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# Supporting Information

## Orthogonally Protected D-Galactosamine Thioglycoside Building Blocks via Highly Regioselective, Double serial and Double Parallel Inversions of $\beta$-D-Thiomannoside

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### Table of Contents

**I. Experimental procedures:**

**II. Spectra**:

**Experimental Section**

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

**Phenyl 3-*O*-Acetyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-mannopyranoside (2a).**

To a solution of **1** (1.2 g, 4.5 mmol) in pyridine (4.8 mL, 59.1 mmol) was added *tert*-butyldiphenylsilyl chloride (2.4 mL, 9.1 mmol). After 12 h, reaction mixture was concentrated and the residue was dissolved in $CHCl_3$ and washed with water. Separated aqueous layer was washed with $CHCl_3$ twice. Combined organic layers were dried over $Na_2SO_4$ and concentrated *in vacuo*.

The crude product so obtained was dissolved in THF (40 ml) and to this clear solution, $Me_2SnCl_2$ (50 mg, 0.2 mmol) and DIPEA (1.6 mL, 9.1 mmol) were added. After 2 min, AcCl (0.35 mL, 5.0 mmol) was added and the solution was stirred at rt for 1.5 h. After complete consumption of the starting material, the reaction was quenched with 3% HCl and extracted with EtOAc (30 mL). Separated organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (40% ethyl acetate: pet ether) to obtain **2a** as a white foam (2.1 g, 84%): $[\alpha]^{20}_{D}$ -50.2 (*c* 3.53, $CHCl_3$); IR ($CHCl_3$) ν 3475, 3019, 2932, 1733, 1428, 1216, 1114, 1067, 758, 669 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 5H, ArH), 7.48-7.35 (m, 10H, ArH), 4.91 (s, 1H, H-1), 4.84 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.30-4.28 (m, 1H, H-2), 4.14-4.09 (m, 1H, H-4), 3.97 (d, *J* = 4.8 Hz, 2H, H-6a, H-6b), 3.50-3.45 (m, 1H, H-5), 2.79 (bs, 1H, OH), 2.25 (d, *J* = 6.2 Hz, 1H, OH), 2.18 (s, 3H, $CH_3$), 1.07 (s, 9H, Si($CH_3$)$_3$); δ 171.1, 135.9, 135.8, 135.7, 134.0, 132.9, 132.7, 131.5, 131.3, 130.1, 129.2, 128.0, 127.86, 127.81, 87.2, 79.7, 77.0, 70.7, 67.0, 64.9, 26.8, 21.3, 19.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{30}H_{36}O_6NaSSi$, 575.1900; found, 575.1860.

**Phenyl 3-*O*-Benzoyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-mannopyranoside (2b).**

The same procedure as described for **2a** was followed for preparation of **2b**, starting from **1** (0.57 g, 2.1 mmol) via selective TBDPS protection at O6 followed by benzoylation at O3 using BzCl (0.27 mL, 2.3 mmol) to obtain **2b** as a white amorphous solid (1.12 g, 87%): $[\alpha]^{20}_{D}$ -30.2 (*c* 2.22, $CHCl_3$); IR ($CHCl_3$) ν 3412, 3019, 2929, 1719, 1216, 1048, 759, 669 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.12-8.10 (m, 2H, ArH), 7.73-7.72 (m, 4H, ArH), 7.71-7.24 (m, 14H, ArH), 5.09 (dd, *J* = 9.8, 3.2 Hz, 1H, H-3), 5.00 (d, *J* = 0.8 Hz, 1H, H-1), 4.43-4.41 (m, 1H, H-2), 4.25 (dt, *J* = 9.8, 3.2 Hz, 1H, H-4), 4.05-3.98 (m, 2H, H-6), 3.59-3.54 (m, 1H, H-5), 2.89 (d, *J* = 3.2 Hz, 1H, OH), 2.41 (d, *J* = 6.4 Hz, 1H, OH), 1.08 (s, 9H, Si($CH_3$)$_3$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.6, 135.87, 135.0, 134.2, 133.7, 133.0, 132.9, 131.5, 130.1, 130.09, 129.6, 129.3, 128.7, 128.0, 127.8, 87.3, 79.7, 76.9, 70.9, 67.2, 64.9, 27.0, 19.4; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{35}H_{38}O_6NaSSi$, 637.2056; found, 637.2054.

**Phenyl 3-*O*-Acetyl-2,4-diazido-2,4-dideoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (5a).**

Trifluoromethanesulfonic anhydride (0.27 mL, 1.6 mmol) was added drop wise at -10 $^oC$ to a stirred solution of phenyl 3-*O*-acetyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-mannopyranoside **2a** (0.15 g, 0.27 mmol) and pyridine (0.28 mL, 3.5 mmol) in $CH_2Cl_2$ (8 mL) and the solution was gradually brought to 10 °C. After 2 h the reaction mixture was concentrated *in vacuo* and the crude product was used for the next step without purification.

The crude product was dissolved in DMF (3 mL) and to this, $NaN_3$ (0.2 g, 3.2 mmol) was added. This reaction mixture was stirred at rt for 10 h and then it was diluted with EtOAc and washed with water. Separated aqueous layer was washed

twice with EtOAc. The combined organic layers were dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (10% ethyl acetate: pet ether) to obtain **5a** as a pale yellowish liquid (0.134 g, 85%): $[\alpha]^{20}_D$ -8.9 (*c* 4.0, $CHCl_3$); IR ($CHCl_3$) ν 3013, 2931, 2858, 2114, 1750, 1472, 1428, 1363, 1275, 1217, 1113, 822, 759, 608, 505 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.66-7.63 (m, 4H, ArH), 7.58-7.51 (m, 2H, ArH), 7.47-7.37 (m, 6H, ArH), 7.31-7.28 (m, 3H, ArH), 4.95 (dd, *J* = 10.0, 3.6 Hz, 1H, H-3), 4.39 (d, *J* = 10.0 Hz, 1H, H-1), 4.16 (d, *J* = 3.6 Hz, 1H, H-4), 3.84-3.70 (m, 2H, H-6a, 6b), 3.72-3.62 (m, 2H, H-2, H-5), 2.19 (s, 3H, $CH_3$), 1.05 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, CDCl3) δ 170.0, 135.7, 133.4, 132.94, 132.89, 131.2, 130.1, 129.2, 128.6, 128.0, 86.9, 77.2, 75.2, 62.3, 59.9, 59.6, 27.0, 20.8, 19.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{30}H_{34}N_6O_4NaSSi$, 625.2029; found, 625.2028.

**Phenyl 2,4-Diazido-3-*O*-benzoyl-2,4-dideoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (5b).**

The same procedure as described for **5a** was followed for triflation of **2b** (2.25 g, 3.66 mmol) and its double displacement with $NaN_3$ to afford **5b** as a pale yellowish liquid (2.0 g, 84%): $[\alpha]^{20}_D$ -18.1 (*c* 0.68, $CHCl_3$); IR ($CHCl_3$) ν 3019, 2928, 2115, 1726, 1216, 1112, 758, 669 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 6.8 Hz, 2H, ArH), 7.66-7.60 (m, 5H, ArH), 7.56-7.40 (m, 10H, ArH), 7.38-7.31 (m, 3H, ArH), 5.24 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3), 4.52 (d, *J* = 10.0 Hz, 1H, H-1), 4.29 (d, *J* = 3.5 Hz, 1H, H-4), 3.90-3.69 (m, 3H, H-6a, 6b & H-5), 3.74 (t, *J* = 10.0 Hz, 1H, H-2), 1.05 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.5, 135.6, 134.0, 133.3, 132.9, 132.8, 131.2, 130.2, 130.1, 129.2, 128.8, 128.6, 128.5, 128.0, 86.9, 77.3, 75.3, 62.3, 60.3, 59.9, 26.9, 19.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. For $C_{35}H_{36}N_6O_4NaSSi$ 687.2186, found 687.2171.

**Phenyl 3-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (6a).**

Trifluoromethanesulfonic anhydride (2.9 mL, 17.5 mmol) and pyridine (2.9 mL, 37.6 mmol) were added sequentially at -10 $^{o}$C to a stirred solution of **2a** (1.6 g, 2.9 mmol) in $CH_2Cl_2$ (65 mL). Then the reaction mixture was gradually warmed to 10 $^{o}$C. After 2 h, reaction mixture was diluted with $CH_2Cl_2$ and washed successively with 1M HCl, aq. $NaHCO_3$ and brine. Separated organic layer was dried over $Na_2SO_4$ and concentrated.

The crude product so obtained was dissolved in acetonitrile (60 mL) and to this, $TBAN_3$ (0.74 g, 2.6 mmol) was added at -30 °C and this reaction was stirred at the same temperature for 20 h. $TBANO_2$ (2.4 g, 8.6 mmol) was added and the reaction mixture was stirred at rt for 1 h. Reaction mixture was diluted with EtOAc and washed with water. Separated organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (1:9 ethyl acetate: pet ether) to obtain **6a** as a pale yellowish viscous liquid (1.0 g, 60%): $[\alpha]^{25}_{D}$ +11.4 (*c* 0.12, $CHCl_3$); IR ($CHCl_3$) ν 3455, 3019, 2932, 2115, 1748, 1523, 1427, 1364, 1217, 928, 770, 669, 623 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H, ArH), 7.69-7.66 (m, 2H, ArH), 7.64-7.61 (m, 2H, ArH), 7.46-7.37 (m, 6H, ArH), 7.30-7.24 (m, 3H, ArH), 4.77 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 4.47 (d, *J* = 10.0 Hz, 1H, H-1), 4.28 (d, *J* = 2.8 Hz, 1H, H-4), 4.02 (dd, *J* = 11.2, 4.0 Hz, 1H, H-6a), 3.92 (dd, *J* = 11.2, 4.0 Hz, 1H, H-6b), 3.85 (t, *J* = 10.0 Hz, 1H, H-2), 3.61 (bs, 1H, OH), 3.51 (t, *J* = 4.0 Hz, 1H, H-5), 2.17 (s, 3H, $CH_3$), 1.07 (s, 9H, $(CH_3)_3$CSi); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.3, 135.8, 135.7, 133.6, 132.4, 132.0, 131.2, 130.27, 130.23, 129.24, 128.5, 128.1, 128.0, 86.5, 76.7, 75.8, 68.4, 65.2, 59.2, 26.8,

21.2, 19.2; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. For $C_{30}H_{35}N_3O_5NaSSi$ 600.1964, found 600.1980.

**Phenyl 2-Azido-3-*O*-benzoyl-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (6b).**

The same procedure as described for **6a** was followed for double serial displacement of **2b** (0.14 g, 0.23 mmol) to obtain **6b** as a pale yellowish viscous liquid (89 mg, 61%): $[\alpha]^{25}_D$ +36.6 (*c* 0.61, $CHCl_3$); IR ($CHCl_3$) ν 3464, 3019, 2931, 2115, 1721, 1602, 1428, 1268, 1216, 1113, 929, 770, 669, 622, 505 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.8 Hz, 2H, ArH), 7.76-7.55 (m, 7H, ArH), 7.47-7.36 (m, 8H, ArH), 7.33-7.24 (m, 3H, ArH), 4.98 (dd, *J* = 10.0, 2.8 Hz, 1H, H-3), 4.55 (d, *J* = 10.0 Hz, 1H, H-1), 4.44 (d, *J* = 2.8 Hz, 1H, H-4), 4.05-3.93 (m, 3H, H-6a, 6b & H-2), 3.60 (t, *J* = 4.0 Hz, 1H, H-5), 3.33 (bs, 1H, OH) 1.06 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.9, 135.8, 135.7, 133.7, 133.5, 132.5, 132.2, 131.5, 130.24, 130.21 130.1, 129.4, 129.2, 128.6, 128.5, 128.12, 128.09, 86.8, 77.5, 76.6, 68.2, 64.9, 59.7, 26.9, 19.2; HRMS calcd for $C_{35}H_{37}O_5SN_3Si$ $[M + Na]^+$ 662.2121, found 662.2112.

**Phenyl 3-*O*-Acetyl-4-azido-4-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (8a).**

Trifluoromethanesulfonic anhydride (0.27 mL, 1.62 mmol) and pyridine (0.28 mL, 3.5 mmol) were added sequentially at -10 °C to a stirred solution of **2a** (0.15 g, 0.27 mmol) in $CH_2Cl_2$ (8 mL). Then the reaction mixture was gradually warmed to 10 °C. After 2 h, it was diluted with $CH_2Cl_2$ and washed successively with 1M HCl, aq. $NaHCO_3$ and brine. Separated organic layer was dried over $Na_2SO_4$, concentrated.

The crude product so obtained was dissolved in acetonitrile (3 mL) and to this, $TBANO_2$ (0.23 g, 0.8 mmol) was added at 0 °C and this reaction was stirred at the

same temperature for 30 min. After that, $TBAN_3$ (0.23 g, 0.8 mmol) was added at 0 °C and the reaction mixture was brought to rt. After stirring at rt for 3 h, reaction mixture was diluted with EtOAc and washed with water. Separated organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (1:9 ethyl acetate: pet ether) to obtain **8a** as a pale yellowish viscous liquid (84 mg, 54%): $[\alpha]^{20}_D$ +3.9 (*c* 1.47, $CHCl_3$); IR ($CHCl_3$) ν 2929, 2851, 2109, 1744, 1218, 1113, 768, 702 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 4H, ArH), 7.50-7.38 (m, 9H, ArH), 7.29-7.27 (m, 2H, ArH), 5.07 (dd, *J* = 9.6, 3.4 Hz, 1H, H-3), 4.50 (d, *J* = 9.6 Hz, 1H, H-1), 4.19 (d, *J* = 3.4 Hz, 1H, H-4), 3.85-3.76 (m, 3H, H-2, H-6a & H-6b), 3.70 (t, *J* = 6.4 Hz, 1H, H-5), 2.19 (s, 3H, $CH_3$), 1.06 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.6, 135.7, 133.0, 132.9, 132.8, 131.6, 130.1, 129.2, 128.4, 128.0, 89.3, 77.28, 76.0, 67.5, 62.4, 60.3, 26.9, 20.9, 19.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{30}H_{35}N_3O_5NaSSi$, 600.1964, found 600.1965.

**Phenyl 4-Azido-3-*O*-benzoyl-4-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (8b).**

The same procedure as described for **8a** was followed for a double serial inversion of **2b** (0.24 g, 0.4 mmol) to obtain **8b** as a pale yellowish viscous liquid (0.14 g, 56%): $[\alpha]^{20}_D$ -28.2 (*c* 0.95, $CHCl_3$); IR ($CHCl_3$) ν 2929, 2111, 1726, 1216, 1113, 768, 669 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 2H, ArH), 7.68-7.58 (m, 5H, ArH), 7.52-7.36 (m, 10H, ArH), 7.30-7.27 (m, 3H, ArH), 5.40 (dd, *J* = 9.6, 3.6 Hz 1H, H-3), 4.59 (d, *J* = 9.6 Hz, 1H, H-1), 4.28 (d, *J* = 3.6 Hz, 1H, H-4), 3.97 (t, *J* = 9.6 Hz, 1H, H-5), 3.89-3.77 (m, 3H, H-5, H-6a & H-6b), 1.06 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.2, 135.7, 133.8, 133.0, 132.8, 131.8, 130.3, 130.1, 129.2,

129.1, 128.7, 128.3, 128.0, 89.5, 77.4, 76.2, 68.0, 62.4, 60.8, 27.0, 19.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{35}H_{37}N_3O_5NaSSi$, 662.2121, found 662.2158.

**Phenyl 4-*O*-Acetyl-2-azido-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (9).**

Trifluoromethanesulfonic anhydride (0.73 mL, 4.3 mmol) and pyridine (0.75 mL, 9.3 mmol) were added sequentially at -10 $^oC$ to a stirred solution of **2a** (0.4 g, 0.72 mmol) in $CH_2Cl_2$ (20 mL). Then the reaction mixture was gradually warmed to 10 $^oC$ over 2 h. After complete consumption of starting material, the reaction mixture was diluted with $CH_2Cl_2$ and washed successively with 1M HCl, aq. $NaHCO_3$ and brine. Separated organic layer was dried over $Na_2SO_4$, and concentrated.

The crude product which was obtained after removal of solvents was dissolved in acetonitrile (30 mL) and to this, $TBAN_3$ (0.2 g, 0.72 mmol) was added at -30 °C and the reaction was stirred at the same temperature for 20 h. Reaction mixture was concentrated to 4 mL and to this, water (0.28 mL, 15.9 mmol) was added and the reaction mixture was kept for reflux at 65 °C for 1 h. The reaction mixture was diluted with EtOAc and washed with water. Separated organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo.* The crude product was purified by column chromatography on silica gel (1:9 ethyl acetate: pet ether) to obtain **9** as a pale yellowish viscous liquid (0.23 g, 56%): $[\alpha]^{20}_D$ -2.5 (*c* 0.56, $CHCl_3$); IR ($CHCl_3$) ν 2930, 2857, 2113, 1744, 1472, 1373, 1233, 1112, 758, 703, 504 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 6H, ArH), 7.57-7.37 (m, 6H, ArH), 7.29-7.27 (m, 3H, ArH), 5.43 (d, *J* = 3.2 Hz, 1H, H-4), 4.46 (d, *J* = 10.0 Hz, 1H, H-1), 3.80-3.77 (m, 2H, H-3 & H-5), 3.75-3.68 (m, 2H, H-6a & H-6b), 3.48 (t, *J* = 10.0 Hz, 1H, H-2), 2.01 (s, 3H, $CH_3$), 1.04 (s, 9H, $(CH_3)_3CSi$); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 171.7, 135.7, 133.1, 133.0, 132.9, 131.9, 130.08, 130.04, 129.1, 128.3, 128.0, 127.97,

127.96, 86.8, 77.3, 73.5, 69.1, 62.6, 61.6, 26.9, 20.8, 19.2; HR-ESI-MS (*m/z*): [M + Na]$^+$ calcd. for $C_{30}H_{35}N_3O_5NaSSi$, 600.1964; found, 600.1940.

**Phenyl 4-*O*-Acetyl-2-azido-3-*O*-chloroacetyl-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (10).**

To a clear solution of **9** (0.4 g, 0.69 mmol) in $CH_2Cl_2$ (4 mL), ClAcCl (0.16 mL, 2.0 mmol), and pyridine (0.0.16 mL, 2.0 mmol) were added at 0 °C. After 30 min, the reaction mixture was concentrated *in vacuo* and chromatographed on silica gel (8% ethyl acetate: pet ether) to obtain desired product **10** as a foam (0.38 g, 85%): $[\alpha]^{20}_D$ -21.0 (*c* 0.63, $CHCl_3$); IR ($CHCl_3$) ν 3019, 2929, 2126, 1745, 1216, 1045, 760, 670 cm$^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63-7.55 (m, 6H, ArH), 7.46-7.36 (m, 6H, ArH), 7.35-7.27 (m, 3H, ArH), 5.52 (d, *J* = 3.0 Hz, 1H, H-4), 4.92 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3), 4.51 (d, *J* = 10.0 Hz, 1H, H-1), 4.03 (d, *J* = 1.4 Hz, 2H, $CH_2$ of ClAc), 3.80-3.74 (m, 2H), 3.66-3.60 (m, 2H) 1.96 (s, 3H, $CH_3$), 1.07 (s, 9H, $(CH_3)_3$CSi); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.2, 166.4, 135.76, 135.75, 133.4, 132.9, 132.8, 131.4, 130.0, 129.2, 128.6, 128.0, 86.9, 77.1, 75.2, 66.3, 61.4, 59.7, 40.6, 26.8, 20.7, 19.2; HR-ESI-MS (*m/z*): [M + Na]$^+$ calcd. for $C_{32}H_{36}N_3O_6NaSSiCl$, 676.1680; found, 676.1728.

**Phenyl 4-*O*-Acetyl-2-azido-3-*O*-chloroacetyl-2-deoxy-1-thio-*β*-D-galactopyranoside (11).**

A solution of TBAF (0.18 mL, 0.18 mmol) and AcOH (20 µL, 0.35 mmol) with pH 7 was added at 0 $^o$C to a solution of **10** (24 mg, 0.035 mmol) in THF (1 mL) and the reaction mixture was stirred at the same temperature overnight. After complete consumption of starting material solvents were removed *in vacuo* and the residue was chromatographed on silica gel (40% ethyl acetate: pet ether) to obtain **11** as a pale yellowish liquid (12 mg, 82%): $[\alpha]^{20}_D$ -12.2 (*c* 0.36, $CHCl_3$); IR ($CHCl_3$) ν 2926, 2854, 2114, 1745, 1375, 1232, 1077, 758 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61-

7.58 (m, 2H, ArH), 7.37-7.35 (m, 3H, ArH), 5.36 (d, *J* = 3.2 Hz, 1H, H-4), 4.93 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.56 (d, *J* = 10.0 Hz, 1H, H-1), 4.03 (d, *J* = 1.8 Hz, 2H, $CH_2$ of ClAc), 3.78-3.69 (m, 3H), 3.53-3.50 (m, 1H), 2.11 (s, 3H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.0, 166.4, 133.6, 131.0, 129.3, 128.9, 86.8, 77.4, 74.8, 67.1, 61.0, 59.8, 40.5, 20.7; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{16}H_{18}N_3O_6NaSCl$, 438.0503; found, 438.0509.

**Phenyl 2-Azido-3-*O*-benzoyl-2,4,6-trideoxy-4-phthalimido-α-D-galactopyranosyl-(1→4)-3-*O*-acetyl-2-azido-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-galactopyranoside (13).** Bromine (26 µL, 0.49 mmol) was added to a solution of **12** (0.11 g, 0.22 mmol) in $CH_2Cl_2$ (3 mL) at 0 °C. After 90 min, toluene was added, the mixture was concentrated and the residue was co-evaporated twice with toluene.

A solution of acceptor **6a** (65 mg, 0.11 mmol) in $CH_2Cl_2$ (1 mL) was added to a suspension of glycosyl bromide, 3 Å MS (0.25 g) and sym. collidine (28 µL, 0.2 mmol) in $CH_2Cl_2$ (1 mL) and kept stirring at -30 °C for 30 min. Then, silver triflate (0.11 g, 0.45 mmol) was added and stirring was continued at the same temperature. After 2 h, triethylamine was added and the reaction mixture was diluted with $CH_2Cl_2$, filtered through celite, and concentrated. The residue was purified by column chromatography on silica gel (20% ethyl acetate: pet ether) to obtain the desired product **13** as a foam (57 mg, 81%): $[\alpha]^{20}_D$ +184.2 (*c* 1.67, $CHCl_3$); IR ($CHCl_3$) ν 2930, 2857, 2111, 1720, 1365, 1329, 1266, 1218, 1106, 1067, 758, 724, 504 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H, ArH), 7.81 (bs, 2H, ArH) 7.73-7.62 (m, 9H, ArH), 7.52-7.29 (m, 11H, ArH), 5.48 (dd, *J* = 11.0, 6.7 Hz, 1H, H-3'), 5.19 (d, *J* = 4.0 Hz, 1H, H-1'), 5.06 (d, *J* = 6.7, 3.7 Hz, 1H, H-4'), 4.88 (dd, *J* = 11.0, 4.0 Hz, 1H, H-2'), 4.83 (dd, *J* = 10.0, 2.6 Hz, 1H, H-3), 4.40 (d, *J* = 10.0 Hz, 1H, H-1), 4.29 (qd, *J* = 6.5, 3.7 Hz, 1H, H-5'), 4.27 (d, *J* = 2.6 Hz, 1H, H-4), 4.13-4.10 (m, 1H, H-

6b), 4.08-3.94 (m, 1H, H-6a), 3.64-3.57 (m, 2H, H-2, H-5), 2.13 (s, 3H, $CH_3$), 1.09 (s, 9H, $(CH_3)_3$CSi), 0.98 (d, *J* = 6.5 Hz, 3H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.7, 165.1, 135.8, 135.7, 134.6, 134.3, 133.7, 133.1, 130.2, 130.17, 130.10, 129.8, 129.2, 128.9, 128.6, 128.1, 128.0, 123.7, 99.0, 85.7, 79.0, 74.8, 73.6, 70.1, 63.9, 61.6, 60.0, 59.5, 52.0, 27.0, 21.3, 19.3, 16.7; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{51}H_{51}N_7O_{10}NaSSi$, 1004.3085; found, 1004.3015.

