Metabolic inhibitors of bacterial glycan biosynthesis

Daniel A. Williams,[1,‡] Kabita Pradhan,[2,‡] Ankita Paul,[2] Ilana R. Olin,[1] Owen T. Tuck,[1] Karen D. Moulton,[1] Suvarn S. Kulkarni[2*] and Danielle H. Dube[1*]

[1]Department of Chemistry & Biochemistry, Bowdoin College,
6600 College Station, Brunswick, Maine 04011
[2]Department of Chemistry, Indian Institute of Technology Bombay,
Powai, Mumbai, 400076, India

Supporting Information

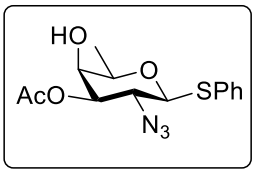
Table of Contents

Chemistry

Synthesis

General. 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 precoated 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) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on 400 MHz and 500 MHz instruments using $CDCl_3$ (D, 99.8%) or CD_3OD (D, 99.8%) 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 interpret proton correlation. ^{19}F was taken to confirm fluorine assignment. Mass spectra were acquired in the ESI mode. Ac_4GlcNAc, Ac_4GlcNAz, Ac_4GalNAz, and Phos-FLAG were synthesized as previously described.[1, 2]

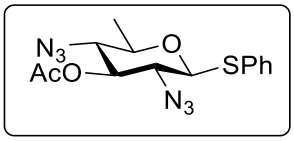
Phenyl 2-azido-3-*O*-acetyl-2,6-dideoxy-1-thio-*β*-D-galactopyranoside (12):



Trifluoromethanesulfonic anhydride (2.30 mL, 13.8 mmol) and dry pyridine (4.4 mL, 55 mmol) were added sequentially to a stirred solution of compound **11** (1.37 g, 4.58 mmol) in dry CH_2Cl_2 (125 mL) and stirred at 0 ºC for 1 h. After complete consumption of starting material, reaction mixture was washed with 1M HCl and aq. $NaHCO_3$ solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried in *vacuum* to give crude 2,4-bis-triflate compound. $TBAN_3$ (1.10 g, 3.89 mmol) was added to the reaction mixture of crude 2,4-bis-triflate compound in dry CH_3CN (140 mL) at -30 ºC and stirred at same temperature for 18 h. After selective inversion at C-2 position (indicated by TLC), reaction mixture was concentrated and kept under high *vacuum* for 15 min. Then, crude compound was dissolved in dry DMF (20 mL) and KNO_2 (3.89 g, 45.8 mmol) was added to it. The reaction was stirred at room

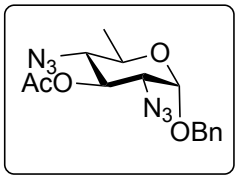
temperature for 5 h. After completion of reaction (indicated by TLC), reaction mixture was diluted with EtOAc (20 mL) and washed with aq. $NaHCO_3$ and brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (25% ethyl acetate: pet ether) to afford compound **12** as brown viscous liquid (1.04 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H, -ArH), 7.35-7.31 (m, 3H, -ArH), 4.77 (dd, J = 10.4, 2.8 Hz, 1H, H-3), 4.45 (d, J = 10.4 Hz, 1H, H-1), 3.84 (d, J = 2.8 Hz, 1H, H-4), 3.71-3.62 (m, 2H, H-2, H-5), 2.14 (s, 3H, -$COCH_3$), 1.32 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 133.39, 131.36, 129.10, 128.91, 128.49, 86.41, 75.92, 74.59, 69.25, 59.35, 20.98, 16.57; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{14}H_{17}N_3NaO_4S$, 346.0810; found, 346.0813.

Phenyl 3-*O*-acetyl-2,4-diazido-2,4,6-trideoxy-1-thio-*β*-D-glucopyranoside (13):



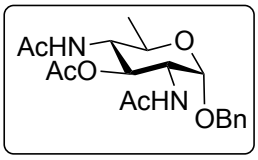
To a clear solution of compound **12** (0.41 g, 1.3 mmol) in dry CH_2Cl_2 (9 mL), trifluoromethanesulfonic anhydride (0.32 mL, 1.9 mmol) and dry pyridine (0.30 mL, 3.8 mmol) were added sequentially at 0 ºC and allowed to stir for 1 h. After completion of starting material (indicated by TLC), the reaction mixture was washed with 1M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated, and dried over *vacuum* to give mono-triflate compound. NaN_3 (1.23 gm, 18.9 mmol) was added to the clear solution of the mono-triflate compound in DMF (7.3 mL) at rt. The mixture was allowed to stir at rt for 5 h. After completion of reaction, the reaction mixture was diluted with EtOAc (25 mL) and washed with brine solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (10% ethyl acetate: pet ether) to afford compound **13** as a white solid (0.34 g, 78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 2H, -ArH), 7.35-7.31 (m, 3H, -ArH), 5.03 (t, J = 10.0 Hz, 1H, H-3), 4.46 (d, J = 10.0 Hz, 1H, H-1), 3.39-3.29 (m, 2H, H-4, H-5), 3.12 (t, J = 9.6 Hz, 1H, H-2), 2.16 (s, 3H, -$COCH_3$), 1.39 (d, J = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.66, 133.79, 132.68, 130.78, 129.13, 128.73, 85.93, 74.96, 74.65, 65.42, 63.15, 20.73, 18.57; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{14}H_{16}N_6NaO_3S$, 371.0897; found, 371.0895.

Benzyl 3-*O*-acetyl-2,4-diazido-2,4,6-trideoxy-*α*-D-glucopyranoside (14):



To donor **13** (0.16 g, 0.46 mmol), benzyl alcohol acceptor (40 µL, 0.32 mmol) and molecular sieves (3Å, 150 mg) were added to dry CH_2Cl_2 (2 mL) and dry Et_2O (2 mL) and stirred at room temperature for 0.5 h. Then NIS (42 mg, 0.92 mmol) and TfOH (20 µL, 0.27 mmol) were added sequentially to the stirring solution at 0 ºC and allowed to stir at the same temperature for 1 h. After complete consumption of donor (indicated by TLC), the reaction mixture was filtered through celite pad and filtrate was dissolved in CH_2Cl_2 followed by a wash with $Na_2S_2O_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography silica gel (10% ethyl acetate: pet ether) to afford *α*-linked *O*-benzylated compound **14** as brown viscous liquid (0.11 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.37(m, 4H, -ArH), 7.36-7.34 (m, 1H, -ArH), 5.49 (t, J = 10.0 Hz, 1H, H-3), 5.00 (d, J = 3.5 Hz, 1H, H-1*α*), 4.76 (d, J = 12.0 Hz, 1H, -CHPh), 4.62 (d, J = 12.0 Hz, 1H, -CHPh), 3.79-3.73 (m, 1H, H-5), 3.22-3.16 (m, 2H, H-2, H-4), 2.20 (s, 3H, -$COCH_3$), 1.33 (d, J = 6.5 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.13, 136.48, 128.45, 128.01, 100.40, 73.57, 70.82, 69.12, 62.84, 60.69, 20.55, 17.26; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{15}H_{18}N_6NaO_4$, 369.1282; found, 369.1282.

Benzyl 2,4-diacetamido-3-*O*-acetyl-2,4,6-trideoxy-*α*-D-glucopyranoside (1):

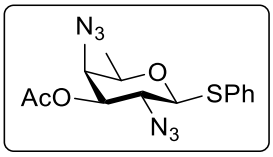


To the stirring solution of compound **14** (0.11 g, 0.32 mmol) in THF (3 mL), activated Zn dust (0.25 g, 3.8 mmol) was added followed by dropwise addition of AcOH (0.3 mL) at rt. Mixture was stirred at rt for 9 h. After complete conversion of azide to amine, zinc was filtered through celite bed, concentrated and dried under high vacuum for 30 min.

The crude di-amine compound was dissolved in THF (2 mL). To the clear solution, Ac_2O (0.12 mL, 1.3 mmol) and DMAP (39 mg, 0.32 mmol) were added sequentially at 0 °C and the mixture was allowed to stir at room temperature for 5 h. After completion of reaction, solvents

were removed in *vacuo* and the crude product was purified by column chromatography silica gel (5% methanol: ethyl acetate) to furnish desired 2,4-diacetamido compound **1** as white solid (0.098 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H, -ArH), 5.80 (d, J = 8.8 Hz, 2H, -NH), 4.99 (t, J = 10.4 Hz, 1H, H-3), 4.85 (d, J = 3.6 Hz, 1H, H-1α), 4.68 (d, J = 12.0 Hz, 1H, -CHPh), 4.47 (d, J = 12.0 Hz, 1H, -CHPh), 4.34 (dt, J = 10.0, 3.6 Hz, 1H, H-4), 3.97 (q, J = 10.0 Hz, 1H, H-2), 3.78-3.71 (m, 1H, H-5), 1.98 (s, 3H, -$OCOCH_3$), 1.91 (s, 3H, -NHAc), 1.88 (s, 3H, -NHAc), 1.20 (d, J = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.17, 170.04, 169.86, 136.92, 128.61, 128.23, 128.14, 96.62, 71.59, 69.76, 67.49, 54.94, 51.79, 23.25, 23.17, 20.84, 17.77; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{19}H_{26}KN_2O_6$, 417.1422; found, 417.1422.

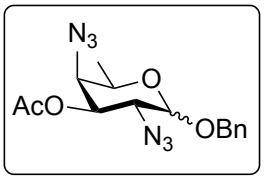
Phenyl 3-*O*-acetyl-2,4-diazido-2,4,6-trideoxy-1-thio-*β*-D-galactopyranoside (15):



Trifluoromethanesulfonic anhydride (0.81 mL, 4.8 mmol) and dry pyridine (0.77 mL, 9.6 mmol) were added sequentially to a stirred solution of compound **11** (0.47 g, 1.6 mmol) in dry CH_2Cl_2 (11 mL) and allowed to stir at 0 ºC for 1 h. After complete consumption of starting material, the reaction mixture was washed with 1M HCl and aq. $NaHCO_3$ solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried over *vacuum* to give bis-triflate compound.

To the solution of bis-triflate compound in DMF (9.1 mL), NaN_3 (1.04 g, 16.0 mmol) was added at rt. After 5 h, reaction mixture was diluted with EtOAc and aq. $NaHCO_3$ and brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography to afford compound **15** (0.483 g, 88%) as white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.52 (m, 2H, ArH), 7.36-7.33 (m, 3H, ArH), 4.90 (dd, J = 10.0, 3.4 Hz, 1H, H-3), 4.40 (d, J = 10.0 Hz, 1H, H-1), 3.82 (d, J = 3.4 Hz, 1H, H-4), 3.70-3.65 (m, 2H, H-2 & H-5), 2.16 (s, 3H, -$COCH_3$), 1.35 (d, J = 6.2 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 133.5, 131.2, 129.2, 128.6, 86.5, 75.5, 73.4, 63.0, 59.3, 20.7, 17.8; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{14}H_{16}N_6NaO_3S$, 371.0897; found, 371.0896.

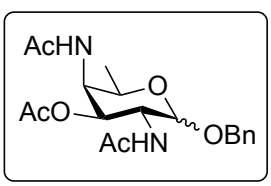
Benzyl 3-*O*-acetyl-2,4-diazido-2,4,6-trideoxy-*α*/*β*-D-galactopyranoside (16):



To donor **15** (0.56 g, 1.6 mmol), benzyl alcohol (0.16 mL, 1.6 mmol) and molecular sieves 3Å (400 mg) were added dry CH_2Cl_2 (6.8 mL), dry Et_2O (6.8 mL) and the solution was stirred at room temperature for 0.5 h. Then NIS (0.72 g, 3.2 mmol) and TfOH (0.11 mL, 1.3 mmol) were added sequentially to the stirring solution at 0 ºC and allowed to stir at same temperature for 1 h. After complete consumption of donor (indicated by TLC), the reaction mixture was filtered out through celite pad and crude filtrate was dissolved in CH_2Cl_2 and washed with $Na_2S_2O_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (10% ethyl acetate: pet ether) to afford compound **16** as brown viscous liquid (0.512 g, 93%, *α*:*β* = 1:1). for *α*-compound: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.37-7.36 (m, 5H, -ArH), 5.44 (dd, *J* = 10.8, 3.6 Hz, 1H, H-3), 4.97 (d, *J* = 3.6 Hz, 1H, H-1*α*), (4.69 (d, *J* = 12.0 Hz, 1H, -CHPh), 4.58 (d, *J* = 12.04 Hz, 1H, -CHPh) , 4.08 (dq, *J* = 7.6, 1.2 Hz, 1H, H-5), 3.91 (dd, *J* = 3.6, 1.6 Hz, 1H, H-4), 3.71 (dd, *J* = 10.8, 3.6 Hz, 1H, H-2), 2.17 (s, -CH_3), 1.22 (d, *J* = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 170.06, 136.61, 129.44, 129.09, 128.82, 128.54, 128.10, 97.03, 71.02, 69.97, 64.79, 64.06, 57.48, 20.56, 17.03.

For *β*-compound: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.38-7.34 (m, 4H, -ArH), 7.33-7.31 (m, 1H, -ArH), 4.93 (d, *J* = 12.0 Hz, 1H, -CHPh), 4.80 (dd, *J* = 11.0, 4.0 Hz, 1H, H-3), 4.66 (d, *J* = 12.0 Hz, 1H, -CHPh), 4.32 (d, *J* = 8.0 Hz, 1H, H-1*β*), 3.79-3.75 (m, 2H, H-2, H-4), 3.64 (dq, *J* = 6.5, 1.5 Hz, 1H, H-5), 2.18 (s, 3H, -CH_3), 1.36 (d, *J* = 6.5 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 170.13, 136.48, 128.45, 128.01, 100.40, 73.57, 70.82, 69.12, 62.84, 60.69, 20.55, 17.26; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{15}H_{18}N_6O_4Na$, 369.1282; found, 369.1282.

Benzyl 2,4-diacetamido-3-*O*-acetyl-2,4,6-trideoxy-*α*/*β*-D-galactopyranoside (2):

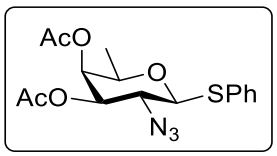


To the stirring solution of compound **16** (0.12 g, 0.35 mmol) in THF (2 mL), activated Zn dust (0.27 g, 3.8 mmol) was added followed by dropwise addition of AcOH (0.2 mL) at rt. Mixture was allowed to stir at rt for 9 h. After complete conversion of azide to amine (indicated by TLC), zinc was filtered through celite bed, concentrated and dried under high vacuum for 30 min.

The crude di-amine was dissolved in THF (2 mL). To the clear solution, Ac_2O (0.13, 1.4 mmol) and DMAP (0.4 mg, 0.003 mmol) were added sequentially at 0 °C, and the mixture was allowed to stir at room temperature for 5 h. After completion of reaction, solvents were removed in vacuo and the crude product was purified by silica gel column chromatography (5% methanol: ethyl acetate) to furnish desired 2,4-diacetamido compound **2** as white solid (0.112 g, 86%, α/β = 1:1). For α-compound: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H, -ArH), 7.34-7.32 (m, 1H, -ArH), 7.31-7.29 (m, 2H, -ArH), 6.48 (bs, 1H, -NH), 5.92 (bs, 1H, -NH), 5.14 (dd, J = 11.5, 4.5 Hz, H-3), 4.88 (d, J = 4.0 Hz, 1H, H-1α), 4.66 (d, J = 12.0 Hz, 1H, -CHPh), 4.47-4.37 (m, 3H, -CHPh, H-2, H-4), 4.21-4.17 (m, 1H, H-5), 2.08 (s, 3H, -$OCOCH_3$), 1.99 (s, 3H, -NHAc), 1.93 (s, 3H, -NHAc), 1.14 (d, J = 6.5 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.27, 171.05, 170.35, 136.93, 128.61, 128.19, 127.95, 96.98, 70.03, 69.37, 65.02, 50.65, 49.43, 48.02, 23.22, 20.98, 16.44.

For β-compound: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 5H, -ArH), 6.04 (bs, 1H, -NH), 5.60 (bs, 1H, -NH), 4.94 (dd, J = 11.2, 4.4 Hz, 1H, H-3), 4.84 (d, J = 12.4 Hz, 1H, -CHPh), 4.53 (d, J = 12.8 Hz, 1H, -CHPh), 4.38-4.33 (m, 2H, H-4, H-1 β), 4.11-3.98 (m, 1H, H-2), 3.68 (q, J = 6.0 Hz, 1H, H-5), 2.03 (s, 3H, -$COCH_3$), 1.95 (s, 3H, -NHAc), 1.88 (s, 3H, -NHAc), 1.18 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.19, 170.83, 170.40, 137.07, 128.49, 128.01, 127.81, 100.73, 71.47, 70.78, 69.59, 50.91, 50.37, 23.39, 23.25, 20.91, 16.62; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{19}H_{26}NaN_2O_6$, 401.1683; found, 401.1686.

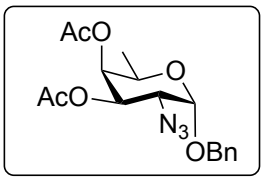
Phenyl 3,4-*O*-diacetyl-2-azido-2,6-dideoxy-1-thio-β-D-galactopyranoside (17):



AcCl (0.30 mL, 4.2 mmol) and dry pyridine (0.33 mL, 4.2 mmol) were added dropwise to a stirring solution of compound **12** (0.45 g, 1.39 mmol) in dry CH_2Cl_2 (4 mL) at 0 °C and allowed to keep at the same temperature over 1 h. After completion of reaction, reaction mixture was

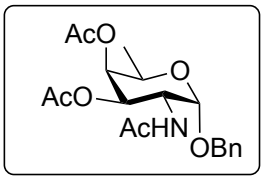
washed with 1 M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over Anhydrous Na_2SO_4, concentrated and purified by column chromatography on silica gel (10% ethyl acetate: pet ether) to give compound **17** as white solid (0.46 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.56 (m, 2H, -ArH), 7.29-7.27 (m, 3H, -ArH), 5.14 (s, 1H, H-4), 4.83 (dd, J = 10.0, 3.2 Hz, 1H, H-3), 4.47 (d, J = 10.0 Hz, 1H, H-1), 3.73 (q, J = 6.0 Hz, 1H, H-5), 3.58 (t, J = 10.0 Hz, 1H, H-2), 2.04 (t, J = 1.6 Hz, 3H, -OCOCH$_3$), 1.95 (t, J = 2.0 Hz, 3H, -OCOCH$_3$), 1.17-1.15 (m, 3H, -CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.25, 169.69, 133.18, 131.52, 128.93, 128.30, 86.14, 76.94, 73.30, 72.96, 69.63, 59.25, 20.61, 20.53, 16.55; HR-ESI-MS (*m/z*): [M + Na]$^+$ calculated for $C_{16}H_{19}N_3O_5NaS$, 388.0938; found, 388.0936.

Benzyl 3,4-*O*-diacetyl-2-azido-2,6-dideoxy-*α*-D-galactopyranoside (18):



To donor **17** (0.17 g, 0.46 mmol), benzyl alcohol (0.03 mL, 0.3 mmol) and molecular sieves 3Å (150 mg) were added dry CH_2Cl_2 (1.1 mL) and dry Et_2O (1.1 mL). The reaction mixture was stirred at room temperature for 0.5 h. Then NIS (0.21 g, 0.93 mmol) and TfOH (0.03 mL, 0.4 mmol) were added sequentially at 0 ºC and stirred at the same temperature for 1 h. After complete consumption of donor **17** (indicated by TLC), 3Å molecular sieve was filtered out through celite pad and the reaction mixture was dissolved in CH_2Cl_2 followed by a wash with $Na_2S_2O_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (10% ethyl acetate: pet ether) to afford exclusively α-linked benzylated compound **18** as a white solid (0.102 g, 87%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.37 (m, 4H, -ArH), 7.36-7.33 (m, 1H, -ArH), 5.43 (dd, J = 11.0, 3.0 Hz, 1H, H-3), 5.31 (dd, J = 3.0, 1.0 Hz, 1H, H-4), 5.06 (d, J = 3.5 Hz, 1H, H-1α), 4.75 (d, J = 12.0 Hz, 1H, -CHPh), 4.64 (d, J = 12.0 Hz, 1H, -CHPh), 4.16 (dq, J = 6.5, 1.0 Hz, 1H, H-5), 3.67 (dd, J = 11.5, 3.5 Hz, 1H, H-2), 2.18 (s, 3H, -OCOCH$_3$), 2.07 (s, 3H, -OCOCH$_3$), 1.13 (d, J = 7.0 Hz, 3H, -CH$_3$); ^{13}C NMR (500 MHz, $CDCl_3$) δ170.41, 169.87, 136.58, 128.55, 128.07, 97.16, 70.70, 70.01, 68.74, 64.94, 57.43, 20.72, 20.64, 15.84; HR-ESI-MS (*m/z*): [M + Na]$^+$ calculated for $C_{17}H_{21}N_3NaO_6$, 386.1323; found, 386.1326.

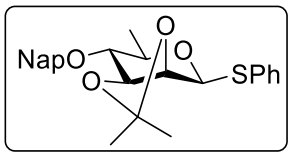
Benzyl 2-acetamido-3,4-*O*-diacetyl-2,6-dideoxy-*α*-D-galactopyranoside (3):



To the stirring solution of compound **18** (0.15 g, 0.41 mmol) in THF (2.5 mL), activated Zn dust (0.32 g, 4.9 mmol) was added followed by dropwise addition of AcOH (0.25 mL) at rt. The mixture was allowed to stir at rt for 9 h. After complete conversion of azide to amine (indicated by TLC), zinc was filtered through celite bed, concentrated and dried under high *vacuum* for 30 min.

Crude amine compound was dissolved in THF (2.5 mL). To the clear solution, Ac_2O (0.15 mL, 1.6 mmol) and DMAP (0.5 mg, 0.004 mmol) were added sequentially at 0 °C, and the mixture was allowed to stir at room temperature for 5 h. After completion of reaction, solvents were removed in *vacuo* and the crude product was purified by column chromatography over silica gel (70% pet ether: ethyl acetate) to furnish desired compound **3** as white solid (0.13 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H, -ArH), 5.60 (d, J = 9.6 Hz, 1H, -NH), 5.19-5.16 (m, 2H, H-3, H-4), 4.92 (d, J = 4.0 Hz, 1H, H-1α), 4.69 (d, J = 11.6 Hz, 1H, -CHPh), 4.58-4.48 (m, 2H, H-2, -CHPh), 4.10 (q, J = 6.8 Hz, 1H, H-5), 2.17 (s, 3H, -OCOCH_3), 1.97 (s, 3H, -OCOCH_3), 1.89 (s, 3H, -NHAc), 1.11 (d, J = 6.8 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.03, 170.78, 169.97, 136.97, 128.63, 128.22, 128.11, 97.21, 70.46, 70.08, 68.89, 65.09, 47.64, 23.30, 20.82, 20.78, 16.03; HR-ESI-MS (*m/z*): $[M + Na]^+$ calculated for $C_{19}H_{25}NNaO_7$, 402.1523; found, 402.1526.

Phenyl 2,3-*O*-(isopropilidene)-4-*O*-napthyl-6-deoxy-1-thio-*β*-D-mannopyranoside (20):

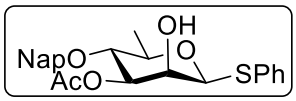


Camphorsulphonic acid (91 mg, 0.39 mmol) was added to the solution of mannose triol compound **19** (1.0 g, 3.9 mmol) in 2,2-DMP (38.2 mL, 312 mmol) and stirred for 1 h at room temperature. After completion of reaction (indicated by TLC), the reaction mixture was

quenched by Et_3N and concentrated under reduced pressure to give acetonide protected compound (1.15 g, quantitatively) as white solid.

2-napthylmethyl bromide (NapBr) (1.72 g, 7.80 mmol) and NaH (0.19 g, 7.8 mmol) were added sequentially to the solution of crude acetonide compound (1.15 g, 3.90 mmol) in dry DMF (19 mL) at 0 ºC and allowed to stir for 1 h at rt. After completion of reaction (indicated by TLC), reaction mixture was dissolved in EtOAc (40 mL) and washed with brine solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography silica gel (3% ethyl acetate: pet ether) to give compound **20** as a white solid (1.39 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 4H, -ArH), 7.57-7.54 (m, 2H, -ArH), 7.52-7.46 (m, 3H, -ArH), 7.35-7.27 (m, 3H, -ArH), 5.07 (d, J = 12.0 Hz, 1H, -CHPh), 5.03 (d, J = 2.0 Hz, 1H, H-1), 4.84 (d, J = 11.6 Hz, 1H-CHPh), 4.67 (dd, J = 5.6, 2.0 Hz, 1H, H-3), 4.28 (t, J = 6 Hz, 1H, H-2), 3.48-3.38 (m, 2H, H-4, H-5), 1.61 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.41 (d, J = 5.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.53, 135.29, 133.23, 133.06, 130.86, 129.00, 128.19, 127.90, 127.75, 127.37, 127.02, 126.18, 126.15, 125.99, 110.53, 84.06, 80.54, 80.08, 76.43, 74.58, 73.06, 28.03, 26.49, 18.64; HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{26}H_{28}NaO_4S$, 459.1601; found, 459.1607.

Phenyl 3-*O*-acetyl-4-*O*-napthyl-6-deoxy-1-thio-*β*-D-mannopyranoside (21):

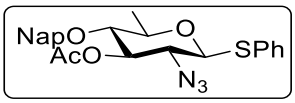


Compound **20** (1.0 g, 2.3 mmol) was dissolved in 80% AcOH (10 mL) and kept at 80 ºC for 1 h. After completion of reaction, the reaction mixture was diluted with EtOAc and washed with $NaHCO_3$ and brine solution. Separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give diol compound as a white solid (0.76 g, 84%).

Me_2SnCl_2 (23 mg, 0.11 mmol), DIPEA (0.83 g, 6.4 mmol) and AcCl (0.2 mL, 2.8 mmol) were added sequentially at rt to the stirring solution of diol compound (0.85 g, 2.1 mmol) in dry THF (20 mL) and allowed to stir for 2 h. After completion of reaction (indicated by TLC), the reaction mixture was diluted with EtOAc and washed with brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (20% ethyl acetate: pet ether) to afford compound **21** as a white solid (0.81 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 3H, -ArH), 7.73 (s, 1H, -ArH), 7.51-7.46 (m,

4H, -ArH), 7.40-7.38 (m, 1H, -ArH), 7.34-7.30 (m, 3H, -ArH), 4.98 (dd, *J* = 9.6, 3.2 Hz, 1H, H-3), 4.90 (s, 1H, H-1), 4.83 (dd, *J* = 11.6, 1.9 Hz, 2H, -CH_2Ph), 4.32 (t, *J* = 2.8 Hz, 1H, H-2), 3.69 (t, *J* = 9.6 Hz, 1H, H-4), 3.54-3.47 (m, 1H, H-5), 2.03 (s, 3H, -CH_3), 1.42 (d, *J* = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.24, 135.38, 133.62, 133.24, 133.02, 131.76, 129.10, 128.26, 127.91, 127.80, 127.69, 126.47, 126.25, 126.06, 125.70, 86.80, 78.22, 76.73, 76.64, 76.41, 75.40, 71.02, 21.09, 18.34; HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{25}H_{26}NaO_5S$, 461.1393; found, 461.1393.

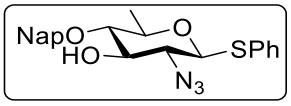
Phenyl 2-azido-3-*O*-acetyl-4-*O*-napthyl-2,6-dideoxy-1-thio-*β*-D-glucopyranoside (22):



Tf_2O (0.51 mL, 3.0 mmol) and dry pyridine (0.48 mL, 6.1 mmol) were added dropwise to the stirring solution of compound **21** (0.88 g, 2.0 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C and allowed to keep at same temperature for 0.5 h. After consumption of starting material, the reaction mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried under *vaccum* to give triflated compound quantitatively.

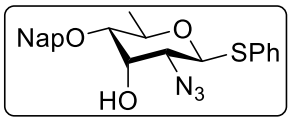
NaN_3 (1.3 g, 20 mmol) was added to the solution of crude triflate compound in dry DMF (7.4 mL). The mixture was kept stirring at rt for 3 h. After completion of reaction, the crude mixture was diluted with EtOAc (30 mL) and washed with brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (5% ethyl acetate: pet ether) to afford compound **22** as a white solid (0.83 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.80 (m, 3H, -ArH), 7.69 (s, 1H, -ArH), 7.59-7.56 (m, 2H, -ArH), 7.49-7.46 (m, 2H, -ArH), 7.37-7.33 (m, 4H, -ArH), 5.16 (t, *J* = 9.2 Hz, 1H, H-3), 4.78 (d, *J* = 11.6 Hz, 1H-CHPh), 4.71 (d, *J* = 11.6 Hz, 1H, -CHPh), 4.52 (d, *J* = 10.4 Hz, 1H, H-1), 3.55-3.48 (m, 1H, H-5), 3.31 (t, *J* = 10.0 Hz, 1H, H-2), 3.23 (t, *J* = 9.6 Hz, 1H, H-4), 1.96 (s, 1H, -CH_3), 1.39 (d, *J* = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.23, 134.92, 133.54, 133.20, 133.04, 129.06, 128.49, 128.33, 127.92, 127.69, 126.61, 126.28, 126.14, 125.70, 85.98, 81.31, 75.93, 75.85, 75.00, 63.75, 20.87, 18.23; HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{25}H_{25}N_3NaO_4S$, 486.1458; found, 486.1460.

Phenyl 2-azido-4-*O*-napthyl-2,6-dideoxy-1-thio-*β*-D-glucopyranoside (23):



To a clear solution of compound **22** (0.80 g, 1.7 mmol) in 1:1 mixture of MeOH (6.8 mL) and CH_2Cl_2 (6.8 mL), 0.2 M NaOMe (0.18 g) was added and kept for 1 h at rt. After complete consumption of starting material, the reaction mixture was neutralized with Amberlite (H+, 1.0 g). The reaction mixture was filtered, concentrated under reduced pressure and purified by column chromatography over silica gel (5% ethyl acetate: pet ether) to give compound **23** as white solid (0.56 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 3H, -ArH), 7.78 (s, 1H, -ArH), 7.59-7.57 (m, 2H, -ArH), 7.50-7.44 (m, 3H, -ArH), 7.34-7.33 (m, 3H, -ArH), 4.91 (dd, J = 17.6, 11.2 Hz, 2H, -CH_2Ph), 4.45 (d, J = 10.0 Hz, 1H, H-1), 3.59 (t, J = 10.4 Hz, 1H, H-3), 3.45-3.38 (m, 1H, H-5), 3.29 (t, J = 9.6 Hz, 1H, H-4), 3.13 (t, J = 9.2 Hz, 1H, H-2), 1.41 (d, J = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.31, 133.28, 133.24, 133.11, 131.65, 129.05, 128.53, 128.32, 127.97, 127.77, 126.85, 126.35, 126.20, 125.81, 86.07, 82.92, 76.76, 75.68, 75.31, 65.50, 18.56; HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{23}H_{23}N_3NaO_3S$, 444.1352; found, 444.1353.

Phenyl 2-azido-4-*O*-napthyl-2,6-dideoxy-1-thio-*β*-D-allopyranoside (24):

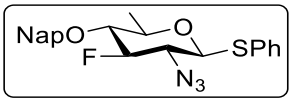


Tf_2O (0.51 mL, 3.1 mmol) and dry pyridine (0.49 mL, 6.1 mmol) were added sequentially in a dropwise manner to the clear solution of compound **23** (0.86 g, 2.1 mmol) in dry CH_2Cl_2 (55.3 mL) at 0 °C and allowed to stir at same temperature for 0.5 h. After reaction completion, the crude mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4 and concentrated to give triflated compound quantitatively.

KNO_2 (2.68 g, 31.5 mmol) was added to the solution of compound in dry DMF (15 mL) and kept stirring at rt for 8 h. After completion of reaction, the crude mixture was diluted with EtOAc (25 mL) and washed with brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (10% ethyl acetate: pet ether) to give compound **24** as a white solid (0.45 g, 53%). ^{1}H NMR (400

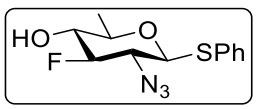
MHz, $CDCl_3$) δ 7.87-7.83 (m, 3H, -ArH), 7.75 (s, 1H, ArH), 7.61- 7.58 (m, 2H, -ArH), 7.52-7.50 (m, 2H, -ArH), 7.46-7.44 (m, 1H, -ArH), 7.34-7.30 (m, 3H, -ArH), 5.08 (d, J = 10.4 Hz, 1H, H-1), 4.78 (d, J = 11.6 Hz, 1H, -CHPh), 4.68 (d, J = 12.0 Hz, 1H, -CHPh), 4.39 (t, J = 2.4 Hz, 1H, H-3), 3.92-3.85 (m, 1H, H-5), 3.13 (t, J = 2.4 Hz, 1H, H-2), 3.11 (t, J = 2.4 Hz, 1H, H-4), 1.34 (d, J = 6.4 Hz, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.47, 133.30, 133.19, 133.16, 131.88, 128.95, 128.63, 128.18, 127.93, 127.81, 127.01, 126.49, 126.38, 125.72, 82.51, 79.45, 71.84, 71.19, 67.98, 61.38, 18.12; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{23}H_{23}N_3NaO_3S$, 444.1352; found, 444.1352.

Phenyl 2-azido-3-fluoro-4-*O*-napthyl-2,3,6-trideoxy-1-thio-*β*-D-glucopyranoside (25):



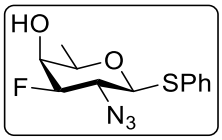
DAST (0.35 mL, 2.7 mmol) was added to a stirring solution of compound **24** (0.38 g, 0.89 mmol) in dry CH_2Cl_2 (4.3 mL) at -20 ºC. After addition of DAST, reaction was stirred at rt for 1 h. After completion of reaction, the reaction was quenched at -20 ºC by dropwise addition of EtOH and the mixture was concentrated and purified by column chromatography over silica gel (5% ethyl acetate: pet ether) to give compound **25** as white solid (0.269 g, 71%).^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 3H, -ArH), 7.78 (s, 1H, -ArH), 7.60-7.35 (m, 8H, -ArH), 5.02 (d, J = 11.2 Hz, 1H-CHPh), 4.78 (s, J = 11.2 Hz, 1H, -CHPh), 4.64 (dt, $J_{3\text{-}F}$, $J_{3\text{-}2,4}$ = 51.6, 8.8 Hz, 1H, H-3), 4.41 (d, J = 10.0 Hz, 1H, H-1), 3.51-3.38 (m, 2H, H-2,H-5) 3.34-3.26 (m, 1H, H-4), 1.38 (d, J = 6.0 Hz, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.92, 133.67, 133.23, 133.14, 131.00, 129.12, 128.63, 128.33, 127.98, 127.74, 127.11, 126.25, 126.15, 126.07, 97.75 (d, $J_{C,F}$ = 233.7 Hz, C-3), 85.17 (d, $J_{C,F}$ = 10.0 Hz, C-1), 80.27 (d, $J_{C,F}$ = 18.7 Hz, C-4), 74.76 (d, $J_{C,F}$ = 11.25 Hz, C-5), 63.72 (d, $J_{C,F}$ = 22.5 Hz, C-2), 18.09; ^{19}F NMR (^1H decoupled) (470 MHz, $CDCl_3$) δ -183.19 (s); HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{23}H_{22}FN_3NaO_2S$, 446.1309; found, 446.1370.

Phenyl 2-azido-3-fluoro-2,3,6-trideoxy-1-thio-*β*-D-glucopyranoside (26):



To a stirring solution of compound **25** (0.170 g, 0.401mmol) in CH_2Cl_2 (25.8 mL) and H_2O (19 mL) recrystallised DDQ (0.16 g, 0.72 mmol) was added and stirred at rt for 3 h. After completion of starting material (indicated by TLC), reaction mixture was quenched with Et_3N, concentrated and purified by column chromatography over silica gel (10% ethyl acetate: pet ether) to afford compound **26** as viscous liquid (0.105 g, 93%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H, -ArH), 7.37-7.36 (m, 3H, -ArH), 4.43 (dd, $J_{1\text{-}F}$, $J_{1\text{-}2}$ = 10.0, 0.5 Hz, 1H, H-1), 4.31 (dt, $J_{3\text{-}F}$, $J_{3\text{-}2}$ = 52.0, 8.5 Hz, 1H, H-3), 3.48-3.36 (m, 3H, H-2,H-4,H-5), 1.41 (d, J = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.63, 130.96, 129.10, 128.65, 97.76 (d, $J_{C,F}$ = 185.0 Hz, C-3) 85.40 (d, $J_{C,F}$ = 6.25 Hz, C-1), 75.05 (d, $J_{C,F}$ = 7.5 Hz, C-5), 73.69 (d, $J_{C,F}$ = 7.5 Hz, C-4), 63.27 (d, $J_{C,F}$ = 16.2 Hz, C-2), 17.62; ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -188.26 (s); HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{12}H_{14}FN_3NaO_2S$, 306.0683; found, 306.0687.

Phenyl 2-azido-3-fluoro-2,3,6-trideoxy-1-thio-*β*-D-galactopyranoside (27):

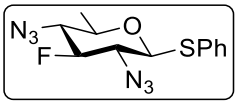


Tf_2O (0.1 mL, 0.63 mmol) and dry pyridine (0.1 mL, 1.26 mmol) were added dropwise to the stirring solution of compound **26** (0.12 g, 0.42 mmol) in dry CH_2Cl_2 (11 mL) at 0 ºC and allowed to stir at 0 ºC for 0.5 h. After complete consumption of starting material, the reaction mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried under *vaccum* to give triflated compound quantitatively.

KNO_2 (0.54 g, 6.3 mmol) was added to the solution of crude triflate compound in dry DMF (3.1 mL) at rt. After complete consumption of starting material, the reaction mixture was diluted with EtOAc (15 mL) and washed with brine solution. Separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (10% ethyl acetate: pet ether) to give compound **27** as a white solid (72 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H, -ArH), 7.35-7.33 (m, 3H, -ArH), 4.38 (ddd, $J_{3\text{-}F}$, $J_{3\text{-}2}$, $J_{3\text{-}4}$= 48.0, 9.6, 3.2 Hz, 1H, H-3), 4.36 (dd, $J_{1\text{-}2}$, $J_{1\text{-}F}$ = 10.0, 0.8 Hz, 1H, H-1), 3.93 (dd, $J_{4\text{-}F}$, $J_{4\text{-}5}$ = 6.8, 2.8 Hz, 1H. H-4), 3.73 (dt, $J_{2\text{-}F}$, $J_{2\text{-}1,3}$ = 12.0, 9.6 Hz, 1H, H-2), 3.69-3.58 (m, 1H, H-5), 1.38 (dd, $J_{6\text{-}5}$, $J_{6\text{-}F}$ = 6.4, 0.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.47, 131.21, 129.10,

128.55, 93.74 (d, $J_{C,F}$ = 187.0 Hz, C-3), 85.73 (d, $J_{C,F}$ = 7.0 Hz, C-1), 73.71 (d, $J_{C,F}$ = 7.0 Hz, C-5), 69.35 (d, $J_{C,F}$ = 16.0 Hz, C-4), 60.05 (d, $J_{C,F}$ = 19.0 Hz, C-2), 16.50 (d, $J_{C,F}$ = 2.0 Hz, -CH_3); ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -189.21 (s); HR-ESI-MS (*m/z*): [M + Na]$^+$calcd. for $C_{12}H_{14}FN_3NaO_2S$, 306.0683; found, 306.0686.

