Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

# Supporting Information

# First Total Synthesis of Trehalose Containing Tetrasaccharides from *Mycobacterium smegmatis*[†]

Manishkumar A. Chaube,[Ŧ] Vikram A. Sarpe,[Ŧ] Santanu Jana and Suvarn S. Kulkarni*

*Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India.*

Email: suvarn@chem.iitb.ac.in

## Table of Contents

**I. Experimental procedures**

**II. Spectra**

## I. Synthetic procedures and characterization data

## Experimental Section

**A. General Methods:** All reactions were conducted under a dry nitrogen atmosphere. Solvents ($CH_2Cl_2$ >99%, THF 99.5%, Acetonitrile 99.8%, DMF 99.5%) were purchased in capped bottles and dried under sodium or $CaH_2$. All other solvents and reagents were used without further purification. All glasswares used were oven dried before use. TLC was performed on pre-coated Aluminium plates of Silica Gel 60 F254 (0.25 mm, E. Merck). Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in ammonium molybdate/cerium (IV) sulfate solution. Silica gel column chromatography was performed using Silica Gel (100-200 mesh or 230-400 mesh) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on 400 and 500 MHz instrument using $CDCl_3$ (D, 99.8%) or $D_2O$ (D, 99.9%) as solvents. Chemical shifts are relative to the deuterated solvent peaks and are in parts per million (ppm). $^1$H-$^1$H COSY was used to confirm proton assignments. Mass spectra were acquired in the ESI mode. Specific rotation experiments were measured at 589 nm (Na) and 25 °C. IR spectra were recorded on an FT-IR spectrometer using CsCl plates.

**Phenyl 2,3,4-tri-*O*-benzoyl-1-thio-*β*-D-glucopyranoside (9):**

To a solution of phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(t-butyldiphenylsilyl)-1-thio-*α*-D-glucopyranoside (0.25 g, 0.30 mmol) in THF (2 mL) was added premixed solution of TBAF (1.52 mL, 1.52 mmol) and AcOH (0.17 mL, 3.04 mmol) at rt and the reaction mixture was stirred for 2 h. After complete conversion of starting material, reaction mixture was concentrated on rotary evaporator and purified by column chromatography to afford compound **9** as a white solid (0.16 g, 90%). $[\alpha]^{20}_D$ +11.9 (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) ν 3436, 3032, 1732, 1600, 1452, 1316, 1282, 1260, 1217, 1026, 765, 709 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.97-7.92 (m, 4H), 7.82-7.80 (m, 2H), 7.55–7.50 (m, 4H), 7.43-7.36 (m, 5H), 7.34-7.32 (m, 3H), 7.28-7.25 (m, 2H), 5.94 (t, *J* = 9.5 Hz, 1H), 5.51-5.45 (m, 2H), 5.06 (d, *J* = 10.0 Hz, 1H), 3.88–3.82 (m, 2H), 3.75 (dd, *J* = 12.5, 4.5 Hz, 1H), 2.52 (bs, 1H, OH); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 166.1, 165.9, 165.2, 133.9, 133.5, 133.4, 133.3, 131.9, 130.1, 130.0, 129.9, 129.3, 129.3, 128.9, 128.7, 128.6, 128.6, 128.5, 86.4, 79.0, 74.2, 70.7, 69.4, 61. 8; HR-ESI-MS (*m/z*): calcd for $C_{33}H_{28}O_8S$ $[M + Na]^+$ 607.1397 found, 607.1405.

### Phenyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(1→6)-2,3,4-tetra-*O*-benzoyl-*β*-D-glucopyranoside (5):

33% HBr in AcOH (1.5 mL) was added to 1,2,3,4,6-penta-*O*-benzoyl glucopyranoside (0.45 gm, 0.64 mmol) at rt and stirred for for 1 h. When the starting material was completely disappeared, reaction was diluted with 50 mL $CH_2Cl_2$ and washed sequentially with sat. solution of $NaHCO_3$ (5 mL), brine (5 mL × 2) and $H_2O$ (5 mL). Then the organic layer was concentrated on rotary evaporator and co evaporated with toluene (2 ml × 3) and kept under high vacuum for 1 h.

To the stirred solution of acceptor **9** (0.25 mg, 0.43 mmol), 3Å MS (400 mg) in $CH_2Cl_2$ (1.5 mL) at rt was added the solution of the 2,3,4,6-tetra-*O*-benzoyl glucosyl bromide in $CH_2Cl_2$ (2.5 mL) and the reaction mixture was stirred for 15 min at rt and then cooled to -40 °C. AgOTf (330 mg, 1.28 mmol) was added to it and reaction was allowed to stir for 1 h. Reaction was quenched by addition of $Et_3N$ (0.5 mL). Reaction mixture was filtered through Celite and washed with $CH_2Cl_2$. combined organic layer was concentrated and purified by column chromatography (1:19 ethyl acetate: toluene) to obtain compound **5** as a white solid (497 mg, 85%). $[\alpha]^{20}_{D}$ +11.6 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 30632927, 2853, 1732, 1602, 1452, 1264, 1178, 1069, 1027, 756, 709 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.06–7.74 (m, 14H), 7.57–7.16 (m, 26H), 5.84 (t, *J* = 9.6 Hz, 1H, H-3′), 5.81 (t, *J* = 9.2 Hz, 1H, H-3), 5.61 (t, *J* = 10.0 Hz, 1H, H-4′), 5.50 (dd, *J* = 9.6, 7.6 Hz, 1H, H-2′), 5.36 (t, *J* = 9.6 Hz, 1H, H-2), 5.26 (t, *J* = 10.0 Hz, 1H, H-4), 4.96 (d, *J* = 7.6 Hz, 1H, H-1′), 4.91 (d, *J* = 10.0 Hz, 1H, H-1), 4.60 (dd, *J* = 12.4, 3.2 Hz, 1H, H6a′), 4.40 (dd, *J* = 12.4, 5.3 Hz, 1H, H6b′), 4.06–4.01 (m, 2H, H-5, H-5′), 4.01–3.95 (m, 2H, H-6ab), $^{13}C$ NMR (100 MHz, $CDCl_3$) *δ* 166.3, 165.9, 165.8, 165.5, 165.4, 165.3, 165.2, 133.7, 133.5, 133.4, 133.2, 131.9, 129.9, 129.9, 129.8, 129.7, 129.4, 129.3, 129.0, 128.9, 128.8, 128.68, 128.64, 128.60, 128.6, 128.5, 128.5, 128.4, 101.2, 86.0, 78.7, 74.2, 73.1, 72.4, 72.0, 70.7, 69.8, 69.7, 68.4, 63.0; HR-ESI-MS (*m/z*): calcd for $C_{67}H_{54}O_{17}S$ $[M + Na]^+$ 1185.2974 found, 1185.2967.

### 2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl-(1→6)-(2,3,4-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(1→6)-(2,3,4,2′,3′-penta-*O*-benzyl)-4′,6′-*O*-benzylidene-*α*,*α*-D-trehalose (11):

A solution of **5** (150 mg, 0.13 mmol) and compound **4** (95 mg, 0.11 mmol) in $CH_2CL_2$ (2 mL) was stirred on activated 3 Å MS (200 mg) for 30 min. The reaction mixture was cooled (0 °C) and NIS (36 mg, 0.16 mmol) and TMSOTf (4 μL, 0.02 mmol) were added. After 30 min, TLC showed that most of the acceptor was consumed. The reaction mixture was diluted with dichloromethane (60 mL), filtered, and the filtrate was washed successively with aqueous sodium thiosulfate (10 mL), water (10 mL), and brine (10 mL). The organic phase was dried over $Na_2SO_4$, concentrated on rotary evaporator and purified by column chromatography to obtain compound **11** (156 mg, 75%). $[\alpha]^{20}_{D}$ +13.0 (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) ν 3065, 3030, 2931, 2858, 1732, 1602, 1496, 1452, 1369, 1264, 1178, 1093, 1027, 756, 710 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.03–8.01 (m, 2H), 7.94–7.83 (m, 8H), 7.78–7.75 (m, 4H), 7.54–7.44 (m, 5H), 7.42–7.30 (m, 14H), 7.30–7.20 (m, 28H), 7.17 (t, *J* = 8.0 Hz, 2H), 6.96 (dd, *J* = 7.4, 3.9 Hz, 2H), 5.79 (t, *J* = 9.5 Hz, 1H), 5.77 (t, *J* = 9.5 Hz, 1H), 5.53 (s, 1H), 5.53–5.41 (m, 3H), 5.36 (t, *J* = 9.5 Hz, 1H), 5.17 (d, *J* = 3.6 Hz, 1H), 5.09 (d, *J* = 3.5 Hz, 1H), 4.97–4.78 (m, 5H), 4.72–4.54 (m, 6H), 4.39–4.36 (m, 2H), 4.35–4.17 (m, 2H), 4.13–3.90 (m, 9H), 3.66–3.33 (m, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) *δ* 166.2, 165.8, 165.4, 165.3, 165.2, 165.0, 139.1, 139.0, 138.6, 138.2, 137.7, 133.6, 133.4, 133.2, 130.0, 129.9, 129.87, 129.7, 129.4, 129.2, 129.0, 128.97, 128.91, 128.6, 128.5, 128.4, 128.36, 128.32, 128.1, 127.99, 127.87, 127.6, 127.5, 126.3, 101.5, 101.3, 100.8, 94.6, 93.9, 82.5, 81.6, 79.4, 79.3, 78.8, 75.5, 75.4, 74.5, 74.1, 73.7, 73.3, 73.0, 72.9, 72.3, 71.9, 71.88, 70.1, 69.9, 69.7, 69.2, 67.5, 63.1, 62.99. HR-ESI-MS (*m/z*): calcd for $C_{115}H_{104}O_{28}$ $[M + Na]^+$ 1955.6606 found, 1956.6608.

**(*β*-D-Glucopyranosyl)-(1→6)-(*β*-D-glucopyranosyl)-(1→6)-*α,α*-D-trehalose (1):**

The solution of **11** (122 mg, 63.08 µmol) in methanolic NaOMe (0.2 M, 5 mL) was stirred at rt for 5 h. Reaction was monitored by LRMS and after complete conversion the reaction mixture was neutralized by addition of acidic resin Amberlite IR 120 H+ (1 g). The resin was filtered off, washed with methanol. The combined organic layer was concentrated, dried and used for next step without purification.

The intermediate obtained in the above step was dissolved in a mixture of EtOH: HOAc (4:1, 5 mL) at rt and $Pd(OH)_2$ (10%, 150 mg) was added to it. The reaction mixture was stirred for 24 h under $H_2$ atmosphere. After complete conversion as indicated by LRMS, the reaction mixture was filtered through Celite and washed with EtOH. The organic layer was concentrated on rotary evaporator and purified by column chromatography on silica gel (100-200 mesh) with gradient elusion (1:9 methanol: $CH_2Cl_2$ to 8:2 methanol: $CH_2Cl_2$) to afford (*β*-D-glucopyranosyl)-(1→6)-(*β*-D-glucopyranosyl)-(1→6)-*α,α*-D-trehalose (**1**) as a white solid (32 mg, 76%). $[\alpha]^{20}_{D}$ +20.9 (*c* 0.67, MeOH); $^1H$ NMR (500 MHz, $CD_3OD$) *δ* 5.15-5.10

(m, 2H, H1, H1’), 4.43 (d, $J$ = 8.0 Hz, 1H), 4.38 (d, $J$ = 8.0 Hz, 1H), 4.15 (d, $J$ = 11.5 Hz, 1H), 4.10 (d, $J$ = 11.5 Hz, 1H), 4.01–3.99 (m, 1H), 3.88–3.78 (m, 8H), 3.70-3.66 (m, 3H), 3.53-3.48 (m, 5H), 3.47-3.30 (m, 3H), 3.23 (t, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, $D_2O$) $\delta$ 102.8, 102.6, 93.3, 93.2, 75.9, 75.7, 75.6, 74.9, 73.1, 72.5, 72.5, 72.2, 71.1, 71.1, 69.7, 69.6, 69.4, 69.3, 68.5, 68.3, 60.7, 60.5; HR-ESI-MS (*m/z*): calcd for $C_{24}H_{42}O_{21}$ $[M + Na]^+$ 689.2111 found, 689.2090.

Note: Due to low solubility of compound **1** in $CD_3OD$, the $^{13}$C NMR spectrum was recorded using $D_2O$ as a solvent.

**Phenyl 4-*O*-benzoyl-2,3-di-*O*-benzyl-6-*O*-*tert*butyldiphenylsilyl-*β*-D-thiogalactopyranoside (7):**

Compound **12** (2.5 g, 6.9 mmol) was dissolved in 80% acetic acid (146 mL, aqueous) and refluxed at 80 °C with stirring for 1 h. Progress of the reaction was monitored by TLC. After 1 h, the reaction mixture was cooled to RT. The reaction mixture was taken in a separating funnel in ethyl acetate. The ethyl acetate layer was washed with $NaHCO_3$ (3 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue on the silica gel (7:1 ethyl acetate: pet ether) yielded the diol product (2.0 g, 96%).

To a solution of diol (2.0 g, 4.42 mmol) in anhydrous acetonitrile (13 mL), imidazole (0.66 g, 9.72 mmol) was added. The solution was stirred for 5 min at RT and TBDPSCl (1.24 mL, 4.86 mmol) was added dropwise. The reaction mixture was stirred at RT in the presence of nitrogen for 1 h. Progress of the reaction was monitored by TLC. After 1 h, the reaction mixture was taken in a separating funnel in ethyl acetate. The ethyl acetate layer was washed with brine (3 × 10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue on the silica gel (1:4 ethyl acetate: pet ether) yielded the C6-OTBDPS protected product (2.32 g, 76%): $[\alpha]^{25}_D$ +0.1 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) $\nu$ 3479, 3066, 2931, 1586, 1427, 1112, 743, 701 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 7.70-7.66 (m, 4H, ArH), 7.56-7.54 (m, 2H, ArH), 7.43-7.40 (m, 4H, ArH), 7.37-7.28 (m, 12H, ArH), 7.23-7.21 (m, 3H, ArH), 4.81 (d, $J$ = 10.5 Hz, 1H, $PhCH_2$), 4.75 (d, $J$ = 10.5 Hz, 1H, $PhCH_2$), 4.71 (s, 2H, $PhCH_2$), 4.60 (d, $J$ = 10.0 Hz, 1H, H-1), 4.10 (bs, 1H, H-4), 3.97-3.89 (m, 2H, H-6), 3.77 (t, $J$ = 9.2 Hz, 1H, H-2), 3.53 (dd, $J$ = 3.0, 9.0 Hz, 1H, H-3), 3.44 (t, $J$ = 5.5 Hz, 1H, H-5), 2.67 (bs, 1H, OH), 1.05 (s, 9H, TBDPS); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 138.4, 137.9, 135.8, 135.7, 134.3, 133.2, 133.1, 131.7, 129.9, 129.0, 128.7, 128.5, 128.4, 128.1, 128.0, 127.96, 127.93, 127.3, 88.0, 82.7, 78.1, 76.9, 75.9, 72.2, 67.1, 63.7, 27.0, 19.34; HR-ESI-MS (*m/z*): calcd for $C_{42}H_{46}O_5SSi$ $[M + Na]^+$ 713.2727, found 713.2724.

To a solution of C6-OTBDPS protected product (2.0 g, 2.89 mmol) in anhydrous dichloromethane (20 mL), anhydrous pyridine (1.2 mL, 14.45 mmol) was added. The solution was stirred for 10 min at 0 °C and benzoyl chloride (0.5 mL, 4.34 mmol) was added dropwise at 0 °C with stirring in the presence of nitrogen. The reaction mixture was slowly warmed to RT and kept stirring for 1 h. Progress of the reaction was monitored by TLC. After 1 h, the reaction mixture was taken in a separating funnel in ethyl acetate. The ethyl acetate layer was washed with brine (3 × 10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue on the silica gel (1:9 ethyl acetate: pet ether) yielded the product **7** (2.18 g, 95%). $[\alpha]^{25}_{D}$ +16.6 (*c* 0.97, $CHCl_3$); IR ($CHCl_3$) $\nu$ 2931, 2857, 1726, 1473, 1452, 1427, 1271, 1111, 745, 701, 504 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.97 (d, 2H, *J* = 7.0 Hz, OBz), 7.66-7.58 (m, 5H, ArH), 7.52-7.50 (m, 2H, ArH), 7.46-7.24 (m, 19H, ArH), 7.14-7.12 (m, 2H, ArH), 5.96 (d, *J* = 3.0 Hz, 1H, H-4), 4.90 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.69 (ABq, *J* = 10.5 Hz, 2H, $PhCH_2$), 4.63 (d, *J* = 9.5 Hz, 1H, H-1), 4.56 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 3.82 (dd, *J* = 2.0, 6.0 Hz, 1H, H-3), 3.80-3.72 (m, 3H, H-5, H-6), 3.66 (t, *J* = 9.2 Hz, 1H, H-2), 1.02 (s, 9H, TBDPS); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 165.6, 138.5, 137.7, 135.7, 135.6, 133.1, 132.9, 130.1, 129.9, 129.8, 129.0, 128.5, 128.3, 127.93, 127.90, 127.8, 127.7, 87.2, 81.7, 77.6, 76.6, 75.8, 72.0, 67.0, 61.8, 26.9, 19.2; HR-ESI-MS (*m/z*): calcd for $C_{49}H_{50}O_6SSi$ $[M + Na]^+$ 817.2990, found 817.2981.

**[4-*O*-benzoyl-2,3-di-*O*-benzyl-6-*O*-*tert*butyldiphenylsilyl-*α*-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (6):**

The solution of the galactosyl thioglycoside donor **7** (0.36 g, 0.45 mmol), the trehalose acceptor **4** (0.32 g, 0.36 mmol) and MS 3Å (0.9 g) in $CH_2Cl_2$: $Et_2O$ (18 mL, 4:1) was stirred under nitrogen atmosphere at RT for about 1 h. The flask was cooled to 0 °C and NIS (146 mg, 0.64 mmol) was added followed by the dropwise addition of TfOH (8 µL, 0.09 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under nitrogen atmosphere for 1 h. The reaction was quenched by adding $NEt_3$ (2-3 drops). The reaction mixture was diluted with $CH_2Cl_2$, filtered through Celite and transferred to a separating funnel. The organic layer was washed with aq. $Na_2S_2O_3$ (2 × 4 mL), $NaHCO_3$, brine, dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue over silica gel (1:3 ethyl acetate: pet ether) yielded the desired trisaccharide **6** (0.45 g, 78%): $[\alpha]^{25}_{D}$ +44.7 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) *ν* 3066, 2932, 2858, 1726, 1602, 1496, 1454, 1428, 1272, 1161, 1027, 754, 698 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) *δ* 8.00 (d, *J* = 10.0 Hz, 2H, OBz), 7.63-7.08 (m, 53H, ArH), 5.91 (s, 1H, H-4), 5.54 (s, 1H, PhCH), 5.14 (d, *J* = 3.5 Hz, 1H, H-1), 5.08 (d, *J* = 2.0 Hz, 2H, 2×H-1), 4.94 (Ap. t, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.85-4.82 (m, 4H), 4.71-4.54 (m, 8H), 4.25-4.20 (m, 1H), 4.16-4.08 (m, 3H), 4.05-3.97 (m, 3H), 3.84 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.70-3.60 (m, 5H), 3.54 (dd, *J* = 3.8, 9.5 Hz, 1H), 3.52-3.49 (m, 1H), 3.40 (dd, *J* = 5.0, 10.0 Hz, 1H), 1.00 (s, 9H, TBDPS); $^{13}$C NMR (125 MHz, $CDCl_3$) *δ* 165.7, 139.1, 139.0, 138.9, 138.8, 138.4, 138.3, 138.2, 137.7, 135.7, 135.6, 133.3, 133.0, 130.5, 130.0, 129.8, 129.7, 129.0, 128.6, 128.5, 128.48, 128.46, 128.40, 128.3, 128.1, 128.08, 128.06, 128.01, 127.89, 127.86, 127.81, 127.77, 127.73, 127.6, 127.58, 127.54, 127.4, 126.3, 101.4, 98.2, 94.6, 94.0, 82.5, 81.8, 79.8, 79.0, 78.7, 75.86, 75.83, 75.6, 75.4, 75.1, 73.6, 73.4, 72.8, 71.6, 69.4, 69.1, 68.2, 65.6, 63.0, 62.0, 26.8, 19.2; HR-ESI-MS (*m/z*): calcd for $C_{97}H_{100}O_{17}Si$ $[M + Na]^+$ 1588.6622, found 1588.6654.

### [4-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (13):

To a solution of compound **6** (0.15 g, 0.10 mmol) in anhydrous THF (2.8 mL), TBAF (0.51 mL, 1 M solution in THF) was added dropwise at 0 °C. The reaction mixture was warmed to RT after 20 min. Progress of the reaction was monitored by TLC. After 6 h, the reaction mixture was taken in a separating funnel in ethyl acetate. The ethyl acetate layer was washed with brine (3 × 10 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue on the silica gel (1:2 ethyl acetate: pet ether) yielded the product **13** (0.117 g, 92%): $[\alpha]^{25}_{D}$ +55.6 (*c* 1.9, $CHCl_3$); IR ($CHCl_3$) *ν* 3486, 3030, 2937, 1722, 1602, 1496, 1454, 1274, 754, 697 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) *δ* 8.00 (d, *J* = 10 Hz, 2H, OBz), 7.59-7.15 (m, 43H, ArH), 5.56 (d, *J* = 2.5 Hz, 1H, H-4), 5.55 (s, 1H, PhCH), 5.15 (d, *J* = 3.5 Hz, 1H, H-1), 5.09 (d, *J* = 3.5 Hz, 1H, H-1), 5.08 (d, *J* = 3.5 Hz, 1H, H-1), 4.96 (Ap. t, *J* = 11.5 Hz, 2H, $PhCH_2$), 4.88-4.83 (m, 3H, $PhCH_2$), 4.78 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.78-4.54 (m, 8H, $PhCH_2$), 4.26 (td, *J* = 5.0, 10.0 Hz, 1H), 4.19 (d, *J* = 10.0 Hz, 1H), 4.14-4.09 (m, 2H), 4.05 (t, *J* = 10.0 Hz, 1H), 3.96 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.93-3.91 (m, 2H), 3.77 (t, *J* = 10.0 Hz, 1H), 3.69-3.63 (m, 3H), 3.61-3.55 (m, 2H), 3.53 (dd, *J* = 2.5, 8.0 Hz, 1H), 3.45 (dd, *J* = 4.0, 9.0 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) *δ* 167.1, 138.9, 138.8, 138.7, 138.6, 138.2, 138.1, 138.0, 137.5, 133.4, 130.0, 129.5, 128.9, 128.54, 128.50, 128.46, 128.41, 128.39, 128.36, 128.31, 128.2, 128.0, 127.9, 127.78, 127.74, 127.71, 127.6, 127.57, 127.50, 126.1, 101.2, 98.2, 94.8, 94.2, 82.4, 81.6, 79.7, 78.9, 78.6, 77.9, 75.5, 75.3, 75.1, 74.9, 73.6, 73.3, 72.5, 71.7, 71.1, 69.3, 69.0, 66.1, 62.9, 61.0; HR-ESI-MS (*m/z*): calcd for $C_{81}H_{82}O_{17}$ $[M + Na]^+$ 1349.5444, found 1349.5463.

**[4-*O*-benzoyl-2,3-di-*O*-benzyl-6-*O*-*tert*butyldiphenylsilyl-*α*-D-galactopyranosyl]-(1→6)-[4-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (14):**

The solution of the galactosyl thioglycoside donor **7** (82 mg, 0.104 mmol), the trisaccharide acceptor **13** (0.11 g, 0.082 mmol) and MS 3Å (0.2 g) in $CH_2Cl_2$: $Et_2O$ (4.6 mL, 4:1) was stirred under nitrogen atmosphere at RT for about 1 h. The flask was cooled to 0 °C and NIS (34 mg, 0.15 mmol) was added followed by the dropwise addition of TfOH (1.8 µL, 0.02 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under nitrogen atmosphere for 1 h. The reaction was quenched by adding $NEt_3$ (1 drop). The reaction mixture was diluted with $CH_2Cl_2$, filtered through Celite and transferred to a separating funnel. The organic layer was washed with aq. $Na_2S_2O_3$ (2 × 4 mL), $NaHCO_3$, brine, dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue over silica gel (1:3 ethyl acetate: pet ether) yielded the desired tetrasaccharide **14** (0.15 g, 89%): $[\alpha]^{25}_{D}$ +42.6 (*c* 1.64, $CHCl_3$); IR ($CHCl_3$) *ν* 2932, 1724, 1602, 1496, 1454, 1428, 1271, 756, 698 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 7.0 Hz, 2H, OBz), 7.94 (d, *J* = 7.0 Hz, 2H, OBz), 7.60-7.08 (m, 66H, ArH), 5.90 (d, *J* = 3.0 Hz, 1H, H-4), 5.87 (d, *J* = 2.5 Hz, 1H, H-4), 5.57 (s, 1H, PhCH), 5.21 (d, *J* = 3.0 Hz, 1H, H-1), 5.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.15 (d, *J* = 3.0 Hz, 1H, H-1), 4.99 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.96 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.90-4.80 (m, 4H, $PhCH_2$), 4.86 (d, *J* = 2.5 Hz, 1H, H-1), 4.78-4.43 (m, 12H, $PhCH_2$), 4.27-4.19 (m, 2H), 4.18 (dd, *J* = 4.0, 10.0 Hz, 1H), 4.16-4.12 (m, 3H), 4.09 (t, *J* = 10.0 Hz, 1H), 4.00 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.98 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.93 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.89-3.86 (m, 2H), 3.85 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.70 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.70-3.60 (m, 6H), 3.58 (dd, *J* = 4.0, 9.0 Hz, 1H), 3.45 (dd, *J* = 3.0, 8.0 Hz, 1H), 0.98 (s, 9H, TBDPS); $^{13}C$ NMR (125 MHz, $CDCl_3$) *δ* 165.9, 165.6, 139.1, 138.9, 138.8, 138.79, 138.73, 138.4, 138.34, 138.31, 138.2, 137.7, 135.68, 135.61, 133.2, 133.0, 132.9, 130.3, 130.2, 130.1, 129.9, 129.79, 129.76, 129.0, 128.6, 128.57, 128.53, 128.46, 128.43, 128.36, 128.34, 128.32, 128.2, 128.17, 128.12, 128.04, 128.01, 127.88, 127.82, 127.78, 127.73, 127.70, 127.66, 127.62, 127.57, 127.54, 127.50, 126.3, 101.3, 98.6, 98.5, 94.7, 94.1, 82.5, 81.8, 79.8, 78.8, 78.7, 77.7, 76.8, 75.78, 75.70, 75.6, 75.5, 75.4, 75.1, 73.5, 73.4, 73.3, 72.8, 72.1, 71.8, 71.5, 69.7, 69.1, 68.6, 68.2, 67.8, 66.5, 66.0, 63.0, 62.1, 26.8, 19.1; HR-ESI-MS (*m/z*): calcd for $C_{124}H_{126}O_{23}Si$ [M + K]$^+$ 2050.8123, found 2050.8121.

### (*α*-D-galactopyranosyl)-(1→6)-(*α*-D-galactopyranosyl)-(1→6)-*α,α*-D-glucopyranosyl)-(1↔1)-*α*-D-glucopyranoside (2):

To a solution of compound **14** (0.14 g, 0.07 mmol) in anhydrous THF (2 mL), TBAF (0.35 mL, 1 M solution in THF) was added dropwise at 0 °C. The reaction mixture was warmed to RT after 20 min. Progress of the reaction was monitored by TLC. After 8 h, the reaction mixture was taken in a separating funnel in ethyl acetate. The ethyl acetate layer was washed with brine (3 × 5 mL). The organic layer was dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue on silica gel (1:2 ethyl acetate: pet ether) yielded the tetrasaccharide mono-ol product (0.124 g, 91%): $[\alpha]^{25}_{D}$ +44.8 (*c* 1.68, $CHCl_3$); IR ($CHCl_3$) *ν* 3485, 3030, 2932, 1722, 1496, 1453, 1273, 1108, 754, 697 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) *δ* 8.10 (d, *J* = 8.0 Hz, 2H, OBz), 8.02 (d, *J* = 8.0 Hz, 2H, OBz), 7.64-7.21 (m, 56H, ArH), 5.91 (d, *J* = 2.5 Hz, 1H, H-4), 5.65 (d, *J* = 2.5 Hz, 1H, H-4), 5.59 (s, 1H, PhCH), 5.24 (d, *J* = 3.5 Hz, 1H, H-1), 5.18 (d, *J* = 4.0 Hz, 1H, H-1), 5.17 (d, *J* = 3.5 Hz, 1H, H-1), 5.02 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.98 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.91 (d, *J* = 3.5 Hz, 1H, H-1), 4.90-4.52 (m, 16H, $PhCH_2$), 4.29-4.26 (m, 3H), 4.18-4.09 (m, 3H), 4.07 (dd, *J* = 4.0, 9.0 Hz, 1H), 4.03 (dd, *J* = 4.0, 9.0 Hz, 1H), 3.97-3.93 (m, 2H), 3.85 (t, *J* = 10.0 Hz, 2H), 3.73-3.71 (m, 4H), 3.67 (t, *J* = 10.0 Hz, 2H), 3.62 (dd, *J* = 2.5, 7.8 Hz, 2H), 3.51 (dd, *J* = 3.0, 8.0 Hz, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) *δ* 167.1, 165.9, 139.1, 139.0, 138.8, 138.5, 138.38, 138.34, 138.28, 138.24, 137.7, 133.5, 133.2, 130.2, 130.1, 129.6, 129.0, 128.63, 128.61, 128.57, 128.55, 128.47, 128.44, 128.38, 128.33, 128.13, 128.10, 128.05, 128.01, 127.9, 127.8, 127.75, 127.73, 127.68, 127.63, 127.5, 126.2, 101.3, 98.9, 98.5, 94.7, 94.0, 82.4, 81.7, 79.8, 78.8, 78.7, 77.7, 76.3, 75.6, 75.4, 75.0, 73.5, 73.4, 73.3, 72.9, 72.1, 71.6, 69.9, 69.2, 69.1, 68.7, 67.8, 66.2, 63.0, 61.2; HR-ESI-MS (*m/z*): calcd for $C_{108}H_{108}O_{23}$ [M + Na]$^+$ 1796.7207, found 1796.7211.

The tetrasaccharide mono-ol product (80 mg, 0.05 mmol) was dissolved in anhydrous methanol (2 mL) followed by the addition of NaOMe (10 mg). The solution was stirred at RT under nitrogen atmosphere for 12 h. The reaction was quenched by adding Amberlite IR120H$^+$ (40 mg). The solution was filtered using methanol. The filtrate was concentrated under reduced pressure and the column chromatography of the residue on silica gel (9:1 ethyl acetate: pet ether) yielded the tetrasaccharide triol product (64 mg, 91%): $[\alpha]^{25}_{D}$ -52.1 (*c* 0.96, $CHCl_3$); IR ($CHCl_3$) *ν* 3463, 3030, 2927, 1497, 1454, 1215, 1091, 1027, 754, 697 cm$^{-1}$; $^1$H

NMR (400 MHz, $CDCl_3$) $\delta$ 7.54-7.21 (m, 50H, ArH), 5.57 (s, 1H, PhCH), 5.21 (d, $J$ = 4.0 Hz, 1H, H-1), 5.13 (d, $J$ = 3.6 Hz, 1H, H-1), 5.01 (d, $J$ = 3.2 Hz, 1H, H-1), 4.99 (d, $J$ = 11.2 Hz, 1H, $PhCH_2$), 4.95 (d, $J$ = 12.0 Hz, 1H, $PhCH_2$), 4.87 (d, $J$ = 4.0 Hz, 1H, H-1), 4.85 (d, $J$ = 11.0 Hz, 1H, $PhCH_2$), 4.74 (Ap. t, $J$ = 11.6 Hz, 6H, $PhCH_2$), 4.69-4.58 (m, 9H, $PhCH_2$), 4.28-4.21 (m, 2H), 4.16-4.10 (m, 3H), 4.07 (t, $J$ = 8.0 Hz, 1H), 4.02 (d, $J$ = 2.8 Hz, 1H), 3.91-3.84 (m, 3H), 3.86 (dd, $J$ = 3.0, 10.0 Hz, 2H), 3.81 (dd, $J$ = 3.0, 10.0 Hz, 2H), 3.78-3.71 (m, 5H), 3.66 (dd, $J$ = 4.0, 10.0 Hz, 2H), 3.62-3.57 (m, 2H), 3.48 (dd, $J$ = 3.6, 9.6 Hz, 1H), 2.94-2.75 (2×bs, OH); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 139.0, 138.9, 138.83, 138.80, 138.4, 138.3, 138.29, 138.21, 138.1, 137.6, 129.0, 128.67, 128.63, 128.55, 128.52, 128.50, 128.47, 128.43, 128.3, 128.08, 128.06, 127.95, 127.93, 127.91, 127.87, 127.85, 127.83, 127.80, 127.77, 127.70, 127.59, 127.53, 126.2, 101.3, 98.6, 98.2, 94.7, 94.1, 82.4, 81.7, 79.8, 78.8, 78.6, 77.8, 77.5, 76.8, 76.0, 75.66, 75.60, 75.3, 74.9, 73.5, 73.4, 73.0, 72.6, 72.4, 71.4, 69.5, 69.1, 68.9, 68.1, 67.6, 67.4, 66.2, 63.1, 63.0; HR-ESI-MS (*m/z*): calcd for $C_{94}H_{100}O_{21}$ $[M + Na]^+$ 1588.6649, found 1588.6690.

