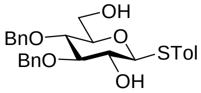
ELECTRONIC SUPPLEMENTARY INFORMATION

Regioselective One-Pot Protection, Protection–Glycosylation and Protection–Glycosylation–Glycosylation of Carbohydrates: A Case Study with D-Glucose

Teng-Yi Huang, Medel Manuel L. Zulueta, and Shang-Cheng Hung*

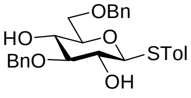
Genomics Research Center & Institute of Chemistry, Academia Sinica, 128, Section 2, Academia Road, Taipei 115, Taiwan

General considerations. CH_2Cl_2 was purified and dried from a safe purification system filled with anhydrous Al_2O_3. Dry CH_3CN was freshly distilled from CaH_2 under N_2 atmosphere. All other reagents were obtained from commercial sources and used without further purification. Water was either distilled or Milli-Q-purified. Flash column chromatography was carried out on Silica Gel 60 (230–400 mesh, E. Merck). TLC was performed on glass plates pre-coated with Silica Gel 60 F254 (0.25 mm, E. Merck); detection was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, and H_2SO_4 in water followed subsequent heating on a hot plate. Specific rotations were taken at ambient conditions and reported in $10^{-1}\cdot deg\cdot cm^2\cdot g^{-1}$; the sample concentrations are in $g\cdot dL^{-1}$. ^1H and ^{13}C NMR spectra were recorded on 400 and 600 MHz spectrometers. Proton peaks were assigned with the aid of 2D NMR techniques (^1H-^1H COSY, HMQC and NOESY). Coupling constants are given in Hz. The hydrogen multiplicities of carbon peaks were determined using DEPT-90 and DEPT-135 experiments.



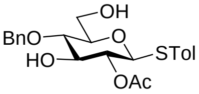
2

4-Methylphenyl 3,4-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (2). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at same temperature for 2 h. Et_3SiH (31 μL, 190 μmol), benzaldehyde (18 μL, 183 μmol) and TMSOTf (5 μL, 26 μmol) were sequentially added to the reaction solution. After stirring for 2.5 h at –78 °C, the reaction flask was moved to 0 °C, and $BH_3 \cdot THF$ (1 M solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture, followed by addition of TMSOTf (16 μL, 0.087 mmol). The solution was kept stirring for another 5 h at 0 °C. The reaction was slowly quenched with MeOH (5 mL) and Et_3N (1 mL) at 0 °C. The mixture was filtered through a pad of Celite, and the filtrate was coevaporated with MeOH under reduced pressure. The residue was partitioned between ethyl acetate and H_2O and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/2) gave the 2,6-diol **2** (70 mg, 86%) as a white solid. m.p. 115–118 °C; $[\alpha]^{28}_{D}$ –29.5 (*c* 0.9 in $CHCl_3$); IR (thin film): ν 3391, 3031, 2875, 1495, 1454, 1090, 807, 733, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.43 (2 H, d, *J* 8.1, Ar-H), 7.38–7.28 (10 H, m, Ar-H), 7.12 (2 H, d, *J* 8.1, Ar-H), 4.94 (1 H, d, *J* 11.3, $ArCH_2$), 4.86 (1 H, d, *J* 11.3, $ArCH_2$), 4.85 (1 H, d, *J* 11.0, $ArCH_2$), 4.64 (1 H, d, *J* 11.0, $ArCH_2$), 4.50 (1 H, d, *J* 9.3, 1-H), 3.89 (1 H, d, *J* 11.8, 6-H_a), 3.72–3.69 (1 H, m, 6-H_b), 3.61 (1 H, t, *J* 9.3, 2-H), 3.52 (1 H, t, *J* 9.3, 3-H), 3.50–3.39 (2 H, m, 4-H, 5-H), 2.71 (1H, d, *J* 1.9, 2-OH), 2.33 (3 H, s, CH_3), 2.27 (1 H, br s, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5 (C), 138.4 (C), 137.8 (C), 133.3 (CH), 129.8 (CH), 128.4 (CH), 127.9 (CH), 127.87 (CH), 127.83 (CH), 127.7 (CH), 127.6 (C), 88.2 (CH), 85.7 (CH), 79.5 (CH), 77.1 (CH), 75.2 (CH_2), 75.0 (CH_2), 72.6 (CH), 61.9 (CH_2), 21.1 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{27}H_{30}O_5SNa$ ($[M + Na]^+$): 489.1712, found: 489.1711.



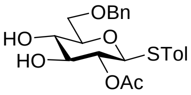
3

4-Methylphenyl 3,6-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (3). TMSOTf (5 *μ*L, 26 *μ*mol) was added to a solution of compound **1** (100 mg, 174 *μ*mol) and benzaldehyde (19 *μ*L, 190 *μ*mol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (31 *μ*L, 190 *μ*mol), benzaldehyde (18 *μ*L, 183 *μ*mol) and TMSOTf (5 *μ*L, 26 *μ*mol) were sequentially added to the reaction solution. After stirring for another 2.5 h at –78 °C, the reaction flask was moved to 0 °C, and Me_2EtSiH (70 *μ*L, 522 *μ*mol) and CH_3CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (6 *μ*L, 35 *μ*mol), and the solution was kept stirring for another 1 h at 0 °C. The reaction was slowly quenched with Et_3N (2 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/2) supplied the 2,4-diol **3** (58mg, 72%) as a white solid. m.p. 95–97 °C; $[\alpha]^{28}_D$ –35.8 (*c* 0.66 in $CHCl_3$); IR (thin film): *ν* 3442, 2919, 1494, 1453, 1361, 1071, 809, 736, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.45–7.42 (2 H, m, Ar-H), 7.38–7.25 (10 H, m, Ar-H), 7.06 (2 H, d, *J* 7.9, Ar-H), 4.93 (1 H, d, *J* 11.6, $ArCH_2$), 4.79 (1 H, d, *J* 11.6, $ArCH_2$), 4.59 (1 H, d, *J* 12.0, $ArCH_2$), 4.55 (1 H, d, *J* 12.0, $ArCH_2$), 4.45 (1 H, d, *J* 9.3, 1-H), 3.78–3.75 (2 H, m, 6-H_a, 6-H_b), 3.60–3.55 (1 H, m, 2-H), 3.51–3.38 (3 H, m, 3-H, 4-H, 5-H), 2.69 (1 H, d, *J* 2.2, OH), 2.52 (1 H, d, *J* 1.6, OH), 2.33 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.44 (C), 138.41 (C), 137.9 (C), 133.5 (CH), 129.7 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 80.4 (CH), 85.1 (CH), 78.5 (CH), 74.8 (CH_2), 73.6 (CH_2), 72.1 (CH), 71.1 (CH), 70.2 (C), 21.1 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{27}H_{30}O_5SNa$ ($[M + Na]^+$) 489.1712, found 489.1711.



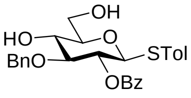
4

4-Methylphenyl 2-*O*-acetyl-4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (4). A solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) was stirred at –78 °C under N_2 atmosphere. TMSOTf (5 μL, 26 μmol) was added to the solution, and the mixture was kept stirring at the same temperature for 2 h. Et_3SiH (31 μL, 191 μmol), 2-NaphCHO (29 mg, 183 μmol) and TMSOTf (5 μL, 26 μmol) were consecutively added to the reaction solution. The resultant mixture was stirred for another 3 h. Ac_2O (25 μL, 261 μmol) and TMSOTf (5 μL, 26 μmol) were consecutively added to the solution. The reaction flask was moved to 0 °C, and the mixture was stirred for 1 h. BH_3·THF (1 M solution in THF, 0.52 mL, 0.52 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 μL, 87 μmol). The solution was kept stirring for another 5 h at 0 °C. H_2O (5 mL) was slowly added to the solution, the whole mixture was vigorously stirred for 5 min, and the aqueous layer was removed from the reaction bottle by using a pipette. DDQ (119 mg, 522 μmol) was then added to the solution. The mixture was stirred at room temperature for another 3 h. The reaction mixture was quenched by saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL), followed by filtration through a pad of Celite. The desired material was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of this residue via flash column chromatography (ethyl acetate/hexanes = 1/2) furnished the desired 3,6-diol **4** (30 mg, 41%) as a white solid. m.p. 106–111 °C; $[\alpha]^{28}_{D}$ –20 (*c* 0.4 in $CHCl_3$); IR (thin film): ν 3438, 2922, 1749, 1493, 1371, 1231, 1043, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35–7.24 (7 H, m, Ar-H), 7.10 (2 H, d, *J* 8.4, Ar-H), 4.79 (1 H, d, *J* 11.3, $ArCH_2$), 4.77 (1 H, t, *J* 9.6, 2-H), 4.69 (1 H, d, *J* 11.3, $ArCH_2$), 4.58 (1 H, d, *J* 9.6, 1-H), 3.88 (1 H, d, *J* 11.8, 6-H_a), 3.78–3.69 (2 H, m, 3-H, 6-H_b), 3.47 (1 H, t, *J* 9.6, 4-H), 3.36 (1 H, ddd, *J* 9.6, 4.4, 2.6, 5-H), 2.66 (1 H, s, 3-OH), 2.31 (3 H, s, CH_3), 2.14 (3 H, s, CH_3), 1.83 (1 H, s, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6 (C), 138.4 (C), 137.8 (C), 133.0 (CH), 129.8 (CH), 128.6 (CH), 128.4 (C), 128.1 (CH), 85.8 (CH), 79.2 (CH), 77.6 (CH), 76.9 (CH), 74.9 (CH_2), 72.6 (CH), 61.9 (CH_2), 21.1 (CH_3), 21.0 (CH_3); HRMS (ESI): *m/z* calcd for $C_{22}H_{26}O_6SNa$ ($[M + Na]^+$): 441.1348, found: 441.1342.



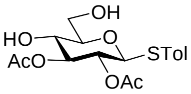
5

4-Methylphenyl 2-*O*-acetyl-6-*O*-benzyl-1-thio-*β*-D-glucopyranoside (5). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol), benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et_3SiH (31 μL, 190 μmol), 2-NaphCHO (29 mg, 183 μmol) and TMSOTf (5 μL, 26 μmol) were consecutively added to the reaction solution and the mixture was stirred at –78 °C for another 3 h. Ac_2O (18 μL, 261 μmol) and TMSOTf (5 μL, 26 μmol) were consecutively added to the solution, the reaction flask was moved to 0 °C, and the mixture was stirred at the same temperature 1 h. Me_2EtSiH (46 μL, 0.348 mmol) and CH_3CN (3 mL) were added to the reaction mixture followed by TMSOTf (6 μL, 35 μmol), and the solution was kept stirring for another 1 h at 0 °C. DDQ (119 mg, 522 μmol) and H_2O (0.1 mL) were added to the solution, and the mixture was stirred at room temperature for 3 h. The reaction mixture was quenched by saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL), then filtered through a pad of Celite. The desired material was extracted with ethyl acetate and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/2) furnished the 3,4-diol **5** (34 mg, 47%) as a white solid. m.p. 155–157 °C; $[\alpha]^{28}_D$ +40.7 (*c* 0.36 in $CHCl_3$); IR (thin film): ν 3491, 2920, 2872, 1723, 1495, 1375, 1268, 1077, 1049, 743, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.26 (7 H, m, Ar-H), 7.04 (2 H, d, *J* 8.3, Ar-H), 4.75 (1 H, t, *J* 9.2, 2-H), 4.57 (1 H, d, *J* 11.8, $ArCH_2$), 4.56 (1 H, d, *J* 9.2, 1-H), 4.53 (1 H, d, *J* 11.8, $ArCH_2$), 3.76 (2 H, d, *J* 4.5, 6-H × 2), 3.59 (1 H, t, *J* 9.2, 3-H), 3.53 (1 H, t, *J* 9.2, 4-H), 3.48–3.43 (1 H, m, 5-H), 3.26 (1 H, br s, OH), 3.00 (1 H, br s, OH), 2.29 (3 H, s, CH_3), 2.14 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (C), 138.3 (C), 137.7 (C), 133.2 (CH), 129.6 (CH), 128.4 (CH), 127.8 (C), 127.7 (CH), 85.9 (CH), 78.1 (CH), 76.7 (CH), 73.7 (CH_2), 72.2 (CH), 72.0 (CH), 70.1 (CH_2), 21.1 (CH_3), 21.0 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{26}O_6SNa$ ($[M + Na]^+$): 441.1348, found: 441.1341.



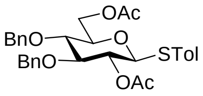
6

4-Methylphenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-*β*-D-glucopyranoside (6). TMSOTf (6.2 μL, 34 μmol) was added to solution of compound **1** (106 mg, 185 μmol), benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1.6 mL) with freshly dried 3 Å molecular sieves (160 mg) at 0 °C under N_2 atmosphere. The mixture was kept stirring at the same temperature for 2 h. After cooling to to –78 °C, Et_3SiH (33 μL, 207 μmol), benzaldehyde (19 μL, 190 μmol) and TMSOTf (3.4 μL, 19 μmol) were sequentially added, and the resulting mixture was stirred at –78 °C for another 3 h. The reaction flask was moved to 0 °C, and Bz_2O (130 mg, 0.56 mmol), and TMSOTf (3.4 μL, 19 μmol) were then added. The reaction flask was gradually warmed up to room temperature and the mixture was stirred at the same temperature for 18 h. 70% $TFA_{(aq)}$ (3 mL) was added to the resulting solution and the mixture was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated $NaHCO_{3(aq)}$, and the desired material was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/1) to afford the 4,6-diol **6** (67 mg, 75%). mp 117–118 °C; $[\alpha]^{22}_{D}$ +12.9 (*c* 1.0 in $CHCl_3$); IR (thin film): ν 3630, 3100, 1724, 1267, 1254, 1094, 1070 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (2 H, m, Ar-H), 7.61–7.57 (1 H, m, Ar-H), 7.49–7.44 (2 H, m, Ar-H), 7.30 (2 H, d, *J* 8.1, Ar-H), 7.21–7.15 (5 H, m, Ar-H), 7.06 (2 H, d, *J* 7.9, Ar-H), 5.20 (1 H, dd, *J* 10.0, 9.0, 2-H), 4.75 (1 H, d, *J* 10.0, 1-H), 4.70 (1 H, d, *J* 11.4, ArCH_2), 4.55 (1 H, d, *J* 11.4, ArCH_2), 3.90 (1 H, ddd, *J* 12.0, 6.6, 3.4, 6-H_a), 3.81–3.75 (1 H, m, 6-H_b), 3.71–3.66 (2 H, m, 3-H, 4-H), 3.46–3.42 (1 H, m, 5-H), 2.37 (1 H, d, *J* 2.2, 4-OH), 2.30 (3 H, s, ArCH_3), 2.11 (1 H, t, *J* 6.6, 6-OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2 (C), 138.4 (C), 137.6 (C), 133.3 (CH), 133.1 (CH), 129.9 (CH), 129.7 (CH), 128.6 (C), 128.51 (CH), 128.49 (CH), 128.0 (CH), 86.6 (CH), 83.9 (CH), 79.4 (CH), 74.8 (CH_2), 72.4 (CH), 70.3 (CH), 62.6 (CH_2), 21.1 (CH_3); HRMS (FAB): *m*/*z* calcd for $C_{27}H_{29}O_6S$ ($[M + H]^+$): 481.1685, found: 481.1696.



7

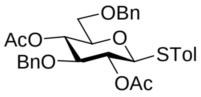
4-Methylphenyl 2,3-di-*O*-acetyl-1-thio-*β*-D-glucopyranoside (7). TMSOTf (5 *μ*L, 26 *μ*mol) was added to a solution of compound **1** (100 mg, 174 *μ*mol) and benzaldehyde (19 *μ*L, 190 *μ*mol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Ac_2O (40 *μ*L, 418 *μ*mol) and TMSOTf (10 *μ*L, 52 *μ*mol) were consecutively added to the solution, and the mixture was stirred at the same temperature. After stirring for 1 h, 70% $TFA_{(aq)}$ (1 mL) was added to the resulting solution, ice-bath was removed, and the reaction was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated $NaHCO_{3(aq)}$ (5 mL), and the desired material was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 2/1) to acquire the 2,3-diacetate **7** (45 mg, 70%) as a colorless oil. $[\alpha]^{28}_{D}$ –28.4 (*c* 0.88, $CHCl_3$); IR (thin film): ν 3441, 2930, 1752, 1374, 1044, 900, 808, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (2 H, d, *J* 8.1, Ar-H), 7.08 (2 H, d, *J* 8.1, Ar-H), 5.03 (1 H, t, *J* 9.6, 2-H), 4.84 (1 H, t, *J* 9.6, 3-H), 4.65 (1 H, d, *J* 9.6, 1-H), 3.87 (1 H, dd, *J* 12.1, 3.3, 6-H_a), 3.77 (1 H, dd, *J* 12.1, 4.3, 6-H_b), 3.66 (1 H, t, *J* 9.6, 4-H), 3.6 (1 H, br s, OH), 3.38 (1 H, ddd, *J* 9.6, 4.3, 3.3, 5-H), 2.69 (1 H, br s, OH), 2.3 (3 H, s, CH_3), 2.05 (3 H, s, CH_3), 2.02 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (C), 169.6 (C), 133.1 (CH), 129.8 (CH), 128.1 (C), 85.9 (CH), 79.6 (CH), 76.8 (CH2), 70.15 (CH), 68.7 (CH), 61.9 (CH_2), 21.1 (CH_3), 20.8 (CH_3), 20.8 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{26}O_6SNa$ ($[M + Na]^+$): 393.0984, found: 393.0992.



8

4-Methylphenyl 2,6-di-*O*-acetyl-3,4-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (8). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (160 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (31 μL, 190 μmol), benzaldehyde (18 μL, 183 μmol) and TMSOTf (5 μL, 26 μmol) were sequentially added to the reaction solution. After stirring at –78 °C for another 2.5 h, the reaction flask was moved to 0 °C. BH_3·THF (1 M solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture followed by TMSOTf (16 μL, 87 μmol), and the solution was kept stirring for another 5 h at 0 °C. Borane was slowly quenched with MeOH (70 μL, 1.74 mmol) at 0 °C, followed by further stirring for 30 min. Et_3N (1.4 mL, 8.7 mmol), Ac_2O (0.66 mL, 6.96 mmol) and DMAP (2 mg, 17.4 μmol) were added to the reaction mixture and the solution was stirred at room temperature for another 12 h. The whole mixture was filtered through a pad of Celite. H_2O was added to the filtrate followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography (ethyl acetate/hexanes = 1/4) to afford the diacetate **8** (74 mg, 77%) as a white solid. m.p. 132–136 °C; $[\alpha]^{28}_D$ +10.9 (*c* 0.76 in $CHCl_3$); IR (thin film): ν 2901, 1742, 1453, 1358, 1238, 1126, 1043, 808, 743, 696 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.36 (2 h, d, *J* 8.1, Ar-H), 7.34–7.24 (8 H, m, Ar-H), 7.23–7.22 (2 H, m, Ar-H), 7.07 (2 H, d, *J* 7.8, Ar-H), 4.94 (1 H, t, *J* 9.8, 2-H), 4.80–4.76 (2 H, m, $ArCH_2$), 4.66 (1 H, d, *J* 11.3, $ArCH_2$), 4.54 (1 H, d, *J* 11.6, $ArCH_2$), 4.51 (1 H, d, *J* 9.8, 1-H), 4.38 (1 H, dd, *J* 11.9, 1.8, 6-H_a), 4.15 (1 H, dd, *J* 11.9, 4.7, 6-H_b), 3.67 (1 H, t, *J*

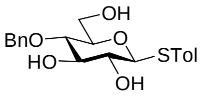
8.7, 3-H), 3.56–3.52 (2 H, m, 4-H, 5-H), 2.31 (3 H, s, CH_3), 2.02 (3 H, s, CH_3), 2.00 (3 H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5 (C), 169.4 (C), 138.1 (C), 137.8 (C), 137.4 (C), 133.18 (CH), 129.4 (CH), 128.5 (C), 128.4 (CH), 128.3 (CH), 127.9 (CH), 128.0 (CH), 127.9 (CH), 127.8(CH), 86.0 (CH), 84.4 (CH), 77.3 (CH), 76.9 (CH), 75.3 (CH_2), 75.0 (CH_2), 71.6 (CH), 62.8 (CH_2), 21.0 (CH_3), 20.9 (CH_3), 20.7 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{31}H_{34}O_7SNa$ ($[M + Na]^+$): 573.1923, found: 573.1924.



9

4-Methylphenyl 2,4-di-*O*-acetyl-3,6-di-*O*-benzyl-1-thio-*β*-D-glucopyranoside (9). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (150 mg) at –78 °C under N_2 atmosphere. The mixture was stirred for 2 h at the same temperature. Et_3SiH (31 μL, 190 μmol), benzaldehyde (18 μL, 183 μmol) and TMSOTf (5 µL, 26 μmol) were sequentially added to the reaction solution. After stirring for another 2.5 h at –78 °C, the reaction flask was moved to 0 °C. Me_2EtSiH (69 μL, 522 μmol) and CH_3CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (5 μL, 26 μmol). The solution was kept stirring for another 1 h at 0 °C. Then, Ac_2O (75 μL, 783 μmol) and TMSOTf (15 μL, 78 μmol) were consecutively added to the mixture, which stirred further for 12 h at the same temperature. The reaction was slowly quenched by Et_3N (2 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/4) to obtain the desired fully protected thioglucoside **9** (40 mg, 42%) as a white solid. m.p. 110–112 °C; $[\alpha]^{28}_{D}$ –12.2 (*c*

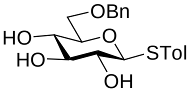
0.76 in $CHCl_3$); IR (thin film): ν 2868, 1749, 1495, 1372, 1220, 1061, 808, 737, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (2 H, d, *J* 8.1, Ar-H), 7.37–7.20 (10 H, m, Ar-H), 7.03 (2 H, d, *J* 8.1, Ar-H), 5.04–5.00 (2 H, m, 2-H, 4-H), 4.62–4.55 (3 H, m, 1-H, $ArCH_2$), 4.53–4.47 (2 H, m, $ArCH_2$), 3.70 (1 H, t, *J* 9.2, 3-H), 3.63–3.54 (3 H, m, 5-H, 6-H × 2), 2.29 (3 H, s, CH_3), 2.04 (3 H, s, CH_3), 1.88 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4 (C), 169.2 (C), 138.1 (C), 137.9 (C), 137.8 (C), 132.9 (CH), 129.6 (CH), 128.7 (C), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.6 (CH), 86.3 (CH), 81.6 (CH), 77.8 (CH), 73.9 (CH_2), 73.6 (CH_2), 71.4 (CH), 70.6 (CH), 69.7 (CH_2), 21.0 (CH_3), 20.9 (CH_3), 20.7 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{31}H_{34}O_7SNa$ ([M + Na]$^+$): 573.1923, found: 573.1926.



10

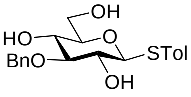
4-Methylphenyl 4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (10). TMSOTf (5 μL, 26 μmol) was added to a mixture of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N_2 atmosphere. After 2 h of stirring at 0 °C, BH_3·THF (1 M solution in THF, 0.87 mL, 0.87 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 μL, 87 μmol). The solution was kept stirring for another 5 h at 0 °C. The reaction was slowly quenched with MeOH (5 mL) and Et_3N (1 mL) at 0 °C, the mixture was filtered through a pad of Celite, and the filtrate was coevaporated with MeOH under reduced pressure. Ethyl acetate and H_2O were added to the residue followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography ($CHCl_3$/MeOH = 20/1) provided the 2,3,6-triol **10**

(53 mg, 81%) as a white solid. m.p. 113–116 °C; $[\alpha]^{28}_{D}$ –41.7 (*c* 0.26 in $CHCl_3$); IR (thin film): ν 3419, 1493, 1028, 807, 751, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (2 H, d, *J* 8, Ar-H), 7.31–7.23 (5 H, m, Ar-H), 7.07 (2 H, d, *J* 8, Ar-H), 4.83 (1 H, d, *J* 11.3, $ArCH_2$), 4.65 (1 H, d, *J* 11.3, $ArCH_2$), 4.47 (1 H, d, *J* 9.7, 1-H), 3.86 (1 H, d, *J* 11.8, 6-H_a), 3.71–3.67 (2 H, m, 2-H, 6-H_b), 3.48 (1 H, br s, OH), 3.44–3.30 (4 H, m, 3-H, 4-H, 5-H, OH), 2.41 (1 H, d, *J* 1.9, 6-OH), 2.30 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4 (C), 138.0 (C), 133.0 (CH), 129.8 (CH), 128.5 (CH), 127.9 (CH), 127.8 (CH), 87.9 (CH), 79.2 (CH), 78 (CH), 76.9 (CH), 74.7 (CH_2), 72.3 (CH), 62.0 (CH_2), 21.1 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_5SNa$ ($[M + Na]^+$): 399.1242, found: 399.1246.



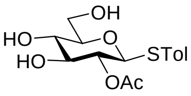
11

4-Methylphenyl 6-*O*-benzyl-1-thio-*β*-D-glucopyranoside (11). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h; then moved to 0 °C afterwards. Me_2EtSiH (46 μL, 0.522 mmol) and CH_3CN (3 mL) were added to the reaction mixture followed by addition of TMSOTf (6 μL, 35 μmol), and the solution was kept stirring for 1 h at 0 °C. TBAF (1.74 mL, 1.74 mmol) was added to the mixture, the reaction flask was gradually warmed up to room temperature, and the solution was kept stirring overnight. The whole mixture was filtered through a pad of Celite, and the filtrate was mixed with saturated $NaHCO_{3(aq)}$ (10 mL). The desired material was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 2/1) to obtain the 2,3,4-triol **11** (32 mg, 51%) as a white solid. m.p. 79–81 °C; $[\alpha]^{28}{}_{D}$ –47.3 (*c* 0.4 in $CHCl_3$); IR (thin film): ν 3375, 2919, 1493, 1453, 1366, 1045, 808, 733, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (2 H, d, *J* 8.1, Ar-H), 7.30–7.21 (5 H, m, Ar-H), 6.97 (2 H, d, *J* 8.1, Ar-H), 4.87 (1 H, br s, OH), 4.35–4.43 (3 H, m, 1-H, $ArCH_2$), 4.28 (1 H, br s, OH), 4.12 (1 H, br s, OH), 3.72 (1 H, dd, *J* 10.9, 2.8, 6-H_a), 3.64 (1 H, dd, *J* 10.9, 4.9, 6-H_b), 3.53–3.38 (3 H, m, 2-H, 3-H, 5-H), 3.3 (1 H, t, *J* 9.1, 4-H), 2.23 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (C), 137.9 (C), 133.0 (CH), 129.7 (CH), 128.5 (CH), 128.4 (CH), 127.8 (CH), 127.67 (CH), 87.9 (CH), 78.7 (CH), 77.9 (CH), 73.6 (CH_2), 71.9 (CH), 70.7(CH), 69.9 (CH_2), 21.1 (CH_3); HRMS (ESI): *m/z* calcd for $C_{20}H_{24}O_5SNa$ ($[M + Na]^+$): 399.1242, found: 399.1248.



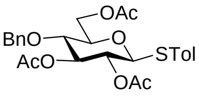
12

4-Methylphenyl 3-O-benzyl-1-thio-β-D-glucopyranoside (12). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N_2 atmosphere. The mixture was stirred for 2 h at the same temperature. Et_3SiH (31 μL, 190 μmol), benzaldehyde (18 μL, 183 μmol) and TMSOTf (5 μL, 26 μmol) were successively added to the solution. After stirring for another 2.5 h at –78 °C, the reaction flask was moved to 0 °C. A 70% aqueous TFA solution (1 mL) was added to the resultant mixture. The reaction was continuously stirred at room temperature for 1 h. The reaction was quenched by saturated $NaHCO_{3(aq)}$, followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 1/1) to afford the 2,4,6-triol **12** (40 mg, 62%) as a white solid. m.p. 136–140 °C; $[\alpha]^{28}_{D}$ –72.4 (*c* 0.6 in $CHCl_3$); IR (thin film): ν 3325, 1493, 1367, 1121, 1035, 808, 751, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.37 (2 H, m, Ar-H), 7.35–7.25 (5 H, m, Ar-H), 7.10 (2 H, d, *J* 7.9, Ar-H), 4.97 (1 H, d, *J* 11.6, $ArCH_2$), 4.74 (1 H, d, *J* 11.6, $ArCH_2$), 4.47 (1 H, d, *J* 9.3, 1-H), 3.87–3.84 (1 H, m, 6-H_a), 3.76–3.70 (1 H, m, 6-H_b), 3.53–3.48 (1 H, m, 2-H), 3.44–3.32 (3 H, m, 3-H, 4-H, 5-H), 2.67 (1 H, d, *J* 2.6, OH), 2.61 (1 H, d, *J* 1.6, OH), 2.32 (3 H, s, CH_3), 2.30–2.27 (1 H, m, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7 (C), 138.4 (C), 133.3 (CH), 129.9 (CH), 128.6 (CH), 128.0 (CH), 127.5 (C), 88.7 (CH), 85.1 (CH), 79.4 (CH), 79.4 (CH), 74.8 (CH_2), 72.5 (CH), 69.9 (CH), 62.6 (CH_2), 21.1 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{20}H_{24}O_5SNa$ ($[M + Na]^+$): 399.1242, found: 399.1235.



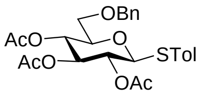
13

4-Methylphenyl 2-*O*-acetyl-1-thio-*β*-D-glucopyranoside (13). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et_3SiH (31 μL, 228 μmol), 2-NaphCHO (29 mg, 183 μmol) and TMSOTf (5 μL, 26 μmol) were consecutively added to the reaction solution. After stirring at –78 °C for 3 h, Ac_2O (25 μL, 261 μmol) and TMSOTf (5 μL,26 μmol) were consecutively added to the solution, the reaction flask was moved to 0 °C, and the mixture was stirred at the same temperature for 1 h. A 70% aqueous TFA (1 mL) was added to the resulting solution, the ice-bath was removed, and the reaction was continuously stirred at room temperature for another 1 h. The reaction was quenched by saturated $NaHCO_{3(aq)}$, followed by extraction with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash column chromatography ($CHCl_3$/MeOH = 15/1) gave the 3,4,6-triol product **13** (30 mg, 53%) as a white solid. m.p. 201–205 °C; $[\alpha]^{28}_{D}$ –63.2 (*c* 0.3 in ethyl acetate); IR (thin film): ν 3510, 3234, 2923, 1721, 1456, 1263, 1040, 810, 720, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.37 (2 H, m, Ar-H), 7.11 (2 H, d, *J* 7.9, Ar-H), 4.73–4.64 (2 H, m, 1-H, 2-H), 3.86 (1 H, dd, *J* 12.1, 2.1, 6-H_a), 3.67 (1 H, dd, *J* 12.1, 5.4, 6-H_b), 3.53 (1 H, t, *J* 8.6, 3-H), 3.38–3.29 (2 H, m, 4-H, 5-H), 2.30 (3 H, s, CH_3), 2.10 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8 (C), 139.0 (CH), 133.4 (CH), 133.1 (C), 130.6 (CH), 87.7 (CH), 82.2 (CH), 77.5 (CH), 74.0 (CH), 71.4 (CH), 62.8 (CH_2), 21.1(CH_3); HRMS (ESI): *m*/*z* calcd for $C_{15}H_{20}O_6SNa$ ($[M + Na]^+$): 351.0878, found: 351.0876.



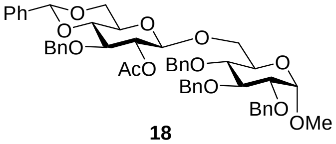
14

4-Methylphenyl 2,3,6-tri-*O*-acetyl-4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (14). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N_2 atmosphere. The mixture was stirred for 2 h at same temperature. BH_3·THF (1 M solution in THF, 0.9 mL, 0.9 mmol) was added to the reaction mixture followed by addition of TMSOTf (16 μL, 87 μmol). After 5 h of stirring at 0 °C, BH_3 was slowly quenched by MeOH (70 μL, 1.74 mmol) at 0 °C, and the mixture was stirred for 30 min. Et_3N (3.6 mL, 26.1 mmol), Ac_2O (1.6 mL, 17.4 mmol) and DMAP (2 mg, 17.4 μmol) were added to the reaction mixture, followed by 12 h of stirring at room temperature. The whole mixture was filtered through a pad of Celite. H_2O was added to the filtrate and the desired material was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue by flash column chromatography (ethyl acetate/hexanes = 1/3) supplied the triacetate **14** (67 mg, 77%) as a white solid. m.p. 95–98 °C; $[\alpha]^{28}_D$ –26.9 (*c* 0.96 in $CHCl_3$); IR (thin film): ν 2945, 1751, 1494, 1366, 1231, 1046, 809, 752, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 (2 H, d, *J* 8.1, Ar-H), 7.31–7.19 (5 H, m, Ar-H), 7.07 (2 H, d, *J* 8.1, Ar-H), 5.23 (1 H, t, *J* 9.6, 2-H), 4.82 (1 H, t, *J* 9.6 Hz, 3-H), 4.59 (1 H, d, *J* 9.6, 1-H), 4.55 (1 H, d, *J* 11.3, $ArCH_2$), 4.51 (1 H, d, *J* 11.3, $ArCH_2$), 4.38 (1 H, d, *J* 11.9, 6-H_a), 4.14 (1 H, dd, *J* 11.9, 3.4, 6-H_b), 3.59–3.53 (2 H, m, 4-H, 5-H), 2.30 (3 H, s, CH_3), 2.04 (3 H, s, CH_3), 2.01 (3 H, s, CH_3), 1.91 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5 (C), 170.0 (C), 169.7 (C), 138.6 (C), 137.3 (C), 133.8 (CH), 129.7 (CH), 128.7 (CH), 128.2 (CH), 128.1 (CH), 127.9 (C), 85.6 (CH), 77.0 (CH), 76.3 (CH), 75.7 (CH), 74.8 (CH_2), 70.6 (CH), 62.8 (CH_2), 21.3 (CH_3), 20.9 ($CH_3 \times 3$); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{30}O_8SNa$ ($[M + Na]^+$): 525.1559, found: 525.1555.



15

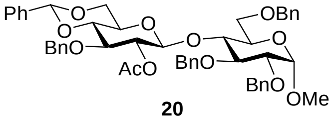
4-Methylphenyl 2,3,4-tri-*O*-acetyl-6-*O*-benzyl-1-thio-*β*-D-glucopyranoside (15). TMSOTf (5 μL, 26 μmol) was added to a solution of compound **1** (100 mg, 174 μmol) and benzaldehyde (19 μL, 190 μmol) in CH_2Cl_2 (1 mL) with freshly dried 3 Å molecular sieves (120 mg) at 0 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h, then Me_2EtSiH (69 μL, 0.522 mmol) and acetonitrile (3 mL) were added to the reaction mixture followed by addition of TMSOTf (5 μL, 26 μmol). After stirring for 1 h at 0 °C, Ac_2O (66 μL, 696 *μ*mol) and TMSOTf (15 *μ*L, 78 *μ*mol) were consecutively added to the solution. Stirring was continued at 0 °C for 12 h. The reaction was slowly quenched by Et_3N (2 mL), the mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. Purification by flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the triacetate **15** (41 mg, 47%) as a white solid. m.p. 92–95 °C; $[\alpha]^{28}_{D}$ –8.8 (*c* 0.55 in $CHCl_3$); IR (thin film): *ν* 2922, 1755, 1494, 1373, 1243, 1219, 1048, 912, 808, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.39–7.27 (7 H, m, Ar-H), 7.04 (2 H, d, *J* 8.4, Ar-H), 5.18 (1 H, t, *J* 9.7, 2-H), 5.00 (1 H, t, *J* 9.7, 3-H), 4.92 (1 H, dd, *J* 9.9, 9.7, 4-H), 4.63 (1 H, d, *J* 9.7, 1-H), 4.52 (1 H, d, *J* 11.8 Hz, $ArCH_2$), 4.47 (1 H, d, *J* 11.8, $ArCH_2$),3.69–3.64 (1 H, m, 5-H), 3.57 (2 H, m, 6-H × 2), 2.30 (3 H, s, CH_3), 2.06 (3 H, s, CH_3), 1.96 (3 H, s, CH_3), 1.90 (3 H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 170.2 (C), 169.5 (C), 169.2 (C), 138.5 (C), 137.8 (C), 133.5 (CH), 129.7 (CH), 128.3 (CH), 127.8 (CH), 127.7 (CH), 85.8 (CH), 77.5 (CH), 74.2 (CH), 73.6 (CH), 70.1 (CH_2), 69.1 (CH), 69.0 (CH_2), 21.1 (CH_3), 20.6 (CH_3 × 3); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{30}O_8SNa$ ($[M + Na]^+$): 525.1559, found: 525.1563.



