Supporting Information

Desymmetrization of Trehalose *via* Regioselective Reductive DIBAL Ring Opening of Benzylidene and Substituted Benzylidene Acetals.

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I. Experimental procedures

General Methods. All reactions were conducted under a dry nitrogen atmosphere. Solvents (CH_2Cl_2 >99%, Toluene >99%) were purchased in capped bottles and dried under CaH_2 or sodium. All other solvents and reagents were used without further purification. All glassware used was oven dried before use. TLC was performed on precoated aluminium plates of silica gel 60 F254 (0.25 mm, E. Merck). Developed TLC plates were visualized under a short-wave UV lamp and by heating plates that were dipped in ammonium molybdate/cerium (IV) sulfate solution. Silica gel column chromatography was performed using Silica Gel (100-200) and employed a solvent polarity correlated with TLC mobility. NMR experiments were conducted on 400 MHz instrument using $CDCl_3$ (D, 99.8%) or CD_3OD (D, 99.9%) as solvents. Chemical shifts are relative to the deuterated solvent peaks and are in parts per million (ppm). ^1H-^1H COSY was used to confirm proton assignments. High resolution mass spectra were acquired in the ESI-TOF (time of flight) mode. Melting points were determined by capillary apparatus. Specific rotation experiments were measured at 589 nm (Na) and 20 °C unless otherwise mentioned. IR spectra were recorded on an FT-IR spectrometer using CsCl plates.

2,3,2′,3′-Tetra-*O*-benzyl-4,6;4′,6′-di-*O*-benzylidene-*α,α*-D-trehalose (6). To the suspension of trehalose (2.0 gm, 5.84 mmol) in DMF (14 mL), benzaldehyde dimethylacetal (2.64 mL, 17.53 mmol) and CSA (270 mg, 1.17 mmol) were added at rt and the reaction mixture was kept on rotary evaporator under 140 mbar pressure and at 60 °C. The reaction was quenched by addition of Et_3N (1 mL, pH>7). Solvents were evaporated on rotary evaporator and the thick glassy liquid was purified by column chromatography (8:2 ethyl acetate: pet ether) to obtain 4,6;4′,6′-di-*O*-benzylidene-*α,α*-D-trehalose[33] as white solid (2.98 gm, 98%).

To a solution of 4,6;4′,6′-di-*O*-(benzylidene)-*α,α*-D-trehalose (2.98 g, 5.75 mmol) in anhydrous DMF (21 mL), was added NaH (60% in oil; 2.3 g, 57.5 mmol) portion wise at rt under N_2 atmosphere. The reaction mixture was cooled to 0 ^oC and benzyl bromide (5.5 mL, 45.98 mmol) followed by TBAI (425 mg, 1.15 mmol) were added to it. Reaction mixture was allowed to stir at room temperature. After 18 h the reaction flask was cooled to 0 °C and quenched by careful addition of MeOH. The reaction mixture was diluted with ethyl acetate (150 mL), washed with brine (15 mL × 5), and dried on anhydrous Na_2SO_4. Organic layer was concentration *in vacuo* and purification of the residue by silica gel column chromatography (3:17 ethyl acetate: pet ether) furnished **6** as a white solid (4.61 g, 90% over 2 steps). $[\alpha]^{20}_D$ +52.64 (*c* 1, $CHCl_3$) [lit[32] $[\alpha]^{20}_D$ +51.3 (*c* 1)]; mp 153-154 ^oC [lit[32]152-153 ^oC]; IR *v* 3066, 3017, 2934, 2865, 1604, 1583, 1454, 1371, 1216, 1089, 987, 757, 698, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.24 (m, 30H), 5.55 (s, 2H, PhC*H*), 5.11 (d, *J* = 3.8 Hz, 2H, H-1 & H-1′), 4.96 (d, *J* = 11.1 Hz, 2H, PhCH_2O), 4.85 (d, *J* = 11.1 Hz, 2H, PhCH_2O), 4.83 (d, *J* = 12.0 Hz, 2H, PhCH_2O), 4.72 (d, *J* = 12.0 Hz, 2H, PhCH_2O), 4.27 (dt, *J* = 10.0, 4.8 Hz, 2H, H5 & H5′), 4.14 (t, *J* = 9.4 Hz, 2H, H3 & H3′), 4.12–4.10 (m, 2H, H4 & H4′), 3.69–3.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.2, 137.7, 129.1, 128.7, 128.5, 128.3, 128.2, 127.9, 127.7, 126.3, 101.4, 95.1, 82.5, 78.9, 78.8, 75.5, 73.98, 69.1, 63.1; HR-ESI-MS (*m/z*): calcd for $C_{54}H_{54}O_{11}$ $[M + H]^+$ 879.3744 found, 879.3719.

2,3,4,2′,3′-Penta-*O*-benzyl-4′,6′-*O*-benzylidene-*α,α*-D-trehalose (7). To a solution of 2,3,2′,3′-tetra-*O*-benzyl-4,6;4′,6′-di-*O*-benzylidene-*α,α*-D-trehalose (**6**) (250 mg, 0.28 mmol) in toluene (2.5 mL), was added 1.5 M DIBAL (supplied as 25wt% solution of DIBAL in toluene; 0.95 mL, 1.42 mmol) in a drop wise manner at -18 ^oC (ice-salt bath) under a N_2 atmosphere and the ice bath was immediately removed. The reaction mixture was stirred for 1.5 h and then quenched by careful addition of methanol (0.5 mL) at 0 ^oC followed by addition of aq. KOH (0.5 mL, 10%) at the same temperature and then brought to rt. The crude product was extracted in CH_2Cl_2 (10 mL × 6), dried on anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography (1:2 ethyl acetate: pet ether) afforded 2,3,4,2′,3′-penta-*O*-benzyl-4′,6′-*O*-benzylidene -*α,α*-D-trehalose **7** as colorless sticky solid (223 mg, 89%). $[\alpha]^{20}_D$ +67.6 (*c* 1, $CHCl_3$); IR *v* 3483, 3065, 2932, 2857, 1662, 1607, 1454, 1369, 1259, 1216, 1155, 1089,

755, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.22 (m, 30H), 5.55 (s, 1H), 5.12 (d, *J* = 3.5 Hz, 2H, H-1 & H-1′), 4.99 (d, *J* = 11.2 Hz, 1H, Ph*CH*$_2$O), 4.96 (d, *J* = 11.6 Hz, 1H, Ph*CH*$_2$O), 4.89–4.63 (m, 8H, Ph*CH*$_2$O), 4.26 (dt, *J* = 10.0, 4.8 Hz, 1H, H5), 4.16–4.05 (m, 4H, H3, H3′, H5′, & H6a), 3.69–3.53 (m, 7H, H2, H2′, H4, H4′, H6a′, H6b, H6b′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.4, 138.2, 138.1, 137.7, 129.1, 128.7, 128.6, 128.55, 128.5, 128.4, 128.2, 128.1, 128.09, 128.02, 127.9, 127.85, 127.82, 127.8, 126.3, 101.4, 95.0, 94.3, 82.5, 81.7, 79.6, 78.9, 78.8, 77.5, 75.8, 75.5, 75.1, 73.8, 73.4, 71.4, 69.2, 63.1, 61.7. HR-ESI-MS (*m/z*): calcd for $C_{54}H_{56}O_{11}$ $[M + H]^+$ 881.3901 found, 881.3903.

6-*O*-Acetyl-2,3,2′,3′-penta-*O*-benzyl-4′,6′-*O*-benzylidene-*α,α*-D-trehalose (7a). To a solution of **7** (90 mg, 102.2 µmol) in CH_2Cl_2 (2 mL), was added Et_3N (128 µL, 919.8 µmol), acetic anhydride (39 µL, 408.8 µmol), and catalytic DMAP (1 mg) and stirred for 8 h. Solvents were evaporated *in vacuo* and residue was purified by column chromatography (2:8 ethyl acetate: pet ether) to obtain compound **7a** (93 mg, 98%). $[\alpha]^{20}_D$ +72.0 (*c* 1, $CHCl_3$); IR *v* 2929, 2857, 1742, 1695, 1604, 1607, 1547, 1454, 1368, 1090, 755, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.30 (m, 30H), 5.60 (s, 1H, Ph*CH*), 5.20 (d, *J* = 3.8 Hz, 1H, H-1), 5.19 (d, *J* = 3.9 Hz, 1H, H-1′), 5.07 (d, *J* = 10.8 Hz, 1H, Ph*CH*$_2$O), 5.02 (d, *J* = 11.1 Hz, 1H, Ph*CH*$_2$O), 4.93–4.85 (m, 4H, Ph*CH*$_2$O), 4.78 (s, 2H, Ph*CH*$_2$O), 4.74 (d, *J* = 11.9 Hz, 1H, Ph*CH*$_2$O), 4.64 (d, *J* = 10.7 Hz, 1H, Ph*CH*$_2$O), 4.31–4.29 (m, 2H, H-5′, H-6a), 4.20–4.07 (m, 5H, H-3, H-3′, H-5, H-6b, H-6a′), 3.74–3.56 (m, 5H, H-2, H-2′, H-4, H-4′, H-6b′), 2.03 (s, 3H, CO*CH*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.9, 138.7, 138.1, 138.0, 137.6, 129.0, 128.7, 128.6, 128.5, 128.3, 128.26, 128.1, 128.05, 127.9, 127.8, 127.7, 126.2, 101.3, 95.2, 94.3, 82.5, 81.8, 79.5, 78.8, 77.3, 75.8, 75.4, 75.2, 73.8, 73.3, 69.19, 69.13, 63.11, 62.9, 20.98; HR-ESI-MS (*m/z*): calcd for $C_{56}H_{58}O_{12}$ $[M + H]^+$ 923.4007 found, 923.4035.

2,3,6,2′,3′-Penta-*O*-benzyl-4′,6′-*O*-benzylidene-*α,α*-D-trehalose (8). A solution of DIBAL in CH_2Cl_2 (1 M solution; 1.14 mL, 1.14 mmol) was added to 2,3,2′,3′-tetra-*O*-benzyl-4,6;4′,6′-di-*O*-benzylidene-*α,α*-D-trehalose **6** (250 mg, 0.28 mmol) in a drop wise manner at 0 °C (ice bath) under a N_2 atmosphere and stirred the reaction at the same temperature for 1.5 h. Reaction mixture was diluted with 5 mL CH_2Cl_2 and quenched by the careful addition of methanol (0.5 mL) at 0 °C followed by addition of aq. KOH (0.5

mL, 10%) at the same temperature and warmed to rt. The crude product was extracted in CH_2Cl_2 (15 mL × 5), dried on anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography (3:17 ethyl acetate: pet ether) afforded 2,3,6,2′,3′-penta-*O*-benzyl-4′,6′-benzylidene-*α,α*-D-trehalose **8** as a white solid (150 mg, 60%). $[\alpha]^{20}_D$ +99.5 (*c* 0.5, dioxane) [lit[19] $[\alpha]^{20}_D$ +95.6 (*c* 1, dioxane)]; mp 118-120 °C [lit[19] 122 °C]; IR *v* 3448, 3063, 3030, 2926, 2858, 1604, 1544, 1496, 1453, 1371, 1091, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.22 (m, 30H), 5.55 (s, 1H, PhC*H*), 5.18 (d, *J* = 3.4 Hz, 1H, H-1), 5.17 (d, *J* = 3.6 Hz, 1H, H-1′), 5.00 (d, *J* = 11.3 Hz, 1H, PhCH_2O), 4.96 (d, *J* = 11.2 Hz, 1H, PhCH_2O), 4.85 (d, *J* = 11.2 Hz, 1H, PhCH_2O), 4.79 (d, *J* = 11.6 Hz, 1H, PhCH_2O), 4.74–4.68 (m, 4H, PhCH_2O), 4.52 (d, *J* = 12.1 Hz, 1H, PhCH_2O), 4.45 (d, *J* = 12.1 Hz, 1H, PhCH_2O), 4.26 (dt, *J* = 10.0, 4.8 Hz, 1H, H-5′), 4.15–4.09 (m, 3H, H-3′, H-5, H6a′), 3.88 (t, *J* = 9.2 Hz, 1H, H-3), 3.70–3.57 (m, 5H, H-2, H2′, H-4, H-4′, H6b′), 3.53–3.45 (m, 2H, H-6a, H-6b), 2.32 (bs, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.92, 138.91, 138.2, 138.1, 138.0, 137.7, 129.0, 128.68, 128.66, 128.5, 128.47, 128.3, 128.1, 128.09, 127.9, 127.89, 127.84, 127.78, 127.73, 126.3, 101.4, 94.98, 94.4, 82.5, 81.2, 79.2, 78.8, 78.7, 75.45, 75.41, 73.7, 73.5, 73.1, 70.8, 69.3, 69.2, 63.1; HR-ESI-MS (*m/z*): calcd for $C_{54}H_{56}O_{11}$ $[M + H]^+$ 881.3901 found, 881.3928.

4-*O*-Acetyl-2,3,2′3′-penta-*O*-benzyl-4′,6′-*O*-benzylidene-*α,α*-D-trehalose (8a). To a solution of **8** (130 mg, 147.6 µmol) in CH_2Cl_2 (2 mL), was added Et_3N (310 µL, 221.33 µmol), acetic anhydride (50 µL, 506.1 µmol), and DMAP (2 mg, 15 µmol) and stirred for 12 h at rt. Solvents were evaporated *in vacuo* and column chromatography (3:17 ethyl acetate: pet ether) of the residue afforded compound **8a** as a sticky solid (119 mg, 87%). $[\alpha]^{20}_D$ +78.24 (*c* 1, $CHCl_3$); IR *v* 3021, 2923, 2857, 1743, 1662, 1604, 1218, 1109, 757, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.21 (m, 30H), 5.57 (s, 1H, PhC*H*), 5.20 (d, *J* = 3.7 Hz, 1H, H-1′), 5.16 (d, *J* = 3.5 Hz, 1H, H-1), 5.09 (t, *J* = 9.7 Hz, 1H, H-4), 4.99 (d, *J* = 11.2 Hz, 1H, PhCH_2O), 4.89 (d, *J* = 11.2 Hz, 1H, PhCH_2O), 4.86 (d, *J* = 11.6 Hz, 1H, PhCH_2O), 4.82–4.65 (m, 5H, PhCH_2O), 4.45 (d, *J* = 11.9 Hz, 1H, PhCH_2O), 4.42 (d, *J* = 11.9 Hz, 1H, PhCH_2O), 4.26 (dt, *J* = 9.9, 4.8 Hz, 1H, H-5′), 4.20–4.13 (m, 3H, H-3′, H-5, H-6a′), 3.97 (t, *J* = 9.7 Hz, 1H, H-3), 3.71–3.60 (m, 4H, H-2, H-2′, H-4′, H6b′), 3.29 (dd, *J* = 10.7, 2.5 Hz, 1H, H-6a), 3.20 (dd, *J* = 10.7, 4.5 Hz, 1H, H-6b), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 138.9, 138.7, 138.3, 137.9, 137.8, 137.7, 129.1,

128.7, 128.5, 128.46, 128.42, 128.36, 128.1, 127.99, 127.98, 127.93, 127.75, 127.73, 126.3, 101.4, 94.6, 94.0, 82.5, 79.2, 79.18, 78.8, 78.7, 77.5, 75.3, 73.8, 73.5, 73.49, 70.4, 69.4, 69.2, 68.5, 63.1, 21.0; HR-ESI-MS (*m/z*): calcd for $C_{56}H_{58}O_{12}$ $[M + Na]^+$ 945.3826 found, 945.3833.

2,3,4,2′,3′,4′-Hexa-*O*-benzyl-*α,α*-D-trehalose (9). $[\alpha]^{20}_D$ +93.4 (*c* 1, $CHCl_3$) [lit[34] $[\alpha]^{24}_D$ +99 (*c* 1, $CHCl_3$)]; IR *v* 3468, 3031, 2928, 2857, 1607, 1585, 1454, 1361, 1211, 1094, 1071, 996, 753, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 30H), 5.13 (d, *J* = 3.6 Hz, 2H), 5.00 (d, *J* = 10.9 Hz, 2H), 4.88 (d, *J* = 10.9 Hz, 2H), 4.87 (d, *J* = 10.9 Hz, 2H), 4.73–4.63 (m, 6H), 4.09–4.04 (m, 4H), 3.59–3.57 (m, 6H), 3.53 (dd, *J* = 9.9, 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.4 138.2, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 127.7, 94.2, 81.8, 79.6, 75.8, 75.2, 73.2, 71.5, 61.7. HR-ESI-MS (*m/z*): calcd for $C_{54}H_{58}O_{11}$ $[M + Na]^+$ 905.3871 found, 905.3884.

2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-4,6;4′,6′-di-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose (10). Trehalose dihydrate (2 g, 5.29 mmol) was refluxed with ethanol (20 mL) for 8 h and then the solvents were evaporated on rotary evaporator and the white solid was dried under high vacuum to remove the traces of ethanol-H_2O to obtain anhydrous trehalose. To a solution of anhydrous trehalose in DMF (14 mL), was added *p*-anisaldehyde dimethyl acetal (3.61 mL, 21.15 mmol) and CSA (246 mg, 1.06 mmol) in one portion (pH~1). The reaction flask was kept on rotary evaporator at 140 mbar pressure and 60 °C for 5 h. Reaction was quenched by addition of Et_3N (2 mL, pH~7). Solvents were removed under reduced pressure to obtain crude product which on purification by column chromatography (8:2 ethyl acetate: pet ether) furnished 4,6;4′,6′-di-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose as a white solid (2.93 gm, 96%). $[\alpha]^{20}_D$ +91.4 (*c* 0.33, CH_3OH); mp 239-242 °C; IR (KBr) *v* 3470, 2939, 2839, 1615, 1588, 1518, 1250, 1077, 983, 829 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.42–7.39 (m, 4H), 6.90–6.86 (m, 4H), 5.51 (s, 2H, Ph*CH*), 5.11 (d, *J* = 3.9 Hz, 2H, H-1, H-1′), 4.19 (dd, *J* = 9.9, 4.9 Hz, 2H), 4.13–4.07 (m, 2H), 4.01 (t, *J* = 9.4 Hz, 2H), 3.78 (s, 6H), 3.70 (t, *J* = 9.9 Hz, 2H), 3.61 (dd, *J* = 9.4, 3.9 Hz, 2H), 3.46 (t, *J* = 9.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 131.6, 128.9, 114.4, 103.1, 96.5, 83.1, 73.8, 71.6, 69.98, 64.3, 55.8; HR-ESI-MS (*m/z*): calcd for $C_{28}H_{34}O_{13}$ $[M + H]^+$ 579.2078 found, 579.2083.

To a solution of 4,6;4′,6′-di-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose (1.52 g, 2.63 mmol) in anhydrous DMF (11 mL), was added NaH (60% in oil; 840 mg, 21.02 mmol) at rt and stirred for 20 min and cooled in ice bath. PMBCl (2.83 mL, 21.02 mmol), and TBAI (0.19 gm, 0.53 mmol) were added sequentially to the reaction and the reaction mixture was warmed to rt. The reaction mixture was then heated to 100 °C and refluxed overnight. After complete conversion, reaction mixture was cooled in ice bath diluted with CH_2Cl_2 (150 mL) and quenched by addition of saturated solution of NH_4Cl (5 mL) at 0 °C. Organic layer was washed with brine (15 mL × 2) followed by water (15 mL × 2), dried on anhydrous Na_2SO_4, concentrated on rotary evaporator and the thick brown syrup was purified by column chromatography (4:6 ethyl acetate: pet ether) to obtain compound **10** (2.7 gm, 97%). $[\alpha]^{20}_D$ +52.64 (*c* 1, $CHCl_3$); IR *v* 3035, 2961, 2847, 1623, 1601, 1454, 1259, 1216, 1177, 831, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 4H), 7.33–7.27 (m, 8H), 6.95–6.82 (m, 12H), 5.52 (s, 2H, Ph*CH*), 5.08 (d, *J* = 3.7 Hz, 2H, H-1, H-1′), 4.86 (d, *J* = 10.7 Hz, 2H), 4.77 (d, *J* = 10.4 Hz, 2H), 4.74 (d, *J* = 11.2 Hz, 2H), 4.65 (d, *J* = 11.2 Hz, 2H), 4.25 (td, *J* = 10.0, 4.9 Hz, 2H), 4.15 (dd, *J* = 10.0, 4.9 Hz, 2H), 4.10 (t, *J* = 9.2 Hz, 2H), 3.83 (s, 6H), 3.78 (s, 6H), 3.74 (s, 6H), 3.69–3.56 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.4, 159.3, 131.2, 130.4, 130.3, 129.8, 129.6, 127.6, 114.0, 113.9, 113.7, 101.4, 94.7, 82.5, 78.6, 77.5, 75.2, 73.6, 69.2, 63.1, 55.5, 55.4, 55.35; HR-ESI-MS (*m/z*): calcd for $C_{60}H_{66}O_{17}$ $[M + Na]^+$ 1081.4198 found, 1081.4244.

2,3,4,2′,3′-Penta-*O*-(*p*-methoxybenzyl)-4′,6′-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose (11). To a solution of 2,3,2′,3′-tetra-*O*-(*p*-methoxybenzyl)-4,6;4′,6′-di-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose **10** (549 mg, 0.52 mmol) in toluene (5 mL), was added a solution of 1.5 M DIBAL (supplied as 25wt% solution of DIBAL in toluene; 1.04 mL, 1.56 mmol) in a drop wise manner at -18 °C (ice-salt bath) under a N_2 atmosphere. The reaction mixture was stirred for 15 min and quenched by careful addition of methanol (0.8 mL), followed by addition of aq. KOH (10%, 0.8 mL) at the same temperature then brought to rt and stirred for 10 min. Product was extracted in CH_2Cl_2 (20 mL × 6), dried on anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography (1:1 ethyl acetate: pet ether) afforded 2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl-4′,6′-(*p*-methoxybenzylidene)-*α,α*-D-trehalose **11** as a white

solid (456 mg, 83%). $[\alpha]^{20}_{D}$ +53.5 (*c* 1, $CHCl_3$); mp 109-111 °C; IR *v* 3432, 2932, 1613, 1586, 1514, 1250, 1082, 823, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.02 (m, 12H), 6.93–6.78 (m, 12H), 5.51 (s, 1H, Ph*CH*), 5.07 (d, *J* = 3.6 Hz, 1H, H-1), 5.04 (d, *J* = 3.6 Hz, 1H, H-1′), 4.90 (d, *J* = 10.4 Hz, 1H, PhCH_2O), 4.81–4.57 (m, 9H, PhCH_2O), 4.22 (dt, *J* = 9.9, 4.8 Hz, 1H, H-5′), 4.13 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6a′), 4.09–4.00 (m, 3H, H-3, H-3′, H-5), 3.82 (s, 3H, OMe), 3.80 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.77 (s, 3H, OMe), 3.76 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.77–3.56 (m, 7H, H-2, H-2′, H-4, H-4′, H6b′, H-6a, H-6b) 1.52 (bt, *J* = 7.3 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 159.4, 159.3, 159.28, 159.24, 131.16, 131.12, 130.6, 130.4, 130.24, 130.22, 129.78, 129.73, 129.6, 129.4, 127.9, 127.53, 113.99, 113.89, 113.82, 113.81, 113.6, 101.3, 94.8, 93.9, 82.4, 81.4, 79.4, 78.5, 78.4, 77.2, 75.4, 75.1, 74.7, 73.2, 73.0, 71.4, 69.3, 69.1, 63.0, 61.8, 55.39, 55.37, 55.34, 55.33, 55.28; HR-ESI-MS (*m/z*): calcd for $C_{60}H_{68}O_{17}$ $[M + Na]^+$ 1083.4349 found, 1083.4344.

2,3,4,2′,3′,4′-Hexa-*O*-(*p*-methoxybenzyl)-*α,α*-D-trehalose (12). $[\alpha]^{20}_{D}$ +73.4 (*c* 1, $CHCl_3$); IR *v* 3435, 2956, 2925, 2851, 1681, 1612, 1513, 1463, 1249, 1172, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.28 (m, 4H), 7.24–7.20 (m, 8H), 6.89–6.85 (m, 8H), 6.81–6.79 (m, 4H), 5.07 (d, *J* = 3.6 Hz, 2H, H-1, H-1′), 4.90 (d, *J* = 10.5 Hz, 2H, PhCH_2O), 4.81 (d, *J* = 10.6 Hz, 2H, PhCH_2O), 4.80 (d, *J* = 10.5 Hz, 2H, PhCH_2O), 4.63–4.56 (m, 6H, PhCH_2O), 4.10–3.98 (m, 4H, H-5, H-5′, H-3, H3′), 3.79 (s, 6H, OMe), 3.77 (s, 6H, OMe), 3.75 (s, 6H, OMe), 3.73–3.57 (m, 4H, 6ab, 6ab′), 3.53 (t, *J* = 9.6 Hz, 2H, H-4, H-4′), 3.47 (dd, *J* = 9.6, 3.6 Hz, 2H, H-2, H-2′), 1.83 (bs, 2H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.3, 159.2, 131.2, 130.6, 130.3, 129.8, 129.7, 129.3, 114.0, 113.91, 113.90, 94.0, 81.4, 79.2, 77.5, 75.4, 74.8, 72.7, 71.5, 61.8, 55.39, 55.37, 55.35; HR-ESI-MS (*m/z*): calcd for $C_{60}H_{70}O_{17}$ $[M + Na]^+$ 1085.4511 found, 1085.4559.

2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-4,6;4′,6′-di-*O*-(2-naphthyl)methylene-*α,α*-D-trehalose (14). To a stirred solution of 2,3,4,6,2′,3′,4′,6′-octa-*O*-trimethylsilyl-*α,α*-D-trehalose **13** (2 g, 2.17 mmol) and freshly activated 3 Å MS (2 g) in CH_2Cl_2 (20 mL), 2-naphthaldehyde (0.75 g, 4.78 mmol) was added and reaction mixture was stirred for 45 min at rt. Reaction mixture was cooled to 0 °C and TMSOTf (119 µL, 0.65 mmol) was added cautiously in a dropwise manner. After 3 h, TBAF (8.7 mL, 8.698 mmol) was added to the reaction mixture stirred overnight at rt. The reaction mixture was filtered

through Celite and washed with CH_2Cl_2. The combined organic layer was concentrated *in vacuo* and purified by column chromatography (7:3 ethyl acetate: pet ether) to afford the 4,6;4′,6′-di-*O*-(naphthyl)methylene trehalose acetal as a white solid (1.29 g, 95%). $[\alpha]^{20}_D$ +35.36 (*c* 1, CH_3OH); mp 193-196 °C; IR (KBr) *v* 3434, 2929, 2857, 1618, 1472, 1175, 1075, 975 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 8.00 (s, 2H), 7.82–7.58 (m, 6H), 7.64–7.61 (m, 2H), 7.51–7.47 (m, 4H), 5.74 (s, 2H), 5.17 (d, *J* = 3.9 Hz, 2H), 4.63 (bs, 1H), 4.29 (dd, *J* = 9.8, 4.9 Hz, 2H), 4.19 (dt, *J* = 9.8, 4.9 Hz, 2H), 4.09 (t, *J* = 9.4 Hz, 2H), 3.80 (t, *J* = 10.1 Hz, 2H), 3.67 (dd, *J* = 9.4, 3.9 Hz, 2H), 3.56 (t, *J* = 9.4 Hz, 2H), ^{13}C NMR (100 MHz, CD_3OD) δ 136.7, 135.2, 134.4, 129.4, 128.8, 128.79, 127.6, 127.3, 126.98, 125.3, 103.2, 96.6, 83.2, 73.9, 71.7, 70.1, 64.4; HR-ESI-MS (*m/z*): calcd for $C_{34}H_{34}O_{11}$ $[M + Na]^+$ 641.1993 found, 641.1997.

To a solution of di-*O*-(naphthyl)methylene trehalose acetal (0.82 g, 1.33 mmol) in anhydrous DMF (7 mL), was added NaH (0.53 g, 13.26 mmol) at rt and stirred for 20 min. Then the reaction was cooled to 0 °C and PMBCl (1.43 mL, 10.60 mmol), TBAI (98 mg, 0.27 mmol) were added sequentially. The reaction mixture was heated to 100 °C and left for stirring overnight. Reaction was cooled to rt and quenched by addition of saturated solution of NH_4Cl (10 mL) at 0 °C. Product was extracted in CH_2Cl_2 (100 mL) and washed with brine (10 × 2), water (10 × 2), dried on anhydrous Na_2SO_4, concentrated on rotary evaporator and the thick brown syrup was purified by column chromatography (1:3 ethyl acetate: pet ether) to obtain compound **14** as a white foam (1.46 g, quantitative). $[\alpha]^{20}_D$ +4.04 (*c* 1, $CHCl_3$); mp 59-61 °C; IR *v* 3011, 2934, 2861, 1612, 1585, 1514, 1249, 1084, 757, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.91–7.83 (m, 6H), 7.63–7.61 (m, 2H), 7.52–7.33 (m, 4H), 7.33–7.28 (m, 8H), 6.84–6.79 (m, 8H), 5.71 (s, 2H), 5.13 (d, *J* = 3.7 Hz, 2H), 4.88 (d, *J* = 10.1 Hz, 2H), 4.79 (d, *J* = 10.8 Hz, 2H), 4.77 (d, *J* = 11.4 Hz, 2H), 4.67 (d, *J* = 11.4 Hz, 2H), 4.31 (dt, *J* = 9.9, 4.8 Hz, 2H), 4.22 (dd, *J* = 9.9, 4.8 Hz, 2H), 4.15 (t, *J* = 9.3 Hz, 2H), 3.82–3.74 (m, 2H), 3.73 (s, 6H), 3.68 (t, *J* = 9.4 Hz, 2H), 3.61 (s, 6H), 3.64–3.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.3, 135.2, 133.7, 133.1, 131.2, 130.3, 129.8, 129.6, 128.6, 128.1, 127.9, 126.6, 126.3, 125.7, 124.1, 114.1, 113.9, 101.5, 94.7, 82.6, 78.7, 78.6, 75.3, 73.7, 69.3, 63.1, 55.4, 55.2; HR-ESI-MS (*m/z*): calcd for $C_{66}H_{66}O_{15}$ $[M + K]^+$ 1137.4039 found, 1137.4010.

2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-4-*O*-(2-naphthyl)methyl-4′,6′-*O*-(2-naphthyl) methylene-*α,α*-D-trehalose (15). To a solution of **14** (150 mg, 0.14 mmol) in toluene (1.5 mL), was added a solution of 1.5 M DIBAL (supplied as 25wt% solution of DIBAL in toluene; 0.45 mL, 0.68 mmol) in a drop wise manner at -18 °C (ice-salt bath) under a N_2 atmosphere and the ice bath was removed. Reaction was completed after 1 h. Reaction flask was cooled to 0 °C and quenched by careful addition of methanol (0.5 mL), followed by addition of aq. KOH (0.5 mL, 10%) at the same temperature. Then the reaction flask warmed to rt and stirred for 10 min. The product was extracted in CH_2Cl_2, dried on anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification using silica gel column chromatography (4:6 ethyl acetate: pet ether) afforded 2,3,2′,3′-tetra-*O*-(*p*-methoxybenzyl-4-(2-naphthyl)methyl-4′,6′-(2-naphthyl)methylene-*α,α*-D-trehalose **15** as a white foam (122 mg, 81%). $[\alpha]^{20}_{D}$ +27.48 (*c* 1, $CHCl_3$); mp 49-52 °C; IR *v* 3480, 2930, 1612, 1514, 1464, 1249, 1084, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (bs, 1H), 7.90–7.80 (m, 6H), 7.74 (s, 1H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.50–7.41 (m, 5H), 7.34–7.22 (m, 8H), 6.85–6.77 (m, 8H), 5.71 (s, 1H), 5.13 (d, *J* = 3.6 Hz, 1H, H-1), 5.10 (d, *J* = 3.6 Hz, 1H, H-1′), 5.04 (d, *J* = 11.2 Hz, 1H, Ph*CH*$_2$O), 4.91 (m, 2H, Ph*CH*$_2$O), 4.83–4.79 (m, 3H, Ph*CH*$_2$O), 4.74–4.61 (m, 4H, Ph*CH*$_2$O), 4.28 (dt, *J* = 9.9, 5.1 Hz, 1H, H-5′), 4.21 (dd, *J* = 10.2, 5.1 Hz, 1H, H-6a′), 4.17–4.07 (m, 3H, H-3, H-3′, H-5), 3.73–3.70 (m, 1H, H-6b′), 3.70 (s, 6H), 3.68–3.66 (m, 3H, H-4′, H-6a, H-6b), 3.65 (s, 3H), 3.62 (s, 3H), 3.61–3.54 (m, 3H, H-4, H-2, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.37, 159.33, 159.28, 159.26, 135.9, 135.1, 133.7, 133.4, 133.1, 133.06, 131.1, 130.3, 130.2, 129.7, 129.5, 129.4, 128.5, 128.4, 128.1, 127.8, 126.8, 126.5, 126.3, 126.27, 126.1, 125.6, 124.0, 114.0, 113.9, 113.88, 113.86, 101.5, 94.7, 93.8, 82.6, 81.4, 79.5, 78.6, 78.5, 77.6, 75.4, 75.2, 73.4, 73.2, 71.4, 69.3, 63.1, 61.8, 55.3, 55.25, 55.21; HR-ESI-MS (*m/z*): calcd for $C_{66}H_{68}O_{15}$ $[M + H]^+$ 1101.4636 found, 1101.4600.

6-*O*-Acetyl-2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-4-*O*-(2-naphthyl)methyl-4′,6′-*O*-(2-naphthyl)methylene-*α,α*-D-trehalose (15a). To a solution of **15** (75 mg, 68.1 µmol) in CH_2Cl_2 (2 mL), was added Et_3N (85 µL, 612.9 µmol), acetic anhydride (20 µL, 204 µmol), and DMAP (1 mg) and stirred for 12 h at rt. Solvents were evaporated *in vacuo* and column chromatography (3:7 ethyl acetate: pet ether) of the residue afforded compound **15a** as a sticky solid (75 mg, 96%). $[\alpha]^{20}_{D}$ +39.2 (*c* 1, $CHCl_3$); IR *v* 2927,

1740, 1612, 1514, 1249, 1085, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (bs, 1H), 7.89–7.82 (m, 6H), 7.71 (s, 1H), 7.63–7.61 (m, 1H), 7.52–7.42 (m, 5H), 7.40–7.22 (m, 8H), 6.85–6.80 (m, 8H), 5.71 (s, 1H), 5.14 (d, *J* = 3.5 Hz, 1H), 5.10 (d, *J* = 3.7 Hz, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.95 (d, *J* = 10.4 Hz, 1H), 4.89 (d, *J* = 10.4Hz, 1H), 4.82–4.79 (m, 2H), 4.75–4.70 (m, 2H), 4.67 (s, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.32–4.17 (m, 3H), 4.15–4.04 (m, 4H), 3.76–3.75 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 3.69–3.66 (m, 1H), 3.65 (s, 3H), 3.63–3.55 (m, 3H) 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 159.4, 159.3, 135.6, 135.1, 133.7, 133.4, 133.2, 133.1, 131.1, 131.0, 130.2, 130.16, 129.8, 129.7, 129.5, 129.4, 128.6, 128.5, 128.1, 127.8, 127.1, 126.6, 126.33, 126.30, 126.28, 126.18, 125.6, 124.0, 114.1, 114.0, 113.9, 101.5, 95.0, 93.9, 82.6, 81.6, 79.4, 78.6, 78.5, 76.9, 75.5, 75.2, 75.1, 73.5, 73.0, 69.3, 69.1, 63.2, 63.0, 55.4, 55.3, 55.28, 20.8; HR-ESI-MS (*m/z*): calcd for $C_{68}H_{70}O_{16}$ $[M + K]^+$ 1181.4295 found, 1181.4287.

2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-6-*O*-(2-naphthyl)methyl-4′,6′-*O*-(-2-naphthyl)methylene-*α,α*-D-trehalose (16). DIBAL (1 M solution of DIBAL in CH_2Cl_2; 0.62 mL, 0.62 mmol) was added to 2,3,2′,3′-tetra-*O*-(*p*-methoxybenzyl)-4,6;4′,6′-di-*O*-(2-naphthyl)methylene-*α,α*-D-trehalose **14** (150 mg, 0.14 mmol) in a drop wise manner at -30 °C. TLC showed maximum conversion in 2 h then the reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched by careful addition of methanol (0.5 mL), followed by addition of aq. KOH (0.5 mL, 10%) at the same temperature. Then the reaction flask warmed to rt and stirred for 10-15 min. The product was extracted in CH_2Cl_2, dried on anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification by silica gel column chromatography (1:3 ethyl acetate: pet ether) afforded 2,3,2′,3′-tetra-*O*-(*p*-methoxybenzyl)-6-*O*-(2-naphthyl)methyl-4′,6′-*O*-(2-naphthyl)methylene-*α,α*-D-trehalose **16** as a sticky solid (80 mg, 52%). $[\alpha]^{22}_D$ +29.44 (*c* 1, $CHCl_3$); IR *v* 3494, 2932, 1612, 1513, 1464, 1249, 1175, 1086, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.88–7.73 (m, 8H), 7.50–7.41 (m, 5H), 7.33–7.28 (m, 6H), 7.17–7.15 (m, 2H), 6.87–6.80 (m, 6H), 6.71 (d, *J* = 8.6 Hz, 2H), 5.70 (s, 1H, Ph*CH*), 5.20 (d, *J* = 3.3 Hz, 1H, H-1′), 5.16 (d, *J* = 3.5 Hz, 1H, H-1), 4.93–4.80 (m, 2H, PhCH_2O), 4.78 (d, *J* = 10.7 Hz, 1H, PhCH_2O), 4.71 (d, *J* = 10.9 Hz, 2H, PhCH_2O), 4.65–4.63 (m, 7H, PhCH_2O), 4.28 (dt, *J* = 9.5, 5.2 Hz, 1H, H-5′), 4.19 (dd, *J* = 10.2, 5.2 Hz, 1H, H6a′), 4.17–4.09 (m, 2H, H-3′, H-5), 3.87 (t, *J* = 9.3 Hz, 1H, H-3), 3.84 (s, 3H), 3.83 (m, 1H, H-6b′), 3.73 (s, 3H), 3.69 (m,

1H, H-4), 3.65 (s, 3H); 3.62 (s, 3H), 3.61–3.55 (m, 5H, H-2, H-2′, H-4′, H-6a, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.29, 159.26, 135.6, 135.2, 133.7, 133.4, 133.1, 133.07, 131.1, 131.0, 130.3, 130.1, 129.8, 129.7, 129.5, 129.4, 128.6, 128.3, 128.1, 128.0, 127.8, 126.6, 126.5, 126.3, 126.2, 125.99, 125.8, 125.6, 124.0, 114.1, 113.86, 113.81, 101.5, 94.8, 94.1, 82.5, 80.8, 79.1, 78.44, 78.41, 75.1, 75.0, 73.9, 73.1, 72.8, 70.9, 70.8, 69.5, 69.3, 63.1, 55.36, 55.34, 55.25, 55.23; HR-ESI-MS (*m/z*): calcd for $C_{66}H_{68}O_{15}$ $[M + H]^+$ 1101.4636 found, 1101.4663.

4-*O*-Acetyl-2,3,2′,3′-Tetra-*O*-(*p*-methoxybenzyl)-6-*O*-(2-naphthyl)methyl-4′,6′-*O*-(-2-naphthyl)methylene-*α,α*-D-trehalose (16a). To a solution of **16** (50 mg, 45.4 µmol) in CH_2Cl_2 (2 mL), was added Et_3N (57 µL, 408.6 µmol), acetic anhydride (13 µL, 136.2 µmol), and DMAP (2 mg) and stirred for 12 h at rt. Solvents were evaporated *in vacuo* and column chromatography (2:8 ethyl acetate: pet ether) of the residue afforded compound **16a** as a white foam (48 mg, 92%). $[\alpha]^{22}_D$ +50.16 (*c* 1, $CHCl_3$); mp 50-52 °C; IR *v* 3018, 2934, 1741, 1612, 1513, 1249, 1216, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.92–7.86 (m, 3H), 7.83–7.78 (m, 2H), 7.73 (s, 1H), 7.64 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.53–7.52 (m, 2H), 7.51–7.42 (m, 3H), 7.34–7.17 (m, 9H), 6.87–6.80 (m, 6H), 6.71–6.69 (m, 2H), 5.74 (s, 1H, Ph*CH*), 5.20 (d, *J* = 3.7 Hz, 1H, H-1′), 5.18 (d, *J* = 3.5 Hz, 1H, H-1), 5.12 (t, *J* = 9.6 Hz, 1H, H-4), 4.92 (d, *J* = 10.8 Hz, 1H, PhCH_2O), 4.83–4.79 (m, 2H, PhCH_2O), 4.72–4.57 (m, 7H, PhCH_2O), 4.34–4.21 (m, 3H, H-5′, H-6a′, H-5), 4.15 (t, *J* = 9.3 Hz, 1H, H-3'), 3.97 (t, *J* = 9.6 Hz, 1H, H-3), 3.82–3.79 (m, 1H, H-6b′), 3.77 (s, 3H), 3.75 (s, 3H), 3.66 (s, 3H), 3.64 (s, 3H), 3.60 (m, 3H, H-2, H-2′, H-4′), 3.42 (dd, *J* = 10.7, 4.7 Hz, 1H, H-6a), 3.35 (dd, *J* = 10.7, 2.6 Hz, 1H H-6b), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.4, 159.3, 159.2, 135.4, 135.1, 133.7, 133.3, 133.1, 133.0, 131.1, 130.9, 130.2, 130.1, 129.6, 129.58, 129.54, 129.3, 128.5, 128.2, 128.1, 128.0, 127.8, 127.76, 126.8, 126.5, 126.3, 126.1, 125.9, 125.6, 124.0, 114.0, 113.8, 113.7, 101.4, 94.4, 93.7, 82.5, 78.9, 78.7, 78.4, 78.3, 77.5, 75.0, 74.8, 73.8, 73.2, 73.0, 70.4, 69.4, 69.3, 68.8, 63.1, 55.33, 55.32, 55.2, 21.0; HR-ESI-MS (*m/z*): calcd for $C_{68}H_{70}O_{16}$ $[M + Na]^+$ 1165.4556 found, 1165.4600.

4-Azido-2,3,6,2′,3′-penta-*O*-(benzyl)-4′,6′-*O*-benzylidene-*α,α*-D-trehalose (17). To the solution of **8** (140 mg, 0.16 mmol) in pyridine (2.5 mL), DMAP (10 mg, 0.08 mmol), and mesyl chloride (43 µL, 0.56 mmol) were added sequentially and reaction mixture was

stirred at rt for 3.5 h. Reaction was cooled to rt and diluted with 50 mL of CH_2Cl_2 and washed with $NaHCO_3$ (10 × 2) followed by brine and water (10 × 1). Organic layer was concentrated on anhydrous rotary evaporator to obtain cream colored solid containing large amount of salt. The crude product was suspended in diethyl ether and the solid was filtered off. The filtrate was concentrated and dried under high vacuum for 2 h and used for next step without any purification.

To the solution mesylate in DMF (5 mL), was added NaN_3 (23 mg, 0.35 mmol) at rt and the reaction mixture was heated to 120 °C and stirred for 12 h. Since reaction was not complete, 20 mg (0.32 mmol) of excess NaN_3 and few drops of H_2O was added to it. After 36 h, reaction was diluted by addition of CH_2Cl_2 and organic layer was washed with water, brine, dried on anhydrous Na_2SO_4. Silica gel column chromatography (1:3 ethyl acetate: pet ether) of the residue furnished **17** as a colorless liquid (114 mg, 79% over 2 steps). $[\alpha]^{22}_D$ +54.0 (*c* 0.2, $CHCl_3$); IR *v* 3032, 2928, 2857, 2109, 1495, 1454, 1369, 1275, 1212, 1097, 751, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60–7.33 (m, 30H), 5.62 (s, 1H, Ph*CH*), 5.23 (d, *J* = 3.9 Hz, 1H, H-1), 5.22 (d, *J* = 4.0 Hz, 1H, H-1′), 5.04 (d, *J* = 11.2 Hz, 1H, PhCH_2O), 4.92–4.74 (m, 7H, PhCH_2O), 4.58–4.45 (m, 2H, PhCH_2O), 4.44–4.49 (m, 1H, H-5), 4.34 (dt, *J* = 9.9, 4.8 Hz, 1H, H-5′), 4.25–4.15 (m, 4H, H-3, H3′, H-4, H6a′), 4.00 (dd, *J* = 9.7, 3.9 Hz, 1H, H-2), 3.75–3.55 (m, 5H, H-2′, H-4′, H-6b′, H-6a, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 138.3, 138.2, 138.1, 137.8, 137.7, 129.0, 128.58, 128.54, 128.49, 128.41, 128.3, 127.9, 127.85, 127.81, 127.7, 127.67, 126.3, 101.3, 94.6, 94.5, 82.4, 78.7, 78.6, 77.8, 75.8, 75.3, 74.0, 73.7, 73.4, 72.9, 69.0, 68.98, 67.9, 62.9, 61.3. HR-ESI-MS (*m/z*): calcd for $C_{54}H_{55}N_3O_{10}$ $[M + H]^+$ 906.3966 found, 906.3967.

4-Acetamido-2,3,6-tri-*O*-acetyl-4-deoxy-α-D-galactopyranosyl 2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranoside (18): To the solution of compound **17** (20 mg, 22.1 μmol) and $Pd(OH)_2$ (10 mg) in MeOH: H_2O: EtOAc (1: 0.2: 0.5 mL) was added 0.1 N of HCl (0.1 mL). The reaction mixture was stirred for 12 h at rt under H_2 atmosphere. Then reaction mixture was filtered through Celite and washed with MeOH (2 mL × 6). Solvents were evaporated on rotary evaporator and the residue was dried under high vacuum. The crude product was dissolved in Et_3N (0.15 mL, 1.10 mmol) and Ac_2O (45 μL, 0.44 mmol), DMAP (1 mg) were added to it. Reaction was stirred overnight at rt.

Solvents were evaporated on rotary evaporator and the residue was chromatographed (8:2 ethyl acetate: pet ether) to furnish compound **18** as a white solid (12 mg, 80% over two steps). $[\alpha]^{22}_{D}$ +76.4 (*c* 0.1, $CHCl_3$) [lit[12] $[\alpha]^{20}_{D}$ +155 (*c* 0.63, $CHCl_3$)]; IR *v* 3362, 3021, 2926, 2853, 1749, 1675, 1371, 1218, 1039, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (d, *J* = 10.0 Hz, 1H), 5.48 (t, *J* = 10.0 Hz, 1H), 5.31–5.25 (m, 3H), 5.08–5.00 (m, 3H), 4.80 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.37–4.34 (m, 1H), 4.26–4.19 (m, 2H), 4.04–4.00 (m, 2H), 3.91 (dd, *J* = 12.0, 4.4 Hz, 1H) 2.12 (s, 3H), 2.11 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 6H), 2.03 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.7, 170.3, 170.1, 170.0, 169.7, 92.2, 91.98, 69.9, 69.8, 68.8, 68.5, 68.3, 67.6, 67.5, 62.4, 61.9, 48.3, 23.4, 20.9, 20.8, 20.78, 20.73. HR-ESI-MS (*m/z*): calcd for $C_{28}H_{39}NO_{18}$ $[M + H]^+$ 678.2245 found, 678.2260.

