Supplementary Methods:

All reactions were run under an atmosphere of nitrogen unless otherwise indicated. Anhydrous solvents were transferred via oven-dried syringe or cannula. Flasks were flame-dried under vacuum and cooled under a stream of nitrogen or argon. Tetrahydrofuran (THF), and dimethoxyethane (DME), Benzene, pyridine, diisopropylamine, triethylamine, diisopropylethylamine, and dimethylsulfoxide, acetonitrile, hexane, toluene, diethyl ether, and dichloromethane were purified with a Solv-Tek solvent purification system by passing through a column of activated alumina. Acetone was distilled from calcium sulfate. Methanol was distilled from magnesium methoxide.

Where indicted, solvents are degassed via freezing in liquid nitrogen and thawing under high vacuum. The above cycle is repeated three times, unless otherwise indicated.

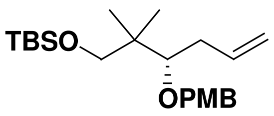
Analytical thin layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (DC-Fertigplatten Krieselgel 60 F_{254}). Preparative column chromatography employing silica gel was performed according to the method of Still. Melting points were determined on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded using a Varian UI-600 (600 MHz), UI-500 (500 MHz) or Varian MERC-400 (400 MHz). Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from tetramethylsilane (TMS) or in ppm relative to the singlet at 7.26 ppm for deuterochloroform. Coupling constants are reported in Hertz (Hz). The following abbreviations are used: s, singlet, d, doublet, t, triplet, q, quartet, m, multiplet.

Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a Varian UI-600 (150 MHz), Varian UI-500 (125 MHz) or Varian MERC-400 (100 MHz). Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to the center line of the triplet at 77.1 ppm for deuterochloroform. ^{13}C NMR spectra were routinely run with broadband decoupling.

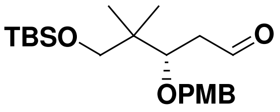
Other refences used: C_6D_6 [7.16 ppm, 128.0 ppm], CD_3CN [1.94 ppm, 118.3 ppm].

Optical rotation data was obtained with a Jasco DIP-360 digital polarimeter at the sodium D line (589 nm) in the solvent and concentration indicated.



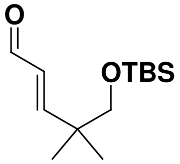
9

Compound 9: To a solution of aldehyde **2**[31] (0.86 g, 4.0 mmol) in dry Et_2O (14 ml) at –90 °C under N_2, was added a solution of (–)-$(Ipc)_2B(allyl)$ (3.5 ml, 3.5 mmol, 1M in pentane) dropwisely. The reaction mixture was stirred at –90 °C for 1h, before MeOH (0.8 ml) was added carefully. The mixture was allowed to warm to rt, and a mixture of THF-water (ca. 1:1, 15 ml) was added, followed by $NaBO_3{\cdot}H_2O$ (1.6 g, 16 mmol). The mixture was stirred vigorously overnight, before water (ca. 20 ml) was added. The mixture was extracted with ether three times and the combined organic fractions were dried over $MgSO_4$. The known homoallyl alcohol[32] was purified via silica gel flash column chromatography (5% ether/petroleum ether, then 5% ethyl acetate/petroleum ether) to give a colorless oil (0.61 g, 67%, 94% ee, determined by chiral GC, 2 °C/min). NaH (0.46 g, 11 mmol) was added to a solution of the above homoallyl alcohol (1.0 g, 3.9 mmol) in DMF (22 ml) at 0 °C. The mixture was stirred at 0 °C for 10 min, and then PMBBr (1.17 g, 5.81 mmol) was added slowly. The reaction mixture was stirred at the same temperature for 2 h, before saturated aqueous NH_4Cl was added. The mixture was extracted with ether four times and the combined organic fractions were dried over $MgSO_4$. The PMB ether **9** was purified via silica gel flash column chromatography (2%, then 5% ether/petroleum ether) to give a colorless oil (1.3 g, 90%). R_F: 0.5 (ether/petroleum ether, 1:9 v/v); $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): +2.33 (c 2.1 g cm^{-3} in DCM); ^1H NMR (C_6D_6, 500 MHz) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.96 (m, 1H), 5.11 (ddd, *J* = 1.5, 3.5, 17 Hz, 1H), 5.02 (ddd, *J* = 1.0, 2.0, 10 Hz, 1H), 4.55 (1H, *J* = 10.5 Hz, 1H), 4.48 (d, *J* = 10.5 Hz, 1H), 3.80 (s, 3H), 3.52 (d, *J* = 14.5 Hz, 1H), 3.43 (dd, *J* = 3.5, 9.0 Hz, 1H), 2.32 (m, 1H), 2.25 (m ,1H), 0.91 (s, 9H), 0.88 (s, 3H), 0.86 (s, 3H), 0.040 (s, 3H), 0.036 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 159.0, 137.6, 131.6, 113.7, 82.7, 74.0, 69.8, 55.3, 40.7, 35.6, 26.0, 21.7, 20.2, 18.3, –5.4, –5.5; IR (film):2955, 2931, 2857, 1614, 1514, 1471, 1249, 1172, 1093, 1040, 851, 837, 775 cm^{-1}.



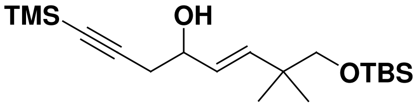
10

Compound 10: According to Jin *et al.*'s procedure[33], to a solution of PMB ether **9** (1.3 g, 3.4 mmol) in 1,4-dioxane/water (30 ml, 3:1) was added 2,6-lutidine (0.74 g, 6.9 mmol), OsO_4 (0.4 ml, 0.068 mmol, 4% in water) and $NaIO_4$ (2.9 g, 13.6 mmol) at rt. The reaction mixture was stirred at rt for 1.5 h, before water (20 ml) and DCM (40 ml) was added. The mixture was extracted with DCM three times and the combined organic fractions were dried over Na_2SO_4. The known aldehyde[16] **10** was purified via silica gel flash column chromatography (5%, then 10% ether/petroleum ether) to give a colorless oil (1.02 g, 87%). R_F: 0.3 (ether:petroleum ether, 1:9 v/v); $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): +5.9 (c 1.1 g cm^{-3} in DCM); Reported: $[\alpha]^{D}_{20}$(deg cm^{3} g^{-1} dm^{-1}): +6.1 (c 1.8 g cm^{-3} in CH_2Cl_2). ^{1}H NMR, ^{13}C NMR and IR are identical to those previously reported.



11

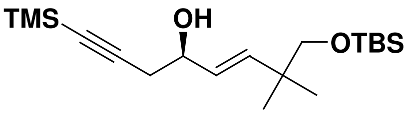
Compound 11: According to Wender *et al.*'s procedure[34], (*Z*)-1-bromo-2-ethoxyethylene (6.0 ml, 48 mmol) was added to a flame-dried flask containing Et_2O (150 ml). The solution was cooled to –78 °C, and *t*-BuLi (60 ml, 1.7 M in pentane) was added dropwise. The reaction was stirred at –78 °C for 30 min. Me_2Zn (22.5 ml, 2.0 M in toluene) was added dropwise, and the reaction was stirred at –78 °C for 30 min. A solution of aldehyde **2** (6.5 g, 30 mmol) in Et_2O (30 ml) was added dropwise, and the reaction was stirred at –78 °C for 2h. The reaction was quenched with saturated $NaHSO_4$ (150 ml) and allowed to warm to rt. The mixture was stirred vigorously for 48 h, during which solid $NaHSO_4$ (5 g) was added every 12 h. The reaction was quenched with saturated $NaHCO_3$. The mixture was extracted with ethyl acetate (150 ml x 3), and the combined organic fractions were dried over Na_2SO_4. Compound **11** was purified via silica gel flash column chromatography (5% Et_2O/petroleum ether, then 10% Et_2O/petroleum ether) to give a colorless oil (7.1 g, 97%). R_F: 0.3 (Et_2O:petroleum ether, 1:19 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.49 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.85 (dd, *J* = 1.0, 16 Hz, 1H), 6.06 (ddd, *J* = 1.0, 7.5, 16 Hz, 1H), 3.40 (s, 2H), 1.06 (s, 6H), 0.86 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 194.6, 165.8, 130.2, 71.0, 39.9, 25.9, 23.3, 18.3, –5.5; IR (film): 2956, 2858, 1696, 1473, 1256, 1103, 838, 776 cm^{-1}; HRMS ($C_{13}H_{26}O_2Si$): Calc'd. 242.1702 (M^{+}), Found 242.1702.



***Rac*-8**

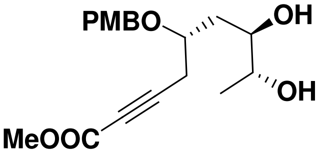
Compound 8: According to Loh *et al.*'s procedure[23], (3-bromo-1-propynyl)-trimethylsilane (63 mg, 0.33 mmol) was added to a mixture of indium powder (38 mg, 0.33 mmol) and InF_3 (2.8 mg, 0.0165 mmol) in THF (0.2 ml) at rt under N_2. The resulting mixture was stirred at rt for 15 min, before a solution of **11** (40 mg, 0.165 mmol) in 0.2 ml THF was added. The mixture was sealed and heated at 65 °C overnight, before it was carefully quenched with 1M NaH_2PO_4 at rt. The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. Compound ***rac*-8** was purified via silica gel flash column chromatography (5% Et_2O/petroleum ether, then 10% Et_2O/petroleum ether) to give a colorless oil (37 mg, 68%). The same reaction on 6.1 g scale gave compound **8** in 65% yield. R_F: 0.35 (Et_2O:petroleum ether, 1:9 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.72 (dd, *J* = 1.0, 20 Hz, 1H), 5.47 (dd, *J* = 8.0, 20 Hz, 1H), 4.20

(m, 1H), 3.28 (s, 2H), 2.45 (dd, *J* = 2.5, 7.5 Hz, 2H), 2.02 (br, 1H), 0.97 (s, 3H), 0.88 (s, 9H), 0.15 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.1, 128.0, 103.0, 87.5, 71.7, 71.1, 38.2, 29.4, 26.0, 24.0, 18.4, 0.2, –5.4; IR (film): 3336 (br), 2958, 2858, 2178, 1464, 1250, 1099, 843 cm^{-1}; HRMS ($C_{15}H_{29}O_2Si_2$+ ^{t}Bu): Calc'd. 297.1706 (M^+– ^{t}Bu), Found 297.1684.



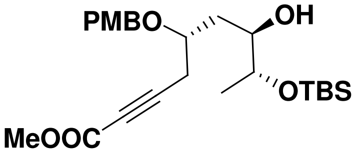
8

Compound (*R*)-8: Dess–Martin periodinane (high quality, 6.95 g, 16.4 mmol) was added to a mixture of ***Rac*-8** (5.49 g, 15.6 mmol) and $NaHCO_3$ (4.2 g, 49.9 mmol) in DCM (66 ml) at 0 °C. The reaction was stirred at rt for 30 min, before being quenched with saturated $Na_2S_2O_3$ and saturated $NaHCO_3$. The mixture was extracted with ethyl acetate (150 ml x 3), and the combined organic fraction was dried over Na_2SO_4. The solvent was removed, and the crude ketone was dissolved with DCM (112 ml). The above solution was cooled to –78 °C, and (*s*)-2-methyl-CBS-oxazaborolidine (0.78 ml, 1M in toluene) was added. The reaction was stirred at –78 °C for 20 min before catechol borane (2.8 g, 23.4 mmol) was added. The resulting solution was stirred at –78 °C for 4 h, and then it was warmed to 0 °C. The reaction was stirred at 0 °C for 1h, before it was quenched with 1M NaH_2PO_4. The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. Compound **8** was purified via silica gel flash column chromatography (5% Et_2O/petroleum ether, then 10% Et_2O/petroleum ether) to give a colorless oil (4.9 g, 90% over two steps, 90% ee, determined by chiral HPLC, OD 205 nm, 0.8 ml/min, 99.5:0.5 heptane/^{i}PrOH). $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): +4.86 (c 0.64 g cm^{-3} in DCM).



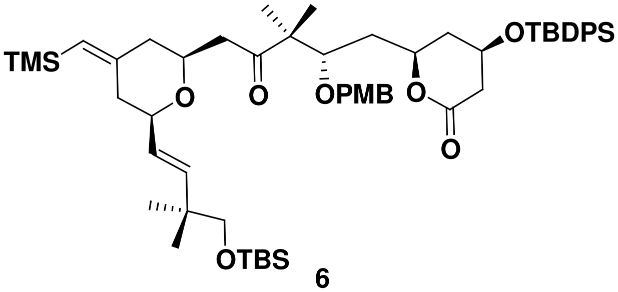
21

Compound 21: $Cu(OTf)_2$ (0.05 mg, 0.00014 mmol) was added to a solution of compound **17** (3.7 mg, 0.014 mol) and $PMBOC(NH)CCl_3$ (5.8 mg, 0.022 mol) in toluene (0.2 ml) at – 10 °C. The reaction mixture was stirred at – 10 °C for 30 min, before it was quenched with saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate three times and the combined organic fractions were dried over Na_2SO_4. The PMB ether was isolated with impurities via silica gel flash column chromatography (10 %, 15% then 20% ethyl acetate/petroleum ether) to give a light yellow oil. The impure PMB ether was then dissolved with freshly distilled MeOH (0.15 ml), and PPTS (3.5 mg, 0.014 mol) was added. The resulting solution was heated at 60 °C for 4 h, before it was poured into aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate three times and the combined organic fractions were dried over Na_2SO_4. Compound **21** was purified via silica gel flash column chromatography (60% ethyl acetate/petroleum ether) to give a colorless oil (4.5 mg, 93% over two steps). R_F: 0.25 (ethyl acetate:petroleum ether, 3:2 v/v); $[\alpha]^{D}_{20}$(deg cm^3 g^{-1} dm^{-1}): +47.9 (c 0.06 g cm^{-3} in DCM); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 4.62 (d, *J* = 11 Hz, 1H), 4.46 (d, *J* = 11 Hz, 1H), 3.93 (m, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.57 (m, 2H), 2.69 (dd, *J* = 5.0, 16.5 Hz, 1H), 2.59 (dd, *J* = 7.0, 17Hz, 1H), 2.60 (br, 1H), 2.32 (br, 1H), 1.75 (dd, *J* = 7.0 Hz, 2H), 1.17 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.6, 154.0, 129.8, 129.6, 114.1, 85.8, 77.3, 73.4, 72.5, 71.7, 70.9, 37.5, 24.2, 19.4; IR (film): 3410 (br), 2955, 2921, 1712, 1259, 1073, 820 cm^{-1}; HRMS ($C_{18}H_{24}O_6$): Calc'd. 359.1471 ($M+Na^+$), Found 359.1478.



4

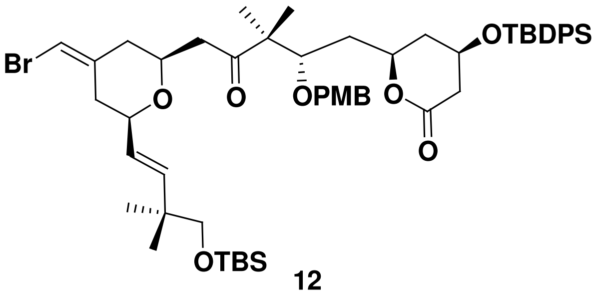
Compound 4: TBSOTf (3.5 mg, 0.013 mmol) was added to a solution of compound **21** (4.5 mg, 0.013 mmol) and 2,6-lutidine (2.1 mg, 0.020 mmol) in DCM (0.13 ml) at –78 °C under N_2. The reaction mixture was stirred at –78 °C for 1 h, before it was poured into saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. Compound **4** was purified via silica gel flash column chromatography (10%, then 15% ethyl acetate/petroleum ether) to give a colorless oil (4.3 mg, 71%). R_F: 0.6 (ethyl acetate:petroleum ether, 3:2 v/v); $[\alpha]^{D}_{20}$(deg cm^3 g^{-1} dm^{-1}): +23.8 (c 0.48 g cm^{-3} in DCM); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (dd, *J* = 2.0, 6.8 Hz, 2H), 6.87 (dd, *J* = 2.0, 6.8 Hz, 2H), 4.61 (d, *J* = 10.8, 1H), 4.50 (d, *J* = 10.8, 1H), 3.96 (m, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.62 (m, 1H), 3.56 (m, 1H), 2.63 (dd, *J* = 5.6, 17.2 Hz, 1H), 2.55 (dd, *J* = 6.4, 17.2 Hz, 1H), 2.34 (d, *J* = 5.6 Hz, 1H), 1.67-1.63 (m, 2H), 11.5 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 9H), 0.082 (s, 3H), 0.075 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.4, 154.1, 130.3, 129.7, 113.9, 86.4, 77.3, 73.7, 72.2, 72.0, 55.4, 52.7, 39.3, 30.4, 25.9, 24.9, 20.2, 18.1, –4.1, –4.8; IR (film): 3552 (br), 2954, 2930, 2857, 1716, 1613, 1514, 1253, 1074, 836 cm^{-1}; HRMS ($C_{24}H_{38}O_6Si$): Calc'd. 473.2335 ($M+Na^+$), Found 473.2335.



