A Concise Enantioselective Synthesis of the Chlorosulfolipid Malhamensilipin A

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SUPPORTING INFORMATION

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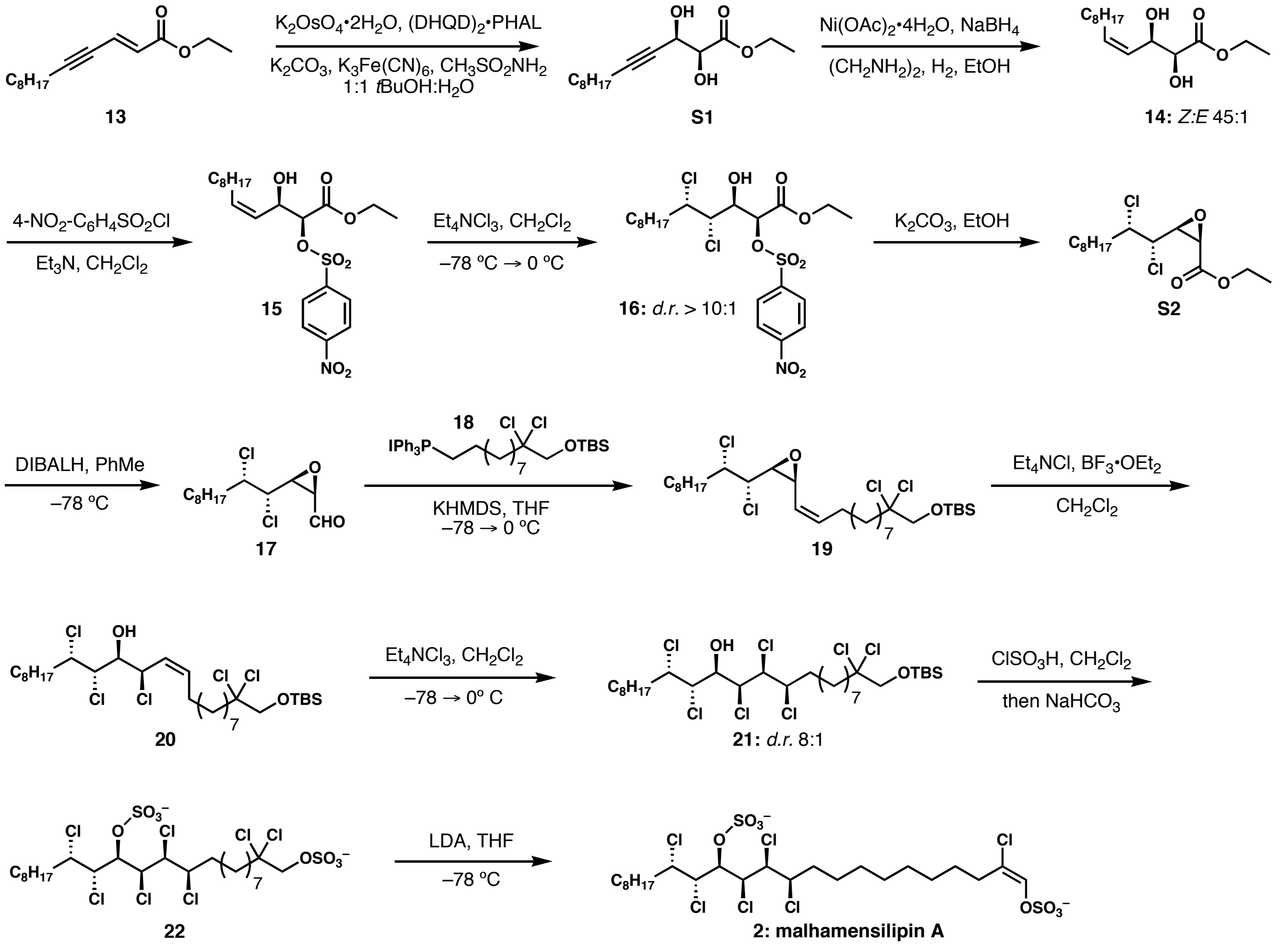
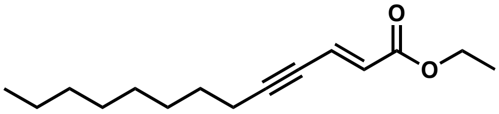
I. General

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker DRX spectrometers at either 500 or 600 MHz (^{1}H) and 125 MHz (^{13}C). Chemical shifts are reported in parts per million (ppm) using the solvent residual as the internal reference. Coupling constants are reported in Hertz (Hz) and the peak multiplicity is listed as follows: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum RXI FT-IR instrument. High-resolution mass spectra were obtained with a Waters LCT Premier mass spectrometer. All column chromatography was performed using Dynamic Adsorbents 230-400 mesh silica gel (SiO_2) with the indicated solvent system, unless otherwise noted. All reactions were conducted under a nitrogen or argon atmosphere using flame-dried or oven-dried glassware. All reaction solvents were dried by passing through activated alumina columns.

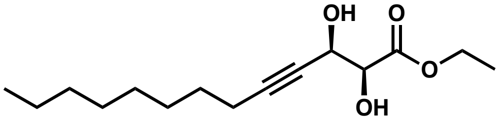
II. Experimental Procedures and Characterization of New Compounds

Synthesis of malhamensilipin A





(*E*)-Ethyl tridec-2-en-4-ynoate (13):
After stirring triethylphosphonoacetate (2.50 mL, 12.5 mmol) and LiBr (4.18 g, 48.3 mmol) in dry THF (230 mL) for 10 min, Et_3N was added to the stirring solution. After stirring for 15 min, undec-2-ynal[1] (1.87 g, 11.2 mmol) was added as a solution in hexanes (2 mL). After stirring at room temperature for 1 h, the reaction was quenched by pouring into saturated aqueous NH_4Cl (100 mL). The layers were separated and the aqueous layer extracted with hexanes (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried with $MgSO_4$, filtered and concentrated. Chromatographic purification (20:1, hexanes:EtOAc) furnished **13**[2] (1.82 g, 7.70 mmol, 69%): R_f = 0.36 (20:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (dt, *J* = 15.8, 2.3 Hz, 1H, H-3), 6.14 (d, *J* = 15.8, 1H, H-2), 4.21 (q, *J* = 7.1 Hz, 2H, $RCO_2C\boldsymbol{H_2}CH_3$), 2.37 (td, *J* = 7.1, 2.2 Hz, 2H, H-6), 1.56 (p, *J* = 5.5 Hz, 2H, H-7), 1.42–1.37 (m, 2H, H-8), 1.32–1.26 (m, 11H), 0.89 (t, *J* = 7.0 Hz, 3H, H-13); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 129.3, 126.1, 100.9, 78.0, 60.6, 31.8, 29.2, 29.1, 28.9, 28.3, 22.7, 19.8, 14.2, 14.1; IR 2929, 2856, 2215, 1716, 1620, 1301, 1178, 962 cm^{-1}; HRMS (CI) *m / z* calcd for $C_{15}H_{24}O_2Na$ $[M+Na]^+$ 259.1674, found 259.1671.



(–)-(2*S*,3*R*)-Ethyl 2,3-dihydroxytridec-4-ynoate (S1):
$K_2OsO_4{\cdot}2H_2O$ (147 mg, 0.390 mmol), $(DHQD)_2PHAL$ (601 mg, 0.772 mmol), $K_3Fe(CN)_6$ (7.62 g, 23.1 mmol) and K_2CO_3 (3.22 g, 23.1 mmol) were vigorously stirred in 140 mL of 1:1 ^{t}BuOH:H_2O at room temperature for 1 h. Methanesulfonamide (728 mg, 7.65 mmol) was added and stirring continued for 30 min. Enyne **13** (1.82 g, 7.70 mmol) was added as a solution in 14 mL of 1:1 ^{t}BuOH:H_2O. The reaction mixture was stirred for 26 h at room temperature, cooled to 0 ºC and quenched by addition of Na_2SO_3 (11.6 g). The ice bath was removed and the mixture was stirred for 30 min at room temperature. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated. Purification by column chromatography (2:1 hexanes:EtOAc) yielded recovered starting ester (336 mg, 1.42 mmol, 18%) and **S1** (1.21 g 4.48 mmol, 58%, >95% ee[3]): R_f = 0.34 (2:1 hexanes:EtOAc); $[\alpha]^{24}_D = -4.1$ (c 0.31, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (d, *J* = 5.5 Hz, 1H, H-3), 4.32 (q, *J* = 7.1 Hz, 2H, $RCO_2C\boldsymbol{H_2}CH_3$), 4.25 (s, 1H, H-2), 3.18 (s, 1H, C2-O**H**), 2.55–2.50 (m, 1H, C3-O***H***), 2.23 (dt, *J* = 7.3, 1.7 Hz, 2H, H-6), 1.51 (p, *J* = 7.5 Hz, 2H, H-7), 1.39–1.24 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H, H-13) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 87.6, 77.4, 74.0, 64.3, 62.6, 32.0, 29.4, 29.3, 29.1, 28.7, 22.9,

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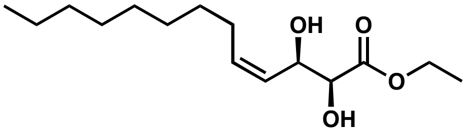
[1] Prepared by formylation of decyne with piperidine carbaldehyde: He, L.; Byun, H.S.; Bittman, R. *J. Org. Chem.* **2000**, *65*, 7627–7633.

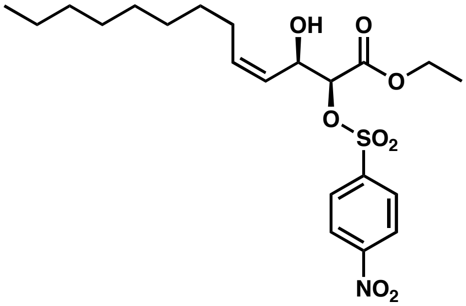
[2] Dixon, D.J.; Lucas, A. C. *Synlett* **2004**, 1092–1094.

[3] The ee was determined by ^{1}H and ^{19}F NMR analysis of the corresponding bis-Mosher esters derived from both enantiomers of Mosher acid (see ref. 1).

18.9, 14.4, 14.3; IR 3434, 2927, 2856, 2232, 1742, 1272 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{15}H_{26}O_4Na$ $[M+Na]^+$ 293.1729, found 293.1732.

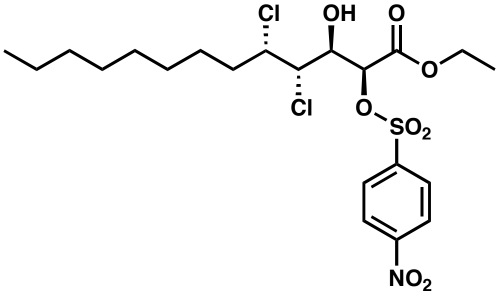


(+)-(2*S*,3*R*,*Z*)-Ethyl 2,3-dihydroxytride-4-enoate (14):
$Ni(OAc)_2{\cdot}4H_2O$ (156 mg, 0.628 mmol) was dissolved in ethanol (10 mL) and then cooled to 0 ºC. $NaBH_4$ (22.5 mg, 0.594 mmol) was added to the vigorously stirring green solution, which immediately turned black upon addition. The reaction flask was stirred at room temperature for five min and ethylenediamine (80.0 μL, 1.20 mmol) was added and stirring was continued for five min more. Alkyne **13** (800 mg, 2.96 mmol) in ethanol (6 mL) was added, the atmosphere was exchanged from argon to hydrogen and the mixture was stirred for 1 h. The reaction mixture was partitioned between water and CH_2Cl_2. After separation of the layers, the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined extracts were filtered through a pad of SiO_2 and the pad was washed with EtOAc until no more diol was visible by TLC. This dark yellow solution was concentrated and filtered two times more through a pad of silica, both times eluting with EtOAc to yield **14** (704 mg, 2.58 mmol, 88%): $R_f = 0.49$ (2:1 toluene:EtOAc); $[\alpha]^{25}_D = +15.9$ (c = 0.304, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67–5.62 (m, 1H, H-5), 5.60–5.55 (m, 1H, H-4), 4.70 (dt, *J* = 10.2, 2.8 Hz, 1H, H-3), 4.35–4.26 (m, 2H, $RCO_2C\boldsymbol{H_2}CH_3$), 4.09 (dd, *J* = 6.1, 2.9 Hz, 1H, H-2), 3.11 (d, *J* = 6.5, 1H, C2-OH), 2.21–2.06 (m, 3H, H-6, C3-OH), 1.41–1.27 (m, 15H), 0.89 (t, *J* = 7.0 Hz, 3H, H-13); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 135.1, 127.5, 74.3, 68.8, 62.3, 32.1, 29.7, 29.6, 29.4 (2C), 28.1, 22.9, 14.4, 14.3; IR 3448, 2925, 1736, 1112 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{15}H_{28}O_4Na$ $[M+Na]^+$ 295.1885, found 295.1880.

