Supporting Information

First total synthesis of ganglioside DSG-A possessing neuritogenic activity

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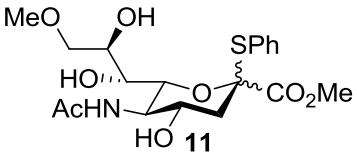
General Materials and Methods.

Chemicals used in reaction were reagent grade and were used without further purification except where noted. All solvents used in reaction were obtained from E. Merck or Acros and were dried by stander procedures[1] before use. Solvents for spectrometers were spectroscopy grade and were purchased from E. Merck company. Solvents used for extraction, and chromatography were technical grade and were distilled prior to use. Reactions were monitored by thin-layer chromatography performed on 0.25 mm TLC aluminium plates of Silica Gel 60 F_{524} (E. Merck) and compound spots were visualized by UV light (254 nm) and by staining with a solution of $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_4H_2O$ (24.0 g) in 6% H_2SO_4 (500 mL). Flash chromatography[2] was carried out using E. Merck Silica Gel 60 (230-400 mesh, 111567.9025).

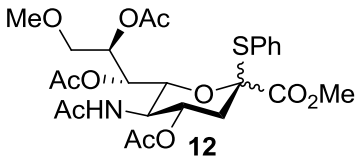
Melting points are uncorrected and were observed using a Yanagimoto Micromelting Point Apparatus. Optical rotations were performed using a Jasco P-1010 polarimeter at the indicated temperature. Infrared spectra were obtained with a Thermo Scientific™ Nicolet™ iS™5 FT-IR Spectrometer, and recorded as neat on KBr plates in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 (300 MHz for ^1H; 75 MHz for ^{13}C) and Bruker Avance II-400 (400 MHz for ^1H; 100 MHz for ^{13}C) FT-NMR instrument. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (δ 0.00) or the residual proton of $CDCl_3$ (δ_H 7.26, δ_C 77.0) as internal standard. COSY, HMQC, and HMBC spectra were applied to the detailed NMR assignments. Stereochemistry of compounds was determined using NOESY. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics Esquire 2000 mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

Experimental Procedures

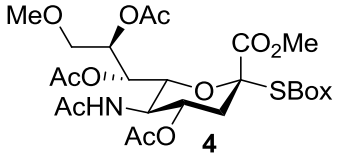


11

Methyl (phenyl-5-acetamido-9-*O*-methyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-2-nonulopyranosid)onate (11) MeONa (0.431 g, 7.88 mmol) was added to a solution of acetate **9** (2.300 g, 3.94 mmol) in dry MeOH (49 mL) at 0 ^{o}C. After stirring for 30 min at room temp, the solution was neutralized with Dowex 50w X 8 [H^+]. The resin was filtered out and washed with MeOH. The filtrate was concentrated under reduced pressure to give a white solid residue **10** (R_f = 0.23 (MeOH/CH_2Cl_2 = 1:5, v/v)). The residue was taken forward to the next step reaction without further purification. The residue was dissolved in dry CH_3CN at room temperature under nitrogen. After stirring for 10 min at -10 ^{o}C, Me_3OBF_4 (0.870 g, 5.91 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (1.6 mL, 11.82 mmol) were quickly added to the above solution and the reaction mixture was stirred at the same temperature for additional 4 h. The reaction mixture was quenched by slowly adding MeOH at -10 ^{o}C and concentrated under reduced pressure. The produced yellowish solid residue were purified by flash column chromatography on silica gel (acetone/CH_2Cl_2 = 1:1, v/v) to afford 1.400 g of a white solid compound **11** as a ca. 1.0:4.0 in mixture of α- and β-stereoisomers in 82% yield over two steps: R_f= 0.38 (acetone/CH_2Cl_2 = 1∶5 (v / v)); FT-IR (neat) ν_{max} 3416, 2948, 2926, 2852, 1725, 1636, 1558, 1472, 1440, 1375, 1278, 1229, 1200, 1125, 1069, 1035, 693 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 7.58 (d, J = 1.2 Hz, 2H), 7.57-7.31 (m, 3H), 4.51 (d, J = 10.8 Hz, 1H), 4.14-4.07 (m, 1H), 3.93-3.86 (m, 2H), 3.67 (dd, J = 10.0, 2.4 Hz, 1H), 3.59-3.53 (m, 2H), 2.69 (dd, J = 13.6, 4.8 Hz, 1H), 1.97 (dd, J = 13.6, 11.6 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3 (C), 169.3 (C), 136.0 (CH), 130.0 (C), 129.2 (CH), 128.6 (CH), 90.2 (C), 74.4 (CH_2), 72.0 (CH), 69.3 (CH), 68.7 (CH), 66.8 (CH), 58.0 (CH_3), 52.7 (CH), 51.7 (CH_3), 40.8 (CH_2), 21.6 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{18}H_{25}NO_8SNa$ 438.1193, Found 438.1198.

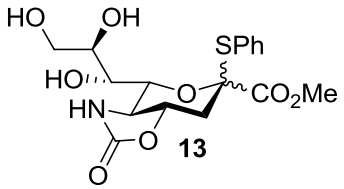


Methyl (phenyl-5-acetamido-4,7,8-tri-*O*-acetyl-3, 5-dideoxy-9-*O*-methyl-2-thio-D-glycero-D-galacto-2-nonulopyranosid)onate (12) To a stirring solution of compound **11** (1.400 g, 3.26 mmol) in dry pyridine (11.0 mL) was slowly added acetic anhydride (1.1 mL, 11.70 mmol) at 0 ^{o}C. The mixture was warmed to room temperature and continuously stirred at this temperature for 48 h. The reaction mixture was carefully quenched with dry MeOH (5.0 mL) to destroy the unreacted acetic anhydride and concentrated in *vacuo*. The observed yellow syrup was purified by flash column chromatography on silica gel using ethyl acetate and *n*-hexane (6:1 (v/v)) as the eluent to give 1.720 g of a white solid per-*O*-acetate **12** as a ca. 1.0:4.1 in mixture of α- and β-stereoisomers in 95% yield: R_f= 0.25 (ethyl acetate:*n*-hexane = 6:1 (v/v)); FT-IR (neat) ν_{max} 3385, 1743, 1663, 1541, 1438, 1372, 1229, 1097, 1035, 941, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.32 (m, 5H), 5.59 (d, *J* = 10.0 Hz, 1H), 5.46 (t, *J* = 2.4 Hz, 1H), 5.40-5.34 (m, 1H), 5.20-5.16 (m, 1H), 4.93 (td, *J* = 8.4, 2.2 Hz, 1H), 4.87-4.81(m, 1H), 4.66 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.13 (q, *J* = 10.4 Hz, 1H), 3.80 (dd, *J* = 11.0, 2.4 Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.41 (dd, *J* = 11.2, 8.4 Hz, 1H), 3.30 (s, 3H), 3.09 (s, 3H), 2.79 (dd, *J* = 12.8, 4.7 Hz, 1H), 2.69 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.14 (dd, *J* = 13.8, 12.0 Hz, 1H), 2.09 (s, 6H), 2.04 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6 (C), 170.9 (C), 170.4 (C), 170.2 (C), 167.9 (C), 136.2 (CH), 135.9 (CH), 129.8 (CH), 129.2 (CH), 128.8 (CH), 89.1 (C), 87.6 (C), 74.3 (CH), 73.2 (CH), 70.0 (CH_2), 69.1 (CH), 59.0 (CH_3), 58.6 (CH_3), 52.6 (CH_3), 49.3 (CH), 49.1 (CH), 37.7 (CH_2), 23.1 (CH_3), 21.2 (CH_3), 20.8 (CH_3), 20.7 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{25}H_{33}NO_{11}SNa$ 578.1667, Found 578.1674.



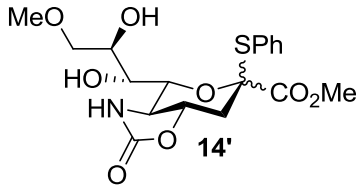
Methyl (benzoxazol-2-yl-5-acetamido-4,7,8-tri-*O*-acetyl -3,5-dideoxy-9-*O*-methyl-2-thio-D-glycero-D-galacto-2-nonulopyranosid)onate (4) A mixture of the thiosialoside **12** (1.720 g, 0.173 mmol), and activated 3 Å powdered molecular sieves (3.090 g) in anhydrous CH_2Cl_2 (31 mL) was stirred at room temperature for 30 minutes under nitrogen to remove any trace amounts of water. The reaction

mixture was then cooled to -10 ℃ followed by addition of iodine monochloride (0.19 mL, 3.71 mmol). After being kept stirring at the same temperature for 3 h, the reaction mixture was filtered through a short pad of Celite and then the filtrate was washed with cold saturated aqueous $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. After the produced white solid chlorinated product (R_f= 0.18 (ethyl acetate – *n*-hexane, 6/1 (v/v)) was completely dissolved in anhydrous CH_2Cl_2 (16 mL), 2-mercaptobenzoxazole (HSBox, 0.700 g, 4.64 mmol) was immediately added at 0 ^oC followed by addition of DIPEA (0.8 mL, 4.64 mmol) dropwise and then the reaction mixture was continuously stirred at room temperature for additional 20 h. The reaction mixture was concentrated under reduced pressure and purification of the syrup crude product via flash column chromatography on silica gel (CH_3CN/CH_2Cl_2 = 1:3, v/v) observed 1.250 g of **4** as a white solid α-stereoisomer in 88% yield (over two steps): R_f= 0.23 (CH_3CN/CH_2Cl_2 = 1/2, v/v); mp = 100-101 ^oC; $[\alpha]^{26}_D$ +31.23 (c 0.15, $CHCl_3$); FT-IR (neat) ν_{max} 1747, 1684, 1669, 1653, 1559, 1540, 1507, 1448, 1372, 1226, 1131, 1091, 1037, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.40-7.32 (m, 2H), 5.29 (dd, *J* = 6.4, 2.0 Hz, 1H), 5.21 (d, *J* = 9.6 Hz, 1H), 5.17-5.14 (m, 1H), 4.97-4.91 (m, 1H), 4.20 (dd, *J* = 10.6, 2.4 Hz, 1H), 4.04 (q, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 3.70 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.32 (dd, *J* = 11.0, 5.6 Hz, 1H), 2.94 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.39 (t, *J* = 12.2 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9 (C), 170.6 (C), 170.3 (C), 170.0 (C), 167.8 (C), 157.0 (C), 152.4 (C), 141.6 (C), 125.9 (CH), 124.7 (CH), 120.1 (CH), 110.8 (CH), 86.5 (C), 75.8 (CH), 71.3 (CH), 70.2 (CH_2), 69.2 (CH), 68.2 (CH), 58.9 (CH_3), 53.6 (CH_3), 48.9 (CH), 38.4 (CH_2), 23.1 (CH_3), 21.1 (CH_3), 20.8 (CH_3), 20.5 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{26}H_{32}NO_{12}SNa$ 619.1568, Found 619.1575.



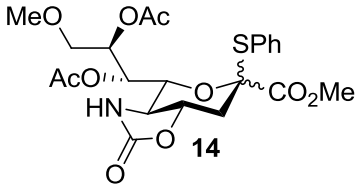
Methyl (Phenyl 5-amino-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-glycero-D-galacto-2-nonulopyranoside)onate (13) Methanesulfonic acid (1.3 mL, 20.02 mmol) was slowly added to a stirred solution of methyl ester **9** (3.851 g, 6.61 mmol) in anhydrous MeOH (22 mL) at 0 ^oC and then the reaction mixture was refluxed under N_2. After 24 h, the reaction mixture was quenched with excess Et_3N at 0 ^oC and then concentrated under reduced pressure to give the syrupy residue (R_f = 0.3,

MeOH:CH_2Cl_2 = 1:3 (v/v)). The residue was taken forward to the next step reaction without further purification. The residue and $NaHCO_3$ (2.812 g, 33.48 mmol) were dissolved in 70 mL of CH_3CN/H_2O (1:2, v/v). A solution of 4-nitrophenyl chloroformate (3.330 g, 16.52 mmol) in CH_3CN (18 mL) was slowly added to the vigorously stirred reaction mixture through an addition funnel at 0 ^oC. After being kept stirring at the same temperature for 3 h, the reaction mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. Purification of the yellow syrup residue via flash column chromatography on silica gel (eluting with EtOAc then EtOAc/MeOH from 15/1 to 5/1, v/v) obtained 1.843 g of **13** as a white solid compound in 74% yield over two steps: R_f = 0.20 (EtOAc/MeOH = 10/1, v/v); FT-IR (neat) ν_{max} 3363, 3016, 2952, 1739, 1475, 1440, 1376, 1302, 1262, 1238, 1178, 1149, 1106, 1066, 1014, 943, 755, 693 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.62-7.60 (m, 2H), 7.41-7.35 (m, 3H), 4.70 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.67-4.60 (m, 1H), 3.83 (dd, *J* = 11.0, 2.4 Hz, 1H), 3.76-3.62 (m, 3H), 3.61 (s, 3H), 3.60-3.59 (m, 1H), 2.89 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.44 (dd, *J* = 12.6, 12.4 Hz, 1H); HRMS-ESI $[M + Na]^+$ Calcd for $C_{17}H_{21}NO_8SNa$ 422.0880, Found 422.0873.

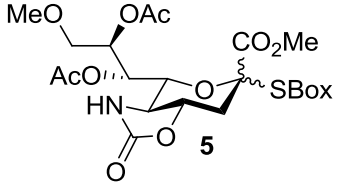


Methyl (phenyl 5-amino-5-*N*,4-*O*-carbonyl-3,5-dideoxy-9-methyl-2-thio-D-glycero-β-D-galacto-2-nonulopyranoside)onate (14') The hydroxyl oxazolidinone **13** was dissolved in dry CH_2Cl_2 (10 mL) at room temperature under nitrogen. After stirring for 10 min at -10 ^oC, Me_3OBF_4 (0.187 g, 1.26 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.2 mL, 1.44 mmol) were quickly added to the above solution and the reaction mixture was stirred at the same temperature for additional 4 h. The reaction mixture was quenched by slowly adding MeOH at -10 ^oC and concentrated under reduced pressure. The produced yellowish syrup residue were purified by flash column chromatography on silica gel (EtOAc/CH_2Cl_2 = 3:1, v/v) to afford 0.148 g of a white solid compound **14'** as a ca. 1.0:4.4 in mixture of α- and β-stereoisomers in 74% yield: R_f = 0.33 (EtOAc/CH_2Cl_2 = 8:1 (v/v)); FT-IR (neat) ν_{max} 3375, 3011, 2926, 1760, 1475, 1440, 1367, 1302, 1263, 1236, 1175, 1149, 1015, 941, 898, 868, 754, 693 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.61-7.31 (m, 5H), 4.69 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.66-4.59 (m, 1H), 3.85-3.80 (m, 1H), 3.66 (dd, *J* = 10.1, 2.6 Hz, 1H), 3.61 (s, 3H), 3.60-3.54 (m, 3H), 3.40 (s, 3H), 2.89 (dd, *J* = 12.8,

4.0 Hz, 1H), 2.43 (t, J = 12.8 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 169.1 (C), 161.1 (C), 136.3 (CH), 129.6 (CH), 129.2 (C), 128.7 (CH), 89.6 (C), 77.8 (CH), 74.0 (CH), 74.0 (CH_2), 70.7 (CH), 68.4 (CH), 58.0 (CH), 52.1 (CH_3), 47.0 (CH_3), 37.0 (CH_2); HRMS-ESI $[M + Na]^+$ Calcd for $C_{18}H_{23}NO_8SNa$ 436.1037, Found 436.1032.



Methyl (phenyl 5-amino-7,8-di-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-9-methyl-2-thio-D-glycero-β-D-galacto-2-nonulopyranoside)onate (14) To a stirring solution of compound **14'** (0.111 g, 0.27 mmol) in dry pyridine (0.9 mL) was slowly added acetic anhydride (1.0 mL, 10.58 mmol) at 0 ^{o}C. The mixture was warmed to room temperature and continuously stirred at this temperature for 8 h. The reaction mixture was carefully quenched with dry MeOH (5.0 mL) to destroy the unreacted acetic anhydride and the concentrated in *vacuo*. The observed yellow syrup was purified by flash column chromatography on silica gel using ethyl acetate and *n*-hexane (1:1 (v/v)) as the eluent to give 0.117 g of a white solid per-*O*-acetate **14** as a ca. 1.0:4.4 in mixture of α- and β-stereoisomers in 97% yield: R_f = 0.54 (ethyl acetate:*n*-hexane = 4:1 (v/v)); FT-IR (neat) ν_{max} 3394, 2925, 1780, 1793, 1475, 1439, 1373, 1301, 1228, 1183, 1145, 1114, 1068, 1022, 940, 852, 754, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 5H), 5.59 (s, 1H), 5.27 (dd, J = 4.8, 3.2 Hz, 1H), 5.14-5.11 (m, 1H), 4.70-4.63 (m, 1H), 4.60 (dd, J = 9.7, 2.8 Hz, 1H), 3.73 (dd, J = 11.2, 2.2 Hz, 1H), 3.58 (s, 3H), 3.50 (dd, J = 11.2, 6.0 Hz, 1H), 3.21 (s, 3H), 3.12 (t, J = 10.4 Hz, 1H), 2.84 (dd, J = 13.0, 3.6 Hz, 1H), 2.27 (t, J = 13.0 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (C), 170.6 (C), 167.7 (C), 159.3 (C), 136.0 (CH), 130.1 (CH), 129.3 (CH), 129.0 (C), 89.2 (C), 76.9 (CH), 73.3 (CH), 71.5 (CH), 71.2 (CH), 70.0 (CH_2), 59.2 (CH_3), 58.8 (CH), 52.8 (CH_3), 36.8 (CH_2), 21.1 (CH_3), 20.7 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{22}H_{27}NO_{10}SNa$ 520.1248, Found 520.1250.

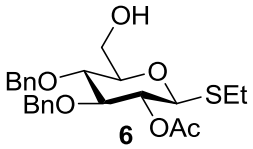


Methyl [benzoxazol-2-yl-7,8-di-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-9-methyl-2-thio-α-D-glycero-D-galacto-2-nonulopyranoside]onate (5) A mixture of the

thiosialoside **14** (0.346 g, 0.70 mmol), and activated 3 Å powdered molecular sieves (1.310 g) in anhydrous CH_2Cl_2 (7.0 mL) was stirred at room temperature for 30 minutes under nitrogen to remove any trace amounts of water. The reaction mixture was then cooled to -10 °C followed by addition of iodine monochloride (0.05 mL, 0.31 mmol). After being kept stirring at the same temperature for 3 h, the reaction mixture was filtered through a short pad of Celite and then the filtrate was washed with cold saturated aqueous $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. After the produced white solid chlorinated product (R_f = 0.45 (ethyl acetate/CH_2Cl_2 = 1/3 (v/v)) was completely dissolved in anhydrous CH_2Cl_2 (3.5 mL), 2-mercaptobenzoxazole (HSBox, 0.171 g, 1.13 mmol) was immediately added at 0 ^oC followed by addition of DIPEA (0.2 mL, 1.21 mmol) dropwise and then the reaction mixture was continuously stirred at room temperature for additional 20 h. The reaction mixture was concentrated under reduced pressure and purification of the yellow syrup crude product via flash column chromatography on silica gel (EtOAc/CH_2Cl_2 = 1:3, v/v) observed 0.264 g of **5** as a white solid ca. 7.5:1.0 in mixture of α- and β-stereoisomers in 70% yield over two steps: R_f = 0.35 (EtOAc/CH_2Cl_2 = 1/3, v/v); FT-IR (neat) ν_{max} 3398, 2926, 1781, 1746, 1498, 1474, 1451, 1371, 1224, 1171, 1122, 1092, 1036, 928, 854, 807, 751, 667, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.56 (m, 2H), 7.39-7.33 (m, 2H), 5.44 (s, 1H), 5.29-5.14 (m, 2H), 4.70-4.66 (m, 1H), 4.34 (d, *J* = 10.0 Hz, 1H), 4.07-4.01 (m, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.60 (d, *J* = 11.4 Hz, 1H), 3.41 (dd, *J* = 11.2, 3.1 Hz, 1H), 3.23 (s, 3H), 3.17-3.09 (m, 2H), 3.05 (s, 3H), 2.95 (dd, *J* = 13.9, 3.0 Hz, 1H), 2.68 (t, *J* = 12.4 Hz, 1H), 2.43 (t, *J* = 13.1 Hz, 1H), 2.08 (s, 3H), 2.06(s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (C), 170.1 (C), 169.7 (C), 167.9 (C), 158.9 (C), 158.8 (C), 157.1 (C), 152.3 (C), 141.5 (C), 126.2 (CH), 125.8 (CH), 124.9 (CH), 124.8 (CH), 120.5 (CH), 120.0 (CH), 110.8 (CH), 89.9 (C), 86.9 (C), 71.2 (CH), 70.6 (CH), 70.2 (CH_2), 70.0 (CH_2), 69.2 (CH), 69.0 (CH), 59.4 (CH_3), 59.0 (CH_3), 58.5 (CH), 57.5 (CH), 53.8 (CH_3), 53.6 (CH_3), 37.9 (CH_2), 36.8 (CH_2); HRMS-ESI $[M + Na]^+$ Calcd for $C_{23}H_{26}N_2O_{11}SNa$ 561.1150, Found 561.1152.

3,4-Di-*O*-benzyl-6-*O*-triisoporpylsilyl-*S*-thiaethyl-β-D-glucopyranose (17) A solution of orthoester **16** (304 mg, 0.53 mmol) and over activated powdered molecular sieves-4 Å (60 mg) in dry CH_2Cl_2 (1.7 mL) was stirred at room temperature for 30 min. The solution was then cooled to 0 °C and 2-mercaptothiazoline (0.2 mL, 3.20 mmol) was added. After keeping stir at 0 ^oC for 10 minutes, TMSOTf (4.8 μL, 0.02 mmol) was added dropwise and the reaction mixture was continuously stirred at same temperature for 1 h. The reaction mixture

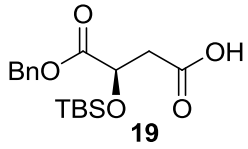
was diluted with CH_2Cl_2 and filtered over Celite. The filtrate was washed with saturated aqueous $NaHCO_3$, and brine. The organic layer was dried with MgSO4, and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:5, v/v) produced 207 mg of colorless syrup compound **12** in 65% yield: R_f = 0.42 (ethyl acetate:*n*-hexane = 1:3 (v/v)); $[\alpha]^{30}_D$ -3.3 (c 0.79, $CHCl_3$); FT-IR (neat) ν_{max} 2936, 2865, 1750, 1227, 1051, 742, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 10H. ArH), 5.00 (t, *J* = 9.3 Hz, 1H), 4.78 (m, CH_2, 4H), 4.33 (d, *J* = 9.9 Hz, 1H), 3.97 (m, 2H), 3.75 (m, 2H), 2.35 (dd, *J* = 9.1, 1.8 Hz, 1H), 2.68 (m, 2H), 1.98 (s, 3H, Ac), 1.21 (t, *J* = 7.5 Hz, 3H), 1.08-1.07 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6 (C), 138.2 (C), 128.7 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 112.5 (C), 84.4 (CH), 82.7 (CH), 80.4 (CH), 77.3 (CH), 75.2 (CH_2), 75.0 (CH_2), 71.8 (CH), 62.3 (CH_2), 22.9 (CH_2), 20.9 (CH_3), 17.9 (CH_3), 14.6 (CH_3), 11.9 (CH).



6

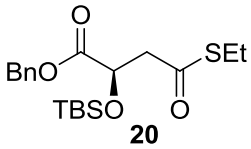
Ethyl 2-*O*-Acetyl-3,4-di-*O*-benzy1-1-thio-β-D-glucopyranoside (6) A solution of orthoester **16** (100 mg, 0.17 mmol) and over activated powdered molecular sieves-3 Å (50 mg) in dry CH_3CN (1.1 mL) was stirred at room temperature for 30 min. The solution was then cooled to 0 ℃ and ethane thiol (0.065 mL, 0.85 mmol) was added. After keeping stir at 0 ^oC for 10 minutes, $HgBr_2$ (13 mg, 0.034 mmol) was quickly added and the reaction mixture was continuously stirred at 60 ^oC for 8 h. To the reaction mixture was added water at 0 ^oC and then was continuously stirred at room temperature for 30 minutes. The reaction mixture was diluted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:3, v/v) produced 76 mg of a white solid compound **6** in 83% yield: R_f = 0.30 (ethyl acetate:*n*-hexane = 1:2 (v/v)); mp = 121-123 ^oC; $[\alpha]^{32}_D$ -6.7 (c 0.23, $CHCl_3$); FT-IR (neat) ν_{max} 3310, 3031, 2961, 2898, 1739, 1468, 1452, 1376, 1359, 1290, 1241, 1120, 1088, 1044, 1025, 980, 904, 743, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 10H), 5.00 (dd, *J* = 10.2, 8.8 Hz, 1H), 4.85-4.64 (m, 4H), 4.41 (d, *J* = 10.0 Hz, 1H), 3.89 (d, *J* = 12.4 Hz, 1H), 3.73-3.62 (m, 3H), 3.43-3.39 (m, 1H), 2.73-2.65 (m, 2H), 1.98 (s, 3H), 1.91 (brs, 1H), 1.25 (t, *J* = 7.4 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7 (C), 138.1 (C), 137.8 (C), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 84.2 (CH), 83.6 (CH), 79.7 (CH), 77.6 (CH_2), 75.3 (CH_2), 75.2 (CH_2), 71.8 (CH), 61.9 (CH_2), 24.1 (CH_2), 21.0 (CH_3), 14.9 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{24}H_{30}O_6SNa$ 469.1655, Found 469.1655.



19

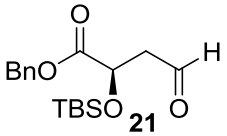
(3*R*)-4-Benzyloxy-3-(*tert*-butyldimethylsilyloxy)-4-oxobutanoic acid (19) To a solution of **18** (0.530 g, 2.4 mmol) in dry DMF (11 mL) was slowly adde NaH (60% dispersion in mineral oil, 0.210 g, 5.3 mmol) at 0 ^oC. After stirring for 30 minutes at 0 ^oC, TBSCl (0.390 g, 2.6 mmol) was added to the reaction mixture and then the reaction mixture was continuously stirred for 2 h at room temperature. After completion of benzylation, the reaction mixture was quenched with water at ice bath, extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The resulting yellow syrup residue was purified by flash column chromatography on silica gel using ethyl acetate and hexane (1:5, v/v) as the eluent to get 0.612 g of **19** as a colorless syrup compound in 74% yield: R_f = 0.13 (EtOAc:*n*-hexane = 1:5 (v/v)); $[\alpha]^{26}_D$ +35.1 (c 0.70, $CHCl_3$); FT-IR (neat) ν_{max} 2954, 2930, 2888, 2858, 1734, 1717, 1472, 1457, 1258, 1215, 1173, 1138, 956, 836, 780, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 5.21-5.13 (m, 2H), 4.65 (dd, J = 7.6, 4.4 Hz, 1H), 2.90-2.72 (m, 2H), 0.85 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7 (C), 171.2 (C), 135.2 (C), 128.5 (CH), 128.4 (CH), 73.0 (C), 68.9 (CH), 67.0 (CH_2), 39.8 (CH_2), 25.5 (CH_3), 18.1 (C); HRMS-ESI $[M - H]^-$ Calcd for $C_{17}H_{25}O_5Si$ 337.1378 , Found 337.1364.



20

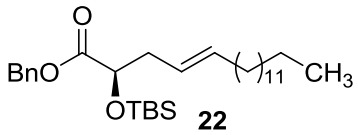
Benzyl (2*R*)-2-(*tert*-butyldimethylsilyloxy)-4-ethylthio-4-oxobutanoate (20) EDCI·HCl (0.281 g, 1.48 mmol) was added to a solution of acid **19** (0.212 g, 0.59 mmol), ethanethiol (88 μL, 1.18 mmol), and DMAP (7 μg, 0.06 mmol) in dry CH_2Cl_2 (3.0 mL) at 0 ^oC. After 10 minutes, the cooling bath was removed and the

reaction mixture was continuously stirred at room temperature for 30 minutes. The reaction mixture was diluted with CH_2Cl_2 at 0 ^oC, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The produced yellow syrup residue was purified by flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:15, v/v) to afford 0.212 g of a colorless syrup thioester **20** in 93% yield: R_f = 0.30 (EtOAc/*n*-hexane = 1:15 (v/v)); $[\alpha]^{26}_D$ +62.6 (c 0.55, $CHCl_3$); FT-IR (neat) ν_{max} 2957, 2930, 2857, 1757, 1687, 1472, 1457, 1362, 1257, 1214, 1186, 1137, 1066, 1004, 969, 939, 838, 813, 780, 751, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 5H), 5.20-5.12 (m, 2H), 4.72 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.96-2.94 (m, 2H), 2.91-2.85 (m, 2H), 1.24 (t, *J* = 7.6 Hz, 3H), 0.85 (s, 9H), 0.03 (d, *J* = 8.8 Hz) , 6H; ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8 (C), 171.9 (C), 135.4 (C), 128.5 (CH), 128.4 (CH), 69.2 (CH), 66.9 (CH_2), 48.7 (CH_2), 25.6 (C), 23.4 (CH_2), 14.6 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{19}H_{30}O_4SiNa$ 405.1526 , Found 405.1528.



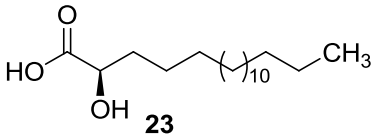
21

Benzyl (2*R*)-2-(*tert*-butyldimethylsilyloxy)-4-oxobutanoate (21) To a solution of ethyl thiol ester **20** (1.102 g, 2.88 mmol) and 10% Pd/C (0.115 g) in acetone (5.8 mL) was added triethylsilane (1.0 mL, 6.51mmol) over a period of 1 h under N_2 at room temperature. The reaction mixture was continuously stirred at room temperature for additional 1 h. The Pd/C was removed through a short pad of SiO_2/Celite and the filter was washed with ethyl acetate, and the filtrate was concentrated under reduced pressure. Purification of the colorless syrup crude product via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:19, v/v) observed 4.910 g of a colorless syrup aldehyde **21** in 91% yield: R_f = 0.10 (EtOAc/*n*-hexane = 1:15 (v/v)); $[\alpha]^{26}_D$ +40.2 (c 0.80, $CHCl_3$); FT-IR (neat) ν_{max} 2954, 2930, 2886, 2857, 1754, 1730, 1462, 1390, 1361, 1257, 1214, 1185, 1137, 1003, 838, 781, 749, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.6 Hz) , 1H, 7.37-7.34 (m, 5H), 5.22-5.14 (m, 2H), 4.73 (t, *J* = 5.8 Hz, 1H), 2.84 (dd, *J* = 6.0, 1.6 Hz, 2H), 0.86 (s, 9H), 0.07 (s, 3H) , 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0 (C), 172.2 (C), 172.0 (C), 135.2 (C), 128.6 (CH), 128.6 (CH), 128.5（CH), 128.5 (CH), 128.5 (CH), 128.4 (CH), 69.0 (CH), 67.7 (CH), 67.0 (CH_2), 48.3 (CH_3), 39.9 (CH_3), 25.6 (CH), 6.6 (CH_3), 5.8 (CH_2); HRMS-ESI $[M + Na]^+$ Calcd for $C_{17}H_{26}O_4SiNa$ 345.1493 , Found 345.1488.



22

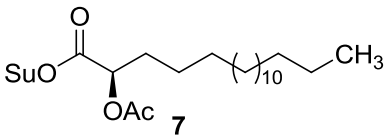
Benzyl (2*R*,4*E*)-2-(*tert*-butyldimethylsilyloxy)-4-octadecenoate (22) A solution of tetradecyltriphenylphosphonium bromide (2.090 g, 3.88 mmol) in dry THF (13 mL) was treated with *n*-butyllithium (1.4 mL, 3.49 mmol, 2.5 M in *n*-hexane) at -78 °C The reaction mixture was kept stirring at the same temperature for 1 h and then a solution of aldehyde **21** (0.501 g, 1.55 mmol) in dry THF (2.6 mL) was slowly added to the above solution. The reaction mixture was stirred at 0 °C for an additional 30 minutes. To this mixture was carefully added saturated aqueous NH_4Cl at 0 °C and the mixture was extracted with ethyl acetate, washed with brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to give a yellow syrup. Purification of this syrup via flash column chromatography on silica gel using CH_2Cl_2 and *n*-hexane (1:4 (v/v)) produced 0.782 g of a colorless syrup **22** as a single *E*-stereoisomers in 82% yield: R_f = 0.23 (CH_2Cl_2: *n*-hexane = 1:4 (v/v)); $[\alpha]^{25}_D$ +9.3 (c 0.50, $CHCl_3$); FT-IR (neat) ν_{max} 2951, 2926, 2854, 1757, 1735, 1463, 1361, 1257, 1136, 1005, 969, 939, 837, 779, 733, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.35 (m, 5H), 5.53-5.34 (m, 2H), 5.20-5.11 (m, 2H), 4.25 (t, *J* = 6.5 Hz, 1H), 2.49 (t, *J* = 6.5 Hz, 2H), 2.00 (dd, *J* = 13.1, 5.4 Hz, 2H), 1.26 (brs, 22H), 0.91-0.88 (m, 2H), 0.04 (s, 3H) , 0.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2 (C), 135.7 (C), 133.1 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 123.8 (CH), 72.4 (CH), 66.5 (CH_2), 33.3 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.4 (CH_2), 25.7 (CH), 22.7 (CH_2), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{31}H_{54}O_3SiNa$ 525.3734, Found 525.3749.



23

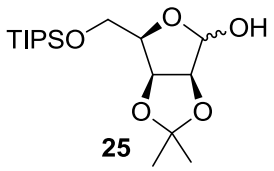
(2*R*)-2-Hydroxyoctadecanoic acid (23) 10% Pd/C (0.004 g) was added to a solution of alkene **22** (40 μg, 0.080 mmol) in EtOAc (0.40 mL). The reaction mixture was stirred under hydrogen (50 psi) at room temperature for 2 h. The Pd/C was removed through a short pad of SiO_2/Celite and the filter was washed with ethyl acetate. The filtrate was concentrated in *vacuo* without further purification to obtain 0.024 g of acid **23** as a white solid in 91% yield: R_f = 0.08 (MeOH/CH_2Cl_2 = 1:9 (v/v)); mp = 115-116 °C; $[\alpha]^{25}_D$ +16.6 (c 0.10, MeOH); FT-IR (neat) ν_{max} 3445, 3412, 2953, 2916, 2849, 1749, 1726, 1471, 1264, 1137, 1104, 1090, 912, 855, 718, 656

cm^{-1}; ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ = 1:2 (v/v)) δ 4.10 (dd, *J* = 7.6, 4.4 Hz, 1H), 1.8-1.58 (m, 2H), 1.41-1.39 (m, 2H), 1.24 (brs, 16H), 0.85 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CD_3OD/CDCl_3$ = 1:2 (v/v)) δ 176.9 (C), 70.2 (CH), 34.2 (CH_2), 31.8 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 24.8 (CH_2), 22.5 (CH_2), 13.6 (CH_3).



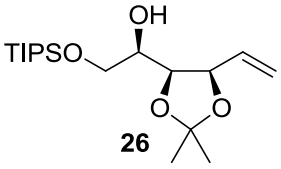
7

2,5-Dioxopyrrolidin-1-yl (2*R*)-2-acetoxyoctadecanoate (7) To a stirring solution of acid **23** (0.150 g, 0.50 mmol) in dry pyridine (2.5 mL) was slowly added acetic anhydride (0.14 mL, 1.50 mmol) at 0 °C. The mixture was warmed to room temperature and continuously stirred at this temperature for 4.5 h. The reaction mixture was diluted with CH_2Cl_2 and neutralized with 1N HCl. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in *vacuo*. The produced yellow syrup residue was taken forward to the next step reaction without further purification. To a solution of the yellow syrup residue, *N*-hydroxysuccinimide (86 mg, 0.75 mmol), and DMAP (6 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (2.5 mL) was added EDCI·HCl (0.240 g, 1.25 mmol) at 0 °C. After 10 minutes, the reaction mixture was stirred at ambient temperature for 3.5 h. The reaction mixture was diluted with CH_2Cl_2 at 0 °C, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The observed yellow syrup residue was purified by flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:3, v/v) to afford 0.190 g of compound **7** as a white solid in 86% yield: R_f = 0.20 (EtOAc/*n*-hexane = 1:3, v/v); mp = 85-86 °C; $[\alpha]^{26}_{D}$ +31.8 (c 0.15, $CHCl_3$); FT-IR (neat) ν_{max} 2915, 2849, 1811, 1762, 1738, 1471, 1372, 1253, 1237, 1225, 1204, 1072, 995, 926 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (t, *J* = 6.4 Hz, 1H), 2.84 (s, 4H), 2.16 (s, 3H), 1.99 (dd, *J* = 15.2, 7.2 Hz, 2H), 1.50 (m, 2H), 1.25 (brs, 26H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0 (C), 168.4 (C), 166.1 (C), 70.3 (CH), 31.9 (CH_2), 31.3 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 25.6 (CH_2), 24.7 (CH_2), 22.7 (CH_2), 20.4 (CH_3), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{24}H_{41}NO_6Na$ 462.2826, Found 462.2832.



25

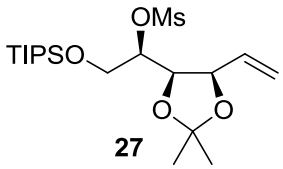
2,3-*O*-Isopropylidenyl-5-*O*-triisopropylsilyl-D-lyxofuranose (25) To a stirred solution of **24** (6.010 g, 32 mmol) and imidazole (6.532 g, 96 mmol) in anhydrous CH_2Cl_2 (210 mL) was added chlorotriisopropylsilane (8.3 mL, 38 mmol) at 0 ^oC. After 10 minutes, the reaction mixture was stirred for additional 1.5 h at room temperature. The reaction mixture was carefully quenched with dry MeOH (2.0 mL) to destroy the unreacted chlorotriisopropylsilane and concentrated in *vacuo*. The resulting residue was dissolved in CH_2Cl_2 and then successively washed with 1N cold aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The produced brown syrup was purified by flash column chromatography on silica (EtOAc/*n*-hexane = 1:6, v/v) to give 10.311 g of a white solid silyl ether **25** as a ca. 1.0:15.0 mixture of α- and β-stereoisomers in 93% yield: R_f = 0.33 (ethyl acetate:*n*-hexane = 1:5 (v/v)); FT-IR (neat) ν_{max} 3431, 2943, 2893, 2867, 1464, 1382, 1372, 1342, 1243, 1210, 1164, 1099, 1016, 998, 919, 881, 793, 682, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 2.0 Hz, 1H), 4.77 (dd, *J* = 5.6, 3.6 Hz, 1H), 4.60 (d, *J* = 4.60 Hz, 1H), 4.29-4.25 (m, 1H), 4.04-3.87 (m, 2H), 2.59-2.59 (m, 1H), 1.43 (s, 3H), 1.31 (s, 3H), 1.08-1.05 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.2 (C), 112.2 (C), 101.0 (CH), 85.5 (CH), 80.8 (CH), 79.7 (CH), 61.5 (CH_2), 26.0 (CH_3), 24.8 (CH_3), 17.9 (CH_3), 17.8 (CH_3), 11.9 (C); HRMS-ESI $[M + Na]^+$ Calcd for $C_{17}H_{34}O_5SiNa$ 369.2058 , Found 369.2068.



26

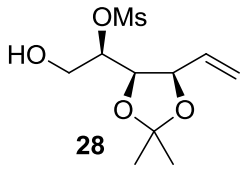
(2*R*,3*S*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-1-*O*-triisopropylsilyl-5-hexene-1,2,3,4-tetra ol (26) A solution of methyltriphenylphosphonium bromide (17.141 g, 48 mmol) in dry THF (200 mL)was treated with potassium *tert*-butoxide (5.042 g, 45 mmol) at 0 ℃. The reaction mixture was kept stirring at the same temperature for 1 h and then a solution of **25** (8.461 g, 24 mmol) in dry THF (40 mL) was slowly added to the above solution. After stirring at 0 ℃ for 20 minutes, the reaction mixture was stirred at room temperature for additional 1 h. The resulting precipitate was filtered out and

washed with ether. The filtrate was washed with saturated aqueous NH_4Cl, and brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to give a yellow syrup. Purification of this syrup via flash column chromatography on silica gel using hexane and ethyl acetate (60:1 → 6:1, v/v) as the eluent produced 6.851 g of a colorless syrup **26** in 83% yield: R_f = 0.38 (ethyl acetate:*n*-hexane = 1:15 (v/v)); $[\alpha]^{25}_D$ -9.5 (c 0.45, $CHCl_3$); FT-IR (neat) ν_{max} 3565, 2942, 2892, 2867, 1464, 1428, 1381, 1247, 1212, 1164, 1118, 1067, 997, 926, 882, 802, 682, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.06 (ddd, *J* = 17.8, 9.6, 8.0 Hz, 1H), 5.37-5.29 (m, 2H), 4.60 (t, *J* = 7.6 Hz, 1H), 4.29 (dd, *J* = 7.0, 3.2 Hz, 1H), 3.70-3.64 (m, 3H), 2.44 (d, *J* = 6.0 Hz, 1H), 1.54 (s, 3H), 1.40 (s, 3H), 1.13-1.01 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6 (CH), 119.1 (CH_2), 108.5 (C), 79.1 (CH), 77.0 (CH), 69.9 (CH), 64.3 (CH_2), 27.1 (CH_3), 24.9 (CH_3), 17.9 (CH_3), 17.9 (CH_3), 11.8 (C); HRMS-ESI $[M + Na]^+$ Calcd for $C_{18}H_{36}O_4SiNa$ 367.2272, Found 367.2275.



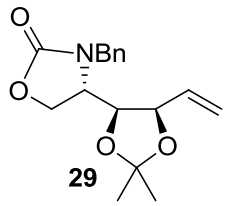
27

(2*R*,3*R*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-2-*O*-methanesulfonyl-1-*O*-triisopropylsilyl -5-hexene-1,2,3,4-tetraol (27) To a solution of **26** (1.020 g, 2.91 mmol) in dry pyridine (9.7 mL) was added dropwise methanesulfonyl chloride (0.67 mL, 8.73 mmol) at 0℃. The reaction mixture was stirred at room temperature for 1 h and concentrated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then successively washed with 1N cold aqueous HCl, saturated aqueous K_2CO_3, and brine. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The produced brown syrup was purified by flash column chromatography on silica (EtOAc/*n*-hexane = 1:25, v/v) to afford 1.193 g of sulfonate compound **27** as a colorless syrup in 90% yield: R_f = 0.30 (ethyl acetate:*n*-hexane = 1:8 (v/v)); $[\alpha]^{25}_D$ -1.2 (c 0.55, $CHCl_3$); FT-IR (neat) ν_{max} 2943, 2892, 2868, 1463, 1361, 1254, 1217, 1177, 1126, 1048, 996, 956, 923, 881, 793, 761, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddd, *J* = 17.8, 9.6, 8.0 Hz, 1H), 5.37-5.22 (m, 2H), 4.65-4.50 (m, 3H), 3.97-3.96 (m, 2H), 3.09 (s, 3H), 1.52 (s, 3H), 1.38 (s, 3H), 1.15-1.03 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6 (CH), 119.6 (CH_2), 108.9 (C), 81.6 (CH), 78.2 (CH), 76.0 (CH), 63.0 (CH_2), 38.6 (CH_3), 27.6 (CH_3), 25.4 (CH_3), 17.8 (CH_3), 17.8 (CH_3), 11.7 (C); HRMS-ESI $[M + Na]^+$ Calcd for $C_{19}H_{38}O_6SSiNa$ 445.2045, Found 445.2051.