***N*-(Benzyloxycarbonyl)-*O*-(4-*O*-acetyl-2-azido-3-*O*-chloroacetyl-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-α-D-galactopyranosyl)-L-serine methylester (15)**.

$Tf_2O$ (19 µL, 0.11 mmol) was added at -60 °C to a cooled solution of **10** (0.05 g, 0.08 mmol) and $Ph_2SO$ (0.05 g, 0.22 mmol) in $CH_2Cl_2$ (4 mL). After 10 min, L-serine derivative **14** (0.04 g, 0.16 mmol) in $CH_2Cl_2$ (1 mL) was added slowly. After stirring the reaction mixture at the same temperature for 1 h, it was diluted with $CH_2Cl_2$ and washed with aq. $NaHCO_3$ and brine. Separated organic layer dried over $Na_2SO_4$, concentrated and chromatographed on silica gel (25% ethyl acetate: pet ether) to afford the desired product **15** as a foam (0.05 g, 74%): $[\alpha]^{20}_D$ +52.6 (*c* 1.83, $CHCl_3$); IR ($CHCl_3$) ν 3018, 2929, 2113, 1749, 1216, 1046, 759, 668 $cm^{-1}$;$^1$H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 5H, ArH), 7.44-7.31 (m, 10H, ArH), 5.66 (d, *J* = 8.4 Hz, 1H, NH), 5.59 (d, *J* = 3.2 Hz, 1H, H-4), 5.36 (dd, *J* = 11.0, 3.2 Hz, 1H, H-3 ), 5.09 (ABq, *J* = 11.3, 5.4 Hz, 2H, $CH_2$), 4.91 (d, *J* = 3.6 Hz, 1H, H-1), 4.58-4.55 (m, 1H, -CH), 4.09-4.02 (m, 5H, H-5, -$CH_2$, -$CH_2$), 3.79 (s, 3H), 3.75-3.63 (m, 1H, H-6a), 3.61-3.54 (m, 2H, H-2, H-6b), 1.98 (s, 3H, $CH_3$), 1.01 (s, 9H, $(CH_3)_3$CSi); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 166.4, 156.2, 136.1, 135.72, 135.71, 132.9, 132.8, 130.8, 130.08, 130.05, 128.7, 128.4, 128.3, 128.0, 99.2, 70.3, 69.5, 67.4, 67.2, 61.2, 57.6, 54.4, 53.0, 40.6 26.8, 20.7, 19.1; HRMS calcd for $C_{38}H_{46}O_{11}SiClN_4$ $[M + H]^+$ 797.2621, found 797.2600.

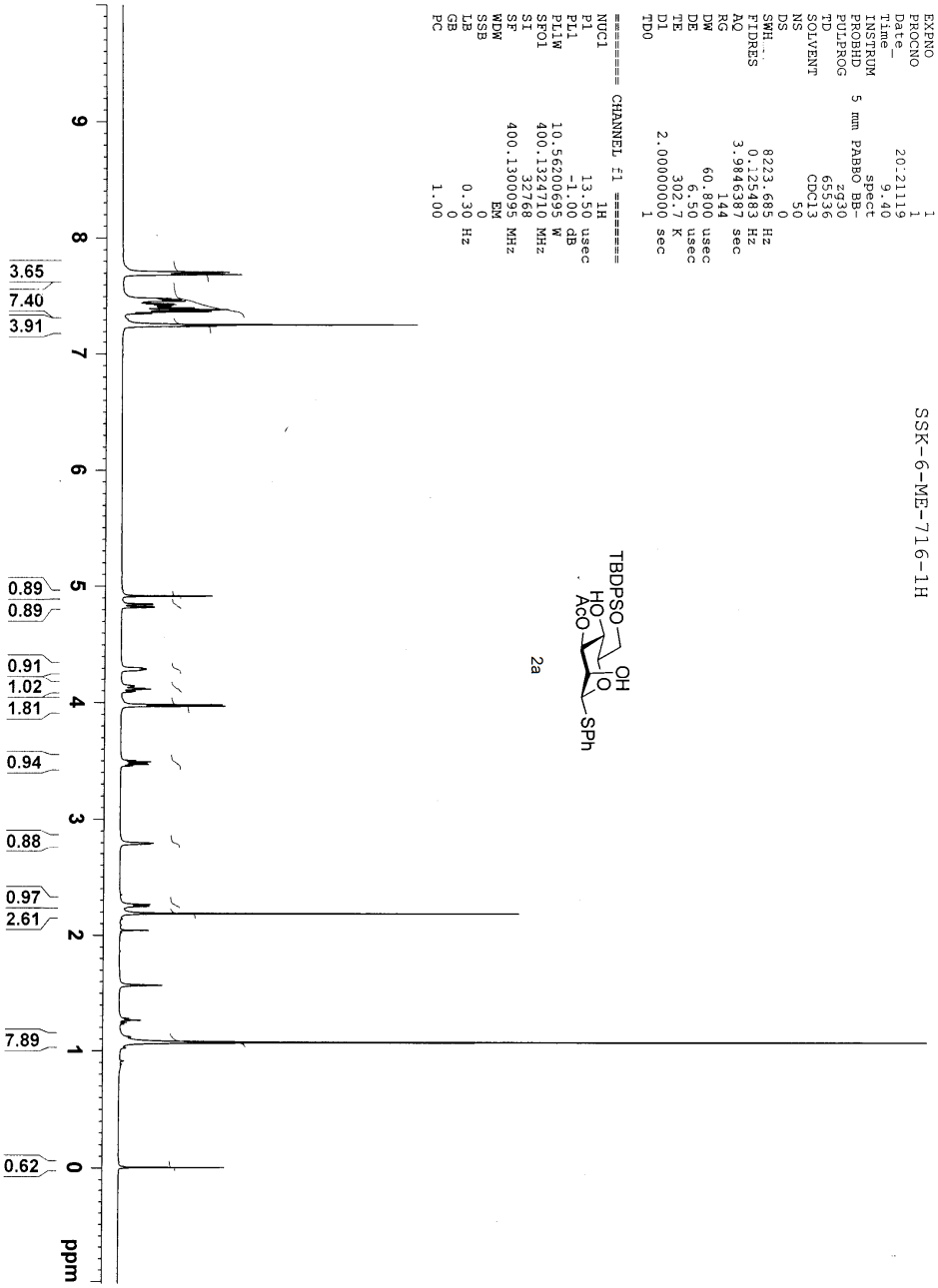
***N*-(Benzyloxycarbonyl)-*O*-(4-*O*-acetyl-2-azido-2-deoxy-6-*O*-*t*-butyldiphenylsilyl-*α*-D-galactopyranosyl)-L-serine methylester (16)**.

Thiourea (0.15 g. 1.9 mmol) was added to a clear solution of **15** (0.23 g, 0.28 mmol) in pyridine (2.8 mL) and EtOH (2.8 mL) and the reaction mixture was kept for reflux at 80 $^{o}$C. After 30 min, solvents were removed and the crude product was chromatographed on silica gel (30% ethyl acetate: pet ether) to afford **16** as a viscous liquid (0.15 g, 78%): $[\alpha]^{20}_{D}$ +30.2 (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) ν 3018, 2975, 2112, 1735, 1427, 1216, 1047, 758, 669 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 5H, ArH), 7.42-7.31 (m, 10H, ArH), 5.68 (d, *J* = 8.4 Hz, 1H, NH), 5.47 (d, *J* = 3.0 Hz, 1H, H-4), 5.12-5.03 (m, 2H, -$CH_2$), 4.86 (d, *J* = 3.6 Hz, 1H, H-1), 4.57-4.55 (m, 1H, -CH), 4.22 (dd, *J* = 10.6, 3.0 Hz, 1H, H-3 ), 4.02-3.90 (m, 3H, H-5, -$CH_2$), 3.78 (s, 3H, $CH_3$), 3.74-3.58 (m, 2H, H-6a, H-6b), 3.40 (dd, *J* = 10.6, 3.6 Hz, 1H, H-2), 2.01 (s, 3H, $CH_3$), 1.02 (s, 9H, *(CH$_3$)$_3$*CSi); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.4, 156.1, 135.7, 133.0, 132.9, 130.1, 130.0, 128.7, 128.4, 128.3, 128.0, 99.3, 70.1, 69.7, 69.4, 67.5, 67.4, 61.4, 60.2, 54.4, 53.0, 26.8, 20.9, 19.2; HRMS calcd for $C_{36}H_{44}O_{10}SiN_4$ $[M + Na]^+$ 743.2719, found 743.2706.

***N*-(Benzyloxycarbonyl)-*O*-(4-*O*-acetyl-2-azido-3-*O*-chloroacetyl-2-deoxy-*α*-D-galactopyranosyl)-L-serine methylester (17)**.

A solution of TBAF (4.2 mL, 4.2 mmol) and AcOH (0.48 mL, 8.27 mmol) with pH 7 was added at 0 $^{o}$C to a clear solution of **15** (0.156 g, 0.195 mmol) in THF (22 mL) and the reaction mixture was stirred at the same temperature overnight. After complete consumption of starting material, solvents were removed in vacuum and chromatographed to obtain **17** as a pale yellowish liquid (0.33 mg, 72%): $[\alpha]^{20}_{D}$ +126.5 (*c* 6.63, $CHCl_3$); IR ($CHCl_3$) ν 3016, 2955, 2113, 1746, 1524, 1438, 1235, 1068, 754, 667 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H, ArH), 6.02 (d,

*J* = 8.0 Hz, 1H, NH), 5.40 (d, *J* = 3.0 Hz, 1H, H-4), 5.32 (dd, *J* = 11.0, 3.0 Hz, 1H, H-3), 5.12 (s, 2H, -$CH_2$), 5.01 (d, *J* = 3.4 Hz, 1H, H-1), 4.58-4.56 (m, 1H, -CH), 4.15-4.04 (m, 5H, H-5, -$CH_2$, -$CH_2$), 3.78 (s, 3H, $CH_3$), 3.74-3.73 (m, 2H, H-2, H-6a), 3.65-3.57 (m, 1H, H-6b), 2.12 (s, 3H, $CH_3$); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.4, 166.5, 156.1, 136.2, 128.7, 128.3, 99.2, 70.7, 69.8, 69.7, 67.9, 67.4, 60.9, 57.6, 54.5, 53.1, 40.6, 20.8; HRMS calcd for $C_{22}H_{27}O_{11}ClN_4$ $[M + Na]^+$ 581.1263, found 581.1269.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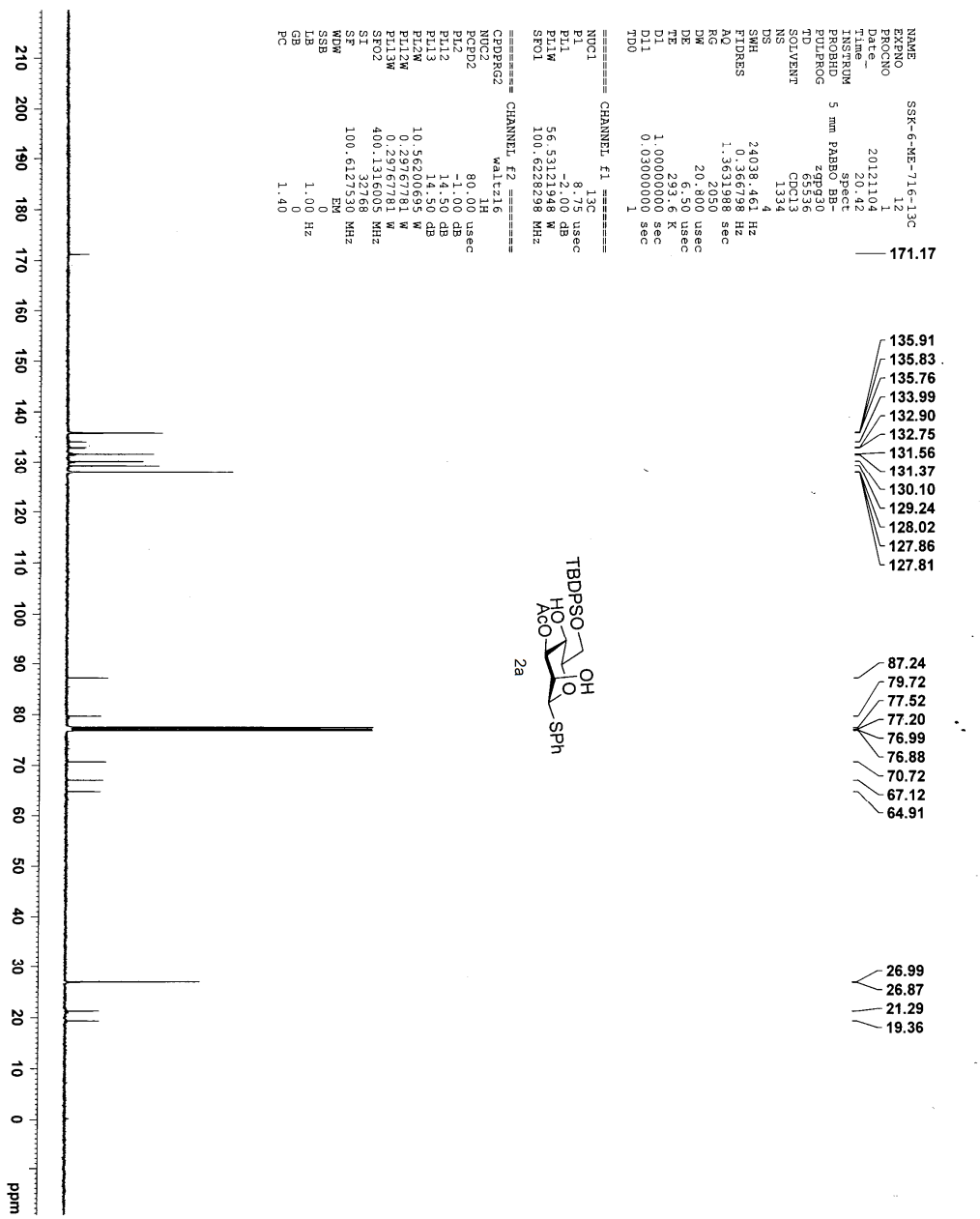

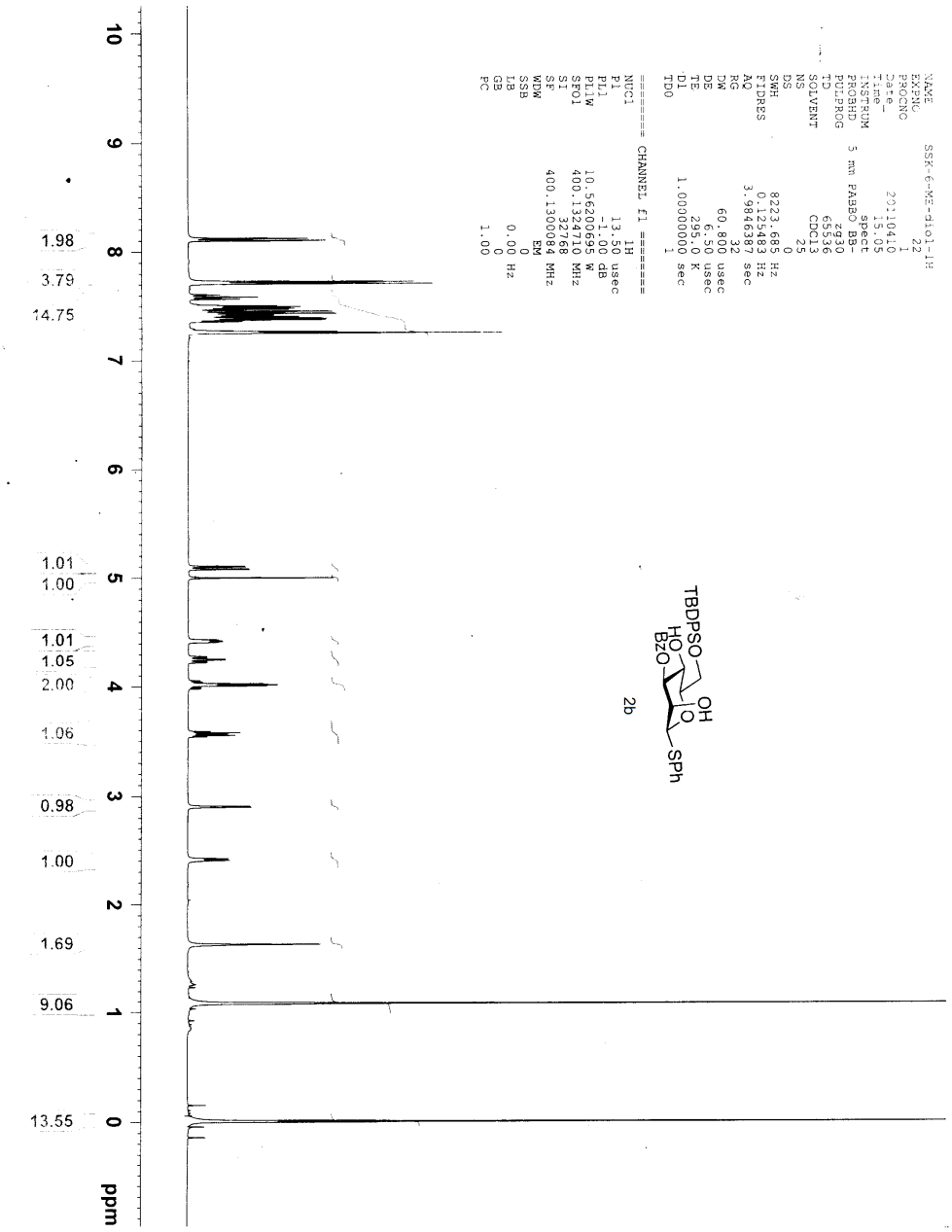

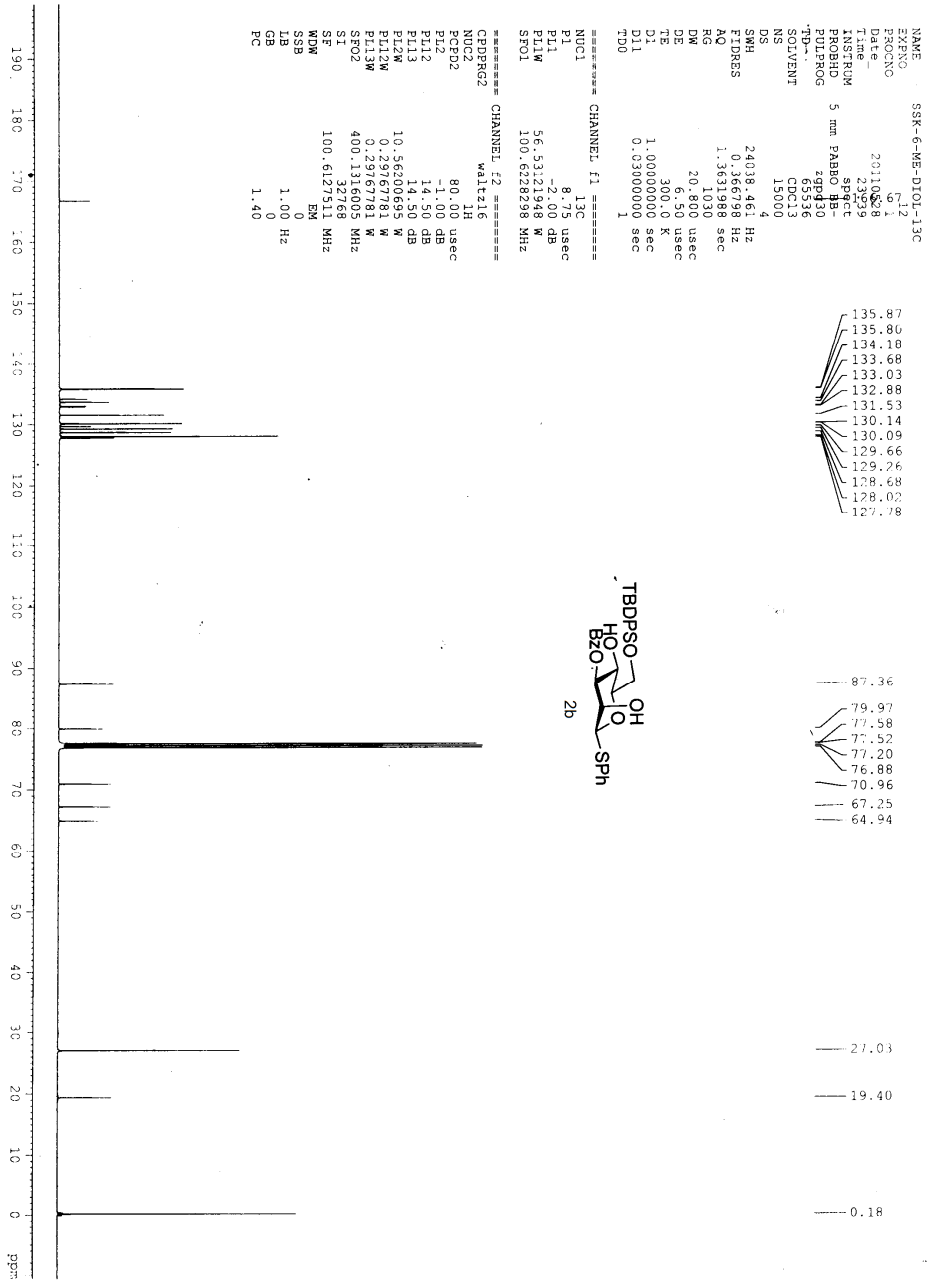
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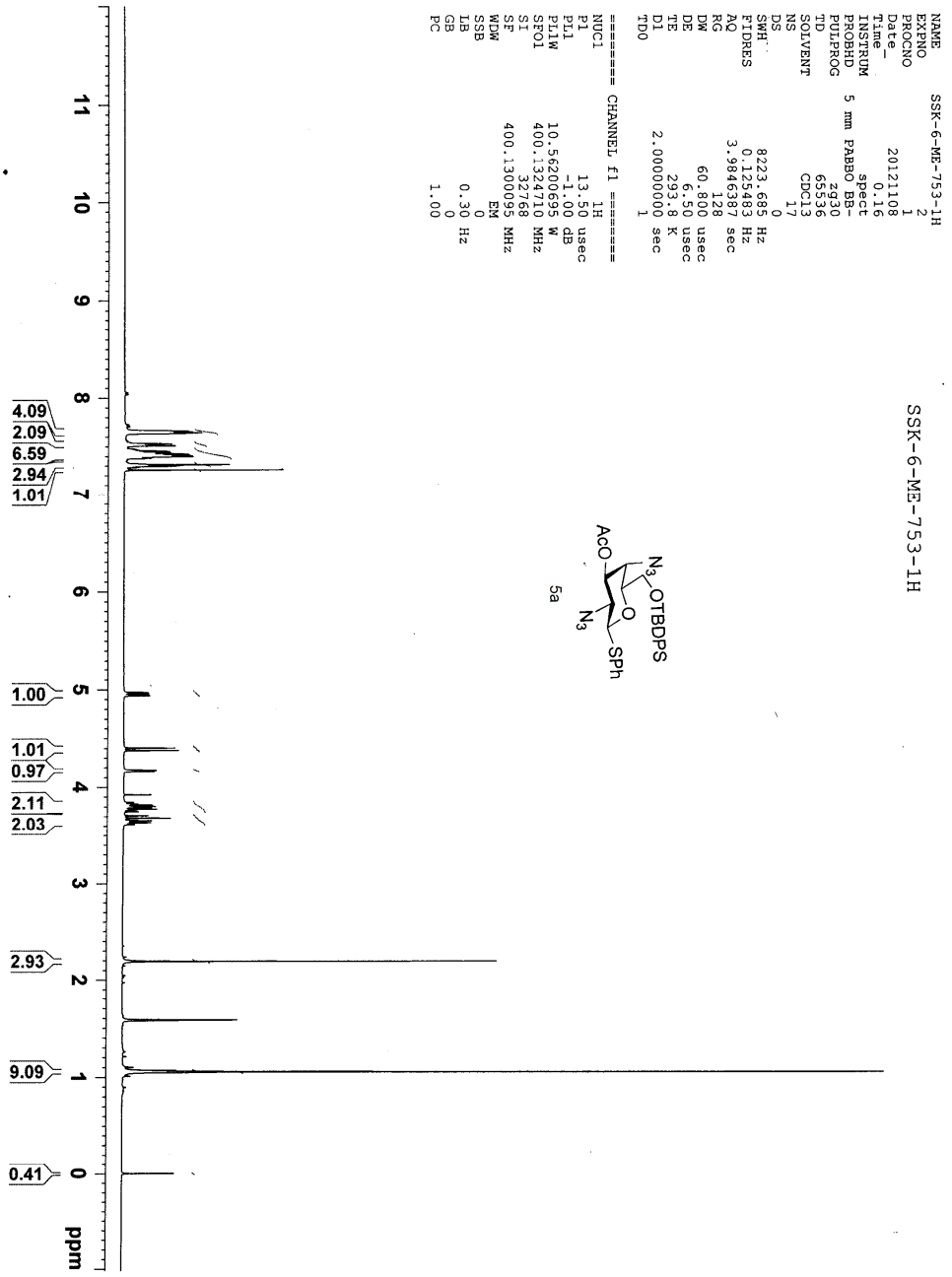
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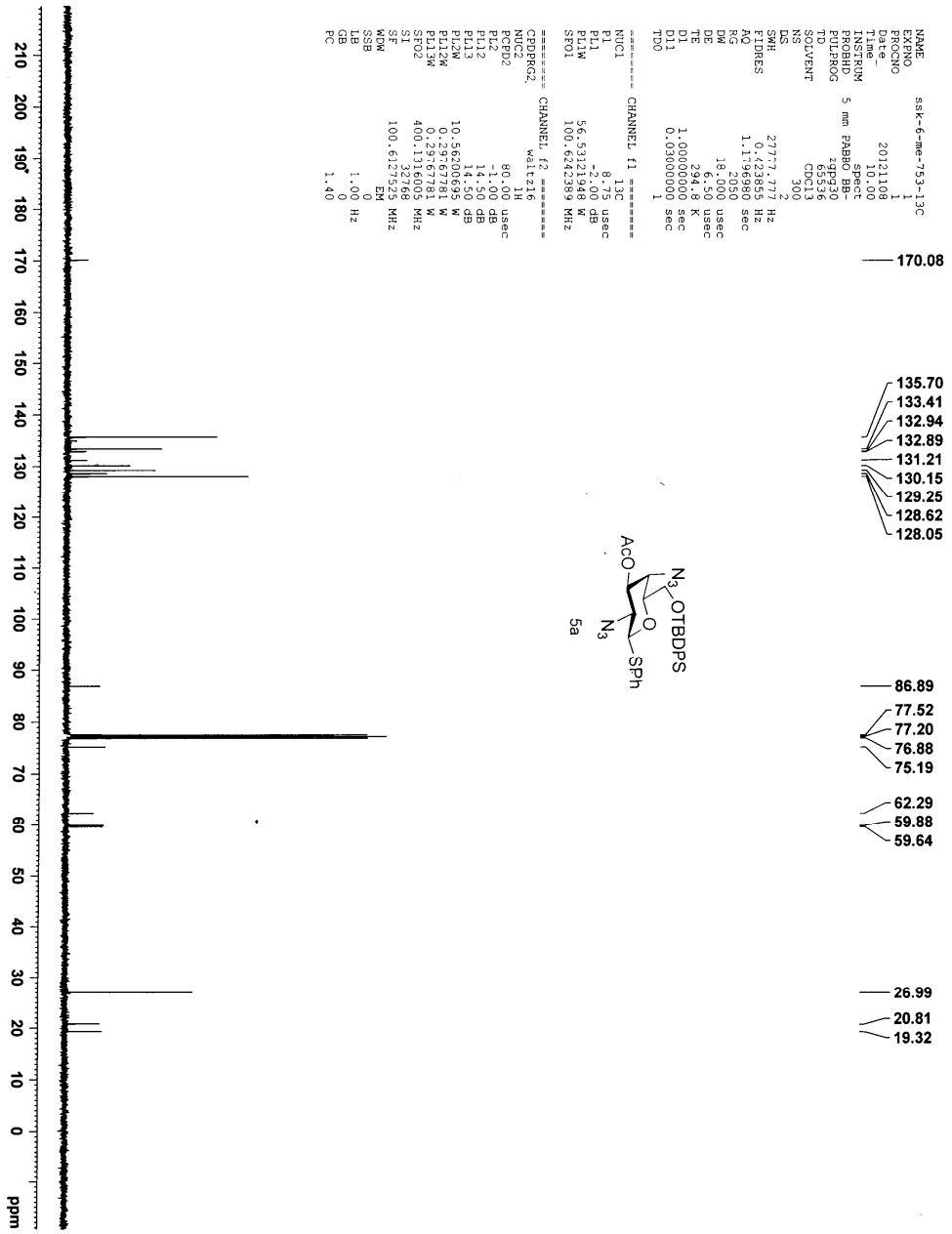