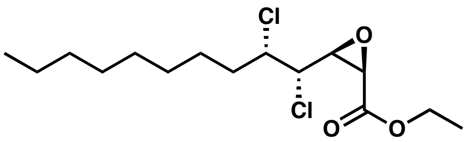


(–)-(2*S*,3*R*,*Z*)-Ethyl 3-hydroxy-2-(4-nitrophenylsulfonyloxy)tridec-4-enoate (15):
Triethylamine (0.49 mL, 3.51 mmol) was added to a solution of diol **14** (704 mg, 2.58 mmol) in CH_2Cl_2 (13 mL). 4-Nitrobenzenesulfonyl chloride (629 mg, 2.84 mmol) was added in a single portion at room temperature and the reaction was stirred for 1 h. The reaction was quenched by addition of 1 M HCl (10 mL). The phases were separated, the organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL), brine (10 mL), dried with Na_2SO_4, filtered and concentrated. Purification by column chromatography (30:1 CH_2Cl_2:EtOAc) yielded **15** (910 mg, 1.99 mmol, 77%): $R_f = 0.44$ (20:1 CH_2Cl_2:EtOAc); $[\alpha]^{24}_D = -40.6$ (c = 0.950, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.9

Hz, 2H, NO_2-C-CH), 8.18 (d, *J* = 8.9 Hz, 2H, OSO_2C-CH), 5.66 (dt, *J* = 10.9, 7.6 Hz, 1H, H-5), 5.40 (ddt, *J* = 10.7, 8.8, 1.4 Hz, 1H, H-4), 4.92–4.87 (m, 2H, H-2, H-3), 4.18 (q, *J* = 7.2 Hz, 2H, $RCO_2C\boldsymbol{H_2}CH_3$), 2.16–2.00 (m, 3H, H-6, OH), 1.38–1.22 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H, H-13); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 151.0, 142.2, 137.3, 129.8 (2C), 124.9, 124.5 (2C), 81.6, 67.8, 62.6, 32.0, 29.6, 29.5, 29.43, 29.41, 28.2, 22.9, 14.3, 14.2; IR 3527, 3108. 2927, 1750, 1535, 1189 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{31}NO_8SNa$ $[M+Na]^+$ 480.1668, found 480.1669.

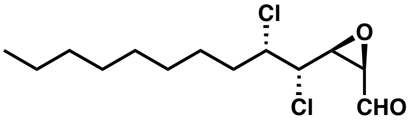


(–)-(2*S*,3*S*,4*S*,5*S*)-Ethyl 4,5-dichloro-3-hydroxy-2-4-nitrophenylsulfonyloxy)tridecanoate (16):
Ester **15** (842 mg, 1.84 mmol) was dissolved in CH_2Cl_2 (6.4 mL) and the reaction mixture was cooled to –78 ºC. Et_4NCl_3 (705 mg, 2.98 mmol) was added to the stirring solution, which was allowed to warm to 0 ºC over 1.5 h. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ (3 mL). The mixture was partitioned between CH_2Cl_2 and water. After separation, the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL), the combined organic extracts were dried over Na_2SO_4, filtered, and concentrated. Purification by column chromatography (40:1 CH_2Cl_2:EtOAc) yielded **16** (803 mg, 1.52 mmol, 83%, >10:1 mixture of diastereomers): R_f = 0.70 (20:1 CH_2Cl_2:EtOAc); $[\alpha]^{24}_D$ = – 19.6 (c = 0.830, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 7.68 (d, *J* = 8.7 Hz, 2H, NO_2–C–CH), 7.54 (d, J = 8.7 Hz, 2H, $ROSO_2$–C–CH), 5.80 (1H, H-2), 4.62 (apparent t, *J* = 9.4, 8.9 Hz, 1H, H-3), 4.27 (dd, *J* = 9.4, 5.4 Hz, 1H, H-5), 4.01 (d, *J* = 9.8 Hz, 1H, H-4) 3.84–3.74 (m, 2H, $RO_2C\boldsymbol{H_2}CH_3$), 2.32 (d, *J* = 8.6 Hz, 1H, O***H***), 1.89–1.82 (m, 1H, H-6), 1.45–1.41 (m, 1H, H-6), 1.37–1.00 (m, 12H), 0.92 (t, *J* = 7.1 Hz, 3H, H-13), 0.78 (t, *J* = 7.2 Hz, 3H, $RO_2CH_2C\boldsymbol{H_3}$) ; ^{13}C NMR (125 MHz, C_6D_6) 167.2, 151.1, 142.2, 129.8 (2C), 124.4 (2C), 78.9, 74.0, 63.3, 63.0, 62.0, 36.9, 32.6, 30.1, 30.0, 29.7, 27.2, 23.4, 14.7, 14.1; IR 3504, 3109, 2928, 2856, 1763, 1534, 1189 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{31}Cl_2NO_8SNa$ $[M+Na]^+$ 550.1045, found 550.1037.

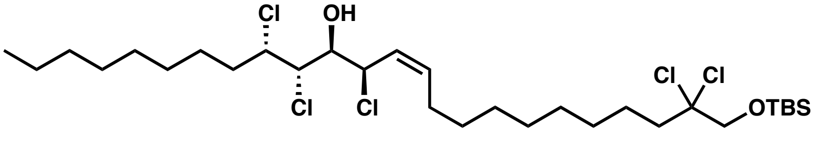


(–)-(2*R*,3*S*,4*S*,5*S*)-Ethyl 4,5-dichloro-2,3-epoxy-tridecananoate (S2):
K_2CO_3 (400 mg, 2.97 mmol) was added to a solution of **16** (782 mg, 1.48 mmol) in EtOH (15 mL). After 6 h, the reaction was deemed complete base on TLC analysis. The reaction solution was poured into saturated aqueous $NaHCO_3$ (10 mL), diluted with water to dissolve the solids, and extracted with CH_2Cl_2 (3 x 10 mL). The combined extracts were washed with brine, dried with Na_2SO_4, filtered and concentrated. The concentrate was filtered through a small plug of SiO_2 and eluted with CH_2Cl_2 to yield **S2** (422 mg, 1.30 mmol, 88%): R_f = 0.34 (1:1 hexanes:CH_2Cl_2); $[\alpha]^{24}_D$ = –65.8 (c = 1.18,

CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 4.44 (d, *J* = 8.6 Hz, 1H, H-4), 4.20 (ddd, *J* = 8.9, 5.0, 2.5 Hz, 1H, H-5), 3.89 (dq *J* = 10.8, 7.1 Hz, 1H, $RCO_2C\boldsymbol{H_2}CH_3$), 3.82 (dq *J* = 10.8, 7.1 Hz, 1H, $RCO_2C\boldsymbol{H_2}CH_3$), 3.50 (dd, *J* = 8.6, 4.3 Hz, 1H, H-3), 3.18 (d, *J* = 4.3 Hz, 1H, H-2), 1.85–1.78 (m, 1H, H-6), 1.55–1.49 (m, 1H, H-6), 1.40–0.95 (m, 12H), 0.89 (t, *J* = 7.2 Hz, 3H, $RCO_2CH_2C\boldsymbol{H_3}$), 0.85 (t, *J* = 7.1 Hz, 1H, H-10) ; ^{13}C NMR (125 MHz, C_6D_6) δ 167.7, 64.1, 62.1, 60.2, 58.0, 52.9, 35.6, 32.5, 30.0, 29.9, 29.5, 26.9, 23.4, 14.7, 14.3; IR 2927, 2856, 1750, 1206 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{15}H_{26}Cl_2O_3Na$ $[M+Na]^+$ 347.1157, found 347.1163.



(–)-(2*R*,3*S*,4*S*,5*S*)-4,5-Dichloro-2,3-epoxytridecanal (17):
DIBAL-H (2.2 mL, 2.2 mmol, 1.0 M in toluene) was added down the neck of a reaction flask cooled to –78 ºC containing ester **S2** (424 mg, 1.30 mmol) in toluene (13 mL). After stirring for 2 h at this temperature, MeOH (10 mL) was slowly added in the same manner as before, and the reaction mixture was stirred for 10 min and warmed to room temperature over 1 h. The reaction mixture was filtered, and the residual solids were exhaustively washed with EtOAc. The residue was subjected to purification via column chromatography (1:1 CH_2Cl_2:hexanes) and yielded **17** (328 mg, 1.2 mmol, 90%) as a white solid (m.p. 58–60 ºC): R_f = 0.21 (1:1 hexanes:CH_2Cl_2); $[\alpha]^{24}_D$ = –35.3 (c = 0.250, CH_2Cl_2); ^{1}H NMR (600 MHz, C_6D_6) δ 8.89 (d, *J* = 1.8 Hz, 1H, H-1), 4.04 (ddd, *J* = 9.2, 4.5, 2.7 Hz, 1H, H-5), 3.71 (dd, *J* = 8.7, 2.6 Hz, 1H, H-4), 3.40 (dd, *J* = 8.7, 4.5 Hz, 1H, H-3), 2.79 (dd, *J* = 4.5, 2.1 Hz, 1H, H-2), 1.77–1.71 (m, 1H, H-6), 1.44–1.39 (m, 1H, H-6), 1.36–1.30 (m, 1H), 1.29–1.24 (m, 2H), 1.23–1.15 (m, 4H), 1.13–1.08 (m, 2H), 1.07–0.98 (m, 3H), 0.91 (t, *J* = 7.2 Hz, 3H, H-13); ^{13}C (125 MHz C_6D_6) δ 195.5, 63.9, 60.0, 59.9, 57.4, 36.3, 32.5, 30.0, 29.9, 29.5, 26.8 23.4, 14.7; IR 2946, 2923, 2853, 1714, 1463, 847, 640 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{13}H_{22}Cl_2O_2Na$ $[M+Na]^+$ 303.0894, found 303.0891.



(+)-(13*R*,14*S*,15*S*,16*S*,*Z*)-1-(*tert*-Butyldimethysilyloxy)-2,2,13,15,16-pentachlorotetracos-11-en-14-ol (20):
Phosphonium salt **18**[4] (479 mg, 0.644 mmol) was dried under vacuum at 75 ºC for 16 h, dissolved in dry THF (3 mL) and cooled to –78 ºC. KHMDS (0.93 mL, 0.46 mmol, 0.5 M solution in toluene) was added and after 5 min the reaction flask was placed in an ice bath and the reaction was stirred for 20 min. The bright orange solution was cooled back to –78 ºC and aldehyde **17** (87 mg, 0.31 mmol) in THF (2 mL) was added via cannula, and the bright orange color dissipated. The bath temperature was

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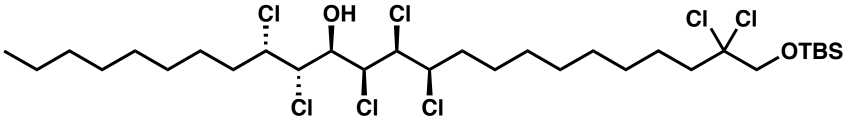
[4] Bedke, D.K.; Shibuya, G.M. Pereira, A.; Gerwick, W.H.; Haines, T.H.; Vanderwal, C.D. *J. Am. Chem. Soc.* **2009**, *131*, 7570–7572.

warmed to 0 °C over 2.5 h and the reaction was quenched with saturated aqueous NH_4Cl (3 mL). The reaction mixture was partitioned between EtOAc and water. The layers were separated and the aqueous layer extracted with pentane (3 x 20 mL). The combined extracts were washed with water (10 mL) and brine (10 mL) and dried with Na_2SO_4. After filtration and concentration, the residue was passed through a plug of SiO_2 to yield crude **19** (151 mg) as a 2:1 (*Z*:*E*) mixture of inseparable isomers (as measured by ^{1}H NMR analysis of the crude reaction mixture) which was used without further purification.