18

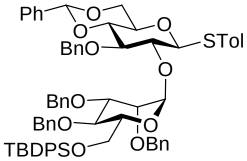
Methyl 6-*O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (18). TMSOTf (9 *μ*L, 52 *μ*mol) was added to a solution of compound **1** (200 mg, 348 *μ*mol) and benzaldehyde (39 *μ*L, 383 *μ*mol) in CH_2Cl_2 (3 mL) with freshly dried 3 Å molecular sieves (400 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et_3SiH (61 *μ*L, 383 *μ*mol), benzaldehyde (37 *μ*L, 366 μmol) and TMSOTf (9 μL, 52 μmol) were consecutively added to the reaction solution. After stirring at –78 °C for 2.5 h, Ac_2O (40 μL, 365 μmol) and TMSOTf (9 μL, 52 μmol) were consecutively added to the solution, the reaction flask was moved to 0 °C, and the mixture was stirred at the same temperature 1 h. The solution of glycosyl acceptor **17** (156 mg, 522 μmol) in CH_2Cl_2 (1 ml), NIS (97 mg, 420 μmol) and TfOH (6 μL, 70 μmol) were sequentially added to the solution at –78 °C. The reaction temperature gradually raised to 0 °C for a period of 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH_2Cl_2, and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the desired adduct **18** (121 mg, 41%) as a white foam. $[\alpha]^{27}_{D}$ +10.7 (*c* 3.4 in $CHCl_3$); IR (thin film): ν 2927, 1752, 1230, 1095, 1070, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.48–7.47 (2 H, m, Ar-H), 7.41–7.25 (23 H, m, Ar-H), 5.46 (1 H, s, ArCH), 4.91–4.88 (2 H, m, 2-H′, $ArCH_2$), 4.85 (1 H, d, *J* 12.1, $ArCH_2$), 4.80–4.76 (2 H, m, $ArCH_2$), 4.72 (1 H, d, *J* 12.0, $ArCH_2$), 4.63–4.60 (2 H, m, $ArCH_2$), 4.57 (1 H, d, *J* 3.6, 1-H), 4.40 (1 H, d, *J* 8.1, 1-H′), 4.37 (1 H, d, *J* 12.0, $ArCH_2$), 4.11 (1 H, dd, *J* 10.5, 4.9, 6-H′$_a$), 3.86–3.80 (2 H, m, 3-H, 4-H), 3.73 (1 H, dd, *J* 10.5, 2.7, 6-H$_a$), 3.63 (1 H, t, *J* 9.3, 3-H), 3.73 (1 H, dd, *J* 10.5, 2.7, 6-H$_a$), 3.59–3.55 (2 H, m, 5-H, 6-H$_b$), 3.50–3.44 (2 H, m, 2-H, 3-H′), 3.40 (1 H, t, *J* 10.3, 6-H′$_b$), 3.36 (3 H, s, OCH_3), 3.12 (1 H, td, *J* 9.7, 5.0, 5-H′), 1.91 (3 H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0 (C), 139.3 (C), 138.3 (C), 137.6 (C), 137.2 (C), 129.0 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.26 (CH), 128.22 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.67 (CH), 127.60 (CH), 127.4 (CH), 127.2 (CH), 126.0 (CH), 101.1 (CH), 100.7 (CH), 98.4 (CH), 81.6 (CH), 79.8 (CH), 78.8 (CH), 78.5 (CH), 75.3 (CH_2), 73.9 (CH_2), 73.6 (CH_2), 73.5 (CH_2), 73.2

(CH), 69.8 (CH), 68.5 (CH_2), 67.4 (CH_2), 65.8 (CH), 55.3 (CH_3), 20.9 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{50}H_{54}O_{12}Na$ ($[M + Na]^+$): 869.3513, found: 869.3499.



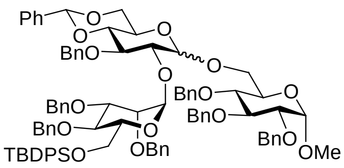
20

Methyl 4-*O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside (20). TMSOTf (5 *μ*L, 32 *μ*mol) was added to a solution of compound **1** (120 mg, 215 *μ*mol) and benzaldehyde (24 *μ*L, 237 *μ*mol) in CH_2Cl_2 (2 mL) with freshly dried 3 Å molecular sieves (240 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at the same temperature for 2 h. Et_3SiH (37 *μ*L, 237 *μ*mol), benzaldehyde (22 *μ*L, 226 *μ*mol) and TMSOTf (5 *μ*L, 32 *μ*mol) were consecutively added to the reaction solution. After stirring at –78 °C for 2.5 h, Ac_2O (20 *μ*L, 226 *μ*mol) and TMSOTf (5 *μ*L, 32 *μ*mol) were consecutively added to the mixture, and the reaction flask was moved to 0 °C, where the mixture was stirred for 1 h. Then, the vessel was cooled again to –78 °C, and a solution of the glycosyl acceptor **19** (120 mg, 323 *μ*mol) in CH_2Cl_2 (1 ml), NIS (60 mg, 258 *μ*mol) and TfOH (4 *μ*L, 43 *μ*mol) were sequentially added to the mixture. Reaction temperature was gradually raised up to 0 °C for a period of 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction. The mixture was filtered through Celite, and the desired material was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the adduct **20** (95 mg, 52%) as a white foam. $[\alpha]^{27}_D$ +4.33 (*c* 3.5 in $CHCl_3$); IR (thin film): *ν* 2871, 1752, 1493, 1229, 1096, 1062, 738, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): *δ* 7.49–7.48 (2 H, m, Ar-H), 7.40–7.23 (23 H, m, Ar-H), 5.55 (1 H, s, PhCH), 5.08 (1 H, t, *J* 8.3, 2-H′), 4.97 (1 H, d, *J* 11.0, $ArCH_2$), 4.87–4.77 (4 H, m, $ArCH_2$), 4.66–4.63 (2 H, m, $ArCH_2$), 4.57 (1 H, d, *J* 3.3, 1-H), 4.51 (1 H, d, *J* 11.0, $ArCH_2$), 4.47 (1 H, d, *J* 8.3, 1-H′), 4.32 (1 H, dd, *J* 10.5, 5.0, $6\text{-H}'_a$), 4.04 (1 H, d, *J* 10.3, 6-H_a), 3.96 (1 H, t, *J* 9.3, 3-H), 3.81–3.67 (5 H, m, 5-H, 6-H_b, 3-H′, 4-H′, $6\text{-H}'_b$), 3.52 (1 H, dd, *J* 9.8, 3.5, 2-H), 3.45 (1 H, t, *J* 9.5, 4-H), 3.40 (1 H, td, *J* 9.7, 5.0, 5-H′), 3.34 (3 H, s, OCH_3), 1.88 (3 H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0 (C), 138.7 (C), 138.2 (C), 138.1 (C), 138.0 (C), 137.1 (C), 129.0 (CH), 128.4 (CH), 128.3 (CH), 128.25 (CH), 128.23 (CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 125.9 (CH), 101.4 (CH), 101.2 (CH), 98.1 (CH), 81.9 (CH), 81.3 (CH), 79.7 (CH), 78.5 (CH), 77.5 (CH), 75.6 (CH_2), 74.8 (CH_2), 74.0 (CH_2), 73.4 (CH_2), 72.6 (CH_2), 69.5 (CH), 68.5 (CH_2), 68.0 (CH_2), 66.3 (CH), 55.1 (CH_3), 20.8 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{50}H_{54}O_{12}Na$ ($[M + Na]^+$): 869.3513, found: 869.3547.



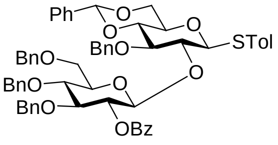
23

4-Methylphenyl 2-*O*-(6-*O*-*tert*-butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-*α*-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (23). TMSOTf (9 μL, 52 μmol) was added to a solution of compound **1** (200 mg, 348 μmol) and benzaldehyde (39 μL, 383 μmol) in CH_2Cl_2 (3 mL) with freshly dried 3 Å molecular sieves (400 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (61 μL, 383 μmol), benzaldehyde (37 μL, 366 μmol) and TMSOTf (9 μL, 52 μmol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor **22** (406 mg, 520 μmol) in CH_2Cl_2 (7.5 ml), NIS (129 mg, 560 μmol), AW-300 molecular sieves (700 mg) and TfOH (16 μL, 104 μmol) were sequentially added to the mixture at –78 °C. The reaction temperature was gradually raised to –40 °C for a period of 3 h. Saturated $NaHCO_{3(aq)}$ (10 mL) and 10% $Na_2S_2O_{3(aq)}$ (10 mL) were added to quench the reaction. The mixture was filtered through Celite followed by extraction with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/4) furnished the adduct **23** (286 mg, 72%) as a white foam. $[\alpha]^{26}_{D}$ +11.04 (*c* 1.2 in $CHCl_3$); IR (thin film): ν 2857, 1494, 1454, 1028, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74–7.72 (2 H, m, Ar-H), 7.64–7.62 (2 H, m, Ar-H), 7.46–7.38 (8 H, m, Ar-H), 7.34–7.22 (20 H, m, Ar-H), 7.17–7.16 (2 H, m, Ar-H), 7.09–7.07 (2 H, m, Ar-H), 7.03–7.00 (1 H, m, Ar-H), 6.94–6.91(2 H, m, Ar-H), 5.63 (1 H, d, *J* 0.7, 1-H′), 5.52 (1 H, s, ArCH), 5.01 (1 H, d, *J* 10.9, $ArCH_2$), 4.84 (1 H, d, *J* 12.7, $ArCH_2$), 4.85–4.78 (3 H, m, $ArCH_2$), 4.71–4.67 (3 H, m, $ArCH_2$), 4.57–4.54 (2 H, m, 1-H, $ArCH_2$), 4.38–4.34 (2 H, m, 6-H_a, 3-H), 3.98–3.96 (2 H, m, 3-H, 2-H′), 3.92 (1 H, d, *J* 9.7, 4-H′), 3.75 (1 H, t, *J* 10.3, 6-H_b), 3.66–3.62 (4 H, m, 2-H, 4-H, 5-H′, 6-H'_a), 3.51 (1 H, dd, *J* 11.3, 1.0, 6-H'_b), 3.51 (1 H, dt, *J* 9.6, 5.1, 5-H), 2.35 (3 H, s, CH_3), 1.04 (9 H, s, *t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1 (C), 138.7 (C), 138.6 (C), 138.2 (C), 137.5 (C), 137.1 (C), 136.0 (CH), 135.6 (CH), 134.1 (C), 133.6 (C), 132.8 (CH), 129.8 (CH), 129.3 (CH), 129.27 (CH), 128.9 (CH), 128.7 (C), 128.5 (CH), 128.3 (CH), 128.23 (CH), 128.21 (CH), 128.16 (CH), 128.10 (CH), 127.9 (CH), 127.7 (CH), 127.53 (CH), 127.52 (CH), 127.49 (CH), 127.44 (CH), 127.38 (CH), 127.31 (CH), 125.9 (CH), 101.1 (CH), 98.0 (CH), 88.6 (CH), 81.7 (CH), 81.2 (CH), 79.8 (CH), 76.0 (CH), 75.14 (CH), 75.13 (CH_2), 75.0 (CH_2), 74.3 (CH), 73.2 (CH), 72.2 (CH_2), 72.1 (CH_2), 70.1 (CH), 68.6 (CH_2), 62.4 (CH_2), 26.8 (CH_3), 21.1 (CH_3), 19.3 (C); HRMS (ESI): *m*/*z* calcd for $C_{70}H_{74}O_{10}SSiNa$ ($[M + Na]^+$): 1157.4670, found 1157.4663.



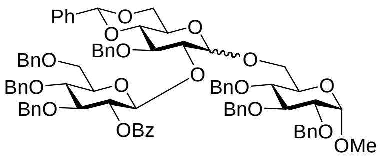
24

Methyl (6-*O*-*tert*-butyldiphenylsilyl-2,3,4-tri-*O*-benzyl-*α*-D-mannopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-*α*/*β*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (24). TMSOTf (4 *μ*L, 23 *μ*mol) was added to a solution of compound **1** (87 mg, 152 *μ*mol) and benzaldehyde (17 *μ*L, 166 *μ*mol) in CH_2Cl_2 (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (27 *μ*L, 166 *μ*mol), benzaldehyde (16 *μ*L, 160 *μ*mol) and TMSOTf (4 *μ*L, 23 *μ*mol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor **22** (176 mg, 226 *μ*mol) in CH_2Cl_2 (3.5 mL), NIS (63 mg, 270 *μ*mol), AW-300 molecular sieves (300 mg) and TfOH (3 *μ*L, 35 *μ*mol) were sequentially added to the mixture at –78 °C. The reaction temperature was gradually raised to –40 °C for a period of 3 h. Then, a solution of glycosyl acceptor **17** (101 mg, 270 *μ*mol) in CH_2Cl_2 (1.5 ml), NIS (56 mg, 240 *μ*mol) and TfOH (7 *μ*L, 75 *μ*mol) were sequentially added to the solution at –40 °C, and the reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH_2Cl_2, and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/6) furnished the trisaccharide **24** (117 mg, 52%, crude *α*/*β* = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69–7.61 (10.1 H, m, Ar-H), 7.45–7.41 (5.5 H, m, Ar-H), 7.38–7.25 (68.2 H, m, Ar-H), 7.23–7.15 (29.7 H, m, Ar-H), 7.12–7.04 (1.5 H, m, Ar-H), 7.01–6.96 (3.9 H, m, Ar-H), 6.89–6.86 (3 H, m, Ar-H), 5.62 (1 H, d, *J* 1.1), 5.50 (1.3 H, s, ArCH), 5.45 (1 H, s, ArCH), 5.06 (1 H, d, *J* 2.8), 5.04 (1 H, d, *J* 1.3), 4.99–4.89 (7.4 H, m), 4.84–4.81 (2.2 H, m), 4.77–4.73 (4 H, m), 4.71–4.60 (13.1 H, m), 4.58–4.55 (4.2 H, m), 4.52–4.47 (3.9 H, m), 4.40–4.35 (4.2 H, m), 4.31–4.26 (2.8 H, m), 4.19–4.16 (1 H, m), 4.12–4.06 (2.4 H, m), 4.02–3.94 (6.1 H, m), 3.91–3.78 (12.9 H, m), 3.74–3.71 (3 H, m), 3.68–3.45 (12.5 H, m), 3.40–3.38 (1.5 H, m), 3.36–3.27 (6 H, m), 3.32 (4 H, s), 1.03 (25.9 H, m); HRMS (ESI): *m*/*z* calcd for $C_{91}H_{98}O_{16}SiNa$ ($[M + Na]^+$): 1497.6522, found: 1497.6523.



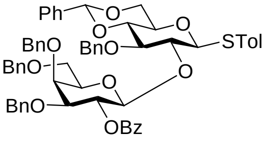
26

4-Methylphenyl 2-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (26). TMSOTf (4 μL, 23 μmol) was added to a solution of compound **1** (87 mg, 152 μmol) and benzaldehyde (17 μL, 166 μmol) in CH_2Cl_2 (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (27 μL, 165 μmol), benzaldehyde (16 μL, 160 μmol) and TMSOTf (4 μL, 23 μmol) were sequentially added to the reaction solution. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor **25** (110 mg, 166 μmol) in CH_2Cl_2 (3 ml), NIS (46 mg, 198 μmol), AW-300 molecular sieves (300 mg) and TfOH (3 μL, 30 μmol) were sequentially added to the solution at –78 °C. The reaction temperature was gradually raised to –60 °C for 3 h. Saturated $NaHCO_{3(aq)}$ (10 mL) and 10% $Na_2S_2O_{3(aq)}$ (10 mL) were added to quench the reaction, and the mixture was filtered through Celite followed by extraction with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/5) furnished the adduct **26** (105 mg, 70%) as a white foam. $[\alpha]^{27}_{D}$ –6.9 (*c* 1.4 in $CHCl_3$); IR (thin film): ν 2866, 1730, 1453, 1266, 1092, 1027, 697 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 (1 H, d, *J* 7.2, Ar-H), 7.52–7.49 (1 H, m, Ar-H), 7.45–7.43 (2 H, m, Ar-H), 7.39–7.37 (4 H, m, Ar-H), 7.34–7.29 (15 H, m, Ar-H), 7.27–7.23 (3 H, m, Ar-H), 7.14–7.11 (5 H, m, Ar-H), 7.09–7.07 (2 H, m, Ar-H), 7.03–7.00 (1 H, m, Ar-H), 5.48 (1 H, s, ArCH), 5.40 (1 H, dd, *J* 9.4, 8.1, 2-H′), 5.26 (1 H, d, *J* 8.1, 1-H′), 4.80–4.78 (2 H, m, ArCH$_2$), 4.76 (1 H, d, *J* 11.2, ArCH$_2$), 4.67–4.65 (4 H, m, 1-H, ArCH$_2$), 4.51 (1 H, d, *J* 11.1, ArCH$_2$), 4.30 (1 H, dd, *J* 10.6, 5.1, 6-H$_a$), 3.94–3.90 (2 H, m, 2-H, 4-H′), 3.87 (1 H, dd, *J* 11.4, 4.1, 6-H$'_a$), 3.82–3.77 (2 H, m, 3-H′, 6-H$'_b$), 3.71 (1 H, t, *J* 10.4, 6-H$_b$), 3.66–3.61 (2 H, m, 3-H, 4-H), 3.51 (1 H, ddd, *J* 9.8, 4.0, 1.7, 5-H′), 3.36 (1 H, dt, *J* 9.5, 5.1, 5-H), 2.33 (3 H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1 (C), 138.4 (C), 138.3 (C), 137.9 (C), 137.8 (C), 137.6 (C), 137.1 (C), 133.0 (CH), 129.8 (C), 129.7 (CH), 129.6 (C), 129.5 (CH), 128.9 (CH), 128.43 (CH), 128.40 (CH), 128.35 (CH), 128.32 (CH), 128.2 (CH), 128.16 (CH), 128.12 (CH), 127.9 (CH), 127.8 (CH), 127.68 (CH), 127.65 (CH), 127.56 (CH), 127.4 (CH), 127.3 (CH), 125.9 (CH), 101.1 (CH), 100.5 (CH), 87.2 (CH), 83.5 (CH), 82.8 (CH), 81.5 (CH), 78.0 (CH), 76.1 (CH), 75.5 (CH_2), 75.1 (CH_2), 74.9 (CH_2), 74.7 (CH_2), 73.9 (CH), 73.87 (CH_2), 69.7 (CH), 68.6 (CH_2), 68.58 (CH_2), 21.1 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{61}H_{60}O_{11}SNa$ ([M + Na]$^+$): 1023.3754, found: 1023.3745.



27

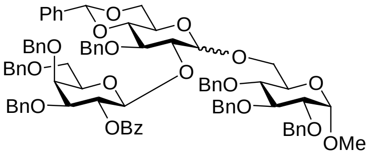
Methyl (2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-*α*/*β*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (27). TMSOTf (4 *μ*L, 23 *μ*mol) was added to a solution of compound **1** (87 mg, 152 *μ*mol) and benzaldehyde (17 *μ*L, 166 *μ*mol) in CH_2Cl_2 (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et3SiH (27 *μ*L, 166 *μ*mol), benzaldehyde (16 *μ*L, 160 *μ*mol) and TMSOTf (4 *μ*L, 23 *μ*mol) were sequentially added to the reaction solution. After stirring –78 °C for 2.5 h, a solution of glycosyl donor **25** (110 mg, 167 *μ*mol) in CH_2Cl_2 (3 ml), NIS (46 mg, 200 *μ*mol), AW-300 molecular sieves (300 mg) and TfOH (3 *μ*L, 30 *μ*mol) were sequentially added to the solution at –78 °C. The reaction temperature was gradually raised to –60 °C for a period of 3 h. Then, a solution of the glycosyl acceptor **17** (84 mg, 228 *μ*mol) in CH_2Cl_2 (1.5 ml), NIS (42 mg, 182 *μ*mol) and TfOH (7 *μ*L, 75 *μ*mol) were sequentially added to the mixture at –60 °C. The reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with CH_2Cl_2, and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) furnished the trisaccharide **27** (131 mg, 65%, crude *α*/*β* = 3/1). For the *α*-isomer: $[\alpha]^{27}_D$ +63.1 (*c* 1.2 in $CHCl_3$); IR (thin film): ν 2859, 1731, 1453, 1365, 1266, 1089, 1027, 736 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.88 (2 H, d, *J* 8.3, Ar-H), 7.42 (1 H, t, *J* 7.4, Ar-H), 7.39–7.34 (6 H, m, Ar-H), 7.32–7.25 (20 H, m, Ar-H), 7.23–7.15 (9 H, m, Ar-H), 7.13–7.10 (5 H, m, Ar-H), 7.06–7.04 (2 H, m, Ar-H), 5.47 (1 H, s, ArCH), 5.38 (1 H, t, *J* 8.5, 2-H″), 5.13 (1 H, d, *J* 3.5, 1-H′), 5.00 (1 H, d, *J* 11.0, $ArCH_2$), 4.96 (1 H, d, *J* 8.5, 1-H″), 4.91 (1 H, d, *J* 11.2, $ArCH_2$), 4.84 (1 H, d, *J* 11.0, ArCH$_2$), 4.79 (1 H, d, *J* 12.0, ArCH$_2$), 4.76 (1 H, d, *J* 10.8, ArCH$_2$), 4.73–4.69 (2 H, m, ArCH$_2$), 4.66–4.64 (2 H, m, ArCH$_2$), 4.60 (1 H, d, *J* 11.2, ArCH$_2$), 4.57 (1 H, d, *J* 11.7, ArCH$_2$), 4.54 (1 H, d, *J* 12.2, ArCH$_2$), 4.51–4.48 (2 H, m, ArCH$_2$), 4.38 (1 H, d, *J* 11.6, ArCH$_2$), 4.20 (1 H, dd, *J* 10.2, 4.9, 6-H′$_a$), 4.02 (1 H, t, *J* 9.3, 3-H), 3.88–3.63 (12 H, m, 2-H, 4-H, 6-H × 2, 2-H′, 3-H′, 4-H′, 6-H′$_b$, 3-H″, 4-H″, 6-H″ × 2), 3.57–3.52 (3 H, m, 5-H, 5-H′, 5-H″), 3.35 (3 H, s, CH$_3$); ^{13}C NMR (150 MHz, CDCl$_3$): δ 164.7 (C), 139.1 (C), 138.6 (C), 138.5 (C), 138.4 (C), 137.9 (C), 137.8 (C), 137.7 (C), 137.4 (C), 132.8 (CH), 129.8 (C), 129.7 (CH), 128.1 (CH), 128.4 (CH), 128.34 (CH), 128.30 (CH), 128.28 (CH), 128.21 (CH), 128.1 (CH), 128.08 (CH), 128.05 (CH), 127.97 (CH), 127.93 (CH), 127.8 (CH), 127.78 (CH), 127.70 (CH), 127.65 (CH), 127.60 (CH), 127.5 (CH), 127.3 (CH), 127.21 (CH), 127.18 (CH), 126.0 (CH), 101.8 (CH), 101.3 (CH), 99.6 (CH), 97.7 (CH), 82.9 (CH), 82.2 (CH), 80.3 (CH), 78.4 (CH), 78.2 (CH), 77.9 (CH), 77.8 (CH), 75.6 (CH$_2$), 75.1 (CH$_2$), 75.0 (CH$_2$), 74.8 (CH$_2$), 74.5 (CH$_2$), 73.7 (CH), 73.3 (CH$_2$), 70.0 (CH), 69.1 (CH$_2$), 68.8 (CH$_2$), 67.0 (CH$_2$), 62.4 (CH), 55.1 (CH$_3$); HRMS (ESI): *m*/*z* calcd for $C_{82}H_{84}O_{17}Na$ ([M + Na]$^+$): 1363.5606, found: 1363.5602. For the β-isomer: IR (thin film): ν 2925, 1731, 1453, 1266, 1093, 737, 697 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.81 (2 H, d, *J* 7.3, Ar-H), 7.46–7.41 (3 H, m, Ar-H), 7.34–7.31 (6 H, m, Ar-H), 7.30–7.21 (26 H, m, Ar-H), 7.17–7.14 (1 H, m, Ar-H), 7.10–7.02 (7 H, m, Ar-H), 5.42 (1 H, s, ArCH), 5.17 (1 H, t, *J* 8.2, 2-H″), 5.11 (1 H, d, *J* 8.2, 1-H″), 5.00–4.97 (2 H, m, ArCH$_2$), 4.85–4.81 (2 H, m, ArCH$_2$), 4.70–4.67 (2 H, m, ArCH$_2$), 4.61–4.51 (4 H, m, 1-H, ArCH$_2$), 4.52–4.48 (4 H, m, 1-H′, ArCH$_2$), 4.39 (1 H, d, *J* 11.4, ArCH$_2$), 4.26–4.24 (2 H, m, 6-H′$_a$, ArCH$_2$), 4.05 (1 H, d, *J* 10.3, 6-H″$_a$), 3.98 (1 H, t, *J* 9.1, 3-H), 3.85 (1 H, t, *J* 7.8, 2-H′), 3.80 (1 H, dd, *J* 10.4, 3.2, 6-H″$_a$), 3.77–3.76 (2 H, m, 4-H, 4-H″), 3.71–3.60 (5 H, m, 6-H × 2, 4-H′, 6-H′$_b$, 3-H″), 3.57–3.48 (3 H, m, 2-H, 3-H′, 5-H″), 3.36 (3 H, s, CH$_3$), 3.34–3.40 (2 H, m, 5-H, 5-H′); ^{13}C NMR (150 MHz, CDCl$_3$): δ 164.9 (C), 139.0 (C), 138.8 (C), 138.4 (C), 138.3 (C), 138.2 (C), 137.8 (C), 137.1 (C), 132.9 (CH), 129.8 (C), 129.7 (CH), 128.9 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.22 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.88 (CH), 127.83 (CH), 127.78 (CH), 127.5 (CH), 127.49 (CH), 127.45 (CH), 127.2 (CH), 125.9 (CH), 102.1 (CH), 101.0 (CH), 100.7 (CH), 97.9 (CH), 82.8 (CH), 82.1 (CH), 82.05 (CH), 81.3 (CH), 80.0 (CH), 78.7 (CH), 78.3 (CH), 77.6 (CH), 75.8 (CH_2), 75.2 (CH_2), 75.1 (CH), 75.0 (CH_2), 74.7 (CH_2), 74.5 (CH_2), 74.0 (CH), 73.3 (CH_2), 73.2 (CH_2), 69.9 (CH), 69.2 (CH_2), 68.7 (CH_2), 68.5 (CH_2), 65.6 (CH), 55.2 (CH_3); HRMS (ESI): *m*/*z* calcd for $C_{82}H_{84}O_{17}Na$ ($[M + Na]^+$): 1363.5606, found: 1363.5601.



29

4-Methylphenyl 2-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (29). TMSOTf (4 *μ*L, 23 *μ*mol) was added to a solution of compound **1** (87 mg, 152 *μ*mol) and benzaldehyde (17 *μ*L, 166 *μ*mol) in CH_2Cl_2 with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (27 *μ*L, 165 *μ*mol), benzaldehyde (16 *μ*L, 160 *μ*mol) and TMSOTf (4 *μ*L, 23 *μ*mol) were sequentially added to the reaction mixture. After stirring at –78 °C for 2.5 h, a solution of glycosyl donor **28** (110 mg, 166 *μ*mol) in CH_2Cl_2 (3 mL), NIS (46 mg, 198 *μ*mol), AW-300 molecular sieves (300 mg) and TfOH (3 *μ*L, 30 *μ*mol) were sequentially added again to the solution at –78 °C. The reaction temperature was gradually raised up to –60 °C for 3 h. Saturated $NaHCO_{3(aq)}$ (10 mL) and 10% $Na_2S_2O_{3(aq)}$ (10 mL) were added to quench the reaction, the mixture was filtered through Celite followed by extraction with

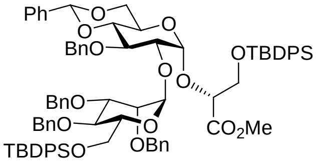
CH_2Cl_2, and the combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/5) furnished the adduct **29** (94 mg, 63%) as a white foam. $[\alpha]^{27}_{D}$ –11.9 (*c* 0.9 in $CHCl_3$); IR (thin film): ν 1731, 1454, 1269, 1095, 751, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 7.93 (2 H, d, *J* 8.1, Ar-H), 7.52 (1 H, t, *J* 7.0, Ar-H), 7.45 (2 H, d, *J* 8.1, Ar-H), 7.40 (2 H, d, *J* 7.0, Ar-H), 7.38–7.31 (14 H, m, Ar-H), 7.28–7.20 (7 H, m, Ar-H), 7.18–7.16 (4 H, m, Ar-H), 7.01 (2 H, d, *J* 8.1, Ar-H), 5.71 (1 H, t, *J* 8.1, 2-H′), 5.47 (1 H, s, ArCH), 5.19 (1 H, d, *J* 8.1, 1-H′), 5.03 (1 H, d, *J* 11.7, $ArCH_2$), 4.68 (1 H, d, *J* 11.8, $ArCH_2$), 4.64–4.61 (2 H, m, 1-H, $ArCH_2$), 4.51 (1 H, d, *J* 11.1, $ArCH_2$), 4.48–4.45 (2 H, m, $ArCH_2$), 4.30 (1 H, dd, *J* 10.6, 5.1, 6-H_a), 4.05 (1 H, d, *J* 2.4, 4-H′), 3.86 (1 H, t, *J* 8.8, 2-H), 3.75 (1 H, t, *J* 8.4, 6-H'_a), 3.69 (1 H, t, *J* 10.4, 6-H_b), 3.65 (1 H, t, *J* 9.2, 3-H), 3.62–3.55 (4 H, m, 3-H′, 4-H′, 5-H′, 6-H'_b), 3.35 (1 H, dt, *J* 9.8, 5.1, 5-H), 2.31 (3 H, s, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.3 (C), 138.6 (C), 138.3 (C), 137.8 (C), 137.7 (C), 137.5 (C), 137.1 (C), 133.7 (CH), 132.9 (CH), 130.0 (C), 129.8 (CH), 129.4 (CH), 128.9 (C), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.26 (CH), 128.20 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.66 (CH), 127.50 (CH), 127.49 (CH), 127.44 (CH), 125.9 (CH), 101.0 (CH), 100.5 (CH), 86.6 (CH), 83.4 (CH), 81.4 (CH), 79.7 (CH), 76.0 (CH), 74.7 (CH_2), 74.4 (CH_2), 73.6 (CH_2), 73.5 (CH), 72.4 (CH), 72.2 (CH), 71.4 (CH), 69.6 (CH), 68.6 (CH_2), 68.3 (CH_2), 21.1 (CH_3); HRMS (ESI): *m/z* calcd for $C_{61}H_{60}O_{11}SNa$ ($[M + Na]^+$): 1023.3754, found: 1023.3733.



30

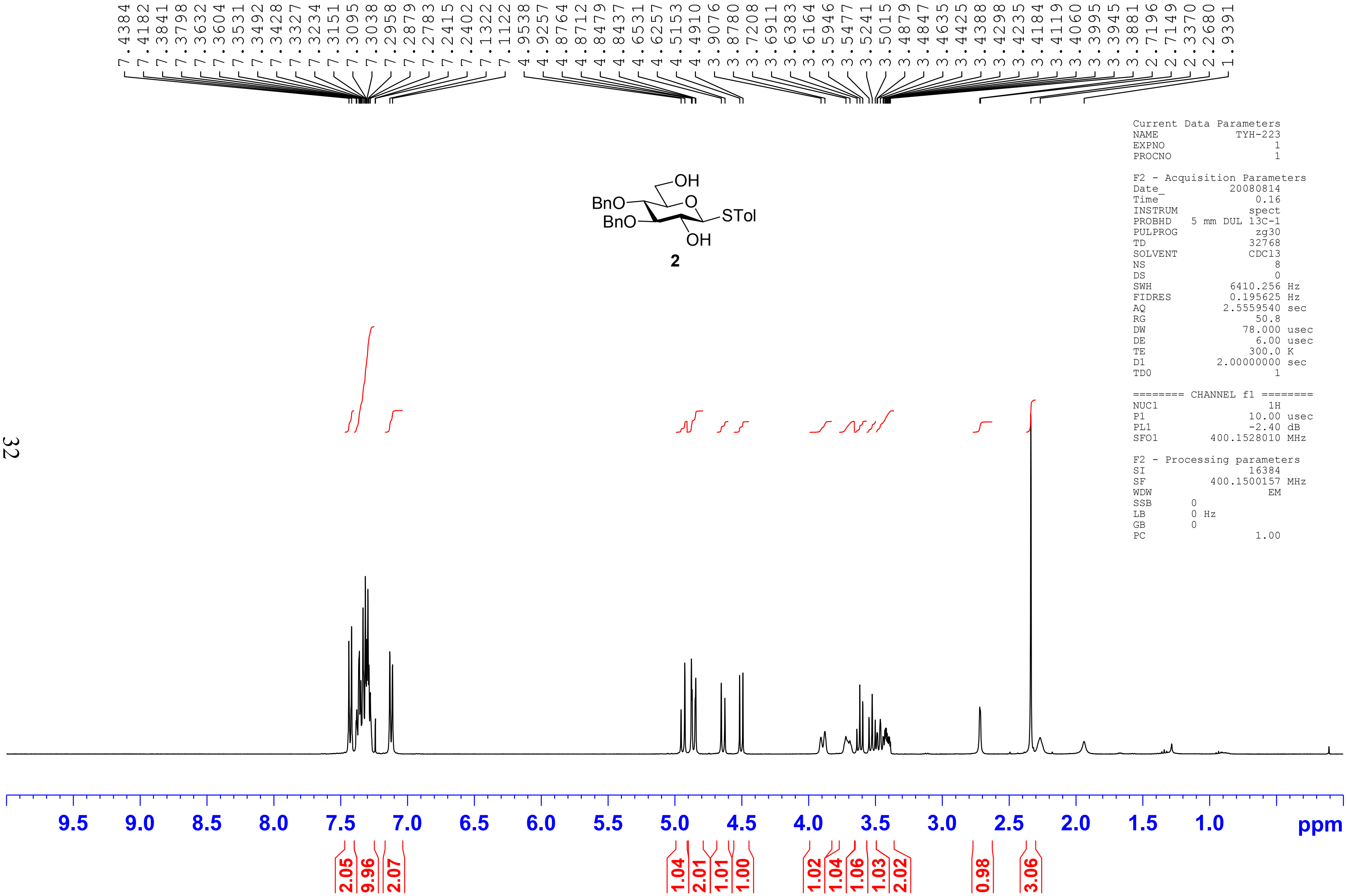
Methyl (2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-*α*/*β*-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside (30). TMSOTf (4 *μ*L, 23 *μ*mol) was added to a solution of compound **1** (87 mg, 152 *μ*mol) and benzaldehyde (17 *μ*L, 166 *μ*mol) in CH_2Cl_2 (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was kept stirring at same temperature for 2 h. Et_3SiH (27 *μ*L, 166 *μ*mol), benzaldehyde (16 *μ*L, 160 *μ*mol) and TMSOTf (4 μL, 23 *μ*mol) were sequentially added to the reaction solution. After 2.5 h of stirring at –78 °C, a solution of the glycosyl donor **28** (110 mg, 167 *μ*mol) in CH_2Cl_2 (3 mL), NIS (46 mg, 200 *μ*mol), AW-300 molecular sieves (300 mg) and TfOH (3 *μ*L, 30 *μ*mol) were sequentially added to the mixture. The reaction temperature was gradually raised to –60 °C for 3 h. Then, a solution of the glycosyl acceptor **17** (84 mg, 228 *μ*mol) in CH_2Cl_2 (1.5 ml), NIS (42 mg, 182 *μ*mol) and TfOH (7 *μ*L, 75 *μ*mol) were sequentially added to the solution at –60 °C. The reaction temperature was gradually raised to 0 °C for 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction, the mixture was filtered through Celite, and the desired material was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/3) provided the trisaccharide **30** (124 mg, 61%, crude *α*/*β* = 2/1) as a white foam. ^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.94–7.92 (2.4 H, m, Ar-H), 7.87–7.86 (2 H, m, Ar-H), 7.51–7.45 (4.5 H, m, Ar-H), 7.43–7.29 (45.8 H, m, Ar-H), 7.26–7.18 (25.5 H, m, Ar-H), 7.17–7.05 (20.4 H, m, Ar-H), 5.69 (1.2 H, t, *J* 8.9), 5.66 (1 H, t, *J* 8.9), 5.48 (1.2 H, s, PhCH), 5.45 (1 H, s, PhCH), 5.10–4.96 (9.1 H, m), 4.92–4.87 (4.1 H, m), 4.84–4.77 (4.2 H, m), 4.73–4.68 (6.1 H, m), 4.65–4.57 (7 H, m), 4.53 (1 H, d, *J* 7.4), 4.48–4.35 (9.4 H, m), 4.29 (1 H, dd, *J* 10.6, 5.1), 4.24–4.19 (2.2 H, m), 4.06–4.00 (4.5 H, m), 3.96 (1 H, d, *J* 2.5), 3.90–3.80 (8.6

H, m), 3.78–3.74 (3.1 H, m), 3.73–3.68 (5.8 H, m), 3.67–3.59 (8.6 H, m), 3.56–3.53 (2.1 H, m), 3.52–3.51 (1.5 h, m), 3.44 (1 H, t, *J* 9.4), 3.38–3.37 (6.6 H, m), 3.36–3.34 (1.2 H, m); HRMS (ESI): *m*/*z* calcd for $C_{82}H_{84}O_{17}Na$ ($[M + Na]^+$): 1363.5606, found: 1363.5580.