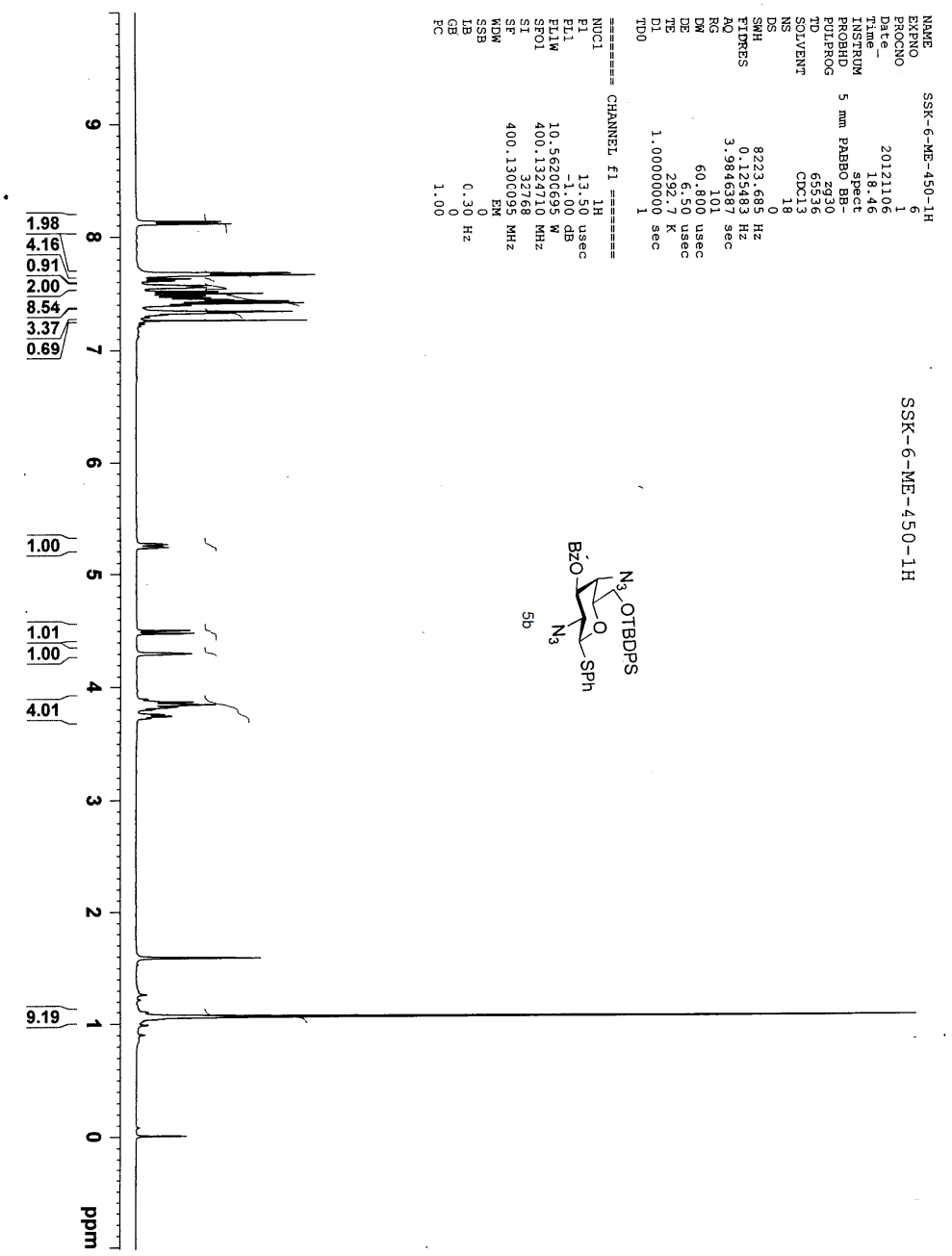

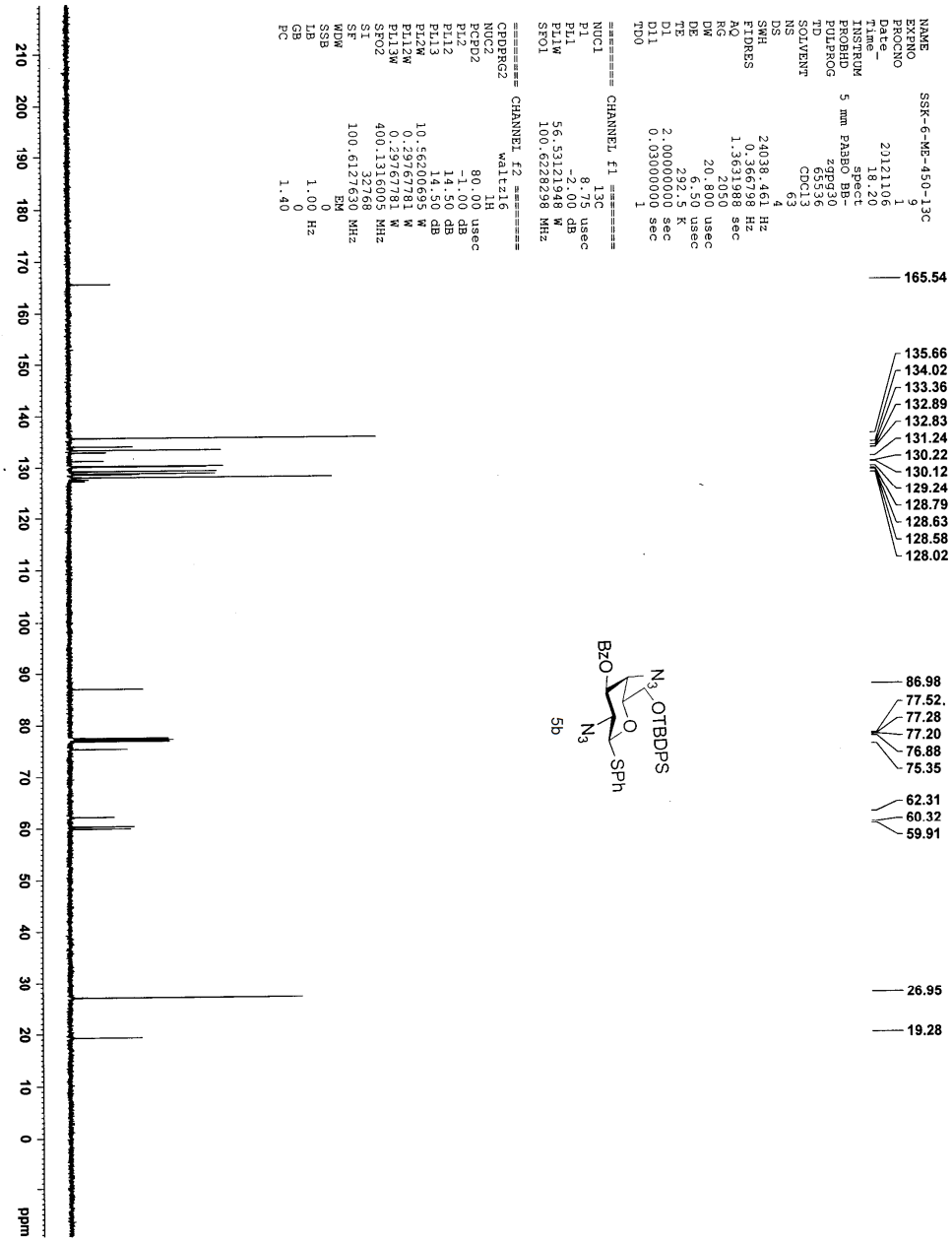

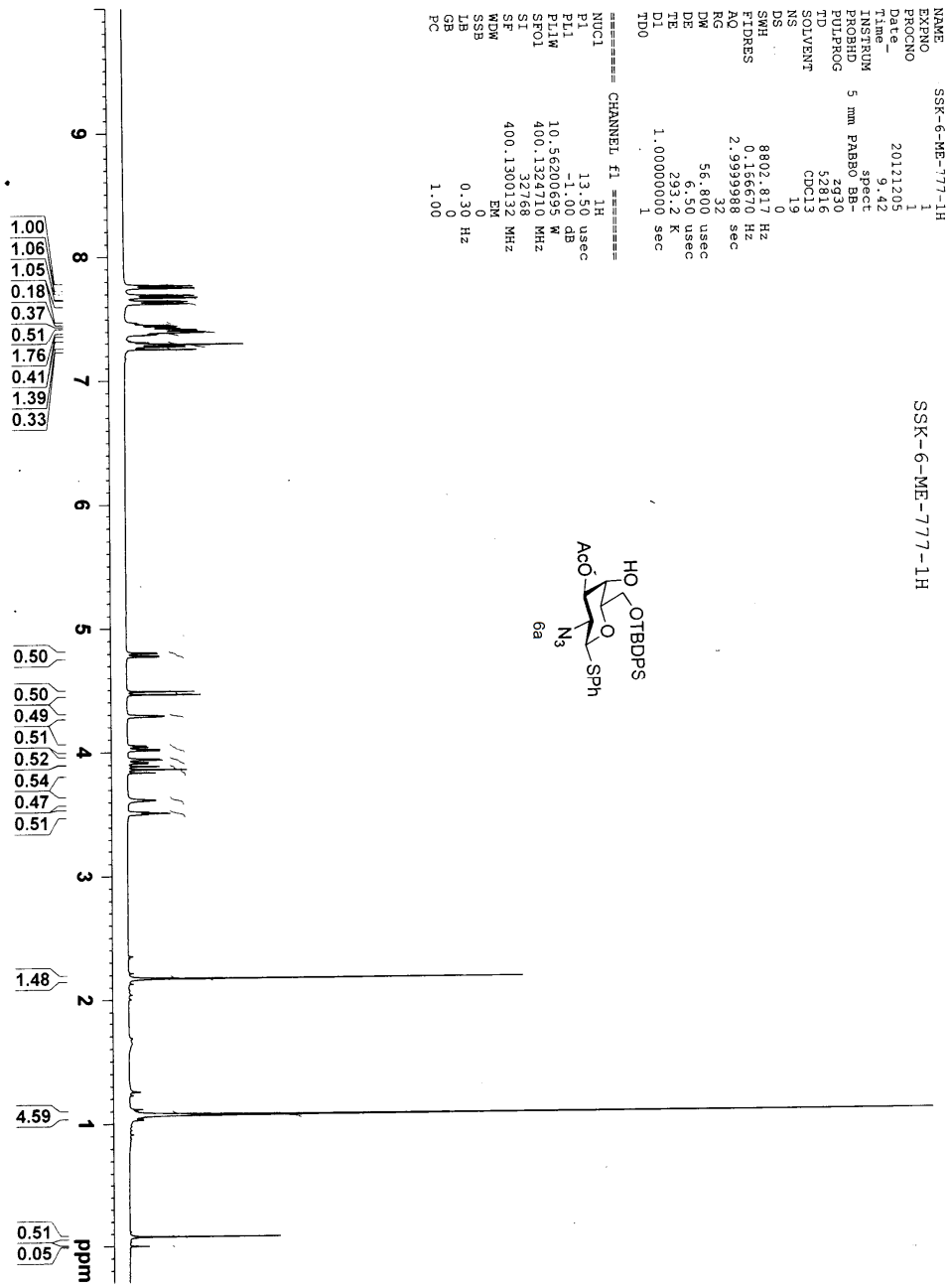

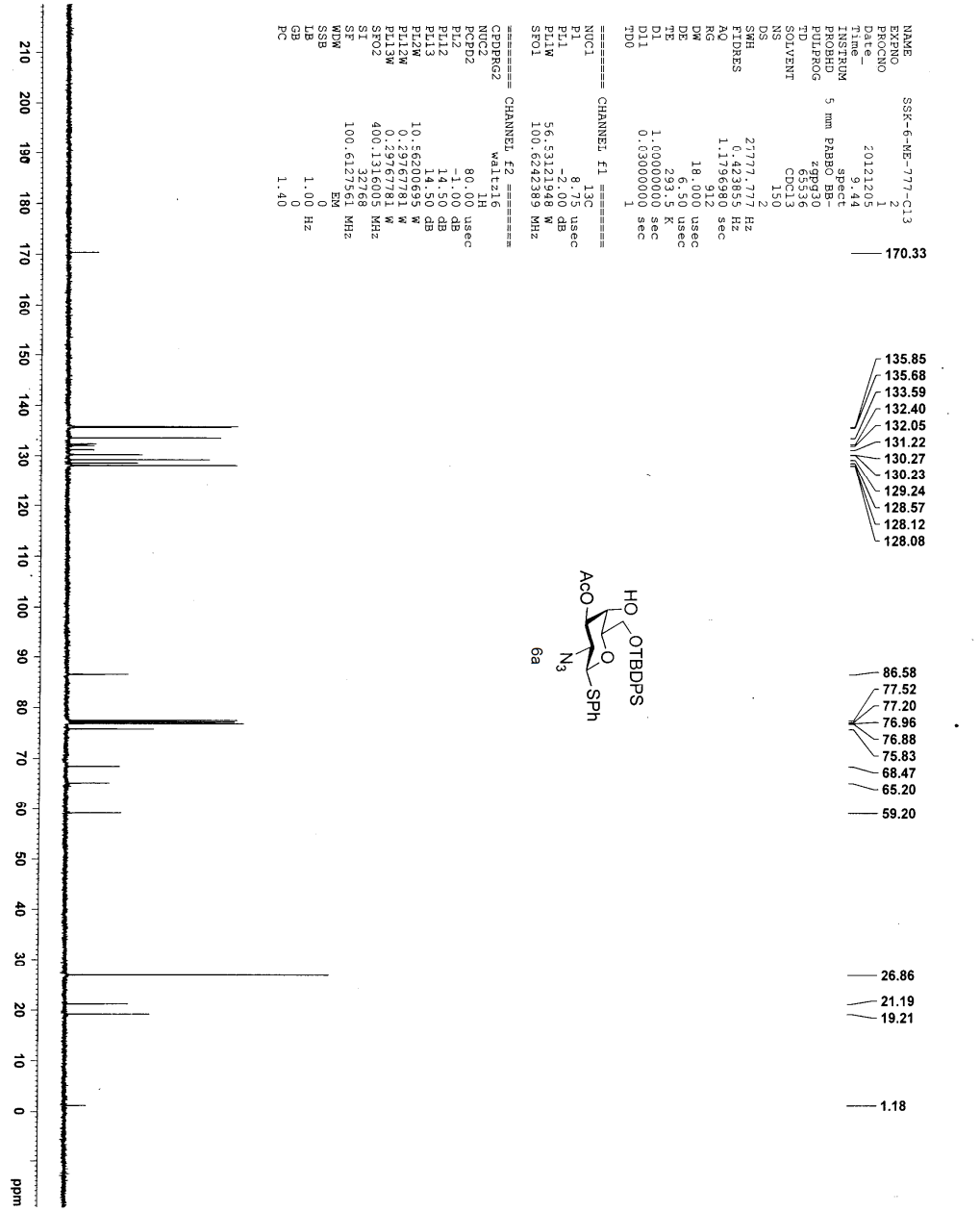

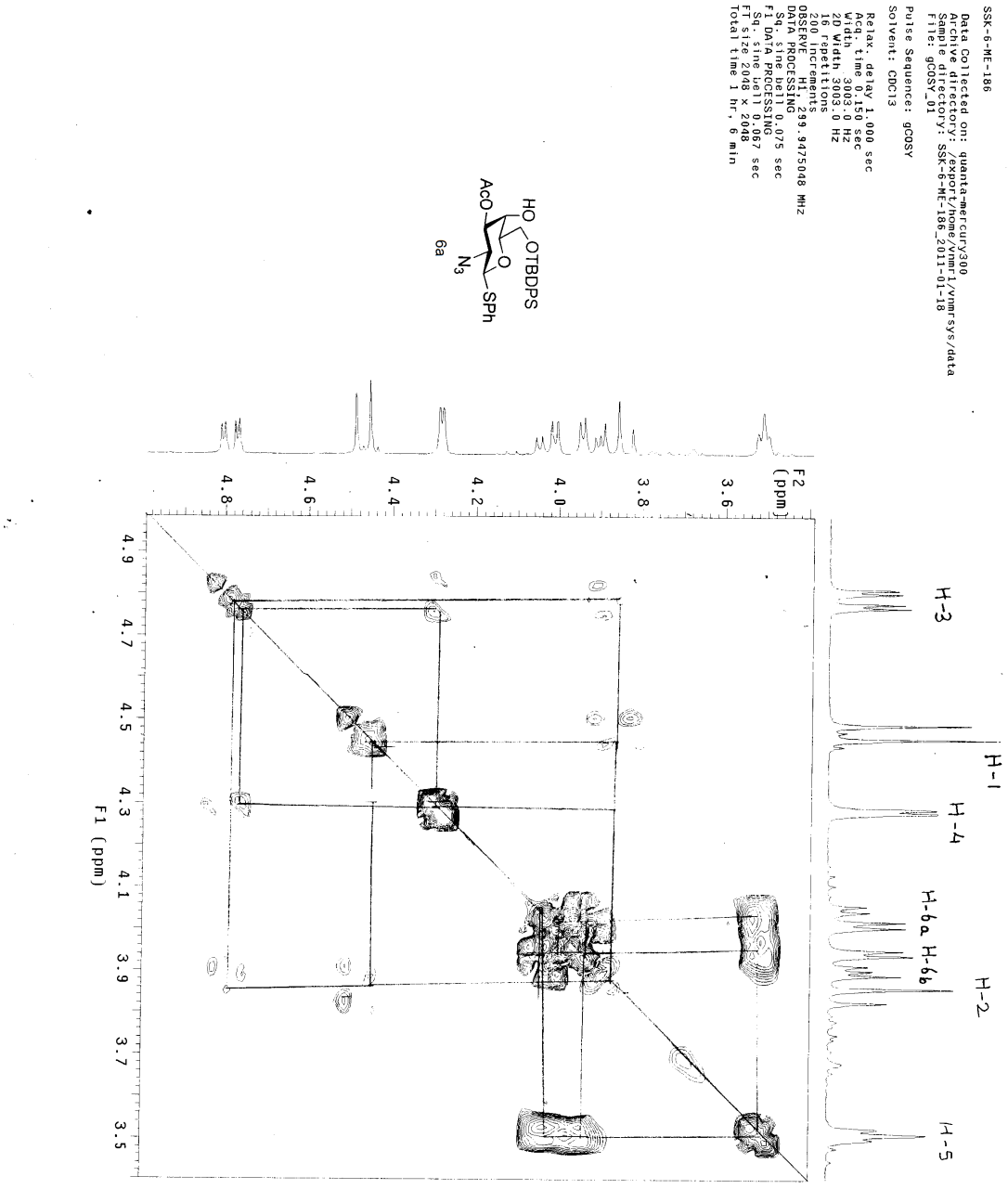
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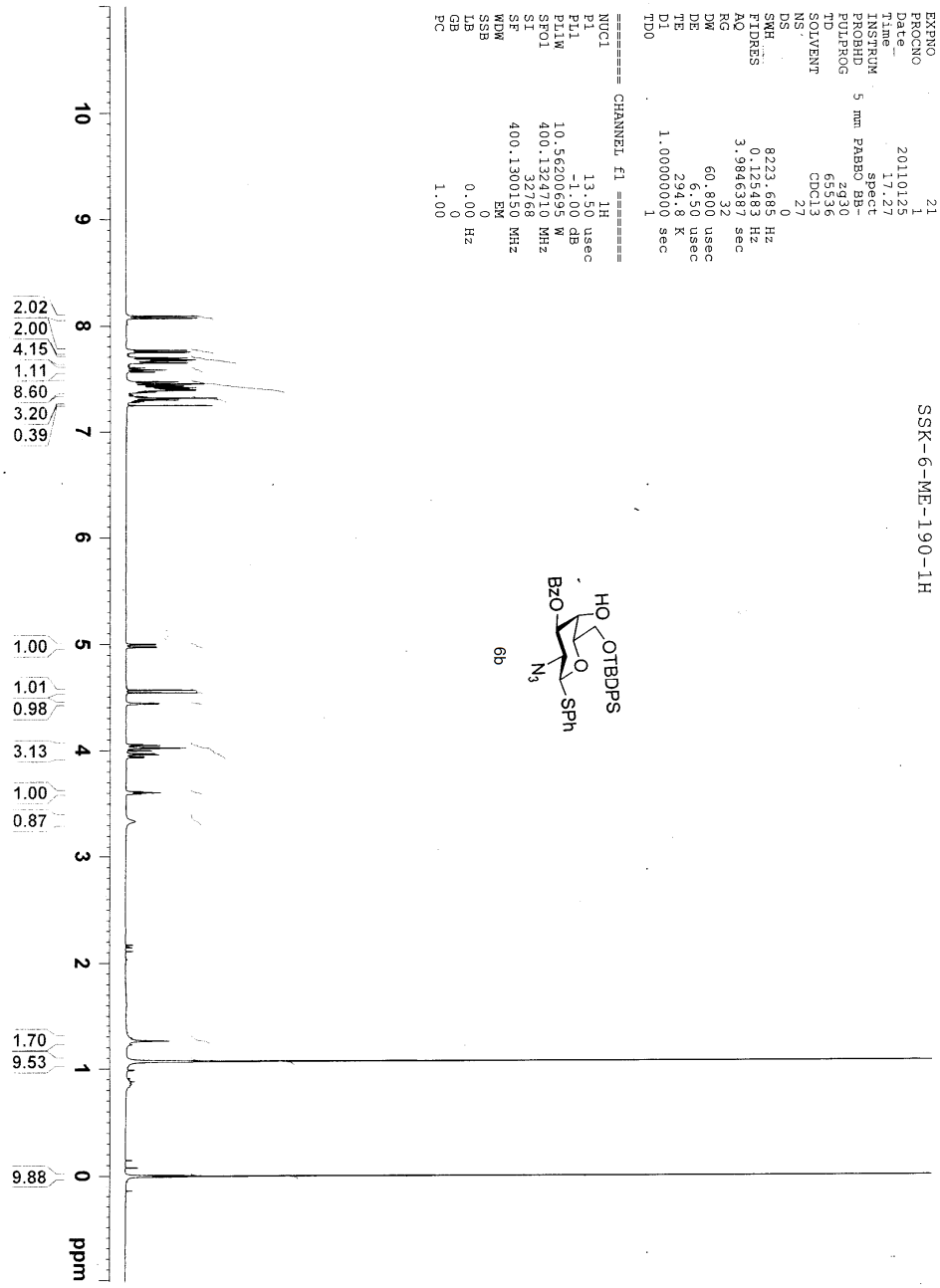