6

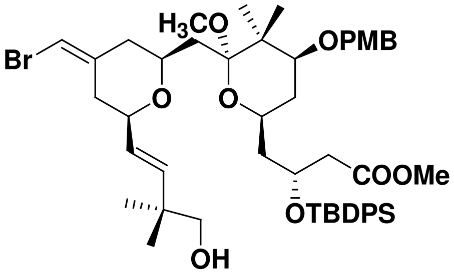
Compound 6: $CpRu(CH_3CN)_3PF_6$ (4.0 mg, 0.0092 mmol) was added to a solution of compound **7** (50 mg, 0.080 mmol) and compound **8** (24.5 mg, 0.069 mmol) in DCM (0.4

ml) at 0 °C. The resulting yellow solution was stirred at rt for 12 h. Compound **6** was purified directly via silica gel flash column chromatography (10%, then 15% ethyl acetate/petroleum ether) to give a colorless foam (23.1 mg, 34%; 80% brsm, 45.6 mg **7** + **8** can be recovered). R_F: 0.3 (ethyl acetate:petroleum ether, 1:9 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}): –21.1 (c 1.27 g cm^{-3} in DCM); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63-7.59 (m, 4H), 7.47-7.44 (m, 2H), 7.43-7.37 (m, 4H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 5.63 (dd, *J* = 0.5, 16 Hz, 1H), 5.40 (dd, *J* = 7.0, 16 Hz, 1H), 5.26 (s, 1H), 4.55 (d, *J* = 11 Hz, 1H), 4.34 (d, *J* = 11 Hz, 1H), 4.03-3.98 (m, 2H), 3.88-3.80 (m, 2H), 3.73 (m, 1H), 3.73 (s, 3H), 3.25 (s, 2H), 3.00 (dd, *J* = 5.5, 17 Hz, 1H), 2.53 (dd, *J* = 7.0, 18 Hz, 1H), 2.47-2.38 (m, 3H), 2.23 (br d, *J* = 13 Hz, 1H), 1.97 (br dd, *J* = 12, 24 Hz, 2H), 1.90 (ddd, *J* = 2.5, 5.5, 14 Hz, 1H), 1.58-1.55 (m, 2H), 1.48 (dd, *J* = 1.5, 10.5, Hz, 1H), 1.18 (s, 3H), 1.08 (s, 3H), 1.03 (s, 9H), 0.93 (s, 3H), 0.92 (s, 3H), 0.88 (s, 9H), 0.09 (s, 9H), 0.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.3, 170.4, 159.2, 152.9, 139.2, 135.73, 135.69, 133.4, 133.2, 130.7, 130.12, 130.06, 129.6, 128.0, 127.9, 127.7, 123.7, 113.8, 79.4, 79.3, 75.1, 74.6, 73.2, 71.8, 65.2, 55.3, 52.6, 45.3, 45.2, 40.6, 39.7, 38.9, 38.1, 37.9, 30.4, 26.9, 26.0, 24.0, 23.7, 20.9, 20.8, 19.1, 18.3, 0.4, –5.4; IR (film): 2956, 2858, 1744, 1702, 1612, 1514, 1249, 1094, 838 cm^{-1}; HRMS ($C_{57}H_{86}O_8Si_3$): Calc'd. 1005.5528 (M+Na$^+$), Found 1005.5520.



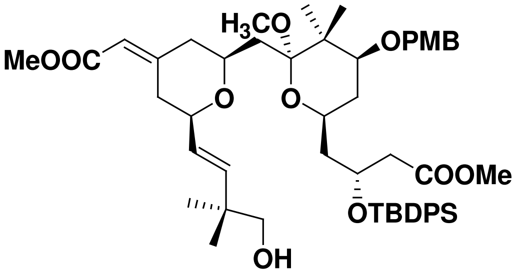
12

Compound 12: NBS (156 mg, 0.876 mmol) was added to a solution of compound **6** (172 mg, 0.175 mmol) in DMF (1.8 ml) at 0 °C. The resulting solution was stirred in the dark for 3 h, before it was poured into a solution of saturated aqueous $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. Compound **12** was purified via silica gel flash column chromatography (10%, then 15% ethyl acetate/petroleum ether) to give a colorless oil (171 mg, 98%). R_F: 0.5 (ethyl acetate:petroleum ether, 1:4 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}): –13.18 (c 0.72 g cm^{-3} in DCM); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63-7.59 (m, 4H), 7.47-7.43 (m, 2H), 7.41-7.37 (m, 4H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 5.98 (s, 1H), 5.67 (dd, *J* = 1.0, 16 Hz, 1H), 5.41 (dd, *J* = 6.5, 16 Hz, 1H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.02-3.97 (m, 2H), 3.84-3.74 (m, 3H), 3.73 (s, 3H), 3.26 (s, 2H), 3.03 (dd, *J* = 5.5, 18 Hz, 1H), 2.80 (br d, *J* = 13.5 Hz, 1H), 2.55 (dd, *J* = 7.0, 18 Hz, 1H), 2.47-2.36 (m, 3H), 1.91 (ddd, *J* = 3.5, 5.5, 14 Hz, 1H), 1.88-1.78 (m, 2H), 1.60-1.54 (m, 2H), 1.47 (m, 1H), 1.18 (s, 3H), 1.09 (s, 3H), 1.03 (s, 9H), 0.95 (s, 3H), 0.94 (s, 3H), 0.89 (s, 9H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.1, 170.4, 159.3, 139.8, 139.6, 135.72, 135.67, 133.4, 133.2, 130.6, 130.1, 130.07, 129.5, 127.95, 127.9, 127.2, 113.8, 100.4, 79.5, 78.0, 75.1, 73.7, 73.1, 71.8, 65.2, 55.3, 52.6, 44.9, 40.4, 39.6, 38.9, 38.2, 38.0, 37.1, 30.4, 26.8, 26.0, 23.9, 23.6, 20.9, 20.8, 19.1, 18.4, –5.4; IR (film): 2957, 2858, 1744, 1706, 1612, 1514, 1472, 1250, 1094, 838 cm^{-1}; HRMS ($C_{54}H_{77}O_8BrSi_2$): Calc'd. 1011.4238 (M+Na$^+$), Found 1011.4239.



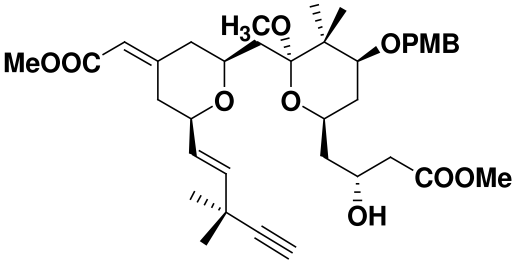
13

Compound 13: CSA (18 mg, 0.080 mmol) was added to a solution of compound **12** (0.88 g, 0.89 mmol) in MeOH (dry, 18 ml) at 0 °C. The resulting solution was stirred at rt for 12 h, before it was poured into saturated aqueous NaHCO$_3$. The mixture was extracted with ethyl acetate three times and the combined organic fractions were dried over Na$_2$SO$_4$. Compound **13** was purified via silica gel flash column chromatography (15%, then 30% ethyl acetate/petroleum ether) to give a colorless oil (0.76 g, 93%). R_F: 0.2 (ethyl acetate:petroleum ether, 1:4 v/v); $[\alpha]^{D}_{20}$(deg cm^3 g^{-1} dm^{-1}): +27.5 (c 0.85 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 400 MHz) δ 7.84-7.80 (m, 4H), 7.26-7.21 (m, 6H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.98 (s, 1H), 5.71 (dd, *J* = 1.2, 16 Hz, 1H), 5.52 (dd, *J* = 5.2, 16 Hz, 1H), 4.58 (m, 1H), 4.38 (d, *J* = 11.2, 1H), 4.18 (d, *J* = 11.2 Hz, 1H), 3.71-3.64 (m, 2H), 3.57 (m, 1H), 3.45 (m, 1H), 3.38 (s, 3H), 3.31 (s, 3H), 3.13 (s, 2H), 2.97 (m, 1H), 2.90 (s, 3H), 2.75-2.65 (m, 2H), 2.26 (brd, *J* = 12 Hz, 1H), 2.18 (dd, *J* = 4.8, 16 Hz, 1H), 1.89 (m, 1H), 1.81-1.65 (m, 4H), 1.51 (m, 1H), 1.20 (s, 3H), 1.17 (s, 9H), 1.14 (s, 3H), 0.91 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 171.6, 159.6, 140.8, 138.2, 136.30, 136.26, 134.4, 134.2, 131.8, 130.1, 129.3, 129.2, 128.0, 127.9, 114.0, 104.3, 100.5, 78.1, 77.2, 74.6, 71.4, 71.2, 69.7, 66.5, 54.7, 51.2, 48.0, 44.7, 43.6, 43.5, 42.4, 39.0, 38.2, 37.6, 33.2, 27.1, 23.9, 23.7, 21.1, 19.5, 16.8; IR (film): 3444, 2933, 1738, 1614, 1514, 1248 cm^{-1}; HRMS ($C_{50}H_{69}O_9BrSi$): Calc'd. 943.3792 (M+Na$^+$), Found 943.3801.



14

Compound 13: A solution of DMF/MeOH/Et$_3$N (4:2:0.06, 23 ml), which was degassed via freeze-pump-thaw technique, was added to a mixture of compound **13** (0.76 g, 0.83 mmol), PdCl$_2$(CH$_3$CN)$_2$ (16 mg, 0.062 mmol) and dppf (103 mg, 0.19 mmol) under CO. The resulting solution was stirred vigorously under CO (1 atm) at 80 °C for 12 h, before it was poured into a brine/water (1:1) solution. The mixture was extracted with ethyl acetate three times and the combined organic fractions were dried over Na_2SO_4. Compound **14** was purified via silica gel flash column chromatography (20%, then 30% ethyl acetate/petroleum ether) to give a colorless oil (0.62 g, 83%; 90% brsm: ca 85 mg compound **13** was recovered). R_F: 0.35 (ethyl acetate:petroleum ether, 2:3 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}) +22.5 (c 0.80 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 500 MHz) δ 7.84 (m, 4H), 7.25-7.16 (m, 8H), 6.81 (d, *J* = 8.5 Hz, 2H), 5.86 (s, 1H), 5.76 (d, *J* = 16 Hz, 1H), 5.57 (dd, *J* = 5.0, 16 Hz, 1H), 4.60 (m, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.29 (d, *J* = 13.5 Hz, 1H), 4.17 (d, *J* = 11.5 Hz, 1H), 3.80 (dd, *J* = 5.0, 11 Hz, 1H), 3.70-3.63 (m, 2H), 3.42 (s, 3H), 3.41 (s, 3H), 3.31 (s, 3H), 3.13 (s, 2H), 2.91 (s, 3H), 2.75 (m, 2H), 2.22-2.16 (m, 2H), 1.98-1.83 (m, 3H), 1.77-1.67 (m, 2H), 1.50 (dt, *J* = 3.5, 12.5 Hz, 1H), 1.21 (s, 3H), 1.19 (s, 9H), 1.14 (s, 3H), 0.90 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 171.6, 166.7, 159.5, 158.0, 138.2, 136.31, 136.28, 135.2, 134.4, 134.2, 131.8, 130.1, 129.4, 129.2, 128.3, 128.2, 114.0, 104.3, 78.1, 78.0, 74.9, 71.5, 71.1, 69.8, 66.6, 54.7, 51.2, 50.6, 48.0, 44.6, 44.2, 43.6, 43.5, 39.4, 38.2, 36.6, 33.1, 30.4, 27.1, 23.8, 23.7, 21.1, 19.5, 16.8; IR (film): 3475 (br), 2952, 2859, 1738, 1718, 1648, 1514, 1430, 1363, 1248 cm^{-1}; HRMS ($C_{52}H_{72}O_{11}Si$): Calc'd. 923.4742 (M+Na$^+$), Found 923.4753.



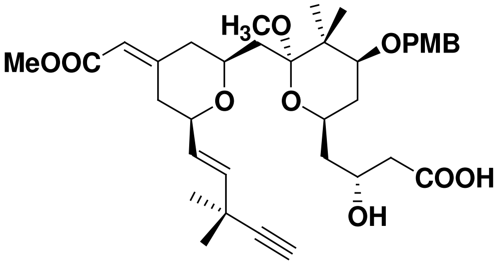
15

Compound 15: Dess–Martin periodinane (1.17 g, 2.76 mmol) was added to a mixture of coupound **14** (0.83 g, 0.92 mmol) and $NaHCO_3$ (1.5 g, 18.4 mmol) in DCM (18 ml) at 0 °C. The reaction was stirred at rt for 30 min, before being quenched with saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the combined organic fraction was dried over Na_2SO_4. The solvent was removed under vacuum, and the aldehyde was purified via silica gel flash column chromatography (10%, then 20% ethyl acetate/petroleum ether) to give a colorless oil (0.73 g, 88%).

The aldehyde was dissolved with freshly distilled MeOH (1.5 ml). Ohira–Bestmann reagent (55.6 mg, 0.289 mmol) and K_2CO_3 (60 mg, 0.435 mmol) were added to above solution at 0 °C. The resulting mixture was stirred for 1h, before it was poured into pH 7.0 buffer. The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. The terminal acetylene was purified via silica gel flash column chromatography (10%, then 15% ethyl acetate/petroleum ether) to give a colorless oil (125 mg, 97%).

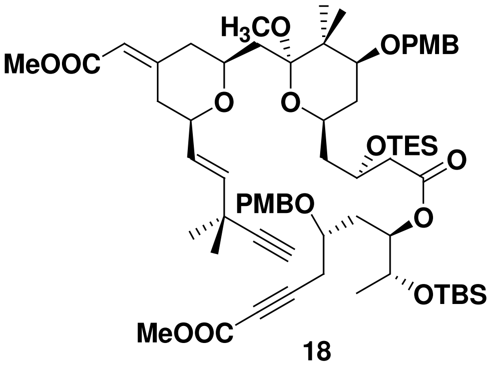
TBAF (1 M buffered with 20 mol % HOAc in THF, 0.24 ml) was added to a solution of the above terminal acetylene (193 mg, 0.216 mmol) in THF (4.0 ml) at rt under N_2. The resulting red solution was stirred at rt for 10 h, before it was poured into pH 7.0 buffer.

The mixture was extracted with ethyl acetate and the combined organic fractions were dried over Na_2SO_4. Compound **15** was purified via silica gel flash column chromatography (15%, 30% then 40% ethyl acetate/petroleum ether) to give a colorless oil (127 mg, 90%, brsm 96%, 13 mg starting material was recovered). R_F: 0.35 (ethyl acetate:petroleum ether, 2:3 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}): +65.7 (c 0.16 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 400 MHz) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.10 (dd, *J* = 5.2, 15.6 Hz, 1H), 5.85 (s, 1H), 5.79 (dd, *J* = 1.6, 15.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.43 (m, 1H), 4.31 (m, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 3.96-3.89 (m, 2H), 3.81 (dd, *J* = 4.4, 11.2 Hz, 1H), 3.76 (m, 1H), 3.41 (s, 3H), 3.36 (s, 3H), 3.30 (s, 3H), 3.13 (s, 3H), 2.34-2.28 (m, 4H), 2.01 (m, 1H), 2.00 (s, 1H), 1.91 (t, *J* = 12 Hz, 1H), 1.79 (dd, *J* = 6.0, 16 Hz, 1H), 1.63 (m, 1H), 1.46-1.36 (m, 4H), 1.26 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 171.7, 166.9, 159.8, 158.1, 136.9, 136.6, 136.5, 134.7, 134.4, 132.0, 130.3, 129.4, 129.0, 128.3, 128.1, 115.0, 114.2, 104.5, 89.7, 78.4, 77.6, 75.2, 71.4, 70.7, 70.0, 66.8, 55.0, 51.4, 50.8, 48.2, 44.9, 44.5, 43.8, 43.7, 39.6, 36.7, 33.7, 33.4, 27.3, 21.4, 19.7, 17.0; IR (film): 3292 (br), 2950, 2858, 1739, 1718, 1651, 1513, 1435, 1247, 1110, 705 cm^{-1}; HRMS ($C_{37}H_{52}O_{10}$): Calc'd. 679.3458 (M+Na$^+$), Found 679.3448.



16

Compound 16: trimethyltin hydroxide (10 mg, 0.055 mmol) was added to a solution of compound **15** (16.5 mg, 0.025 mmol) in dry DCE (0.7 ml) at rt under N_2. The resulting mixture was stirred at 80 °C for 12 h. Compound **16** was purified directly via silica gel flash column chromatography (40%, 60%, 80% ethyl acetate/petroleum ether, then 5%, 10% MeOH in DCM) to give a colorless oil (13.5 mg, 84%). R_F: 0.25 (ethyl acetate:petroleum ether, 4:1 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}): +70.7 (c 0.07 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 400 MHz) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.10 (dd, *J* = 4.8, 15.6 Hz, 1H), 5.88 (s, 1H), 5.80 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 11.2 , 1H), 4.37–4.24 (m, 2H), 4.29 (d, *J* = 11.2 Hz, 1H), 3.94-3.73 (m, 4H), 3.47 (s, 3H), 3.31 (s, 3H), 3.10 (s, 3H), 2.35-2.23 (m, 3H), 2.03 (s, 1H), 2.00-1.88 (m, 2H), 1.75 (dd, *J* = 5.2, 16 Hz, 1H), 1.59 (br d, *J* = 13.6 Hz, 1H), 1.44 (t, *J* = 12.4 Hz, 1H), 1.36-1.28 (m, 3H), 1.25 (s, 3H), 1.24 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ 176.6, 166.8, 159.6, 157.7, 136.9, 131.8, 129.3, 128.7, 127.8, 125.8, 114.8, 114.0, 104.3, 89.5, 78.3, 77.5, 75.2, 71.4, 70.5, 65.5, 64.7, 54.7, 50.8, 48.2, 44.2, 43.7, 42.1, 39.4, 36.5, 33.5, 32.6, 21.0, 16.9; IR (film): 3446 (br), 3296, 2949, 1715, 1651, 1514, 1247, 1088 cm^{-1}; HRMS ($C_{36}H_{50}O_{10}$): Calc'd. 665.3302 (M+Na$^+$), Found 665.3301.