32

Methyl 3-*O*-*tert*-butyl-(2*R*)-2-*O*-[3-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-*α*-D-mannopyranosyl)-4,6-*O*-benzylidene-*α*-D-glucopyranosyl]-2,3-dihydroxypropanoate (32). TMSOTf (4 *μ*L, 23 *μ*mol) was added to a solution of compound **1** (87 mg, 152 *μ*mol) and benzaldehyde (17 *μ*L, 166 *μ*mol) in CH_2Cl_2 (1.5 mL) with freshly dried 3 Å molecular sieves (200 mg) at –78 °C under N_2 atmosphere. The mixture was stirred at same temperature for 2 h. Et_3SiH (27 *μ*L, 166 *μ*mol), benzaldehyde (16 *μ*L, 160 *μ*mol) and TMSOTf (4 *μ*L, 23 *μ*mol) were sequentially added to the reaction solution. After 2.5 h of stirring at –78 °C, a solution of the glycosyl donor **22** (176 mg, 176 *μ*mol) in CH_2Cl_2 (3.5 ml), NIS (61 mg, 270 *μ*mol), AW-300 molecular sieves (300 mg) and TfOH (3 *μ*L, 35 *μ*mol) were sequentially added to the solution at –78 °C. The reaction temperature was gradually raised to –40 °C for a period of 3 h. Then, a solution of the glycerate **31** (97 mg, 270 *μ*mol) in CH_2Cl_2 (1.5 ml), NIS (34 mg, 146 *μ*mol) and TfOH (7 *μ*L, 75 *μ*mol) were sequentially added to the mixture at –40 °C, and the reaction temperature was gradually raised to 0 °C for a period of 2 h. Saturated $NaHCO_{3(aq)}$ (5 mL) and 10% $Na_2S_2O_{3(aq)}$ (5 mL) were added to quench the reaction. The mixture was filtered through Celite, followed by extraction with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the residue via flash column chromatography (ethyl acetate/hexanes = 1/6) delivered the MMG backbone **32** (70 mg, 34%). $[\alpha]^{24}_{D}$ +24.4 (*c* 3.1 in $CHCl_3$); IR (thin film): δ 2930, 2857, 1752, 1427, 1112, 1044, 737, 698 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79–7.70 (8 H, m, Ar-H), 7.48–7.46 (4 H, m, Ar-H), 7.43–7.35 (11 H, m, Ar-H), 7.33–7.25 (13 H, m, Ar-H), 7.24–7.18 (6 H, m, Ar-H), 7.11–7.09 (1 H, m, Ar-H), 7.03–7.01 (2 H, m, Ar-H), 5.59 (1 H, s, 1′-H), 5.49 (1 H, s, ArCH), 5.35 (1 H, s, 1-H), 4.99 (1 H, d, *J* 11.1, $ArCH_2$), 4.90 (1 H, d, *J* 12.2, $ArCH_2$), 4.85 (1 H, d, *J* 12.2, $ArCH_2$), 4.78 (1 H, d, *J* 10.9, $ArCH_2$), 4.74 (1 H, d, *J* 10.9, $ArCH_2$), 4.63 (1 H, d, *J* 11.1, $ArCH_2$), 4.54–4.48 (3 H, m, glycerate-CH, $ArCH_2$), 4.20 (1 H, dd, *J* 10.3, 4.8, 6-H_a), 4.16–4.15 (5 H, m, 2′-H, 3′-H, 4′-H, 5-H, glycerate-CH_2), 4.04–4.03 (2 H, m, 2-H, 3-H), 4.00 (1 H, dd, *J* 10.8, 2.4, glycerate-CH_2), 3.91–3.84 (3 H, m, 5-H, 6′-H × 2), 3.77 (3 H, s, OCH_3), 3.68 (1 H, t, *J* 10.3, 6-H_b), 3.60 (1 H, t, *J* 8.9, 4-H), 1.07–1.06 (18 H, m, *t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.0 (C), 139.14 (C), 139.11 (C), 138.6 (C), 138.3 (C), 137.4 (C), 135.9 (CH), 135.7 (CH), 135.5 (CH), 133.9 (C), 133.6 (C), 133.1 (C), 132.8 (C), 129.8 (CH), 129.4 (CH), 129.3 (CH), 128.8 (CH), 128.2 (CH), 128.1 (CH), 128.09 (CH), 128.06 (CH), 128.04 (CH), 127.8 (CH), 127.79 (CH), 127.75 (CH), 127.6 (CH), 127.5 (CH), 127.45 (CH), 127.43 (CH), 127.3 (CH), 127.2 (CH), 127.1 (CH), 127.0 (CH), 126.0 (CH), 101.3 (CH), 94.5 (CH), 93.9 (CH), 81.9 (CH), 80.1 (CH), 75.4 (CH_2), 75.2 (CH), 74.9 (CH_2), 74.6 (CH), 74.3 (CH), 73.0 (CH), 72.4 (CH), 72.3 (CH_2), 71.5 (CH_2), 68.8 (CH_2), 64.9 (CH_2), 63.3 (CH_2), 62.8 (CH), 51.9 (CH_3), 26.9 (CH_3), 26.7 (CH_3), 19.3 (C), 19.2 (C); HRMS (ESI): *m*/*z* calcd for $C_{83}H_{92}O_{14}Si_2Na$ ($[M + Na]^+$): 1391.5923, found: 1391.5970.



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D1            2.00000000 sec
TD0                     1

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PL1                 -2.40 dB
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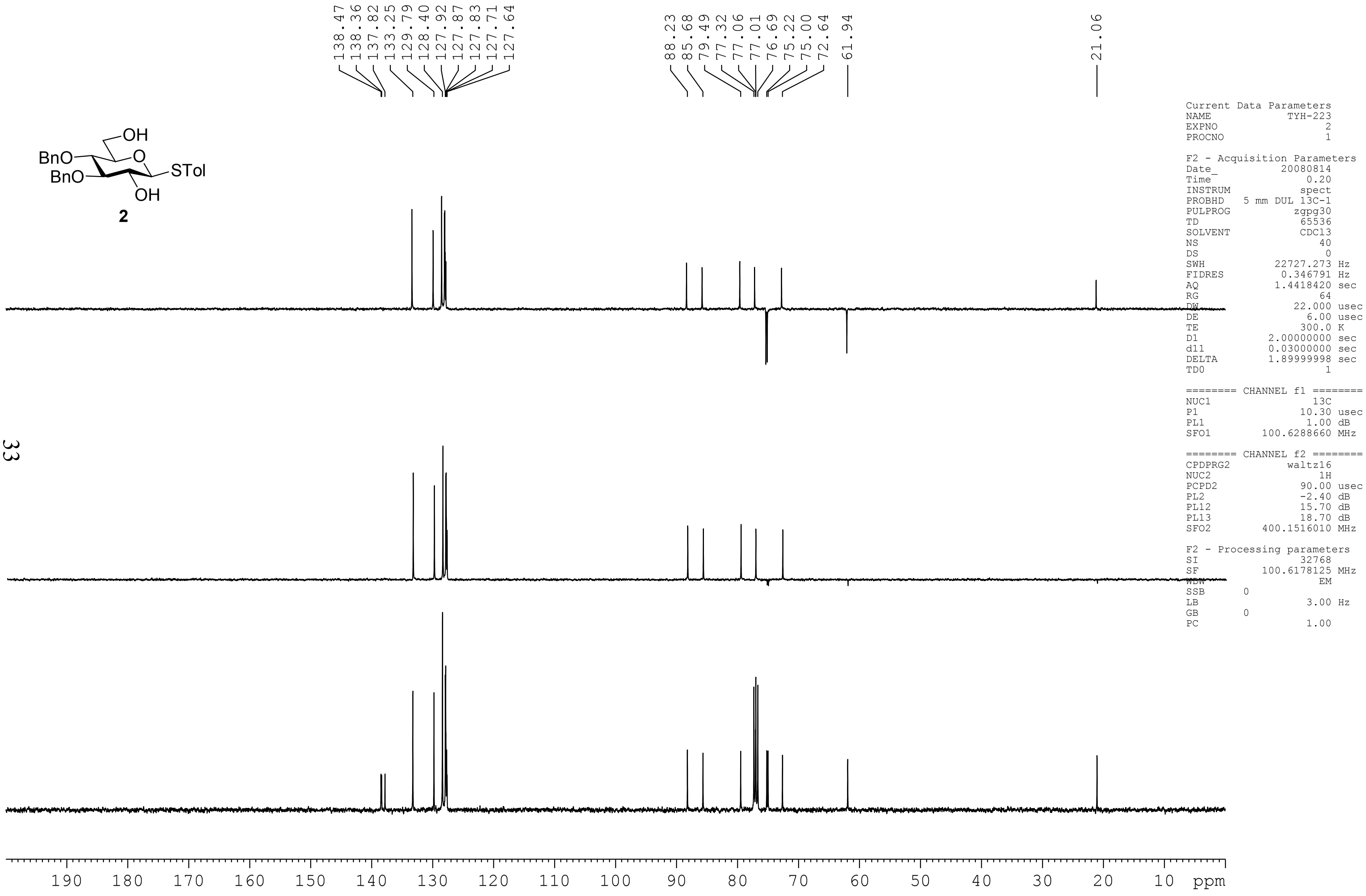

2

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PL1                 1.00 dB
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======== CHANNEL f2 ========
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PCPD2              90.00 usec
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PL12               15.70 dB
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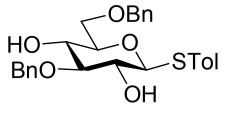

3

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TD0                     1

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F2 - Processing parameters
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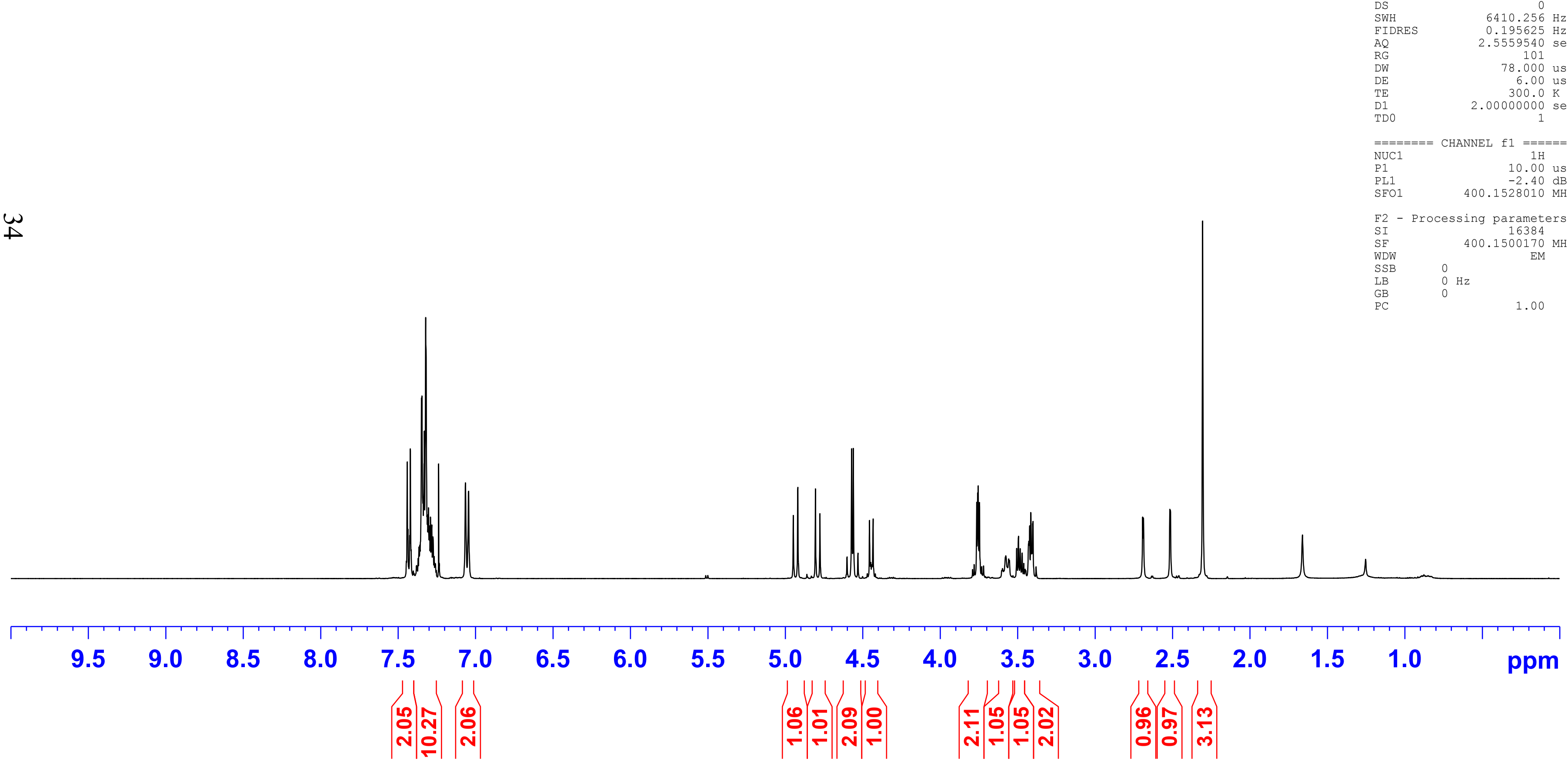
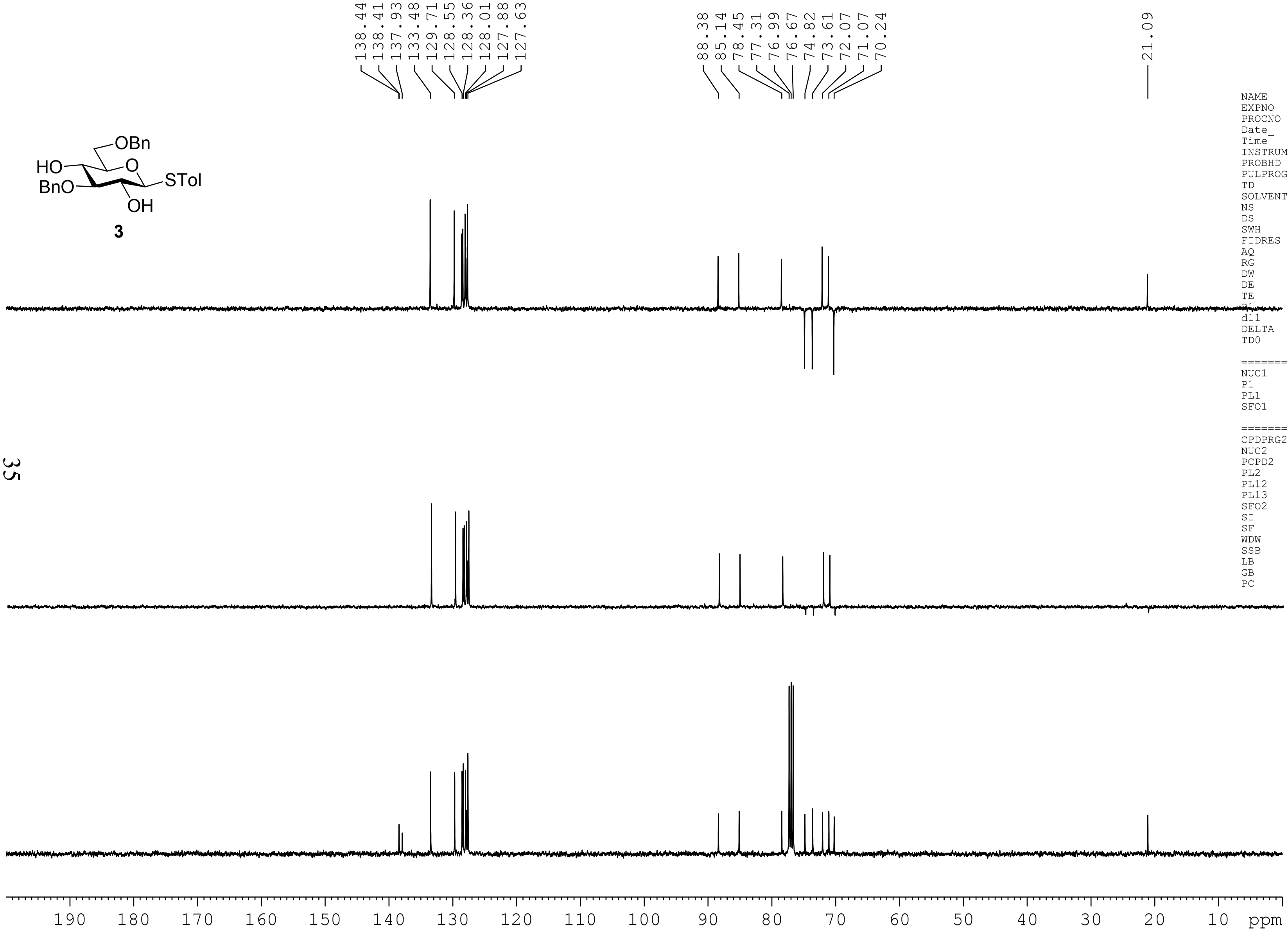
PC                   1.00
```



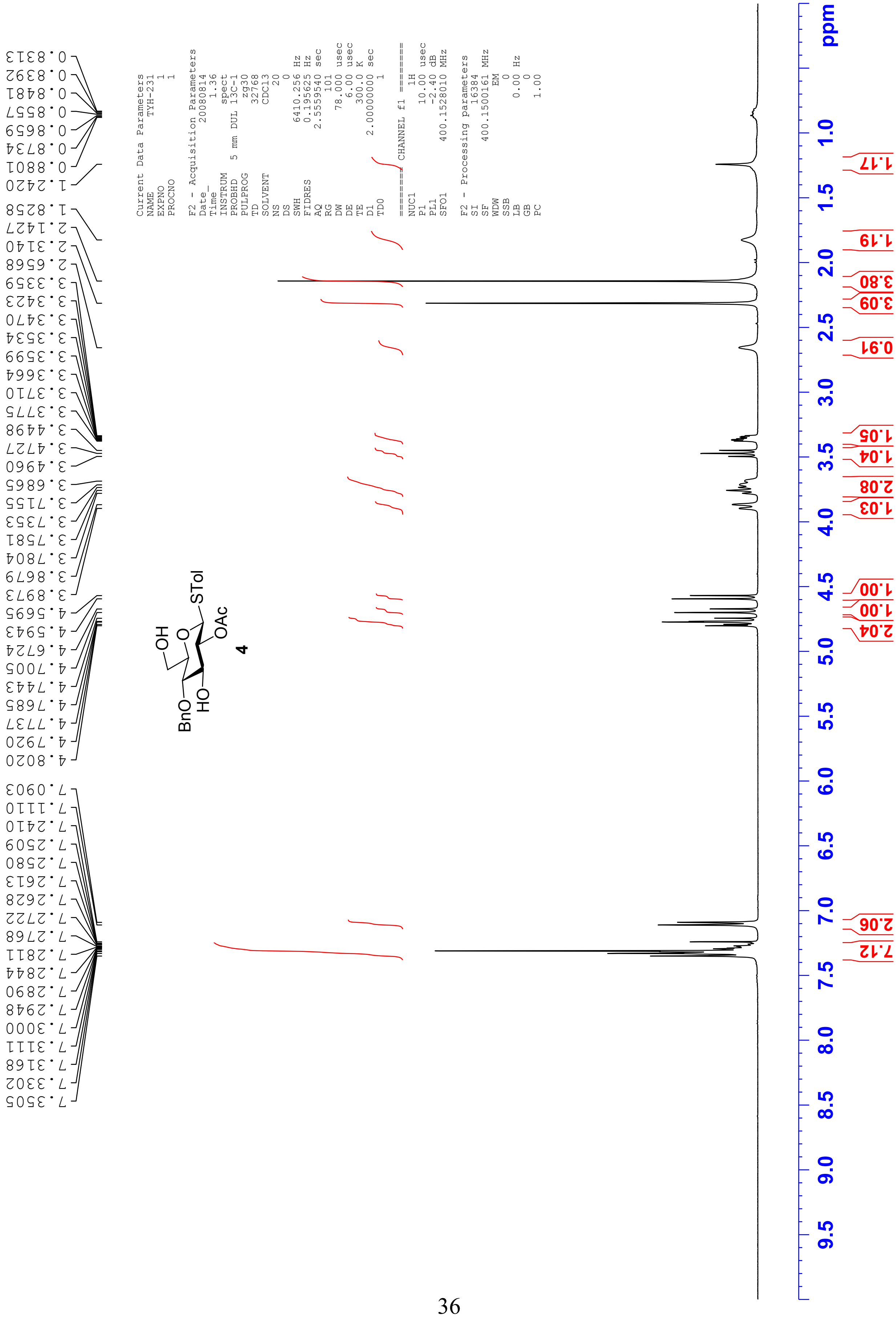


3

```
NAME              TYH-225
EXPNO                   3
PROCNO                  1
Date_            20080814
Time                 0.44
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    100
DS                      0
SWH            22727.273 Hz
FIDRES          0.346791 Hz
AQ             1.4418420 sec
RG                     64
DW                 22.000 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.30 usec
PL1                  1.00 dB
SFO1          100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -2.40 dB
PL12                15.70 dB
PL13                18.70 dB
SFO2          400.1516010 MHz
SI                  32768
SF            100.6178047 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.00
```


0.8313
0.8392
0.8481
0.8557
0.8659
0.8734
0.8801
1.2420
1.8258
2.1427
2.3140
2.6568
3.3359
3.3423
3.3470
3.3534
3.3599
3.3664
3.3710
3.3775
3.4498
3.4727
3.4960
3.6865
3.7155
3.7353
3.7581
3.7804
3.8679
3.8973
4.5695
4.5943
4.6724
4.7005
4.7443
4.7685
4.7737
4.7920
4.8020
7.0903
7.1110
7.2410
7.2509
7.2580
7.2613
7.2628
7.2722
7.2768
7.2811
7.2844
7.2890
7.2948
7.3000
7.3111
7.3168
7.3302
7.3505
Current Data Parameters
NAME TYH-231
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080814
Time 1.36
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 20
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 101
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.40 dB
SFO1 400.1528010 MHz
F2 - Processing parameters
SI 16384
SF 400.1500161 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
BnO
HO
OH
O
STol
OAc
4
1.17
1.19
3.80
3.09
0.91
1.05
1.04
2.08
1.03
1.00
1.00
2.04
2.06
7.12
ppm
1.0
1.5
2.0
2.5
3.0
3.5
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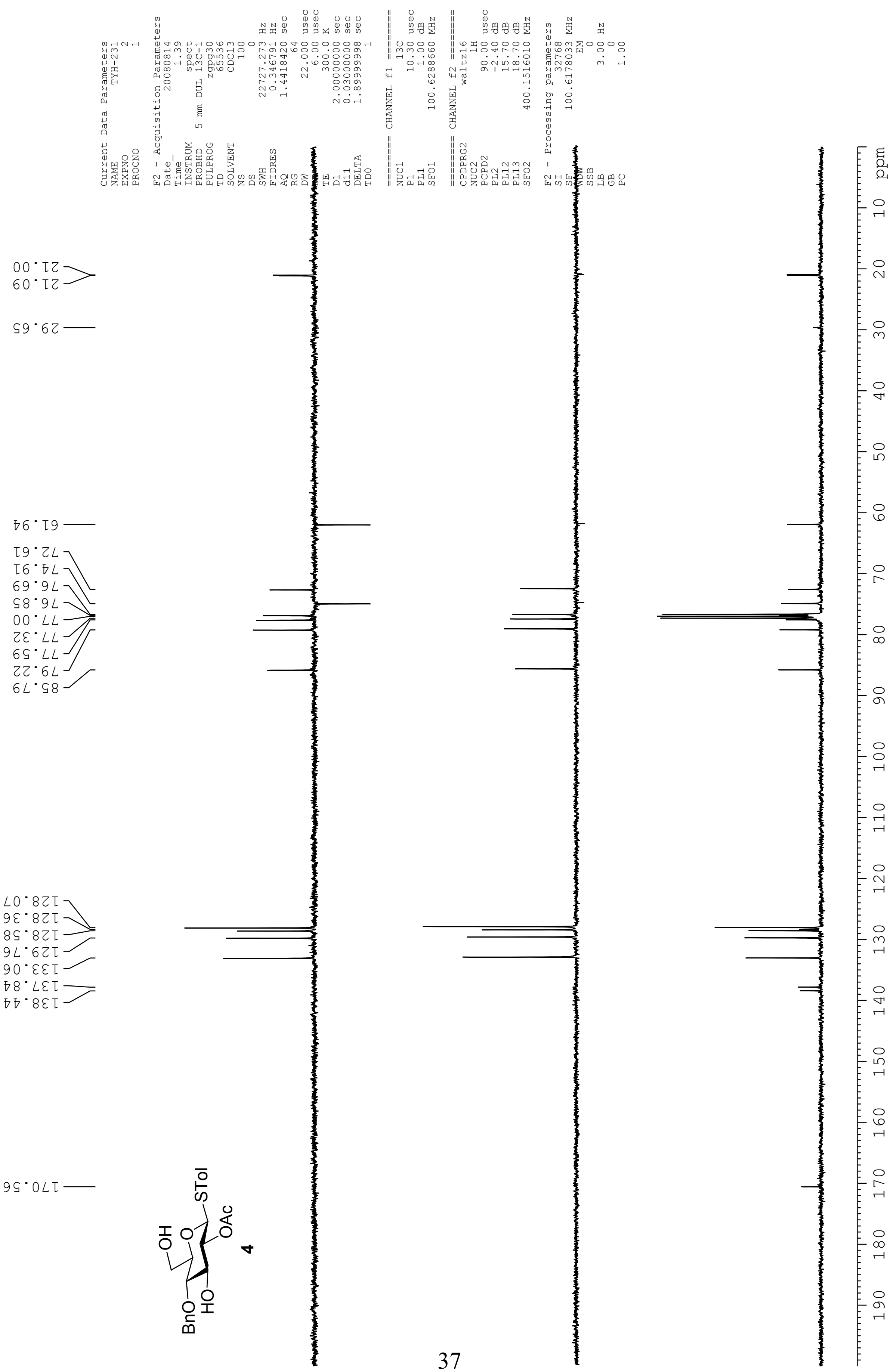
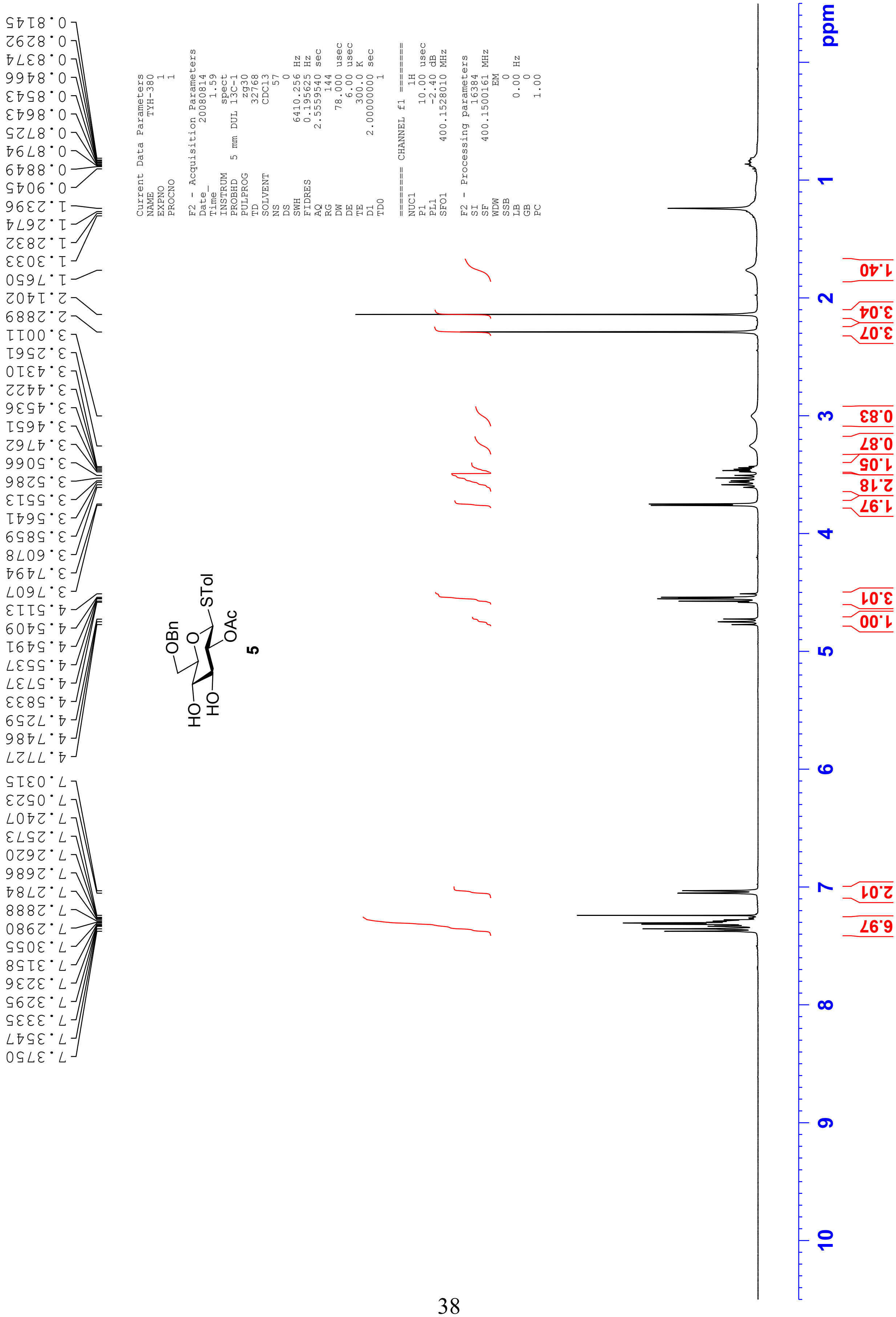
7.0
7.5
8.0
8.5
9.0
9.5


Current Data Parameters
NAME TYH-231
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080814
Time 1.39
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 100
DS 0
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 64
DW 22.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 1.00 dB
SFO1 100.6288660 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.40 dB
PL12 15.70 dB
PL13 18.70 dB
SFO2 400.1516010 MHz
F2 - Processing parameters
SI 32768
SF 100.6178033 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
21.00
21.09
29.65
61.94
72.61
74.91
76.69
76.85
77.00
77.32
77.59
79.22
85.79
128.07
128.36
128.58
129.76
133.06
137.84
138.44
170.56
BnO
HO
OH
O
STol
OAc
4
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

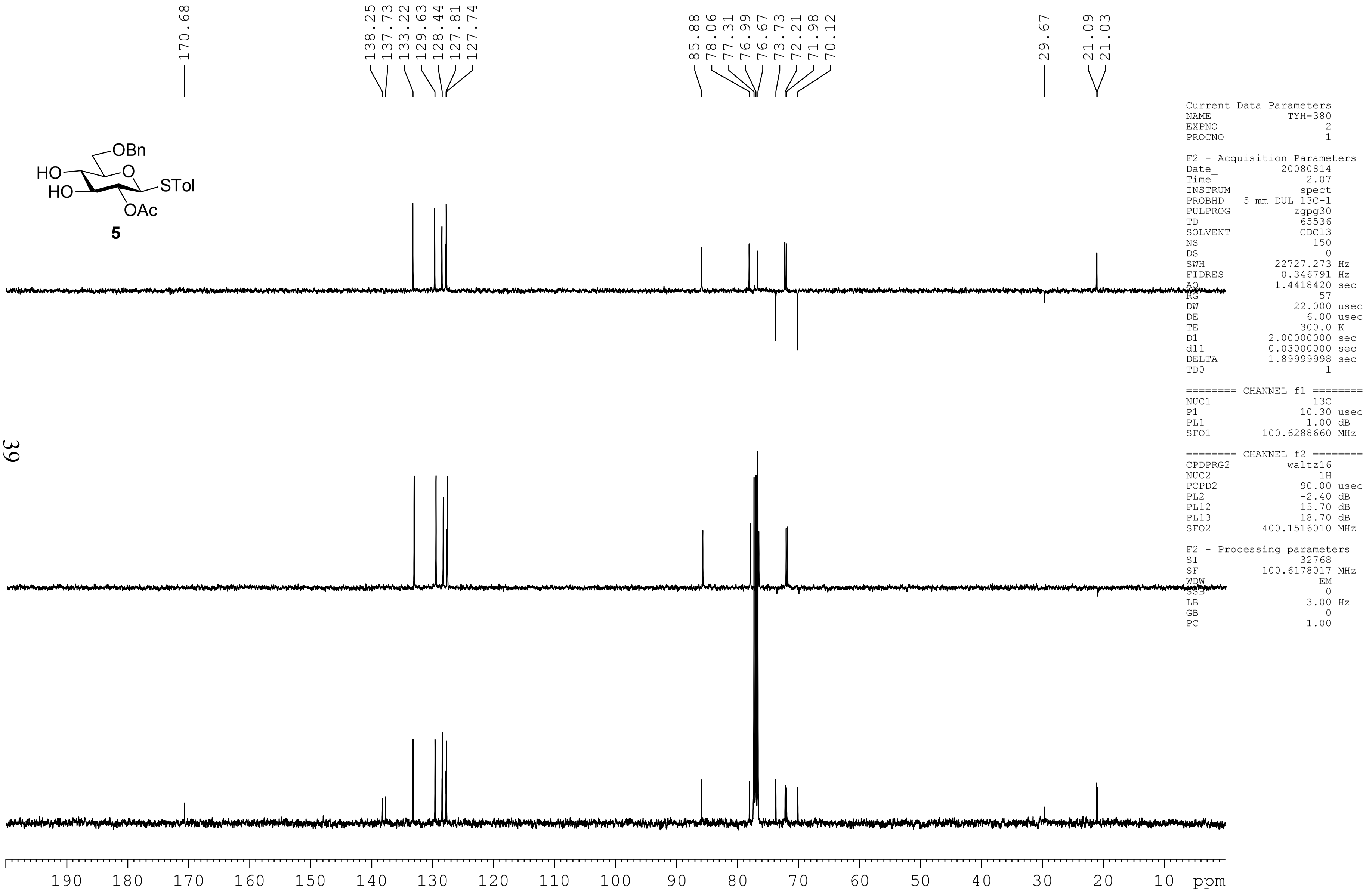