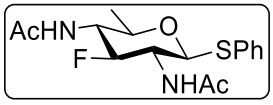
Phenyl 2,4-diazido-3-fluoro-2,3,4,6-tetradeoxy-1-thio-*β*-D-glucopyranoside (28):



Trifluoromethanesulphonic anhydride (0.11 mL, 0.67 mmol) and dry pyridine (0.10 mL, 1.3 mmol) were added dropwise to the stirring solution of compound **27** (0.13 g, 0.44 mmol) in dry CH_2Cl_2 (2.2 mL) at 0 ºC and allowed to stir at same temperature for 0.5 h. After complete conversion of starting material, the reaction mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried under *vaccum* to give triflated compound quantitatively.

NaN_3 (0.29 g, 4.4 mmol) was added to the solution of crude triflate compound in dry DMF (1.6 mL) and kept stirring at rt for 3 h. After complete consumption of starting material, the reaction mixture was diluted with EtOAc (20 mL) and washed with brine solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified on silica gel (5% ethyl acetate: pet ether) to give compound **28** as a white solid (0.11 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H, -ArH), 7.36-7.35 (m, 3H, -ArH), 4.36 (dt, $J_{3\text{-}F}$, $J_{3\text{-}2,4}$ = 51.0, 8.5 Hz, 1H, H-3), 4.37 (d, J = 10.0 Hz, 1H, H-1), 3.44 (dt, $J_{2\text{-}F}$, $J_{2\text{-}1,3}$ = 12.5, 9.0 Hz, 1H, H-2), 3.29-3.21 (m, 2H, H-4, H-5), 1.40 (d, J = 5.5 Hz, 1H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.95, 130.45, 129.17, 128.89, 95.43 (d, $J_{C,F}$ = 187.5 Hz, C-3), 85.23 (d, $J_{C,F}$ = 6.2 Hz, C-1), 74.18 (d, $J_{C,F}$ = 3.1 Hz, C-5), 65.60 (d, $J_{C,F}$ = 16.25 Hz, C-4), 63.22 (d, $J_{C,F}$ = 17.5 Hz, C-2), 18.35; ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -183.24 (s); HR-ESI-MS (*m/z*): [M + Na]$^+$calcd. for $C_{12}H_{13}FN_6NaOS$, 331.0748; found, 331.0760.

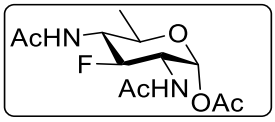
Phenyl 2,4-diacetamido-3-fluoro-2,3,4,6-tetradeoxy-1-thio-*β*-D-glucopyranoside (29):



To the stirring solution of compound **28** (0.19 g, 0.62 mmol) in THF (3.6 mL), activated Zn dust (0.58 g, 7.4 mmol) was added followed by dropwise addition of AcOH (0.35 mL) at rt. The reaction mixture was allowed to stir at rt for 8 h. After complete conversion of azide to amine (indicated by TLC), the reaction mixture was filtered through celite bed, concentrated and dried under high *vacuum* for 30 min.

Crude di-amine compound was dissolved in THF (4.1 mL). To the clear solution, Ac_2O (23 mL, 2.48 mmol) and DMAP (4 mg, 0.06 mmol) were added sequentially at 0 °C, and the mixture was allowed to stir at room temperature for 4 h. After completion of reaction, solvents were removed in *vacuo* and the crude product was purified by column chromatography over silica gel (80% ethyl acetate: pet ether) to furnish desired product **29** as a white solid (0.16 g, 75%). ^{1}H NMR (500 MHz, CD_3OD) δ 7.51-7.49 (m, 2H, -ArH), 7.31-7.29 (m, 3H, -ArH), 4.84 (bs, 1H, H-1), 4.58 (dt, $J_{3\text{-F}}$, $J_{3\text{-2,4}}$ = 51.5, 10.0 Hz, 1H, H-3), 3.84 (q, J = 10.5 Hz, 1H, H-2), 3.73 (q, J = 10.0 Hz, 1H, H-4), 3.56-3.50 (m, 1H, H-5), 2.01 (s, 3H, -$COCH_3$), 1.98 (s, 3H, -$COCH_3$), 1.22 (d, J = 6.5 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, CH_3OD) δ 172.11, 171.95, 133.05, 131.91, 128.57, 127.47, 91.57 (d, $J_{C,F}$ = 187.5 Hz, C-3), 85.44 (d, $J_{C,F}$ = 7.5 Hz, C-1), 74.16 (d, $J_{C,F}$ = 6.2 Hz, C-5), 55.78 (d, $J_{C,F}$ = 16.2 Hz, C-4), 54.17 (d, $J_{C,F}$ = 17.5 Hz, C-2), 21.44, 21.32, 16.78; ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -189.98 (s); HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{16}H_{21}FN_2NaO_3S$, 363.1149; found, 363.1145.

Acetyl 2,4-diacetamido-3-fluoro-2,3,4,6-tetradeoxy-*α*-D-glucopyranoside (4):

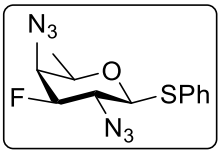


To the stirring solution of compound **29** (0.094 g, 0.28 mmol) in THF (3.2 mL) and H_2O (0.8 mL), NBS (0.147 g, 0.828 mmol) was added at 0 ºC and allowed to stir for 15 min at rt. After complete consumption of starting material, the reaction mixture was concentrated under reduced pressure and kept in high *vacuum* overnight to provide hemiacetal compound quantitatively.

To crude hemiacetal compound in dry CH_2Cl_2 (2.0 mL), Ac_2O (0.26 mL, 2.8 mmol), Et_3N (0.38 mL, 2.8 mmol) and DMAP (3 mg, 0.03 mmol) were added sequentially at 0 ºC and stirred for 5 h at rt. After reaction completion, the reaction mixture was concentrated and purified by column chromatography over silica gel (3% methanol: ethyl acetate) to obtain compound **4** as yellow viscous liquid (74 mg, 75%). ^{1}H NMR (500 MHz, CD_3OD) δ 6.13 (t, J = 3.5 Hz, 1H, H-

1α), 4.74 (dt, $J_{3\text{-F}}$, $J_{3\text{-}2,4}$ = 51.8 Hz, 10.3 Hz, 1H, H-3), 4.57 (bs, 1H), 4.28 (dt, $J_{2\text{-}1,3}$, $J_{2\text{-F}}$ = 10.8 Hz, 3.6 Hz, 1H, H-2), 3.94-3.84 (m, 2H, H-4, H-5), 2.14 (s, 3H, -$COCH_3$), 2.00 (s, 1H, -NHAc), 1.97 (s, 1H, -NHAc), 1.20 (d, J = 6.2 Hz, 3H, -CH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 172.33, 172.10, 169.36, 90.68 (d, $J_{C,F}$ = 9.9 Hz, C-1), 88.55 (d, $J_{C,F}$ = 182.5 Hz, C-3), 68.46 (d, $J_{C,F}$ = 6.2 Hz, C-5), 55.48 (d, $J_{C,F}$ = 16.73 Hz, C-4), 52.30 (d, $J_{C,F}$ = 17.8 Hz, C-2), 21.34, 20.87, 19.24, 16.69; HR-ESI-MS (*m/z*): $[M + K]^+$ calcd. for $C_{12}H_{19}FKN_2O_5$, 329.0910; found, 329.0906.

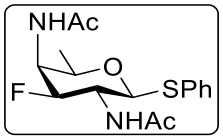
Phenyl 2,4-diazido-3-fluoro-2,3,4,6-tetradeoxy-1-thio-β-D-galactopyranoside (30):



Tf_2O (0.17 mL, 1.03 mmol) and dry pyridine (0.17 mL, 2.1 mmol) were added dropwise to the stirring solution of compound **26** (0.19 g, 0.69 mmol) in dry CH_2Cl_2 (3.5 mL) at 0 ºC and allowed to stir at the same temperature for 0.5 h. After complete conversion of starting material, the reaction mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and dried under *vaccum* to give triflated compound quantitatively.

NaN_3 (0.45 g, 6.9 mmol) was added to the solution of crude triflate compound in dry DMF (2.4 mL) at rt. After 3 h, the reaction mixture was diluted with EtOAc (20 mL) and washed with brine solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (5% ethyl acetate: pet ether) to give compound **30** as a white solid (0.150 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H, -ArH), 7.35-7.34 (m, 3H, -ArH), 4.55 (ddd, $J_{3\text{-F}}$, $J_{3\text{-}2}$, $J_{3\text{-}4}$ = 47.6, 9.2, 4.0 Hz, 1H, H-3), 4.31 (dd, $J_{1\text{-}2}$, $J_{1\text{-F}}$ = 9.2, 0.8 Hz, 1H, H-1), 3.87-3.84 (m, 1H, H-4), 3.73 (dt, $J_{2\text{-F}}$, $J_{2\text{-}1,3}$ = 14.0, 9.6 Hz, 1H, H-2), 3.62-3.57 (m, 1H, H-5), 1.38 (dd, $J_{6\text{-}5}$, $J_{6\text{-F}}$ = 6.4, 0.4 Hz, 1H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.45, 130.94, 129.11, 128.61, 93.39 (d, $J_{C,F}$ = 192.0 Hz, C-3), 85.81 (d, $J_{C,F}$ = 7.0 Hz, C-1), 72.61 (d, $J_{C,F}$ = 5.0 Hz, C-5), 63.16 (d, $J_{C,F}$ = 15.0 Hz, C-4), 60.11 (d, $J_{C,F}$ = 17.0 Hz, C-5), 17.60 (d, $J_{C,F}$ = 3.0 Hz, -CH_3); ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -184.73 (s); HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{12}H_{13}FN_6NaOS$, 331.0748; found, 331.0762.

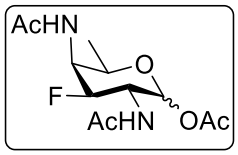
Phenyl 2,4-diacetamido-3-fluoro-2,3,4,6-tetradeoxy-1-thio-*β*-D-galactopyranoside (31):



To the stirring solution of compound **30** (0.11 g, 0.32 mmol) in THF (3 mL), activated Zn dust (250 mg, 3.8 mmol) was added followed by dropwise addition of AcOH (0.3 mL) at rt. The mixture was allowed to stir at rt for 8 h. After complete conversion of azide to amine (indicated by TLC), the mixture was filtered through celite pad, concentrated and dried under high *vacuum* for 30 min.

Crude di-amine compound was dissolved in THF (2 mL). To the clear solution, Ac_2O (0.12 mL, 1.3 mmol) and DMAP (4 mg, 0.03 mmol) were added sequentially at 0 °C, and the reaction mixture was allowed to stir at room temperature for 4 h. After completion of reaction, solvents were removed in *vacuo* and the crude product was purified by column chromatography over silica gel (80% ethyl acetate: pet ether) to furnish desired derivative **31** as a brown viscous liquid (0.198 g, 72%). ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.49-7.47 (m, 2H, -ArH), 7.32-7.24 (m, 3H, -ArH), 5.99 (d, J = 9.6 Hz, 1H, -NHAc), 4.81 (d, J = 10.4 Hz, 1H, H-1), 4.72 (ddd, $J_{3\text{-}F}$, $J_{3\text{-}2}$, $J_{3\text{-}4}$ = 48.0, 10.4, 4.4 Hz, 1H, H-3), 4.53-4.50 (m, 1H, H-4), 4.06-3.98 (m, 1H, H-2), 3.69-3.68 (m, 1H, H-5), 1.98 (s, 3H, -NHAc), 1.92 (s, 3H, -NHAc), 1.17 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.40, 171.36, 133.11, 132.18, 129.01, 127.96, 90.06 (d, $J_{C,F}$ = 191.0 Hz, C-3), 86.54 (d, $J_{C,F}$ = 8.0 Hz, C-1), 72.87, (d, $J_{C,F}$ = 6.0 Hz, C-5), 51.06 (d, $J_{C,F}$ = 15.0 Hz, C-4), 50.56, (d, $J_{C,F}$ = 19.0 Hz, C-2), 23.32, 23.14, 16.81; ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -191.81 (s); HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{16}H_{21}FN_2NaO_3S$, 363.1149; found, 363.1171.

Acetyl 2,4-diacetamido-3-fluoro-2,3,4,6-tetradeoxy-*α*/*β*-D-galactopyranoside (5):

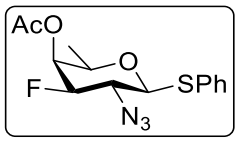


To the stirring solution of compound **31** (0.067 g, 0.20 mmol) in THF (2.3 mL) and H_2O (0.6 mL), NBS (0.105 g, 0.590 mmol) was added at 0 ºC and the reaction was stirred for 30 min at rt.

After completion of reaction, the reaction mixture was concentrated under reduced pressure and kept under high *vacuum* overnight.

Ac_2O (0.1 mL, 1.0 mmol), Et_3N (0.14 mL, 1.0 mmol) and DMAP (2.5 mg, 0.02 mmol) were added sequentially to the crude compound in dry CH_2Cl_2 (1.4 mL) at 0 ºC and stirred for 4 h at rt. The reaction mixture was then concentrated and purified by column chromatography over silica gel (5% methanol: ethyl acetate) to obtain compound **5** as a white solid (34 mg, 70%, α:β = 5:1). ^{1}H NMR (400 MHz,CD_3OD) δ 6.13 (t, J = 4.4 Hz, 1H, H-1α), 4.85-4.72 (m, 1H, H-3), 4.61-4.59 (m, 1H, H-4), 4.51 (dt, $J_{2\text{-}1,3}$, $J_{2\text{-}F}$ = 10.4, 4.0 Hz, 1H, H-2), 4.22-4.20 (m, 1H, H-5), 2.13 (s, 3H, -$COCH_3$), 2.06 (s, 3H, -NHAc), 1.95 (s, 3H, -NHAc), 1.11 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz,CD_3OD) δ 173.16, 172.44, 169.62, 90.98 (d, $J_{C,F}$ = 10.0 Hz, C-1), 86.68 (d, $J_{C,F}$ = 187.0 Hz, C-3), 66.92 (d, $J_{C,F}$ = 6.0 Hz, C-5), 48.23 (d, $J_{C,F}$ = 4.9 Hz, C-4), 47.06 (d, $J_{C,F}$ = 22.0 Hz, C-2), 20.99, 20.95, 19.28, 15.26; HR-ESI-MS (*m/z*): $[M + Na]^+$calcd. for $C_{12}H_{19}FKN_2O_5$, 329.0910; found, 329.0909.

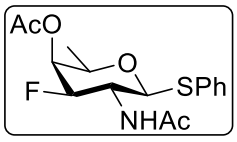
Phenyl 4-*O*-acetyl-2-azido-3-fluoro-2,3,6-trideoxy-1-thio-β-D-galactopyranoside (32):



AcCl (0.02 mL, 0.33 mmol) and dry pyridine (0.03 mL, 0.33 mmol) were added dropwise to the stirring solution of compound **27** (64 mg, 0.22 mmol) in dry CH_2Cl_2 (1.5 mL) at 0 °C and allowed to stir at rt. After 1 h, the reaction mixture was washed with 1 M HCl and aq. $NaHCO_3$ solution. The separated organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography over silica gel (5% ethyl acetate: pet ether) to give compound **32** as brown viscous liquid (54 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H, -ArH), 7.35-7.33 (m, 3H, -ArH), 5.33 (ddd, $J_{4\text{-}F,}$ $J_{4\text{-}3,}$ $J_{4\text{-}5}$ = 6.0, 3.6, 0.8 Hz, 1H, H-4), 4.46 (ddd, $J_{3\text{-}F}$, $J_{3\text{-}2}$, $J_{3\text{-}4}$ = 46.8, 9.6, 3.6 Hz, 1H, H-3), 4.40 (d, J = 9.6 Hz, 1H, H-1), 3.73-3.65 (m, 2H, H-2, H-5), 2.19 (s, 3H, -$COCH_3$), 1.24 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.09, 133.48, 131.22, 128.98, 128.54, 91.08 (d, $J_{C,F}$ = 193.0 Hz, C-3), 85.72 (d, $J_{C,F}$ = 7.0 Hz, C-1), 72.61 (d, $J_{C,F}$ = 5.0 Hz, C-5), 69.42 (d, $J_{C,F}$ = 16.0 Hz, C-4), 60.43 (d, $J_{C,F}$ = 18.0 Hz, C-2), 20.59, 16.58 (d, $J_{C,F}$ = 2.0 Hz, -CH_3); ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -

189.87 (s). HR-ESI-MS (*m/z*): [M + Na]$^+$calcd. for $C_{14}H_{16}FN_3NaO_3S$, 348.0789; found, 331.0781.

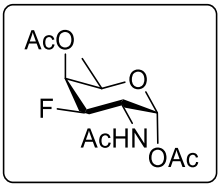
Phenyl 4-*O*-acetyl-2-acetamido-3-fluoro-2,3,6-trideoxy-1-thio-*β*-D-galactopyranoside (33):



To compound **32** (0.11 g, 0.32 mmol) in THF (3 mL), activated Zn dust (250 mg, 3.8 mmol) was added followed by dropwise addition of AcOH (0.3 mL) at rt. The mixture was allowed to stir at same temperature for 8 h. After complete conversion of azide to amine, the reaction was filtered through celite pad, concentrated and dried under high *vacuum* for 30 min.

Crude di-amine compound was dissolved in THF (2 mL). To the clear solution, Ac_2O (0.12 mL, 1.3 mmol) and DMAP (4 mg, 0.03 mmol) were added sequentially at 0 °C, and the mixture was allowed to stir at room temperature for 4 h. After completion of reaction, solvents were removed in *vacuo* and the crude product was purified by column chromatography over silica gel (50% ethyl acetate: pet ether) to furnish desired substrate **33** as brown viscous liquid (0.084 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H, -ArH), 7.27-7.26 (m, 3H, -ArH), 6.59 (d, J = 8.0 Hz, 1H, -NH), 5.34 (s, 1H, H-4), 5.06 (d, J = 10.8 Hz, 1H, H-1), 4.97 (ddd, $J_{3\text{-F}}$, $J_{3\text{-2}}$, $J_{3\text{-4}}$ = 37.0, 10.0, 3.0 Hz, 1H, H-3), 4.04-3.96 (m, 1H, H-2), 3.74-3.72 (m, 1H, H-5), 2.08 (s, 3H, -NHAc), 1.99 (s, 3H, -NHAc), 1.18 (d, J = 6.0 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.18, 170.55, 133.09, 132.01, 128.94, 127.77, 88.56 (d, $J_{C,F}$ = 191.2 Hz, C-3), 85.43 (d, $J_{C,F}$ = 7.5 Hz, C-1), 72.38 (d, $J_{C,F}$ = 5.7 Hz, C-5), 70.01, (d, $J_{C,F}$ = 15.0 Hz, C-4) 52.10, (d, $J_{C,F}$ = 18.7 Hz, C-2), 23.49, 20.64, 16.57; ^{19}F NMR (^{1}H decoupled) (470 MHz, $CDCl_3$) δ -192.47 (s); HR-ESI-MS (*m/z*): [M + Na]$^+$calcd. for $C_{16}H_{20}FNNaO_4S$, 364.0989; found, 364.0983.

Acetyl 4-*O*-acetyl-2-acetamido-3-fluoro-2,3,6-trideoxy-*α*-D-galactopyranoside (6):



To the stirring solution of compound **33** (0.080 g, 0.23 mmol) in THF (2.8 mL) and H_2O (0.70 mL), NBS (0.125 g, 0.703 mmol) was added at 0 ºC and the reaction was stirred for 30 min at rt. After completion of reaction, the reaction mixture was concentrated under reduced pressure and kept in high *vacuum* overnight.

Then Ac_2O (0.11 mL, 1.1 mmol), Et_3N (0.16 mL, 1.1 mmol) and DMAP (3 mg, 0.02 mmol) were added sequentially to crude amine compound in dry CH_2Cl_2 (1.69 mL) at 0 ºC and stirred at rt. After 4 h, the reaction mixture was concentrated and purified by column chromatography over silica gel (70% ethyl acetate: pet ether) to obtain compound **6** as a white solid (0.051 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (t, J = 4.0 Hz, 1H, H-1α), 5.45 (dd, J = 4.4, 2.8 Hz, 1H, H-4), 4.80 (bs, 1H, H-2), 4.73 (ddd, $J_{3\text{-}F}$, $J_{3\text{-}2}$, $J_{3\text{-}4}$ = 38.0, 10.8, 3.2 Hz, 1H, H-3), 4.10-4.07 (m, 1H, H-5), 2.20 (s, 3H, -$COCH_3$), 2.15 (s, 3H, -$COCH_3$), 2.02 (s, 3H, -NHAc), 1.17 (d, J = 6.4 Hz, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.49, 170.29, 168.87, 91.88 (d, $J_{C,F}$ = 9.0 Hz, C-1), 86.64 (d, $J_{C,F}$ = 191.0 Hz, C-3), 69.69 (d, $J_{C,F}$ = 16.0 Hz, C-4), 67.09 (d, $J_{C,F}$ = 5.0 Hz, C-5), 47.49 (d, $J_{C,F}$ = 19.0 Hz, C-2), 23.27, 20.97, 20.69, 16.07; LR-ESI-MS (*m/z*): [M + Na]$^+$calcd. for $C_{12}H_{18}FKNO_6$, 330.0755; found, 330.3450.

Biology

General. All biological reagents were obtained from commercial suppliers and used without further purification. *Helicobacter pylori* strain G27[3] was a gift from Manuel Amieva (Stanford University). Glycosylation mutant (ΔGT, HPG27_580::Cm^R) was a gift from Nina Salama (Fred Hutchinson Cancer Research Center); it is *H. pylori* G27 insertionally inactivated in HPG27_580 with a chloramphenicol resistance cassette[4]. Other bacterial cells (*C. jejuni* ATCC 33560; *B. fragilis* ATCC 23745) were purchased from ATCC and grown according to the supplier's instructions.

Bacterial growth conditions. Three bacterial species were used to examine the effect of metabolic inhibitors. *H. pylori* was grown on horse blood agar plates (4% Columbia agar, 5% horse blood, 10 μg/mL vancomycin, 5 μg/mL cefsulodin, 0.3 μg/mL polymixin B, 5 μg/mL trimethoprim, and 8 μg/mL amphotericin B) or in Brucella Broth (with 10% Fetal Bovine Serum (FBS) and 6 μg/mL vancomycin) in 14% CO_2 at 37 °C. *C. jejuni* was grown on 4% Müller-

Hinton agar plates or in Müller-Hinton broth in 14% CO_2 at 37 °C. *B. fragilis* was grown on brain-heart infusion plates (1.5% Bacto agar, 3.7% brain-heart infusion broth, 0.5% yeast extract, and 15 μg/mL hematin porcine) or in brain-heart infusion broth (3.7% brain-heart infusion broth, 0.5% yeast extract, and 15 μg/mL hematin porcine). *B. fragilis* cultures were incubated at 37 °C under anaerobic conditions generated using an Oxoid AnaeroGen 2.5L Sachet (Thermo Scientific).[5]

Rationale for and construction of *H. pylori* glycosylation mutant strain. Targeted insertional inactivation[6] was employed to mutate the putative glycosyltransferase gene HpG27_580 within *H. pylori* G27. This gene was chosen as it encodes a glycosyltransferase gene from family GT-25 with unknown function; though this gene has homology to JHP0563, a β-1,3-galactosyltransferase essential for production of type 1 Lewis antigens on lipopolysaccharide in J99 *H. pylori*, mutating this gene in *H. pylori* strain G27 has no effect on lipopolysaccharide biosynthesis based on reports in the literature[7] and our own unpublished observations. Therefore, we explored the role of this gene in glycoprotein biosynthesis within strain G27. Toward this end, a mutant strain containing the *Campylobacter coli* chloramphenicol acetyl transferase (cat) resistance cassette (Cm^R) within HpG27_580 was produced. Genomic DNA (gDNA) from this mutant was used in the generation of the *H. pylori* G27 mutant transformant used in this study. The patch method was used to transform wildtype *H. pylori* G27 with mutant gDNA. Briefly, log-phase *H. pylori* G27 in Brucella Broth was placed in patches onto HBA plates, incubated for five hours in a 14% CO_2 incubator at 37 °C, and then mixed with 10 μg of mutant gDNA. These patches were incubated for 24 hours in a 14% CO_2 incubator at 37 °C, then plated onto HBA containing chloramphenicol (Cm) for selection of *H. pylori* mutants for 7-10 days. Individual transformants were propagated from single colonies and stored at -80 °C in brain heart infusion freezing media. Polymerase Chain Reaction (PCR) amplification of HpG27_580 from genomic DNA using a forward primer (5'-acatatggtttttagaaaaattaaaagaaaactc-3') and a reverse primer (5'-ctctagattaaacctctttaggggtttttaa-3') was used to confirm the presence and size of the insertionally inactivated target gene (580::Cm^R) within the *H. pylori* mutant strain ΔGT (Supplemental Figure 2A). This mutant strain exhibits a defective glycoprotein biosynthesis fingerprint (Supplemental Figure 2B), indicating HpG27_580 plays a role in glycoprotein biosynthesis.

Metabolic labeling of *H. pylori.* *H. pylori* from a frozen stock was streaked onto agar plates using a sterile tip applicator and then incubated in Brucella broth under microaerophilic conditions (see *Bacterial growth conditions*). After 3-4 days of growth on plates, *H. pylori* were inoculated at an OD_{600} of 0.1-0.4 in liquid media supplemented with 0.5 mM of Ac_4GlcNAc, 0.5 mM of Ac_4GlcNAz, or 0.5 mM Ac_4GlcNAz and varying concentrations (0.5 mM - 2 mM) of compounds **1**-**10**. After metabolic labeling for 3-4 days in liquid media, *H. pylori* were centrifuged at 3500 rpm using a Sorvall Legend RT^+ centrifuge (Thermo Scientific, Waltham, MA) and washed three times with PBS.

Metabolic labeling of *C. jejuni.* *C. jejuni* from a frozen stock was streaked onto agar plates using a sterile tip applicator and then incubated in liquid broth under microaerophilic conditions (see *Bacterial growth conditions*). After 3 days of growth on plates, *C. jejuni* were inoculated at an OD_{600} of 0.1-0.2 in liquid media supplemented with 1 mM of Ac_4GlcNAc, 1 mM of Ac_4GalNAz, or 1 mM Ac_4GalNAz and varying concentrations (0.5 mM - 2 mM) of compounds **1**-**8**. After metabolic labeling for 4 days in liquid media, *C. jejuni* were centrifuged at 3500 rpm using a Sorvall Legend RT^+ centrifuge (Thermo Scientific, Waltham, MA) and washed three times with PBS.

Metabolic labeling of *B. fragilis.* *B. fragilis* from a frozen stock was streaked onto agar plates using a sterile tip applicator and then incubated in liquid broth under anaerobic conditions (see *Bacterial growth conditions*). After overnight growth on plates, *B. fragilis* were inoculated at an OD_{600} of 0.1-0.2 in liquid media supplemented with 0.1 mM of Ac_4GlcNAc, 0.1 mM of Ac_4GalNAz, or 0.1 mM Ac_4GalNAz and varying concentrations (0.5 mM - 2 mM) of compounds **1**-**8**. After metabolic labeling for 2 days in liquid media, *B. fragilis* were centrifuged at 3500 rpm using a Sorvall Legend RT^+ centrifuge (Thermo Scientific, Waltham, MA) and washed three times with PBS.

SDS-PAGE and Western blot analysis of azide-labeled glycans. To probe for azide-labeled glycans produced by cells, metabolically labeled and rinsed cells were lysed in lysis buffer (20 mM Tris-HCl, pH 7.4, 1% Igepal, 150 mM NaCl, 1 mM EDTA) containing protease inhibitor

cocktail (Sigma Aldrich, St. Louis, MO) for 15-30 minutes at room temperature. Lysates were pelleted at 10,000 rpm using an Eppendorf microcentrifuge, then protein concentrations of supernatants were measured using the DC Protein Assay (Bio-Rad, Hercules, CA) and standardized to equal concentrations (~2 mg/mL). Standardized samples were subsequently reacted 1:1 with 500 μM Phos-FLAG at 37°C overnight, then analyzed by SDS-PAGE and Western blot. In preparation for electrophoresis, reacted samples were combined in a 1:1 ratio with 2X SDS reducing loading buffer and boiled at 95 °C for 5-10 minutes. Samples (20 μg), alongside a molecular weight ladder (EZ-Run Prestained Rec Protein Ladder, Fisher Scientific), were loaded onto a 12% Tris-HCl SDS-PAGE gel with a 4% stacking layer. After electrophoresis at 200 V for 60 minutes on ice, proteins were transferred to a nitrocellulose membrane (Bio-Rad – Amersham, GE Healthcare Life Sciences) at 100 V for 1 hour or stained with Coomassie (Stain: 45% deionized water, 45% Methanol, 10% acetic acid, 0.25% Coomassie brilliant blue/Destain: 50% deionized water, 40% methanol, 10% acetic acid) to visualize equal protein loading. Immunoblots were blocked for 1 hour with 5% non-fat dried milk in 0.05% TBS-T buffer (5 mM Tris-HCl, 0.05% Tween-20 (BioRad), pH 7.4). Anti-FLAG-HRP (Sigma Aldrich; 1:1000 dilution in blocking buffer) was employed to visualize FLAG-tagged proteins via chemiluminescence (SuperSignal West Pico Chemiluminescent Substrate) with the G:BOX Chemi XRQ gel documentation system (Syngene).

Lectin binding flow cytometry experiments with *H. pylori*. *H. pylori* were cultured for four days in rich liquid media supplemented with 2 mM of compounds **1**-**6** or without any additional supplement (wildtype), then thoroughly washed with 1X PBS prior to incubation with Alexa Fluor 488-conjugated *Concanavilin A* (ConA) lectin (15 μg/ml in 1X PBS; Thermo Fischer, Waltham, MA; ex: 488/em: 519) for 45 mins at 37 °C in 14% CO_2. As a control, ConA was pre-incubated with 400 mM mannose for 60 mins at 37 °C prior to binding to untreated (wildtype) *H. pylori*. Cells were then washed three times with 1X PBS and analyzed by flow cytometry using a BD Accuri C6 (BD Biosciences) instrument, with 10,000 live cells gated for each replicate experiment. Labeling was performed in triplicate and is reported as number of cells versus fluorescence intensity in histogram plots. Alternatively, flow cytometry data are reported as the mean fluorescence intensity (MFI) of a population of cells from replicate experiments, as calculated using FlowJo software (Ashland, OR).

Flow cytometry experiments with *B. fragilis*. To complement Western blot analyses, the presence of azides on *B. fragilis* was also probed via flow cytometry. For these experiments, metabolically labeled *B. fragilis* were washed with FACS buffer (1X PBS containing 1% fetal bovine serum (FBS)), then reacted with Alexa Fluor 488 DBCO (Click Chemistry Tools) for strain-promoted azide-alkyne cycloaddition detection of azides. In this case, whole cells metabolically labeled as described above (see *Metabolic labeling of B. fragilis*) were reacted with 20 μM Alexa Fluor Dye 488 DBCO (AF488-DBCO; ex: 488/em: 519) for 5 hours in the dark. Cells were then rinsed with PBS supplemented with 1% BSA, and analyzed using a BD Accuri C6 (BD Biosciences) instrument, with 30,000 live cells gated for each replicate experiment. Labeling was performed in triplicate and is reported as number of cells versus fluorescence intensity in histogram plots. Alternatively, flow data are reported as the mean fluorescence intensity (MFI) of a population of cells from replicate experiments, as calculated using FlowJo software (Ashland, OR).

Growth curves. Growth was measured over the course of 4-5 days. Bacteria were inoculated at a starting optical density at 600 nm (OD_{600}) of ~0.2-0.5 into culture tubes containing 3 mL of liquid media (see *Bacterial growth conditions*) supplemented with 1 mM (*H. pylori*) or 2 mM (*C. jejuni*) of the indicated compound **1**-**8**. Untreated wildtype (WT) or glycosylation mutant (ΔGT) cells were grown in parallel under analogous conditions. Cultures were kept at 37°C and 14% CO_2 with gentle shaking. The OD_{600} of each culture was measured using spectrophotometry (SPECTROstarNano plate reader) at the indicated timepoints.

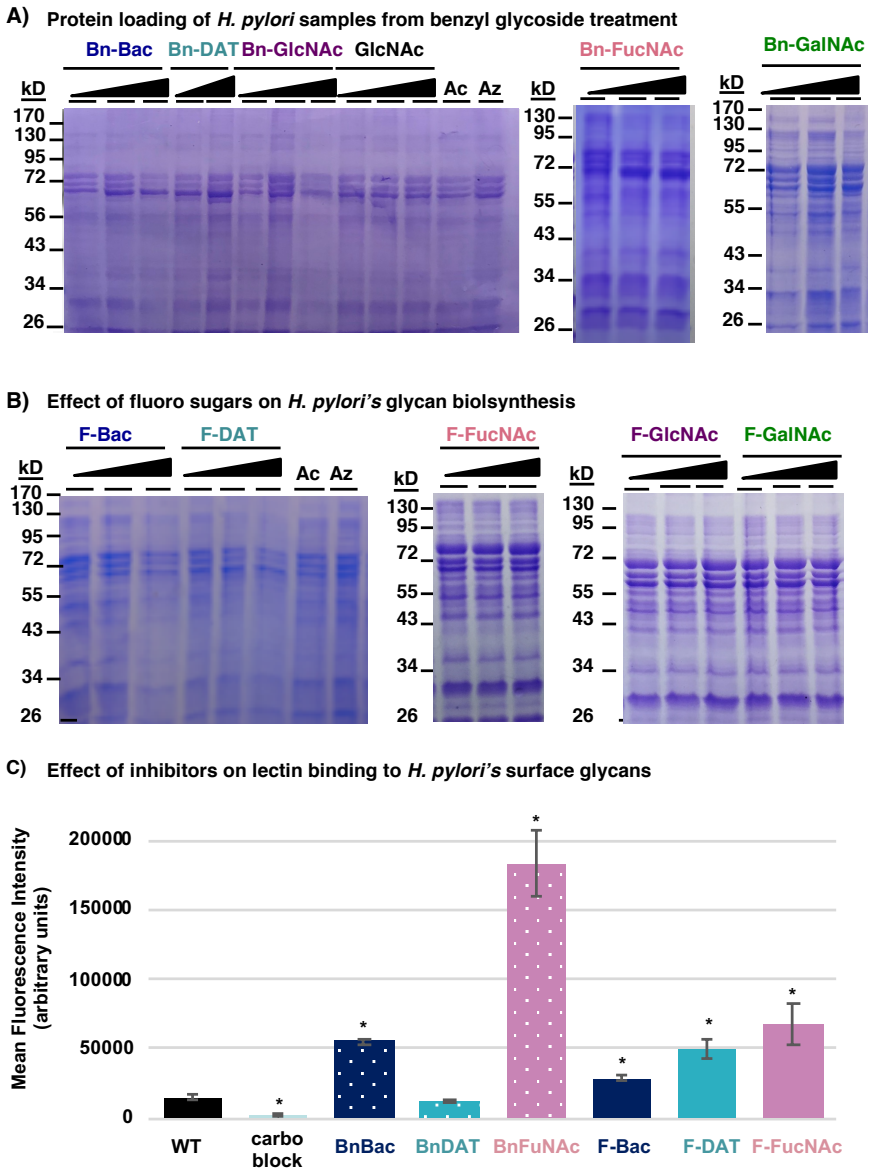
Viability assessment. Viability of inhibitor-treated or untreated wildtype *H. pylori* was assessed over the course of 4 days by enumerating colony forming units (CFUs) or by scoring percent of live cells. *H. pylori* were inoculated at a starting optical density at 600 nm (OD_{600}) of ~0.2-0.3 into culture tubes containing 3 mL of Brucella Broth supplemented with 2 mM of the indicated compound or left untreated (wildtype). To measure CFUs, cells were harvested at 0, 2, or 4 days, serially diluted, and grown on horse blood agar plates in triplicate under microaerophilic conditions. The number of colony forming units were enumerated after five days of incubation, once colonies became visible and could be counted. In parallel to scoring CFUs, percentage of

live cells in cultures was measured using the LIVE/DEAD BacLight Bacterial Viability and Counting Kit (Invitrogen) according to manufacturer's instructions. Briefly, cells were rinsed with 0.85% NaCl three times before staining with LIVE/DEAD BacLight Bacterial Viability solution (Invitrogen), consisting of propidium iodide and SYTO 9 diluted in 0.85% NaCl according to manufacturer's instructions. The cells were kept in the dark for 15 min and then analyzed by flow cytometry using a BD Accuri C6 (BD Biosciences) instrument, with 50,000 live cells gated for each replicate experiment. Cells were scored as live or dead by using gates established with live and dead controls. The number of dead (red) and live (green) *Hp* cells were counted using FlowJo software (Ashland, OR) to determine the percentage of live *Hp* (percentage live cells = 100*[(# live cells)/(# live cells + # dead cells)]).

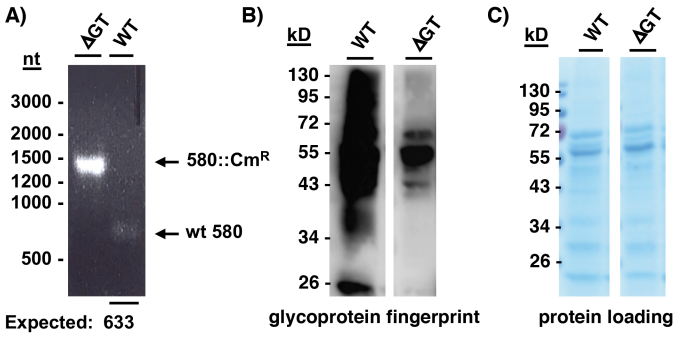
Motility assays. The ability of the bacteria to swarm in the presence of different inhibitors was monitored over the course of 4-8 days using a soft agar motility assay. Bacteria were standardized to an OD_{600} of 1.0 and grown overnight in liquid media supplemented with with 1 mM (*H. pylori*) or 2 mM (*C. jejuni*) of compounds **1-8**. After overnight incubation, 1 mL of each sample was centrifuged at 5000 rpm for 10 minutes using a Sorvall Legend RT^+ centrifuge (Thermo Scientific, Waltham, MA). Pelleted cells were resuspended in 50 µL of Brucella Broth, and 10 µL was plated into soft agar Brucella Broth plates (4% agar and 10% fetal bovine serum) and incubated at 37°C and 14% CO_2. *H. pylori* colony diameter was measured for daily.

