

**General Methods.** All reaction glassware, transfer syringes and cannulae were oven-dried or flame dried under high vacuum. All commercial materials were used without further purification unless otherwise noted. The following solvents were distilled under positive pressure of dry nitrogen immediately before use: THF and diethyl ether from sodium-benzophenone ketyl, and  $\text{CH}_2\text{Cl}_2$ , toluene, and benzene from  $\text{CaH}_2$ . Anhydrous solvents were also obtained by passing them through dried alumina column. All the reactions were performed under dry nitrogen or argon. NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra were recorded on a Bruker AMX-400 MHz spectrometer and a Bruker Avance DRX-500 MHz spectrometer, referenced to TMS ( $^1\text{H}$  NMR,  $\delta$  0.00) or  $\text{CDCl}_3$  ( $^{13}\text{C}$  NMR,  $\delta$  77.00) peaks unless otherwise noted. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer and optical rotations were measured with a JASCO DIP-370 digital polarimeter. Analytical thin-layer chromatography was performed on E. Merck silica gel 60 F<sub>254</sub> plate (0.25  $\mu\text{m}$ ). Compounds were visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Flash column chromatography was performed using the indicated solvent on E. Merck silica gel 60 (40–63  $\mu\text{m}$ ) or Sigma H-Type silica gel (10–40  $\mu\text{m}$ ) for normal phase and EM Science Lichroprep RP-18 (15–25  $\mu\text{m}$ ) for reverse phase. Melting points are obtained with Electrothermal melting point apparatus (series no. 9100) and are uncorrected. Azeotropic drying was performed by concentrating the solution of the sample in appropriate amount of anhydrous benzene with a rotary evaporator more than twice and further drying *in vacuo*.

**Tetraol Lactal 11.** A solution of **10** (1.35 g, 2.01 mmol) in dry THF (10 mL) under N<sub>2</sub> was treated with a solution of TBAF (2.41 mL, 2.41 mmol, 1M in THF). After 18 h, the reaction mixture was diluted with absolute MeOH (10 mL) and treated with a solution of MeONa (0.200 mL, 25 wt % in MeOH). After 4.5 h, the reaction mixture was neutralized with Dowex50-x8 (0.8 g, washed and dried), filtered, and rinsed with MeOH. The crude product was purified with flash chromatography (20% EtOAc in CH<sub>2</sub>Cl<sub>2</sub>-5% MeOH in CH<sub>2</sub>Cl<sub>2</sub>) to give **11** (0.866 g, 88%):  $[\alpha]_D^{23} = -2.14^\circ$  (c 0.99, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 3390, 3064, 3031, 2873, 1646, 1497, 1455, 1410, 1368, 1246, 1212, 1145, 1066, 911, 898, 821, 736, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.24-7.18 (m, 10H), 6.31 (d, 1H, *J* = 6.1 Hz), 4.75 (dd, 1H, *J* = 5.8, 2.8 Hz), 4.55-4.66 (m, 4H), 4.37 (d, 1H, *J* = 7.6 Hz), 4.14 (s, 1H), 4.07 (s, 3H), 3.87-3.82 (m, 4H), 3.65-3.60 (m, 3H), 3.55 (t, 1H, *J* = 8.6 Hz), 3.37 (d, 1H, *J* = 8.7 Hz), 3.21 (m, 1H), 2.94 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 138.4, 137.7, 128.39, 128.37, 127.84, 127.75, 127.6, 127.5, 103.4, 99.9, 76.4, 74.1, 73.9, 73.42, 73.39, 73.1, 71.2, 69.6, 68.8, 67.9, 67.0, 61.4; LRMS (EI) calcd for C<sub>26</sub>H<sub>32</sub>O<sub>9</sub>·Na [M + Na]<sup>+</sup> 511, found 511.

**Levulinate Lactal 12.** To a mixture of tetraol **11** (2.10 g, 4.30 mmol) and CMPI (2.20 g, 8.60 mmol) in 55 mL of dry 1,4-dioxane under N<sub>2</sub> at RT was added levulinic acid. (0.528 mL, 5.16 mmol) and distilled Et<sub>3</sub>N (3.60 mL, 25.8 mmol). After 42 h. of stirring, the reaction mixture was poured into sat. NaHCO<sub>3(aq)</sub> (70 mL) and extracted with EtOAc (3 x 150 mL). The combined organic layers were washed with sat. NaHCO<sub>3(aq)</sub> (2 x 50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Chromatographic separation with 3-5% MeOH in CH<sub>2</sub>Cl<sub>2</sub> gave the desired levulinate **12** (1.62 g, 64%) along with the starting material **11** (0.363 g, 17%):  $[\alpha]_D^{23} = +4.7^\circ$  (c 0.23, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film)

3411, 3063, 3030, 2913, 2871, 1736, 1718, 1648, 1496, 1453, 1404, 1363, 1245, 1209, 1157, 1070, 911, 740, 699  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, 0.08 M in  $\text{CDCl}_3$ )  $\delta$  7.35-7.24 (m, 10H), 6.39 (dd, 1H,  $J = 6.2, 1.0$  Hz), 4.83 (dd, 1H,  $J = 6.2, 3.2$  Hz), 4.64-4.54 (m, 4H), 4.50 (d, 1H,  $J = 7.7$  Hz), 4.32 (dd, 1H,  $J = 11.4, 5.9$  Hz), 4.23-4.09 (m, 5H), 3.94 (dd, 1H,  $J = 11.3, 4.6$  Hz), 3.81 (t, 1H,  $J = 3.6$  Hz), 3.73-3.60 (3H, m), 3.55-3.46 (2H, m), 3.33 (d, 1H,  $J = 4.4$  Hz), 2.71-2.58 (m, 2H), 2.50-2.37 (m, 2H), 2.12 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz, 0.08 M in  $\text{CDCl}_3$ )  $\delta$  206.7, 172.7, 144.7, 138.3, 137.6, 128.40, 128.36, 127.9, 127.8, 127.6, 103.1, 100.1, 76.4, 73.8 (2C), 73.0, 72.4, 71.5, 70.0, 68.2, 68.0, 63.1, 37.8, 29.7, 27.7; LRMS (EI) calcd for  $\text{C}_{31}\text{H}_{38}\text{O}_{11}\cdot\text{Na}$   $[\text{M}+\text{Na}]^+$  609, found 609.

**6-*O*-Triisopropylsilyl-3-*O*-triphenylsilyl Glucal (14).** To a solution of 6-TIPS glucal (10.2g, 33.9 mmol),  $\text{Et}_3\text{N}$  (9.44 ml, 67.7 mmol), and DMAP (0.207 g, 1.69 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (250 mL) under  $\text{N}_2$  at  $-10^\circ\text{C}$  was added TPSCl (10.4 g, 34.2 mmol, dissolved in 50 mL of  $\text{CH}_2\text{Cl}_2$ ) dropwise over the period of 15 min. The reaction mixture was allowed to warm to RT and stirred for 5 h. Then, it was washed with  $\text{H}_2\text{O}$  (2 x 500 mL), sat.  $\text{NaHCO}_3(\text{aq})$  (1 x 500 mL), brine (1 x 500 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated to dryness. Flash chromatography of residue with 5-50% EtOAc in Hexanes gave 14 (13.6 g, 72%) as a colorless oil:  $[\alpha]_D^{23} = +0.73^\circ$  ( $c$  2.7,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 2942, 2865, 1644, 1463, 1429, 1244, 1116, 1048, 883  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd, 6H,  $J = 8.0, 1.6$  Hz), 7.45-7.35 (m, 9H), 6.23 (dd, 1H,  $J = 6.0, 1.6$  Hz), 4.56 (dd, 1H,  $J = 6.1, 2.4$  Hz), 4.47 (m, 1H), 4.06-4.00 (m, 2H), 3.98-3.95 (dd, 1H,  $J = 11.0, 3.7$  Hz), 3.80-3.75 (m, 1H), 2.37 (d, 1H,  $J = 4.0$  Hz), 1.13-1.03 (m, 21H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 135.5, 134.3, 130.1, 127.9, 102.9, 78.0, 71.0, 70.9, 63.3, 17.9, 11.9; LRMS (EI) calcd for  $\text{C}_{33}\text{H}_{44}\text{O}_4\text{Si}\cdot\text{NH}_4$   $[\text{M} + \text{NH}_4]^+$  578, found 578.

**4-O-Fucosyl-3-hydroxyl Glucal 16.** To a mixture of  $\text{AgClO}_4$  (0.883 g, 4.26 mmol),  $\text{SnCl}_2$  (0.808 g, 4.26 mmol) and flame dried 4 Å M.S. (10.7 g) under  $\text{N}_2$  at  $0^\circ\text{C}$  was added via cannula a solution of disilylglucal **14** (2.39 g, 4.26 mmol), tribenzylfucosyl fluoride **15** (1.86 g, 4.26 mmol) and di-*tert*-butylpyridine (0.957 mL, 4.26 mmol) in freshly distilled ether (45 mL). The reaction mixture was stirred at 22 h at RT with exclusion of light. The reaction mixture was filtered through a pad of silica gel with the help of EtOAc, and further rinsed with EtOAc (100 mL). The filtrate was washed with sat.  $\text{NaHCO}_3(\text{aq})$  (2 x 100 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. The crude product was dissolved in 45 mL of MeOH-THF (2:1) and the resulting solution was treated with anhydrous  $\text{K}_2\text{CO}_3$  (0.8 g). After 20 h of stirring, the reaction mixture was diluted with  $\text{Et}_2\text{O}$  (100 mL), filtered through a pad of silica gel, concentrated, and chromatographed (10% EtOAc in hexanes) to give **16** (1.95 g, 64%):  $[\alpha]_D^{23} = -15.3^\circ$  ( $c$  1.6,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3453, 2941, 2865, 1650, 1454, 1235, 1103, 1060, 1028, 883, 737  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.26 (m, 15H), 6.36 (dd, 1H,  $J = 6.0, 1.6$  Hz), 4.99 (d, 1H,  $J = 3.6$  Hz), 4.98 (d, 1H,  $J = 11.5$  Hz), 4.85 (d, 1H,  $J = 11.8$  Hz), 4.78-4.62 (m, 5H), 4.30 (m, 1H), 4.24 (m, 1H), 4.14-4.06 (m, 3H), 3.96-3.87 (m, 3H), 3.70 (d, 1H,  $J = 1.8$  Hz), 3.49 (dd, 1H,  $J = 9.8, 6.8$  Hz), 1.16 (d, 3H,  $J = 6.5$  Hz), 1.08-0.99 (m, 21H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 138.7, 138.34, 138.25, 128.41, 128.40, 128.3, 128.2, 127.70, 127.65, 127.6, 127.3, 101.4, 99.7, 80.5, 79.2, 77.5, 77.4, 75.8, 74.9, 73.4, 73.3, 68.7, 68.0, 63.1, 18.0, 16.5, 12.0; LRMS (EI) calcd for  $\text{C}_{42}\text{H}_{58}\text{O}_8\text{Si}\cdot\text{NH}_4$   $[\text{M} + \text{NH}_4]^+$  736, found 735.

**Le<sup>a</sup> Trisaccharide Glycal 19.** A solution of 6-*O*-TIPS-3,4-cyclocarbonate galactal (1.95 g, 5.94 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (10 mL), was treated with 3,3'-

dimethyldioxirane (90 mL, ca. 0.07 M) at 0°C, stirred for 30 min. and concentrated by stream of N<sub>2</sub>. To the resulting oil was added a solution of acceptor **16** (1.98 g, 2.76 mmol) in dry THF (20 mL). The resulting solution was cooled to 0°C and treated with 1M ZnCl<sub>2</sub> in THF (6.00 mL, 6.00 mmol). The reaction mixture was concentrated by N<sub>2</sub> stream after removing cooling bath and stirred for 2.5 h at RT. The reaction mixture was diluted EtOAc (100 mL), washed with sat. NaHCO<sub>3(aq)</sub> (2 x 50 mL), H<sub>2</sub>O (2 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness. Flash chromatography of residue with 10-15% EtOAc in hexanes gave **18** (2.23 g, 76%) as white form. To a solution of trisaccharide glucal **18** (2.23g, 2.10 mmol), Et<sub>3</sub>N (1.46 mL, 10.5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) under N<sub>2</sub> at 0°C was added TBSOTf (0.772 mL, 3.15 mmol). After 1h of stirring, the reaction was diluted with EtOAc-hexanes (1:1, 100 mL), washed with sat. NaHCO<sub>3(aq)</sub> (2 x 50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. Flash chromatography with 5% EtOAc in hexanes gave TBS ether **19** (2.33 g, 94%, 71% over 2 steps) of as a white foam:  $[\alpha]_D^{23} = -46.0^\circ$  (*c* 0.09, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 2943, 2866, 1821, 1693, 1644, 1556, 1504, 1462, 1384, 1360, 1253, 1105, 1049, 882, 839, 782, 737, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.21 (m, 15H), 6.40 (d, 1H, *J* = 6.2 Hz), 5.21 (d, 1H, *J* = 3.6 Hz), 4.95 (d, 1H, *J* = 11.4 Hz), 4.87 (dd, 1H, *J* = 7.6, 1.0 Hz), 4.84 (d, 1H, *J* = 11.6 Hz), 4.78-4.68 (m, 4H), 4.64 (d, 1H, *J* = 11.4 Hz), 4.59-4.56 (m, 2H), 4.39 (m, 1H), 4.27 (1, 1H, *J* = 6.6 Hz), 4.12-4.04 (m, 4H), 3.96 (dd, 1H, *J* = 10.2, 2.6 Hz), 3.90-3.82 (m, 4H), 3.72 (d, 1H, *J* = 1.7 Hz), 3.67 (t, 1H, *J* = 5.1 Hz), 1.13 (d, 3H, *J* = 6.4 Hz), 1.10-1.01 (m, 42H), 0.89 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.0, 145.2, 138.8, 138.7, 138.6, 128.23, 128.17, 128.1, 127.8, 127.42, 127.39, 127.3, 127.2, 98.6, 97.2, 97.1, 79.9, 78.8, 78.1, 77.7, 76.1, 75.0, 73.9, 73.5, 72.6, 72.0, 71.3, 71.2, 71.0,

66.4, 61.4, 61.3, 25.6, 18.0, 17.93, 17.87, 17.8, 16.7, 12.0, 11.8, -4.5, -5.1; HRMS calcd for  $C_{64}H_{100}O_{14}Si_3 \cdot Na$   $[M + Na]^+$  1199.6320, found 1199.6330.