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(1→6)-2,3,4,2′,3′-penta-*O*-benzyl-4′,6′-*O*-benzylidene-*α*,*α*-D-trehalose (21). To the stirred solution of acceptor **7** (170 mg, 0.19 mmol), 3Å MS in CH_2Cl_2 (1.5 mL) at rt was added the solution of the 2,3,4,6-tetra-*O*-benzoyl glucosyl bromide **20** (202 mg, 0.29 mmol) in CH_2Cl_2 (2.5 mL) and the reaction mixture was stirred for 15 min at rt and then cooled to -50 °C. AgOTf (100 mg, 0.39 mmol) was added to it and reaction was allowed to stir for 1 h. Reaction was quenched by addition of Et_3N (0.5 mL) and the content was filtered through Celite washed with CH_2Cl_2. Organic layer was concentrated and purified by column chromatography (1:5 ethyl acetate: pet ether) to obtain compound **21** as a white solid (255 mg, 91%). $[\alpha]^{22}_{D}$ +46.36 (*c* 1, $CHCl_3$); mp 48-50 °C; IR *v* 3031, 2926, 2854, 1733, 1452, 1265, 1091, 1071, 757, 710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.12–8.10 (m, 1H), 7.99–7.97 (m, 2H), 7.91–7.81 (m, 4H), 7.50–6.99 (m, 43H), 5.90 (t, *J* = 9.6 Hz, 1H), 5.68 (t, *J* = 9.6 Hz, 1H), 5.59 (dd, *J* = 9.6, 7.6 Hz, 1H), 5.55 (s, 1H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.08 (d, *J* = 3.6 Hz, 1H), 4.92 (t, *J* = 11.2 Hz, 1H), 4.84 (t, *J* = 8.4 Hz, 1H), 4.75–4.68 (m, 3H), 4.65–4.60 (m, 4H), 4.54 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.38 (d, *J* = 11.2 Hz, 2H), 4.23–4.18 (m, 2H), 4.13–4.07 (m, 4H), 3.95–3.90 (m, 2H), 3.66 (t, *J* = 10.8 Hz, 1H), 3.60 (t, *J* = 9.3 Hz, 1H), 3.52 (dd, *J* = 9.2, 3.6 Hz, 1H), 3.49–3.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.0, 165.3, 165.1, 139.0, 138.97, 138.5, 138.3, 138.2, 137.7, 133.8, 133.6, 133.4, 133.3, 130.3, 129.99, 129.95, 129.93, 129.88, 129.7, 129.2, 129.0, 128.95, 128.88, 128.65, 128.59, 128.56, 128.5, 128.4, 128.39, 128.35, 128.1,

127.9, 127.85, 127.80, 127.7, 127.7, 127.6, 126.3, 101.3, 94.8, 94.2, 82.5, 81.7, 79.4, 79.2, 78.8, 77.5, 75.5, 75.4, 74.7, 73.7, 73.3, 72.9, 72.3, 71.9, 69.9, 69.8, 69.2, 63.5, 63.0; HR-ESI-MS (*m/z*): calcd for $C_{88}H_{82}O_{20}$ $[M + Na]^+$ 1481.5292 found, 1482.5275.

6-*O*-(2,3,4,6-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(1→6)-*α*,*α*-D-trehalose (21a). To the stirred solution of **21** (166 mg, 0.11 mmol), 3 Å MS in EtOH: EtOAc (3:2, 5 mL) at rt was added Pd/C (10%, 50 mg) and reaction was stirred for 25 h under H_2 atmosphere. Reaction was filtered through Celite and washed with EtOH. The organic layer was concentrated on rotary evaporator and purified by column chromatography (1:9 methanol: chloroform) to afford 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-gluco-pyranosyl)-(1→6)-*α*,*α*-D-trehalose (**21a**) as a white foam (98 mg, 94%). $[\alpha]^{22}_D$ +68.4 (*c* 1, CH_3OH); mp 48-50 °C; IR (KBr) *ν* 3425, 2931, 1731, 1602, 1267, 1110, 988, 709 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.96–7.91 (m, 4H), 7.84–7.82 (m, 2H), 7.73–7.71 (m, 2H), 7.57–7.42 (m, 3H), 7.42–7.25 (m, 7H), 7.19 (t, *J* = 7.9 Hz, 2H), 5.98 (t, *J* = 9.6 Hz, 1H), 5.68 (t, *J* = 9.6 Hz, 1H), 5.47 (dd, *J* = 9.7, 7.9 Hz, 1H), 5.12 (d, *J* = 7.9 Hz, 1H), 4.95 (d, *J* = 3.7 Hz, 1H), 4.89 (d, *J* = 3.7 Hz, 1H), 4.60 (dd, *J* = 12.4, 3.3 Hz, 1H), 4.50 (t, *J* = 12.4, 4.3 Hz, 1H), 4.35 (td, *J* = 9.8, 3.8 Hz, 1H), 4.17 (d, *J* = 9.6 Hz, 1H), 3.95–3.91 (m, 1H), 3.78–3.68 (m, 5H), 3.60 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.31–3.20 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 167.1, 167.0, 166.8, 134.77, 134.6, 134.5, 130.97, 130.90, 130.79, 130.77, 130.6, 130.5, 130.2, 130.1, 129.7, 129.6, 129.5, 102.6, 94.8, 94.7, 74.6, 74.56, 74.5, 73.8, 73.7, 73.1, 73.0, 72.5, 72.1, 71.9, 71.2, 70.4, 64.3, 62.8; HR-ESI-MS (*m/z*): calcd for $C_{46}H_{48}O_{20}$ $[M + Na]^+$ 943.2631 found, 943.2642.

6-*O*-(*β*-D-Glucopyranosyl)-(1→6)-*α*,*α*-D-trehalose (3). The solution of **21a** (75 mg, 0.08 mmol) in methanolic NaOMe (0.2 M, 3 mL) was stirred at rt for 75 min. After complete conversion, reaction mixture was neutralized by addition of acidic resin Amberlite IR 120 (120 mg). The resin was filtered off, washed with methanol. The organic layer was concentrated and residue was purified by silica gel column chromatography (6:3.5:0.5 ethyl acetate: methanol: water) to obtain **3** as a white foam (38 mg, 93%). $[\alpha]^{22}_D$ +64.8 (*c* 1, $CHCl_3$) [lit[39] $[\alpha]^{24}_D$ +90 (*c* 1, $CHCl_3$)]; IR (KBr) *ν* 3411, 2930, 1566, 1414, 1151, 1038, 990, 940, 654 cm^{-1}; ^1H NMR (400 MHz, D_2O) 5.14 (d, *J* = 3.7 Hz, 1H), 5.13 (d, *J* = 3.7 Hz, 1H), 4.45 (d, *J* = 7.9 Hz, 1H), 4.11 (d, *J* = 9.8 Hz, 1H), 3.92–3.76 (m, 7H), 3.75–3.64 (m, 3H), 3.63–3.58 (m, 2H), 3.52 (t, *J* = 9.5 Hz, 1H), 3.50-

3.39 (m, 3H), 3.26 (dd, *J* = 9.2, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 102.6, 93.2, 75.8, 75.6, 72.99, 72.4, 72.3, 72.1, 71.1, 70.9, 70.8, 69.6, 69.5, 69.2, 68.1, 60.6, 60.4; HR-ESI-MS (*m/z*): calcd for $C_{18}H_{32}O_{16}$ $[M + Na]^+$ 527.1583 found, 527.1595.

6-*O*-Oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl)-4′,6′-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose (22). To a solution of 2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl-4′,6′-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose **11** (0.69 g, 0.65 mmol) in CH_2Cl_2 (6 mL), was added a solution of oleic acid (308 µL, 0.98 mmol), DCC (0.27 g, 1.30 mmol), DMAP (16 mg, 0.13 mmol) in CH_2Cl_2 (4 mL) in a drop wise manner at 0 °C. The reaction mixture was stirred for 7 h at rt. Solvents were evaporated on rotary evaporator and the residue was purified by column chromatography (3:17 ethyl acetate: pet ether) to afford 6-*O*-oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl-4′,6′-*O*-(*p*-methoxybenzylidene)-*α,α*-D-trehalose **22** as a yellowish sticky liquid (715 mg, 83%). $[\alpha]^{22}_D$ +51.2 (*c* 1, $CHCl_3$); IR *v* 3021, 2873, 1735, 1602, 1355, 1135, 1047, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.33–7.21 (m, 10H), 6.94–6.82 (m, 12H), 5.52 (s, 1H, Ph*CH*), 5.39–5.30 (m, 2H), 5.12 (d, *J* = 3.6 Hz, 1H, H-1), 5.08 (d, *J* = 3.6 Hz, 1H, H-1′), 4.93 (d, *J* = 10.4 Hz, 1H, PhCH_2O), 4.86 (d, *J* = 10.8 Hz, 1H, PhCH_2O), 4.82 (d, *J* = 10.4 Hz, 1H, PhCH_2O), 4.80 (d, *J* = 10.0 Hz, 1H, PhCH_2O), 4.76 (d, *J* = 10.8 Hz, 1H, PhCH_2O), 4.71 (d, *J* = 11.6 Hz, 1H, PhCH_2O), 4.66 (s, 2H, PhCH_2O), 4.61 (d, *J* = 11.6 Hz, 1H, PhCH_2O), 4.46 (d, *J* = 10.4 Hz, 1H, PhCH_2O), 4.25–4.20 (m, 3H, H-5, H-6a, H6b), 4.14 (dd, *J* = 10.4, 4.8 Hz, 1H, H-6a′), 4.10–4.00 (m, 3H, H-3, H-3′, H-5′), 3.83 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.787 (s, 3H), 3.76 (s, 3H) 3.73–3.49 (m, 5H, H-2, H-2′, H-4, H-4′, H6b′), 2.28 (t, *J* = 7.6 Hz, 2H), 2.20–2.01 (m, 4H), 1.60–1.58 (m, 2H), 1.39–1.28 (m, 20H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 160.1, 159.5, 159.43, 159.40, 159.36, 159.31, 131.14, 131.1, 130.4, 130.24, 130.22, 130.2, 129.89, 129.85, 129.80, 129.5, 127.6, 114.1, 113.99, 113.9, 113.7, 101.3, 95.0, 94.0, 82.5, 81.5, 79.4, 78.6, 78.4, 77.5, 77.4, 75.5, 75.2, 74.9, 73.4, 73.0, 69.3, 69.2, 63.1, 62.8, 55.46, 55.42, 55.40, 55.35, 34.3, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 27.38, 27.34, 25.1, 22.9, 14.3. HR-ESI-MS (*m/z*): calcd for $C_{78}H_{100}O_{18}$ $[M + Na]^+$ 1347.6802 found, 1347.6808.

6-*O*-Oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl)-*α,α*-D-trehalose (22a). Solution of 6-*O*-oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl-4′,6′-*O*-(*p*-methoxybenzylidene) -*α,α*-

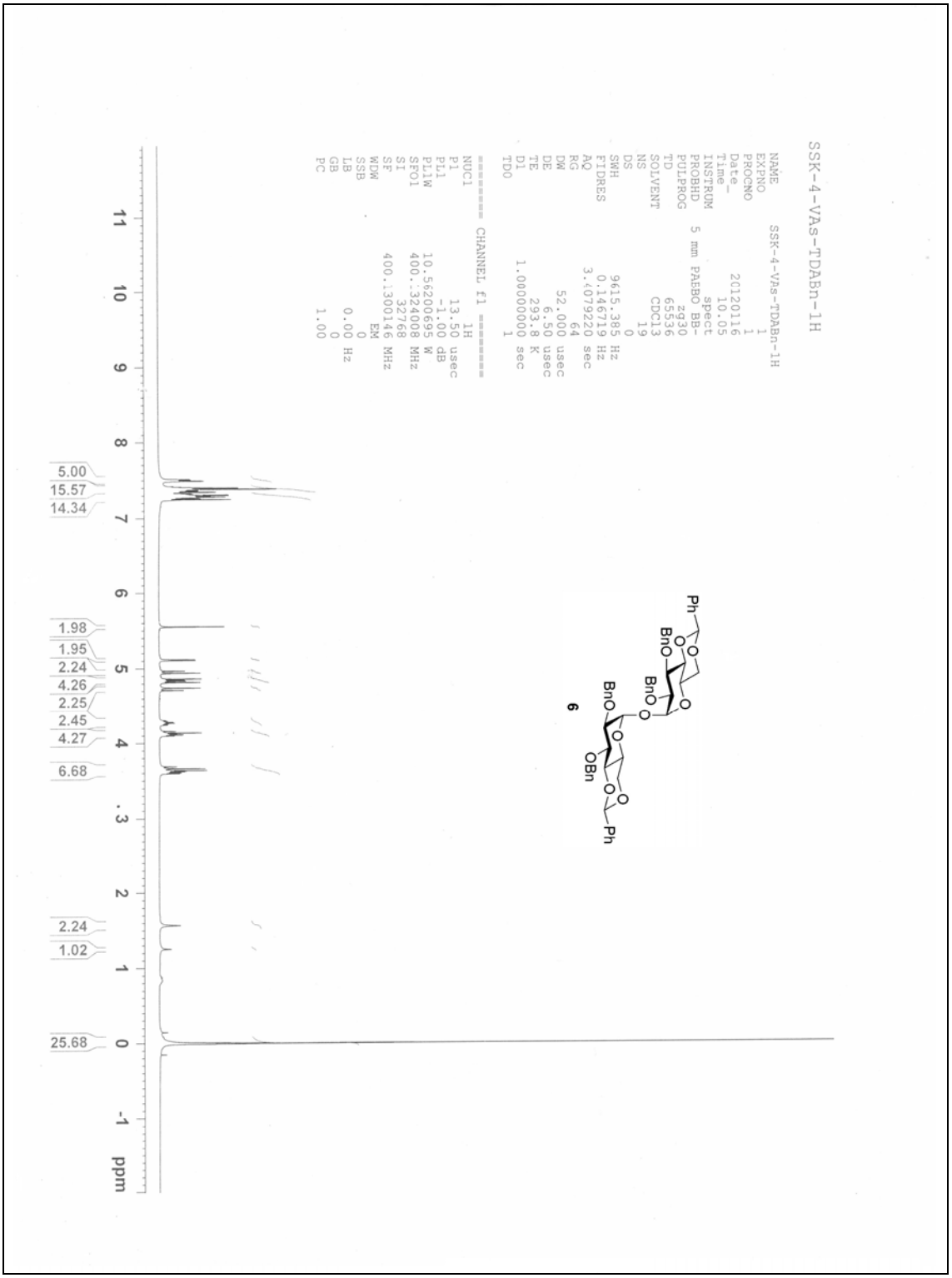
D-trehalose **22** (200 mg, 0.15 mmol) in 90% aqueous acetic acid (4 mL), was refluxed at 60 °C for 25 min. After cooling to rt, solvents were evaporated on rotary evaporator at 36-37 °C. Co-evaporation with toluene followed by purification by column chromatography (4:6 ethyl acetate: pet ether) afforded the desired 4′,6′-diol, 6-*O*-oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl)-*α,α*-D-trehalose **22a** as a yellowish sticky liquid (156 mg, 87%). $[\alpha]^{22}_{D}$ +59.44 (*c* 1, $CHCl_3$); IR *v* 3456, 3010, 2927, 2846, 1736, 1612, 1583, 1514, 1459, 1250, 820, 758 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 10H), 6.90–6.82 (m, 10H), 5.37–5.32 (m, 2H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.11 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 10.4 Hz, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 10.4 Hz, 1H), 4.81 (d, *J* = 10.4 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.64 (s, 2H), 4.61 (s, 2H), 4.47 (d, *J* = 10.4 Hz, 1H), 4.24–4.21 (m, 2H), 4.12–4.09 (m, 1H), 4.05–3.98 (m, 2H), 3.85–3.81 (m, 1H), 3.812 (s, 3H), 3.809 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.67 (d, *J* = 3.6 Hz, 2H), 3.56–3.47 (m, 4H), 2.28–2.24 (m, 2H), 2.01–1.97 (m, 4H),1.58–1.56 (m, 2H), 1.24–1.23 (m, 20H), 0.90–0.87 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 159.5, 159.44, 159.42, 159.35, 130.98, 130.90, 130.3, 130.16, 130.13, 129.95, 129.85, 129.78, 129.72, 129.4, 129.36, 114.1, 114.0, 113.99, 113.96, 94.1, 93.9, 81.5, 80.6, 79.2, 78.9, 77.5, 75.5, 74.9, 72.8, 72.5, 71.5, 70.5, 69.3, 62.8, 62.4, 55.4, 55.37, 55.35, 34.3, 32.0, 29.9, 29.8, 29.7, 29.5, 29.3, 29.27, 27.35, 27.31, 25.0, 22.8, 22.0, 14.3; HR-ESI-MS (*m/z*): calcd for $C_{70}H_{93}O_{17}$ $[M + H]^+$ 1206.6491 found, 1206.6465.

6-*O*-(13-Methylmyristoyl)-6′-oleoyl-*O*-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl)-*α,α*-D-trehalose (23). To a solution of 13-methylmyristic acid (25 mg, 0.11 mmol), DCC (30 mg, 0.14 mmol), DMAP (3 mg, 19.11 µmol) in CH_2Cl_2 (2 mL) was added a solution of 6-*O*-oleoyl-2,3,4,2′,3′-penta-*O*-(*p*-methoxybenzyl)-*α,α*-D-trehalose **22a** (115 mg, 95.31 µmol) in CH_2Cl_2 (2 mL), in a drop wise manner at 0 °C. The reaction mixture was stirred for 5 h at same temperature. Solvents were evaporated on rotary evaporator and pure 6-*O*-oleoyl-6′-*O*-(13-methylmyristoyl)-2,3,4,2′,3′-penta-*O*-(*p*-methoxy benzyl)-*α,α*-D-trehalose **23** was obtained by column chromatography (1:6 ethyl acetate: pet ether) as a colorless sticky liquid (90 mg, 65%). $[\alpha]^{22}_{D}$ +18.4 (*c* 1, $CHCl_3$); IR *v* 3535, 3020, 2928, 2854, 2253, 1735, 1612, 1514, 1251, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 10H), 6.82–6.74 (m, 10H), 5.27–5.24 (m, 2H), 5.05 (d, *J* = 3.1 Hz, 1H, H-1), 5.04 (d, *J* = 2.2 Hz, 1H, H-1′), 4.84 (d, *J* = 10.9 Hz, 1H, PhCH_2O), 4.81 (d, *J* = 11.5 Hz, 1H,

PhC*H*$_2$O), 4.75–4.72 (m, 2H, PhC*H*$_2$O), 4.65 (d, *J* = 10.8 Hz, 1H, PhC*H*$_2$O), 4.55 (d, *J* = 12.0 Hz, 4H, PhC*H*$_2$O), 4.38 (d, *J* = 10.8 Hz, 1H, PhC*H*$_2$O), 4.27 (dd, *J* = 12.3, 3.7 Hz, 1H, H-6a), 4.16–4.14 (m, 2H, H-5′, H-6b′), 4.05–3.99 (m, 2H, H-5, H-6a′), 3.90–3.87 (m, 2H, H-3′, H6b), 3.72–3.73 (m, 1H, H-3), 3.73 (s, 3H), 3.729 (s, 6H), 3.71 (s, 3H), 3.70 (s, 3H), 3.48–3.39 (m, 3H, H-2, H-2′, H-4′), 3.32 (bt, *J* = 9.1 Hz, 1H, H-4), 2.60 (bs, 1H, OH), 2.19 (q, *J* = 8.0 Hz, 4H), 1.93–1.90 (m, 4H), 1.50–1.40 (m, 6H),1.19–1.17 (m, 35H), 1.01–1.06 (m, 2H), 0.82–0.79 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.7, 159.6, 159.5, 159.4, 131.0, 130.9, 130.3, 130.2, 130.1, 130.0, 129.9, 129.7, 129.4, 129.3, 114.1, 114.06, 114.03, 94.4, 94.3, 81.5, 80.4, 79.3, 78.7, 75.5, 75.3, 75.0, 72.9, 72.6, 70.2, 70.0, 69.4, 62.9, 62.8, 55.44, 55.41, 39.2, 34.3, 34.25, 32.1, 30.1, 29.9, 29.88, 29.86, 29.82, 29.78, 29.69, 29.63, 29.48, 29.41, 29.35, 29.30, 28.1, 27.6, 27.4; HR-ESI-MS (*m/z*): calcd for $C_{85}H_{122}O_{18}$ $[M + Na]^+$ 1453.8523 found, 1453.8560.

6-*O*-(13-Methyltetradecanoyl)-6′-*O*-oleoyl-*α,α*-trehalose/ Maradolipid (2). Compound **23** (140 mg, 98 μmol) was dissolved in CH_2Cl_2 (2.4 ml) and H_2O (0.6 ml). DDQ (223 mg, 980 μmol) was added to the reaction mixture and reaction was stirred at rt. Reaction was completed after 4 h. Solvents were saturated by addition of brine 2-3 drops, and excess DDQ was quenched by addition of sat. $NaHCO_3$ and stirred for 5 min. The crude product was extracted in CH_2Cl_2 and 5% MeOH in CH_2Cl_2. The brown colored impurities were removed by fast-filter column on silica in CH_2Cl_2-methanol (8% to 12%) followed by careful column chromatography (1:9 methanol CH_2Cl_2) to afford compound **2** as a white solid (59 mg, 73%). $[\alpha]^{22}_D$ +37.24 (*c* 1, $CHCl_3$); IR *v* 3352, 2925, 2853, 1733, 1465, 984, 761 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 5.39–5.31 (m, 2H, CH=CH), 5.05 (d, *J* = 3.6 Hz, 2H, H-1, H-1′), 4.35 (d, *J* = 11.7 Hz, 2H, H-6a, H-6a′), 4.20 (dd, *J* = 11.7, 5.3 Hz, 2H, H-6b, H-6b′), 4.03–3.99 (m, 2H, H-5, H-5′), 3.78 (t, *J* = 9.4 Hz, 2H, H-3, H-3′), 3.47 (dd, *J* = 9.4, 3.6 Hz, 2H, H-2, H-2′), 3.36–3.31 (m, 2H, H-4, H-4′), 2.34 (t, *J* = 7.4 Hz, 4H), 2.04–2.01 (m, 4H), 1.64–1.60 (m, 4H), 1.56–1.46 (m, 1H), 1.33–1.30 (m, 36H), 1.18–1.17 (m, 2H), 0.90–0.85 (m, 9H); ^{13}C NMR (100 MHz, CD_3OD) δ 175.6, 131.0, 130.9, 95.2, 74.6, 73.2, 72.0, 71.5, 64.5, 40.4, 35.2, 33.2, 31.2, 30.96, 30.90, 30.87, 30.7, 30.6, 30.5, 30.4, 30.3, 29.3, 28.7, 28.3, 26.2, 23.8, 23.2, 14.6; HR-ESI-MS (*m/z*): calcd for $C_{45}H_{82}O_{13}$ $[M + Na]^+$ 853.5653 found, 853.5660.

II Spectra.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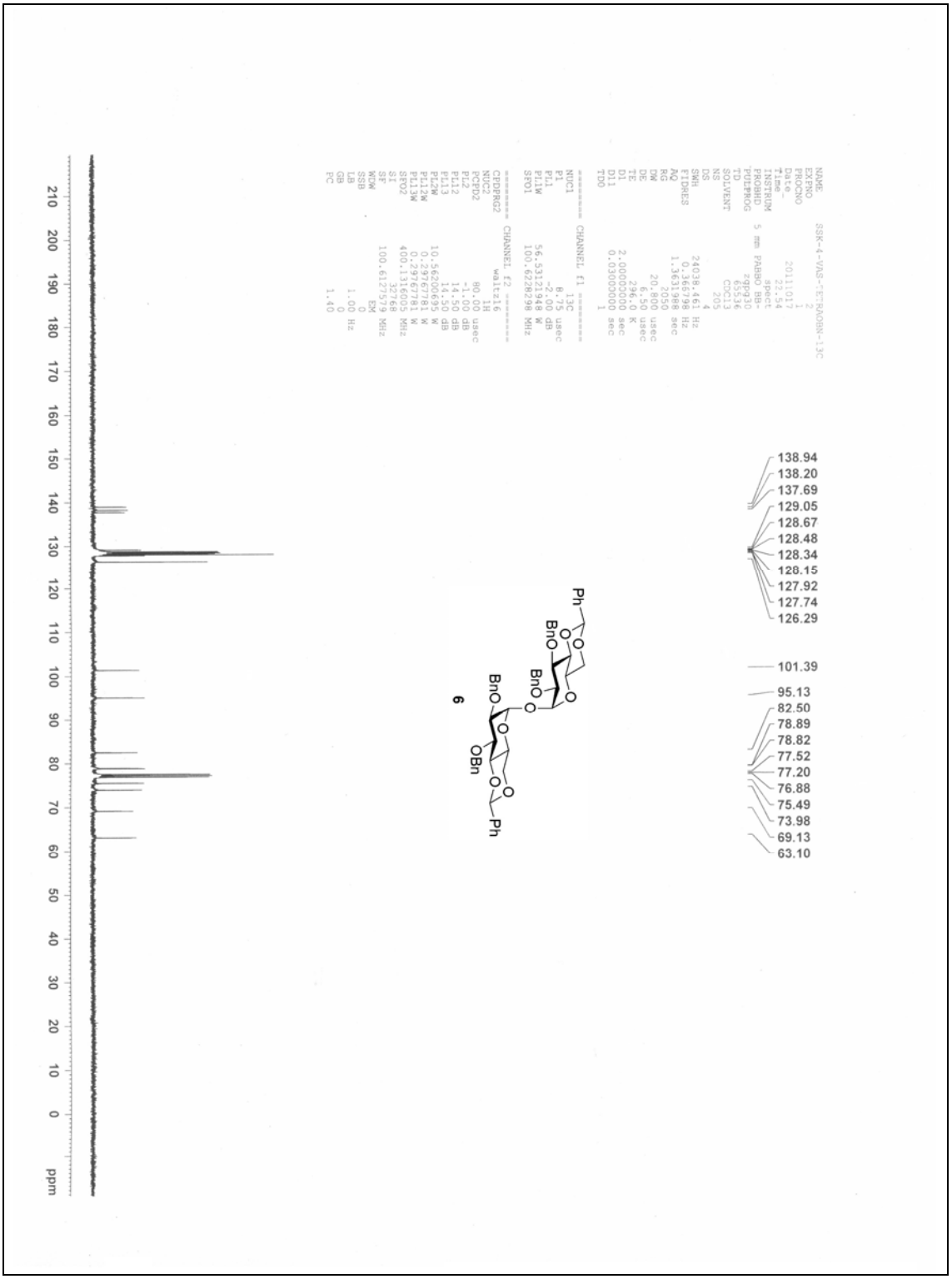
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73.98
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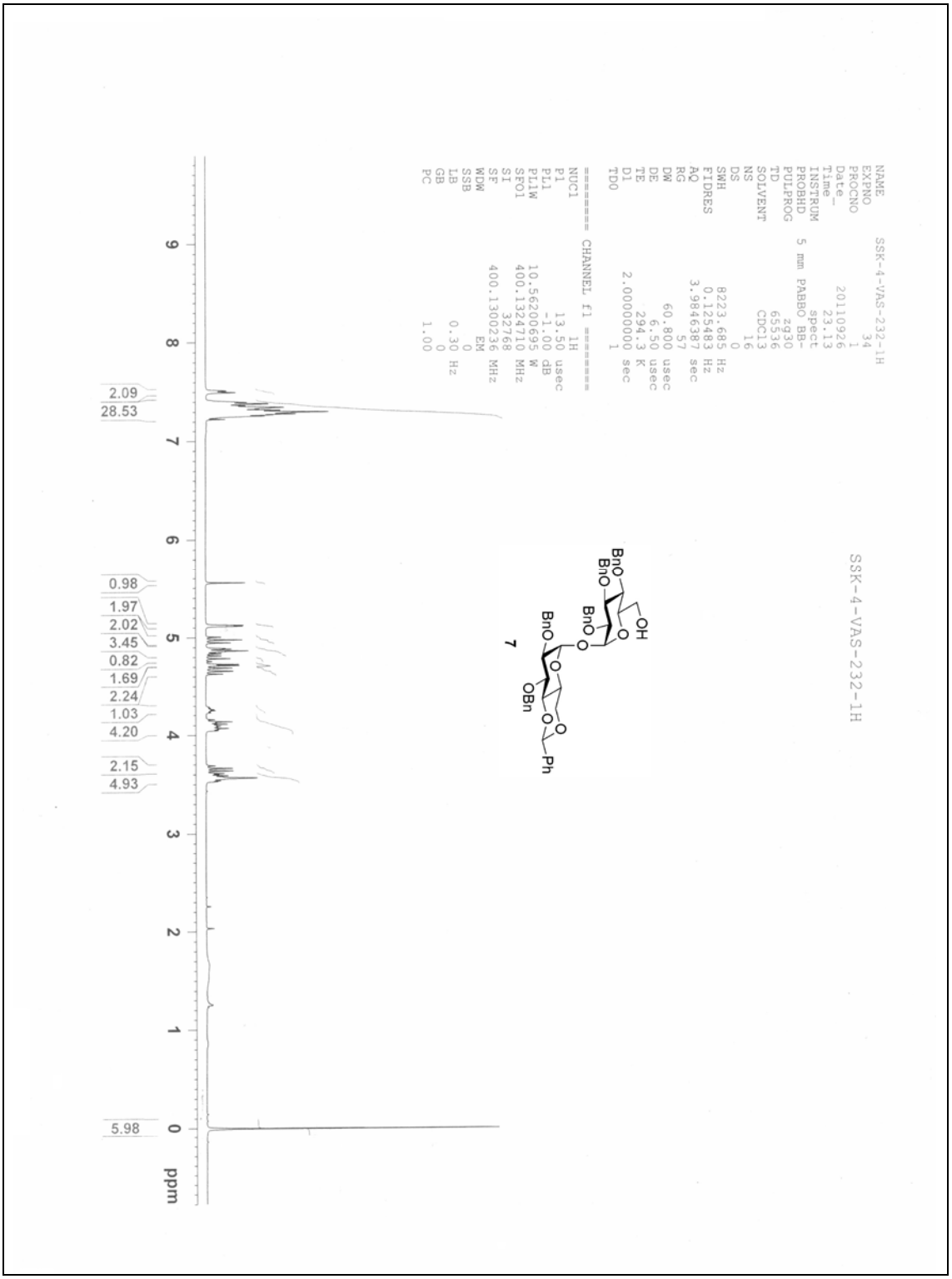
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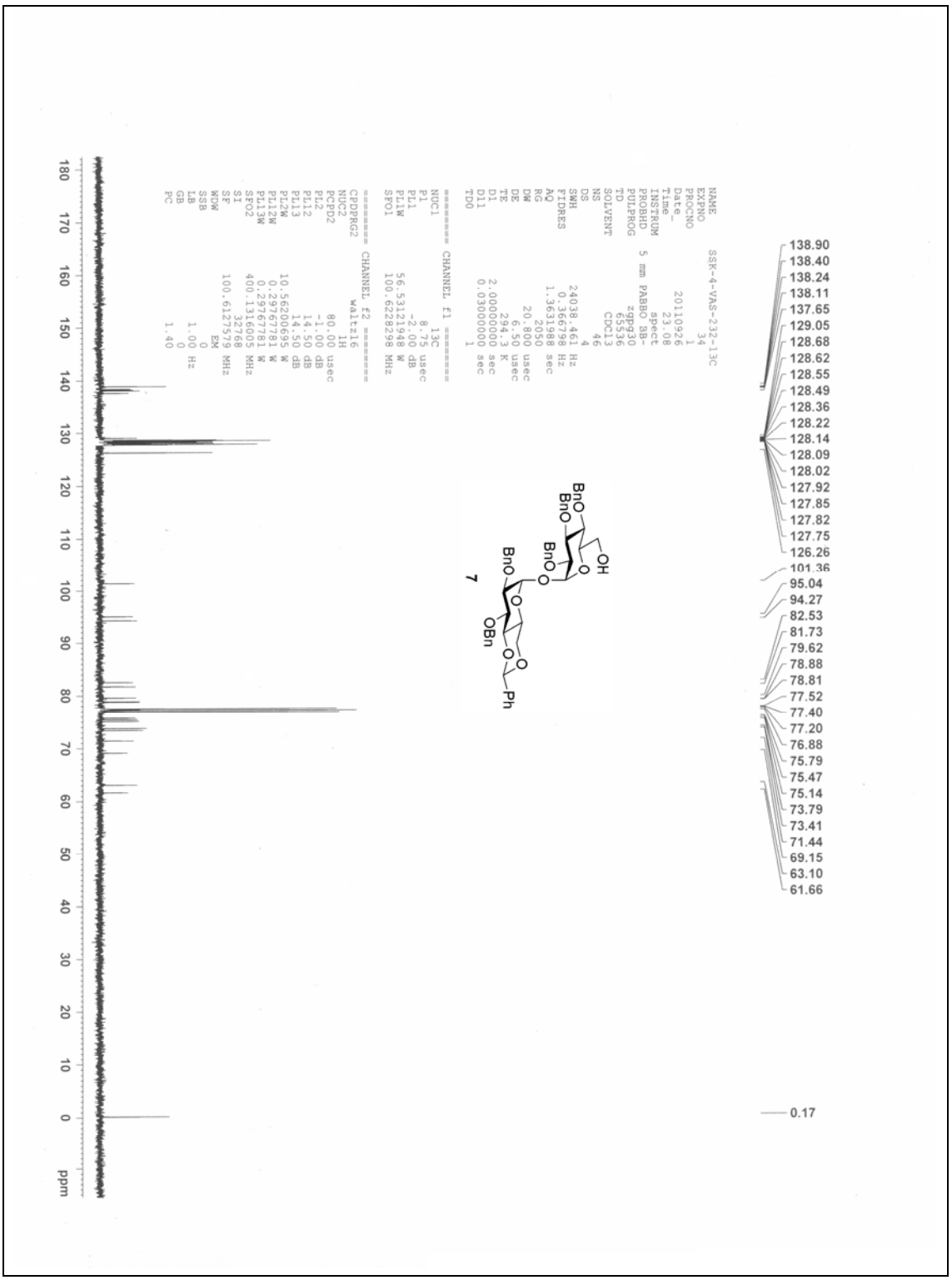
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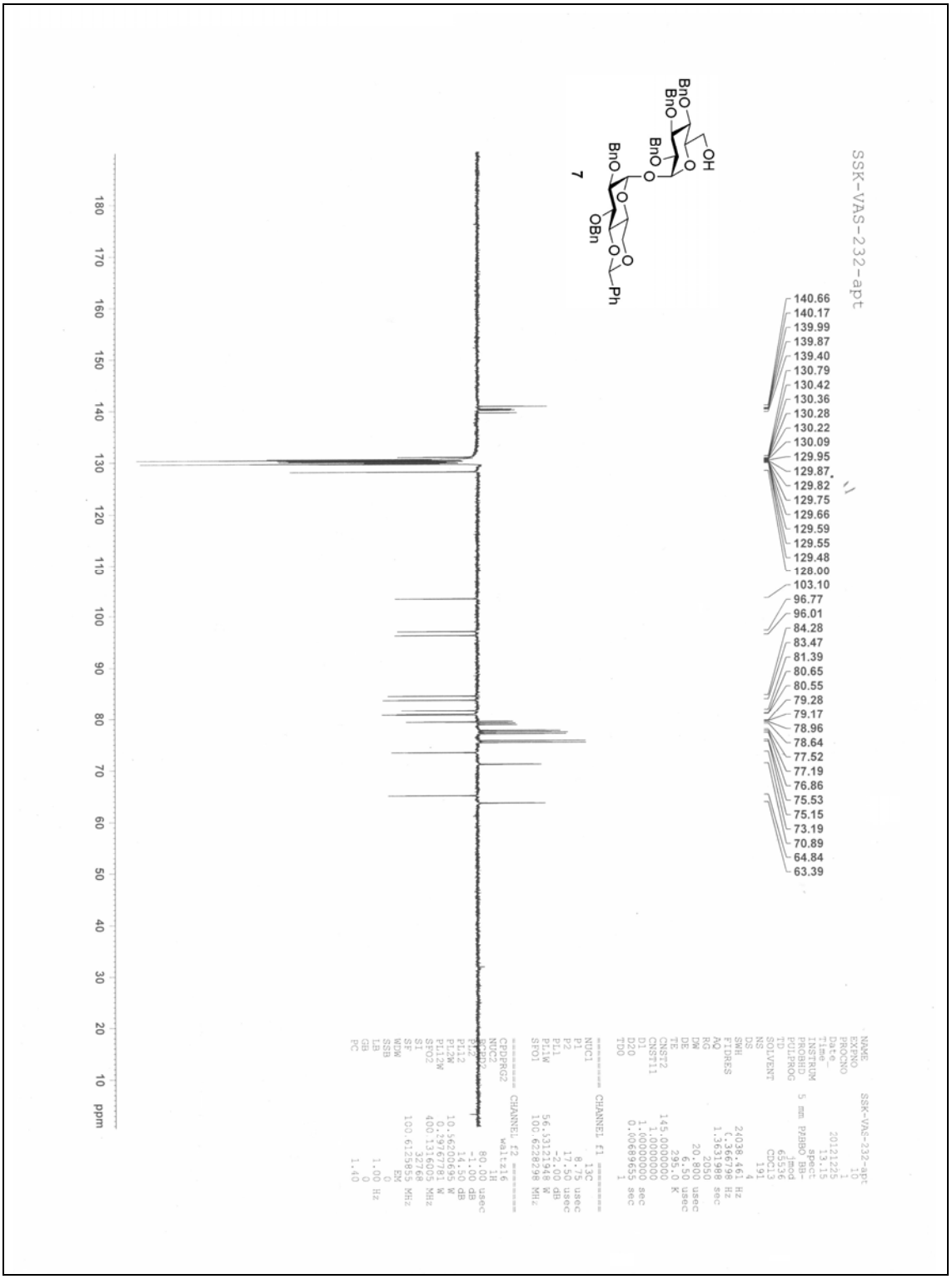
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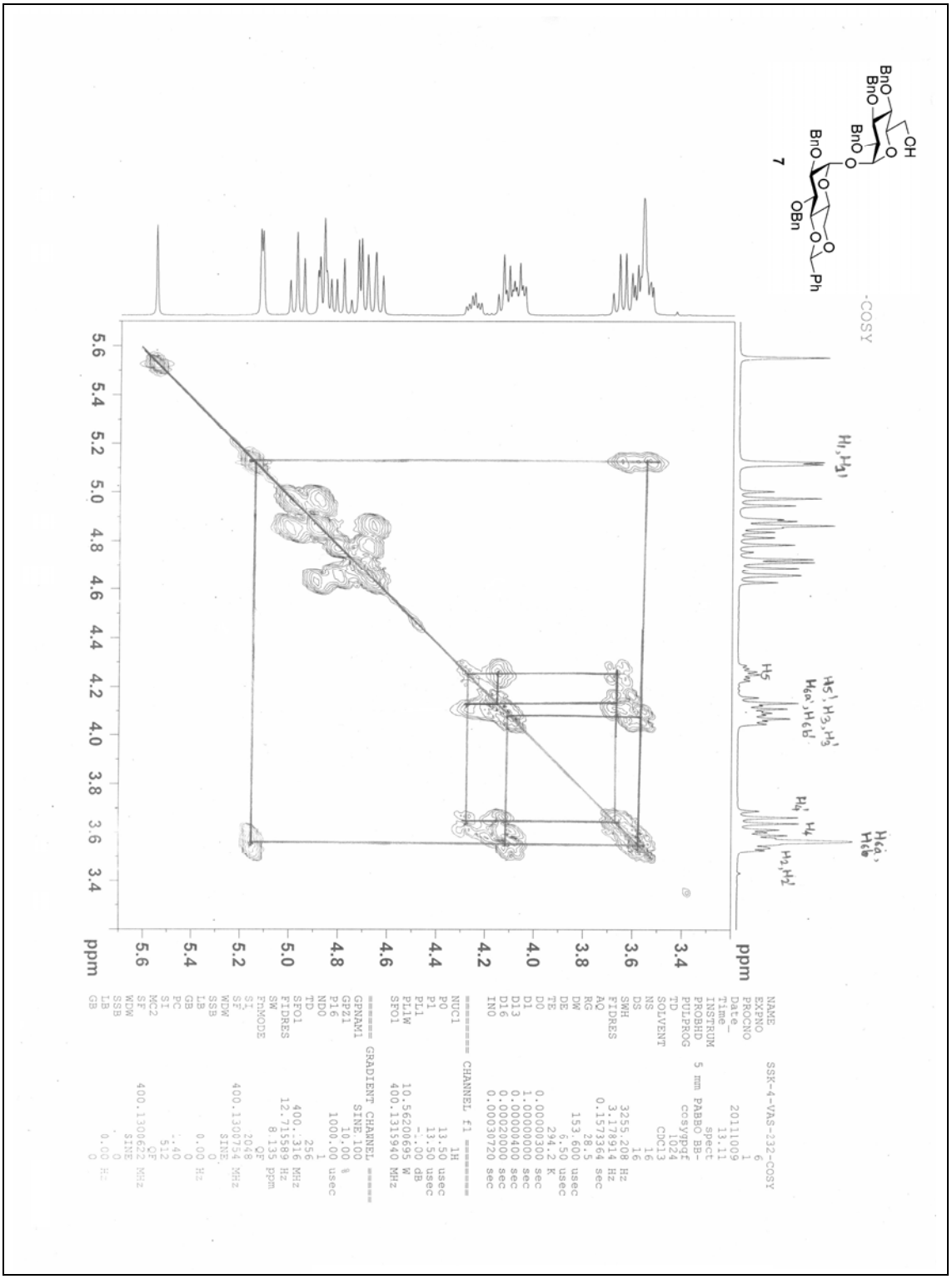
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O
Ph
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H6a',H6b'
H4'
H4
H2,H2'
H6a,
H6b
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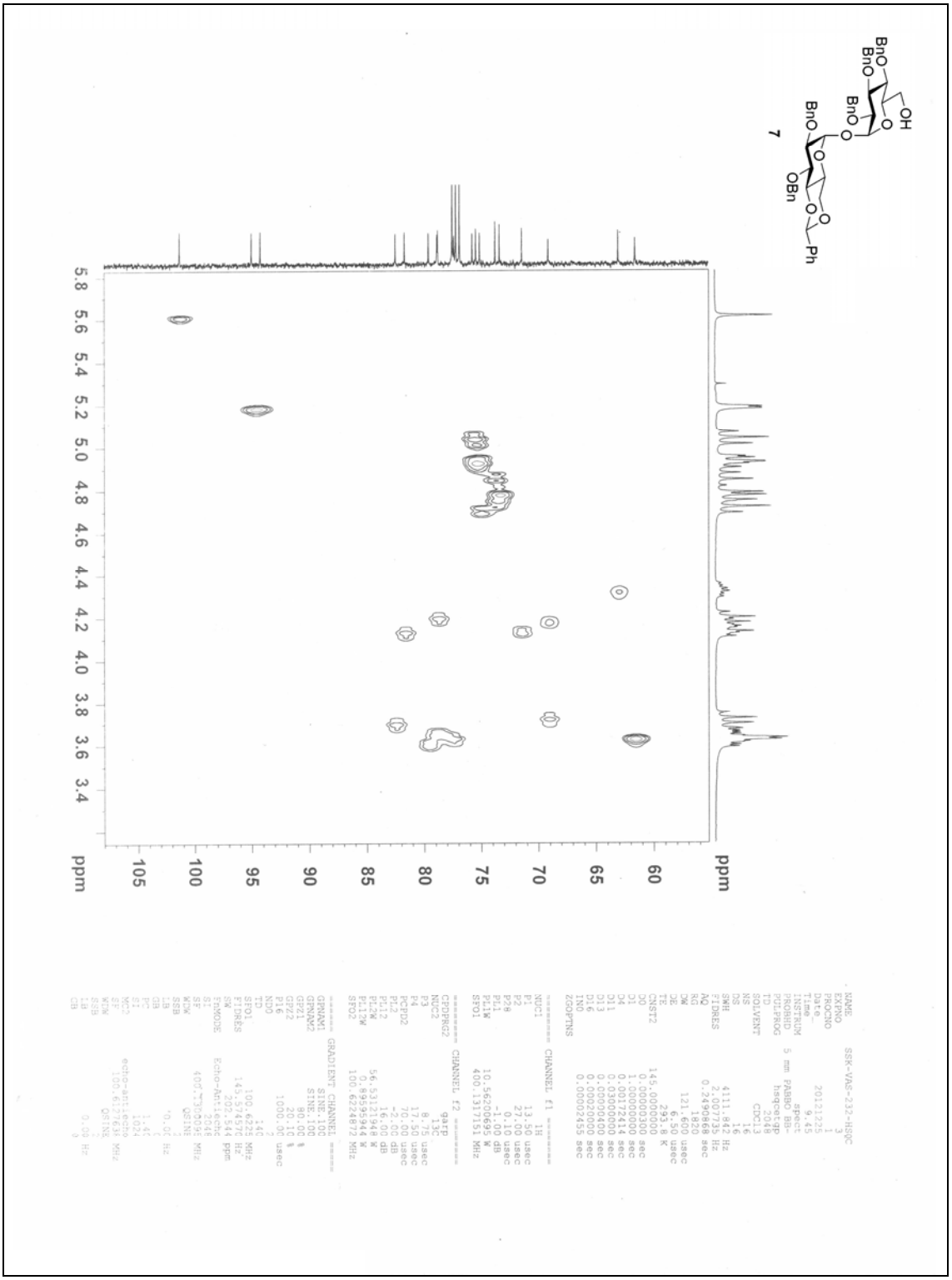
3.6
3.4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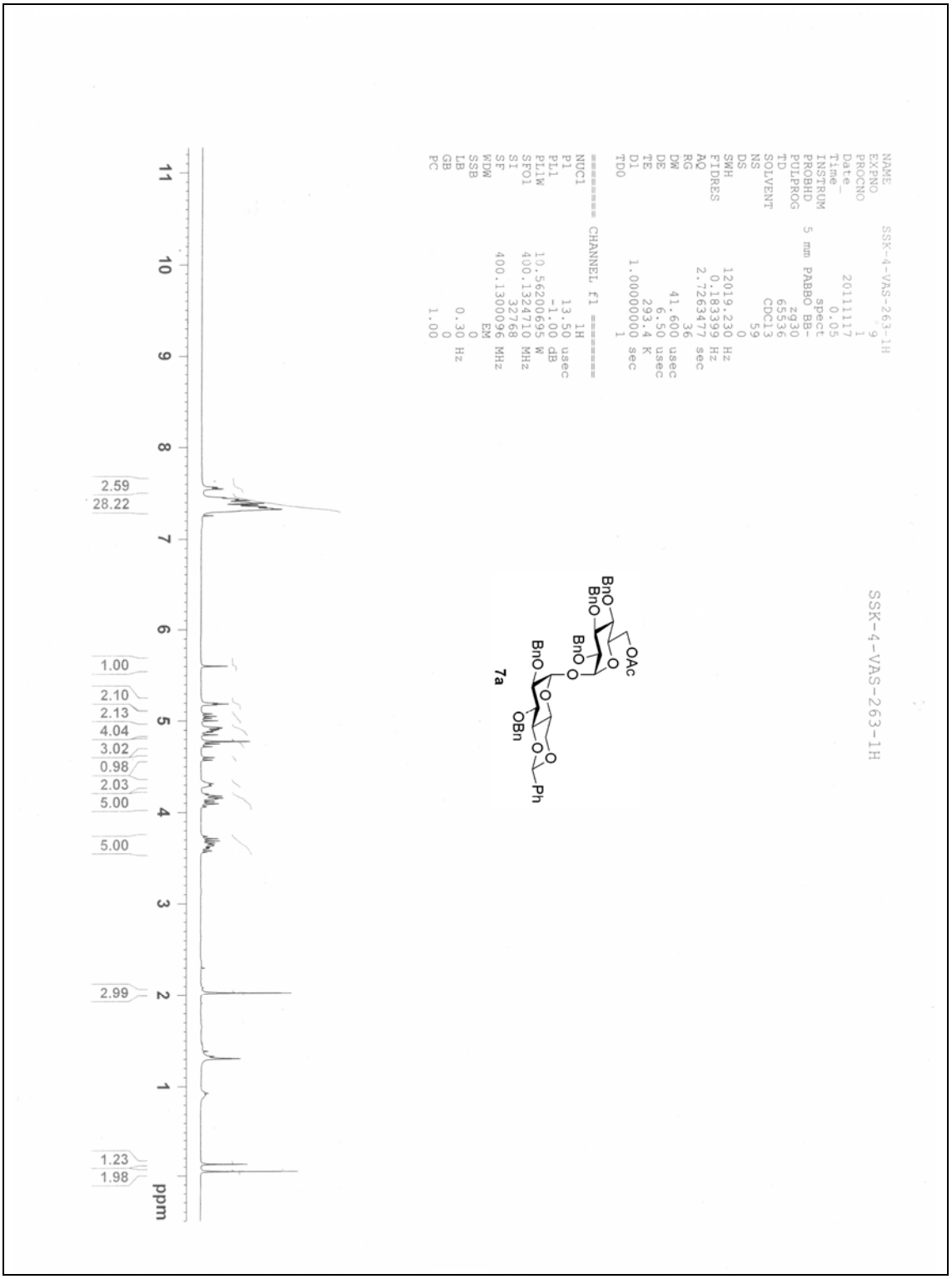
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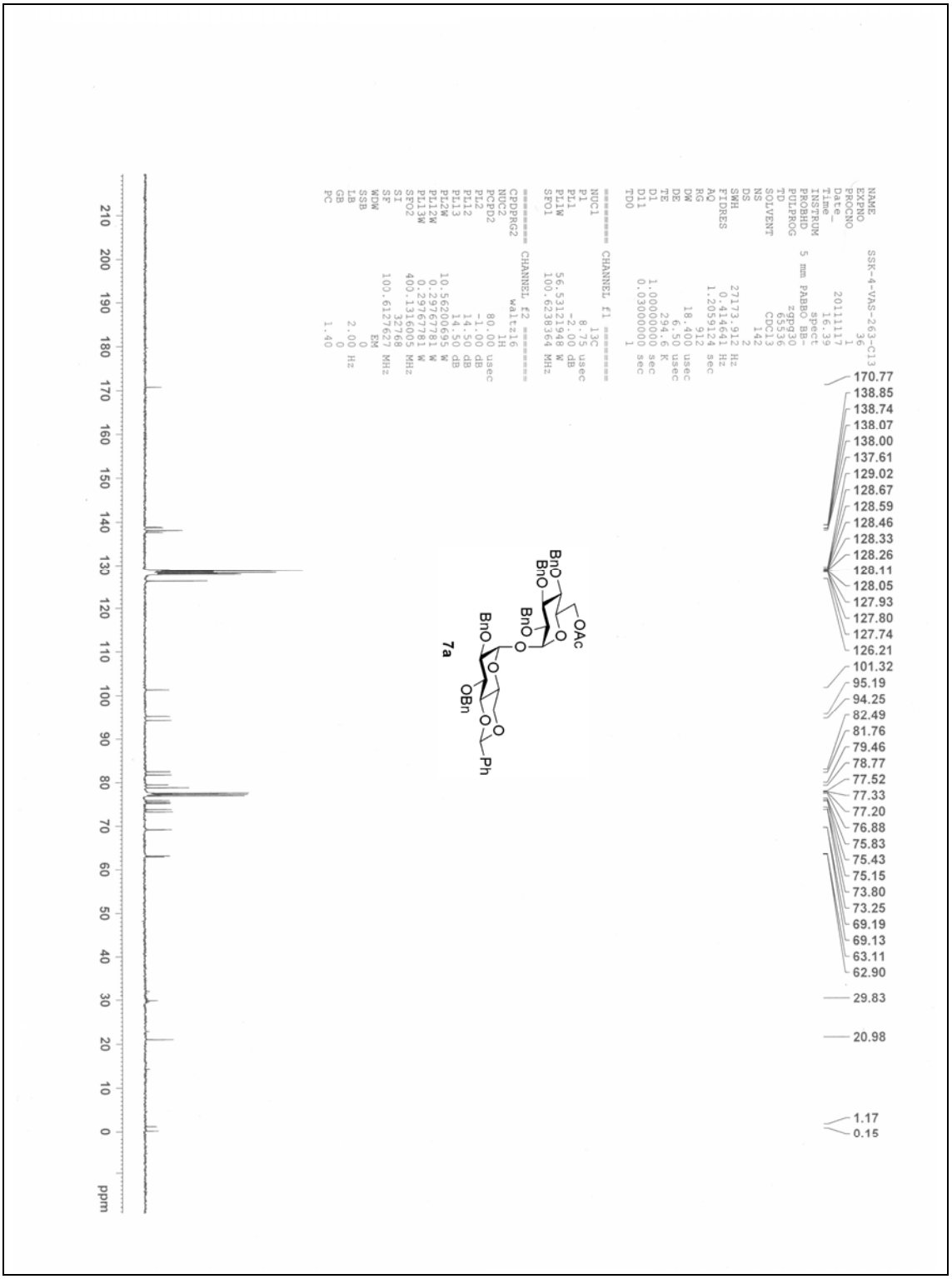

