SUPPORTING INFORMATION

Expeditious Synthesis of Bacterial, Rare Sugar Building Blocks to Access the Prokaryotic Glycome

Madhu Emmadi, and Suvarn S. Kulkarni*

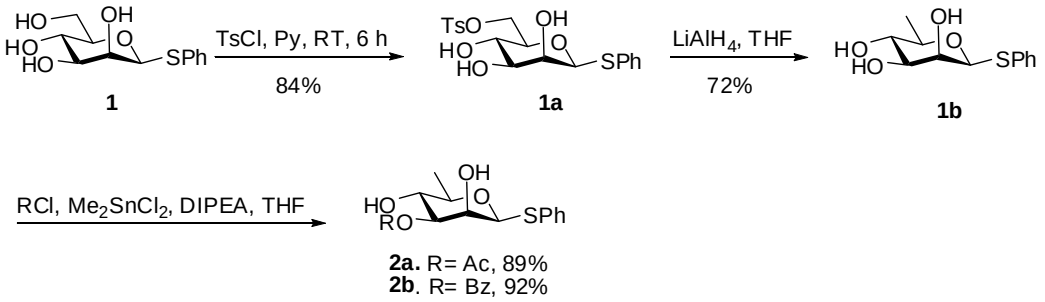
Department of Chemistry, Indian Institute of Technology Bombay,Mumbai, India.

Email: suvarn@chem.iitb.ac.in

Table of Contents

I. Experimental Procedures

Synthesis of diols 2a and 2b:



Phenyl 6-*O*-Tosyloxy-1-thio-*β*-D-mannopyranoside (1a):

To a cooled solution of phenyl-1-thio-*β*-D-mannopyranoside **1** (9.5 g, 35.1 mmol) in pyridine (80 mL) was added a solution of TsCl (7.3 g, 38.6 mmol) in pyridine (54 mL) at 0 °C. The reaction mixture was gradually brought to rt and stirred for 6 h. After completion of starting material, solvents were evaporated under reduced pressure and the crude product was chromatographed (ethyl acetate/pet ether = 3/2, v/v) to obtain the desired product **1a** as a foam (12.5 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H, ArH), 7.36-7.33 (m, 2H, ArH), 7.18-7.16 (m, 6H, ArH), 4.81 (s, 1H, H-1), 4.34-4.32 (m, 2H), 4.22 (d, *J* = 3.0 Hz, 1H), 3.79 (t, *J* = 9.6 Hz, 1H, H-4), 3.68-3.65 (m, 1H), 3.50-3.45 (m, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 134.7, 132.4, 130.5, 130.0, 128.9, 128.0, 127.0, 87.0, 77.7, 74.7, 72.5, 69.7, 66.9, 21.6; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{19}H_{22}O_7NaS_2$, 449.0705; found, 449.0746.

Phenyl 6-Deoxy-1-thio-*β*-D-mannopyranoside (1b):

A solution of **1a** (6.2 g, 14.6 mmol) in THF (110 mL) was added dropwise to a suspension of LAH (1.7 g, 43.8 mmol) in THF (38 mL) at 0 °C and the solution was refluxed for 2 h at 80 °C. After complete consumption of starting material the reaction mixture was brought to 0 °C and LAH was quenched with a drop wise addition of EtOAc followed by water, the so formed precipitate was dissolved in 2N H_2SO_4 (100 mL) and extracted with EtOAc (300 mL x 2). Separated organic layer was dried over Na_2SO_4, concentrated and chromatographed (ethyl acetate/pet ether = 3/2, v/v) to obtain **1b** as a white solid (3.73 g, 72%). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.45-7.43

(m, 2H, ArH), 7.31-7.28 (m, 2H, ArH), 7.22-7.18 (m, 1H, ArH), 5.04 (s, 1H, H-1), 4.20 (bs, 3H, OH), 4.09 (s, 1H), 3.58 (dd, J = 9.0, 3.2 Hz, 1H), 3.44 (t, J = 9.0 Hz, 1H), 3.40-3.34 (m, 1H), 1.29 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 137.6, 130.0, 129.7, 127.0, 87.5, 77.0, 75.7, 73.8, 73.3, 18.4; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{12}H_{16}O_4NaS$, 279.0667; found, 279.0663.

Phenyl 3-*O*-Acetyl-6-deoxy-1-thio-β-D-mannopyranoside (2a):

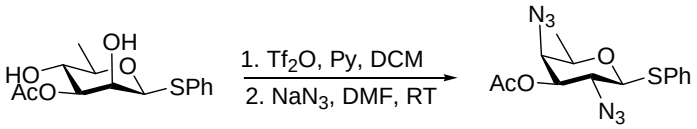
Me_2SnCl_2 (85 mg, 0.39 mmol) and DIPEA (2.7 mL, 15.6 mmol) were sequentially added to a stirred solution of **1b** (2.0 g, 7.8 mmol) in THF (40 mL). To this, AcCl (0.61 mL, 8.58 mmol) was added, after 1h the reaction mixture was quenched with 3% HCl and extracted with EtOAc (100 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (40% ethyl acetate: pet ether) to afford **2a** as a white solid (89%, 2.08 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H, ArH), 7.31-7.24 (m, 3H, ArH), 4.88 (d, J = 0.8 Hz, 1H, H-1), 4.75 (dd, J = 9.6, 3.2 Hz 1H, H-3), 4.28 (dd, J = 3.2, 0.8 Hz, 1H, H-2), 3.71 (t, J = 9.6 Hz, 1H, H-4), 3.45-3.38 (m, 1H, H-5), 2.15 (s, 3H, CH_3), 1.39 (d, J = 6.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 133.8, 131.6, 129.2, 127.8, 87.0, 77.0, 76.9, 70.1, 70.5, 21.3, 18.0; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{14}H_{18}O_5NaS$, 321.0773; found, 321.0776.

Phenyl 3-*O*-Benzoyl-6-deoxy-1-thio-β-D-mannopyranoside (2b):

Me_2SnCl_2 (85 mg, 0.39 mmol) and DIPEA (2.7 mL, 15.6 mmol) were added to a stirred solution of **1b** (2.0 g, 7.8 mmol) in THF (40 mL). To this, BzCl (1.0 mL, 8.58 mmol) was added, after 1h the reaction mixture was quenched with 3% HCl and extracted with EtOAc (100 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated *in vacuo*, and purified by column chromatography (25% ethyl acetate: pet ether) to afford **2b** as a white solid (92%, 2.6 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H, ArH), 7.56-7.54 (m, 1H, ArH), 7.48-7.46 (m, 2H, ArH), 7.41-7.37 (m, 2H, ArH), 7.32-7.25 (m, 3H, ArH), 5.00 (dd, J = 9.6, 3.2 Hz, 1H, H-3), 4.93 (d, J = 0.8 Hz, 1H, H-1), 4.40 (dd, J = 3.2, 0.8 Hz, 1H, H-2), 3.86 (t, J = 9.6 Hz, 1H, H-4), 3.48-3.44 (m, 1H, H-5), 1.41 (d, J = 6.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 134.0, 133.7, 131.5, 130.0, 129.4, 129.2, 128.6, 127.8, 87.1,

77.6, 76.8, 71.1, 70.7, 18.1; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{19}H_{20}O_5NaS$, 383.0929; found, 383.0941.

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

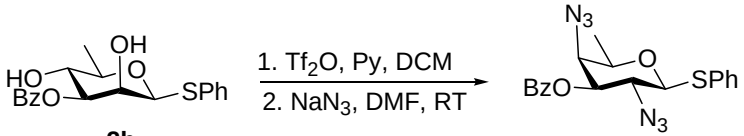


2a 82% Over 2 steps **3a**

Trifluoromethanesulfonic anhydride (6.1 mL, 36.9 mmol) was added dropwise at -10 ^oC to a stirred solution of **2a** (1.8 g, 6.0 mmol) and pyridine (6.3 mL, 78.4 mmol) in CH_2Cl_2 (55 mL) and this solution was gradually brought to 10 ^oC over 2 h. After complete consumption of starting material, as indicated by TLC, the reaction mixture was concentrated *in vacuo* and the crude product was used for the next step without any purification.

The crude product which was obtained in the above step was dissolved in DMF (40 mL) and to this, NaN_3 (3.9 g, 60 mmol) was added. The reaction mixture was stirred at rt for 8 h and then it was diluted with EtOAc (50 mL) and washed with water. Separated aqueous layer was washed with EtOAc (50 mL x 2). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The desired product was purified by column chromatography (10% ethyl acetate: pet ether) to obtain **3a** as a pale yellowish liquid (1.72 g, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H, ArH), 7.34-7.33 (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, CH_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*): $[M + Na]^+$ calcd. for $C_{14}H_{16}N_6O_3NaS$, 371.0902; found, 371.0905.

Phenyl 2,4-Diazido-3-*O*-benzoyl-2,4,6-trideoxy-1-thio-β-D-galactopyranoside (3b):

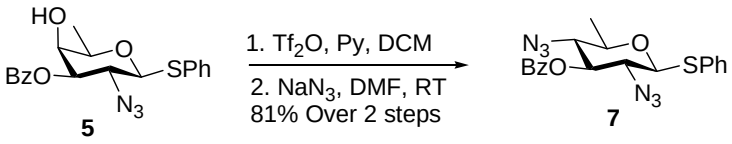


2b 85% Over 2 steps **3b**

Trifluoromethanesulfonic anhydride (3.4 mL, 20.0 mmol) was added drop wise at -10 ^{o}C to a stirred solution of **2b** (1.2 g, 3.3 mmol) and pyridine (3.5 mL, 43.1 mmol) in CH_2Cl_2 (42 mL) and the solution was gradually brought to 10 ^{o}C over 2 h. After complete consumption of starting material, reaction mixture was concentrated *in vacuo* and the crude product was used for the next step without any purification.

The crude product which was obtained in the above step was dissolved in DMF (28 mL) and to this, NaN_3 (2.15 g, 33.2 mmol) was added. This reaction mixture was stirred at rt for 8 h and then it was diluted with EtOAc (50 mL) and washed with water. Separated aqueous layer was washed with EtOAc (50 mL x 2). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The desired product was purified by column chromatography (10% ethyl acetate: pet ether) to obtain **3b** as a pale yellowish liquid (1.15 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.07 (m, 2H, ArH), 7.64-7.59 (m, 3H, ArH), 7.50-7.46 (m, 2H, ArH), 7.38-7.35 (m, 3H, ArH), 5.18 (dd, *J* = 10.0, 3.5 Hz 1H, H-3), 4.49 (d, *J* = 10.0 Hz, 1H, H-1), 3.85 (dd, *J* = 3.5, 1.0 Hz, 1H, H-4), 3.80-3.77 (m, 2H, H-2 & H-5), 1.39 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 133.9, 133.4, 131.2, 130.1, 129.1, 128.7, 128.5, 128.4, 86.6, 75.8, 73.6, 63.1, 59.8, 17.8; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{19}H_{18}N_6O_3NaS$, 433.1059; found, 433.1039.

Phenyl 2,4-Diazido-3-*O*-benzoyl-2,4,6-trideoxy-1-thio-β-D-glucopyranoside (7):

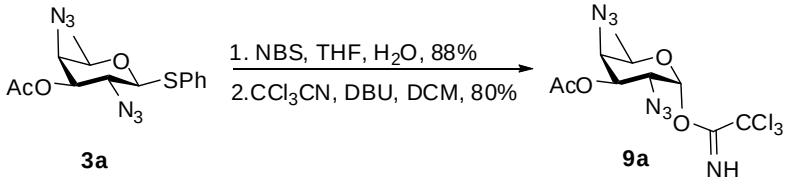


Trifluoromethanesulfonic anhydride (30 µL, 0.18 mmol) was added drop wise at -10 ^{o}C to a stirred solution of **5** (58 mg, 0.15 mmol) and pyridine (75 µL, 0.9 mmol) in CH_2Cl_2 (1 mL) and this solution was gradually brought to 10 ^{o}C over 2 h. After complete consumption of starting material, reaction mixture was concentrated *in vacuo* and the crude product was used for the next step without purification.

The crude product which was obtained in above step was dissolved in DMF (1.2 mL) and to this, NaN_3 (0.1 g, 1.5 mmol) was added. The reaction mixture was stirred at rt for 10 h and then it 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 (10% ethyl acetate: pet ether) to

afford **7** as a white solid (51 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H, ArH), 7.63-7.59 (m, 3H, ArH), 7.49-7.45 (m, 2H, ArH), 7.38-7.35 (m, 3H, ArH), 5.28 (t, *J* = 10.0 Hz, 1H, H-3), 4.57 (d, *J* = 10.0 Hz, 1H, H-1), 3.49-3.44 (m, 2H, H-2 & H-5), 3.29 (t, *J* = 10.0 Hz, 1H, H-4), 1.45 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 133.9, 133.8, 130.9, 130.1, 129.3, 128.9, 128.8, 128.7, 86.3, 75.3, 75.1, 65.9, 63.6, 18.8; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{19}H_{18}N_6O_3NaS$, 433.1059; found, 433.1055.

3-*O*-Acetyl-2,4-diazido-2,4,6-trideoxy-α-D-galactopyranoside Trichloroacetimidate (9a):

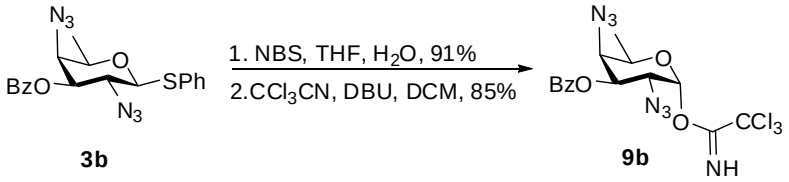


3a **9a**

NBS (1.0 g, 6.0 mmol) was added at 0 °C to a cooled solution of **3a** (0.7 g, 2.0 mmol) in THF: H_2O (30 mL, 4:1). After 10 min. reaction mixture was brought to rt and stirred for 30 min. Then solvents were evaporated and the crude product was purified by column chromatography on silica gel (20% ethyl acetate: pet ether) to afford the desired hemiacetal as a viscous liquid (0.45 g, 88%).

DBU (70 µL, 0.47 mmol) was added at -5 ^{o}C to the solution of hemiacetal (0.4 g, 1.56 mmol) and Cl_3CCN (1.9 mL, 19.0 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture was stirred at the same temperature for 1 h. The mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (10% ethyl acetate: pet ether) to afford **9a** as a white foam (0.5 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H, NH), 6.39 (d, *J* = 3.6 Hz, 1H, H-1), 5.39 (dd, *J* = 10, 3.4 Hz, 1H, H-3), 4.27 (q, *J* = 6.4 Hz, 1H, H-5), 4.10-4.03 (m, 2H, H-2 & H-4), 2.22 (s, 3H, CH_3), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 160.8, 94.8, 90.9, 71.6, 67.6, 63.5, 57.1, 20.8, 17.3.

3-*O*-Benzoyl-2,4-diazido-2,4,6-trideoxy-α-D-galactopyranoside Trichloroacetimidate (9b):



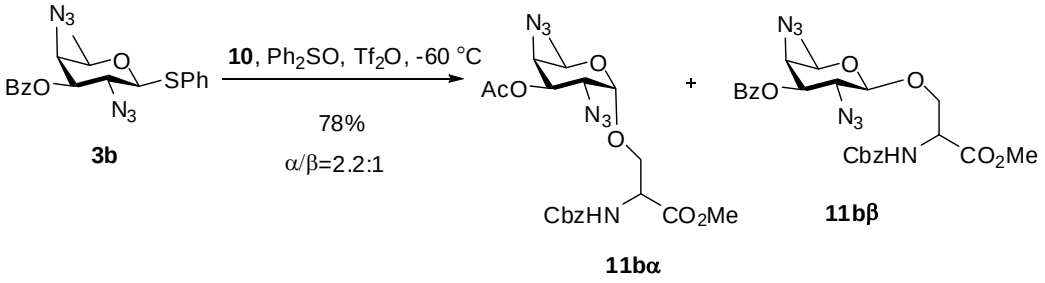
3b **9b**

NBS (0.34 g, 1.9 mmol) was added at 0 °C to a cooled solution of **3b** (0.26 g, 0.64 mmol) in THF: H_2O (9.5 mL, 4:1). After 10 min. reaction mixture was brought to rt and stirred for 30 min. Then solvents were evaporated and the crude product was purified by column chromatography on silica gel (20% ethyl acetate: pet ether) to afford the desired hemiacetal as a viscous liquid (0.18 g, 91%).

DBU (26 µL, 0.17 mmol) was added at -5 ^oC to the solution of hemiacetal (0.18 g, 0.57 mmol) and Cl_3CCN (0.7 mL, 7.0 mmol) in CH_2Cl_2 (3.5 mL) and the reaction mixture was stirred at the same temperature for 1 h. The mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (10% ethyl acetate: pet ether) to afford **9b** as a white foam (0.22 g, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H, NH), 8.12 (d, J = 7.8 Hz, 2H, ArH), 7.63 (t, J = 7.8 Hz, 1H, ArH), 7.52 (t, J = 7.8 Hz, 2H, ArH), 6.47 (d, J = 3.6 Hz, 1H, H-1), 5.67 (dd, J = 10.8, 3.4 Hz, 1H, H-3), 4.38 (q, J = 6.4 Hz, 1H, H-5), 4.23 (dd, J = 10.8, 3.6 Hz, 1H, H-2), 4.18-4.17 (m, 1H, H-4), 1.33 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 160.8, 134.1, 130.2, 128.8, 128.5, 94.9, 90.9, 71.7, 67.9, 63.8, 57.6, 17.3.

Stereoselective glycosylation of L-serine acceptor 10 with various donors:

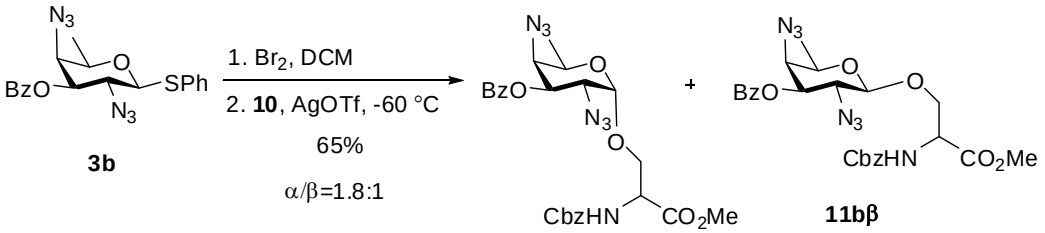
A. Thioglycoside 3b using Ph_2SO/Tf_2O as promoter:



Tf_2O (6 µL, 0.34 mmol) was added at -60 °C to a cooled solution of 3**b** (0.1 g, 0.24 mmol) and Ph_2SO (0.15 g, 0.68 mmol) in CH_2Cl_2 (10 mL). After 10 min. aminoacid (0.12 g, 0.48 mmol) in DCM (3 mL) added slowly and after stirring the reaction mixture at the same temperature for 1 h, diluted with DCM and washed with aq. $NaHCO_3$ and brine. Separated organic layer dried over Na_2SO_4, concentrated and

chromatographed to yield the desired product **11b** as white solid (0.11 g, 78%, α/β = 2.2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ (for α-isomer **11b**α) 8.10 (d, *J* = 7.2 Hz, 2H, ArH), 7.63-7.59 (m, 1H, ArH), 7.50-7.46 (m, 2H, ArH), 7.38-7.32 (m, 5H, ArH), 5.82 (d, *J* = 8.2 Hz, 1H, NH), 5.57 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3), 5.18 (s, 2H, CH_2 of Cbz), 4.91 (d, *J* = 3.6 Hz, 1H, H-1), 4.57-4.55 (m, 1H, -CH), 4.15-3.98 (m, 4H, H-4, H-5, CH_2), 3.79 (s, 3H, CH_3), 3.69 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 1.25 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 165.7, 156.0, 134.0, 130.2, 128.8, 128.7, 128.4, 128.3, 99.3, 70.8, 69.5, 67.3, 65.6, 64.2, 57.8, 54.5, 53.1, 17.2.
^{1}H NMR (400 MHz, $CDCl_3$) δ (for β-isomer **11b**β) 8.09 (d, *J* = 7.8 Hz, 2H, ArH), 7.63-7.60 (m, 1H, ArH), 7.50-7.46 (m, 2H, ArH), 7.36-7.30 (m, 5H, ArH), 5.80 (d, *J* = 8.2 Hz, 1H, NH), 5.13 (s, 2H, CH_2 of Cbz), 5.07 (dd, *J* = 10.4, 3.6 Hz, 1H, H-3), 4.56-4.54 (m, 1H, -CH), 4.35-4.32 (m, 1H, –CH_2), 4.30 (d, *J* = 8.0 Hz, 1H, H-1), 3.92-3.80 (m, 3H, H-2, H-4, 1H of –CH_2), 3.77 (s, 3H, CH_3), 3.66 (q, *J* = 6.4 Hz, H-5), 1.33 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 165.6, 136.4, 134.0, 130.1, 128.7, 128.64, 128.60, 128.2, 128.1, 102.6, 73.5, 69.7, 69.5, 67.1, 63.0, 61.0, 54.3, 52.9, 17.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{20}H_{25}N_7O_8Na$, 576.5137; found, 576.5129.

B. Glycosyl bromide 8 using AgOTf as promoter:

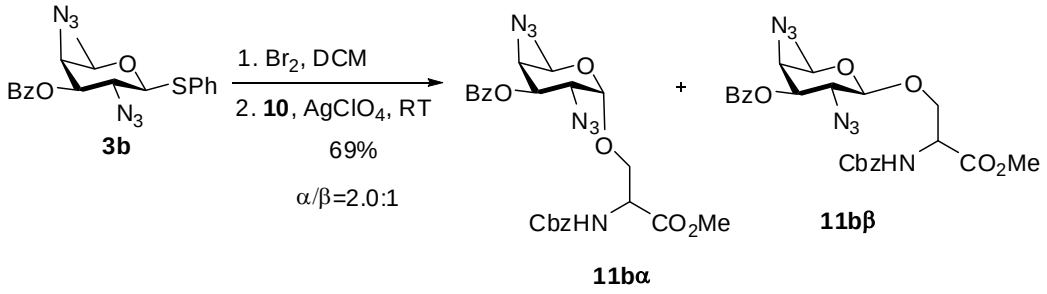


Bromine (0.08 mL, 1.5 mmol) was added to a solution of 3**b** (0.28 g, 0.68 mmol) in CH_2Cl_2 (10 mL). After 1 h, toluene was added, the mixture was concentrated, and the residue was co-evaporated twice with toluene.

The residue which was obtained after solvents removal was dissolved in CH_2Cl_2 (3 mL) and added to a solution of aminoacid **10** (0.10 g, 0.4 mmol) in CH_2Cl_2 (5 mL) containing molecular sieves. The mixture was stirred under nitrogen for 30 min at rt, after which the temperature was lowered to -50 °C and silver triflate (0.19 g, 0.75 mmol) was added. After 2 h triethylamine was added, and the stirring

was continued for 10 min. The mixture was diluted with CH_2Cl_2, filtered through celite, and concentrated. The residue was purified by silica gel chromatography to give the desired product 11b as a white solid (0.1 g, 65%, α/β = 1.8:1)

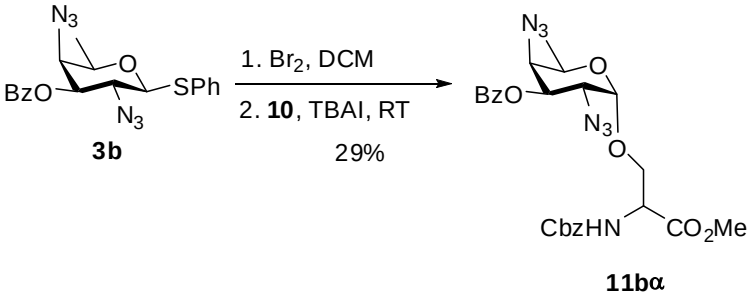
C. Glycosyl bromide 8 using $AgClO_4$ as promoter:



Bromine (0.07 mL, 1.4 mmol) was added to a solution of 3**b** (0.24 g, 0.64 mmol) in CH_2Cl_2 (8 mL). After 1 h, toluene was added, the mixture was concentrated, and the residue was co-evaporated twice with toluene.

A premixed solution of aminoacid acceptor **10** (0.10 g, 0.38 mmol) and glycosyl bromide **8** in CH_2Cl_2 (5 mL) was added to a solution of $AgClO_4$,(0.16 g, 0.76 mmol) and MS in CH_2Cl_2 (6 mL) over aperiod of 20 min. After 8 h, triethylamine was added, and the stirring was continued for 10 min. The mixture was diluted with CH_2Cl_2, filtered through celite, and concentrated. The residue was purified by silica gel chromatography to give the desired product 11b as a white solid (0.1 g, 69%, α/β = 2.0:1)

D. Glycosyl bromide 8 using TBAI as promoter:



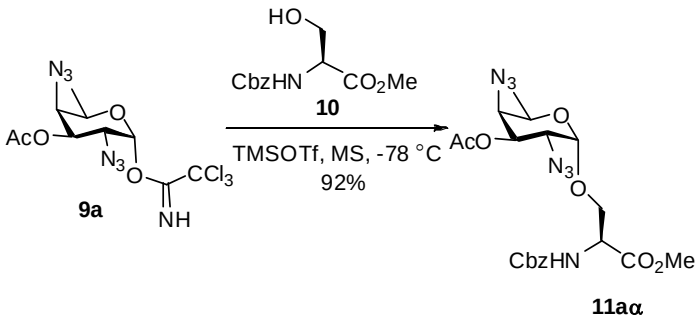
Bromine (35 μL, 0.66 mmol) was added to a solution of 3**b** (0.12 g, 0.29 mmol) in CH_2Cl_2 (4mL). After 1 h, toluene was added, the mixture was concentrated, and the residue was co-evaporated twice with toluene.

The residue in CH_2Cl_2 (1.5 mL) was added to a solution of aminoacid acceptor **10** (0.11 g, 0.4 mmol), MS, TBAI (0.33 g, 0.87 mmol), and DIPEA (40 μL, 0.33

mmol) in CH_2Cl_2 (2 mL). After 6 h the mixture was diluted with CH_2Cl_2, filtered through celite, and concentrated. The residue was purified by silica gel chromatography to give the desired product **11b** as a white solid (0.05 g, 29%, only α-isomer).

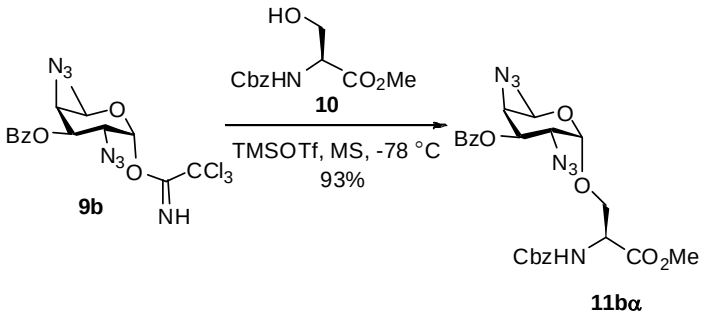
E. Imidate 9a/9b using TMSOTf as promoter:

***N*-(Benzyloxycarbonyl)-*O*-(3-*O*-acetyl-2,4-diazido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine methylester (11aα)**:



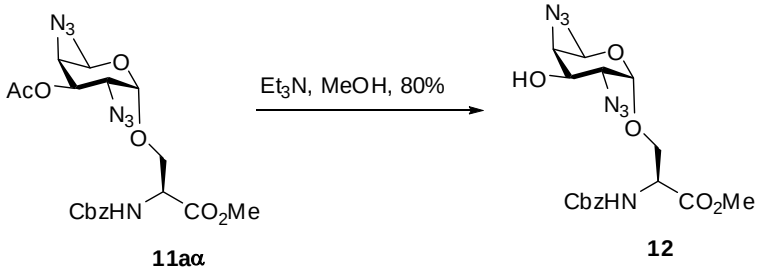
TMSOTf (75 µL, 0.38 mmol, diluted with 1.2 mL of THF) was added drop wise to a suspension of imidate **9a** (0.3 g, 0.76 mmol), the aminoacid derivative **10** (0.29 g, 1.1 mmol) and 3 Å MS (1.0 g) in THF (6.5 mL) at -78 ^{o}C and the reaction mixture was allowed to stir at the same temperature for 4 h. The mixture was diluted with CH_2Cl_2, filtered through celite, and concentrated. The residue was purified by silica gel chromatography (20% ethyl acetate: pet ether) to give the desired product **11aα** as a viscous liquid (0.35 g, 92%, only α-isomer). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H, ArH), 5.85 (d, J = 8.0 Hz, 1H, NH), 5.28 (dd, J = 10.0, 3.4 Hz, 1H, H-3), 5.12 (s, 2H, CH_2 of Cbz), 4.83 (d, J = 3.6 Hz, 1H, H-1), 4.55-4.52 (m, 1H, -CH), 4.05-4.00 (m, 3H, H-5 & -CH_2), 3.87 (d, J = 3.4 Hz, 1H, H-4), 3.77 (s, 3H, CH_3), 3.60 (dd, J = 10.0, 3.6 Hz, 1H, H-2), 2.16 (s, 3H, CH_3), 1.20 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 156.0, 136.2, 128.7, 128.4, 128.2, 99.0, 77.4, 70.6, 69.3, 67.3, 65.3, 63.9, 57.3, 54.4, 53.0, 20.7, 17.1; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{20}H_{25}N_7O_8Na$, 514.1662; found, 514.1635.

***N*-(Benzyloxycarbonyl)-*O*-(3-*O*-benzoyl-2,4-diazido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine methylester (11bα)**:



TMSOTf (29 µL, 0.14 mmol, diluted with 0.5 mL of THF) was added drop wise to a suspension of imidate **9b** (0.13 g, 0.29 mmol), the aminoacid derivative **10** (0.11 g, 0.43 mmol) and 3 Å MS (0.4 g) in THF (2.5 mL) at -78 ^{o}C and the reaction mixture was allowed to stir at the same temperature for 4 h. The mixture was diluted with CH_2Cl_2, filtered through celite, and concentrated. The residue was purified by silica gel chromatography (20% ethyl acetate: pet ether) to give the desired product **11bα** as a viscous liquid (0.15 g, 93%, only α-isomer).

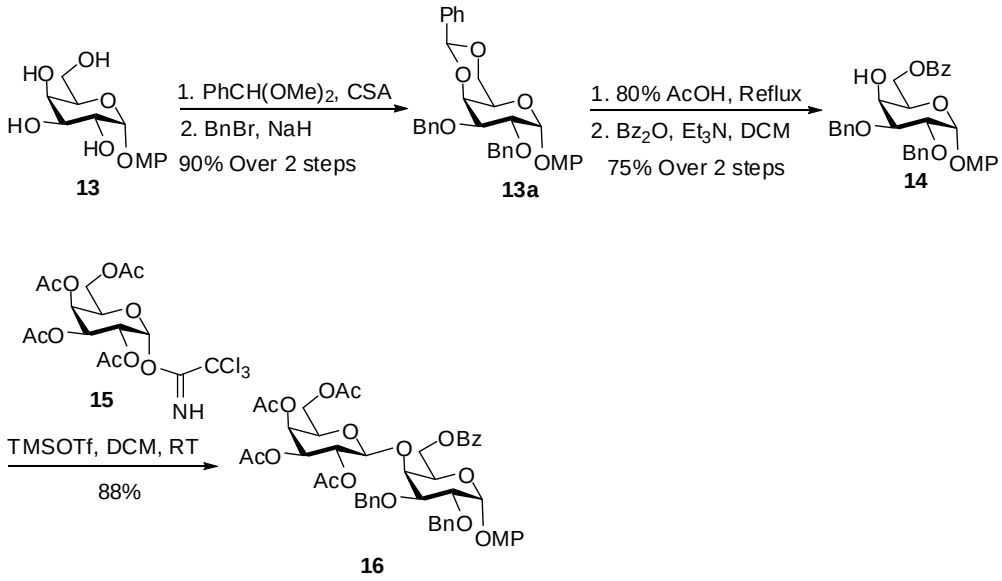
***N*-(Benzyloxycarbonyl)-*O*-(2,4-diazido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine methylester (12)**:



Et_3N (1 mL) was added to a clear solution of **11aα** (0.2 g, 0.4 mmol) in MeOH (4 mL) and the reaction mixture kept for stirring at rt overnight in dark. After complete consumption of starting material solvents were removed *in vacuo* and the crude product was chromatographed by silica gel column chromatography (30% ethyl acetate: pet ether) to afford **12** as a viscous liquid (0.152 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H, ArH), 5.80 (d, *J* = 8.0 Hz, 1H, NH), 5.12 (d, *J* = 2.0 Hz, 2H, CH_2 of Cbz), 4.83 (d, *J* = 3.6 Hz, 1H, H-1), 4.56-4.52 (m, 1H, -CH), 4.14

(dd, J = 10.0, 3.6 Hz, 1H, H-3), 4.10-3.93 (m, 3H, H-5 & -CH_2), 3.77 (s, 3H, CH_3), 3.70 (d, J = 3.6 Hz, 1H, H-4), 3.39 (dd, J = 10.0, 3.6 Hz, 1H, H-2), 1.24 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.1, 136.1, 128.6, 128.4, 128.2, 98.8, 68.9, 68.2, 67.3, 66.5, 65.8, 60.0, 54.4, 52.3, 17.2; HR-ESI-MS (*m/z*): [M + Na]$^+$ calcd. for $C_{18}H_{23}N_7O_7Na$, 472.1557; found, 472.1578.