28

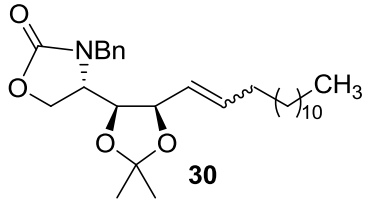
(2*R*,3*R*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-2-*O*-methanesulfonyl-5-hexene-1,2,3,4-tetraol (28) To a solution of silyl ether **27** (7.623 g, 18 mmol) in anhydrous THF (100 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 M, 20 mL, 20 mmol) at 0 ^{o}C and then the mixture was continuously stirred for 20 minutes at room temperature. After the reaction mixture was concentrated in *vacuo*, the resulting yellow syrup residue was purified by flash column chromatography on silica gel using ethyl acetate and hexane (1:1, v/v) as the eluent to afford 4.611 g of a colorless syrup compound **28** in 96% yield: R_f = 0.25 (ethyl acetate/*n*-hexane = 1:1 (v/v)); $[\alpha]^{25}_{D}$ -5.7 (c 0.60, $CHCl_3$); FT-IR (neat) ν_{max} 3526, 2988, 2940, 1639, 1354, 1251, 1219, 1173, 1075, 1043, 971, 925, 872, 801 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 17.8, 9.4, 8.4 Hz, 1H), 5.43-5.35 (m, 2H), 4.68-4.59 (m, 2H), 4.42 (dd, *J* = 7.6, 6.4 Hz, 1H), 3.91-3.79 (m, 2H), 3.14 (s, 3H), 2.43 (brs, 1H), 1.52 (s, 3H), 1.38(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0 (CH), 120.4 (CH_2), 109.3 (C), 82.1 (CH), 78.3 (CH), 76.0 (CH), 61.8 (CH_2), 38.8 (CH_3), 27.5 (CH_3), 25.4 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{10}H_{18}O_6SNa$ 289.0716, Found 289.0713.



29

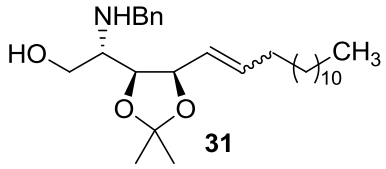
(4*S*)-3-benzyl-4-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-1,3-oxazolidin-2-one (29) To a solution of mesylate **28** (3.201 g, 12.02 mmol) in dry THF (30 mL) was slowly added benzyl isocyanate (1.8 mL, 13.22 mmol) at 0 ℃ and then quickly added NaH (60% dispersion in mineral oil, 1.443 g, 36.06 mmol). After stirring at 0 ℃ for 15 minutes, the reaction mixture was stirred at room temperature for additional 4 h. The reaction mixture was diluted with CH_2Cl_2 and then successively washed with saturated aqueous NH_4Cl, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:2, v/v) obtained 2.951 g of oxazolidinone **29** as a white solid in 81% yield: R_f = 0.18

(ethyl acetate:*n*-hexane = 1:2 (v/v)); mp = 110-111 ^{o}C; $[\alpha]^{24}_{D}$ -1.77 (c 0.11, $CHCl_3$); FT-IR (neat) ν_{max} 3479, 3089, 3064, 3031, 2988, 2935, 1747, 1644, 1606, 1477, 1426, 1382, 1260, 1212, 1166, 1070, 1034, 1016, 936, 879, 762, 704, 679 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 5.60-5.52 (m, 1H), 5.37-5.22 (m, 2H), 4.84 (d, 1H, *J* = 15.6 Hz), 4.66 (t, 1H, *J* = 7.0 Hz), 4.39 (dd, 1H, *J* = 7.4, 2.0 Hz), 4.35 (dd, 1H, *J* = 8.8, 5.2 Hz), 4.21 (d, 1H, *J* = 15.6 Hz), 4.15 (t, 1H, *J* = 8.8 Hz), 3.64-3.60 (m, 1H), 1.54 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (C), 135.8 (C), 132.2 (CH), 128.8 (CH), 127.9 (CH), 127.8 (CH), 119.1 (CH_2), 109.3 (C), 76.8 (C), 74.2 (CH), 62.8 (CH_2), 54.9 (CH), 45.9 (CH_2), 26.4 (CH_3), 24.4 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{17}H_{21}NO_4Na$ 326.1363, Found 326.1366.



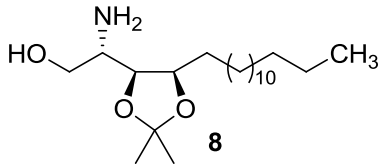
30

(4*S*)-3-benzyl-4-((4*S*,5*R*)-2,2-dimethyl-5-((1*E*/*Z*)-1-tetradecenyl)-1,3-dioxolan-4-yl)-1,3-oxazolidin-2-one (30) To a solution of the alkene **29** (0.525 g, 1.73 mmol) and 1-tetradecene (1.9 ml, 6.93 mmol) in anhydrous CH_2Cl_2 (58 ml) was added Grubbs II catalyst (1 mg, 1.18 μmol) and then the mixture was was heated at reflux for 24 h. The reaction mixture was concentrated in *vacuo* and the resulting yellow syrup residue was purified by flash column chromatography on silica gel using ethyl acetate and hexane (1:4, v/v) as the eluent to get 0.772 g of colorless syrup **30** as a ca. 16:1 mixture of *E*- and *Z*-stereoisomers in 94% yield: R_f = 0.30 (EtOAc:*n*-hexane = 1:3 (v/v)); FT-IR (neat) ν_{max} 2925, 2854, 1751, 1456, 1424, 1382, 1259, 1211, 1165, 1094, 1069, 1035, 994, 883, 761, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 5.79-5.72 (m, 1H), 5.55-5.48 (m, 1H), 5.09 (dd, *J* = 15.4, 7.2 Hz, 1H), 4.99 (t, *J* = 7.7 Hz, 1H), 4.93 (d, *J* = 15.5 Hz, 1H), 4.86 (d, *J* = 15.2 Hz, 1H), 4.64 (t, *J* = 7.4 Hz, 1H), 4.40-4.28 (m, 2H), 4.19-4.09 (m, 2H), 3.60-3.56 (m, 1H), 3.48-3.45 (m, 1H), 1.98-1.96 (m, 2H), 1.52 (s, 3H), 1.34 (s, 3H), 1.25 (brs, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (C), 137.2 (CH), 135.9 (C), 128.8 (CH), 127.9 (CH), 127.8 (CH), 123.5 (CH), 109.0 (C), 74.2 (CH), 62.9 (CH_2), 55.1 (CH), 45.8 (CH_2), 32.4 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 26.4 (CH_3), 24.4 (CH_3), 22.7 (CH_2), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{29}H_{45}NO_4Na$ 494.3241, Found 494.3234.



31

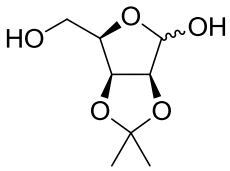
(2*S*,3*S*,4*R*,5*E*)-(-)-2-(*N*-Benzylamino)-3,4-*O*-isopropylidenyl-5-octadecene-1,3,4-triol (31*E*) and (2*S*,3*S*,4*R*,5*Z*)-(+)-2-(*N*-benzylamino)-3,4-*O*-isopropylidenyloctadecene-1,3,4-triol (31*Z*) NaOH (294 mg, 12.20 mmol) was added to a solution of oxazolidinone **30** (410 mg, 0.71 mmol) in MeOH/H_2O (15 mL, 8/1 (v/v)) at 0 ^oC and then the reaction mixture was continuously stirred under reflux condition for 6 h. The reaction mixture was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel using (ethyl acetate/*n*-hexane = 1:3, v/v) furnished 0.632 g of a white solid amino alkenol **31*E*** and a colorless syrup compound **31*Z*** in 94% yield: **31*Z***: R_f = 0.15 (ethyl acetate : *n*-hexane = 1:3 (v/v)); $[\alpha]^{26}_D$ -22.1 (c 0.30, $CHCl_3$); FT-IR (neat) ν_{max} 3452, 2925, 2853, 1467, 1453, 379, 1369, 1245, 1217, 1169, 1061, 972, 875, 735, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H), 5.68 (td, *J* = 10.8, 7.6 Hz, 1H), 5.48 (t, *J* = 10.2 Hz, 1H), 5.01 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.18 (t, *J* = 7.2 Hz, 1H), 3.81-3.68 (m, 4H), 2.80-2.76 (m, 1H), 2.17-2.08 (m, 1H), 2.01-1.93 (m, 1H), 1.47 (s, 3H), 1.37 (s, 3H), 1.30-1.22 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7 (C), 135.5 (CH), 128.4 (CH), 128.2 (CH), 127.2 (CH), 124.9 (CH), 108.4 (C), 77.8 (CH), 73.1 (CH), 60.5 (CH_2), 57.9 (CH), 51.1 (CH), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 27.8 (CH_2), 27.7 (CH_3), 25.3 (CH_3), 22.7 (CH_2), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{28}H_{48}NO_3Na$ 446.3629, Found 446.3624; **31*E***: R_f = 0.20 (ethyl acetate : *n*-hexane = 1:3 (v/v)); mp = 66-67 ^oC; $[\alpha]^{26}_D$ +13.0 (c 0.90, $CHCl_3$); FT-IR (neat) ν_{max} 3454, 2984, 2925, 2853, 1454, 1379, 1369, 1244, 1217, 1166, 1049, 871, 734, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 5.85-5.77 (m, 1H), 5.52 (dd, *J* = 15.2, 8.4 Hz, 1H), 4.62 (dd, *J* = 8.2, 6.4 Hz, 1H), 4.12 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.83-3.63 (m, 4H), 2.79-2.75 (m, 1H), 2.23 (bs, 2H), 2.04 (q, *J* = 6.8 Hz, 2H), 1.46 (s, 3H), 1.35 (s, 3H), 1.34 (bs, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9 (C), 136.5 (CH), 128.4 (CH), 128.1 (CH), 127.2 (CH), 125.2 (CH), 108.3 (C), 78.9 (CH), 77.9 (CH), 60.3 (CH_2), 58.0 (CH), 51.1 (CH_2), 32.5 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 27.8 (CH_3), 25.3 (CH_3), 22.7 (CH_2), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{28}H_{48}NO_3Na$ 446.3629, Found 446.3626.



8

(2*S*,3*S*,4*R*)-(+)-2-Amino-3,4-*O*-isopropylidenyloctadecane-1,3,4-triol (8) 10% Pd/C (0.101 g) was added to a solution of alkene **31** (0.490 g, 1.10 mmol) in EtOH (11 mL). The reaction mixture was stirred under hydrogen (50 psi) at room temperature for 4 h. The Pd/C was removed through a short pad of SiO_2/Celite and the filter was washed with ethyl acetate. The filtrate was concentrated in *vacuo* to obtain 0.389 g of **8** as a colorless syrup in 99% yield: R_f = 0.13 ($MeOH/CH_2Cl_2$ = 1:1 (v/v)); $[\alpha]^{25}_D$ +31.7 (c 0.15, $CHCl_3$); FT-IR (neat) ν_{max} 3361, 3305, 2985, 2923, 2853, 1465, 1378, 1368, 1246, 1218, 1166, 1064, 873, 720 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 4.18-4.14 (m, 1H), 3.92 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.76 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.50 (dd, *J* = 10.8, 6.8 Hz, 1H), 2.89-2.85 (m, 1H), 1.55 (m, 2H), 1.39 (s, 3H), 1.31 (s, 3H), 1.29 (brs, 24H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 107.8 (C), 78.5 (CH), 77.6 (CH), 63.9 (CH_2), 51.4 (CH), 31.7 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 27.2 (CH_3), 25.8 (CH_2), 24.7 (CH_3), 22.3 (CH_2), 13.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{21}H_{43}NO_3Na$ 380.3135, Found 380.3136.

Procedures of Large Scale for Preparing Compound 8



2,3-*O*-isopropylidene-α-D-lyxofuranose (24) To a stirred suspension of D-(-)-lyxose (50.000 g, 0.33 mol) in anhydrous acetone (1.7 L, 0.2 M) was added dropwise conc. H_2SO_4 (1.78 mL, 0.33 x 10^{-1} mol) at 0 °C. After stirring at 0 °C for 10 min, the reaction mixture was continually stirred at room temperature for additional 2 h until a clear solution was achieved. The mixture was neutralized with solid $Ba(OH)_2$ at 0 °C. The solid was filtered out through a short pad of Celite and the Celite pad was washed with ethyl acetate. The filtrate was concentrated under reduced pressure to give a colorless syrup residue. The residue was purified via flash column chromatography on silica gel using ethyl acetate and *n*-hexane (2:1 v/v) as

the eluent to obtain 50.667 g of white solid **15** as a ca. 1.0:15.0 mixture of α- and β-stereoisomers in 80% yield: R_f = 0.35 (ethyl acetate).

2,3-*O*-Isopropylidenyl-5-*O*-triisopropylsilyl-D-lyxofuranose (25) To a stirred solution of **24** (47.653 g, 0.25 mol) and imidazole (34.109 g, 0.50 mmol) in anhydrous CH_2Cl_2 (1.7 L) was added chlorotriisopropylsilane (58.51 mL, 0.28 mol) at 0 ^oC. After 10 minutes, the reaction mixture was stirred for additional 1.5 h at room temperature. The reaction mixture was carefully quenched with dry MeOH (16 mL) to destroy the unreacted chlorotriisopropylsilane and concentrated in *vacuo*. The resulting residue was dissolved in CH_2Cl_2 and then successively washed with 1N cold aqueous HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The produced brown syrup was purified by flash column chromatography on silica (EtOAc/*n*-hexane = 1:6, v/v) to give 78.326 g of a white solid silyl ether **25** as a ca. 1.0:15.0 mixture of α- and β-stereoisomers in 90% yield: R_f = 0.33 (ethyl acetate:*n*-hexane = 1:5 (v/v)).

(2*R*,3*S*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-1-*O*-triisopropylsilyl-5-hexene-1,2,3,4-tetraol (26) A solution of methyltriphenylphosphonium bromide (144.652 g, 0.40 mol) in dry THF (1.4 L)was treated with potassium *tert*-butoxide (36.305 g, 0.32 mmol) at 0 ℃. The reaction mixture was kept stirring at the same temperature for 1 h and then a solution of **25** (70.300 g, 0.20 mol) in dry THF (280 mL) was slowly added to the above solution. After stirring at 0 ℃ for 20 minutes, the reaction mixture was stirred at room temperature for additional 1 h. The resulting precipitate was filtered out and washed with ether. The filtrate was washed with saturated aqueous NH_4Cl, and brine, dried over $MgSO_4$, filtered and evaporated under reduced pressure to give a yellow syrup. Purification of this syrup via flash column chromatography on silica gel using hexane and ethyl acetate (60:1 → 6:1, v/v) as the eluent produced 55.916 g of a colorless syrup **26** in 80% yield: R_f = 0.38 (ethyl acetate:*n*-hexane = 1:15 (v/v))

(2*R*,3*R*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-2-*O*-methanesulfonyl-1-*O*-triisopropylsilyl-5-hexene-1,2,3,4-tetraol (27) To a solution of **26** (49.970 g, 0.14 mol) in dry pyridine (483 mL) was added dropwise methanesulfonyl chloride (34 mL, 0.43 mol) at 0℃. The reaction mixture was stirred at room temperature for 1 h and concentrated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and then successively washed with 1N cold aqueous HCl, saturated aqueous K_2CO_3, and brine. The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The

produced brown syrup was purified by flash column chromatography on silica (EtOAc/*n*-hexane = 1:25, v/v) to afford 57.004 g of sulfonate compound **27** as a colorless syrup in 93% yield.

(2*R*,3*R*,4*R*)-(-)-3,4-*O*-Isopropylidenyl-2-*O*-methanesulfonyl-5-hexene-1,2,3,4-tetraol (28) To a solution of silyl ether **27** (52.300 g, 0.12 mol) in anhydrous THF (412 mL) was added a solution of tetrabutylammonium fluoride in THF (1.0 M, 124 mL, 1.3 mol) at 0 ^{o}C and then the mixture was continuously stirred for 20 minutes at room temperature. After the reaction mixture was concentrated in *vacuo*, the resulting yellow syrup residue was purified by flash column chromatography on silica gel using ethyl acetate and hexane (1:1, v/v) as the eluent to afford 28.284 g of a colorless syrup compound **28** in 86% yield: R_f = 0.25 (ethyl acetate/*n*-hexane = 1:1 (v/v)).

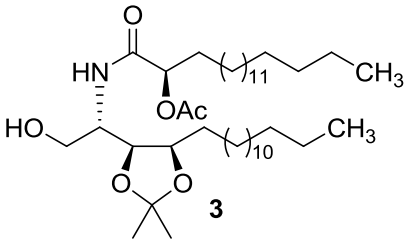
(4*S*)-3-benzyl-4-((4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl)-1,3-oxazolidin-2-one (29) To a solution of mesylate **28** (20.168 g, 76 mmol) in dry THF (189 mL) was slowly added benzyl isocyanate (10 mL, 83 mmol) at 0 ℃ and then quickly added NaH (60% dispersion in mineral oil, 9.098 g, 227 mmol). After stirring at 0 ℃ for 15 minutes, the reaction mixture was stirred at room temperature for additional 4 h. The reaction mixture was diluted with CH_2Cl_2 and then successively washed with saturated aqueous NH_4Cl, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel (EtOAc/*n*-hexane = 1:2, v/v) obtained 19.068 g of oxazolidinone **29** as a white solid in 83% yield: R_f = 0.18 (ethyl acetate:*n*-hexane = 1:2 (v/v)).

(4*S*)-3-benzyl-4-((4*S*,5*R*)-2,2-dimethyl-5-((1*E*/*Z*)-1-tetradecenyl)-1,3-dioxolan-4-yl)-1,3-oxazolidin-2-one (30) To a solution of the alkene **29** (15.333 g, 50.60 mmol) and 1-tetradecene (55 mL, 0.20 mol) in anhydrous CH_2Cl_2 (633 mL) was added Grubbs II catalyst (90 mg, 0.11 mmol) and then the mixture was was heated at reflux for 28 h. The reaction mixture was concentrated in *vacuo* and the resulting yellow syrup residue was purified by flash column chromatography on silica gel using ethyl acetate and hexane (1:4, v/v) as the eluent to get 22.653 g of colorless syrup **30** as a ca. 16:1 mixture of *E*- and *Z*-stereoisomers in 95% yield: R_f = 0.30 (EtOAc:*n*-hexane = 1:3 (v/v)).

(2*S*,3*S*,4*R*,5*E*)-(-)-2-(*N*-Benzylamino)-3,4-*O*-isopropylidenyl-5-octadecene-1,3,4-t

riol (31*E*) and (2*S*,3*S*,4*R*,5*Z*)-(+)-2-(*N*-benzylamino)-3,4-*O*-isopropylidenylocta-decene-1,3,4-triol (31*Z*) NaOH (25.928 g, 0.65 mol) was added to a solution of oxazolidinone **30** (17.769 g, 37.67 mmol) in MeOH/H_2O (796 mL, 8/1 (v/v)) at 0 °C and then the reaction mixture was continuously stirred under reflux condition for 6 h. The reaction mixture was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the resulting yellow syrup residue via flash column chromatography on silica gel using (ethyl acetate/*n*-hexane = 1:3, v/v) furnished 15.782 g of a white solid amino alkenol **31*E*** and a colorless syrup compound **31*Z*** in 94% yield: **31*Z***: R_f = 0.15 (ethyl acetate : *n*-hexane = 1:3 (v/v)).

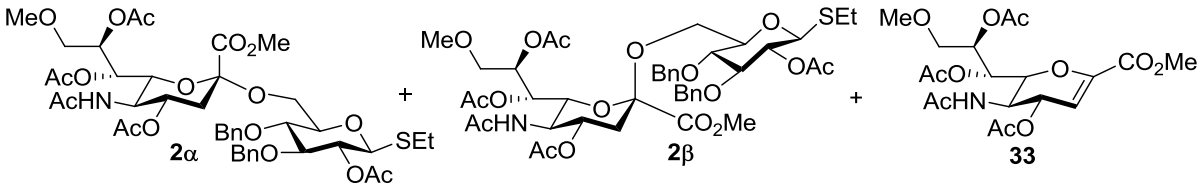
(2*S*,3*S*,4*R*)-(+)-2-Amino-3,4-*O*-isopropylidenyloctadecane-1,3,4-triol (8) 10% Pd/C (0.892 g) was added to a solution of alkene **31** (15.782 g, 35.41 mmol) in EtOH (354 mL). The reaction mixture was stirred under hydrogen balloon at room temperature for 9 h. The Pd/C was removed through a short pad of SiO_2/Celite and the filter was washed with ethyl acetate. The filtrate was concentrated in *vacuo* to obtain 12.465 g of **8** as a colorless syrup in 99% yield: R_f = 0.13 (MeOH/CH_2Cl_2 = 1:1 (v/v)).



3

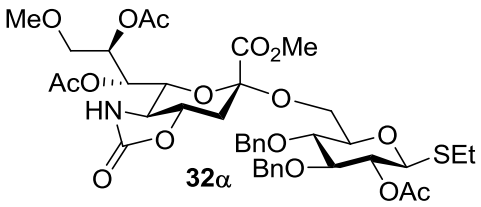
(2*R*)-1-(((1*S*)-1-((4*S*,5*R*)-2,2-Dimethyl-5-tetradecyl-1,3-dioxolan-4-yl)-2-hydroxy ethyl)amino)-1-oxooctadecan-2-yl ethanoate (3) Amino **8** (0.182 g, 0.50 mmol) and succinimidyl ester **7** (0.240 g, 0.55 mmol) was dissolved in THF (10 mL) and then Et_3N (0.16 mL, 1.15 mmol) was slowly added to the above solution at 0 °C. After being stirred for 4 h at room temperature, the reaction mixture was concentrated under reduced pressure. Purification of the syrup crude product via flash column chromatography on silica gel using EtOAc/*n*-hexane (1:3, v/v) as the eluent observed 0.320 g of a white solid amide **3** in 94% yield: R_f = 0.43 (EtOAc:*n*-hexane = 1:1 (v / v)); mp = 83-84 °C; $[\alpha]^{26}_D$ +23.9 (c 0.30, $CHCl_3$); FT-IR (neat) ν_{max} 3446, 2917, 2850, 1743, 1654, 1559, 1533, 1467, 1457, 1377, 1236, 1065, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.55 (d, 1H, *J* = 8.8 Hz), 5.10 (dd, 1H, *J* = 7.0, 5.2 Hz), 4.18-4.13 (m, 2H), 4.08-4.05 (m, 1H), 3.88 (dd, *J* = 11.0, 2.8 Hz, 1H),

3.62 (dd, *J* = 11.0, 2.4 Hz, 1H), 2.61 (brs, 1H), 1.84-1.77 (m, 2H), 1.51 (brs, 1H), 1.45 (s, 3H), 1.33 (s, 3H), 1.24 (brs, 52H), 0.86 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9 (C), 169.9 (C), 108.2 (C), 77.9 (CH), 77.7 (CH), 74.3 (CH), 63.0 (CH_2), 49.9 (C), 31.9 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.5 (CH_3), 26.8 (CH_2), 25.2 (CH_3), 24.9 (CH_2), 22.7 (CH_2), 21.0 (CH_3), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{41}H_{79}NO_6Na$ 704.5786, Found 704.5800.

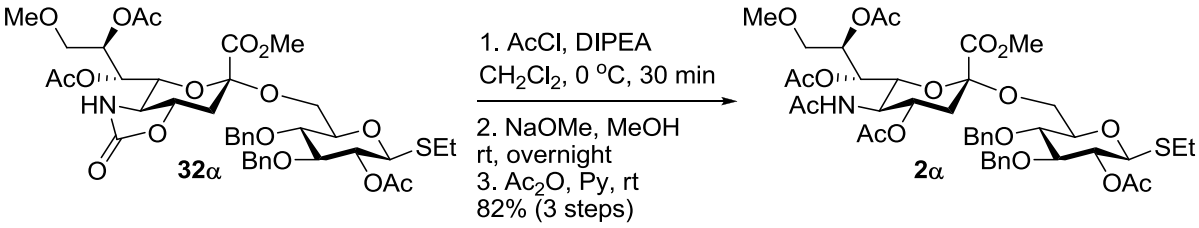


Ethyl (methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-β-D-glucopyranoside (2α) and β-isomer (2β) A mixture of the thiosialoside **4** (0.566 g, 0.98 mmol), and glucopyranoside acceptor **6** (0.436 g, 0.98 mmol), and activated 3 Å powdered molecular sieves (0.980 g, 1.000 g/mmol) in anhydrous THF (9.8 mL) was stirred at room temperature for 1 h under nitrogen to remove any trace amounts of water. The reaction mixture was then cooled to -40 ℃ followed by addition of AgOTf (0.378 g, 1.47 mmol). After being kept stirring at the same temperature for 1.5 h, the reaction mixture was carefully quenched with triethylamine and then filtered through a short pad of Celite. The filtrate was washed with cold saturated aqueous Na_2CO_3, cold saturated aqueous $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The produced yellow syrup residue was purified by flash column chromatography on silica (EtOAc) to afford 402 mg of a white solid disaccharide **2α** in 46% yield, 131 mg of a colorless syrup disaccharide **2β** in 15% yield, and 131 mg of a colorless syrup glycal **33** in 30% yield: **2α**: R_f = 0.4 (EtOAc); mp = 83-84 °C; $[\alpha]^{26}_D$ -11.3 (c 0.10, $CHCl_3$); FT-IR (neat) ν_{max} 3447, 1744, 1685, 1654, 1647, 1637, 1370, 1229, 1129, 1035, 753, 721, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 10H), 5.36-5.30 (m, 2H), 5.10 (d, *J* = 9.6 Hz, 1H), 4.90-4.84 (m, 1H), 4.82-4.64 (m, 4H), 4.33 (d, *J* = 10.0 Hz, 1H), 4.14 (dd, *J* = 11.0, 4.4 Hz, 1H), 4.09-4.02 (m, 2H), 3.75 (s, 3H), 3.72 (t, *J* = 11.2 Hz, 1H), 3.62 (t, *J* = 9.0 Hz, 1H), 3.60 (d, *J* = 11.2 Hz, 1H), 3.50 (dd, *J* = 11.0, 2.4 Hz, 1H), 3.42 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.27 (s, 3H), 3.23 (dd, *J* = 10.8, 4.4 Hz, 1H), 2.73-2.59 (m, 3H), 2.13 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.86 (s, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0

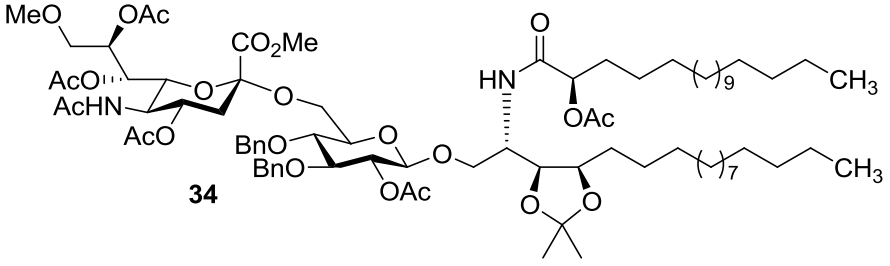
(C), 170.3 (C), 170.1 (C), 170.0 (C), 169.7 (C), 167.9 (C), 138.2 (C), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 98.7 (C), 84.1 (CH), 83.5 (CH), 78.2 (CH), 77.4 (CH), 75.2 (CH_2), 75.1 (CH_2), 72.4 (CH), 71.7 (CH), 71.0 (CH_2), 69.1 (CH), 68.6 (CH), 67.5 (CH), 63.5 (CH_2), 59.1 (CH_3), 52.8 (CH_3), 49.4 (CH), 38.1 (CH_2), 24.1 (CH_2), 23.2 (CH_3), 21.3 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.7 (CH_3), 15.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{43}H_{57}NO_{17}SNa$ 914.3237, Found 914.3239; **2β**: R_f = 0.5 (EtOAc); $[\alpha]^{25}_D$ +3.0 (c 0.10, $CHCl_3$); FT-IR (neat) ν_{max} 2930, 1747, 1688, 1547, 1530, 1498, 1453, 1371, 1229, 1120, 1085, 1038, 943, 753, 699, 667, 604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 10H), 5.91 (d, *J* = 10.0 Hz, 1H), 5.33 (dd, *J* = 3.6, 2.4 Hz, 1H), 5.27-5.18 (m, 2H), 4.98 (t, *J* = 9.6 Hz, 1H), 4.85-4.67(m, 4H), 4.43 (d, *J* = 10.0 Hz, 1H), 4.32 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.16 (q, *J* =10.4 Hz, 1H), 3.97 (dd, *J* = 11.0, 2.8 Hz, 1H), 3.83 (t, *J* = 9.4 Hz, 1H), 3.77-3.77 (m, 2H), 3.69 (s, 3H), 3.66 (t, *J* = 9.8 Hz, 1H), 3.49-3.44 (m, 2H), 3.33 (s, 3H), 2.76 (dd, *J* = 14.8, 7.2 Hz, 2H), 2.45 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.91 (t, *J* = 12.2 Hz, 1H), 1.86 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 (C), 170.5 (C), 170.4 (C), 170.1 (C), 169.5 (C), 167.1 (C), 138.1 (C), 138.0 (C), 128.4 (CH), 127.9 (CH), 127.9 (CH), 127.8 (CH), 127.8 (CH), 97.7 (C), 83.9 (CH), 83.9 (CH), 77.6 (CH), 76.8 (CH), 75.2 (CH_2), 75.0 (CH_2), 72.8 (CH), 71.9 (CH), 71.6 (CH), 71.1 (CH_2), 69.2 (CH), 68.8 (CH), 60.5 (CH_2), 59.0 (CH_3), 52.6 (CH_3), 48.6 (CH), 37.1 (CH_2), 24.5(CH_2), 23.1(CH_3), 21.1(CH_3), 20.9 (CH_3), 20.8 (CH_3), 14.7 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{43}H_{57}NO_{17}SNa$ 914.3228, Found 914.3239; **33**: R_f = 0.3 (EtOAc); $[\alpha]^{26}_D$ +6.1 (c 0.10, $CHCl_3$); FT-IR (neat) ν_{max} 1746, 1662, 1540, 1438, 1373, 1222, 1139, 1111, 1030, 976, 855, 760, 640 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01 (d, *J* = 3.6 Hz, 1H), 5.79 (d, *J* = 8.4 Hz, 1H), 5.51 (t, *J* = 4.2 Hz, 1H), 5.45-5.42 (m, 1H), 5.30-5.26 (m, 1H), 4.45-4.38 (m, 2H), 3.84 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.79 (s, 3H), 3.48 (dd, *J* = 11.0, 6.4 Hz, 1H), 3.36 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8 (C), 170.3 (C), 170.2 (C), 170.0 (C), 161.7 (C), 145.0 (C), 107.8 (CH), 76.8 (CH), 71.1 (CH), 70.0 (CH_2), 68.0 (CH), 67.6 (CH), 59.1 (CH_3), 52.6 (CH_3), 46.4 (CH), 23.2 (CH_3), 21.0 (CH_3), 20.9 (CH_3), 20.8 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{19}H_{27}NO_{11}Na$ 468.1476, Found 468.1470.



Ethyl (methyl 7,8-di-*O*-acetyl-4,5-N,O-carbonyl-3,5-dideoxy-9-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-β-D-glucopyranoside (32α) A mixture of the thiosialoside **5** (0.030 g, 0.056 mmol), and glucopyranoside acceptor **6** (0.048 g, 0.012 mmol), and activated 3 Å powdered molecular sieves (0.080 g, 1.000 g/mmol) in anhydrous CH_2Cl_2 (1.1 mL) was stirred at room temperature for 1 h under nitrogen to remove any trace amounts of water. The reaction mixture was then cooled to -40 ℃ followed by addition of AgOTf (0.025 g, 0.096 mmol). After being kept stirring at the same temperature for 18 h, the reaction mixture was carefully quenched with triethylamine and then filtered through a short pad of Celite. The filtrate was washed with cold saturated aqueous Na_2CO_3, cold saturated aqueous $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The produced yellow syrup residue was purified by flash column chromatography on silica (EtOAc/*n*-hexane = 1:1.5, v/v) to afford 40 mg of disaccharide **32α** as a white solid α-stereoisomer in 93% yield: R_f = 0.4 (EtOAc:*n*-hexane = 1:1, v/v); mp = 71-72 ^oC; $[\alpha]^{25}_D$ +0.1 (c 0.15, $CHCl_3$); FT-IR (neat) ν_{max} 3402, 3029, 2930, 1782, 1747, 1455, 1372, 1300, 1225, 1151, 1084, 1082, 921, 754, 700, 667, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 10H, ArH), 5.42-5.38 (m, 1H, H-8), 5.35 (s, 1H, NH), 5.23 (dd, *J* = 10.0, 1.6 Hz, H-7, 1H), 4.99 (t, *J* = 9.4 Hz, H-12, 1H), 4.79-4.64 (m, 4H, $ArCH_2$), 4.34 (d, *J* = 10.0 Hz, H-11, 1H), 4.23 (dd, *J* = 9.8, 2.0 Hz, H-6, 1H), 4.10 (dd, *J* = 11.0, 4.8 Hz, H-16, 1H), 3.96-3.90 (m, H-4, 1H), 3.73 (s, 3H, COOMe), 3.67-3.63 (m, H-14, H-13, 2H), 3.56 (dd, *J* = 11.0, 1.6 Hz, H-16, 1H), 3.48 (dd, *J* = 11.4, 2.0 Hz, H-9, 1H), 3.45-3.42 (m, H-15, 1H), 3.33-3.29 (m, H-9', 1H), 3.29 (s, OMe, 3H), 3.01 (t, *J* = 10.4 Hz, H-, 1H 5), 2.95 (dd, *J* = 11.8, 3.6 Hz, H-3, 1H), 2.71-2.64 (m, S*CH*$_2$CH$_3$, 2H), 2.16 (s, Ac, 3H), 2.03 (t, *J* = 13.0 Hz, H-3', 1H), 1.97 (s, Ac, 3H), 1.27 (t, *J* = 7.4 Hz, SCH_2*CH*$_3$, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (C),170.1 (C), 169.8 (C), 168.2 (C), 159.4 (C), 100.3 (C), 138.3 (CH), 128.5 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 84.3 (CH), 83.7 (CH), 77.6 (CH), 73.7 (CH), 71.8 (CH), 69.2 (CH), 67.9 (CH), 58.1 (CH), 75.3 (CH_2), 75.1 (CH_2), 70.8 (CH_2), 64.3 (CH_2), 59.6 (CH_3), 53.0 (CH_3), 37.6 (CH_2), 24.3 (CH_2), 21.3 (CH_3), 21.1 (CH_3), 20.1 (CH_3), 15.2 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{40}H_{51}NO_{16}SNa$ 856.2821, Found 856.2831.

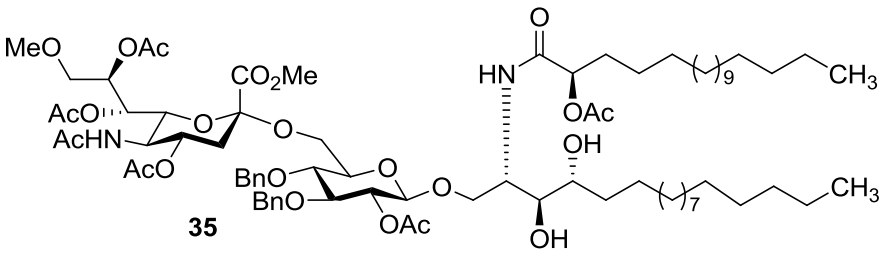


Ethyl (methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-β-D-glucopyranoside (2α) To a stirred solution of compound **32α** (0.010 g, 0.012 mmol) in dry CH_2Cl_2 (1.2 mL) was successively added EtN(*i*-Pr)$_2$ (0.021 mL, 0.120 mmol), and AcCl (0.009 mL, 0.120 mmol) at 0 °C. After stirring at 0 °C for 30 minutes, the reaction mixture was concentrated in *vacuo* to observe a brown syrup residue (R_f= 0.25 (EtOAc:CH_2Cl_2 = 1:6, v/v)). The brown syrup residue was taken forward to the next step reaction without further purication. A solution of brown syrup residue in anhydrous MeOH (1.2 mL) was treated with MeONa (0.006 g, 0.120 mmol) at 0 °C and then the reaction mixture was heated at 50 °C. After the reaction was complete, monitored by TLC, the solution was neutralized with Dowex 50w X 8 [H^+]. The resin was filtered out and washed with MeOH. The filtrate was concentrated under reduced pressure to give a brown syrup residue (R_f = 0.10 (EtOAc)). The residue was taken forward to the next step reaction without further purification. The brown residue was dissolved in dry pyridine (1.2 mL) and then treated with acetic anhydride (0.007 mL, 0.072 mmol) at 0 °C. The mixture was warmed to room temperature and continuously stirred at this temperature for 24 h. The reaction mixture was carefully quenched with dry MeOH (5.0 mL) to destroy the unreacted acetic anhydride and the concentrated in *vacuo*. The observed brown syrup was purified by flash column chromatography on silica gel using ethyl acetate and CH_2Cl_2 (1:1 (v/v) as the eluent to give 9 mg of disaccharide **2α** (R_f= 0.18 (ethyl acetate/CH_2Cl_2 = 1/1, v/v) as a white solid compound in 82% yield over three steps.



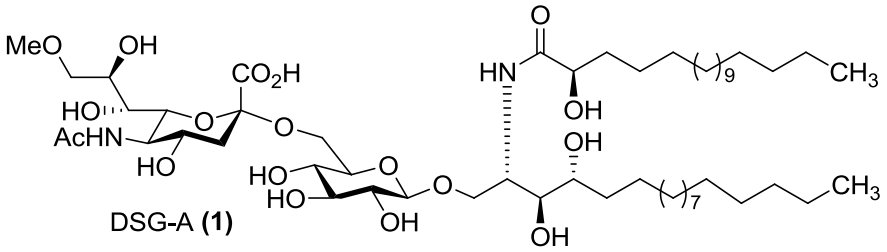
(Methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)-2- *O*-acetyl-3,4-di-*O*-benzyl-β-D-gluco

pyranoside (1→1)-(2*S*,3*S*,4*R*)-2-(1-[(2*R*)-2-acetoxy-1-oxoctadecyl]amino)-3,4-*O*-isopropylidenyloctadecane-1,3,4-triol (34) A mixture of the disaccharide donor **2α** (0.140 g, 0.16 mmol), phytoceramide derivative **3** (0.118 g, 0.17 mmol), and activated 3 Å powdered molecular sieves (170 mg, 1.000 g/mmol) in anhydrous CH_2Cl_2 (7.9 mL) was stirred at room temperature for 1 h under nitrogen to remove any trace amounts of water. The reaction mixture was then cooled to -70 °C followed by addition of *N*-iodosuccinimide (88 mg, 0.39 mmol) and AgOTf (40 mg, 0.16 mmol). After being kept stirring at the same temperature for 2 h, the reaction mixture was carefully quenched with triethylamine and then filtered through a short pad of Celite. The filtrate was washed with cold saturated aqueous Na_2CO_3, cold saturated aqueous $Na_2S_2O_3$, and brine, dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The produced yellow syrup residue was purified by flash column chromatography on silica (EtOAc/CH_2Cl_2 = 1:2, v/v) to obtain 237 mg of a colorless syrup ganglioside **34** as a β-stereoisomer in 82% yield: R_f = 0.28 (EtOAc/CH_2Cl_2 = 1:1 (v/v)); $[\alpha]^{26}_D$ +10.0 (c 0.10, $CHCl_3$); FT-IR (neat) ν_{max} 3323, 2925, 2854, 1748, 1666, 1531, 1455, 1370, 1231, 1040, 727, 663, 582 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 10H), 6.22 (d, *J* = 8.4 Hz, 1H), 5.32 (brs, 2H), 5.10-5.05 (m, 2H), 4.93-4.84 (m, 3H), 4.74 (t, *J* = 10.0 Hz, 2H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.31 (d, *J* = 8.0 Hz, 1H), 4.20-3.99 (m, 7H), 3.76 (s, 3H), 3.74 (t, *J* = 9.6 Hz, 1H), 3.61-3.56 (m, 3H), 3.48-3.42 (m, 2H), 3.27 (s, 3H), 3.18 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.65 (dd, *J* = 12.8, 4.8 Hz, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 1.95 (t, *J* = 11.8 Hz, 1H), 1,92 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H), 1.80-1.78 (m, 2H), 1.51 (brs, 2H), 1.42 (s, 3H), 1.33 (s, 3H), 1.25 (brs, 52H), 0.88 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 (C), 170.3 (C), 170.0 (C), 169.9 (C), 169.9 (C), 169.4 (C), 169.4 (C), 168.0 (C), 138.2 (C), 128.4 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 108.0 (C), 101.0 (CH), 98.7 (C), 82.5 (CH), 77.7 (CH), 75.8 (CH), 75.0 (CH_2), 74.9 (CH_2), 74.2 (CH), 74.0 (CH), 73.1 (CH), 72.5 (CH), 70.9 (CH_2), 69.0 (CH), 68.9 (CH_3), 68.4 (CH), 67.5 (CH), 59.2 (CH_3), 52.8 (CH_3), 49.4 (CH), 48.0 (CH), 31.9 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.1 (CH_3), 26.6 (CH_2), 25.8 (CH_3), 24.8 (CH_2), 23.2 (CH_3), 22.7 (CH_2), 21.3 (CH_3), 21.1 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.6 (CH_3), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{82}H_{130}N_2O_{23}Na$ 1533.8953, Found 1533.8957.



35

(Methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→6)-2- *O*-acetyl-3,4-di-*O*-benzyl-β-D-gluco pyranoside (1→1)-(2*S*,3*S*,4*R*)-2-(1-[(2*R*)-2-acetoxy-1-oxooctadecyl]amino) octadecane-1,3,4-triol (35) The isopropylidene acetal **34** (40 mg, 26.00 μmol) was dissolved in a solution of 80% aqueous AcOH (3.3 mL) at 0 ^{o}C and then the mixture was continuously stirred for 3 h at 85 ^{o}C. The reaction mixture was co-evaporated with toluene. Purification of the got syrup crude product via flash column chromatography on silica gel (EtOAc/*n*-hexane = 3:1, v/v) afforded 35 mg of **35** as a colorless syrup compound in 90% yield: R_f= 0.13 (EtOAc/*n*-hexane = 3:1 (v/v)); $[\alpha]^{25}_{D}$ +18.3 (c 0.10, $CHCl_3$); FT-IR (neat) ν_{max} 3365, 2924, 2853, 1748, 1663, 1558, 1540, 1498, 1456, 1370, 1231, 1129, 1074, 1040, 751, 699, 605 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 10H), 6.54 (d, *J* = 8.8 Hz, 1H), 5.33 (brs, 2H), 5.15-5.09 (m, 2H), 4.92-4.86 (m, 2H), 4.82-4.62 (m, 4H), 4.35 (d, *J* = 7.6 Hz, 1H), 4.18-4.00 (m, 5H), 3.77 (s, 3H), 3.72-3.41 (m, 8H), 3.27 (s, 3H), 3.20 (dd, *J* = 11.0, 7.2 Hz, 1H), 2.61 (dd, *J* = 12.6, 4.0 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H), 1.82-1.80 (m, 2H), 1.62-1.24 (m, 60H), 0.87 (t, *J* = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9 (C), 170.3 (C), 170.1 (C), 170.0 (C), 169.7 (C), 169.6 (C), 167.9 (C), 138.1 (C), 138.0 (C), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 100.9 (CH), 98.7 (C), 82.2 (CH), 77.8 (CH), 75.1 (CH_2), 74.0 (CH), 73.5 (CH), 72.9 (CH), 72.5 (CH), 72.1 (CH), 71.0 (CH_2), 68.9 (CH), 68.5 (C), 67.5 (CH), 63.5 (C), 59.2 (CH_3), 52.9 (CH_3), 49.9 (CH_3), 49.4 (C), 27.8 (CH_2), 32.0 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.0 (C), 24.8 (C), 23.2 (CH_3), 22.7 (CH_2), 21.3 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.8 (CH_3), 20.6 (CH_3), 14.1 (CH_3), 14.1 (CH_3); HRMS-ESI $[M + Na]^+$ Calcd for $C_{79}H_{126}N_2O_{23}Na$ 1493.8644, Found 1493.8623.