The tetrasaccharide triol (60 mg, 0.04 mmol) and 20% $Pd(OH)_2/C$ (140 mg) in acetic acid: water (20 mL, 1:1) was stirred under hydrogen atmosphere for 20 h. the solution was filtered through Celite pad and concentrated under reduced pressure and the column chromatography of the residue on silica gel (7:3 methanol: $CH_2Cl_2$) yielded the tetrasaccharide product **2** (26 mg, 98%): $[\alpha]^{25}_D$ +81.9 (*c* 0.52, MeOH: $H_2O$ = 1:1); $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 5.14 (d, $J$ = 3.5 Hz, 1H, H-1), 5.13 (d, $J$ = 3.5 Hz, 1H, H-1), 4.93 (d, $J$ = 4.0 Hz, 2H, H-1), 4.13-4.06 (m, 2H), 3.94-3.86 (m, 6H), 3.85-3.76 (m, 7H), 3.75-3.66 (m, 5H), 3.56-3.51 (m, 2H), 3.41-3.34 (m, 2H); $^{13}$C NMR (125 MHz, $D_2O$) $\delta$ 97.9, 97.6, 93.4, 93.3, 72.8, 72.5, 72.2, 70.9, 70.4, 69.7, 69.6, 69.5, 69.3, 69.2, 68.7, 68.3, 68.2, 66.4, 65.3, 61.1, 60.5; HR-ESI-MS (*m/z*): calcd for $C_{24}H_{42}O_{21}$ $[M + Na]^+$ 689.2111, found 689.2117.

Note: Due to low solubility of compound **2** in $CD_3OD$, the $^{13}$C NMR spectrum was recorded using $D_2O$ as a solvent.

**Phenyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (8):**

To an ice-cooled solution of phenyl 2,3,4-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside (0.28 g, 0.516 mmol) in $CH_2Cl_2$ (3 mL) were added pyridine (0.21 mL, 2.58 mmol) and BzCl (0.09 mL, 0.774 mmol). The mixture was stirred at rt for 30 minutes, then diluted with $CH_2Cl_2$ (10 mL) and washed with $NaHCO_3$ solution (2X5 mL), dried on anhydrous $Na_2SO_4$ and concentrated in vacuo. Purification by silica gel column chromatography (1:4 ethyl acetate: pet ether) afforded Phenyl 6-*O*-Benzoyl-2,3,4-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside **8** as white solid (0.327 g, 98%). $[\alpha]^{20}_{D}$ +4.388 (*c* 0.67, $CHCl_3$); IR ($CHCl_3$) ν 3030, 2101, 1719, 1454, 1274, 1067, 752, 698 cm$^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 8.03 (d, *J* = 7.2 Hz, 2H, ArH), 7.62-7.11 (m, 23H, ArH), 4.95-4.85 (m, 4H, $CH_2Ph$), 4.76-4.61 (m, 4H, $CH_2Ph$, H1, H6b), 4.43 (dd, *J* = 11.6, 4.8 Hz, 1H, H6a), 3.77 (t, *J* = 8.8 Hz, 1H, H3), 3.68-3.67 (m, 1H, H5), 3.66 (t, *J* = 8.8 Hz, 1H, H4), 3.53 (t, *J* = 9.2 Hz, 1H, H2); $^{13}C$ NMR (125 MHz, $CDCl_3$) *δ* 166.3, 138.3, 138.1, 137.7, 134.7, 133.4, 133.3, 132.5, 130.7, 130.1, 129.9, 129.0, 129.0, 128.7, 128.64, 128.57, 128.35, 128.27, 128.22, 128.11, 128.08, 128.04, 127.8, 87.5, 86.9, 80.9, 77.7, 77.4, 76.2, 75.6, 75.4, 63.7; HRMS calcd for $C_{40}H_{38}O_6S$ $[M +Na]^+$ 669.2281, found 669.2271.

**[2,3-di-*O*-benzyl-4-*O*-benzoyl-6-*O*-tertbutyldiphenylsilyl-α-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-2,3,6-tri-O-benzyl-*α*-D-glucopyranoside (15):**

To a solution of compound **11** (100 mg, 0.064 mmol) in $CH_2Cl_2$ (1 mL), was added 1 M $Et_3SiH$ (in THF) at 0 °C (ice bath) under a $N_2$ atmosphere, after 10 min TfOH was added in a drop wise manner. The reaction mixture was stirred for 1 h and then quenched by addition of $NaHCO_3$ solution at the same temperature and then brought to rt. The crude product was extracted in $CH_2Cl_2$ (10 mL × 2), dried on anhydrous $Na_2SO_4$ and concentrated *in vacuo*. Purification by silica gel column chromatography (1:4 ethyl acetate: pet ether) afforded compound **15** as colorless sticky solid (60 mg, 60%) along with benzylidene acetal hydrolyzed byproduct (25%, 23.6 mg). $[\alpha]^{20}_{D}$ +50.1 (*c* 1.84, $CHCl_3$); IR ($CHCl_3$) ν 3464, 3030, 2932, 2778, 1726, 1496, 1454, 1361, 1272, 1215, 1110, 754, 698 cm$^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 8.0 (d, *J* = 7.2 Hz, 2H, ArH), 7.64-7.10 (m, 53H, ArH), 5.90 (d, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 5.16 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.90 (t, *J* = 11.2 Hz, 2H, $CH_2Ph$), 4.88-4.44 (m, 14H, $CH_2Ph$), 4.17-3.97 (m, 5H), 3.9-3.81 (m, 2H), 3.77 (t, *J* = 9.6 Hz, 1H), 3.67-3.63 (m, 4H), 3.56-3.46 (m, 4H), 3.38 (dd, *J* = 9.6, 3.6 Hz, 1H), 1.01 (s, 9H, $CH_3$); $^{13}C$ NMR (125 MHz, $CDCl_3$) *δ* 165.7, 139.2, 138.98 138.9, 138.8, 138.4, 138.4, 138.1, 135.7, 135.6, 133.3, 133.0, 130.5 130.0, 129.9, 129.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 98.3, 93.9, 93.8, 81.8, 81.1, 79.8, 79.1, 77.9, 75.8, 75.8, 75.6, 75.4, 75.2, 73.8, 73.0, 72.8, 72.7, 71.6, 70.9, 70.7, 69.5, 69.4, 68.2, 65.6, 62.1, 26.9, 19.2; HRMS calcd for $C_{97}H_{102}O_{17}Si$ $[M +Na]^+$ 1589.6778, found 1589.6784.

**[2,3-di-*O*-benzyl-4-*O*-benzoyl-6-*O*-*tert*butyldiphenylsilyl-*α*-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-4-*O*-acetyl-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside:**

Pyridine (4.6 µL, 0.05 mmol) and DMAP (0.3 mg, 0.0025 mmol) was added to a clear solution of **15** (18.0 mg, 0.01 mmol) in $CH_2Cl_2$ (0.5 mL) at rt. Next, acetic anhydride (2.3 µL, 0.02 mmol) was to the reaction mixture. Then, the reaction mixture was kept at room temperature for 1 h. After complete consumption of starting material, the reaction mixture was concentrated *in vacuo* and the obtained residue was purified by silica gel chromatography (1:4 ethyl acetate: pet ether) to obtain C4-OAc compound as a sticky solid (17.5 mg, 95%). $[\alpha]^{20}_{D}$ +45.8 (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) ν 3029, 2931, 2856, 1805, 1745, 1725, 1454, 1361, 1272, 1162, 1107, 754, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.00 (d, *J* = 7.2 Hz, 2H, ArH), 7.64-7.06 (m, 53H, ArH), 5.89 (d, *J* = 2.4 Hz, 1H), 5.17 (t, *J* = 3.2 Hz, 1H), 5.09 (d, *J* = 3.6 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 4.96 (d, *J* = 11.2 Hz, 1H, $CH_2Ph$), 4.88-4.81 (m, 4H, $CH_2Ph$), 4.67-4.36 (m, 12H, $CH_2Ph$) 4.15-4.11 (m, 2H), 4.07-3.97 (m, 3H), 3.94 (t, *J* = 9.5 Hz, 1H), 3.83 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.77 (t, *J* = 9.6 Hz, 1H), 3.71-3.52 (m, 5H), 3.37 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.27-3.2 (m, 2H), 1.86 (s, 3H. $CH_3$), 1.01 (s, 9H, $CH_3$); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 169.8, 165.7, 139.2, 138.98 138.9, 138.8, 138.4, 138.4, 138.1, 135.7, 135.6, 133.3, 133.0, 130.5 130.0, 129.9, 129.8, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 98.3, 93.4, 81.8, 81.1, 79.8, 79.1, 77.9, 75.8, 75.8, 75.6, 75.4, 75.2, 73.8, 73.0, 72.8, 72.7, 71.6, 70.9, 70.7, 69.5, 69.4, 68.2, 65.6, 62.1, 26.9, 21.1, 19.2; HRMS calcd for $C_{99}H_{104}O_{18}Si$ $[M+Na]^+$ 1631.6890, found 1631.6854.

**[4-*O*-benzoyl-2,3-di-*O*-benzyl-6-*O*-*tert*butyldiphenylsilyl-*α*-D-galactopyranosyl]-(1→6)-(2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(1↔1)-(2,3,6-tri-*O*-benzyl-*α*-D-glucopyranosyl)-(4→1)-2,3,4-tri-*O*-benzyl-6-*O*-benzoyl-*α*-D-glucopyranoside (16):**

The solution of the donor **8** (0.06 g, 0.0893 mmol), acceptor **15** (0.07 g, 0.045 mmol) and MS 3Å (180 mg) in $CH_2Cl_2/Et_2O$ (2.1/1.5 mL) was stirred under nitrogen atmosphere at RT for 10 minutes. The flask was cooled to 0 °C and NIS (0.03 g, 0.134 mmol) was added followed by the dropwise addition of TfOH (2.4 µL, 0.027 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under nitrogen atmosphere for 2 h. The reaction was quenched by adding $NEt_3$ (2-3 drops). The reaction mixture was diluted with $CH_2Cl_2$, filtered through Celite and transferred to a separating funnel. The organic layer was washed with aq. $Na_2S_2O_3$ (2 × 4 mL), $NaHCO_3$, brine, dried over $Na_2SO_4$, filtered and concentrated. Column chromatography of the residue over silica gel yielded the desired tetrasaccharide **16** (0.075 g, 80%). $[\alpha]^{20}_{D}$

+45.1 (*c* 1.31, $CHCl_3$); IR ($CHCl_3$) ν 3028, 2932, 2858, 1724, 1496, 1453, 1360, 1273, 1216, 1107, 754, 697 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) *δ* 8.0 (t, *J* = 8.4 Hz, 4H, ArH), 7.64-7.07 (m, 71H, ArH), 5.9 (bs, 1H), 5.56 (d, *J* = 1.6 Hz, 1H), 5.21 (d, *J* = 3.6 Hz, 1H), 5.17 (d, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 5.03-4.43 (m, 22H, $CH_2Ph$), 4.32 (bs, 2H), 4.17-3.93 (m, 9H), 3.45-3.56 (m, 8H), 3.5-3.45 (m, 3H), 3.39 (dd, *J* = 9.6, 3.6 Hz, 1H), 1.01 (s, 9H, $CH_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) *δ* 166.3, 165.7, 139.3, 139.2, 138.9, 138.7, 138.5, 138.4, 138.2, 138.2, 138.0, 138.0, 135.7, 135.6, 133.3, 133.1, 133.0, 130.5, 130.2, 130.0, 129.9, 129.8, 129.2, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.34, 128.28, 128.24, 128.17, 128.07, 127.85, 127.73, 127.71, 127.63, 127.6, 127.53, 127.44, 127.41, 127.1, 126.8, 98.3, 97.1, 94.0, 93.5, 81.96, 81.9, 81.5, 80.0, 79.8, 79.4, 77.9, 77.8, 75.9, 75.8, 75.7, 75.4, 75.17, 74.18, 74.0, 73.5, 72.99, 72.9, 72.8, 71.6, 70.63, 69.62, 69.5, 68.7, 68.2, 65.6, 63.5, 62.1, 26.9, 19.2; HRMS calcd for $C_{131}H_{134}O_{23}Si$ [M +Na]$^+$ 2125.8977, found 2125.8968.

***α*-D-galactopyranosyl-(1→6)-*α*-D-glucopyranosyl-(1↔1)-*α*-D-glucopyranosyl-(4→1)-*α*-D-glucopyranoside (3):**

To a solution of compound **16** (0.07 g, 0.033 mmol) in THF (1 mL) was added TBAF (0.17 mL, 0.166 mmol) at rt and the reaction mixture was stirred for 2 h. After complete conversion of starting material, reaction mixture was concentrated on rotary evaporator and purified by column chromatography to afford C6-OH derivative of compound **16** as a sticky solid (0.057 g, 92%). $[\alpha]^{20}_D$ +53.5 (*c* 0.6, $CHCl_3$); IR ($CHCl_3$) ν 3463, 3029, 2928, 1722, 1453, 1360, 1274, 1216, 1158, 1106, 1070, 1027, 753, 697 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) *δ* 8.00 (t, *J* = 8.3 Hz, 4H, ArH), 7.64-7.07 (m, 61H, ArH), 5.90 (bs, 1H), 5.53 (d, *J* = 3.2 Hz, 1H), 5.22 (d, *J* = 3.6 Hz, 1H), 5.17 (d, *J* = 3.6 Hz, 1H), 5.06-5.03 (m, 2H), 4.97-4.44 (m, 21H, $CH_2Ph$), 4.31 (bs, 2H), 4.17-3.90 (m, 10H), 3.81-3.42 (m, 11H); $^{13}$C NMR (125 MHz, $CDCl_3$) *δ* 167.3, 166.3, 139.3, 139.1, 138.85, 138.71, 138.66, 138.37, 138.21, 138.18, 138.15, 138.09, 138.04, 133.57, 133.15, 130.18, 129.86, 129.78, 129.66, 128.67, 128.61, 128.59, 128.49, 128.43, 128.29, 128.24, 128.17, 128.11, 128.05, 128.0, 127.95, 127.87, 127.85, 127.75, 127.72, 127.68, 127.62, 127.44, 127.39, 127.09, 126.82, 126.78, 98.36, 97.16, 94.25, 93.79, 81.96, 81.87, 81.5, 80.02, 79.73, 79.6, 78.09, 77.82, 75.92, 75.73, 75.67, 75.39, 75.24, 75.13, 74.27, 74.17, 73.5, 73.1, 72.99, 72.62, 71.84, 71.3, 70.7, 69.6, 69.4, 68.7, 66.3, 63.5, 61.2; HRMS calcd for $C_{115}H_{116}O_{23}Si$ [M +Na]$^+$ 1887.7794, found 1887.7808

The solution of C6-OH derivative of compound **16** (35 mg, 18.8 µmol) in methanolic NaOMe (0.2 M, 1 mL) was stirred at rt for 5 h. Reaction was monitored by LRMS and after complete conversion the reaction mixture was neutralized by addition of acidic resin

Amberlite IR 120 H+ (100 mg). The resin was filtered off, washed with methanol. The combined organic layer was concentrated, dried and used for next step without purification.

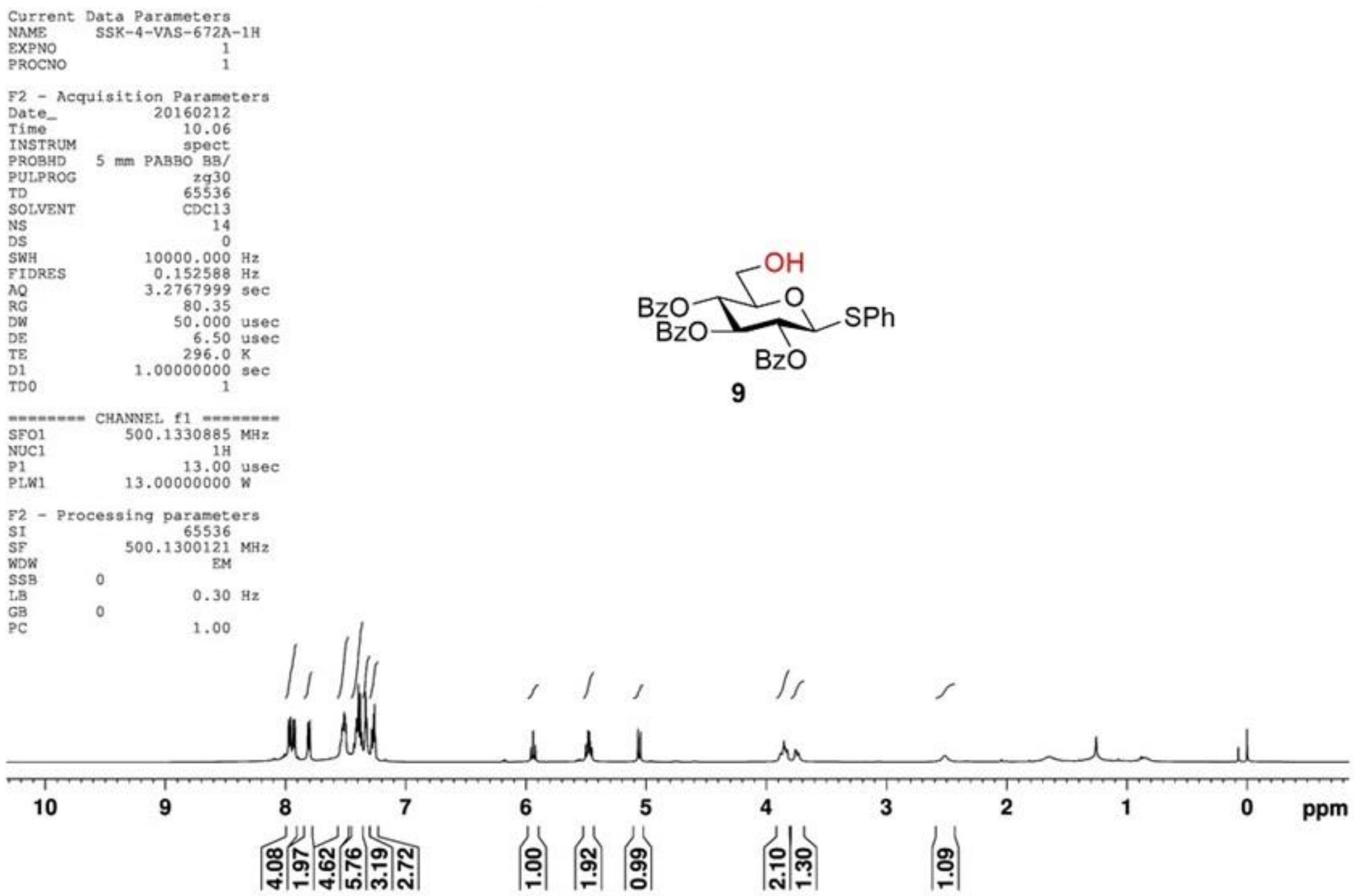
The intermediate obtained in the above step was dissolved in 50% aqueous AcOH (5 mL) at rt and $Pd(OH)_2$ (10%, 50 mg) was added to it. The reaction mixture was stirred for 24 h under $H_2$ atmosphere. After complete conversion as indicated by LRMS, the reaction mixture was filtered through Celite and washed with MeOH. The organic layer was concentrated on rotary evaporator and purified by column chromatography on silica gel (100-200 mesh) with gradient elusion (1:9 methanol: $CH_2Cl_2$ to 8:2 methanol: $CH_2Cl_2$) to afford desired product **3** as a white solid (11.5 mg, 92% over two steps).

$[\alpha]^{20}_{D}$ +65.96 (*c* 0.5, MeOH:$H_2O$ = 1:1); $^1H$ NMR (500 MHz, $CD_3OD$) $\delta$ 5.25 (bs, 1H), 5.15(bs, 2H), 4.85 (bs, 1H), 4.13-4.02 (m, 2H), 3.97-3.88 (m, 5H), 3.85-3.80 (m, 6H), 3.77-3.68 (m, 5H), 3.66-3.61 (m, 3H), 3.56-3.49 (m, 2H), 3.44-3.40 (m, 1H); $^{13}C$ NMR (125 MHz, $CD_3OD$: MeOD 1:1) $\delta$ 100.6, 98.2, 93.64, 93.55, 78.6, 73.4, 73.0, 72.3, 71.4, 71.1, 71.0, 70.7, 70.1, 69.9, 69.7, 69.4, 68.7, 65.6, 61.1, 60.9, 60.6; HRMS calcd for $C_{24}H_{42}O_{21}$ $[M+Na]^+$ 689.2111, found 689.2113.

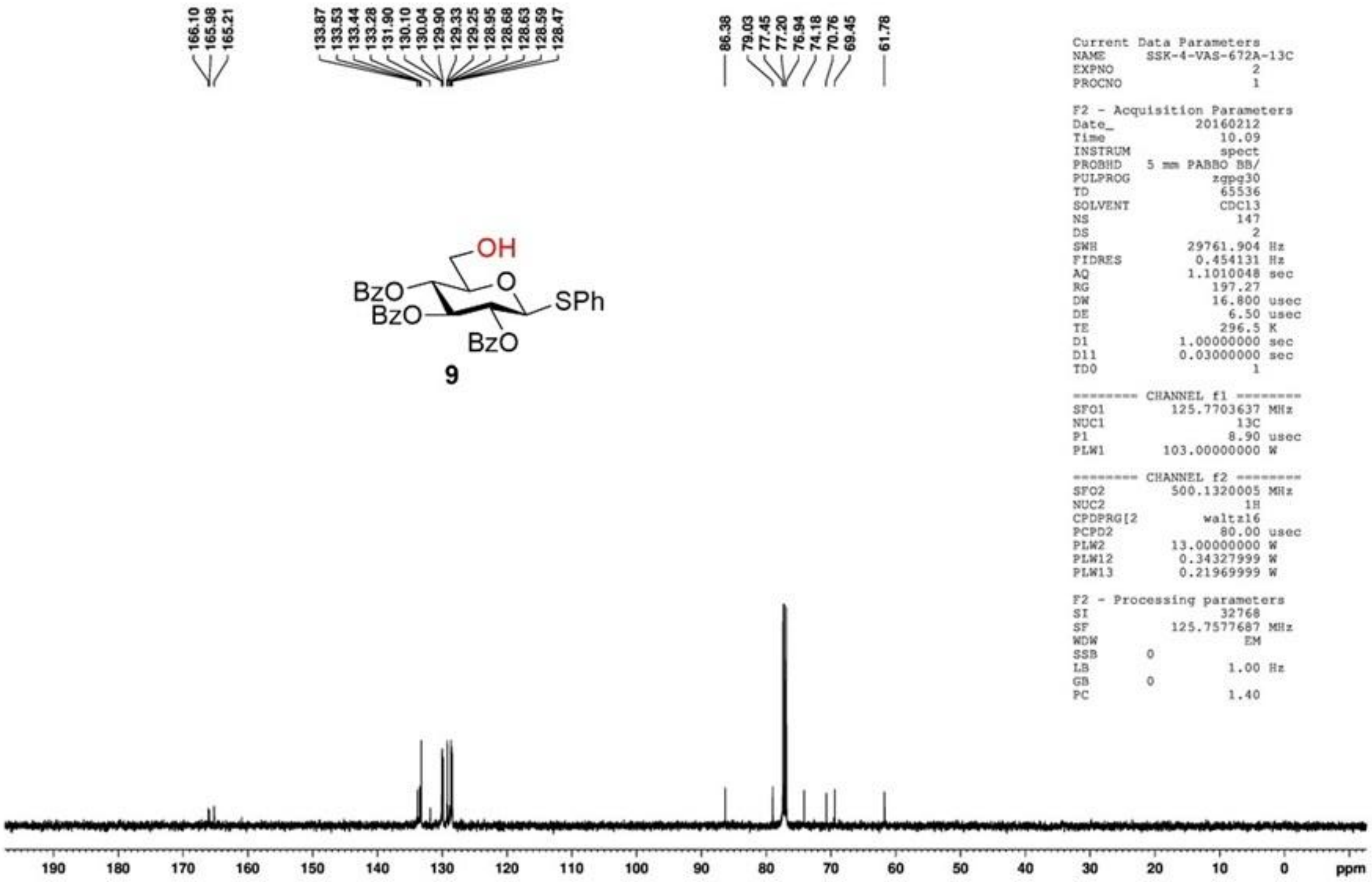
Note: Due to low solubility of compound **3** in $CD_3OD$, the $^{13}C$ NMR spectrum was recorded using $CD_3OD$: $D_2O$ (1:1) mixture as a solvent.

## II. Spectra

SSK-4-VAS-672A-1H



```
Current Data Parameters
NAME     SSK-4-VAS-672A-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160212
Time                 10.06
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      14
DS                       0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                   80.35
DW                  50.000 usec
DE                    6.50 usec
TE                   296.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                   13.00 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1300121 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
```

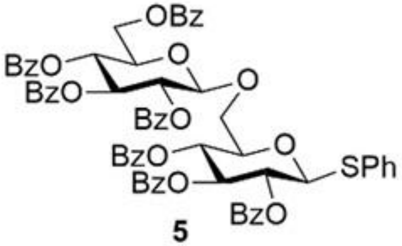


9

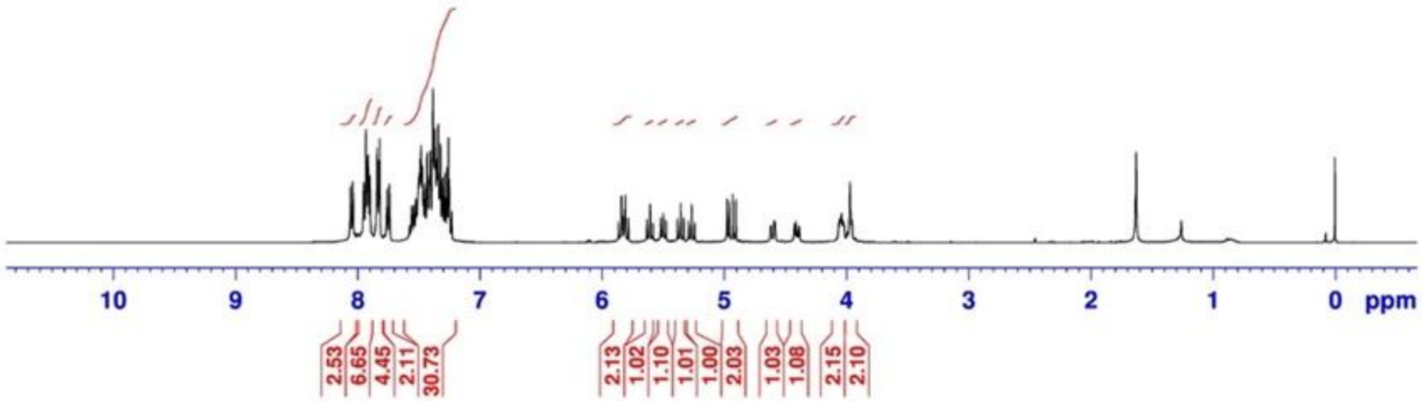
```
Current Data Parameters
NAME     SSK-4-VAS-672A-13C
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_            20160212
Time                10.09
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    147
DS                      2
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 197.27
DW                 16.800 usec
DE                   6.50 usec
TE                  296.5 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                 13C
P1                   8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                  32768
SF           125.7577687 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

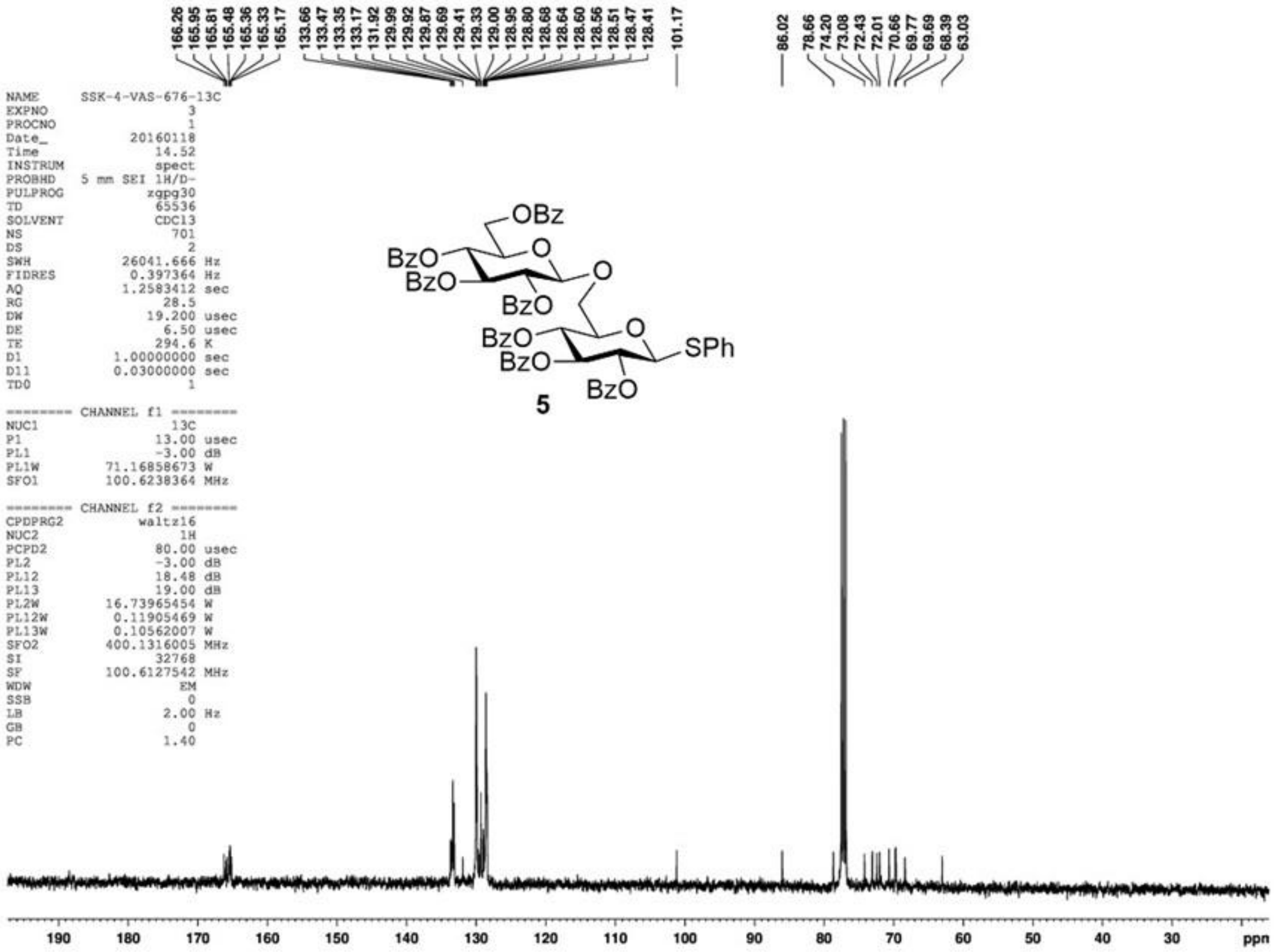
```
NAME      SSK-4-VAS-676-1H
EXPNO                    4
PROCNO                   1
Date_             20160118
Time                 15.21
INSTRUM              spect
PROBHD    5 mm SEI 1H/D-
PULPROG               zg30
TD                   54274
SOLVENT              CDCl3
NS                      75
DS                       0
SWH               8223.685 Hz
FIDRES            0.151522 Hz
AQ               3.2999091 sec
RG                      32
DW                  60.800 usec
DE                    6.50 usec
TE                   294.5 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.75 usec
PL1                  -1.00 dB
PL1W           10.56200695 W
SFO1           400.1324710 MHz
SI                   32768
SF             400.1300102 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

SSK-4-VAS-676-1H



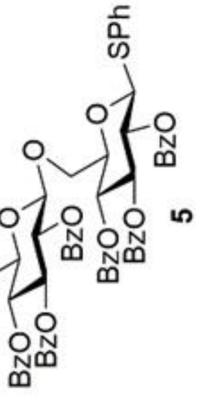
5



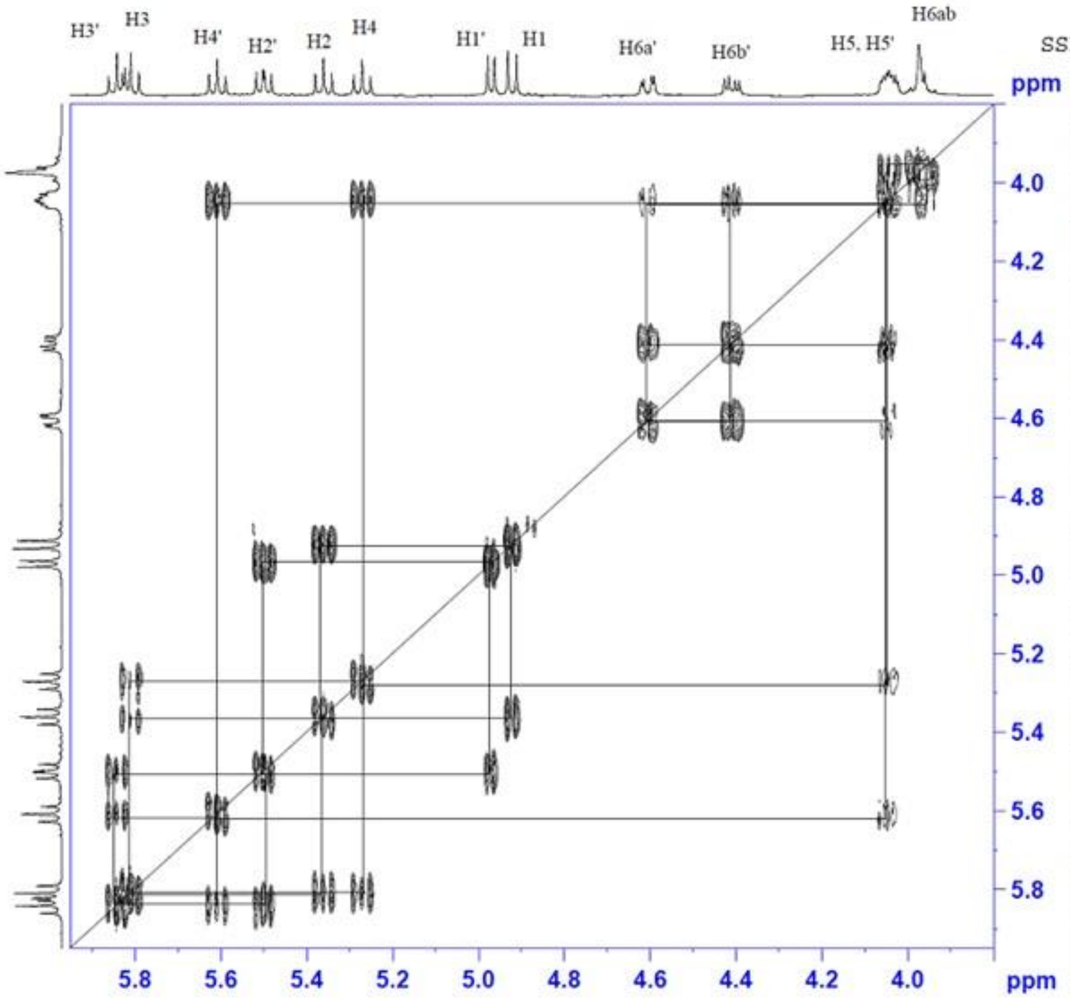


5

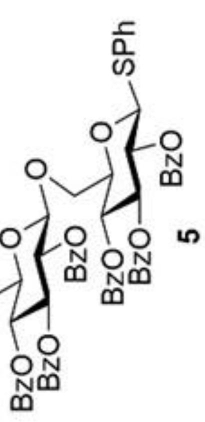
```
NAME       SSK-4-VAS-676-13C
EXPNO                      3
PROCNO                     1
Date_               20160118
Time                   14.52
INSTRUM                spect
PROBHD     5 mm SEI 1H/D-
PULPROG              zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       701
DS                         2
SWH             26041.666 Hz
FIDRES           0.397364 Hz
AQ              1.2583412 sec
RG                      28.5
DW                 19.200 usec
DE                   6.50 usec
TE                  294.6 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                 13.00 usec
PL1                -3.00 dB
PL1W         71.16858673 W
SFO1         100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               18.48 dB
PL13               19.00 dB
PL2W         16.73965454 W
PL12W         0.11905469 W
PL13W         0.10562007 W
SFO2         400.1316005 MHz
SI                     32768
SF           100.6127542 MHz
WDW                       EM
SSB                        0
LB                   2.00 Hz
GB                         0
PC                      1.40
```