_p_-Methoxyphenyl 2,3,4,6-Tetra-_O_-acetyl-β-D-galctopyranosyl-(1→4)-6-_O_-Benzoyl-2,3-dibenzyl-α-D-galactopyranoside (16):



_p_-Methoxyphenyl 4,6-Benzylidene-2,3-dibenzyl-α-D-galactopyranoside (13a): Camphorsulfonic acid (0.38 g, 1.6 mmol) was added to a solution of *p*-methoxyphenyl α-D-galactopyranoside **13** (1.9 g, 6.6 mmol) in acetonitrile (25 mL). After 10 min, benzaldehyde dimethyl acetal (1.2 mL, 8.0 mmol) was added drop wise to it and the mixture was kept for stirring at rt for 30 min. Then the reaction was quenched with triethylamine until the pH was adjusted to 7, and then the solvents were removed *in vacuo*.

The crude product which was obtained after removal of solvents was dissolved in DMF (25 mL) and to this, NaH (0.8 g, 33.3 mmol) was added at 0 ^{o}C. After 10 min, BnBr (3.4 mL, 20.0 mmol) was added and kept for stirring at rt overnight. Then reaction mixture was quenched with water and extracted with EtOAc twice. Combined orgnic layers were concentrated and chromatographed on silica gel (10% ethyl acetate: pet ether) to afford **13a** as a white solid (3.3 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.29 (m, 15H, ArH), 7.03 (d, J = 9.0 Hz, 2H, ArH), 6.78 (d, J =

9.0 Hz, 2H, ArH), 5.53 (d, J = 2.0 Hz, 1 H, H-1), 5.51 (s, 1H, benzylidene), 4.91-4.69 (m, 4H, $ArCH_2$), 4.27-4.17 (m, 4H), 3.99 (dd, J = 12.0, 1.6 Hz, 1H), 3.78 (s, 3H, CH_3), 3.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 151.0, 138.8, 138.5, 137.7, 128.9, 128.6, 128.4, 128.2, 127.9, 127.7, 127.69, 127.64, 126.3, 117.7, 114.5, 101.0, 97.3, 76.0, 75.3, 74.6, 73.6, 72.2, 69.4, 63.2, 55.6; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{34}H_{34}O_7Na$, 577.2202; found, 577.2192.

***p*-Methoxyphenyl 6-Benzoyl-2,3-dibenzyl-α-D-galactopyranoside (14):**

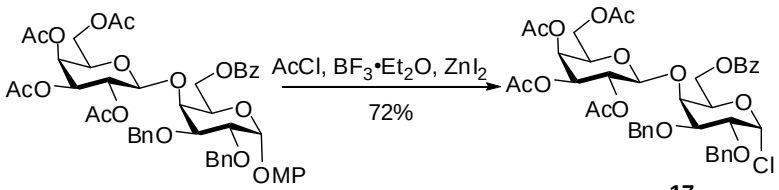
A solution of **13a** (0.65 g, 1.1 mmol) in 80% aq. acetic acid solution (26 mL) was stirred at 80 °C for 1.5 h. After complete consumption of starting material solvents were removed *in vacuo* and the residue was azeotroped with toluene twice. The crude product which was obtained after solvent removal was dissolved in CH_2Cl_2 (20 mL) and to this, Et_3N (1.5 mL, 10.6 mmol), and Bz_2O (0.37 g, 1.6 mmol) were added. After 6 h, solvents were evaporated *in vacuo* and the residue was chromatographed on silica gel (10% ethyl acetate: pet ether) to obtain the desired compound **14** as a white solid (0.5 g, 75%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H, ArH), 7.56-7.52 (m, 1H, ArH), 7.42-7.27 (m, 12H, ArH), 7.02 (d, J = 9.0 Hz, 2H, ArH), 6.67 (d, J = 9.0 Hz, 2H, ArH), 5.38 (d, J =3.6 Hz, 1H, H-1), 4.91-4.72 (m, 4H, $ArCH_2$), 4.54-4.46 (m, 2H), 4.29-4.26 (m, 1H), 4.12-4.09 (m, 2H), 4.02-3.99 (m, 1H), 3.70 (s, 3H, CH_3), 2.61 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 155.2, 150.7, 138.2, 138.0, 133.2, 129.9, 128.5, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 118.7, 114.5, 97.0, 75.6, 73.5, 73.2, 68.5, 68.0, 64.3, 55.6; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{34}H_{34}O_8Na$, 593.2151; found, 593.2129.

***p*-Methoxyphenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galctopyranosyl-(1→4)-6-*O*-Benzoyl-2,3-dibenzyl-α-D-galactopyranoside (16):**

TMSOTf (3 µL, 0.015 mmol) was added drop wise to a suspension of imidate **15** (0.25 g, 0.5 mmol), acceptor **14** (0.23 g, 0.4 mmol) and 3 Å MS (0.3 g) at rt and the reaction mixture was stirred at the same temperature for 4 h. The mixture was diluted with CH_2Cl_2 filtered through celite and concentrated. The residue was purified by silica gel chromatography (30% ethyl acetate: pet ether) to give the desired product **16** as a foam (0.32 g, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H, ArH), 7.55-7.53 (m, 1H, ArH), 7.51-7.27 (m, 12H, ArH), 6.96 (d, J = 9.0 Hz, 2H, ArH),

6.61 (d, *J* = 9.0 Hz, 2H, ArH), 5 .37 (d, *J* = 3.3 Hz, 1H, H-4'), 5 .33 (d, *J* = 3.6 Hz, 1H, H-1), 5.22 (ap.t, *J* = 10.0, 7.8 Hz, IH, H-2'), 5.02 (dd, *J* = 10.0, 3.3 Hz, 1H, H-3'), 4.91-4.61 (m, 5H, H-1' & $ArCH_2$), 4.52 (dd, *J* = 12.0, 3.4 Hz, 1H, H-6b), 4.27 (ap.t, *J* = 12.0, 8.4 Hz, 1H, H-6a), 4.25 (dd, *J* = 8.4, 3.4 Hz, 1H, H-5), 4.10-4.08 (m, 4H, H-3, H-4, H-6'a & H-6'b), 3.94 (dd, *J* = 10.0, 3.6 Hz, 1H, H-2), 3.83 (t, *J* = 6.4 Hz, 1H, H-5'), 3.68 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.83 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 169.7, 166.2, 155.0, 150.6, 138.3, 138.2, 132.9, 129.9, 129.6, 128.54, 128.50, 128.23, 127.97, 127.92, 127.8, 118.6, 114.3, 102.3, 97.0, 77.81, 76.8, 76.7, 76.4, 73.9, 73.6, 70.8, 70.4, 68.9, 68.6, 66.8, 64.8, 61.4, 55.4, 20.8, 20.7, 20.6; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{48}H_{52}O_{17}Na$, 923.3102; found, 923.3087.

2,3,4,6-Tetra-*O*-acetyl-β-D-galctopyranosyl-(1→4)-6-*O*-Benzoyl-2,3-dibenzyl-α-D-galactopyranoside Chloride (17):

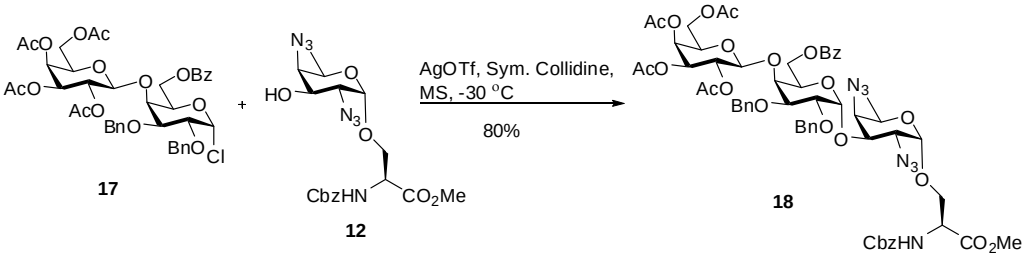


16 **17**

$BF_3{\cdot}Et_2O$ (90 µL, 0.7 mmol) was added to a solution of disacharide **16** (0.18 g, 0.2 mmol), and AcCl (0.14 mL, 1.9 mmol) in $CHCl_3$ (4 mL) at 0 °C. After 5 min, ZnI_2 (3 mg) was added and the reaction mixture was brought to rt. After stirring at rt for 45 min., the reaction mixture was diluted with CH_2Cl_2 and washed with aq. $NaHCO_3$ and brine. Separated organic layer was dried over Na_2SO_4, concentrated and chromatographed on silica gel (30% ethyl acetate: pet ether) to afford the glycosyl chloride **17** as a foam (0.12 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H, ArH), 7.49-7.47 (m, 1H, ArH), 7.38-7.11 (m, 12H, ArH), 5.99 (d, *J* = 3.6 Hz, 1H, H-1), 5.28 (d, *J* = 3.4 Hz, 1H, H-4'),), 5.22 (ap.t, *J* = 10.0, 7.8 Hz, 1H, H-2'), 4.93 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3'), 4.79-4.53 (m, 6H, H-1', H-5 & $ArCH_2$), 4.32-4.27 (m, 2H, H-6a & H-6b), 4.02-3.84 (m, 5H, H-2, H-3, H-4, H-6'a & H-6'b), 3.74 (t, *J* = 6.4 Hz, IH, H-5'), 2.06 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.74 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.5, 170.3, 169.9, 166.3, 138.1, 137.7, 133.3, 129.9, 129.8, 129.1, 128.7, 128.5, 128.3, 128.2, 128.07, 128.03, 125.4, 102.5, 94.4, 77.27, 76.57, 76.4, 74.2, 73.5, 71.5, 70.8, 70.5, 69.1, 66.8, 64.1,

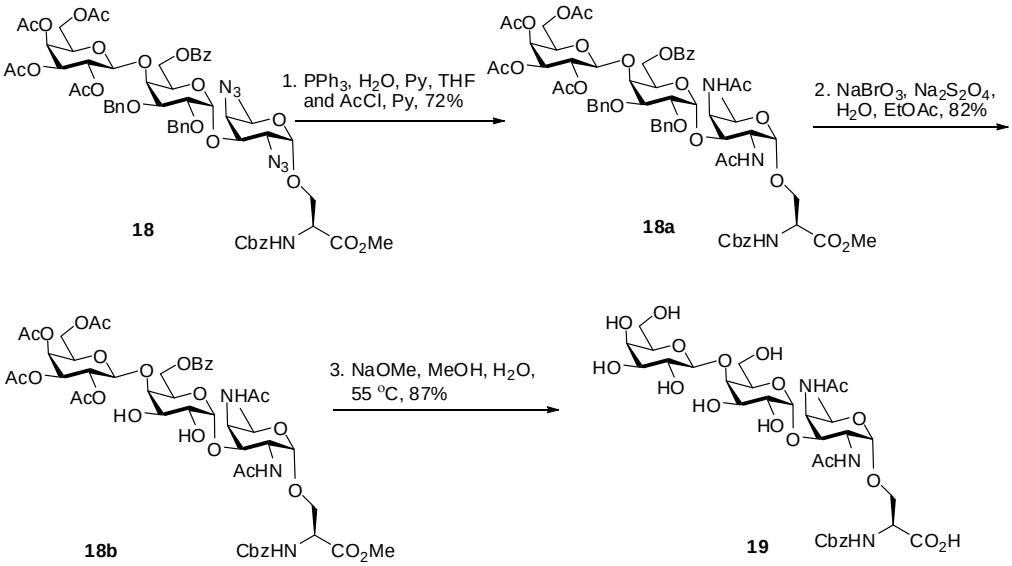
61.4, 20.9, 20.8, 20.78, 20.7; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{41}H_{45}O_{15}NaCl$, 835.2345; found, 835.2369.

***N*-(Benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-galctopyranosyl-(1→4)-6-*O*-Benzoyl-2,3-dibenzyl-*α*-D-galactopyranosyl-(1→3)-2,4-diazido-2,4,6-trideoxy-*α*-D-galactopyranosyl)-L-serine methylester (18)**:



AgOTf (0.18 g, 0.7 mmol) was added to a premixed solution of glycosyl chloride **17** (0.28 g, 0.35 mmol), acceptor **12** (0.13 g, 0.29 mmol), sym. collidene (45 µL, 0.32 mmol) and 3 Å MS in CH_2Cl_2 (8 mL) at -30 °C and the reaction mixture was stirred at the same temperature for 3 h. The reaction mixture was quenched with Et_3N and the mixture was filtered through celite. Filtrate was concentrated *in vacuo* and chromatograped on silica gel (35% ethyl acetate: pet ether) to obtain **18** as a viscous liquid (0.28 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H, ArH), 7.56-7.54 (m, 1H, ArH), 7.44-7.30 (m, 17H, ArH), 5.78 (d, *J* = 8.0 Hz, 1H, NH), 5.33 (d, *J* = 3.0 Hz, 1H, H-4''), 5.22 (ap.t, *J* = 10.0, 7.8 Hz, 1H, H-2''), 5.11 (s, 2H, CH_2 of Cbz), 5.01-4.98 (m, 2H, H-3" & H-1), 4.86-4.79 (m, 2H, $ArCH_2$), 4.74 (d, *J* = 3.6 Hz, 1H, H-1'), 4.68-4.54 (m, 4H, H-1", H-6'a & $ArCH_2$), 4.48-4.46 (m, 1H, CH), 4.41-4.30 (m, 2H), 4.06-3.82 (m, 5H), 3.78-3.70 (m, 5H), 3.68 (s, 3H, CH_3), 3.60 (s, 1H), 3.34 (dd, *J* = 10.0, *J* = 3.6 Hz, 1H, H-2'), 2.12 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.04 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.2, 169.8, 166.4, 156.0, 138.5, 138.4, 136.2, 133.0, 130.3, 129.7, 128.7, 128.68, 128.65, 128.46, 128.43, 128.2, 128.16, 128.13, 128.10, 127.7, 102.3, 101.0, 99.6, 77.9, 77.87, 76.7, 74.6, 73.8, 70.9, 70.4, 69.6, 69.2, 67.3, 66.9, 65.7, 64.3, 63.9, 61.3, 58.8, 54.5, 52.9, 21.0, 20.8, 20.7, 20.6, 17.1; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{59}H_{67}O_{22}N_7Na$, 1248.4237; found, 1248.4272.

***N*-(Benzyloxycarbonyl)-*O*-(β-D-galctopyranosyl-(1→4)-α-D-galactopyranosyl-(1→3)-2,4-diacetimido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine (19)**:



***N*-(Benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galctopyranosyl-(1→4)-6-*O*-Benzoyl-2,3-dibenzyl-α-D-galactopyranosyl-(1→3)-2,4-diacetimido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine methylester (18a)**:

Pyridine (0.15 mL, 1.9 mmol) and water (35 µL, 1.9 mmol) were added to a clear solution of trisaccharide **18** (0.23 g, 0.19 mmol) and PPh_3 (0.2 g, 0.77 mmol) in THF (4 mL) and then the reaction mixture was kept for reflux for 4 h at 70 °C. Then solvents were removed *in vacuo* and the crude product was dissolved in pyridine (3 mL) and Ac_2O (0.36 mL, 3.8 mmol) was added. After stirring the reaction mixture at rt for 10 h solvents were removed under reduced pressure and the crude product was chromatographed on silica gel (60% ethyl acetate: pet ether) to obtain **18a** as a foam (0.175 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.4 Hz, 2H, ArH), 7.60 (t, *J* = 7.4 Hz, 1H, ArH), 7.46 (t, *J* = 7.4 Hz, 1H, ArH), 7.33-7.14 (m, 16H, ArH), 6.82 (d, *J* = 9.4 Hz, 1H, NH), 6.33 (d, *J* = 9.6 Hz, 1H, NH), 6.18 (d, *J* = 9.6 Hz, 1H, NH), 5.43 (d, *J* = 3.2 Hz, 1H, H-4''), 5.32 (d, *J* = 2.7 Hz, 1H, H-1), 5.22 (ap.t, *J* = 10.0, 8.0 Hz, IH, H-2''), 5.03 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3''), 4.96 (d, *J* = 12.0 Hz, 1H, $ArCH_2$), 4.81-4.76 (m, 2H), 4.71-4.66 (m, 3H), 4.57-4.46 (m, 6H), 4.30-4.26 (m, 2H), 4.14-3.75 (m, 9H), 3.72 (s, 3H, CH_3), 3.68-3.66 (m, 1H), 2.17 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.63 (s, 3H, CH_3),

1.10 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 171.0, 170.4, 170.3, 170.2, 169.7, 169.0, 156.3, 138.4, 136.2, 134.0, 130.2, 129.1, 128.8, 128.5, 128.3, 128.0, 127.9, 127.7, 127.5, 127.4, 102.2, 99.0, 91.6, 77.4, 76.8, 75.4, 74.1, 73.0, 70.9, 70.3, 68.9, 68.5, 68.3, 66.7, 66.07, 66.0, 62.8, 60.8, 54.6, 52.6, 48.1, 47.5, 22.97, 22.94, 20.8, 20.7, 16.7; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{63}H_{75}O_{24}N_3Na$, 1280.4638; found, 1280.4702.

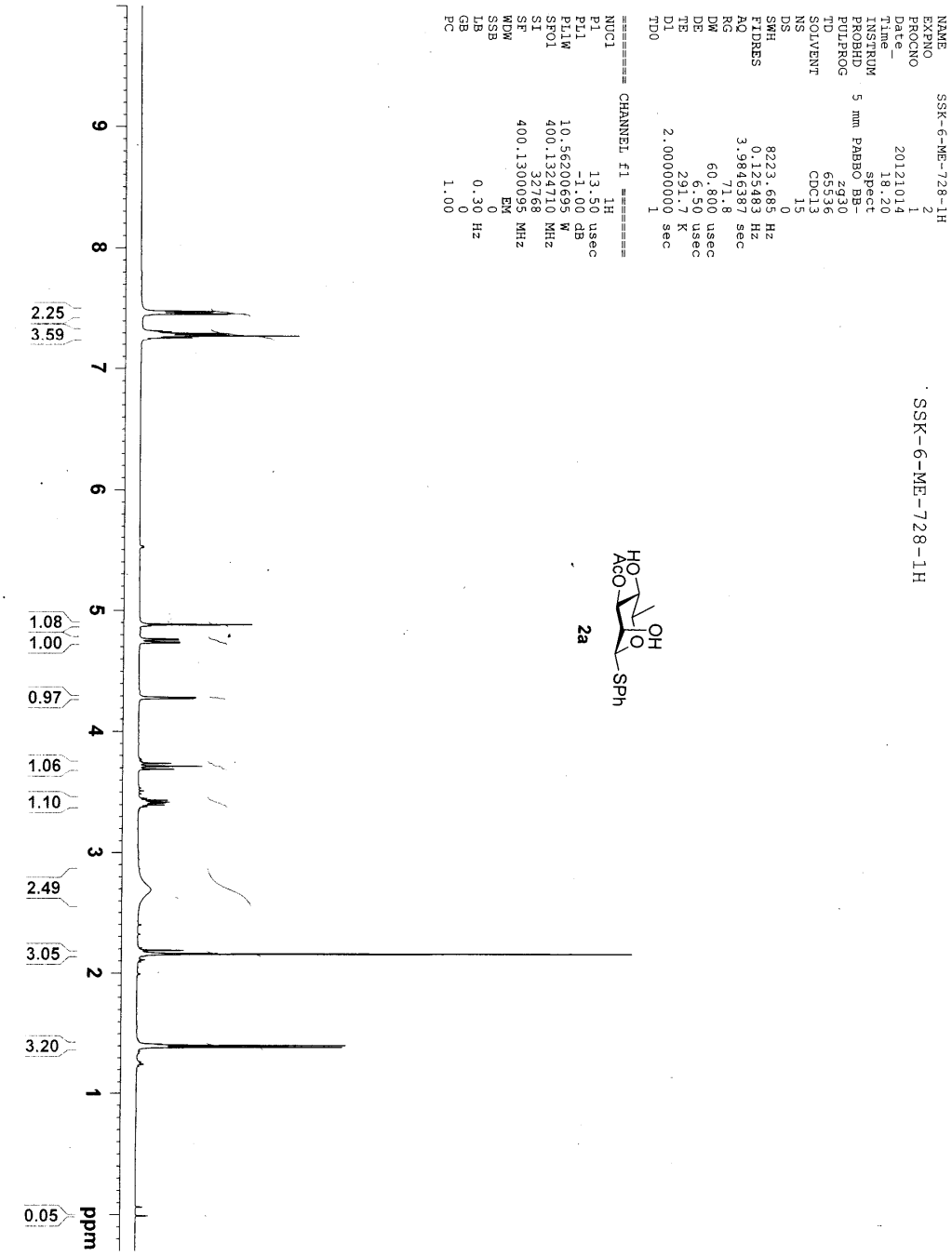
***N*-(Benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galctopyranosyl-(1→4)-6-*O*-Benzoyl-α-D-galactopyranosyl-(1→3)-2,4-diacetimido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine methylester (18b)**:

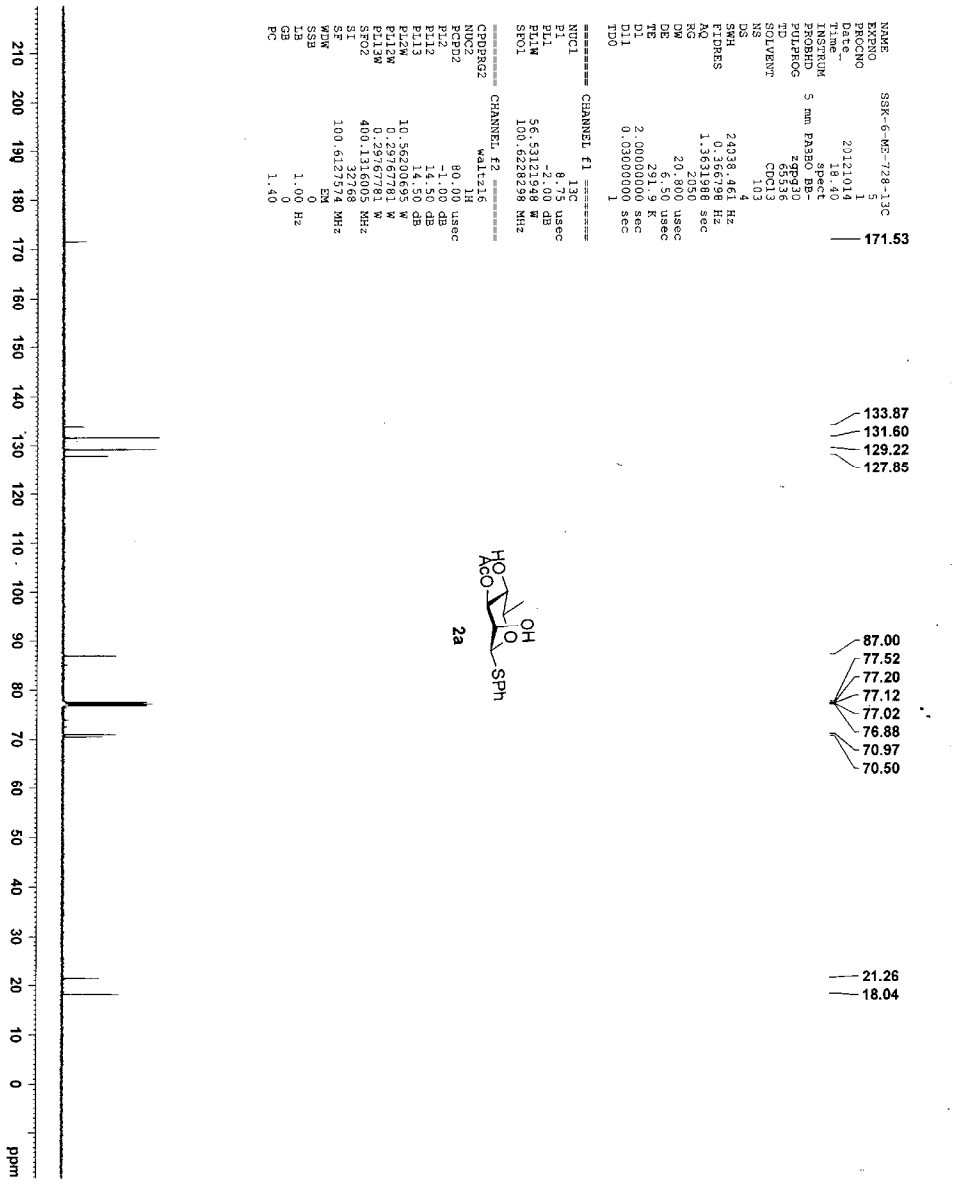
A solution of $NaBrO_3$ (0.07 g, 0.47 mmol) in water (1.5 mL) was added to a clear solution of **18a** (0.1 g, 0.08 mmol) in EtOAc (1.1 mL). To this biphasic layer a solution of $Na_2S_2O_4$ (0.07 g, 0.0.4 mmol) in water (2 mL) was added dropwise over 5 min. After 45 min. reaction mixture was quenched with aq. $Na_2S_2O_3$ solution and extracted with EtOAc (30 mL x 3). Combined organic layers dried over Na_2SO_4, concentrated and chromatographed on silica gel (5% methanol: ethyl acetate) to afford the desired product **18b** as a white solid (70 mg, 82%). ^1H NMR (400 MHz, CD_3OD) δ 8.07 (d, J = 7.4 Hz, 2H, ArH), 7.51 (t, J = 7.4 Hz, 1H, ArH), 7.47 (t, J = 7.4 Hz, 2H, ArH), 7.30-7.28 (m, 5H, ArH), 5.43 (d, J = 1.8 Hz, 1H), 5.14-5.01 (m, 5H), 4.90 (m, 1H), 4.74 (d, J = 1.8 Hz, 1H), 4.57 (t, J = 9.2 Hz, 1H), 4.46 (t, J = 4.0 Hz, 1H), 4.40-4.39 (m, 1H), 4.28-4.22 (m, 2H), 4.10-3.85 (m, 8H), 3.79-3.75 (m, 1H), 3.72 (s, 3H, CH_3), 3.71-3.68 (m, 1H), 3.57 (dd, J = 10.0, 3.6 Hz, 1H), 2.11 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.09 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD) δ 173.3, 171.7, 170.7, 170.4, 170.3, 170.2, 169.9, 166.5, 156.7, 136.2, 133.0, 129.4, 129.2, 128.2, 127.9, 127.5, 127.3, 101.7, 98.4, 96.8, 76.3, 73.3, 70.6, 69.8, 69.4, 69.0, 68.7, 67.4, 66.9, 66.2, 64.9, 62.4, 60.6, 54.2, 51.4, 49.5, 21.5, 21.0, 19.5, 18.9, 18.8, 15.3; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{49}H_{64}O_{24}N_3Na$, 1078.3880; found, 1078.3940.

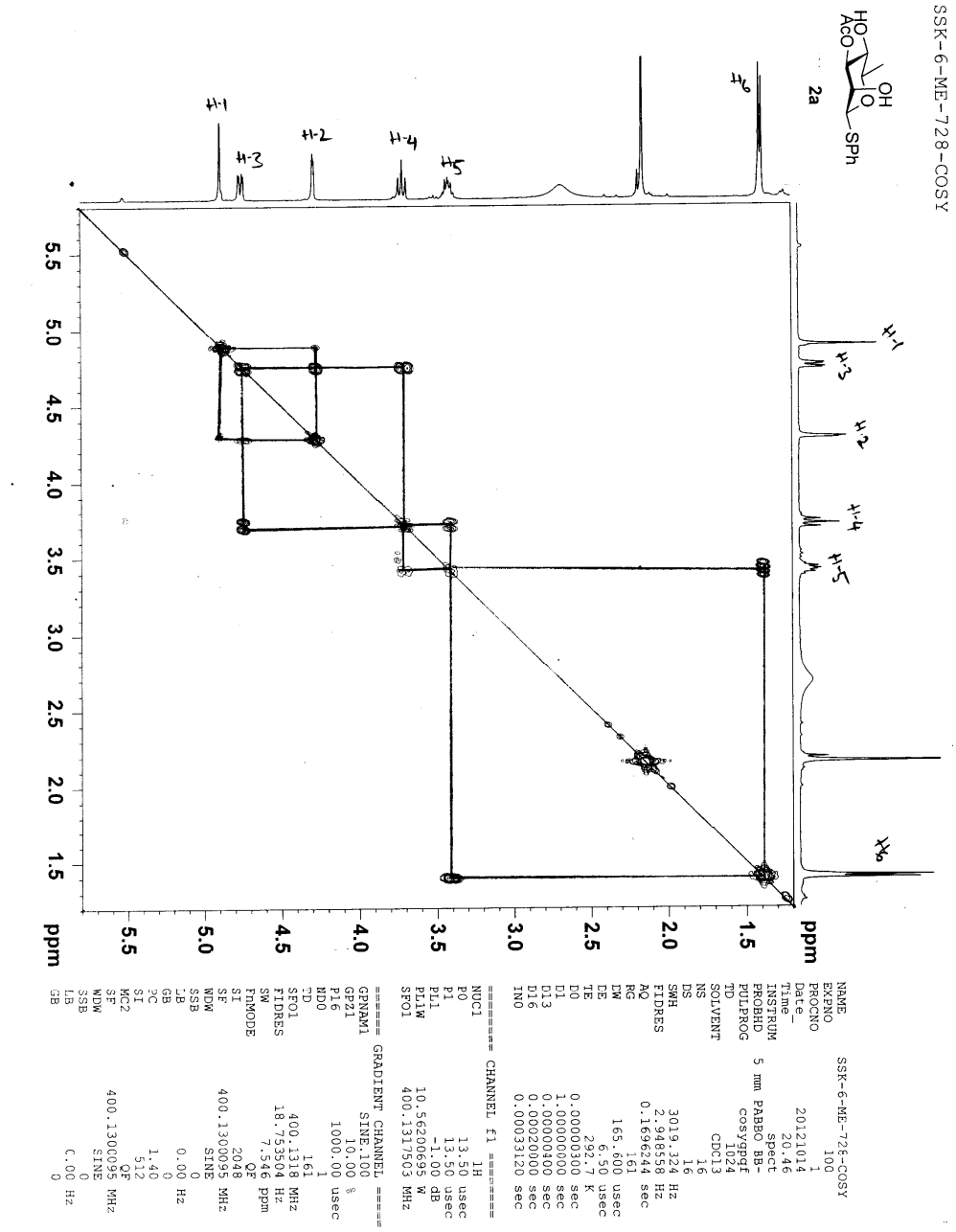
***N*-(Benzyloxycarbonyl)-*O*-(β-D-galctopyranosyl-(1→4)-α-D-galactopyranosyl-(1→3)-2,4-diacetimido-2,4,6-trideoxy-α-D-galactopyranosyl)-L-serine (19)**:

A solution of NaOMe (35 mg) in MeOH (2 mL) was added to a clear solution of **18b** (33 mg, 0.03 mmol) in MeOH (2 mL) and water (2 mL) at 50 °C (pH 10). After stirring the reaction mixture at the same temperature for 20 h, the reaction miture was neutralized with AcOH until the pH adjusted to 6. Then solvents were removed under reduced pressure and the crude product was chromatographed on silica gel (7:2:1 ethyl acetate: MeOH: H_2O) to afford the desired product **19** as a white solid (20 mg, 87%). ^{1}H NMR (400 MHz, CD_3OD) δ 7.38-7.29 (m, 5H, ArH), 5.12-5.08 (m, 2H), 4.99-4.90 (m, 2H), 4.74-4.69 (m, 1H), 4.43 (d, J = 8.0 Hz, 1H), 4.35-4.32 (m, 1H), 4.24-4.15 (m, 2H), 4.06-3.94 (m, 3H), 3.87-3.79 (m, 2H), 3.77-3.61 (m, 8H), 3.58-3.45 (m, 2H), 2.03, 2.02 (2s, 3H, CH_3), 2.02, 1.89 (2s, 3H, CH_3), 1.05, 1.03 (2d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD) δ 176.8, 174.9, 174.0, 173.8, 170.5, 158.3, 158.1, 138.3, 129.15, 129.09, 129.02, 107.0, 99.7, 99.1, 98.2, 97.9, 80.5, 77.1, 75.3, 74.5, 74.2, 73.3, 72.0, 71.9, 71.1, 71.0, 70.5, 67.7, 67.1, 66.3, 66.1, 62.9, 62.7, 61.5, 57.7, 51.3, 51.1, 50.1, 24.1, 23.2, 23.1, 22.7, 17.0; HR-ESI-MS (*m/z*): $[M + Na]^+$ calcd. for $C_{33}H_{49}O_{19}N_3Na$, 814.2858; found, 814.2849.