```
Current Data Parameters
NAME          TYH-380
EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
Date_        20080814
Time             1.59
INSTRUM         spect
PROBHD   5 mm DUL 13C-1
PULPROG          zg30
TD              32768
SOLVENT         CDCl3
NS                 57
DS                  0
SWH          6410.256 Hz
FIDRES       0.195625 Hz
AQ          2.5559540 sec
RG                144
DW             78.000 usec
DE               6.00 usec
TE              300.0 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
NUC1               1H
P1              10.00 usec
PL1             -2.40 dB
SFO1      400.1528010 MHz

F2 - Processing parameters
SI              16384
SF        400.1500161 MHz
WDW                EM
SSB                 0
LB               0.00 Hz
GB                  0
PC               1.00
```



5

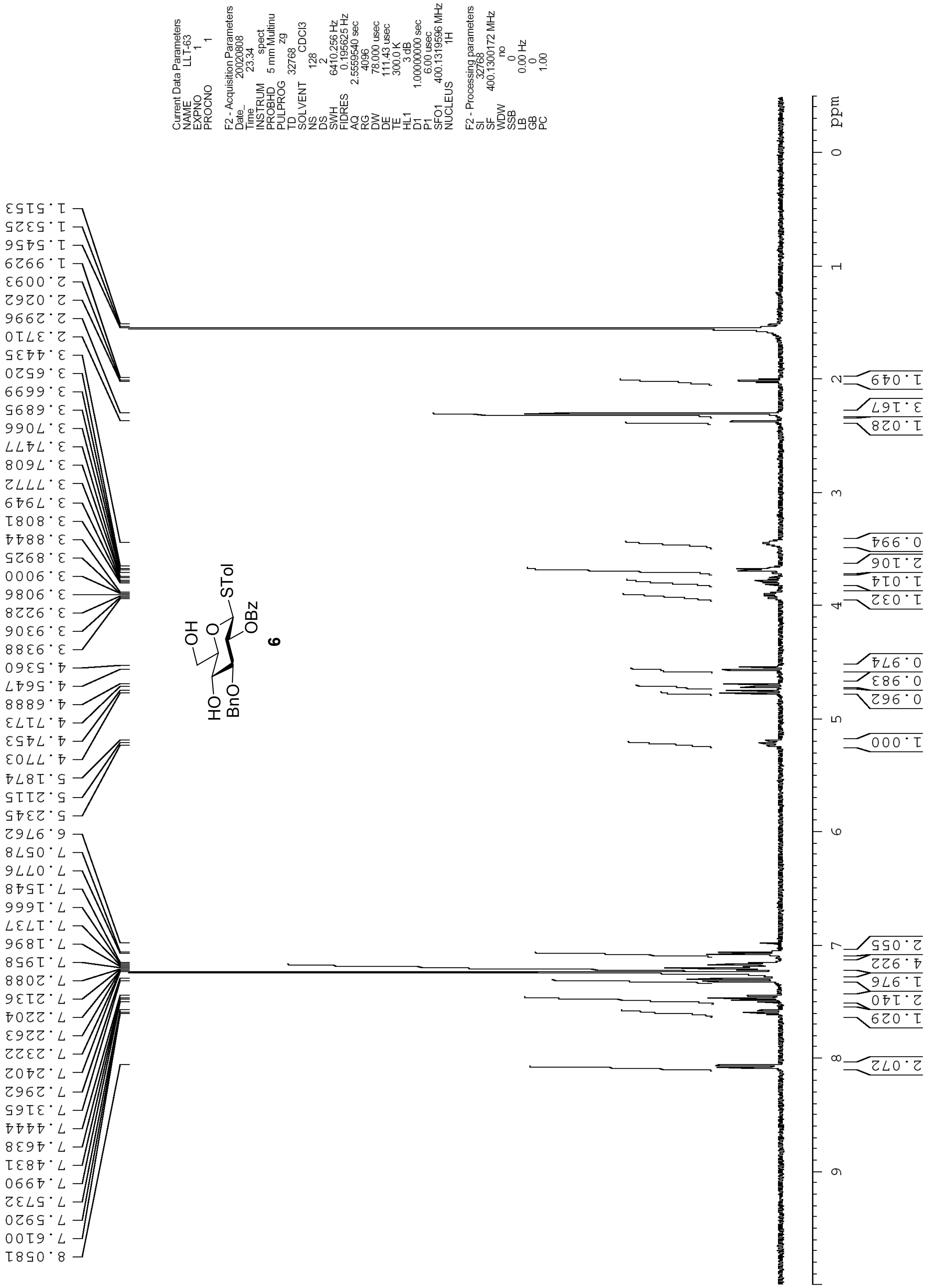
```
Current Data Parameters
NAME             TYH-380
EXPNO                  2
PROCNO                 1

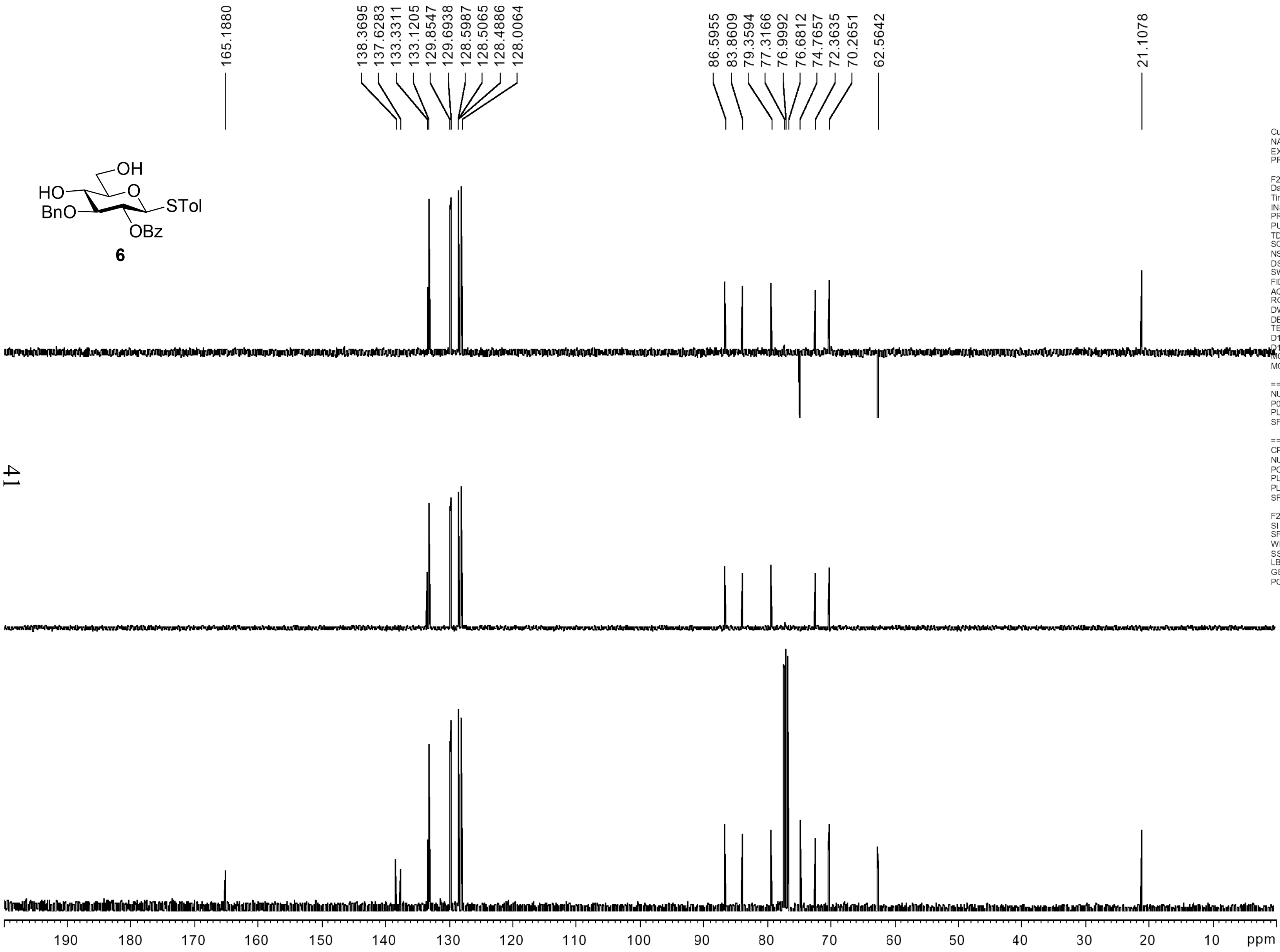
F2 - Acquisition Parameters
Date_           20080814
Time                2.07
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   150
DS                     0
SWH          22727.273 Hz
FIDRES        0.346791 Hz
AQ           1.4418420 sec
RG                    57
DW              22.000 usec
DE                6.00 usec
TE               300.0 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1         100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2         400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF           100.6178017 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```


Current Data Parameters
NAME LLT-63
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20020808
Time 23.34
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 128
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 4096
DW 78.000 usec
DE 111.43 usec
TE 300.0 K
HL1 3 dB
D1 1.00000000 sec
P1 6.00 usec
SFO1 400.1319596 MHz
NUCLEUS 1H
F2 - Processing parameters
SI 32768
SF 400.1300172 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1.5153
1.5325
1.5456
1.9929
2.0093
2.0262
2.2996
2.3710
3.4435
3.6520
3.6699
3.6895
3.7066
3.7477
3.7608
3.7772
3.7949
3.8081
3.8844
3.8925
3.9000
3.9086
3.9228
3.9306
3.9388
4.5360
4.5647
4.6888
4.7173
4.7453
4.7703
5.1874
5.2115
5.2345
6.9762
7.0578
7.0776
7.1548
7.1666
7.1737
7.1896
7.1958
7.2088
7.2136
7.2204
7.2263
7.2322
7.2402
7.2962
7.3165
7.4444
7.4638
7.4831
7.4990
7.5732
7.5920
7.6100
8.0581
OH
O
STol
HO
BnO
OBz
6
1.049
3.167
1.028
0.994
2.106
1.014
1.032
0.974
0.983
0.962
1.000
2.055
4.922
1.976
2.140
1.029
2.072
ppm
0
1
2
3
4
5
6
7
8
9



6

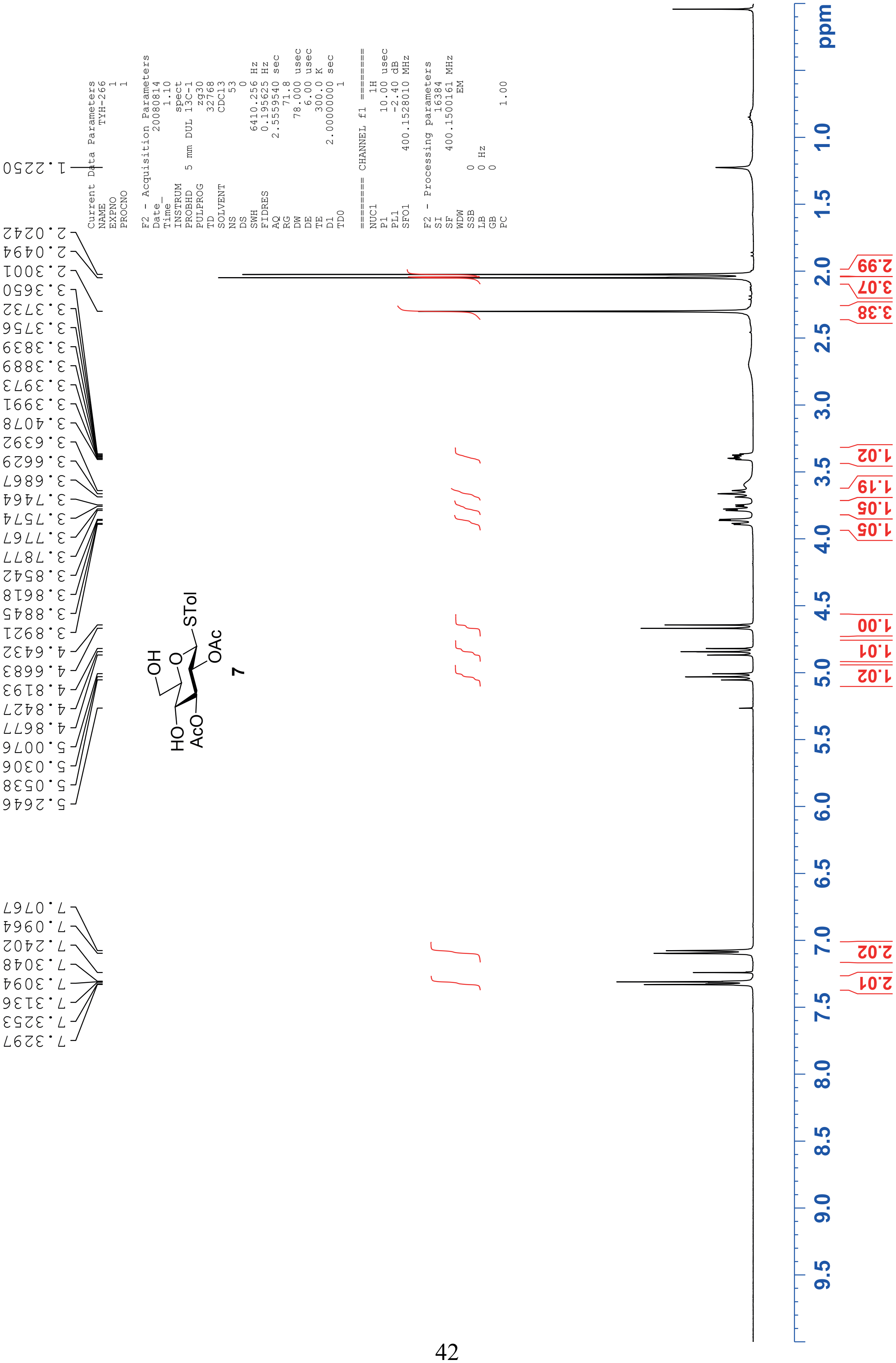
```
Current Data Parameters
NAME          LLT-265-P
EXPNO                 2
PROCNO                1

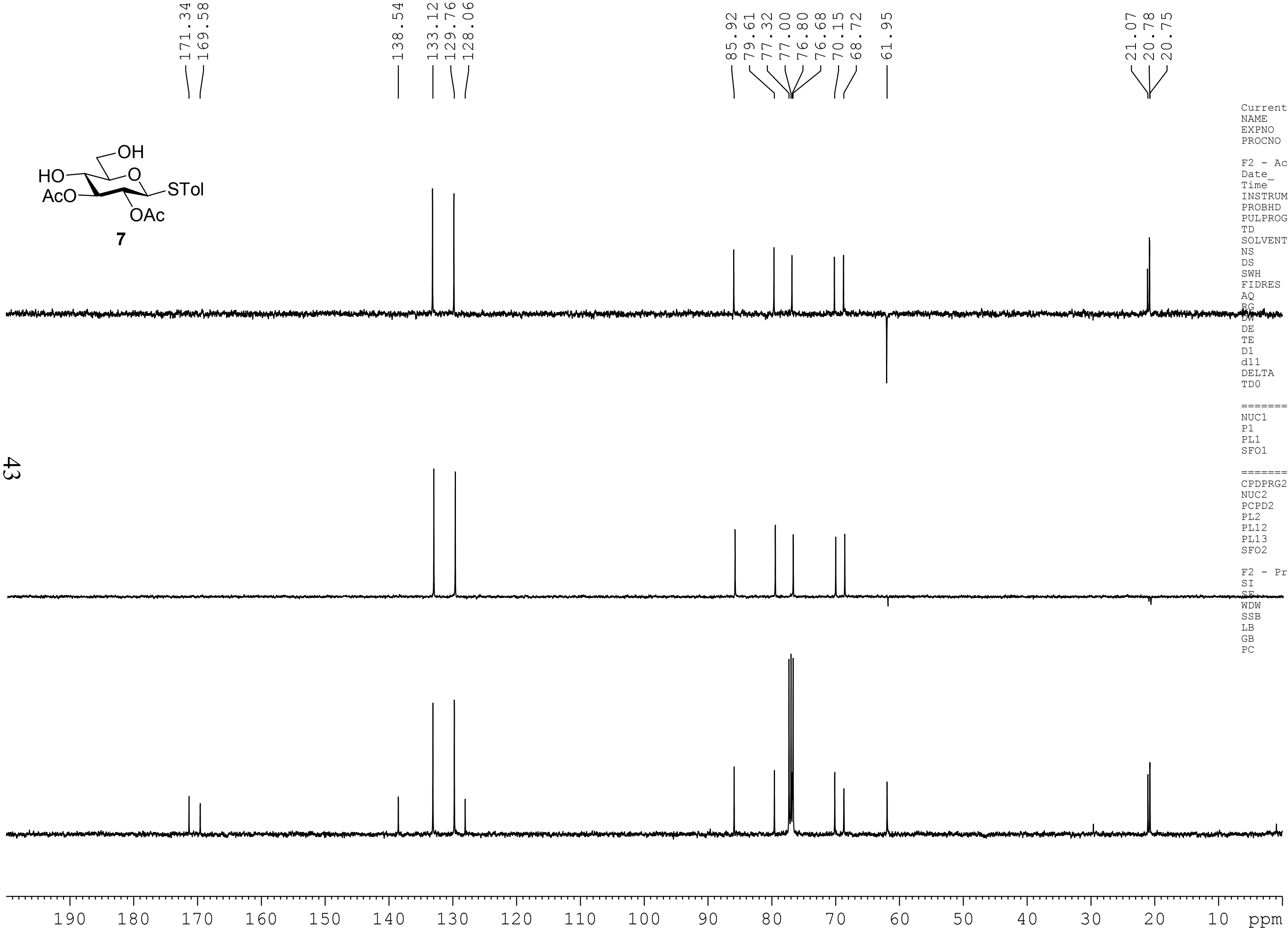
F2 - Acquisition Parameters
Date_          20040306
Time              20.57
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG           zg0dc
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH          23980.814 Hz
FIDRES        0.731836 Hz
AQ          0.6832628 sec
RG                645.1
DW             20.850 usec
DE               6.00 usec
TE              296.5 K
D1         3.00000000 sec
D11        0.03000000 sec
MCREST     0.00000000 sec
MCWRK      0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P0                 5.00 usec
PL1               -2.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             95.00 usec
PL2               -2.00 dB
PL12              16.50 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127737 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```


1.2250
2.0242
2.0494
2.3001
3.3650
3.3732
3.3756
3.3839
3.3889
3.3973
3.3991
3.4078
3.6392
3.6629
3.6867
3.7464
3.7574
3.7767
3.7877
3.8542
3.8618
3.8845
3.8921
4.6432
4.6683
4.8193
4.8427
4.8677
5.0076
5.0306
5.0538
5.2646
7.0767
7.0964
7.2402
7.3048
7.3094
7.3136
7.3253
7.3297
Current Data Parameters
NAME TYH-266
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080814
Time 1.10
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 53
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 71.8
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.40 dB
SFO1 400.1528010 MHz
F2 - Processing parameters
SI 16384
SF 400.1500161 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
HO
AcO
OH
O
STol
OAc
7
2.99
3.07
3.38
1.02
1.19
1.05
1.05
1.00
1.01
1.02
2.02
2.01
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5



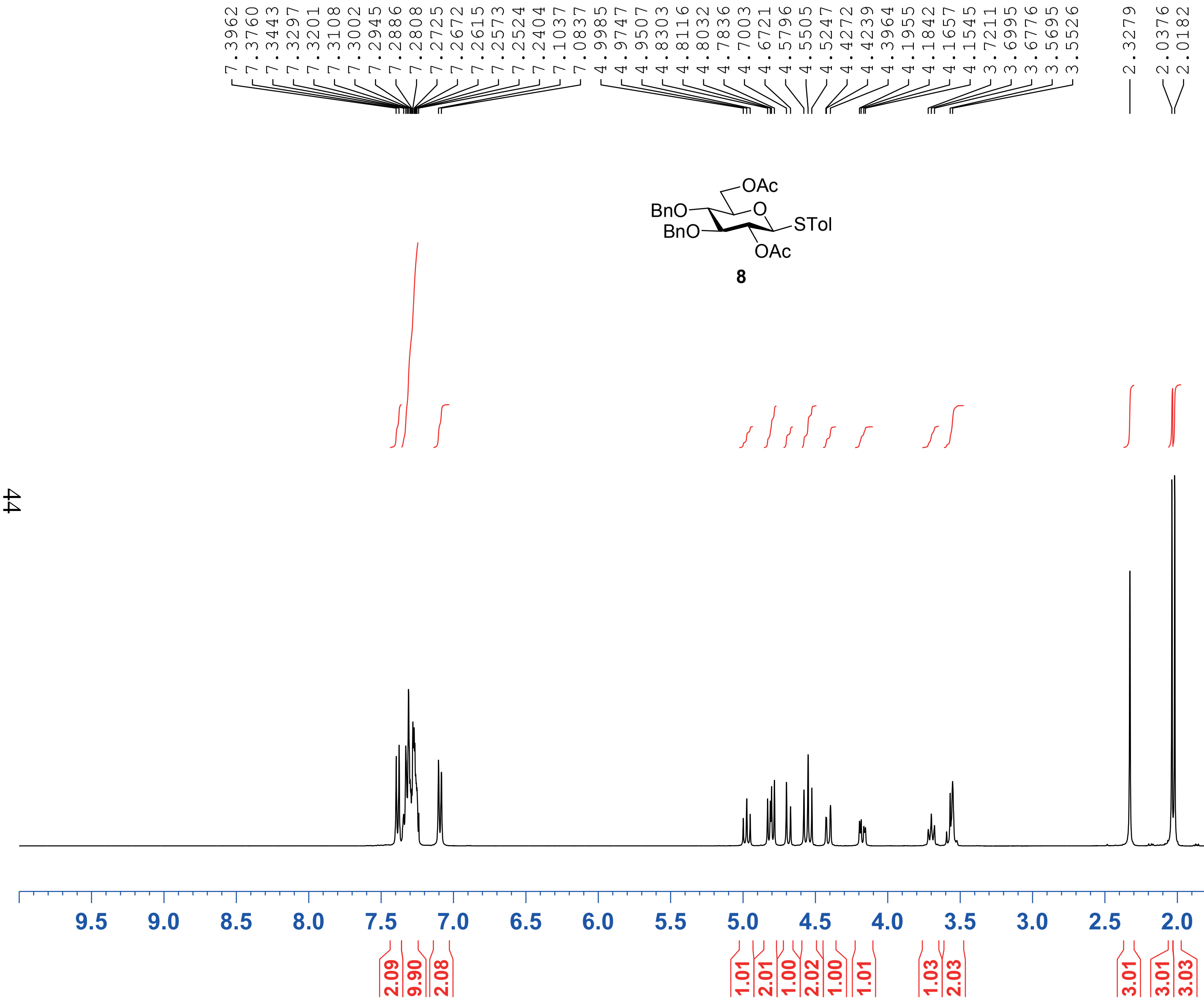
```
Current Data Parameters
NAME             TYH-266
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080814
Time                1.18
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     0
SWH           22727.273 Hz
FIDRES         0.346791 Hz
AQ            1.4418420 sec
RG                    57
DW               22.000 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1         100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2         400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF           100.6178040 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```

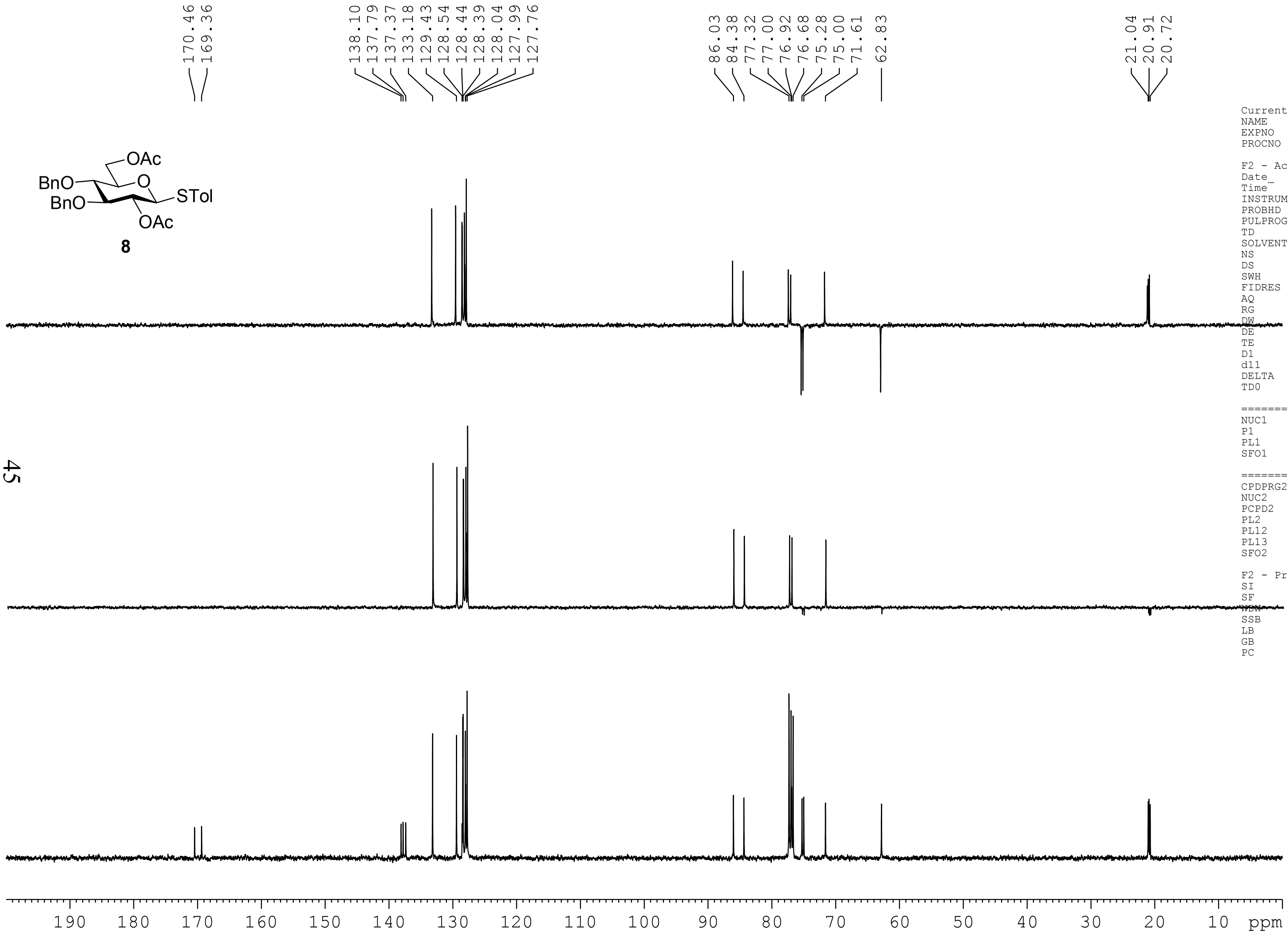


```
Current Data Parameters
NAME             TYH-291
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080814
Time                3.02
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    31
DS                     0
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                  50.8
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -2.40 dB
SFO1         400.1528010 MHz

F2 - Processing parameters
SI                 16384
SF           400.1500160 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



8

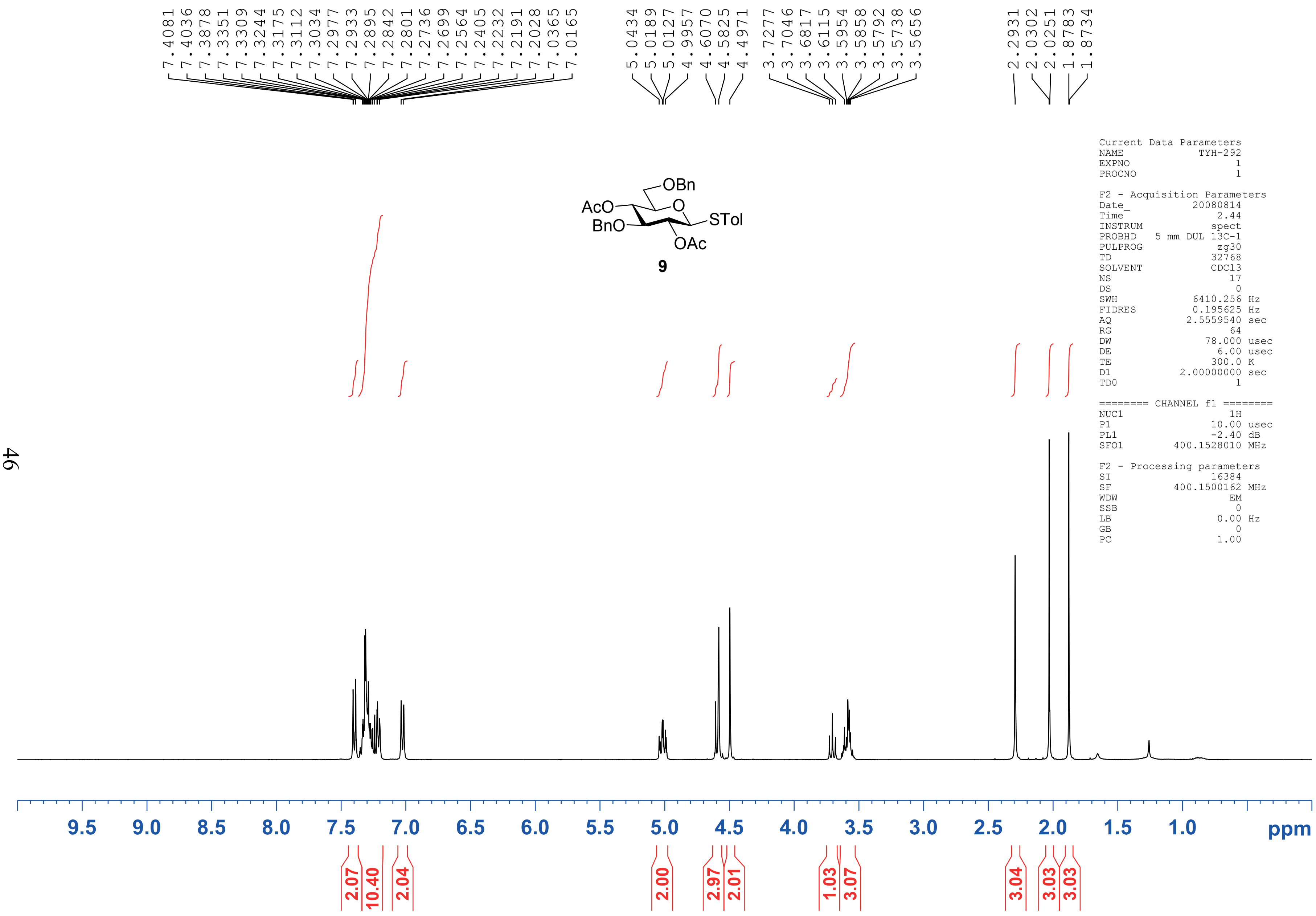
```
Current Data Parameters
NAME             TYH-291
EXPNO                  2
PROCNO                 1

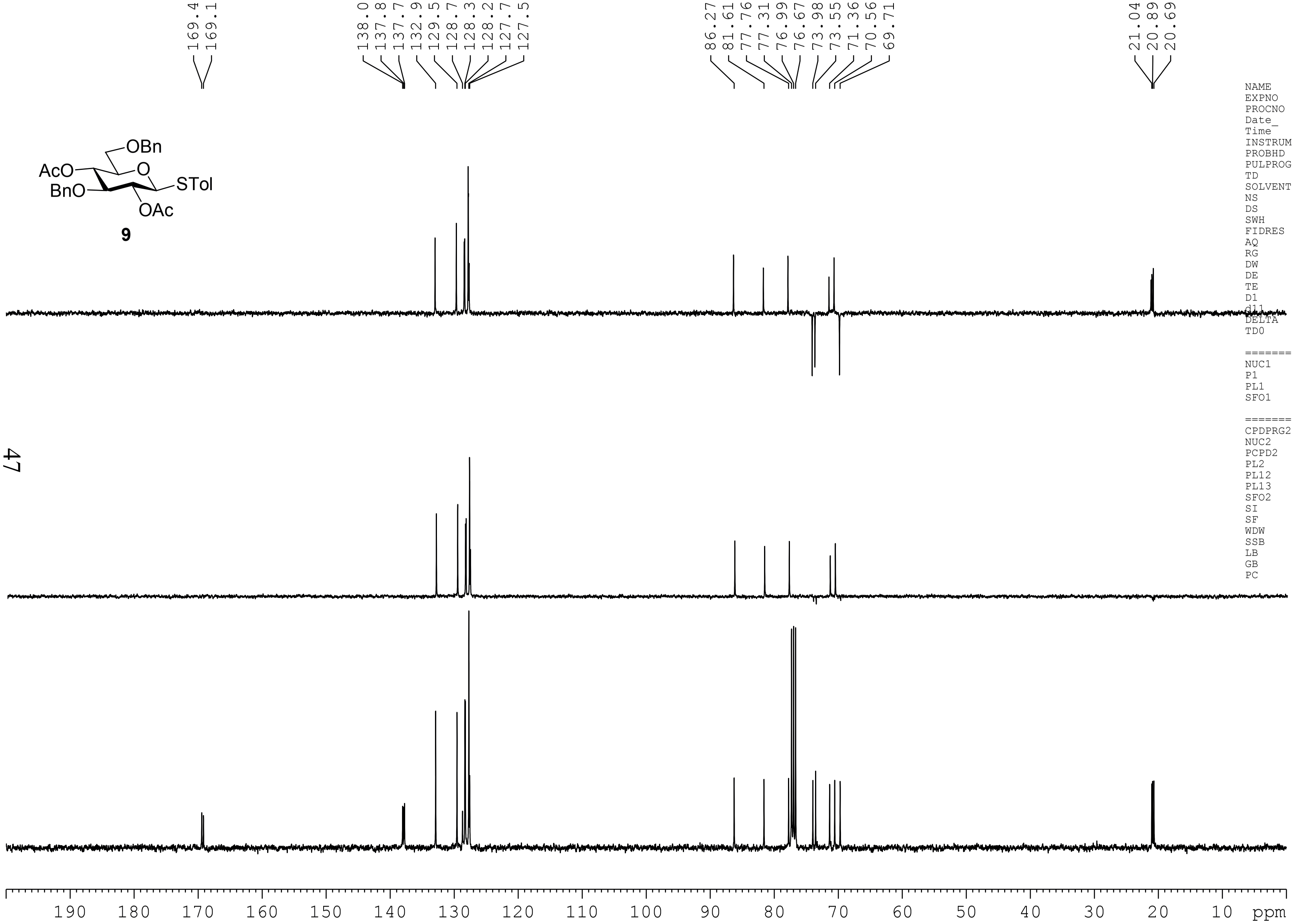
F2 - Acquisition Parameters
Date_           20080814
Time                3.07
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    94
DS                     0
SWH            22727.273 Hz
FIDRES          0.346791 Hz
AQ             1.4418420 sec
RG                    64
DW                22.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1         100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2         400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF           100.6178117 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```