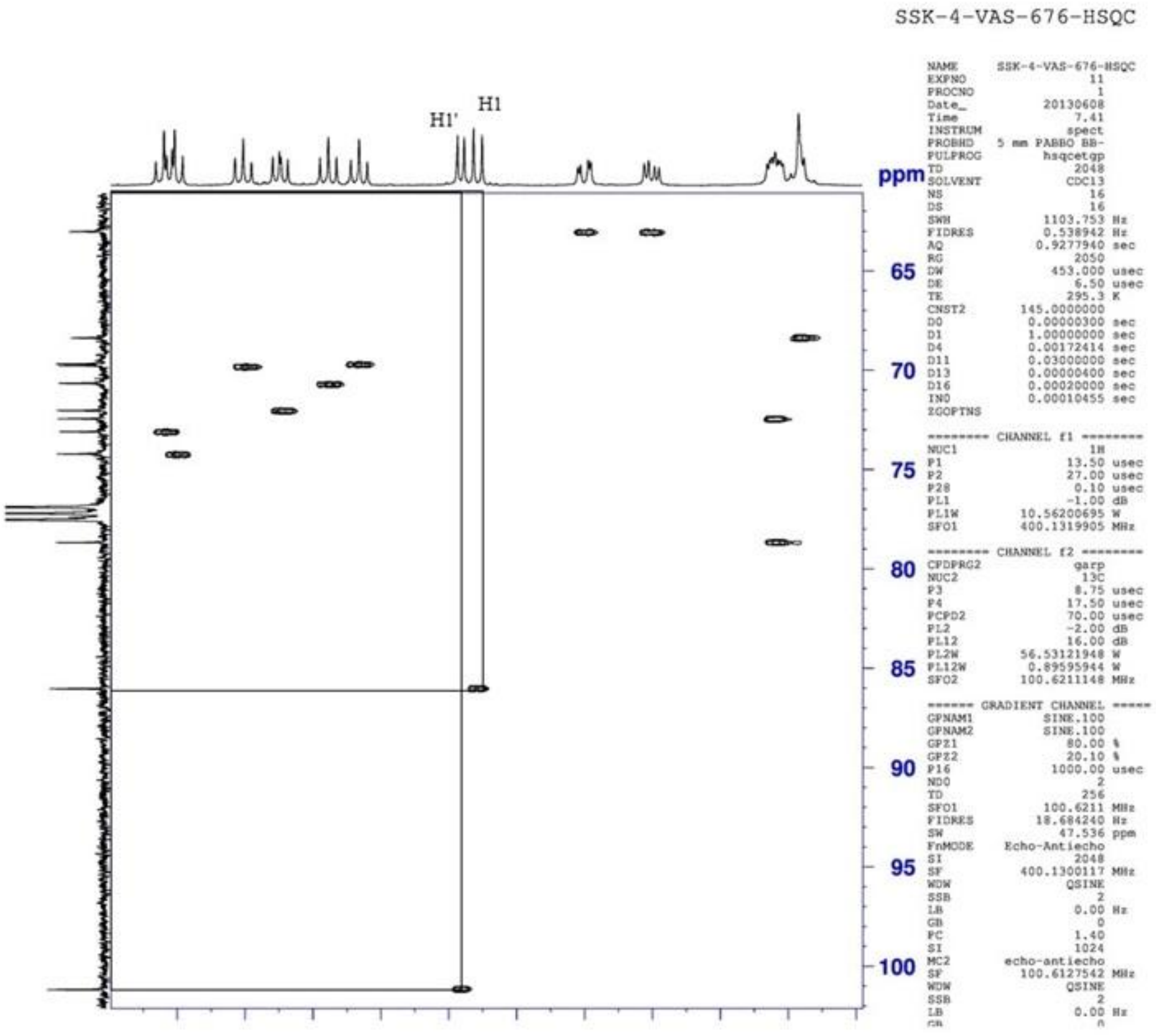
**5**



```
SSK-4-VAS-676-cosy

Current Data Parameters
NAME     SSK-4-VAS-676-cosy
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160205
Time                 10.02
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG         cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                      16
DS                       8
SWH               1254.181 Hz
FIDRES            0.612393 Hz
AQ               0.8164693 sec
RG                  177.33
DW                 398.667 usec
DE                    6.50 usec
TE                   297.6 K
D0              0.00000300 sec
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00079740 sec

======== CHANNEL f1 ========
SFO1           500.1324210 MHz
NUC1                    1H
P0                   13.00 usec
P1                   13.00 usec
P17                2500.00 usec
PLW1           13.00000000 W
PLW10           3.25000000 W

------ GRADIENT CHANNEL -----
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                      55
SFO1              500.1324 MHz
FIDRES           22.801376 Hz
SW                   2.507 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1300125 MHz
WDW                  QSINE
SSB      0
LB       0 Hz
GB       0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300125 MHz
WDW                  QSINE
SSB      0
LB       0 Hz
GB       0
```



**5**

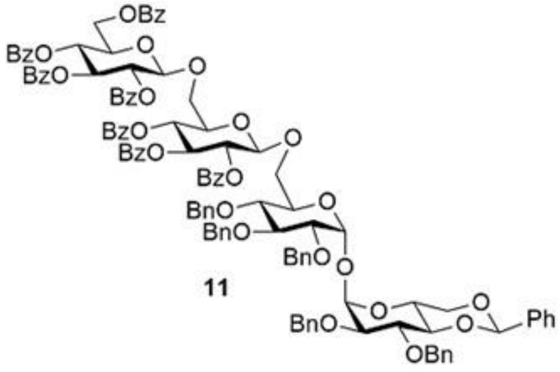


SSK-4-VAS-676-HSQC

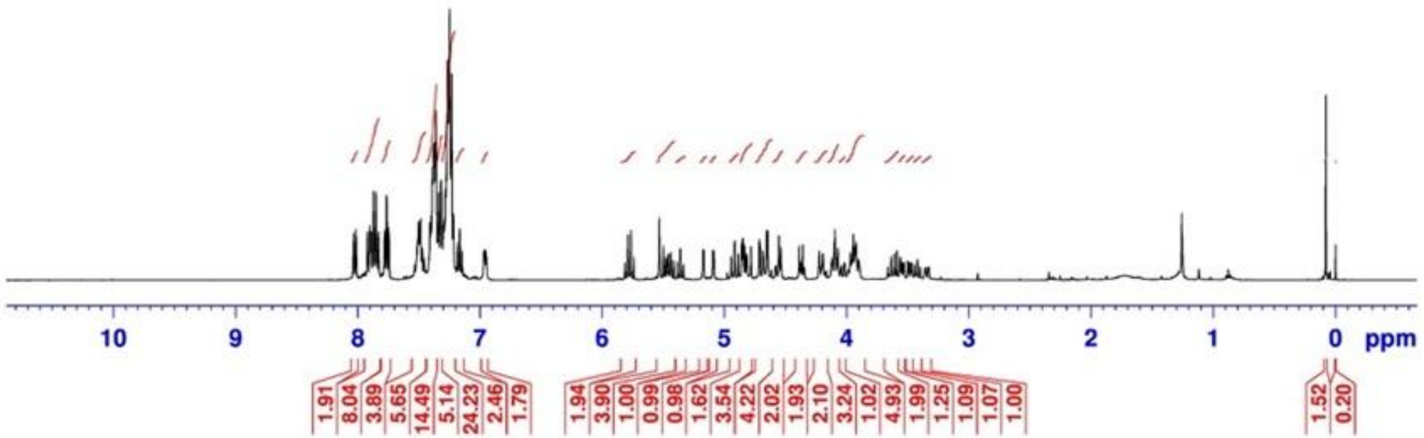
```
NAME          SSK-4-VAS-676-HSQC
EXPNO                         11
PROCNO                         1
Date_                   20130608
Time                        7.41
INSTRUM                    spect
PROBHD       5 mm PABBO BB-
PULPROG                 hsqcetgp
TD                          2048
SOLVENT                    CDCl3
NS                            16
DS                            16
SWH                     1103.753 Hz
FIDRES                  0.538942 Hz
AQ                     0.9277940 sec
RG                          2050
DW                       453.000 usec
DE                          6.50 usec
TE                         295.3 K
CNST2               145.0000000
D0                    0.00000300 sec
D1                    1.00000000 sec
D4                    0.00172414 sec
D11                   0.03000000 sec
D13                   0.00000400 sec
D16                   0.00020000 sec
IN0                   0.00010455 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                          1H
P1                         13.50 usec
P2                         27.00 usec
P28                         0.10 usec
PL1                        -1.00 dB
PL1W                 10.56200695 W
SFO1                 400.1319905 MHz

======== CHANNEL f2 ========
CPDPRG2                     garp
NUC2                         13C
P3                          8.75 usec
P4                         17.50 usec
PCPD2                      70.00 usec
PL2                        -2.00 dB
PL12                       16.00 dB
PL2W                 56.53121948 W
PL12W                 0.89595944 W
SFO2                 100.6211148 MHz

====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPNAM2                  SINE.100
GPZ1                       80.00 %
GPZ2                       20.10 %
P16                      1000.00 usec
ND0                            2
TD                           256
SFO1                    100.6211 MHz
FIDRES                 18.684240 Hz
SW                        47.536 ppm
FnMODE            Echo-Antiecho
SI                          2048
SF                   400.1300117 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
GB                             0
PC                          1.40
SI                          1024
MC2               echo-antiecho
SF                   100.6127542 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
```

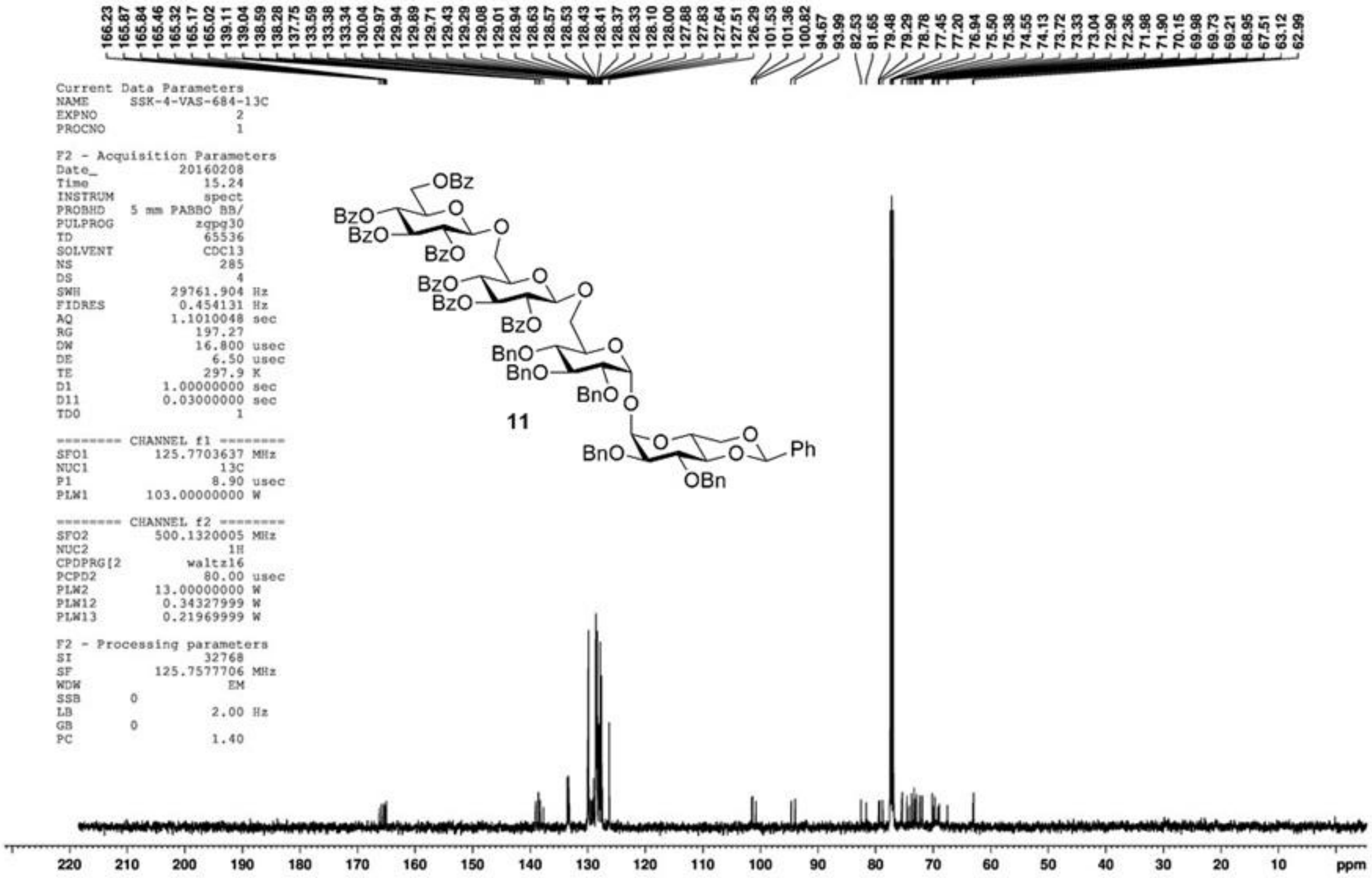
```
NAME       SSK-4-VAS-684-1H
EXPNO                     3
PROCNO                    1
Date_              20130619
Time                   1.32
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    49340
SOLVENT               CDCl3
NS                       17
DS                        0
SWH                8223.685 Hz
FIDRES             0.166674 Hz
AQ                2.9999220 sec
RG                       32
DW                   60.800 usec
DE                     6.50 usec
TE                    295.3 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    13.50 usec
PL1                   -1.00 dB
PL1W            10.56200695 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300202 MHz
WDW                      EM
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```

SSK-4-VAS-684-1H



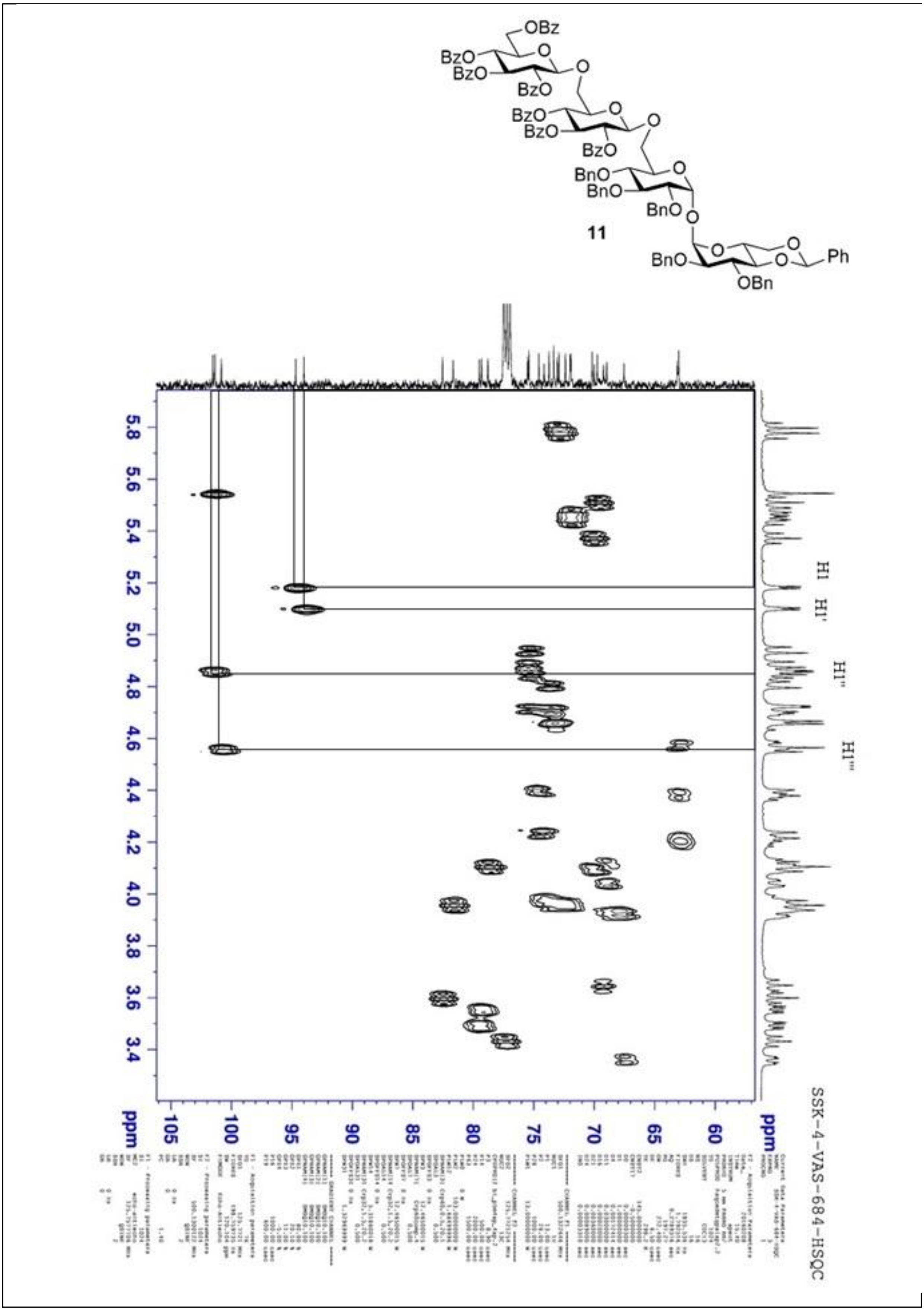
11





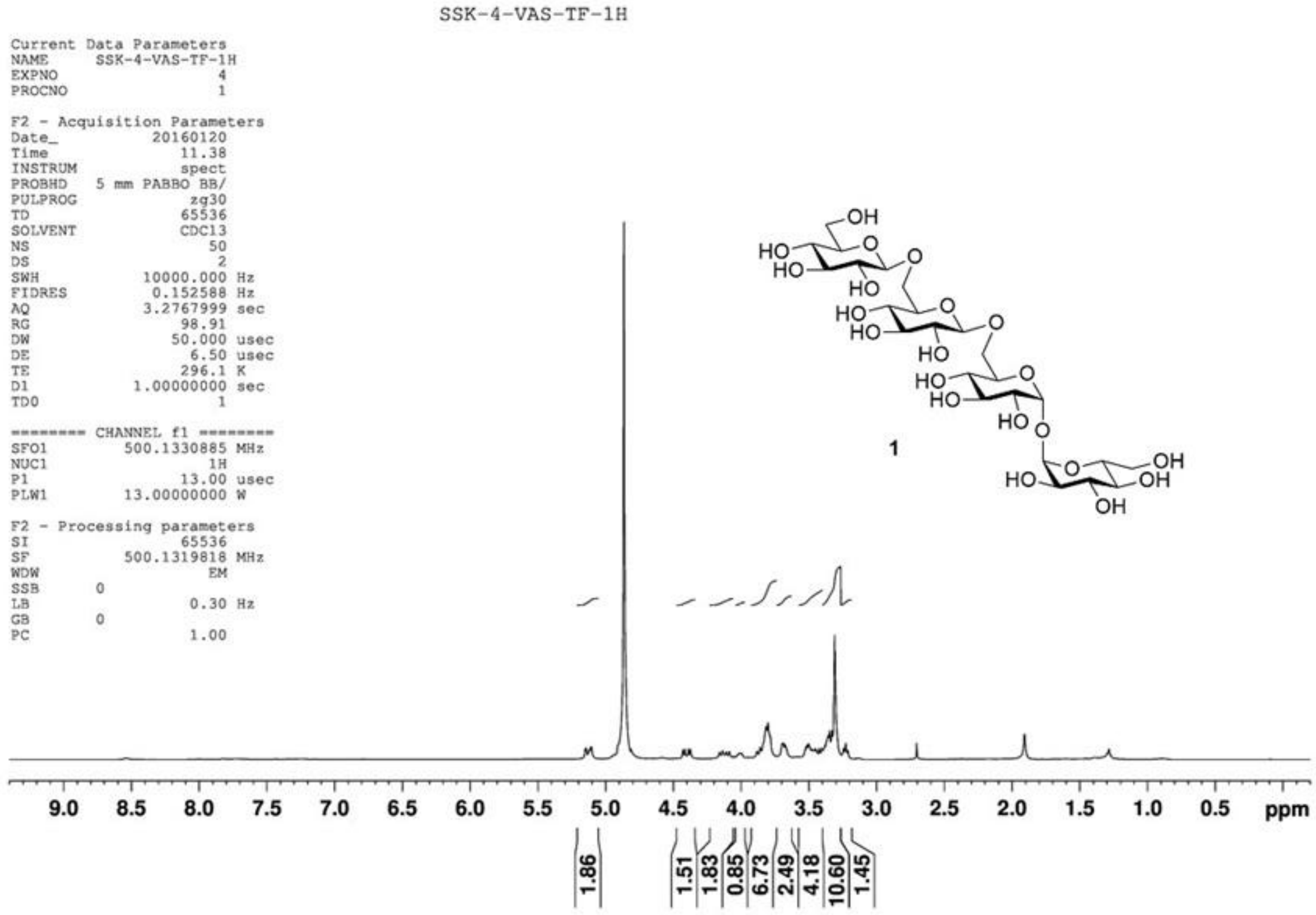
11

```
Current Data Parameters
NAME      SSK-4-VAS-684-13C
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_          20160208
Time              15.24
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  285
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                 6.50 usec
TE                297.9 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                13C
P1                 8.90 usec
PLW1       103.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        13.00000000 W
PLW12        0.34327999 W
PLW13        0.21969999 W

F2 - Processing parameters
SI                32768
SF          125.7577706 MHz
WDW                  EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.40
```



**11**

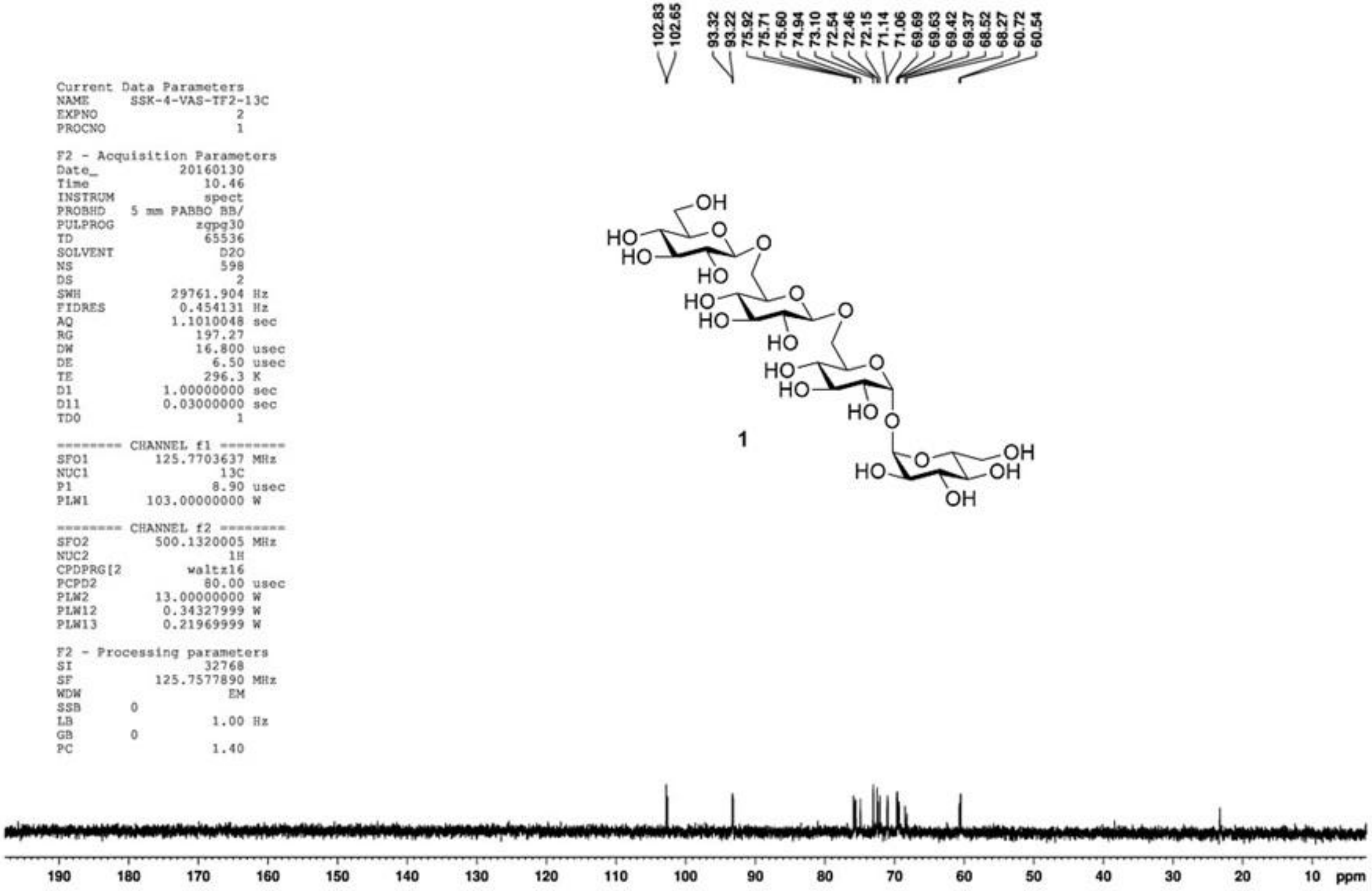
OBz
BzO
BzO
BzO
BzO
BzO
BzO
BnO
BnO
BnO
BnO
OBn
Ph
H1
H1'
H1''
H1'''
ppm
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
60
65
70
75
80
85
90
95
100
105
SSK-4-VAS-684-HSQC



SSK-4-VAS-TF-1H

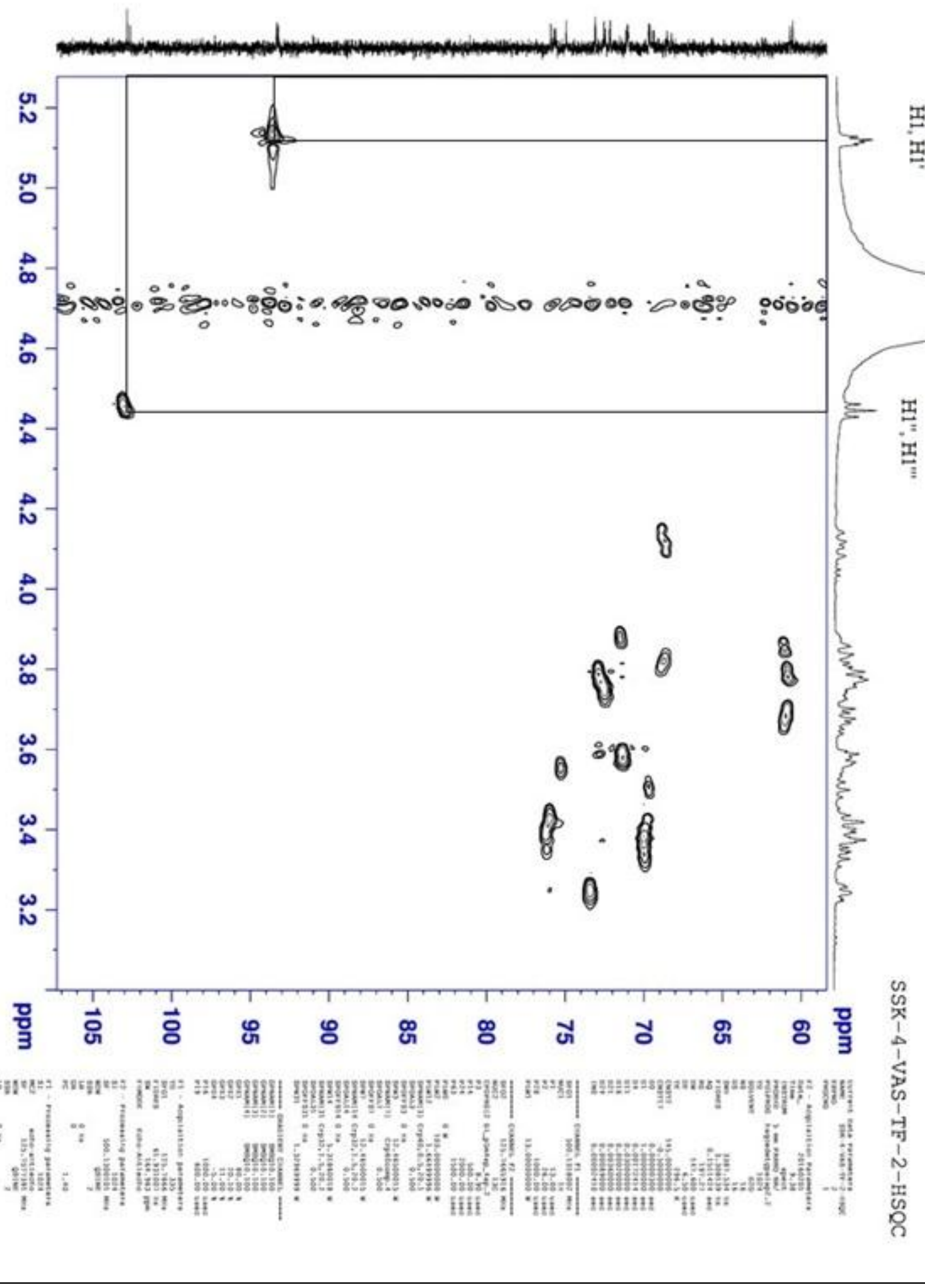
```
Current Data Parameters
NAME       SSK-4-VAS-TF-1H
EXPNO                    4
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160120
Time                 11.38
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      50
DS                       2
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                   98.91
DW                  50.000 usec
DE                    6.50 usec
TE                   296.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                   13.00 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1319818 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