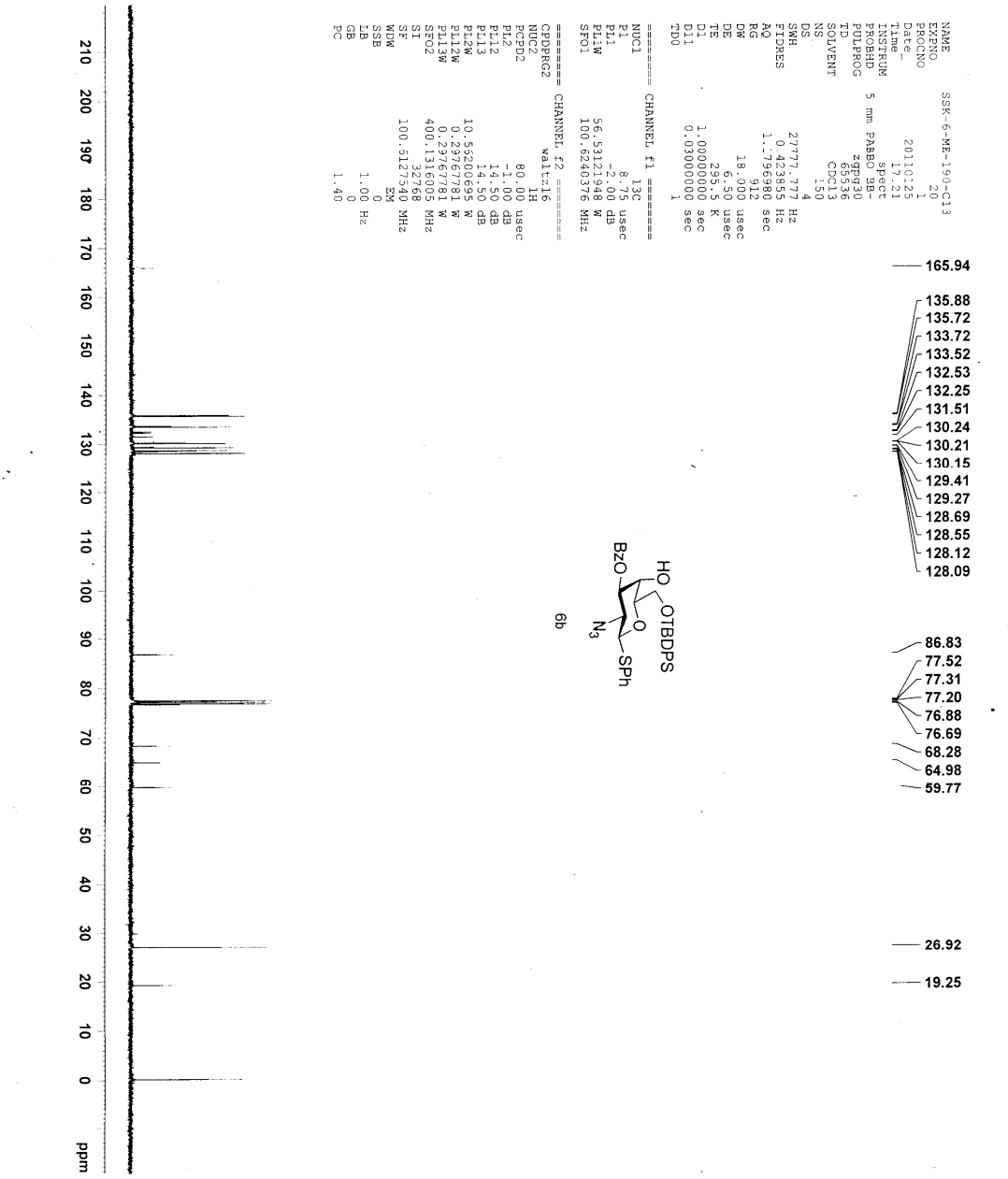
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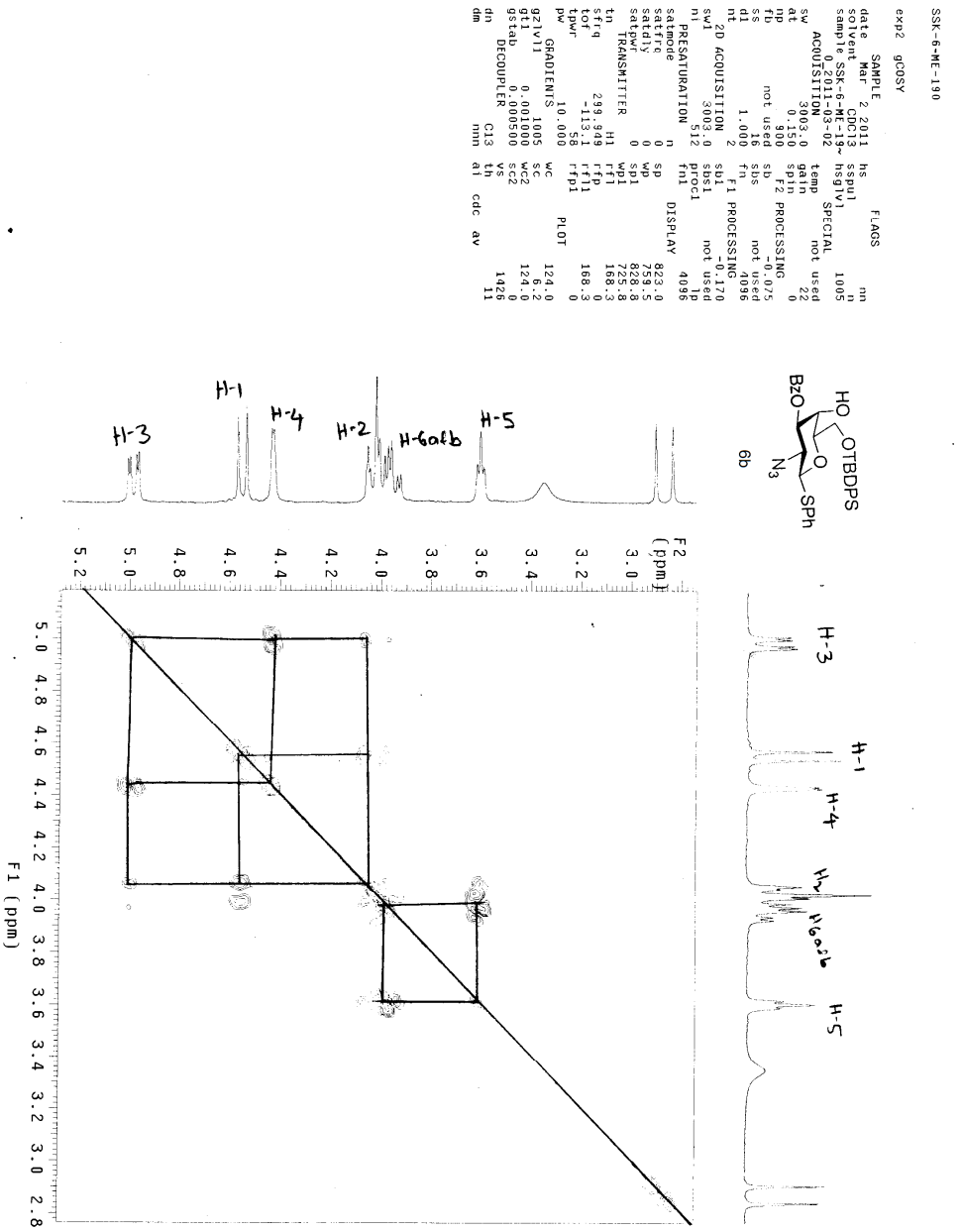
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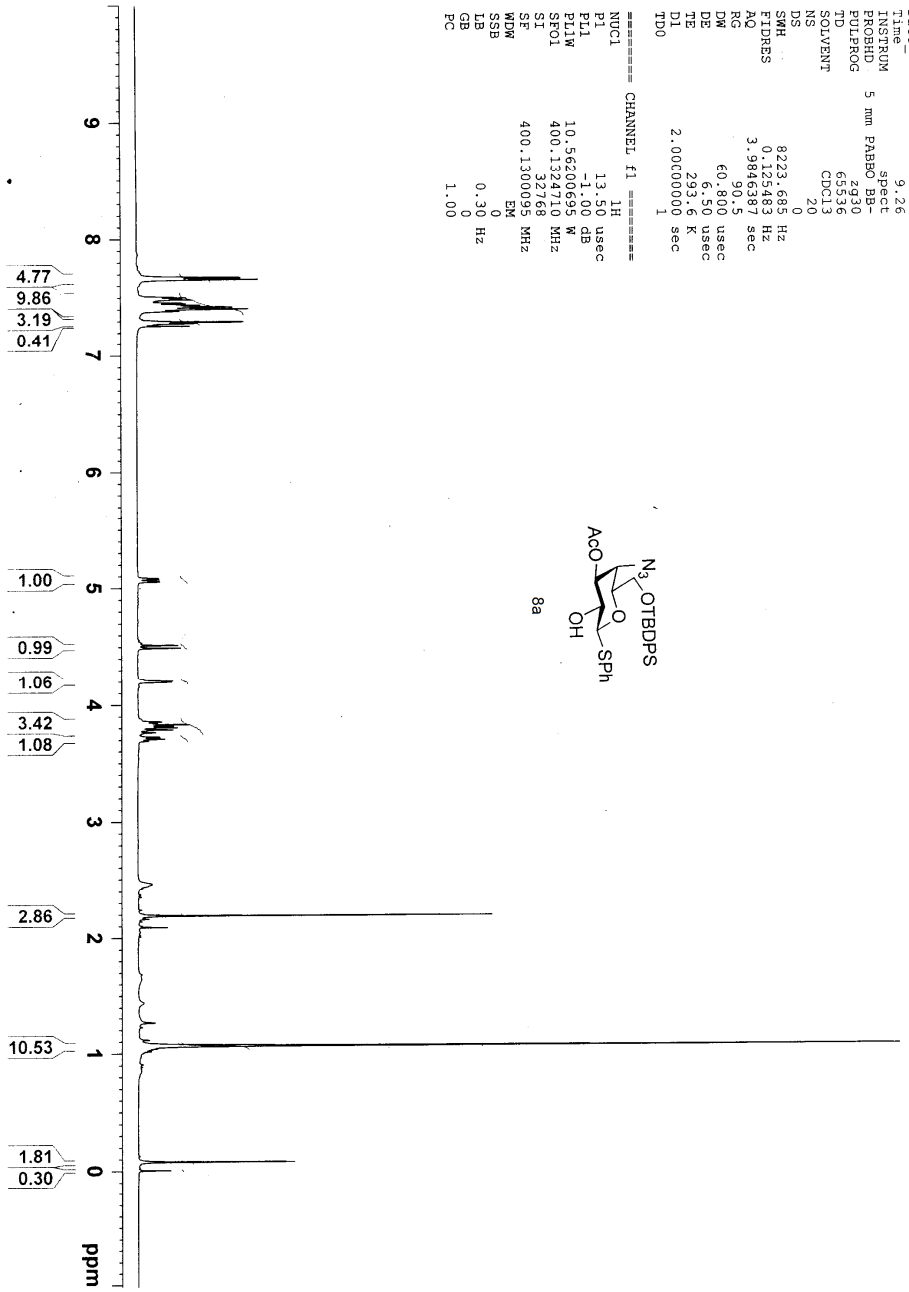
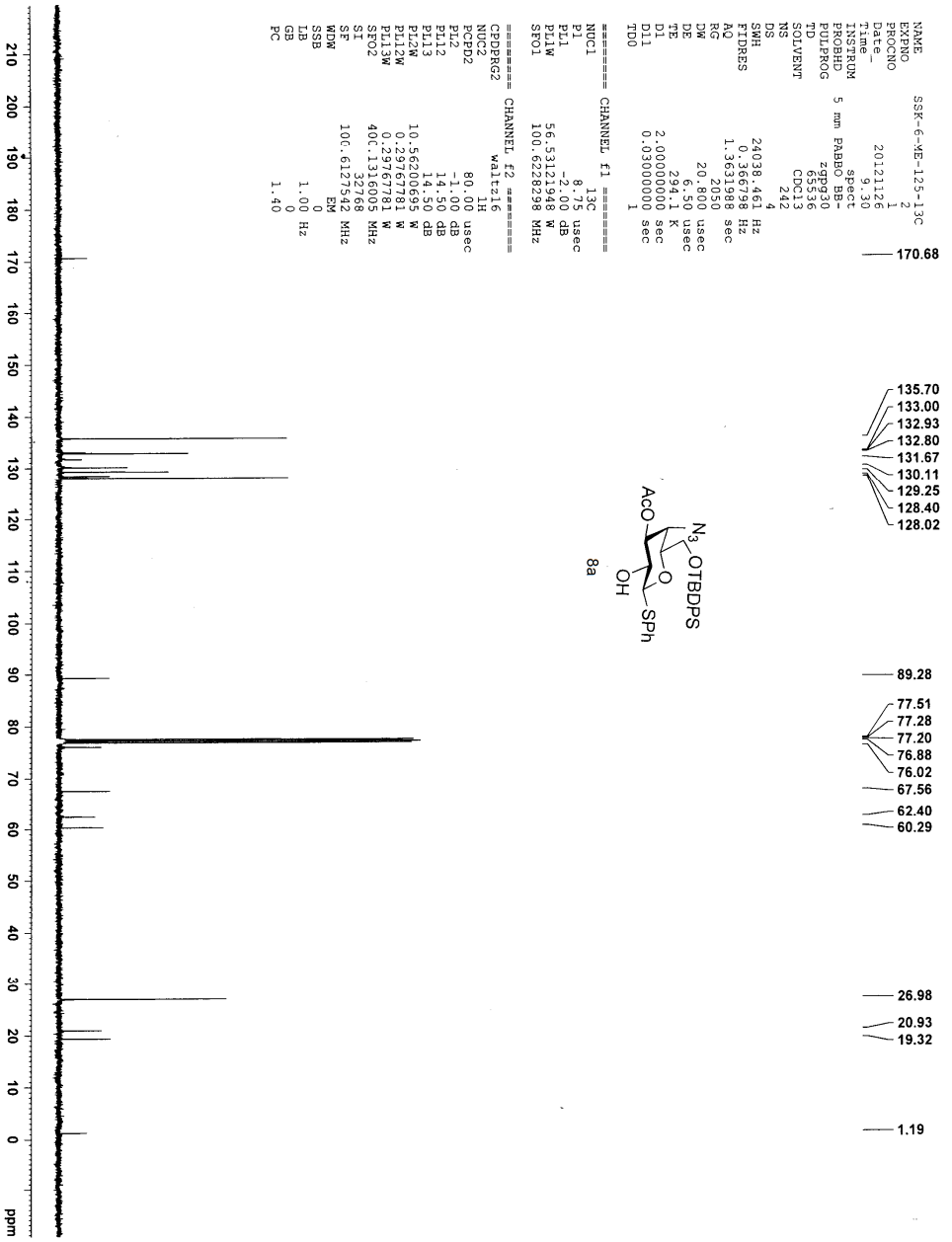
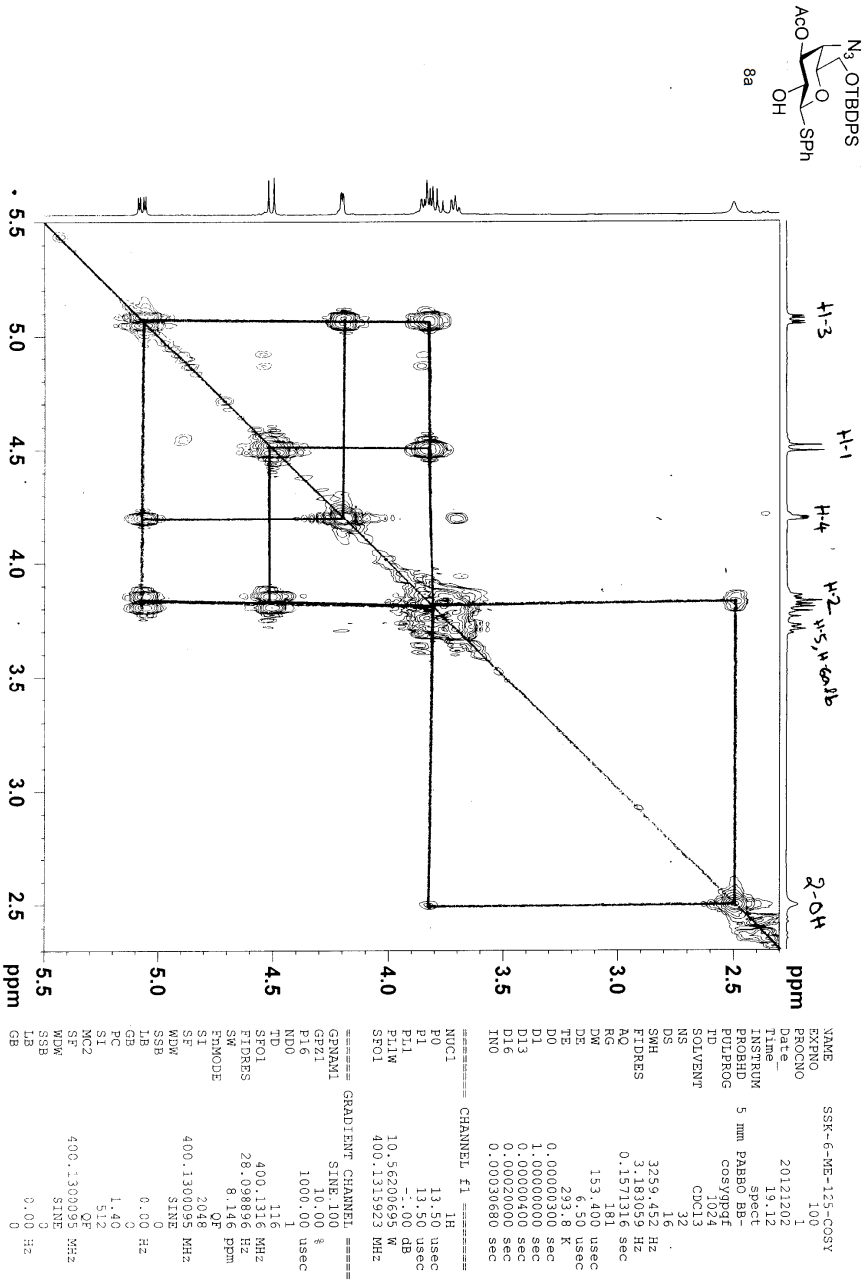
F1 (ppm)