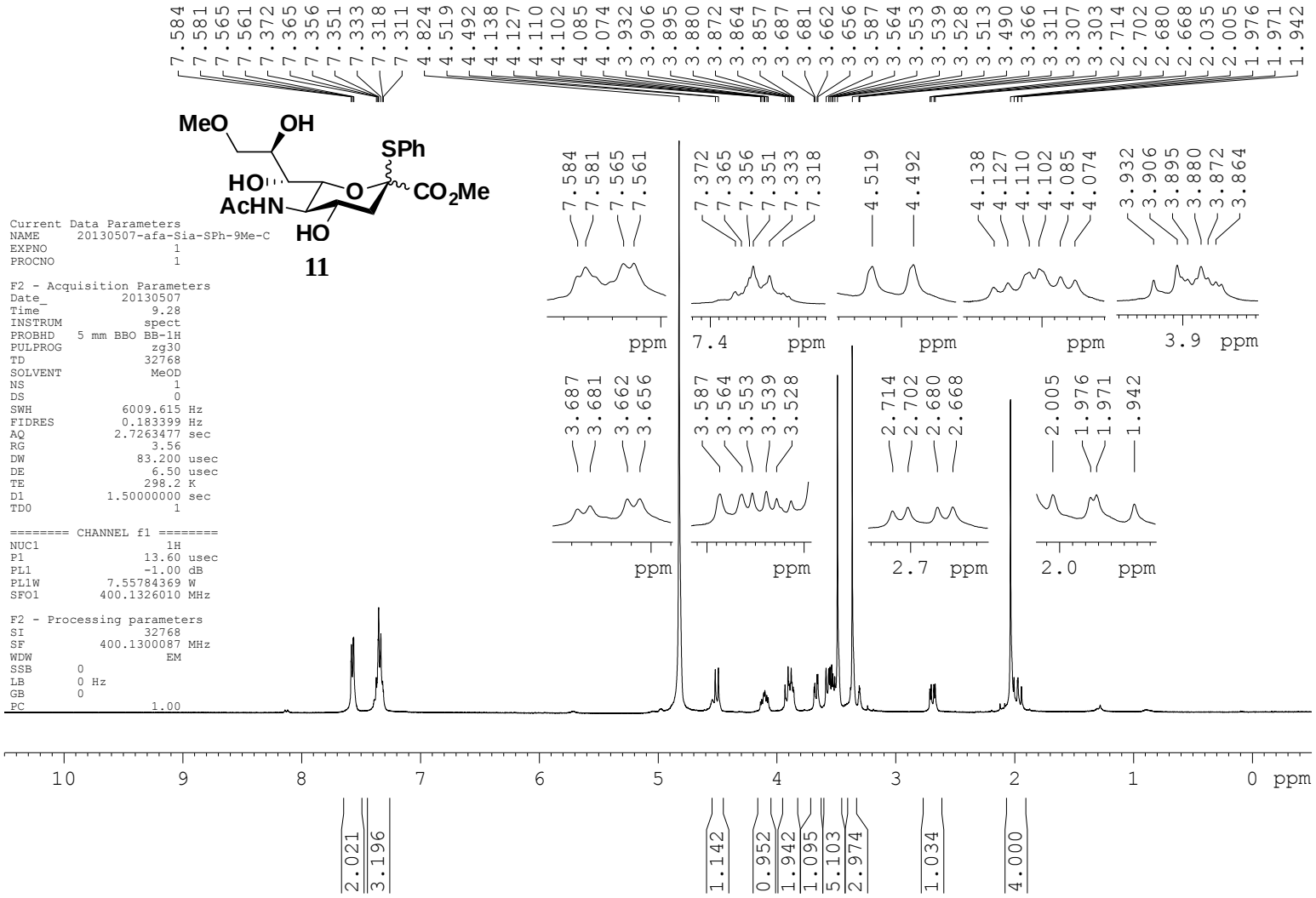


DSG-A (**1**)

Synthesis of Target Compound DSG-A (1) To a solution of ganglycoside derivative **35** (40 mg, 27.00 μmol) in EtOAc (2.7 mL) was added 20% $Pd(OH)_2/C$ (10 mg) at room temperature. The reaction mixture was stirred under hydrogen (50 psi) at room temperature for 1 h. The $Pd(OH)_2/C$ was removed through a short pad of SiO_2/Celite and the filter was washed with EtOAc. The filtrate was concentrated in *vacuo*. The resulting colorless syrup tetraol, without further purification, was dissolved in dry MeOH (0.27 mL) and then MeONa (1 mg, 0.027 mmol) was added to this solution at 0 ^oC. After stirring for 1.5 h at room temp, H_2O was added to the reaction mixture. After completing the soapnification, the solution was neutralized with Dowex 50w X 8 [H^+]. The resin was filtered out and washed with MeOH/CH_2Cl_2 (2:1, v/v). The filtrate was concentrated under reduced pressure to give a white solid residue. After recrystallization (MeOH/CH_2Cl_2/EtOAc) of the afforded residue, the residue retaining in mother liquor was purified by flash column chromatography on silica gel (MeOH/CH_2Cl_2 = 1:2 (v/v)) to yield 28 mg of DSG-A (**1**) as a white solid compound in 96% yield: R_f = 0.13 (MeOH/CH_2Cl_2 = 1:2 (v/v)); ^{1}H NMR (800 MHz, $CD_3OD/CDCl_3$ = 2:1, v/v) δ 4.17 (d, *J* = 8.0 Hz, 1H), 4.11-4.09 (m, 1H), 3.99-3.95 (m, 2H), 3.92 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.88-3.86 (m, 1H), 3.66-3.56 (m, 6H), 3.49 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.46-3.43 (m, 2H), 3.41-3.37 (m, 2H), 3.29 (s, 3H), 3.28 (t, *J* = 9.6 Hz, 1H), 3.25-3.24 (m, 1H), 3.12 (dd, *J* = 8.8, 8.0 Hz, 1H), 2.74 (dd, *J* = 12.4, 4.0 Hz, 1H), 1.94 (s, 3H), 1.68-1.64 (m, 1H), 1.56-1.49 (m, 4H), 1.23-1.18 (brs, 52H), 0.80 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR(200 MHz, $CD_3OD/CDCl_3$ = 2:1, v/v) δ 176.8 (C), 175.4 (C), 174.1 (C), 104.3 (CH), 101.2 (C), 77.1 (CH), 76.0 (CH), 74.8 (CH_2), 74.7 (CH), 74.6 (CH), 73.9 (CH), 72.8 (CH), 72.7 (CH), 71.1 (CH), 70.8 (CH), 70.0 (CH_2), 69.9 (CH), 69.0 (CH), 63.6 (CH_2), 59.4 (CH_3), 53.9 (CH), 51.3 (CH), 42.1 (CH_2), 35.5 (CH_2), 32.8 (CH_2), 32.8 (CH_2), 32.3 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 30.6 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 26.9 (CH_2), 26.0 (CH_2), 23.5 (CH_2), 22.6 (CH_3), 14.4 (CH_3); HRMS-ESI [M – H]$^-$ Calcd for $C_{54}H_{101}N_2O_{18}Na$ 1065.7065, Found 1065.7059.

References

1. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed; Pergamon Press: New York, 1980.
2. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 29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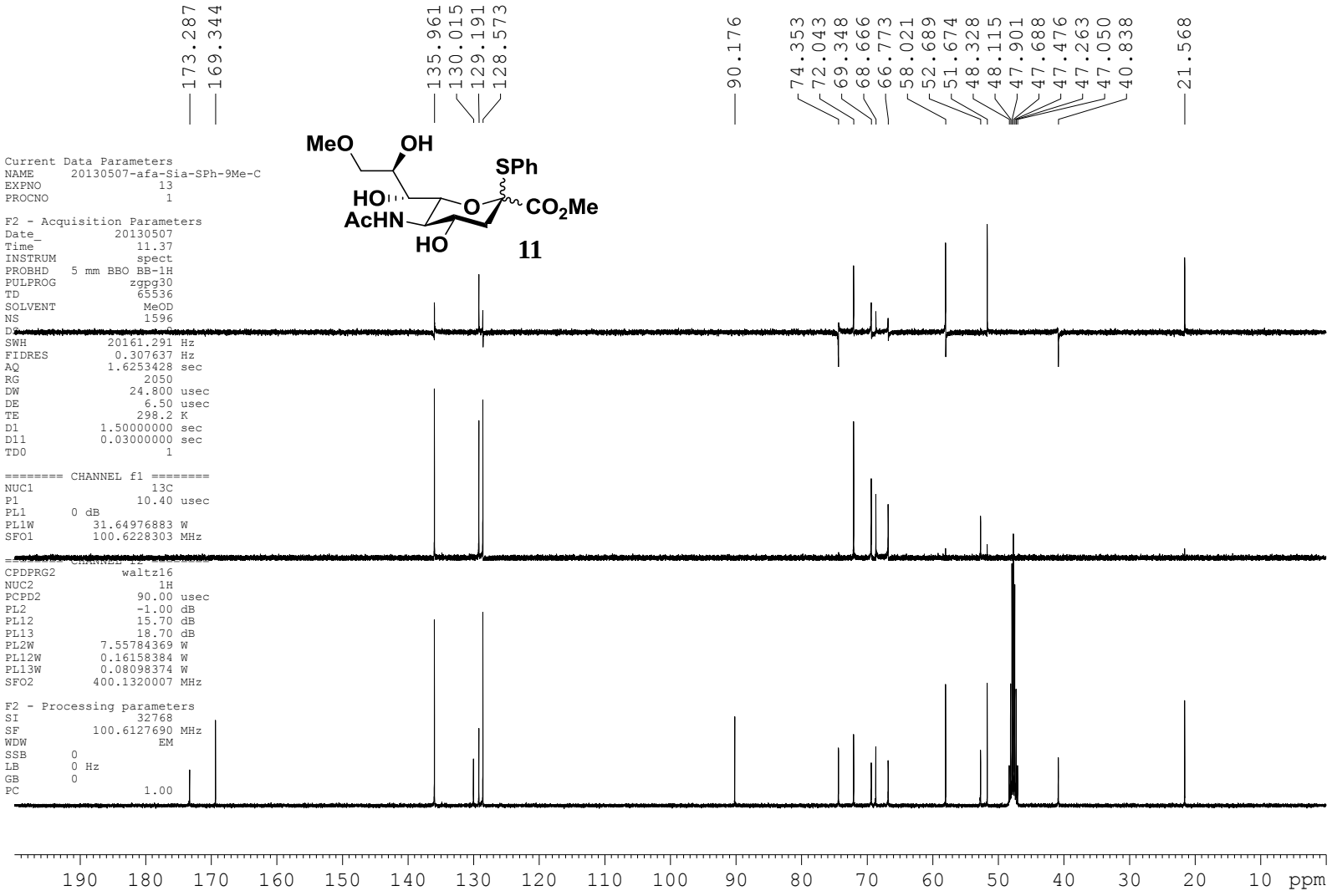
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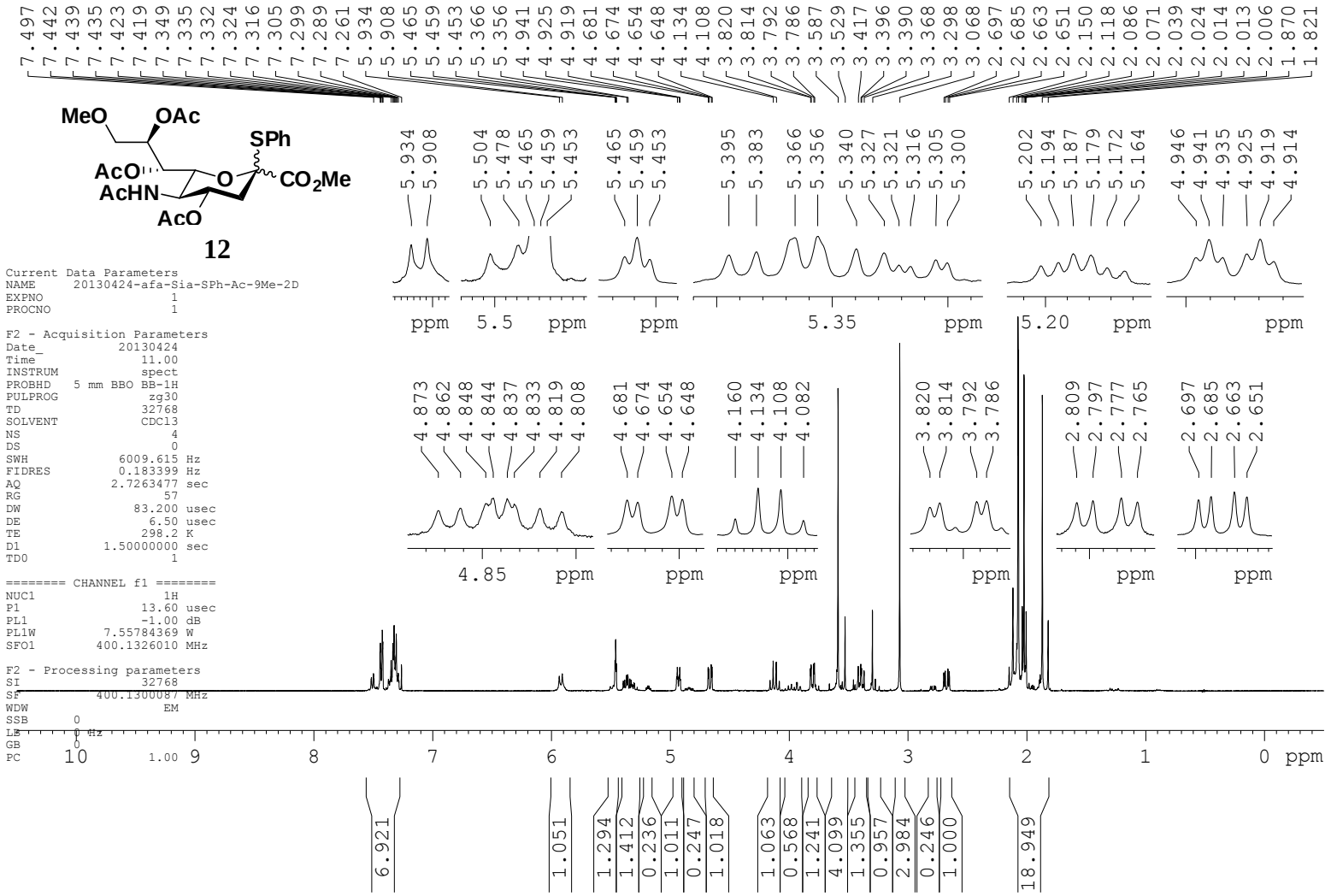
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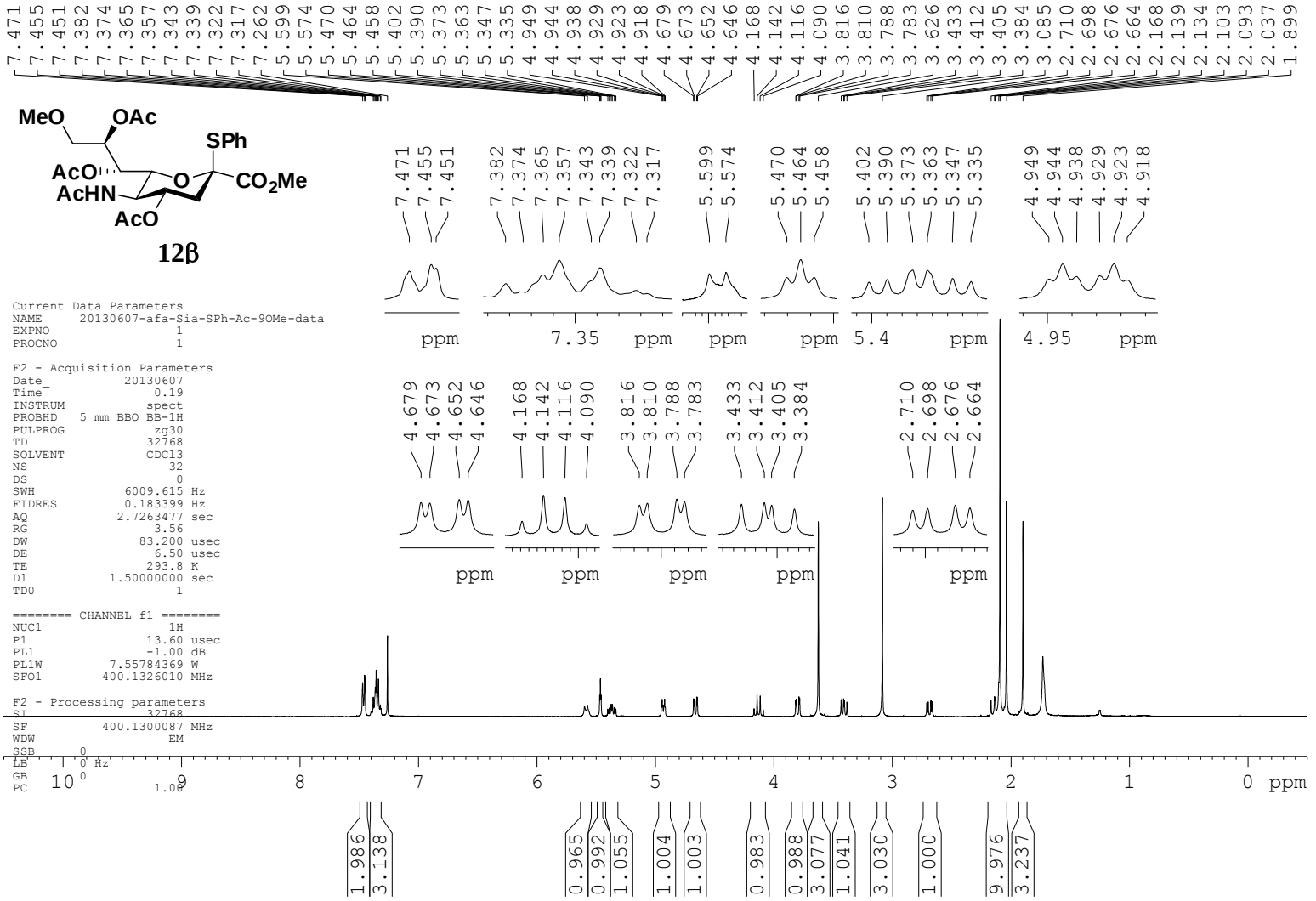
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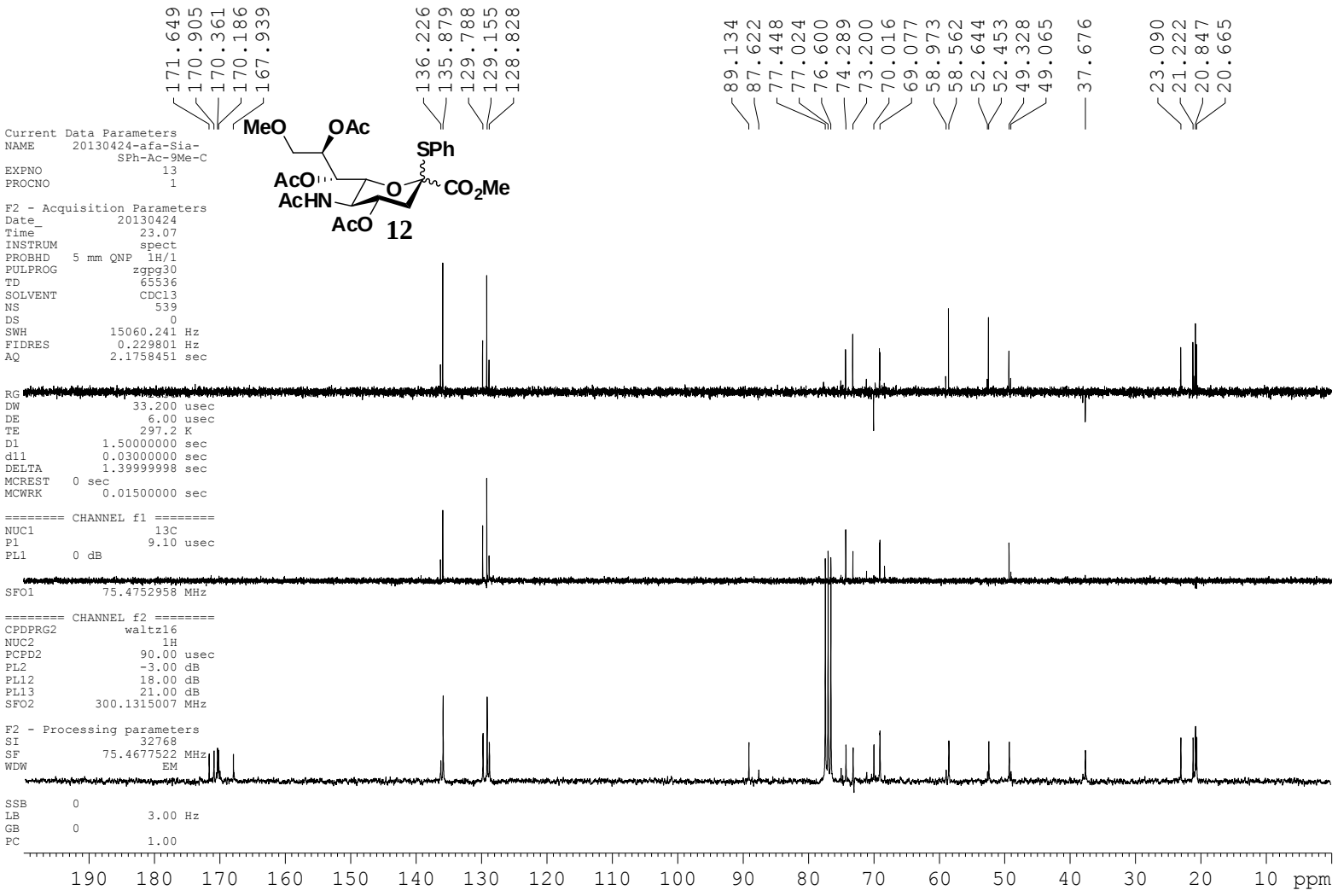
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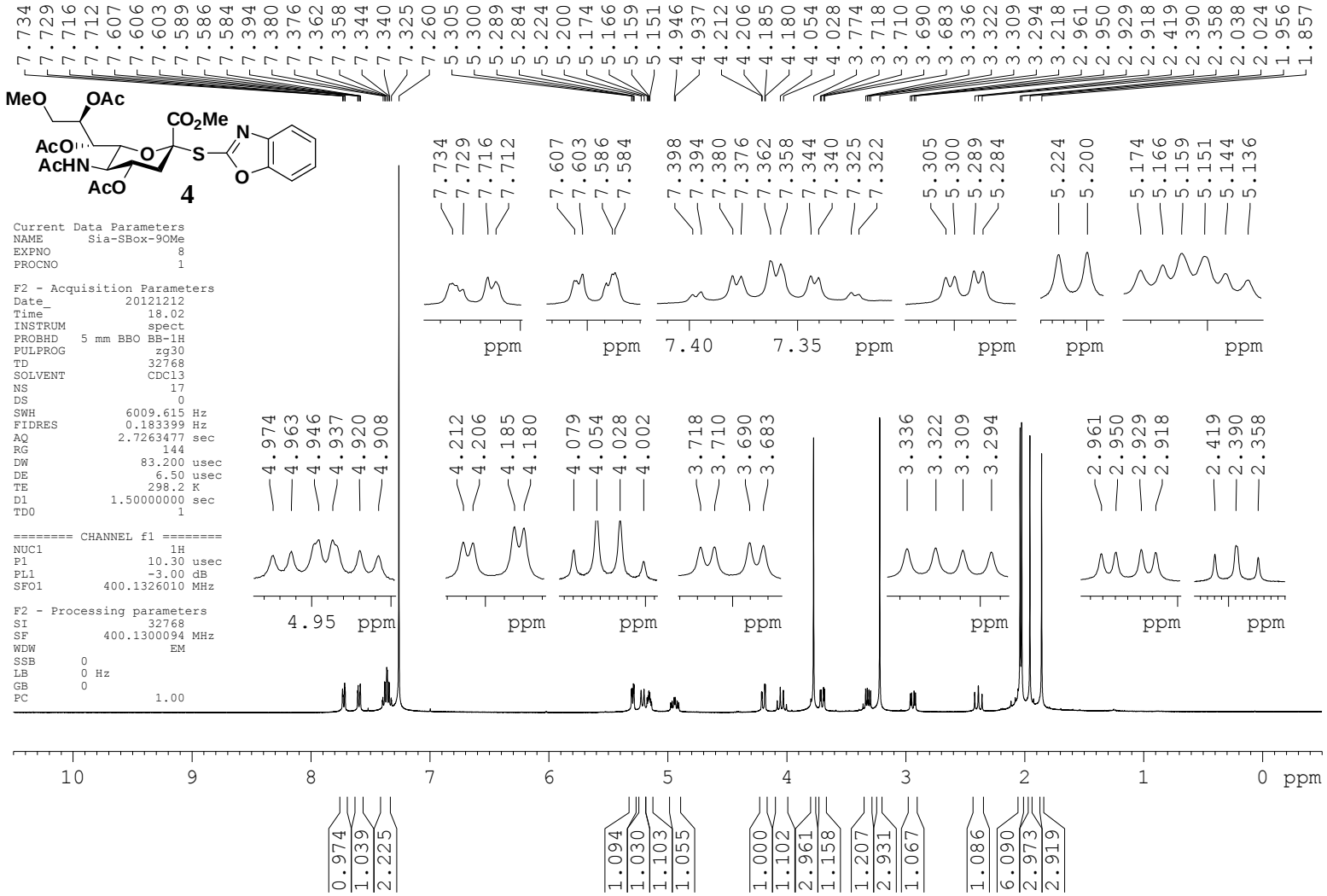
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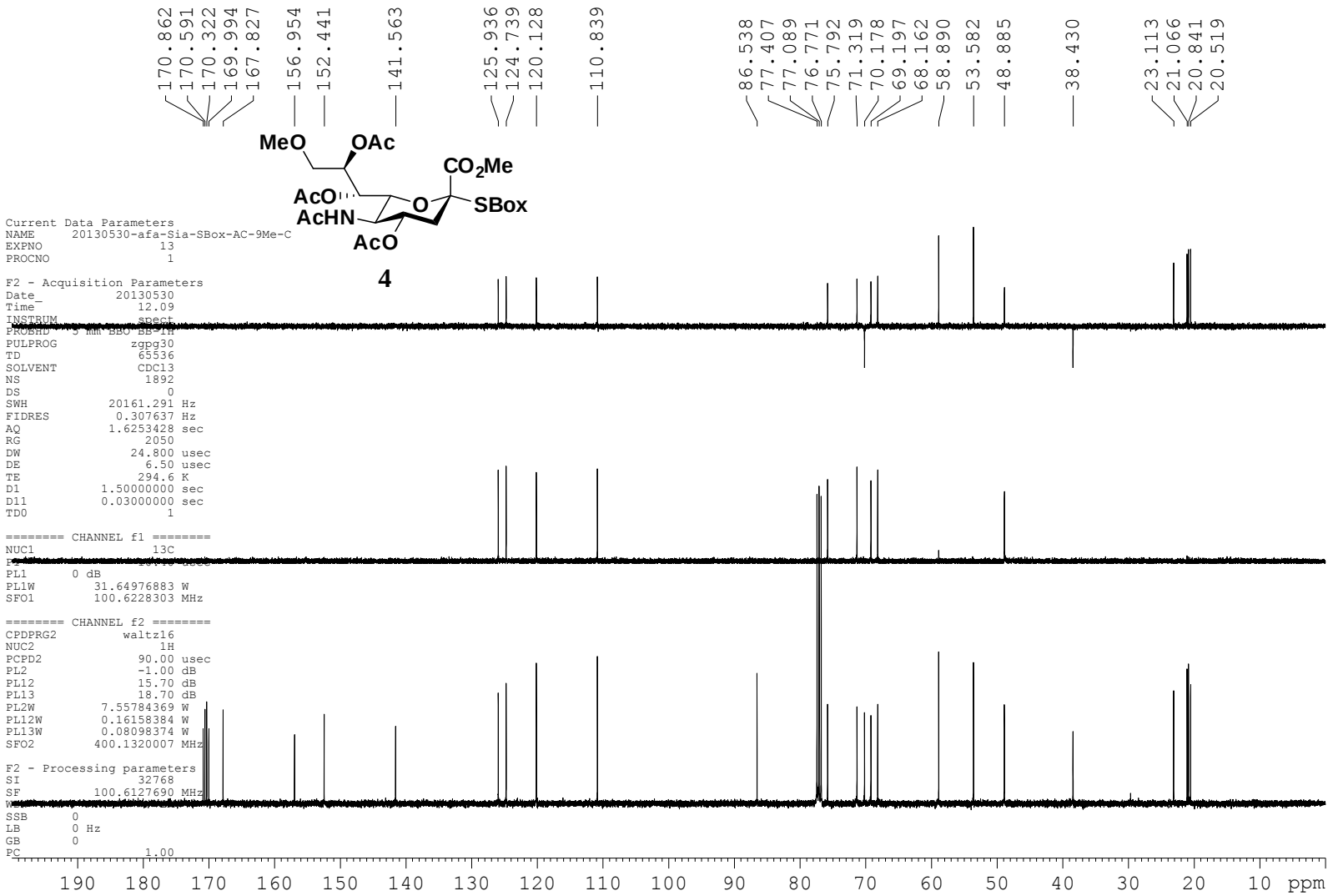
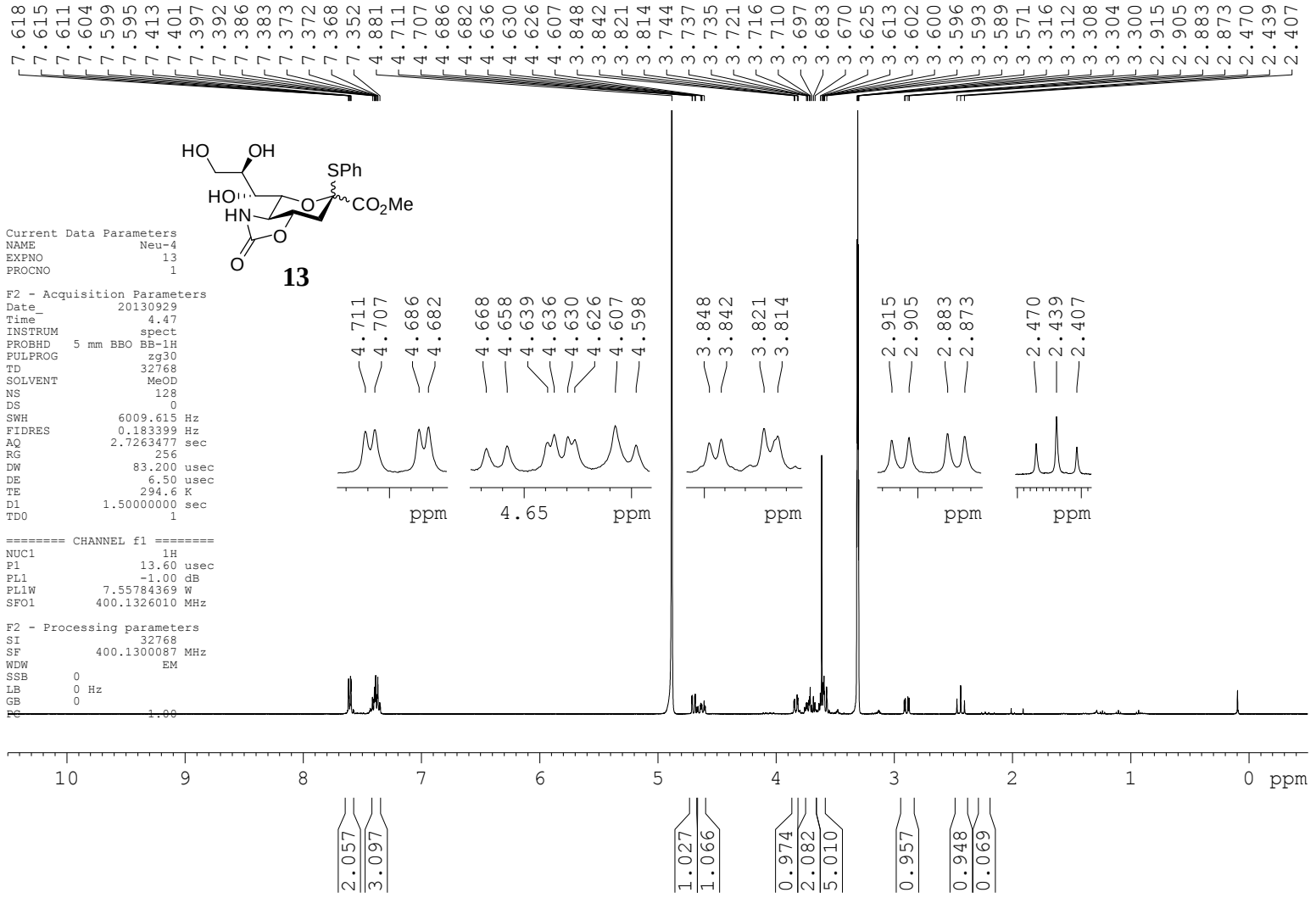
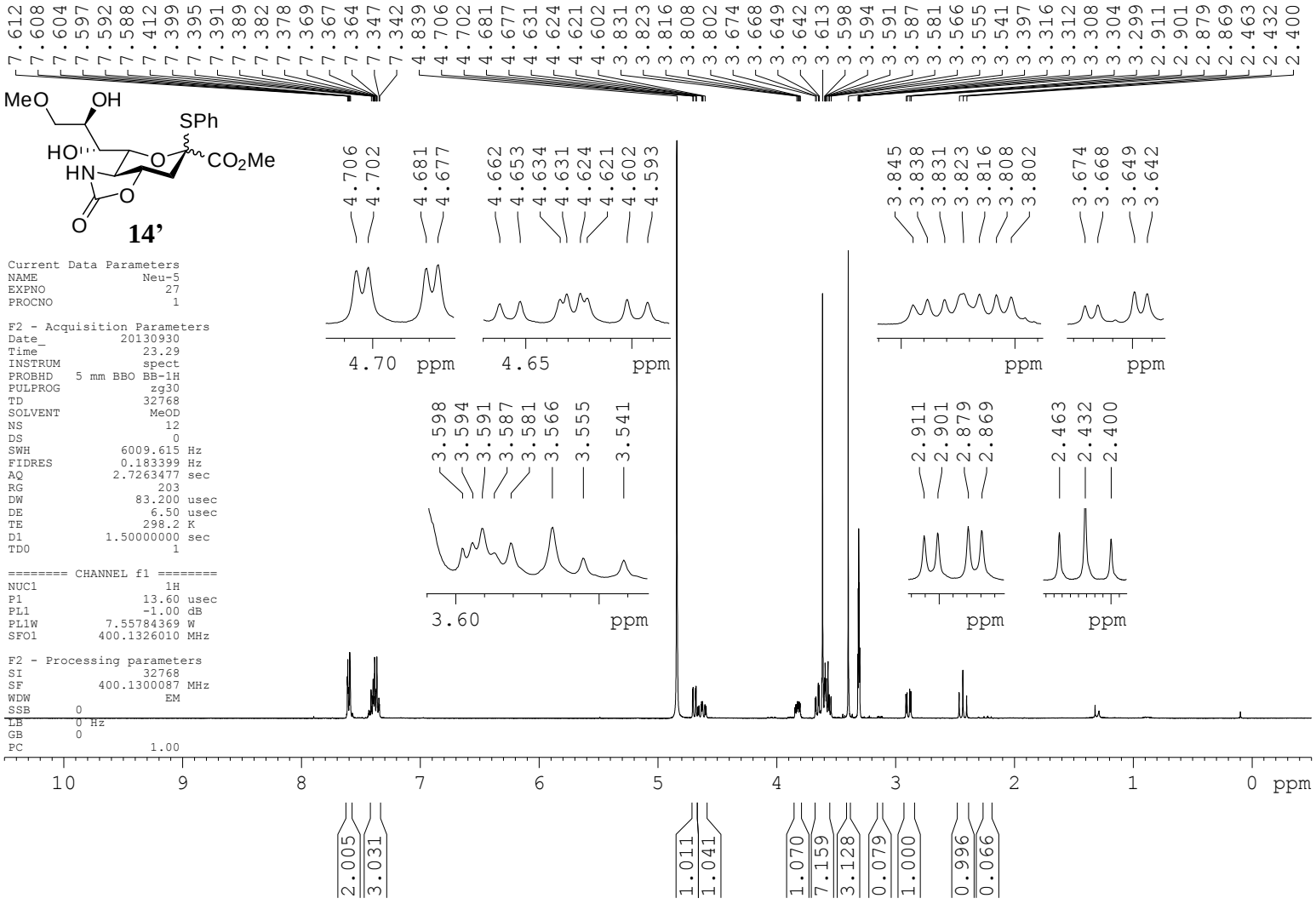
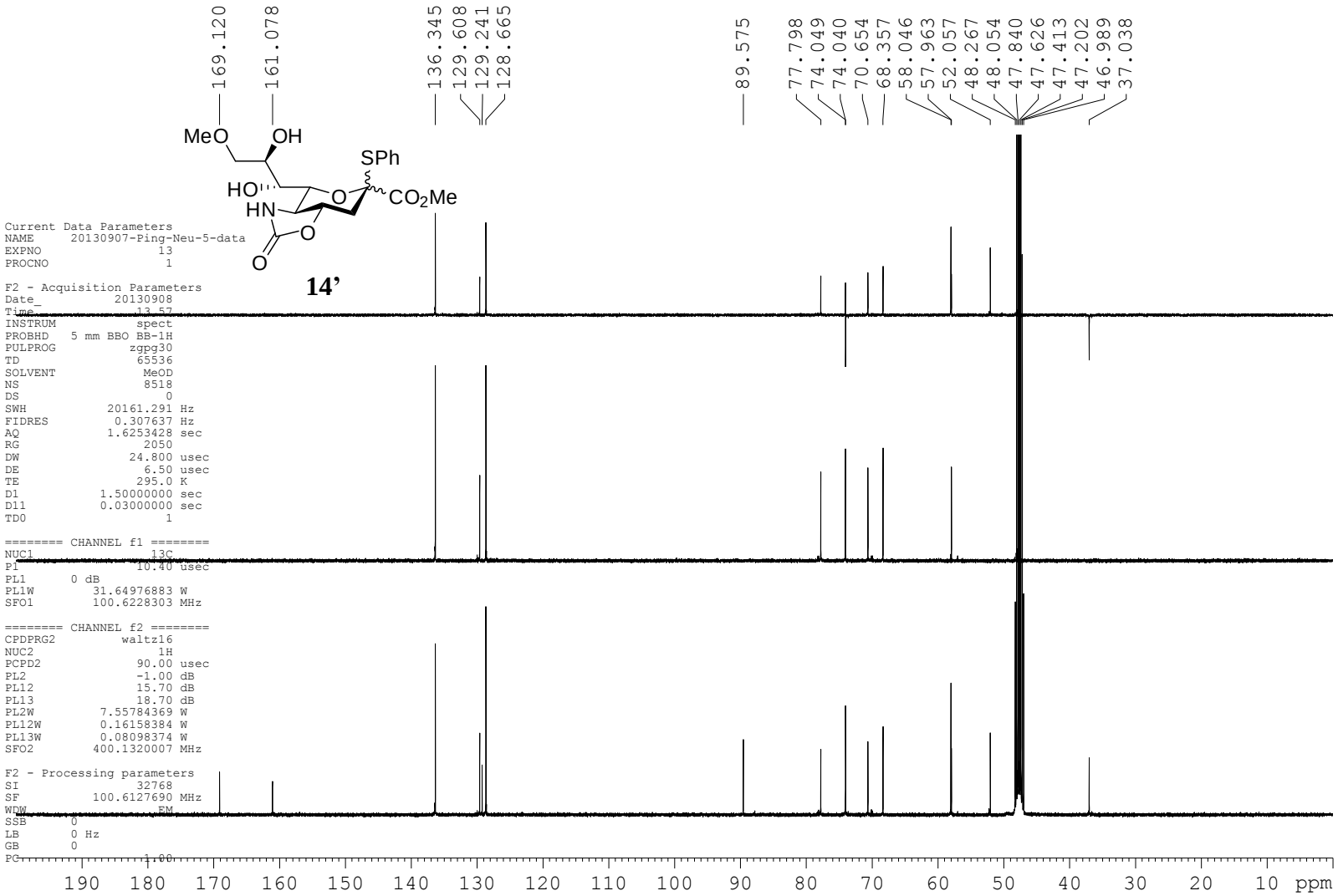
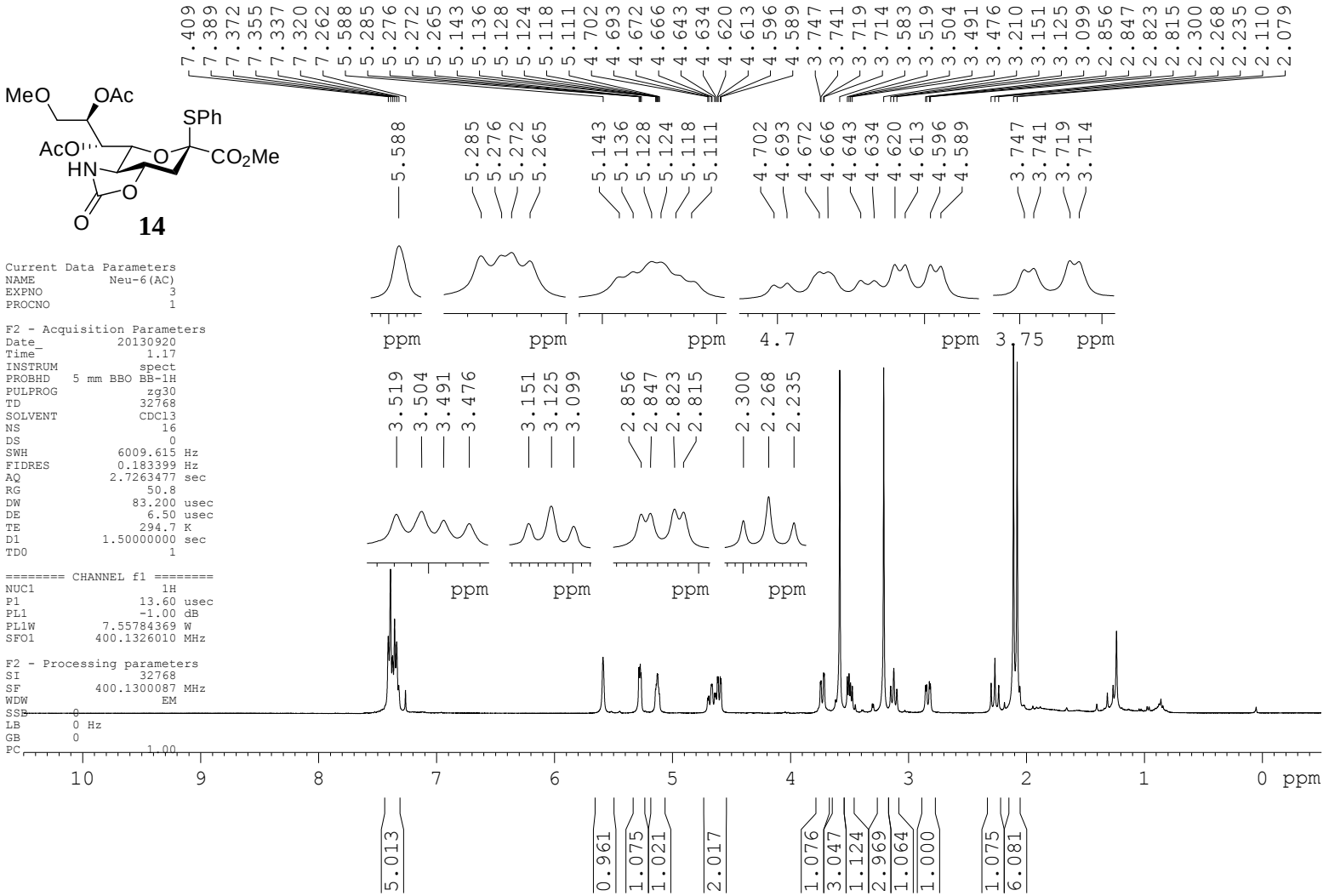
1.207 2.931 1.067
1.086 6.090 2.973 2.919