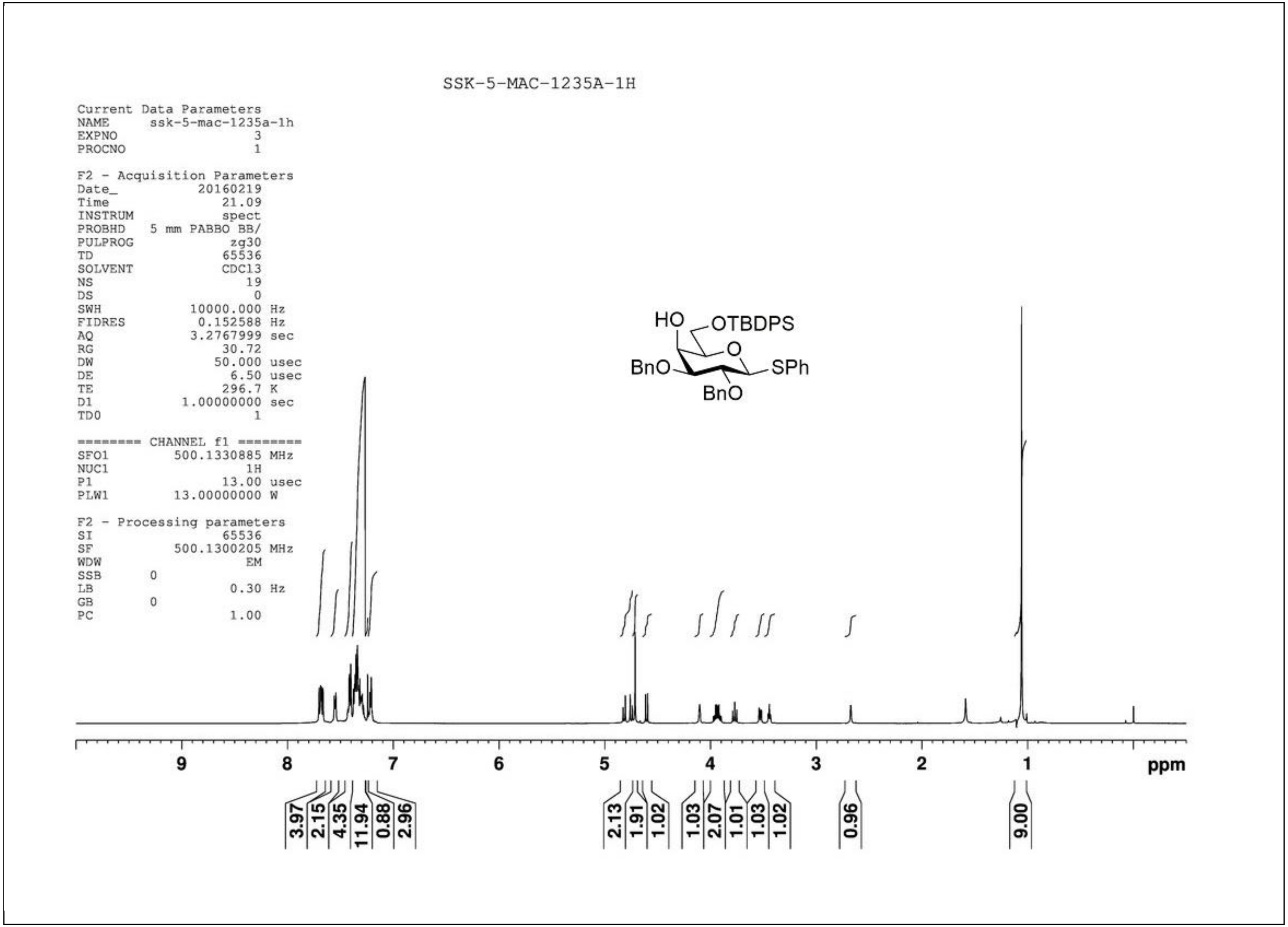
1



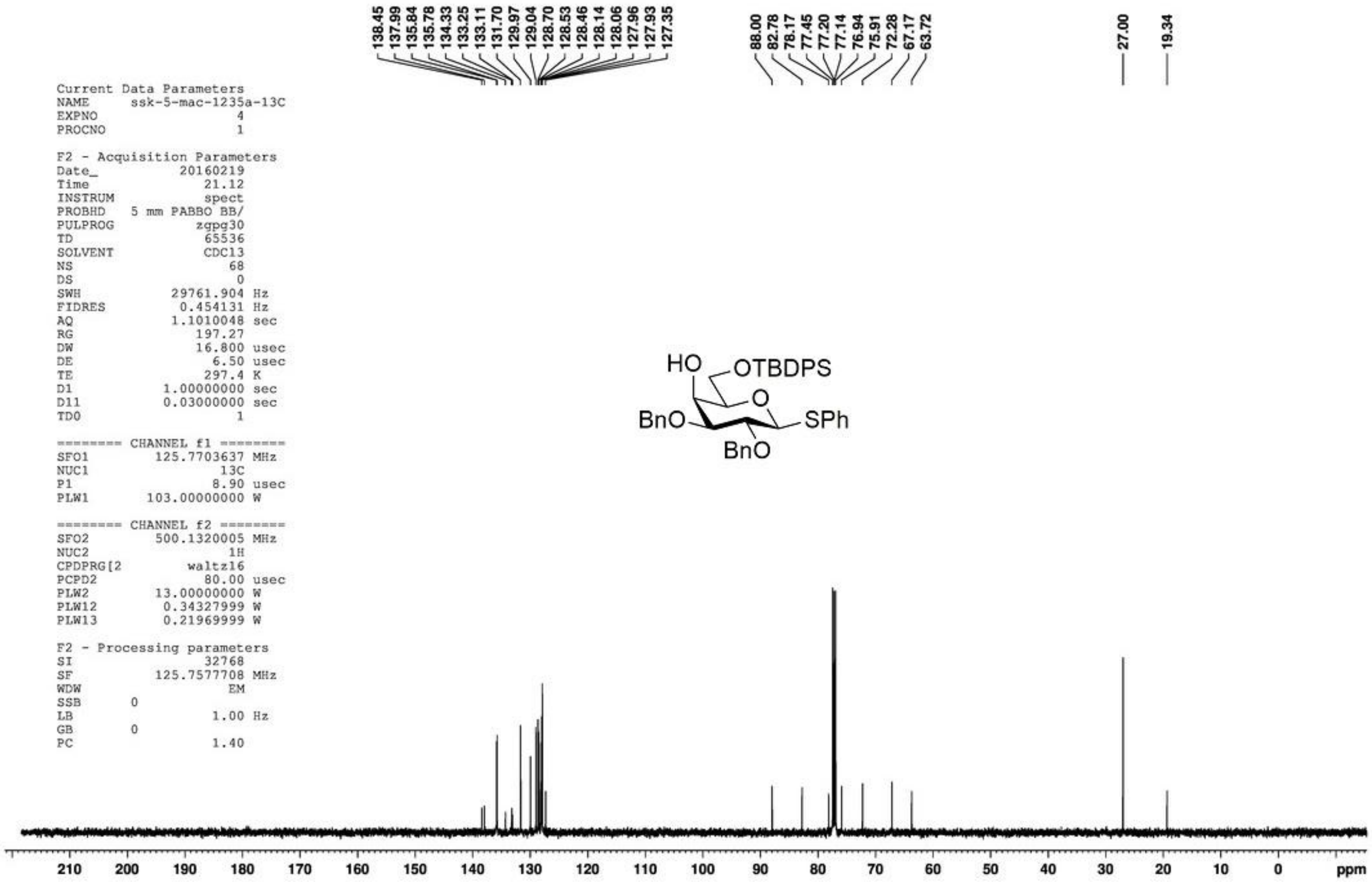
1

```
Current Data Parameters
NAME      SSK-4-VAS-TF2-13C
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160130
Time                 10.46
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT                D2O
NS                     598
DS                       2
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   296.3 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                   32768
SF            125.7577890 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```


H1,H1'
H1'',H1'''
SSK-4-VAS-TF-2-HSQC
ppm
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
105
100
95
90
85
80
75
70
65
60

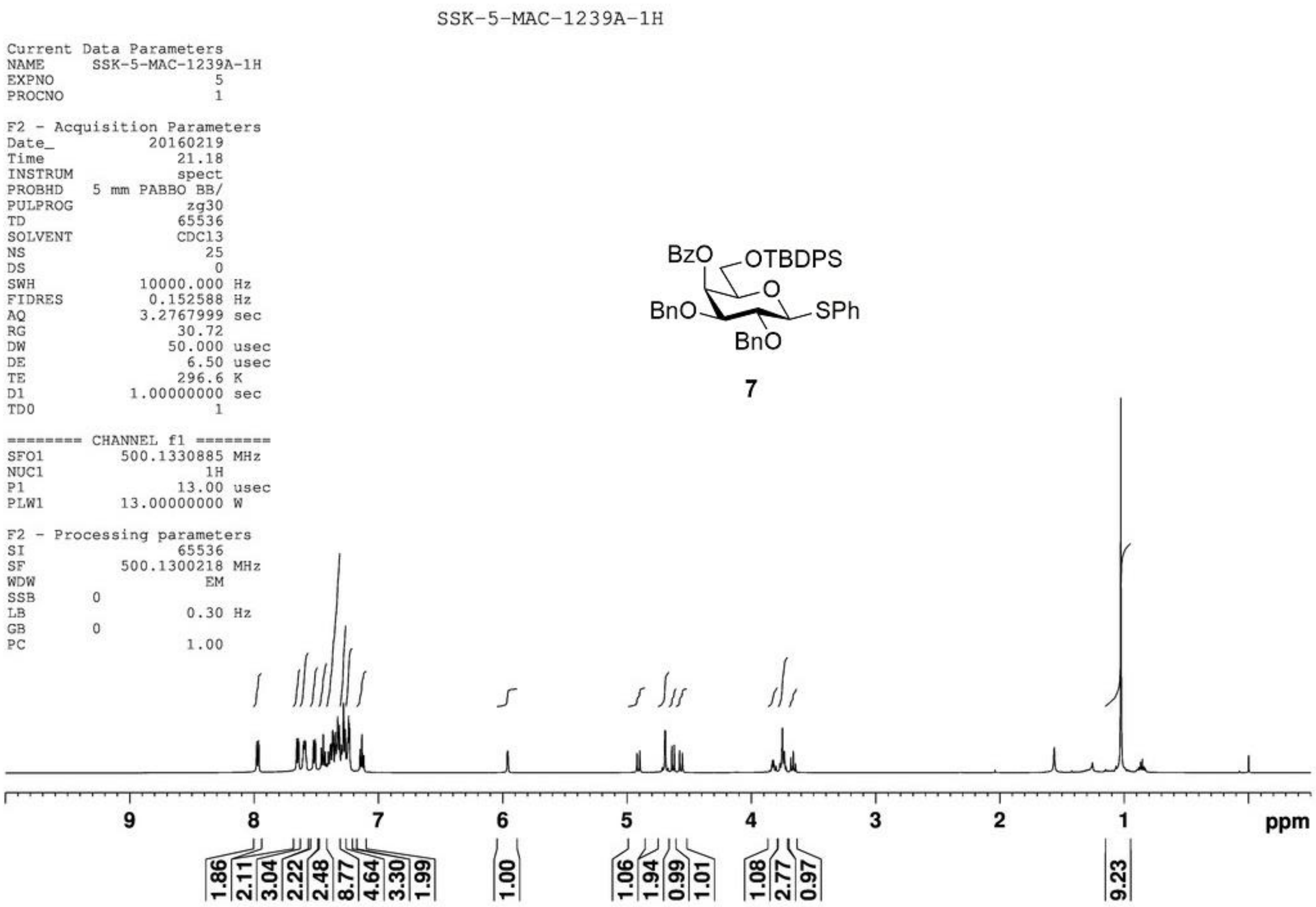

SSK-5-MAC-1235A-1H

```
Current Data Parameters
NAME     ssk-5-mac-1235a-1h
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160219
Time                  21.09
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       19
DS                        0
SWH               10000.000 Hz
FIDRES             0.152588 Hz
AQ                3.2767999 sec
RG                    30.72
DW                   50.000 usec
DE                     6.50 usec
TE                    296.7 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            500.1330885 MHz
NUC1                     1H
P1                    13.00 usec
PLW1            13.00000000 W

F2 - Processing parameters
SI                    65536
SF              500.1300205 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```



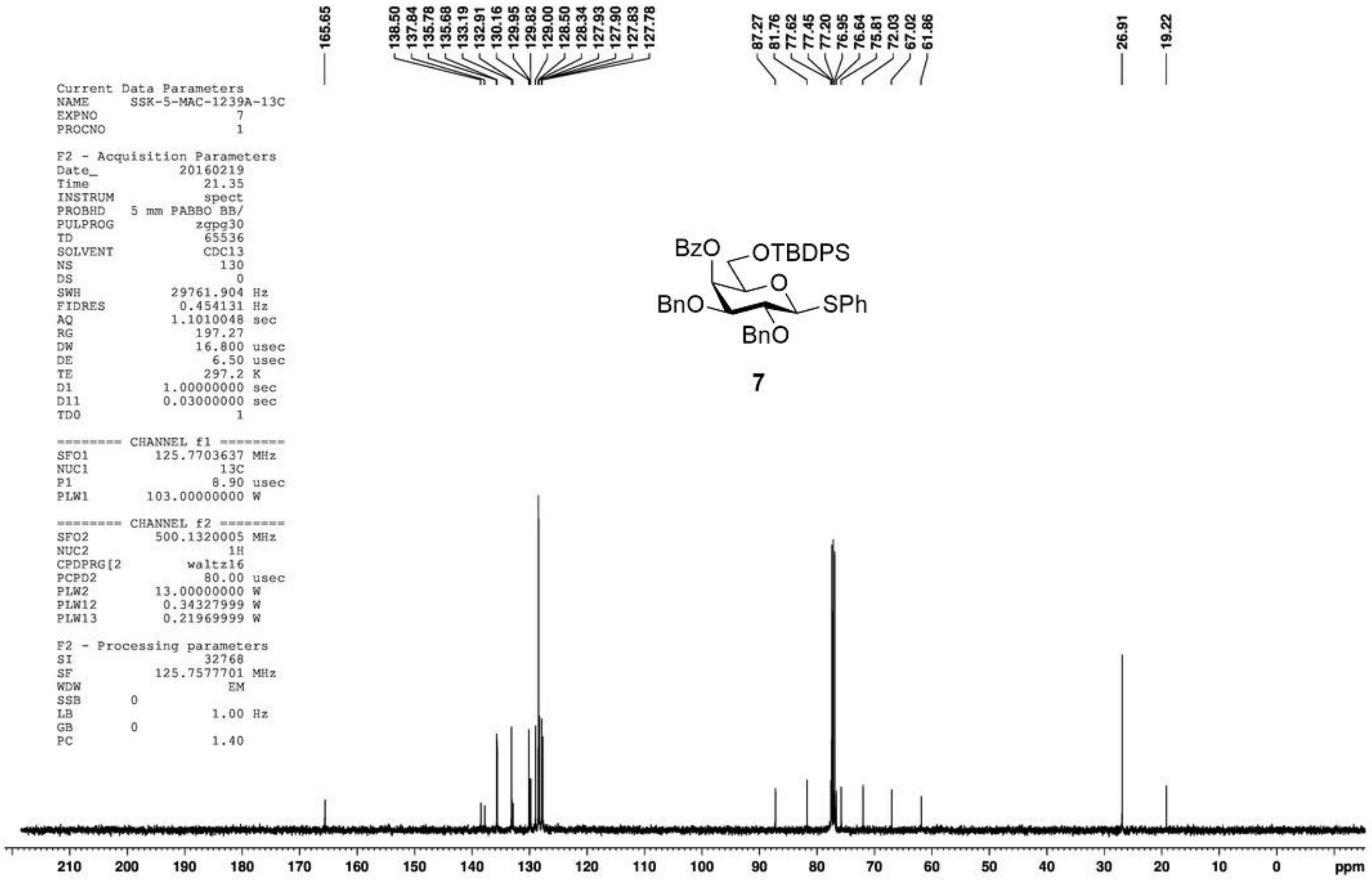
```
Current Data Parameters
NAME     ssk-5-mac-1235a-13C
EXPNO               4
PROCNO              1

F2 - Acquisition Parameters
Date_          20160219
Time              21.12
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  68
DS                   0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010048 sec
RG              197.27
DW              16.800 usec
DE               6.50 usec
TE              297.4 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1       125.7703637 MHz
NUC1               13C
P1                8.90 usec
PLW1      103.00000000 W

======== CHANNEL f2 ========
SFO2       500.1320005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       13.00000000 W
PLW12       0.34327999 W
PLW13       0.21969999 W

F2 - Processing parameters
SI               32768
SF         125.7577708 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

SSK-5-MAC-1239A-1H



```
Current Data Parameters
NAME     SSK-5-MAC-1239A-1H
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160219
Time                  21.18
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       25
DS                        0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  30.72
DW                 50.000 usec
DE                   6.50 usec
TE                  296.6 K
D1             1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                     1H
P1                    13.00 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                    65536
SF            500.1300218 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

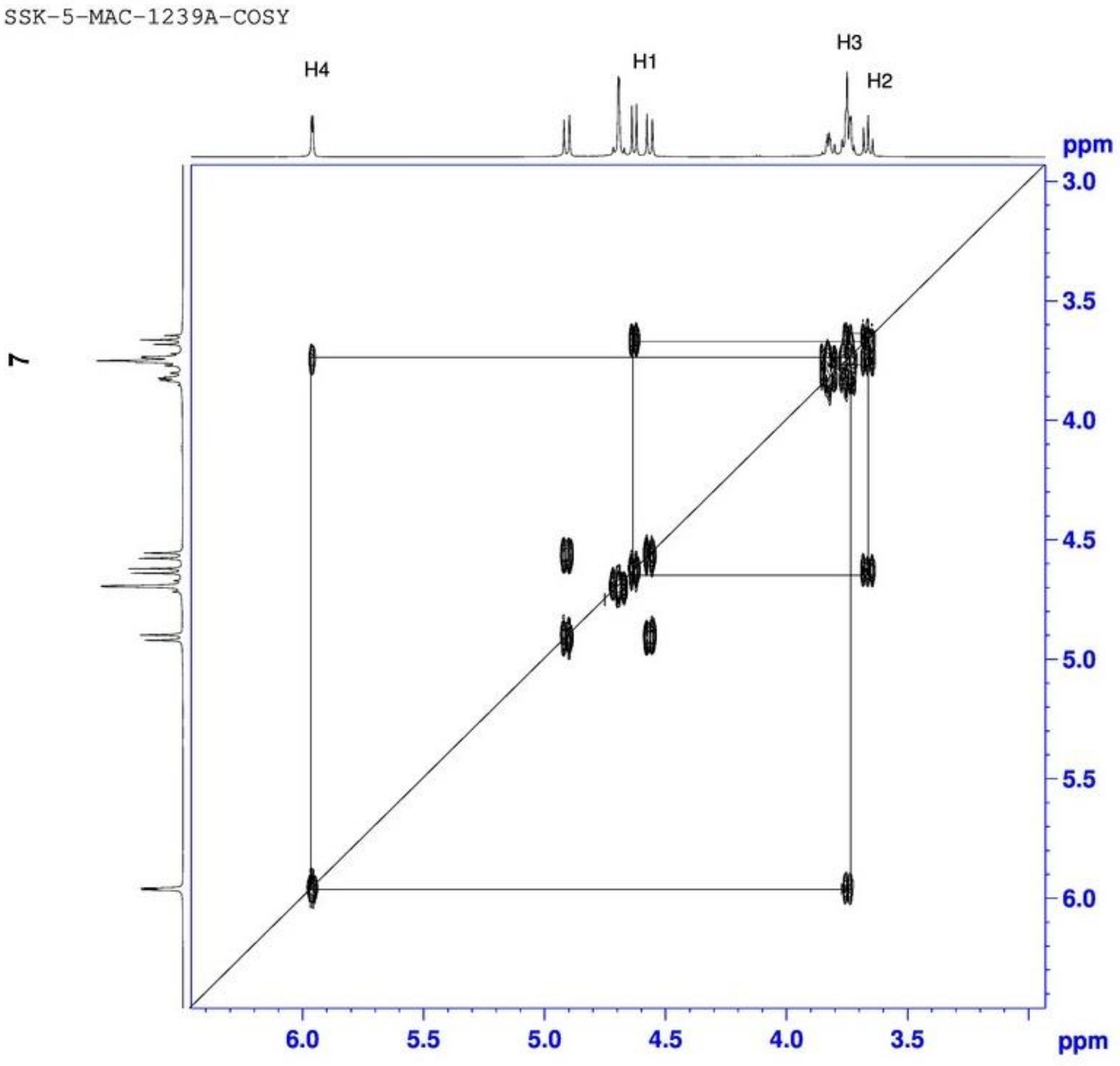
**7**



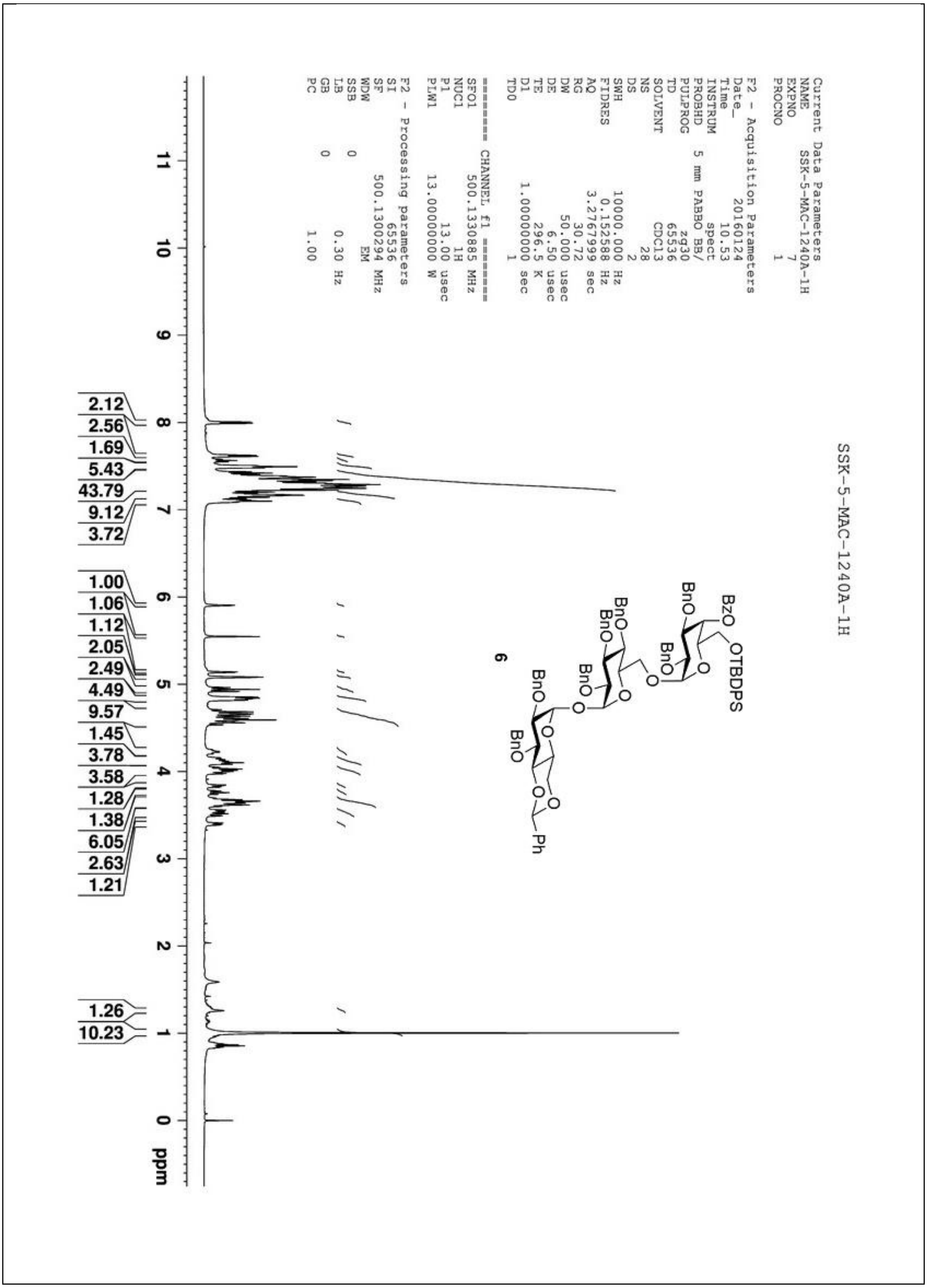
```
Current Data Parameters
NAME     SSK-5-MAC-1239A-13C
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160219
Time               21.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  130
DS                    0
SWH          29761.904 Hz
FIDRES        0.454131 Hz
AQ           1.1010048 sec
RG               197.27
DW               16.800 usec
DE                 6.50 usec
TE                297.2 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       125.7703637 MHz
NUC1                13C
P1                 8.90 usec
PLW1      103.00000000 W

======== CHANNEL f2 ========
SFO2       500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        13.00000000 W
PLW12        0.34327999 W
PLW13        0.21969999 W

F2 - Processing parameters
SI                32768
SF         125.7577701 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

7

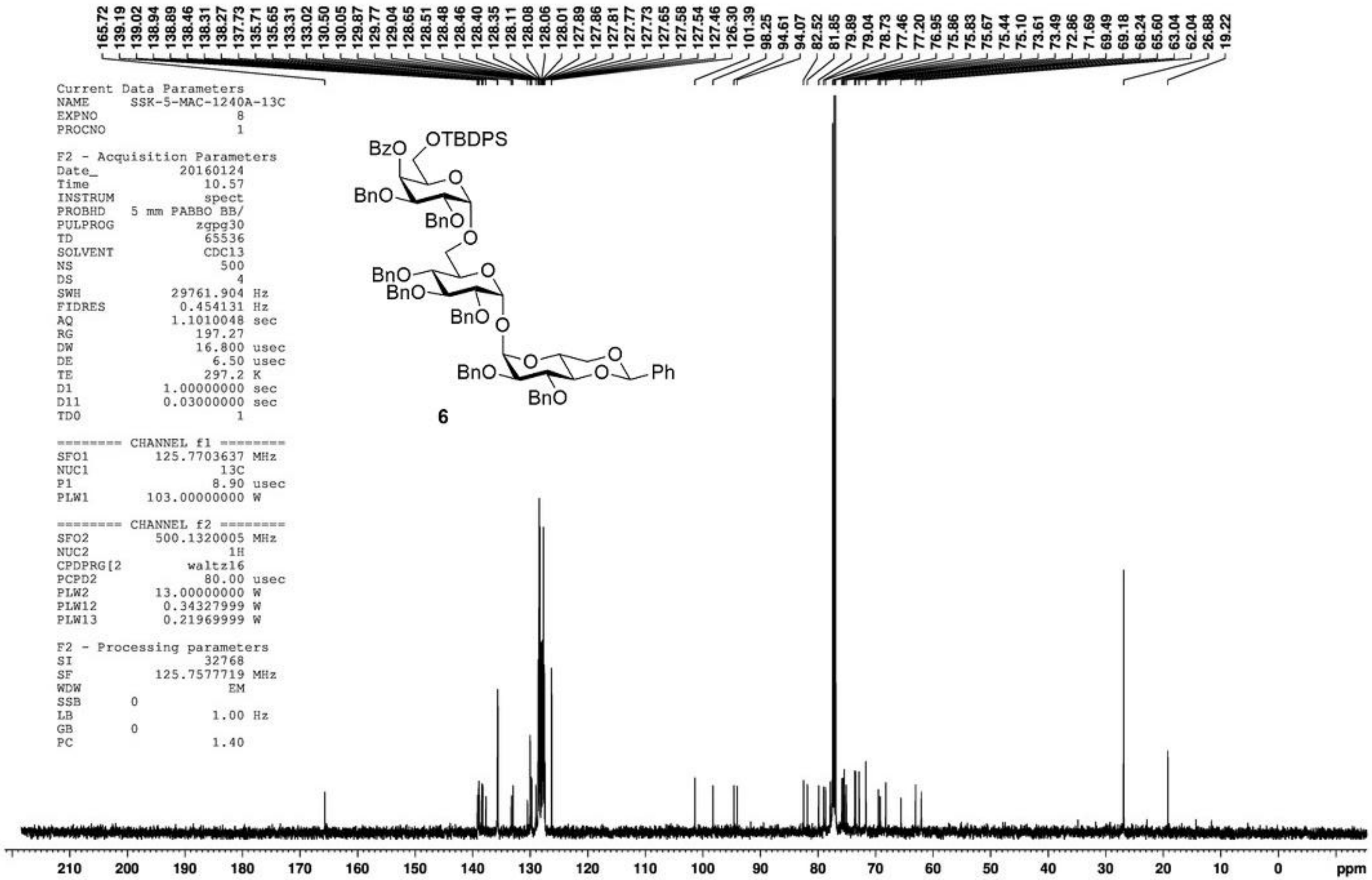
**7**



```
Current Data Parameters
NAME      SSK-5-MAC-1239A-COSY
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160219
Time                 21.21
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG          cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                       8
DS                       0
SWH               1765.537 Hz
FIDRES            0.862078 Hz
AQ               0.5799936 sec
RG                   61.42
DW                 283.200 usec
DE                    6.50 usec
TE                   296.6 K
D0              0.00000300 sec
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00056640 sec

======== CHANNEL f1 ========
SFO1           500.1323702 MHz
NUC1                    1H
P0                   13.00 usec
P1                   13.00 usec
P17                2500.00 usec
PLW1           13.00000000 W
PLW10           3.25000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                      58
SFO1              500.1324 MHz
FIDRES           30.440289 Hz
SW                   3.530 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1300218 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300218 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
```

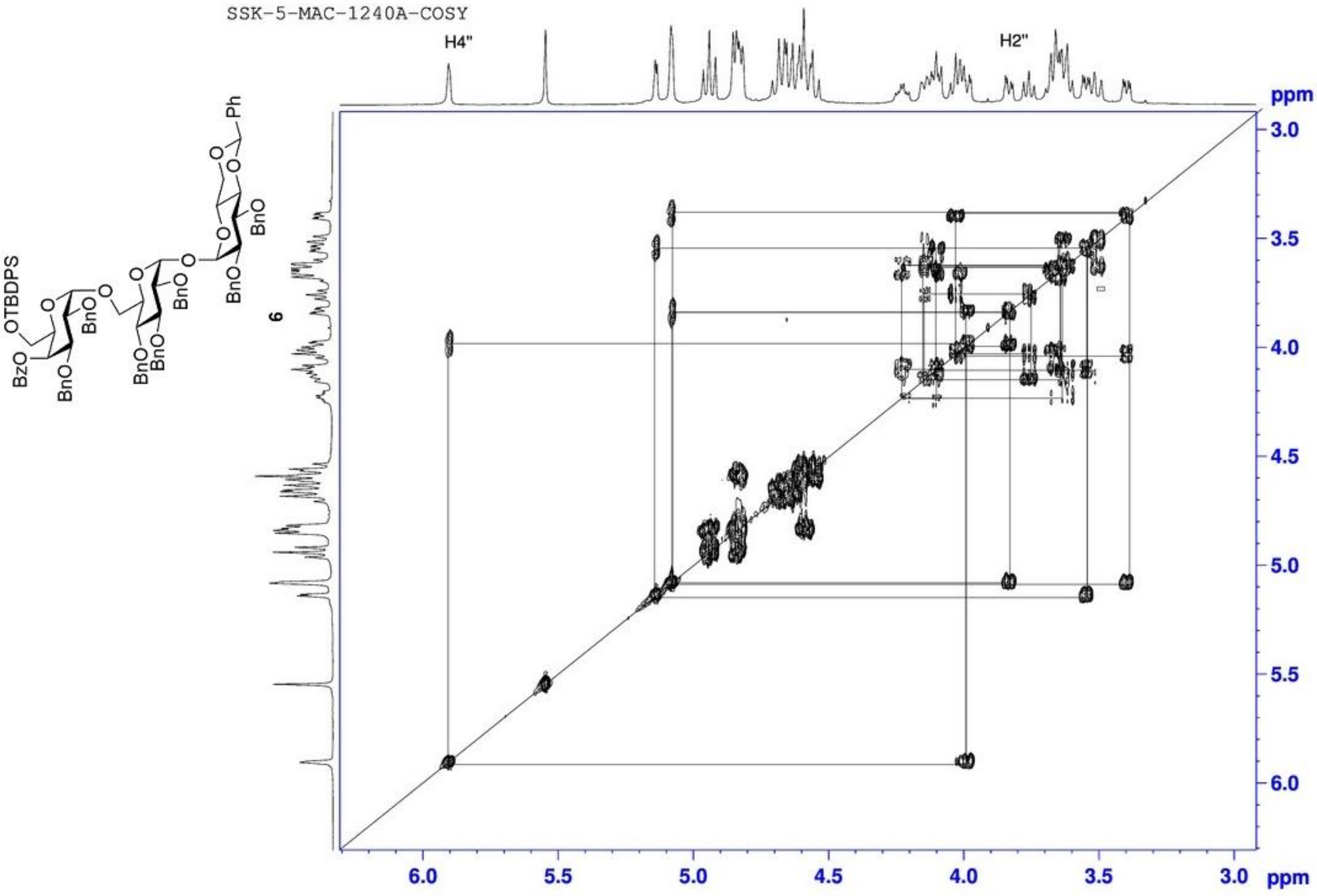


```
Current Data Parameters
NAME          SSK-5-MAC-1240A-1H
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160124
Time               10.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    28
DS                     2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                 30.72
DW                50.000 usec
DE                  6.50 usec
TE                 296.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         13.00000000 W

F2 - Processing parameters
SI                 65536
SF           500.1300294 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



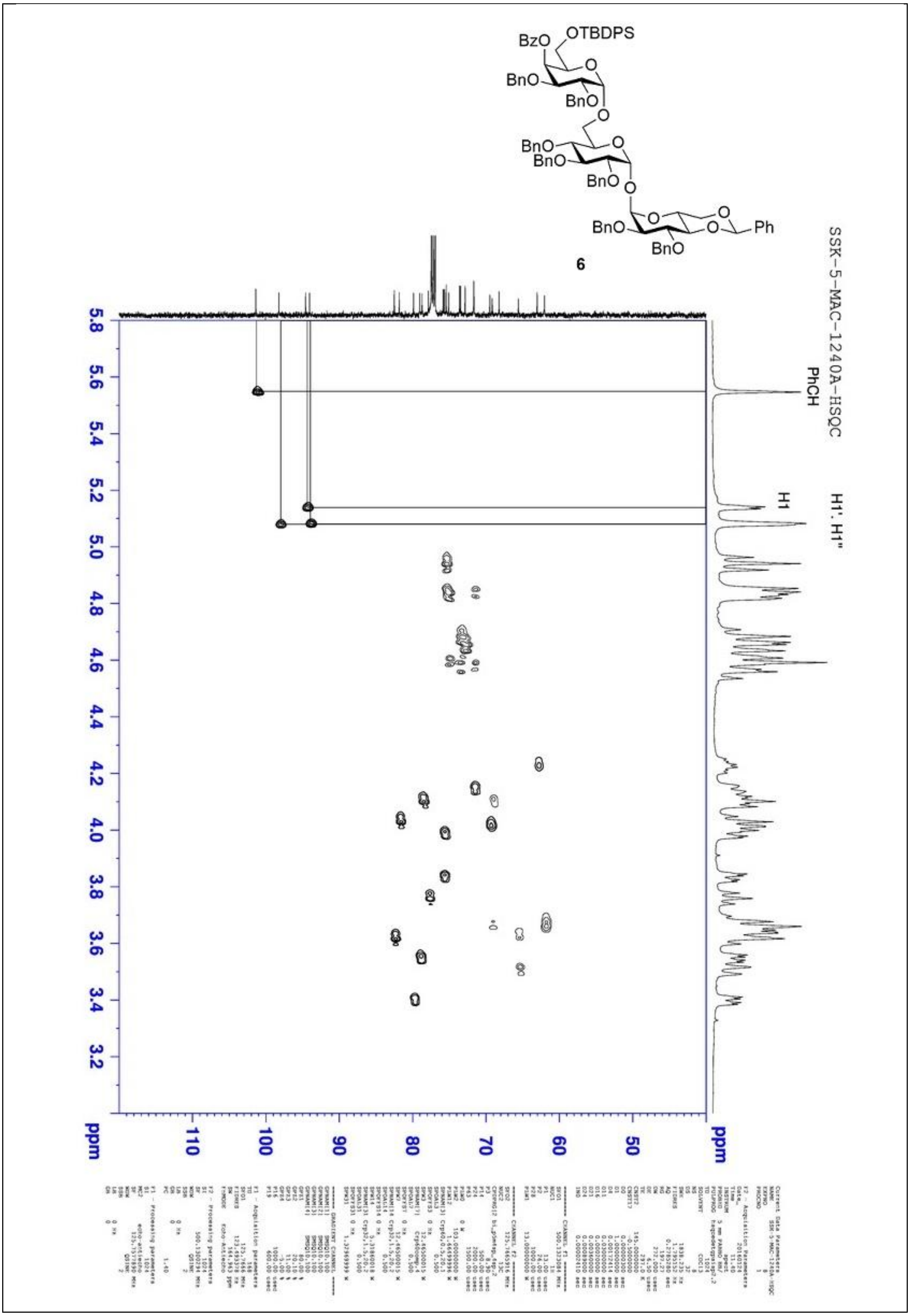
**6**

```
Current Data Parameters
NAME     SSK-5-MAC-1240A-13C
EXPNO                  8
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160124
Time               10.57
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   500
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                197.27
DW                16.800 usec
DE                  6.50 usec
TE                 297.2 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                 13C
P1                  8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                 32768
SF           125.7577719 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



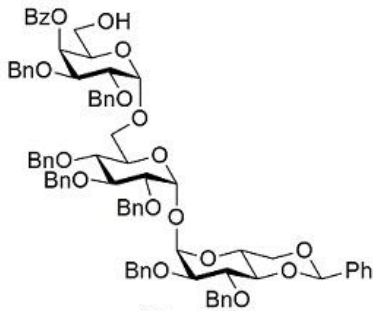
6