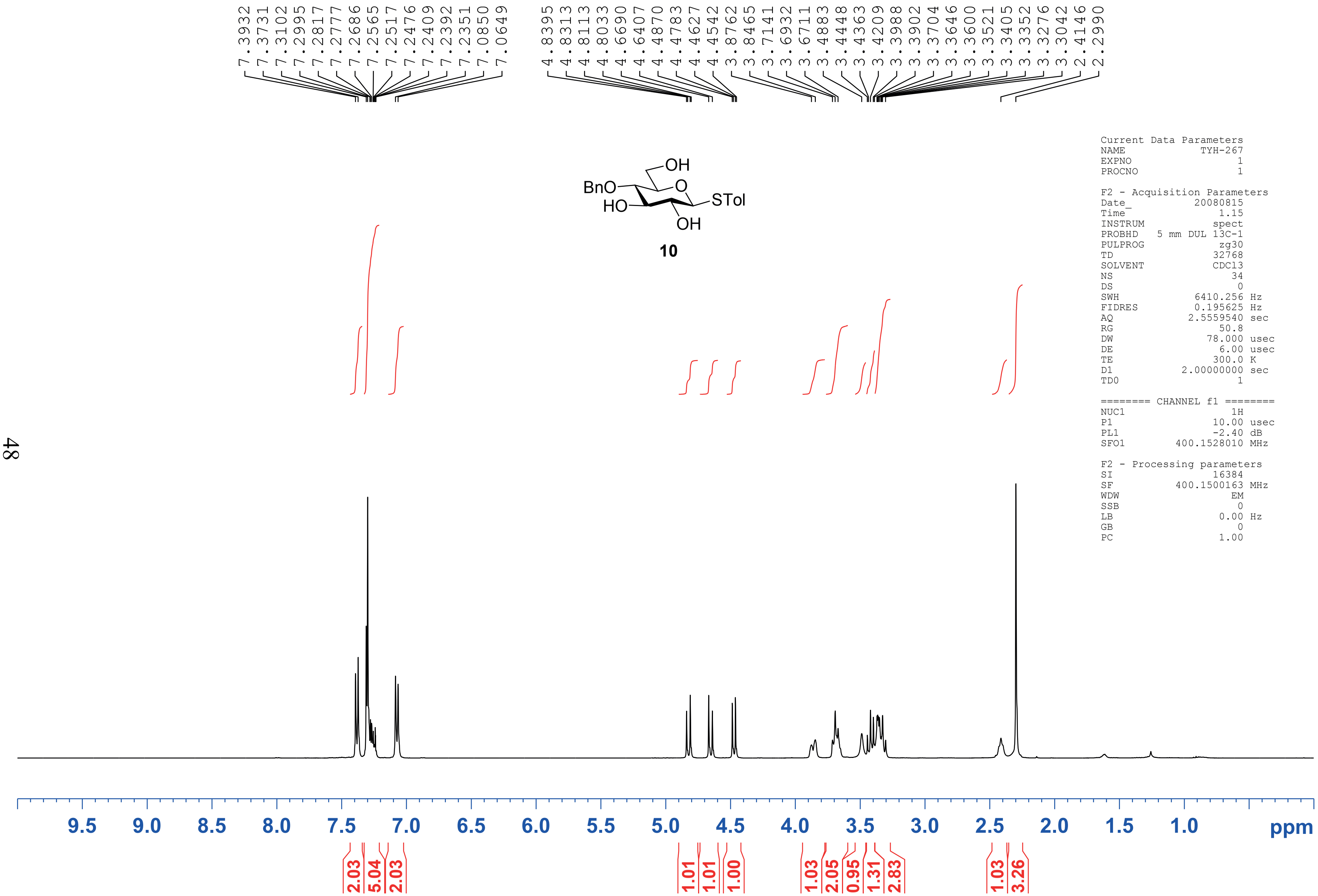

7.4081
7.4036
7.3878
7.3351
7.3309
7.3244
7.3175
7.3112
7.3034
7.2977
7.2933
7.2895
7.2842
7.2801
7.2736
7.2699
7.2564
7.2405
7.2232
7.2191
7.2028
7.0365
7.0165
5.0434
5.0189
5.0127
4.9957
4.6070
4.5825
4.4971
3.7277
3.7046
3.6817
3.6115
3.5954
3.5858
3.5792
3.5738
3.5656
2.2931
2.0302
2.0251
1.8783
1.8734
OBn
AcO
BnO
O
STol
OAc
9
Current Data Parameters
NAME TYH-292
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080814
Time 2.44
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 17
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 64
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.40 dB
SFO1 400.1528010 MHz
F2 - Processing parameters
SI 16384
SF 400.1500162 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.07
10.40
2.04
2.00
2.97
2.01
1.03
3.07
3.04
3.03
3.03



```
NAME             TYH-292
EXPNO                  2
PROCNO                 1
Date_           20080814
Time                2.48
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   89
DS                    0
SWH           22727.273 Hz
FIDRES         0.346791 Hz
AQ            1.4418420 sec
RG                   64
DW               22.000 usec
DE                 6.00 usec
TE                300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1         100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2         400.1516010 MHz
SI                 32768
SF           100.6178082 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```



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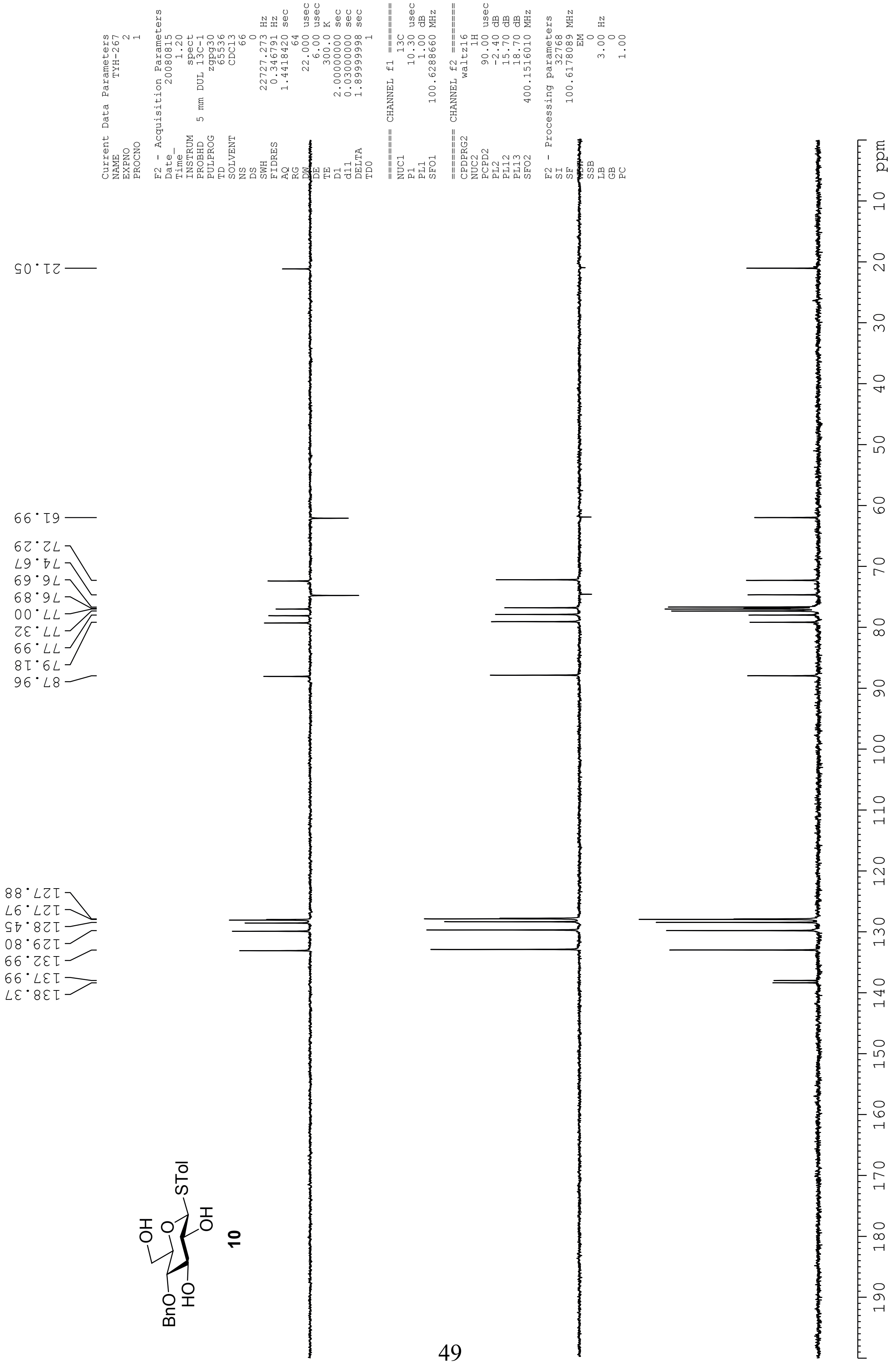
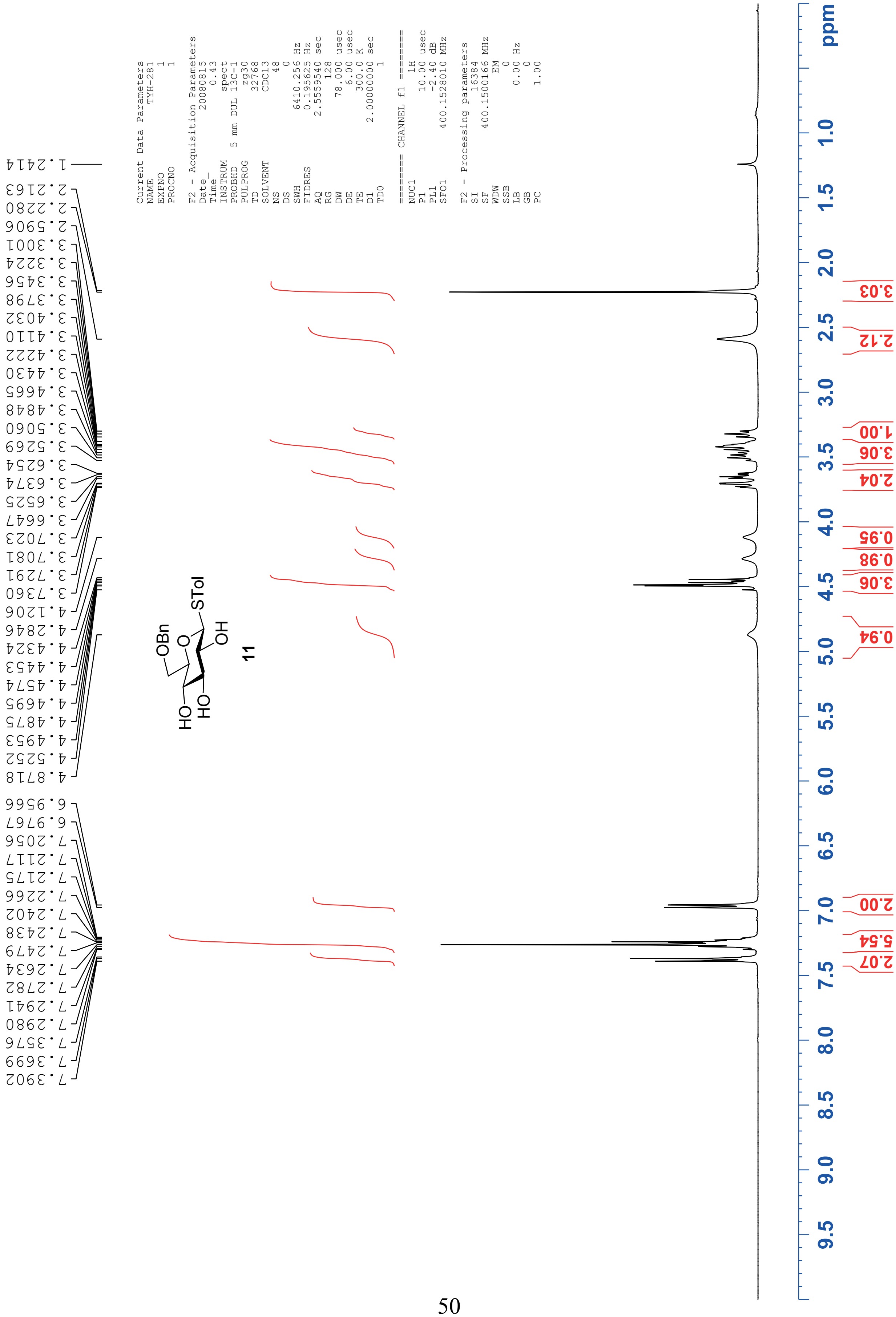
```
Current Data Parameters
NAME              TYH-267
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080815
Time                 1.15
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     34
DS                      0
SWH              6410.256 Hz
FIDRES           0.195625 Hz
AQ              2.5559540 sec
RG                   50.8
DW                 78.000 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                 -2.40 dB
SFO1          400.1528010 MHz

F2 - Processing parameters
SI                  16384
SF            400.1500163 MHz
WDW                    EM
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```


Current Data Parameters
NAME TYH-267
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080815
Time 1.20
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 66
DS 0
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 64
DW 22.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 1.00 dB
SFO1 100.6288660 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.40 dB
PL12 15.70 dB
PL13 18.70 dB
SFO2 400.1516010 MHz
F2 - Processing parameters
SI 32768
SF 100.6178089 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
21.05
61.99
72.29
74.67
76.69
76.89
77.00
77.32
77.99
79.18
87.96
127.88
127.97
128.45
129.80
132.99
137.99
138.37
BnO
HO
OH
O
OH
STol
10
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


1.2414
2.2163
2.2280
2.5906
3.3001
3.3224
3.3456
3.3798
3.4032
3.4110
3.4222
3.4430
3.4665
3.4848
3.5060
3.5269
3.6254
3.6374
3.6525
3.6647
3.7023
3.7081
3.7291
3.7360
4.1206
4.2846
4.4324
4.4453
4.4574
4.4695
4.4875
4.4953
4.5252
4.8718
6.9566
6.9767
7.2056
7.2117
7.2175
7.2266
7.2402
7.2438
7.2479
7.2634
7.2782
7.2941
7.2980
7.3576
7.3699
7.3902
Current Data Parameters
NAME TYH-281
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080815
Time 0.43
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 48
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 128
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.40 dB
SFO1 400.1528010 MHz
F2 - Processing parameters
SI 16384
SF 400.1500166 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
OBn
O
STol
HO
HO
OH
11
3.03
2.12
1.00
3.06
2.04
0.95
0.98
3.06
0.94
2.00
5.54
2.07
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
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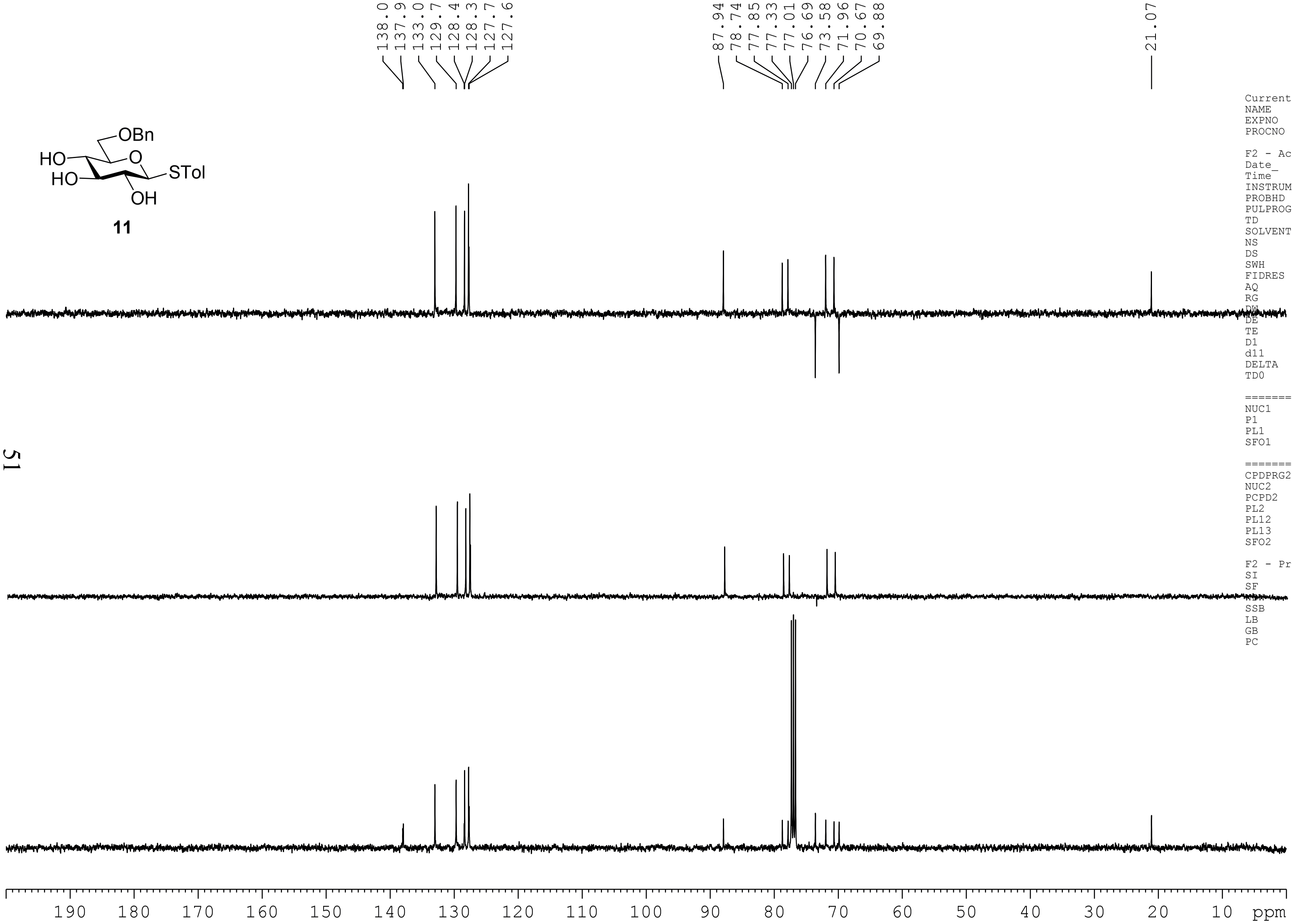
8.0
8.5
9.0
9.5



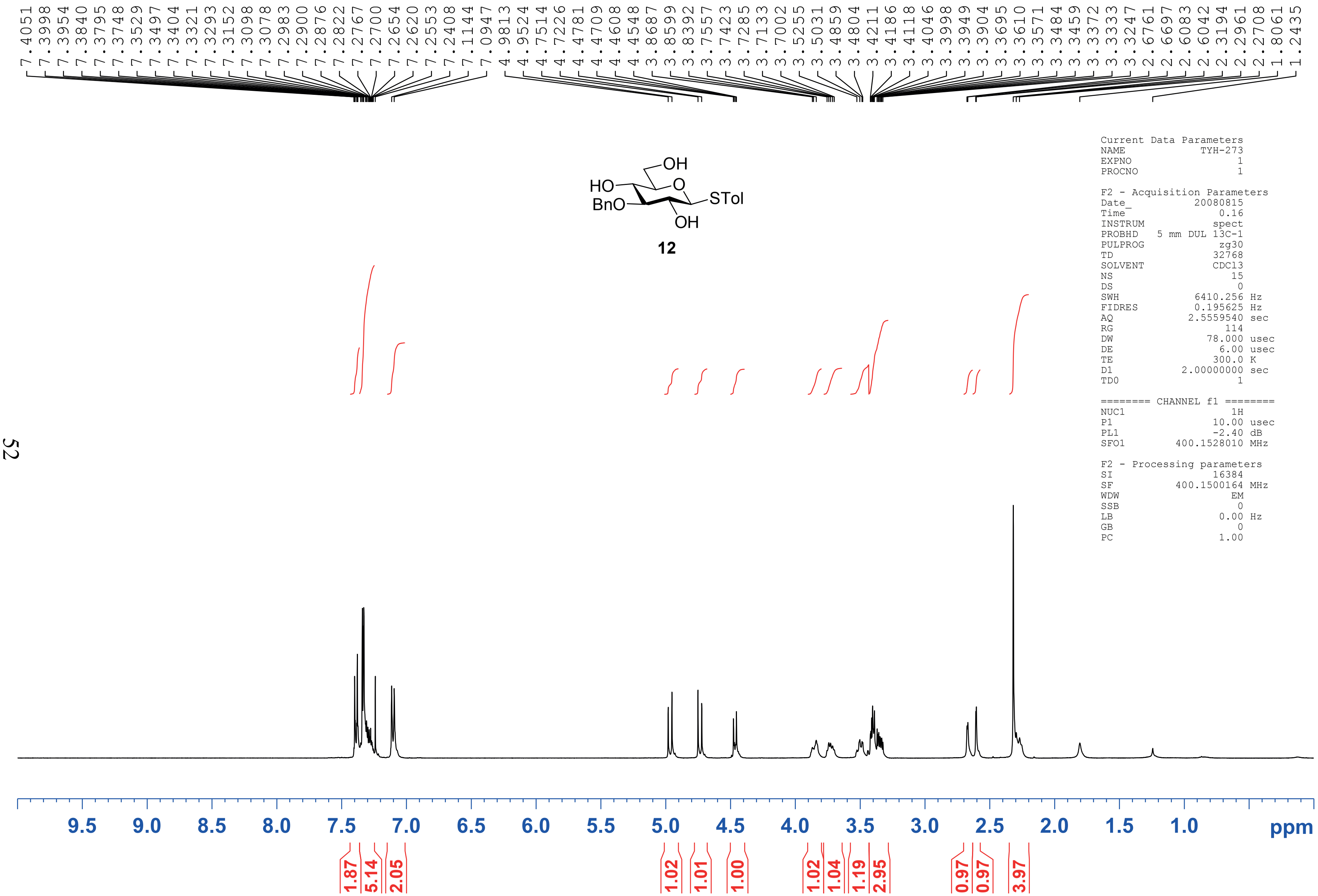
```
Current Data Parameters
NAME              TYH-281
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080815
Time                 0.57
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    100
DS                      0
SWH            22727.273 Hz
FIDRES          0.346791 Hz
AQ             1.4418420 sec
RG                     57
DW                 22.000 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.30 usec
PL1                  1.00 dB
SFO1          100.6288660 MHz

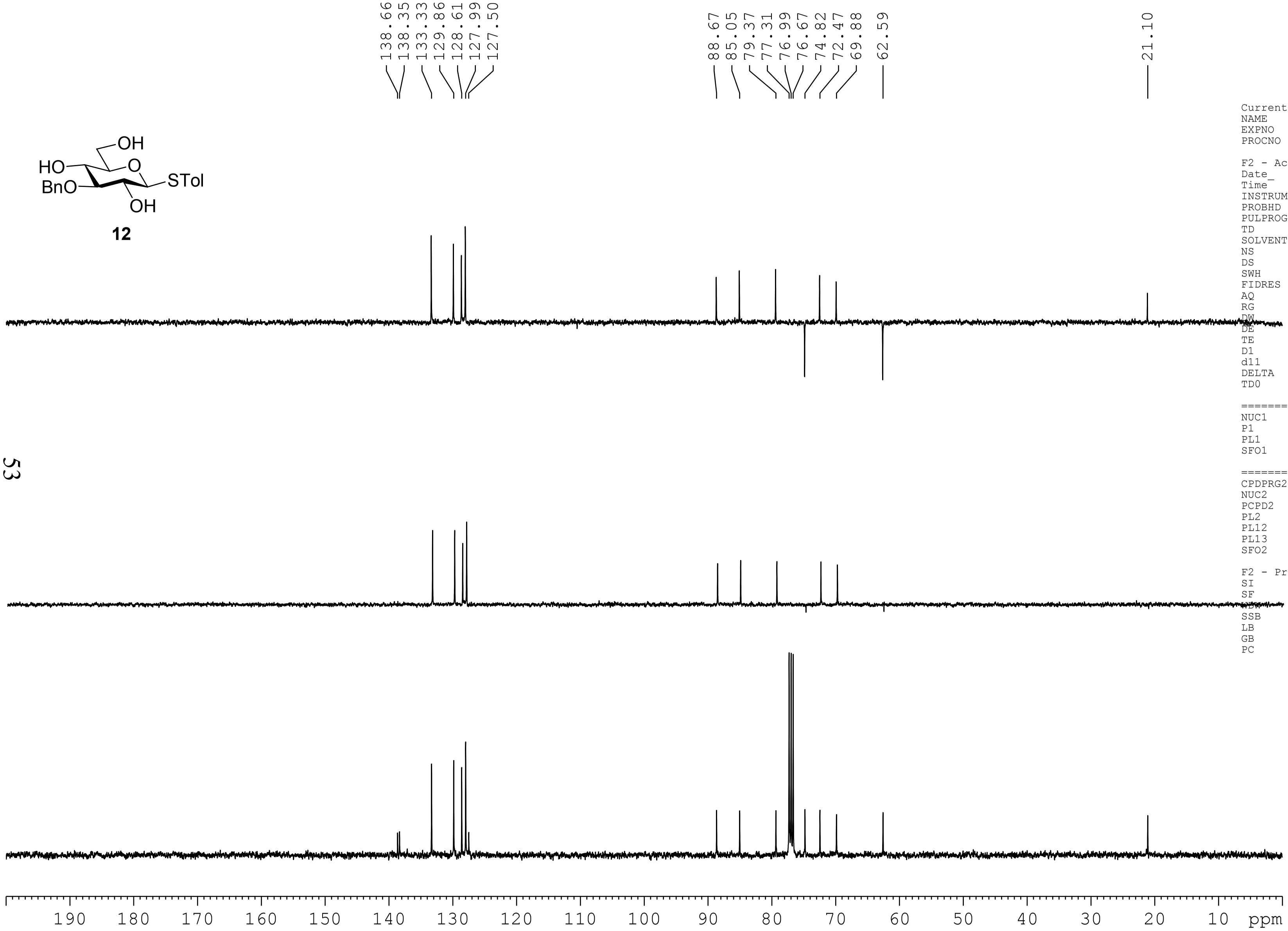
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -2.40 dB
PL12                15.70 dB
PL13                18.70 dB
SFO2          400.1516010 MHz

F2 - Processing parameters
SI                  32768
SF            100.6178001 MHz
WDW                    EM
SSB                     0
LB                   3.00 Hz
GB                      0
PC                   1.00
```


7.4051
7.3998
7.3954
7.3840
7.3795
7.3748
7.3529
7.3497
7.3404
7.3321
7.3293
7.3152
7.3098
7.3078
7.2983
7.2900
7.2876
7.2822
7.2767
7.2700
7.2654
7.2620
7.2553
7.2408
7.1144
7.0947
4.9813
4.9524
4.7514
4.7226
4.4781
4.4709
4.4608
4.4548
3.8687
3.8599
3.8392
3.7557
3.7423
3.7285
3.7133
3.7002
3.5255
3.5031
3.4859
3.4804
3.4211
3.4186
3.4118
3.4046
3.3998
3.3949
3.3904
3.3695
3.3610
3.3571
3.3484
3.3459
3.3372
3.3333
3.3247
2.6761
2.6697
2.6083
2.6042
2.3194
2.2961
2.2708
1.8061
1.2435
Current Data Parameters
NAME TYH-273
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080815
Time 0.16
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 15
DS 0
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 114
DW 78.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -2.40 dB
SFO1 400.1528010 MHz
F2 - Processing parameters
SI 16384
SF 400.1500164 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
HO
BnO
OH
O
STol
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.87
5.14
2.05
1.02
1.01
1.00
1.02
1.04
1.19
2.95
0.97
0.97
3.97

12

12



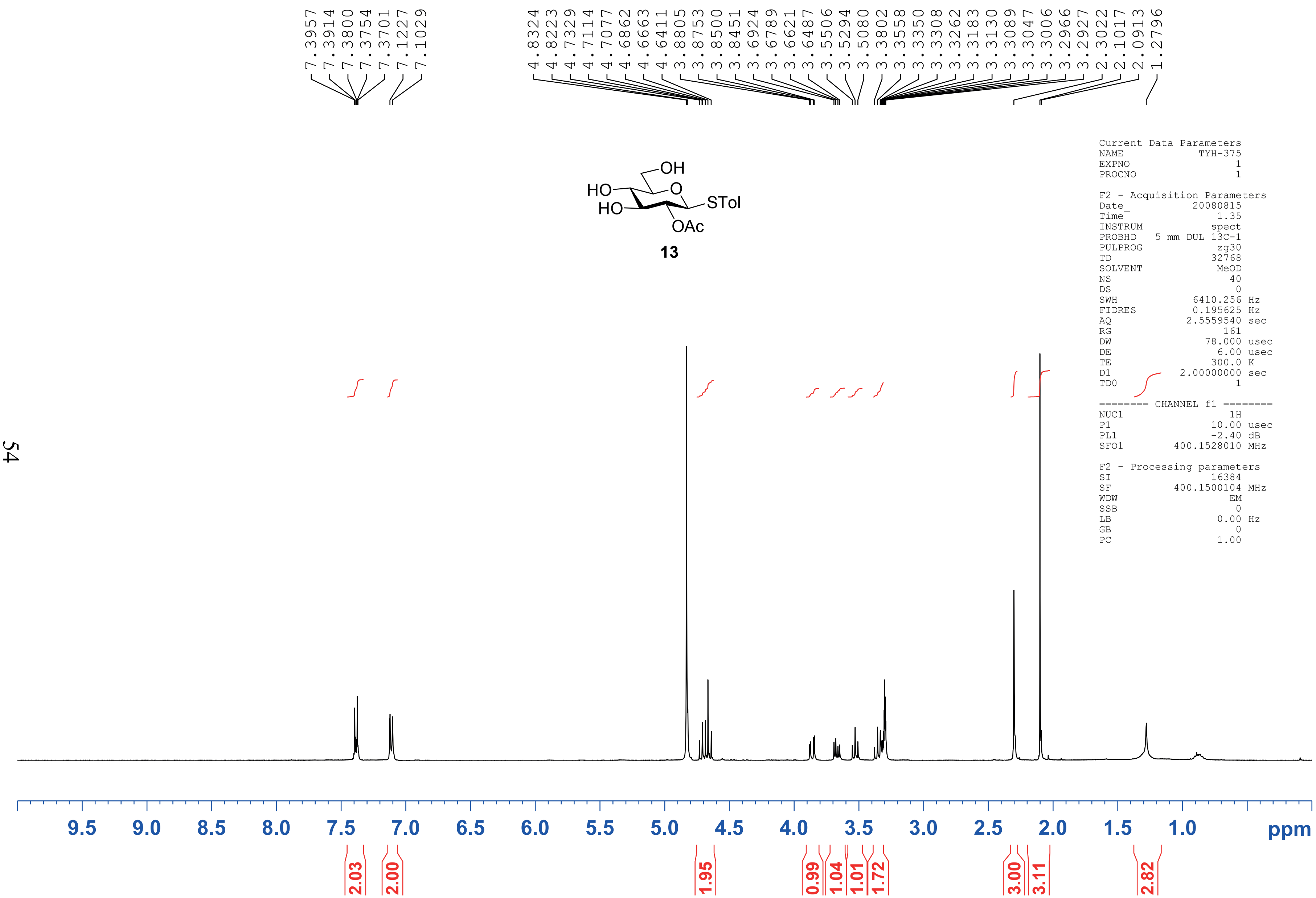
```
Current Data Parameters
NAME             TYH-273
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080815
Time                0.21
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   100
DS                     0
SWH          22727.273 Hz
FIDRES        0.346791 Hz
AQ           1.4418420 sec
RG                  50.8
DW                22.000 usec
DE                  6.00 usec
TE                 300.0 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1       100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2       400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF         100.6178035 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```

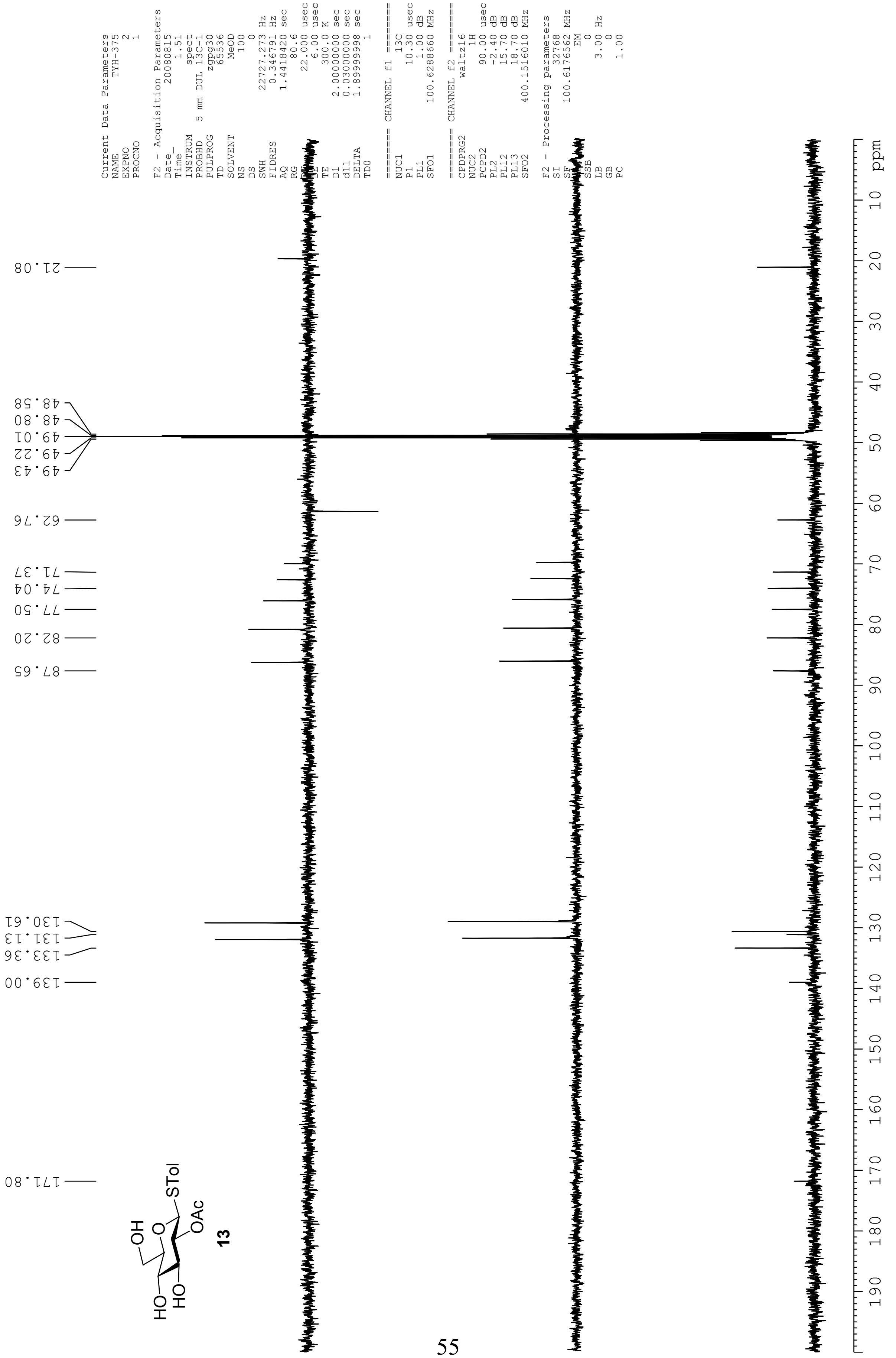


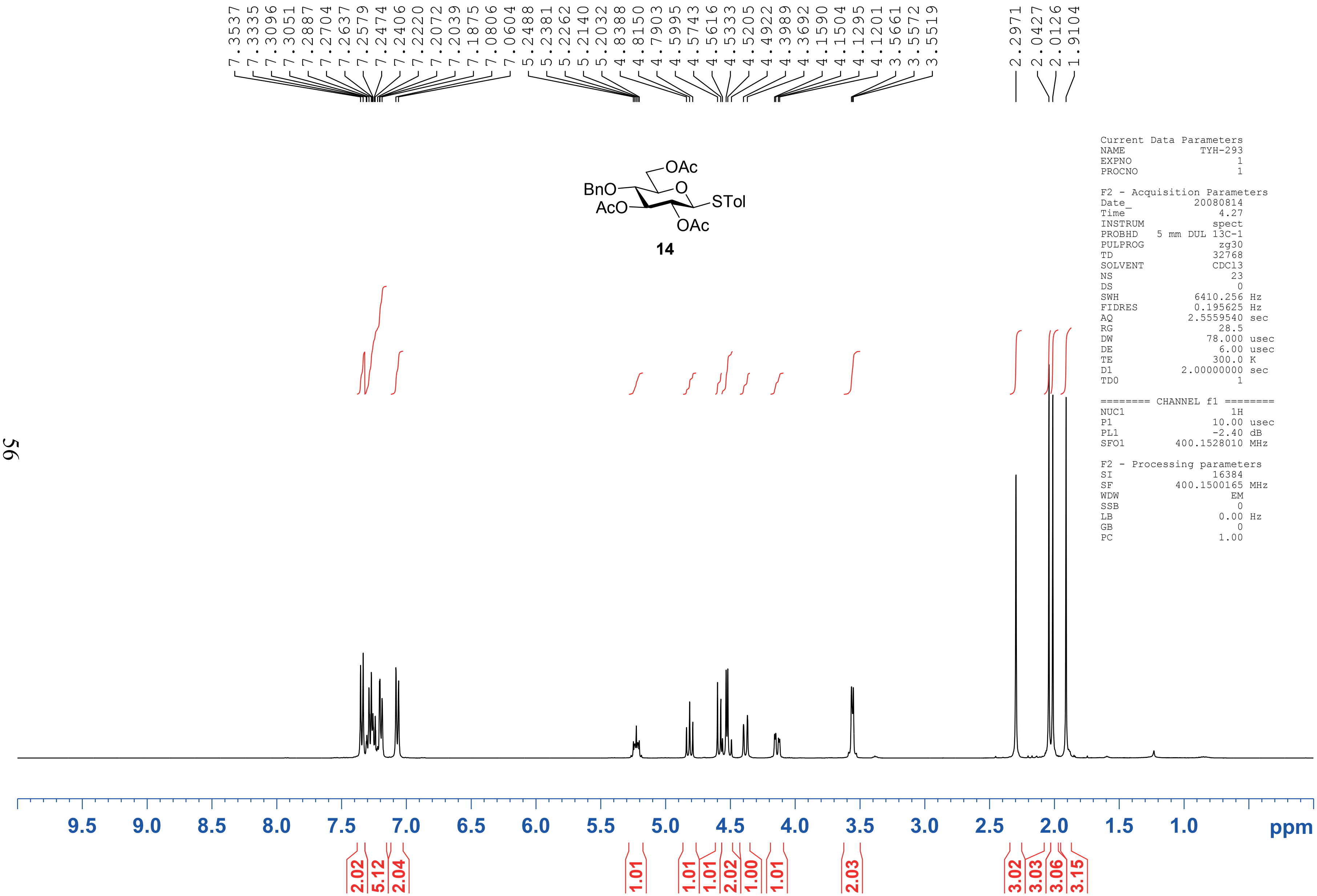
```
Current Data Parameters
NAME             TYH-375
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080815
Time                1.35
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT             MeOD
NS                    40
DS                     0
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                   161
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -2.40 dB
SFO1         400.1528010 MHz