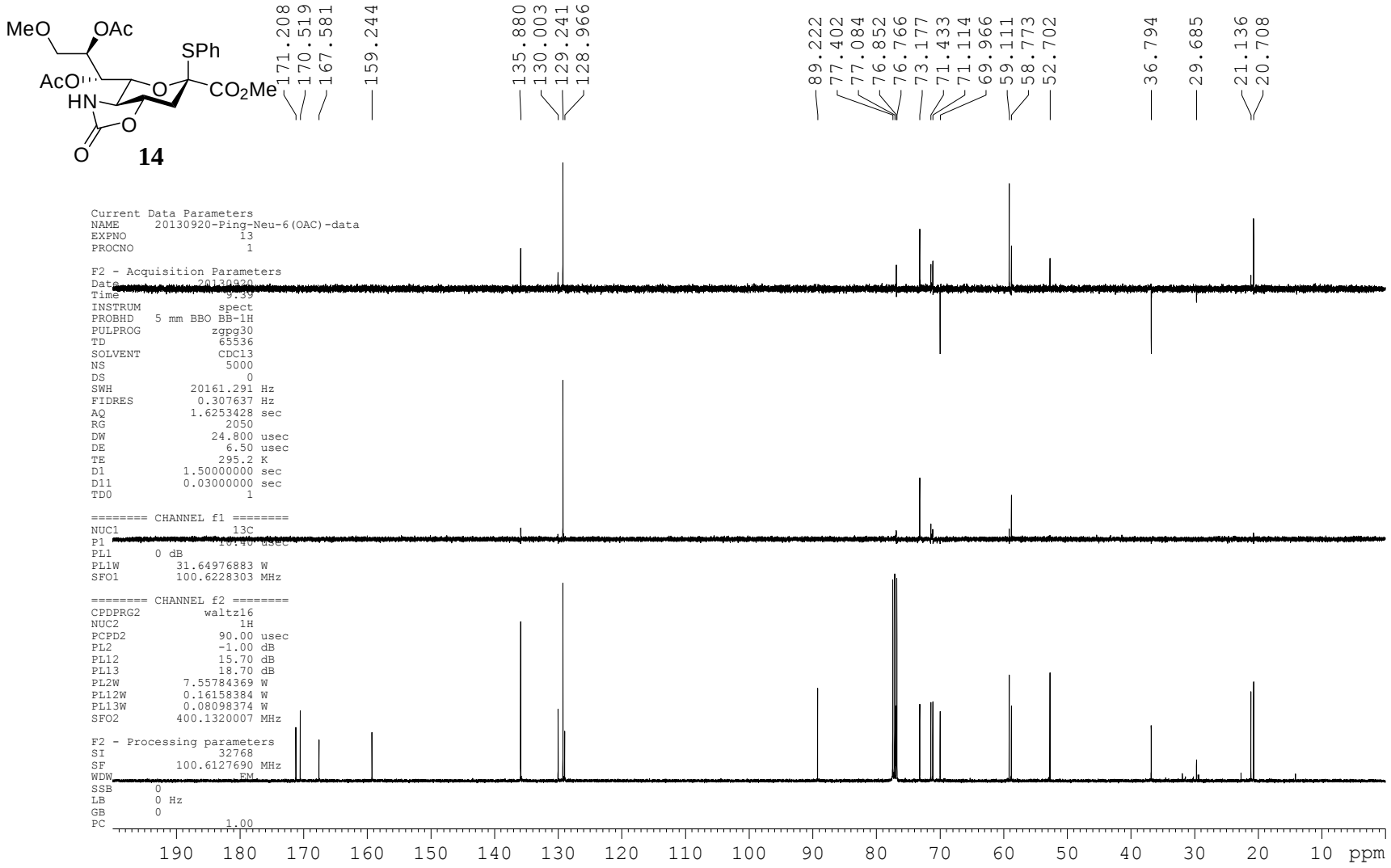

170.862
170.591
170.322
169.994
167.827
156.954
152.441
141.563
125.936
124.739
120.128
110.839
86.538
77.407
77.089
76.771
75.792
71.319
70.178
69.197
68.162
58.890
53.582
48.885
38.430
23.113
21.066
20.841
20.519
MeO
OAc
CO2Me
AcO
AcHN
O
SBox
AcO
4
Current Data Parameters
NAME 20130530-afa-Sia-SBox-AC-9Me-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130530
Time 12.09
INSTRUM spect
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1892
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.6 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

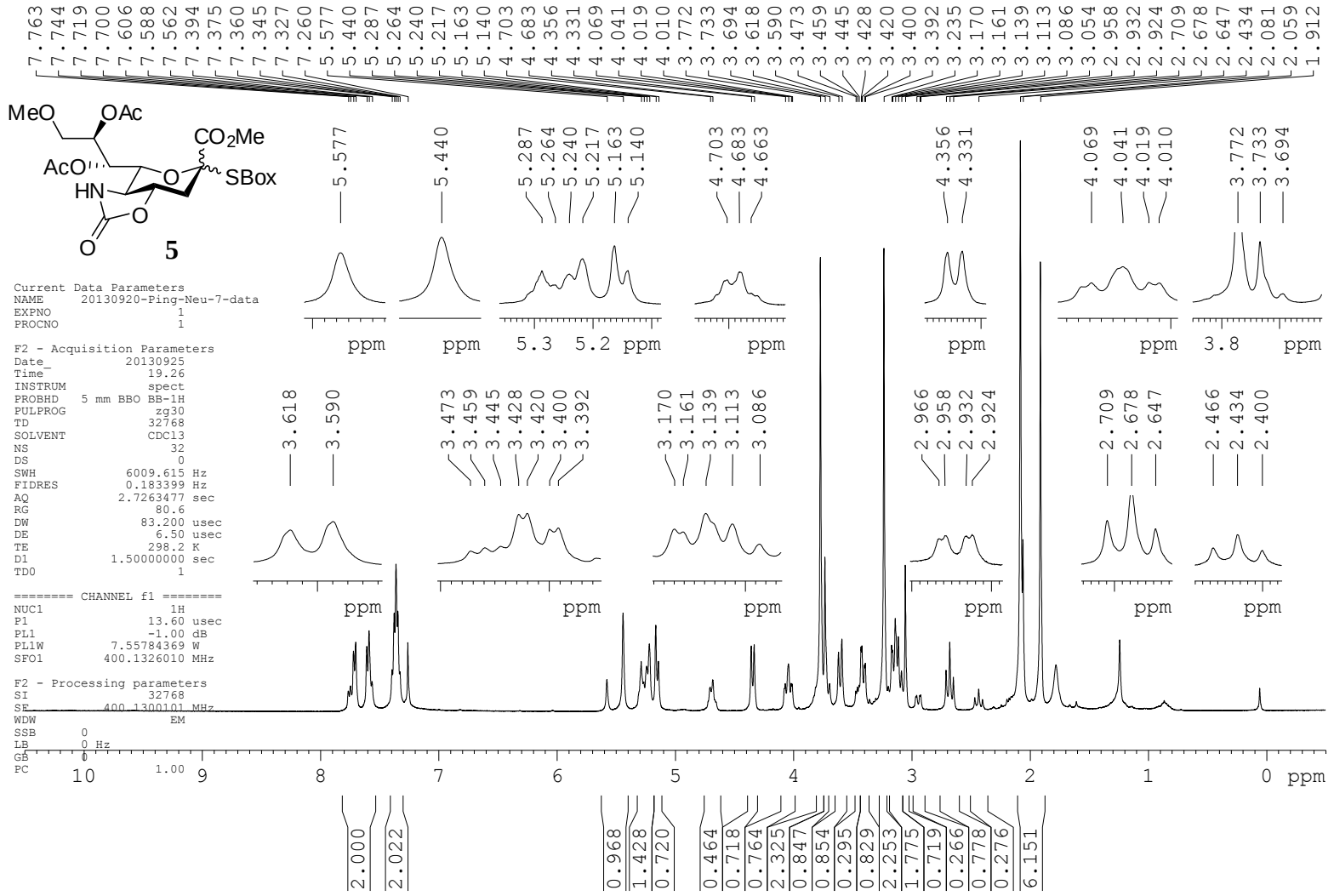

7.618 7.615 7.611 7.604 7.599 7.595 7.413 7.401 7.397 7.392 7.386 7.383 7.373 7.372 7.368 7.352 4.881 4.711 4.707 4.686 4.682 4.636 4.630 4.626 4.607 3.848 3.842 3.821 3.814 3.744 3.737 3.735 3.721 3.716 3.710 3.697 3.683 3.670 3.625 3.613 3.602 3.600 3.596 3.593 3.589 3.571 3.316 3.312 3.308 3.304 3.300 2.915 2.905 2.883 2.873 2.470 2.439 2.407
HO OH SPh HO HN O CO2Me O O
13
Current Data Parameters
NAME Neu-4
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130929
Time 4.47
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 128
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 256
DW 83.200 usec
DE 6.50 usec
TE 294.6 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
4.711 4.707 4.686 4.682
4.668 4.658 4.639 4.636 4.630 4.626 4.607 4.598
3.848 3.842 3.821 3.814
2.915 2.905 2.883 2.873
2.470 2.439 2.407
ppm
4.65
ppm
ppm
ppm
ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
2.057 3.097
1.027 1.066
0.974 2.082 5.010
0.957
0.948 0.069

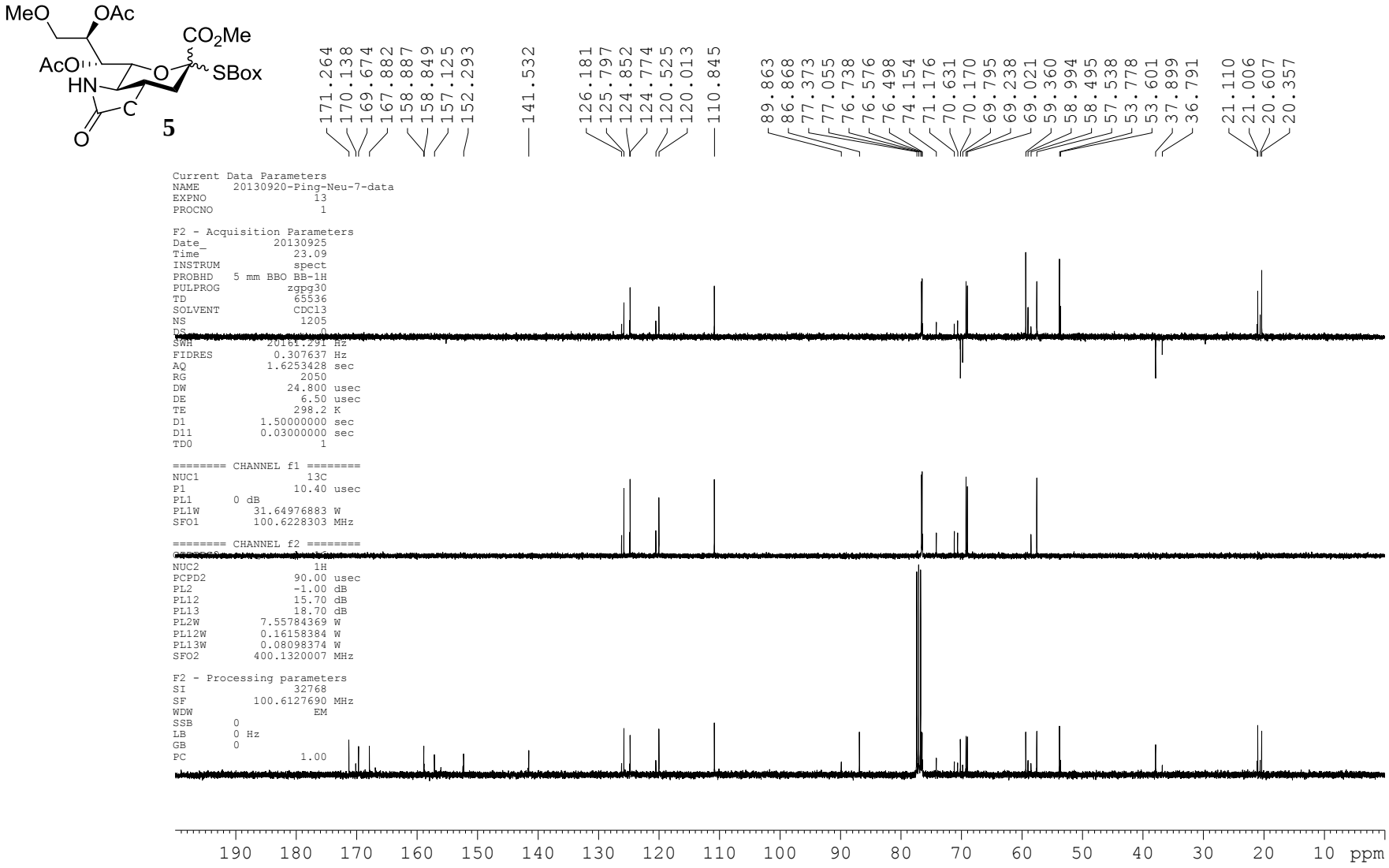

7.612 7.608 7.604 7.597 7.592 7.588 7.412 7.399 7.395 7.391 7.389 7.382 7.378 7.369 7.367 7.364 7.347 7.342
4.839 4.706 4.702 4.681 4.677 4.631 4.624 4.621 4.602 3.831 3.823 3.816 3.808 3.802 3.674 3.668 3.649 3.642 3.613 3.598 3.594 3.591 3.587 3.581 3.566 3.555 3.541 3.397 3.316 3.312 3.308 3.304 3.299 2.911 2.901 2.879 2.869 2.463 2.432 2.400
MeO
OH
SPh
HO
HN
O
CO2Me
O
O
14'
Current Data Parameters
NAME Neu-5
EXPNO 27
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130930
Time 23.29
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 12
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 203
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
4.70 ppm
4.65 ppm
3.60 ppm
ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
2.005 3.031 1.011 1.041 1.070 7.159 3.128 0.079 1.000 0.996 0.066

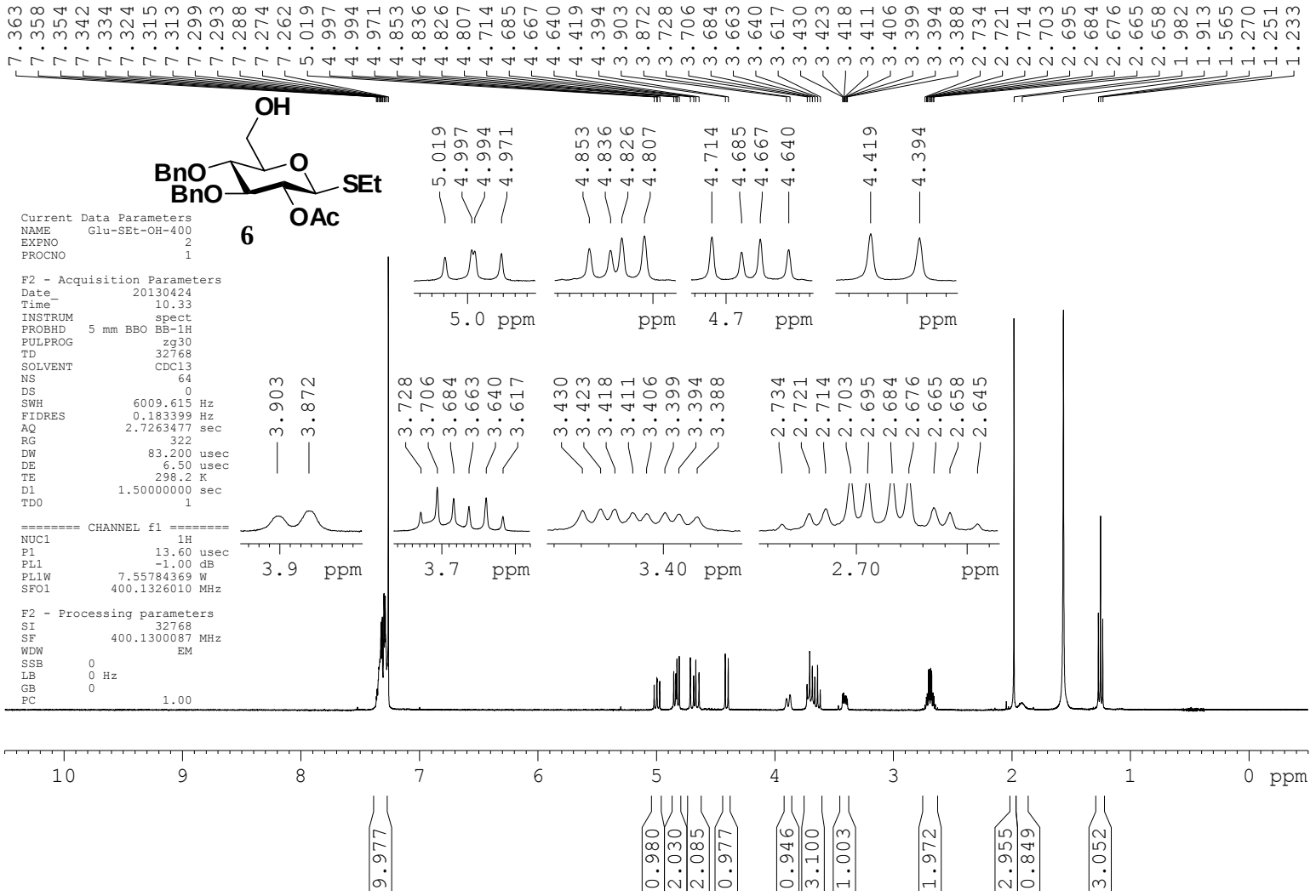

169.120
161.078
136.345
129.608
129.241
128.665
89.575
77.798
74.049
74.040
70.654
68.357
58.046
57.963
52.057
48.267
48.054
47.840
47.626
47.413
47.202
46.989
37.038
MeO
OH
SPh
HO
HN
O
CO2Me
O
O
14'
Current Data Parameters
NAME 20130907-Ping-Neu-5-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130908
Time 13.57
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 8518
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 295.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

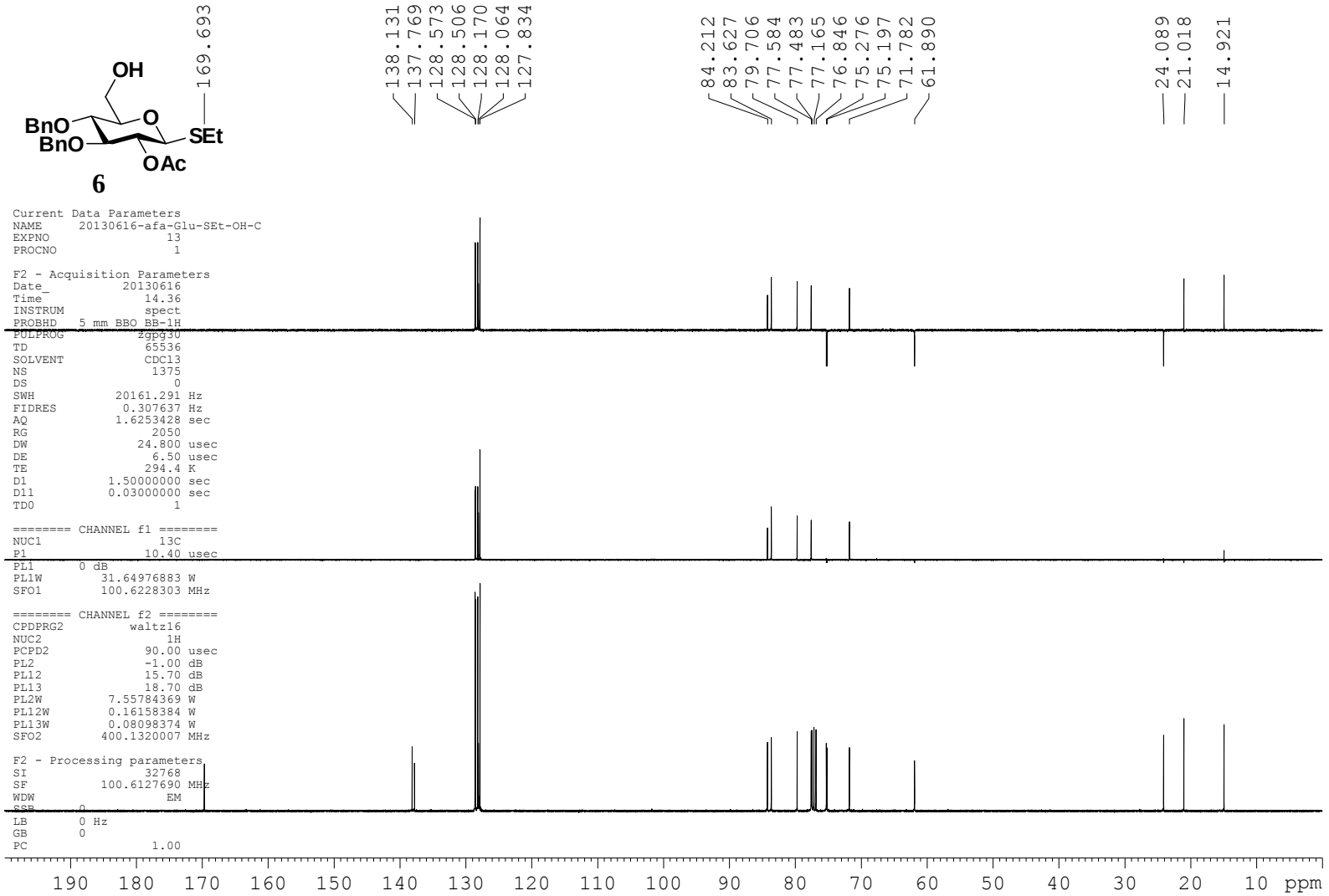

MeO
OAc
SPh
AcO
HN
O
CO2Me
O
O
14
Current Data Parameters
NAME Neu-6(AC)
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130920
Time 1.17
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 50.8
DW 83.200 usec
DE 6.50 usec
TE 294.7 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
7.409 7.389 7.372 7.355 7.337 7.320 7.262 5.588 5.285 5.276 5.272 5.265 5.143 5.136 5.128 5.124 5.118 5.111 4.702 4.693 4.672 4.666 4.643 4.634 4.620 4.613 4.596 4.589 3.747 3.741 3.719 3.714 3.583 3.519 3.504 3.491 3.476 3.210 3.151 3.125 3.099 2.856 2.847 2.823 2.815 2.300 2.268 2.235 2.110 2.079
ppm
4.7
3.75
3.519 3.504 3.491 3.476 3.151 3.125 3.099 2.856 2.847 2.823 2.815 2.300 2.268 2.235
10 9 8 7 6 5 4 3 2 1 0 ppm
5.013 0.961 1.075 1.021 2.017 1.076 3.047 1.124 2.969 1.064 1.000 1.075 6.081


MeO
OAc
SPh
AcO
HN
O
CO2Me
O
O
14
171.208
170.519
167.581
159.244
135.880
130.003
129.241
128.966
89.222
77.402
77.084
76.852
76.766
73.177
71.433
71.114
69.966
59.111
58.773
52.702
36.794
29.685
21.136
20.708
Current Data Parameters
NAME 20130920-Ping-Neu-6(OAC)-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5000
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 295.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MeO
OAc
CO2Me
AcO
O
SBox
HN
O
O
O
5
Current Data Parameters
NAME 20130920-Ping-Neu-7-data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130925
Time 19.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 80.6
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
2.000
2.022
0.968
1.428
0.720
0.464
0.718
0.764
2.325
0.847
0.854
0.295
0.829
2.253
1.775
0.719
0.266
0.778
0.276
6.151


MeO
OAc
CO2Me
AcO
O
SBox
HN
C
O
5
171.264
170.138
169.674
167.882
158.887
158.849
157.125
152.293
141.532
126.181
125.797
124.852
124.774
120.525
120.013
110.845
89.863
86.868
77.373
77.055
76.738
76.576
76.498
74.154
71.176
70.631
70.170
69.795
69.238
69.021
59.360
58.994
58.495
57.538
53.778
53.601
37.899
36.791
21.110
21.006
20.607
20.357
Current Data Parameters
NAME 20130920-Ping-Neu-7-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130925
Time 23.09
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1205
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.363 7.358 7.354 7.342 7.334 7.324 7.315 7.313 7.299 7.293 7.288 7.274 7.262 5.019 4.997 4.994 4.971 4.853 4.836 4.826 4.807 4.714 4.685 4.667 4.640 4.419 4.394 3.903 3.872 3.728 3.706 3.684 3.663 3.640 3.617 3.430 3.423 3.418 3.411 3.406 3.399 3.394 3.388 2.734 2.721 2.714 2.703 2.695 2.684 2.676 2.665 2.658 1.982 1.913 1.565 1.270 1.251 1.233
OH
BnO
BnO
O
SEt
OAc
6
Current Data Parameters
NAME Glu-SEt-OH-400
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130424
Time 10.33
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 322
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.019 4.997 4.994 4.971
4.853 4.836 4.826 4.807
4.714 4.685 4.667 4.640
4.419 4.394
5.0 ppm
ppm
4.7 ppm
ppm
3.903 3.872
3.728 3.706 3.684 3.663 3.640 3.617
3.430 3.423 3.418 3.411 3.406 3.399 3.394 3.388
2.734 2.721 2.714 2.703 2.695 2.684 2.676 2.665 2.658 2.645
3.9 ppm
3.7 ppm
3.40 ppm
2.70 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
9.977
0.980 2.030 2.085 0.977
0.946 3.100 1.003
1.972
2.955 0.849
3.052


169.693
138.131
137.769
128.573
128.506
128.170
128.064
127.834
84.212
83.627
79.706
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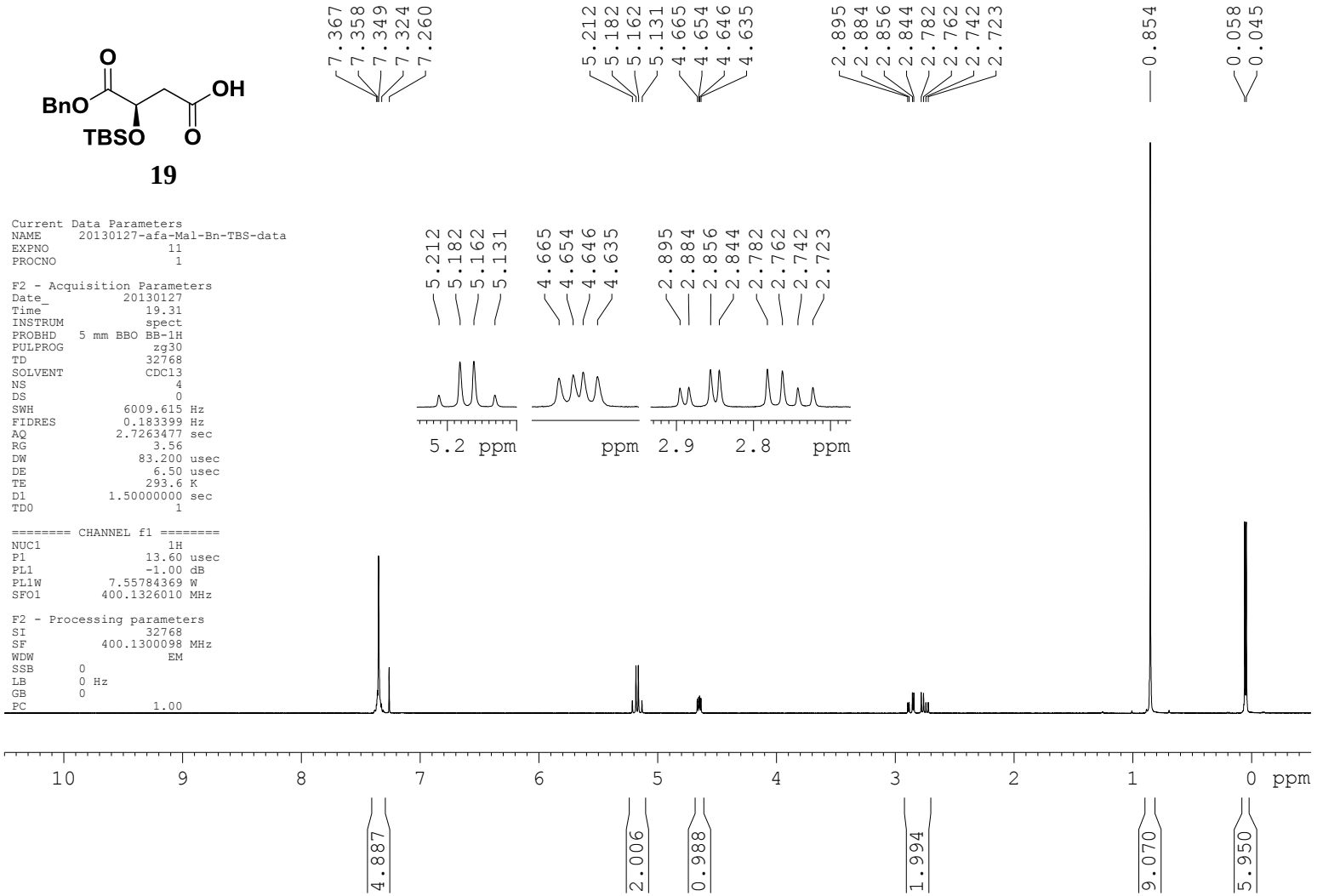
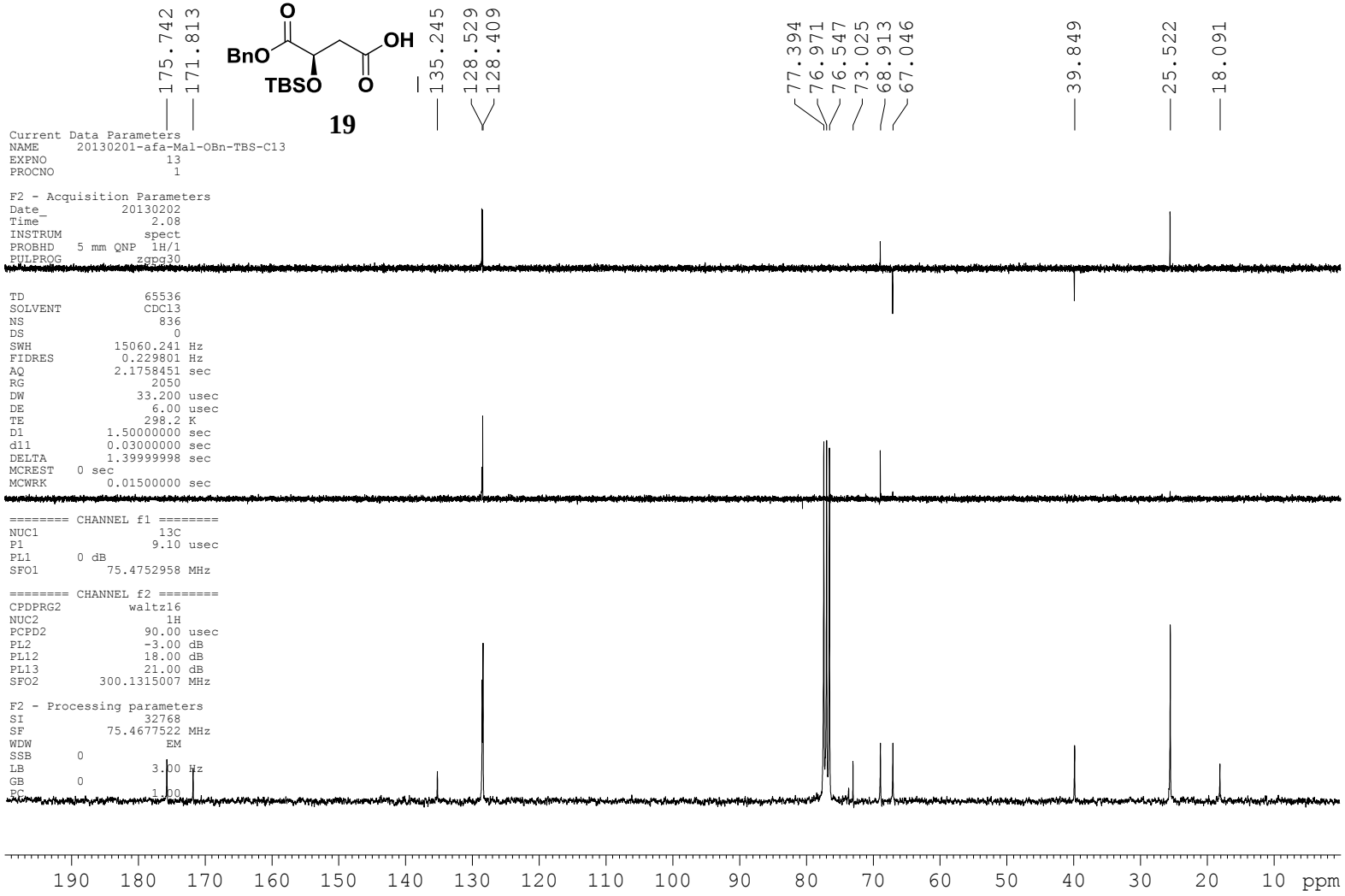
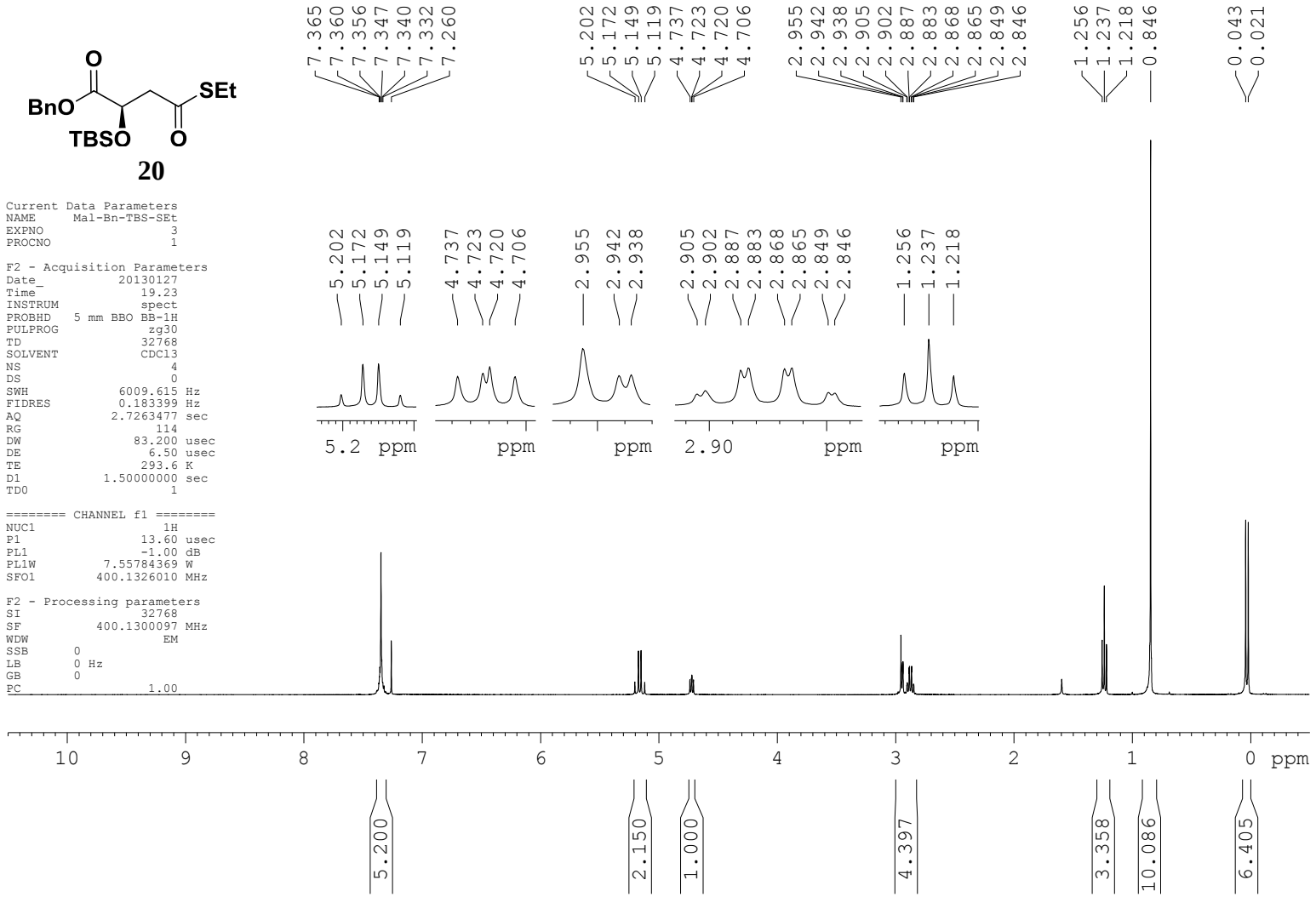
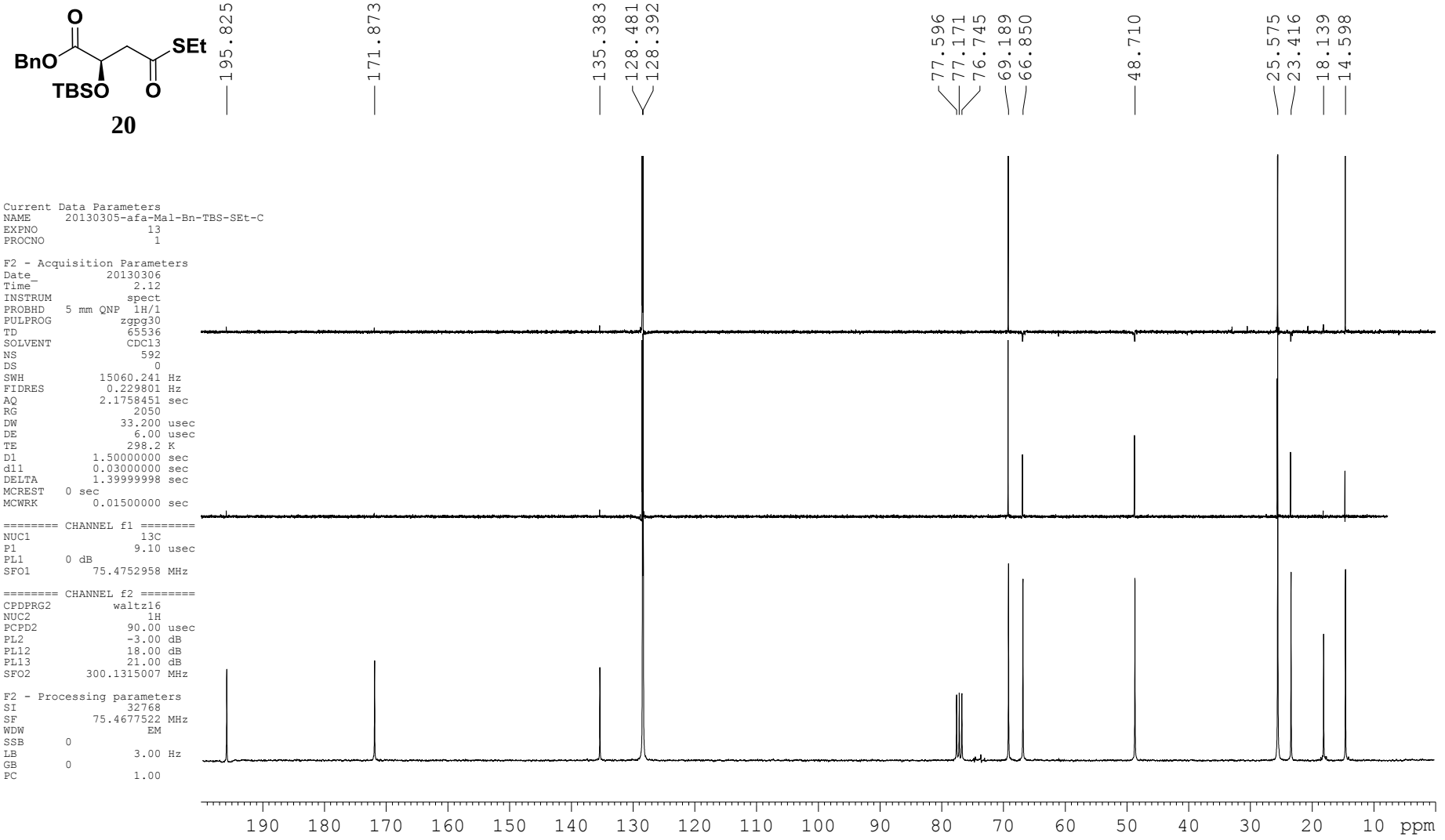
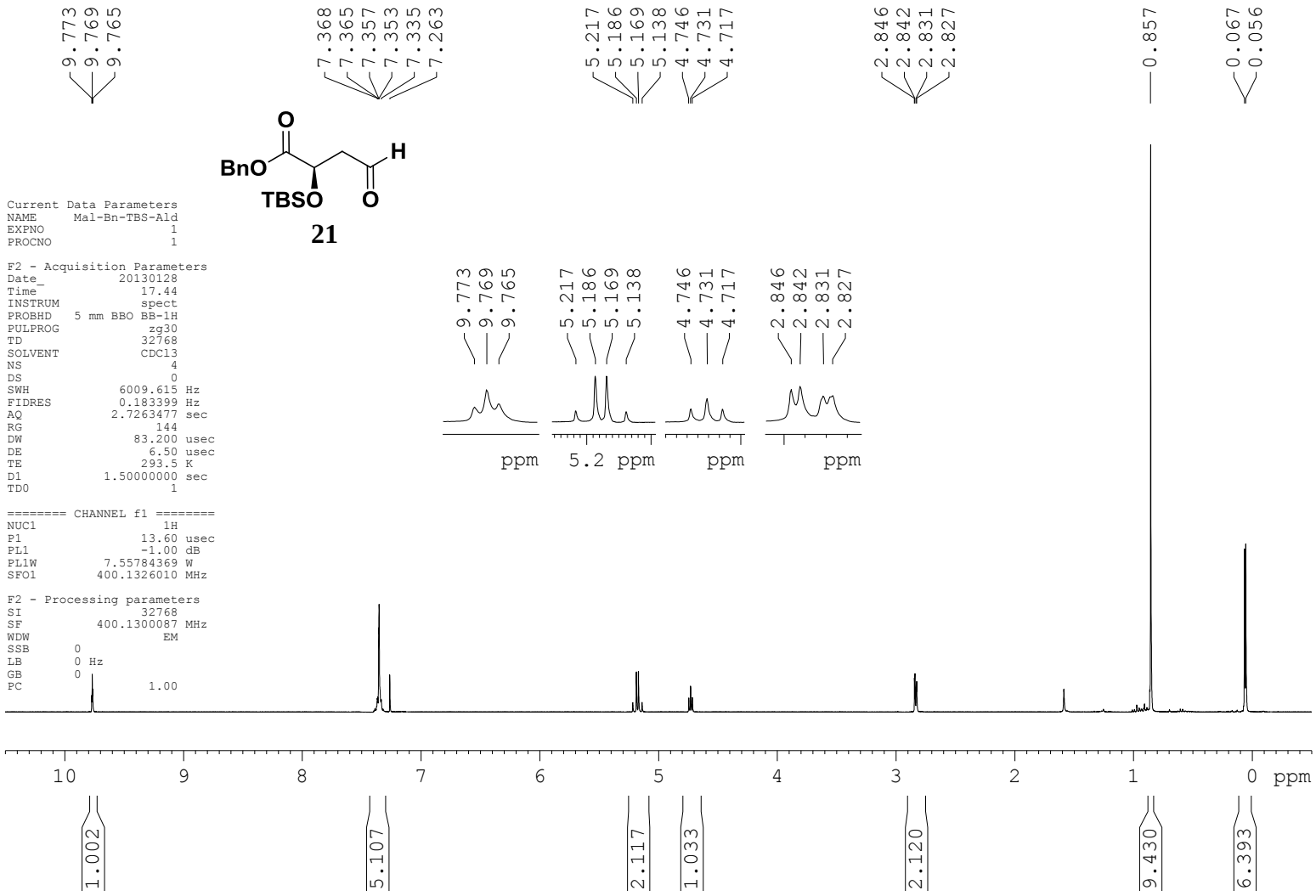
77.483
77.165
76.846
75.276
75.197
71.782
61.890
24.089
21.018
14.921
OH
O
BnO
BnO
SEt
OAc
6
Current Data Parameters
NAME 20130616-afa-Glu-SEt-OH-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130616
Time 14.36
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1375
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.4 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