```
Current Data Parameters
NAME      SSK-5-MAC-1240A-COSY
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160124
Time                 11.13
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG         cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                       8
DS                       8
SWH               1694.915 Hz
FIDRES            0.827595 Hz
AQ               0.6041600 sec
RG                   61.42
DW                 295.000 usec
DE                    6.50 usec
TE                   297.1 K
D0              0.00000300 sec
D1              1.00000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00059000 sec

======== CHANNEL f1 ========
SFO1           500.1323365 MHz
NUC1                    1H
P0                   13.00 usec
P1                   13.00 usec
P17                2500.00 usec
PLW1           13.00000000 W
PLW10           3.25000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SMSQ10.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     114
SFO1              500.1323 MHz
FIDRES           14.867678 Hz
SW                   3.389 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1300294 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
PC                    1.40

F1 - Processing parameters
SI                    1024
MC2                     QF
SF             500.1300294 MHz
WDW                  QSINE
SSB       0
LB        0 Hz
GB        0
```

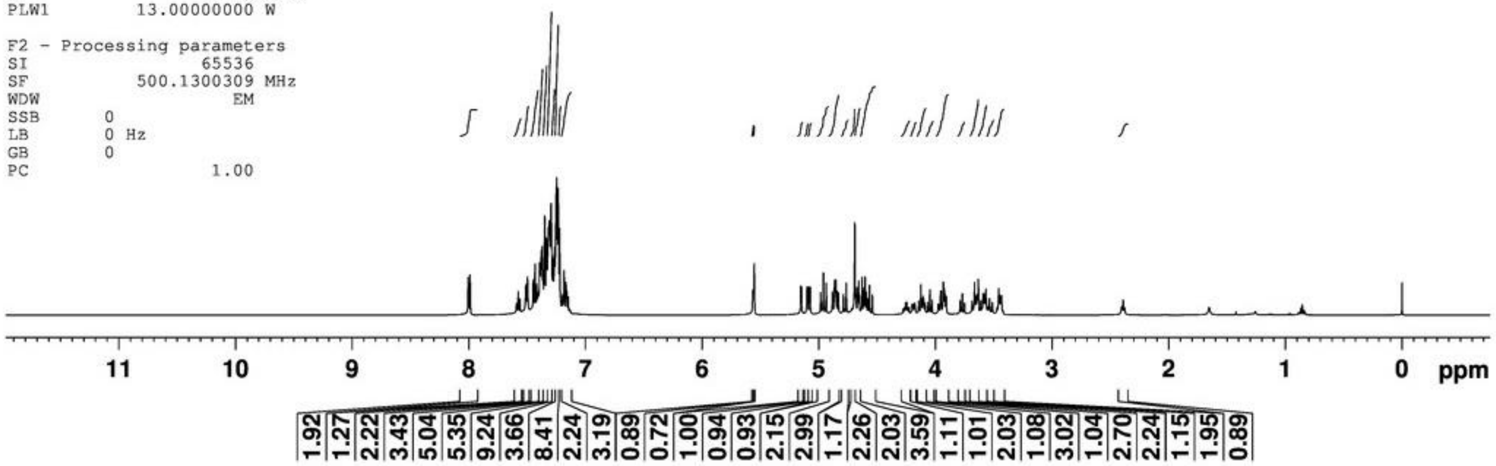

SSK-5-MAC-1240A-HSQC
PhCH
H1
H1', H1"
6
BzO
OTBDPS
BnO
O
Ph
ppm
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
110
100
90
80
70
60
50

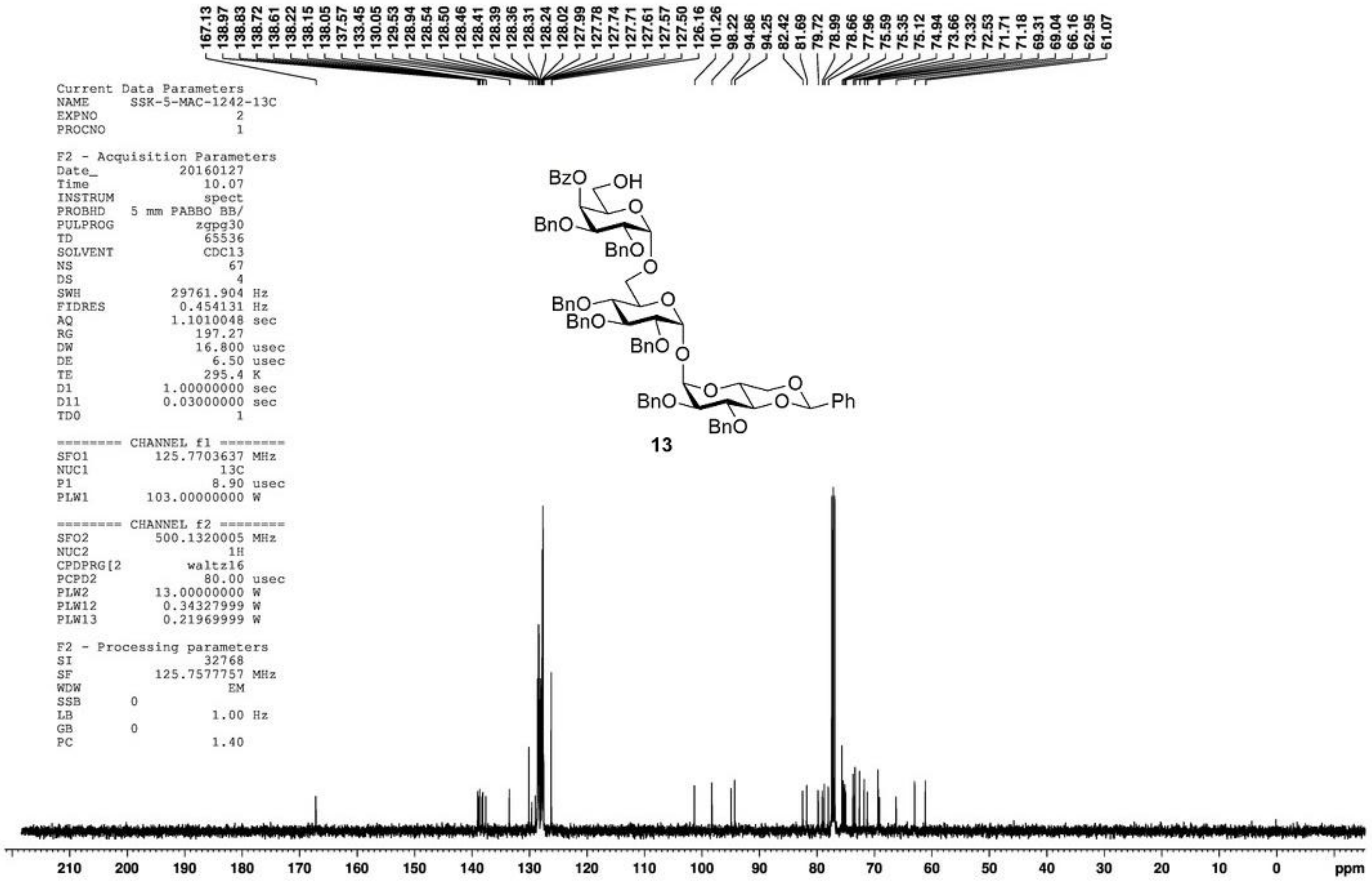
SSK-5-MAC-1242-1H

```
Current Data Parameters
NAME     SSK-5-MAC-1242-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160127
Time                 10.03
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                   30.72
DW                  50.000 usec
DE                    6.50 usec
TE                   294.6 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                    1H
P1                   13.00 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                   65536
SF           500.1300309 MHz
WDW                     EM
SSB      0
LB       0 Hz
GB       0
PC                    1.00
```



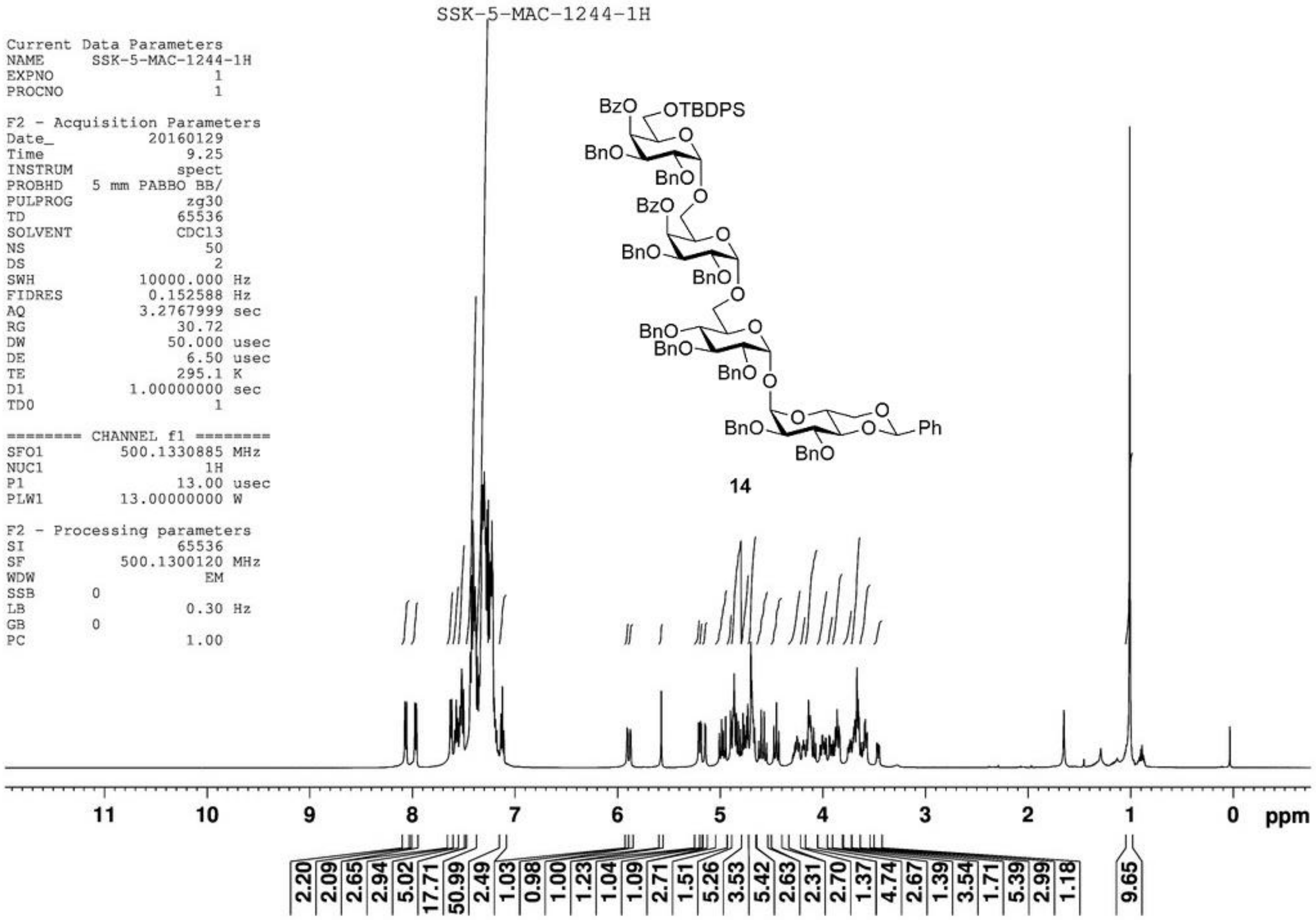
13





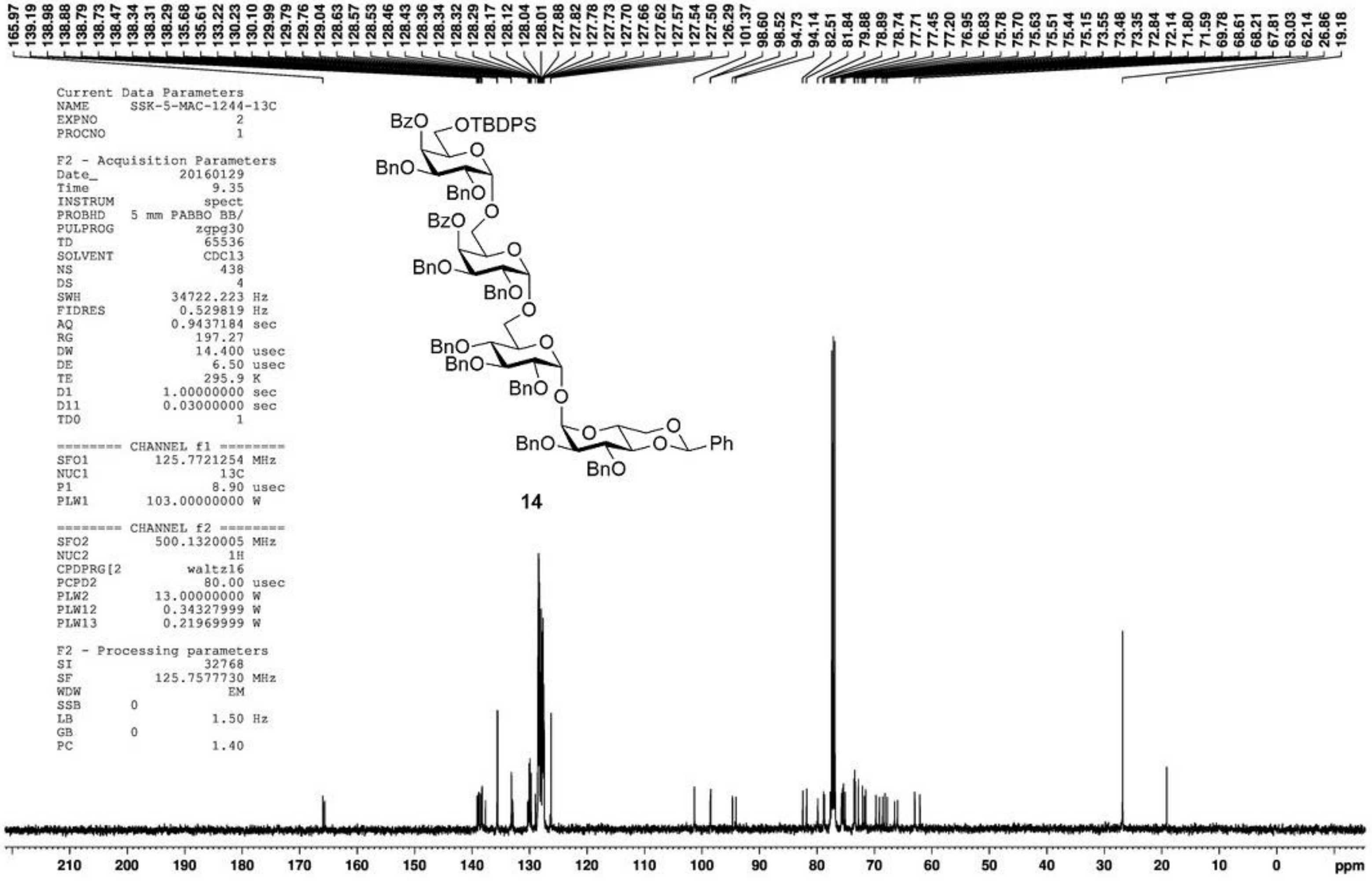
```
Current Data Parameters
NAME     SSK-5-MAC-1242-13C
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160127
Time                 10.07
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      67
DS                       4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   295.4 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                   32768
SF            125.7577757 MHz
WDW                     EM
SSB        0
LB                    1.00 Hz
GB         0
PC                    1.40
```

13



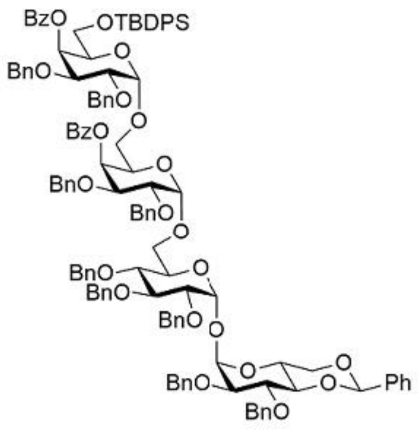
14

```
Current Data Parameters
NAME     SSK-5-MAC-1244-1H
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160129
Time                  9.25
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      50
DS                       2
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                   30.72
DW                  50.000 usec
DE                    6.50 usec
TE                   295.1 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                    1H
P1                   13.00 usec
PLW1           13.00000000 W

F2 - Processing parameters
SI                   65536
SF            500.1300120 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



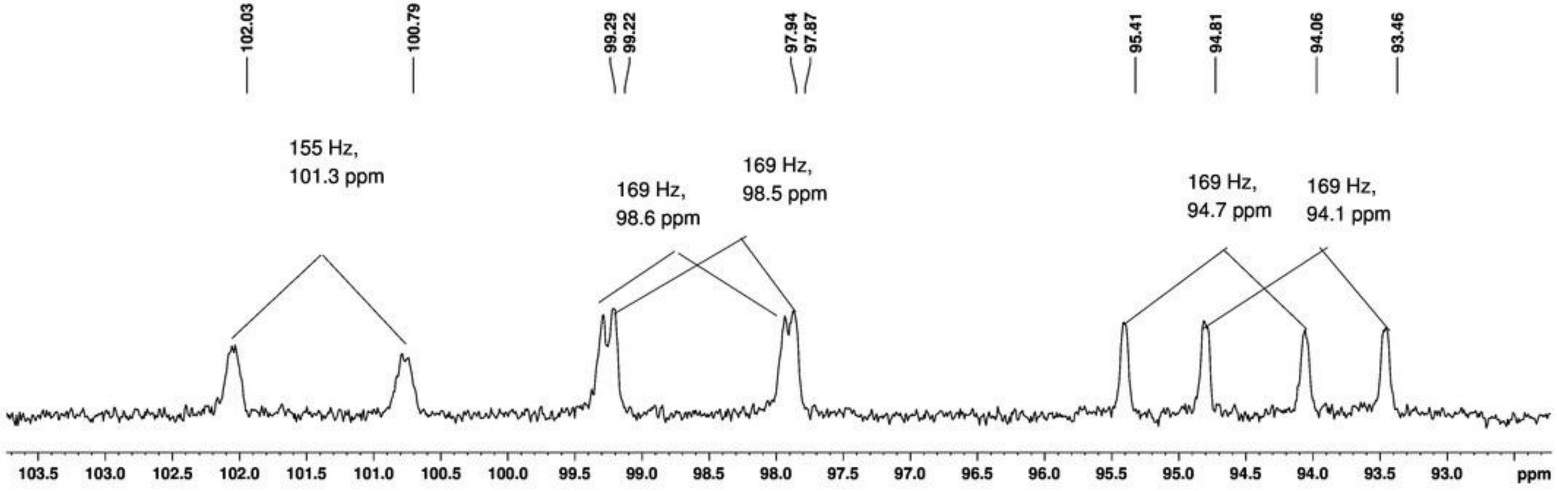
14

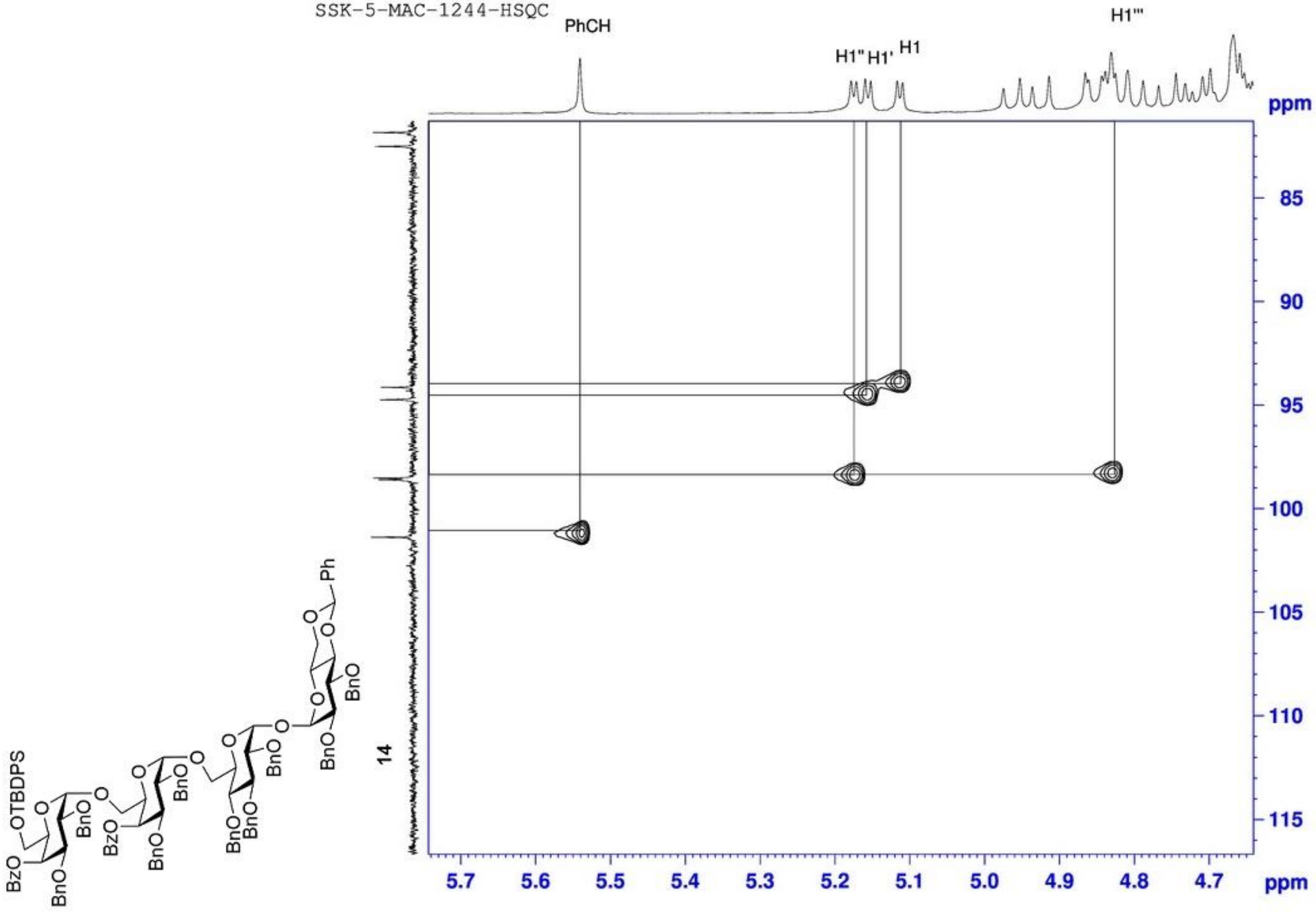
```
Current Data Parameters
NAME     SSK-5-MAC-1244-13C
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160129
Time                   9.35
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      438
DS                        4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ            0.9437184 sec
RG                   197.27
DW               14.400 usec
DE                 6.50 usec
TE                  295.9 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         125.7721254 MHz
NUC1                     13C
P1                 8.90 usec
PLW1          103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2             80.00 usec
PLW2           13.00000000 W
PLW12           0.34327999 W
PLW13           0.21969999 W

F2 - Processing parameters
SI                     32768
SF           125.7577730 MHz
WDW                       EM
SSB        0
LB                   1.50 Hz
GB         0
PC                      1.40
```



**14**

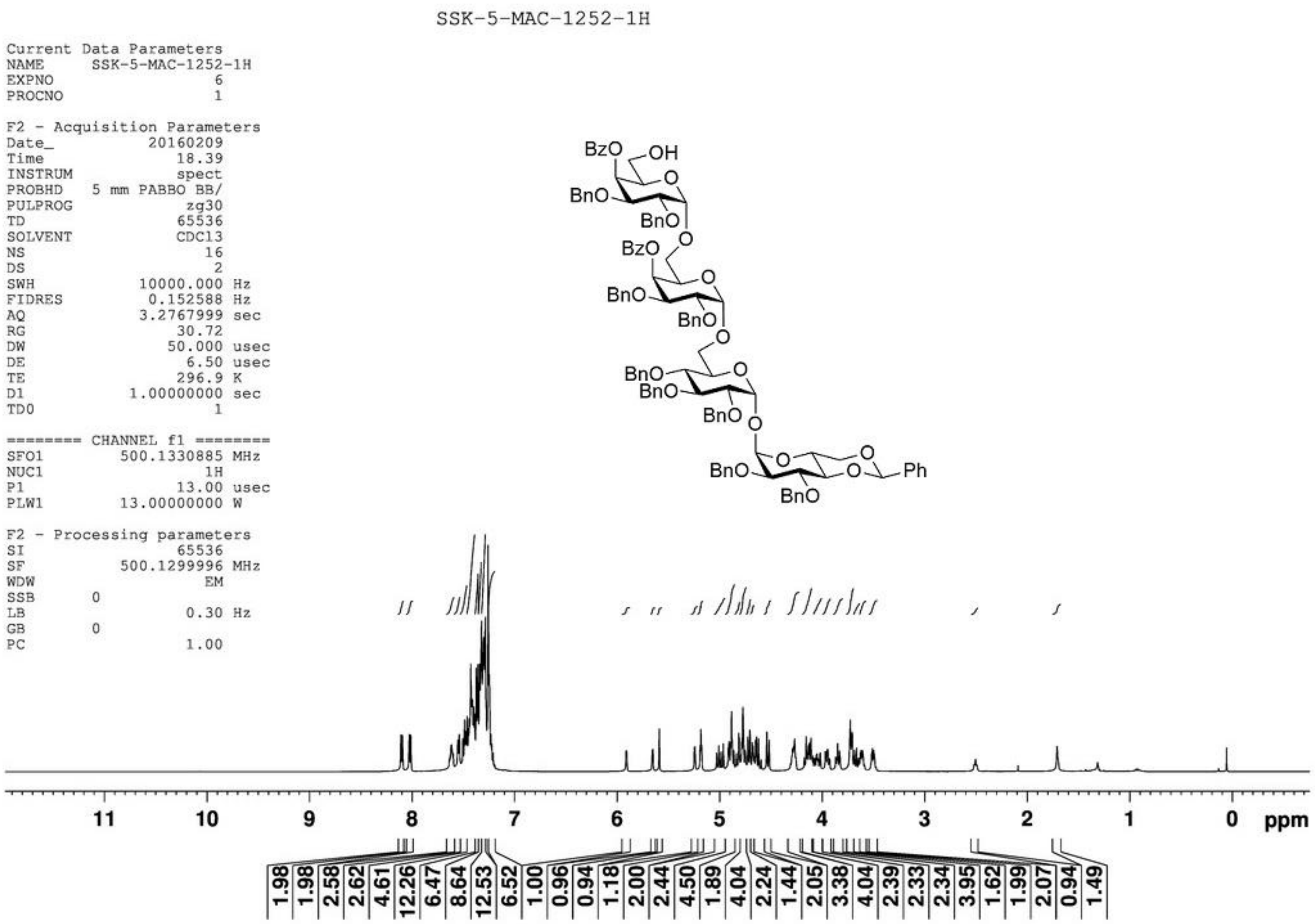
SSK-5-MAC-1244-HcoupledC13



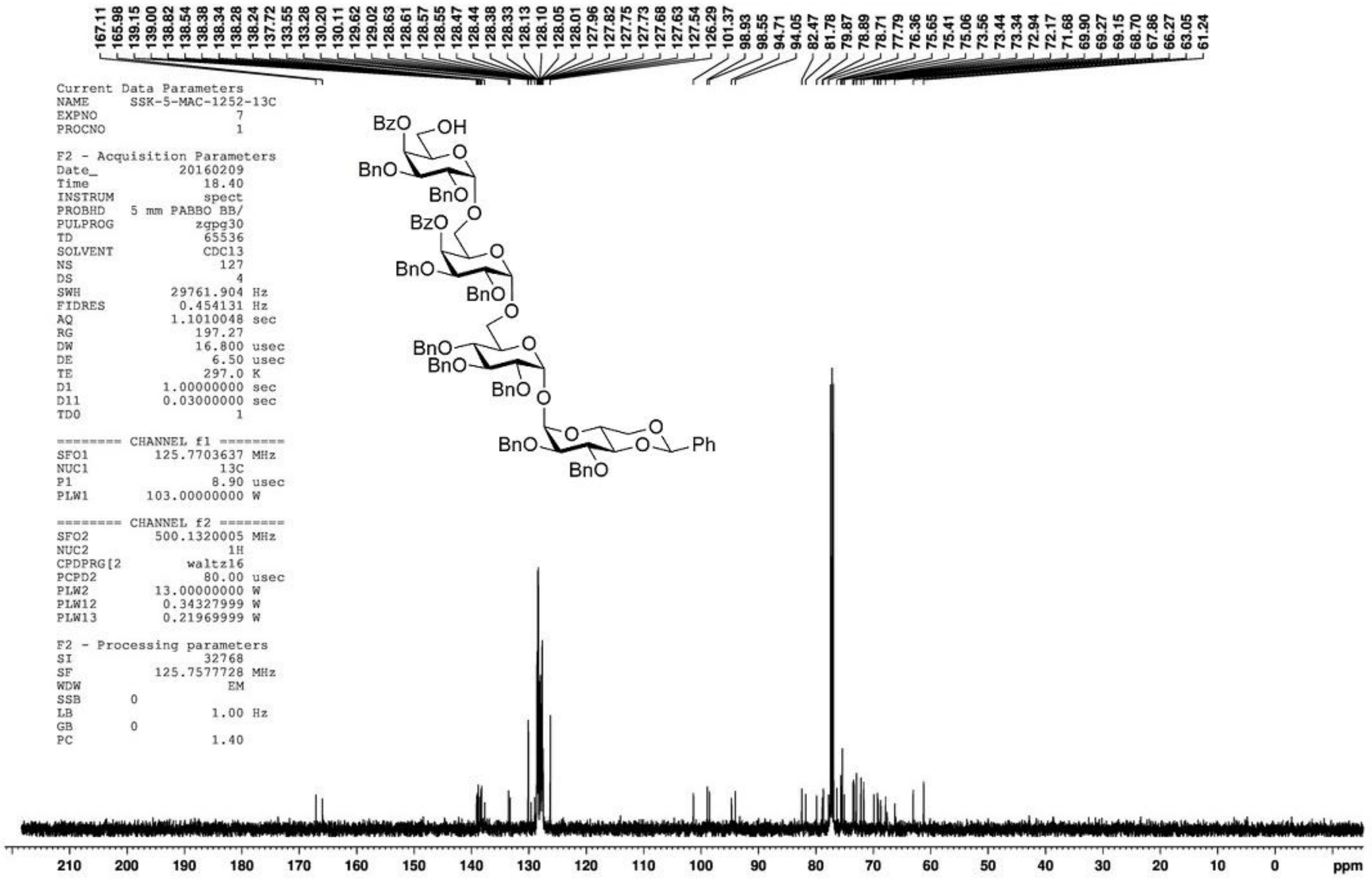


14

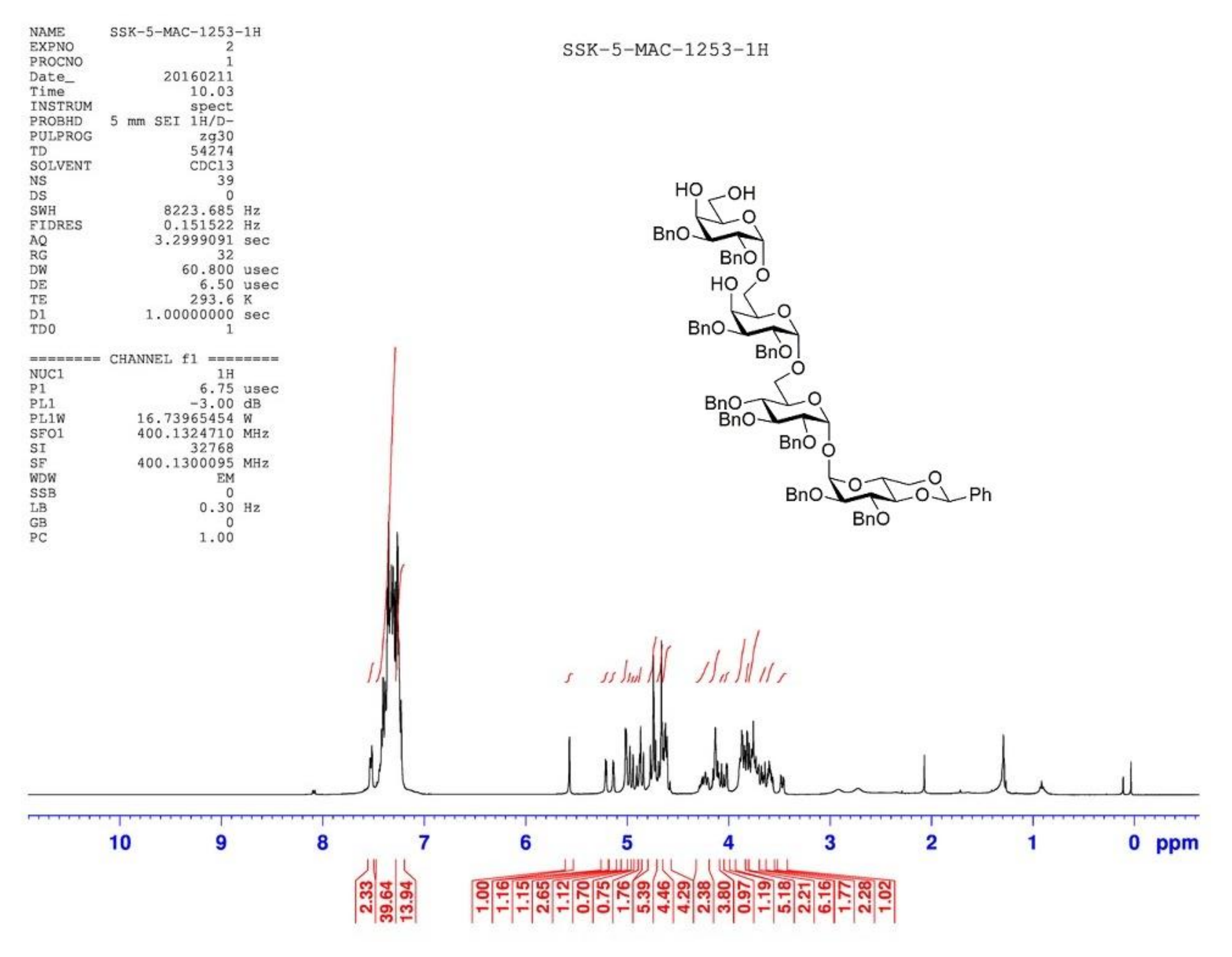
```
Current Data Parameters
NAME     SSK-5-MAC-1244-HSQC
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_           20160130
Time                0.17
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG  hsqcedetgpsisp2.2
TD                  1024
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             1677.852 Hz
FIDRES          1.638528 Hz
AQ             0.3051520 sec
RG                197.27
DW               298.000 usec
DE                  6.50 usec
TE                 296.7 K
CNST2        145.0000000
CNST17        -0.5000000
D0            0.00000300 sec
D1            1.00000000 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
D21           0.00360000 sec
D24           0.00089000 sec
IN0           0.00002410 sec

======== CHANNEL f1 ========
SFO1        500.1322925 MHz
NUC1                 1H
P1                13.00 usec
P2                26.00 usec
P28             1000.00 usec
PLW1        13.00000000 W

======== CHANNEL f2 ========
SFO2        125.7665916 MHz
NUC2                13C
CPDPRG[2 bi_p5m4sp_4sp.2
P3                 8.90 usec
P14              500.00 usec
P24             2000.00 usec
P63             1500.00 usec
PLW0      0 W
PLW2       103.00000000 W
PLW12        1.66499996 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3              0.500
SPOFFS3   0 Hz
SPW3         12.46500015 W
SPNAM[7]     Crp60comp.4
SPOAL7              0.500
SPOFFS7   0 Hz
SPW7         12.46500015 W
SPNAM[14 Crp32,1.5,20.2
SPOAL14             0.500
SPOFFS14 0 Hz
SPW14         5.31860018 W
SPNAM[31 Crp32,1.5,20.2
SPOAL31             0.500
SPOFFS31 0 Hz
SPW31         1.32969999 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPNAM[4]      SMSQ10.100
GPZ1               80.00 %
GPZ2               20.10 %
GPZ3               11.00 %
GPZ4               -5.00 %
P16              1000.00 usec
P19               600.00 usec

F1 - Acquisition parameters
TD                    256
SFO1          125.7666 MHz
FIDRES       81.042534 Hz
SW             164.963 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF          500.1300300 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2          echo-antiecho
SF          125.7577890 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
```