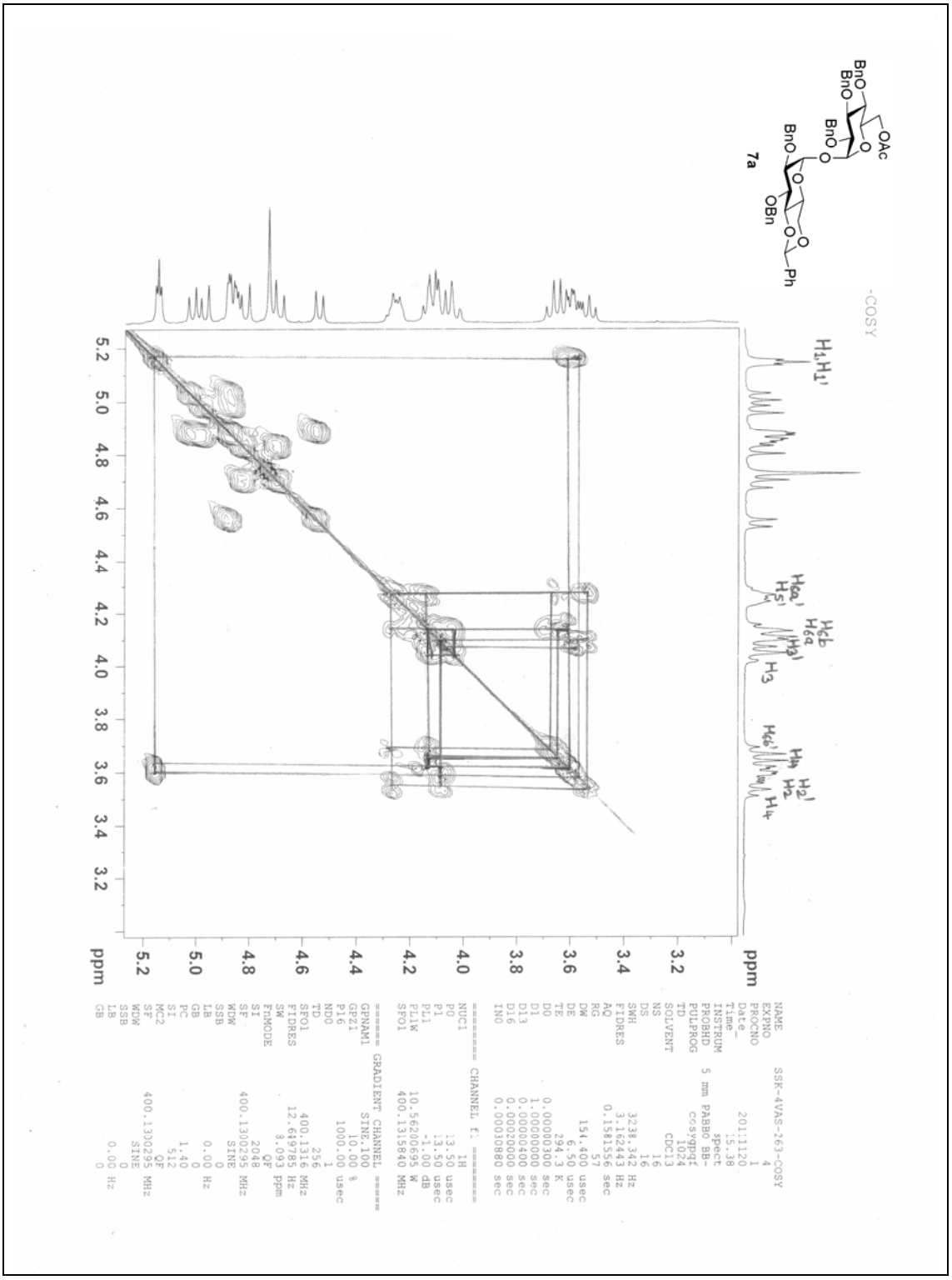
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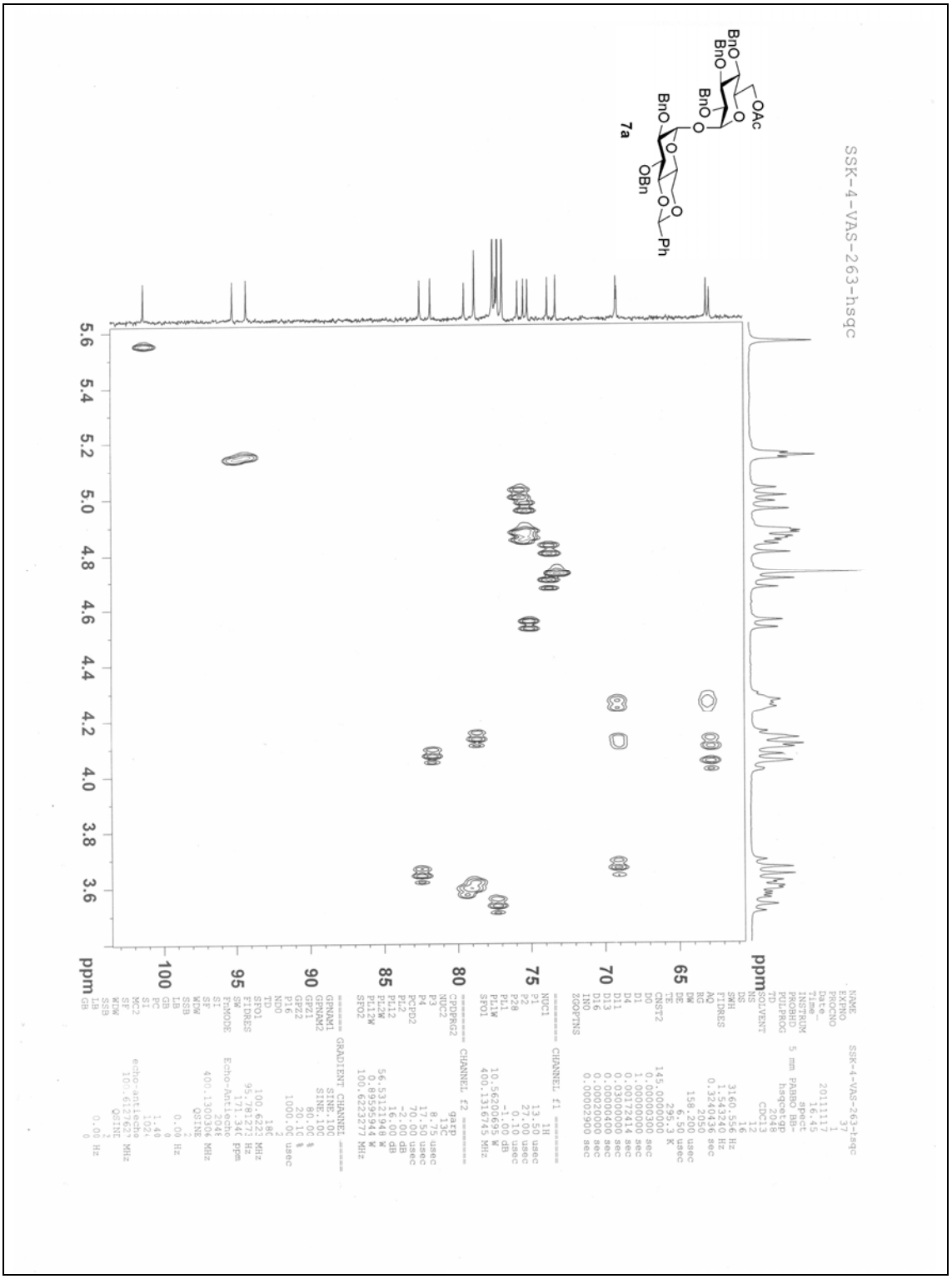
3.2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Ph
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95
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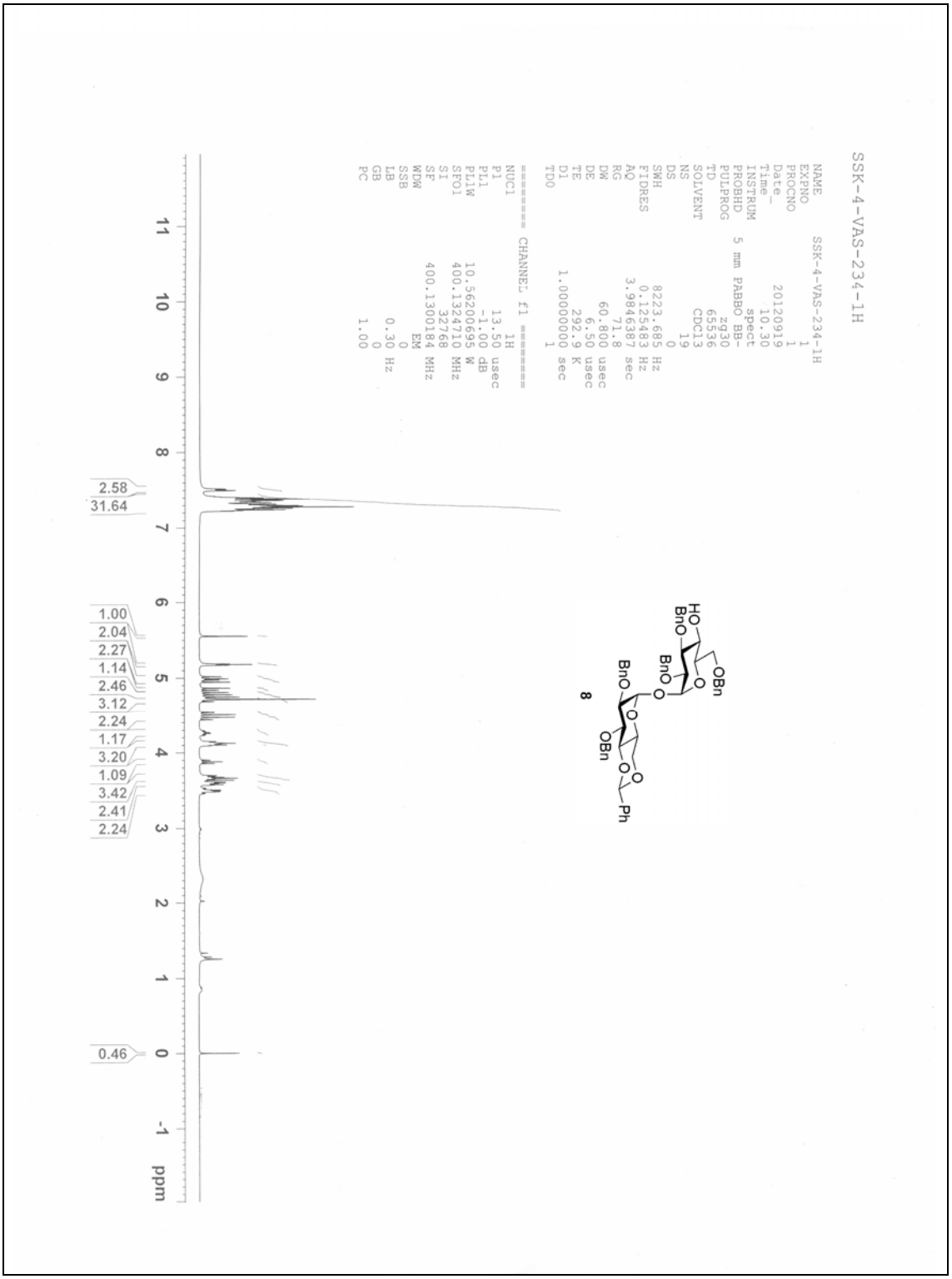
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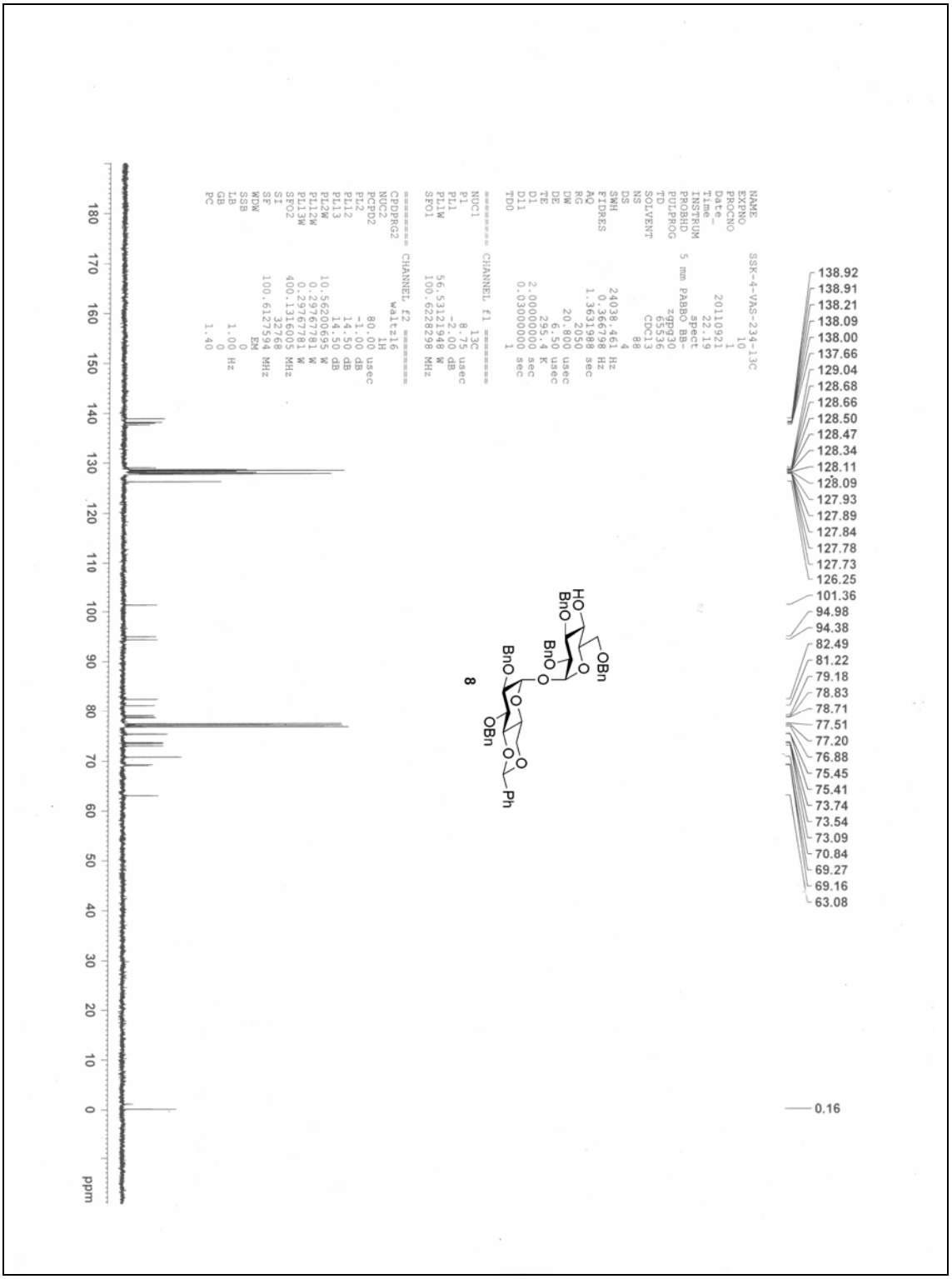
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DE 6.50 usec
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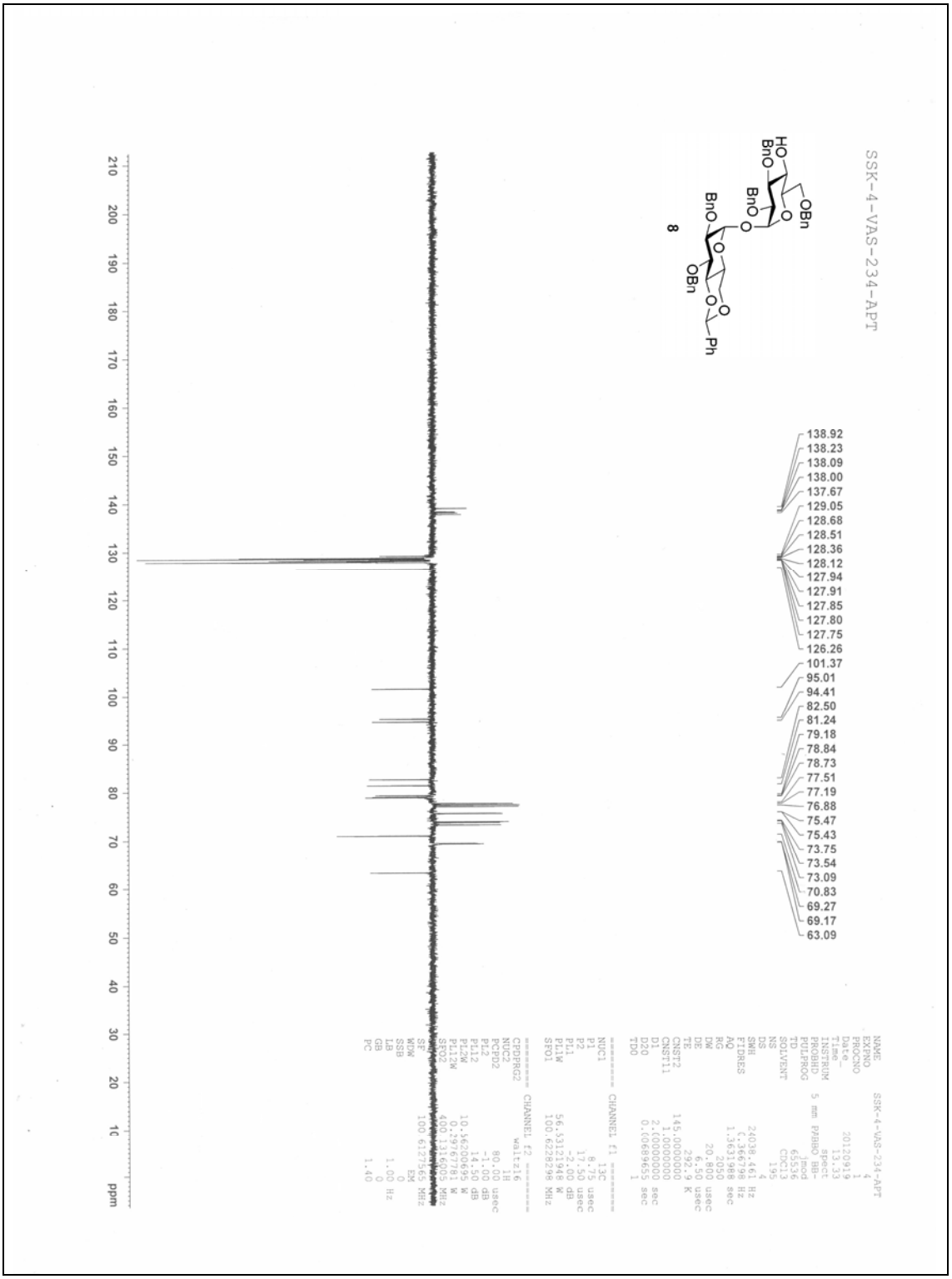
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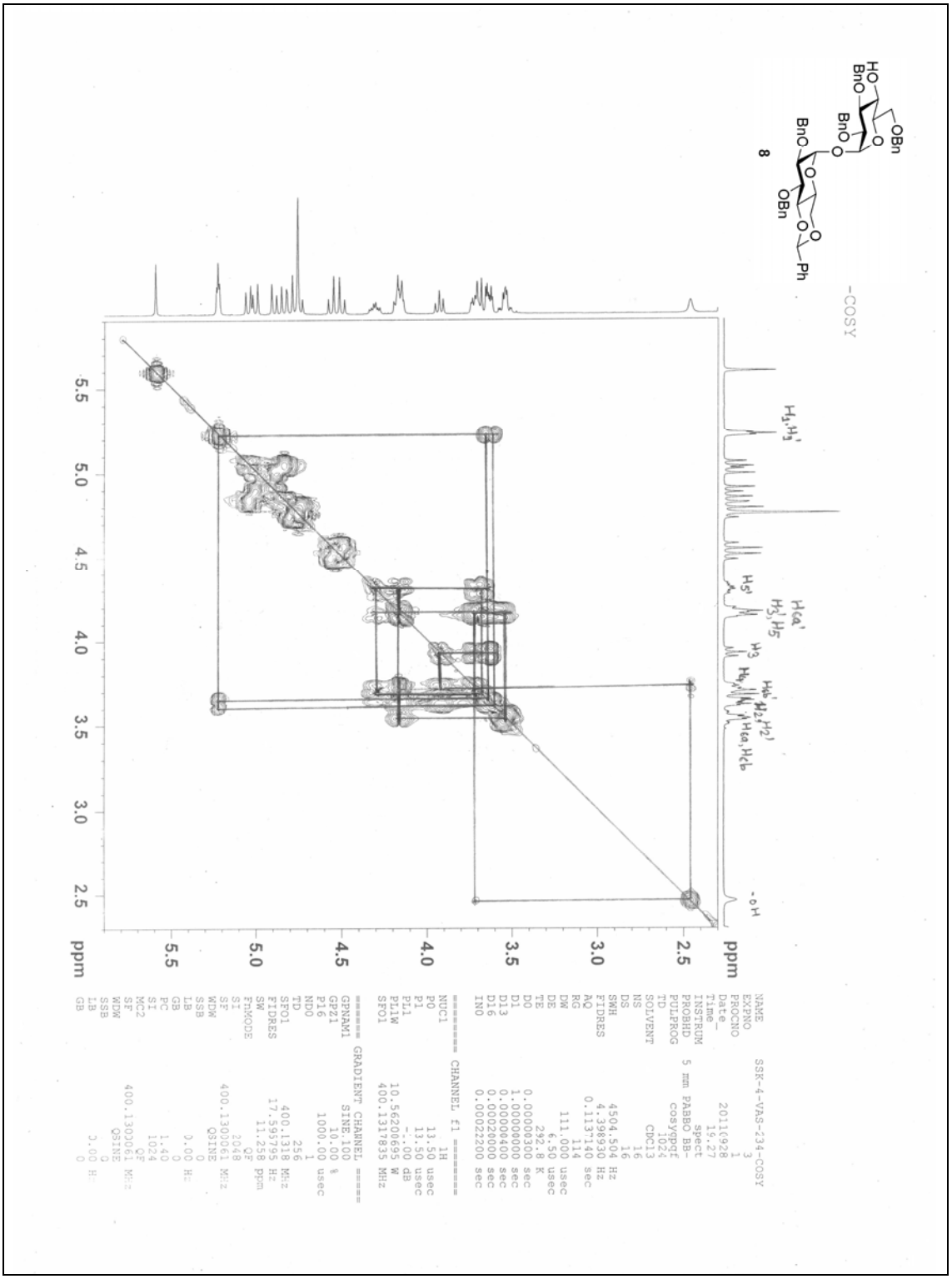

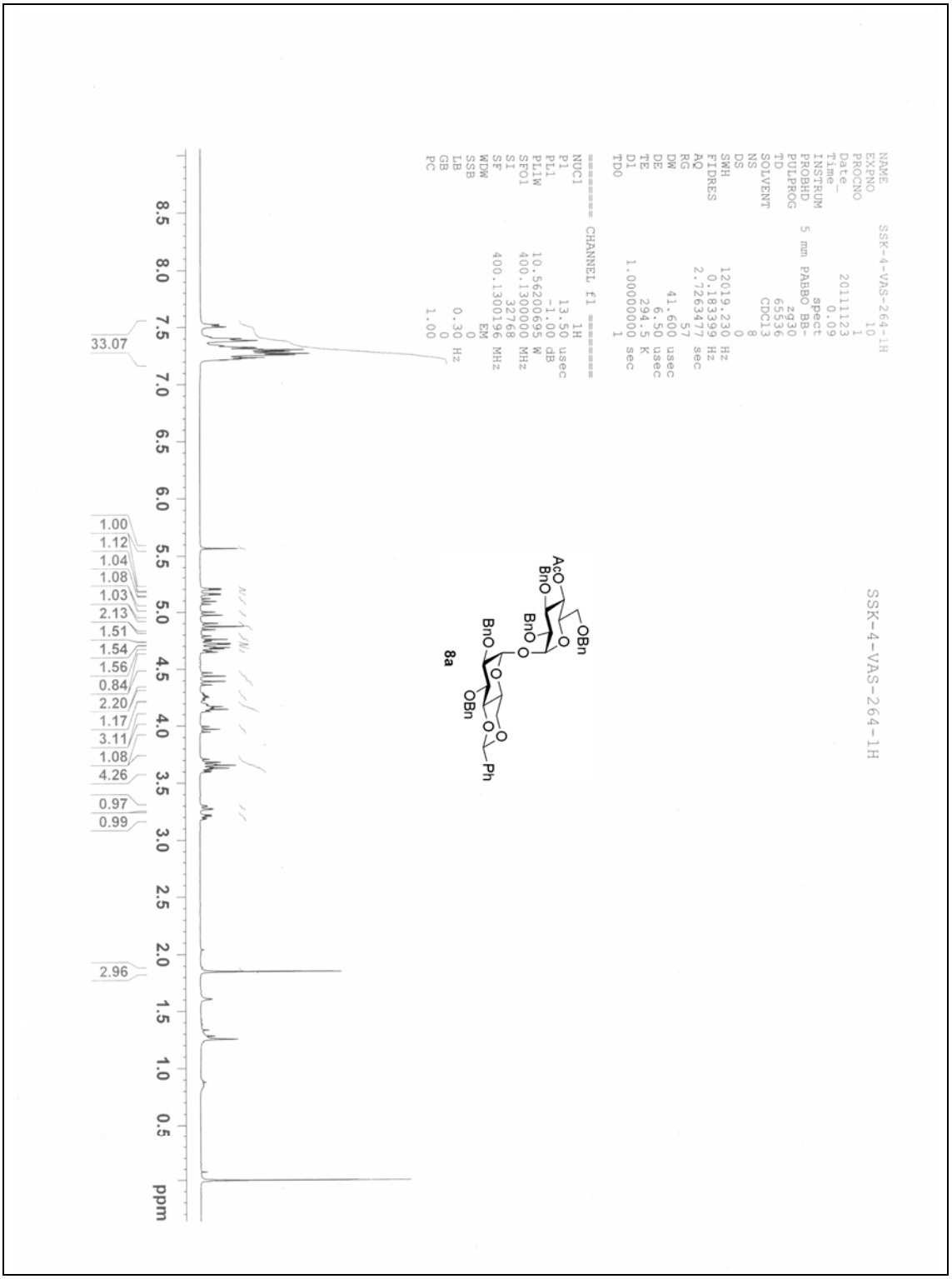
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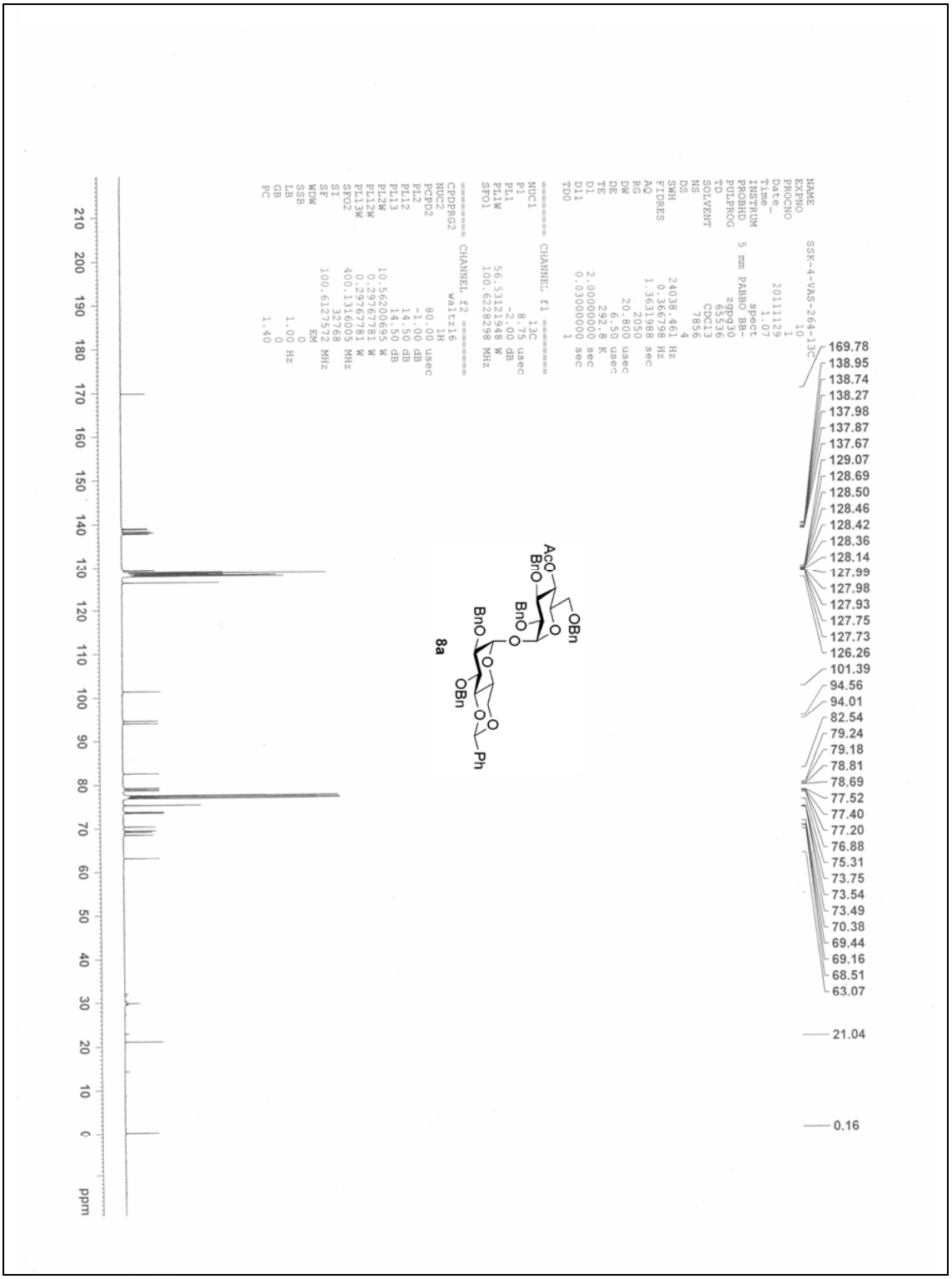
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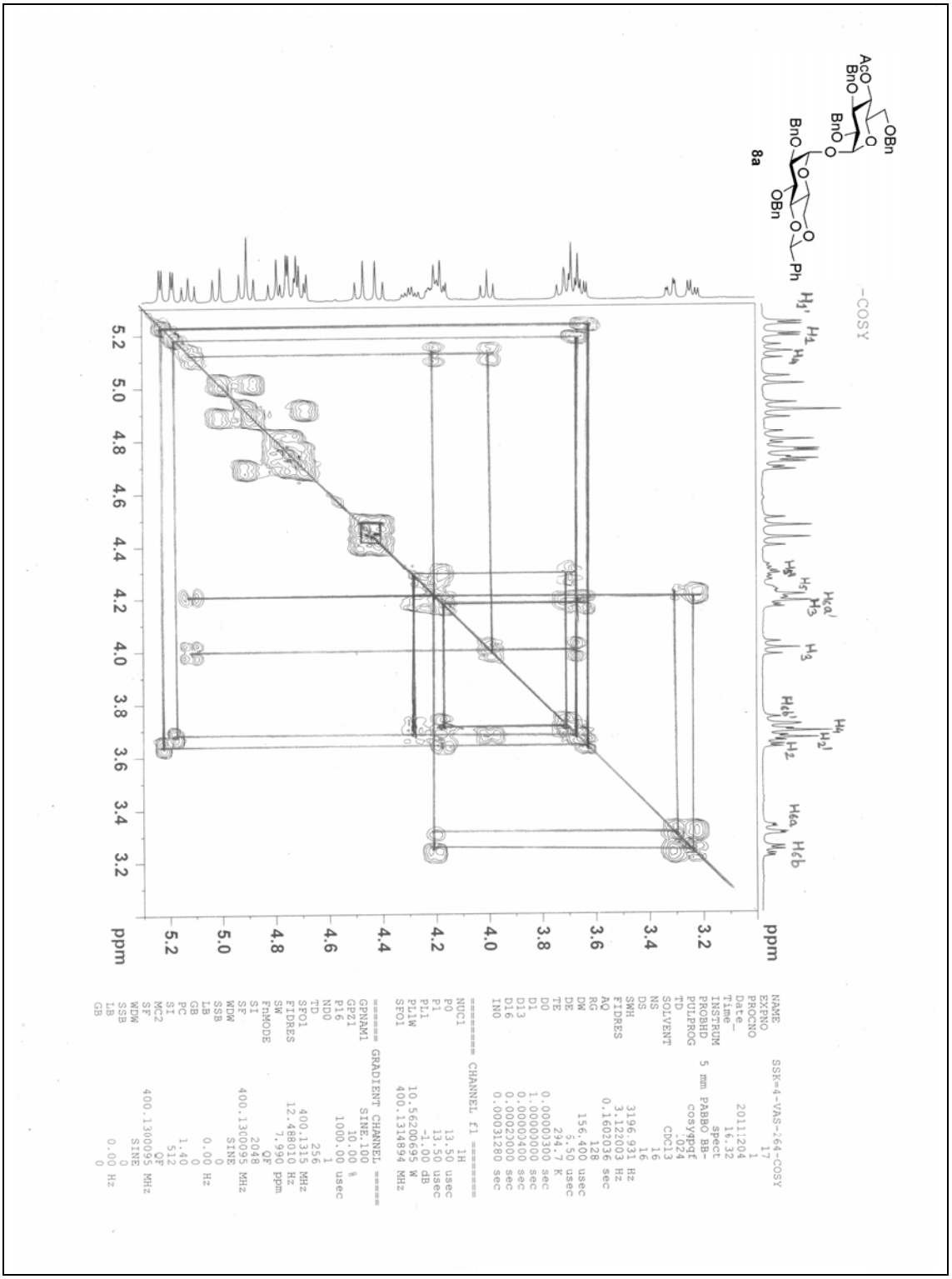
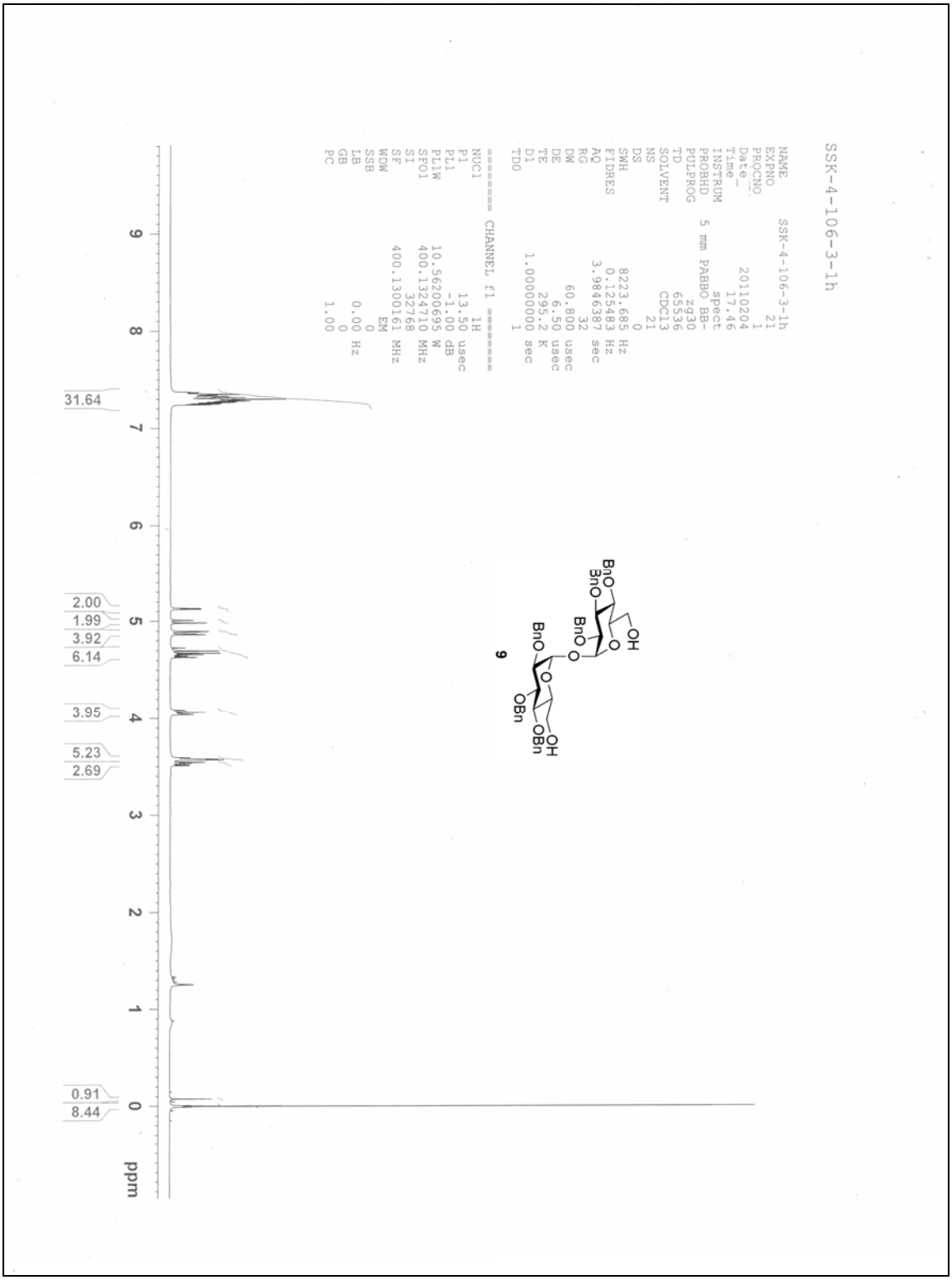
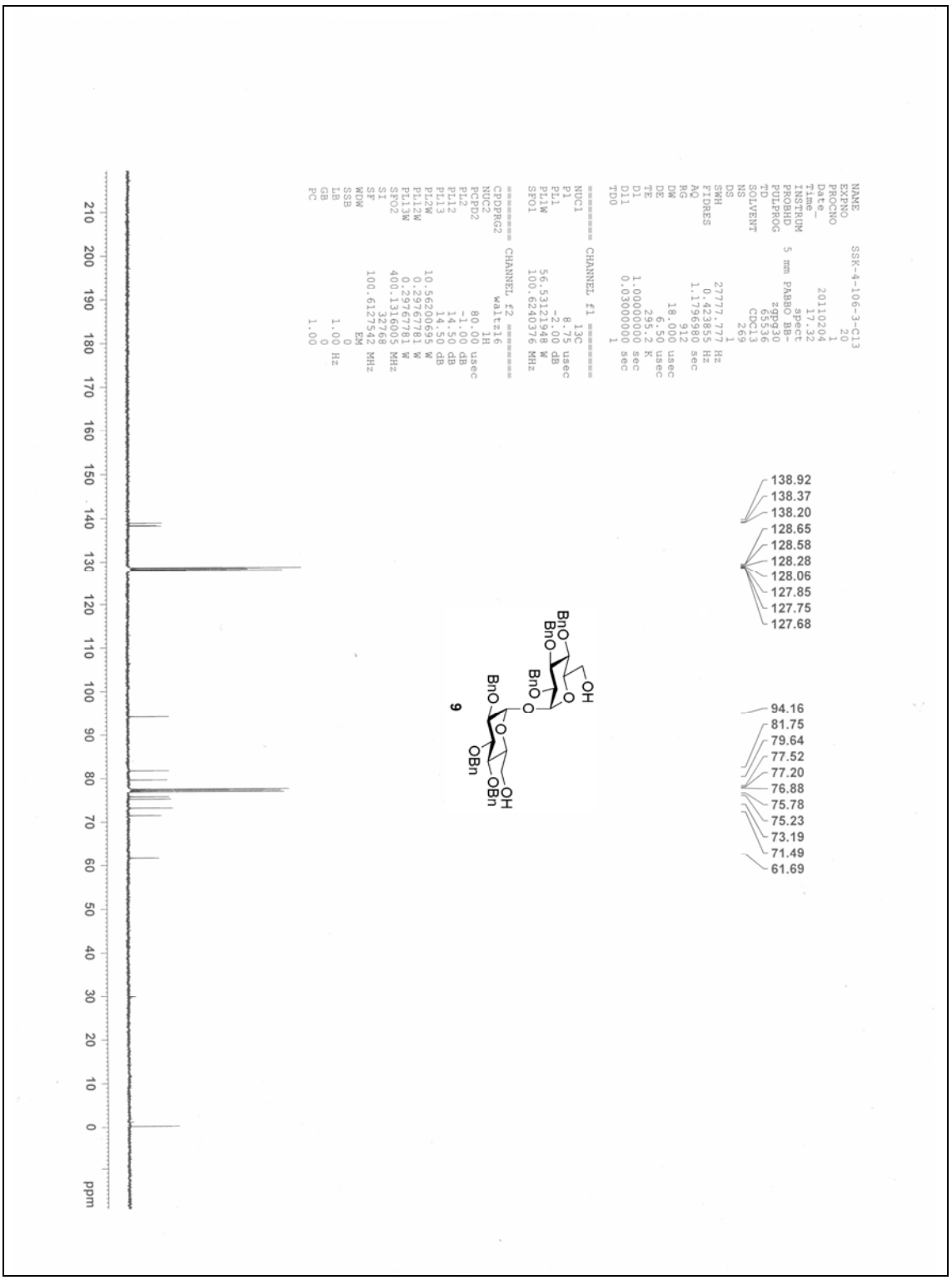
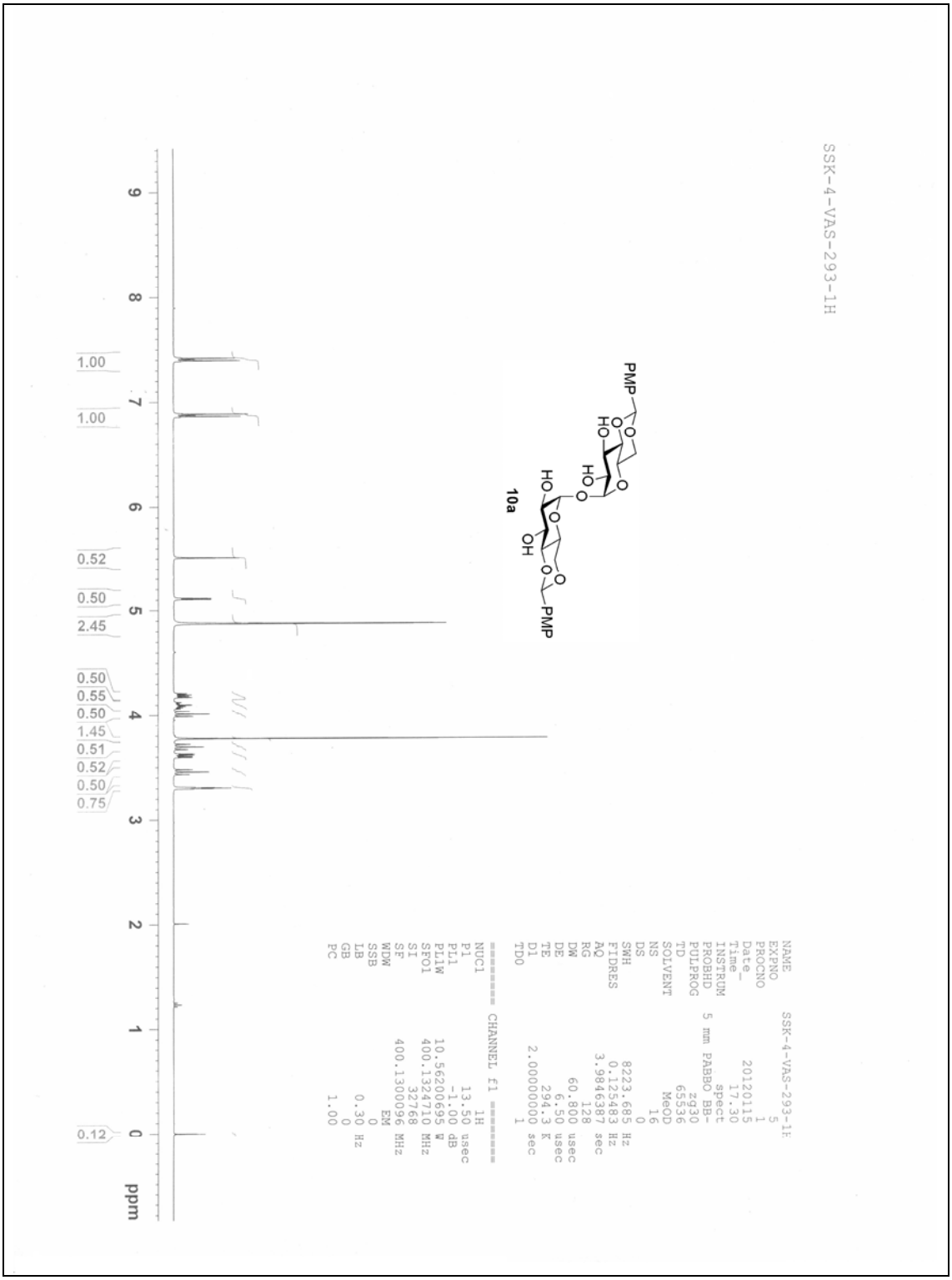
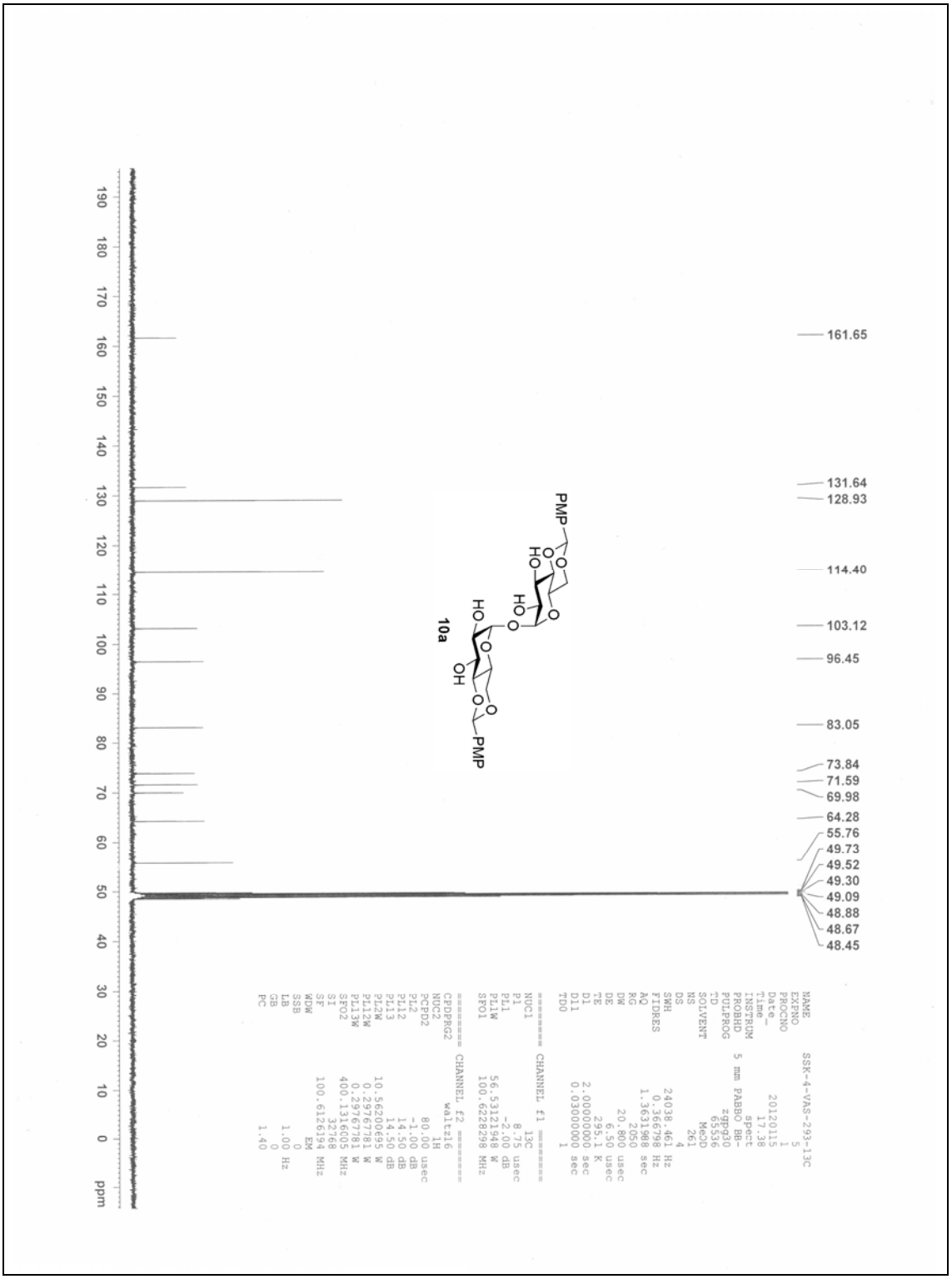
169.78
138.95
138.74
138.27
137.98
137.87
137.67
129.07
128.69
128.50
128.46
128.42
128.36
128.14
127.99
127.98
127.93
127.75
127.73
126.26
101.39
94.56
94.01
82.54
79.24
79.18
78.81
78.69
77.52
77.40
77.20
76.88
75.31
73.75
73.54
73.49
70.38
69.44
69.16
68.51
63.07
21.04
0.16
ppm