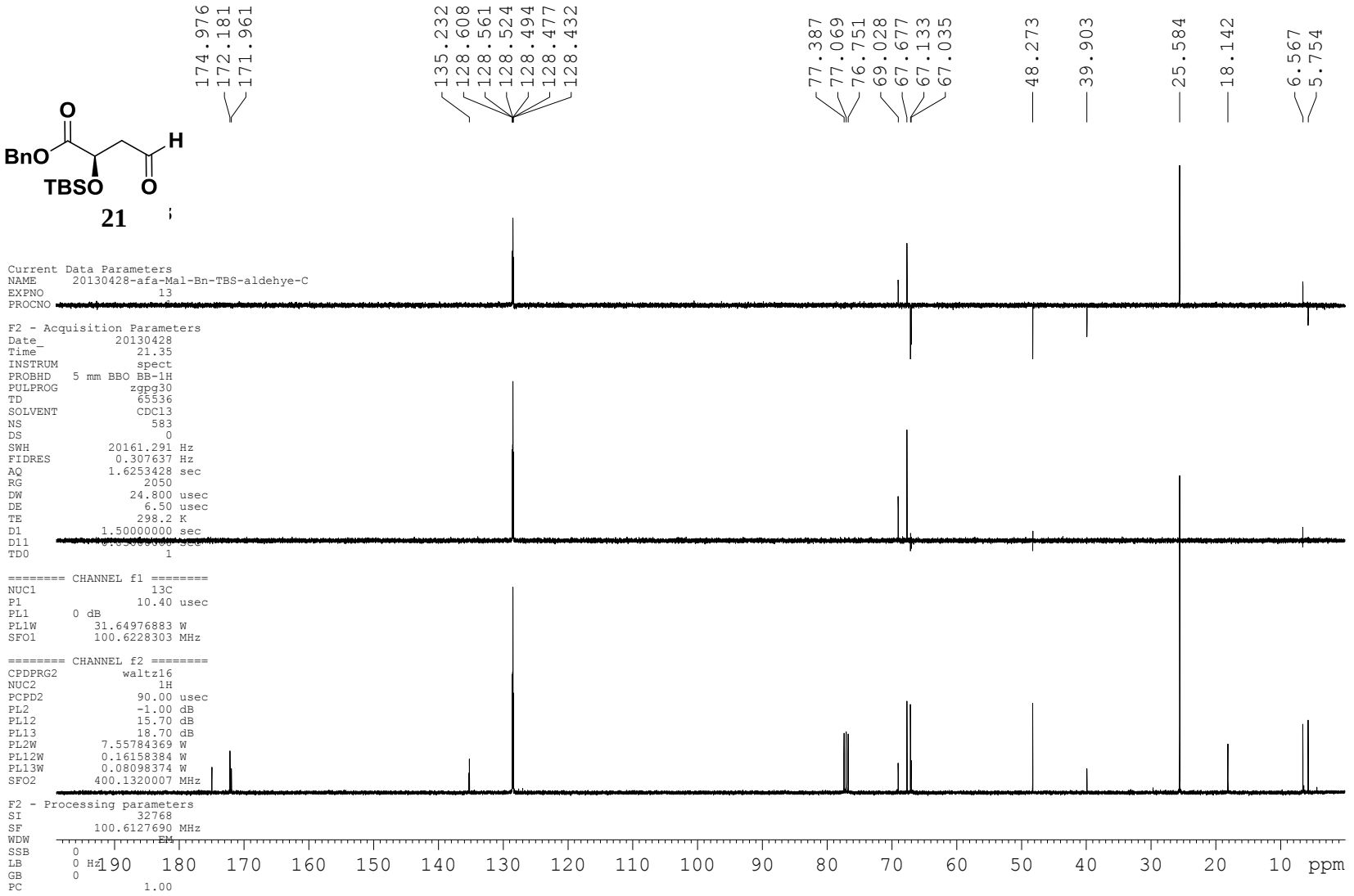

BnO
OH
TBSO
O
O
19
Current Data Parameters
NAME 20130127-afa-Mal-Bn-TBS-data
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130127
Time 19.31
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 3.56
DW 83.200 usec
DE 6.50 usec
TE 293.6 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300098 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
7.367
7.358
7.349
7.324
7.260
5.212
5.182
5.162
5.131
4.665
4.654
4.646
4.635
2.895
2.884
2.856
2.844
2.782
2.762
2.742
2.723
0.854
0.058
0.045
5.2 ppm
ppm
2.9
2.8
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
4.887
2.006
0.988
1.994
9.070
5.950

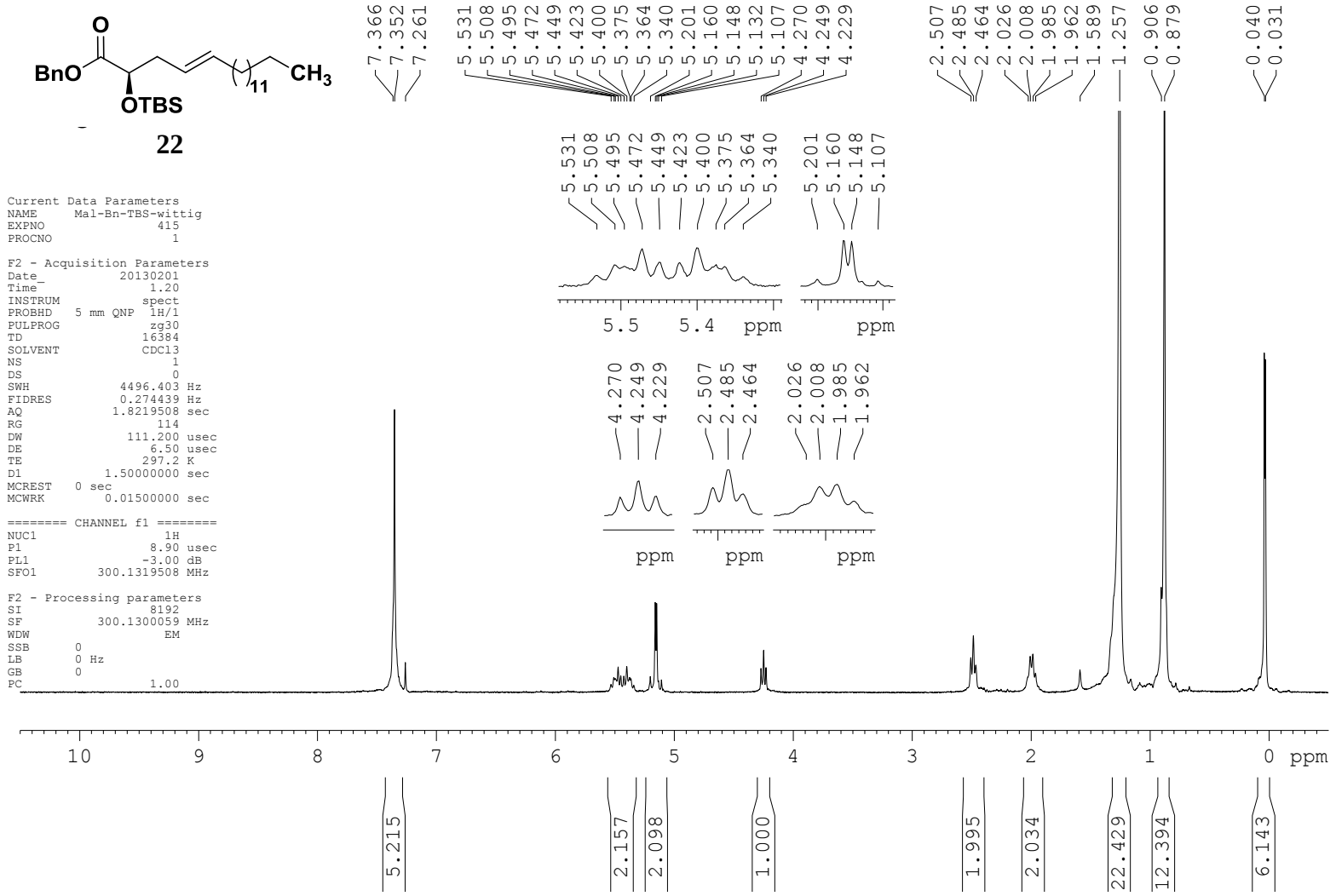

175.742
171.813
135.245
128.529
128.409
77.394
76.971
76.547
73.025
68.913
67.046
39.849
25.522
18.091
BnO
OH
TBSO
O
19
Current Data Parameters
NAME 20130201-afa-Mal-OBn-TBS-C13
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130202
Time 2.08
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 836
DS 0
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 2050
DW 33.200 usec
DE 6.00 usec
TE 298.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 75.4677522 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

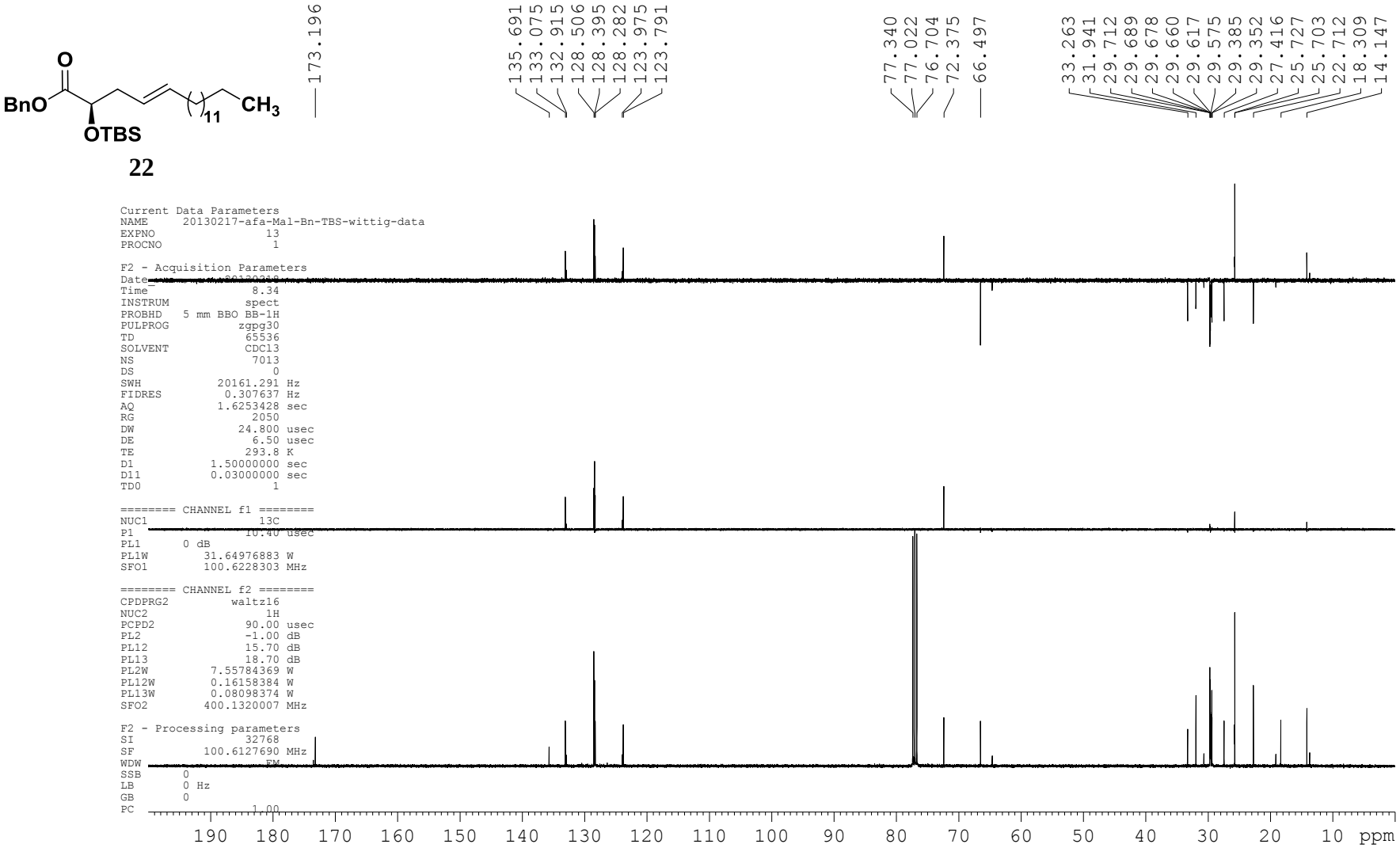

BnO
TBSO
SEt
O
O
O
20
7.365 7.360 7.356 7.347 7.340 7.332 7.260
5.202 5.172 5.149 5.119
4.737 4.723 4.720 4.706
2.955 2.942 2.938 2.905 2.902 2.887 2.883 2.868 2.865 2.849 2.846
1.256 1.237 1.218
0.846
0.043 0.021
Current Data Parameters
NAME Mal-Bn-TBS-SEt
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130127
Time 19.23
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 114
DW 83.200 usec
DE 6.50 usec
TE 293.6 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300097 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.2 ppm
2.90 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
5.200
2.150
1.000
4.397
3.358
10.086
6.405


O
BnO
SEt
TBSO
O
20
195.825
171.873
135.383
128.481
128.392
77.596
77.171
76.745
69.189
66.850
48.710
25.575
23.416
18.139
14.598
Current Data Parameters
NAME 20130305-afa-Mal-Bn-TBS-SEt-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130306
Time 2.12
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 592
DS 0
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 2050
DW 33.200 usec
DE 6.00 usec
TE 298.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 75.4677522 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

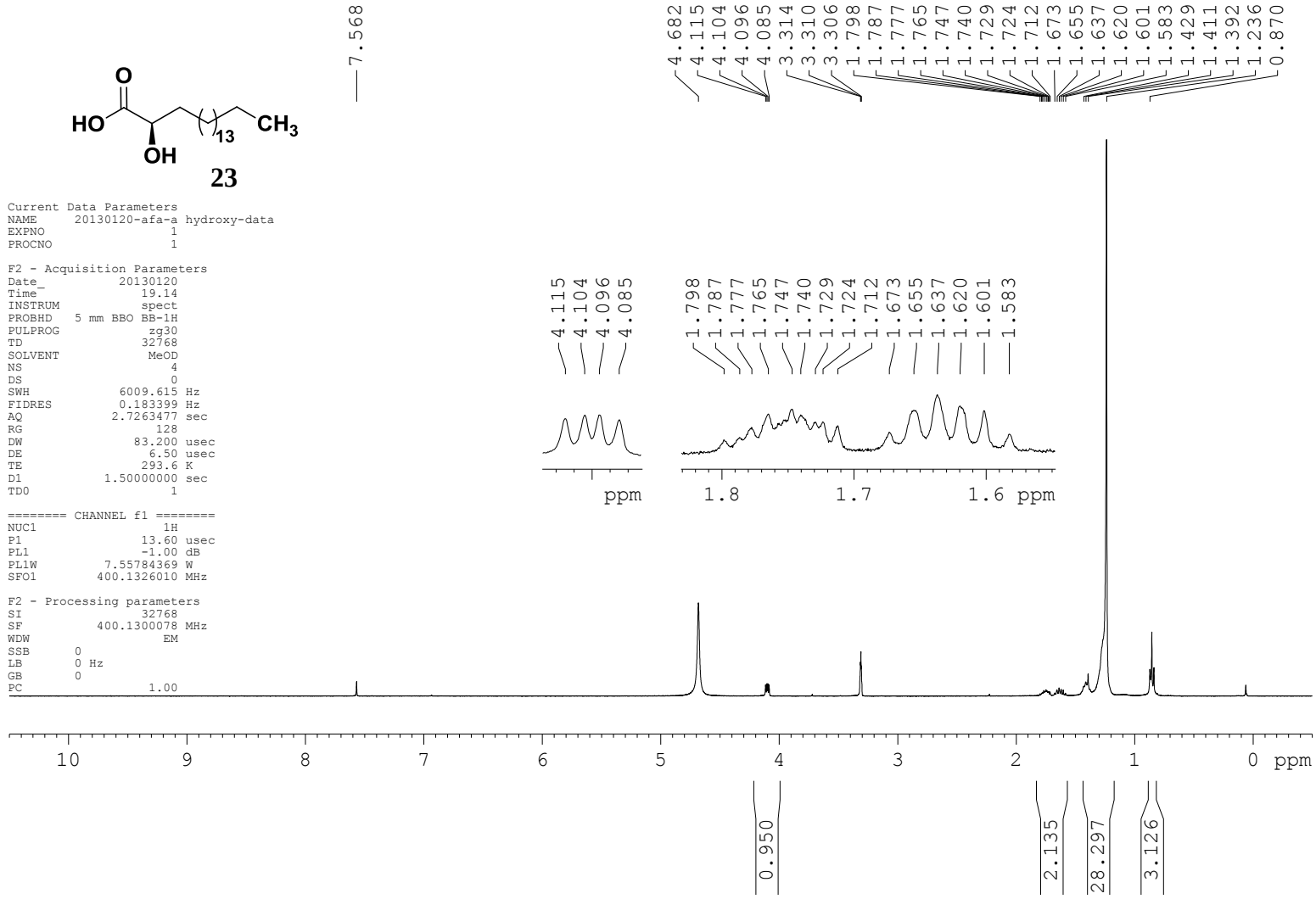

9.773
9.769
9.765
7.368
7.365
7.357
7.353
7.335
7.263
5.217
5.186
5.169
5.138
4.746
4.731
4.717
2.846
2.842
2.831
2.827
0.857
0.067
0.056
BnO
TBSO
O
H
21
Current Data Parameters
NAME Mal-Bn-TBS-Ald
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130128
Time 17.44
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 144
DW 83.200 usec
DE 6.50 usec
TE 293.5 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
5.2 ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
1.002
5.107
2.117
1.033
2.120
9.430
6.393

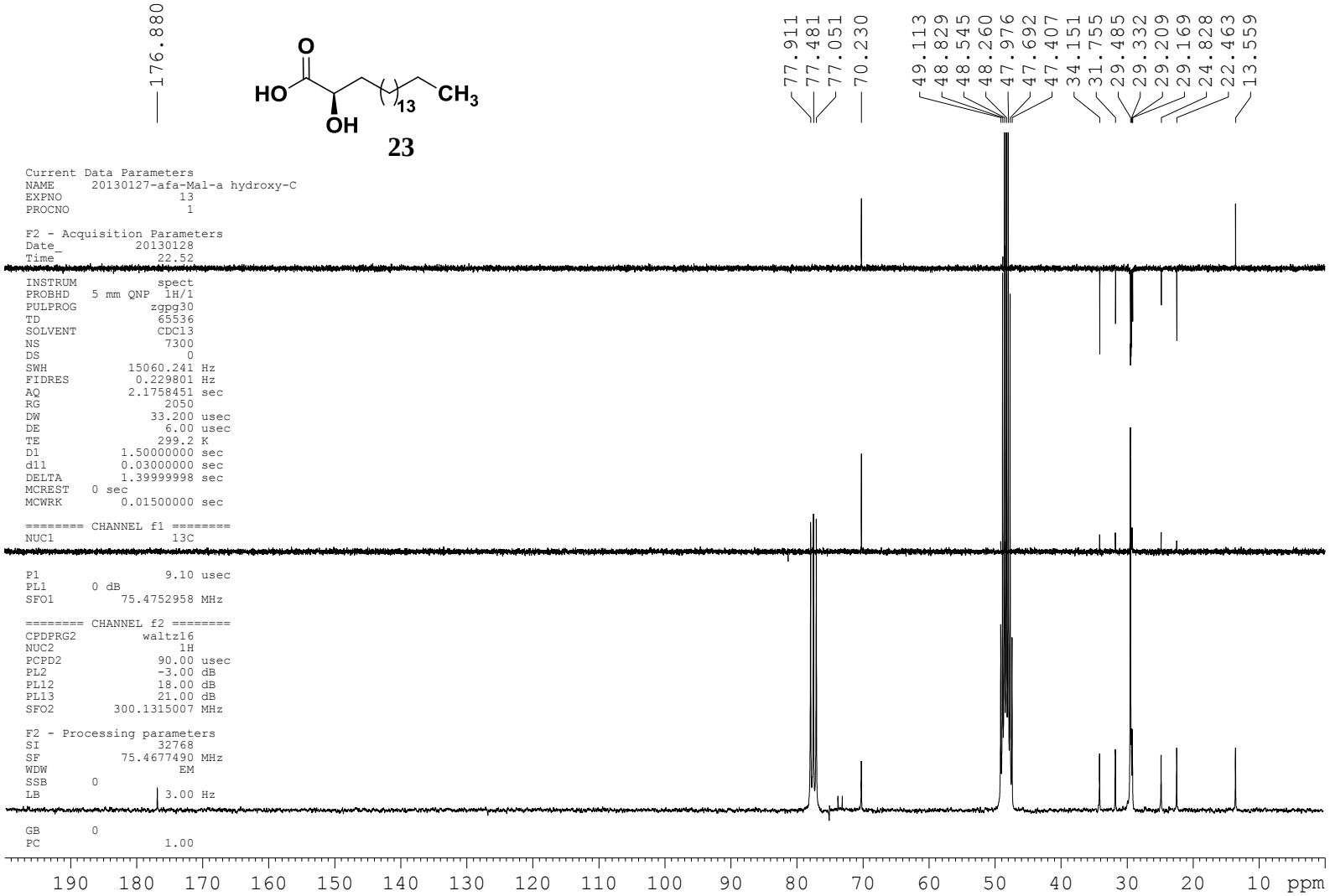

174.976
172.181
171.961
135.232
128.608
128.561
128.524
128.494
128.477
128.432
77.387
77.069
76.751
69.028
67.677
67.133
67.035
48.273
39.903
25.584
18.142
6.567
5.754
BnO
TBSO
O
H
21
Current Data Parameters
NAME 20130428-afa-Mal-Bn-TBS-aldehye-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130428
Time 21.35
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 583
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

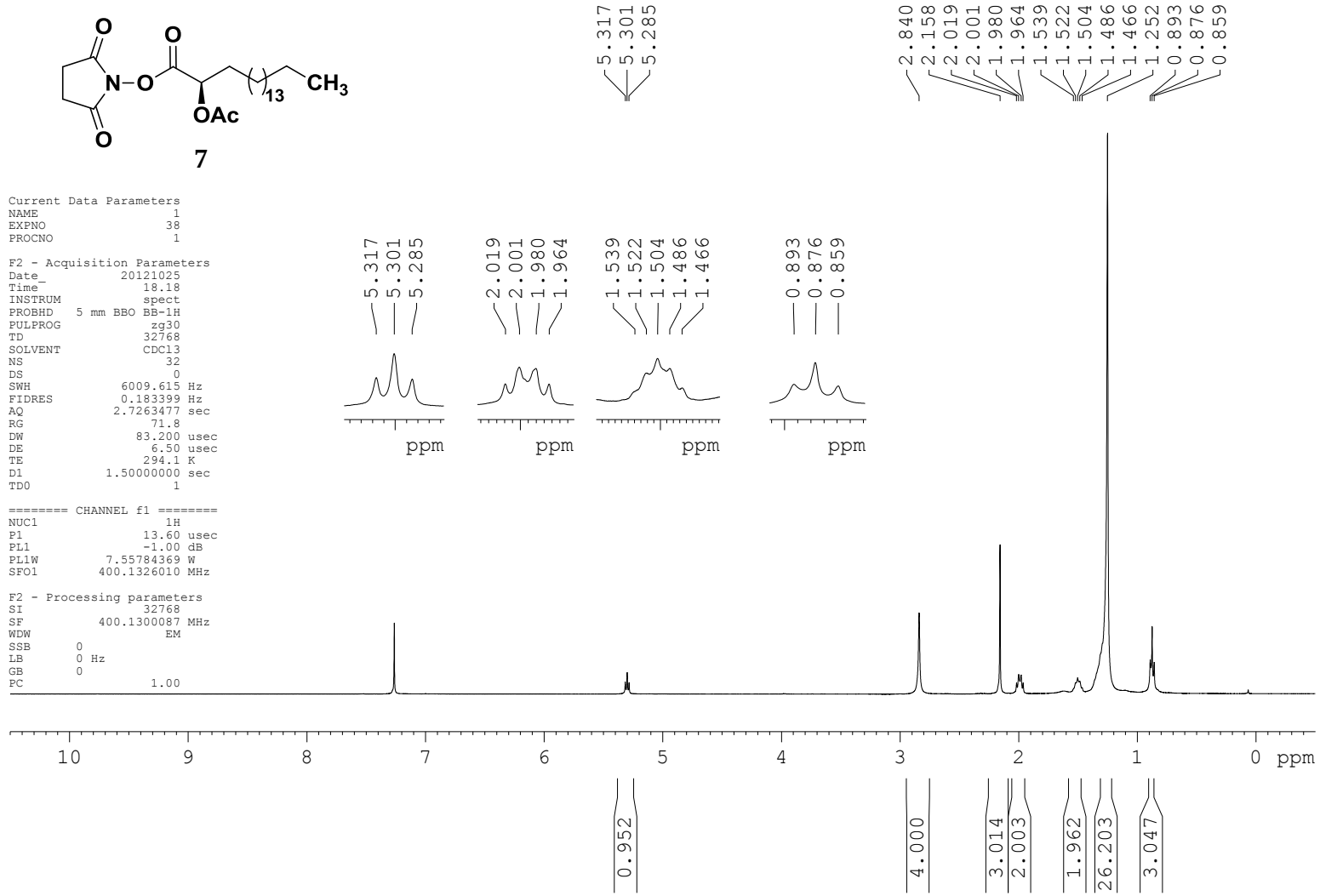

BnO
O
OTBS
11
CH3
22
Current Data Parameters
NAME Mal-Bn-TBS-wittig
EXPNO 415
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130201
Time 1.20
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 1
DS 0
SWH 4496.403 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 114
DW 111.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.50000000 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 8.90 usec
PL1 -3.00 dB
SFO1 300.1319508 MHz
F2 - Processing parameters
SI 8192
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
7.366
7.352
7.261
5.531
5.508
5.495
5.472
5.449
5.423
5.400
5.375
5.364
5.340
5.201
5.160
5.148
5.132
5.107
4.270
4.249
4.229
2.507
2.485
2.464
2.026
2.008
1.985
1.962
1.589
1.257
0.906
0.879
0.040
0.031
5.5
5.4
ppm
10
9
8
7
6
5
4
3
2
1
0
5.215
2.157
2.098
1.000
1.995
2.034
22.429
12.394
6.143

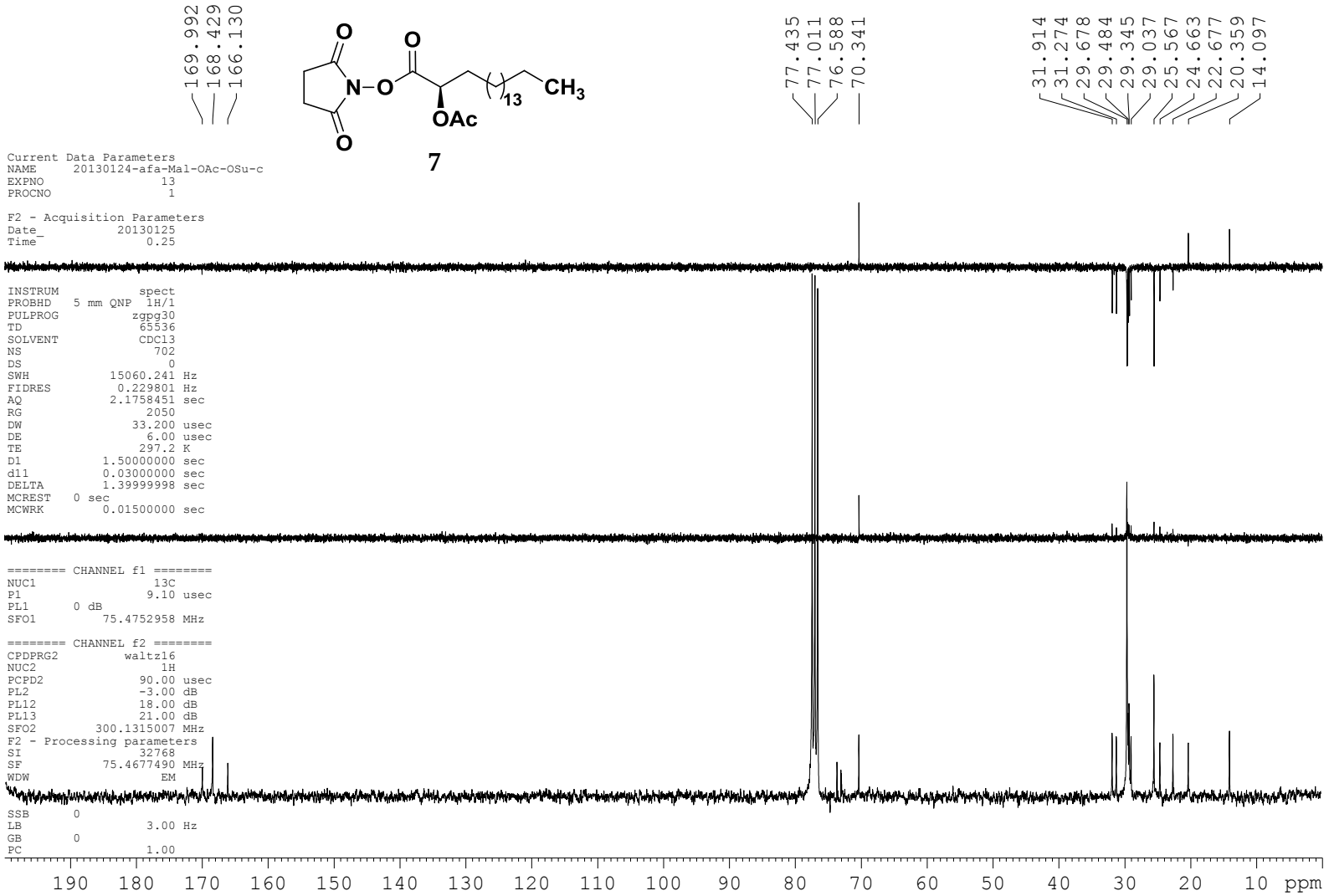

O
BnO
OTBS
11
CH3
173.196
135.691
133.075
132.915
128.506
128.395
128.282
123.975
123.791
77.340
77.022
76.704
72.375
66.497
33.263
31.941
29.712
29.689
29.678
29.660
29.617
29.575
29.385
29.352
27.416
25.727
25.703
22.712
18.309
14.147
Current Data Parameters
NAME 20130217-afa-Mal-Bn-TBS-wittig-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Time 8.34
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7013
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 293.8 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

22


HO
O
OH
13
CH3
23
7.568
4.682
4.115
4.104
4.096
4.085
3.314
3.310
3.306
1.798
1.787
1.777
1.765
1.747
1.740
1.729
1.724
1.712
1.673
1.655
1.637
1.620
1.601
1.583
1.429
1.411
1.392
1.236
0.870
Current Data Parameters
NAME 20130120-afa-a hydroxy-data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130120
Time 19.14
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 4
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 128
DW 83.200 usec
DE 6.50 usec
TE 293.6 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
1.8
1.7
1.6 ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
0.950
2.135
28.297
3.126


176.880
77.911
77.481
77.051
70.230
49.113
48.829
48.545
48.260
47.976
47.692
47.407
34.151
31.755
29.485
29.332
29.209
29.169
24.828
22.463
13.559
HO
O
OH
13
CH3
23
Current Data Parameters
NAME 20130127-afa-Mal-a hydroxy-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130128
Time 22.52
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 7300
DS 0
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 2050
DW 33.200 usec
DE 6.00 usec
TE 299.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7
Current Data Parameters
NAME 1
EXPNO 38
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121025
Time 18.18
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 71.8
DW 83.200 usec
DE 6.50 usec
TE 294.1 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.317
5.301
5.285
2.840
2.158
2.019
2.001
1.980
1.964
1.539
1.522
1.504
1.486
1.466
1.252
0.893
0.876
0.859
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
0.952
4.000
3.014
2.003
1.962
26.203
3.047


169.992
168.429
166.130
O
O
N–O
O
OAc
13
CH3
77.435
77.011
76.588
70.341
31.914
31.274
29.678
29.484
29.345
29.037
25.567
24.663
22.677
20.359
14.097
Current Data Parameters
NAME 20130124-afa-Mal-OAc-OSu-c
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130125
Time 0.25
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 702
DS 0
SWH 15060.241 Hz
FIDRES 0.229801 Hz
AQ 2.1758451 sec
RG 2050
DW 33.200 usec
DE 6.00 usec
TE 297.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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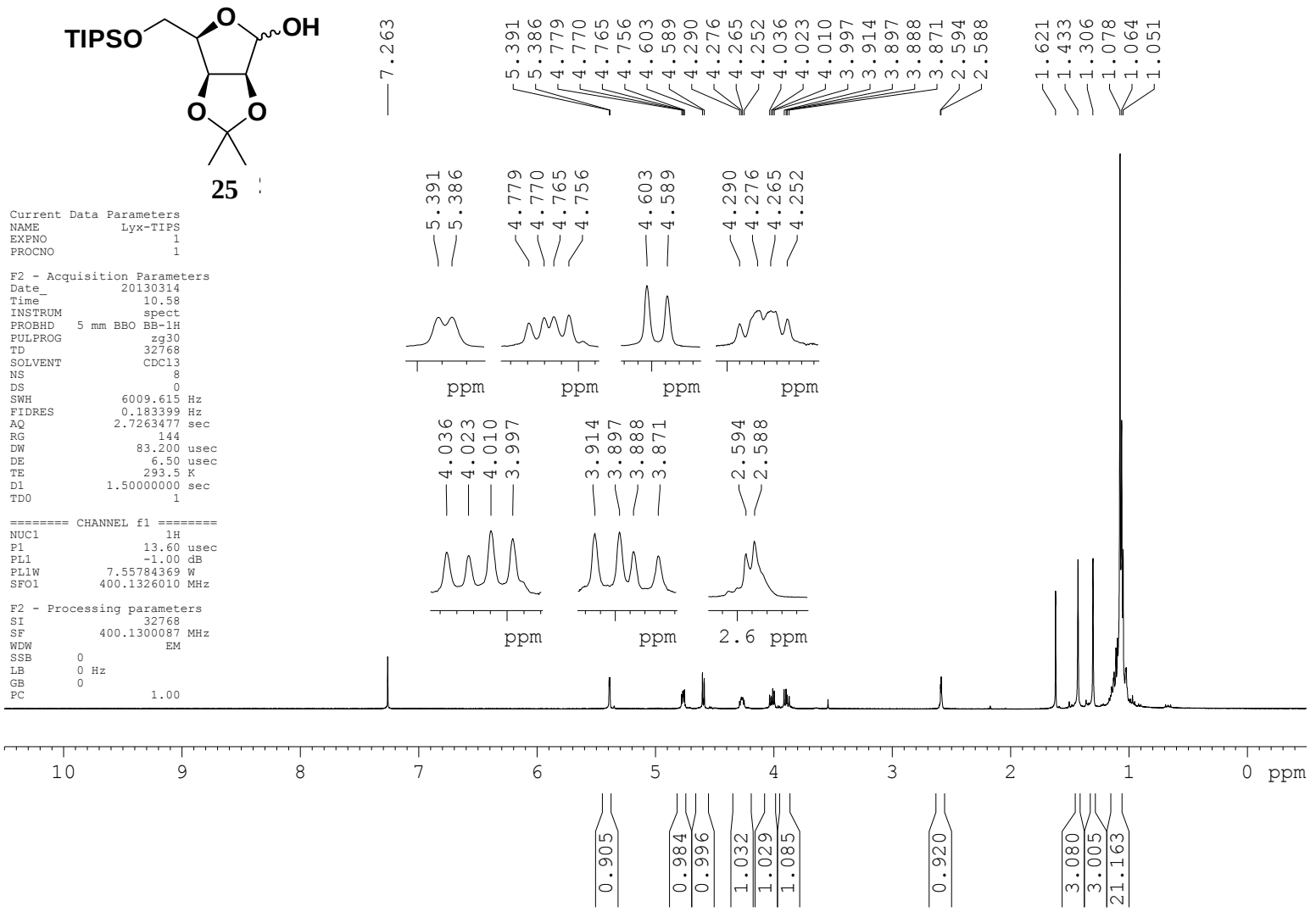
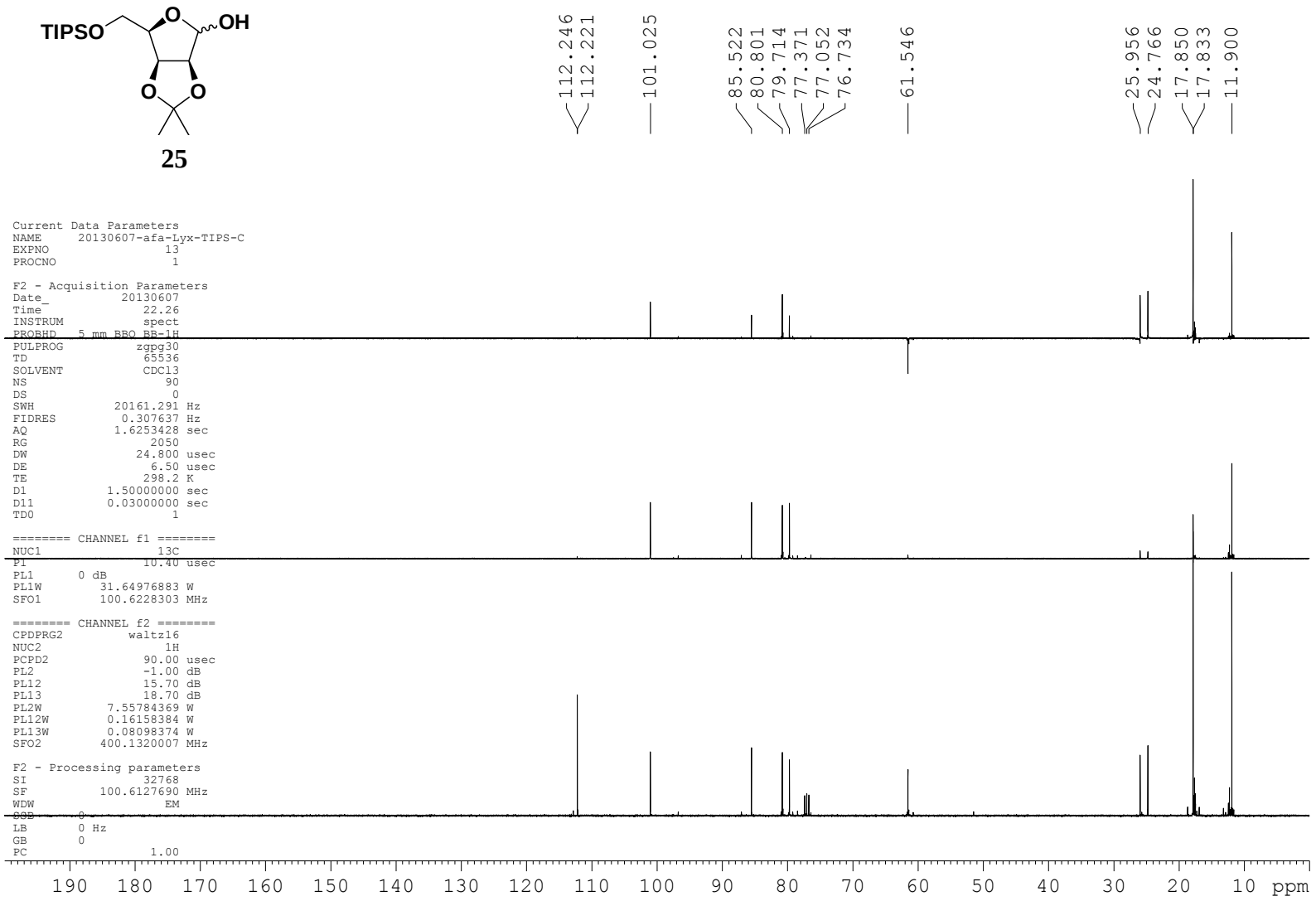
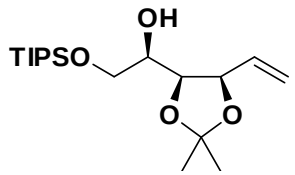

TIPSO
O
OH
O
O
25
7.263
5.391
5.386
4.779
4.770
4.765
4.756
4.603
4.589
4.290
4.276
4.265
4.252
4.036
4.023
4.010
3.997
3.914
3.897
3.888
3.871
2.594
2.588
1.621
1.433
1.306
1.078
1.064
1.051
ppm
2.6 ppm
Current Data Parameters
NAME Lyx-TIPS
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130314
Time 10.58
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 144
DW 83.200 usec
DE 6.50 usec
TE 293.5 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
0.905
0.984
0.996
1.032
1.029
1.085
0.920
3.080
3.005
21.163


TIPSO
O
OH
O
O
25
112.246
112.221
101.025
85.522
80.801
79.714
77.371
77.052
76.734
61.546
25.956
24.766
17.850
17.833
11.900
Current Data Parameters
NAME 20130607-afa-Lyx-TIPS-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130607
Time 22.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 90
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