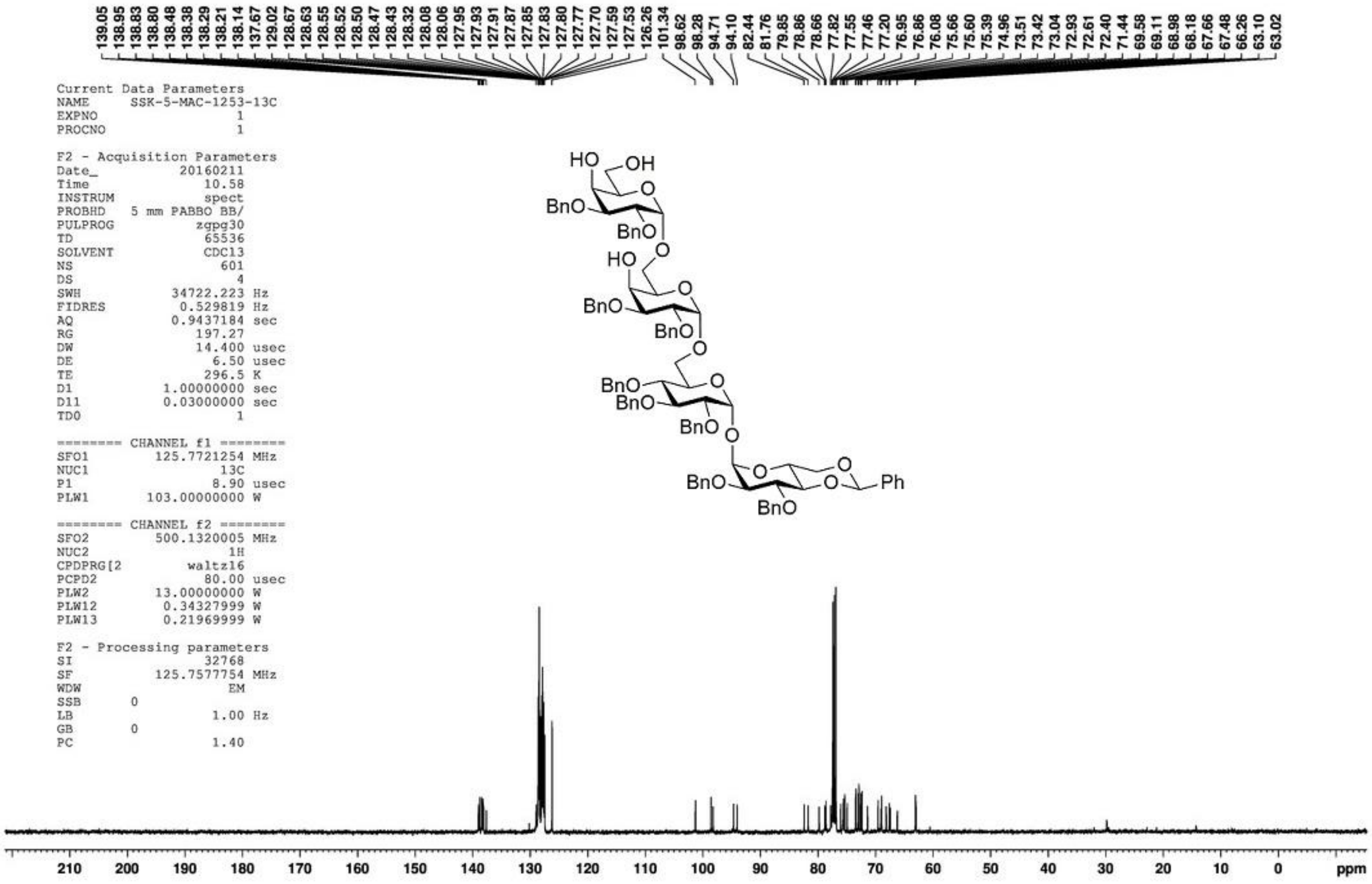
```
Current Data Parameters
NAME     SSK-5-MAC-1252-1H
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20160209
Time                18.39
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  30.72
DW                 50.000 usec
DE                   6.50 usec
TE                  296.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  13.00 usec
PLW1          13.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1299996 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



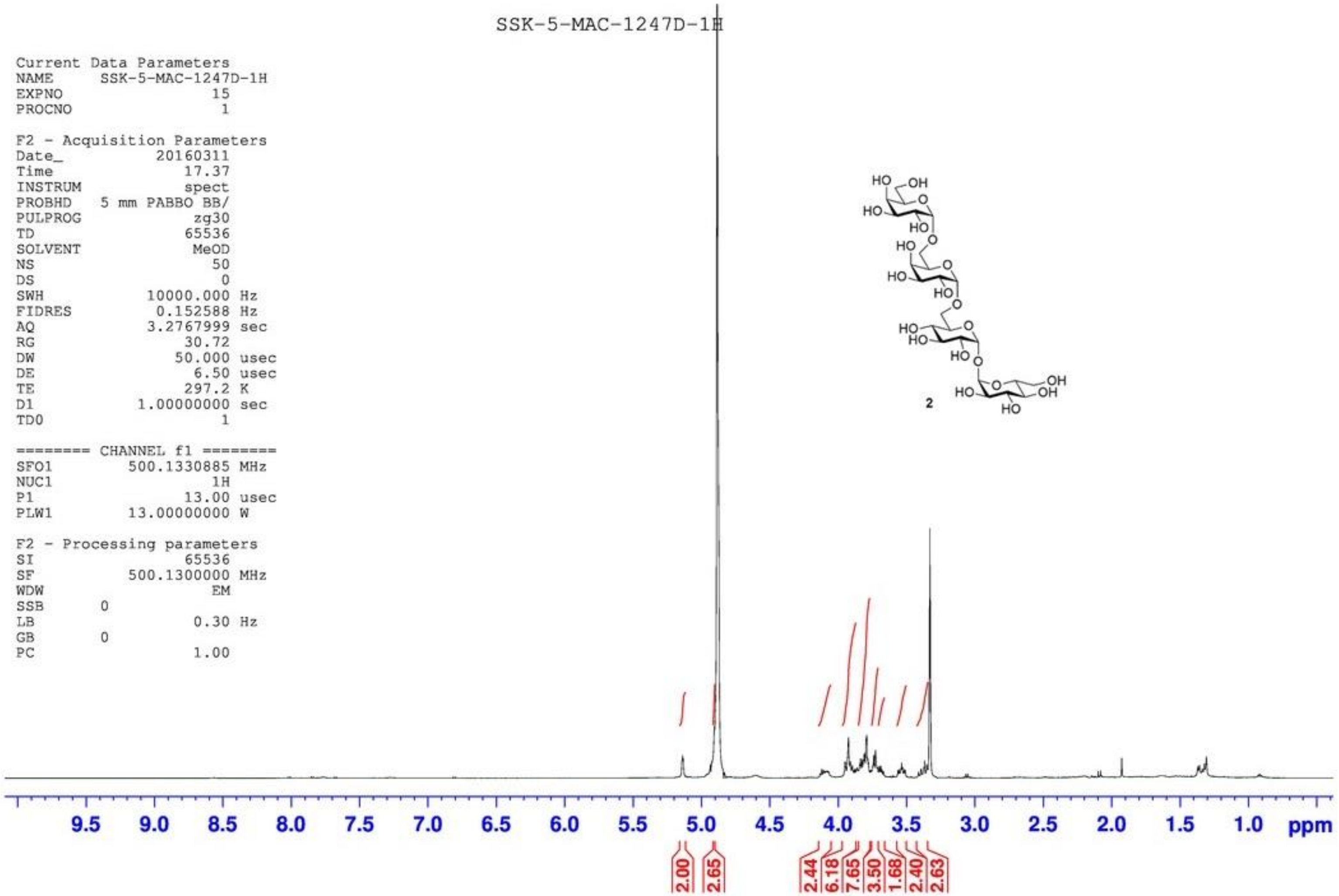
```
Current Data Parameters
NAME     SSK-5-MAC-1252-13C
EXPNO                     7
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160209
Time                  18.40
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     127
DS                       4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   297.0 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                     13C
P1                      8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                     32768
SF            125.7577728 MHz
WDW                       EM
SSB       0
LB                      1.00 Hz
GB        0
PC                      1.40
```



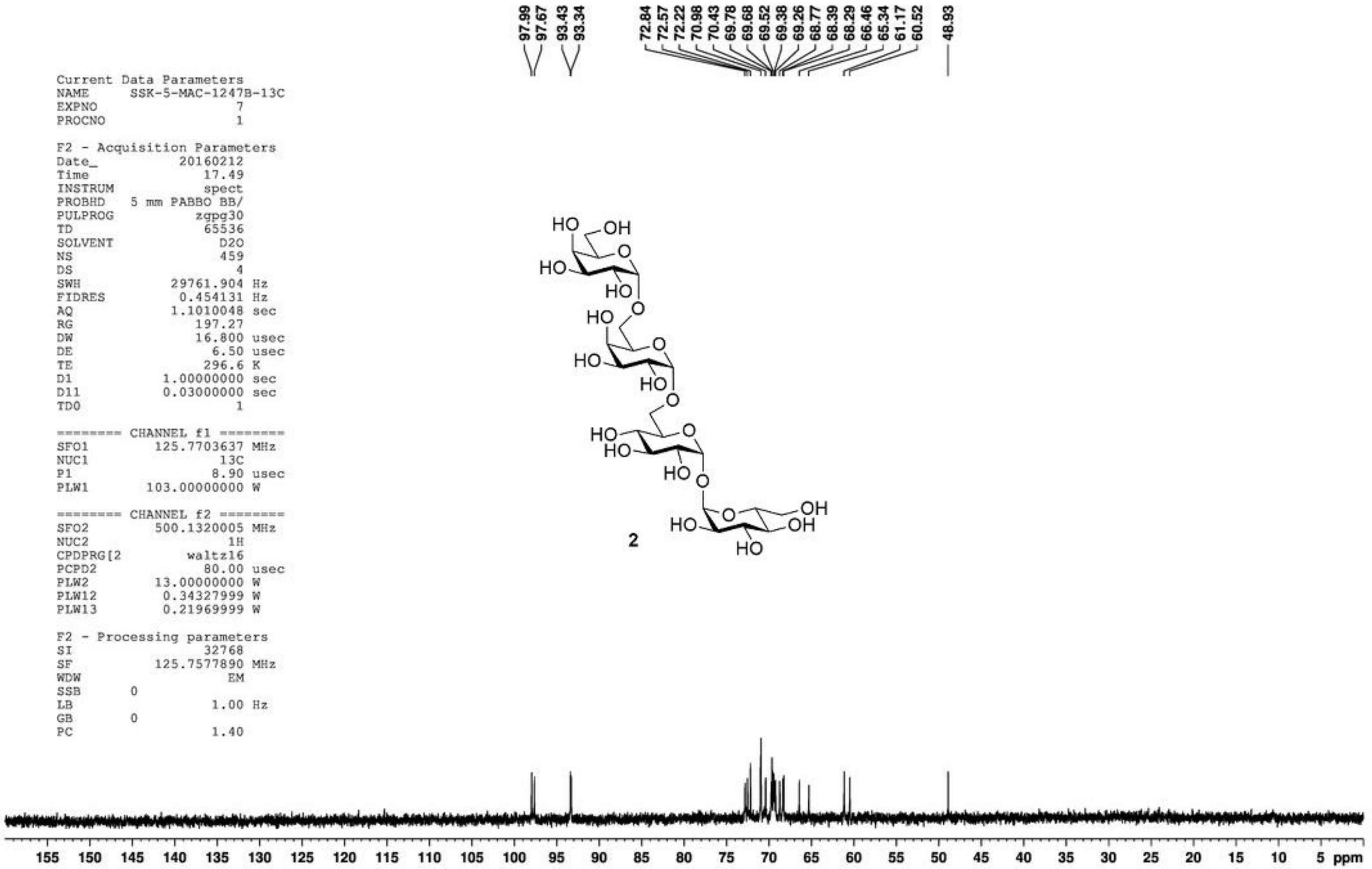
```
NAME       SSK-5-MAC-1253-1H
EXPNO                    2
PROCNO                   1
Date_             20160211
Time                 10.03
INSTRUM              spect
PROBHD    5 mm SEI 1H/D-
PULPROG               zg30
TD                   54274
SOLVENT              CDCl3
NS                      39
DS                       0
SWH               8223.685 Hz
FIDRES            0.151522 Hz
AQ               3.2999091 sec
RG                      32
DW                  60.800 usec
DE                    6.50 usec
TE                   293.6 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    6.75 usec
PL1                  -3.00 dB
PL1W           16.73965454 W
SFO1           400.1324710 MHz
SI                   32768
SF             400.1300095 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
Current Data Parameters
NAME     SSK-5-MAC-1253-13C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160211
Time                  10.58
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      601
DS                        4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ            0.9437184 sec
RG                   197.27
DW               14.400 usec
DE                 6.50 usec
TE                  296.5 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1        125.7721254 MHz
NUC1                    13C
P1                 8.90 usec
PLW1       103.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2             80.00 usec
PLW2        13.00000000 W
PLW12        0.34327999 W
PLW13        0.21969999 W

F2 - Processing parameters
SI                    32768
SF          125.7577754 MHz
WDW                      EM
SSB      0
LB                  1.00 Hz
GB       0
PC                     1.40
```

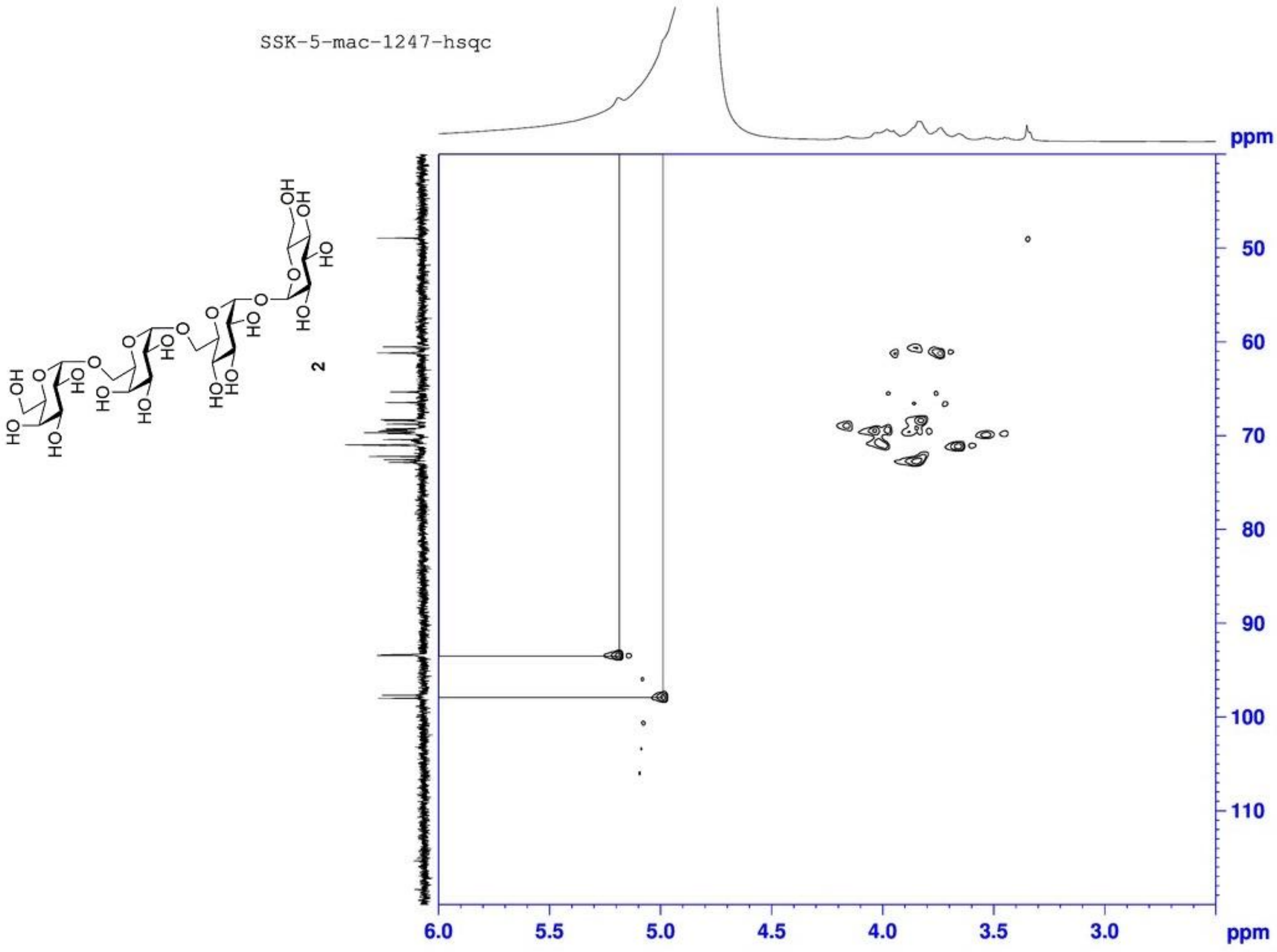


```
Current Data Parameters
NAME      SSK-5-MAC-1247D-1H
EXPNO                     15
PROCNO                     1

F2 - Acquisition Parameters
Date_               20160311
Time                   17.37
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                 zg30
TD                     65536
SOLVENT                 MeOD
NS                        50
DS                         0
SWH            10000.000 Hz
FIDRES          0.152588 Hz
AQ             3.2767999 sec
RG                     30.72
DW                50.000 usec
DE                  6.50 usec
TE                   297.2 K
D1            1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                      1H
P1                 13.00 usec
PLW1         13.00000000 W

F2 - Processing parameters
SI                     65536
SF           500.1300000 MHz
WDW                       EM
SSB      0
LB                   0.30 Hz
GB       0
PC                      1.00
```

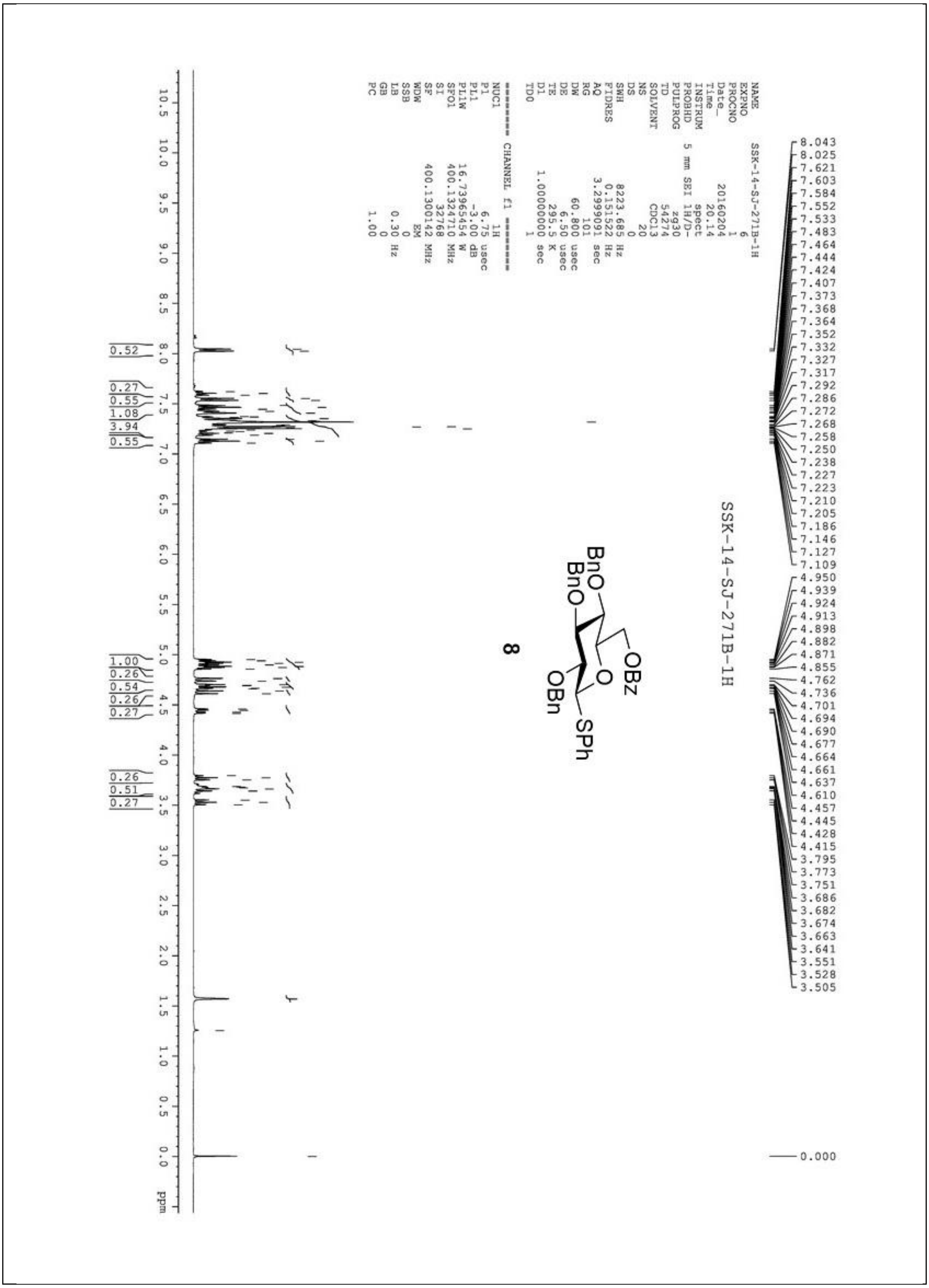


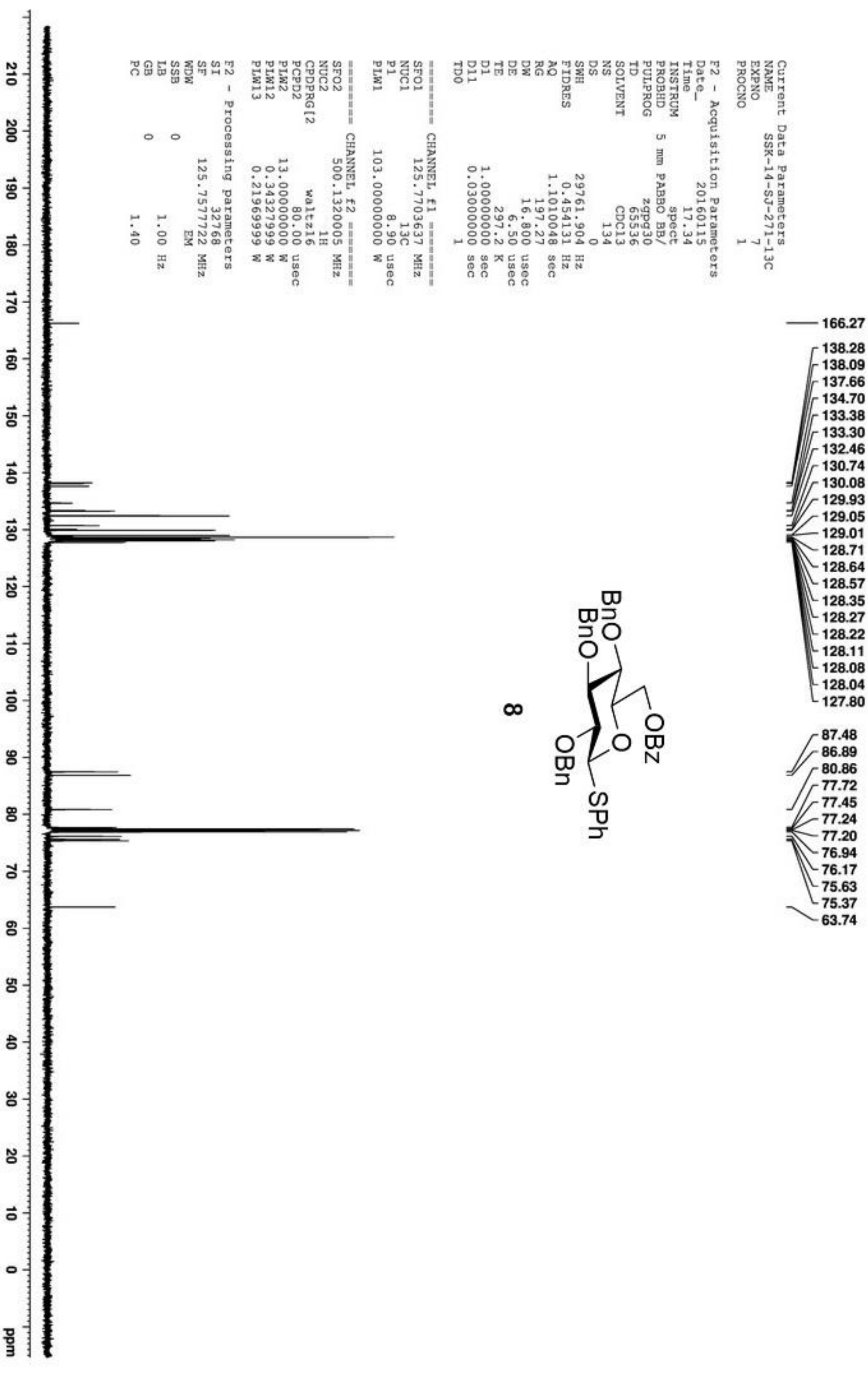
2

```
Current Data Parameters
NAME     SSK-5-MAC-1247B-13C
EXPNO                      7
PROCNO                     1

F2 - Acquisition Parameters
Date_               20160212
Time                   17.49
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT                 D2O
NS                      459
DS                        4
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                   197.27
DW                   16.800 usec
DE                     6.50 usec
TE                    296.6 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                     13C
P1                      8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                     32768
SF            125.7577890 MHz
WDW                       EM
SSB       0
LB                      1.00 Hz
GB        0
PC                      1.40
```

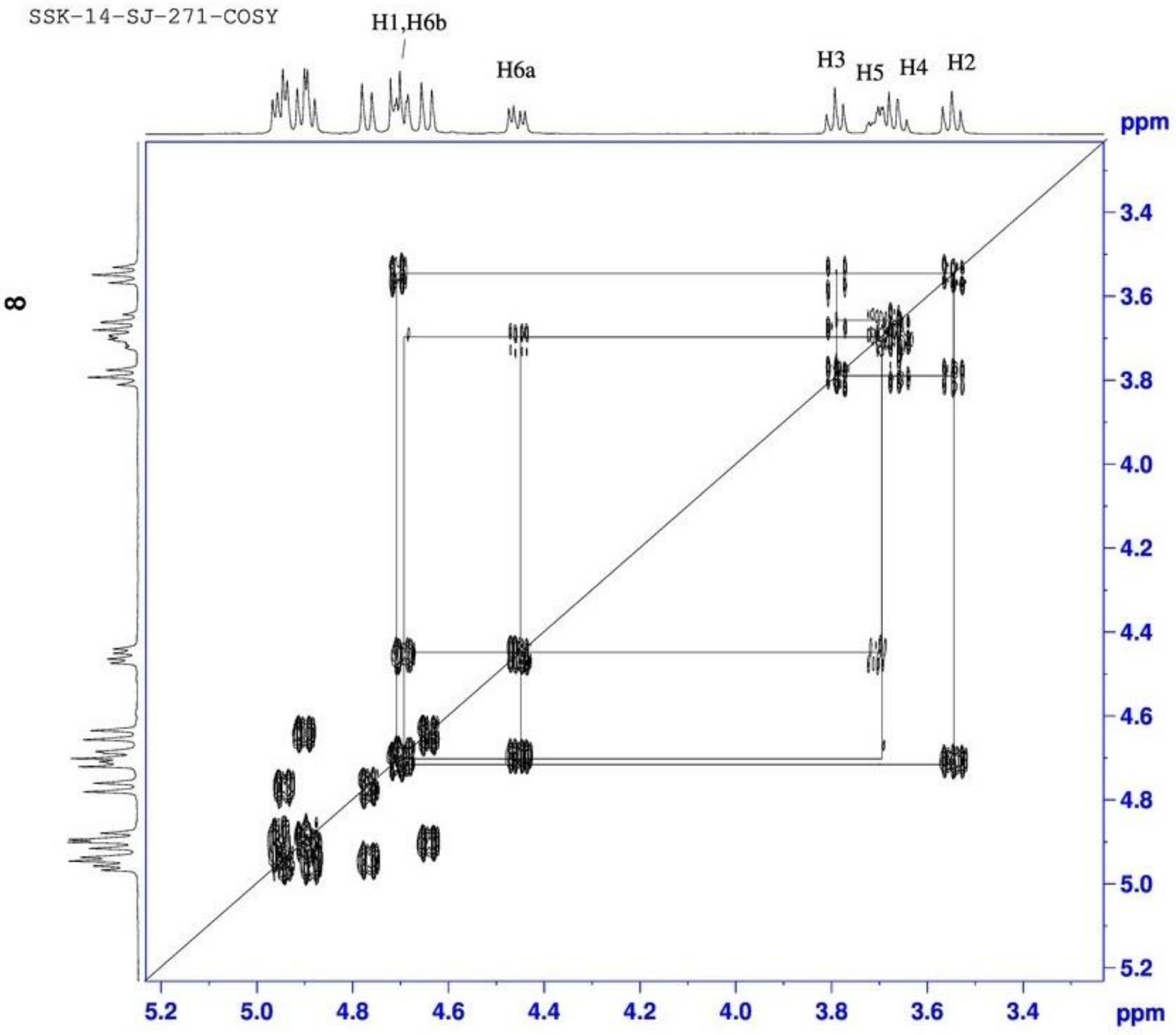


```
Current Data Parameters
NAME       SSK-5-mac-1247-hsqc
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_             20160214
Time                 22.27
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG  hsqcedetgpsisp2.2
TD                    1024
SOLVENT                D2O
NS                       8
DS                      32
SWH               3517.824 Hz
FIDRES            3.435375 Hz
AQ               0.1455445 sec
RG                  197.27
DW                 142.133 usec
DE                    6.50 usec
TE                   296.6 K
CNST2          145.0000000
CNST17          -0.5000000
D0              0.00000300 sec
D1              1.00000000 sec
D4              0.00172414 sec
D11             0.03000000 sec
D16             0.00020000 sec
D21             0.00360000 sec
D24             0.00089000 sec
IN0             0.00002410 sec

======== CHANNEL f1 ========
SFO1          500.1320643 MHz
NUC1                   1H
P1                  13.00 usec
P2                  26.00 usec
P28               1000.00 usec
PLW1          13.00000000 W