F2 - Processing parameters
SI                 16384
SF           400.1500104 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```


Current Data Parameters
NAME TYH-375
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080815
Time 1.51
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 100
DS 0
SWH 22727.273 Hz
FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 80.6
DW 22.000 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
PL1 1.00 dB
SFO1 100.6288660 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.40 dB
PL12 15.70 dB
PL13 18.70 dB
SFO2 400.1516010 MHz
F2 - Processing parameters
SI 32768
SF 100.6176562 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00
21.08
48.58
48.80
49.01
49.22
49.43
62.76
71.37
74.04
77.50
82.20
87.65
130.61
131.13
133.36
139.00
171.80
HO
HO
OH
O
OAc
STol
13
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

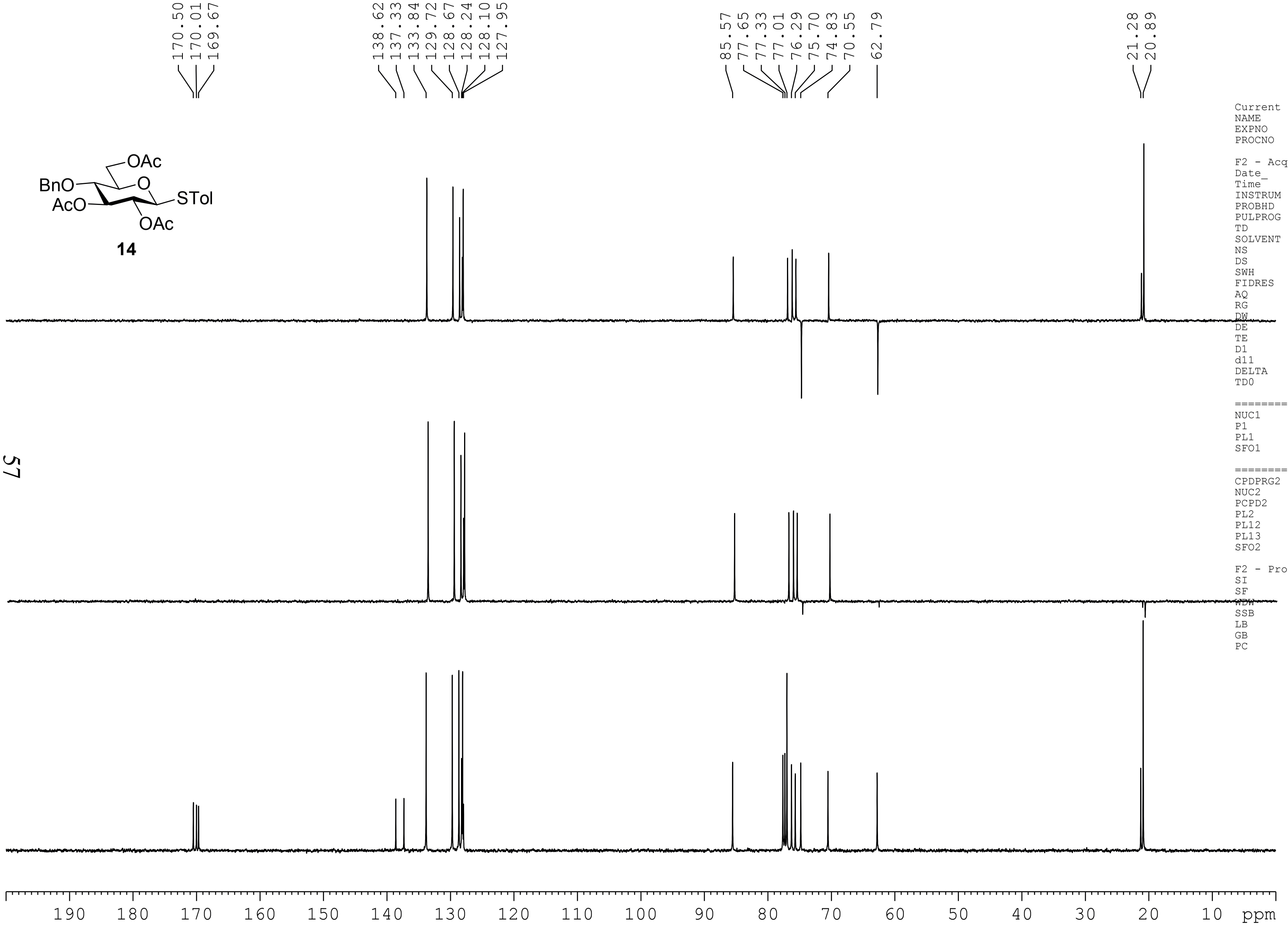


```
Current Data Parameters
NAME             TYH-293
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080814
Time                4.27
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    23
DS                     0
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                  28.5
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -2.40 dB
SFO1         400.1528010 MHz

F2 - Processing parameters
SI                 16384
SF           400.1500165 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



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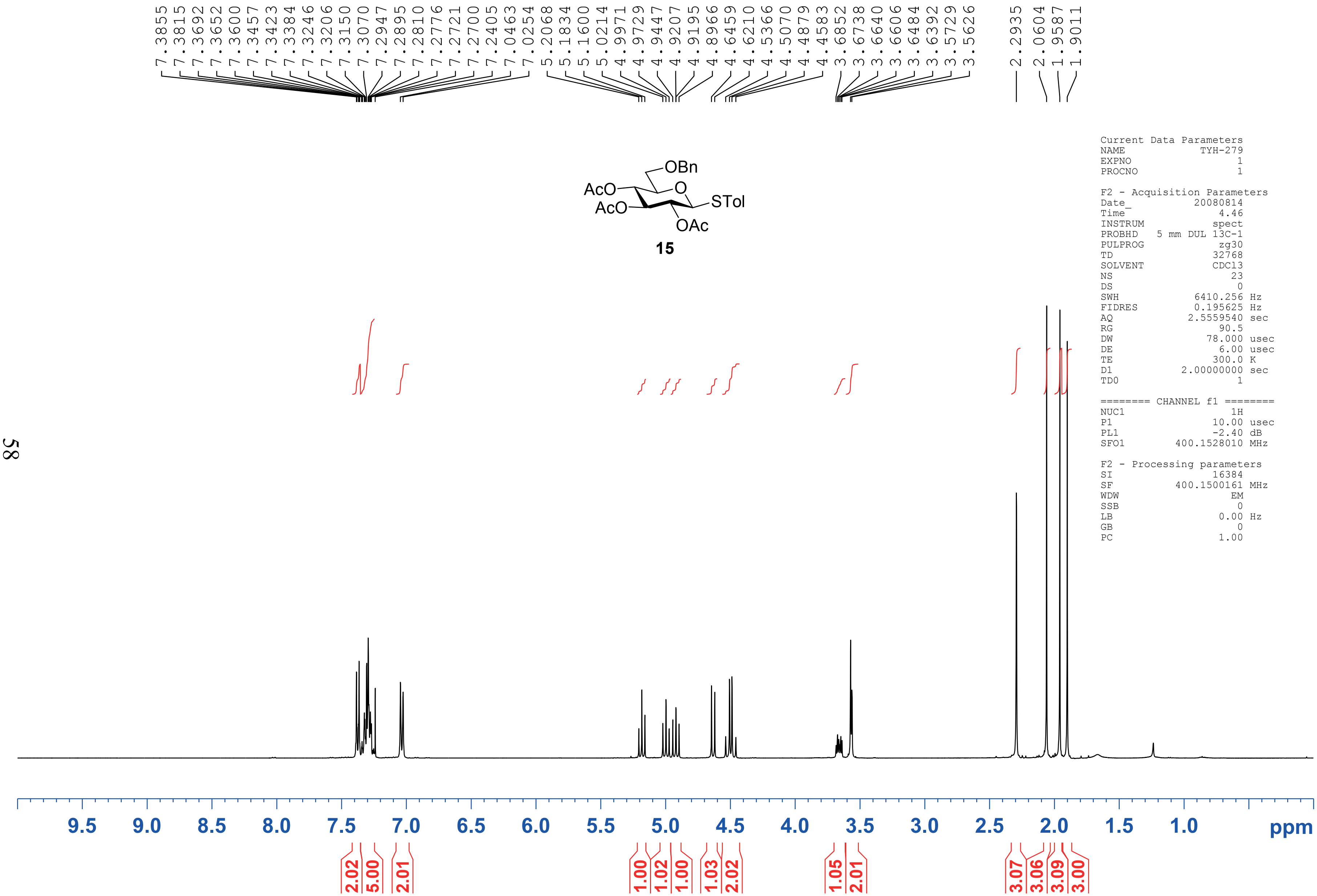
```
Current Data Parameters
NAME             TYH-293
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080814
Time                4.33
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    82
DS                     0
SWH            22727.273 Hz
FIDRES          0.346791 Hz
AQ             1.4418420 sec
RG                  71.8
DW                22.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1         100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2         400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF           100.6177875 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```



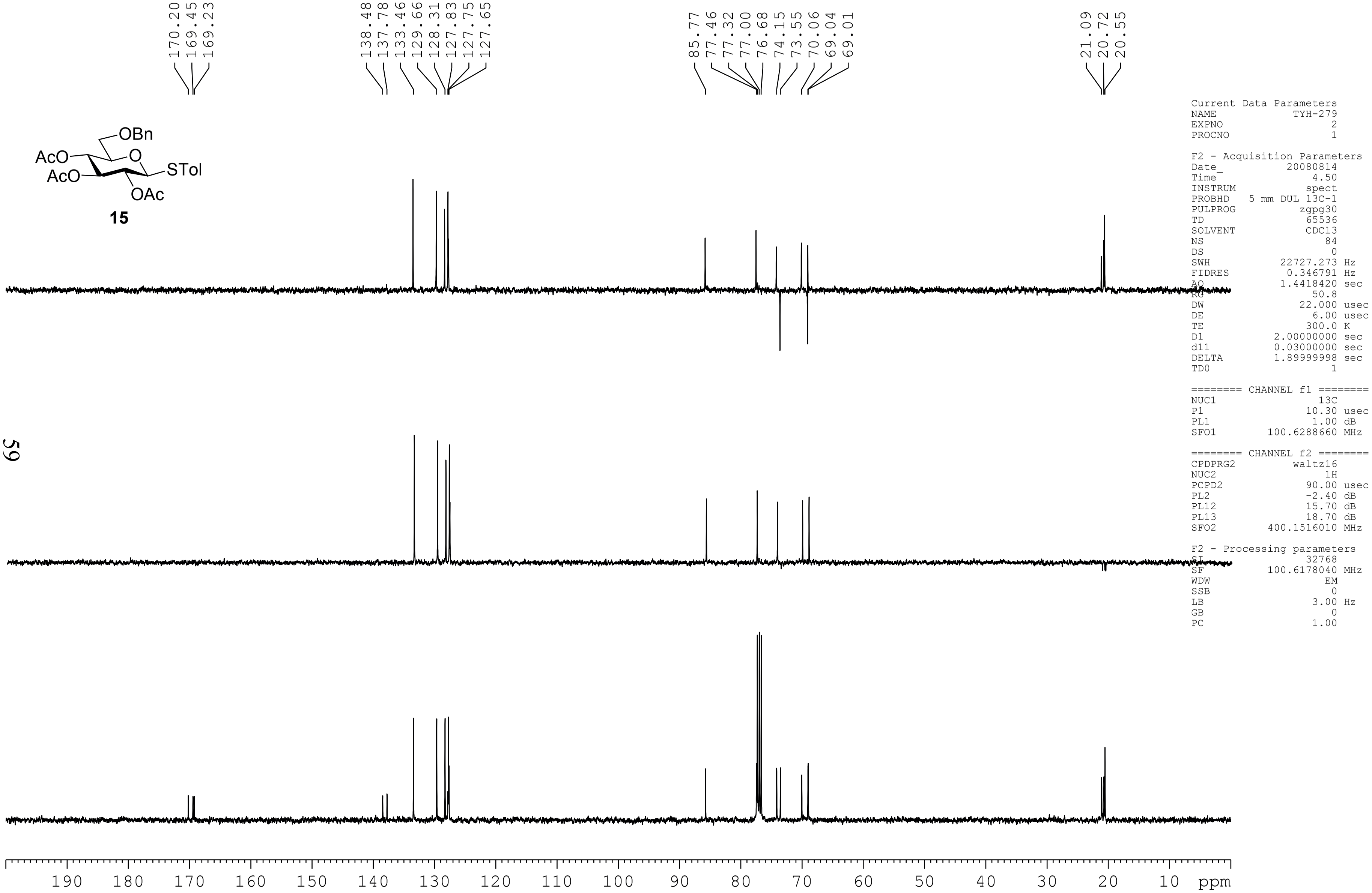
15

```
Current Data Parameters
NAME             TYH-279
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080814
Time                4.46
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    23
DS                     0
SWH             6410.256 Hz
FIDRES          0.195625 Hz
AQ             2.5559540 sec
RG                  90.5
DW                78.000 usec
DE                  6.00 usec
TE                 300.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -2.40 dB
SFO1         400.1528010 MHz

F2 - Processing parameters
SI                 16384
SF           400.1500161 MHz
WDW                   EM
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



15

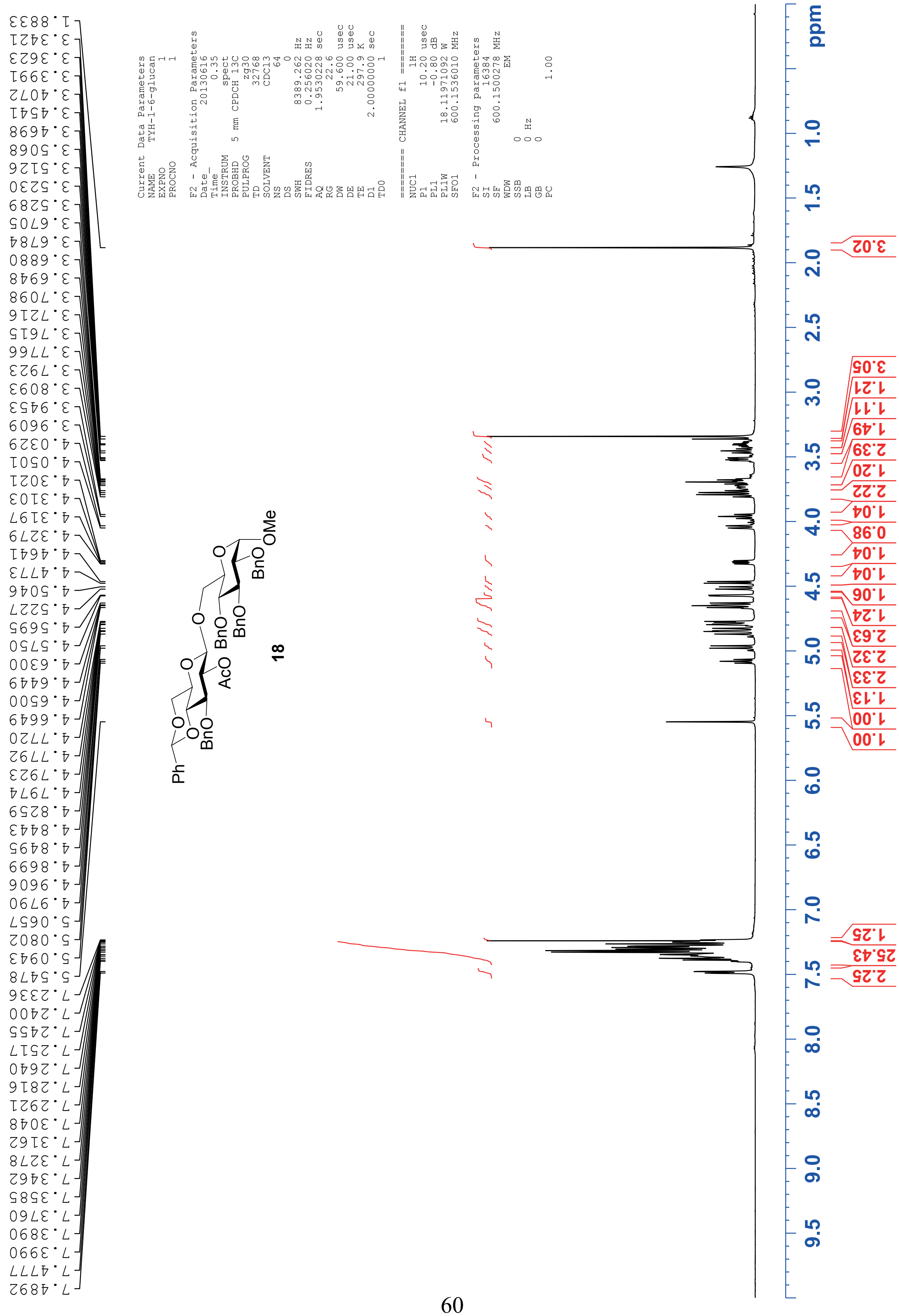
```
Current Data Parameters
NAME              TYH-279
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080814
Time                 4.50
INSTRUM             spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    84
DS                     0
SWH           22727.273 Hz
FIDRES         0.346791 Hz
AQ            1.4418420 sec
RG                  50.8
DW                22.000 usec
DE                  6.00 usec
TE                 300.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
PL1                 1.00 dB
SFO1        100.6288660 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -2.40 dB
PL12               15.70 dB
PL13               18.70 dB
SFO2        400.1516010 MHz

F2 - Processing parameters
SI                 32768
SF          100.6178040 MHz
WDW                   EM
SSB                    0
LB                  3.00 Hz
GB                     0
PC                  1.00
```


Current Data Parameters
NAME TYH-1-6-glucan
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130616
Time 0.35
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 8389.262 Hz
FIDRES 0.256020 Hz
AQ 1.9530228 sec
RG 22.6
DW 59.600 usec
DE 21.00 usec
TE 297.9 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 -0.80 dB
PL1W 18.11971092 W
SFO1 600.1536010 MHz
F2 - Processing parameters
SI 16384
SF 600.1500278 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
1.8833
3.3421
3.3623
3.3991
3.4072
3.4541
3.4698
3.5068
3.5126
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3.5289
3.6705
3.6784
3.6880
3.6948
3.7098
3.7216
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3.9453
3.9609
4.0329
4.0501
4.3021
4.3103
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4.3279
4.4641
4.4773
4.5046
4.5227
4.5695
4.5750
4.6300
4.6449
4.6500
4.6649
4.7720
4.7792
4.7923
4.7974
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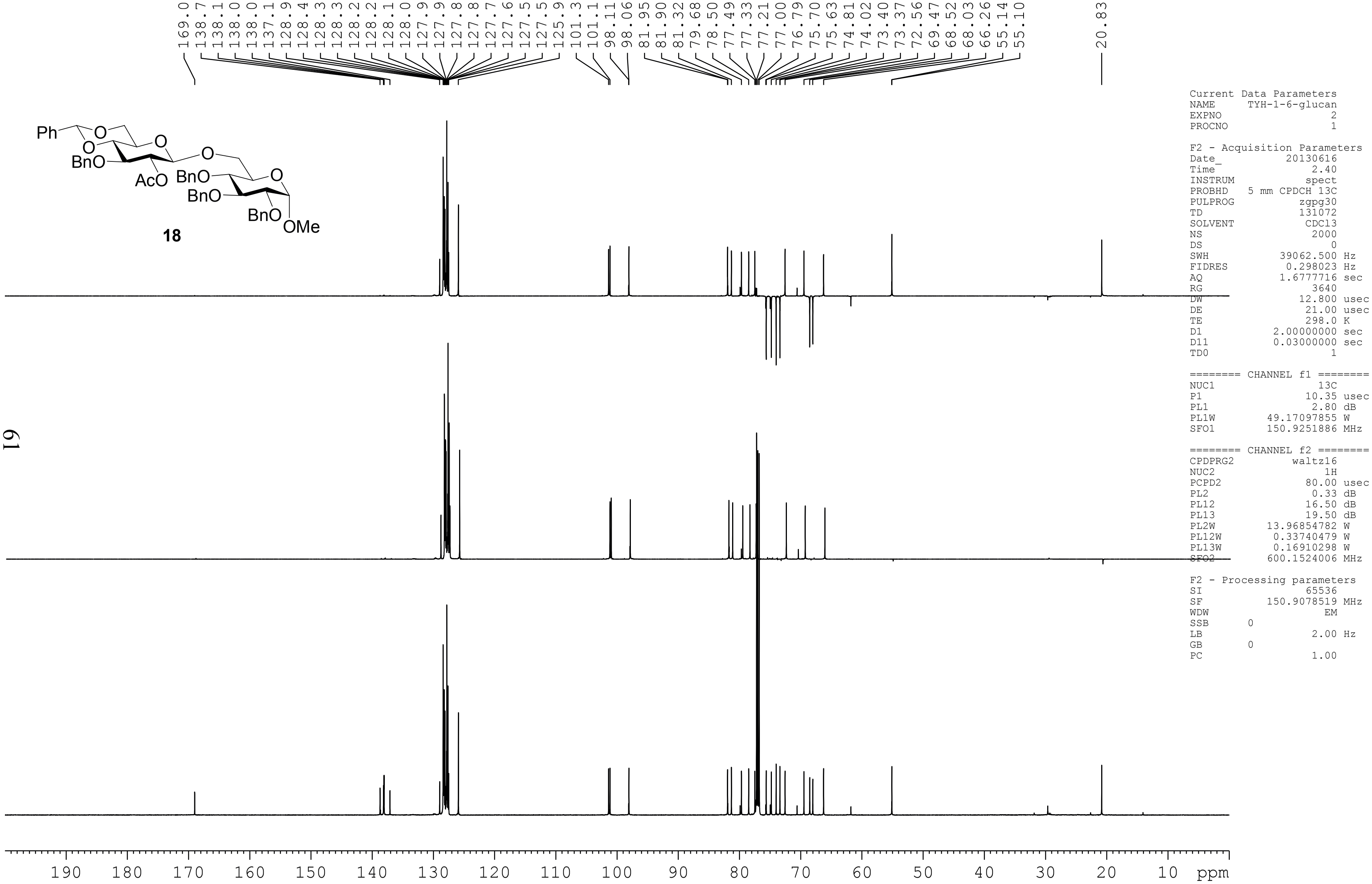
4.9790
5.0657
5.0802
5.0943
5.5478
7.2336
7.2400
7.2455
7.2517
7.2640
7.2816
7.2921
7.3048
7.3162
7.3278
7.3462
7.3585
7.3760
7.3890
7.3990
7.4777
7.4892
3.02
3.05
1.21
1.11
1.49
2.39
1.20
2.22
1.04
0.98
1.04
1.04
1.06
1.24
2.63
2.32
2.33
1.13
1.00
1.00
1.25
25.43
2.25
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
Ph
O
O
BnO
O
AcO
O
BnO
BnO
BnO
O
BnO
O
OMe

18



18

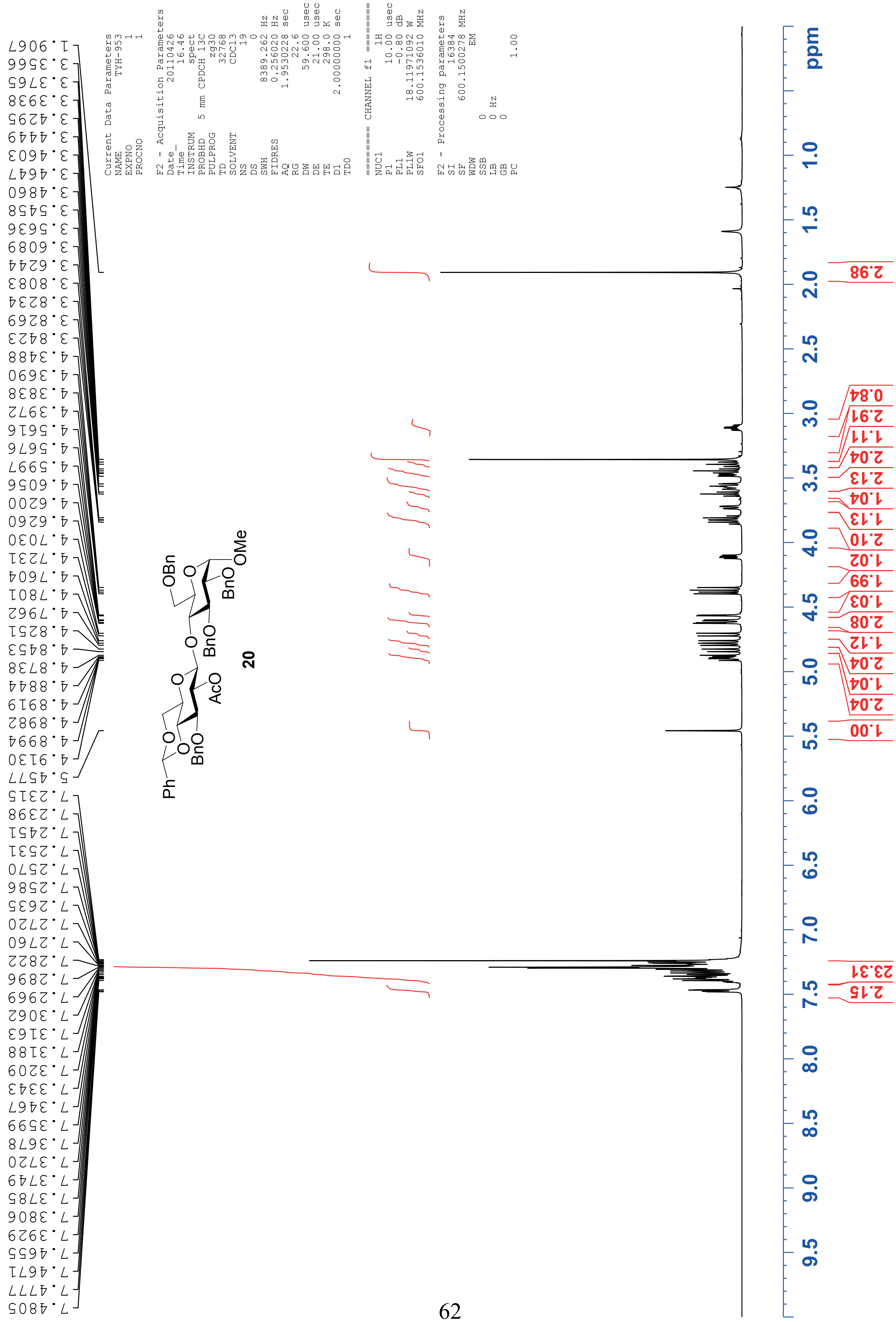
```
Current Data Parameters
NAME      TYH-1-6-glucan
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130616
Time_               2.40
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                131072
SOLVENT            CDCl3
NS                  2000
DS                     0
SWH            39062.500 Hz
FIDRES          0.298023 Hz
AQ             1.6777716 sec
RG                  3640
DW                12.800 usec
DE                 21.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.35 usec
PL1                 2.80 dB
PL1W         49.17097855 W
SFO1         150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.33 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         13.96854782 W
PL12W         0.33740479 W
PL13W         0.16910298 W
SFO2         600.1524006 MHz

F2 - Processing parameters
SI                 65536
SF           150.9078519 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```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3.3566
3.3765
3.3938
3.4295
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3.4860
3.5458
3.5636
3.6089
3.6244
3.8083
3.8234
3.8269
3.8423
4.3488
4.3690
4.3838
4.3972
4.5616
4.5676
4.5997
4.6056
4.6200
4.6260
4.7030
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4.7604
4.7801
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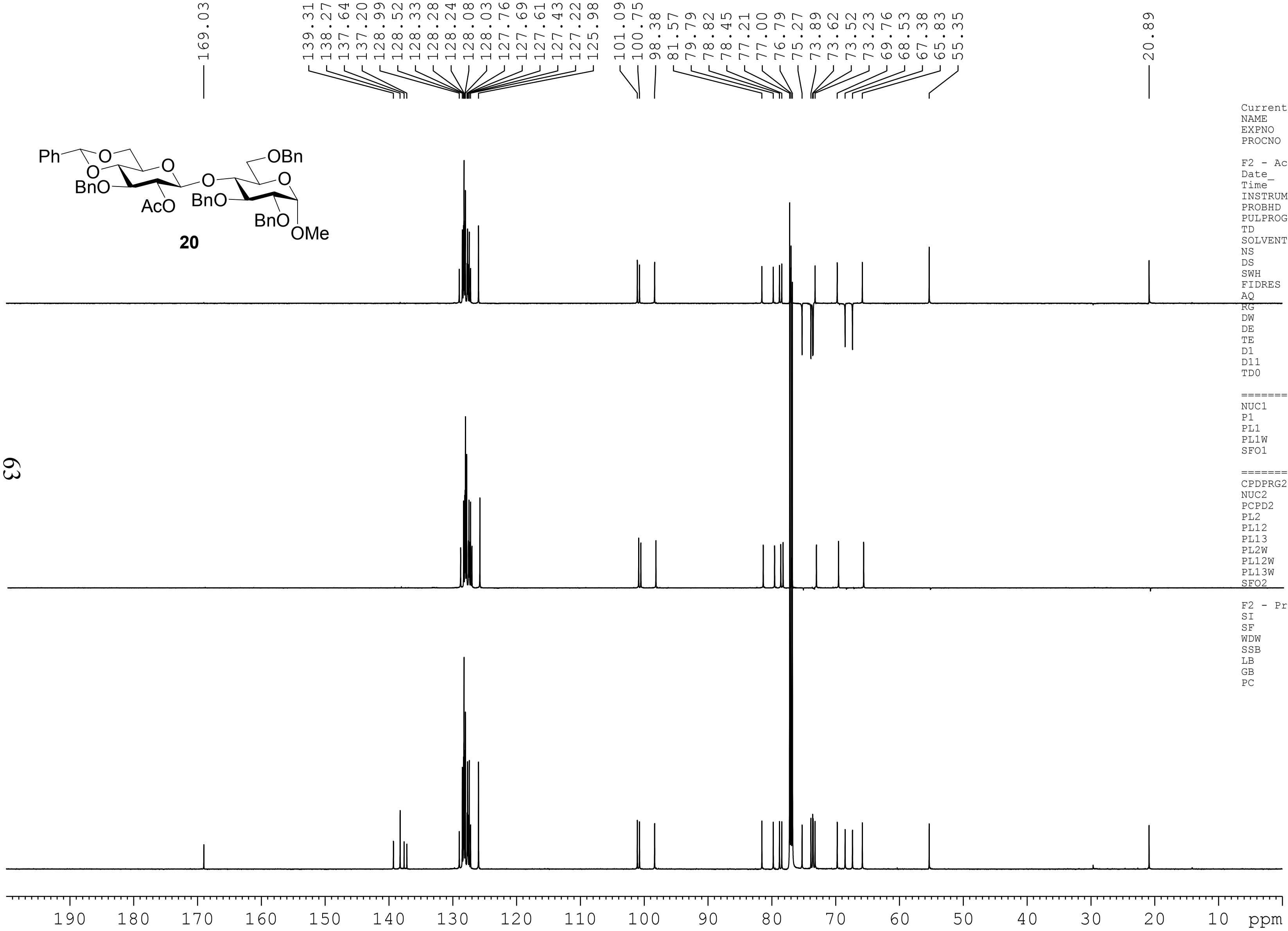
4.8994
4.9130
5.4577
7.2315
7.2398
7.2451
7.2531
7.2570
7.2586
7.2635
7.2720
7.2760
7.2822
7.2896
7.2969
7.3062
7.3163
7.3188
7.3209
7.3343
7.3467
7.3599
7.3678
7.3720
7.3749
7.3785
7.3806
7.3929
7.4655
7.4671
7.4777
7.4805
Current Data Parameters
NAME TYH-953
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110426
Time 16.46
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 19
DS 0
SWH 8389.262 Hz
FIDRES 0.256020 Hz
AQ 1.9530228 sec
RG 22.6
DW 59.600 usec
DE 21.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.80 dB
PL1W 18.11971092 W
SFO1 600.1536010 MHz
F2 - Processing parameters
SI 16384
SF 600.1500278 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
OBn
O
OMe
BnO
O
BnO
O
AcO
O
O
BnO
Ph
20
2.98
0.84
2.91
1.11
2.04
2.13
1.04
1.13
2.10
1.02
1.99
1.03
2.08
1.12
2.04
1.04
2.04
1.00
23.31
2.15
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5