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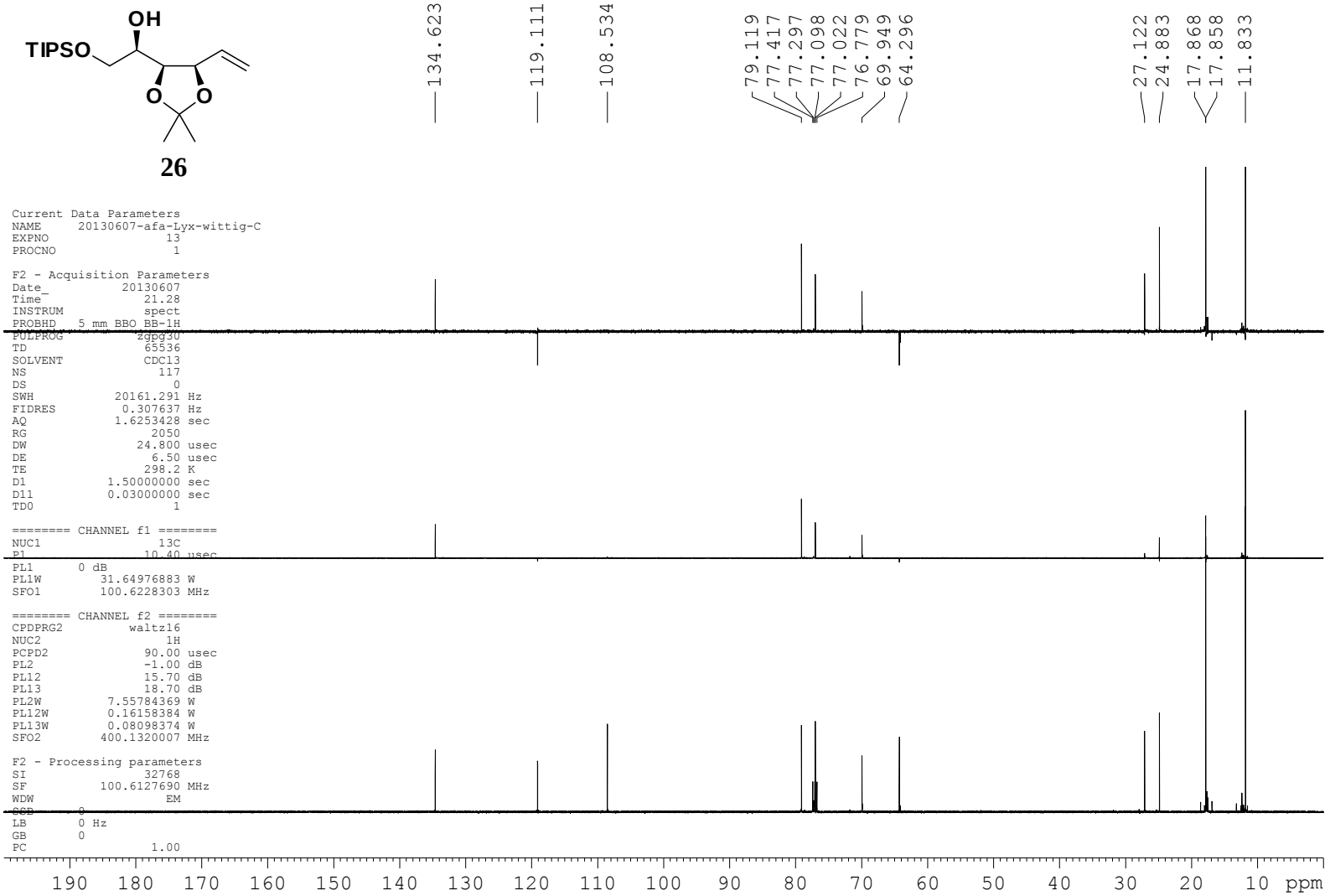
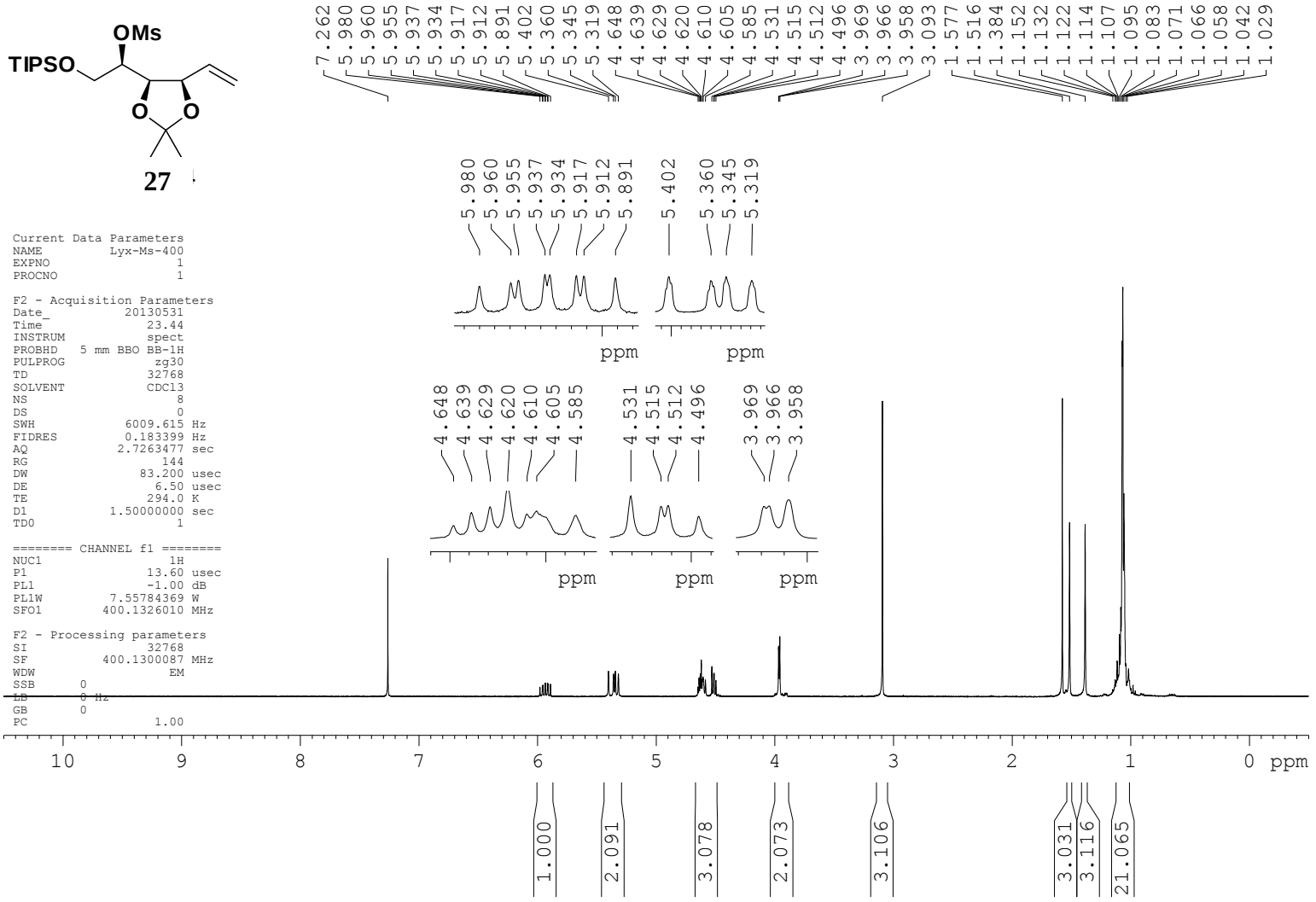
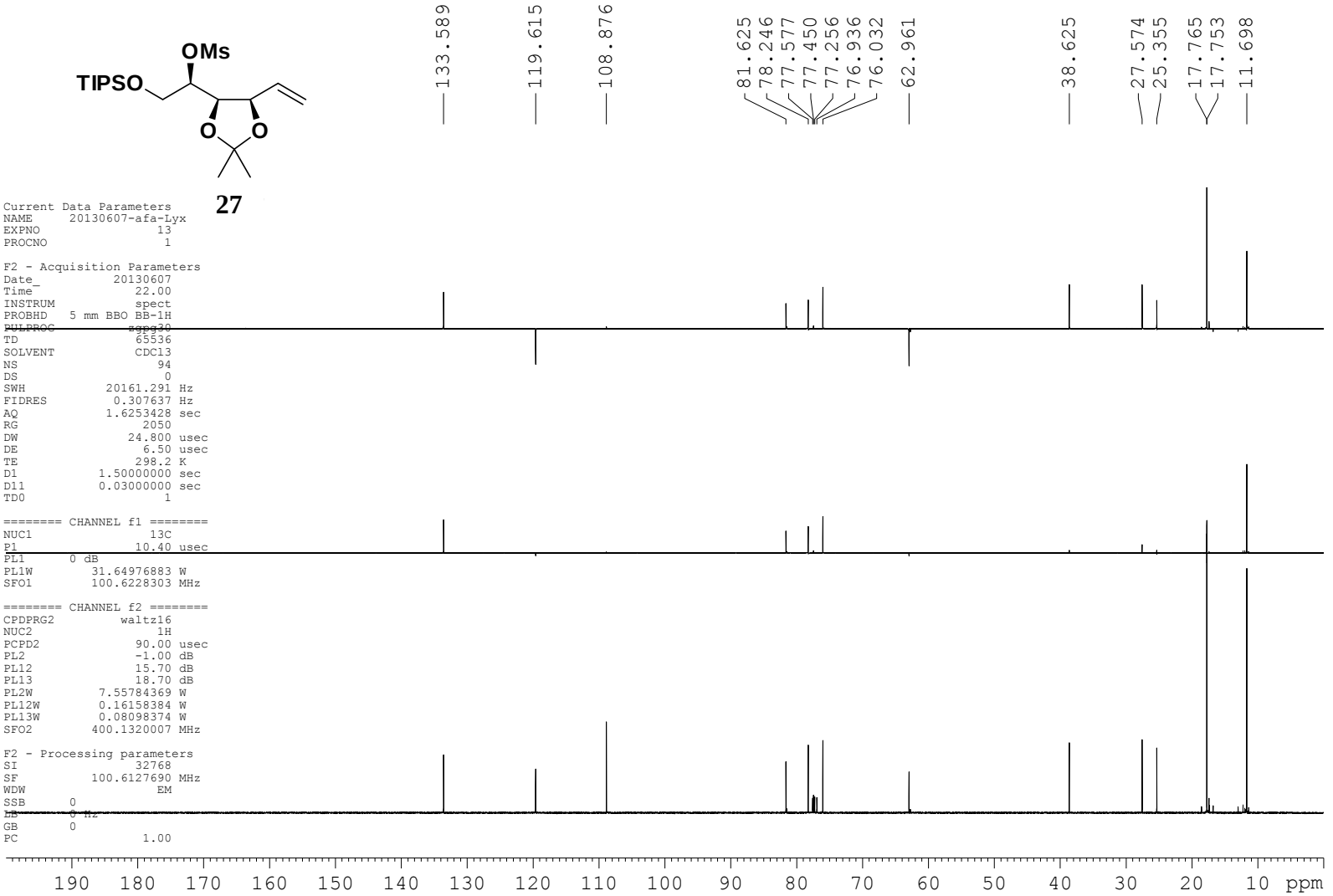
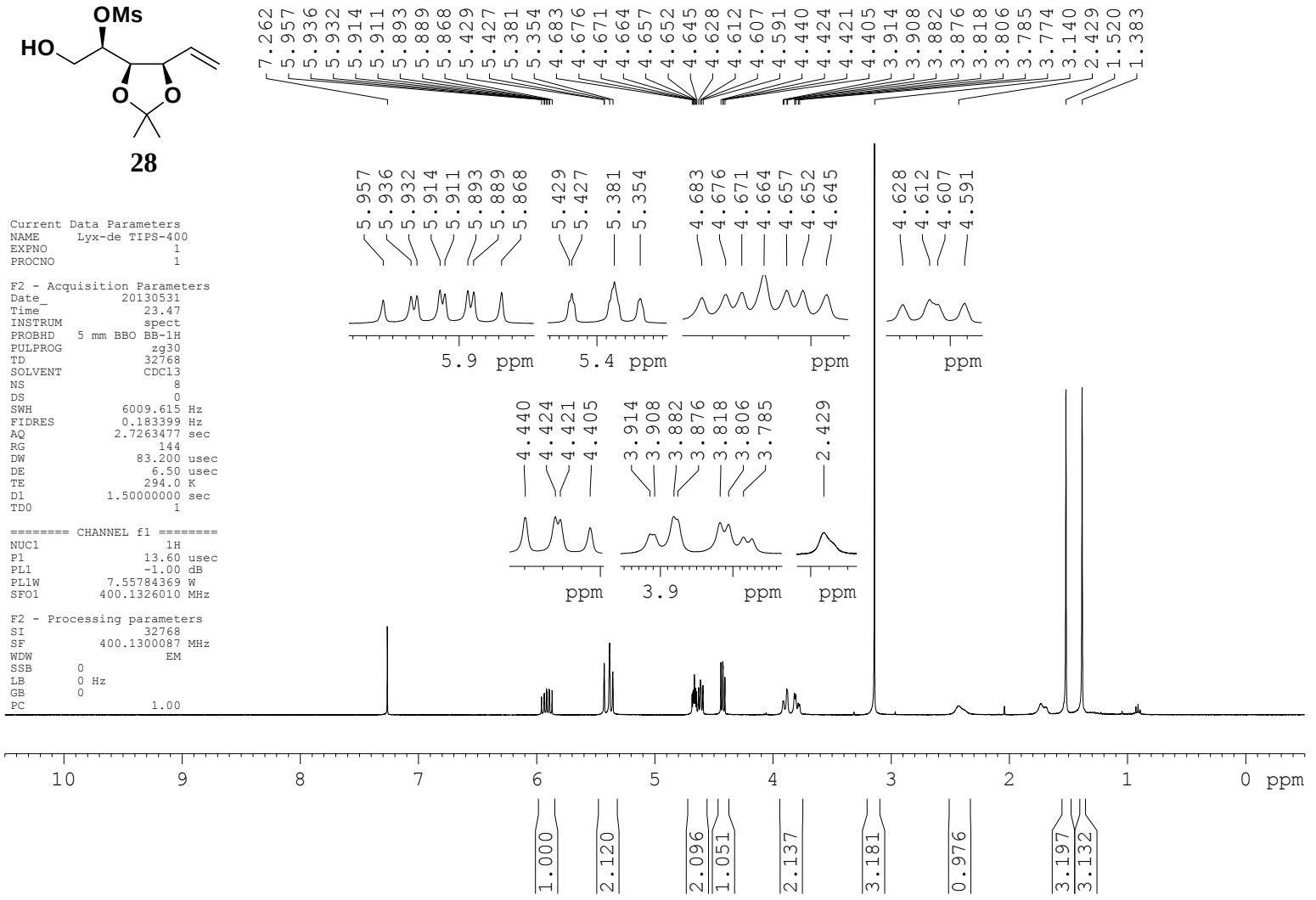
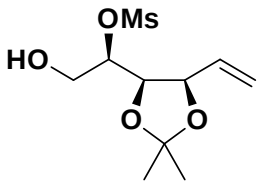
```
Current Data Parameters
NAME      Lyx-wittig-400
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130601
Time              14.36
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   14
DS                    0
SWH            6009.615 Hz
FIDRES        0.183399 Hz
AQ            2.7263477 sec
RG                  228
DW                83.200 usec
DE                 6.50 usec
TE                294.0 K
D1           1.50000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.60 usec
PL1               -1.00 dB
PL1W         7.55784369 W
SFO1        400.1326010 MHz

F2 - Processing parameters
SI                32768
SF          400.1300087 MHz
WDW                  EM
SSB       0
LB        0 Hz
GB        0
PC                1.00
```


OH
TIPSO
O
O
26
134.623
119.111
108.534
79.119
77.417
77.297
77.098
77.022
76.779
69.949
64.296
27.122
24.883
17.868
17.858
11.833
Current Data Parameters
NAME 20130607-afa-Lyx-wittig-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130607
Time 21.28
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 117
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OMs
TIPSO
O
O
27
7.262
5.980
5.960
5.955
5.937
5.934
5.917
5.912
5.891
5.402
5.360
5.345
5.319
4.648
4.639
4.629
4.620
4.610
4.605
4.585
4.531
4.515
4.512
4.496
3.969
3.966
3.958
3.093
1.577
1.516
1.384
1.152
1.132
1.122
1.114
1.107
1.095
1.083
1.071
1.066
1.058
1.042
1.029
Current Data Parameters
NAME Lyx-Ms-400
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130531
Time 23.44
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 144
DW 83.200 usec
DE 6.50 usec
TE 294.0 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
2.091
3.078
2.073
3.106
3.031
3.116
21.065

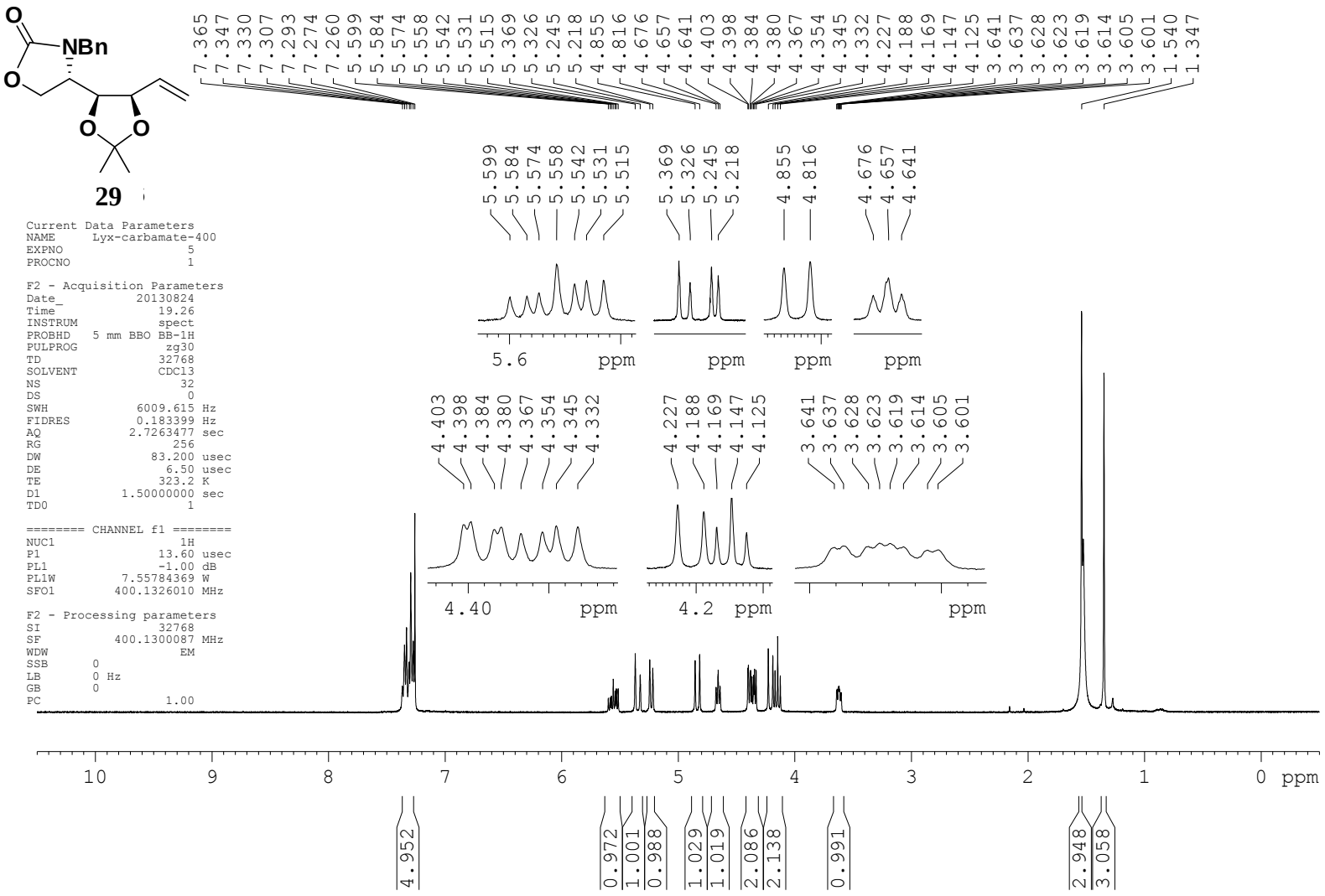

OMs
TIPSO
O
O
27
133.589
119.615
108.876
81.625
78.246
77.577
77.450
77.256
76.936
76.032
62.961
38.625
27.574
25.355
17.765
17.753
11.698
Current Data Parameters
NAME 20130607-afa-Lyx
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130607
Time 22.00
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 94
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

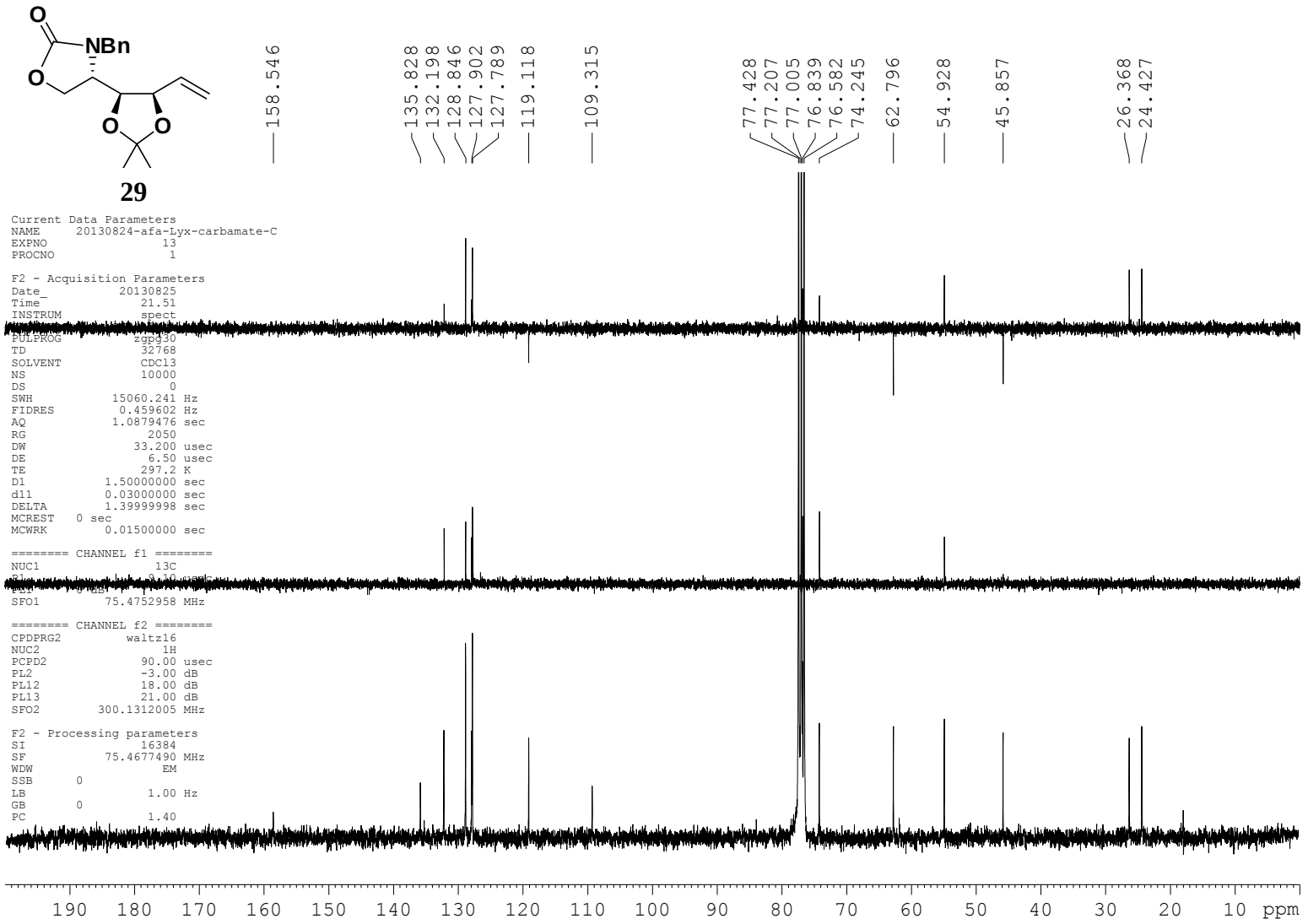

OMs
HO
O
O
28
7.262
5.957
5.936
5.932
5.914
5.911
5.893
5.889
5.868
5.429
5.427
5.381
5.354
4.683
4.676
4.671
4.664
4.657
4.652
4.645
4.628
4.612
4.607
4.591
4.440
4.424
4.421
4.405
3.914
3.908
3.882
3.876
3.818
3.806
3.785
3.774
3.140
2.429
1.520
1.383
Current Data Parameters
NAME Lyx-de TIPS-400
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130531
Time 23.47
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 144
DW 83.200 usec
DE 6.50 usec
TE 294.0 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.9 ppm
5.4 ppm
ppm
ppm
ppm
3.9
ppm
ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
2.120
2.096
1.051
2.137
3.181
0.976
3.197
3.132

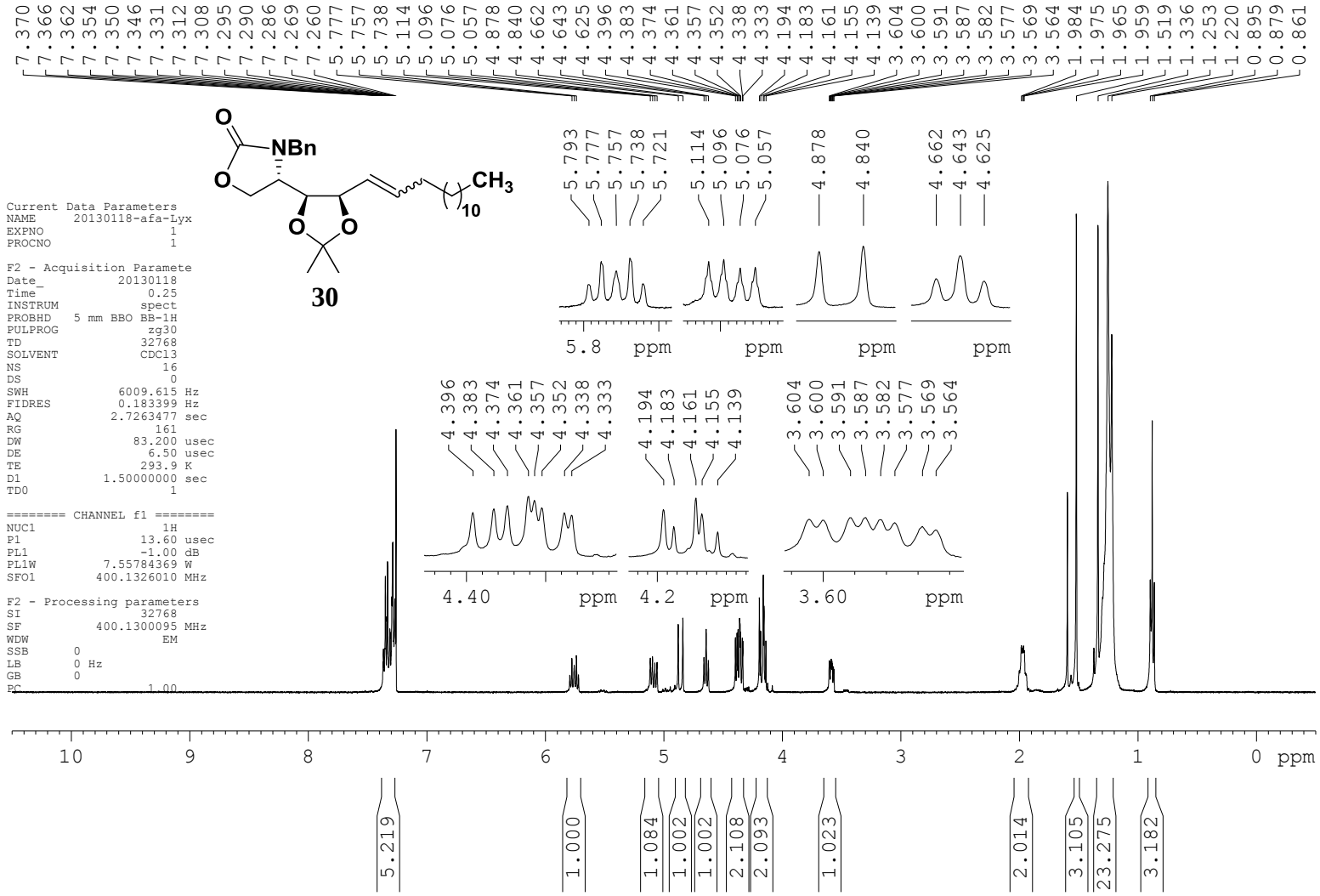

OMs
HO
O
O

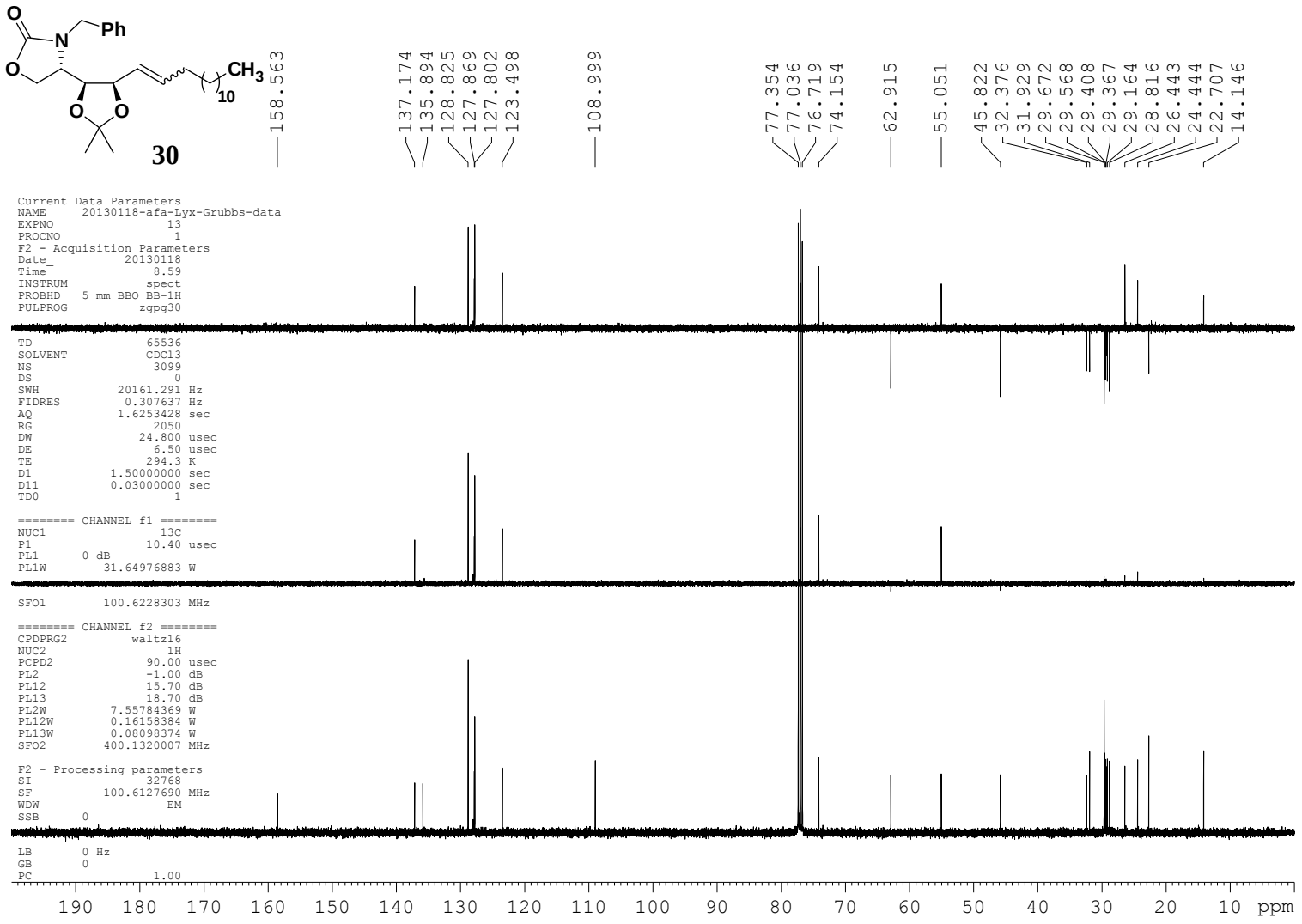
28

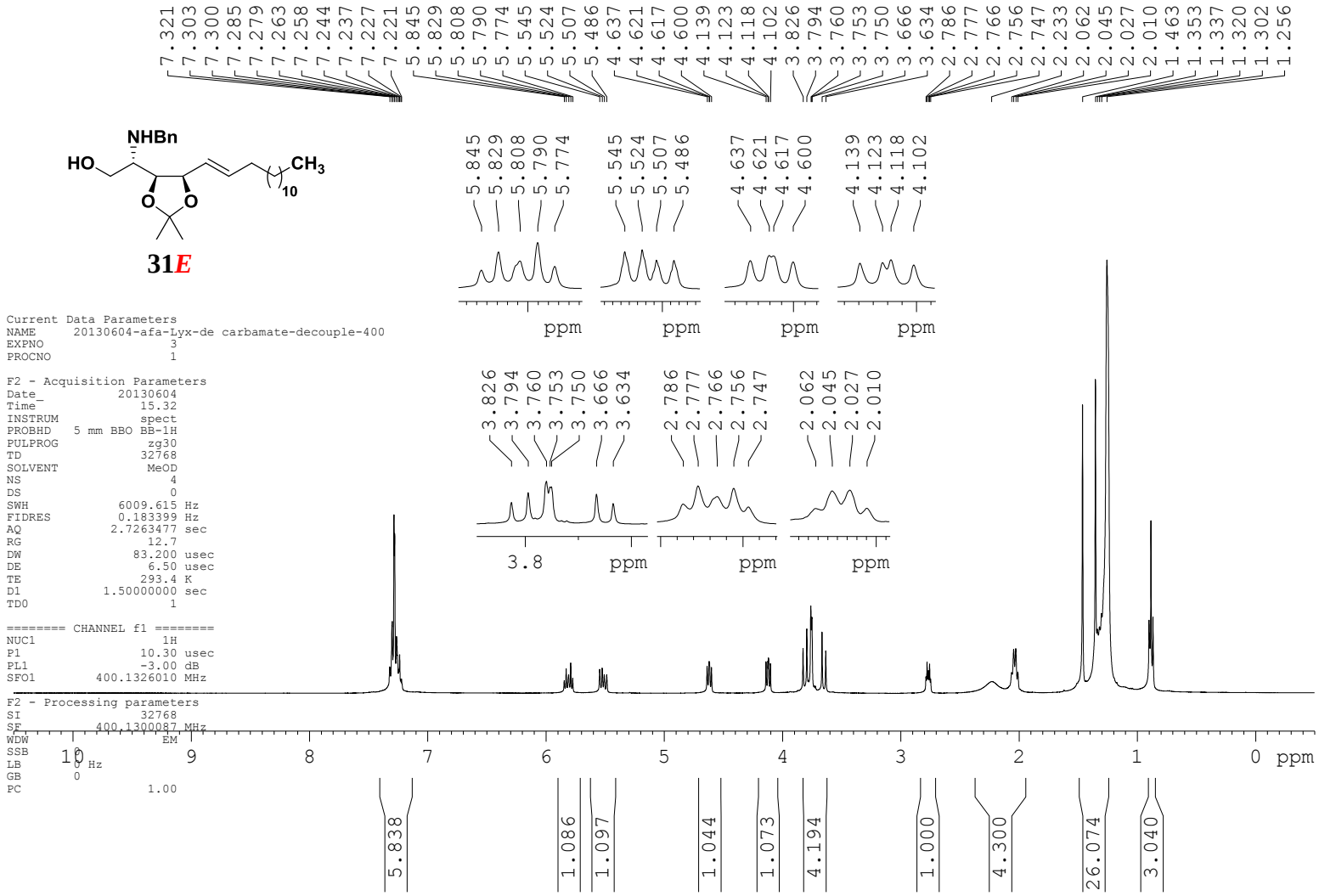
132.992
120.439
109.256
82.135
78.298
77.566
77.247
76.928
76.007
61.826
38.802
27.543
25.427
Current Data Parameters
NAME 20130607-afa-Lyx-de TIPS-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date 20130607
Time 22.45
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 81
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

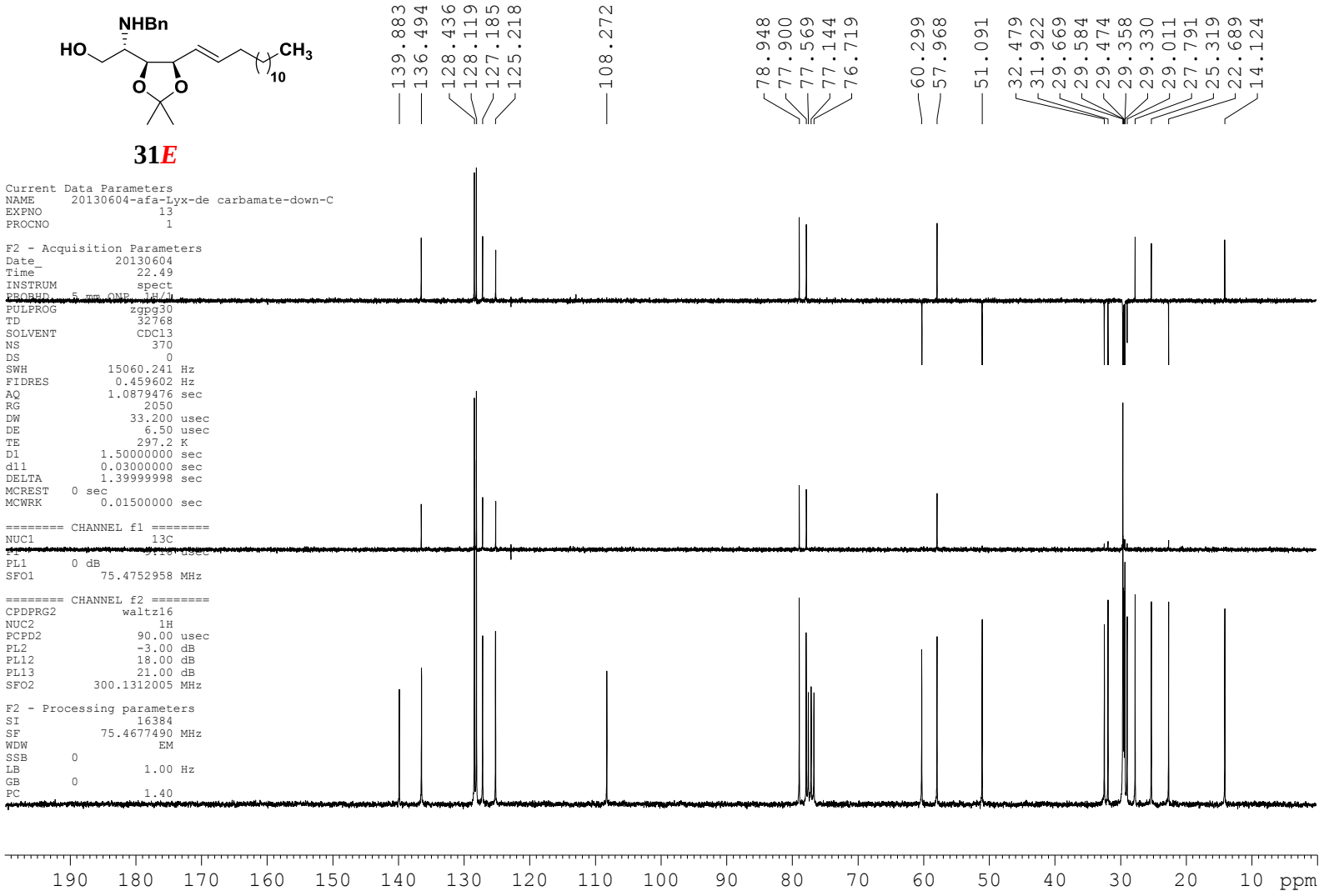

NBn
O
O
O
O
29
7.365 7.347 7.330 7.307 7.293 7.274 7.260 5.599 5.584 5.574 5.558 5.542 5.531 5.515 5.369 5.326 5.245 5.218 4.855 4.816 4.676 4.657 4.641 4.403 4.398 4.384 4.380 4.367 4.354 4.345 4.332 4.227 4.188 4.169 4.147 4.125 3.641 3.637 3.628 3.623 3.619 3.614 3.605 3.601 1.540 1.347
Current Data Parameters
NAME Lyx-carbamate-400
EXPNO 5
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130824
Time 19.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 256
DW 83.200 usec
DE 6.50 usec
TE 323.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.6 ppm
4.40 ppm
4.2 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
4.952
0.972 1.001 0.988
1.029 1.019
2.086 2.138
0.991
2.948 3.058

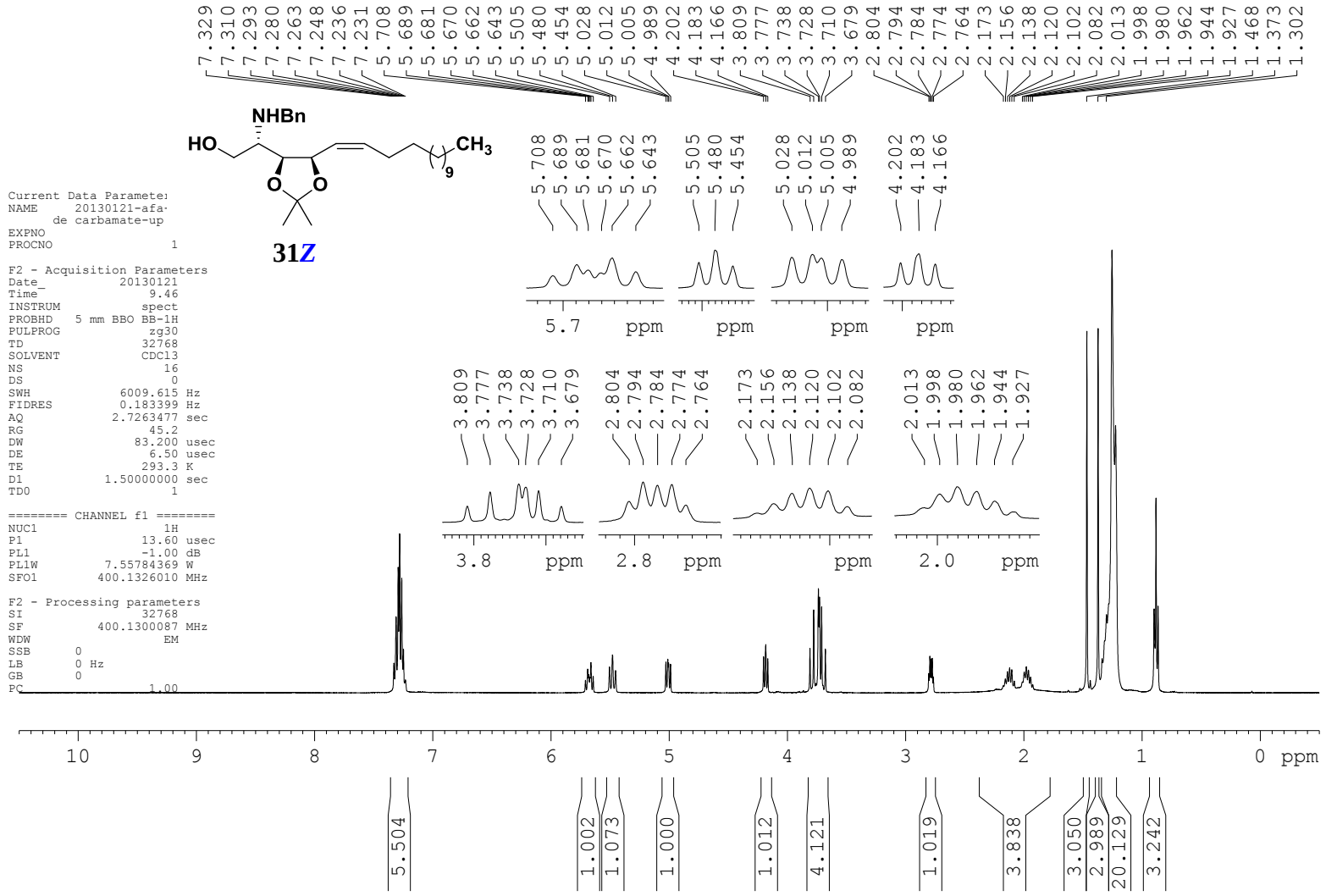

NBn
O
O
O
O
158.546
135.828
132.198
128.846
127.902
127.789
119.118
109.315
77.428
77.207
77.005
76.839
76.582
74.245
62.796
54.928
45.857
26.368
24.427
29
Current Data Parameters
NAME 20130824-afa-Lyx-carbamate-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130825
Time 21.51
INSTRUM spect
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 10000
DS 0
SWH 15060.241 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 2050
DW 33.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 16384
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