======== CHANNEL f2 ========
SFO2          125.7665916 MHz
NUC2                  13C
CPDPRG[2 bi_p5m4sp_4sp.2
P3                   8.90 usec
P14                500.00 usec
P24               2000.00 usec
P63               1500.00 usec
PLW0       0 W
PLW2         103.00000000 W
PLW12          1.66499996 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3              0.500
SPOFFS3   0 Hz
SPW3          12.46500015 W
SPNAM[7]     Crp60comp.4
SPOAL7              0.500
SPOFFS7   0 Hz
SPW7          12.46500015 W
SPNAM[14 Crp32,1.5,20.2
SPOAL14             0.500
SPOFFS14 0 Hz
SPW14          5.31860018 W
SPNAM[31 Crp32,1.5,20.2
SPOAL31             0.500
SPOFFS31 0 Hz
SPW31          1.32969999 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[2]       SMSQ10.100
GPNAM[3]       SMSQ10.100
GPNAM[4]       SMSQ10.100
GPZ1                80.00 %
GPZ2                20.10 %
GPZ3                11.00 %
GPZ4                -5.00 %
P16               1000.00 usec
P19                600.00 usec

F1 - Acquisition parameters
TD                    227
SFO1             125.7666 MHz
FIDRES          91.395981 Hz
SW                164.963 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                   1024
SF            500.1299683 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
PC                   1.40

F1 - Processing parameters
SI                   1024
MC2         echo-antiecho
SF            125.7577651 MHz
WDW                 QSINE
SSB                     2
LB         0 Hz
GB         0
```

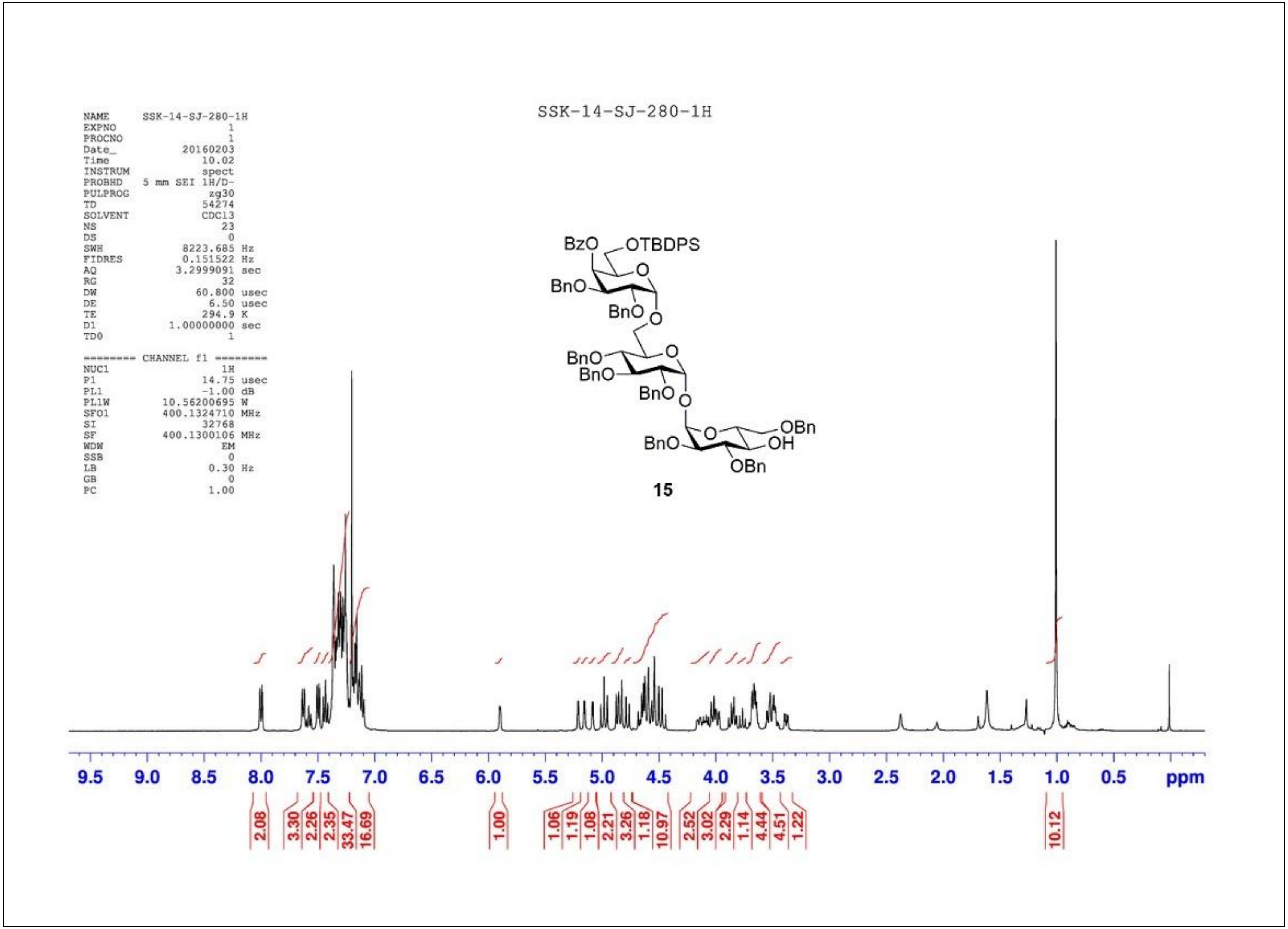

SSK-14-SJ-271B-1H
NAME SSK-14-SJ-271B-1H
EXPNO 6
PROCNO 1
Date_ 20160204
Time 20.14
INSTRUM spect
PROBHD 5 mm SEI 1H/D-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 20
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2999091 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 6.75 usec
PL1 -3.00 dB
PL1W 16.73965454 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
8.043
8.025
7.621
7.603
7.584
7.552
7.533
7.483
7.464
7.444
7.424
7.407
7.373
7.368
7.364
7.352
7.332
7.327
7.317
7.292
7.286
7.272
7.268
7.258
7.250
7.238
7.227
7.223
7.210
7.205
7.186
7.146
7.127
7.109
4.950
4.939
4.924
4.913
4.898
4.882
4.871
4.855
4.762
4.736
4.701
4.694
4.690
4.677
4.664
4.661
4.637
4.610
4.457
4.445
4.428
4.415
3.795
3.773
3.751
3.686
3.682
3.674
3.663
3.641
3.551
3.528
3.505
0.000
OBz
BnO
BnO
O
OBn
SPh
8
0.52
0.27
0.55
1.08
3.94
0.55
1.00
0.26
0.54
0.26
0.27
0.26
0.51
0.27
10.5
10.0
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
0.5
0.0
ppm

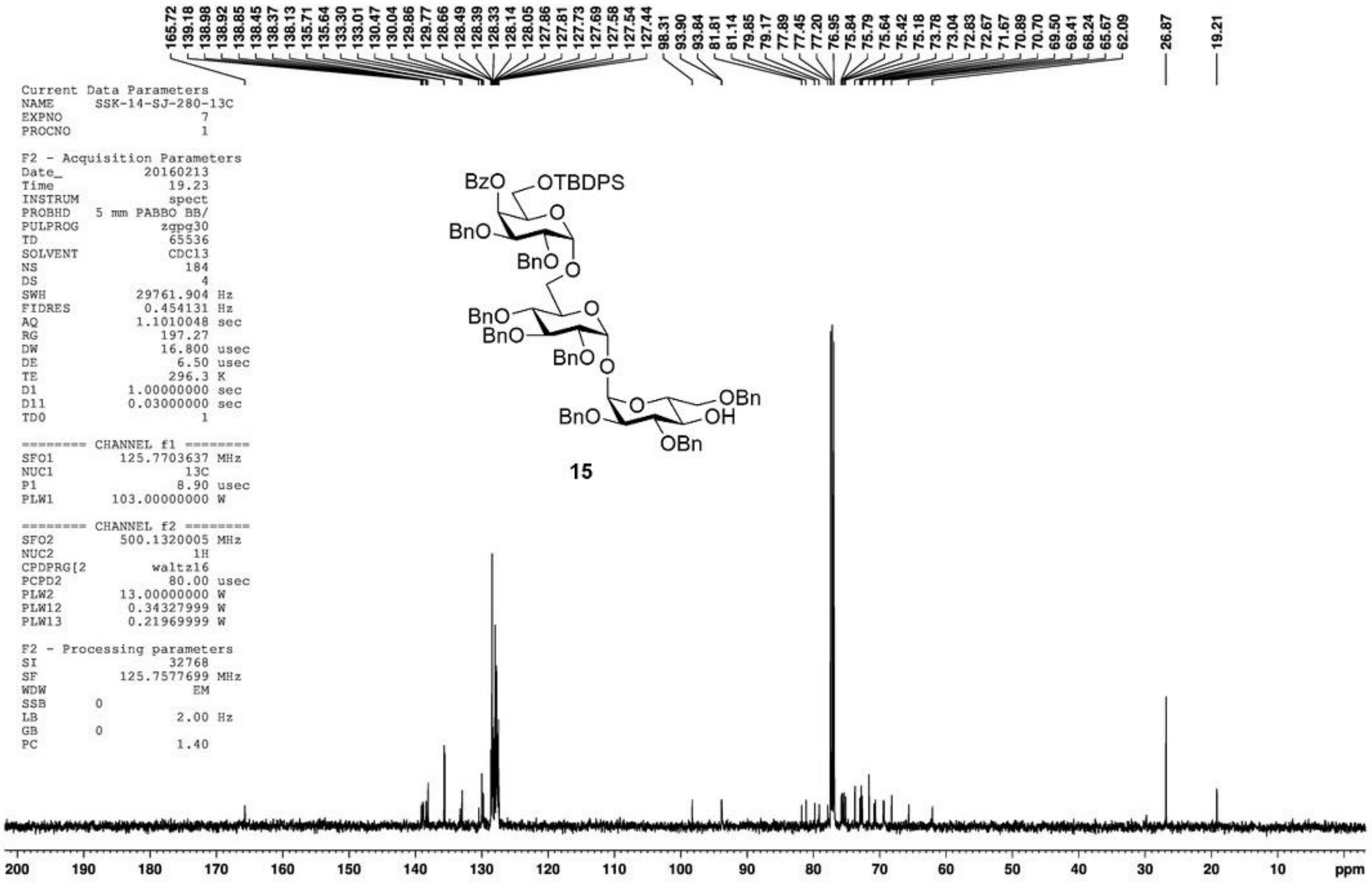
Current Data Parameters
NAME SSK-14-SJ-271-13C
EXPNO 7
PROCNO 1
F2 - Acquisition Parameters
Date_ 20160115
Time 17.34
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 134
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 13.00000000 W
PLW12 0.34327999 W
PLW13 0.21969999 W
F2 - Processing parameters
SI 32768
SF 125.7577722 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
166.27
138.28
138.09
137.66
134.70
133.38
133.30
132.46
130.74
130.08
129.93
129.05
129.01
128.71
128.64
128.57
128.35
128.27
128.22
128.11
128.08
128.04
127.80
87.48
86.89
80.86
77.72
77.45
77.24
77.20
76.94
76.17
75.63
75.37
63.74
BnO
BnO
OBz
O
OBn
SPh
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

**8**



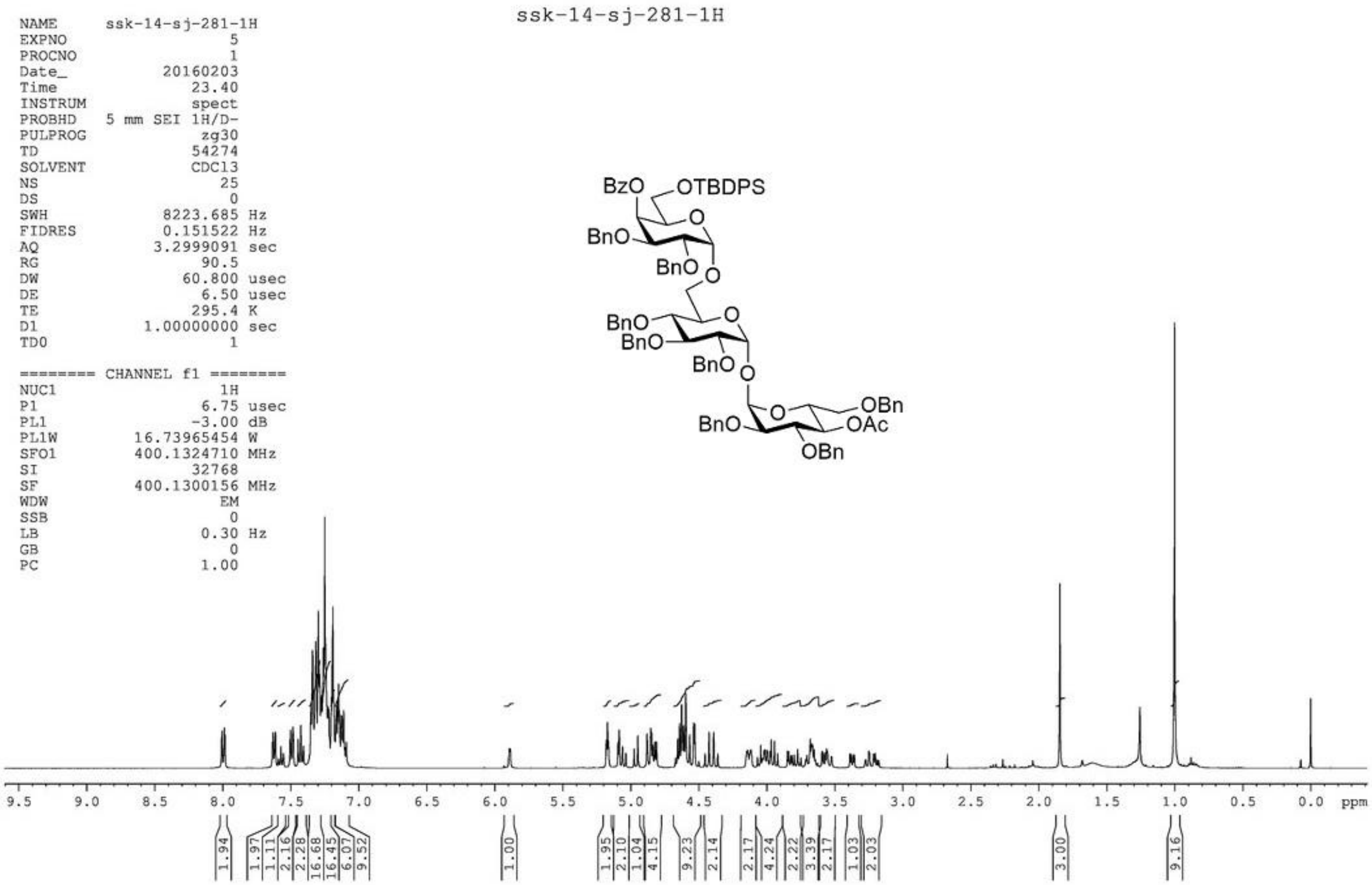
```
Current Data Parameters
NAME     SSK-14-SJ-271-COSY
EXPNO                     9
PROCNO                    1

F2 - Acquisition Parameters
Date_              20160115
Time                  17.39
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG          cosygpppqf
TD                     2048
SOLVENT               CDC13
NS                        8
DS                        0
SWH                1000.400 Hz
FIDRES             0.488477 Hz
AQ                1.0235904 sec
RG                   134.65
DW                  499.800 usec
DE                     6.50 usec
TE                    296.4 K
D0               0.00000300 sec
D1               1.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
D16              0.00020000 sec
IN0              0.00099960 sec

======== CHANNEL f1 ========
SFO1            500.1321279 MHz
NUC1                     1H
P0                    13.00 usec
P1                    13.00 usec
P17                 2500.00 usec
PLW1            13.00000000 W
PLW10            3.25000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]         SMSQ10.100
GPZ1                  10.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       51
SFO1               500.1321 MHz
FIDRES            19.615690 Hz
SW                    2.000 ppm
FnMODE                   QF

F2 - Processing parameters
SI                     1024
SF              500.1300113 MHz
WDW                   QSINE
SSB        0
LB         0 Hz
GB         0
PC                     1.40

F1 - Processing parameters
SI                     1024
MC2                      QF
SF              500.1300113 MHz
WDW                   QSINE
SSB        0
LB         0 Hz
GB         0
```


SSK-14-SJ-280-1H
NAME SSK-14-SJ-280-1H
EXPNO 1
PROCNO 1
Date_ 20160203
Time 10.02
INSTRUM spect
PROBHD 5 mm SEI 1H/D-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 23
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2999091 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300106 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
BzO
OTBDPS
BnO
BnO
O
BnO
BnO
BnO
O
BnO
O
OBn
OH
OBn
15
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
0.5
ppm
2.08
3.30
2.26
2.35
33.47
16.69
1.00
1.06
1.19
1.08
2.21
3.26
1.18
10.97
2.52
3.02
2.29
1.14
4.44
4.51
1.22
10.12

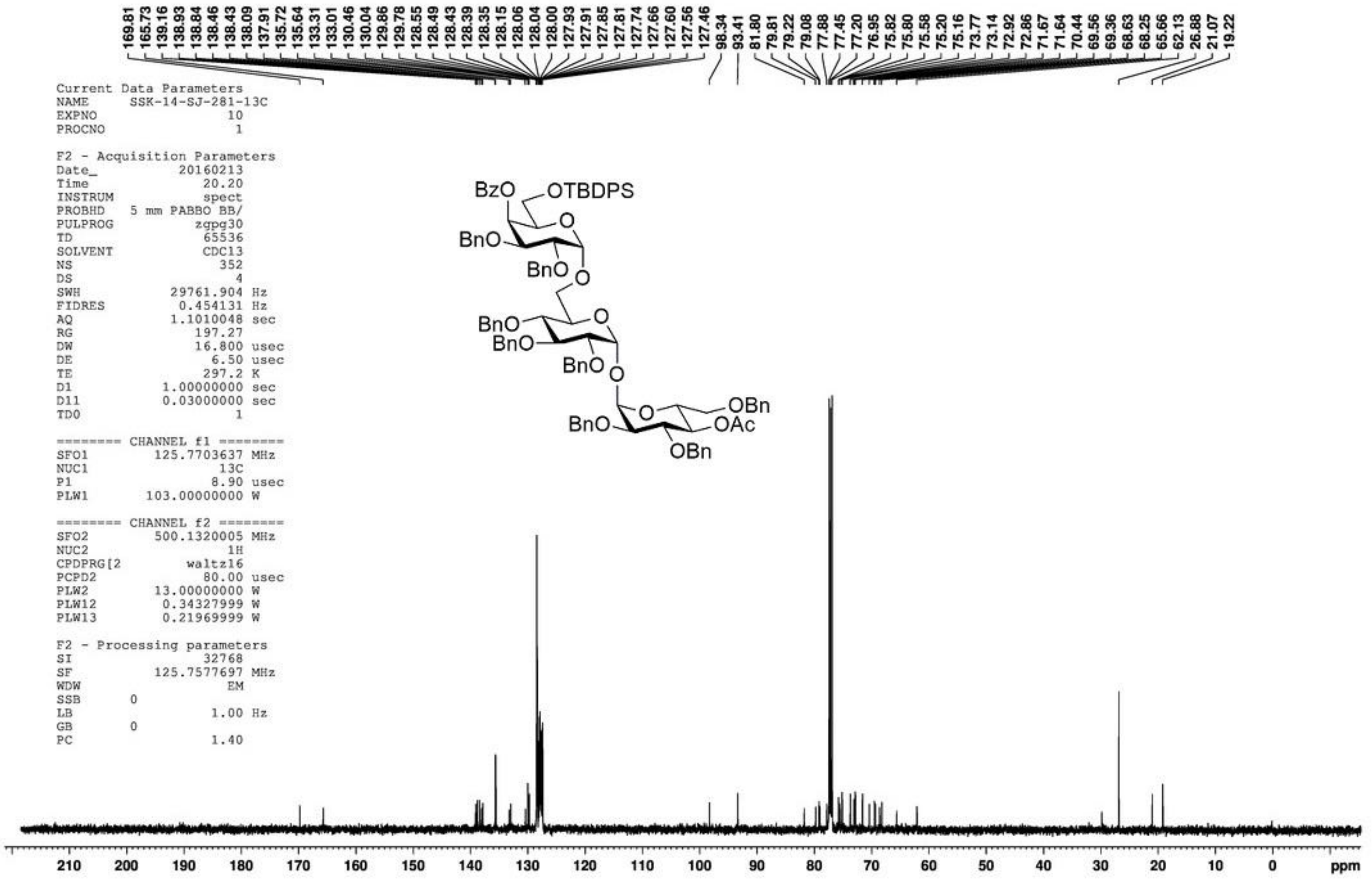


```
Current Data Parameters
NAME     SSK-14-SJ-280-13C
EXPNO              7
PROCNO             1

F2 - Acquisition Parameters
Date_          20160213
Time              19.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  184
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               197.27
DW               16.800 usec
DE                 6.50 usec
TE                296.3 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1       125.7703637 MHz
NUC1               13C
P1                8.90 usec
PLW1      103.00000000 W

======== CHANNEL f2 ========
SFO2       500.1320005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            80.00 usec
PLW2       13.00000000 W
PLW12       0.34327999 W
PLW13       0.21969999 W

F2 - Processing parameters
SI                32768
SF         125.7577699 MHz
WDW                  EM
SSB      0
LB                 2.00 Hz
GB       0
PC                 1.40
```

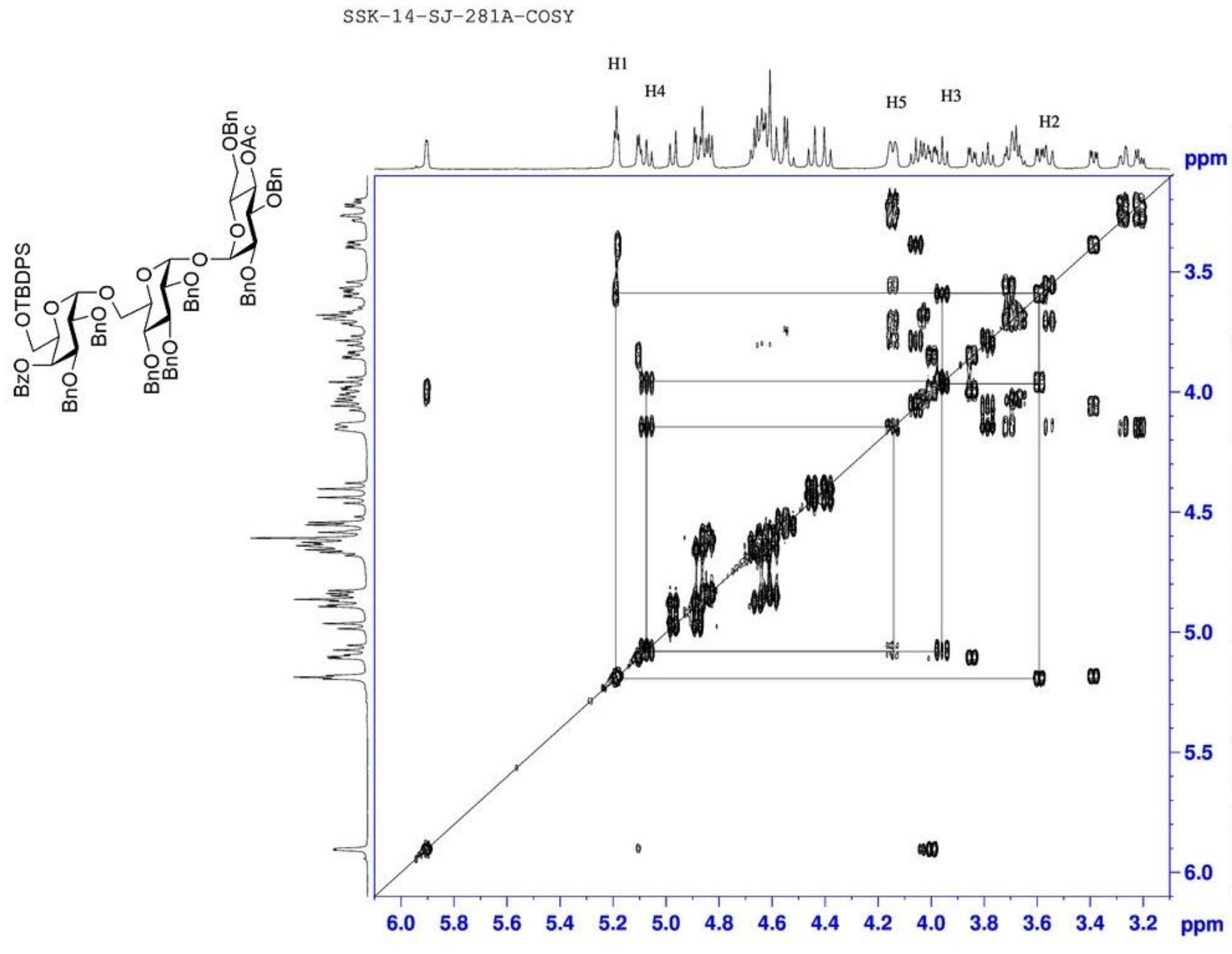
15



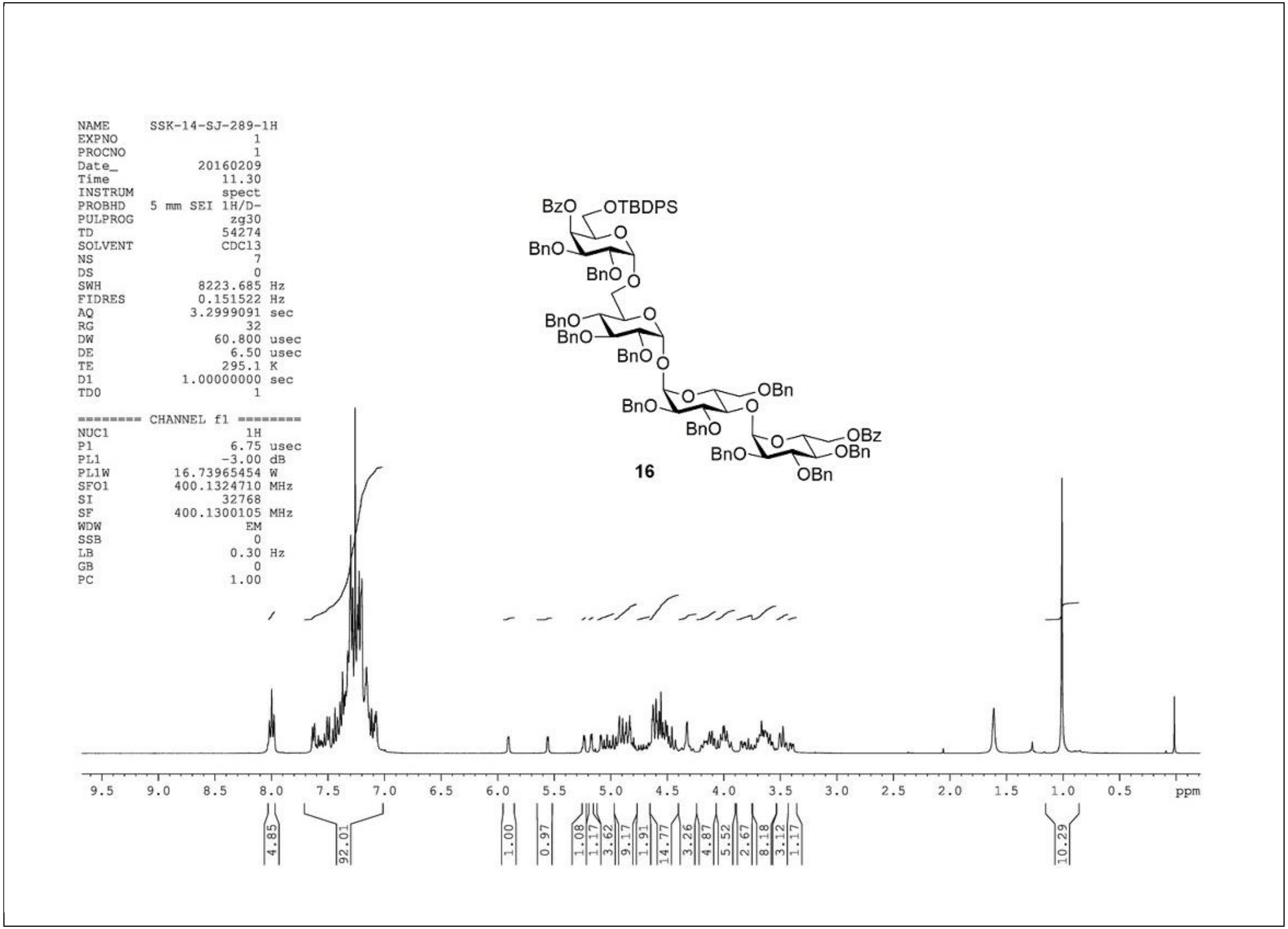
```
NAME         ssk-14-sj-281-1H
EXPNO                       5
PROCNO                      1
Date_                20160203
Time                    23.40
INSTRUM                 spect
PROBHD       5 mm SEI 1H/D-
PULPROG                  zg30
TD                      54274
SOLVENT                 CDCl3
NS                         25
DS                          0
SWH                  8223.685 Hz
FIDRES               0.151522 Hz
AQ                  3.2999091 sec
RG                       90.5
DW                     60.800 usec
DE                       6.50 usec
TE                      295.4 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       6.75 usec
PL1                     -3.00 dB
PL1W              16.73965454 W
SFO1              400.1324710 MHz
SI                      32768
SF                400.1300156 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```



```
Current Data Parameters
NAME     SSK-14-SJ-281-13C
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160213
Time                 20.20
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDC13
NS                     352
DS                       4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   297.2 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                   32768
SF           125.7577697 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

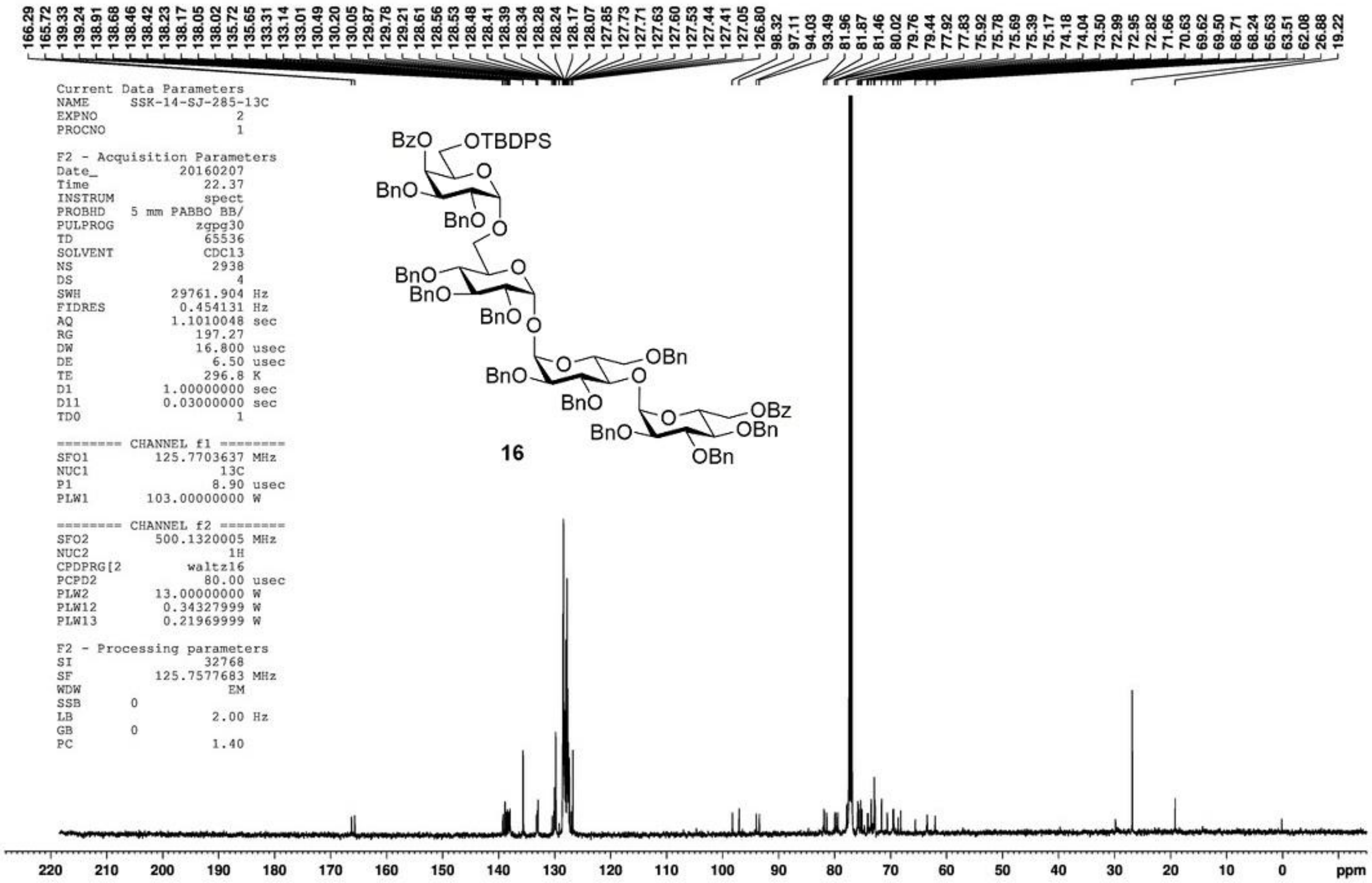


```
Current Data Parameters
NAME     SSK-14-SJ-281A-COSY
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160205
Time               11.01
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        cosygpppqf
TD                  2048
SOLVENT            CDC13
NS                    16
DS                     8
SWH             1731.302 Hz
FIDRES          0.845362 Hz
AQ             0.5914624 sec
RG                119.07
DW               288.800 usec
DE                  6.50 usec
TE                 297.3 K
D0            0.00000300 sec
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00057760 sec