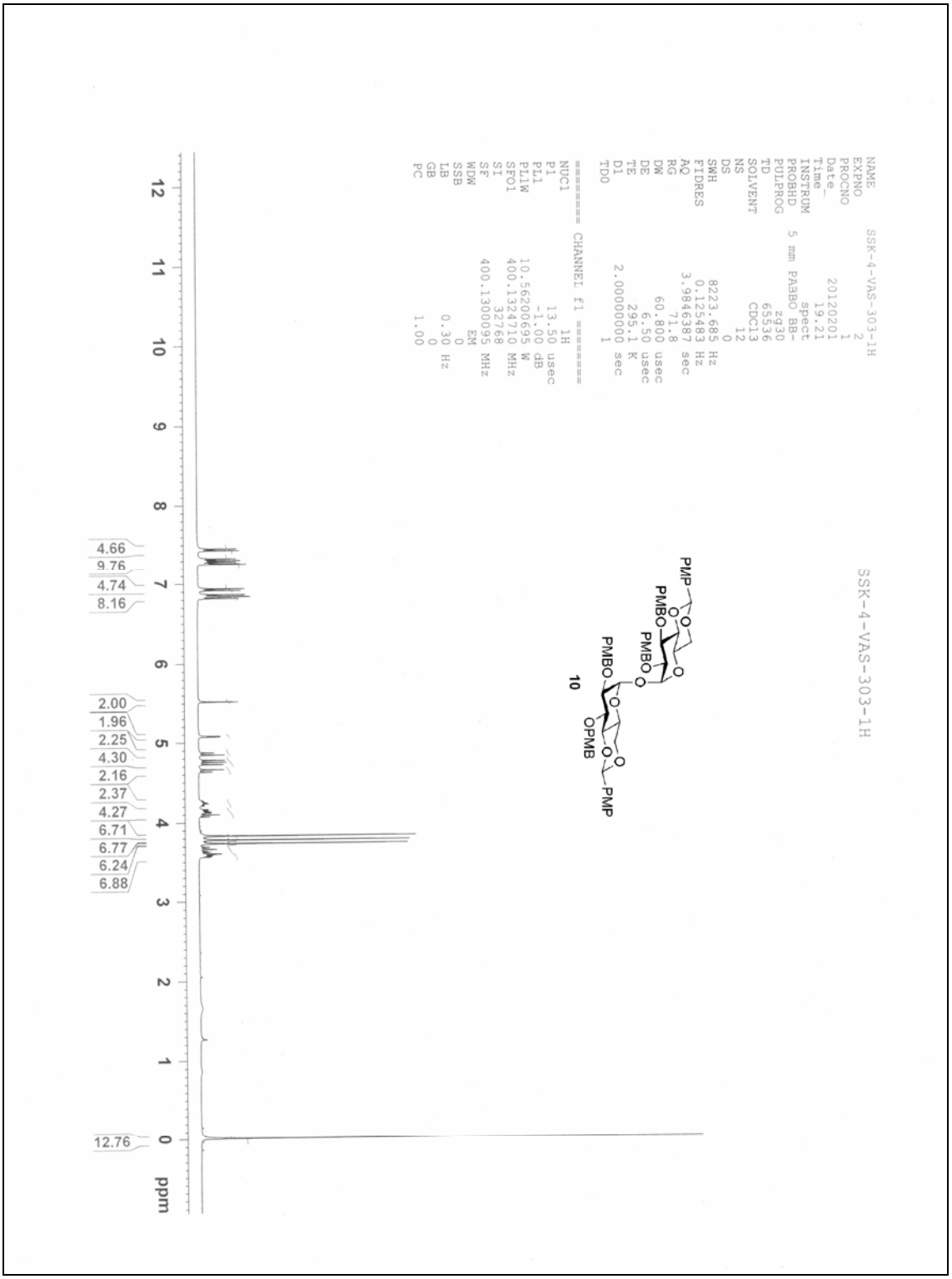

8a
-COSY
ppm
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2

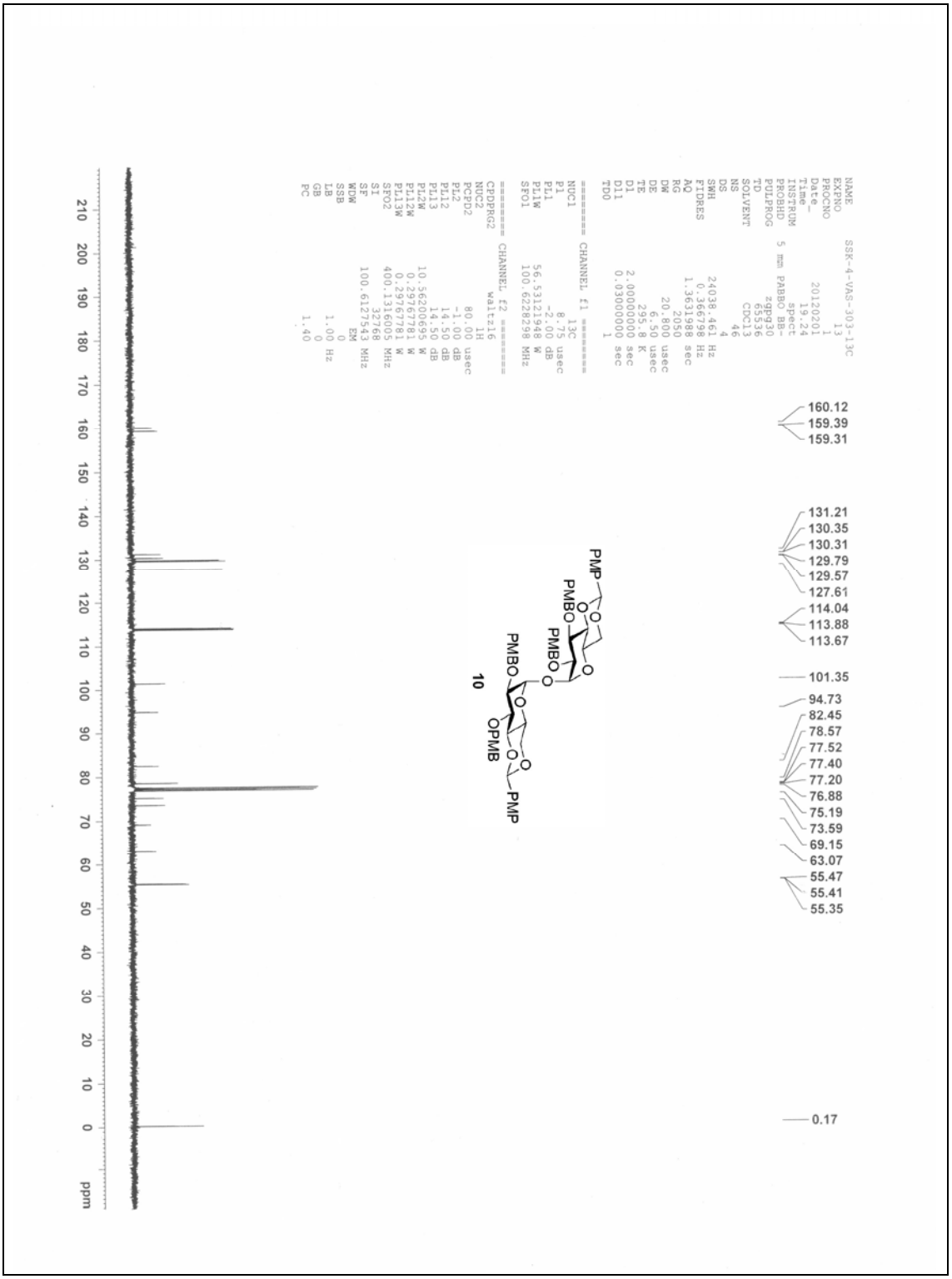

SSK-4-106-3-1h
NAME SSK-4-106-3-1h
EXPNO 21
PROCNO 1
Date_ 20110204
Time_ 17.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 21
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PLIW 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300161 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
31.64
2.00
1.99
3.92
6.14
3.95
5.23
2.69
0.91
8.44
ppm
9
BnO
BnO
BnO
BnO
OBn
OBn
OH
OH

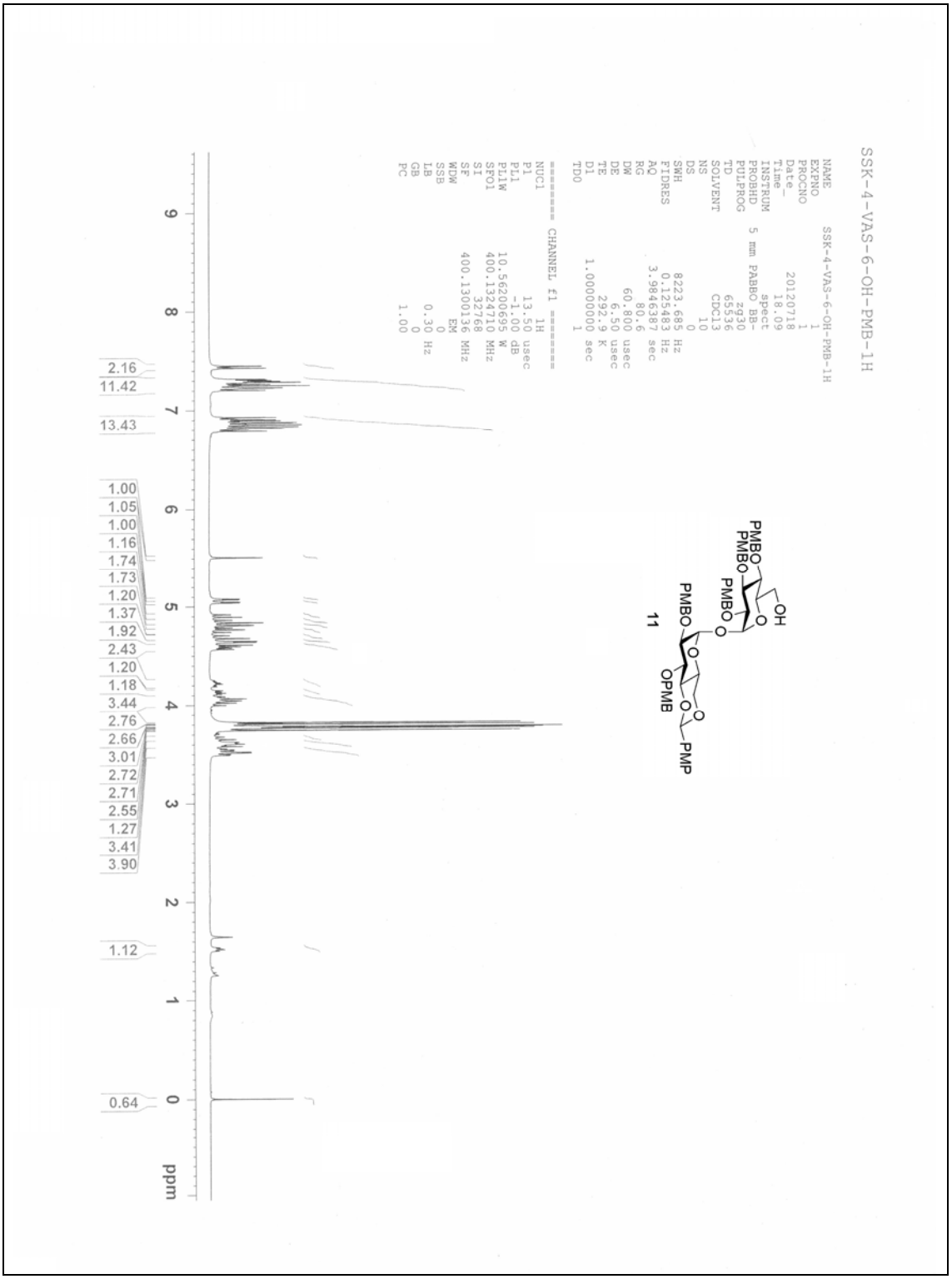

NAME SSK-4-106-3-C13
EXPNO 20
PROCNO 1
Date_ 20110204
Time 17.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 269
DS 4
SWH 27777.777 Hz
FIDRES 0.423855 Hz
AQ 1.1796980 sec
RG 912
DW 18.000 usec
DE 6.50 usec
TE 295.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.6240376 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 100.6127542 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
138.92
138.37
138.20
128.65
128.58
128.28
128.06
127.85
127.75
127.68
94.16
81.75
79.64
77.52
77.20
76.88
75.78
75.23
73.19
71.49
61.69
9
BnO
BnO
BnO
BnO
OH
OBn
OBn
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

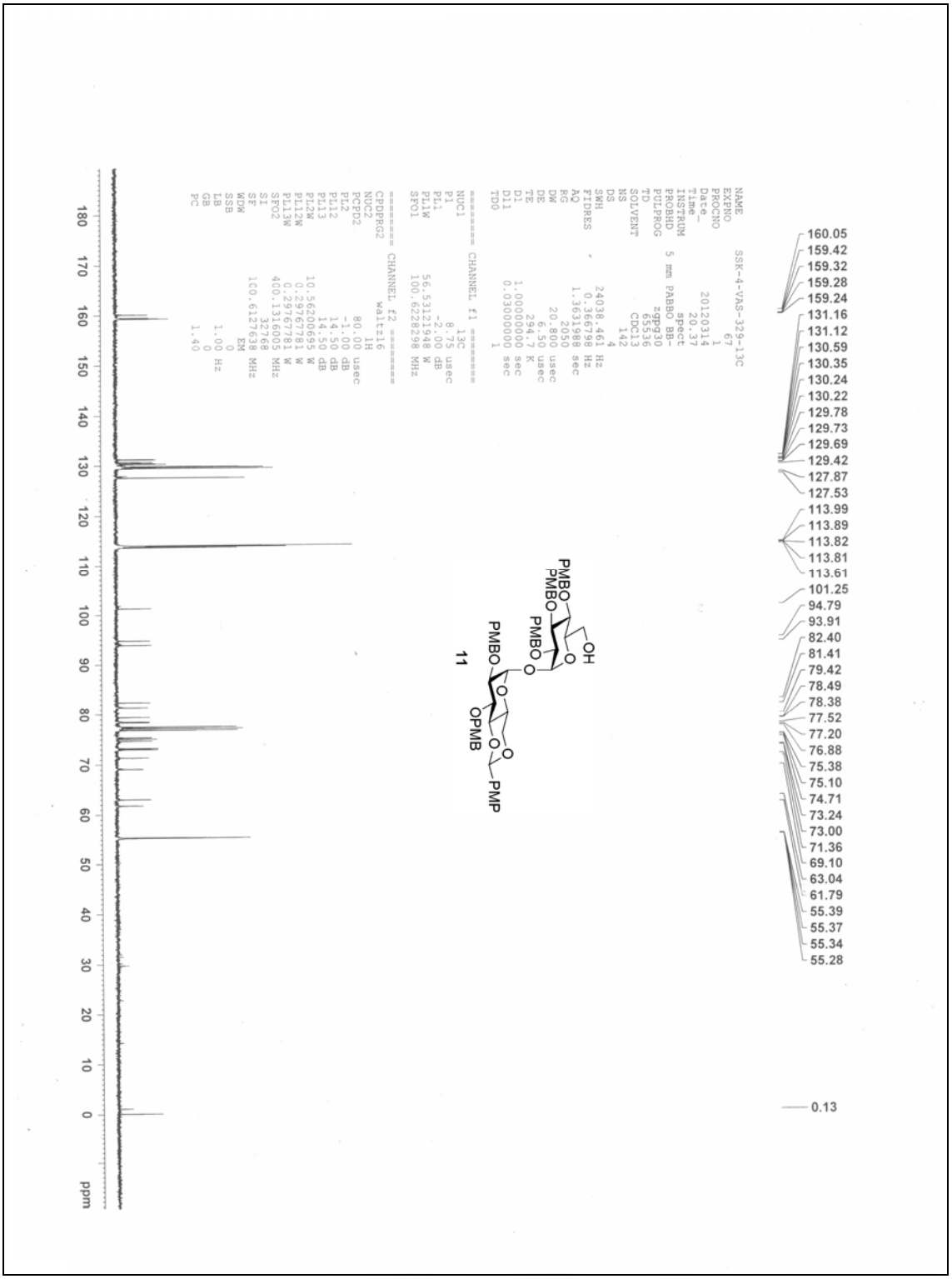


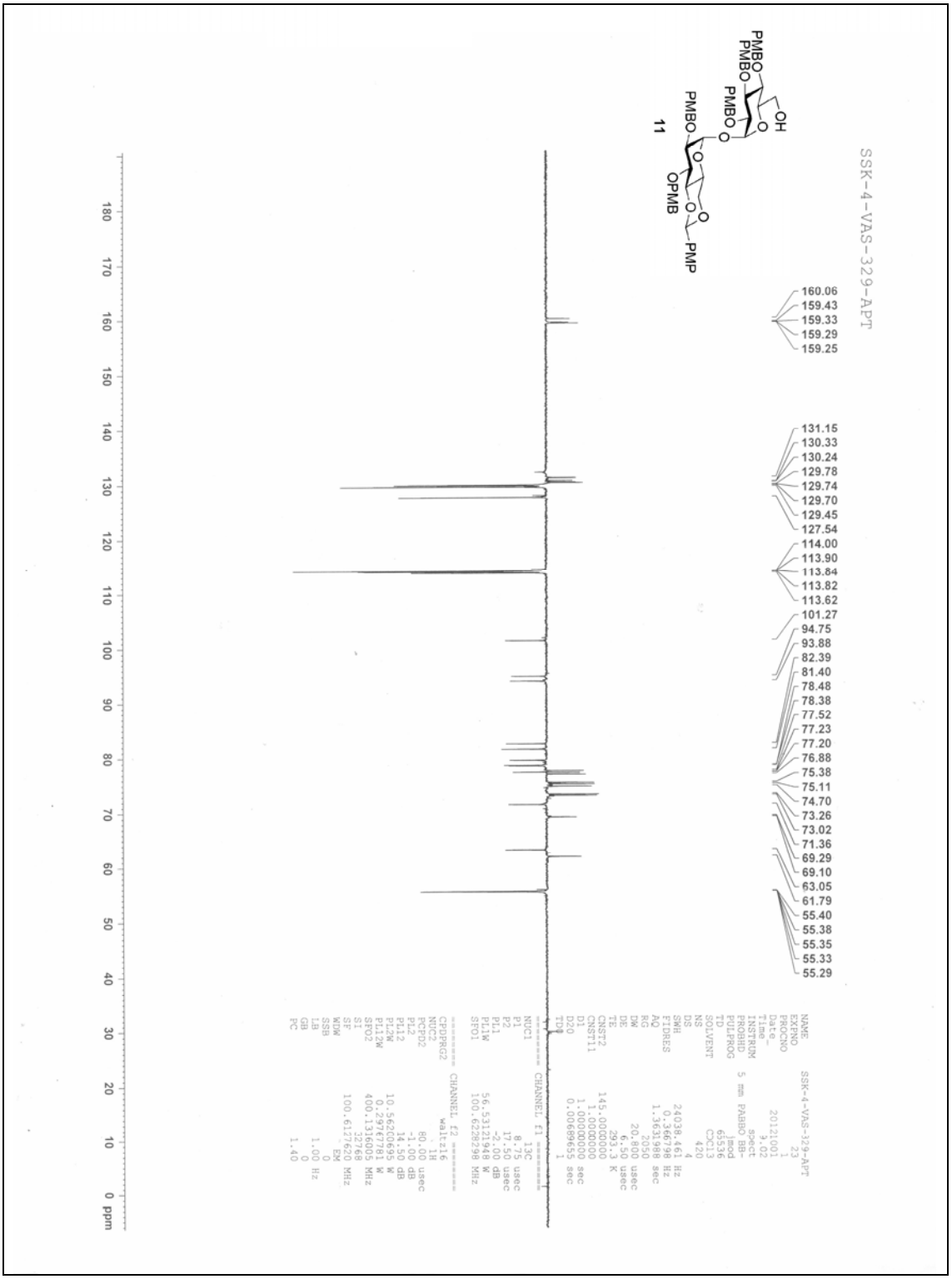


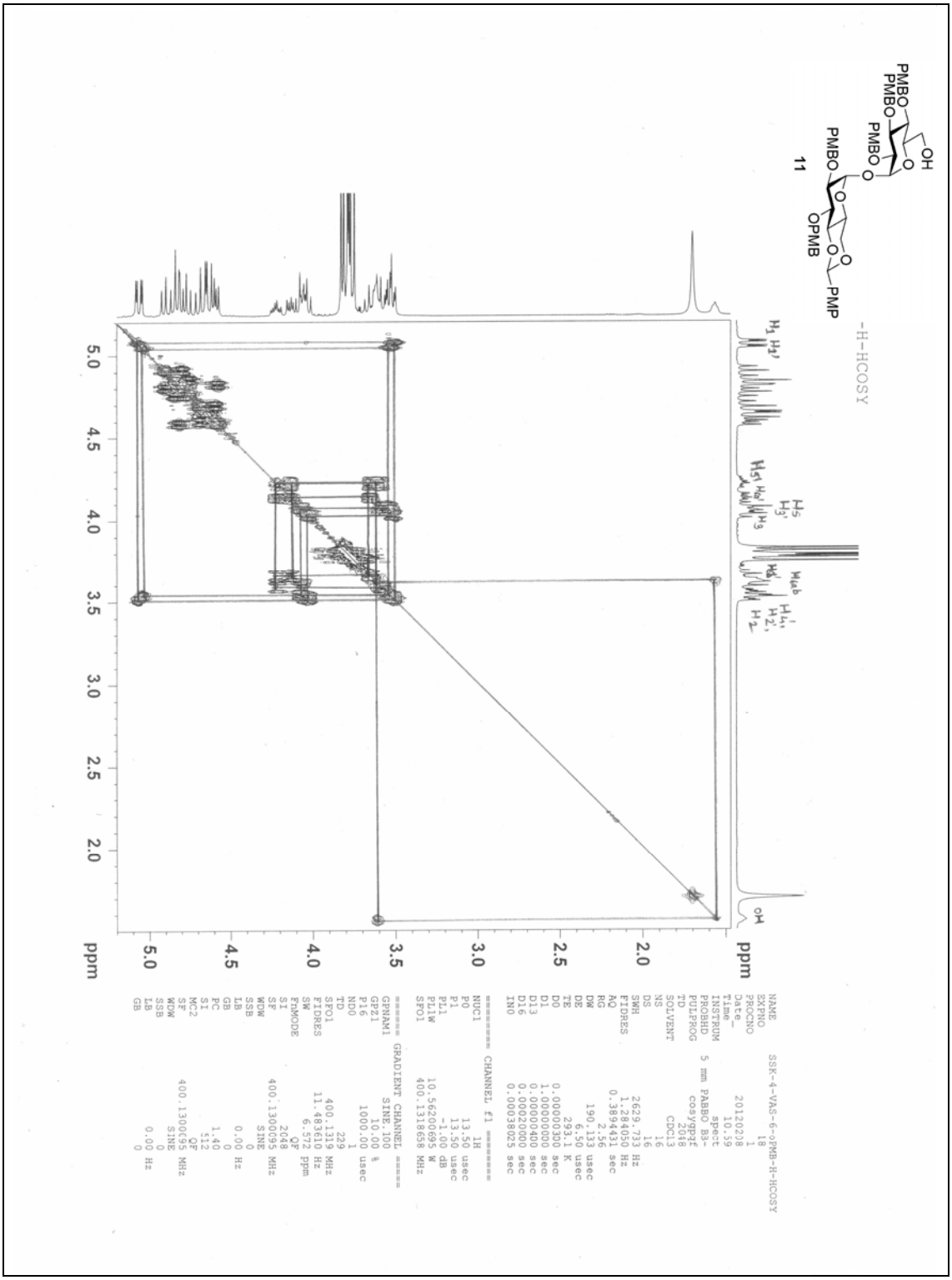

SSK-4-VAS-303-1H
PMP
PMBO
PMBO
PMBO
OPMB
PMP
10
4.66
9.76
4.74
8.16
2.00
1.96
2.25
4.30
2.16
2.37
4.27
6.71
6.77
6.24
6.88
12.76
ppm

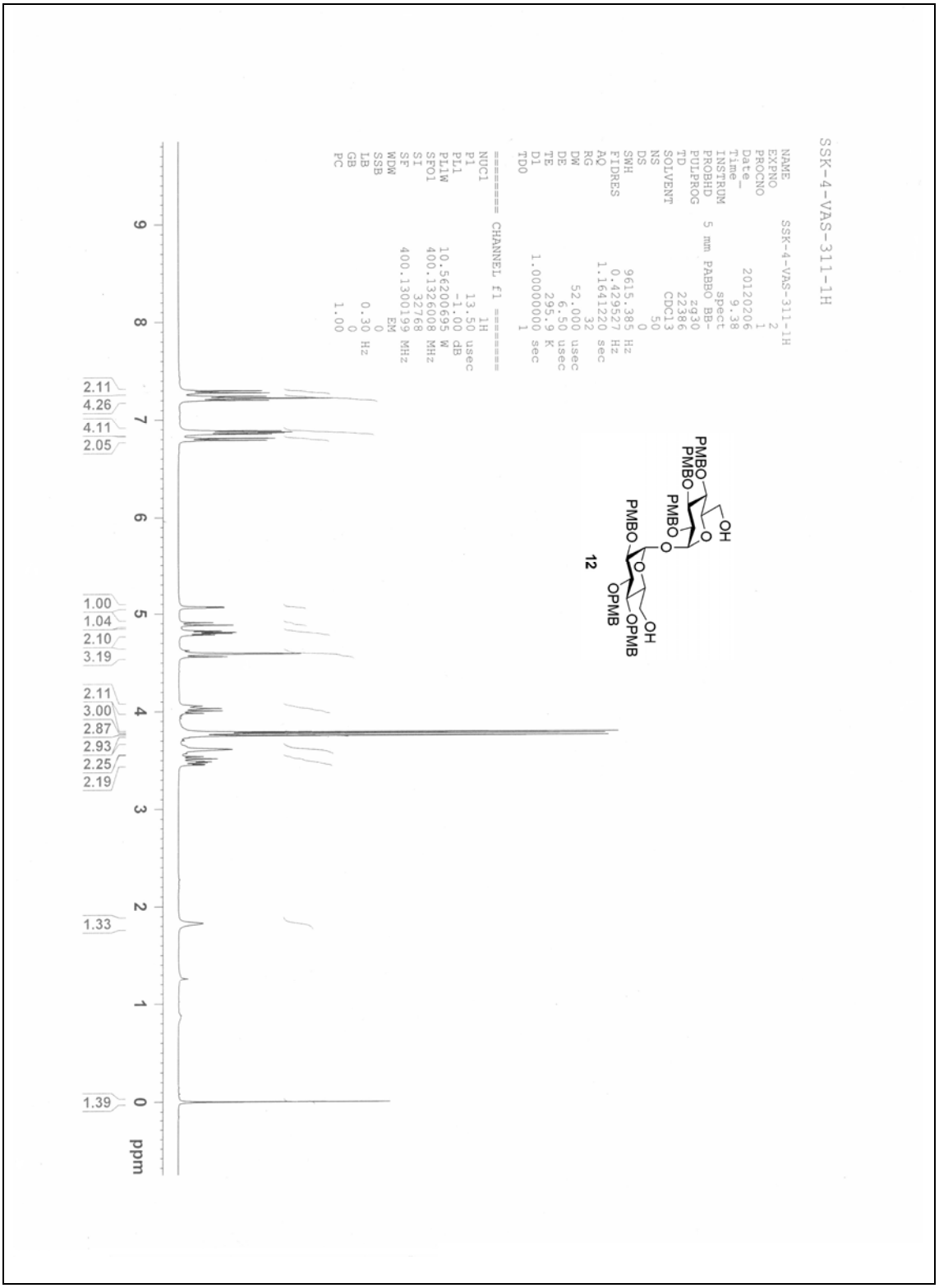

NAME SSK-4-VAS-303-13C
EXPNO 13
PROCNO 1
Date_ 20120201
Time_ 19.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 46
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.53121948 W
SFO1 100.622898 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 100.6127543 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160.12
159.39
159.31
131.21
130.35
130.31
129.79
129.57
127.61
114.04
113.88
113.67
101.35
94.73
82.45
78.57
77.52
77.40
77.20
76.88
75.19
73.59
69.15
63.07
55.47
55.41
55.35
0.17
PMP
PMBO
PMBO
PMBO
PMBO
OPMB
PMP
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

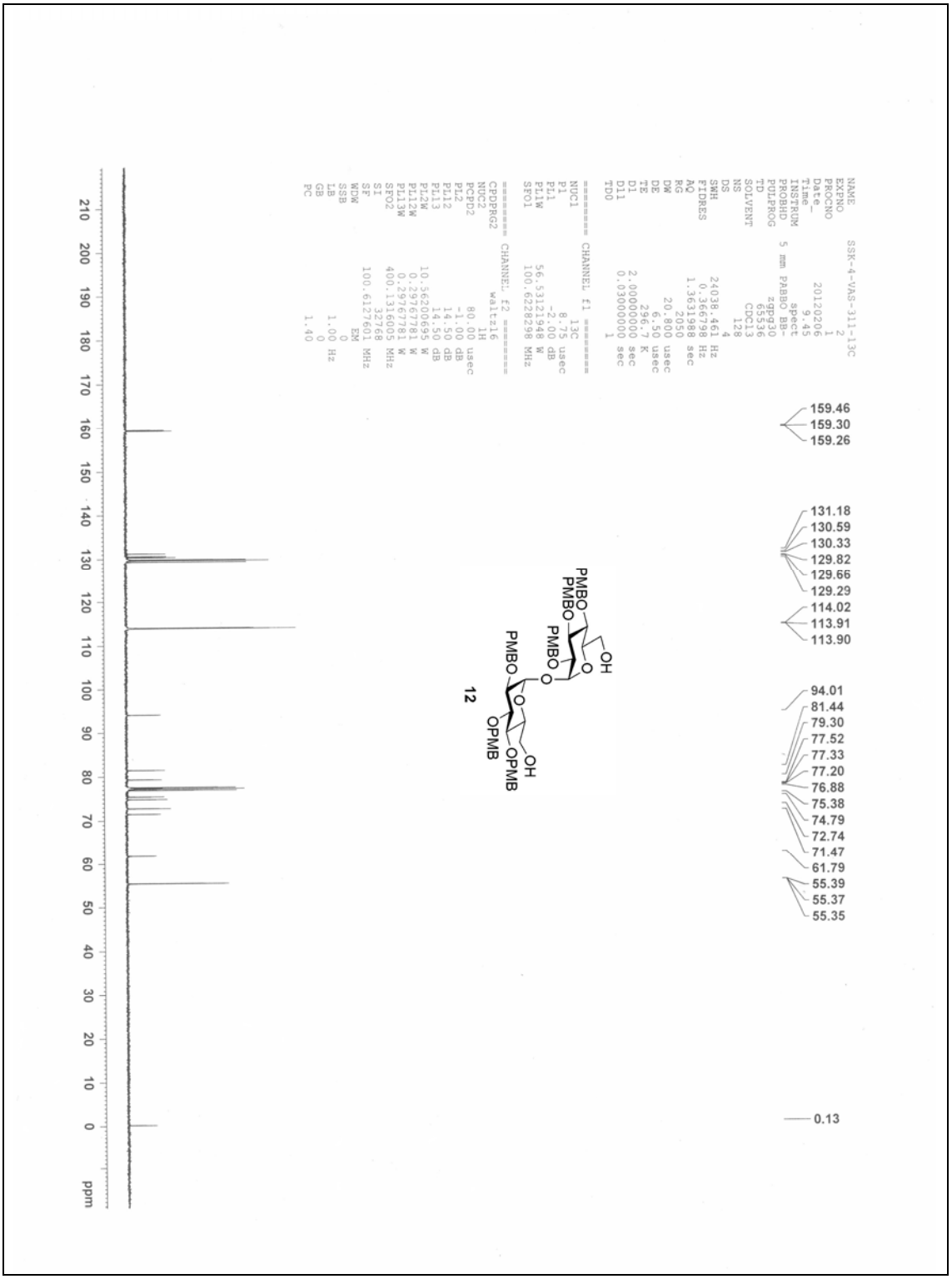

SSK-4-VAS-6-OH-PMB-1H
NAME SSK-4-VAS-6-OH-PMB-1H
EXPNO 1
PROCNO 1
Date_ 20120718
Time_ 18.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 80.6
DW 60.800 usec
DE 6.50 usec
TE 292.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PLIW 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300136 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
PMBO
PMBO
PMBO
OH
PMBO
OPMB
PMP
11
2.16
11.42
13.43
1.00
1.05
1.00
1.16
1.74
1.73
1.20
1.37
1.92
2.43
1.20
1.18
3.44
2.76
2.66
3.01
2.72
2.71
2.55
1.27
3.41
3.90
1.12
0.64
ppm

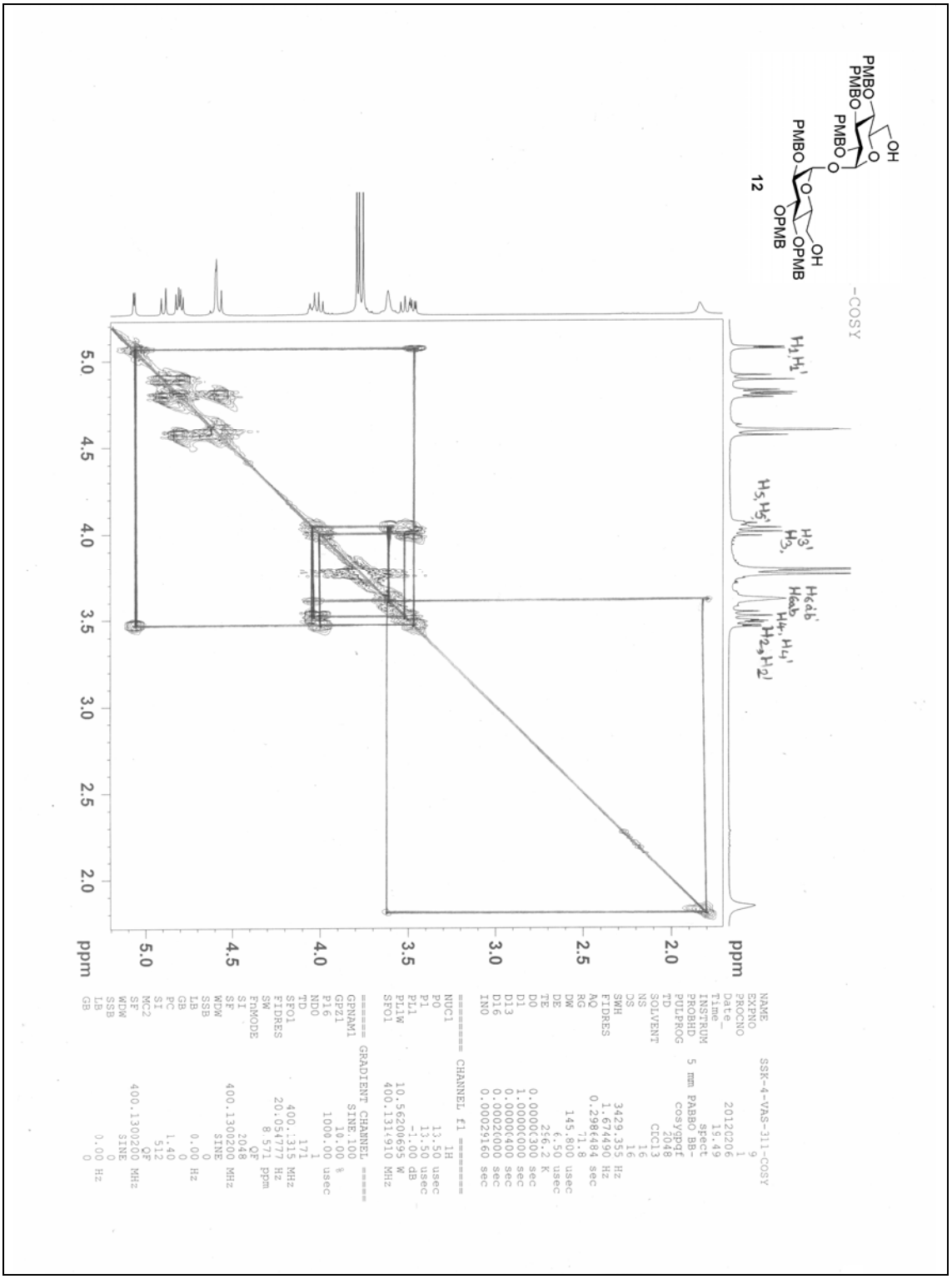

160.05
159.42
159.32
159.28
159.24
131.16
131.12
130.59
130.35
130.24
130.22
129.78
129.73
129.69
129.42
127.87
127.53
113.99
113.89
113.82
113.81
113.61
101.25
94.79
93.91
82.40
81.41
79.42
78.49
78.38
77.52
77.20
76.88
75.38
75.10
74.71
73.24
73.00
71.36
69.10
63.04
61.79
55.39
55.37
55.34
55.28
0.13
PMBO
PMBO
PMBO
PMBO
OH
OPMB
PMP
11
ppm