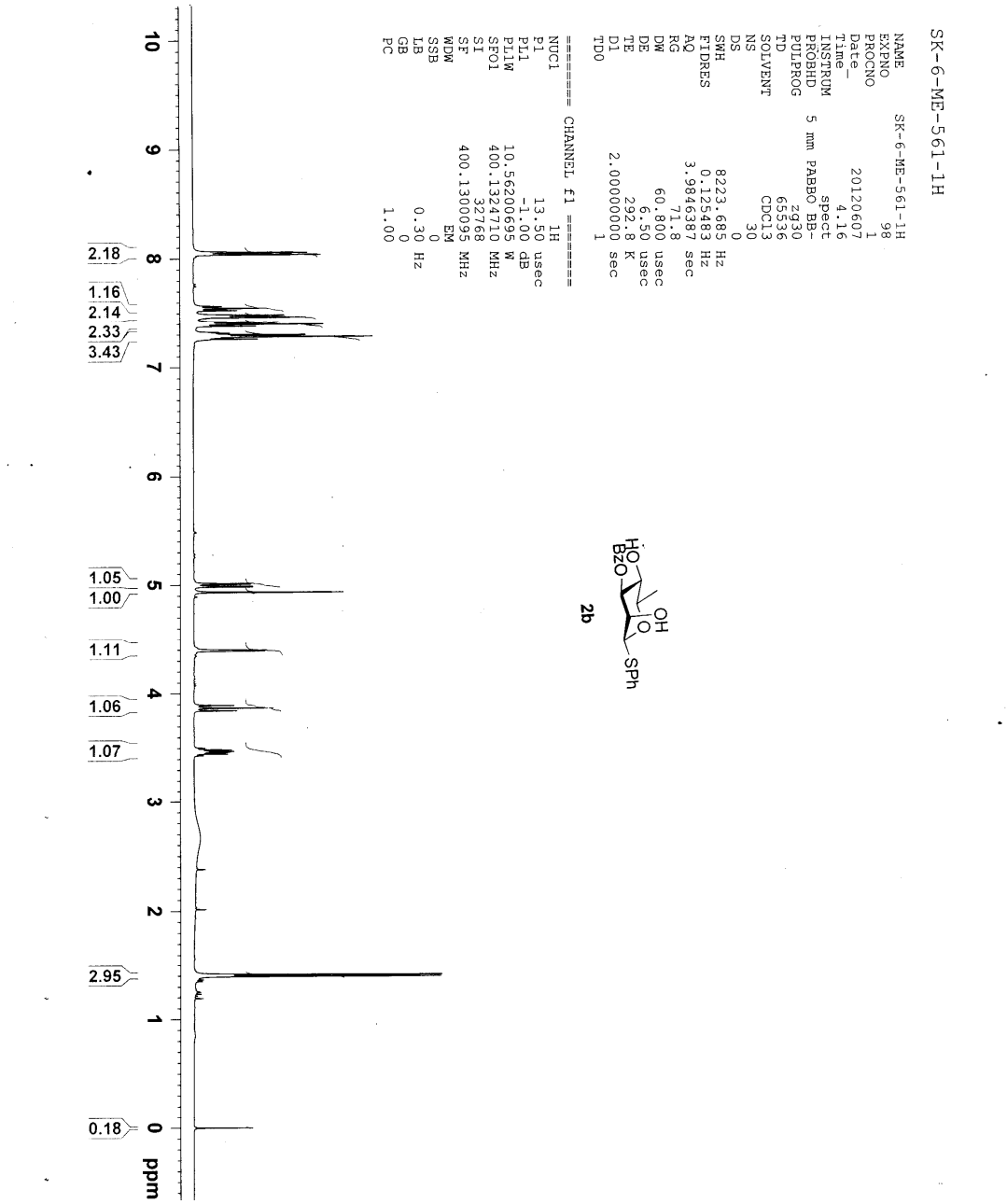
II.Spectra:

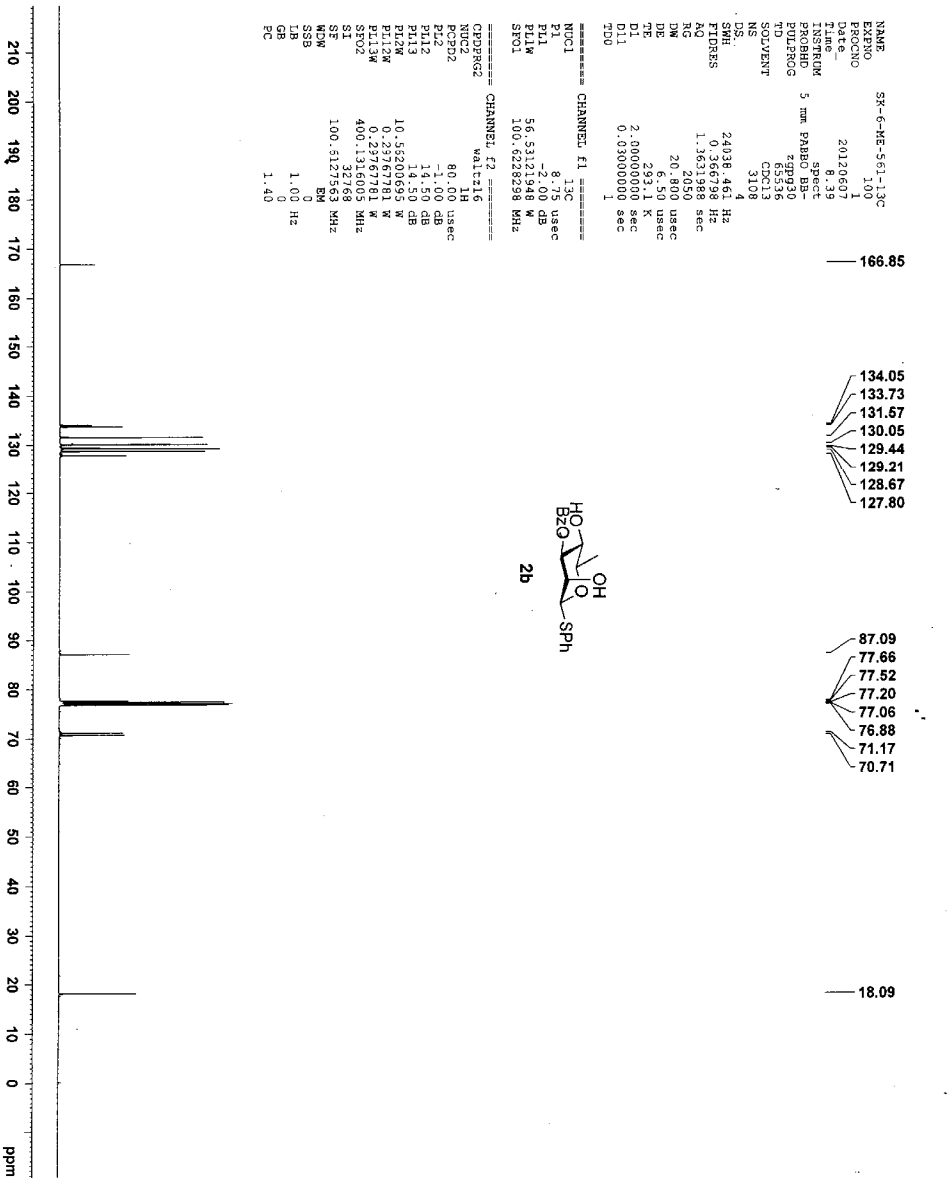

NAME SSK-6-ME-728-1H
EXPNO 2
PROCNO 1
Date_ 20121014
Time_ 18.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 15
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 291.7 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-728-1H
HO
AcO
OH
O
SPh
2a
2.25
3.59
1.08
1.00
0.97
1.06
1.10
2.49
3.05
3.20
0.05
ppm

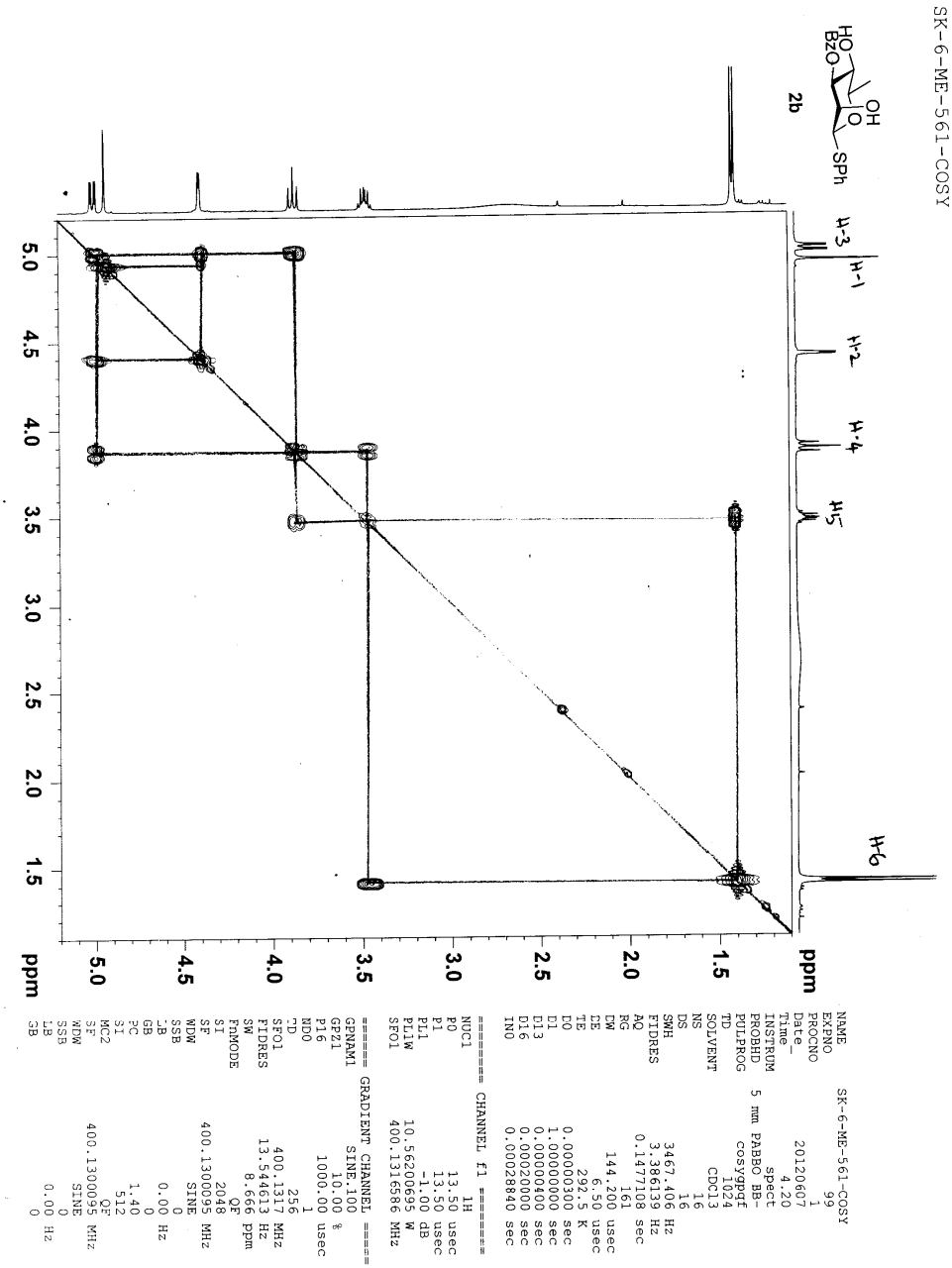

NAME SSK-6-MS-728-13C
EXPNO 5
PROCNO 1
Date_ 20121014
Time 18.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 103
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.363968 sec
RG 20.2050
DW 20.800 usec
DE 6.50 usec
TE 291.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56290695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127574 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.53
133.87
131.60
129.22
127.85
87.00
77.52
77.20
77.12
77.02
76.88
70.97
70.50
21.26
18.04
HO
AcO
OH
O
SPh
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

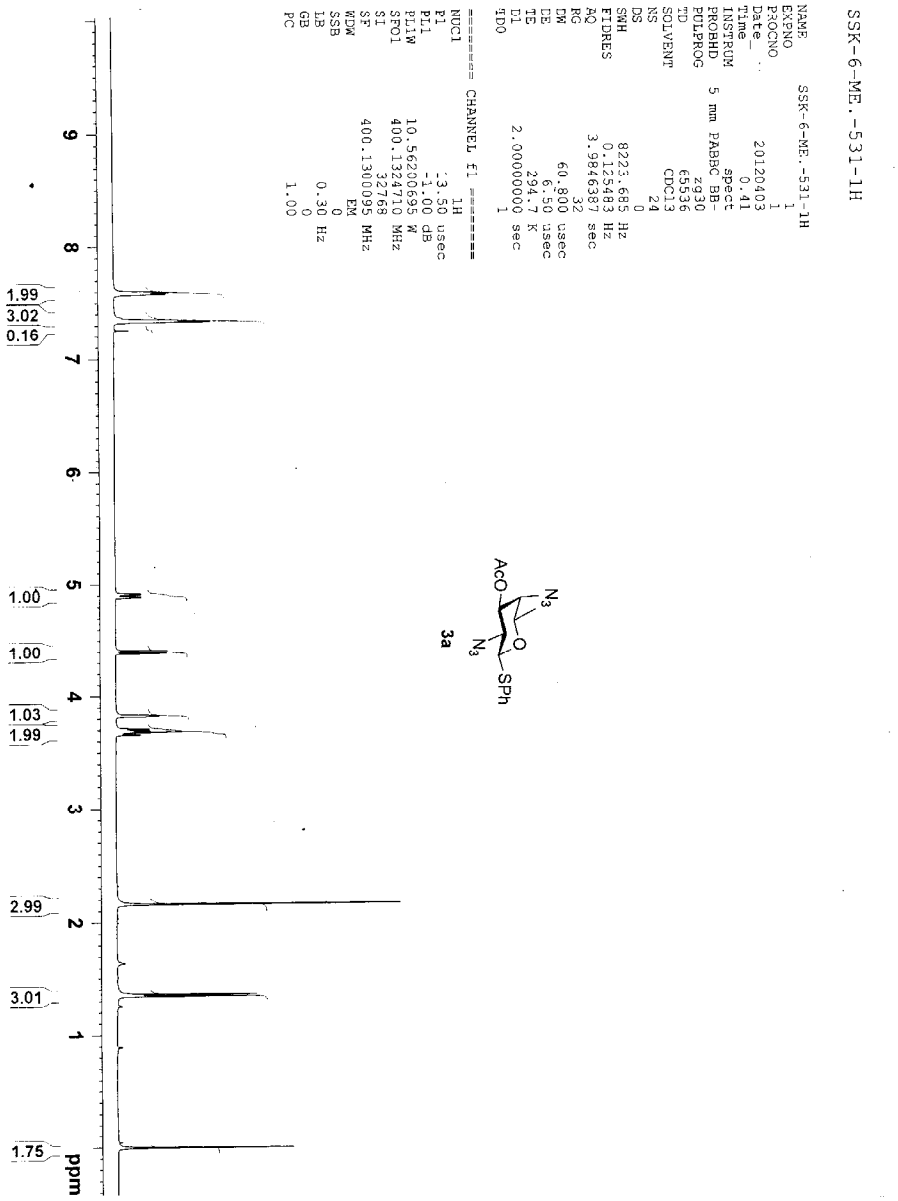


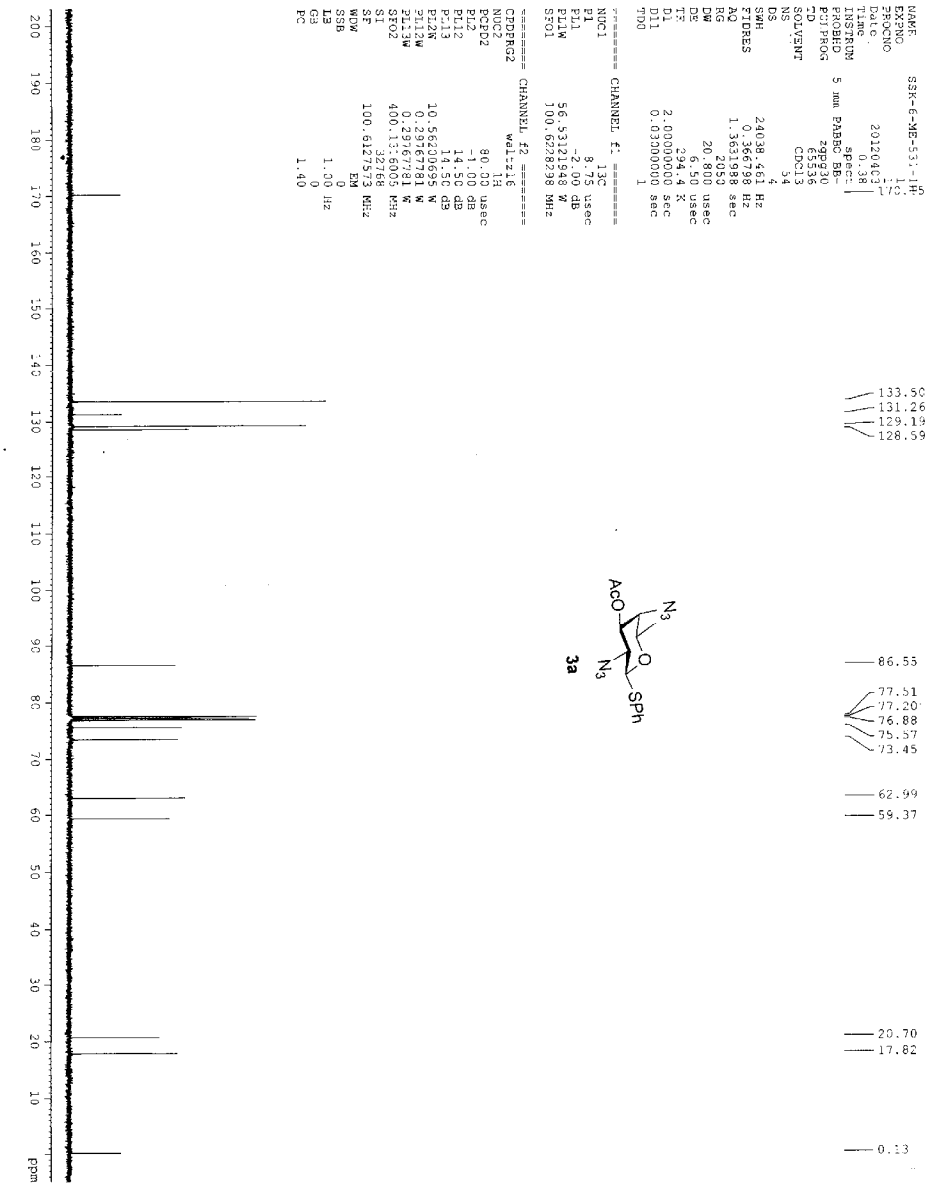

```
NAME                    SSK-6-ME-728-COSY
EXPNO                                 100
PROCNO                                  1
Date_                        20121014
Time_                            20.46
INSTRUM                           spect
PROBHD     5 mm PABBO BB-
PULPROG                        cosygpqf
TD                                   1024
SOLVENT                           CDCl3
NS                                     16
DS                                     16
SWH                          3019.324 Hz
FIDRES                       2.948558 Hz
AQ                           0.1696244 sec
RG                                    161
DW                           165.600 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
IN0                       0.00033120 sec

======== CHANNEL f1 ========
NUC1                               1H
P0                           13.50 usec
P1                           13.50 usec
PL1                           1.00 dB
PLIW                         10.56200695 W
SFO1                         400.1317503 MHz

====== GRADIENT CHANNEL =====
GPNAM1                    SINE.100
GP21                        10.00 %
P16                       1000.00 usec
MDO                                1
TD                               161
SFO1                         400.1318 MHz
FIDRES                       18.753504 Hz
SW                            7.546 ppm
FnMODE                             QF
SI                               2048
SF                           400.1300095 MHz
WDW                             SINE
SSB                                0
LB                                 0
GB                            0.00 Hz
PC                                 1.40
SI                                 512
MC2                                QF
SF                           400.1300095 MHz
WDW                             SINE
SSB                                0
LB                             C.00 Hz
GB                                 0
```

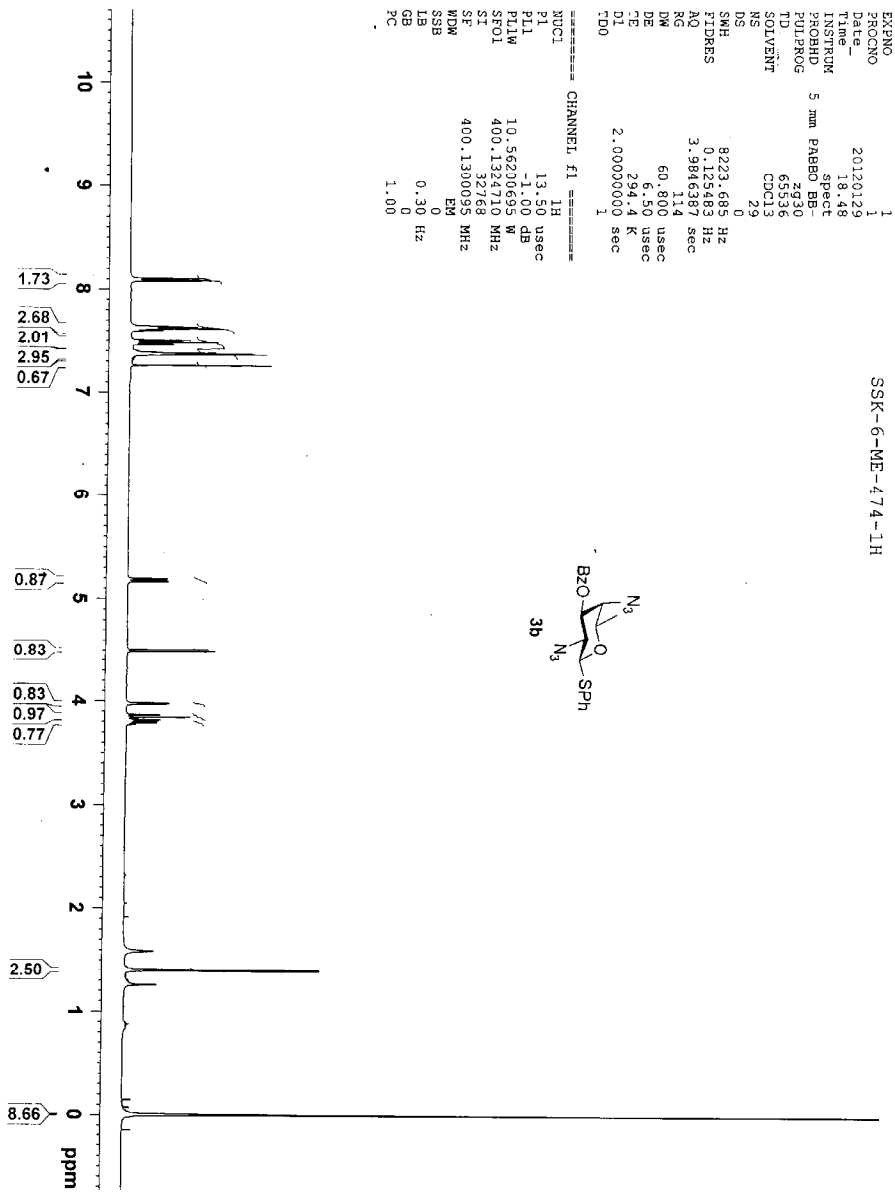

SK-6-ME-561-1H
NAME SK-6-ME-561-1H
EXPNO 98
PROCNO 1
Date_ 20120607
Time_ 4.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 30
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 71.8
DW 60.800 usec
DE 6.50 usec
TE 292.8 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
HO
BzO
OH
O
SPh
2b
2.18
1.16
2.14
2.33
3.43
1.05
1.00
1.11
1.06
1.07
2.95
0.18
10
9
8
7
6
5
4
3
2
1
0
ppm

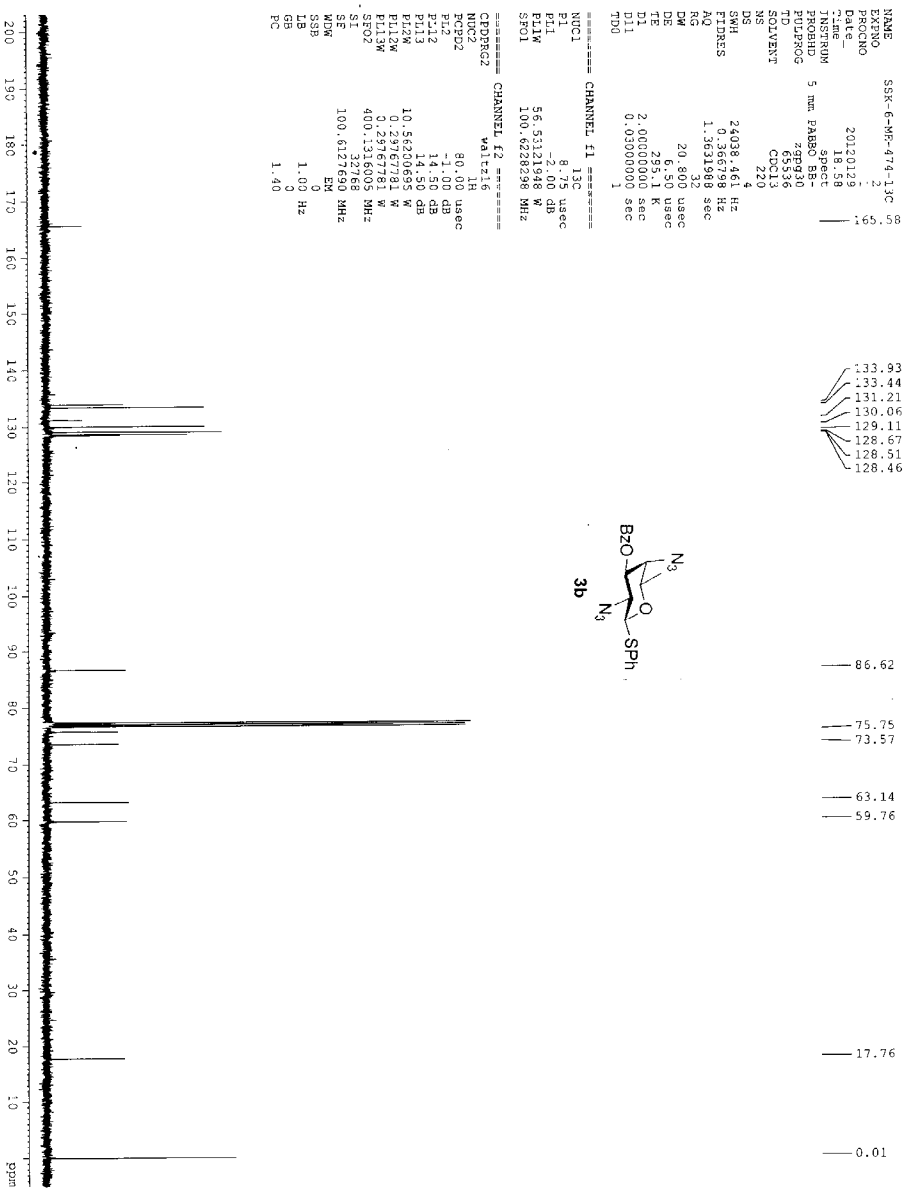

NAME SK-6-ME-561-13C
EXPNO 100
PROCNO 1
Date_ 20120607
Time 8.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3108
DS 4
SWH 24038.462 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 20.1
DW 20.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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
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 32768
SF 100.6127563 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
166.85
134.05
133.73
131.57
130.05
129.44
129.21
128.67
127.80
87.09
77.66
77.52
77.20
77.06
76.88
71.17
70.71
18.09
HO
BzO
OH
O
SPh
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

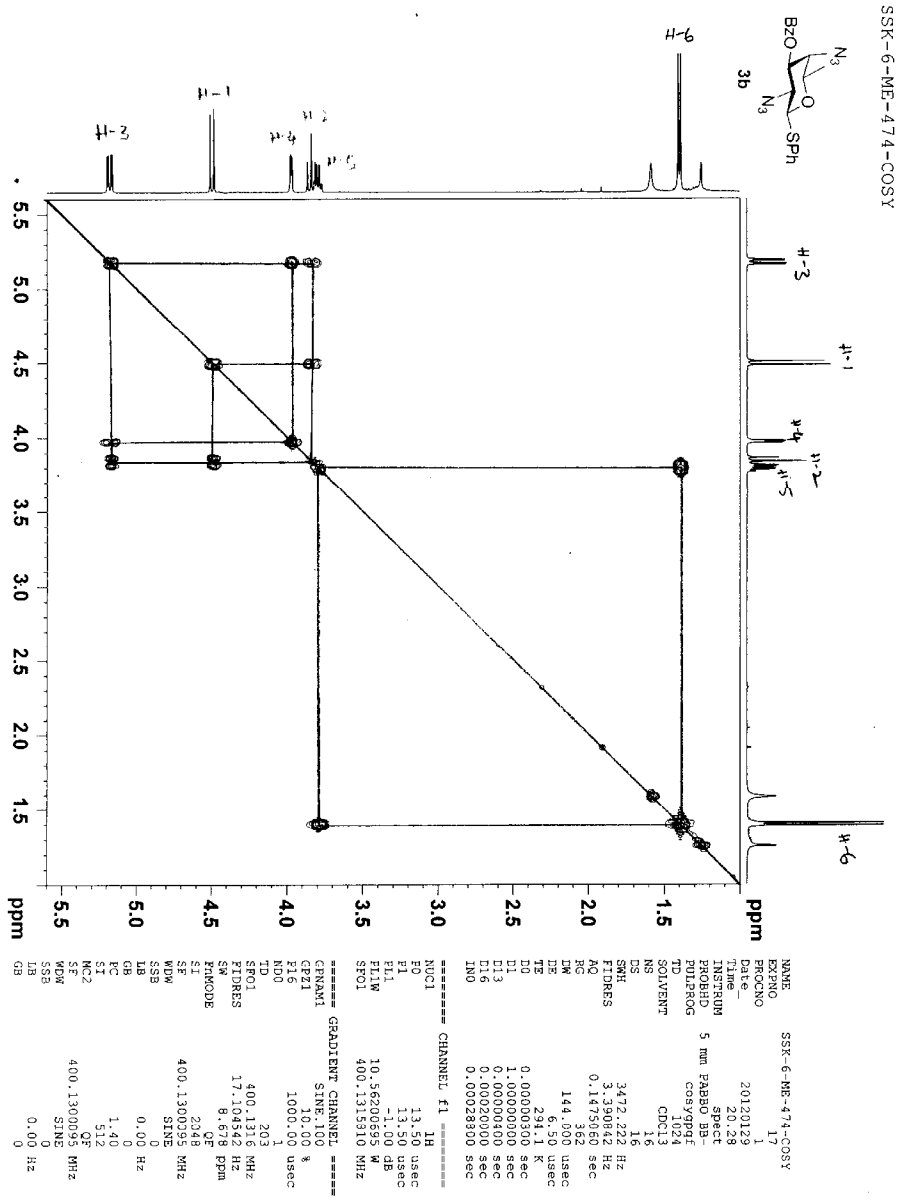

SK-6-ME-561-COSY
2b
H-3
H-1
H-2
H-4
H-5
H-6
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
NAME SK-6-ME-561-COSY
EXPNO 99
PROCNO 1
Date_ 20120607
Time 4.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3467.406 Hz
FIDRES 3.386139 Hz
AQ 0.1477108 sec
RG 161
DW 144.200 usec
DE 6.50 usec
TE 292.5 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
INO 0.00028840 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1316586 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1317 MHz
FIDRES 13.544613 Hz
SW 8.666 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