======== CHANNEL f1 ========
SFO1         500.1322978 MHz
NUC1                  1H
P0                 13.00 usec
P1                 13.00 usec
P17              2500.00 usec
PLW1         13.00000000 W
PLW10         3.25000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            500.1323 MHz
FIDRES         13.525796 Hz
SW                 3.462 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           500.1300125 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.1300125 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
```



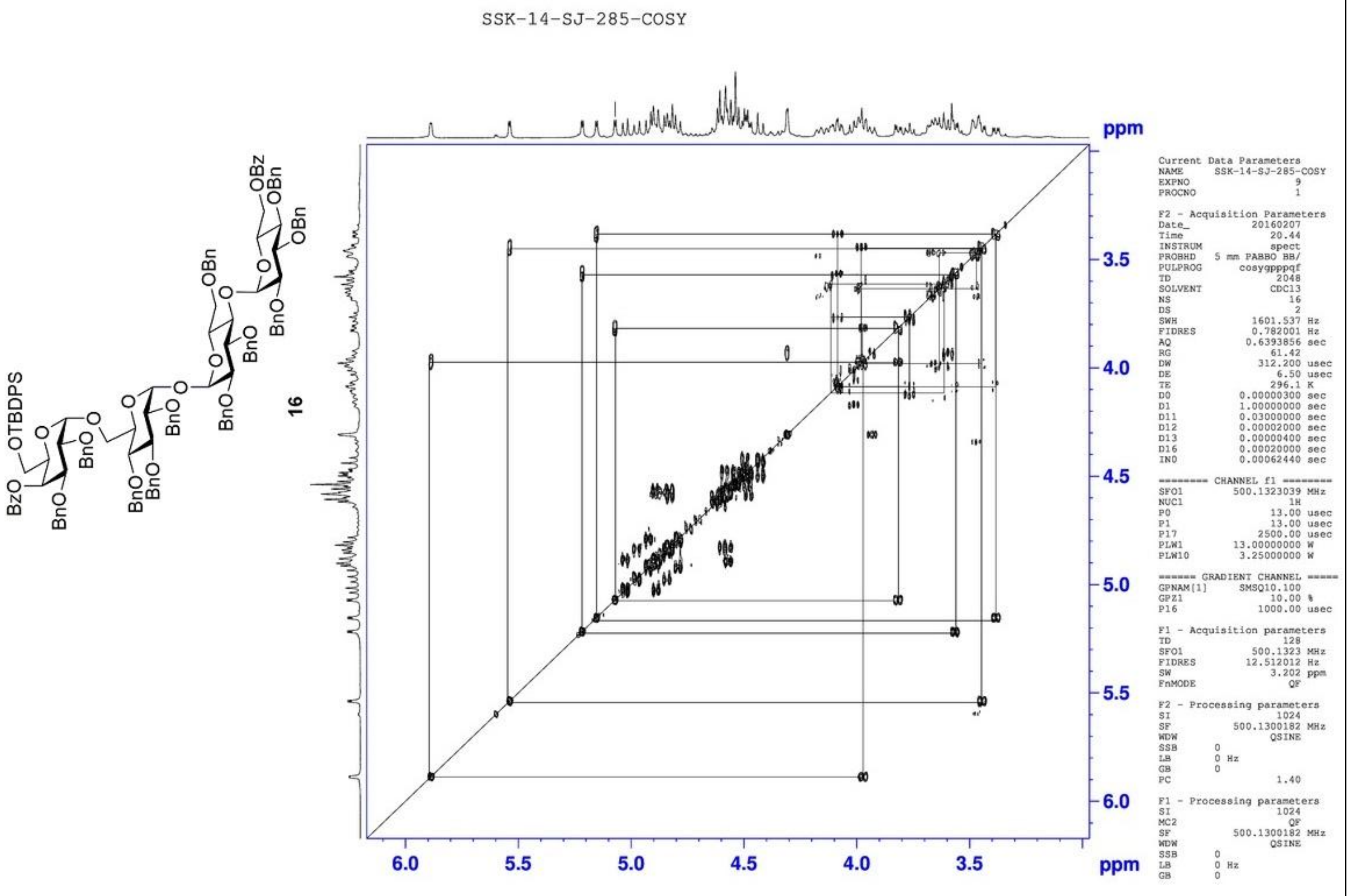
```
NAME      SSK-14-SJ-289-1H
EXPNO                    1
PROCNO                   1
Date_             20160209
Time                 11.30
INSTRUM              spect
PROBHD    5 mm SEI 1H/D-
PULPROG               zg30
TD                   54274
SOLVENT              CDCl3
NS                       7
DS                       0
SWH               8223.685 Hz
FIDRES            0.151522 Hz
AQ               3.2999091 sec
RG                      32
DW                  60.800 usec
DE                    6.50 usec
TE                   295.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    6.75 usec
PL1                  -3.00 dB
PL1W           16.73965454 W
SFO1           400.1324710 MHz
SI                   32768
SF             400.1300105 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

**16**



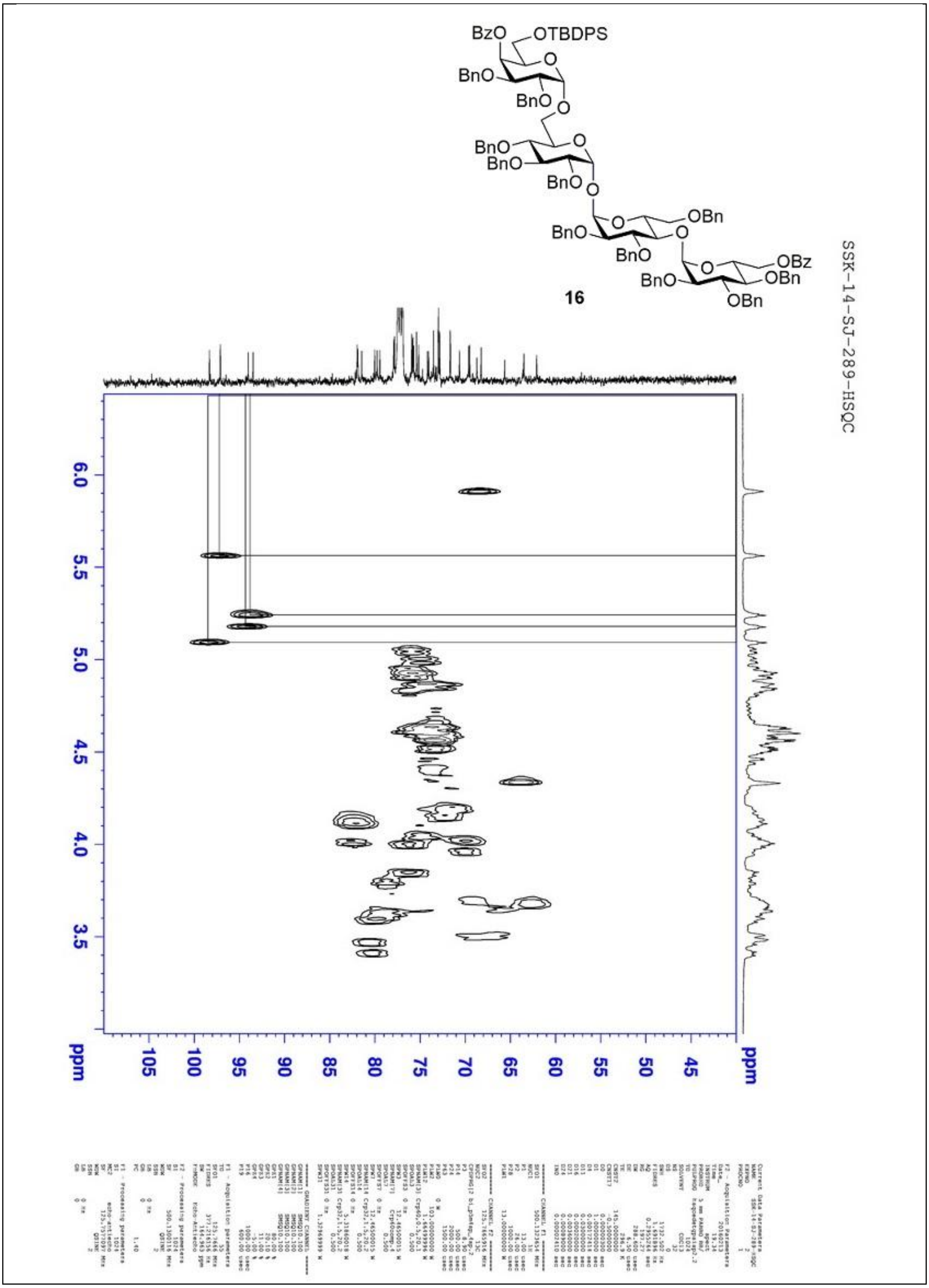
16

```
Current Data Parameters
NAME     SSK-14-SJ-285-13C
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160207
Time                 22.37
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2938
DS                       4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   296.8 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           13.00000000 W
PLW12           0.34327999 W
PLW13           0.21969999 W

F2 - Processing parameters
SI                   32768
SF           125.7577683 MHz
WDW                     EM
SSB      0
LB                    2.00 Hz
GB       0
PC                    1.40
```

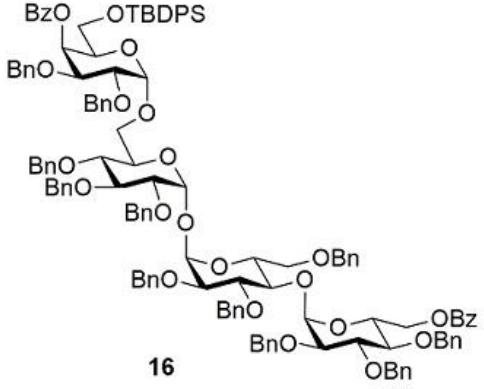


16

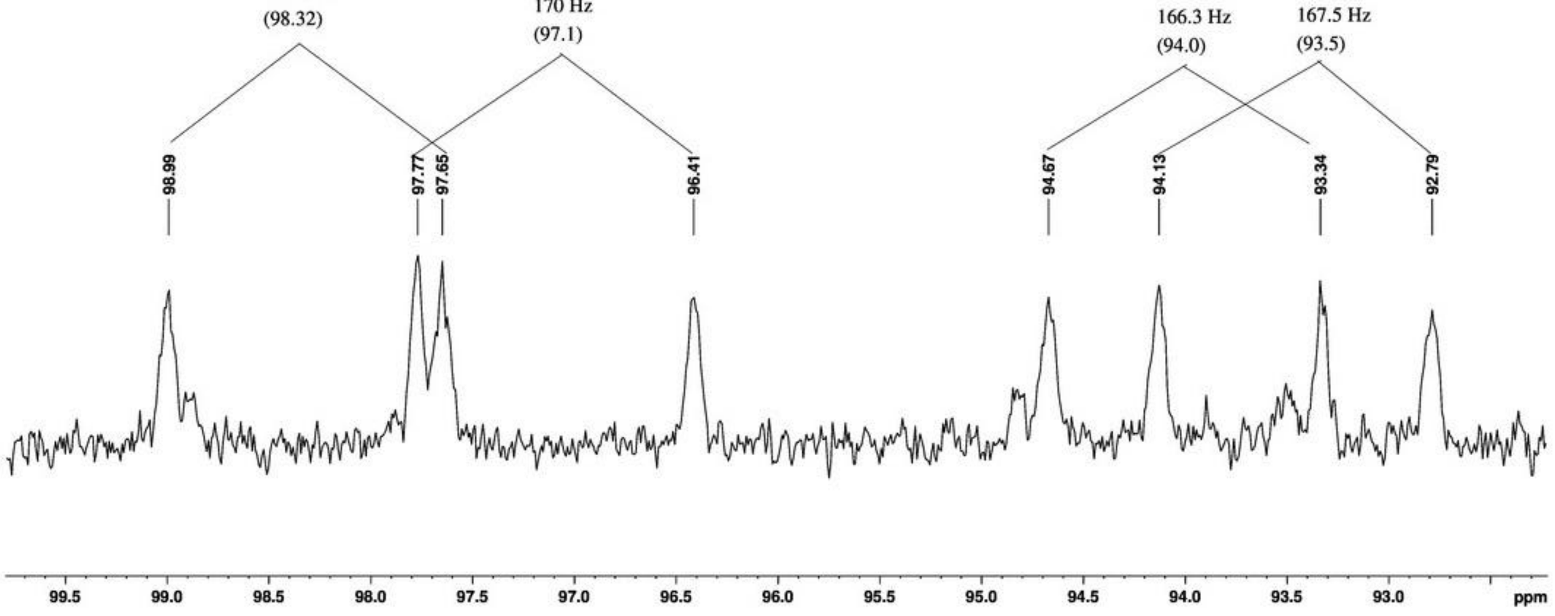
```
Current Data Parameters
NAME      SSK-14-SJ-285-COSY
EXPNO                  9
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160207
Time               20.44
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG       cosygpppqf
TD                  2048
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             1601.537 Hz
FIDRES          0.782001 Hz
AQ             0.6393856 sec
RG                 61.42
DW               312.200 usec
DE                  6.50 usec
TE                 296.1 K
D0            0.00000300 sec
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00062440 sec

======== CHANNEL f1 ========
SFO1         500.1323039 MHz
NUC1                  1H
P0                 13.00 usec
P1                 13.00 usec
P17              2500.00 usec
PLW1         13.00000000 W
PLW10         3.25000000 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPZ1               10.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   128
SFO1            500.1323 MHz
FIDRES         12.512012 Hz
SW                 3.202 ppm
FnMODE                QF

F2 - Processing parameters
SI                  1024
SF           500.1300182 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
PC                  1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           500.1300182 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
```


SSK-14-SJ-289-HSQC
16
BzO
OTBDPS
BnO
BnO
O
BnO
BnO
BnO
O
OBn
BnO
BnO
O
OBz
BnO
OBn
OBn
6.0
5.5
5.0
4.5
4.0
3.5
ppm
105
100
95
90
85
80
75
70
65
60
55
50
45
ppm

SSK-14-SJ-289-CH COUPLING

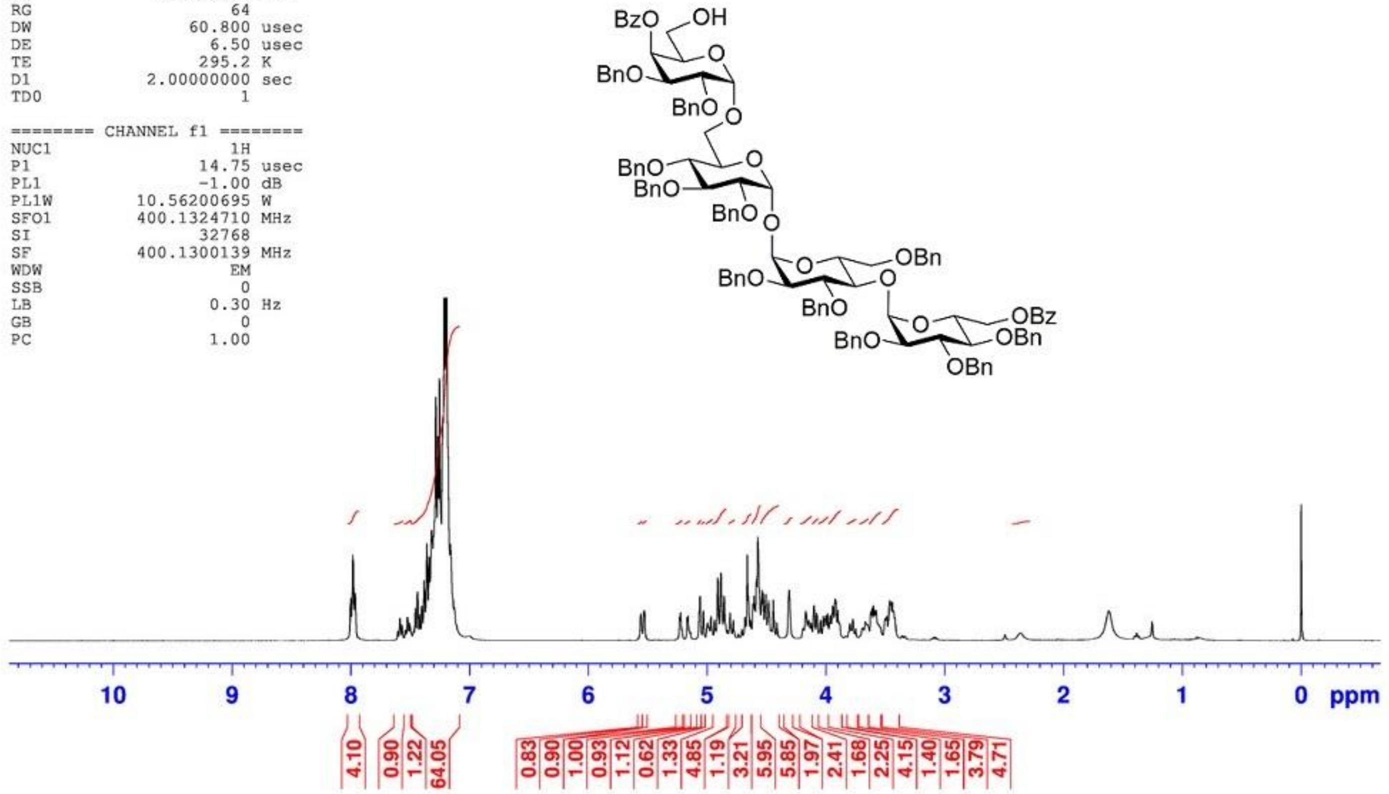


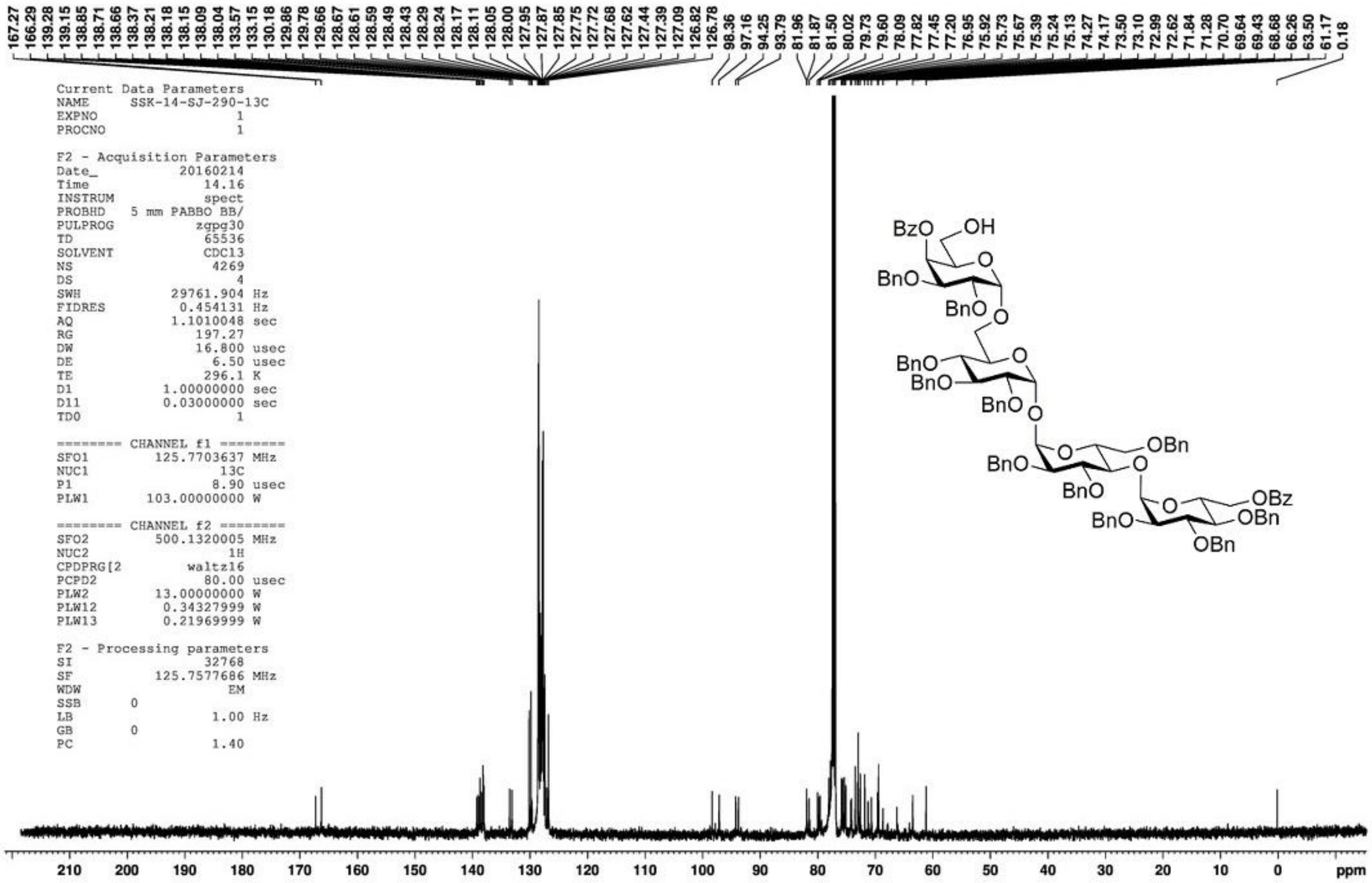
**16**



```
NAME       SSK-14-SJ-290-1H
EXPNO                     3
PROCNO                    1
Date_              20160210
Time                  22.53
INSTRUM               spect
PROBHD   5 mm SEI 1H/D-
PULPROG                zg30
TD                    54274
SOLVENT               CDCl3
NS                       13
DS                        0
SWH                8223.685 Hz
FIDRES             0.151522 Hz
AQ                3.2999091 sec
RG                       64
DW                   60.800 usec
DE                     6.50 usec
TE                    295.2 K
D1               2.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.75 usec
PL1                   -1.00 dB
PL1W            10.56200695 W
SFO1            400.1324710 MHz
SI                    32768
SF              400.1300139 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

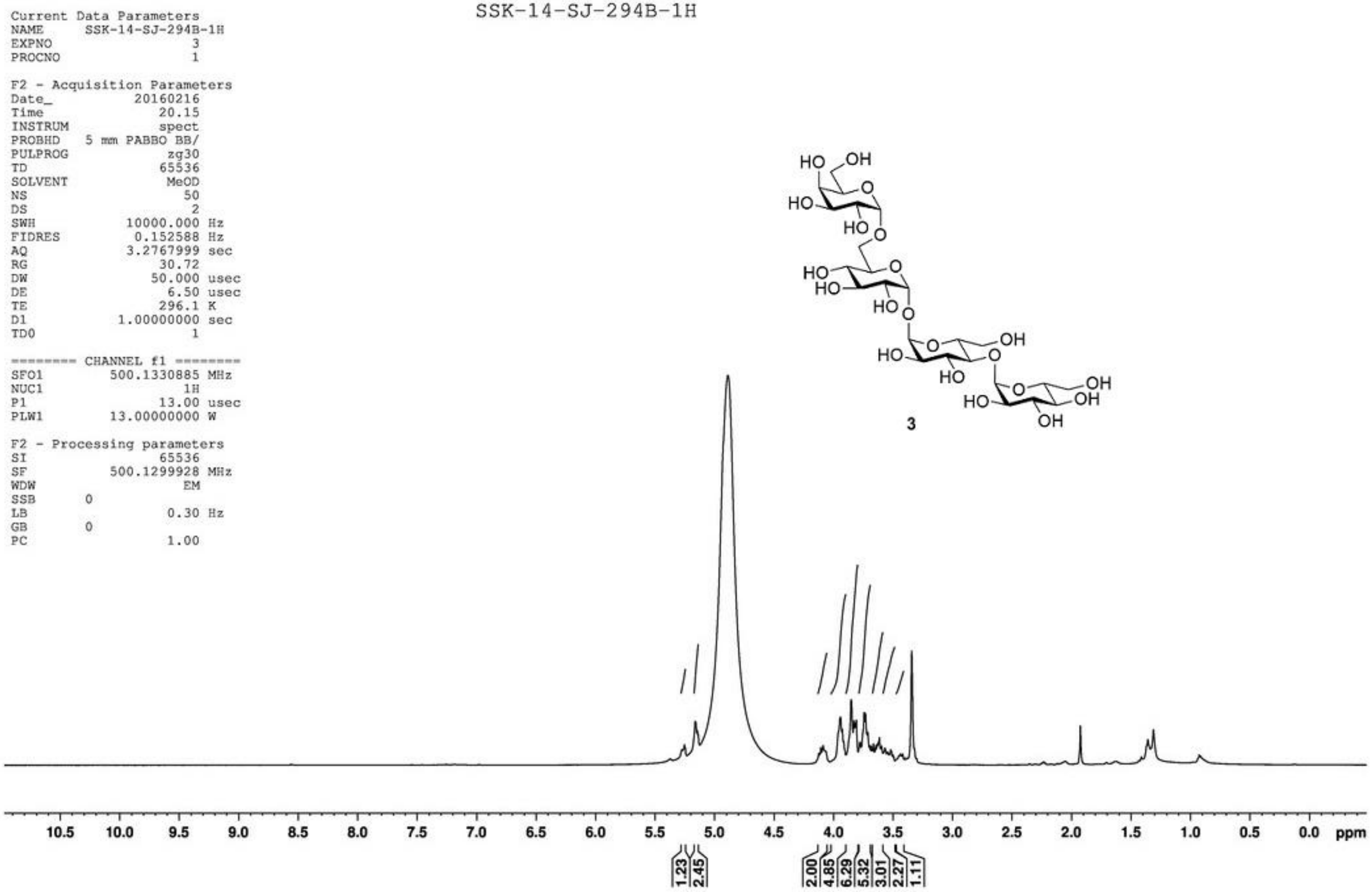
SSK-14-SJ-290-1H



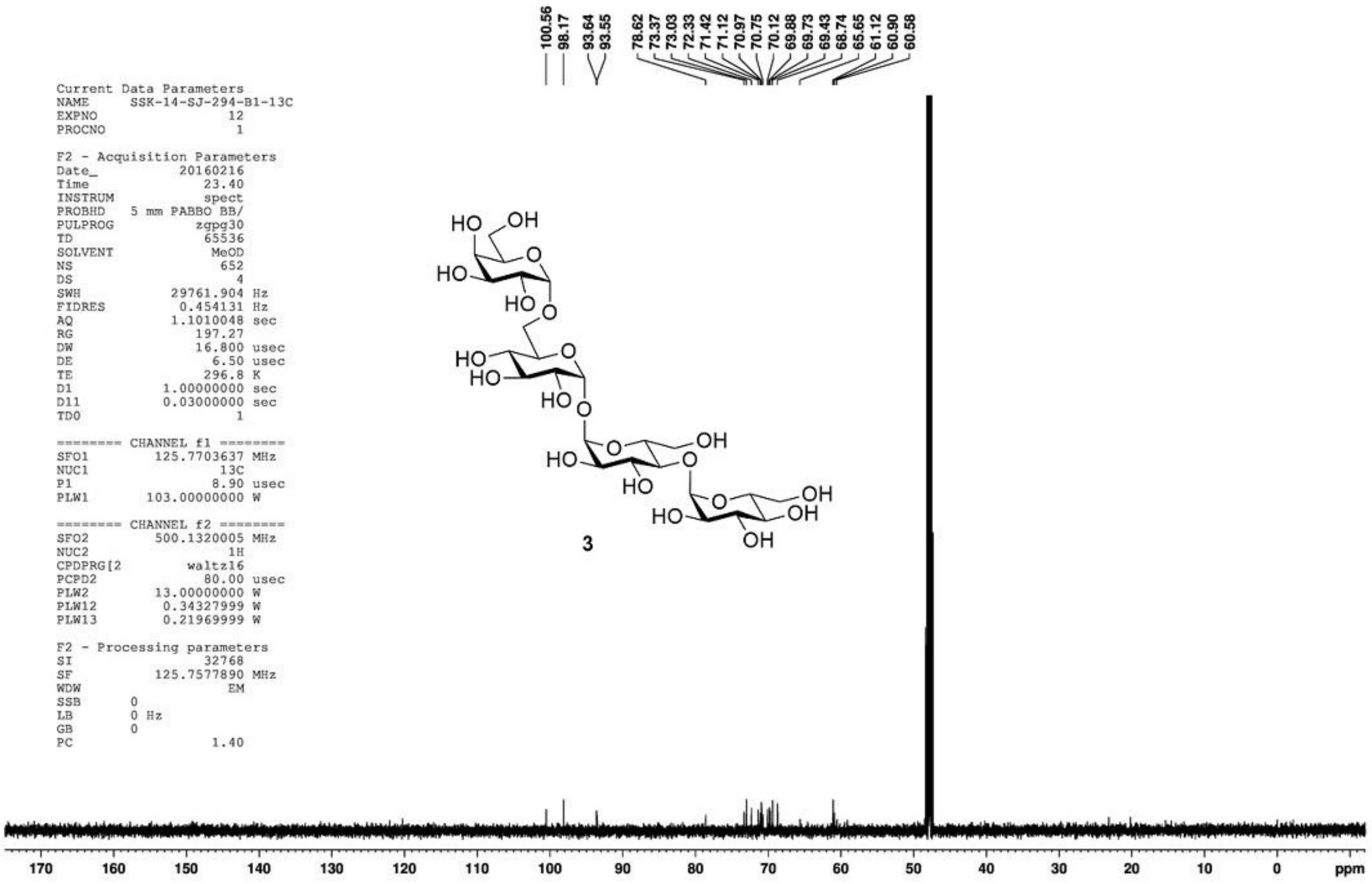


```
Current Data Parameters
NAME     SSK-14-SJ-290-13C
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20160214
Time                 14.16
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    4269
DS                       4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   296.1 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                   13C
P1                    8.90 usec
PLW1        103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2         13.00000000 W
PLW12         0.34327999 W
PLW13         0.21969999 W

F2 - Processing parameters
SI                   32768
SF           125.7577686 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

SSK-14-SJ-294B-1H

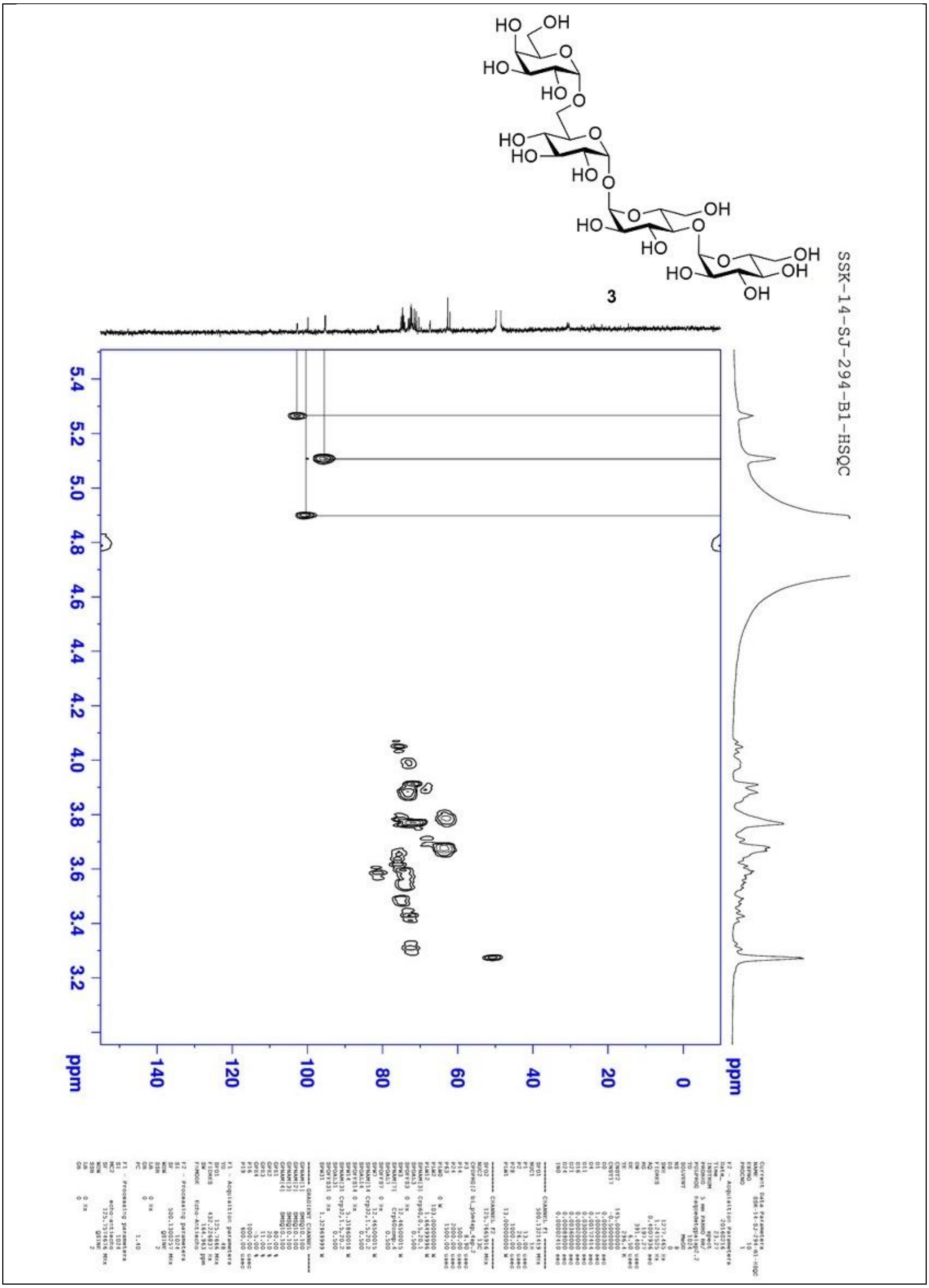


```
Current Data Parameters
NAME      SSK-14-SJ-294B-1H
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_            20160216
Time                20.15
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     50
DS                      2
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  30.72
DW                 50.000 usec
DE                   6.50 usec
TE                  296.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  13.00 usec
PLW1          13.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1299928 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```



3

```
Current Data Parameters
NAME     SSK-14-SJ-294-B1-13C
EXPNO                      12
PROCNO                      1

F2 - Acquisition Parameters
Date_              20160216
Time                  23.40
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT               MeOD
NS                     652
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                  197.27
DW                  16.800 usec
DE                    6.50 usec
TE                   296.8 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                     13C
P1                      8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                      1H
CPDPRG[2             waltz16
PCPD2                  80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                     32768
SF            125.7577890 MHz
WDW                       EM
SSB      0
LB       0 Hz
GB       0
PC                      1.40
```


SSK-14-SJ-294-B1-HSQC
3
HO
OH
O
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
140
120
100
80
60
40
20
0
ppm