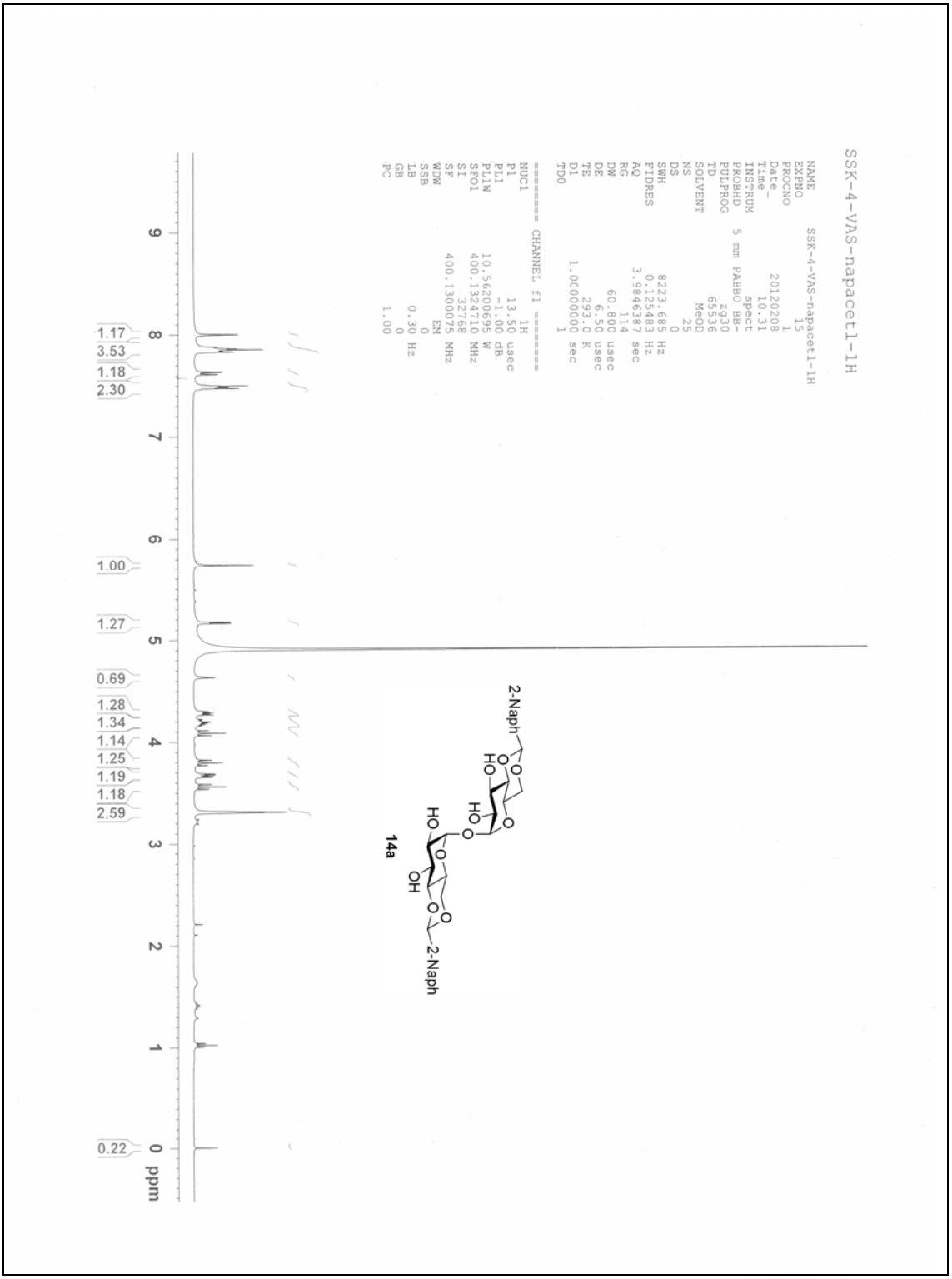

SSK-4-VAS-329-APT
11
PMBO
PMBO
PMBO
PMBO
OH
PMBO
OPMB
PMP
160.06
159.43
159.33
159.29
159.25
131.15
130.33
130.24
129.78
129.74
129.70
129.45
127.54
114.00
113.90
113.84
113.82
113.62
101.27
94.75
93.88
82.39
81.40
78.48
78.38
77.52
77.23
77.20
76.88
75.38
75.11
74.70
73.26
73.02
71.36
69.29
69.10
63.05
61.79
55.40
55.38
55.35
55.33
55.29
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

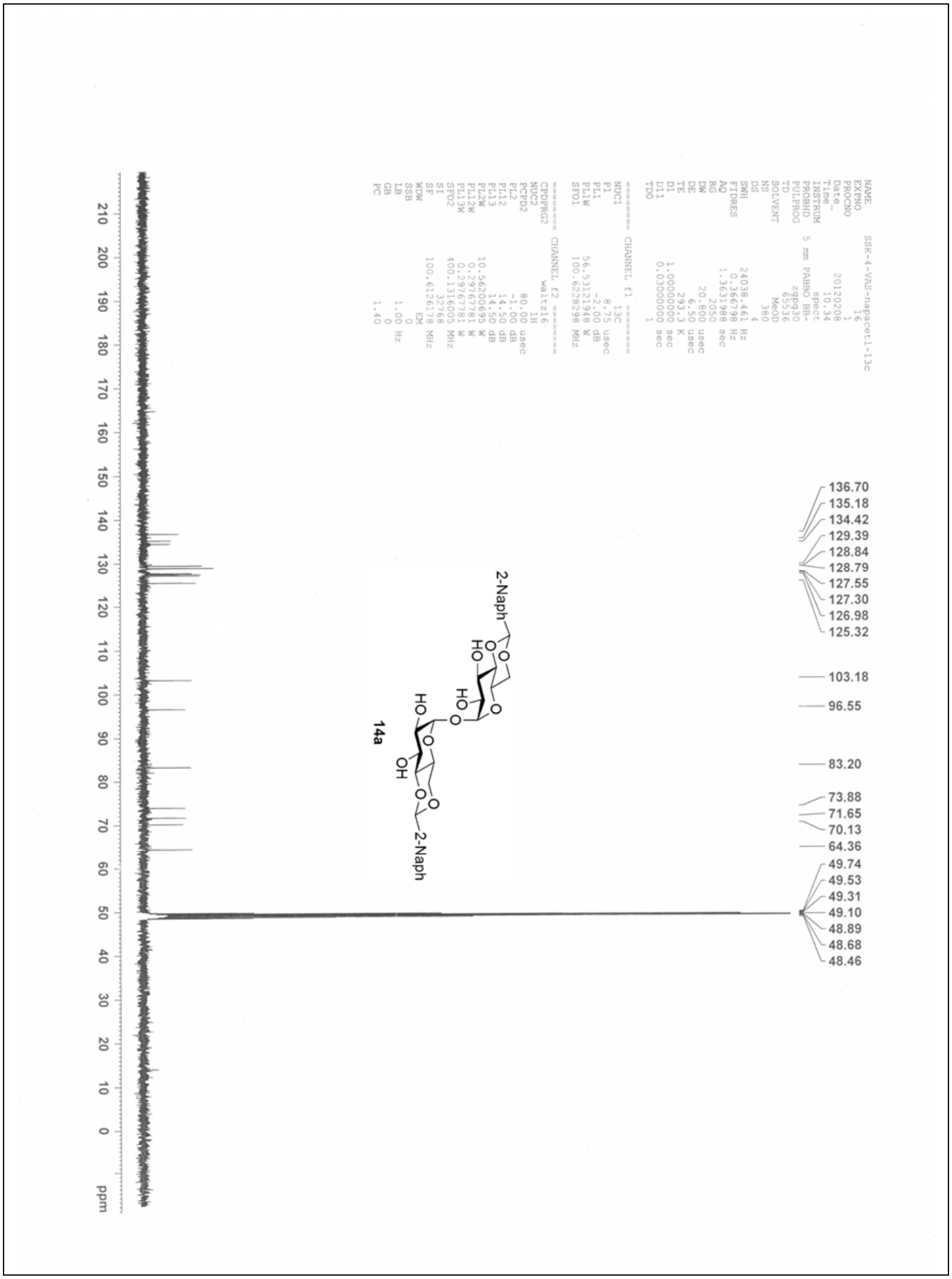

PMBO
PMBO
PMBO
PMBO
OH
OPMB
PMP
11
-H-HCOSY
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0

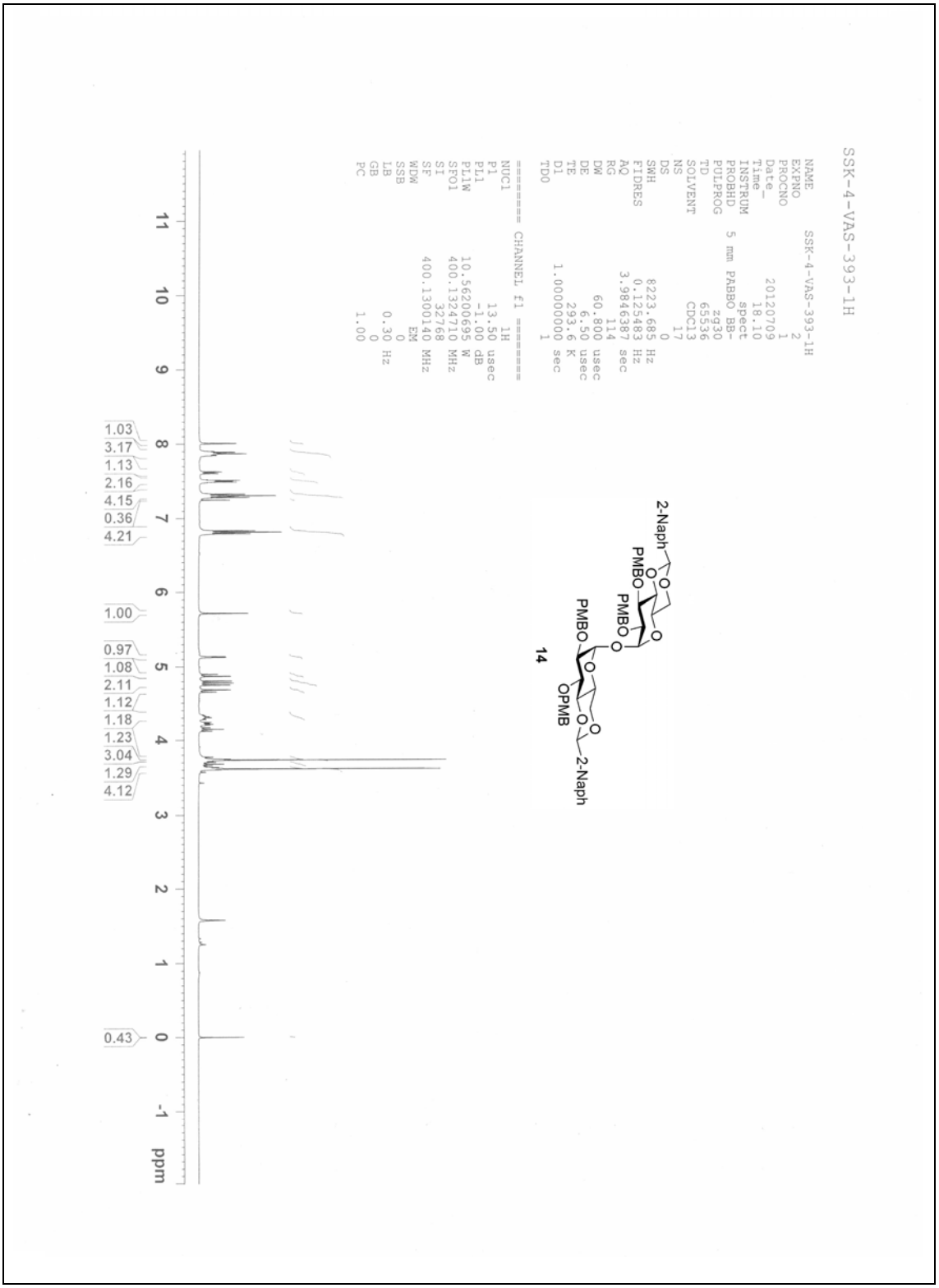

SSK-4-VAS-311-1H
NAME SSK-4-VAS-311-1H
EXPNO 2
PROCNO 1
Date_ 20120206
Time_ 9.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 22386
SOLVENT CDCl3
NS 50
DS 0
SWH 9615.385 Hz
FIDRES 0.429527 Hz
AQ 1.1641220 sec
RG 32
DW 52.000 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1326008 MHz
SI 32768
SF 400.1300199 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
PMBO
PMBO
PMBO
PMBO
OH
O
O
O
O
OPMB
OPMB
OH
12
2.11
4.26
4.11
2.05
1.00
1.04
2.10
3.19
2.11
3.00
2.87
2.93
2.25
2.19
1.33
1.39
9
8
7
6
5
4
3
2
1
0
ppm

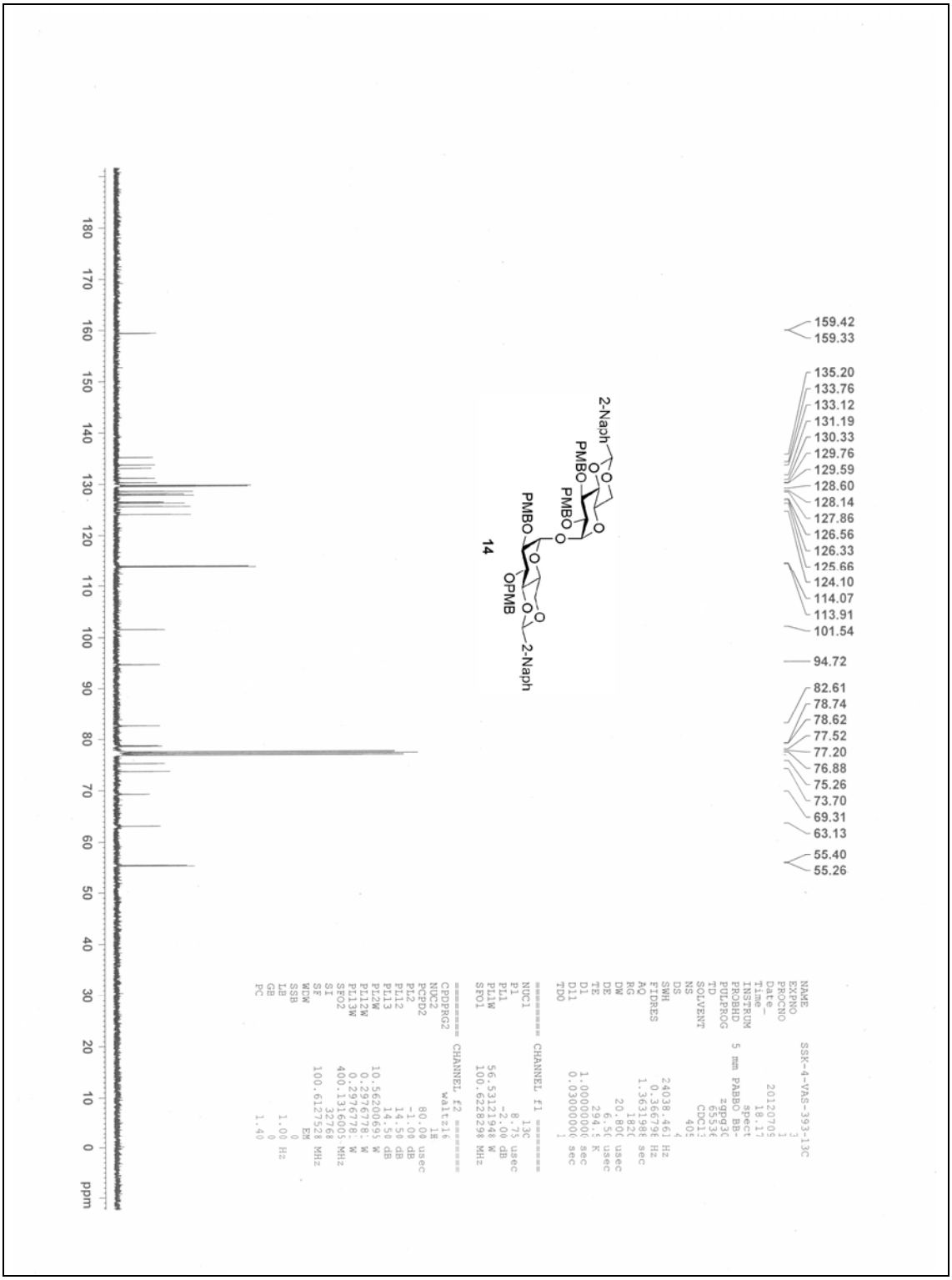

159.46
159.30
159.26
131.18
130.59
130.33
129.82
129.66
129.29
114.02
113.91
113.90
94.01
81.44
79.30
77.52
77.33
77.20
76.88
75.38
74.79
72.74
71.47
61.79
55.39
55.37
55.35
0.13
PMBO
PMBO
PMBO
PMBO
OH
OH
OPMB
OPMB
O
O
O
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

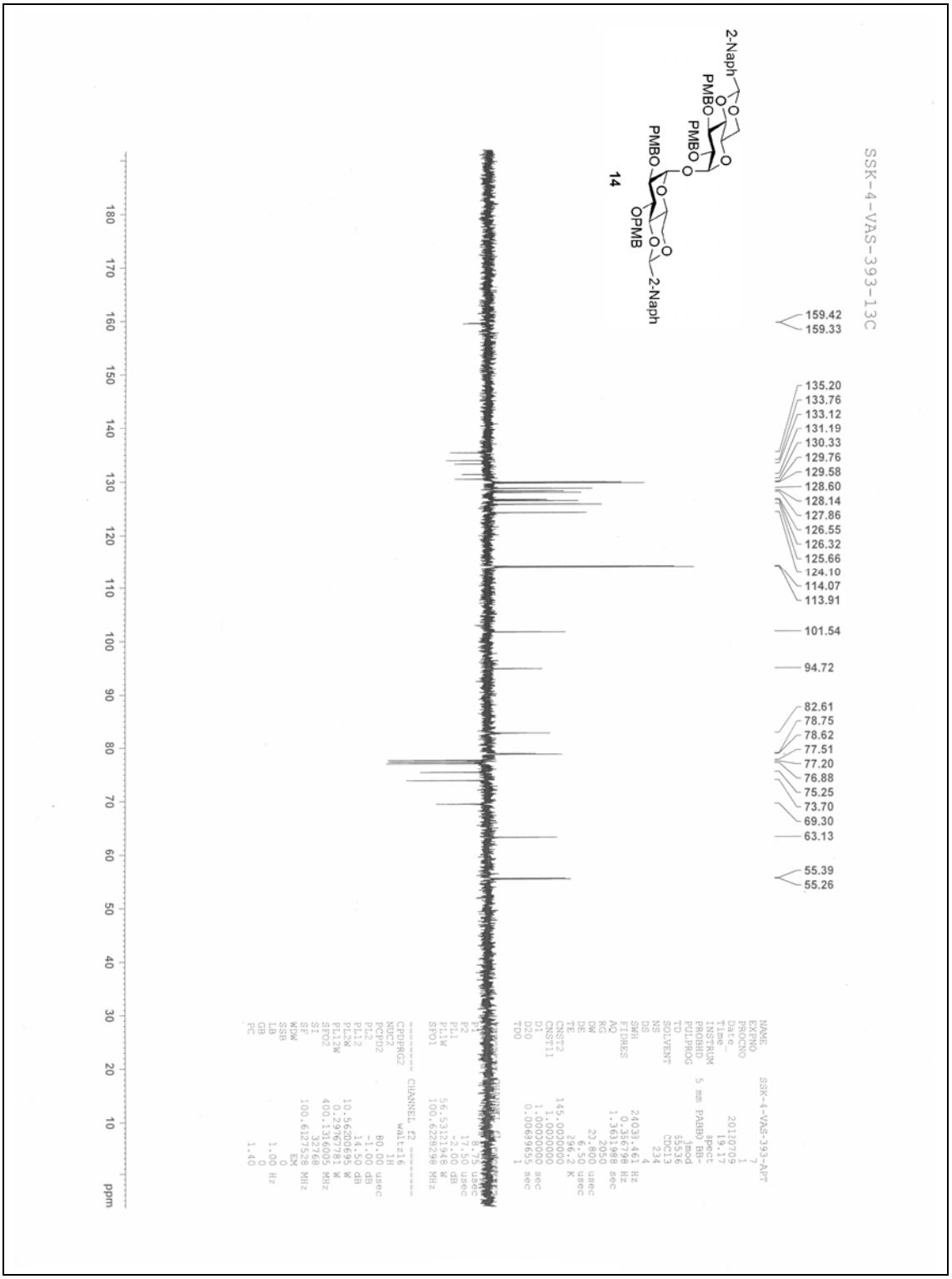

PMBO
PMBO
PMBO
PMBO
OH
O
PMBO
O
OPMB
OH
OPMB
12
-COSY
H1,H1'
H5,H5'
H3'
H3,
H6ab'
H6ab
H4, H4'
H2,H2'
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm

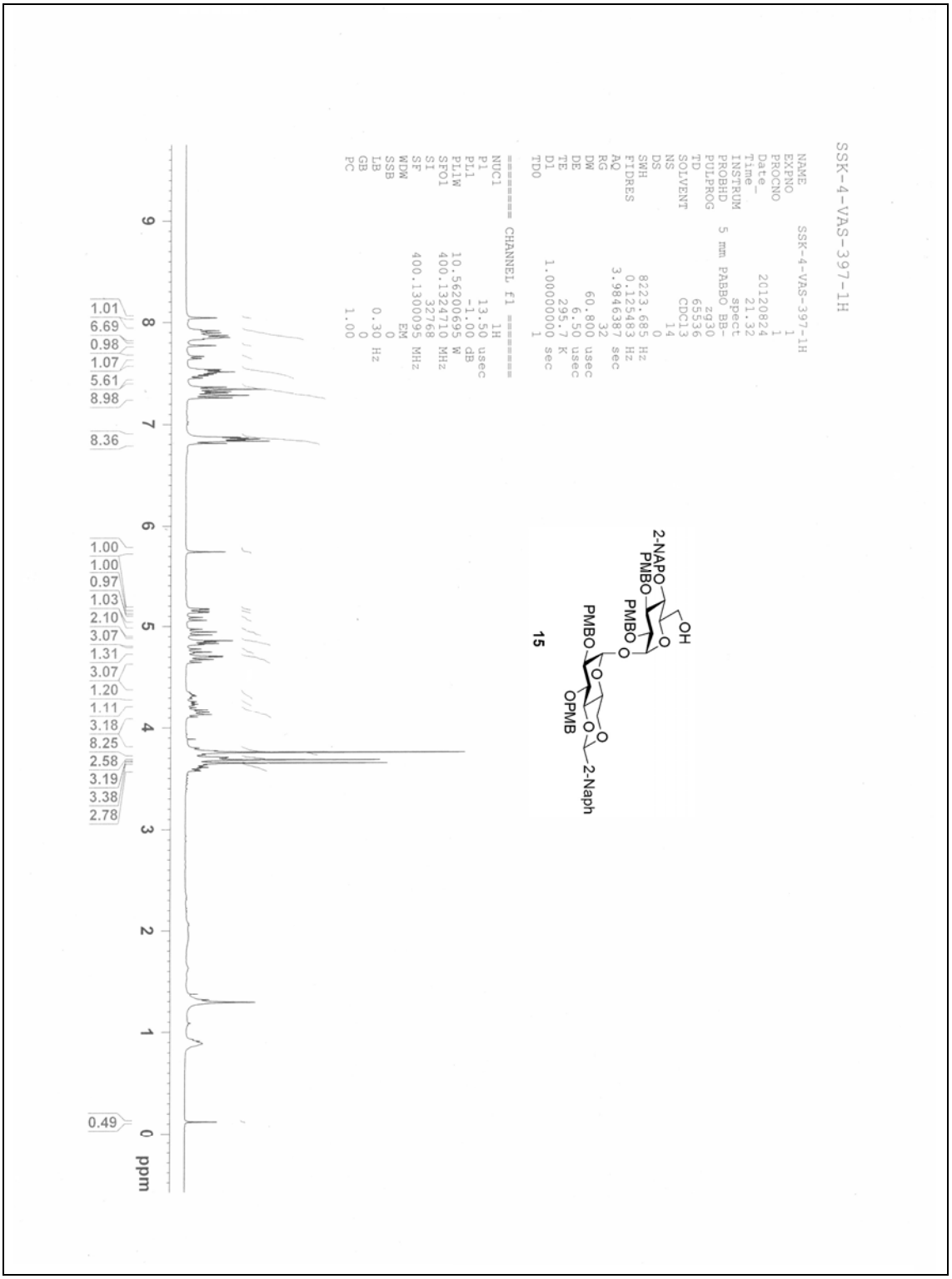

SSK-4-VAS-napacetl-1H
NAME SSK-4-VAS-napacetl-1H
EXPNO 19
PROCNO 1
Date_ 20120208
Time 10.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 25
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 293.0 K
D1 1.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.17
3.53
1.18
2.30
1.00
1.27
0.69
1.28
1.34
1.14
1.25
1.19
1.18
2.59
0.22
9
8
7
6
5
4
3
2
1
0
ppm
2-Naph
HO
HO
HO
HO
OH
2-Naph
14a

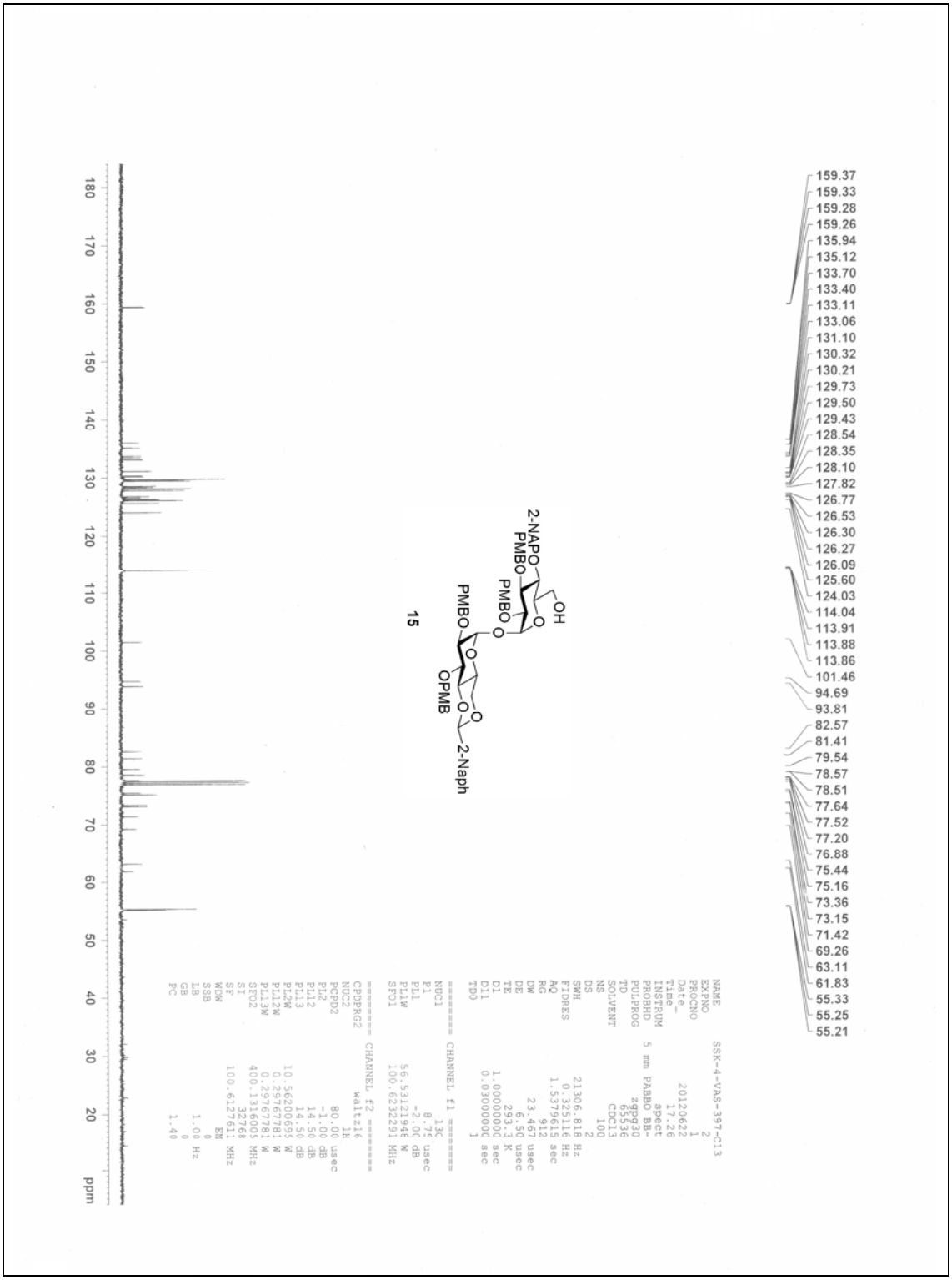

136.70
135.18
134.42
129.39
128.84
128.79
127.55
127.30
126.98
125.32
103.18
96.55
83.20
73.88
71.65
70.13
64.36
49.74
49.53
49.31
49.10
48.89
48.68
48.46
2-Naph
14a
ppm

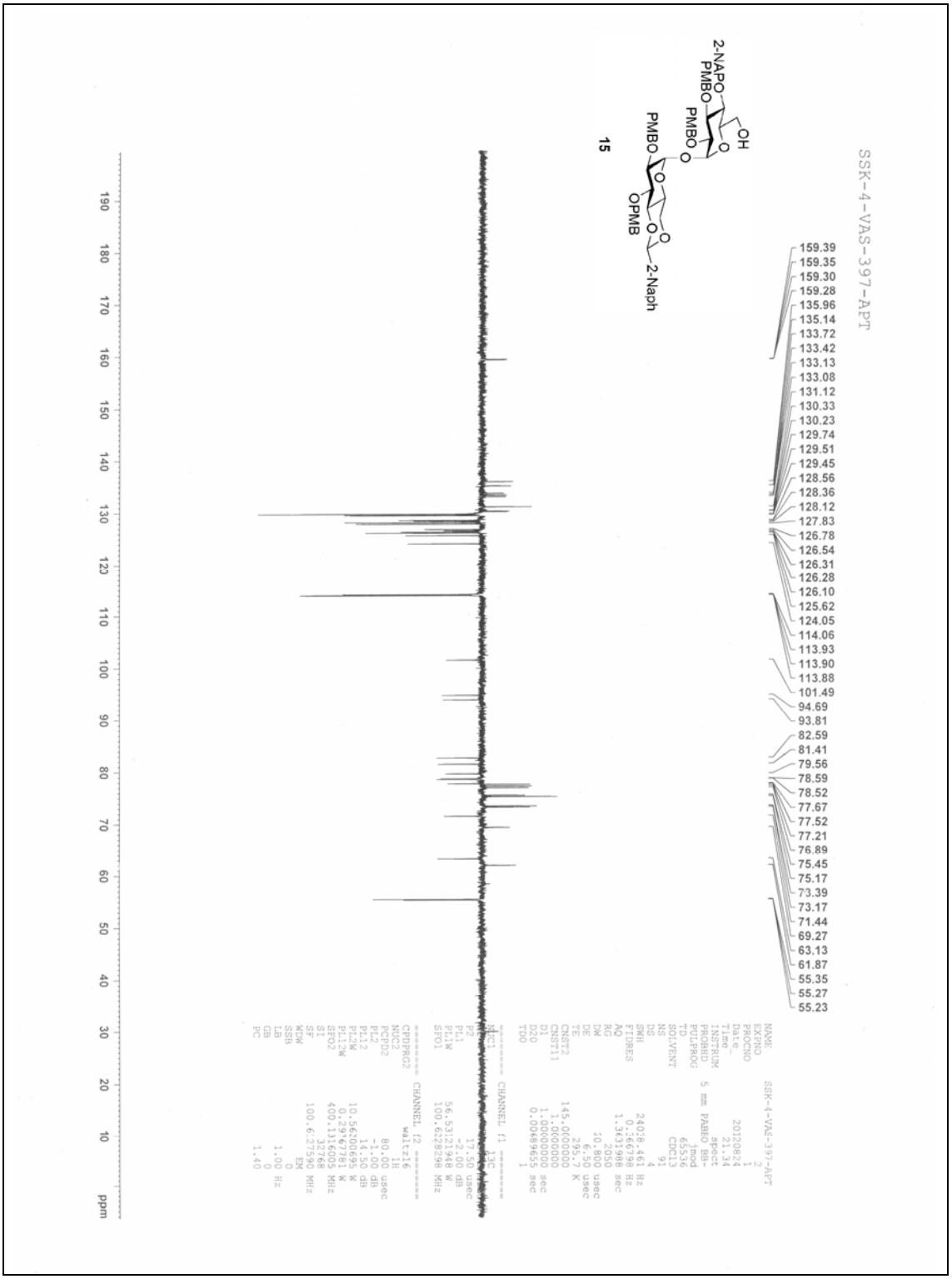

SSK-4-VAS-393-1H
NAME SSK-4-VAS-393-1H
EXPNO 2
PROCNO 1
Date_ 20120709
Time_ 18.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 293.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
2-Naph
PMBO
PMBO
PMBO
OPMB
2-Naph
14
1.03
3.17
1.13
2.16
4.15
0.36
4.21
1.00
0.97
1.08
2.11
1.12
1.18
1.23
3.04
1.29
4.12
0.43
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

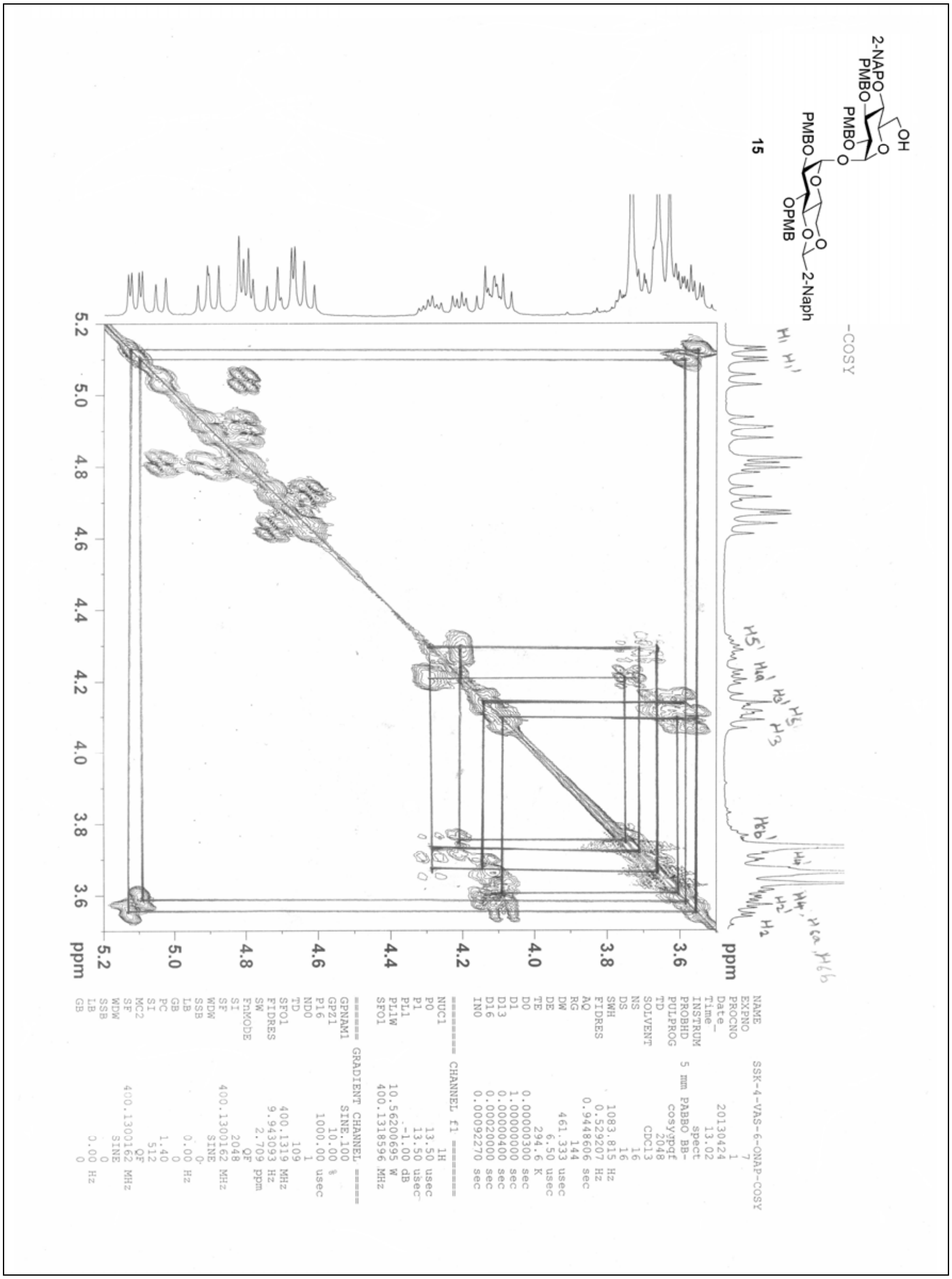

2-Naph
PMBO
PMBO
PMBO
OPMB
2-Naph
14
159.42
159.33
135.20
133.76
133.12
131.19
130.33
129.76
129.59
128.60
128.14
127.86
126.56
126.33
125.66
124.10
114.07
113.91
101.54
94.72
82.61
78.74
78.62
77.52
77.20
76.88
75.26
73.70
69.31
63.13
55.40
55.26
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

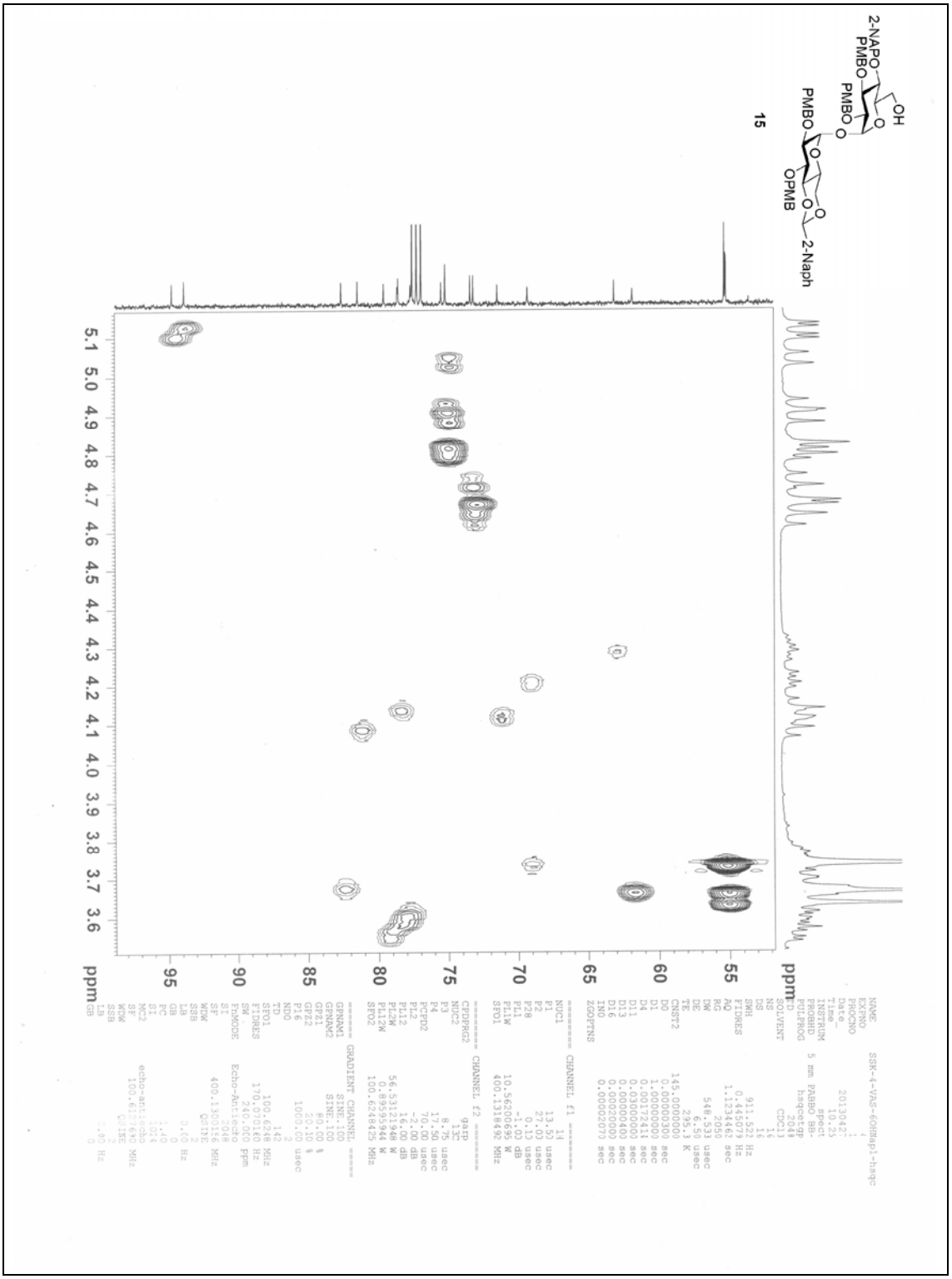

SSK-4-VAS-393-13C
2-Naph
PMBO
PMBO
PMBO
OPMB
2-Naph
14
159.42
159.33
135.20
133.76
133.12
131.19
130.33
129.76
129.58
128.60
128.14
127.86
126.55
126.32
125.66
124.10
114.07
113.91
101.54
94.72
82.61
78.75
78.62
77.51
77.20
76.88
75.25
73.70
69.30
63.13
55.39
55.26
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

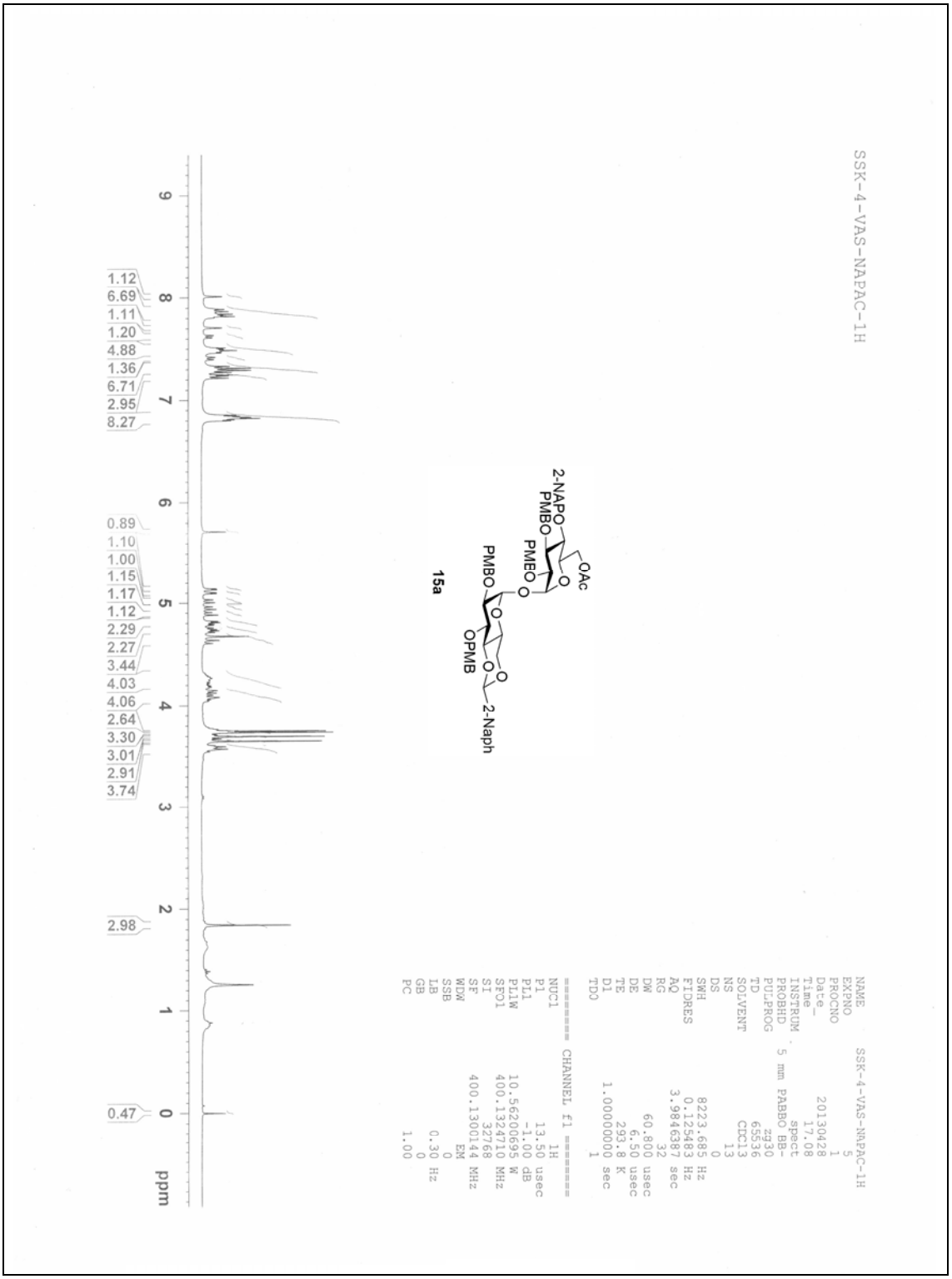

SSK-4-VAS-397-1H
NAME SSK-4-VAS-397-1H
EXPNO 1
PROCNO 1
Date_ 20120824
Time_ 21.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 14
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.01
6.69
0.98
1.07
5.61
8.98
8.36
1.00
1.00
0.97
1.03
2.10
3.07
1.31
3.07
1.20
1.11
3.18
8.25
2.58
3.19
3.38
2.78
0.49
9
8
7
6
5
4
3
2
1
0
ppm
2-NAPO
PMBO
PMBO
PMBO
OPMB
OH
2-Naph
15

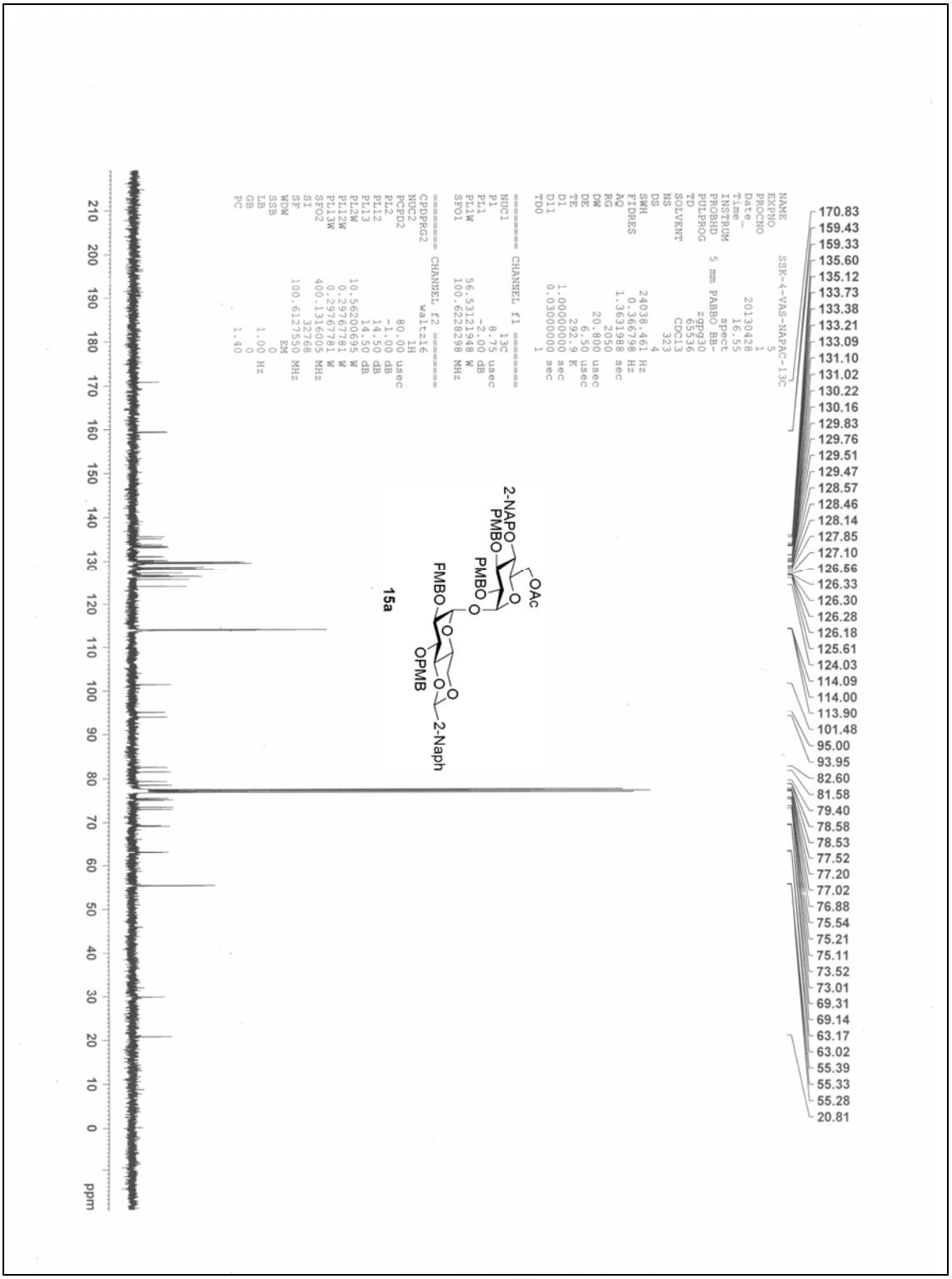

159.37
159.33
159.28
159.26
135.94
135.12
133.70
133.40
133.11
133.06
131.10
130.32
130.21
129.73
129.50
129.43
128.54
128.35
128.10
127.82
126.77
126.53
126.30
126.27
126.09
125.60
124.03
114.04
113.91
113.88
113.86
101.46
94.69
93.81
82.57
81.41
79.54
78.57
78.51
77.64
77.52
77.20
76.88
75.44
75.16
73.36
73.15
71.42
69.26
63.11
61.83
55.33
55.25
55.21
2-NAPO
PMBO
PMBO
OH
PMBO
OPMB
2-Naph
15
NAME SSK-4-VAS-397-C13
EXPNO 2
PROCNO 1
Date_ 20120622
Time_ 17.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 100
DS 2
SWH 21306.816 Hz
FIDRES 0.325216 Hz
AQ 1.5378613 sec
RG 203
DW 23.460 usec
DE 25.50 usec
TE 298.0 K
D1 1.0000000 sec
D11 0.0300000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13c
P1 8.75 usec
PL1 -2.06 dB
PL1W 56.53121946 W
SFO1 100.6232291 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 100.6127617 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