**Le<sup>a</sup> Iodosulfonamide 20.** To a mixture of trisaccharide glycal **19** (0.564 g, 0.479 mmol), benzenesulfonamide (0.169 g, 1.05 mmol), and 4 Å molecular sieves (0.7 g) in 5 mL  $CH_2Cl_2$  was added  $I(sym-coll)_2ClO_4$  (0.494 g, 1.05 mmol) at 0°C. The reaction mixture was stirred at 0°C under  $N_2$  with exclusion of light. After 2 h of stirring, the reaction mixture was diluted with EtOAc (100 mL) and filtered through a pad of silica gel. The filtrate was washed with sat.  $Na_2S_2O_3(aq)$  (3 x 150 mL), sat.  $CuSO_4(aq)$  (2 x 150 mL), and brine (1 x 150 mL), dried over  $Na_2SO_4$ , and concentrated. The crude oil was purified by flash column chromatography (7% EtOAc in hexanes) to yield iodosulfonamide **20** (0.625 g, 89%):  $[\alpha]_D^{23} = -65.2^\circ$  ( $c$  1.12,  $CHCl_3$ ); IR ( $CHCl_3$  film) 3275, 3065, 3031, 2942, 2865, 1838, 1821, 1464, 1381, 1344, 1254, 1206, 1161, 1109, 1044, 960, 919, 882, 840, 811, 781, 753  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.86 (dd, 2H,  $J = 7.5, 1.1$  Hz), 7.50 (t, 1H,  $J = 7.5$  Hz), 7.41-7.19 (m, 17H), 5.74 (d, 1H,  $J = 9.6$  Hz), 5.48 (m, 1H), 4.95-4.92 (m, 2H), 4.86-4.71 (m, 5H), 4.66-4.59 (m, 3H), 4.39 (m, 1H), 4.09-4.06 (m, 2H), 3.98-3.92 (m, 2H), 3.87-3.81 (m, 5H), 3.73 (b, 1H), 3.62 (dd, 1H,  $J = 10.6, 3.6$  Hz), 3.35 (b, 1H), 3.23 (b, 1H), 1.10 (d, 3H,  $J = 6.8$  Hz), 1.08-0.95 (m, 42H), 0.93 (s, 9H), 0.23 (s, 3H), 0.17 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  153.6, 141.0, 138.9, 138.8, 138.5, 132.6, 128.7, 128.3, 128.2, 128.1, 127.7, 127.5, 127.4, 127.3, 102.0, 97.6, 82.4, 79.4, 77.2, 75.5, 75.0, 74.9, 73.6, 73.5, 72.6, 72.3, 71.6, 70.7, 66.5, 60.8, 60.5, 27.6, 25.7, 18.0, 17.92, 17.87, 17.8, 16.8, 11.81, 11.76, -3.9, -4.9; HRMS (FAB) calcd for  $C_{70}H_{106}INO_{16}SSi_3 \cdot Na$   $[M + Na]^+$  1482.5480, found 1482.5440.

**Pentasaccharide 21.** A mixture of levulinate **12** (2.09 g, 3.56 mmol) and  $(\text{Bu}_3\text{Sn})_2\text{O}$  (1.04 mL, 1.96 mmol) in  $\text{C}_6\text{H}_6$  (70 mL) was heated at reflux with azeotropic removal of water for 12 h. The reaction mixture was then concentrated by a stream of  $\text{N}_2$  and then in vacuo. The stannyl ether formed above was dissolved in dry THF (13 mL). To a mixture of iodosulfonamide **20** (0.556 g, 0.381 mmol), freshly activated 4 Å M.S. (3 g) and  $\text{AgBF}_4$  (0.888 g, 4.56 mmol) was added the tin ether solution via cannula at RT. The reaction mixture was heated at 45°C for 31.5 h. Then, additional  $\text{AgBF}_4$  (0.277 g, 1.45 mmol) in THF (1.5 mL) was added to the mixture. After stirred at 45°C for 68 h totally, the reaction mixture was filtered through a pad of celite and rinsed with EtOAc (200 mL). The filtrate was washed with sat.  $\text{NaHCO}_3(\text{aq})$  (3 x 70 mL), brine (70 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated to dryness. Flash column chromatography of residue with 30% EtOAc in hexanes gave desired product **21** (0.329 g, 45%) as a white foam. Levulinate **12** (1.707 g) was also recovered by elution with 3% MeOH in  $\text{CH}_2\text{Cl}_2$ :  $[\alpha]_D^{23} = -57.9^\circ$  (*c* 1.68,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3586, 2942, 2856, 1819, 1739, 1718, 1648, 1455, 1362, 1103  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84-7.82 (d, 2H, *J* = 7.6 Hz), 7.50 (t, 1H, *J* = 7.4 Hz), 7.40 (t, 2H, *J* = 8.1 Hz), 7.38-7.21 (m, 25H), 6.59 (d, 1H, *J* = 7.2 Hz), 6.41 (dd, 1H, *J* = 6.0, 0.8 Hz), 4.98-4.94 (m, 2H), 4.87-4.75 (m, 6H), 4.70-4.58 (m, 8H), 4.42 (d, 1H, *J* = 7.9 Hz), 4.29-4.05 (m, 9H), 4.00-3.65 (m, 12H), 3.55-3.48 (m, 2H), 3.34 (t, 1H, *J* = 7.0 Hz), 3.27 (b, 1H), 3.22 (t, 1H, *J* = 8.6 Hz), 2.95 (dd, 1H, *J* = 9.4, 3.2 Hz), 2.70-2.56 (m, 2H), 2.42 (t, 2H, *J* = 6.4 Hz), 2.12 (s, 3H), 1.11-1.00 (m, 45H), 0.85 (s, 9H), 0.10 (s, 3H), 0.00 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  206.3, 172.5, 153.9, 144.5, 140.0, 138.6, 138.30, 138.26, 138.1, 137.5, 132.6, 128.8, 128.6, 128.5, 128.41, 128.40, 128.2, 128.0, 127.9, 127.8, 127.71, 127.69, 127.5, 127.2, 102.6, 101.0

(2C), 100.2, 94.7, 81.1, 80.2, 79.7, 79.6, 76.9, 76.5, 76.2, 75.2, 74.7, 74.6, 74.4, 73.7, 73.6, 73.2, 73.1, 72.0, 71.8, 70.83, 70.82, 70.7, 68.0, 67.9, 67.1, 63.8, 63.1, 61.0, 58.3, 37.7, 29.7, 27.7, 25.7, 17.96, 17.95, 17.9, 17.8, 16.6, 11.78, 11.75, -4.5, -5.2; HRMS (FAB) calcd for  $C_{101}H_{143}NO_{27}SSi_3 \cdot Na$   $[M + Na]^+$  1940.8770, found 1940.8770.

**Pentasaccharide Triol 22.** A solution of pentasaccharide **21** (0.329 g, 0.172 mmol) in  $CH_2Cl_2$  (25 mL) was treated sequentially with pyridine (0.880 mL) and hydrazine (0.880 mL, 0.880 mmol, 1M in pyridine-AcOH (3:2)) at RT. The reaction mixture was stirred at RT for 1.5 h. Then, it was diluted with EtOAc (150 mL), washed with sat.  $NaHCO_{3(aq)}$  (2 x 50 mL), sat.  $CuSO_{4(aq)}$  (2 x 50 mL),  $H_2O$  (50 mL), brine (50 mL), and concentrated *in vacuo*. Flash column chromatography of residue with 30% EtOAc in hexanes afforded **22** (0.290 g, 93%) as a white foam:  $[\alpha]_D^{23} = -69.1^\circ$  (*c* 0.29,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 3511, 3064, 3030, 2926, 2864, 1647, 1462, 1347, 1253, 1105, 882  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.86 (d, 2H,  $J = 7.6$  Hz), 7.52-7.20 (m, 28H), 6.41 (d, 1H,  $J = 6.2$  Hz), 5.77 (d, 1H,  $J = 8.0$  Hz), 4.97 (d, 1H,  $J = 3.7$  Hz), 4.94 (d, 1H,  $J = 11.6$  Hz), 4.87 (dd, 1H,  $J = 6.1, 2.7$  Hz), 4.85 (d, 1H,  $J = 2.6$  Hz), 4.81 (m, 1H), 4.75 (d, 1H,  $J = 11.6$  Hz), 4.69-4.64 (m, 4H), 4.62-4.61 (m, 3H), 4.59-4.55 (m, 2H), 4.42 (d, 1H,  $J = 7.8$  Hz), 4.28 (m, 1H), 4.16-4.11 (m, 2H), 4.07-4.03 (m, 3H), 4.00 (d, 1H,  $J = 4.5$  Hz), 3.97-3.75 (m, 8H), 3.72-3.59 (m, 4H), 3.56 (t, 1H,  $J = 6.0$  Hz), 3.42-3.38 (m, 2H), 3.22 (s, 1H), 3.04-3.02 (m, 2H), 2.41 (s, 1H), 2.17 (dd, 1H,  $J = 9.2, 3.2$  Hz), 1.10 (d, 3H,  $J = 6.8$  Hz), 1.08-1.02 (m, 42H), 0.86 (m, 9H), 0.10 (s, 3H), 0.02 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  153.8, 144.7, 140.1, 138.6, 138.33, 138.28, 138.1, 137.5, 132.6, 128.8, 128.6, 128.49, 128.46, 128.4, 128.2, 128.0, 127.9, 127.74, 127.73, 127.6, 127.5, 127.2, 102.8, 101.2, 100.9, 100.3, 95.0, 81.8, 79.9, 79.7, 79.3, 78.7, 76.9, 76.1, 75.3, 75.0,



74.8, 74.4, 74.1, 73.7, 73.2, 72.8, 71.7, 71.1, 70.7, 68.7, 68.1, 67.3, 63.4, 62.5, 61.0, 58.1, 25.7, 18.0, 17.9, 17.8, 16.6, 11.80, 11.78, -4.5, -5.2; HRMS (FAB) calcd for  $C_9H_{137}NO_{25}SSi_3 \cdot Na$   $[M + Na]^+$  1842.8410, found 1842.8440.

**Disaccharide Glycal 25.** To a mixture of disaccharide **24** (2.01 g, 2.74 mmol) and PMBCl (0.410 mL, 3.01 mmol) in dry DMF (40 mL) was added NaH (60% in oil, 0.131 g, 3.29 mmol) at 0°C. The reaction mixture was stirred at RT for 1.5 h, diluted with EtOAc (200 mL), and poured into sat.  $NaHCO_3(aq)$  (70 mL). The organic layer was separated, washed with  $H_2O$  (3 x 50 mL), sat.  $NaHCO_3(aq)$  (50 mL), and brine (50 mL), dried over  $Na_2SO_4$ , and concentrated *in vacuo*. Flash column chromatography of crude material with 8% EtOAc in hexanes gave **25** (1.90g, 83%) as a colorless oil:  $[\alpha]_D^{23} = -87.5^\circ$  (*c* 1.13,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 2866, 1723, 1649, 1612, 1514, 1453, 1271, 1109, 883, 713  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04-8.02 (m, 2H), 7.57 (m, 1H), 7.45-7.42 (m, 2H), 7.34-7.17 (m, 12H), 6.87 (d, 2H,  $J = 8.8$  Hz), 6.39 (d, 1H,  $J = 6.0$  Hz), 5.41 (d, 1H,  $J = 2.8$  Hz), 4.96 (d, 1H,  $J = 3.6$  Hz), 4.83 (d, 1H,  $J = 12.2$  Hz), 4.80 (d, 1H,  $J = 11.5$  Hz), 4.78-4.73 (m, 2H), 4.67 (d, 1H,  $J = 12.2$  Hz), 4.63 (d, 1H,  $J = 8.4$  Hz), 4.60 (d, 1H,  $J = 8.8$  Hz), 4.37 (d, 1H,  $J = 7.0$  Hz), 4.11 (q, 1H,  $J = 6.5$  Hz), 4.05-3.96 (m, 4H), 3.89 (dd, 1H,  $J = 10.1, 3.6$  Hz), 3.85-3.80 (m, 4H), 1.18-1.07 (m, 21H), 0.95 (d, 3H,  $J = 6.5$  Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.2, 159.3, 145.0, 138.5, 138.3, 133.0, 130.5, 130.0, 129.9, 128.3, 128.2, 127.8, 127.7, 127.5, 113.9, 98.4, 94.9, 78.7, 76.1, 74.7, 74.1, 74.0, 73.4, 72.4, 71.9, 71.6, 65.0, 61.9, 55.3, 18.01, 17.98, 16.1, 12.0; LRMS (EI) calcd for  $C_{50}H_{64}O_{10}Si \cdot NH_4$   $[M + NH_4]^+$  870, found 870.