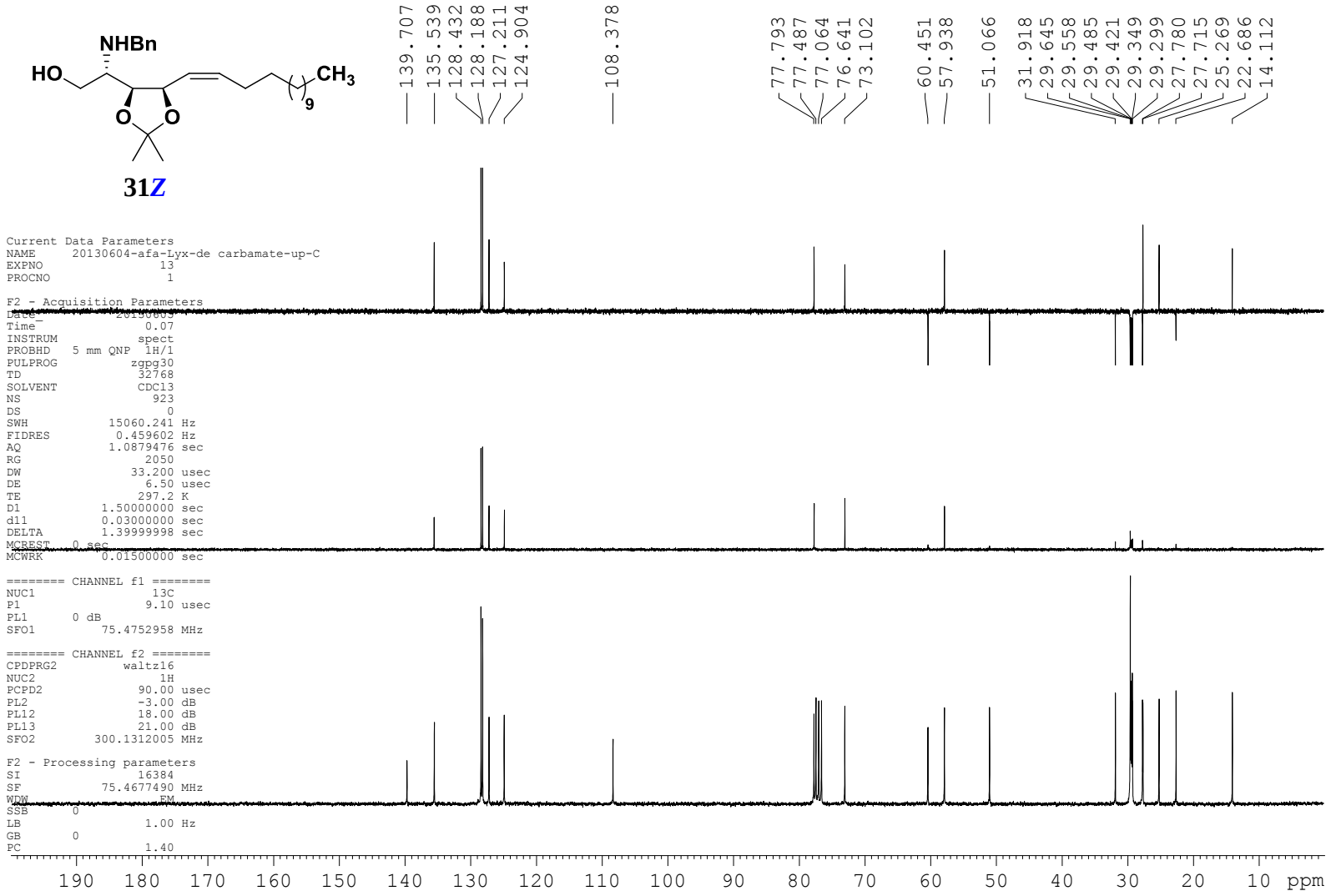

7.370 7.366 7.362 7.354 7.350 7.346 7.331 7.312 7.308 7.295 7.290 7.286 7.269 7.260 5.777 5.757 5.738 5.114 5.096 5.076 5.057 4.878 4.840 4.662 4.643 4.625 4.396 4.383 4.374 4.361 4.357 4.352 4.338 4.333 4.194 4.183 4.161 4.155 4.139 3.604 3.600 3.591 3.587 3.582 3.577 3.569 3.564 1.984 1.975 1.965 1.959 1.519 1.336 1.253 1.220 0.895 0.879 0.861
NBn
CH3
10
30
Current Data Parameters
NAME 20130118-afa-Lyx
EXPNO 1
PROCNO 1
F2 - Acquisition Paramete
Date_ 20130118
Time 0.25
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 161
DW 83.200 usec
DE 6.50 usec
TE 293.9 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.793 5.777 5.757 5.738 5.721
5.114 5.096 5.076 5.057
4.878 4.840
4.662 4.643 4.625
5.8 ppm
4.396 4.383 4.374 4.361 4.357 4.352 4.338 4.333
4.194 4.183 4.161 4.155 4.139
3.604 3.600 3.591 3.587 3.582 3.577 3.569 3.564
4.40 ppm
4.2 ppm
3.60 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
5.219
1.000
1.084
1.002
1.002
2.108
2.093
1.023
2.014
3.105
23.275
3.182

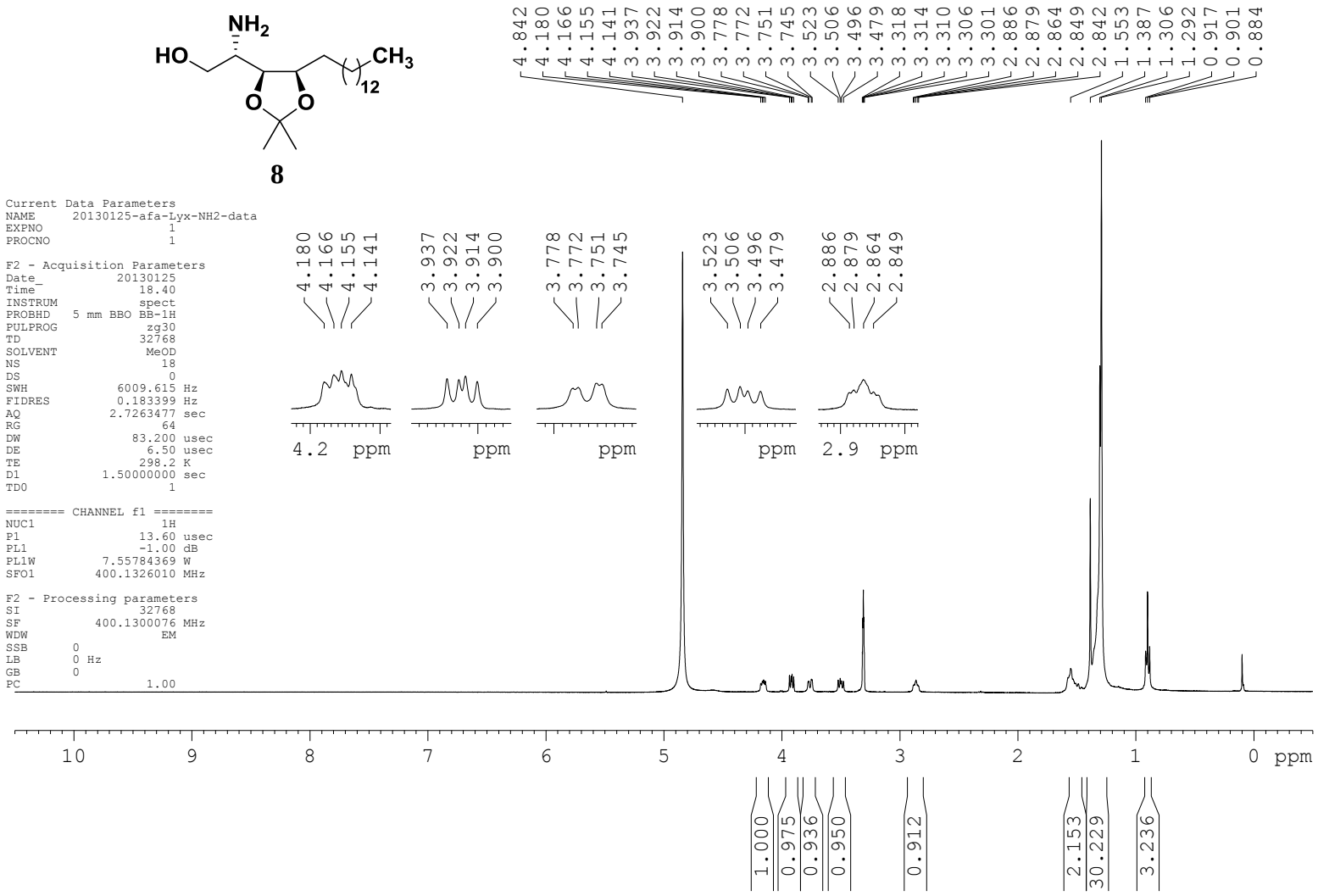

O
N
Ph
O
O
O
CH3
10
30
158.563
137.174
135.894
128.825
127.869
127.802
123.498
108.999
77.354
77.036
76.719
74.154
62.915
55.051
45.822
32.376
31.929
29.672
29.568
29.408
29.367
29.164
28.816
26.443
24.444
22.707
14.146
Current Data Parameters
NAME 20130118-afa-Lyx-Grubbs-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130118
Time 8.59
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3099
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.3 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

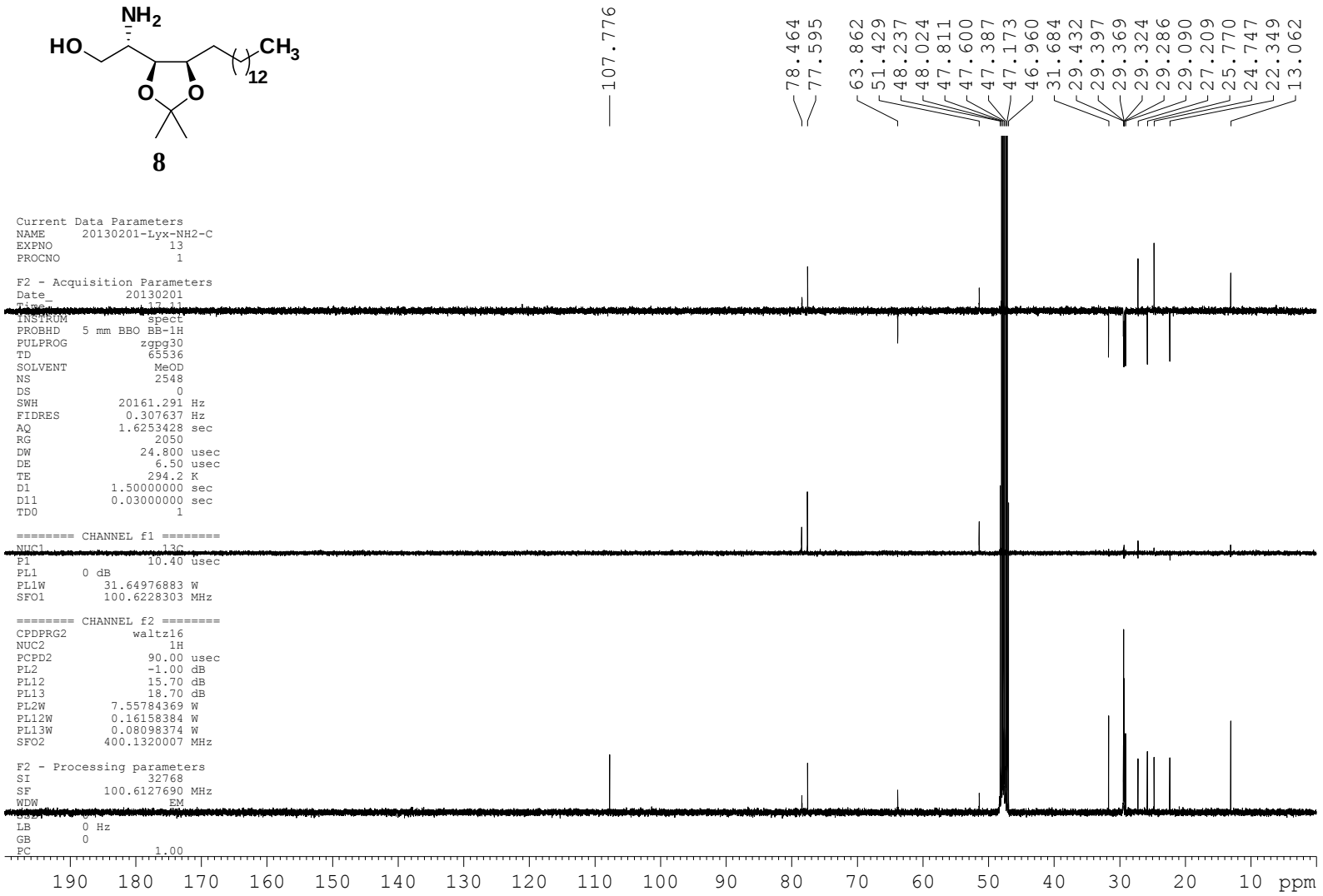

7.321 7.303 7.300 7.285 7.279 7.263 7.258 7.244 7.237 7.227 7.221 5.845 5.829 5.808 5.790 5.774 5.545 5.524 5.507 5.486 4.637 4.621 4.617 4.600 4.139 4.123 4.118 4.102 3.826 3.794 3.760 3.753 3.750 3.666 3.634 2.786 2.777 2.766 2.756 2.747 2.233 2.062 2.045 2.027 2.010 1.463 1.353 1.337 1.320 1.302 1.256
NHBn
HO
CH3
10
O
O
31E
Current Data Parameters
NAME 20130604-afa-Lyx-de carbamate-decouple-400
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130604
Time 15.32
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 4
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 12.7
DW 83.200 usec
DE 6.50 usec
TE 293.4 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 -3.00 dB
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
5.838
1.086
1.097
1.044
1.073
4.194
1.000
4.300
26.074
3.040

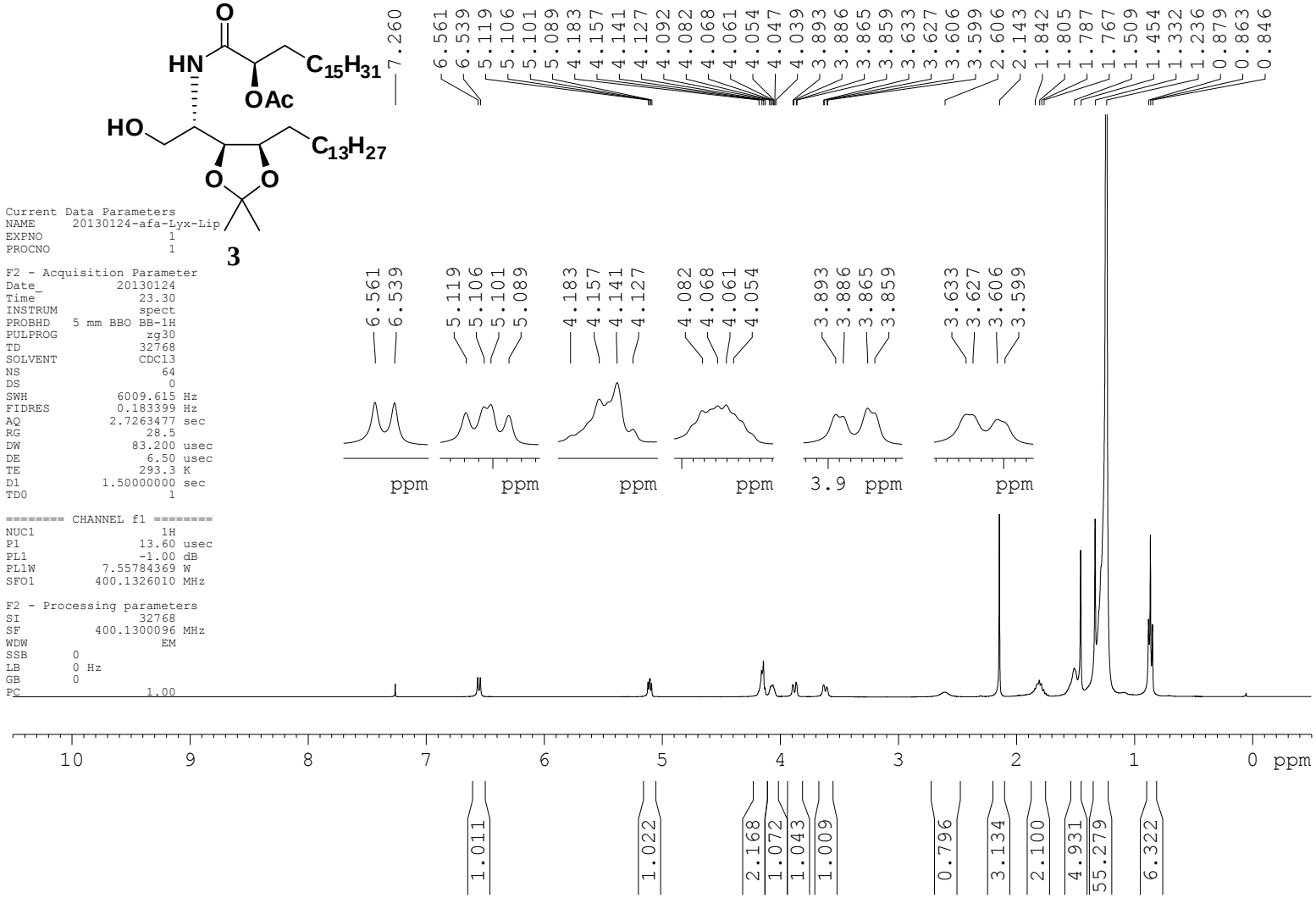

NHBn
HO
O
O
CH3
10
139.883
136.494
128.436
128.119
127.185
125.218
108.272
78.948
77.900
77.569
77.144
76.719
60.299
57.968
51.091
32.479
31.922
29.669
29.584
29.474
29.358
29.330
29.011
27.791
25.319
22.689
14.124
31E
Current Data Parameters
NAME 20130604-afa-Lyx-de carbamate-down-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130604
Time 22.49
INSTRUM spect
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 370
DS 0
SWH 15060.241 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 2050
DW 33.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 16384
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

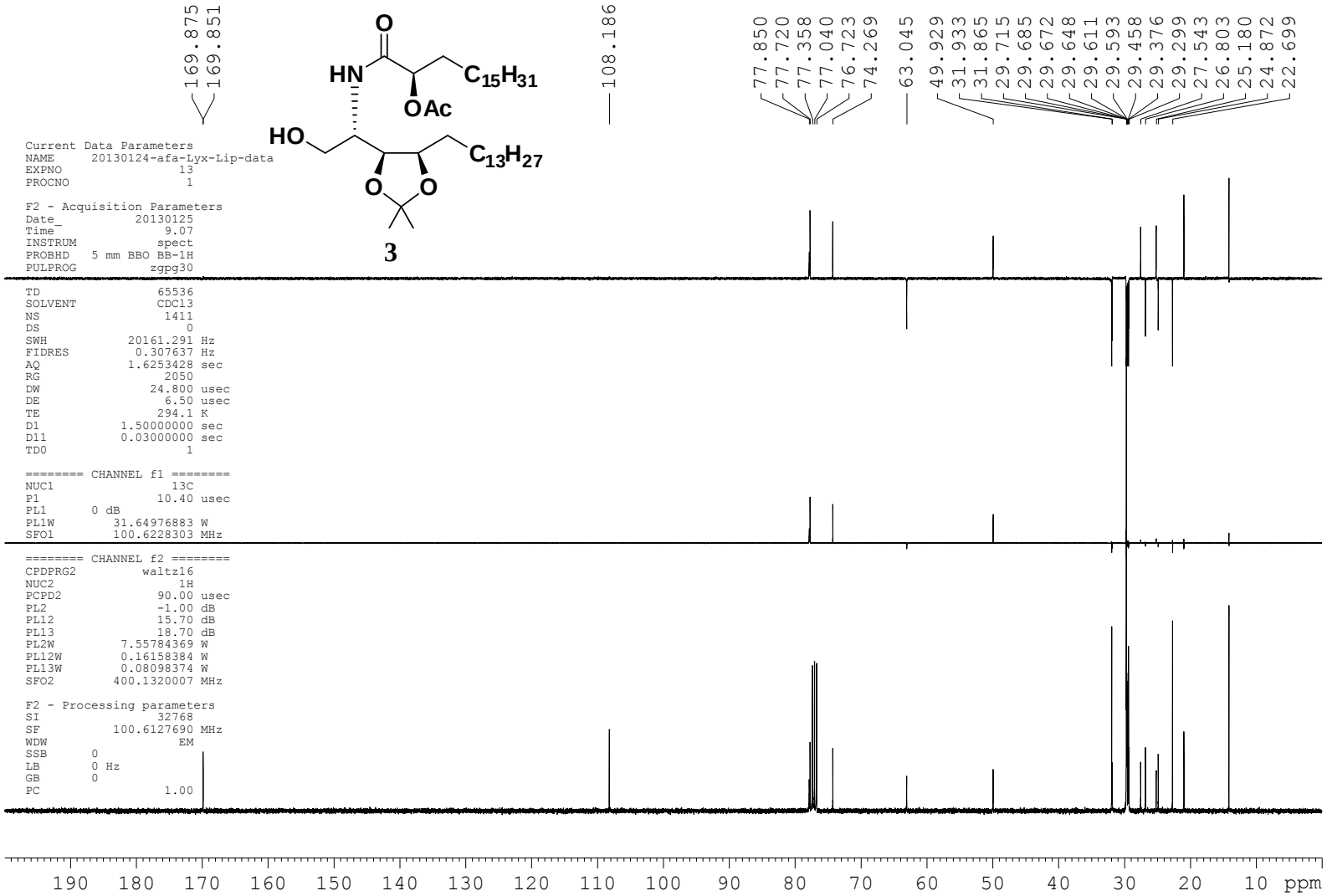

7.329 7.310 7.293 7.280 7.263 7.248 7.236 7.231 5.708 5.689 5.681 5.670 5.662 5.643 5.505 5.480 5.454 5.028 5.012 5.005 4.989 4.202 4.183 4.166 3.809 3.777 3.738 3.728 3.710 3.679 2.804 2.794 2.784 2.774 2.764 2.173 2.156 2.138 2.120 2.102 2.082 2.013 1.998 1.980 1.962 1.944 1.927 1.468 1.373 1.302
NHBn
HO
CH3
9
O
O
31Z
Current Data Parameter
NAME 20130121-afa·
de carbamate-up
EXPNO
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130121
Time 9.46
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 45.2
DW 83.200 usec
DE 6.50 usec
TE 293.3 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.7 ppm
3.8 ppm
2.8 ppm
2.0 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
5.504
1.002
1.073
1.000
1.012
4.121
1.019
3.838
3.050
2.989
20.129
3.242

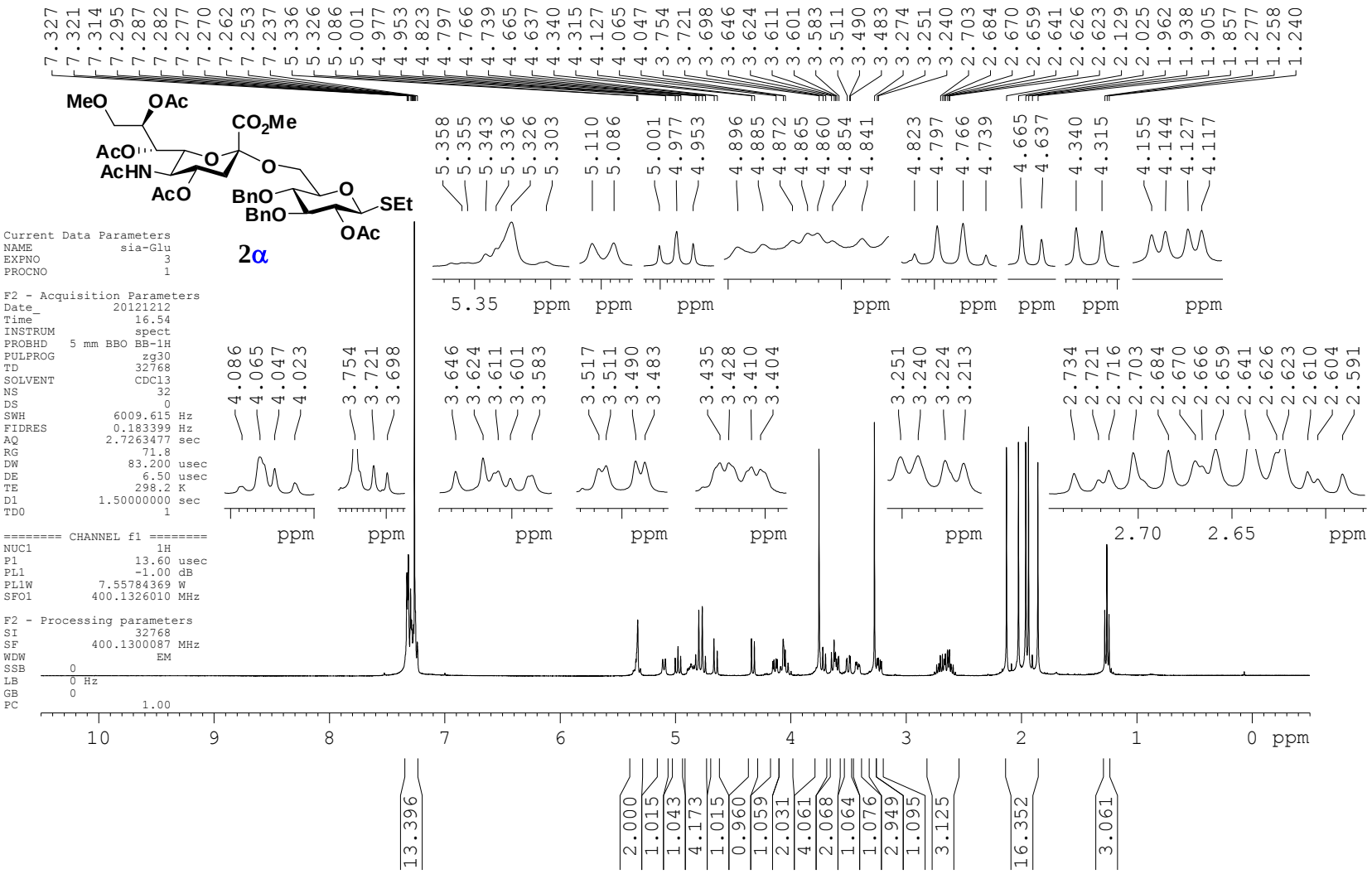

NHBn
HO
O
O
CH3
9
31Z
139.707
135.539
128.432
128.188
127.211
124.904
108.378
77.793
77.487
77.064
76.641
73.102
60.451
57.938
51.066
31.918
29.645
29.558
29.485
29.421
29.349
29.299
27.780
27.715
25.269
22.686
14.112
Current Data Parameters
NAME 20130604-afa-Lyx-de carbamate-up-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Time 0.07
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDC13
NS 923
DS 0
SWH 15060.241 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 2050
DW 33.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 16384
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

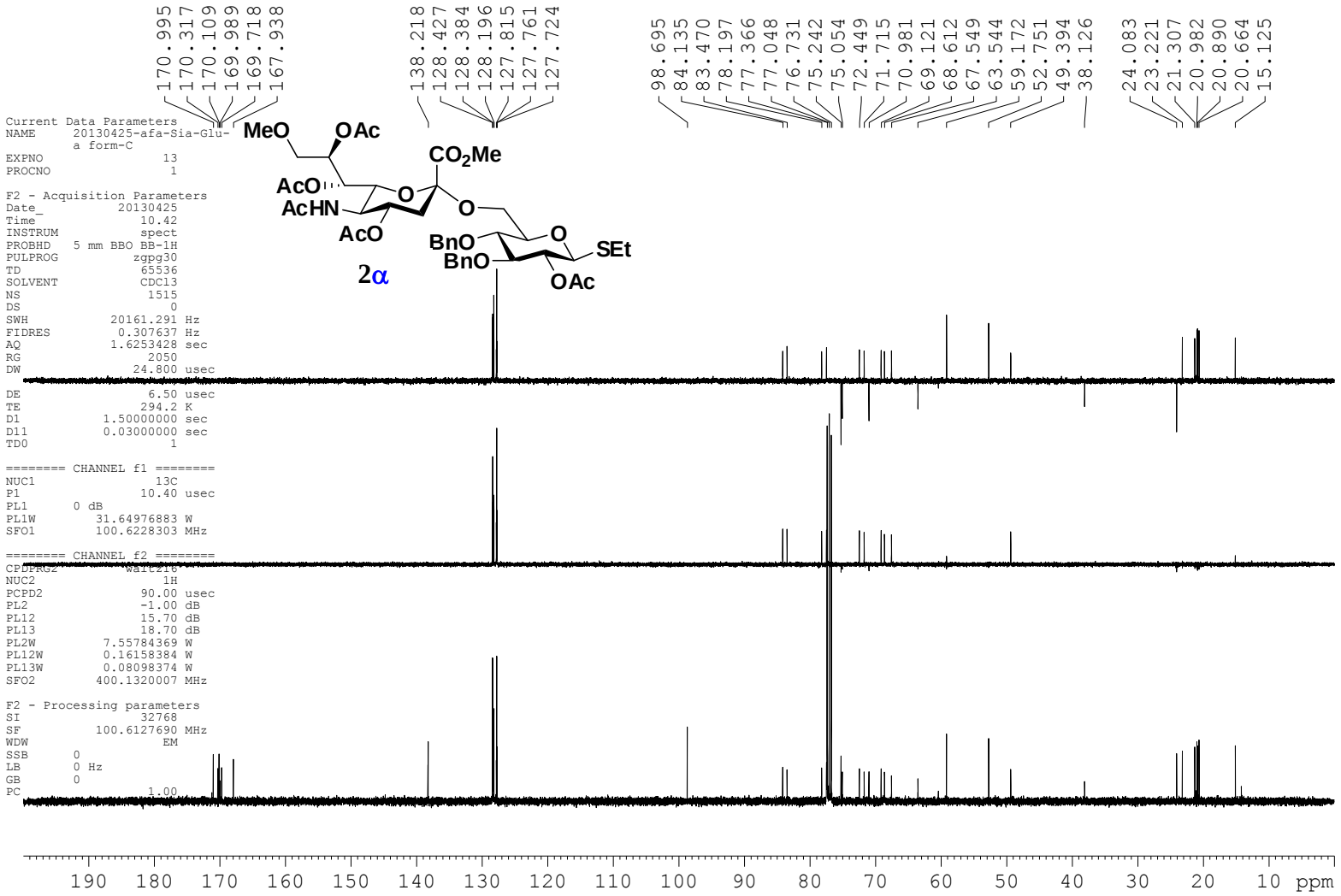

NH2
HO
CH3
12
O
O
8
4.842
4.180
4.166
4.155
4.141
3.937
3.922
3.914
3.900
3.778
3.772
3.751
3.745
3.523
3.506
3.496
3.479
3.318
3.314
3.310
3.306
3.301
2.886
2.879
2.864
2.849
2.842
1.553
1.387
1.306
1.292
0.917
0.901
0.884
Current Data Parameters
NAME 20130125-afa-Lyx-NH2-data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130125
Time 18.40
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 18
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 64
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300076 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
4.180
4.166
4.155
4.141
3.937
3.922
3.914
3.900
3.778
3.772
3.751
3.745
3.523
3.506
3.496
3.479
2.886
2.879
2.864
2.849
4.2 ppm
ppm
ppm
ppm
2.9 ppm
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.975
0.936
0.950
0.912
2.153
30.229
3.236

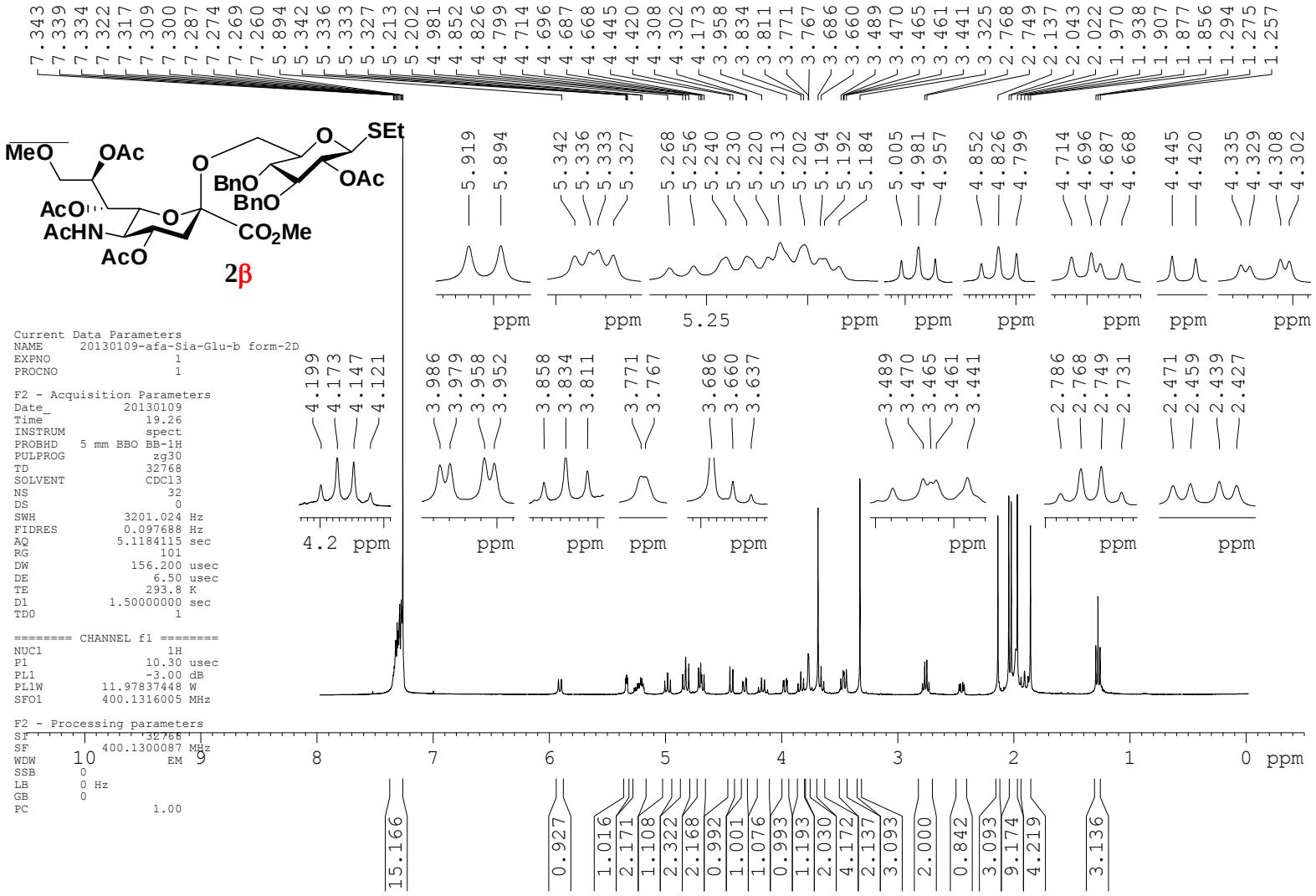

NH2
HO
CH3
12
O
O
8
107.776
78.464
77.595
63.862
51.429
48.237
48.024
47.811
47.600
47.387
47.173
46.960
31.684
29.432
29.397
29.369
29.324
29.286
29.090
27.209
25.770
24.747
22.349
13.062
Current Data Parameters
NAME 20130201-Lyx-NH2-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130201
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 2548
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

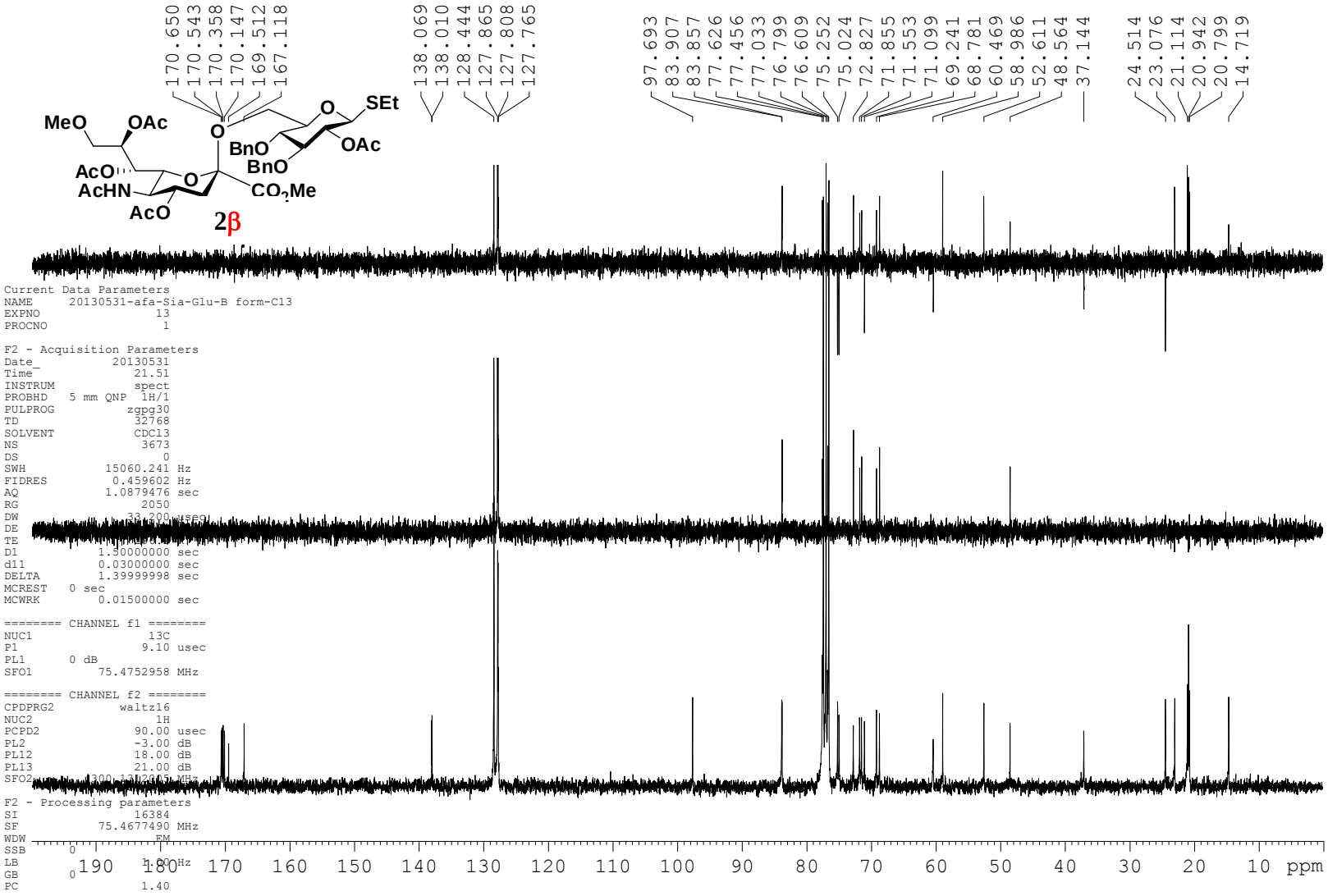

HN
O
OAc
C15H31
HO
C13H27
O
O
3
7.260
6.561
6.539
5.119
5.106
5.101
5.089
4.183
4.157
4.141
4.127
4.092
4.082
4.068
4.061
4.054
4.047
4.039
3.893
3.886
3.865
3.859
3.633
3.627
3.606
3.599
2.606
2.143
1.842
1.805
1.787
1.767
1.509
1.454
1.332
1.236
0.879
0.863
0.846
Current Data Parameters
NAME 20130124-afa-Lyx-Lip
EXPNO 1
PROCNO 1
F2 - Acquisition Parameter
Date_ 20130124
Time 23.30
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 28.5
DW 83.200 usec
DE 6.50 usec
TE 293.3 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
3.9
10
9
8
7
6
5
4
3
2
1
0 ppm
1.011
1.022
2.168
1.072
1.043
1.009
0.796
3.134
2.100
4.931
55.279
6.322

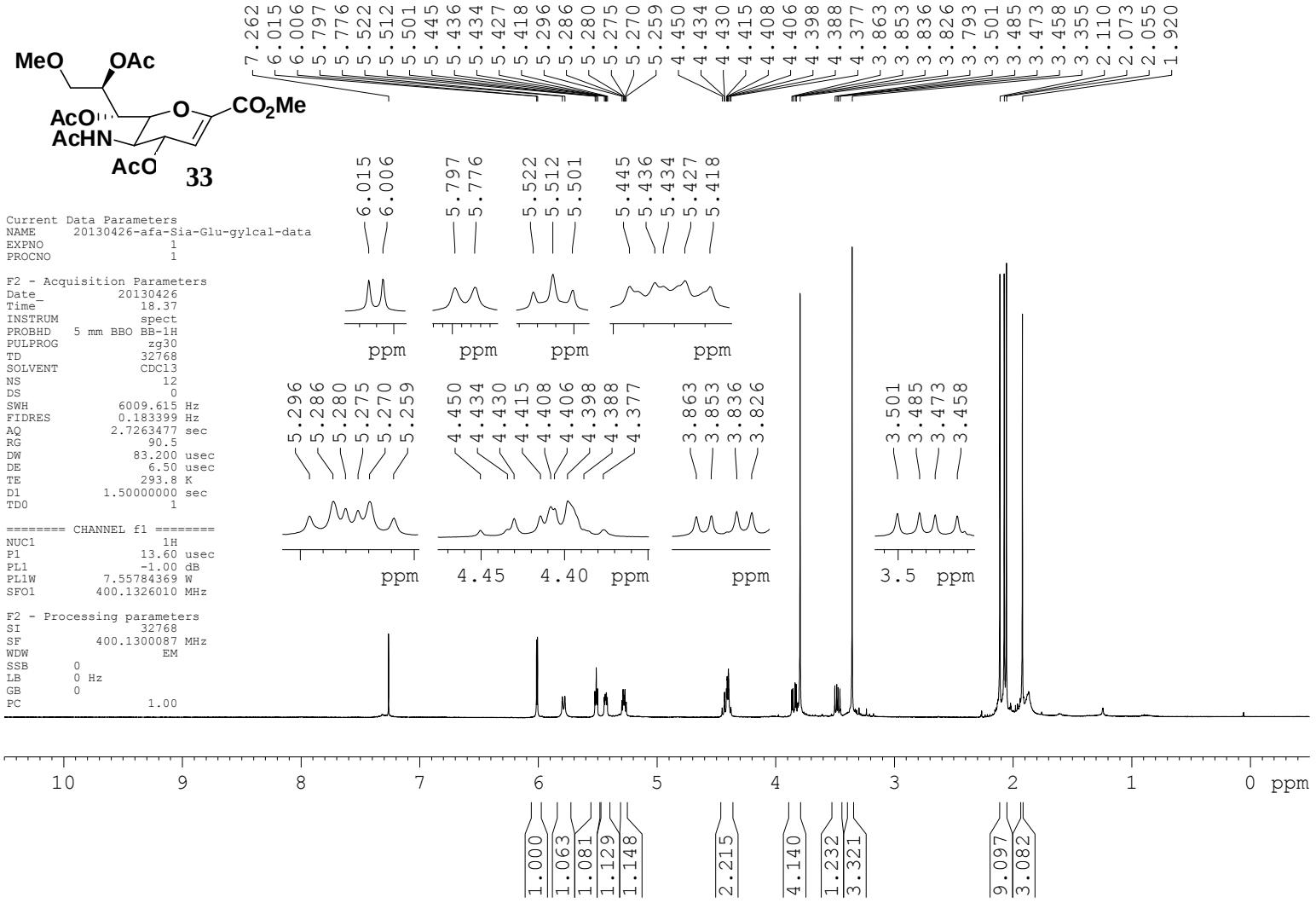

169.875
169.851
108.186
77.850
77.720
77.358
77.040
76.723
74.269
63.045
49.929
31.933
31.865
29.715
29.685
29.672
29.648
29.611
29.593
29.458
29.376
29.299
27.543
26.803
25.180
24.872
22.699
HN
O
C15H31
OAc
HO
C13H27
O
O
3
Current Data Parameters
NAME 20130124-afa-Lyx-Lip-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130125
Time 9.07
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1411
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.1 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