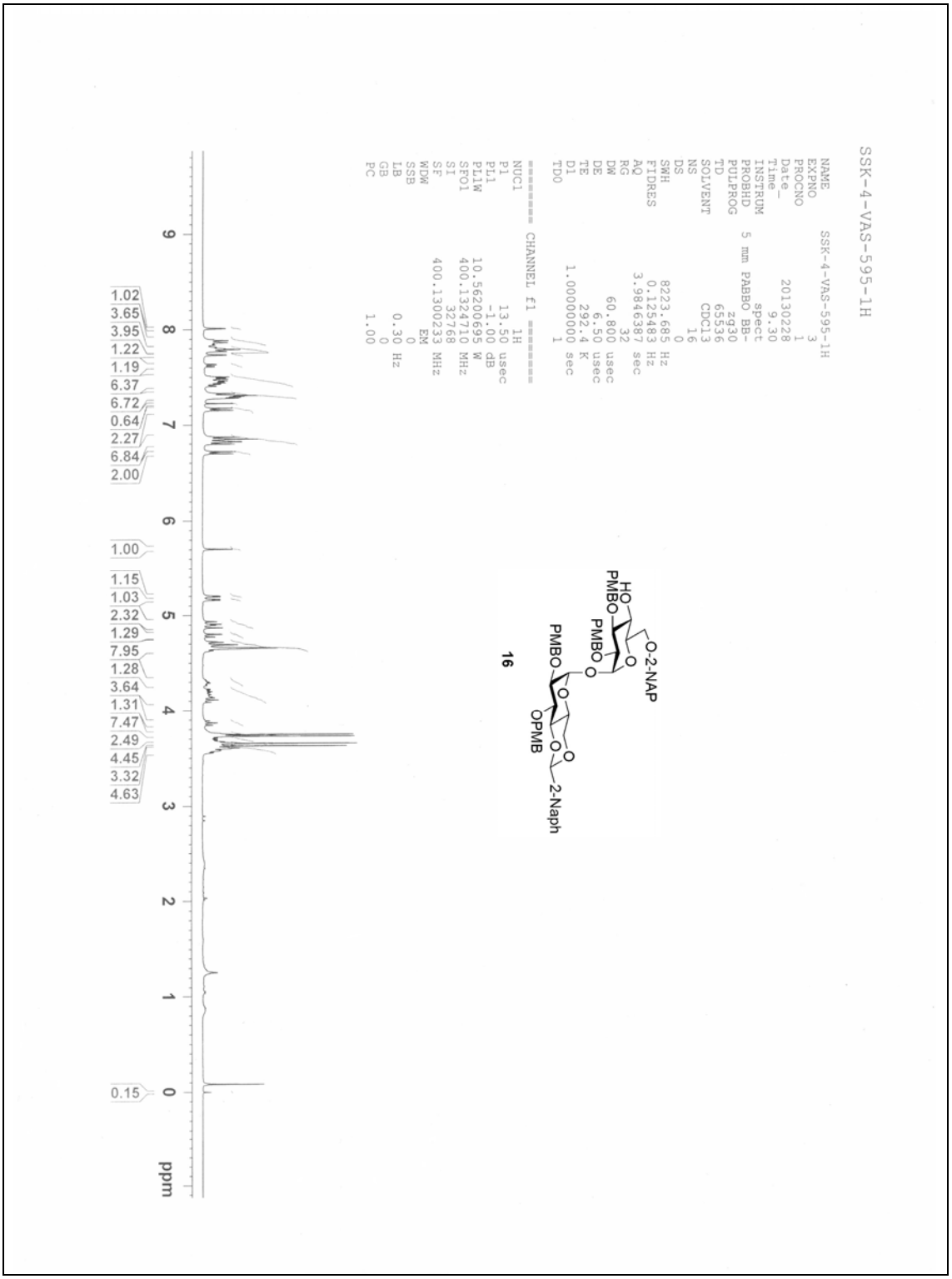

SSK-4-VAS-397-APT
15
2-NAPO
PMBO
PMBO
OH
PMBO
OPMB
2-Naph
159.39
159.35
159.30
159.28
135.96
135.14
133.72
133.42
133.13
133.08
131.12
130.33
130.23
129.74
129.51
129.45
128.56
128.36
128.12
127.83
126.78
126.54
126.31
126.28
126.10
125.62
124.05
114.06
113.93
113.90
113.88
101.49
94.69
93.81
82.59
81.41
79.56
78.59
78.52
77.67
77.52
77.21
76.89
75.45
75.17
73.39
73.17
71.44
69.27
63.13
61.87
55.35
55.27
55.23
NAME SSK-4-VAS-397-APT
EXPNO 2
PROCNO 1
Date_ 20120824
Time 21.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 91
DS 4
SWH 24038.461 Hz
FIDRES 0.366799 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.7 K
CNST2 145.0000000
CNST11 100.0000000
D1 1.0000000 sec
D20 0.00689655 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P2 17.50 usec
PL1 -2.00 dB
PL1W 56.53125748 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.50 dB
PL2W 10.56600695 W
PL12W 0.29767781 W
SFO2 400.1316005 MHz
SF 100.6275596 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
190 180 170 160 150 140 130 122 110 100 90 80 70 60 50 40 30 20 10 ppm

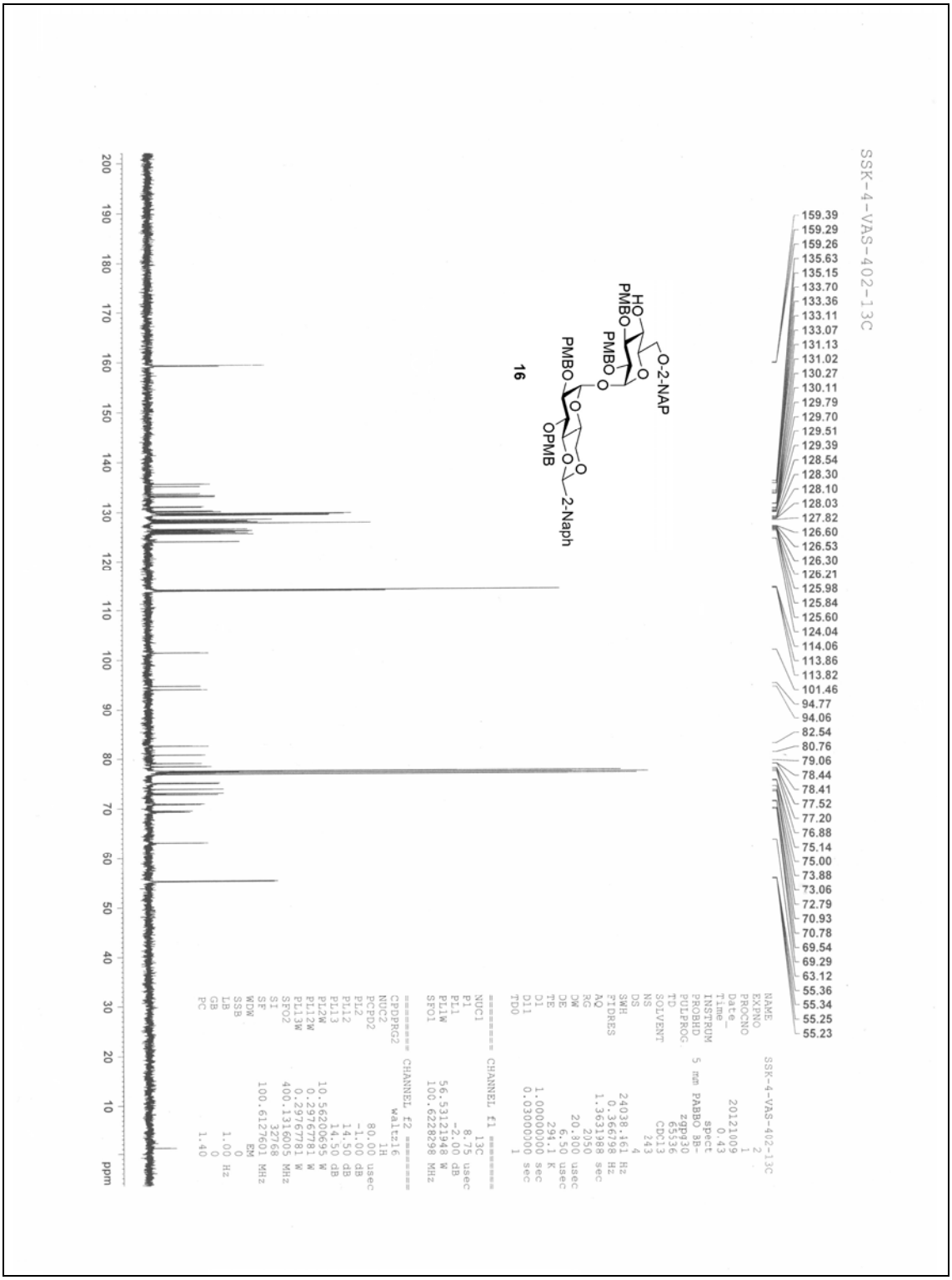

2-NAPO
PMBO
PMBO
PMBO
OH
OPMB
2-Naph
15
-COSY
ppm
SSK-4-VAS-6-ONAP-COSY

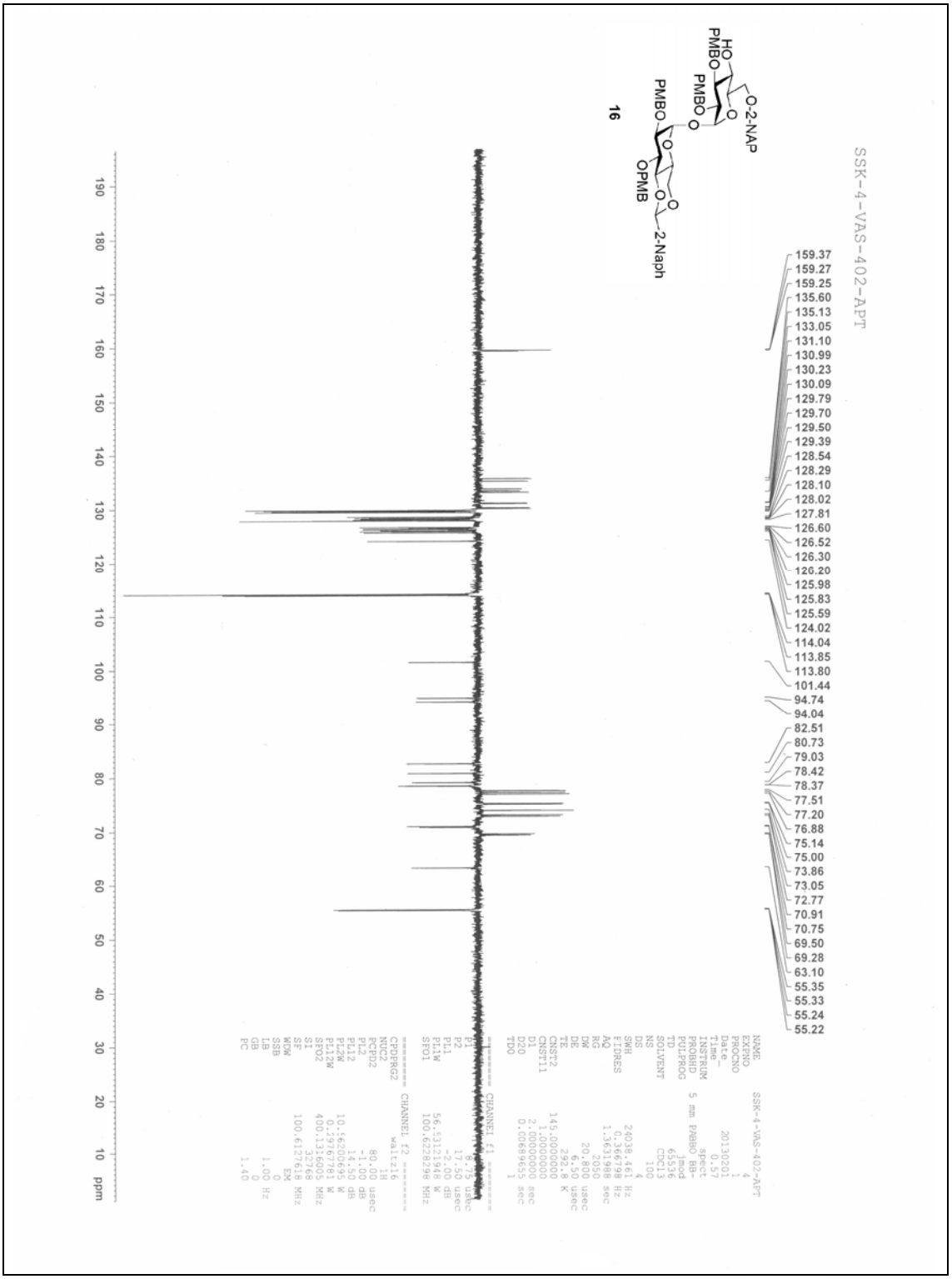

2-NAPO
PMBO
PMBO
OH
PMBO
OPMB
2-Naph
15
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6
ppm
95
90
85
80
75
70
65
60
55
ppm

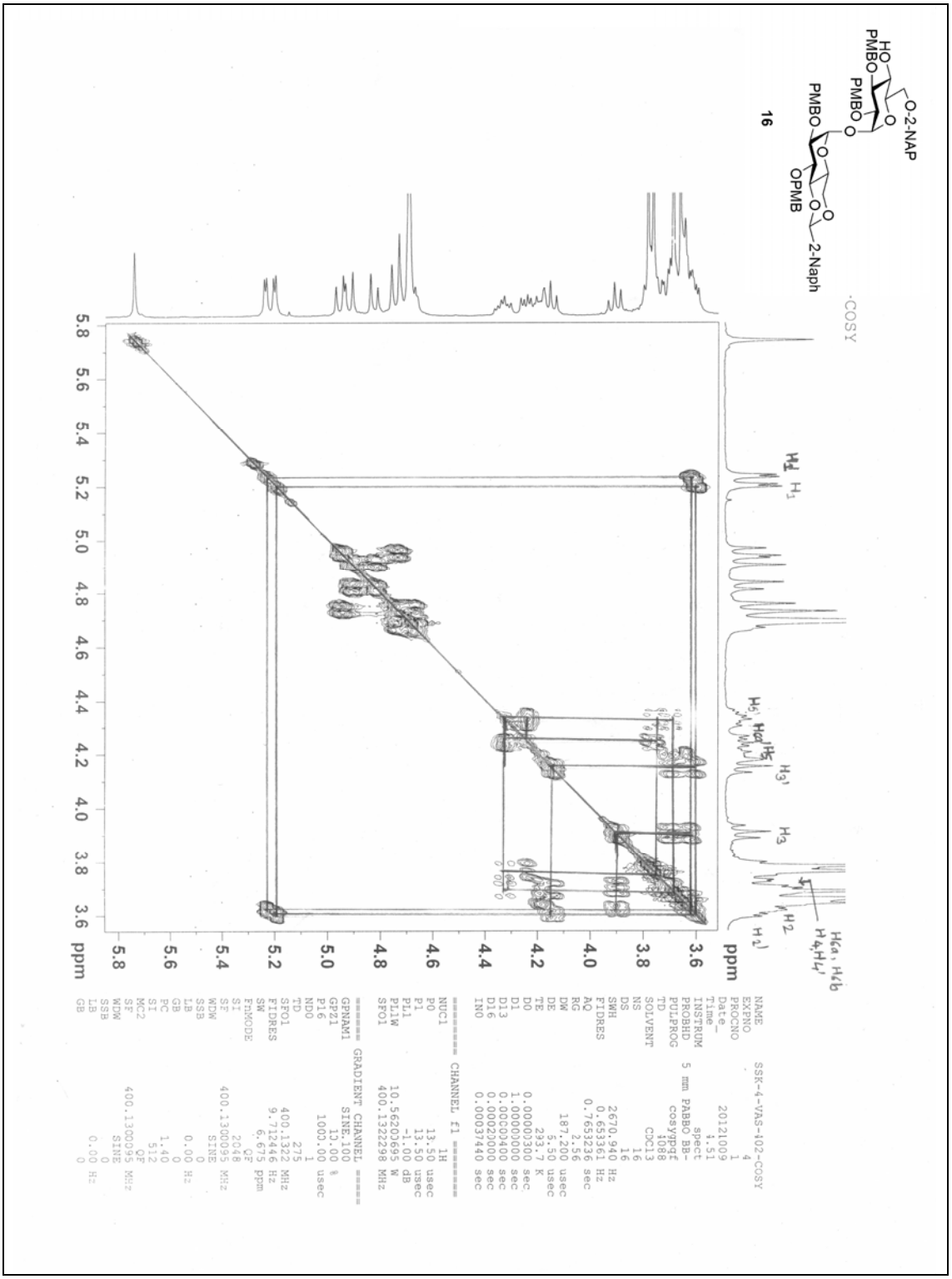

SSK-4-VAS-NAPAC-1H
2-NAPO
PMBO
PMEO
OAc
PMBO
OPMB
2-Naph
15a
NAME SSK-4-VAS-NAPAC-1H
EXPNO 5
PROCNO 1
Date_ 20130428
Time 17.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 293.8 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PLIW 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300144 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.12
6.69
1.11
1.20
4.88
1.36
6.71
2.95
8.27
0.89
1.10
1.00
1.15
1.17
1.12
2.29
2.27
3.44
4.03
4.06
2.64
3.30
3.01
2.91
3.74
2.98
0.47
9
8
7
6
5
4
3
2
1
0
ppm

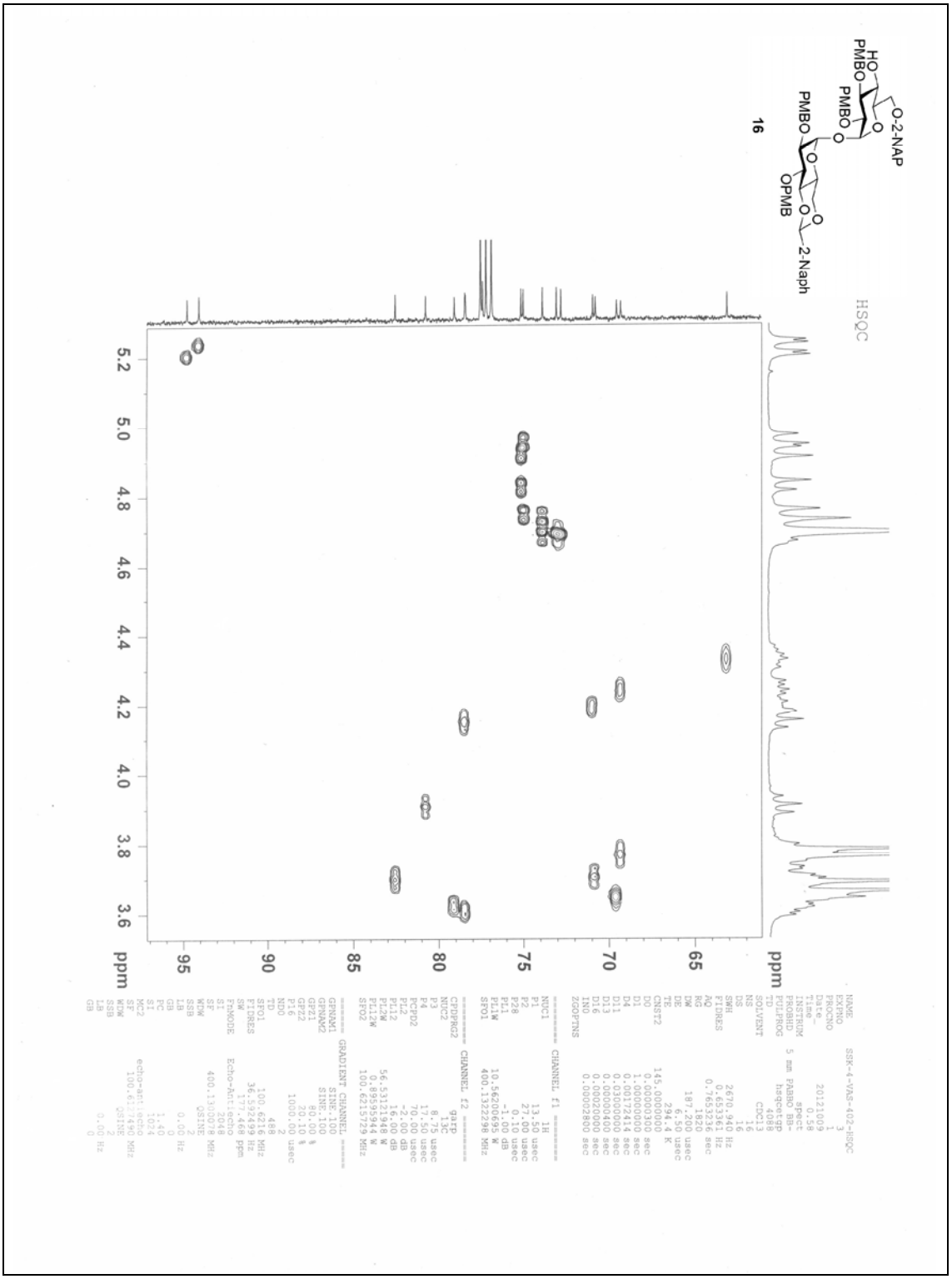


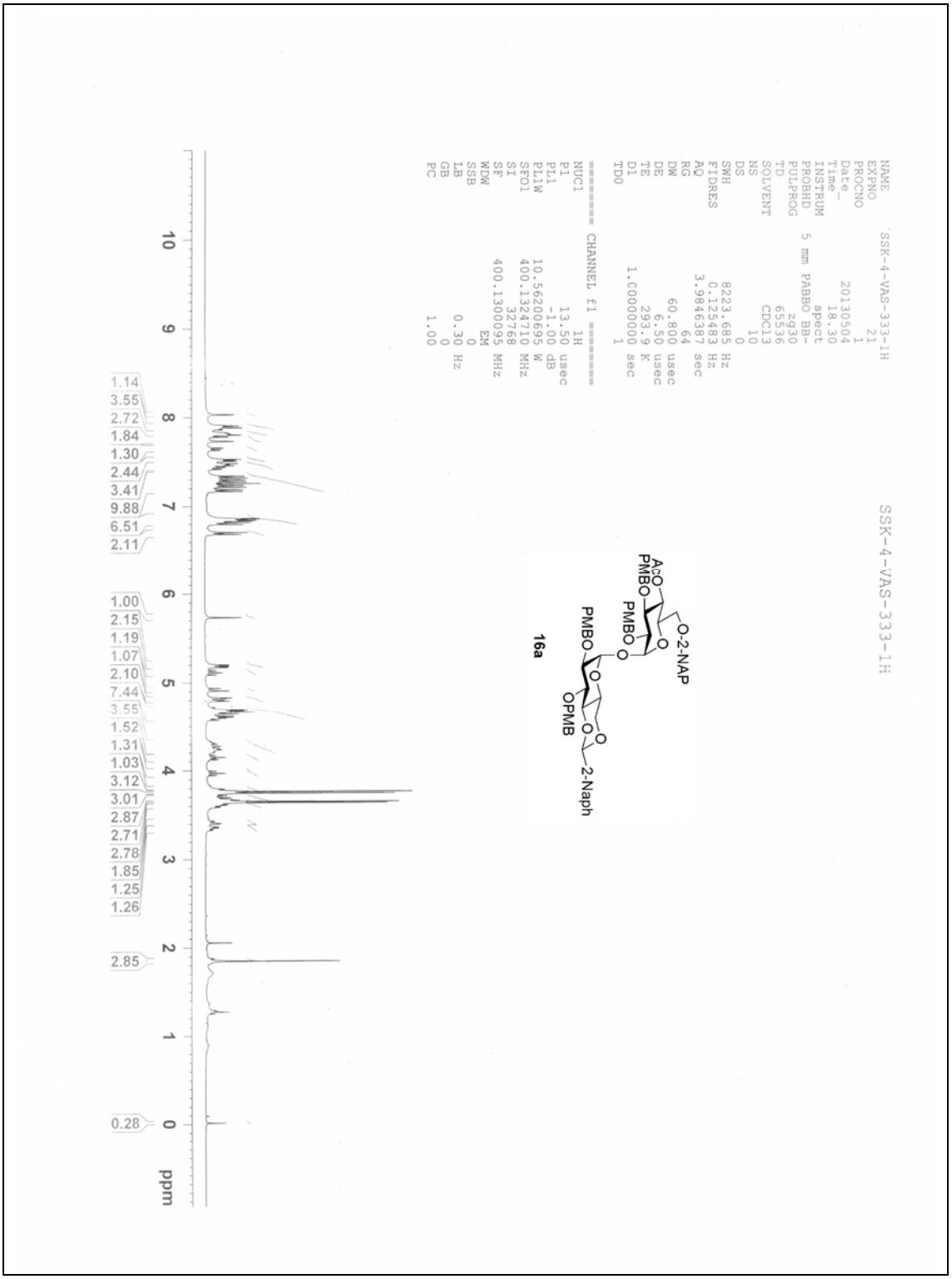


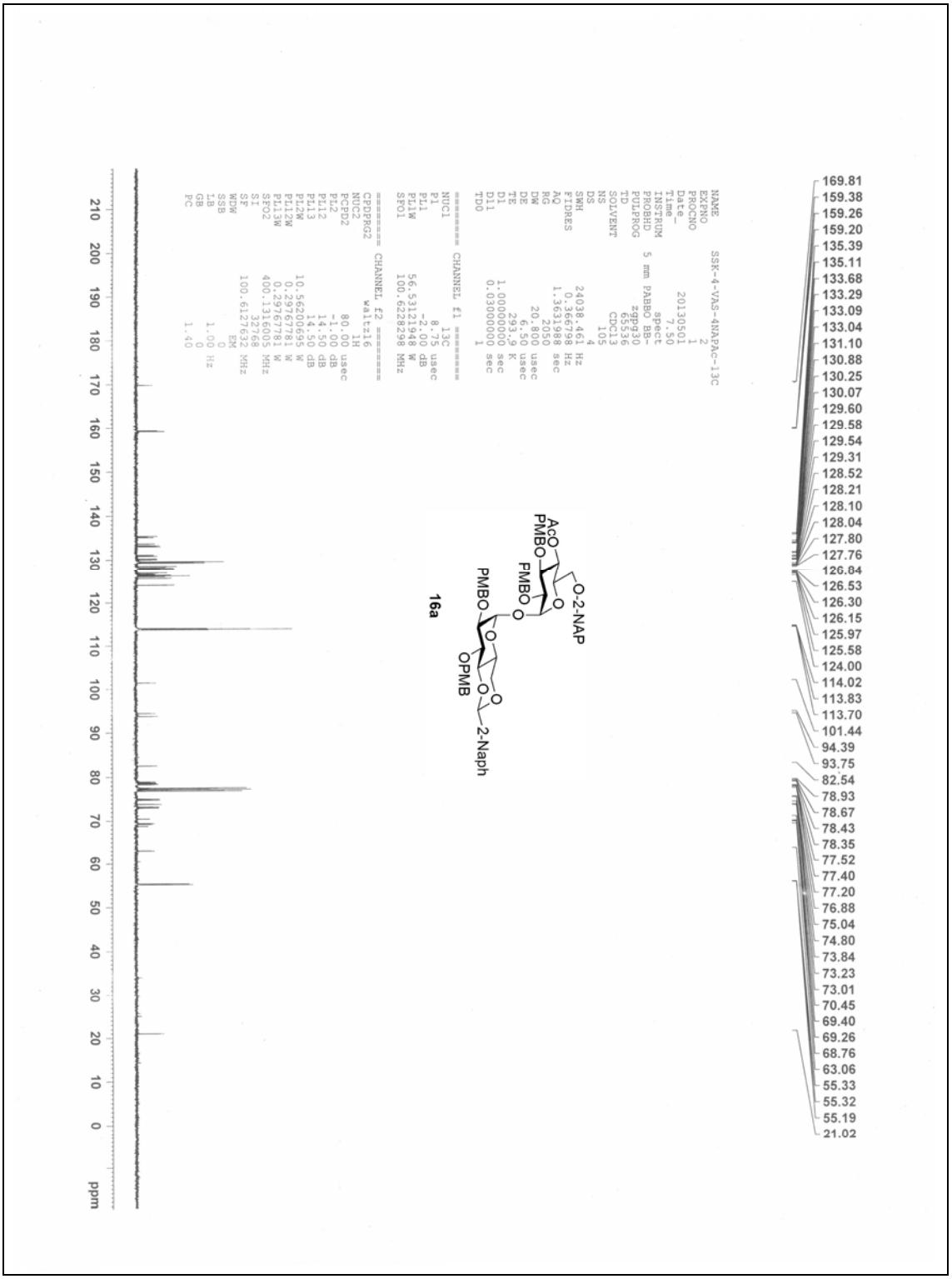

SSK-4-VAS-402-13C
159.39
159.29
159.26
135.63
135.15
133.70
133.36
133.11
133.07
131.13
131.02
130.27
130.11
129.79
129.70
129.51
129.39
128.54
128.30
128.10
128.03
127.82
126.60
126.53
126.30
126.21
125.98
125.84
125.60
124.04
114.06
113.86
113.82
101.46
94.77
94.06
82.54
80.76
79.06
78.44
78.41
77.52
77.20
76.88
75.14
75.00
73.88
73.06
72.79
70.93
70.78
69.54
69.29
63.12
55.36
55.34
55.25
55.23
HO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
16
NAME SSK-4-VAS-402-13C
EXPNO 2
PROCNO 1
Date_ 20121009
Time_ 0.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 243
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 294.1 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 100.622898 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 100.6127601 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

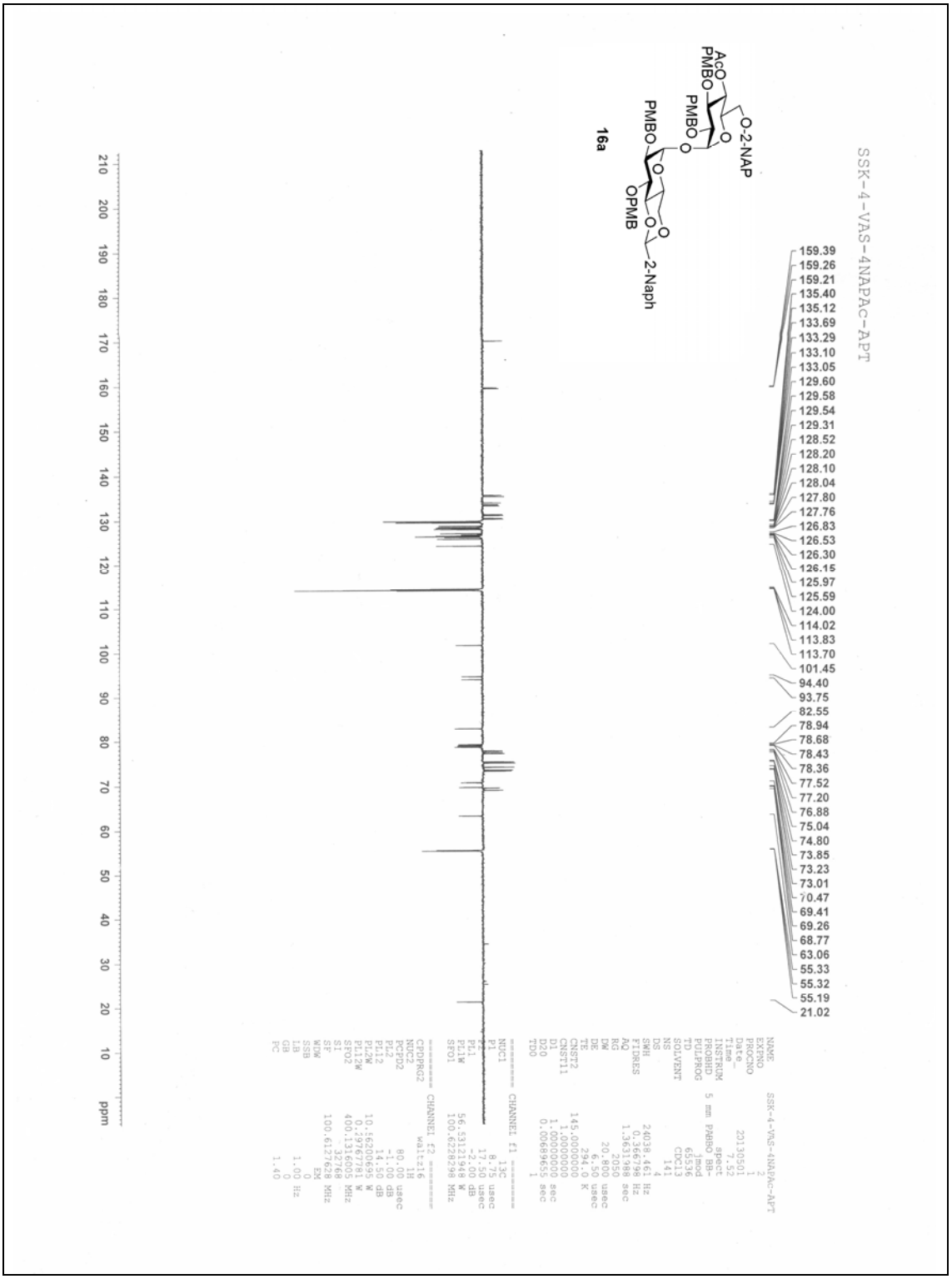

SSK-4-VAS-402-APT
16
HO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
159.37
159.27
159.25
135.60
135.13
133.05
131.10
130.99
130.23
130.09
129.79
129.70
129.50
129.39
128.54
128.29
128.10
128.02
127.81
126.60
126.52
126.30
126.20
125.98
125.83
125.59
124.02
114.04
113.85
113.80
101.44
94.74
94.04
82.51
80.73
79.03
78.42
78.37
77.51
77.20
76.88
75.14
75.00
73.86
73.05
72.77
70.91
70.75
69.50
69.28
63.10
55.35
55.33
55.24
55.22
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

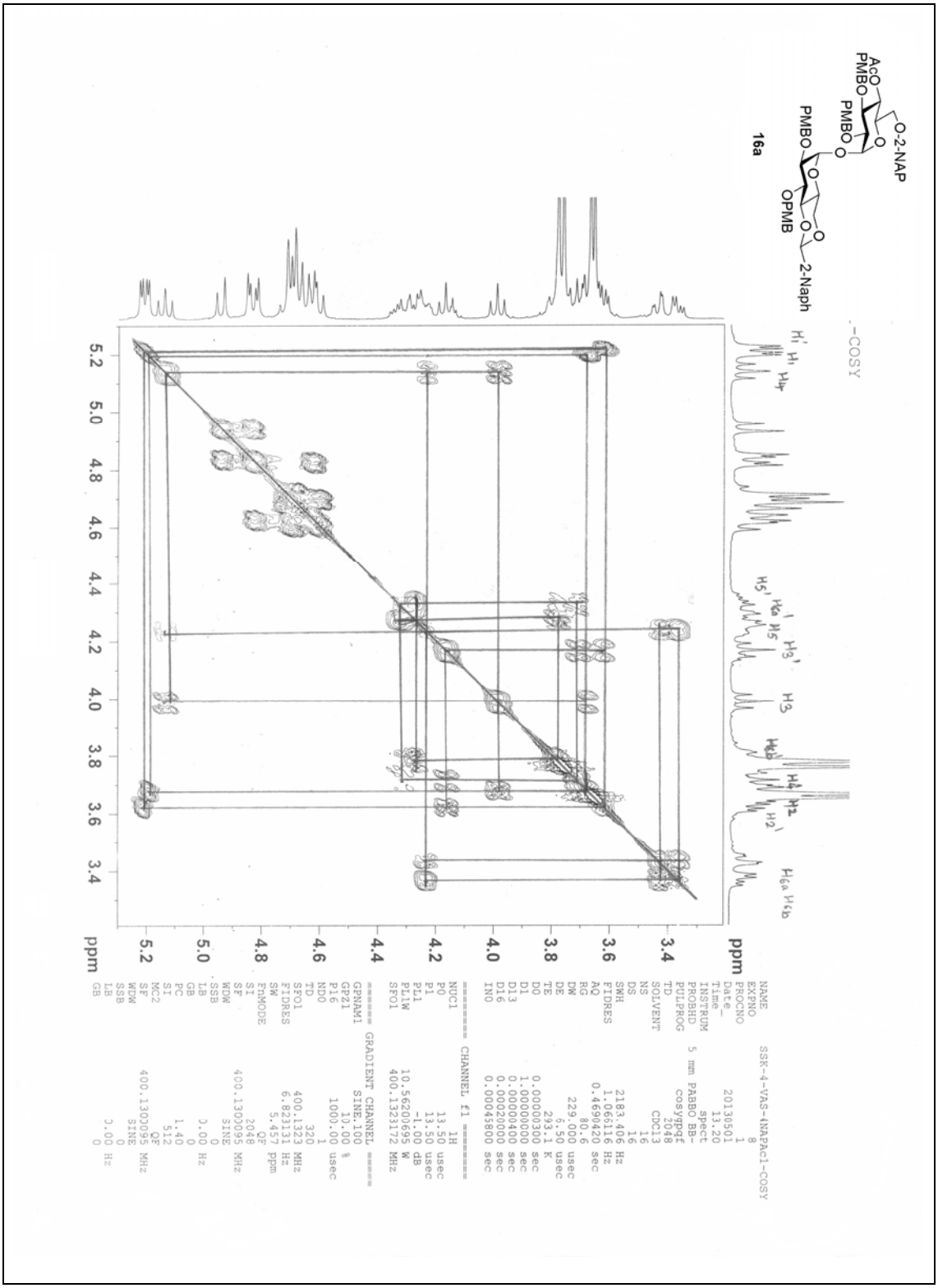

HO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
16
COSY
H1
H1'
H5
H4a
H5'
H3'
H3
H2
H2'
H4a, H4b
H4',H4'
ppm
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6

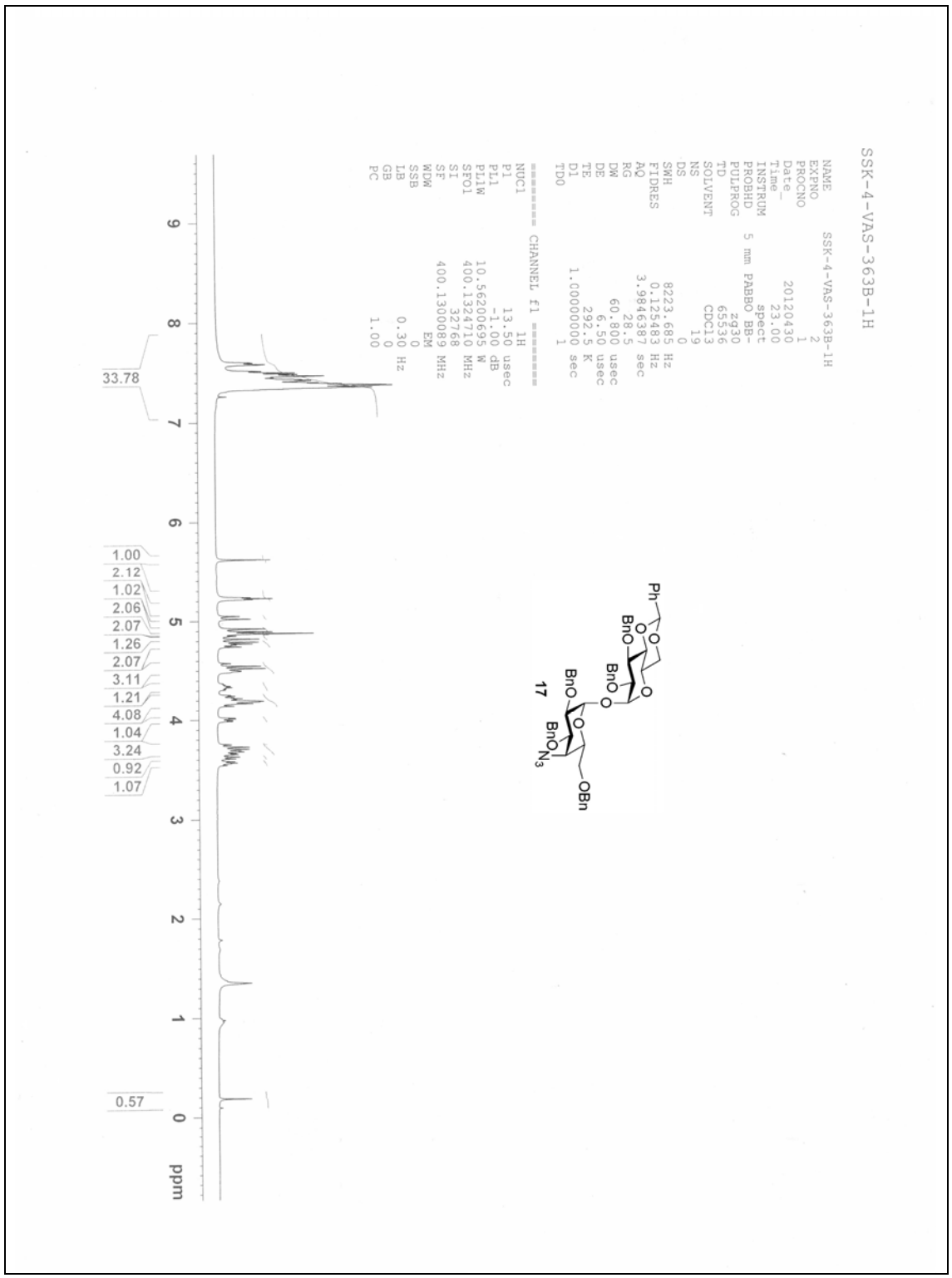

HO
PMBO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
16
HSQC
ppm
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
95
90
85
80
75
70
65

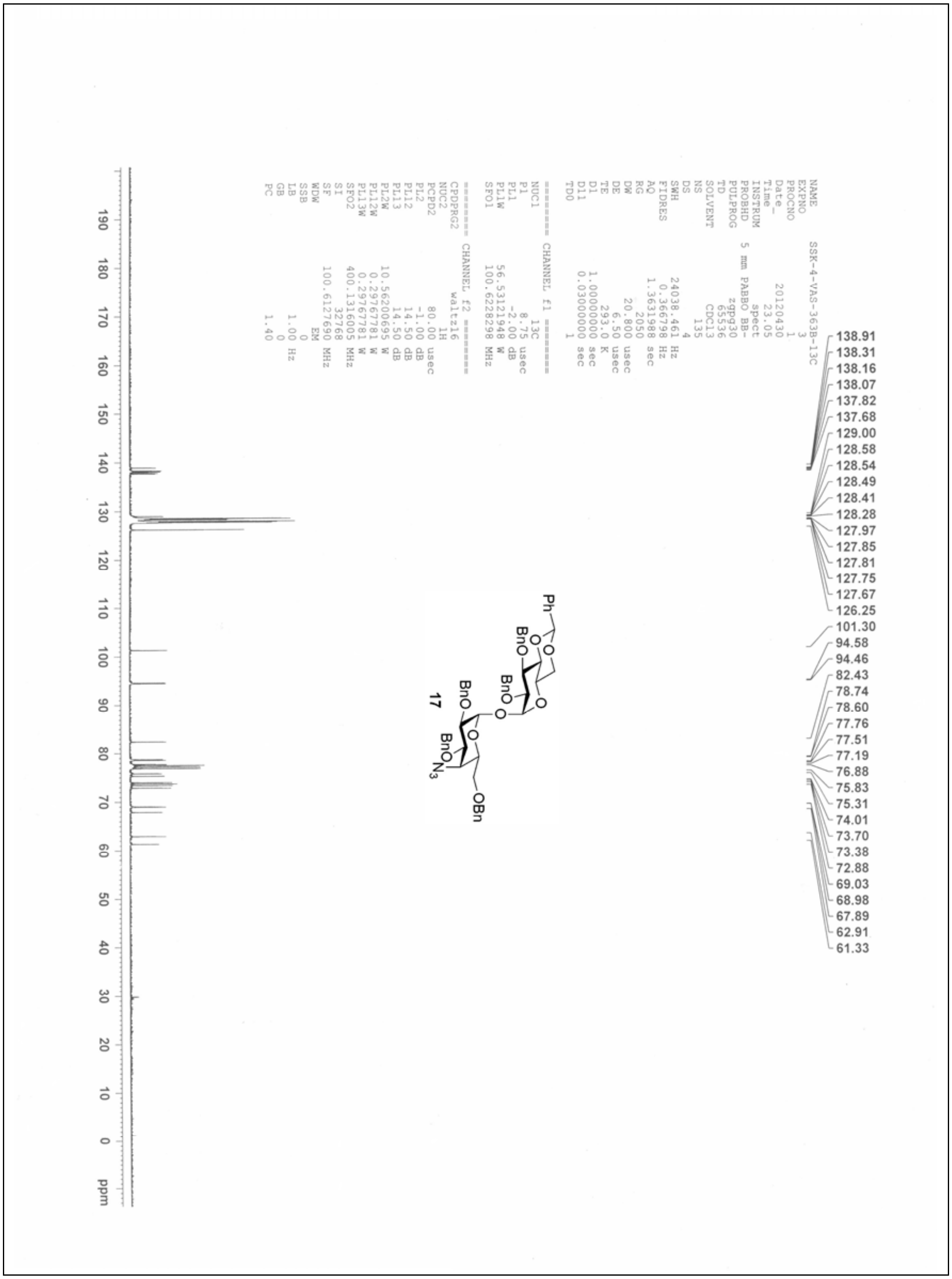

SSK-4-VAS-333-1H
16a
AcO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
ppm

