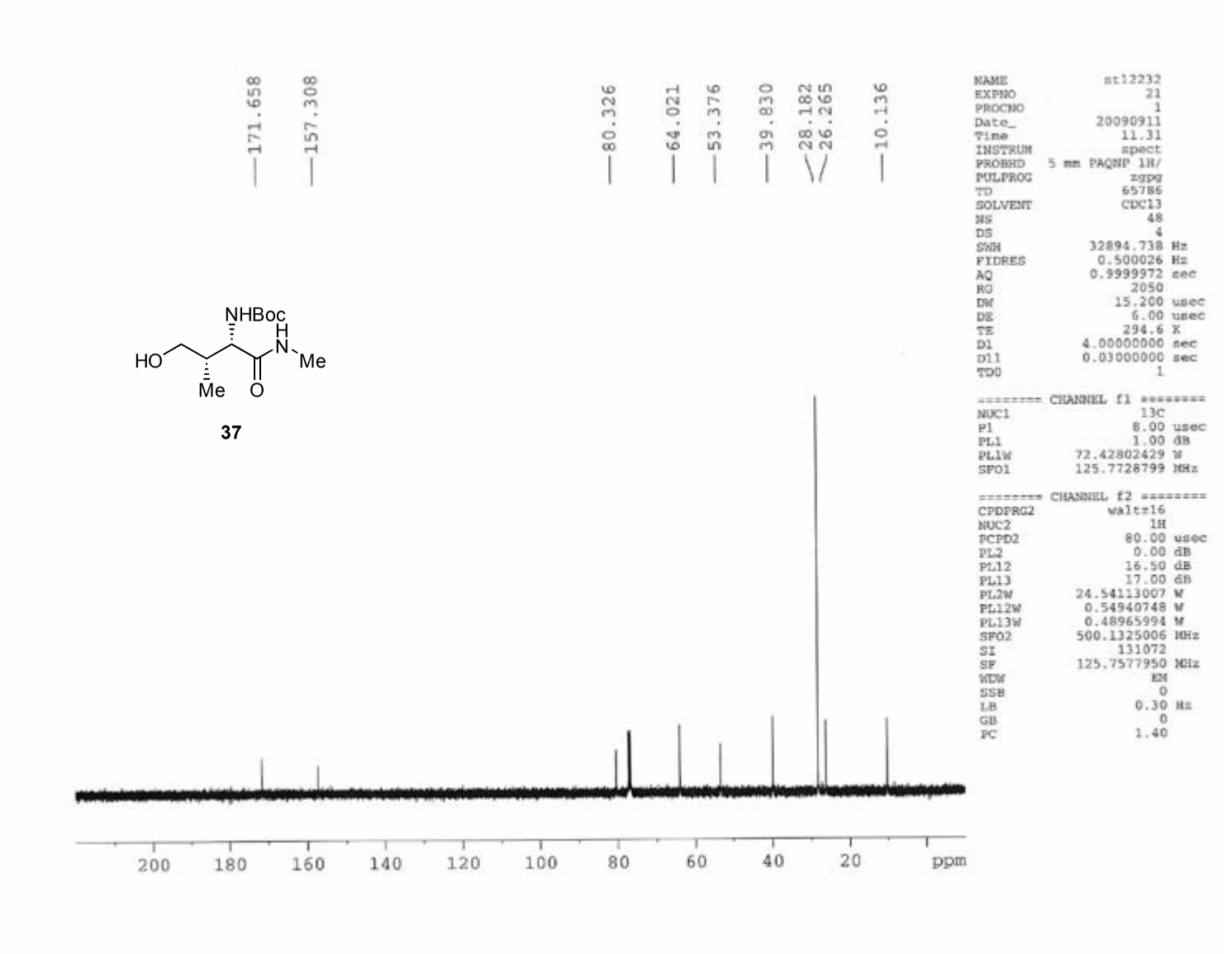

7.335
6.498
4.529
4.380
4.373
3.494
3.484
3.475
3.465
3.389
3.370
3.350
2.831
2.821
2.658
2.647
0.785
0.771
BnO
Me
N3
O
H
N
Me
19
3.97
0.95
2.06
0.89
1.07
1.06
3.02
1.00
3.11
ppm
NAME st12231
EXPNO 2
PROCNO 1
Date_ 20090910
Time 10.08
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 57
DW 66.667 usec
DE 71.43 usec
TE 294.3 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

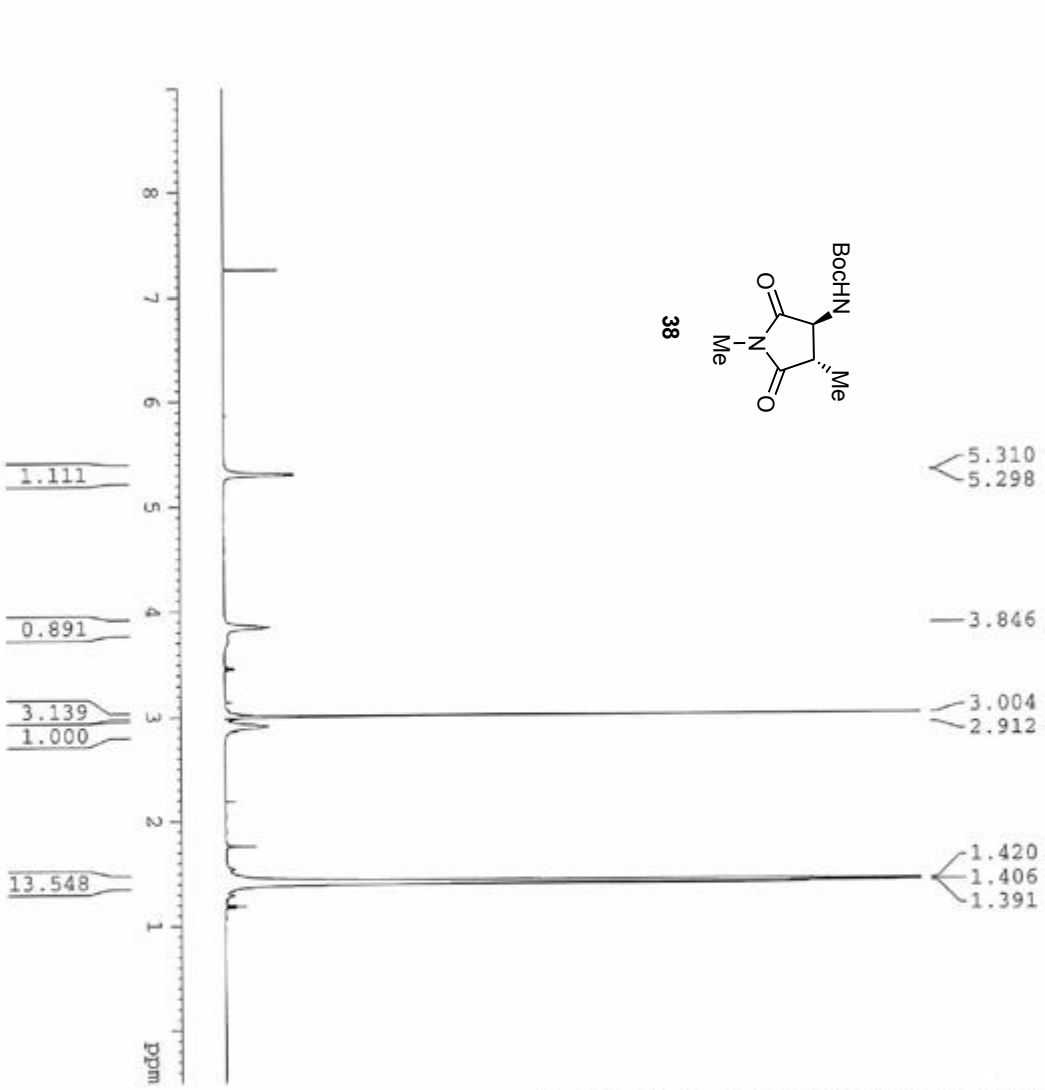

169.838
138.005
128.409
127.771
127.710
73.034
71.589
65.703
36.380
26.134
10.734
N3
H
N
Me
BnO
Me
O
19
200
180
160
140
120
100
80
60
40
20
ppm
NAME st12231
EXPNO 21
PROCNO 1
Date_ 20090910
Time 10.14
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 16
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 294.6 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577890 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

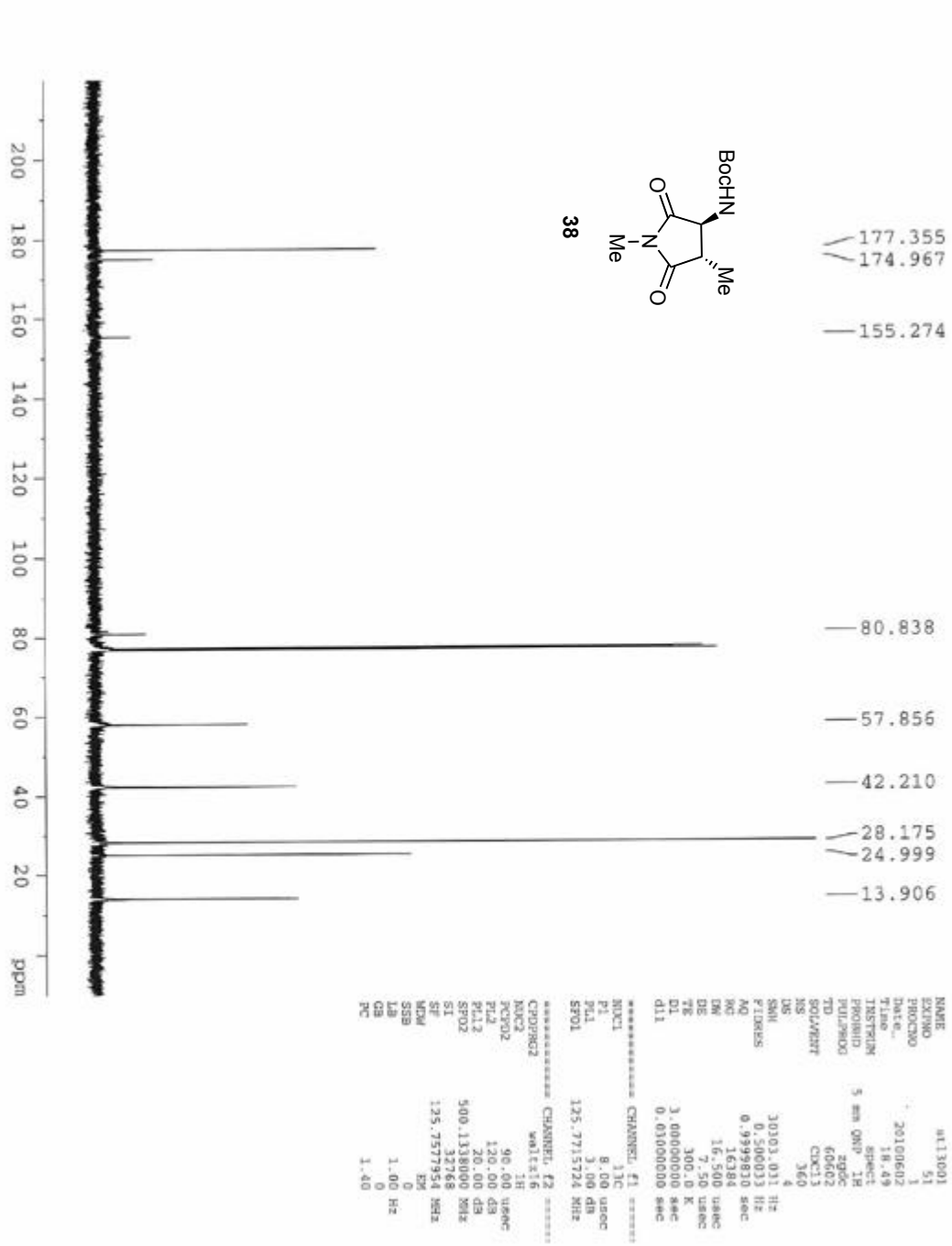


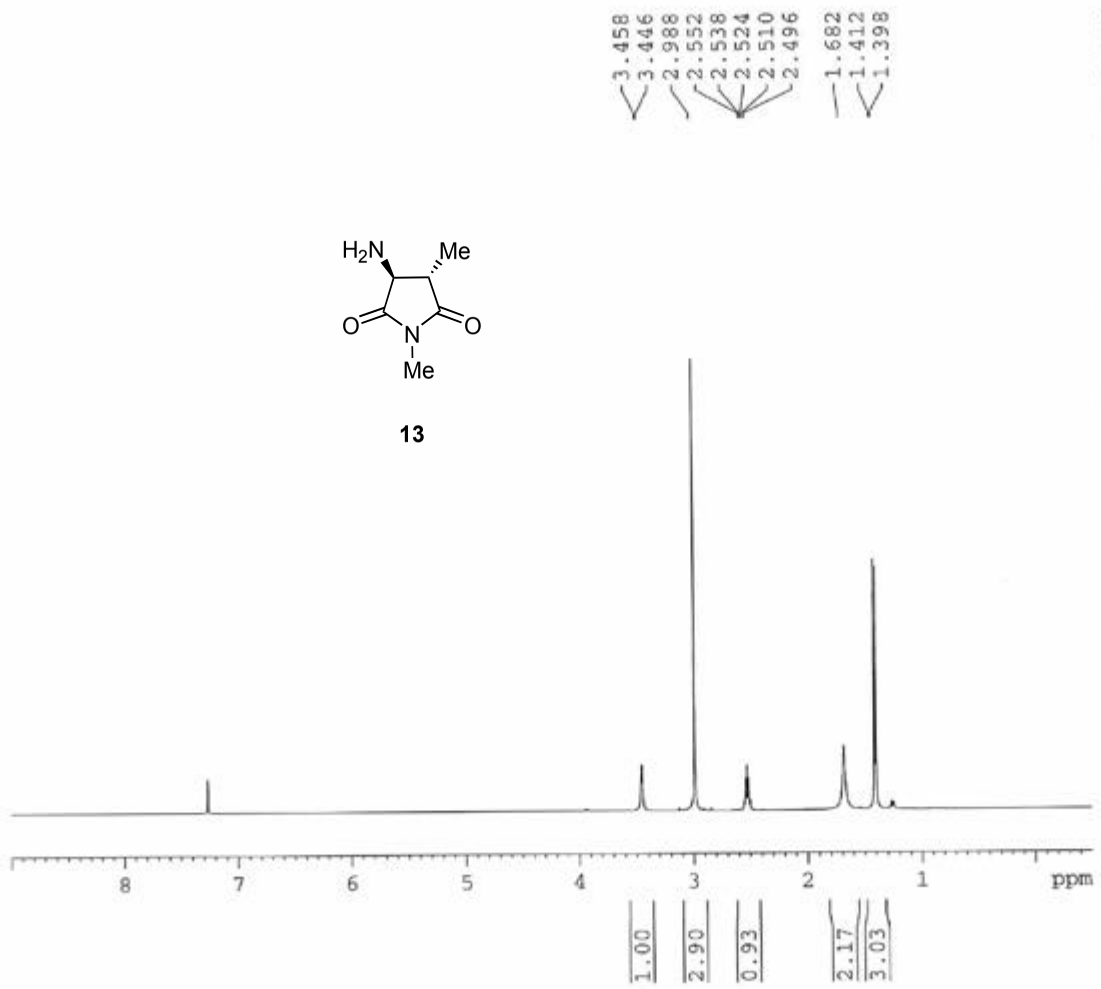
NAME st12232
EXPNO 2
PROCNO 1
Date_ 20090911
Time 11.24
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 45.2
DW 66.667 usec
DE 71.43 usec
TE 294.2 K
D1 3.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

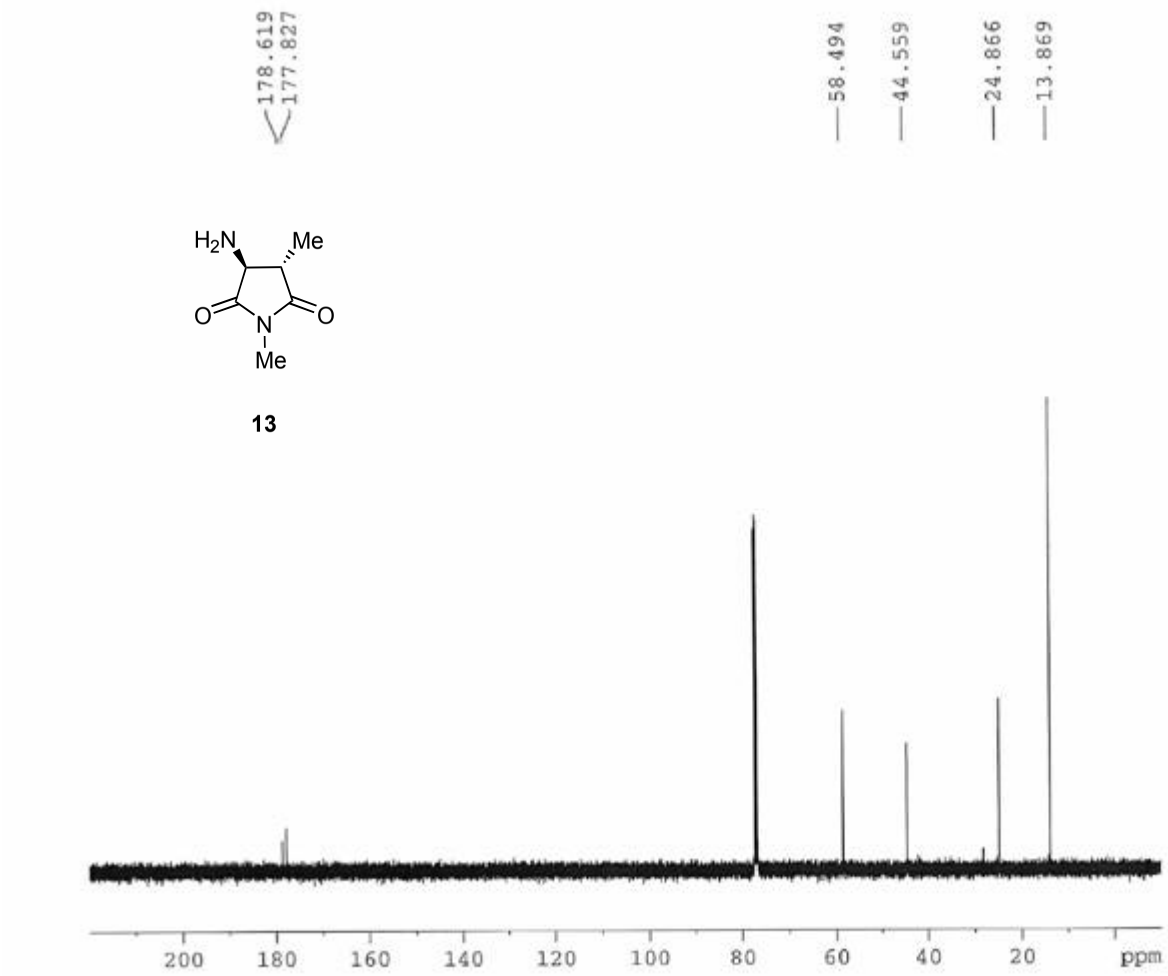

171.658
157.308
80.326
64.021
53.376
39.830
28.182
26.265
10.136
NHBoc
H
N
HO
Me
Me
O
37
200
180
160
140
120
100
80
60
40
20
ppm
NAME st12232
EXPNO 21
PROCNO 1
Date_ 20090911
Time 11.31
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 48
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 usec
DE 6.00 usec
TE 294.6 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577950 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40


38
BocHN
Me
N
Me
O
O
5.310
5.298
3.846
3.004
2.912
1.420
1.406
1.391
1.111
0.891
3.139
1.000
13.548
ppm

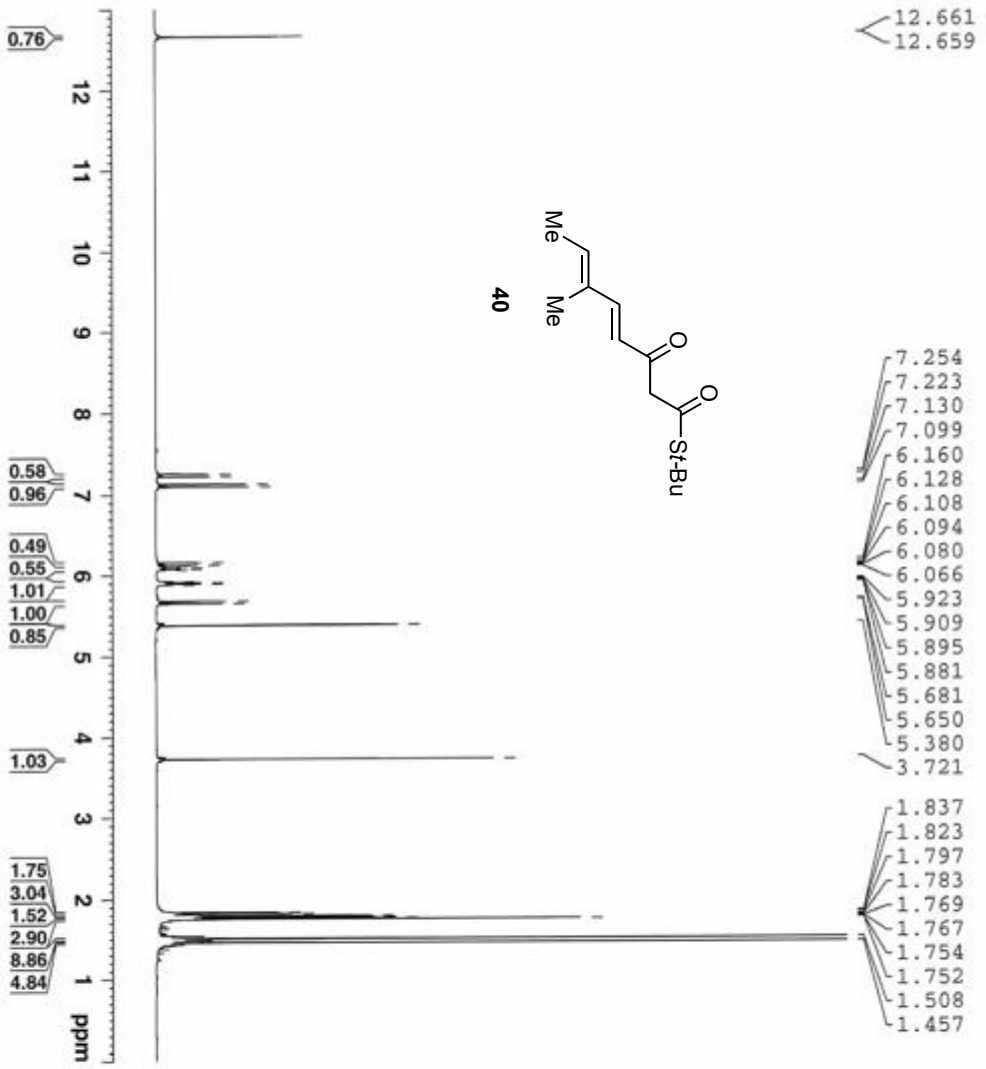

BocHN
Me
N
Me
O
O
38
177.355
174.967
155.274
80.838
57.856
42.210
28.175
24.999
13.906
200
180
160
140
120
100
80
60
40
20
ppm

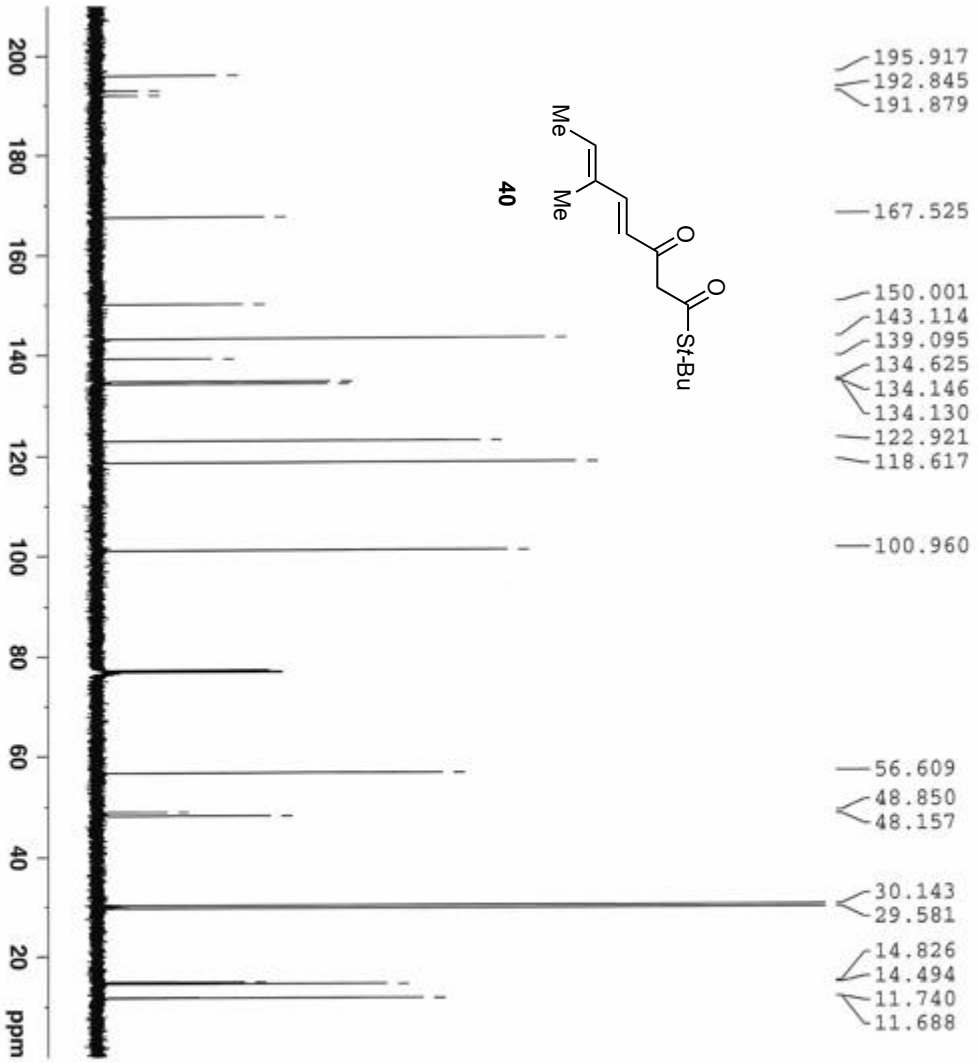


NAME	st12247
EXPNO	1
PROCNO	1
Date_	20090920
Time	12.57
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zg
TD	44998
SOLVENT	CDCl3
NS	8
DS	0
SWH	7500.000 Hz
FIDRES	0.166674 Hz
AQ	2.9999166 sec
RG	256
DW	66.667 usec
DE	71.43 usec
TE	294.1 K
D1	3.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	12.00 usec
PL1	0.00 dB
PL1W	24.54113007 W
SFO1	500.1335009 MHz
SI	16384
SF	500.1300076 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

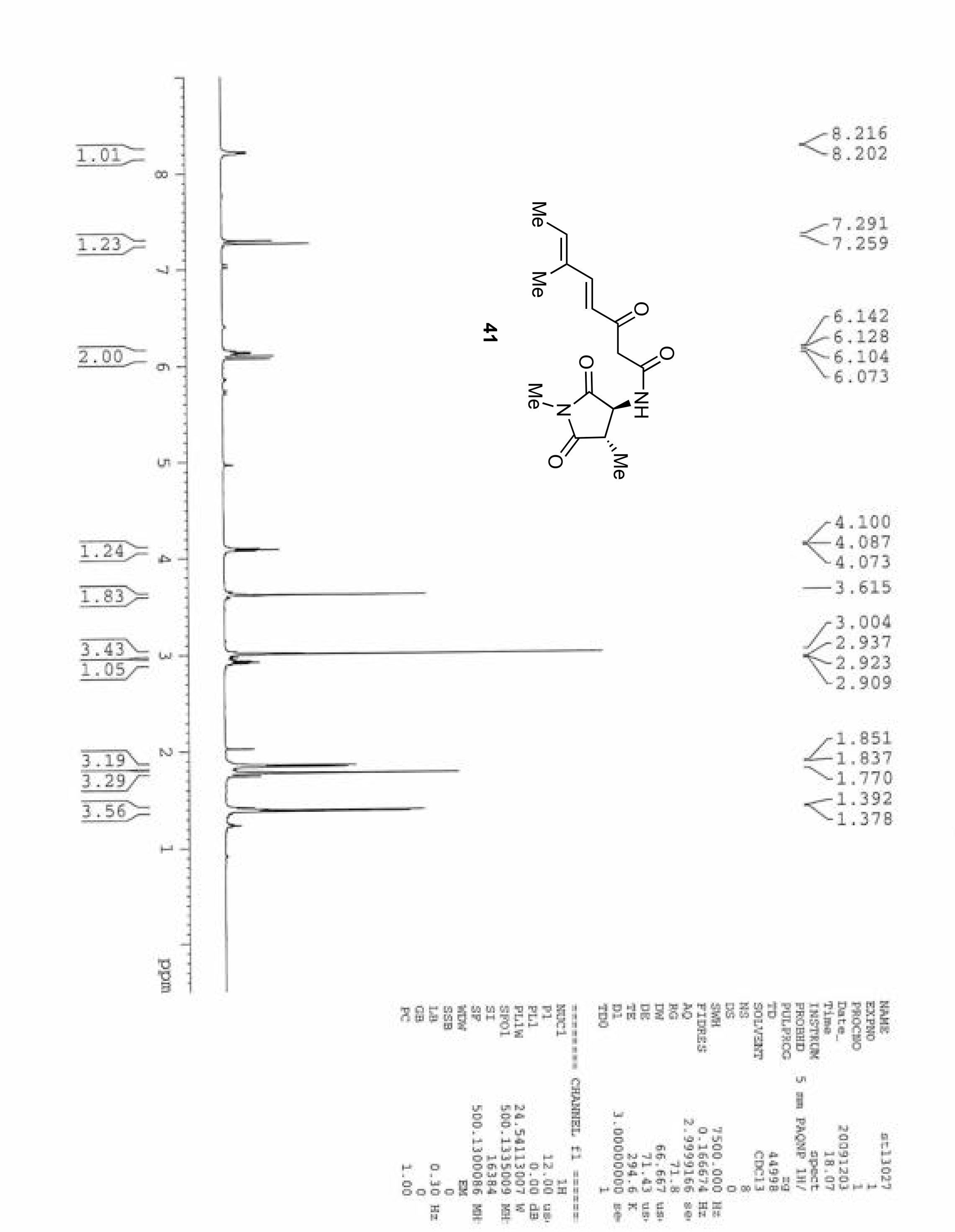


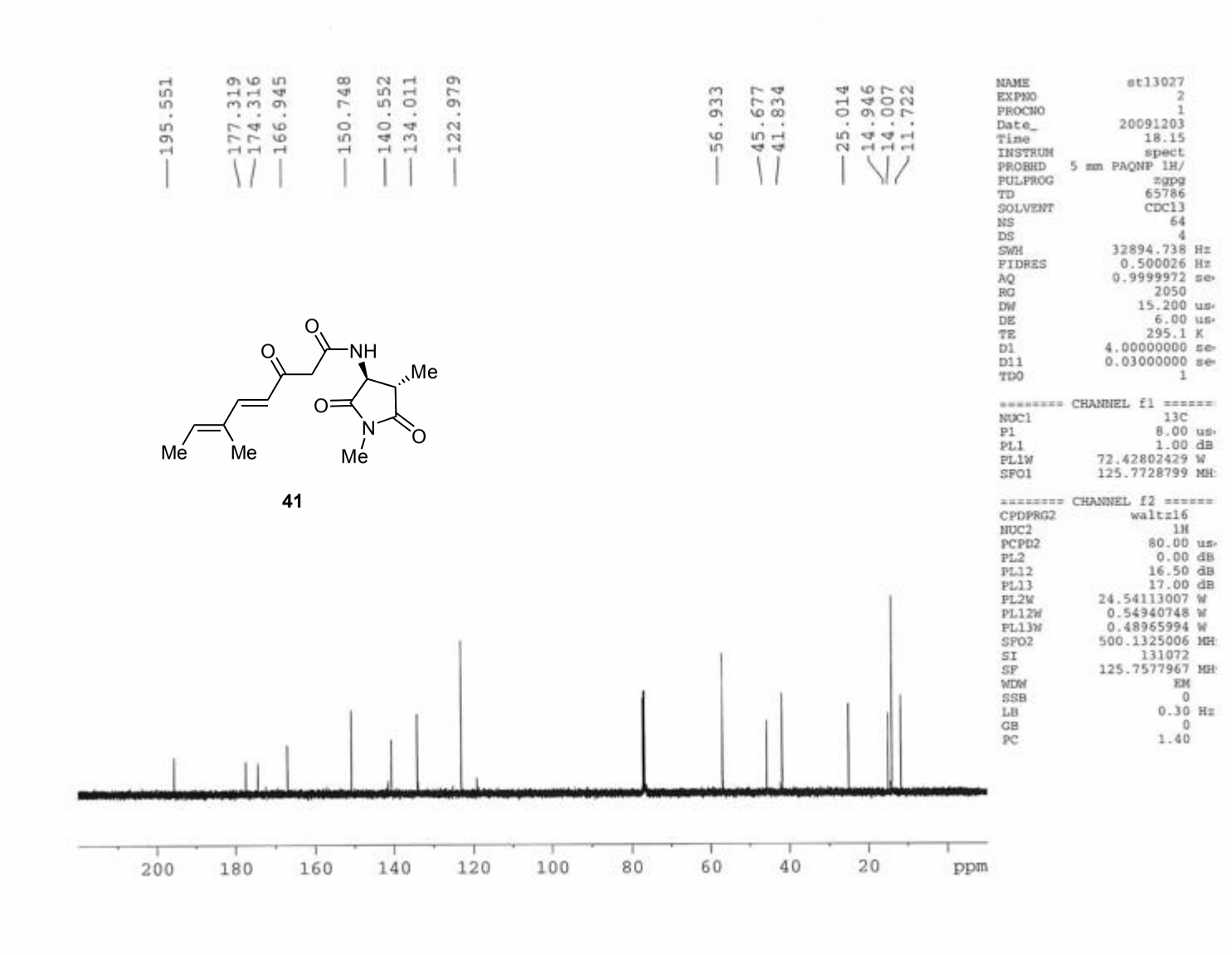
NAME	st12235
EXPNO	2
PROCNO	1
Date_	20090913
Time	13.30
INSTRUM	spect
PROBHD	5 mm PAQNP 1H/
PULPROG	zgpg
TD	65786
SOLVENT	CDCl3
NS	160
DS	4
SWH	32894.738 Hz
FIDRES	0.500026 Hz
AQ	0.9999972 sec
RG	2050
DW	15.200 usec
DE	6.00 usec
TE	295.1 K
D1	4.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.00 usec
PL1	1.00 dB
PL1W	72.42802429 W
SFO1	125.7728799 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	16.50 dB
PL13	17.00 dB
PL2W	24.54113007 W
PL12W	0.54940748 W
PL13W	0.48965994 W
SFO2	500.1325006 MHz
SI	131072
SF	125.7577890 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.40