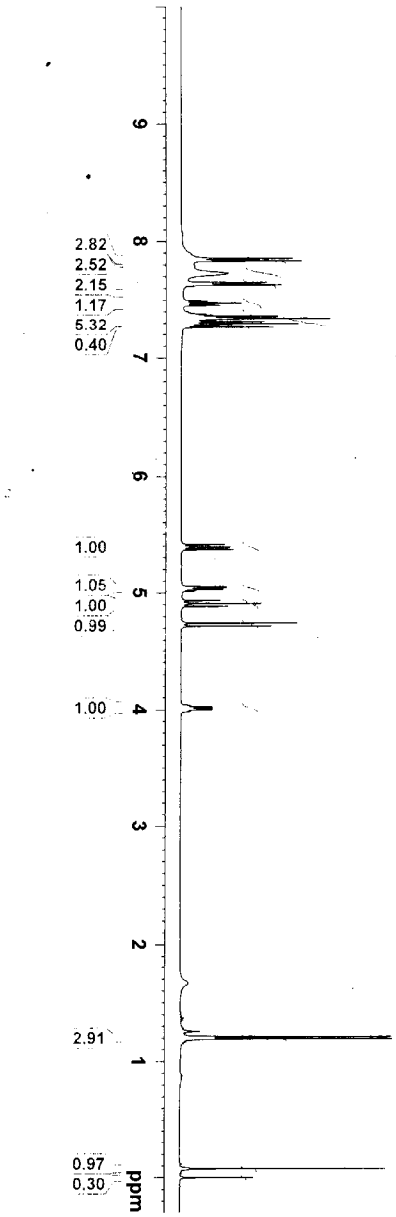

SSK-6-ME.-531-1H
NAME SSK-6-ME.-531-1H
EXPNO 1
PROCNO 1
Date_ 20120403
Time_ 0.41
INSTRUM spect
PROBHD 5 mm PABBC BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 294.7 K
D1 2.00000000 sec
D0 1
======== CHANNEL f1 ========
NUC1 1H
P1 -3.50 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
1.99
3.02
0.16
1.00
1.00
1.03
1.99
2.99
3.01
1.75
ppm
AcO
N3
O
N3
SPh
3a


AcO
N3
N3
O
SPh
3a
133.50
131.26
129.19
128.59
86.55
77.51
77.20
76.88
75.57
73.45
62.99
59.37
20.70
17.82
0.13
ppm


NAME SSK-6-ME-474-1H
EXPNO 1
PROCNO 1
Date_ 20120129
Time_ 18.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 29
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 294.4 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56220695 W
SFO1 400.1334710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-474-1H
3b
BzO
N3
O
N3
SPh
1.73
2.68
2.01
2.95
0.67
0.87
0.83
0.83
0.97
0.77
2.50
8.66
ppm

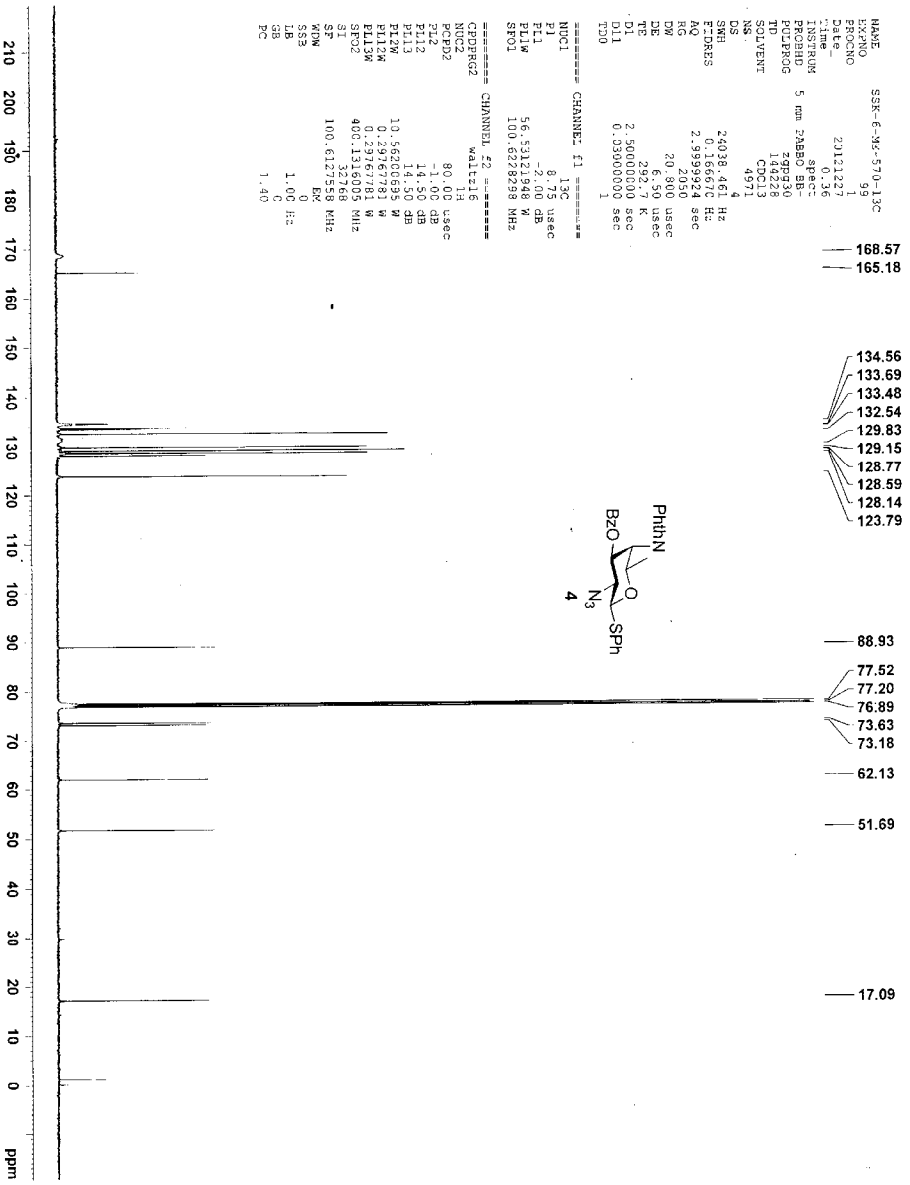

NAME SSK-6-MP-474-13C
EXPNO 2
PROCNO 1
Date_ 20120129
Time 18.58
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 220
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631980 sec
RG 32
DW 20.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
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
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56209183 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
BzO
N3
N3
O
SPh
3b
165.58
133.93
133.44
131.21
130.06
129.11
128.67
128.51
128.46
86.62
75.75
73.57
63.14
59.76
17.76
0.01
ppm

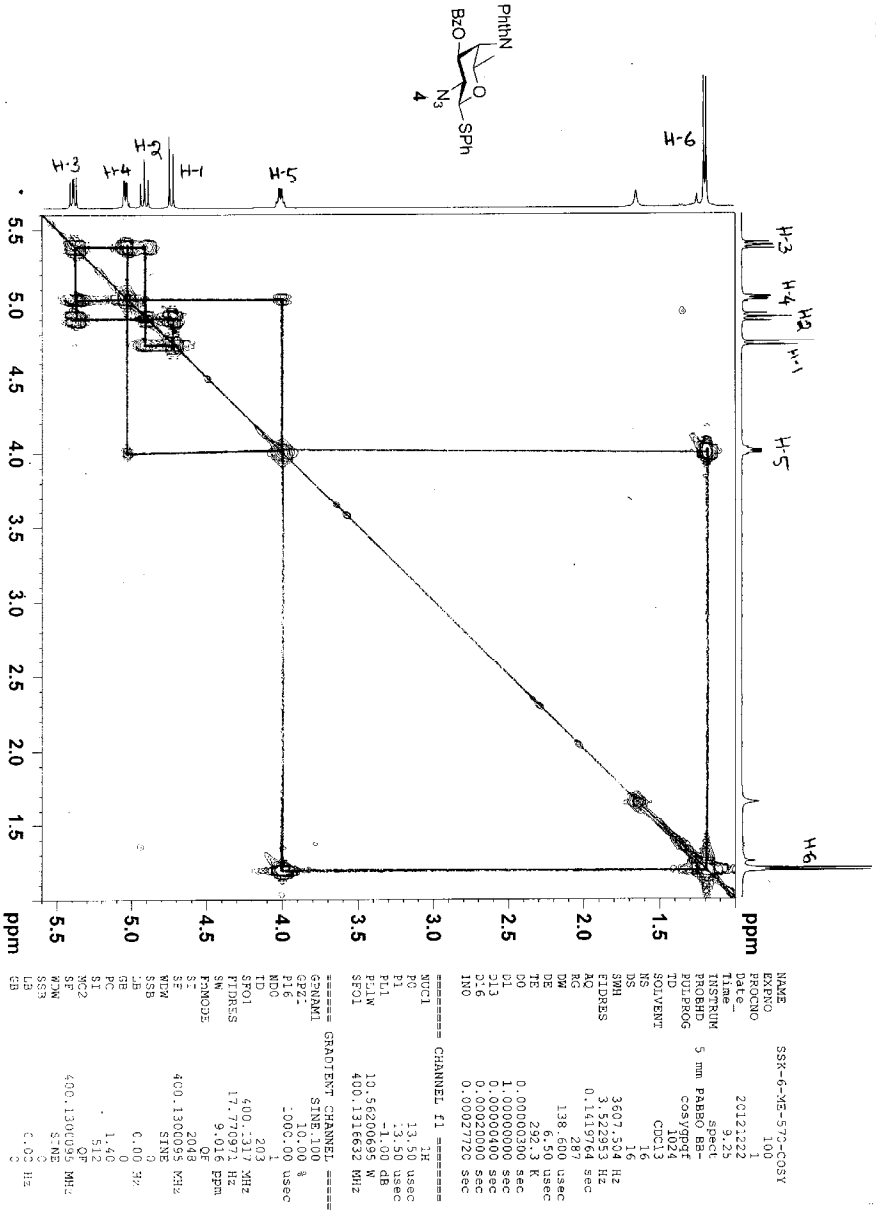

SSK-6-ME-474-COSY
3b
BzO
SPh
H-6
H-3
H-1
H-4
H-2
H-5
ppm
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
NAME SSK-6-ME-474-COSY
EXPNO 17
PROCNO 1
Date_ 20120129
Time 20.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3472.222 Hz
FIDRES 3.390842 Hz
AQ 0.1475060 sec
RG 362
DW 144.000 usec
DE 6.50 usec
TE 294.1 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
INO 0.00028900 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1315510 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 80.00 %
P16 1000.00 usec
NDO 1
TD 203
SFO1 400.1316 MHz
FIDRES 17.104542 Hz
SW 8.678 ppm
FnMODE QF
SI 2048
SF 400.1300295 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

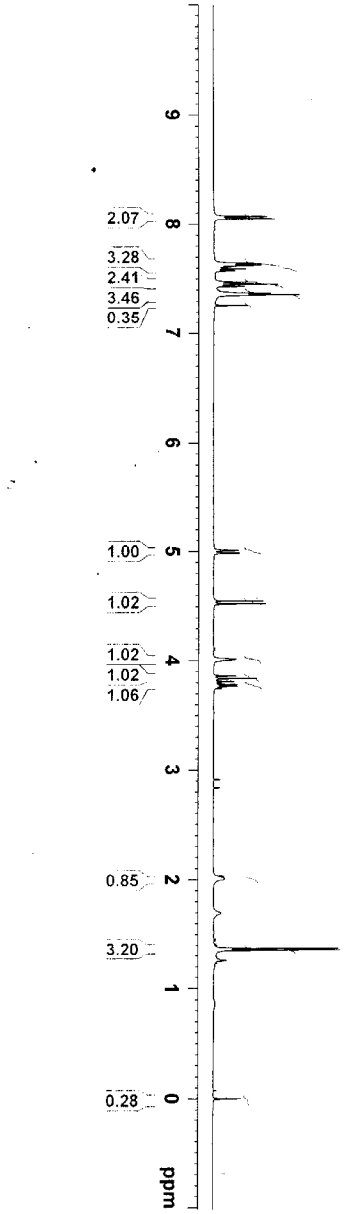


SSK-6-ME-570-H1

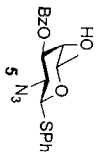
```
NAME                 SSK-6-ME-570-H1
EXPNO                             1
PROCNO                            1
Date_                      20121221
Time                         21.12
INSTRUM                       spect
PROBHD     5 mm PABBO BB-
PULPROG                    zg30
TD                            65536
SOLVENT                     CDCl3
NS                               11
DS                                0
SWH                        8223.685 Hz
FIDRES                     0.125483 Hz
AQ                         3.9846387 sec
RG                               32
DW                         60.800 usec
DE                          6.50 usec
TE                          292.9 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                         400.1300084 MHz
WDW                              EM
SSB                               0
LB                         0.30 Hz
GB                                0
PC                         1.00
```


NAME SSK-6-Ms-570-13C
EXPNO 99
PROCNO 1
Date_ 20121227
Time 0.156
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 144228
SOLVENT CDCl3
NS 4971
DS 4
SWH 24038.461 Hz
FIDRES 0.166670 Hz
AQ 2.999924 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 292.7 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 100.6278298 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 100.6127558 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
168.57
165.18
134.56
133.69
133.48
132.54
129.83
129.15
128.77
128.59
128.14
123.79
88.93
77.52
77.20
76.89
73.63
73.18
62.13
51.69
17.09
PhthN
BzO
O
N3
SPh
4
ppm

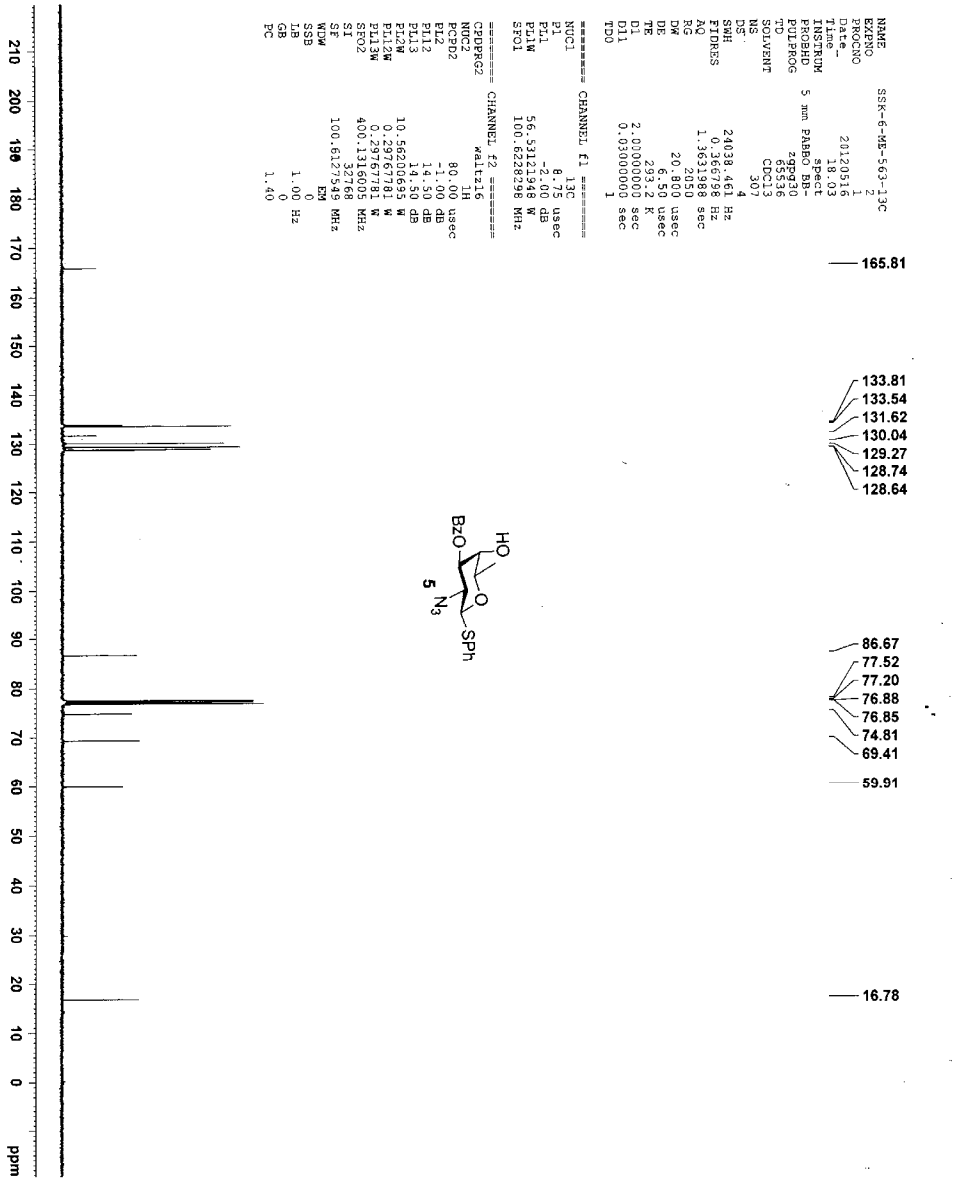

SSK-6-ME-570-COSY
PhthN
BzO
O
N3
4
SPh
H-3
H-4
H-2
H-1
H-5
H-6
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
NAME SSK-6-ME-570-COSY
EXPNO 100
PROCNO 1
Date_ 20121222
Time 9.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3607.504 Hz
FIDRES 3.522953 Hz
AQ 0.1419904 sec
RG 203
DW 138.600 usec
DE 6.50 usec
TE 292.3 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00002000 sec
IN0 0.00027720 sec
======== CHANNEL f1 ========
NUC1 1H
PC 1.00
P1 13.50 usec
PL1 -3.50 usec
PL1W -1.00 dB
SFO1 10.56200695 W
400.1316632 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 203
SFO1 400.1317 MHz
FIDRES 17.770971 Hz
SW 9.016 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

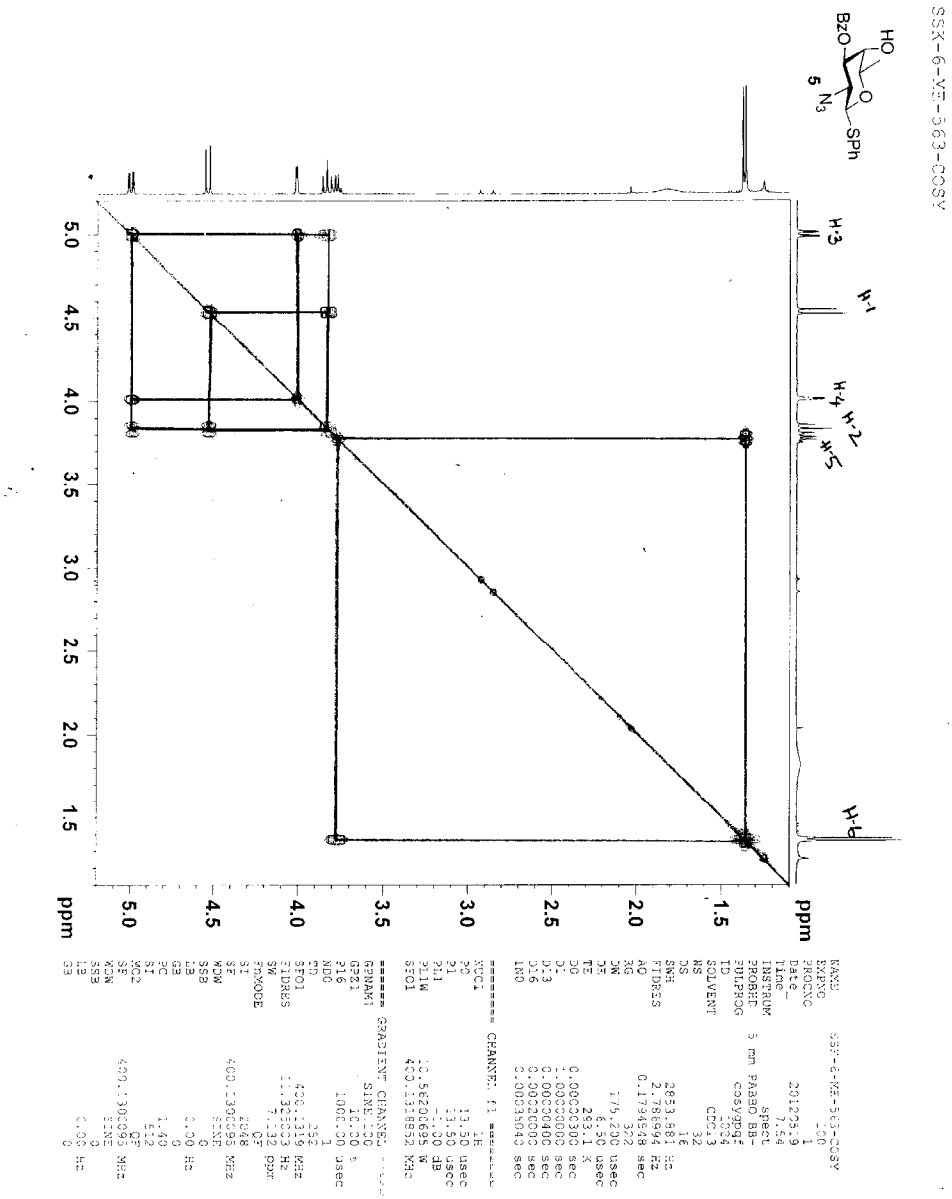


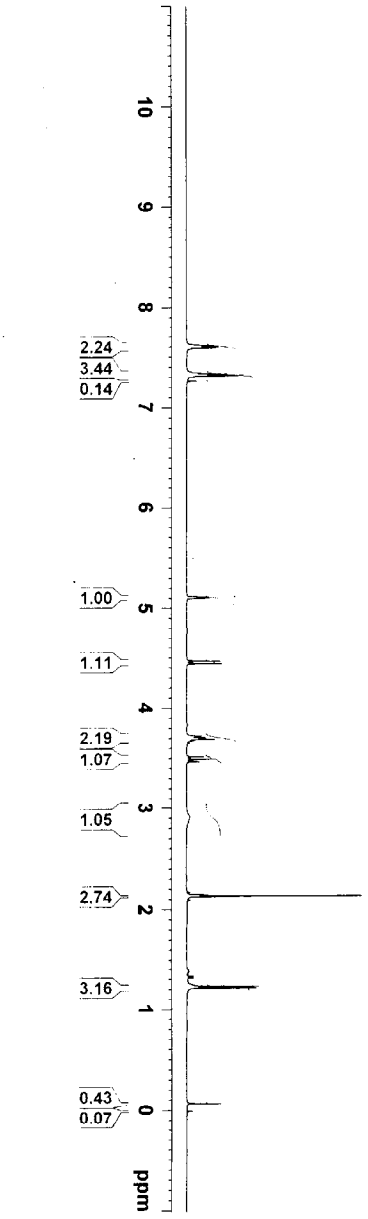

```
NAME                 SSK-6-ME-563-1H
EXPNO                             1
PROCNO                            1
Date_                      20120516
Time_                         18.01
INSTRUM                       spect
PROBHD     5 mm PABBO BB-
PULPROG                       zg30
TD                           65536
SOLVENT                     CDCl3
NS                               11
DS                                0
SWH                      8223.685 Hz
FIDRES                   0.125403 Hz
AQ                       3.9846387 sec
RG                            90.5
DW                           60.800 usec
DE                            6.50 usec
TE                           293.1 K
D1                    2.00000000 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                  400.1300095 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
```



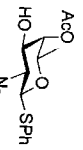
SSK-6-ME-563-1H


NAME SSK-6-ME-563-13C
EXPNO 2
PROCNO 1
Date_ 20120516
Time_ 18.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 304
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 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 100.6228398 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 100.6127549 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
165.81
133.81
133.54
131.62
130.04
129.27
128.74
128.64
86.67
77.52
77.20
76.88
76.85
74.81
69.41
59.91
16.78
HO
BzO
O
5
N3
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

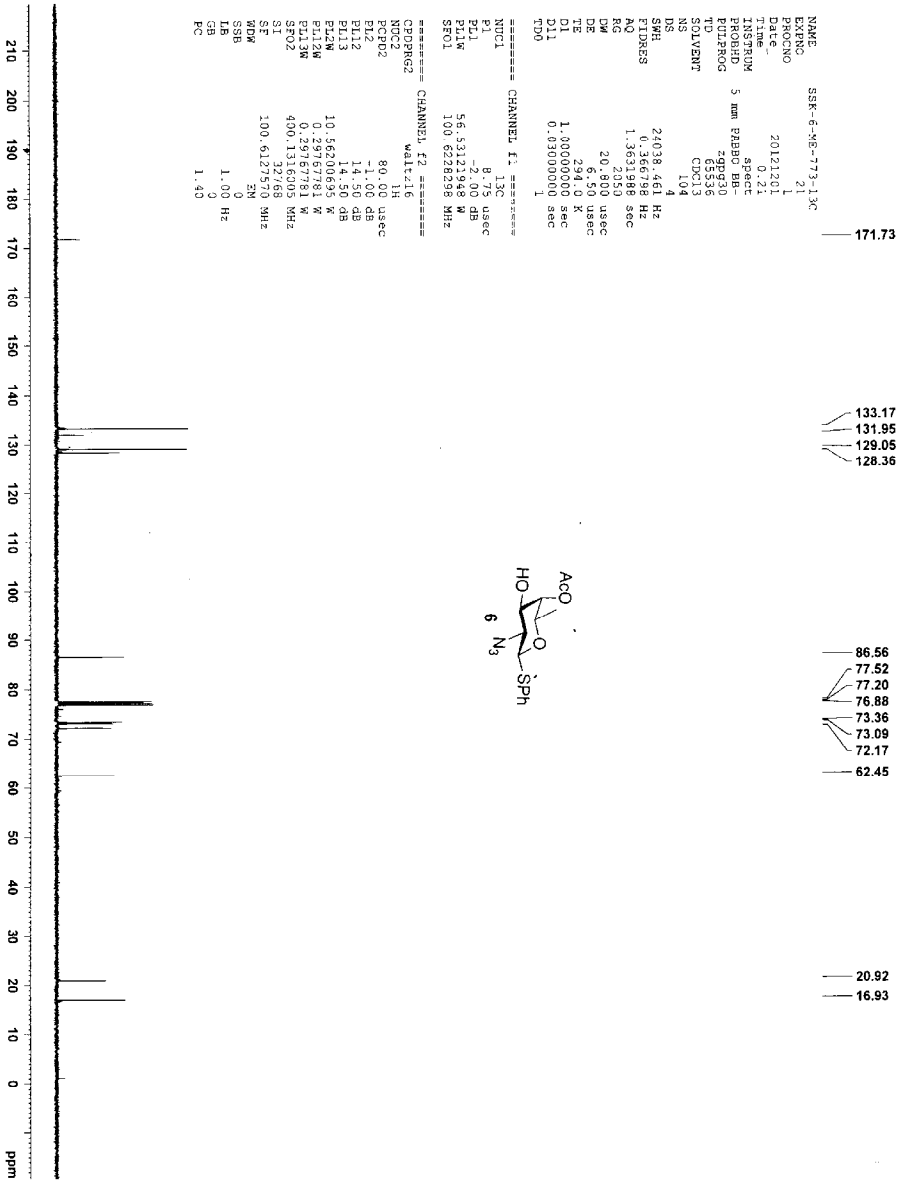

SSK-6-MS-563-COSY
HO
BzO
5
N3
SPh
H-3
H-1
H-4
H-2
H-5
H-6
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

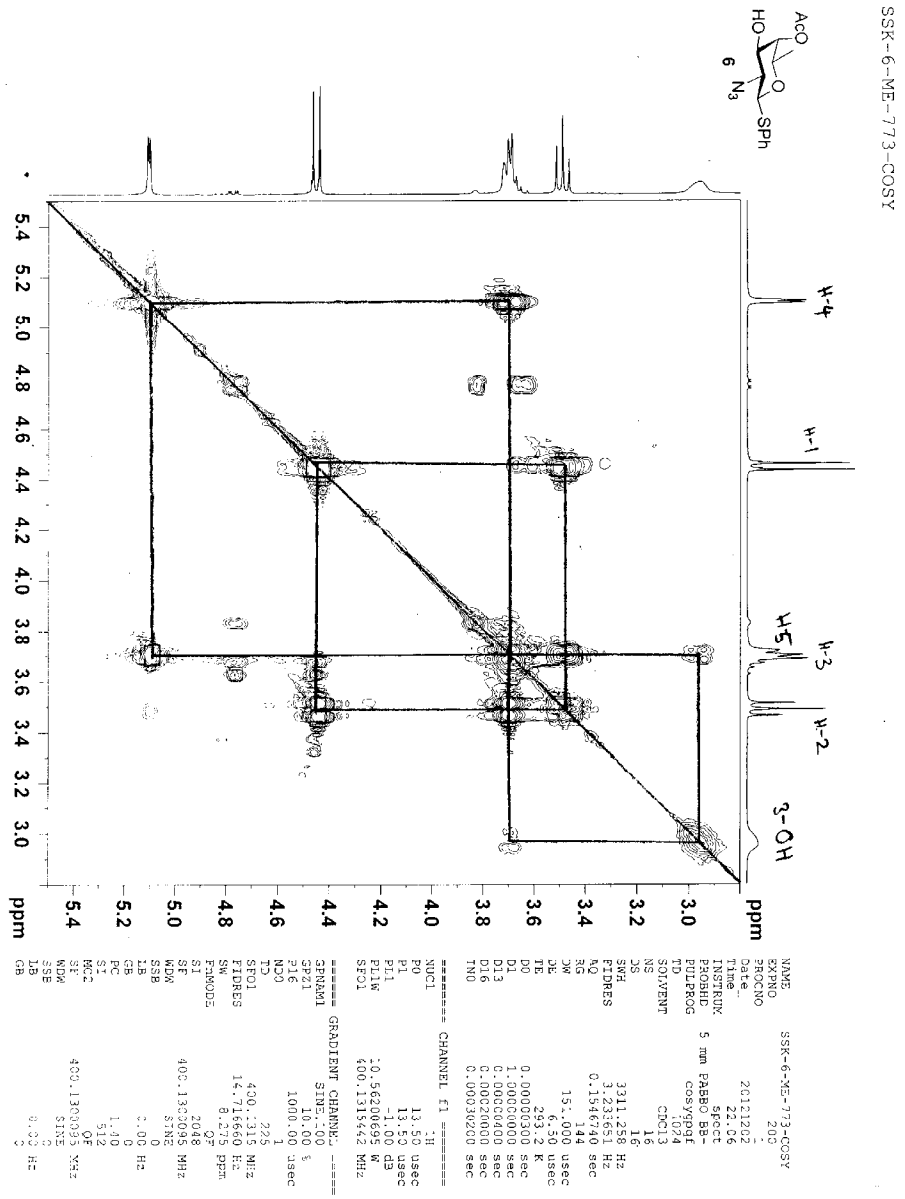


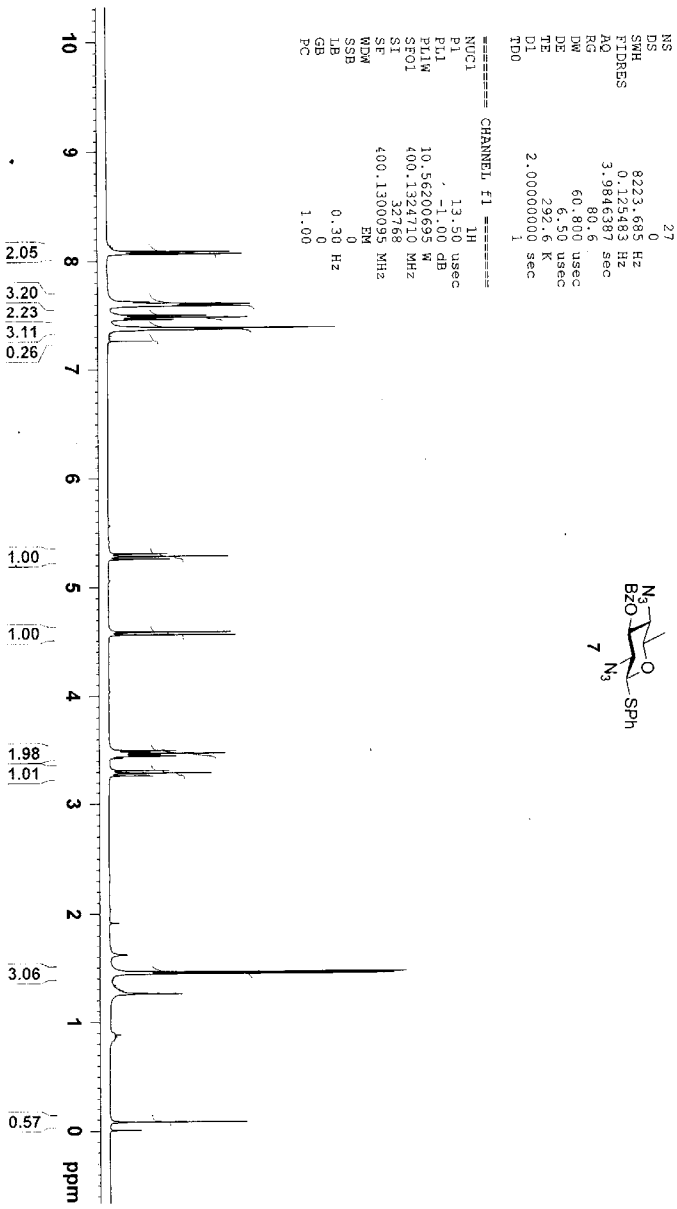

```
NAME                 SSK-6-ME-773-1H
EXPNO                             9
PROCNO                            1
Date_                      20121130
Time_                      23.19
INSTRUM                       spect
PROBHD     5 mm PABBO BB-
PULPROG                       zg30
TD                           65536
SOLVENT                     CDCl3
NS                              14
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                          293.8 K
D1                         2.00000000 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                         400.1300095 MHz
WDW                              EM
SSB                               0
LB                         0.30 Hz
GB                                0
PC                         1.00
```