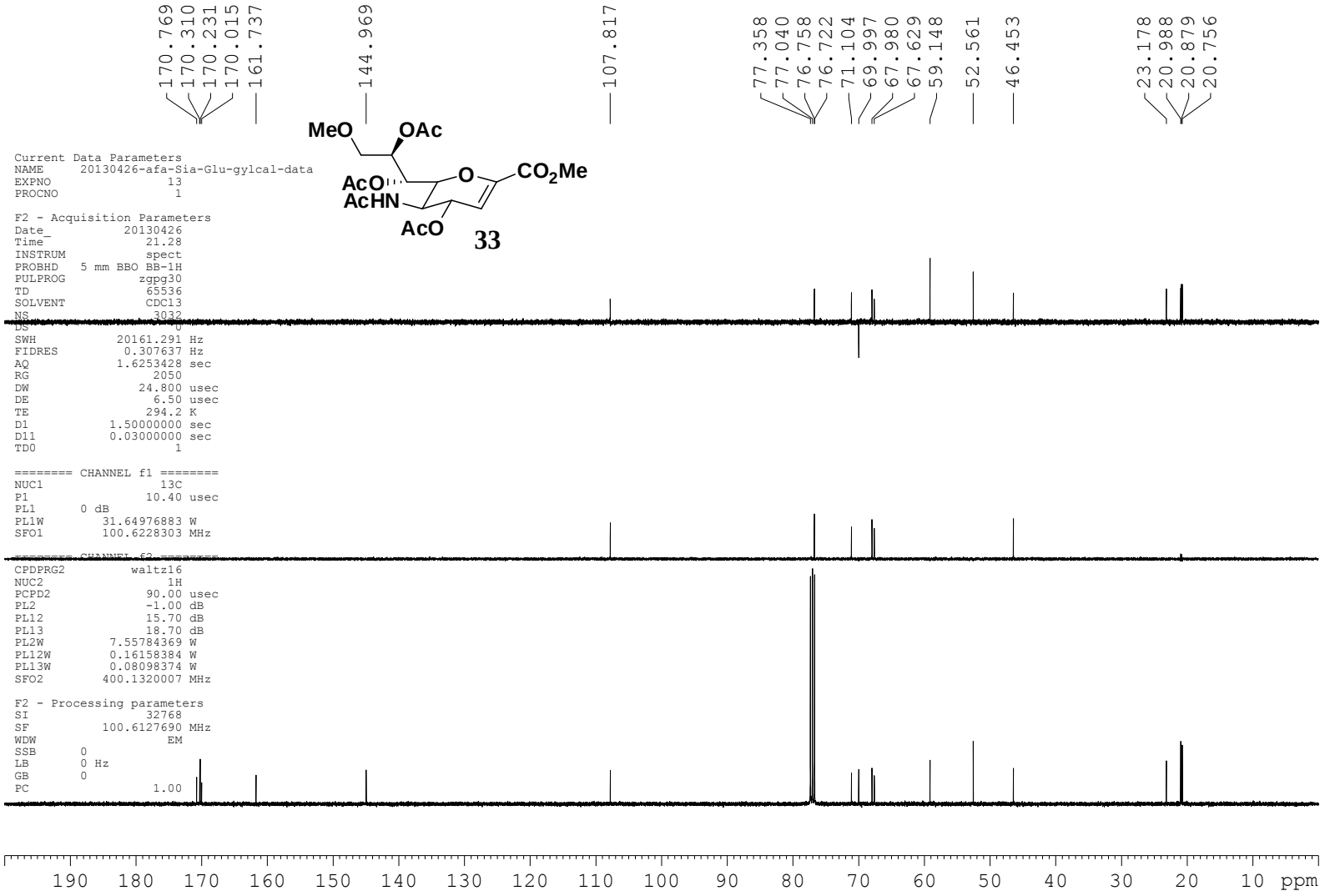

MeO
OAc
CO2Me
AcO
AcHN
AcO
BnO
BnO
SEt
OAc
2α
Current Data Parameters
NAME sia-Glu
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121212
Time 16.54
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 71.8
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
7.327 7.321 7.314 7.295 7.287 7.282 7.277 7.270 7.262 7.253 7.237 5.336 5.326 5.086 5.001 4.977 4.953 4.823 4.797 4.766 4.739 4.665 4.637 4.340 4.315 4.127 4.065 4.047 3.754 3.721 3.698 3.646 3.624 3.611 3.601 3.583 3.511 3.490 3.483 3.274 3.251 3.240 2.703 2.684 2.670 2.659 2.641 2.626 2.623 2.129 2.025 1.962 1.938 1.905 1.857 1.277 1.258 1.240
5.358 5.355 5.343 5.336 5.326 5.303 5.110 5.086 5.001 4.977 4.953 4.896 4.885 4.872 4.865 4.860 4.854 4.841 4.823 4.797 4.766 4.739 4.665 4.637 4.340 4.315 4.155 4.144 4.127 4.117
4.086 4.065 4.047 4.023 3.754 3.721 3.698 3.646 3.624 3.611 3.601 3.583 3.517 3.511 3.490 3.483 3.435 3.428 3.410 3.404 3.251 3.240 3.224 3.213 2.734 2.721 2.716 2.703 2.684 2.670 2.666 2.659 2.641 2.626 2.623 2.610 2.604 2.591
5.35 ppm
2.70 2.65 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
13.396 2.000 1.015 1.043 4.173 1.015 0.960 1.059 2.031 4.061 2.068 1.064 1.076 2.949 1.095 3.125 16.352 3.061

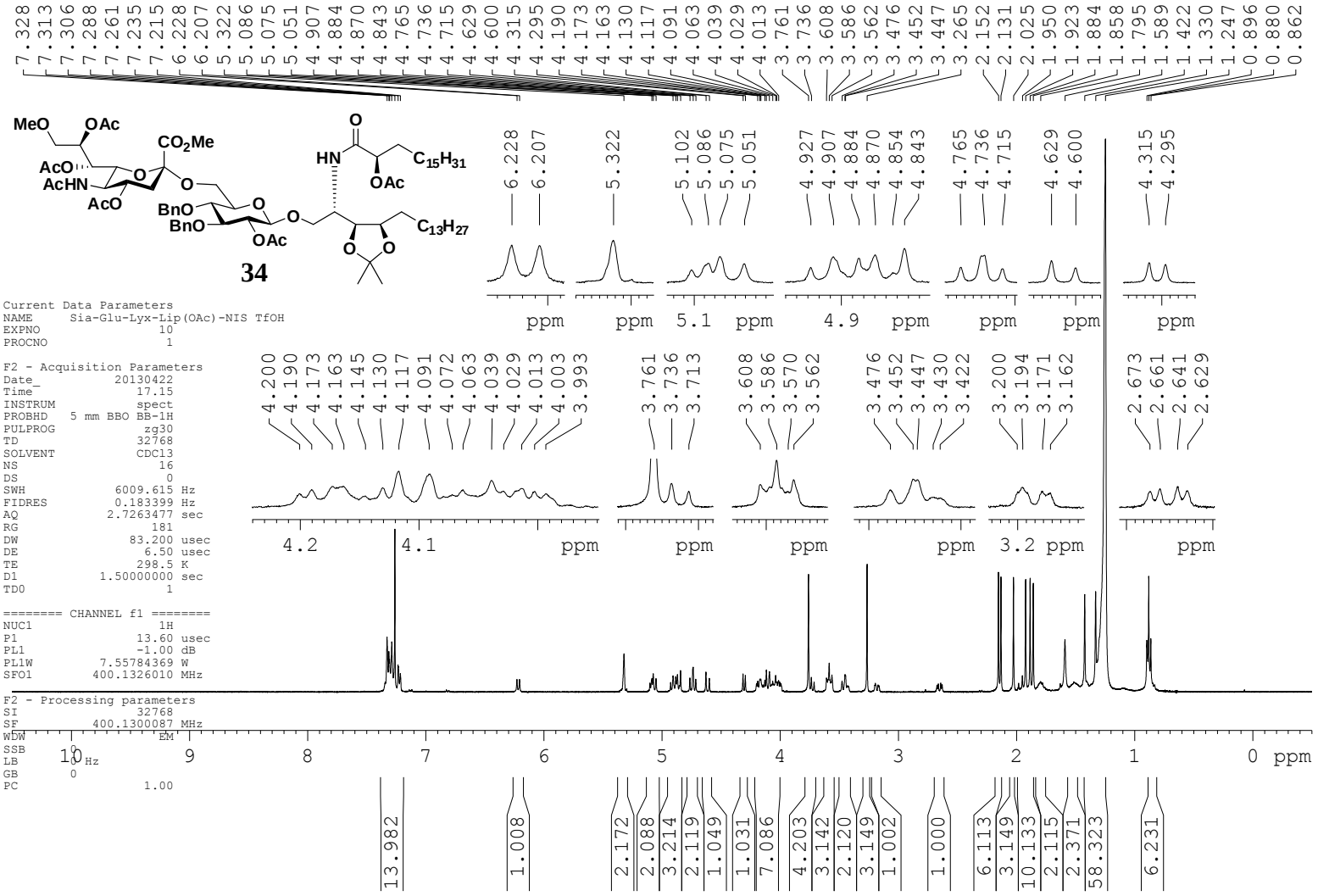

170.995
170.317
170.109
169.989
169.718
167.938
138.218
128.427
128.384
128.196
127.815
127.761
127.724
98.695
84.135
83.470
78.197
77.366
77.048
76.731
75.242
75.054
72.449
71.715
70.981
69.121
68.612
67.549
63.544
59.172
52.751
49.394
38.126
24.083
23.221
21.307
20.982
20.890
20.664
15.125
MeO
OAc
CO2Me
AcO
AcHN
AcO
BnO
BnO
SEt
OAc
2α
Current Data Parameters
NAME 20130425-afa-Sia-Glu-a form-C
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130425
Time 10.42
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1515
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

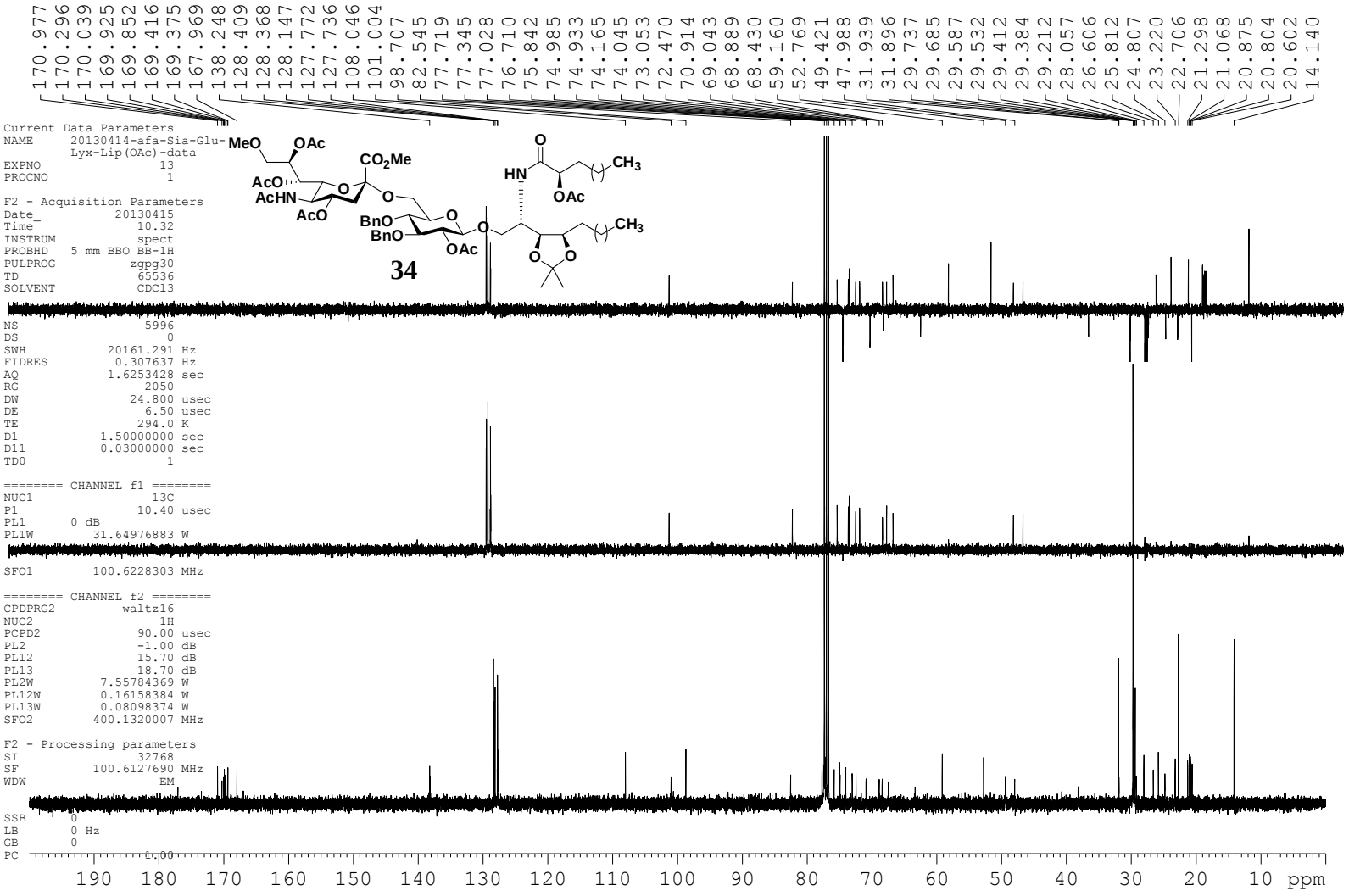

7.343 7.339 7.334 7.322 7.317 7.309 7.300 7.287 7.274 7.269 7.260 5.894 5.342 5.336 5.333 5.327 5.213 5.202 4.981 4.852 4.826 4.799 4.714 4.696 4.687 4.668 4.445 4.420 4.308 4.302 4.173 3.958 3.834 3.811 3.771 3.767 3.686 3.660 3.489 3.470 3.465 3.461 3.441 3.325 2.768 2.749 2.137 2.043 2.022 1.970 1.938 1.907 1.877 1.856 1.294 1.275 1.257
MeO
OAc
AcO
AcHN
AcO
O
BnO
BnO
O
SEt
OAc
CO2Me
2β
5.919 5.894 5.342 5.336 5.333 5.327 5.268 5.256 5.240 5.230 5.220 5.213 5.202 5.194 5.192 5.184 5.005 4.981 4.957 4.852 4.826 4.799 4.714 4.696 4.687 4.668 4.445 4.420 4.335 4.329 4.308 4.302
ppm
5.25
4.199 4.173 4.147 4.121 3.986 3.979 3.958 3.952 3.858 3.834 3.811 3.771 3.767 3.686 3.660 3.637 3.489 3.470 3.465 3.461 3.441 2.786 2.768 2.749 2.731 2.471 2.459 2.439 2.427
4.2 ppm
Current Data Parameters
NAME 20130109-afa-Sia-Glu-b form-2D
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130109
Time 19.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 3201.024 Hz
FIDRES 0.097688 Hz
AQ 5.1184115 sec
RG 101
DW 156.200 usec
DE 6.50 usec
TE 293.8 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 -3.00 dB
PL1W 11.97837448 W
SFO1 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
15.166 0.927 1.016 2.171 1.108 2.322 2.168 0.992 1.001 1.076 0.993 1.193 2.030 4.172 2.137 3.093 2.000 0.842 3.093 9.174 4.219 3.136

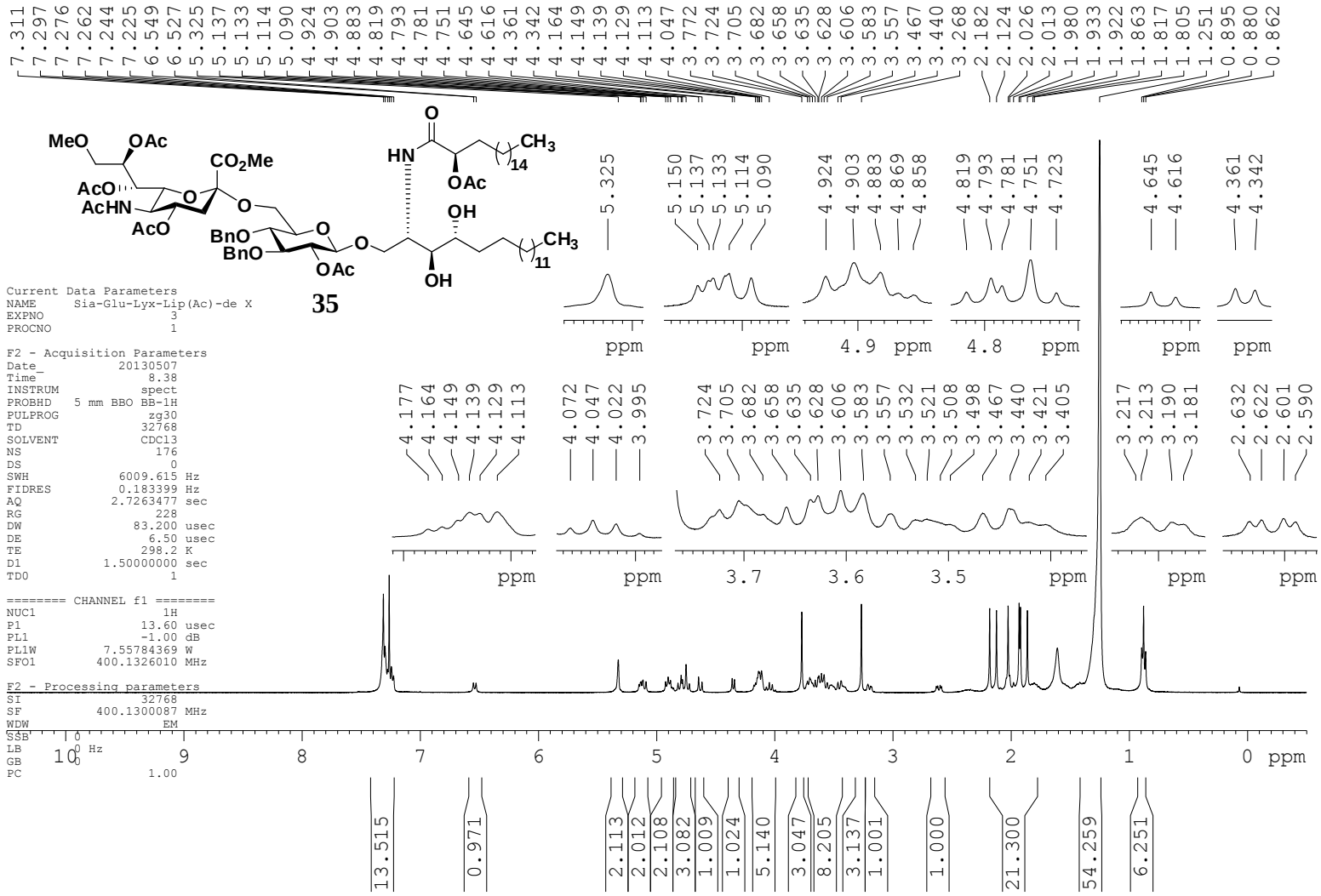

170.650
170.543
170.358
170.147
169.512
167.118
138.069
138.010
128.444
127.865
127.808
127.765
97.693
83.907
83.857
77.626
77.456
77.033
76.799
76.609
75.252
75.024
72.827
71.855
71.553
71.099
69.241
68.781
60.469
58.986
52.611
48.564
37.144
24.514
23.076
21.114
20.942
20.799
14.719
MeO
OAc
AcO
AcHN
AcO
O
O
BnO
BnO
SEt
OAc
CO2Me
2β
Current Data Parameters
NAME 20130531-afa-Sia-Glu-B form-C13
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130531
Time 21.51
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3673
DS 0
SWH 15060.241 Hz
FIDRES 0.459602 Hz
AQ 1.0879476 sec
RG 2050
DW 33.200 usec
DE
TE
D1 1.30000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.10 usec
PL1 0 dB
SFO1 75.4752958 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -3.00 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2
F2 - Processing parameters
SI 16384
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

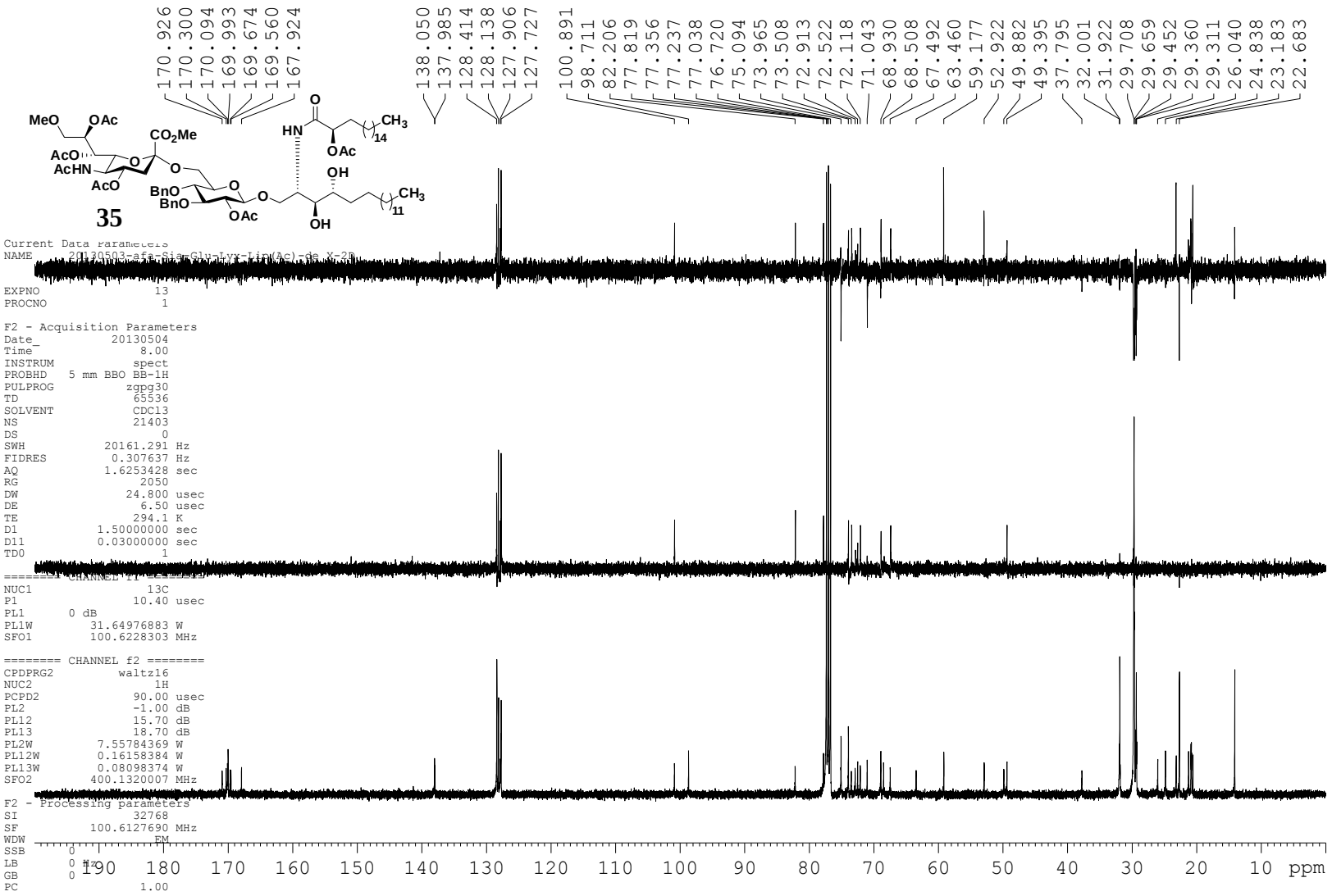

MeO
OAc
AcO
AcHN
AcO
O
CO2Me
33
7.262
6.015
6.006
5.797
5.776
5.522
5.512
5.501
5.445
5.436
5.434
5.427
5.418
5.296
5.286
5.280
5.275
5.270
5.259
4.450
4.434
4.430
4.415
4.408
4.406
4.398
4.388
4.377
3.863
3.853
3.836
3.826
3.793
3.501
3.485
3.473
3.458
3.355
2.110
2.073
2.055
1.920
Current Data Parameters
NAME 20130426-afa-Sia-Glu-gylcal-data
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130426
Time 18.37
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 12
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 90.5
DW 83.200 usec
DE 6.50 usec
TE 293.8 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
ppm
4.45
4.40
3.5
10
9
8
7
6
5
4
3
2
1
0
1.000
1.063
1.081
1.129
1.148
2.215
4.140
1.232
3.321
9.097
3.082

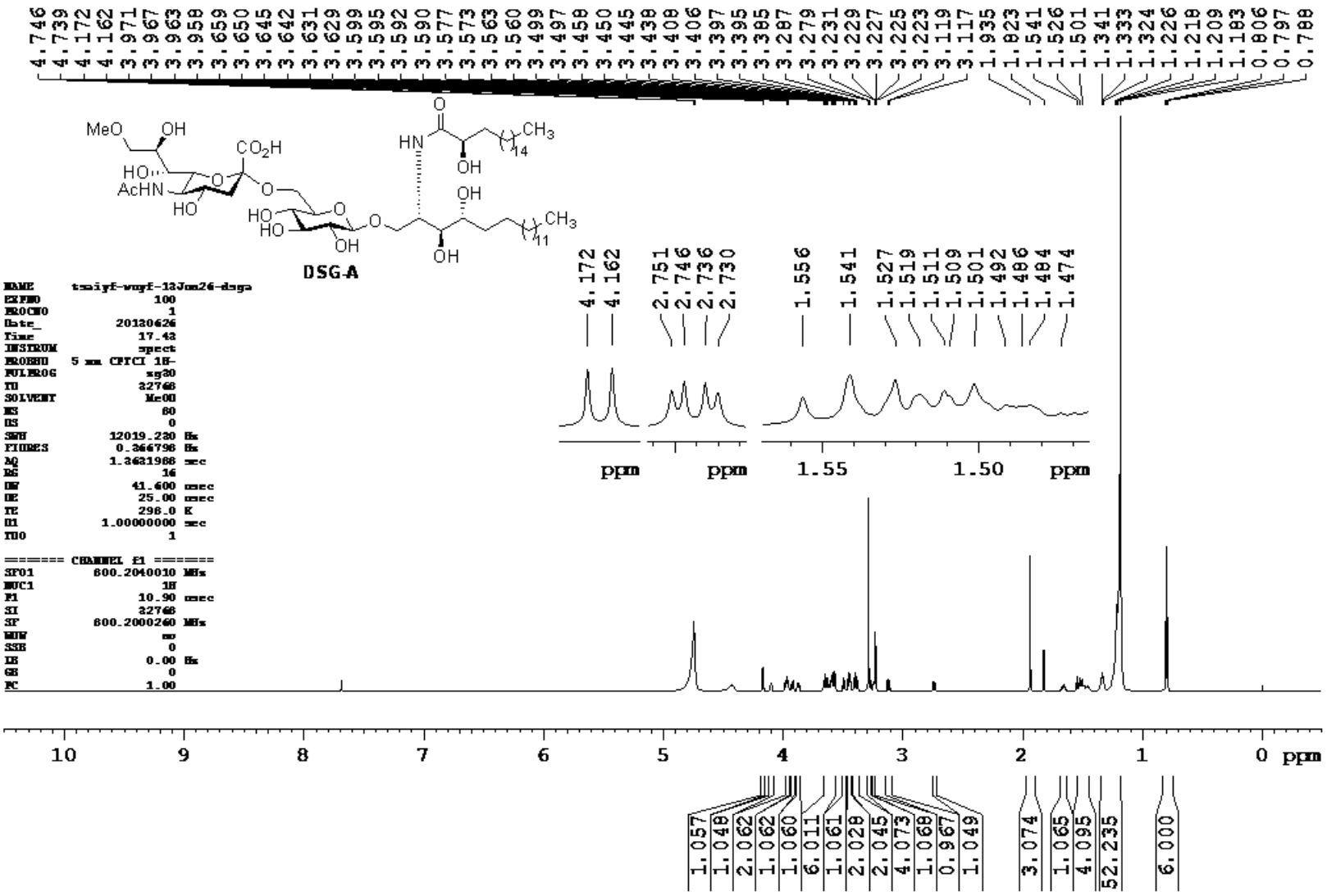

170.769
170.310
170.231
170.015
161.737
144.969
107.817
77.358
77.040
76.758
76.722
71.104
69.997
67.980
67.629
59.148
52.561
46.453
23.178
20.988
20.879
20.756
MeO
OAc
AcO
AcHN
AcO
O
CO2Me
33
Current Data Parameters
NAME 20130426-afa-Sia-Glu-gylcal-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130426
Time 21.28
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3032
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.2 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

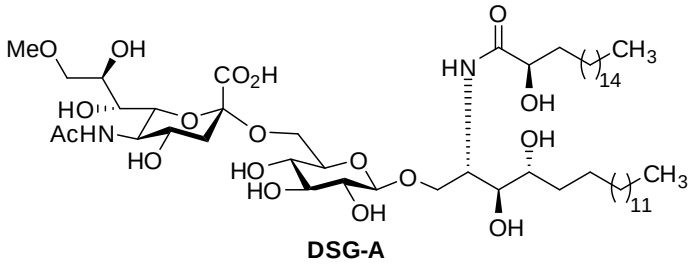

34
Current Data Parameters
NAME Sia-Glu-Lyx-Lip(OAc)-NIS TfOH
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130422
Time 17.15
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 181
DW 83.200 usec
DE 6.50 usec
TE 298.5 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
13.982
1.008
2.172
2.088
3.214
2.119
1.049
1.031
7.086
4.203
3.142
2.120
3.149
1.002
1.000
6.113
3.149
10.133
2.115
2.371
58.323
6.231


170.977
170.296
170.039
169.925
169.852
169.416
169.375
167.969
138.248
128.409
128.368
128.147
127.772
127.736
108.046
101.004
98.707
82.545
77.719
77.345
77.028
76.710
75.842
74.985
74.933
74.165
74.045
73.053
72.470
70.914
69.043
68.889
68.430
59.160
52.769
49.421
47.988
31.939
31.896
29.737
29.685
29.587
29.532
29.412
29.384
29.212
28.057
26.606
25.812
24.807
23.220
22.706
21.298
21.068
20.875
20.804
20.602
14.140
Current Data Parameters
NAME 20130414-afa-Sia-Glu-Lyx-Lip(OAc)-data
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130415
Time 10.32
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5996
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.0 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
MeO
OAc
CO2Me
AcO
AcHN
AcO
BnO
BnO
OAc
HN
OAc
CH3
CH3
34
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

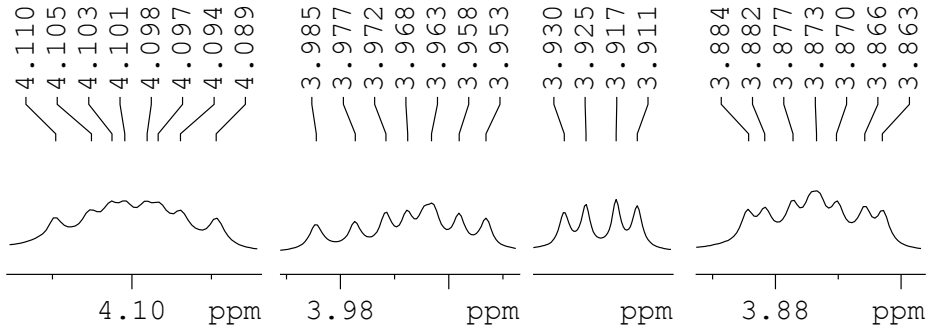

7.311 7.297 7.276 7.262 7.244 7.225 6.549 6.527 5.325 5.137 5.133 5.114 5.090 4.924 4.903 4.883 4.819 4.793 4.781 4.751 4.645 4.616 4.361 4.342 4.164 4.149 4.139 4.129 4.113 4.047 3.772 3.724 3.705 3.682 3.658 3.635 3.628 3.606 3.583 3.557 3.467 3.440 3.268 2.182 2.124 2.026 2.013 1.980 1.933 1.922 1.863 1.817 1.805 1.251 0.895 0.880 0.862
MeO OAc CO2Me AcO AcHN AcO BnO BnO OAc O HN OAc CH3 14 OH O CH3 11 OH
35
Current Data Parameters
NAME Sia-Glu-Lyx-Lip(Ac)-de X
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130507
Time 8.38
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 176
DS 0
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 228
DW 83.200 usec
DE 6.50 usec
TE 298.2 K
D1 1.50000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.60 usec
PL1 -1.00 dB
PL1W 7.55784369 W
SFO1 400.1326010 MHz
F2 - Processing parameters
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
5.325 5.150 5.137 5.133 5.114 5.090 4.924 4.903 4.883 4.869 4.858 4.819 4.793 4.781 4.751 4.723 4.645 4.616 4.361 4.342
4.177 4.164 4.149 4.139 4.129 4.113 4.072 4.047 4.022 3.995 3.724 3.705 3.682 3.658 3.635 3.628 3.606 3.583 3.557 3.532 3.521 3.508 3.498 3.467 3.440 3.421 3.405 3.217 3.213 3.190 3.181 2.632 2.622 2.601 2.590
ppm 4.9 4.8 3.7 3.6 3.5
10 9 8 7 6 5 4 3 2 1 0 ppm
13.515 0.971 2.113 2.012 2.108 3.082 1.009 1.024 5.140 3.047 8.205 3.137 1.001 1.000 21.300 54.259 6.251

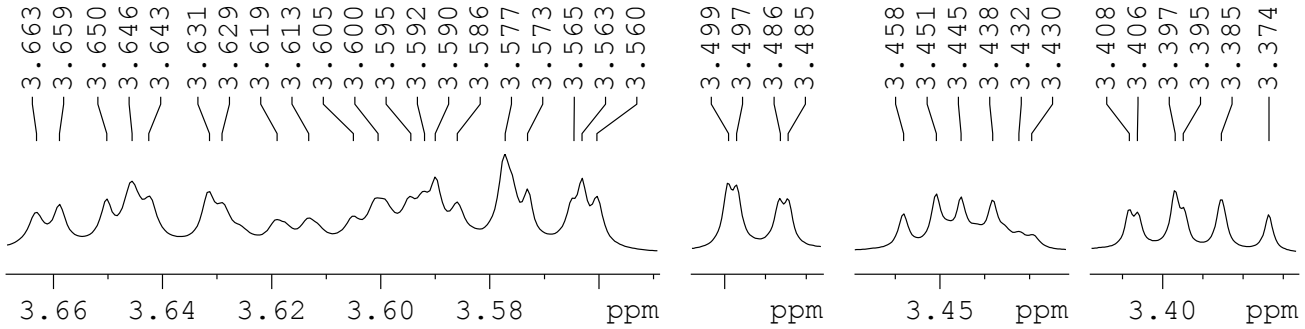

170.926
170.300
170.094
169.993
169.674
169.560
167.924
138.050
137.985
128.414
128.138
127.906
127.727
100.891
98.711
82.206
77.819
77.356
77.237
77.038
76.720
75.094
73.965
73.508
72.913
72.522
72.118
71.043
68.930
68.508
67.492
63.460
59.177
52.922
49.882
49.395
37.795
32.001
31.922
29.708
29.659
29.452
29.360
29.311
26.040
24.838
23.183
22.683
35
Current Data Parameters
NAME 20130503-afa-Sia-Glu-tyx-Lip(Ac)-de X-2h
EXPNO 13
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130504
Time 8.00
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 21403
DS 0
SWH 20161.291 Hz
FIDRES 0.307637 Hz
AQ 1.6253428 sec
RG 2050
DW 24.800 usec
DE 6.50 usec
TE 294.1 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1
NUC1 13C
P1 10.40 usec
PL1 0 dB
PL1W 31.64976883 W
SFO1 100.6228303 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.70 dB
PL13 18.70 dB
PL2W 7.55784369 W
PL12W 0.16158384 W
PL13W 0.08098374 W
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

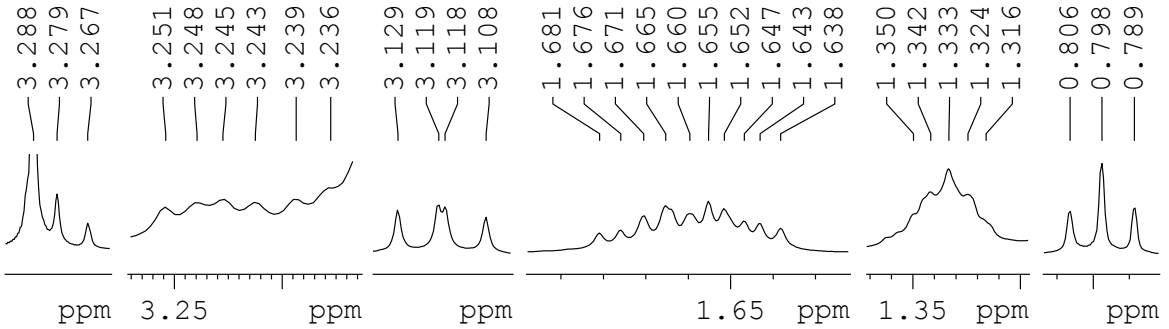

4.746 4.739 4.172 4.162 3.971 3.967 3.963 3.958 3.659 3.650 3.645 3.642 3.631 3.629 3.599 3.595 3.592 3.590 3.577 3.573 3.563 3.560 3.499 3.497 3.458 3.450 3.445 3.438 3.408 3.406 3.397 3.395 3.385 3.287 3.279 3.231 3.229 3.227 3.225 3.223 3.119 3.117 1.935 1.823 1.541 1.526 1.501 1.341 1.333 1.324 1.226 1.218 1.209 1.183 0.806 0.797 0.788
MeO OH CO2H HO AcHN HO HO HO HO OH HN O OH CH3 14 OH CH3 11
DSG-A
4.172 4.162 2.751 2.746 2.736 2.730 1.556 1.541 1.527 1.519 1.511 1.509 1.501 1.492 1.486 1.484 1.474
ppm ppm 1.55 1.50 ppm
NAME tsaiyf-wuyf-13Jun26-dsga
EXPNO 100
PROCNO 1
Date_ 20130626
Time 17.43
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 80
DS 0
SWH 12019.230 Hz
FIDRES 0.366796 Hz
AQ 1.3631968 sec
RG 16
DW 41.600 usec
DE 25.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
======= CHANNEL f1 =======
SFO1 600.2040010 MHz
NUC1 1H
P1 10.90 usec
SI 32768
SF 600.2000260 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
1.057 1.048 2.062 1.062 1.060 6.011 1.061 2.028 2.045 4.073 1.068 0.967 1.049 3.074 1.065 4.095 52.235 6.000



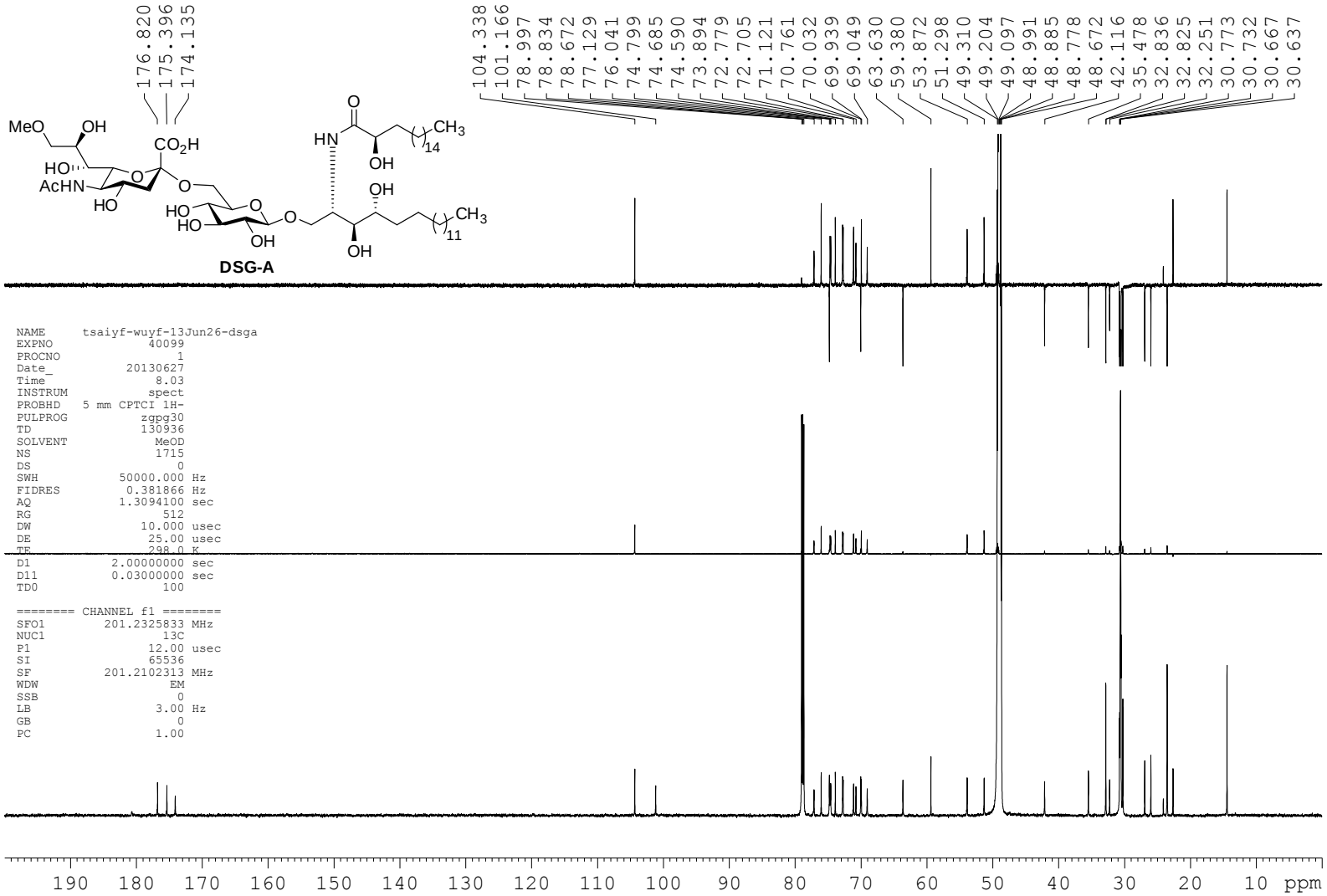
DSG-A

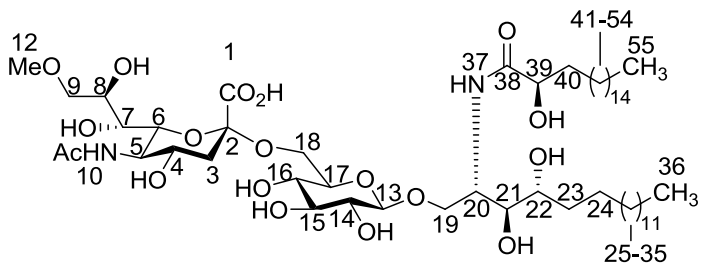







```
NAME      tsaiyf-wuyf-13Jun26-dsga
EXPNO                100
PROCNO                 1
Date_           20130626
Time                17.43
INSTRUM             spect
PROBHD   5 mm CPTCI 1H-
PULPROG              zg30
TD                  32768
SOLVENT              MeOD
NS                     80
DS                      0
SWH            12019.230 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                     16
DW                41.600 usec
DE                25.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         800.2040010 MHz
NUC1                  1H
P1                 10.90 usec
SI                 32768
SF           800.2000260 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```


176.820
175.396
174.135
104.338
101.166
78.997
78.834
78.672
77.129
76.041
74.799
74.685
74.590
73.894
72.779
72.705
71.121
70.761
70.032
69.939
69.049
63.630
59.380
53.872
51.298
49.310
49.204
49.097
48.991
48.885
48.778
48.672
42.116
35.478
32.836
32.825
32.251
30.773
30.732
30.667
30.637
MeO
OH
HO
AcHN
HO
CO2H
O
HO
HO
OH
HN
OH
14
CH3
OH
OH
11
CH3
DSG-A
NAME tsaiyf-wuyf-13Jun26-dsga
EXPNO 40099
PROCNO 1
Date_ 20130627
Time 8.03
INSTRUM spect
PROBHD 5 mm CPTCI 1H-
PULPROG zgpg30
TD 130936
SOLVENT MeOD
NS 1715
DS 0
SWH 50000.000 Hz
FIDRES 0.381866 Hz
AQ 1.3094100 sec
RG 512
DW 10.000 usec
DE 25.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 100
======== CHANNEL f1 ========
SFO1 201.2325833 MHz
NUC1 13C
P1 12.00 usec
SI 65536
SF 201.2102313 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



DSG-A

```
NAME      tsaiyf-wuyf-13Jun26-dsga
EXPNO              83
PROCNO              1
Date_        20130627
Time             5.54
INSTRUM         spect
PROBHD    5 mm CPTCI 1H-
PULPROG      cosygpqf
TD               2048
SOLVENT          MeOD
NS                  6
DS                  4
SWH         9615.385 Hz
FIDRES      4.695012 Hz
AQ          0.1065460 sec
RG                203
DW             52.000 usec
DE             25.00 usec
TE             298.0 K
D0          0.00000300 sec
D1          1.00000000 sec
D13         0.00000400 sec
D16         0.00020000 sec
IN0         0.00010400 sec

======== CHANNEL f1 ========
SFO1      800.2040010 MHz
NUC1            1H
P0             5.45 usec
P1            10.90 usec
ND0               1
TD              512
SFO1        800.204 MHz
FIDRES    18.780048 Hz
SW          12.016 ppm
FnMODE           QF
SI              2048
SF        800.2000242 MHz
WDW             SINE
SSB                0
LB              0.00 Hz
GB                 0
PC              1.00
SI              2048
MC2              QF
SF        800.2000238 MHz
WDW             SINE
SSB                0
LB              0.00 Hz
GB                 0
```