**Iodosulfonamide 26.** A mixture of disaccharide glycal **25** (0.411 g, 0.491 mmol),  $PhSO_2NH_2$  (0.193 g, 1.23 mmol) and 4 Å M.S. (0.470 g), in  $CH_2Cl_2$  (4 mL) was

stirred at RT for 15 min. The reaction mixture was cooled to 0°C, treated with I(*sym*-coll)<sub>2</sub>ClO<sub>4</sub> (0.575 g, 1.23 mmol) and stirred for 1h. Then, it was diluted with EtOAc (100 mL), washed with sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3(aq)</sub> (2 x 50 mL), sat. CuSO<sub>4(aq)</sub> (2 x 30 mL), and brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated to dryness. Flash column chromatography of crude material with 20% EtOAc in hexanes afforded **26** (0.483 g, 88%) as a colorless glass:  $[\alpha]_D^{23} = -86.9^\circ$  (*c* 0.78, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 3268, 3064, 2941, 1723, 1612, 1514, 1451, 1271, 1094, 883 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04-8.02 (m, 2H), 7.87-7.85 (m, 2H), 7.60-7.52 (m, 2H), 7.47-7.39 (m, 6H), 7.36-7.30 (m, 5H), 7.27-7.18 (m, 3H), 7.12-7.10 (m, 2H), 6.84-6.82 (m, 2H), 5.74 (d, 1H, *J* = 7.6 Hz), 5.59 (d, 1H, *J* = 6.8 Hz), 5.46 (d, 1H, *J* = 2.4 Hz), 5.03 (d, 1H, *J* = 3.3 Hz), 4.82-4.75 (m, 3H), 4.61-4.52 (m, 4H), 4.23 (t, 1H, *J* = 6.2 Hz), 4.12-4.02 (m, 2H), 3.92 (dd, 1H, *J* = 10.0, 3.3 Hz), 3.79 (s, 3H), 3.66 (dd, 1H, *J* = 11.3, 2.0 Hz), 3.10 (dd, 1H, *J* = 8.9, 3.9 Hz), 3.04 (d, 1H, *J* = 9.3 Hz), 2.97 (d, 1H, *J* = 11.3 Hz), 1.11-1.02 (m, 21H), 1.00 (d, 3H, *J* = 6.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.2, 159.4, 140.6, 138.2, 138.1, 133.1, 132.8, 130.2, 130.0, 129.9, 129.4, 128.4 (2C), 128.22, 128.18, 127.9, 127.8, 127.5, 127.4, 113.9, 95.5, 84.6, 76.0, 75.0, 74.7, 74.5, 73.7, 73.4, 71.7, 71.4, 66.0, 61.0, 55.3, 29.6, 18.1, 18.0, 16.2, 11.9; HRMS (FAB) calcd for C<sub>56</sub>H<sub>70</sub>INO<sub>12</sub>SSi·Na [M + Na]<sup>+</sup> 1158.3330, found 1158.3360.

**Thioglycoside 27.** To a solution of iodosulfonamide **26** (0.515 g, 0.460 mmol) in dry DMF (1.5 mL) was added EtSH (0.170 mL, 2.30 mmol) at -40°C. Immediately, LHMDS (1M in THF, 1.38 mL, 1.38 mmol) was added to the reaction mixture at -40°C. The reaction mixture was stirred at -40 - -15°C for 30 min, allowed to warm to RT and stirred for additional 30 min. The reaction mixture was diluted with EtOAc (30 mL),

washed with sat.  $\text{NH}_4\text{Cl}_{(\text{aq})}$  (2 x 20 mL),  $\text{H}_2\text{O}$  (3 x 20 mL), and brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated to dryness. Careful flash chromatography of crude material with 15% EtOAc in hexanes gave **27** (0.462 g, 95%) as a colorless glass:  $[\alpha]_{\text{D}}^{23} = -76.6^\circ$  ( $c$  1.01,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3200, 2940, 2866, 1722, 1612, 1515, 1453, 1321, 1271, 1159, 1091  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d, 2H,  $J = 7.4$  Hz), 7.61-7.55 (m, 3H), 7.50-7.18 (m, 17H), 6.90 (d, 2H,  $J = 8.5$  Hz), 6.54 (d, 1H,  $J = 4.2$  Hz), 5.74 (d, 1H,  $J = 3.0$  Hz), 5.57 (d, 1H,  $J = 3.4$  Hz), 4.97 (d, 1H,  $J = 9.4$  Hz), 4.95 (d, 1H,  $J = 10.5$  Hz), 4.88 (d, 1H,  $J = 10.1$  Hz), 4.79 (d, 1H,  $J = 10.1$  Hz), 4.75 (dd, 1H,  $J = 10.0, 3.2$  Hz), 4.67-4.58 (m, 3H), 4.02 (dd, 1H,  $J = 10.0, 3.4$  Hz), 3.94 (d, 1H,  $J = 2.6$  Hz), 3.83 (d, 1H,  $J = 9.5$  Hz), 3.81 (s, 3H), 3.72-3.62 (m, 3H), 3.22 (d, 1H,  $J = 8.9$  Hz), 2.39-2.32 (m, 2H), 1.26 (d, 3H,  $J = 6.5$  Hz), 1.51-1.05 (m, 21H), 0.90 (t, 3H,  $J = 7.5$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 159.5, 142.8, 138.6, 137.6, 133.0, 131.6, 130.33, 130.26, 130.2, 129.9, 128.7, 128.5, 128.44, 128.36, 128.04, 127.99, 127.96, 127.3, 127.0, 113.9, 100.1, 85.4, 82.4, 80.3, 78.1, 77.9, 76.9, 75.0, 72.2, 71.3, 71.2, 66.7, 62.2, 57.7, 55.2, 23.3, 18.01, 17.97, 16.7, 14.0, 11.9; HRMS (FAB) calcd for  $\text{C}_{58}\text{H}_{75}\text{NO}_{12}\text{S}_2\text{Si}\cdot\text{Na}$   $[\text{M} + \text{Na}]^+$  1092.4400, found 1092.4440.

**Galactosyl Donor 28.** To a solution of azeotropically dried 6-*O*-TIPS-3,4-cyclocarbonate galactal (1.99 g, 6.06 mmol), in 7 mL  $\text{CH}_2\text{Cl}_2$  was added a solution of DMDO in acetone (240 mL of ca. 0.05 M solution) at  $0^\circ\text{C}$ . The reaction mixture was stirred at  $0^\circ\text{C}$  under  $\text{N}_2$  for 1 h. After 1 h of stirring, the volatiles were removed by  $\text{N}_2$  stream until around 10 mL of solvent was left. Then the reaction mixture was again dissolved in 14 mL anhydrous benzene, and the volatiles were evaporated again with  $\text{N}_2$  stream. The resulting oil was further dried *in vacuo* for 2 h. The crude epoxide was

dissolved in 10 mL THF and was treated with EtSH (11.6 mL, 15.1 mmol) and ZnCl<sub>2</sub> (6.06 mL, 6.06 mmol, 1M solution in THF) at -20°C. The reaction was stirred under N<sub>2</sub> for 3 h. while the reaction mixture was allowed to warm to 0°C. Then the volatiles were again removed by N<sub>2</sub> stream. The clear colorless oil was dissolved in EtOAc and poured into a separatory funnel containing cold sat. NaHCO<sub>3(aq)</sub>. (100 mL). Then, the organic layer was washed with sat. NaHCO<sub>3(aq)</sub> (2 x 150 mL), brine (1 x 150mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude oil obtained was dissolved in 10 mL CH<sub>2</sub>Cl<sub>2</sub> and DMAP (1.11g, 9.09 mmol) and Ac<sub>2</sub>O (0.858 mL, 9.09 mmol) were added to the solution at RT. The reaction mixture was stirred at RT under N<sub>2</sub> overnight. The reaction mixture was diluted with EtOAc and washed with sat NaHCO<sub>3(aq)</sub> (3 x 50 mL), brine (1 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The reaction mixture was purified by column chromatography (13% - 20 % EtOAc in hexanes) to yield **2.31** (0.627 g, 23%) as an oil:  $[\alpha]_D^{23} = -23.1^\circ$  (*c* 0.97, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 2943, 2867, 1816, 1751, 1463, 1372, 1221, 1121, 882 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.08 (dd, 1H, *J* = 8.0, 5.6 Hz), 4.90 (dd, 1H, *J* = 7.6, 2.0 Hz), 4.81 (dd, 1H, *J* = 7.2, 5.6 Hz), 4.57 (d, 1H, *J* = 8.0 Hz), 3.99-3.91 (m, 2H), 3.87 (dt, 1H, *J* = 7.0, 2.0 Hz), 2.78-2.63 (m, 2H), 1.25 (t, 3H, *J* = 6.8 Hz), 1.07-1.03 (m, 21H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.0, 153.3, 82.0, 76.0, 75.7, 74.1, 70.1, 61.4, 24.2, 20.8, 17.8, 14.5, 11.8; LRMS (EI) calcd for C<sub>20</sub>H<sub>36</sub>O<sub>7</sub>SSi·NH<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup> 466, found 466.

**Heptasaccharide 29.** A mixture of ethylthioglycoside **27** (0.126 g, 0.117 mmol), pentasaccharide acceptor **22** (0.107 g, 0.0590 mmol) and freshly activated 4 Å molecular sieves (0.69 g) in Et<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> (3 mL, 2:1) was stirred at RT for 15 min and cooled to -40°C. The reaction mixture was treated with di-*tert*-butylpyridine (0.106 mL, 0.470

mmol), methyltriflate (0.053 mL, 0.47 mmol) at  $-40^{\circ}\text{C}$  and stirred at  $-10^{\circ}\text{C}$  for 24 h. Then, it was quenched with  $\text{Et}_3\text{N}$  (2 mL) and stirred for additional 15 min at RT. The reaction mixture was diluted with EtOAc (30 mL), filtered through a pad of silica gel, washed with sat.  $\text{NaHCO}_3(\text{aq})$  (2 x 10 mL), and brine (10 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated to dryness. Flash column chromatography of crude material with 20% EtOAc in hexanes gave **29** (0.0858 g, 52%) with  $\alpha$ -isomer (0.0365 g, 80% purity) as a colorless glass:  $[\alpha]_D^{23} = -68.5^{\circ}$  ( $c$  1.01,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3589, 3196, 3064, 3031, 2941, 2866, 1820, 1723, 1650, 1613, 1515, 1496, 1325, 1098, 882  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10-8.08 (m, 2H), 7.87-7.85 (m, 2H), 7.59 (m, 1H), 7.53-7.45 (m, 8H), 7.39-7.16 (m, 41H), 6.91-6.87 (m, 2H), 6.78 (d, 1H,  $J = 3.6$  Hz), 6.39 (dd, 1H,  $J = 6.0, 1.0$  Hz), 6.08 (d, 1H,  $J = 7.2$  Hz), 5.70 (d, 1H,  $J = 2.4$  Hz), 5.46 (d, 1H,  $J = 3.2$  Hz), 5.02 (d, 1H,  $J = 3.6$  Hz), 4.95 (d, 1H,  $J = 10.6$  Hz), 4.90 (d, 1H,  $J = 6.1$  Hz), 4.88-4.83 (m, 5H), 4.81 (d, 1H,  $J = 4.6$  Hz), 4.78-4.69 (m, 3H), 4.62-4.50 (m, 11H), 4.22-4.18 (m, 2H), 4.12-3.97 (m, 9H), 3.95-3.88 (m, 5H), 3.86-3.82 (m, 2H), 3.81 (s, 3H), 3.77-3.72 (m, 3H), 3.62-3.46 (m, 5H), 3.40 (s, 1H), 3.36 (t, 1H,  $J = 6.9$  Hz), 3.27 (t, 1H,  $J = 8.7$  Hz), 3.10-3.06 (m, 3H), 2.85 (dd, 1H,  $J = 9.6, 6.1$  Hz), 2.29 (s, 1H), 2.07 (s, 1H), 1.23 (d, 3H,  $J = 6.4$  Hz), 1.12 (d, 3H,  $J = 6.4$  Hz), 1.10-1.00 (m, 63H), 0.87 (s, 9H), 0.13 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 159.5, 153.9, 144.3, 143.4, 139.9, 138.7, 138.6, 138.4, 138.2, 137.7, 137.6, 133.0, 132.7, 131.3, 130.3, 130.22, 130.18, 129.9, 128.9, 128.8, 128.52, 128.50, 128.44, 128.43, 128.39, 128.3, 128.2, 128.0, 127.9, 127.81, 127.76, 127.7, 127.6, 127.50, 127.45, 127.3, 127.2, 126.5, 114.0, 102.8, 102.2, 101.2, 100.1, 95.8, 80.9, 80.62, 80.56, 79.9, 79.6, 79.0, 78.1, 77.6, 77.2, 76.2, 75.9, 75.7, 74.9, 74.8, 74.7, 74.3, 74.2, 73.7, 73.6, 73.5, 73.1, 72.5, 72.0, 71.9, 71.6, 71.2, 71.0, 70.8,

67.9, 67.5, 67.1, 66.7, 66.6, 63.0, 62.0, 60.9, 58.7, 58.2, 55.3, 25.7, 18.04, 18.01, 17.90, 17.85, 16.6, 11.9, 11.84, 11.78, -4.4, -5.2; LRMS (EI) calcd for  $C_{152}H_{206}N_2O_{37}S_2Si_4 \cdot NH_4$   $[M + NH_4]^+$  2845, found 2847.