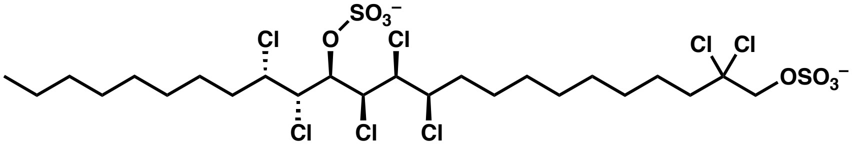
Allylic epoxide **19** (2:1 mix of *Z:E* diastereomers, 145 mg, 0.234 mmol) was dissolved in CH_2Cl_2 (4 mL), Et_4NCl (1.99 g, 12.0 mmol) was added and the mixture stirred until clear. $BF_3{\cdot}OEt_2$ (0.155 mL, 1.24 mmol) was added and the solution was stirred for 30 min at room temperature and quenched by pouring into water. After the layers were separated, the aqueous layer was extracted three times with CH_2Cl_2 (3 x 10 mL). The combined organic extracts were washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography to yield **20** (65.8 mg, 0.100 mmol, 32%, two steps) R_f = 0.35 (2:1 hexane:CH_2Cl_2); $[\alpha]^{24}_D$ = +22.6 (c = 0.695, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_3OD) δ 5.79 (t, *J* = 10.3 Hz, 1H, H-12), 5.61 (dt, *J* = 10.8, 7.7 Hz, 1H, H-11), 5.32 (d, *J* = =10.0 Hz, H-10), 4.59 (ddd, *J* = 8.8, 5.2, 1.4 Hz, 1H, H-16), 4.18 (dd, *J* = 9.4, 1.4 Hz, 1H, H-15), 3.83 (d, *J* = 9.4 Hz, 1H, H-14), 2.22–2.19 (m, 4H, H-3, H-10), 1.98–1.92 (m, 1H, H-17), 1.86–1.79 (m, 1H, H-17), 1.61-1.51 (m, 3H), 1.47–1.29 (m, 23H) 0.93 (s, 9H, SiC(C$\boldsymbol{H_3}$)$_3$), 0.91 (t, *J* = 6.8 Hz, 3H, H-24), 0.13 (s, 6H, Si(C$\boldsymbol{H_3}$)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.6, 126.4, 93.7, 75.1, 72.3, 65.1, 61.7, 59.6, 43.7, 36.7, 32.1, 29.6, 29.5, 29.47, 29.41, 29.34, 29.278, 29.267, 29.245, 27.9, 26.8, 26.0 (3C), 25.0, 22.9, 18.5, 14.3, –5.1 (2C); IR 3482, 2928, 2857, 1458, 1257, 1119, 839, 779 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{30}H_{57}Cl_5O_2SiNa$ $[M+Na]^+$ 675.2468, found 675.2493 .



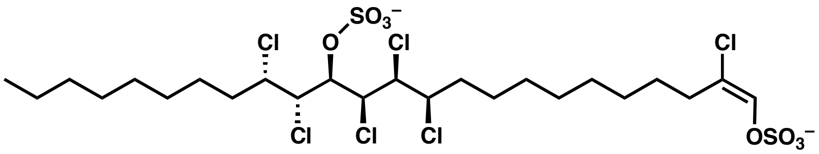
(+)-(11*R*,12*S*,13*R*,14*S*,15*S*,16*S*)-1-(*tert*-Butyldimethysilyloxy)-2,2,11,12,13,15,16-pentachlorotetracosan-14-ol (21):

A solution of **20** (110 mg, 0.168 mmol) in CH_2Cl_2 (1.6 mL) at –78 °C was treated with Et_4NCl_3 (79.5 mg, 0.336 mmol). After 1.5 h, the flask was warmed to room temperature and quenched with a 1:1 solution of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (1 mL). The mixture was diluted with water (5 mL) and CH_2Cl_2 (5 mL), and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic extracts were dried with Na_2SO_4, filtered and concentrated. Purification via column chromatography (3:1 pentane:CH_2Cl_2) yielded **21** as a >8:1 mixture of diastereomers (117 mg, 97%): R_f = 0.18 (3:1 hexanes:CH_2Cl_2); $[\alpha]^{24}_D$ = +2.5 (c = 0.285, CH_2Cl_2); ^{1}H NMR (500 MHz, C_6D_6) δ 5.13 (d, *J* = 8.6, 1.1 Hz, 1H H-13), 4.52 (t, *J* = 9.2 Hz, 1H, H-14), 4.30 (ddd, *J* = 9.5, 2.3,1.6 Hz, 1H, H-16), 4.19 (dd, *J* = 8.6 Hz, 2.2 Hz, 1H, H-12), 4.09 (ddd, *J* = 8.1, 5.7, 2.3 Hz, 1H, H-11), 3.95 (dd, *J* = 9.2, 1.6 Hz, 1H, H-15), 3.92 (s, 2H, H-1), 2.26–2.23 (m, 2H, H3), 1.94 (q, *J* = 9.9 Hz, 1H, H-17), 1.85–1.78 (m, 1H, H-10), 1.72–1.63 (m, 4H, OH, H-10, H-4), 1.51–1.43 (m, 2H, H-17), 1.35–1.00 (m, 20H), 0.931 (s, 9H, SiC(C$\boldsymbol{H_3}$)$_3$), 0.926 (t, *J* = 7.1 Hz, 3H, H-24), 0.026 (s, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 94.3, 73.0, 72.4, 68.5, 68.4, 65.4, 62.1, 61.9, 44.4, 37.3, 36.9, 32.6, 30.1, 30.0, 29.9, 29.83, 29.77, 29.7, 29.6, 27.3, 26.8, 26.3, 25.6, 23.4, 18.8, 14.7, –5.0;

IR 2929, 2856, 1463, 1257, 1119 cm^{-1}; HRMS (ESI) *m / z* calcd for $C_{30}H_{57}Cl_7O_2SiNa$ $[M+Na]^+$ 745.1845, found 745.1839.



(+)-(11*R*,12*S*,13*S*,14*R*,15*S*,16*S*)-2,2,11,12,13,15,16-heptachlorotetracosane-1,14-diyl disulfate (22): Silyl ether **21** (21 mg, 0.029 mmol) was dissolved in dry CH_2Cl_2 (1.45 mL, 0.02 M) and $ClSO_3H$ (approx. 0.15 mL, 0.031 mmol) was added via Pasteur pipette. A brown color immediately resulted. After sitting for 10 min the solution was transferred via pipette into 10 mL of vigorously stirred saturated aqueous $NaHCO_3$ with 500 mg of added solid $NaHCO_3$. The aqueous solution was concentrated and the solids extracted by stirring the solids for 10 min with *n*-butanol (4 mL) and then decanting and filtering the liquid through a cotton filter. After repeating this extraction three times, the *n*-butanol was evaporated to leave **22** as an off-white solid (20 mg, 0.024 mmol, 83%): $R_f = 0.16$ (6:1 CH_2Cl_2:MeOH); $[\alpha]^{24}_D = +6.4$ (c = 0.50, MeOH); ^{1}H NMR (600 MHz, CD_3OD, 330 K) δ 5.05 (dd, *J* = 9.1, 0.72 Hz, 1H, H-14), 4.95 (ddd, *J* = 8.8, 4.3, 1.7 Hz, 1H, H-11), 4.85 (dd, *J* = 9.9, 0.81 Hz, 1H, H-13), 4.78 (ddd, *J* = 8.8, 5.4, 1.0 Hz, 1H, H-16), 4.66 (dd, *J* = 9.9, 1.7 Hz, 1H, H-12), 4.34 (s, 2H, H-1), 4.28 (dd, *J* = 9.1, 1.1 Hz, 1H, H-15), 2.28–2.24 (m, 2H, H-3), 1.98–1.92 (m, 2H), 1.89–1.81 (m, 2H), 1.67–1.65 (m, 2H), 1.64–1.50 (m, 2H), 1.47–1.27 (m, 20H), 0.90 (t, *J* = 7.1 Hz, 3H, H-24); ^{13}C NMR (125 MHz, CD_3OD) δ 91.3, 77.6, 75.7, 69.2, 67.7, 66.2, 63.2, 62.2, 45.3, 38.6, 37.9, 33.2, 30.7, 30.6, 30.5, 30.47, 30.3, 30.24, 30.22, 27.8, 27.4, 26.0, 23.9, 14.6; HRMS (ESI) *m / z* calcd for $C_{24}H_{41}Cl_7O_8S_2$ $[M]^{2-}$ 383.0037, found 383.0052.

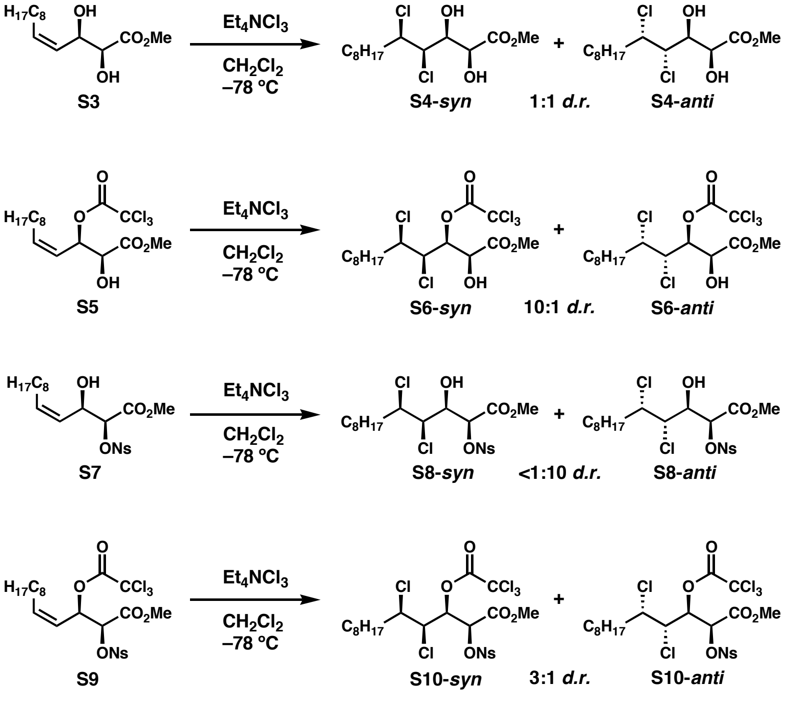


(+)–(11*R*,12*S*,13*S*,14*R*,15*S*,16*S*,*E*)-2,11,12,13,15,16-hexachlorotetracos-1-ene-1,14-diyl disulfate (malhamensilipin A, 2):

To a cold (–78 ºC) solution of **22** (9.4 mg, 0.012 mmol) in THF (0.96 mL, 0.012 M) was added LDA (0.14 mL, 0.37 M in THF, freshly prepared from newly distilled diisopropylamine and *n*-BuLi/hexanes) dropwise by syringe over 30 seconds. The solution was stirred at –78 ºC for 75 min and saturated aqueous $NaHCO_3$ (1.5 mL) was added. The solution was warmed to ambient temperature over 10 min and then concentrated. The solids were triturated with *n*BuOH (4 x 5 mL), and the combined extracts were filtered and concentrated to give a brown gum (5.2 mg). The crude product was purified by column chromatography (1. E. Merck HP silica, 1:2 MeCN:CH_2Cl_2, then 2. E. Merck HP silica, 1:6 MeOH:CH_2Cl_2) to give a white gum (2.7 mg, ca. 90% purity, 26%): $R_f = 0.16$ (6:1 CH_2Cl_2:MeOH); $[\alpha]^{24}_D = +7.0$ (c = 0.130, MeOH); ^{1}H NMR (600 MHz, CD_3OD, 330 K) δ 6.73 (s, 1H), 5.04 (dd, *J* = 9.1, 0.72 Hz, 1H), 4.95 (ddd, *J* = 8.8, 4.3, 1.7 Hz, 1H), 4.84 (dd, *J* = 9.9, 0.81 Hz, 1H), 4.79 (ddd, *J* = 8.8, 5.4, 1.0 Hz, 1H), 4.65 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.28 (dd, *J* = 9.1, 1.1 Hz, 1H), 2.43 (t, *J* = 6.1, 2H), 1.97–1.92 (m, 2H), 1.87–1.82 (m, 2H), 1.63–1.57 (m, 2H), 1.56–1.50 (m, 2H), 1.48–1.41 (m, 2H), 1.39–1.27 (m, 20H), 0.90 (t, *J* = 5.9, 3H); ^{13}C NMR δ 136.5, 125.4, 77.5, 69.2, 67.7, 66.2, 63.4, 62.2., 38.6, 37.9, 33.2, 32.0, 30.71, 30.69, 30.66, 30.5 (2 C), 30.2, 30.0, 28.0, 27.8, 27.5, 23.9, 14.6; HRMS (ESI) *m* / *z* calcd for $C_{24}H_{40}Cl_6O_8S_2$ $[M]^{2-}$ 365.0154, found 365.0143.

III. Dichlorination Diastereoselectivity for Derivatives of Diol S3

Diol **S3** (the methyl ester corresponding to **14**—our early studies toward malhamensilipin A were performed with methyl esters) and three derivatives were evaluated for the diastereoselectivity of dichlorination of the alkene. Analysis of the crude reaction mixture of the dichlorination of **S3** revealed a 1:1 mixture of diastereomers; these products were never separated. This selectivity is perfectly consistent with that previously observed and reported by us for *Z*-allylic alcohol dichlorinations under these conditions.[5] The allylic trichloroacetate derivative **S5** was dichlorinated with high *syn*-selectivity (10:1) in accord with our previous studies.[5] The identity of **S6-*syn*** was verified by conversion to a diastereomer of **21**, whose relative configuration was secured by *J*-based configurational analysis. Dichlorination of nosyl ester **S7** demonstrated essentially complete selectivity in the formation of **S8-*anti***, in line with the conversion of **15** to **16** described in detail in this disclosure. Finally, **S9** delivered the *syn*-product with marginal selectivity. Conversion of products **S6** into **S10** by nosylation and **S8** into **S10** by trichloroacetylation showed that all assignments were self-consistent. In all cases, NMR spectra of the crude reaction mixtures demonstrated clean reactivity. Complete details are forthcoming in a full paper.