20

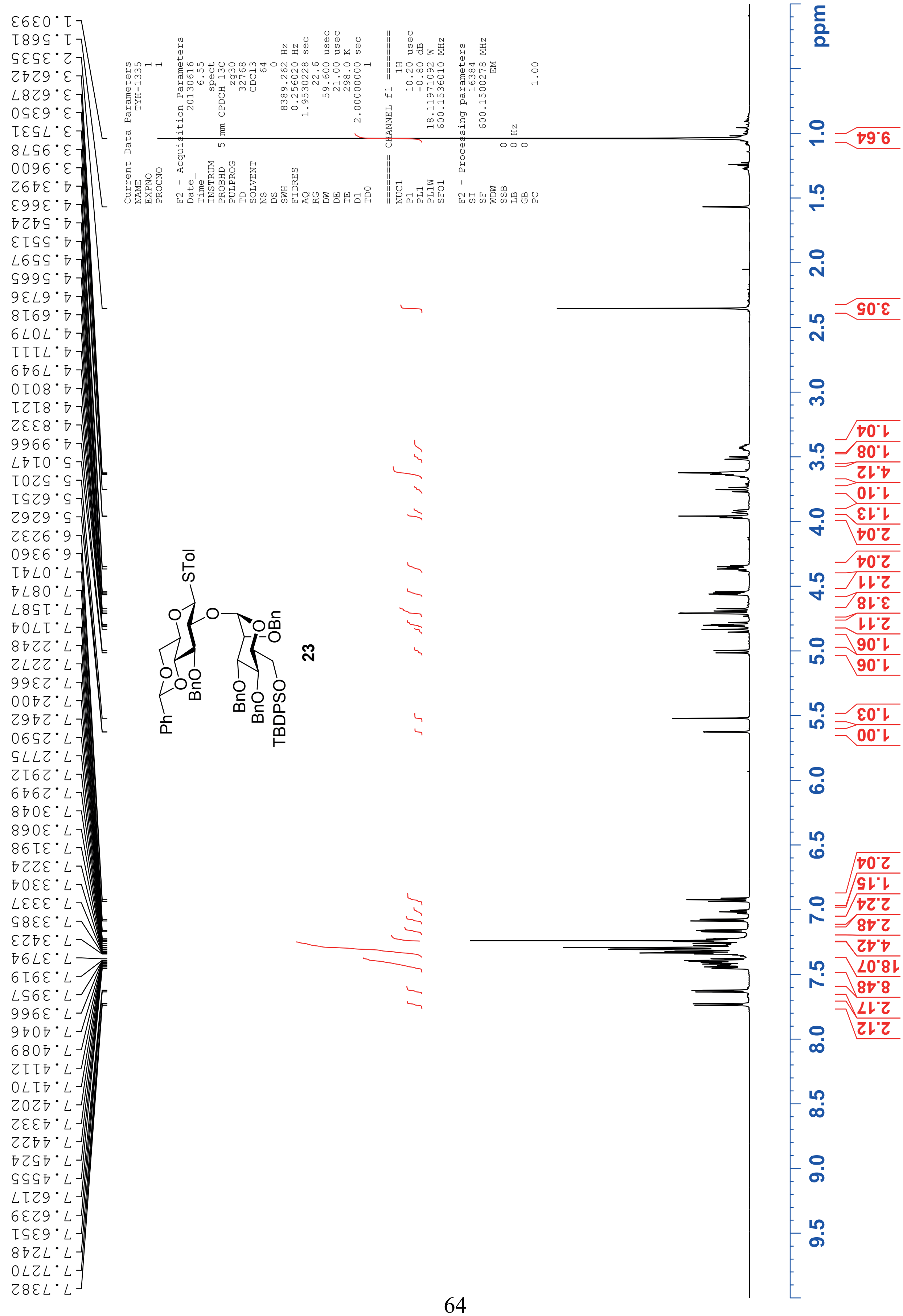
```
Current Data Parameters
NAME              TYH-953
EXPNO                   2
PROCNO                  1

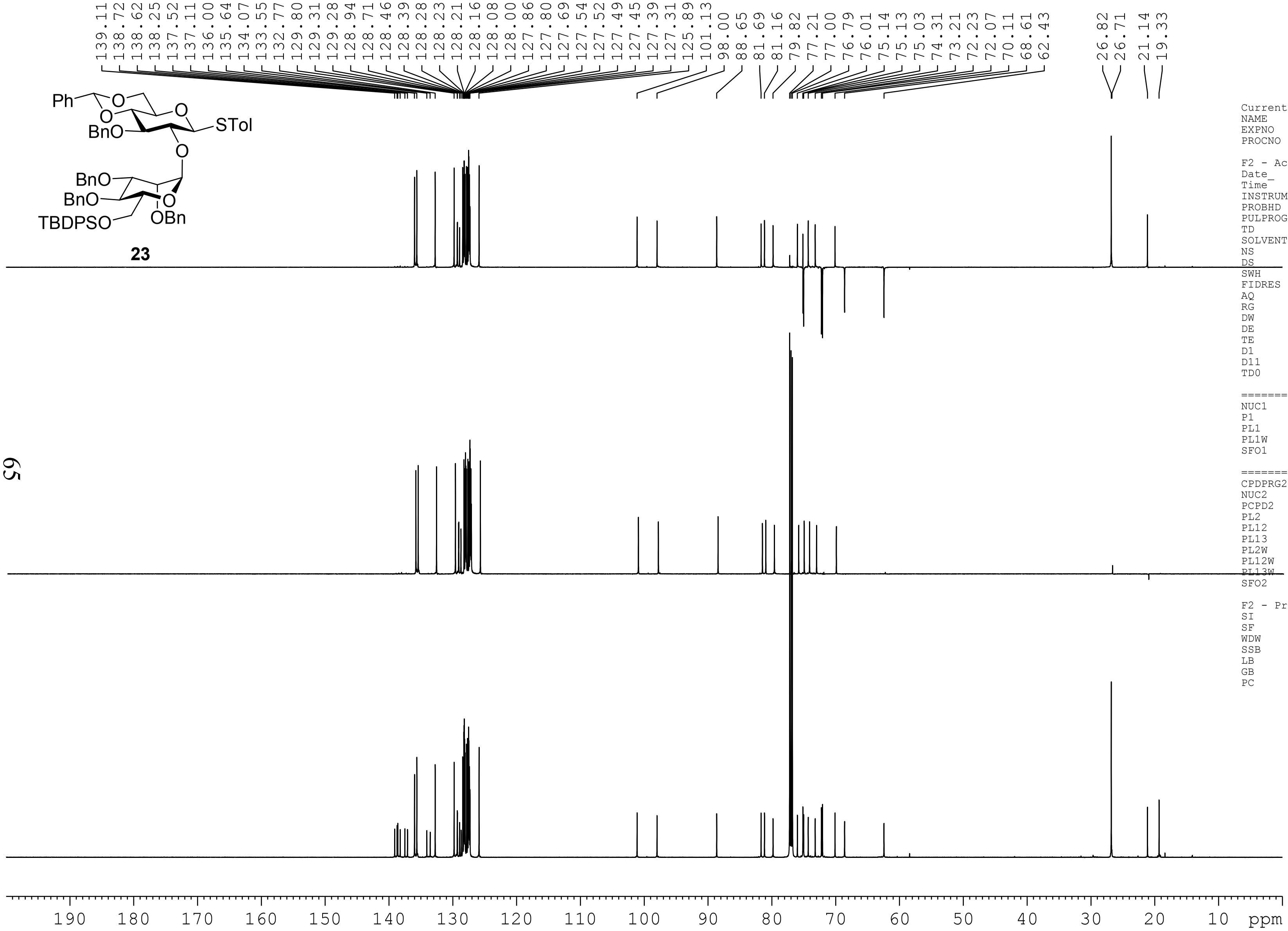
F2 - Acquisition Parameters
Date_            20110426
Time                22.11
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                131072
SOLVENT            CDCl3
NS                   600
DS                     0
SWH         39370.078 Hz
FIDRES       0.300370 Hz
AQ          1.6646644 sec
RG                  7290
DW             12.700 usec
DE              21.00 usec
TE              298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1               10.50 usec
PL1               2.80 dB
PL1W       49.17097855 W
SFO1      150.9251915 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            80.00 usec
PL2               0.33 dB
PL12             17.18 dB
PL13             20.18 dB
PL2W       13.96854782 W
PL12W       0.28850359 W
PL13W       0.14459431 W
SFO2      600.1539010 MHz

F2 - Processing parameters
SI                 65536
SF        150.9078498 MHz
WDW                   EM
SSB      0
LB                3.00 Hz
GB       0
PC                 1.00
```


Current Data Parameters
NAME TYH-1335
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130616
Time 6.55
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 8389.262 Hz
FIDRES 0.256020 Hz
AQ 1.9530228 sec
RG 22.6
DW 59.600 usec
DE 21.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 -0.80 dB
PL1W 18.11971092 W
SFO1 600.1536010 MHz
F2 - Processing parameters
SI 16384
SF 600.1500278 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
1.0393
1.5681
2.3535
3.6242
3.6287
3.6350
3.7531
3.9578
3.9600
4.3492
4.3663
4.5424
4.5513
4.5597
4.5665
4.6736
4.6918
4.7079
4.7111
4.7949
4.8010
4.8121
4.8332
4.9966
5.0147
5.5201
5.6251
5.6262
6.9232
6.9360
7.0741
7.0874
7.1587
7.1704
7.2248
7.2272
7.2366
7.2400
7.2462
7.2590
7.2775
7.2912
7.2949
7.3048
7.3068
7.3198
7.3224
7.3304
7.3337
7.3385
7.3423
7.3794
7.3919
7.3957
7.3966
7.4046
7.4089
7.4112
7.4170
7.4202
7.4332
7.4422
7.4524
7.4555
7.6217
7.6239
7.6351
7.7248
7.7270
7.7382
Ph
O
O
BnO
O
STol
O
O
OBn
BnO
BnO
TBDPSO
23
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
9.64
3.05
1.04
1.08
4.12
1.10
1.13
2.04
2.04
2.11
3.18
2.11
1.06
1.06
1.03
1.00
2.04
1.15
2.24
2.48
4.42
18.07
8.48
2.17
2.12



23

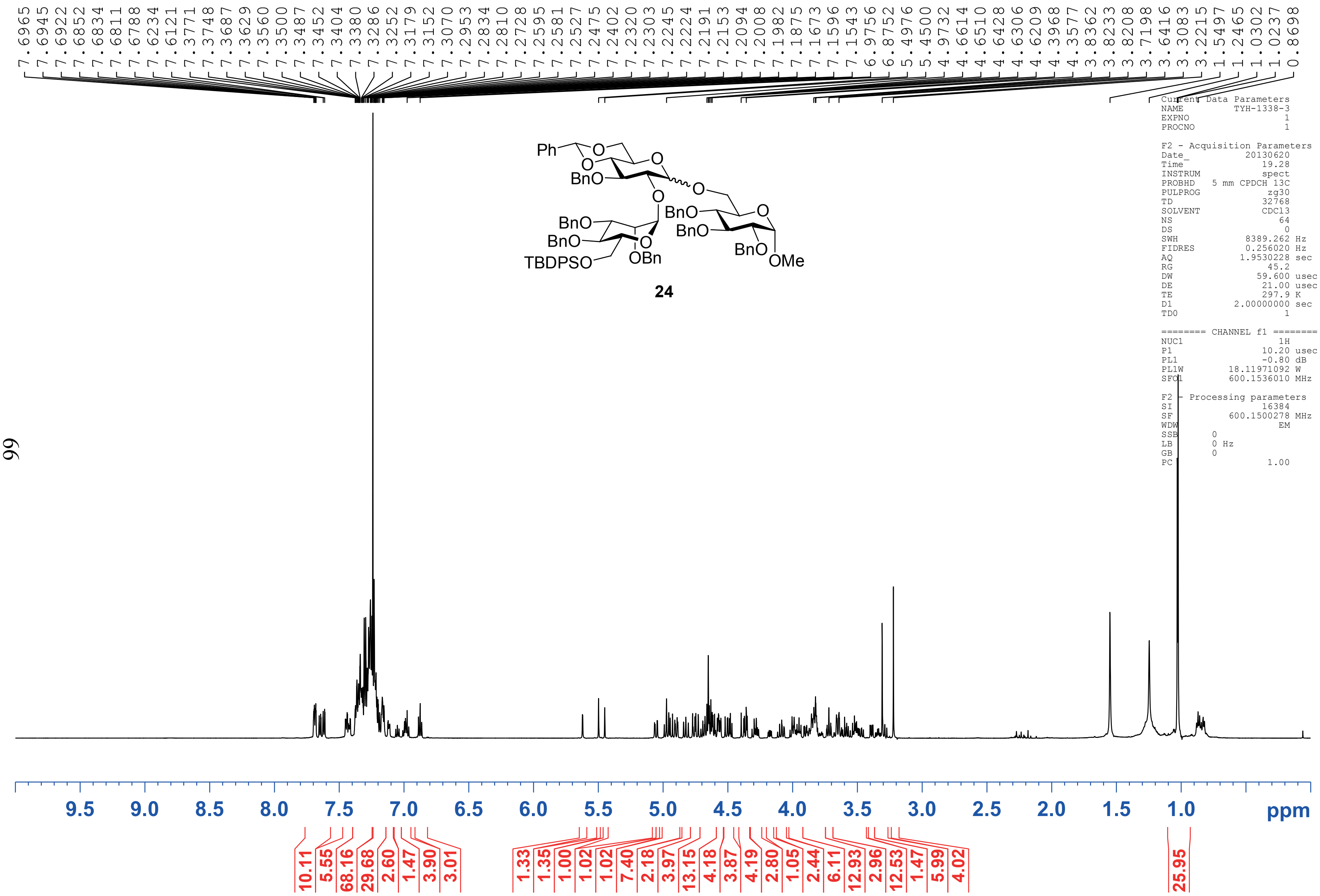
```
Current Data Parameters
NAME            TYH-1335
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130616
Time                9.00
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG          zgpg30
TD                131072
SOLVENT            CDCl3
NS                  2000
DS                     0
SWH            39062.500 Hz
FIDRES          0.298023 Hz
AQ             1.6777716 sec
RG                  3640
DW                12.800 usec
DE                 21.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.35 usec
PL1                 2.80 dB
PL1W         49.17097855 W
SFO1        150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.33 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         13.96854782 W
PL12W         0.33740479 W
PL13W         0.16910298 W
SFO2        600.1524006 MHz

F2 - Processing parameters
SI                 65536
SF           150.9078499 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```



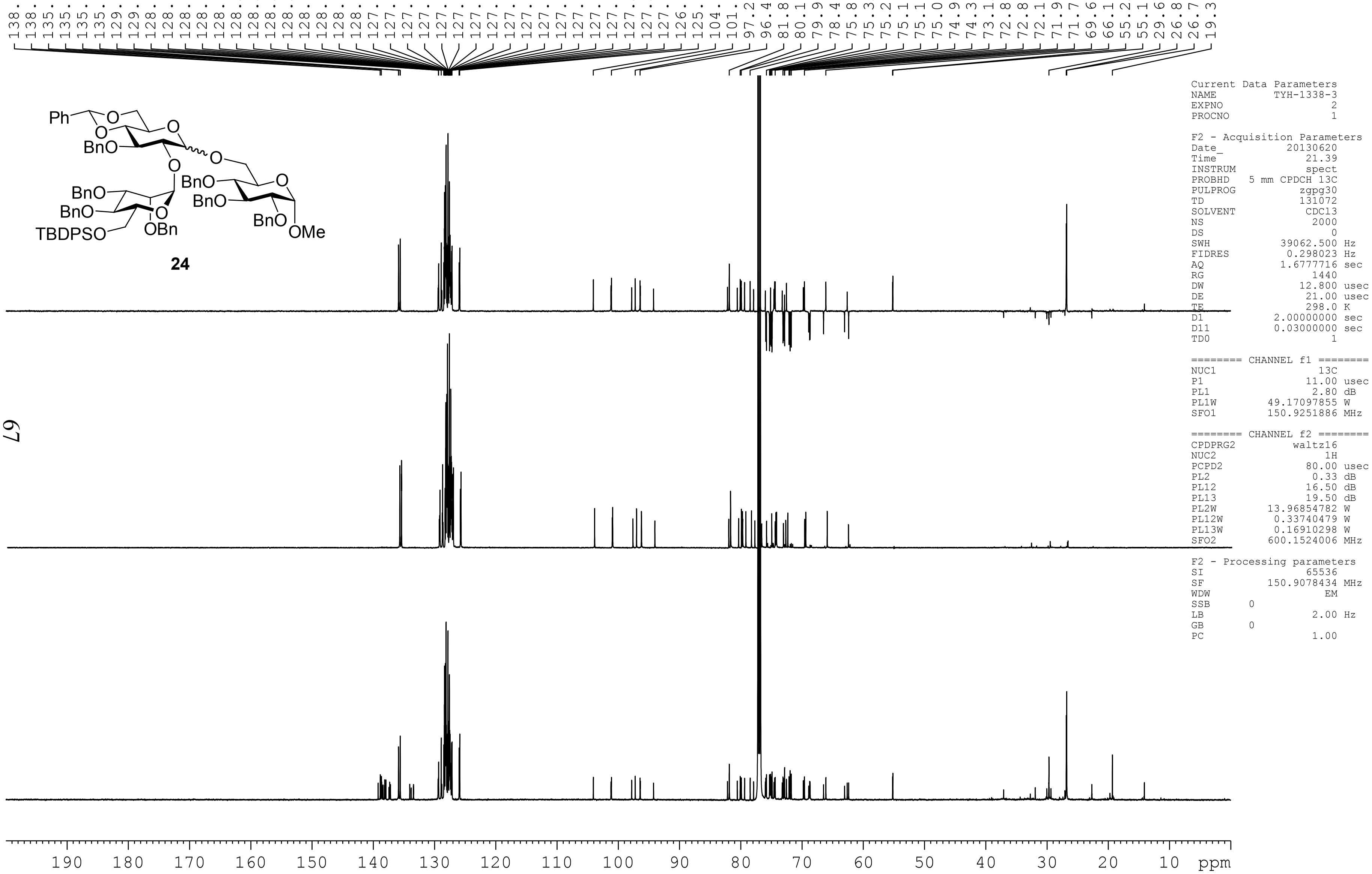
24

```
Current Data Parameters
NAME          TYH-1338-3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130620
Time               19.28
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             8389.262 Hz
FIDRES          0.256020 Hz
AQ             1.9530228 sec
RG                  45.2
DW                59.600 usec
DE                 21.00 usec
TE                 297.9 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                -0.80 dB
PL1W         18.11971092 W
SFO1         600.1536010 MHz

F2 - Processing parameters
SI                 16384
SF           600.1500278 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



24

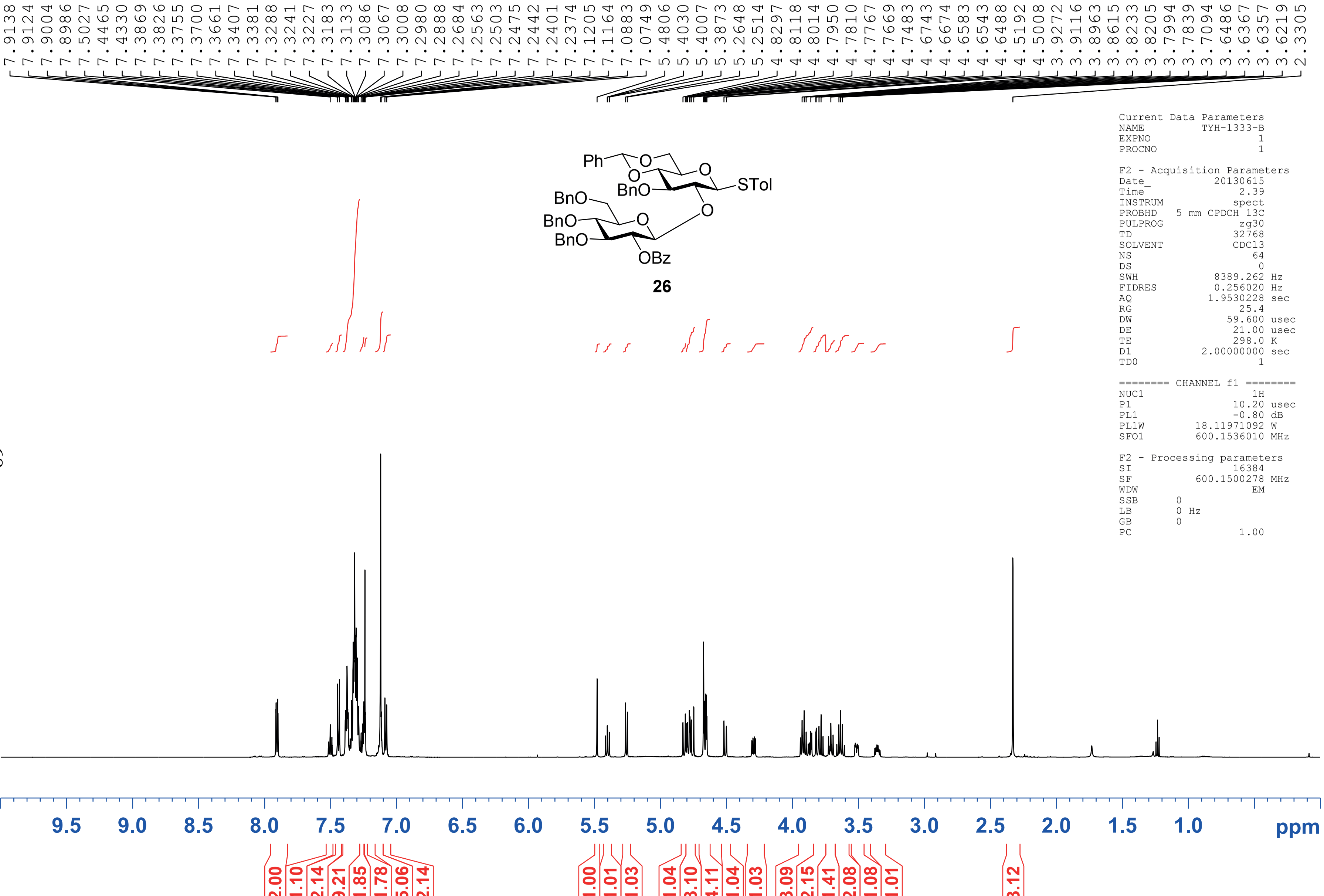
```
Current Data Parameters
NAME           TYH-1338-3
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130620
Time                21.39
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                 131072
SOLVENT             CDCl3
NS                   2000
DS                      0
SWH             39062.500 Hz
FIDRES           0.298023 Hz
AQ              1.6777716 sec
RG                   1440
DW                 12.800 usec
DE                  21.00 usec
TE                  298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

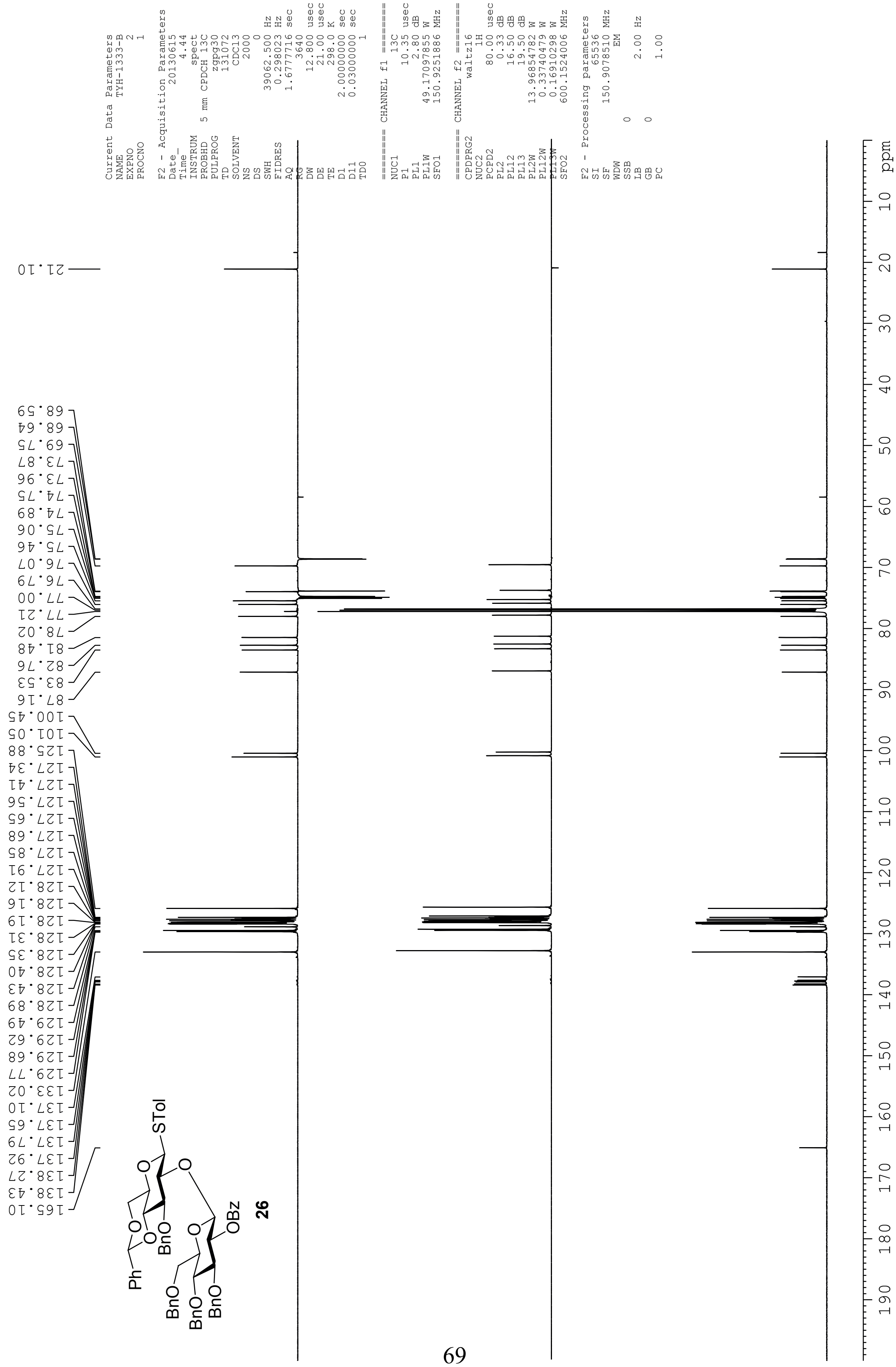
======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  2.80 dB
PL1W          49.17097855 W
SFO1         150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.33 dB
PL12                16.50 dB
PL13                19.50 dB
PL2W          13.96854782 W
PL12W          0.33740479 W
PL13W          0.16910298 W
SFO2         600.1524006 MHz

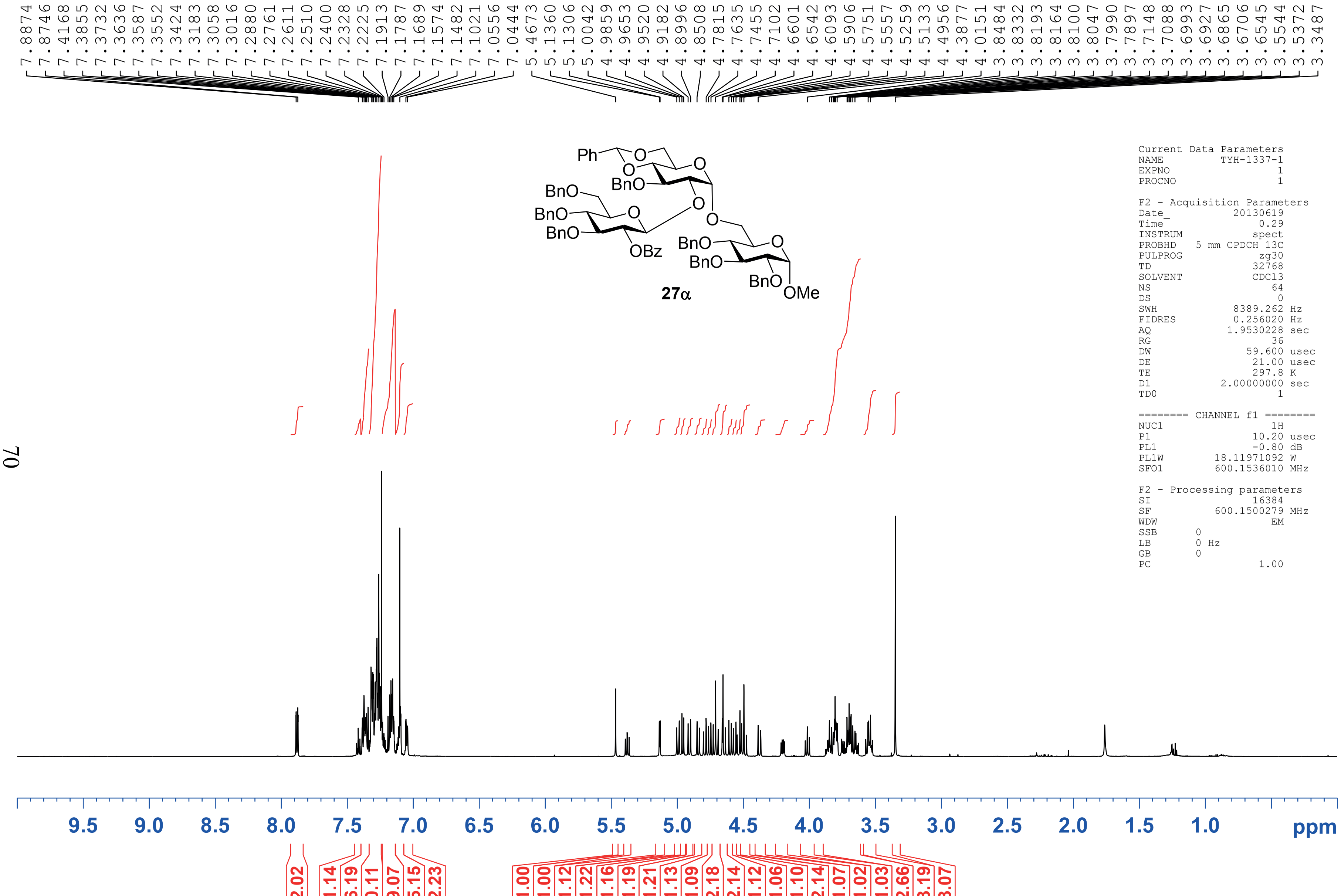
F2 - Processing parameters
SI                  65536
SF           150.9078434 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   1.00
```


7.9138
7.9124
7.9004
7.8986
7.5027
7.4465
7.4330
7.3869
7.3826
7.3755
7.3700
7.3661
7.3407
7.3381
7.3288
7.3241
7.3227
7.3183
7.3133
7.3086
7.3067
7.3008
7.2980
7.2888
7.2684
7.2563
7.2503
7.2475
7.2442
7.2401
7.2374
7.1205
7.1164
7.0883
7.0749
5.4806
5.4030
5.4007
5.3873
5.2648
5.2514
4.8297
4.8118
4.8014
4.7950
4.7810
4.7767
4.7669
4.7483
4.6743
4.6674
4.6583
4.6543
4.6488
4.5192
4.5008
3.9272
3.9116
3.8963
3.8615
3.8233
3.8205
3.7994
3.7839
3.7094
3.6486
3.6367
3.6357
3.6219
2.3305
Current Data Parameters
NAME TYH-1333-B
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130615
Time 2.39
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 0
SWH 8389.262 Hz
FIDRES 0.256020 Hz
AQ 1.9530228 sec
RG 25.4
DW 59.600 usec
DE 21.00 usec
TE 298.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 -0.80 dB
PL1W 18.11971092 W
SFO1 600.1536010 MHz
F2 - Processing parameters
SI 16384
SF 600.1500278 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
Ph
O
O
O
BnO
STol
O
BnO
BnO
O
BnO
OBz
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
1.10
2.14
19.21
1.85
1.78
5.06
2.14
1.00
1.01
1.03
1.04
3.10
4.11
1.04
1.03
3.09
2.15
1.41
2.08
1.08
1.01
3.12

26


Current Data Parameters
NAME TYH-1333-B
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130615
Time 4.44
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 131072
SOLVENT CDCl3
NS 2000
DS 0
SWH 39062.500 Hz
FIDRES 0.298023 Hz
AQ 1.6777716 sec
RG 3640
DW 12.800 usec
DE 21.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.35 usec
PL1 2.80 dB
PL1W 49.17097855 W
SFO1 150.9251886 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.33 dB
PL12 16.50 dB
PL13 19.50 dB
PL2W 13.96854782 W
PL12W 0.33740479 W
PL13W 0.16910298 W
SFO2 600.1524006 MHz
F2 - Processing parameters
SI 65536
SF 150.9078510 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00
21.10
68.59
68.64
69.75
73.87
73.96
74.75
74.89
75.06
75.46
76.07
76.79
77.00
77.21
78.02
81.48
82.76
83.53
87.16
100.45
101.05
125.88
127.34
127.41
127.56
127.65
127.68
127.85
127.91
128.12
128.16
128.19
128.31
128.35
128.40
128.43
128.89
129.49
129.62
129.68
129.77
133.02
137.10
137.65
137.79
137.92
138.27
138.43
165.10
STol
O
O
O
O
Ph
BnO
O
BnO
BnO
BnO
OBz
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm

26



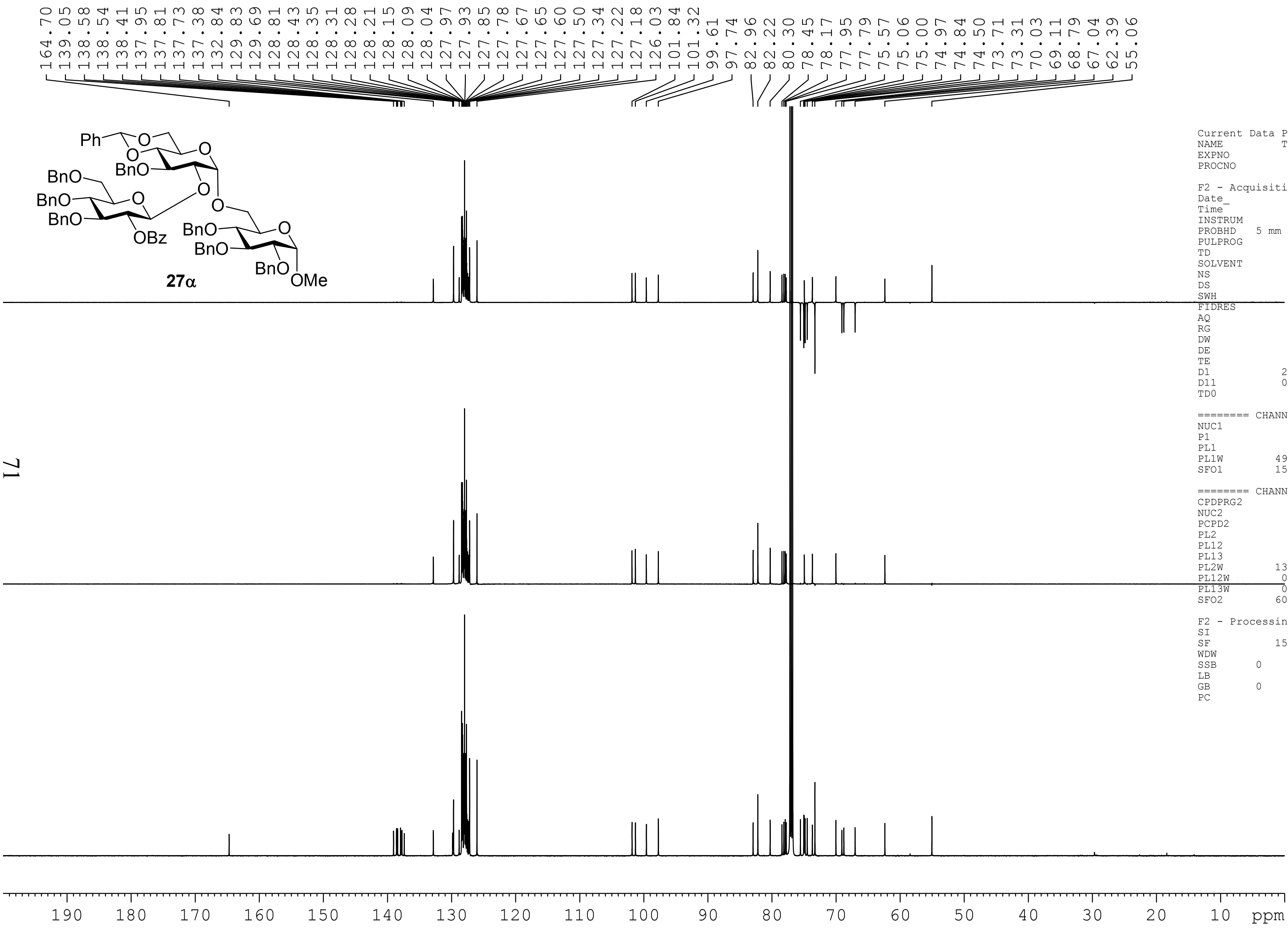
27α

```
Current Data Parameters
NAME          TYH-1337-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130619
Time                0.29
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             8389.262 Hz
FIDRES          0.256020 Hz
AQ             1.9530228 sec
RG                    36
DW                59.600 usec
DE                 21.00 usec
TE                 297.8 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                -0.80 dB
PL1W         18.11971092 W
SFO1         600.1536010 MHz

F2 - Processing parameters
SI                 16384
SF           600.1500279 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



27α

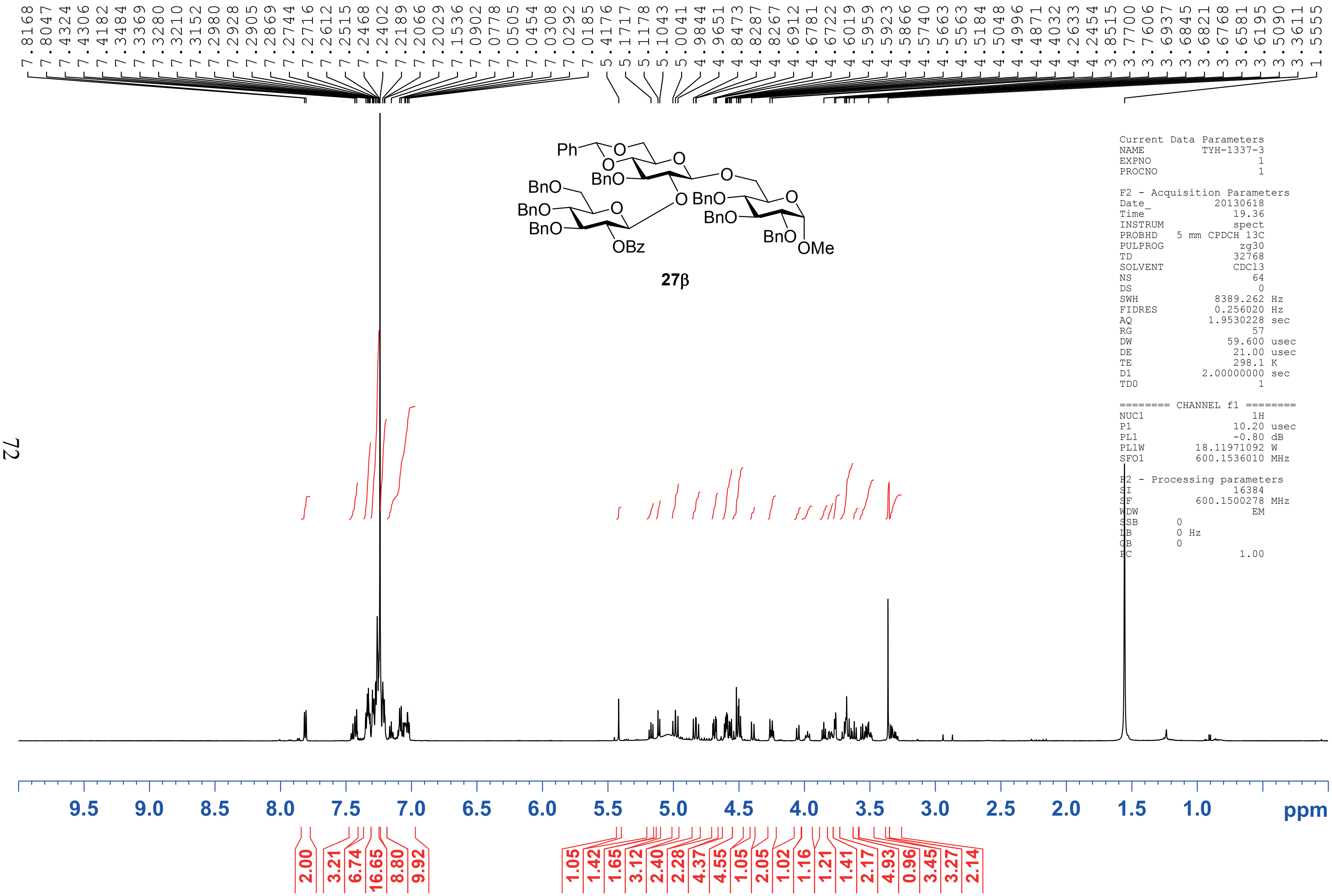
```
Current Data Parameters
NAME           TYH-1337-1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130619
Time                 2.03
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                 131072
SOLVENT             CDCl3
NS                   1500
DS                      0
SWH             39062.500 Hz
FIDRES           0.298023 Hz
AQ              1.6777716 sec
RG                   3640
DW                 12.800 usec
DE                  21.00 usec
TE                  298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.35 usec
PL1                  2.80 dB
PL1W          49.17097855 W
SFO1          150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.33 dB
PL12                16.50 dB
PL13                19.50 dB
PL2W          13.96854782 W
PL12W          0.33740479 W
PL13W          0.16910298 W
SFO2          600.1524006 MHz