**Diacetyl Hepta 30.** To a solution of heptasaccharide **29** (0.102 g, 0.0360 mmol), and DMAP (0.0088 g, 0.072 mmol) in  $CH_2Cl_2$  (3 mL), was added  $Ac_2O$  (0.0068 mL, 0.072 mmol) at  $0^\circ C$ . The reaction mixture was stirred at  $0^\circ C$  for 2 h. After the solvent was evaporated, the residue was diluted with EtOAc (30 mL), washed with sat.  $NaHCO_{3(aq)}$  (2 x 10 mL),  $H_2O$  (10 mL), and brine (10 mL), dried over  $Na_2SO_4$  and concentrated to dryness. Column chromatography of residue with 20% EtOAc in hexanes afforded monoacetylated product (0.100 g, 97%) as a colorless glass. The monoacetylated product was directly used to further protection. To a solution of monoacetylated compound (0.0600 mg, 0.0209 mmol),  $Et_3N$  (0.0291 mL, 0.209 mmol), and DMAP (0.0128 mg, 0.105 mmol) in  $CH_2Cl_2$  (1.39 mL) was added  $Ac_2O$  (0.020 mL, 0.209 mmol) at  $0^\circ C$ . Then, the reaction mixture was slowly concentrated by a stream of  $N_2$  to ca. 0.2 mL at  $0^\circ C$  for 30 min. It was diluted with EtOAc (50 mL), washed with sat.  $NaHCO_{3(aq)}$  (2 x 30 mL), brine (30 mL), dried over  $Na_2SO_4$  and concentrated to dryness. Flash column chromatography of crude material with 6% EtOAc in  $CHCl_3$  afforded diacetylated product **30** (0.0355 g, 58%) as a colorless glass:  $[\alpha]_D^{23} = -59.0^\circ$  ( $c$  0.44,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 3354, 2939, 2866, 1837, 1820, 1750, 1725, 1650, 1454, 1366, 1327, 1250, 1159, 1094, 1065, 882  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.09 (d, 2H,  $J = 7.2$  Hz), 7.88 (d, 2H,  $J = 8.2$  Hz), 7.62-7.46 (m, 9H), 7.40-7.21 (m, 39H), 6.93 (d, 1H,  $J = 2.6$  Hz), 6.87 (d, 2H,  $J = 8.6$  Hz), 6.38 (d, 1H,  $J = 6.4$  Hz), 5.69 (d, 1H,  $J = 2.4$  Hz), 5.38 (d, 1H,  $J = 2.8$  Hz), 5.03 (dd, 1H,  $J = 10.1, 8.1$  Hz), 5.01-4.97 (m, 2H), 4.94-

4.88 (m, 4H), 4.84-4.76 (m, 4H), 4.73-4.68 (m, 5H), 4.64-4.56 (m, 6H), 4.52-4.46 (m, 6H), 4.38 (d, 1H,  $J = 9.5$  Hz), 4.28-4.23 (m, 3H), 4.13 (m, 1H), 4.07-4.04 (m, 2H), 3.99-3.96 (m, 2H), 3.89-3.74 (m, 12H), 3.71-3.64 (m, 3H), 3.58 (dd, 1H,  $J = 10.2, 3.3$  Hz), 3.53 (d, 1H,  $J = 7.4$  Hz), 3.48-3.41 (m, 3H), 3.29 (t, 1H,  $J = 9.2$  Hz), 3.16-3.12 (m, 2H), 3.08-3.05 (m, 1H), 2.47 (dd, 1H,  $J = 11.6, 9.6$  Hz), 1.96 (s, 3H), 1.72 (s, 3H), 1.22 (d, 2H,  $J = 6.4$  Hz), 1.10 (d, 3H,  $J = 6.4$  Hz), 1.08-0.96 (m, 63H), 0.81 (s, 9H), 0.05 (s, 3H), -0.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 169.2, 166.2, 159.5, 153.8, 143.9, 142.9, 139.0, 138.9, 138.5, 138.4, 138.3, 138.2, 138.1, 137.4, 133.0, 132.6, 130.9, 130.2, 130.1, 130.0, 129.8, 129.0, 128.8, 128.5, 128.44, 128.43, 128.39, 128.34 (several peaks), 128.3, 128.17, 128.16, 128.1, 127.9, 127.8, 127.74, 127.71, 127.66, 127.52, 127.50, 127.4, 127.22, 127.18, 113.9, 103.4, 102.3, 100.7, 100.2, 99.9, 99.1, 95.6, 80.9, 80.7, 80.1, 79.7, 79.5, 78.3, 77.4, 77.1, 76.8, 75.9, 75.7, 75.1, 74.91, 74.86, 74.8, 74.7, 74.4, 74.2, 73.9, 73.7, 73.4, 73.2, 73.0, 72.3, 71.8, 71.7, 71.2, 71.0, 70.3, 70.2, 68.0, 67.1, 62.6, 60.8, 58.5, 58.3, 55.2, 25.6, 20.8, 20.6, 18.03, 17.96, 17.9, 17.84, 17.79, 16.8, 16.5, 11.9, 11.79, 11.75, -4.2, -5.5; HRMS (FAB)  $\text{C}_{156}\text{H}_{210}\text{N}_2\text{O}_{39}\text{S}_2\text{Si}_4\cdot\text{Na}$   $[\text{M} + \text{Na}]^+$  calcd 2934.2927 found 2934.2980.

**Hepta Acceptor 31.** To a solution of **30** (0.168 g, 0.0577 mmol) and di-*tert*-butylpyridine (0.039 mL, 0.17 mmol) in  $\text{CH}_2\text{Cl}_2$ - $\text{H}_2\text{O}$  (18:1, 3.2 mL) was added DDQ (0.0524 g, 0.230 mmol) at RT. The reaction mixture was stirred vigorously for 3.5 h. It was diluted with EtOAc (30 mL) and washed with sat.  $\text{NaHCO}_3(\text{aq})$  (20 mL). The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with sat.  $\text{NaHCO}_3(\text{aq})$  (2 x 20 mL), and brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. Flash column chromatography of crude material with 5% EtOAc

in C<sub>6</sub>H<sub>6</sub> provided **31** with recovered **30** (29.8 mg). This recovered **30** was re-subjected to the same reaction. Thus, 0.0903 g (57%) of **31** was obtained as a colorless glass:  $[\alpha]_D^{23} = -63.2^\circ$  (*c* 1.36, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 3469, 2942, 2866, 1820, 1752, 1726, 1454, 1367, 1269, 1094 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, 2H, *J* = 8.5 Hz), 7.89 (d, 4H, *J* = 8.5 Hz), 7.61-7.43 (m, 7H), 7.41-7.19 (m, 37H), 6.36 (d, 1H, *J* = 6.2 Hz), 6.25 (d, 1H, *J* = 1.4 Hz), 5.60 (d, 1H, *J* = 2.4 Hz), 5.12 (d, 1H, *J* = 3.5 Hz), 5.08-5.03 (m, 2H), 4.98 (d, 1H, *J* = 7.9 Hz), 4.93-4.86 (m, 4H), 4.83-4.75 (m, 6H), 4.69-4.63 (m, 5H), 4.61 (d, 1H, *J* = 4.4 Hz), 4.59 (d, 1H, *J* = 4.2 Hz), 4.56 (d, 1H, *J* = 6.9 Hz), 4.52 (d, 1H, *J* = 1.5 Hz), 4.47 (d, 1H, *J* = 7.3 Hz), 4.33 (d, 1H, *J* = 7.9 Hz), 4.22-4.14 (m, 2H), 3.89-3.83 (m, 4H), 3.81-3.70 (m, 8H), 3.68-3.62 (m, 2H), 3.59 (s, 1H), 3.54 (dd, 1H, *J* = 11.8, 3.8 Hz), 3.47 (dd, 1H, *J* = 7.2, 6.1 Hz), 3.31-3.12 (m, 5H), 2.94 (t, 1H, *J* = 8.0 Hz), 2.04 (s, 3H), 1.78 (s, 3H), 1.13 (d, 3H, *J* = 6.4 Hz), 1.06-0.99 (m, 63H), 0.85 (s, 9H), 0.08 (s, 3H), -0.09 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.3, 169.1, 166.0, 153.8, 144.2, 140.2, 139.3, 138.8, 128.6, 128.4, 128.3, 138.1, 137.9, 137.6, 133.2, 132.6, 132.0, 129.9, 129.8, 129.3, 129.0, 128.7, 128.54, 128.51, 128.47, 128.43, 128.39, 128.35, 128.31, 128.27, 128.2, 128.12, 128.08, 128.05, 127.9, 127.81, 127.78, 127.7, 127.6, 127.4, 127.3, 102.4, 102.2, 101.1, 100.9, 99.7, 99.5, 95.6, 85.7, 80.8, 80.2, 79.7, 79.4, 76.9, 76.0, 75.7, 75.6, 75.3, 74.8, 74.7, 74.0, 73.8, 73.5, 73.1 (several peaks), 72.3, 72.2, 71.9, 71.81, 71.78, 70.8, 70.6, 70.5, 70.0, 68.2, 67.5, 67.1, 66.9, 63.6, 62.7, 60.9, 58.7, 58.6, 53.4, 25.7, 20.8, 20.7, 18.00, 17.97, 17.92, 17.89, 17.8, 16.8, 16.3, 11.9, 11.8, -4.1, -5.3.

**Fully Protected N3 Major 32.** A mixture of thioglycoside **28** (0.0243 mg, 0.0540 mmol), glycosylacceptor **31** (0.0296 mg, 0.0105 mmol) and freshly activated 4 Å molecular sieves (0.31 g) in Et<sub>2</sub>O-CH<sub>2</sub>Cl<sub>2</sub> (2.1 mL, 4:3) was stirred at RT for 15 min.



Then, the reaction mixture was treated with di-*tert*-butylpyridine (0.062 mL, 0.27 mmol), methyltriflate (0.031 mL, 0.27 mmol) and stirred at RT for 12 h. The reaction mixture was quenched by addition of Et<sub>3</sub>N (1 mL) and stirred for additional 15 min. After being diluted with EtOAc (50 mL), the solution was washed with sat. NaHCO<sub>3(aq)</sub> (2 x 20 mL), brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. Flash column chromatography of crude material with 7% EtOAc in CHCl<sub>3</sub> afforded **32** (0.0331 g, 96%) as a colorless glass:  $[\alpha]_D^{23} = -62.4^\circ$  (*c* 1.11, CHCl<sub>3</sub>); FTIR (CHCl<sub>3</sub> film) 3215, 2942, 2866, 1821, 1750, 1727, 1651, 1454, 1367, 1249, 1105 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, 2H, *J* = 8.5 Hz), 7.89 (d, 2H, *J* = 8.5 Hz), 7.65 (d, 2H, *J* = 8.4 Hz), 7.61-7.42 (m, 6H), 7.40-7.18 (m, 38H), 6.49 (d, 1H, *J* = 4.4 Hz), 6.37 (d, 1H, *J* = 6.4 Hz), 5.69 (d, 1H, *J* = 3.0 Hz), 5.43 (d, 1H, *J* = 5.2 Hz), 5.40 (d, 1H, *J* = 3.4 Hz), 5.03 (dd, 1H, *J* = 10.0, 8.0 Hz), 4.95-4.89 (m, 6H), 4.86-4.79 (m, 4H), 4.76-4.66 (m, 7H), 4.62 (d, 1H, *J* = 5.4 Hz), 4.61 (d, 1H, *J* = 6.8 Hz), 4.59 (d, 1H, *J* = 5.5 Hz), 4.56 (d, 1H, *J* = 6.8 Hz), 4.54-4.49 (m, 4H), 4.48-4.44 (m, 2H), 4.35 (q, 1H, *J* = 6.8 Hz), 4.26 (d, 1H, *J* = 3.0 Hz), 4.20-4.14 (m, 3H), 4.08-4.04 (m, 2H), 4.00-3.92 (m, 2H), 3.90-3.63 (m, 17H), 3.57-3.48 (m, 2H), 3.45-3.37 (m, 3H), 3.23 (d, 1H, *J* = 9.7 Hz), 3.16 (t, 1H, *J* = 7.3 Hz), 3.11-3.07 (m, 1H), 2.6 (dd, 1H, *J* = 11.4, 9.2 Hz), 1.96 (s, 3H), 1.74 (s, 3H), 1.64 (s, 3H), 1.20 (d, 3H, *J* = 6.5 Hz), 1.13-0.99 (m, 87H), 0.83 (s, 9H), 0.06 (s, 3H), -0.14 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.3, 169.2, 166.2, 153.8, 153.0, 144.1, 142.4, 139.2, 138.9, 138.5, 138.4, 138.3, 137.6, 133.0, 132.6, 131.3, 130.0, 129.9, 129.0, 128.7, 128.6, 128.48, 128.46, 128.4, 128.34, 128.31, 128.26, 128.2, 128.1, 128.02, 127.98, 127.9, 127.83, 127.76, 127.7, 127.59, 127.57, 127.55, 127.3, 127.2, 127.1, 122.5, 102.9, 102.4, 100.8, 99.9, 99.4, 98.0, 96.8, 95.7, 80.9, 80.2, 79.7, 79.4, 77.9, 76.8, 75.8, 74.9, 74.8, 74.7, 74.5,

74.2, 73.8, 73.72, 73.66, 73.5, 73.3, 73.1, 72.3, 72.0, 71.8, 71.7, 71.2, 71.1, 71.0, 70.6, 70.1, 69.8, 68.7, 68.1, 68.0, 67.9, 67.2, 66.3, 63.0, 62.7, 60.9, 60.8, 58.6, 58.0, 25.6, 22.5, 20.8, 20.7, 18.01, 17.98, 17.9, 17.8, 16.9, 16.5, 11.9, 11.84, 11.80, -4.2, -5.4; HRMS calcd for  $C_{166}H_{232}N_2O_{45}S_2Si_5Na$   $[M + Na]^+$  3200.4110, found 3200.4030.

**Tetrasaccharide 48.** Azeotropically dried thioglycoside **47** (0.226 g, 0.241 mmol), lactal **43** (0.0916 g, 0.135 mmol), and 1.64 g of flame dried 4 Å M.S. were suspended in the mixed solvent system of  $CH_2Cl_2$  and  $Et_2O$  (3 mL and 6 mL respectively). The reaction mixture was treated with 1,4-di-*tert*-butylpyridine (0.112 mL, 0.484 mmol) and stirred at RT for 10 min. Then, the reaction mixture was cooled to -40°C and treated with MeOTf (0.109 mL, 0.963 mmol). The reaction mixture was stirred while the temperature was allowed to warm to RT slowly during the period of 6 h. The reaction mixture was quenched by addition of  $Et_3N$  (0.6 mL). The reaction mixture was stirred for 10 min and filtered through a pad of silica gel with the help of plenty of EtOAc. The clear filtrate was washed with sat.  $NaHCO_{3(aq)}$  (3 x 75 mL), brine (1 x 75 mL), and dried over  $Na_2SO_4$ . Resulting crude oil was further purified by column chromatography with 10% EtOAc in hexanes to yield tetrasaccharide **48** (0.146 g, 70%) as white foam:  $[\alpha]_D^{23} = -11.7^\circ$  ( $c$  0.18,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 3494, 3360, 3063, 3030, 2951, 2913, 2874, 1957, 1810, 1737, 1719, 1649, 1605, 1586, 1548, 1496, 1454, 1413, 1368, 1338, 1243, 1208, 1161, 1092, 1037, 939, 912, 812, 740, 699  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.83 (m, 2H), 7.50-7.27 (m, 33H), 6.43 (dd, 1H,  $J = 6.3, 0.8$  Hz), 4.90 (dd, 1H,  $J = 5.5, 4.2$  Hz), 4.85 (d, 1H,  $J = 11.3$  Hz), 4.71 (m, 2H), 4.64 (s, 2H), 4.60 (s, 2H), 4.58-4.50 (m, 9H), 4.41 (m, 2H), 4.33-4.26 (m, 3H), 4.23 (t, 1H,  $J = 4.2$  Hz), 4.12 (m, 1H), 3.92 (dd, 1H,  $J = 10.7, 4.7$  Hz), 3.85 (m, 2H), 3.74-3.63 (m, 5H), 3.57-3.41

(m, 6H), 3.37 (t, 1H,  $J = 6.4$  Hz), 3.23 (m, 1H), 2.85 (s, 1H), 2.64 (m, 2H), 2.44 (m, 2H), 2.10 (s, 3H), 0.79 (t, 9H,  $J = 8.0$  Hz), 0.37 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  206.4, 172.5, 153.8, 144.4, 141.0, 138.9, 138.7, 138.2, 137.6, 137.5, 136.9, 132.6, 129.0, 128.6, 128.52, 128.49, 128.40, 128.35, 128.24, 128.17, 127.99, 127.96, 127.94, 127.87, 127.86, 127.8, 127.72, 127.65, 127.5, 127.4, 102.2, 101.6, 99.6, 99.5, 79.2, 78.9, 77.8, 77.6, 75.7, 75.6, 74.6, 74.4, 74.3, 73.9, 73.8, 73.4, 73.3, 72.9, 72.5, 72.0, 71.6, 70.4, 70.3, 68.9, 68.4, 68.0, 67.7, 63.6, 59.0, 37.9, 29.7, 27.9, 6.0, 4.7; HRMS (FAB) calcd for  $\text{C}_{84}\text{H}_{99}\text{NO}_{23}\text{SSi}\cdot\text{Na}$   $[\text{M} + \text{Na}]^+$  1572.5996, found 1572.6018.