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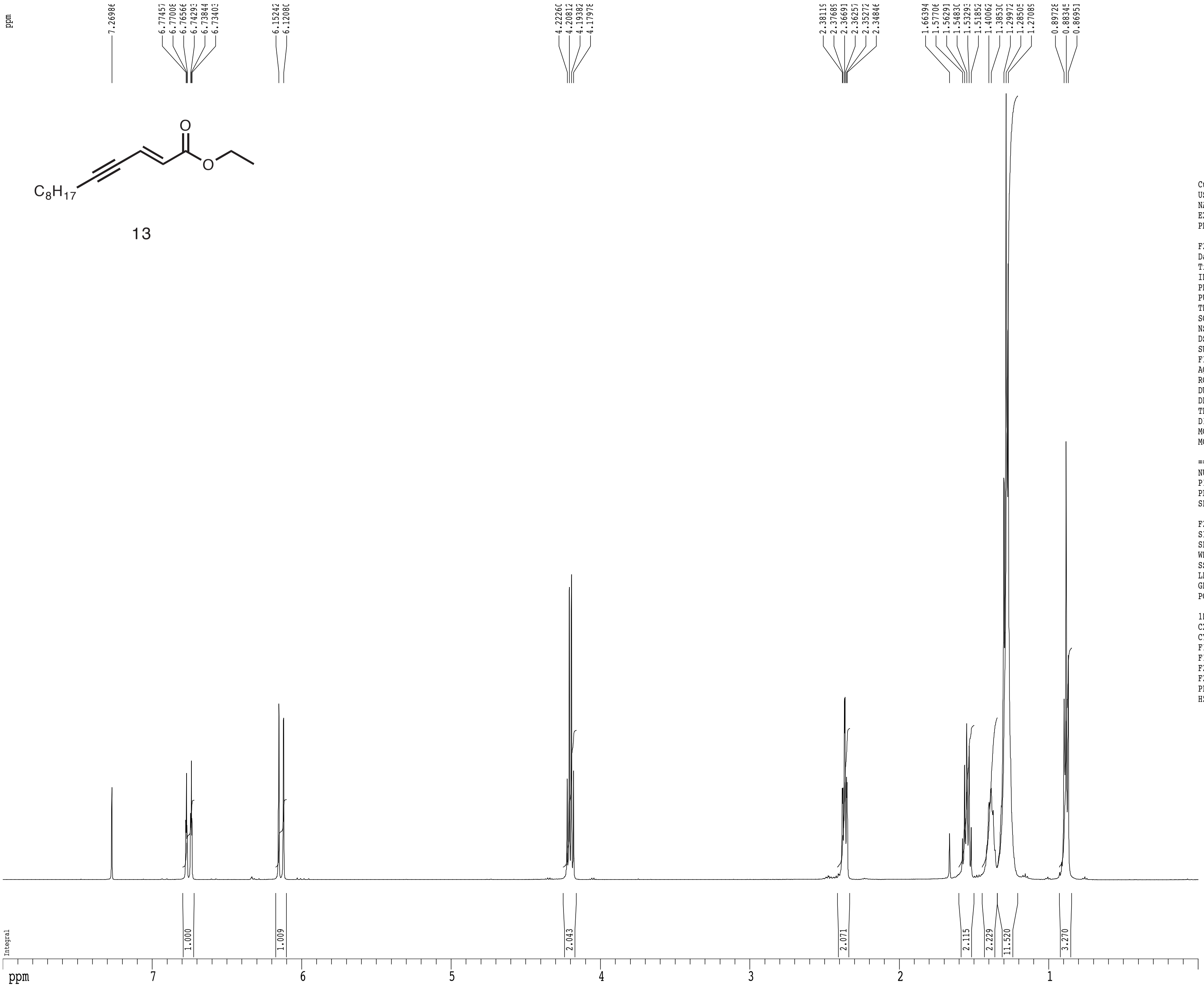
[5] Shibuya, G. M.; Kanady, J. S.; Vanderwal, C. D. *J. Am. Chem. Soc.* **2008**, *130*, 12514–12518.

IV. NMR Spectra

1H spectrum



13

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PROCNO                 1

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MCWRK         0.01500000 sec

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PL1                 1.60 dB
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GB                     0
PC                  4.00