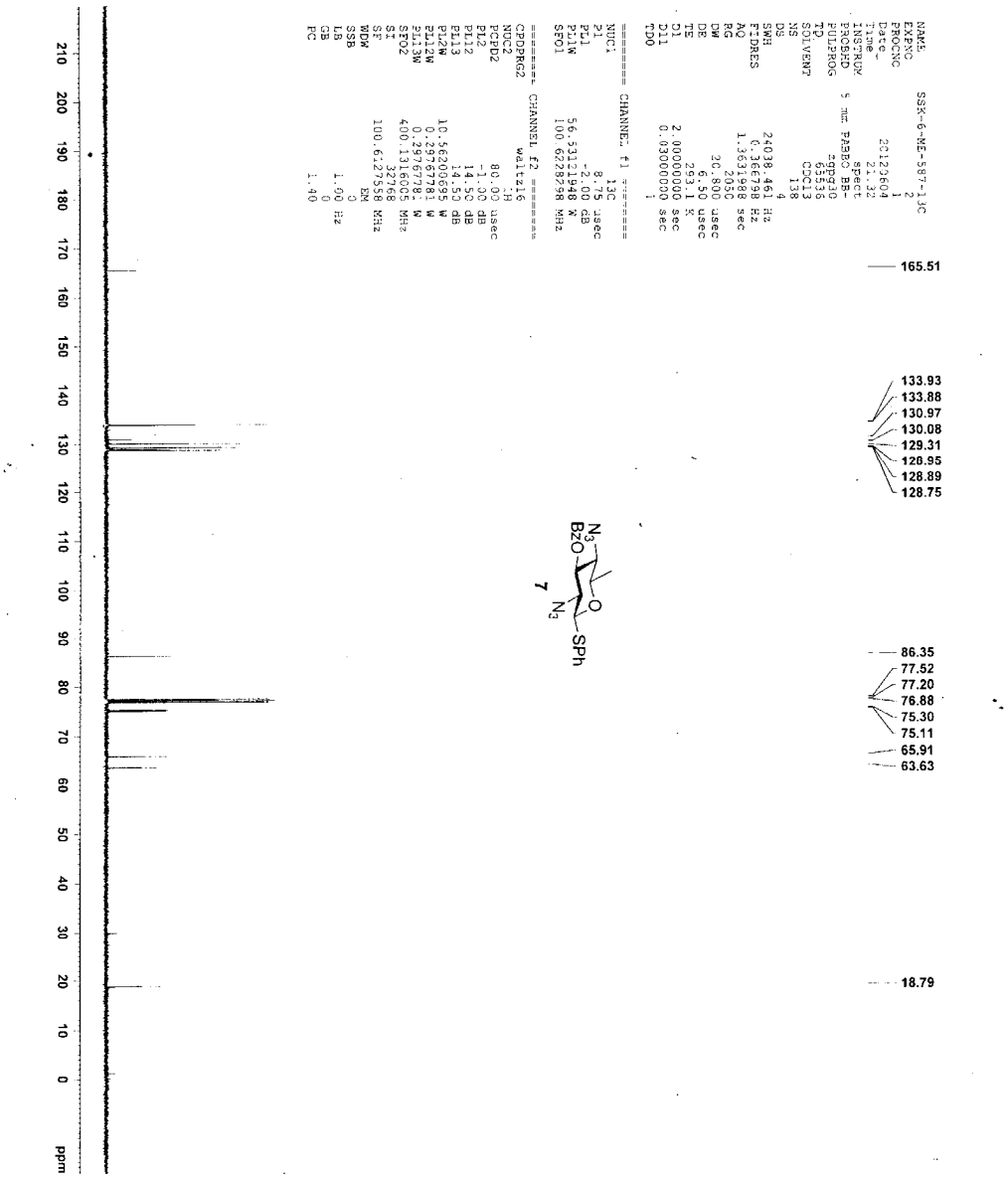


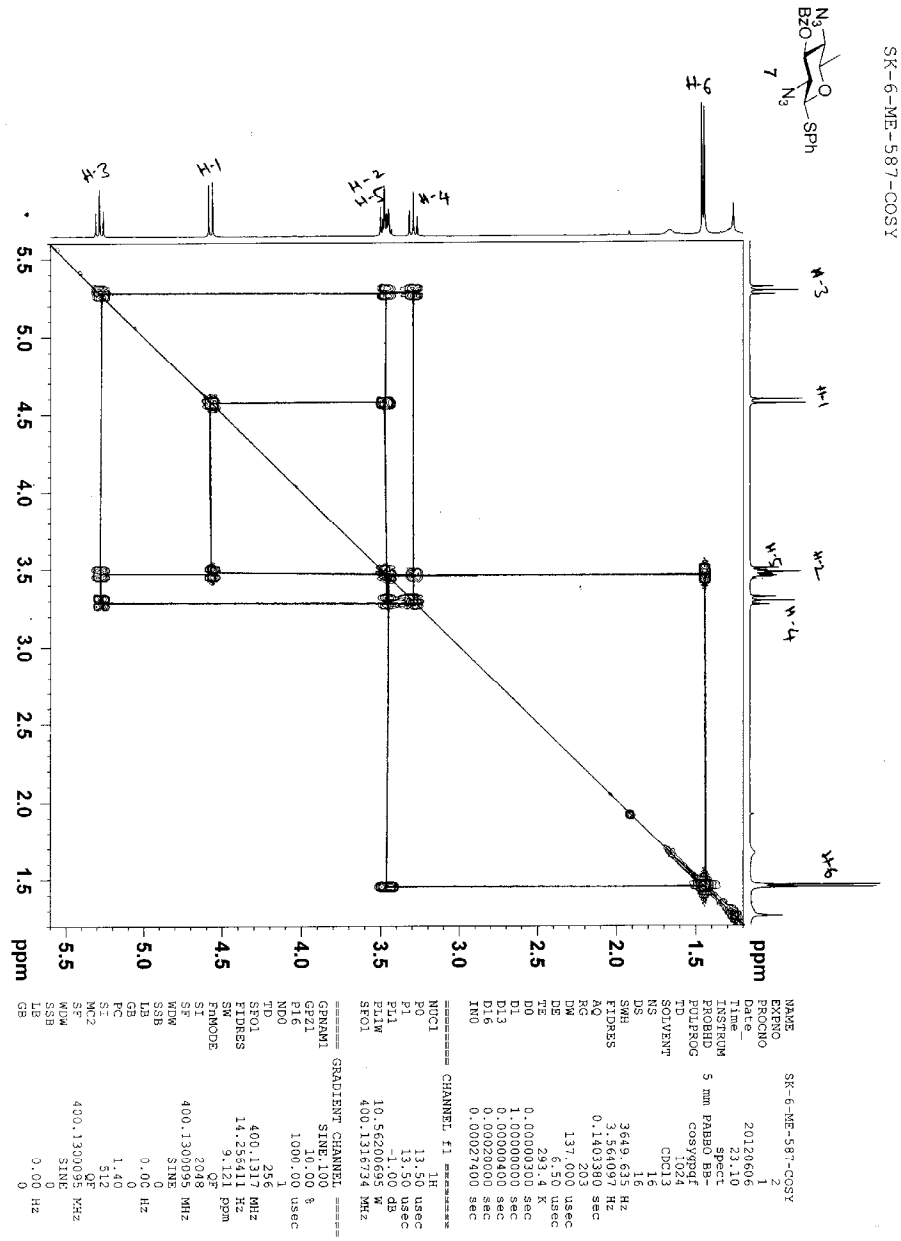
SSK-6-ME-773-1H


NAME SSK-6-ME-773-13C
EXPNO 21
PROCNO 1
Date_ 20121201
Time_ 0.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 104
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 294.0 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 100.6127570 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
171.73
133.17
131.95
129.05
128.36
86.56
77.52
77.20
76.88
73.36
73.09
72.17
62.45
20.92
16.93
AcO
HO
O
6
N3
SPh
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

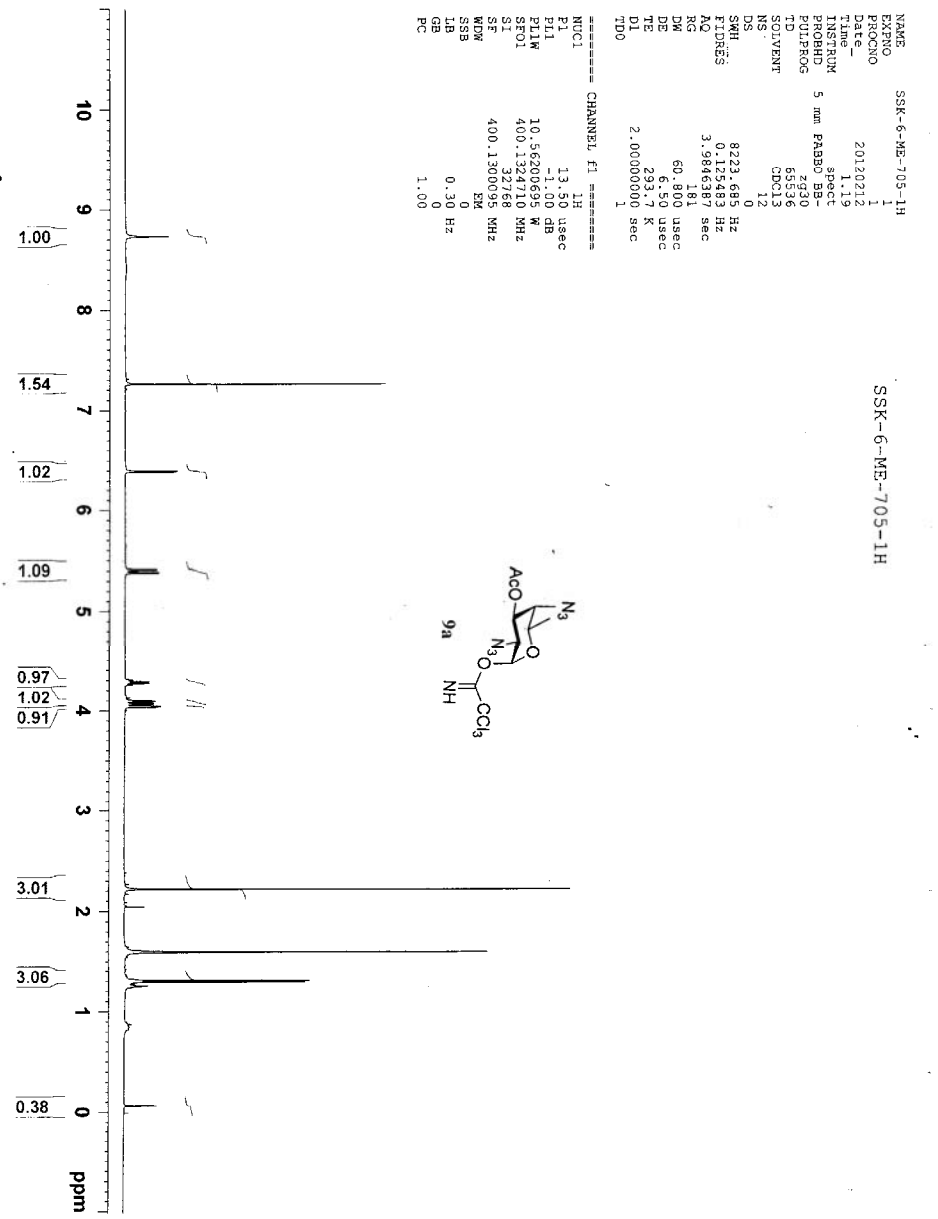

SSK-6-ME-773-COSY
AcO
HO
O
6
N3
SPh
H-4
H-1
H5
H-3
H-2
3-OH
ppm
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0
NAME SSK-6-ME-773-COSY
EXPNO 203
PROCNO 1
Date_ 20121202
Time 22.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CHCl3
NS 16
DS 16
SWH 3311.258 Hz
FIDRES 3.233651 Hz
AQ 0.1546740 sec
RG 144
DW 151.000 usec
DE 6.50 usec
TE 293.2 K
D0 0.00030300 sec
D1 1.00000000 sec
D13 0.00000000 sec
D16 0.00020000 sec
TN0 0.00030200 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1315442 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NC0 1
TD 225
SFO1 400.1315 MHz
FIDRES 14.716660 Hz
SW 8.275 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 2
LB 0.30 Hz
GB 0

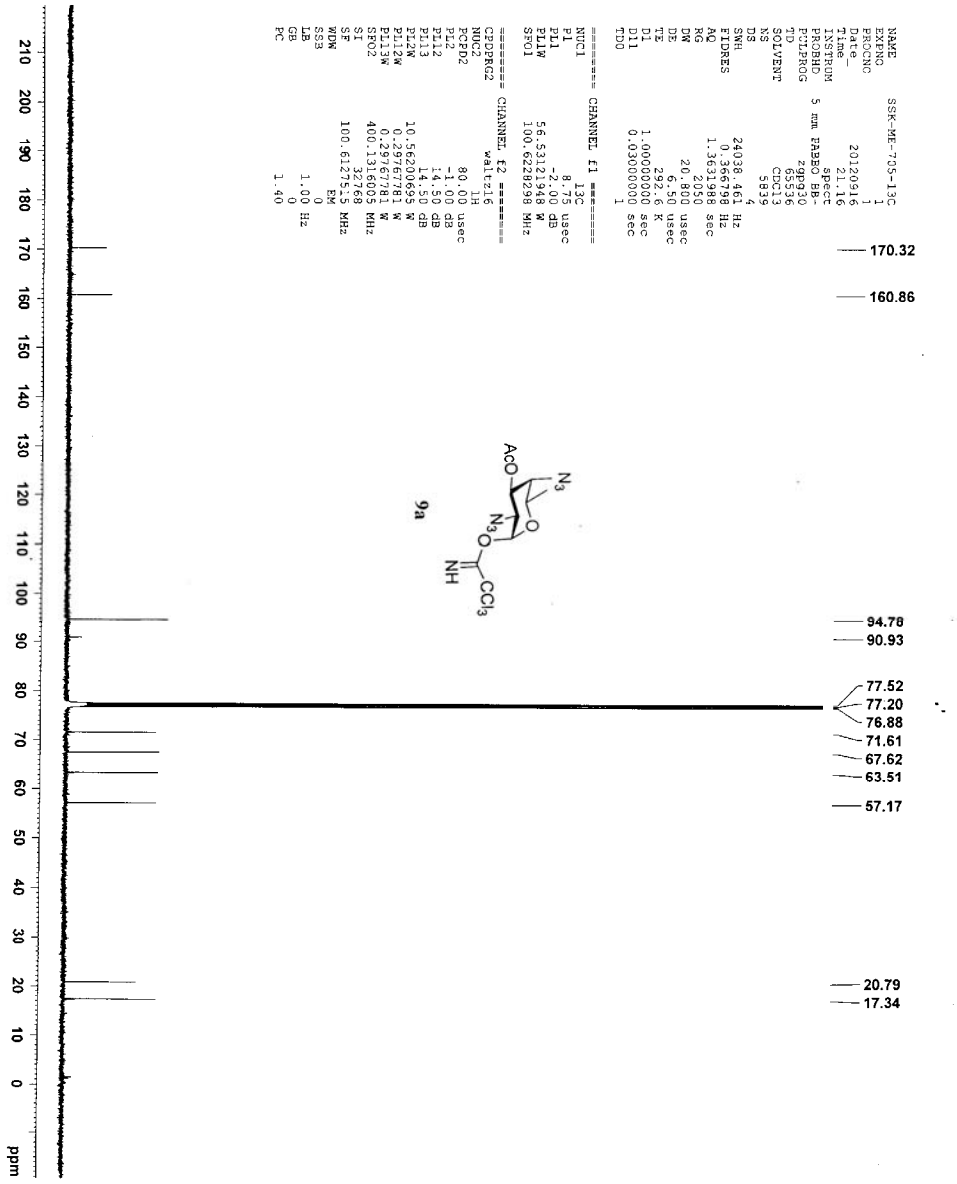

SSK-6-ME-537-1H
NAME SSK-6-ME-537-1H
EXPNO 1
PROCNO 1
Date_ 20120604
Time_ 21.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 27
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846307 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 2.00000000 sec
TD0 1
======== CHANNEL 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
2.05
3.20
2.23
3.11
0.26
1.00
1.00
1.98
1.01
3.06
0.57
10
9
8
7
6
5
4
3
2
1
0
ppm
N3
BzO
O
7
N3
SPh

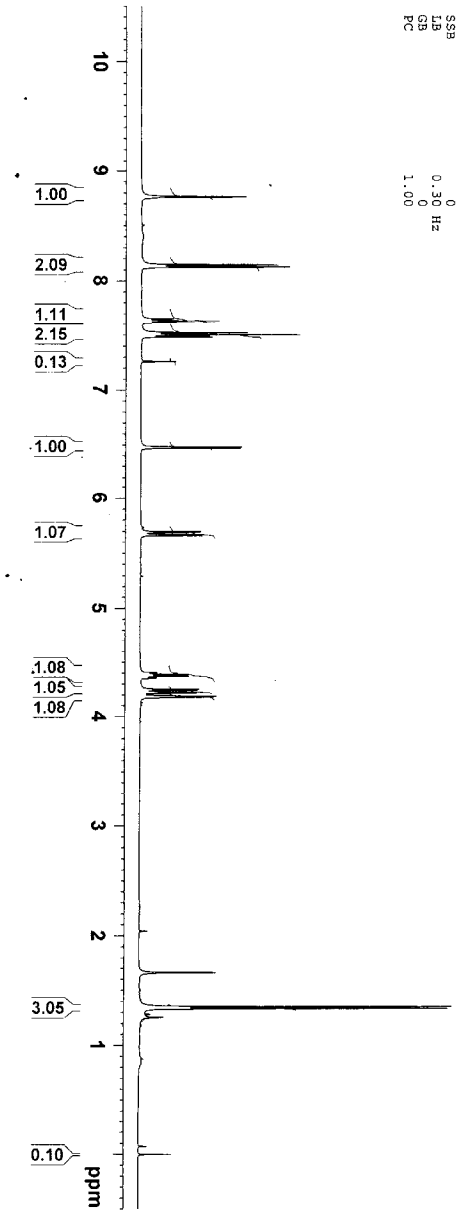

NAME SSK-6-ME-ISO-1-13C
EXPNO 2
PROCNO 1
Date_ 20122604
Time 21.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 138
DS 8
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631968 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6228748 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 131072
SF 100.6127558 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
165.51
133.93
133.88
130.97
130.08
129.31
128.95
128.89
128.75
86.35
77.52
77.20
76.88
75.30
75.11
65.91
63.63
18.79
BzO
N3
O
SPh
N3
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

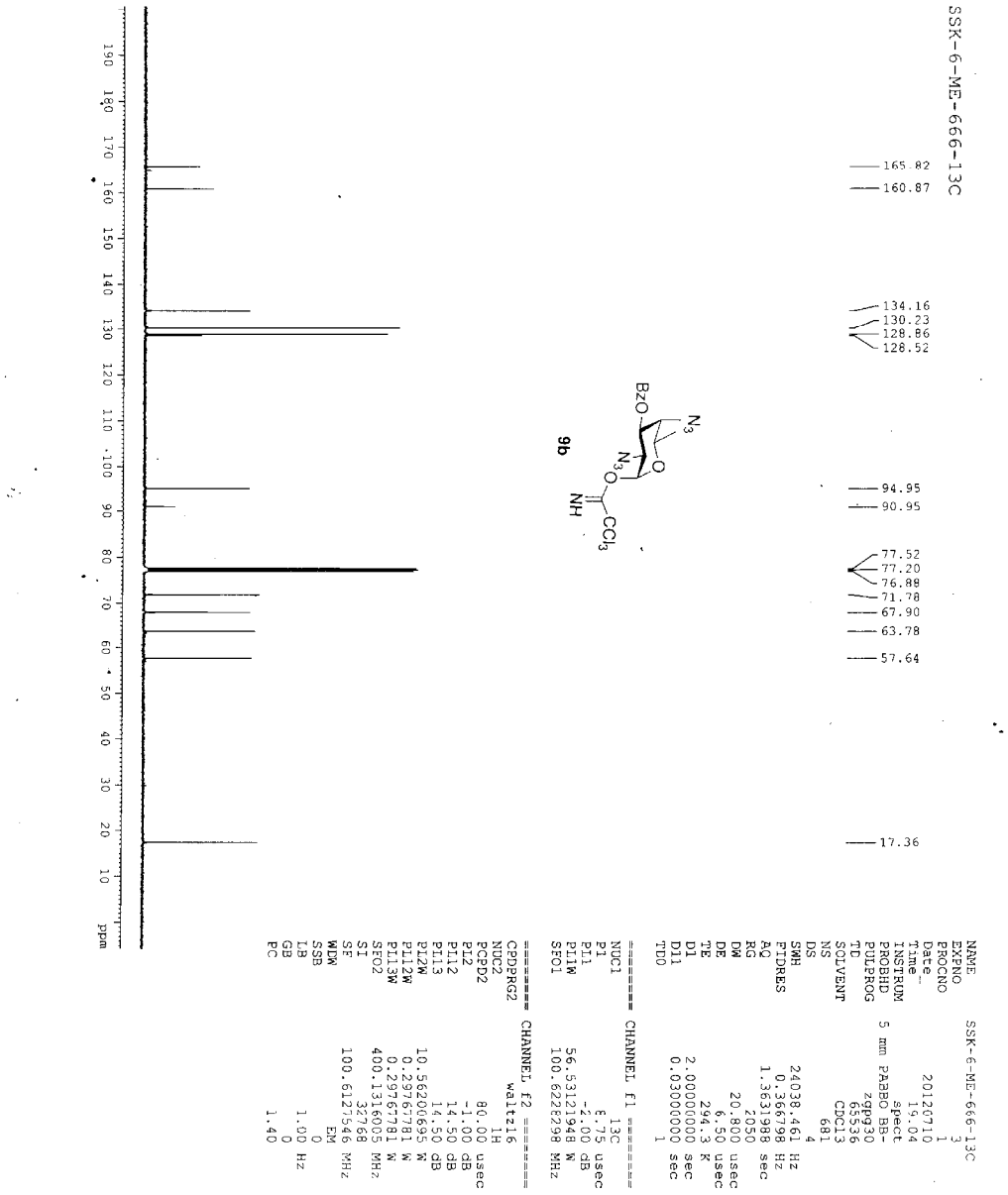


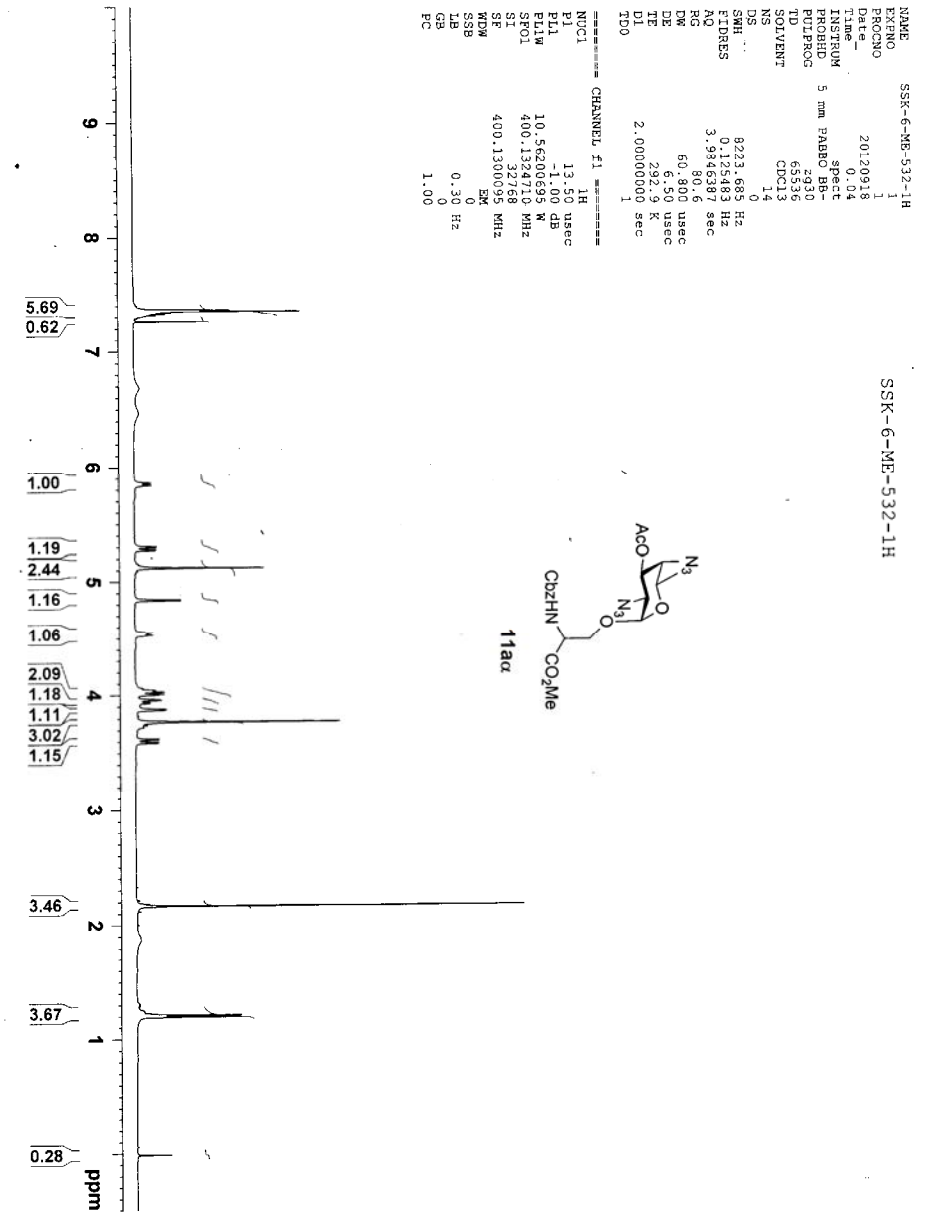

```
NAME                   SK-6-ME-587-COSY
EXPNO                                2
PROCNO                               1
Date_                         20120606
Time                             23.10
INSTRUM                          spect
PROBHD     5 mm PABBO BB/
PULPROG                  cosygpqf
TD                               1024
SOLVENT                       CDCl3
NS                                  16
DS                                  16
SWH                         3649.635 Hz
FIDRES                         3.564097 Hz
AQ                             0.1403380 sec
RG                                 203
DW                             137.000 usec
DE                               6.50 usec
TE                             293.4 K
D0                          0.00000300 sec
D1                          1.00000000 sec
D13                         0.00000400 sec
D16                         0.00020000 sec
IN0                         0.00027400 sec

========== CHANNEL f1 ==========
NUC1                              1H
P0                             13.50 usec
P1                             13.50 usec
PL1                            -1.00 dB
PL1W                    10.56200695 W
SFO1                   400.1316734 MHz

====== GRADIENT CHANNEL =====
GPNAM1                    SINE.100
GPZ1                         10.00 %
P16                        1000.00 usec
NDO                               1
TD                              256
SFO1                   400.1317 MHz
FIDRES                 14.255411 Hz
SW                          9.121 ppm
FnMODE                         QF
SI                            2048
SF                     400.1300095 MHz
WDW                          SINE
SSB                             0
LB                           0.00 Hz
GB                              0
PC                           1.40
SI2                           512
MC2                        QF
SF                     400.1300095 MHz
WDW                          SINE
SSB                             0
LB                           0.00 Hz
GB                              0
```

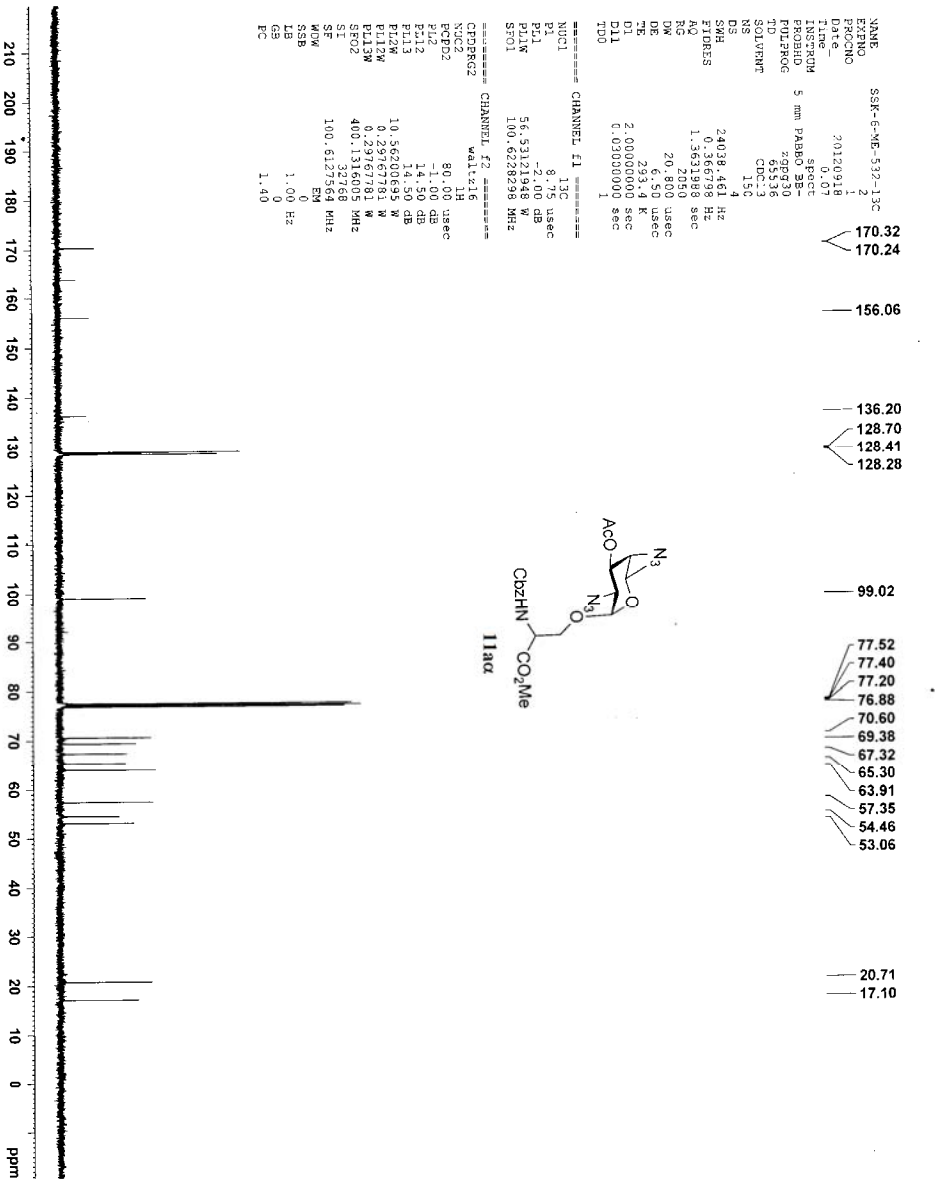

SSK-6-ME-705-1H
NAME SSK-6-ME-705-1H
EXPNO 1
PROCNO 1
Date_ 20120212
Time 1.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.50 usec
TE 293.7 K
D1 2.00000000 sec
TD0 1
========== CHANNEL f1 ==========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
AcO
N3
N3
O
O
NH
CCl3
9a
1.00
1.54
1.02
1.09
0.97
1.02
0.91
3.01
3.06
0.38
10
9
8
7
6
5
4
3
2
1
0
ppm