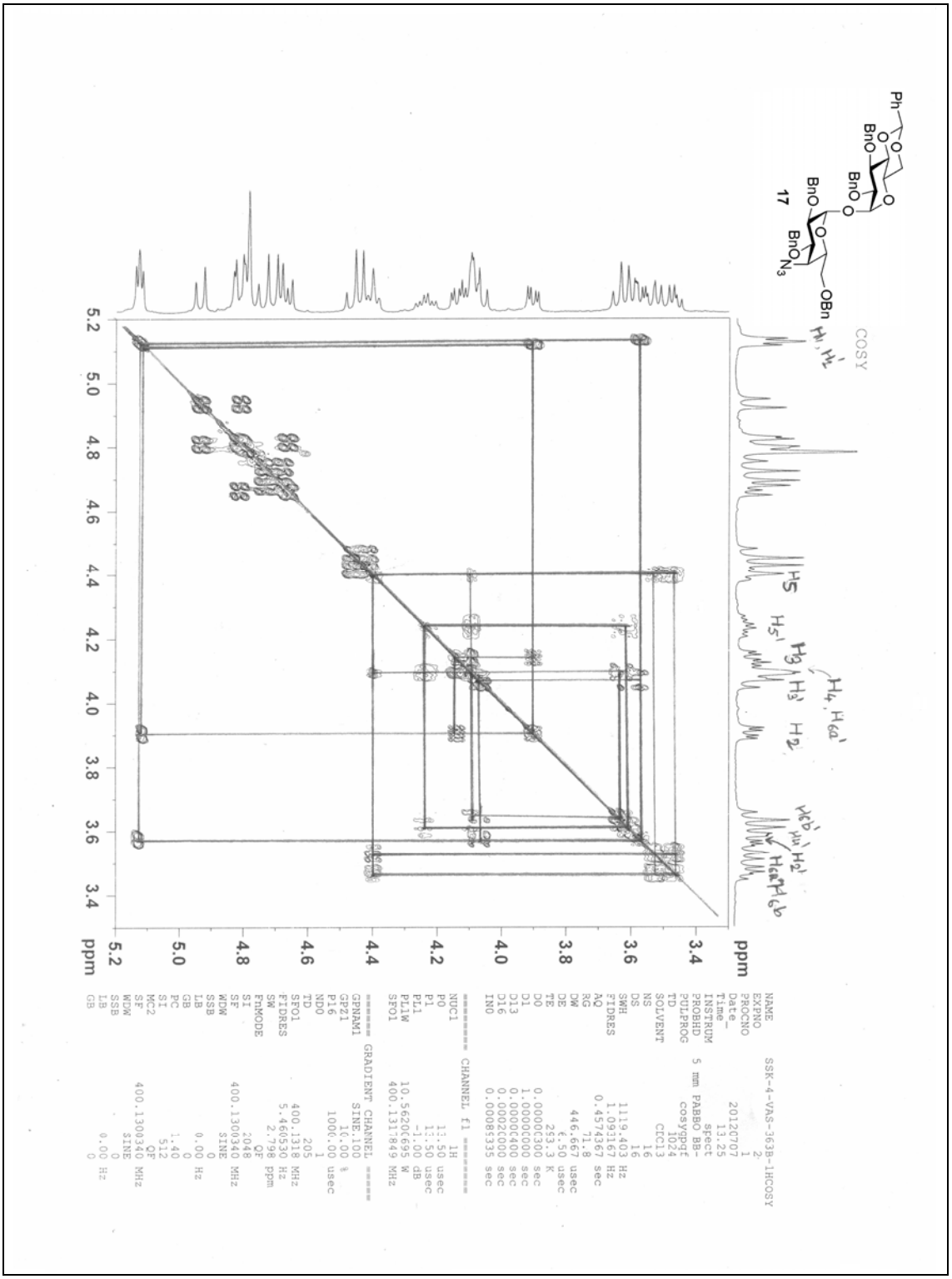

AcO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
16a
NAME SSK-4-VAS-4NAPAc-13C
EXPNO 2
PROCNO 1
Date_ 20130501
Time 7.50
INSTRUM spect
PROBHD 5 mm PABBO BB-0
PULPROG zgpg30
SOLVENT CDCl3
NS 105
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.5312948 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 100.6127632 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
169.81
159.38
159.26
159.20
135.39
135.11
133.68
133.29
133.09
133.04
131.10
130.88
130.25
130.07
129.60
129.58
129.54
129.31
128.52
128.21
128.10
128.04
127.80
127.76
126.84
126.53
126.30
126.15
125.97
125.58
124.00
114.02
113.83
113.70
101.44
94.39
93.75
82.54
78.93
78.67
78.43
78.35
77.52
77.40
77.20
76.88
75.04
74.80
73.84
73.23
73.01
70.45
69.40
69.26
68.76
63.06
55.33
55.32
55.19
21.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

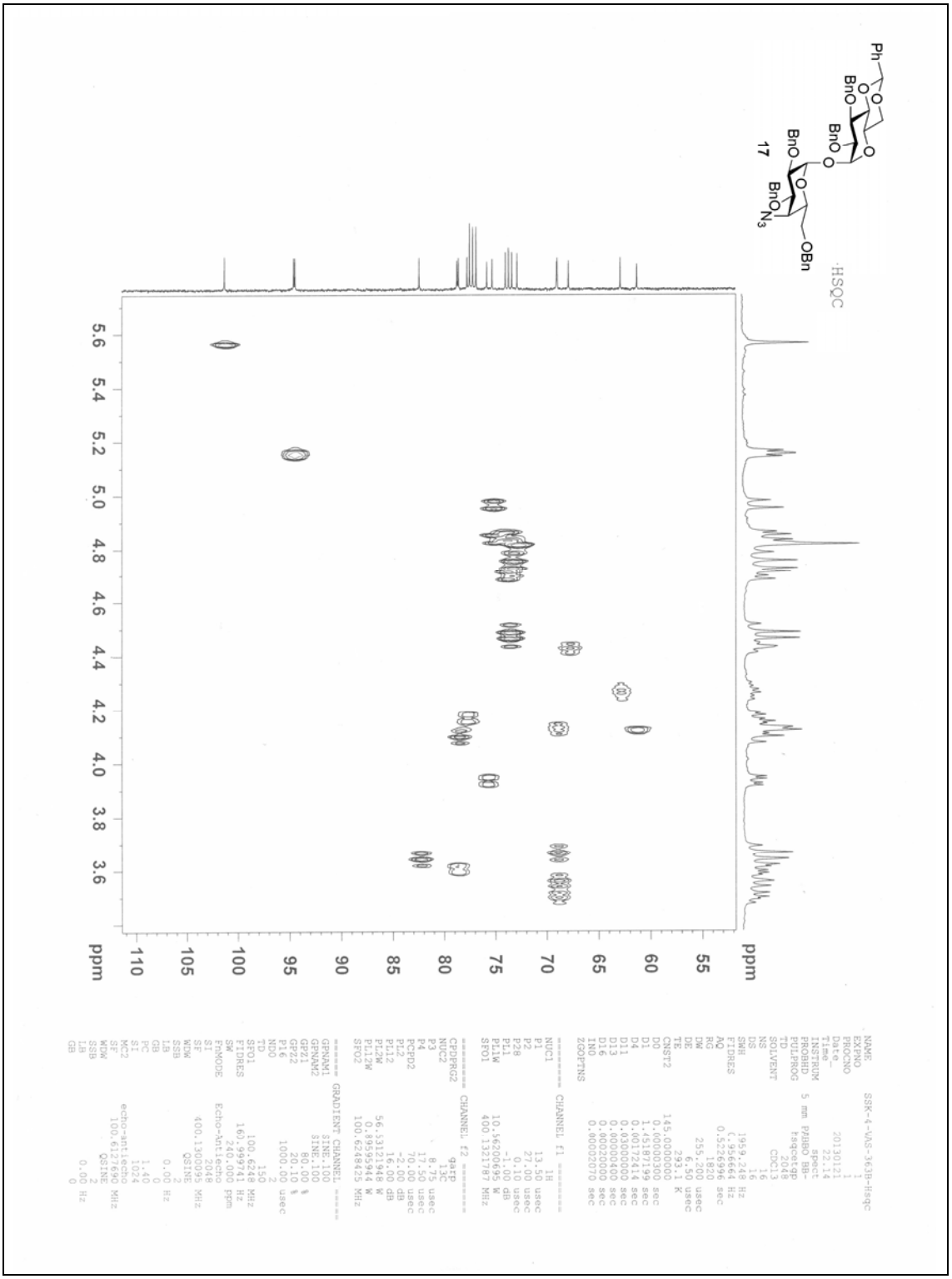

SSK-4-VAS-4NAPAc-APT
16a
AcO
PMBO
PMBO
O-2-NAP
PMBO
OPMB
2-Naph
159.39
159.26
159.21
135.40
135.12
133.69
133.29
133.10
133.05
129.60
129.58
129.54
129.31
128.52
128.20
128.10
128.04
127.80
127.76
126.83
126.53
126.30
126.15
125.97
125.59
124.00
114.02
113.83
113.70
101.45
94.40
93.75
82.55
78.94
78.68
78.43
78.36
77.52
77.20
76.88
75.04
74.80
73.85
73.23
73.01
70.47
69.41
69.26
68.77
63.06
55.33
55.32
55.19
21.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

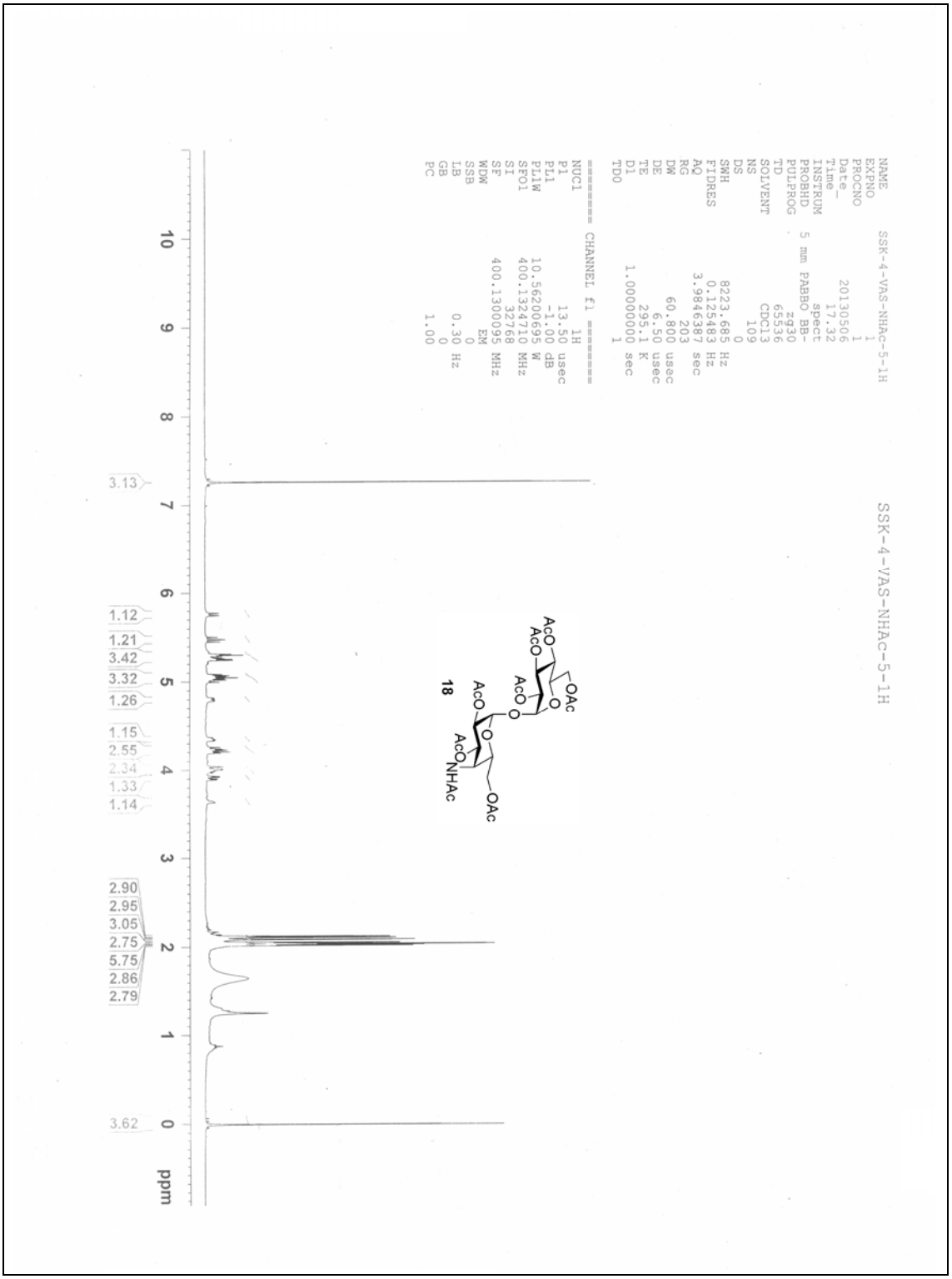

AcO
PMBO
PMBO
PMBO
O-2-NAP
OPMB
2-Naph
16a
-COSY
ppm
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4

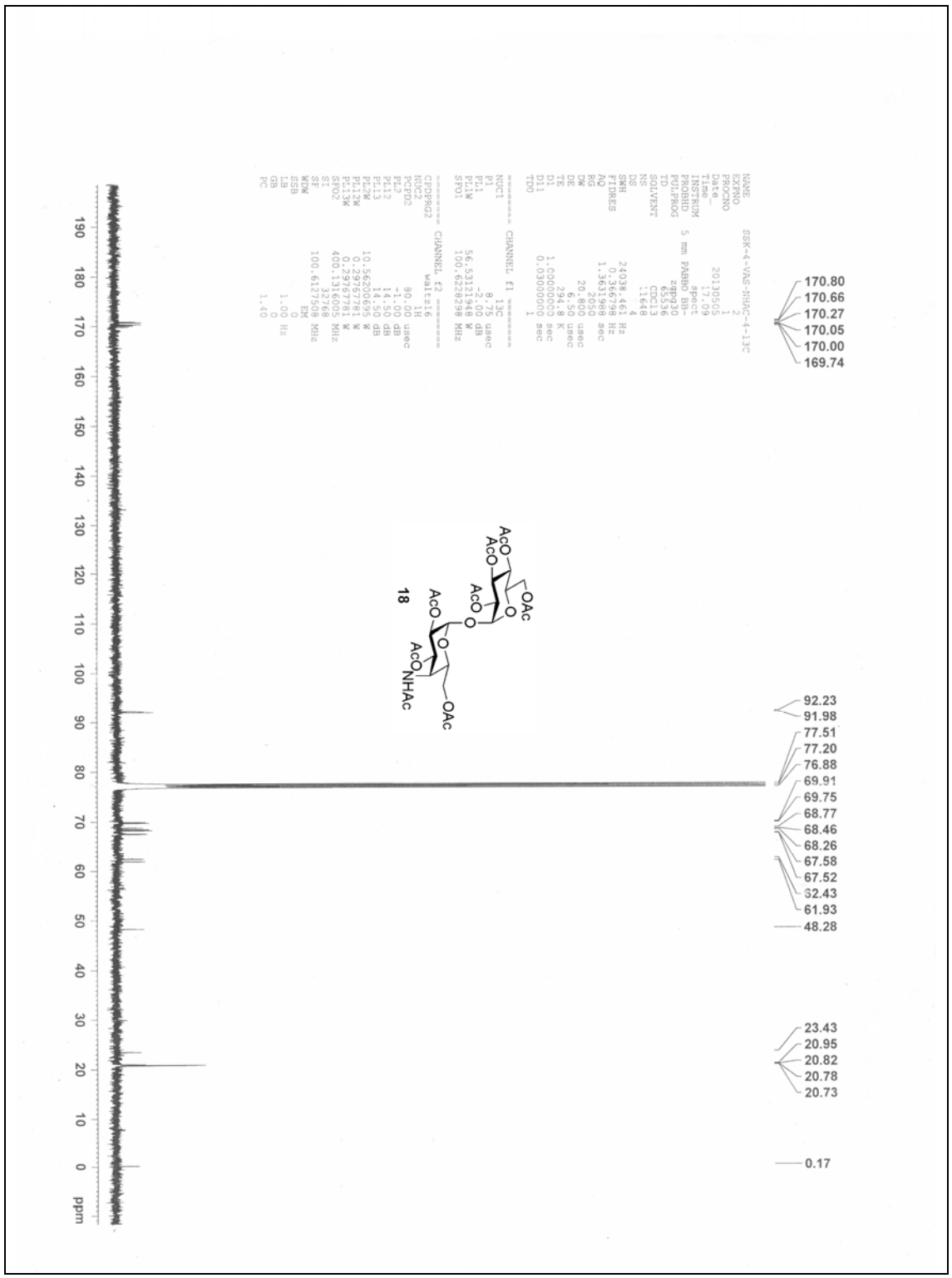

SSK-4-VAS-363B-1H
NAME SSK-4-VAS-363B-1H
EXPNO 2
PROCNO 1
Date_ 20120430
Time 23.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 19
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 28.5
DW 60.800 usec
DE 6.50 usec
TE 292.5 K
D1 1.0000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
33.78
1.00
2.12
1.02
2.06
2.07
1.26
2.07
3.11
1.21
4.08
1.04
3.24
0.92
1.07
0.57
ppm
Ph
BnO
BnO
BnO
BnO
N3
OBn
17

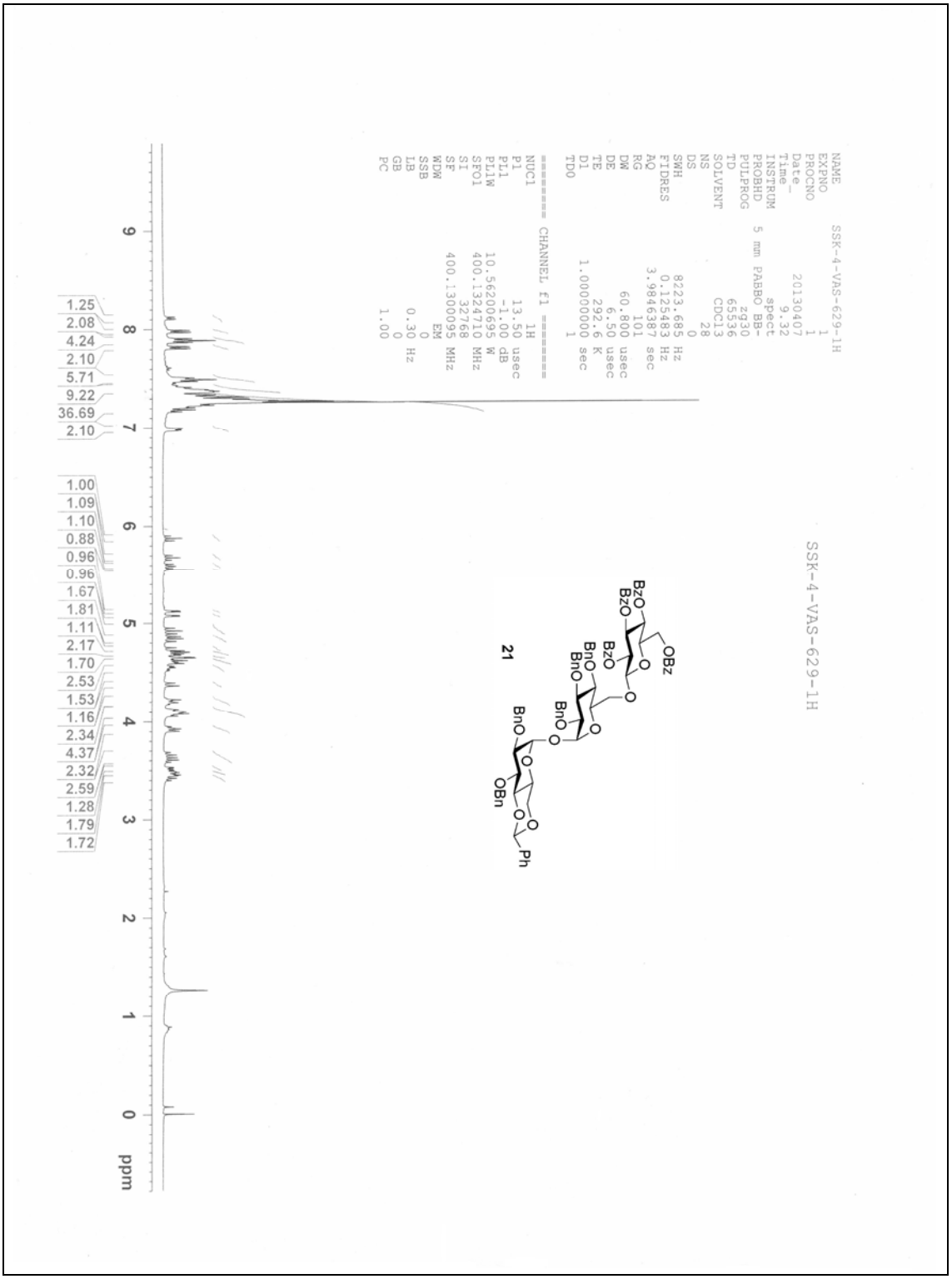

138.91
138.31
138.16
138.07
137.82
137.68
129.00
128.58
128.54
128.49
128.41
128.28
127.97
127.85
127.81
127.75
127.67
126.25
101.30
94.58
94.46
82.43
78.74
78.60
77.76
77.51
77.19
76.88
75.83
75.31
74.01
73.70
73.38
72.88
69.03
68.98
67.89
62.91
61.33
17
ppm

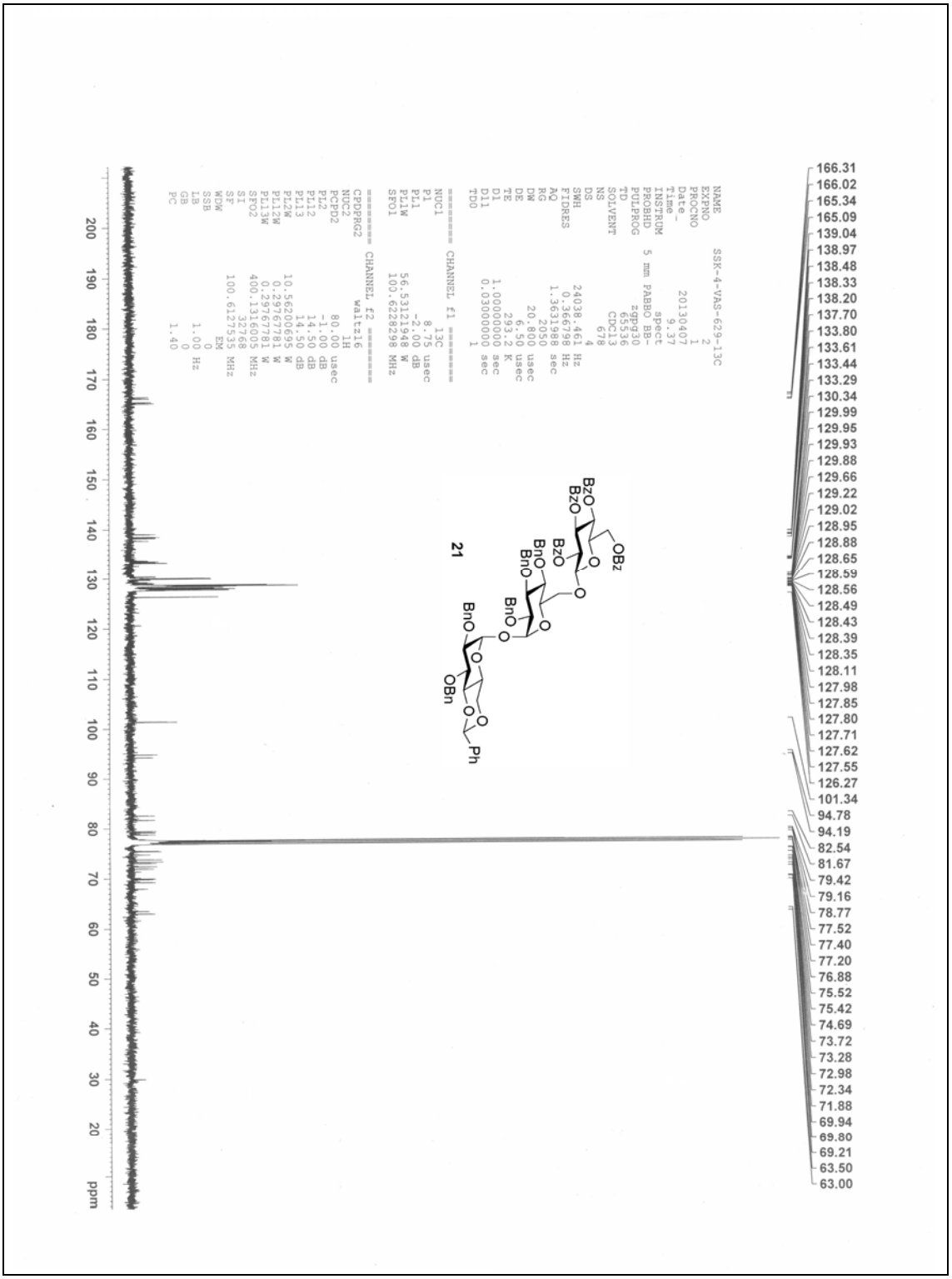

Ph
BnO
BnO
BnO
BnO
17
BnO
N3
OBn
COSY
H1, H1'
H5
H5'
H3
H3'
H4, H6a'
H2
H6b', H2'
H6a, H6b
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
NAME SSK-4-VAS-363B-1HCOSY
EXPNO 2
PROCNO 1
Date_ 20120707
Time_ 13.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 16
DS 16
SWH 1119.403 Hz
FIDRES 1.093167 Hz
AQ 0.457436? sec
RG 71.8
DW 446.667 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 0.00085335 sec
======== CHANNEL f1 ========
NUC1 1H
P0 11.50 usec
P1 11.50 usec
PL1 -1.00 dB
PL1W 10.56206695 W
SFO1 400.1311849 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GP21 10.00 %
P16 1000.00 usec
NDO 1
TD 205
SFO1 400.1318 MHz
FIDRES 5.460530 Hz
SW 2.798 ppm
FnMODE QF
SI 2048
SF 400.1300340 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 512
MC2 QF
SF 400.1300340 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

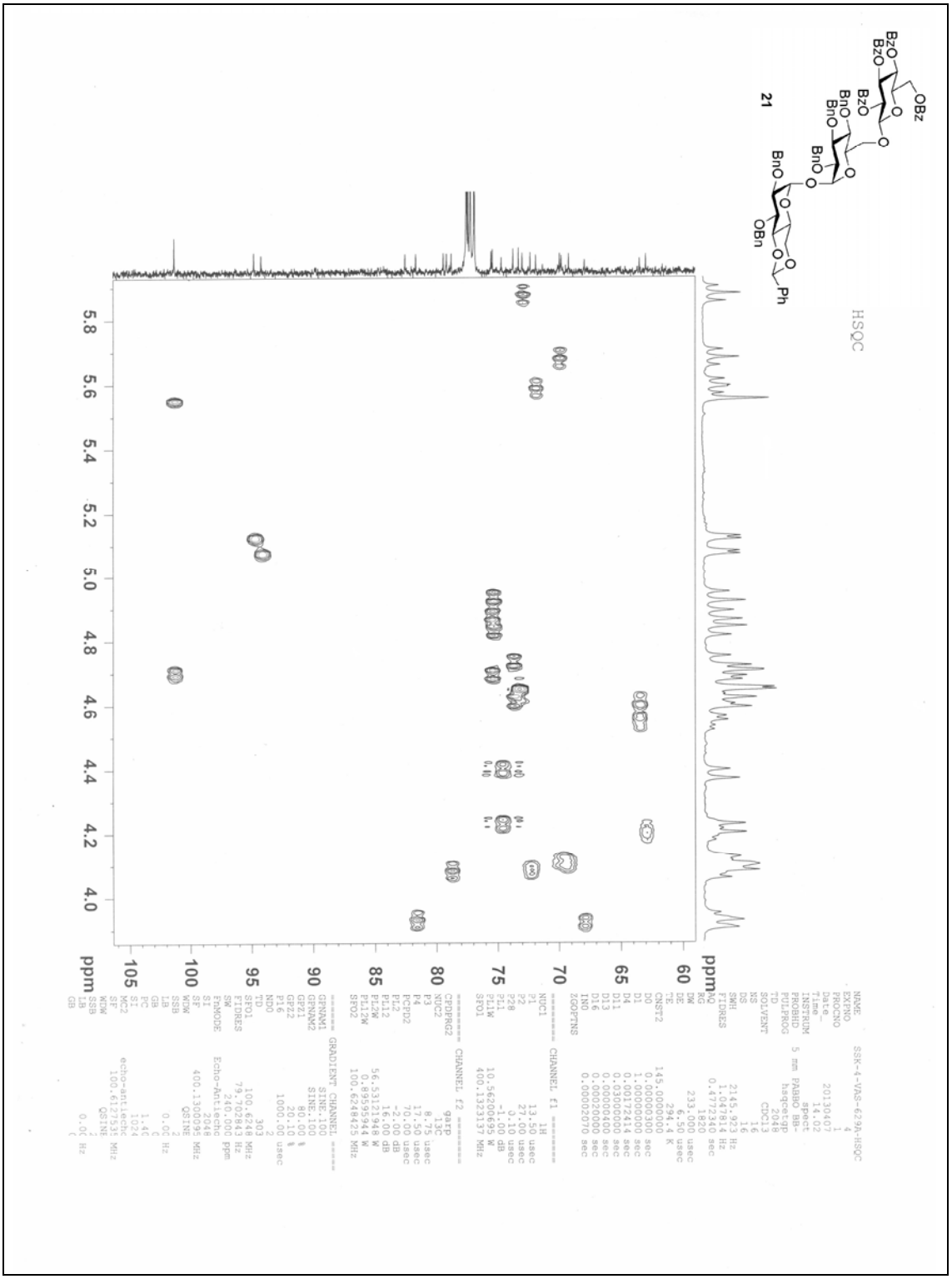

Ph
BnO
BnO
BnO
BnO
BnO
N3
OBn
17
HSQC
ppm
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
110
105
100
95
90
85
80
75
70
65
60
55

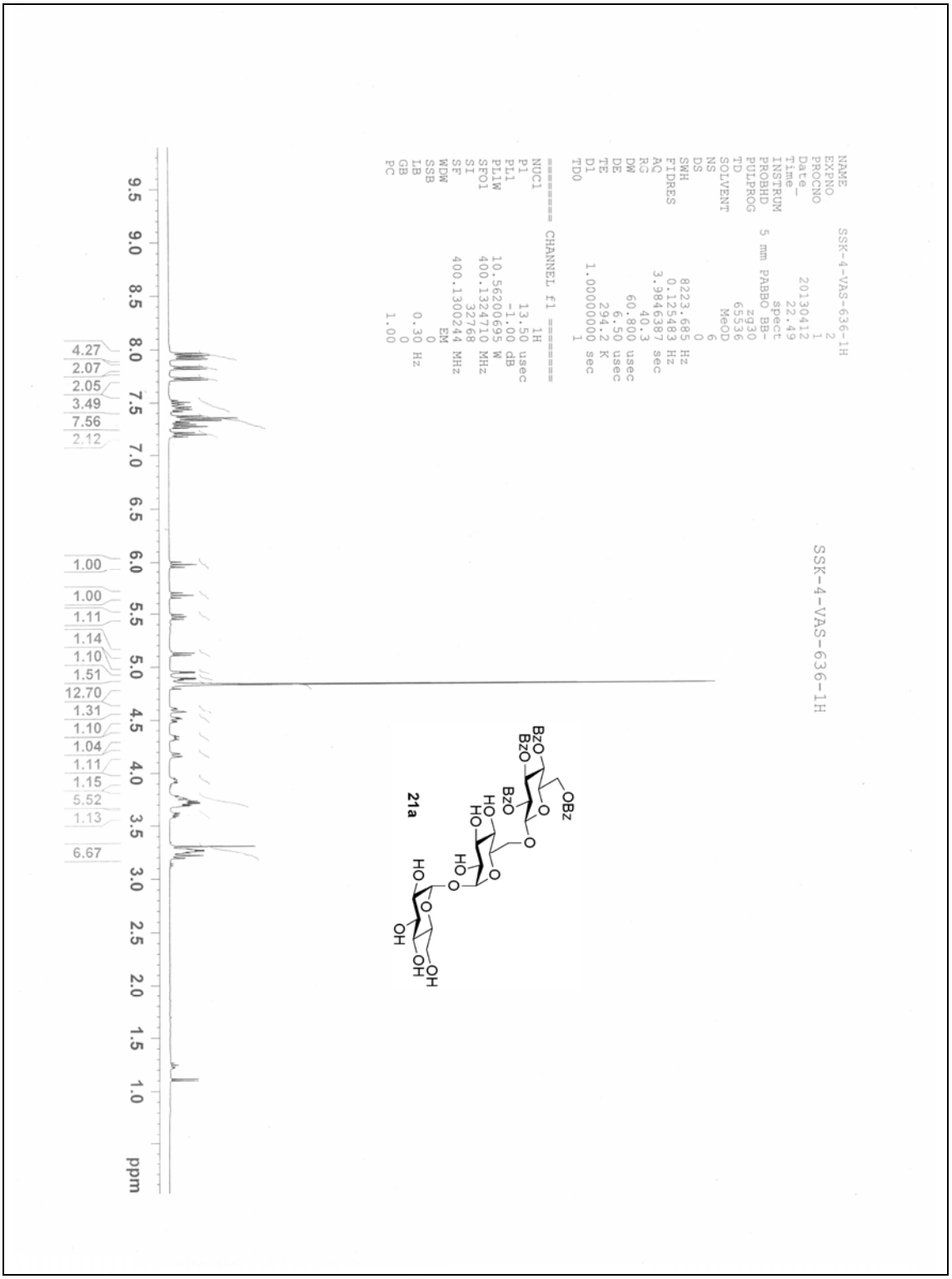

SSK-4-VAS-NHAc-5-1H
NAME SSK-4-VAS-NHAc-5-1H
EXPNO 1
PROCNO 1
Date_ 20130506
Time 17.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 109
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
18
3.13
1.12
1.21
3.42
3.32
1.26
1.15
2.55
2.34
1.33
1.14
2.90
2.95
3.05
2.75
5.75
2.86
2.79
3.62
10
9
8
7
6
5
4
3
2
1
0
ppm

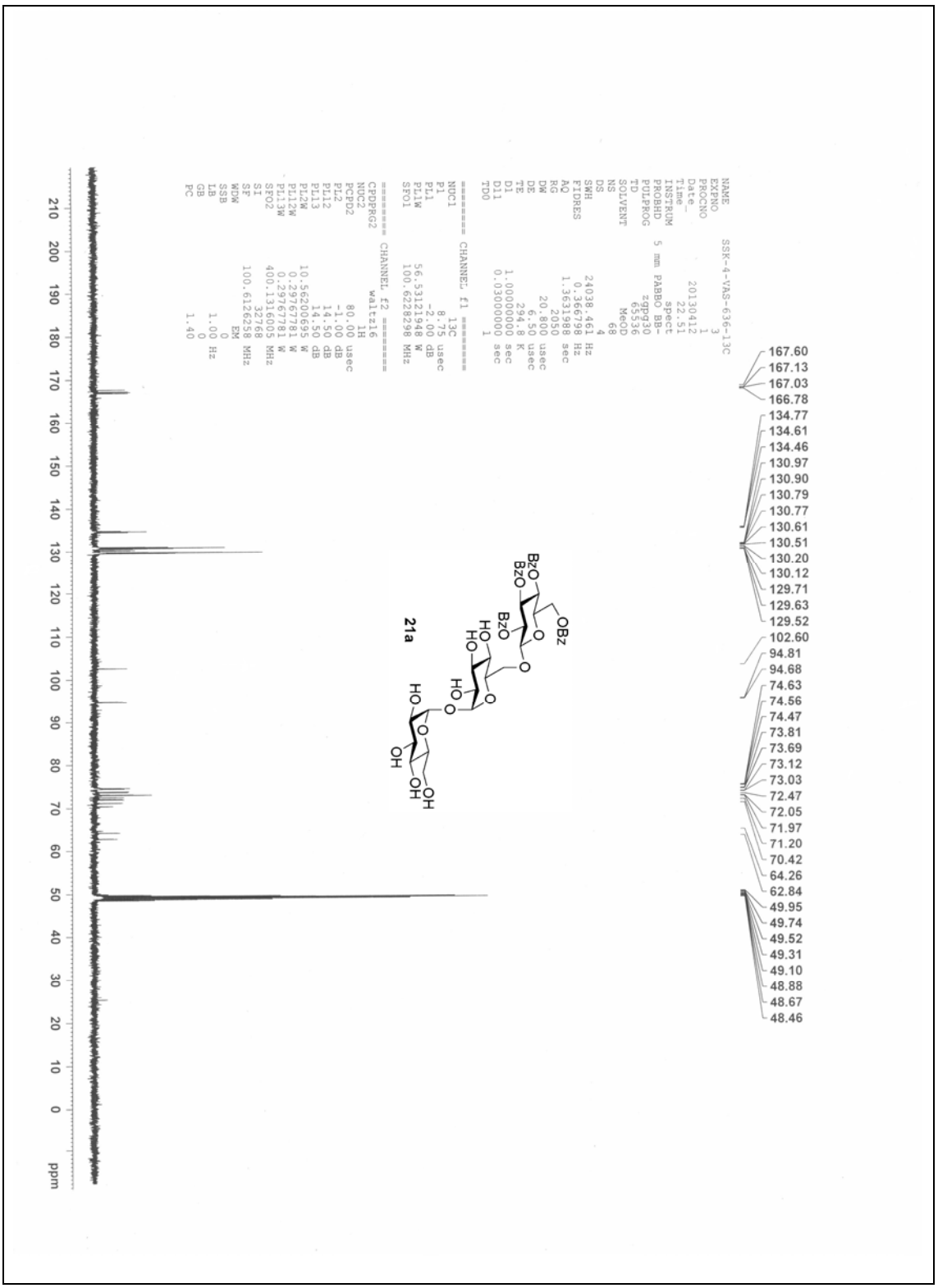

18
AcO
AcO
AcO
AcO
AcO
AcO
NHAc
OAc
OAc
170.80
170.66
170.27
170.05
170.00
169.74
92.23
91.98
77.51
77.20
76.88
69.91
69.75
68.77
68.46
68.26
67.58
67.52
32.43
61.93
48.28
23.43
20.95
20.82
20.78
20.73
0.17
ppm

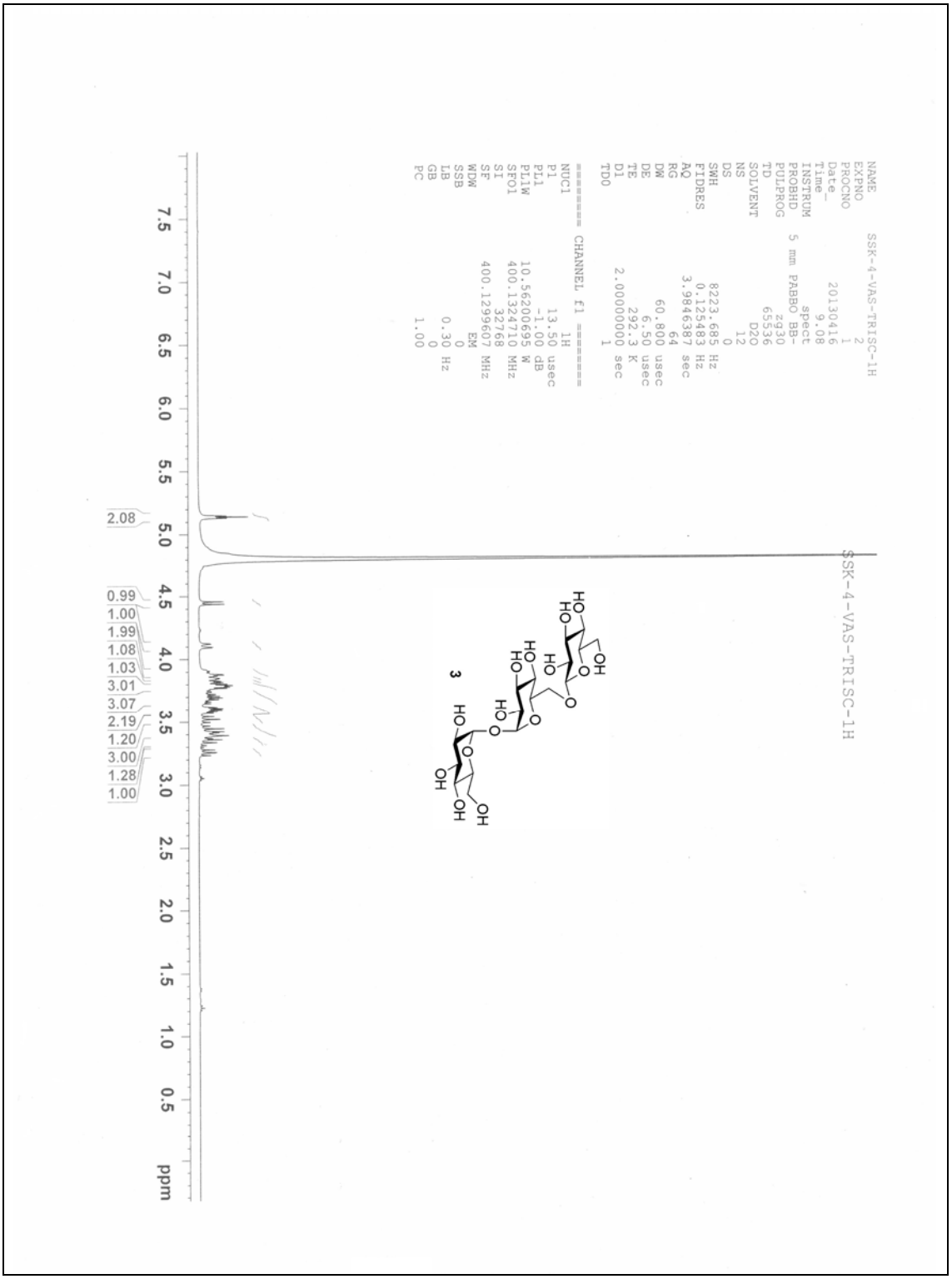

NAME SSK-4-VAS-629-1H
EXPNO 1
PROCNO 1
Date_ 20130407
Time_ 9.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 28
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-4-VAS-629-1H
21
BzO
BzO
BzO
BnO
BnO
BnO
BnO
OBz
OBn
Ph
1.25
2.08
4.24
2.10
5.71
9.22
36.69
2.10
1.00
1.09
1.10
0.88
0.96
0.96
1.67
1.81
1.11
2.17
1.70
2.53
1.53
1.16
2.34
4.37
2.32
2.59
1.28
1.79
1.72
9
8
7
6
5
4
3
2
1
0
ppm

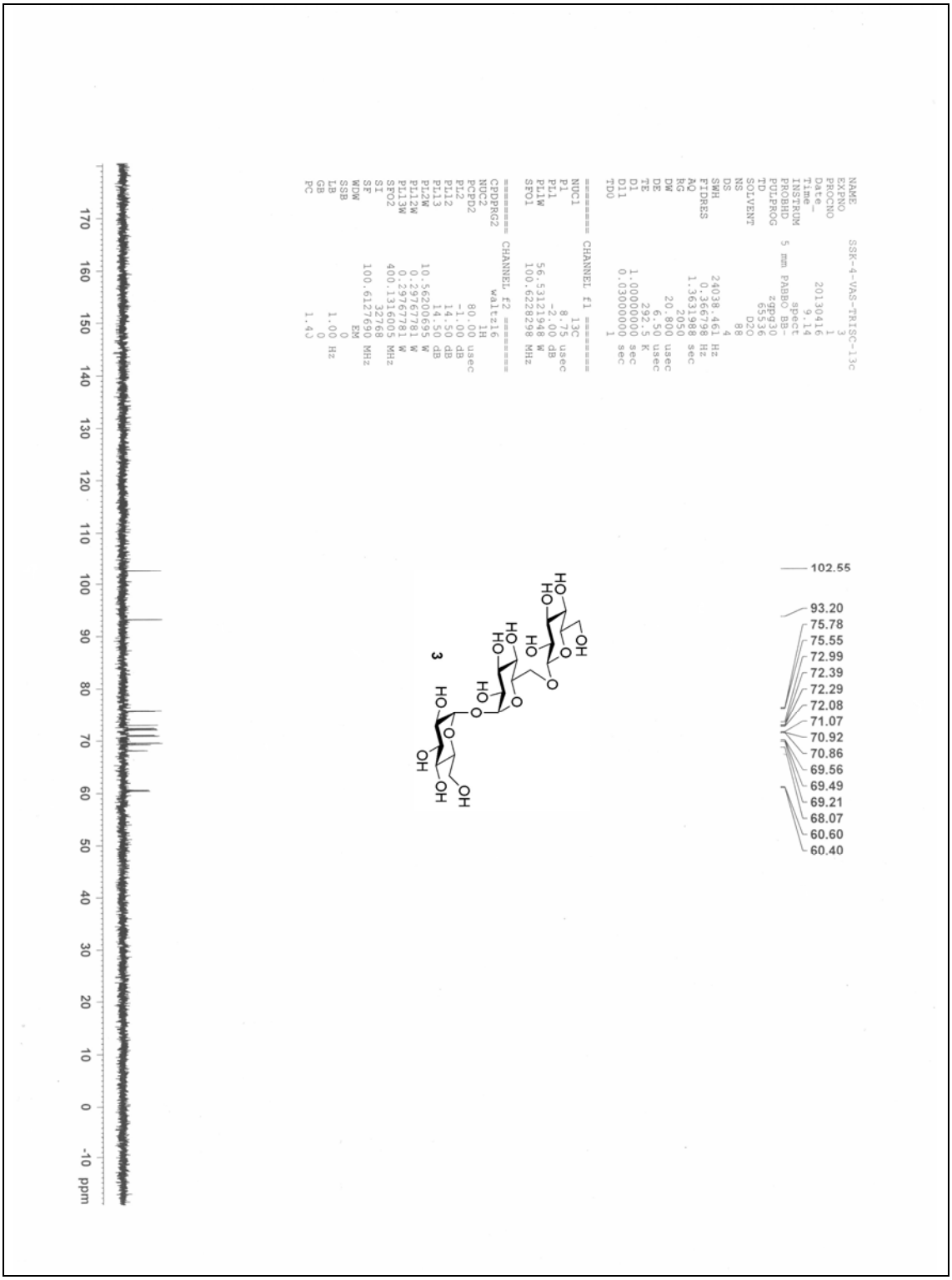

21
BzO
BzO
OBz
BzO
BnO
BnO
BnO
BnO
OBn
Ph
NAME SSK-4-VAS-629-13C
EXPNO 2
PROCNO 1
Date_ 20130407
Time_ 9.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 678
DS 4
SWH 24038.461 Hz
FIDRES 0.366998 Hz
AQ 1.3631488 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.2 K
D1 1.00000000 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 100.6127535 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
166.31
166.02
165.34
165.09
139.04
138.97
138.48
138.33
138.20
137.70
133.80
133.61
133.44
133.29
130.34
129.99
129.95
129.93
129.88
129.66
129.22
129.02
128.95
128.88
128.65
128.59
128.56
128.49
128.43
128.39
128.35
128.11
127.98
127.85
127.80
127.71
127.62
127.55
126.27
101.34
94.78
94.19
82.54
81.67
79.42
79.16
78.77
77.52
77.40
77.20
76.88
75.52
75.42
74.69
73.72
73.28
72.98
72.34
71.88
69.94
69.80
69.21
63.50
63.00
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