**Acetylated Tetrasaccharide 54.** To a solution of tetrasaccharide **48** (0.0274 g, 0.0177 mmol) and catalytic amount of DMAP in  $\text{CH}_2\text{Cl}_2$  (3 mL) were added pyridine (0.0183 mL, 0.226 mmol) and  $\text{Ac}_2\text{O}$  (0.0183 mL, 0.194 mmol). The reaction mixture was stirred at RT for 15 h. The reaction mixture was then concentrated with rotary evaporator without work-up. The resulting oil was purified by column chromatography with 30% EtOAc in hexanes to yield acetyl protected tetrasaccharide **54** (0.0259 g, 92%) as white foam:  $[\alpha]_D^{23} = -1.33^\circ$  ( $c$  0.3,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3327, 3064, 3031, 2913, 2874, 1808, 1744, 1720, 1649, 1497, 1453, 1413, 1369, 1342, 1238, 1161, 1092, 912, 813, 739, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d, 2H,  $J = 7.6$  Hz), 7.48-7.24 (m, 33H), 6.38 (d, 1H,  $J = 5.9$  Hz), 5.33 (d, 1H,  $J = 3.2$  Hz), 4.90 (dd, 1H,  $J = 6.0$ , 4.0 Hz), 4.82 (d, 1H,  $J = 11.4$  Hz), 4.71 (d, 1H,  $J = 7.4$  Hz), 4.65-4.43 (m, 14H), 4.42 (d, 1H,  $J = 11.4$  Hz), 4.24 (m, 2H), 4.13 (m, 2H), 4.03 (m, 2H), 3.87-3.80 (m, 2H), 3.75 (m, 2H), 3.69-3.61 (m, 7H), 3.40 (m, 1H), 3.36-3.31 (m, 3H), 2.60 (m, 2H), 2.42 (m, 2H), 2.13 (s, 3H), 2.08 (s, 3H), 0.76 (t, 9H,  $J = 7.9$  Hz), 0.41 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  206.3, 172.2, 170.1, 153.8, 144.5, 141.9, 138.9, 138.6, 138.2, 138.0, 137.5,

137.0, 132.2, 128.7, 128.4, 128.33, 128.27, 128.0, 127.9, 127.80, 127.78, 127.7, 127.6, 127.54, 127.48, 127.2, 102.3, 101.8, 100.2, 99.6, 79.9, 78.6, 78.5, 76.7, 75.6, 75.50, 75.46, 74.7, 74.3, 73.9, 73.7, 73.4, 73.22, 73.17, 72.9, 71.7, 71.2, 70.6, 70.1, 69.4, 68.6, 67.8, 67.5, 62.3, 59.6, 37.8, 29.6, 27.8, 20.8, 6.8, 4.6; HRMS (FAB) calcd for  $C_{86}H_{101}NO_{24}SSi-Na [M + Na]^+$  1614.6101, found 1614.6090.

**Tetrasaccharide Acceptor 55.** The hydrazine solution was prepared by mixing of pyridine, hydrazine, and AcOH (0.6 mL, 0.032 mL, and 0.4 mL respectively). To a solution of acetylated tetrasaccharide **54** (0.244 g, 0.153 mmol) in  $CH_2Cl_2$  (20 mL) were added pyridine (0.764 mL, 9.22 mmol) and the hydrazine solution (0.764 mL, 0.764 mmol) at RT. Upon addition of the hydrazine solution, the reaction mixture became cloudy. The reaction mixture was stirred at RT for 3 h, diluted with EtOAc (100 mL), and the resulting organic solution was washed with sat.  $NaHCO_{3(aq)}$  (4 x 120 mL), sat.  $CuSO_{4(aq)}$  (2 x 120 mL), brine (1 x 120 mL). The resulting organic layer was dried over  $Na_2SO_4$ . After the purification of the crude product with column chromatography using 35% EtOAc in hexanes, the free hydroxy tetrasaccharide **55** (0.218 g, 95%) was obtained as colorless oil:  $[\alpha]_D^{23} = -1.38^\circ$  ( $c$  0.4,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 3356, 3064, 3031, 2951, 2875, 1810, 1745, 1648, 1497, 1454, 1370, 1342, 1241, 1163, 1091, 910, 812, 736, 699  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.83 (d, 2H,  $J = 7.7$  Hz), 7.48-7.26 (m, 33H), 6.41 (d, 1H,  $J = 6.0$  Hz), 5.23 (s, 1H), 4.88 (m, 1H), 4.76 (d, 1H,  $J = 11.4$  Hz), 4.67-4.43 (m, 16H), 4.23-4.13 (m, 4H), 3.83-3.52 (m, 11H), 3.44-3.34 (m, 6H), 2.91 (br s, 1H), 2.15 (s, 3H), 0.78 (t, 9H,  $J = 7.9$  Hz), 0.32 (m, 6H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  172.3, 153.7, 144.5, 141.7, 138.7, 138.4, 137.9, 137.8, 137.4, 136.9, 132.1, 128.6, 128.3, 128.22, 128.15, 127.9, 127.8, 127.68, 127.66, 127.6, 127.52, 127.46, 127.41, 127.35,

127.1, 102.2, 101.9, 100.0, 99.7, 79.8, 78.13, 78.10, 76.5, 76.0, 75.8, 75.1, 74.5, 74.3, 73.6, 73.5, 73.3, 73.2, 73.0, 72.9, 72.4, 70.5, 70.4, 70.1, 68.6, 67.7, 67.4, 60.1, 59.4, 20.7, 6.7, 4.5; HRMS (FAB) calcd for  $C_{81}H_{95}NO_{22}SSi\cdot Na$   $[M + Na]^+$  1516.5733, found 1516.5756.

**Hexasaccharide 56.** The azeotropically dried mixture of the hydroxy tetrasaccharide **55** (0.0705 g, 0.0472 mmol) and thioglycoside **47** (0.0883 g, 0.0943 mmol) was mixed with 0.6 g of flame dried 4 Å M.S. The mixture was suspended in  $Et_2O$  and  $CH_2Cl_2$  (3.4 mL and 1.7 mL respectively). The resulting milky white suspension was treated with 2,4-di-*tert*-butylpyridine (0.0437 mL, 0.189 mmol) and stirred at RT for 15 min. Then, the reaction mixture was cooled to  $-40^\circ C$  and treated with MeOTf (0.0427 mL, 0.377 mmol) at  $-40^\circ C$ . The reaction mixture was stirred while it was allowed to be warm slowly to RT during the period of 24 h. The reaction mixture was treated with 1 mL of  $Et_3N$ , diluted with EtOAc (*ca.* 50 mL), and filtered through a pad of silica gel. The filtrate was washed with sat.  $NaHCO_{3(aq)}$  (4 x 50 mL), brine (1 x 50 mL), and dried over  $Na_2SO_4$ . Chromatographic purification of the crude product with the solvent gradient of 10% EtOAc in hexanes-40% EtOAc in hexanes provided hexasaccharide **56** (0.0790 g, 71%) as white foam:  $[\alpha]_D^{23} = -2.47^\circ$  (*c* 0.5,  $CHCl_3$ ); FTIR ( $CHCl_3$  film) 3326, 3031, 2947, 2876, 2163, 2051, 1953, 1811, 1747, 1648, 1491, 1451, 1370, 1337, 1236, 1160, 1094, 1041, 911, 814, 740, 698  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.89 (d, 2H,  $J = 7.5$  Hz), 7.83 (d, 2H,  $J = 7.4$  Hz), 7.49-7.14 (m, 51H), 6.38 (d, 1H,  $J = 5.7$  Hz), 5.21 (d, 1H,  $J = 2.2$  Hz), 4.83-4.40 (m, 27H), 4.34 (t, 1H,  $J = 8.3$  Hz), 4.30 (d, 1H,  $J = 12.0$  Hz), 4.23 (d, 1H,  $J = 6.7$  Hz), 4.17 (d, 1H,  $J = 6.3$  Hz), 4.08 (m, 1H), 3.94 (m, 2H), 3.82 (m, 2H), 3.77-3.64 (m, 12H), 3.55 (m, 1H), 3.45-3.31 (m, 9H),

3.27 (t, 1H,  $J = 7.2$  Hz), 2.75 (d, 1H,  $J = 7.9$  Hz), 2.19 (s, 3H), 0.84 (t, 9H,  $J = 8.0$  Hz), 0.74 (t, 9H,  $J = 8.0$  Hz), 0.44 (m, 6H), 0.25 (m, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 153.8, 144.3, 142.2, 142.0, 138.9, 138.5, 137.98, 137.96, 137.51, 137.45, 137.1, 136.9, 132.1, 131.78, 128.7, 128.6, 128.4, 128.33, 128.28, 128.2, 128.0, 127.9, 127.82, 127.78, 127.73, 127.71, 127.66, 127.63, 127.55, 127.5, 127.4, 127.10, 127.07, 102.2, 102.0, 101.9, 100.3, 100.2, 99.9, 80.4, 78.73, 78.70, 78.5, 78.4, 77.2, 76.6, 76.1, 75.8, 75.4, 75.3, 74.8, 74.6, 74.4, 73.93, 73.90, 73.73, 73.66, 73.62, 73.60, 73.43, 73.36, 73.14, 73.12, 71.7, 70.5, 70.3, 68.5, 68.0, 67.9, 67.5, 67.4, 60.0, 59.7, 20.9, 7.0, 6.8, 4.8, 4.6; HRMS (FAB) calcd for  $\text{C}_{127}\text{H}_{150}\text{N}_2\text{O}_{34}\text{S}_2\text{Si}_2\cdot\text{Na}$   $[\text{M} + \text{Na}]^+$  2389.8948, found 2389.8950.

**Hexasaccharide Acceptor 57.** To a solution of hexa **56** (0.142 g, 0.0600 mmol) in 11 mL THF were added AcOH (0.0206 mL, 0.360 mmol) and TBAF (0.360 mL, 1M solution in THF) at RT. The reaction mixture was stirred at RT for 25 h. Then, the reaction mixture was diluted with EtOAc (50 mL), and the resulting organic solution was washed with sat.  $\text{NaHCO}_3(\text{aq})$  (4 x 50 mL),  $\text{H}_2\text{O}$  (5 x 50 mL), brine (1 x 50 mL), and dried over  $\text{Na}_2\text{SO}_4$ . Chromatographic purification of the crude product with 2% MeOH in  $\text{CH}_2\text{Cl}_2$  afforded hexasaccharide diol **57** (0.128 g, quantitative) as colorless oil:  $[\alpha]_D^{23} = +3.42^\circ$  ( $c$  0.59,  $\text{CHCl}_3$ ); FTIR ( $\text{CHCl}_3$  film) 3475, 3338, 3063, 3030, 2924, 2870, 1959, 1808, 1746, 1647, 1605, 1586, 1496, 1454, 1371, 1328, 1238, 1206, 1162, 1098, 1055, 940, 911, 737, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d, 2H,  $J = 7.6$  Hz), 7.83 (d, 2H,  $J = 7.5$  Hz), 7.45-7.24 (m, 51H), 6.27 (d, 1H,  $J = 6.0$  Hz), 5.37 (d, 1H,  $J = 7.9$  Hz), 5.22 (s, 1H), 4.84 (m, 2H), 4.74-4.10 (m, 29H), 4.00 (t, 1H,  $J = 6.1$  Hz), 3.93 (t, 1H,  $J = 6.3$  Hz), 3.84-3.25 (m, 26H), 3.14 (t, 1H,  $J = 9.1$  Hz), 2.72 (d, 1H,  $J = 9.1$  Hz), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 153.6, 153.5, 144.5, 142.4, 142.0, 138.8,