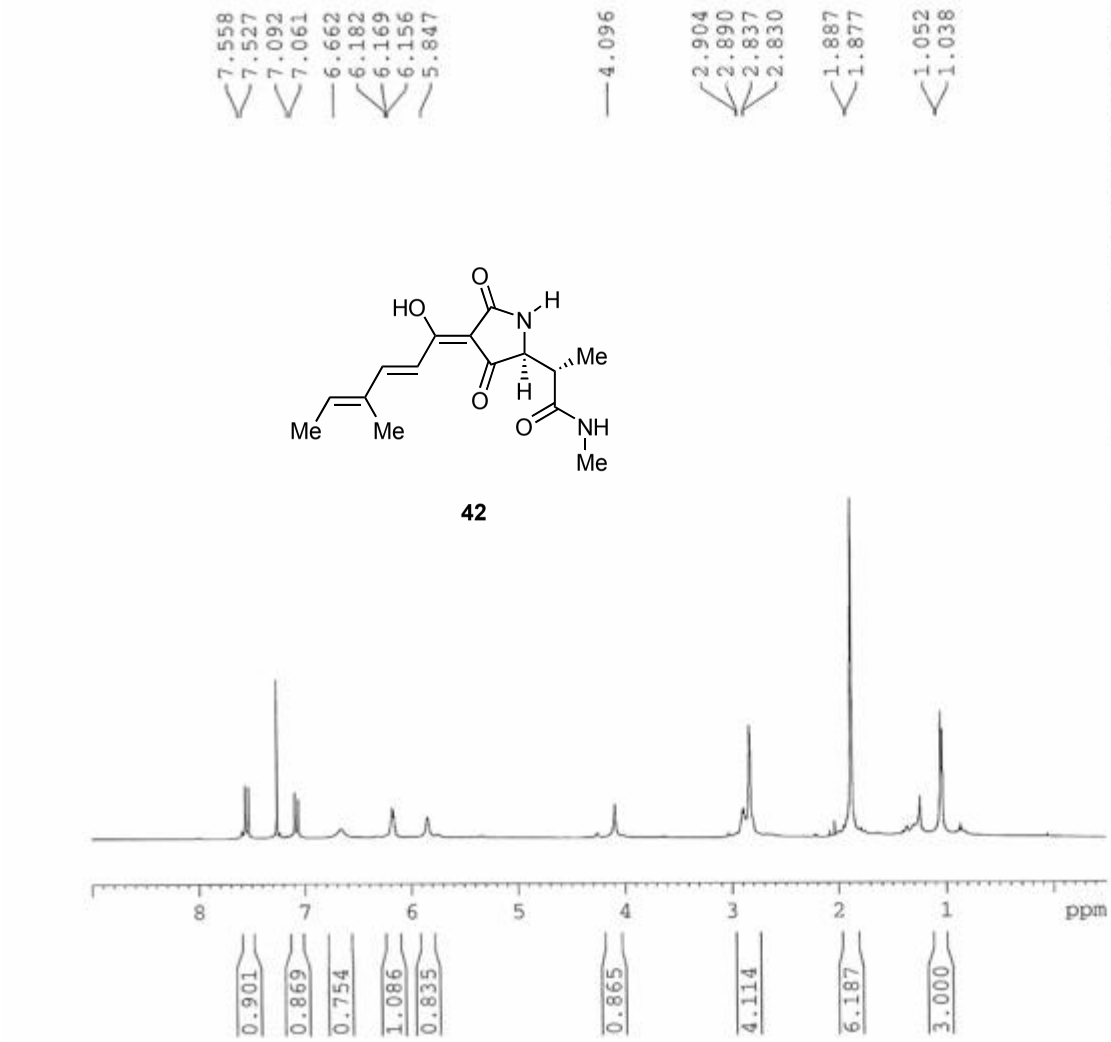

12.661
12.659
7.254
7.223
7.130
7.099
6.160
6.128
6.108
6.094
6.080
6.066
5.923
5.909
5.895
5.881
5.681
5.650
5.380
3.721
1.837
1.823
1.797
1.783
1.769
1.767
1.754
1.752
1.508
1.457
0.76
0.58
0.96
0.49
0.55
1.01
1.00
0.85
1.03
1.75
3.04
1.52
2.90
8.86
4.84
ppm
Me
Me
O
O
St-Bu
40
NAME st13010
EXPNO 1
PROCNO 1
Date_ 20091124
Time 14.16
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 36
DW 66.667 usec
DE 71.43 usec
TE 294.7 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1W 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300073 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

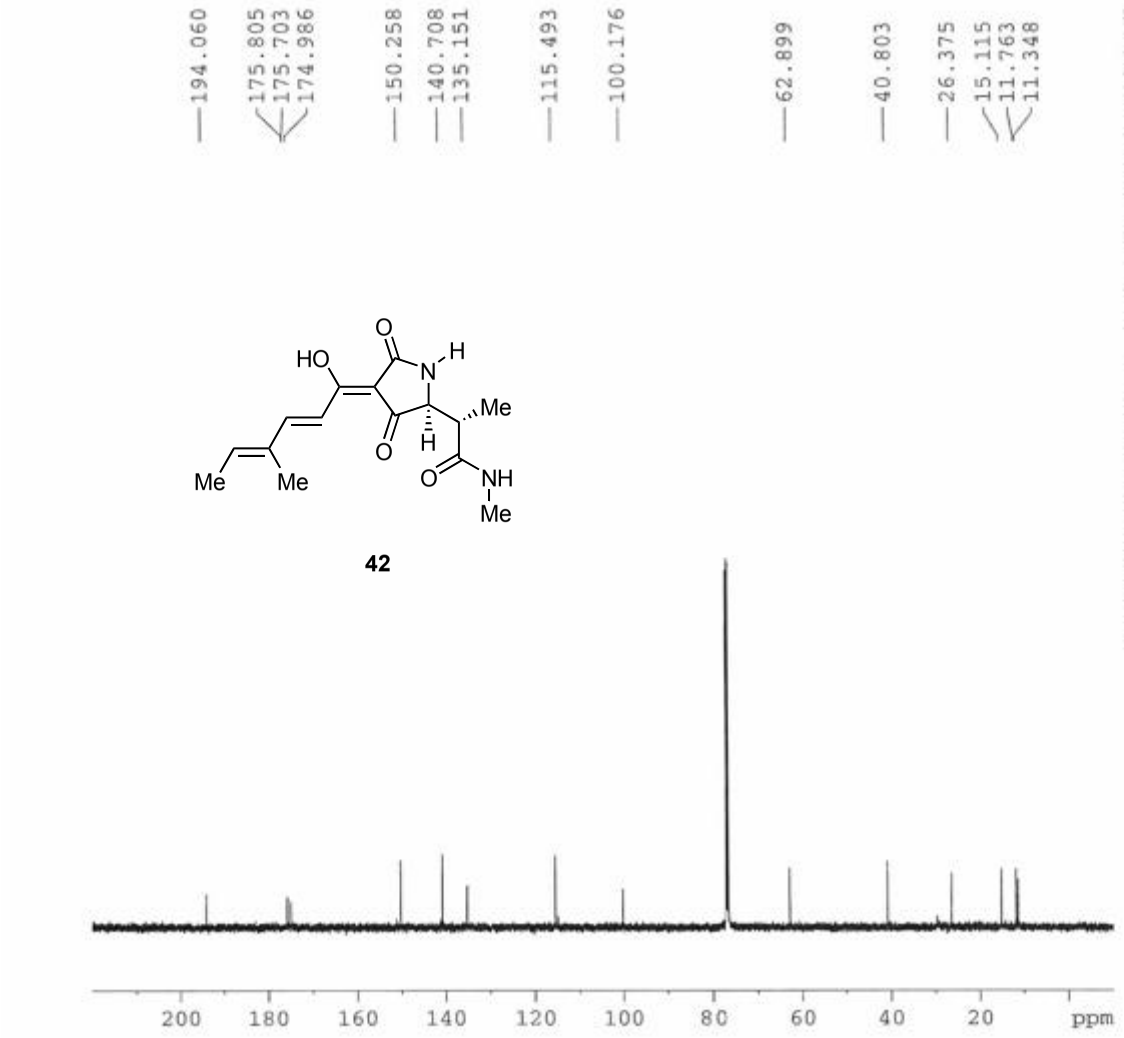



```
NAME                                    stl3010
EXPNO                                         2
PROCNO                                        1
Date_                               20091124
Time                                    14.23
INSTRUM                                 spect
PROBHD                 5 mm PAQNP 1H/
PULPROG                                 zgpg
TD                                     65786
SOLVENT                                CDCl3
NS                                        64
DS                                         4
SWH                                32894.738 Hz
FIDRES                                 0.500026 Hz
AQ                                     0.9999972 sec
RG                                        2050
DW                                      15.200 usec
DE                                       6.00 usec
TE                                      295.2 K
D1                                     4.00000000 sec
D11                                    0.03000000 sec
TD0                                           1

======== CHANNEL f1 ========
NUC1                                       13C
P1                                        8.00 usec
PL1                                       1.00 dB
PL1W                                72.42802429 W
SFO1                               125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                                waltz16
NUC2                                       1H
PCPD2                                    80.00 usec
PL2                                       0.00 dB
PL12                                     16.50 dB
PL13                                     17.00 dB
PL2W                                24.54113007 W
PL12W                                0.54940748 W
PL13W                                0.48965994 W
SFO2                               500.1325006 MHz
SI                                       131072
SF                                 125.7577945 MHz
WDW                                        EM
SSB                                         0
LB                                       0.30 Hz
GB                                          0
PC                                       1.40
```


41
Me
Me
O
O
NH
O
O
N
Me
Me
8.216
8.202
7.291
7.259
6.142
6.128
6.104
6.073
4.100
4.087
4.073
3.615
3.004
2.937
2.923
2.909
1.851
1.837
1.770
1.392
1.378
1.01
1.23
2.00
1.24
1.83
3.43
1.05
3.19
3.29
3.56
ppm

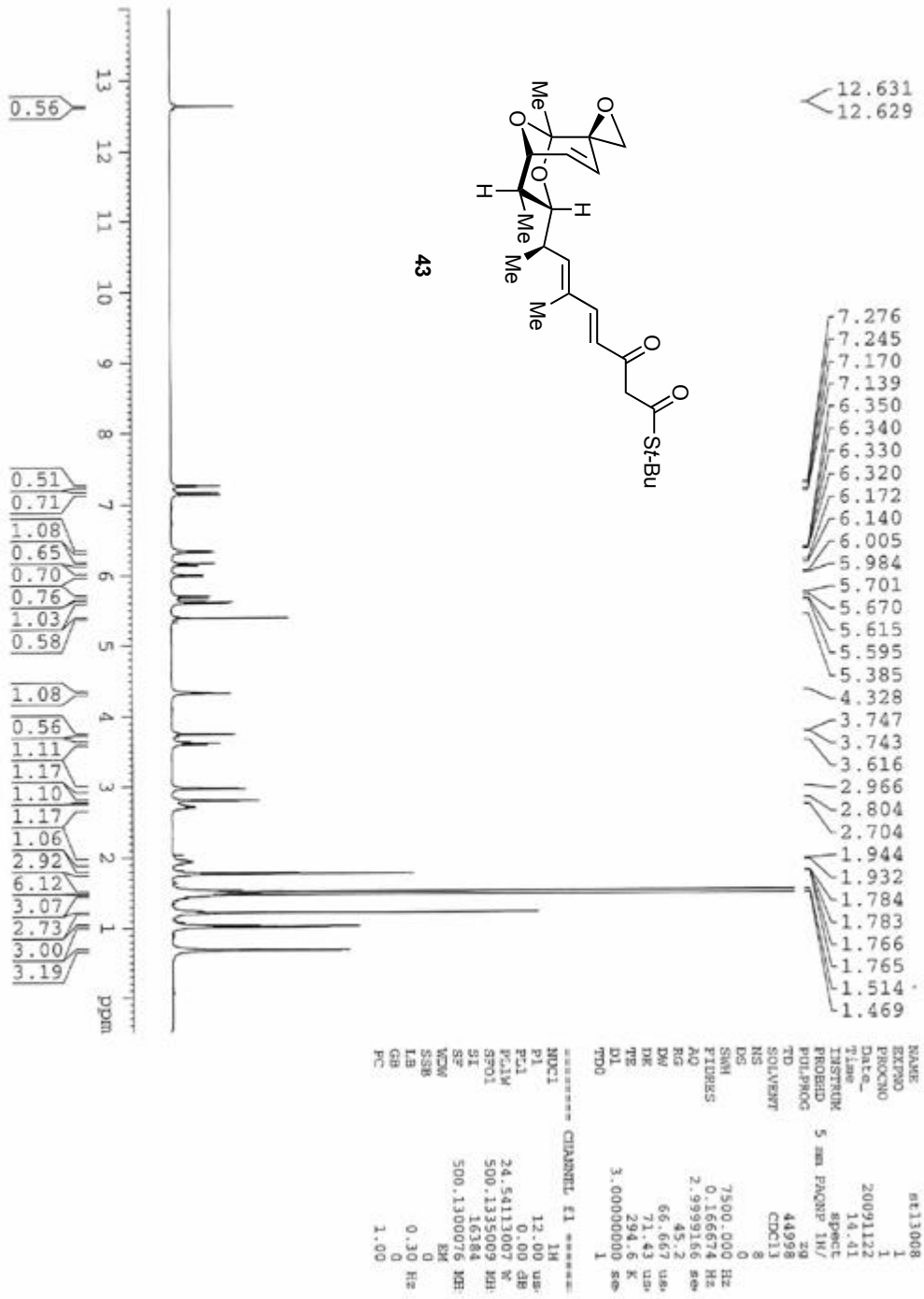

195.551
177.319
174.316
166.945
150.748
140.552
134.011
122.979
56.933
45.677
41.834
25.014
14.946
14.007
11.722
O
O
NH
Me
O
N
O
Me
Me
Me
41
NAME st13027
EXPNO 2
PROCNO 1
Date_ 20091203
Time 18.15
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 64
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 se
RG 2050
DW 15.200 us
DE 6.00 us
TE 295.1 K
D1 4.00000000 se
D11 0.03000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 13C
P1 8.00 us
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MH
======== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 us
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MH
SI 131072
SF 125.7577967 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

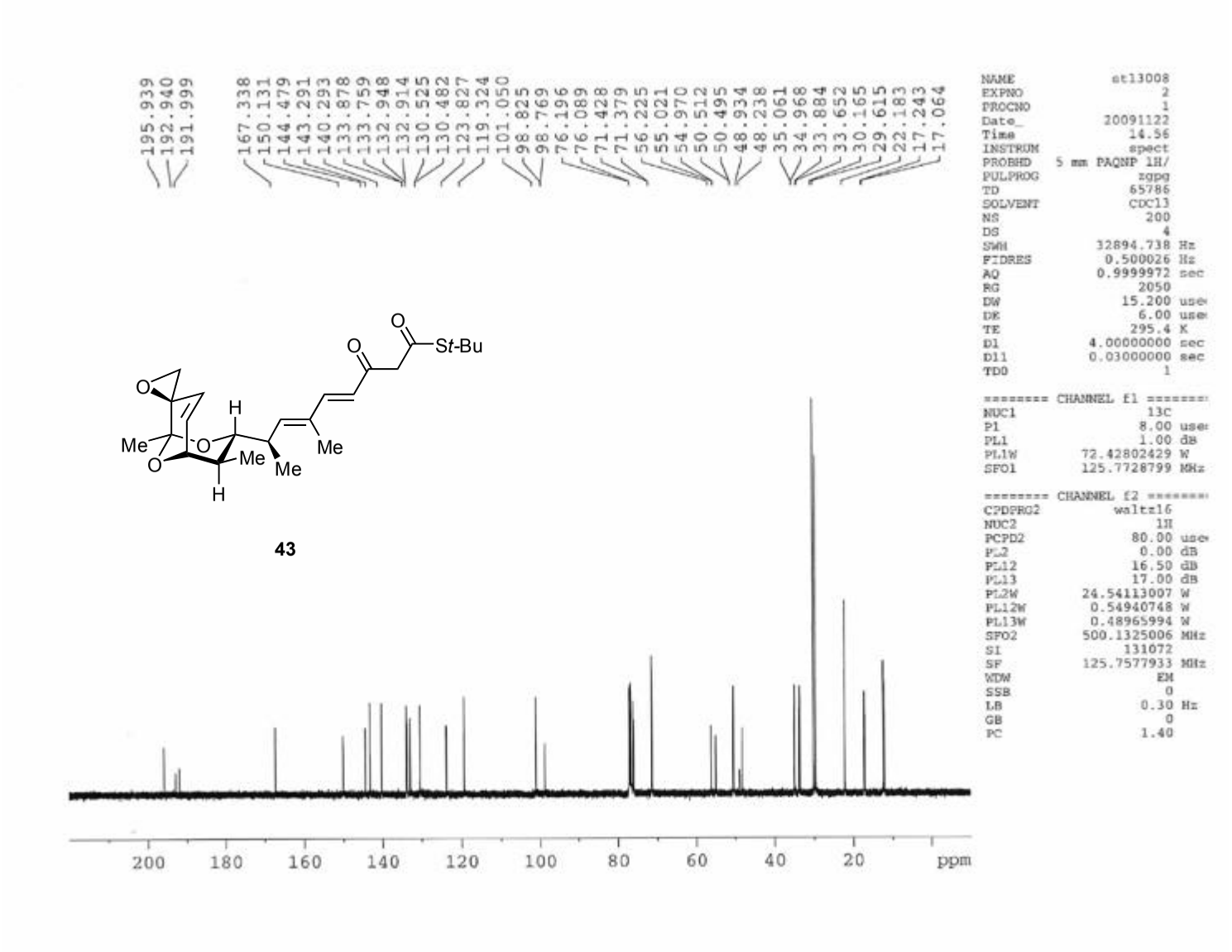

7.558
7.527
7.092
7.061
6.662
6.182
6.169
6.156
5.847
4.096
2.904
2.890
2.837
2.830
1.887
1.877
1.052
1.038
NAME stĪ3228
EXPNO 8
PROCNO 1
Date_ 20101125
Time 18.59
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT Aceton
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 128
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz
SI 65536
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
O
N
H
Me
O
H
Me
Me
O
NH
Me
42
8
7
6
5
4
3
2
1
ppm
0.901
0.869
0.754
1.086
0.835
0.865
4.114
6.187
3.000

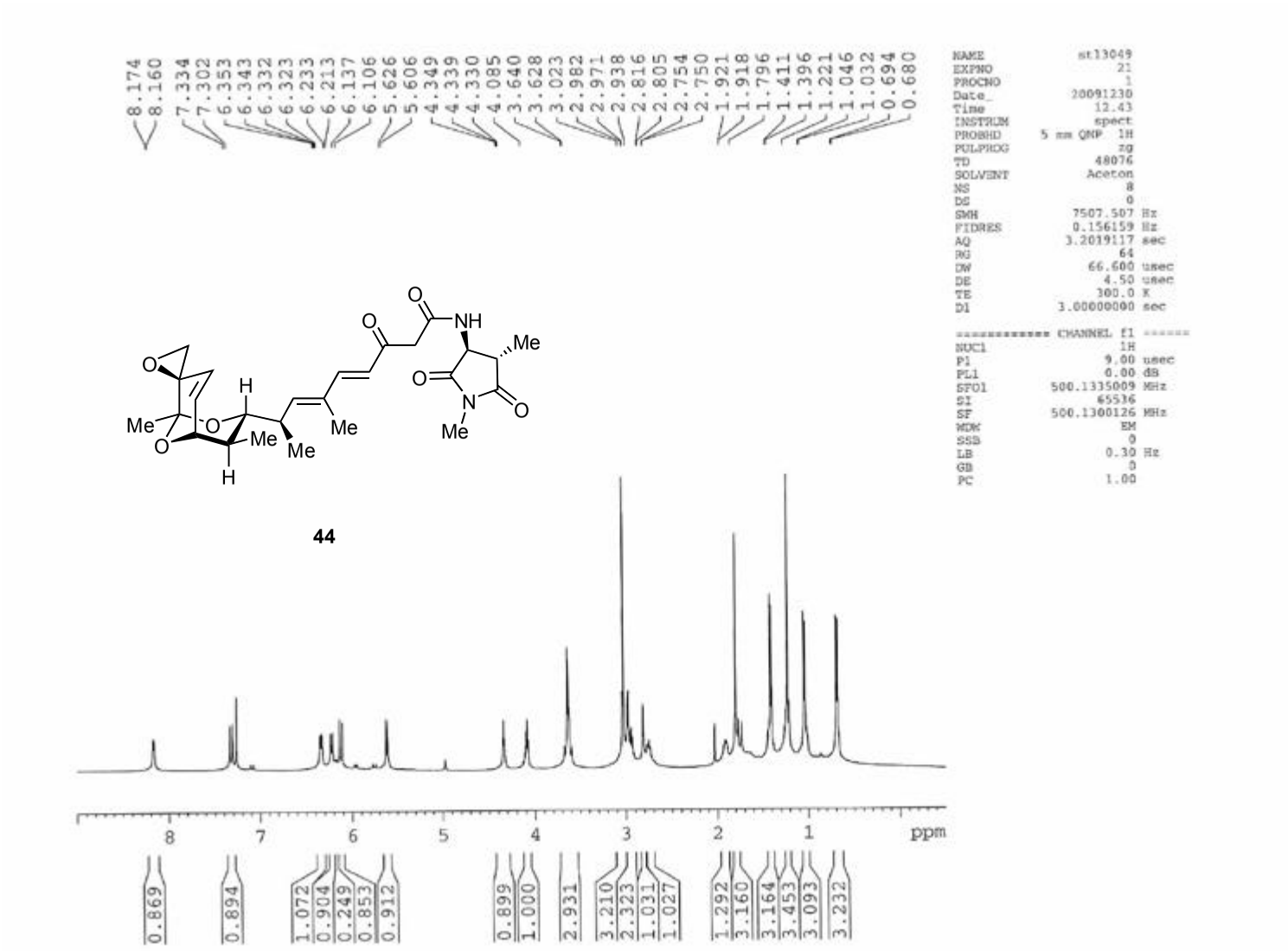


42

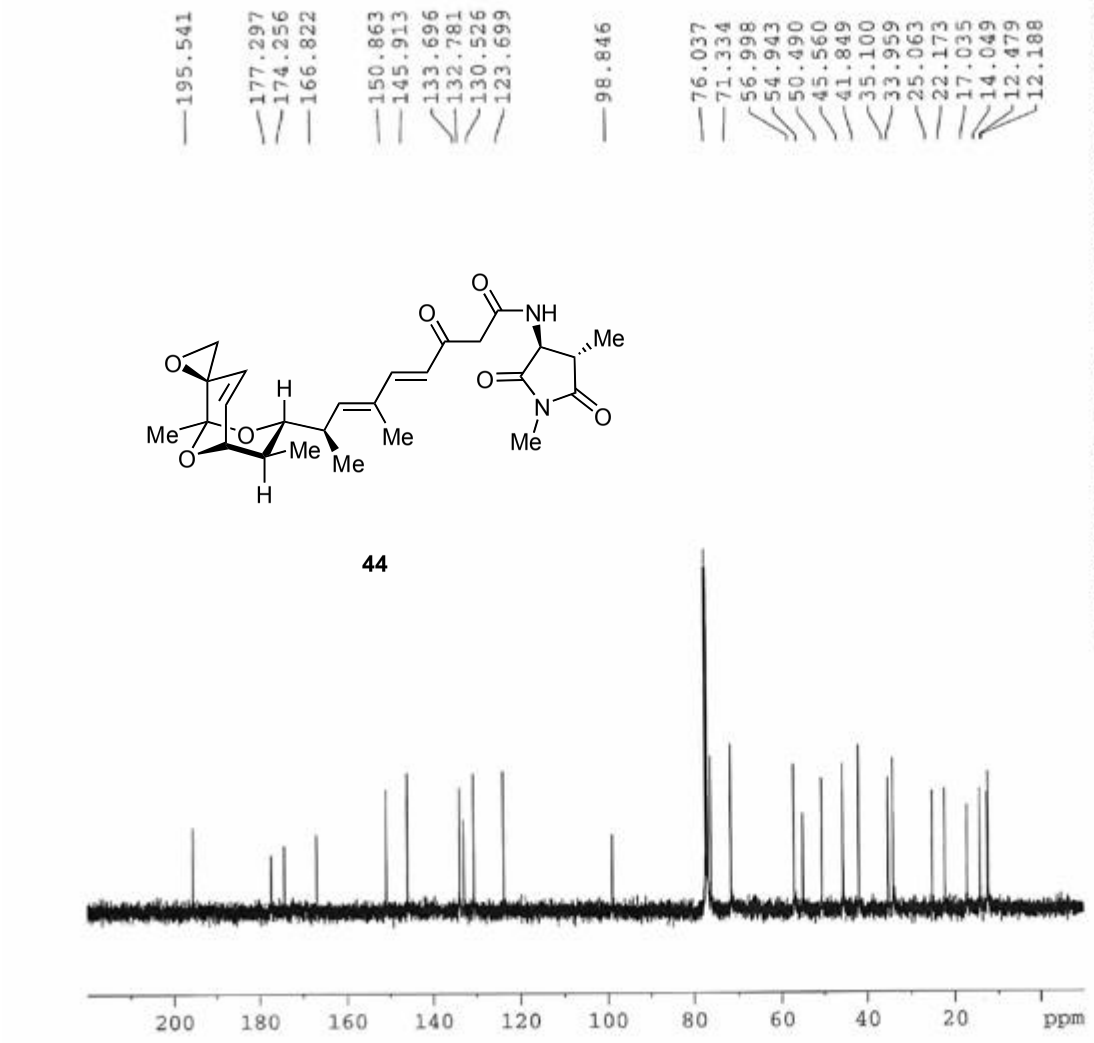
NAME	st13228
EXPNO	81
PROCNO	1
Date_	20101125
Time	19.16
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	280
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	16384
DW	16.500 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
======	CHANNEL f1 ======
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
======	CHANNEL f2 ======
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7577932 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

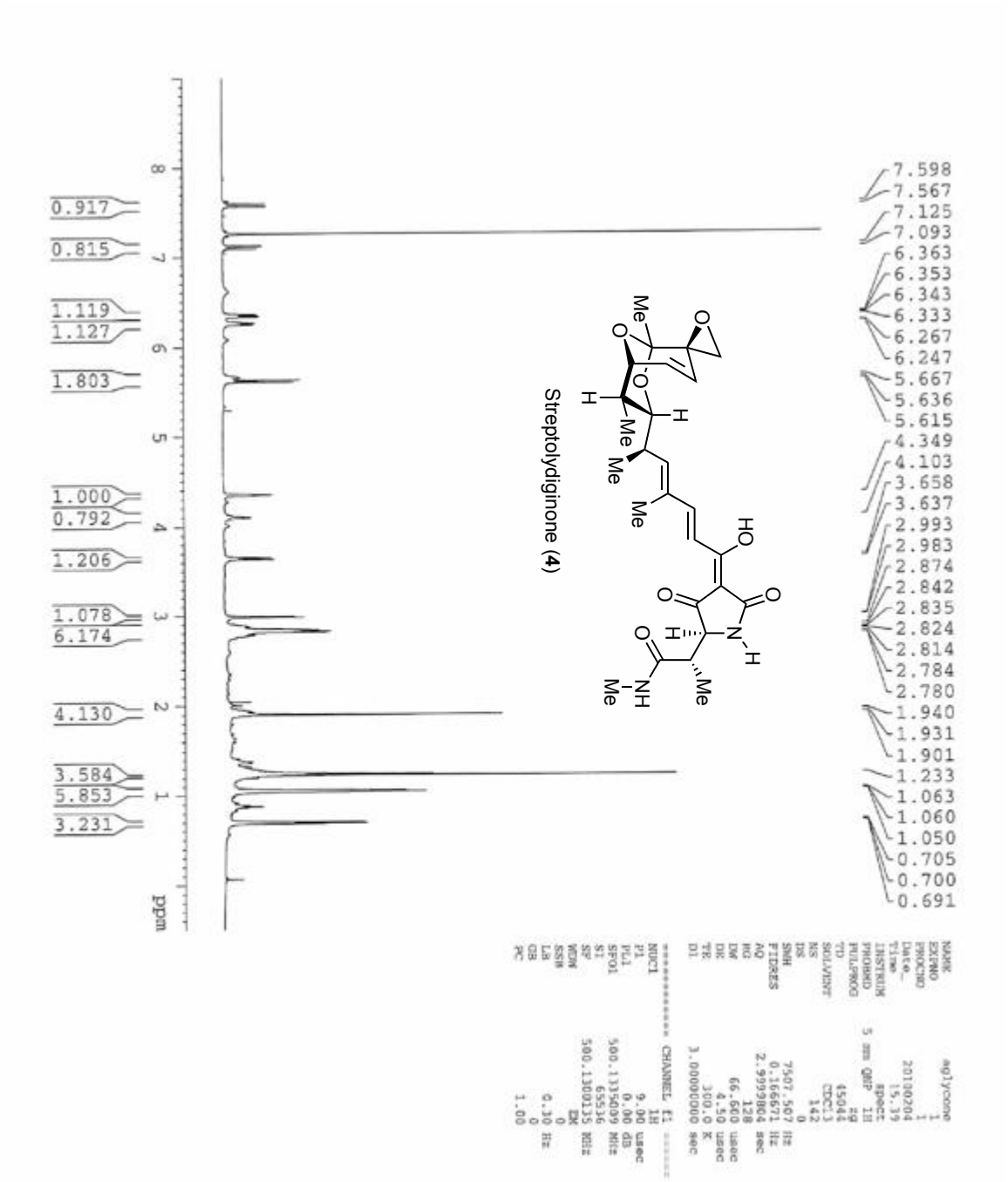

43
St-Bu
Me
Me
Me
Me
H
H
O
O
O
O
O
O
12.631
12.629
7.276
7.245
7.170
7.139
6.350
6.340
6.330
6.320
6.172
6.140
6.005
5.984
5.701
5.670
5.615
5.595
5.385
4.328
3.747
3.743
3.616
2.966
2.804
2.704
1.944
1.932
1.784
1.783
1.766
1.765
1.514
1.469
0.56
0.51
0.71
1.08
0.65
0.70
0.76
1.03
0.58
1.08
0.56
1.11
1.17
1.10
1.17
1.06
2.92
6.12
3.07
2.73
3.00
3.19
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
NAME st13008
EXPNO 1
PROCNO 1
Date_ 20091122
Time 14.41
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 sec
RG 45.2
DW 66.667 usec
DE 71.43 usec
TE 294.6 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL1M 24.54113007 W
SFO1 500.1335009 MHz
SI 16384
SF 500.1300076 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