Biofilm formation assays. Biofilm formation was measured over the course of 4 days for *H. pylori* and *C. jejuni* cultured in the presence of compounds **1-8** using a literature protocol[8]. Bacteria were standardized to an OD_{600} of 1.0 in liquid media (see *Bacterial growth conditions*), and aliquoted into the side wells of a 96 well plate in three replicates. To the experimental wells, 1 mM (*H. pylori*) or 2 mM (*C. jejuni*) of compounds **1-8** was added. The bacteria were incubated for 4 days at 37 °C and 14% CO_2. After incubation, liquid was removed and wells were gently washed with sterile water. Then biofilm was stained with 0.30% crystal violet and incubated at room temperature for 10-15 minutes. The wells were washed 3-4 times with sterile water and allowed to dry. Biofilm was imaged and then quantified by adding 300 µL acetic acid in water to solubilize the crystal violet. The absorbance at 562 nm was measured using a SPECTROstar^{Nano} plate reader.

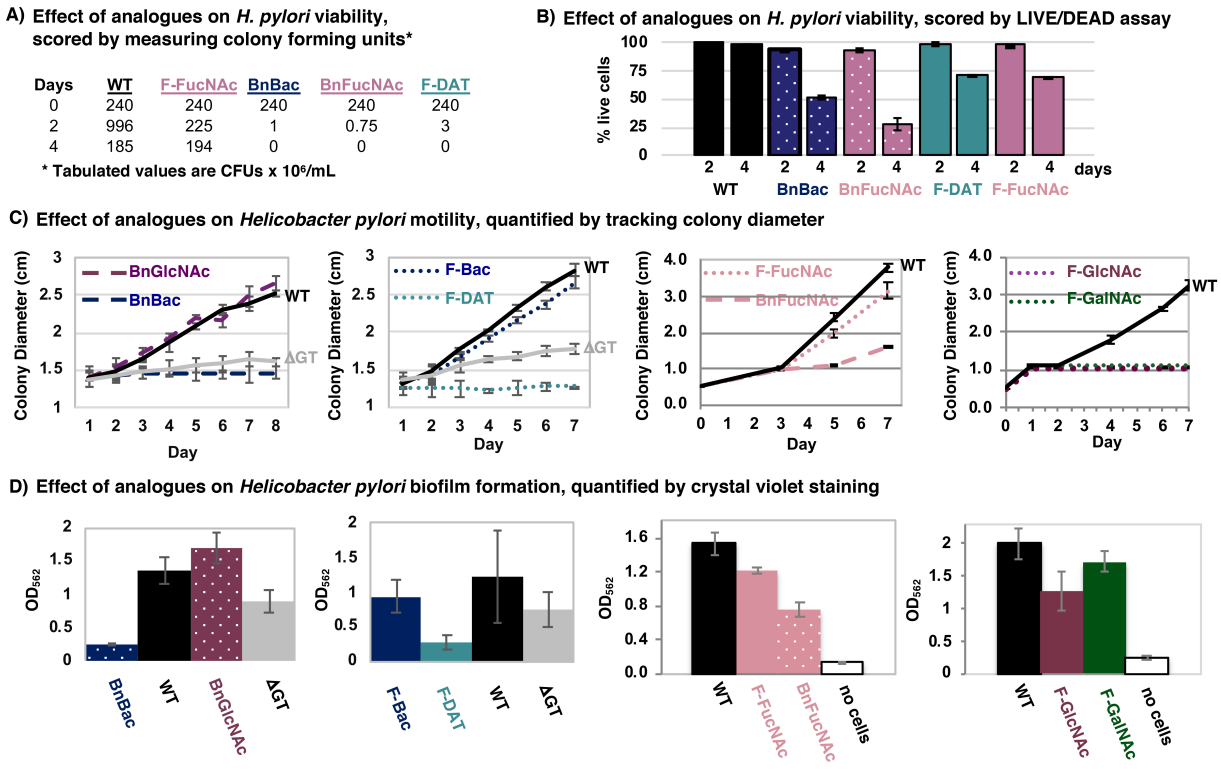
Supplemental Figures



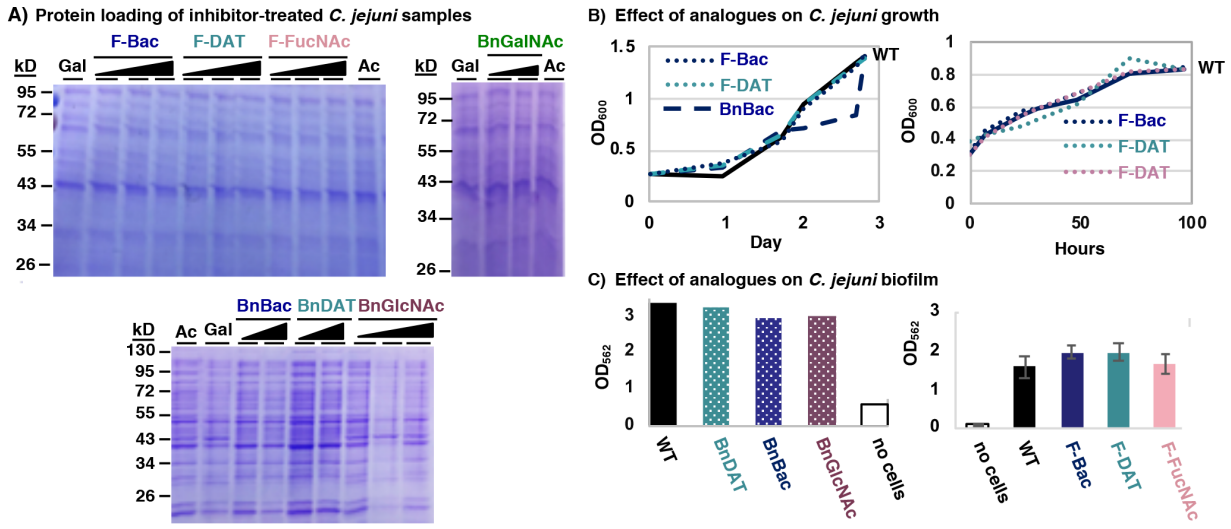
Supplemental Figure 1. Protein loading for samples presented in Figure 3, and graphical depiction of flow cytometry data from Figure 3C. A, B) Coomassie staining of electrophoresed samples from Figure 3 reveal that all Western samples contain roughly equivalent protein levels. C) Mean fluorescence intensity (MFI) of *H. pylori* cell populations probed with ConA. These MFIs correspond to the flow cytometry histograms in Figure 3C. Asterisks (*) indicate samples that were significantly statistically different from wildtype (WT) untreated cells as measured by a Student's t-test (p-value < 0.01). Error bars represent the standard deviation of triplicate samples.



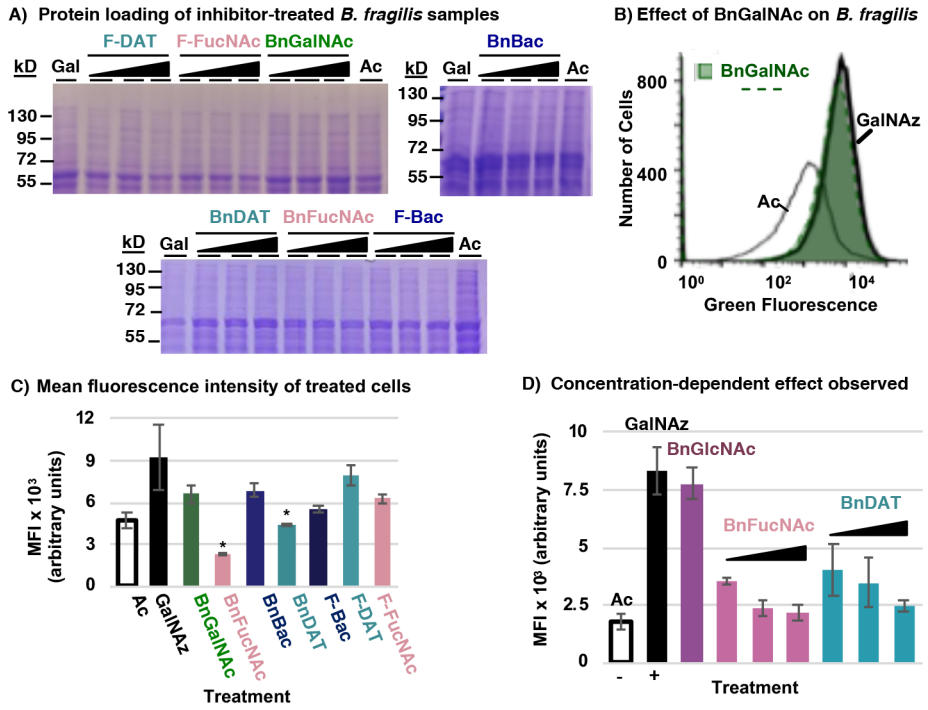
Supplemental Figure 2. Glycoprotein biosynthesis is impeded in ΔGT versus wildtype (WT) *H. pylori*. A) Characterization of an *H. pylori* G27 glycosylation mutant strain (ΔGT, HPG27_580::Cm^R), which contains a chloramphenicol transferase (cat) cassette (Cm^R) within gene HPG27_580. PCR amplification of HPG27_580 from wildtype G27 and from ΔGT, followed by analysis on agarose gel, revealed the expected 633 nucleotide (nt) gene present in WT G27. A substantially larger amplification product was observed in ΔGT, consistent with insertional inactivation of the target gene HPG27_580 with the chloramphenicol transferase cassette (580::Cm^R). B) Comparison of the azide-labeled glycoprotein profile in G27 wildtype (WT) *H. pylori* versus in ΔGT. In this experiment, *H. pylori* strains were grown for four days in media supplemented with 1.0 mM Ac_4GlcNAz (Az), then harvested by lysis. The presence of azides in cellular glycoproteins was detected by reacting lysates with 250 μM Phos-FLAG for 12 h at 37 °C and then analyzing samples via Western blot with anti-FLAG antibody. C) Protein loading for samples presented in Figure B. Coomassie staining of electrophoresed samples reveal that these Western samples contain roughly equivalent protein levels. Note that the WT and ΔGT samples were prepared and analyzed in parallel; images are cropped to remove intervening sample lanes. The data shown are representative of replicates ($n \geq 2$). This genetic interruption of *H. pylori*'s general protein glycosylation system occurs by an as-yet uncharacterized mechanism that does not influence lipopolysaccharide structure in *H. pylori* G27.[7]



Supplemental Figure 3. *Helicobacter pylori* viability, motility, and biofilm production is hindered by metabolic inhibitors. A, B) *H. pylori* were cultured in liquid media containing 2 mM of the indicated inhibitor or no inhibitor (WT) and scored for viability by (A) enumerating colony forming units (CFUs) and (B) measuring percent of live cells in each sample at 0, 2 and 4 days, as noted. C) *H. pylori* were cultured overnight in liquid media containing 1 mM of the indicated inhibitor, then plated on soft agar. Colony diameter was monitored daily. D) *H. pylori* were cultured for 4 days in edge wells of 96 well plates in the presence or absence of 1 mM of the indicated inhibitors. Biofilm was subsequently stained by crystal violet, resuspended in 30% acetic acid, and quantified by measurement of optical density at 562 nm (OD_{562}) via spectrophotometry. Error bars represent the standard deviation of triplicates. WT = wildtype *H. pylori* treated with no inhibitor. ΔGT = glycosyltransferase mutant.



Supplemental Figure 4. Metabolic inhibitors do not have a significant effect on growth or biofilm formation in *Campylobacter jejuni*. A) Protein loading for samples presented in Figure 5A. Coomassie staining of electrophoresed samples from Figure 5A reveal that all Western samples contain roughly equivalent protein levels. Note that BnBac samples were treated with 1 and 2 mM compound, BnDAT samples were treated with 0.5 and 2 mM compound, and all others were treated with 0.5, 1, and 2 mM of the indicated metabolic inhibitor. B) *C. jejuni* were cultured in media containing 2 mM of the indicated inhibitors and scored for growth each day by monitoring optical density at 600 nm (OD_{600}). C) *C. jejuni* were cultured for 4 days in 96 well plates in the presence or absence of 2 mM of the indicated inhibitors. Biofilm was subsequently stained by crystal violet, resuspended in 30% acetic acid, and quantified by measurement of optical density at 562 nm (OD_{562}) via spectrophotometry.



Supplemental Figure 5. Metabolic inhibitors have a subtle effect on *Bacteroides fragilis'* glycan biosynthesis. A) Protein loading for samples presented in Figure 6A. Coomassie staining of electrophoresed samples from Figure 6A reveal that all Western samples contain roughly equivalent protein levels. B, C) Flow cytometry-based assay to measure levels of azide-labeled glycans on *B. fragilis*. *B. fragilis* were treated with 1 mM metabolic inhibitors (**1-6, 8**) and 0.1 mM Ac_4GalNAz for two days, with 0.1 mM Ac_4GalNAz (GalNAz) in the absence of inhibitor, or with the azide-free control sugar Ac_4GlcNAc (Ac), then probed for the presence of azide-labeled glycans on cells by reaction with 20 μM DIBO-488 and subsequent flow cytometry analysis. B) Flow cytometry histograms of treated cell populations indicate BnGalNAc has a minimal effect on glycan biosynthesis. C) Mean fluorescence intensity (MFI) of treated cell populations was measured by flow cytometry analysis. These MFIs correspond to the flow cytometry histograms in Figure 6B and panel B of this figure. BnFucNAc and BnDAT treatments (*) were significantly statistically different from Ac_4GalNAz (GalNAz)-treated cells as measured by a Student's t-test (p-value < 0.05). D) Effect of increasing concentrations of BnFucNAc and BnDAT on *B. fragilis* azide-labeled glycans. *B. fragilis* were treated with increasing concentration of BnFucNAc (3) and BnDAT (2) in tandem with 0.1 mM Ac_4GalNAz for two days, then reacted with 20 μM DIBO-488 and mean fluorescence intensity (MFI) of each cell population was measured by flow

cytometry analysis. Error bars represent the standard deviation of triplicate samples. Triangles indicate relative concentration, with the shortest point representing 0.5 mM and the tallest part representing 2 mM of the indicated compound.

Supplemental References

1. Luchansky, S. J.; Hang, H. C.; Saxon, E.; Grunwell, J. R.; Yu, C.; Dube, D. H.; Bertozzi, C. R., Constructing azide-labeled cell surfaces using polysaccharide biosynthetic pathways. *Methods in Enzymology* **2003,** *362*, 249-72.
2. Laughlin, S. T.; Bertozzi, C. R., Metabolic labeling of glycans with azido sugars and subsequent glycan-profiling and visualization via Staudinger ligation. *Nature Protocols* **2007,** *2* (11), 2930 - 2944.
3. Baltrus, D. A.; Amieva, M. R.; Covacci, A.; Lowe, T. M.; Merrell, D. S.; Ottemann, K. M.; Stein, M.; Salama, N. R.; Guillemin, K., The complete genome sequence of *Helicobacter pylori* strain G27. *Journal of Bacteriology* **2009,** *191* (1), 447-448.
4. Salama, N. R.; Shepherd, B.; Falkow, S., Global transposon mutagenesis and essential gene analysis of *Helicobacter pylori*. *Journal of Bacteriology* **2004,** *186* (23), 7926-7935.
5. Brigham, C.; Caughlan, R.; Gallegos, R.; Dallas, M. B.; Godoy, V. G.; Malamy, M. H., Sialic acid (N-acetyl neuraminic acid) utilization by *Bacteroides fragilis* requires a novel N-acetyl mannosamine epimerase. *Journal of Bacteriology* **2009,** *191* (11), 3629-38.
6. Baldwin, D. N.; Shepherd, B.; Kraemer, P.; Hall, M. K.; Sycuro, L. K.; Pinto-Santini, D. M.; Salama, N. R., Identification of *Helicobacter pylori* genes that contribute to stomach colonization. *Infection and Immunity* **2007,** *75* (2), 1005-1016.
7. Li, H.; Marceau, M.; Yang, T.; Liao, T.; Tang, X.; Hu, R.; Xie, Y.; Tang, H.; Tay, A.; Shi, Y.; Shen, Y.; Yang, T.; Pi, X.; Lamichhane, B.; Luo, Y.; Debowski, A. W.; Nilsson, H.-O.; Haslam, S. M.; Mulloy, B.; Dell, A.; Stubbs, K. A.; Marshall, B. J.; Benghezal, M., East-Asian *Helicobacter pylori* strains synthesize heptan-deficient lipopolysaccharide. *PLOS Genetics* **2019,** *15* (11), e1008497.
8. O'Toole, G. A., Microtiter dish biofilm formation assay. *Journal of Visualized Experiments* **2011,** DOI: 10.3791/2437..

SSK-17-KP-548-1H

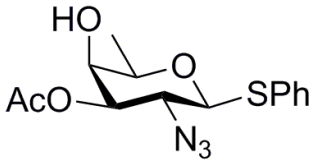
7.603 7.598 7.592 7.584 7.579 7.351 7.342 7.338 7.330 7.325 7.315 7.310

4.796 4.789 4.771 4.763 4.469 4.443 3.840 3.833 3.707 3.691 3.676 3.659 3.651 3.625