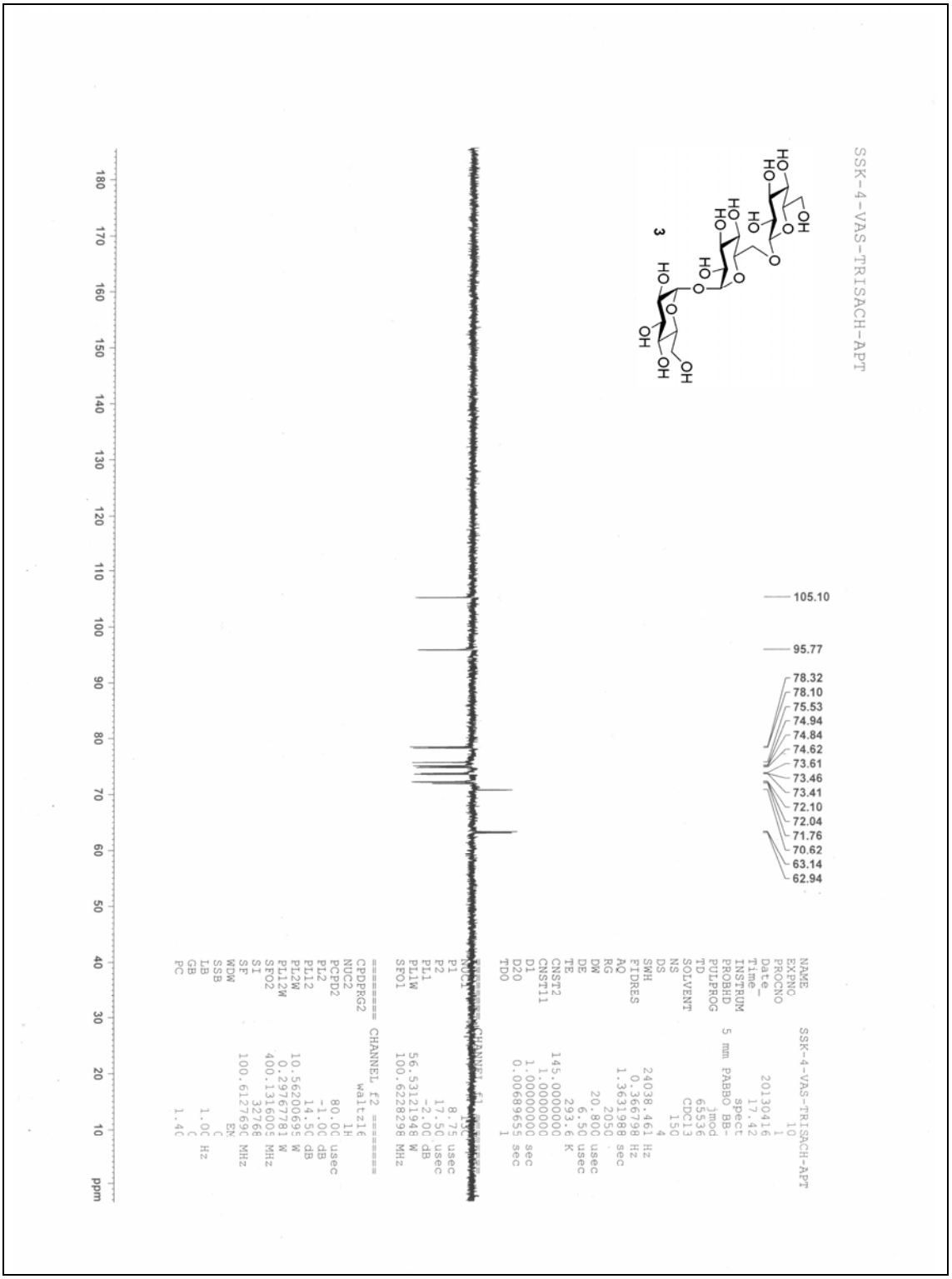

21
HSQC
ppm
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
105
100
95
90
85
80
75
70
65
60

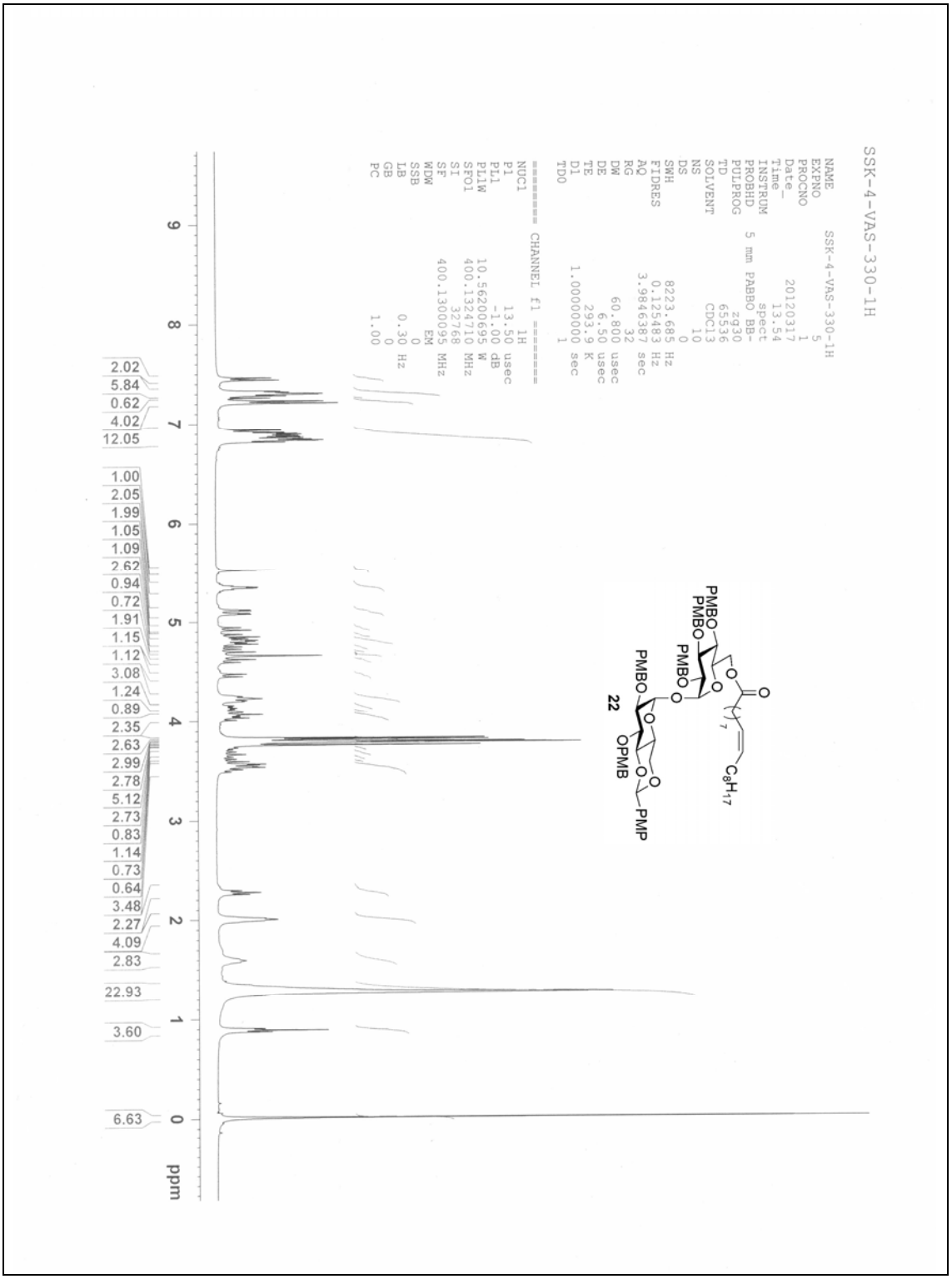


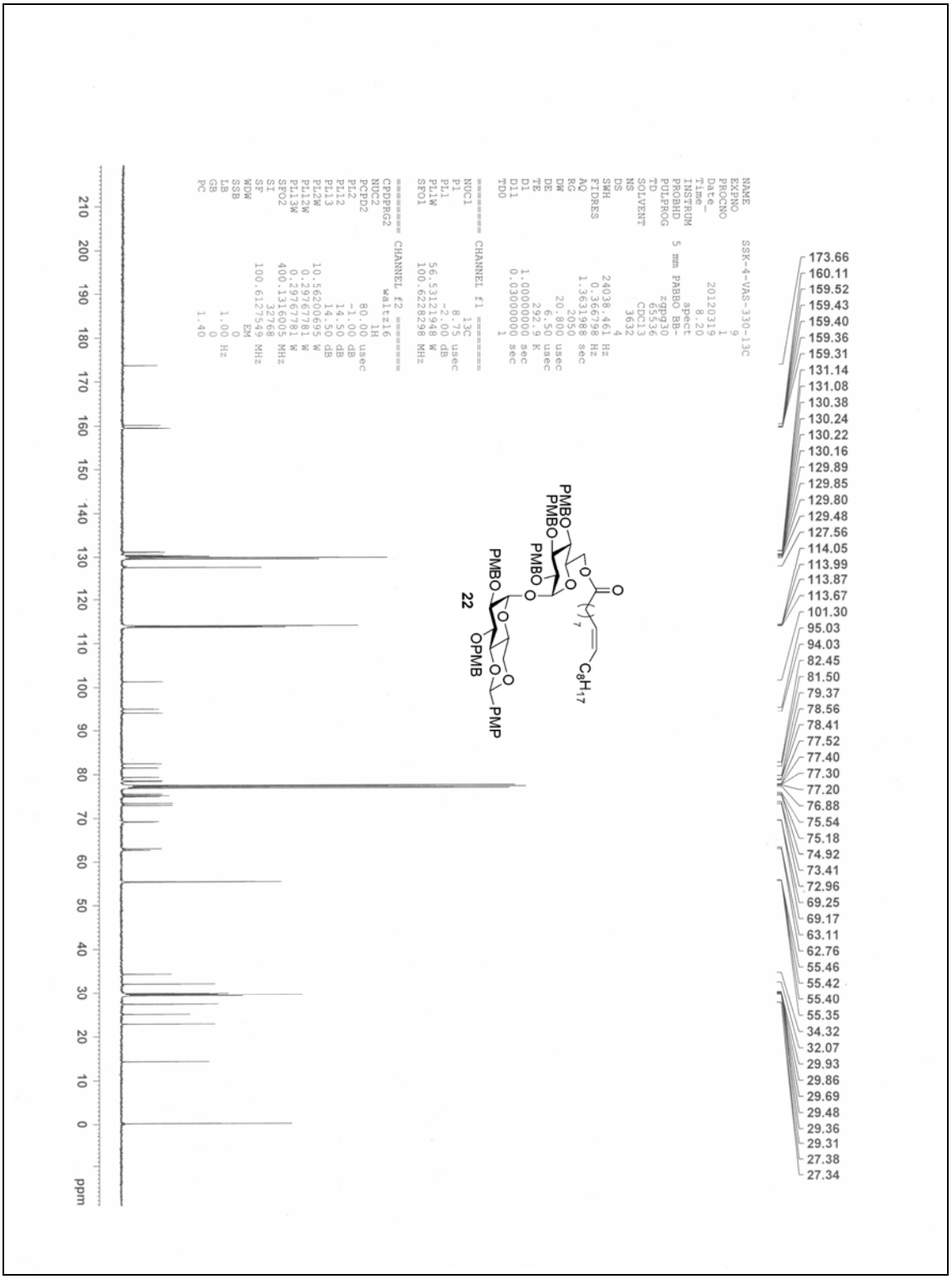

21a
167.60
167.13
167.03
166.78
134.77
134.61
134.46
130.97
130.90
130.79
130.77
130.61
130.51
130.20
130.12
129.71
129.63
129.52
102.60
94.81
94.68
74.63
74.56
74.47
73.81
73.69
73.12
73.03
72.47
72.05
71.97
71.20
70.42
64.26
62.84
49.95
49.74
49.52
49.31
49.10
48.88
48.67
48.46
ppm

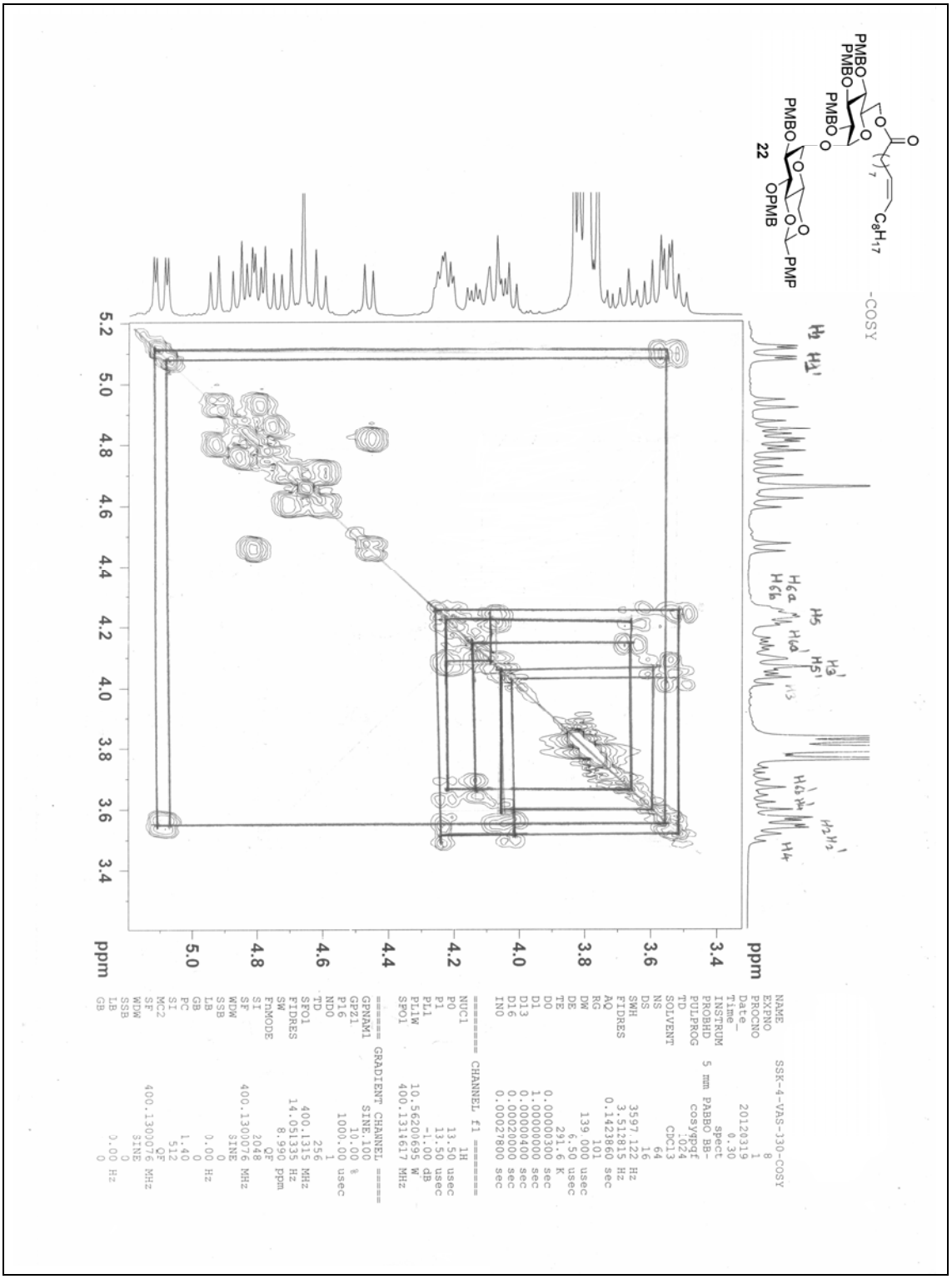

NAME SSK-4-VAS-TRISC-1H
EXPNO 2
PROCNO 1
Date_ 20130416
Time 9.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT D2O
NS 12
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 292.3 K
D1 2.00000000 sec
TDO 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299607 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
SSK-4-VAS-TRISC-1H
3
2.08
0.99
1.00
1.99
1.08
1.03
3.01
3.07
2.19
1.20
3.00
1.28
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

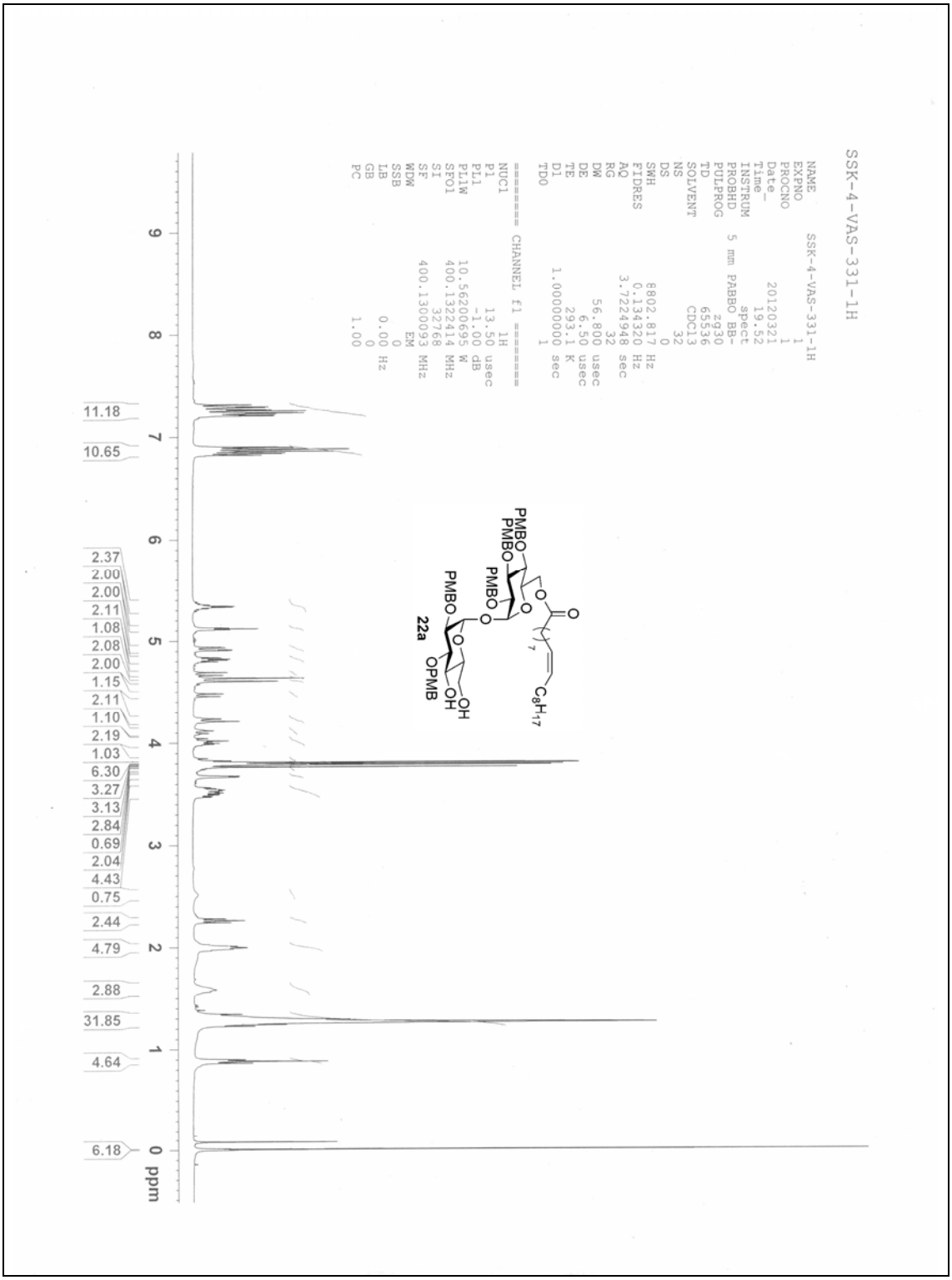

NAME SSK-4-VAS-TRISC-13c
EXPNO 3
PROCNO 1
Date_ 20130416
Time 9.14
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 88
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.363198 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 292.5 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.75 usec
PL1 -2.00 dB
PL1W 56.5312148 W
SFO1 100.622829 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 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
102.55
93.20
75.78
75.55
72.99
72.39
72.29
72.08
71.07
70.92
70.86
69.56
69.49
69.21
68.07
60.60
60.40
3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

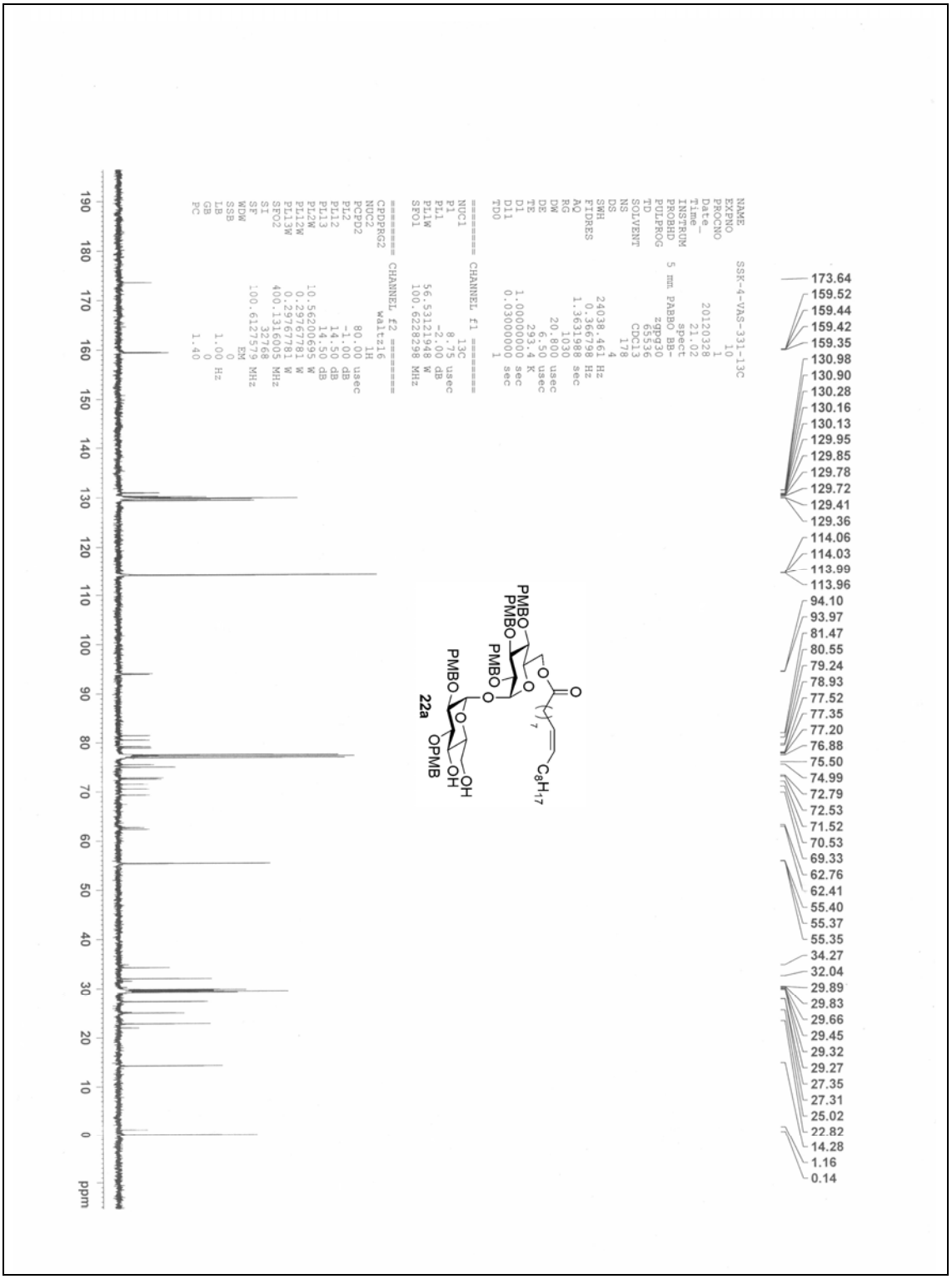

SSK-4-VAS-TRISACH-APT
3
105.10
95.77
78.32
78.10
75.53
74.94
74.84
74.62
73.61
73.46
73.41
72.10
72.04
71.76
70.62
63.14
62.94
NAME SSK-4-VAS-TRISACH-APT
EXPNO 10
PROCNO 1
Date_ 20130416
Time 17.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 150
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 293.6 K
CNST2 145.0000000
CNST11 1.0000000
D1 1.00000000 sec
D20 0.00689655 sec
TD0 1
CHANNEL f1
P1 8.75 usec
P2 17.50 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
PL2W 10.56200695 W
PL12W 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
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

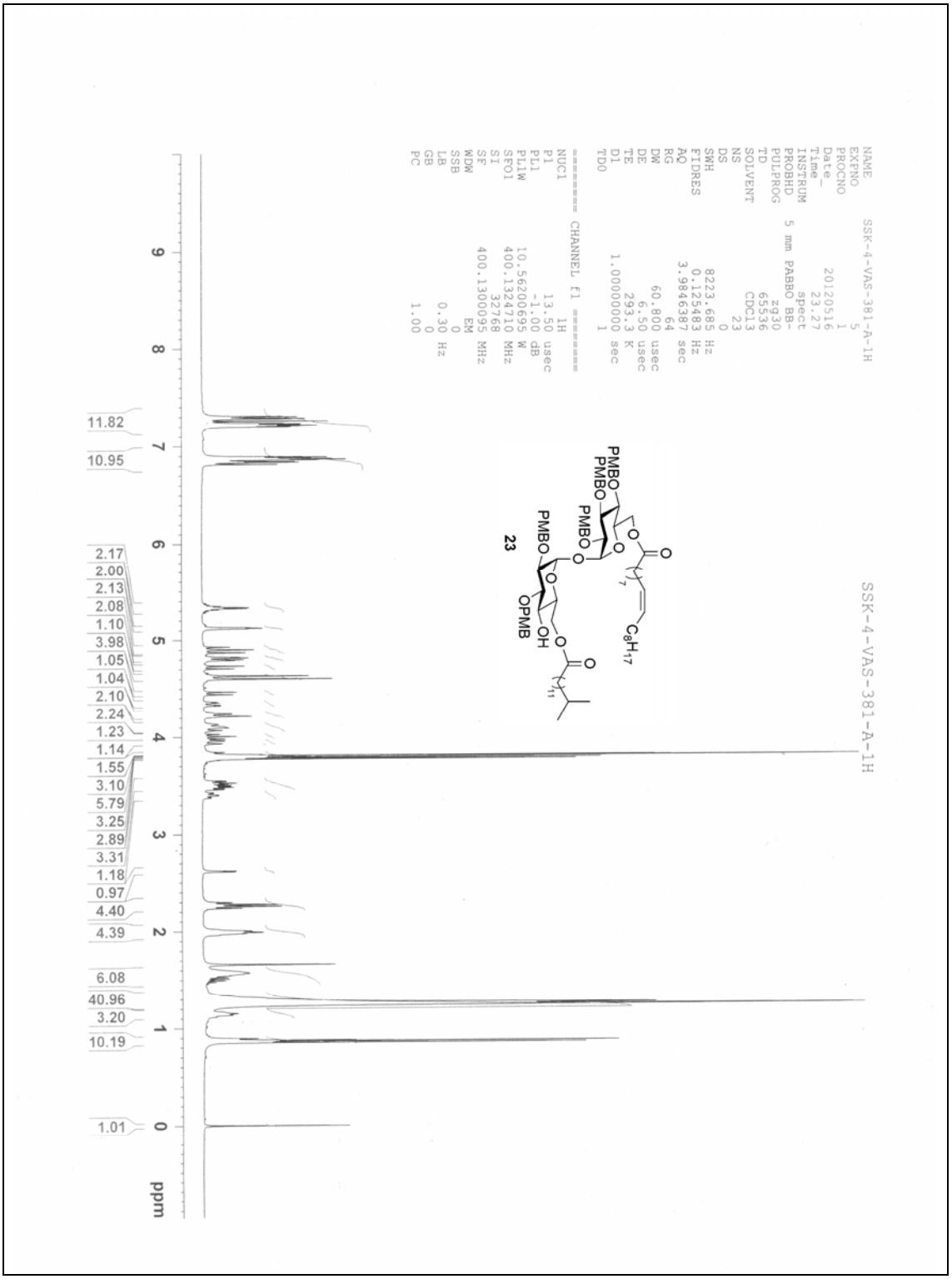

SSK-4-VAS-330-1H
NAME SSK-4-VAS-330-1H
EXPNO 5
PROCNO 1
Date_ 20120317
Time_ 13.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 10
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 32
DW 60.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 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
PMBO
PMBO
PMBO
PMBO
OPMB
22
PMP
C8H17
2.02
5.84
0.62
4.02
12.05
1.00
2.05
1.99
1.05
1.09
2.62
0.94
0.72
1.91
1.15
1.12
3.08
1.24
0.89
2.35
2.63
2.99
2.78
5.12
2.73
0.83
1.14
0.73
0.64
3.48
2.27
4.09
2.83
22.93
3.60
6.63
9
8
7
6
5
4
3
2
1
0
ppm

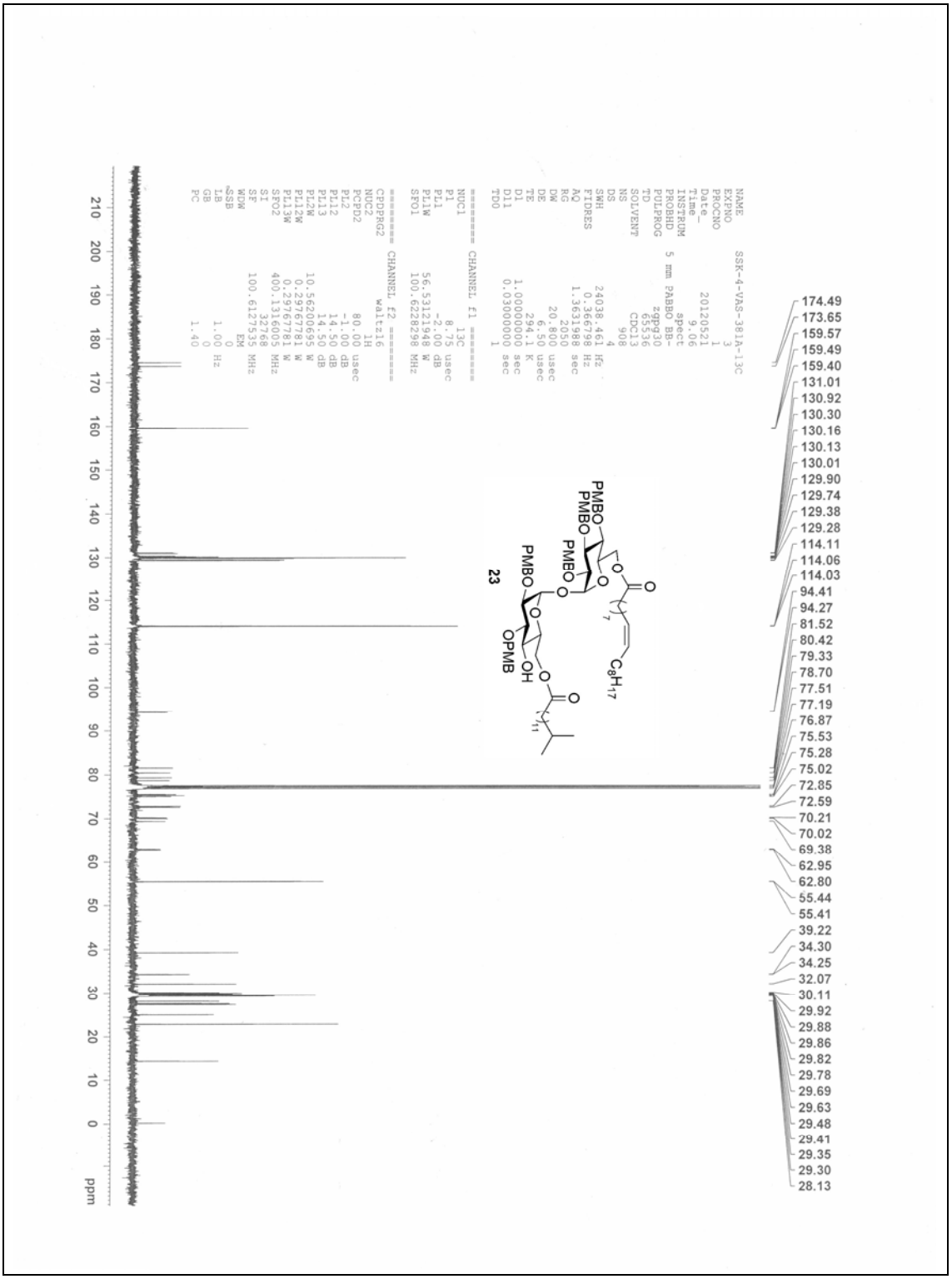


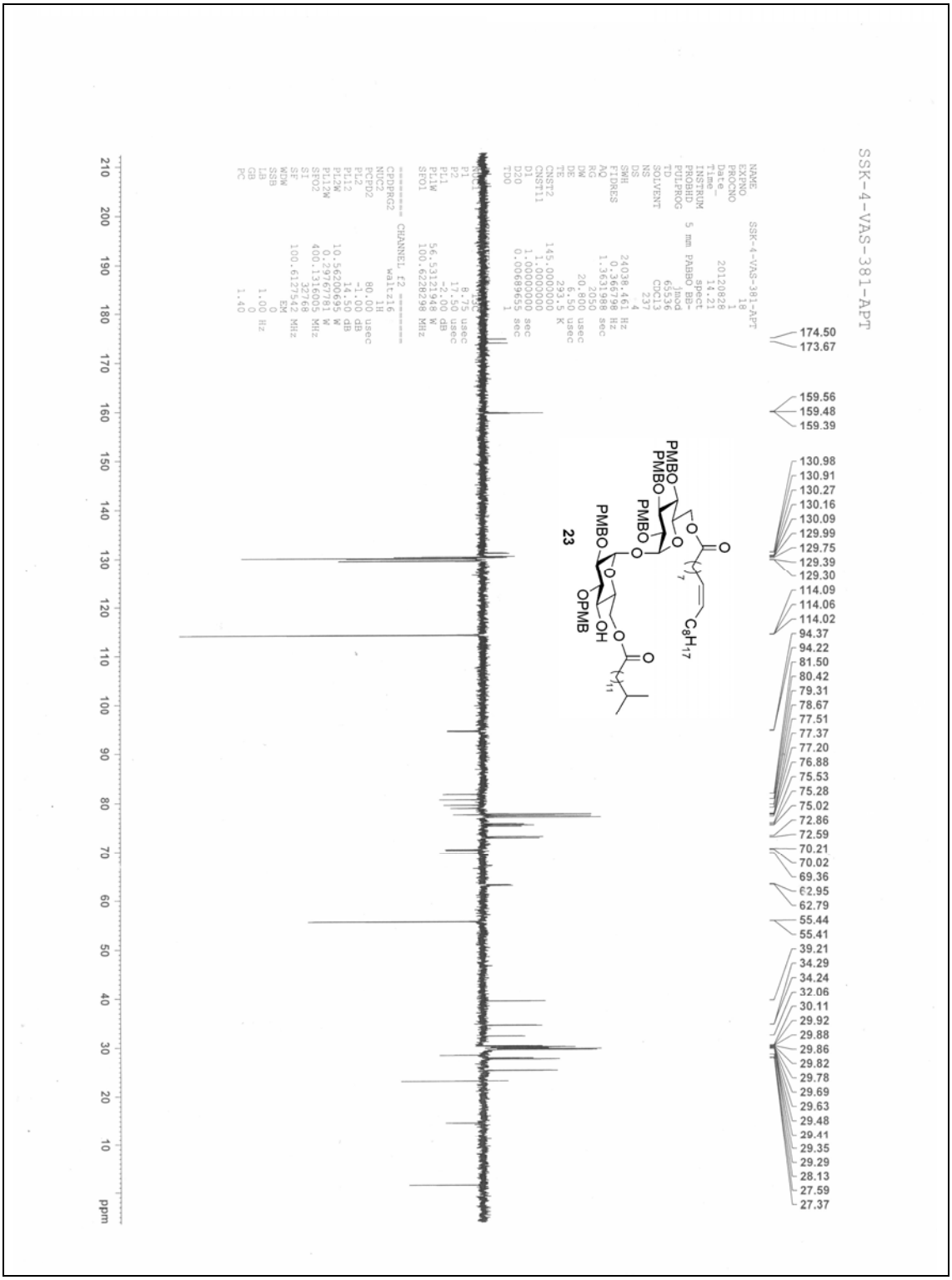

PMBO
PMBO
PMBO
PMBO
22
OPMB
PMP
C_8H_{17}
-COSY
H2 H2'
H6a H6b
H5
H6a'
H5'
H3'
H3
H6b' H6a'
H2 H2'
H4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
NAME SSK-4-VAS-130-COSY
EXPNO 8
PROCNO 1
Date_ 20120319
Time_ 0.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 1024
SOLVENT CDCl3
NS 64
DS 16
SWH 3597.122 Hz
FIDRES 3.512815 Hz
AQ 0.1423860 sec
RG 101
DW 139.000 usec
DE 6.50 usec
TE 291.6 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00027800 sec
======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1316017 MHz
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
NDO 1
TD 256
SFO1 400.1315 MHz
FIDRES 14.051335 Hz
SW 8.990 ppm
FnMODE QF
SI 2048
SF 400.1300076 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 512
MC2 QF
SF 400.1300076 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

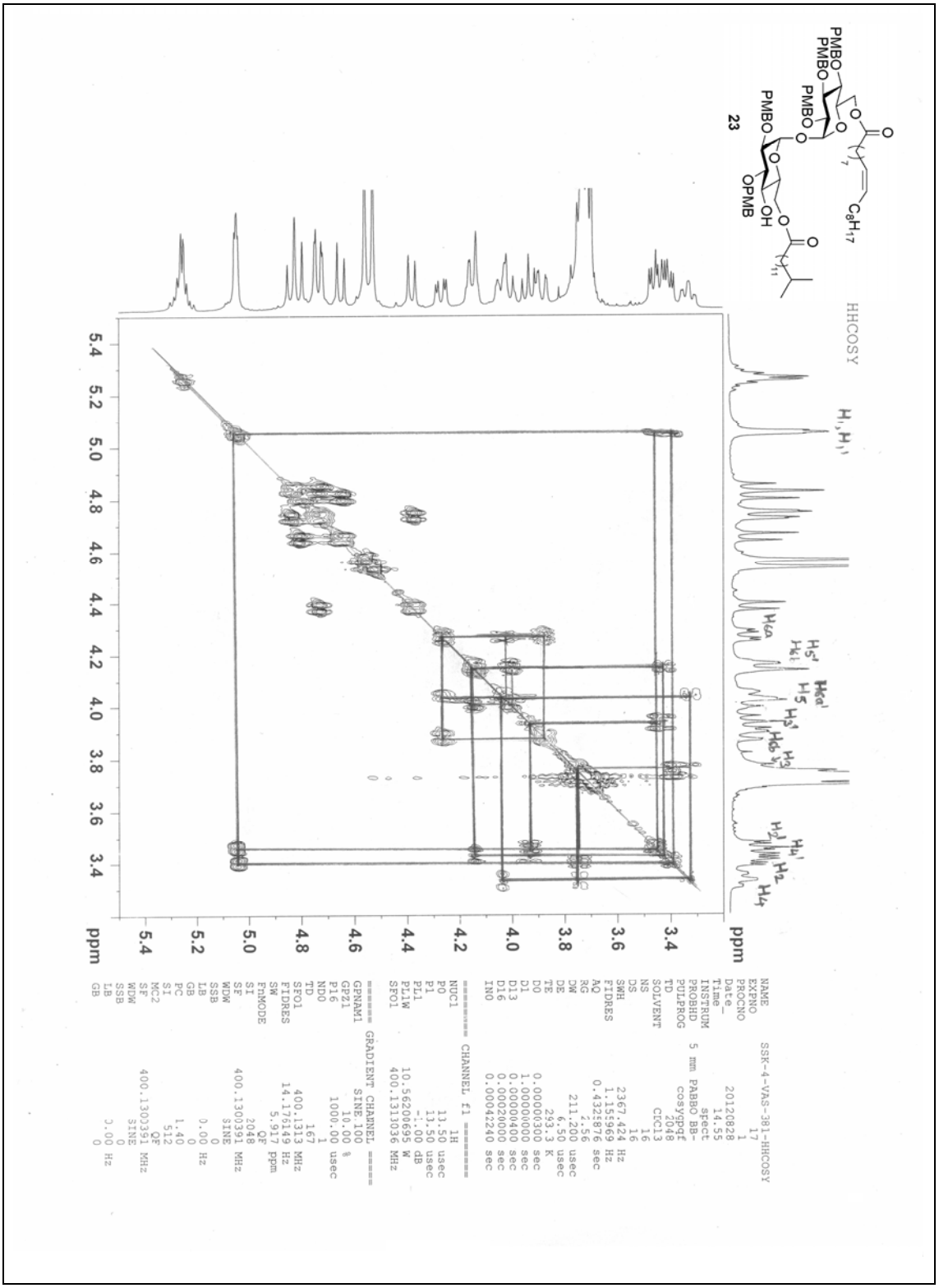


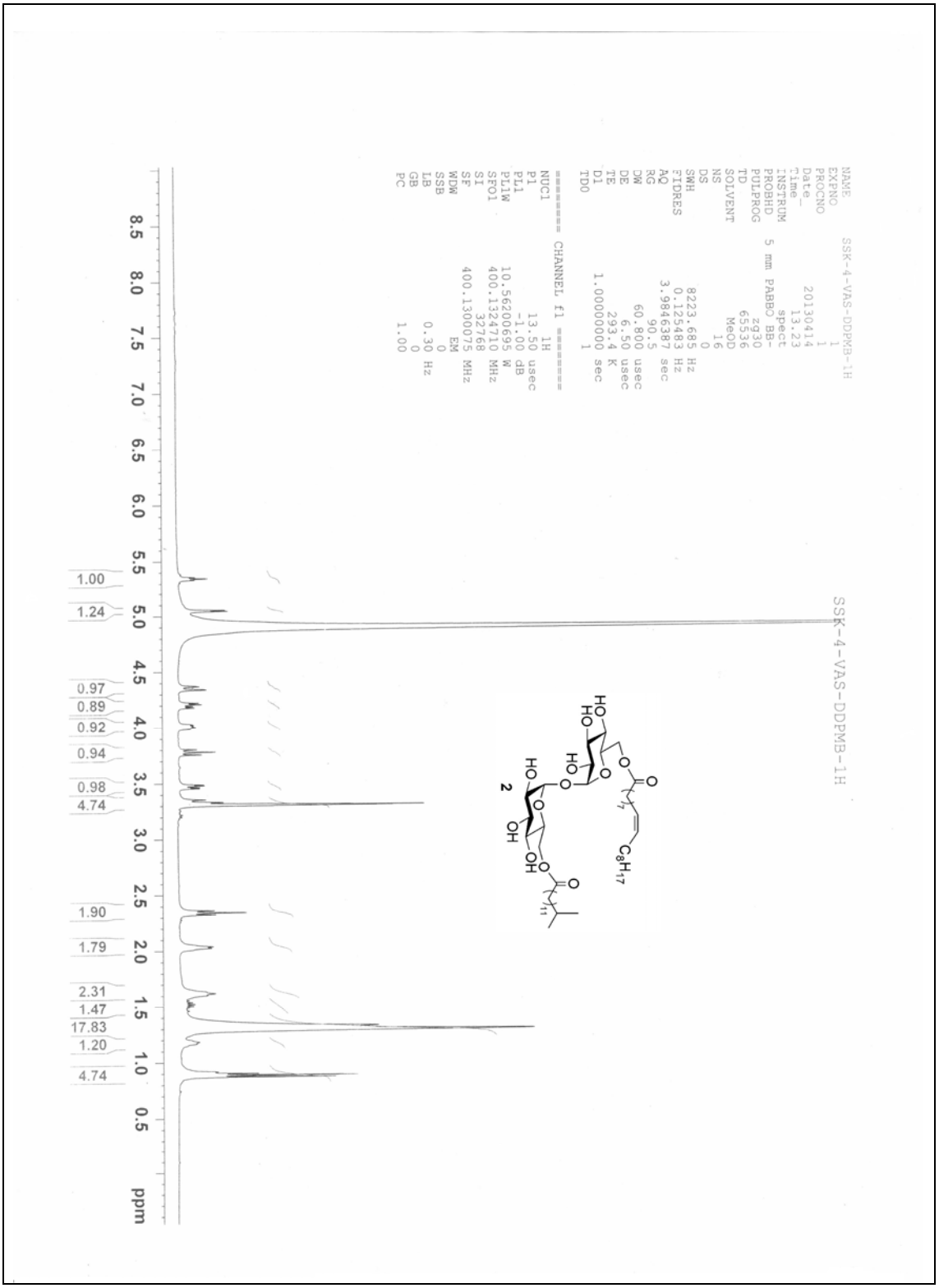



SSK-4-VAS-381-A-1H
PMBO
PMBO
PMBO
PMBO
OPMB
OH
23
C_8H_{17}
11.82
10.95
2.17
2.00
2.13
2.08
1.10
3.98
1.05
1.04
2.10
2.24
1.23
1.14
1.55
3.10
5.79
3.25
2.89
3.31
1.18
0.97
4.40
4.39
6.08
40.96
3.20
10.19
1.01
ppm






PMBO
PMBO
PMBO
PMBO
OPMB
OH
C_8H_{17}
23
HHCOSY
$H_1, H_{1'}$
ppm
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
NAME SSR-4-VAS-381-HHCOSY
EXPNO 17
PROCNO 1
Date_ 20120828
Time_ 14.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 2367.424 Hz
FIDRES 1.155969 Hz
AQ 0.432587876 sec
RG 2.56
DW 211.200 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 0.00042240 sec
CHANNEL f1
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1311036 MHz
GRADIENT CHANNEL
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
ND0 1
TD 167
SFO1 400.1313 MHz
FIDRES 14.176149 Hz
SW 5.917 ppm
FnMODE QF
SI 2048
SF 400.1300391 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 512
MC2 QF
SF 400.1300391 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0


SSK-4-VAS-DDPMB-1H
NAME SSK-4-VAS-DDPMB-1H
EXPNO 1
PROCNO 1
Date_ 20130414
Time 13.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 293.4 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 400.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1.00
1.24
0.97
0.89
0.92
0.94
0.98
4.74
1.90
1.79
2.31
1.47
17.83
1.20
4.74
ppm