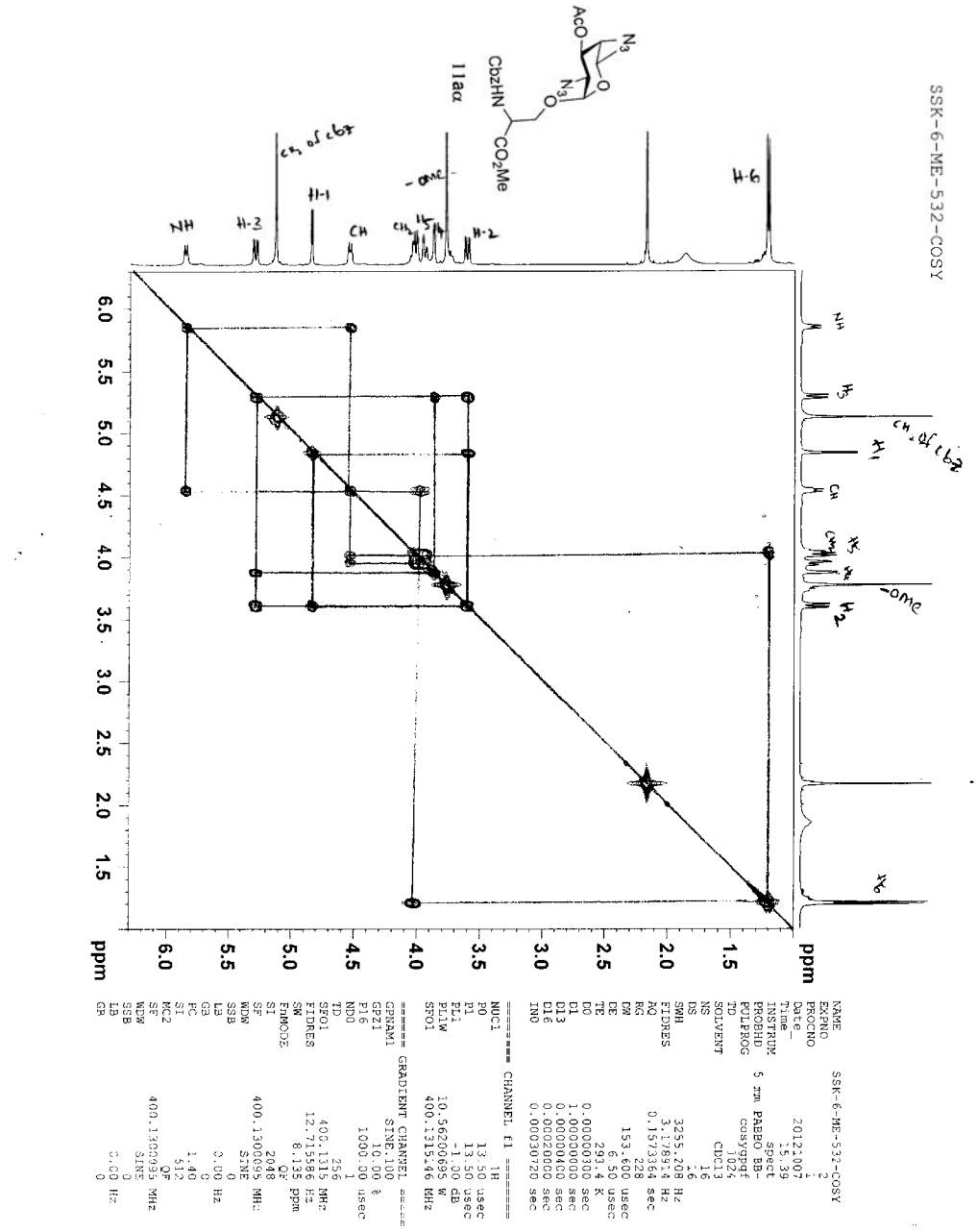

NAME SSK-ME-705-13C
EXPNO 1
PROCNO 1
Date_ 20120916
Time_ 21.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5859
DS 2
SWH 24038.461 Hz
FIDRES 0.366796 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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 400.1316049 MHz
SI 131072
SF 100.6127525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcO
N3
N3
O
O
NH
CCl3
9a
170.32
160.86
94.78
90.93
77.52
77.20
76.88
71.61
67.62
63.51
57.17
20.79
17.34
ppm

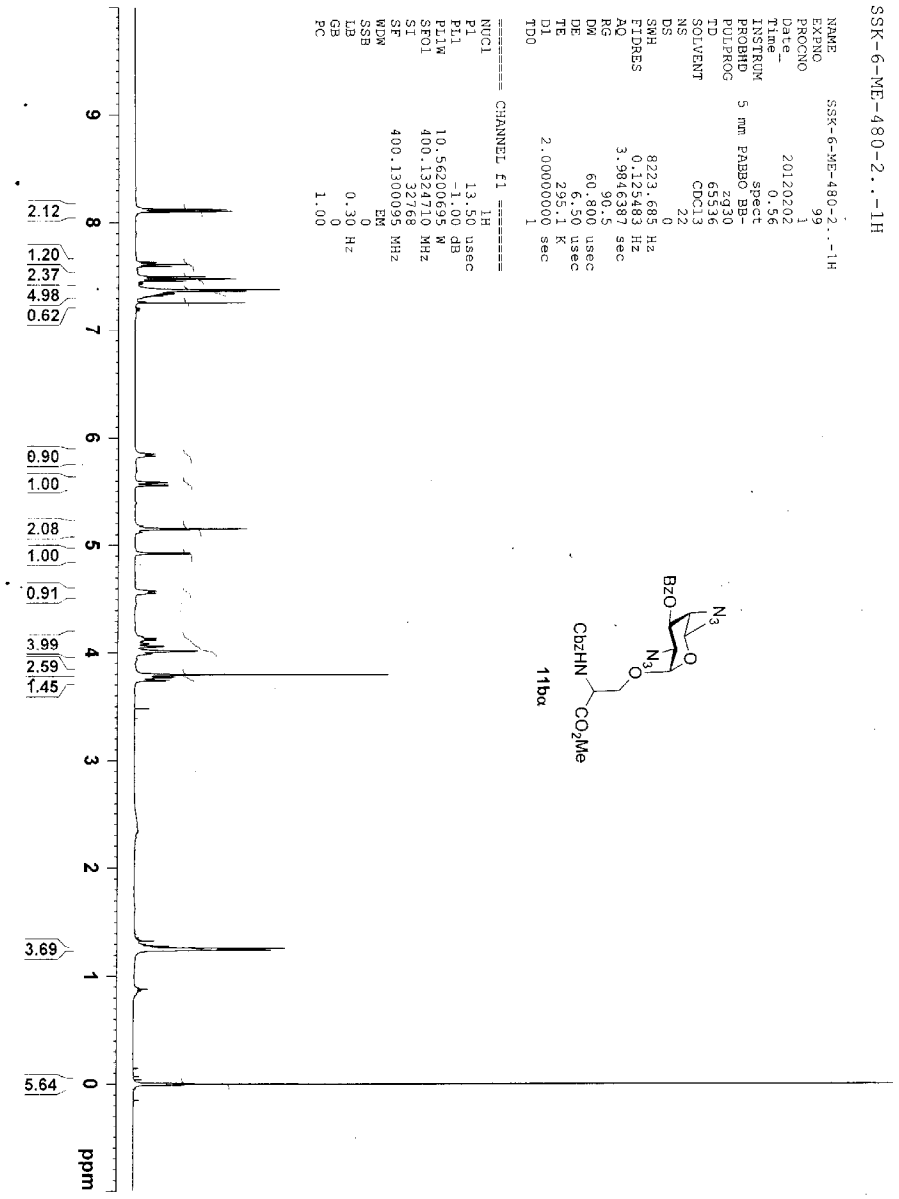


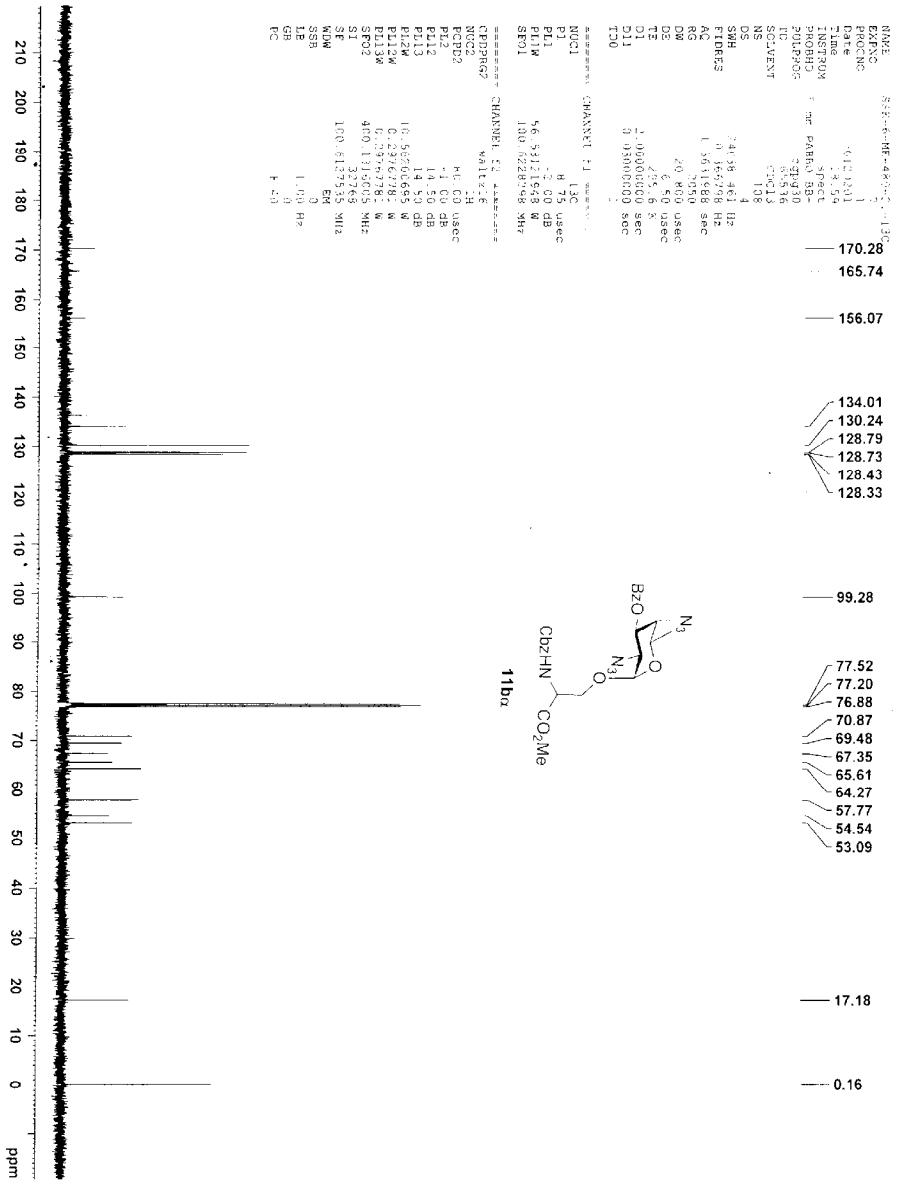

SSK-6-ME-666-13C
165.82
160.87
134.16
130.23
128.86
128.52
94.95
90.95
77.52
77.20
76.88
71.78
67.90
63.78
57.64
17.36
BzO
N3
O
N3
O
NH
CCl3
96
ppm
NAME SSK-6-ME-666-13C
EXPNO 3
PROCNO 1
Date_ 20120710
Time 15.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 681
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 6.75 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 100.6127546 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

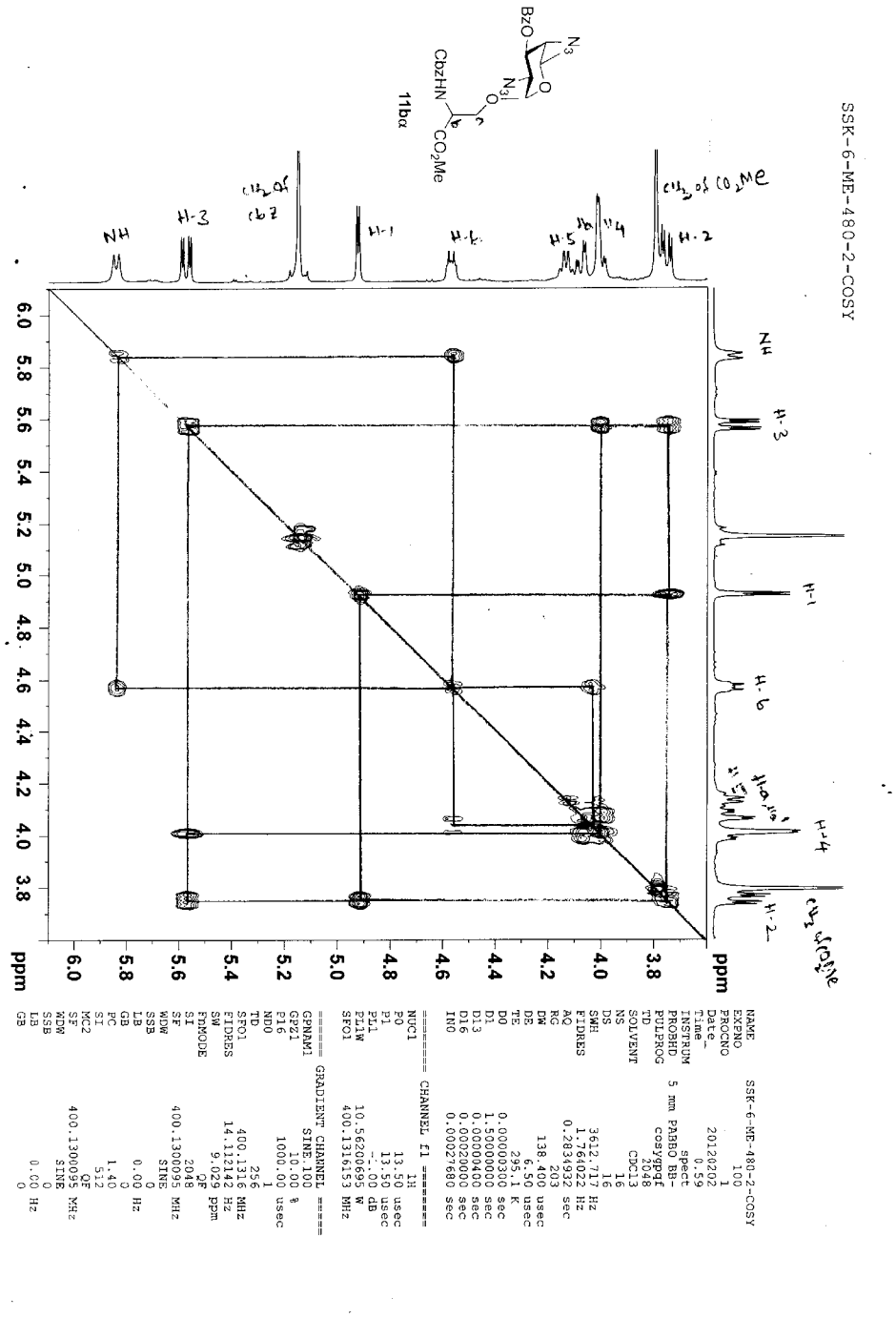


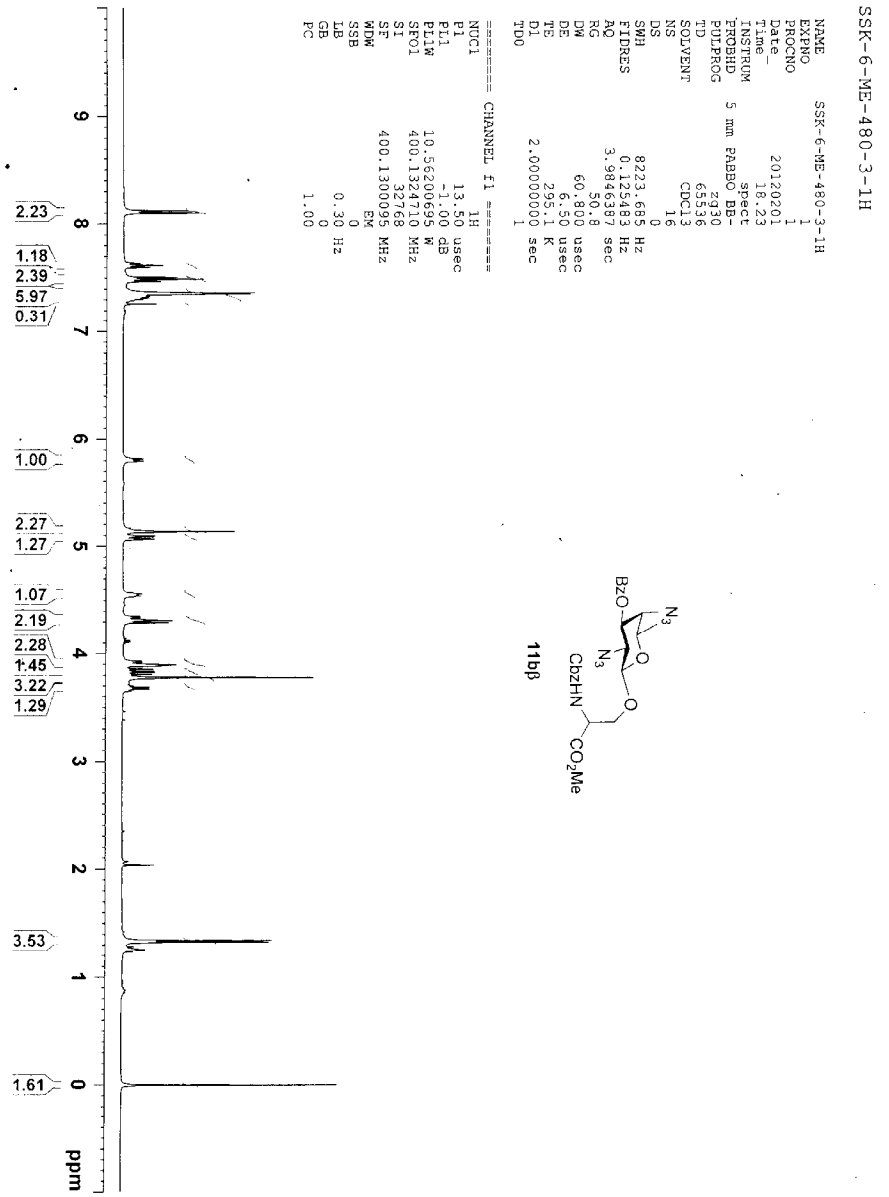

NAME SSK-6-ME-532-13C
EXPNO 2
PROCNO 1
Date_ 20120918
Time_ 0.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 154
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.35 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 10.56200981 W
PL12W 0.22967781 W
PL13W 0.22967781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127564 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
AcO
N3
N3
O
CbzHN
CO2Me
11aα
170.32
170.24
156.06
136.20
128.70
128.41
128.28
99.02
77.52
77.40
77.20
76.88
70.60
69.38
67.32
65.30
63.91
57.35
54.46
53.06
20.71
17.10
ppm

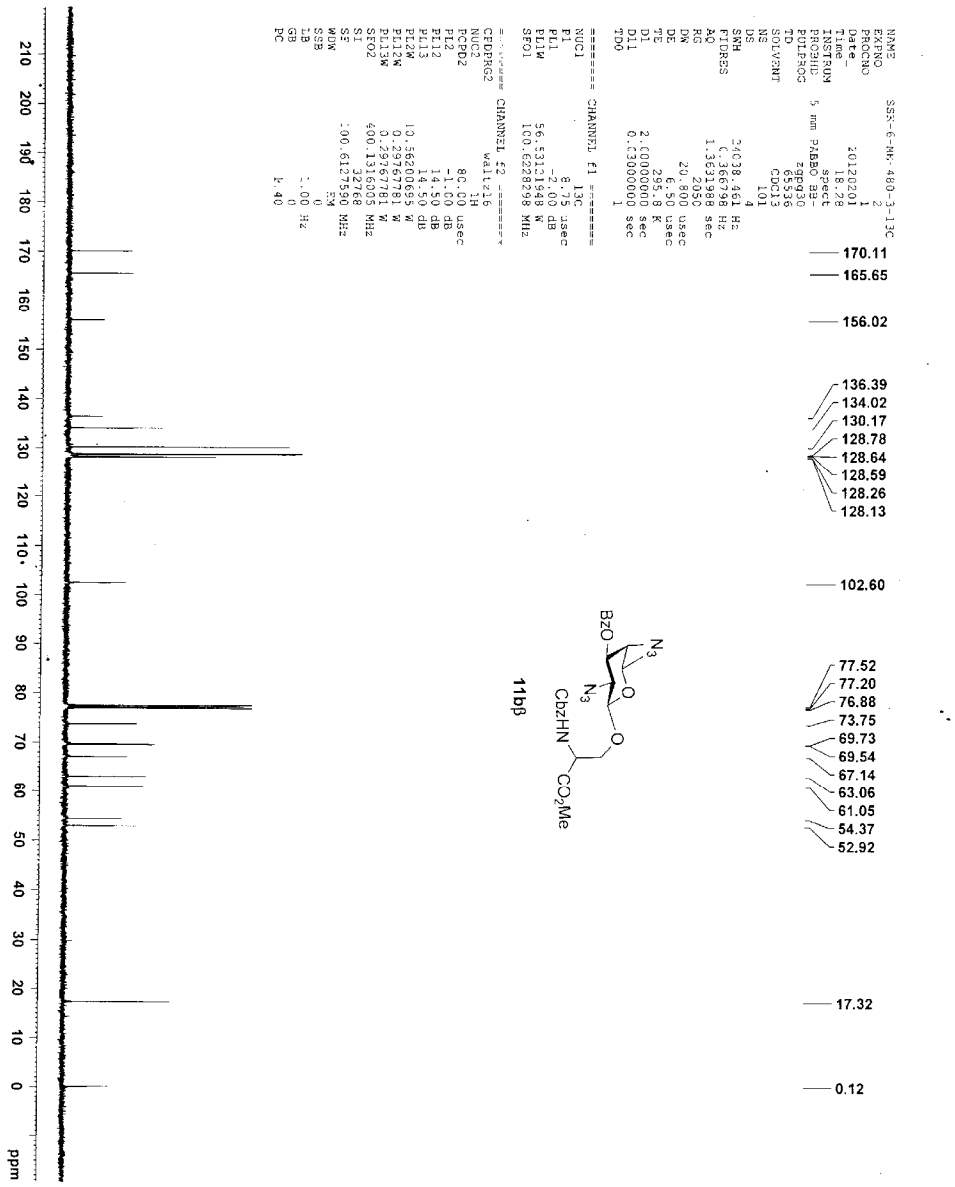

SSK-6-ME-532-COSY
11aα
AcO
N3
CbzHN
CO2Me
NH
H-3
H-1
CH
H-2
H-6
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
NAME SSK-6-ME-532-COSY
EXPNO 2
PROCNO 1
Date_ 20121007
Time_ 15.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 3255.208 Hz
FIDRES 3.178914 Hz
AQ 0.1573364 sec
RG 228
DW 153.600 usec
DE 6.50 usec
TE 293.4 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
INO 0.00030720 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1315.46 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 16.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1315 MHz
FIDRES 12.715586 Hz
SW 8.135 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

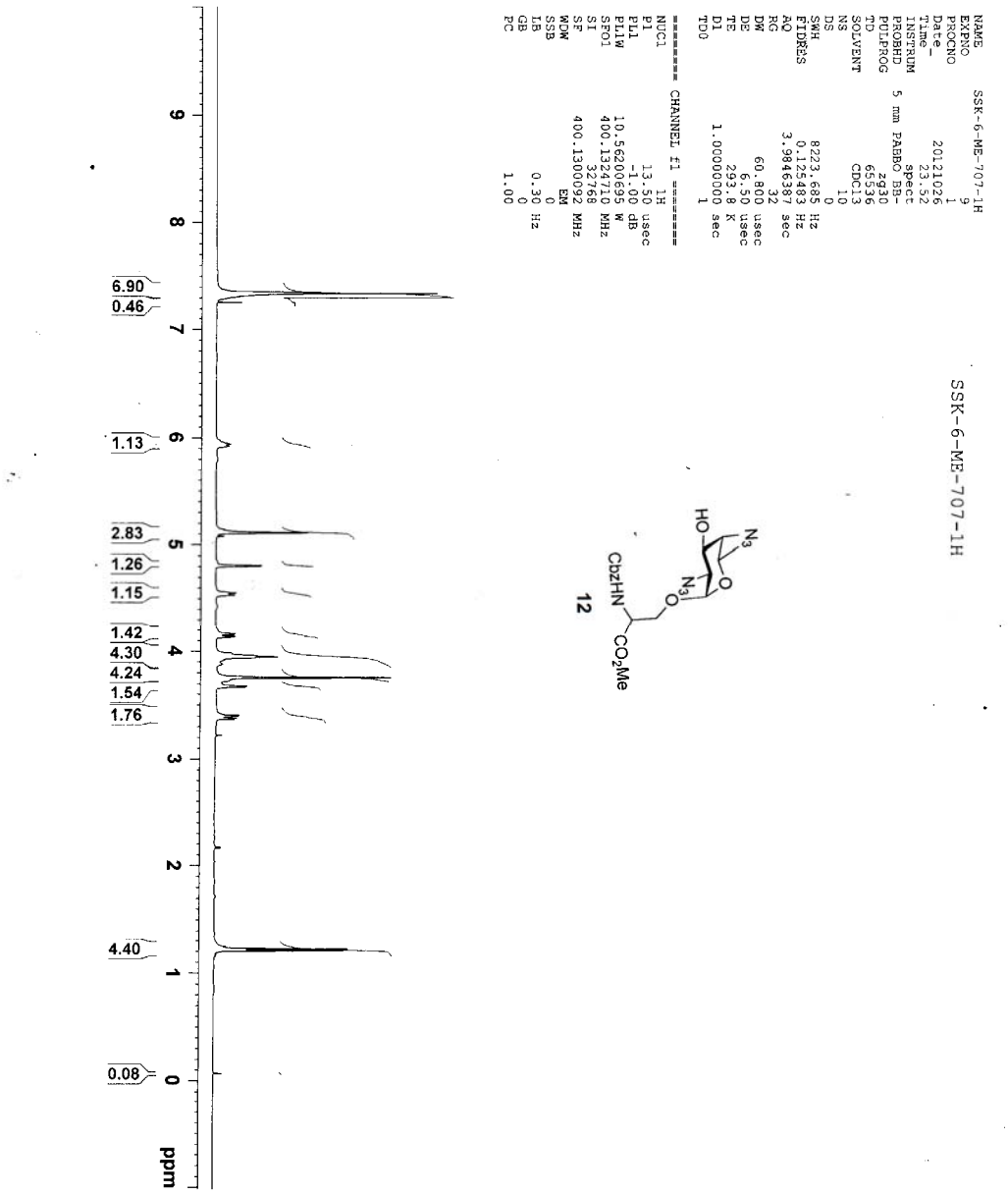


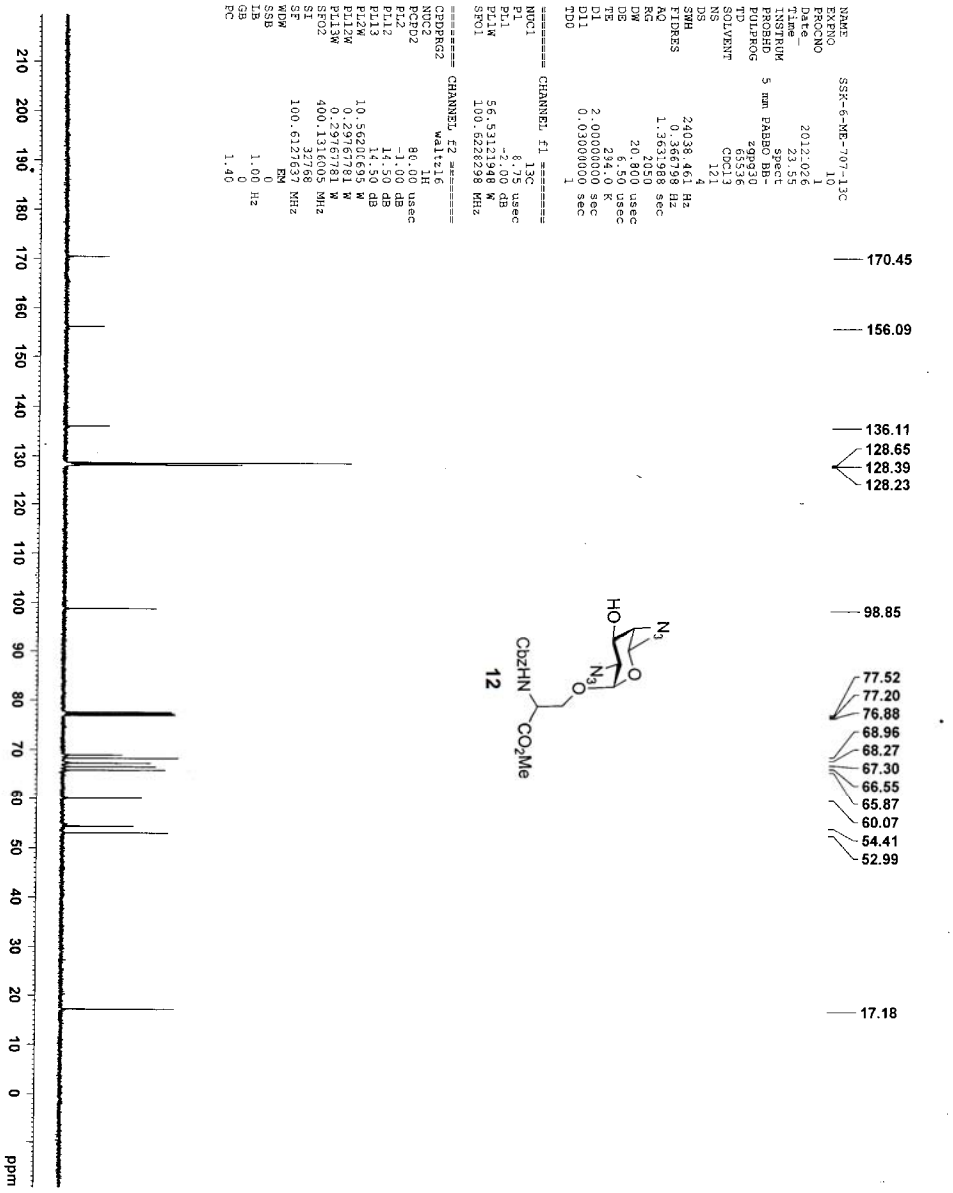

170.28
165.74
156.07
134.01
130.24
128.79
128.73
128.43
128.33
99.28
77.52
77.20
76.88
70.87
69.48
67.35
65.61
64.27
57.77
54.54
53.09
17.18
0.16
BzO
N3
N3
O
O
Cbz-HN
CO2Me
11bα