1D NMR plot parameters
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CY                 15.00 cm
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F1               4001.76 Hz
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F2                  0.00 Hz
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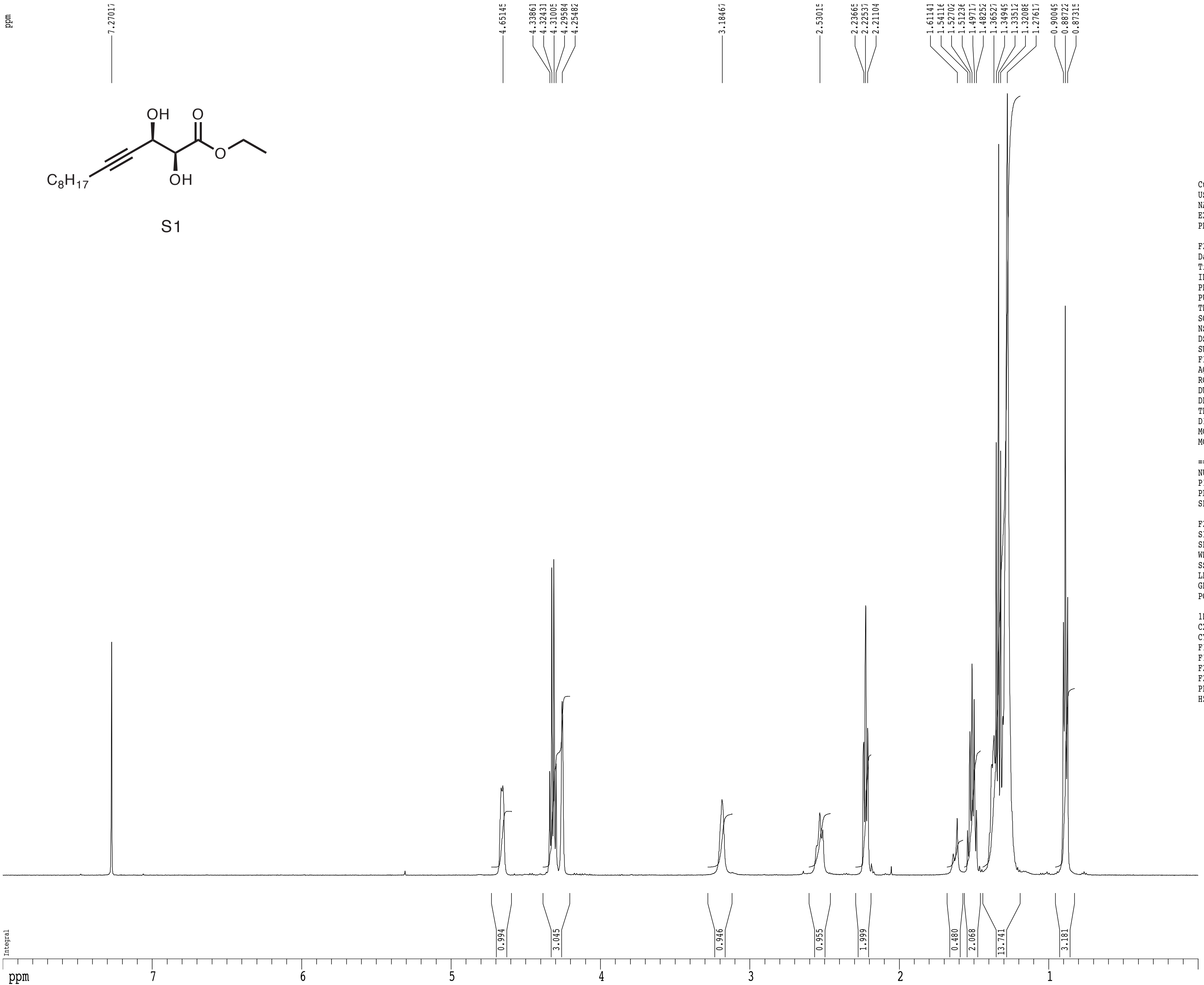
HZCM           175.51581 Hz/cm
```

1H spectrum

S1



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TD                 81728
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DS                     2
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MCWRK         0.01500000 sec

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P1                  7.50 usec
PL1                 1.60 dB
SFO1         500.2235015 MHz

F2 - Processing parameters
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SF           500.2200261 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  4.00

1D NMR plot parameters
CX                 22.80 cm
CY                 15.00 cm
F1P                8.000 ppm
F1               4001.76 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.35088 ppm/cm
HZCM           175.51581 Hz/cm
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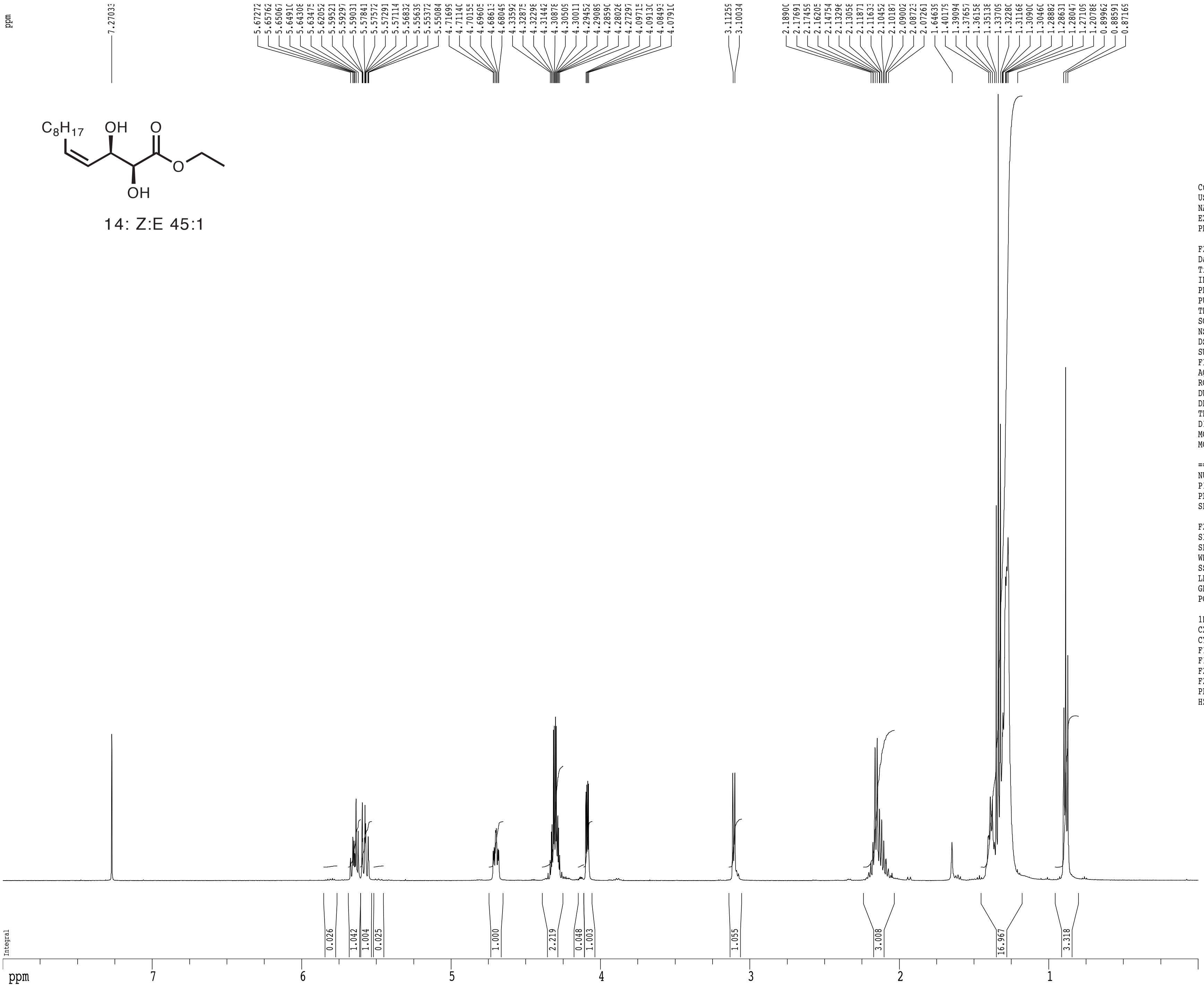
1H spectrum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DS                     2
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WDW                   EM
SSB                    0
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1D NMR plot parameters
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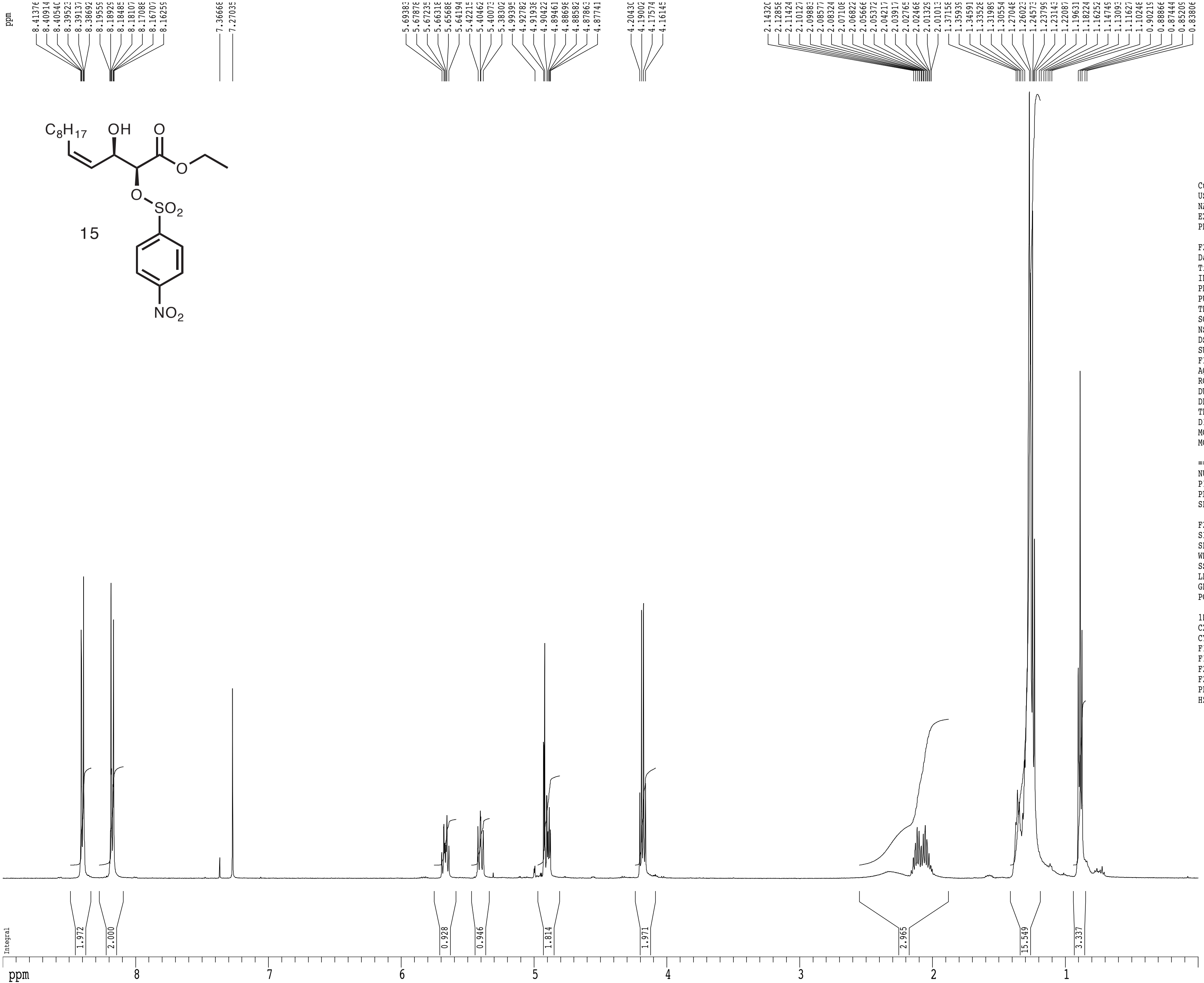
1H spectrum



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DS                   2
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DE                6.00 usec
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PL1              -3.00 dB
SFO1       499.6234973 MHz

F2 - Processing parameters
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1D NMR plot parameters
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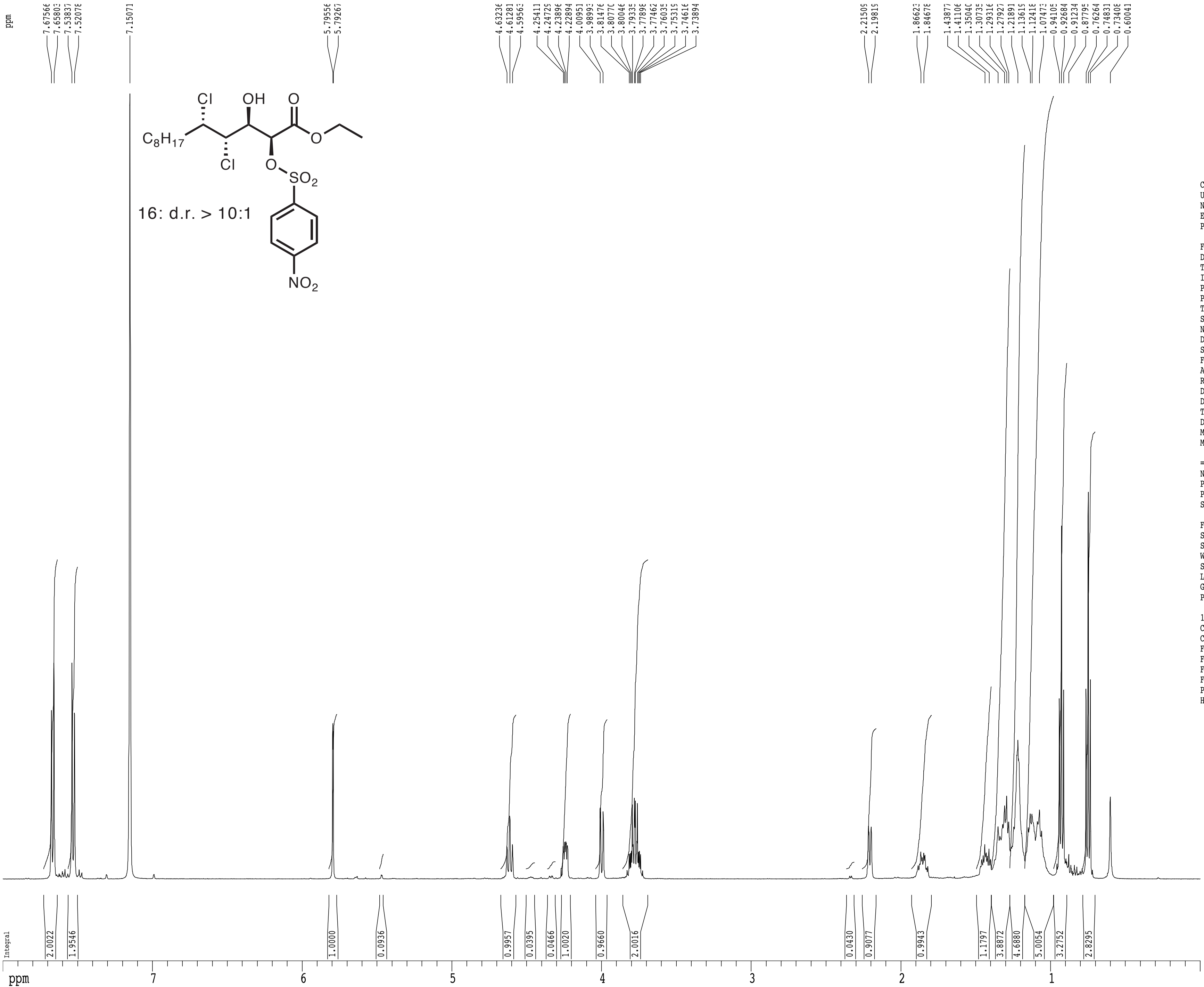
1H spectrum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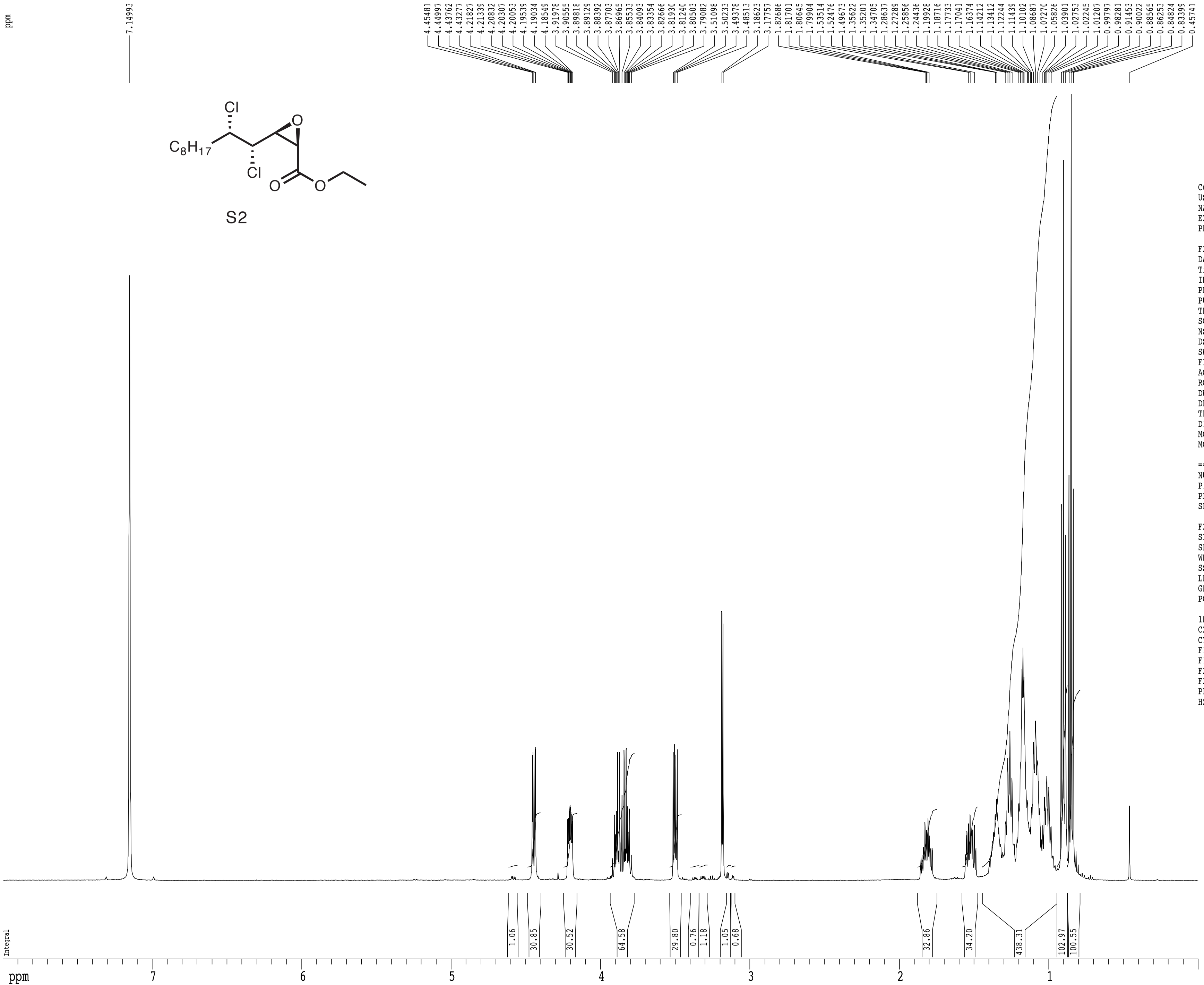
1H spectrum


S2

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MCREST        0.00000000 sec
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======== CHANNEL f1 ========
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PL1                -3.00 dB
SFO1         499.6234973 MHz

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1D NMR plot parameters