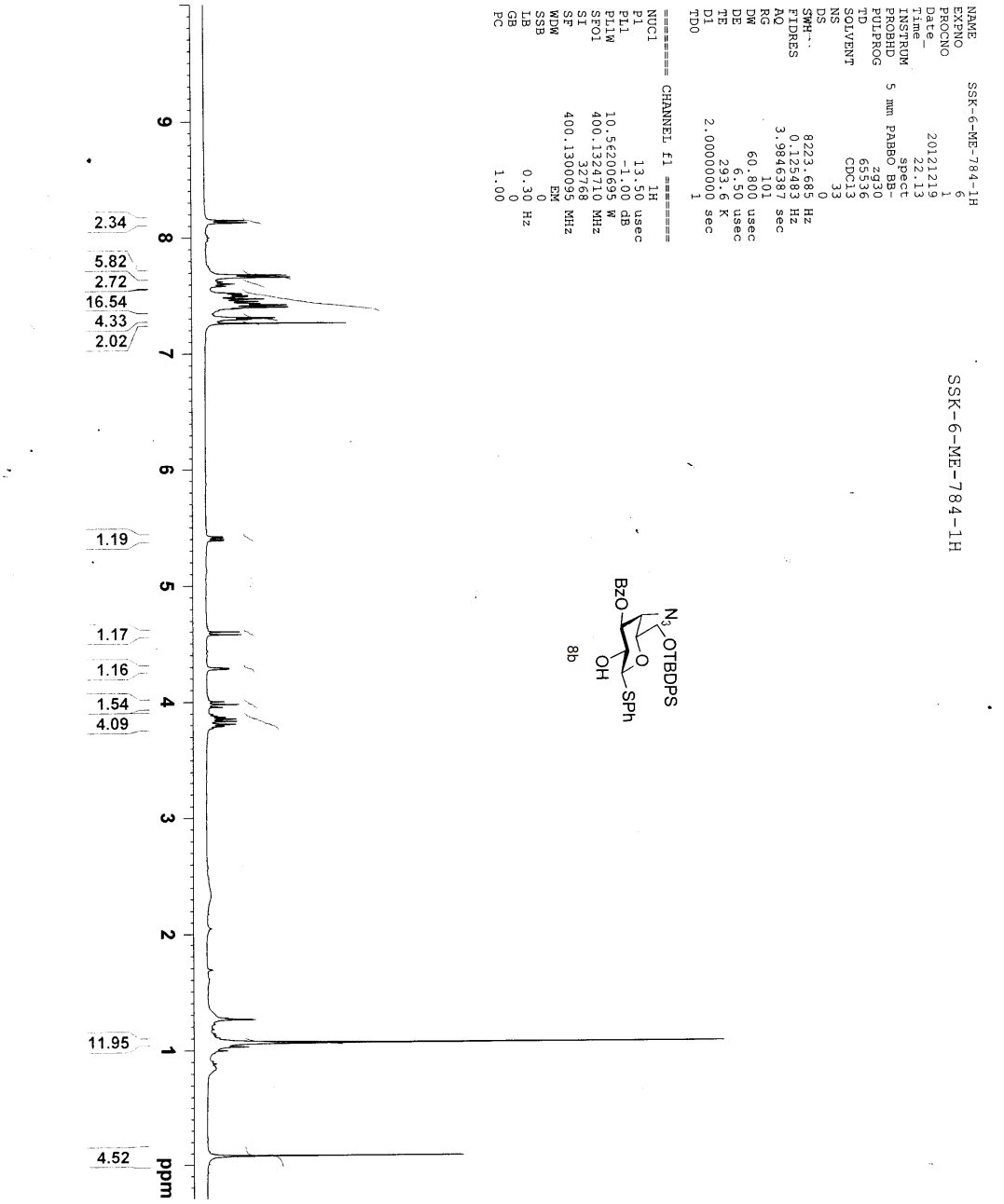


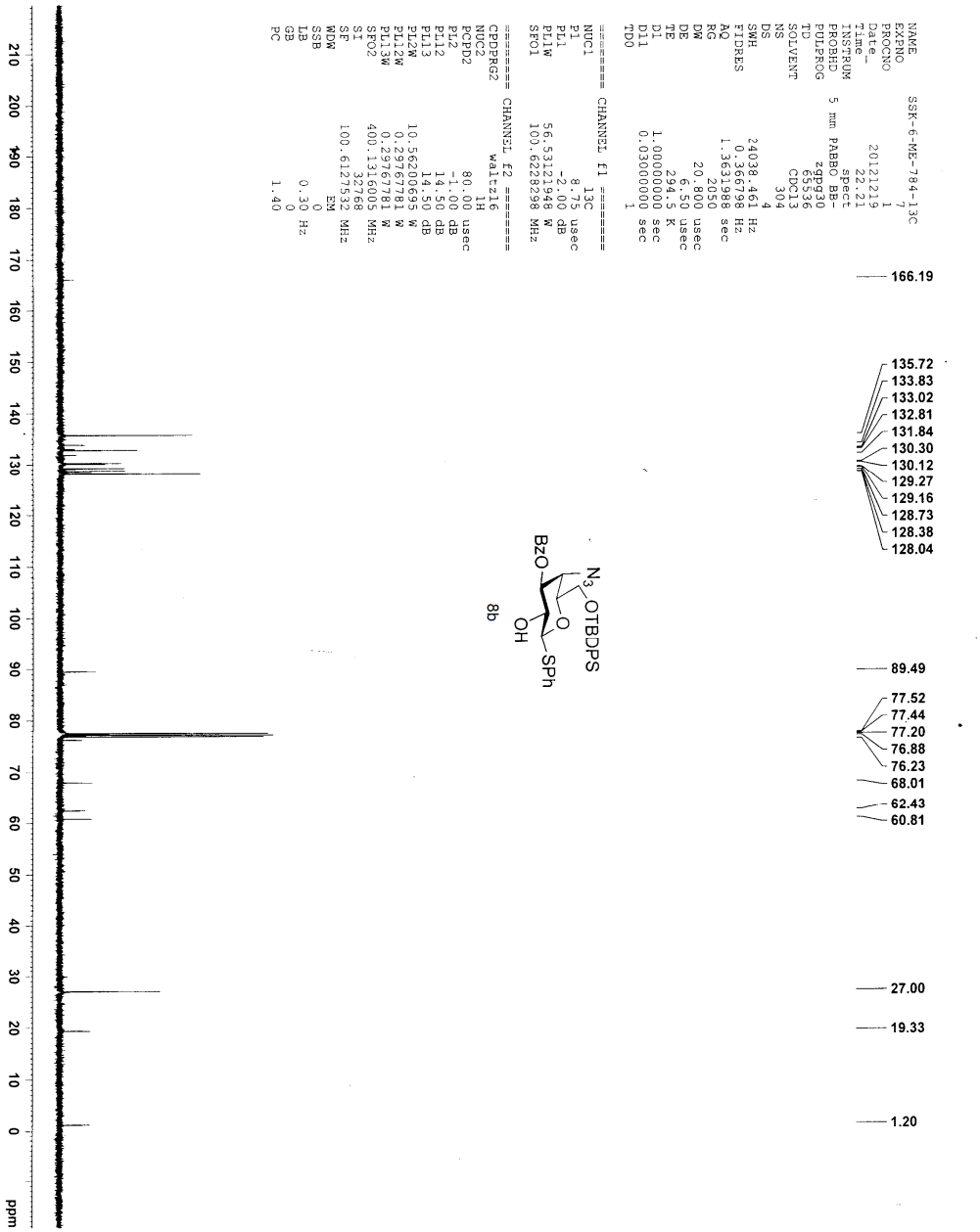

NAME SSK-6-ME-125-13C
EXPNO 2
PROCNO 1
Date_ 20121126
Time 9.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 242
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631598 sec
RG 203
DW 20.800 usec
DE 26.31 usec
TE 294.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL12 -1.00 dB
PL13 14.50 dB
PL12W 10.56200695 W
PL13W 0.23767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127542 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcO
OH
O
N3
OTBDPS
SPh
8a
170.68
135.70
133.00
132.93
132.80
131.67
130.11
129.25
128.40
128.02
89.28
77.51
77.28
77.20
76.88
76.02
67.56
62.40
60.29
26.98
20.93
19.32
1.19
ppm

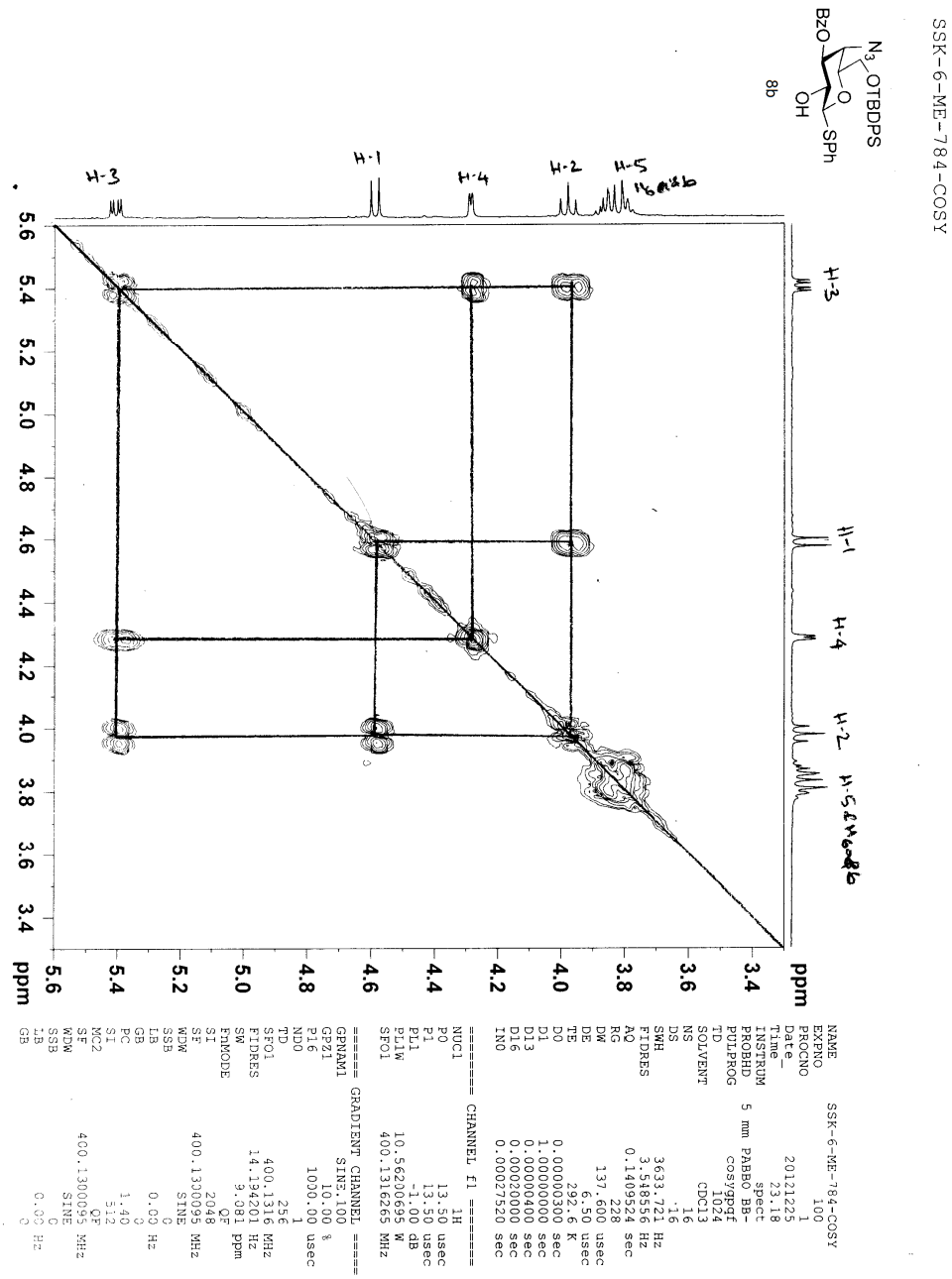
SSK-6-ME-125-COSY

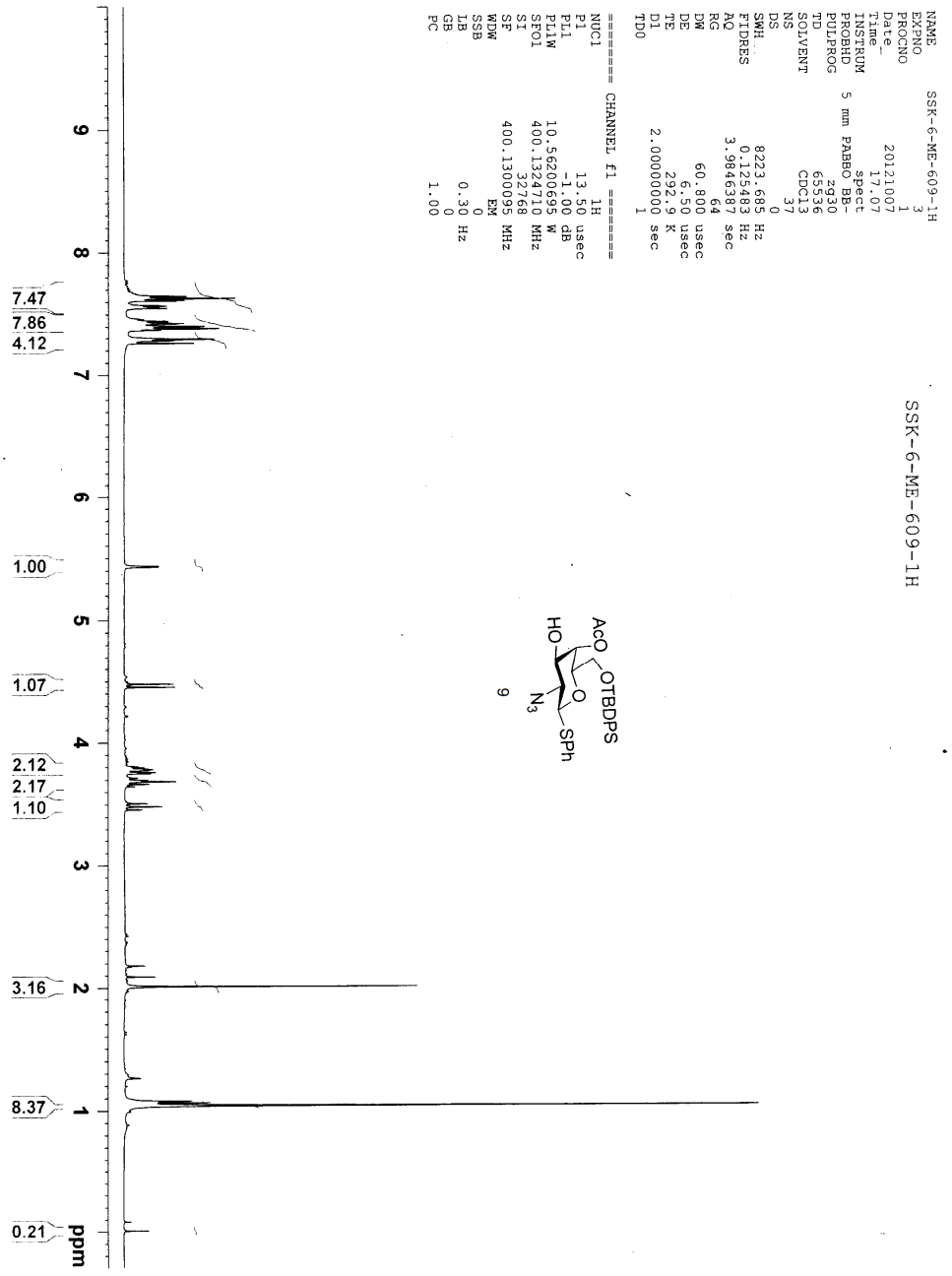


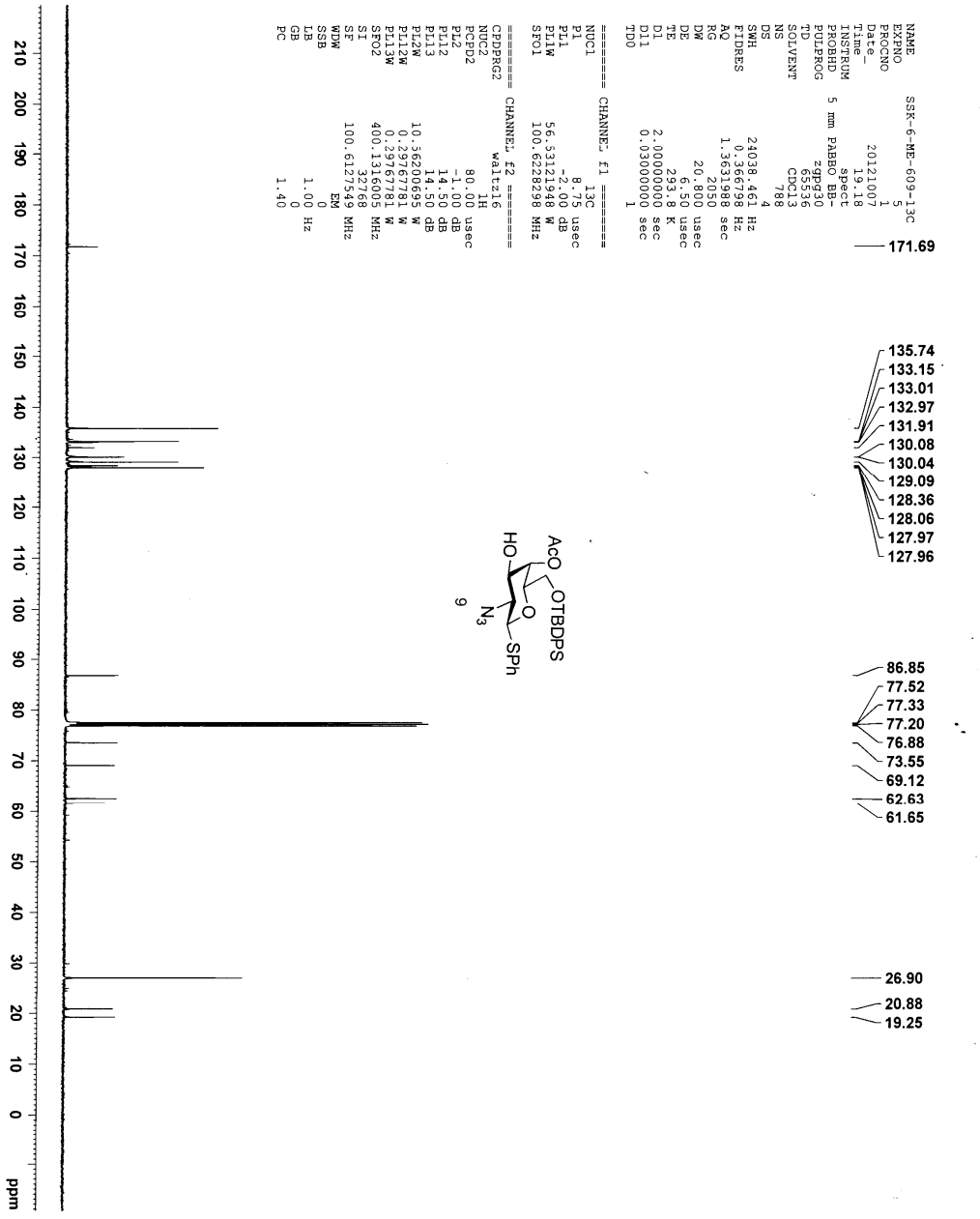

```
NAME                 SSK-6-ME-125-COSY
EXPNO                     100
PROCNO                      1
Date_              20121202
Time                   19.12
INSTRUM                 spect
PROBHD     5 mm PABBO BB-
PULPROG             cosygpqf
TD                      1024
SOLVENT                 CDCl3
NS                        32
DS                        16
SWH                 3259.452 Hz
FIDRES              3.183059 Hz
AQ                  0.1571316 sec
RG                        181
DW                  153.400 usec
DE                    6.50 usec
TE                    293.8 K
D0                  0.00000300 sec
D1                  1.00000000 sec
D13                 0.00000400 sec
D16                 0.00020000 sec
IN0                 0.00033680 sec

======== CHANNEL f1 ========
NUC1                      1H
P0                     13.50 usec
P1                     13.50 usec
PL1                    -1.00 dB
PL1W        10.56200695 W
SFO1        400.1315923 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPZ1                   10.00 %
P16                  1000.00 usec
NDO                         1
TD                        116
SFO1        400.1316 MHz
FIDRES              28.098896 Hz
SW                   8.146 ppm
FnMODE                     QF
SI                       2048
SF          400.1300095 MHz
WDW                  SINE
SSB                         0
LB                   0.00 Hz
GB                          0
PC                       1.40
SI                       512
MC2                        QF
SF          400.1300095 MHz
WDW                  SINE
SSB                         0
LB                   0.00 Hz
GB                          0
```



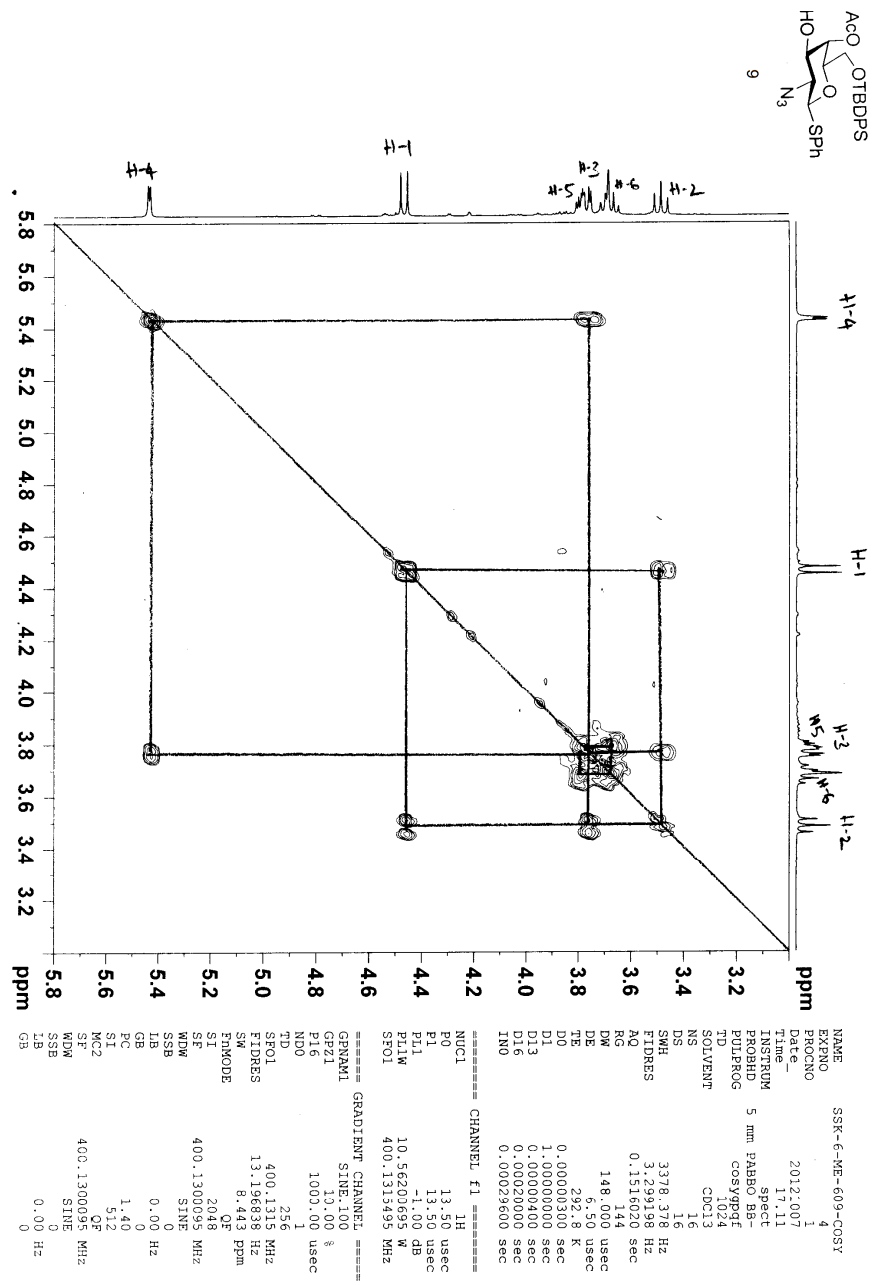



SSK-6-ME-784-COSY
8b
H-3
H-1
H-4
H-2
H-5
ppm
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
NAME SSK-6-ME-784-COSY
EXPNO 100
PROCNO 1
Date_ 20121225
Time_ 23.18
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3633.721 Hz
FIDRES 3.548556 Hz
AQ 0.1409524 sec
RG 228
DW 137.600 usec
DE 6.50 usec
TE 292.6 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00027520 sec
========== CHANNEL f1 ==========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56220695 W
SFO1 400.1316265 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GP21 10.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1316 MHz
FIDRES 14.134201 Hz
SW 9.081 ppm
FnMODE QF
2048
SF 400.1300095 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 512
MC2 QF
SF 400.1300095 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

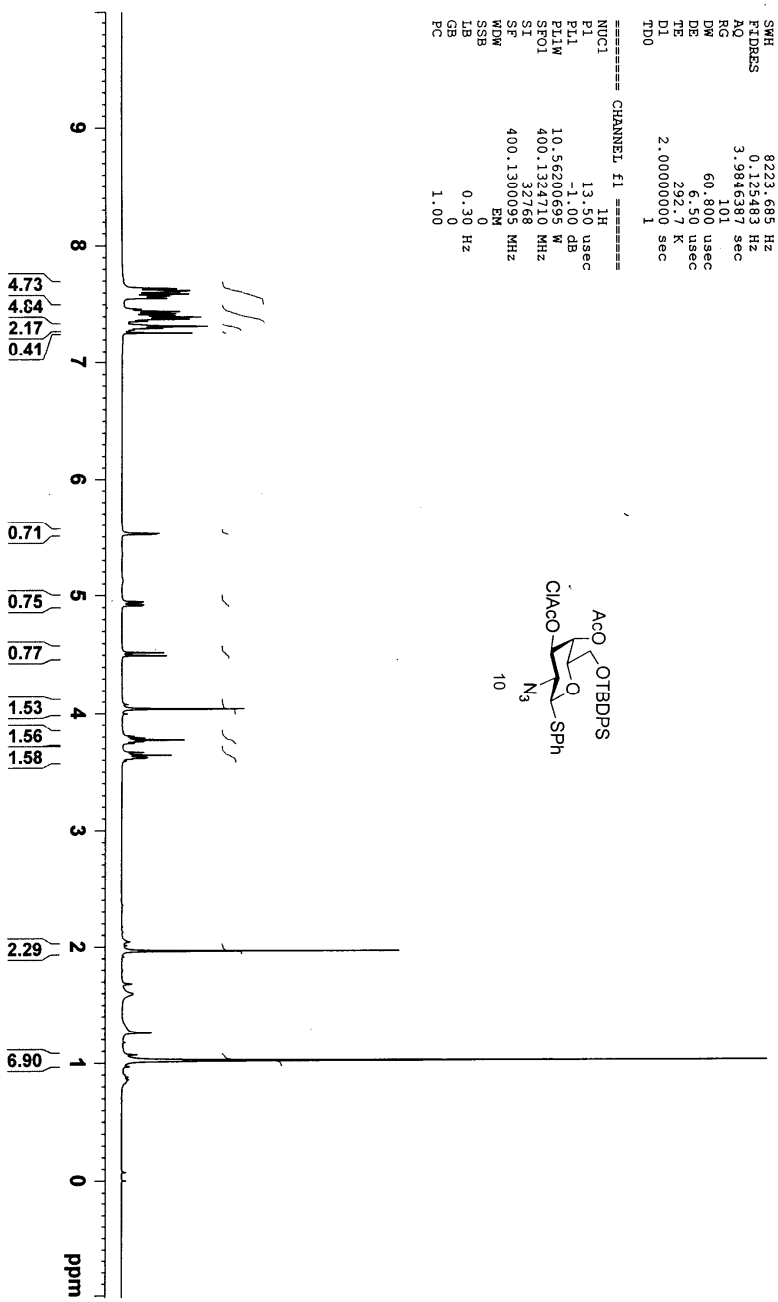

NAME SSK-6-ME-609-1H
EXPNO 3
PROCNO 1
Date_ 20121007
Time_ 17.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 37
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 292.9 K
D1 2.00000000 sec
TDO 1
========== CHANNEL f1 ==========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-609-1H
AcO
OTBDPS
HO
O
N3
SPh
9
7.47
7.86
4.12
1.00
1.07
2.12
2.17
1.10
3.16
8.37
0.21
ppm