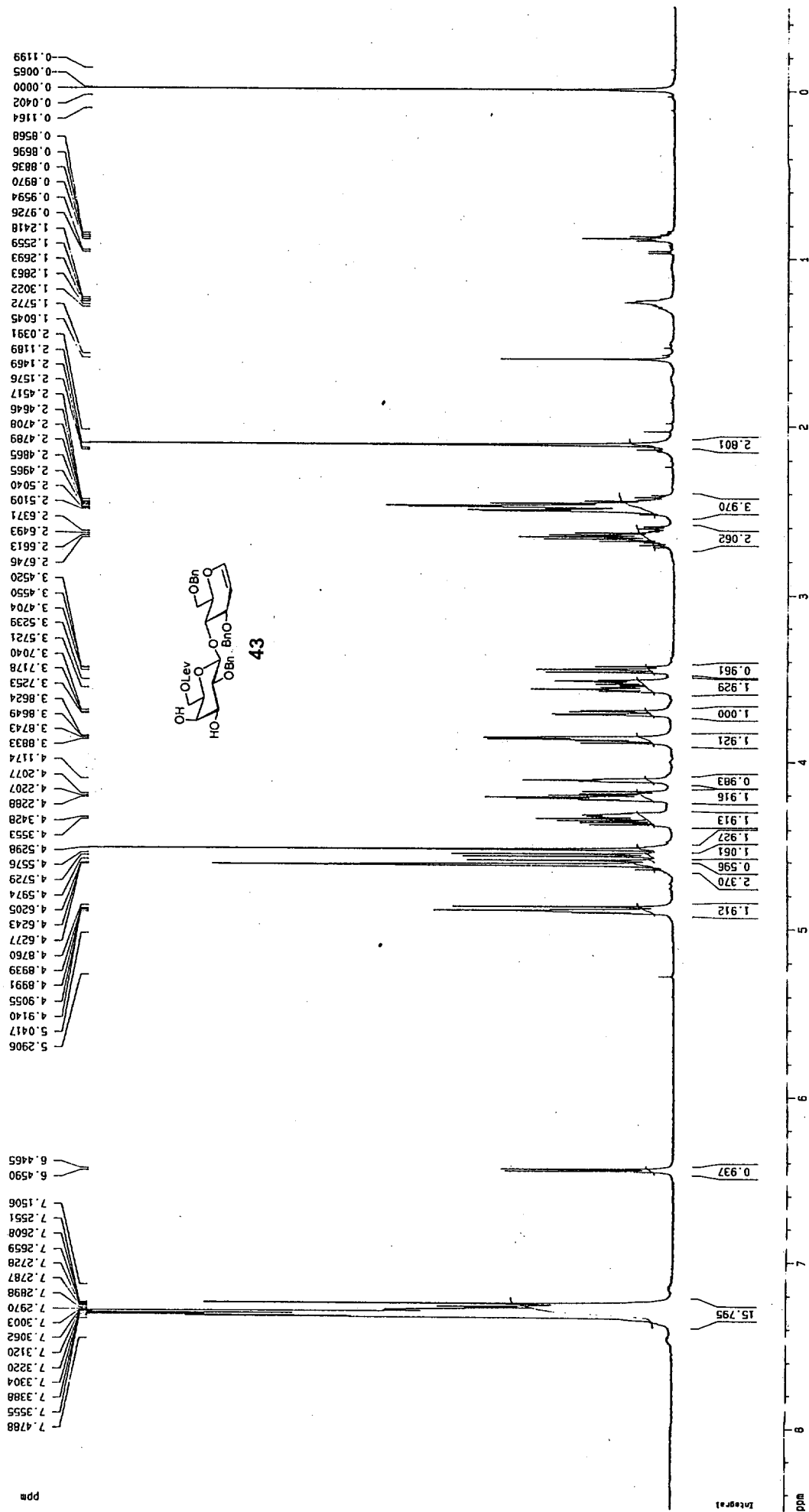
138.5, 138.2, 138.1, 137.8, 137.1, 136.5, 136.4, 131.9, 131.7, 128.6, 125.53, 128.47, 128.4, 128.32, 128.27, 128.03, 128.01, 127.9, 127.82, 127.79, 127.71, 127.67, 127.61, 127.58, 127.53, 127.50, 127.29, 127.27, 102.1, 102.0, 101.5, 100.4, 100.2, 99.5, 81.0, 80.8, 80.2, 77.2, 76.9, 76.7, 76.5, 76.2, 76.13, 76.10, 76.0, 74.6, 74.5, 73.93, 73.86, 73.8, 73.7, 73.6, 73.5, 73.29, 73.27, 73.2, 73.1, 73.0, 72.9, 71.3, 70.3, 69.9, 69.7, 68.4, 68.1, 67.9, 67.7, 67.6, 59.2, 59.0, 21.0; LRMS (ESI) calcd for  $C_{113}H_{120}N_2O_{33}S_2 \cdot Na$   $[M + Na]^+$  2119.7, found 2121.1.

**Octasaccharide 58.** To a mixture of azeotropically dried hexasaccharide **57** (0.0840 g, 0.0390 mmol), fucosyl fluoride **23** (0.0884 g, 0.196 mmol), and freshly activated 4Å M.S. (1.4 g) in anhydrous toluene (6.5 mL) was added di-*tert*-butylpyridine (0.062 mL, 0.28 mmol), and the resulting suspension was stirred at RT for 10 min. The reaction mixture was cooled to -15°C and was treated with the solution of Sn(OTf)<sub>2</sub> (0.0570 g, 0.137 mmol) in THF (0.650 mL) *via* canular. After being stirred at -7°C for 24 h, the reaction mixture was quenched by addition of Et<sub>3</sub>N (2 mL) at -7°C. The reaction mixture was diluted with EtOAc (100 mL), washed with sat. NaHCO<sub>3(aq)</sub> (3 x 50 mL), brine (1 x 50 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>. Flash column chromatography of crude material with 35% EtOAc in hexanes afforded octasaccharide **58** (0.082 g, 70%) as white foam along with monofucosylated product (0.018 g, 18%):  $[\alpha]_D^{23} = -64.2^\circ (c\ 0.73, CHCl_3)$ ; FTIR(CHCl<sub>3</sub> film) 2923, 2871, 1812, 1745, 1721, 1452, 1271, 1163, 1094, 738, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.05 (d, 2H, *J* = 7.3 Hz), 8.02 (d, 2H, *J* = 7.3 Hz), 7.82 (d, 2H, *J* = 7.3 Hz), 7.59-7.54 (m, 4H), 7.46-7.43 (m, 6H), 7.37-7.16 (m, 65H), 7.09-7.08 (m, 2H), 6.91 (d, 1H, *J* = 3.4 Hz), 6.41-6.40 (m, 2H), 5.57 (d, 1H, *J* = 2.3 Hz), 5.54 (d, 1H, *J* = 2.3 Hz), 5.20 (d, 1H, *J* = 3.2 Hz), 5.13 (d, 1H, *J* = 3.6 Hz), 4.99-4.97 (m,

2H), 4.89 (dd, 1H,  $J = 6.0, 3.8$  Hz), 4.83 (d, 2H,  $J = 10.4$  Hz), 4.78 (d, 1H,  $J = 11.7$  Hz), 4.74-4.73 (m, 1H), 4.71-4.44 (m, 25H), 4.39 (d, 1H,  $J = 12.0$  Hz), 4.34-4.26 (m, 6H), 4.19-4.16 (m, 3H), 4.11 (dt, 1H,  $J = 4.6$  Hz), 4.06 (br-s, 1H), 4.00 (br-s, 1H), 3.95 (dd, 1H,  $J = 10.0, 3.3$  Hz), 3.89-3.85 (m, 3H), 3.82-3.77 (m, 2H), 3.76-3.61 (m, 12H), 3.56-3.54 (m, 1H), 3.51-3.47 (m, 2H), 3.41 (br-d, 1H,  $J = 9.3$  Hz), 3.32-3.23 (m, 3H), 3.20-3.18 (m, 1H), 2.87 (dd, 1H,  $J = 10.3, 6.4$  Hz), 2.78 (t, 1H,  $J = 6.0$  Hz), 2.10 (s, 3H), 1.02 (t, 6H,  $J = 5.8$  Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 166.2, 166.1, 153.74, 153.66, 144.4, 142.8, 142.3, 138.8, 138.5, 138.3, 138.2, 138.0, 137.8, 137.7, 137.6, 137.51, 137.46, 137.4, 137.3, 133.0, 132.6, 132.2, 128.7, 128.54, 128.46, 128.43, 128.37, 128.33, 128.31, 128.29, 128.26, 128.12, 128.10, 128.06, 128.01, 127.96, 127.92, 127.89, 127.85, 127.8, 127.72, 127.70, 127.67, 127.65, 127.6, 127.5, 102.0, 101.8, 101.7, 100.0, 99.9, 99.74, 99.69 (2C), 80.0, 79.8, 79.4, 78.51, 78.46, 78.4, 76.9, 76.5, 76.0, 75.7, 75.3, 75.1, 74.84, 74.76, 74.7, 74.6, 74.5, 73.9, 73.7, 73.5, 73.44, 73.40, 73.2, 72.2, 71.9, 71.4, 71.2, 71.1, 70.7, 70.6, 70.5, 69.5, 68.5, 68.4, 67.9, 67.40, 67.36, 66.2, 66.0, 59.1, 58.8, 20.9, 16.4, 16.2; LRMS (EI) calcd for  $\text{C}_{169}\text{H}_{174}\text{N}_2\text{O}_{44}\text{S}_2\cdot\text{Na}$   $[\text{M} + 2\text{Na}]^{2+}$  1522.5 for  $z=2$ , found 1522.6.



HKim 2',3,6-tribenzyl-6'-Levulinatelactal



HKim DRX500 2',3,6-tribenzyloxy-6'-Levulatelactal

ppm

206.497

172.681

144.505

138.531

138.158

137.968

128.511

128.355

128.296

127.911

127.741

127.634

127.579

127.496

99.527

102.328

78.590

77.256

77.001

76.748

75.681

74.552

73.302

73.052

72.810

71.993

71.535

70.466

68.089

67.814

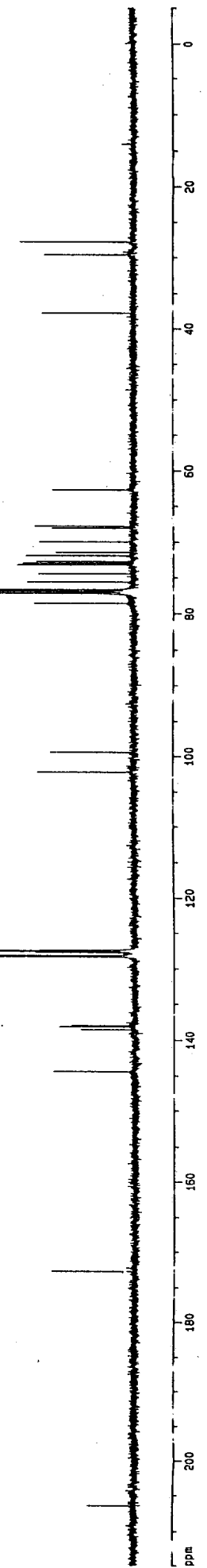
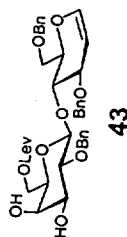
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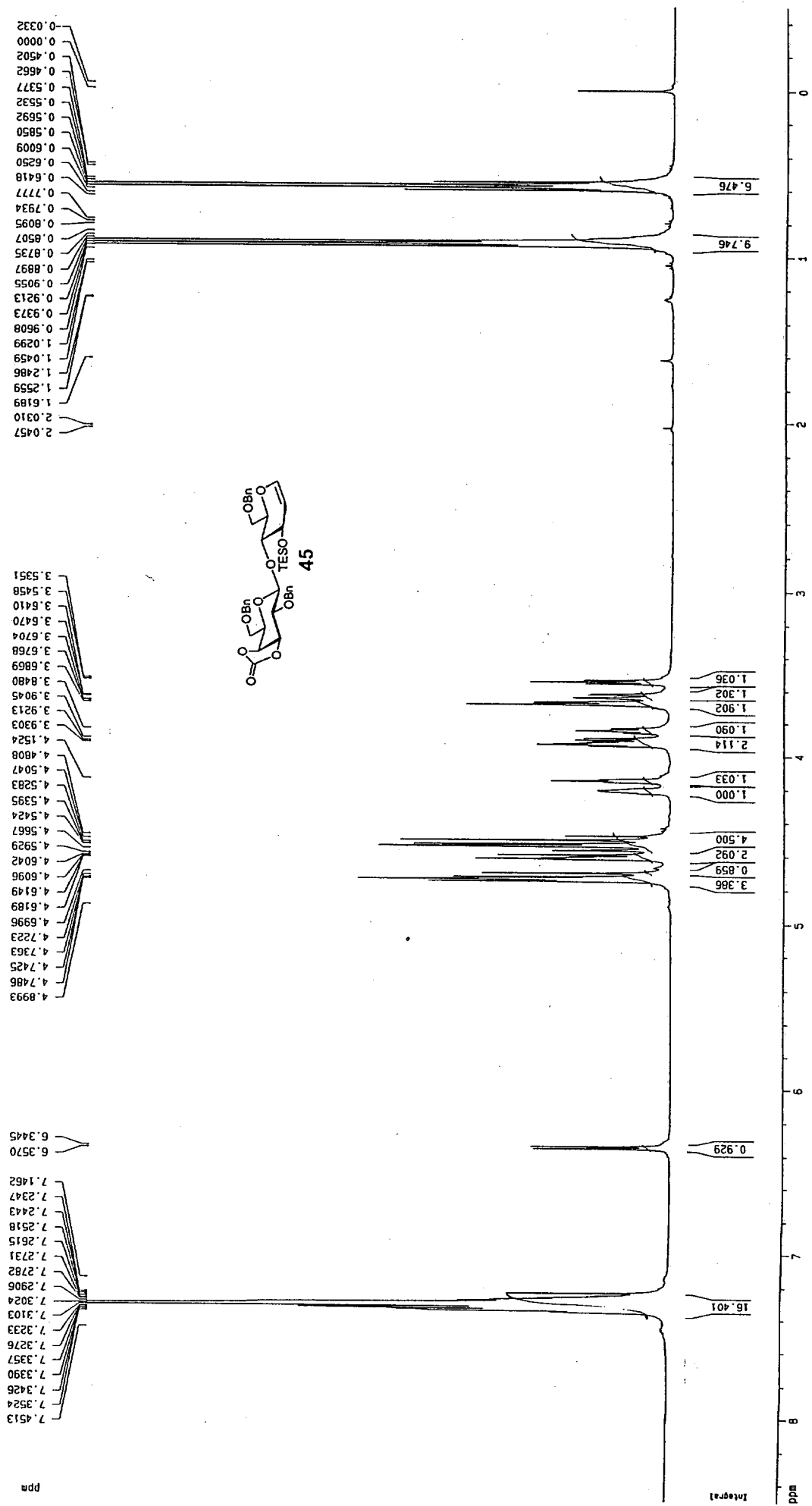
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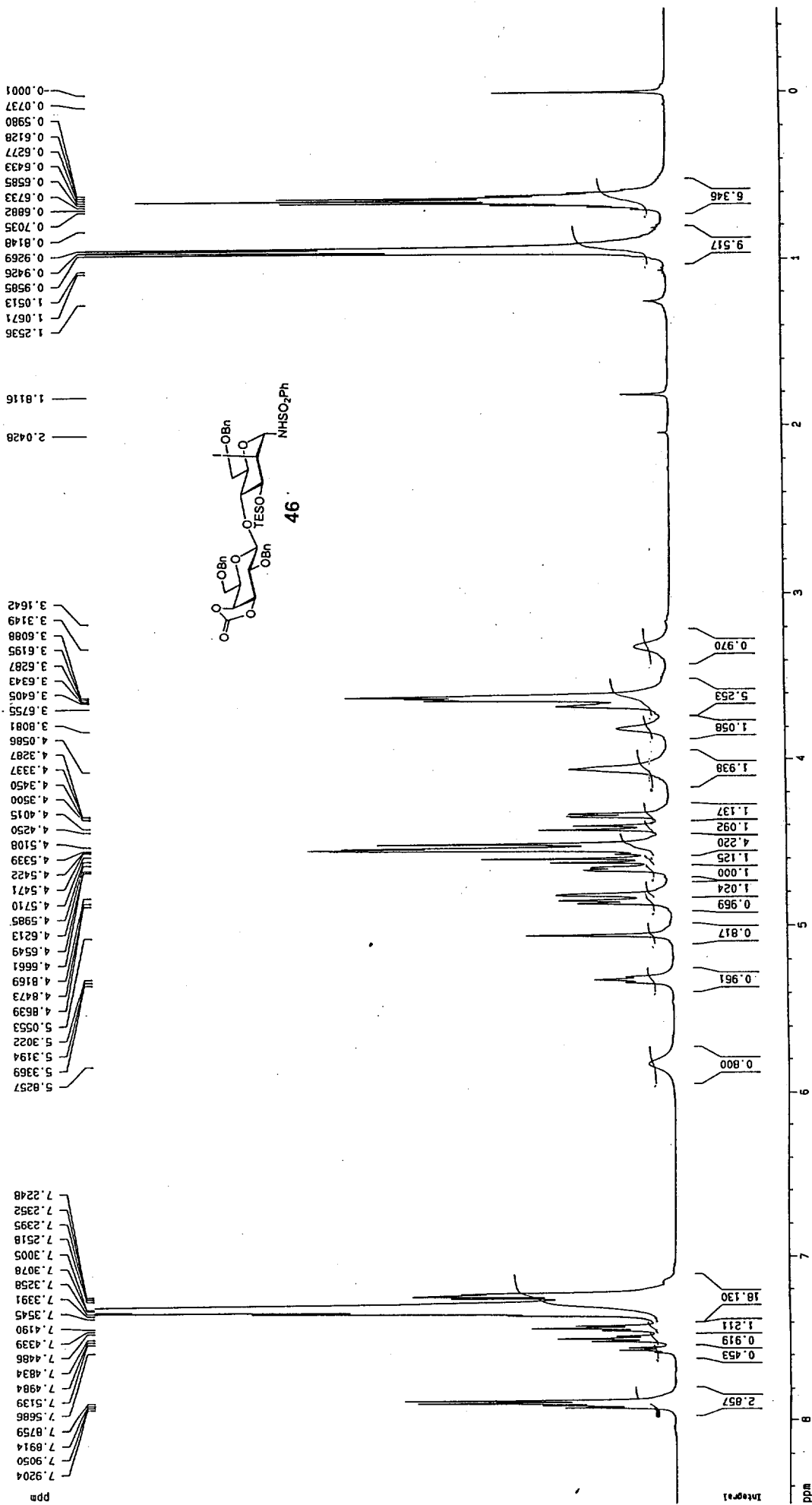