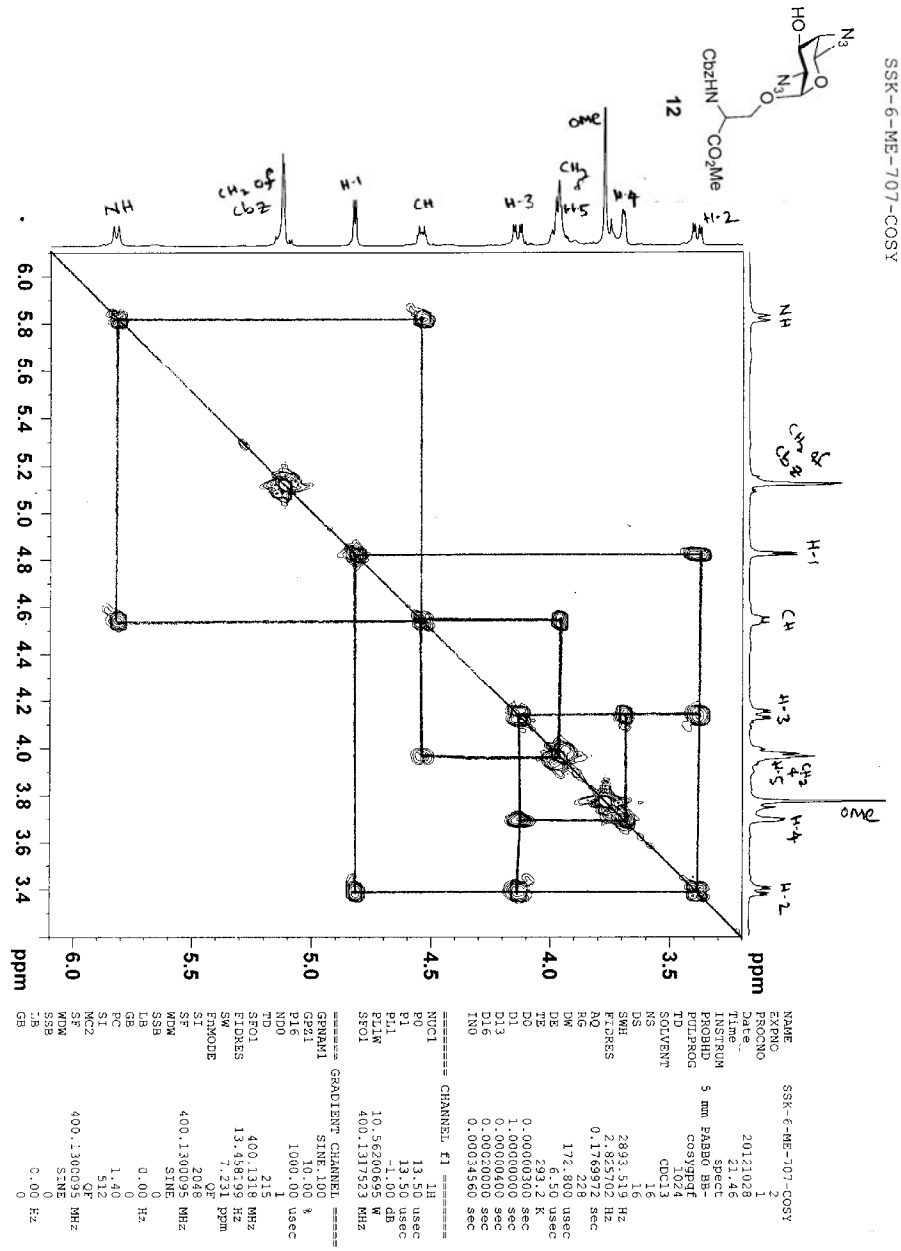

SSK-6-ME-480-2-COSY
11bα
BzO
CbzHN
CO2Me
NH
H-3
H-1
H-6
H-4
H-2
ppm
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
NAME SSK-6-ME-480-2-COSY
EXPNO 100
PROCNO 1
Date_ 20120202
Time_ 0.59
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 3612.717 Hz
FIDRES 1.764022 Hz
AQ 0.2834932 sec
RG 203
DW 138.400 usec
DE 6.50 usec
TE 295.1 K
D0 0.00000300 sec
D1 1.50000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00027680 sec
CHANNEL f1
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1316153 MHz
GRADIENT CHANNEL
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1316 MHz
FIDRES 14.112142 Hz
SW 9.029 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



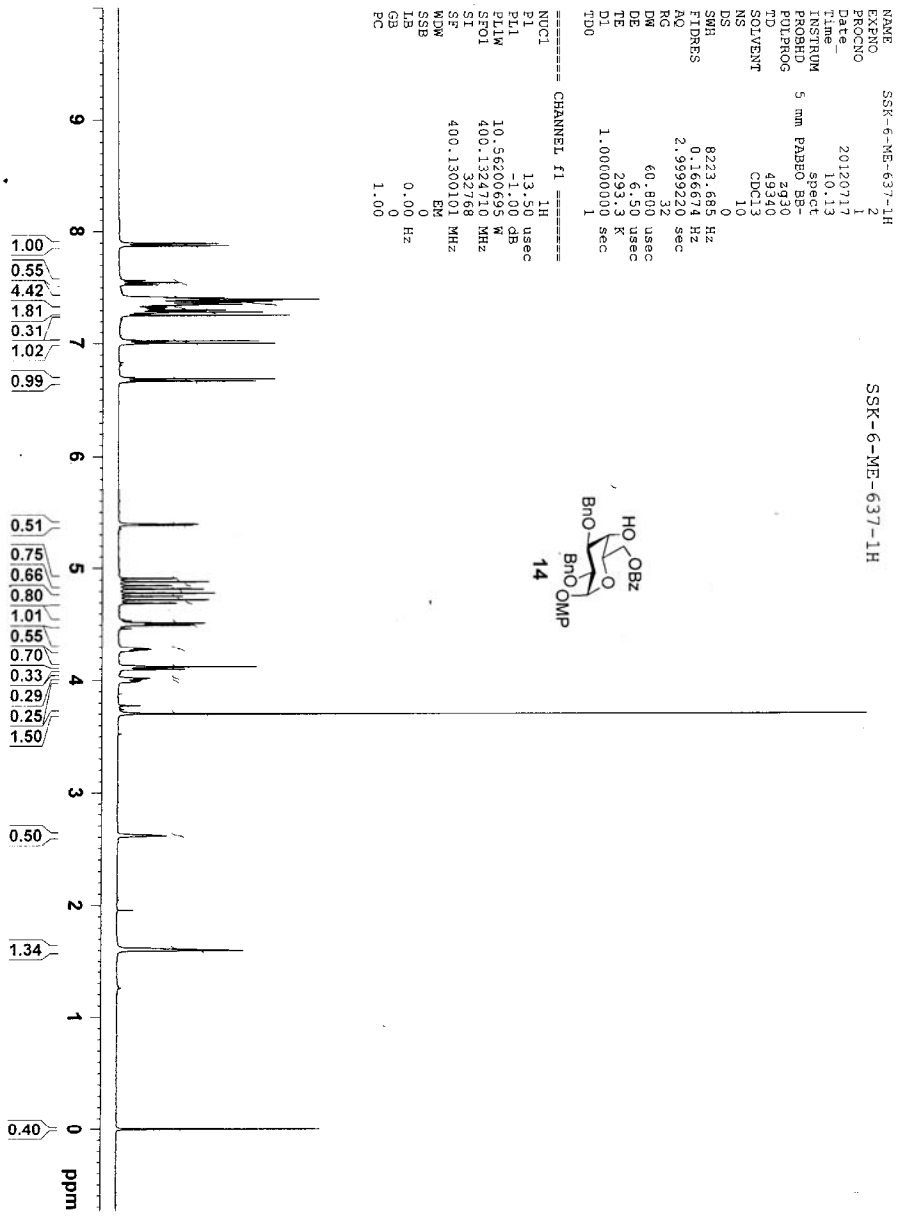

170.11
165.65
156.02
136.39
134.02
130.17
128.78
128.64
128.59
128.26
128.13
102.60
77.52
77.20
76.88
73.75
69.73
69.54
67.14
63.06
61.05
54.37
52.92
17.32
0.12
BzO
N3
N3
CbzHN
CO2Me
11bβ
ppm

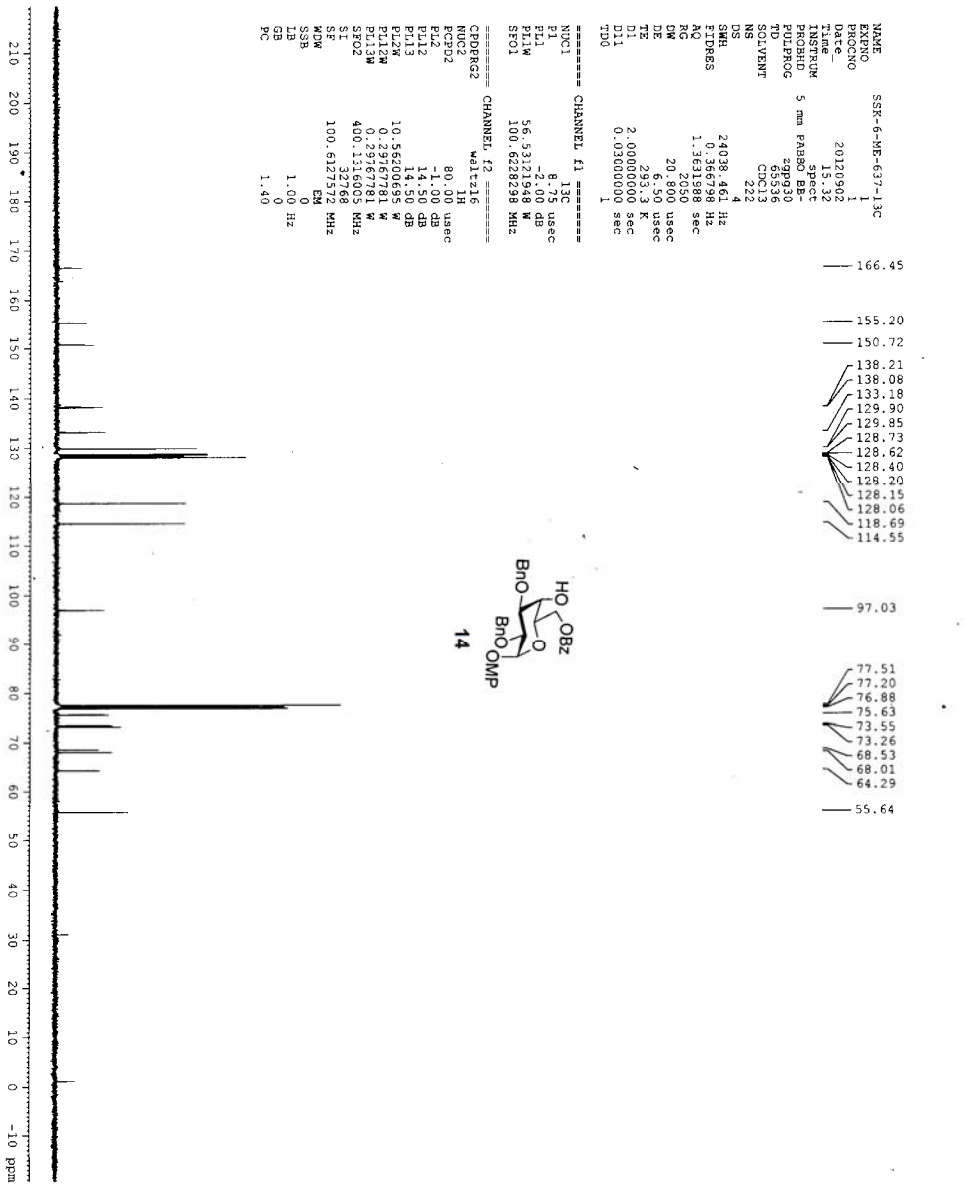

NAME SSK-6-ME-707-1H
EXPNO 9
PROCNO 1
Date_ 20121026
Time 23.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 293.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-707-1H
12
HO
N3
N3
O
O
CbzHN
CO2Me
6.90
0.46
1.13
2.83
1.26
1.15
1.42
4.30
4.24
1.54
1.76
4.40
0.08
9
8
7
6
5
4
3
2
1
0
ppm

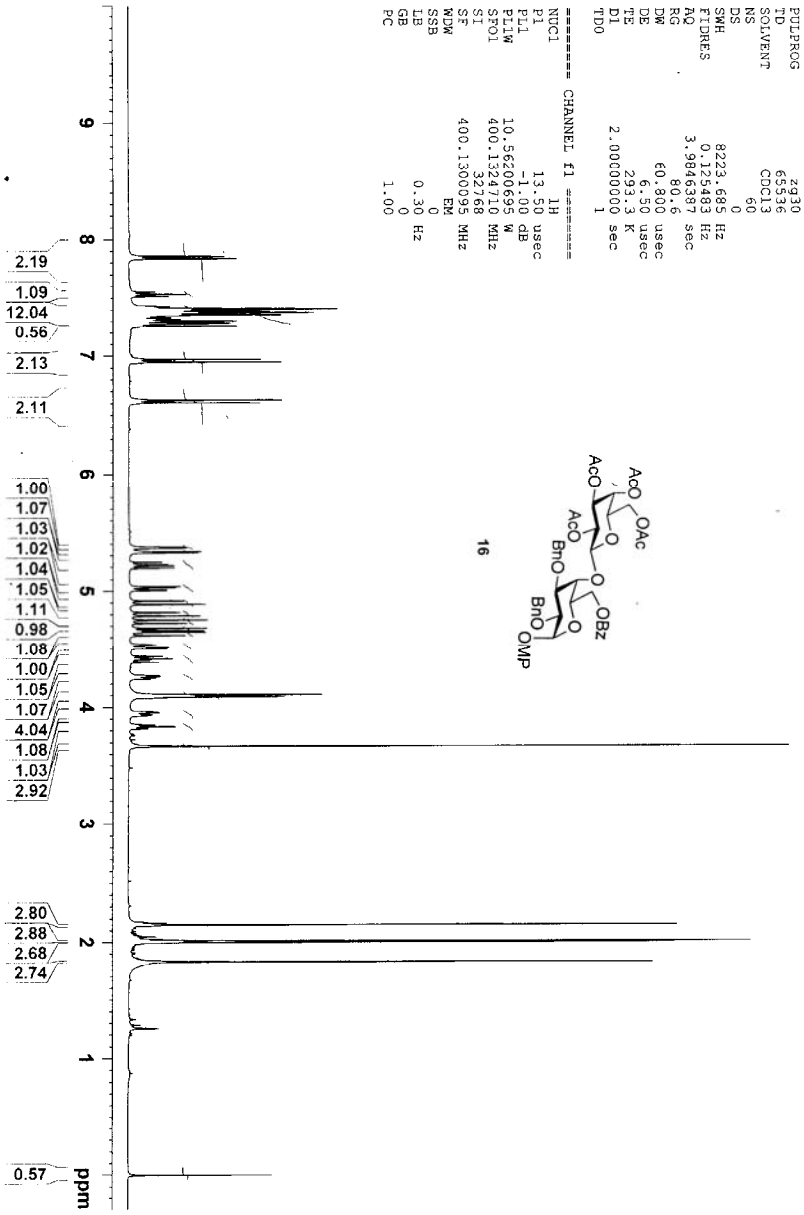

NAME SSK-6-ME-707-13C
EXPNO 10
PROCNO 1
Date_ 20121026
Time 23.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 121
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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
PL2 -1.00 dB
PL12 14.50 dB
PL13 14.50 dB
PL2W 10.56201695 W
PL12W 0.29767781 W
PL13W 0.29767781 W
SFO2 400.1324005 MHz
SI 100.6127637 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
HO
N3
O
N3
O
CbzHN
CO2Me
12
170.45
156.09
136.11
128.65
128.39
128.23
98.85
77.52
77.20
76.88
68.96
68.27
67.30
66.55
65.87
60.07
54.41
52.99
17.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

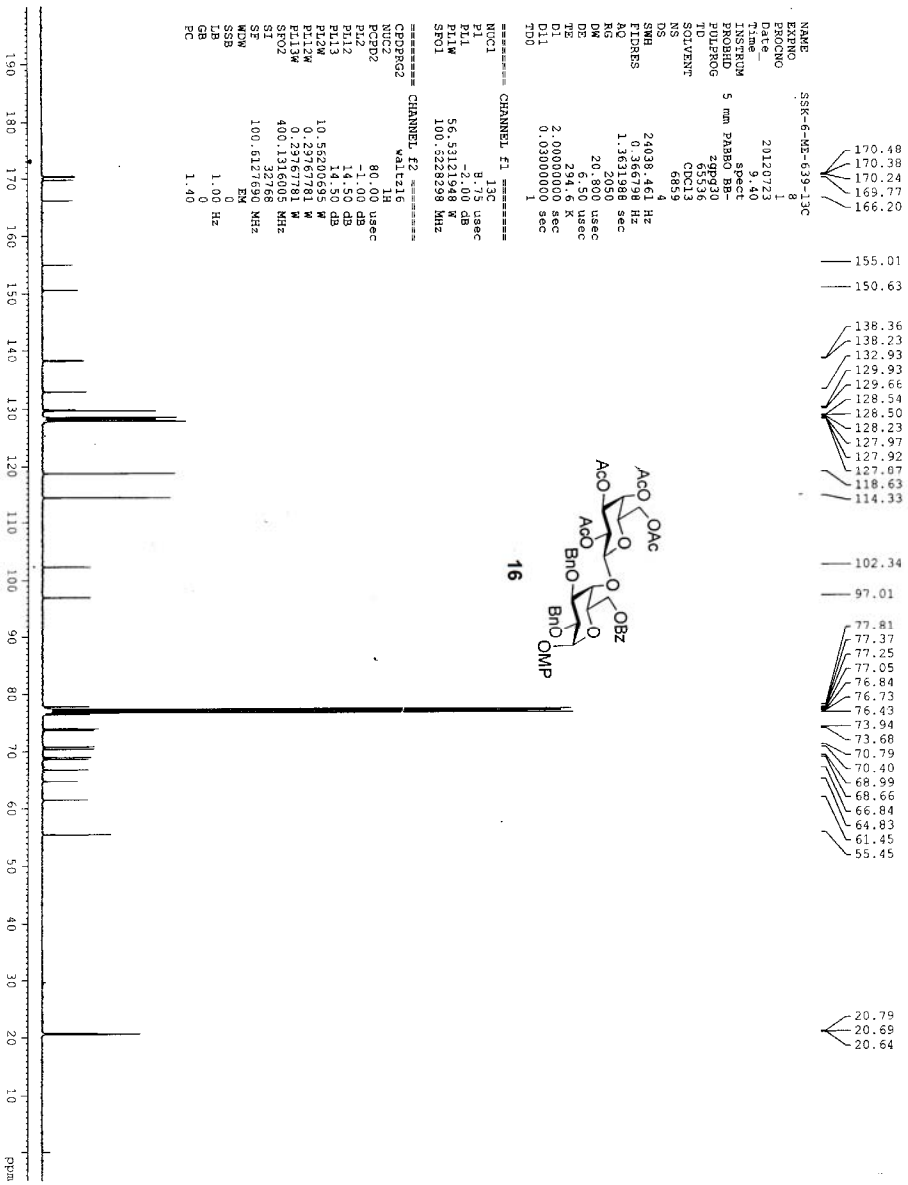


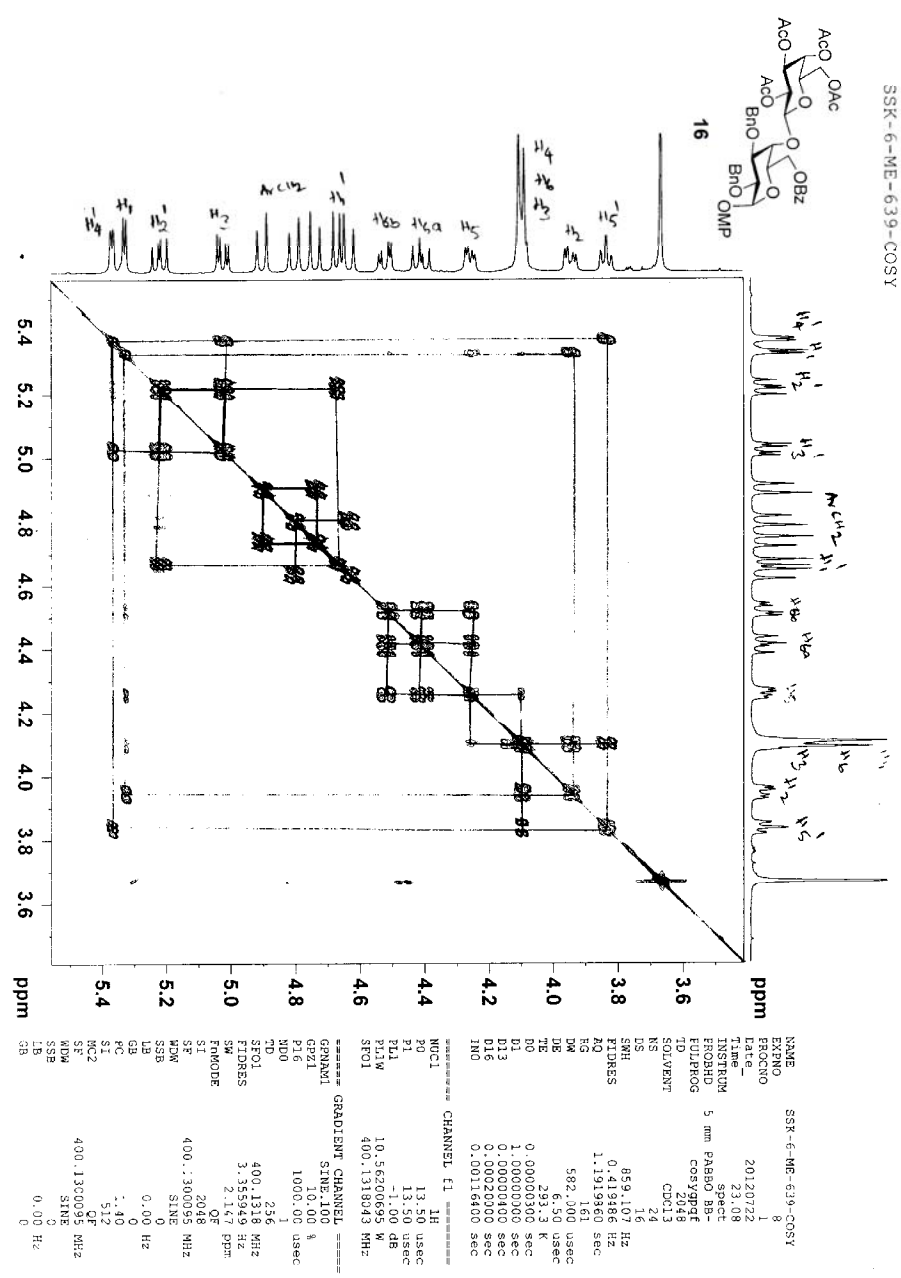
NAME SSK-6-ME-707-COSY
EXPNO 1
PROCNO 1
Date_ 20121028
Time_ 21.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 2893.519 Hz
FIDRES 2.825702 Hz
AQ 0.1769972 sec
RG 228
DW 172.800 usec
DE 6.50 usec
TE 293.2 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00034560 sec
========== CHANNEL f1 ==========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1317523 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 215
SFO1 400.1318 MHz
FIDRES 13.458299 Hz
SW 7.231 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

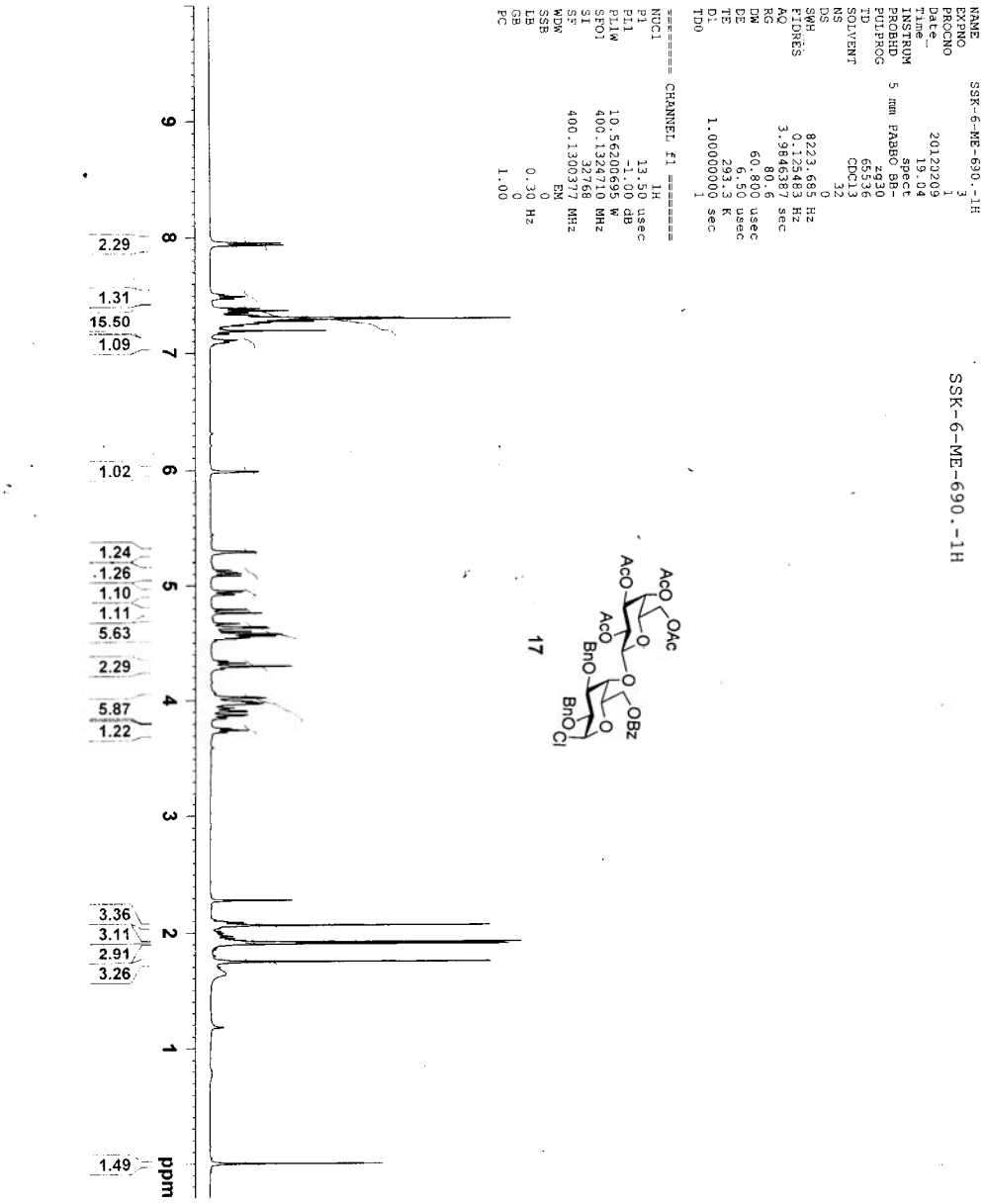

NAME SSK-6-ME-637-1H
EXPNO 2
PROCNO 1
Date_ 20120717
Time_ 10.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 49340
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.166674 Hz
AQ 2.9999220 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
SSK-6-ME-637-1H
BnO
BnO
OMP
HO
OBz
14
1.00
0.55
4.42
1.81
0.31
1.02
0.99
0.51
0.75
0.66
0.80
1.01
0.55
0.70
0.33
0.29
0.25
1.50
0.50
1.34
0.40
ppm

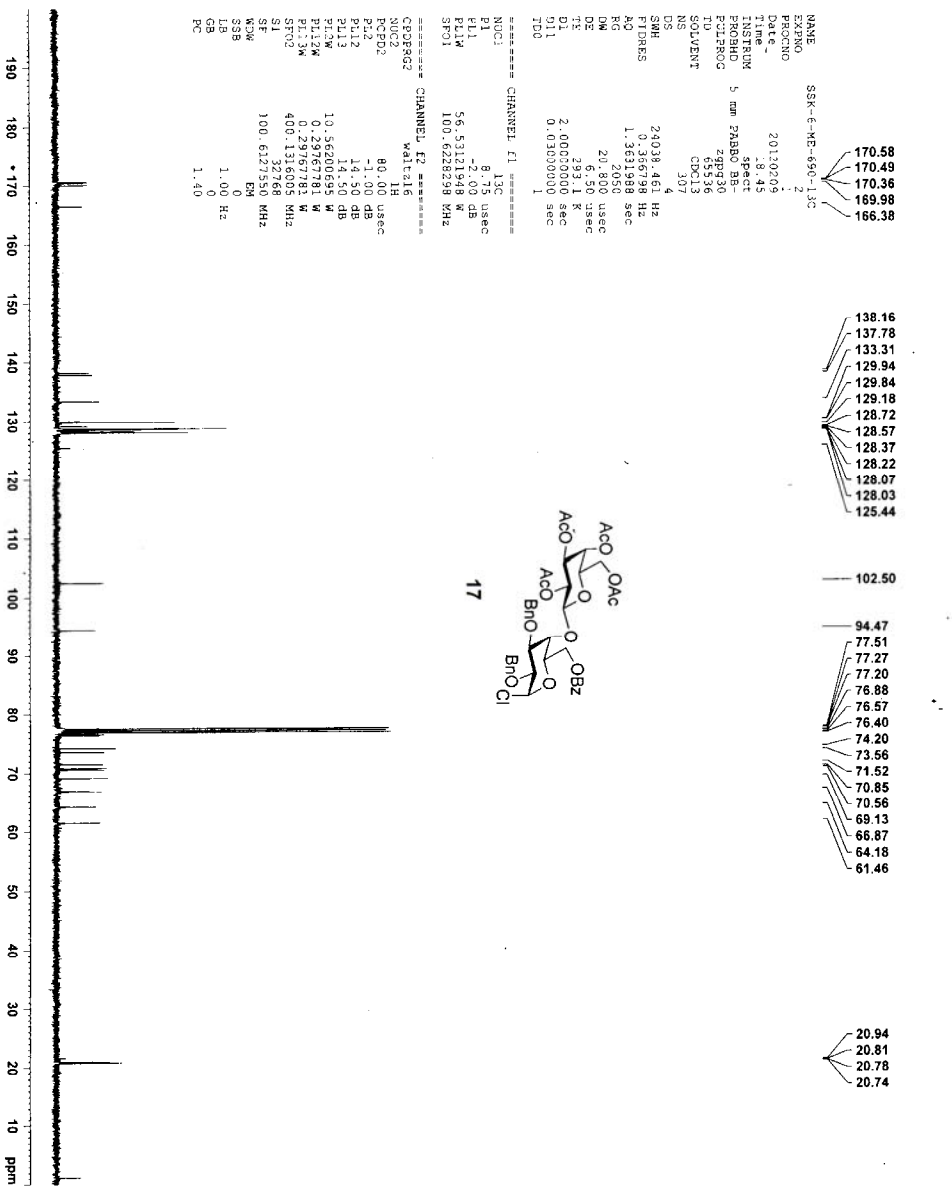

NAME SSK-6-ME-637-13C
EXPNO 1
PROCNO 1
Date_ 20120902
Time_ 15.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 222
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.363188 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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
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 100.6127572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
166.45
155.20
150.72
138.21
138.08
133.18
129.90
129.85
128.73
128.62
128.40
128.20
128.15
128.06
118.69
114.55
97.03
77.51
77.20
76.88
75.63
73.55
73.26
68.53
68.01
64.29
55.64
HO
OBz
BnO
O
BnO
OMP
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