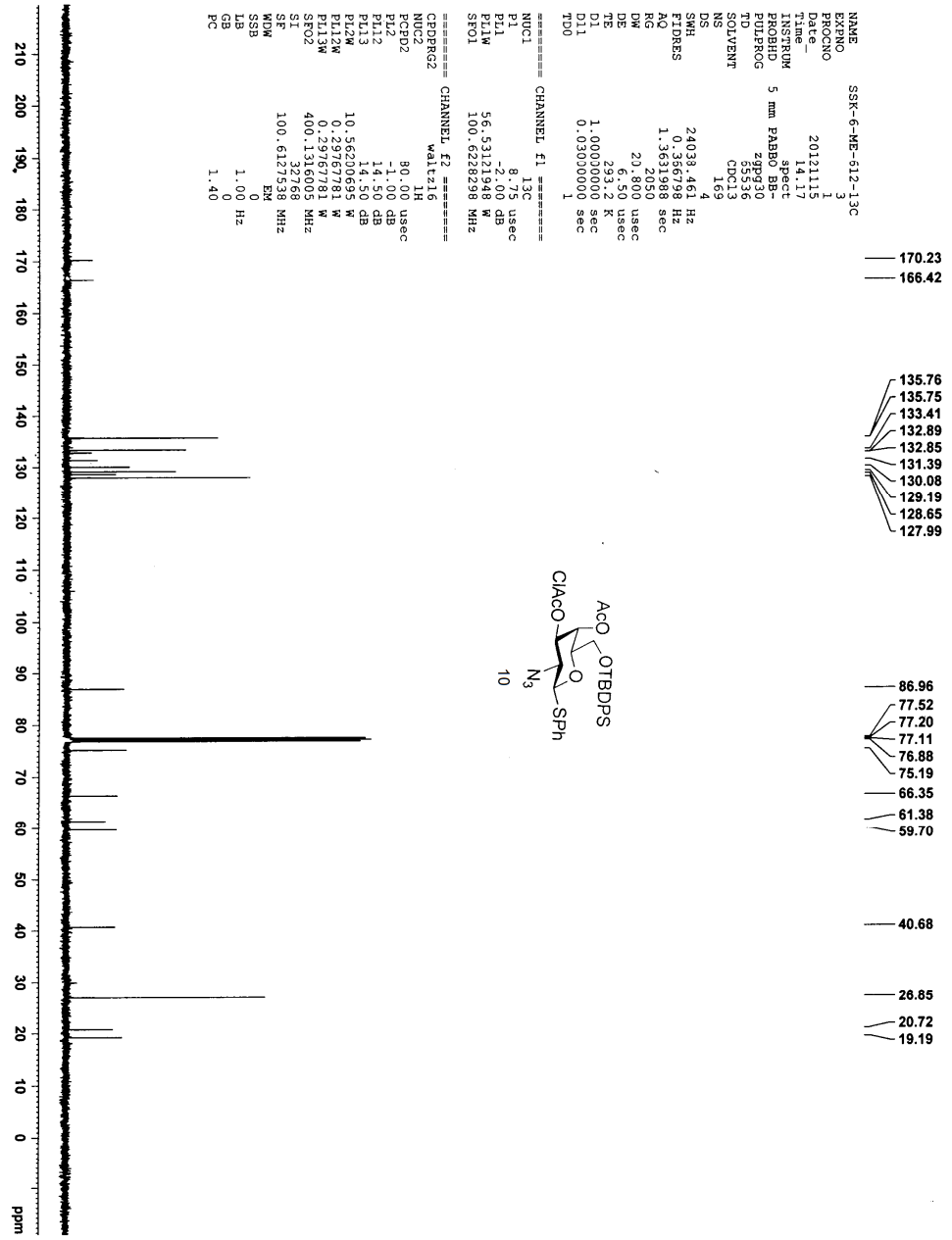


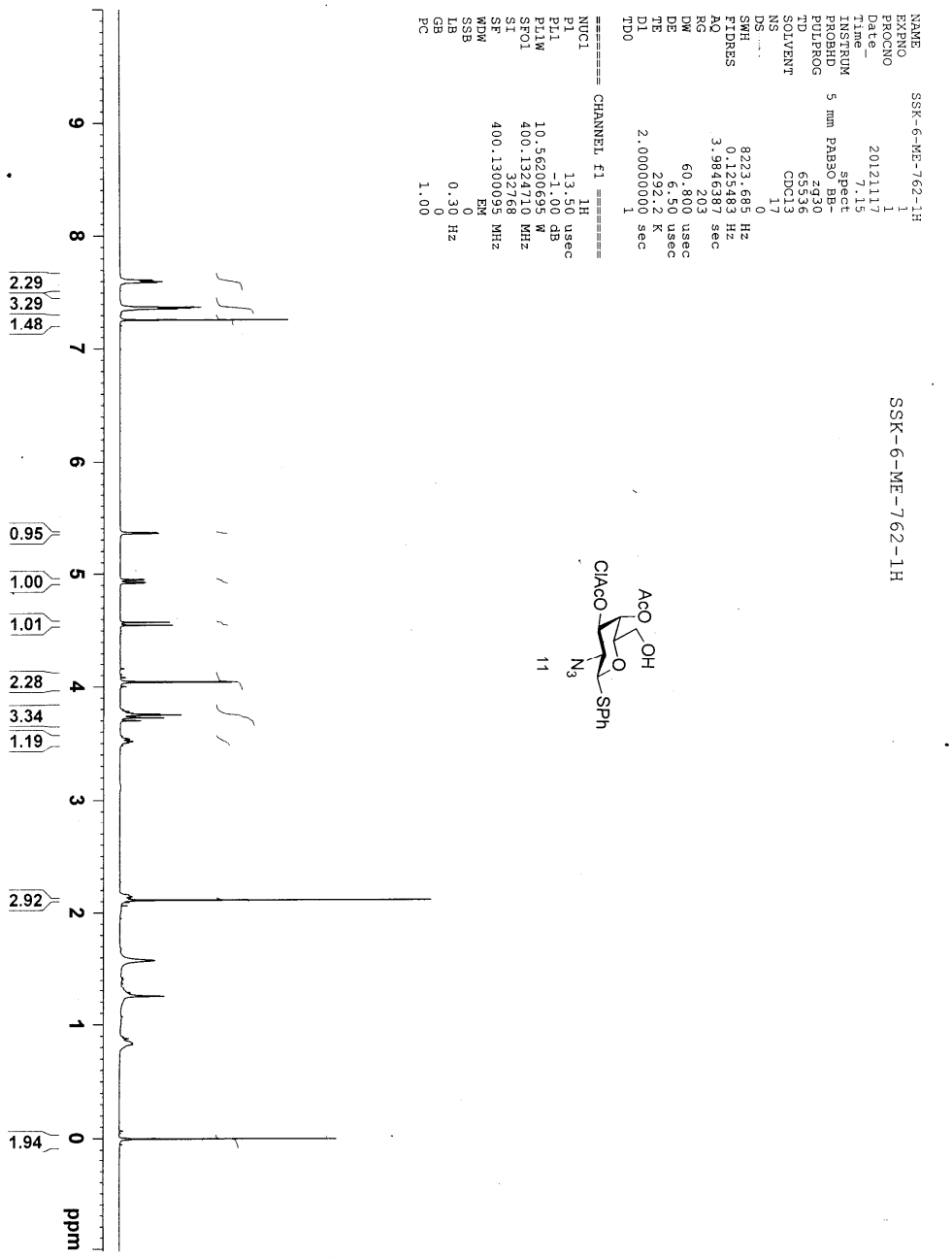
SSK-6-ME-609-COSY

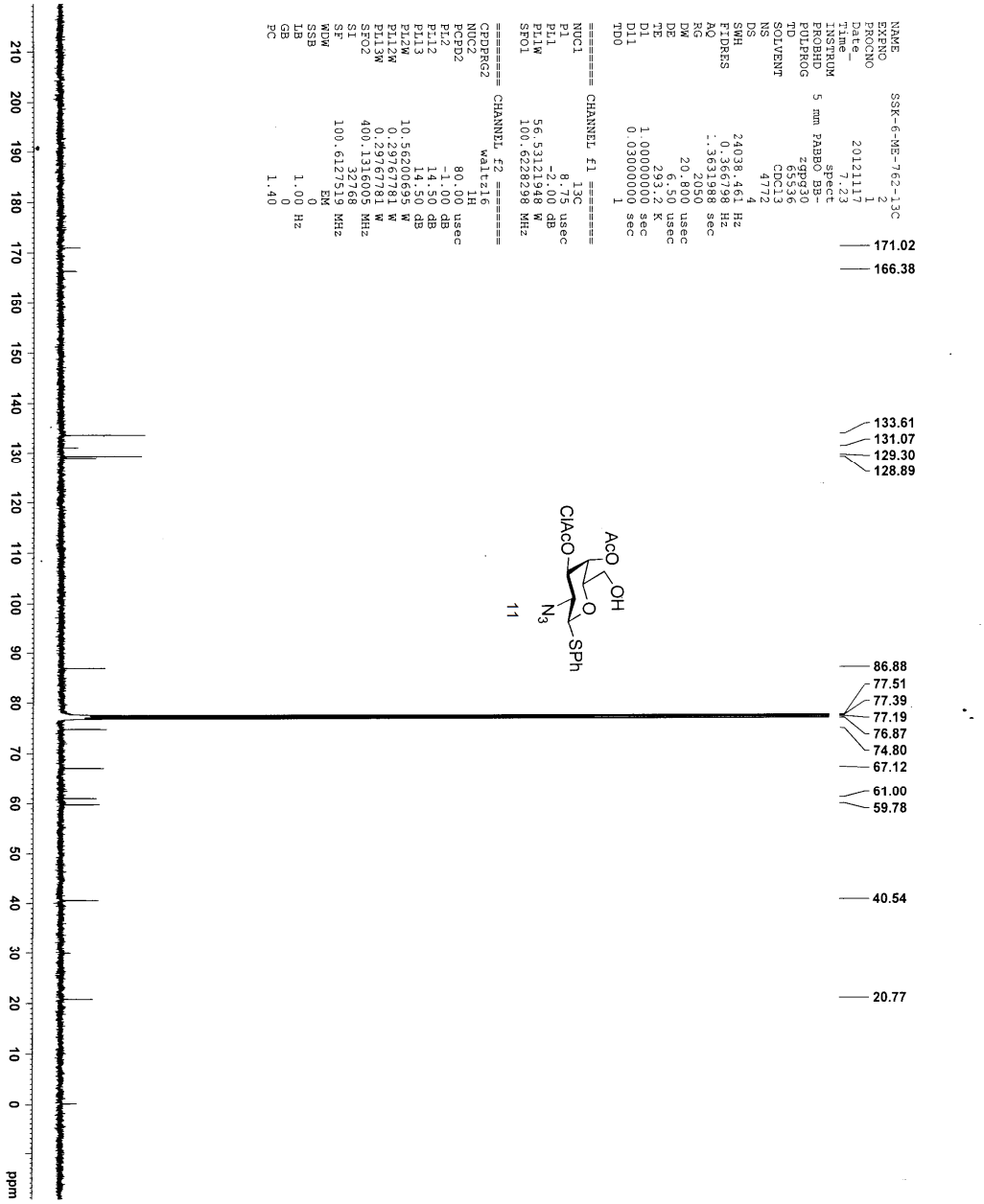



```
NAME                                SSK-6-ME-609-COSY
EXPNO                                               4
PROCNO                                              1
Date_                                      2012:007
Time_                                         17.11
INSTRUM                                        spect
PROBHD                    5 mm PABBO BB-
PULPROG                                   cosygpqf
TD                                            1024
SOLVENT                                     CDCl3
NS                                             16
DS                                             16
SWH                                      3378.378 Hz
FIDRES                                   3.299198 Hz
AQ                                       0.1516020 sec
RG                                           144
DW                                       148.000 usec
DE                                         6.50 usec
TE                                        292.8 K
D0                                    0.00000300 sec
D1                                    1.00000000 sec
D13                                   0.00000400 sec
D16                                   0.00020000 sec
IN0                                   0.00029600 sec

======== CHANNEL f1 ========
NUC1                                          1H
P0                                         13.50 usec
P1                                         13.50 usec
PL1                                        -1.00 dB
PLW1                                  10.56203695 W
SFO1                                  400.1315495 MHz

====== GRADIENT CHANNEL =====
GPNAM1                                  SINE.100
GPZ1                                       10.00 %
P16                                      1000.00 usec
NDO                                            1
TD                                           256
SFO1                                  400.1315 MHz
FIDRES                                13.196838 Hz
SW                                     8.443 ppm
FnMODE                                        QF
SI                                          2048
SF                    400.1300095 MHz
WDW                                         SINE
SSB                                            0
LB                                      0.00 Hz
GB                                             0
PC                                          1.40
SI                                           512
MC2                                           QF
SF                    400.1300095 MHz
WDW                                         SINE
SSB                                            0
LB                                      0.00 Hz
GB                                             0
```

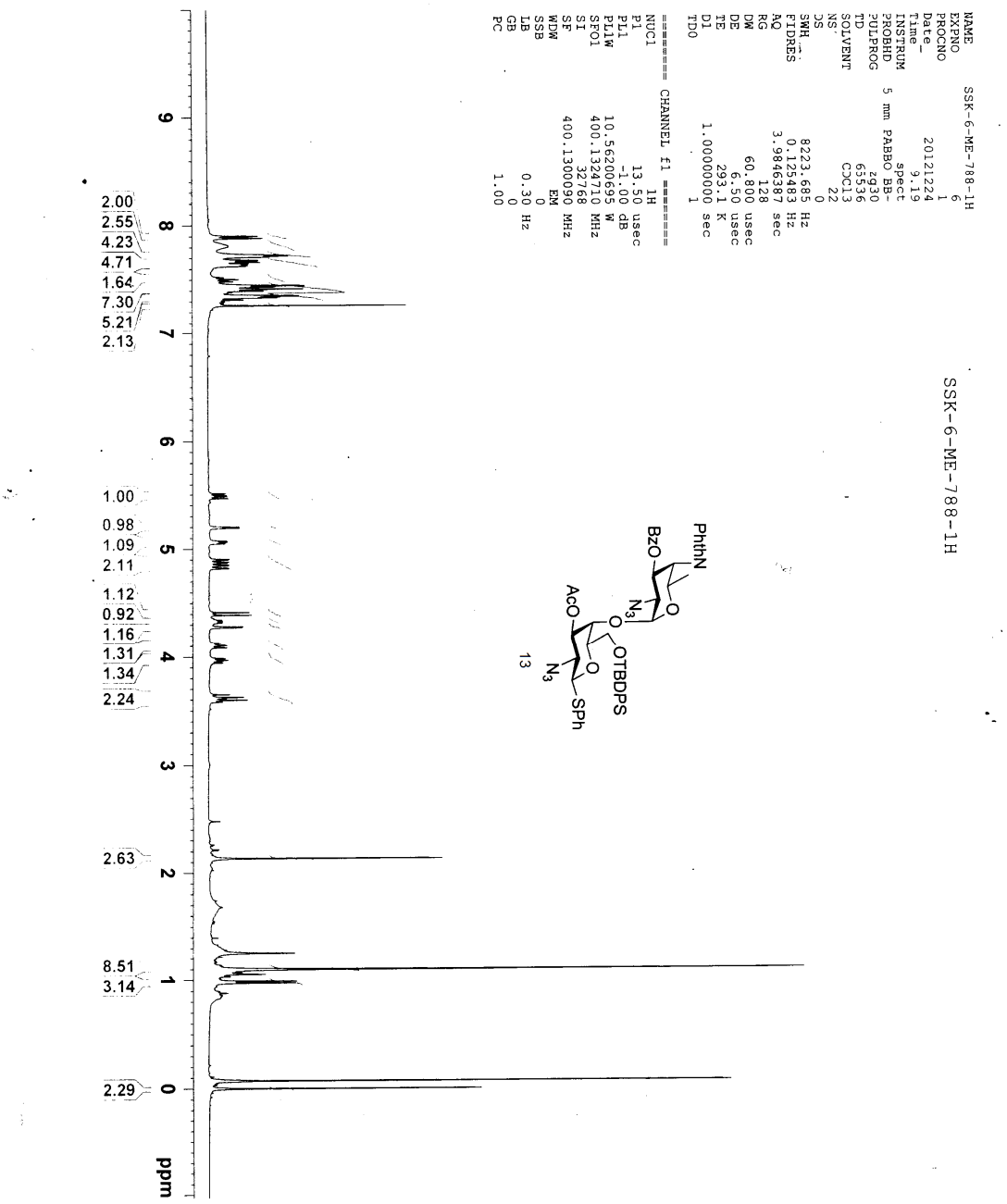


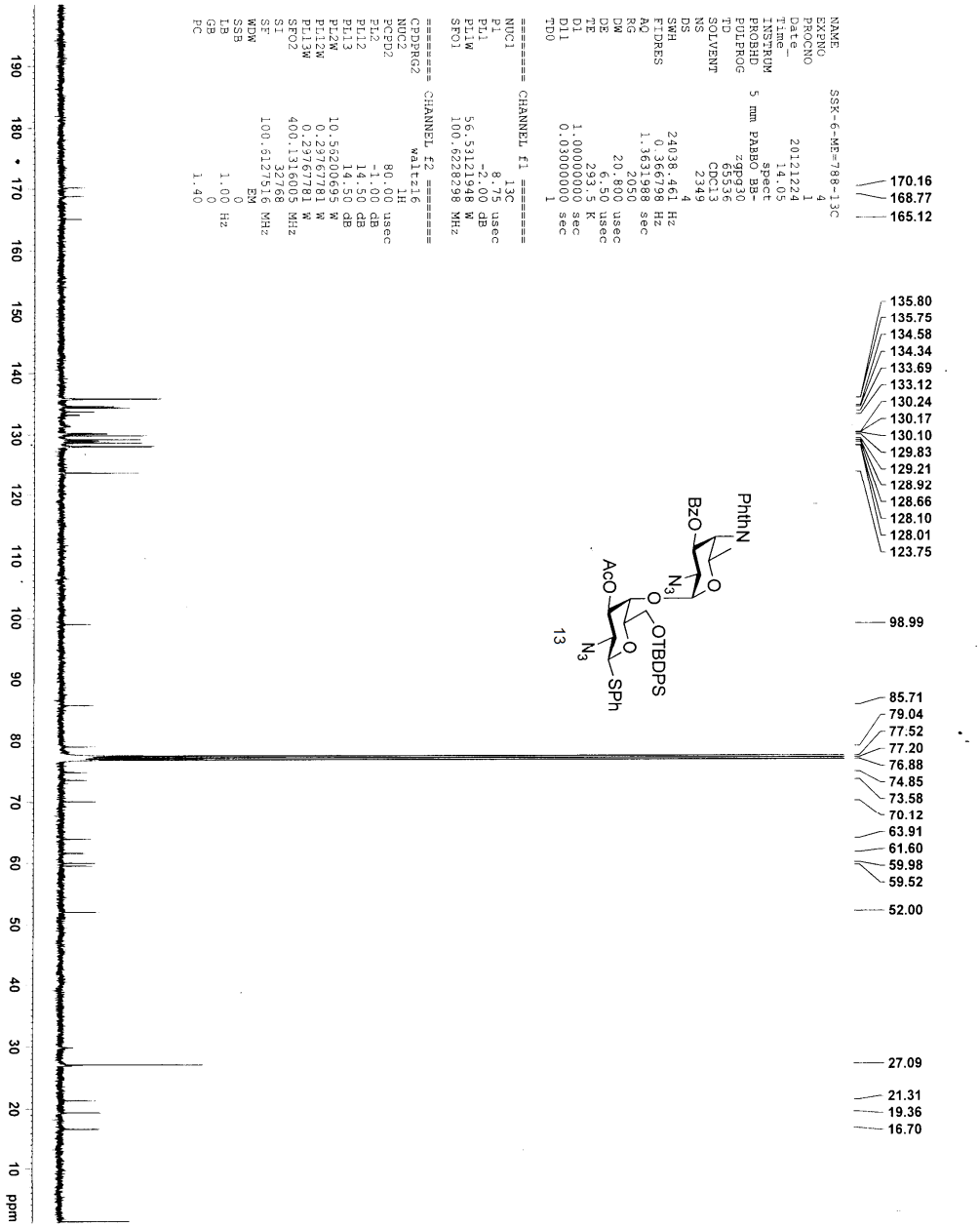

NAME SSK-6-ME-612-13C
EXPNO 3
PROCNO 1
Date_ 20121115
Time_ 14.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 169
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56200695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127538 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.23
166.42
135.76
135.75
133.41
132.89
132.85
131.39
130.08
129.19
128.65
127.99
86.96
77.52
77.20
77.11
76.88
75.19
66.35
61.38
59.70
40.68
26.85
20.72
19.19
AcO
OTBDPS
ClAcO
O
N3
SPh
10
ppm

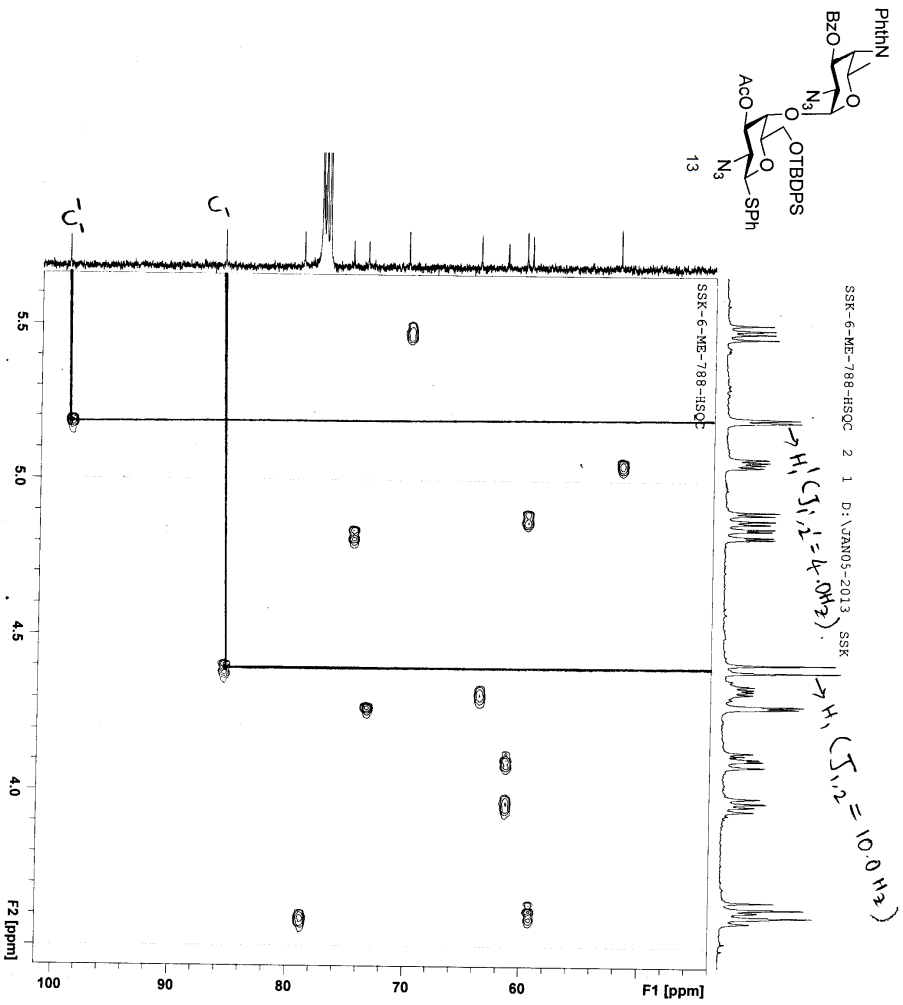

NAME SSK-6-ME-762-1H
EXPNO 1
PROCNO 1
Date_ 20121117
Time_ 7.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 292.2 K
D1 2.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PLIW 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-762-1H
AcO
OH
ClAcO
O
N3
SPh
11
2.29
3.29
1.48
0.95
1.00
1.01
2.28
3.34
1.19
2.92
1.94
ppm