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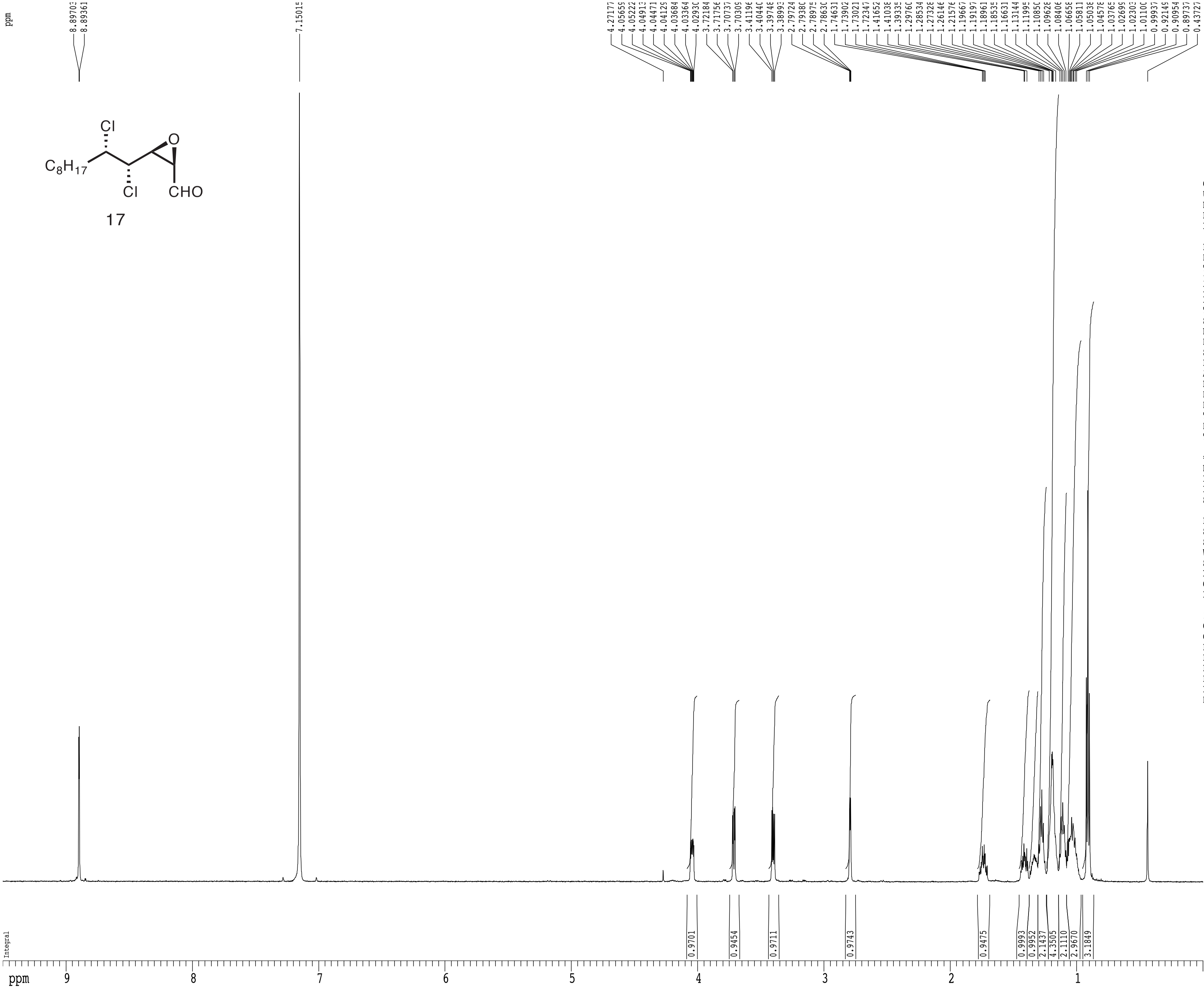
1H spectrum



17

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PROCNO                 1

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======== CHANNEL f1 ========
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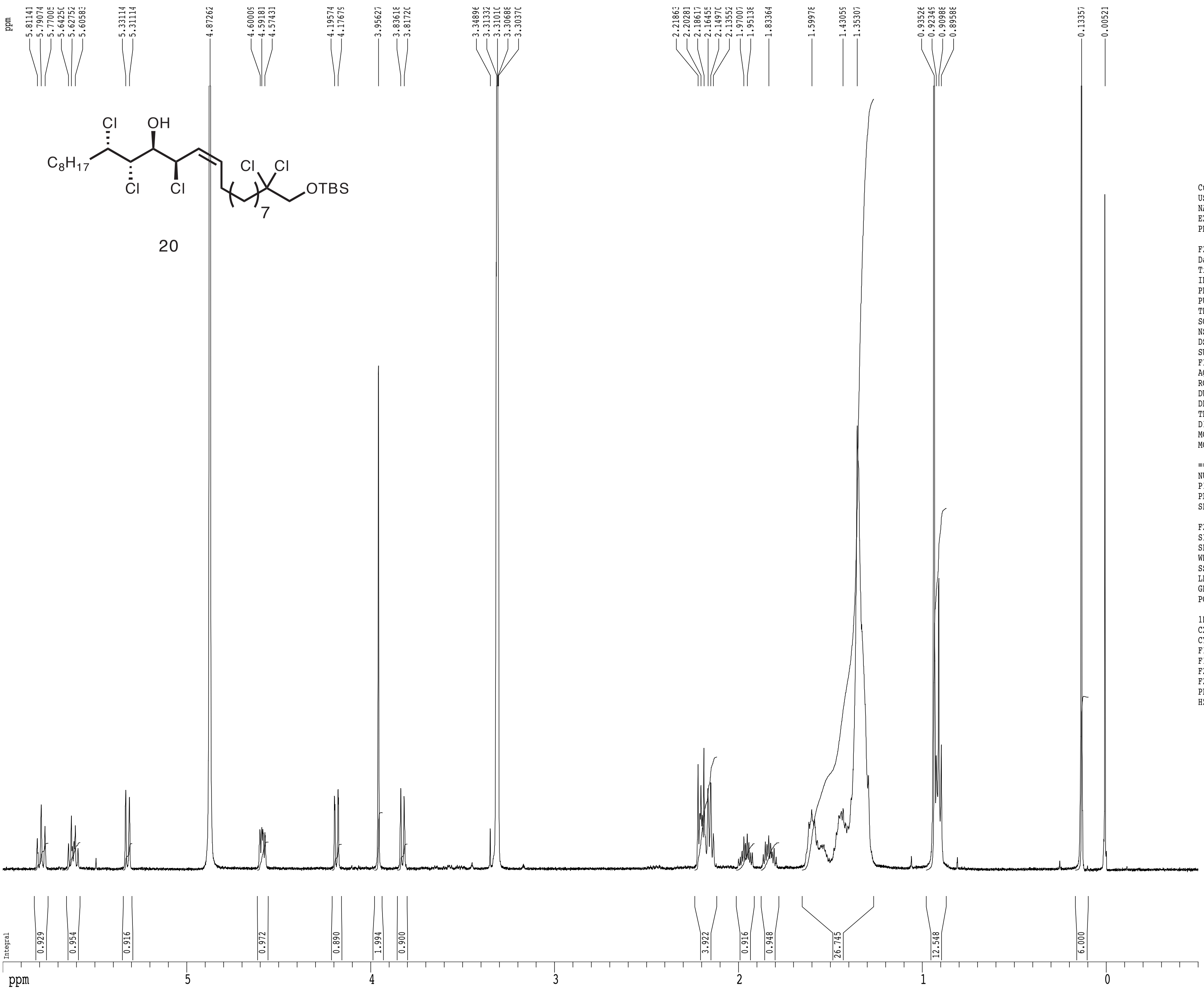
1H spectrum



20

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PULPROG             zg30
TD                 81728
SOLVENT            CDCl3
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DS                     2
SWH             8012.820 Hz
FIDRES          0.098043 Hz
AQ             5.0998774 sec
RG                   4.5
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TE                 298.0 K
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MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.50 usec
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1D NMR plot parameters
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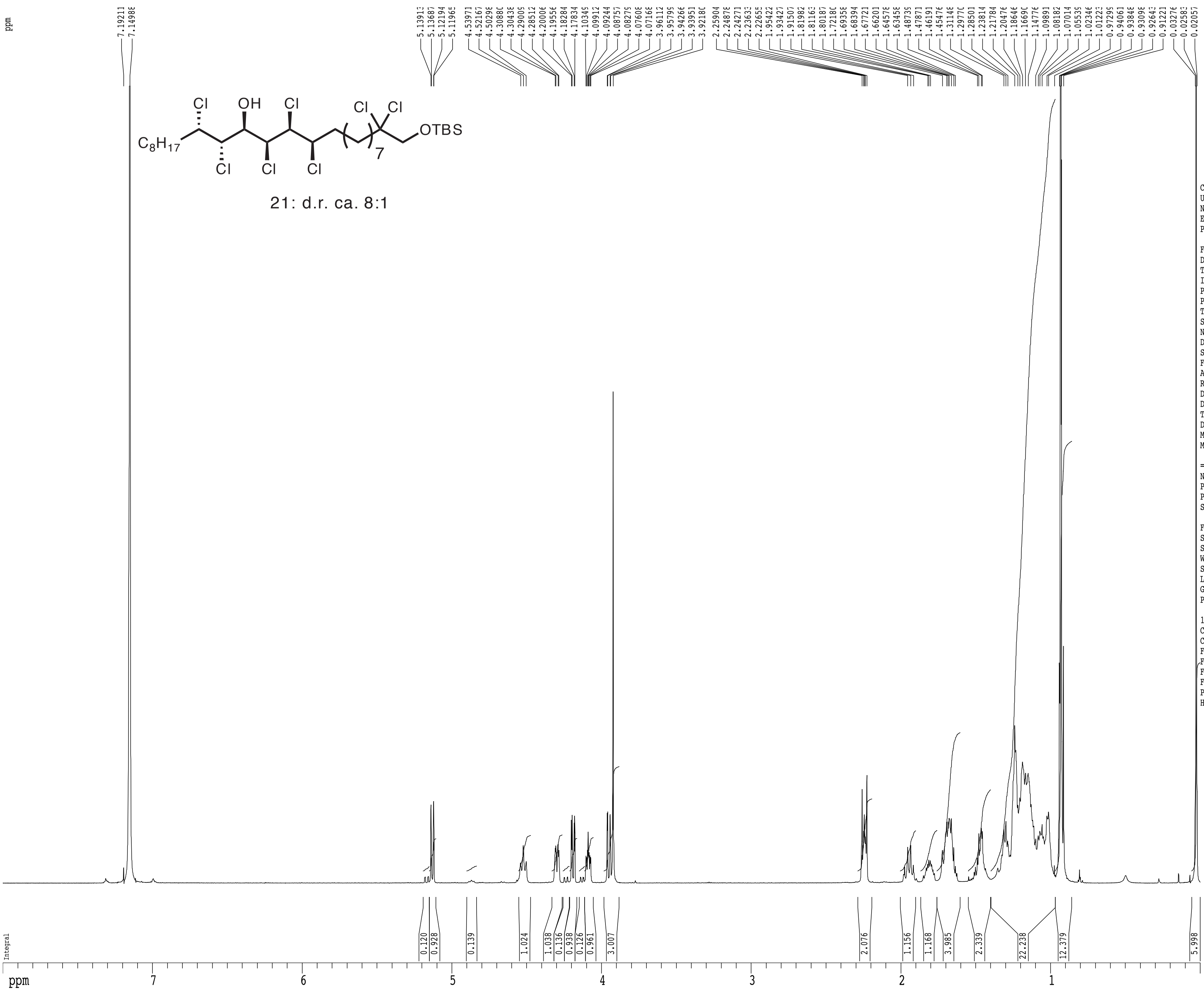
1H spectrum



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PROCNO 1

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DS 2
SWH 8012.820 Hz
FIDRES 0.098043 Hz
AQ 5.0998774 sec
RG 6.3
DW 62.400 usec
DE 6.00 usec
TE 298.0 K
D1 0.10000000 sec
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MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 7.50 usec
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1D NMR plot parameters
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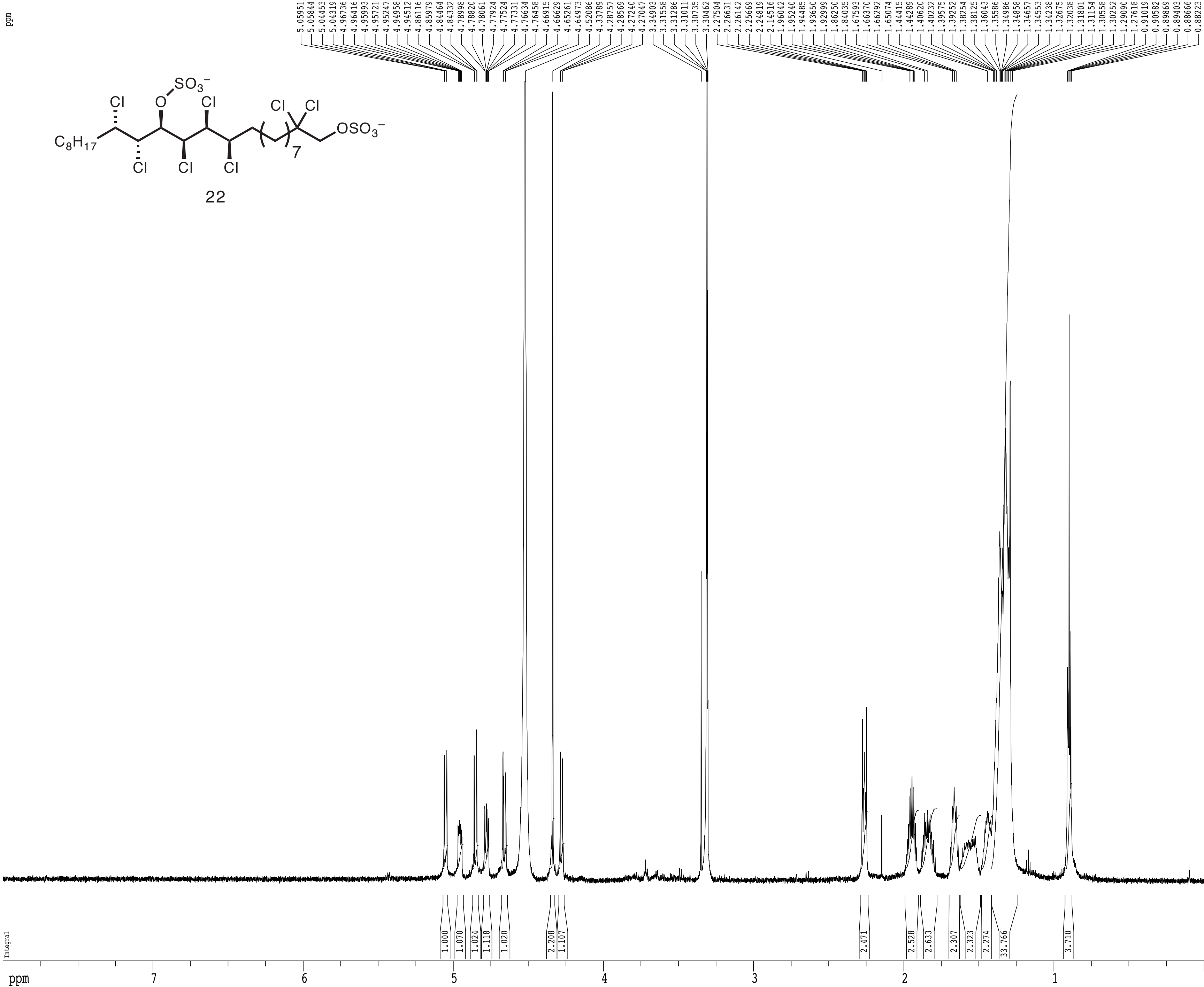
1H spectrum

22



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DS                       2
SWH            9615.385 Hz
FIDRES         0.098178 Hz
AQ            5.0928259 sec
RG                     256
DW              52.000 usec
DE                6.00 usec
TE                 330.0 K
D1           0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                8.00 usec
PL1               -1.00 dB
SFO1        600.1342009 MHz

F2 - Processing parameters
SI                   65536
SF          600.1300191 MHz
WDW                     GM
SSB                      0
LB                -0.61 Hz
GB                  0.2995
PC                    0.50

1D NMR plot parameters
CX                 22.80 cm
CY                 69.64 cm
F1P                8.000 ppm
F1               4801.04 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM         0.35088 ppm/cm
HZCM         210.57195 Hz/cm
```
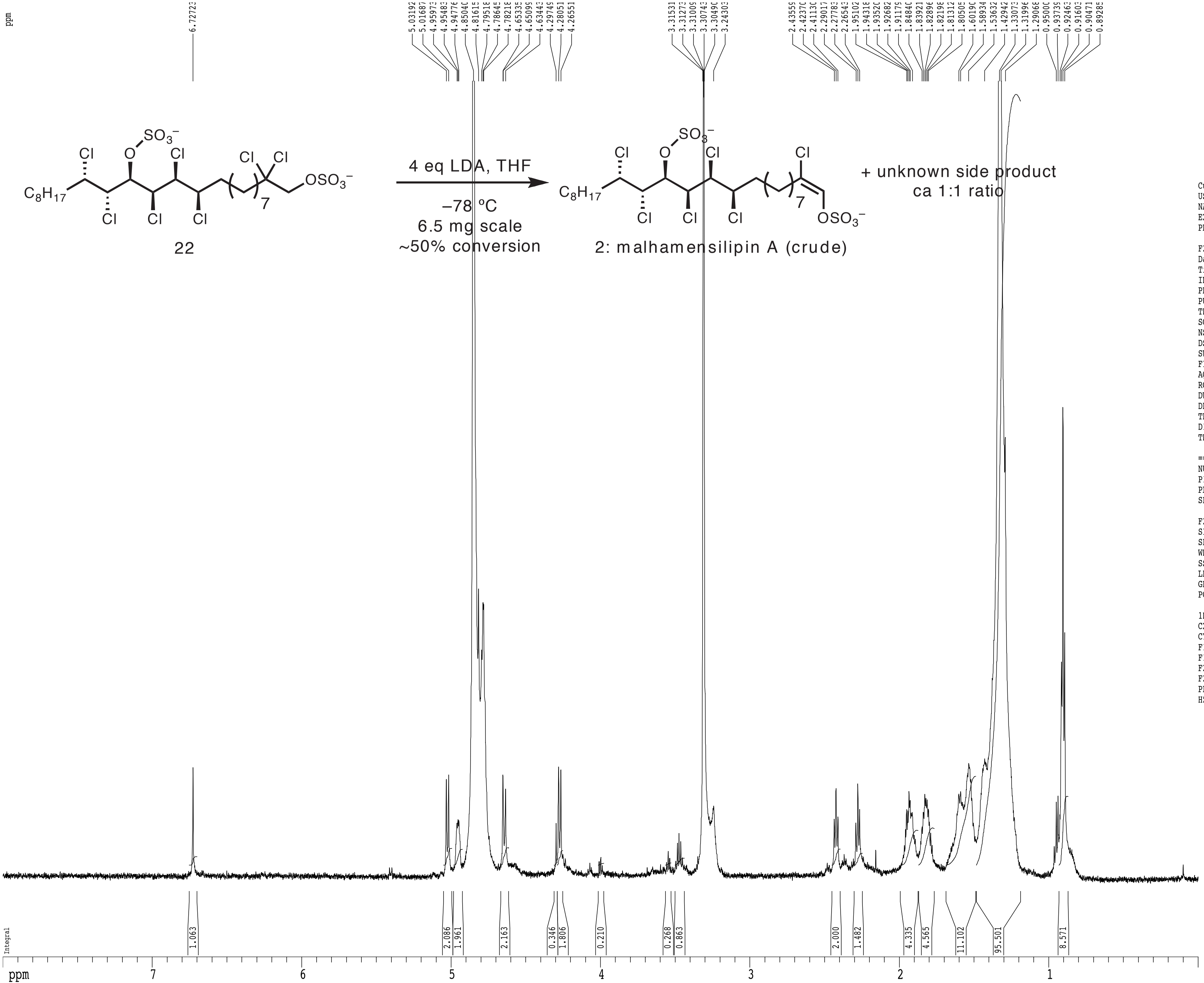
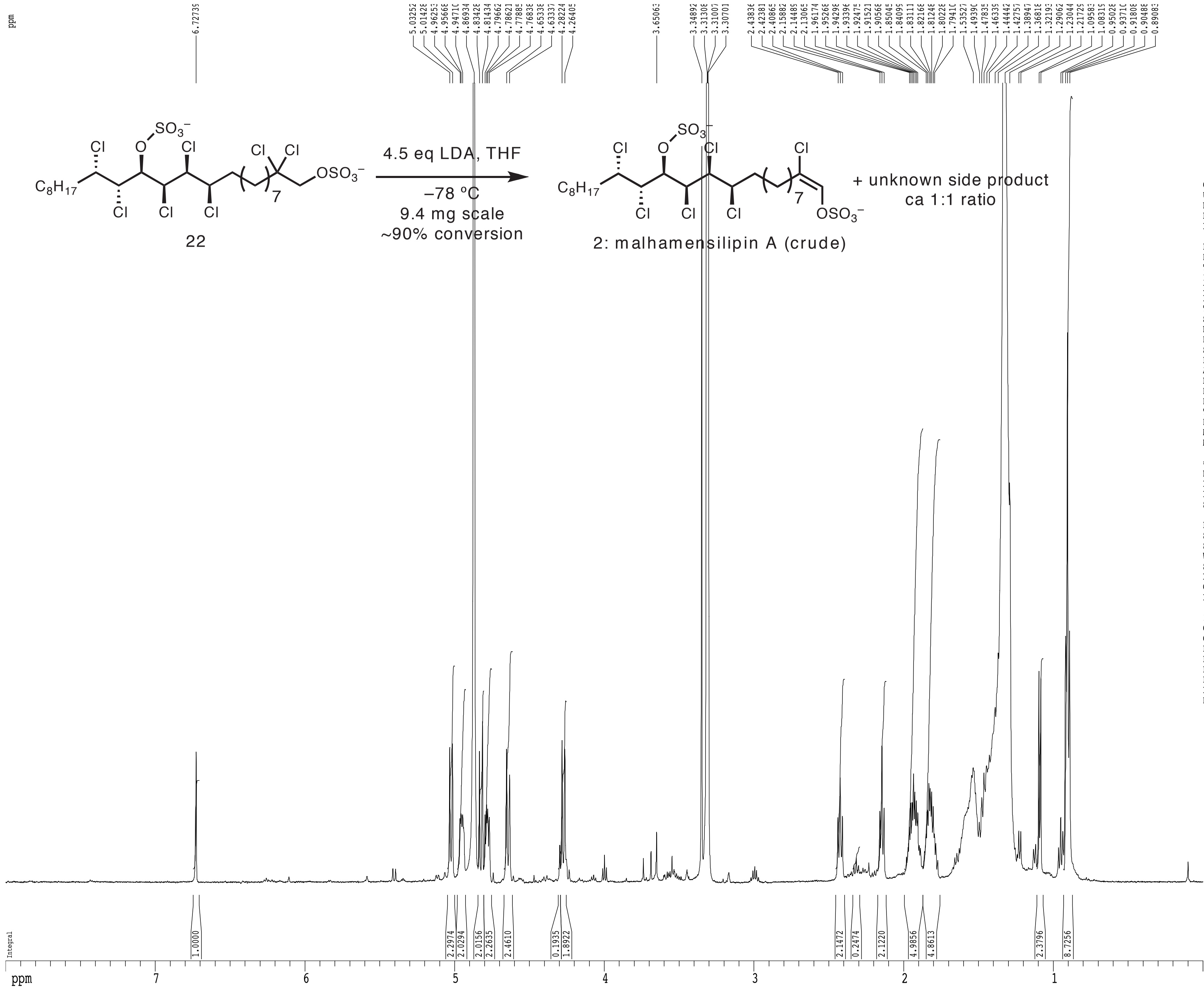