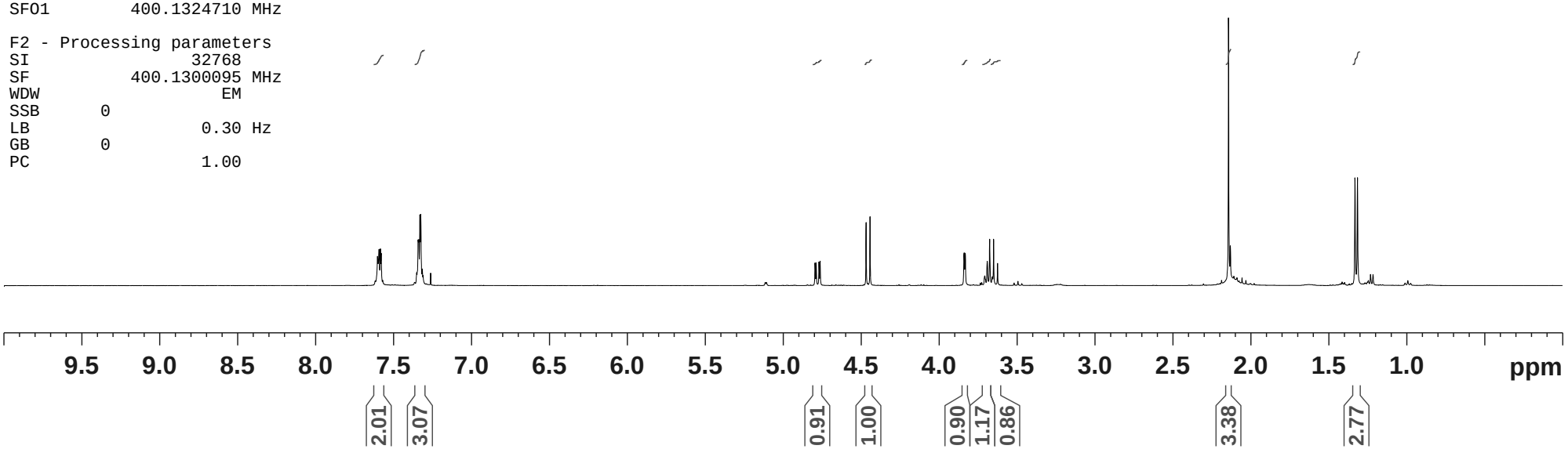
2.143

1.332 1.316

```
Current Data Parameters
NAME     SSK-17-KP-548-1H
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20190717
Time              15.36
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                54274
SOLVENT           CDCl3
NS                    6
DS                    0
SWH            8223.685 Hz
FIDRES        0.151522 Hz
AQ           3.2998593 sec
RG                 71.8
DW               60.800 usec
DE                6.50 usec
TE                297.4 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

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



12



Current Data Parameters
NAME SSK-17-KP-548-13C
EXPNO 3
PROCNO 1

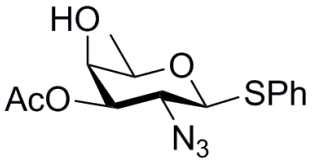
F2 - Acquisition Parameters
Date_ 20190717
Time 15.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 15
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 1030
DW 19.200 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ======
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

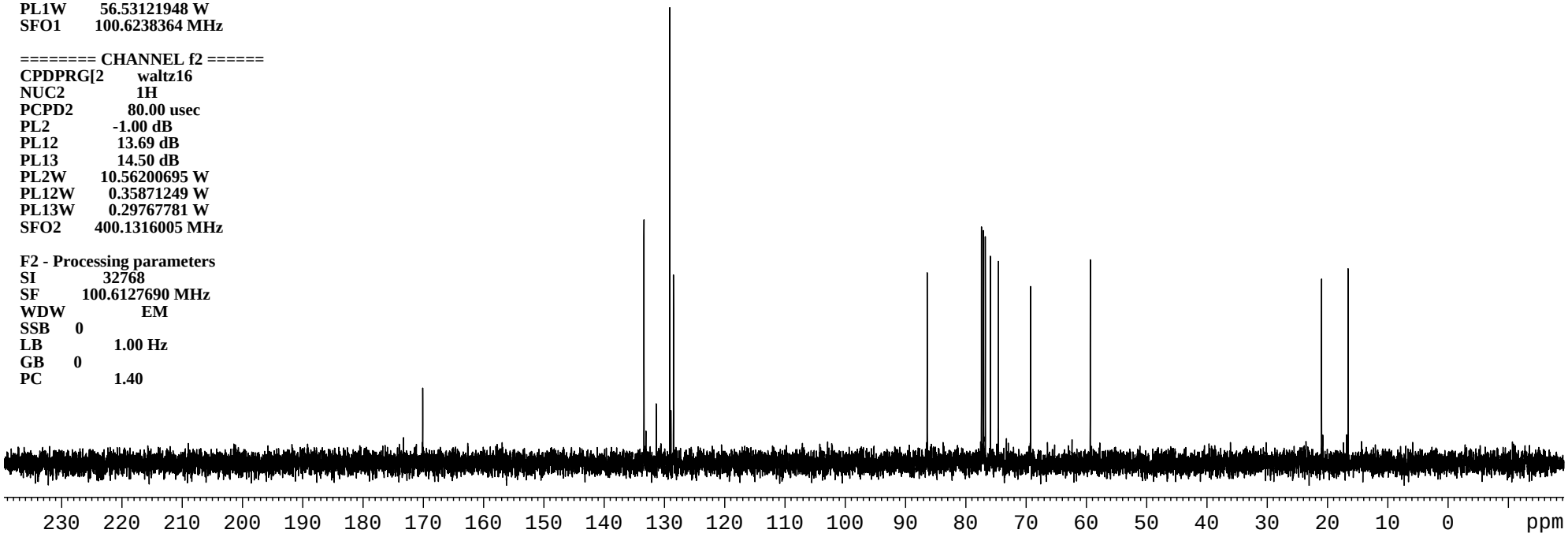
======== CHANNEL f2 ======
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

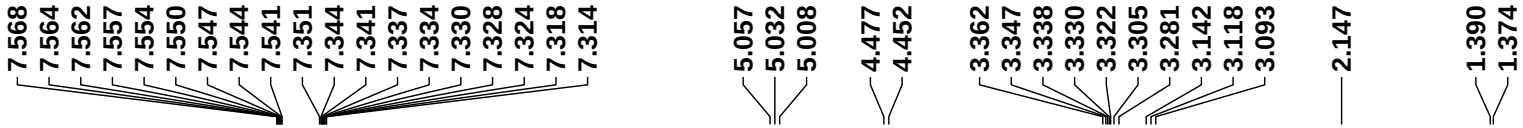
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

170.09
133.39
131.36
129.10
128.91
128.49
86.41
77.40
77.08
76.76
75.92
74.59
69.25
59.35
20.98
16.57



12





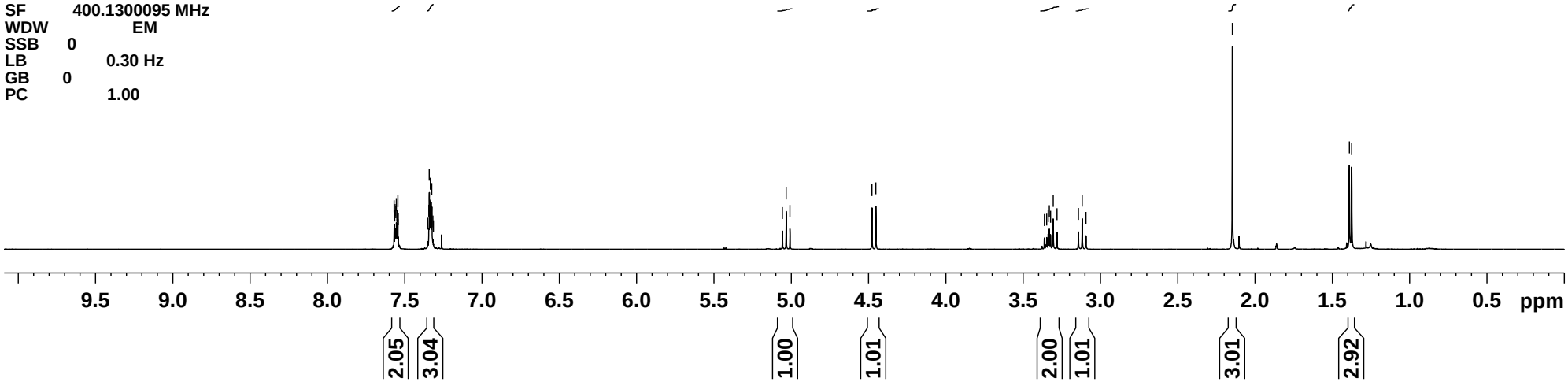
Current Data Parameters
NAME SSK-17-KP-551-H
EXPNO 2
PROCNO 1

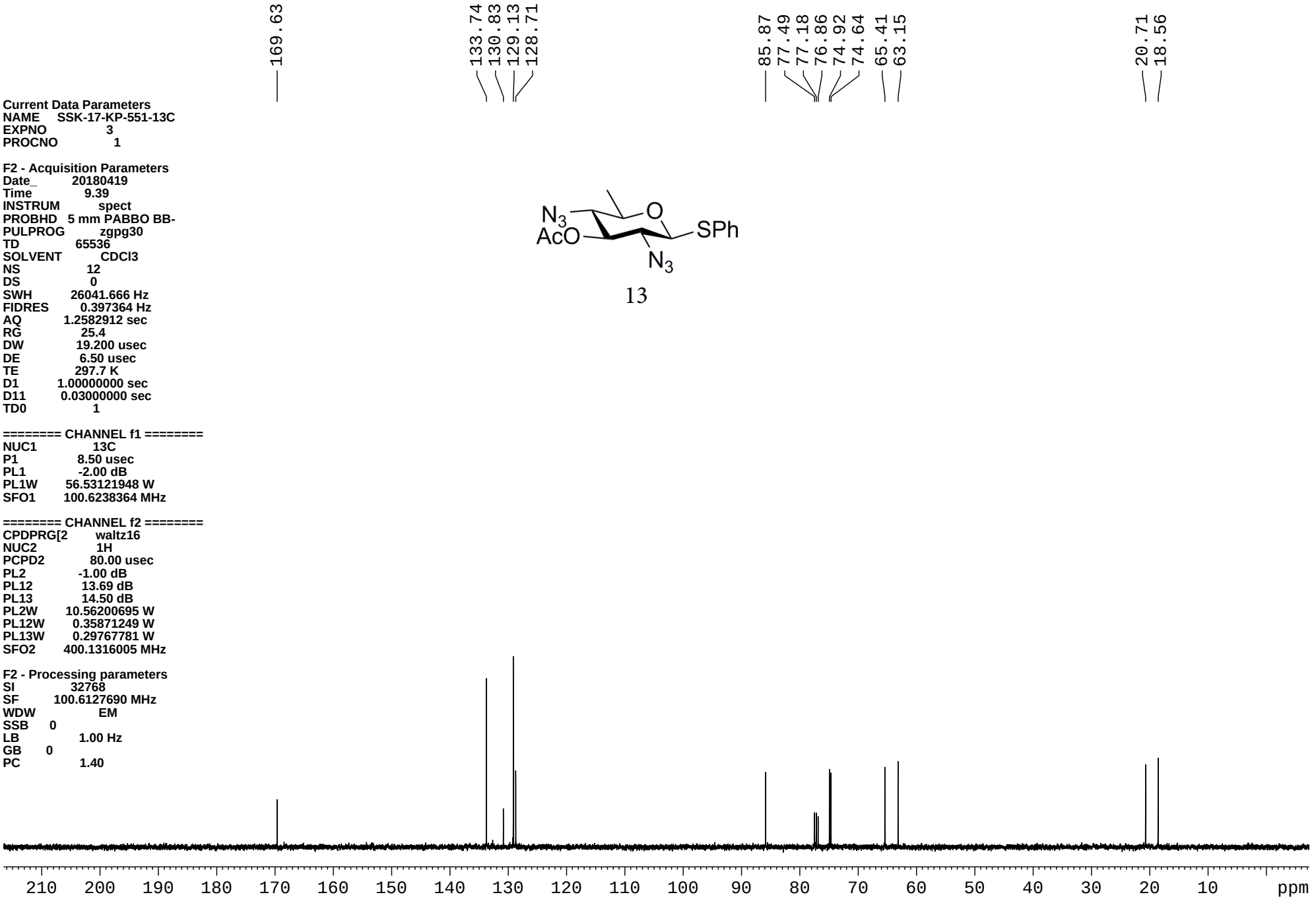
F2 - Acquisition Parameters
Date_ 20180419
Time 9.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 12
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

13




169.63
133.74
130.83
129.13
128.71
85.87
77.49
77.18
76.86
74.92
74.64
65.41
63.15
20.71
18.56
Current Data Parameters
NAME SSK-17-KP-551-13C
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180419
Time 9.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 12
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 25.4
DW 19.200 usec
DE 6.50 usec
TE 297.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N3
AcO
O
SPh
N3
13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

7.404 7.397 7.395 7.379 7.377 7.374 7.366 7.359 7.357 7.353 7.349

5.518 5.498 5.478 5.006 4.999 4.769 4.745 4.637 4.613 3.787 3.775 3.767 3.762 3.754 3.750 3.742 3.730 3.223 3.204 3.184 3.178 3.164 3.157 2.202

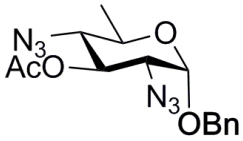
1.333 1.320

Current Data Parameters
NAME SSK-17-KP-562-1H
EXPNO 2
PROCNO 1

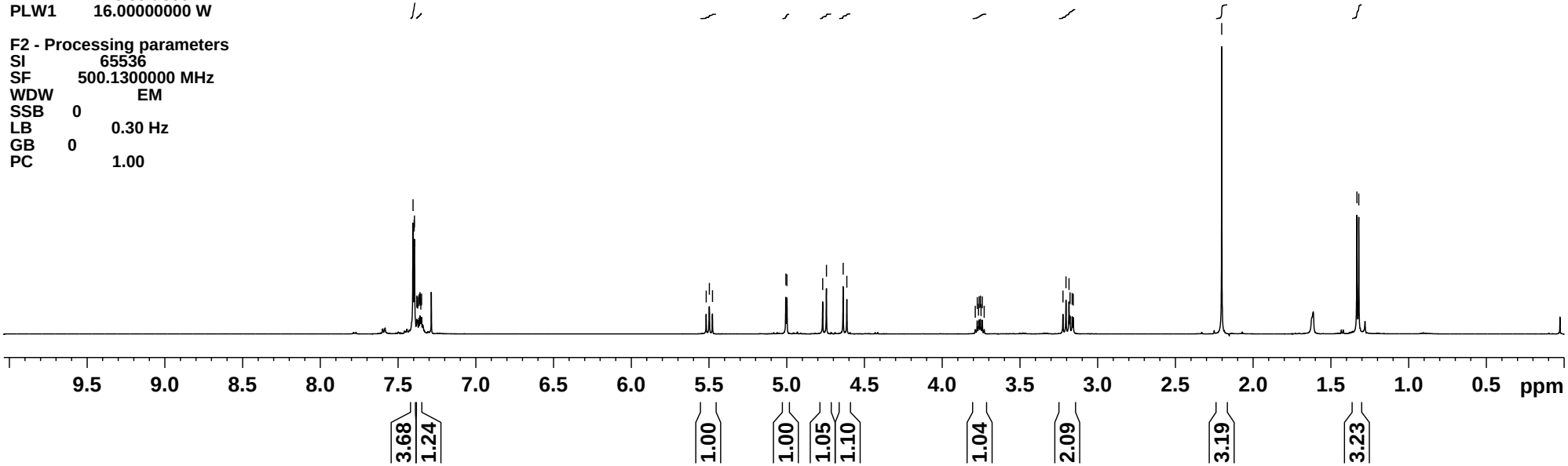
F2 - Acquisition Parameters
Date_ 20180427
Time 22.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 98.91
DW 50.000 usec
DE 6.50 usec
TE 297.5 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

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



14



169.83
136.61
136.25
129.45
128.58
128.20
127.58
96.73
77.29
77.03
76.78
70.75
69.82
66.38
66.35
61.26
20.79
18.18

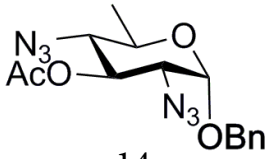
Current Data Parameters
NAME SSK-17-KP-562-13C
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180427
Time 23.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 75
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 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

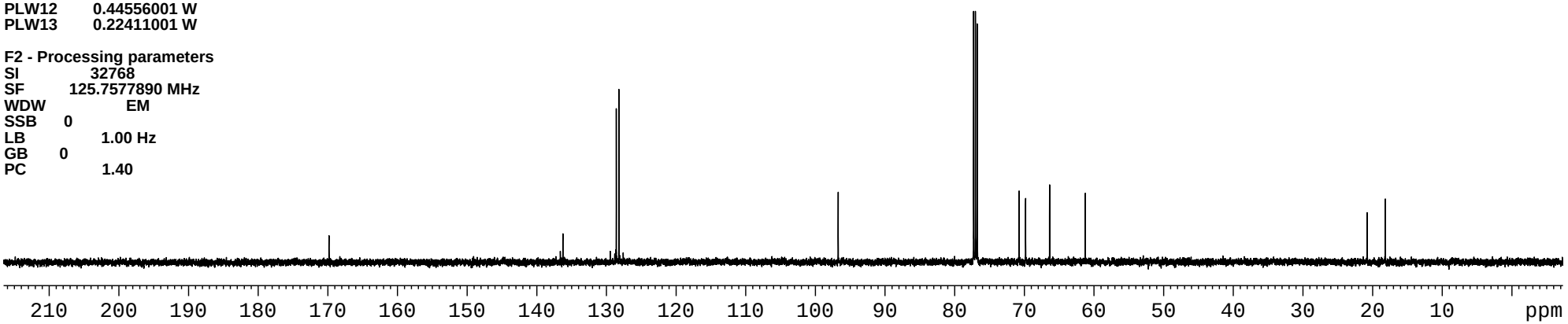
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W

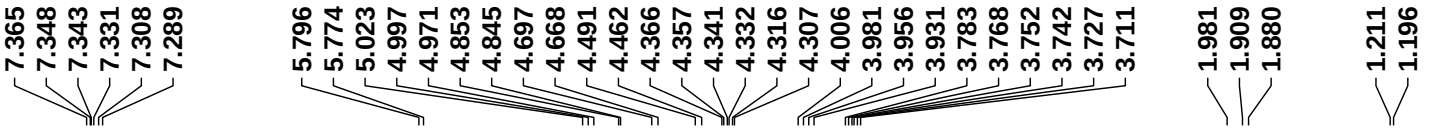
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

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



14



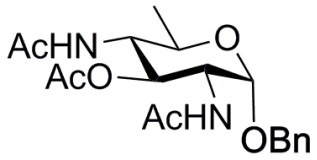


Current Data Parameters
NAME SSK-17-KP-BACNHAcOBn-1H
EXPNO 3
PROCNO 1

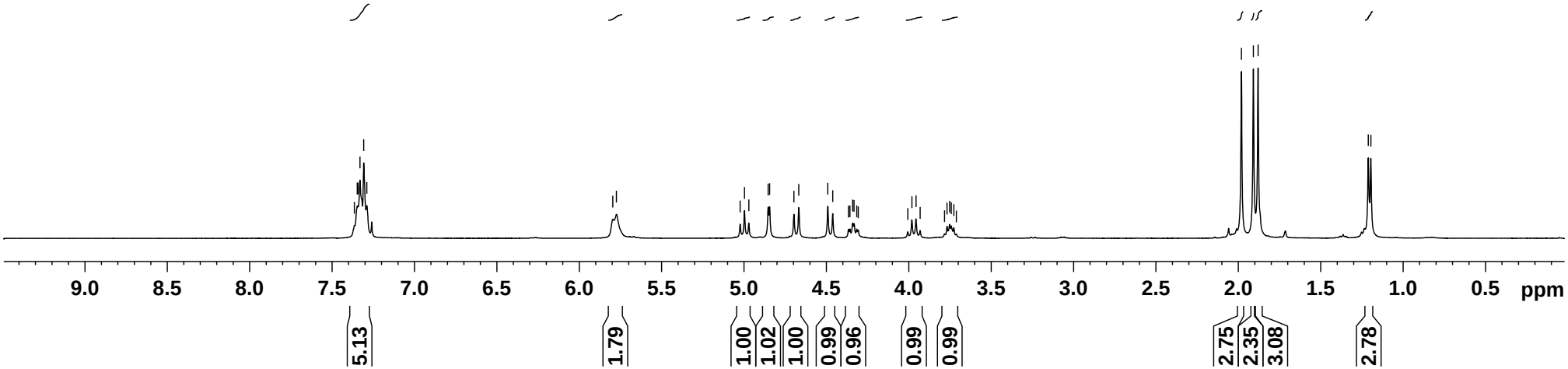
F2 - Acquisition Parameters
Date_ 20190301
Time 18.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1

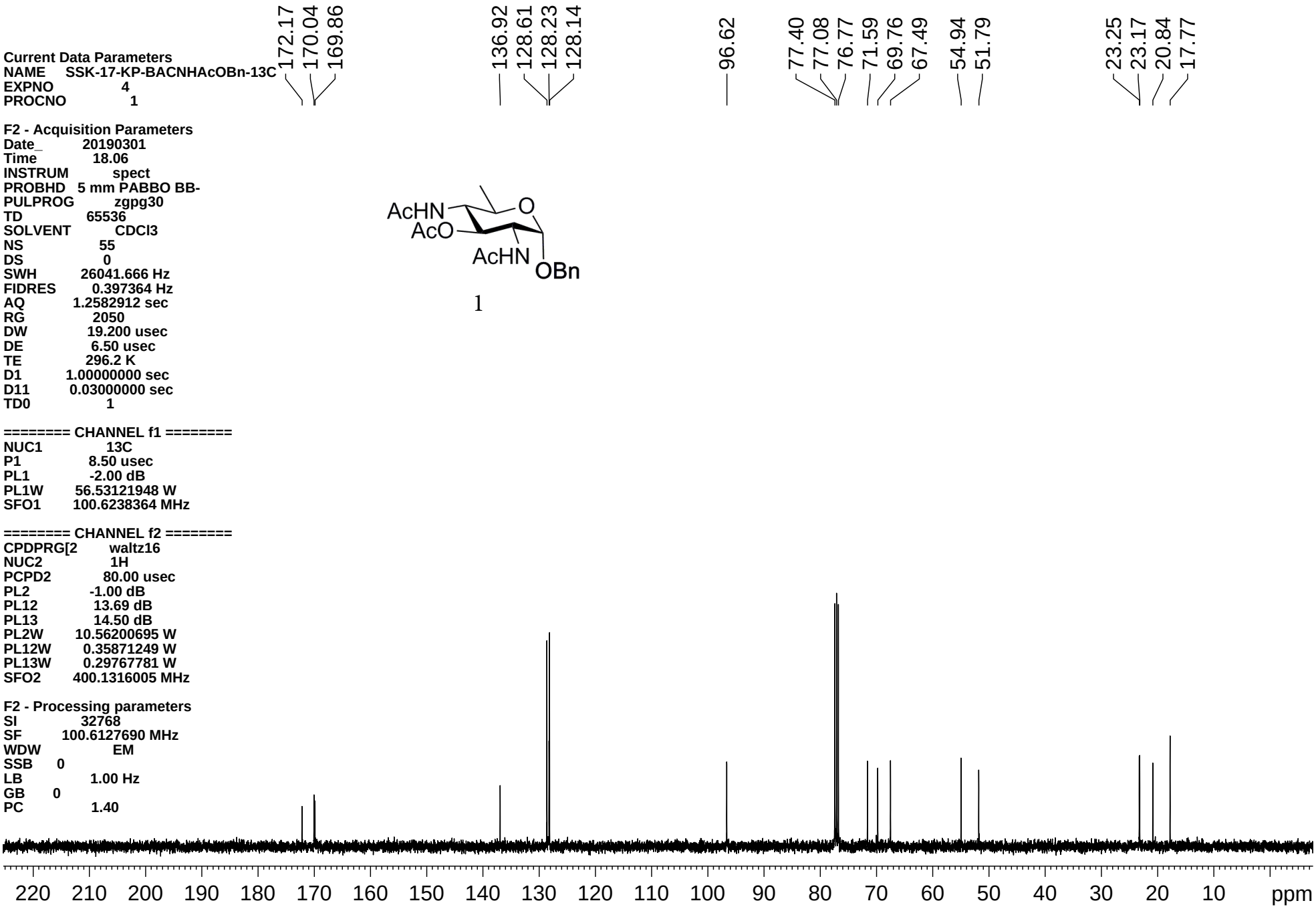
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

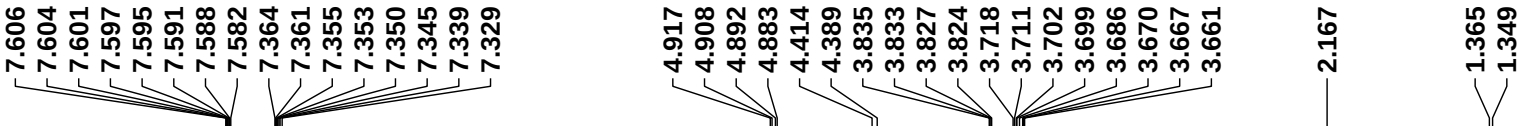
F2 - Processing parameters
SI 32768
SF 400.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



1




172.17
170.04
169.86
136.92
128.61
128.23
128.14
96.62
77.40
77.08
76.77
71.59
69.76
67.49
54.94
51.79
23.25
23.17
20.84
17.77
Current Data Parameters
NAME SSK-17-KP-BACNHAcOBn-13C
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190301
Time 18.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 55
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcHN
O
AcO
AcHN
OBn
1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

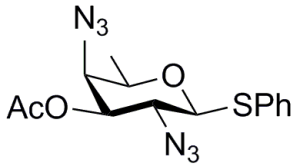


Current Data Parameters
NAME SSK-17-KP-539-1H
EXPNO 1
PROCNO 1

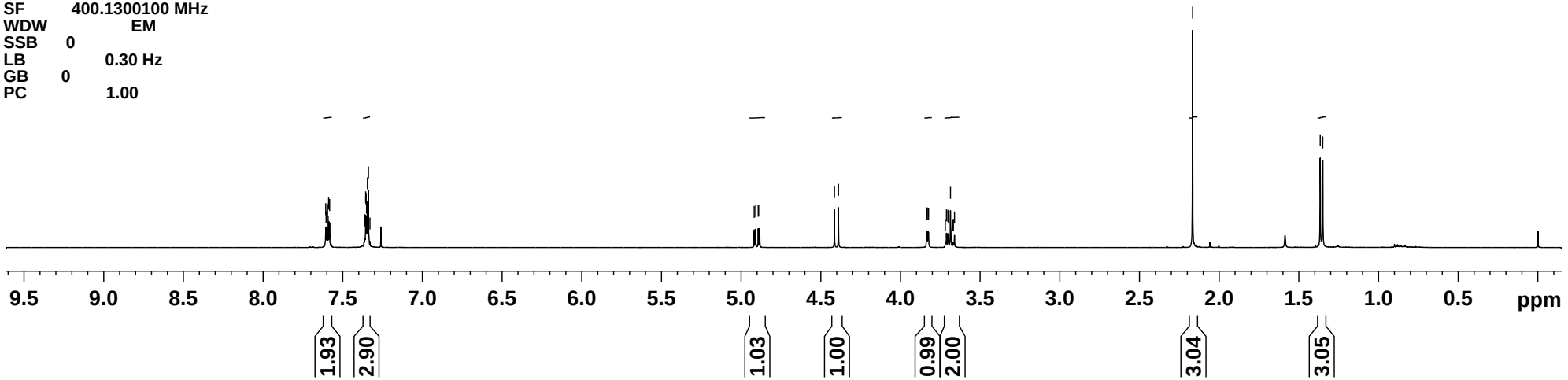
F2 - Acquisition Parameters
Date_ 20180222
Time 15.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

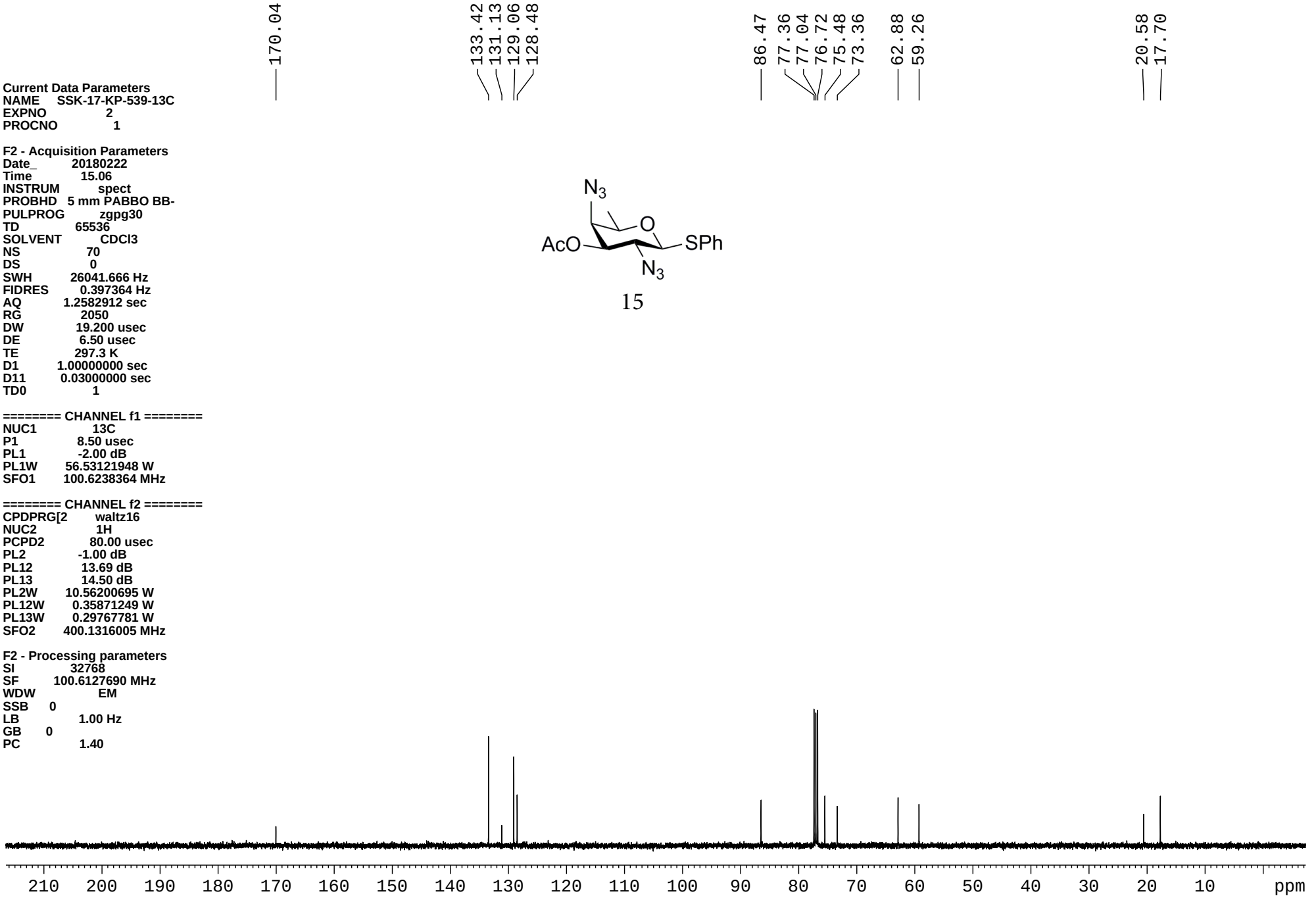
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

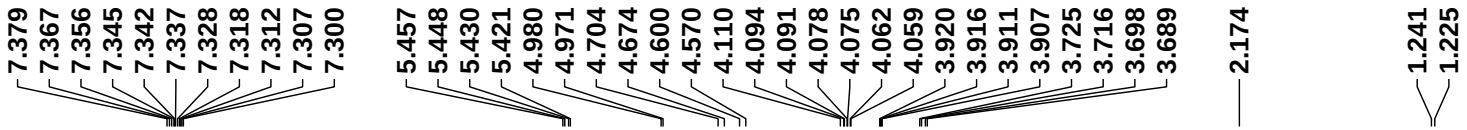
F2 - Processing parameters
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



15




170.04
133.42
131.13
129.06
128.48
86.47
77.36
77.04
76.72
75.48
73.36
62.88
59.26
20.58
17.70
Current Data Parameters
NAME SSK-17-KP-539-13C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180222
Time 15.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 70
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
N3
O
AcO
SPh
N3
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

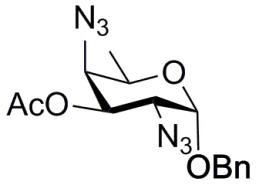


Current Data Parameters
NAME SSK-17-KP-DAT-OBn-UP-1H
EXPNO 4
PROCNO 1

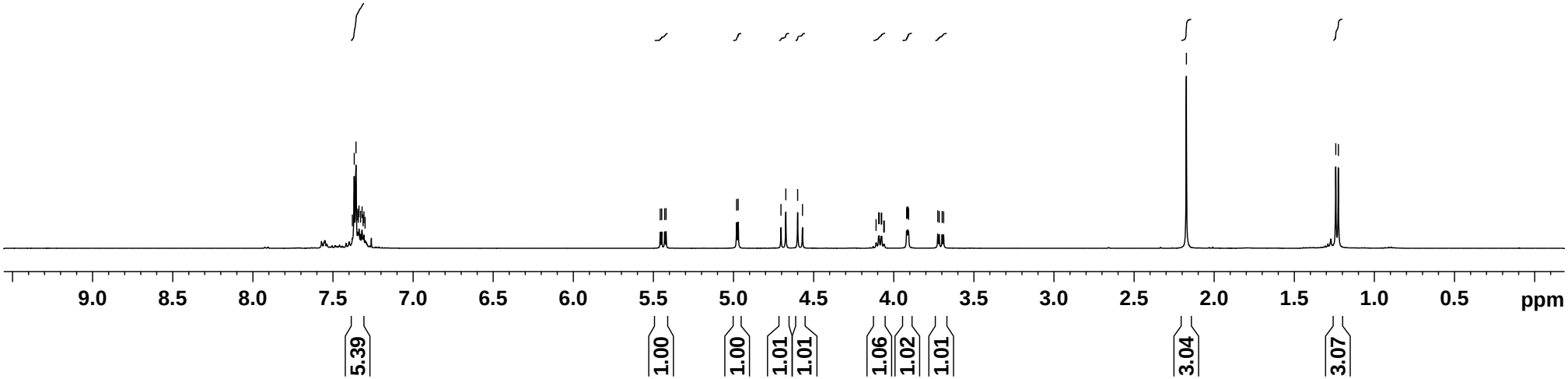
F2 - Acquisition Parameters
Date_ 20190204
Time 16.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



16



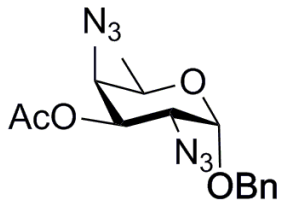
Current Data Parameters
NAME SSK-17-KP-DAT-OBn-UP-13C
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190204
Time 16.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

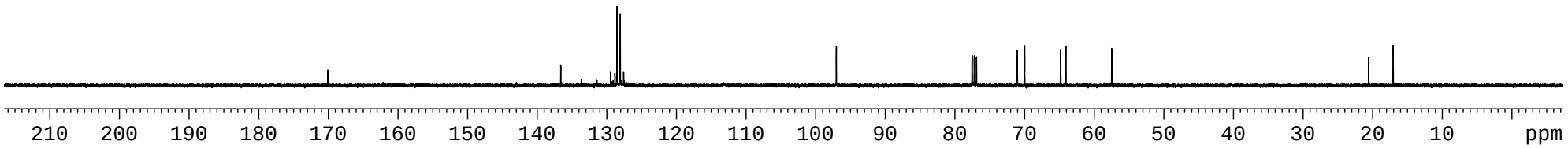
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

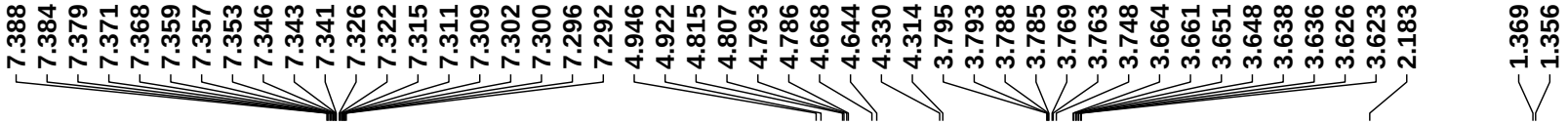
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



16



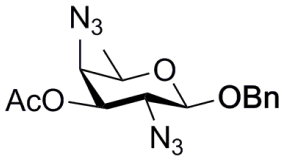


Current Data Parameters
NAME SSK-17-KP-542-1H
EXPNO 6
PROCNO 1

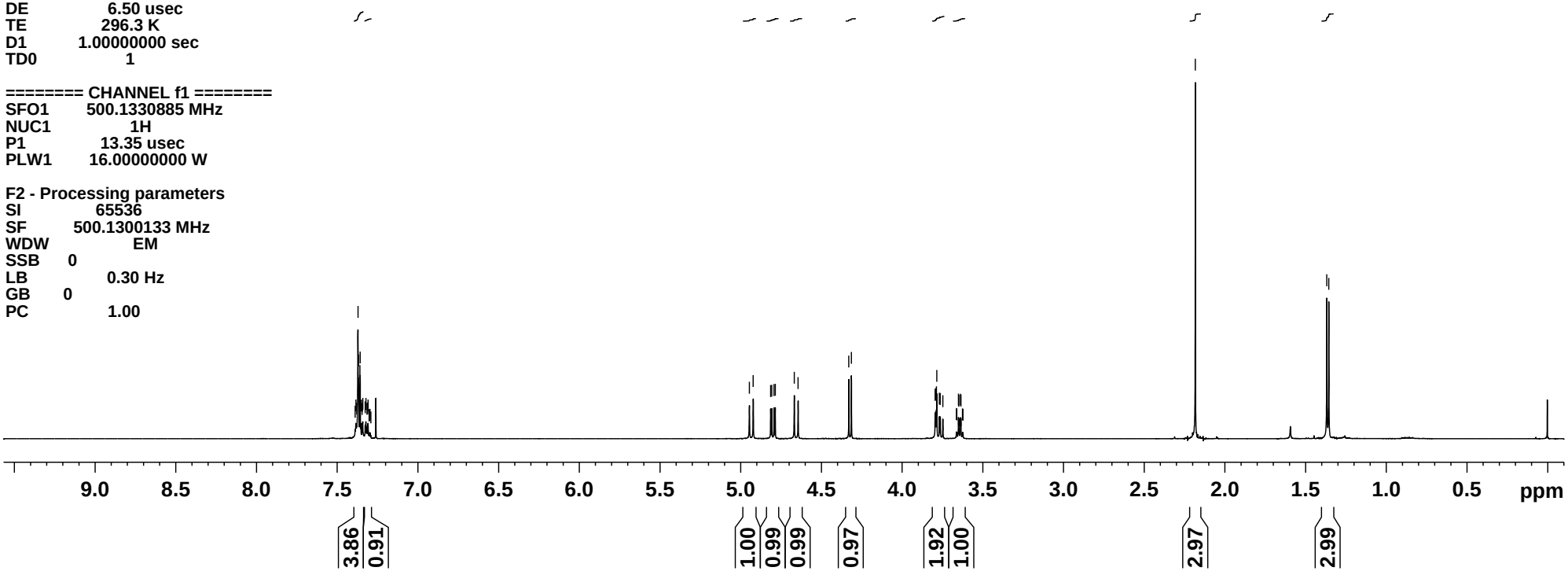
F2 - Acquisition Parameters
Date_ 20180225
Time 15.06
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 80.35
DW 50.000 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1

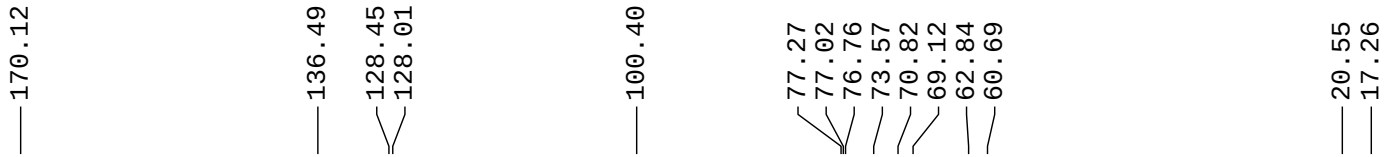
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300133 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



16





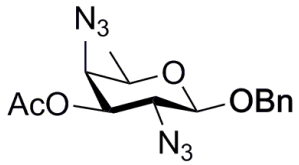
Current Data Parameters
NAME SSK-17-KP-542-13C
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180225
Time 15.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 109
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 296.5 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

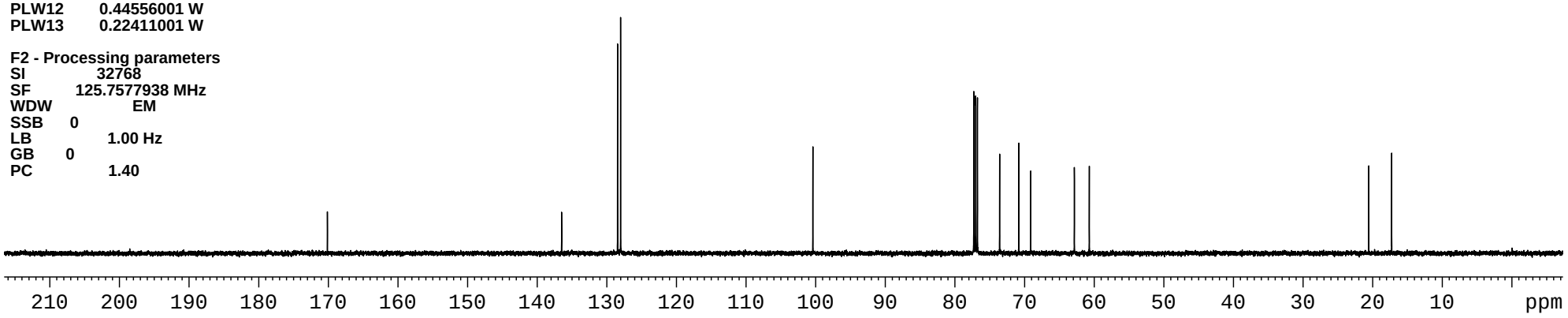
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W

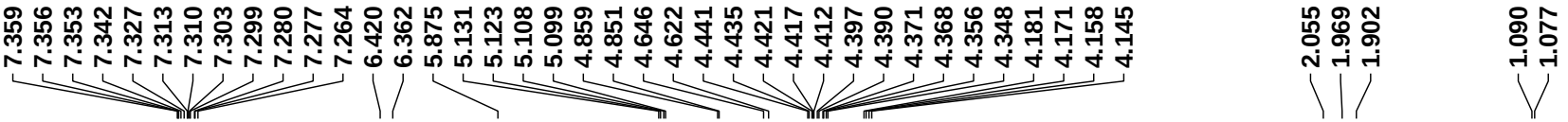
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

F2 - Processing parameters
SI 32768
SF 125.7577938 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



16



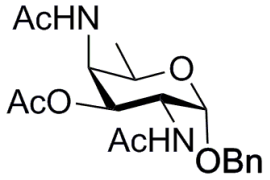


Current Data Parameters
NAME SSK-17-KP-DAT-NHAC-1H
EXPNO 4
PROCNO 1

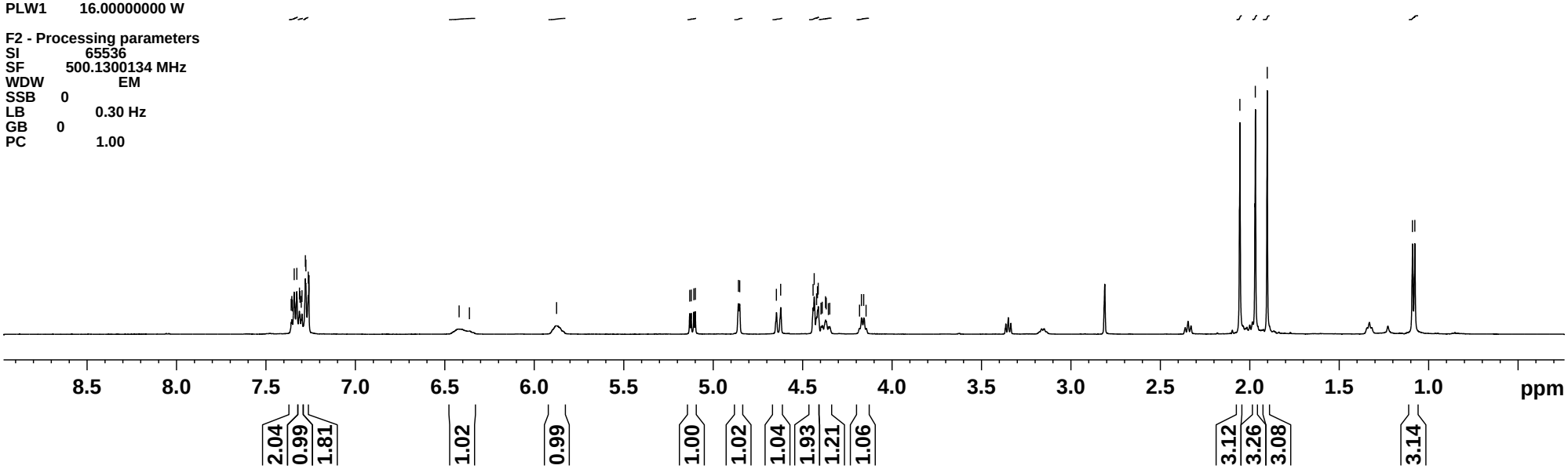
F2 - Acquisition Parameters
Date_ 20190208
Time 21.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1

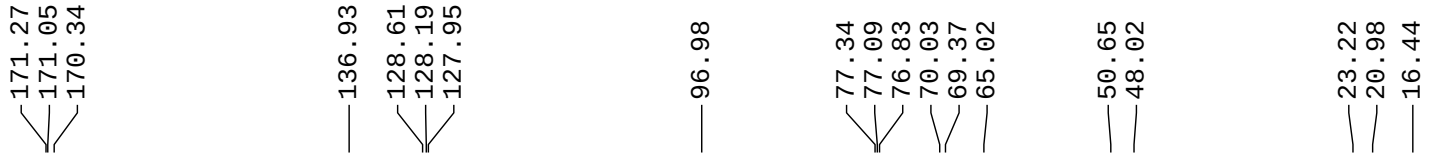
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300134 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



2





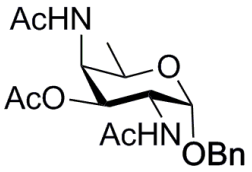
Current Data Parameters
NAME SSK-17-KP-DAT-NHAC-13C
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190208
Time 21.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 47
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 295.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

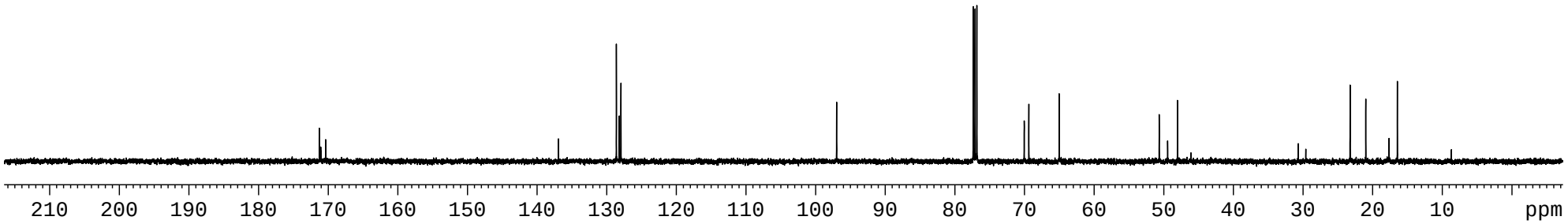
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 8.90 usec
PLW1 103.00000000 W

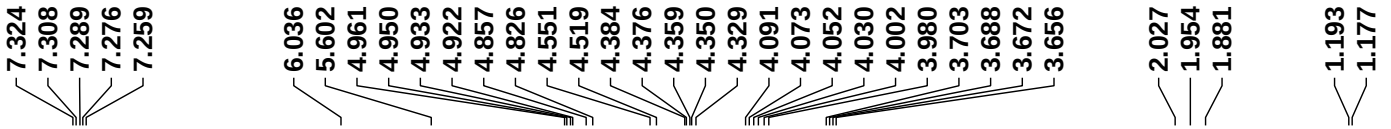
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

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



2



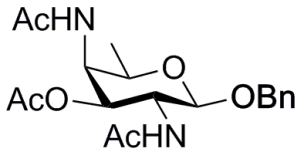


Current Data Parameters
NAME ssk-17-kp-dat-nhac-b-1H
EXPNO 7
PROCNO 1

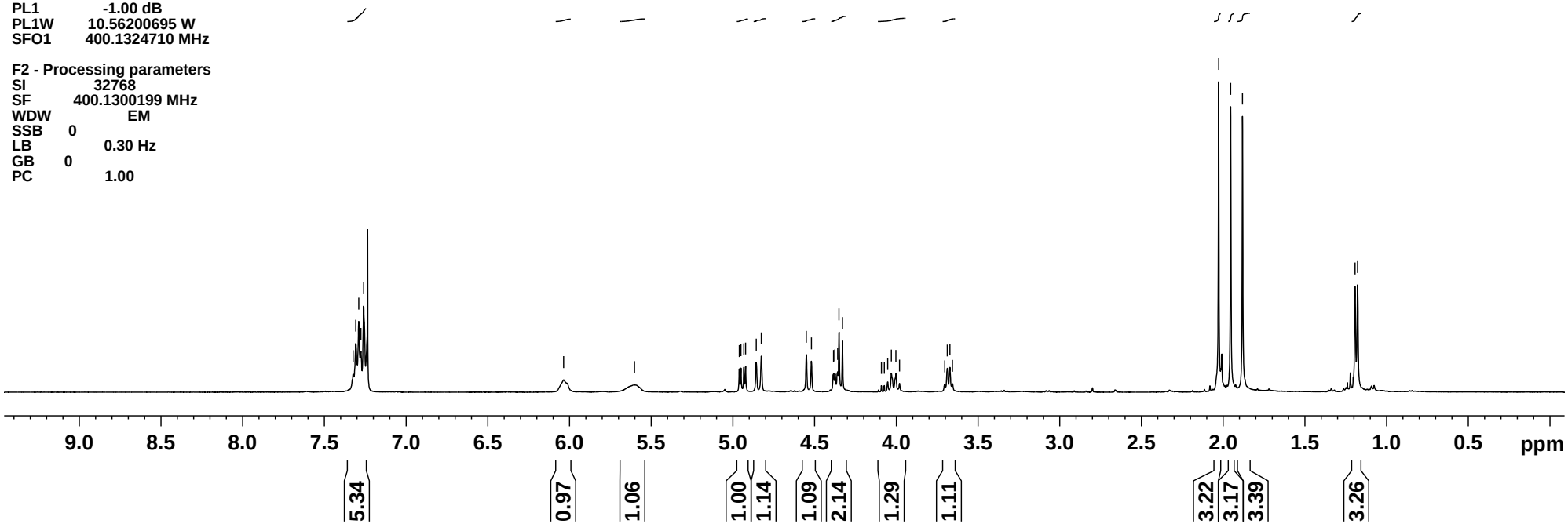
F2 - Acquisition Parameters
Date_ 20190215
Time 2.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 20
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1

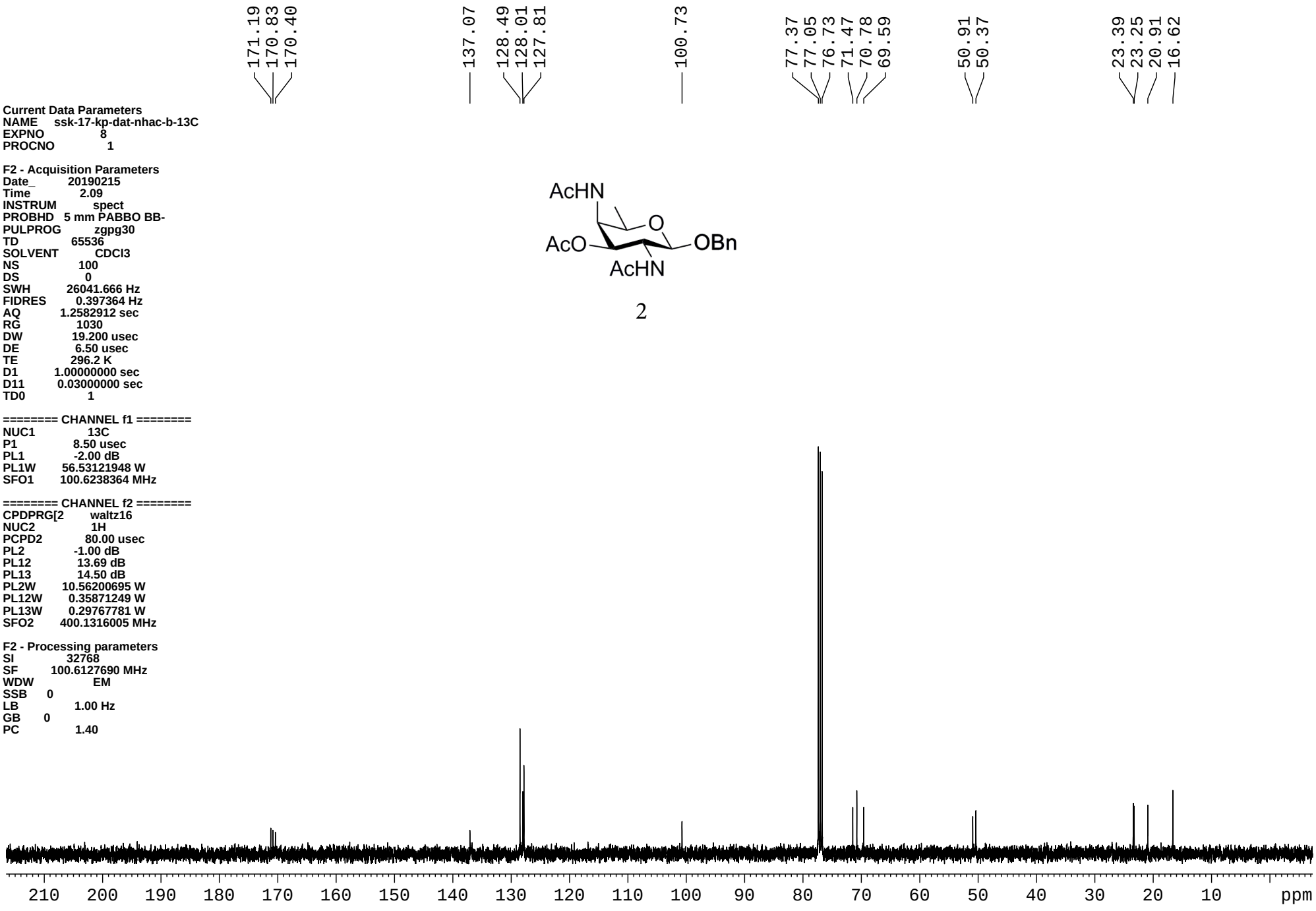
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

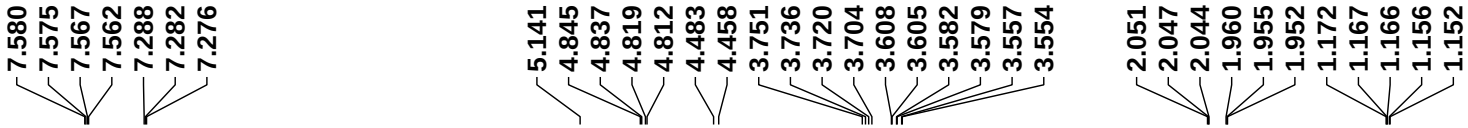
F2 - Processing parameters
SI 32768
SF 400.1300199 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



2




171.19
170.83
170.40
137.07
128.49
128.01
127.81
100.73
77.37
77.05
76.73
71.47
70.78
69.59
50.91
50.37
23.39
23.25
20.91
16.62
Current Data Parameters
NAME ssk-17-kp-dat-nhac-b-13C
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190215
Time 2.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 1030
DW 19.200 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcHN
O
AcO
OBn
AcHN
2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

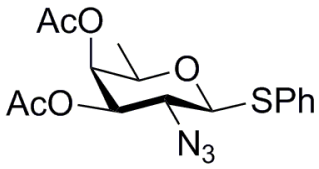


Current Data Parameters
NAME SSK-17-KP-549-1H
EXPNO 1
PROCNO 1

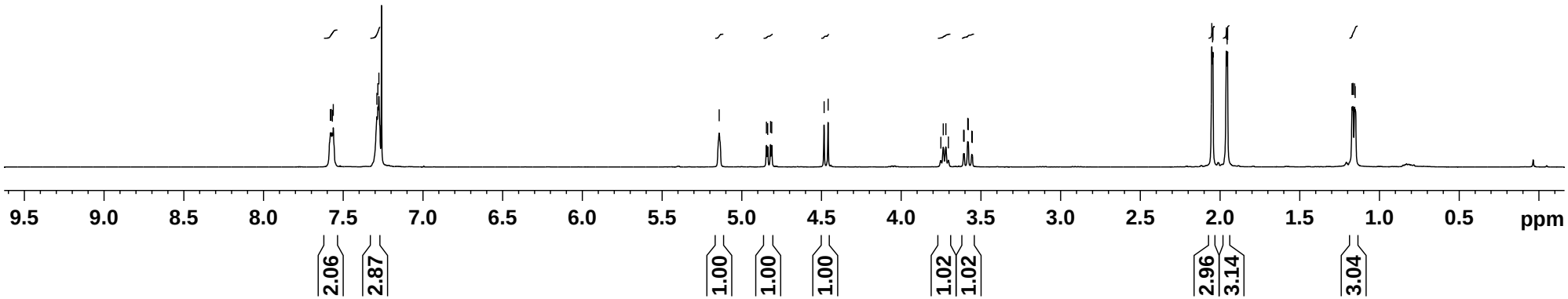
F2 - Acquisition Parameters
Date_ 20180313
Time 14.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 12.7
DW 60.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

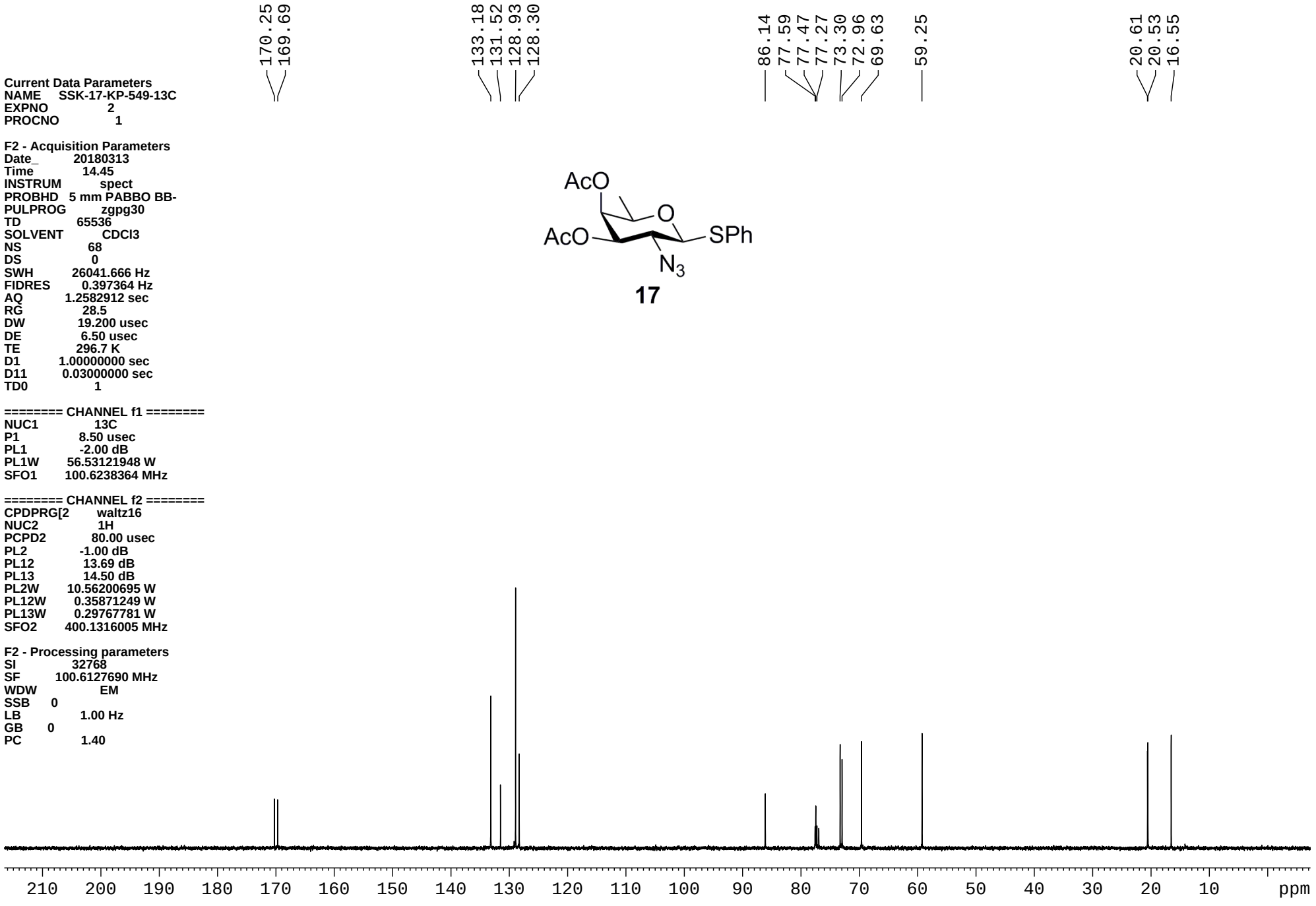
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

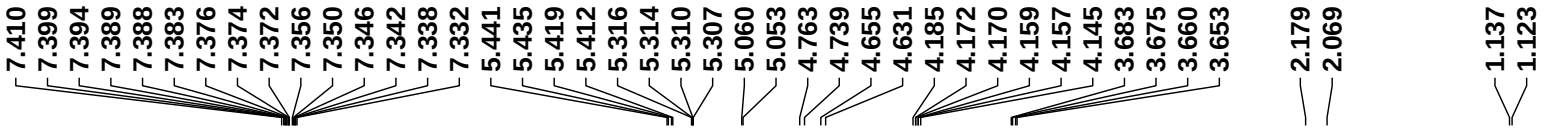
F2 - Processing parameters
SI 32768
SF 400.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



17




170.25
169.69
133.18
131.52
128.93
128.30
86.14
77.59
77.47
77.27
73.30
72.96
69.63
59.25
20.61
20.53
16.55
AcO
AcO
O
SPh
N3
17
Current Data Parameters
NAME SSK-17-KP-549-13C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180313
Time 14.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 68
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 28.5
DW 19.200 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

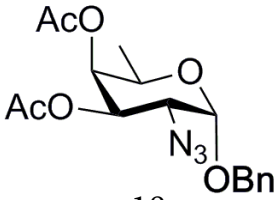


Current Data Parameters
NAME SSK-17-KP-552-1H
EXPNO 2
PROCNO 1

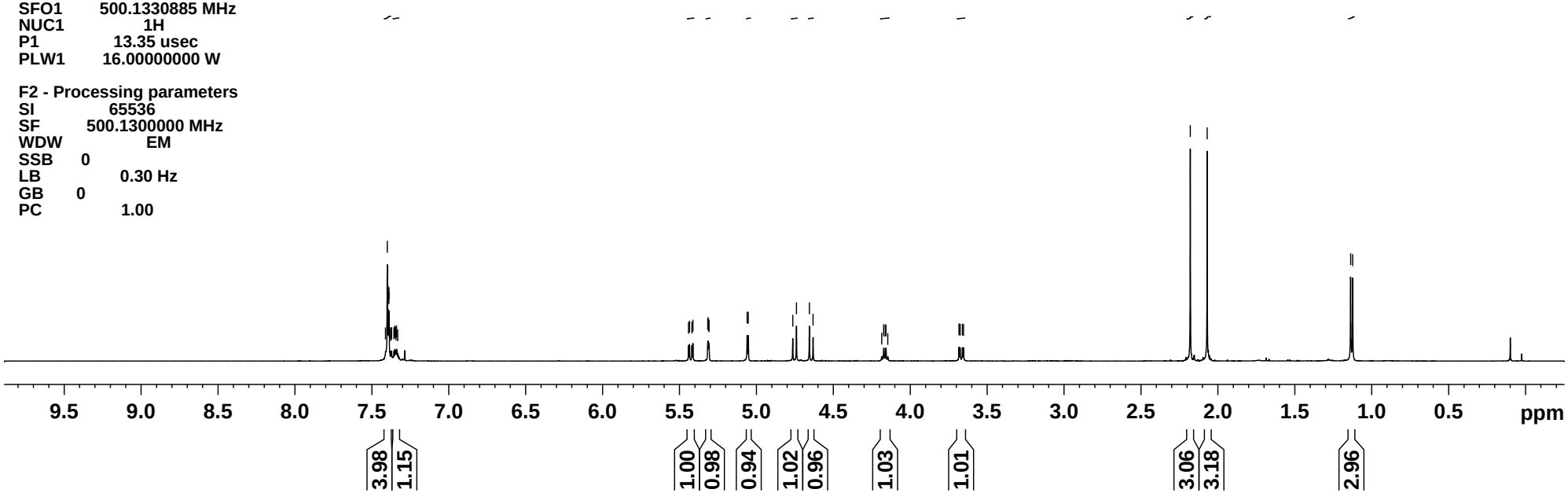
F2 - Acquisition Parameters
Date_ 20180313
Time 16.13
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

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



18



SSK-17-KP-552-13C

Current Data Parameters
NAME SSK-17-KP-552-13C
EXPNO 3
PROCNO 1

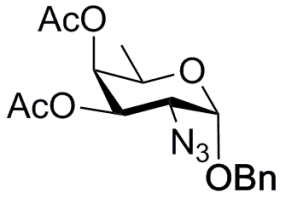
F2 - Acquisition Parameters
Date_ 20180313
Time 16.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 30
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

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

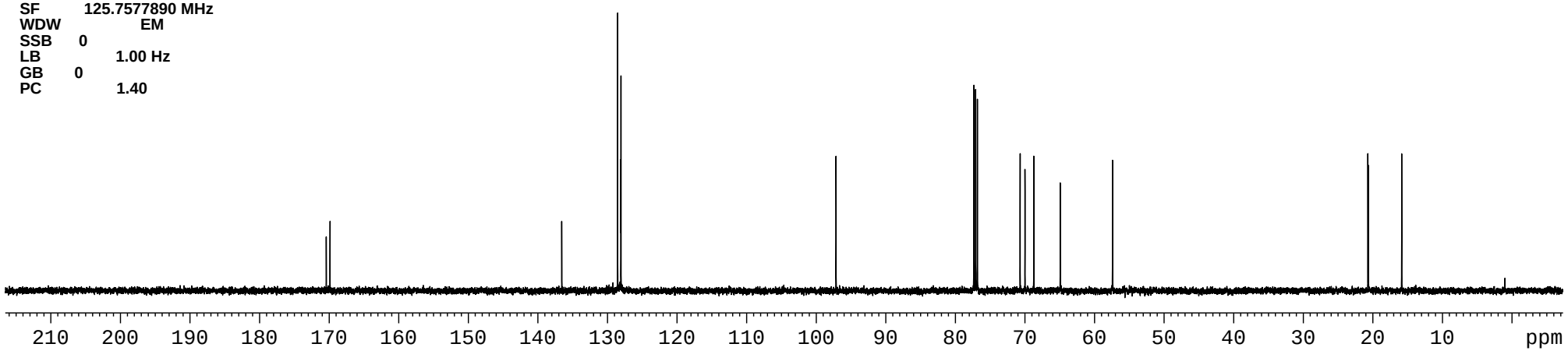
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

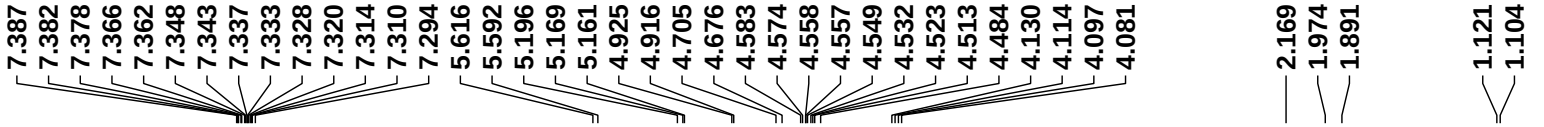
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

170.41
169.87
136.58
128.55
128.07
97.16
70.70
70.01
68.74
64.94
57.43
20.72
20.64
15.86



18



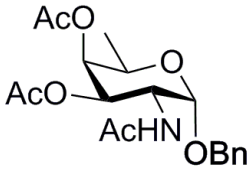


Current Data Parameters
NAME SSK-17-KP-FUCOSENHAC-OBn-1H
EXPNO 3
PROCNO 1

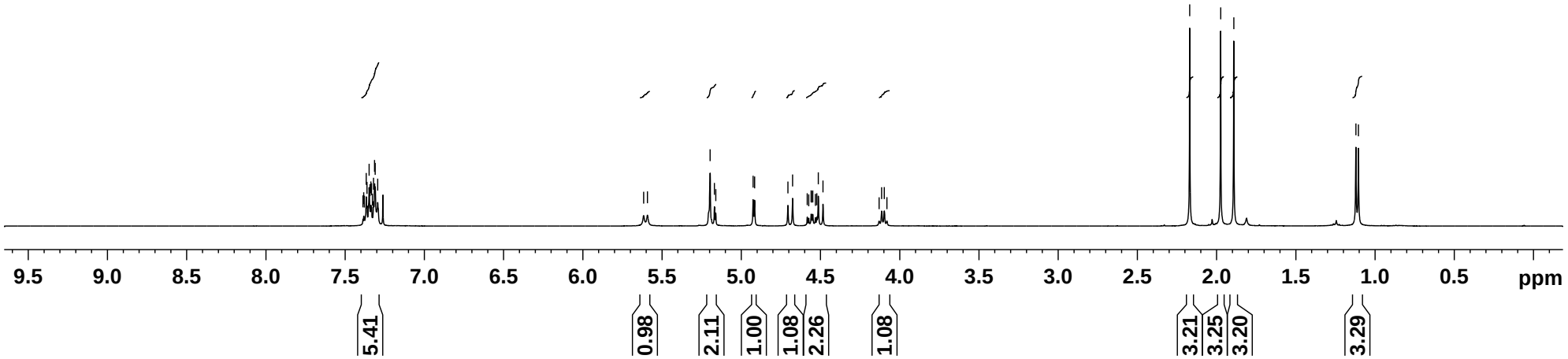
F2 - Acquisition Parameters
Date_ 20190227
Time 16.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1

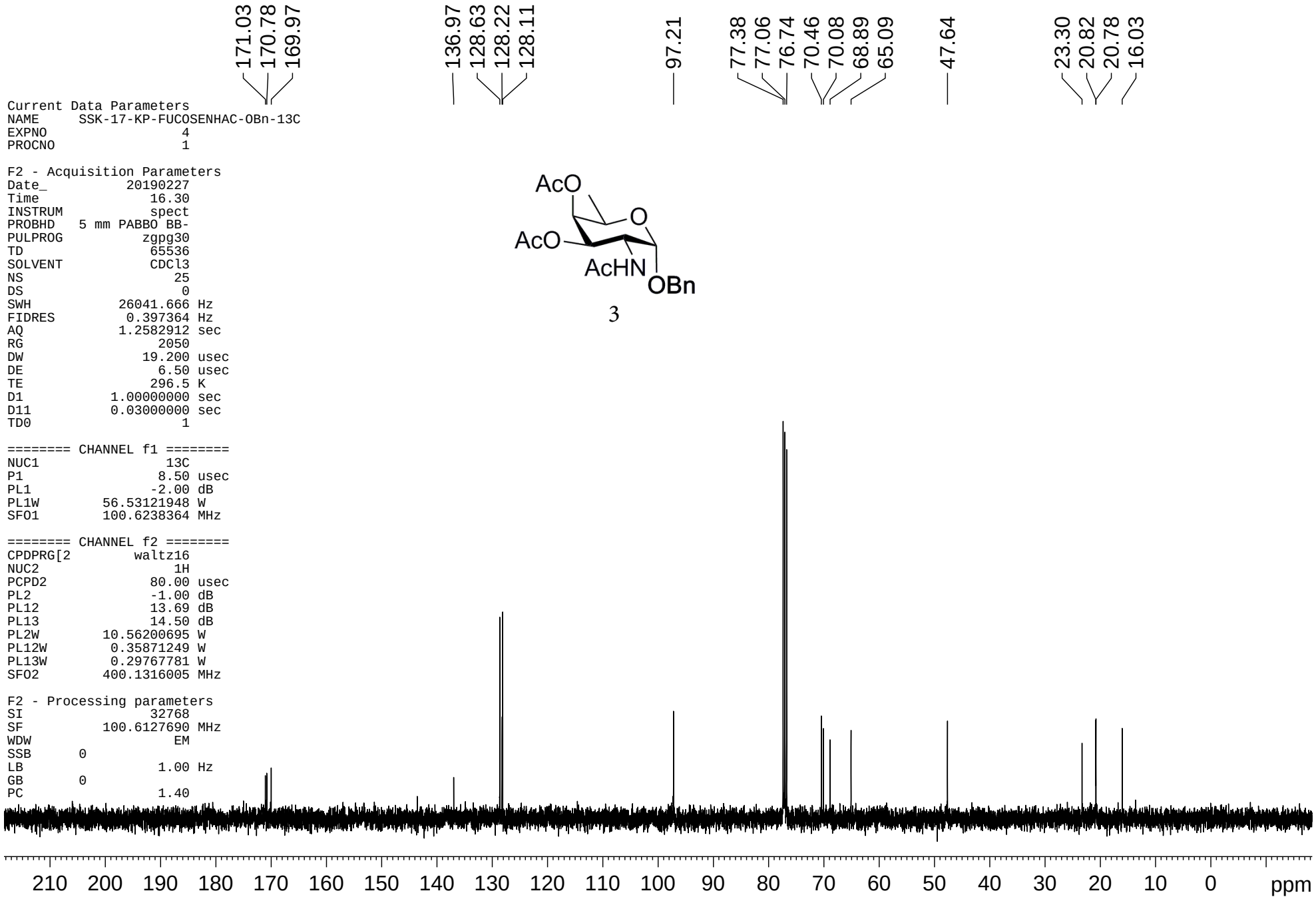
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

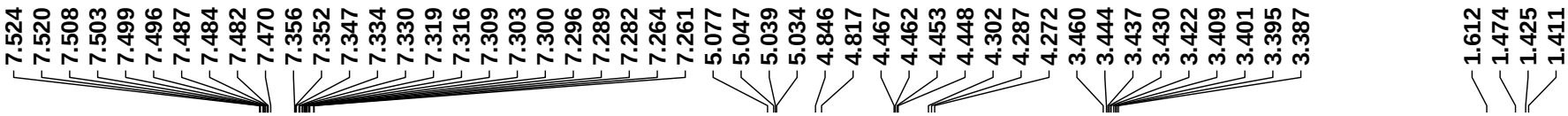
F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



3



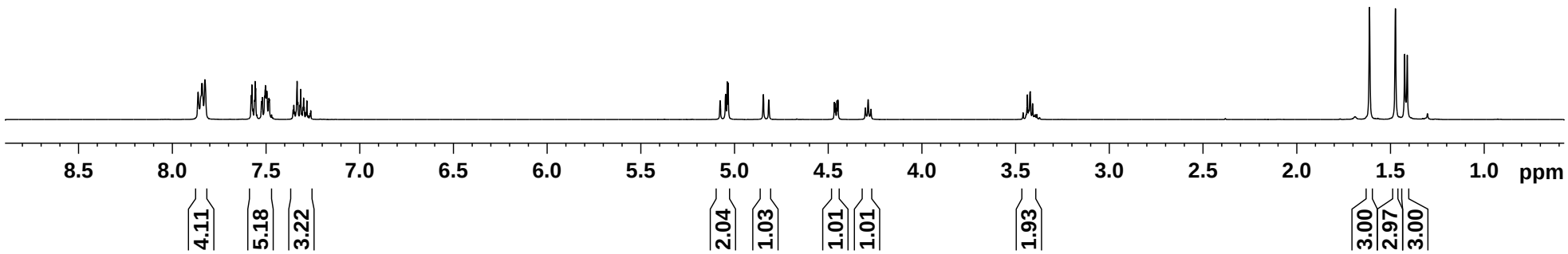

171.03
170.78
169.97
136.97
128.63
128.22
128.11
97.21
77.38
77.06
76.74
70.46
70.08
68.89
65.09
47.64
23.30
20.82
20.78
16.03
Current Data Parameters
NAME SSK-17-KP-FUCOSENHAC-OBn-13C
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190227
Time 16.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 25
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcO
O
AcO
AcHN
OBn
3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



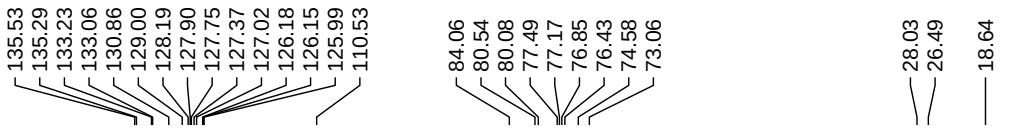
SSK-23-AP-149-1H