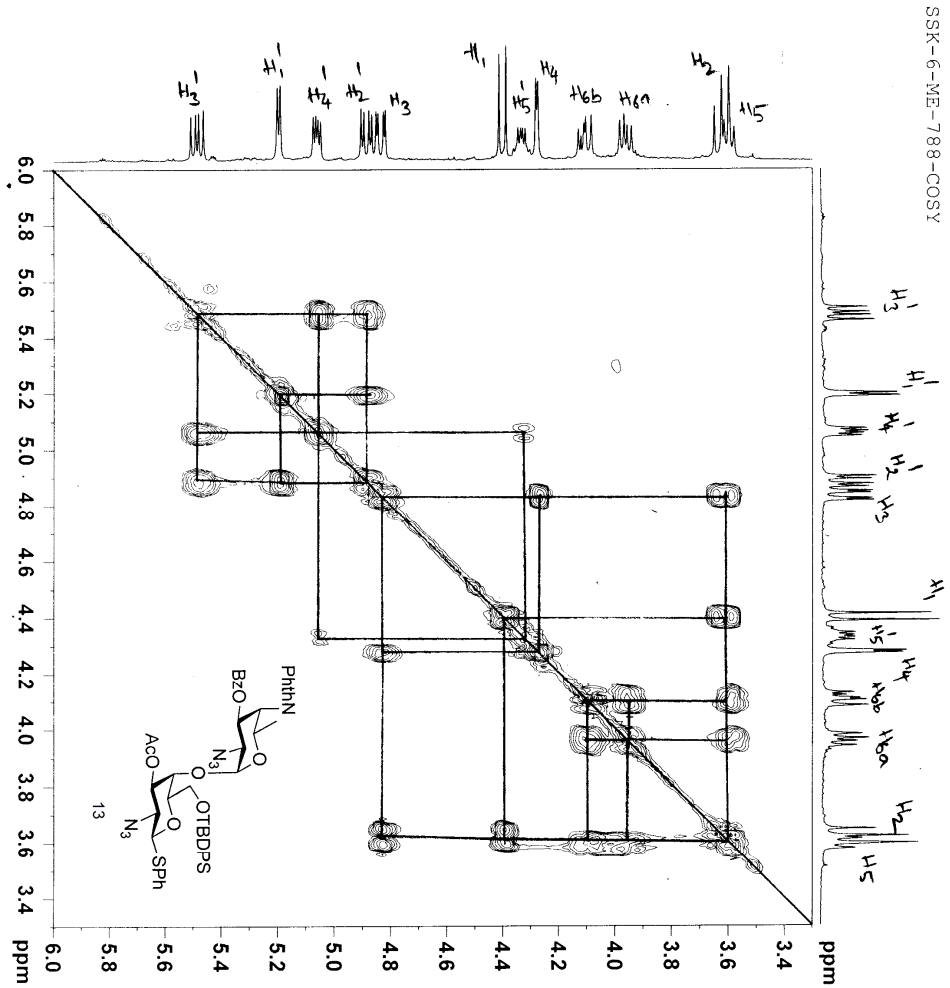



11

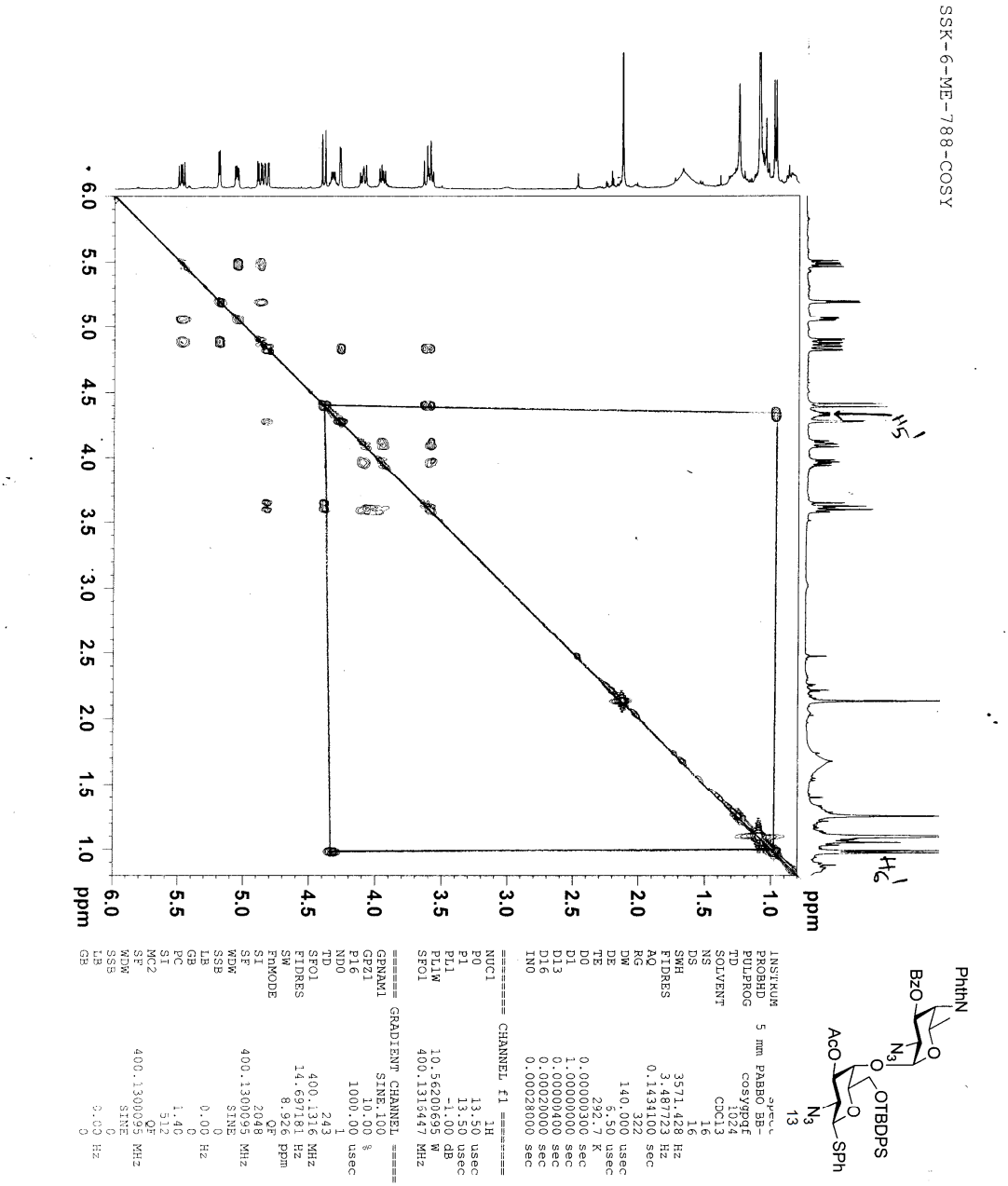


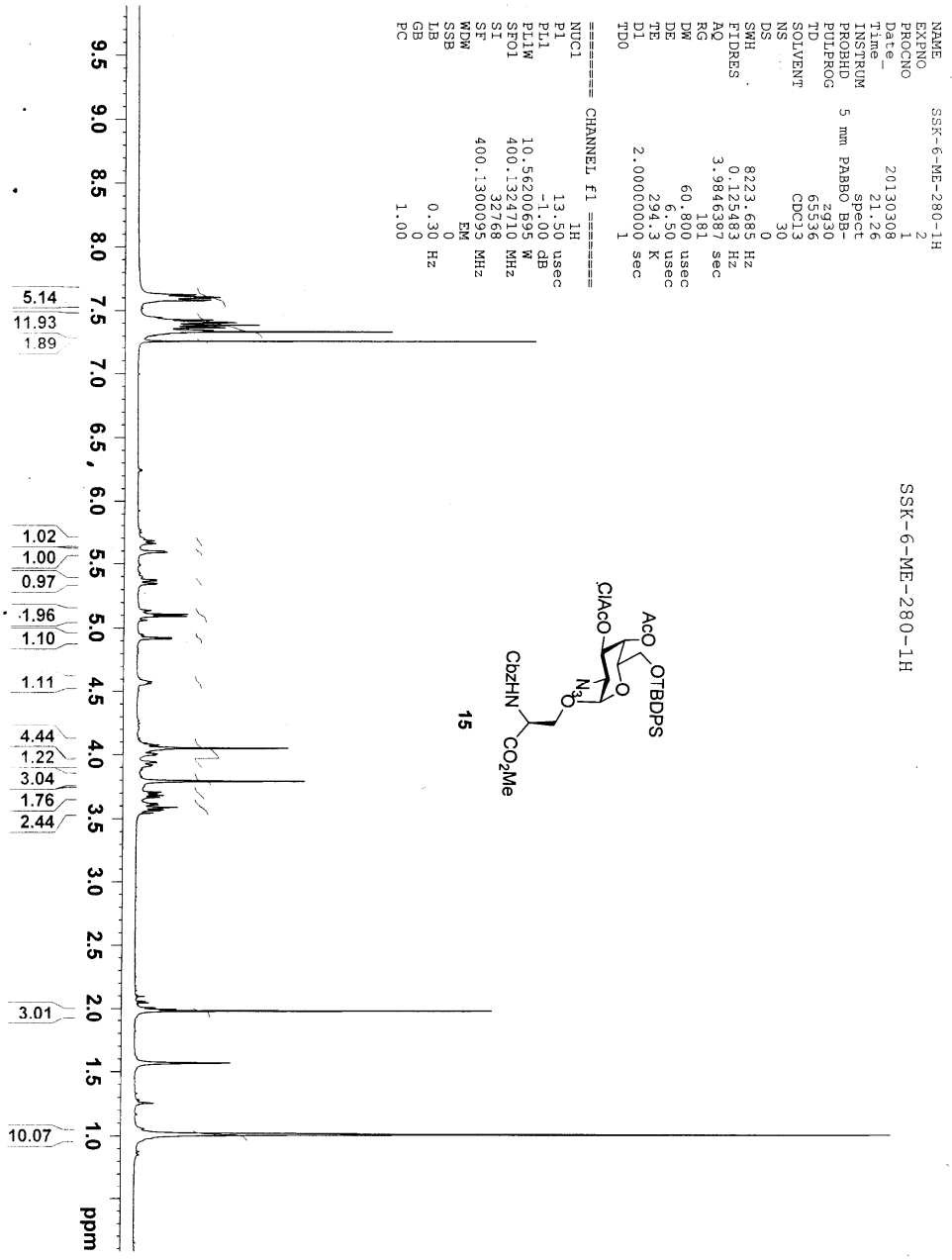

NAME SSK-6-ME-788-13C
EXPNO 4
PROCNO 1
Date_ 20121224
Time_ 14.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2349
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.55200695 W
PL12W 0.23767781 W
PL13W 0.23767781 W
SFO2 400.1316005 MHz
SI 131072
SF 100.6127516 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.16
168.77
165.12
135.80
135.75
134.58
134.34
133.69
133.12
130.24
130.17
130.10
129.83
129.21
128.92
128.66
128.10
128.01
123.75
98.99
85.71
79.04
77.52
77.20
76.88
74.85
73.58
70.12
63.91
61.60
59.98
59.52
52.00
27.09
21.31
19.36
16.70
PhthN
BzO
N3
O
AcO
OTBDPS
O
N3
SPh
13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

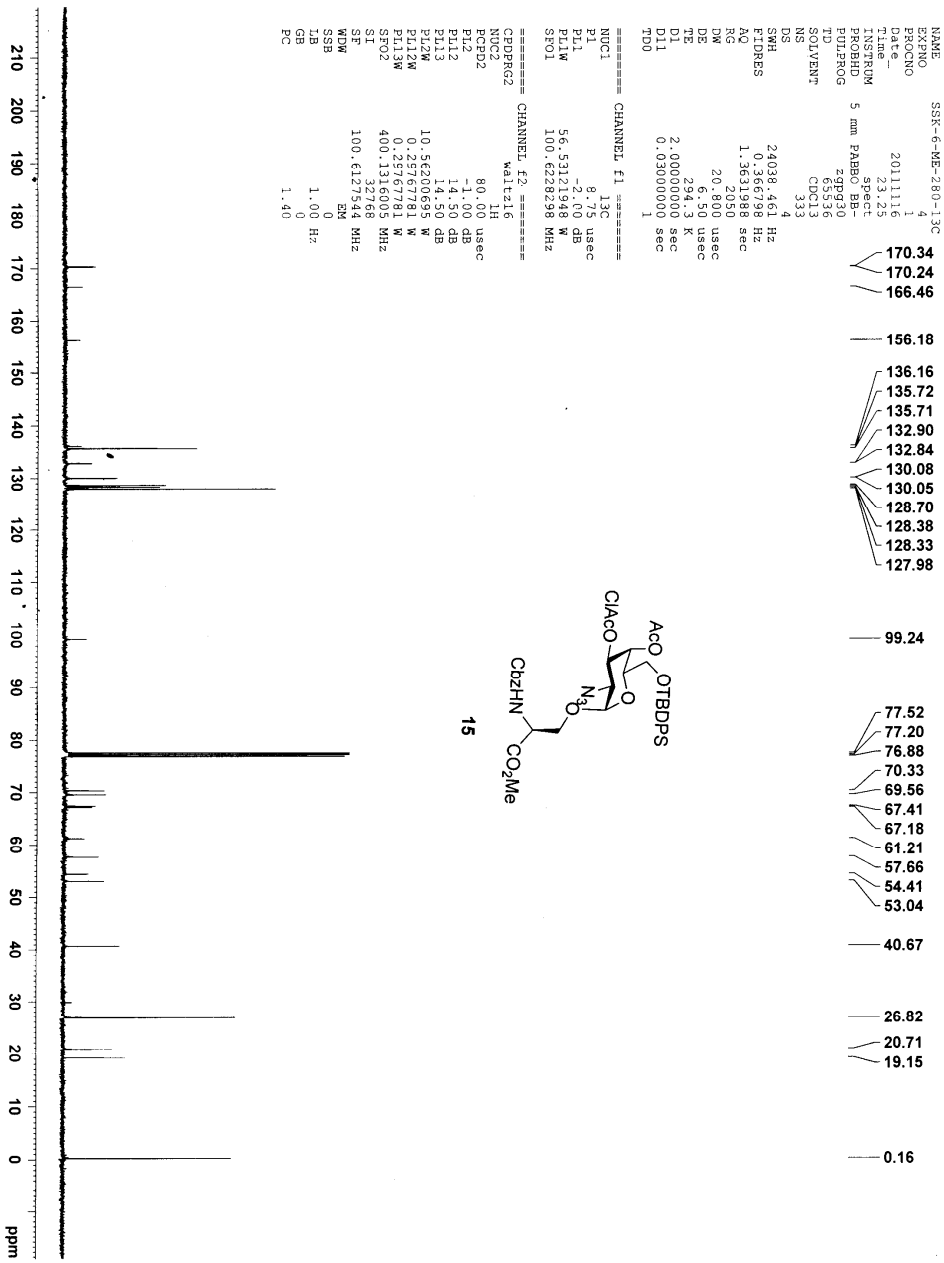


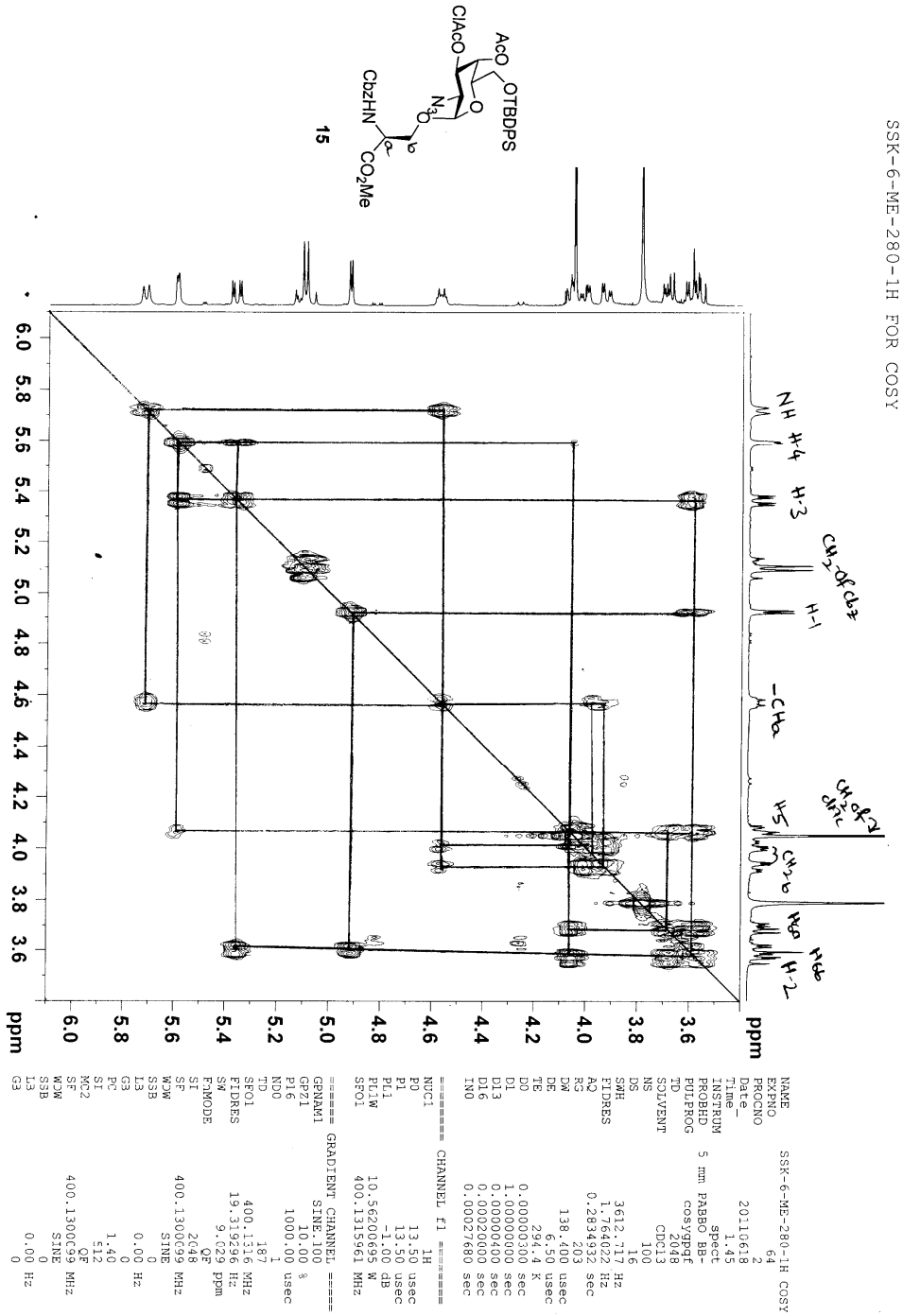



```
NAME                 SSK-6-ME-788-COSY
EXPNO                                 2
PROCNO                                1
Date_                          20121224
Time_                             18.04
INSTRUM                            spect
PROBHD     5 mm PABBO BB-
PULPROG                   cosygpqf
TD                                 1024
SOLVENT                          CDCl3
NS                                   16
DS                                   16
SWH                          3571.428 Hz
FIDRES                       3.487723 Hz
AQ                           0.1434100 sec
RG                                  322
DW                           140.000 usec
DE                             6.50 usec
TE                             292.7 K
D0                           0.00000300 sec
D1                           1.00000000 sec
D13                          0.00000400 sec
D16                          0.00020000 sec
INO                          0.00028000 sec

======== CHANNEL f1 ========
NUC1                               1H
P0                           13.50 usec
P1                           13.50 usec
PL1                          -1.00 dB
PL1W                 10.56200695 W
SFO1                 400.1316447 MHz

====== GRADIENT CHANNEL =====
GPNAM1                    SINE.100
GPZ1                         10.00 %
P16                        1000.00 usec
NDO                                1
TD                                 243
SFO1                 400.1316 MHz
FIDRES               14.697181 Hz
SW                           6.926 ppm
FnMODE                        QF
SI                                2048
SF                   400.1300095 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.40
SI                              512
MC2                            QF
SF                   400.1300095 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0
```

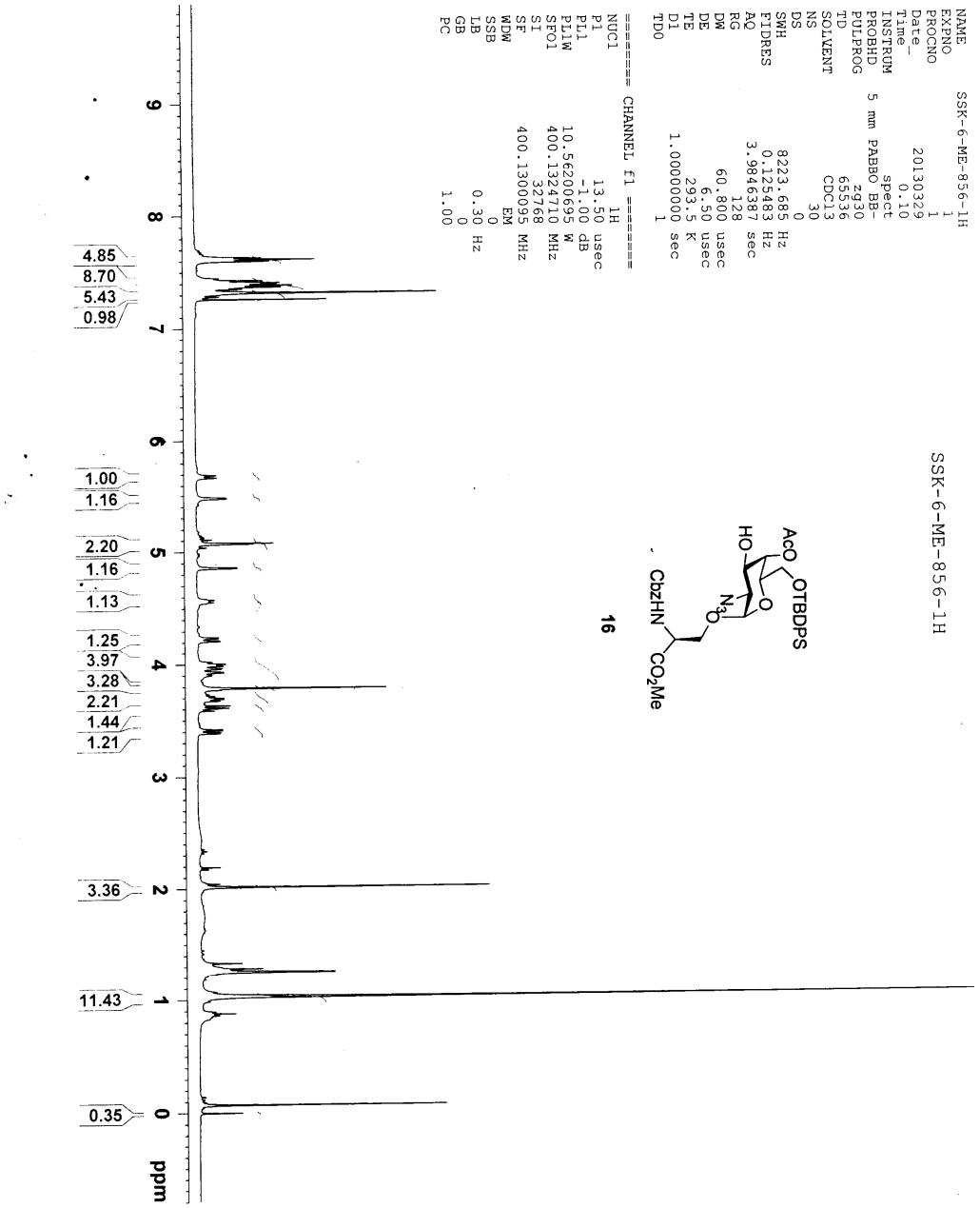

SSK-6-ME-788-COSY
PhthN
BzO
N3
O
OTBDPS
AcO
SPh
N3
13
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