1H spectrum

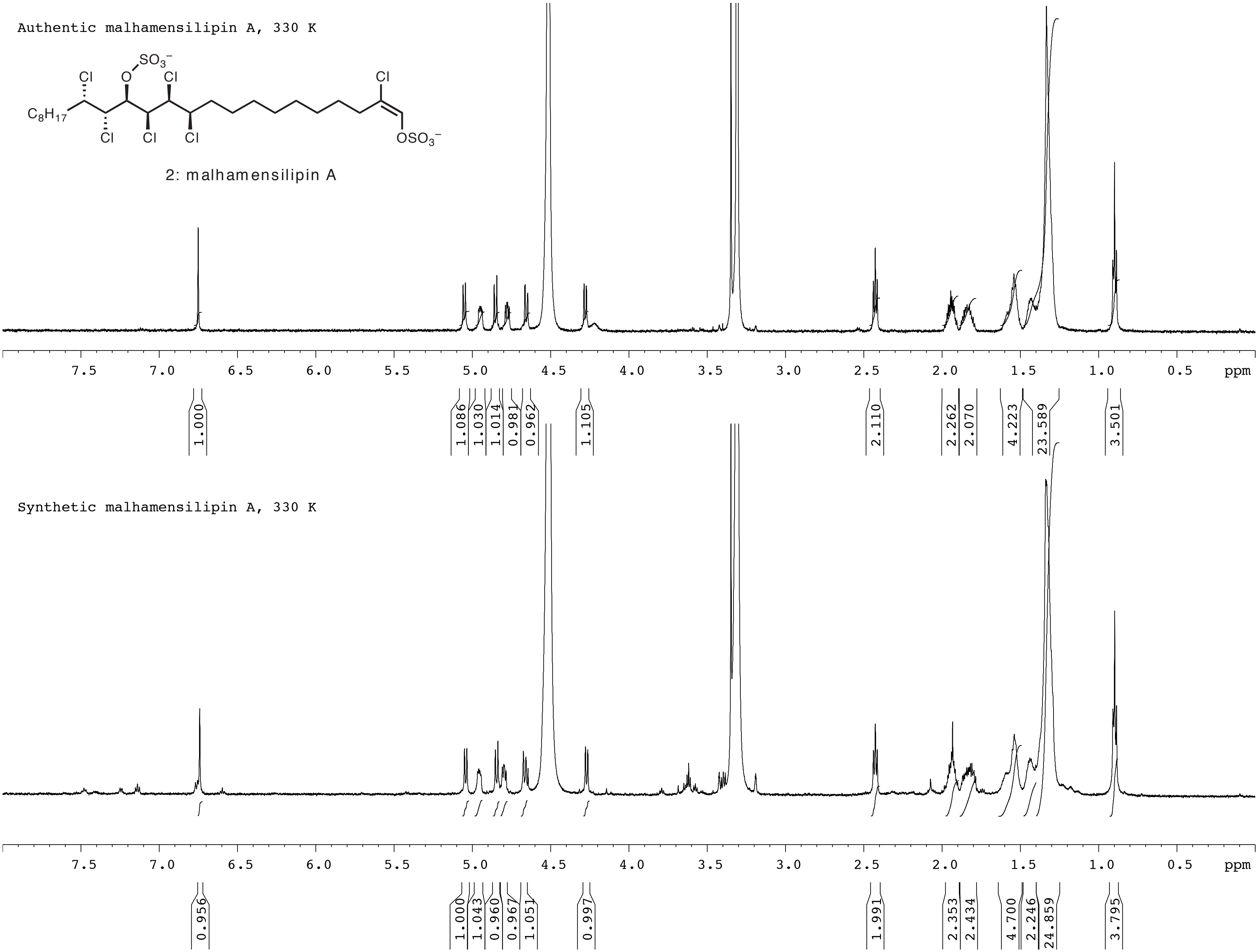


```
Current Data Parameters
USER              grants
NAME           GS6_173_c
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091111
Time               11.47
INSTRUM            av600
PROBHD   5 mm TBI 1H/13
PULPROG             zg30
TD                 97938
SOLVENT           CDCl3T
NS                    16
DS                     2
SWH             9615.385 Hz
FIDRES          0.098178 Hz
AQ             5.0928259 sec
RG                  1440
DW                52.000 usec
DE                  6.00 usec
TE                 298.0 K
D1           0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.00 usec
PL1                -1.00 dB
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300200 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY                 95.98 cm
F1P                8.000 ppm
F1               4801.04 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            0.35088 ppm/cm
HZCM           210.57195 Hz/cm
```