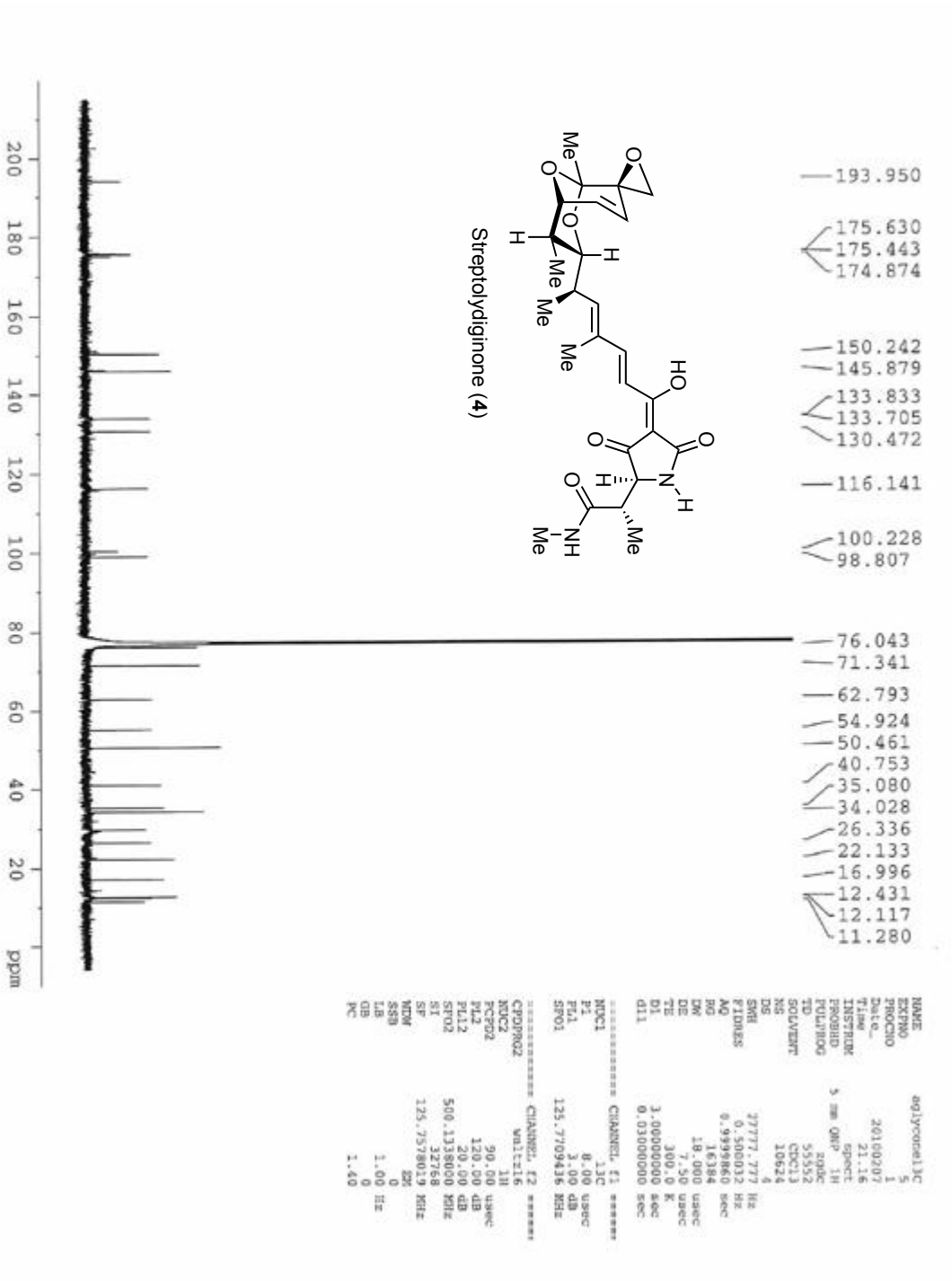

195.939
192.940
191.999
167.338
150.131
144.479
143.291
140.293
133.878
133.759
132.948
132.914
130.525
130.482
123.827
119.324
101.050
98.825
98.769
76.196
76.089
71.428
71.379
56.225
55.021
54.970
50.512
50.495
48.934
48.238
35.061
34.968
33.884
33.652
30.165
29.615
22.183
17.243
17.064
St-Bu
Me
Me
Me
Me
H
H
43
NAME st13008
EXPNO 2
PROCNO 1
Date_ 20091122
Time 14.56
INSTRUM spect
PROBHD 5 mm PAQNP 1H/
PULPROG zgpg
TD 65786
SOLVENT CDCl3
NS 200
DS 4
SWH 32894.738 Hz
FIDRES 0.500026 Hz
AQ 0.9999972 sec
RG 2050
DW 15.200 use
DE 6.00 use
TE 295.4 K
D1 4.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 use
PL1 1.00 dB
PL1W 72.42802429 W
SFO1 125.7728799 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0.00 dB
PL12 16.50 dB
PL13 17.00 dB
PL2W 24.54113007 W
PL12W 0.54940748 W
PL13W 0.48965994 W
SFO2 500.1325006 MHz
SI 131072
SF 125.7577933 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

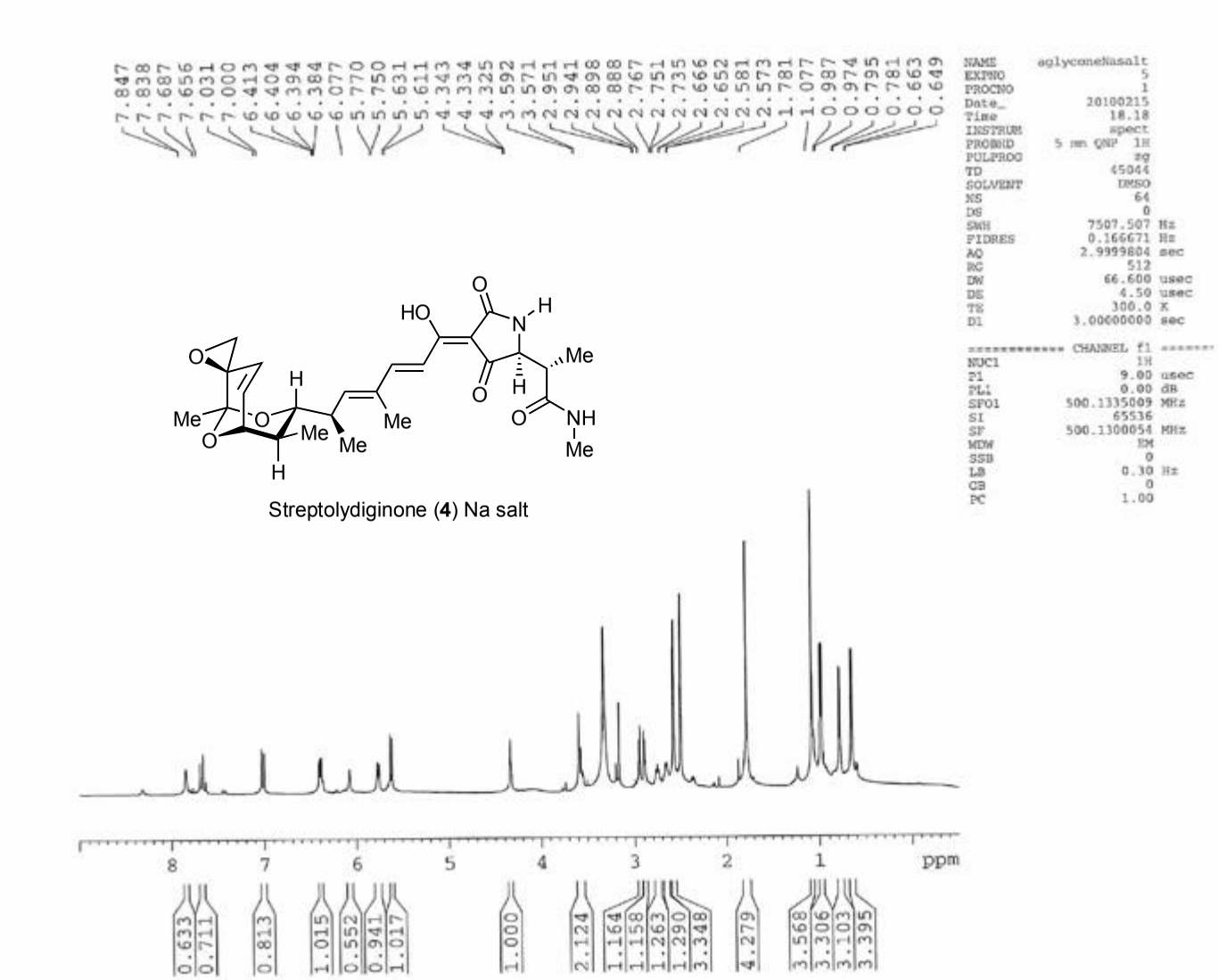

8.174
8.160
7.334
7.302
6.353
6.343
6.332
6.323
6.233
6.213
6.137
6.106
5.626
5.606
4.349
4.339
4.330
4.085
3.640
3.628
3.023
2.982
2.971
2.938
2.816
2.805
2.754
2.750
1.921
1.918
1.796
1.411
1.396
1.221
1.046
1.032
0.694
0.680
NAME st13049
EXPNO 21
PROCNO 1
Date_ 20091230
Time 12.43
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 48076
SOLVENT Aceton
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.156159 Hz
AQ 3.2019117 sec
RG 64
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz
SI 65536
SF 500.1300126 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
O
NH
Me
O
H
Me
O
Me
Me
Me
Me
O
N
O
O
H
8
7
6
5
4
3
2
1
ppm
0.869
0.894
1.072
0.904
0.249
0.853
0.912
0.899
1.000
2.931
3.210
2.323
1.031
1.027
1.292
3.160
3.164
3.453
3.093
3.232

44

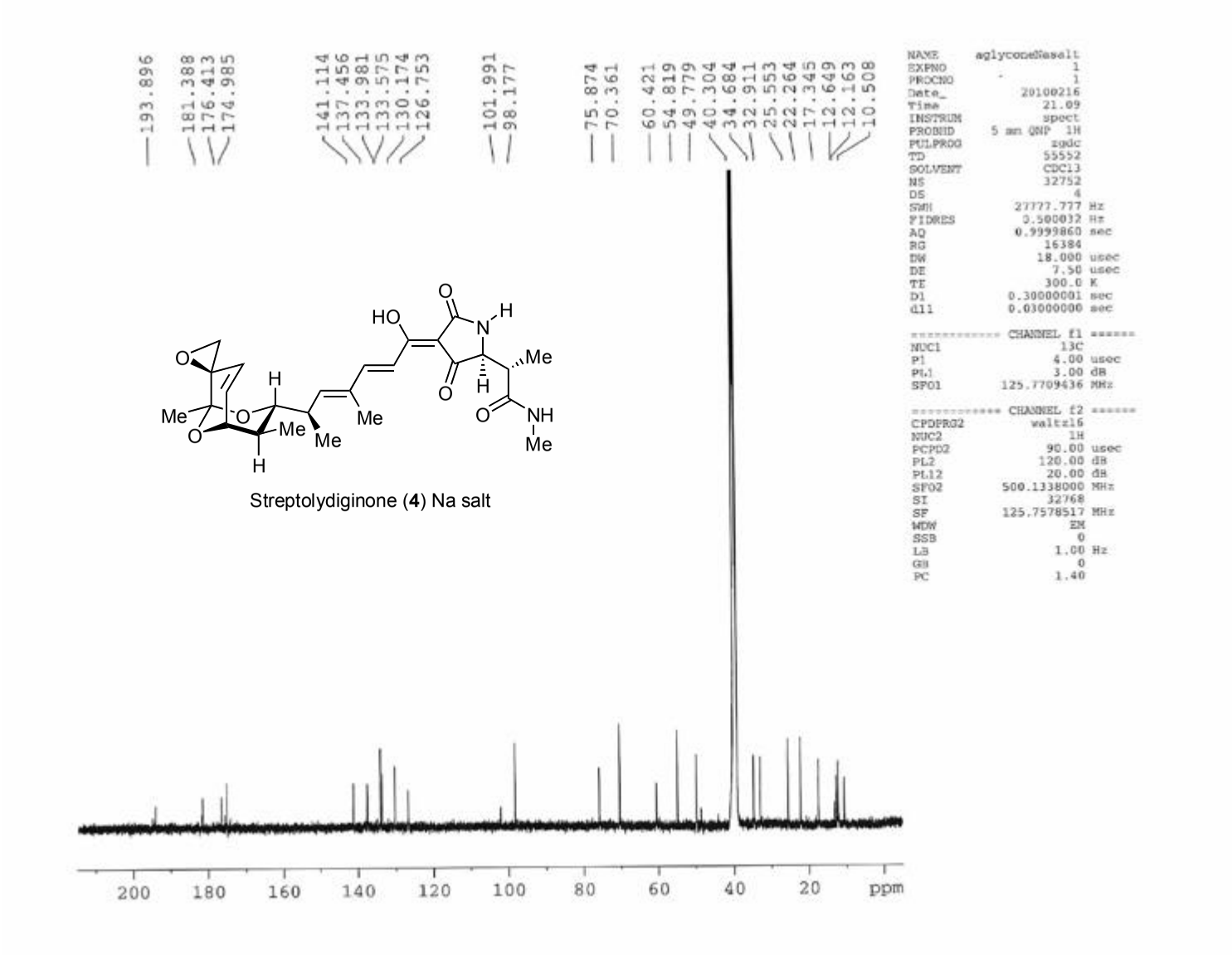

195.541
177.297
174.256
166.822
150.863
145.913
133.696
132.781
130.526
123.699
98.846
76.037
71.334
56.998
54.943
50.490
45.560
41.849
35.100
33.959
25.063
22.173
17.035
14.049
12.479
12.188
NAME st13049
EXPNO 2
PROCNO 1
Date_ 20091230
Time 12.26
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 65356
SOLVENT CDCl3
NS 161
DS 0
SWH 32679.738 Hz
FIDRES 0.500027 Hz
AQ 0.9999968 sec
RG 16384
DW 15.300 usec
DE 7.50 usec
TE 300.0 K
D1 4.00000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7728299 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 500.1338000 MHz
SI 32768
SF 125.7577960 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
NH
Me
H
Me
Me
Me
Me
Me
O
O
O
O
O
N
Me
H
44
200
180
160
140
120
100
80
60
40
20
ppm


Streptolydiginone (4)
7.598
7.567
7.125
7.093
6.363
6.353
6.343
6.333
6.267
6.247
5.667
5.636
5.615
4.349
4.103
3.658
3.637
2.993
2.983
2.874
2.842
2.835
2.824
2.814
2.784
2.780
1.940
1.931
1.901
1.233
1.063
1.060
1.050
0.705
0.700
0.691
0.917
0.815
1.119
1.127
1.803
1.000
0.792
1.206
1.078
6.174
4.130
3.584
5.853
3.231
ppm

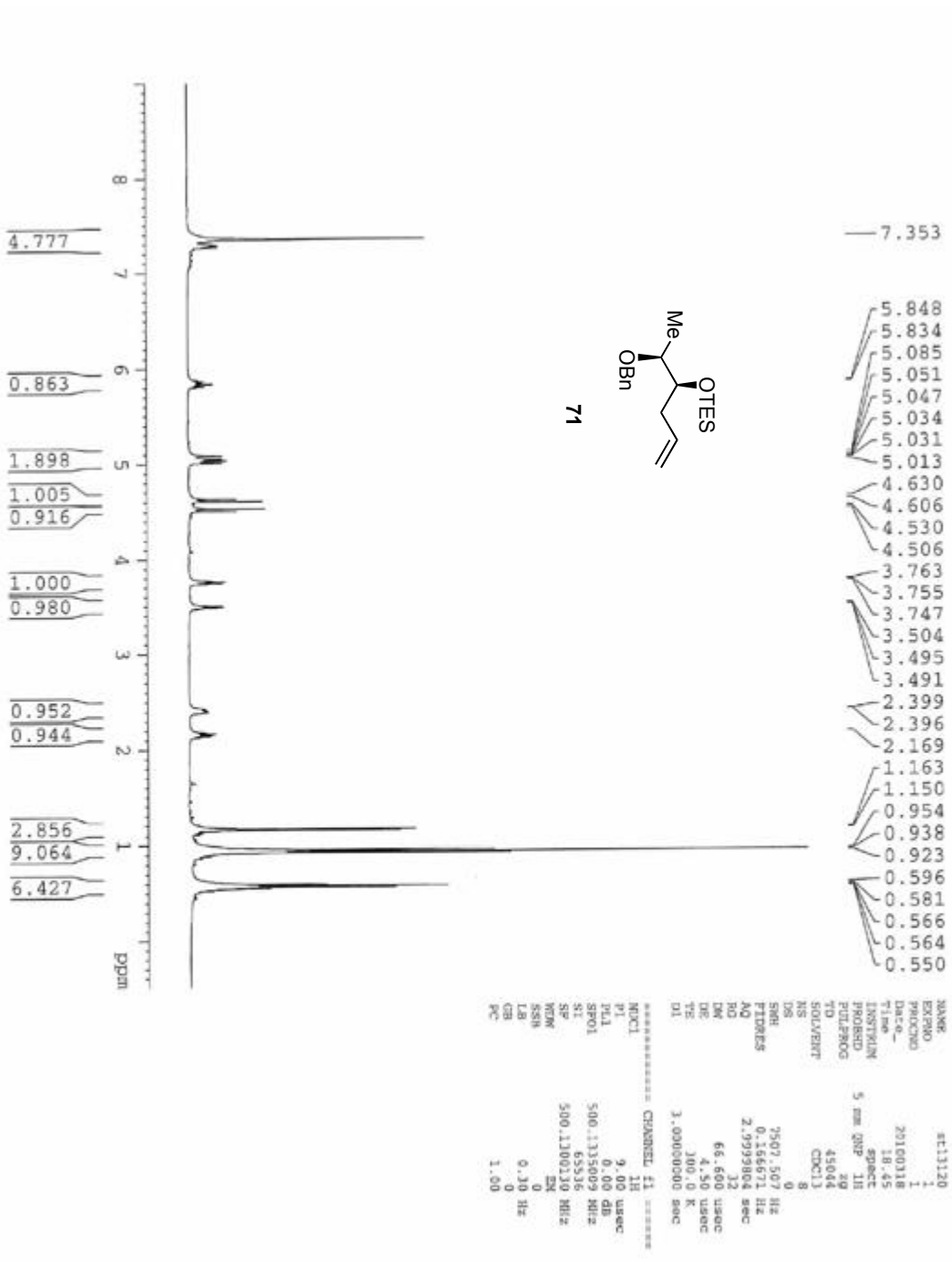

Streptolydigiinone (4)
193.950
175.630
175.443
174.874
150.242
145.879
133.833
133.705
130.472
116.141
100.228
98.807
76.043
71.341
62.793
54.924
50.461
40.753
35.080
34.028
26.336
22.133
16.996
12.431
12.117
11.280
200
180
160
140
120
100
80
60
40
20
ppm

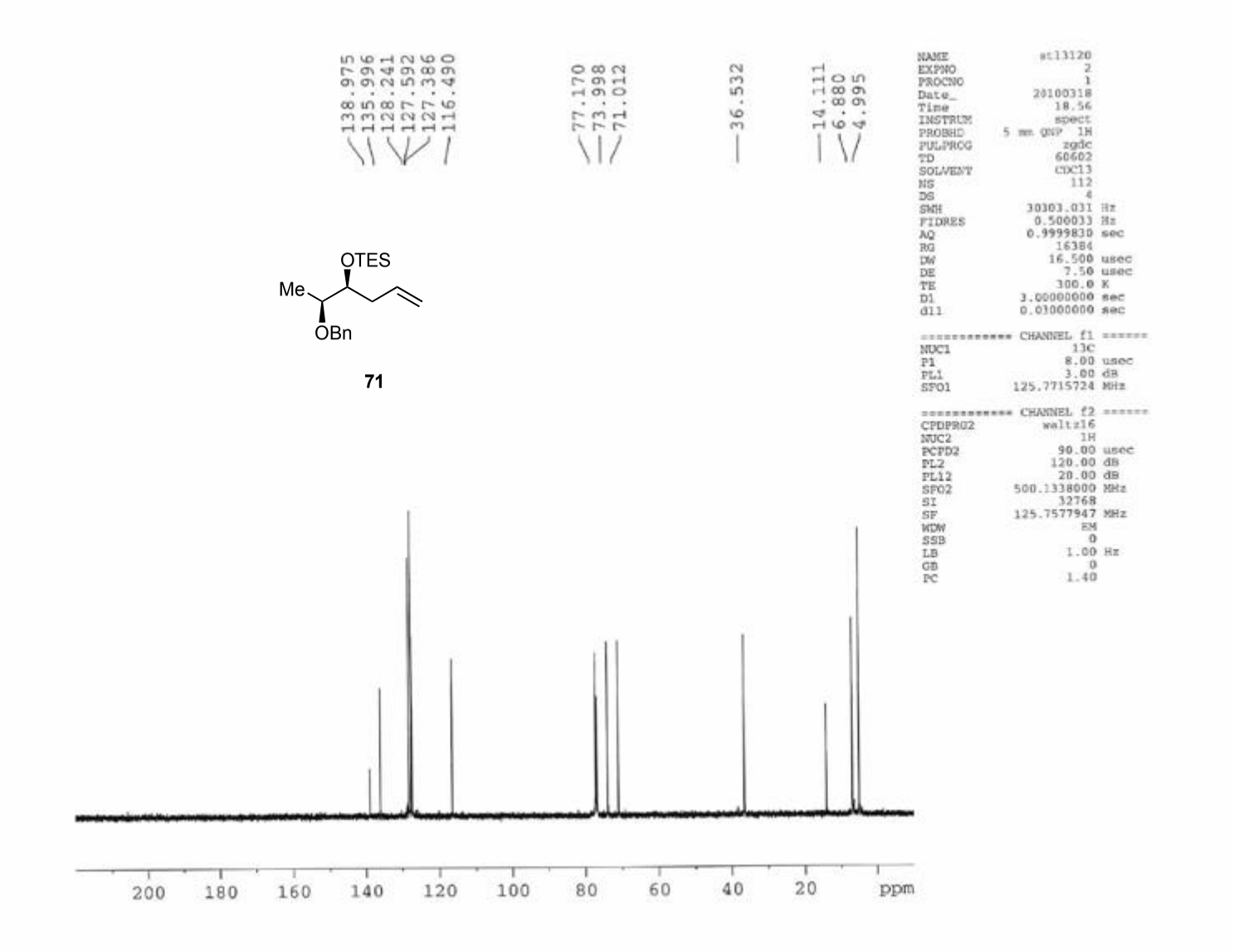


Streptolydiginone (**4**) Na salt

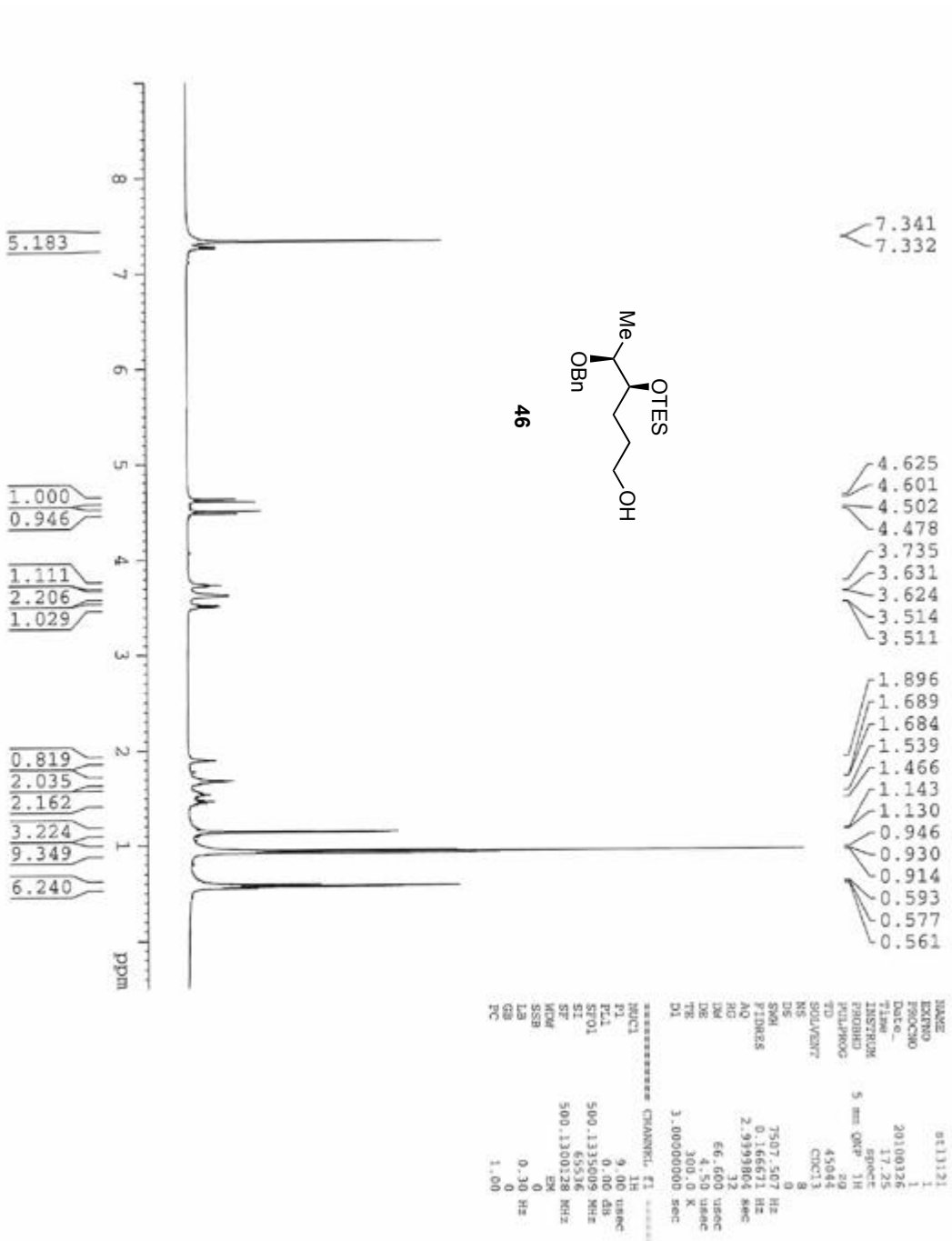


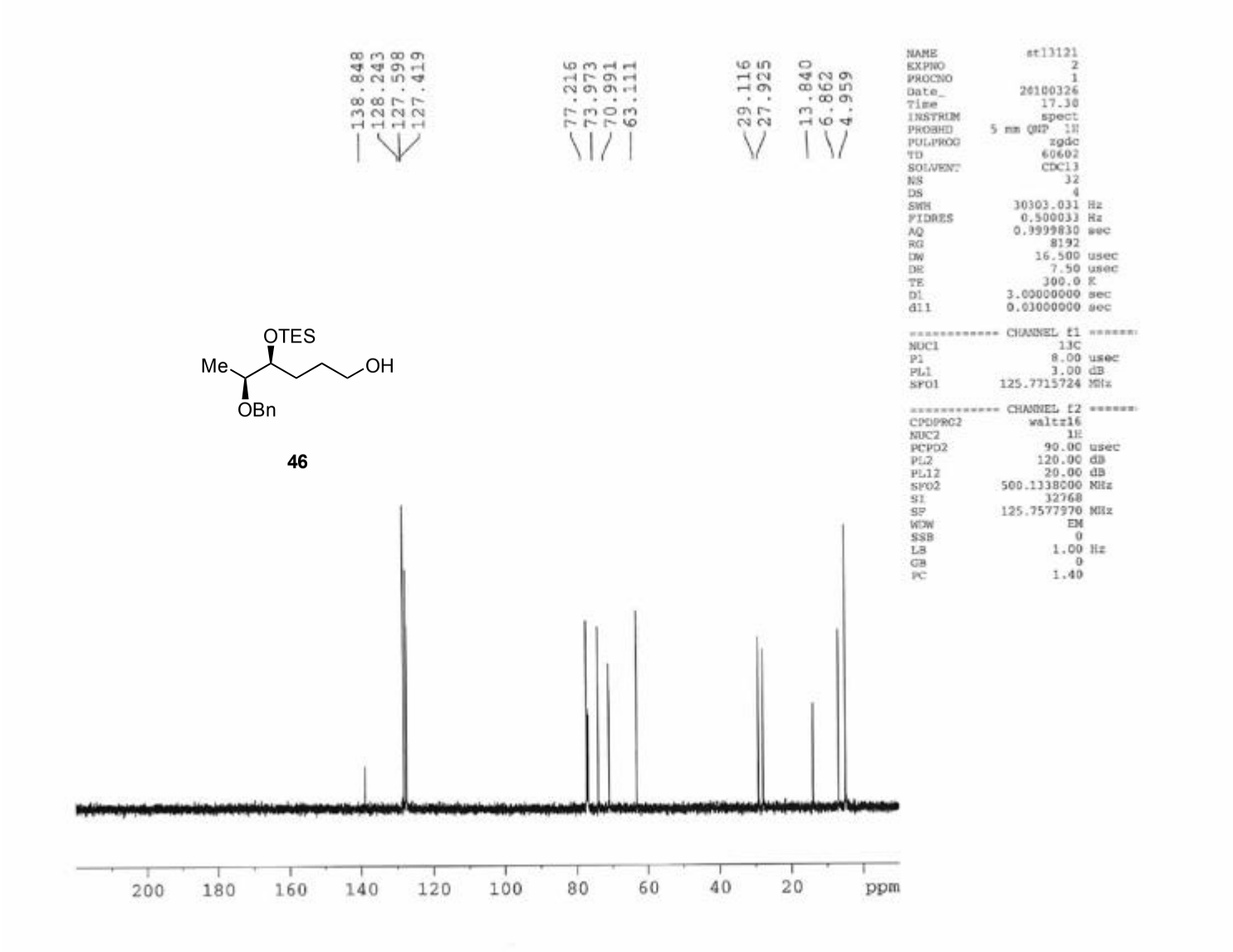
Streptolydiginone (**4**) Na salt


4.777
0.863
1.898
1.005
0.916
1.000
0.980
0.952
0.944
2.856
9.064
6.427
ppm
Me
OBn
OTES
71
7.353
5.848
5.834
5.085
5.051
5.047
5.034
5.031
5.013
4.630
4.606
4.530
4.506
3.763
3.755
3.747
3.504
3.495
3.491
2.399
2.396
2.169
1.163
1.150
0.954
0.938
0.923
0.596
0.581
0.566
0.564
0.550

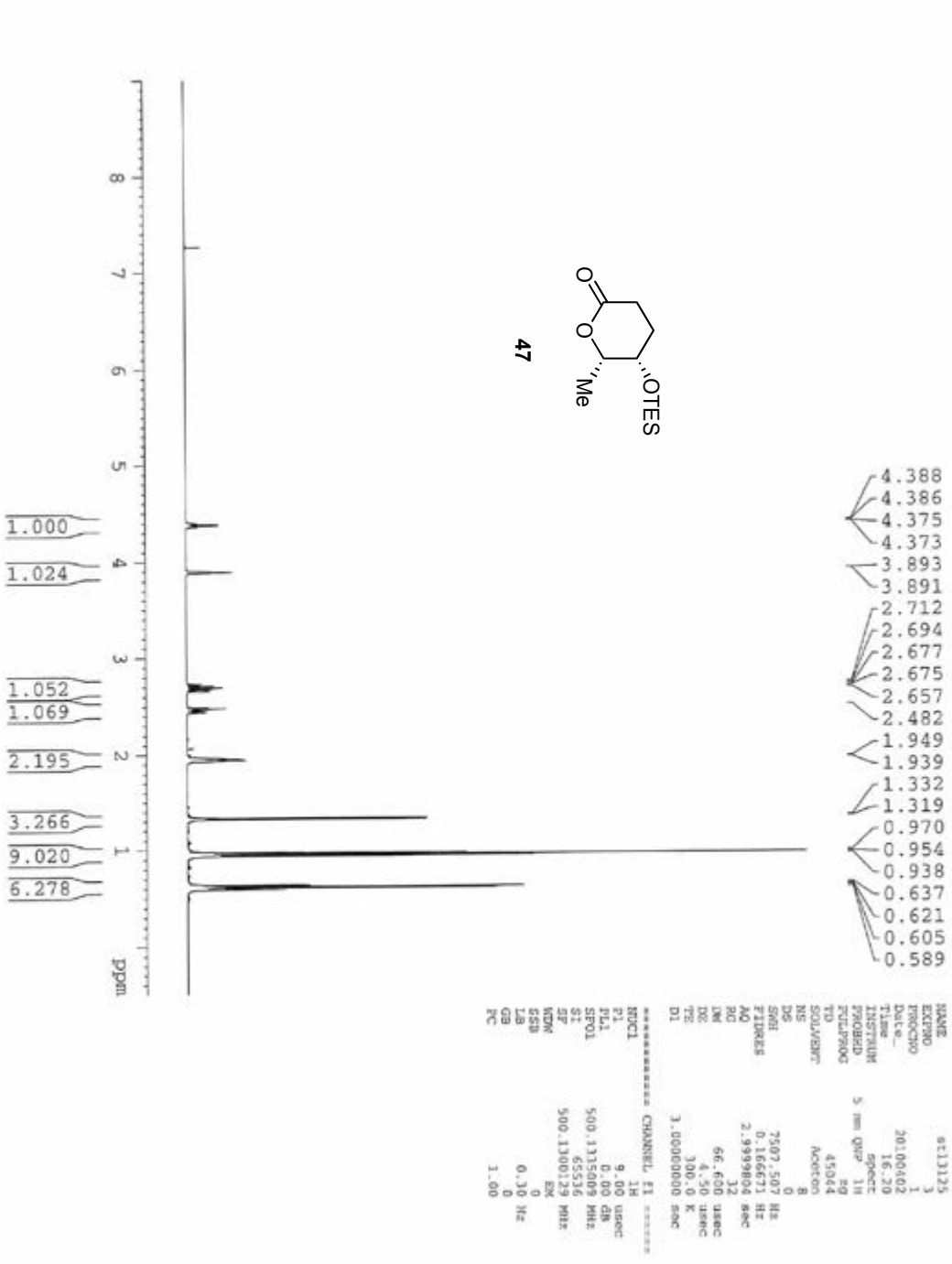


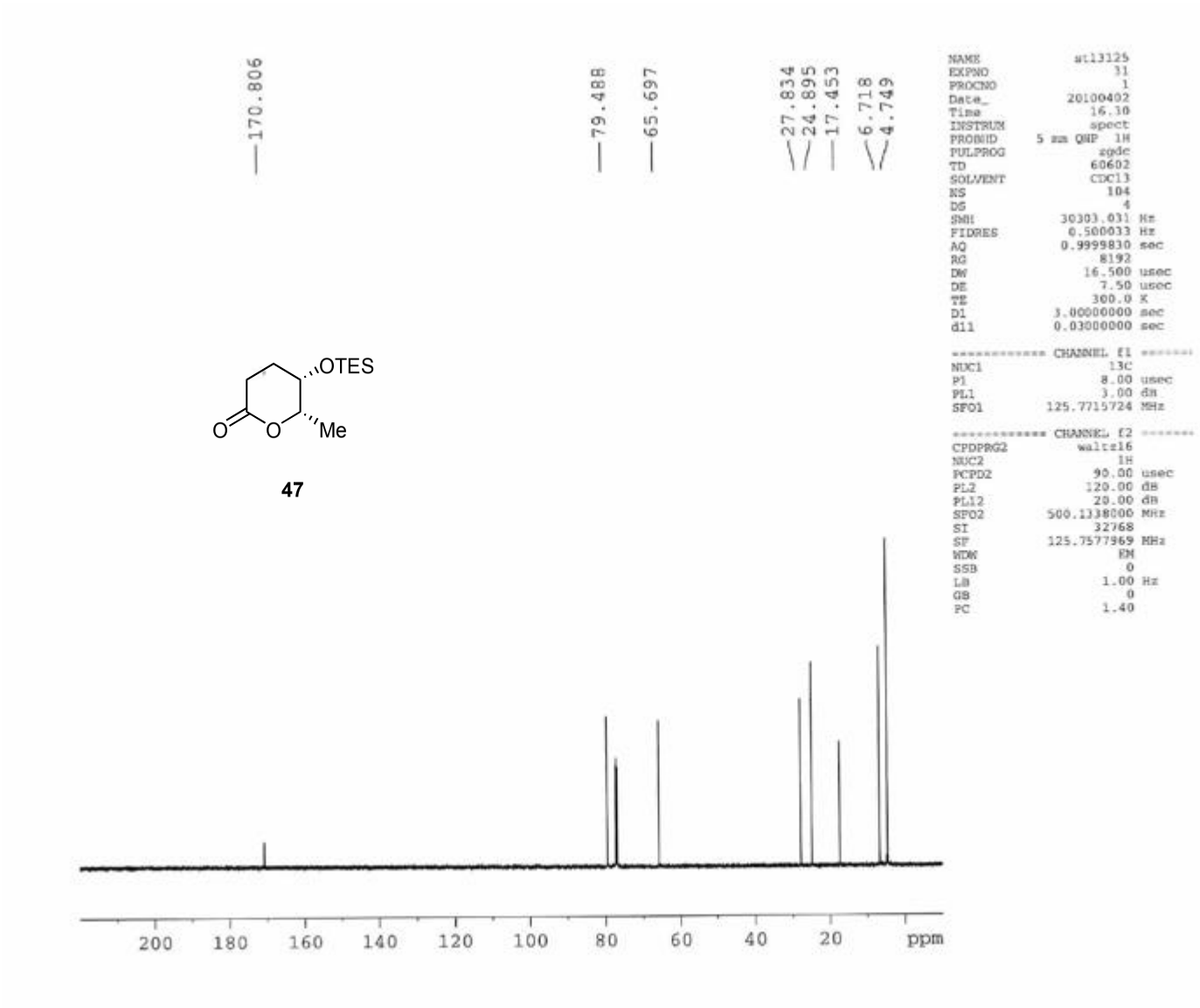

```
NAME                 st13120
EXPNO                      2
PROCNO                     1
Date_               20100318
Time                   18.56
INSTRUM                spect
PROBHD     5 mm QNP  1H
PULPROG                zgdc
TD                    60602
SOLVENT               CDCl3
NS                      112
DS                        4
SWH              30303.031 Hz
FIDRES           0.500033 Hz
AQ               0.9999830 sec
RG                    16384
DW                 16.500 usec
DE                  7.50 usec
TE                 300.0 K
D1              3.00000000 sec
d11             0.03000000 sec

======== CHANNEL f1 ======
NUC1                  13C
P1                 8.00 usec
PL1                3.00 dB
SFO1         125.7715724 MHz

======== CHANNEL f2 ======
CPDPRG2           waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2               120.00 dB
PL12               20.00 dB
SFO2         500.1338000 MHz
SI                 32768
SF           125.7577947 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```


46
OBn
Me
OTES
OH
7.341
7.332
4.625
4.601
4.502
4.478
3.735
3.631
3.624
3.514
3.511
1.896
1.689
1.684
1.539
1.466
1.143
1.130
0.946
0.930
0.914
0.593
0.577
0.561
5.183
1.000
0.946
1.111
2.206
1.029
0.819
2.035
2.162
3.224
9.349
6.240
ppm

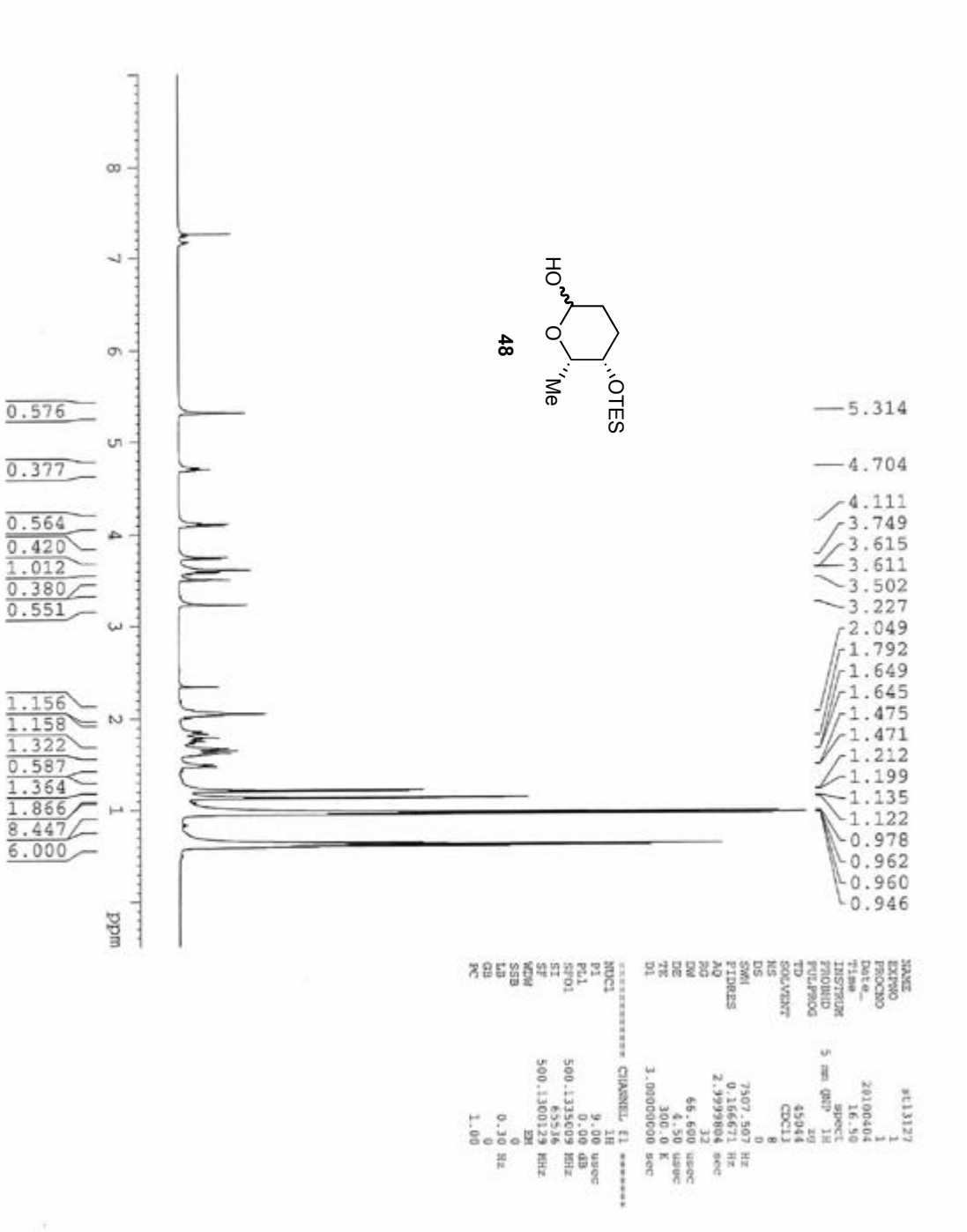


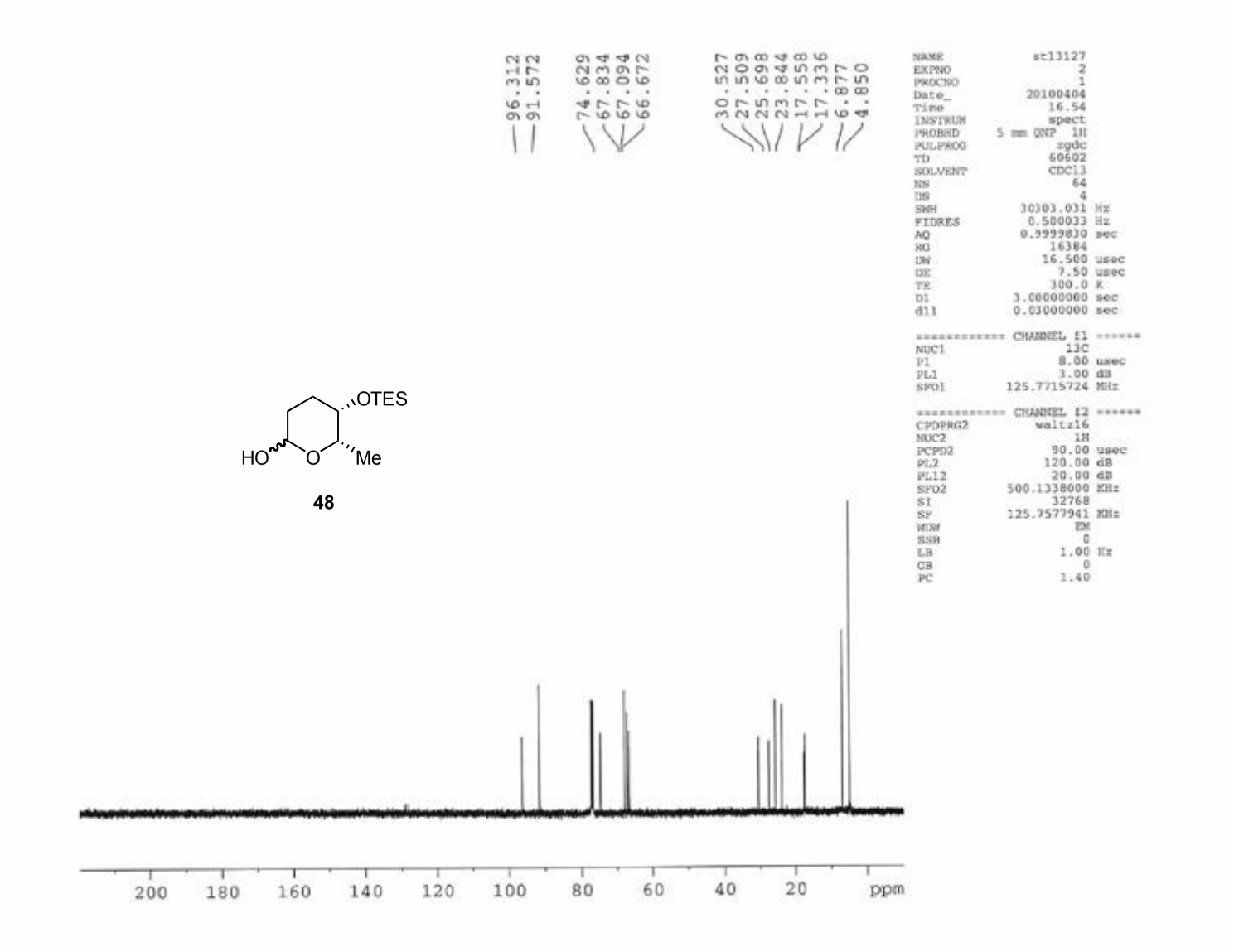
NAME	st13121
EXPNO	2
PROCNO	1
Date_	20100326
Time	17.30
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	32
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	8192
DW	16.500 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
==========	CHANNEL f1 =======
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
==========	CHANNEL f2 =======
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7577970 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

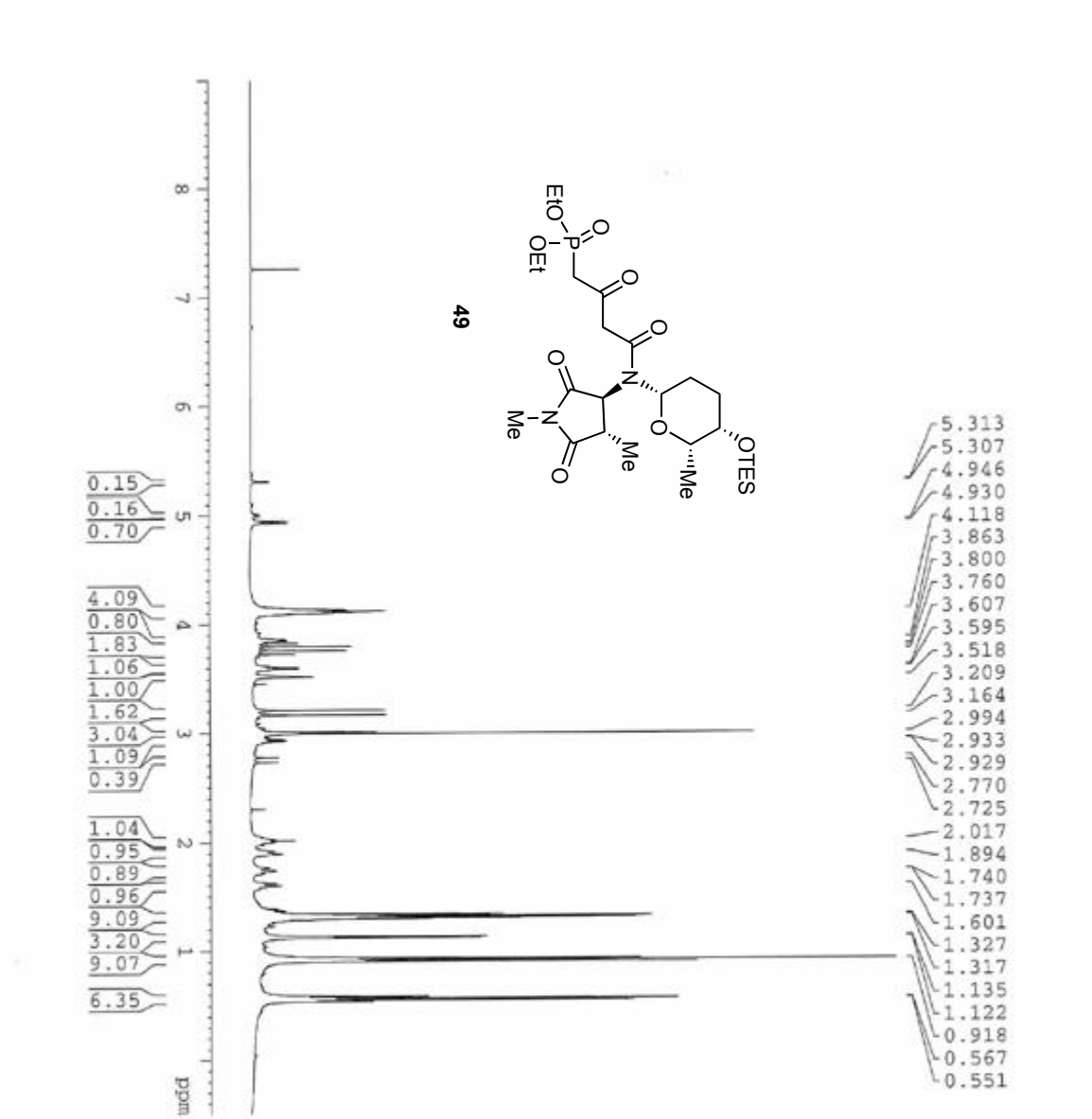

47
OTES
Me
4.388
4.386
4.375
4.373
3.893
3.891
2.712
2.694
2.677
2.675
2.657
2.482
1.949
1.939
1.332
1.319
0.970
0.954
0.938
0.637
0.621
0.605
0.589
1.000
1.024
1.052
1.069
2.195
3.266
9.020
6.278
ppm

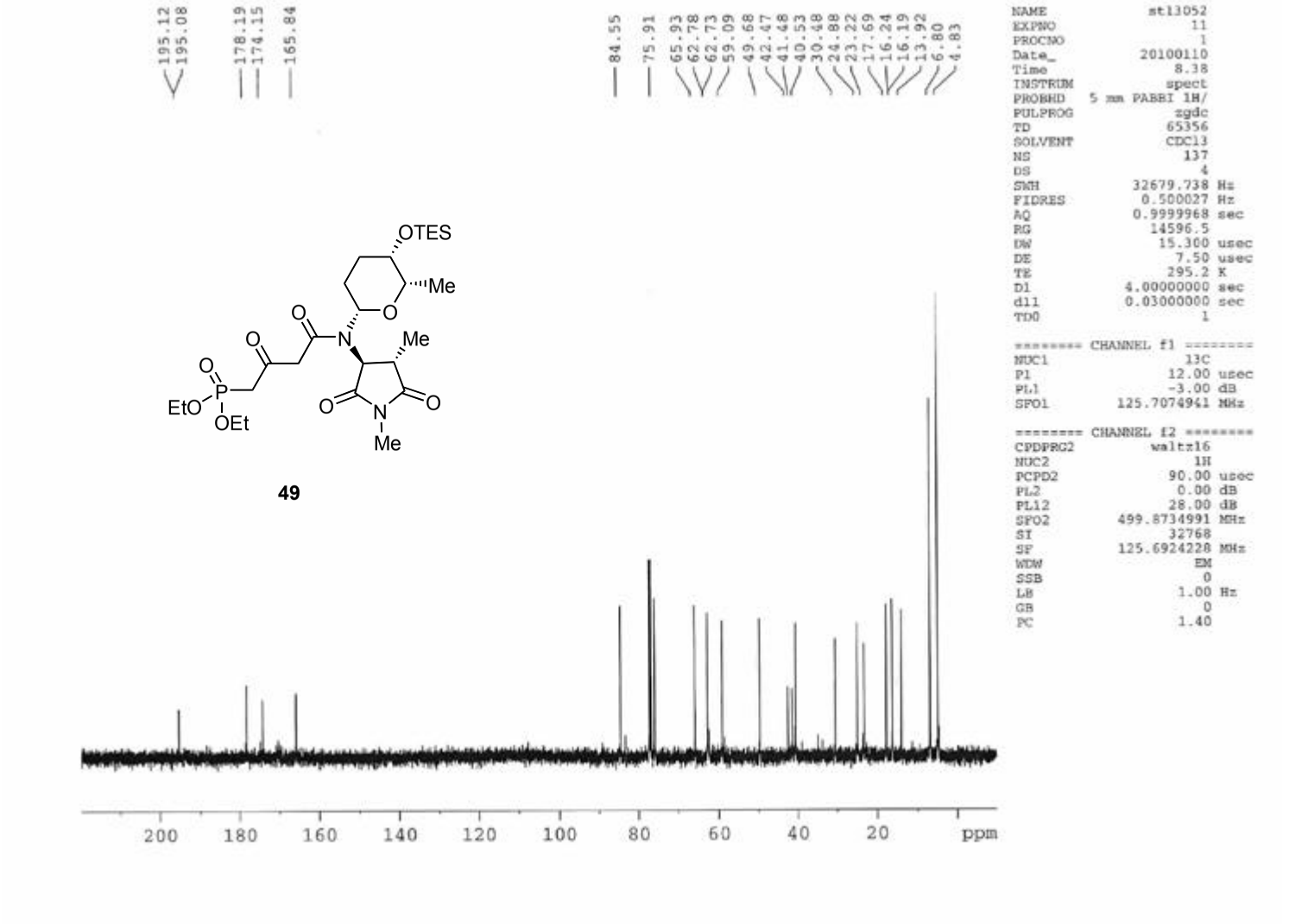


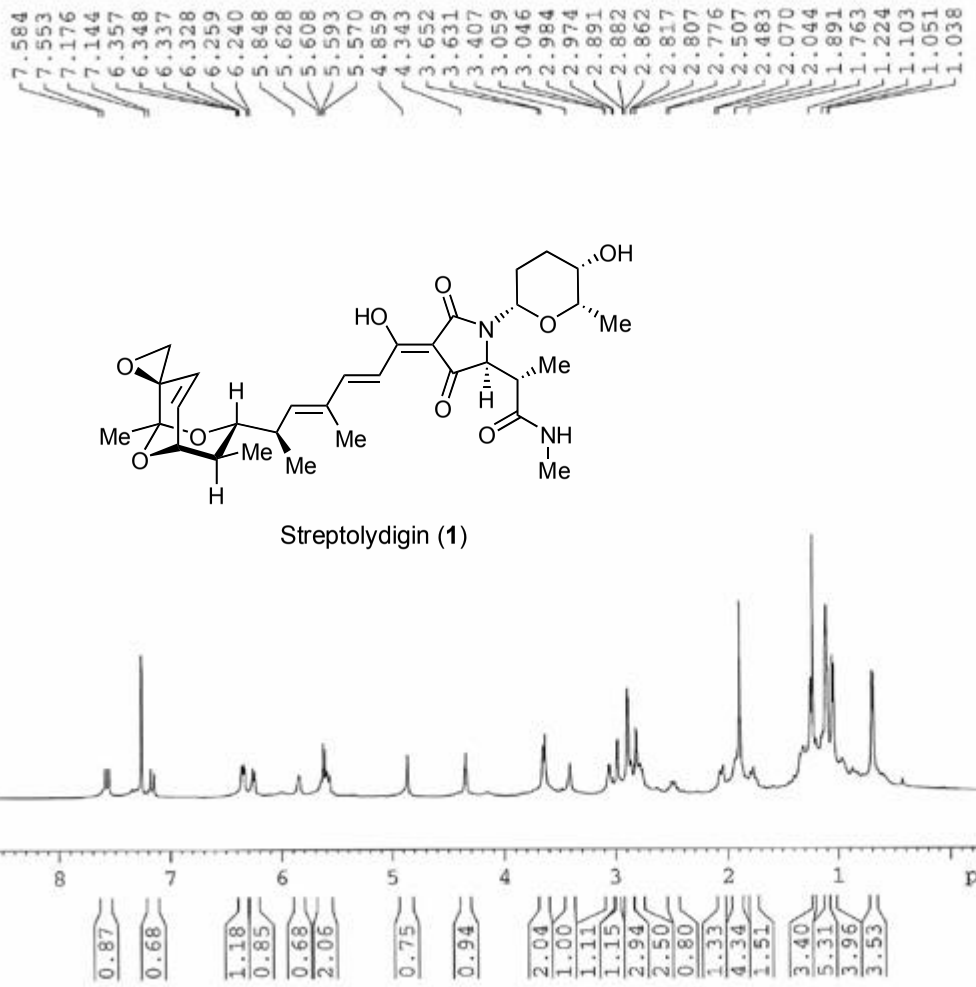
NAME	at13125
EXPNO	31
PROCNO	1
Date_	20100402
Time	16.10
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	104
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	8192
DW	16.500 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
========== CHANNEL f1 =======	
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
========== CHANNEL f2 =======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7577969 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

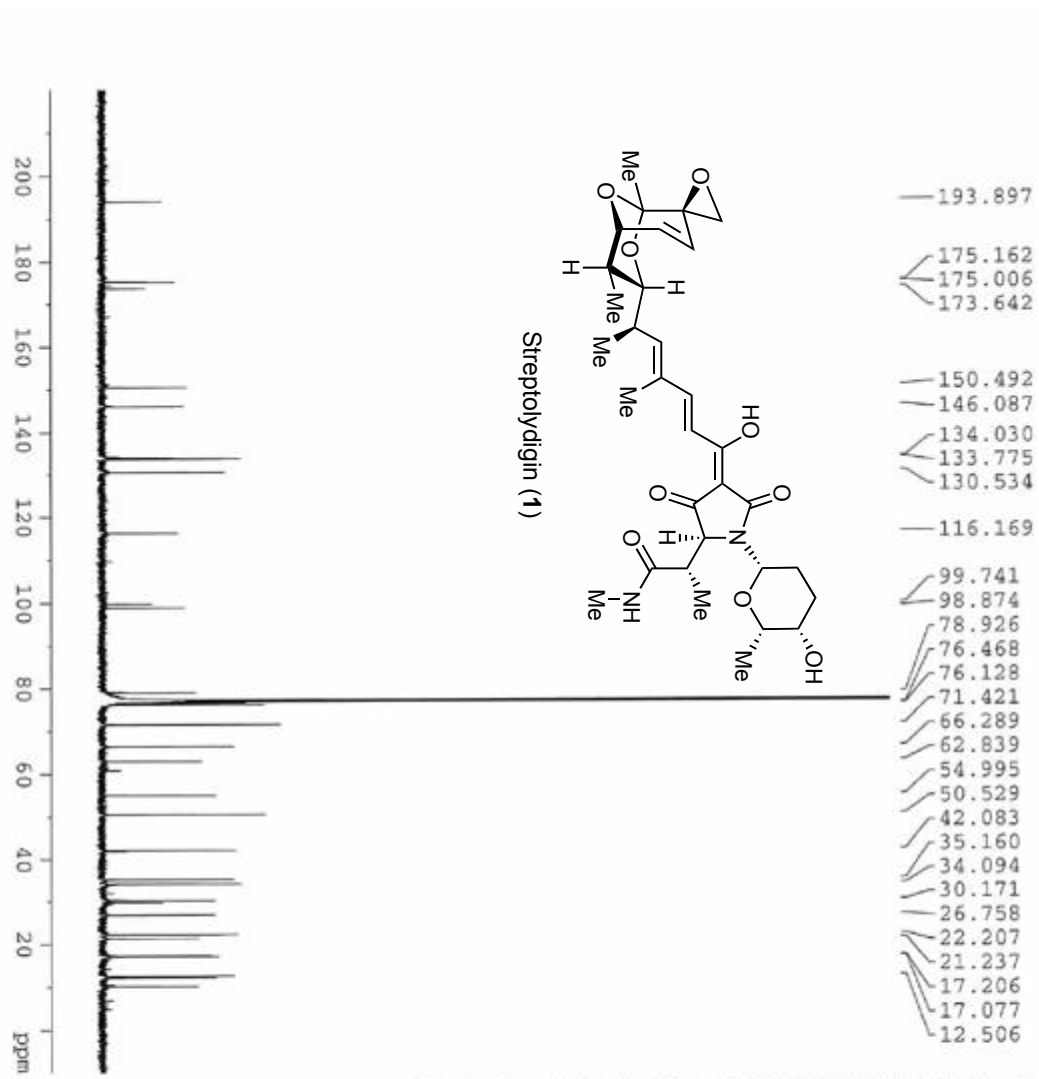

HO
O
Me
OTES
48
5.314
4.704
4.111
3.749
3.615
3.611
3.502
3.227
2.049
1.792
1.649
1.645
1.475
1.471
1.212
1.199
1.135
1.122
0.978
0.962
0.960
0.946
0.576
0.377
0.564
0.420
1.012
0.380
0.551
1.156
1.158
1.322
0.587
1.364
1.866
8.447
6.000
ppm


96.312
91.572
74.629
67.834
67.094
66.672
30.527
27.509
25.698
23.844
17.558
17.336
6.877
4.850
NAME st13127
EXPNO 2
PROCNO 1
Date_ 20100404
Time 16.54
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 60602
SOLVENT CDCl3
NS 64
DS 4
SWH 30303.031 Hz
FIDRES 0.500033 Hz
AQ 0.9999830 sec
RG 16384
DW 16.500 usec
DE 7.50 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec
CHANNEL f1
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7715724 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 500.1338000 MHz
SI 32768
SF 125.7577941 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OTES
HO
O
Me
48
200
180
160
140
120
100
80
60
40
20
ppm

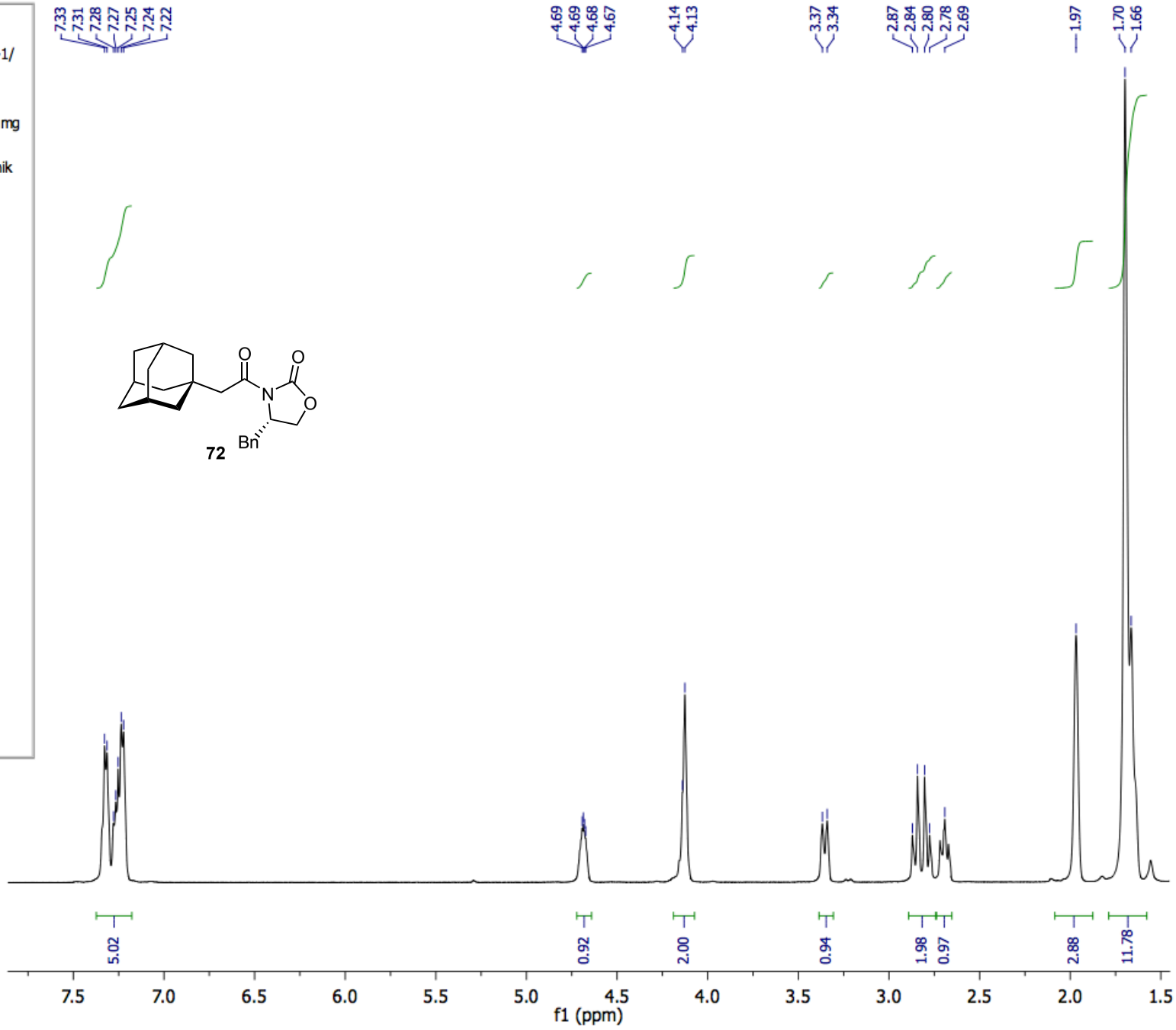

49
OTES
Me
Me
Me
EtO
OEt
ppm
0.15
0.16
0.70
4.09
0.80
1.83
1.06
1.00
1.62
3.04
1.09
0.39
1.04
0.95
0.89
0.96
9.09
3.20
9.07
6.35
5.313
5.307
4.946
4.930
4.118
3.863
3.800
3.760
3.607
3.595
3.518
3.209
3.164
2.994
2.933
2.929
2.770
2.725
2.017
1.894
1.740
1.737
1.601
1.327
1.317
1.135
1.122
0.918
0.567
0.551


195.12
195.08
178.19
174.15
165.84
84.55
75.91
65.93
62.78
62.73
59.09
49.68
42.47
41.48
40.53
30.48
24.88
23.22
17.69
16.24
16.19
13.92
6.80
4.83
OTES
Me
O
O
N
Me
O
O
P
EtO
OEt
O
N
O
Me
49
NAME st13052
EXPNO 11
PROCNO 1
Date_ 20100110
Time 8.38
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgdc
TD 65356
SOLVENT CDCl3
NS 137
DS 4
SWH 32679.738 Hz
FIDRES 0.500027 Hz
AQ 0.9999968 sec
RG 14596.5
DW 15.300 usec
DE 7.50 usec
TE 295.2 K
D1 4.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 12.00 usec
PL1 -3.00 dB
SFO1 125.7074941 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 28.00 dB
SFO2 499.8734991 MHz
SI 32768
SF 125.6924220 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm

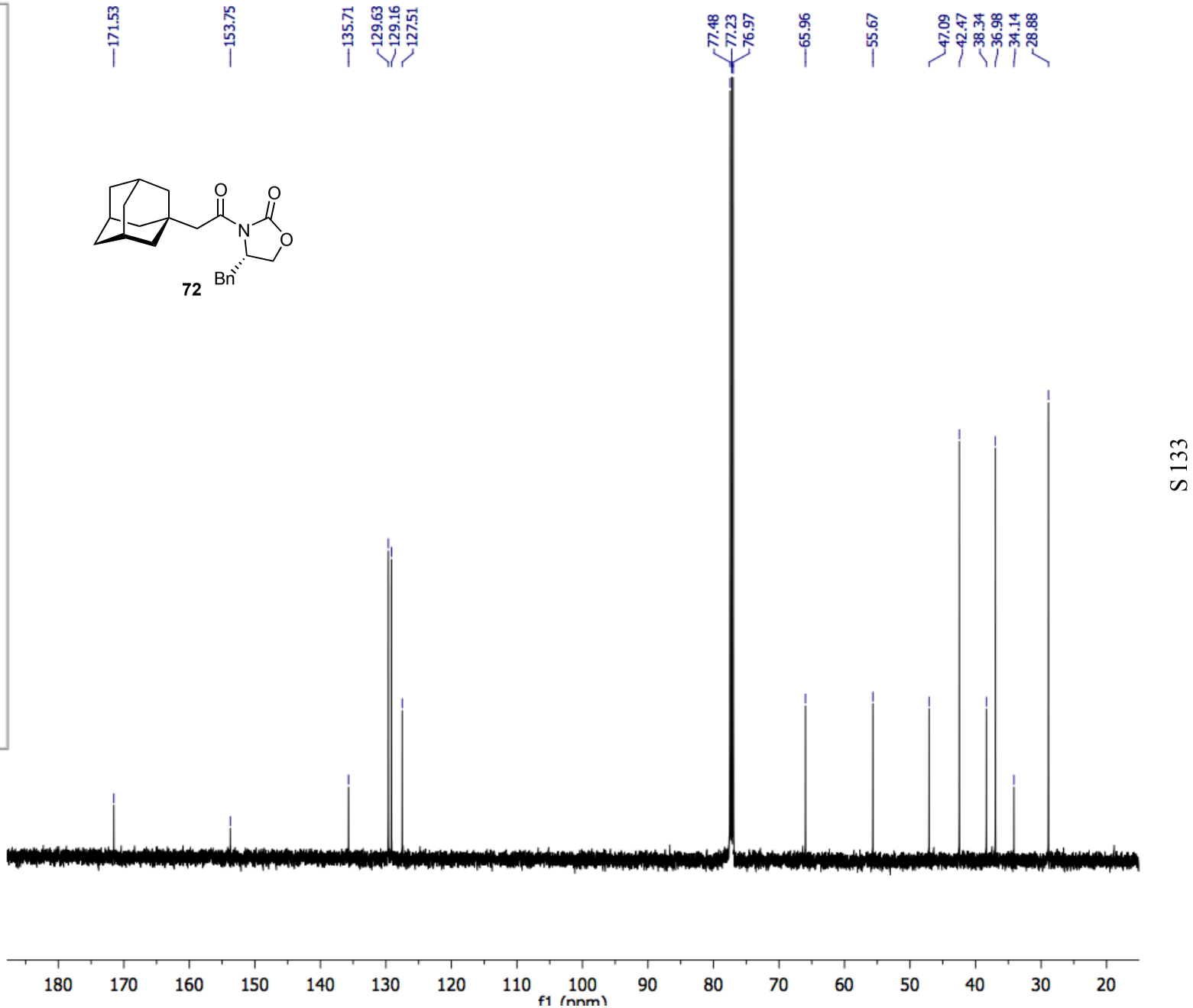

7.584
7.553
7.176
7.144
6.357
6.348
6.337
6.328
6.259
6.240
5.848
5.628
5.608
5.593
5.570
4.859
4.343
3.652
3.631
3.407
3.059
3.046
2.984
2.974
2.891
2.882
2.862
2.817
2.807
2.776
2.507
2.483
2.070
2.044
1.891
1.763
1.224
1.103
1.051
1.038
NAME st13141
EXPNO 2
PROCNO 1
Date_ 20100420
Time 10.36
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg
TD 45044
SOLVENT Acetone
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 128
DW 66.600 usec
DE 7.50 usec
TE 295.6 K
D1 3.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 5.35 usec
PL1 0.00 dB
SFO1 499.8734991 MHz
SI 32768
SF 499.8700197 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Streptolydigin (1)
8
7
6
5
4
3
2
1
ppm
0.87
0.68
1.18
0.85
0.68
2.06
0.75
0.94
2.04
1.00
1.11
1.15
2.94
2.50
0.80
1.33
4.34
1.51
3.40
5.31
3.96
3.53


Streptolydigin (1)
193.897
175.162
175.006
173.642
150.492
146.087
134.030
133.775
130.534
116.169
99.741
98.874
78.926
76.468
76.128
71.421
66.289
62.839
54.995
50.529
42.083
35.160
34.094
30.171
26.758
22.207
21.237
17.206
17.077
12.506
200
180
160
140
120
100
80
60
40
20
ppm

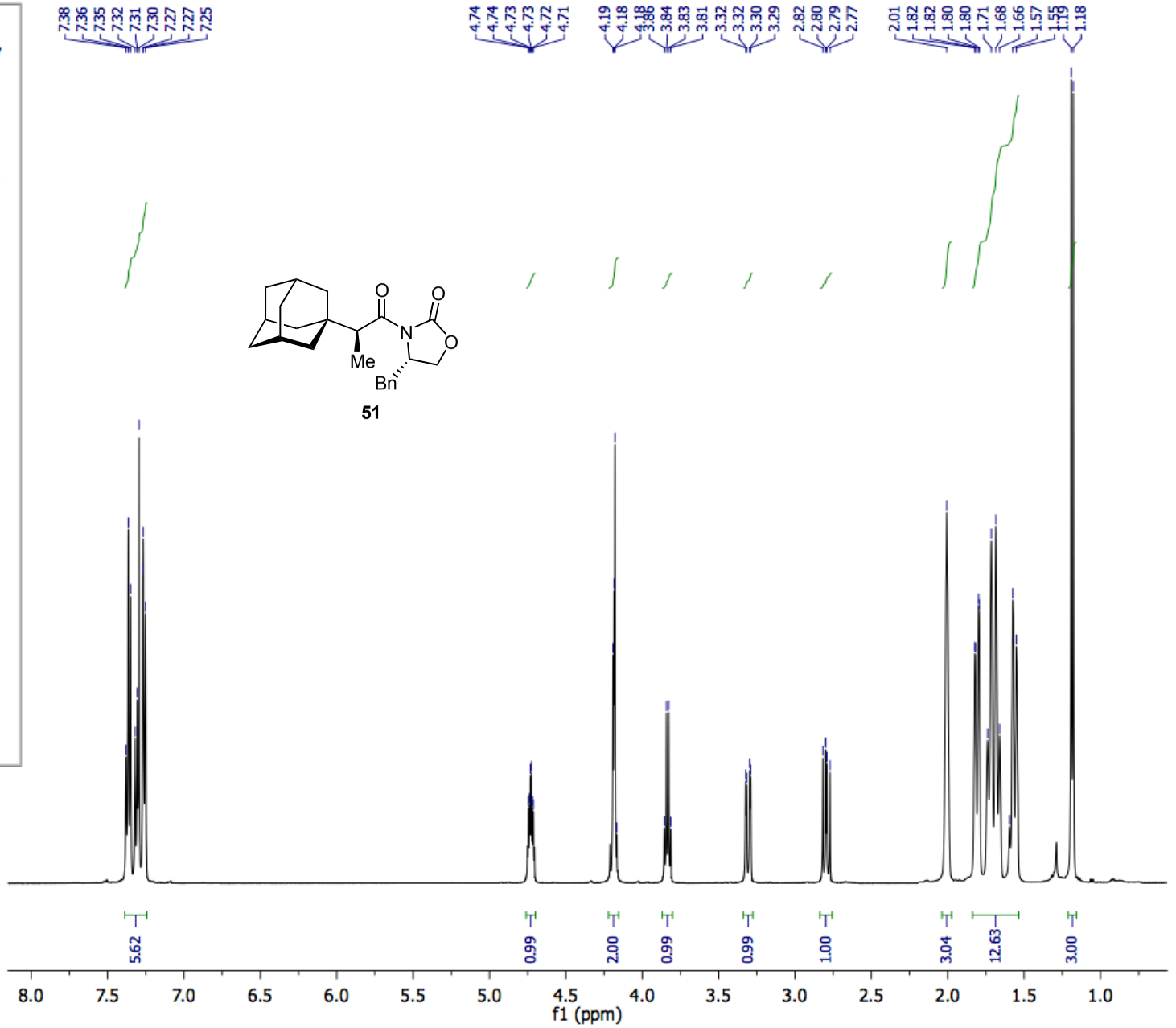
Parameter	Value
Data File Name	E:/ NMR Spectra/ 500-1/ 22/ pdata/ 1/ 1r
Title	AM
Comment	97/ 10/ 17, #5, 122.5 mg
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Owner	jschwans
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
0 Temperature	300.0
1 Pulse Sequence	zg
2 Number of Scans	32
3 Receiver Gain	128
4 Relaxation Delay	3.0000
5 Pulse Width	9.0000
6 Acquisition Time	3.0000
7 Acquisition Date	2011-01-23T13:24:00
8 Modification Date	2011-02-17T16:13:10
9 Spectrometer Frequency	500.13
0 Spectral Width	8012.8
1 Lowest Frequency	-1523.8
2 Nucleus	1H
3 Acquired Size	24038
4 Spectral Size	65536



	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 25/ fid
2	Title	AM
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	ajurkiew
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	150
13	Receiver Gain	8192
14	Relaxation Delay	4.0000
15	Pulse Width	8.0000
16	Acquisition Time	1.7933
17	Acquisition Date	2011-01-23T14:42:00
18	Modification Date	2011-03-14T07:26:54
19	Spectrometer Frequency	125.76
20	Spectral Width	31446.5
21	Lowest Frequency	-6317.1
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072

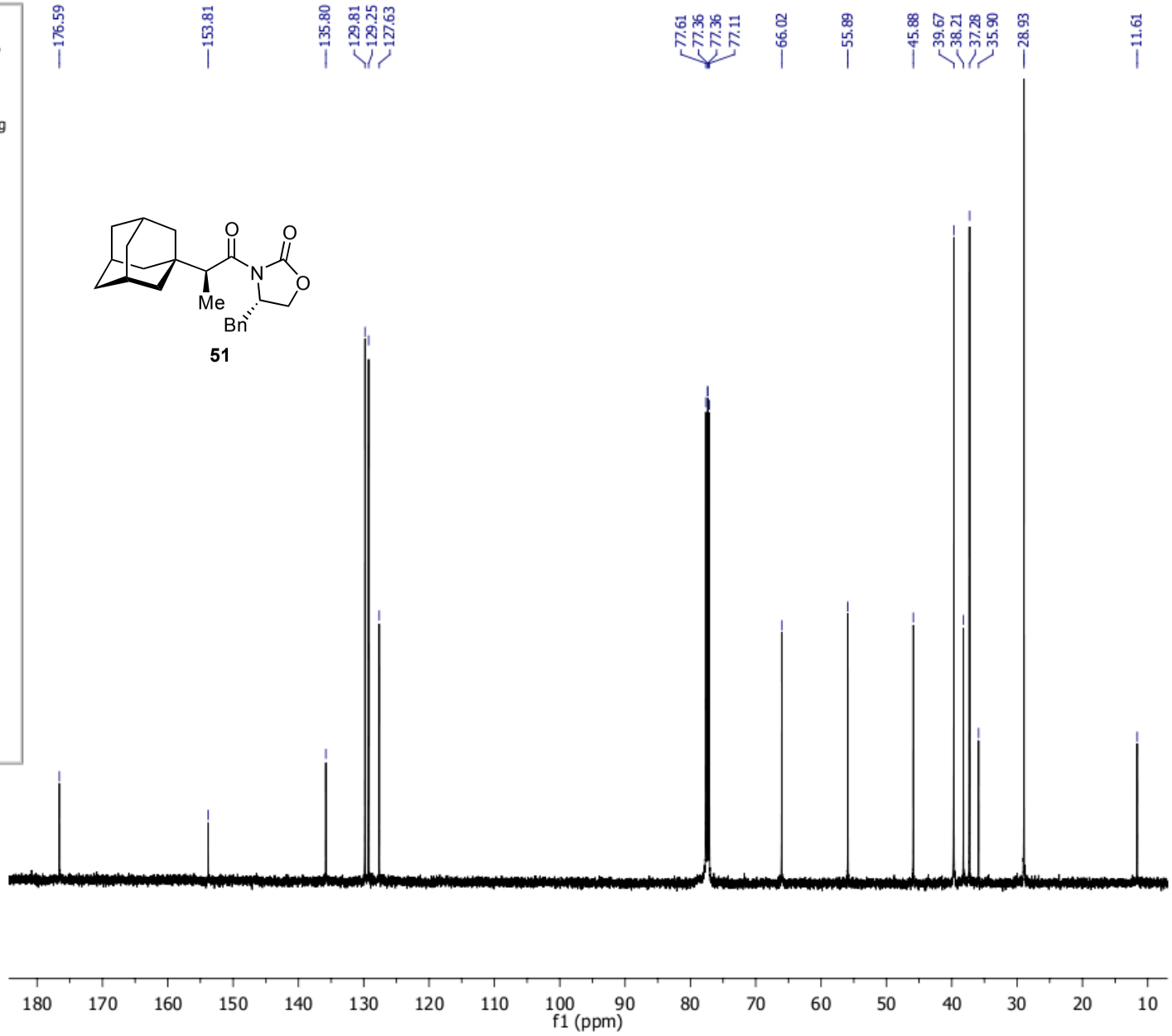


	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-2/ 74/ fid
2	Title	500-2
3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	zg
12	Number of Scans	32
13	Receiver Gain	51
14	Relaxation Delay	10.0000
15	Pulse Width	8.0000
16	Acquisition Time	2.9999
17	Acquisition Date	2011-02-19T04:18:31
18	Modification Date	2011-02-19T11:18:34
19	Spectrometer Frequency	499.87
20	Spectral Width	10000.0
21	Lowest Frequency	-2000.8
22	Nucleus	1H
23	Acquired Size	29999
24	Spectral Size	65536

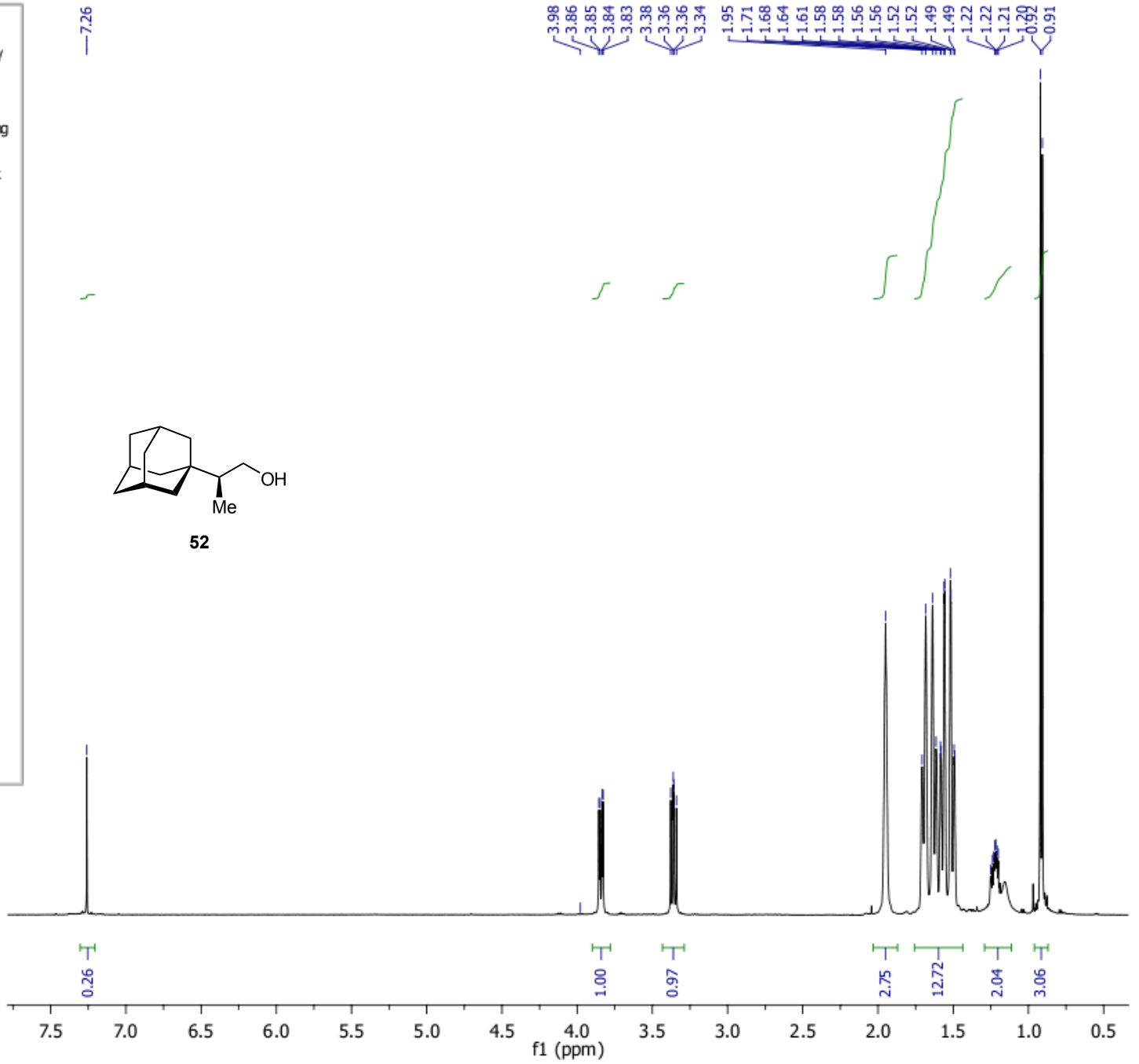


51

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 37/ fid
2	Title	500-1
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	ajurkiew
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	500
13	Receiver Gain	8192
14	Relaxation Delay	3.0000
15	Pulse Width	8.0000
16	Acquisition Time	1.5000
17	Acquisition Date	2011-03-04T11:35:57
18	Modification Date	2011-03-04T11:31:10
19	Spectrometer Frequency	125.76
20	Spectral Width	37594.0
21	Lowest Frequency	-9374.6
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072

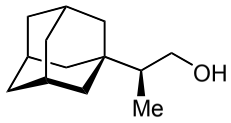


	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 29/ fid
2	Title	AM
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	ajurkiew
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zg
12	Number of Scans	32
13	Receiver Gain	64
14	Relaxation Delay	3.0000
15	Pulse Width	9.0000
16	Acquisition Time	3.0000
17	Acquisition Date	2011-01-31T13:33:00
18	Modification Date	2011-03-02T09:28:38
19	Spectrometer Frequency	500.13
20	Spectral Width	8012.8
21	Lowest Frequency	-1519.5
22	Nucleus	1H
23	Acquired Size	24038
24	Spectral Size	65536



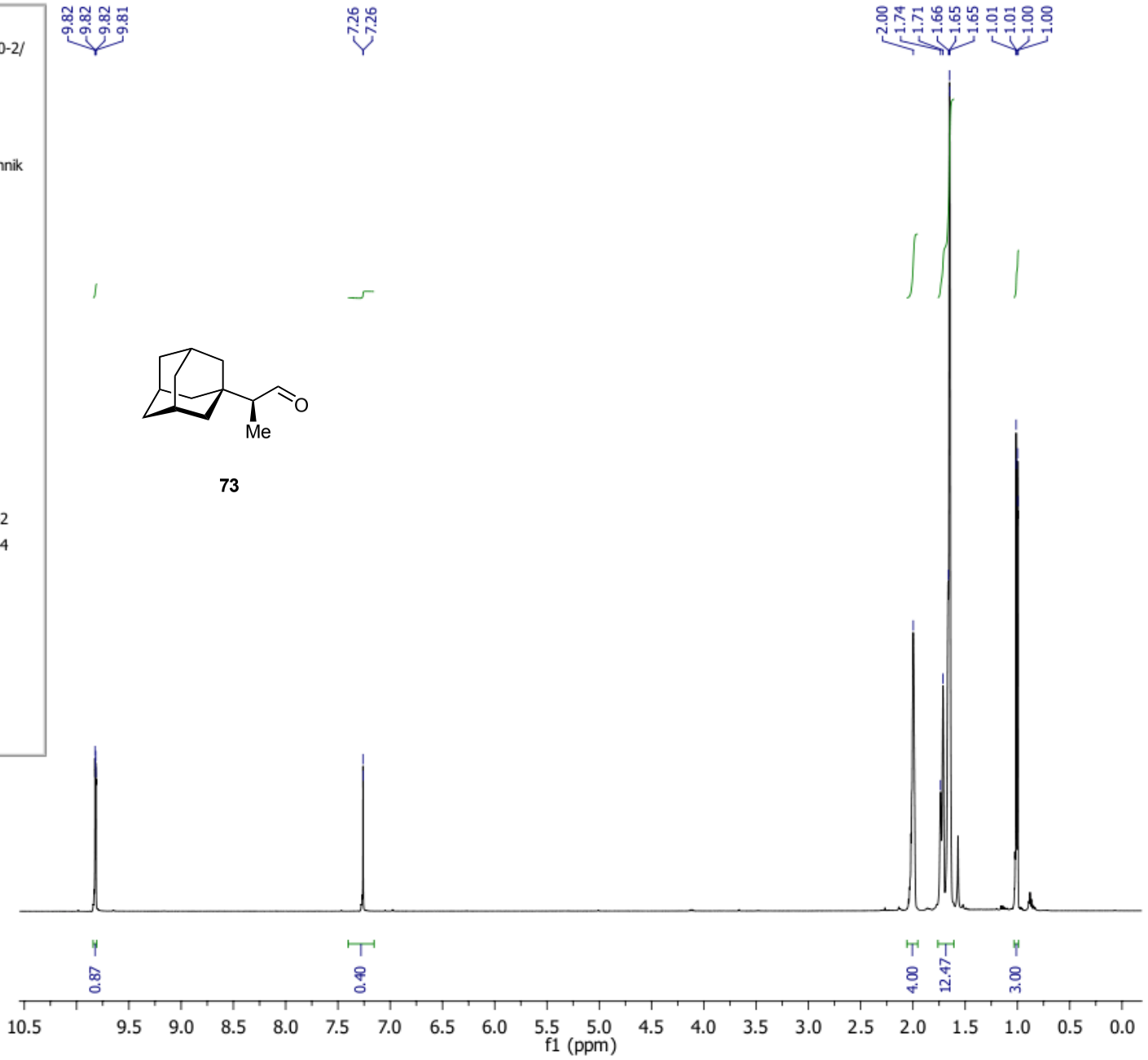
52

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 32/ fid
2	Title	AM
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	ajurkiew
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	20
13	Receiver Gain	4096
14	Relaxation Delay	4.0000
15	Pulse Width	8.0000
16	Acquisition Time	3.0000
17	Acquisition Date	2011-01-31T14:51:00
18	Modification Date	2011-03-02T09:29:00
19	Spectrometer Frequency	125.76
20	Spectral Width	18797.0
21	Lowest Frequency	-0.4
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072



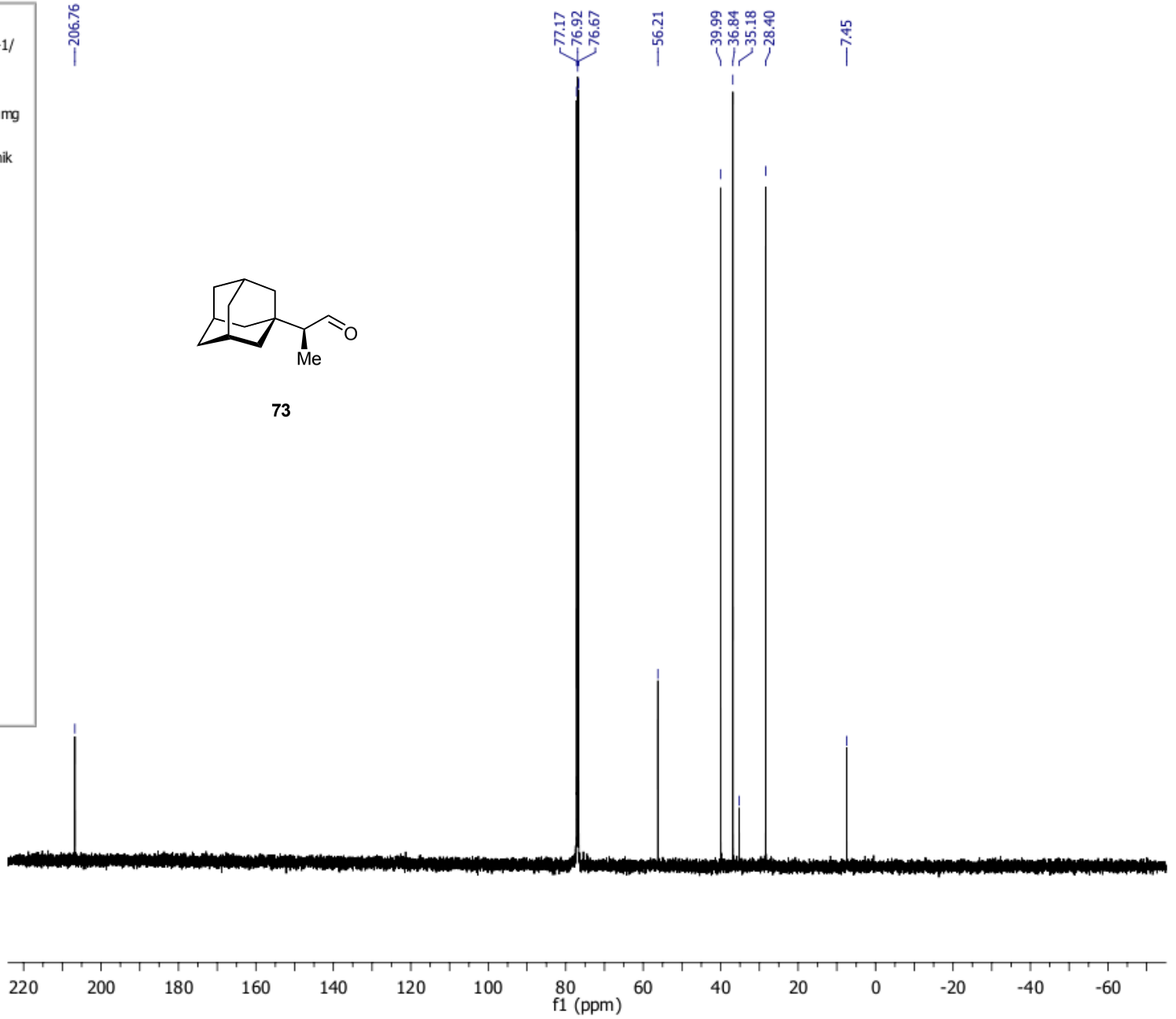
52

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-2/ 93/ fid
2	Title	500-2
3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.7
11	Pulse Sequence	zg
12	Number of Scans	32
13	Receiver Gain	57
14	Relaxation Delay	10.0000
15	Pulse Width	5.3500
16	Acquisition Time	2.9999
17	Acquisition Date	2011-03-14T04:28:42
18	Modification Date	2011-03-14T10:28:44
19	Spectrometer Frequency	499.87
20	Spectral Width	10000.0
21	Lowest Frequency	-2018.8
22	Nucleus	1H
23	Acquired Size	29999
24	Spectral Size	65536



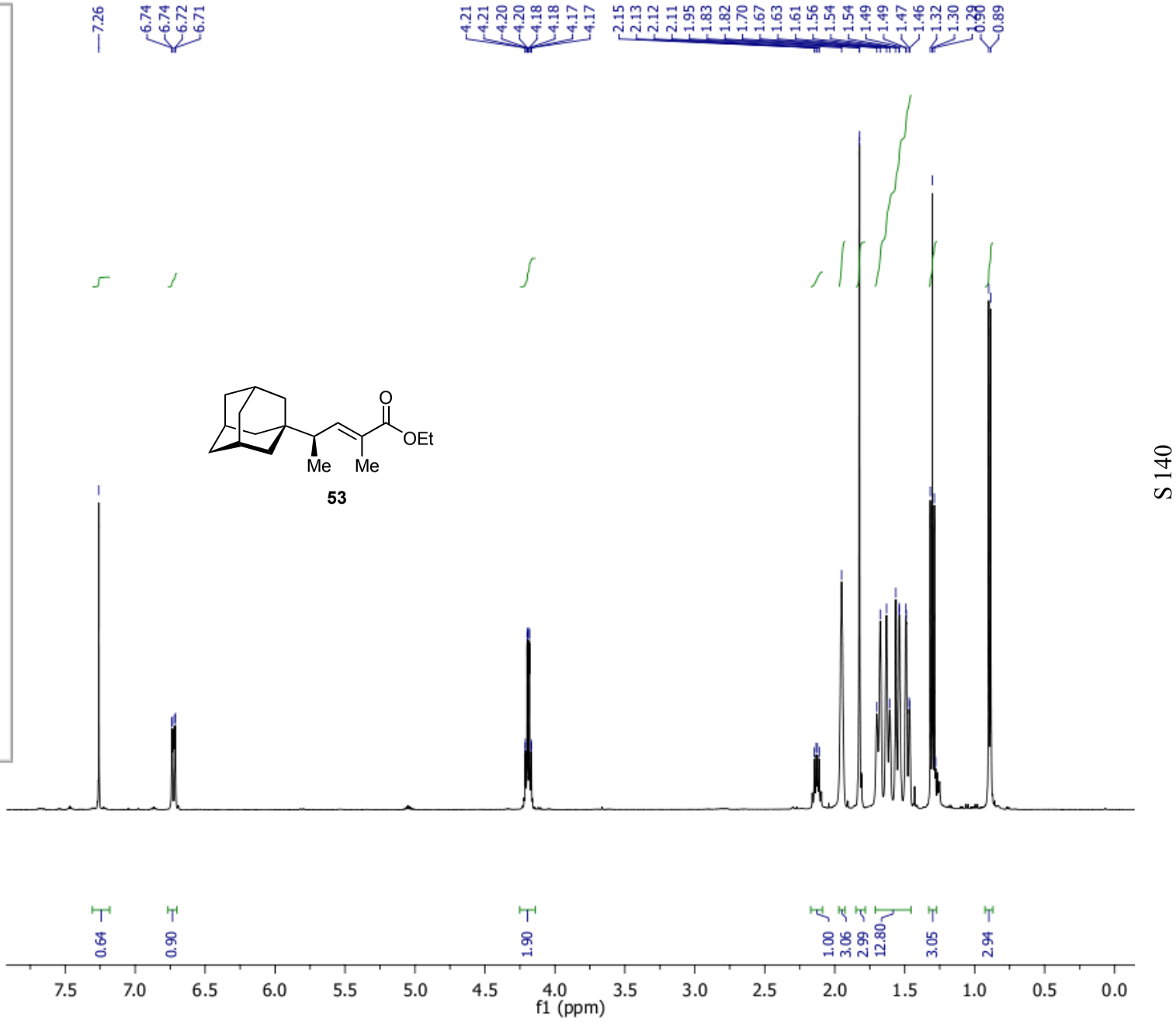
73

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 42/ fid
2	Title	500-1
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	jschwans
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	500
13	Receiver Gain	8192
14	Relaxation Delay	4.0000
15	Pulse Width	8.0000
16	Acquisition Time	1.5000
17	Acquisition Date	2011-03-10T09:28:56
18	Modification Date	2011-03-14T07:29:40
19	Spectrometer Frequency	125.76
20	Spectral Width	37594.0
21	Lowest Frequency	-9428.0
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072



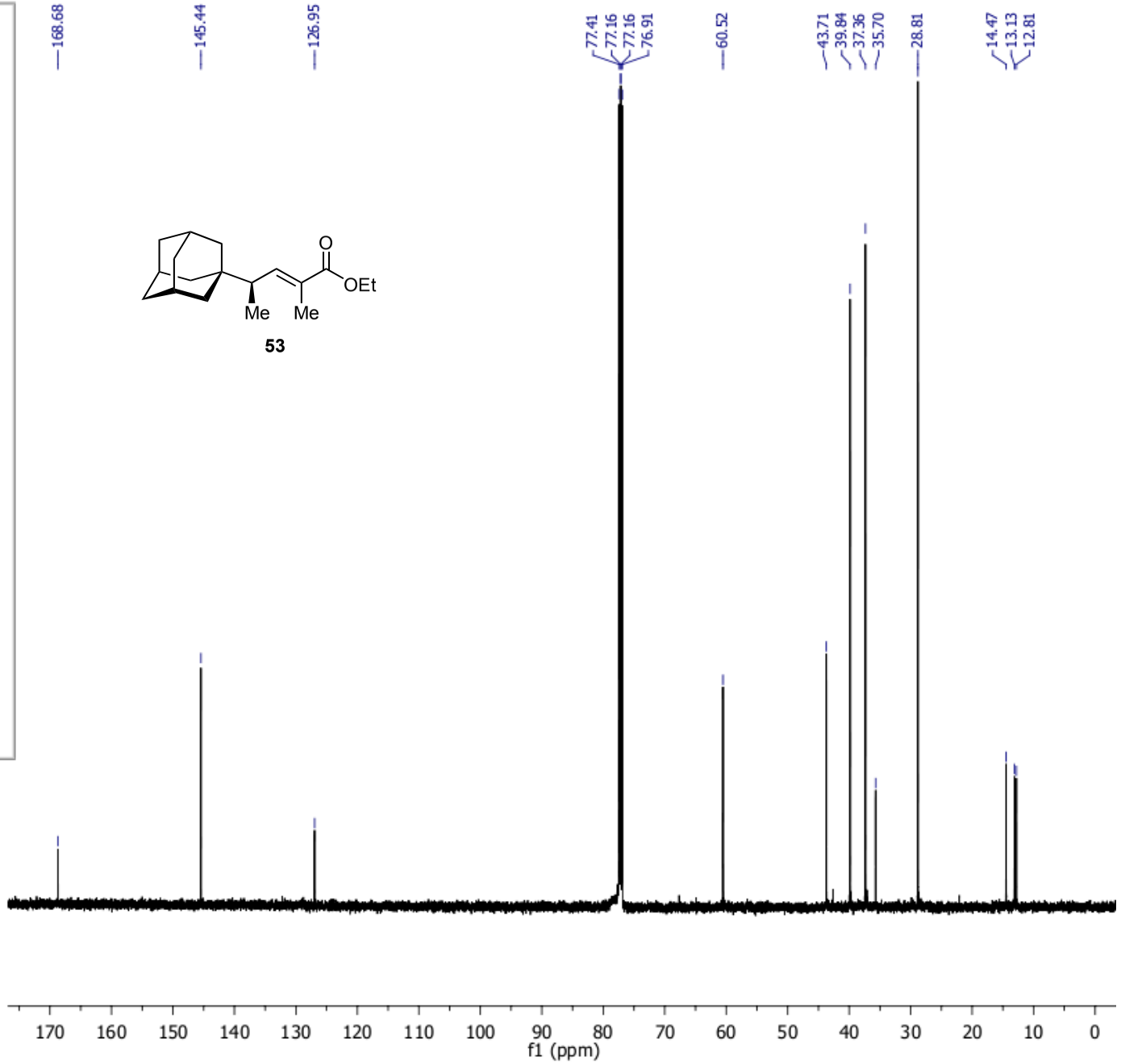
73

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-2/ 82/ fid
2	Title	500-2
3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	Acetone
10	Temperature	294.8
11	Pulse Sequence	zg
12	Number of Scans	32
13	Receiver Gain	51
14	Relaxation Delay	10.0000
15	Pulse Width	8.0000
16	Acquisition Time	2.9999
17	Acquisition Date	2011-02-23T05:31:13
18	Modification Date	2011-02-23T12:31:14
19	Spectrometer Frequency	499.87
20	Spectral Width	10000.0
21	Lowest Frequency	-2018.8
22	Nucleus	1H
23	Acquired Size	29999
24	Spectral Size	65536

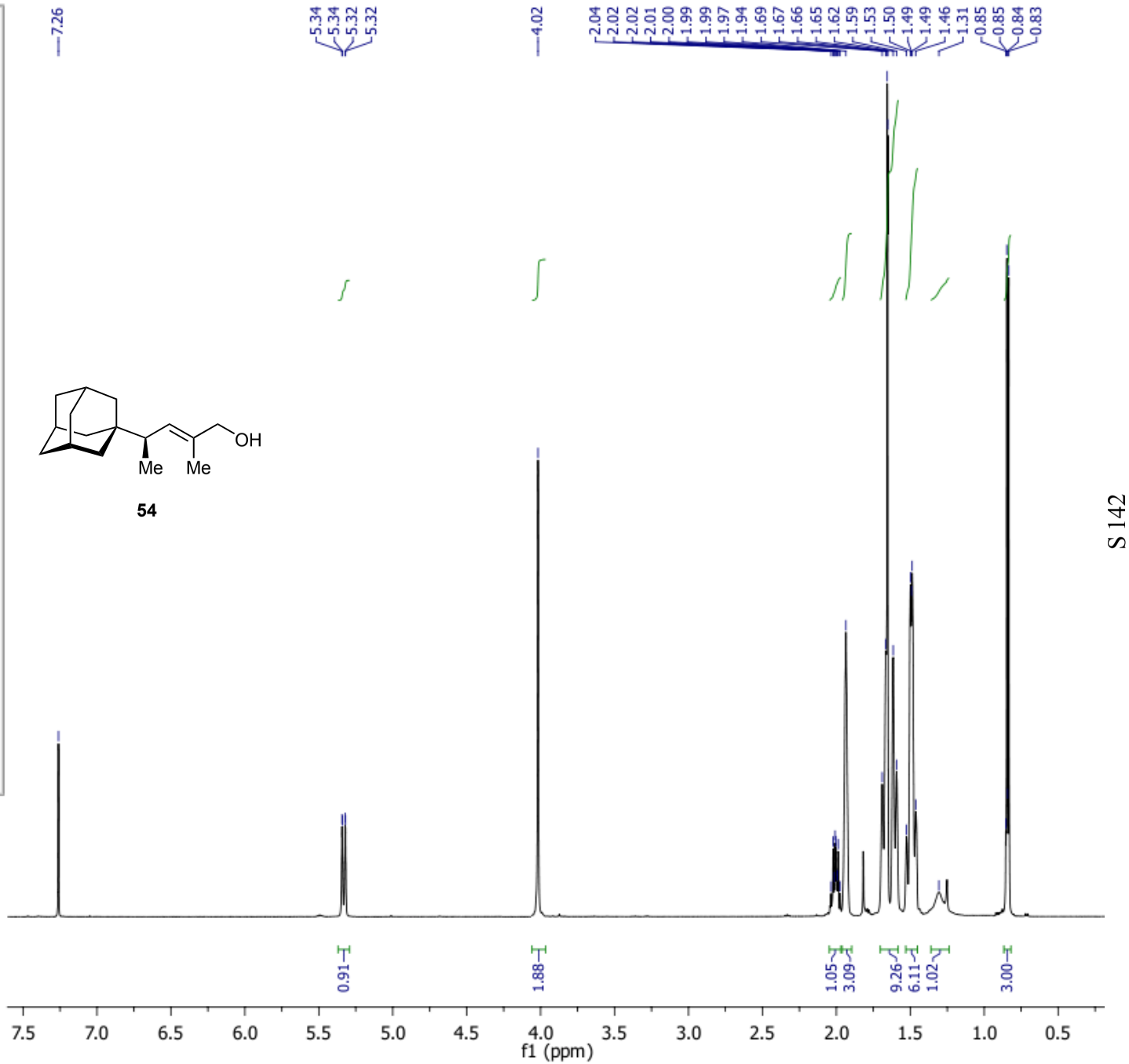


53

	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-1/ 36/ fid
2	Title	500-1
3	Comment	97/ 10/ 17, #5, 122.5 mg
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	ajurkiew
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	600
13	Receiver Gain	8192
14	Relaxation Delay	4.0000
15	Pulse Width	8.0000
16	Acquisition Time	1.5000
17	Acquisition Date	2011-02-28T09:56:14
18	Modification Date	2011-03-02T09:29:26
19	Spectrometer Frequency	125.76
20	Spectral Width	37594.0
21	Lowest Frequency	-9398.2
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072



	Parameter	Value
1	Data File Name	E:/ NMR Spectra/ 500-2/ 92/ fid
2	Title	500-2
3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	294.9
11	Pulse Sequence	zg
12	Number of Scans	32
13	Receiver Gain	32
14	Relaxation Delay	10.0000
15	Pulse Width	8.0000
16	Acquisition Time	2.9999
17	Acquisition Date	2011-03-08T05:50:27
18	Modification Date	2011-03-08T12:50:30
19	Spectrometer Frequency	499.87
20	Spectral Width	10000.0
21	Lowest Frequency	-2018.3
22	Nucleus	1H
23	Acquired Size	29999
24	Spectral Size	65536



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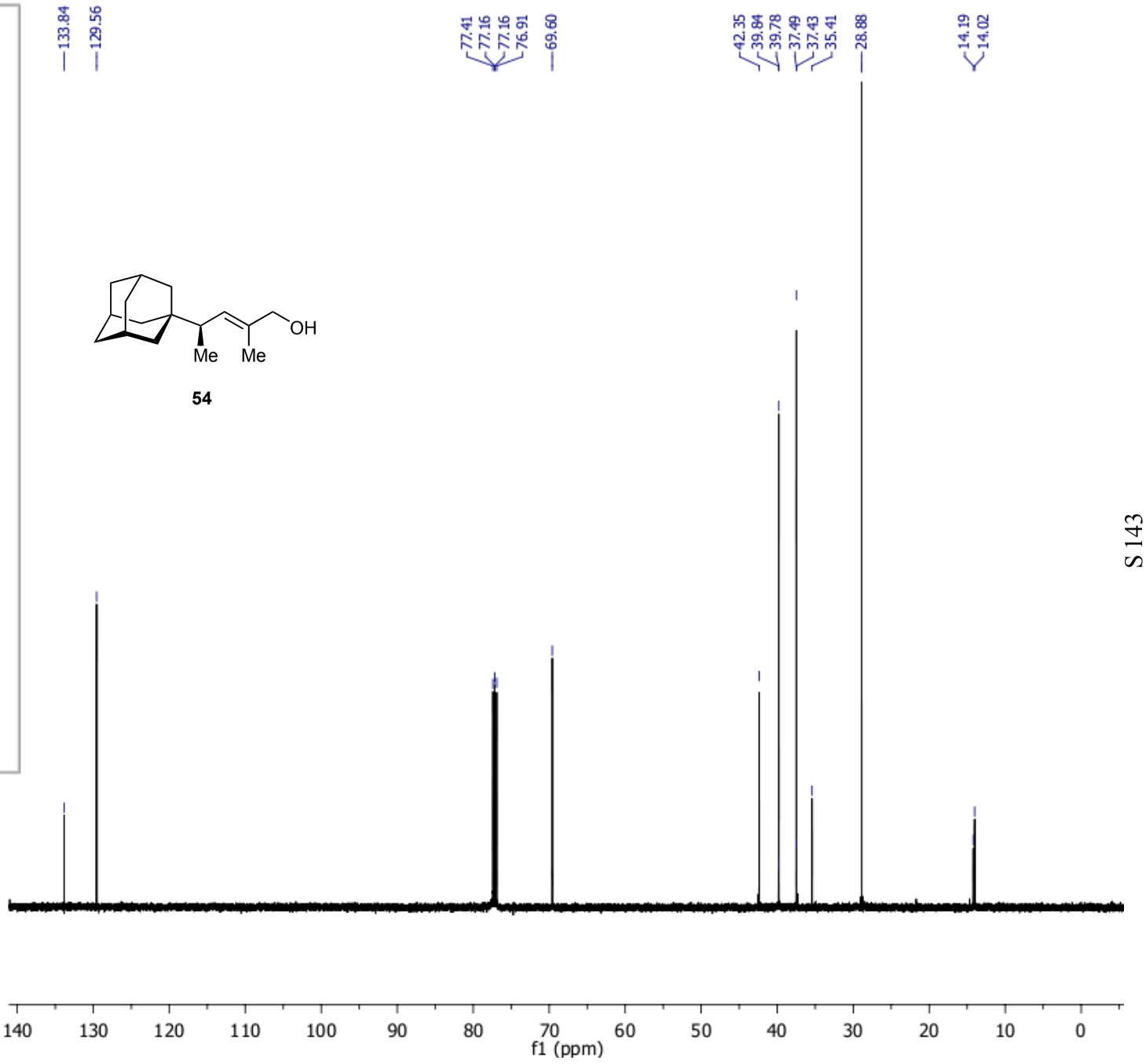
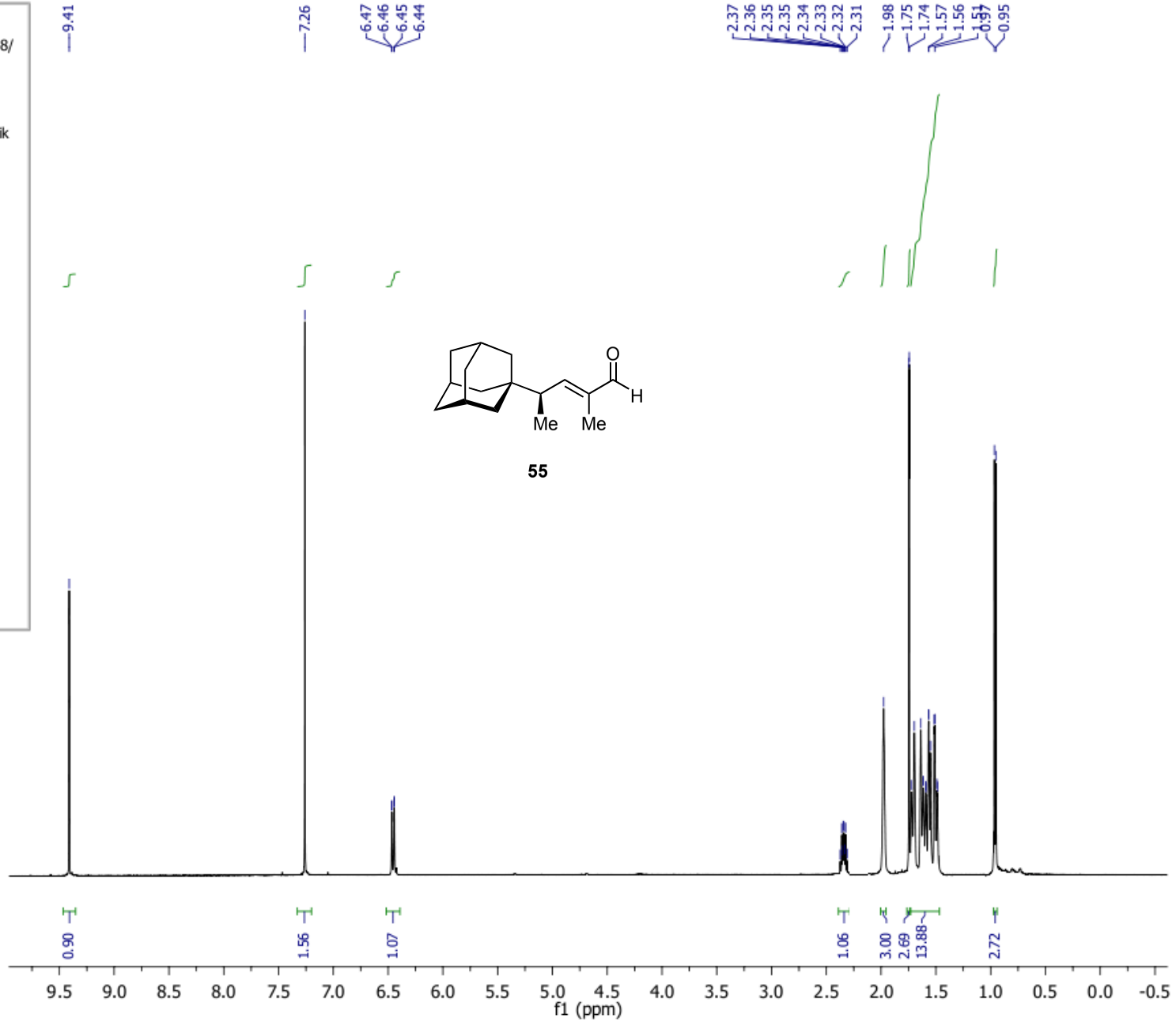
	Parameter	Value
1	Data File Name	E:/ 46/ fid
2	Title	E:
3	Comment	
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	jschwans
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDCl3
10	Temperature	300.0
11	Pulse Sequence	zgdc
12	Number of Scans	600
13	Receiver Gain	8192
14	Relaxation Delay	3.0000
15	Pulse Width	8.0000
16	Acquisition Time	1.5000
17	Acquisition Date	2011-03-15T08:26:07
18	Modification Date	2011-03-15T07:37:30
19	Spectrometer Frequency	125.77
20	Spectral Width	37594.0
21	Lowest Frequency	-9398.1
22	Nucleus	13C
23	Acquired Size	56390
24	Spectral Size	131072



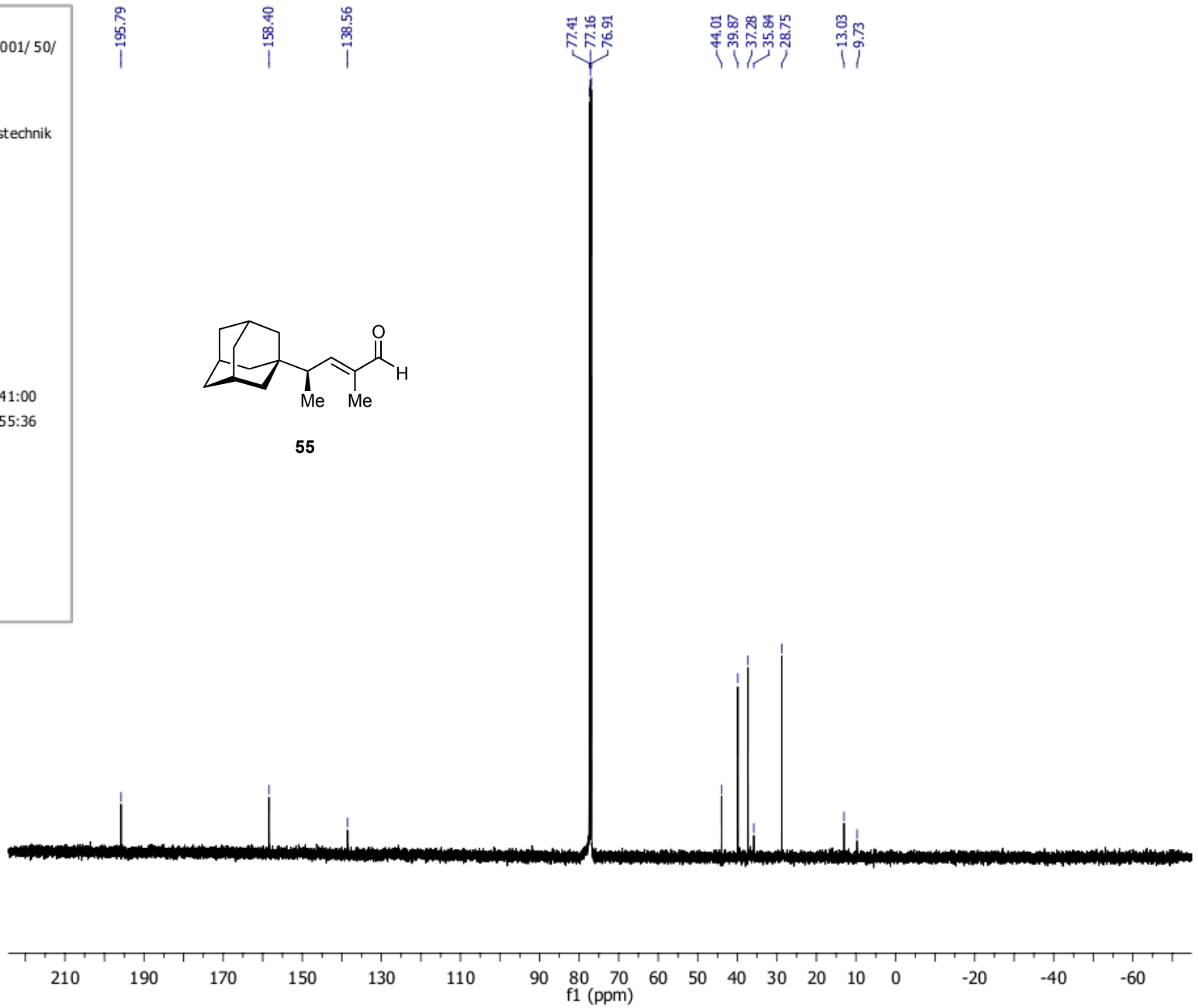
54

	Parameter	Value
1	Data File Name	E:/ all nmr/ AM 5001/ 48/ fid
2	Title	AM
3	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
4	Owner	jschwans
5	Spectrometer	spect
6	Temperature	300.0
7	Pulse Sequence	zg
8	Number of Scans	16
9	Receiver Gain	256
10	Relaxation Delay	10.0000
11	Pulse Width	9.0000
12	Acquisition Time	3.0000
13	Acquisition Date	2011-03-16T13:31:00
14	Modification Date	2011-04-19T14:55:30
15	Spectrometer Frequency	500.13
16	Spectral Width	8012.8
17	Lowest Frequency	-1519.3
18	Nucleus	1H
19	Acquired Size	24038
20	Spectral Size	65536

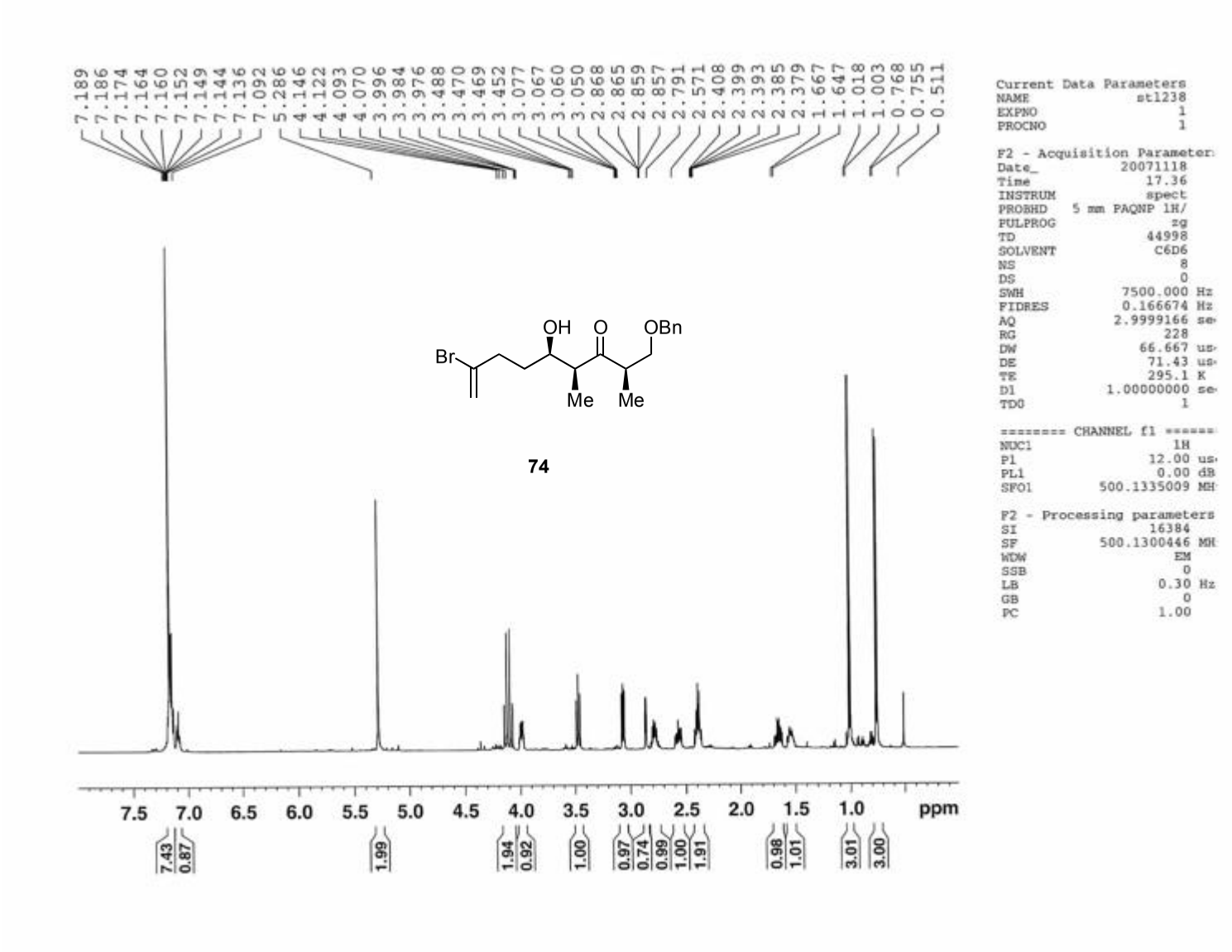


55

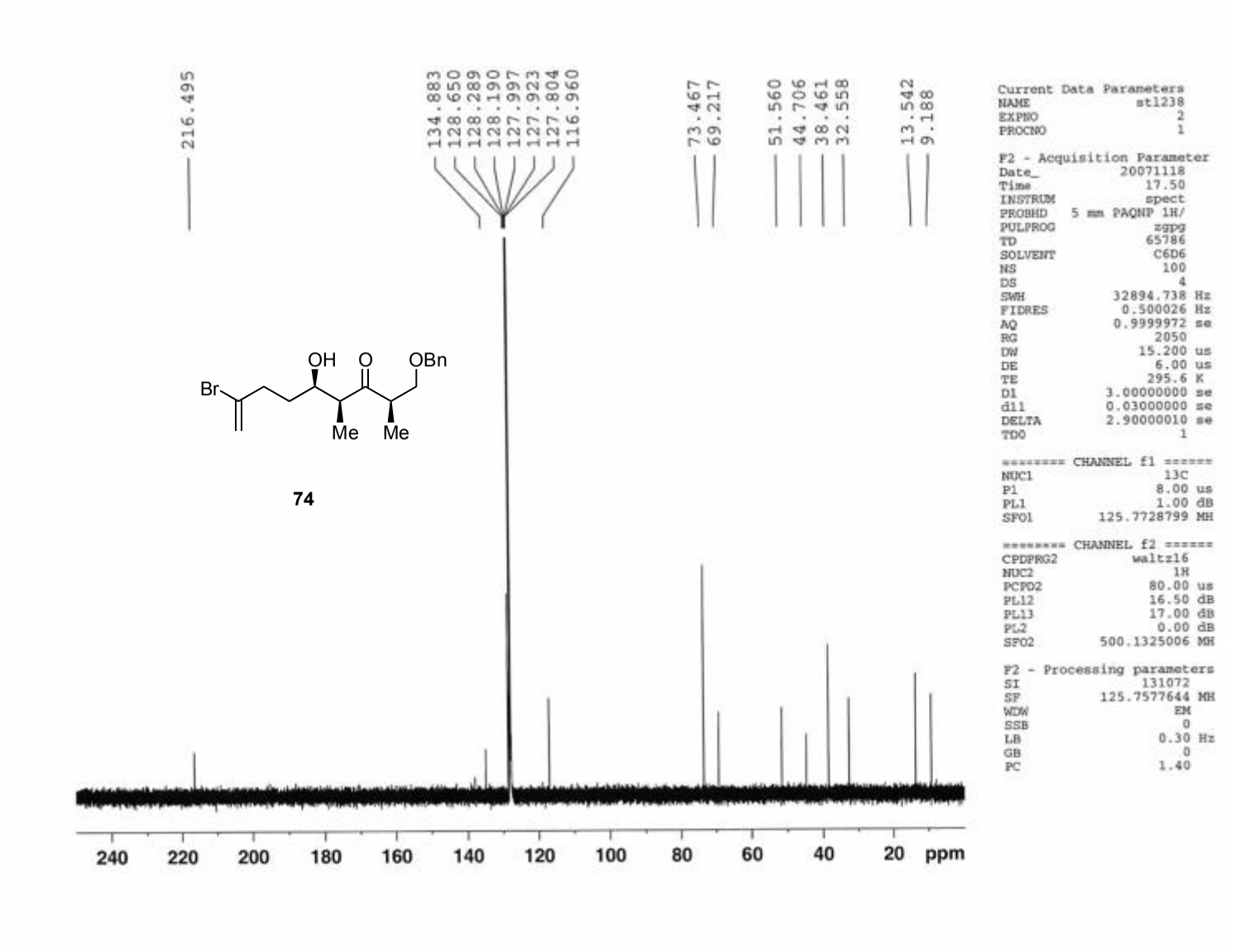
	Parameter	Value
1	Data File Name	E:/ all nmr/ AM 5001/ 50/ fid
2	Title	AM
3	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
4	Owner	jschwans
5	Spectrometer	spect
6	Temperature	300.0
7	Pulse Sequence	zgdc
8	Number of Scans	650
9	Receiver Gain	8192
10	Relaxation Delay	3.0000
11	Pulse Width	8.0000
12	Acquisition Time	1.5000
13	Acquisition Date	2011-03-16T18:41:00
14	Modification Date	2011-04-19T14:55:36
15	Spectrometer Frequency	125.76
16	Spectral Width	37594.0
17	Lowest Frequency	-9397.7
18	Nucleus	13C
19	Acquired Size	56390
20	Spectral Size	131072



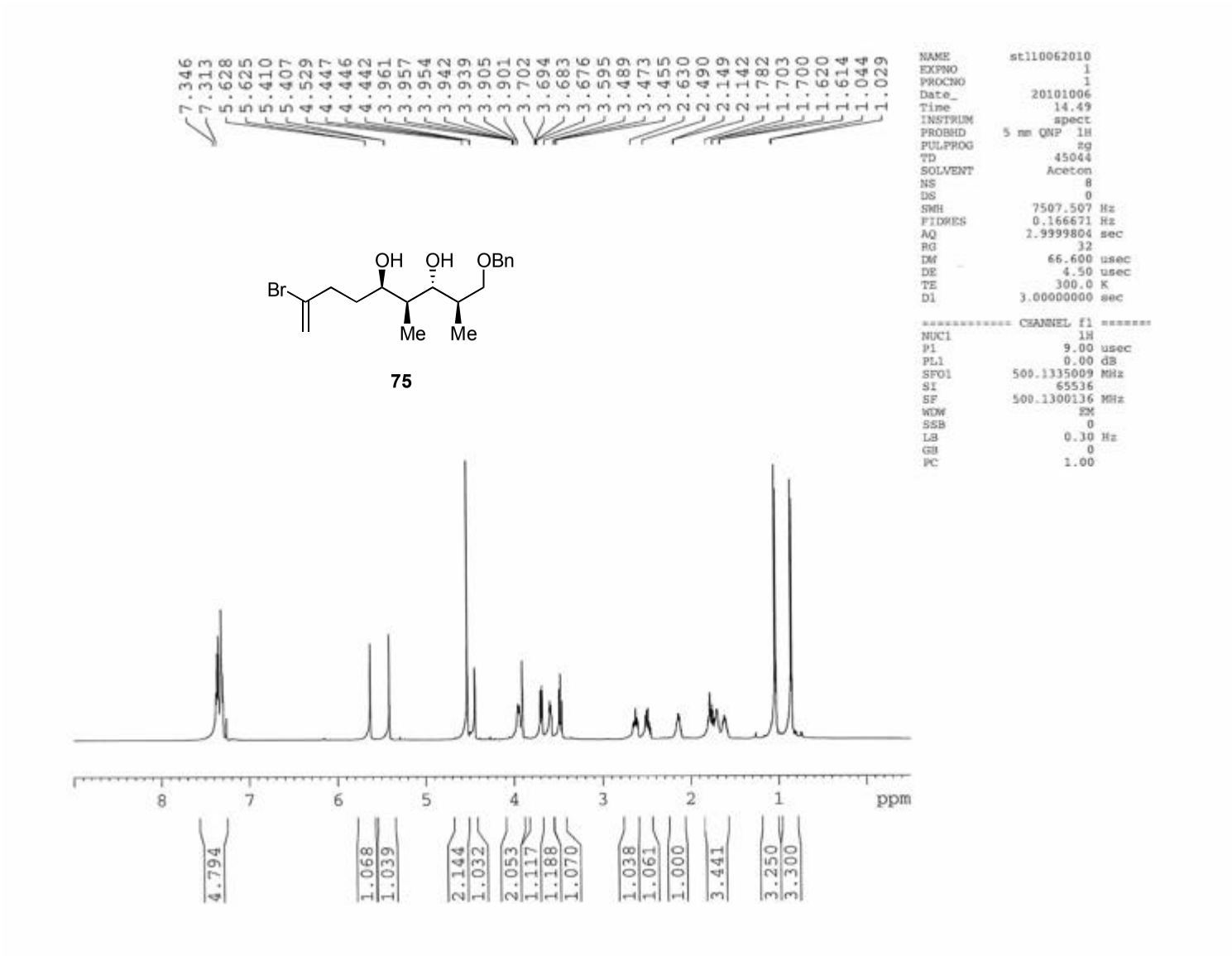
55



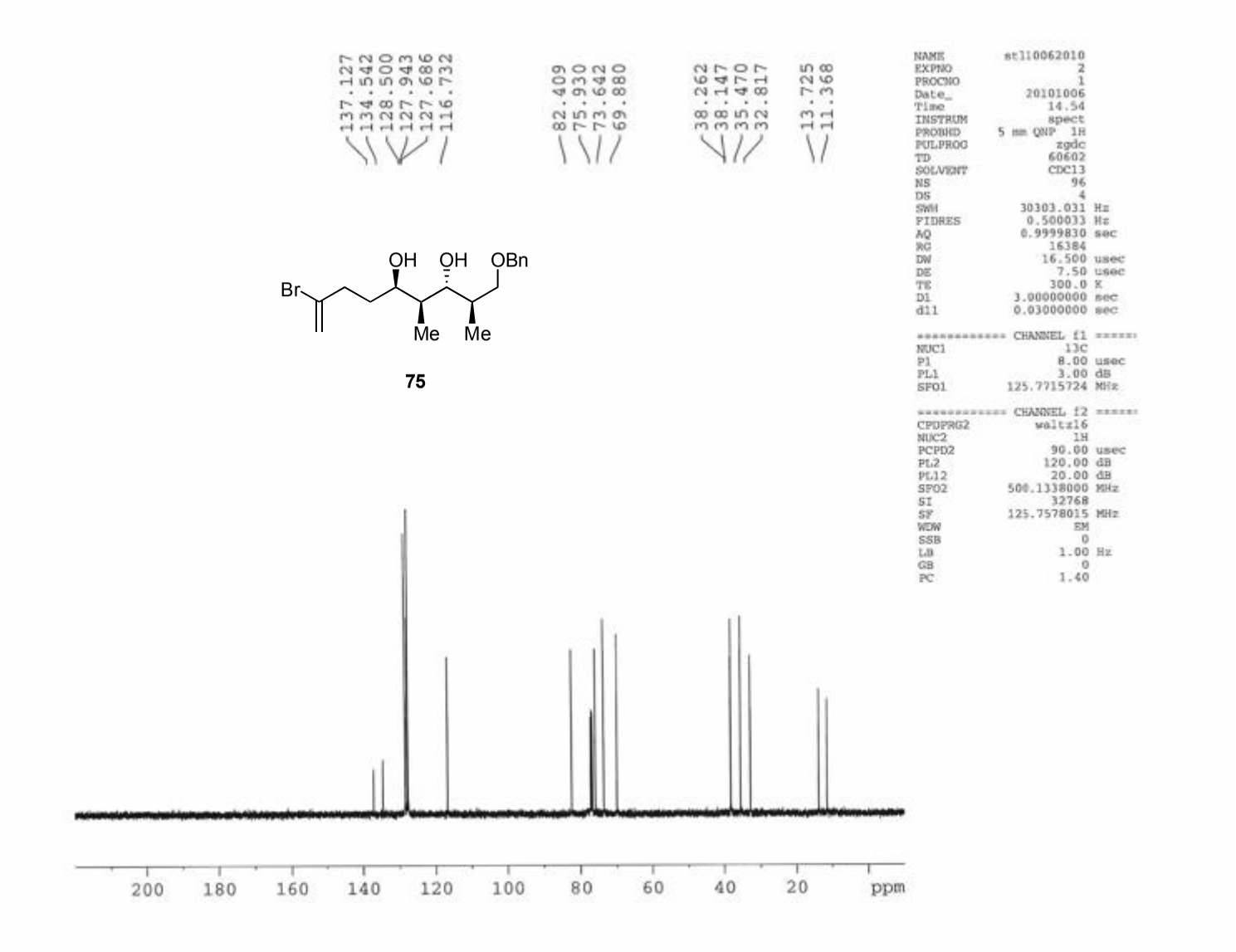

```
Current Data Parameters
NAME                  st1238
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameter
Date_              20071118
Time                  17.36
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG                 zg
TD                     44998
SOLVENT                C6D6
NS                         8
DS                         0
SWH                7500.000 Hz
FIDRES                0.166674 Hz
AQ                 2.9999166 se
RG                       228
DW                    66.667 us
DE                    71.43 us
TE                    295.1 K
D1                 1.00000000 se
TD0                        1

======== CHANNEL f1 ======
NUC1                      1H
P1                    12.00 us
PL1                    0.00 dB
SFO1           500.1335009 MH

F2 - Processing parameters
SI                     16384
SF             500.1300446 MH
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00
```



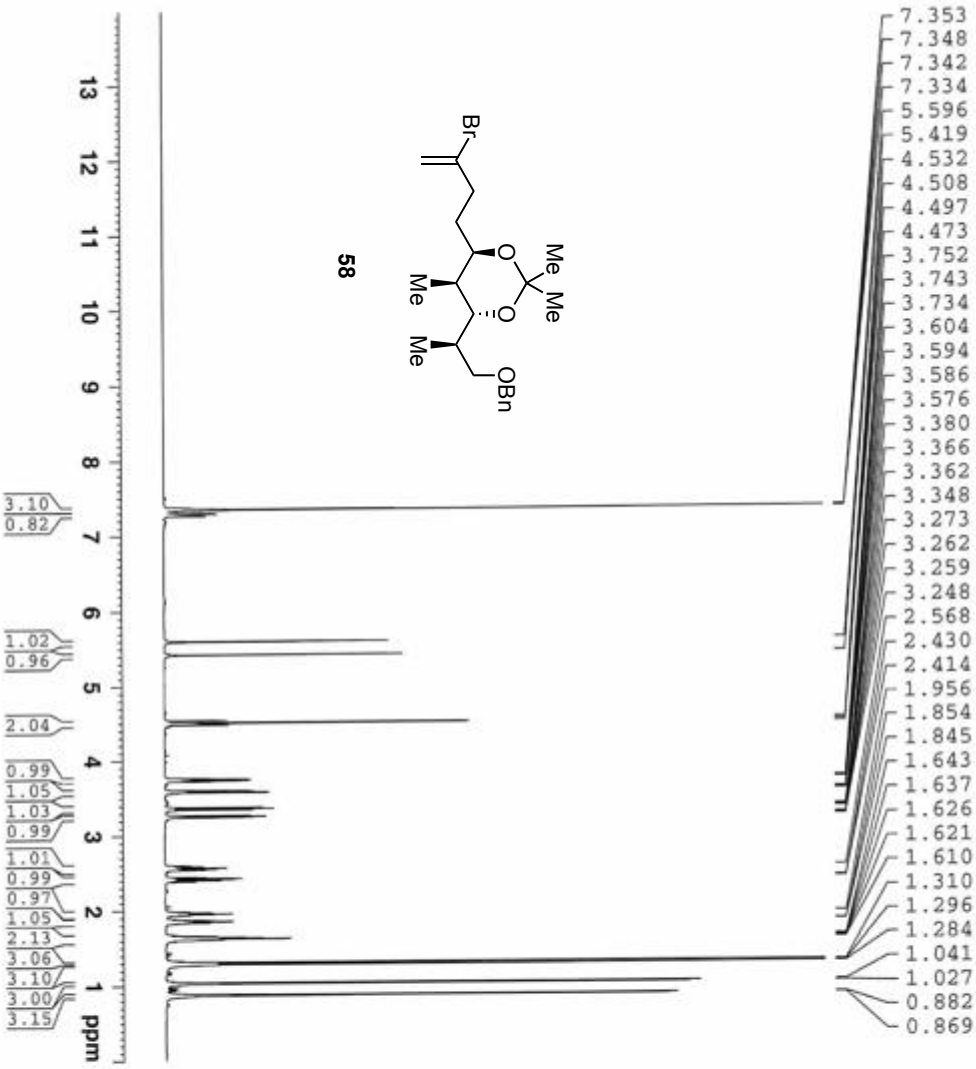

```
Current Data Parameters
NAME                  stl238
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameter
Date_              20071118
Time                  17.50
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zgpg
TD                    65786
SOLVENT               C6D6
NS                      100
DS                        4
SWH               32894.738 Hz
FIDRES            0.500026 Hz
AQ                0.9999972 se
RG                     2050
DW                  15.200 us
DE                   6.00 us
TE                   295.6 K
D1                3.00000000 se
d11               0.03000000 se
DELTA             2.90000010 se
TD0                        1

======== CHANNEL f1 ======
NUC1                    13C
P1                   8.00 us
PL1                  1.00 dB
SFO1          125.7728799 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                    1H
PCPD2               80.00 us
PL12                16.50 dB
PL13                17.00 dB
PL2                  0.00 dB
SFO2          500.1325006 MH

F2 - Processing parameters
SI                    131072
SF            125.7577644 MH
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                    1.40
```

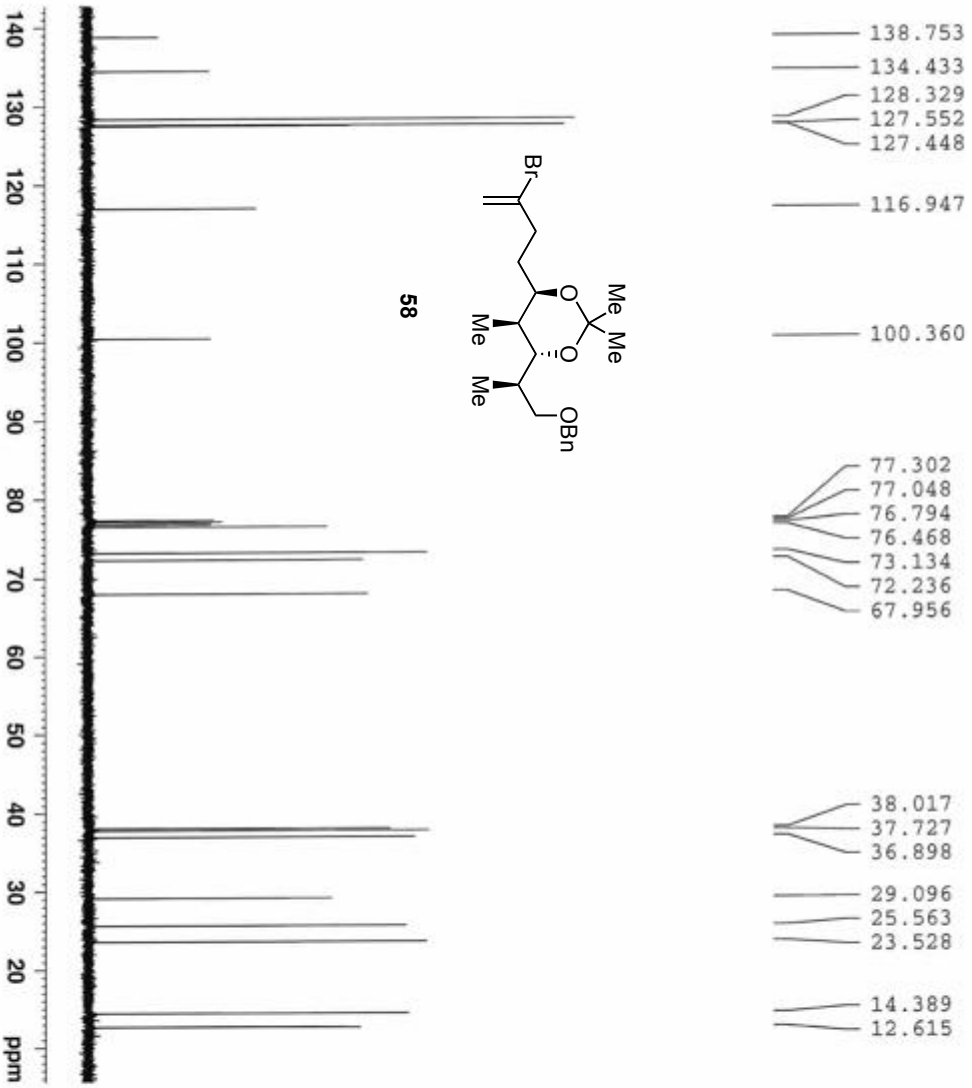

7.346
7.313
5.628
5.625
5.410
5.407
4.529
4.447
4.446
4.442
3.961
3.957
3.954
3.942
3.939
3.905
3.901
3.702
3.694
3.683
3.676
3.595
3.489
3.473
3.455
2.630
2.490
2.149
2.142
1.782
1.703
1.700
1.620
1.614
1.044
1.029
NAME st110062010
EXPNO 1
PROCNO 1
Date_ 20101006
Time 14.49
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT Aceton
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 32
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec
CHANNEL f1
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz
SI 65536
SF 500.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
OH
OBn
Br
Me
Me
8
7
6
5
4
3
2
1
ppm
4.794
1.068
1.039
2.144
1.032
2.053
1.117
1.188
1.070
1.038
1.061
1.000
3.441
3.250
3.300

75

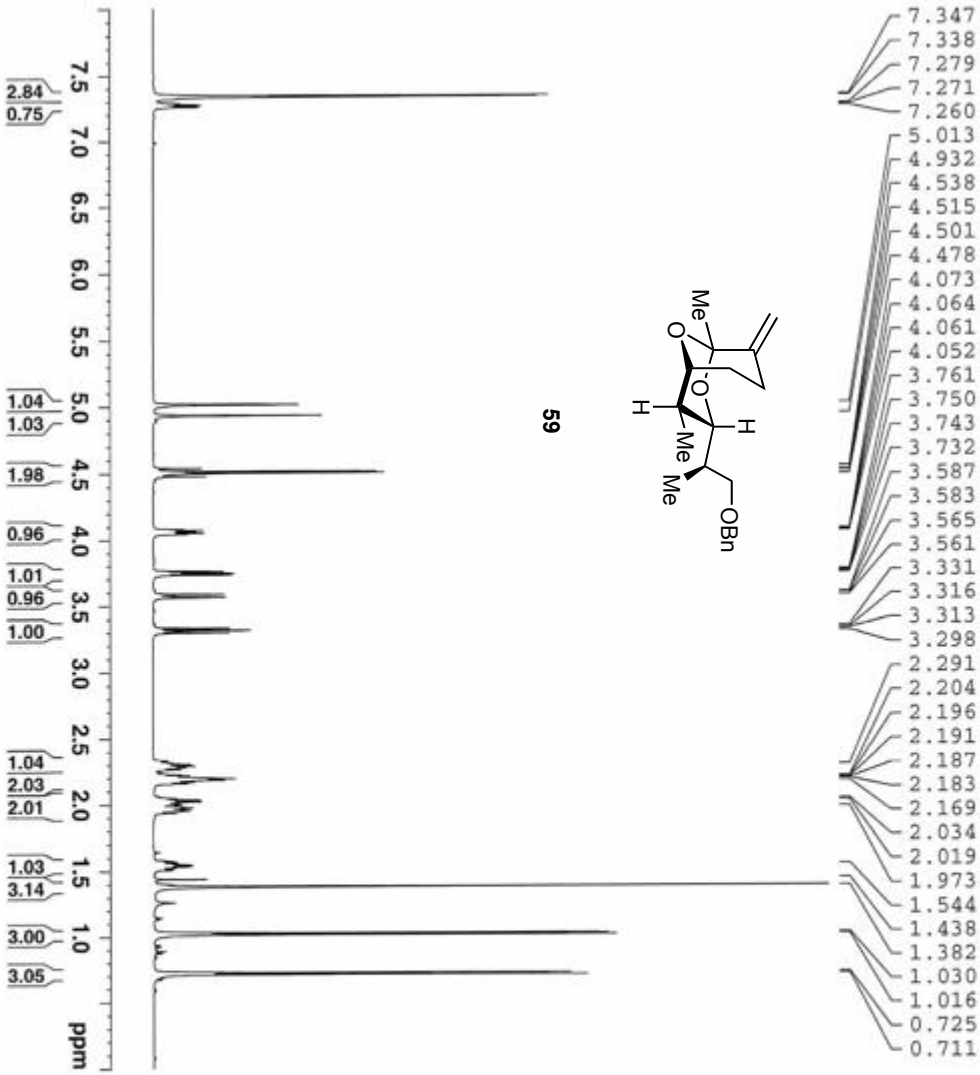


NAME	st110062010
EXPNO	2
PROCNO	1
Date_	20101006
Time	14.54
INSTRUM	spect
PROBHD	5 mm QNP 1H
PULPROG	zgdc
TD	60602
SOLVENT	CDCl3
NS	96
DS	4
SWH	30303.031 Hz
FIDRES	0.500033 Hz
AQ	0.9999830 sec
RG	16384
DW	16.500 usec
DE	7.50 usec
TE	300.0 K
D1	3.00000000 sec
d11	0.03000000 sec
========== CHANNEL f1 ======	
NUC1	13C
P1	8.00 usec
PL1	3.00 dB
SFO1	125.7715724 MHz
========== CHANNEL f2 ======	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	120.00 dB
PL12	20.00 dB
SFO2	500.1338000 MHz
SI	32768
SF	125.7578015 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

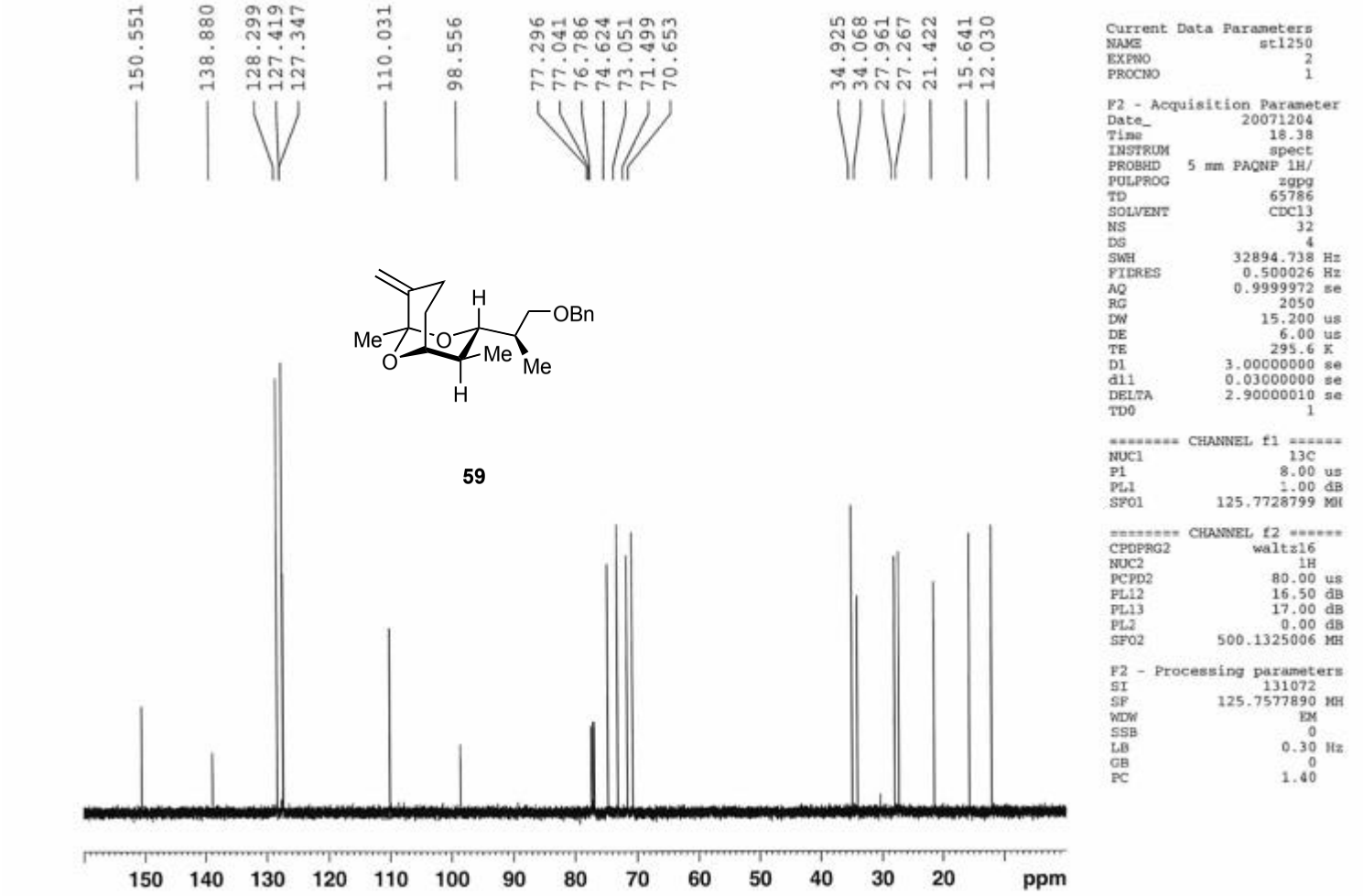

7.353
7.348
7.342
7.334
5.596
5.419
4.532
4.508
4.497
4.473
3.752
3.743
3.734
3.604
3.594
3.586
3.576
3.380
3.366
3.362
3.348
3.273
3.262
3.259
3.248
2.568
2.430
2.414
1.956
1.854
1.845
1.643
1.637
1.626
1.621
1.610
1.310
1.296
1.284
1.041
1.027
0.882
0.869
Br
Me Me
Me
Me
OBn
58
3.10
0.82
1.02
0.96
2.04
0.99
1.05
1.03
0.99
1.01
0.99
0.97
1.05
2.13
3.06
3.10
3.00
3.15
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
Current Data Parameters
NAME st1244
EXPNO 1
PROCNO 1
F2 - Acquisition Parameter
Date_ 20071129
Time 12.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 44998
SOLVENT CDCl3
NS 8
DS 0
SWH 7500.000 Hz
FIDRES 0.166674 Hz
AQ 2.9999166 se
RG 32
DW 66.667 us
DE 6.00 us
TE 295.0 K
D1 1.00000000 se
TD0 1
======== CHANNEL f1 ======
NUC1 1H
P1 11.80 us
PL1 0.00 dB
SFO1 500.1335009 MH
F2 - Processing parameters
SI 16384
SF 500.1300073 MH
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



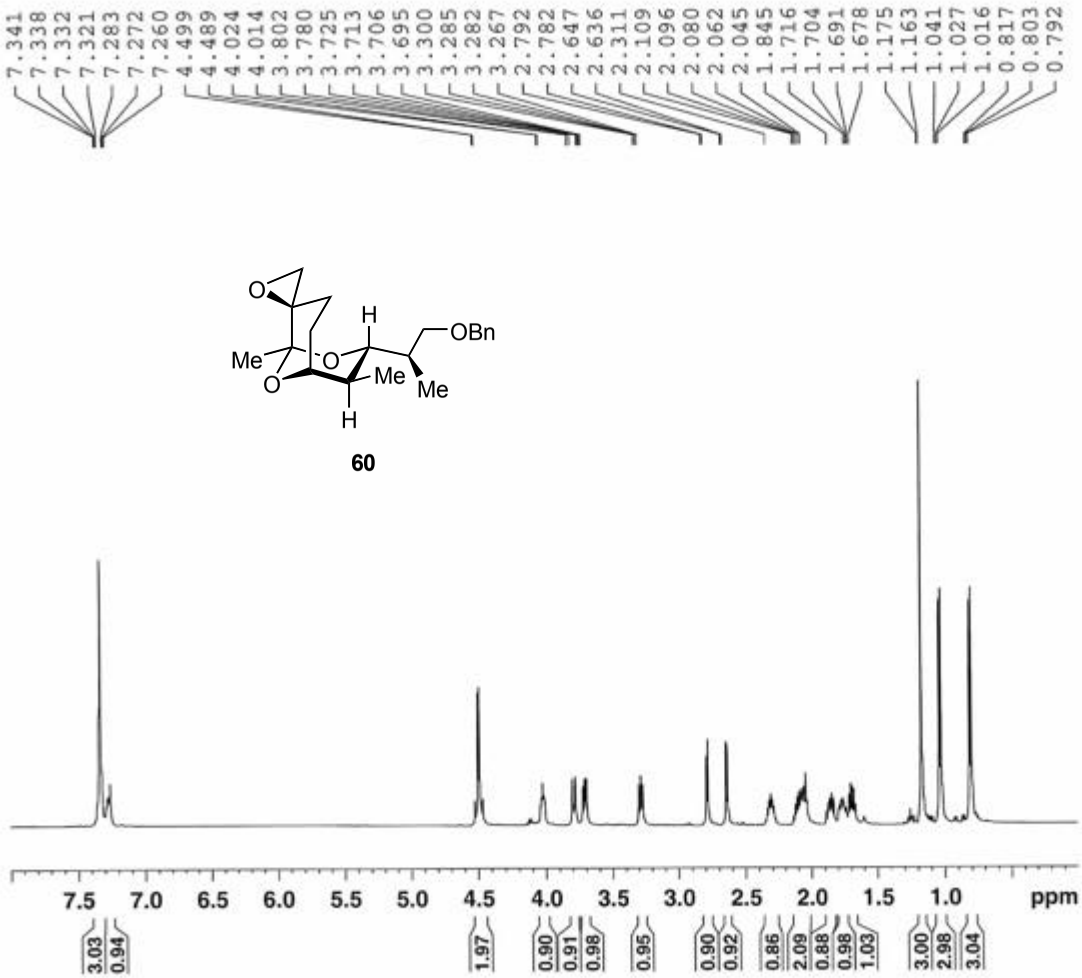

```
Current Data Parameters
NAME                  st1244
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20071129
Time                  12.28
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                zgpg
TD                    65786
SOLVENT               CDCl3
NS                       32
DS                        0
SWH                32894.738 Hz
FIDRES             0.500026 Hz
AQ                 0.9999972 sec
RG                      2050
DW                    15.200 usec
DE                     6.00 usec
TE                   295.7 K
D1                 3.00000000 sec
d11                0.03000000 sec
DELTA              2.90000010 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      7.50 usec
PL1                     0.50 dB
SFO1           125.7728799 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL12                   17.60 dB
PL13                   18.00 dB
PL2                    -2.00 dB
SFO2           500.1325006 MHz

F2 - Processing parameters
SI                       131072
SF             125.7577890 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.40
```



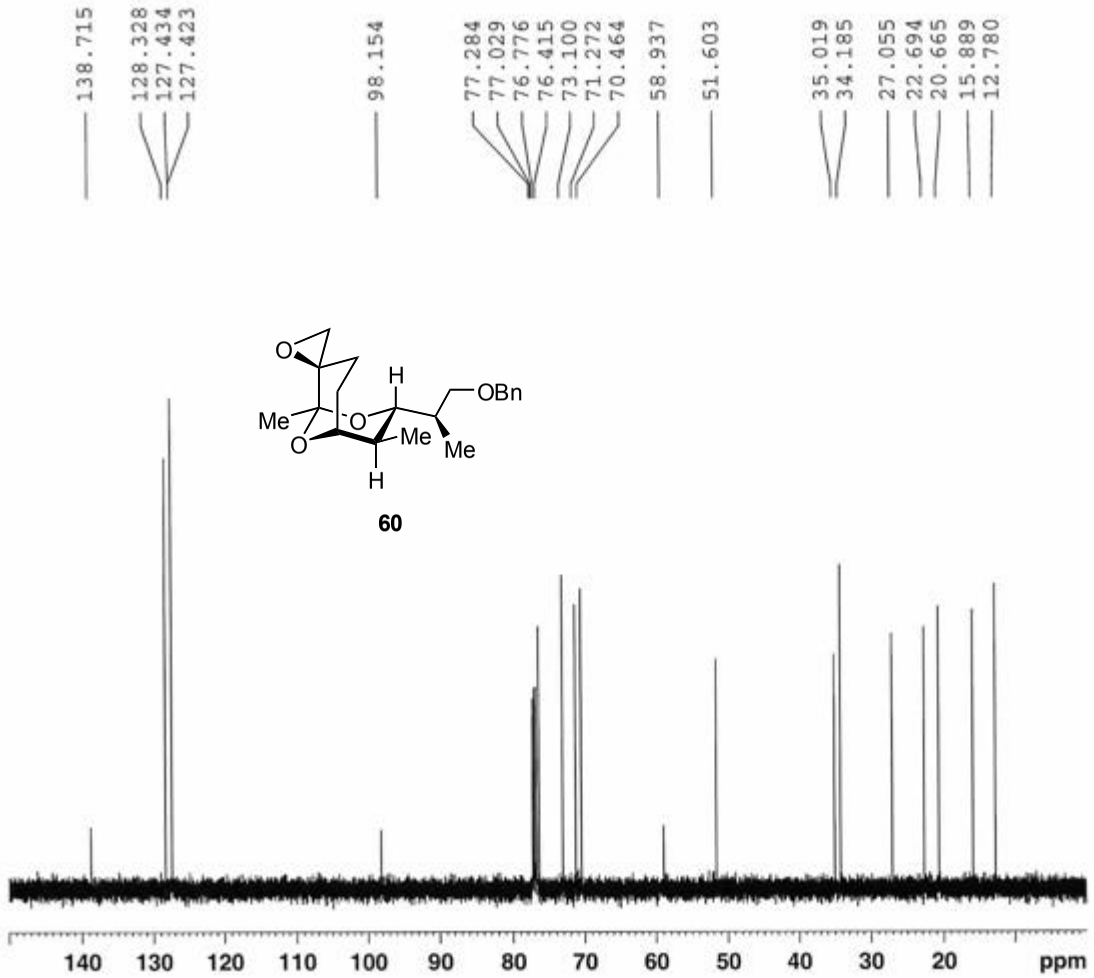

```
Current Data Parameters
NAME                  st1250
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20071204
Time                   18.29
INSTRUM                spect
PROBHD   5 mm PAQNP 1H/
PULPROG                zg
TD                     44998
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                7500.000 Hz
FIDRES                0.166674 Hz
AQ                 2.9999166 se
RG                      50.8
DW                    66.667 us
DE                    71.43 us
TE                    295.0 K
D1                 1.00000000 se
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 us
PL1                     0.00 dB
SFO1          500.1335009 MHz

F2 - Processing parameters
SI                     16384
SF            500.1300084 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



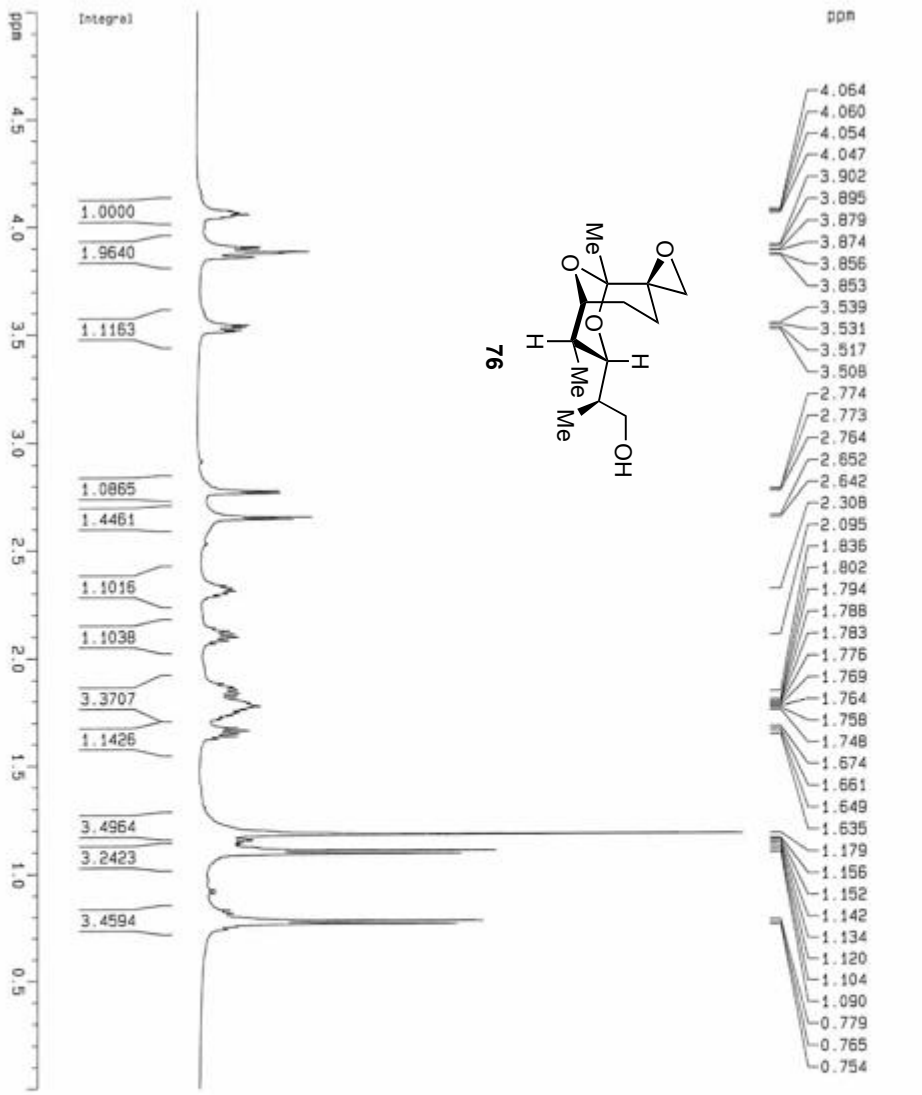

```
Current Data Parameters
NAME                  st1250
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameter
Date_               20071204
Time                   18.38
INSTRUM                spect
PROBHD   5 mm PAQNP 1H/
PULPROG                zgpg
TD                    65786
SOLVENT               CDCl3
NS                       32
DS                        4
SWH               32894.738 Hz
FIDRES            0.500026 Hz
AQ                0.9999972 se
RG                     2050
DW                   15.200 us
DE                    6.00 us
TE                   295.6 K
D1                3.00000000 se
d11               0.03000000 se
DELTA             2.90000010 se
TD0                        1

======== CHANNEL f1 ======
NUC1                     13C
P1                    8.00 us
PL1                   1.00 dB
SFO1            125.7728799 MH

======== CHANNEL f2 ======
CPDPRG2             waltz16
NUC2                     1H
PCPD2                80.00 us
PL12                 16.50 dB
PL13                 17.00 dB
PL2                   0.00 dB
SFO2            500.1325006 MH

F2 - Processing parameters
SI                     131072
SF              125.7577890 MH
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.40
```




```
Current Data Parameters
NAME                  st1257
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameter
Date_              20071210
Time                  10.44
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG                  zg
TD                    44998
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                7500.000 Hz
FIDRES            0.166674 Hz
AQ                2.9999166 se
RG                      128
DW                   66.667 us
DE                   71.43 us
TE                   294.9 K
D1                1.00000000 se
TD0                       1

======== CHANNEL f1 ======
NUC1                      1H
P1                   12.00 us
PL1                   0.00 dB
SFO1           500.1335009 MH

F2 - Processing parameters
SI                    16384
SF             500.1300085 MH
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
```




```
Current Data Parameters
NAME                  stl257
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameter
Date_              20071210
Time                  10.51
INSTRUM               spect
PROBHD   5 mm PAQNP 1H/
PULPROG               zgpg
TD                   65786
SOLVENT              CDCl3
NS                      64
DS                       4
SWH               32894.738 Hz
FIDRES            0.500026 Hz
AQ                0.9999972 se
RG                    2050
DW                  15.200 us
DE                   6.00 us
TE                  295.3 K
D1               3.00000000 se
d11              0.03000000 se
DELTA            2.90000010 se
TD0                        1

======== CHANNEL f1 ======
NUC1                    13C
P1                    8.00 us
PL1                   1.00 dB
SFO1          125.7728799 MH

======== CHANNEL f2 ======
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 us
PL12                 16.50 dB
PL13                 17.00 dB
PL2                   0.00 dB
SFO2          500.1325006 MH

F2 - Processing parameters
SI                    131072
SF            125.7577890 MH
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.40
```



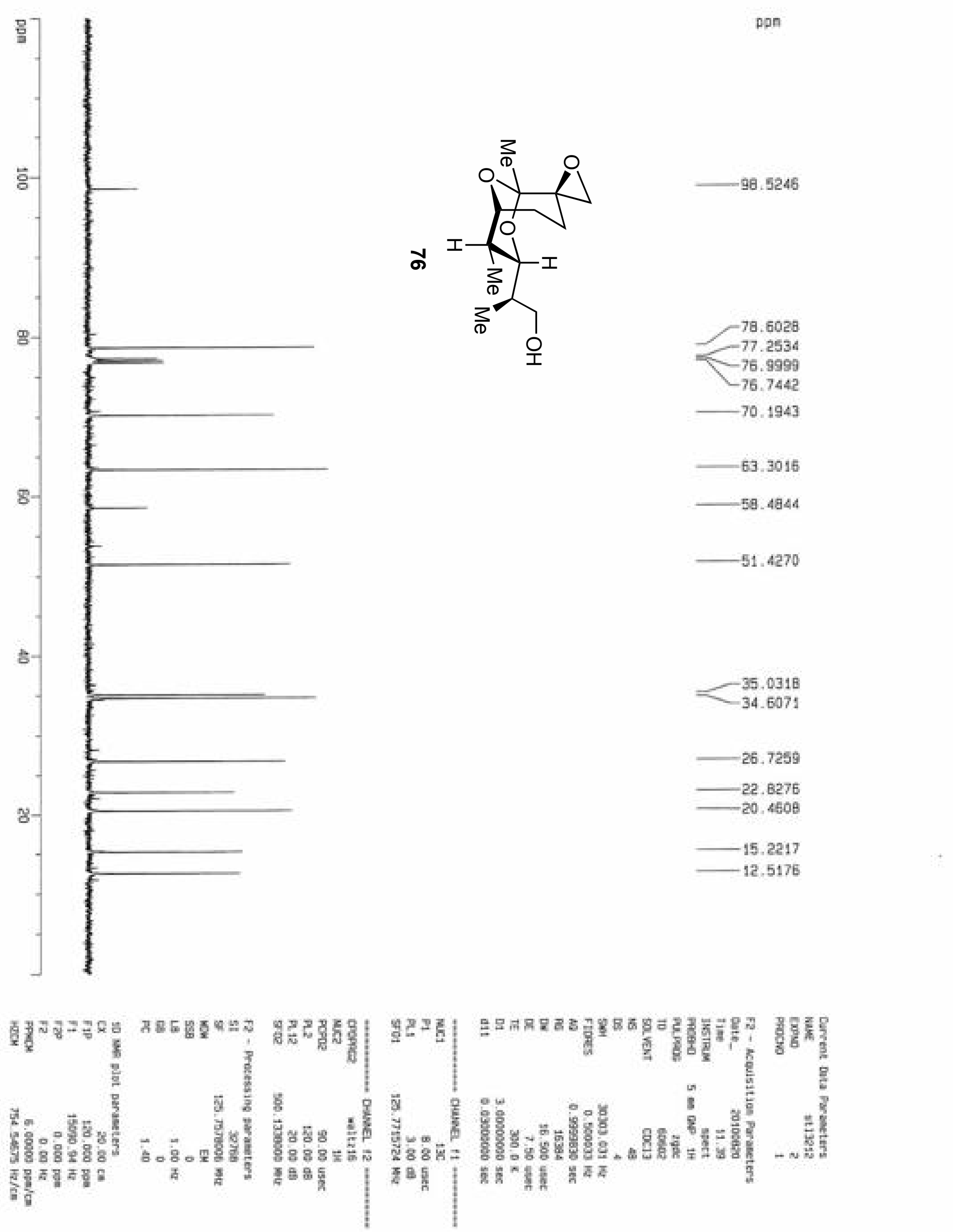
Current Data Parameters
NAME st13212
EXPNO 1
PROCNO 1

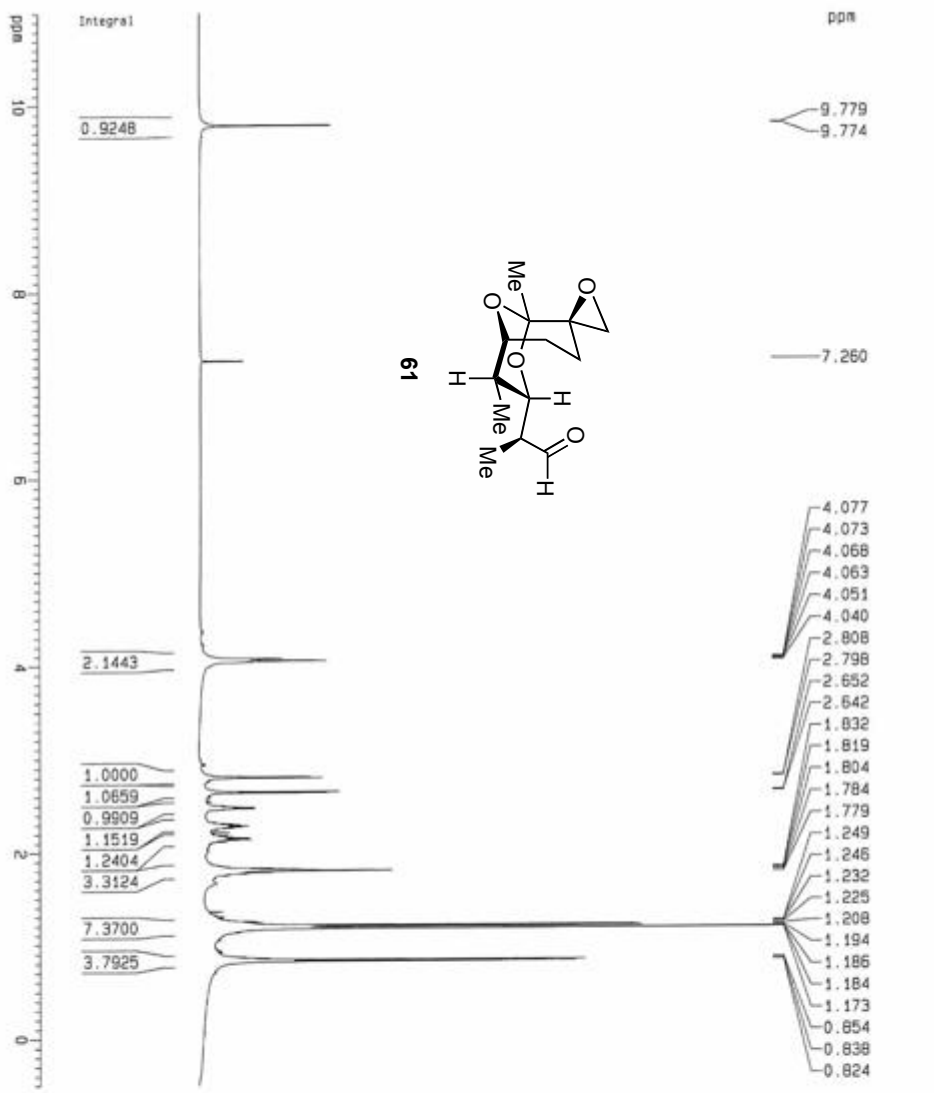
F2 - Acquisition Parameters
Date_ 20100820
Time 11.34
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT Acetone
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 16
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1330009 MHz

F2 - Processing parameters
SI 65536
SF 500.1300122 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 5.000 ppm
F1 2500.65 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.25000 ppm/cm
HZCM 125.03250 Hz/cm


ppm
98.5246
78.6028
77.2534
76.9999
76.7442
70.1943
63.3016
58.4844
51.4270
35.0318
34.6071
26.7259
22.8276
20.4608
15.2217
12.5176
76



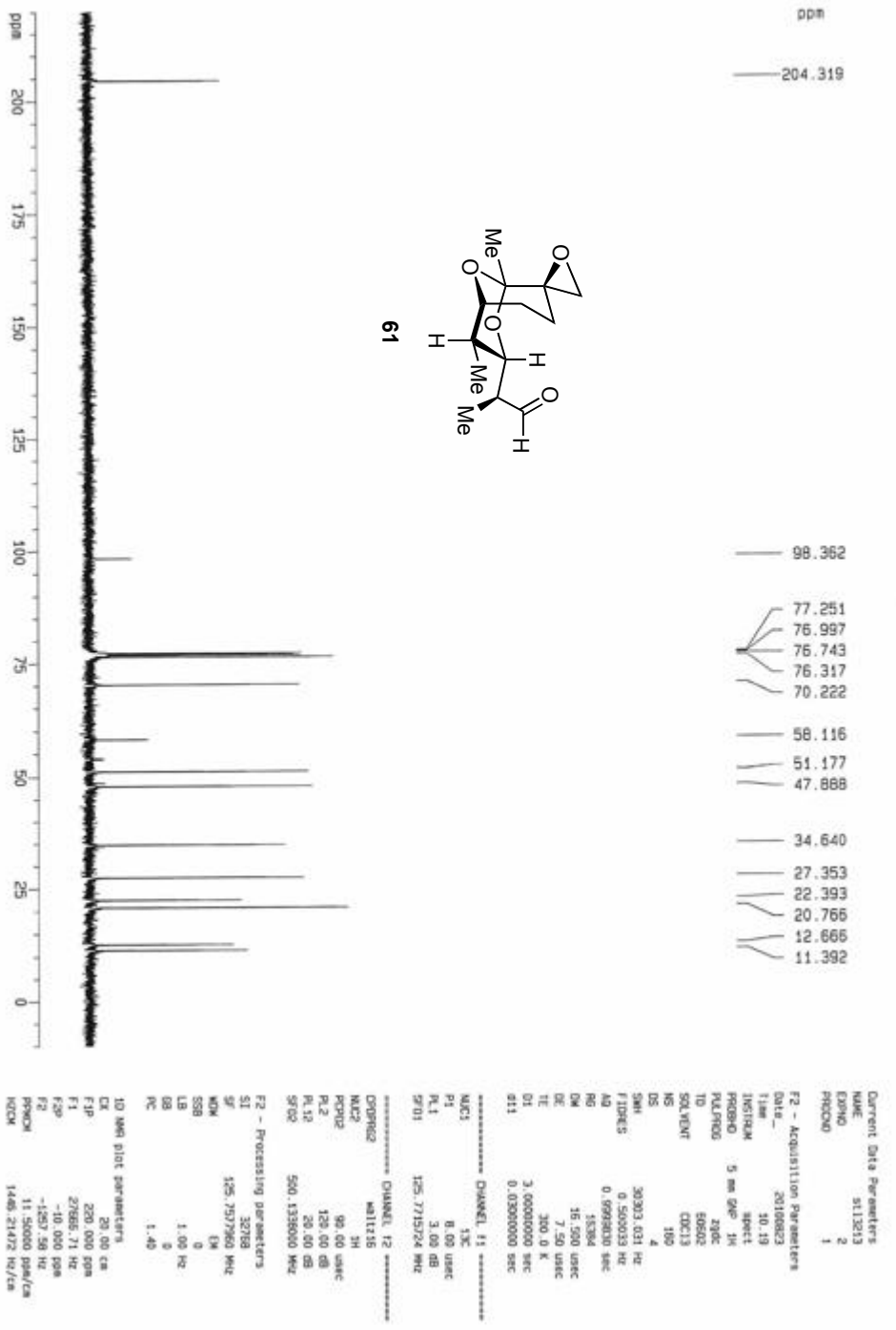
Current Data Parameters
NAME st13213
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150623
Time 10.14
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT Aceton
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9979804 sec
RG 32
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz

F2 - Processing parameters
SI 65536
SF 500.1300128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.57500 ppm/cm
HZCM 287.5747 Hz/cm



Current Data Parameters
NAME st1213
EXPNO 2
PROCNO 1

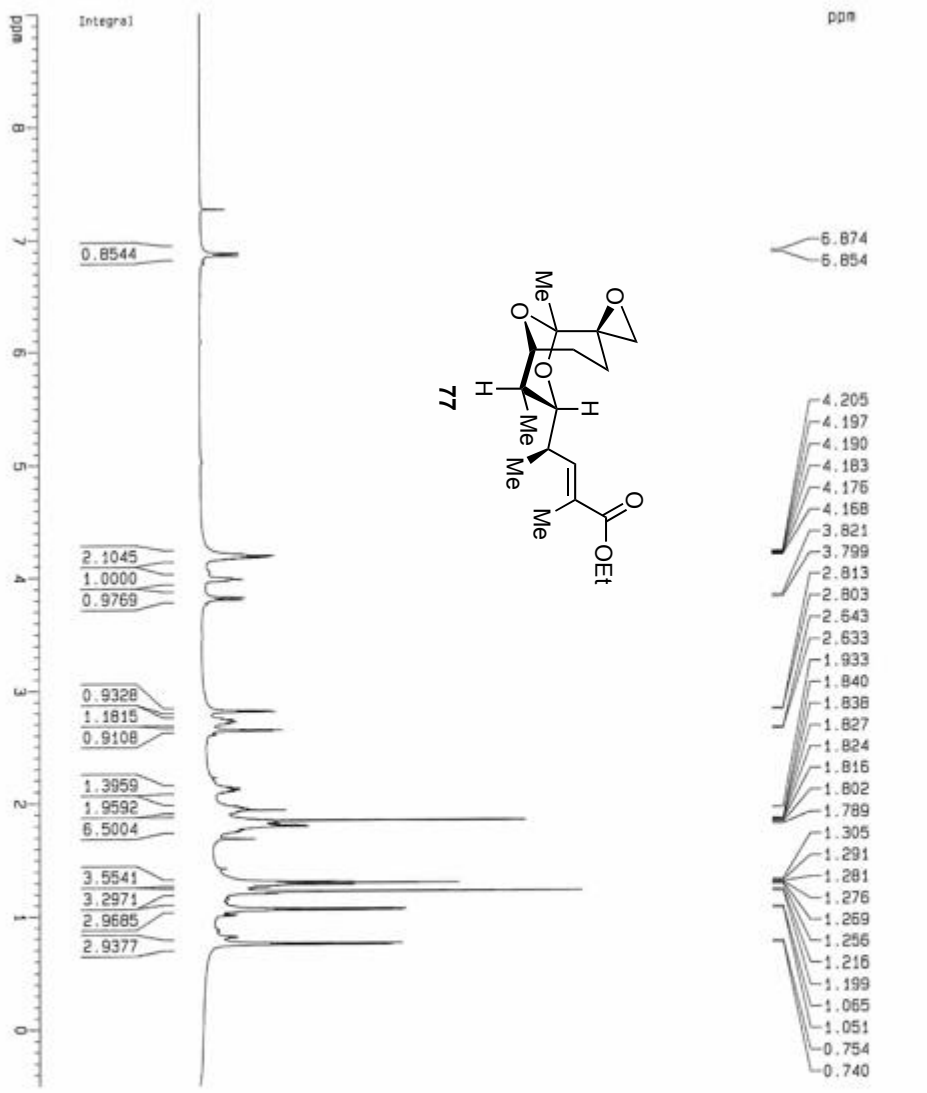
F2 - Acquisition Parameters
Date_ 20160823
Time 10.19
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 65502
SOLVENT CDCl3
NS 160
DS 4
SWH 30303.031 Hz
FIDRES 0.505033 Hz
AQ 0.9998830 sec
RG 153184
DW 16.500 usec
DE 7.50 usec
TE 320.0 K
D1 3.00000000 sec
d11 0.03000000 sec

---------- CHANNEL f1 ----------
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SFO1 125.7715724 MHz

---------- CHANNEL f2 ----------
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 20.00 dB
SFO2 500.1330000 MHz

F2 - Processing parameters
SI 32768
SF 125.7577960 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 27665.71 Hz
F2P -10.000 ppm
F2 -1257.58 Hz
PPMCM 11.50000 ppm/cm
HZCM 1446.21472 Hz/cm



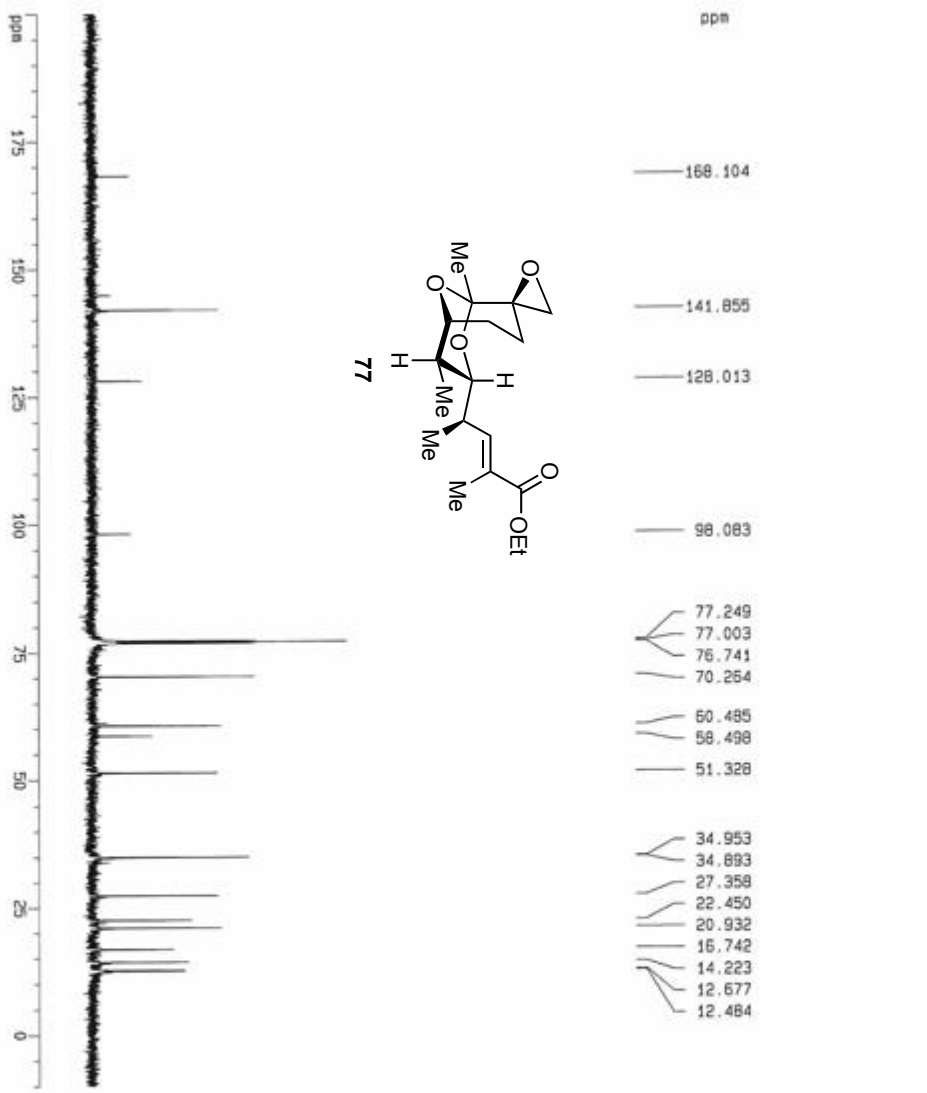
Current Data Parameters
NAME sli214
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100823
Time 16.07
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 45044
SOLVENT Aceton
NS 8
DS 0
SWH 7507.507 Hz
FIDRES 0.166671 Hz
AQ 2.9999804 sec
RG 32
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec

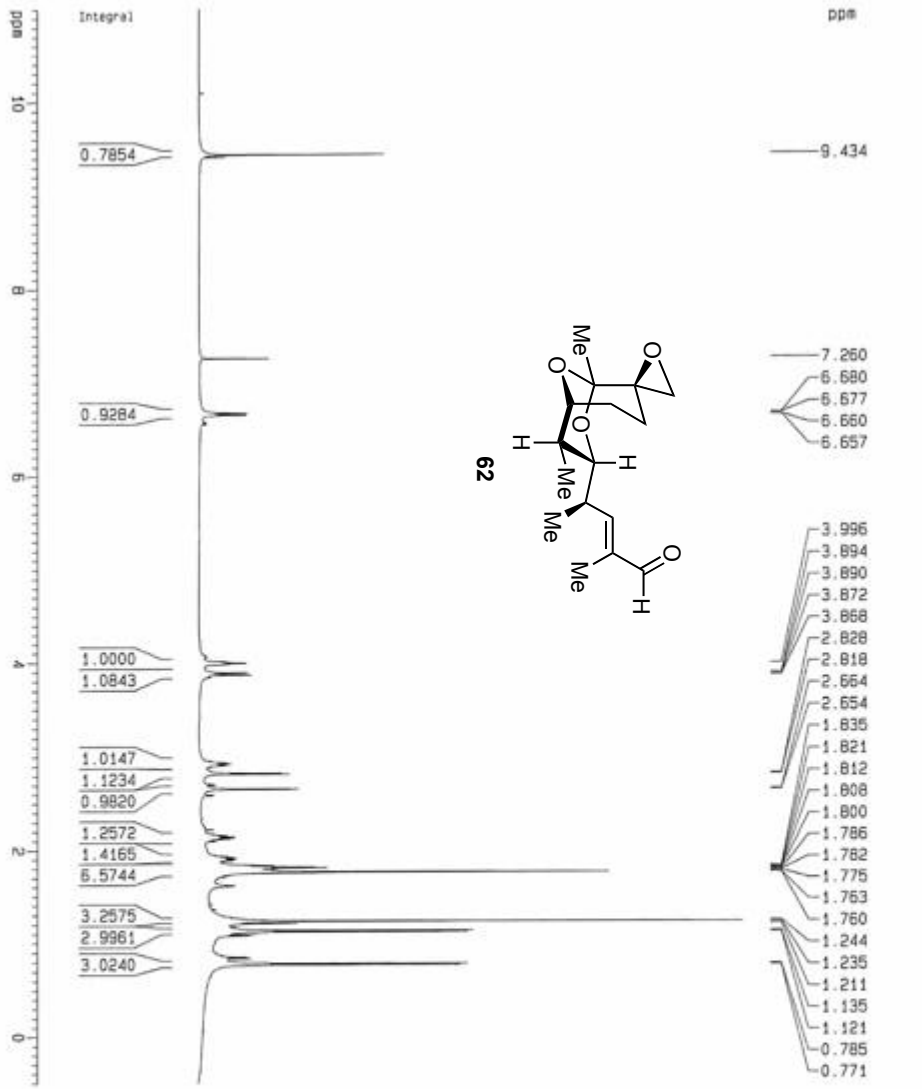
========== CHANNEL f1 ==========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 500.1335009 MHz

F2 - Processing parameters
SI 65536
SF 500.1300128 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 9.000 ppm
F1 4501.17 Hz
F2P -0.500 ppm
F2 -250.07 Hz
PPMCM 0.47500 ppm/cm
HZCM 237.56175 Hz/cm

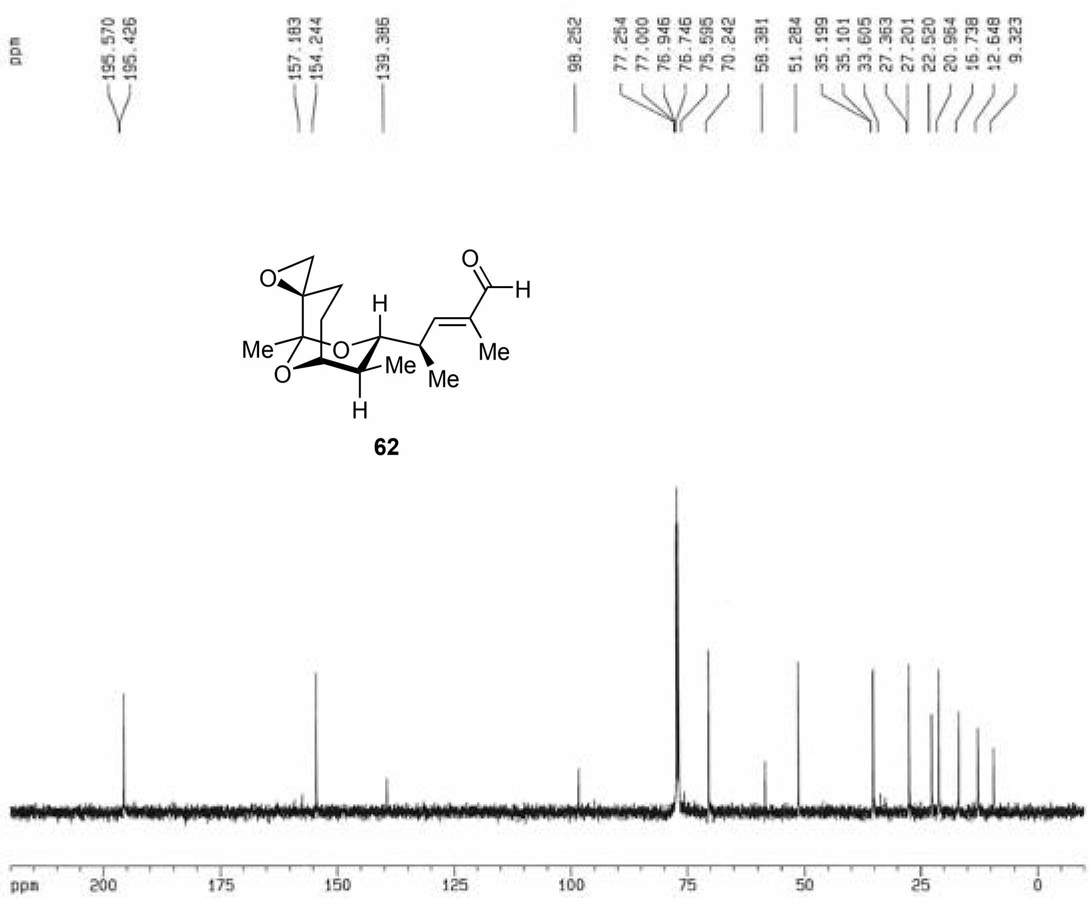



```
Current Data Parameters
NAME                  st13214
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100823
Time                   16.13
INSTRUM                spect
PROBHD     5 mm QNP 1H
PULPROG                zgdc
TD                    65662
SOLVENT               CDCl3
NS                      160
DS                        4
SWH                30303.031 Hz
FIDRES              0.500033 Hz
AQ                  0.9999830 sec
RG                      16384
DW                     16.500 usec
DE                      7.50 usec
TE                     300.0 K
D1                  3.00000000 sec
d11                 0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       8.00 usec
PL1                      3.00 dB
SFO1             125.7715724 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                    120.00 dB
PL12                    20.00 dB
SFO2             500.1338000 MHz

F2 - Processing parameters
SI                        32768
SF               125.7577960 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      200.000 ppm
F1                     25151.56 Hz
F2P                     -10.000 ppm
F2                     -1257.58 Hz
PPMCM                  10.50000 ppm/cm
HZCM                1320.45691 Hz/cm
```



62

```
Current Data Parameters
NAME                  st13216
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100825
Time                   11.29
INSTRUM                spect
PROBHD     5 mm QNP 1H
PULPROG                 zg
TD                      45044
SOLVENT                 Acetone
NS                      8
DS                      0
SWH                7507.507 Hz
FIDRES             0.166671 Hz
AQ                 2.9999804 sec
RG                      64
DW                 66.600 usec
DE                 4.50 usec
TE                 300.0 K
D1                 3.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 9.00 usec
PL1                0.00 dB
SFO1          500.1135009 MHz

F2 - Processing parameters
SI                     65536
SF            500.1300129 MHz
WDW                    EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                11.000 ppm
F1                 5501.43 Hz
F2P                -0.550 ppm
F2                 -256.07 Hz
PPMCM              0.57550 ppm/cm
HZCM               287.5747 Hz/cm
```



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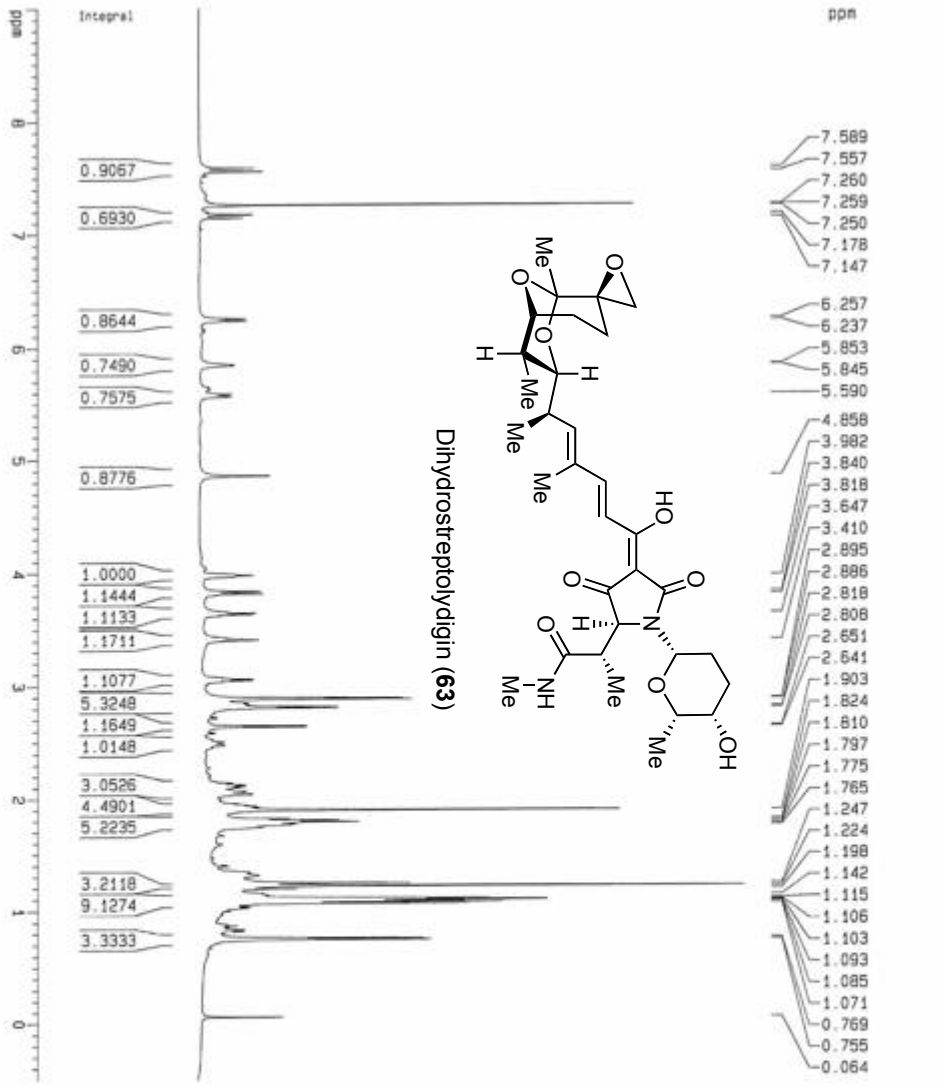
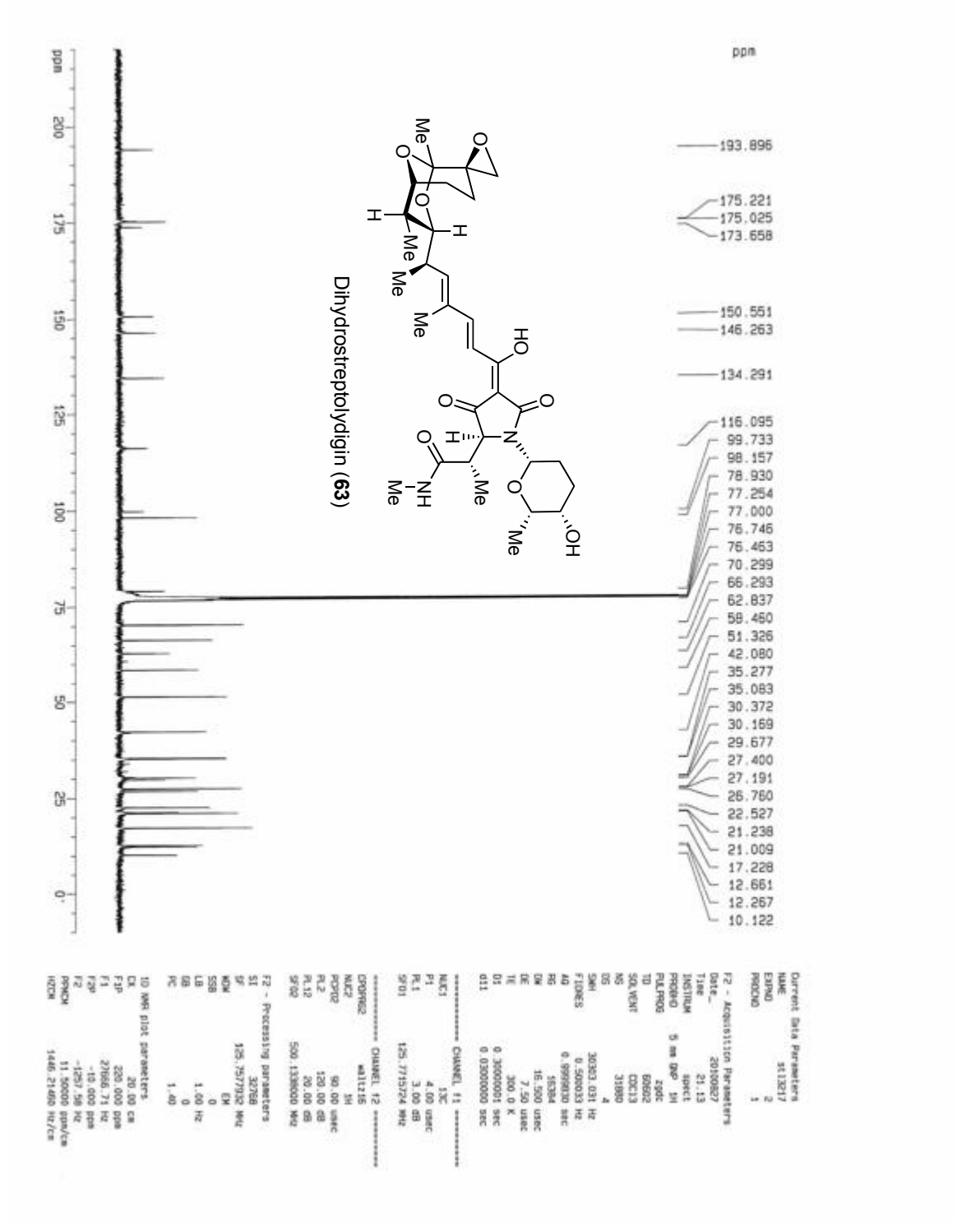
```
Current Data Parameters
NAME            st13256
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_          20100825
Time              11.32
INSTRUM           spect
PROBHD     5 mm QNP 1H
PULPROG            zgdc
TD                60602
SOLVENT           CDCl3
NS                  272
DS                    4
SWH          30303.031 Hz
FIDRES        0.500033 Hz
AQ           0.9999830 sec
RG                16384
DW               16.500 usec
DE                 7.50 usec
TE                300.0 K
D1           3.00000000 sec
d11          0.03000000 sec

============ CHANNEL f1 ==========
NUC1                13C
P1                 8.00 usec
PL1                3.00 dB
SFO1        125.7715724 MHz

============ CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2              120.00 dB
PL12              20.00 dB
SFO2        500.1338000 MHz

F2 - Processing parameters
SI                32768
SF          125.7577932 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P             220.000 ppm
F1             27666.71 Hz
F2P             -10.000 ppm
F2             -1257.58 Hz
PPMCM          11.50000 ppm/cm
HZCM         1446.21460 Hz/cm
```




```
Current Data Parameters
NAME                  st13217
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100826
Time               17.15
INSTRUM            spect
PROBHD     5 mm QNP 1H
PULPROG             zg
TD                  45044
SOLVENT             Acetone
NS                  32
DS                  0
SWH                 7507.507 Hz
FIDRES              0.166671 Hz
AQ                  2.999804 sec
RG                  128
DW                  66.600 usec
DE                  4.50 usec
TE                  300.0 K
D1                  3.00000000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                  9.00 usec
PL1                 0.00 dB
SFO1                500.1335009 MHz

F2 - Processing parameters
SI                  65536
SF                  500.1300138 MHz
WDW                 EM
SSB                 0
LB                  0.30 Hz
GB                  0
PC                  1.00

1D NMR plot parameters
CX                  20.00 cm
F1P                 9.000 ppm
F1                  4501.17 Hz
F2P                 -0.500 ppm
F2                  -250.07 Hz
PPMCM               0.47500 ppm/cm
HZCM                237.56175 Hz/cm
```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175.221
175.025
173.658
150.551
146.263
134.291
116.095
99.733
98.157
78.930
77.254
77.000
76.746
76.463
70.299
66.293
62.837
59.460
51.326
42.080
35.277
35.083
30.372
30.159
29.677
27.400
27.191
26.760
22.527
21.238
21.009
17.228
12.661
12.267
10.122