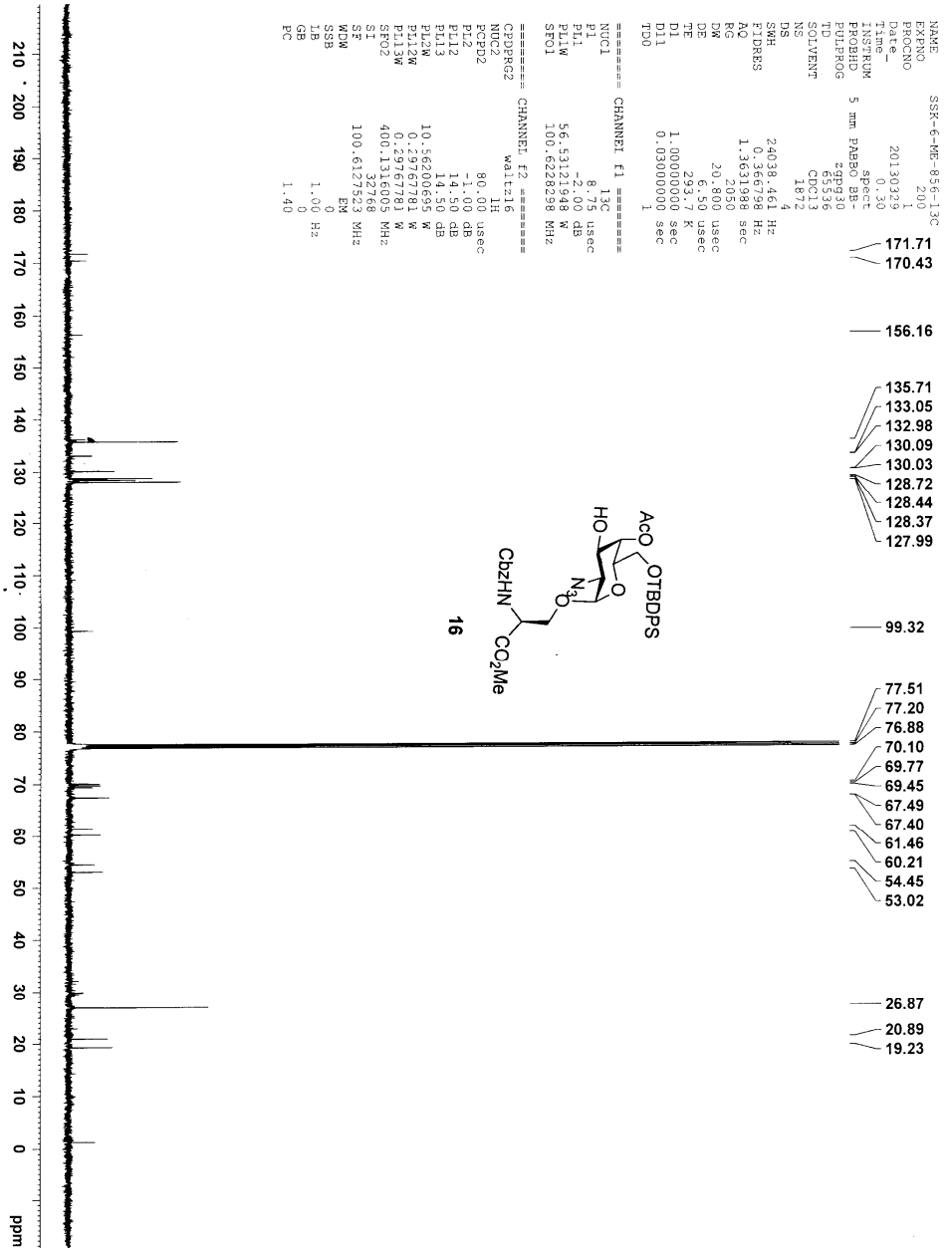


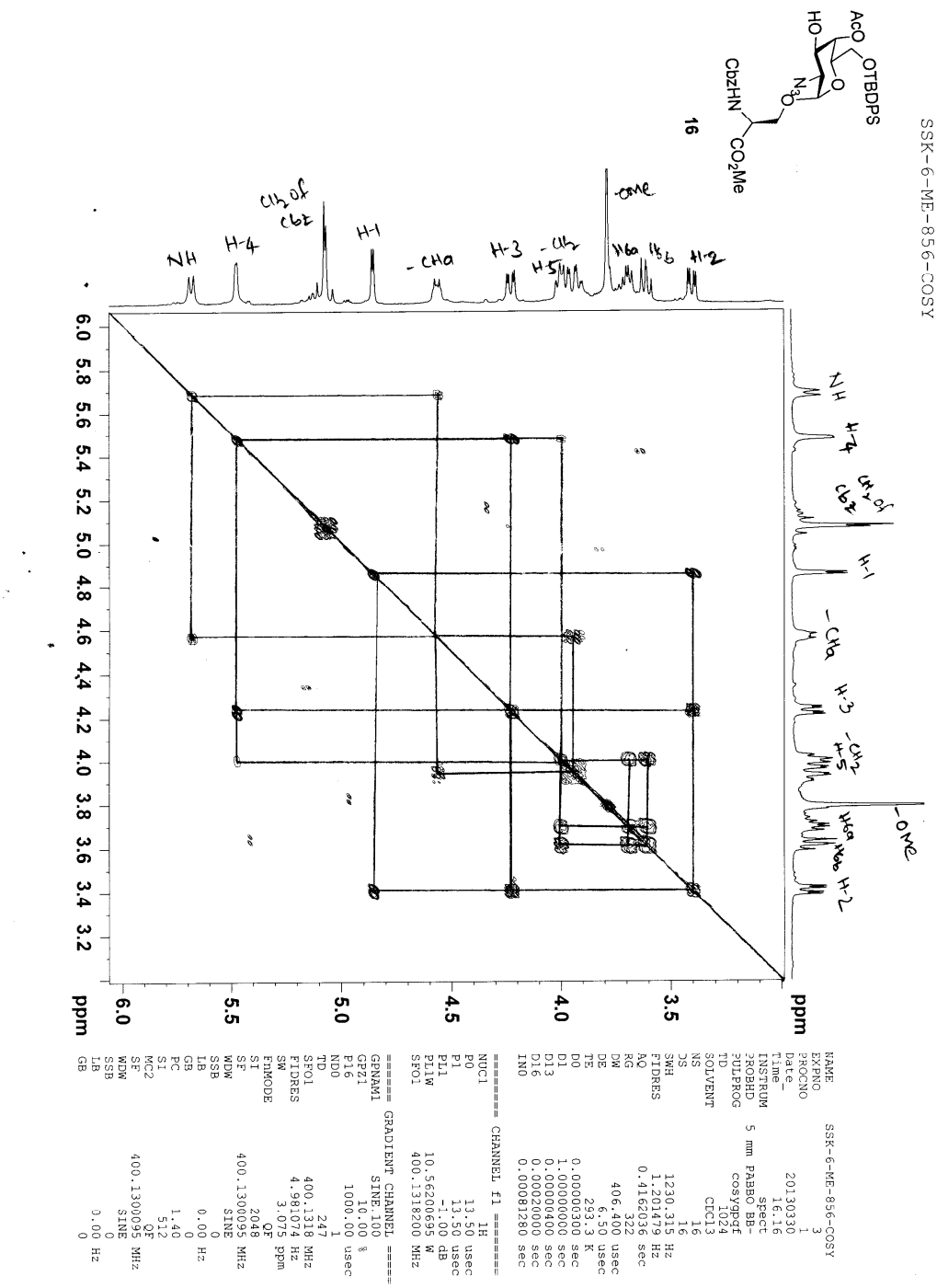




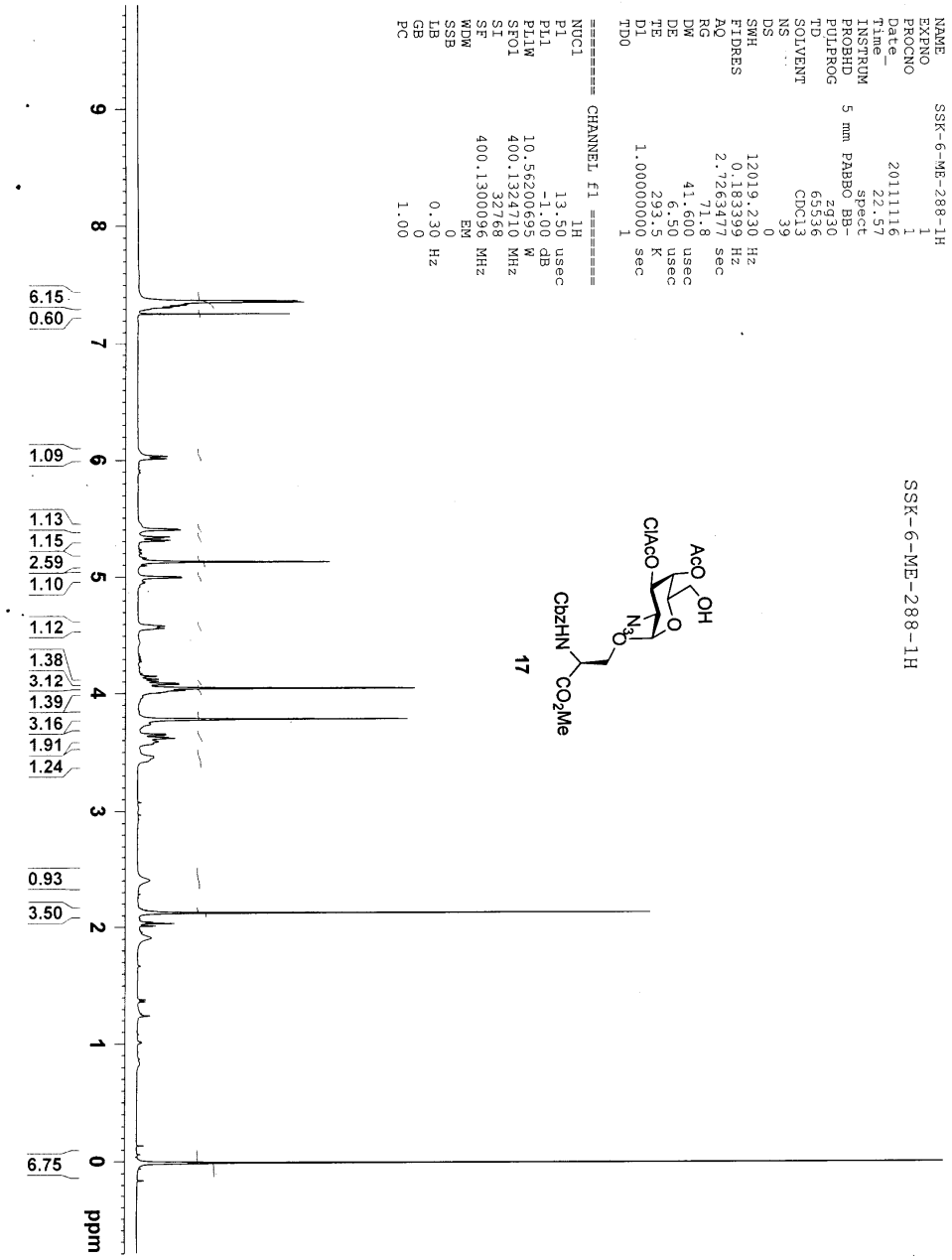

```
NAME                    SSK-6-ME-280-1H COSY
EXPNO                   64
PROCNO                  2
Date_                   20110618
Time_                   1.45
INSTRUM                 spect
PROBHD                  5 mm PABBO BB-
PULPROG                 cosygpqf
TD                      2048
SOLVENT                 CDCl3
NS                      100
DS                      16
SWH                     3612.717 Hz
FIDRES                  1.764022 Hz
AQ                      0.2834932 sec
RG                      203
DW                      138.400 usec
DE                      6.50 usec
TE                      294.4 K
D0                      0.00000300 sec
D1                      1.00000000 sec
D13                     0.00000400 sec
D16                     0.00020000 sec
TNO                     0.00027680 sec

========== CHANNEL f1 ==========
NUC1                    1H
P0                      13.50 usec
P1                      13.50 usec
PL1                     -1.00 dB
PL1W                    10.56206695 W
SFO1                    400.1319961 MHz

====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPZ1                    10.00 %
P16                     1000.00 usec
ND0                     1
TD                      187
SFO1                    400.1316 MHz
FIDRES                  19.319296 Hz
SW                      9.029 ppm
FnMODE                  QF
SI                      2048
SF                      400.1300099 MHz
WDW                     SINE
SSB                     0
LB                      0.00 Hz
GB                      0
PC                      1.40
SI                      ±12
MC2                     QF
SF                      400.1300099 MHz
WDW                     SINE
SSB                     0
LB                      0.00 Hz
GB                      0
```

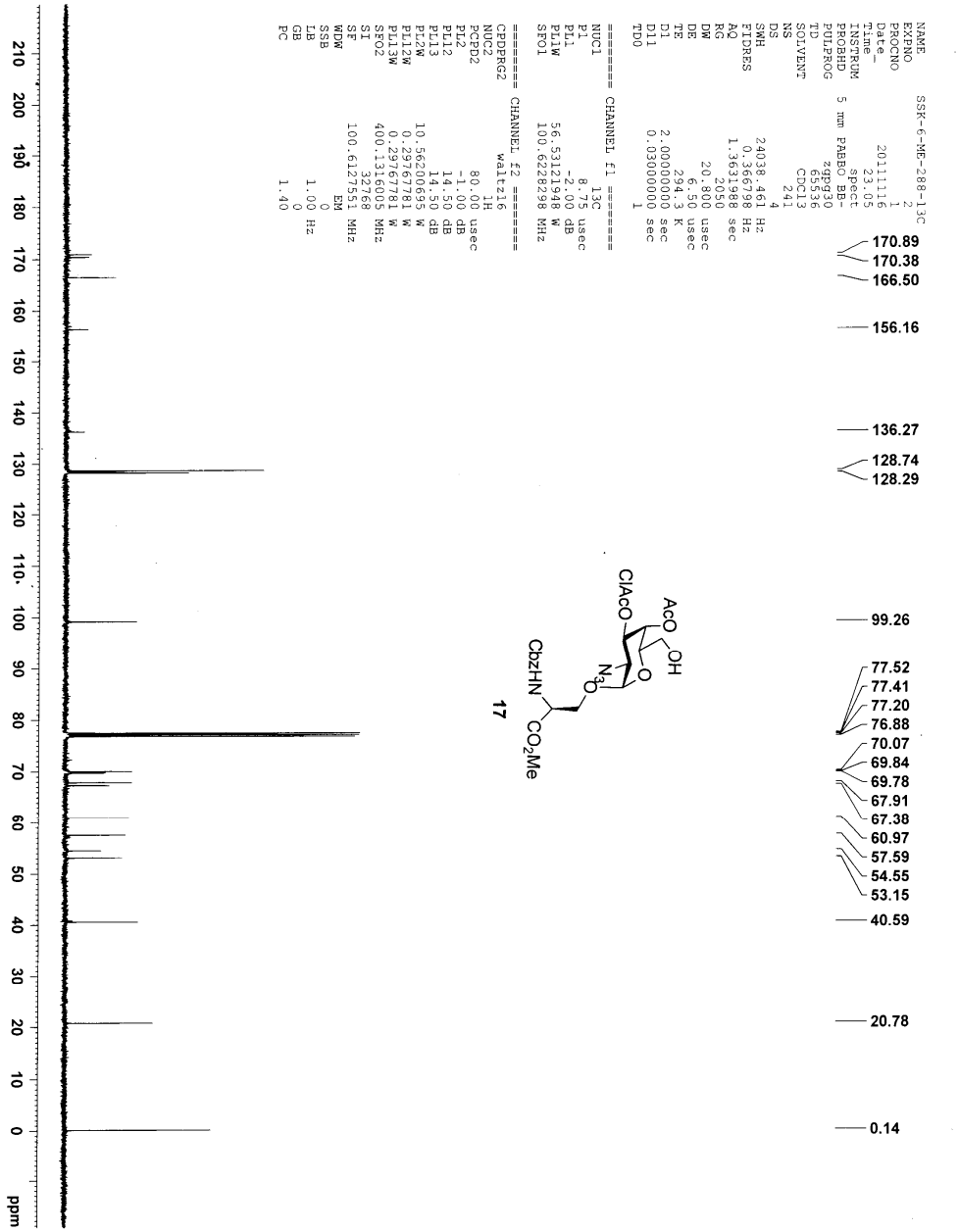


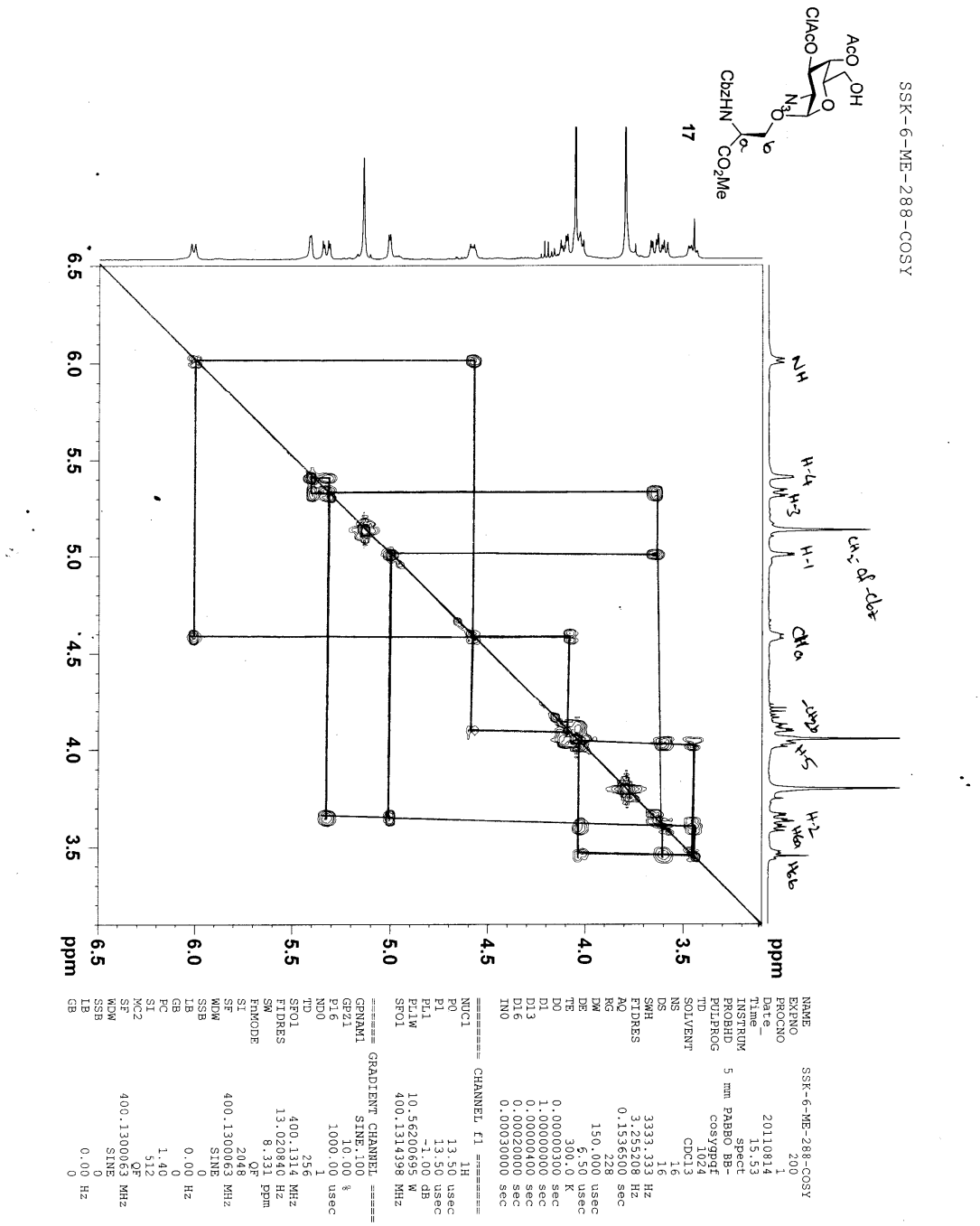





```
NAME                    SSK-6-ME-856-COSY
EXPNO                                  3
PROCNO                                 1
Date_                           20130330
Time                                16.16
INSTRUM                             spect
PROBHD     5 mm PABBO BB-
PULPROG                         cosygpqf
TD                                  1024
SOLVENT                           cdcl3
NS                                    16
DS                                    16
SWH                           1230.315 Hz
FIDRES                        1.201479 Hz
AQ                            0.416203€ sec
RG                                   322
DW                              406.400 usec
DE                                 6.50 usec
TE                                293.3 K
D0                          0.00000300 sec
D1                          1.00000000 sec
D13                         0.00000400 sec
D16                         0.00020000 sec
IN0                         0.00081280 sec

========== CHANNEL f1 ==========
NUC1                               1H
P0                              13.50 usec
P1                              13.50 usec
PL1                             -1.00 dB
PL1W                    10.56200695 W
SFO1                   400.1318200 MHz

====== GRADIENT CHANNEL =====
GPNAM1                     SINE.100
GPZ1                          10.00 %
P16                         1000.00 usec
NDO                                1
TD                               247
SFO1                   400.1318 MHz
FIDRES                    4.981074 Hz
SW                        3.075 ppm
FnMODE                          QF
ST                              2048
SF                     400.1300095 MHz
WDW                          SINE
SSB                             0
LB                           0.00 Hz
GB                              0
PC                           1.40
SI                              512
MC2                              QF
SF                     400.1300095 MHz
WDW                          SINE
SSB                             0
LB                           0.00 Hz
GB                              0
```


NAME SSK-6-ME-288-1H
EXPNO 1
PROCNO 1
Date_ 20111116
Time_ 22.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 39
DS 0
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 71.8
DW 41.600 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-288-1H
ClAcO
AcO
OH
O
N3
CbzHN
CO2Me
17
6.15
0.60
1.09
1.13
1.15
2.59
1.10
1.12
1.38
3.12
1.39
3.16
1.91
1.24
0.93
3.50
6.75
9
8
7
6
5
4
3
2
1
0
ppm






```
NAME                    SSK-6-ME-288-COSY
EXPNO                   200
PROCNO                  1
Date_                   20110814
Time                    15.53
INSTRUM                 spect
PROBHD                  5 mm PABBO BB-
PULPROG                 cosygpqf
TD                      1024
SOLVENT                 CDCl3
NS                      16
DS                      16
SWH                     3333.333 Hz
FIDRES                  3.255208 Hz
AQ                      0.153600 sec
RG                      228
DW                      150.000 usec
DE                      6.50 usec
TE                      300.0 K
D0                      0.00000300 sec
D1                      1.00000000 sec
D13                     0.00000400 sec
D16                     0.00020000 sec
IN0                     0.00030000 sec
======== CHANNEL f1 ========
NUC1                    1H
P0                      13.50 usec
P1                      13.50 usec
PL1                     -1.00 dB
PL1W                    10.56200695 W
SFO1                    400.1314398 MHz
====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPZ1                    10.00 %
P16                     1000.00 usec
ND0                     1
TD                      256
SFO1                    400.1314 MHz
FIDRES                  13.020840 Hz
SW                      8.331 ppm
FnMODE                  QF
SI                      2048
SF                      400.1300063 MHz
WDW                     SINE
SSB                     0
LB                      0.00 Hz
GB                      0
PC                      1.40
SI1                     512
MC2                     QF
SF                      400.1300063 MHz
WDW                     SINE
SSB                     0
LB                      0.00 Hz
GB                      0
```