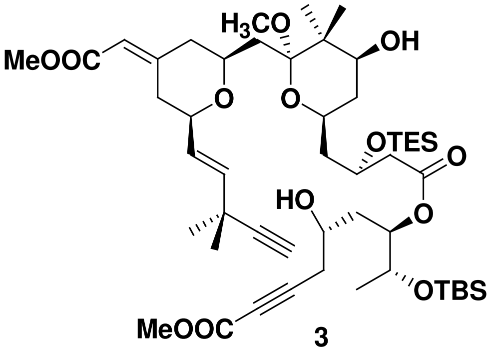


18

Compound 18: To a solution of hydroxyacid **16** (74 mg, 0.12 mmol) in DCM (2.5 ml) was added freshly distilled 2,6-lutidine (62 mg, 0.58 mmol) at –10 ^{o}C, followed by dropwise addition of freshly distilled TESOTf (67 mg, 0.25 mmol). The resulting solution was stirred at the same temperature for 20 min, before poured into pH 7.0 buffer. The mixture was extracted with ethyl acetate five times and the combined organic fractions were dried over Na_2SO_4. The TES ether-acid **5** was purified via **quick** silica gel flash column chromatography (10%, 20% then 30% ethyl acetate/petroleum ether) to give a colorless foam (73 mg, 79%). (Significant decomposition has been observed when slower chromatography was applied.)

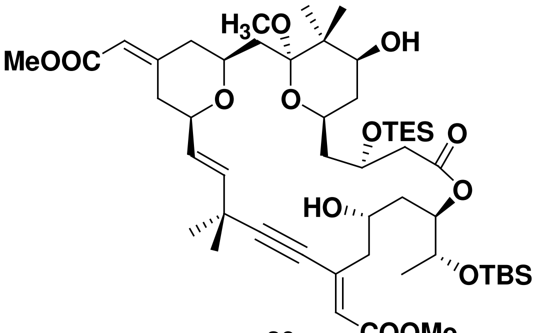
To a solution of TES ether-acid **5** (17.0 mg, 0.0225 mmol) in dry toluene (0.5 ml) was added Et_3N (4.8 mg, 0.047 mmol) at rt under N_2, followed by dropwise addition of freshly distilled 2,4,6-trichlorobenzoyl chloride (5.6 mg, 0.024 mmol) at rt. The resulting solution was stirred at rt for 1 h, before a solution of alcohol **4** (10.1 mg, 0.0225 mmol) and DMAP (6.9 mg, 0.056 mmol) in toluene (0.75 ml) was added. The resulting mixture was stirred at rt for another 1h, before poured into pH 7.0 buffer. The mixture was extracted with ethyl acetate four times and the combined organic fractions were dried over Na_2SO_4. The ester **18** was purified via silica gel flash column chromatography (10%, then 20% ethyl acetate/petroleum ether) to give a colorless foam (25 mg, 92%). R_F: 0.35 (ethyl acetate:petroleum ether, 1:4 v/v); $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): +62.6 (c 0.11 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 500 MHz) δ 7.41 (d, *J* =8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.07 (dd, *J* = 5.0, 15.5 Hz, 1H), 5.93 (s, 1H), 5.79 (dd, *J* = 1.5, 15.5 Hz, 1H), 5.48 (ddd, *J* = 2.0, 4.0, 10.5 Hz, 1H), 4.60 (m, 1H), 4.53 (d, *J* = 10.5, 1 H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.42 (d, *J* = 10.5 Hz, 1H), 4.32 (brd, *J* = 15.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 3.97 (m, 1H), 3.88-3.83 (2H), 3.79 (m, 1H), 3.67 (m ,1H), 3.45 (s, 3H), 3.33 (s, 3H), 3.30 (s, 3H), 3.28 (s, 3H), 3.27 (s, 3H), 2.70 (br s, 1H), 2.69 (d, *J* = 2.0 Hz, 1H), 2.38-2.25 (4H), 2.07-1.89 (6H), 2.01 (s, 1H), 1.84 (dd, *J* = 5.0, 16 Hz, 1H), 1.80 (m, 1H), 1.65 (m, 1H), 1.57 (dd, *J* = 9.5, 19.5 Hz, 2H), 1.29 (s, 3H), 1.22 (s, 3H), 1.21 (s, 6H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.07 (t, *J* = 6.5 Hz, 9H), 1.00 (3, 9H), 0.72 (m, 6H), 0.17 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 170.9, 166.7, 159.8, 159.6, 157.7, 153.9, 136.8, 131.7, 130.5, 130.1, 129.3, 128.7, 128.3, 128.1, 127.9, 114.9, 114.1, 114.03, 113.96, 104.5, 89.4, 85.8, 78.5, 77.5, 75.6, 75.1, 73.6, 73.4, 72.1, 71.5, 70.5, 68.7, 67.8, 66.2, 54.74, 54.70, 52.0, 50.6, 48.3, 44.9, 44.3, 43.7, 43.6, 39.5, 36.4, 34.4, 33.8, 33.5, 29.8, 26.01, 25.96, 24.5, 21.2, 18.6, 18.2, 17.0, 7.3, 5.7, –4.6, –4.7;

IR (film): 2927, 2240, 1717, 1651, 1614, 1514, 1463, 1377, 1250, 1075 cm^{-1}; HRMS ($C_{66}H_{100}O_{15}Si_2$): Calc'd. 1211.6499 (M+Na$^+$), Found 1211.6484.



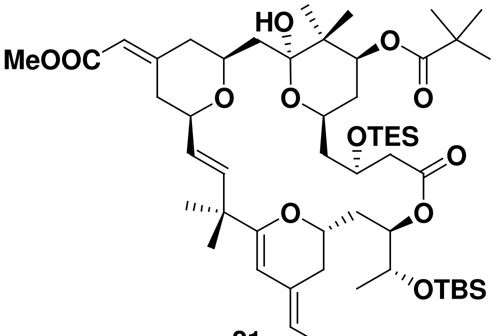
3

Compound 3: DDQ (14 mg, 0.063 mmol) was added to a mixture of ester **18** (15.0 mg, 0.0126 mmol) in DCM (2.6 ml) and pH 7.0 buffer (0.26 ml) at 0 °C, and then the ice-bath was removed. The resulting mixture was stirred for 1.5 h, before another portion of DDQ (7.5 mg, 0.033 mmol) and pH 7.0 buffer (0.15 ml) was added at rt. The resulting mixture was stirred at rt for 1 h, before saturated aqueous $NaHCO_3$ was added. The mixture was extracted with ethyl acetate four times and the combined organic fractions were dried over Na_2SO_4. The residue was purified by silica gel flash column chromatography (20%, 30% then 40% ethyl acetate/petroleum ether) to give diol **3** (5.5 mg, 46%) and the mono-PMB ether (7.8 mg, 58%). The mono-PMB ether can be re-subjected to the same DDQ deprotection procedure to give diol **3** in 50% yield. R_F: 0.35 (ethyl acetate:petroleum ether, 3:7 v/v); $[\alpha]^D_{20}$(deg cm^3 g^{-1} dm^{-1}): –43.8 (c 0.21 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 500 MHz) δ 6.09 (dd, *J* = 5.0, 15.5 Hz, 1H), 5.90 (s, 1H), 5.82 (d, *J* = 15.5 Hz, 1H), 5.29 (m, 1H), 4.50 (m, 1H), 4.28 (d, *J* = 13.5 Hz, 1H), 4.01 (dd, *J* = 4.5, 11 Hz, 1H), 4.00-3.73 (6H), 3.44 (s, 3H), 3.22 (s, 3H), 3.21 (s, 3H), 2.67 (dd, *J* = 6.5, 10.5 Hz, 2H), 2.36-2.24 (3H), 2.16 (dd, *J* = 5.5, 17 Hz), 2.02 (s, 1H), 2.02-1.91 (4H), 1.83 (dd, *J* = 5.5 15.5 Hz, 1H), 1.80-1.74 (3H), 1.59-1.45 (4H), 1.23 (s, 3H), 1.22 (s, 3H), 1.17 (s, 6H), 1.13 (d, *J* = 6.0 Hz, 3H), 1.04 (t, *J* = 8.0 Hz, 9H), 0.99 (s, 9H), 0.66 (m, 6H), 0.17 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 171.7, 166.8, 157.8, 154.4, 136.8, 128.7, 128.3, 128.1, 127.9, 125.8, 114.8, 104.4, 89.4, 87.2, 77.5, 75.3, 75.2, 74.3, 70.7, 70.5, 68.6, 67.4, 65.9, 65.8, 52.0, 50.7, 48.2, 44.4, 44.1, 43.6, 42.9, 39.5, 37.0, 36.5, 36.0, 33.5, 30.4, 29.8, 28.0, 26.01, 25.96, 20.9, 18.5, 18.2, 15.8, 7.2, 5.6, 5.5, –4.6, –4.7; IR (film): 3453 (br), 2927, 2240, 1718, 1650, 1614, 1435, 1378, 1254, 1075 cm^{-1}; HRMS ($C_{50}H_{84}O_{13}Si_2$): Calc'd. 971.5348 (M+Na$^+$), Found 971.5354.



20

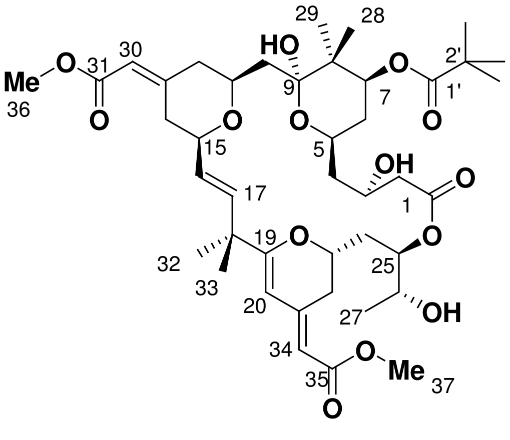
Compound 20: To a mixture of $Pd(OAc)_2$ (4.4 mg, 0.02 mmol) and TDMPP [tris(2,6-dimethoxyphenyl)phosphine] (11.2 mg, 0.025 mmol) was added freshly distilled toluene (1 ml). The mixture was stirred at rt for 30 min, and the resulting red solution (0.02 ml, ca. 0.0004 mmol) was slowly added a solution of di-yne **3** (3.2 mg, 0.0034 mmol) in freshly distilled toluene (1.6 ml) under N_2. The reaction was stirred at rt for 3 days, before it was filtered through a short plug of silica gel. The solvent was removed under vacuum and the macrocycle **20** was purified via silica gel flash column chromatography (20%, 30% then 40% ethyl acetate/petroleum ether) to give a white paste (1.8 mg, 56%). R_F: 0.35 (ethyl acetate:petroleum ether, 3:7 v/v); $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): –43.8 (c 0.21 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 500 MHz) δ 6.32 (s, 1H), 6.12 (dd, *J* = 3.5, 15.5 Hz, 1H), 5.89 (d, *J* = 15 Hz, 1H), 5.73 (s, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 4.67 (m, 1H), 4.36 (d, *J* = 13 Hz, 1H), 4.31 (m, 1H), 4.12 (d, *J* = 11 Hz, 1H), 4.03-4.00 (2H), 3.91 (m ,1H), 3.86 (m ,1H), 3.40 (s, 3H), 3.38 (t, *J* = 7.5 Hz, 1H), 3.26 (s, 3H), 3.21 (s, 3H), 3.16 (dd, *J* = 5.0, 14.5 Hz, 1H), 2.68 (dd, *J* = 3.0, 16 Hz, 1H), 2.62 (dd, *J* = 9.0, 16 Hz, 1H), 2.21 (dd, *J* = 8.0, 16 Hz, 1H), 2.00 (m 1H), 1.92-1.84 (4H), 1.65-1.53 (3H), 1.46 (m, 1H), 1.36-1.29 (2H), 1.24 (s, 3H), 1.22 (s, 3H), 1.19 (d, *J* = 6.5 Hz, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.07 (t, *J* = 8.0 Hz, 9H), 0.98 (s, 9H), 0.66 (m, 6H), 0.16 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 172.3, 166.5, 157.7, 140.2, 134.9, 129.1, 128.2, 127.9, 125.1, 114.8, 103.5, 102.0, 83.9, 76.4, 75.1, 74.3, 70.0, 68.7, 67.4, 66.9, 65.9, 50.9, 50.6, 49.1, 46.5, 44.6, 43.2, 42.8, 40.6, 40.2, 37.2, 36.8, 36.4, 34.6, 30.2, 29.8, 29.6, 26.0, 20.6, 18.5, 18.3, 16.6, 7.35, 6.0, –4.68, –4.72; IR (film): 3442 (br), 2924, 2853, 1717, 1650, 1614, 1435, 1376, 1256, 1151, 1107 cm^{-1}; HRMS ($C_{50}H_{84}O_{13}Si_2$): Calc'd. 971.5348 (M+Na$^+$), Found 971.5341.



21

Compound 21: To a mixture of $Au(PPh_3)_3Cl$ (10.2 mg, 0.020 mmol) and $AgSbF_6$ (7.0 mg, 0.020 mmol) was added dry DCM (0.5 ml) at rt under N_2. The resulting mixture was stirred in the dark for 15 min, and a purple precipitate was formed. The supernatant solution (0.01 ml) was transferred to a mixture of compound **20** (1.8 mg, 0.0017 mmol) and $NaHCO_3$ (1.8 mg, 0.021 mmol) in DCM/CH_3CN (10:1, 0.5 ml) at 0 ^{o}C under N_2. The resulting reaction mixture was stirred vigorously overnight, before it was poured into a mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (ca 1:1), and then the mixture was extracted with ethyl acetate four times and the combined organic fractions were dried over Na_2SO_4. The dihydropyran intermediate was purified via **quick** silica gel flash column chromatography (10%, 20% then 30% ethyl acetate/petroleum ether) to give a colorless foam (1.4 mg, 73%).

To a solution of the above dihydropyran (1.9 mg, 0.0020 mmol) in DCM (0.10 ml) was added DMAP (20 mg, 0.16 mmol) and Piv_2O (18 mg, 0.10 mmol) at rt under N_2. The resulting solution was sealed and stirred at 52 ^{o}C for 2 h, before it was cooled to rt and MeOH (0.10 ml) was added. The solution was stirred at rt for 10 min, and the solvent was removed under vacuum. The pivalate ester **21** was purified directly via silica gel flash column chromatography (10%, 15% then 20% ethyl acetate/petroleum ether) to give a white paste (1.3 mg, 62%). R_F: 0.30 (ethyl acetate:petroleum ether, 1:9 v/v); $[\alpha]^{D}_{20}$(deg cm^3 g^{-1} dm^{-1}): +52.6 (c 0.12 g cm^{-3} in DCM); ^{1}H NMR (C_6D_6, 400 MHz) δ 6.06 (d, *J* = 16.2 Hz, 1H), 5.81 (s, 1H), 5.79 (s, 1H), 5.60 (brs, 1H), 5.52 (dd, *J* = 6.0, 15.4 Hz, 1H), 5.33 (dd, *J* = 3.6, 11.5 Hz, 1H), 5.24 (brs, 1H), 5.10 (dd, *J* = 4.7, 11.6 Hz, 1H), 4.48-4.42 (2H), 4.30 (d, *J* = 14 Hz, 1H), 4.20 (m, 1H), 3.81-3.71 (2H), 3.62 (t, *J* = 12 Hz, 1H), 3.50 (s, 3H), 3.47 (s, 3H), 3.39-3.28 (2H), 2.50 (dd, *J* = 10, 16.6 Hz, 1H), 2.30 (t, *J* = 16 Hz, 1H), 2.02-1.93 (2H), 1.80-1.40 (9H), 1.26 (s, 3H), 1.21(s, 3H), 1.18 (s, 9H), 1.11 (t, *J* = 7.7 Hz, 9H), 1.07 (d, *J* = 6.5 Hz, 3H), 1.06 (s, 6H), 1.05 (s, 9H), 0.75-0.69 (m, 6H), 0.26 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (C_6D_6, 125 MHz) δ 177.6, 172.3, 168.7, 167.3, 166.1, 156.0, 150.4, 138.4, 127.9, 127.3, 115.3, 109.6, 101.4, 78.8, 75.2, 74.0, 73.9, 73.0, 72.2, 69.2, 68.4, 67.3, 50.6, 50.4, 45.2, 45.0, 42.4, 42.2, 41.1, 39.1, 36.5, 36.3, 34.0, 32.8, 32.1, 30.2, 27.3, 26.4, 26.1, 23.3, 18.4, 17.1, 15.3, 7.3, 5.5, 1.4, –4.7, –4.8; IR (film): 3442 (br), 2954, 2927, 2855, 1729, 1612, 1434, 1376, 1231, 1152, 1044 cm^{-1}; HRMS ($C_{50}H_{84}O_{13}Si_2$): Calc'd. 1041.5761 (M+Na$^+$), Found 1041.5764.