F2 - Processing parameters
SI                  65536
SF            150.9078469 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   1.00
```



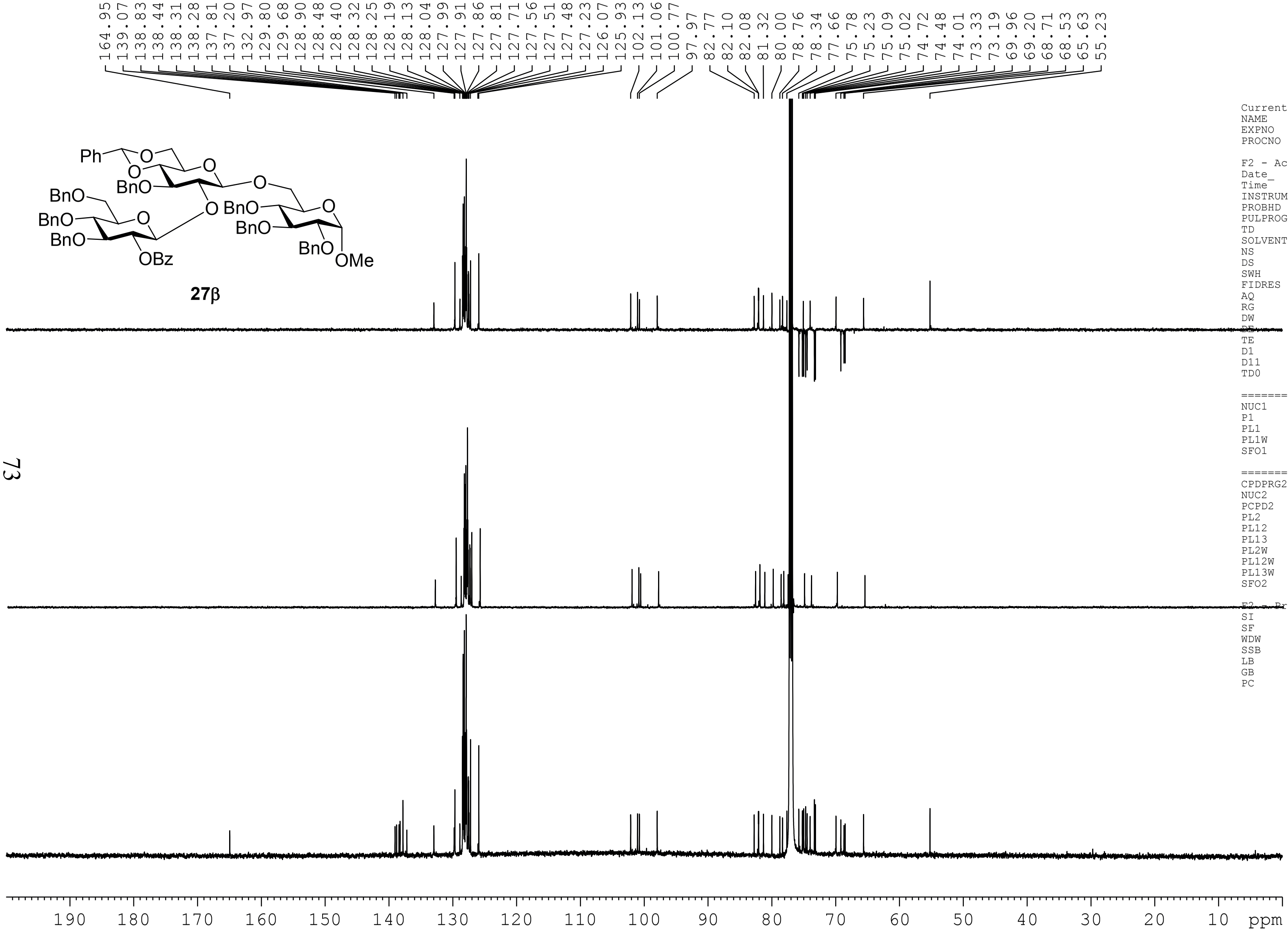
27β

```
Current Data Parameters
NAME          TYH-1337-3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130618
Time               19.36
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             8389.262 Hz
FIDRES          0.256020 Hz
AQ             1.9530228 sec
RG                    57
DW                59.600 usec
DE                 21.00 usec
TE                 298.1 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                -0.80 dB
PL1W         18.11971092 W
SFO1         600.1536010 MHz

F2 - Processing parameters
SI                 16384
SF           600.1500278 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



27β

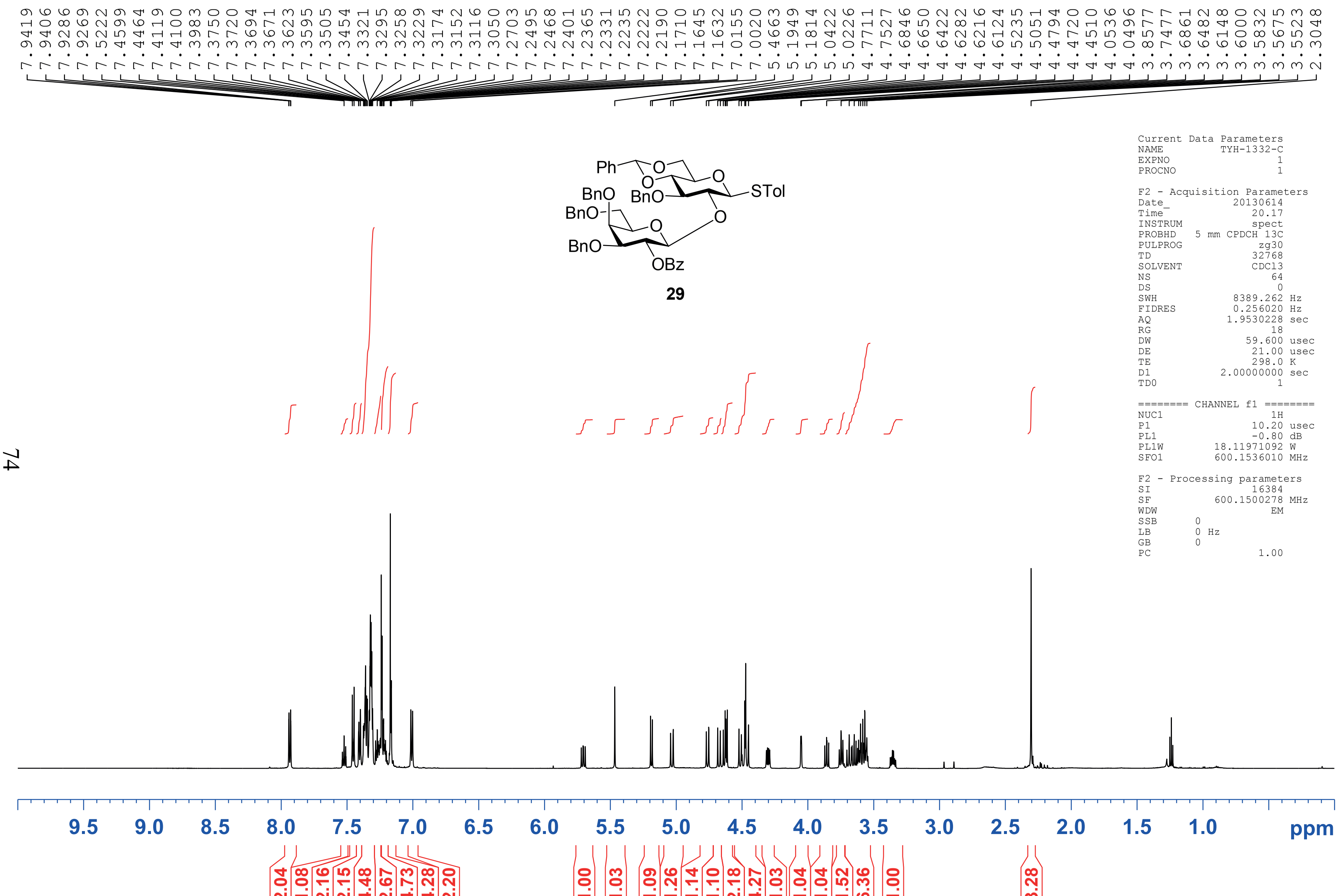
```
Current Data Parameters
NAME          TYH-1337-3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130618
Time               21.12
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG          zgpg30
TD                131072
SOLVENT            CDCl3
NS                  1500
DS                     0
SWH            39062.500 Hz
FIDRES          0.298023 Hz
AQ             1.6777716 sec
RG                  1290
DW                12.800 usec
DE                 21.00 usec
TE                 297.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.35 usec
PL1                 2.80 dB
PL1W         49.17097855 W
SFO1         150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.33 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         13.96854782 W
PL12W         0.33740479 W
PL13W         0.16910298 W
SFO2         600.1524006 MHz

F2 - Processing parameters
SI                 65536
SF           150.9078380 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```



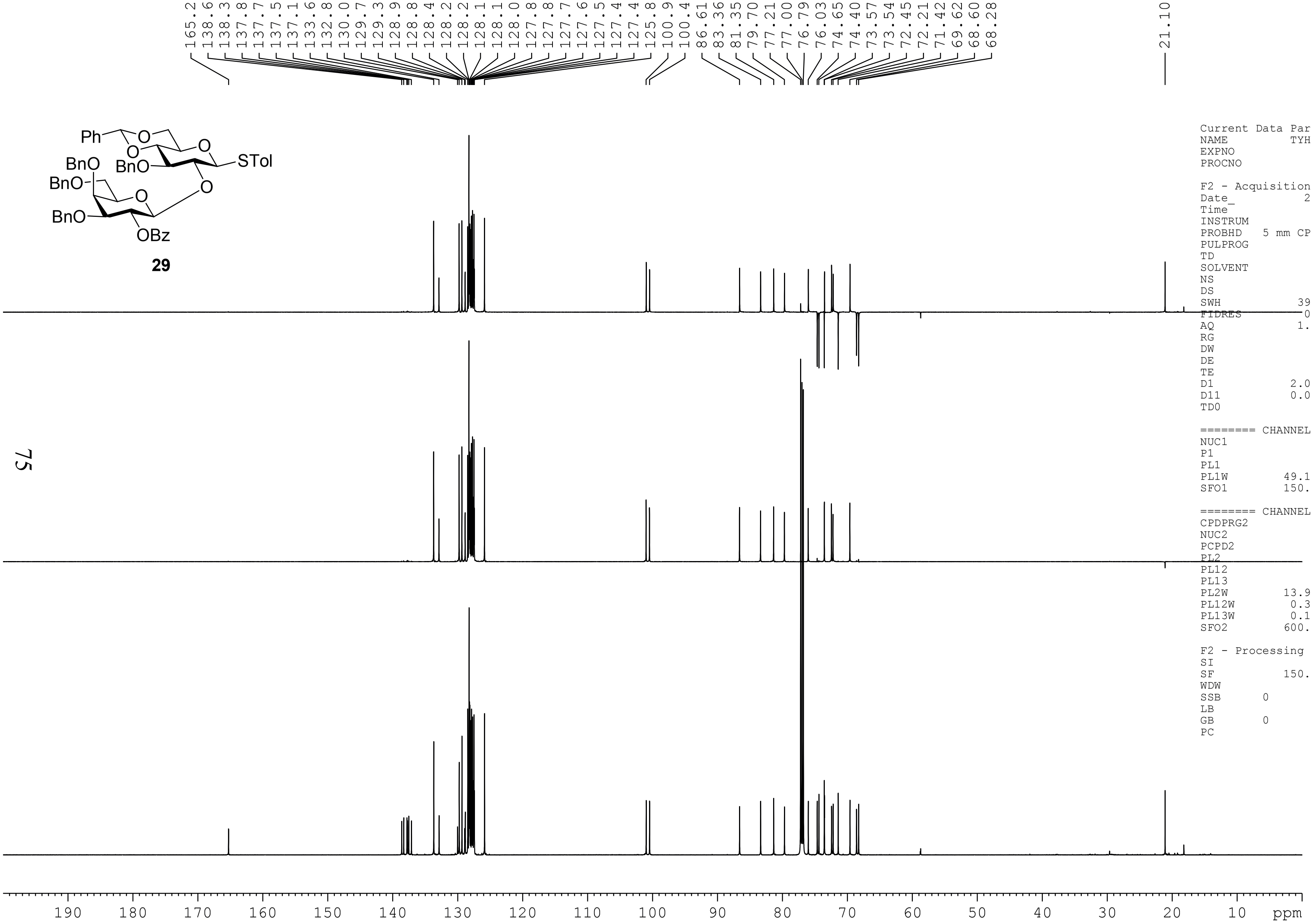
29

```
Current Data Parameters
NAME          TYH-1332-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130614
Time               20.17
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             8389.262 Hz
FIDRES          0.256020 Hz
AQ             1.9530228 sec
RG                    18
DW                59.600 usec
DE                 21.00 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                -0.80 dB
PL1W         18.11971092 W
SFO1         600.1536010 MHz

F2 - Processing parameters
SI                 16384
SF           600.1500278 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



29

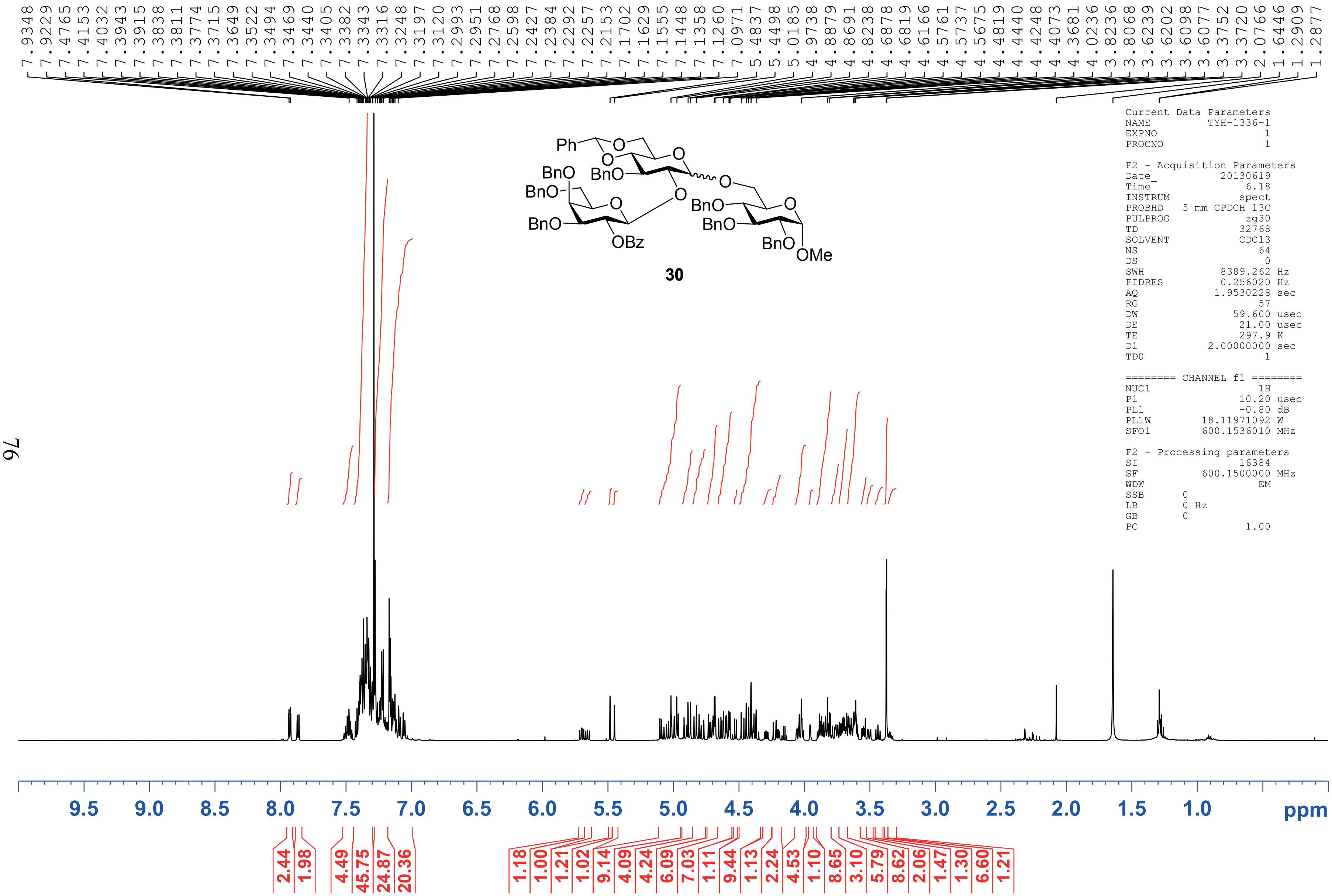
```
Current Data Parameters
NAME          TYH-1332-C
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130614
Time               20.21
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                131072
SOLVENT            CDCl3
NS                  2000
DS                     0
SWH            39062.500 Hz
FIDRES          0.298023 Hz
AQ             1.6777716 sec
RG                  1030
DW                12.800 usec
DE                 21.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.35 usec
PL1                 2.80 dB
PL1W         49.17097855 W
SFO1         150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.33 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         13.96854782 W
PL12W         0.33740479 W
PL13W         0.16910298 W
SFO2         600.1524006 MHz

F2 - Processing parameters
SI                 65536
SF           150.9078535 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```

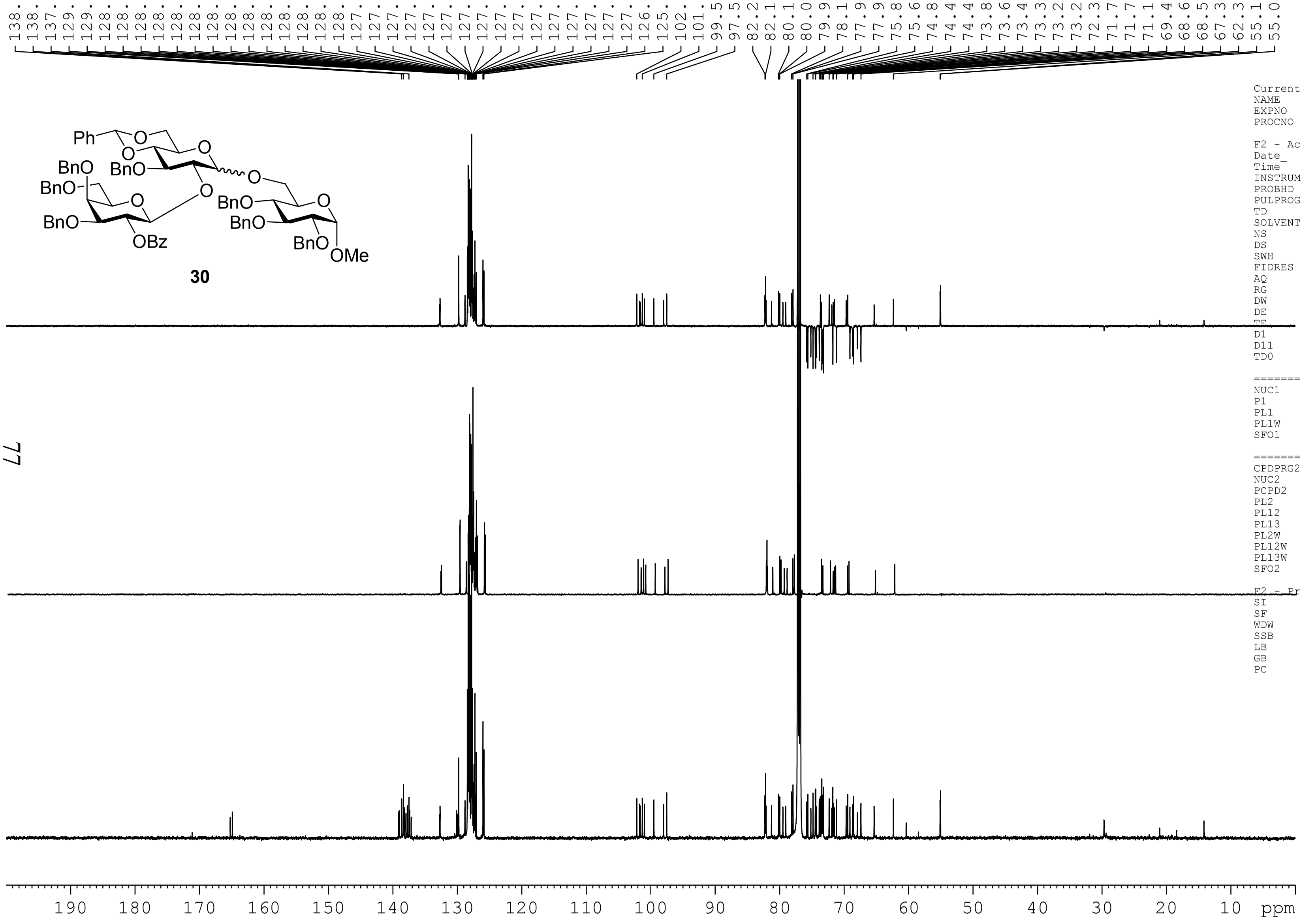


```
Current Data Parameters
NAME          TYH-1336-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130619
Time                6.18
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             8389.262 Hz
FIDRES          0.256020 Hz
AQ             1.9530228 sec
RG                    57
DW                59.600 usec
DE                 21.00 usec
TE                 297.9 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.20 usec
PL1                -0.80 dB
PL1W         18.11971092 W
SFO1         600.1536010 MHz

F2 - Processing parameters
SI                 16384
SF           600.1500000 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



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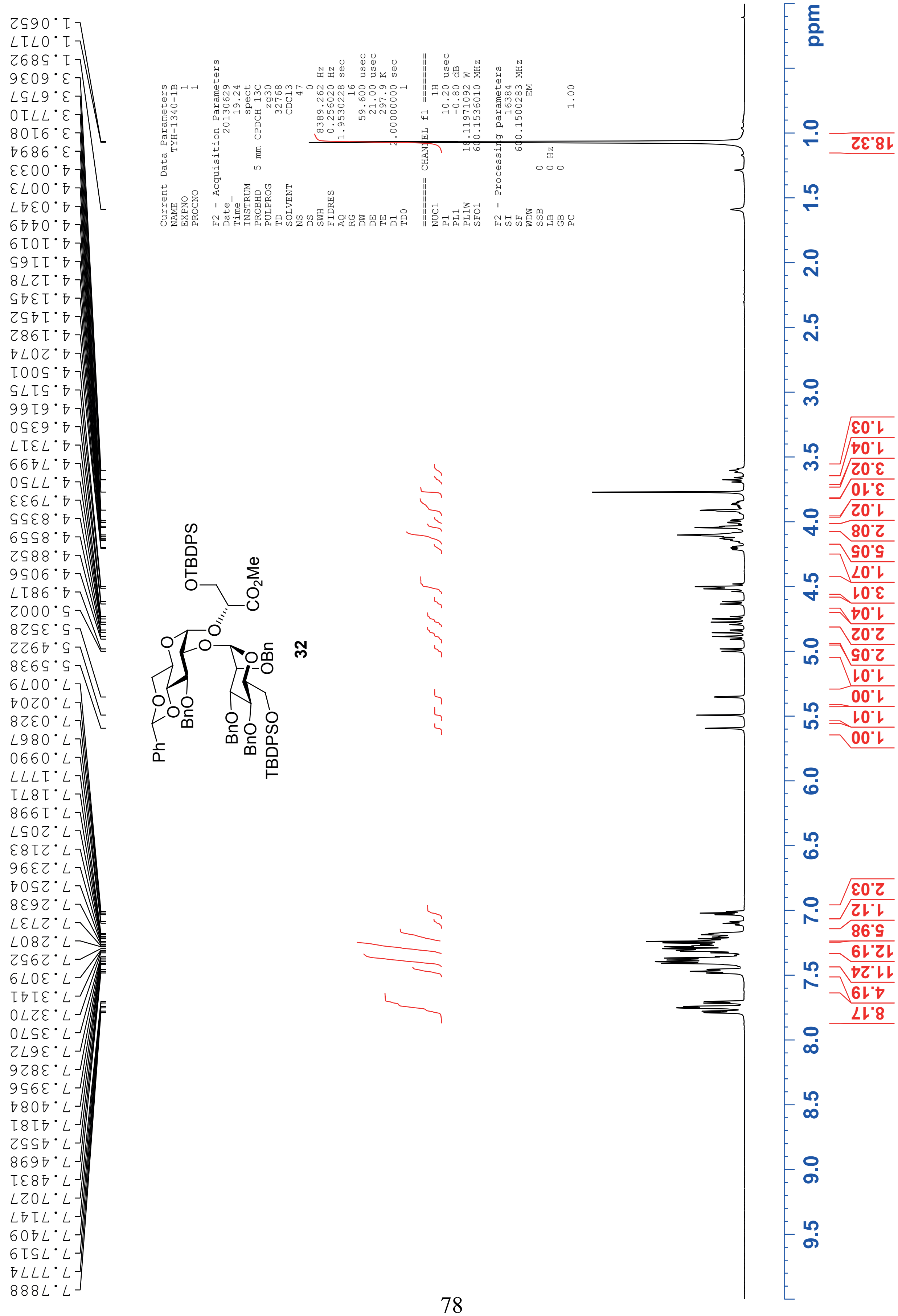
```
Current Data Parameters
NAME          TYH-1336-1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130619
Time                7.21
INSTRUM            spect
PROBHD   5 mm CPDCH 13C
PULPROG          zgpg30
TD                131072
SOLVENT            CDCl3
NS                  1000
DS                     0
SWH            39062.500 Hz
FIDRES          0.298023 Hz
AQ             1.6777716 sec
RG                  3640
DW                12.800 usec
DE                 21.00 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.35 usec
PL1                 2.80 dB
PL1W         49.17097855 W
SFO1         150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 0.33 dB
PL12               16.50 dB
PL13               19.50 dB
PL2W         13.96854782 W
PL12W         0.33740479 W
PL13W         0.16910298 W
SFO2         600.1524006 MHz

F2 - Processing parameters
SI                 65536
SF           150.9078440 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  1.00
```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1.0717
1.5892
3.6036
3.6757
3.7710
3.9108
3.9894
4.0033
4.0073
4.0347
4.0449
4.1019
4.1165
4.1278
4.1345
4.1452
4.1982
4.2074
4.5001
4.5175
4.6166
4.6350
4.7317
4.7499
4.7750
4.7933
4.8355
4.8559
4.8852
4.9056
4.9817
5.0002
5.3528
5.4922
5.5938
7.0079
7.0204
7.0328
7.0867
7.0990
7.1777
7.1871
7.1998
7.2057
7.2183
7.2396
7.2504
7.2638
7.2737
7.2807
7.2952
7.3079
7.3141
7.3270
7.3570
7.3672
7.3826
7.3956
7.4084
7.4181
7.4552
7.4698
7.4831
7.7027
7.7147
7.7409
7.7519
7.7774
7.7888
Current Data Parameters
NAME TYH-1340-1B
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130629
Time 19.24
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 47
DS 0
SWH 8389.262 Hz
FIDRES 0.256020 Hz
AQ 1.9530228 sec
RG 16
DW 59.600 usec
DE 21.00 usec
TE 297.9 K
D1 2.0000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PL1 -0.80 dB
PL1W 18.11971092 W
SFO1 600.1536010 MHz
F2 - Processing parameters
SI 16384
SF 600.1500283 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
Ph
O
O
BnO
O
O
OTBDPS
CO2Me
BnO
BnO
TBDPSO
OBn
18.32
1.03
1.04
3.02
3.10
1.02
2.08
5.05
1.07
3.01
1.04
2.02
2.05
1.01
1.00
1.01
1.00
2.03
1.12
5.98
12.19
11.24
4.19
8.17
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
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6.0
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8.5
9.0
9.5

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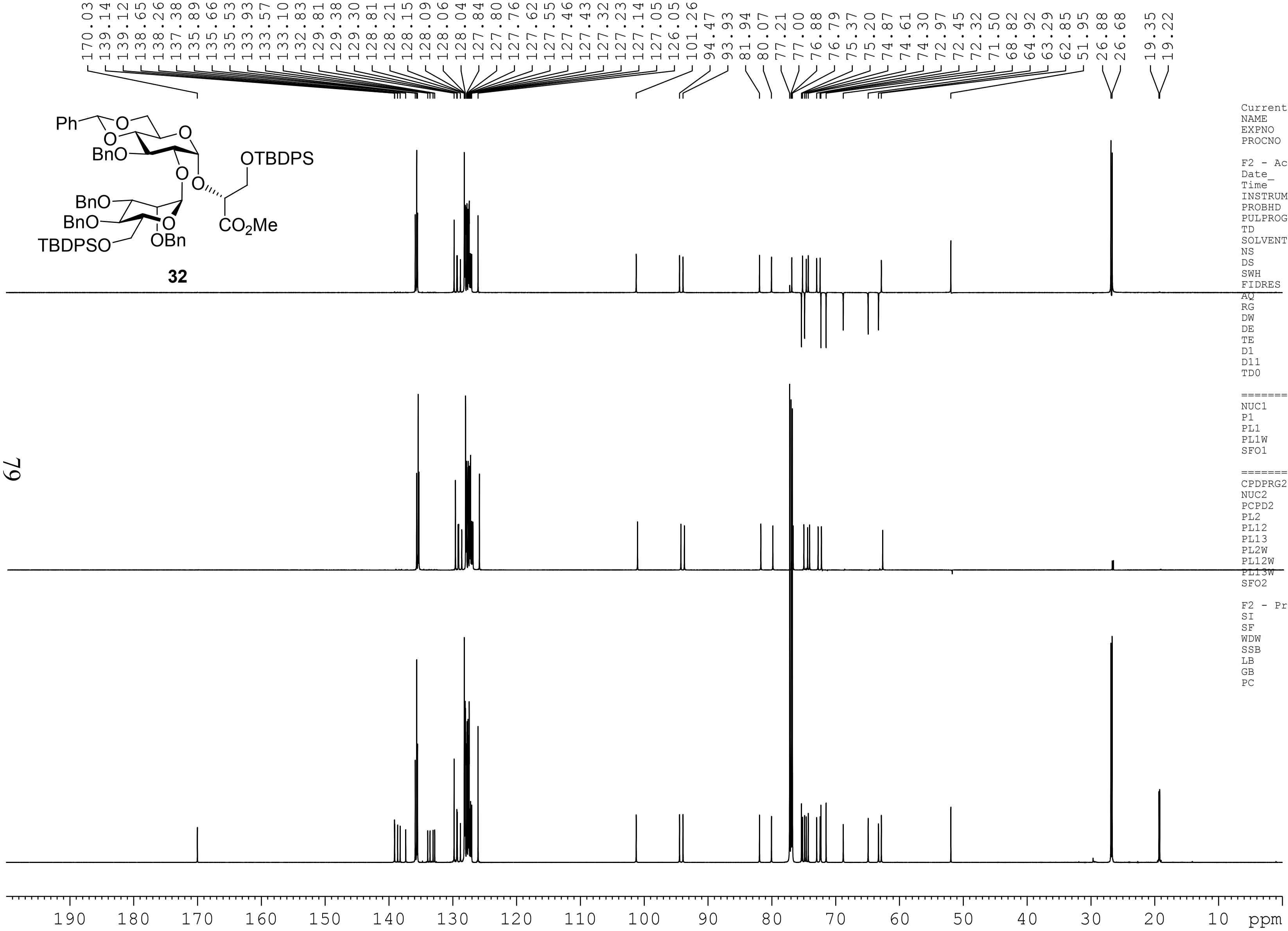

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```
Current Data Parameters
NAME          TYH-1340-1B
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130629
Time                19.26
INSTRUM             spect
PROBHD   5 mm CPDCH 13C
PULPROG           zgpg30
TD                 131072
SOLVENT             CDCl3
NS                   5000
DS                      0
SWH             39062.500 Hz
FIDRES           0.298023 Hz
AQ              1.6777716 sec
RG                   3640
DW                 12.800 usec
DE                  21.00 usec
TE                  297.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  2.80 dB
PL1W          49.17097855 W
SFO1          150.9251886 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.33 dB
PL12                16.50 dB
PL13                19.50 dB
PL2W          13.96854782 W
PL12W          0.33740479 W
PL13W          0.16910298 W
SFO2          600.1524006 MHz

F2 - Processing parameters
SI                  65536
SF            150.9078511 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   1.00
```