```
Current Data Parameters
NAME    SSK-23-AP-149-1H
EXPNO              5
PROCNO             1

F2 - Acquisition Parameters
Date_         20180627
Time              5.19
INSTRUM          spect
PROBHD  5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT          CDCl3
NS                13
DS                 0
SWH          8223.685 Hz
FIDRES        0.151522 Hz
AQ           3.2998593 sec
RG                32
DW              60.800 usec
DE               6.50 usec
TE              296.3 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

F2 - Processing parameters
SI              32768
SF          400.1300095 MHz
WDW                EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

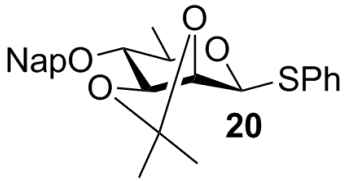
20



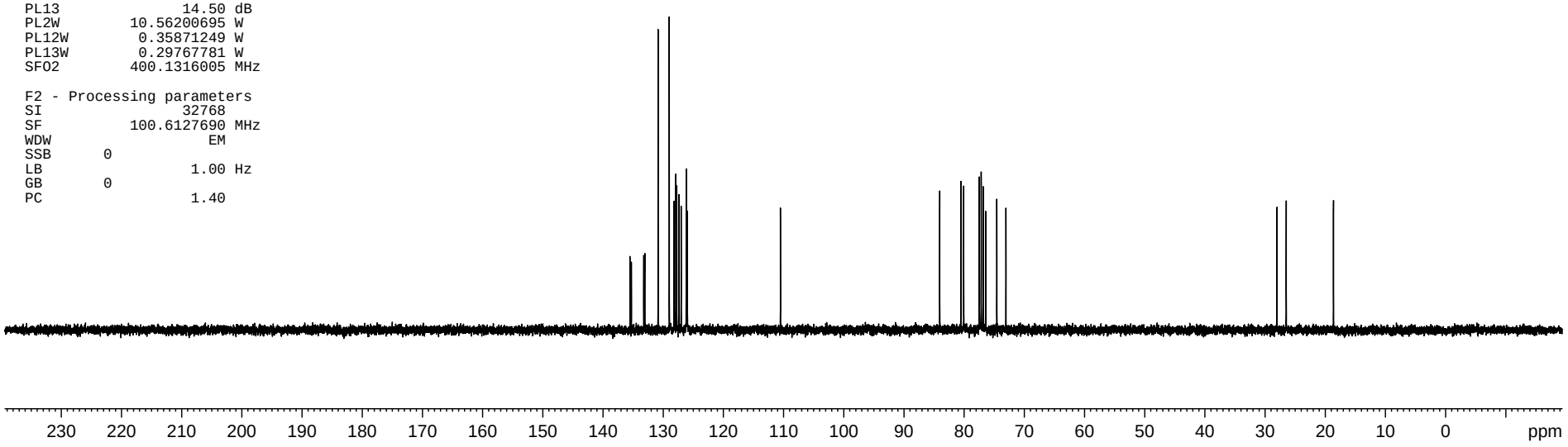
SSK-23-AP-149-13C

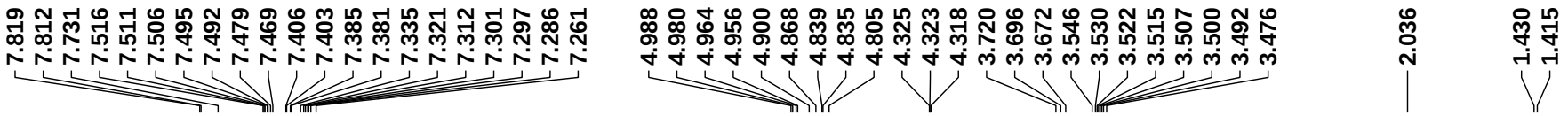



```
Current Data Parameters
NAME     SSK-23-AP-149-13C
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_          20180627
Time               5.20
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   23
DS                    0
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ            1.2582912 sec
RG                  724
DW               19.200 usec
DE                6.50 usec
TE               296.4 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W        56.53121948 W
SFO1       100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W        10.56200695 W
PL12W        0.35871249 W
PL13W        0.29767781 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



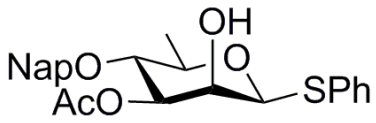
20



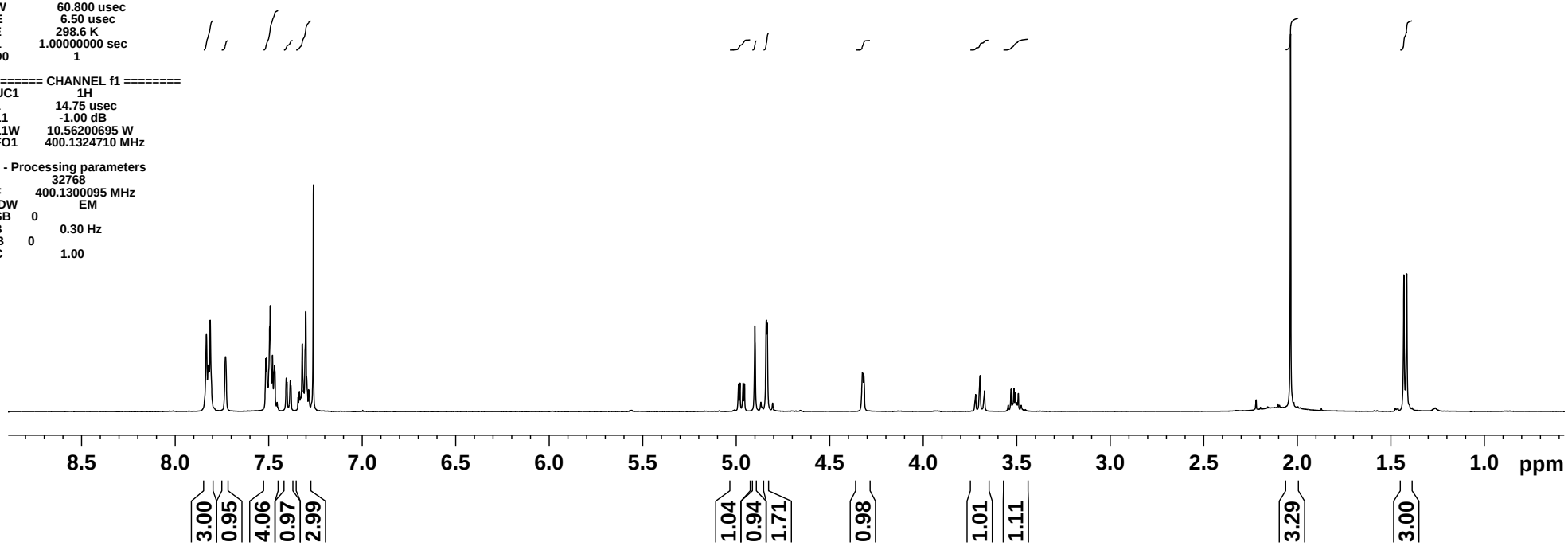


SSK-23-AP-137-1H

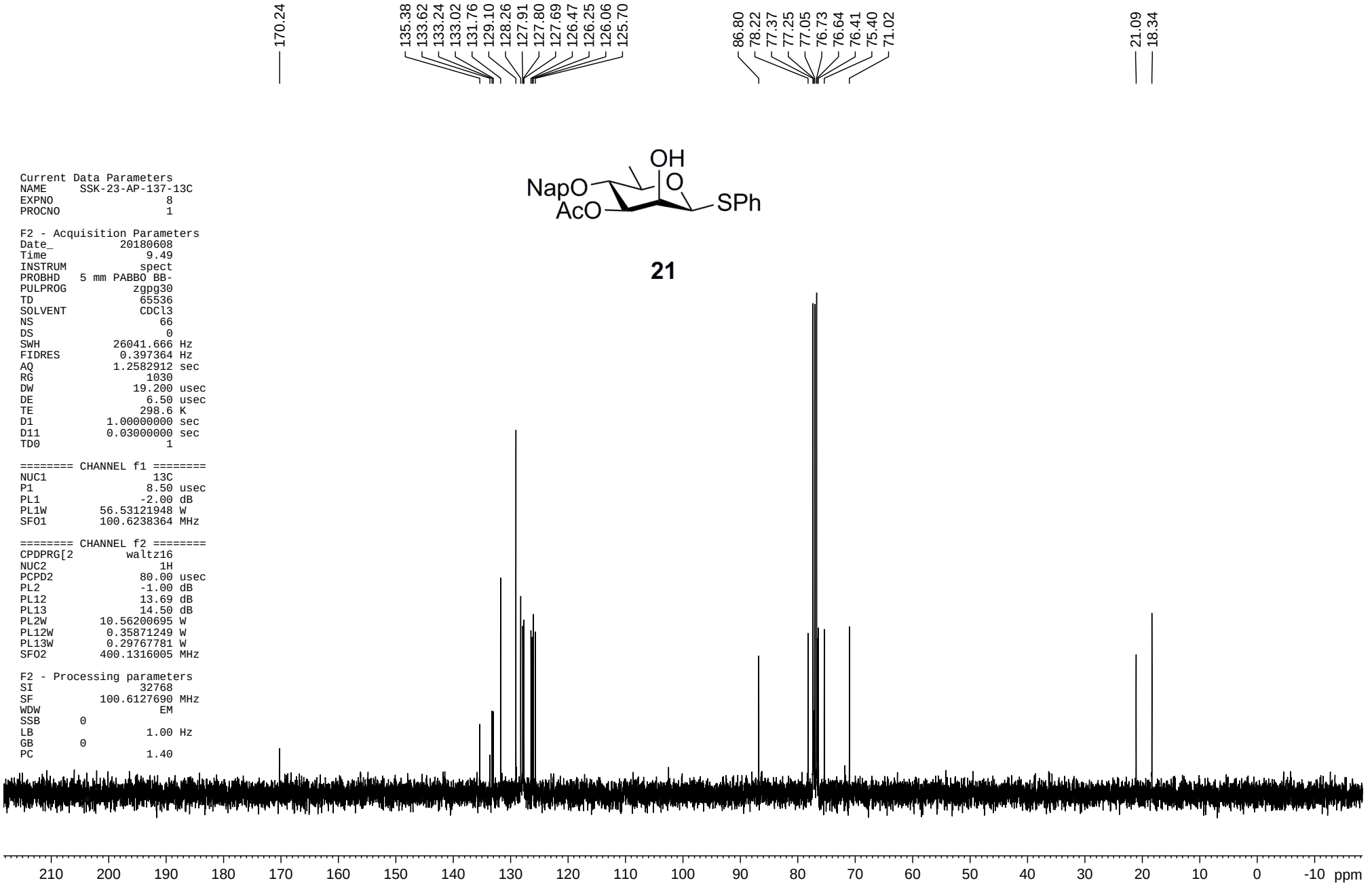
```
Current Data Parameters
NAME    SSK-23-AP-137-1H
EXPNO              7
PROCNO             1

F2 - Acquisition Parameters
Date_         20180608
Time              9.46
INSTRUM           spect
PROBHD  5 mm PABBO BB-
PULPROG           zg30
TD               54274
SOLVENT           CDCl3
NS                  28
DS                   0
SWH           8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                 114
DW                60.800 usec
DE                 6.50 usec
TE                298.6 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

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                EM
SSB     0
LB                 0.30 Hz
GB      0
PC                 1.00
```

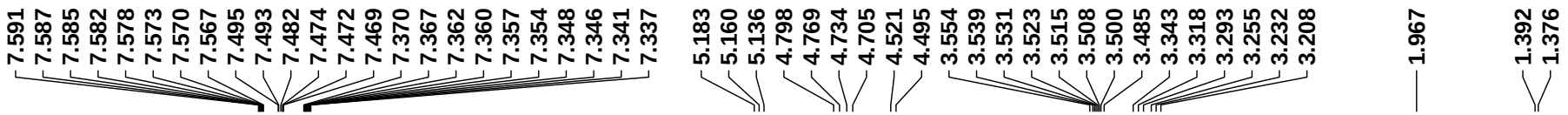


21



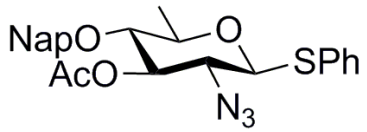
SSK-23-AP-137-13C



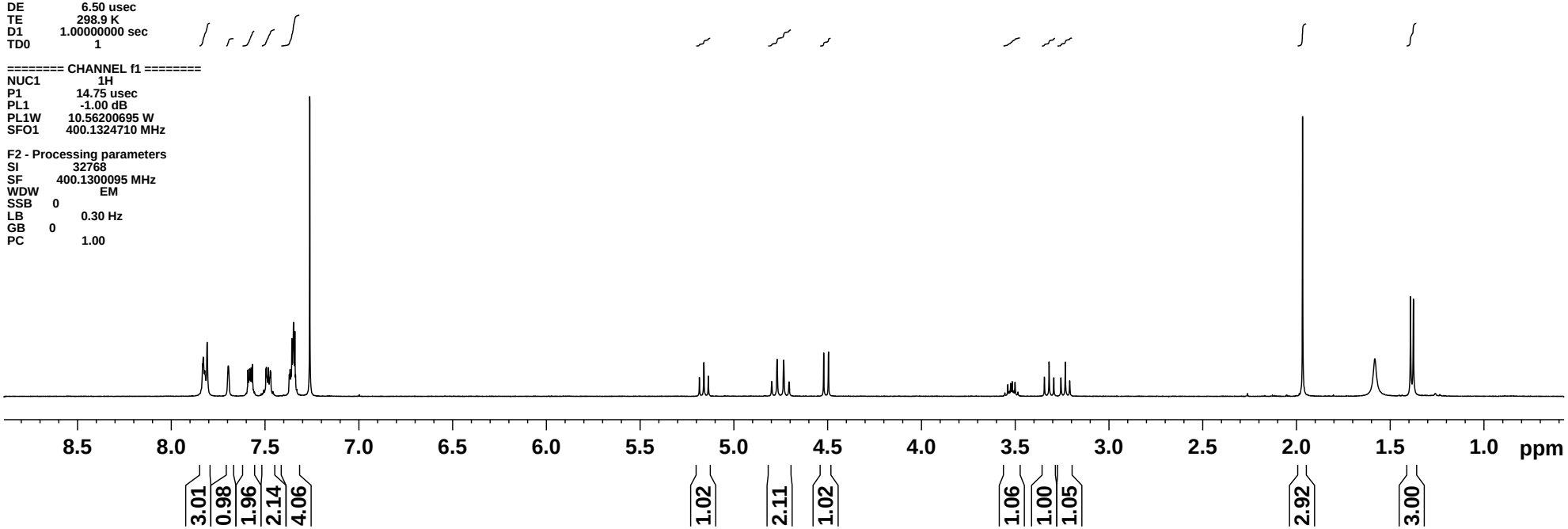


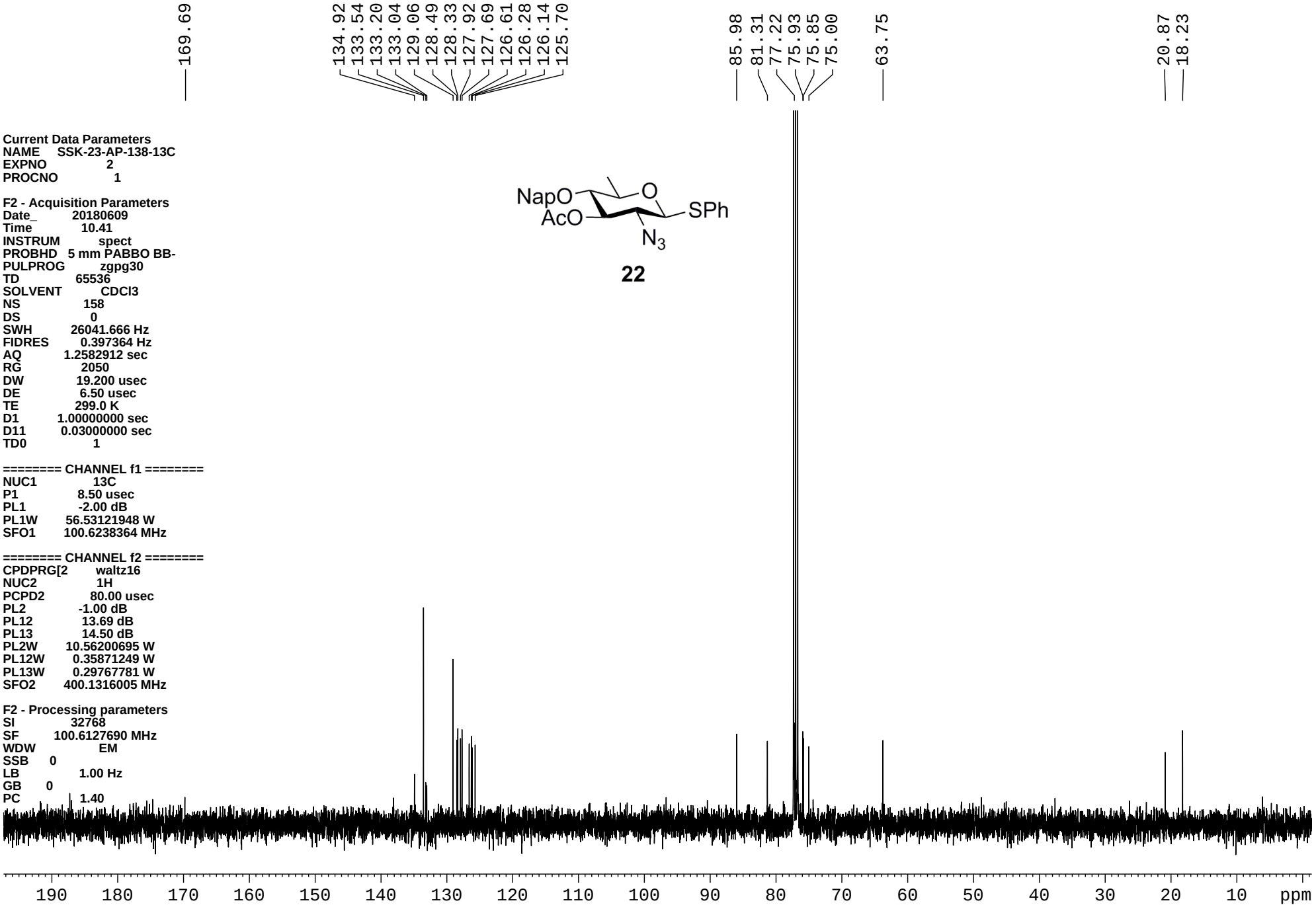
SSK-23-AP-138-1H

```
Current Data Parameters
NAME    SSK-23-AP-138-1H
EXPNO             1
PROCNO            1

F2 - Acquisition Parameters
Date_         20180609
Time            10.40
INSTRUM          spect
PROBHD  5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT          CDCl3
NS                 8
DS                 0
SWH           8223.685 Hz
FIDRES         0.151522 Hz
AQ           3.2998593 sec
RG               181
DW             60.800 usec
DE              6.50 usec
TE             298.9 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

F2 - Processing parameters
SI              32768
SF          400.1300095 MHz
WDW                EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```



22




169.69
134.92
133.54
133.20
133.04
129.06
128.49
128.33
127.92
127.69
126.61
126.28
126.14
125.70
85.98
81.31
77.22
75.93
75.85
75.00
63.75
20.87
18.23
NapO
AcO
O
SPh
N3
22
Current Data Parameters
NAME SSK-23-AP-138-13C
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180609
Time 10.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 158
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 299.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

SSK-23-AP-139-1H

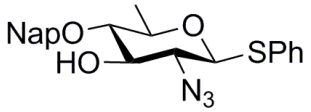
7.860 7.849 7.839 7.828 7.781 7.598 7.594 7.588 7.580 7.576 7.508 7.496 7.484 7.468 7.447 7.444 7.347 7.338 7.333 4.947 4.919 4.903 4.874 4.454 4.429 3.616 3.593 3.570 3.456 3.441 3.432 3.425 3.417 3.410 3.402 3.387 3.319 3.295 3.270 3.153 3.130 3.107 1.411 1.396

Current Data Parameters
NAME SSK-23-AP-139-1H
EXPNO 7
PROCNO 1

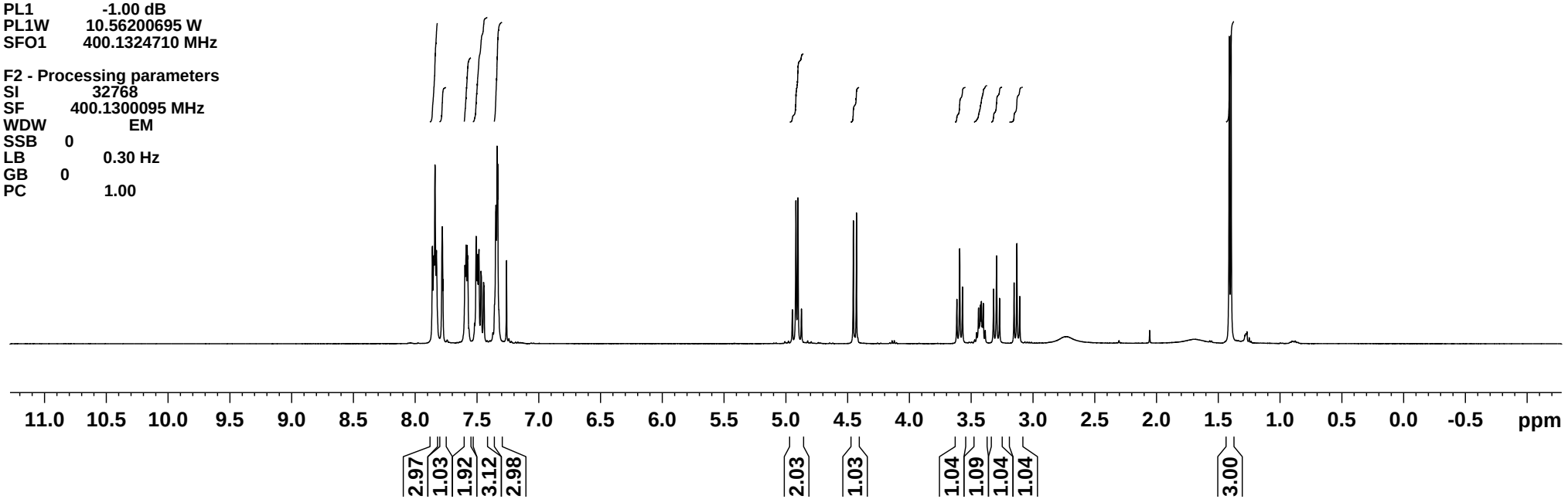
F2 - Acquisition Parameters
Date_ 20180610
Time 5.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 14
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