HKim DRX500 2',6',6'-tribenzy]-3-TES-3',4'-carbonate-lactal

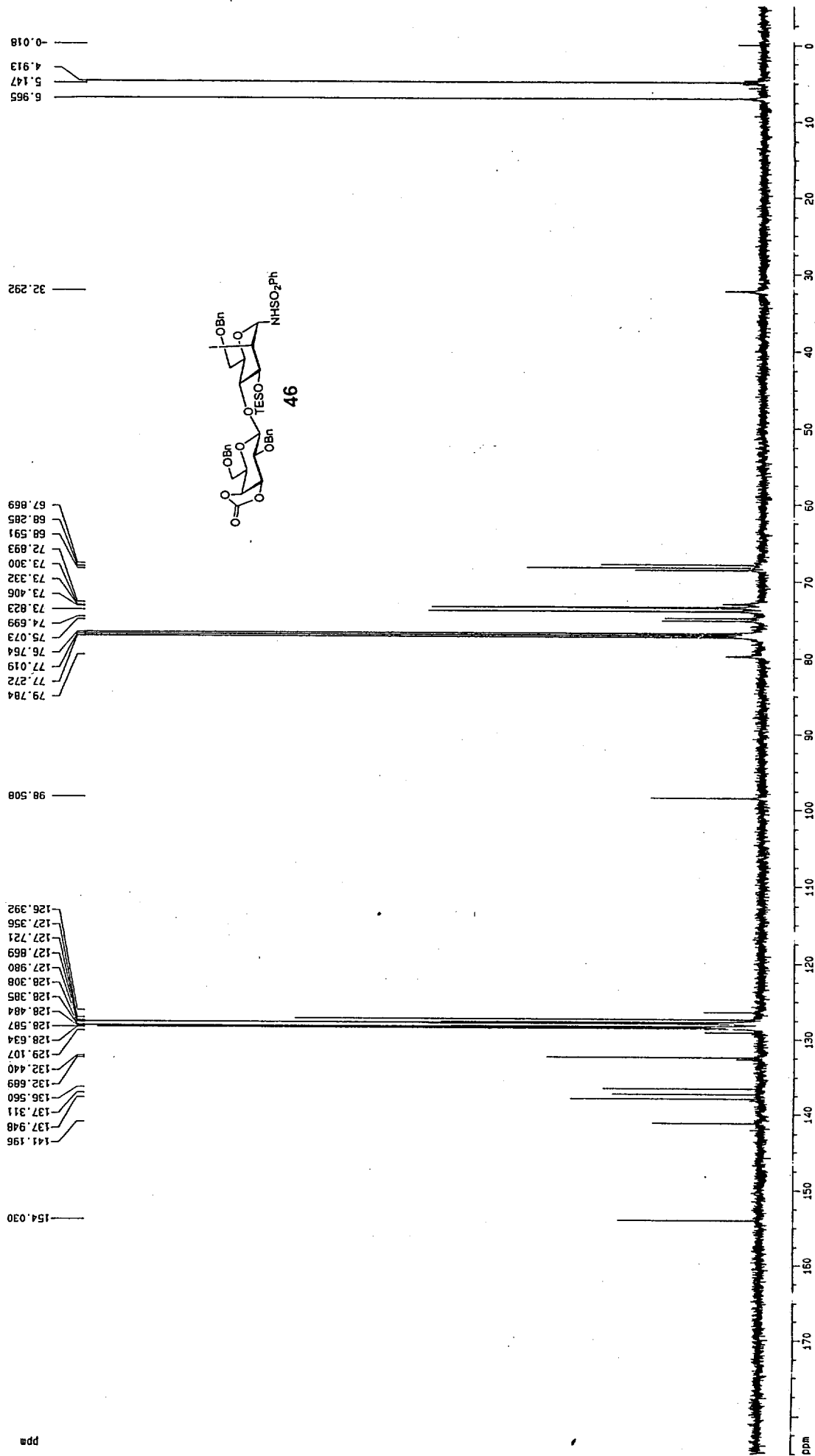




HKim DRX500 N3 minor lactose iododisulfonamide



HKim DRX500 minor\_N3 iodosalfonamide disaccharide

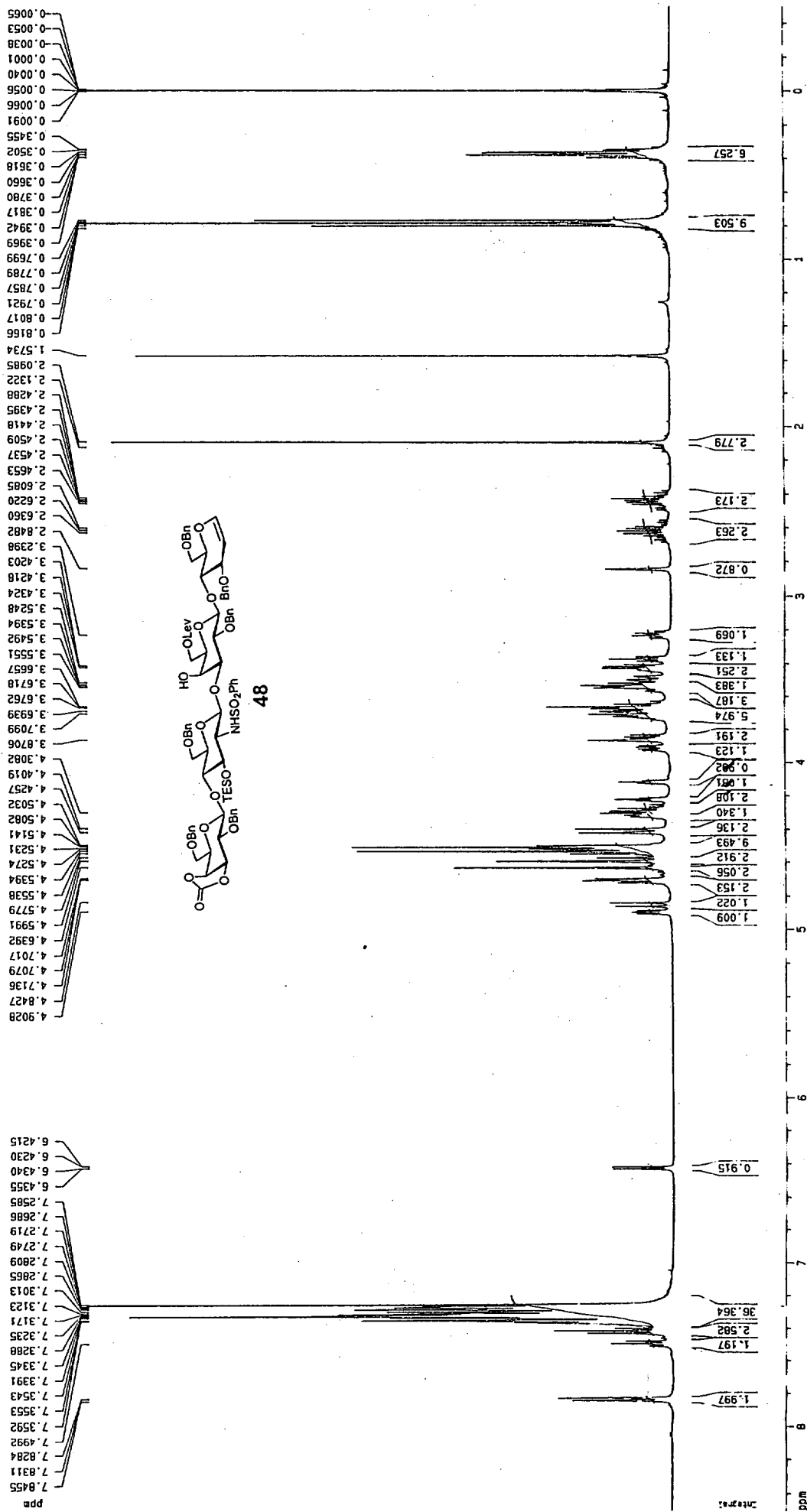




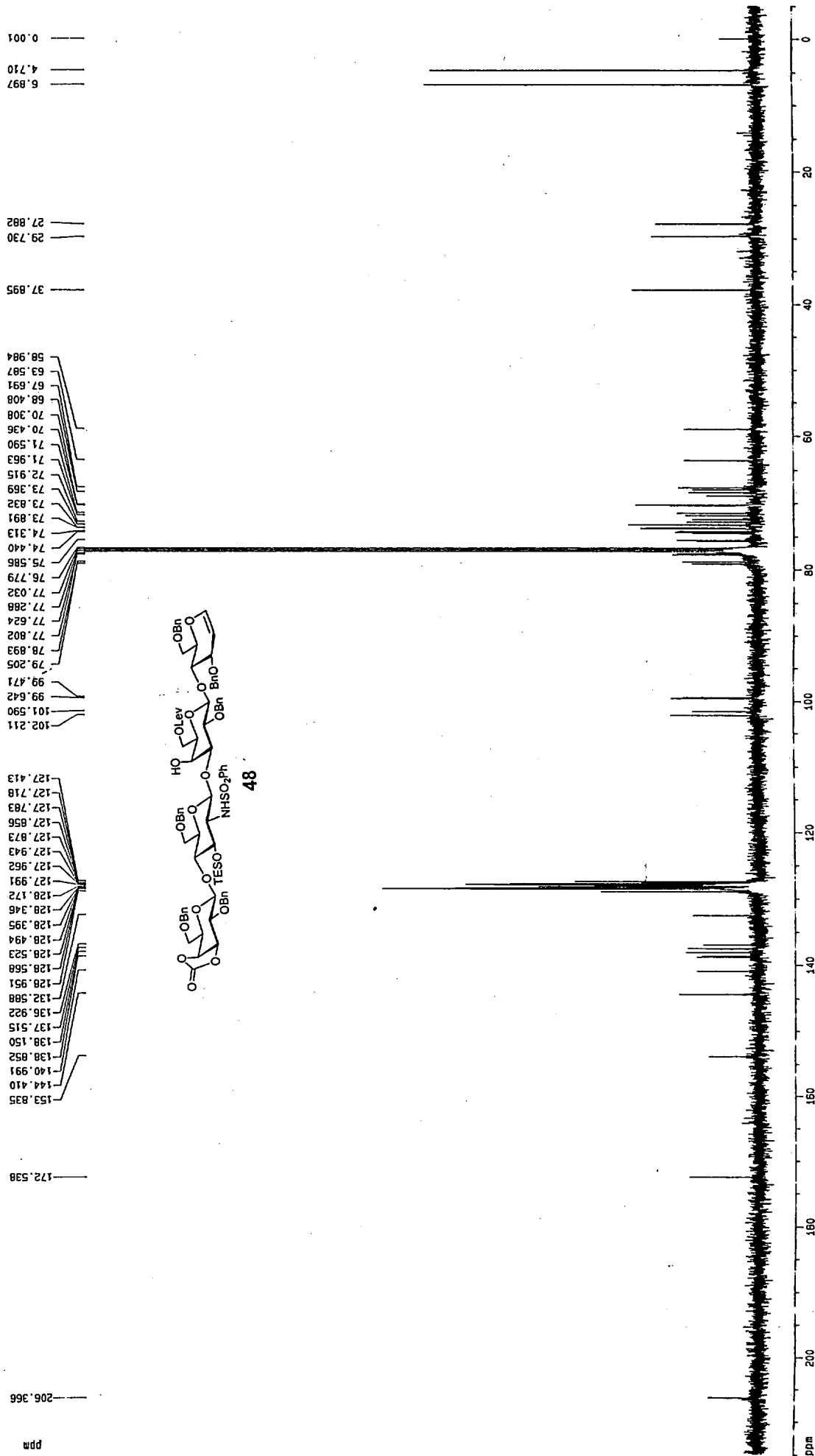




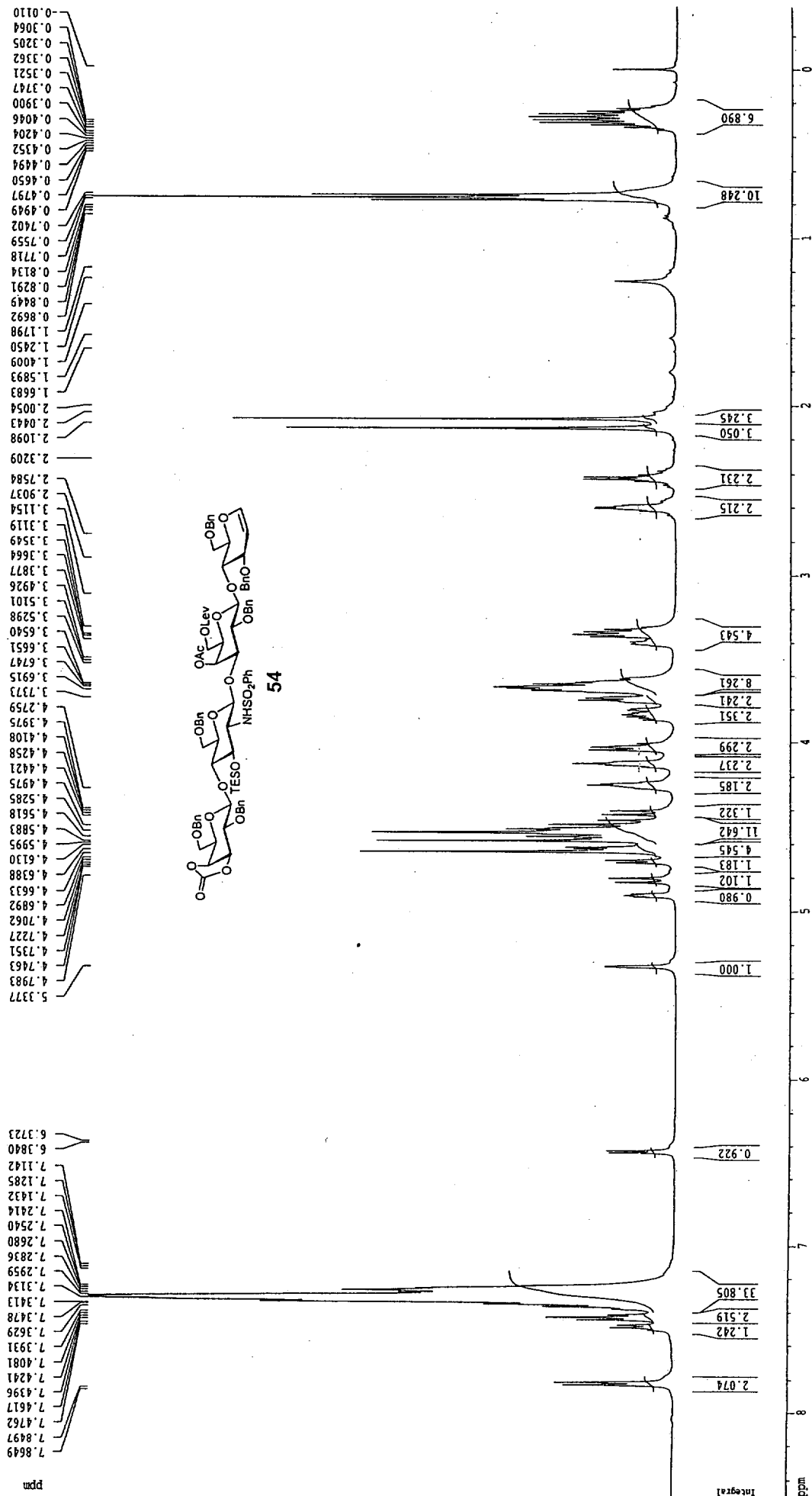
HKim DRX500 minor N3 tetra w/o OAc and w/ Lev



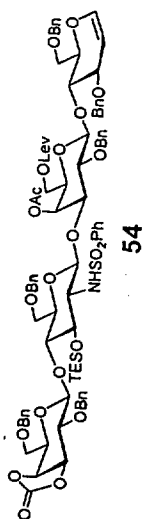
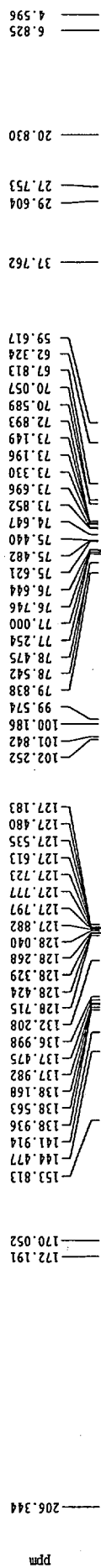
HK1.r. DRX500 3058 purified by HPLC



HKlm DRX500 N3 minor tetra w/ OAc, Olev

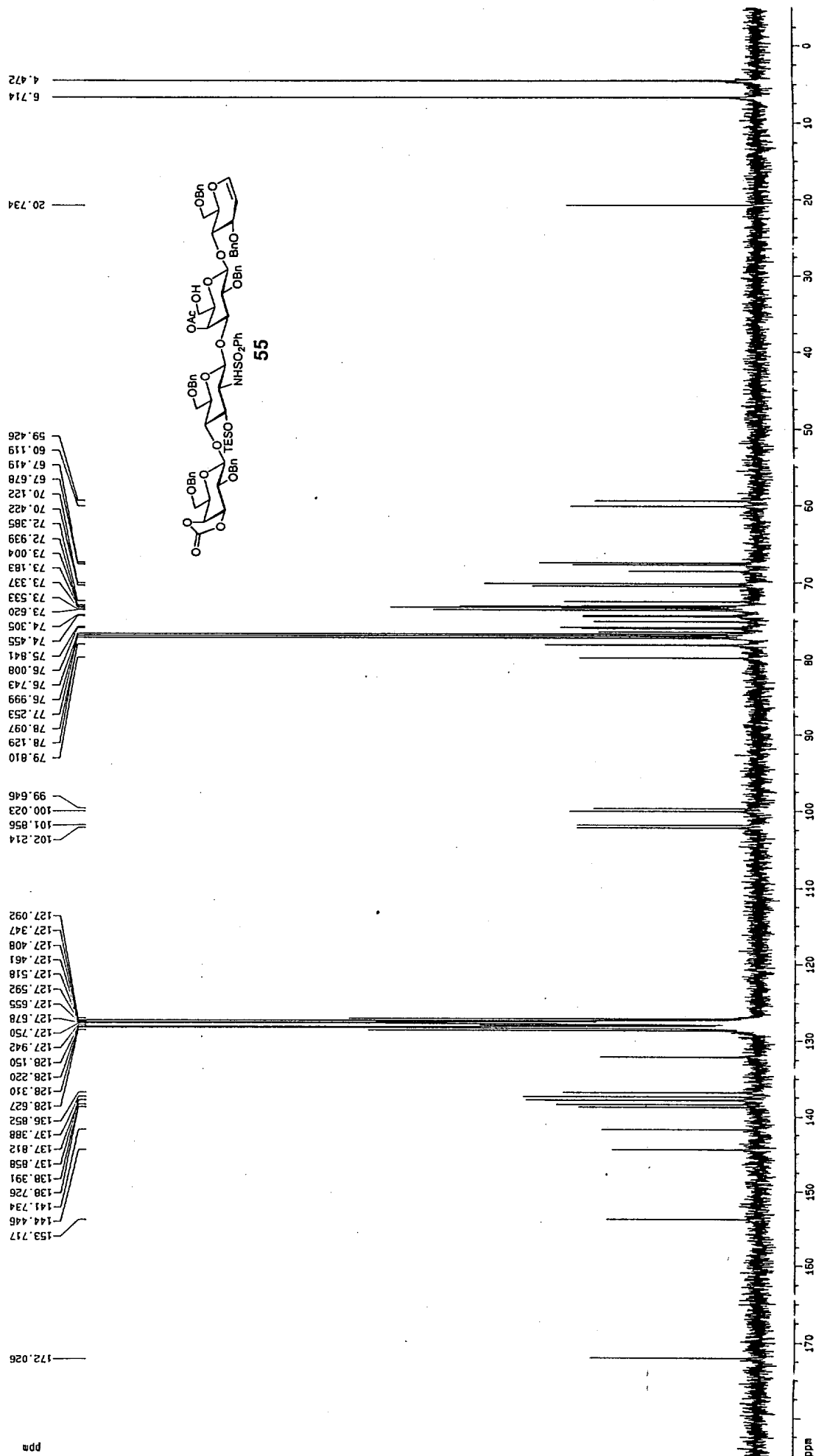


HKim DRX500 N3 minor tetra w/ OAc, OLev

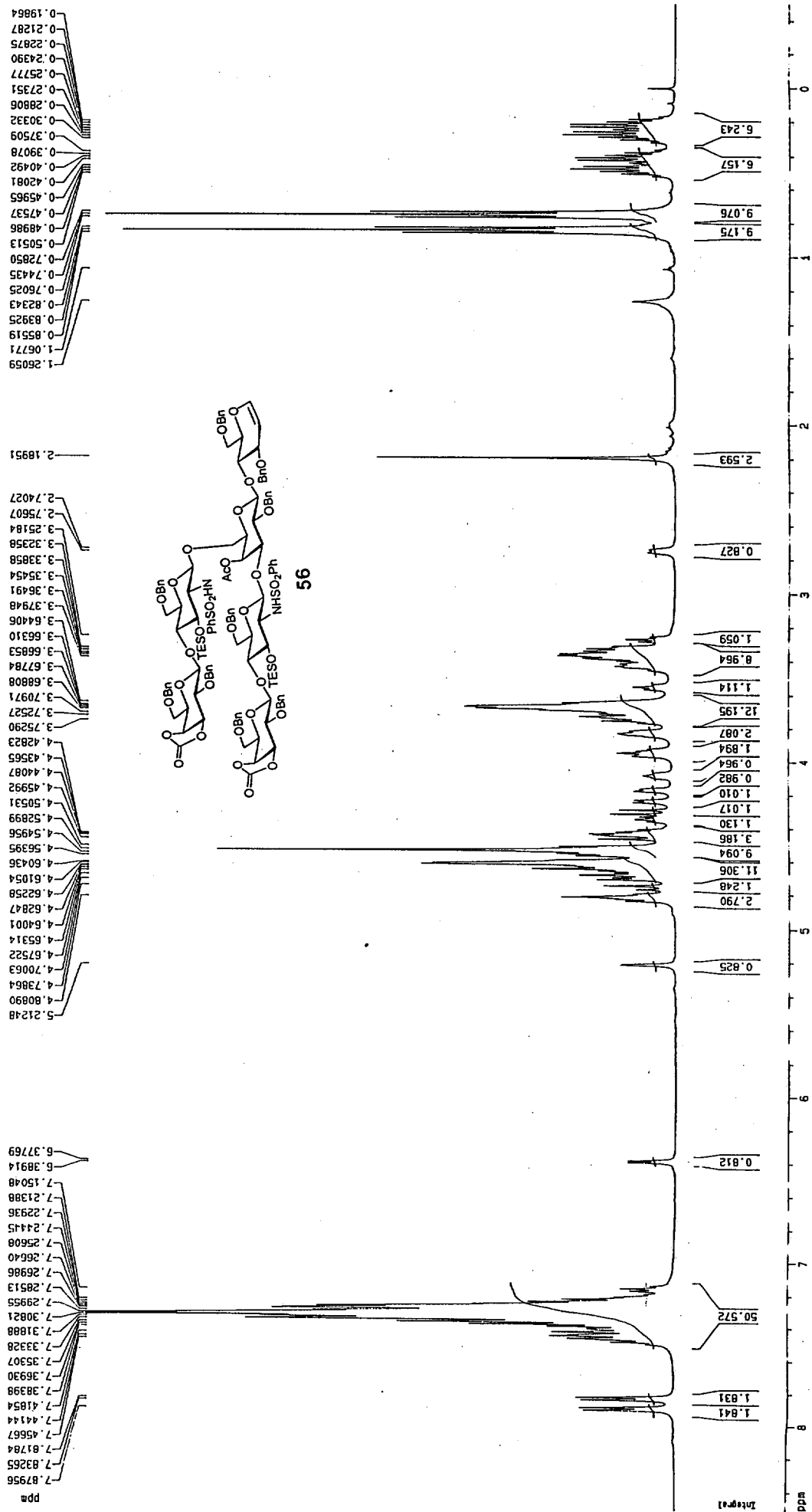




HK1m DRX500 N3 minor tetra de-Lev



HKim DRX500 minor N3 Hexa w/ OAc



HK1m DRX500 N3 minor hexa w DAC