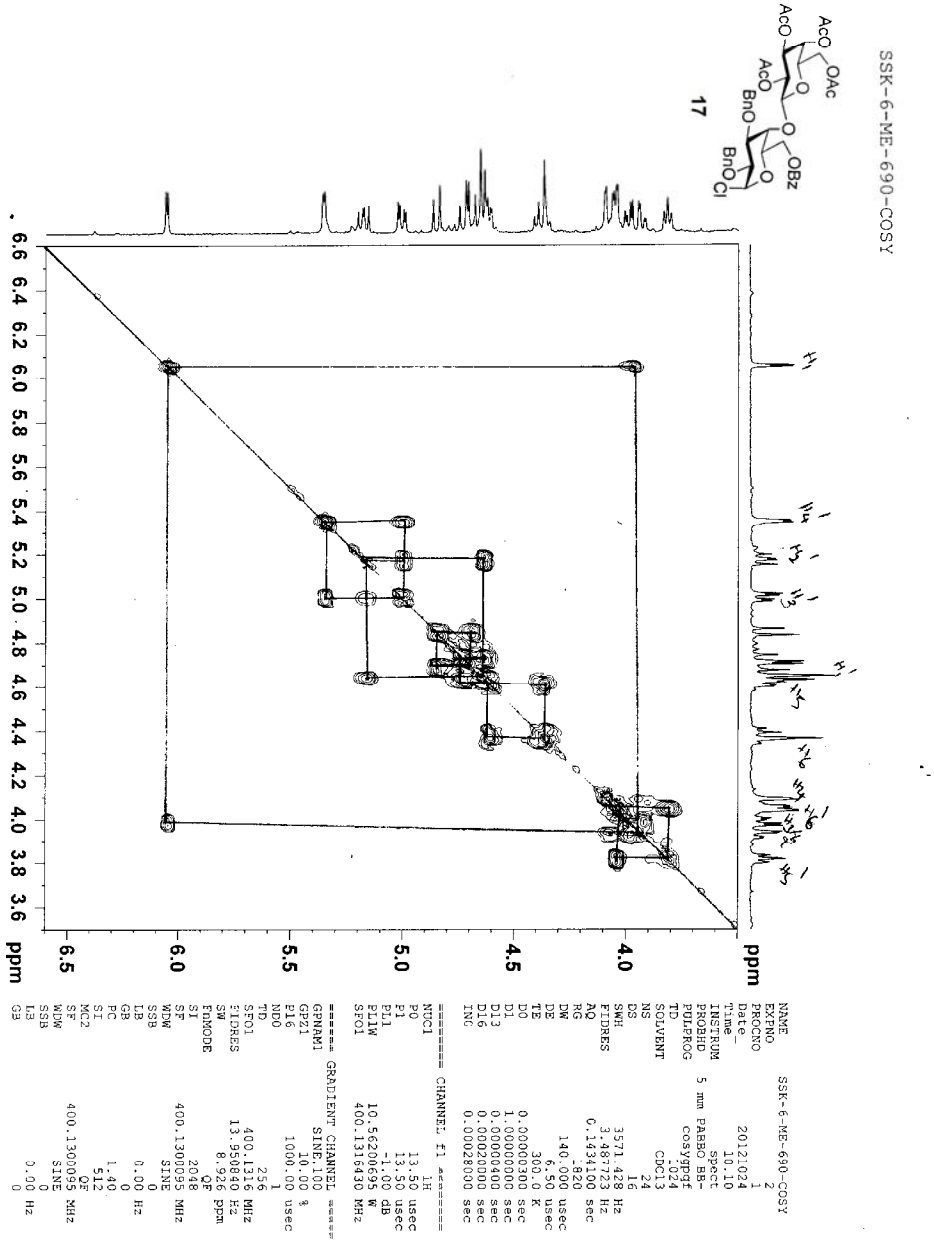

NAME SSK-6-ME-639-1H
EXPNO 1
PROCNO 1
Date_ 20120722
Time_ 23.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 60
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 293.3 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-6-ME-639-1H
16
2.19
1.09
12.04
0.56
2.13
2.11
1.00
1.07
1.03
1.02
1.04
1.05
1.11
0.98
1.08
1.00
1.05
1.07
4.04
1.08
1.03
2.92
2.80
2.88
2.68
2.74
0.57
ppm

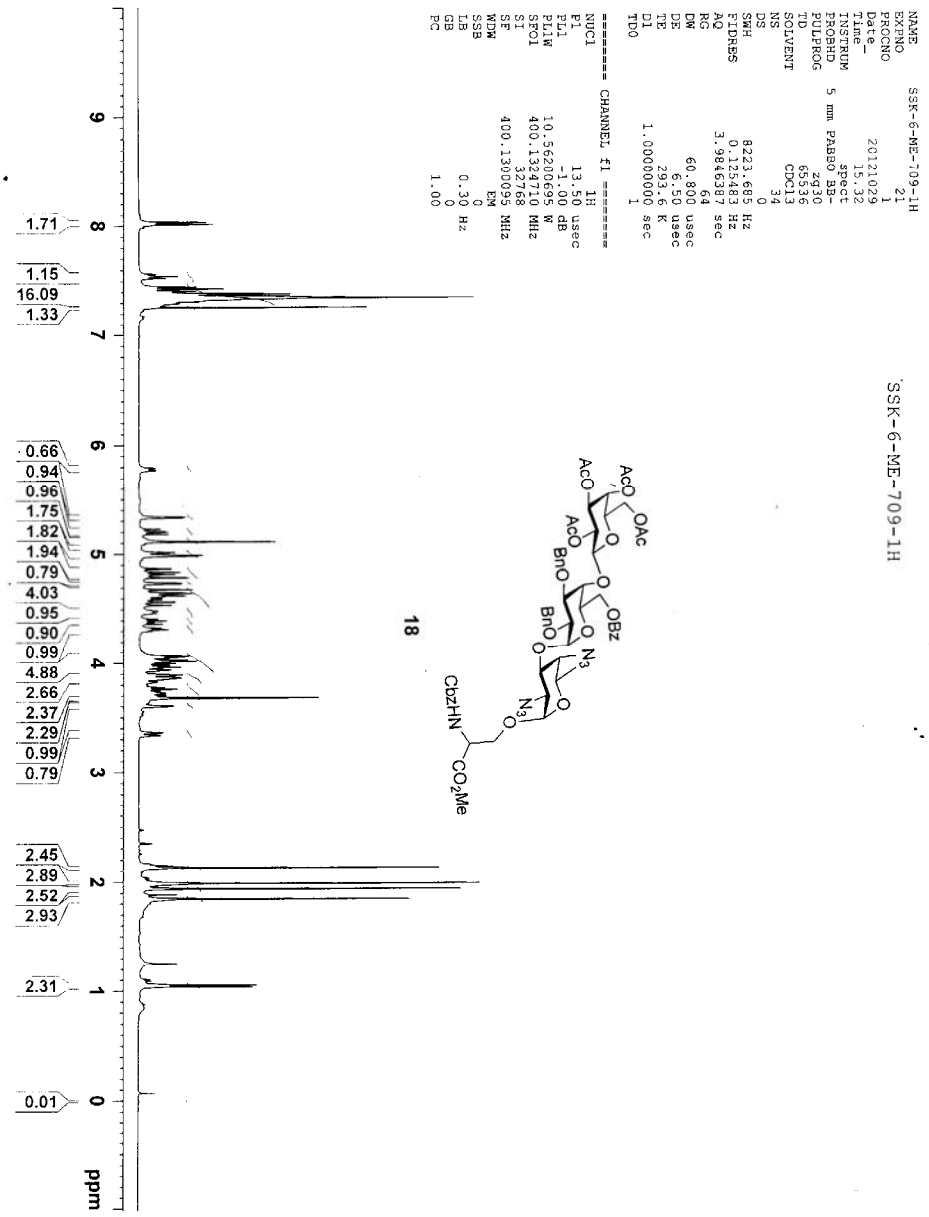

NAME SSK-6-ME-639-13C
EXPNO 8
PROCNO 1
Date_ 20120723
Time 9.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 6859
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.5228298 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 0.23767781 W
PL13W 0.23767781 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
16
AcO
AcO
AcO
OAc
BnO
BnO
OBz
OMP
170.48
170.38
170.24
169.77
166.20
155.01
150.63
138.36
138.23
132.93
129.93
129.66
128.54
128.50
128.23
127.97
127.92
127.87
118.63
114.33
102.34
97.01
77.81
77.37
77.25
77.05
76.84
76.73
76.43
73.94
73.68
70.79
70.40
68.99
68.66
66.84
64.83
61.45
55.45
20.79
20.69
20.64
ppm

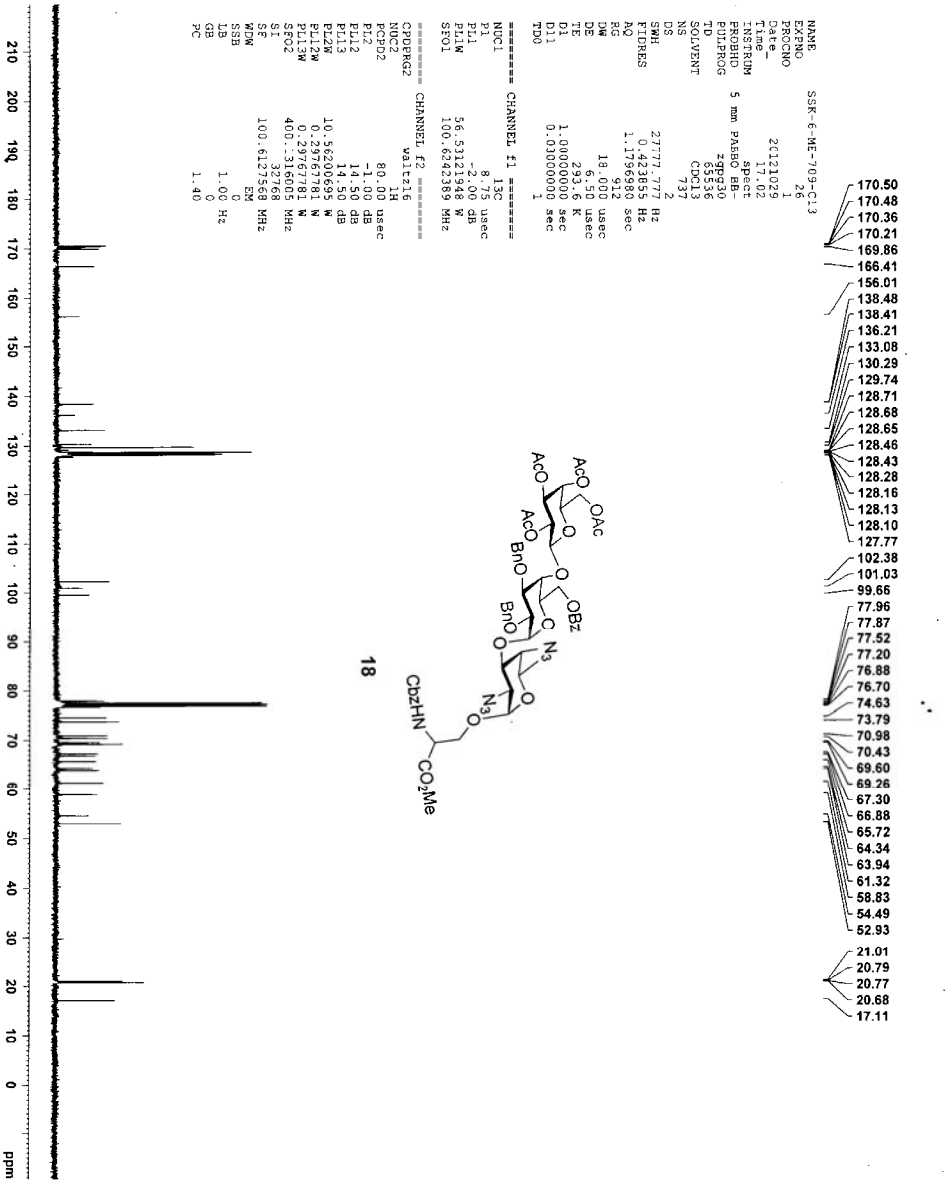

SSK-6-ME-639-COSY
AcO
OAc
AcO
AcO
BnO
OBz
BnO
OMP
16
ppm
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6

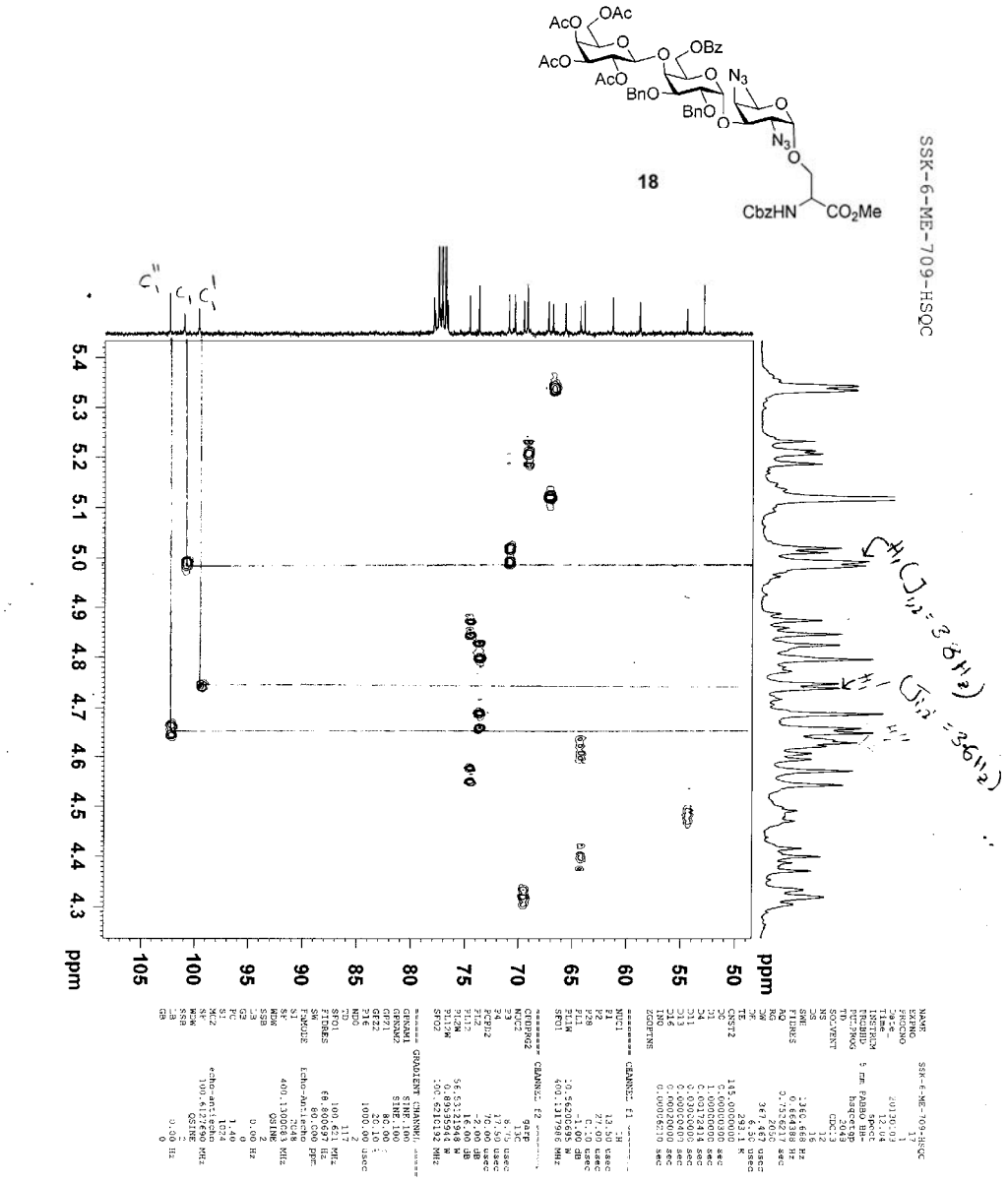


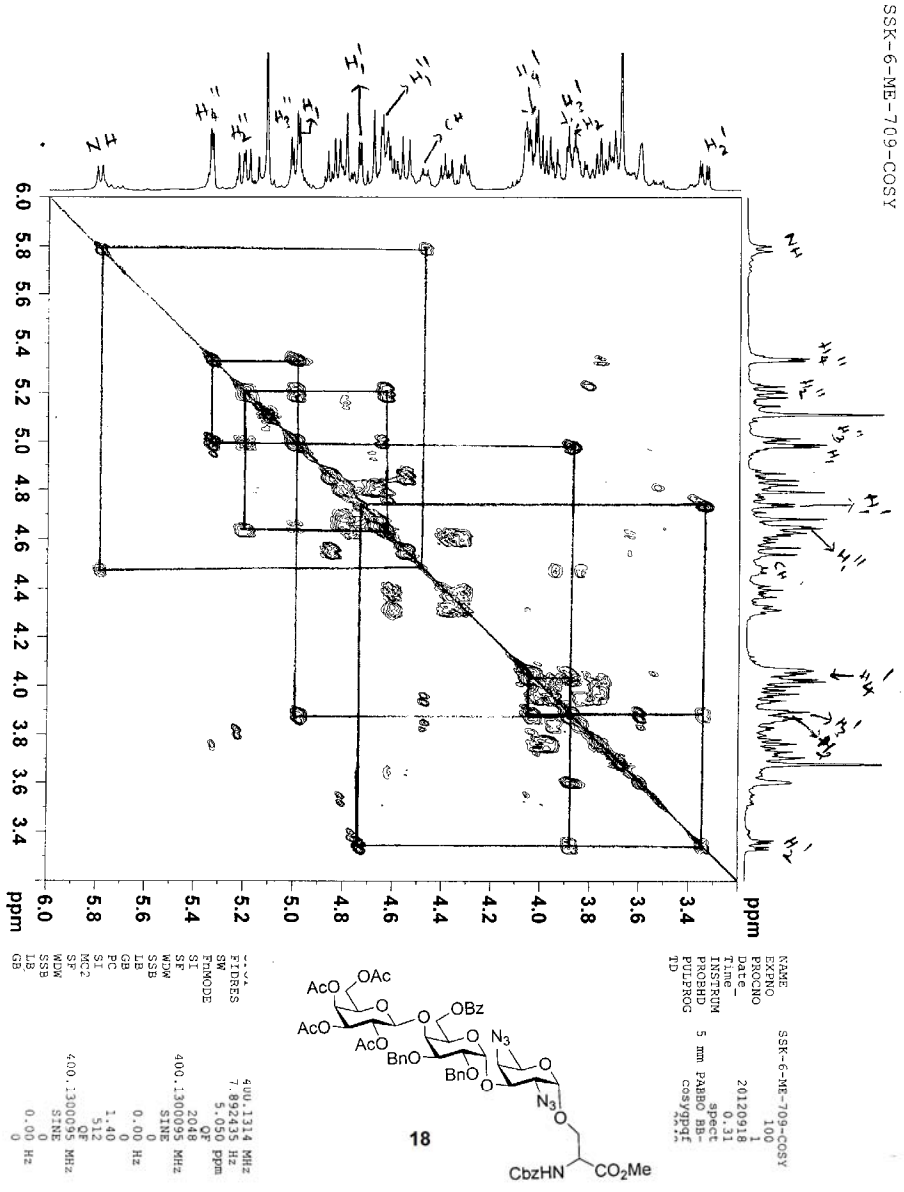

NAME SSK-6-ME-69C-13C
EXPNO 2
PROCNO 1
Date_ 20130206
Time_ 18.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 307
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 293.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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
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 100.6127550 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
170.58
170.49
170.36
169.98
166.38
138.16
137.78
133.31
129.94
129.84
129.18
128.72
128.57
128.37
128.22
128.07
128.03
125.44
102.50
94.47
77.51
77.27
77.20
76.88
76.57
76.40
74.20
73.56
71.52
70.85
70.56
69.13
66.87
64.18
61.46
20.94
20.81
20.78
20.74
17
AcO
AcO
AcO
OAc
BnO
O
O
OBz
BnO
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

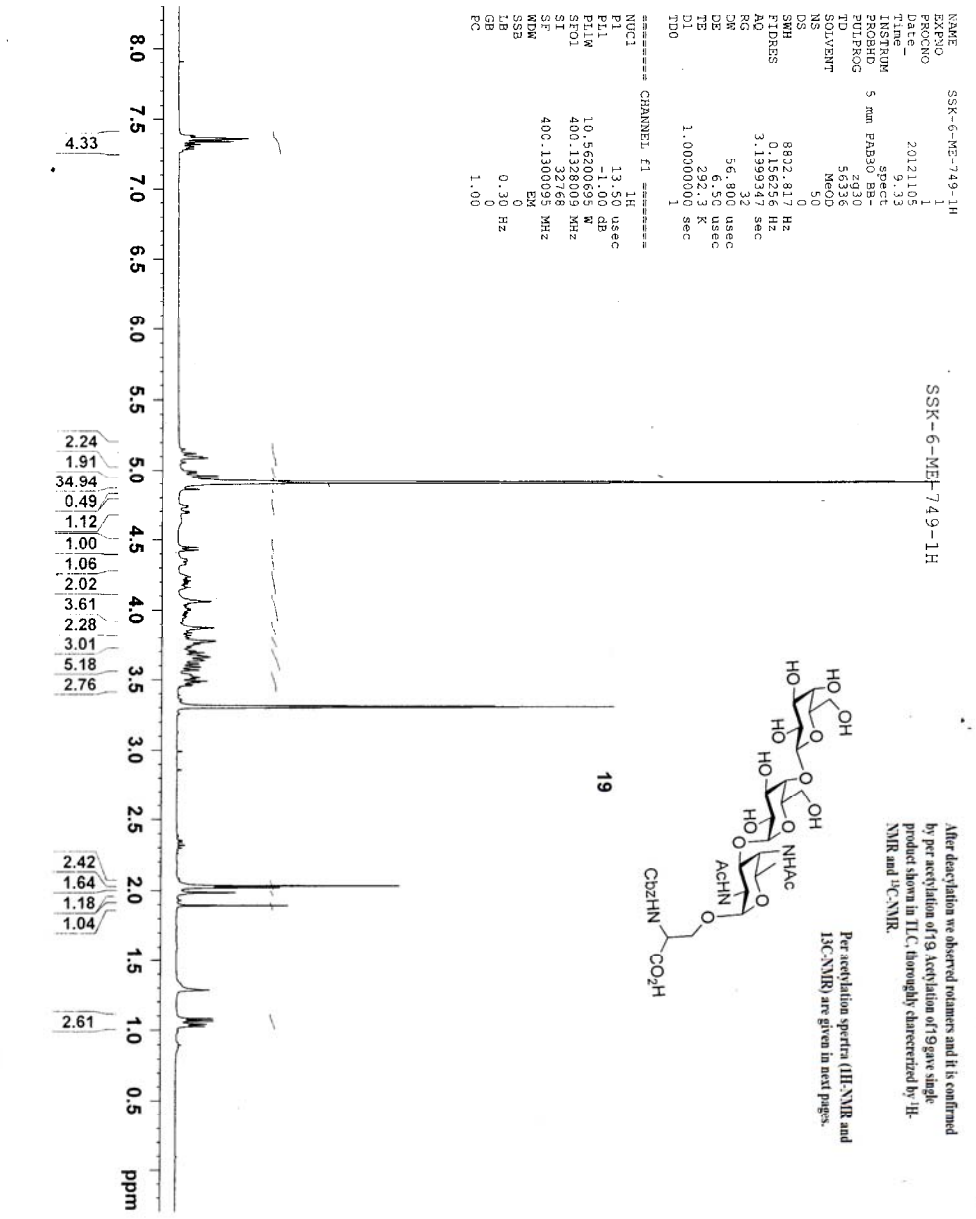

SSK-6-ME-690-COSY
17
AcO
AcO
AcO
BnO
BnO
Cl
OAc
OBz
ppm
6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6
6.5
6.0
5.5
5.0
4.5
4.0
NAME SSK-6-ME-690-COSY
EXPNO 2
PROCNO 1
Date_ 20121024
Time 10.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 24
DS 16
SWH 3571.428 Hz
FIDRES 3.487723 Hz
AQ 0.1434100 sec
RG 820
DW 140.000 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
INO 0.00028000 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -11.00 dB
PLW1 10.56200695 W
SFO1 400.1316430 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1316 MHz
FIDRES 13.950840 Hz
SW 8.926 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


NAME SSK-6-ME-709-1H
EXPNO 21
PROCNO 1
Date_ 20121029
Time_ 15.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 34
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 293.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PLW1 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-709-1H
18
1.71
1.15
16.09
1.33
0.66
0.94
0.96
1.75
1.82
1.94
0.79
4.03
0.95
0.90
0.99
4.88
2.66
2.37
2.29
0.99
0.79
2.45
2.89
2.52
2.93
2.31
0.01
ppm


NAME SSK-6-ME-709-C13
EXPNO 26
PROCNO 1
Date_ 20121029
Time_ 17.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 737
DS 2
SWH 27777.777 Hz
FIDRES 0.423655 Hz
AQ 1.179680 sec
RG 512
DW 18.000 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53122330 W
SFO1 100.6242389 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 400.3160005 MHz
SI 32768
SF 100.6127568 MHz
WDW EM
SSB 1.00 Hz
LB 0
GB
PC 1.40
170.50
170.48
170.36
170.21
169.86
166.41
156.01
138.48
138.41
136.21
133.08
130.29
129.74
128.71
128.68
128.65
128.46
128.43
128.28
128.16
128.13
128.10
127.77
102.38
101.03
99.66
77.96
77.87
77.52
77.20
76.88
76.70
74.63
73.79
70.98
70.43
69.60
69.26
67.30
66.88
65.72
64.34
63.94
61.32
58.83
54.49
52.93
21.01
20.79
20.77
20.68
17.11
AcO
AcO
AcO
OAc
O
BnO
O
OBz
C
N3
BnO
O
N3
O
O
CbzHN
CO2Me
18
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

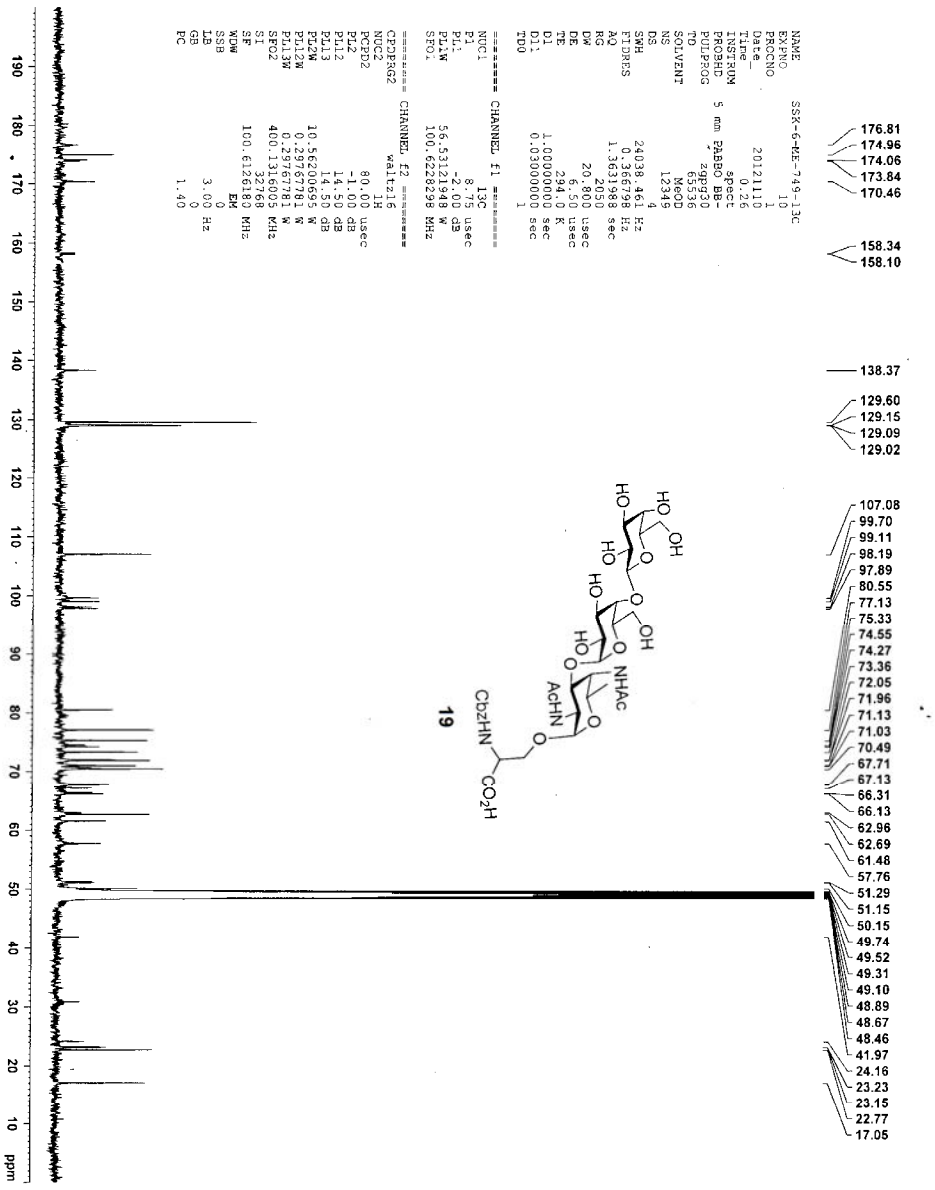

18
SSK-6-ME-709-HSQC
ppm
ppm


SSK-6-ME-709-COSY
ppm
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
AcO
OAc
AcO
OBz
AcO
BnO
BnO
N3
N3
CbzHN
CO2Me
18



After deacetylation we observed rotamers and it is confirmed by per acetylation of 19. Acetylation of 19 gave single product shown in TLC, thoroughly characterized by ^{1}H-NMR and ^{13}C-NMR.

Per acetylation spectra (^{1}H-NMR and ^{13}C-NMR) are given in next pages.

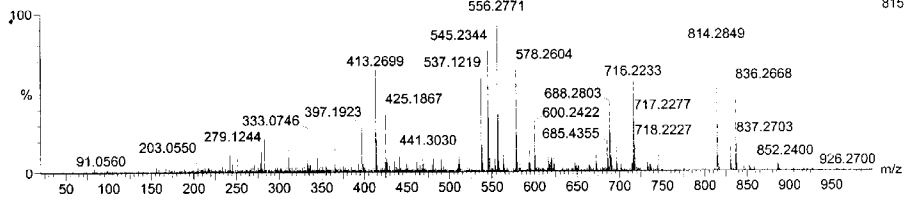

NAME SSK-6-ME-749-13C
EXPNO 10
PROCNO 1
Date_ 20121110
Time 0.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD3OD
NS 12349
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 294.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== 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 100.6126180 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
176.81
174.96
174.06
173.84
170.46
158.34
158.10
138.37
129.60
129.15
129.09
129.02
107.08
99.70
99.11
98.19
97.89
80.55
77.13
75.33
74.55
74.27
73.36
72.05
71.96
71.13
71.03
70.49
67.71
67.13
66.31
66.13
62.96
62.69
61.48
57.76
51.29
51.15
50.15
49.74
49.52
49.31
49.10
48.89
48.67
48.46
41.97
24.16
23.23
23.15
22.77
17.05
19
ppm

Elemental Composition Report **Page 1**

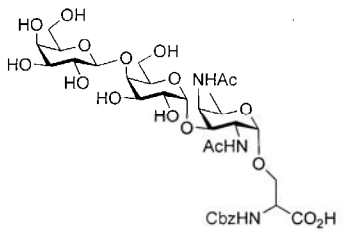
Single Mass Analysis (displaying only valid results)
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
307 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Waters(Micromass) : Q-Tof micro(YA-105) Dept. Of Chemistry - I.I.T.(B) 21-Dec-201223:54:18
C33H49N3O19
SSK-6-ME-749 40 (0.400) AM (Cen,4, 80.00, Ht,5000.0,556.28,1.00); Sm (Md, 6.00); Sb (5,40.00); Cm (28:41) TOF MS ES+
815



Minimum:				-1.5		
Maximum:		50.0	20.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
814.2849	814.2858	-0.9	-1.2	10.5	1	C33 H49 N3 O19 Na



19