23



SSK-23-AP-139-13C

135.31
133.28
133.24
133.11
131.65
129.05
128.53
128.32
127.97
127.77
126.85
126.35
126.20
125.81

86.07
82.92
77.40
77.26
77.08
76.76
75.68
75.31
65.50

18.36

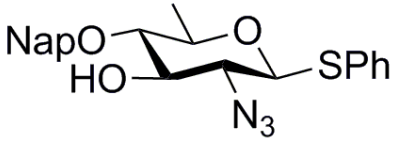
Current Data Parameters
NAME SSK-23-AP-139-13C
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180610
Time 5.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 28
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 28.5
DW 19.200 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

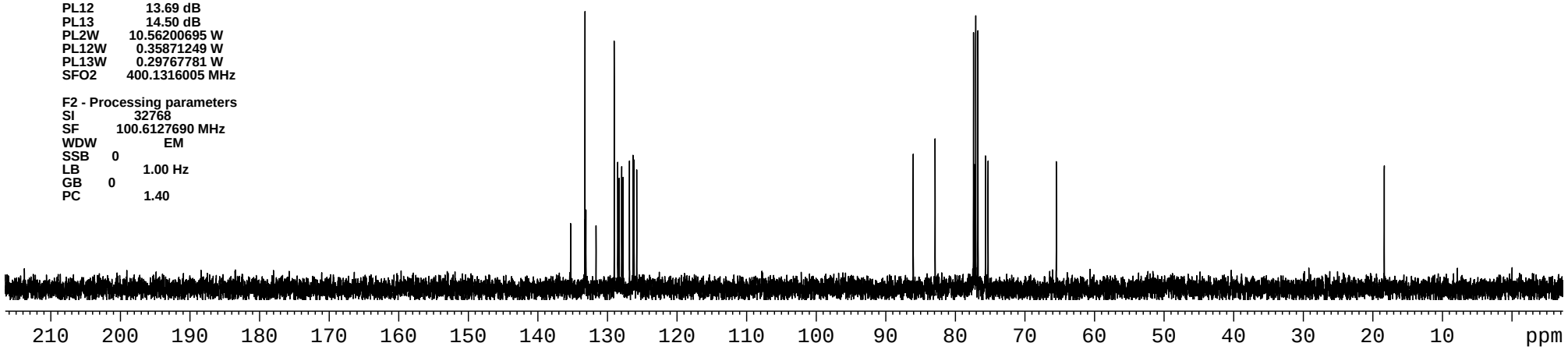
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



23



SSK-23-AP-141-1H

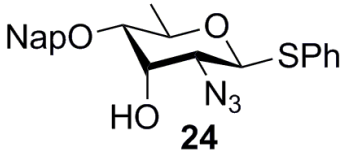
7.865 7.854 7.846 7.831 7.752 7.612 7.604 7.601 7.593 7.588 7.529 7.524 7.519 7.516 7.511 7.506 7.464 7.461 7.443 7.440 7.342 7.332 7.327 7.319 7.314 7.305 5.089 5.063 4.799 4.770 4.696 4.666 4.402 4.396 4.389 3.926 3.911 3.902 3.895 3.887 3.880 3.872 3.856 3.145 3.139 3.132 3.120 3.114 3.109 1.347 1.331

Current Data Parameters
NAME SSK-23-AP-141-1H
EXPNO 5
PROCNO 1

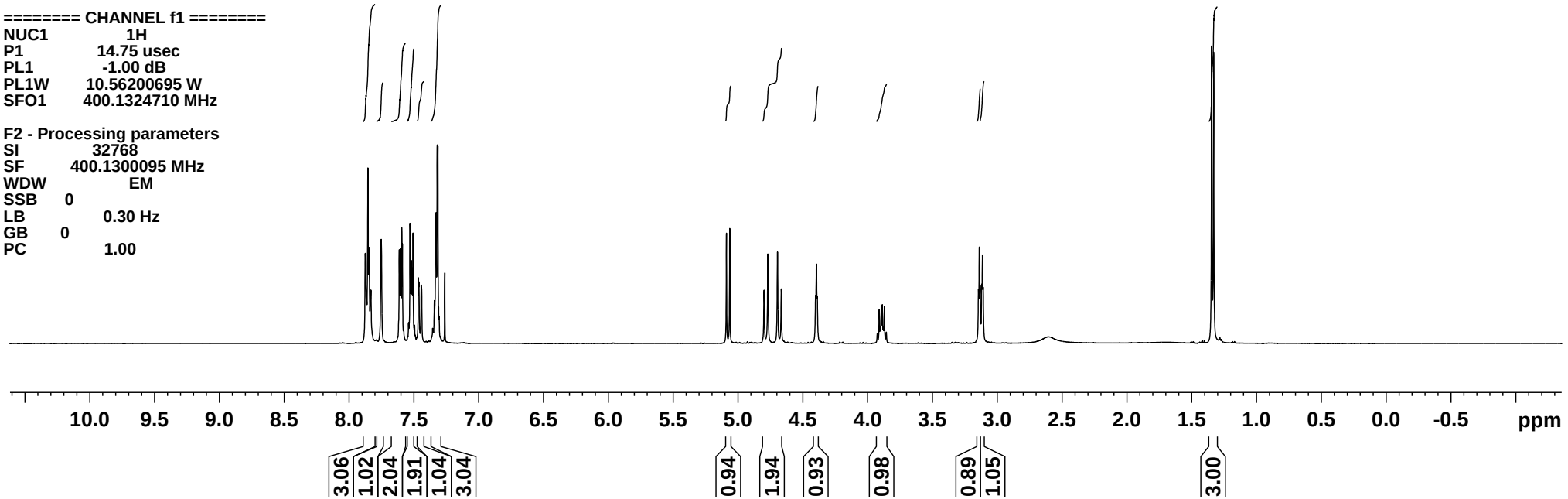
F2 - Acquisition Parameters
Date_ 20180612
Time 5.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



24



SSK-23-AP-141-13C

Current Data Parameters
NAME SSK-23-AP-141-13C
EXPNO 6
PROCNO 1

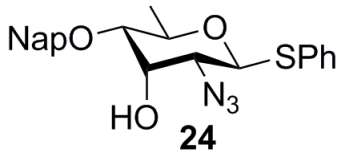
F2 - Acquisition Parameters
Date_ 20180612
Time 5.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 15
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

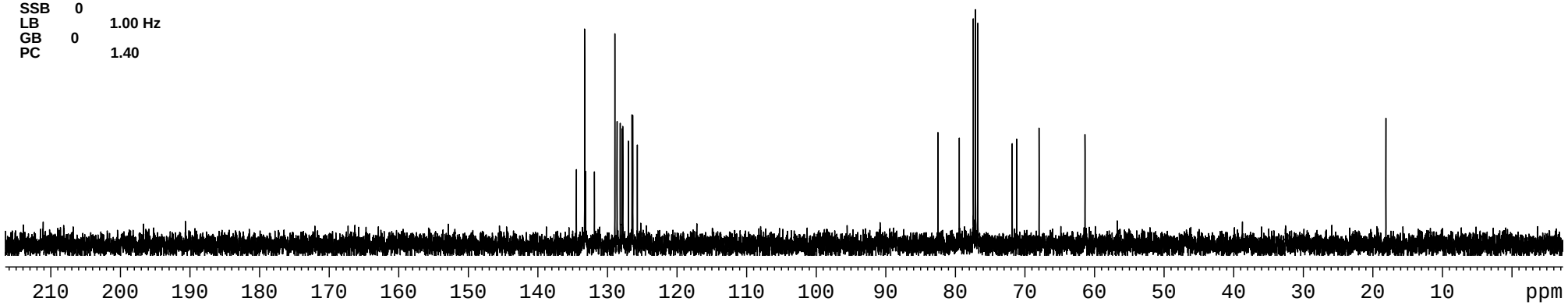
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

134.47
133.30
133.19
133.16
131.88
128.95
128.63
128.18
127.93
127.81
127.01
126.49
126.38
125.72
82.51
79.45
71.84
71.19
67.98
61.38
18.12

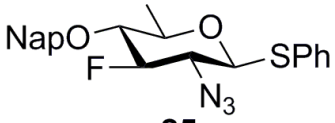


24



SSK-23-AP-143-1H

7.861 7.843 7.837 7.783 7.603 7.595 7.592 7.589 7.586 7.582 7.579 7.513 7.501 7.489 7.480 7.476 7.458 7.455 7.367 7.359 7.351 5.039 5.011 4.801 4.773 4.644 4.623 4.601 4.516 4.494 4.472 4.413 4.388 3.512 3.489 3.487 3.479 3.463 3.456 3.454 3.431 3.420 3.412 3.409 3.396 3.381 3.341 3.320 3.311 3.297 3.290 3.267 1.392 1.377



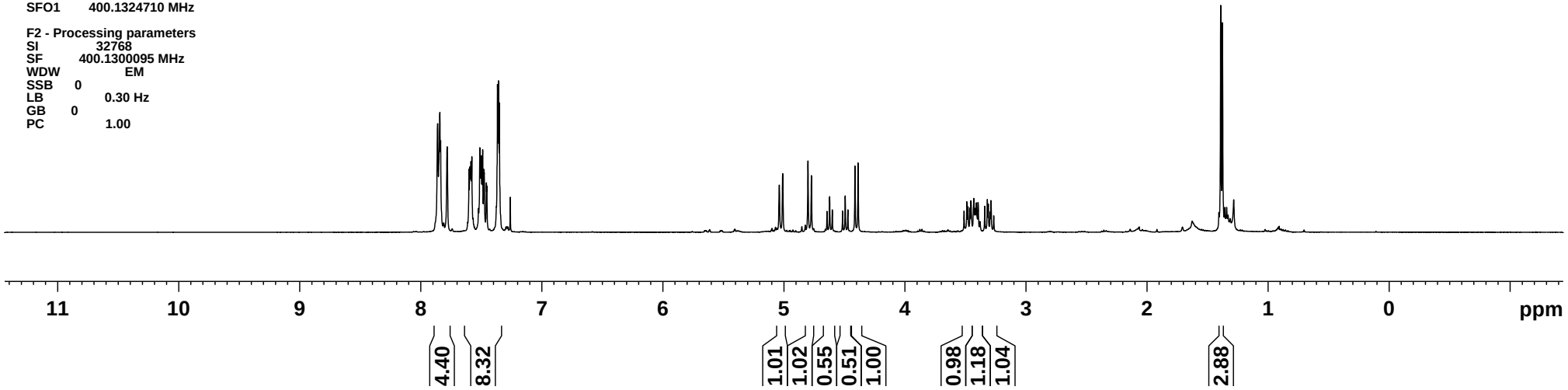
25

Current Data Parameters
NAME SSK-23-AP-143-1H
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180613
Time 5.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 20
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 297.4 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

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



SSK-23-AP-143-13C

Current Data Parameters
NAME SSK-23-AP-143-13C
EXPNO 6
PROCNO 1

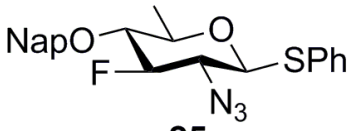
F2 - Acquisition Parameters
Date_ 20180613
Time 5.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 50
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 2050
DW 19.200 usec
DE 6.50 usec
TE 297.5 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

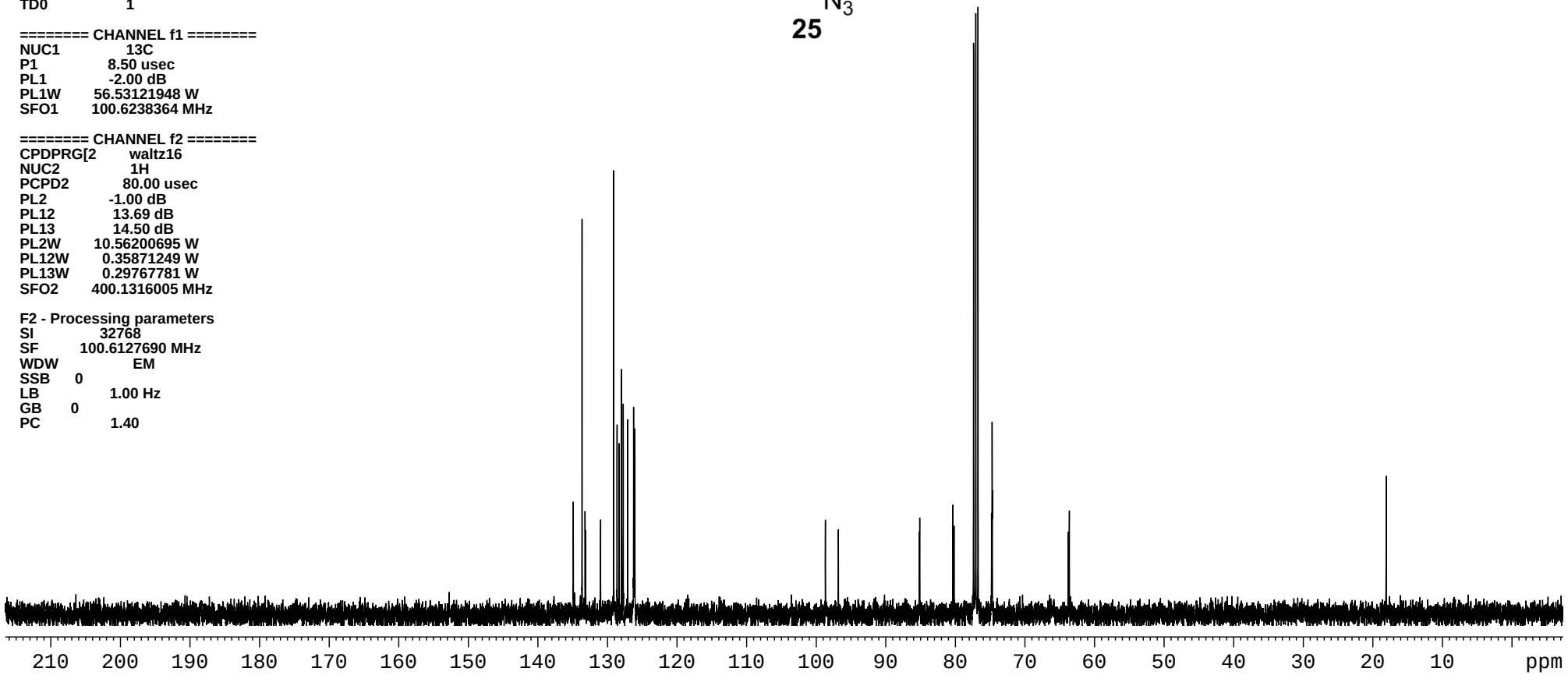
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

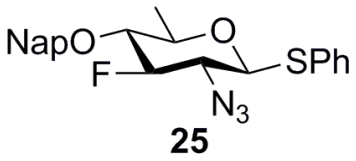
134.92
133.67
133.23
133.14
131.00
129.12
128.63
128.33
127.98
127.74
127.11
126.25
126.15
126.07
98.69
96.82
85.21
85.13
80.35
80.20
77.39
77.08
76.76
74.81
74.72
63.81
63.63
18.09



25



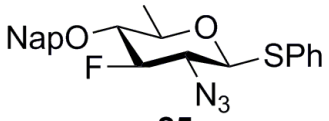
SSK-23-AP-25-F-19F



25

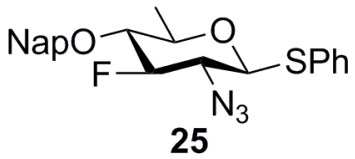
```
Current Data Parameters
NAME     SSK-23-AP-25-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time              22.33
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                   11
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

SSK-23-AP-143-HHCOSY

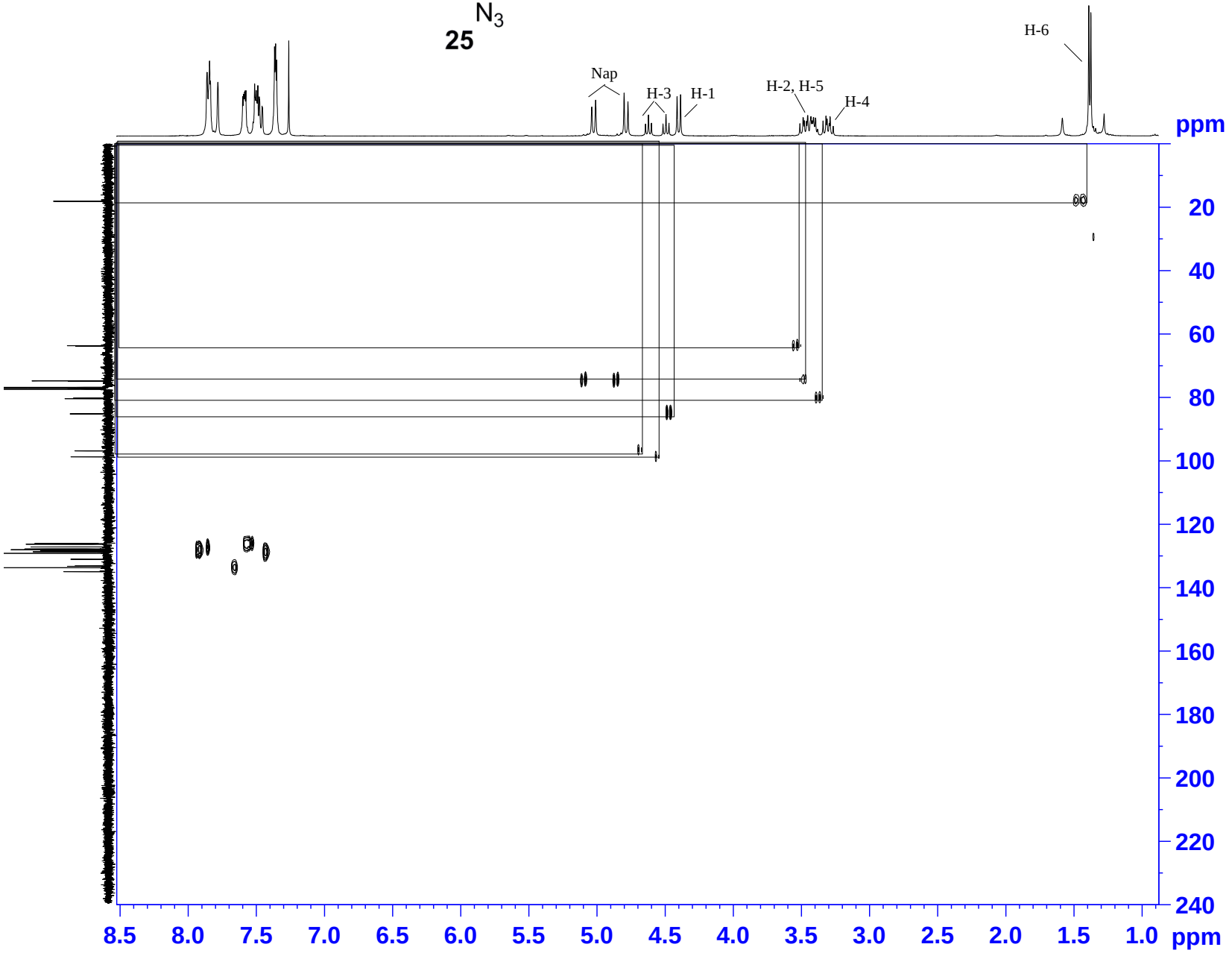


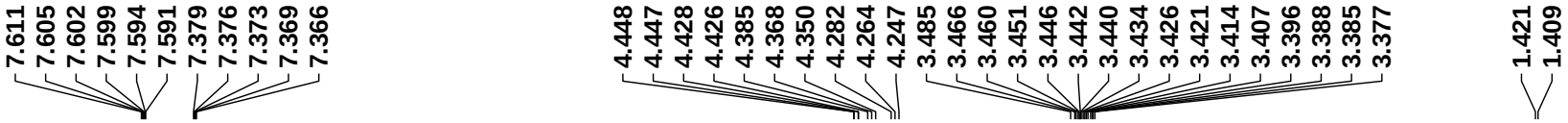
25

SSK-23-AP-150'-HSQC

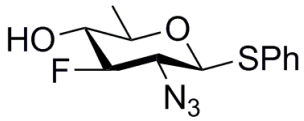


25





SSK-23-AP-152-1H



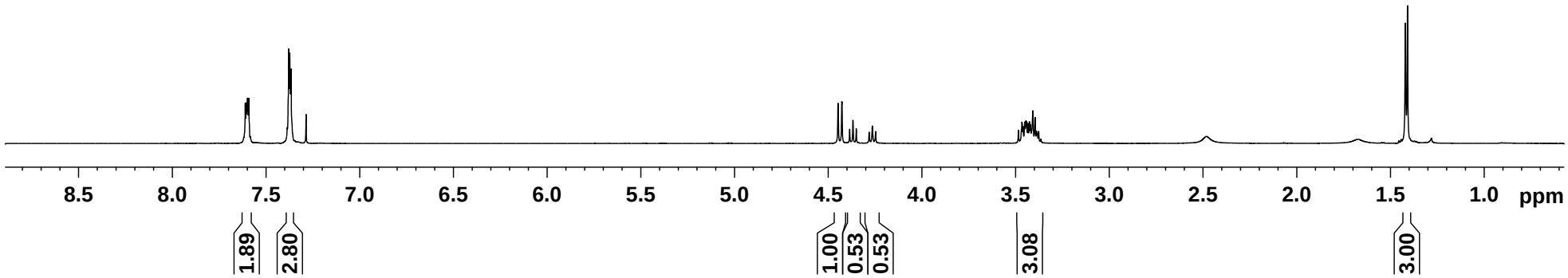
26

Current Data Parameters
NAME SSK-23-AP-152-1H
EXPNO 5
PROCNO 1

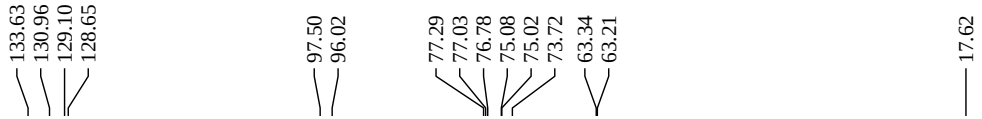
F2 - Acquisition Parameters
Date_ 20180628
Time 17.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 98.91
DW 50.000 usec
DE 6.50 usec
TE 300.6 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

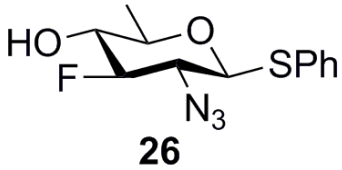
F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



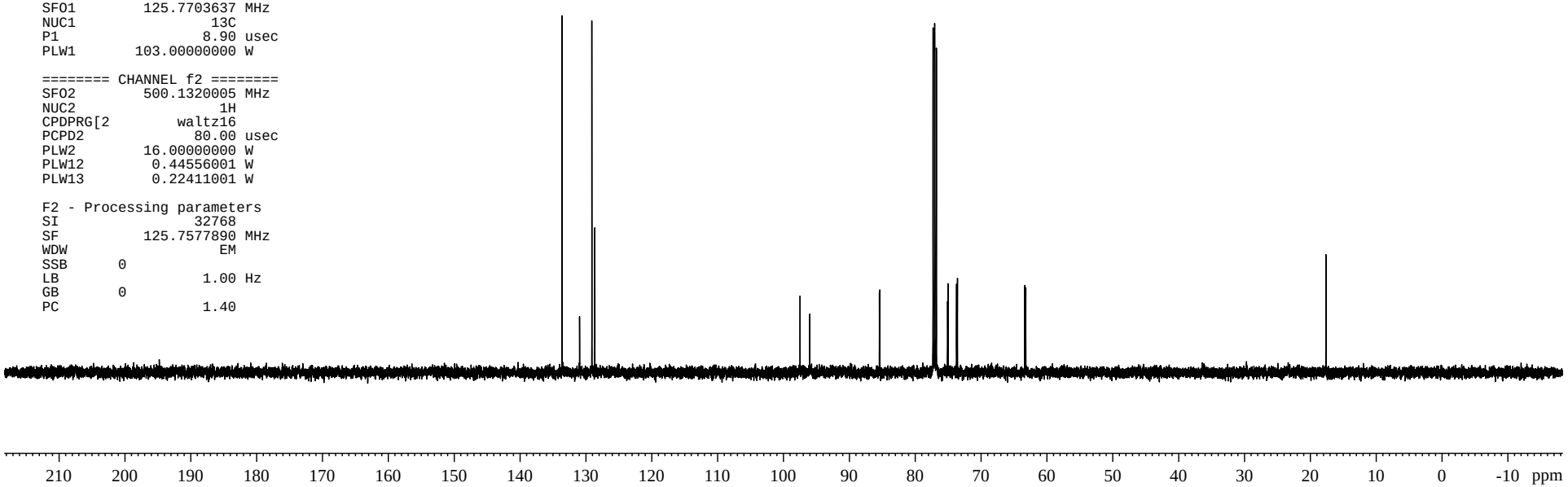
SSK-23-AP-152-13C




```
Current Data Parameters
NAME     SSK-23-AP-152-13C
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180628
Time              17.20
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   50
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               300.6 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        16.00000000 W
PLW12        0.44556001 W
PLW13        0.22411001 W

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



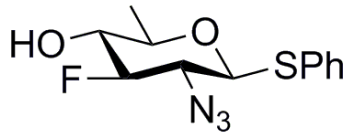
26



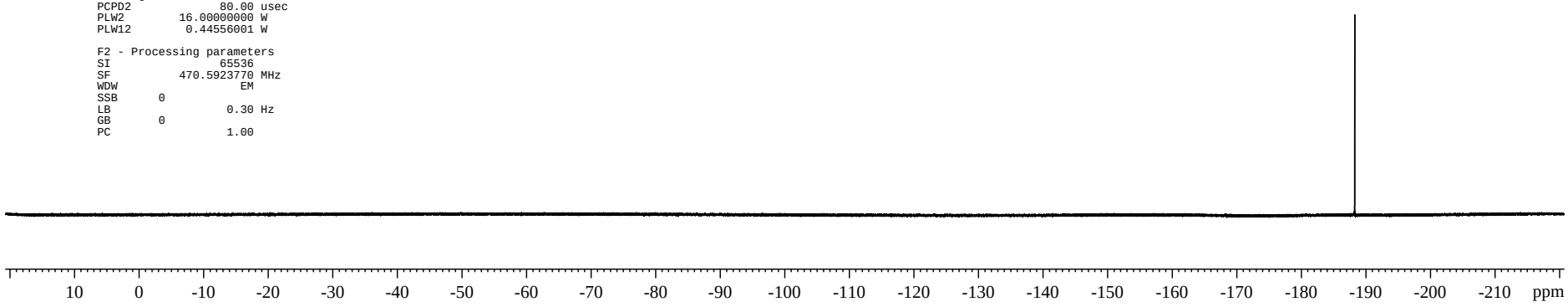
SSK-23-AP-26-F-19F

-188.26

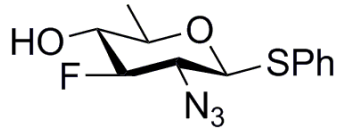
```
Current Data Parameters
NAME     SSK-23-AP-26-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time              22.26
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                   17
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



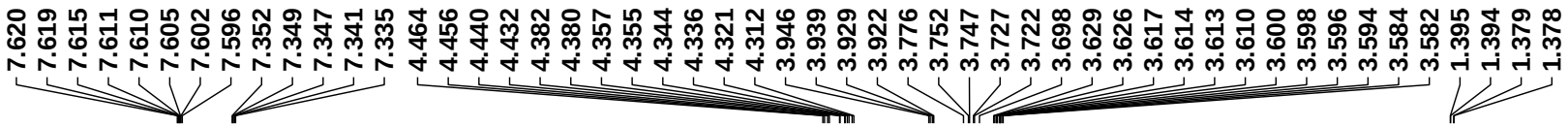
26



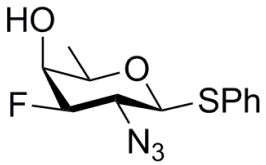
SSK-23-AP-152-HHCOSY



26



SSK-23-AP-166-1H



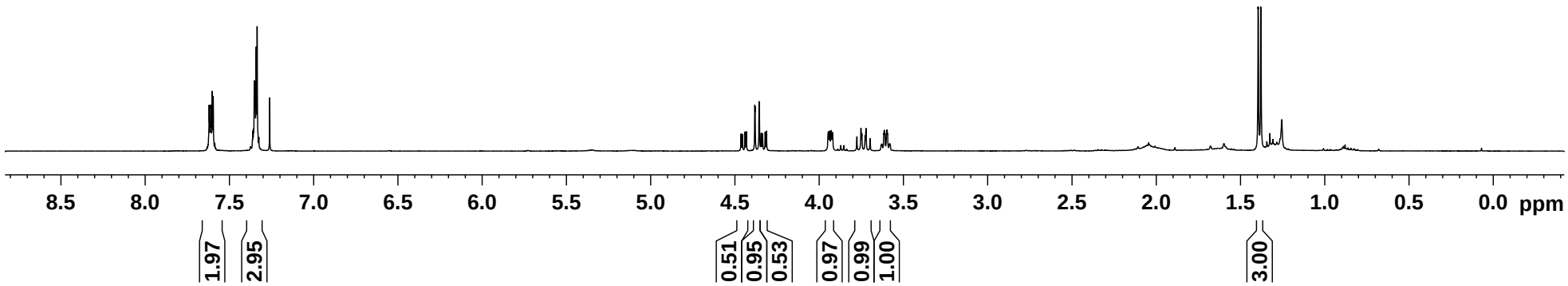
27

Current Data Parameters
NAME SSK-23-AP-166-1H
EXPNO 5
PROCNO 1

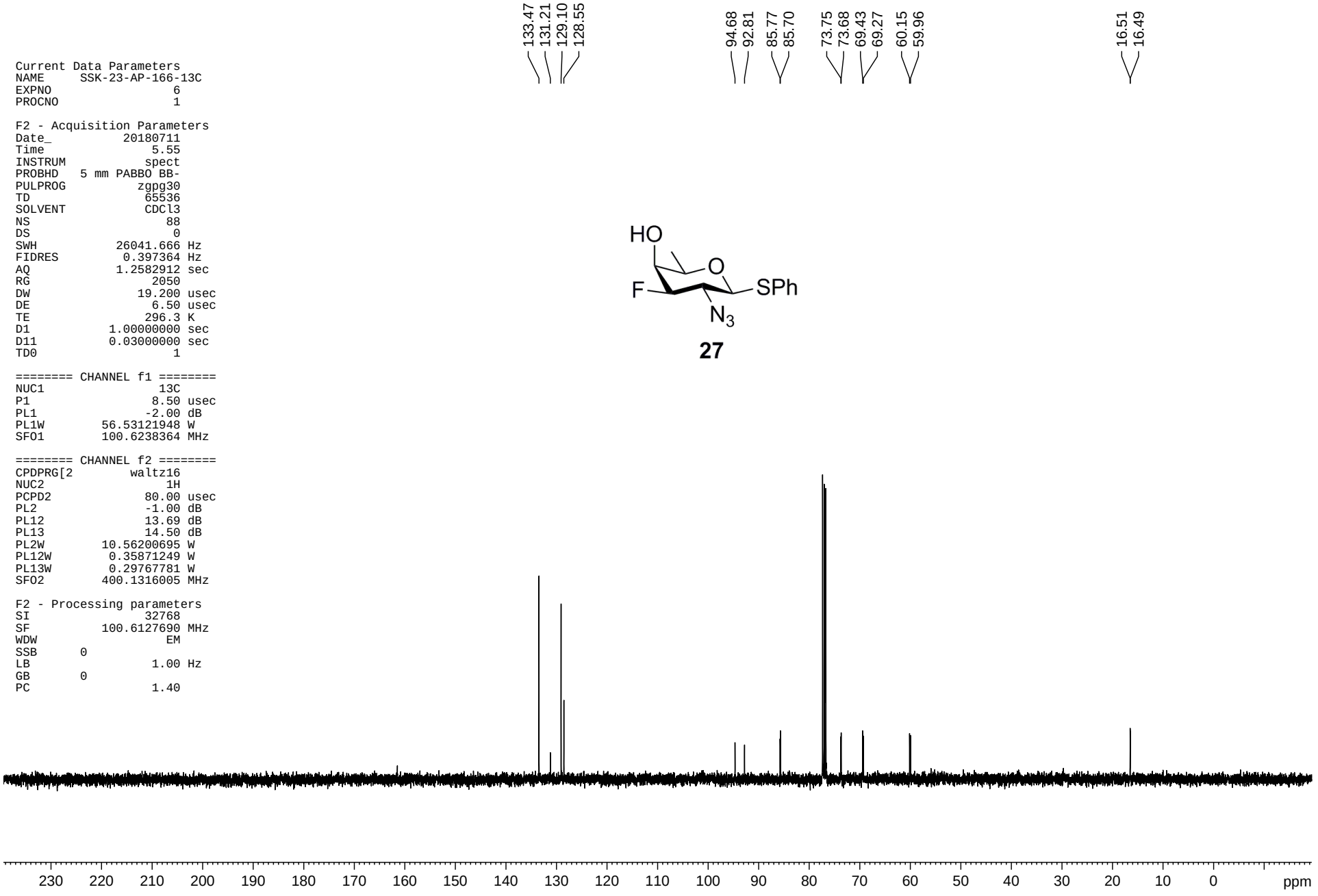
F2 - Acquisition Parameters
Date_ 20180711
Time 5.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 30
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

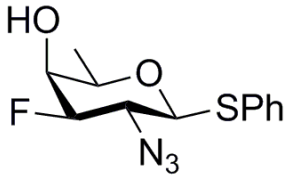


SSK-23-AP-166-13C



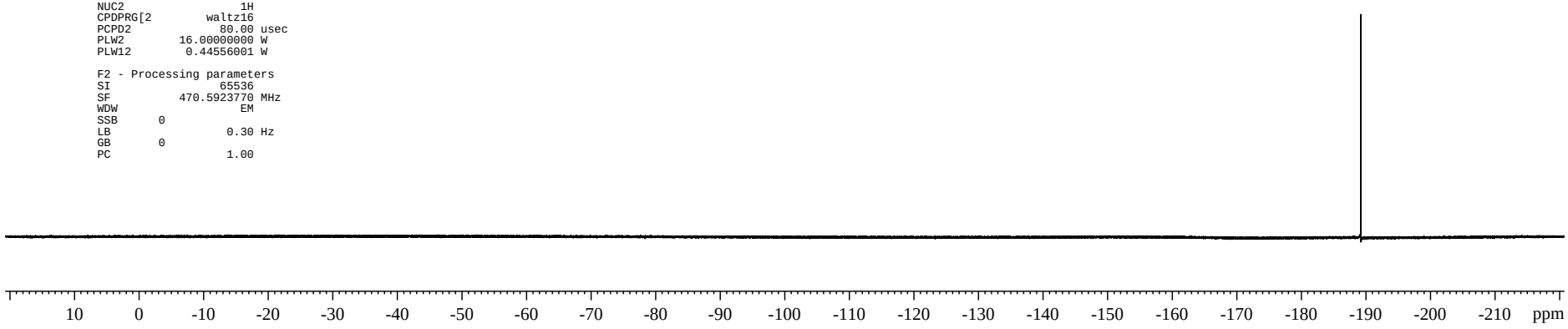

```
Current Data Parameters
NAME      SSK-23-AP-166-13C
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180711
Time                5.55
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    88
DS                     0
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                  2050
DW                19.200 usec
DE                 6.50 usec
TE                296.3 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.50 usec
PL1                 -2.00 dB
PL1W        56.53121948 W
SFO1        100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                13.69 dB
PL13                14.50 dB
PL2W        10.56200695 W
PL12W        0.35871249 W
PL13W        0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF          100.6127690 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

SSK-23-AP-27-F-19F

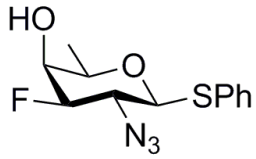


27

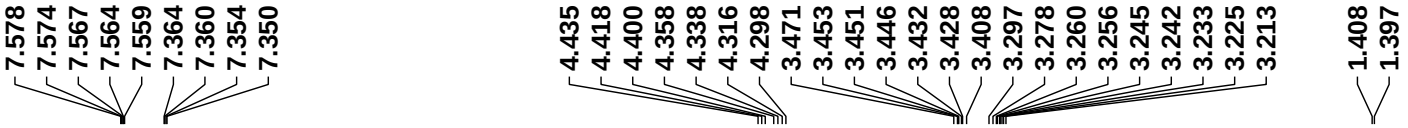
```
Current Data Parameters
NAME     SSK-23-AP-27-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time              22.29
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                   12
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



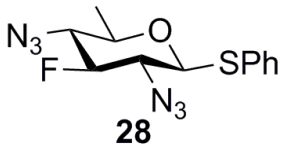
SSK-23-AP-166-HHCOSY



27

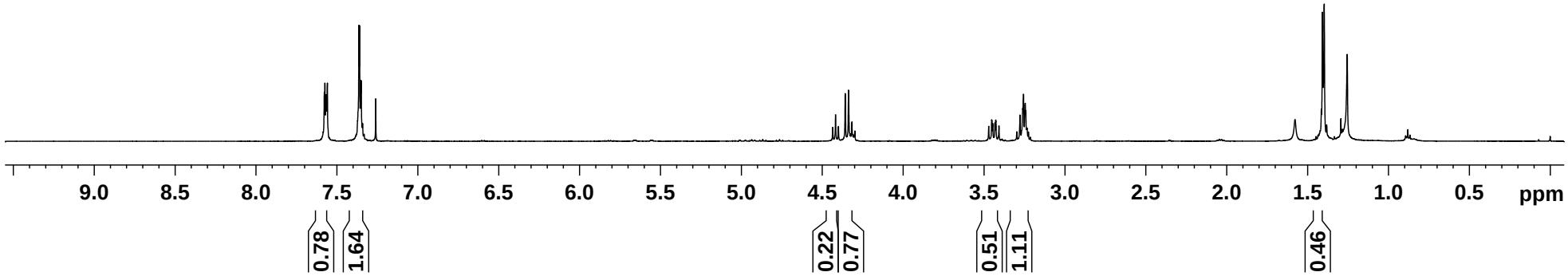


SSK-23-AP-112-1H



28