1H spectrum



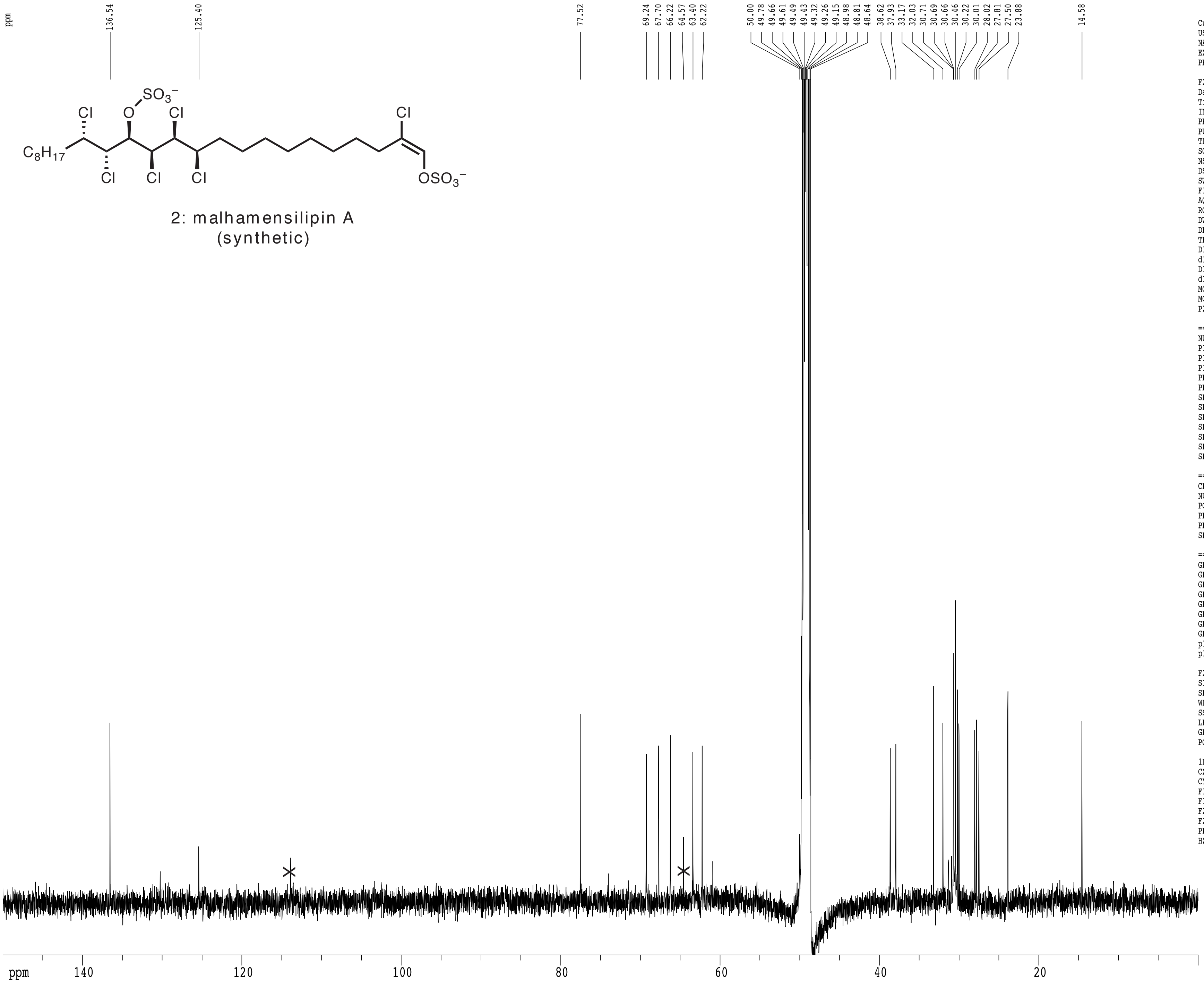
```
Current Data Parameters
USER                grants
NAME             GS6_178_c
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20091205
Time                 17.17
INSTRUM            cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG               zg30
TD                   81728
SOLVENT              CD3OD
NS                      16
DS                       2
SWH            8012.820 Hz
FIDRES         0.098043 Hz
AQ            5.0998774 sec
RG                     5.7
DW              62.400 usec
DE                6.00 usec
TE                 298.0 K
D1          0.10000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                7.50 usec
PL1                1.60 dB
SFO1        500.2235015 MHz

F2 - Processing parameters
SI                   65536
SF          500.2200188 MHz
WDW                     EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    4.00

1D NMR plot parameters
CX                22.80 cm
CY                95.37 cm
F1P              8.000 ppm
F1              4001.76 Hz
F2P              0.000 ppm
F2                 0.00 Hz
PPMCM        0.35088 ppm/cm
HZCM       175.51581 Hz/cm
```


Authentic malhamensilipin A, 330 K

2: malhamensilipin A

Synthetic malhamensilipin A, 330 K

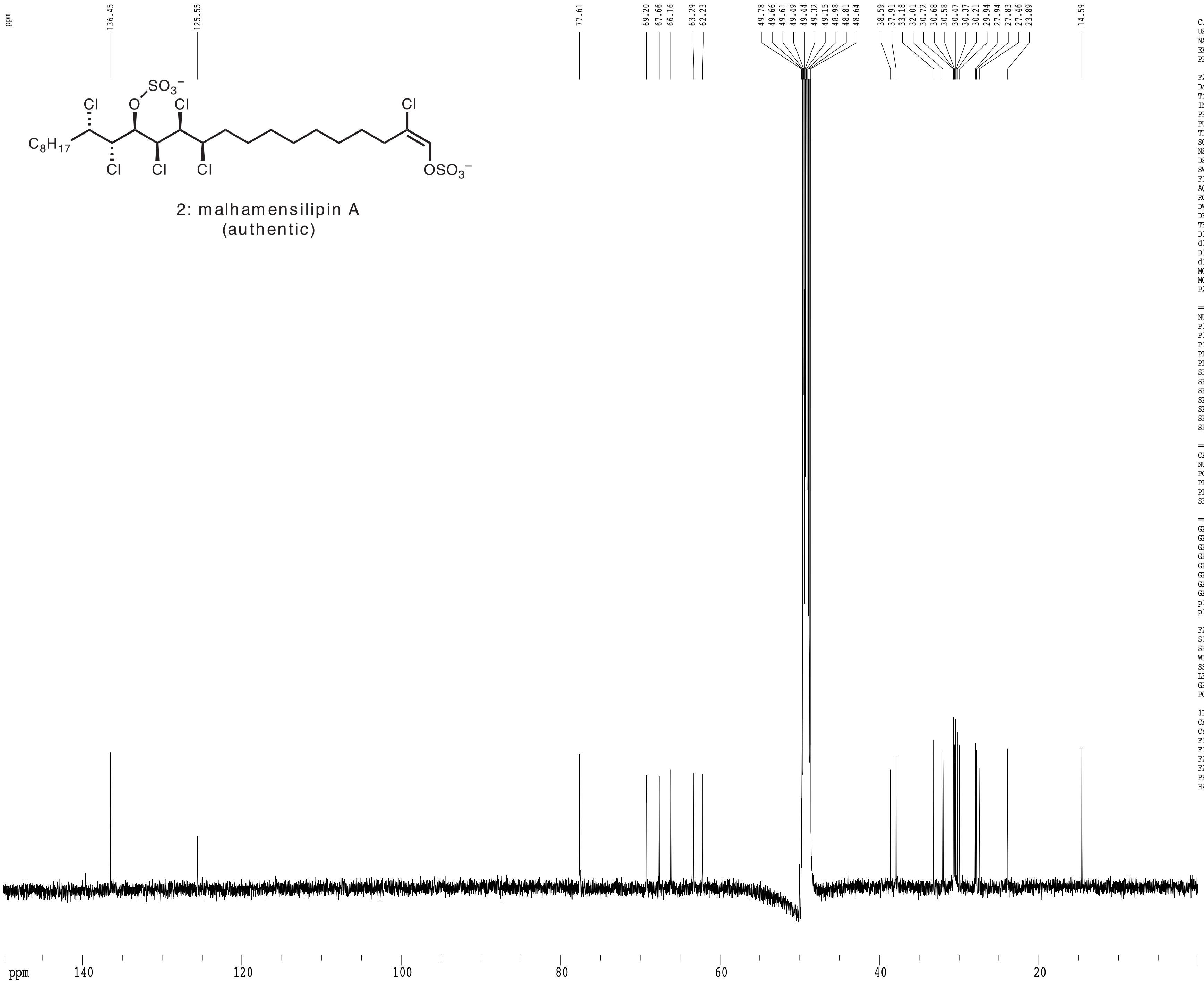
Z-restored spin-echo 13C spectrum with 1H decoupling



2: malhamensilipin A
(synthetic)

```
Current Data Parameters
USER              grants
NAME      GS6_178_13C-45-99
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091211
Time               21.47
INSTRUM          cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                 65418
SOLVENT            CDCl3
NS                 29514
DS                    16
SWH            30303.031 Hz
FIDRES          0.463222 Hz
AQ             1.0794470 sec
RG                7298.2
DW                16.500 usec
DE                  6.00 usec
TE                 300.0 K
D1            0.25000000 sec
d11           0.03000000 sec
D16           0.00020000 sec
d17           0.00019600 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec
P2                 31.00 usec

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.50 usec
P11               500.00 usec
P12              2000.00 usec
PL0               120.00 dB
PL1                -1.00 dB
SFO1         125.7942548 MHz
SP1                 3.20 dB
SP2                 3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1              0.00 Hz
SPOFF2              0.00 Hz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                 1.60 dB
PL12               24.60 dB
SFO2         500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPX1                0.00 %
GPX2                0.00 %
GPY1                0.00 %
GPY2                0.00 %
GPZ1               30.00 %
GPZ2               50.00 %
p15               500.00 usec
p16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF           125.7802256 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.80 cm
CY               1124.60 cm
F1P              150.000 ppm
F1              18867.03 Hz
F2P                0.000 ppm
F2                  0.00 Hz
PPMCM            6.57895 ppm/cm
HZCM           827.50153 Hz/cm
```

Z-restored spin-echo 13C spectrum with 1H decoupling



2: malhamensilipin A
(authentic)

```
Current Data Parameters
USER            grants
NAME     GS6_178_auth_malA_13C
EXPNO                3
PROCNO               1

F2 - Acquisition Parameters
Date_          20091216
Time              20.25
INSTRUM         cryo500
PROBHD   5 mm CPTCI 1H-
PULPROG  SpinEchopg30gp.prd
TD                65418
SOLVENT           CDCl3
NS                30720
DS                   16
SWH           30303.031 Hz
FIDRES         0.463222 Hz
AQ            1.0794470 sec
RG               7298.2
DW               16.500 usec
DE                 6.00 usec
TE                298.0 K
D1           0.25000000 sec
d11          0.03000000 sec
D16          0.00020000 sec
d17          0.00019600 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec
P2                31.00 usec

======== CHANNEL f1 ========
NUC1                13C
P1                15.50 usec
P11              500.00 usec
P12             2000.00 usec
PL0              120.00 dB
PL1               -1.00 dB
SFO1        125.7942548 MHz
SP1                3.20 dB
SP2                3.20 dB
SPNAM1   Crp60,0.5,20.1
SPNAM2      Crp60comp.4
SPOFF1             0.00 Hz
SPOFF2             0.00 Hz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                1.60 dB
PL12              24.60 dB
SFO2        500.2225011 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPX1               0.00 %
GPX2               0.00 %
GPY1               0.00 %
GPY2               0.00 %
GPZ1              30.00 %
GPZ2              50.00 %
p15              500.00 usec
p16             1000.00 usec

F2 - Processing parameters
SI                65536
SF          125.7802260 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 2.00

1D NMR plot parameters
CX                22.80 cm
CY               507.24 cm
F1P             150.000 ppm
F1             18867.03 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           6.57895 ppm/cm
HZCM          827.50153 Hz/cm
```