Bryostatin 16 (1)

Bryostatin 16 (1): To a solution of pivalate ester **21** (1.0 mg, 0.001 mmol) in THF (0.05 ml) was added TBAF (0.005 ml, 0.005 mmol, 1M) at 0 °C. The resulting solution was allowed to slowly warm to rt and stirred for 4 h. The reaction mixture was diluted with ethyl acetate and pH 7.0 buffer was added. The mixture was extracted with ethyl acetate five times and the combined organic fractions were dried over Na_2SO_4. The residue was purified by reverse phase HPLC (RP C-18 column, CH_3CN in H_2O from 65% to 95%) to give **1** as a white paste (0.4 mg, ca 52%). R_F: 0.35 (ethyl acetate:petroleum ether, 4:1 v/v); $[\alpha]^{D}{}_{20}$(deg cm^3 g^{-1} dm^{-1}): +81 (c 0.04 g cm^{-3} in MeOH); IR (film): 3359 (br), 2958, 2917, 2849, 1722, 1702, 1605, 1614, 1433, 1375, 1259, 1154, 1099 cm^{-1}; HRMS ($C_{42}H_{62}O_{14}$): Calc'd. 913.4037 (M+Na$^+$), Found 913.4038.

^{1}H NMR (CD_3CN, 600 MHz) [reported ^{1}H NMR (CD_3CN, 400 MHz)] (δ, ppm):

Reported	Found
5.92 (d, *J* = 16 Hz, 1H)	5.92 (d, *J* = 15.8 Hz, 1H)
5.75 (brs, 1H)	5.75 (brs, 1H)
5.50 (brs, 1H)	5.50 (brs, 1H)
5.47 (brs, 1H)	5.47 (brs, 1H)
5.41 (dd, *J* = 7.3, 16 Hz, 1H)	5.41 (dd, *J* = 7.2, 15.9 Hz, 1H)
5.20 (brd, *J* = 11 Hz, 1H)	5.20 (ddd, *J* = 1.8, 4.2, 11.6 Hz, 1H)
5.10 (dd, *J* = 5, 12 Hz, 1H)	5.10 (dd, *J* = 5.1, 11.9 Hz, 1H)
4,16 (m, 1H),* 4.12 (m, 1H)*	4.20-4.08 (m, 2H)*
3.98 (brdd, *J* = 7.3, 12 Hz, 1H)	3.99 (ddd, *J* = 2.0, 7.2, 11.7 Hz, 1H)
3.82 (brt *J* = 11 Hz, 1H), 3.78 (1H)*	
3.76 (1H)*	3.86-3.75 (m, 3H)*
3.68 (1H)*	3.68 (1H)*
3.66 (s, 3H)	3.66 (s, 3H)
3.61 (s, 3H)	3.61 (s, 3H)
3.57 (brd, *J* = 17 Hz, 1H)	3.57 (brd, *J* = 17.1 Hz, 1H)
unreported	3.06 (d, *J* = 9.2 Hz, 1H) [C(3)HO**H**]
unreported	2.91 (d, *J* = 5.8 Hz, 1H) [C(26)HO**H**]
2.47 (2H)*	2.48 (d, *J* = 3.2 Hz, 1H)
	2.46 (d, *J* = 10.1 Hz, 1H)
2.25 (brdd, *J* = 11, 17 Hz, 1H)	2.26 (1H)*
2.23 (1H)*	2.23 (1H)*
2.18 (1H)*	2.18 (1H)*
1.98 (brt, *J* = 11 Hz, 1H)	1.98 (1H)**
1.89 (1H)*	1.89 (1H)*
1.88 (m, 1H)*	1.87 (m, 1H)*
1.86 (1H)*	1.85 (1H)*
1.78 (dd, *J* = 3, 15 Hz, 1H)	1.78 (dd, *J* = 3.4, 15.2 Hz, 1H)
1.67 (m, 1H)*, 1.64 (m, 2H)*	1.68-1.62 (m, 3H)*
1.40 (dt, *J* = 12, 12 Hz, 1H)	1.40 (dt, *J* = 12.1, 12.1 Hz, 1H)
1.21 (s, 3H)	1.21 (s, 3H)
1.19 (s, 3H)	1.19 (s, 3H)

1.16 (s, 9H)	1.16 (s, 9H)
1.10 (d, J = 6.6 Hz, 3H)	1.10 (d, J = 6.6 Hz, 3H)
0.97 (s, 3H)	0.97 (s, 3H)
0.89 (s, 3H)	0.89 (s, 3H)

---

[*] Couplings for these signals were obscured.

[**] Overlapping with the peak of CH$_3$CN, detectable from gCOSY.

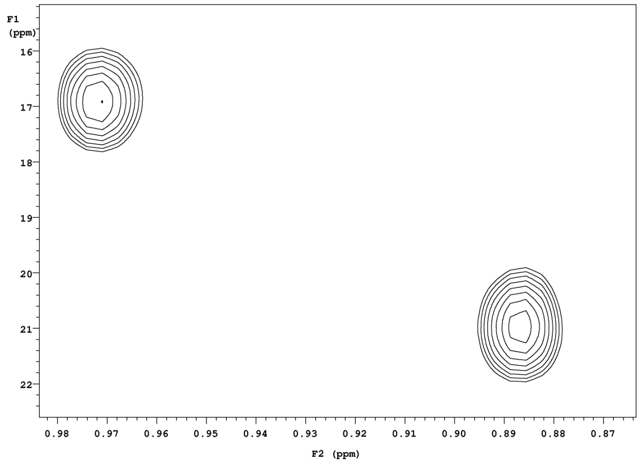
^{13}C NMR (CD$_3$CN, 150 MHz), determined from gHSQC and gHMBC (δ, ppm) [reported ^{13}C NMR (CD$_3$CN, 100 MHz)]

Position	Reported	Found[a]	Found[b]
1	172.8	172.7	172.7
2	42.9	42.7	42.7
3	67.4	67.4	67.4
4	42.5	42.4	42.4
5	66.0	65.8	65.8
6	34.3	34.1	34.1
7	73.5	73.5	73.5
8	41.9	41.9	41.9
9	102.5	102.4	102.4
10	43.0	42.8	42.8
11	74.4	74.2	74.2
12	45.3	45.2	45.2
13	158.9	158.5	158.5
14	36.5	36.3	36.3
15	79.9	79.4	79.4
16	128.2	128.1	128.1
17	139.5	139.4	139.4
18	42.1	42.0	42.0
19	151.9	151.9	169.8 (see 21, 35)
20	101.6	101.5	101.5
21	168.2	168.2	151.9 (see 19, 35)
22	32.8	32.7	32.7
23	73.5	73.2	73.2
24	36.5	36.3	36.3
25	73.5	73.4	73.4
26	69.0	68.9	68.9
27	19.1	18.9	18.9
28	21.3	21.0	17.0 (see 29)
29	17.2	17.0	21.0 (see 28)
30	114.8	114.8	114.8
31	167.8	167.5	167.5

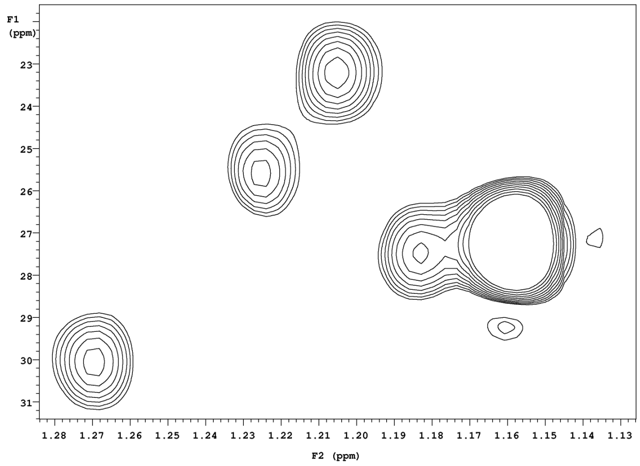
32	27.7	27.5	23.2 (see 33)
33	23.4	23.2	27.5 (see 32)
34	108.9	108.8	108.8
35	170.0	169.8	168.2 (see 19, 21)
36	51.6	51.4	51.4
37	51.2	51.1	51.1
1’	178.5	178.5	178.5
2’	39.6	39.5	39.5
3’-5’	27.5	27.3	27.3

---

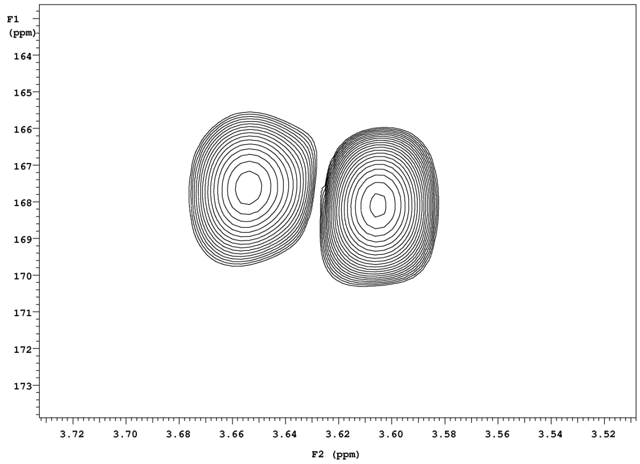
a) Chemical shift according to the original assignment
b) Chemical shift according to our new assignment
From gHSQC, correlations from 0.97 (H28) to 17.0, and from 0.89 (H29) to 21.0 were observed to support our C28-29 assignment.



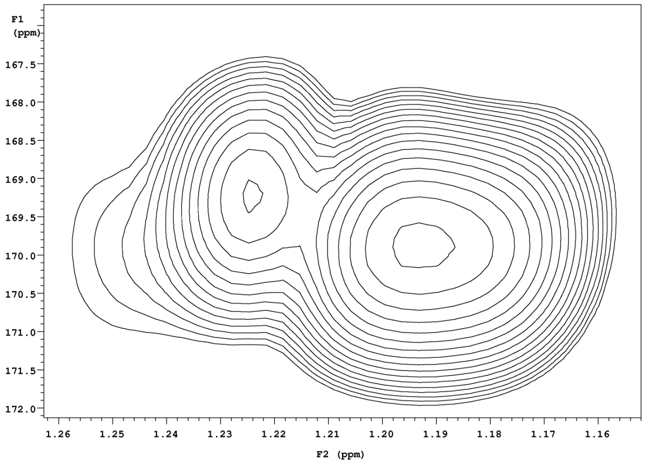
From gHSQC, correlations from 1.21 (H32) to 23.2, and from 1.19 (H33) to 27.5 were observed to support our C32-33 assignment.



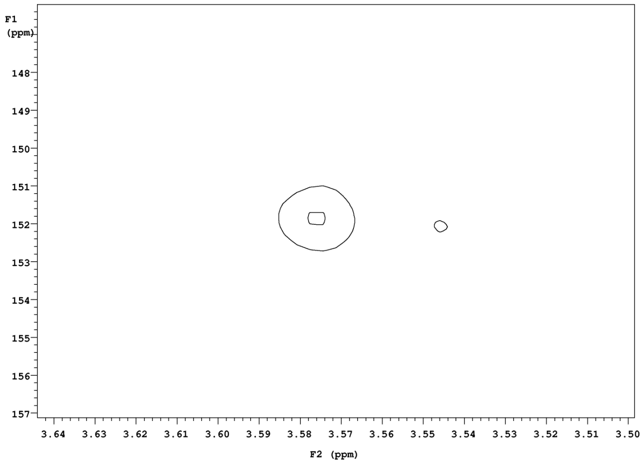
From gHMBC, correlations from 3.61 (H37) to 168.2 was observed to support our C35 assignment.



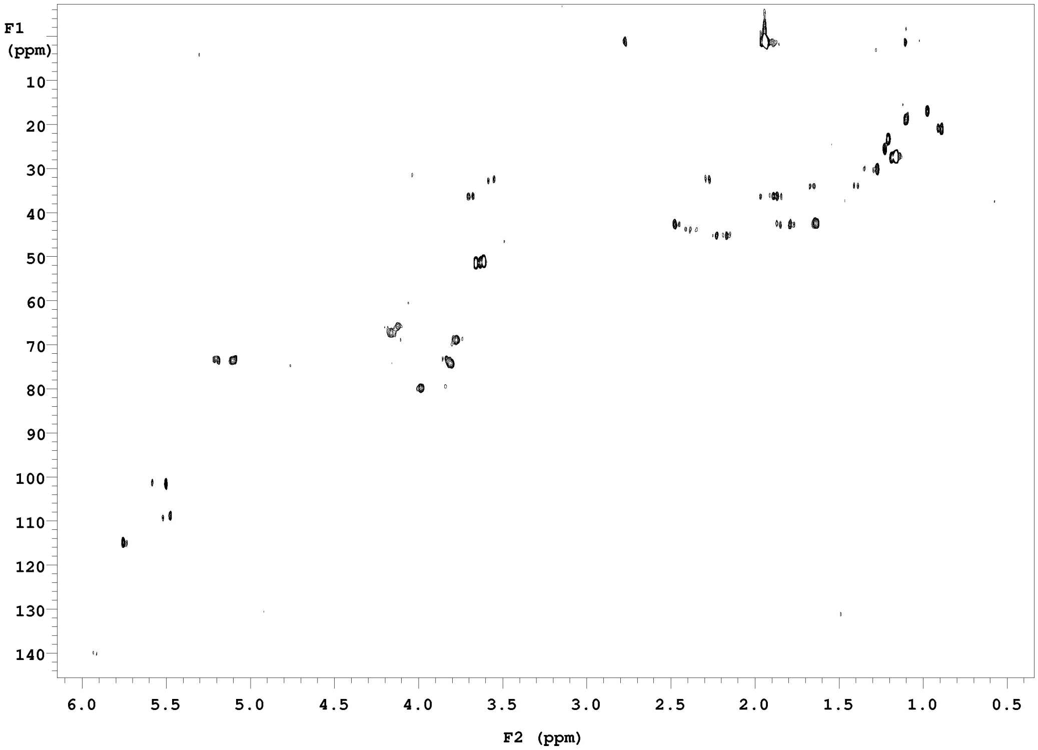
From gHMBC, correlations from 1.21 (H32) and 1.19 (H33) to 169.8 was observed to support our C19 assignment.



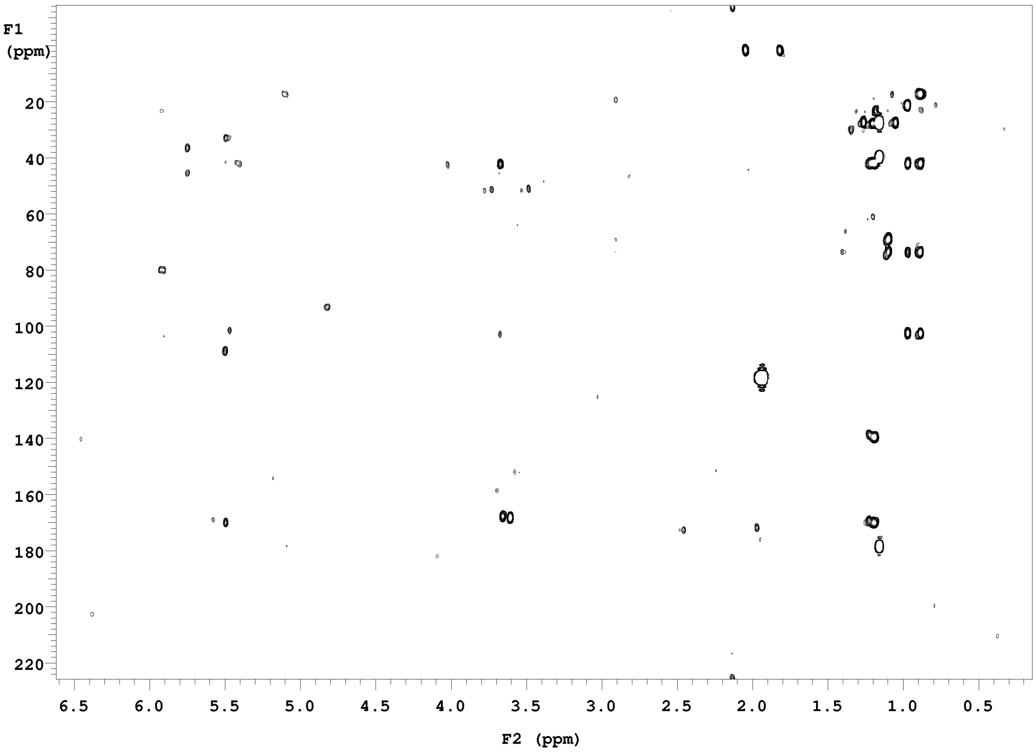
From gHMBC, correlation from 3.57 (H22) to 151.9 was observed to support our C21 assignment.



Full gHSQC spectrum:

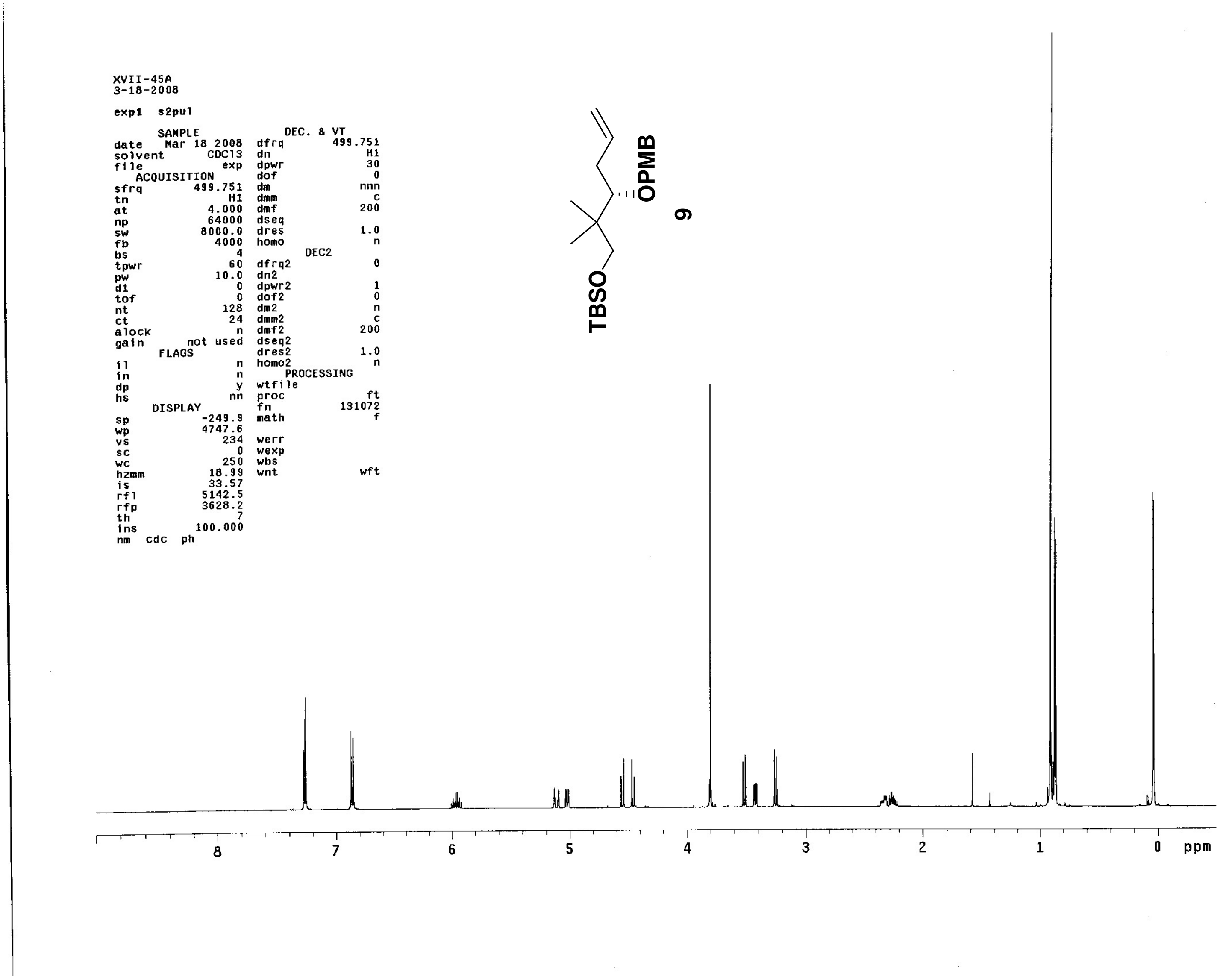


Full gHMBC spectrum:



References:

31. Large quantities of **2** are readily available in two steps from commercially available inexpensive 2,2-dimethyl-propane-1,3-diol (see ref 21). Small quantities of **2** are available from SALOR.
32. Bode, J. W.; Gauthier, Jr. D. R. & Carreira, E. M. Facile enantioselective synthesis of a key homoallylic alcohol building block for polyketide synthesis: TiF_4-BINOL catalyzed allylsilylation with allyl trimethylsilane. *Chem. Commun.* 2560-2561 (2001).
33. Yu, W.; Mei, Y.; Kang, Y.; Hua, Z. & Jin, Z. Improved procedure for the oxidative cleavage of olefins by OsO_4-$NaIO_4$ *Org. Lett.* **6**, 3217-3219 (2004).
34. Wender, P. A. *et al.* The practical synthesis of a novel and highly potent analogue of bryostatin. *J. Am. Chem. Soc.* **124**, 13648-13649 (2002).



9

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XVII-45A
3-18-2008

exp1  s2pul

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   ACQUISITION       dof                 0
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tn               H1  dmm                 c
at            4.000  dmf               200
np            64000  dseq
sw           8000.0  dres              1.0
fb             4000  homo                n
bs                4             DEC2
tpwr             60  dfrq2               0
pw             10.0  dn2
d1                0  dpwr2               1
tof               0  dof2                0
nt              128  dm2                 n
ct               24  dmm2                c
alock             n  dmf2              200
gain       not used  dseq2
      FLAGS          dres2             1.0
il                n  homo2               n
in                n        PROCESSING
dp                y  wtfile
hs               nn  proc               ft
     DISPLAY         fn             131072
sp           -249.9  math                f
wp           4747.6
vs              234  werr
sc                0  wexp
wc              250  wbs
hzmm          18.99  wnt               wft
is            33.57
rfl          5142.5
rfp          3628.2
th                7
ins         100.000
nm  cdc  ph
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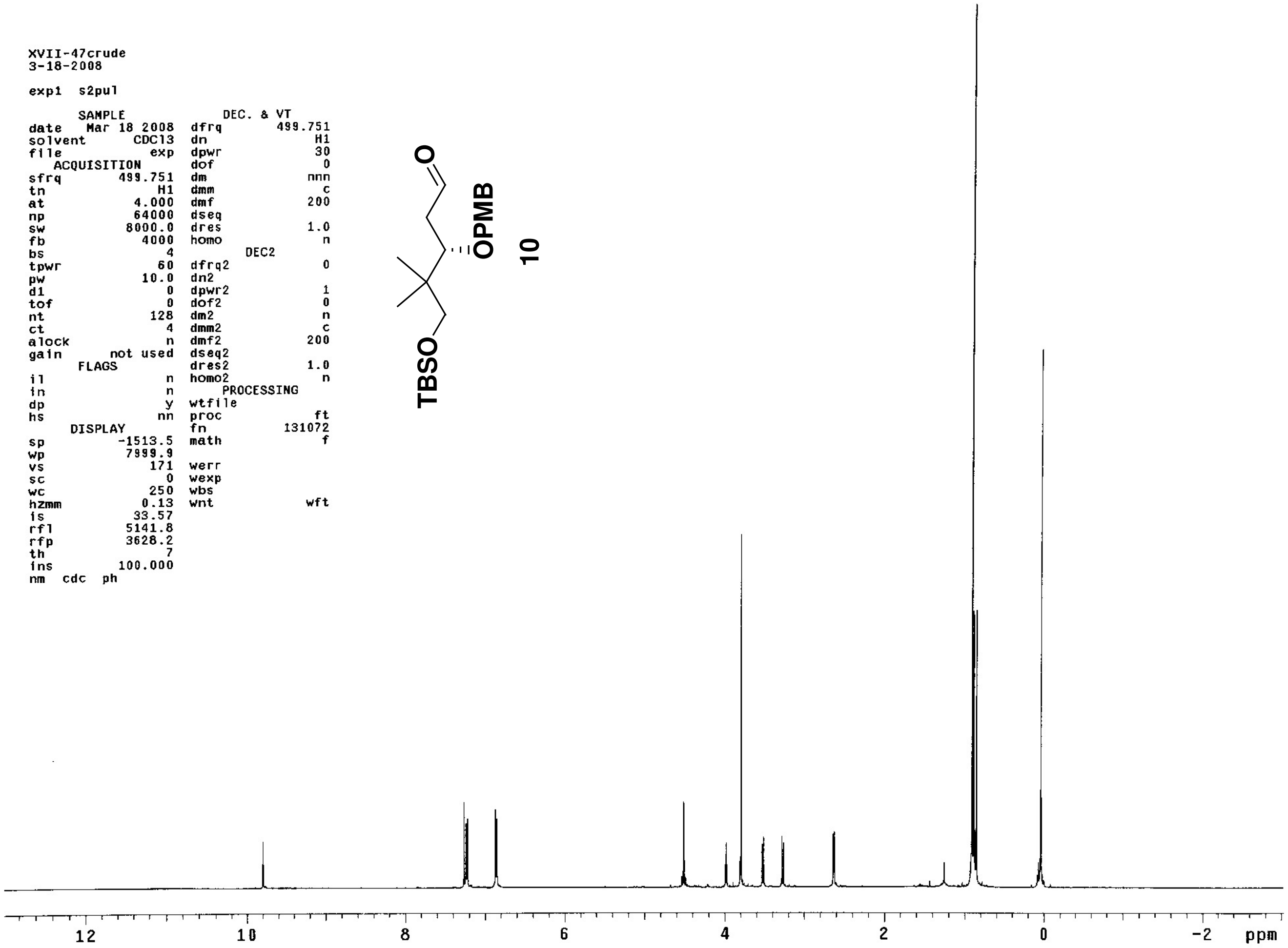

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XVII-47crude
3-18-2008

exp1  s2pul

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solvent      CDC13  dn               H1
file           exp  dpwr             30
   ACQUISITION      dof               0
sfrq       499.751  dm              nnn
tn              H1  dmm               c
at           4.000  dmf             200
np           64000  dseq
sw          8000.0  dres            1.0
fb            4000  homo              n
bs               4          DEC2
tpwr            60  dfrq2             0
pw            10.0  dn2
d1               0  dpwr2             1
tof              0  dof2              0
nt             128  dm2               n
ct               4  dmm2              c
alock            n  dmf2            200
gain      not used  dseq2
      FLAGS         dres2           1.0
il               n  homo2             n
in               n      PROCESSING
dp               y  wtfile
hs              nn  proc             ft
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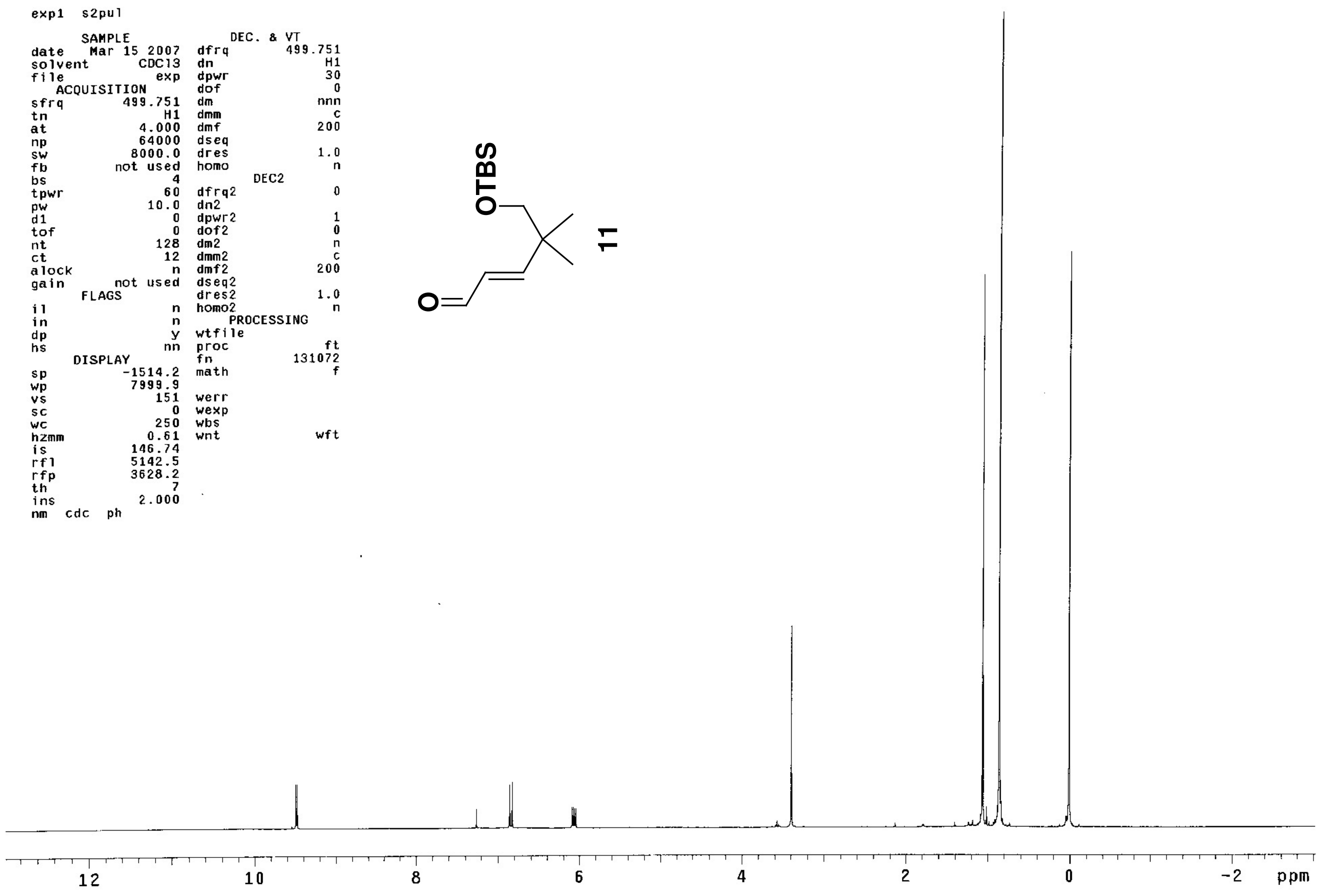
sp         -1513.5  math              f
wp          7999.9
vs             171  werr
sc               0  wexp
wc             250  wbs
hzmm          0.13  wnt             wft
is           33.57
rfl         5141.8
rfp         3628.2
th               7
ins        100.000
nm  cdc  ph
```

10



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XII-16A
03-15-2007

exp1  s2pul

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date   Mar 15 2007  dfrq         499.751
solvent       CDCl3  dn                H1
file            exp  dpwr              30
   ACQUISITION       dof                0
sfrq        499.751  dm               nnn
tn               H1  dmm                c
at            4.000  dmf              200
np            64000  dseq
sw           8000.0  dres             1.0
fb         not used  homo               n
bs                4           DEC2
tpwr             60  dfrq2              0
pw             10.0  dn2
d1                0  dpwr2              1
tof               0  dof2               0
nt              128  dm2                n
ct               12  dmm2               c
alock             n  dmf2             200
gain       not used  dseq2
      FLAGS          dres2            1.0
il                n  homo2              n
in                n       PROCESSING
dp                y  wtfile
hs               nn  proc              ft
     DISPLAY         fn            131072
sp          -1514.2  math               f
wp           7999.9
vs              151  werr
sc                0  wexp
wc              250  wbs
hzmm           0.61  wnt              wft
is           146.74
rfl          5142.5
rfp          3628.2
th                7
ins           2.000
nm  cdc  ph
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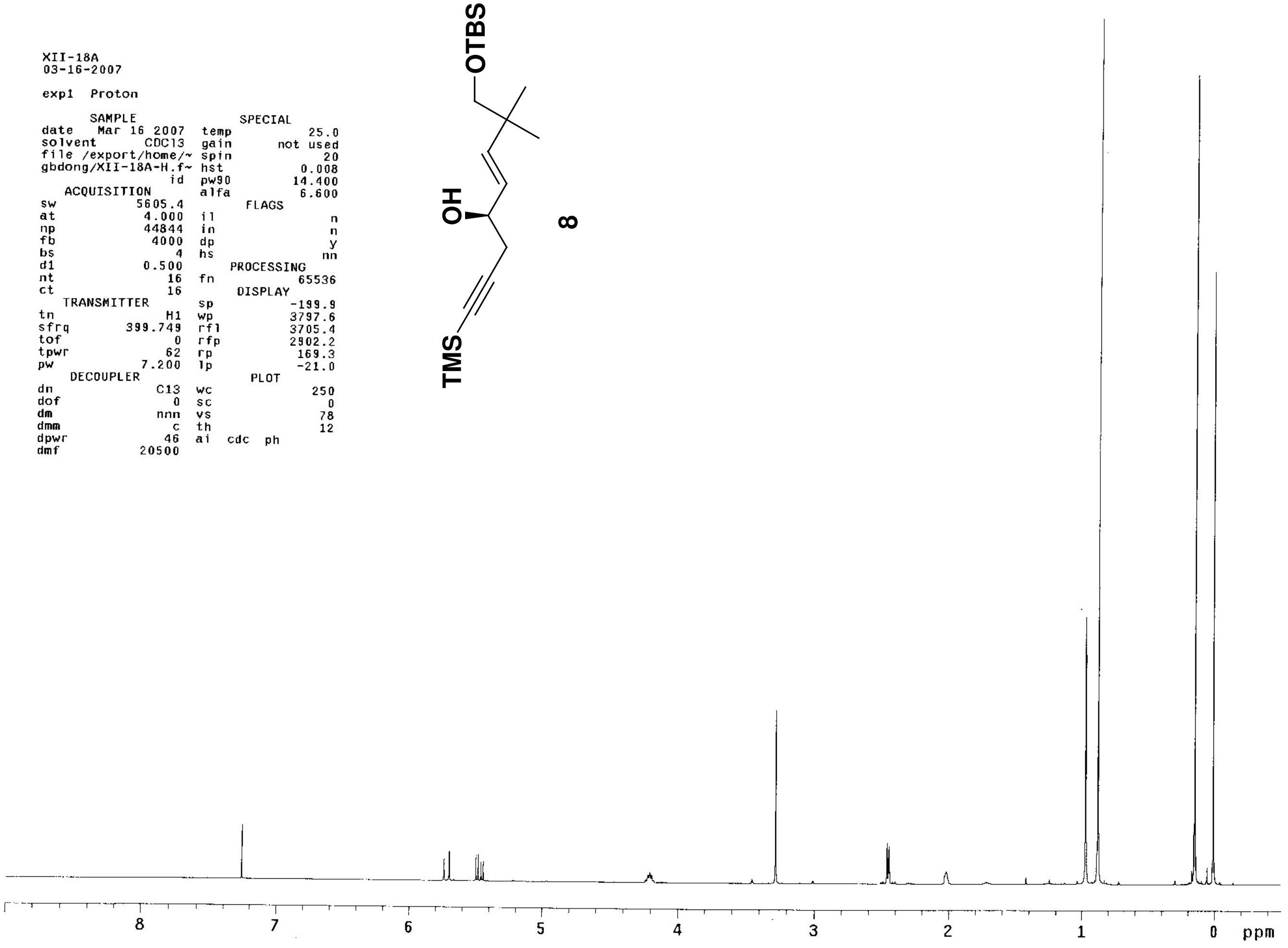

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XII-18A
03-16-2007

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gbdong/XII-18A-H.f~ hst              0.008
                id  pw90            14.400
   ACQUISITION      alfa             6.600
sw          5605.4           FLAGS
at           4.000  il                   n
np           44844  in                   n
fb            4000  dp                   y
bs               4  hs                  nn
d1           0.500        PROCESSING
nt              16  fn               65536
ct              16          DISPLAY
   TRANSMITTER      sp              -199.9
tn              H1  wp              3797.6
sfrq       399.749  rfl             3705.4
tof              0  rfp             2902.2
tpwr            62  rp               169.3
pw           7.200  lp               -21.0
   DECOUPLER                 PLOT
dn             C13  wc                 250
dof              0  sc                   0
dm             nnn  vs                  78
dmm              c  th                  12
dpwr            46  ai   cdc   ph
dmf          20500
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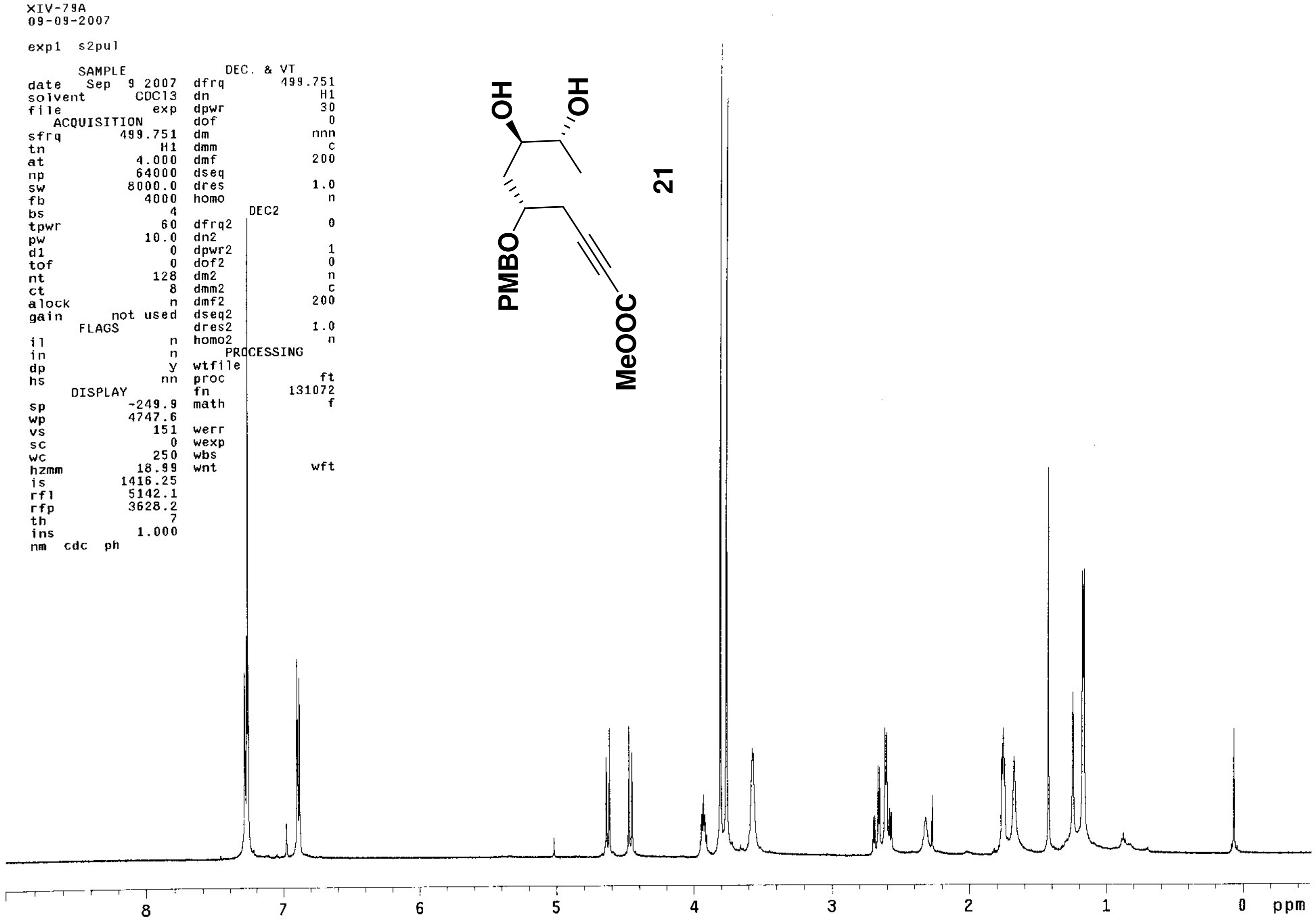
8



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XIV-79A
09-09-2007

exp1  s2pul

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tn               H1   dmm               c
at            4.000   dmf             200
np            64000   dseq
sw           8000.0   dres            1.0
fb             4000   homo              n
bs                4          DEC2
tpwr             60   dfrq2             0
pw             10.0   dn2
d1                0   dpwr2             1
tof               0   dof2              0
nt              128   dm2               n
ct                8   dmm2              c
alock             n   dmf2            200
gain       not used   dseq2
        FLAGS         dres2           1.0
il                n   homo2             n
in                n        PROCESSING
dp                y   wtfile
hs               nn   proc             ft
       DISPLAY        fn           131072
sp           -249.9   math              f
wp           4747.6
vs              151   werr
sc                0   wexp
wc              250   wbs
hzmm          18.99   wnt             wft
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rfl          5142.1
rfp          3628.2
th                7
ins           1.000
nm  cdc  ph
```
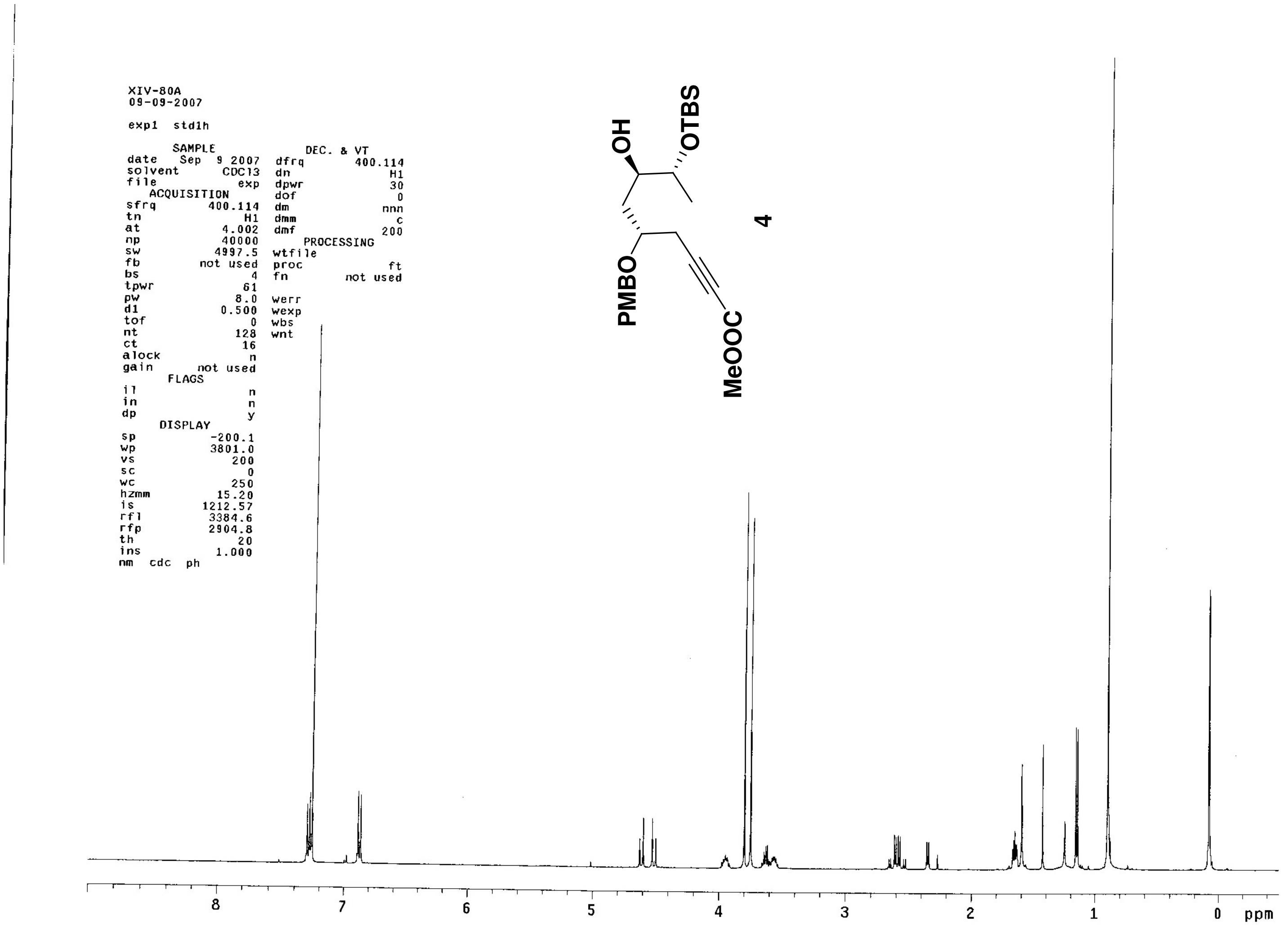

21



4

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XIV-80A
09-09-2007

exp1  std1h

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file            exp  dpwr              30
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sfrq        400.114  dm               nnn
tn               H1  dmm                c
at            4.002  dmf              200
np            40000       PROCESSING
sw           4997.5  wtfile
fb         not used  proc              ft
bs                4  fn          not used
tpwr             61
pw              8.0  werr
d1            0.500  wexp
tof               0  wbs
nt              128  wnt
ct               16
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
     DISPLAY
sp           -200.1
wp           3801.0
vs              200
sc                0
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nm  cdc  ph
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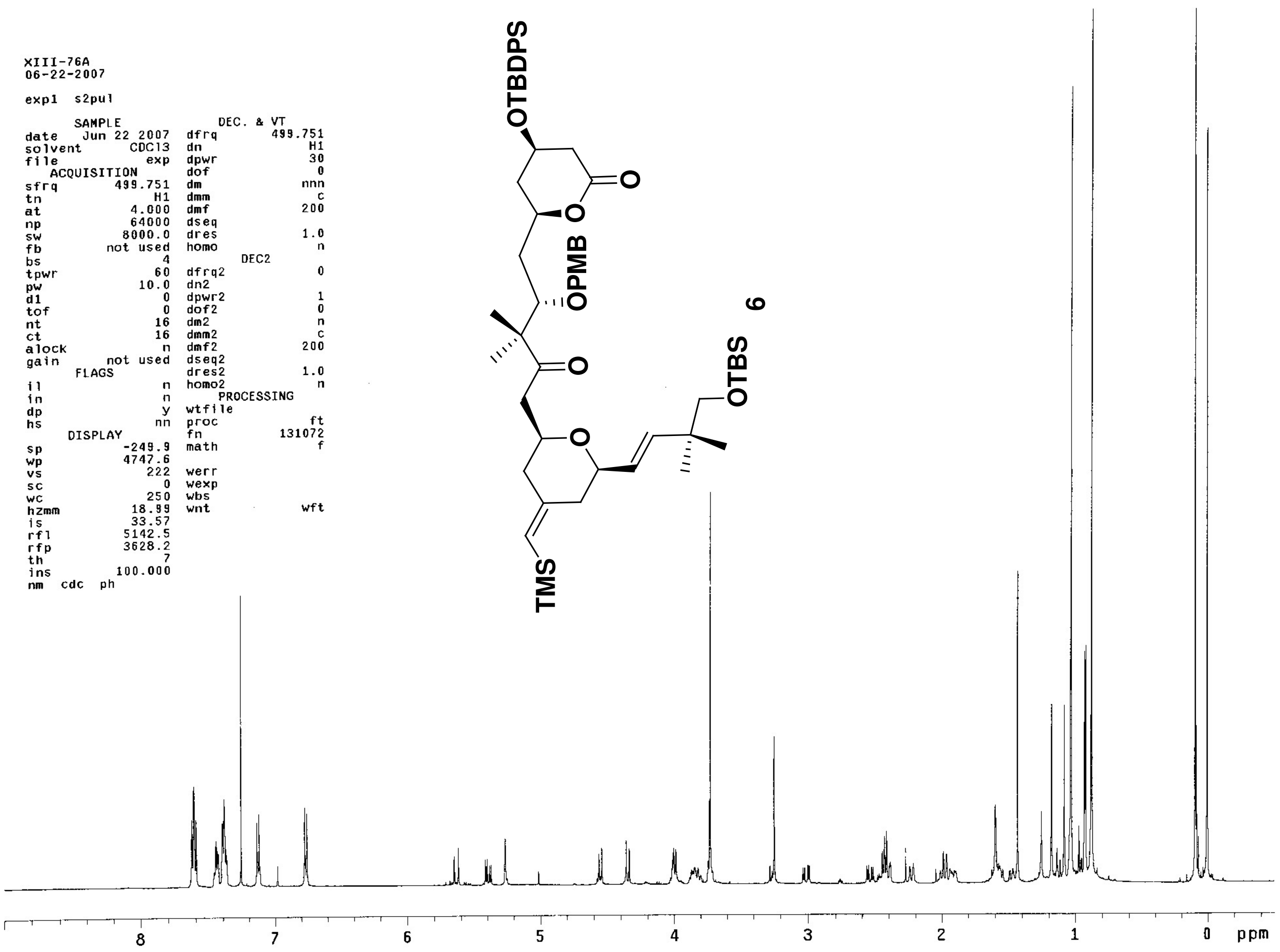

6

```
XIII-76A
06-22-2007

exp1  s2pul

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file           exp   dpwr               30
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sfrq       499.751   dm                nnn
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at           4.000   dmf               200
np           64000   dseq
sw          8000.0   dres              1.0
fb        not used   homo                n
bs               4          DEC2
tpwr            60   dfrq2               0
pw            10.0   dn2
d1               0   dpwr2               1
tof              0   dof2                0
nt              16   dm2                 n
ct              16   dmm2                c
alock            n   dmf2              200
gain      not used   dseq2
      FLAGS          dres2             1.0
il               n   homo2               n
in               n        PROCESSING
dp               y   wtfile
hs              nn   proc               ft
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sp          -249.9   math                f
wp          4747.6
vs             222   werr
sc               0   wexp
wc             250   wbs
hzmm         18.99   wnt               wft
is           33.57
rfl         5142.5
rfp         3628.2
th               7
ins        100.000
nm  cdc  ph
```
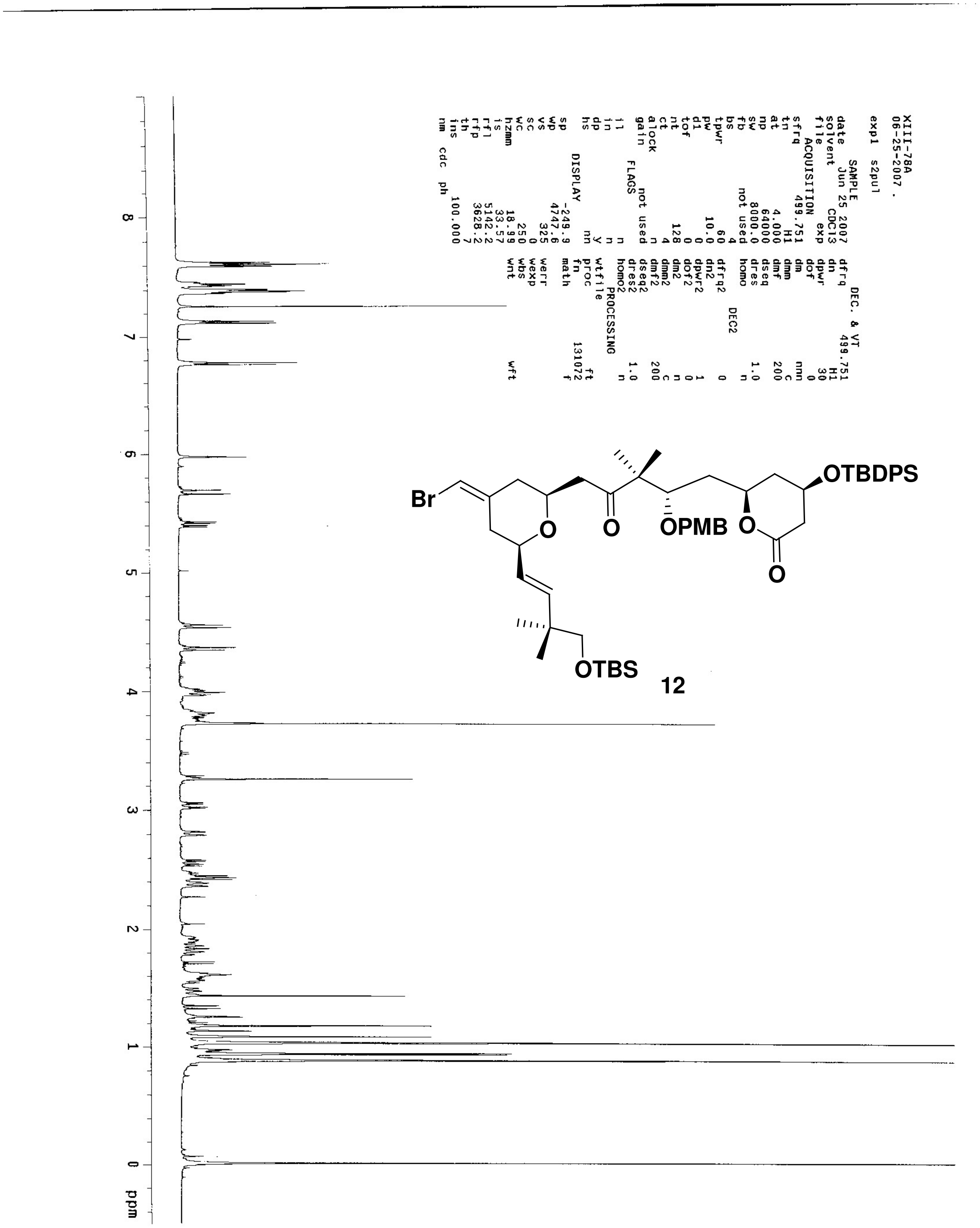
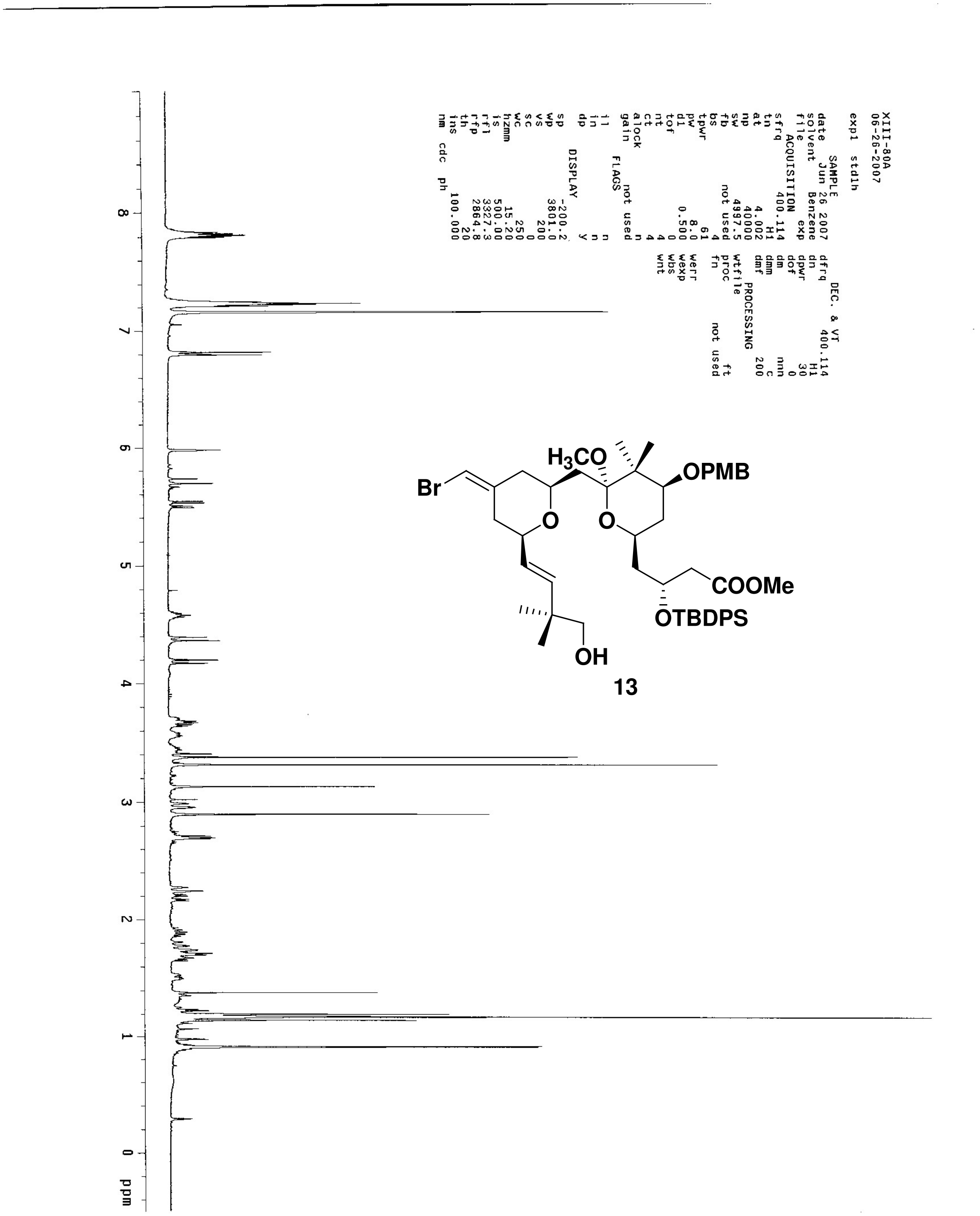
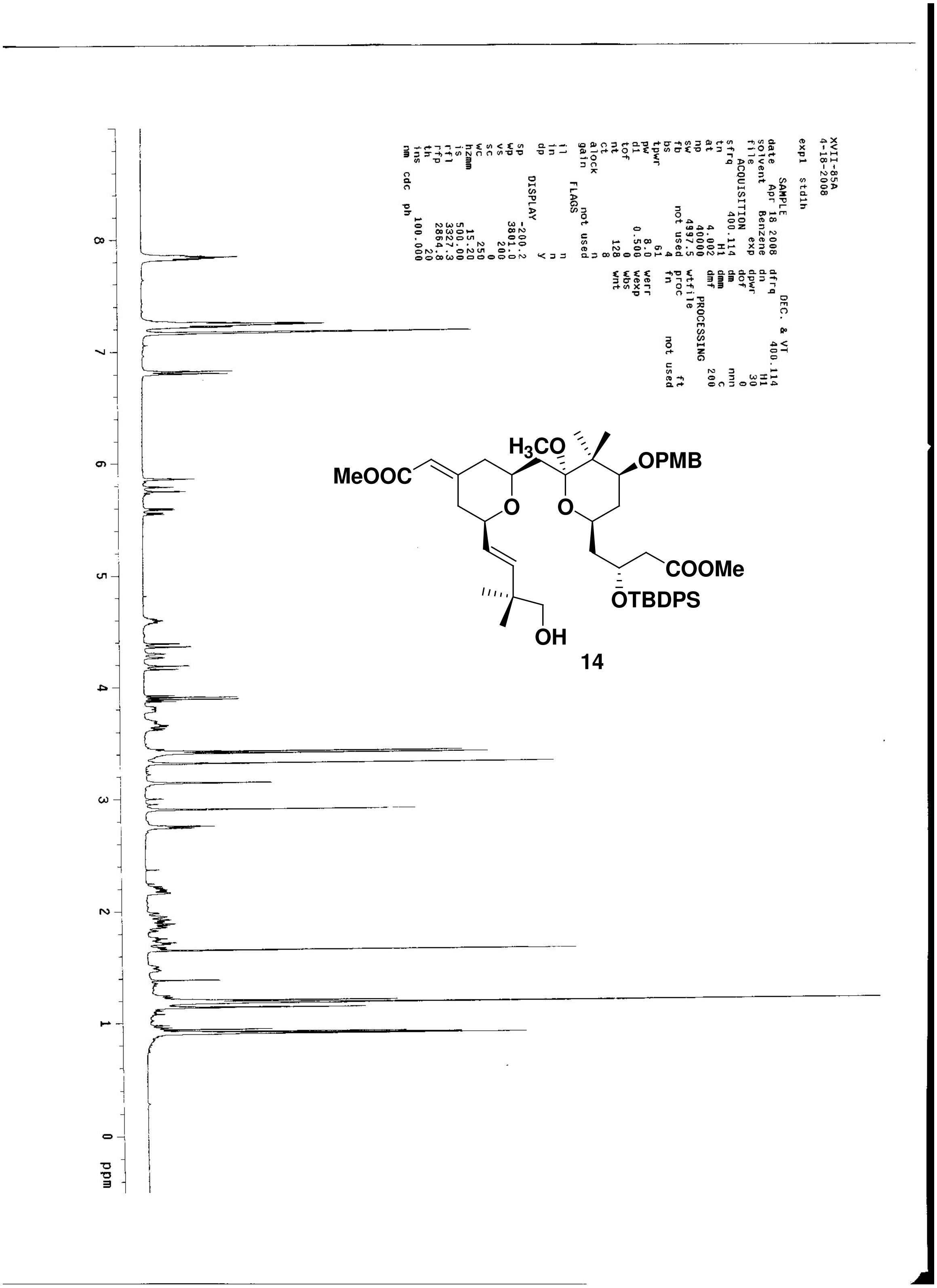


XIII-78A
06-25-2007 .
exp1 s2pul
SAMPLE
date Jun 25 2007
solvent CDCl3
file exp
ACQUISITION
sfrq 499.751
tn H1
at 4.000
np 64000
sw 8000.0
fb not used
bs 4
tpwr 60
pw 10.0
d1 0
tof 0
nt 128
ct 4
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 4747.6
vs 325
sc 0
wc 250
hzmm 18.99
is 33.57
rfl 5142.2
rfp 3628.2
th 7
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.751
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
PROCESSING
wtfile
proc ft
fn 131072
math f
werr
wexp
wbs
wnt wft
Br
O
O
OPMB
O
O
OTBDPS
OTBS
8
7
6
5
4
3
2
1
0
ppm

12

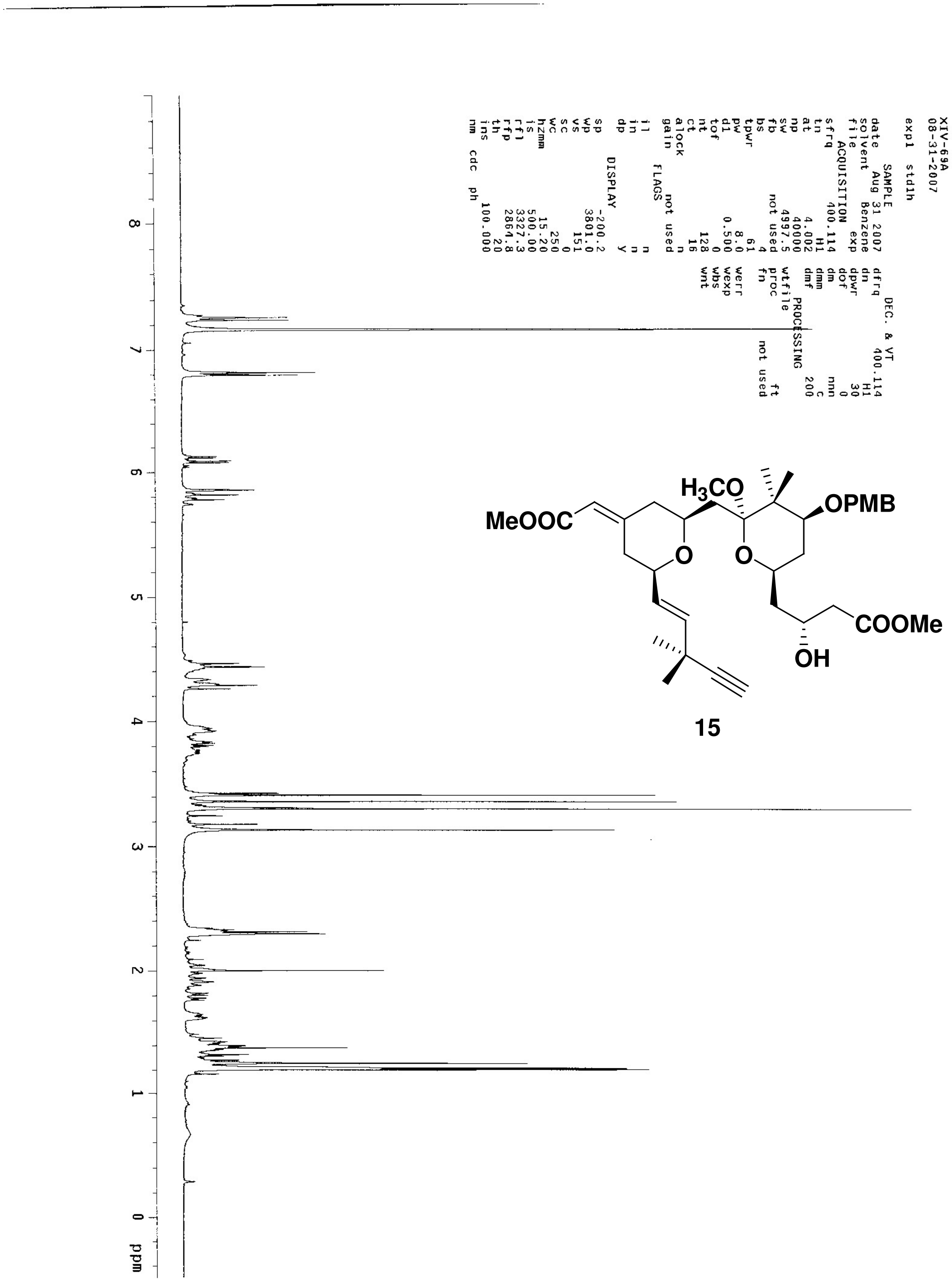


```
XIII-80A
06-26-2007

exp1  std1h

      SAMPLE             DEC. & VT
date    Jun 26 2007   dfrq      400.114
solvent     Benzene   dn             H1
file            exp   dpwr           30
   ACQUISITION        dof             0
sfrq        400.114   dm            nnn
tn               H1   dmm             c
at            4.002   dmf           200
np            40000      PROCESSING
sw           4997.5   wtfile
fb         not used   proc           ft
bs                4   fn       not used
tpwr             61
pw              8.0   werr
d1            0.500   wexp
tof               0   wbs
nt                4   wnt
ct                4
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
      DISPLAY
sp           -200.2
wp           3801.0
vs              200
sc                0
wc              250
hzmm          15.20
is           500.00
rfl          3327.3
rfp          2864.8
th               20
ins         100.000
nm  cdc  ph
```

13

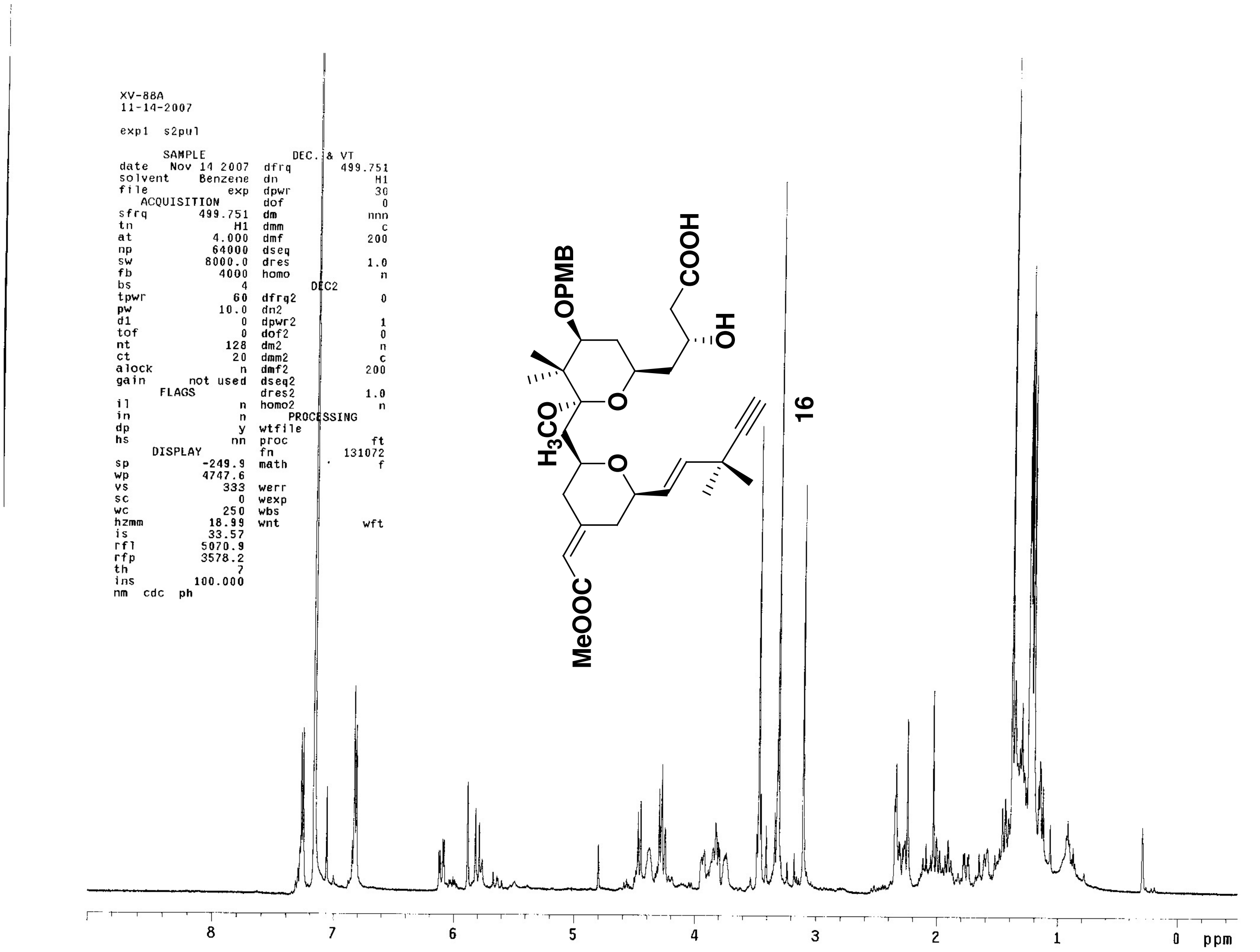

XVII-85A
4-18-2008
exp1 std1h
SAMPLE
date Apr 18 2008
solvent Benzene
file exp
ACQUISITION
sfrq 400.114
tn H1
at 4.002
np 40000
sw 4997.5
fb not used
bs 4
tpwr 61
pw 8.0
d1 0.500
tof 0
nt 128
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -200.2
wp 3801.0
vs 200
sc 0
wc 250
hzmm 15.20
is 500.00
rfl 3327.3
rfp 2864.8
th 20
ins 100.000
nm cdc ph
DEC. & VT
dfrq 400.114
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
MeOOC
H3CO
OPMB
O
O
COOMe
OTBDPS
OH
8
7
6
5
4
3
2
1
0
ppm

14



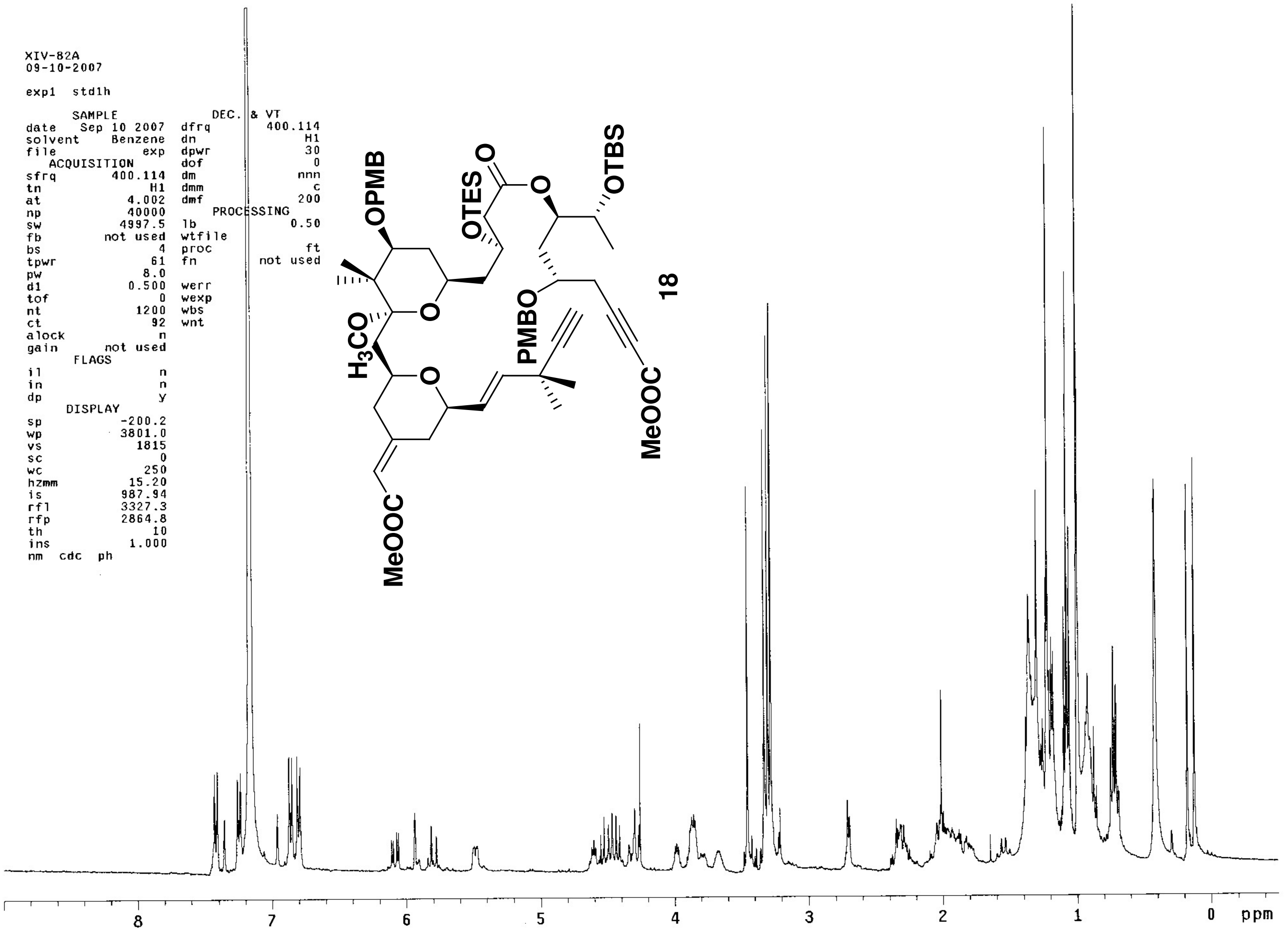
15

```
XIV-69A
08-31-2007

exp1  std1h

        SAMPLE                    DEC. & VT
date     Aug 31 2007    dfrq          400.114
solvent      Benzene    dn                 H1
file             exp    dpwr               30
     ACQUISITION        dof                 0
sfrq         400.114    dm                nnn
tn                H1    dmm                 c
at             4.002    dmf               200
np             40000         PROCESSING
sw            4997.5    wtfile
fb          not used    proc               ft
bs                 4    fn           not used
tpwr              61
pw               8.0    werr
d1             0.500    wexp
tof                0    wbs
nt               128    wnt
ct                16
alock              n
gain        not used
        FLAGS
il                 n
in                 n
dp                 y
        DISPLAY
sp            -200.2
wp            3801.0
vs               151
sc                 0
wc               250
hzmm           15.20
is            500.00
rfl           3327.3
rfp           2864.8
th                20
ins          100.000
nm  cdc  ph
```



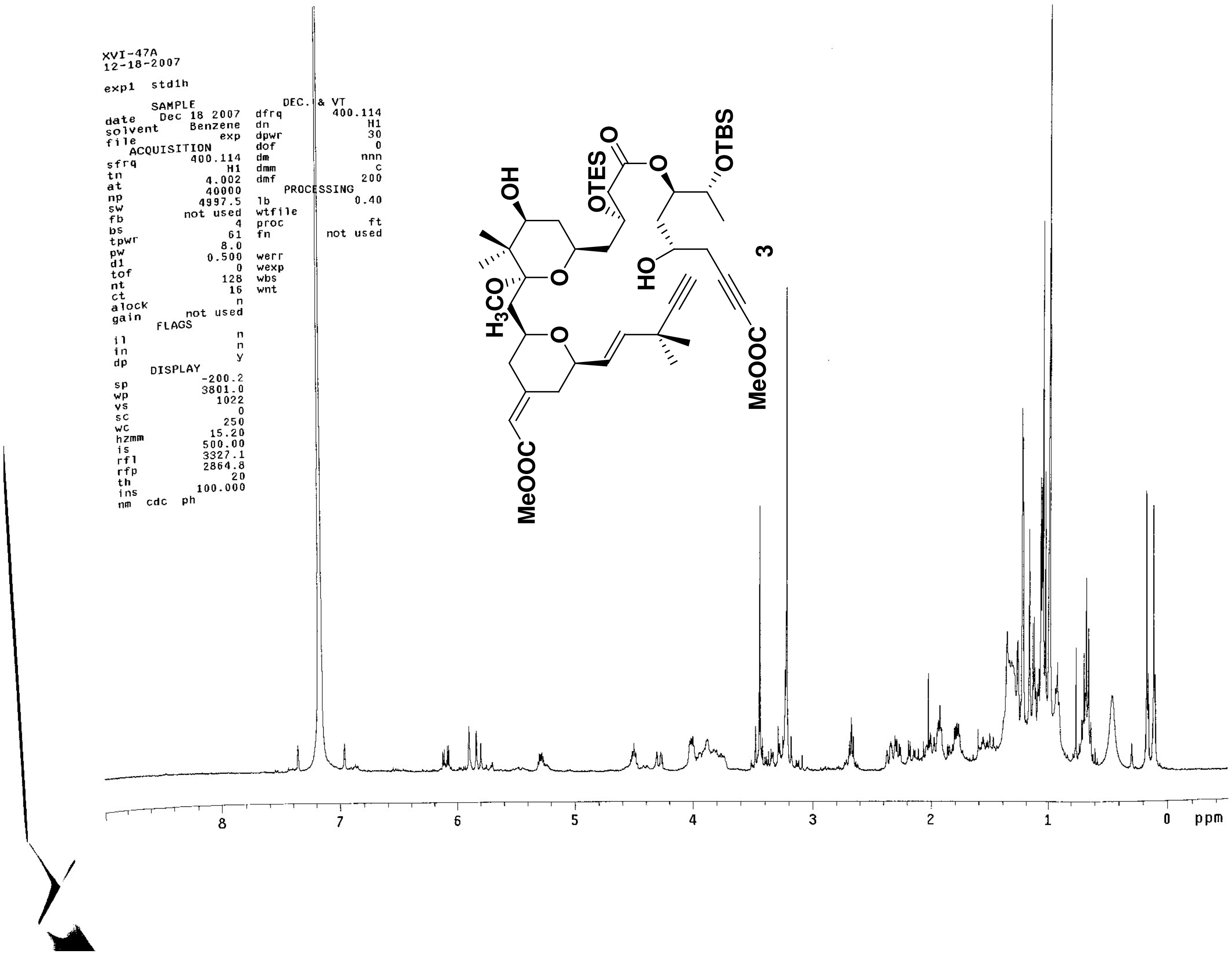
```
XV-88A
11-14-2007

exp1  s2pul

      SAMPLE                 DEC. & VT
date   Nov 14 2007  dfrq         499.751
solvent    Benzene  dn                H1
file           exp  dpwr              30
   ACQUISITION      dof                0
sfrq       499.751  dm               nnn
tn              H1  dmm                c
at           4.000  dmf              200
np           64000  dseq
sw          8000.0  dres             1.0
fb            4000  homo               n
bs               4          DEC2
tpwr            60  dfrq2              0
pw            10.0  dn2
d1               0  dpwr2              1
tof              0  dof2               0
nt             128  dm2                n
ct              20  dmm2               c
alock            n  dmf2             200
gain      not used  dseq2
      FLAGS         dres2            1.0
il               n  homo2              n
in               n        PROCESSING
dp               y  wtfile
hs              nn  proc              ft
     DISPLAY        fn            131072
sp          -249.9  math               f
wp          4747.6
vs             333  werr
sc               0  wexp
wc             250  wbs
hzmm         18.99  wnt              wft
is           33.57
rfl         5070.9
rfp         3578.2
th               7
ins        100.000
nm  cdc  ph
```

16



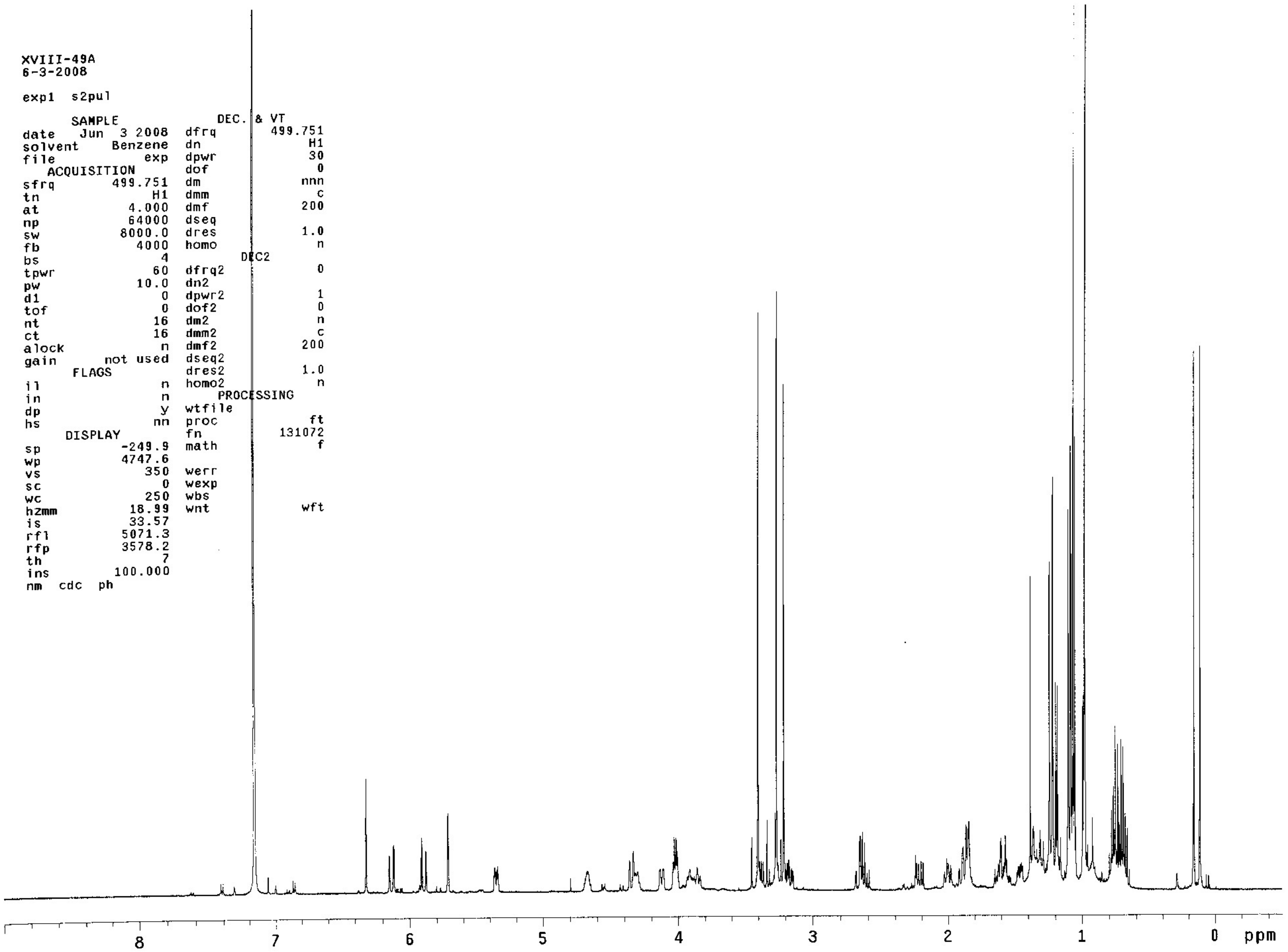
```
XIV-82A
09-10-2007

exp1  std1h

       SAMPLE               DEC. & VT
date    Sep 10 2007   dfrq        400.114
solvent     Benzene   dn               H1
file            exp   dpwr             30
    ACQUISITION       dof               0
sfrq        400.114   dm              nnn
tn               H1   dmm               c
at            4.002   dmf             200
np            40000         PROCESSING
sw           4997.5   lb             0.50
fb         not used   wtfile
bs                4   proc             ft
tpwr             61   fn         not used
pw              8.0
d1            0.500   werr
tof               0   wexp
nt             1200   wbs
ct               92   wnt
alock             n
gain       not used
       FLAGS
il                n
in                n
dp                y
      DISPLAY
sp           -200.2
wp           3801.0
vs             1815
sc                0
wc              250
hzmm          15.20
is           987.94
rfl          3327.3
rfp          2864.8
th               10
ins           1.000
nm  cdc  ph
```

18



```
XVI-47A
12-18-2007

exp1  std1h

      SAMPLE                  DEC. & VT
date    Dec 18 2007  dfrq          400.114
solvent     Benzene  dn                 H1
file            exp  dpwr               30
    ACQUISITION      dof                 0
            400.114  dm                nnn
sfrq             H1  dmm                 c
tn            4.002  dmf               200
at            40000         PROCESSING
np           4997.5  lb               0.40
sw         not used  wtfile
fb                4  proc               ft
bs               61  fn           not used
tpwr            8.0
pw            0.500  werr
d1                0  wexp
tof             128  wbs
nt               16  wnt
ct                n
alock      not used
gain      FLAGS
                  n
il                n
in                y
dp       DISPLAY
             -200.2
sp           3801.0
wp             1022
vs                0
sc              250
wc            15.20
hzmm         500.00
is           3327.1
rfl          2864.8
rfp              20
th          100.000
ins
nm   cdc   ph
```

3



```
XVIII-49A
6-3-2008

exp1  s2pul

      SAMPLE                  DEC. & VT
date   Jun  3 2008   dfrq          499.751
solvent     Benzene  dn                 H1
file            exp  dpwr               30
   ACQUISITION       dof                 0
sfrq        499.751  dm                nnn
tn               H1  dmm                 c
at            4.000  dmf               200
np            64000  dseq
sw           8000.0  dres              1.0
fb             4000  homo                n
bs                4          DEC2
tpwr             60  dfrq2               0
pw             10.0  dn2
d1                0  dpwr2               1
tof               0  dof2                0
nt               16  dm2                 n
ct               16  dmm2                c
alock             n  dmf2              200
gain       not used  dseq2
      FLAGS          dres2             1.0
il                n  homo2               n
in                n        PROCESSING
dp                y  wtfile
hs               nn  proc               ft
     DISPLAY         fn             131072
sp           -249.9  math                f
wp           4747.6
vs              350  werr
sc                0  wexp
wc              250  wbs
hzmm          18.99  wnt               wft
is            33.57
rfl          5071.3
rfp          3578.2
th                7
ins         100.000
nm  cdc  ph
```