```
Current Data Parameters
NAME     SSK-23-AP-112-1H
EXPNO              10
PROCNO              1

F2 - Acquisition Parameters
Date_          20180429
Time             18.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD               65536
SOLVENT            CDCl3
NS                 54
DS                  0
SWH          10000.000 Hz
FIDRES         0.152588 Hz
AQ           3.2767999 sec
RG               85.91
DW               50.000 usec
DE                6.50 usec
TE               297.4 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                1H
P1               13.35 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI               65536
SF          500.1300128 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```



SSK-23-AP-112-13C

Current Data Parameters
NAME SSK-23-AP-112-13C
EXPNO 11
PROCNO 1

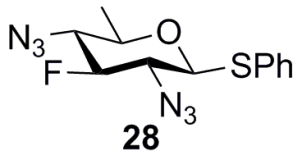
F2 - Acquisition Parameters
Date_ 20180429
Time 18.45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 57
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

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

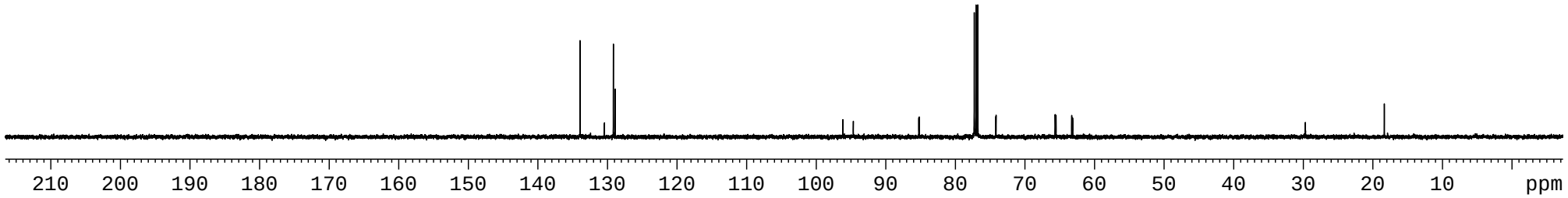
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

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

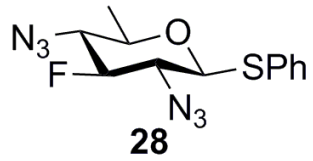
133.95, 130.45, 129.17, 128.89, 96.18, 94.68, 85.26, 85.21, 74.21, 74.16, 65.67, 65.54, 63.29, 63.15, 18.35



28

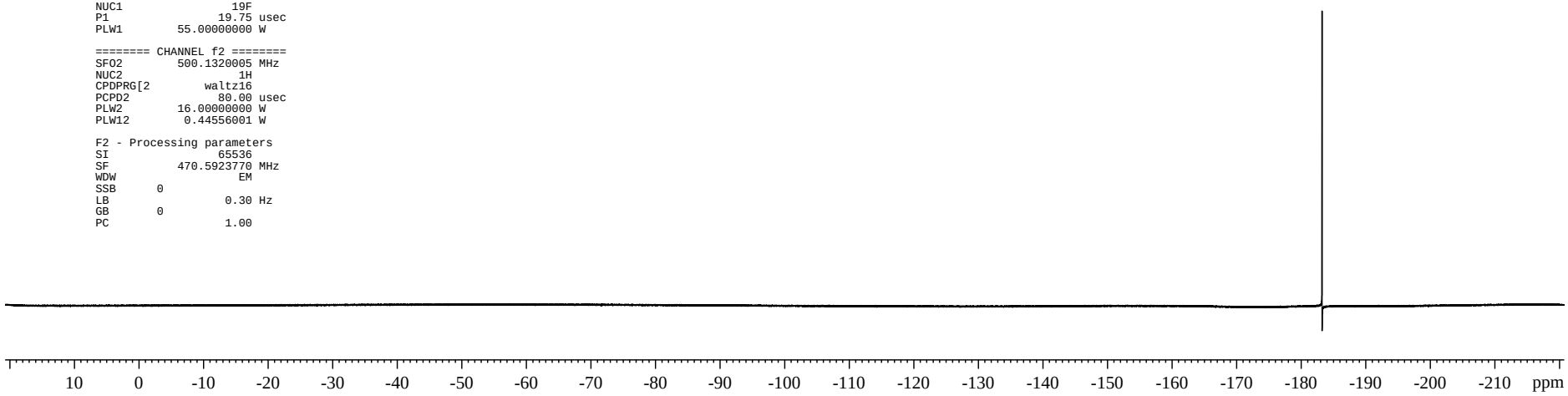


SSK-23-AP-28-F-19F

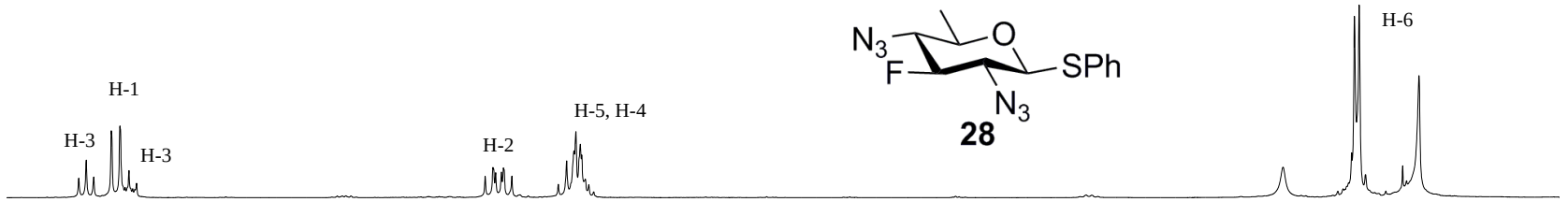


28

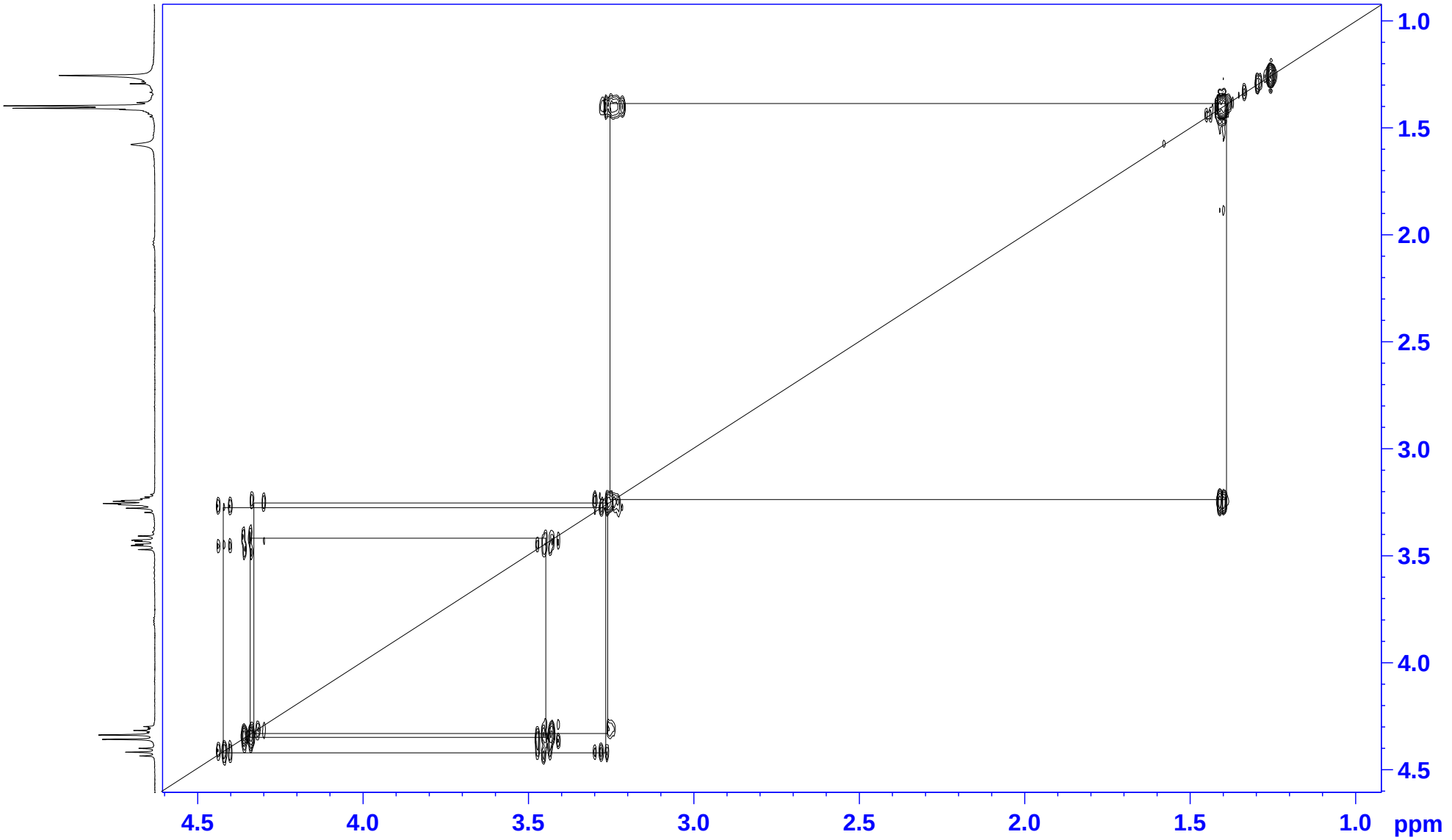
```
Current Data Parameters
NAME     SSK-23-AP-28-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time              22.36
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                   29
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE               296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



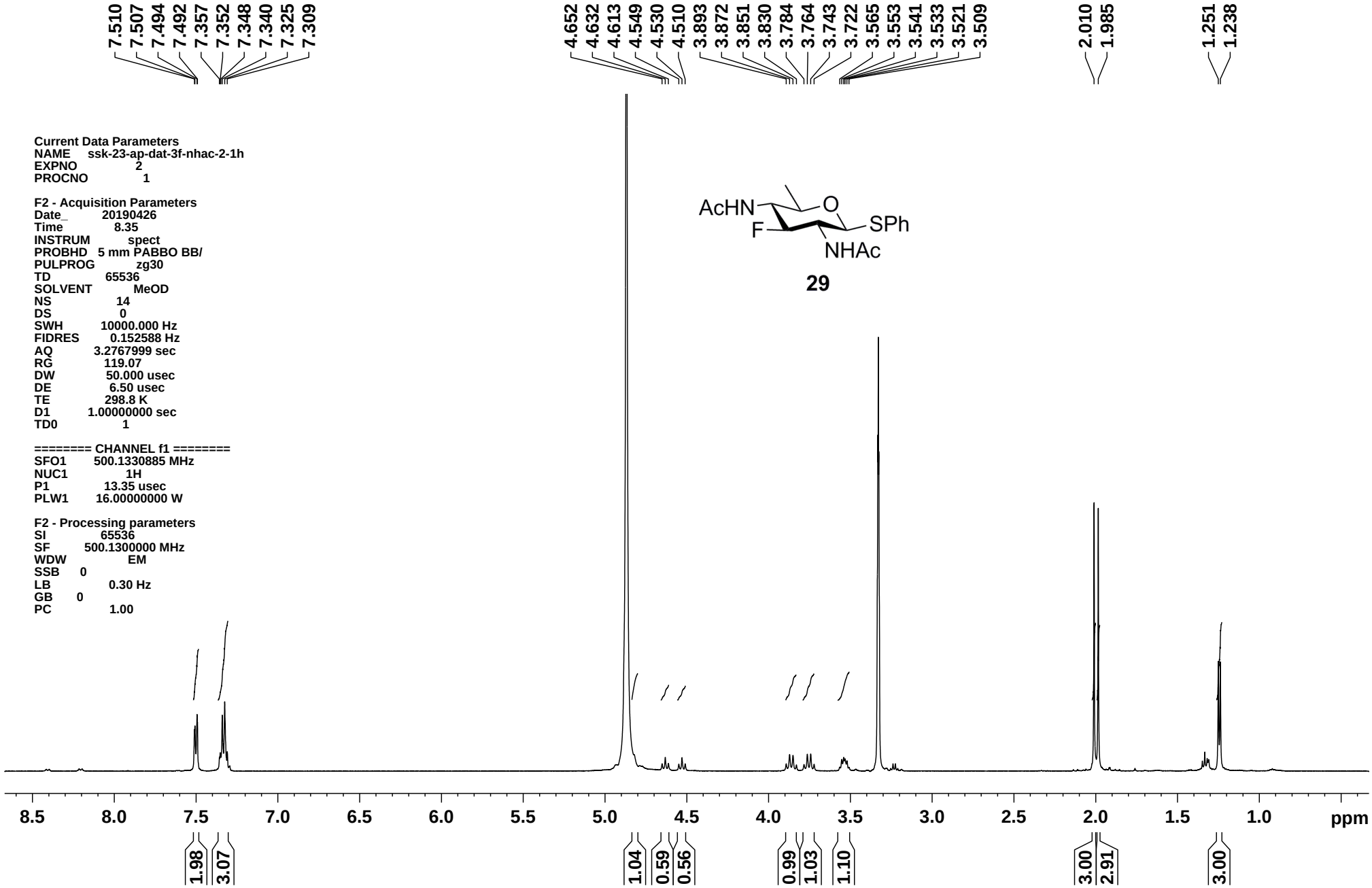
SSK-23-AP-112-HHCOSY



28



ssk-23-ap-dat-3f-nhac-2



Current Data Parameters
NAME ssk-23-ap-dat-3f-nhac-2-1h
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190426
Time 8.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 14
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 119.07
DW 50.000 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

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

ssk-23-ap-dat-3f-nhac-2-13c

Current Data Parameters
NAME ssk-23-ap-dat-3f-nhac-2-13c
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190426
Time 8.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 554
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 299.0 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 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

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

172.11
171.95
133.05
131.91
128.57
127.47
92.32
90.82
85.47
85.41
74.19
74.14
55.85
55.72
54.24
54.10
21.44
21.32
16.78

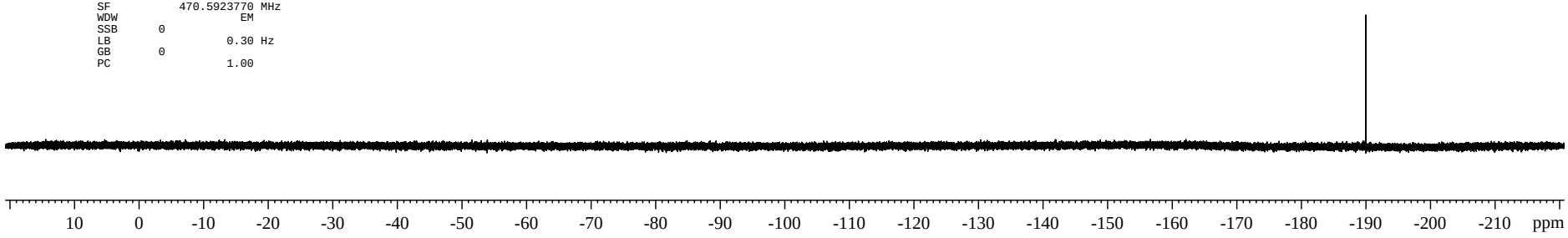
29

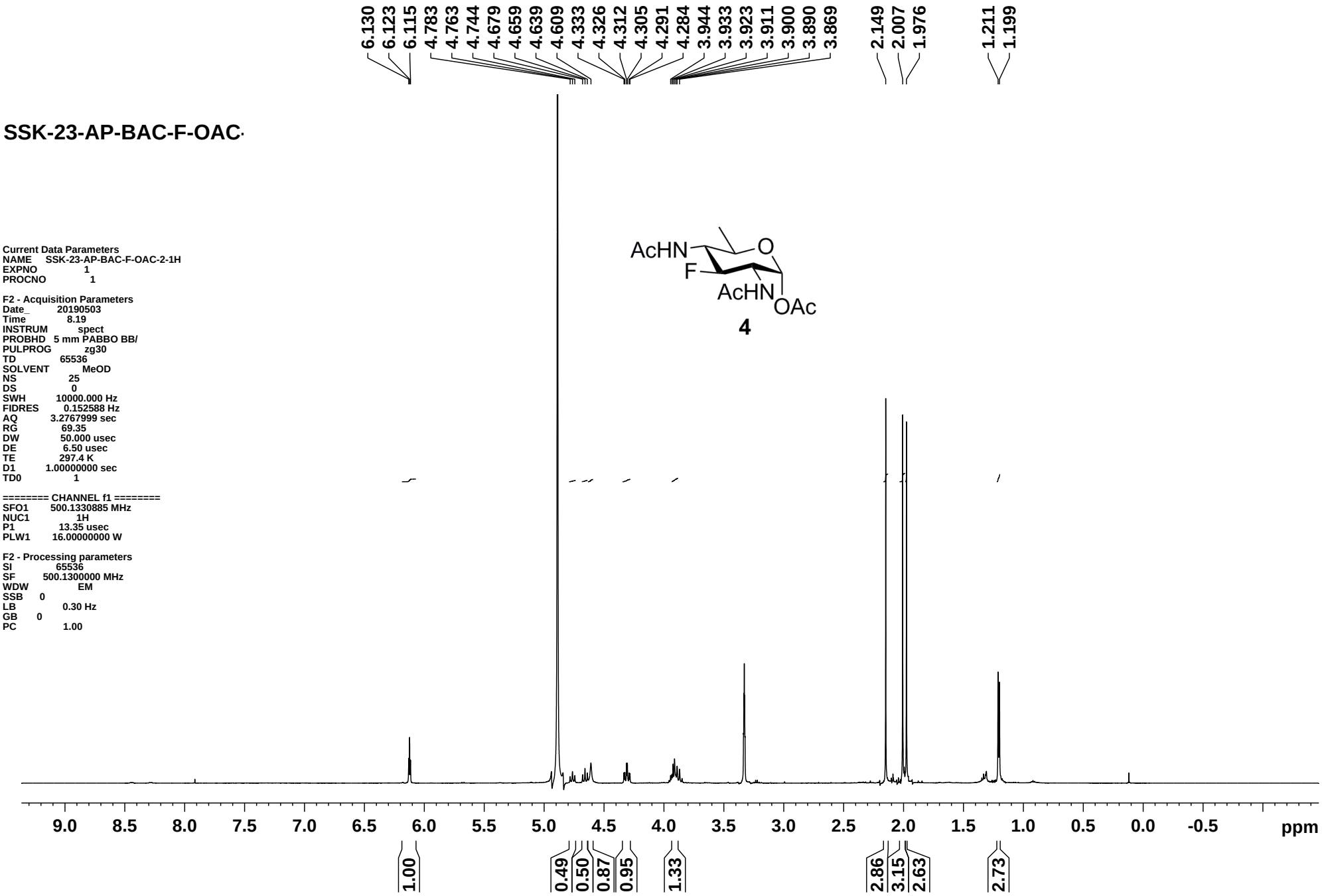
SSK-23-AP-3F-BAC-NHAC-19F

-189.98

29

```
Current Data Parameters
NAME     SSK-23-AP-3F-BAC-NHAC-19F
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20190905
Time              22.45
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT            MeOD
NS                   17
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE               296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```




6.130
6.123
6.115
4.783
4.763
4.744
4.679
4.659
4.639
4.609
4.333
4.326
4.312
4.305
4.291
4.284
3.944
3.933
3.923
3.911
3.900
3.890
3.869
2.149
2.007
1.976
1.211
1.199
SSK-23-AP-BAC-F-OAC-
Current Data Parameters
NAME SSK-23-AP-BAC-F-OAC-2-1H
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190503
Time 8.19
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 25
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 69.35
DW 50.000 usec
DE 6.50 usec
TE 297.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
AcHN
O
F
AcHN
OAc
4
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
-0.5
ppm
1.00
0.49
0.50
0.87
0.95
1.33
2.86
3.15
2.63
2.73

SSK-23-AP-255-BAC-F-13CNEW

Current Data Parameters
NAME SSK-23-AP-255-BAC-F-13CNEW
EXPNO 7
PROCNO 1

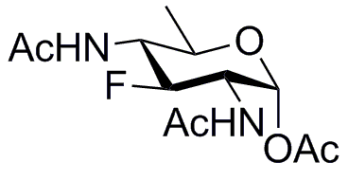
F2 - Acquisition Parameters
Date_ 20181001
Time 16.33
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 364
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 197.27
DW 16.800 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

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

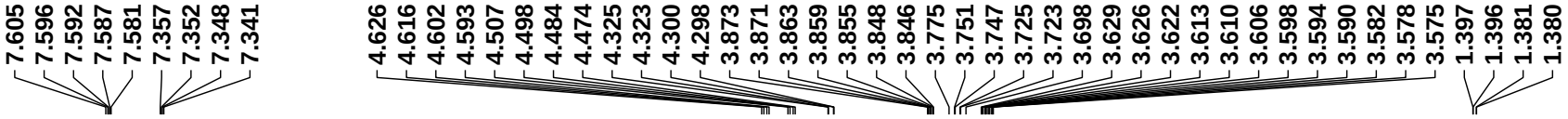
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W

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

172.33
172.10
169.36
90.72
90.64
89.29
87.81
68.49
68.44
55.55
55.42
52.38
52.24
21.34
20.87
19.25
16.59



4



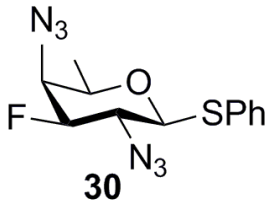
SSK-23-AP-156-1H

Current Data Parameters
NAME SSK-23-AP-156-1H
EXPNO 17
PROCNO 1

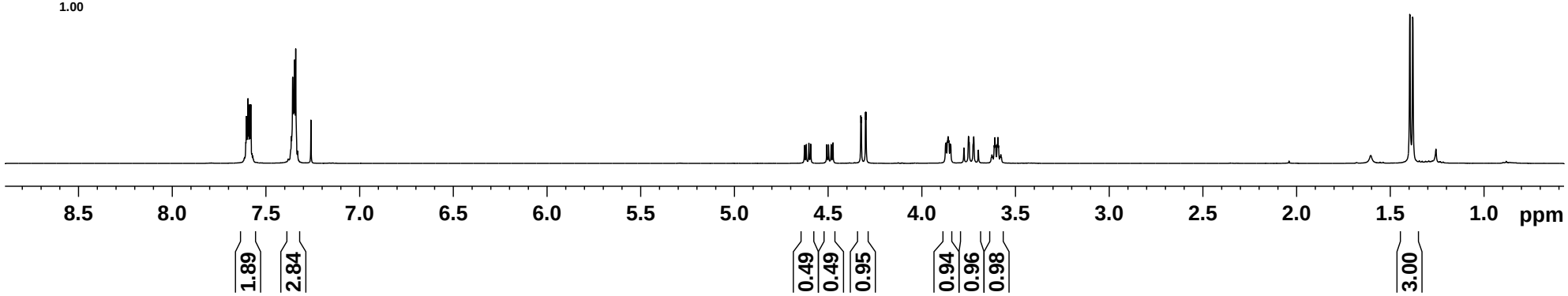
F2 - Acquisition Parameters
Date_ 20180703
Time 13.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 40
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

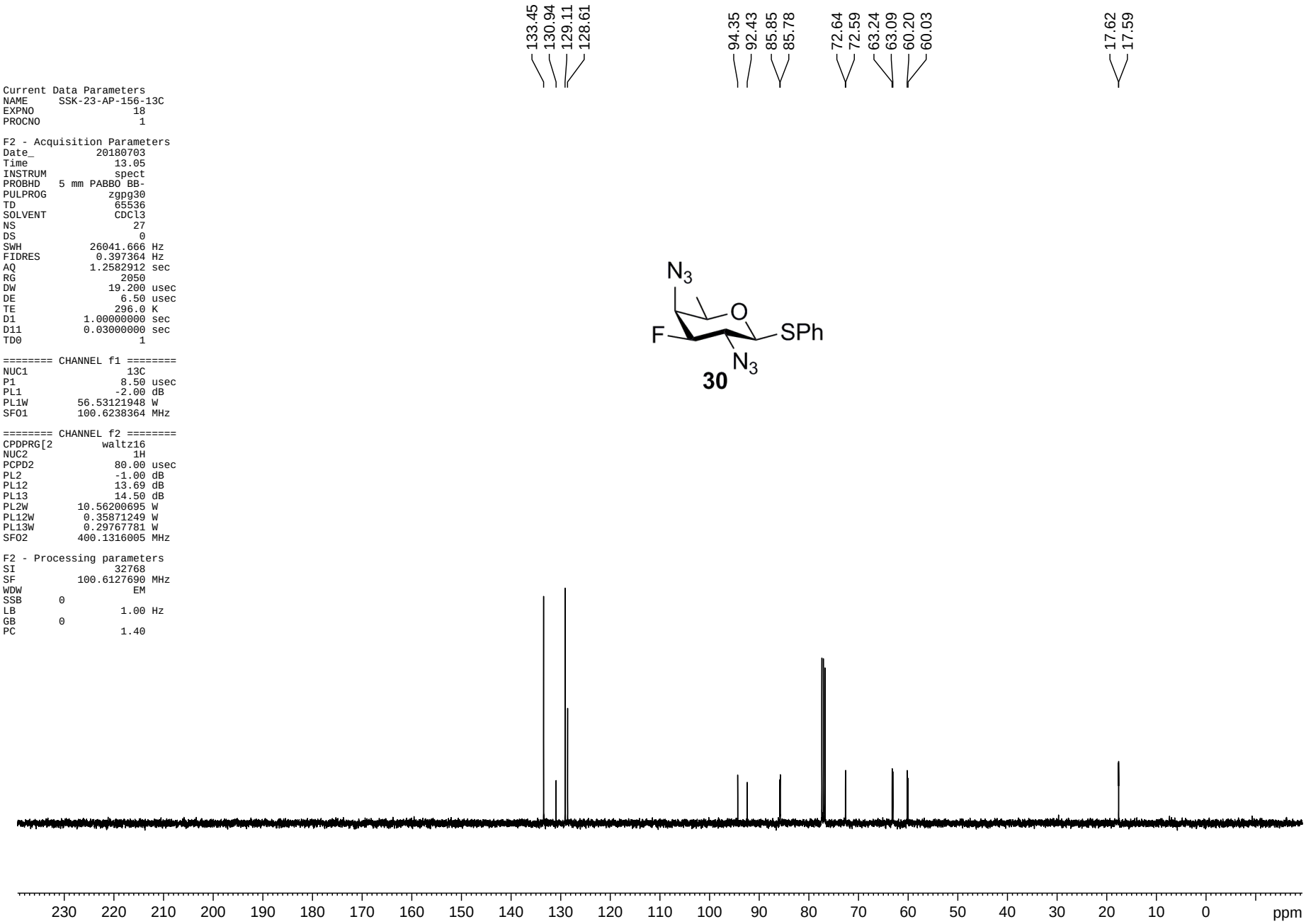
F2 - Processing parameters
SI 32768
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



30

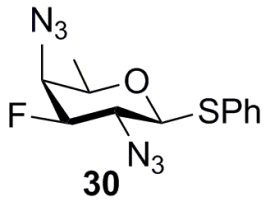


SSK-23-AP-156-13C




```
Current Data Parameters
NAME      SSK-23-AP-156-13C
EXPNO                   18
PROCNO                   1

F2 - Acquisition Parameters
Date_           20180703
Time               13.05
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   27
DS                    0
SWH           26041.666 Hz
FIDRES         0.397364 Hz
AQ            1.2582912 sec
RG                 2050
DW               19.200 usec
DE                6.50 usec
TE                296.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W        56.53121948 W
SFO1        100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W        10.56200695 W
PL12W        0.35871249 W
PL13W        0.29767781 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127690 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

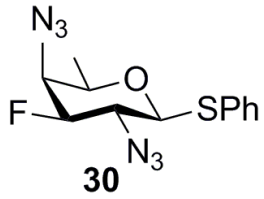
SSK-23-AP-30-F-19F



30

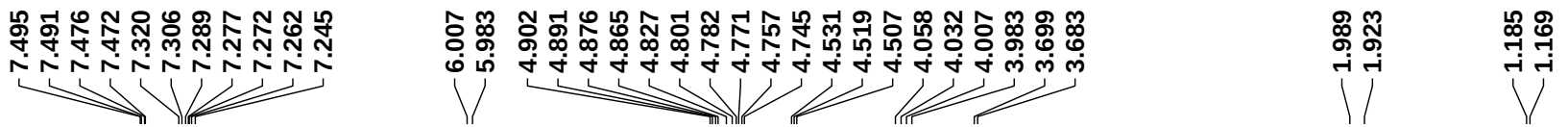
```
Current Data Parameters
NAME     SSK-23-AP-30-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time             22.23
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD              131072
SOLVENT           CDCl3
NS                   11
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE               296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

SSK-23-AP-156-HHCOSY



30

sk-23-ap-dat-f-nhac-1h

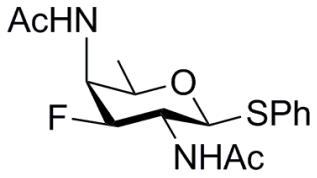


Current Data Parameters
NAME ssk-23-ap-dat-f-nhac-1h
EXPNO 1
PROCNO 1

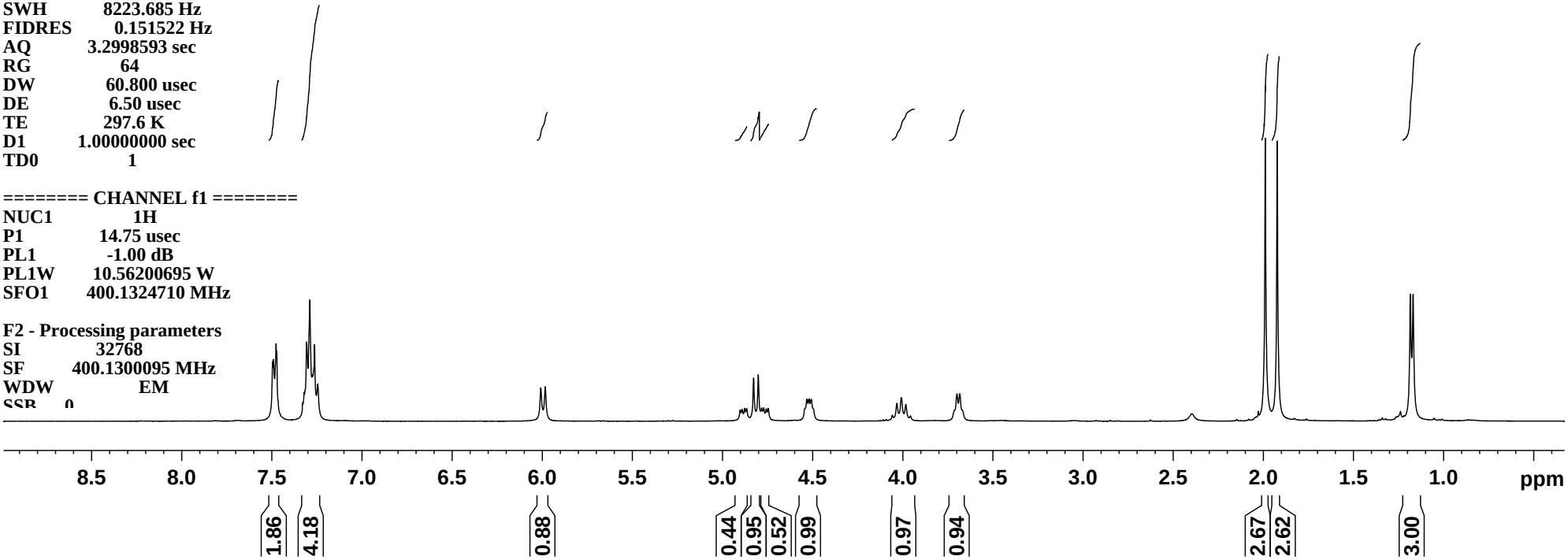
F2 - Acquisition Parameters
Date_ 20190313
Time 3.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 54274
SOLVENT CDCl3
NS 12
DS 0
SWH 8223.685 Hz
FIDRES 0.151522 Hz
AQ 3.2998593 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
TD0 1

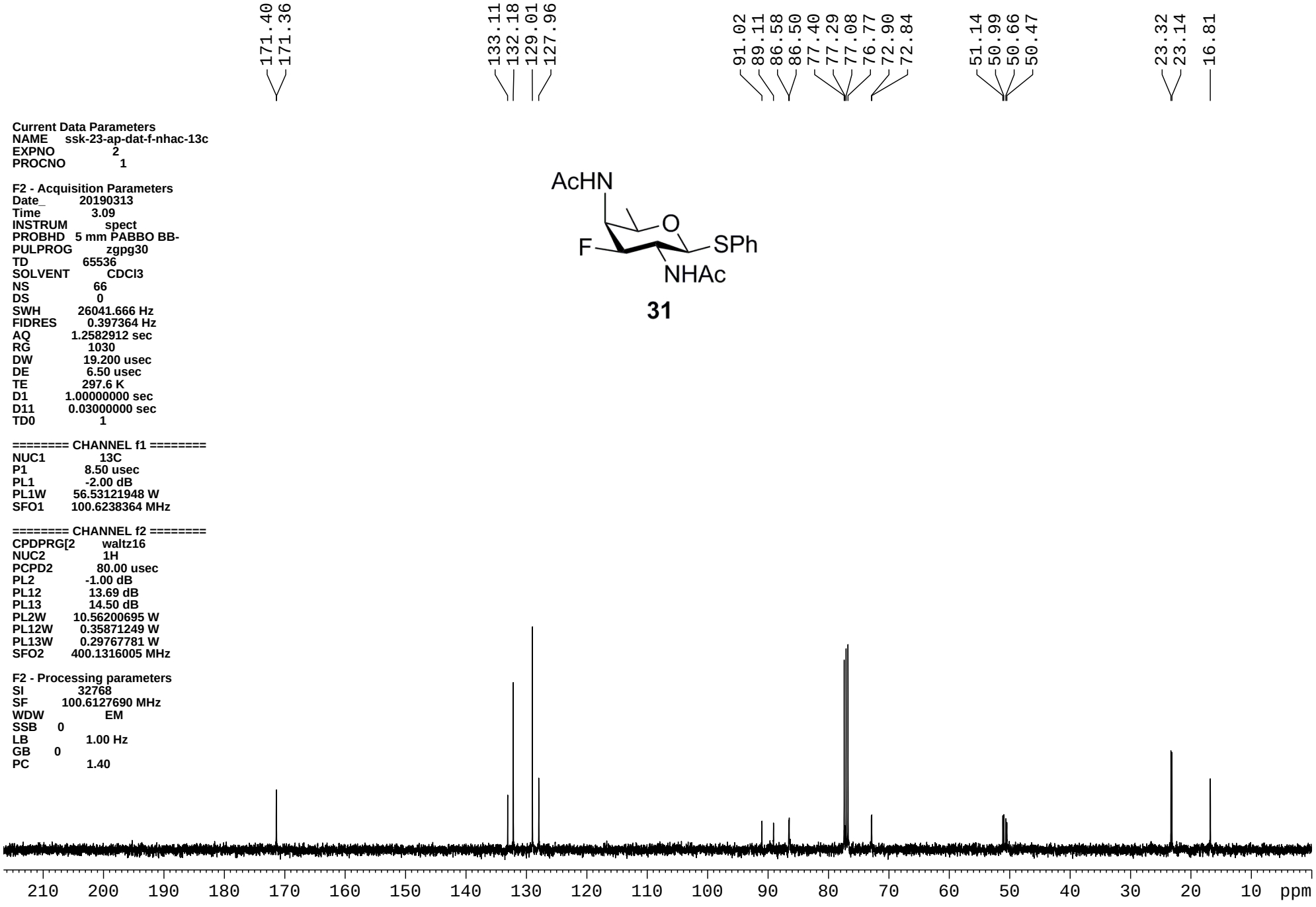
======== CHANNEL f1 ========
NUC1 1H
P1 14.75 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0



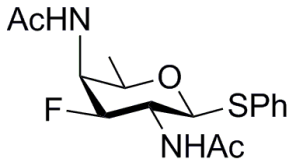
31




171.40
171.36
133.11
132.18
129.01
127.96
91.02
89.11
86.58
86.50
77.40
77.29
77.08
76.77
72.90
72.84
51.14
50.99
50.66
50.47
23.32
23.14
16.81
Current Data Parameters
NAME ssk-23-ap-dat-f-nhac-13c
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190313
Time 3.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 66
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 1030
DW 19.200 usec
DE 6.50 usec
TE 297.6 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcHN
O
F
SPh
NHAc
31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

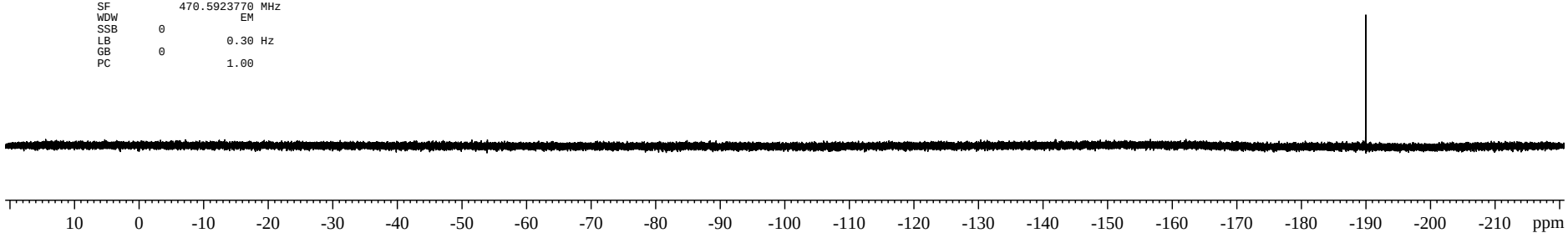
SSK-23-AP-3F-BAC-NHAC-19F

-189.98

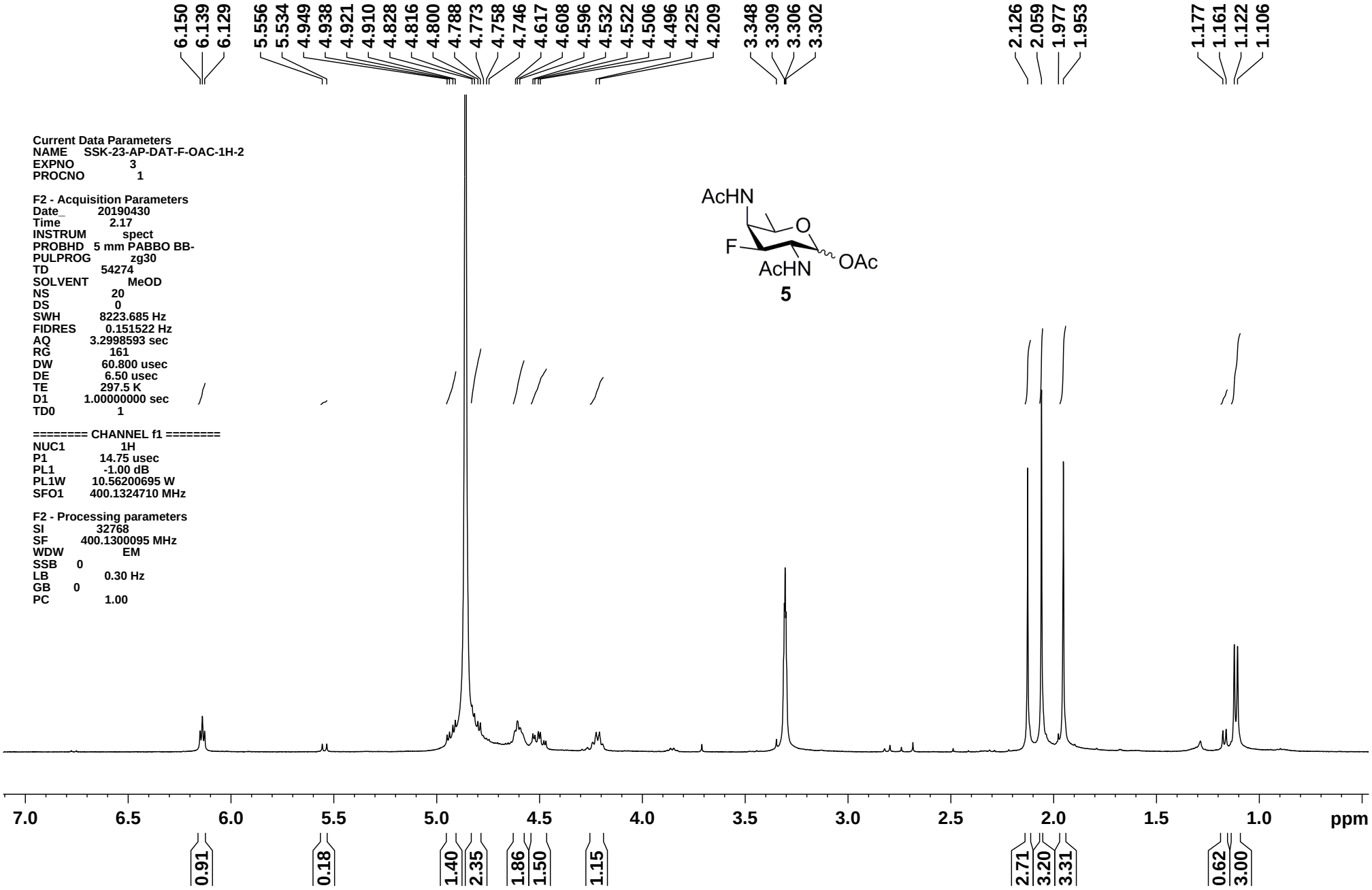


31

```
Current Data Parameters
NAME     SSK-23-AP-3F-BAC-NHAC-19F
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20190905
Time              22.45
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT            MeOD
NS                   17
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                 19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



SSK-23-AP-DAT-F-OAC-



SSK-23-AP-246-13C

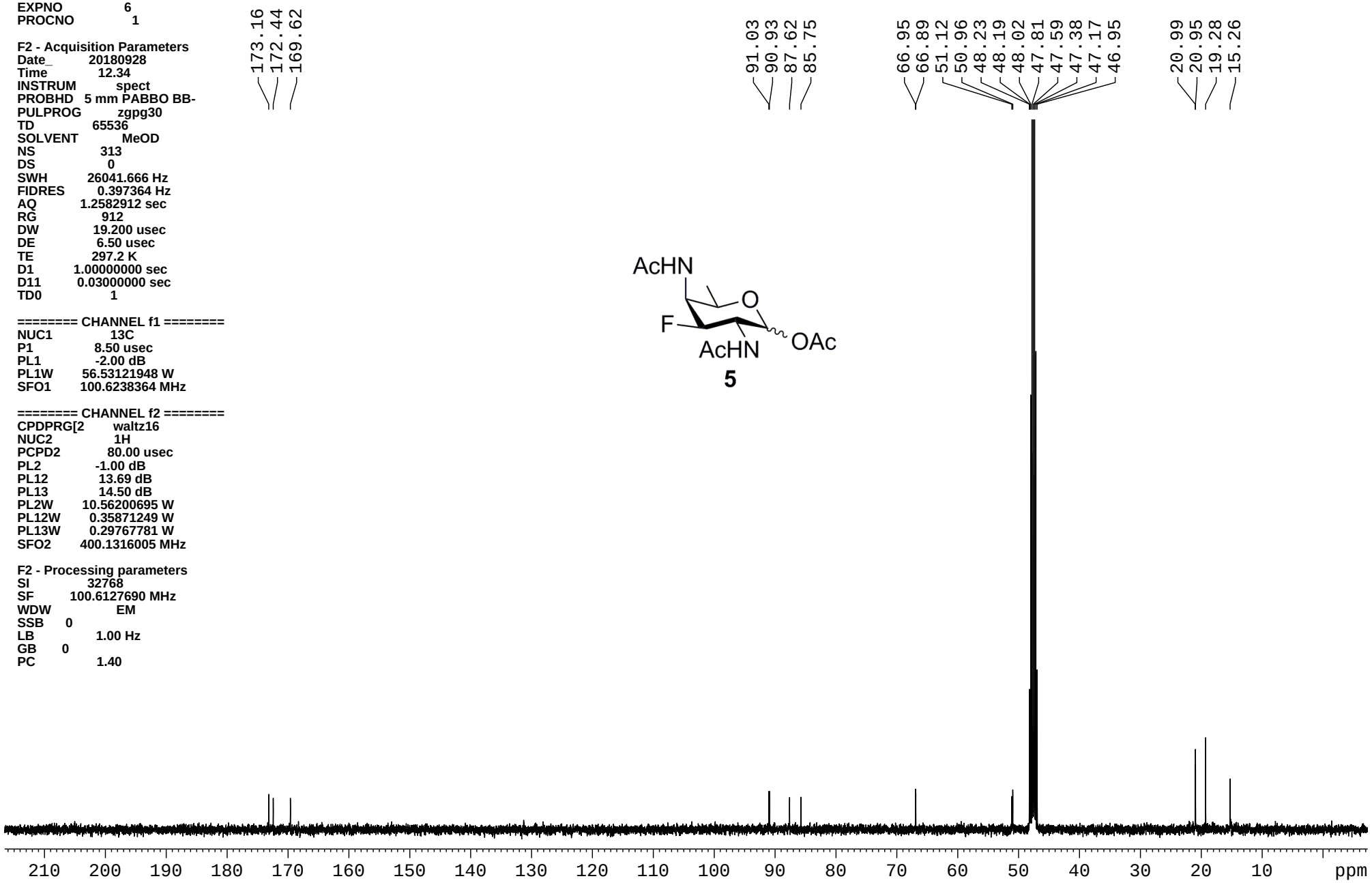
Current Data Parameters
NAME SSK-23-AP-246-13C
EXPNO 6
PROCNO 1

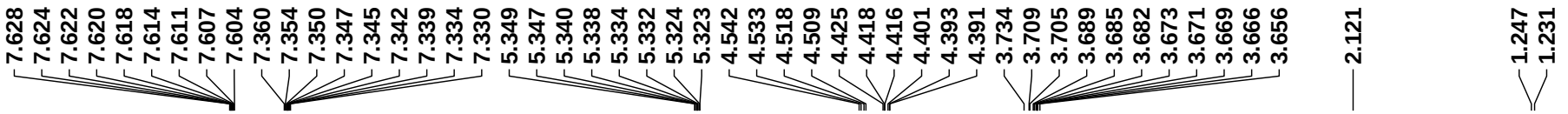
F2 - Acquisition Parameters
Date_ 20180928
Time 12.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 313
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 912
DW 19.200 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz

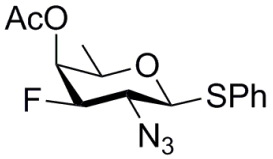
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



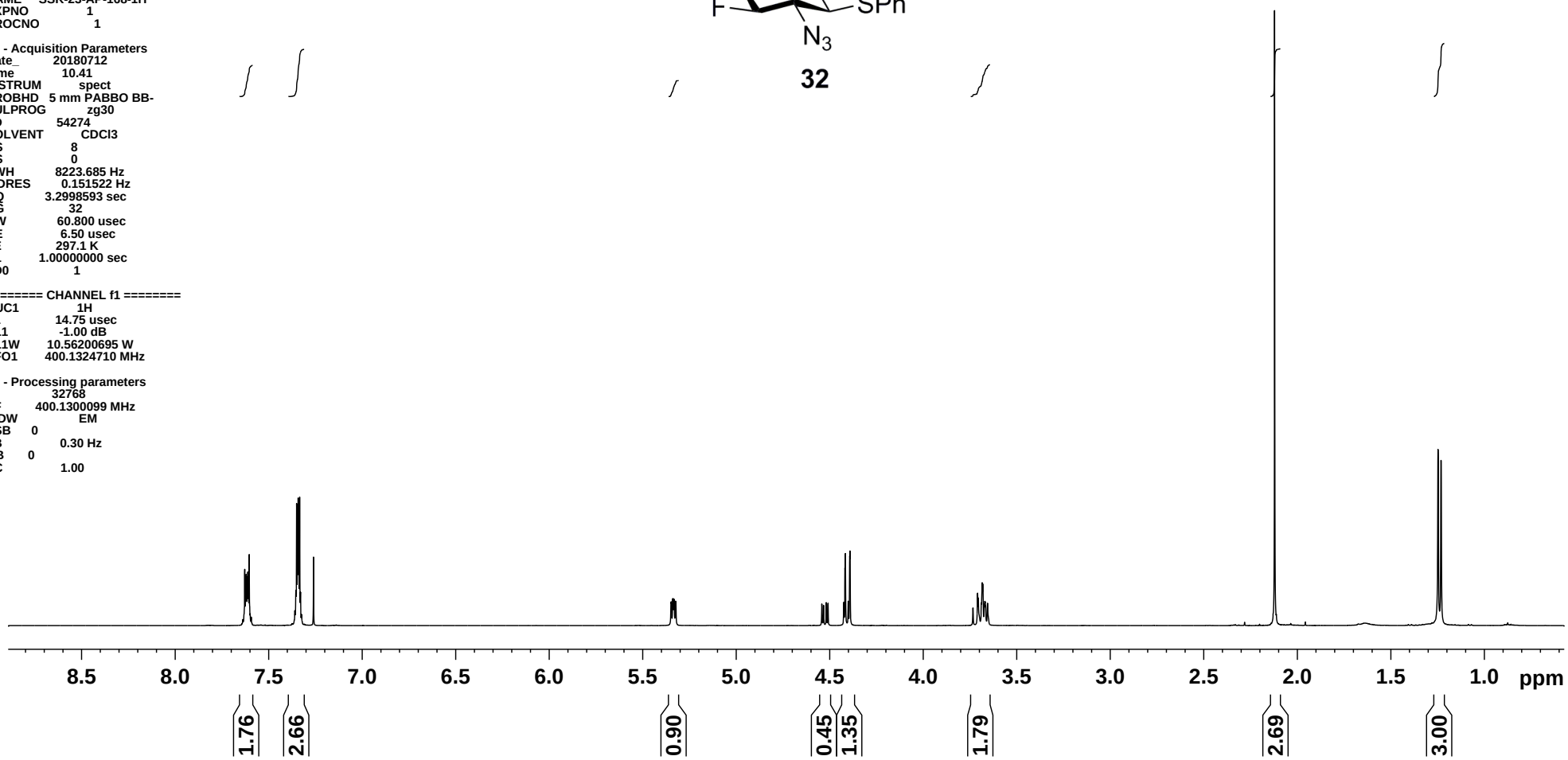


SSK-23-AP-168-1H

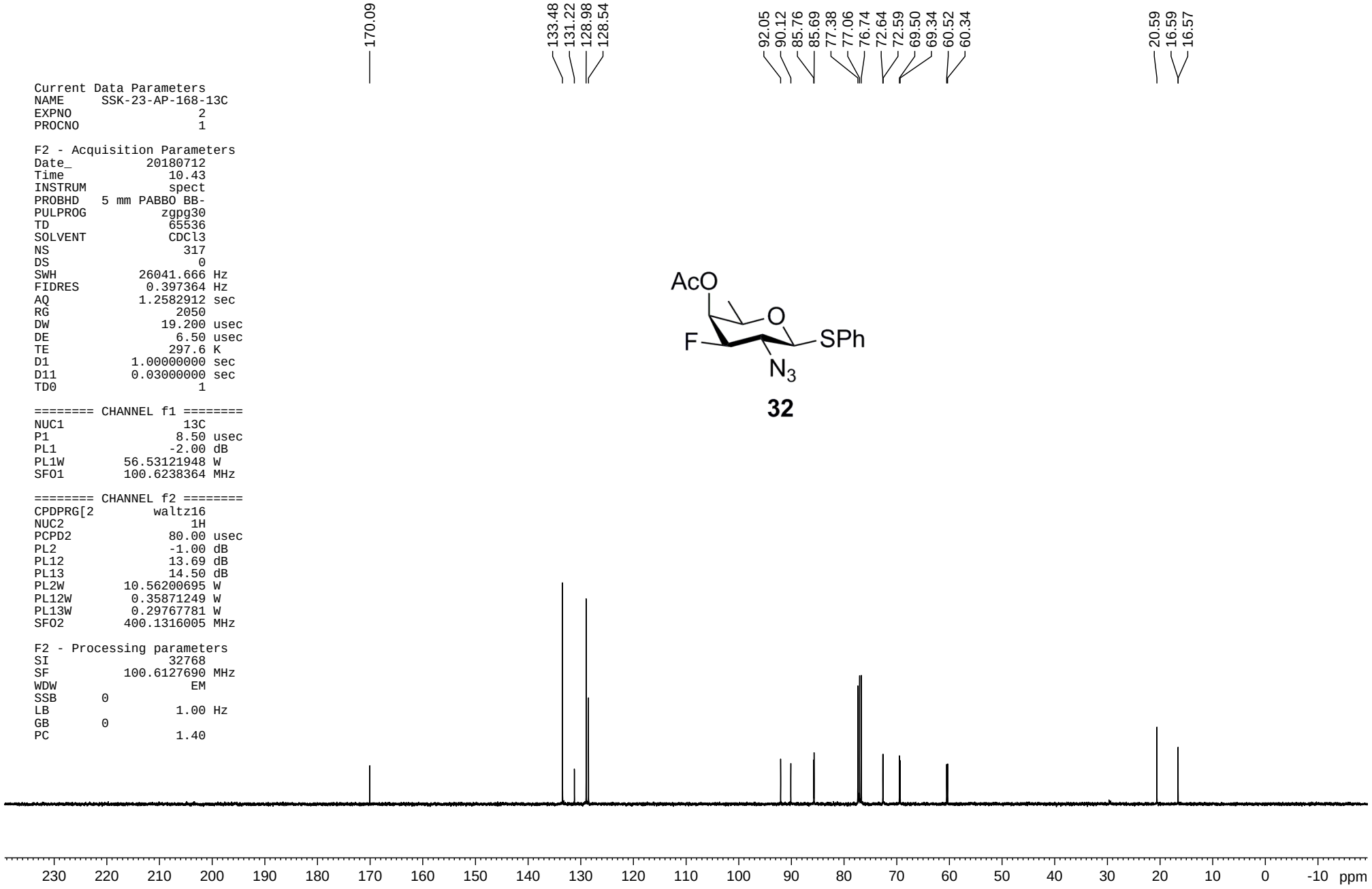


32

```
Current Data Parameters
NAME    SSK-23-AP-168-1H
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_         20180712
Time            10.41
INSTRUM          spect
PROBHD  5 mm PABBO BB-
PULPROG          zg30
TD              54274
SOLVENT          CDCl3
NS                 8
DS                 0
SWH           8223.685 Hz
FIDRES         0.151522 Hz
AQ            3.2998593 sec
RG                32
DW              60.800 usec
DE               6.50 usec
TE              297.1 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

F2 - Processing parameters
SI              32768
SF          400.1300099 MHz
WDW                EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```



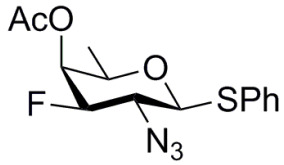
SSK-23-AP-168-13C




```
Current Data Parameters
NAME     SSK-23-AP-168-13C
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180712
Time               10.43
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                   317
DS                     0
SWH            26041.666 Hz
FIDRES          0.397364 Hz
AQ             1.2582912 sec
RG                  2050
DW                19.200 usec
DE                 6.50 usec
TE                297.6 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                -2.00 dB
PL1W         56.53121948 W
SFO1         100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.69 dB
PL13               14.50 dB
PL2W         10.56200695 W
PL12W         0.35871249 W
PL13W         0.29767781 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

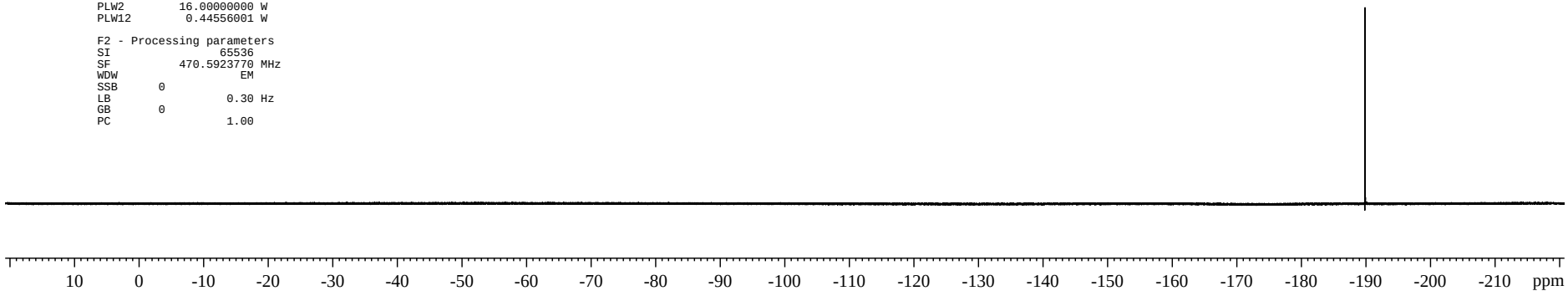
SSK-23-AP-32-F-19F

-189.87

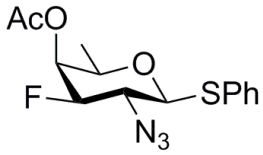


32

```
Current Data Parameters
NAME     SSK-23-AP-32-F-19F
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_          20190905
Time              22.40
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.8 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                65536
SF          470.5923770 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```



SSK-23-AP-168-HHCOSY



32

ssk-23-ap-fuc-3f-nhac-2

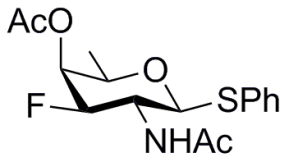
7.480 7.468 7.272 7.260 6.605 6.589 5.348 5.079 5.058 5.029 5.009 4.935 4.929 4.915 4.909 4.038 4.019 4.000 3.981 3.961 3.741 3.729 2.083 1.990 1.190 1.178

Current Data Parameters
NAME ssk-23-ap-fuc-3f-nhac-2-1h
EXPNO 2
PROCNO 1

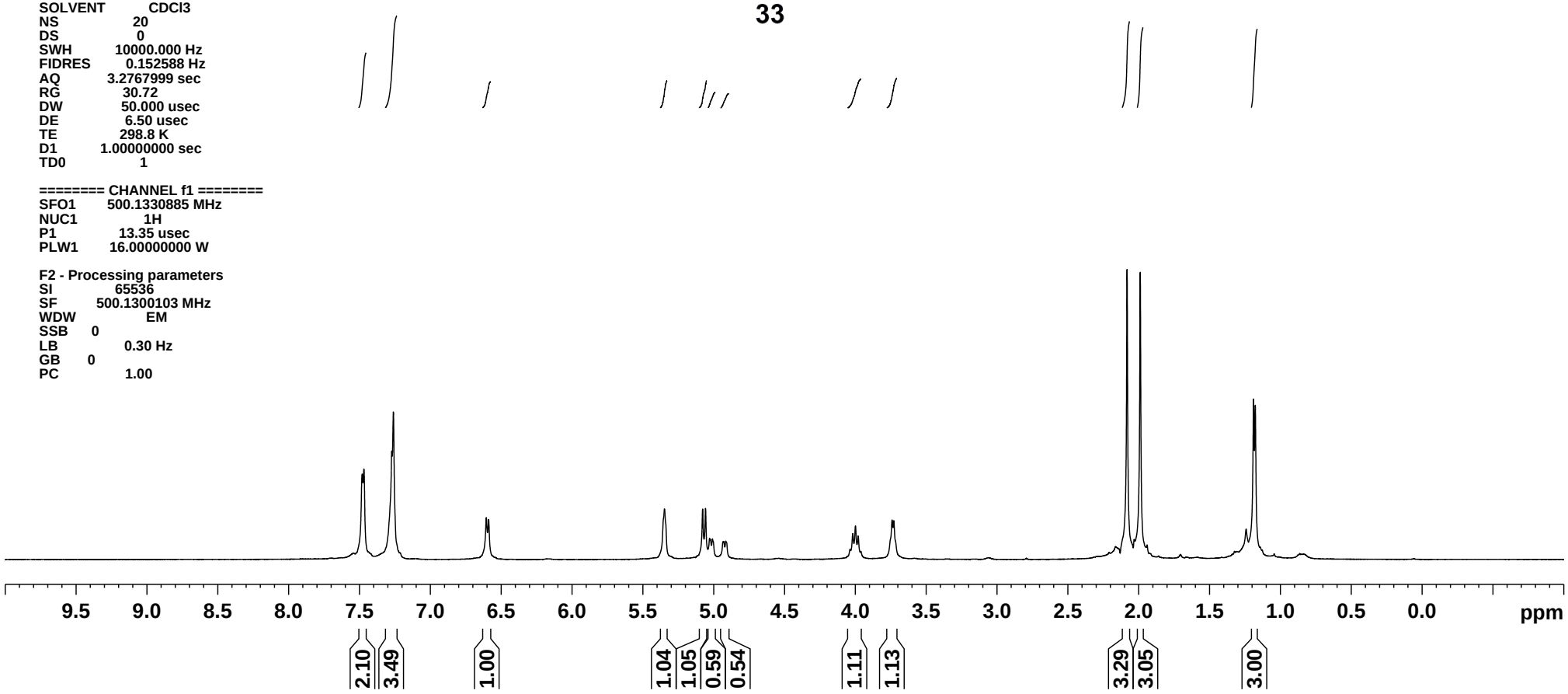
F2 - Acquisition Parameters
Date_ 20190426
Time 9.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 30.72
DW 50.000 usec
DE 6.50 usec
TE 298.8 K
D1 1.00000000 sec
TD0 1

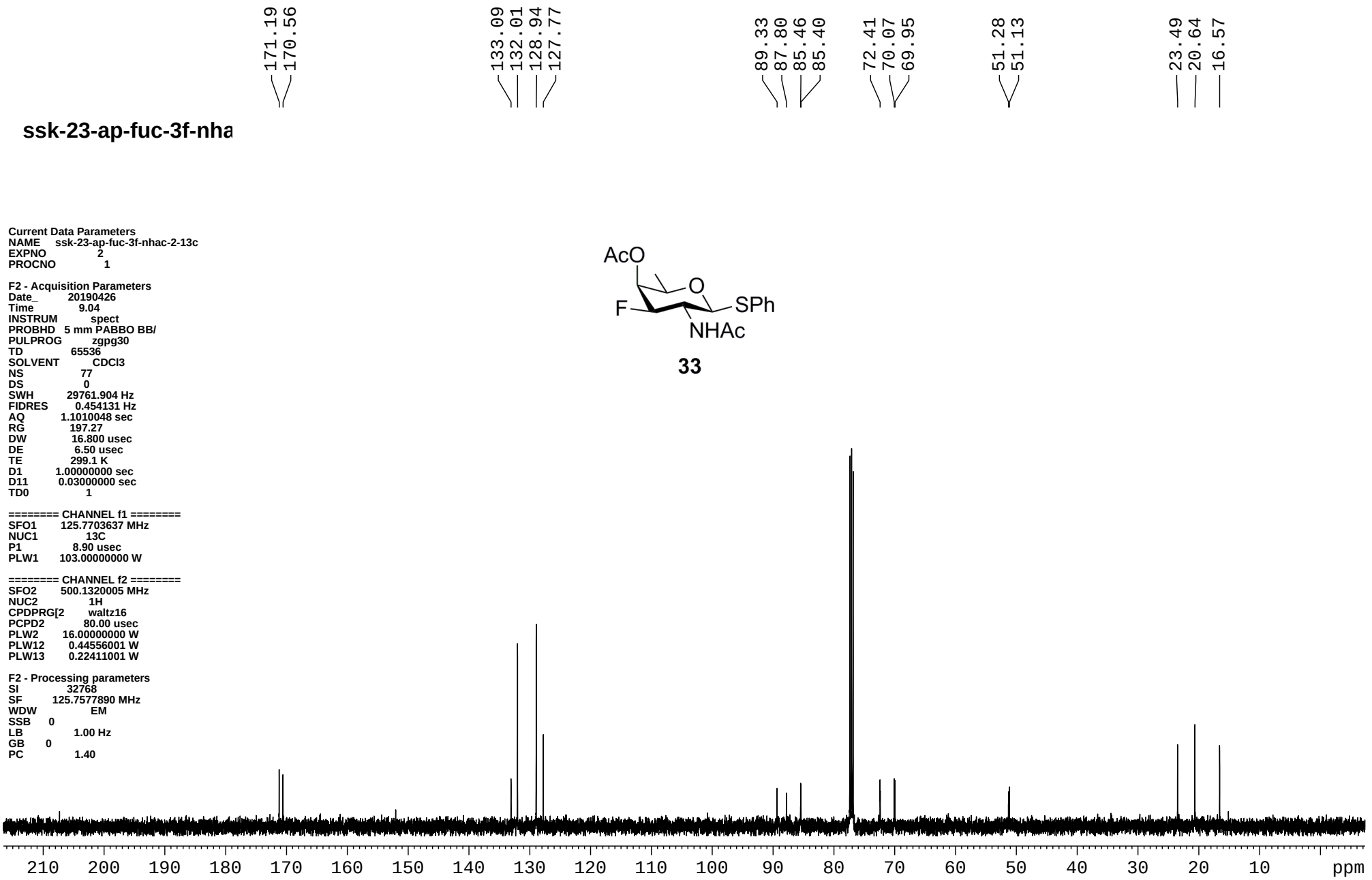
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 13.35 usec
PLW1 16.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

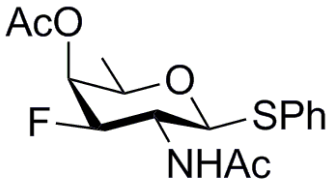


33



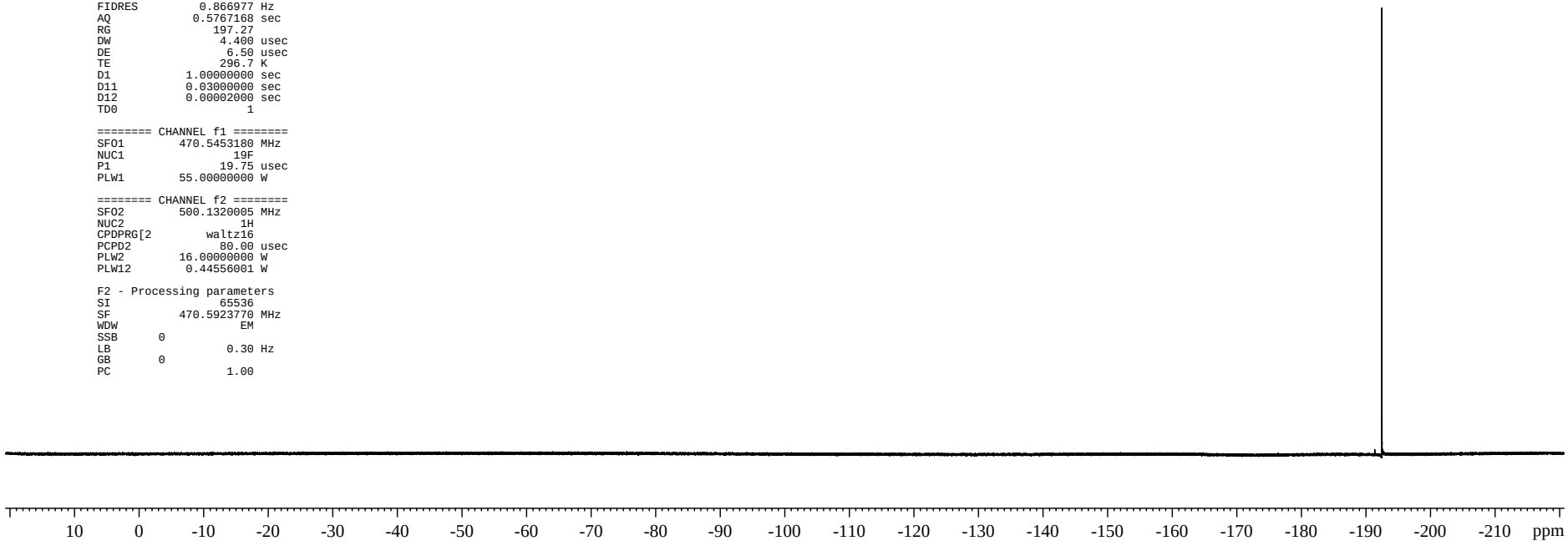

171.19
170.56
133.09
132.01
128.94
127.77
89.33
87.80
85.46
85.40
72.41
70.07
69.95
51.28
51.13
23.49
20.64
16.57
ssk-23-ap-fuc-3f-nha
Current Data Parameters
NAME ssk-23-ap-fuc-3f-nhac-2-13c
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20190426
Time 9.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 77
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 299.1 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 16.00000000 W
PLW12 0.44556001 W
PLW13 0.22411001 W
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcO
O
F
SPh
NHAc
33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

SSK-23-AP-3F-FUC-NHAC-19F

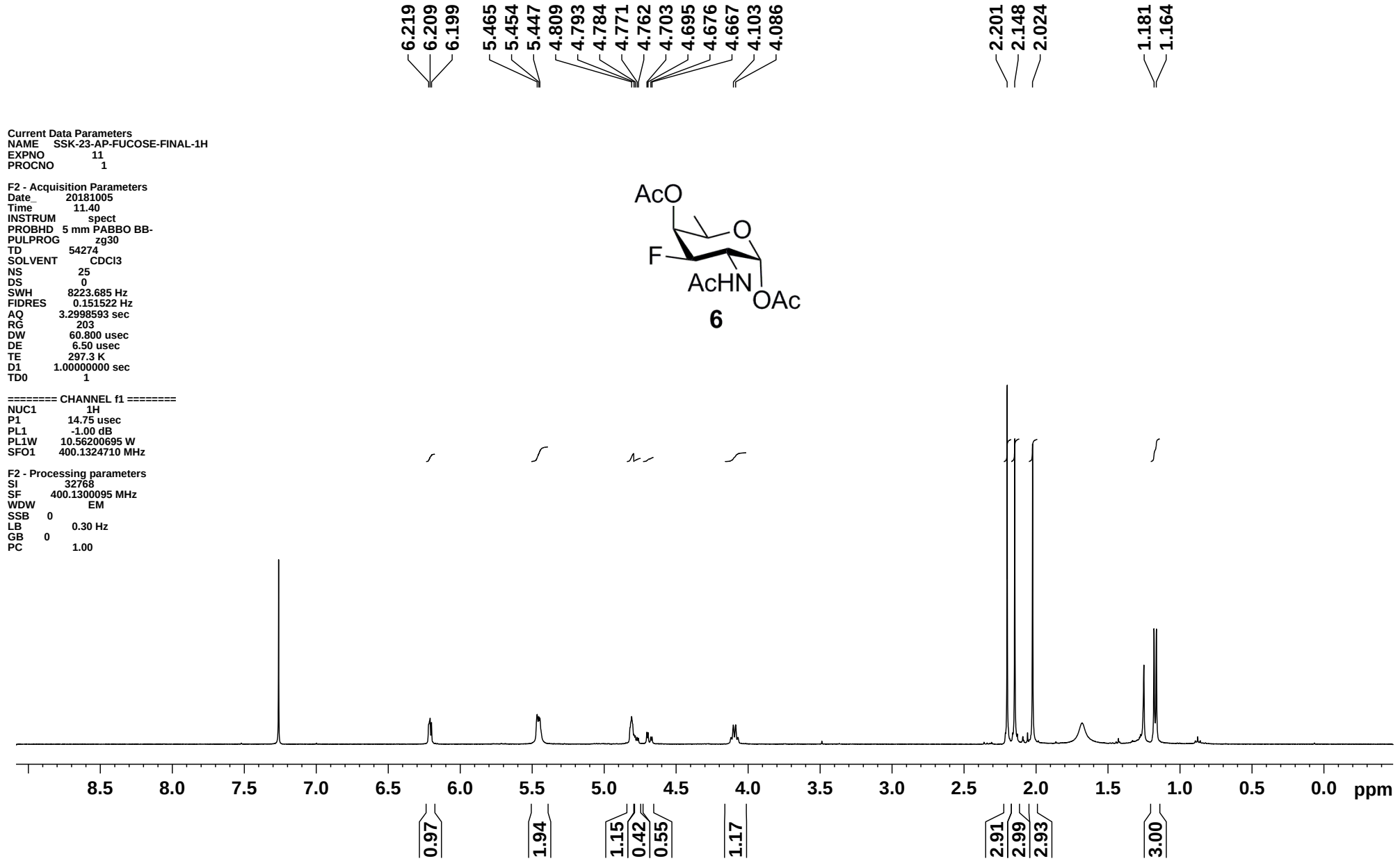


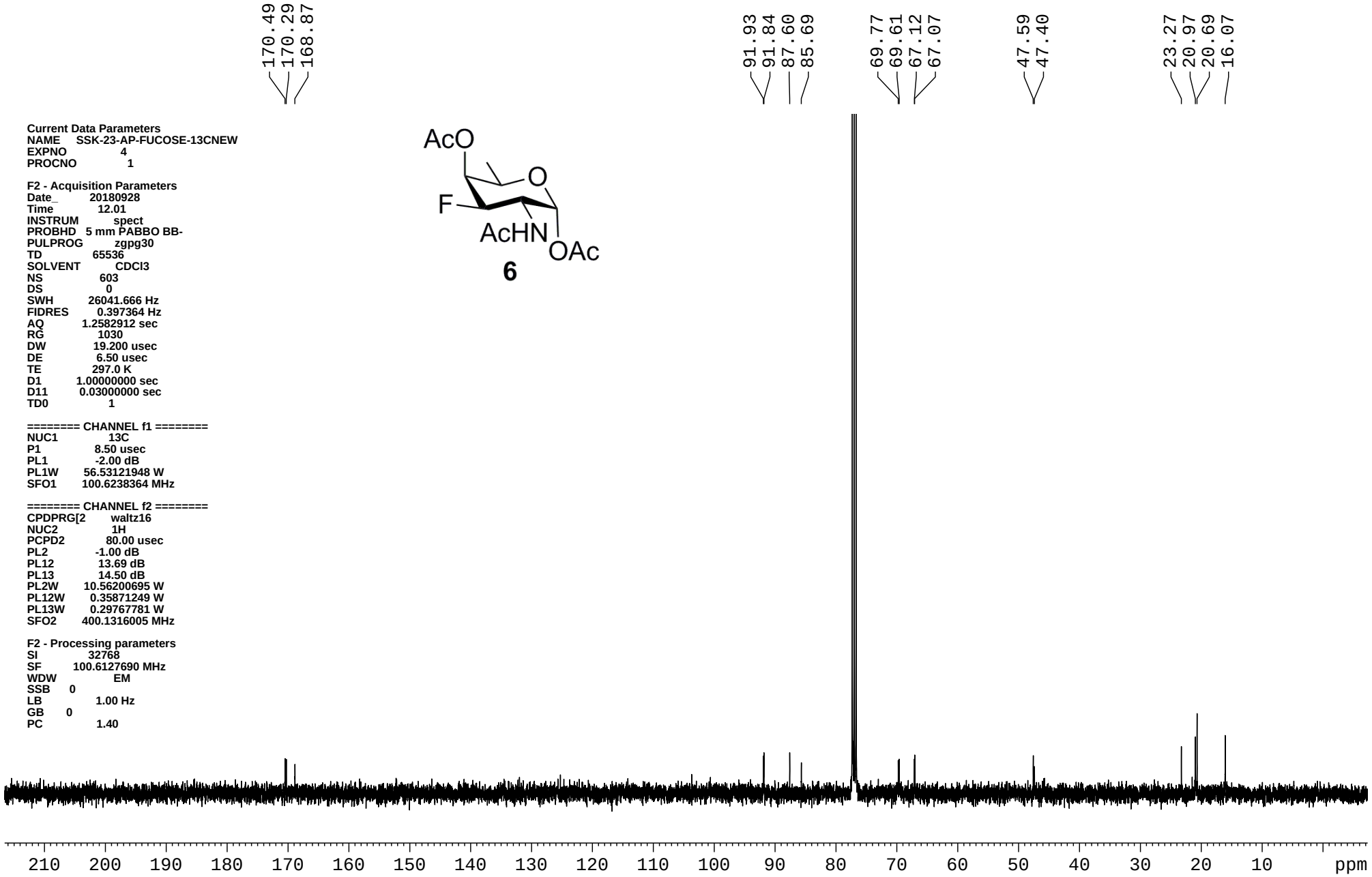
33

```
Current Data Parameters
NAME     SSK-23-AP-3F-FUC-NHAC-19F
EXPNO                 7
PROCNO                1

F2 - Acquisition Parameters
Date_          20190905
Time              22.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG      zgfhigqn.2
TD               131072
SOLVENT            CDCl3
NS                     8
DS                     0
SWH          113636.367 Hz
FIDRES         0.866977 Hz
AQ            0.5767168 sec
RG               197.27
DW                4.400 usec
DE                6.50 usec
TE                296.7 K
D1           1.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        470.5453180 MHz
NUC1                 19F
P1                19.75 usec
PLW1        55.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2        16.00000000 W
PLW12        0.44556001 W

F2 - Processing parameters
SI                 65536
SF          470.5923770 MHz
WDW                   EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



SSK-23-AP-FUCOSE-FINAL-1H




170.49
170.29
168.87
91.93
91.84
87.60
85.69
69.77
69.61
67.12
67.07
47.59
47.40
23.27
20.97
20.69
16.07
AcO
O
F
AcHN
OAc
6
Current Data Parameters
NAME SSK-23-AP-FUCOSE-13CNEW
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20180928
Time 12.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 603
DS 0
SWH 26041.666 Hz
FIDRES 0.397364 Hz
AQ 1.2582912 sec
RG 1030
DW 19.200 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6238364 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 13.69 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.35871249 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm