Supporting Information

A Modular Synthesis of Heparan Sulfate Oligosaccharides for Structure-Activity Relationship Studies

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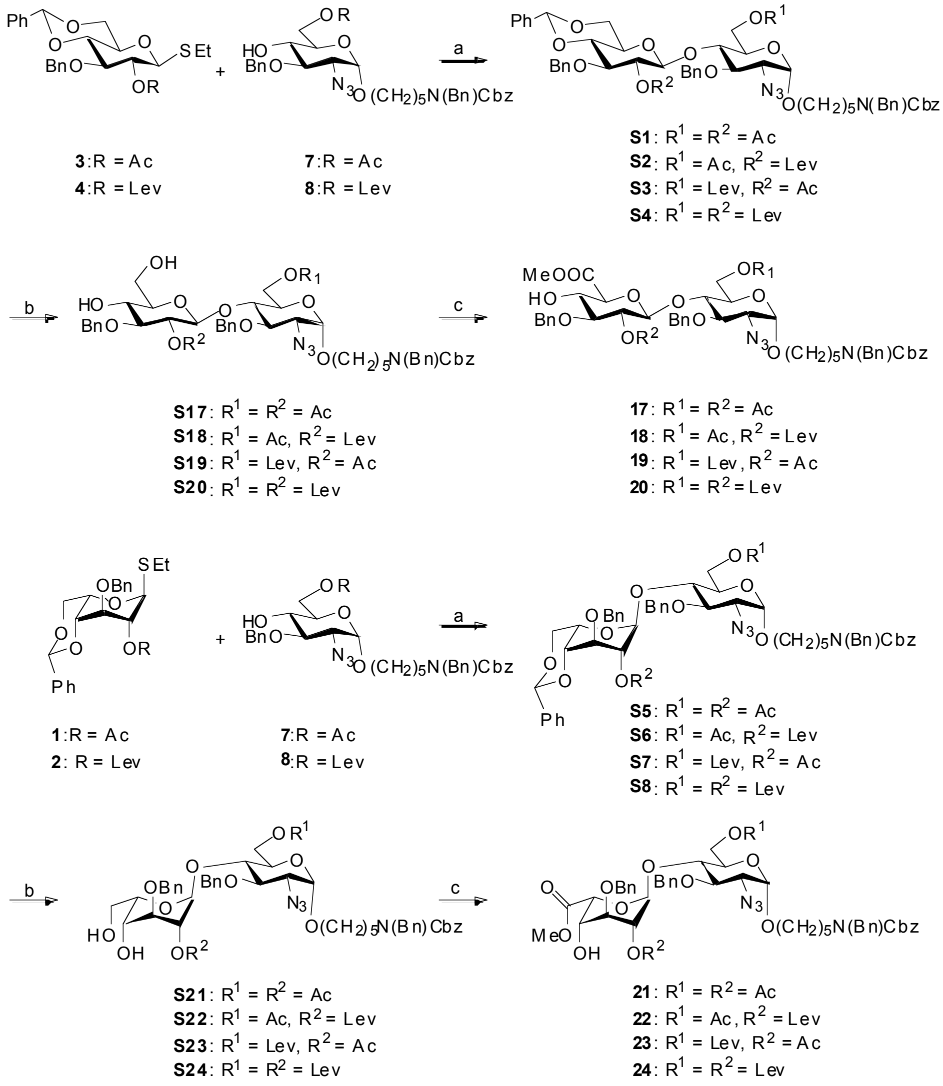
General procedures: All moisture sensitive reactions were performed under an argon atmosphere by using vacuum dried glassware. All commercial materials were used without purification, unless otherwise noted. CH_2Cl_2 was freshly distilled from calcium hydride under nitrogen prior to use. Toluene, DMF, diethylether, methanol and THF were purchased anhydrous and used without further purification. Molecular sieves (4Å) were flame activated *in vacuo* prior to use. All reactions were performed at room temperature unless specified otherwise. TLC-analysis was conducted on Silica gel 60 F_{254} (EMD Chemicals Inc.) with detection by UV-absorption (254 nm) were applicable, and by spraying with 20% sulfuric acid in ethanol followed by charring at ~150^{o}C or by spraying with a solution of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ (25 g/L) in 10% sulfuric acid in ethanol followed by charring at ~150^{o}C. Column chromatography was performed on silica gel G60 (Silicycle, 60-200 μm, 60 Å) or on Bondapak C-18 (Waters). ^{1}H and ^{13}C NMR spectra were recorded on a Varian inova-300 (300/75 MHz), a Varian inova-500 (500/125 MHz) and a Varian inova-600 (600/150 MHz) spectrometer equipped with sun workstations. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. NMR data is presented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}HNMR, ^{13}C NMR, COSY and HSQC experiments. Optical rotations were measured using a Jasco P-1020 polarimeter. Mass spectra were recorded on an Applied Biosystems 4700 MALDI-TOF proteomics analyzer. The matrix used was 2,5-dihydroxy-benzoicacid (DHB) and ultamark 1621 as the internal standard. The ESI-MS spectra were recorded on 9.4 T Bruker Apex Ultra QeFTMS (Billerica, MA) mass spectrometer.



Scheme A (a) NIS, TMSOTf, 0°C, DCM; (b) (i) EtSH, *p*-TsOH, DCM, 1 h, room temperature or DCM:TFA:H_2O, 30 min, room temperature; ii) TEMPO, BAIB, DCM, H_2O, 1 h, room temperature; iii) CH_2N_2, THF, 0°C; (c) (i) FmocCl, Py, DMAP, 0°C to room temperature; (ii) HF·Py, THF, room temperature, 18 h; (iii) CCl_3CN, K_2CO_3, 0°C, DCM.

Ethyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α/β-L-idopyranoside (**1**): A solution of compound **35** (1.0 g, 2.48 mmol) in pyridine: acetic anhydride (4/1,v/v, 0.2 M) was stirred for 6 hr at ambient temperature. The mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using a gradient of hexanes/EtOAc (85/15, v/v) to obtain **1** (1.04 g, 93%). $[\alpha]_D^{25}$ -30.4 (*c* = 1, $CHCl_3$); ^{1}HNMR (300MHz, $CDCl_3$): δ 7.51-7.31 (m, 10H, CH

Aromatic), 5.50 (s, 1H, C*H* benzylidene α), 5.44 (m, 2H, H2α, C*H* benzylidene β), 5.08 (s, 1H, H1α), 5.05 (s, 1H, H1β), 4.96 (bs, 1H, H2β), 4.83 (d, 1H, *J* = 7.2 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 7.2 Hz, CH*H*Bn), 4.66 (d, 1H, *J* = 7.2 Hz, C*H*HBn), 4.60 (d, 1H, *J* = 7.2 Hz, CH*H*Bn), 4.35 (d, 1H, *J* = 7.5 Hz, H6aβ), 4.30 (s, 1H, H5α), 4.27 (d, 1H, *J* = 7.5 Hz, H6aα), 4.12 (dd, 1H, *J* = 0.9 Hz, *J* = 6.6 Hz, H6bα), 4.04 (dd, 1H, *J* = 0.9 Hz, *J* = 6.6 Hz, H6bβ), 3.97 (s, 1H, H4α), 3.91 (s, 1H, H4β), 3.87 (bs, 1H, H3β), 3.74 (s, 1H, H3α), 3.69 (s, 1H, H5β), 2.80-2.75 (m, 2H,CH_2SEt α), 2.71-2.61 (m, 2H,CH_2SEt β), 2.06 (s, 3H, CH_3 Ac), 2.05 (s, 3H, CH_3 Ac), 1.33-1.30 (m, 6H, CH_3SEt α/β). ^{13}CNMR (75.5 MHz,$CDCl_3$): δ 170.5, 170.0, 137.9, 137.9, 137.2, 129.0, 128.9, 128.6, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 126.5, 126.4, 126.3, 126.1, 125.9, 101.3, 100.9, 100.8, 95.6, 82.3, 82.2, 79.9, 77.4, 77.0, 76.5, 75.1, 73.5, 73.2, 77.2, 72.9, 72.7, 72.3, 72.2, 72.1, 71.9, 71.9, 71.7, 69.6, 69.5, 69.4, 69.4, 69.0, 68.7, 68.7, 68.6, 68.2, 68.2, 67.8, 67.4, 66.9, 65.4, 64.9, 63.6, 61.1, 59.7, 26.6, 26.1, 25.3, 21.0, 20.9, 20.7, 14.9, 14.8, 14.7. HRMS-MALDI: ($M + Na^+$) calcd. 467.1504, found: 467.1576

Ethyl 2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α/β-L-idopyranoside (**2**): A solution of DCC (0.51 g, 2.48 mmol) and DMAP (0.03 g, 0.25 mmol) in DCM (2 mL) was added to a solution of compound **35** (0.5 g, 1.24 mmol) and levulinic acid (0.21 g, 1.86 mmol) in DCM (0.2 M) at 0 ^{0}C. After stirring for 4 hr at ambient temperature, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using a gradient of hexanes/EtOAc (75/25, v/v) to obtain **2** (0.45 g, 89%). $[\alpha]_D^{25}$ -90.9 (*c* = 2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.31 (m, 10H, CH Aromatic), 5.51 (s, 1H, C*H* benzylidene α), 5.46 (s, 1H, C*H* benzylidene β), 5.41 (s, 1H, H2α), 5.09 (s, 1H, H1α), 5.03-5.04 (m, 1H, H1β), 4.97–4.98 (bs, 1H, H2β), 4.83 (d, 1H, *J* = 7.2 Hz, C*H*HBn), 4.78 (d, 1H, J = 11.7 Hz, CH*H*Bn), 4.66 (d, 1H, J = 11.7 Hz, C*H*HBn), 4.57 (d, 1H, J = 11.7 Hz, CH*H*Bn), 4.35 (d, 1H, J = 12.6 Hz, H6aβ), 4.29-4.25 (m, 2H, H6aα, H5α), 4.10 (dd, 1H, J = 1.8 Hz, J = 10.5 Hz, H6bα), 4.04 (dd, 1H, J = 2.7 Hz, J = 10.8 Hz, $H6_b\beta$), 3.97 (s, 1H, H4α), 3.91 (bs, 1H, H4β), 3.85 (bs, 1H, J = 2.4 Hz, H3β), 3.71-3.68 (m, 2H, H3α, H5β), 2.80-2.53 (m, 12H, CH_2 SEt α/β, 4 x CH_2 Lev α/β), 1.99 (s, 3H, CH_3 Lev), 1.98 (s, 3H, CH_3 Lev), 1.33-1.27 (m, 6H, CH_3 SEtα/β). ^{13}CNMR (75.5 MHz,$CDCl_3$): δ 206.4, 171.7, 138.0, 137.3, 128.9, 128.5128.4, 128.3, 128.0, 128.0, 127.8, 127.8, 127.7, 127.6, 126.3, 126.2, 126.1, 100.9, 82.4, 77.4, 77.9, 76.6, 73.8, 73.1, 72.9, 72.1, 72.0, 69.8, 68.3, 67.9, 67.3, 63.2, 59.8, 37.9, 37.8, 37.6, 29.6, 29.5, 28.3, 28.2, 28.0, 26.7, 14.9. HRMS-MALDI: (M + Na^+) calcd. 523.1766 found 523.1796

Ethyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D- glucopyranoside (**3**): A solution of compound **36** (13.9 g, 34.5 mmol) in pyridine: acetic anhydride (4/1, v/v, 0.2 M) was stirred for 6 hr at ambient temperature. TLC (hexanes/EtOAc, 70/30, v/v) indicated the consumption of the starting material, after which the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using a gradient of hexanes/EtOAc (80/20, v/v) to obtain **1** (13.0 g, 85%). $[\alpha]_D^{25}$ -5.7 (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.25 (10H, CH Aromatic), 5.58 (s, 1H, C*H* benzylidene), 5.09-5.02 (m, 1H,H2), 4.89 (d, 1H, J = 12.0 Hz, C*H*HBn), 4.68 (d, 1H, J = 12.0 Hz, CH*H*Bn), 4.48 (d, 1H, J = 10.2 Hz, H1), 4.38 (dd, 1H, J = 4.8 Hz, J = 5.7 Hz,H6a), 3.82-3.71 (m, 3H, H3, H4, H6b), 3.503-3.46 (m, 1H, H5), 2.74-2.67 (m, 2H, CH_2SEt), 2.01 (s, 1H, CH_3 Ac), 1.25 (t, 3H, J = 7.5 Hz, CH_3SEt). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.3, 138.1, 138.1, 137.1, 128.9, 128.2, 128.2, 127.7, 127.6, 125.9, 101.1, 84.1, 81.4, 79.6, 77.4, 77.0, 76.6, 74.2, 71.1, 70.5, 68.5, 23.8, 20.8, 14.7. HRMS-MALDI: (M + Na$^+$) calcd. 467.1504, found: 467.1585

Ethyl 2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**4**): A solution of DCC (0.5 g, 1.24 mmol) and DMAP (0.03 g, 0.25 mmol) in DCM (2 mL) was added to a solution of compound **36** (0.5 g, 1.24 mmol) and levulinoylic acid (0.21 g, 1.86 mmol) in DCM (0.2 M) at 0 ^{0}C. After stirring for 4hr at ambient temperature TLC (hexanes/EtOAc, 70/30, v/v) indicated the consumption of the starting material, the mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using a gradient of hexanes/EtOAc to obtain **2** (0.42 g, 70%). $[\alpha]_D^{25}$ -22.9 (*c* = 1, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$): δ 7.47-7.25 (10H, CH Aromatic), 5.58 (s, 1H, C*H* benzylidene), 5.08-5.02 (m, 1H, H2), 4.89 (d, 1H, *J* = 12.0 Hz , C*H*HBn), 4.68 (d, 1H, *J* = 12.0 Hz , CH*H*Bn), 4.48 (d, 1H, *J* = 9.9 Hz, H1), 4.38 (dd, 1H, *J* = 4.8 Hz, *J* = 5.7 Hz, H6a), 3.81-3.71 (m, 3H, H3, H4, H6b), 3.50-3.47 (m, 1H, H5), 2.75-2.64 (m, 4H, CH_2 SEt, CH_2 Lev), 2.54 (t, 2H, *J* = 6.6 Hz, CH_2 Lev), 2.17 (s, 3H, CH_3 Lev), 1.25 (t, 3H, *J* = 7.5 Hz, CH_3 SEt). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 171.4, 138.1, 137.1, 129.0, 128.2, 127.9, 127.6, 125.9, 101.2, 84.1, 81.4, 79.5, 77.4, 77.0, 76.6, 74.3, 71.6, 70.6, 68.5, 37.8, 29.8, 27.9, 24.0, 14.8. HRMS-MALDI: (M + Na$^+$) calcd. 523.1766, found 523.1773.

Dimethylthexylsilyl 6-*O*-acetyl-2-azido-3-*O*-benzy2-deoxy-β-D-glucopyranoside (**5**): To a solution of compound **31** (1.62 g, 3.70 mmol) in DCM (62 mL) was added acetic acid (0.44 g, 7.4 mmol) and 2-chloromethyl pyridinium iodide (CMPI) (2.36 g, 9.25 mmol). The mixture was stirred for 15 minutes at room temperature followed by the addition of 1,4-

diazabicyclo[2,2,2]octane (DABCO) (0.980 g, 8.75 mmol). Stirring was continued until TLC indicated consumption of starting material (~ 1.5 hr). The reaction mixture was filtered through Celite, diluted with EtOAc (40 mL), and washed with brine (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and the filtrate concentrated *in vacuo*. Silica gel column chromatography of the residue (hexanes/EtOAc, 75/25, v/v) afforded **5** (1.20 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.24 (m, 5H, CH aromatic), 4.93 (d, 1H, *J* = 11.4 Hz, CH*H*Bn), 4.71 (d, 1H, *J* = 11.4 Hz, C*H*HBn), 4.50 (d, 1H, *J* = 7.2 Hz, H1), 4.28 (m, 2H, H6a, H6b), 3.46-3.36 (m, 2H, H4, H5), 3.28 (dd, *J* = 7.2 Hz, *J* = 9.7 Hz, 1H, H2), 3.10 (dd, *J* = 8.0 Hz, *J* = 9.7 Hz, 1H, H3), 2.05 (s, 3H, CH_3 Lev), 1.65-1.56 [m, 1H, $CH(CH_3)_2$], 0.89-0.87 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.18-0.17 [2s, 6H, $Si(CH_3)_2$]. HRMS-MALDI: (M + Na^+) calcd. 502.2349, found 502.2367.

Dimethylthexylsilyl 6-*O*-levulinoyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (6): To a solution of **31** (1.82 g, 4.16 mmol) in DCM (70 mL) was added levulinic acid (0.96 g, 8.32 mmol) and 2-chloromethyl pyridinium iodide (CMPI) (2.66 g, 10.4 mmol). The mixture was stirred for 15 minutes at room temperature followed by the addition of 1,4-diazabicyclo[2,2,2]octane (DABCO) (1.77 g, 15.8 mmol). Stirring was continued until TLC indicated consumption of the starting material (~ 2 hr). The reaction mixture was filtered through Celite, diluted with EtOAc (50 mL), and washed with brine (2 x 25 mL). The combined organic layers were dried ($MgSO_4$), filtered, the filtrate was concentrated *in vacuo*. Silica gel column chromatography (Hexanes/EtOAc, 75/25, v/v) afforded **6** (2.0 g, 89%). $[\alpha]_D^{25}$ +24.2 (*c* = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.07 (m, 5H, CH Aromatic), 4.94 (d, 1H, *J* = 11.3 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 11.3 Hz, CH*H*Bn), 4.50 (d, 1H, *J* = 7.6 Hz, H1), 4.36 (dd, 1H, *J* =

5.0 Hz, *J* = 11.7 Hz, H6a), 4.30 (bd, *J* = 11.7, 1H, H6b), 3.48-3.39 (m, 2H, H4, H5), 3.30 (dd, 1H, *J* = 7.6 Hz, *J* = 10.0 Hz, H2), 3.21 (dd, 1H, *J* = 8.5 Hz, *J* = 10.0 Hz, H3), 2.76-2.72 (m, 2H, C*H*$_2$ Lev), 2.59 (m, 3H, C*H*$_2$ Lev, 4-O*H*), 2.17 (s, 3H, C*H*$_3$ Lev), 1.70-1.62 [m, 1H, C*H*(CH$_3$)$_2$], 0.89-0.87 [4s, 12H, C(C*H*$_3$)$_2$ and CH(C*H*$_3$)$_2$], 0.18-0.17 [2s, 6H, Si(C*H*$_3$)$_2$]. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.8, 173.2, 138.1, 128.7, 128.1, 97.1, 82.1, 75.0, 73.6, 70.2, 68.3, 63.5, 37.9, 33.9, 29.8, 27.9, 24.8, 19.9, 19.8, 18.5, 18.4, -2.1, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 558.2611, found 558.2637.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glycopyranoside (28)**: Trichloroacetimidate **27** (25.4 g, 53.0 mmol) and *N*-(benzyl)-*N*-benzyloxycarbonyl-5-aminopentan-1-ol (20.9 g, 64.0 mmol) were co-evaporated with toluene (3 x 50 mL) and dissolved in a mixture of DCM (120 mL) and diethyl ether (400 mL) and stirred in the presence of powdered molecular sieves (3*Å*, 40 g) for 1hr at room temperature. TMSOTf (2.65 mmol, 0.480 ml) was slowly added to the mixture at -20°C. After stirring at -20°C for 1h, the reaction mixture was allowed to reach room temperature and then quenched with pyridine (0.5 mL). After filtration, the reaction mixture was extracted with saturated sodium bicarbonate (500 mL), brine (2 x 200 mL) and dried (MgSO$_4$). The organic layers were filtered and the filtrate concentrated *in vacuo*. NMR of the crude residue indicated α/β ratio of 3:1. Silica gel column chromatography (hexanes/EtOAc, 80/20, v/v) provided the pure α-glycoside **28** (23.2g, 68%). $[\alpha]_D^{25}$ +10.8 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.45-7.10 (m, 10H, CH Aromatic), 5.44 (dd, 1H, *J* = 9.2 Hz, *J* = 10.3 Hz, H3), 5.24-5.14 (m, 2H, C*H*$_2$ Cbz), 5.04 (dd, 1H, *J* = 9.9 Hz, H4), 4.51 (bs, 2H, NC*H*$_2$Bn), 4.24 (dd, 1H, *J* = 3.4 Hz, *J* = 12.4 Hz, H6a), 4.10-3.94 (m, 2H, H6b, H5), 3.76-3.58 (m, 1H, OC*H*H Linker), 3.54- 3.36 (m, 1H, OCH*H* Linker), 3.34-3.15 (m, 3H, H2, C*H*$_2$N Linker), 2.09- 2.03 (3s, 9H, 3 x C*H*$_3$ Ac), 1.70-1.40 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}CNMR (75.5 MHz, CDCl$_3$): δ 170.5, 169.9, 169.6, 137.8, 136.9, 128.9, 128.5, 128.4, 128.2 127.9, 127.8, 127.2, 97.8, 70.3, 68.6, 68.5, 67.5, 67.1, 61.8, 60.7, 50.4, 50.1, 46.9, 46.1, 28.9, 27.8, 27.3, 23.3, 20.6 20.5. HRMS-MALDI: (M + Na$^+$) calcd. 663.2637, found 663.2656.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glycopyranoside (30)**: CH$_3$ONa in MeOH (0.5 M) was added to **28** (13.7 g, 22.0 mmol) dissolved in MeOH (80 mL) until the reaction mixture reached pH 12. The mixture was stirred overnight until TLC (chloroform/MeOH, 9/1, v/v) indicated the completion of the reaction. After neutralization with Dowex 50-H$^+$ resin, the mixture was filtered through Celite and concentrated *in vacuo*. Silica gel column chromatography of the residue (chloroform/MeOH (95/5→93/7, v/v) provided (11.0 g, 97%) of the deacetylated compound which was directly used in the next step. *p*-toluene sulfonic acid (100 mg, 0.52 mmol) was added to the solution of the starting material (11.0 g, 21.4 mmol) and benzaldehyde dimethyl acetal (5.06 g, 33.0 mmol) in CH$_3$CN (110 mL). After 16 hr, the reaction mixture was neutralized with triethylamine and concentrated *in vacuo*. Silica gel chromatography of the residue (hexanes/EtOAc, 80/20→70/30, v/v) provided **30** (10.0g, 76%). $[\alpha]_D^{25}$ +45 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.55-7.10 (m, 15H, Aromatic), 5.46 (s, 1H, benzylidene), 5.24-5.16 (m, 2H, C*H*$_2$Cbz), 4.86 (bs, 1H, H1), 4.50 (bs, 2H, NC*H*$_2$Bn), 4.30-4.18 (m, 2H, H6a, H3), 3.88-3.62 (m, 3H, H5, H6b, OC*H*H Linker), 3.50 (t, 1H, *J* = 9.1 Hz, H4), 3.47-3.33 (m, 1H, CH*H* Linker), 3.32-3.16 (m, 3H, incl. H2: dd, *J* = 3.7 Hz, *J* = 10.2 Hz, C*H*$_2$N Linker), 2.75 (d, 1H, *J* = 3.0 Hz, 3-O*H*), 1.67-1.53 (m, 4H, 2 x C*H*$_2$Linker), 1.45-1.34 (m, 2H, C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 137.8, 136.8, 129.3, 128.5, 128.4, 128.3, 127.9, 127.8, 127.2, 102.0, 98.5, 81.9, 68.8, 68.6, 68.4, 67.1, 63.0, 62.4, 29.0, 27.8, 27.4, 23.2. HRMS-MALDI: (M + Na^+) calcd. 625.2640, found 625. 2721.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-3-*O*-benzyl-2-deoxy-α-D-glycopyranoside (32)**: NaH (1.0 g, 26.0 mmol) was added to a solution **30** (10.0 g, 16.6 mmol) in DMF (85 mL). The mixture was stirred for 30 minutes at room temperature prior to addition of benzyl bromide (3.69 g, 21.5 mmol). The reaction was followed by TLC (hexanes/EtOAc, 2/1, v/v). After stirring overnight at room temperature, the reaction was quenched with acetic acid (0.5 mL) and concentrated *in vacuo*. The residue was dissolved in EtOAc (500 mL), washed with water and brine (2 x 100mL) and dried ($MgSO_4$), filtered and concentrated *in vacuo*. Silica gel chromatography of the residue (hexanes/EtOAc, 95/15→70/30, v/v) provided *N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glycopyranoside (10.8 g, 93%). $[\alpha]_D^{25}$ +58 (*c* = 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.45-7.10 (m, 15H, Aromatic), 5.60 (s, 1H, C*H* benzylidene), 5.24-5.16 (m, 2H, CH_2 Cbz), 4.96 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.90- 4.78 (m, 2H, CH*H*Bn, H1), 4.50 (bs, 2H, NCH_2Bn), 4.28 (dd, 1H, *J* = 4.4 Hz, *J* = 9.9 Hz, H6a), 4.08 (dd, 1H, *J* = 9.1 Hz, *J* = 10.2 Hz, H3), 3.91-3.60 (m, 4H, incl. H4, H5, H6b, OC*H*H Linker), 3.42-3.17 (m, 4H, OCH*H* Linker, CH_2N Linker, H2), 1.70-1.40 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 156.8, 156.3, 137.8, 136.8, 128.5, 128.4, 128.3, 128.2 127.9, 127.8, 127.3, 101.4, 98.5 (C1), 82.8, 76.0, 75.0, 66.9, 67.1 62.9, 62.7, 50.53, 50.25, 47.0, 46.1, 29.0, 27.8, 27.4 23.2. HRMS-MALDI: (M + Na^+) calcd. 692.321, found 692.3321.

A solution of *N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glycopyranoside (4.6 g, 6.6 mmol) in acetic acid (60 mL) and H_2O (6 mL) was heated at 90°C. After 1 hr, TLC (hexanes/EtOAc, 2/1, v/v) indicated the consumption of the starting material. The reactions mixture was co-evaporated with an excess of toluene and the residue was purified using silica gel chromatography (hexanes/EtOAc, 60/40, v/v) affording **32** (6.9g, 92%). $[\alpha]_D^{25}$ +54 (*c* = 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.10 (m, 15H, CH Aromatic), 5.24-5.12 (m, 2H, C*H*$_2$ Cbz), 4.96-4.78 (m, 3H, C*H*HBn, CH*H*Bn, H1), 4.51 (bs, 2H, NC*H*$_2$Bn), 3.85-3.55 (m, 6H, H3, H4, H5, H6a, H6b, OC*H*H Linker), 3.50-3.18 (m, 4H, H2, OCH*H* Linker, C*H*$_2$N Linker), 1.70-1.20 [m, 6H, $(CH_2)_3$]. ^{13}CNMR (75.5 MHz, $CDCl_3$): δ 156.8, 156.4, 138.1, 137.7, 136.4, 128.5, 128.4 128.0, 127.9, 127.8, 127.3, 127.2, 97.8 C1, 79.8, 74.9, 72.0, 71.2, 68.0, 67.7, 67.3, 62.8, 62.7, 62.2*,* 50.4, 47.3, 46.0, 28.7, 27.8, 27.1, 23.4. HRMS-MALDI : (M + Na^+) calcd. 622.2797, found 622.2810.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-2-azido-6-*O*-levulinoyl-3-*O*-benzyl-2-deoxy-α-D-glycopyranoside (8)**: To a solution of **32** (2.0 g, 3.30 mmol) in DCM (45mL) was added levulinic acid (0.42 g, 3.63 mmol) and 2-chloromethyl pyridinium iodide (CMPI) (2.10 g, 8.25 mmol). The mixture was stirred for 15 minutes at room temperature and then cooled to -20°C followed by the addition of 1,4-diazabicyclo[2,2,2]octane (1.29 g, 11.55 mmol). The reaction mixture was allowed to warm up slowly to room temperature. Stirring was continued until TLC (hexanes/EtOAc, 1/1, v/v) indicated consumption of starting material (~ 1.5 hr). The reaction mixture was filtered through Celite, diluted with EtOAc (100 mL) and washed with a 5% solution of NaCl (2 x 25 mL). The organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. Silica gel column chromatography of the residue (hexanes/EtOAc, 26/74, v/v) afforded **6** (3.80 g, 82%). $[\alpha]_D^{25}$ +63 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, 95:5 CD_3COCD_3/CD_3OD): δ 7.40-7.10 (m, 15H, CH Aromatic), 5.22-5.12 (m, 2H, C*H*$_2$ Cbz), 5.0 (d, 1H, *J* = 11.2 Hz, C*H*HBn), 4.92-4.83 (m, 1H, H1), 4.78 (d, 1H, *J* = 11.2 Hz, CH*H*Bn), 4.54 (bs, 2H, NCH_2Bn), 4.17 (bd, 1H, *J* = 11.8 Hz, H6a), 4.20 (dd, 1H, *J* = 6.2 Hz, *J* = 11.8 Hz, H6b), 3.86-3.77 (m, 2H, H3, H5), 3.77-3.64 (m, 1H, OC*H*H Linker), 3.60 (dd, 1H, *J* = 9.1 Hz, *J* = 9.5Hz, H4), 3.48-3.36 (m, 1H, OC*H*H Linker), 3.32-3.22 (m, 3H incl. H2: dd, *J* = 3.4 Hz, *J* = 10.2 Hz, CH_2N Linker), 2.76-2.71 (t, 2H, *J* = 6.5 Hz, CH_2 Lev), 2.52 (t, 2H, *J* = 6.5 Hz, CH_2 Lev), 2.11 (s, 3H, CH_3 Ac), 1.67-1.53 (m, 4H, 2 x CH_2 Linker), 1.45-1.34 (m, 2H, CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.5, 173.3, 138.0, 137.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.2, 97.8, 79.3, 75.0, 70.8, 70.6, 70.0, 68.1, 67.1, 63.1, 62.7, 50.3, 47.3 46.0, 37.8, 29.7, 28.8, 27.7, 27.3, 23.5. HRMS-MALDI: (M + Na^+) calcd. 725.3157, found 725.3145.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glycopyranoside) (7)**: To a solution of compound **32** (1.5 g, 2.50 mmol) in DCM (45 mL) was added acetic acid (0.165 g, 2.50 mmol) and 2-chloromethyl pyridinium iodide (CMPI) (1.59 g, 6.25 mmol). The mixture was stirred for 15 minutes at room temperature and then cooled to -20°C followed by the addition of 1,4-diazabicyclo[2,2,2]octane (0.98 g, 8.75 mmol).The reaction was slowly warmed to room temperature in about 1.5hr and the progress of the reaction was monitored by TLC (hexanes/EtOAc, 1/1, v/v). The reaction mixture was filtered through Celite, diluted with EtOAc (100 mL) and washed with 5% solution of NaCl (2 x 25 mL). The organic layers were dried ($MgSO_4$), filtered and the filtrate was concentrated *in vacuo*. Silica gel column chromatography of the residue (hexanes/EtOAc, 75/25, v/v) provided **7** (1.10 g, 68%). $[\alpha]_D^{25}$ +50 (*c* = 1.00, $CHCl_3$); ^{1}HNMR (500 MHz, 95:5 CD_3COCD_3/CD_3OD): δ 7.40-7.10 (m, 15H, CH Aromatic), 5.22-5.12 (m, 2H, CH_2 Cbz), 5.00 (d, 1H, *J* = 11.2 Hz, C*H*HBn), 4.92-4.84 (m, 1H, H1), 4.78 (d, 1H, *J* = 11.2 Hz, CH*H*Bn), 4.54 (bs, 1H, NCH_2Bn), 4.14 (bd, 1H, *J* = 11.8 Hz, H6a), 4.20 (dd, 1H, *J* = 6.2 Hz, *J* = 11.8 Hz, H6b), 3.86-3.77 (m, 2H, H3, H5), 3.77-3.64 (m, 1H, OC*H*H Linker), 3.60 (dd, 1H, *J* = 9.1 Hz, *J* = 9.5 Hz, H4), 3.48-3.36 (m, 1H, OC*H*H Linker), 3.32-3.22 (m, 3H incl. H2: dd, *J* = 3.4 Hz, *J* = 10.2 Hz, H2, CH_2N Linker), 2.00 (s, 3H, CH_3 Ac), 1.67-1.53 (m, 4H, 2 x CH_2 Linker), 1.45-1.34 (m, 2H, CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 171.6, 156.7, 156.2, 137.9, 137.8, 136.8, 136.5, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.3, 87.9, 79.4, 75.1, 70.9, 70.6, 70.0, 68.1, 67.2, 62.9, 62.8, 50.4, 47.3, 46.0, 28.8, 27.3, 23.5, 23.3, 20.7. HRMS-MALDI: (M + Na^+) calcd. 669.2895, found 669.2901.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (37): Glycosyl donor **3** (25 m g, 0.056 mmol) was coupled with acceptor **5** (22.5 mg, 0.047 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **37** (33 mg, 81%). $[\alpha]_D^{25}$ +4.8 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.25 (m, 15H, CH Aromatic), 5.48 (s, 1H, C*H* benzylidene), 5.00 (t, 1H, *J* = 8.5 Hz, H2^B), 4.87 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.86 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.78 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.52 (d, 1H, *J* = 8.0 Hz, H1^B), 4.46 (d, 1H, *J* = 7.5 Hz, H1^A), 4.41 (dd, 1H, *J* = 1.5 Hz, *J* = 11.5 Hz, H6a^A), 4.09-4.05 (m, 2H, H6a^B, H6b^A), 3.72-3.65 (m, 3H, H3^B, H4^A, H4^B), 3.45-3.41 (m, 2H, H5^A, H6b^B), 3.36-3.27 (m, 3H, H2^A, H3^A, H5^B), 2.06 (s, 3H, CH_3 Ac), 2.00 (s, 3H, CH_3 Ac), 1.62-1.56 [m, 1H, $CH(CH_3)_2$], 0.88-0.86 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.17-0.15 [2s, 6H, Si $(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.4, 169.3, 138.4, 138.0, 137.0, 129.0, 128.3, 128.2, 128.2, 127.7, 127.7, 127.6, 127.3, 125.9, 101.6, 101.1, 96.7, 81.4, 80.8, 78.6, 78.3, 77.4, 77.0, 76.5, 75.1, 74.2, 73.2, 72.8, 68.4, 68.3, 66.3, 62.4, 33.9, 24.8, 20.7, 19.9, 19.8, 18.4, 18.3, -2.2, -3.3. HRMS-MALDI: (M + Na^+) calcd. 884.3765, found 884.3772.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (38): Glycosyl donor **4** (25 mg, 0.056 mmol) was coupled with acceptor **5** (22.5 mg, 0.047 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **38** (30 mg, 75%). $[\alpha]_D^{25}$ -86.3 (*c* = 0.22, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.45-7.25 (m, 15H, CH Aromatic), 5.48 (s,1H, C*H* benzylidene), 5.00 (t, 1H, *J* = 9.0 Hz, H2^B), 4.88-4.84 (m, 2H, C*H*HBn, CH*H*Bn), 4.76 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.64 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.53 (d, 1H, *J* = 8.0 Hz, H1^B), 4.47 (d, 1H, *J* = 7.5 Hz, H1^A), 4.41 (dd, 1H, *J* = 4.0 Hz, *J* = 10.0 Hz, H6a^A), 4.14-4.09 (m, 2H, H6b^A, H6a^B), 3.73-3.68 (m, 2H, H3^B, H4^A), 3.57-3.55 (m, 1H, H5^A), 3.43 (t, 1H, *J* = 10.0 Hz, H5^B), 3.34 (t, 1H, *J* = 9.5 Hz, H4^B), 3.31-3.27 (m, 2H, H2^A, H3^A), 2.81-2.74 (m, 1H, C*H*H Lev), 2.65-2.55 (m, 2H, CH_2 Lev), 2.40-2.34 (m, 1H, CH*H* Lev), 2.16 (s, 3H, CH_3 Lev), 2.06 (s, 3H, CH_3Ac),1.66-1.54 [m, 1H, C*H*(CH$_3$)$_2$], 0.88-0.86 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.17-0.16 [2s, 6H, Si (CH$_3$)$_2$].^{13}C NMR (75.5 MHz, CDCl$_3$): δ 205.9, 171.2, 170.4, 138.4, 138.0, 136.9, 128.9, 128.2, 128.1, 127.7, 127.5, 127.5, 127.4, 125.9, 101.4, 101.1, 96.6, 81.3, 80.7, 78.6, 78.0, 77.4, 77.0, 76.6, 75.1, 74.2, 73.4, 72.6, 68.4, 68.3, 66.2, 62.4, 37.5, 33.8, 29.7, 27.6, 24.7, 20.7, 19.9, 19.8, 18.4, 18.3, -2.2, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 940.4022, found 940.5577.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (39): Glycosyl donor **3** (2.2 g, 5.15 mmol) was coupled with acceptor **6** (2.3 g, 4.29 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **39** (3.65 g,, 3.97 mmol, 92%). $[\alpha]_D^{25}$ +4.8 (*c* = 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.45-7.25 (m, 15H, CH Aromatic), 5.48 (s,1H, C*H* benzylidene), 5.00 (t, 1H, *J* = 8.0 Hz, $H2^B$), 4.89 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.85 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.76 (d, 1H, *J*= 10.5 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.60 (d, 1H, *J* = 8.0 Hz, $H1^B$), 4.46 (d, 1H, *J* = 7.0 Hz, $H1^A$), 4.37 (dd, 1H, *J* = 1.5 Hz, *J* = 11.5 Hz, $H6a^A$), 4.14-4.08 (m, 2H, $H6a^B$, $H6b^A$), 3.78 (t, 1H, *J* = 9.5 Hz, $H3^B$), 3.74-3.66 (m, 3H, $H4^A$, $H5^B$, $H4^B$), 3.42-3.40 (m, 2H, $H6b^B$, $H5^A$), 3.35-3.26 (m, 2H, $H2^A$, $H3^A$), 2.82-2.67 (m, 2H, CH_2 Lev), 2.62-2.51 (m, 2H, CH_2 Lev), 2.17 (s, 3H, CH_3 Lev), 2.00 (s, 3H, CH_3 Ac), 1.67-1.61 [m, 1H, $CH(CH_3)_2$], 0.88-0.86 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.17-0.16 [2s, 6H, Si $(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 172.3, 169.4, 138.4, 138.2, 137.1, 129.0, 128.3, 128.2, 127.6, 127.6, 127.5, 126.0, 101.5, 101.1, 96.7, 81.5, 80.8, 78.7, 77.9, 77.4, 77.0, 76.6, 75.2, 74.3, 73.3, 72.8, 66.1, 62.4, 37.8, 33.9, 29.8, 29.7, 27.8, 24.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI: (M + Na^+) calcd. 940.4029, found 940.5577.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (40): Glycosyl donor **4** (101.1 mg, 0.202 mmol) was coupled with acceptor **6** (90.0 mg, 0.168 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **40** (100 mg, 75%). $[\alpha]_D^{25}$ -6.0 (*c* = 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.45-7.25 (m, 15H, CH Aromatic), 5.48 (s,1H, C*H* benzylidene), 5.01 (t, 1H, *J* = 8.5 Hz, $H2^B$), 4.90 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.85 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 13.0 Hz, CH*H*Bn), 4.62 (d, 1H, *J* = 8.5 Hz, $H1^B$), 4.49 (d, 1H, *J* = 7.5 Hz, $H1^A$), 4.41 (dd, 1H, *J* = 1.5 Hz, *J* = 12.0 Hz, $H6a^A$), 4.22 (dd, 1H, *J* = 5.5 Hz, *J* = 11.5 Hz, $H6b^A$), 4.14-4.12 (m, 1H, H6a^B), 3.82 (t, 1H, *J* = 9.0 Hz, H3^B), 3.76 (t, 1H, *J* = 9.0 Hz, H4^A), 3.69-3.66 (m, 2H, H4^B, H6b^B) 3.59-3.56 (m, 1H, H5^A), 3.48-3.40 (m, 1H, H5^B), 3.35 (t, 1H, *J* = 10.0 Hz, H2^A), 3.30-3.27 (m, 1H, H3^A), 2.84-2.50 (m, 5H, 2x CH_2 Lev and C*H*H Lev) 2.40-2.32 (m, 1H, CH*H* Lev), 2.17 (s, 3H, CH_3 Lev), 2.16 (s, 3H, CH_3 Lev), 1.69-1.62-1.55 [m, 1H, C*H*(CH_3)$_2$], 0.89-0.86 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.17-0.16 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 172.6, 171.6, 138.7, 138.5, 137.4, 129.2, 128.4, 128.4, 127.9, 127.8, 127.7, 126.2, 101.6, 101.4, 96.9, 81.8, 81.0, 79.0, 78.1, 77.6, 77.2, 76.8, 75.5, 74.5, 73.8, 72.9, 66.2, 62.9, 38.0, 37.8, 34.1, 30.0, 30.0, 28.1, 27.9, 20.13, 20.1, 18.7, 18.6. HRMS-MALDI: (M + Na$^+$) calcd. 996.4290, found 996.5958.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (49): Glycosyl donor **1** (110.6 mg, 0.249 mmol) was coupled with the acceptor **5** (100 mg, 0.208 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **49** (162 mg, 90%). $[\alpha]_D^{25}$-6.8 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.25 (m, 15H, CH Aromatic), 5.30 (s,1H, C*H* benzylidene), 4.98 (bs, 2H, H2^B, H1^B), 4.85 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.65 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.55 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.53 (m, 2H, H1^A, H6a^A), 4.05 (dd, 1H, *J* = 5.5 Hz, *J* = 12.0 Hz, H6b^A), 3.90 (bs, 1H, H5^B), 3.84-3.78 (m, 3H, H4^A, H4^B, H6a^B), 3.72-3.70 (m, 1H, H3^B), 3.49-3.45 (m, 1H, H5^A), 3.37-3.35 (m, 1H, H2^A), 3.24 (t, 1H, *J* = 9.5 Hz, H3^A), 3.18 (dd, 1H, *J* = 2.0 Hz, *J* = 13.0 Hz, H6b^B), 2.06 (s, 3H, CH_3 Ac), 2.05 (s 3H, CH_3 Ac), 1.67-1.54 [m, 1H, C*H*(CH_3)$_2$], 0.90-0.88 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.19-0.17 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.4, 170.2, 138.1, 137.9, 137.6, 128.9, 128.4, 128.3, 128.0, 127.9, 127.9, 127.6, 127.4, 127.1, 126.1, 100.4, 98.0, 97.0, 81.2, 77.4, 77.0, 76.5, 75.0, 74.9, 73.8, 73.7, 73.5, 72.1, 69.0,69.0, 67.1, 62.3, 60.3, 33.9, 24.8, 20.9, 20.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 884.3765, found 884.5333.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (50): Glycosyl donor **2** (124.6 mg, 0.249 mmol) was coupled with acceptor **5** (100 mg, 0.208 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **50** (170 mg, 66%) $[\alpha]_D^{25}$ -12.0 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.254 (m, 15H, CH Aromatic), 5.30 (s,1H, C*H* benzylidene), 4.97 (bd, 2H, *J* = 14.5 Hz, H2^B, H1^B), 4.83 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.63 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.55-4.49 (m, H, H1^A, H6a^A, CH*H*Bn), 4.08 (dd, 1H, *J* = 5.0 Hz, *J* = 11.5 Hz, H6b^A), 3.89 (bs, 1H, H5^B), 33.84-3.79 (m, 3H, H4^A, H4^B, H6a^B), 3.68 (bs, 1H, H3^B), 3.49-3.45 (m, 1H, H5^A), 3.36 (t, 1H, *J* = 10.0 Hz, H2^A), 3.24 (t, 1H, *J* = 9.5 Hz, H3^A), 3.17 (d, 1H, *J* = 13.0 Hz, H6b^B), 2.64-2.62 (m, 2H, CH_2 Lev), 2.56-2.52 (m, 2H, CH_2 Lev), 2.06 (s, 3H, CH_3 Lev), 2.02 (s, 3H, CH_3 Ac), 1.67-1.54 [m, 1H, C*H*(CH_3)$_2$], 0.90-0.88 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.19-0.17 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.2, 171.8, 170.5, 138.1, 137.9, 137.6, 128.9, 128.4, 128.3, 128.1, 127.9, 127.6, 127.4, 126.1, 100.4, 97.9, 97.0, 81.2, 77.4, 77.0, 76.6, 75.0, 75.0, 73.9, 73.7, 73.5, 72.1, 69.1, 69.0, 67.1, 62.3, 60.3, 37.7, 33.9, 29.6, 28.1, 24.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 940.4022, found 940.5577.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (**51**): Glycosyl donor **1**

(100 mg, 0.22 mmol) was coupled with the acceptor **6** (96.4 mg, 0.18 mmol) according to the general reacted procedure for synthesis of disaccharides to give disaccharide **51** (156.9 mg, 95%). $[\alpha]_D^{25}$ +21.0 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.06 (m, 15H, CH Aromatic), 5.12 (s,1H, C*H* benzylidene), 4.80-4.79 (m, 1H, H2^B), 4.77 (s, 1H, H1^B), 4.65 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.57 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.47 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.37 (d, 2H, *J* = 11.0 Hz, H6a^A, CH*H*Bn), 4.34 (d, 1H, *J* = 7.5 Hz, H1^A), 3.86 (dd, 1H, J = 6.0 Hz, *J*= 12.0 Hz, H6b^A), 3.73 (bs, 1H, H5^B), 3.65-3.3.60 (m, 3H, H4^A, H4^B, H6a^B), 3.68 (bt, 1H, *J* = 3.0 Hz, H3^B), 3.30-3.28 (m, 1H, H5^A), 3.36 (t, 1H, *J* = 7.5 Hz, H2^A), 3.02 (t, 1H, *J* = 9.5 Hz, H3^A), 3.00 (d, *J* = 13.0 Hz, 1H, H6b^B), 2.58-2.54 (m, 2H, CH_2 Lev), 2.42-2.39 (m, 2H, CH_2 Lev), 1.98 (s, 3H, CH_3 Lev), 1.88 (s, 3H, CH_3 Ac), 1.49-1.45 [m, 1H, $CH(CH_3)_2$], 0.72-0.70 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.018-0.00 [2s, 6H, Si $(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.3, 172.1, 170.2, 138.1, 138.0, 137.6, 129.1, 128.9, 128.4, 128.4, 128.3, 128.0, 127.9, 127.6, 127.4, 126.1, 100.5, 97.9, 97.0, 81.2, 77.4, 77.0, 76.6, 75.0, 74.9, 73.8, 73.5, 73.5, 72.1, 69.1, 69.0, 67.0, 62.6, 60.2, 37.9, 33.9, 29.8, 29.7, 27.9, 24.8, 21.0, 19.9, 19.8, 18.5, 18.4, -2.1, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 940.4029, found 940.5577.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (52): Glycosyl donor **2** (140 mg, 0.280 mmol) was coupled with acceptor **6** (140 mg, 0.260 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **52** (200 mg, 80%). $[\alpha]_D^{25}$ -11.2 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.25 (m, 15H, CH Aromatic), 5.30 (s,1H, C*H* benzylidene), 4.98-4.97 (m, 1H, H2^B), 4.92 (bs, 1H, H1^B), 4.82 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.74 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.55-4.51 (m, 3H, H1^A, H6a^A, CH*H*Bn), 4.07 (dd, 1H, *J* = 5.5 Hz, *J* = 12.0 Hz, H6b^A), 3.89 (bs, 1H, H5^B), 3.84-3.79 (m, 3H, H4^A, H4^B, H6a^B), 3.68 (bt, 1H, *J* = 3.0 Hz, H3^B), 3.49-3.45 (m, 1H, H5^A), 3.38-3.34 (m, 1H, H2^A), 3.23 (t, 1H, *J* = 9.0 Hz, H3^A), 3.18 (dd, 1H, *J* = 1.5 Hz, *J* = 12.5 Hz, H6b^B), 2.78-2.68 (m, 2H, CH_2 Lev), 2.66-2.60 (m, 2H, CH_2 Lev), 2.58-2.51 (m, 4H, 2 x CH_2 Lev), 2.17 (s, 3H, CH_3 Lev), 2.01 (s, 3H, CH_3 Lev), 1.67-1.54 [m, 1H, C*H*(CH_3)$_2$], 0.90-0.88 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.19-0.17 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 206.3 172.1, 171.9, 138.1, 138.0, 137.6, 128.9, 128.3, 128.2, 128.0, 127.9, 127.9, 127.6, 127.4, 126.6, 100.4, 97.8, 96.9, 81.2, 77.4, 77.0, 76.5, 75.0, 74.9, 73.9, 73.4, 73.4, 72.1, 69.0, 69.0, 67.0, 62.5, 60.2, 37.9, 37.7, 33.9, 29.7, 29.6, 28.1, 27.9, 24.7, 19.9, 19.8, 18.4, 18.3,-2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 996.4290, found 996.5962.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside (S1)**: Glycosyl donor **3** (82.1 mg, 0.185 mmol) was coupled with acceptor **7** (100 mg, 0.154 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S1** (120 mg, 75%). $[\alpha]_D^{25}$ +53.4 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.24(m, 20H, CH Aromatic), 5.47 (s, 1H, C*H* benzylidene), 5.17 (bd, 2H, *J* = 17.5 Hz, CH_2 Cbz), 5.03 (t, 1H, *J* = 8.5 Hz, H2^B), 4.96 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.86 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.81-4.75 (bd, 2H, H1^A, CH*H*Bn), 4.63 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.51 (bd, 3H, *J* = 8.0 Hz, H1^B and NCH_2Bn), 4.39 (d, 1H, *J* = 11.5 Hz, H6a^A), 4.13 (bd, 1H, *J* = 11.5 Hz, H6b^A),4.06 (dd, 1H, *J* = 4.5 Hz, *J* = 10.0 Hz, H6a^B), 3.89 (t, 1H, *J* = 9.5 Hz, H4^A), 3.75-3.74 (m, 2H, H5^A, OC*H*H Linker), 3.68 (t, 2H, *J* = 5.0 Hz, H3^B, H4^B), 3.65-3.34

(m, 1H, OCH*H* Linker), 3.44-3.22 (m, 6H, H2^{A}, H5^{B}, H3^{A}, H6b^{B}, C*H*$_2$N Linker), 2.07 (s, 3H, C*H*$_3$ Ac), 2.00 (s, 3H, C*H*$_3$ Ac), 1.66-1.24 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$):δ 170.4, 169.3, 138.4, 138.0, 137.9, 137.0, 129.1, 128.5, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 127.4, 125.9, 101.6, 101.1, 97.5, 81.4, 78.7, 78.4, 77.8, 77.4, 77.0, 76.6, 75.0, 74.3, 73.2, 68.8, 68.3, 67.2, 66.3, 62.9, 62.1, 50.6, 50.2, 47.0, 46.1, 29.7, 28.9, 27.9, 23.3, 22.7, 20.8, 20.8. HRMS-MALDI: (M + Na^{+}) calcd. 1051.4316, found 1051.6359.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside (S2)**: Glycosyl donor **4** (92.61 mg, 0.185 mmol) was coupledwith acceptor **7** (100 mg, 0.154 mmol) according to the general glycosylation procedure for synthesis of disaccharides to obtain disaccharide **S2** (160 mg, 95%). $[\alpha]_D^{25}$ +50.1 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.44-7.24 (m, 25H, CH Aromatic), 5.47 (s,1H, C*H* benzylidene), 5.17 (bd, 2H, *J* = 17.0 Hz, C*H*$_2$Cbz), 5.04 (t, 1H, *J* = 8.5 Hz, H2^{B}), 4.96 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.86 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.81 (bd, 2H, *J* = 12.0 Hz, H1^{A}), 4.75 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.64 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.52- 4.49 (m, 3H, H1^{B}, NC*H*$_2$Bn), 4.39 (dd, 1H, *J* = 1.5 Hz, *J* = 12.0 Hz, H6a^{A}), 4.29 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz, H6b^{A}), 4.10 (dd, 1H, *J* = 4.5 Hz, *J* = 10.5 Hz, H6b^{B}), 3.98 (bd, 1H, *J* = 9.5 Hz, H5^{A}), 3.92 (t, 1H, *J* = 9.5 Hz, H3^{A}), 3.79 (t, 1H, *J* = 9.0 Hz, H4^{A}), 3.72-3.66 (m, 3H, H3^{B}, H4^{B}, OC*H*H Linker), 3.38-3.21 (m, 6H, H2^{A}, H5^{B}, H6b^{B}, C*H*$_2$N Linker), 2.84-2.78 (m, 1H, C*H*H Lev), 2.64-2.52 (m, 2H, C*H*$_2$ Lev), 2.39-2.30 (m, 1H, CH*H* Lev), 2.10 (bd, 3H, *J* = 12.5 Hz, C*H*$_3$ Lev), 2.08 (s, 3H, C*H*$_3$ Ac), 1.70-1.51 (m, 4H, 2 x C*H*$_2$ Linker), 1.39-1.25 (m, 2H, C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 205.7, 171.3, 170.6, 156.7, 156.1, 138.4, 1381, 137.9, 136.9, 129.0, 128.5, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.2, 127.9, 101.5, 101.1, 97.4, 81.4, 78.8, 78.2, 77.7, 77.4, 77.0, 76.5, 75.1, 74.3, 73.4, 68.5, 68.3, 68.3, 68.1, 67.1, 66.2, 62.9, 62.3, 50.5, 50.2, 47.0, 46.1, 37.5, 29.7, 29.6, 28.9, 27.9, 27.6, 27.4, 23.2, 20.9. HRMS-MALDI: (M + Na$^+$) calcd. 1084.4682, found 1080.6445.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S3)**: Glycosyl donor **3** (1.51 g, 3.41 mmol) was coupled with acceptor **8** (2.0 g, 2.84 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S3** (2.65 g, 85%). $[\alpha]_D^{25}$ +31.5 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.47-7.26 (m, 25H, CH Aromatic), 5.48 (s, 1H, C*H* benzylidene), 5.19 (bd, 2H, *J* = 17.5 Hz, C*H*$_2$ Cbz), 5.05 (t, 1H, *J* = 9.0 Hz, H2^B), 5.02 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.88 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.81 (bd, 2H, *J* = 13.0 Hz, H1^A), 4.75 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.67 (d, 1H, *J* = 8.0 Hz, H1^B), 4.65 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.51 (bs, 2H, NC*H*$_2$Bn), 4.29 (bs, 2H, H6a$_b$^{A}), 4.11 (dd, 1H, *J* = 5.0 Hz, *J* = 10.5 Hz, H6a^B), 3.90 (t, 1H, *J* = 9.5 Hz, H3^A), 3.87-3.82 (m, 2H, H3^B, H4^A), 3.78-3.75 (m, 1H, H5^A), 3.70 (t, 1H, *J* = 9.5 Hz, H4^B), 3.67-3.58 (m, 1H, OC*H*H Linker), 3.50 (ddd, 1H, *J* = 4.5 Hz, *J* = 9.5 Hz, *J* = 14.0 Hz, H5^B), 3.44-3.23 [m, 5H, incl. H2^A: t, *J* = 10.0 Hz, H6b^B: dd, *J* = 3.0 Hz, *J* = 10.0 Hz, C*H*$_2$N Linker and OCH*H* Linker], 2.89-2.82 (m, 1H, C*H*H Lev), 2.73- 2.67 (m, 1H, C*H*H Lev), 2.64- 2.58 (m, 1H, CH*H* Lev), 2.54-2.50 (m, 1H, C*H*H Lev), 2.17 (s, 3H, C*H*$_3$ Lev), 2.03 (s, 3H, C*H*$_3$ Ac), 1.70-1.46 (m**,** 4H**,** 2 x C*H*$_2$ Linker), 1.38-1.22 (m, 2H, C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.1, 172.4, 169.4, 168.5, 138.4, 138.2, 137.9, 137.2, 136.8, 128.9, 128.5, 128.4, 128.3, 128.2, 128.2, 127.8, 127.6, 127.6, 127.5, 127.4, 127.2, 125.9, 113.9, 101.4, 101.1, 97.5, 81.6, 78.8, 78.1, 77.7, 77.4, 77.0, 76.5, 75.0, 74.3, 73.3, 68.8, 68.4, 67.1, 65.9, 62.8, 62.1, 50.5, 50.2, 37.8, 29.7, 29.7, 29.3, 28.9, 27.8, 27.4, 23.2, 20.8. HRMS-MALDI: (M + Na$^+$) calcd. 1084.4682, found 1080.644.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S4)**: Glycosyl donor **4** (85.1 mg, 0.170 mmol) was coupled with acceptor **8** (100 mg, 0.142 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S4** (150 mg, 0.131 mmol, 92%). $[\alpha]_D^{25}$ +34.9 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.24 (m, 25H, CH Aromatic), 5.47 (s,1H, C*H* benzylidene), 5.17 (bd, 2H, *J* = 16.5 Hz, CH_2 Cbz), 5.06-5.01 (m, 2H, H2^B, C*H*HBn), 4.85 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.81 (bd, 1H, *J* = 11.0 Hz, H1^A), 4.73 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.68 (d, 1H, *J* = 8.0 Hz, H1^B), 4.64 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.49 (bs, 2H, NCH_2Bn), 4.44 (dd, 1H, *J* = 4.5 Hz, *J* = 12.5 Hz, H6a^A), 4.33 (dd, 1H, *J* = 2.0 Hz, *J* = 12.5 Hz, H6b^A), 4.11 (dd, 1H, *J* = 4.5 Hz, *J* = 10.0 Hz, H6b^B), 4.00 (bd, 1H, *J* = 9.5 Hz, H5^A), 3.92 (t, *J* = 9.5 Hz, 1H, H3^A), 3.88-3.83 (m, 2H, H4^A, H3^B), 3.67 (t, 2H, *J* = 9.5 Hz, H4^B, OC*H*H Linker), 3.54 (ddd, 1H, *J* = 5.0 Hz, *J* = 10.0 Hz, *J* = 19.5 Hz, H5^B), 3.37-3.21 (m, 5H, incl. : H2^A: t, *J* = 10.5 Hz, H6b^B: dd, *J* = 3.5 Hz, *J* = 10.5 Hz), CH_2N Linker and OCH*H* Linker), 2.90-2.78 (m, 2H, CH_2 Lev), 2.72-2.46 (m, 5H, 2 x CH_2 Lev and C*H*H Lev), 2.39-2.30 (m, 1H, CH*H* Lev), 2.16 (s, 3H, CH_3 Lev), 2.10 (bd, 3H, *J* = 12.0 Hz, CH_3 Lev), 1.63-1.52 (m, 4H, 2 x CH_2 Linker), 1.35-1.25 (m, 2H, CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.2, 205.8, 172.5, 171.4, 138.5, 138.4, 137.9, 137.2, 136.7, 128.9, 128.5, 128.4, 128.2, 128.2, 127.9, 127.8, 127.6, 127.6, 127.5, 127.2, 126.0, 101.3, 101.1 , 97.5 , 81.6, 78.9, 78.1, 77.7, 77.4, 77.0, 76.6, 75.1, 74.3, 73.6, 68.5, 68.5, 68.1, 67.1, 65.9, 62.9, 62.5, 50.5, 50.2, 47.0, 46.1, 37.8, 37.6, 29.8, 29.7, 28.9, 27.9, 27.7, 23.9. HRMS-MALDI: (M + Na$^+$) calcd. 1140.4943, found 1136.6748.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside (S5)**: Glycosyl donor **1** (82.1 mg, 0.185 mmol) was coupled with acceptor **7** (100 mg, 0.154 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S5** (140 mg, 0.135 mmol, 88%). $[\alpha]_D^{24}$ +22.7 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.25 (m, 25H, CH Aromatic), 5.28 (s, 1H, C*H* benzylidene), 5.17 (bd, 2H, *J* = 15.0 Hz, C*H*$_2$ Cbz), 5.00 (bs, 1H, H2^B), 4.98 (bs, 1H, H1^B), 4.86 (bd, 1H, *J* = 12.5 Hz, H1^A), 4.80 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.75 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.65 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.62 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.50 (bd, 2H, *J* = 7.0 Hz, NC*H*$_2$Bn), 4.46 (dd, 1H, *J* = 12.0 Hz, H6a^A), 4.14 (d, 1H, *J* = 12.5 Hz, H6b^A), 3.87-3.83 (m, 5H, H5^A, H3^A, H4^A, H4^B, H5^B), 3.77 (d, 1H, *J* = 13.0 Hz, H6a^B), 3.71 (t, 1H, *J* = 3.0 Hz, H3^B), 3.69-3.60 (m, 1H, OC*H*H Linker), 3.46-3.22 (m, 3H, C*H*$_2$N Linker, OCH*H* Linker), 3.36 (dd, 1H, *J* = 3.0 Hz, *J* = 9.5 Hz, H2^A), 3.09 (d, 1H, *J* = 11.5 Hz, H6b^B), 2.09 (s, 3H, C*H*$_3$ Ac), 2.07 (s, 3H, C*H*$_3$ Ac), 1.70-1.40 (m, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.6, 170.2, 138.0, 137.9, 137.6, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 127.4, 126.1, 100.4, 98.1, 97.5, 78.5, 77.4, 77.0, 76.6, 74.9, 74.6, 74.0, 73.8, 72.0, 69.4, 69.0, 68.2, 67.2, 67.1, 63.6, 62.3, 60.3, 29.7, 29.0, 23.3, 21.0. HRMS-MALDI: (M + Na$^+$) calcd. 1051.4316, found 1051.4595.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-**

glucopyranoside (S6): Glycosyl donor **2** (92.6 mg, 0.185 mmol) was coupled with the acceptor **7** (100 mg, 0.154 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S5** (140 mg, 83%) $[\alpha]_D^{25}$ +37.9 (*c* = 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.44-7.24 (m, 25H, CH Aromatic), 5.29 (s, 1H, C*H* benzylidene), 5.17 (bd, 2H, *J* = 14.5 Hz, CH_2 Cbz), 5.01 (bs, 1H, $H2^B$), 4.95 (bs, 1H, $H1^B$), 4.86 (bd, 1H, *J* = 14.0 Hz, $H1^A$), 4.79 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.75 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.60 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.50 (bd, 2H, *J* = 7.0 Hz, NCH_2Bn), 4.45 (dd,1H, *J* = 12.5 Hz, $H6a^A$), 4.17 (d, 1H, *J* = 12.0 Hz, $H6b^A$), 3.85-3.82 (m, 5H, $H5^A$, $H3^A$, $H4^A$, $H4^B$, $H5^B$), 3.77 (d, 1H, *J* = 13.0 Hz, $H6a^B$), 3.69 (t, 1H, *J* = 3.0 Hz, $H3^B$), 3.69-3.60 (m, 1H, OC*H*H Linker), 3.46-3.22 (m, 3H, CH_2N Linker, OCH*H*Linker), 3.34 (dd, 1H, *J* = 3.0 Hz, *J* = 9.5 Hz, $H2^A$), 3.09 (d, 1H, *J* = 11.5 Hz, $H6b^B$), 2.64-2.59 (m, 2H, CH_2 Lev), 2.56-2.50 (m, 2H, CH_2 Lev), 2.07 (s, 3H, CH_3 Lev), 2.01 (s, 3H, CH_3 Ac), 1.70-1.40 (m, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 171.9, 170.6, 138.1, 138.0, 137.9, 137.6, 128.9, 128.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.8, 127.6, 127.4, 126.1, 100.4, 98.0, 97.5, 78.5, 77.4, 77.0, 76.6, 74.9, 74.6, 74.0, 73.8, 72.1, 69.3, 69.1, 68.2, 67.1, 67.1, 63.6, 62.3, 60.3, 50.5, 50.2, 37.9, 34.1, 32.1, 29.9, 29.8, 29.2, 28.3, 23.5, 22.9, 21.2, 14.3. HRMS-MALDI: $(M + Na^+)$ calcd. 1084.4681, found 1080.4642.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S7)**: Glycosyl donor **1** (100 mg, 0.22 mmol) was coupled with acceptor **8** (126.5 mg, 0.18 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S7** (160 mg, 81%). $[\alpha]_D^{25}$ +32.3 (*c* = 1.00, $CHCl_3$); δ 7.45-

7.27 (m, 25H, CH Aromatic), 5.30 (s, 1H, C*H* benzylidene), 5.19 (bd, 2H, *J* = 16.0 Hz, CH_2 Cbz), 5.01 (bs, 1H, H2^B), 4.97 (s, 1H, H1^B), 4.87 (bd, 1H, *J* = 12.5 Hz, H1^A), 4.80 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.77 (d, 1H, *J* = 12.5 Hz, C*H*HBn), 4.66 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.63 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.52 (bd, 3H, *J* = 11.0 Hz, NCH_2Bn, H6a^A), 4.15 (d, 1H, *J* = 11.0 Hz, H6b^A), 3.89-3.78 (m, 5H, H5^A, H3^A, H4^A, H4^B, H5^B), 3.79 (d, 1H, *J* = 13.0 Hz, H6$_a^B$), 3.73 (t, 1H, *J* = 3.0 Hz, H3^B), 3.69-3.60 (m, 1H, OC*H*H Linker), 3.46-3.22 (m, 3H, CH_2N Linker, OCH*H* Linker), 3.36 (dd, 1H, *J* = 3.0 Hz, *J* = 9.0 Hz, H2^A), 3.13 (d, 1H, *J* = 12.5 Hz, H6b^B), 2.77-2.74 (m, 2H, CH_2 Lev), 2.62-2.60 (m, 2H, CH_2 Lev), 2.15 (s, 3H, CH_3 Lev), 2.08 (s, 3H, CH_3 Ac), 1.70-1.40 (m**,** 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.3, 172.2, 170.2, 138.0, 138.0, 137.9, 137.6, 136.8, 128.9, 128.5, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.6, 127.3, 127.2, 126.1, 100.4, 97.9, 97.4, 78.5, 77.4, 77.0, 76.6, 75.0, 74.8, 74.6, 73.7, 72.0, 70.0, 69..3, 69.0, 68.1, 67.1, 66.9, 63.6, 62.7, 62.4, 60.2, 50.5, 50.2, 47.1, 46.1, 37.8, 29.7, 29.6, 29.0, 27.9, 27.4, 23.3, 20.9. HRMS-MALDI: (M + Na$^+$) calcd. 1084.4681, found 1080.4642.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S8)**: Glycosyldonor **2** (100 mg, 0.199 mmol) was coupled with the acceptor **8** (116.6 mg, 0.166 mmol) according to the general glycosylation procedure for synthesis of disaccharides to give disaccharide **S8** (180 mg, 95%). $[\alpha]_D^{25}$ +37.3 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.38-7.16 (m, 25H, CH Aromatic), 5.21 (s, 1H, C*H* benzylidene), 5.09 (bs, 2H, CH_2 Cbz), 4.93 (t, 1H, *J* = 2.4 Hz, H2^B), 4.85 (bs, 1H, H1^B), 4.79(bs, 1H, H1^A), 4.72 (d, 1H, *J* = 10.8 Hz, C*H*HBn), 4.70 (d, 1H, *J* = 11.7 Hz, C*H*HBn), 4.58 (d, 1H, *J* = 11.4 Hz, CH*H*Bn), 4.55 (d, 1H, *J* = 11.1 Hz, CH*H*Bn), 4.43 (t, 3H, *J* = 3.0 Hz, NCH_2Bn, H6a^A), 4.15 (d, 1H, *J* =

12.6 Hz, H6b^A), 3.78-3.73 (m, 5H, H5^A, H3^A, H4^A, H4^B, H5^B), 3.68 (s, 1H, H6a^B), 3.73 (t, 1H, *J* = 3.0 Hz, H3^B), 3.63-3.52 (m, 1H, OC*H*H Linker), 3.42-3.12 (m, 3H, C*H*$_2$N Linker, OCH*H* Linker), 3.36 (dd, 1H, *J* = 3.3 Hz, *J* = 9.3 Hz, H2^A), 3.02 (d, 1H, *J* = 11.7 Hz, H6b^B), 2.77-2.74 (m, 2H, C*H*$_2$ Lev), 2.62-2.60 (m, 2H, C*H*$_2$ Lev), 2.15 (s, 3H, C*H*$_3$ Lev), 2.08 (s, 3H, C*H*$_3$ Ac), 1.70-1.40 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.4, 206.3, 172.1, 171.9, 138.0, 138.0, 137.8, 137.6, 136.8, 128.8, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.5, 127.3, 127.2, 126.1, 100.4, 97.7, 97.4, 78.4, 77.4, 77.2, 77.0, 76.5, 74.8, 74.5, 73.7, 73.6, 72.0, 69.3, 69.0, 68.1, 67.1, 66.9, 63.6, 62.4, 60.1, 50.5, 50.2, 47.0, 46.1, 37.8, 37.7, 30.8, 29.7, 29.6, 29.5, 29.0, 28.1, 27.9, 27.4, 23.2. HRMS-MALDI: (M + Na$^+$) calcd. 1140.4943, found 1136.6748.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S9): Disaccharide **37** (0.427 g, 0.495 mmol) was dissolved in DCM:TFA:H$_2$O (0.06 M) (10/1/0.1, v/v) and treated according to the general procedure for benzylidene acetal cleavage to give **S9** (0.290 g, 75%). $[\alpha]_D^{25}$ +16.20 (*c*=1.00, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.37-7.25 (m, 10H, CH Aromatic), 4.97 (t, 1H, *J* = 9.5 Hz, H2^B), 4.87 (d, 1H, *J* = 10.0 Hz, C*H*HBn), 4.78 (d, 1H, *J* = 15.0 Hz, C*H*HBn), 4.72 (d, 1H, *J* = 10.0 Hz, CH*H*Bn), 4.64 (d, 1H, *J* = 10.0 Hz, CH*H*Bn), 4.58 (d, 1H, *J* = 10.0 Hz, H1^A), 4.44 (dd, 1H, *J* = 2.0 Hz, *J* = 10.0 Hz, H6a^A), 4.39 (d, 1H, *J* = 10.0 Hz, H1^B), 4.06 (dd, 1H, *J* = 7.0 Hz, *J* = 12.0 Hz, H6b^A), 3.64-3.54 (m, 3H, H4^B, H4^A,H6a^B), 3.48-3.42 (m, 2H, H5^A, H3^B), 3.35-3.28 (m, 3H, H2^A, H3^A,H6b^B), 3.20-3.16 (m, 1H, H5^A), 2.06 (s, 3H, C*H*$_3$ Ac), 2.00 (s, 3H, C*H*$_3$ Ac), 1.65-1.61 [m, 1H, C*H*(CH$_3$)$_2$], 0.88-0.86 [4s, 12H, C(C*H*$_3$)$_2$ and CH(C*H*$_3$)$_2$], 0.17-0.15 [2s, 6H, Si(C*H*$_3$)$_2$].^{13}C NMR (75.5 MHz,CDCl$_3$): δ 170.5, 169.4, 138.3, 137.9, 128.7, 128.4, 128.1, 127.8, 127.7, 127.1, 101.0, 96.7, 82.8, 80.6, 78.0, 77.4, 77.0, 76.6, 75.4, 75.1, 74.7, 73.3, 72.9, 70.5, 68.5, 62.4, 62.1, 33.9, 24.8, 20.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.2, -3.3. HRMS-MALDI: (M + Na^+) calcd. 796.34527, found 796.3431.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S10): Disaccharide **38** (0.255 g, 0.277 mmol) was dissolved in DCM:TFA:H_2O (0.06 M) (10/1/0.1, v/v) and treated according to the general procedure for benzylidene acetal cleavage to give **S10** (0.20 g, 87%). ^1H NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H, CH Aromatic), 4.97 (t, 1H, *J* = 8.5 Hz, $H2^B$), $[\alpha]_D^{25}$ +27.1 (*c* = 0.024, $CHCl_3$); 4.87 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.79 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.76 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.62 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.50-4.48 (m, 2H, $H1^A$, $H6a^A$), 4.40 (d, 1H, *J* = 7.5 Hz, $H1^B$), 4.11 (dd, 1H, *J* = 6.0 Hz, *J* = 12.0 Hz, $H6b^A$), 3.61-3.56 (m, 2H, $H4^B$, $H6a^B$), 3.53 (t, 1H, *J* = 9.0 Hz, $H5^A$), 3.47 (t, 1H, *J* = 9.0 Hz,$H3^B$), 3.36-3.27 (m, 3H, $H2^A$, $H3^A$, $H6b^B$), 3.20-3.17 (m, 1H, $H5^B$), 2.81-2.58 (m, 3H, CH_2 Lev, C*H*H Lev), 2.47-2.41 (m, 1H, CH*H* Lev), 2.17 (s, CH_3 Lev), 2.08 (s, 1H, CH_3 Ac), 1.68-1.62 [m, 1H, C*H*(CH_3)$_2$], 0.89-0.86 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.18-0.16 [2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz,$CDCl_3$): δ 206.1, 171.5, 170.6, 138.3, 138.1, 128.6, 128.4, 128.0, 127.7, 127.2, 100.9, 96.7, 82.9, 80.7, 77.9, 77.4, 77.0, 76.6, 75.4, 75.2, 74.7, 73.6, 72.7, 70.5, 68.5, 62.6, 62.1, 37.5, 33.9, 29.8, 27.7, 24.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI : (M + Na^+) calcd. 852.3714, found 852.5162.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S11): Disaccharide **39** (3.65 g, 3.97

mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S11** (2.8 g, 85%). $[\alpha]_D^{25}$ +30.6 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.26 (m, 10H, CH Aromatic), 4.97 (t, 1H, *J* = 9.0 Hz, H2^B), 4.90 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.77 (d, 1H, *J*= 11.0 Hz, CH*H*Bn), 4.72 (d, 1H, *J*= 11.5 Hz, C*H*HBn), 4.65 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.47 (d, 1H, *J* = 8.0 Hz, H1^A), 4.46 (d, 1H, *J* = 7.0 Hz, H1^B), 4.35 (dd, 1H, *J* = 1.5 Hz, *J* = 11.5 Hz, H6a^A), 4.17 (dd, 1H, *J* = 5.0 Hz, *J* = 11.5 Hz, H6b^A), 3.71 (t, 1H, *J* = 9.5 Hz, H4^B),3.64-3.59 (m, 2H, H4^B, H3^B), 3.56 (ddd, 1H, *J* = 3.5 Hz, *J* = 9.0 Hz, *J* = 18.0 Hz, H6^B), 3.45-3.41 (m, 1H, H5^A), 3.37-3.27 (m, 4H, H2^A, H3^A, H6B, H5^B), 2.85-2.81 (m, 1H, C*H*H Lev), 2.75-2.67 (m, 1H, CH*H* Lev), 2.65-2.52 (m, 2H, 2 x CH_2 Lev), 2.06 (s, 3H, CH_3 Ac), 2.19 (s 3H, CH_3 Lev), 2.04 (s, 3H, CH_3 Ac), 1.65-1.61 [m, 1H, C*H*(CH_3)$_2$], 0.90-0.87 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.17-0.16 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz,$CDCl_3$): δ 206.5, 172.4, 169.5, 138.3, 138.1, 128.6, 128.4, 128.0, 127.8, 127.7, 127.3, 100.8, 96.8, 82.9, 80.6, 77.4, 77.0, 76.6, 75.5, 75.2, 74.6, 73.3, 72.8, 70.8, 68.5, 62.3, 37.7, 33.9, 29.8, 29.7, 27.8,24.8, 20.9, 19.9, 19.8, 18.5, 18.4, -2.1, -3.2. HRMS-MALDI: (M + Na^+) calcd. 852.3714, found 852.5162.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S12): Disaccharide **40** (0.377 g, 0.387 mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S12** (0.297 g, 87%). $[\alpha]_D^{25}$ -9.1 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.26 (m, 10H, CH Aromatic), 4.96 (t, 1H, *J* = 8.5 Hz, H2^B), 4.90 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.75 (d, 2H, *J* = 11.5 Hz, CH*H*Bn and C*H*HBn), 4.65 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.489 (t, 2H, *J* = 7.5 Hz, H1^B and H1^A), 4.38, (dd, 1H, *J* = 1.5 Hz, *J* = 11.5 Hz, $H6a^{A}$), 4.25 (dd, 1H, *J* = 4.5 Hz, *J* = 12.0 Hz, $H6b^{A}$), 3.73 (t, 1H, *J* = 9.5 Hz, $H4^{A}$), 3.62-3.57 (m, 3H, $H3^{B}$, $H5^{A}$,$H6a^{B}$), 3.51 (t, 1H, *J* = 9.0 Hz, $H4^{B}$), 3.365-3.271 (m, 4H, $H2^{A}$, $H3^{A}$, $H5^{B}$, $H6b^{B}$), 3.56-3.58[m, 6H, 3 x $C\mathit{H}_2$ Lev], 2.43-2.38 (m, 2H, $C\mathit{H}_2$ Lev), 2.38-2.18 (2s 3H, $C\mathit{H}_3$ Lev), 1.80-1.62 [m, 1H, $C\mathit{H}(CH_3)_2$], 0.89-0.87 [4s, 12H, $C(C\mathit{H}_3)_2$ and $CH(C\mathit{H}_3)_2$], 0.17-0.16 [2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.6, 206.1, 172.4, 171.5, 138.4, 138.3, 128.6, 128.3, 127.9, 127.7, 127.3, 100.7 , 96.7 , 82.9, 80.6, 77.4, 77.0, 76.6, 75.4, 75.2, 74.6, 73.6, 72.6, 70.9, 68.5, 62.7, 62.3, 37.7, 37.6, 33.9, 29.9, 29.8, 27.8, 24.8, 19.9, 19.8, 18.4, 18.4, -2.1, -3.2. HRMS-MALDI: ($M + Na^{+}$) calcd. 908.3977, found 908.5037.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (S13): Disaccharide **49** **(**120 mg, 0.131mmol) was dissolved in DCM and treated according to the general procedure for benzylidene acetal cleavage. Silica gel column chromatography of the residue (Toluene/EtOAc, 9/1→65/35, v/v) afforded **S13** (116 mg, 65%). $[\alpha]_D^{25}$ -21(*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.07 (m, 10H, CH Aromatic), 4.79 (t, 1H, *J* = 1.2 Hz, $H2^{B}$), 4.70 (bs, 1H, $H1^{B}$), 4.65 (d, 1H, *J* = 10.0 Hz, C*H*HBn), 4.61 (d, 1H, *J* = 11.3 Hz, CH*H*Bn), 4.46(d, *J* = 11.3, 1H, C*H*HBn), 4.39(d, *J* = 7.6 Hz,1H, $H1^{A}$), 4.36 (d, 1H, *J* = 10.0 Hz, CH*H*Bn), 4.33 (dd, 1H, *J* = 2.3 Hz, *J* = 12.2 Hz, $H6a^{A}$),4.10 (bt, 1H, *J* = 5.2 Hz, $H5^{B}$), 4. 97 (dd, 1H, *J* = 5.6 Hz, *J* = 12.0 Hz, $H6b^{A}$), 3.67 (t, 1H, *J* = 9.5 Hz, $H4^{A}$), 3.50 (t, 1H, *J* = 2.6 Hz, $H3^{B}$), 3.45 (bd, 1H, *J* = 9.6 Hz, $H4^{B}$), 3.34 (ddd, 1H, *J* =2.3 Hz, *J*= 5.4 Hz, *J* = 9.5 Hz, $H5^{A}$), 3.22 (dd, 1H, *J* = 7.6 Hz, *J* = 10.0 Hz, $H2^{A}$), 3.18 (d, 1H, *J* = 6.0 Hz, *J* = 12.0 Hz, $H6a^{B}$), 3.10 (t, 1H, *J* = 9.7 Hz, $H3^{A}$), 3.05 (m, 1H, $H6b^{B}$), 2.40 (d, 1H, *J* = 9.6, O*H*), 1.94-1.92 (2s, 6H, 2 x $C\mathit{H}_3$ Ac), 1.52-1.43[m, 1H, $C\mathit{H}(CH_3)_2$], 0.76-0.73 [4s, 12H, $C(C\mathit{H}_3)_2$ and $CH(C\mathit{H}_3)_2$], 0.05-0.03 [2s, 6H, $Si(C\mathit{H}_3)_2$].

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.45, 169.48, 137.59, 137.47, 128.5, 128.14, 128.11, 128.03, 127.92, 97.8, 97.04, 81.30, 75.43, 75.09, 73.50, 73.43, 72.24, 69.2, 67.72, 67.50, 67.0, 62.71, 62.37, 33.95, 24.80, 20.99, 20.83, 19.94, 19.83, 18.50, 18.36, -2.21, -3.31. HRMS-MALDI: (M + Na^+) calcd. 796.3447, found 796.3451.

Dimethylthexylsilyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-β-D-glucopyranoside (S14): Disaccharide **50 (**170mg, 0.137 mmol) was dissolved inDCM:TFA:H_2O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S14** (71.5 mg, 55%). $[\alpha]_D^{25}$ +45.6 (*c* = 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.25-7.07 (m, 10H, CH Aromatic), 4.79 (t, 1H, *J* = 1.1 Hz, $H2^B$), 4.70 (bs, 1H, $H1^B$), 4.64 (d, 1H, *J* = 10.3 Hz, C*H*HBn), 4.61 (d, 1H, *J* = 11.3 Hz, CH*H*Bn), 4.46 (d, 1H, *J* = 11.3 Hz, C*H*HBn), 4.39 (d, 1H, *J* = 7.6 Hz, $H1^A$), 4.36 (d, 1H, *J* = 10.3 Hz, CH*H*Bn), 4.32 (dd, 1H, *J* = 2.3 Hz, *J* = 12.0 Hz, $H6a^A$), 4.08 (t, 1H,*J* = 5.1 Hz, $H5^B$), 3.96 (dd, 1H, *J* = 5.2 Hz, *J* = 12.0 Hz, $H6b^A$), 3.70 (t, 1H, *J* = 9.4 Hz, $H4^A$), 3.51 (t, 1H, *J* = 2.4 Hz, $H3^B$), 3.46 (bs, 1H, $H4^A$), 3.33 (ddd, 1H, *J* = 2.3 Hz, *J* = 5.1 Hz, *J* = 9.5 Hz, $H5^A$), 3.24-3.18 (m, 2H, $H2^A$, $H6a^B$), 3.10 (t, 1H, *J* = 9.4 Hz, $H3^A$), 3.05-3.04 (m, 1H, $H6b^B$), 2.61 (t, 2H, CH_2 Lev), 2.56 (bd, 1H, *J* = 6.4 Hz, O*H*), 2.42 (t, 2H, CH_2 Lev), 2.03-1.93 (2s, 6H, CH_3 Ac, CH_3 Lev), 1.52-1.43[m, 1H, $CH(CH_3)_2$], 0.76-0.74[4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.05-0.03 [2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.45, 169.48, 137.59, 137.47, 128.5, 128.14, 128.11, 128.03, 127.92, 97.8, 97.04, 81.30, 75.43, 75.09, 73.50, 73.43, 72.24, 69.2, 67.72, 67.50, 67.0, 62.71, 62.37, 33.95, 24.80, 20.99, 20.83, 19.94, 19.83, 18.50, 18.36, -2.21, -3.31. HRMS-MALDI: (M + Na^+) calcd. 852.3714, found 852.5162.

Dimethylthexylsilyl *O*-(2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S15): Disaccharide **51 (**120 mg, 0.131mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v)(0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S15** (90 mg, 82%). $[\alpha]_D^{25}$ +24 (*c* = 1, CHCl$_3$): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.31-7.15 (m, 10H, CH Aromatic), 4.86 (bs, 1H, H2^B), 4.74 (s, 1H, H1^B), 4.71 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.67 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.53 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.47-4.43 (m, 2H, C*H*HBn, H1^A), 4.39 (dd, 2H, *J* = 2.0 Hz, *J* = 12.0 Hz , H6a^A), 4.16 (t, 1H, *J* = 2.0 Hz, H5^B), 4.06 (dd, 1H, *J* = 5.0 Hz, *J* = 12.5 Hz, H6b^A), 3.78 (t, 1H, *J* = 9.5 Hz, H4^A), 3.57 (bs, 1H, H3^B), 3.57 (bs, 1H, H4^B), 3.42-3.39 (m, 1H, H5^A), 3.30-3.26 (m, 2H, H2^A, H6a^B), 3.19-3.12 (m, 1H, H3^A, H6b^B), 2.68-2.67 (m, 2H, C*H*$_2$ Lev), 2.52-2.50 (m, 2H, C*H*$_2$ Lev), 2.10 (s, 3H, C*H*$_3$ Lev), 2.03 (s, 3H, C*H*$_3$ Ac), 1.49-1.45 [m, 1H, C*H*(CH$_3$)$_2$], 0.72-0.70 [4s, 12H, C(C*H*$_3$)$_2$ and CH(C*H*$_3$)$_2$], 0.018-0.00 [2s, 6H, Si (CH$_3$)$_2$]. HRMS-MALDI: (M + Na$^+$) calcd. 852.3714, found 852.5162.

Dimethylthexylsilyl -*O*-(2-*O*-levulinoyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-β-D-glucopyranoside (S16): Disaccharide **52 (**140 mg, 0.195 mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S16** (50 mg, 30%), $[\alpha]_D^{25}$ +24 (*c* = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.31-7.15 (m, 10H, CH Aromatic), 4.93 (bs, 1H, H2^B), 4.80 (s, 1H, H1^B), 4.77-4.43 (m, 2H, C*H*HBn, C*H*HBn),4.59 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.53-4.49 (m, 2H, C*H*HBn, H1^A), 4.45 (dd, 2H, *J* = 2.5 Hz, *J* = 12.5 Hz , H6a^A), 4.20 (t, 1H, *J* = 2.0 Hz, H5^B), 4.14 (dd, 1H, *J* = 4.5 Hz, *J* = 12.5 Hz, H6b^A), 3.86 (t, 1H, *J* = 9.5 Hz, H4^A), 3.65 (bs, 1H, *J* = 3 Hz, H3^B), 3.60 (bs, 1H, H4^B), 3.48-3.45 (m, 1H, H5^A), 3.38-3.33 (m, 2H, H2^A, H6a^B), 3.25-3.19 (m, 1H, H3^A, H6b^B), 2.78-2.71 (m, 2H, CH_2 Lev), 2.65-2.54 (m, 2H, CH_2 Lev), 2.17-2.16 (2s, 6H, 2 x CH_3 Lev), 1.65-1.59[m, 1H, CH(CH$_3$)$_2$], 0.90-0.87 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.019-0.018 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz,CDCl$_3$): δ 206.5, 206.5, 172.0, 171.6, 137.6, 137.5, 128.4, 128.3, 128.1, 128.1, 127.9, 97.4, 97.0, 81.2, 77.4, 77.0, 76.6, 75.4, 75.3, 73.3, 72.9, 72.3, 69.2, 67.8, 67.1, 62.7, 62.5, 37.8, 37.9, 33.9, 29.8, 29.7, 28.0, 27.9, 24.8, 19.9, 19.8, 18.5, 18.4, -2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 908.3977, found 908.5037.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside (S17)**: Disaccharide **S1** (120 mg, 0.116 mmol) was dissolved in DCM:TFA:H$_2$O (10/1/0.1, v/v/v) (0.06M) and treated according to the general procedure for benzylidene acetal cleavageto give **S17** (85 mg,78%). $[\alpha]_D^{23}$ +21.1 (c = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.31-7.07 (m, 25H, CH Aromatic), 5.12-5.1 (bd, 2H, J = 17.5 Hz, CH_2 Cbz), 4.94-4.88 (m, 2H, H2^B, CHHBn), 4.66 (d, 1H, J =12.0 Hz, CHHBn), 4.60 (d, 1H, J = 11.5 Hz, CHHBn), 4.44 (bd, 2H, J = 7.5 Hz, NCH_2Bn), 4.35-4.31 (m, 2H, H1^A, H6a^A), 4.07 (bd, 1H, J = 12.0 Hz, H6b^A),3.81 (bt, 1H, J = 8.5 Hz, H3^A), 3.75-3.69 (bm, 1H, 5H^A), 3.64 (t, 1H, J = 9.0 Hz, 4H^A), 3.56-3.44 (m, 3H, OCHH Linker, H6a^B, H4^B), 3.41-3.11 (m, 7H, H3^B, OCHH Linker, H2^A, NCH_2 Linker, H6b^B, H5^B), 2.35 (bs, 1H, OH), 2.02 (s, 3H, CH_3 Ac), 1.97 (s, 3H, CH_3 Lev), 1.35-1.17 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 170.5, 169.4, 138.3, 137.9, 137.8, 136.7, 129.0, 128.7, 128.5, 128.4, 128.2, 128.1,127.9, 127.8, 127.7, 127.7, 127.3, 127.1, 125.3, 101.0 (C1^B), 97.5 (C1^A), 83.0, 78.1, 77.7, 77.4, 77.0, 76.6, 75.5, 74.9, 74.7, 73.3, 70.7, 68.8, 68.3, 67.2, 63.0, 62.1, 50.5, 50.2, 47.0, 46.1, 29.7, 28.9, 27.8, 27.4, 23.3, 20.9, 20.8. HRMS-MALDI: (M + Na^{+}) calcd. 940.4106, found 940.4055.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside (S18)**: Disaccharide **S2** (40 mg,0.037 mmol) was dissolved in DCM:TFA:H$_2$O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S18** (35 mg, 94%). [α]$_{D}^{25}$ +47.0 (*c* = 1.00, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.39-7.25 (m, 20H, CH Aromatic), 5.17 (bd, 2H, C*H*$_2$ Cbz), 5.01-4.95 (m, 2H, H2^{B}, C*H*HBn), 4.83-4.81 (bd, 1H, *J* = 11.0 Hz, H1^{A}), 4.78 (d, 2H, *J* = 11.0 Hz,CH*H*Bn, C*H*HBn), 4.62 (d, 1H, *J* = 11.5 Hz,CH*H*Bn), 4.51-4.49 (m, 2H, NC*H*$_2$Bn),4.46 (dd, 1H, *J* = 2.00 Hz, *J* = 12.5 Hz, H6a^{A}), 4.39 (d, 1H, *J*= 8.0 Hz, H1^{B}), 4.29 (dd, 1H, *J* = 4.5 Hz, *J* = 12.5 Hz, H6b^{A}), 3.98 (d, 1H, *J* = 9.0 Hz, H5^{A}), 3.91 (t, 1H, *J* = 9.5 Hz, H3^{A}), 3.75-3.66 (m, 2H, H4^{A}, OC*H*H Linker), 3.60 (dd, 1H, *J* = 3.0 Hz, *J* = 12.0 Hz, H6a^{B}),3.53-3.45 (m, 2H, H3^{B}, H4^{B}), 3.30-3.16 (m, 4H, H5^{B}, H2^{A},H6b^{B}, C*H*$_2$N Linker, OCH*H* Linker), 2.81-2.78 (m, 1H, C*H*H Lev), 2.65-2.59 (m, 2H, C*H*$_2$ Lev), 2.42-2.39 (m, CH*H* Lev), 1.63-1.21 (2m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 205.7, 171.5, 170.6, 156.7, 156.1, 138.4, 138.1, 137.9, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.3, 127.0, 101.0, 97.4, 83.0, 78.1, 77.7, 77.4, 77.0, 76.6, 75.4, 74.9, 74.8, 73.6, 70.6, 68.6, 68.1, 67.1, 63.1, 62.4, 62.2, 50.5, 50.2, 46.5, 46.1, 37.5, 29.7, 29.7, 28.9, 27.8, 23.3, 20.9. HRMS-MALDI: (M + Na^{+}) calcd. 996.43682, found 996.4386.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S19)**: Disaccharide **S3** (2.65 g, 2.44 mmol) was dissolved in DCM:TFA:H$_2$O (10/1/0.1, v/v/v)

(0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S19** (1.79 g, 88%). $[\alpha]_D^{25}$ +23.0 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.18 (m, 20H, CH Aromatic), 5.10 (bd, 2H, *J* = 17.5 Hz, C*H*₂ Cbz), 4.94-4.90 (m, 2H, H2^B, C*H*HBn), 4.74 (bd, 1H, *J* = 13.0 Hz, H1^A), 4.70 (d, 1H, *J*= 11.0 Hz, H1^B) 4.65 (d, 1H, *J* = 12.0 Hz, C*H*HBn,), 4.60 (d, 1H,*J* = 12.0 Hz, C*H*HBn), 4.45-4.42 (m, 2H, CH*H*Bn, NC*H*₂Bn), 4.25 (bd, 1H, *J* = 12.0, H6a^A), 4.17 (d, 1H, *J* = 12.5 Hz, H6b^A), 3.83-3.81 (m, 1H, H4^A), 3.72-3.61 (bd, 2H, incl. H5^A: *J* = 5.0 Hz, OC*H*H Linker), 3.59-3.52 (m, 2H, incl. H3^B : t, 1H, *J* = 9.0 Hz, H6a^B: dd, 1H, *J* = 3.0 Hz, *J* = 12.0 Hz), 3.45 (m, 1H, H4^B), 3.36-3.34 (m, 1H, H5^B), 3.24-3.14 (m, 4H, H2^A,H3^A, H6b^B, C*H*₂N Linker), 2.81-2.78 (m, 1H, C*H*H Lev), 2.65-2.59 (m, 2H, C*H*₂ Lev), 2.42-2.39 (m, CH*H* Lev), 1.65-1.21 (m, 6H, 3 x C*H*₂ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.6, 172.4, 169.6, 138.3, 138.1, 137.8, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.2, 100.8, 97.6, 82.9, 77.7, 77.6, 77.4, 77.0, 76.5, 75.5, 75.0, 74.6, 73.3, 71.1, 68.8, 68.3, 67.1, 63.0, 62.3, 62.2, 50.5, 50.2, 47.0, 46.1, 37.7, 29.8, 28.9, 27.7, 27.4, 23.2, 20.9. HRMS-MALDI: (M + Na$^+$) calcd. 996.43682, found 996.4386.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside (S20)**: Disaccharide **S4** (140 mg, 0.123 mmol) DCM:TFA:H_2O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S20** (100 mg, 77%). $[\alpha]_D^{25}$ +52.1 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.26 (m, 20H, CH Aromatic), 5.17 (bd, 2H, *J* = 17.0 Hz, C*H*₂Cbz), 5.02-4.97 (m, 2H, H2^B, C*H*HBn), 4.83 (d, 1H, *J* = 9.5 Hz, H1^A), 4.78 (d, 1H, *J* = 10.5 Hz, C*H*HBn), 4.77 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.65 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.53 (d, 1H, *J*= 8.0 Hz, H1^B), 4.48 (m, 2H, H6a^A, NC*H*₂Bn), 4.28 (d, 1H, J = 10.5 Hz, H6b^{A}), 4.00 (d, 1H, J = 10.0 Hz, H5^{A}), 3.92 (t, 1H, J = 10.0 Hz, H3^{A}), 3.80 (t, 1H, J = 9.5 Hz, H4^{A}), 3.68 (m, 2H, H3^{B}, OC*H*H Linker), 3.60 (dd, 1H, J = 2.5 Hz, J = 10.5 Hz, H6a^{B}), 3.53 (ddd, 1H, J = 4.0 Hz, J = 9.5 Hz, J = 18.5 Hz, H4^{B}), 3.46-3.43 (ddd, 1H, J = 3.0 Hz, J = 6.0 Hz, J = 15.5 Hz, H6b^{B}), 3.34-3.21 (m, 4H, H5^{B}, H2^{A}, CH_2N Linker), 2.92-2.79 (m, 2H, CH_2 Lev), 2.71-2.61 (m, 4H, 2 x CH_2 Lev), 2.56-2.36 (m, 2H, CH_2 Lev), 2.18 (s, 3H, CH_3 Lev), 2.11 (bd, 3H, J = 10.0 Hz, CH_3 Lev), 1.61-1.25 (2m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.7, 205.8, 172.5, 171.5, 138.5, 138.3, 137.9, 136.7, 128.6, 128.5, 128.4, 127.9, 127.8, 127.7, 127.3, 127.1, 100.8, 97.6, 83.0, 77.9, 77.7, 77.4, 77.0, 76.5, 75.3, 75.0, 74.6, 73.7, 71.1, 68.6, 68.1, 67.1, 63.1, 62.6, 62.4,50.5, 50.2, 46.5, 46.1 37.7, 37.6, 29.9, 29.7, 29.7, 28.9, 27.8, 23.2. HRMS-MALDI: (M + Na^{+}) calcd. 1052.4630, found 1052.4660.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside** (**S21**): Disaccharide **S5 (**130 mg, 0.135mmol) was dissolved in DCM:TFA:H$_2$O (10/1/0.1, v/v/v) (0.06 M) and treated according the general procedure for benzylidene acetal cleavage to give **S21** (80 mg, 67%). $[\alpha]_D^{24}$ +51.0 (c = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.44-7.26 (m, 25H, CH Aromatic), 5.18 (bd, 2H, J = 15.0 Hz, CH_2Cbz), 4.97 (bs, 1H, H2^{B}), 4.89-4.85 (m, 2H, H1^{A}, H1^{B}), 4.77-4.75 (m, 2H, C*H*HBn, C*H*HBn), 4.61 (d, 1H,J = 11.5 Hz, CH*H*Bn), 4.57 (d, 1H, J = 12.5 Hz, CH*H*Bn), 4.50 (bd, 2H, J = 6.5Hz, NCH_2Bn), 4.40 (d, 1H, J = 12.5 Hz, H6), 4.22-4.20 (m, 2H, H5^{A}, H6a^{B}), 3.86-3.81 (m, 3H, H5^{A},H4^{A}, H3^{A}), 3.70-3.58 (m, 3H, OCH*H* Linker, H3^{B}, H4^{B}), 3.44-3.16 (m, 5H, OC*H*H Linker, incl. H2^{A}: dd, J = 3.0 Hz, J = 9.5 Hz at 3.34, H6a^{B}, CH_2N Linker), 2.09 (s, 3H, CH_3 Ac), 2.08 (s, 3H, CH_3 Ac), 1.68-1.26 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 170.5, 169.4, 156.2,137.8, 137.5, 137.4, 136.7, 128.5, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.3, 97.8, 97.5, 78.8, 77.4, 77.0, 76.5, 75.1, 74.9, 73.6, 72.1, 69.2, 69.2, 68.2, 67.6, 67.4, 67.1, 67.0, 63.8, 62.9, 62.6, 62.2, 50.5, 50.2, 47.0, 46.1, 29.6, 29.0, 27.8, 27.4, 23.3, 20.9, 20.8. HRMS-MALDI: (M + Na$^+$) calcd. 940.4106, found 940.4123.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-levulinoyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-acetyl-2-deoxy-α-D-glucopyranoside** (**S22**): Disaccharide **S6 (**140 mg, 0.129 mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v/v) (0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S22** (84.7 mg, 60%). $[\alpha]_D^{25}$ +53.3 (*c* = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.11 (m, 20H, CH Aromatic), 5.12-5.1 (bd, 2H, *J* = 15.0 Hz, C*H*$_2$Cbz), 4.89 (bs, 1H, H2^B), 4.81-4.77 (m, 2H, H1^A, H1^B), 4.70-4.66 (m, 2H, 2 x C*H*HBn), 4.54 (d, 1H, *J* = 11.3 Hz, CH*H*Bn), 4.50 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.45 (bd, 1H, *J* = 6.9 Hz, NC*H*$_2$Bn), 4.34 (bd, 1H, *J* =12.2 Hz, H6a^A), 4.14-4.11 (m, 2H, H6b^A, H5^B), 3.83-3.73 (m, 3H, H4^A, H5^A, H3^A), 3.58-3.51 (m, 3H, OCH*H* Linker, H3^B, H4^B), 3.38-3.07 (m, 6H, OC*H*H Linker, H6a^B, NC*H*$_2$ Linker, H3^B, H6b^B), 2.70 (t, 2H, *J* = 5.5 Hz, C*H*$_2$ Lev), 2.53-2.47 (m, 3H, C*H*$_2$ Lev, O*H*), 2.1 (s, 3H, C*H*$_3$ Ac), 2.01 (s, 3H, C*H*$_3$ Lev), 1.61-1.15 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.3, 171.6, 170.6, 137.9, 137.6, 137.5, 128.5-127.3,97.7, 97.5, 78.8, 75.2, 75.0, 73.5, 72.2, 69.2, 68.2, 67.6, 67.5, 67.2, 67.0, 63.8, 63.0, 62.3, 50.6, 50.2, 47.0, 37.9, 29.7, 29.6,29.1, 28.0, 23.3, 20.9. HRMS-MALDI: (M + Na$^+$) calcd. 996.43682, found 996.4386.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyl)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-2-deoxy-α-D-glucopyranoside** (**S23**): Disaccharide **S7** (160 mg, 0.147 mmol) was dissolved in DCM:TFA:H_2O (10/1/0.1, v/v/v)

(0.06 M) and treated according to the general procedure for benzylidene acetal cleavage to give **S23** (110 mg, 75%). $[\alpha]_D^{24}$ +42 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.11 (bd, 2H, J = 16.0 Hz, CH_2Cbz), 4.90 (bs, 1H, H2^B), 4.80 (bd, 2H, J = 11.5 Hz, H1^A), 4.75 (bs, 1H, H1^B), 4.70-4.66 (m, C*H*HBn, C*H*HBn), 4.55-4.51 (m, 2H,CH*H*Bn, CH*H*Bn), 4.47-4.41(bd, 2H, J = 7.0 Hz, NCH_2Bn), 4.32(d, 1H, J = 12.0 Hz, H6a^A), 4.18 (bd, 1H, J = 12.0 Hz, H6b^A), 4.11 (t, 1H, J = 5.0 Hz, H5^B), 3.84-3.74 (m, 3H, H5^A, H4^A, H3^A), 3.68-3.50 (m, 3H, H3^B, OC*H*H Linker, H4^B), 3.38-3.16 (m, 4H, OCH*H* Linker, H2^A, CH_2N Linker), 3.12 (dd, 1H, J = 4.5 Hz, J = 12.0 Hz, H6b^B), 2.74-2.45 (m, 4H, 2 x CH_2 Lev), 2.10 (s, 3H, CH_3 Lev), 1.88 (s, 3H, CH_3 Ac), 1.60-1.16 (m, 6H, 3 x CH_2 Linker). HRMS-MALDI: (M + Na$^+$) calcd. 996.43682, found 996.4386.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**41**): Compound **S9** (0.29 g, 0.37 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **41** (230 mg, 76%, two steps). $[\alpha]_D^{25}$ +20.5 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H, CH Aromatic), 4.97 (m, 2H, H2^B, C*H*HBn), 4.83-4.78 (m, 2H, CH*H*Bn, C*H*HBn), 4.68 (d, 1H, J = 12.0 Hz, CH*H*Bn), 4.58 (d, 1H, J = 8.0 Hz, H1^B), 4.46 (d, 1H, J = 8.0 Hz, H1^A), 4.37 (dd, 1H, J = 2.5 Hz, J = 12.0 Hz, H6a^A), 4.12- 4.06 (m, 2H, H6b^A, H5^B), 3.91 (m, 1H, H4^B), 3.67 (m, 1H, H4^A), 3.63 (m, 1H, H3^B), 3.57 (s, 3H, CO_2CH_3), 3.49 (t, 1H, J = 9.0 Hz, H5^A), 3.37 (t, 1H, J = 10.0 Hz, H3^A),3.30 (t, 1H, J = 8.0 Hz, H2^A), 2.06 (s, 3H, CH_3 Ac), 1.99 (s, 3H, CH_3 Ac), 1.67-1.61 [m, 1H, C*H*$(CH_3)_2$], 0.88-0.86 [4s, 12H, C$(CH_3)_2$ and CH$(CH_3)_2$], 0.17-0.15 [2s, 6H, Si$(CH_3)_2$]. HRMS-MALDI: (M + Na$^+$) calcd. 824.3401, found 824.3415.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**42**): Compound **S10** (0.20 g, 0.24 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **42** (150 mg, 72%, two steps). $[\alpha]_D^{25}$ +4.7 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H, CH Aromatic), 4.98-4.94 (m, 2H, H2^B, C*H*HBn), 4.80 (d, 1H, *J* = 12.0 Hz, C*H*HBn), 4.77 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.72 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.58 (d, 1H, *J* = 8.5 Hz, H1^B), 4.48 (d, 1H, *J* = 8.0 Hz, H1^A), 4.32 (dd, 1H, *J* = 2.5 Hz, *J* = 11.5 Hz, H6a^A), 4.18 (dd, 1H, *J* = 6.5 Hz, *J* = 11.5 Hz, H6b^A), 3.91 (t, 1H, *J* = 9.5 Hz, H4^B), 3.71 (t, 1H, *J* = 8.5 Hz, H4^A), 3.64 (d, 1H, *J* = 10.0 Hz, H5^B), 3.58-3.52 (m, 1H, H5^A), 3.56 (s, 3H, CO_2CH_3), 3.50 (t, 1H, *J* = 9.0 Hz, H3^B), 3.38 (t, 1H, *J* = 8.5 Hz, H3^A), 3.32-3.29 (m, 1H, H2^A), 2.92 (bs, 1H, 4-O*H*), 2.78-2.74 (m, 1H, C*H*H Lev) 2.72-2.53 (m, 2H, CH_2 Lev), 2.43-2.37 (m, 1H, CH*H* Lev), 2.18 (s, 3H, CH_3 Lev), 2.00 (s, 3H, CH_3 Ac), 1.67-1.61 [m, 1H, $CH(CH_3)_2$], 0.88-0.86 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.16-0.15 [2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 171.3, 170.6, 169.2, 138.7, 138.1, 128.4, 128.2, 127.8, 127.3, 127.2, 101.1, 96.7, 81.3, 81.0, 78.3, 77.4, 77.0, 76.6, 74.8, 74.6, 74.1, 72.8, 72.5, 72.0, 68.6, 62.7, 52.6, 37.6, 33.9, 29.8, 29.7, 27.7, 24.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.2, -3.2. HRMS-MALDI: (M + Na^+) calcd. 880.3664, found 880.3683.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**43**): Compound **S11** (3.65 g, 4.40 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **43** (3.3 g, 88%, two steps). $[\alpha]_D^{24}$ +17.1

(c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H, CH Aromatic), 4.97 (m, 2H, H2^B, C*H*HBn), 4.82 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.73 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.68 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.640 (d, 1H, *J* = 8.0 Hz, H1^B), 4.46 (d, 1H, *J* = 7.5 Hz, H1^A), 4.32 (dd, 1H, *J* = 1.0 Hz, *J* = 10.5 Hz, H6a^A), 4.18 (dd, 1H, *J* = 5.0 Hz, *J* = 11.5 Hz, H6b^A), 3.93 (t, 1H, *J* = 9.5 Hz,H4^B), 3.85 (d, 1H, *J* = 9.5 Hz, H5^B), 3.78 (t, 1H, *J* = 9.0 Hz, H4^A), 3.63 (t, 1H, *J* = 9.0 Hz, H3^B), 3.54 (s, 3H, CO_2CH_3), 3.42-3.40 (m, 1H, H5^A), 3.35 (t, 1H, *J* = 10.0 Hz, H3^A), 3.30 (t, 1H, *J* = 7.5 Hz, H2^A), 3.02 (bs, 1H, 4-O*H*), 2.87-2.81 (m, 1H, C*H*H Lev) 2.72-2.49 (m, 3H, CH_2 Lev, CH*H* Lev), 2.18 (s, 3H, CH_3 Lev), 2.00 (s, 3H, CH_3 Ac), 1.67-1.61 [m, 1H, C*H*(CH_3)$_2$], 0.88-0.86 [4s, 12H, C(CH_3)$_2$, CH(CH_3)$_2$], 0.16-0.15 [2s, 6H, Si(CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.5, 172.3, 169.4, 169.4, 138.6, 138.2, 128.4, 128.1, 127.7, 127.6, 127.4, 127.3, 101.0, 96.7, 81.3, 80.9, 77.9, 77.4, 77.0, 76.6, 74.9, 74.5, 74.0, 72.6, 72.5, 72.1, 68,4, 62.5, 52.5, 37.8, 33.9, 29.8, 27.7, 24.7, 20.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI: (M + Na^+) calcd. 880.3664, found 880.3683.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**44**): Compound **S12** (0.297 g, 0.33 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **44** (217.2 mg, 71%, 2 steps). $[\alpha]_D^{25}$ -7.2 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 10H, CH Aromatic), 4.95-4.89 (m, 2H, H2^B, C*H*HBn), 4.74 (d, *J* = 12.0 Hz, 1H, CH*H*Bn), 4.63 (d, *J* = 12.0 Hz, 1H, C*H*HBn), 4.62 (d, *J* = 11.0 Hz, 1H, CH*H*Bn), 4.640 (d, *J* = 8.0 Hz, 1H, H1^B), 4.41 (d, *J* = 7.5 Hz, 1H, H1^A), 4.28 (dd, *J* = 2.0 Hz, *J* = 12.0 Hz, 1H, H6a^A), 4.21 (dd, *J* = 4.5 Hz, *J* = 12.0 Hz, 1H, H6b^A), 3.85 (bd, 1H, *J* = 3.5 Hz, H4^B, H5^B), 3.75 (t, 1H, *J* = 8.5 Hz, H4^A), 3.63-3.57 (m, 1H, H3^B), 3.52-3.48(m, 1H, H5^A), 3.46(s, 3H, CO$_2$C*H*$_3$), 3.29 (t, 1H, *J* = 8.0 Hz, H3^A), 3.25-3.21 (m, 1H, H2^A), 2.87 (bs, 1H, 4-O*H*), 2.81-2.41 (m, 8H, 4 xC*H*$_2$ Lev) 2.11 (s, 3H, C*H*$_3$ Lev), 2.08 (s, 3H, C*H*$_3$ Lev), 1.67-1.61 [m, 1H, C*H*(CH$_3$)$_2$], 0.88-0.86 [4s, 12H, C(C*H*$_3$)$_2$ and C(C*H*$_3$)$_2$], 0.16-0.15 [2s, 6H, Si(C*H*$_3$)$_2$]. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.6, 206.0, 172.4, 171.3, 169.5, 138.7, 138.3, 129.0, 128.3, 128.1, 127.6, 127.5, 127.2, 100.9, 96.7, 81.4, 80.9, 77.8, 77.4, 76.9, 76.5, 75.0, 74.5, 74.0, 72.8, 72.4, 72.1, 68.5, 62.7, 52.5, 37.8, 37.5, 33.9, 33.6, 31.9, 30.1, 29.8, 29.7, 29.6, 29.3, 27.8, 27.7, 26.6, 24.8, 23.1, 22.6, 19.9, 19.8, 18.4, 18.3, 14.0, -2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 936.3926, found 936.3956

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**53**): Compound **S13** (116 mg, 0.149 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **53** (63.7 mg, 54%, two steps). $[\alpha]_D^{25}$ +16.2 (*c* = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.24-7.13 (m, 10H, CH Aromatic), 4.93 (s, 1H, H1^B), 4.83 (bs, 1H, H5^B), 4.79 (bs, 1H, H2^B), 4.61 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.60 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.56 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.51 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.39-4.34 (m, 2H, H1^A, H6a^A), 4.99 (dd, 1H, *J* = 5.5 Hz, *J* = 12.0 Hz, H6b^A), 3.85 (bd, 1H, *J* =11.0 Hz, H4^B), 3.70 (t, 1H, *J* = 9.5 Hz, H4^A), 3.60 (bs, 1H, H3^B), 3.36(s, 3H, CO$_2$C*H*$_3$), 3.34-3.32 (m, 1H, H5^A), 3.22 (dd, 1H, *J* = 8.0 Hz, *J* = 10.0 Hz, H2^A), 3.14 (t, 1H, *J* = 10.0 Hz, H3^A),2.52 (d, 1H, *J* =11.5 Hz, 4-O*H*), 1.95 (s, 3H, C*H$_3$* Ac), 1.92 (s, 3H, C*H$_3$* Ac), 1.58-1.51 [m, 1H, C*H*(CH$_3$)$_2$], 0.77-0.75 [4s, 12H, C(C*H*$_3$)$_2$ and CH(C*H*$_3$)$_2$], 0.06-0.05 [2s, 6H Si(C*H*$_3$)$_2$]. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 173.8, 172.7, 172.5, 141.3, 140.6, 132.0, 131.8, 131.5, 131.4, 131.3, 131.1, 130.7, 130.6, 129.3, 101.2, 100.3, 84.3, 80.8, 80.6, 80.4, 79.9, 79.3, 78.2, 77.9, 77.7, 76.5, 75.6, 72.2, 71.7, 71.0, 70.4, 70.2, 65.7, 55.4, 37.2, 28.1, 24.3, 24.2, 24.1, 23.2, 23.1, 21.8, 21.7, -2.2, -3.2. HRMS-MALDI: (M + Na^+) calcd. 824.3401, found 824.3415.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**54**): Compound **S14** (71 mg, 0.086 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **54** (56.6 mg, 76%, two steps). $[\alpha]_D^{25}$ +24.3 (*c* = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$: δ 7.25-7.11 (m, 10H, CH Aromatic), 4.93 (s, 1H, H1^B), 4.81 (d, 1H,*J* = 1.7 Hz, H5^B), 4.79 (bs, 1H, H2^B), 4.62 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.59 (d, 1H, *J* = 11.4 Hz, C*H*HBn), 4.55 (d, 1H, *J* = 11.4Hz, CH*H*Bn), 4.51 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.39 (d, 1H, *J* = 7.7 Hz, H1^A), 4.34 (dd, 1H, *J* = 2.0 Hz, *J* = 11.9 Hz, H6a^A), 4.00 (dd, 1H, *J* = 4.8 Hz, *J* = 11.7 Hz, H6b^A), 3.86 (bd, 1H, *J* = 8.6, H4^B), 3.72 (t, 1H, *J* = 9.3 Hz, H4^A), 3.61 (bs, 1H, H3^B), 3.36 (s, 1H, $CO_2C\mathit{H}_3$), 3.33 (ddd,1H, *J* = 3.3 Hz, *J* = 5.7 Hz, *J* = 10.1 Hz, H5^A), 3.22 (dd, 1H, *J* = 7.7 Hz, *J* = 9.9 Hz, H2^A), 3.12 (t, 1H, *J* = 9.2 Hz, H3^A), 2.64 (dd, 2H, *J* = 2.7 Hz, *J* = 7.0 Hz, $C\mathit{H}_2$ Lev), 2.54 (d, 1H, *J* = 10.4 Hz, 4-O*H*), 2.44 (t, 1H, *J* = 7.0 Hz, $C\mathit{H}_2$ Lev), 2.05 (s, 3H, $C\mathit{H}_3$ Lev), 1.95(s, 3H, $C\mathit{H}_3$ Ac), 1.54-1.42 [m, 1H, $C\mathit{H}(CH_3)_2$], 0.77-0.75 [4s, 12H, $C(C\mathit{H}_3)_2$ and $CH(C\mathit{H}_3)_2$], 0.06-0.05 [2s, 6H, $Si(C\mathit{H}_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 171.3, 171.1, 170.5, 169.4, 138.0, 137.3, 128.4, 128.1, 128.0, 127.9, 127.4, 127.3, 97.9, 97.0, 77.4, 77.0, 76.6, 74.7, 74.6, 74.5, 73.2, 72.3, 68.9, 68.4, 67.6, 67.3, 62.3, 52.0, 37.8, 33.9, 29.6, 29.7, 27.9, 24.8, 22.7, 20.8, 19.9, 19.8, 18.4, 18.4, -2.2, -3.3. HRMS-MALDI: (M + Na^+) calcd. 880.3664, found 880.3683.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**55**): Compound **S15** (90 mg, 0.108 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **55** (56.5 mg, 60%, two steps). $[\alpha]_D^{25}$ +32.2 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.14 (m, 10H, CH Aromatic), 4.89 (s, 1H, H1^B), 4.83 (bs, 1H, H5^B), 4.80 (bs, 1H, H2^B), 4.61 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.56 (m, 2H, C*H*HBn, CH*H*Bn), 4.50 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.39-4.37 (m, 2H, H1^A, H6a^A), 4.00 (dd, 1H, *J* = 4.0 Hz, *J* = 11.0 Hz, H6b^A), 3.84 (bd, 1H, *J* = 8.0 Hz, H4^B), 3.71 (t, 1H, *J* = 9.5 Hz, H4^A), 3.60 (bs, 1H, H3^B), 3.36(s, 1H, CO_2CH_3), 3.33-3.30 (m, 1H, H5^A), 3.21 (t, 1H, *J* = 10.0 Hz, H2^A), 3.11 (t, 1H, *J* = 10.0 Hz, H3^A), 2.66-2.63 (m, 2H, CH_2 Lev), 2.53-2.47 (m, 3H, CH_2 Lev, 4-O*H*), 2.07 (s, 3H, CH_3 Lev), 1.97(s, 3H, CH_3 Ac), 1.54–1.52 [m, 1H, $CH(CH_3)_2$], 0.77-0.75 [4s, 12H, $C(CH_3)_2$and $CH(CH_3)_2$], 0.06-0.05 [2s, 6H , $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.4, 172.2, 169.4, 169.3, 138.0, 137.3, 128.5, 128.2, 128.1, 128.0, 127.5, 127.3, 97.8,97.0, 77.5, 77.0, 76.6, 74.6, 74.5, 74.3, 73.2, 72.2, 68.9, 68.3, 67.7, 67.0, 62.5, 52.0, 49.3, 37.8, 33.9, 29.8, 29.7, 29.3, 27.9, 24.8, 22.7, 21.0, 19.9, 19.8, 18.5, 18.4,-2.2, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 880.3664, found 880.3683.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**56**): Compound **S16** (50 mg, 0.056 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure to give **56** (27 mg, 53%, two steps). $[\alpha]_D^{25}$ -40.9 (*c* =1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.25 (m, 10H, CH Aromatic), 4.99 (s, 1H, H2^B), 4.91 (bs, 2H, H1^B, H5^B), 4.73 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.66 (bs, 2H, CH*H*Bn, C*H*HBn), 4.61 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.49 (d, 1H, *J* = 7.5 Hz, H1^A), 4.46 (dd, 1H, *J* = 2.0 Hz, *J* = 12.5 Hz, H6a^A), 4.11 (dd, 1H, *J* = 5.0 Hz, *J* = 12.5 Hz, H6b^A), 3.97 (bd, 1H, *J* = 9.0 Hz, H4^B), 3.85 (t, 1H, *J* = 9.5Hz, H4^A), 3.73 (t, 1H, *J* = 2.5 Hz, H3^B), 3.47 (s, 3H, CO_2CH_3), 3.45-3.44 (m, 1H, H5^A), 3.34-3.30 (m, 1H, H2^A), 3.22 (t, 1H, *J* = 9.0 Hz, H3^A), 2.80-2.73 [m, 4H, 2 x CH_2 Lev], 2.61-2.58 [m, 4H, 2 x CH_2 Lev], 2.19 (s, 3H, CH_3 Lev), 2.17 (s, 3H, CH_3 Lev), 1.67-1.63 [m, 1H, $CH(CH_3)_2$], 0.90-0.88 [4s, 12H, $C(CH_3)_2$, $CH(CH_3)_2$], 0.19-0.17 [2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.5, 206.3, 172.1, 171.3, 169.4, 138.0, 137.3, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.5, 127.3, 97.7, 97.0, 81.0, 77.4, 77.0, 76.6, 74.7, 74.5, 74.3, 72.3, 68.9, 68.4, 67.7, 67.3, 62.5, 51.9, 37.8, 37.8, 33.9, 33.7, 31.9, 30.1, 29.8, 29.7, 29.3, 27.9, 24.8, 19.9, 19.8, 18.4, 18.3, 14.1, -2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 936.3926, found 936.3956.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-α-D-glucopyranoside** (**17**): Compound **S17** (85 mg, 0.090 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography of the residue (toluene/EtOAc, 50/50, v/v) afforded **17** (57.4 mg, 66%, two steps). $[\alpha]_D^{25}$ +25.5 (*c* =1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.13 (m, 20H, CH Aromatic), 5.14-5.11 (m, 2H, CH_2 Cbz), 5.01 (d, 1H, *J* = 11.2 Hz, C*H*HBn), 4.94 (t, 1H, *J* = 8.7 Hz, H2^B), 4.78 (d, 1H, *J* = 11.8 Hz, C*H*HBn), 4.75 (bd, 1H, *J* = 12.0 Hz, H1^A), 4.69 (d, 1H, *J* = 11.2 Hz, C*H*HBn), 4.64 (d, 1H, *J* = 11.8 Hz, CH*H*Bn), 4.53 (d, 1H, *J* = 7.9Hz, H1^B), 4.45 (bd, 2H,*J* = 5.8HzNCH_2Bn), 4.33 (bd, 1H, *J* = 11.7 Hz, H6a^A), 4.10 (bm, 1H, H6$_b$^{A}), 3.90-3.86 (m, 2H, H4^B, H3^A) 3.72-3.71 (m, 2H, H4^A, H5^A), 3.61-3.59(bm, 2H,H5^B, OC*H*H Linker), 3.48 (s, 3H, CO_2CH_3), 3.45 (t, 1H, *J* = 9.3 Hz, H3^B), 3.36-3.17 (bm, 4H, OCH*H* Linker, C*H*$_2$N Linker), 3.02 (d, 1H, *J* = 2.4 Hz, 4-O*H*), 2.03-1.98 (2s, 6H, 2 x C*H*$_3$ Ac), 1.55-1.19 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 170.7, 169.6, 169.5, 138.8, 138.1, 128.8-127.5,101.5, 97.9, 81.6, 78.7, 78.2, 77.7, 77.5, 77.3, 76.9, 75.0, 74.9, 74.5, 72.8, 72.3, 68.8, 68.7, 67.4, 63.1, 62.5, 60.6, 52.9, 50.8, 50.5, 47.3, 46.4, 29.2, 28.1, 23.5, 21.3, 21.1, 21.0. HRMS-MALDI: (M + Na$^+$) calcd. 991.3952, found 991.3975.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-α-D-glucopyranoside** (**18**): Compound **S18** (35 mg, 0.035 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography of the residue (toluene/EtOAc, 50/50, v/v) afforded **18** (28 mg, 77%, two steps). $[\alpha]_D^{25}$ 20.3 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.24 (m, 20H, CH Aromatic), 5.16-5.11 (m, 2H, C*H*$_2$Cbz), 5.08 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 5.01 (m, 1H, H2^B), 4.82 (bd, *J* = 12.0 Hz, 1H,H1^A, C*H*HBn), 4.71-4.65 (m, 2H,CH*H*Bn, CH*H*Bn), 4.57 (d, 1H, *J* = 8.0 Hz, H1^B), 4.49 (bs, 2H, NC*H*$_2$Bn), 4.48 (dd, 1H, *J* = 2.0 Hz, *J* = 12.5 Hz, H6a^A), 4.28 (dd,1H, *J* = 4.5 Hz, *J* = 12.5 Hz, H6b^A), 3.96-3.81 (m, 3H, H3^A, H5^A, H4^B), 3.72 (t, 1H, *J* = 9.5 Hz, H5^B), 3.68-3.64 (m, 2H, H4^A OC*H*H Linker), 3.55-3.51 (m, 1H, H3^B), 3.51 (s, 3H, CO_2CH_3), 3.41-3.36 (m, 1H, OCH*H* Linker), 3.27-3.20 (m, 3H, H2^A, C*H*$_2$N Linker), 2.94 (s, 1H, 4-O*H*), 2.79-2.74 (m, 0.5H, C*H*H Lev), 2.71-2.61 (m, 1.5H, C*H*$_2$ Lev), 2.56-2.36 (m, 0.5H, C*H*H Lev), 2.18 (bs, 6H, C*H*$_3$ Ac, C*H*$_3$ Lev), 1.61-1.26 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 205.8, 171.3, 170.6, 169.2, 138.6, 138.1, 137.9, 128.4, 128.2, 127.8, 127.7, 127.7, 127.3, 101.2, 97.5, 81.4, 78.4, 78.0, 77.4, 76.9, 76.5, 74.8, 74.6, 74.1, 72.8, 72.0, 68.3, 68.1, 67.1, 62.8, 62.4, 52.6, 37.5, 37.3, 33.6, 33.3, 32.3, 31.9, 30.6, 30.1, 30.0, 29.6, 29.3, 28.9, 27.8, 27.7, 26.6, 26.3, 23.2, 23.1, 22.6, 22.6, 20.9, 14.1, 14.1. HRMS-MALDI: (M + Na^+) calcd. 1047.4215, found 1047.4223.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-*O*-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside** (**19**): Compound **S19** (1.79 g, 1.84 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography of the residue (toluene/EtOAc, 50/50, v/v) afforded **19** (1.5 g, 79%, two steps). $[\alpha]_D^{25}$ +47.3 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.18 (m, 20H, CH Aromatic), 5.19-5.13 (m, 2H, C*H*$_2$Cbz, C*H*HBn), 5.02 (t, 1H, *J* = 8.5 Hz, H2^B), 4.86-4.80 (m, 1H, H1^A, C*H*HBn), 4.71-4.65 (m, 3H, CH*H*Bn, CH*H*Bn, H1^B), 4.48 (bd, 2H, *J* = 6.5 Hz, NC*H*$_2$Bn), 4.36 (bd, 1H, *J* = 11.5 Hz, H6a^A), 4.23 (d, 1H, *J* = 12.0 Hz, H6b^A), 4.02 (d, 1H, *J* = 9.5 Hz, H5^B), 3.97-3.86 (m, 3H, H3^A, H4^A, H4^B), 3.76 (bs, 1H, H5^A), 3.69 (t, 1H, *J* = 9.0 Hz, H3^B), 3.64-3.56 (m, 1H, OC*H*H), 3.50 (s, 3H, CO_2CH_3), 3.42-3.19 (m, 4H, H2^A, C*H*$_2$N Linker, OCH*H* Linker), 2.92-2.86 (m, 1H, C*H*H Lev), 2.70-2.61 (m, 2H, C*H*$_2$ Lev), 2.51-2.46 (m, 2H, CH*H* Lev), 2.18 (s, 3H, C*H*$_3$ Lev), 2.01 (s, 3H, C*H*$_3$ Ac),1.61-1.56 (m, 2H, C*H*$_2$ Linker), 1.34-1.26 (m, 2H, C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 172.4, 169.6, 169.4, 138.6, 138.3, 137.9, 128.5, 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 127.3, 101.0, 97.7, 81.3, 78.2, 77.8, 77.4, 77.0, 76.6, 75.0, 74.5, 74.0, 72.5, 72.3, 68.6, 68.3, 67.1, 62.8, 62.2, 52.5, 50.5, 50.2, 47.0, 46.1, 37.8, 29.8, 28.9, 27.8, 23.2, 20.8. HRMS-MALDI: (M + Na^+) calcd. 1047.4215, found 1047.4223.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-*O*-2-*O*-levulinoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside** (**20**): Compound **S20** (100 mg, 0.097 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography of the residue (toluene/EtOAc, 50/50, v/v) afforded **20** (70 mg, 67%, two steps). $[\alpha]_D^{25}$ -18.4 (c =1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.26 (m, 20H, CH Aromatic), 5.19-5.15 (m, 2H, C*H*HBn, C*H*₂ Cbz), 5.02 (t, 1H, *J* = 8.0 Hz, H2^B), 4.83 (bd, 1H, *J* = 12.0 Hz, H1^A, C*H*HBn), 4.71-4.65 (m, 3H, CH*H*Bn, CH*H*Bn, H1^B), 4.48 (dd, 1H, *J* = 2.0 Hz, *J* = 12.5 Hz, H6a^A), 4.48 (bd, 2H, *J* = 8.0 Hz, NCH_2Bn), 4.28 (d, 1H, *J* = 11.0 Hz, H6b^A), 4.10 (d, 1H, *J* = 10.0 Hz, H5^B), 4.01 (bd, 1H, *J* = 8.5 Hz, H5^A), 3.96-3.89 (m, 3H, H3^A, H4^A, H4^B), 3.72 (t, 1H, *J* = 9.0 Hz, H3^B), 3.68-3.64 (m, 1H, OC*H*H Linker), 3.47 (s, 3H, CO_2CH_3), 3.39-3.19 (m, 4H, H2^A, CH_2N Linker, OCH*H* Linker), 2.92-2.79 (m, 2H, CH_2 Lev), 2.71-2.61 (m, 4H, 2 x CH_2 Lev), 2.56-2.36 (m, CH_2 Lev), 2.18 (s, 3H, CH_3 Lev), 2.11 (bd, 3H, *J* = 10.1 Hz, CH_3 Lev), 1.61-1.56 (m, 6H, 3 x CH_2 Linker. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.8, 205.8, 172.5, 169.7, 138.8, 138.4, 137.9, 136.8, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 127.5, 127.2, 101.0, 97.7, 81.4, 78.3, 77.9, 77.4, 77.0, 76.6, 75.2, 74.5, 74.0, 72.8, 72.3, 68.3, 68.1, 67.1, 62.8, 62.6, 52.4, 50.5, 50.2, 46.1, 37.9, 37.5, 29.8, 29.7, 29.6, 28.9, 27.8, 27.7, 23.2. HRMS-MALDI: (M + Na$^+$) calcd. 1103.4477, found 1103.4456.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-3-*O*-benzyl-2-*O*-acetyl)-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-α-D-glucopyranoside** (**21**): Compound **S21** (80 mg, 0.087 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography (toluene/EtOAc, 50/50, v/v) afforded **21** (70 mg, 83%, two steps).

$[\alpha]_D^{25}$ +98.3 (c = 1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36-7.26 (m, 20H, CH Aromatic), 5.17 (bd, 2H, J = 14.0 Hz, CH_2 Cbz), 5.07 (s, 1H, H1^B), 4.98-4.90 (m, 1H, H2^B, H5^B), 4.84 (bd, 2H, J = 14.5 Hz, H1^A), 4.74 (bd, 2H, J = 11.0 Hz, C*H*HBn, C*H*HBn), 4.66-4.62 (m, 2H, CH*H*Bn, CH*H*Bn), 4.49-4.47(m, 2H, NCH_2Bn, H6a^A), 4.22 (bd, 1H, J = 12.0 Hz, H6b^A), 3.95 (bs, 1H, H4^B), 3.86-3.82 (m, 3H, H4^A, H3^A), 3.71 (bs, 1H, H3^B), 3.65-3.52 (m, 2H, OC*H*H Linker, H5^A), 3.47 (s, 3H, CO_2CH_3), 3.40-3.18 (m, 4H incl.: d, J = 9.0 Hz at 3.27, H2^A, OCH*H* Linker, CH_2N Linker), 2.06 (s, 3H, CH_3 Ac), 2.07 (s, 3H, CH_3 Ac), 1.61-1.19 (m, 6H, 3 x CH_2 Linker). HRMS-MALDI: (M + Na$^+$) calcd. 991.3952, found 991.3975.

_N_-(Benzyl)-benzyloxycarbonyl-5-aminopentyl _O_-(methyl-3-_O_-benzyl-2-_O_-levulinoyl)-α-L-idopyranosyluronate)-(1→4)-_O_-2-azido-3-_O_-benzyl-2-deoxy-6-_O_-acetyl-α-D-glucopyranoside (**22**): Compound **S22** (84.7 mg, 0.087 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography (toluene/EtOAc, 9/1 to 1/1, v/v) afforded **22** (65.6 mg, 73%, two steps). $[\alpha]_D^{25}$ 21.1 (c = 1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.32-7.13 (m, 20H, CH Aromatic), 5.13 (bd, 2H, J = 13.2 Hz, CH_2 Cbz), 5.03 (s, 1H, H1^B), 4.90 (bs, 1H, H2^B), 4.83-4.79 (m, 2H, H5^B, H1^A), 4.72-4.70 (m, 2H, C*H*HBn, C*H*HBn), 4.61-4.57 (m, 2H, CH*H*Bn, CH*H*Bn), 4.46 (bd, 2H, J = 7.0 Hz, NCH_2Bn), 4.35 (bd, 1H, J = 12.5 Hz, H6a^A), 4.19 (bd, 1H, J = 12.5 Hz, H6b^A), 3.93 (bd, 1H, J = 9.2 Hz, H4^B), 3.86-3.78 (m, 3H, H4^A, H3^A, H5^A), 3.69 (bs, 1H, H3^B), 3.63-3.53 (m, 1H, OC*H*H Linker), 3.43 (s, 3H, CO_2CH_3), 3.40-3.18 (m, 4H incl.: dd, J = 3.5 Hz, J = 10.3 Hz at 3.27, H2^A, OCH*H* Linker, CH_2N Linker),2.69-2.63 (m, 4H, 2 x CH_2 Lev), 2.51-2.49 (m, 2H, 2 x CH_2 Lev), 2.05 (s, 3H, CH_3 Ac), 2.11 (s, 3H, CH_3 Lev), 1.61-1.19 (m, 6H, 3 x CH_2 Linker).^{13}CNMR(75.5 MHz, $CDCl_3$): δ 206.1, 172.3, 171.1, 170.6, 169.5, 156.1, 137.8, 137.8, 137.3, 136.8, 128.5, 128.4, 128.1, 128.1, 128.0, 127.8, 127.3, 127.3, 97.9, 97.6, 78.3, 77.5, 77.2, 77.0, 76.6, 75.0, 74.6, 74.3 72.3, 69.0, 68.7, 68.2, 67.5, 67.1, 63.3, 62.2, 60.3, 51.9, 50.5, 50.2, 47.0, 46.1, 37.7, 29.6, 29.0, 27.9, 27.4, 23.2, 21.0, 20.8, 14.1. HRMS-MALDI: (M + Na$^+$) calcd. 1047.4215, found 1047.4223.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-α-D-glucopyranoside** (**23**): Compound **S23** (263 mg, 0.211 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography of the residue (toluene/EtOAc 1/1 to1/2, v/v) afforded **23** (210 mg, 97%). $[\alpha]_D^{25}$ +23.4 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.19 (m, 20H, Aromatic), 5.23-5.15 (m, 2H, C*H*$_2$ Cbz), 5.04 (bs, 1H, H1^B), 4.96 (bs, 1H, H2^B), 4.92 (bs, 1H, H5^B), 4.89-4.83 (m, 1H, H1^A), 4.80-4.73 (m, 2H, C*H*HBn, C*H*HBn), 4.69-4.62 (m, 2H, CH*H*Bn, CH*H*Bn), 4.55-4.48 (bs, 2H, NC*H*$_2$Bn), 4.44 (dd, 1H, *J* = 1.5 Hz, *J* = 12.2 Hz, H6a^A), 4.24 (bd, 1H, H6b^A), 3.93 (bs, 1H, H4^B), 3.94-3.78 (m, 3H, H3^A, H4^A, H5^A), 3.74 (t, 1H, *J* = 2.5Hz, H3^B), 3.70-3.59 (m, 1H, OC*H*H Linker), 3.52- 3.18 (7H incl. CO_2CH_3: s, 3.48, H2^A: dd, 3.33, *J* = 3.3 Hz, *J* = 10.0Hz, OCH*H* Linker, C*H*$_2$N Linker), 2.82-2.75 (m, 2H, C*H*$_2$ Lev), 2.72-2.55 (m, 2H C*H*$_2$ Lev), 2.20 (s, 3H, C*H*$_3$ Lev), 2.10 (s, 3H, C*H*$_3$ Ac), 1.72-1.40 (m, 4H, C*H*$_2$ Linker), 1.40-1.20 (m , 2H, C*H*$_2$ Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 201.4172.3, 168.4 168.3, 156.6, 156.4, 136.9, 136.8 136.2, 127.5, 127.4, 127.2, 127.1, 126.9, 126.8, 126.4, 126.3, 96.8, 96.6, 77.3, 73.7, 73.4, 71.2, 68.0, 67.4, 67.2, 66.7, 66.1, 66.0, 62.4, 61.4, 51.0, 49.9, 46.8, 46.0, 36.8, 28.8, 28.0, 26.9, 22.3, 29.9. HRMS-MALDI: (M + Na$^+$) calcd. 1047.4215, found 1047.4223.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-(methyl 2-*O*-levulinoyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-α-D-glycopyranoside** (**24**): Compound **S24** (400 mg, 0.380 mmol) was subjected to TEMPO/BAIB mediated oxidation and esterification using diazomethane according to the general procedure. Silica gel chromatography (toluene/EtOAc 1/1, v/v) provided **24** (299 mg, 73%). $[\alpha]_D^{25}$ +28 (*c* = 1, $CHCl_3$); ^1H NMR (500MHz, $CDCl_3$): δ 7.40-7.15 (m, 20H, CH Aromatic), 5.18-5.12 (m, 2H, CH_2 Cbz), 4.99 (bs, 1H, H1^B), 4.92 (bs, 1H, H2^B), 4.86, 4.78 (m, 2H, H1^A, H5^B), 4.75-4.70 (m, 2H, C*H*HBn, C*H*HBn), 4.62-4.58 (m, 2H, CH*H*Bn, CH*H*Bn), 4.51-4.45 (m, 2H, NCH_2Bn), 4.39 (dd, 1H, *J* = 1.5 Hz, *J* = 12.3Hz, H6a^A), 4.20 (bd, 1H, *J* = 12.3 Hz, H6b^A), 3.94 (bd, 1H, *J* = 10.5 Hz, H4^B), 3.88 (t, 1H, *J* = 9.1Hz, H4^A), 3.85-3.74 (m, 2H, H3^A, H5^A), 3.71 (t, 1H, *J* = 2.7 Hz, H3^B), 3.68-3.54 (m, 1H, OC*H*H Linker), 3.45 (s, 3H, CO_2CH_3), 3.44 –3.17 (m, 3H, incl. H2^A: dd, 3.36, *J* = 3.5 Hz, *J* = 10.1 Hz, OC*H*H Linker), 2.80-2.50 (m, 8H, 4 x CH_2 Lev), 2.16 (s, 3H, CH_3 Lev), 2.14 (s, 3H, CH_3 Lev), 1.64-1.48 (m, 4H, CH_2 Linker), 1.38-1.24 (m, 2H, CH_2 Linker). ^{13}C NMR ($CDCl_3$): δ 206.6, 206.3, 172.2, 171.4, 169.4, 156.6, 156.1,137.9, 137.8, 137.2, 136.8, 128.5, 128.4, 128.1, 127.9, 127.8, 127.4, 127.3, 97.7, 97.5, 78.3, 74.5, 74.4, 72.3, 68.9, 68.5, 68.1, 67.6, 67.4, 67.1, 63.3, 62.4, 51.9, 50.5, 50.2, 47.0, 46.1, 37.8, 37.7, 29.8, 29.7, 28.0, 27.9, 23.2. HRMS-MALDI: (M + Na^+) calcd. 1103.4477, found 1103.4456.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**9**): Disaccharide **41** (63 mg, 0.078 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **9** (50 mg, 62%). $[\alpha]_D^{25}$ +34.3 (*c* = 1, $CHCl_3$); ^1H

NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 20H, CH Aromatic), 5.06-5.00 (m, 2H, H4^{B}, H2^{B}), 4.95 (d, 1H, *J* = 12.0, C*H*HBn), 4.82 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.66 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.62 (d, 1H, *J* = 8.0 Hz, H1^{B}), 4.53 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.46 (d, 1H, *J* = 7.5 Hz, H1^{A}), 4.42 (dd, 1H, *J* = 7.0 Hz, *J* = 10.5 Hz, C*H*H Fmoc), 4.37-4.31 (m, 2H, CH*H* Fmoc, H6b^{A}), 4.20 (t, 1H, *J* = 7.5 Hz, C*H* Fmoc), 4.08 (dd, 1H, *J* = 6.5 Hz, *J* = 11.5 Hz, H6a^{A}), 3.82 (d, 1H, H5^{B}), 3.71 (t, 1H, *J* = 9.0 Hz, H3^{B}), 3.64 (t, 1H, *J* = 9.5 Hz, H4^{A}), 3.46 (s, 1H, CO_2CH_3), 3.47-3.44 (m, 1H, H5^{A}), 3.39 (t, 1H,*J* = 9.5 Hz, H3^{A}), 3.30-3.26 (m, 1H, H2^{A}), 2.05 (s, 3H, CH_3 Ac), 1.92 (s, 3H, CH_3 Ac), 1.66-1.61 [m, 1H, $CH(CH_3)_2$], 0.88-0.86 [4s, 12H, $C(CH_3)_2$, $CH(CH_3)_2$], 0.16-0.15 [2s, 6H, $Si(CH_3)_2$]. HRMS-MALDI: (M + Na^+) calcd. 1046.4082, found 1046.4091.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-4-*O*-(9-O-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-cetyl-β-D-glucopyranoside (**10**): Disaccharide **42** (20 mg, 0.023 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography (toluene/EtOAc 95/5 to 90/10, v/v) afforded **10** (17 mg, 68%). $[\alpha]_D^{25}$-9.6 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.02(m, 20H, CH Aromatic), 4.93-4.87 (m, 2H, H4^{B}, H2^{B}), 4.81 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.63 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.47-4.46(m, 2H, C*H*HBn, H1^{B}), 4.42 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.33 (d, 1H, *J* = 8.0 Hz, H1^{A}), 4.27-4.22 (m, 2H, C*H*H Fmoc, H6a^{A}), 4.17-4.13 (m, 1H, CH*H*Fmoc), 4.04 (t, 1H, *J* = 7.0 Hz, C*H* Fmoc), 3.96 (dd, 1H, *J* = 6.5 Hz, *J* = 12.0 Hz, H6b^{A}), 3.68 (d, 1H, *J* = 10.0 Hz, H5^{B}), 3.57 (t, 1H, *J* = 9.5 Hz, H3^{B}), 3.52 (t, 1H, *J* = 8.5 Hz, H4^{A}), 3.42-3.39 (m, 1H, H5^{A}), 3.31 (s, 3H, CO_2CH_3), 3.21 (t, 1H, *J* = 8.5 Hz, H3^{A}), 3.13 (t, 1H, *J* = 8.0 Hz, H2^{A}), 2.61-2.55 (m, 1H, C*H*H

Lev), 2.50-2.36 (m, 2H, CH_2 Lev), 2.23-2.17 (m, 1H, CH*H* Lev), 1.99 (s, 3H, CH_3 Lev), 1.19 (s, 3H, CH_3 Ac), 1.51-1.45[m, 1H, C*H*(CH_3)$_2$], 0.72-0.70 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.014-0.00 [2s, 6H, Si(CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.0, 171.2, 170.6, 168.6, 167.0, 153.9, 143.2, 142.9, 141.3, 138.6, 137.5, 128.3, 128.2, 127.9, 127.7, 127.7, 127.3, 127.2, 125.1, 125.0, 120.1, 101.0, 96.7, 81.0, 79.4, 78.7, 77.4, 77.06, 76.6, 75.0, 74.8, 74.4, 72.5, 72.4, 68.7, 62.7, 61.0, 58.3, 52.6, 46.6, 37.5, 33.9, 29.8, 29.7, 27.6, 24.8, 20.8, 19.9, 19.8, 18.4, 18.3, -2.2, -3.2. HRMS-MALDI: (M + Na^+) calcd. 1102.4344, found 1102.4363.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside) (**11**): Disaccharide **43** (30 mg, 0.033 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography of the residue (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **11** (30 mg, 81%). $[\alpha]_D^{25}$ +14.2 (*c* = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.02. (m, 20H, CH Aromatic), 4.93-4.87 (m, 3H, H4^B, H2^B, C*H*HBn), 4.60 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.55 (d, 1H, *J* = 8.0 Hz, H1^B),4.51 (d, 1H, *J* = 11.5 Hz, C*H*HBn), 4.40 (d, 1H, *J* = 12.0 Hz, CH*H*Bn), 4.30 (d, 1H, *J* = 7.5 Hz, H1^A), 4.25 (dd, 1H, *J* = 7.0 Hz, *J* = 10.5 Hz, C*H*H Fmoc), 4.16-4.13 (m, 2H, CH*H* Fmoc, H6a^A), 4.06-4.00 (m, 2H, H6b^A, C*H* Fmoc), 3.95-3.86 (m, 1H, H5^B), 3.73 (t, 1H, *J* = 9.5 Hz, H3^B), 3.60 (t, 1H, *J* = 9.5 Hz, H4^A),3.30 (s, 3H, CO_2CH_3), 3.26-3.24 (m, 1H, H5^A), 3.21 (t, 1H, *J* = 9.0 Hz, H3^A), 3.12 (t, 1H, *J* = 8.0 Hz, H2^A),2.72-2.66 (m, 1H, C*H*H Lev), 2.58-2.52 (m, 1H, CH*H* Lev), 2.49-2.42 (m, 1H, C*H*H Lev), 2.39-2.33 (m, 1H, CH*H* Lev), 2.19 (s, 3H, CH_3 Lev), 2.04 (s, 3H, CH_3 Ac), 1.67-1.61 [m, 1H, C*H*(CH_3)$_2$], 0.88-0.86 [4s, 12H, C(CH_3)$_2$ and CH(CH_3)$_2$], 0.16-0.15 [2s, 6H, Si (CH_3)$_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.5, 172.4, 169.2, 167.2, 154.0, 143.3, 143.0, 141.2, 138.6, 137.6, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.3, 127.1, 125.1, 125.0, 120.0, 100.9, 96.8, 80.8, 79.4, 78.3, 77.4, 77.0, 76.6, 75.2, 75.0, 74.3, 72.5, 72.4, 72.3, 70.3, 68.6, 62.4, 52.6, 46.6, 37.9, 33.9, 29.8, 29.7, 27.8, 24.8, 20.7, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI: (M + Na$^+$) calcd. 1102.4344, found 1102.4363.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**12**): Disaccharide **44** (40 mg, 0.043 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography of the residue (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **12** (40 mg, 82%). $[\alpha]_D^{25}$ +15.5 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.20 (m, 25H, CH Aromatic), 5.10-5.04 (m, 3H, H4^B, H2^B, C*H*HBn), 4.74-4.71(m, 2H, CH*H*Bn, H1^B), 4.66 (d, *J* = 11.5 Hz, 1H, C*H*HBn), 4.60 (d, *J* = 11.5 Hz, 1H, CH*H*Bn), 4.47 (d, *J* = 7.5 Hz, 1H, H1^A), 4.40 (dd, *J* = 7.0 Hz, *J* = 10.5 Hz, 1H, H6a^A), 4.34 (dd, *J* = 1.5 Hz, *J* = 11.5 Hz, 1H, H6b^A), 4.30-4.26 (m, 2H, C*H*H Fmoc, CH*H* Fmoc), 4.20 (t, 1H, *J* = 7.5 Hz, C*H* Fmoc), 3.14 (d, 1H, *J* = 10.0 Hz, H5^B), 3.89 (t, 1H, *J* = 9.5 Hz, H3^B), 3.76 (t, 1H, *J* = 8.5 Hz, H4^A), 3.42-3.40 (m, 1H, H5^A), 3.46 (s, 3H, $CO_2C\mathit{H}_3$), 3.37 (t, 1H, *J* = 9.5 Hz, H3^A), 3.27 (t, 1H, *J* = 8.0 Hz, H2^A), 2.88-2.49 (m, 8H, 4 x $C\mathit{H}_2$ Lev) 2.21 (s, 3H, $C\mathit{H}_3$ Lev), 1.15 (s, 3H, $C\mathit{H}_3$ Lev), 1.66-1.61 [m, 1H, $C\mathit{H}(CH_3)_2$], 0.88-0.86 [4s, 12H, $C(C\mathit{H}_3)_2$ and $CH(C\mathit{H}_3)_2$], 0.16-0.15 [2s, 6H, Si $(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.6, 206.0, 172.5, 171.2, 167.3, 154.0, 143.3, 143.0, 141.2, 138.7, 137.8, 128.5, 128.2, 128.1, 127.9, 127.6, 127.5, 127.3, 127.1, 126.2, 126.1, 125.8, 125.1, 125.0, 120.0, 100.8 , 96.8, 80.9, 79.5, 78.2, 77.9, 77.4, 77.0, 76.6, 75.1, 74.4, 72.7, 72.3, 72.2, 70.3, 68.6, 67.3, 62.7, 62.6, 52.5, 46.5, 37.5, 33.9, 29.7, 27.9, 27.6, 24.8, 19.9, 19.8, 18.4, 18.3, -2.1, -3.2. HRMS-MALDI: (M + Na^+) calcd. 1135.4709, found 1135.4715.

Dimethylthexylsilyl *O*-(methyl-2-*O*-acetyl-3-*O*-benzyl4-*O*-(9-fluorenylmethoxycarbonyl) -α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-α-D-glucopyranoside (**13**): Disaccharide **53** (19.3 mg, 0.023 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography (Toluene/EtOAc, 95/5 to 90/10) afforded **13** (18 mg, 76%). $[\alpha]_D^{25}$ -32.4 (*c* = 0.7, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.74-7.73 (m, 2H, CH Aromatic), 7.55-7.54 (m, 2H,CH Aromatic), 7.39-7.21 (m, 25H, CH Aromatic), 5.13 (bs, 1H, $H1^B$), 4.99-4.98 (m, 2H, $H5^B$, $H4^B$), 4.85 (bs, 1H, $H2^B$), 4.73-4.69 (m, C*H*HBn, C*H*HBn, CH*H*Bn), 4.61 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.53-4.48 (m, 2H, $H1^A$, $H6a^A$), 4.42 (dd, 1H, *J* = 7.3 Hz, *J* = 10.4 Hz, C*H*H Fmoc), 4.33 (dd, 1H, *J* = 7.3 Hz *J* = 10.4 Hz, CH*H* Fmoc), 4.19 (t, 1H, *J* = 7.3 Hz, C*H* Fmoc), 4.12 (dd, 1H, *J* = 5.3 Hz, *J* = 12.0 Hz, $H6_b{}^A$), 3.86-3.83 (m, 2H, $H3^B$, $H4^A$), 3.45-3.44 (m, 4H incl. s at 3.44 : CO_2CH_3, $H5^A$), 3.33 (t, 1H, *J* = 7.8 Hz, *J* = 9.8 Hz, $H2^A$), 3.23 (t, 1H, *J* = 9.3 Hz, *J* = 9.6 Hz, $H3^A$), 2.06-1.96 (s, 6H, CH_3 Ac), 1.65-1.53 [m, 1H, $CH(CH_3)_2$], 0.88-0.75 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.17-0.16 [2s, 6H,$Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.5, 169.9, 168.3, 154.2, 143.2, 143.0, 141.3, 141.3, 137.9, 137.2, 128.5, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 127.1, 125.1, 125.0, 120.1, 97.5, 97.0, 80.9, 80.6, 77.4, 77.2, 77.0, 76.6, 74.7, 73.3, 72.8, 72.8, 72.6, 71.2, 70.2, 68.9, 67.3, 66.8, 62.2, 52.2, 46.6, 33.9, 29.7, 24.8, 2 20.8, 20.8, 19.9, 19.8, 18.5, 18.3,-2.2, -3.3. HRMS-MALDI: (M + Na^+) calcd. 1046.4082, found 1046.4091.

Dimethylthexylsilyl *O*-(methyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-2-*O*-levulinoyl-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-acetyl-β-D-glucopyranoside (**14**): Disaccharide **54** (15 mg, 0.017 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography of the residue (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **14** (16.9 mg, 90%). $[\alpha]_D^{25}$ –16.1 (*c* = 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.72 (m, 2H, CH Aromatic), 7.55-7.54 (m, 2H,CH Aromatic), 7.39-7.20 (m, 24H, CH Aromatic), 5.10 (bs, 1H, H1^B), 4.99 (d, 1H, *J* = 3.0 Hz, *J* = 4.0 Hz, H4^B), 4.97 (t, 1H, *J* = 3.0 Hz, H5^B), 4.86 (t, 1H, *J* = 2.3 Hz, H2^B), 4.72 (d, 1H, *J* = 11.3 Hz, C*H*H*Bn*), 4.70-4.67 (m, 2H, C*H*HBn*,* CH*H*Bn), 4.60 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.50-4.46 (m, 2H, H1^A, H6a^A), 4.45 (dd, 1H, *J* = 7.3 Hz, *J* = 10.5 Hz, C*H*H Fmoc), 4.35 (dd, 1H, *J* = 7.3 Hz, *J* = 10.5 Hz, CH*H* Fmoc), 4.19 (t, 1H, *J* = 7.3 Hz, C*H* Fmoc), 4.12 (dd, 1H, *J* = 5.0 Hz, *J* = 12.1 Hz, H6b^A), 3.88-3.84 (m, 2H, H3^B, H4^A), 3.46 (ddd, 1H, *J* = 2.2 Hz, *J* = 4.8 Hz, *J* = 11.9 Hz, H5^A), 3.42 (s, 3H, CO_2CH_3), 3.32 (dd, 1H, *J* = 7.6 Hz, *J* = 9.9 Hz, H2^A), 3.22 (t, 1H, *J* = 9.3 Hz, H3^A), 2.81-2.54 (m, 2H, CH_2 Lev), 2.55-2.40 (m, 3H, CH_2 Lev), 2.07 (s, 3H, CH_3 Lev), 2.04 (s, 3H, CH_3 Ac),1.64-1.42 [m, 1H, $CH(CH_3)_2$], 0.88-0.85 [4s, 12H,$C(CH_3)_2$ and $CH(CH_3)_2$], 0.12-0.11 (2s, 6H, $Si(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 171.7, 170.6, 168.3, 154.3, 143.2, 143.1, 141.3, 141.3, 137.9, 137.3, 128.4, 128.2, 128.0, 127.9, 127.5, 127.4, 127.12, 125.1, 125.0, 124.3, 120.1, 97.5, 97.0, 80.9, 77.4,77.0, 76.6, 74.8, 74.7, 73.2, 72.9, 72.7, 71.2, 70.1, 68.9, 67.3, 66.8, 62.3, 52.2, 46.6, 37.6, 33.9, 29.5, 27.9, 24.8, 20.8, 20.9, 19.9, 19.8, 18.4, 18.5, 18.3, -2.2, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 1102.4344, found 1102.4363.

Dimethylthexylsilyl *O*-(methyl 2-*O*-acetyl-3-*O*-benzyl4-*O*-(9-fluorenylmethoxycarbonyl)-β-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levylinyl-β-D-

glucopyranoside (**15**): Disaccharide **55** (56.5 mg, 0.065 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography of the residue (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **15** (51.4 mg, 73%). $[\alpha]_D^{25}$ +13 (*c* = 1.5, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74-7.73 (m, 2H, C*H* Aromatic), 7.54-7.53 (m, 2H,C*H*Aromatic), 7.28-7.08 (m, 25H, *CH* Aromatic), 5.07 (bs, 1H, H1^B), 4.99 (d, 1H, *J* = 2.6 Hz, H5^B), 4.97 (t, 1H, *J* = 3.2 Hz, H4^B), 4.84 (bs, 1H, H2^B), 4.72 (d, 1H, *J* =11.3 Hz, C*H*HBn), 4.69 (d, 1H, *J* = 11.3 Hz,CH*H*Bn), 4.66 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.60 (d, 1H, *J* = 11.0 Hz, CH*H*Bn), 4.55 (dd, 1H, *J* = 2.0 Hz, *J* = 12.0 Hz, H6a^A), 4.49 (d, 1H, *J* = 7.3 Hz, H1^A), 4.41 (dd, 1H, 7.3 Hz, 10.4Hz, C*H*H Fmoc), 4.32 (dd, 1H, *J* = 7.3 Hz, *J* = 10.4 Hz, CH*H* Fmoc), 4.18 (t, 1H, *J* = 7.3 Hz, C*H* Fmoc), 4.08 (dd, 1H, *J* = 4.9 Hz, *J* = 12.0 Hz, H6b^A), 3.87-3.84 (m, 2H, H3^B, H4^A), 3.46-3.43 (m, 4H incl. s at 3.43: CO$_2$C*H*$_3$’ H5^A), 3.43 (dd, 1H, *J* = 7.8 Hz, *J* = 9.9 Hz , H2^A), 3.11 (t, 1H, *J* = 9.3 Hz, H3^A), 2.81-2.42 (m, 1H, C*H*$_2$ Lev),2.72-2.(m, 1H, C*H*$_2$ Lev), 2.54-(m, 2H,C*H*$_2$ Lev), 2.13 (s, 3H, C*H*$_3$ Lev), 1.94 (s, 3H, C*H*$_3$ Ac),1.60-1.52 [m, 1H, C*H*(CH$_3$)$_2$], 0.84-0.81 [4s, 12H, C(C*H*$_3$)$_2$ and CH(C*H*$_3$)$_2$], 0.12-0.11 [2s, 6H, Si(C*H*$_3$)$_2$]. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.6, 172.1, 169.9, 168.3, 154.2, 143.2,143.0, 141.3, 141.3, 137.9, 137.1, 128.5, 128.2, 128.1, 128.0, 127.9, 127.5, 127.4, 127.1, 127.0, 125.0, 124.9, 120.1, 97.3, 97.0, 80.9, 77.4,77.0, 76.6, 74.8, 74.1, 73.2, 72.8, 72.7, 71.2, 70.1, 68.9, 67.1, 66.6, 62.4, 52.1, 46.6, 37.9, 33.9, 29.7, 29.6, 28.0, 24.8, 20.8, 20.8, 19.9, 19.8, 18.4, 18.3,-2.2, -3.3. HRMS-MALDI: (M + Na$^+$) calcd. 1102.4344, found 1102.4363.

Dimethylthexylsilyl *O*-(methyl-2-*O*-levulinoyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-β-D-glucopyranoside (**16**): Compound **56** (20 mg, 0.0218 mmol) was prepared according to the general procedure for synthesis of Fmoc protected disaccharides. Silica gel chromatography of the residue (toluene/EtOAc, 95/5 to 90/10, v/v) afforded **16** (17 mg, 68%). $[\alpha]_D^{25}$ +17 (c = 1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.75-7.19 (m, 25H, CH Aromatic), 5.04 (bs, 1H, $H5^B$), 4.98 (bs, 2H, $H2^B$, $H1^B$), 4.86 (bs, 2H, $H4^B$), 4.73 (d, 1H, *J* = 11.0 Hz, C*H*HBn), 4.69 (d, 1H, *J* = 11.5 Hz, CH*H*Bn), 4.66 (d, 1H, *J* = 11.0, C*H*HBn), 4.58 (d, 1H, *J* = 10.5 Hz, CH*H*Bn), 4.54 (dd, 1H, *J* = 2.0 Hz, *J* = 12.0 Hz, $H6a^A$), 4.50 (d, 1H, *J* = 8.0 Hz, $H1^A$), 4.45 (dd, 1H, *J* = 7.5 Hz, *J* = 10.5 Hz, C*H*H Fmoc), 4.37 (dd, 1H, *J* = 7.5 Hz, *J* = 10.5 Hz, CH*H* Fmoc), 4.20 (t, 1H, *J* = 7.0 Hz, C*H* Fmoc), 4.11 (dd, 1H, *J* = 4.5 Hz, *J* = 12.0 Hz, $H6b^A$), 3.911-3.87 (m, 2H, $H3^B$, $H4^A$), 3.48-3.45 (m, 1H, $H5^A$), 3.43 (s, 3H, CO_2CH_3) 3.33 (dd, 1H, *J* = 7.5 Hz, *J* = 10.0 Hz, $H2^A$), 3.22 (t, 1H, *J* = 9.5 Hz, $H3^A$), 2.86-2.70 (m, 3H, CH_2 Lev, C*H*H Lev), 2.61-2.48 (m, 5H, 2 x CH_2 Lev, CH*H* Lev), 2.18 (s, 3H, CH_3 Lev), 2.06 (s, 3H, CH_3 Lev), 1.68-1.60 [m, 1H, $CH(CH_3)_2$], 0.90-0.88 [4s, 12H, $C(CH_3)_2$ and $CH(CH_3)_2$], 0.19-0.17 [2s, 6H, Si $(CH_3)_2$]. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 206.3, 172.1, 171.7, 168.3, 154.2, 143.2, 141.3, 137.9, 137.2, 128.4, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 127.1, 125.1, 125.0, 120.0, 97.1, 97.0, 80.9, 77.4, 77.0, 76.6, 74.8, 74.0, 73.1, 72.9, 72.7, 71.2, 70.1, 68.9, 67.1, 66.5, 62.5, 52.1, 46.6, 37.9, 37.6, 33.9, 33.7, 31.9, 30.1, 29.7, 29.5, 29.3, 28.1, 27.9, 24.8, 22.7, 19.9, 19.8, 18.4, 18.3, 14.1, 14.1, -2.1, 3.2. HRMS-MALDI: ($M + Na^+$) calcd. 1135.4709, found 1135.4715.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)]-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside** (**70**): Glycosylation of disaccharide acceptor **19** (93.0 mg, 0.086 mmol) with disaccharide donor **47** (73.4 mg, 0.072 mmol) according to the general procedure for preparation of tetrasaccharides followed by silica gel chromatography (toluene/EtOAc, 60/40, v/v) provided tetrasaccharide **71** (85 mg, 61%). $[\alpha]_D^{25}$ +27.8 (*c* = 0.93, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.75-7.73 (m, 2H, CH Aromatic), 7.56-7.53 (m, 2H, CH Aromatic), 7.41-7.17(m, 34H, CH Aromatics), 5.35 (d, 1H, *J* = 3.6 Hz, $H1^C$), 5.21 (d, 1H, *J* = 11.4 Hz, C*H*HBn), 5.16 (bd, 2H, *J* = 15.0 Hz, CH_2 Cbz), 5.10-5.05 (m, 3H, $H2^B$, $H2^D$, $H4^D$), 4.80-4.77 (m, 2H, $H1^A$, CH*H*Bn), 4.74 (d, 1H, *J* = 7.9 Hz, $H1^B$), 4.73 (d,1H, *J* = 7.6 Hz, $H1^D$), 4.67-4.54 (m, 6H, 3 x CH_2Bn), 4.47(m, 2H, NCH_2Bn), 4.41-4.34 (m, 4H, C*H*H Fmoc, $H6a^A$, $H6a^C$, $H5^D$), 4.27 (dd, 1H, *J* = 7.6 Hz, *J* = 10.4 Hz, CH*H* Fmoc), 4.20-4.12 (m, 5H, C*H* Fmoc, $H6b^A$, $H6b^C$, $H4^B$, $H5^B$), 3.98 (t, 1H, *J* = 9.5 Hz, $H3^B$), 3.94 (t, 1H, *J* = 9.0 Hz, $H3^D$), 3.92-3.83 (m, 3H, $H4^A$, $H4^C$, $H3^A$), 3.72-3.68 (m, 3H, $H5^A$, $H3^A$, OC*H*H Linker), 3.59-3.55 (bm, 2H, OCH*H* Linker, $H5^C$), 3.44 (s, 3H, CO_2CH_3), 3.42 (s, 3H, CO_2CH_3), 3.27-3.19 (m, 4H incl. H2: dd, *J* = 3.6 Hz, *J* = 10.3 Hz at 3.25, $H2^A$, CH_2N Linker), 2.97-2.91 (m, 2H, 2 x CH_2 Lev), 2.76-2.56 (m, 4H, 2 x CH_2 Lev), 2.48-2.37 (m, 2H, CH_2 Lev) , 2.20, 2.19, 2.00, 1.98 (4s, 12H, 2 x CH_3 Ac, 2 x CH_3 Lev), 1.58-1.24 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.1, 205.8, 172.3, 171.7, 171.5, 168.2, 168.3, 167.4, 166.5, 166.4, 153.1, 153.0, 142.7, 142.6, 142.4, 141.7, 141.6, 141.4, 140.3 128.7-127.5, 125.4, 125.3, 120.3, 101.4 ($C1^D$), 101.0 ($C1^B$), 98.1 ($C1^A$), 97.5 ($C1^C$), 79.7, 78.6, 78.4, 78.0, 77.7, 75.7, 75.6, 75.0, 74.7, 74.4, 73.3, 72.7, 72.6, 70.5, 69.3, 68.9, 68.7, 67.4, 63.0, 62.3, 61.8, 52.8, 50.7, 50.6, 38.2, 30.0, 29.2, 28.2, 23.5, 21.0, 20.9. HRMS-MALDI: (M + Na^+) calcd. 1966.7373, found 1943.7335.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-(methyl-2-*O*-acetyl-3-*O*-benzyl-α-L-**

idopyranosyluronate)]-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside (**71**): Glycosylation of disaccharide acceptor **23** (112 mg, 0.103 mmol) with disaccharide donor **47** (127 mg, 0.124 mmol) according to the general procedure for preparation of tetrasaccharides followed by silica gel chromatography (hexane/EtOAc, 60/40, v/v) provided tetrasaccharide **71** (125 mg, 62%). $[\alpha]_D^{25}$ +26 (*c* = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.73-7.71(m, 2H, CH Aromatic), 7.55-7.50 (m, 2H, CH Aromatic), 7.42-7.14 (m, 34H, CH Aromatics), 5.23-5.18 (m, 2H, H1^B, C*H*HBn), 5.18-5.13 (m, 2H, CH_2 Cbz), 5.11-5.04 (m, 2H, H2^D, H4^D), 4.93-4.89 (m, 2H, H1^C, H2^B), 4.83-4.77 (m, 2H, CH_2Bn, H1^A), 4.73 (d, 1H, *J* = 8.1 Hz, H1^D), 4.55-4.70 (m, 6H, 2 x CH_2Bn, CH*H*Bn, H5^B at 4.61), 4.51- 4.46 (m, 2H, NCH_2Bn), 4.43-4.37 (m, 5H, CH_2 Fmoc, H6a^A, H6a^C, H5^D at 4.28), 4.21-4.14 (m, 3H, 2 x H6, C*H* Fmoc), 3.99-3.94 (m, 2H, H4^B, H3^D), 3.92-3.86 (m, 2H, H4^C, H3^B), 3.83-3.75 (m, 3H, H3^A, H5^A, H5^C), 3.67-3.57 (m, 2H, incl. OC*H*H Link, H3^C: dd at 3.65 *J* = 8.7 Hz, *J* = 10.5 Hz), 3.52 and 3.43 (2s, 6H, 2 x CO$_2$CH_3), 3.43-3.17 (m, 5H, incl. H2^A, H2^C: dd at 3.23 *J* = 3.5 Hz, *J* = 10.5 Hz, OCH*H* Linker, CH_2N Linker), 2.30-3.00 (m, 8H, 4 x CH_2 Lev), 2.20-1.96 (4s, 12H, 2 x CH_3 Ac, 2 x CH_3 Lev), 1.72-1.40 (m, 4H, 2 x CH_2 Linker), 1.40-1.20 (m , 2H, CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.8, 206.3, 172.5, 172.3, 170.0, 169.6, 169.0, 167.4, 154.0, 143.3, 143.0, 141.3, 141.2, 138.1, 138.0, 137.9, 137.7, 137.4, 128.5-127.1, 125.1, 125.0, 120.0, 100.5 (C1^B), 98.0 (C1^C), 97.5 (C1^A), 97.4 (C1^D), 79.3, 78.2, 77.6, 77.2, 75.8, 75.4, 75.3, 74.7, 74.3, 74.2, 73.5, 72.9, 72.4, 72.8, 70.3, 69.7, 69.1, 69.0, 68.2, 67.0. HRMS-MALDI: (M + Na$^+$) calcd. 1966.7373, found 1966.7442.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-α-L-idopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-**

deozy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)]-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside (**72**): Glycosylation of disaccharide acceptor **19** (90 mg, 0.083 mmol) with donor **59** (107 mg, 0.100 mmol) was performed according to the general procedure for preparation of tetrasaccharides followed by chromatography (toluene/EtOAc, 75/25, v/v) providing tetrasaccharide **72** (104 mg, 64%). $[\alpha]_D^{25}$ +19 (c = 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.70 (m, 2H, CH Aromatics), 7.54-7.50 (m, 2H, CH Aromatics), 7.42-7.14 (m, 36 H, CH Aromatics), 5.36 (d, 1H, J = 3.6 Hz, H1^C), 5.19-5.13 (m, 2H, CH_2 Cbz,), 5.13-5.08 (m, 3H, H1^D, H2^B, C*H*HBn), 4.94 (t, 1H, J = 4.0 Hz, H4^D), 4.86-4.82 (m, 3H, H2^D, H5^D, C*H*HBn), 4.82-4.76 (m, 1H, H1^A), 4.75-4.58 (m, 7H, 2 C*H*HBn, 4 x CH*H*Bn, and H1^B at 4.71), 4.51-4.45 (m, 2H, CH_2NBn), 4.45-4.38 (m, 2H, H6a^C, C*H*H Fmoc), 4.38-4.32 (m, 2H, H6a^A, CH*H* Fmoc), 4.23-4.16 (m, 4H, CH_2C*H* Fmoc, H6b^A, H4^B, H5^B), 4.10 (dd, 1H, J = 11.2 Hz, J = 3.3 Hz, H6b^C), 3.95-3.91 (m, 1H, H3^B), 3.90-3.82 (m, 4H, H3^A, H3^B, H3^D, H4^C), 3.76-3.70 (m, 1H, H5^A), 3.67 (dd, 1H, J = 9.1 Hz, J = 9.0 Hz, H3^C), 3.64-3.56 (m, 2H, H5^C, OC*H*H Linker), 3.48 (s, 3H, CO_2CH_3), 3.42-3.16 (m, 8H, incl. CO_2CH_3: s at 3.42, H2^C: dd J = 3.8 Hz, J = 10.3 Hz at 3.31, OCH*H* Linker, CH_2N Linker, H2^A), 2.80-2.45 (m, 8H, 4 x CH_2 Lev), 2.20-1.95 (4s, 12H, 2 x CH_3 Ac, 2 x CH_3 Lev), 1.74-1.44 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.7, 206.6, 171.5, 172.1, 171.4, 170.8, 169.8, 169.2, 168.4, 168.1, 154.1, 143.1, 142.9, 141.2, 138.3, 137.8, 137.6, 137.5, 137.1, 136.8, 128.5-127.0, 125.0, 124.9, 120.0, 101.0 (C1^B), 97.7 (C1^D), 97.4 (C1^B), 97.2 (C1^A), 81.9, 78.3, 78.1, 77.7, 77.2, 75.5, 75.3, 74.8, 74.5, 74.4, 74.3, 73.0, 72.0, 71.6, 70.8, 70.1, 69.5, 68.6, 68.3, 68.1, 67.3, 67.1, 63.4, 62.8, 62.0, 61.4, 55.7, 52.4, 52.1, 50.5, 50.2, 47.0, 46.5, 46.0, 37.9, 37.5, 34.8, 29.7, 29.6, 25.4, 25.2, 24.8, 24.6, 23.2. HRMS-MALDI: (M + Na$^+$) calcd. 1966.7373, found 1966.7372.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-α-L-idopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside (73)**: Glycosylation of disaccharide acceptor **23 (**123.4mg, 0.1140 mmol) with donor **59** (97.4 mg, 0.0950 mmol) was performed according to the general procedure for preparation of tetrasaccharides followed by silica chromatography (hexanes/EtOAc, 60/40 to 50/50, v/v) providing tetrasaccharide **73** (114.6 mg, 62%). $[\alpha]_D^{23}$ +30.4 (*c* = 1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68-7.65 (m, 2H, CH Aromatic), 7.48-7.42 (m, 2H, CH Aromatic), 7.32-7.15 (m, 34H, CH Aromatic), 5.17-5.10 (m, 3H incl. $H1^B$: d, *J* = 2.9 Hz at 5.16, CH_2 Cbz), 5.1 (d, 1H, *J* = 2.7 Hz, $H1^D$), 4.95 (t, 1H, *J* = 3.9 Hz, $H4^D$), 4.91 (t, 1H, *J* = 3.8 Hz, $H2^B$), 4.88 (d, 1H, *J* = 3.4 Hz, $H1^C$), 4.86 (d, 1H, *J* = 3.4 Hz, $H5^D$), 4.83 (t, 1H, *J* = 3.4 Hz, $H2^D$), 4.80-4.57 (m, 10H incl. $H1^A$: 4.79, $H5^B$: d, *J* = 3.2 Hz at 4.75, 4 x CH_2Bn), 4.48-4.40 (m, 5H, NCH_2Bn, $H6a^A$, $H6a^C$, C*H*H Fmoc), 4.35 (dd, 1H, *J* = 7.6 Hz, *J* = 10.5 Hz, CH*H* Fmoc), 4.2-7.17 (m, 2H, $H6b^A$, C*H* Fmoc), 4.11 (dd, 1H, *J* = 2.44 Hz, *J* = 12.7 Hz, $H6b^C$), 3.96 (t, 1H, *J* = 3.9 Hz, $H4^B$), 3.92-3.88 (m, 2H, $H4^C$, $H3^B$), 3.86-3.74 (m, 5H, $H3^D$, $H4^A$, $H5^A$, $H3^A$, $H5^C$), 3.65-3.6 (m, 2H, incl. OC*H*H Linker, $H3^C$: t, *J* = 9.7 Hz at 3.62), 3.45 and 3.44 (2s, 6H, 2 x CO_2CH_3), 3.33-3.17 (bm, 1H, OCH*H* Linker), 3.29-3.27 (m, 2H incl. $H2^A$: dd, *J* = 2.4 Hz, *J* = 12.4 Hz at 3.28), 3.20-3.10 (bm, 2H, CH_2N Linker), 2.83-2.69 (m, 4H, 2 x CH_2 Lev), 2.66-2.52 (m, 4H, 2 x CH_2 Lev) , 2.15-1.98 (4s, 12H, 2 x CH_3 Ac, 2 x CH_3 Lev), 1.34-1.23 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 206.9, 206.7, 172.6, 172.4, 170.3, 170.0, 169.5, 168.7, 143.4, 143.2, 141.5, 138.1, 137.7, 137.4, 137.3, 128.8-127.4, 125.2, 120.4, 98.2 ($C1^B$), 97.8 ($C1^D$), 97.5 ($C1^A$), 97.3

(C1^{C}), 78.5, 78.3, 77.7, 77.5, 77.2, 76.8, 75.6, 74.9, 74.8, 74.5, 73.7, 73.6, 73.4, 72.7, 71.8, 70.4, 69.9, 69.3, 69.1, 68.6, 68.4, 67.5, 67.4, 63.5, 62.6, 62.1, 52.4, 52.1 46.8, 38.1, 38.0, 30.0, 29.9, 29.3, 28.3, 28.2, 23.5, 21.1, 21.0. HRMS-MALDI: (M + Na^{+}) calcd. 1966.7373, found 1966.7362.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-α-L-idopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deozy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-3-*O*-benzyl-2-*O*-levulinoyl-α-L-idopyranosyluronate)]-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)** (**74**): Glycosylation of disaccharide acceptor **19 (**107 mg, 0.099 mmol) with donor **59** (128 mg, 0.119 mmol) was performed according to the general procedure for preparation of tetrasaccharides followed by silica gel chromatography (hexanes/EtOAc, 60/40 to 50/50, v/v) providing tetrasaccharide **72** (80 mg, 51%). $[\alpha]_D^{25}$ +30 (*c* = 1, $CHCl_3$); ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.78-7.73 (m, 2H, CH Aromatics), 7.59-7.53 (m, 2H, CH Aromatics), 7.35-7.12 (m, 34H, CH Aromatic), 5.19-5.13 (m, 3H incl. H1^{B}: d, *J* = 3.4 Hz at 5.18, CH_2 Cbz), 5.12 (d, 1H, *J* = 3.0 Hz, H1^{D}), 5.02 (d, 1H, *J* = 3.5 Hz, H1^{C}), 4.96-4.91 (m, 2H, H2^{B}, H4^{D}), 4.86 (d, 1H, *J* = 3.6 Hz, H5^{D}), 4.82 (t, 1H, *J* = 3.6 Hz, H2^{D}), 4.81-4.59 (m, 10H, incl. H1^{A} at 4.80, H5^{B} at 4.70, 4 x CH_2Bn), 4.50-4.46 (m, 2H, CH_2NBn), 4.46-4.38 (m, 3H, H6a^{A}, H6a^{C}, C*H*H Fmoc), 4.35 (dd, 1H, *J* = 7.5 Hz, *J* = 8.3 Hz, CH*H* Fmoc), 4.13 (bd, *J* = 12.5 Hz, H6b^{A}), 4.18 (t, 1H, *J* = 7.3Hz, C*H* Fmoc), 4.12 (dd, 1H, *J* = 3.1 Hz, *J* = 12.5 Hz, H6b^{C}), 3.98 (t, 1H, *J* = 4.4 Hz, H4^{B}), 3.94 (t, 1H, *J* = 4.4 Hz, H3^{B}), 3.92-3.83 (m, 5H, H3^{A}, H3^{D}, H4^{A}, H4^{C}, H5^{A}), 3.76-3.20 (m, 1H, H5^{C}), 3.67-3.55 (m, 2H, incl. H3^{C}: t at 3.61 *J* = 9.0 Hz, OC*H*H Linker), 3.56 (s, 3H, CO_2CH_3), 3.45 (s, 3H, CO_2CH_3), 3.43-3.17 (m, 5H, incl. H2^{C}: dd at 3.27, OCH*H* Linker, H2^{A}, CH_2N Linker), 2.76-

2.42 (m, 8H, 4 x C*H*$_2$ Lev), 2.10, 2.09, 2.05, 2.94 (4s, 12H, 1 x C*H*$_3$ Ac, 3 x C*H*$_3$ Lev), 1.72-1.20 (m, 6H, 3 x C*H*$_2$ Linker). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 206.5, 206.4, 206.1, 172.3, 172.1, 169.7, 169.3, 168.5, 154.1, 143.1, 143.0, 141.3, 141.2, 137.8, 137.5, 137.4, 137.1, 136.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.1, 124.9, 120.0, 97.8 (C1^B), 97.5 (C1^D), 97.3 (C1^C), 96.6 (C1^A), 78.2, 78.0, 77.0, 75.4, 74.6, 74.3, 73.5, 73.3, 73.2, 72.9, 72.4, 71.8, 71.6, 71.4, 70.5, 70.2, 69.5, 69.3, 69.0, 68.9, 68.8, 68.3, 68.1, 67.3, 67.1, 64.3, 63.2, 62.4, 61.8, 52.1, 51.8, 50.5, 50.2, 47.0, 46.5, 46.2, 37.8, 37.7, 29.8, 29.7, 29.6, 28.9, 28.0, 27.9, 27.6, 23.2, 20.8. HRMS-MALDI: (M + Na$^+$) calcd. 2022.7743, found 2022.7783.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate))-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl 2-O-levulinoyl-3-*O*-benzyl-α-L-idopyranosyluronate)]-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)** (**75**): Glycosylation of disaccharide acceptor **24** (274mg, 0.254 mmol) with donor **47** (329 mg, 0.305 mmol) was performed according to the general procedure for preparation of tetrasaccharides followed by silica gel chromatography (Hexanes/EtOAc 60/40 to 50/50) providing tetrasaccharide **75** (282 mg, 59%). $[\alpha]_D^{25}$ +19 (*c* = 1, CHCl$_3$); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.75-7.71 (m, 2H CH Aromatics) 7.58-7.52 (m, 2H, CH Aromatics), 7.42-7.16 (m, 34H, CH Aromatics), 5.23 (d, 1*H,J* = 4.4 Hz, H1^B), 5.20 (d, 1H, *J* = 11.1 Hz, C*H*HBn), 5.18-5.12 (m, 2H C*H*$_2$ Cbz), 5.10-5.04 (m, 2H, H2^D, H4^D), 5.02 (d, 1H, *J* = 3.5 Hz, H1^C), 4.92 (t, 1H, *J* = 3.0 Hz, H2^B), 4.82-4.77 (m, 2H, H1^A, C*H*HBn), 4.74-4.55 (m, 9H, incl. H5^B at 4.57, 4 x C*H*$_2$Bn), 4.50-4.45 (m, 2H, C*H*$_2$NBn), 4.43-4.14 (m, 8H, incl. H5^D at 4.31, H6a^A, H6b^A, H6a^C, H6b^C, C*H*$_2$ Fmoc, C*H* Fmoc), 3.99-3.80 (m, 8H, H3^A, H3^B, H3^D, H4^A, H4^B, H4^C, H5^A, H5^C), 3.67-3.57 (m, 2H, incl. H3^C: dd at 3.64 *J* = 8.5 Hz, *J* = 10.2 Hz, OC*H*H Linker), 3.53 (s, 3H, CO$_2$CH_3), 3.45-3.18 (m, 8H incl. CO$_2$CH_3: s at 3.43, H2^C: dd at 3.24 *J* = 3.5 Hz, *J* = 10.4 Hz, H2^A, OCH*H* Linker, CH_2N Linker), 12.80-2.40 (m, 8H, 4 x CH_2 Lev), 2.20-1.95 (4s, 12H, 1 x CH_3 Ac, 3 x CH_3 Lev), 1.64-1.24 (m, 6H, 3 x CH_2 Linker). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 206.8, 206.4, 206.1, 172.5, 172.4 172.0, 169.6, 169.0, 167.4, 156.6, 156.1, 154.0, 143.3, 143.0, 141.2, 138.2, 138.0, 137.9, 137.7, 137.5, 136.8, 128.5,128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.4, 127.2, 127.1, 125.1, 125.0, 124.0, 122.9, 120.0, 100.5 (C1^B), 97.9 (C1^C), 97.4 (C1^A), 97.1 9 (C1^D), 79.3, 78.1, 77.6, 75.9, 75.3, 74.8, 74.3, 73.6, 72.6, 72.4, 72.3, 70.3, 70.0, 69.6, 69.0, 68.9, 68.0, 67.1, 63.1, 62.5, 62.3, 61.7,52.5, 52.1, 50.5, 50.2, 47.0, 46.5, 46.1, 38.0, 37.8, 376, 29.7, 29.6, 28.9, 27.8, 27.6, 23.2, 20.6. HRMS-MALDI: (M + Na$^+$) calcd. 2022.7743, found 2022.7982.

***N*-(Benzyl)-benzyloxycarbonyl-5-aminopentyl *O*-[(methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-α-L-idopyranosyluronate)-(1→4)-*O*-(2-azido-3-*O*-benzy-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside)-(1→4)-*O*-(methyl-2-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranosyluronate)]-(1→4)-*O*-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranoside (63)**: Trichloroacetimidate donor **59** (221.8 mg, 0. 2052 mmol) was coupled with the acceptor **19** (174.9 mg, 0.1710 mmol) in the presence of TMSOTf (0.0257 mmol, 4.63 mL) according to the general procedure to give tetrasaccharide **61** (289 mg, 64%). Tetraaccharide **61** was subjected to Fmoc cleavage according to the general procedure to obtain acceptor **62** (209.9 mg, 82%). Acceptor **62** (209.9 mg, 0.1219 mmol) was coupled with the donor **47** (171 mg, 0.1585 mmol) according to the general procedure to obtain hesxasaccharide **63** (209.3 mg, 65%). $[\alpha]_D^{25}$ +167 (*c* = 0.22, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H, CH Aromatics), 7.56-7.52 (m, 2H, CH Aromatics), 7.40-7.17 (m,40H, CH Aromatics), 5.34 (d, 1H, *J* = 3.7 Hz, H1^C), 5.25 (d, 1H, *J* = 4.9 Hz,H1^D) , 5.20-5.039 (m, 7H, CH_2Bn, CH_2 Cbz, H2^B, H2^F, H4^F), 4.97 (d, 1H, *J* = 3.4 Hz, H1^E), 4.87 (t, 1H, *J* = 5.6 Hz, H2^D), 4.83-4.77 (m, 3H incl.CH_2Bn, H1^A at 4.80), 4.73-4.7 (m, 3H incl. H1^F at 4.73, H1^B at 4.72, CH_2Bn), 4.68-4.55 (m, 7H, CH_2Bn), 4.47-4.45 (m, 4H incl. NCH_2Bn, H5^B at 4.56, C*H*H Fmoc), 4.41-4.25 (m, 5H, H6a^A, H6a^E, H6a^C, H5^F at 4.28, CH*H* Fmoc), 4.19-4.11 (m, 6H, H6b^E, H6b^A, H6b^C, H5^B, H4^B), 3.98-3.92 (m, 3H, H3^F, H3^B, H4^D), 3.91-3.80 (m, 5H, H3^D, H4^E, H4^A, H3^A, H5^E), 3.79 (t, 1H, *J* = 9.5 Hz, H4^C), 3.73-3.70 (bm, 1H, H5^A), 3.68-3.60 (m, 2H incl. H3^C: t, *J* = 9.52 Hz, *J* = 10.3 Hz at 3.7, H3^E: t, *J* = 8.79 Hz at 3.64), 3.58-3.51 (m, 5H incl. CO_2CH_3^{D}: s at 3.56, H5^C at 3.54, OC*H*H Linker), 3.43 (s, 3H, CO_2CH_3^{F}), 3.39 (s, 3H, CO_2CH_3^{B}), 3.28-3.19 (m, 6H, H2^C: dd, *J* = 3.6 Hz, *J* = 10.3 Hz at 3.28, H2^E, H2^A, OCH*H* Linker, CH_2N Linker), 2.75-2.54 (m, 6H, 3 x CH_2 Lev), 2.49-2.39 (m, 6H, 3 x CH_2 Lev), 2.19-1.94 (6s, 36H, 3 x CH_3 Lev, 3x CH_3 Ac), 1.65-1.23 (m, 6H, 3 x CH_2Linker). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 206.8, 206.7, 206.5, 172.6, 172.5, 172.4, 169.9, 169.8, 169.3, 169.0, 168.2,167.44, 154.0, 143.3, 143.0, 141.3, 141.2, 138.4, 138.1, 137.8, 137.7, 137.6, 137.4, 128.5-127.1, 125.1, 125.0, 120.0, 101.1, 100.5 (C1^F), 98.0 (C1^D), 97.8 (C1^E), 97.7, 97.2 (C1^C), 82.0, 79.3, 78.4, 78.0, 77.7, 77.6, 77.4, 75.7, 75.5, 75.4, 75.3, 75.0, 74.5, 74.4, 74.3, 74.2, 73.3, 73.1, 72.4, 72.3, 70.5, 70.3, 70.2, 69.5, 69.2, 68.6, 67.2, 63.1, 62.8, 62.5, 62.1, 61.7, 61.6, 52.6, 52.4, 52.2, 50.6, 50.3, 47.1, 46.6, 46.2, 38.1, 38.0, 37.9, 37.8, 31.9, 29.8, 29.7, 29.6, 29.4, 28.9, 27.9, 27.8, 27.7, 27.4, 23.2, 22.7, 20.8, 20.7, 20.6. HRMS-MALDI: (M + Na^+) calcd. 2663.9856, found 2663.9900.

Hexasaccharide Deprotection: Synthesis of Hexasaccharide (**69**):

Cleavage of Lev esters: Hexasaccharide **63** (73.5 mg, 0.028 mmol) was de-levulinoylated according to the general procedure for cleavage of levulinoyl ester to give **64** as a colorless oil (59.2 mg, 90%). ^{1}H NMR (500 MHz, CD$_3$OCD$_3$): δ 7.72-7.70 (m, 2H, CH Aromatic), 7.57-7.55 (m, 2H, CH Aromatics), (m, 40H, CH Aromatics), 5.47 (d, 1H, J = 3.7 Hz, H1^{c}), 5.38 (d, 1H, J = 4.0 Hz, H1^{D}), 5.22-512 (m, 4H, CH$_2$ Cbz, 2 x CHHBn), 5.09-5.06 (m, 3H incl. H1^{E} at 5.02, H2^{B}, H2^{F}), 5.04-4.91 (m, 5H, H2^{D}, H4^{F}, H1^{F}, H1^{B}, CHHBn), 4.87-4.75 (m, 6H incl. 4 x CH$_2$Bn, H1^{A} at 4.80), 4.64-4.49 (m, 7H, 5 x CH$_2$Bn, CH$_2$ Fmoc, NCH$_2$Bn),4.30 (t, 1H, J = 6.6 Hz, CH Fmoc), 4.21-4.12 (m, 3H, H5^{F}, H4^{B}, H5^{B}), 4.07 (t, 1H, J = 5. 2 Hz, H3^{D}), 4.03-3.92 (m, 5H, H3^{F}, H3^{B}, H4^{C}, H4^{E}, H4^{A}), 3.88-3.71 (m, 10H, H3^{A}, H3^{E}, H3^{C}, H6a^{A}, H6a^{E}, H6a^{C}, H6b^{E}, H6b^{A}, H6b^{C}, H5^{E}), 3.62 (m, 5H incl. s at 3.62: CO$_2$CH$_3$, OCHH Linker, H5^{A}), 3.53, 3.51 (2s, 6H, CO$_2$CH$_3$$^{\text{B or D}}$, CO$_2CH_3$$^{\text{B or D}}$), 3.46-3.43 (m, 2H, H2^{C}, H5^{C}), 3.43-3.38 (bm, 1H, OCHH Linker), 3.45 (dd, 1H, J = 3.7 Hz, J = 10.4 Hz, H2^{C}), 3.30 (dd, 1H, J = 3.3 Hz, J = 10.4 Hz, H2^{E}), 3.25-3.23 (m, 3H incl. H2^{A}: dd, J = 3.0 Hz, J = 10.2 Hz at 3.25, CH$_2$N Linker), 2.10-2.05 (3s, 9H, 3 x CH$_3$ Ac), 1.56-1.28 (m, 6H, 3x CH$_2$ Linker). HRMS-MALDI: (M + Na$^+$) calcd. 2369.8753, found 2369.8722.

O-sulfation: Hexasaccharide **64** (59.2 mg, 0.025 mmol) was dissolved in DMF (1.76 mL) and O-sulfated according to the general procedure for O-sulfation providing **65** as sodium salt (53.3 mg, 80%). $[\alpha]_D^{23}$ -32.1 (*c* = 1.3, CHCl$_3$); ^{1}H NMR (500 MHz, CD$_3$OCD$_3$): δ7.85-7.80 (m, 2H, CH Aromatic), 7.66-7.60 (m, 2H, CH Aromatics), 7.50-7.21 (m, 40H, CH Aromatic), 5.42 (bs, 1H, H1^{D}), 5.36 (d, 1H, *J* = 3.8 Hz, H1^{C}), 5.33 (d, 1H, *J* = 8.2 Hz, H1^{B}), 5.25 (d, 1H, *J* = 8.2 Hz, H1^{F}), 5.18-5.15 (m, 3H, C*H*$_2$ Cbz, C*H*HBn), 5.11-5.09 (m, 2H, H2^{D}, CH*H*Bn), 5.03-4.99 (m, 4H, C*H*HBn, H2^{B}, H2^{F}, H1^{E}), 4.95 (t, 1H, *J* = 9.6 Hz, H4^{F}), 4.92 (d, 1H, *J* = 1.8 Hz, H5^{D}), 4.87-4.48

(m, 12H incl. H1^A: bs at 4.87, 8 x CH*H*Bn, NCH$_2$Bn, C*H*H Fmoc,),4.42 (dd, 1H, *J* = 6.8 Hz, *J* =10.5 Hz, CH*H* Fmoc), 4.36-4.32 (m, 5H, H5^B, H6a^A, H6a^E, H6a^C, H5^F), 4.27 (t, 1H, *J* = 6.8 Hz, C*H* Fmoc), 4.23-4.4.16 (m, 4H, H6b^E, H6b^A, H6b^C, H4^B), 4.10-4.01 (m, 6H, H3^B, H4^D, H3^F, H3^D, H4^E, H4^A), 3.94 (t, 1H, *J* = 9.6 Hz, H4^C), 3.85-3.81 (bm, 9H, H5^E, H3^A, H5^C, H3^C, H3^E, OC*H*H Linker, CO_2CH_3^{D}), 3.59 (dd, 1H, *J* = 3.6 Hz, *J* = 10.4 Hz, H2^C), 3.53, 3.52 (2s, 6H, CO_2CH_3^{F}, CO_2CH_3^{B}), 3.37-3.35 (m, 2H incl. H2^C: dd, *J* = 3.5 Hz, *J* = 10.4 Hz at 3.36, H2^E, OCH*H* Linker), 3.29-3.20 (bm, 3H, H2^A, C*H*$_2$N Linker), 2.15, 2.11, 2.00 (3s, 9H, 3 x C*H*$_3$ Ac), 1.56-1.25 (m, 6H, 3 x C*H*$_2$ Linker). ESI-MS: *m/z:* calcd. for $C_{122}H_{128}N_{10}Na_3O_{47}S_3$: 1292.3710, found: 1292.3712 [M-2H]$^{2-}$; calcd. $C_{122}H_{127}N_{10}Na_3O_{47}S_3$: 861.2449, found: 861.2446 [M-3H]$^{3-}$.

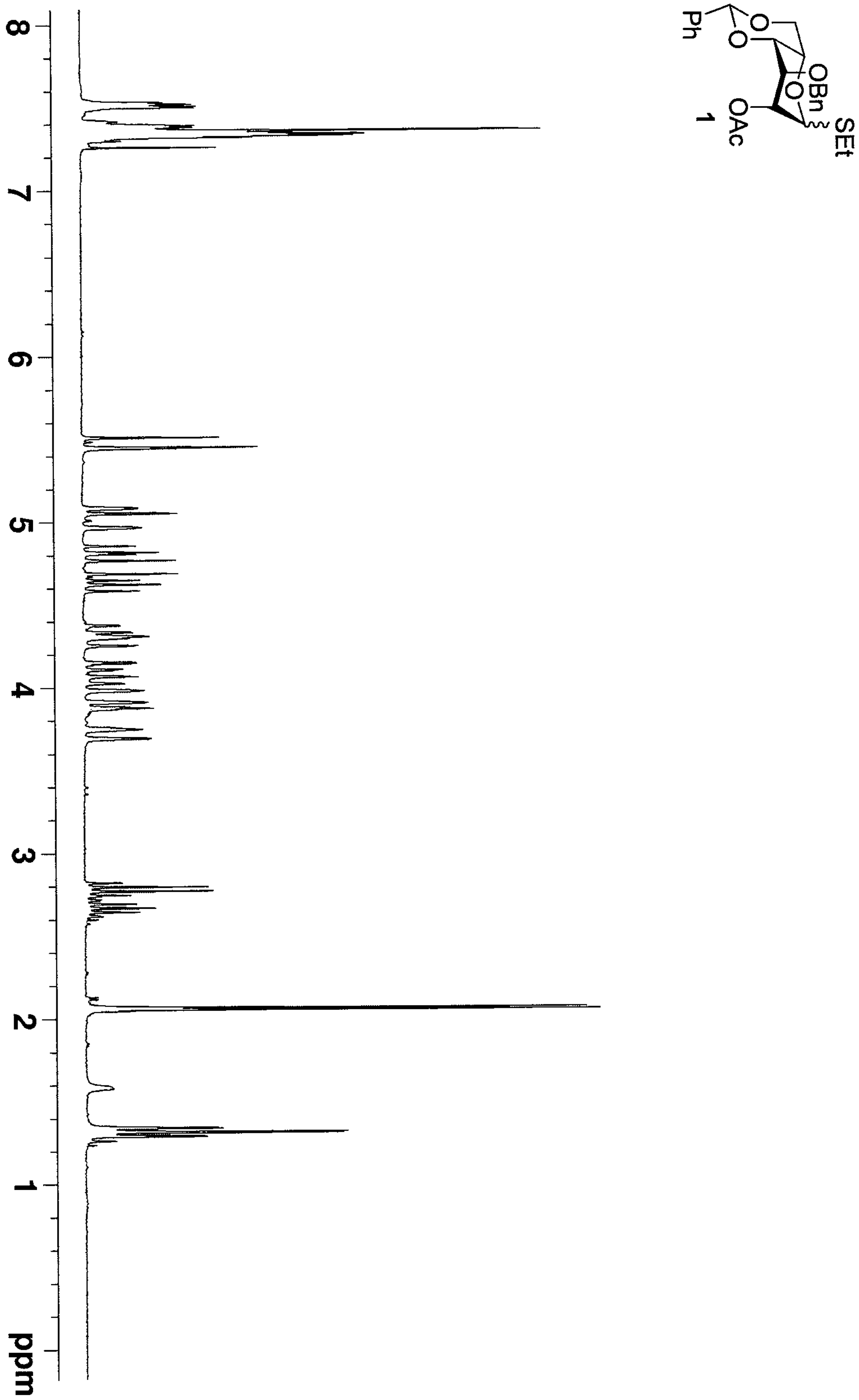
Fmoc cleavage and saponification of methyl esters and de-O-acetylation: Hexasaccharide **65** (53.3 mg, 0.020 mmol*)* was dissolved in DMF (1.25 mL) and subjected to Fmoc cleavage according to the general procedure. The resulting product was directly used in the next step. The compound (33.0 mg, 0.0124 mmol) was dissolved in THF (1.4 mL) and subjected to saponification and de-*O*-acetylation according to the general procedure of saponification of methyl ester and de-*O*-acetylation to give **66** as sodium salt (23.9 mg, 82%). $[\alpha]_D^{23}$ +36.9 (*c* = 0.48, CH_3OH); ^{1}H NMR (500 MHz, CD_3OCD_3): δ 7.47-7.19 (m, 40H, CH Aromatic), 5.53 (d, 1H, *J* = 3.5 Hz, H1^c), 5.30 (bs, 1H, H1^E), 5.17-4.56 (m, 18H incl. H1^E at 5.14, H1^B at 4.90, H1^A at 4.82, H1^F at 4.8, H5^D, C*H*$_2$ Cbz, 6 x C*H*$_2$Bn), 4.51-4.31 (m, 8H, NC*H*$_2$Bn, H6a^A, H6a^C, H6a^E, H6b^A, H6b^E, H6b^C), 4.27-4.20 (m, 4H, H3^D, H4^D, H5^A, H5^E), 4.08-3.82 (m, 8H, H4^E, H4^C, H4^A, H5^B, H3^E, H3^C, H3^A,H2^D, H3^D), 3.72 (t, 1H, *J* = 8.9 Hz, H3^B), 3.59-3.47 (m, 5H, OC*H*$_2$ Linker, H4^A, H4^F, H2), 3.51-3.47 (m, 2H incl. H2^E: dd, *J* = 3.2 Hz, *J* = 9.8 Hz at 3.50, H3^F), 3.89 (t, 1H, *J* = 9.8 Hz, H2^B), 3.34-3.24 (m, 2H, C*H*$_2$N Linker), 3.18 (m, 1H, H2^A), 3.14 (dd, 1H, *J* = 3.5 Hz, *J* = 9.8 Hz, H2^C), 1.57-1.28 (m, 6H, 3 x C*H*$_2$ Linker). ESI-MS*:m/z*: calcd. for

$C_{98}H_{104}N_{10}Na_6O_{42}S_3$: 1097.2976, found: 1097.2973 $[M-2H]^{2-}$; calcd. $C_{98}H_{103}N_{10}Na_6O_{42}S_3$: 731.1960, found: 731.1951 $[M-3H]^{3-}$.

Reduction of azide group: Hexasacharide **66** (23.9 mg, 0.0102 mmol) was dissolved in 1:1 mixture of THF and (0.1 M) NaOH (0.102 mL, 0.102 mmol, 10 eq. per azido group) and subjected to azide reduction to obtain hexasaccharide **67** (17.3 mg, 65%). ^{1}HNMR (500 MHz, CD_3OCD_3): δ 7.50-7.18 (m, 40H, CH Aromatics), 5.49 (d, 1H, *J* = 3.1 Hz, H1^c), 5.24 (d, 1H, *J* = 3.7 Hz, H1^D), 5.18-5.00 (m, 7H, C*H*$_2$Cbz, 2 x C*H*$_2$Bn, H1^E at 5.10), 4.82-4.61 (m, 11H incl. H1^F at 4.76, H1^B at 4.68, H1^A at 4.66, H5^D at 4.72, 3 x C*H*$_2$Bn, CH*H*Bn), 4.56-4.33 (m, 6H, NC*H*$_2$Bn, H6a^A, H6a^C, H6a^E, C*H*HBn), 4.32-4.22 (m, 4H, H4^D, H6b^A, H6b^E, H6b^C), 4.16-4.03 (m, 5H, H5^C, H5^E, H4C, H4^E, H4^B), 3.93 (t, 1H, *J* = 9.3 Hz, H3^E), 3.90-3.75 (m, 5H, H2^D, H5^B, H3^C, H3^D, H3^B), 3.66-3.56 (m, 4H, OC*H*H Linker, H2^B, H4^F, H3^A), 3.51 (t, 1H, *J* = 8.9 Hz, H3^F), 3.40 (t, 1H, *J* = 9.1 Hz, H2^F), 3.32-3.23 (m, under CD_2HOD OCH*H* Linker, C*H*$_2$N Linker), 3.00 (bd, 1H, *J* = 8.9 Hz, H2^E), 2.80-2.72 (m, 2H incl. H2^C at 2.79, H2^A at 2.74), 1.55-1.21 (m, 6H, 3 x C*H*$_2$ Linker). ESI-MS:*m/z*: calcd. for $C_{98}H_{110}N_4Na_6O_{42}S_3$: 1058.3119, found: 1058.3131 $[M-2H]^{2-}$; calcd. for $C_{98}H_{109}N_4Na_6O_{42}S_3$: 705.2055 found: 705.2047 $[M-3H]^{3-}$.

Selective N-sulfation^2**:** Hexasaccharide **67** (17.3 mg, 0.008 mmol) was subjected to selective *N*-sulfation to obtain hexasaccharide **68** (10.2 mg,50 μmol). $[\alpha]_D^{23}$+ 59.9 (*c* = 0.47, CH_3OH). ^{1}H NMR (500 MHz, CD_3OCD_3): δ7.53-7.15 (m, 40H, CH Aromatics), 5.65 (d, 1H, *J* = 3.1Hz, H1^c), 5.33 (bs, 1H, H1^E), 5.25 (bs, 1H, H1^E), 5.18-5.08 (m, 4H incl. H1^A at 5.10, C*H*$_2$Cbz, C*H*HBn), 4.94-4.58 (m, under CD_3OH peak, 14H incl. H5^D at 4.82, H1^F at 4.83, H5^D at 4.76, eleven C*H*HBn), 4.51-4.19 (m, 9H, NC*H*$_2$Bn, H6a^A, H6a^C, H6a^E, H6b^A, H6b^E, H6b^C, H4^D), 4.11-3.79 (m, 6H, H5^C, H4^B, H5^E, H5^B, H4^E, H2^D), 3.90-3.79 (m, 5H, H5^A, H4^A, H3^C, H3^B, H3^E), 3.70-3.54 (m, 6H, H5^F, OC*H*H Linker, H3^A, H4^F, H2^B, H3^F), 3.47-3.23 (m, 7H, H2^C, H2^E, H2^A, H2^B, OCH*H* Linker, C*H*$_2$N Linker), 1.67-1.28 (m, 6H, 3 x C*H*$_2$ Linker). ESI-MS: *m/z*: calcd. for $C_{98}H_{107}N_4Na_9O_{51}S_6$: 1178.2471, found: 1178.2475 $[M-2H]^{2-}$; calcd. for $C_{98}H_{106}N_4Na_9O_{51}S_6$: 705.2055, found 705.2047 $[M-3H]^{3-}$.

Global debenzylation: A solution of the hexasaccharide **68** (10.2 mg, 0.004 mmol) in (CH_3OH/H_2O 1:1, v/v) (1 mL) was subjected to debenzylation according to the general procedure for global debenzylation to give hexasaccharide **69** (4.8 mg, 67%). NMR data reported in the experimental section of paper.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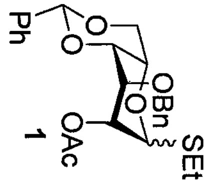

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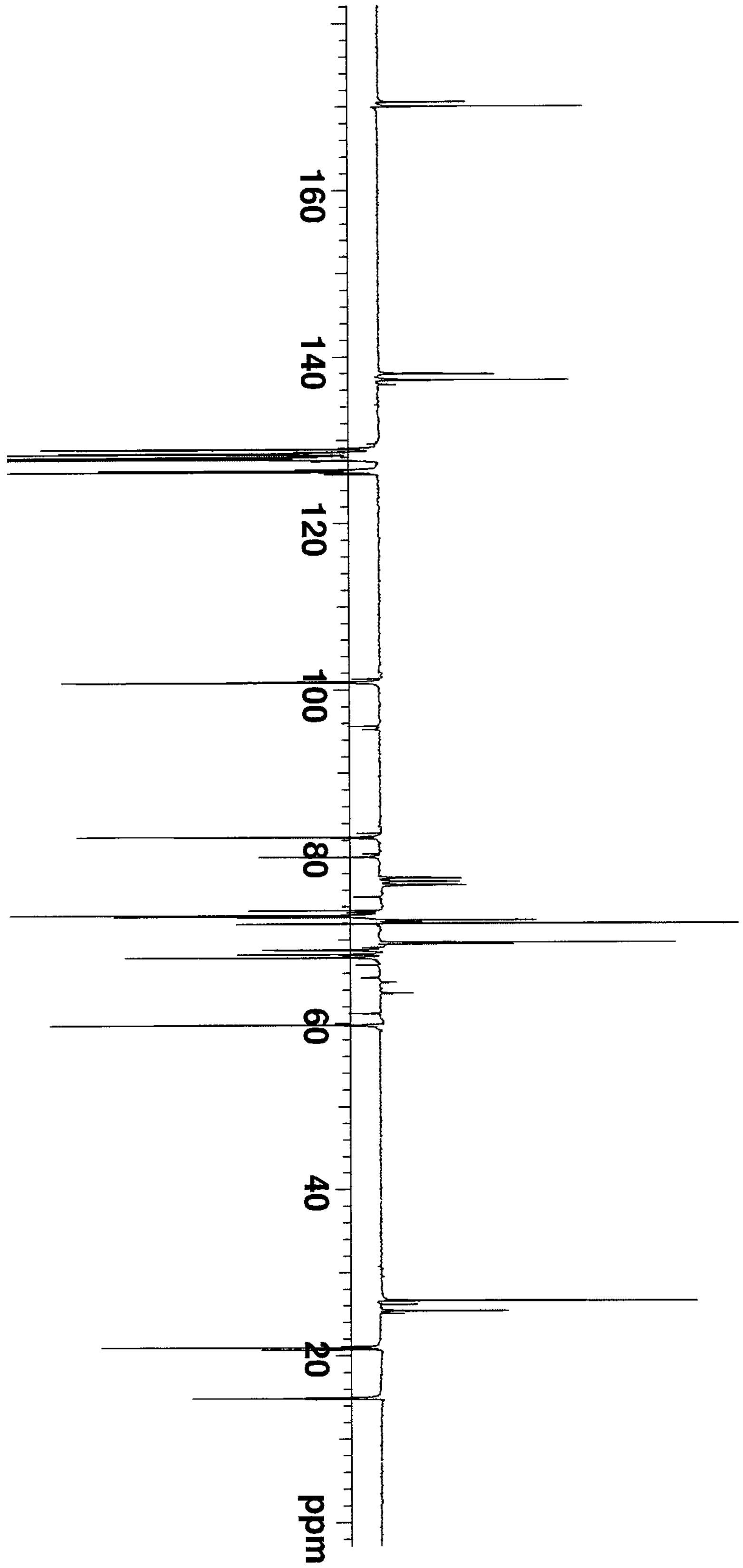
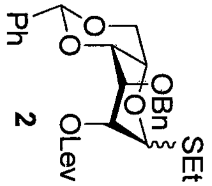
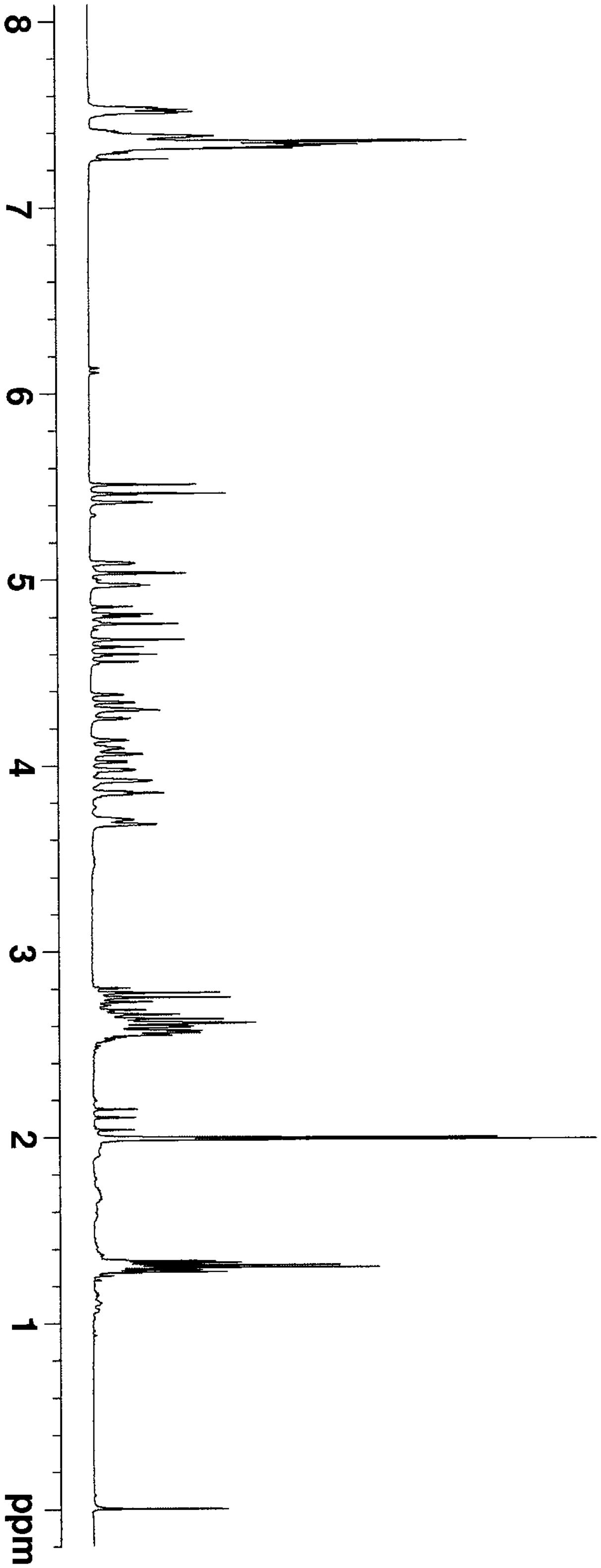
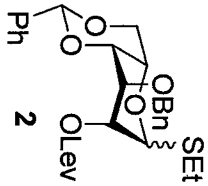


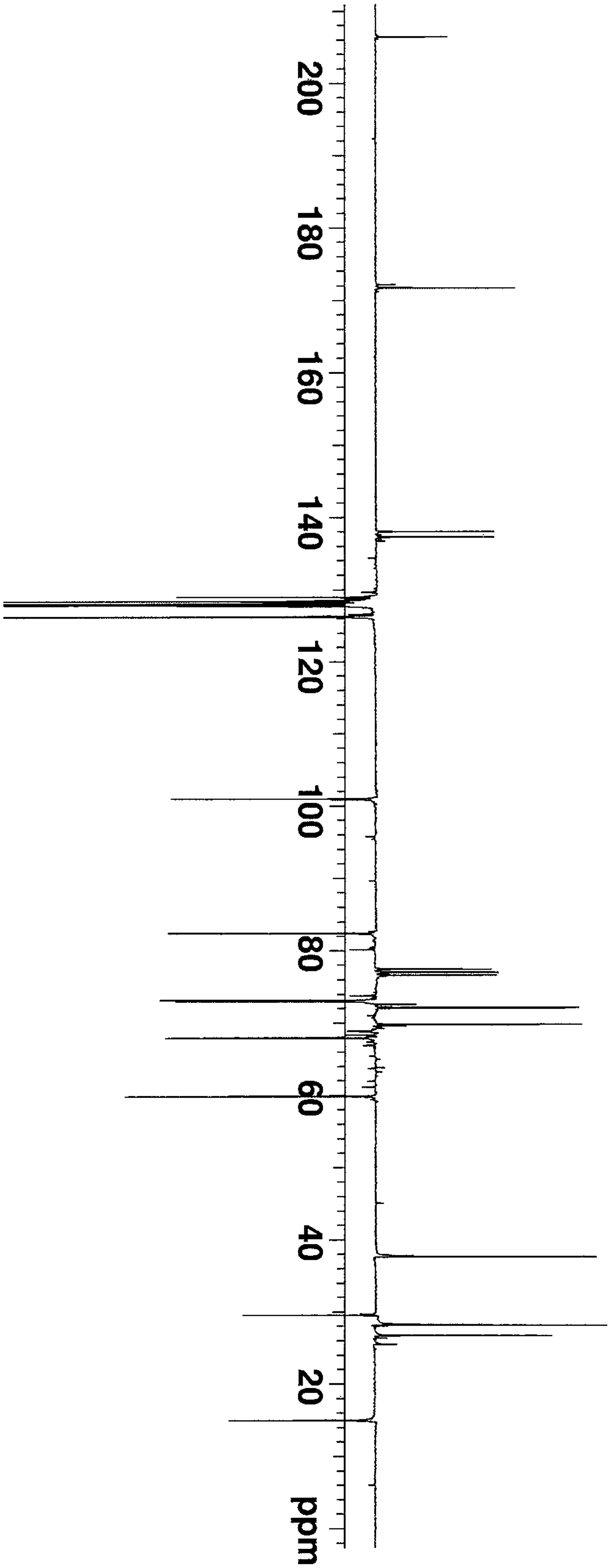


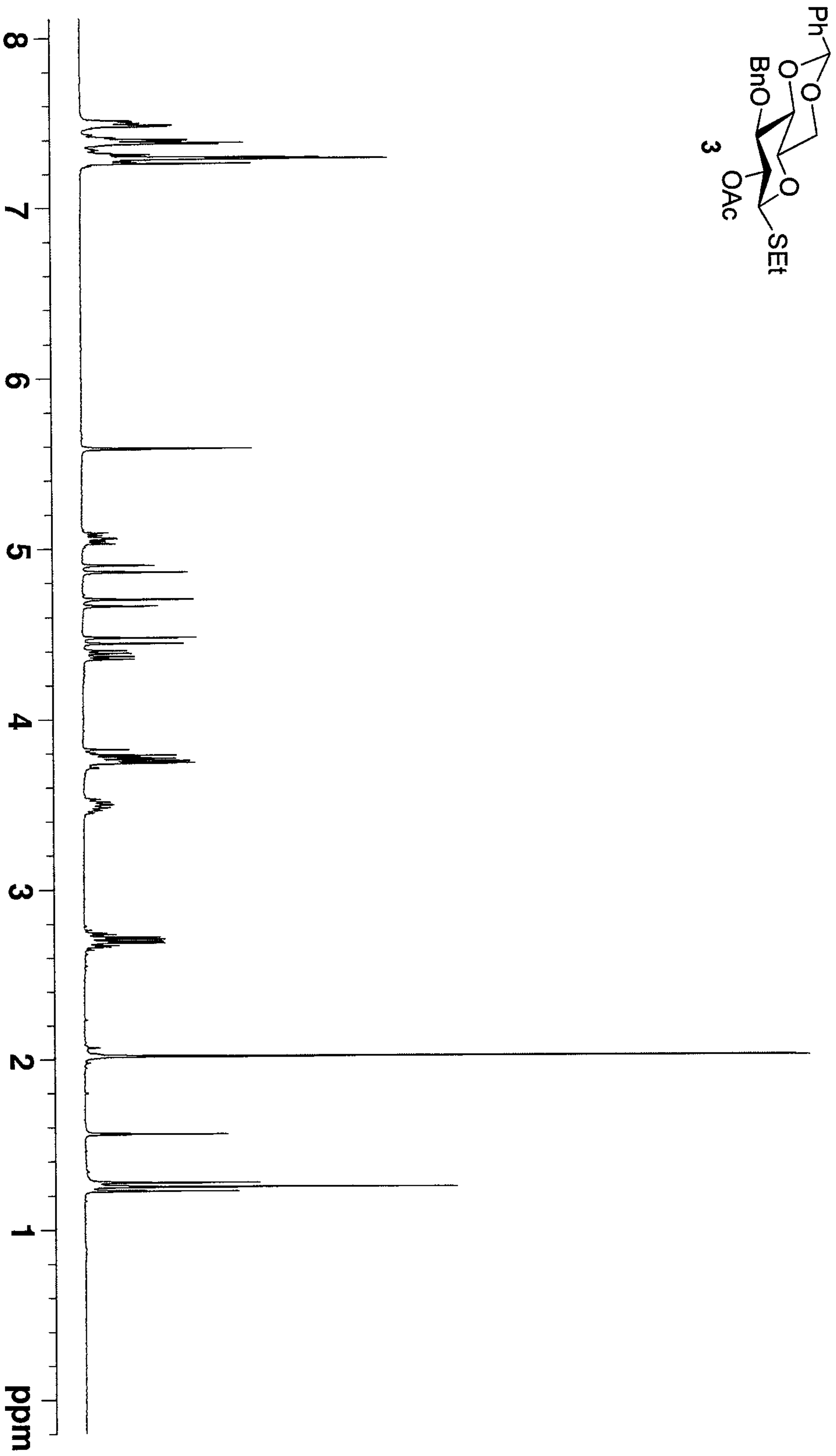
2



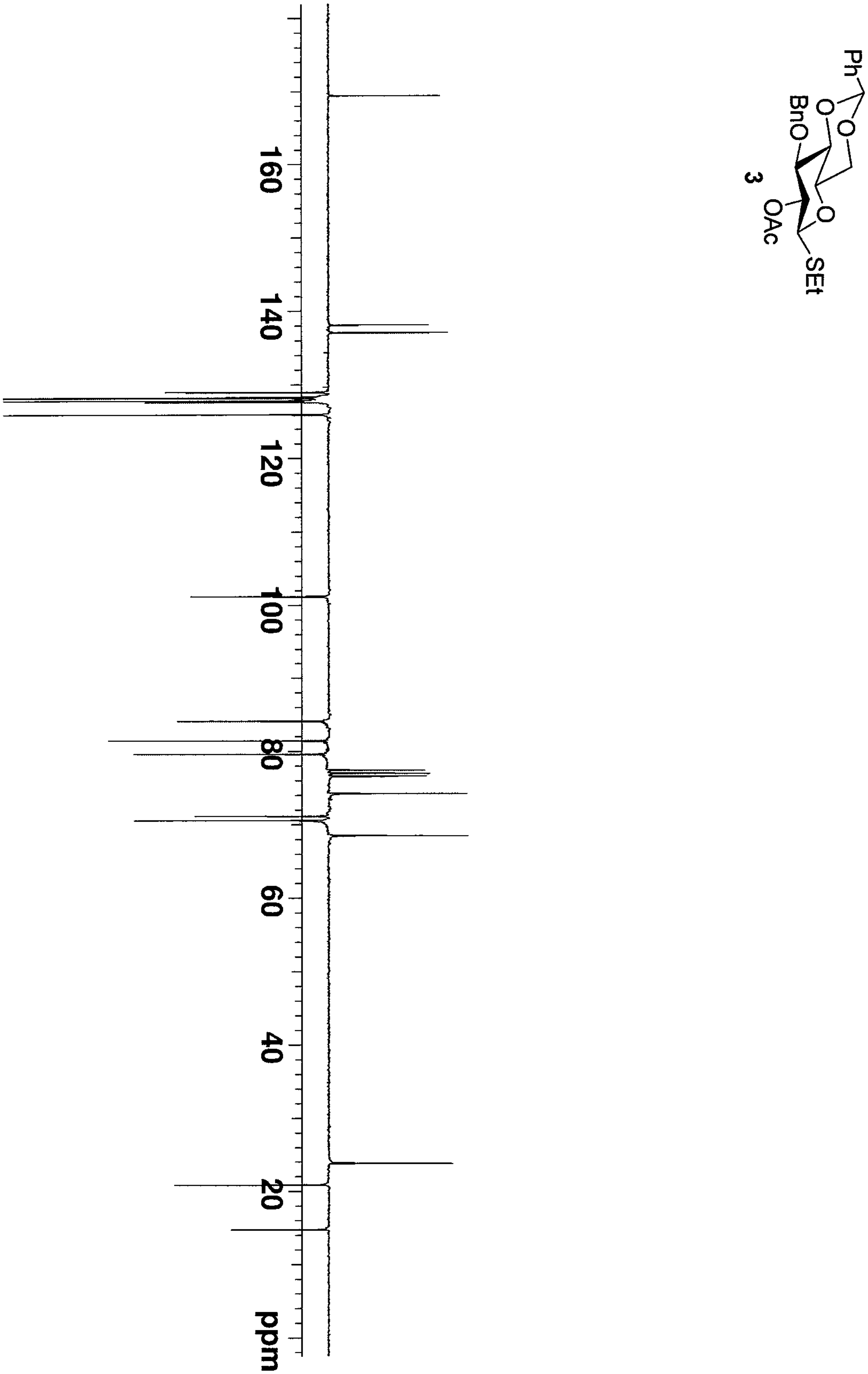


2

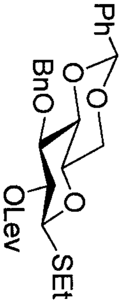




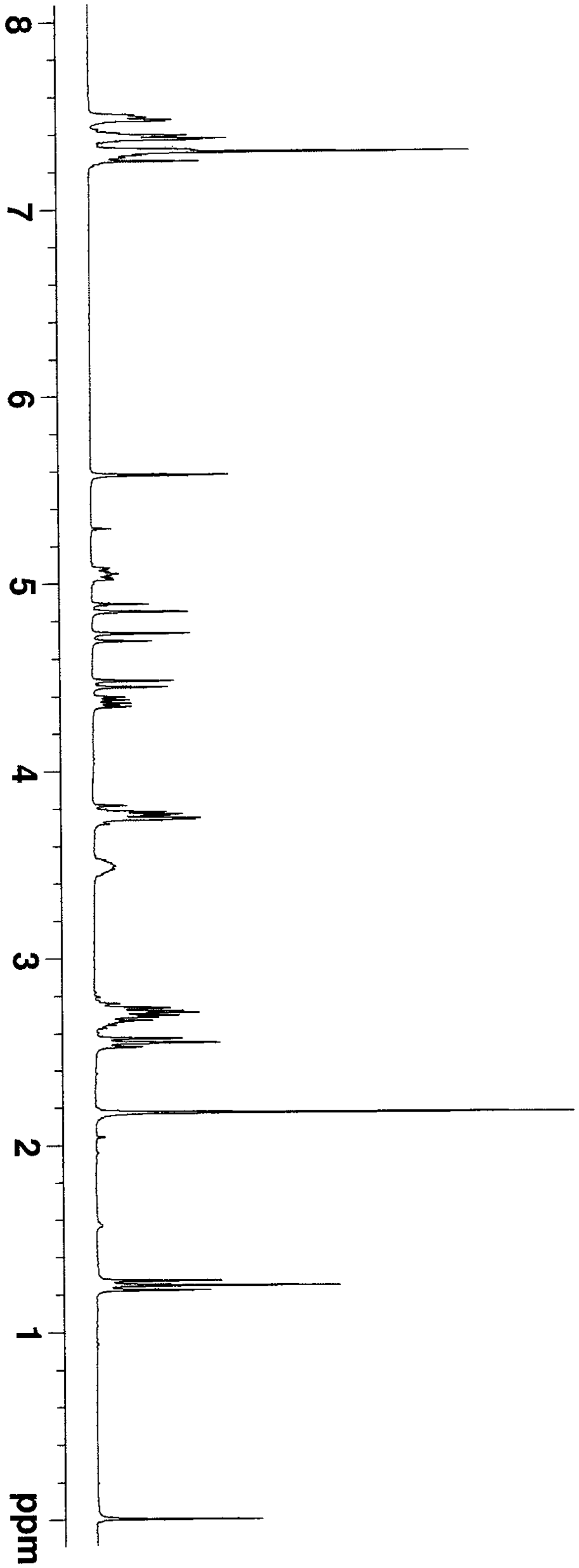
3

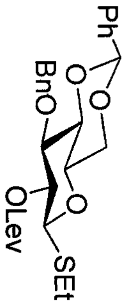


3

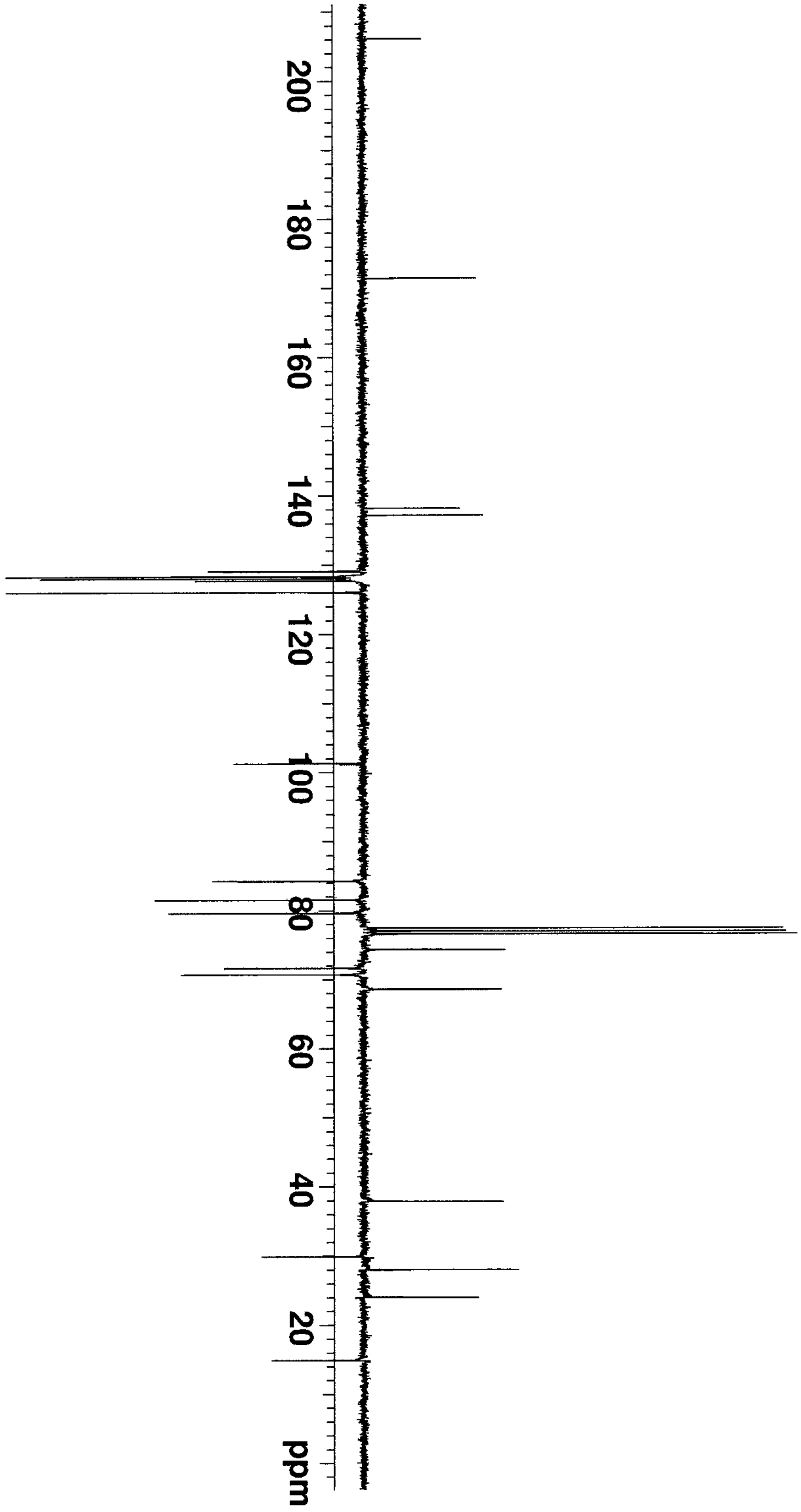


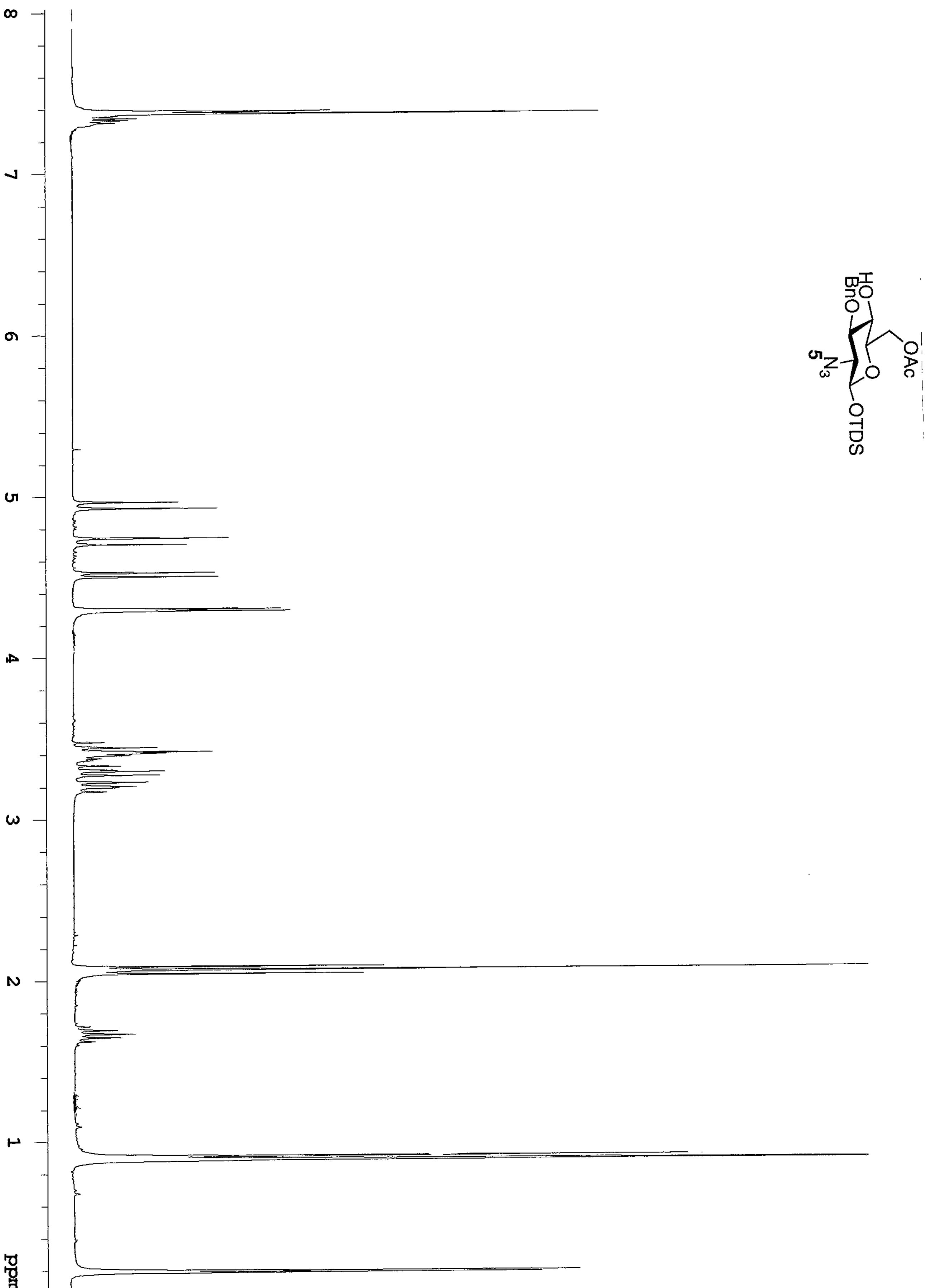
4

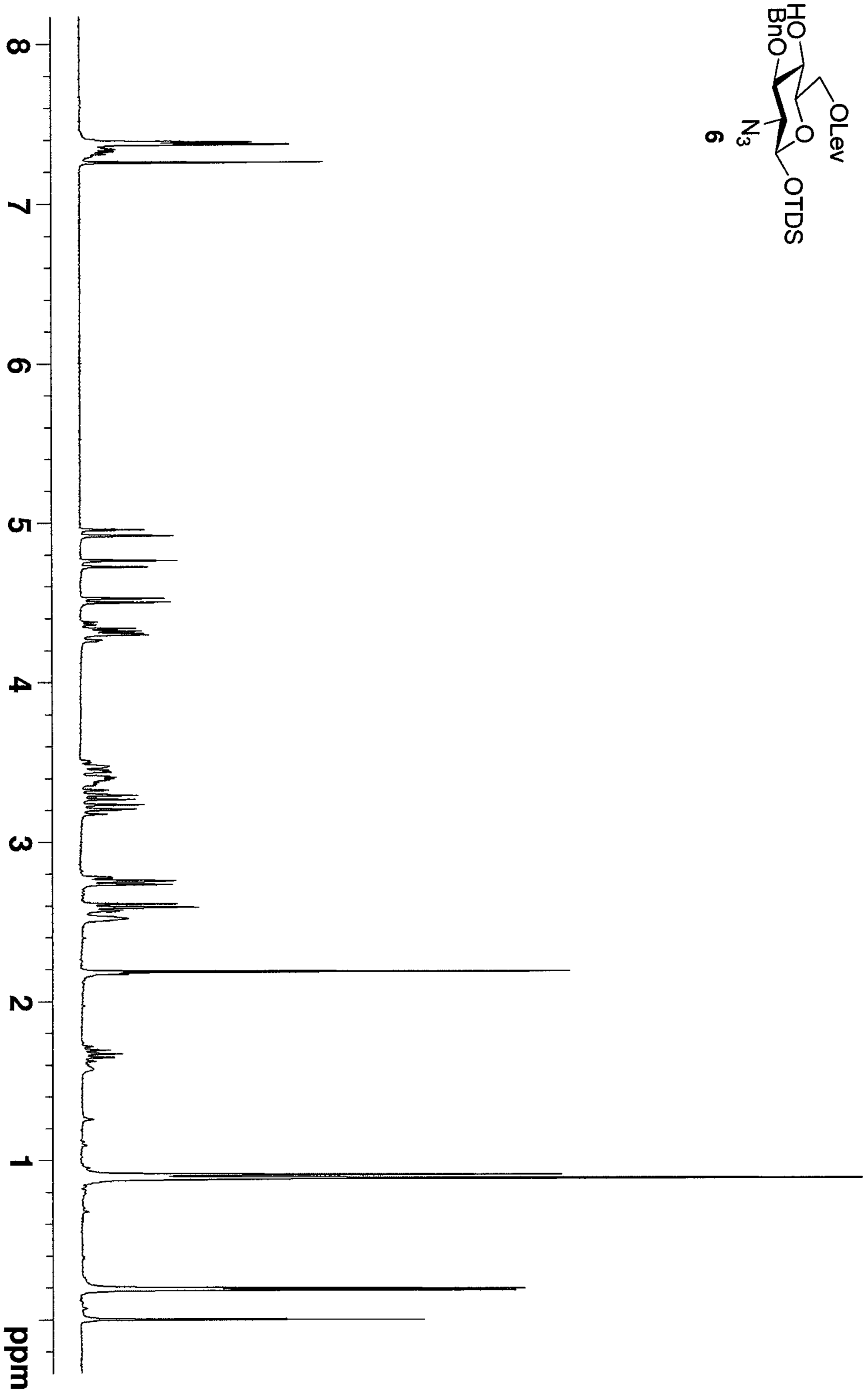




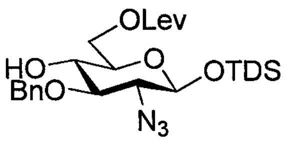
4



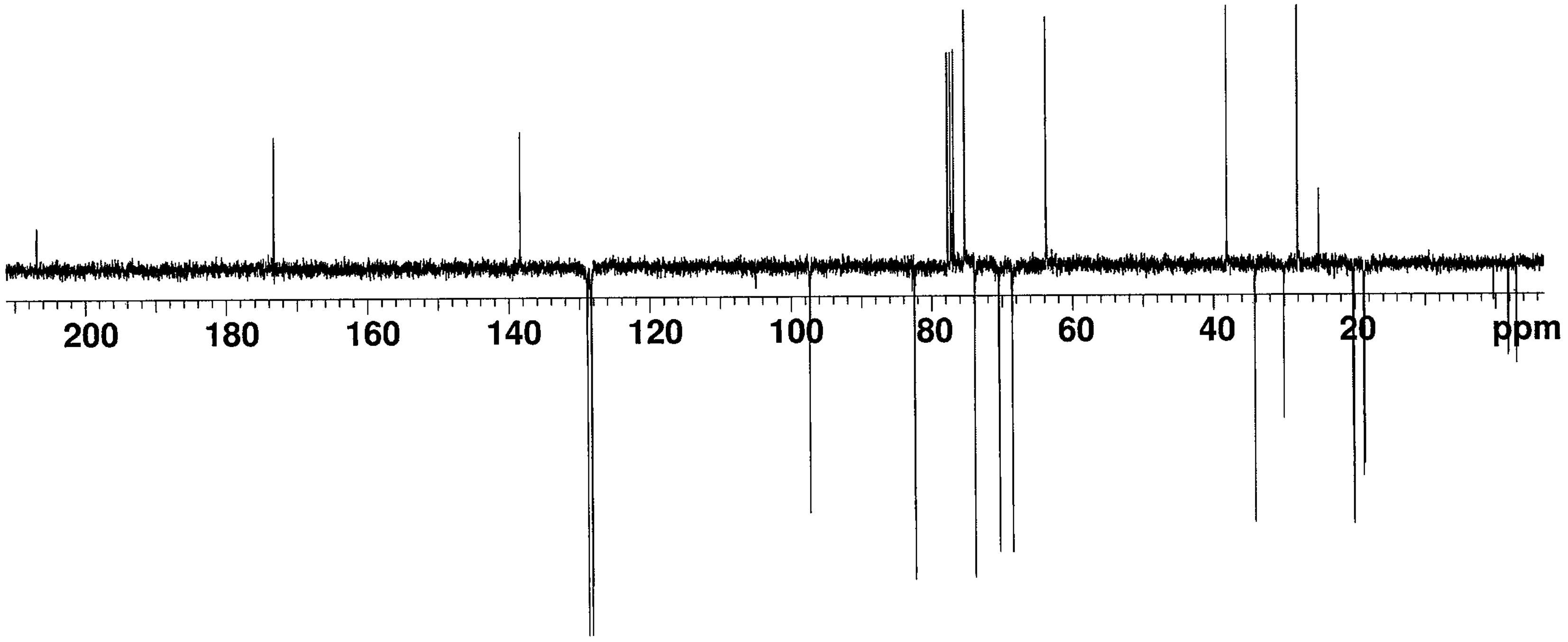

8
7
6
5
4
3
2
1
ppm
OAc
HO
BnO
O
N3
OTDS
5

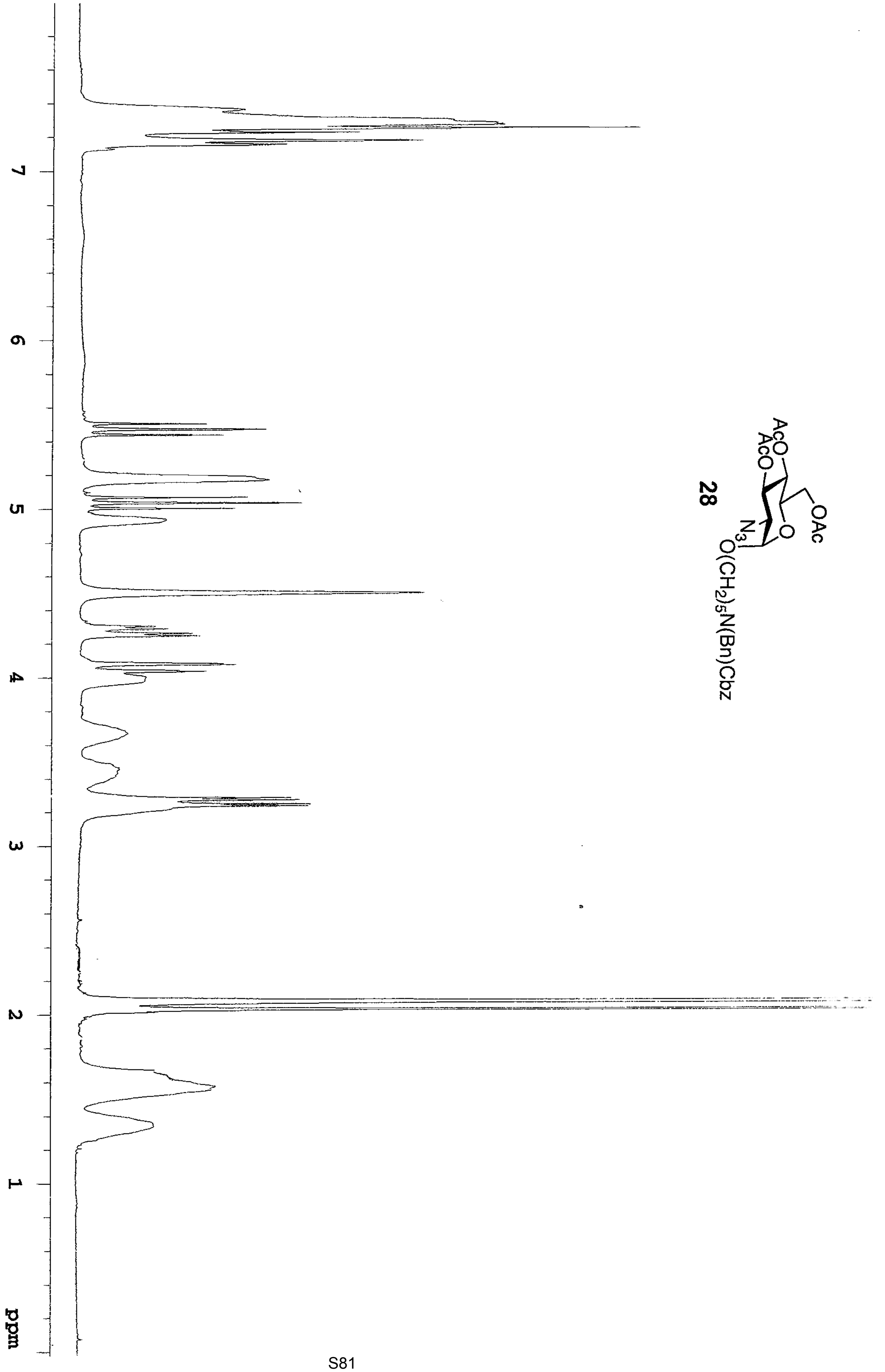


OLev
HO
BnO
O
N_3
OTDS
6
8
7
6
5
4
3
2
1
ppm

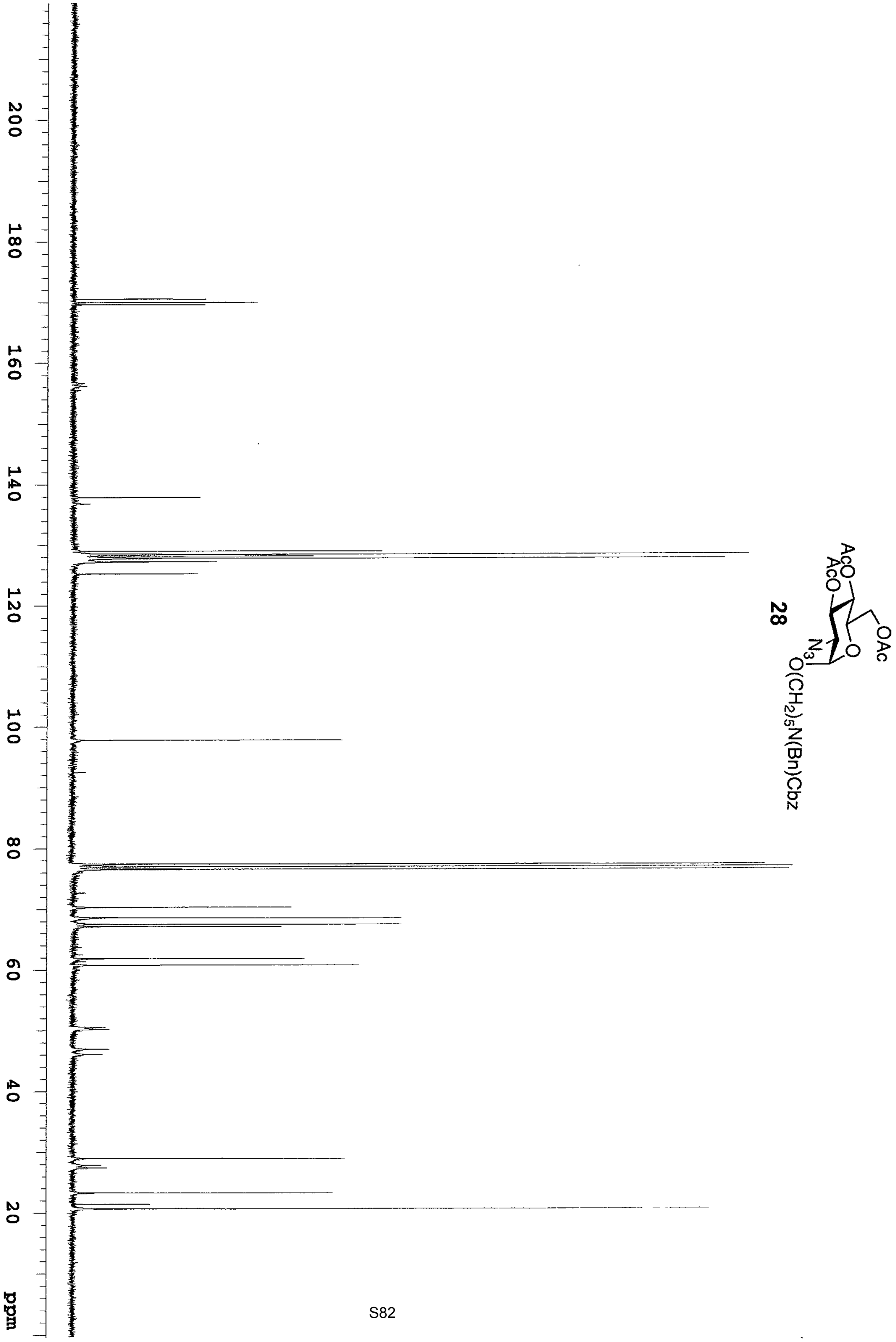


6

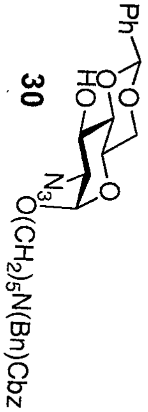




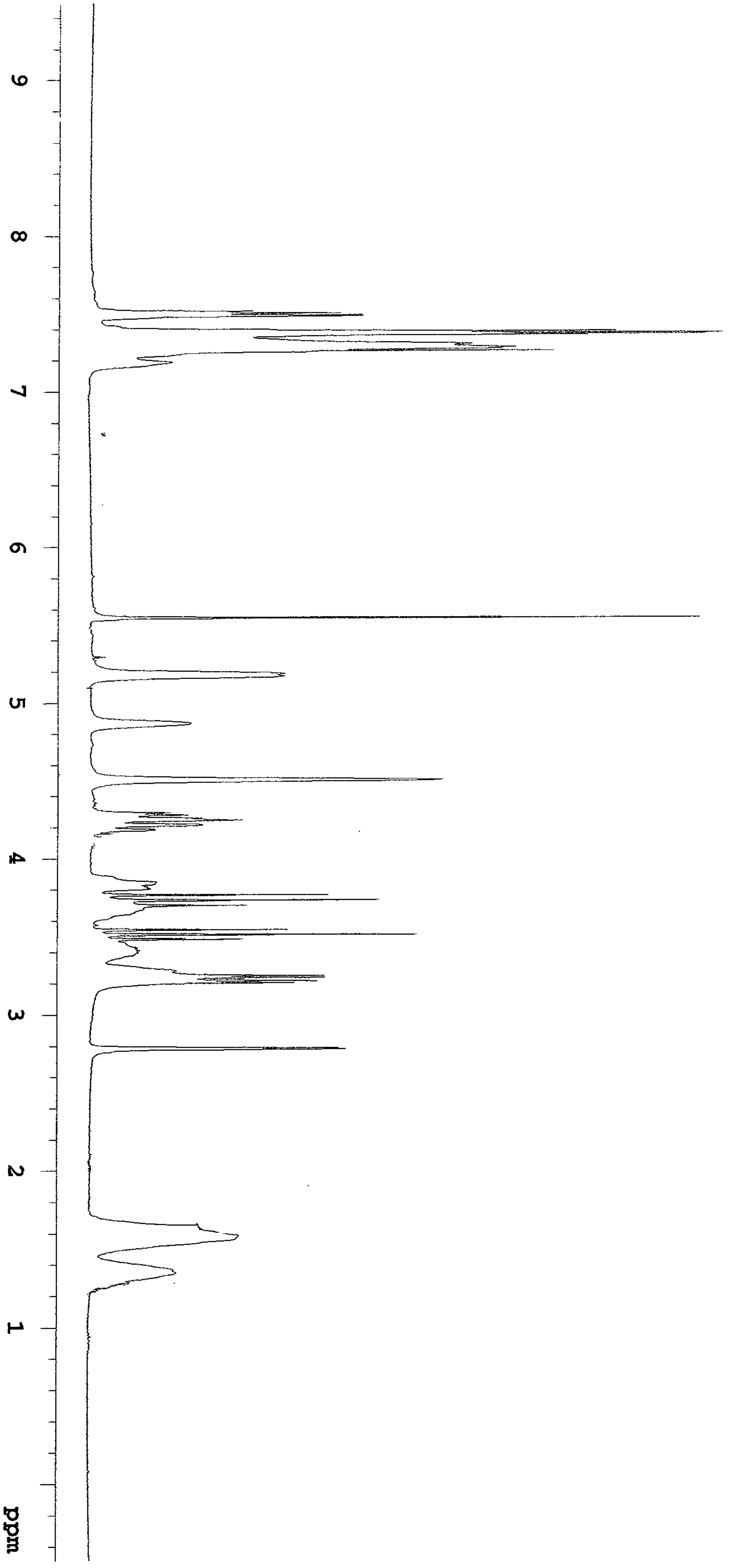
28

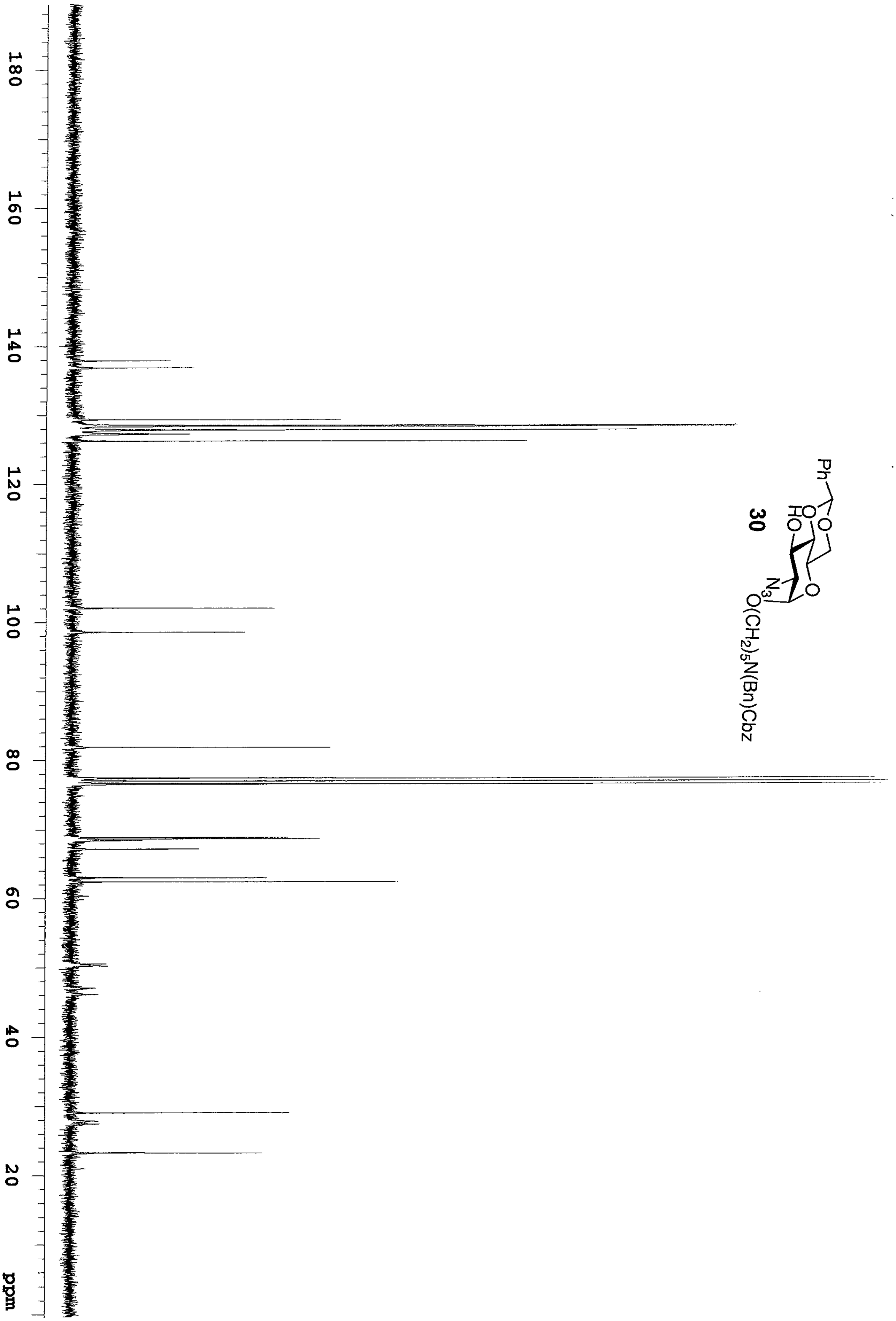

200
180
160
140
120
100
80
60
40
20
ppm
AcO
AcO
OAc
O
N_3
$O(CH_2)_5N(Bn)Cbz$

28

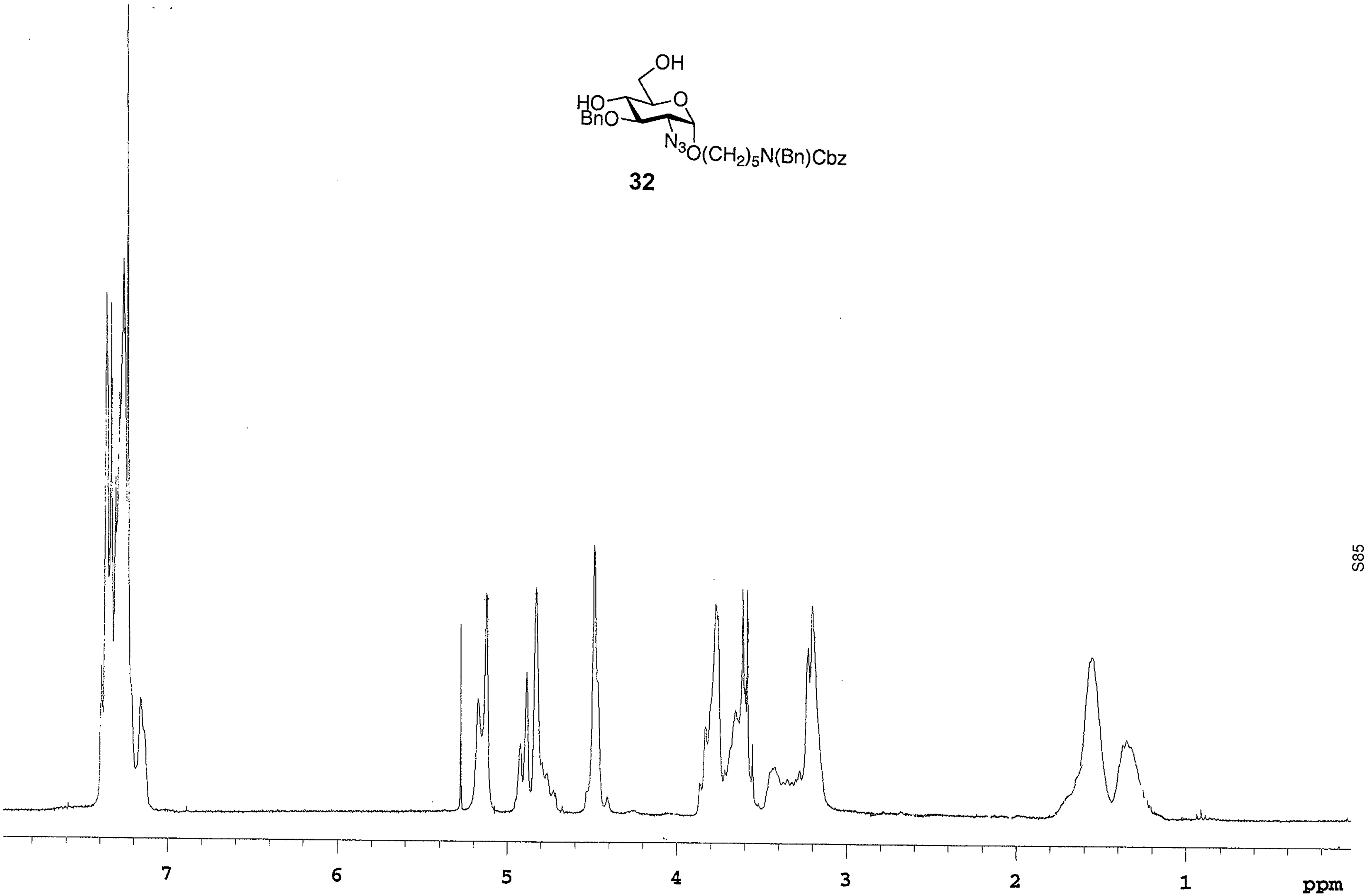


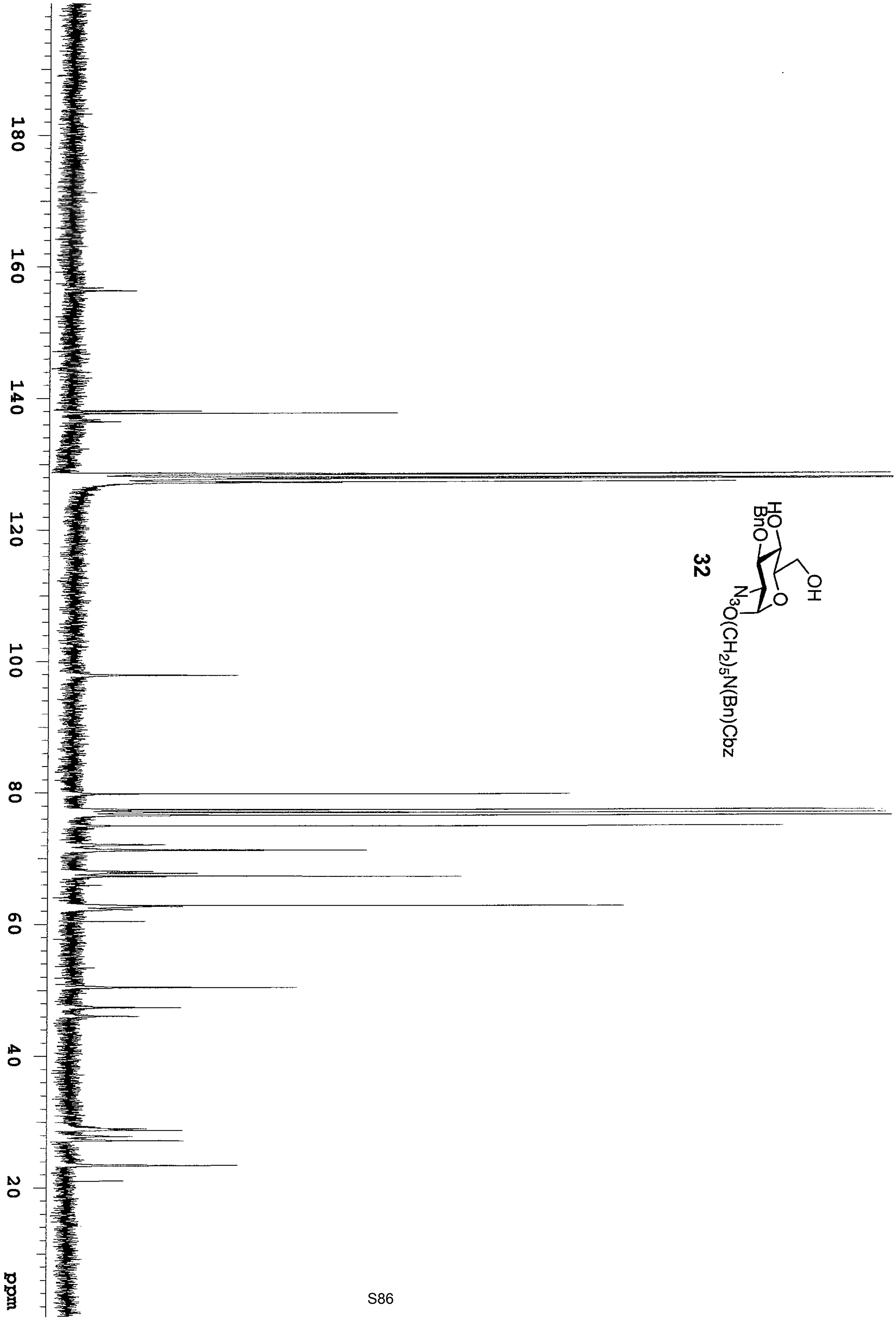
30



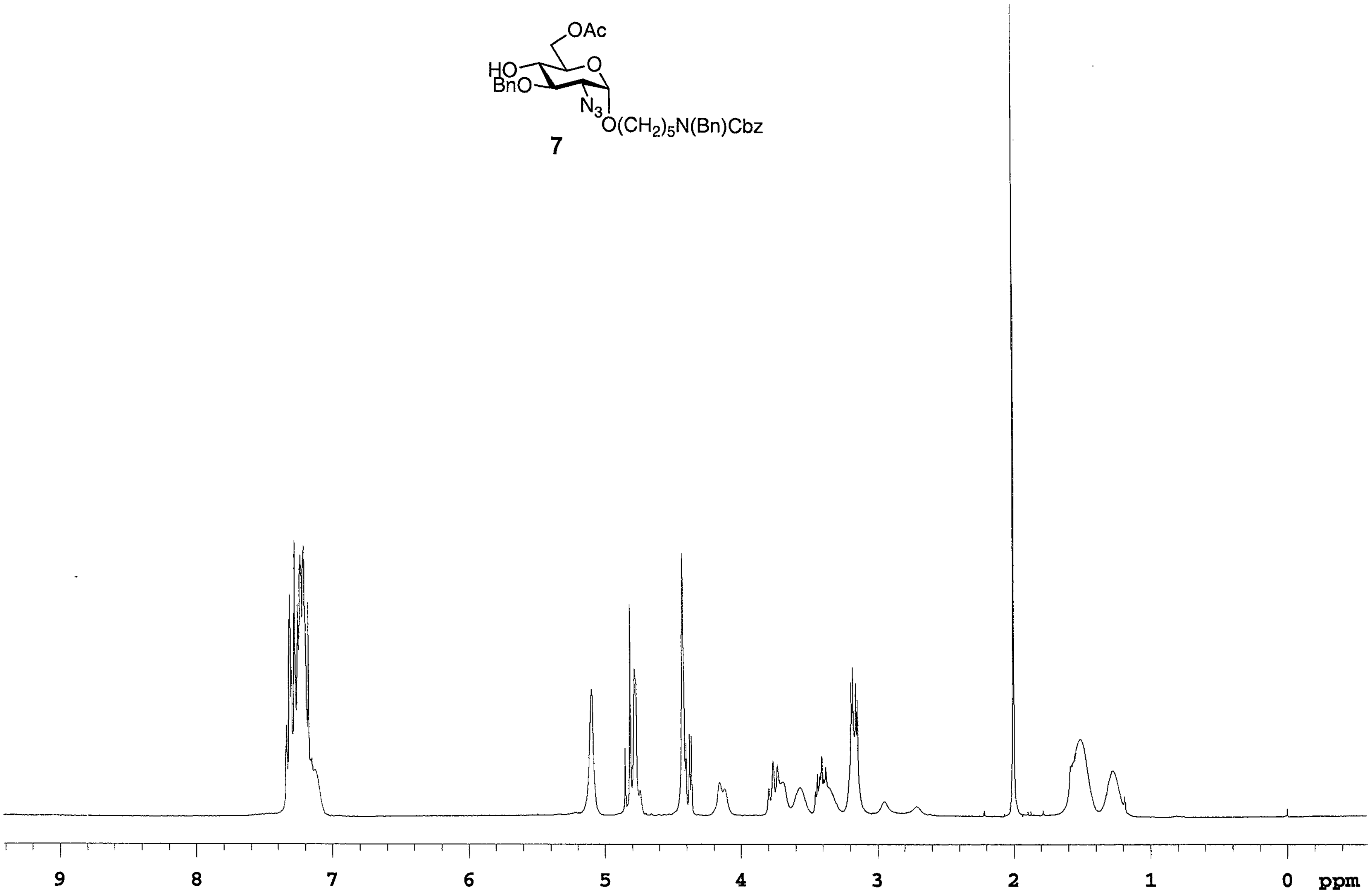


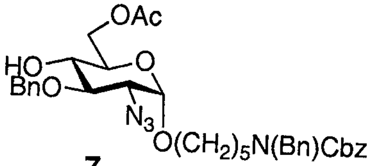
30


32

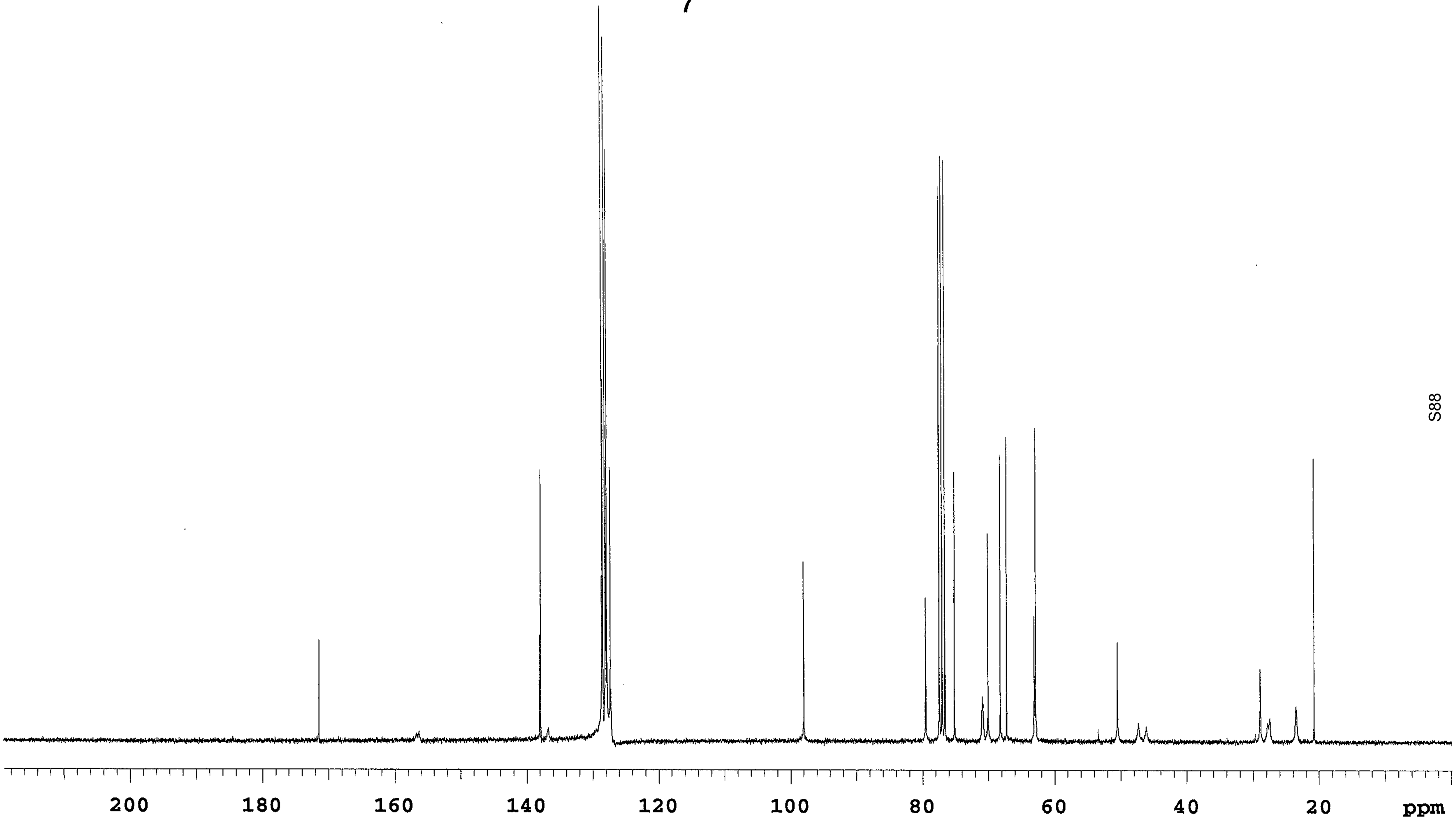


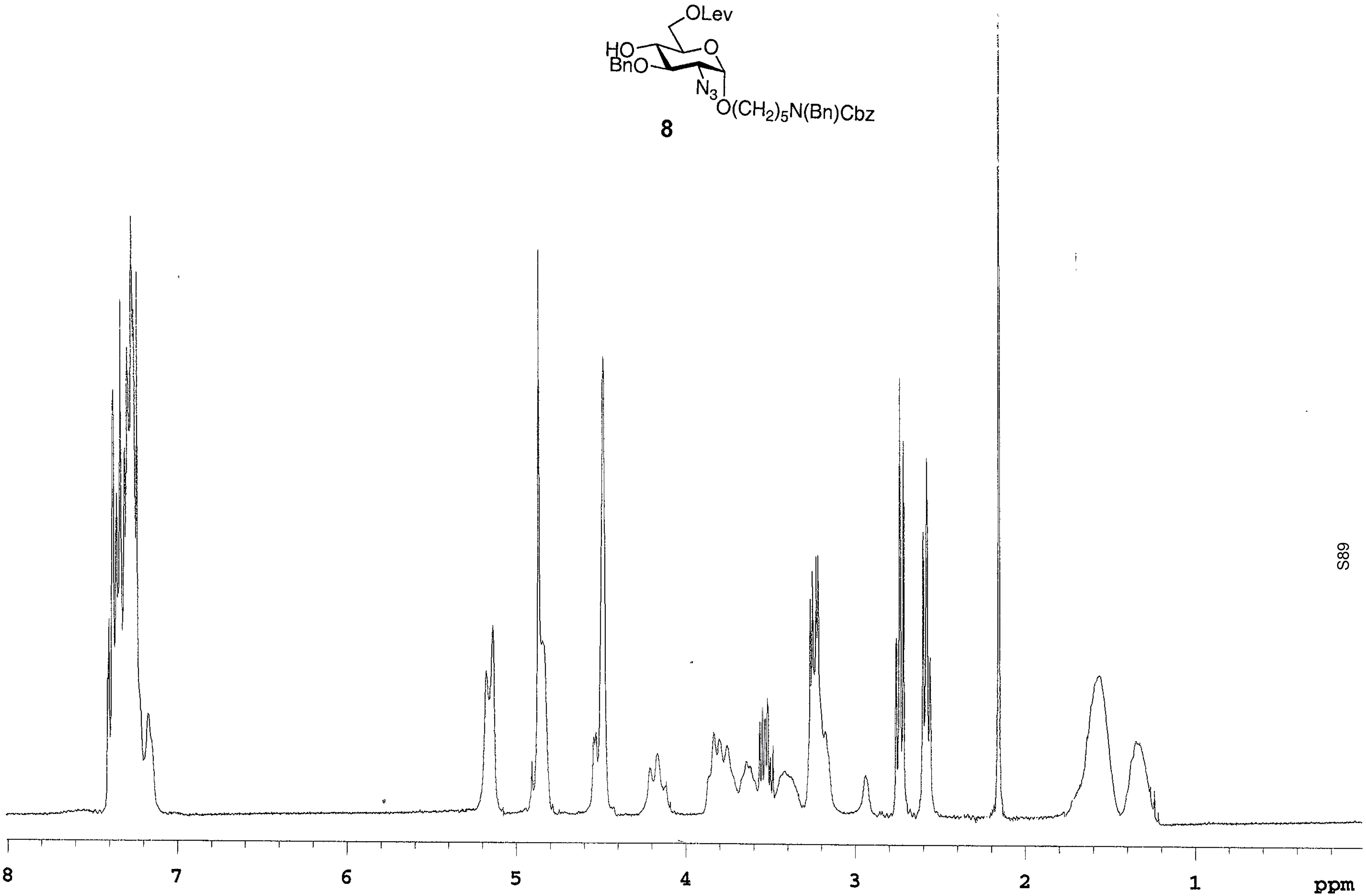
32


OAc
HO
BnO
O
N3
O(CH2)5N(Bn)Cbz
7
9
8
7
6
5
4
3
2
1
0
ppm

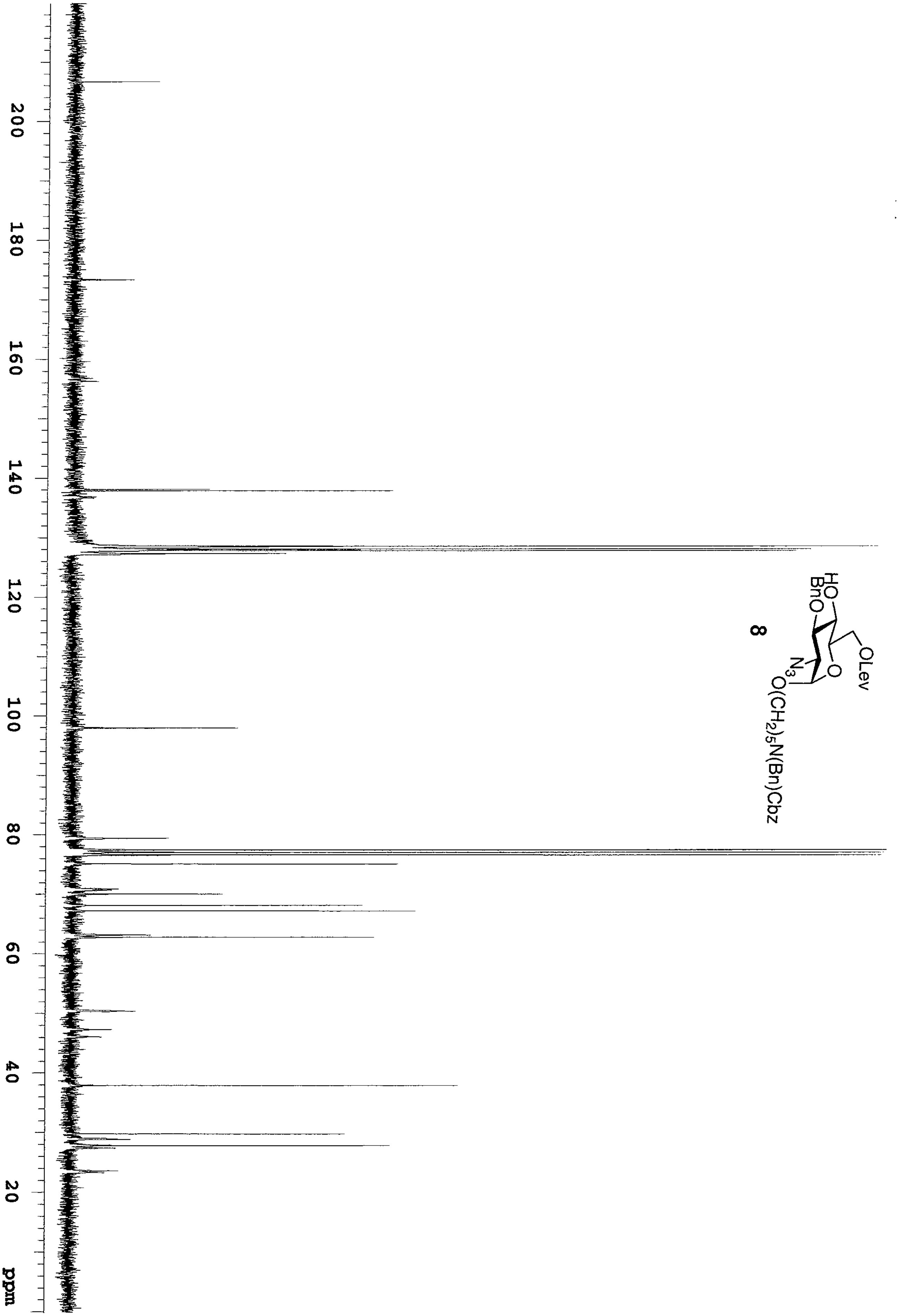

OAc
HO
BnO
O
N$_3$
O(CH$_2$)$_5$N(Bn)Cbz

7

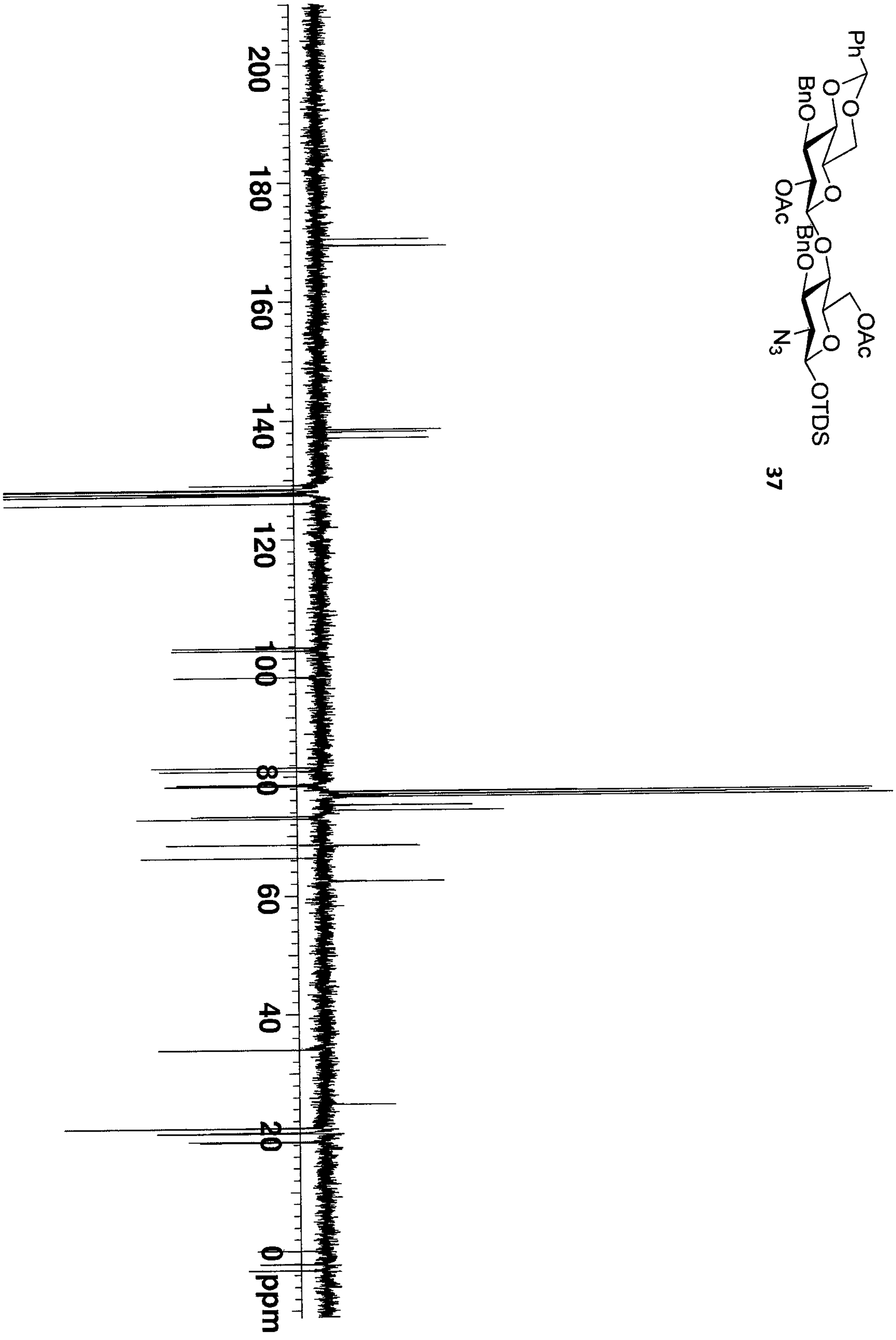

200
180
160
140
120
100
80
60
40
20
ppm



8

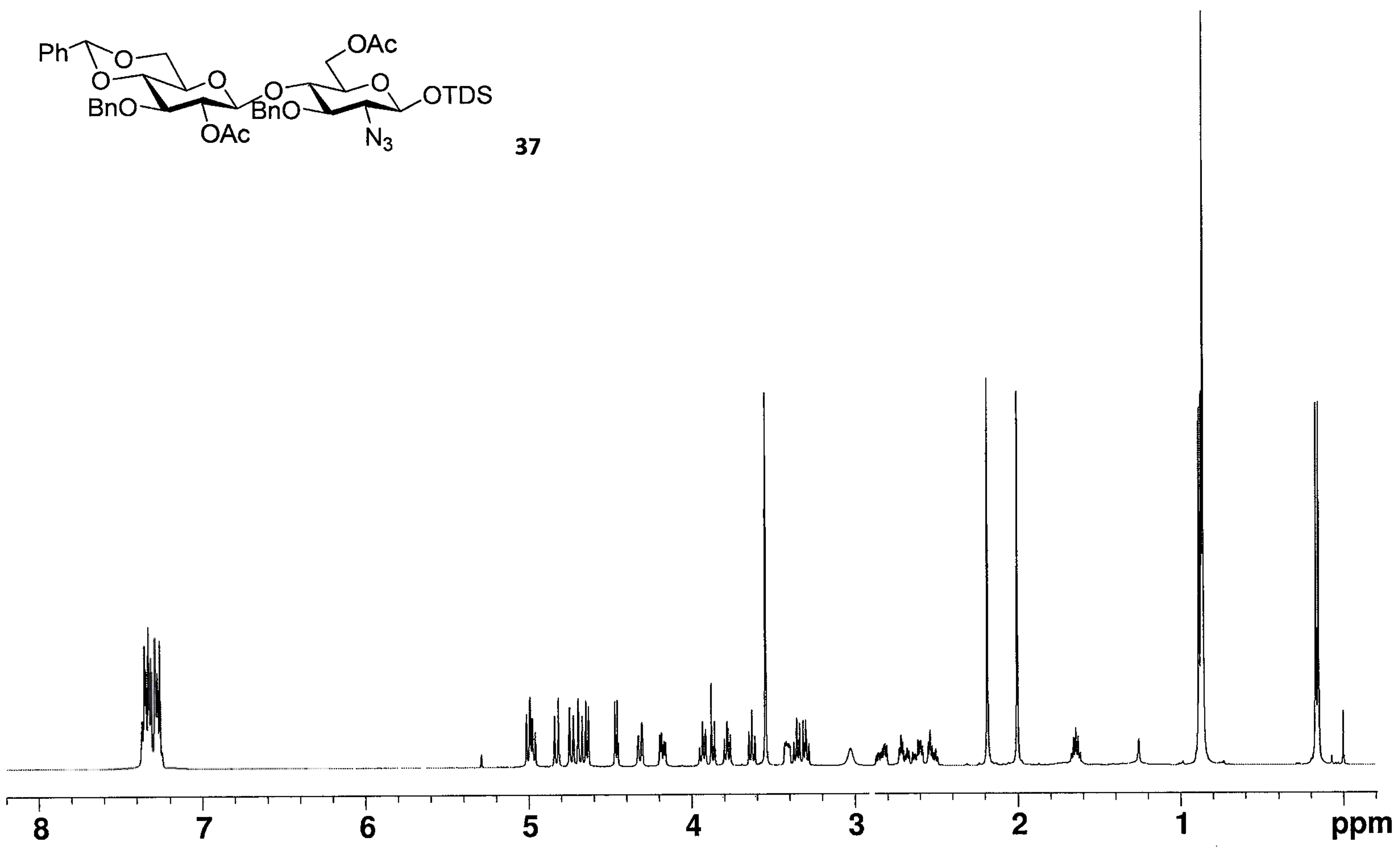


200
180
160
140
120
100
80
60
40
20
ppm
HO
BnO
OLev
O
N3
O(CH2)5N(Bn)Cbz
8

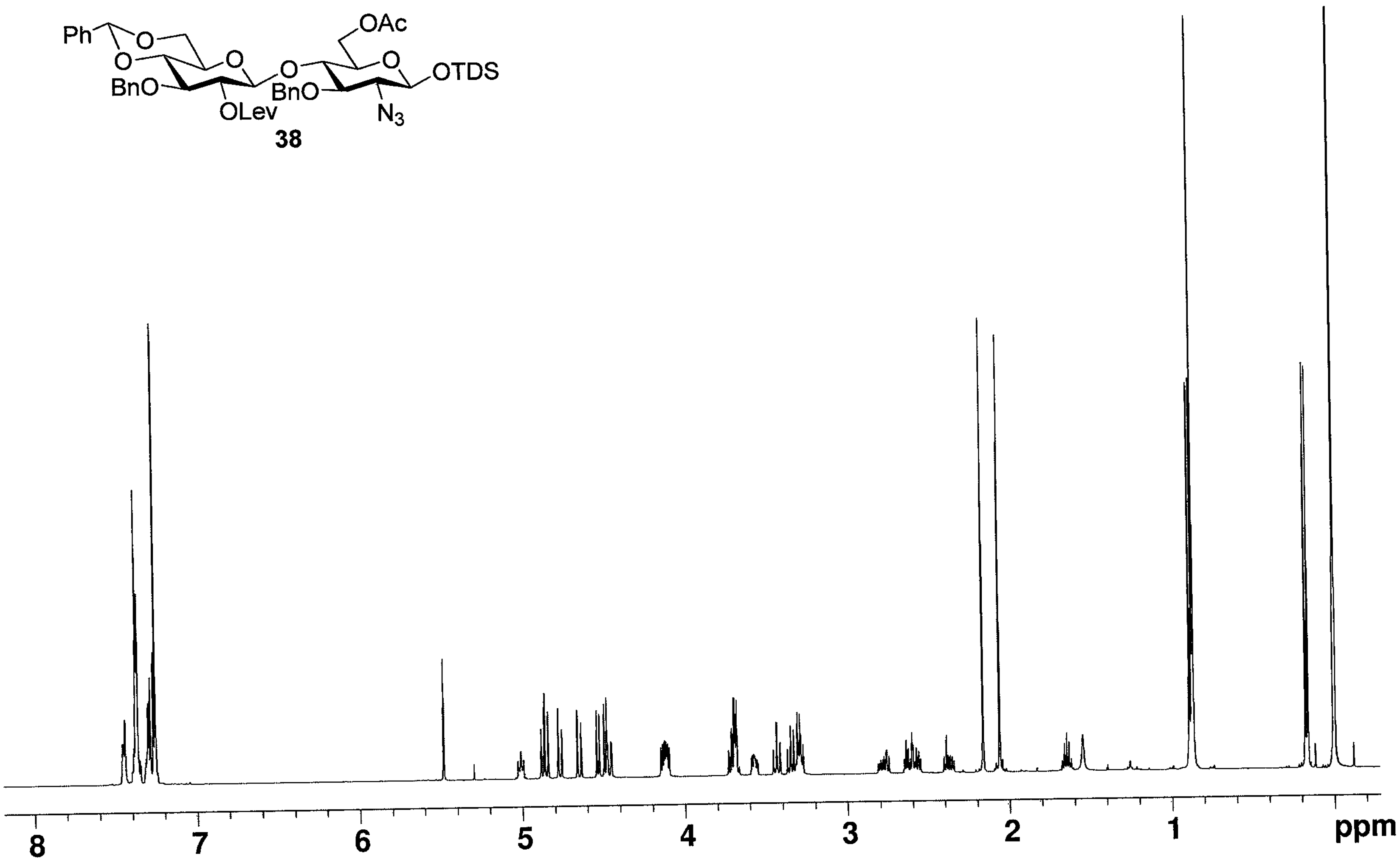

Ph
O
O
BnO
O
OAc
BnO
O
O
OAc
N_3
O
OTDS

37

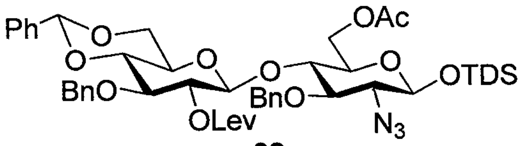
200
180
160
140
120
100
80
60
40
20
0
ppm



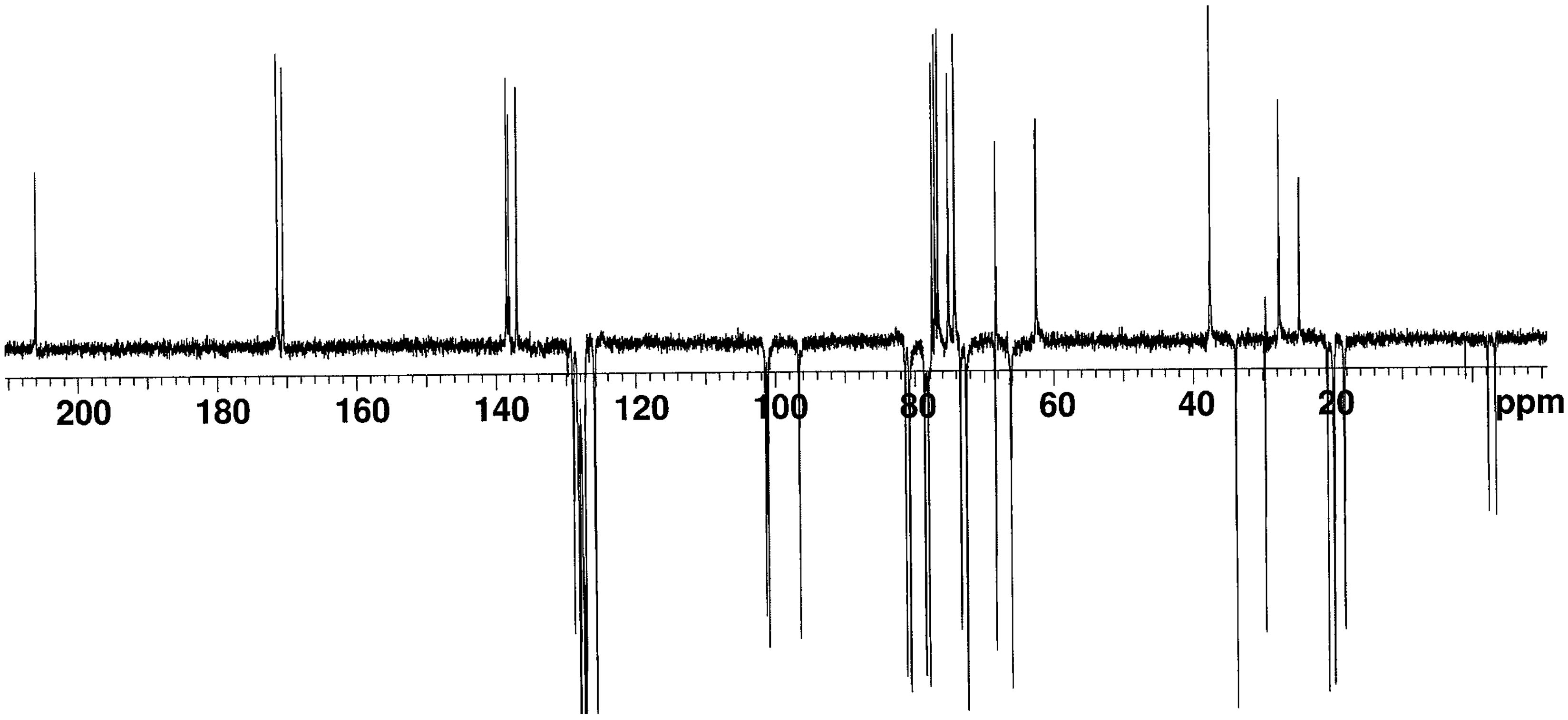
37

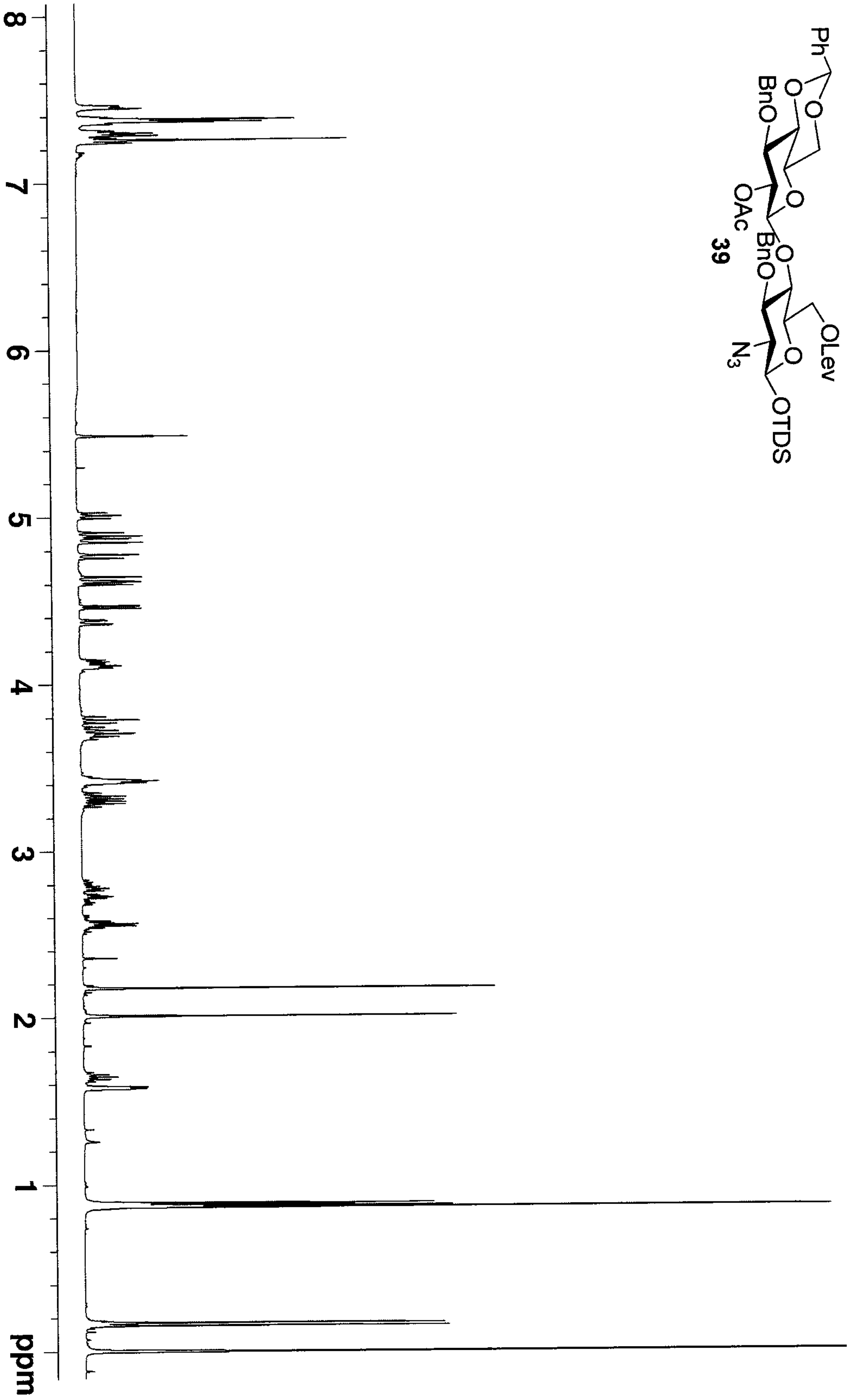


38

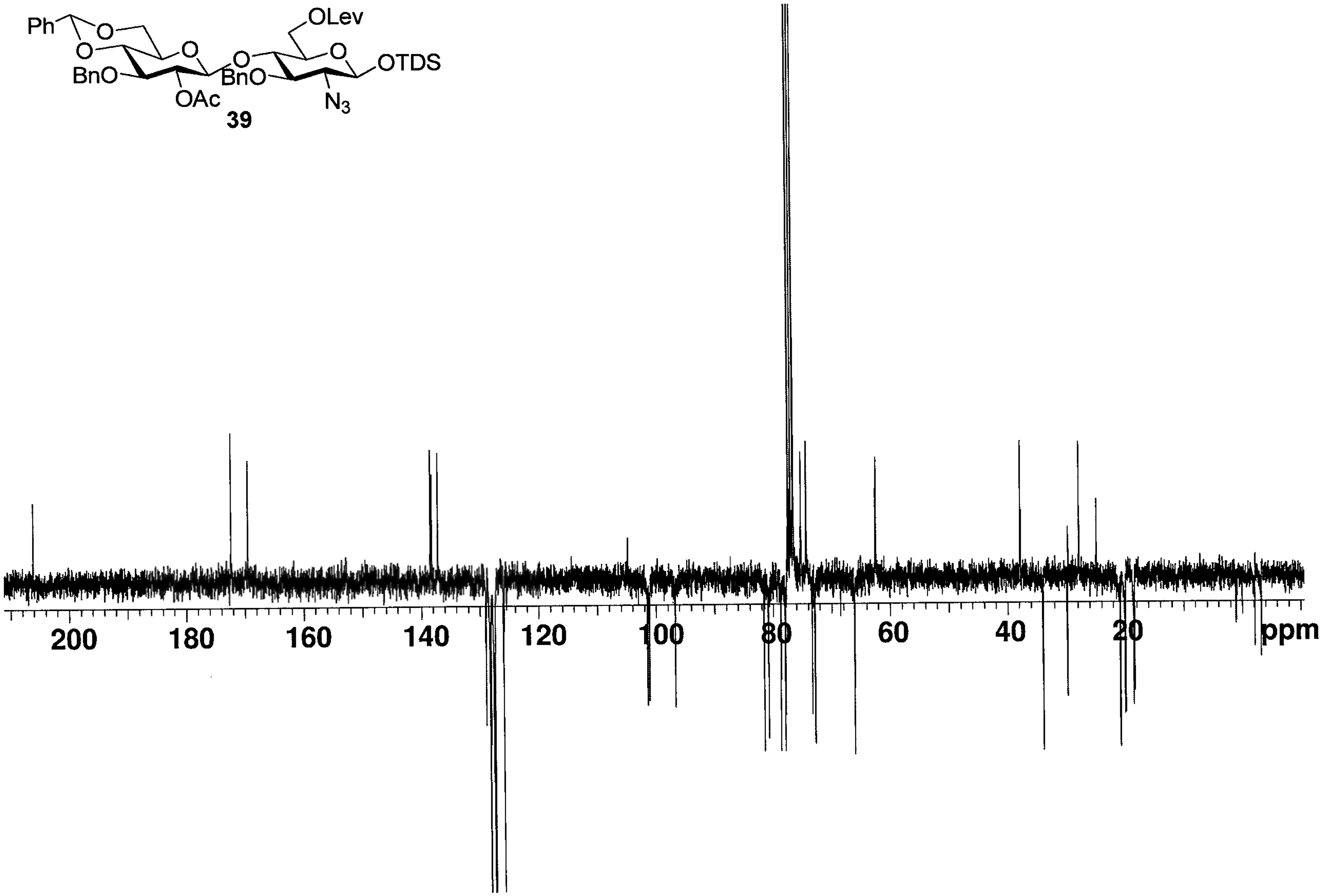

Ph
O
O
BnO
O
OLev
O
BnO
OAc
O
OTDS
N3

38


200
180
160
140
120
100
80
60
40
20
ppm

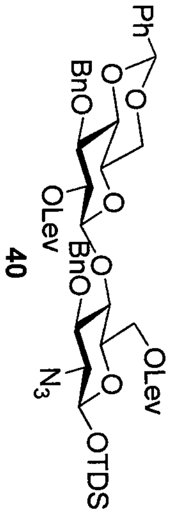


39

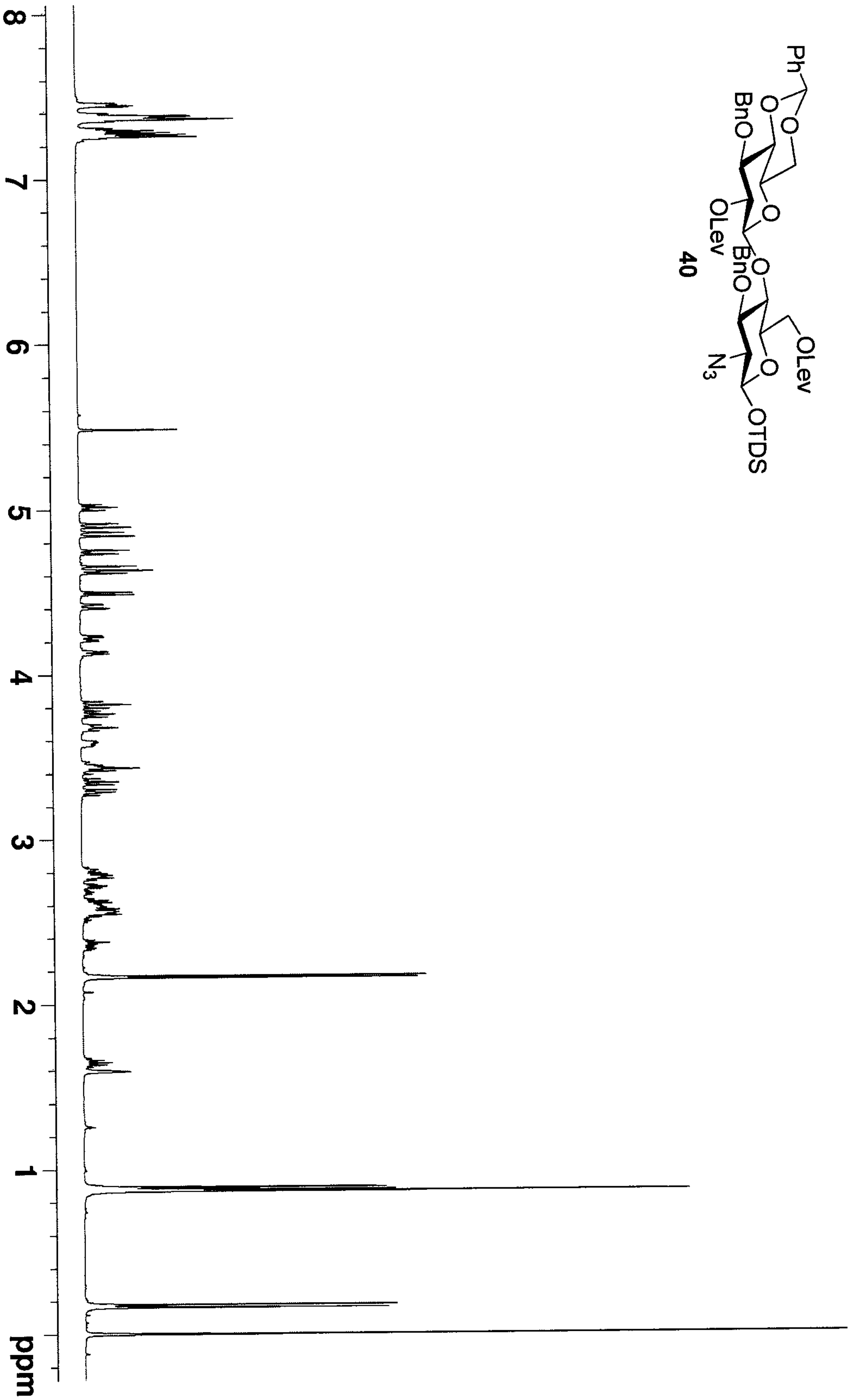


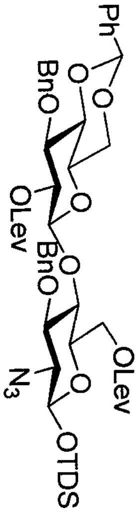
39

Ph
O
O
BnO
OAc
O
BnO
O
OLev
O
OTDS
N3
200
180
160
140
120
100
80
60
40
20
ppm

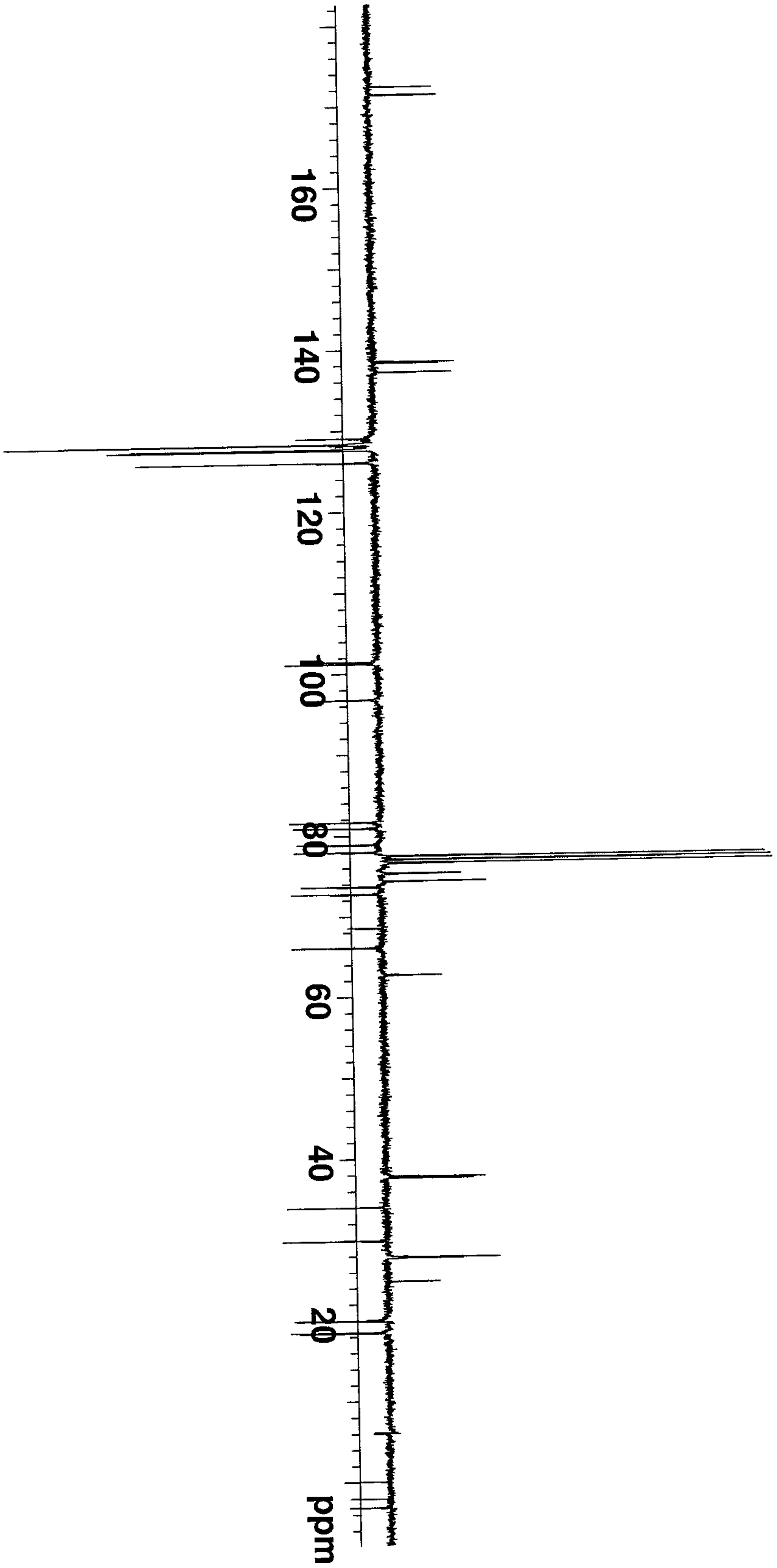


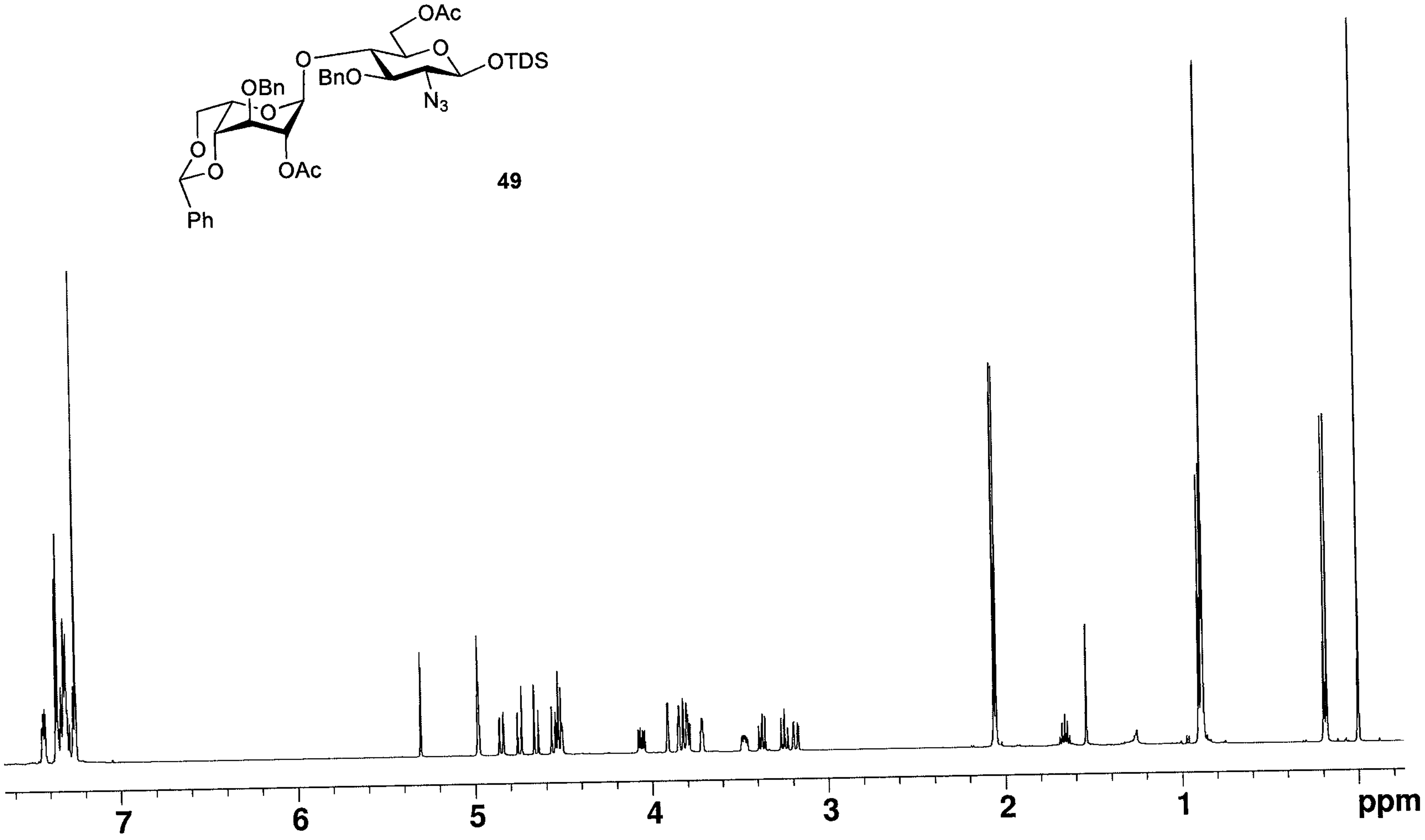
40



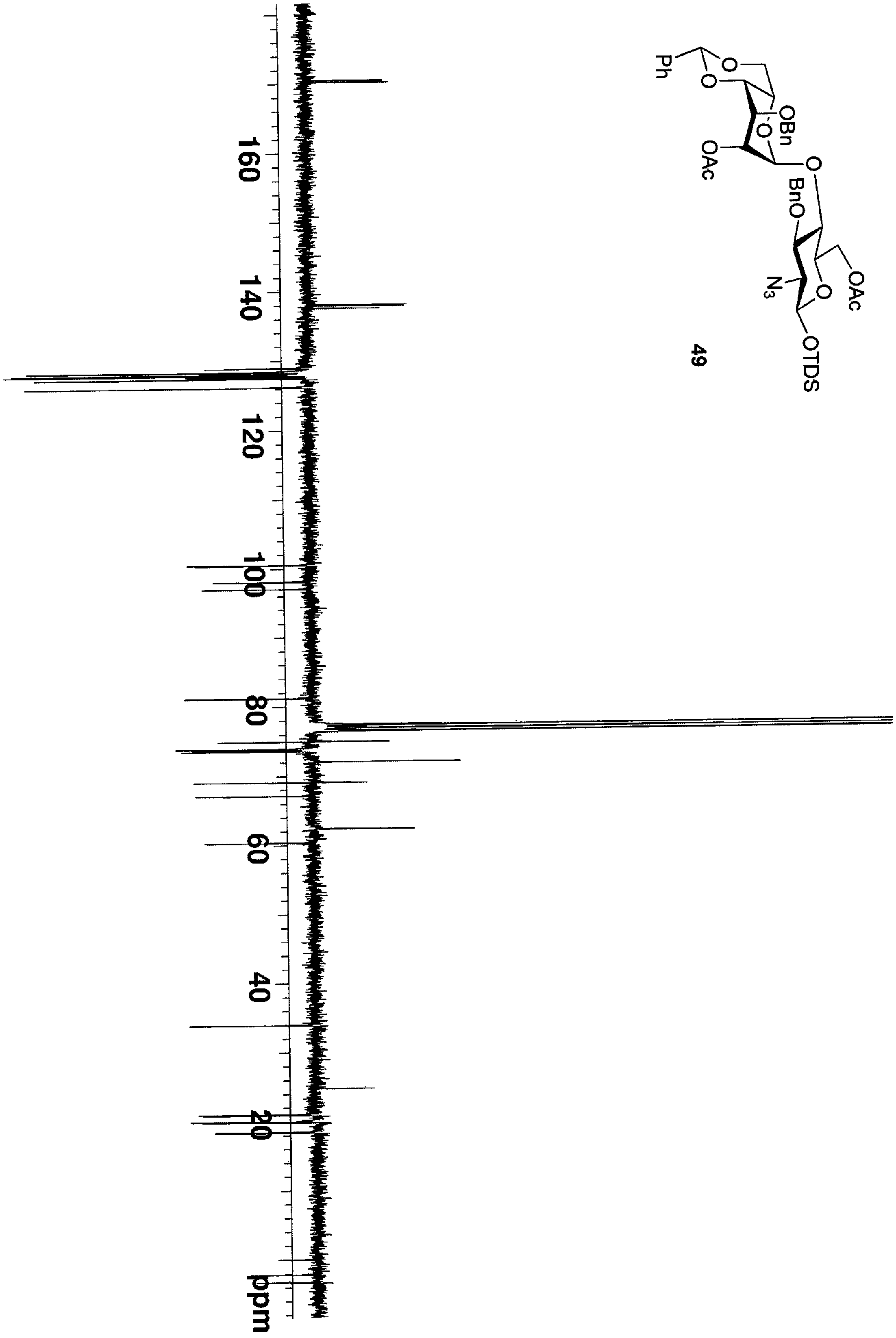

Ph
O
O
BnO
O
OLev
O
BnO
O
OLev
O
N3
OTDS

40

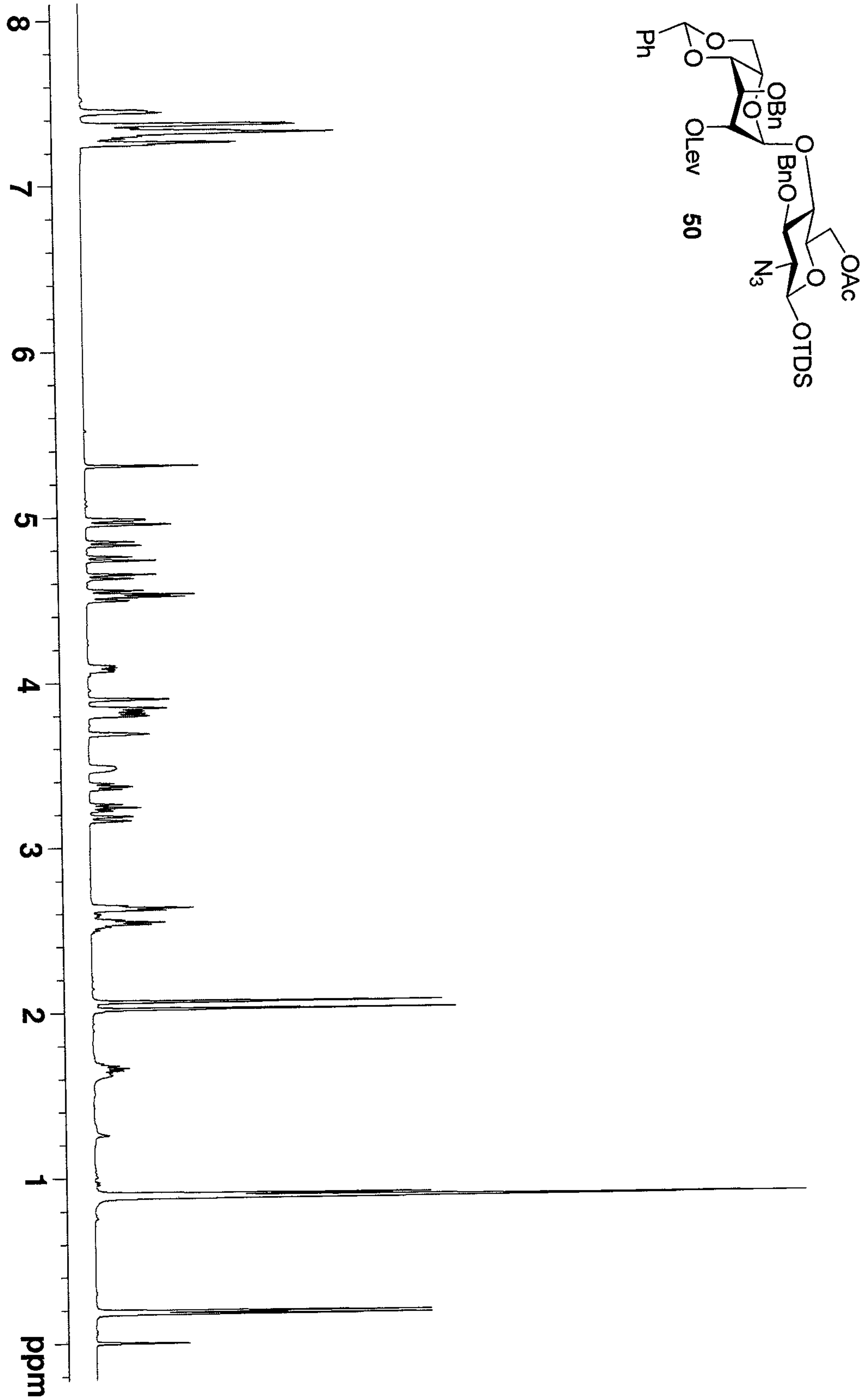

160
140
120
100
80
60
40
20
ppm



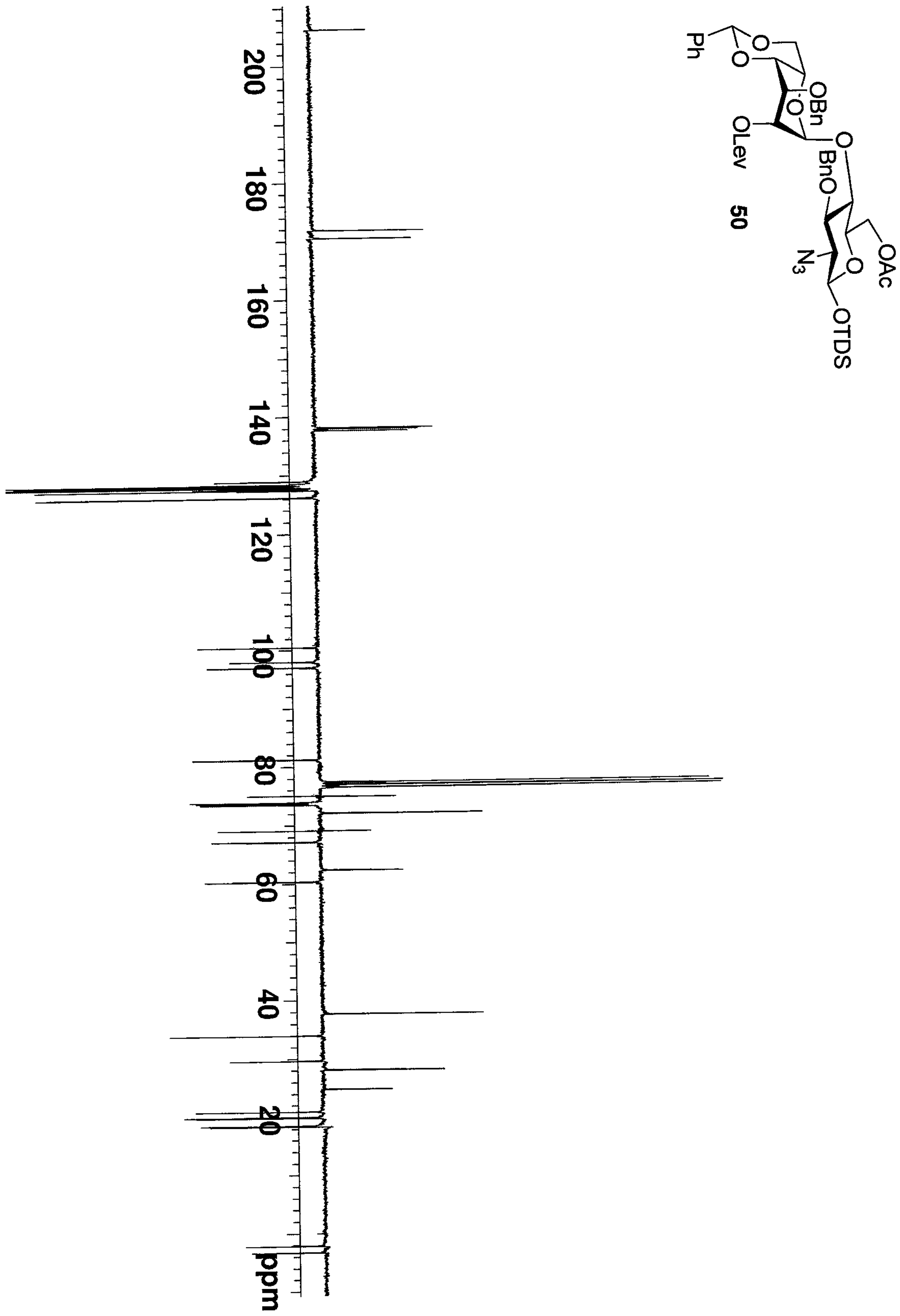
49



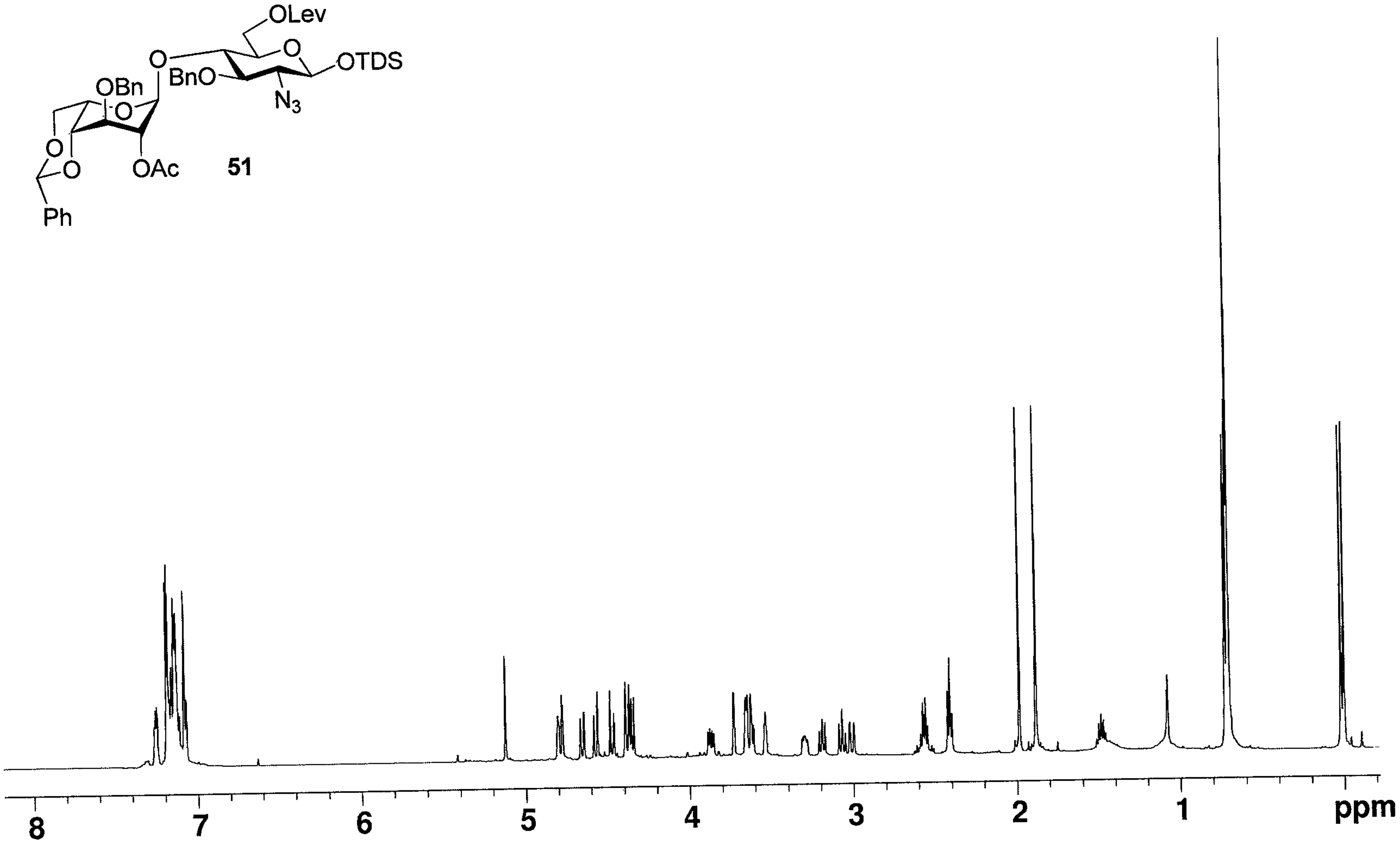
49

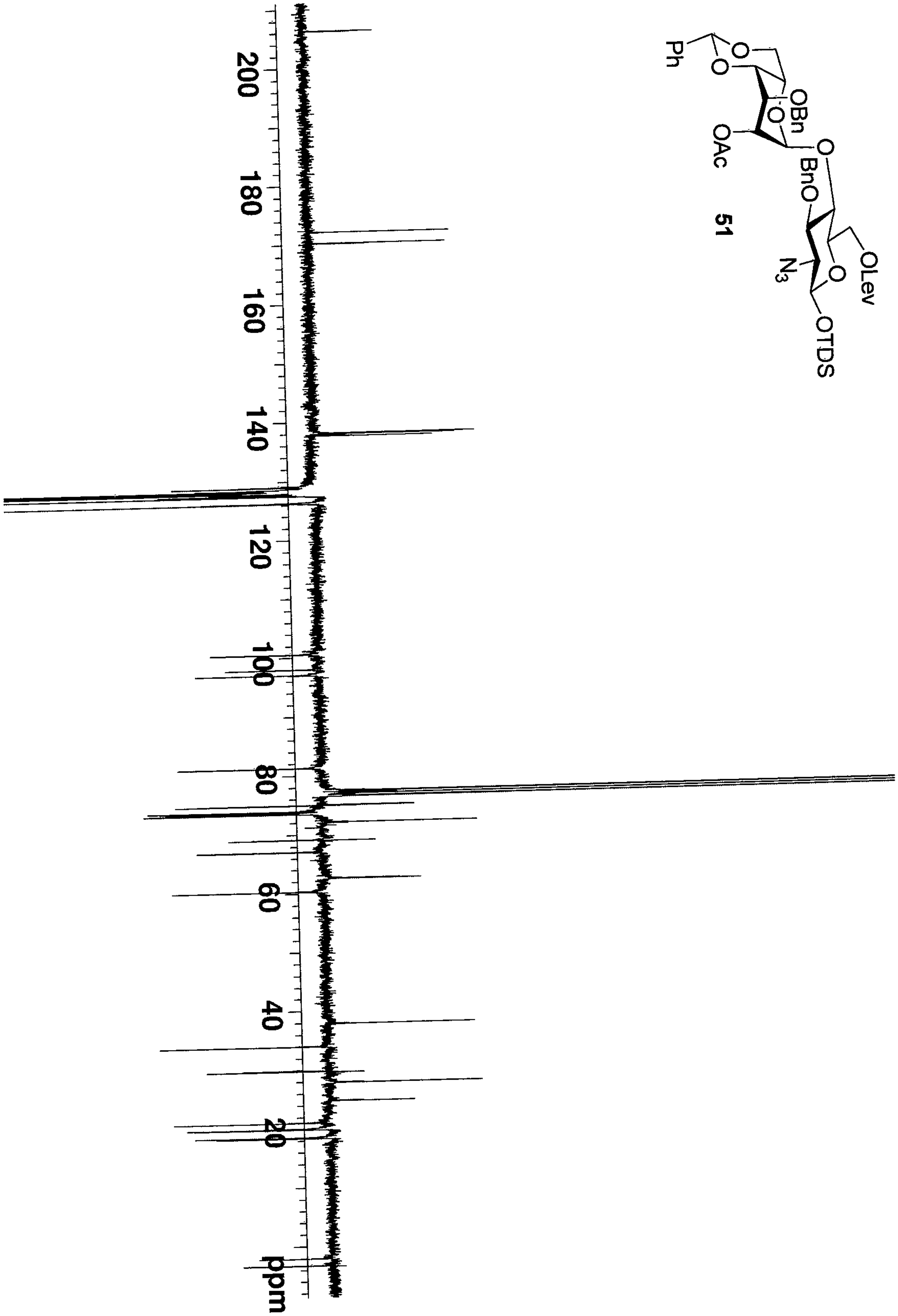


50

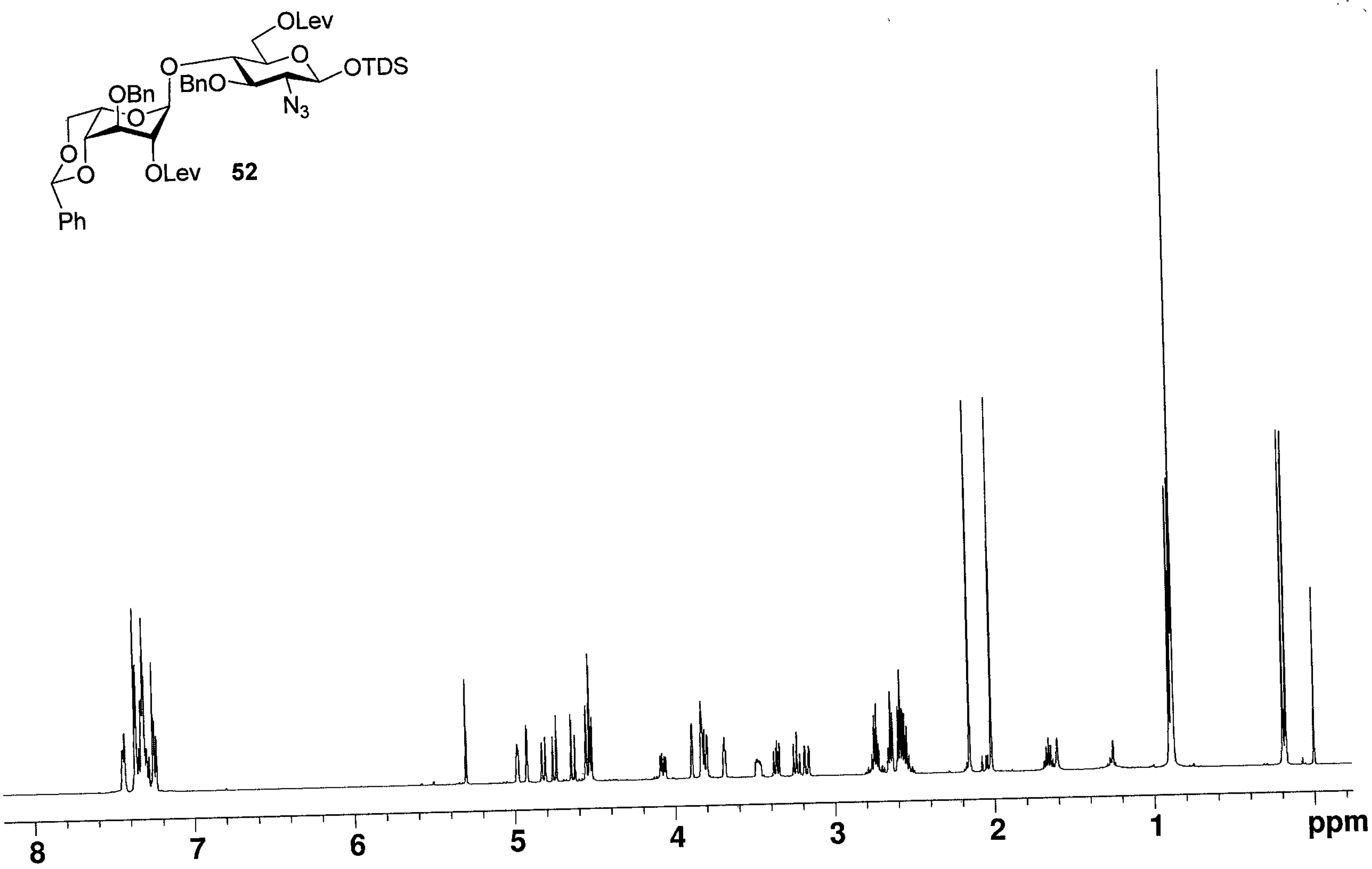

OAc
O
OTDS
N$_3$
BnO
O
OBn
O
OLev
Ph
O
O
200
180
160
140
120
100
80
60
40
20
ppm

50

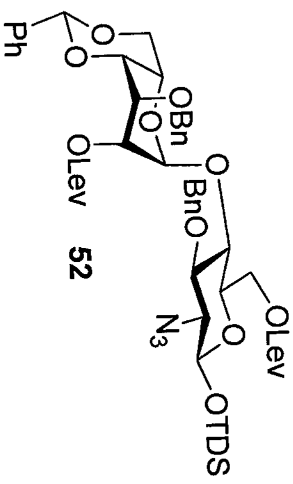

51


OLev
O
OTDS
N3
BnO
O
OBn
O
O
O
Ph
OAc
200
180
160
140
120
100
80
60
40
20
ppm

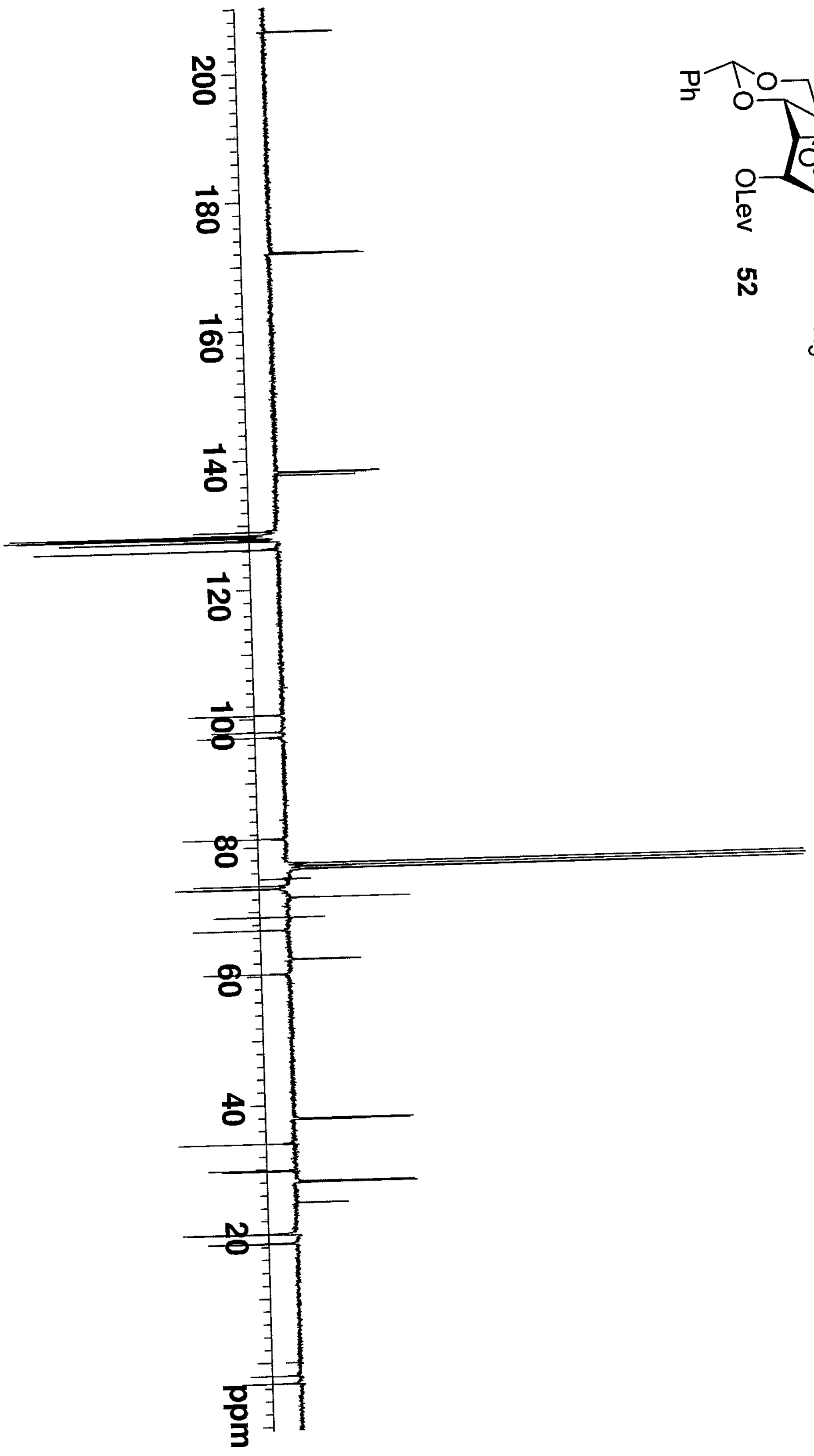
51

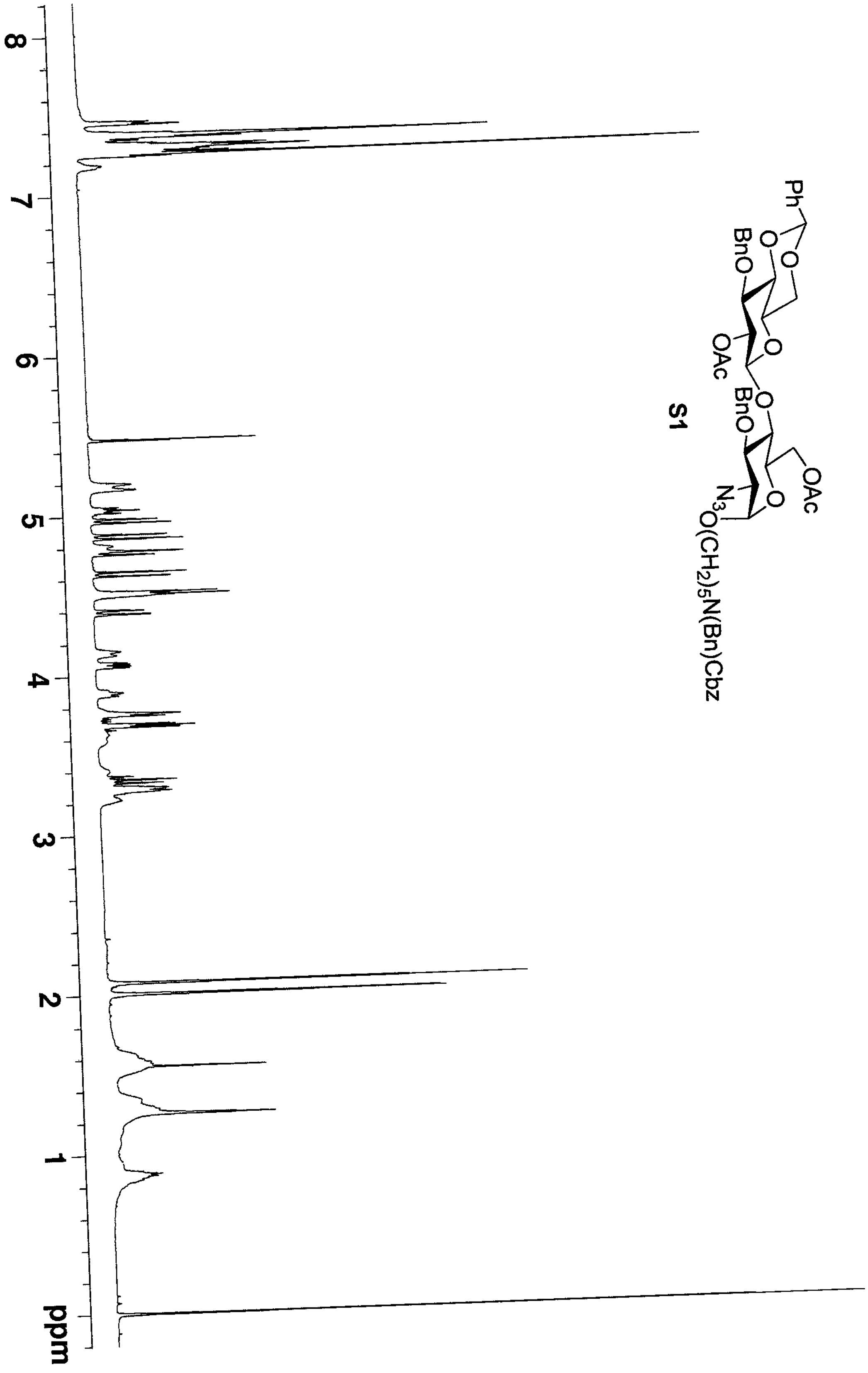


52

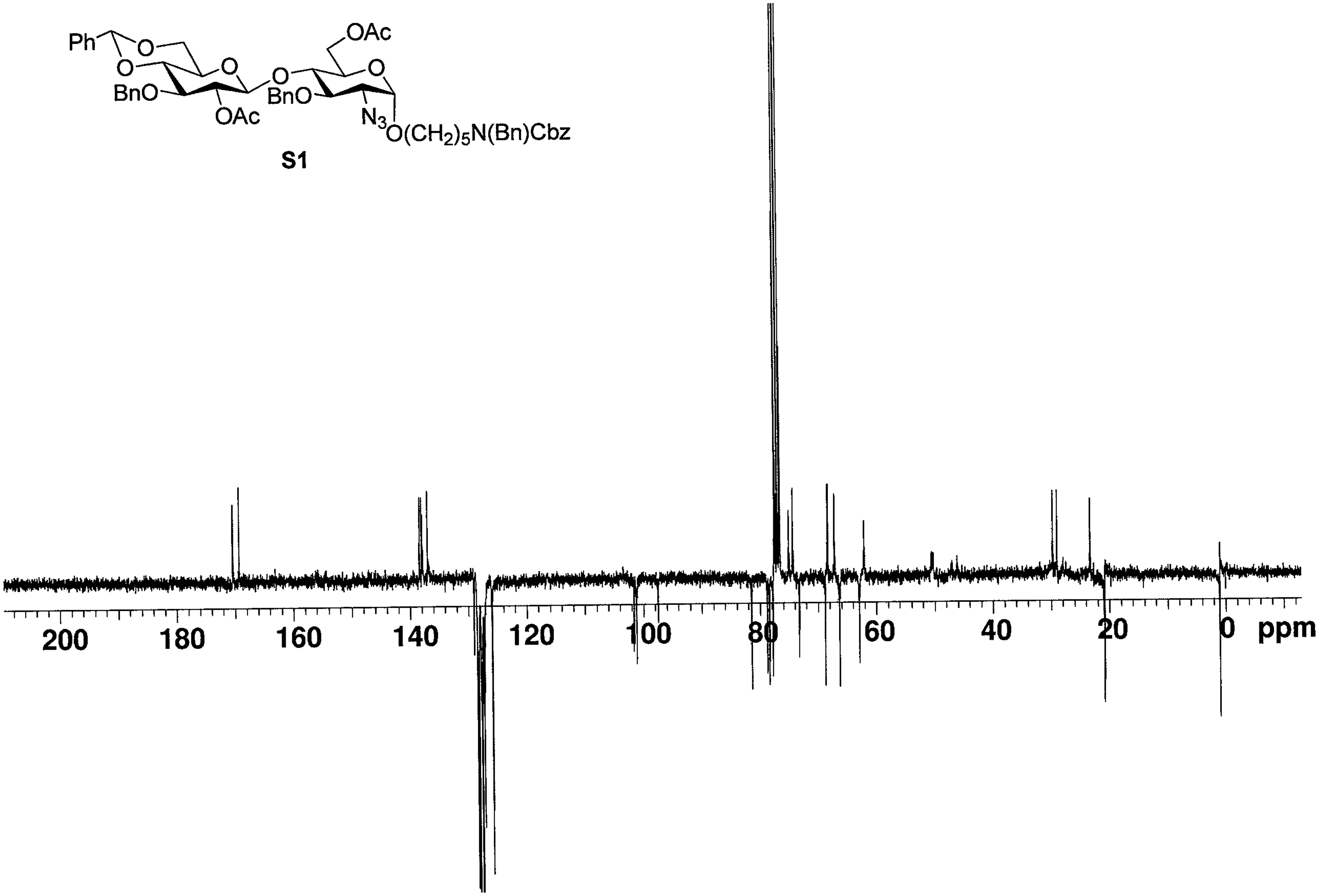

OLev
OTDS
O
N3
BnO
O
O
OBn
O
O
OLev
Ph

52

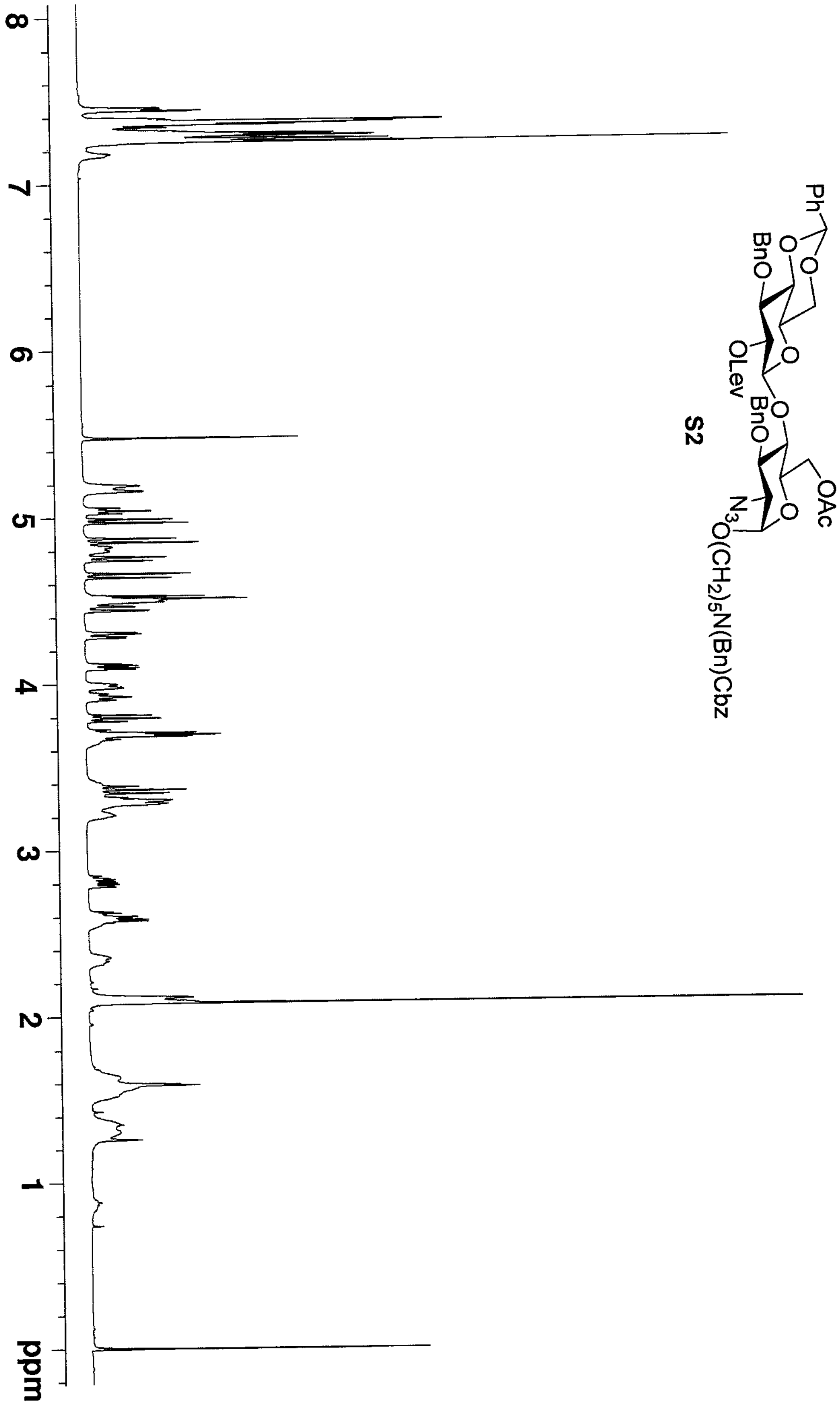

200
180
160
140
120
100
80
60
40
20
ppm



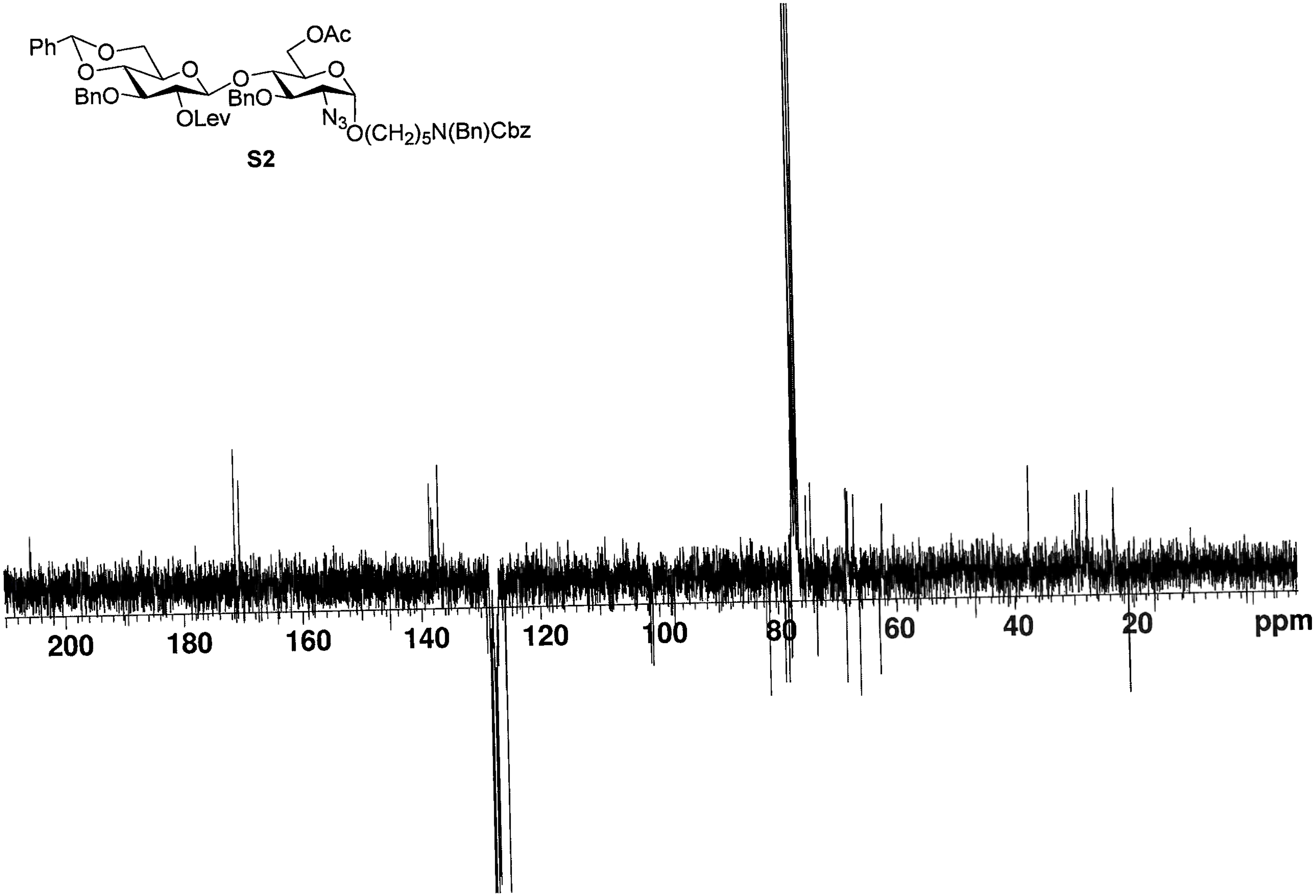
S1


Ph
O
O
BnO
OAc
O
OAc
O
BnO
N_3
$O(CH_2)_5N(Bn)Cbz$
200
180
160
140
120
100
80
60
40
20
0
ppm

S1

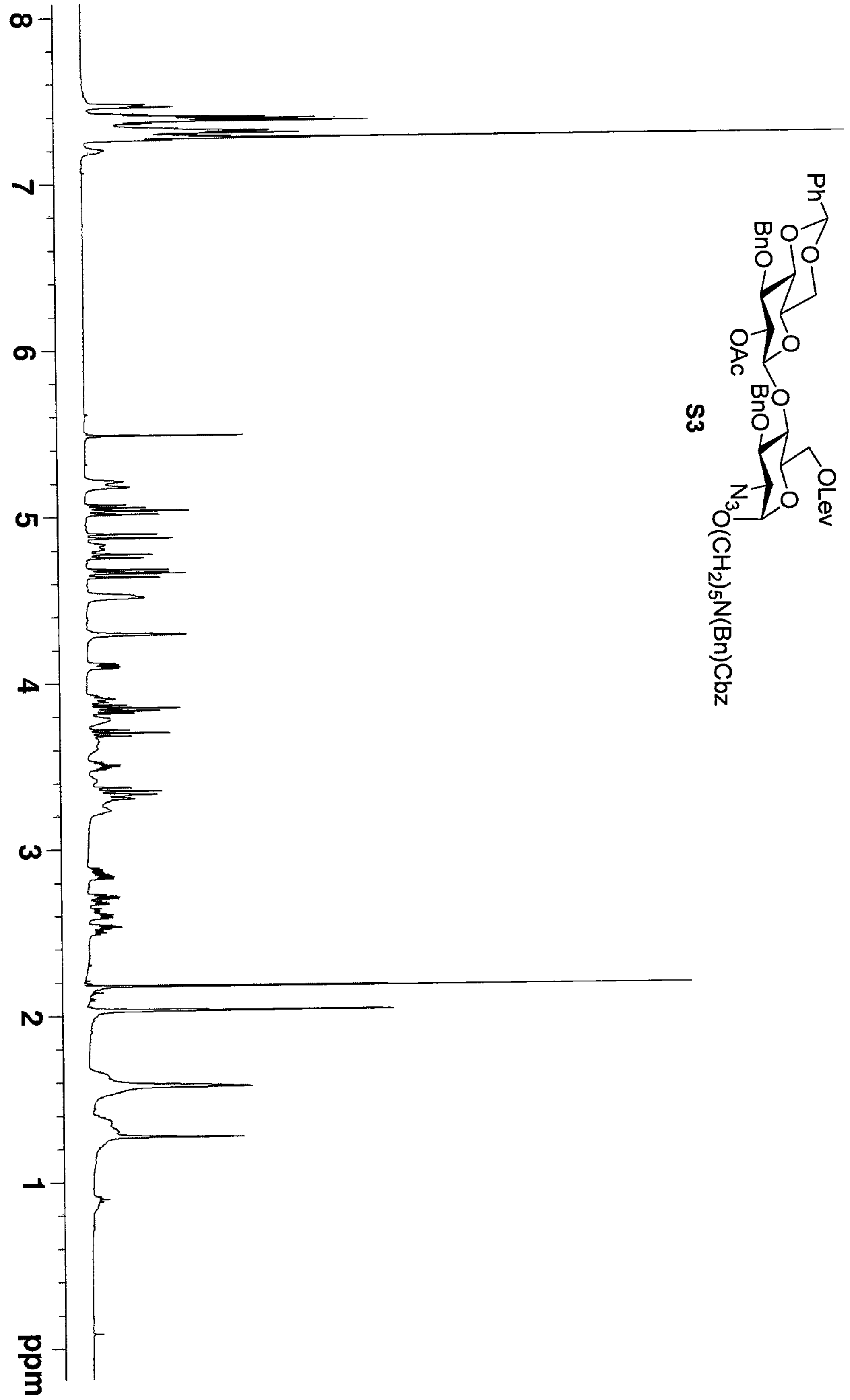


S2

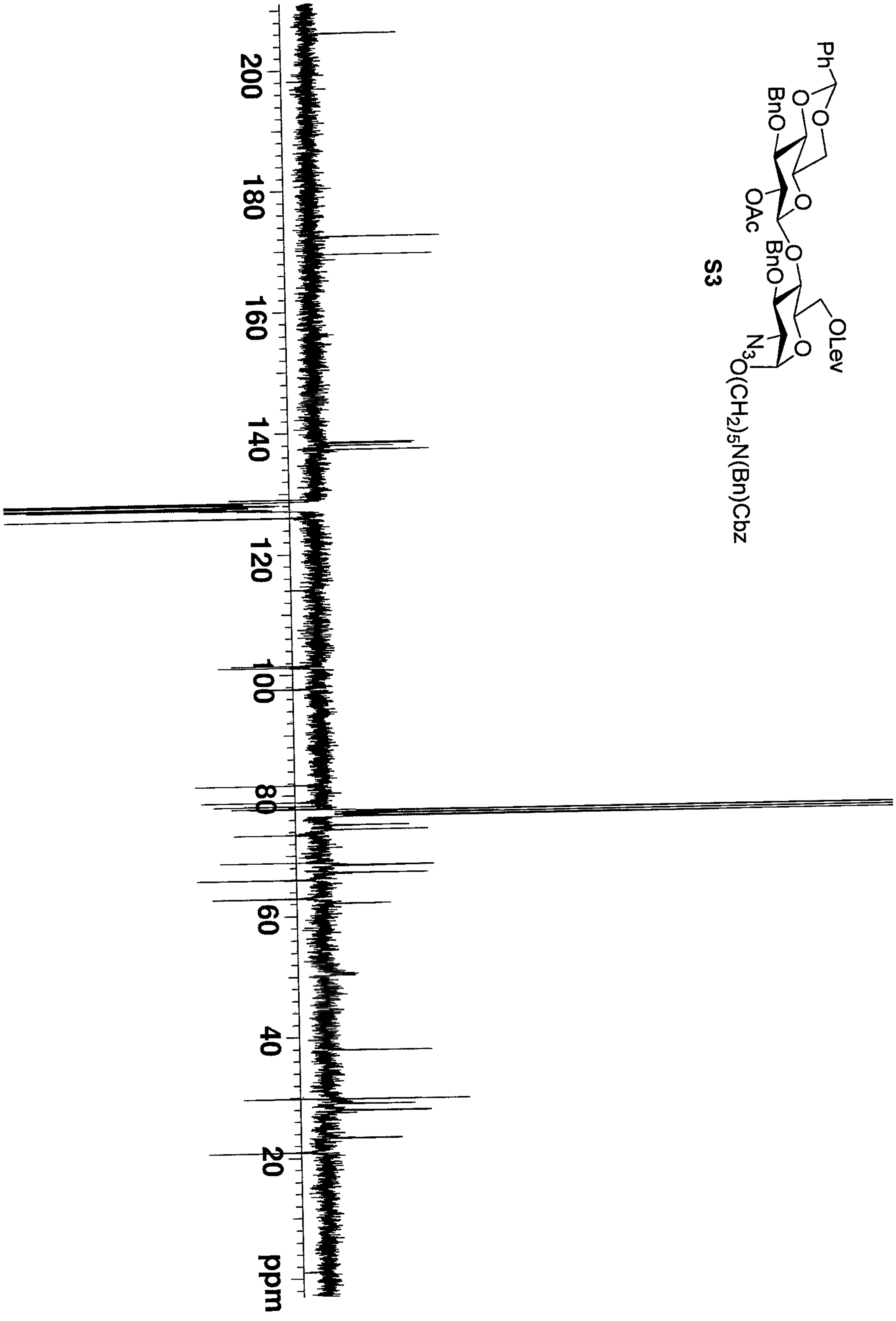

Ph
O
O
BnO
OLev
O
O
BnO
OAc
O
N3
O(CH2)5N(Bn)Cbz

S2

200
180
160
140
120
100
80
60
40
20
ppm

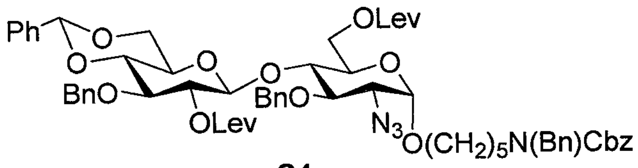


S3

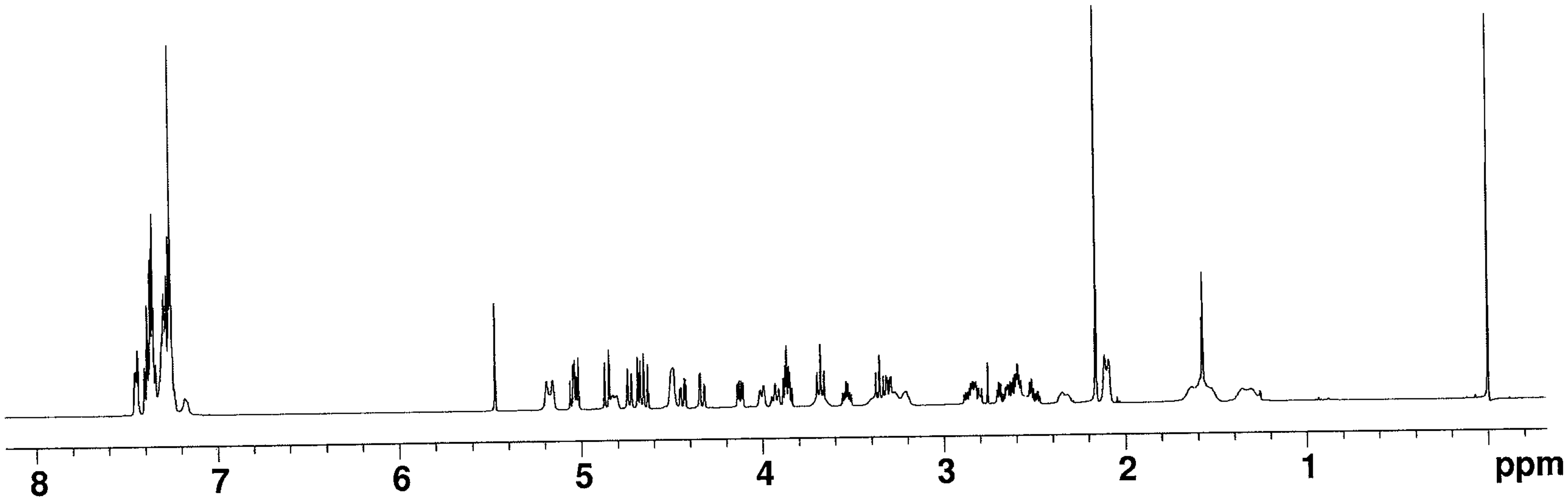


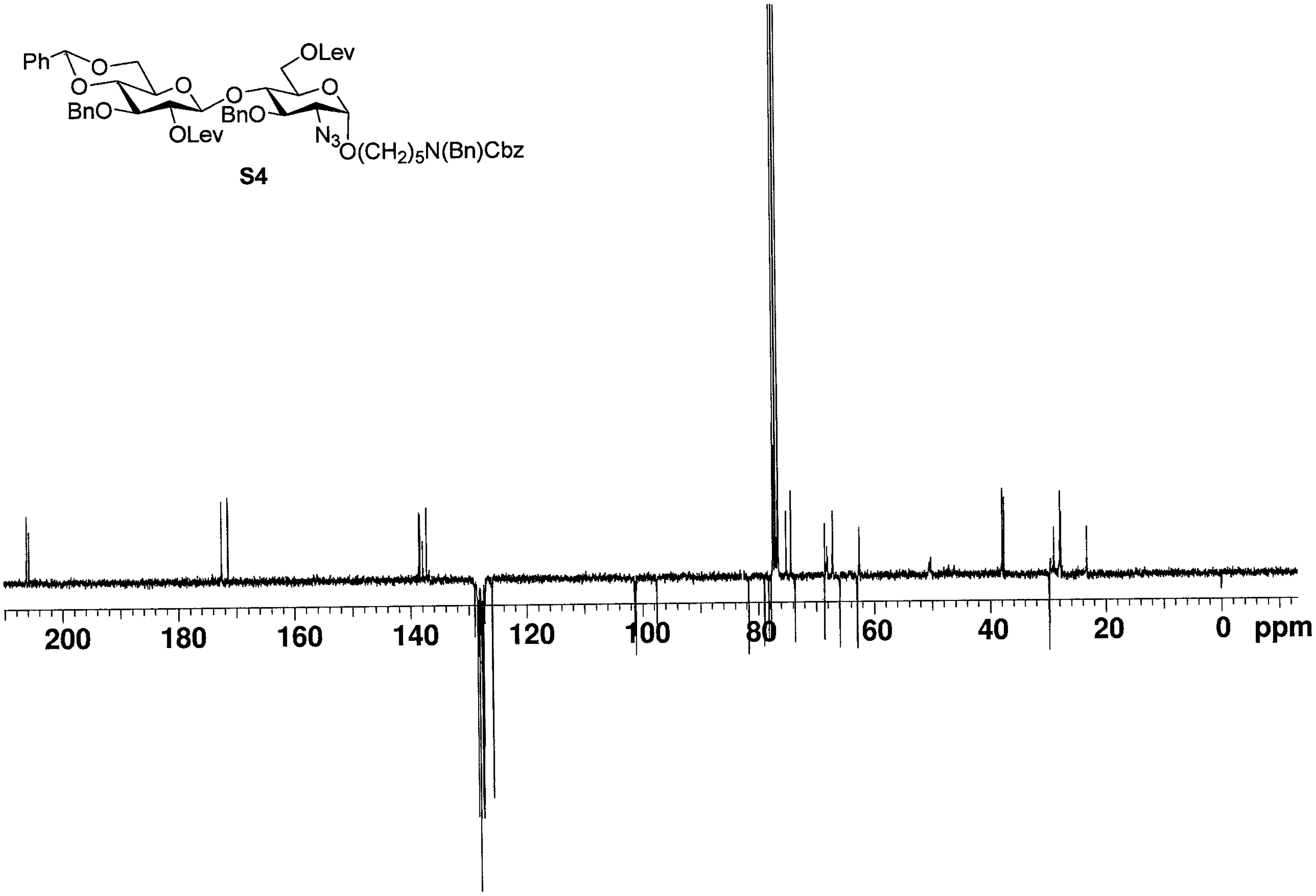
S3

Ph
O
O
BnO
OAc
O
O
BnO
O
OLev
N3
O(CH2)5N(Bn)Cbz
200
180
160
140
120
100
80
60
40
20
ppm

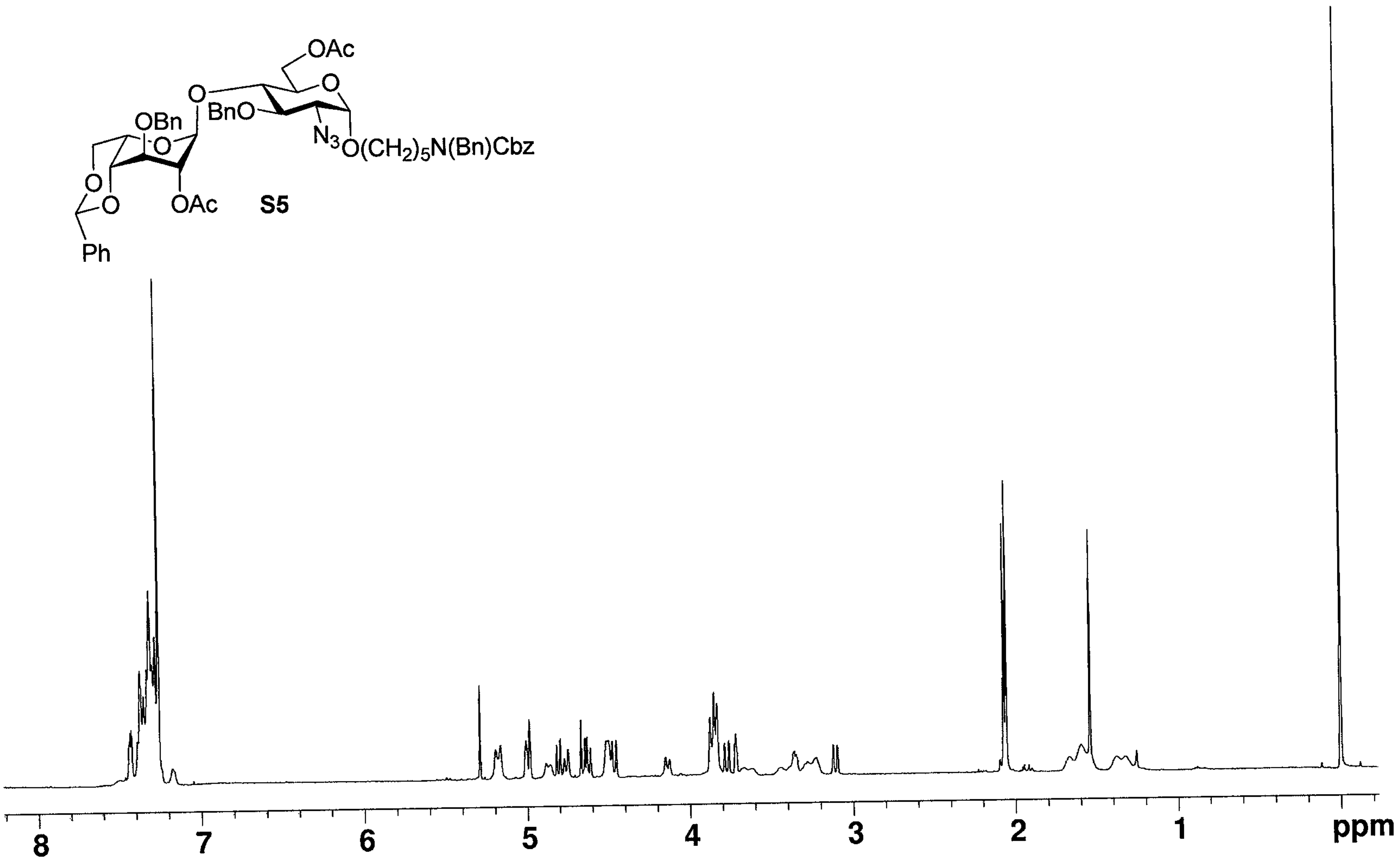


S4

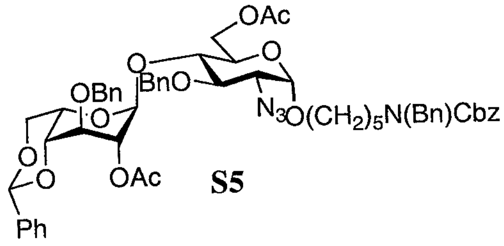



Ph
O
O
BnO
O
OLev
O
BnO
OLev
O
N3
O(CH2)5N(Bn)Cbz
200
180
160
140
120
100
80
60
40
20
0
ppm

S4



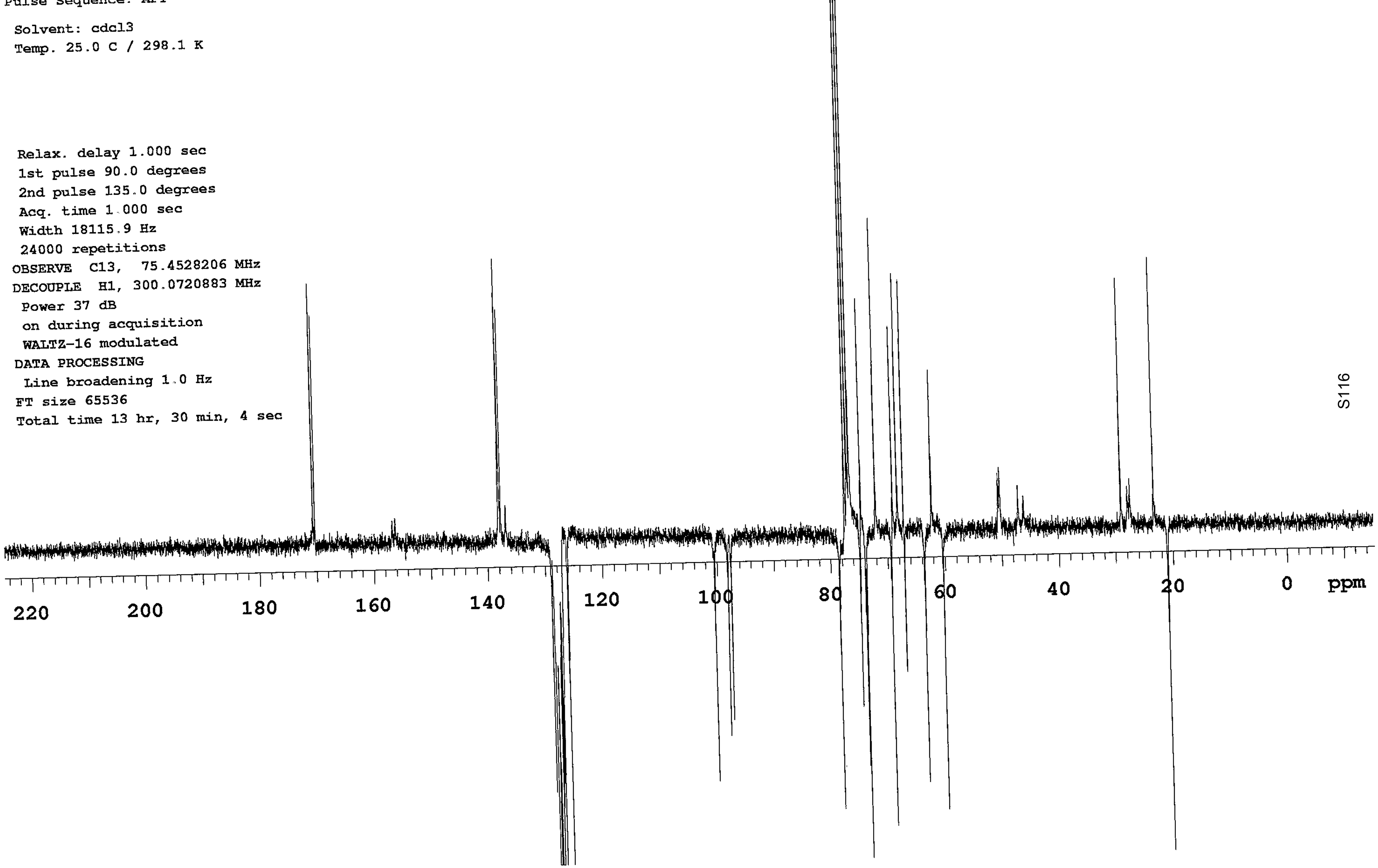
S5

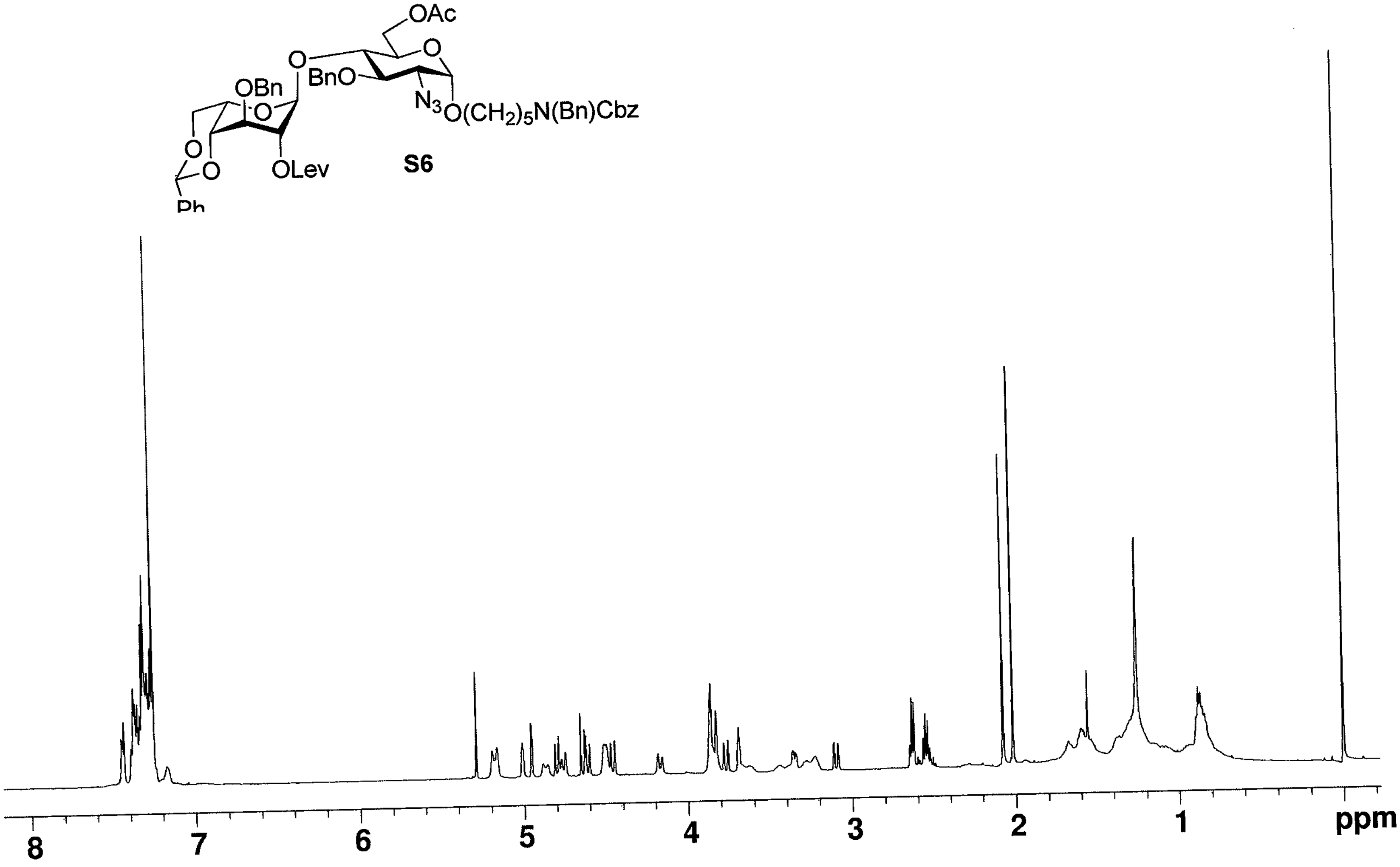

S5

Pulse Sequence: APT

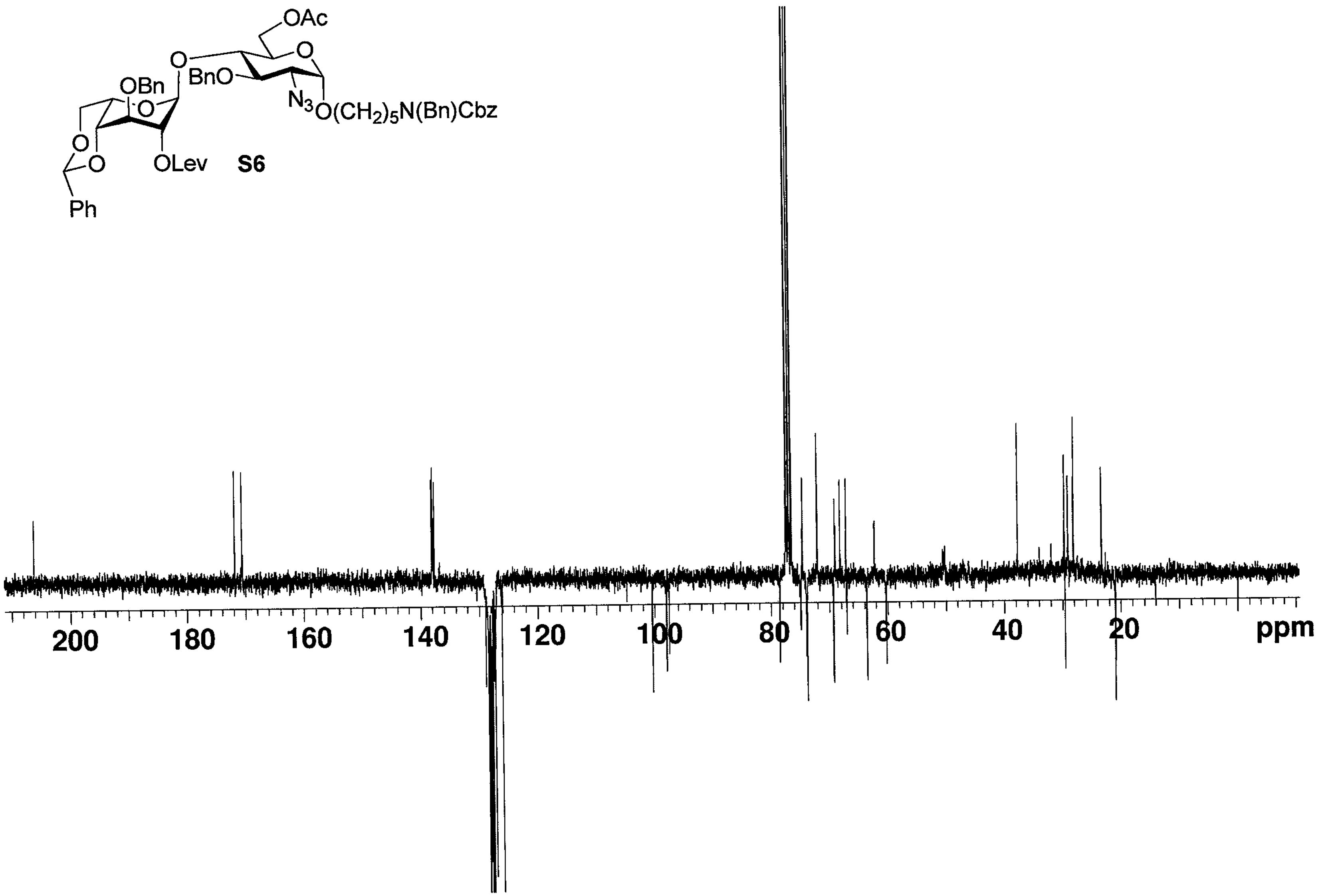
Solvent: cdcl3
Temp. 25.0 C / 298.1 K

Relax. delay 1.000 sec
1st pulse 90.0 degrees
2nd pulse 135.0 degrees
Acq. time 1.000 sec
Width 18115.9 Hz
24000 repetitions
OBSERVE C13, 75.4528206 MHz
DECOUPLE H1, 300.0720883 MHz
Power 37 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 13 hr, 30 min, 4 sec



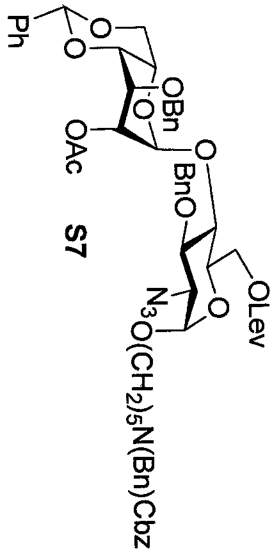


S6

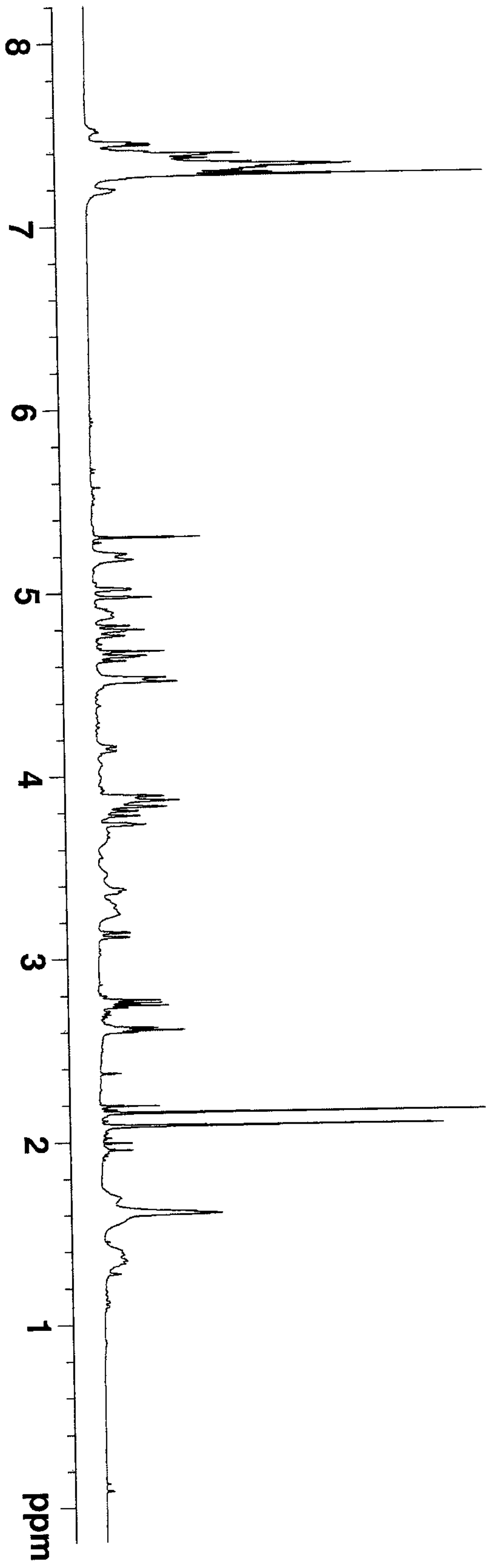


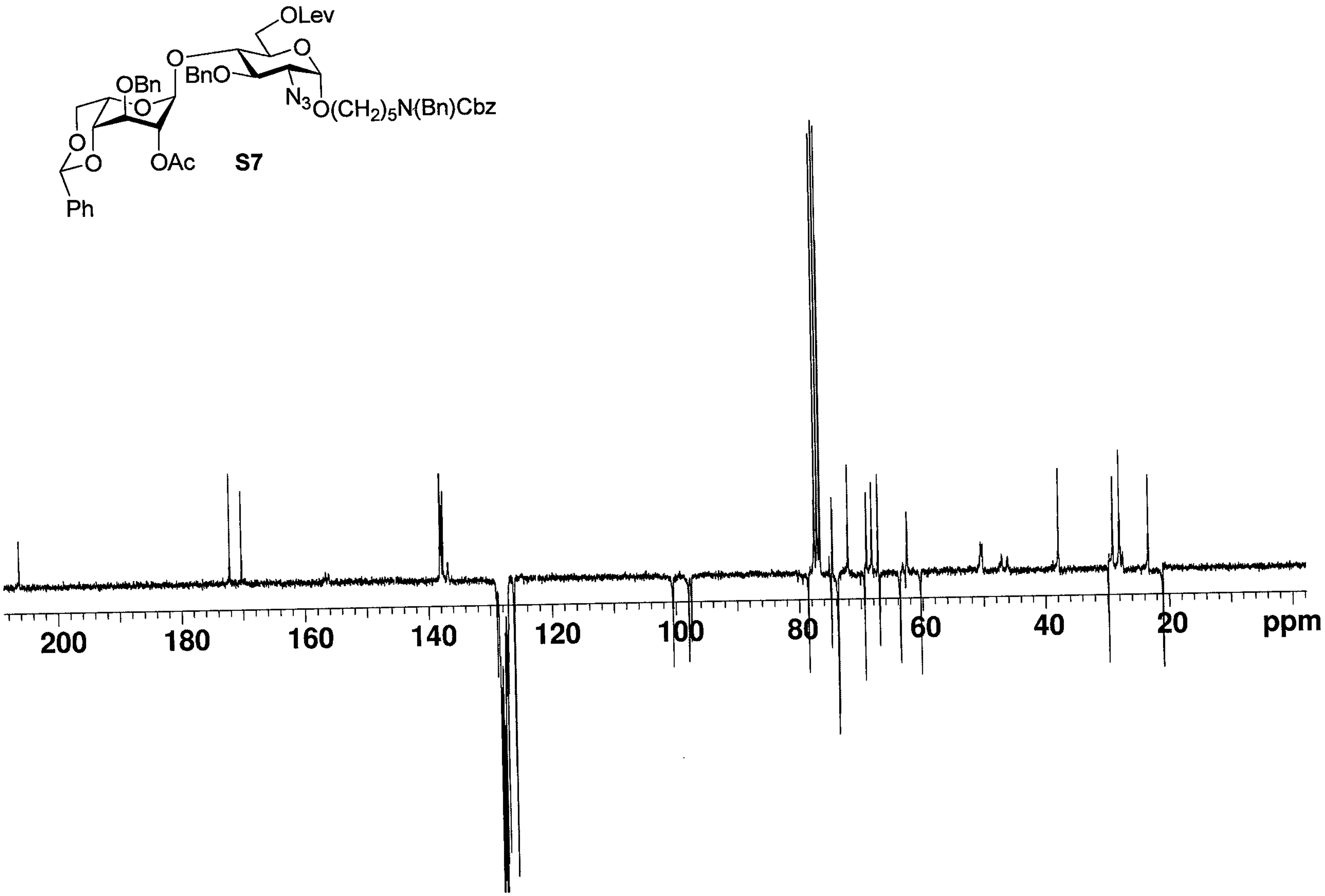
S6

OAc
O
BnO
OBn
O
N_3
O(CH$_2$)$_5$N(Bn)Cbz
O
O
OLev
Ph
200
180
160
140
120
100
80
60
40
20
ppm

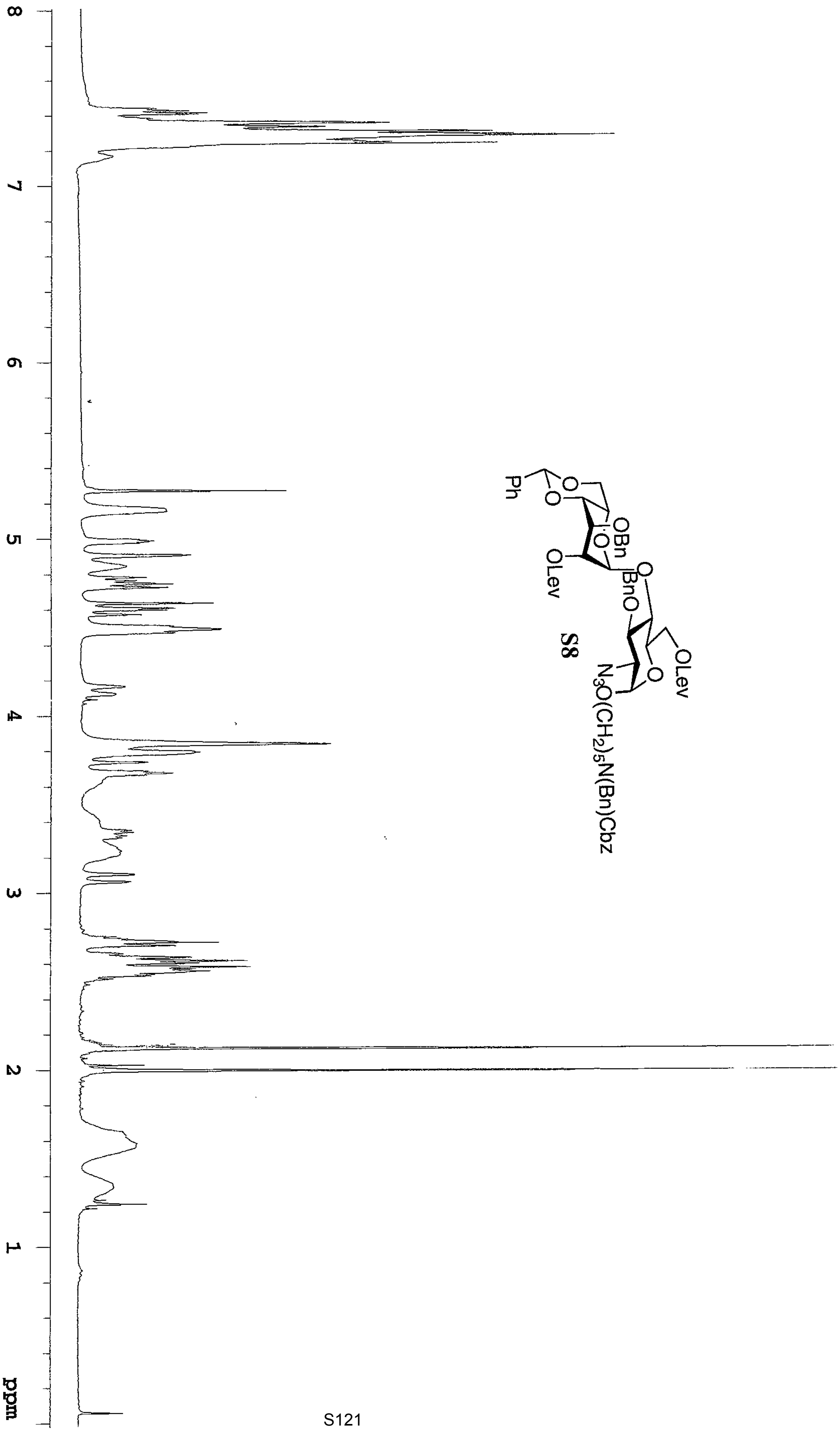


S7

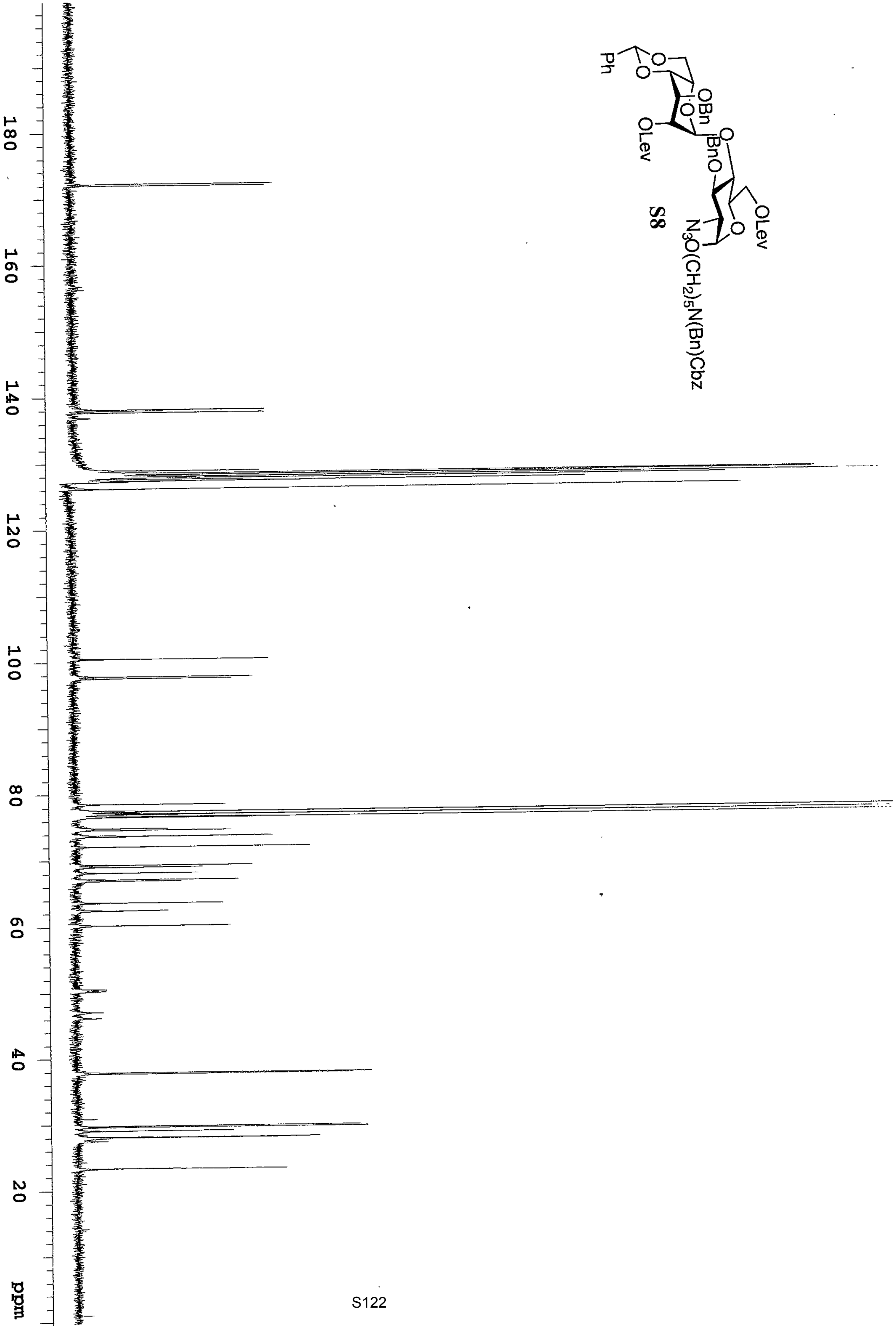



OLev
O
BnO
OBn
O
N3
O(CH2)5N(Bn)Cbz
O
O
OAc
Ph
200
180
160
140
120
100
80
60
40
20
ppm

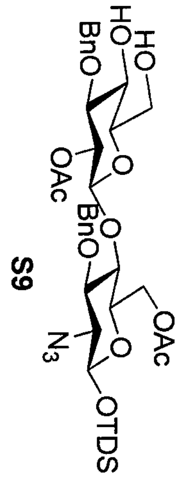
S7



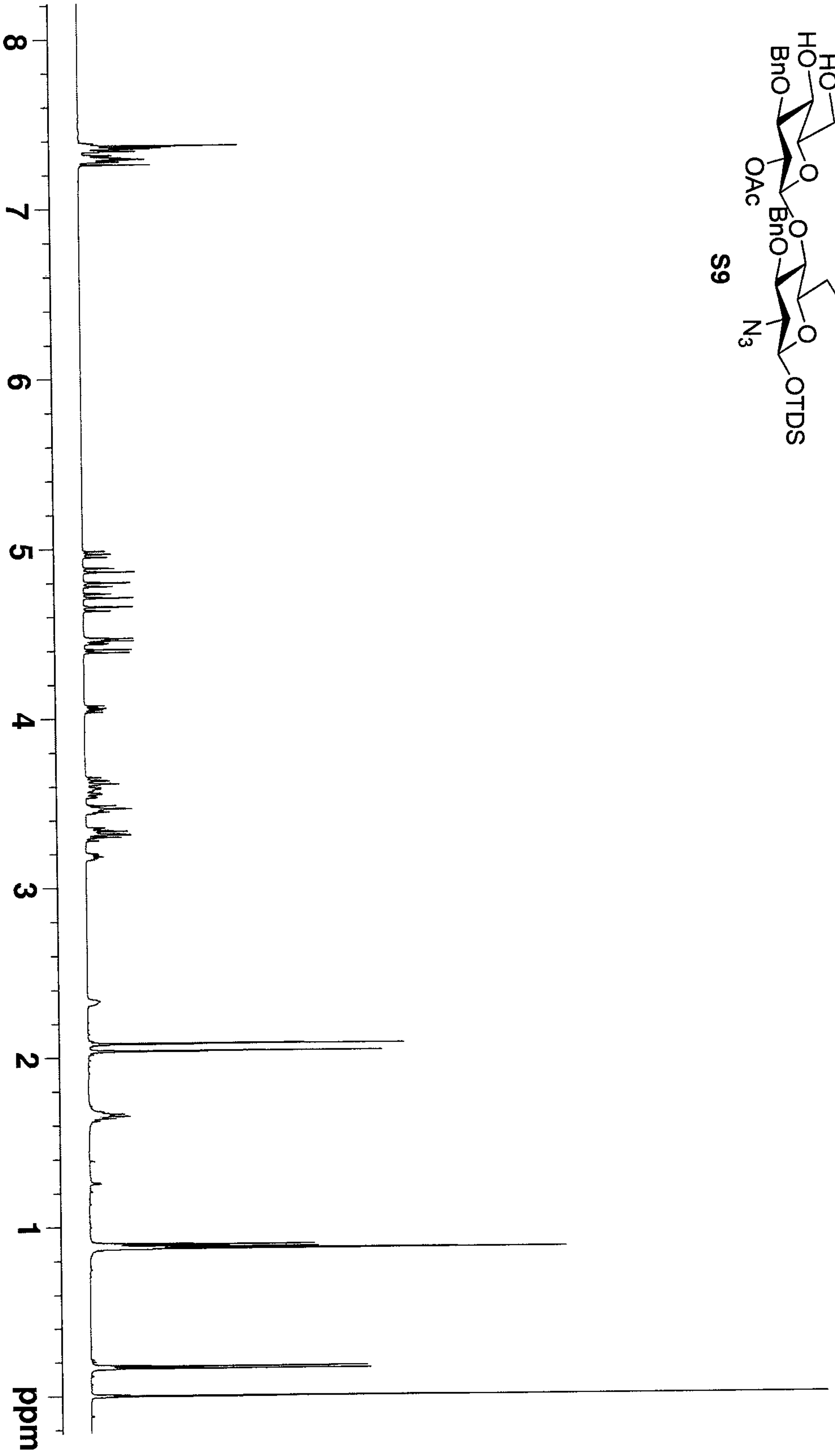
S8

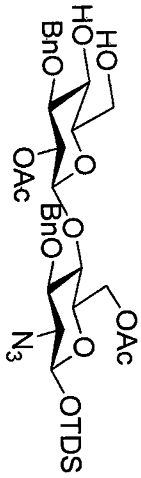

180
160
140
120
100
80
60
40
20
ppm
OLev
O
O
BnO
N3O(CH2)5N(Bn)Cbz
OBn
O
O
O
Ph
OLev

S8

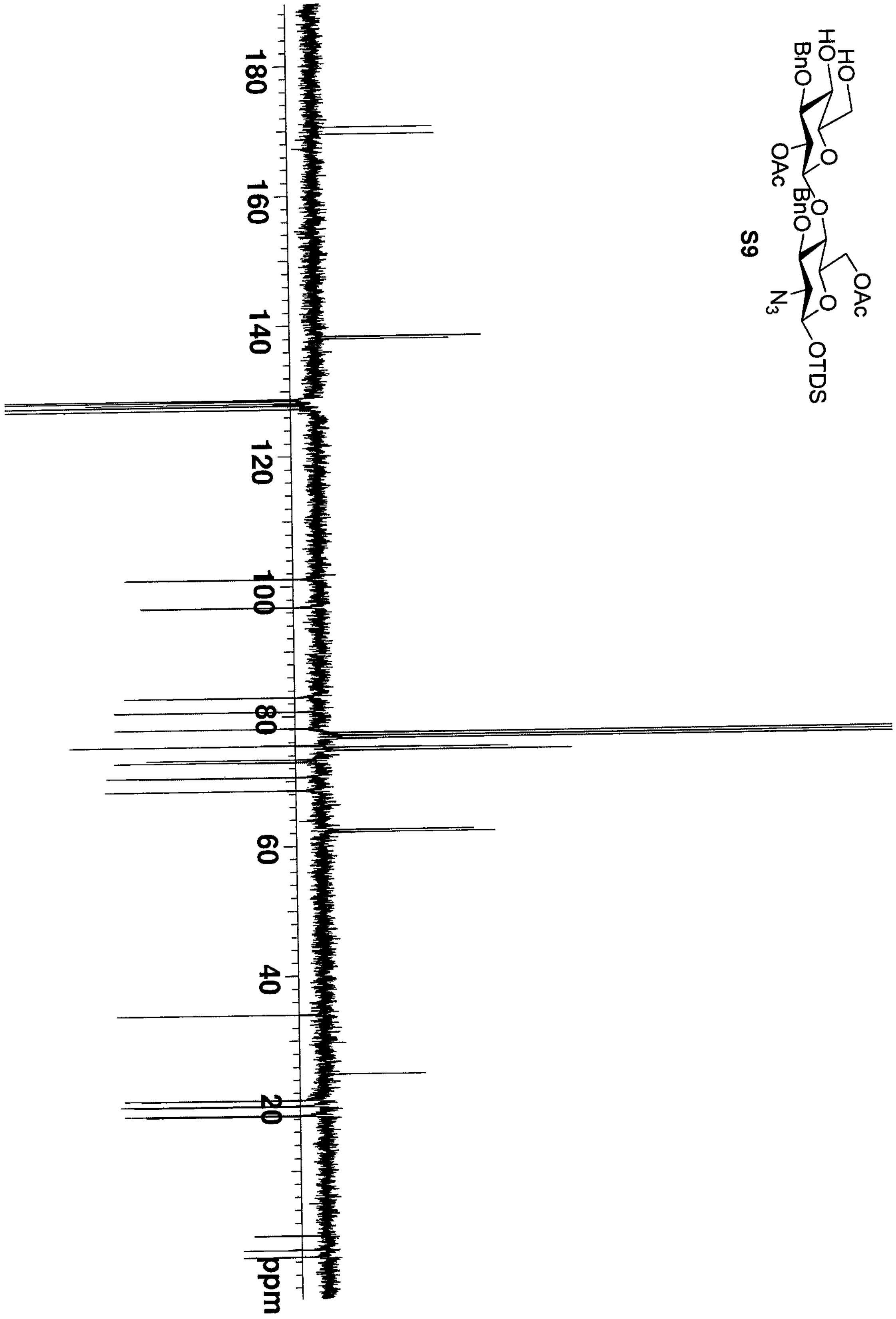


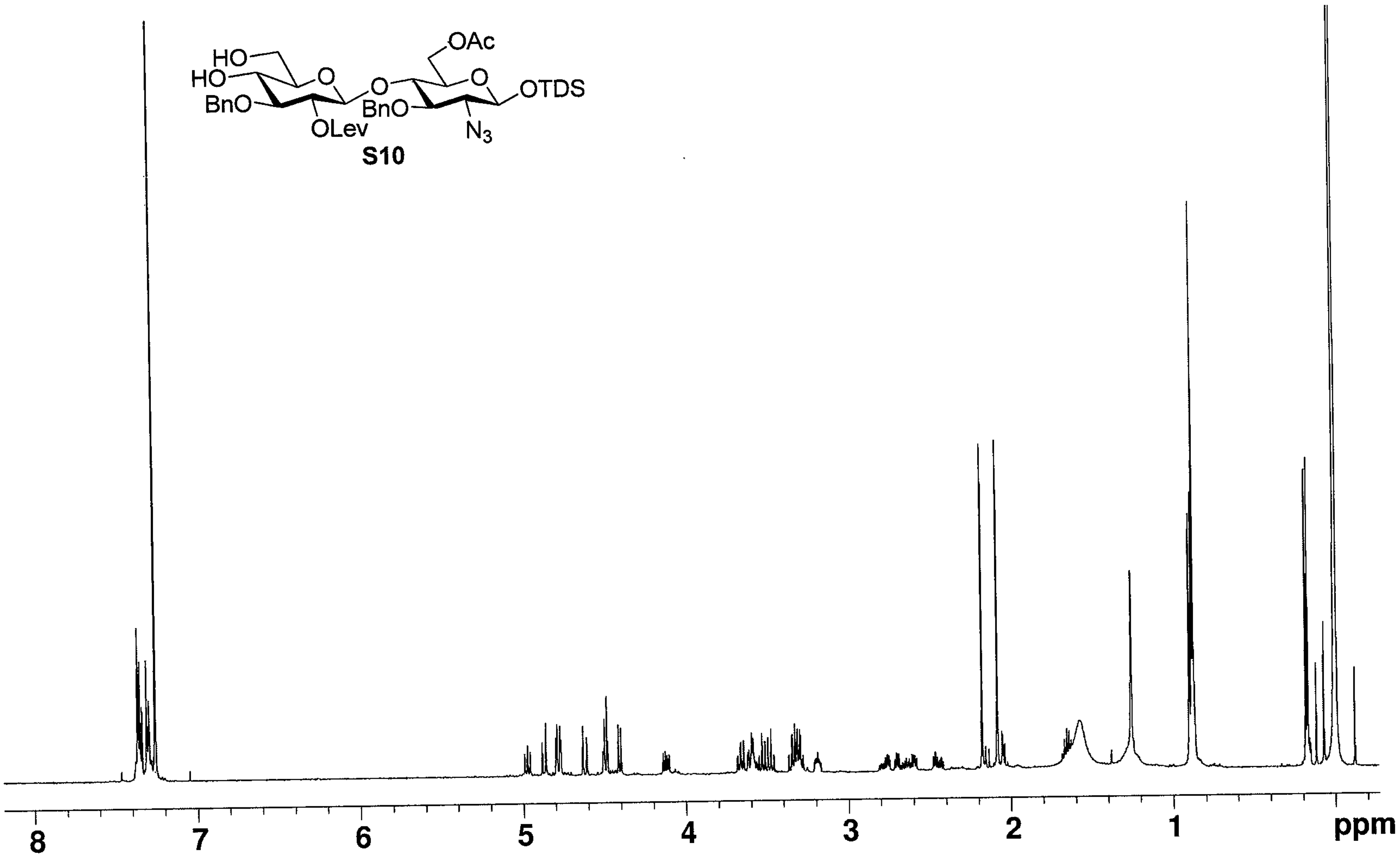
S9



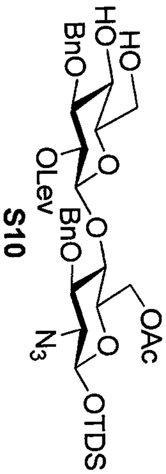

HO
HO
BnO
O
OAc
O
BnO
OAc
O
N3
OTDS

S9

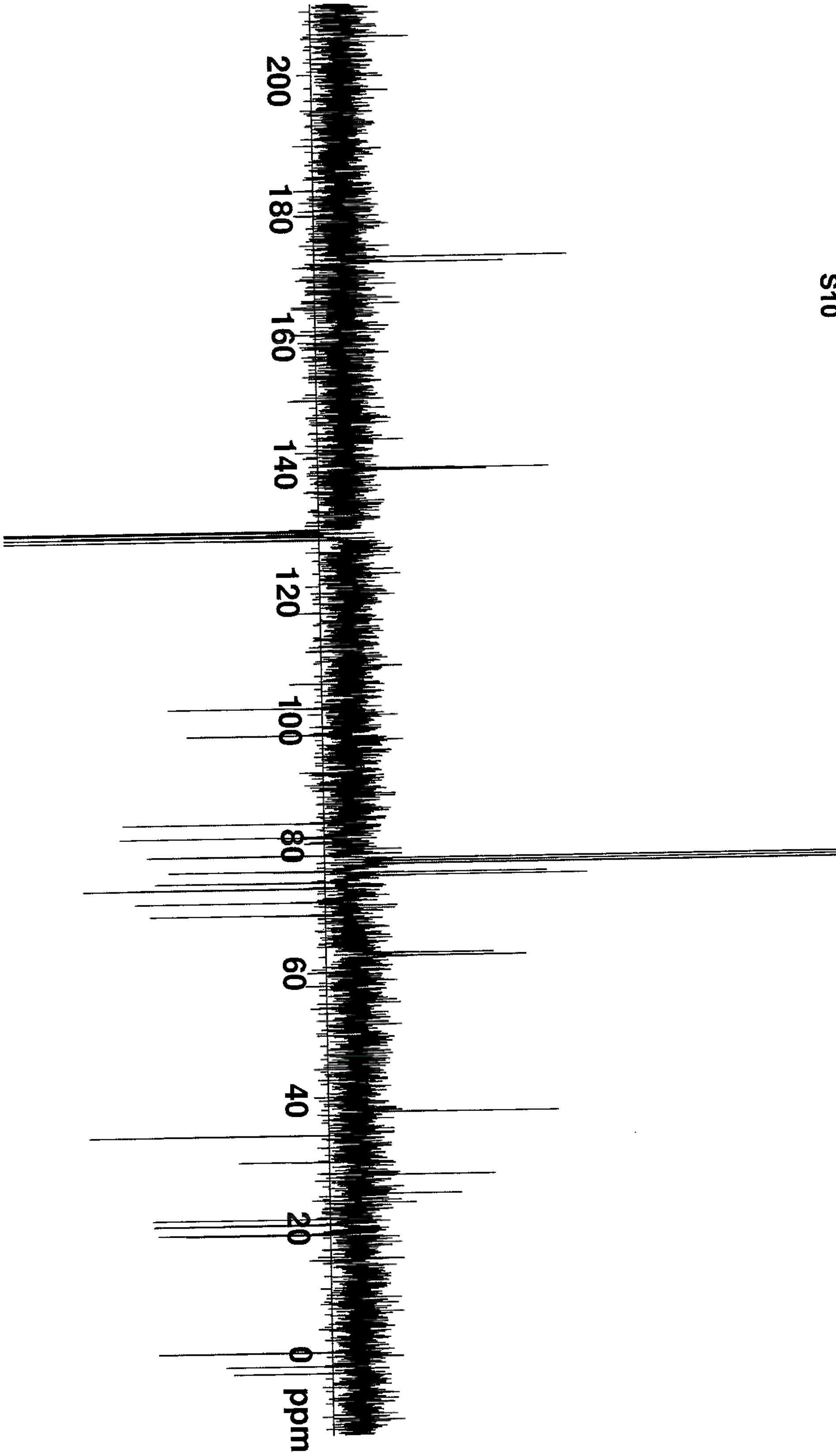

180
160
140
120
100
80
60
40
20
ppm

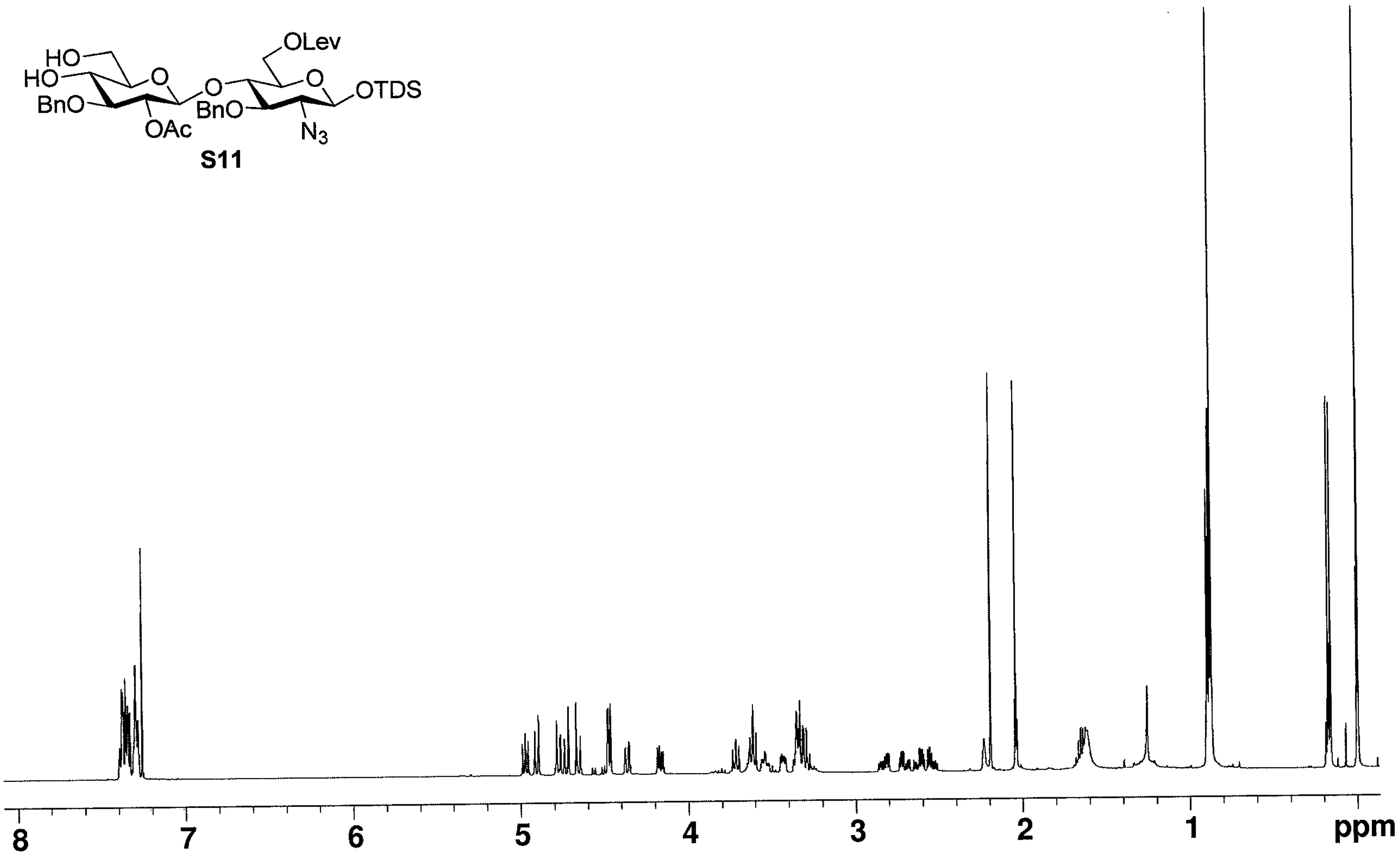


S10

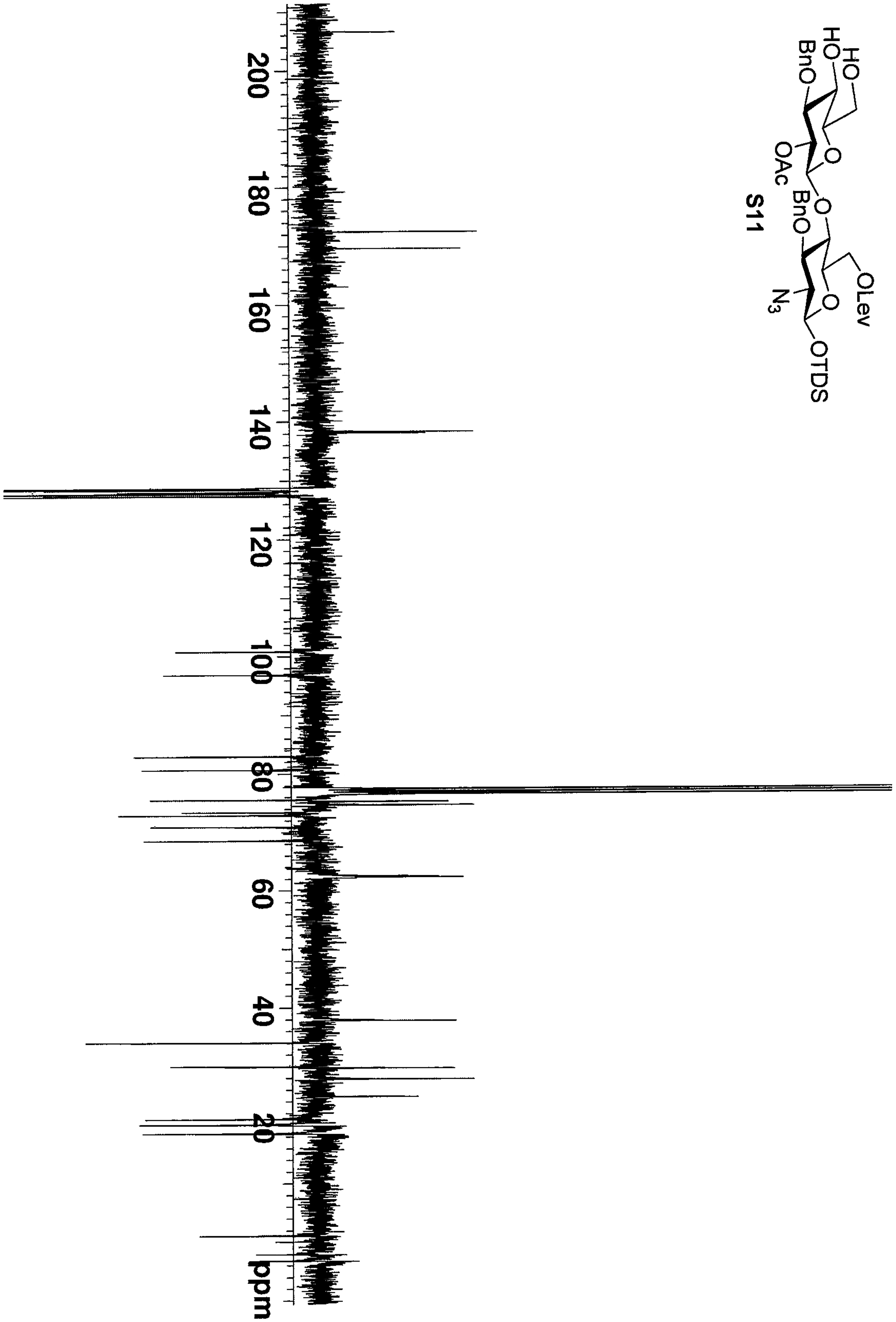

HO
HO
BnO
O
OLev
BnO
O
O
OAc
N3
OTDS

S10


200
180
160
140
120
100
80
60
40
20
0
ppm

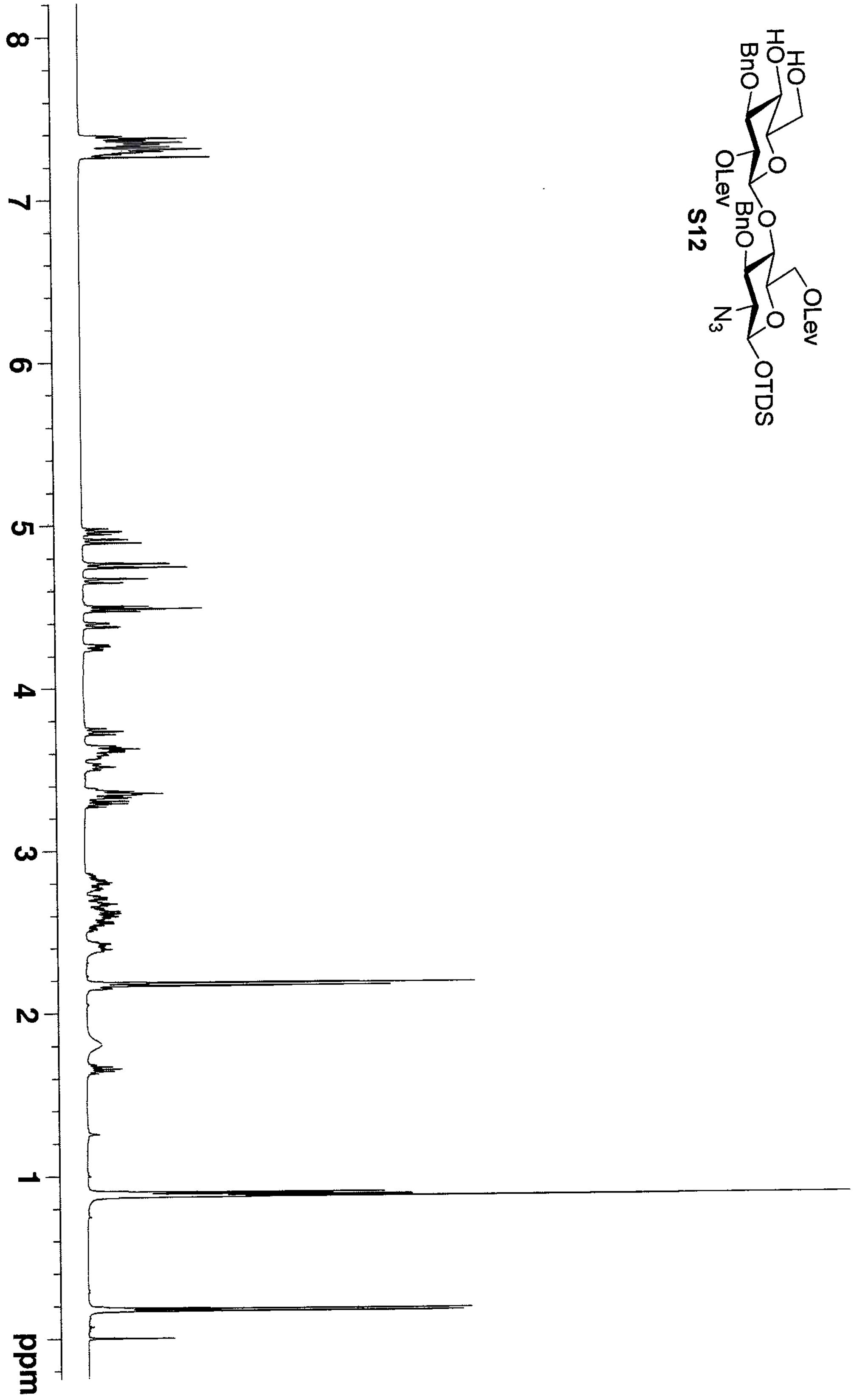


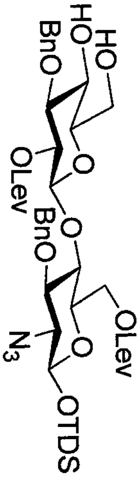
S11


HO
HO
BnO
O
OAc
O
BnO
OLev
O
N3
OTDS
200
180
160
140
120
100
80
60
40
20
ppm

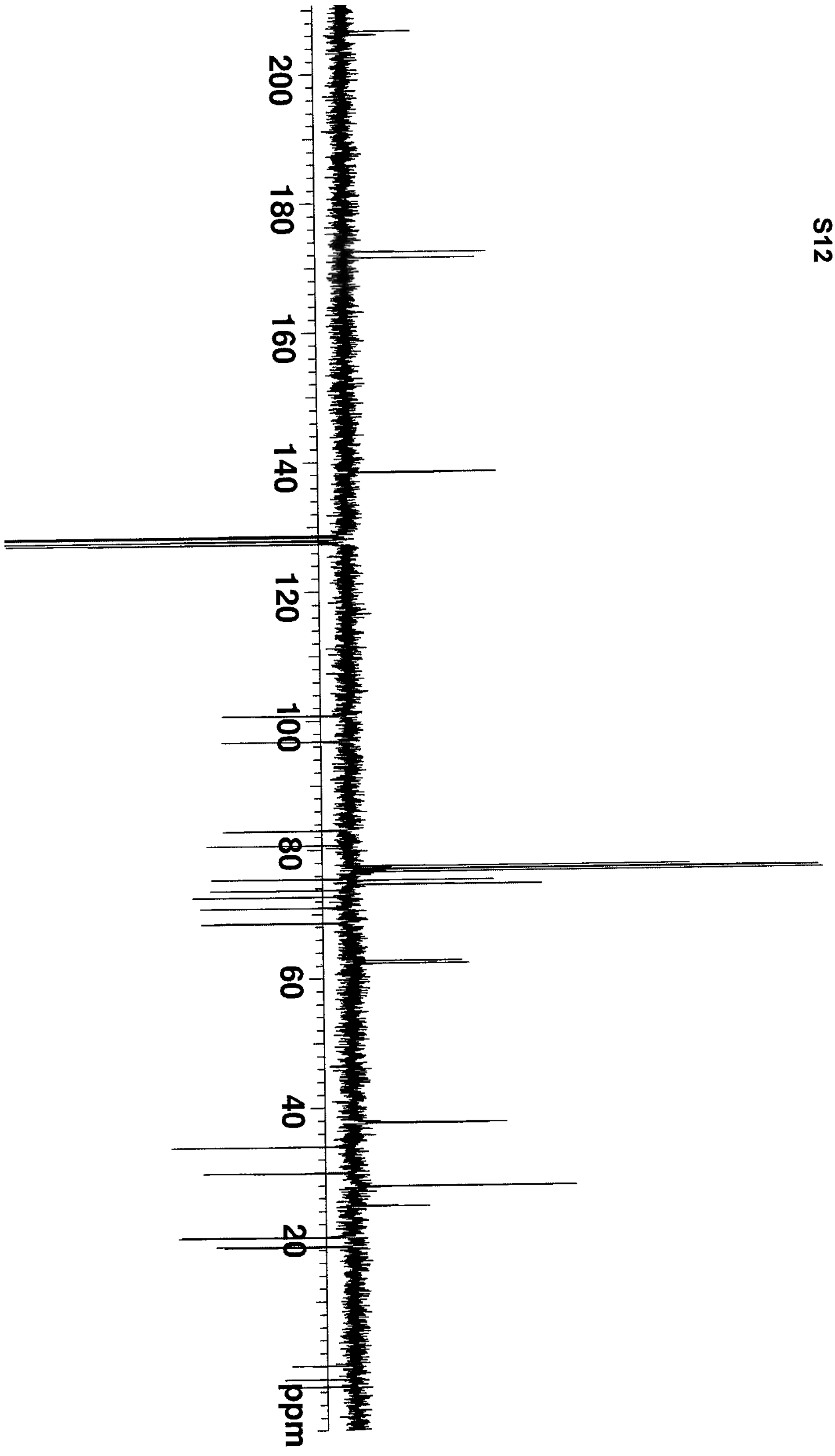
S11

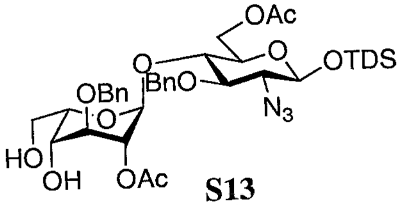
S12



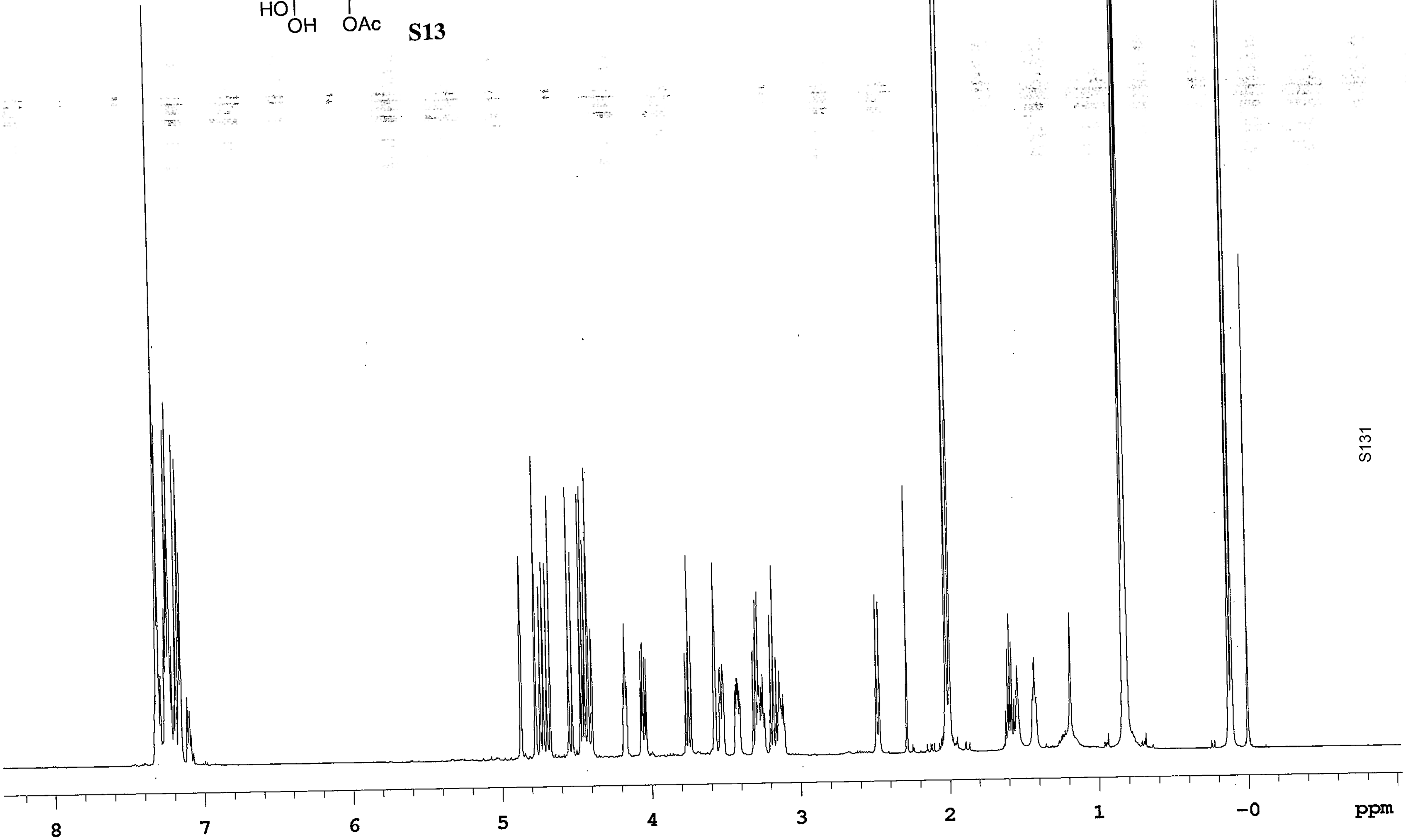

HO
HO
BnO
O
OLev
O
BnO
OLev
O
N3
OTDS

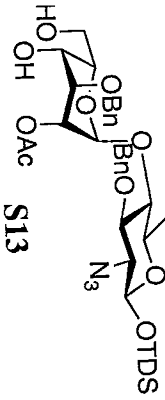
S12


200
180
160
140
120
100
80
60
40
20
ppm

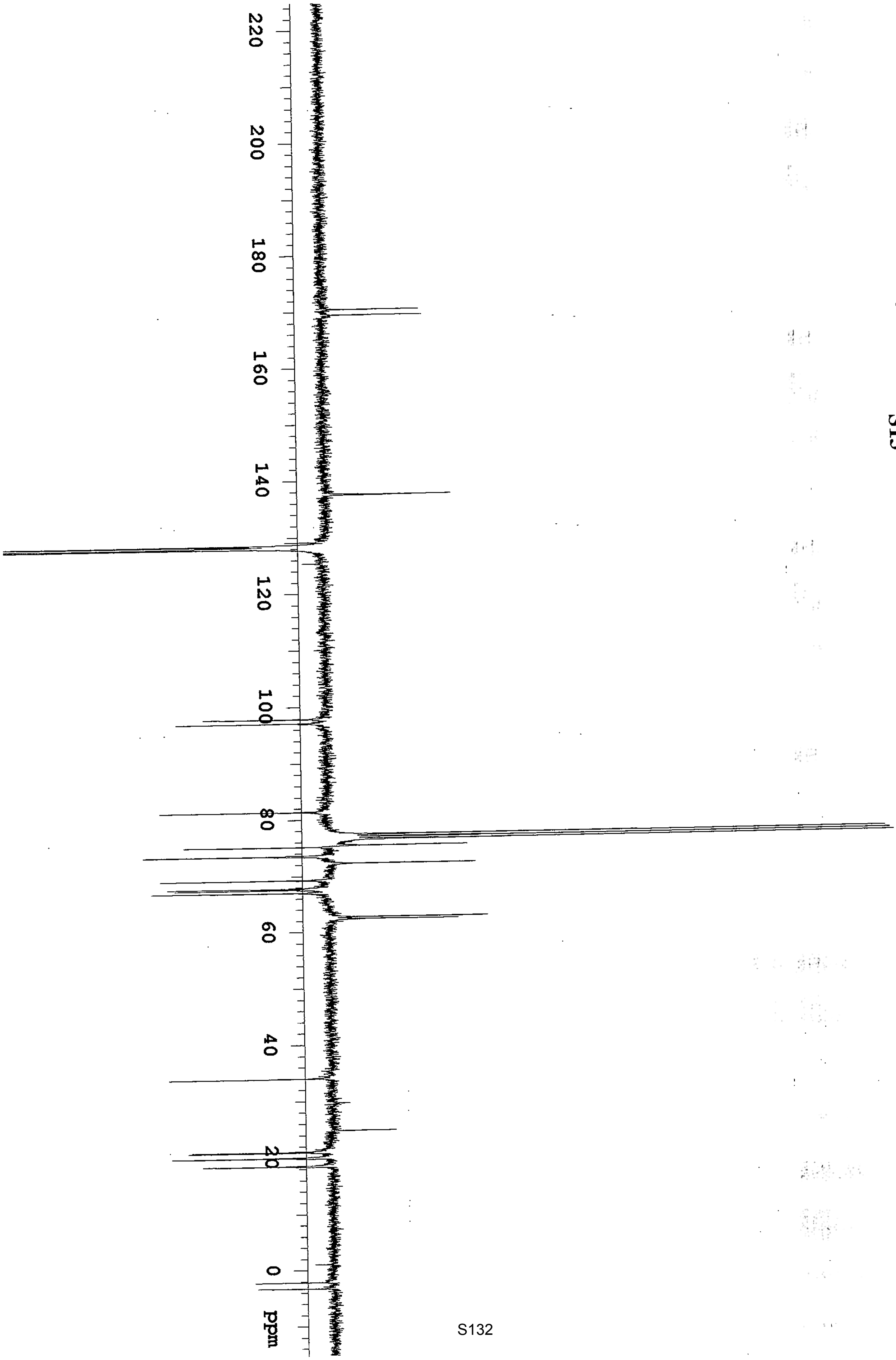


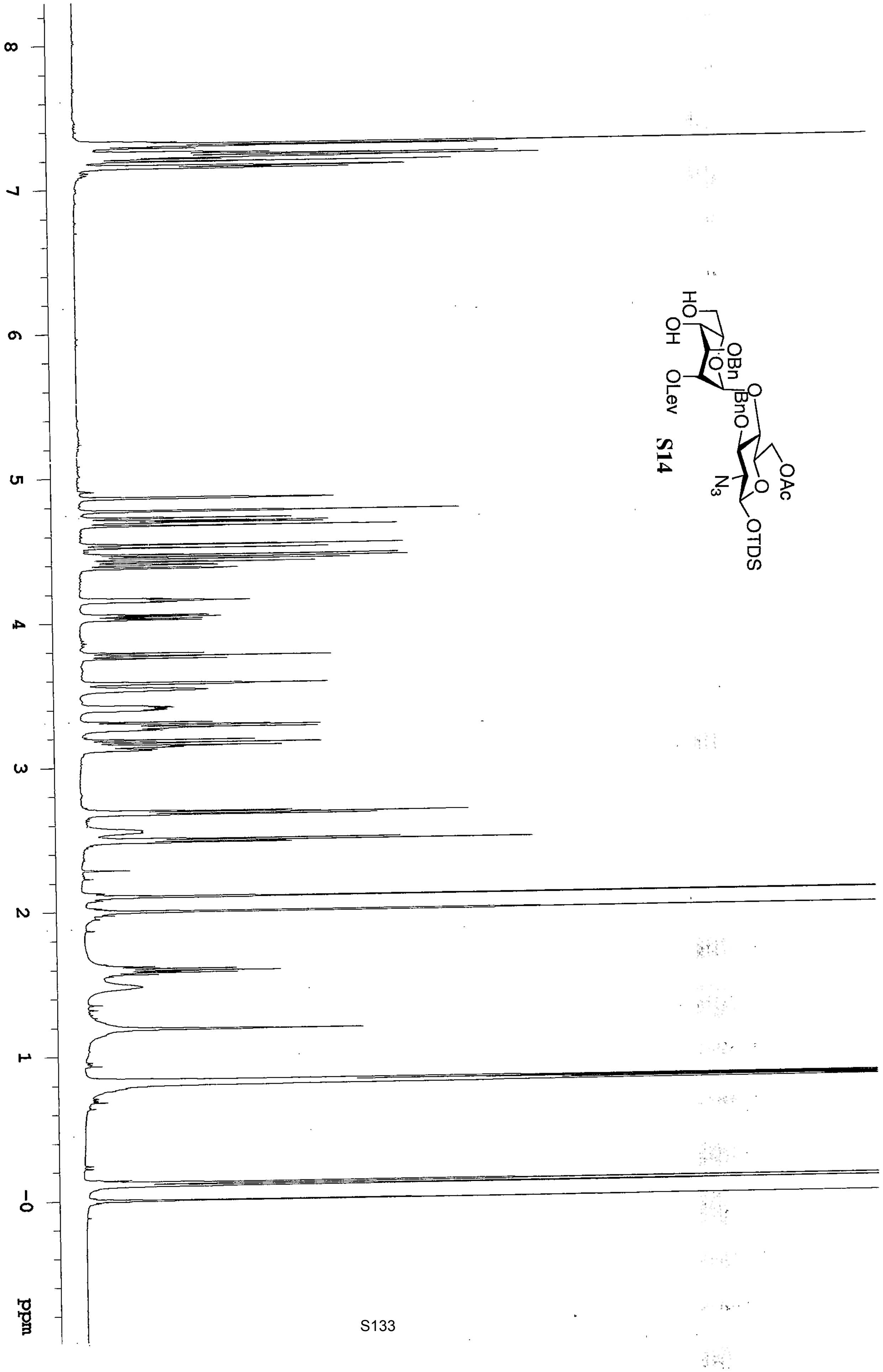
S13



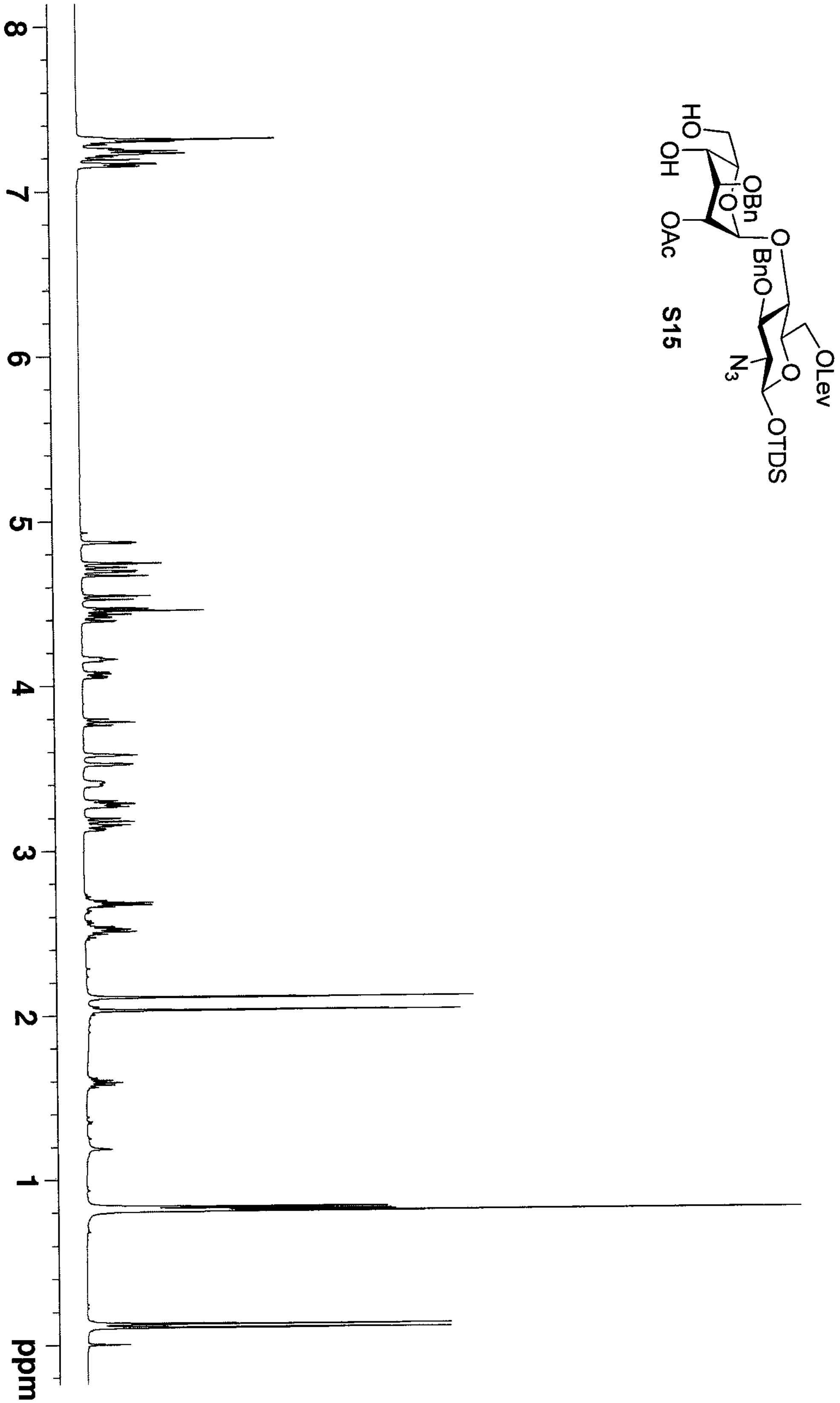

OAc
O
OTDS
N3
BnO
O
OBn
O
HO
OH
OAc

S13

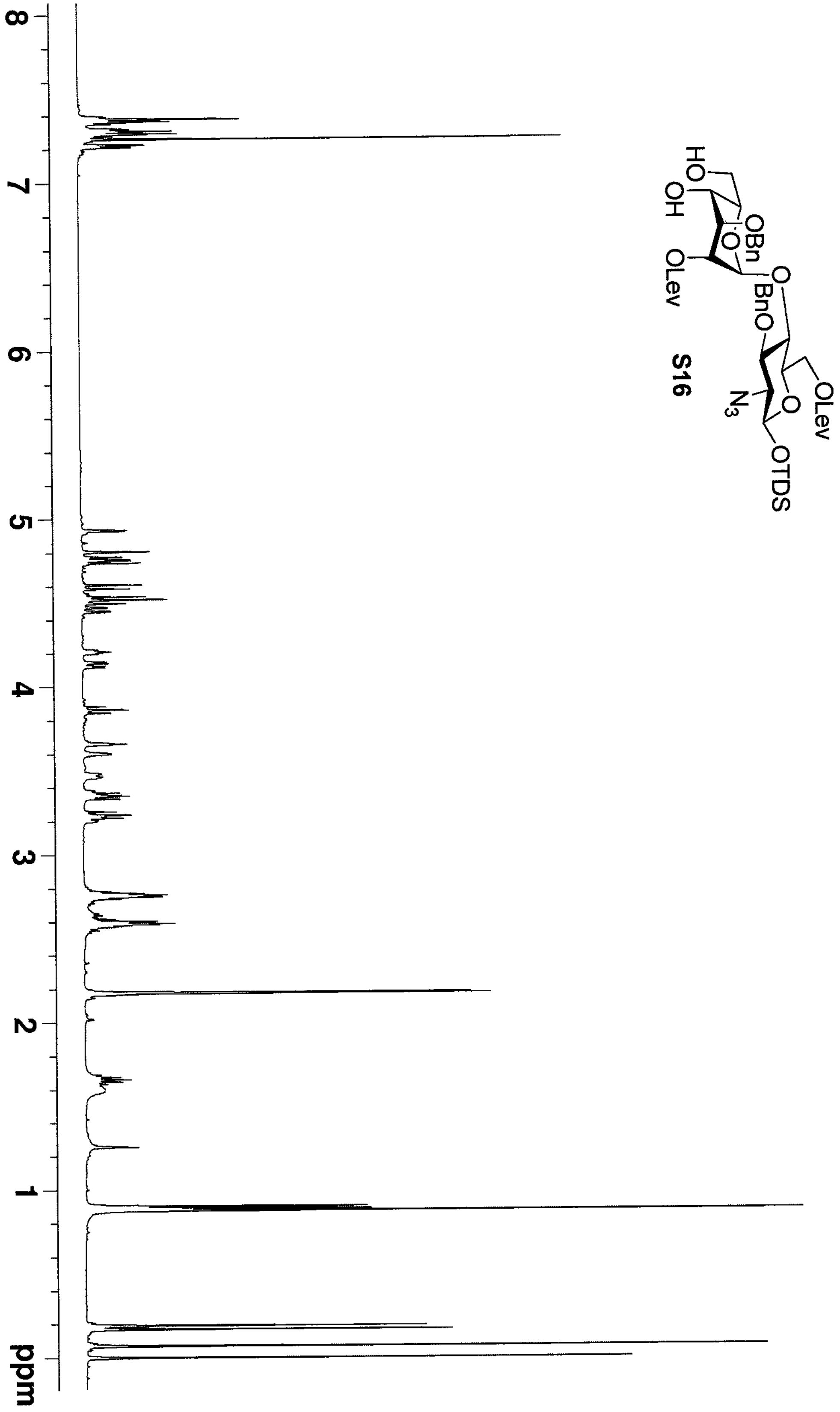

220
200
180
160
140
120
100
80
60
40
20
0
ppm



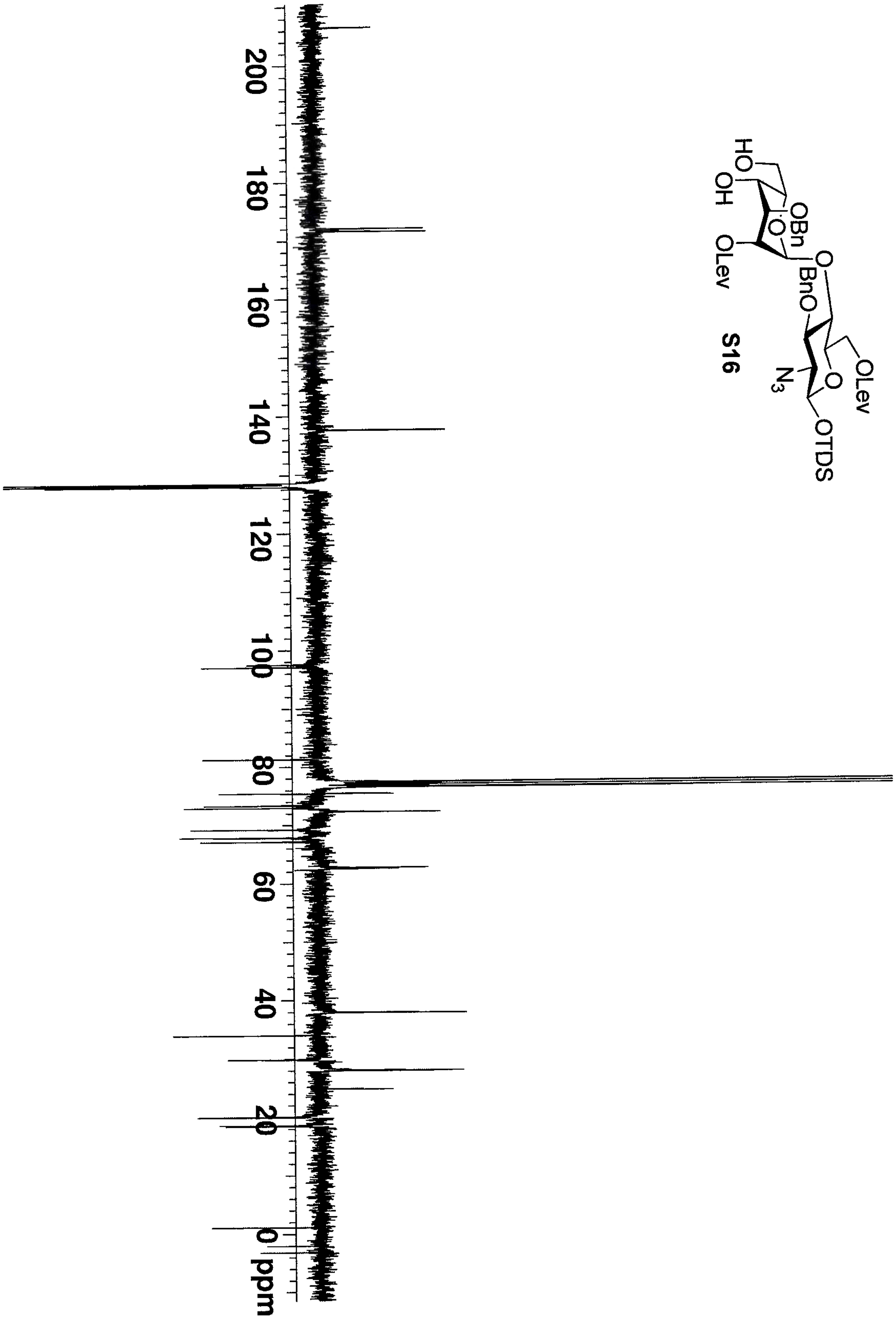
S14



S15

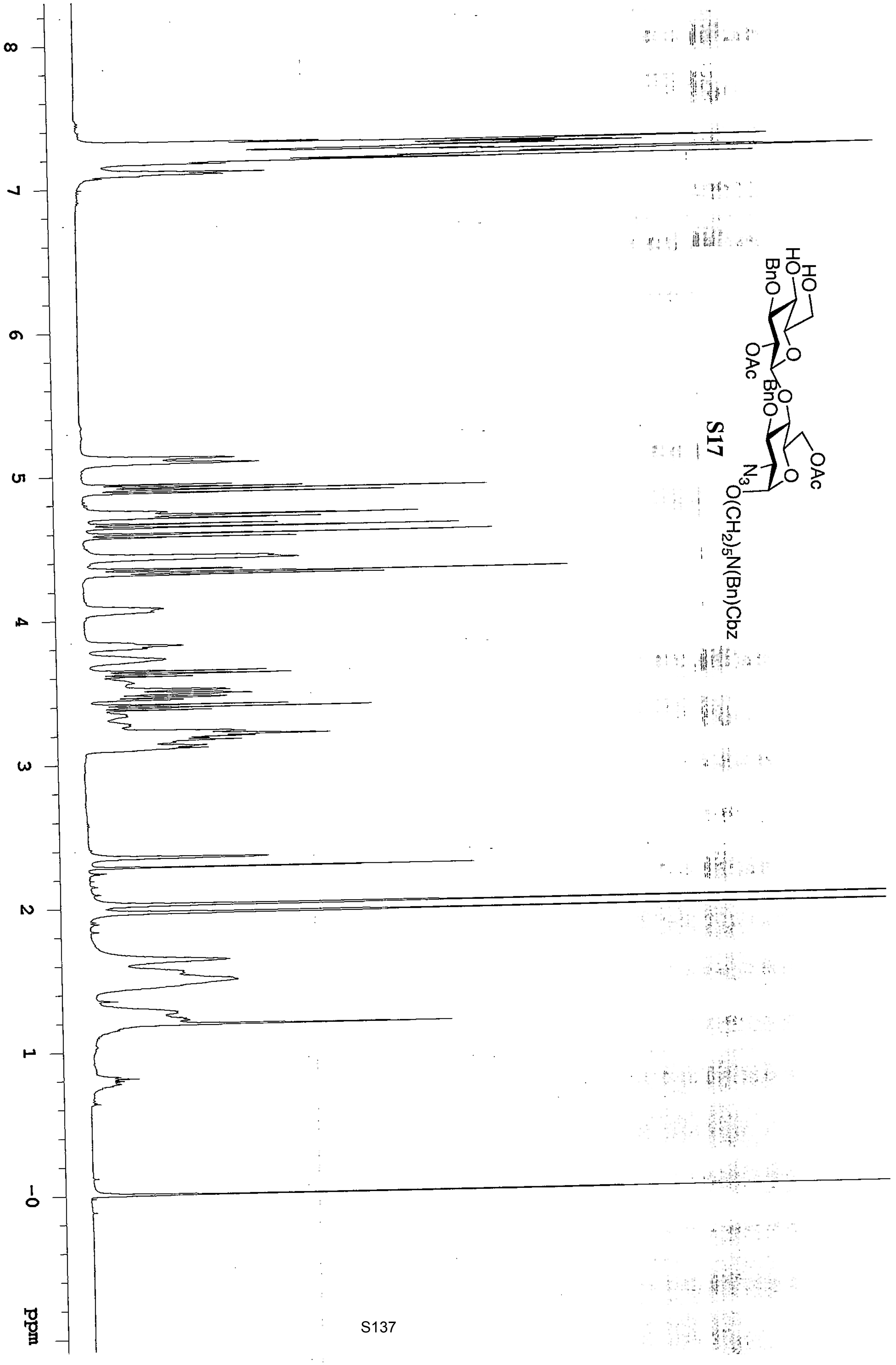


S16

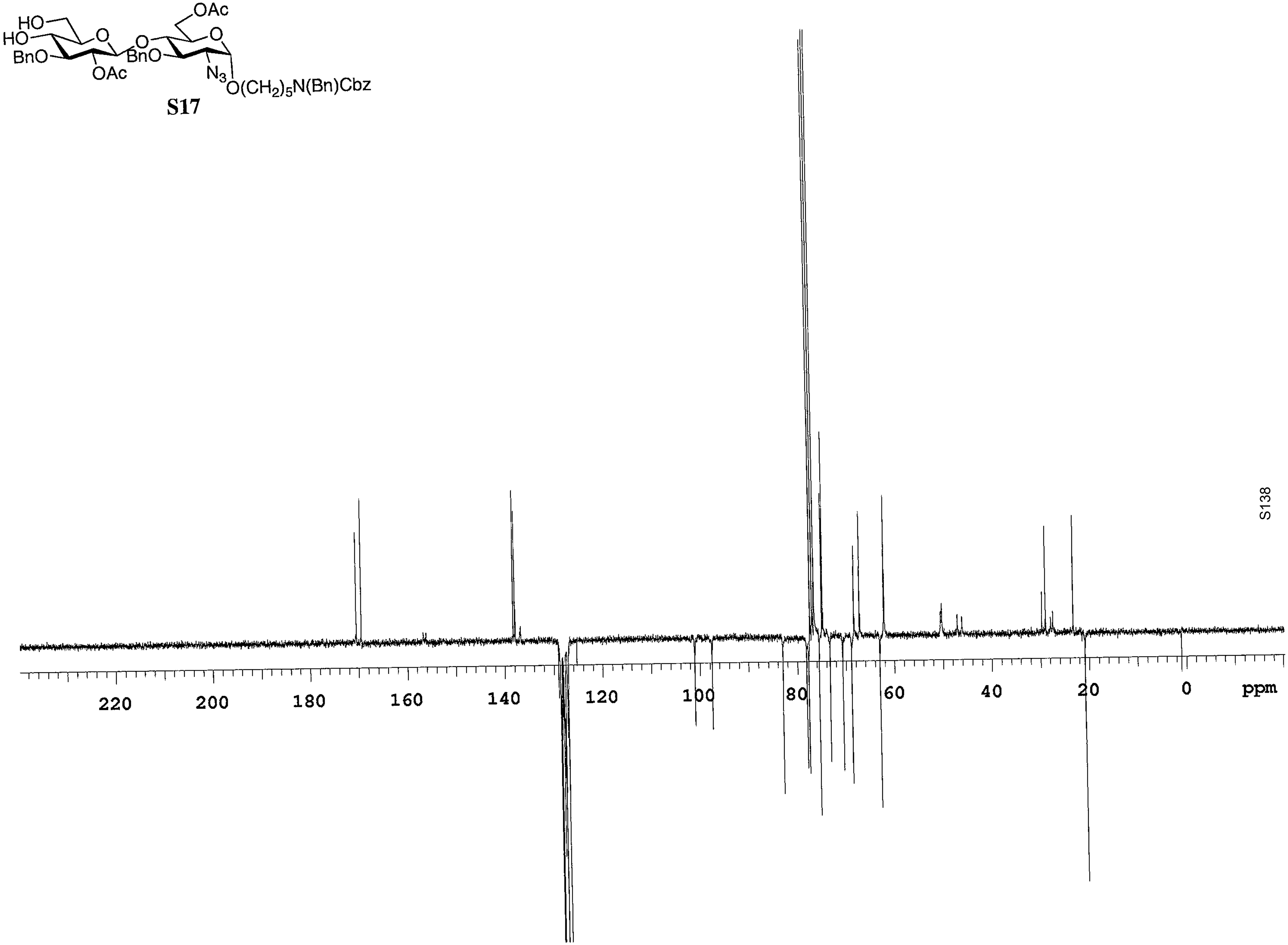

OLev
O
OTDS
N3
BnO
O
OBn
O
HO
OH
OLev

S16

200
180
160
140
120
100
80
60
40
20
0
ppm

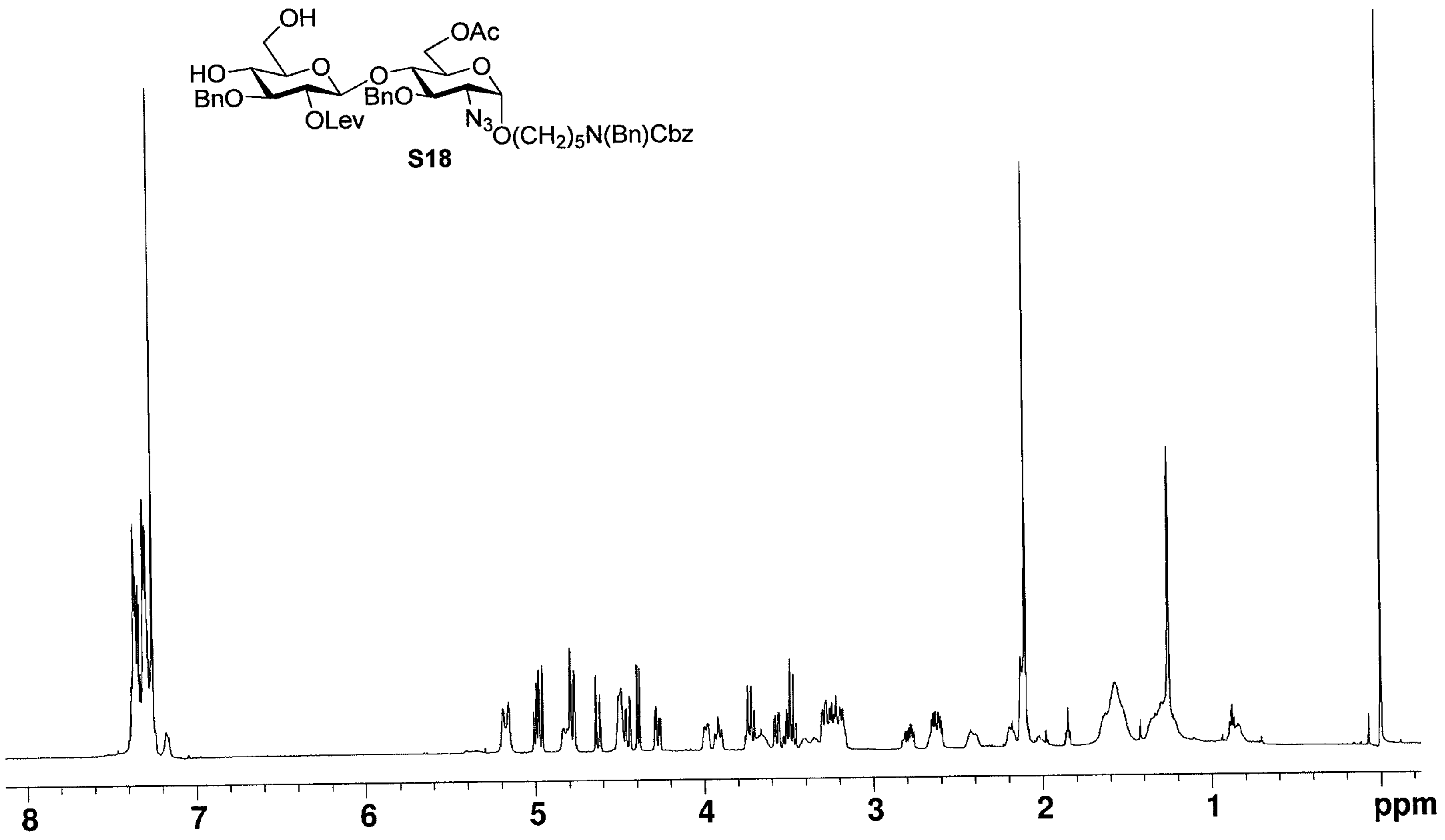


S17

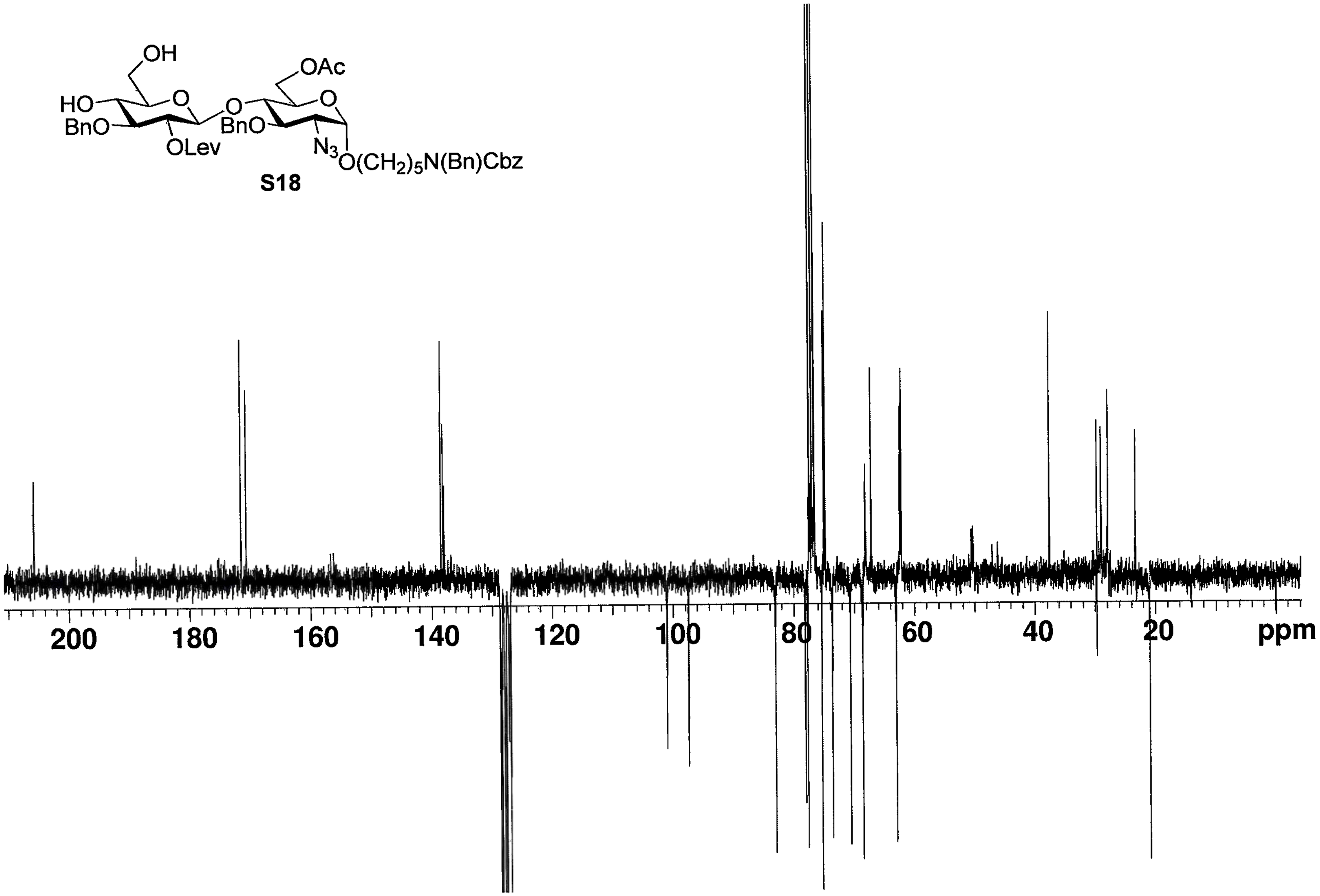


S17

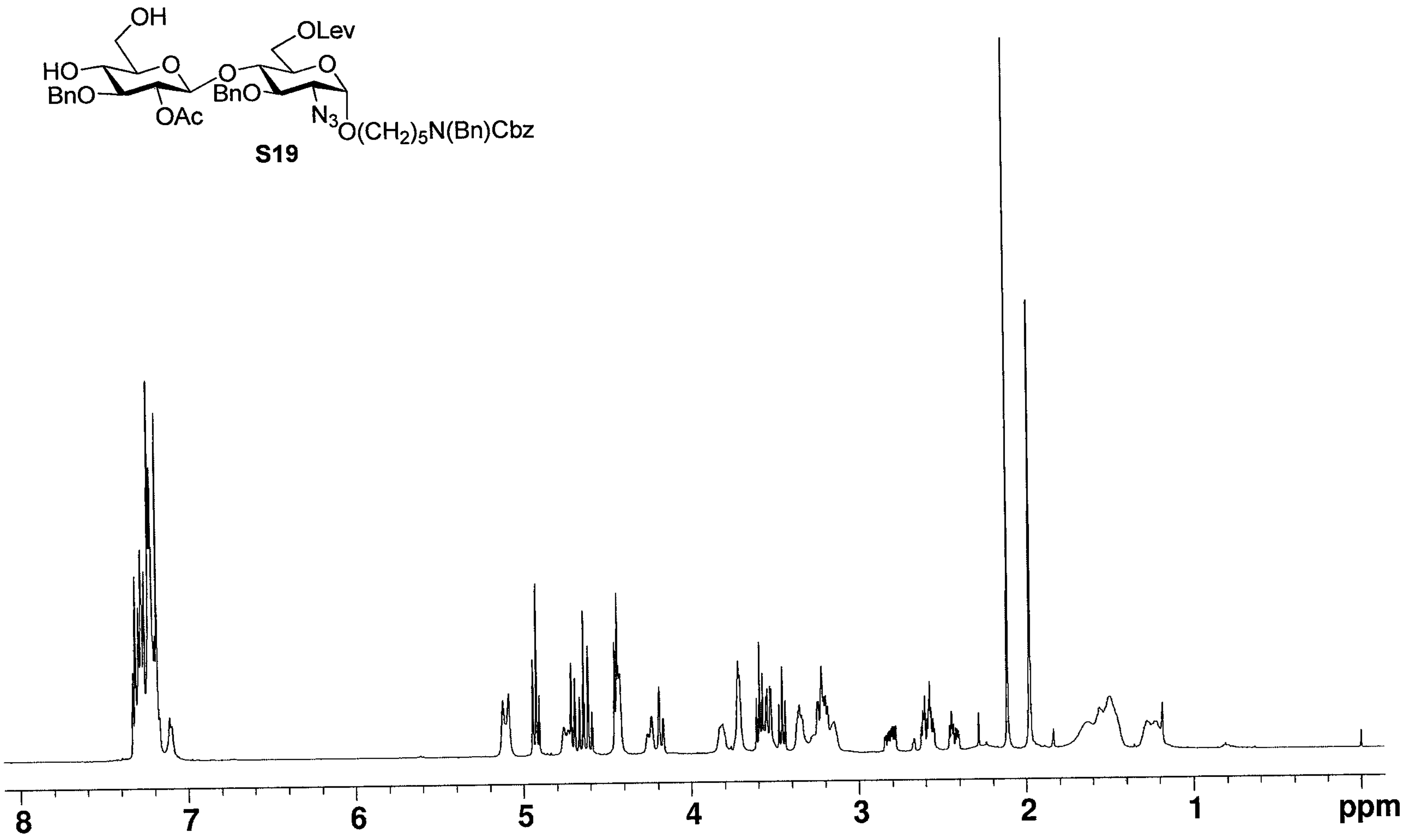
HO
HO
BnO
OAc
BnO
OAc
N_3
$O(CH_2)_5N(Bn)Cbz$
220
200
180
160
140
120
100
80
60
40
20
0
ppm



S18



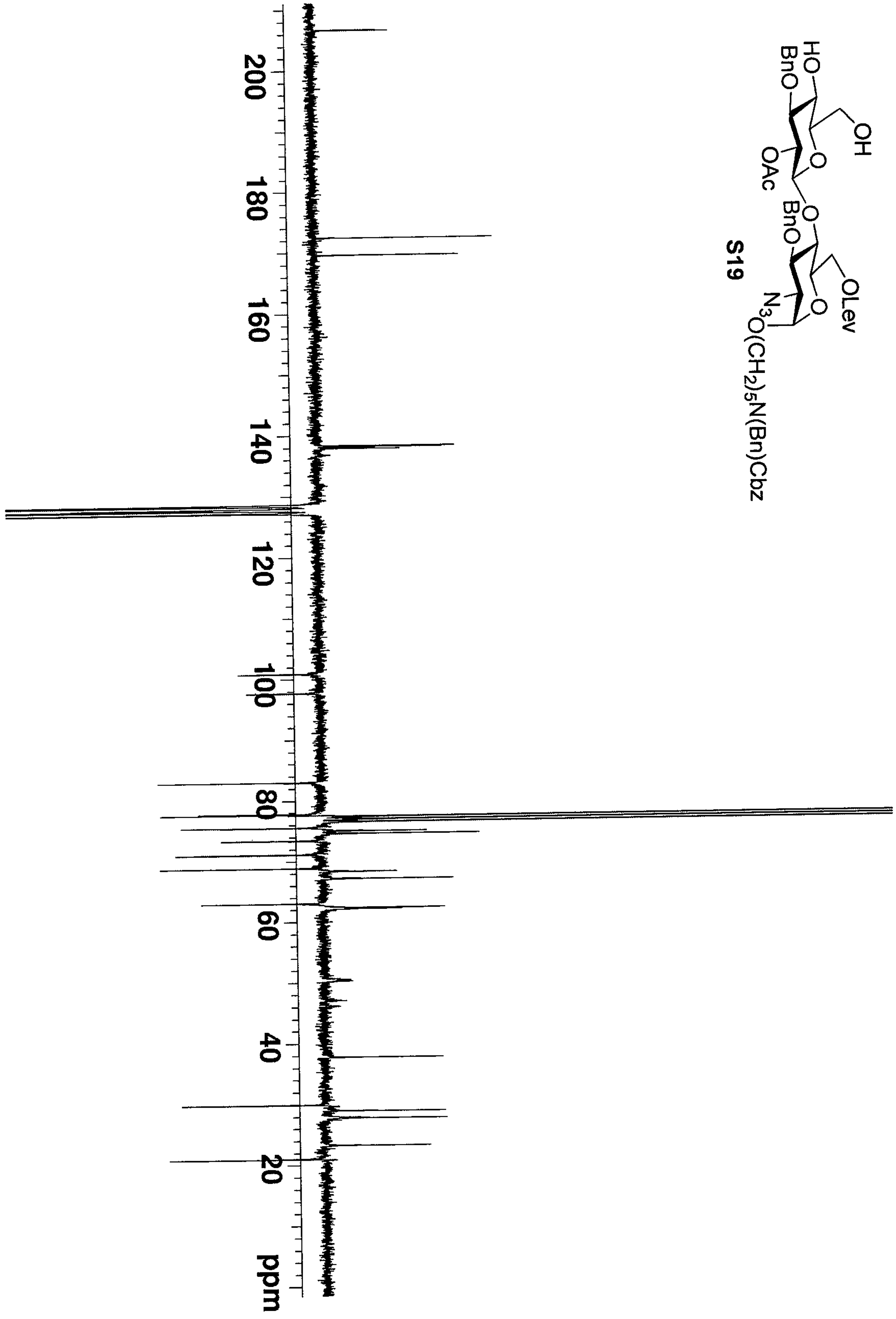
S18

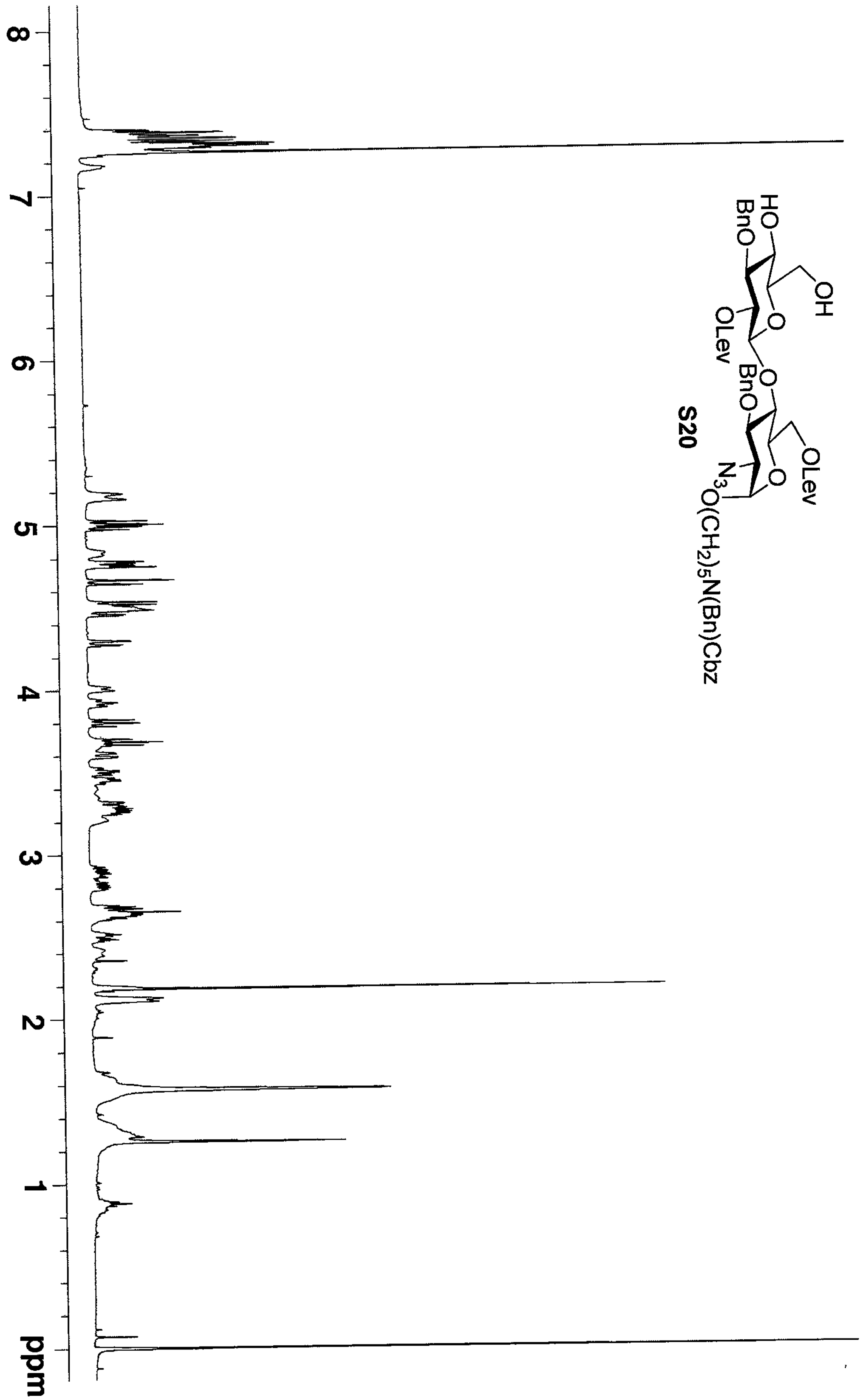


S19

OH
HO
BnO
O
OAc
O
BnO
O
OLev
O
N3
O(CH2)5N(Bn)Cbz

S19

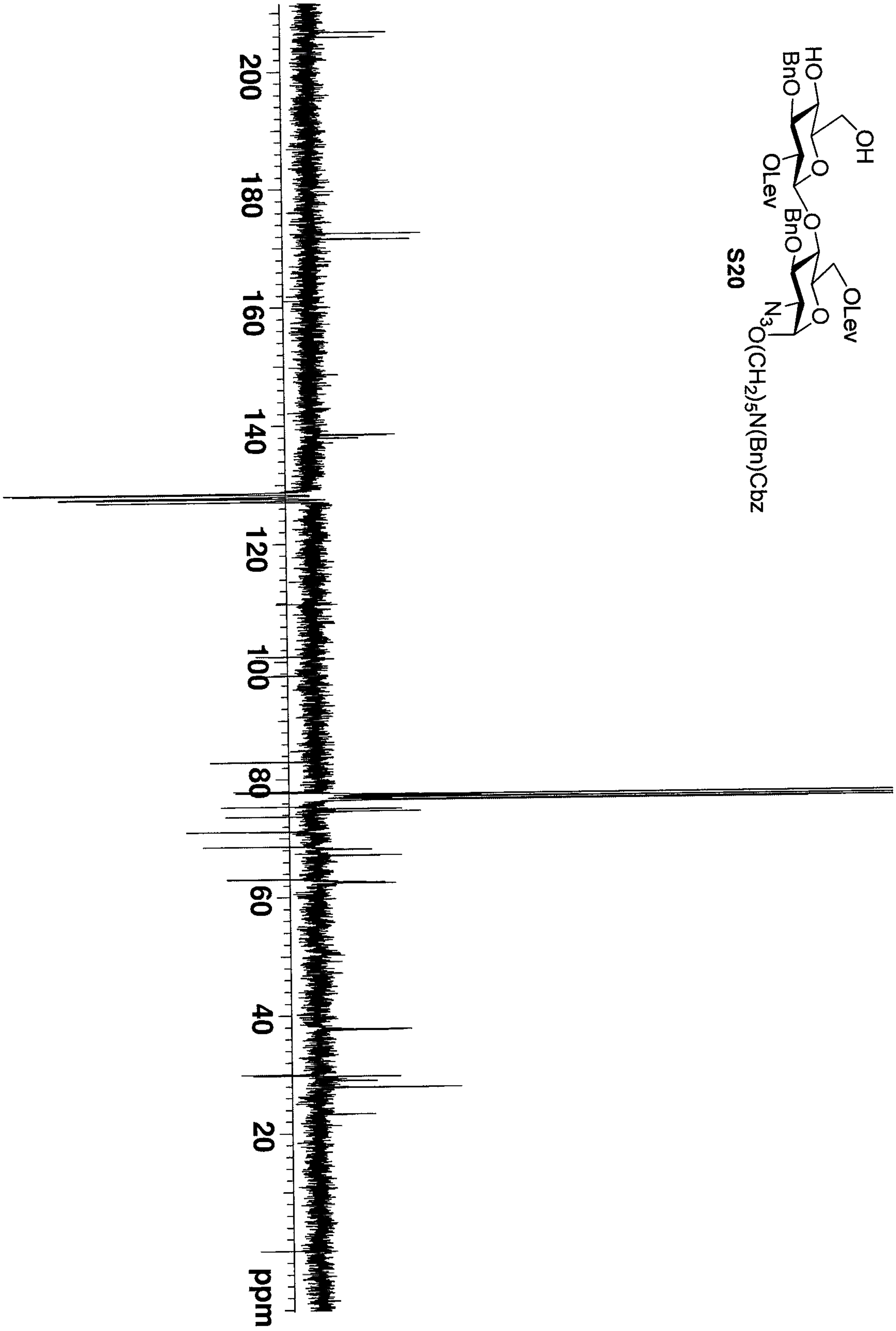

200
180
160
140
120
100
80
60
40
20
ppm



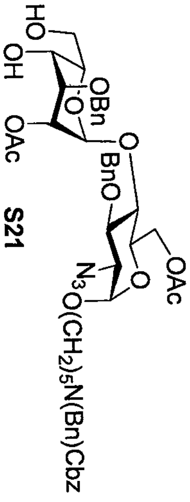
S20

OH
HO
BnO
O
OLev
O
BnO
OLev
O
N3
O(CH2)5N(Bn)Cbz

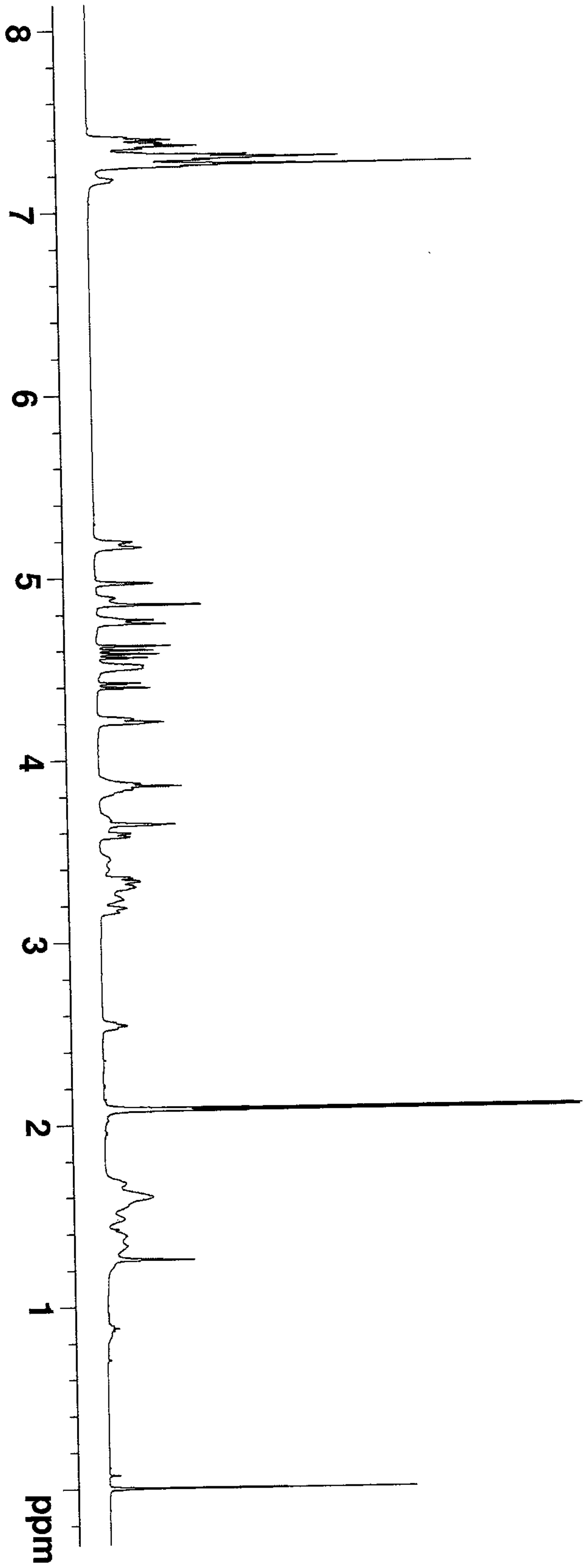
S20

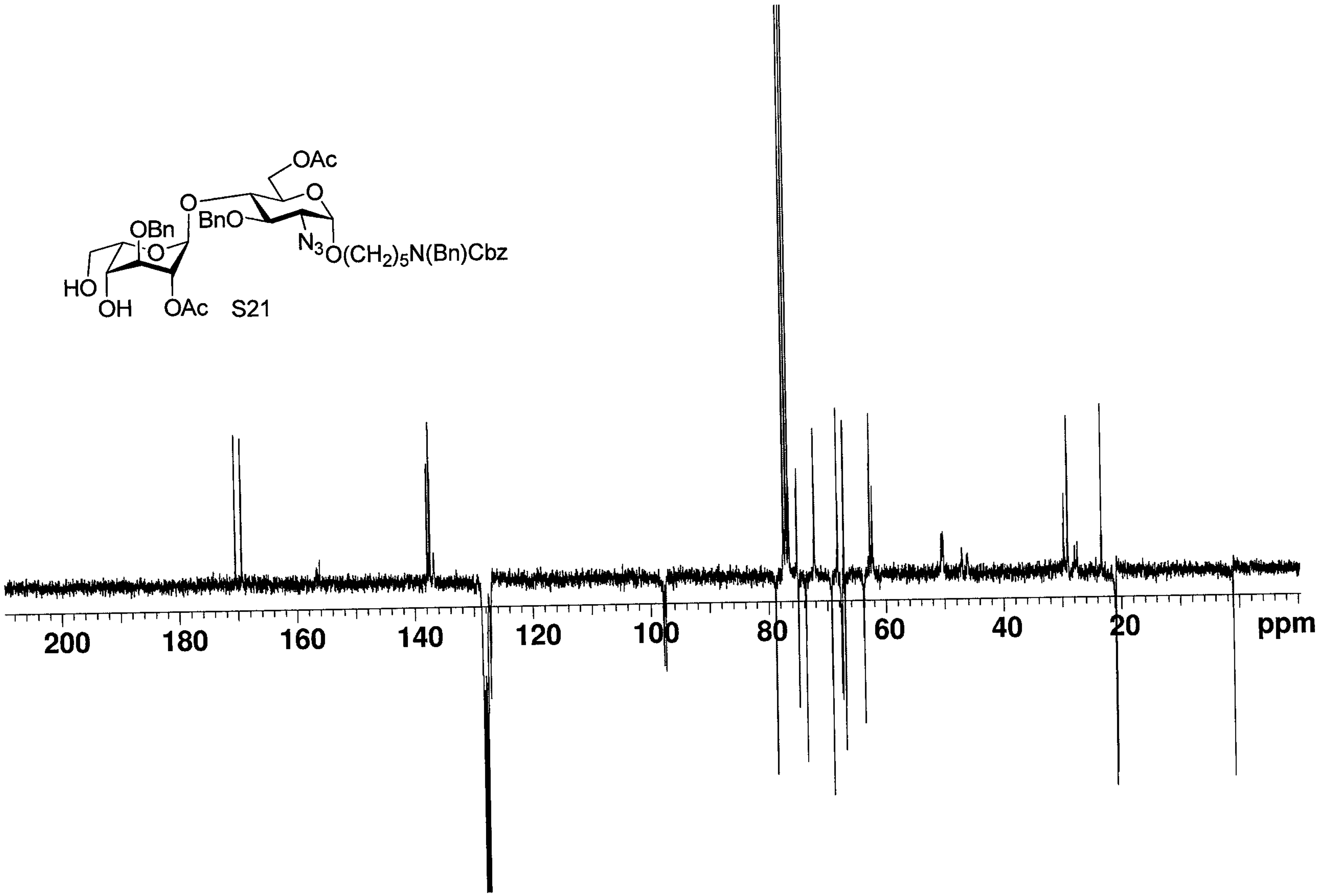


200
180
160
140
120
100
80
60
40
20
ppm



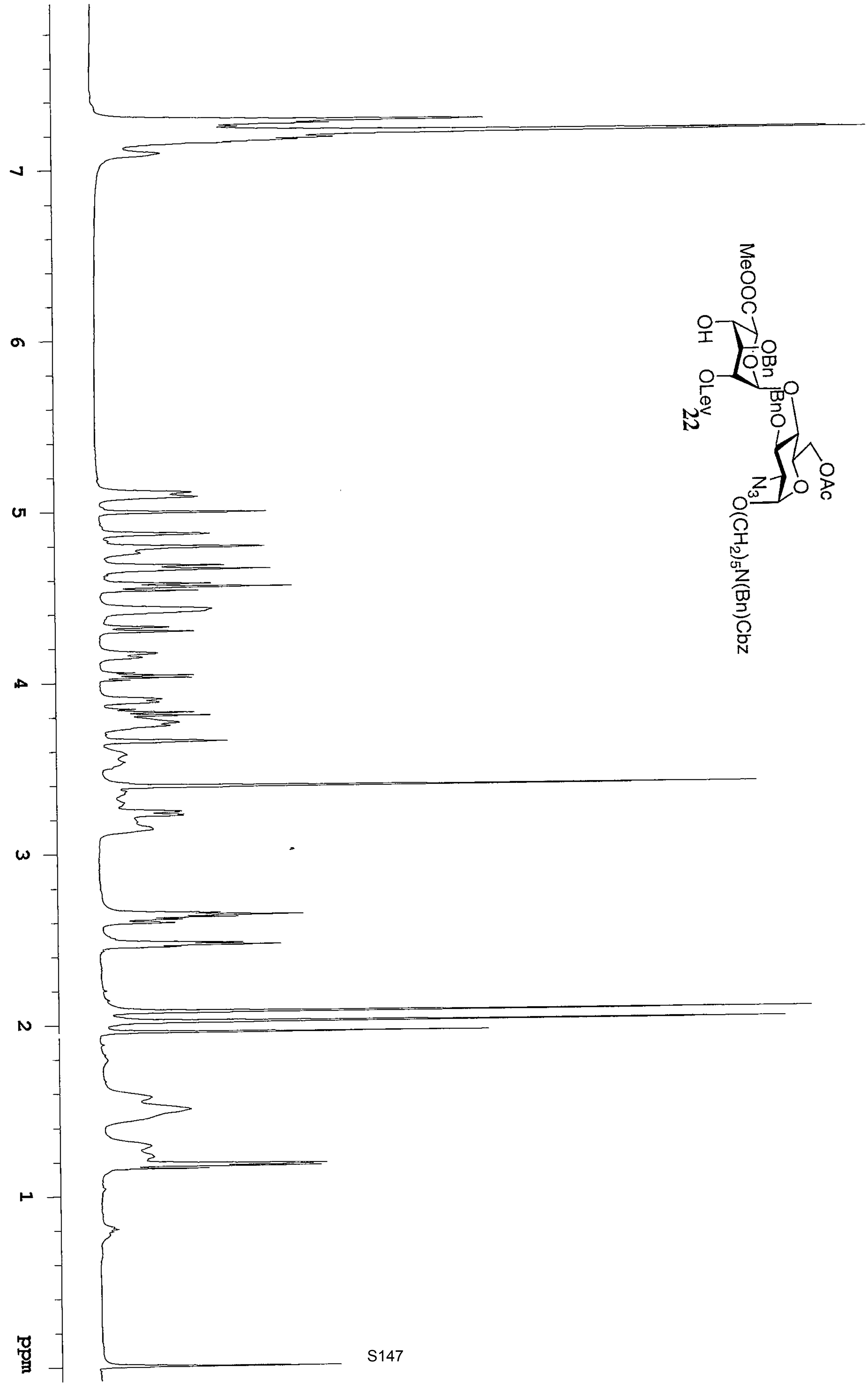
S21



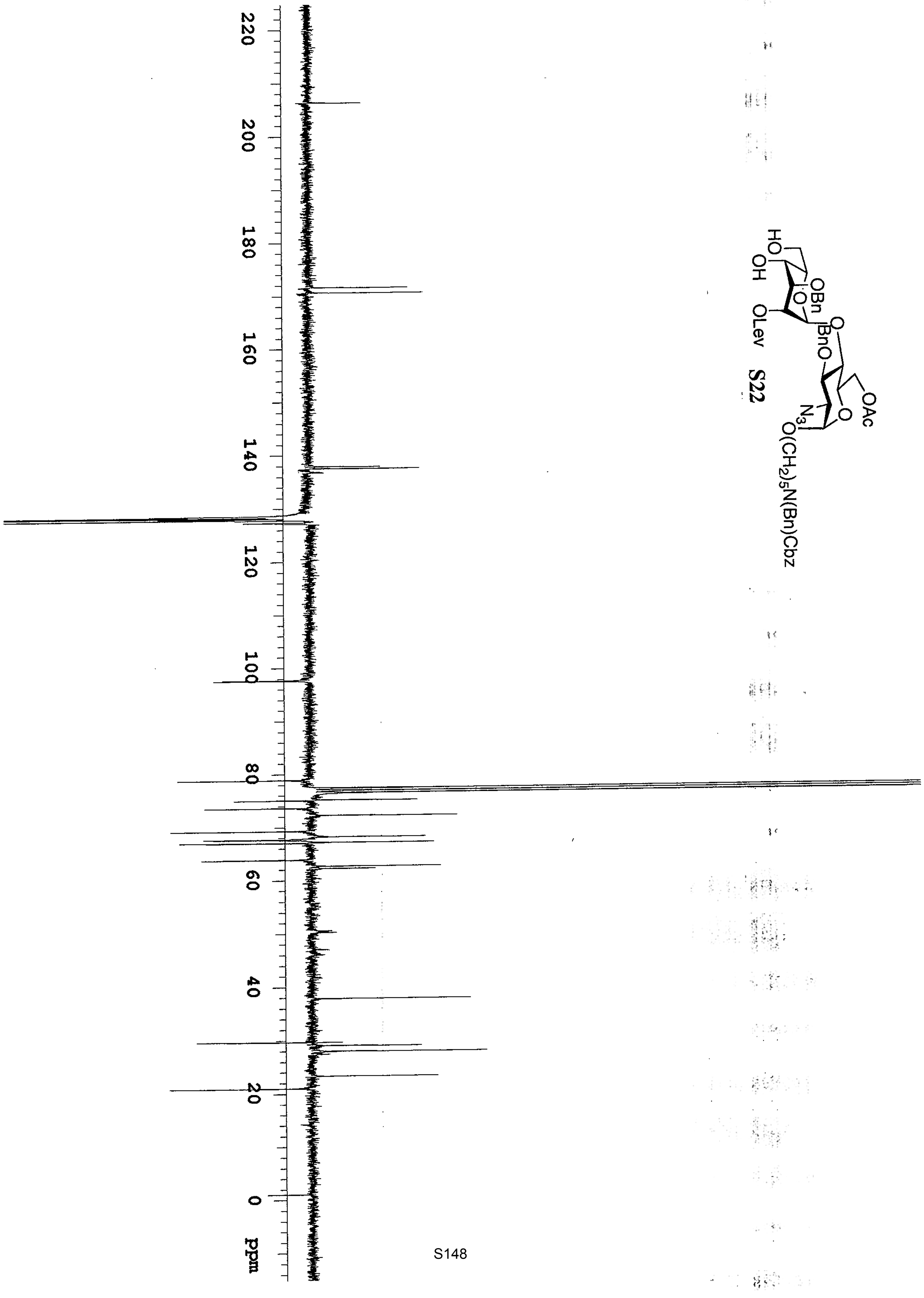

OAc
O
O
OBn
BnO
O
N3
O(CH2)5N(Bn)Cbz
HO
OH
OAc

S21

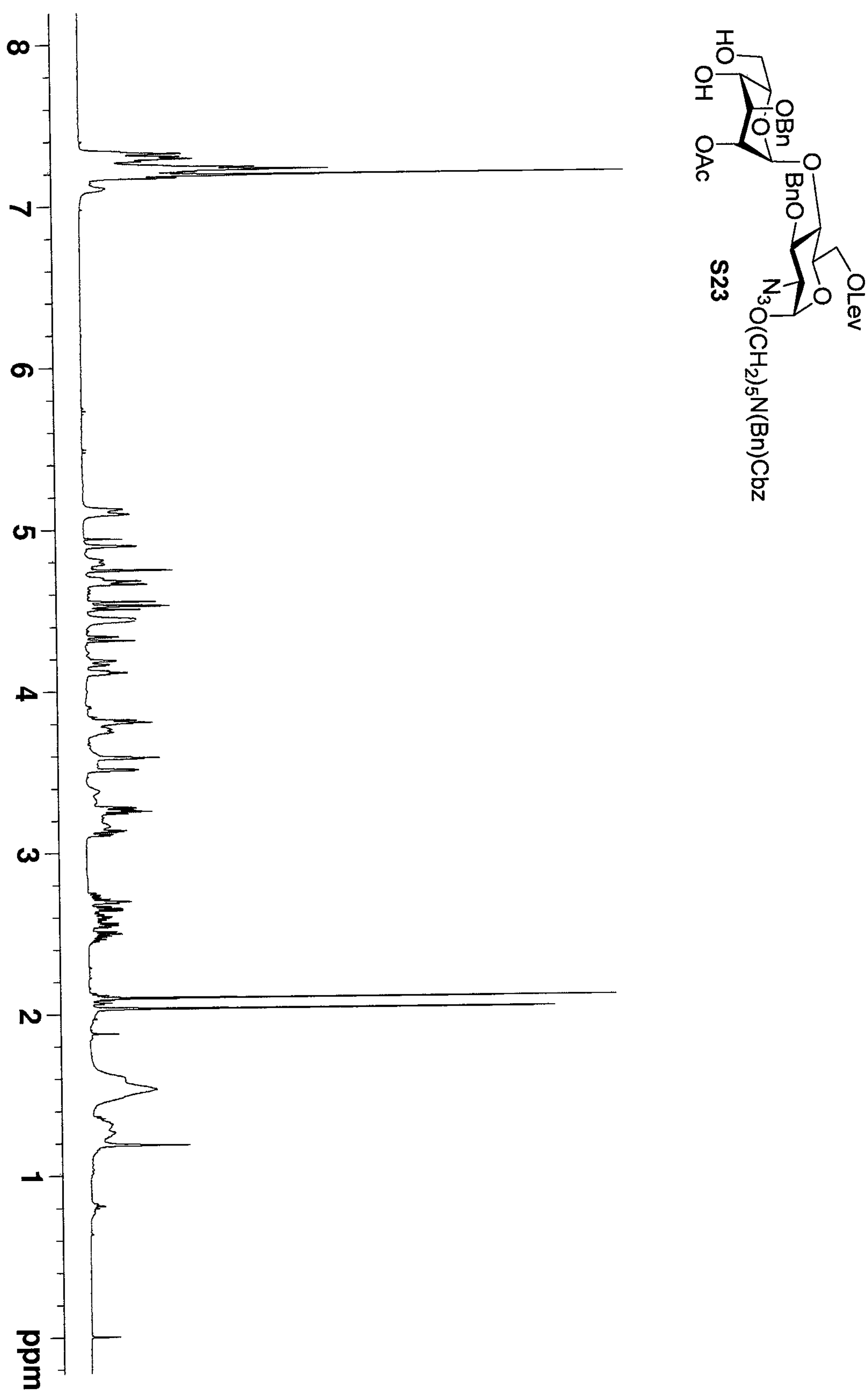
200
180
160
140
120
100
80
60
40
20
ppm



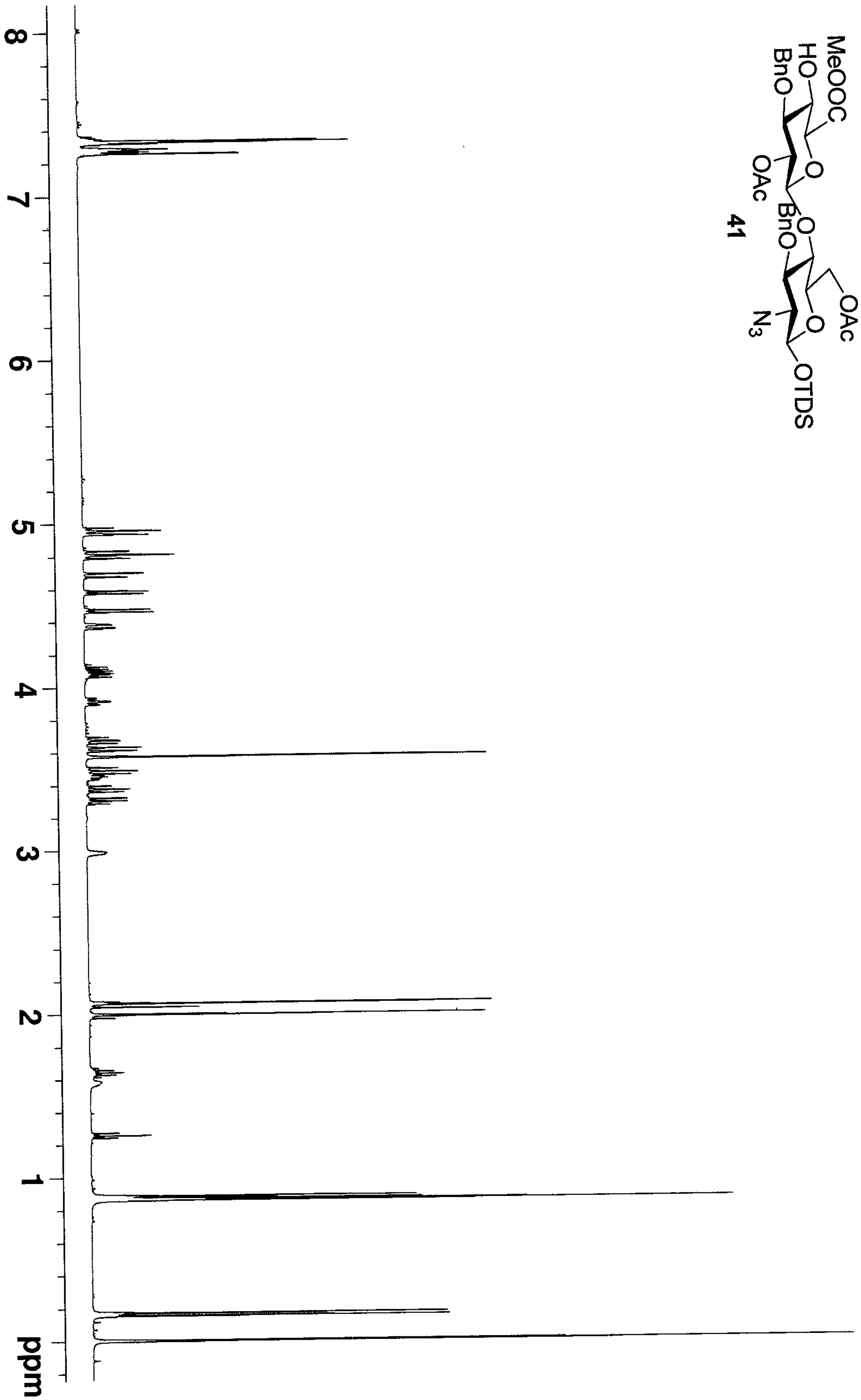
7
6
5
4
3
2
1
ppm
MeOOC
OH
OBn
O
OLev
BnO
O
OAc
O
N$_3$
O(CH$_2$)$_5$N(Bn)Cbz
22


S22

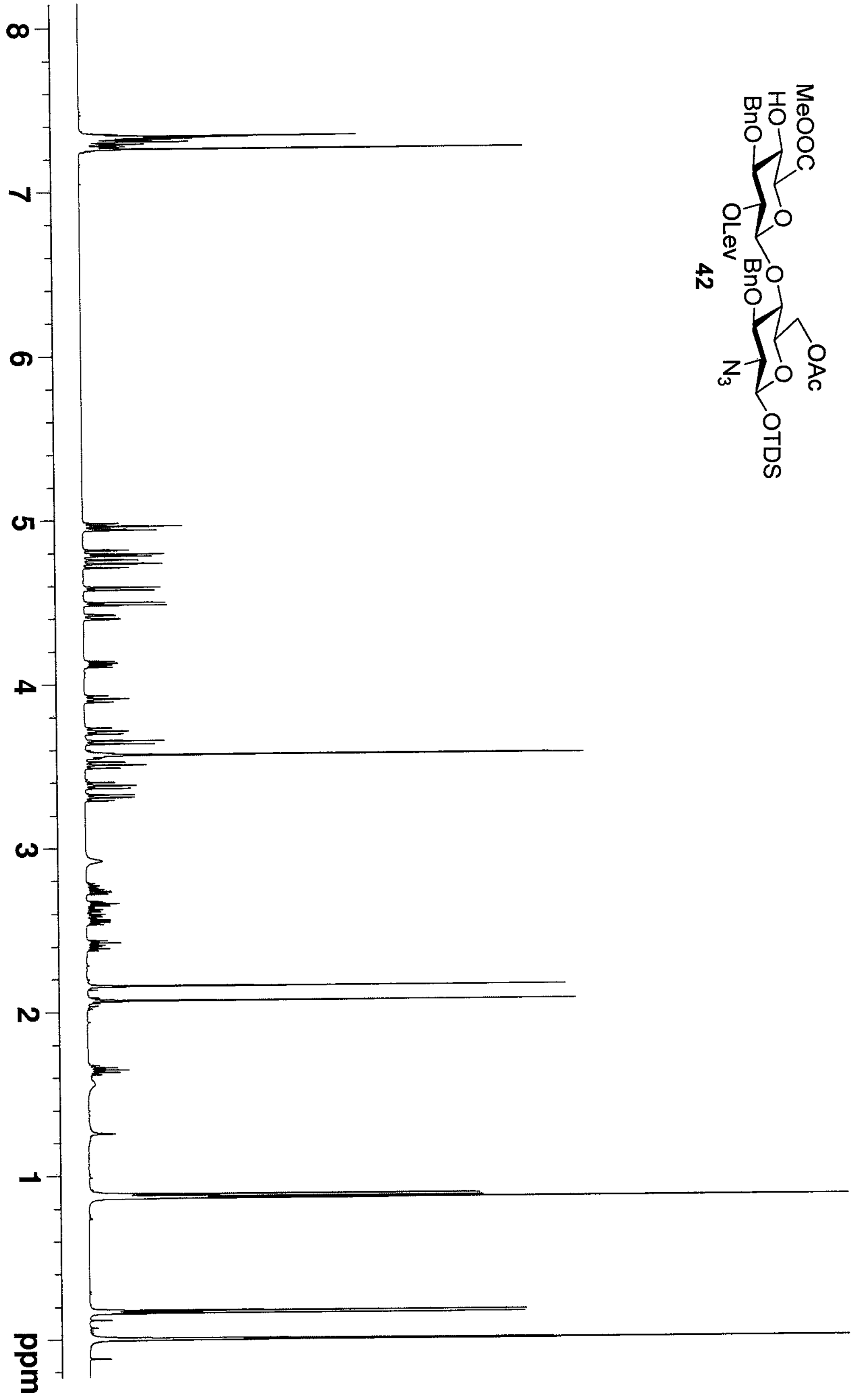
OAc
O
O
BnO
N3
O(CH2)5N(Bn)Cbz
O
OBn
HO
OH
OLev
220
200
180
160
140
120
100
80
60
40
20
0
ppm



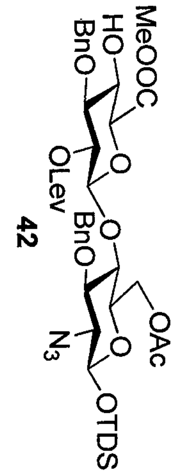
S23



41

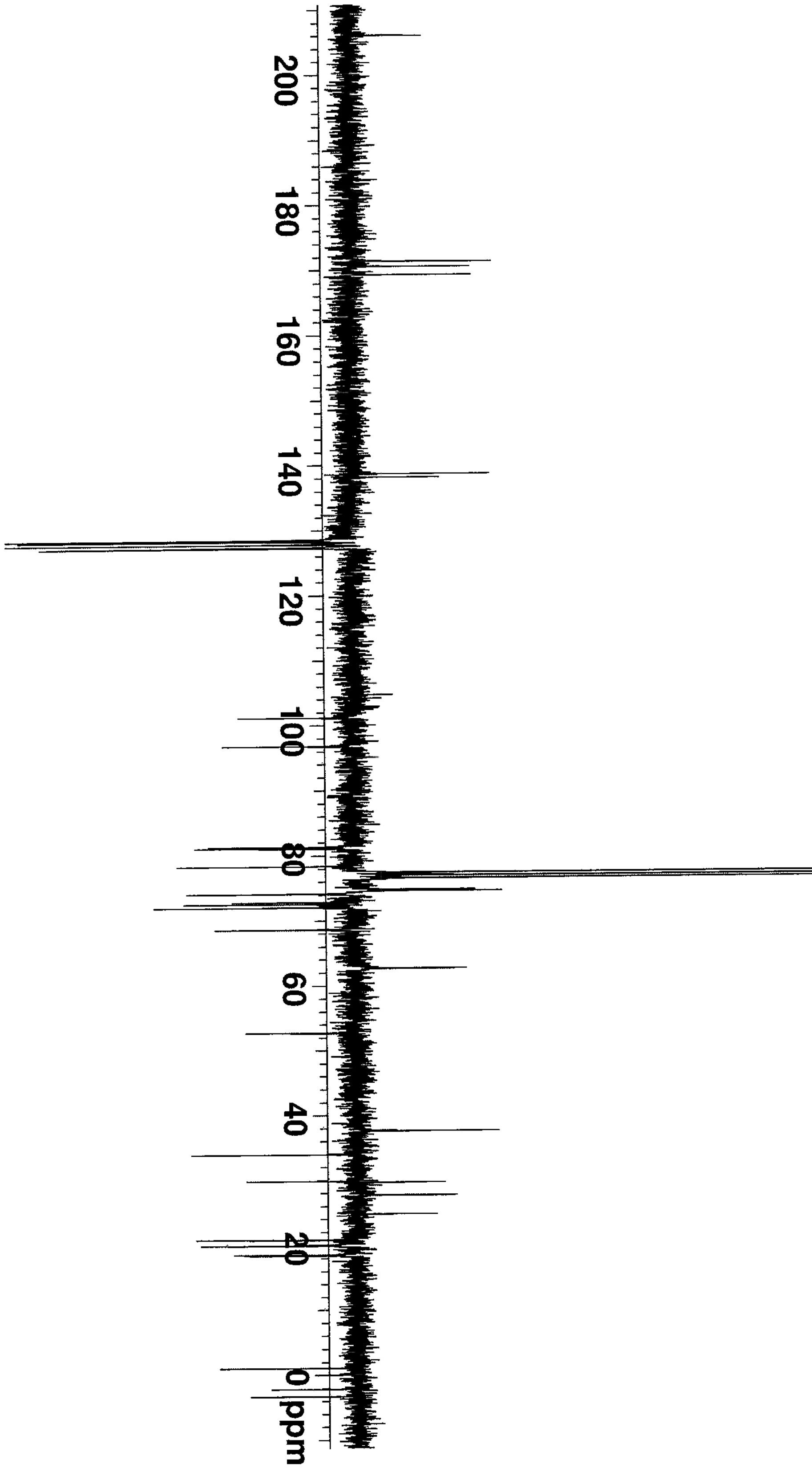


42



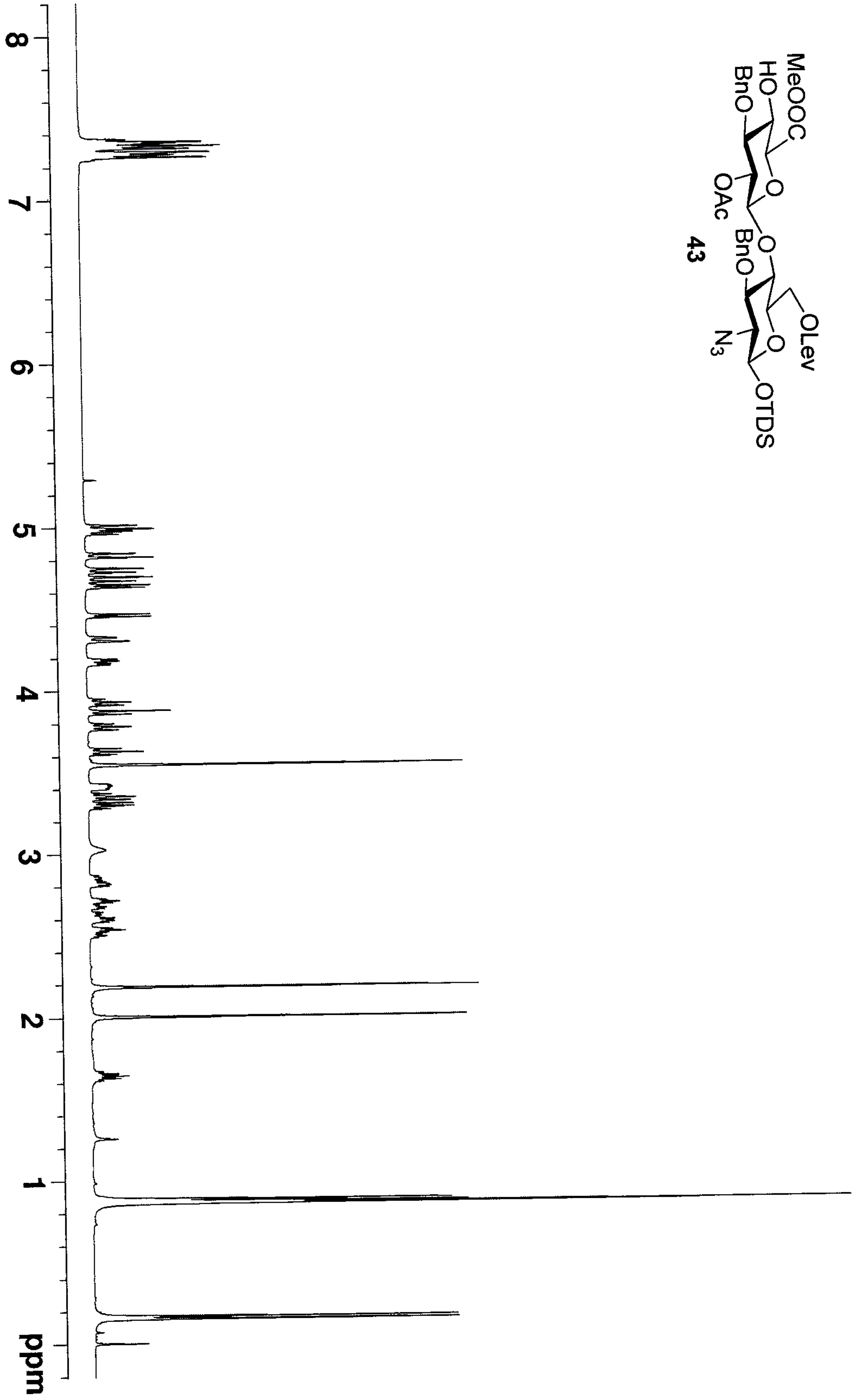
MeOOC
HO
BnO
O
OLev
O
BnO
OAc
O
N$_3$
OTDS

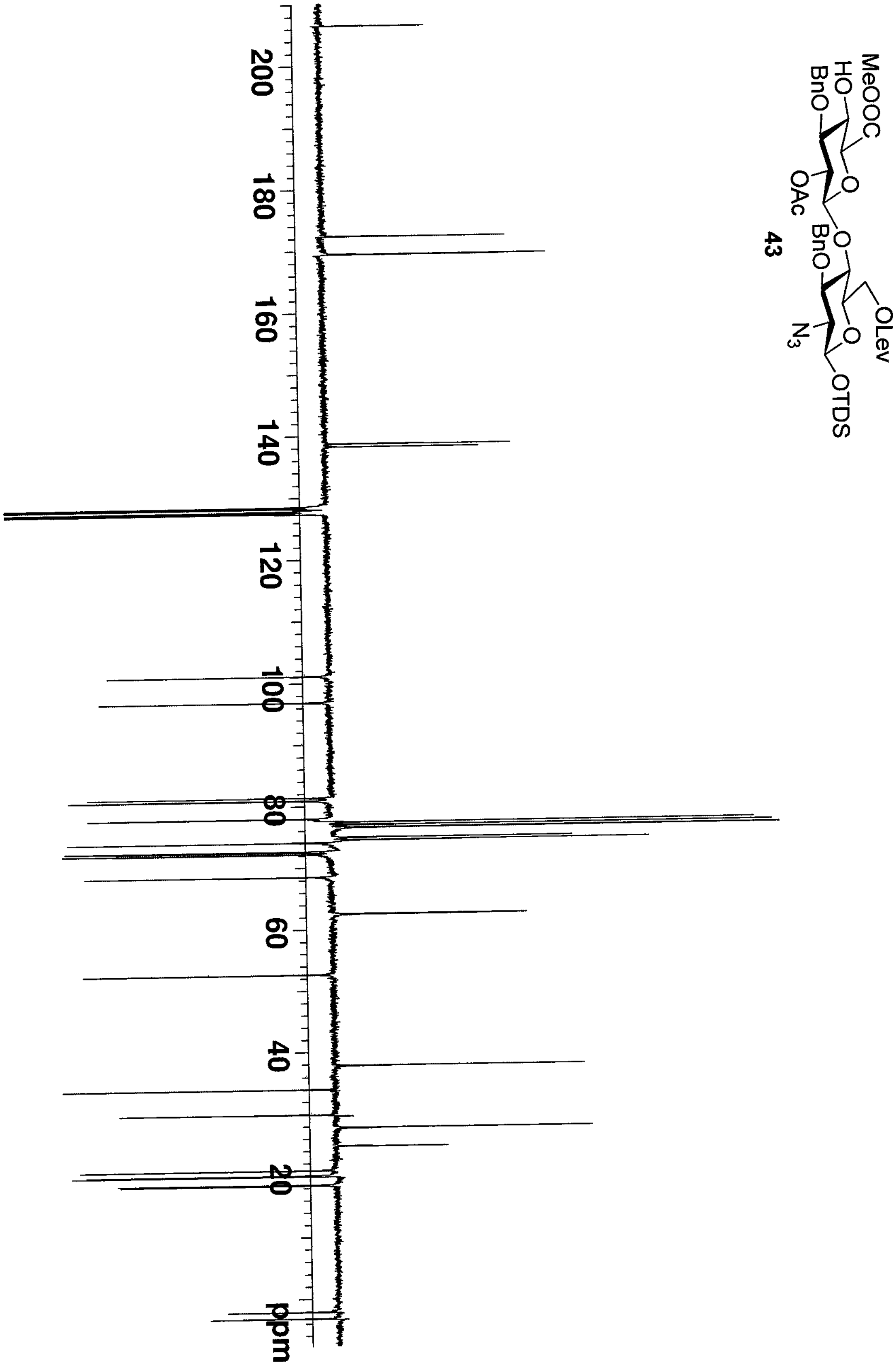
42



200
180
160
140
120
100
80
60
40
20
0
ppm

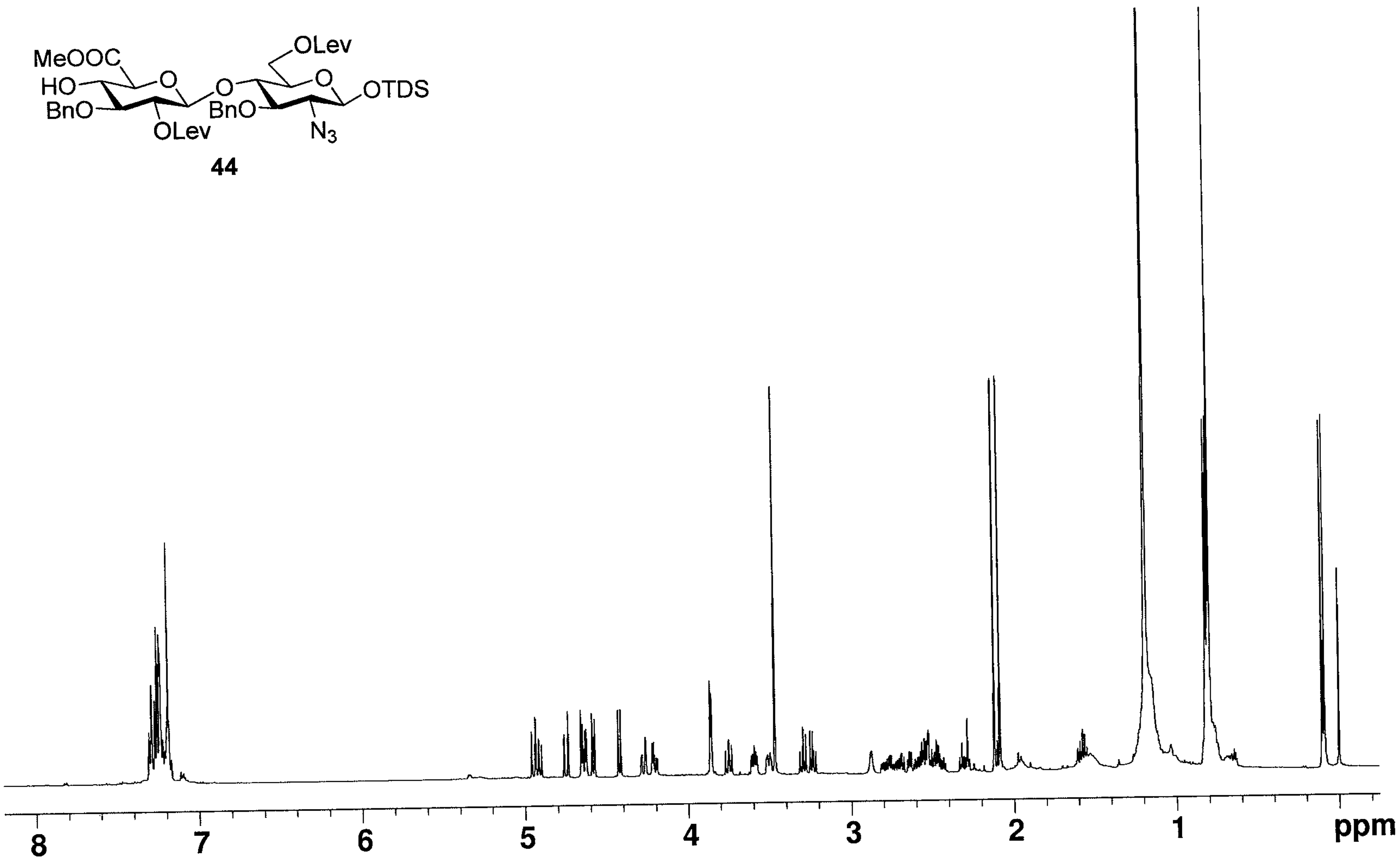
43





43

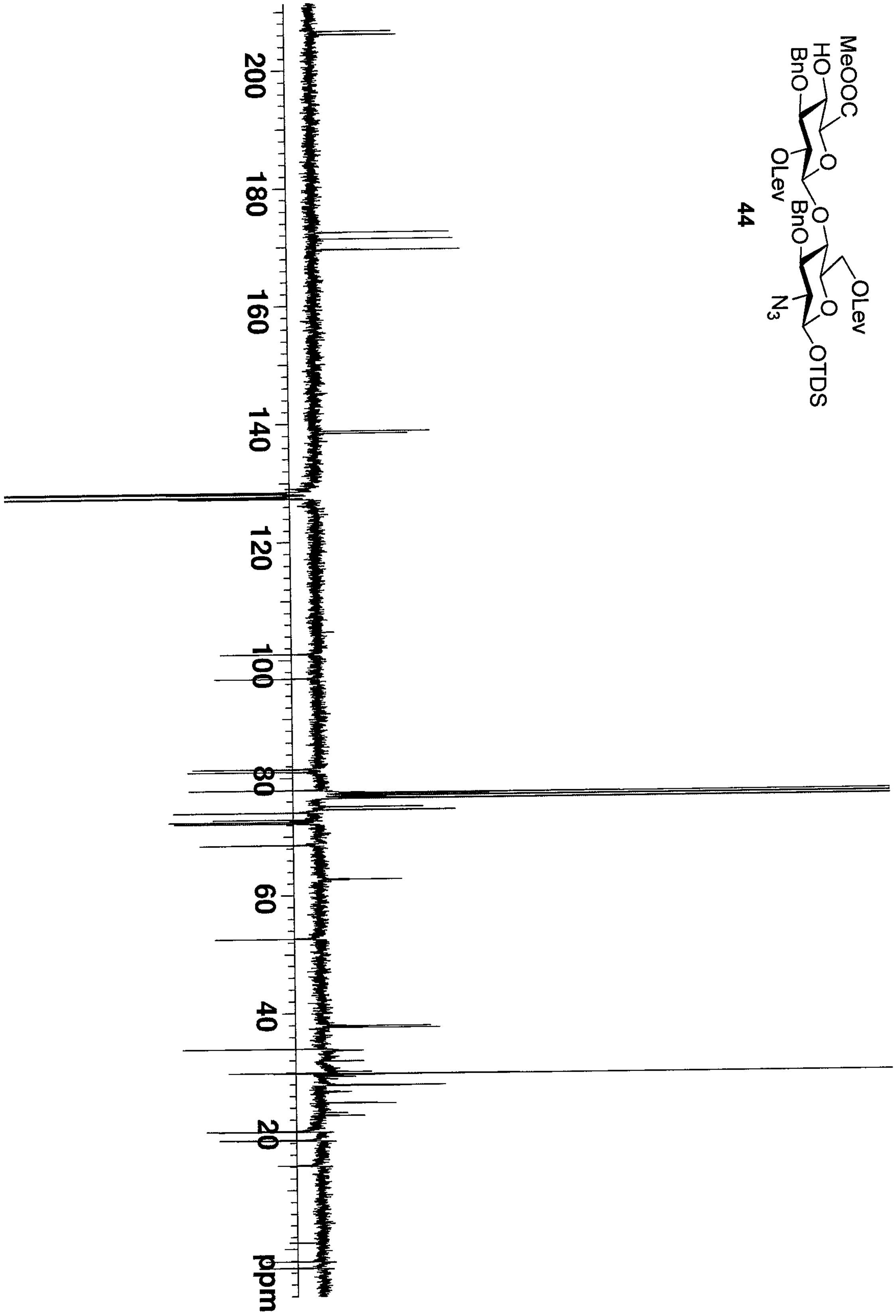
MeOOC
HO
BnO
O
OAc
O
BnO
O
OLev
N3
OTDS
200
180
160
140
120
100
80
60
40
20
ppm

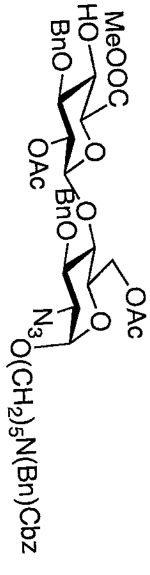


44

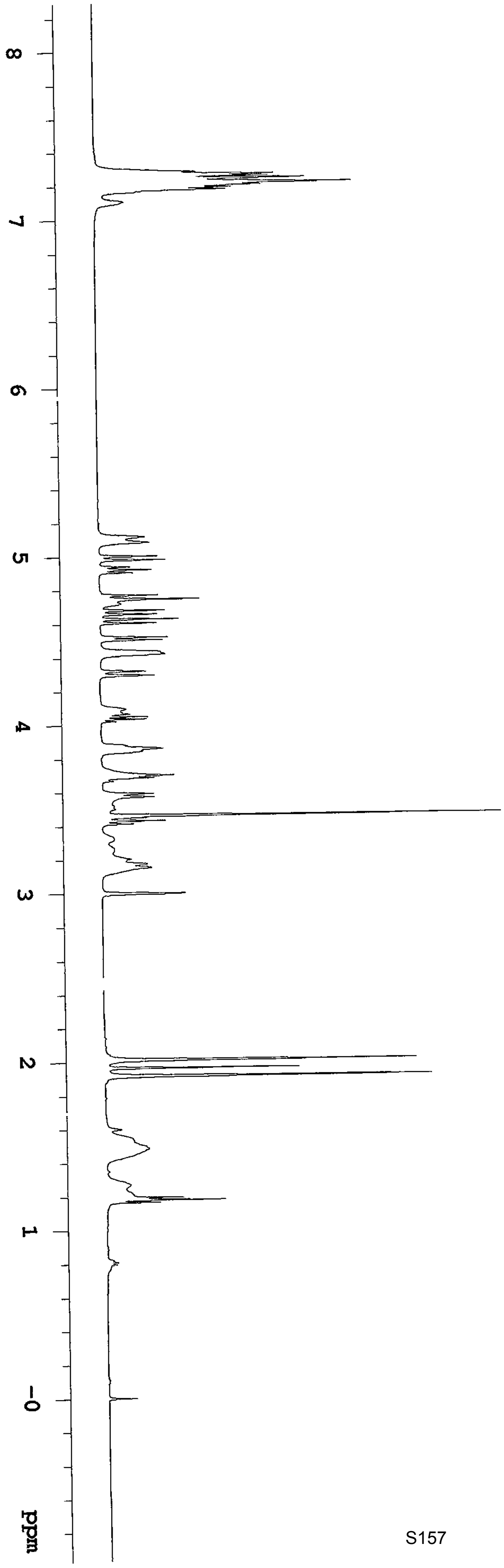
MeOOC
HO
BnO
O
OLev
O
BnO
O
OLev
N$_3$
OTDS

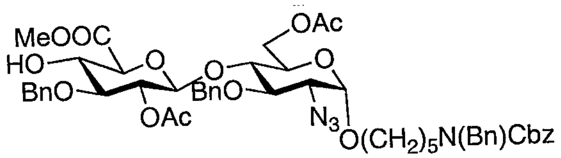
44


200
180
160
140
120
100
80
60
40
20
ppm

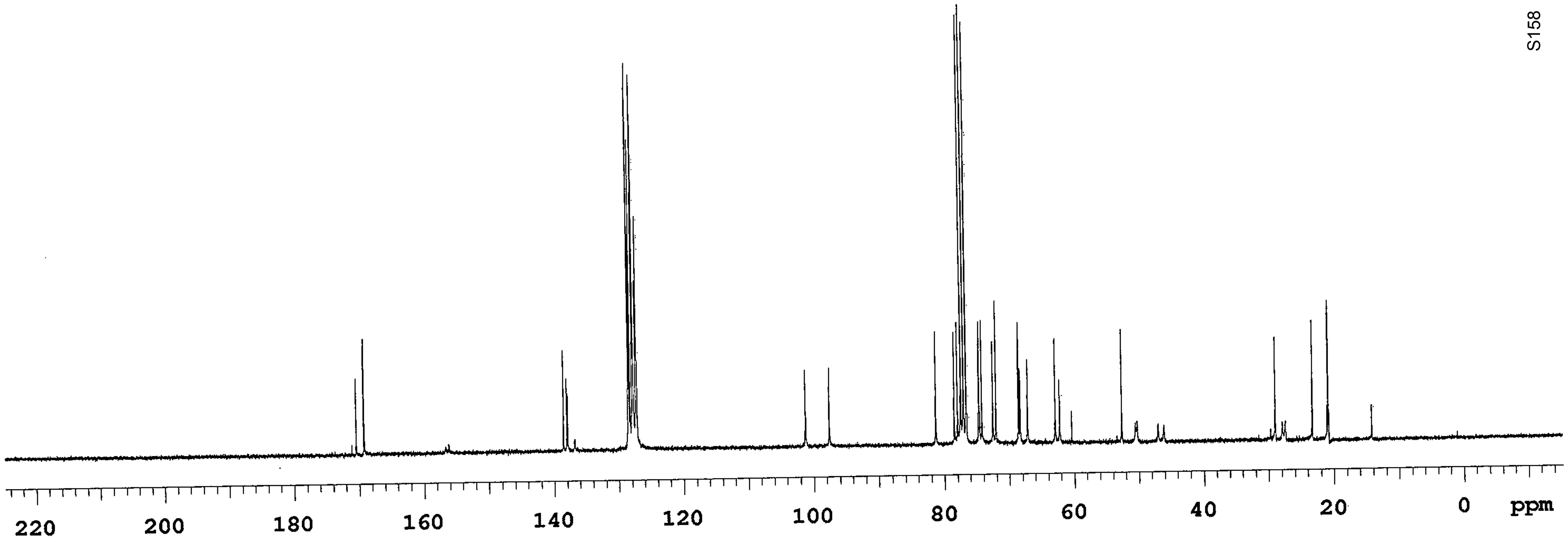


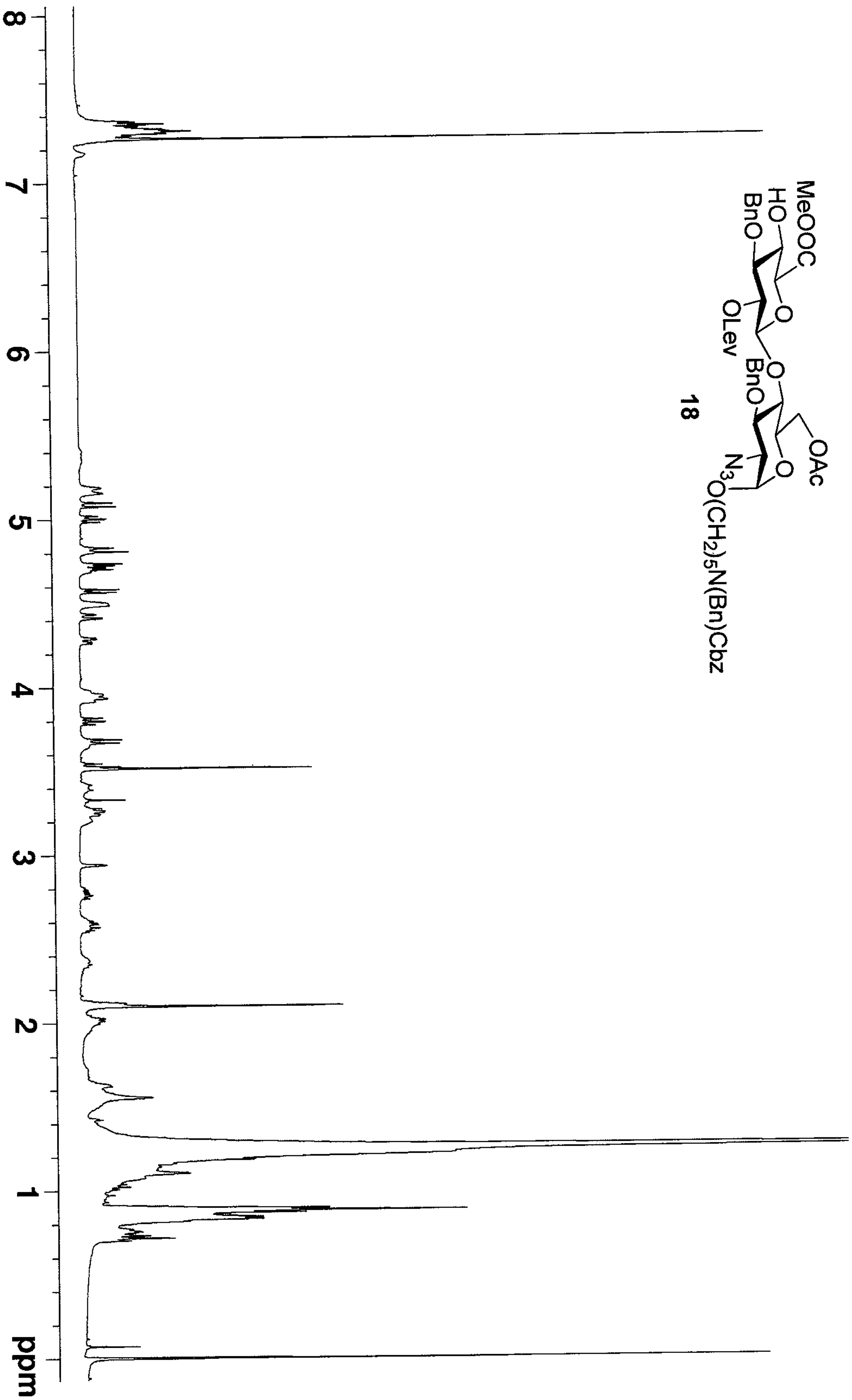
17




MeOOC
HO
BnO
O
OAc
O
BnO
OAc
O
N3
O(CH2)5N(Bn)Cbz

17

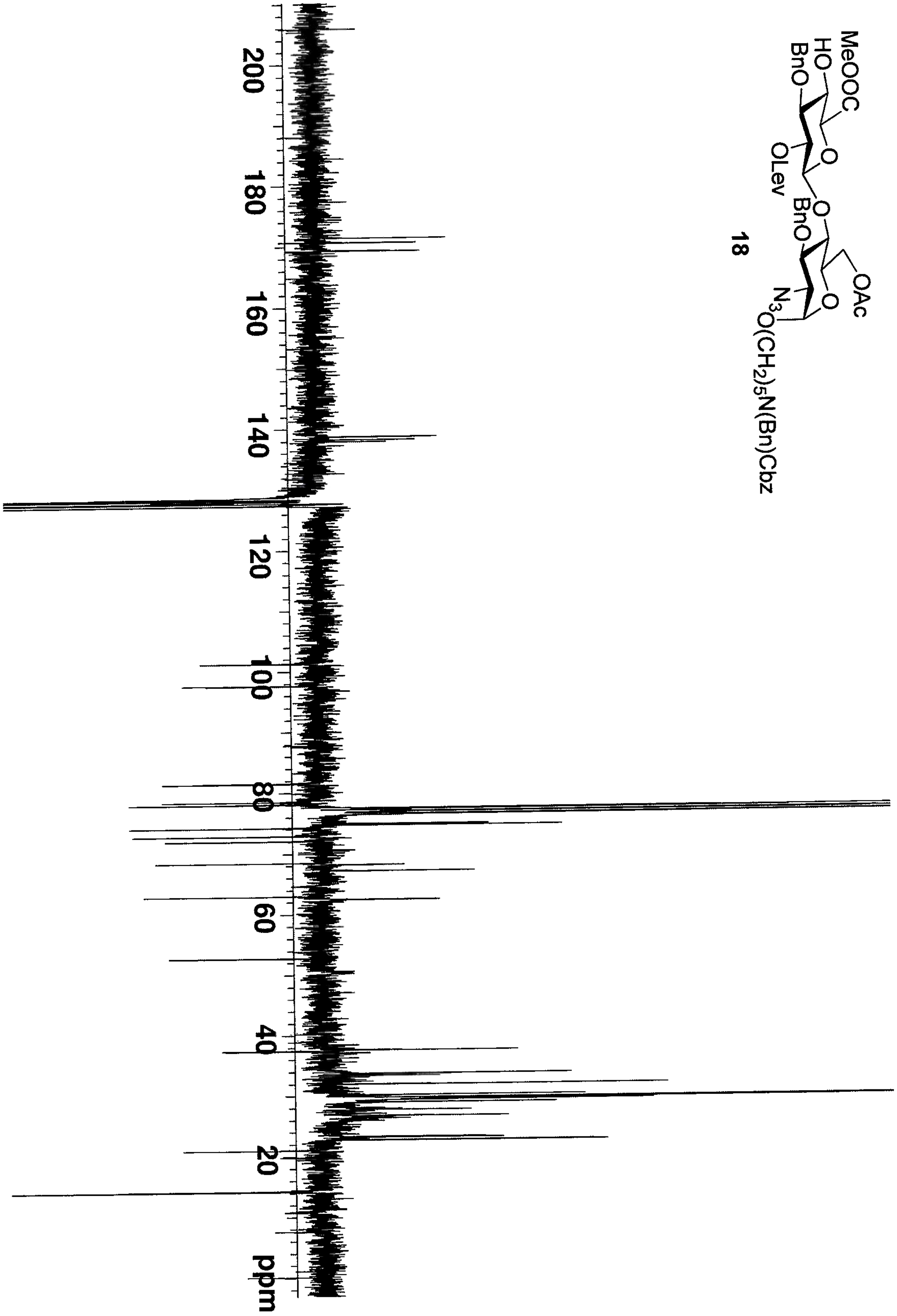

220
200
180
160
140
120
100
80
60
40
20
0
ppm

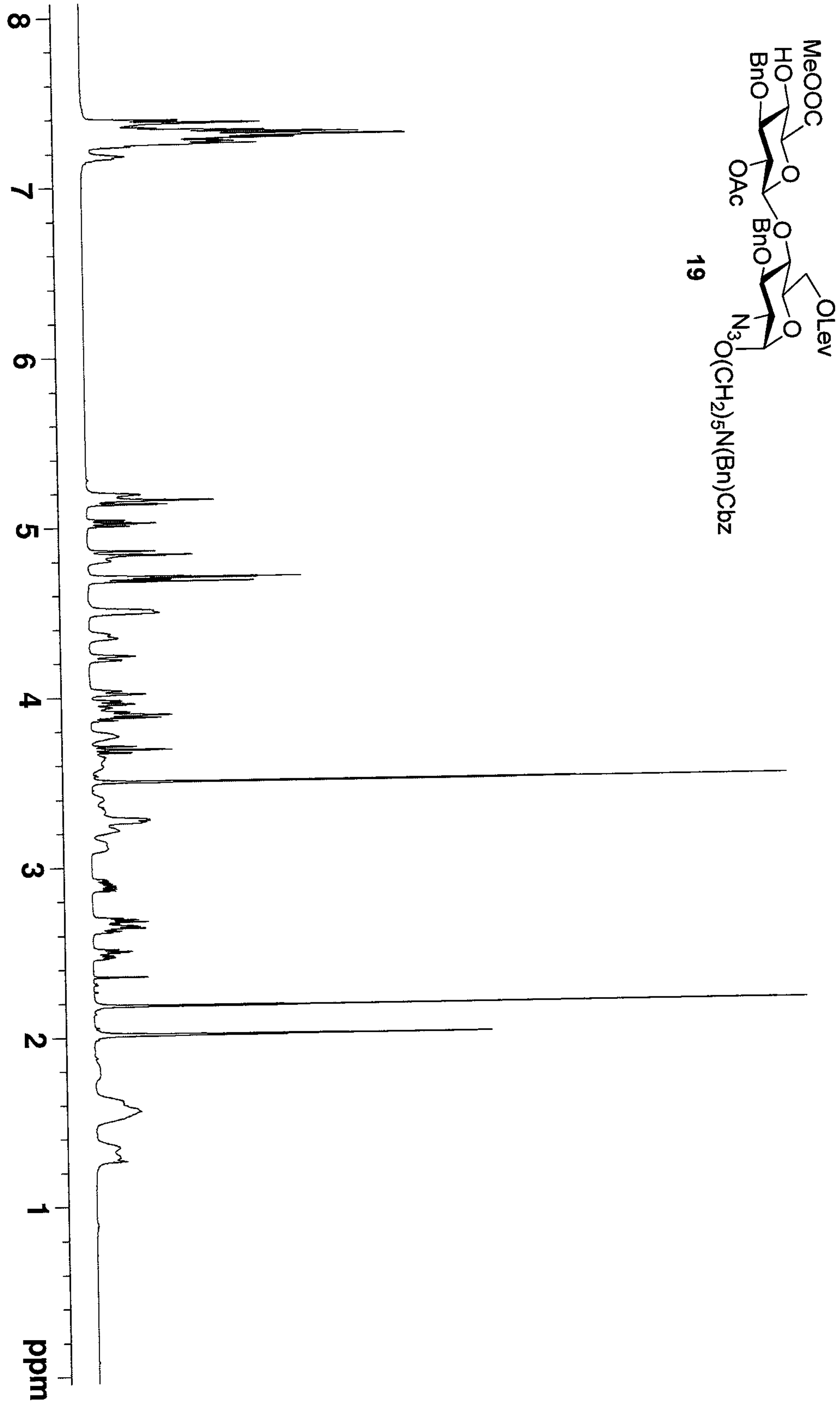


18

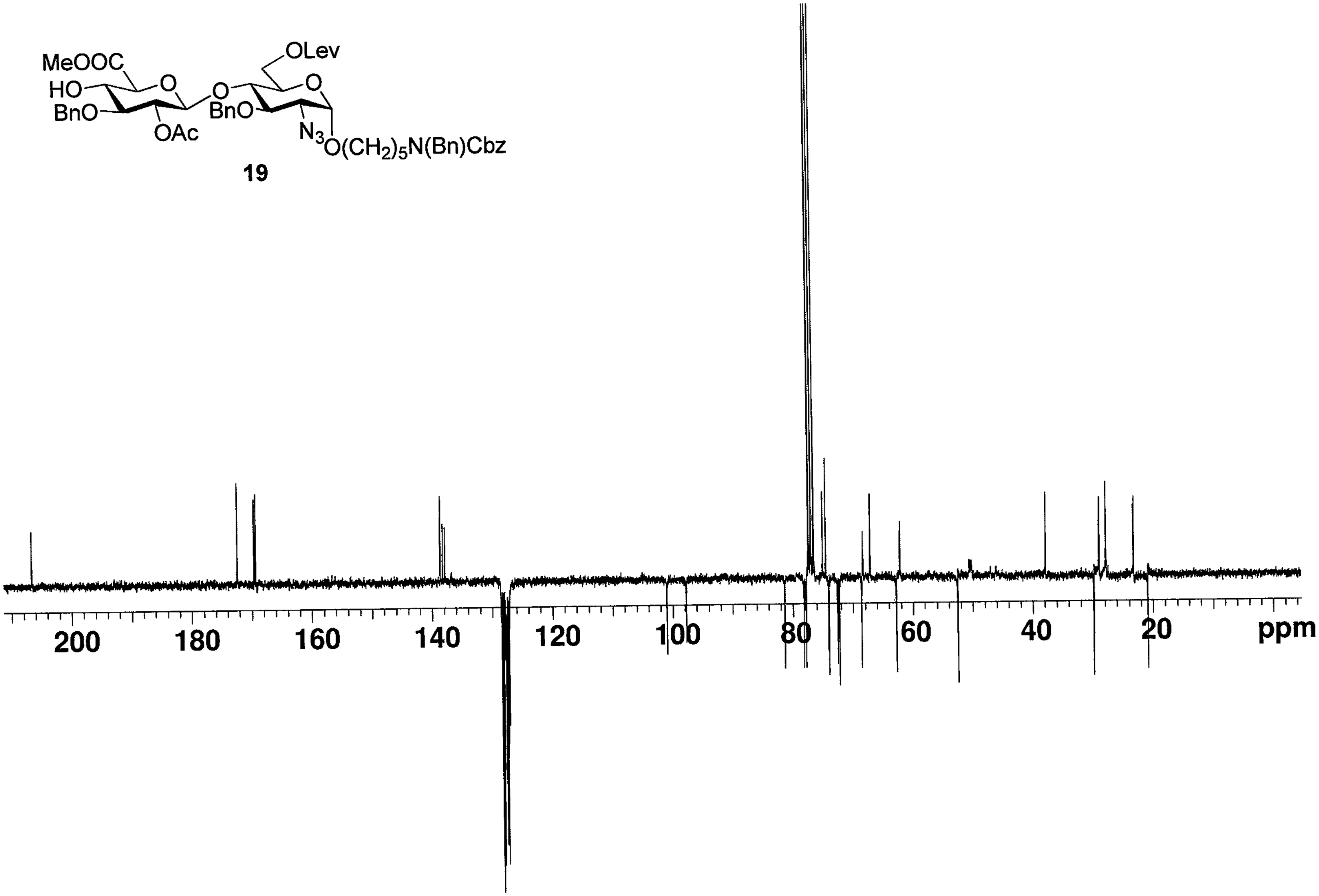
MeOOC
HO
BnO
O
OLev
O
BnO
OAc
O
N3
O(CH2)5N(Bn)Cbz

18


200
180
160
140
120
100
80
60
40
20
ppm

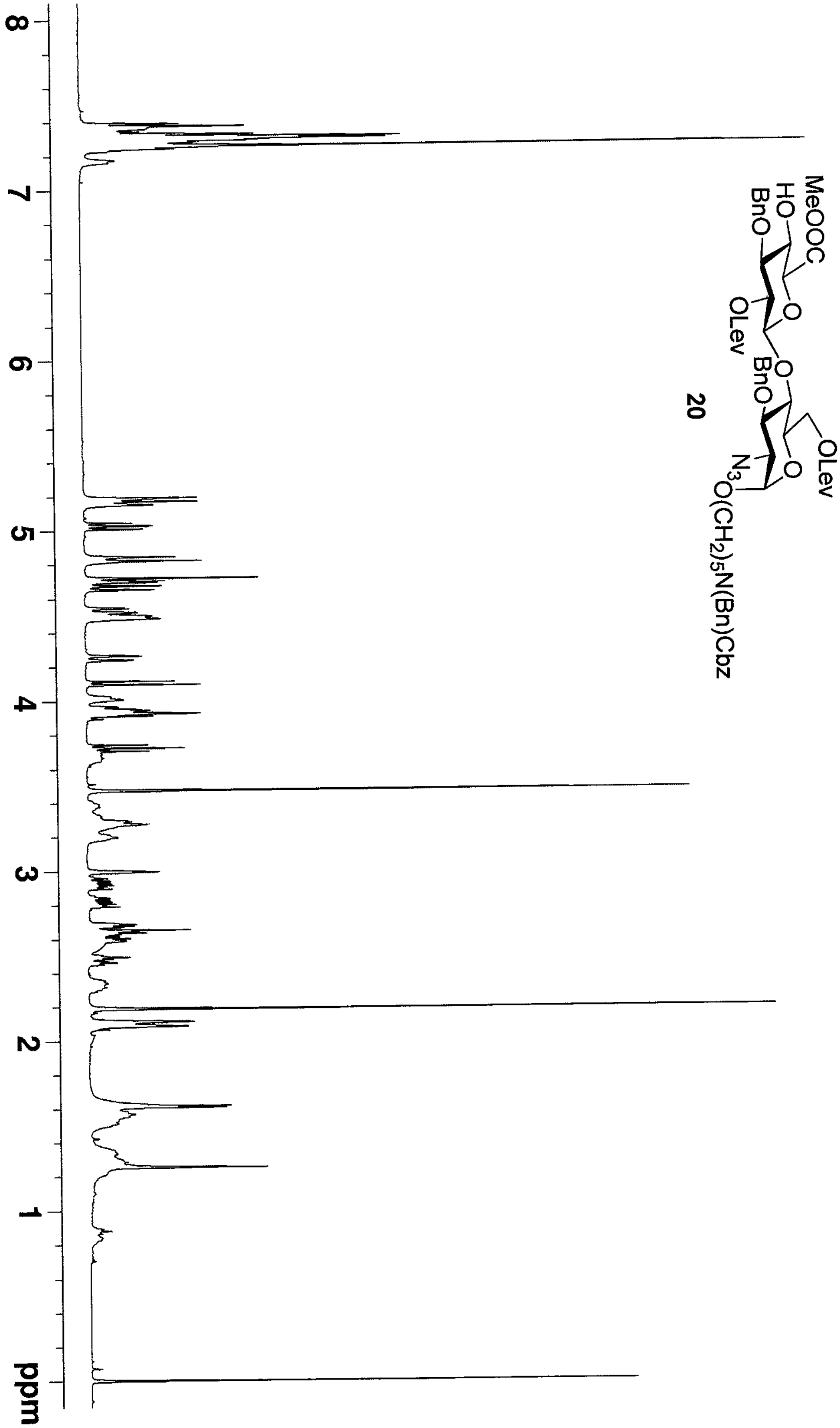


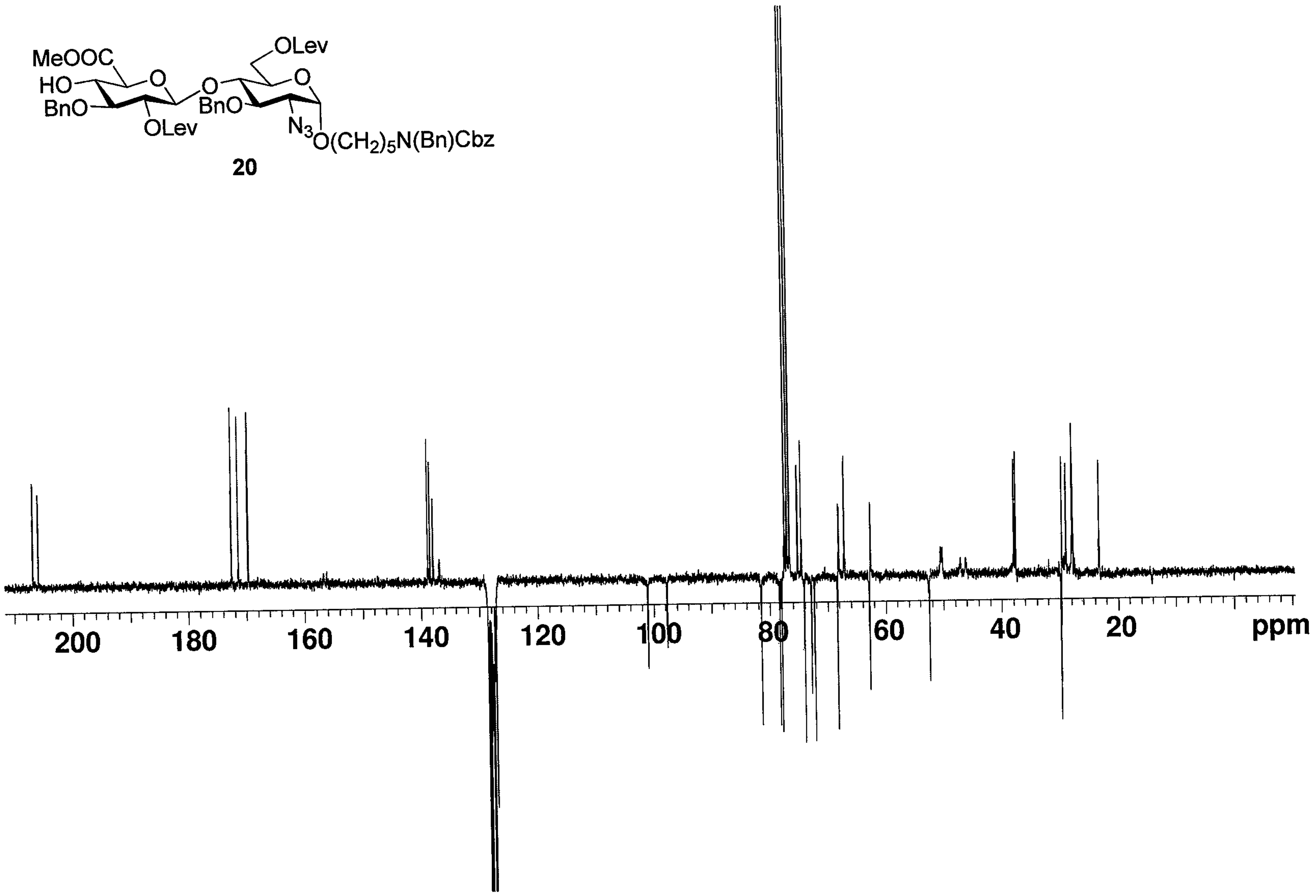
19


MeOOC
HO
BnO
O
OAc
O
BnO
OLev
O
N3
O(CH2)5N(Bn)Cbz

19

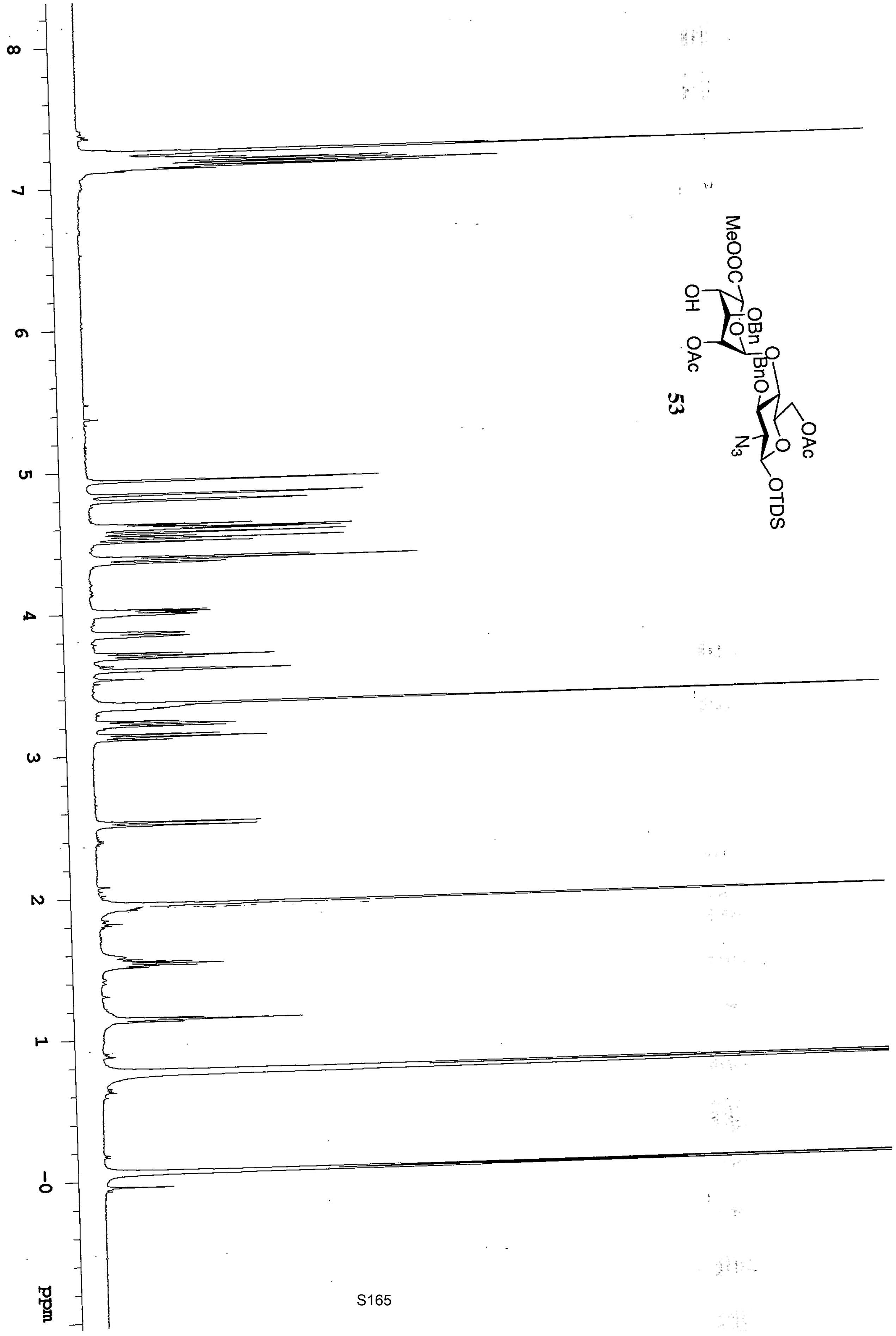
200
180
160
140
120
100
80
60
40
20
ppm

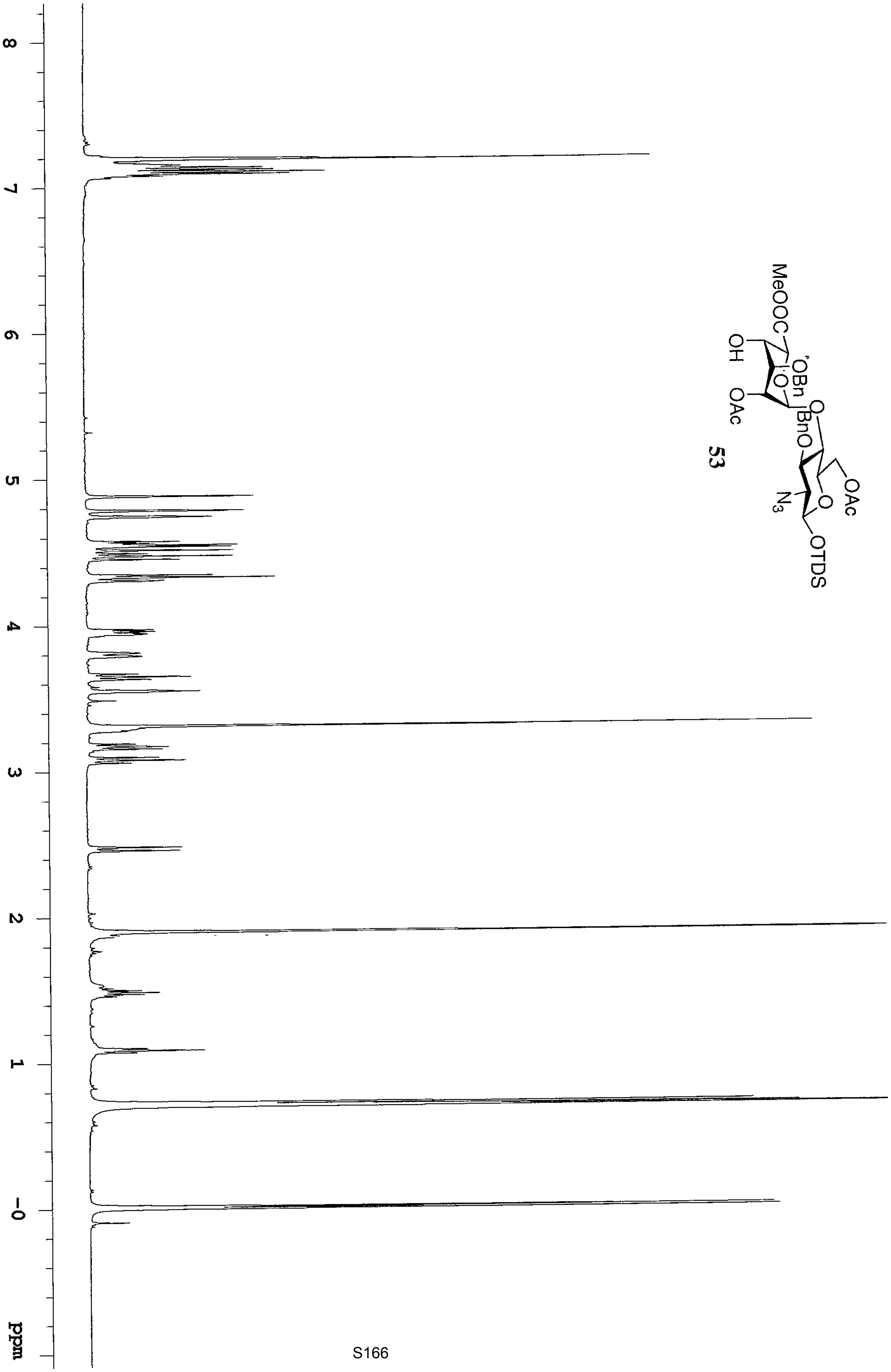

MeOOC
HO
BnO
O
OLev
O
BnO
O
OLev
N3
O(CH2)5N(Bn)Cbz
20
8
7
6
5
4
3
2
1
ppm



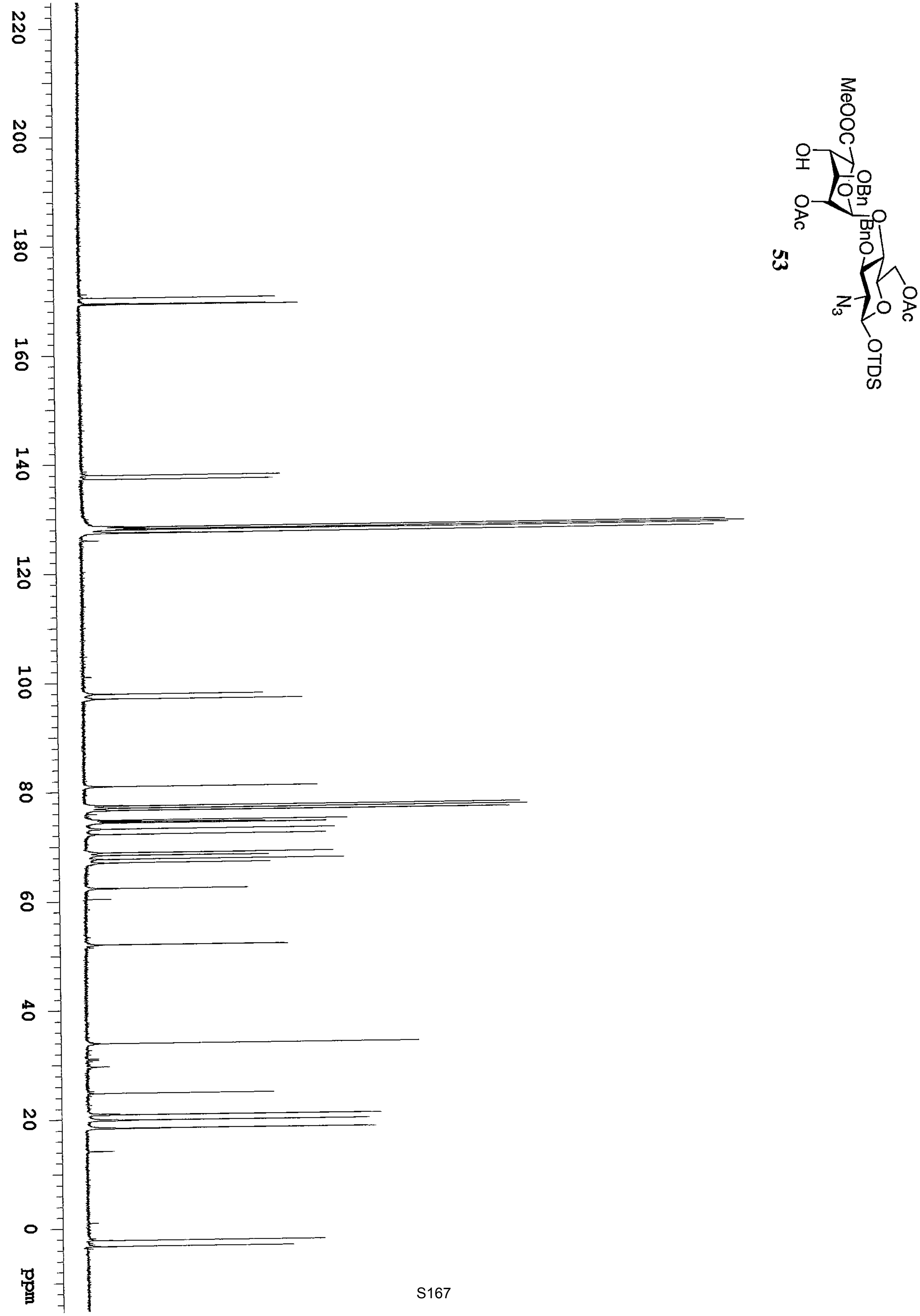
20

MeOOC
HO
BnO
O
OLev
O
BnO
O
OLev
N3
O(CH2)5N(Bn)Cbz
200
180
160
140
120
100
80
60
40
20
ppm

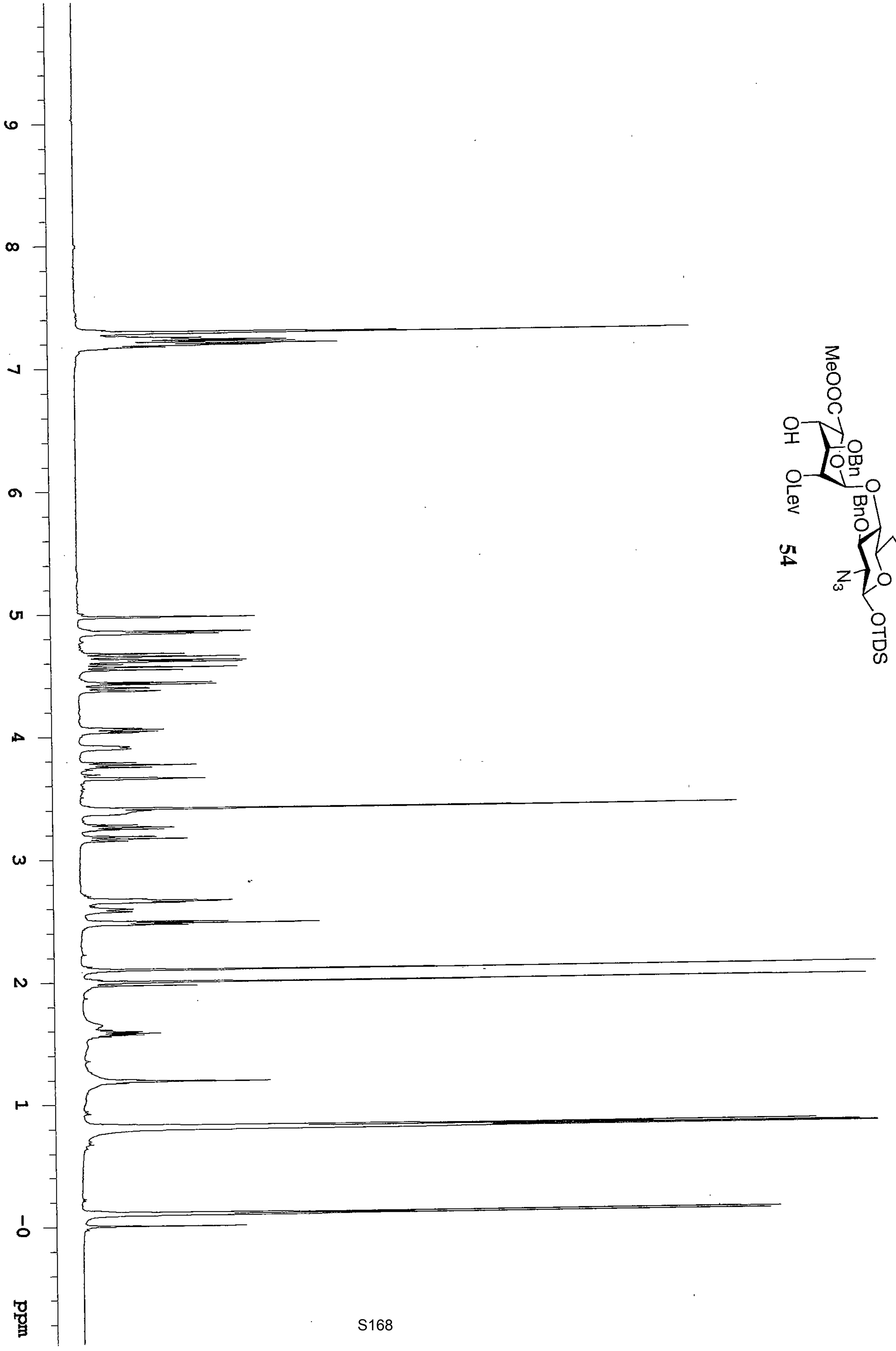

53



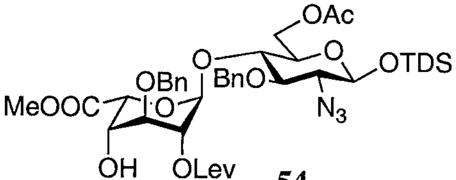
53


MeOOC
OH
OBn
O
OAc
O
BnO
OAc
O
N3
OTDS
220
200
180
160
140
120
100
80
60
40
20
0
ppm

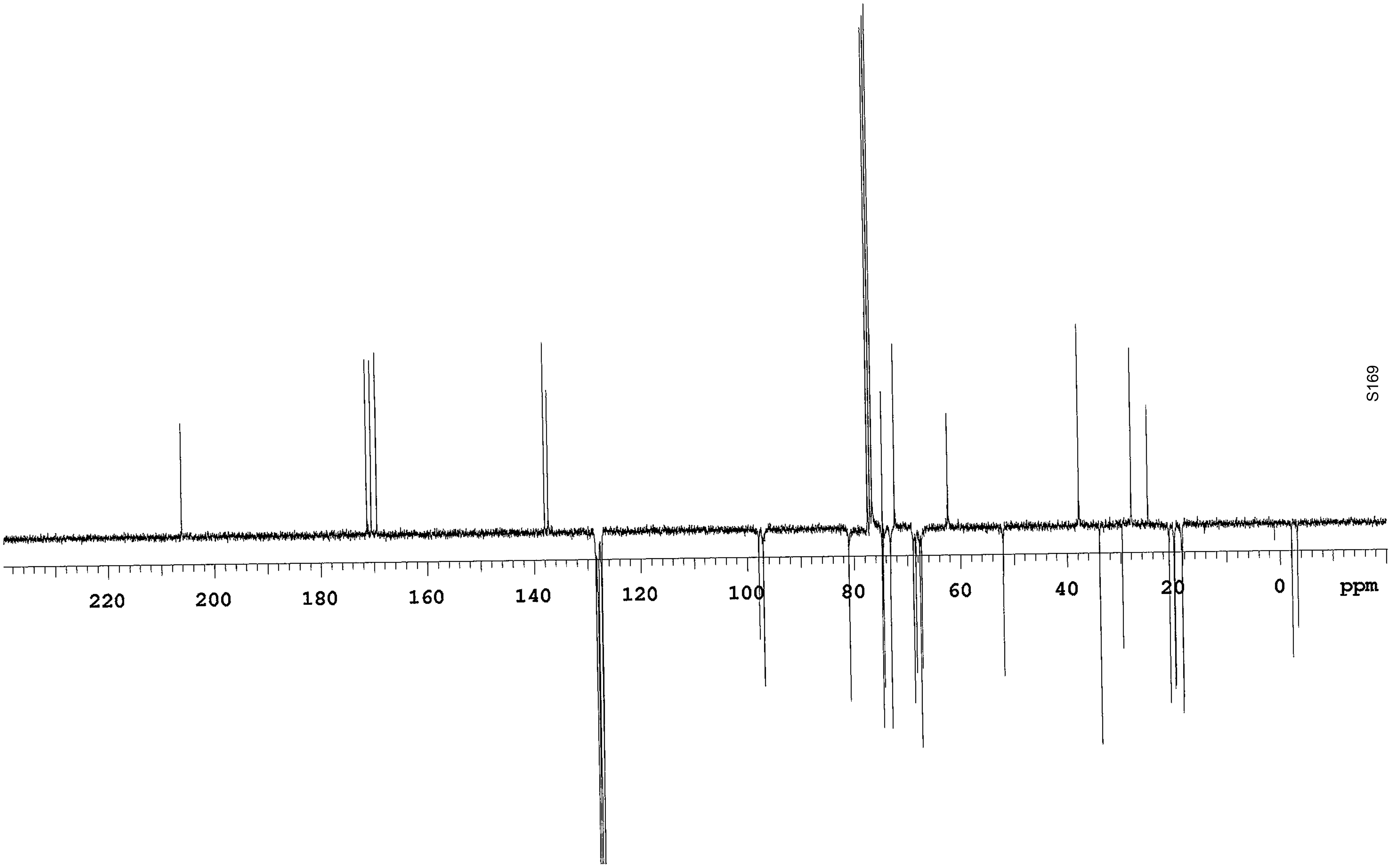
53

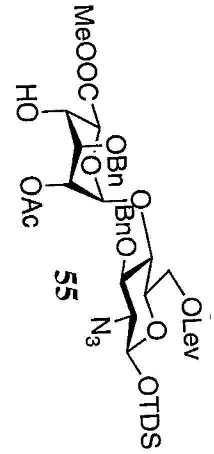


54

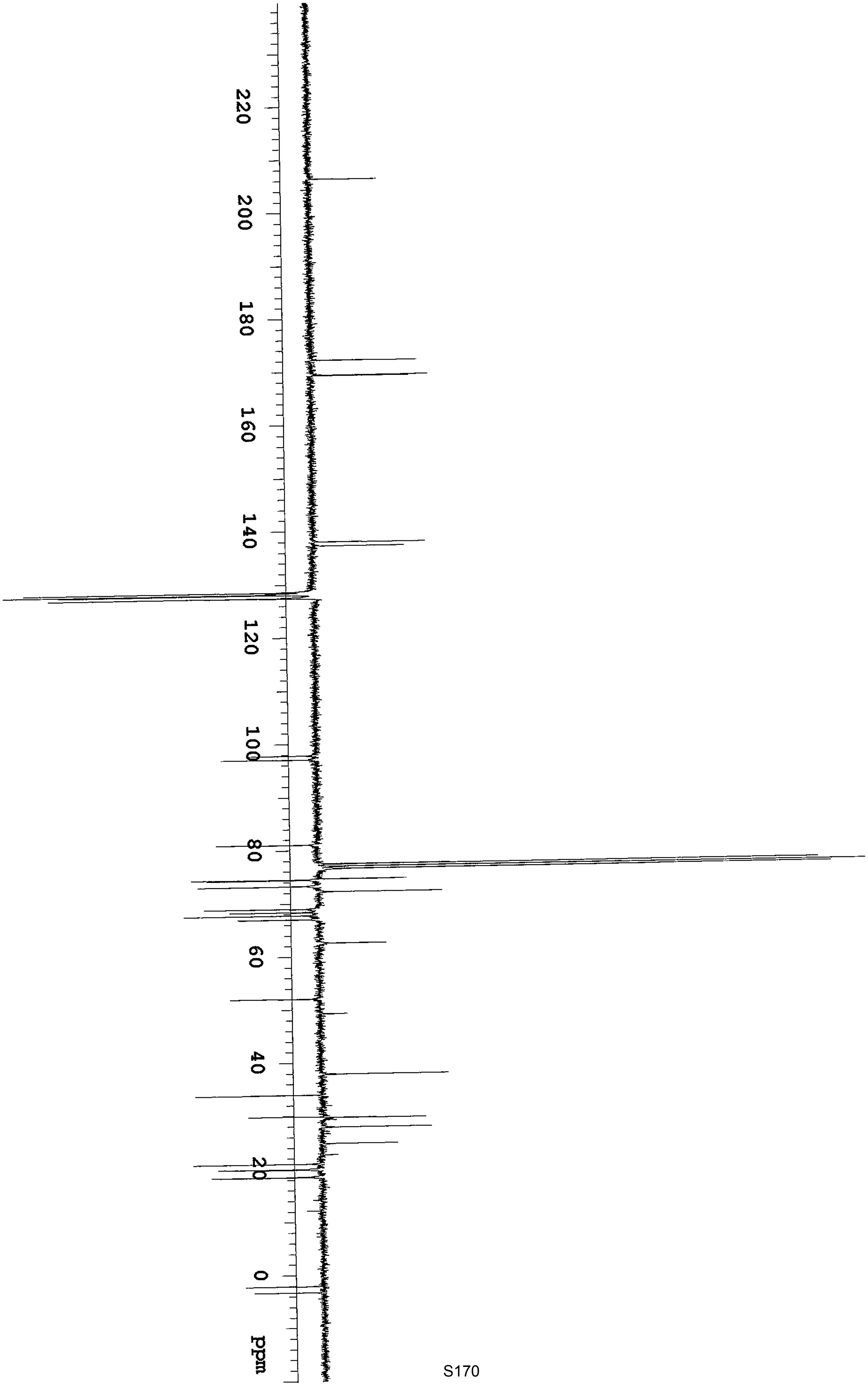

MeOOC
OBn
O
O
BnO
OAc
O
OTDS
N$_3$
OH
OLev

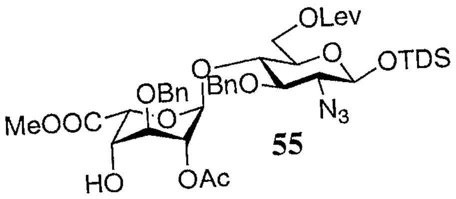
54


220
200
180
160
140
120
100
80
60
40
20
0
ppm

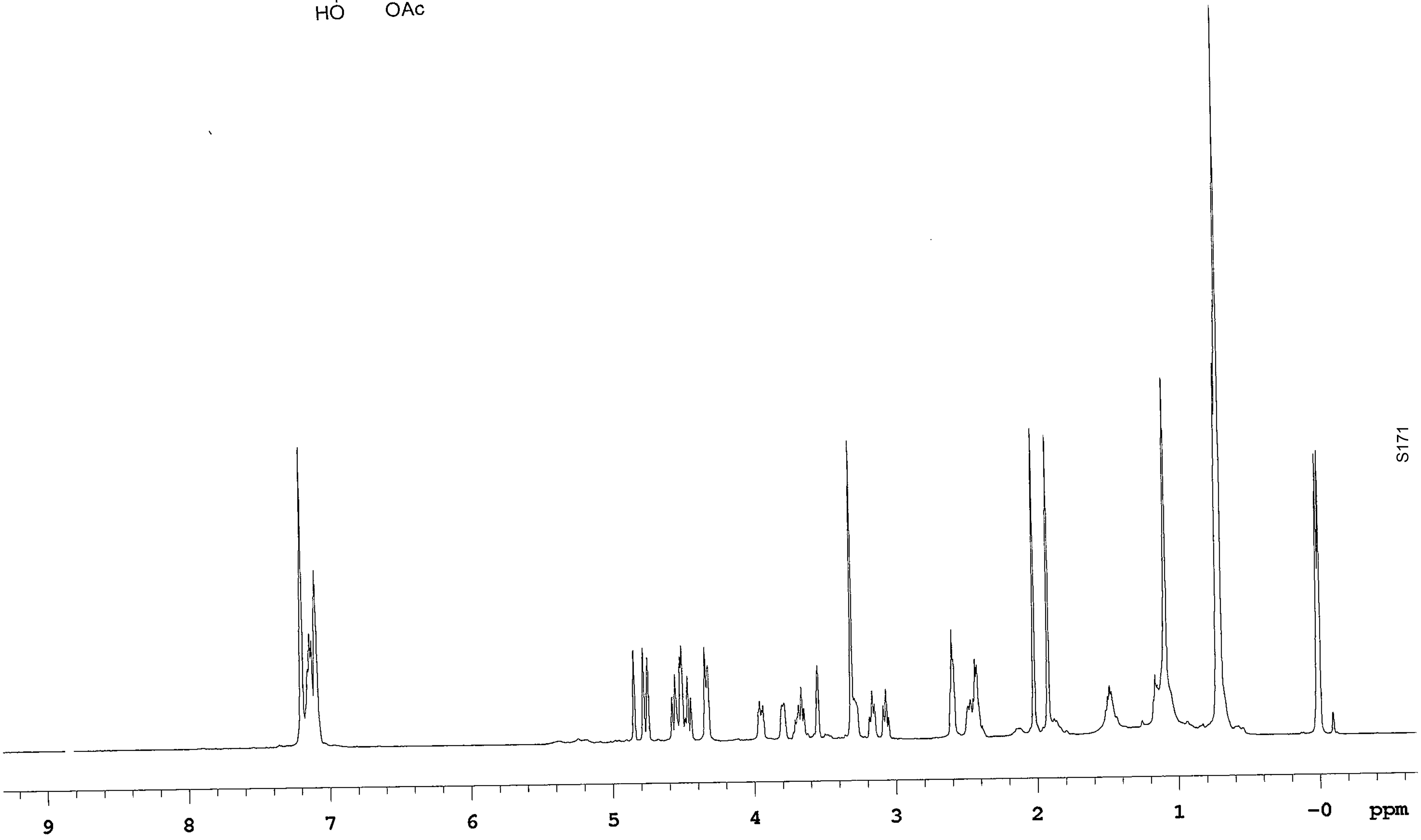

MeOOC
HO
OBn
O
OAc
BnO
O
OLev
O
N3
OTDS

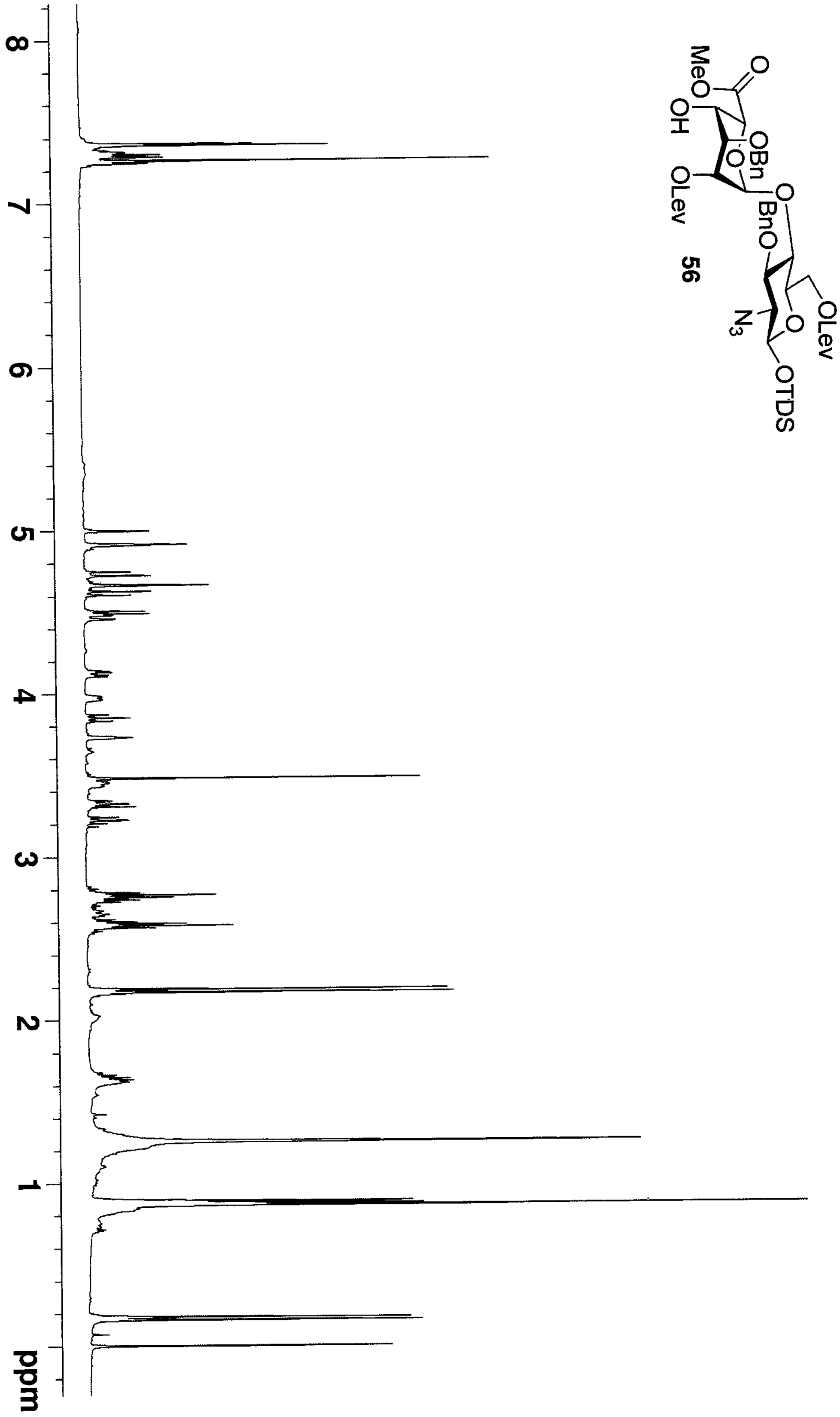
55


220
200
180
160
140
120
100
80
60
40
20
0
ppm



55

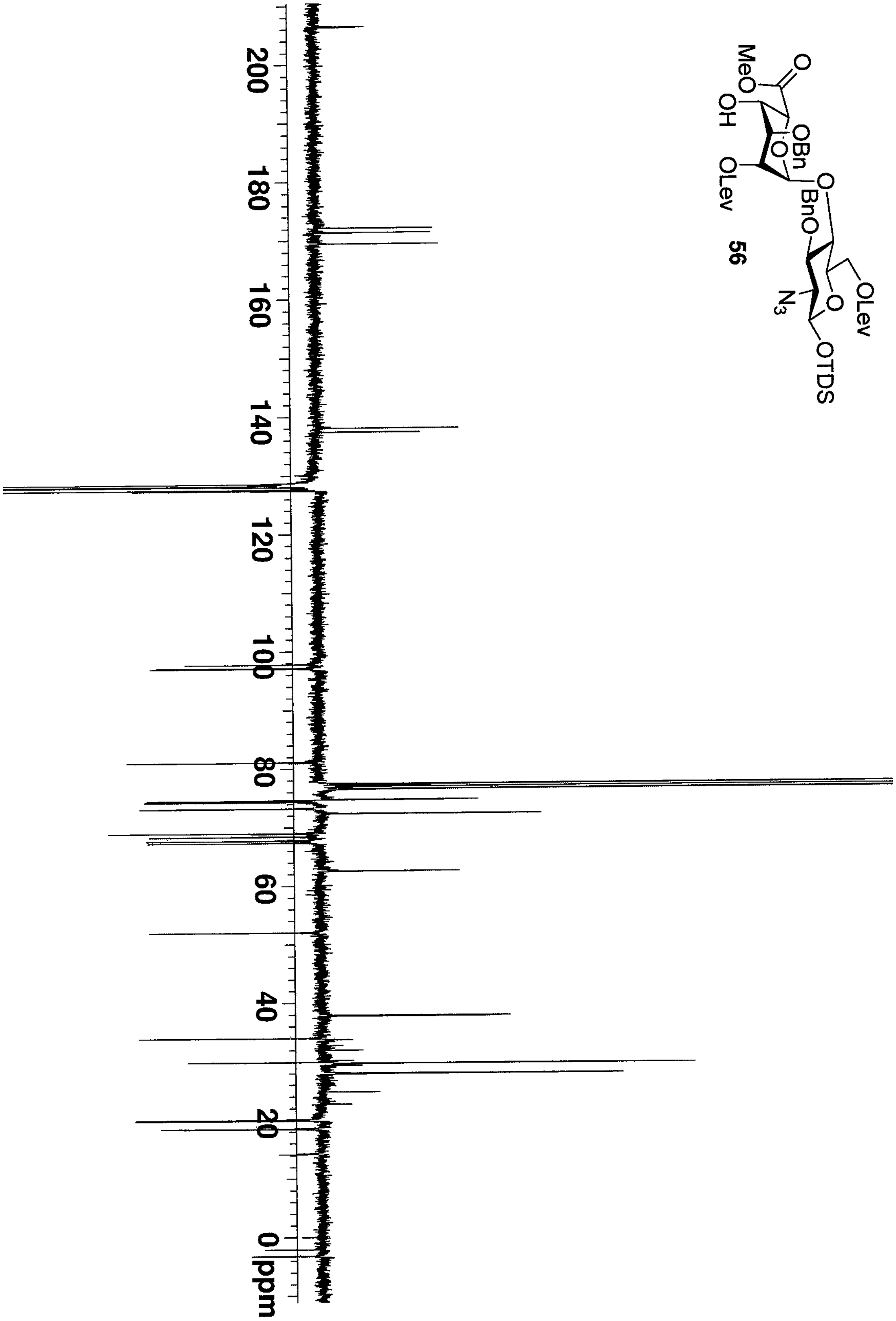


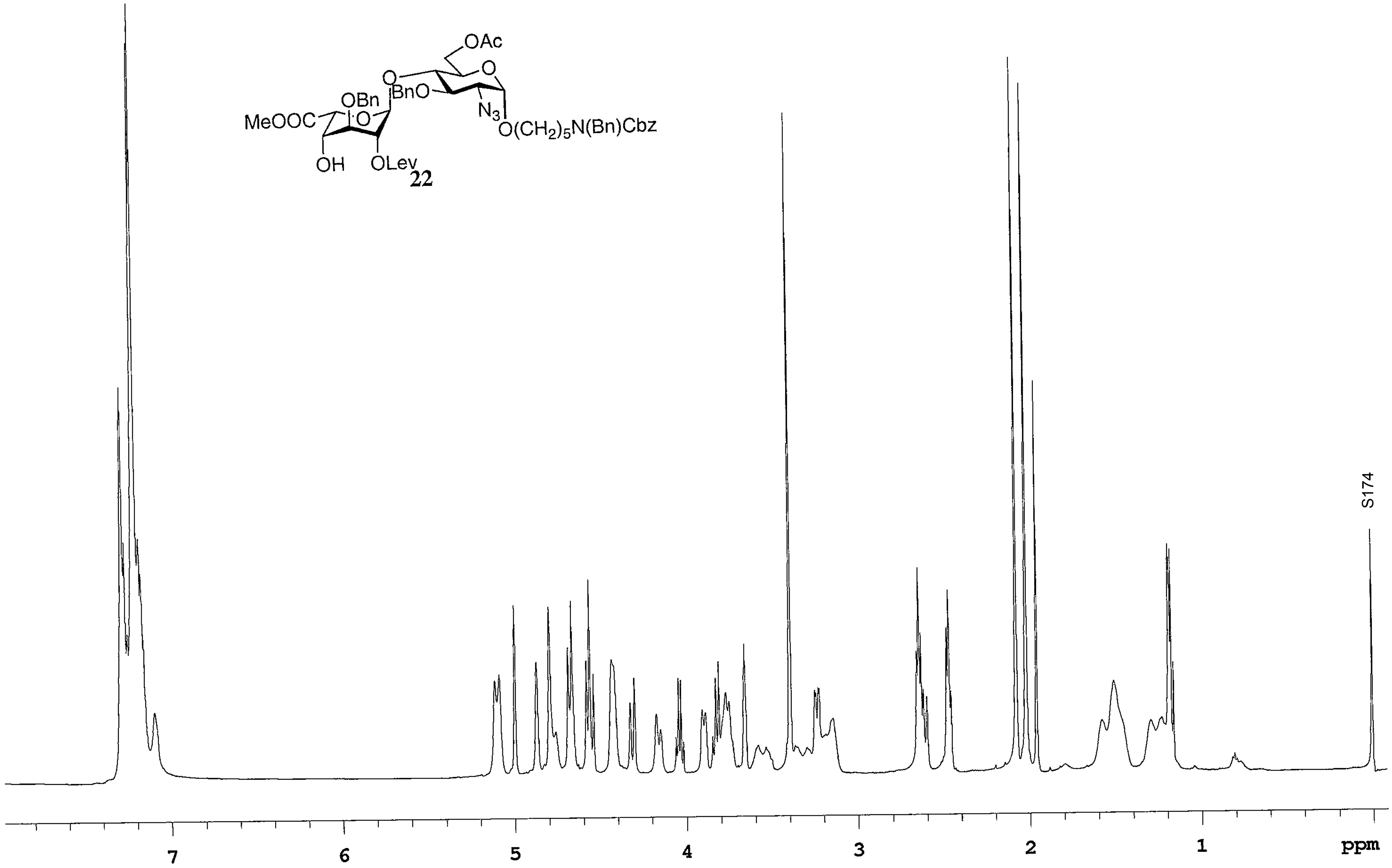


56

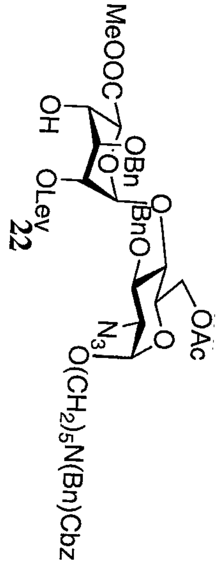
O
MeO
OH
OBn
O
OLev
O
BnO
OLev
O
N3
OTDS

56

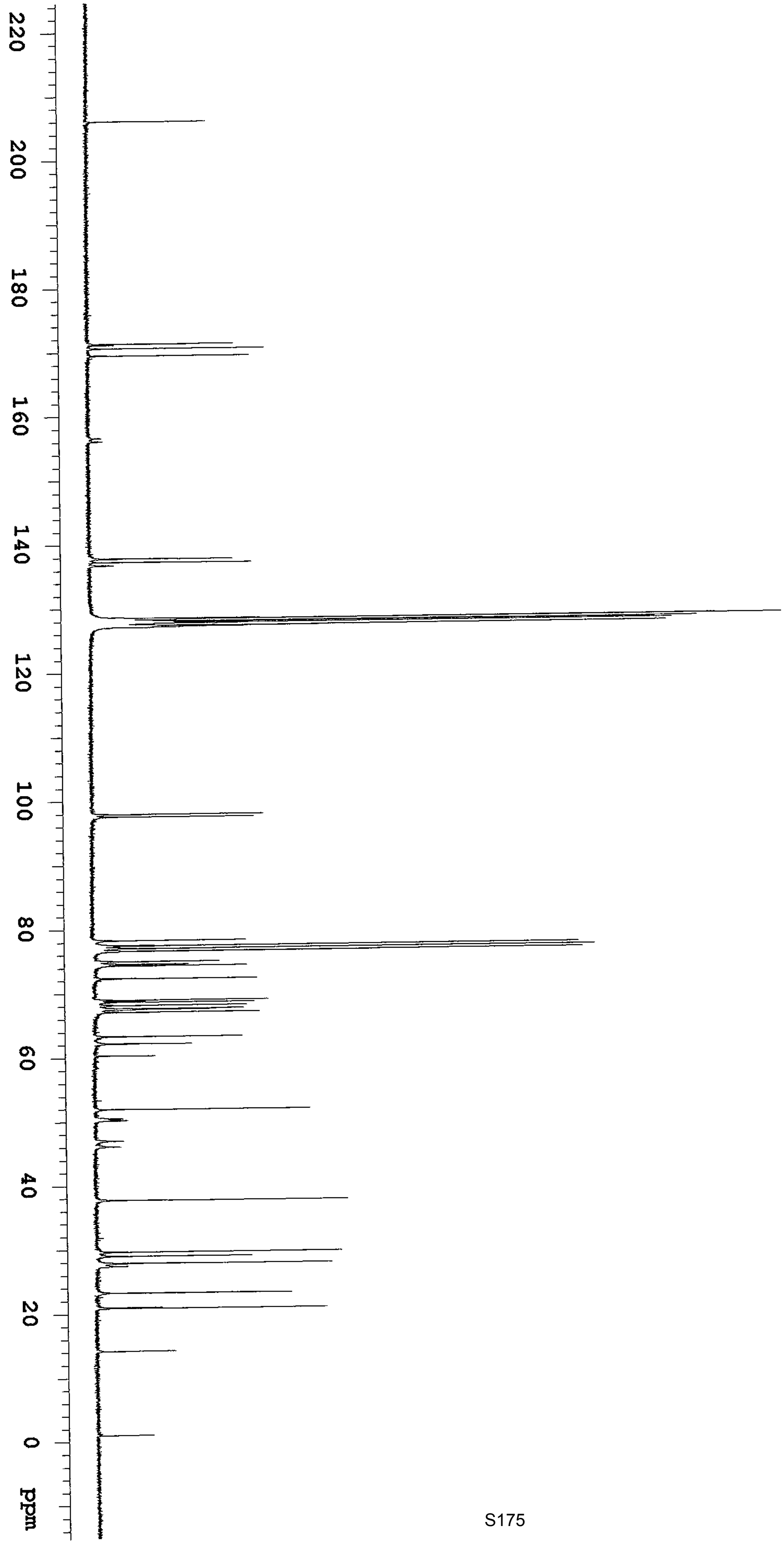

200
180
160
140
120
100
80
60
40
20
0
ppm

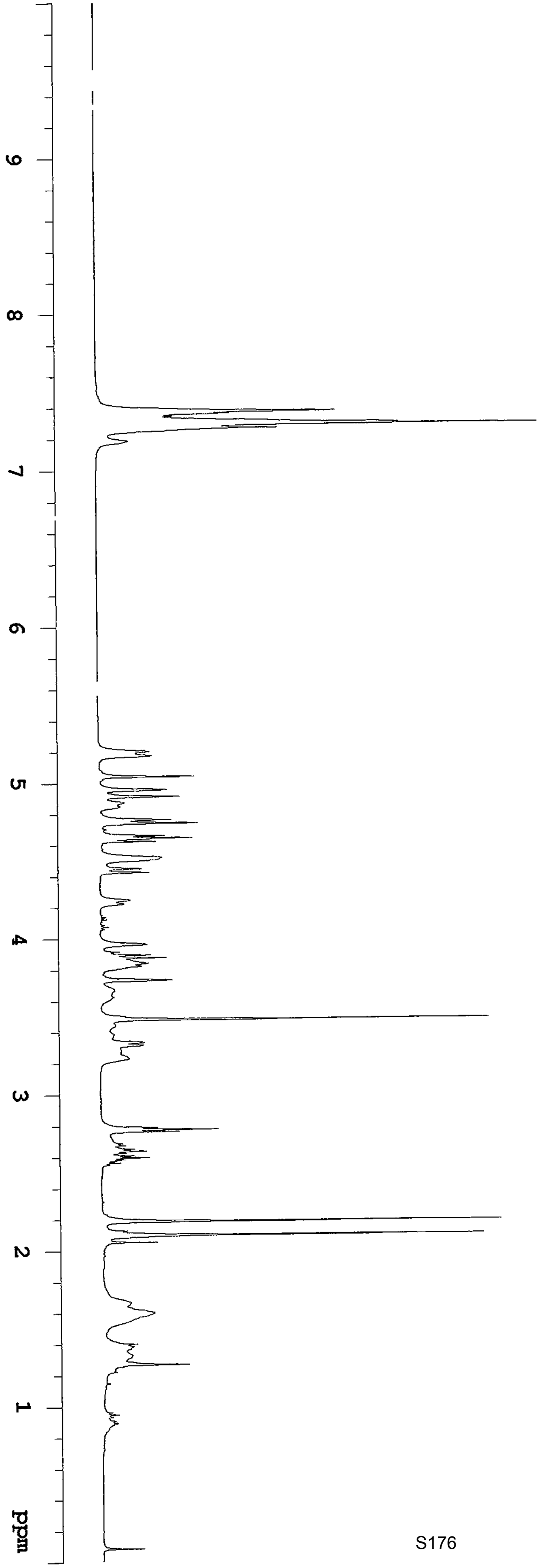


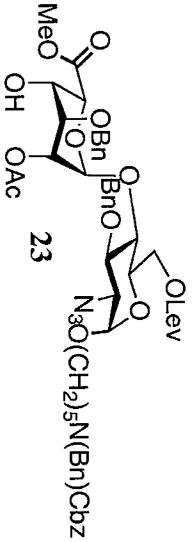
22


MeOOC
OBn
O
OH
OLev
BnO
O
OAc
O
N3
O(CH2)5N(Bn)Cbz

22


220
200
180
160
140
120
100
80
60
40
20
0
ppm



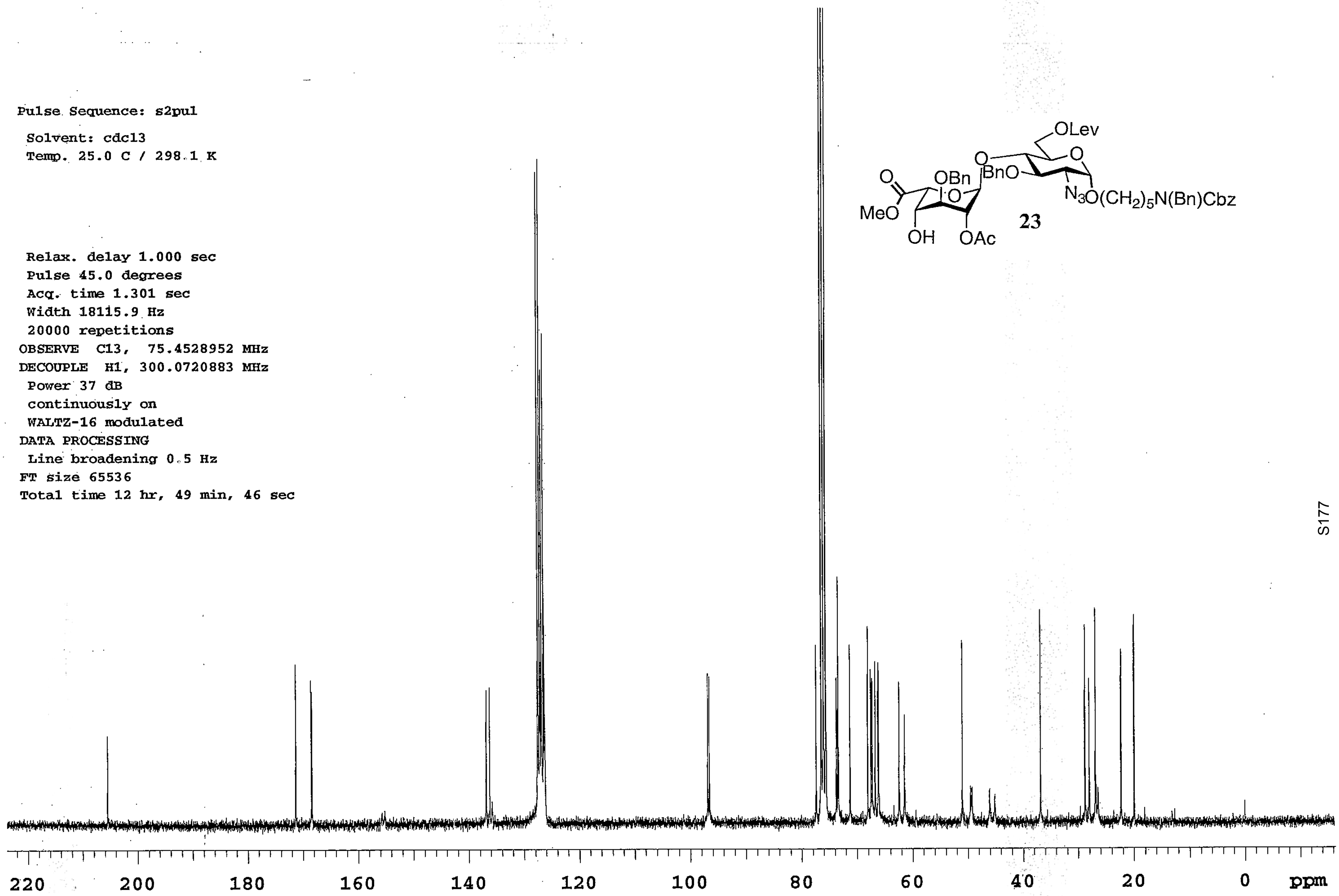


23

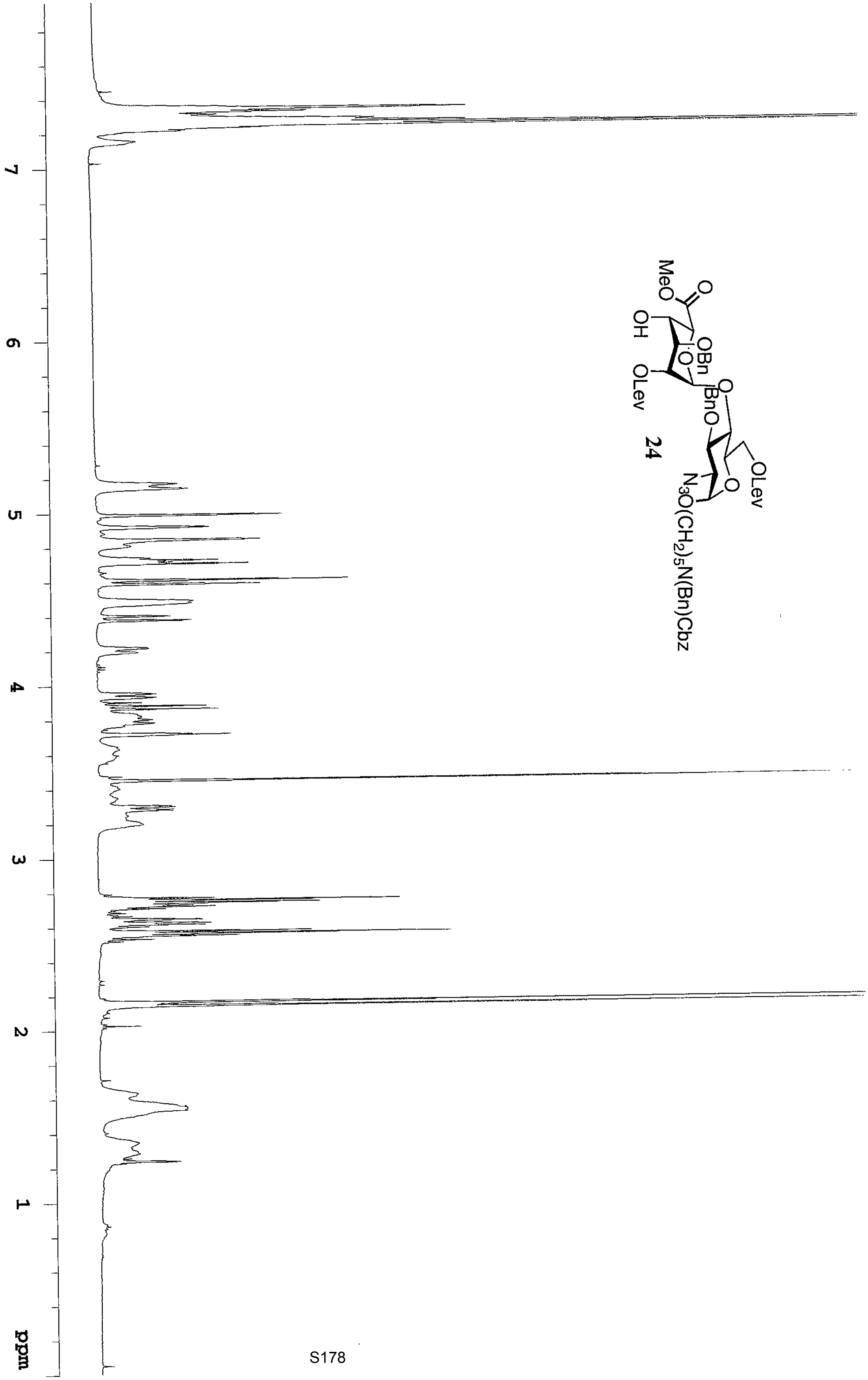
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K

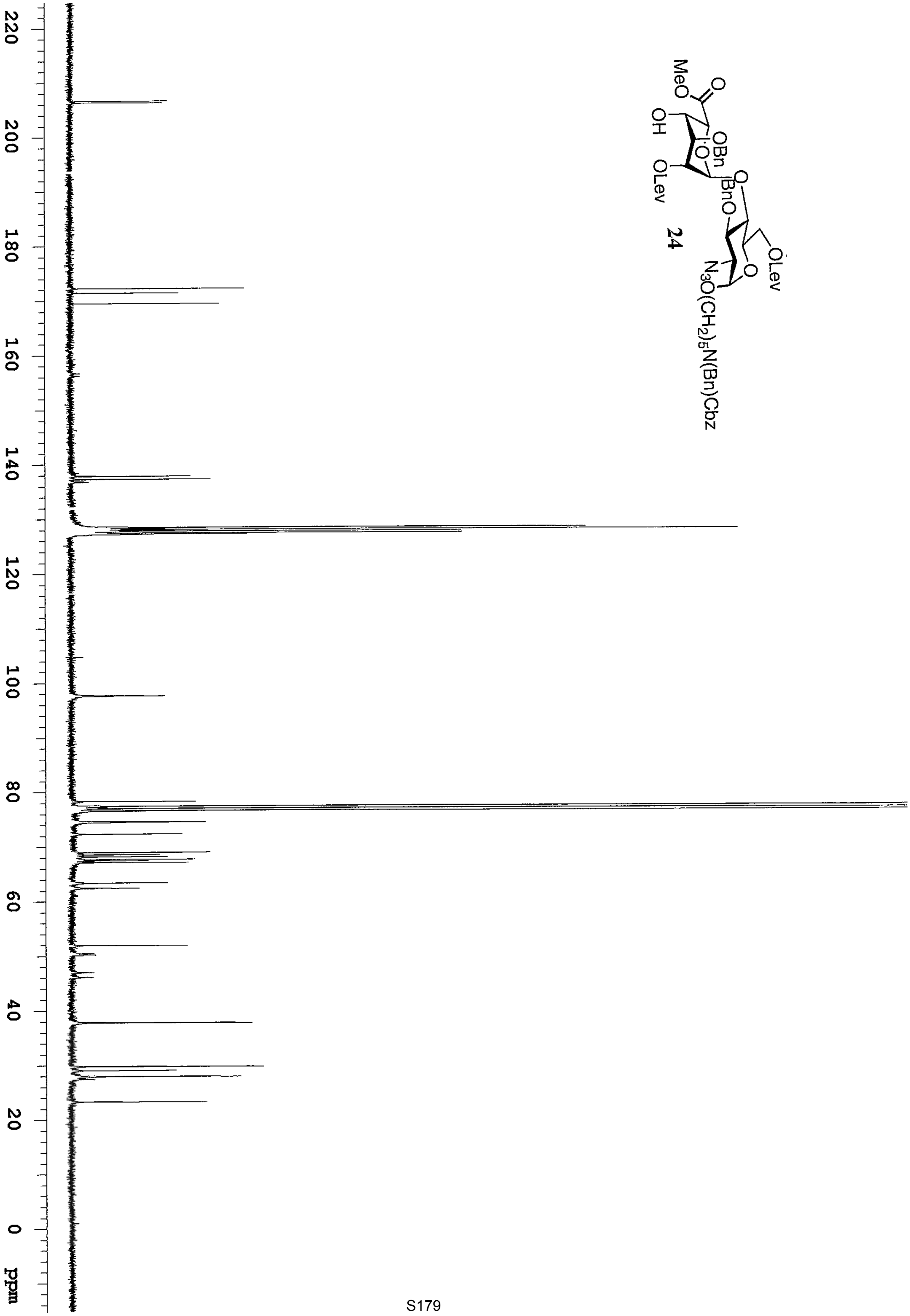
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.301 sec
Width 18115.9 Hz
20000 repetitions
OBSERVE C13, 75.4528952 MHz
DECOUPLE H1, 300.0720883 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 hr, 49 min, 46 sec



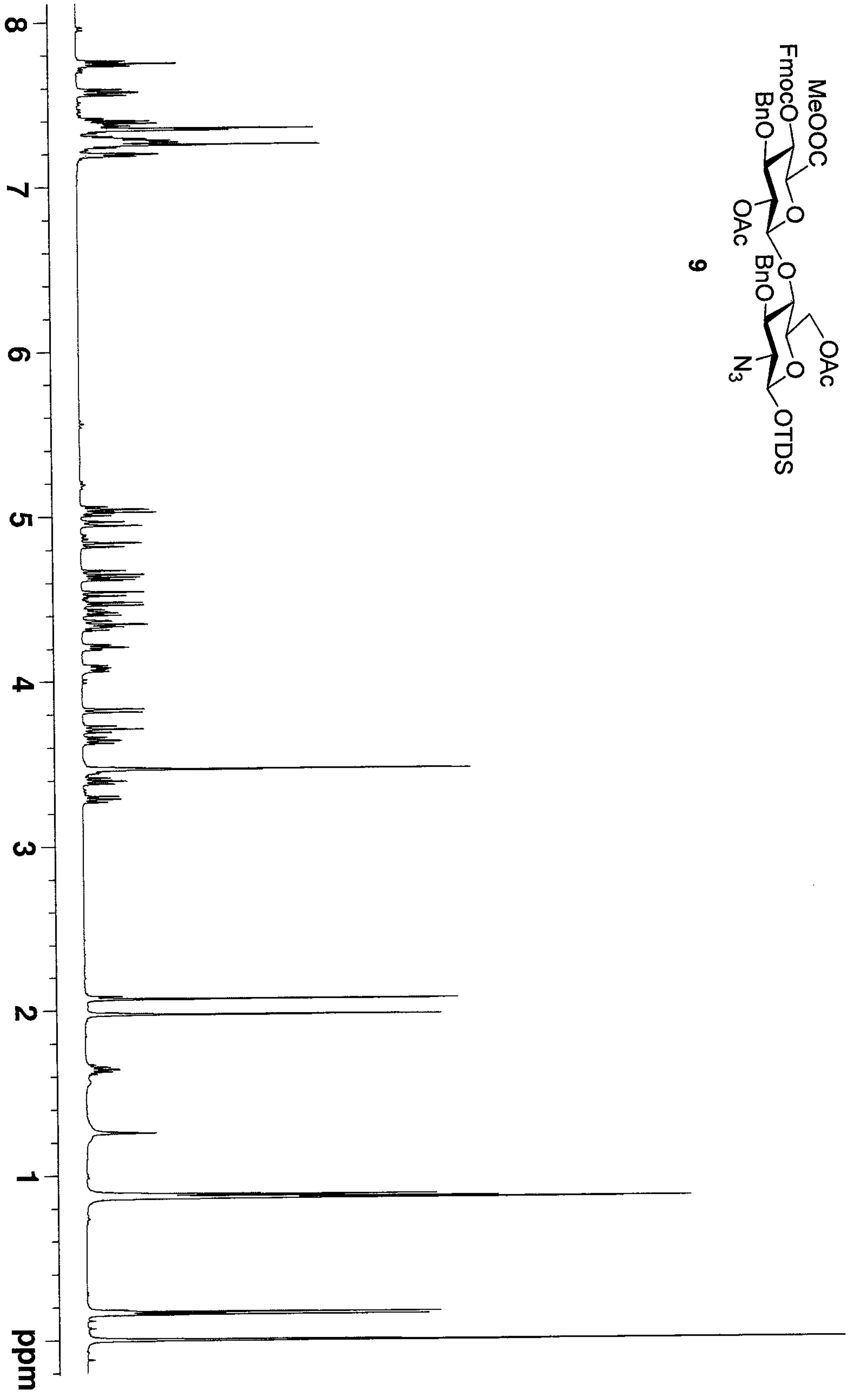
23



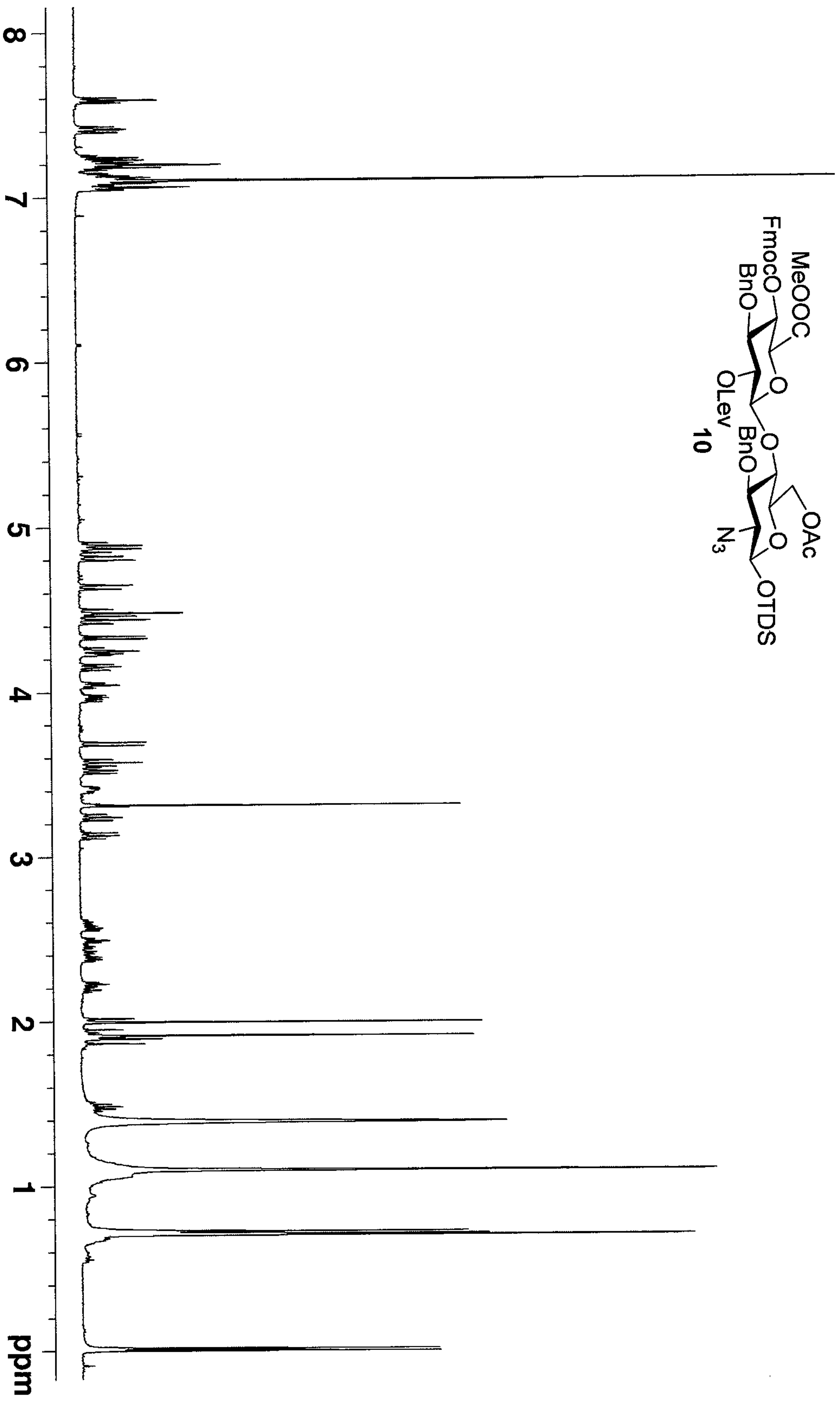
7
6
5
4
3
2
1
ppm
MeO
O
OH
OBn
O
OLev
BnO
O
OLev
O
N3
O(CH2)5N(Bn)Cbz
24


OLev
O
N3
O(CH2)5N(Bn)Cbz
BnO
O
OBn
O
MeO
OH
OLev
220
200
180
160
140
120
100
80
60
40
20
0
ppm

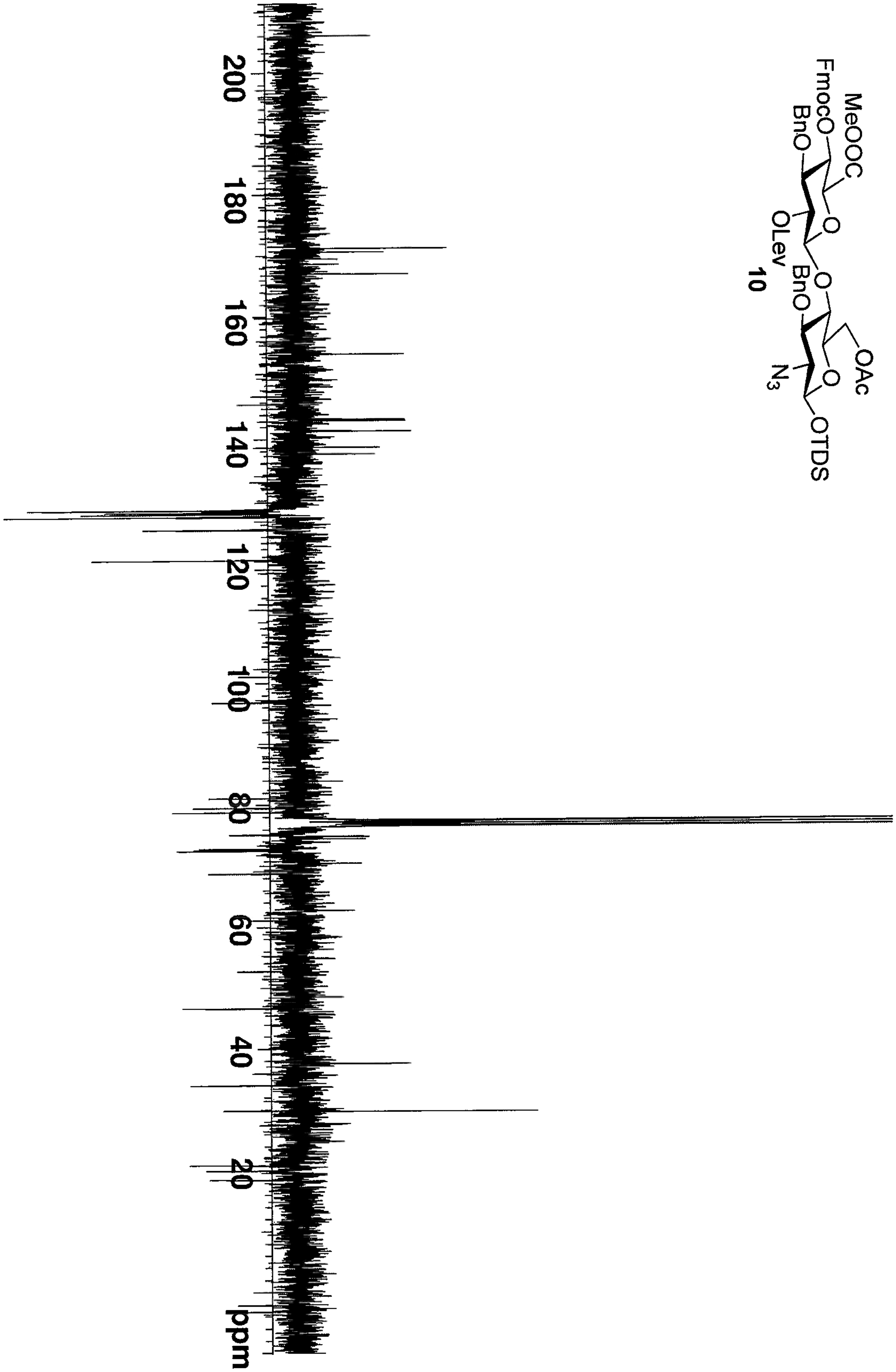
24

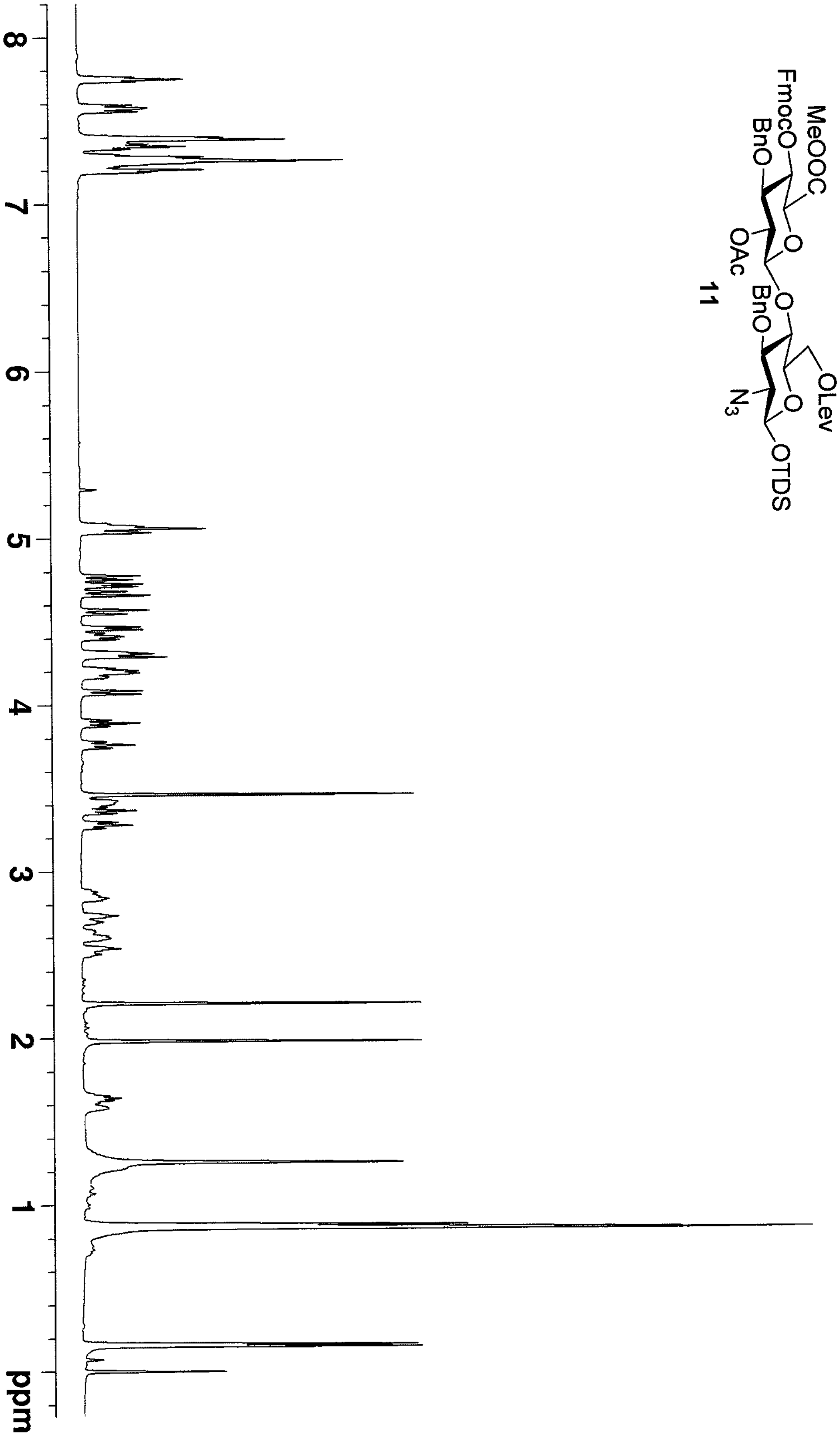


9

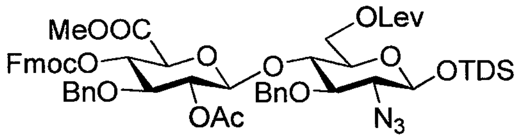


10

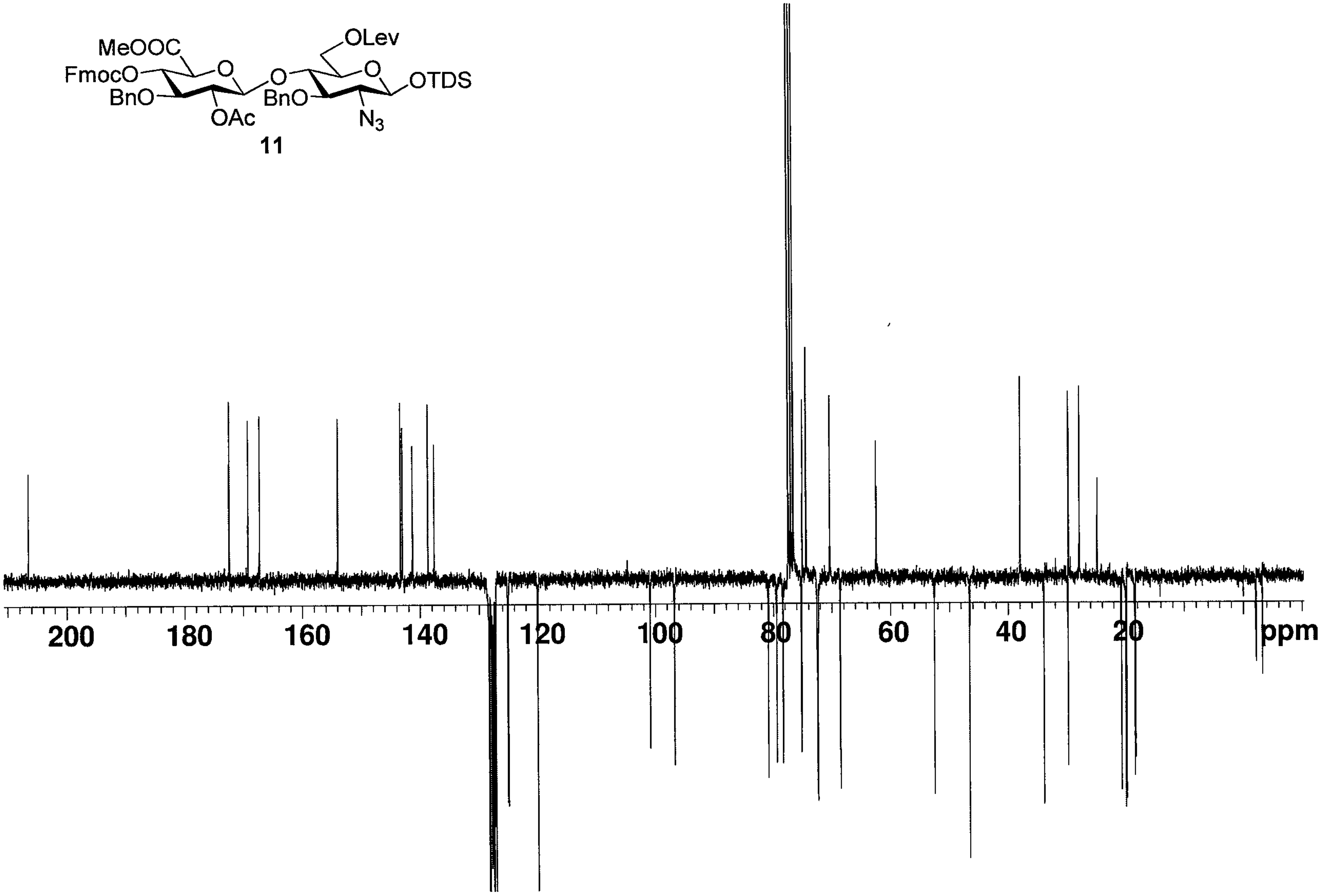

MeOOC
FmocO
BnO
O
OLev
BnO
O
OAc
N_3
O
OTDS
10
200
180
160
140
120
100
80
60
40
20
ppm

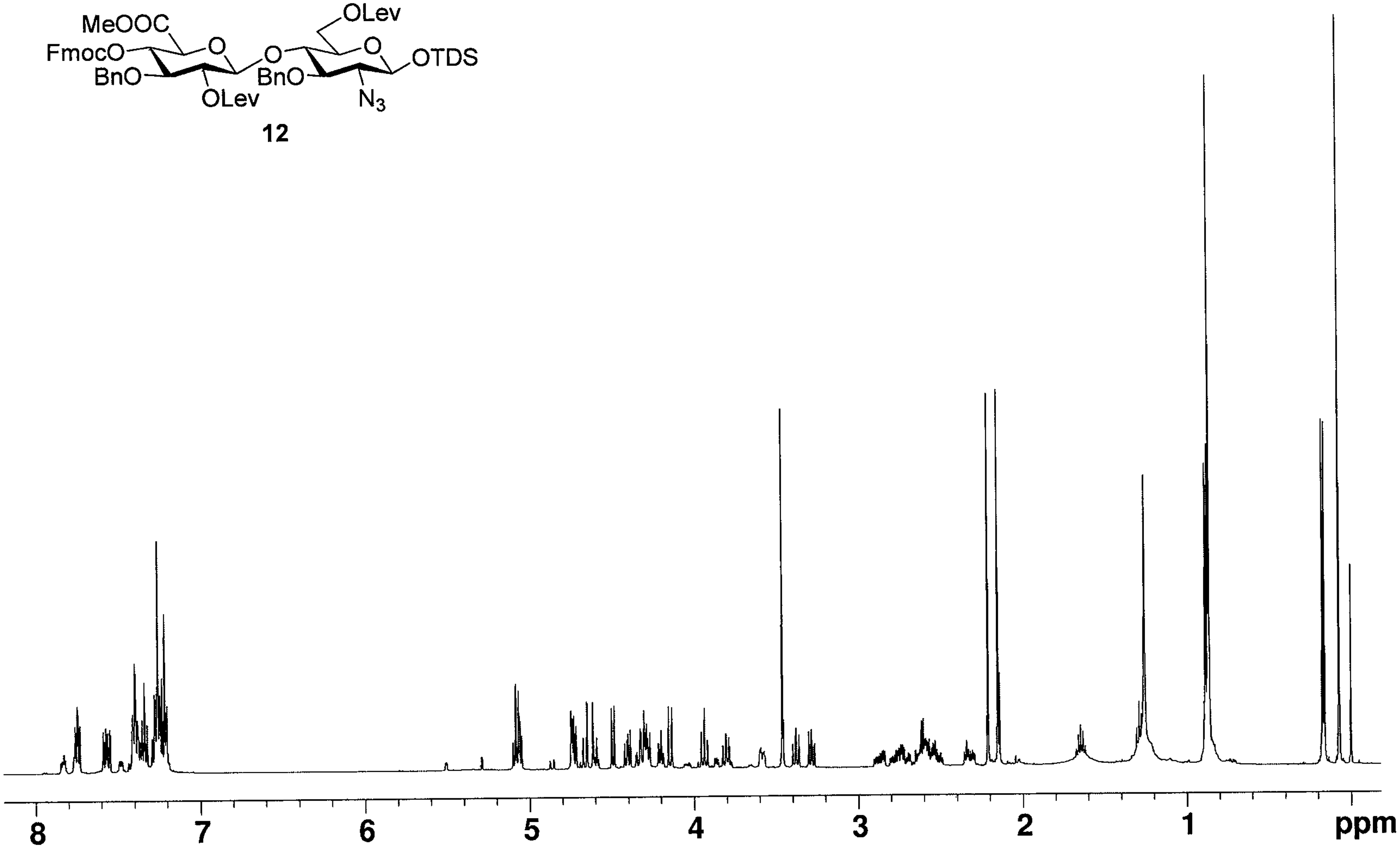


11

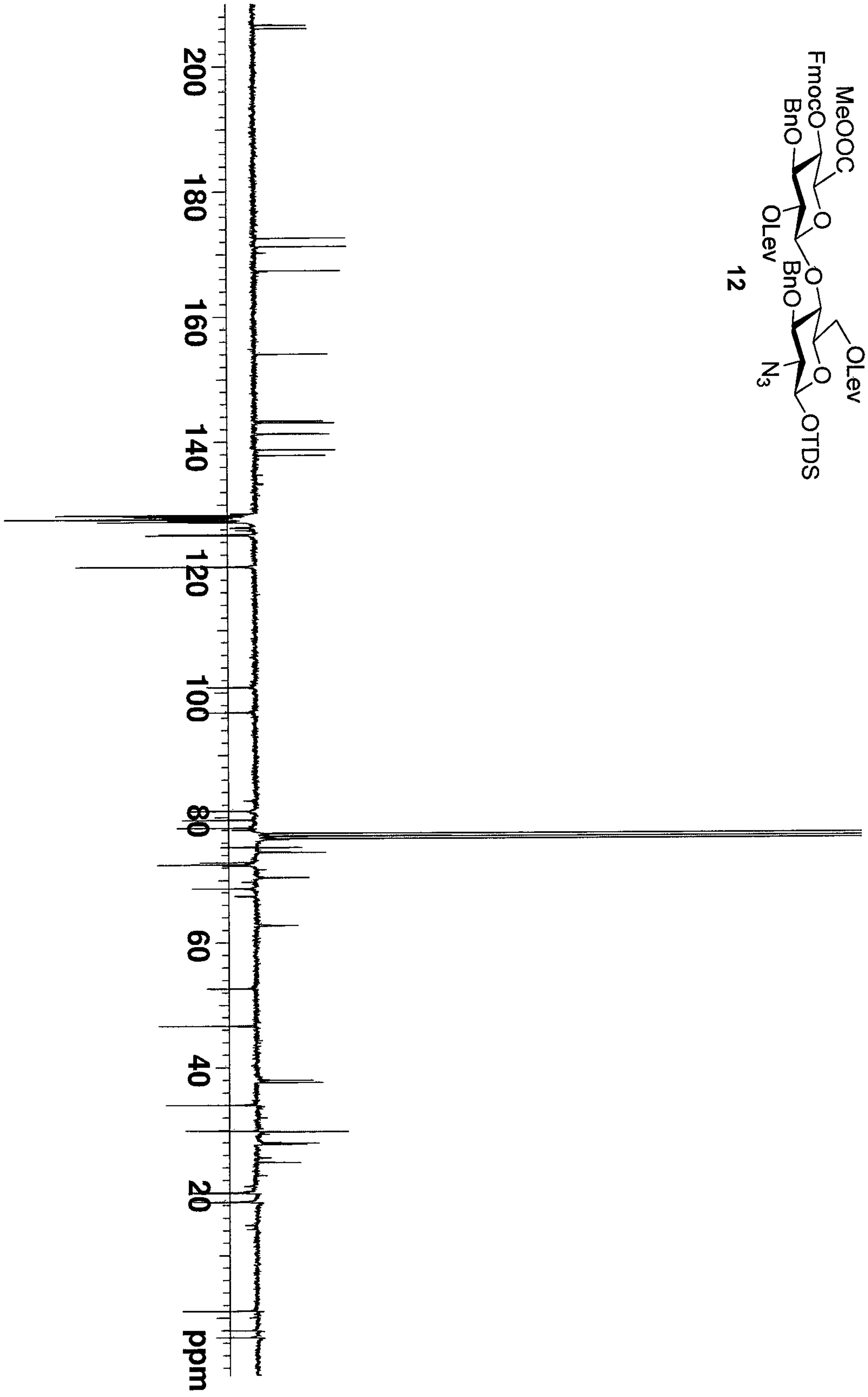

MeOOC
FmocO
BnO
OAc
BnO
N3
OLev
OTDS
O
O
O

11

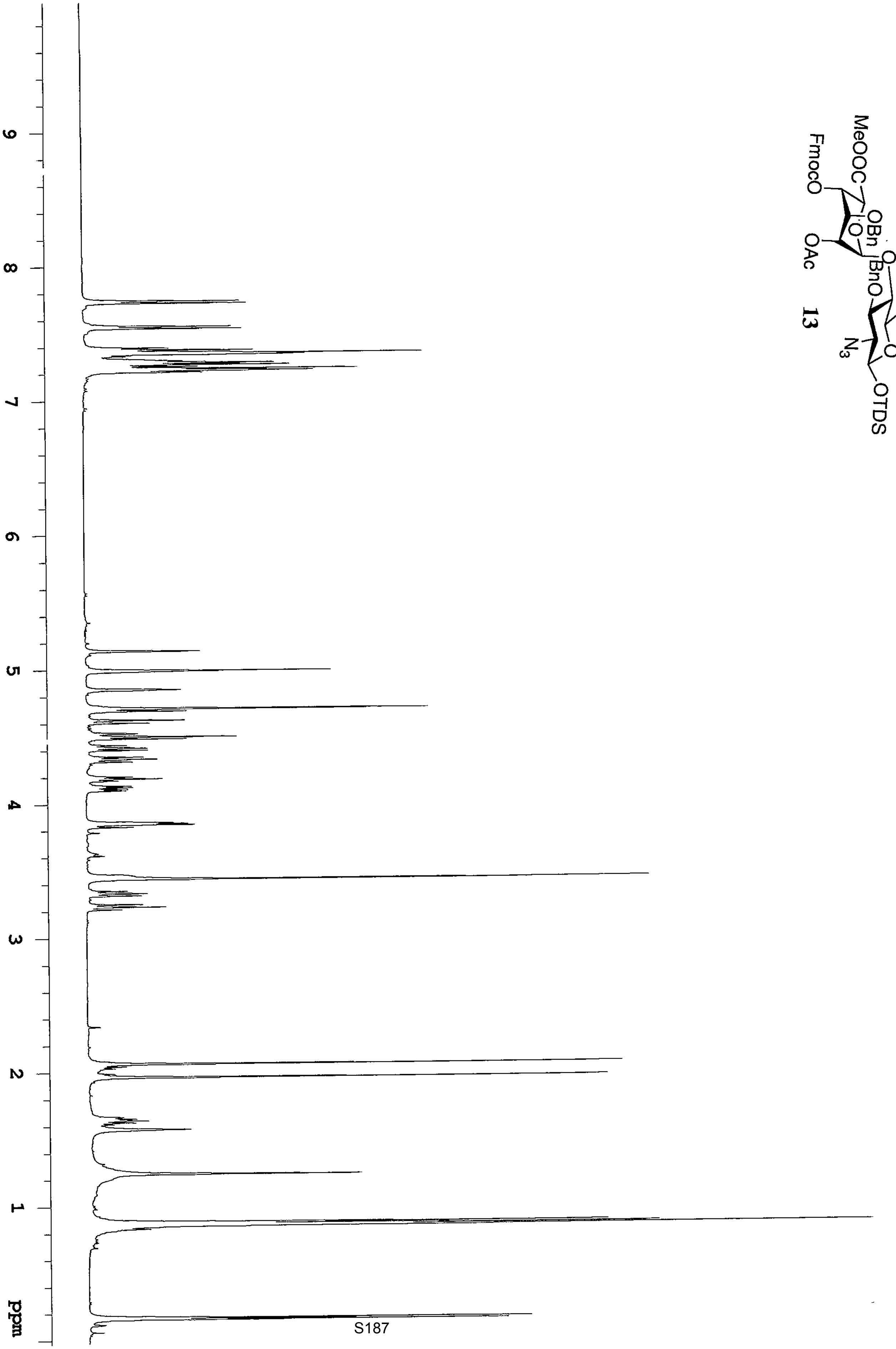

200
180
160
140
120
100
80
60
40
20
ppm



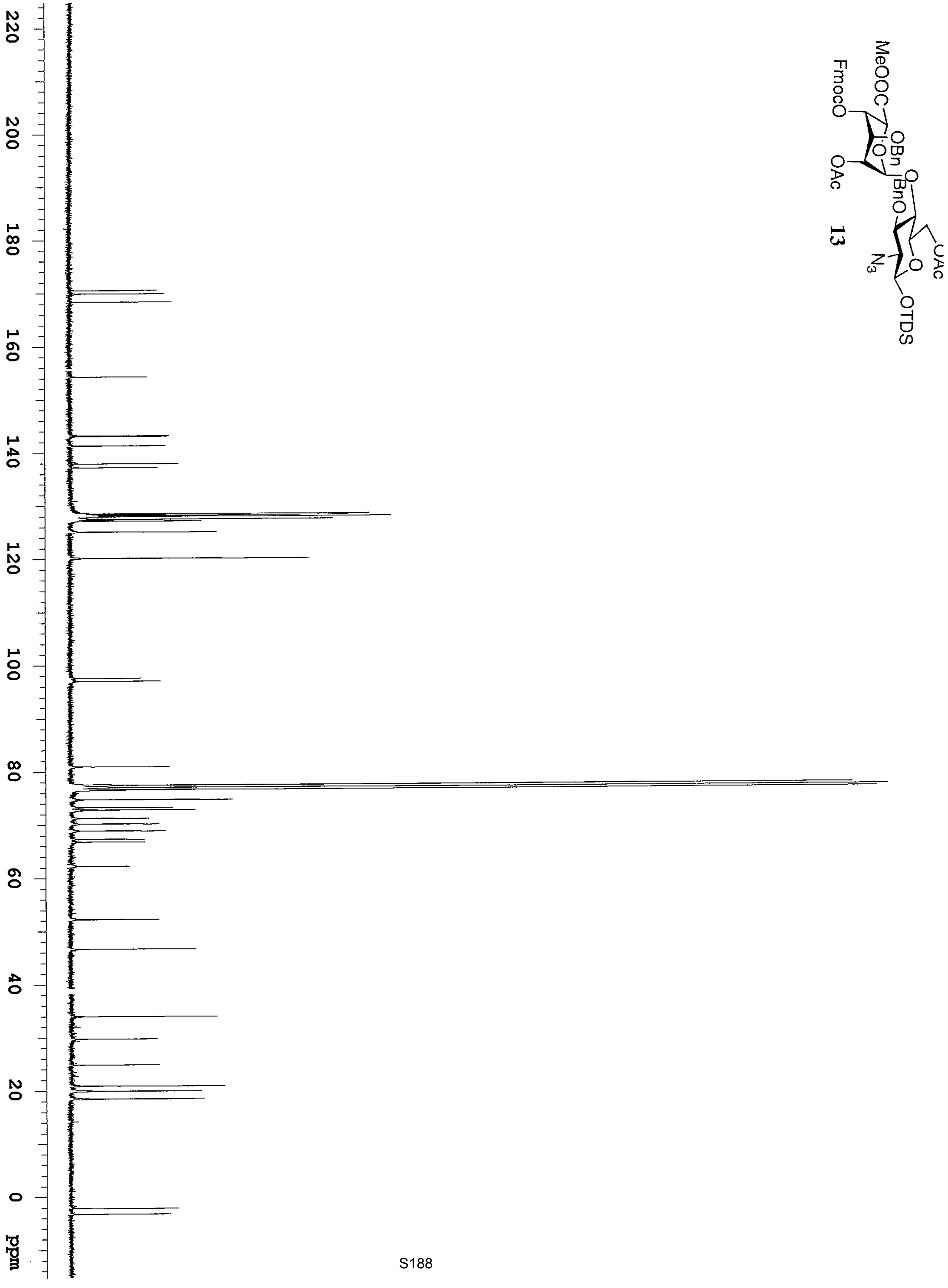
12

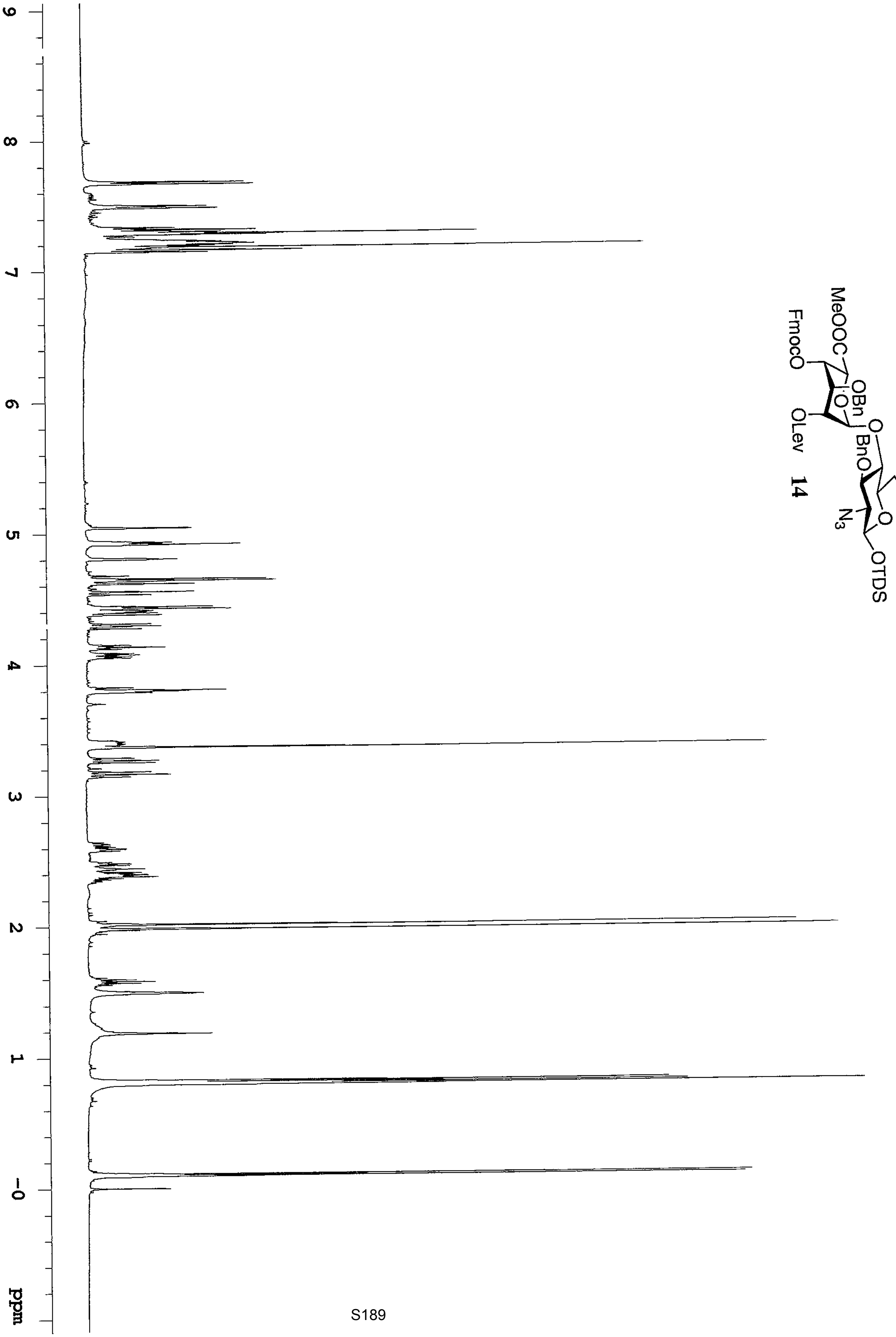

MeOOC
FmocO
BnO
O
OLev
O
BnO
O
OLev
N_3
OTDS
200
180
160
140
120
100
80
60
40
20
ppm

12

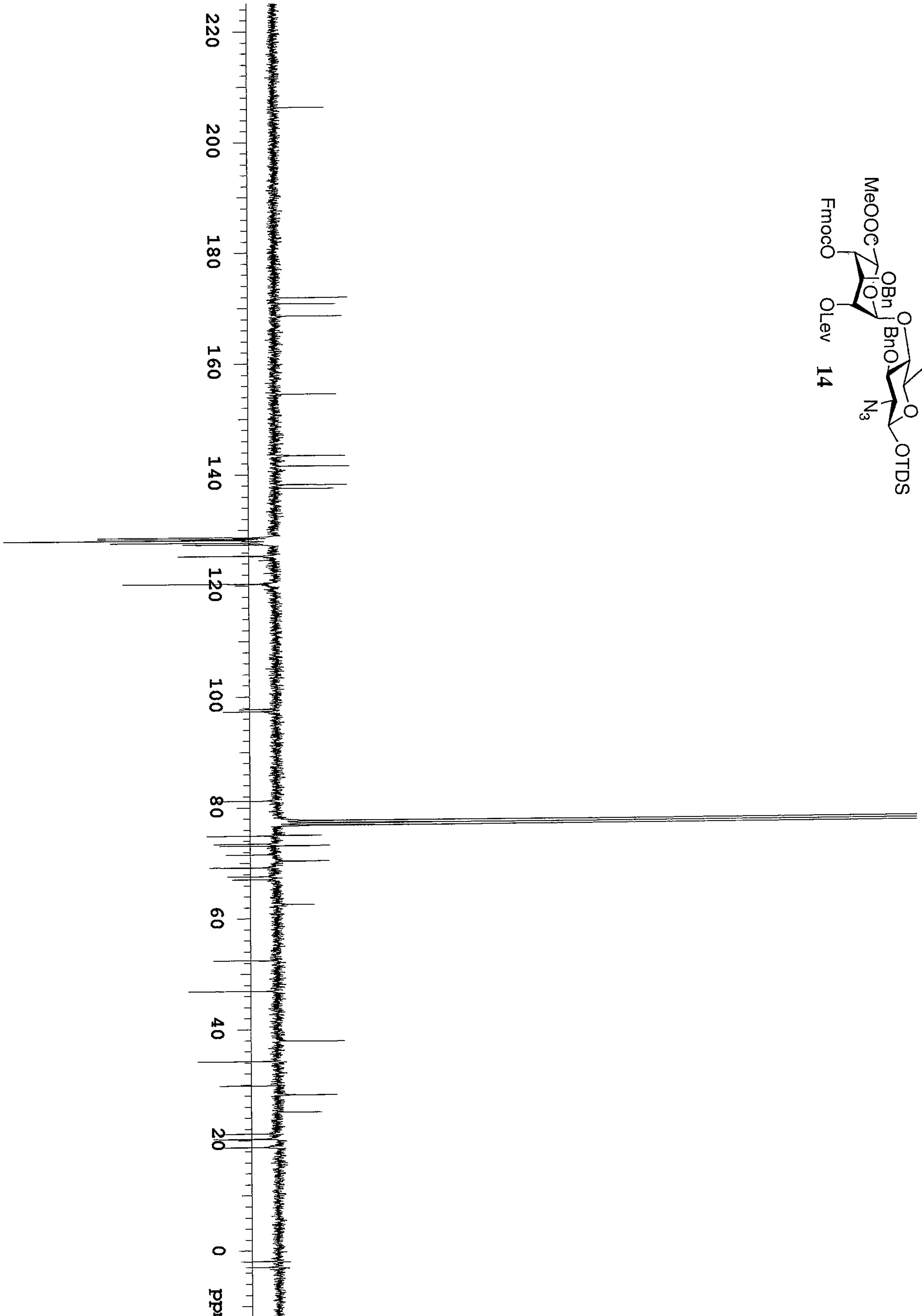


13


MeOOC
OBn
O
O
BnO
OAc
O
N3
OTDS
FmocO
OAc
13
220
200
180
160
140
120
100
80
60
40
20
0
ppm

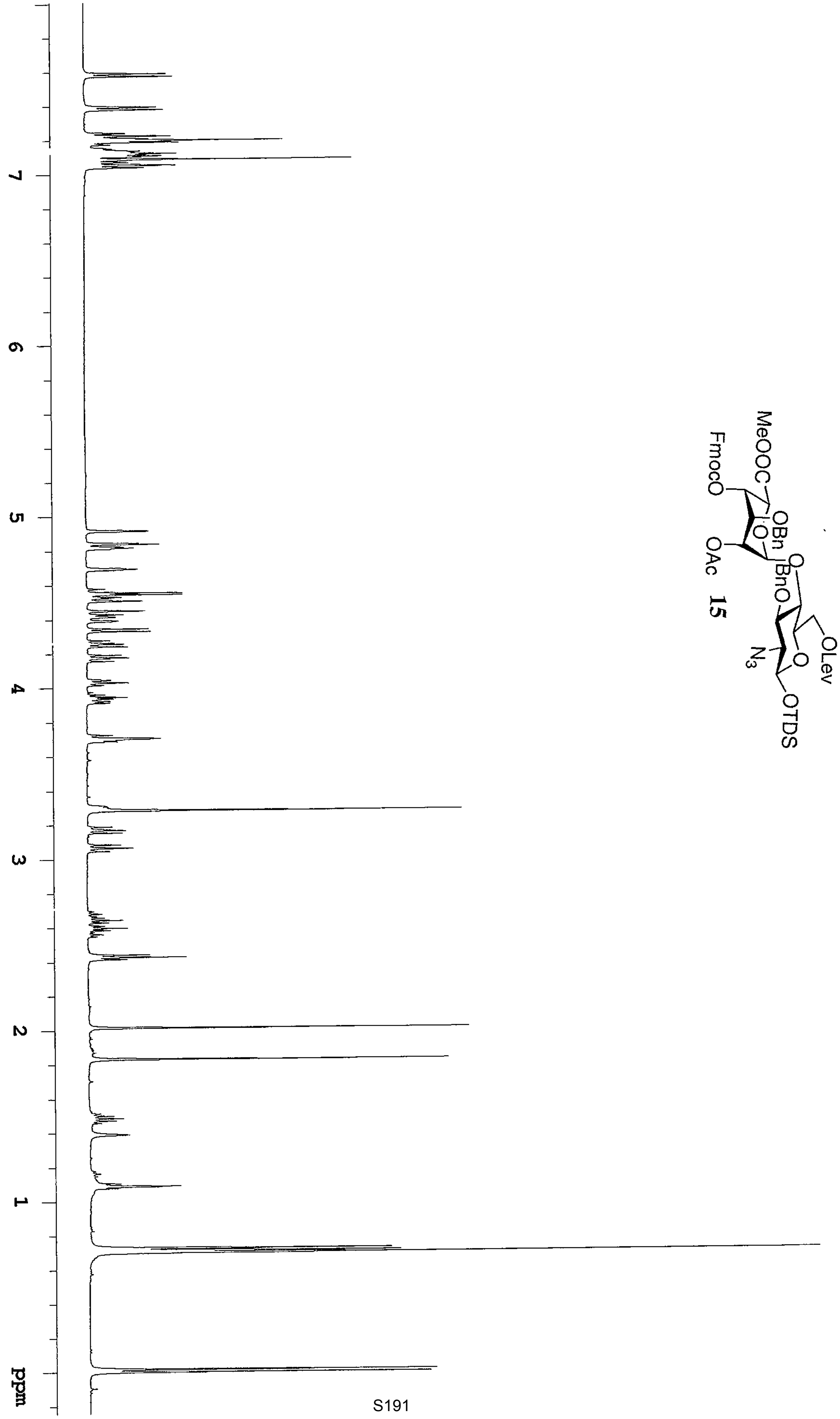


14

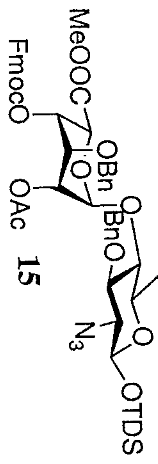


MeOOC
FmocO
OBn
O
OLev
O
BnO
OAc
O
N$_3$
OTDS
220
200
180
160
140
120
100
80
60
40
20
0
ppm

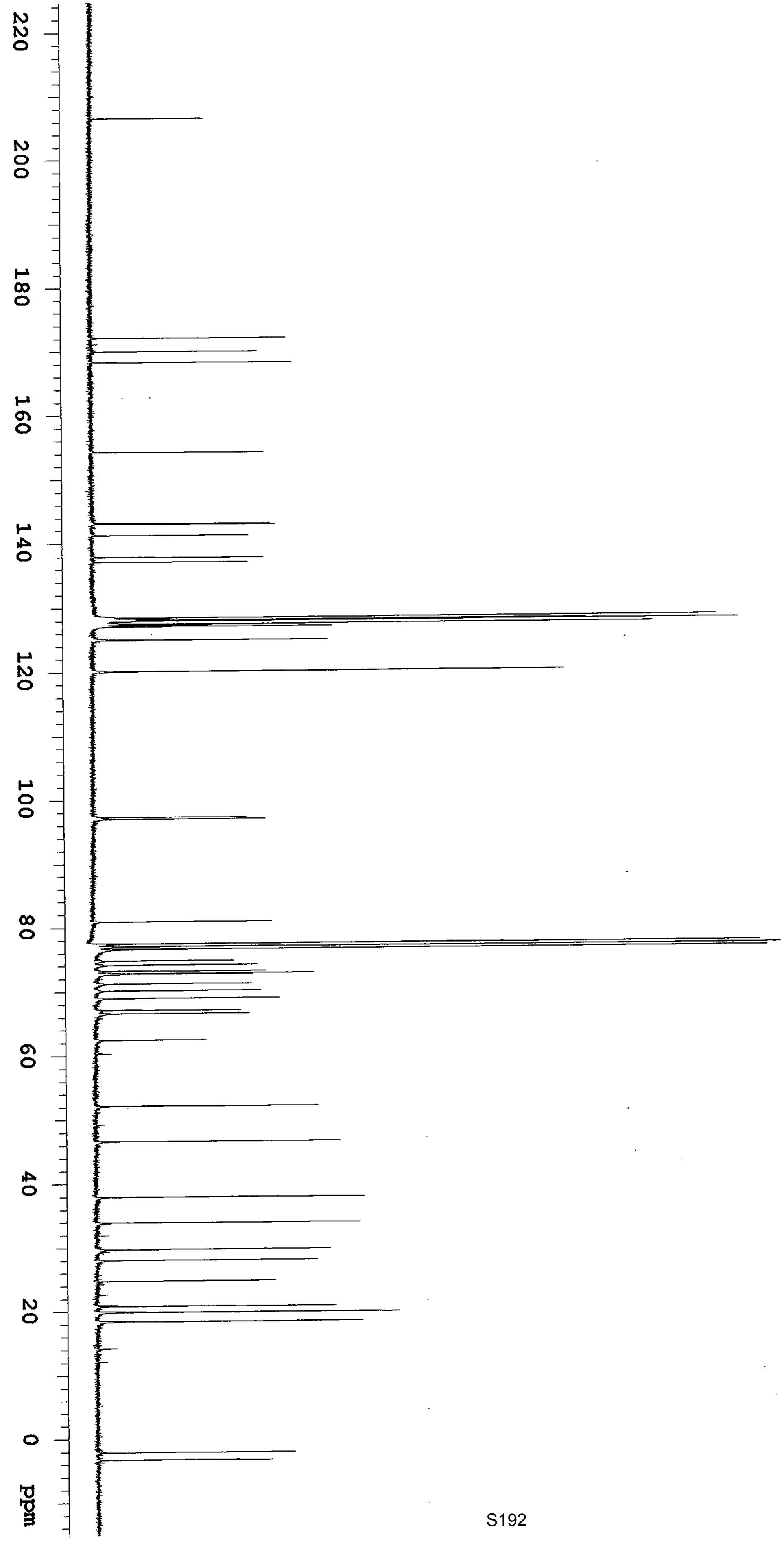
14

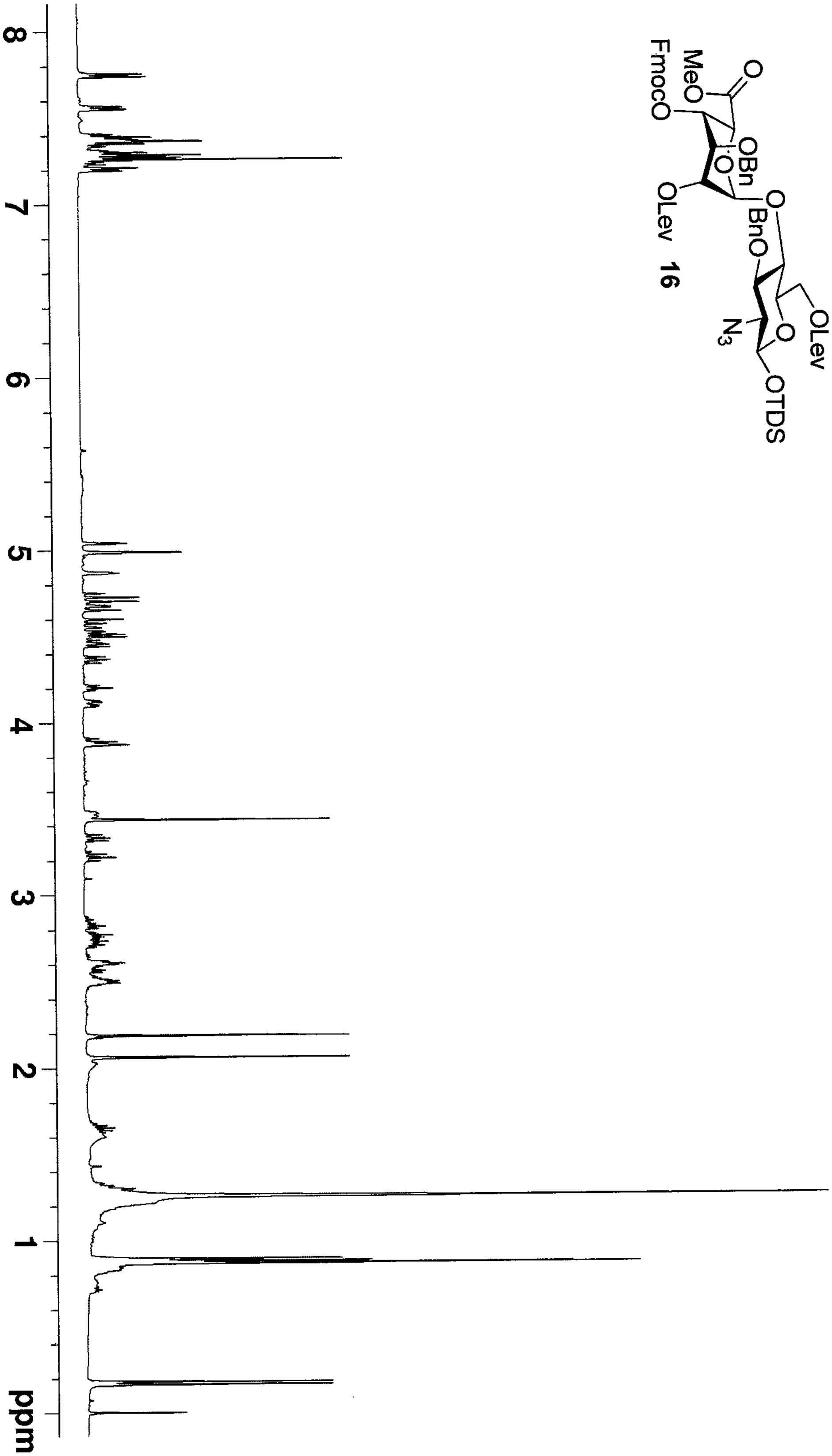


15


MeOOC
FmocO
OBn
O
BnO
OAc
OLev
O
N3
OTDS

15

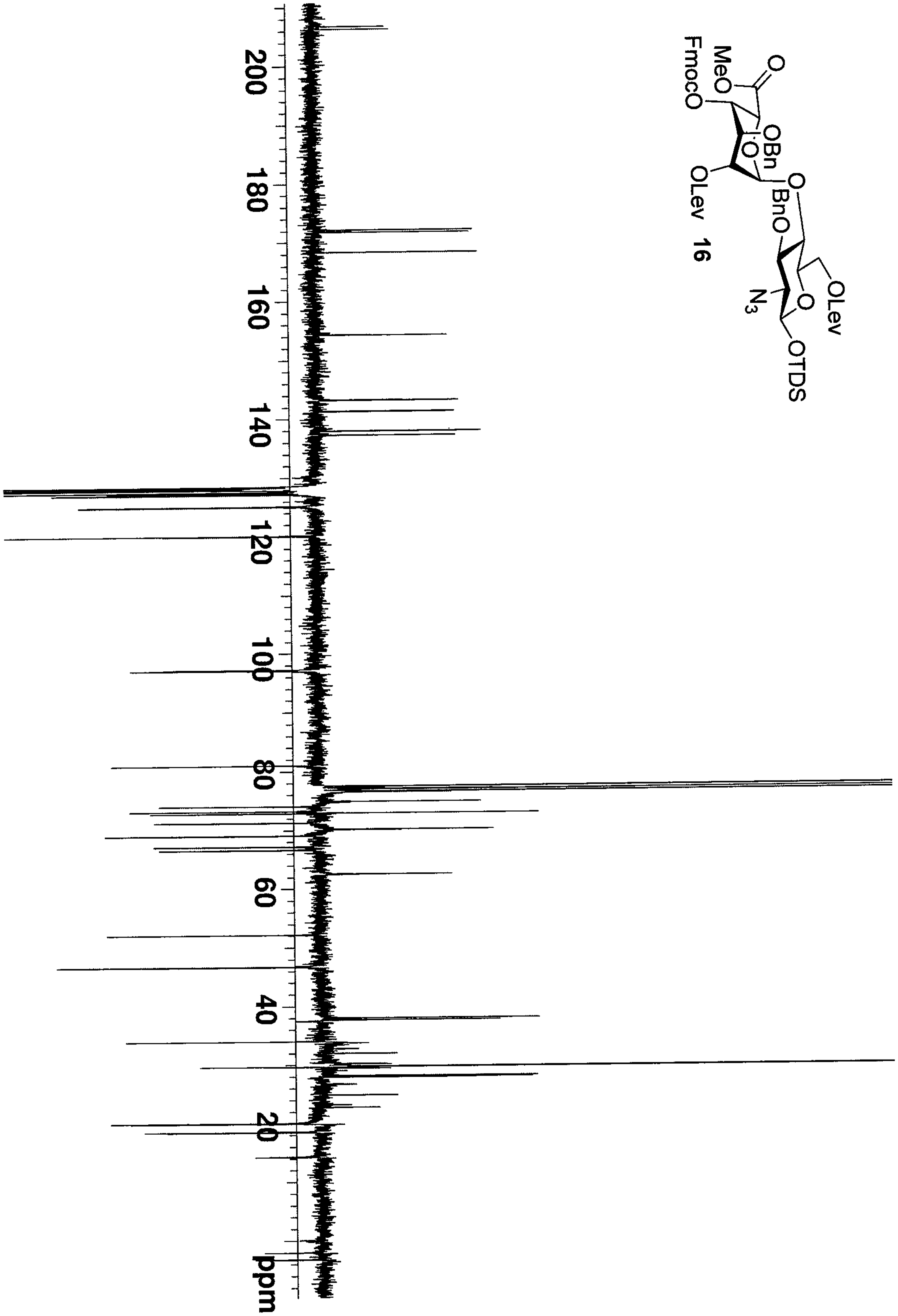

220
200
180
160
140
120
100
80
60
40
20
0
ppm

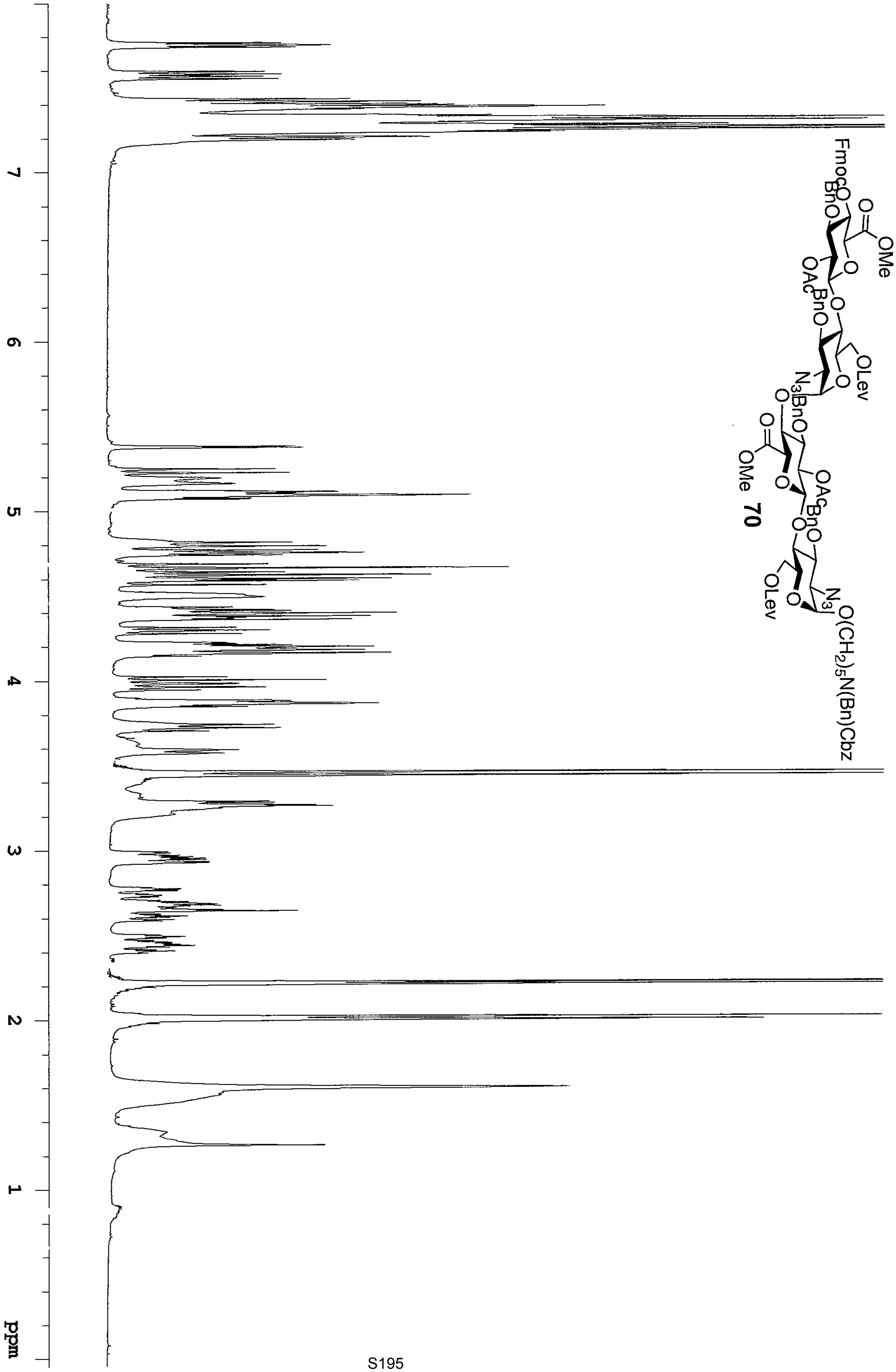


16

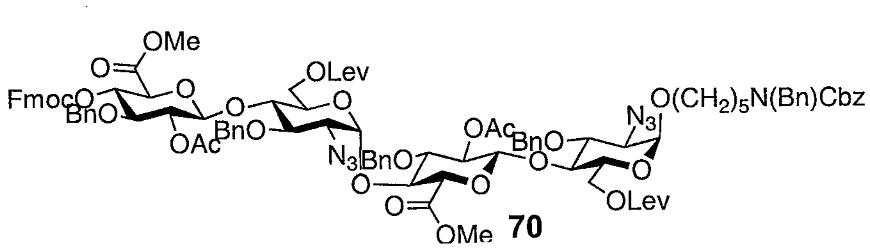
OLev
O
OTDS
N$_3$
BnO
O
OBn
O
O
MeO
FmocO
OLev

16

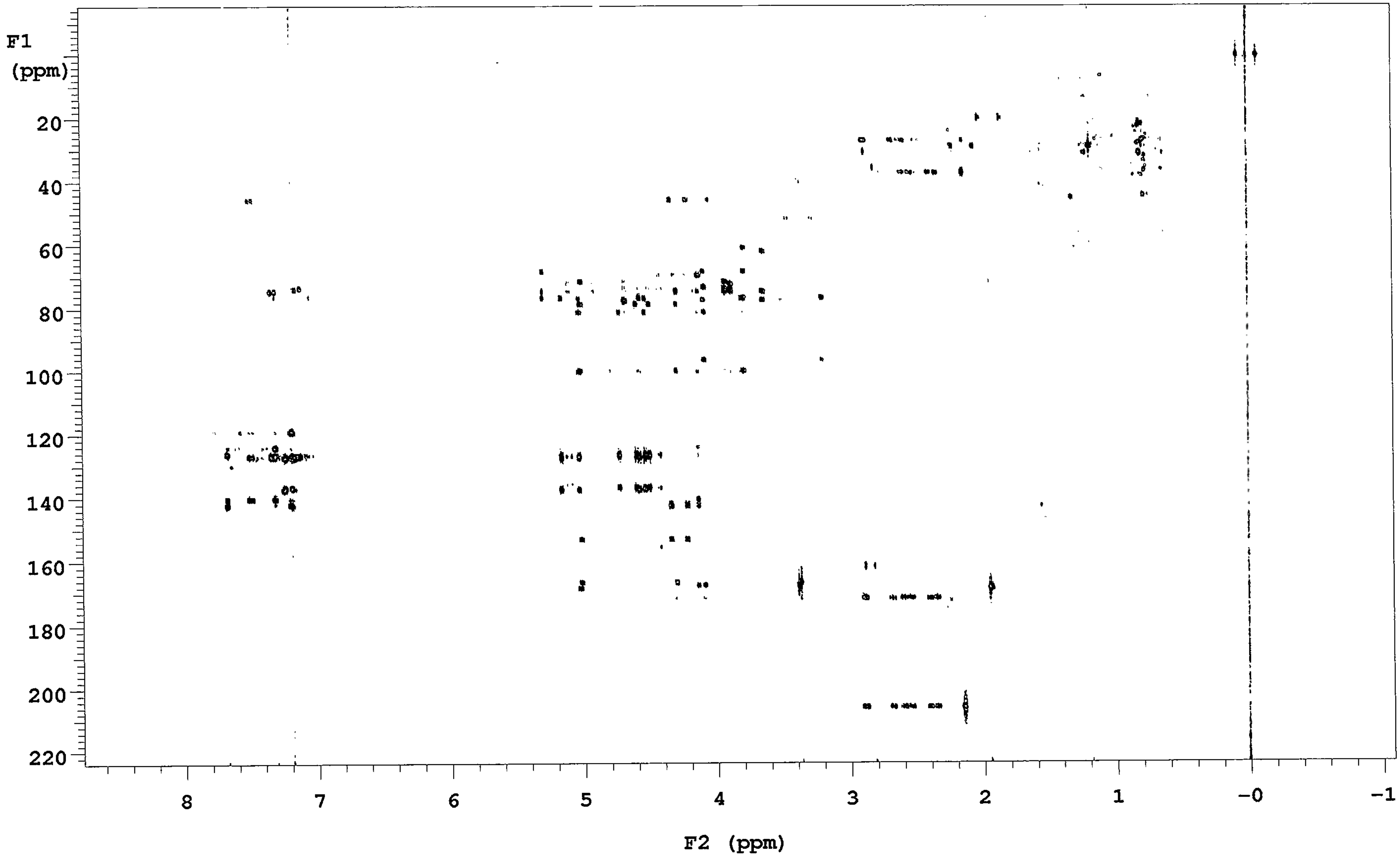

200
180
160
140
120
100
80
60
40
20
ppm

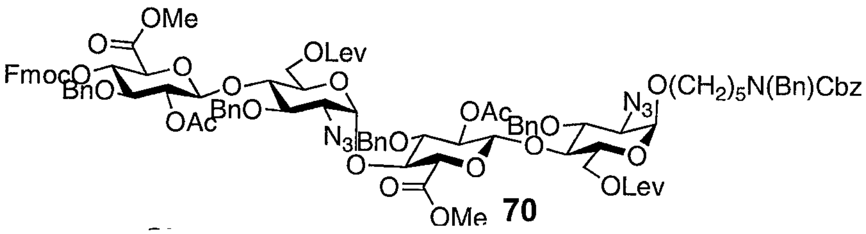

7
6
5
4
3
2
1
ppm
FmocO
BnO
OMe
O
OAc
BnO
OLev
N3
BnO
O
OMe
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz

70

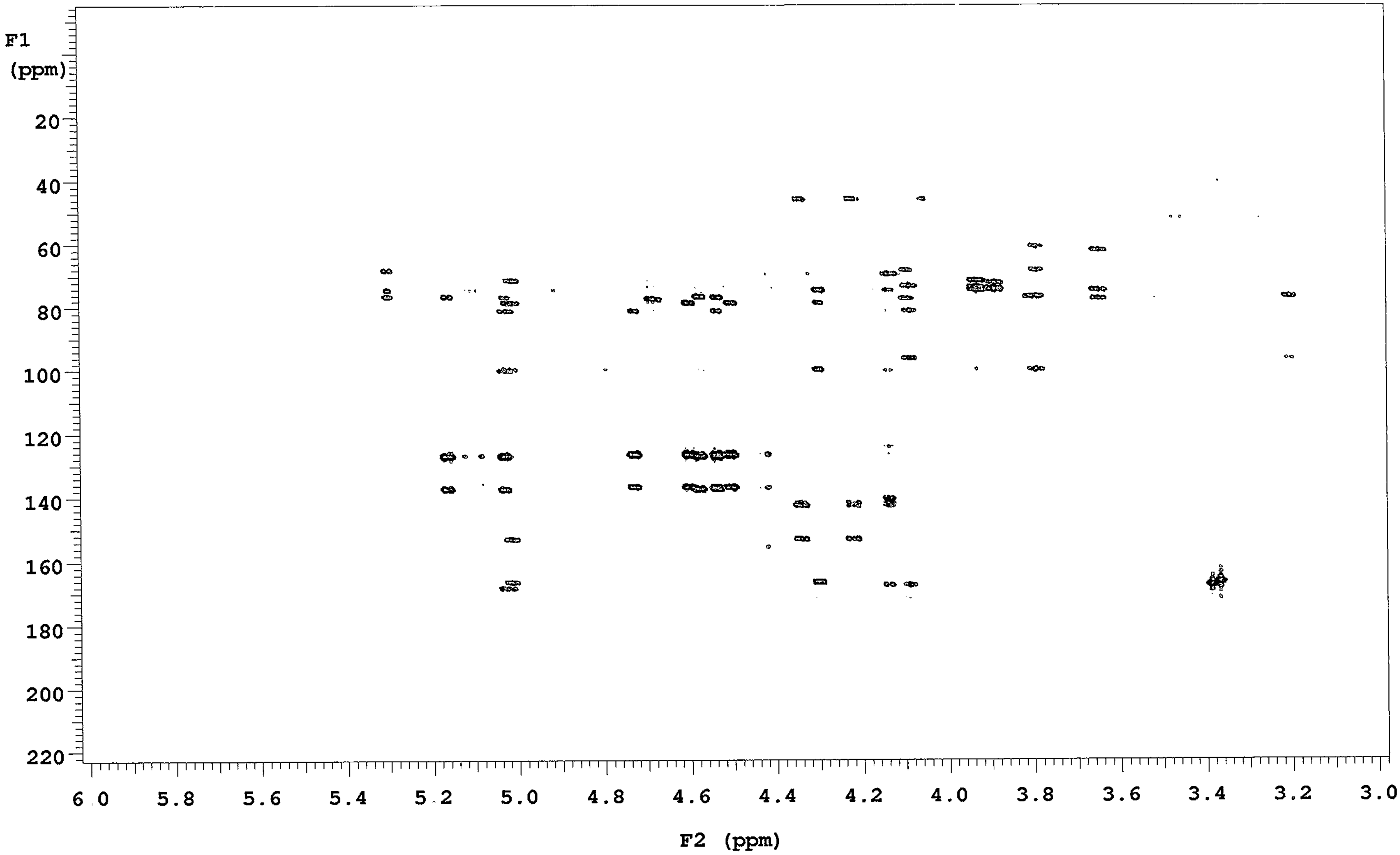


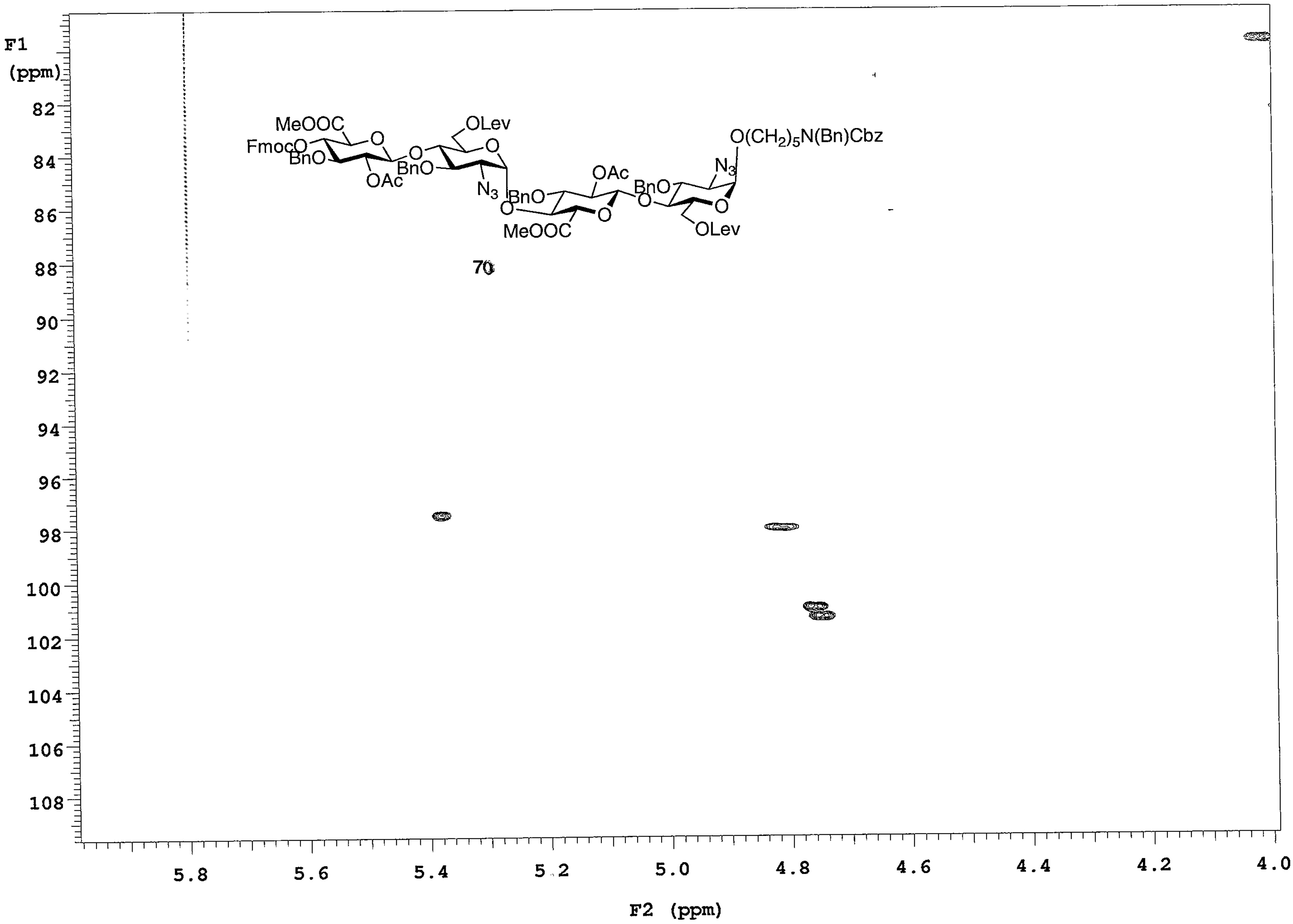
70



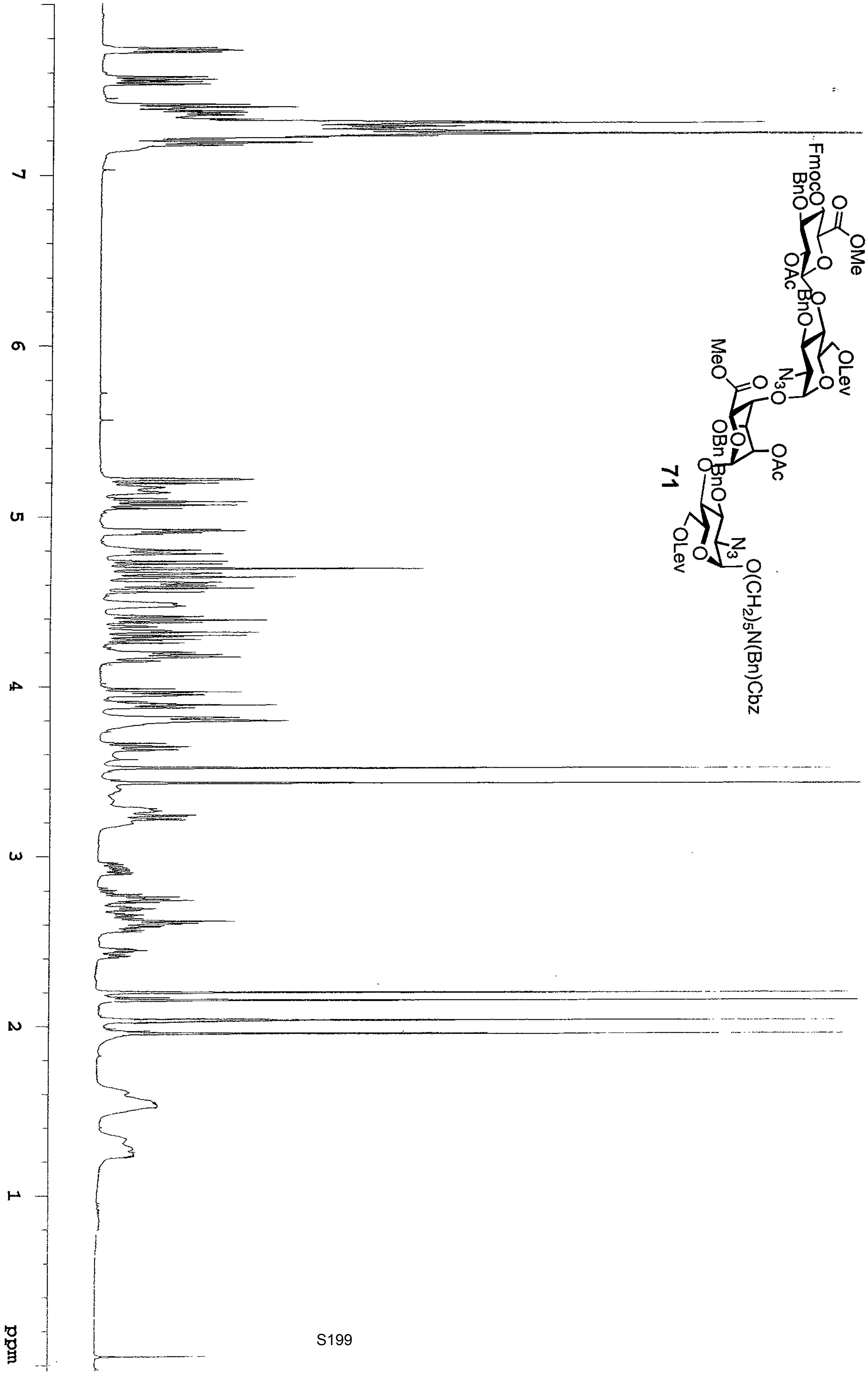

OMe
O
FmocO
BnO
O
OAc
BnO
O
OLev
O
N3
BnO
O
O
OMe
OAc
O
BnO
O
O
OLev
N3
O(CH2)5N(Bn)Cbz

70


F1
(ppm)
20
40
60
80
100
120
140
160
180
200
220
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
F2 (ppm)

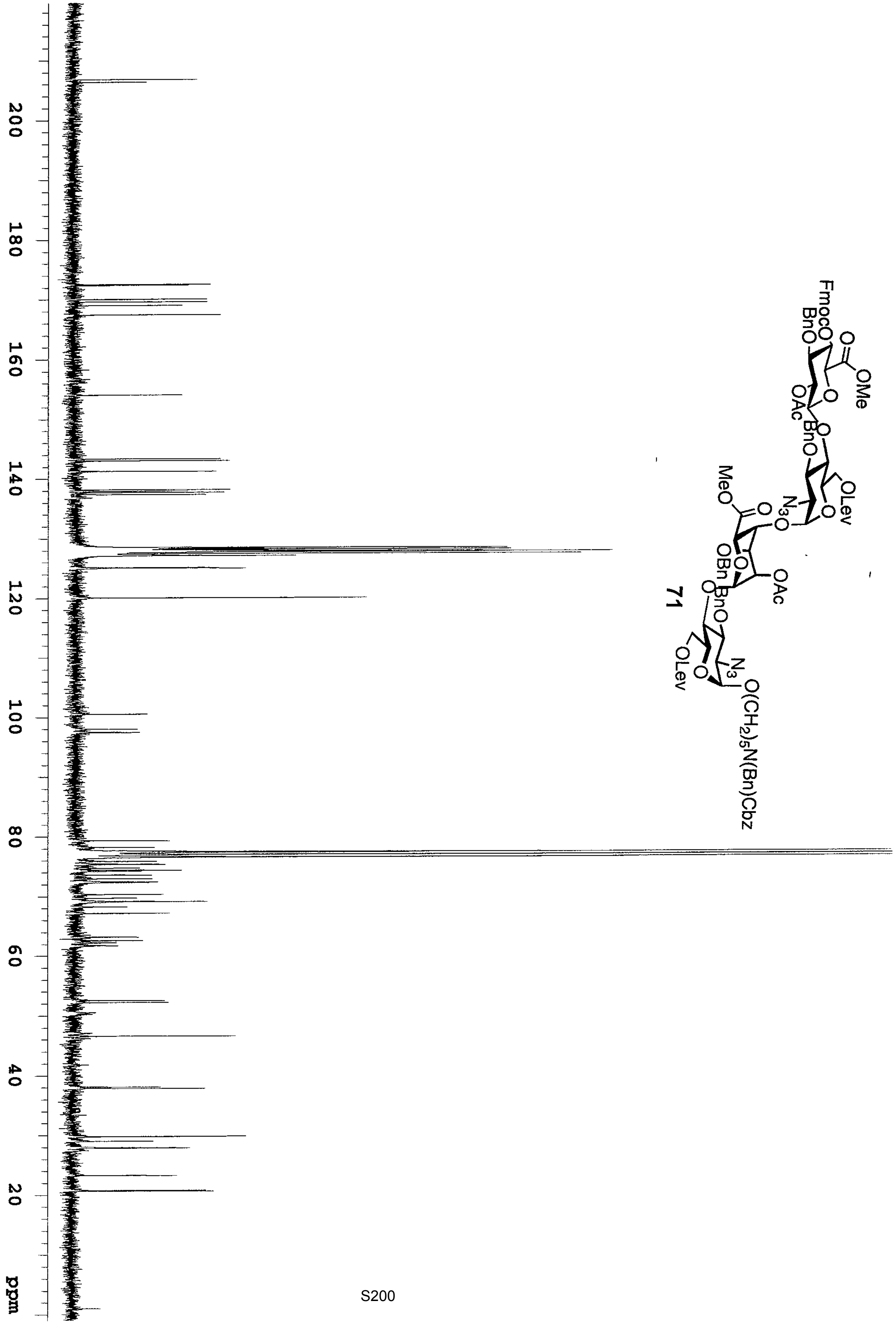

F1
(ppm)
82
84
86
88
90
92
94
96
98
100
102
104
106
108
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
F2 (ppm)
MeOOC
FmocO
BnO
OAc
BnO
OLev
N3
BnO
MeOOC
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz

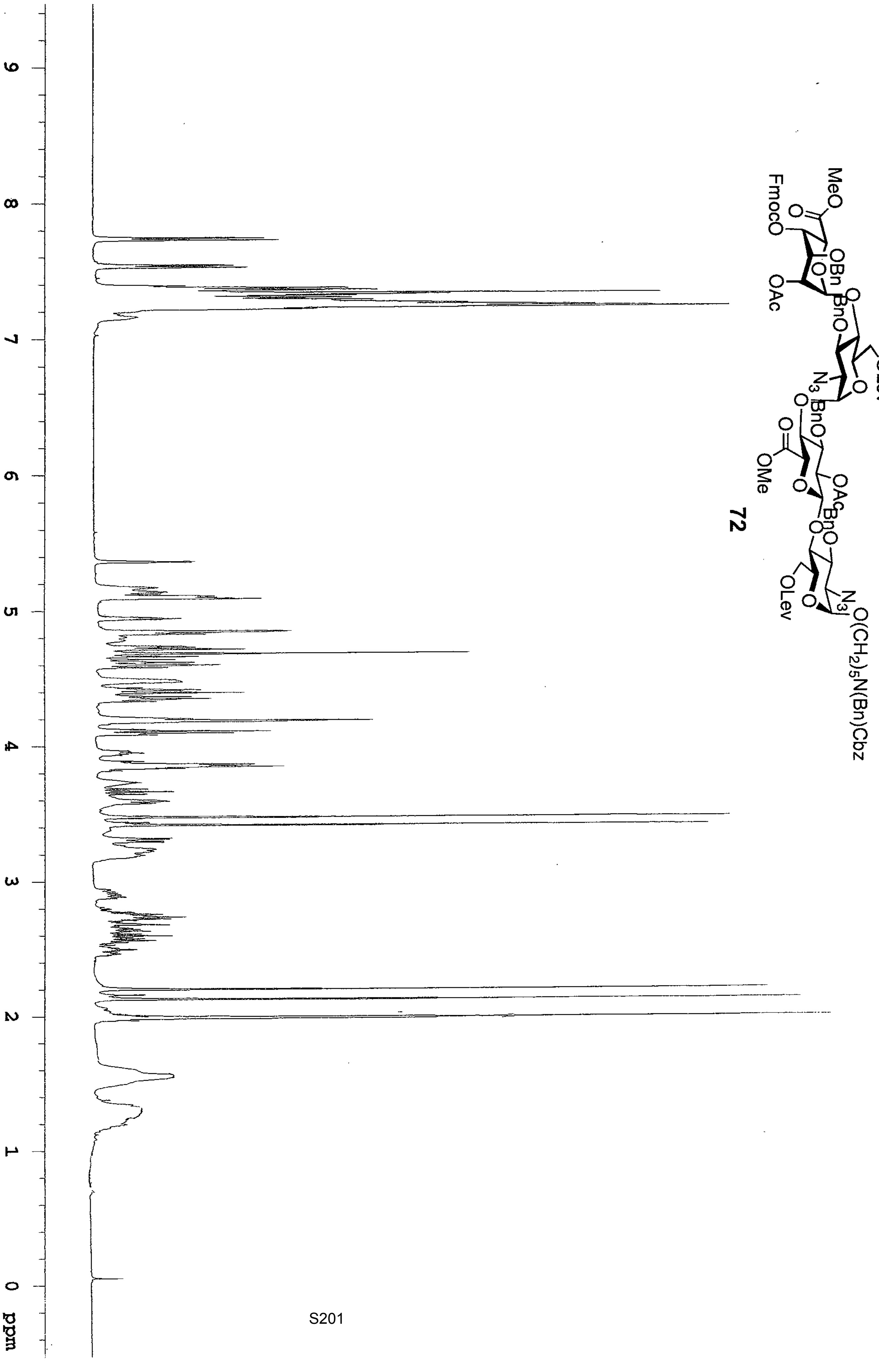
70



7
6
5
4
3
2
1
ppm
FmocO
BnO
OMe
O
OAc
BnO
OLev
N3
MeO
OBn
OAc
BnO
OLev
O(CH2)5N(Bn)Cbz

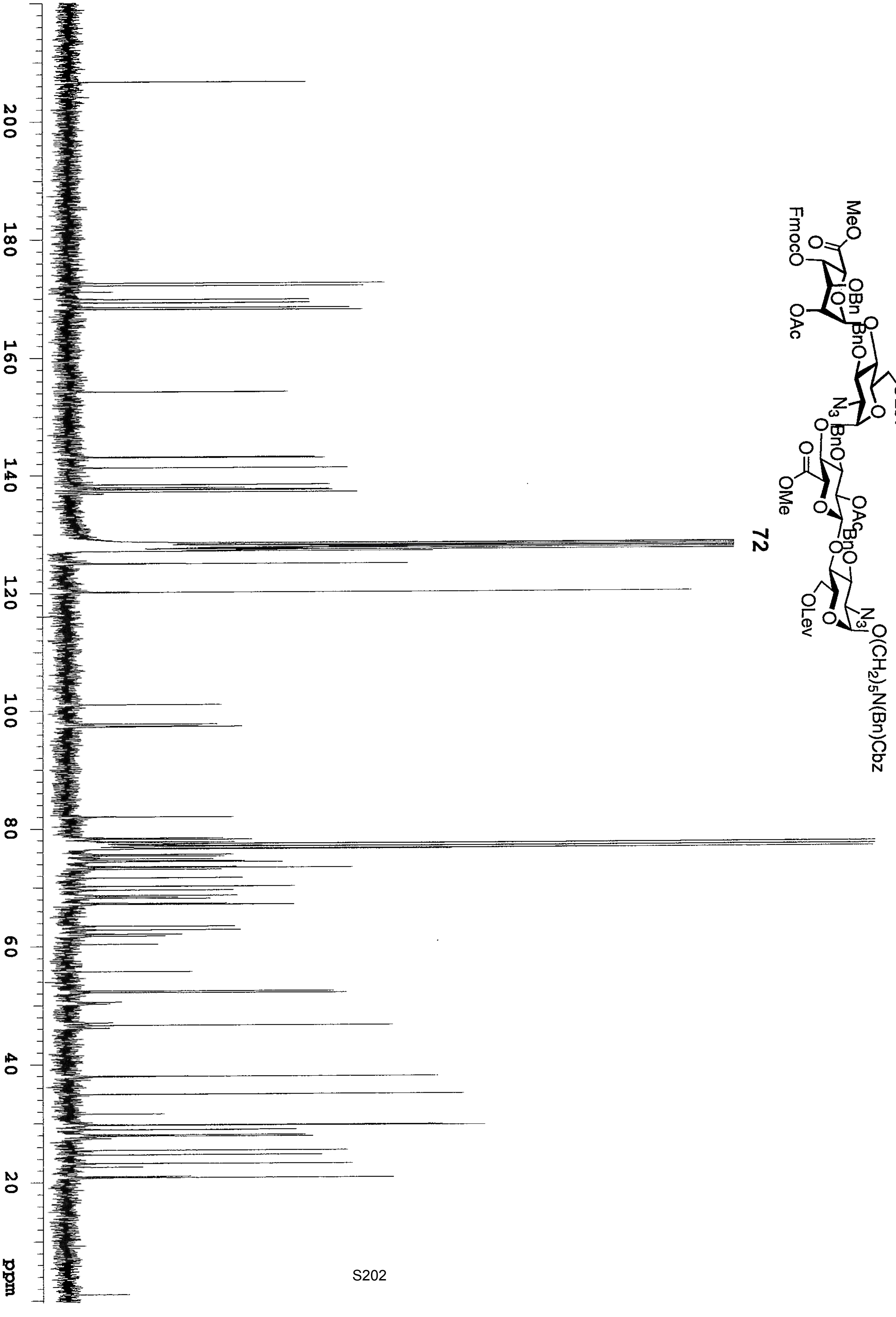
71


200
180
160
140
120
100
80
60
40
20
ppm
FmocO
BnO
OMe
O
O
OAc
BnO
O
O
OLev
N3
O
MeO
O
O
OBn
O
OAc
BnO
O
O
N3
O(CH2)5N(Bn)Cbz
OLev
71



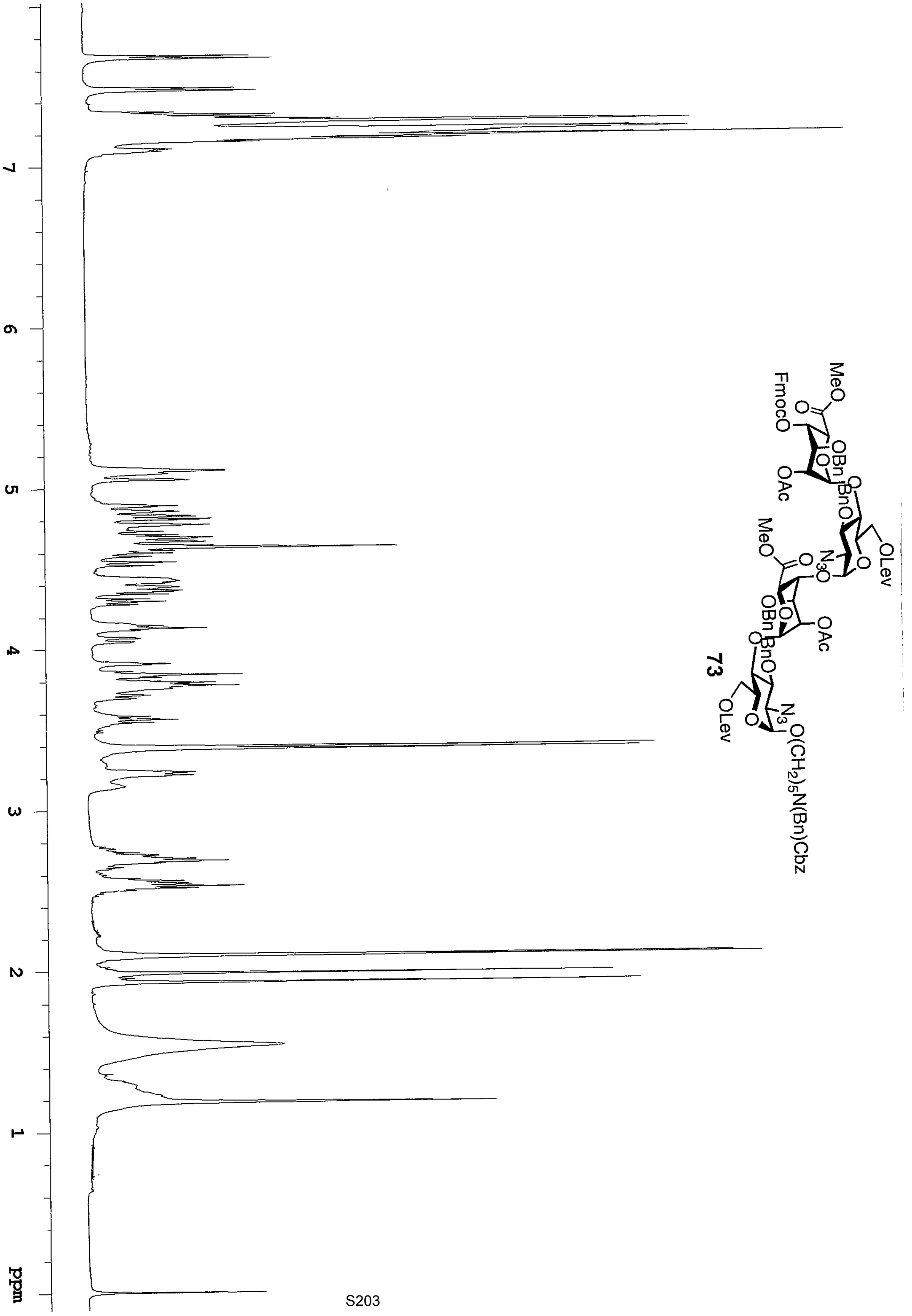
MeO
FmocO
OBn
OAc
BnO
OLev
N3
BnO
OMe
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz
9
8
7
6
5
4
3
2
1
0
ppm

72



200
180
160
140
120
100
80
60
40
20
ppm
MeO
FmocO
OBn
OAc
BnO
OLev
N3
BnO
OMe
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz

72



73

7
6
5
4
3
2
1
ppm
MeO
O
FmocO
OBn
O
OAc
BnO
O
OLev
N3
O
MeO
O
OBn
O
OAc
BnO
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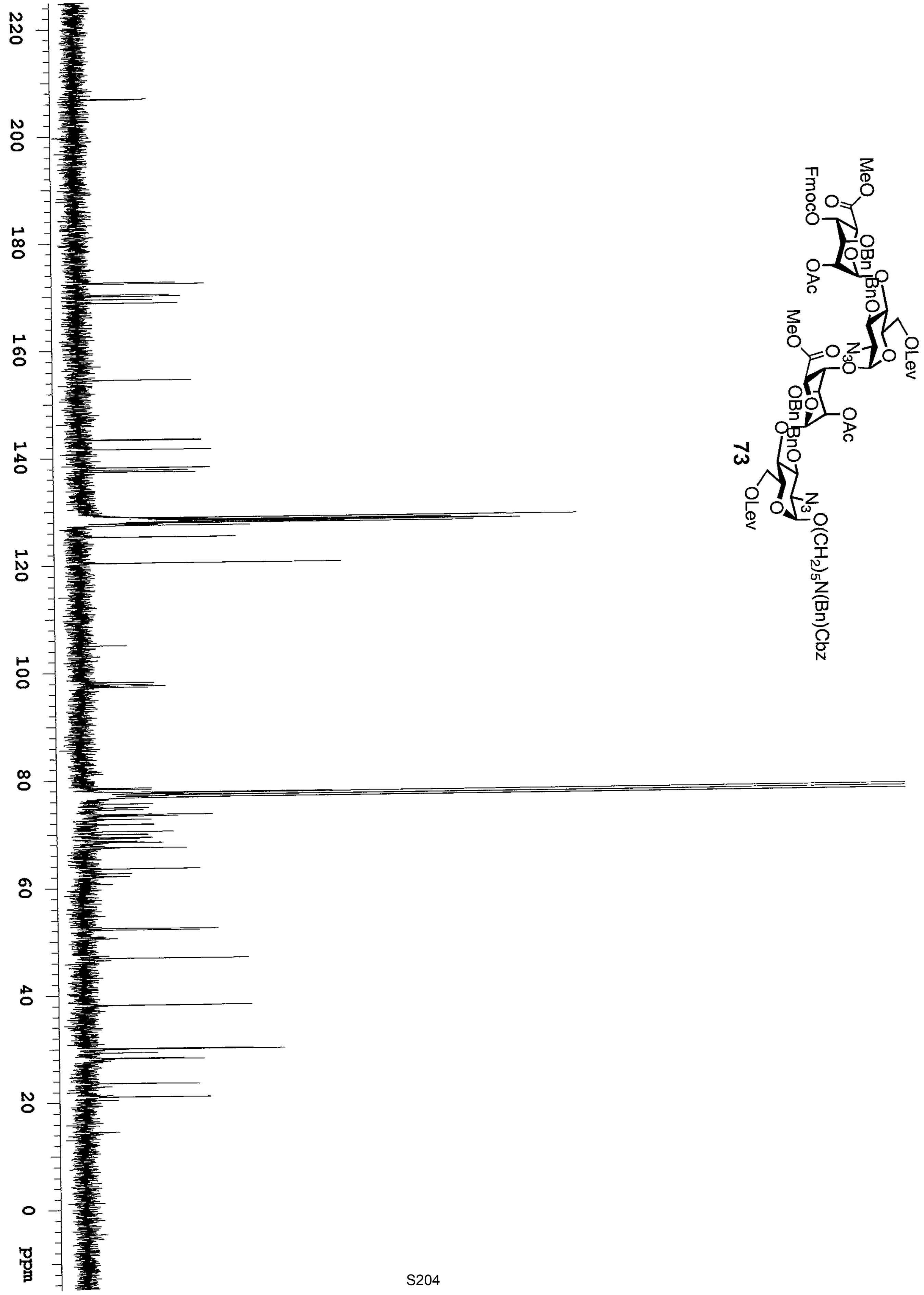
OLev
N3
O(CH2)5N(Bn)Cbz



220
200
180
160
140
120
100
80
60
40
20
0
ppm
MeO
FmocO
OBn
OAc
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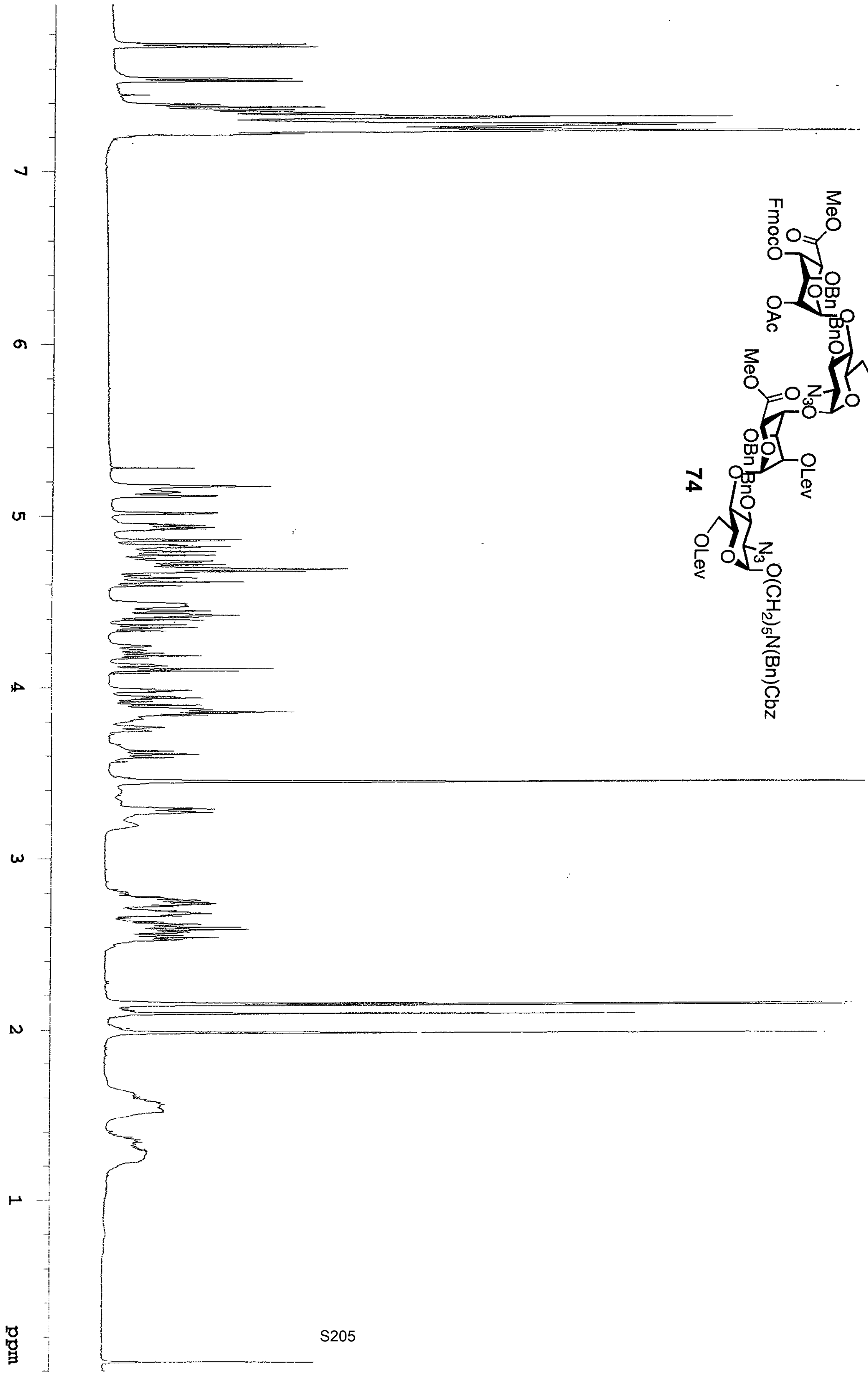
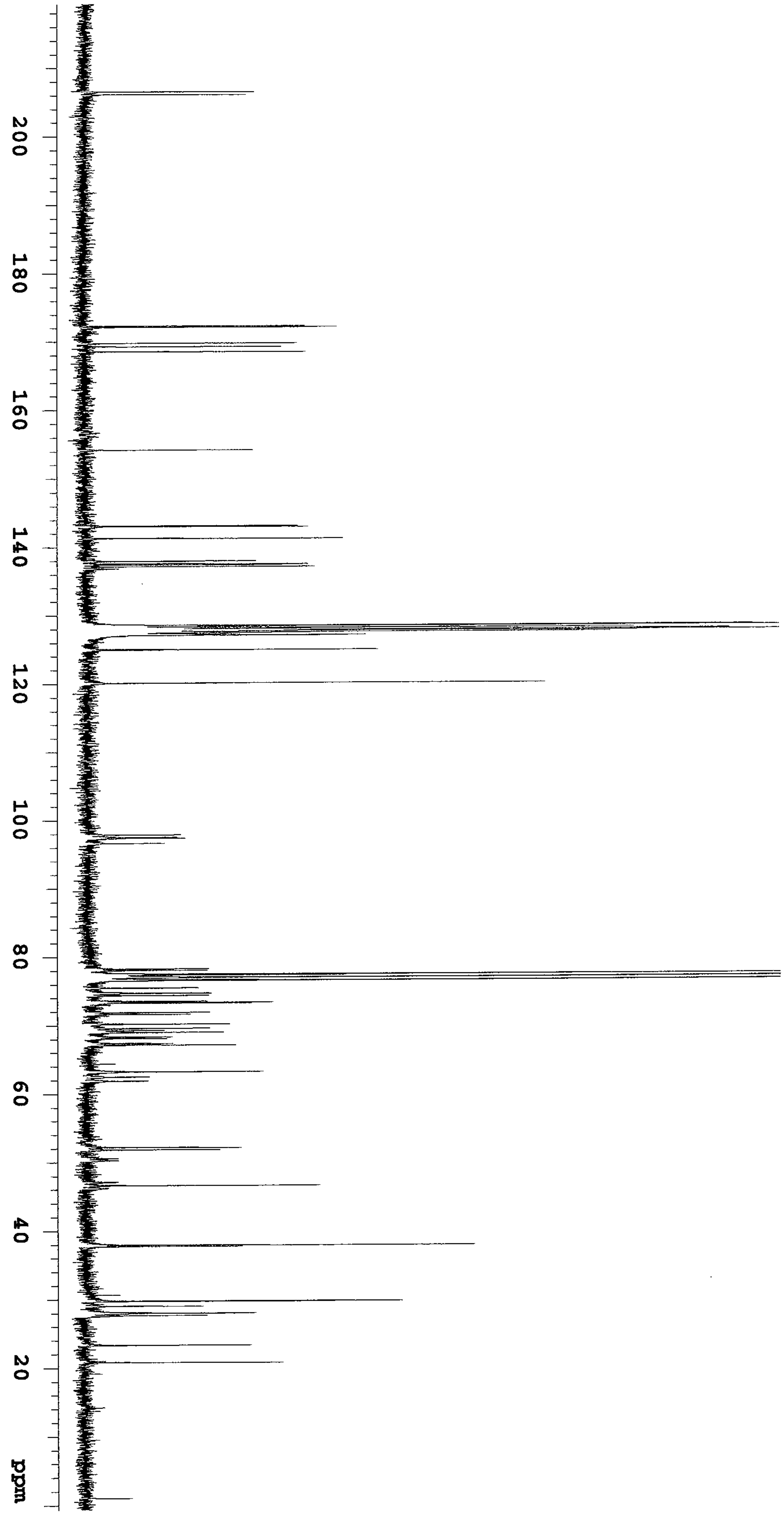
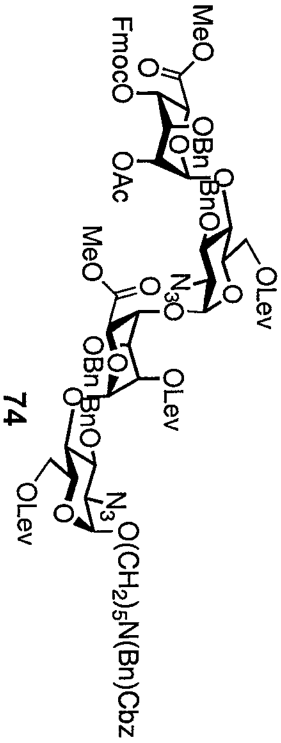
OLev
N3
MeO
OAc
OBn
BnO
N3
OLev
O(CH2)5N(Bn)Cbz

73

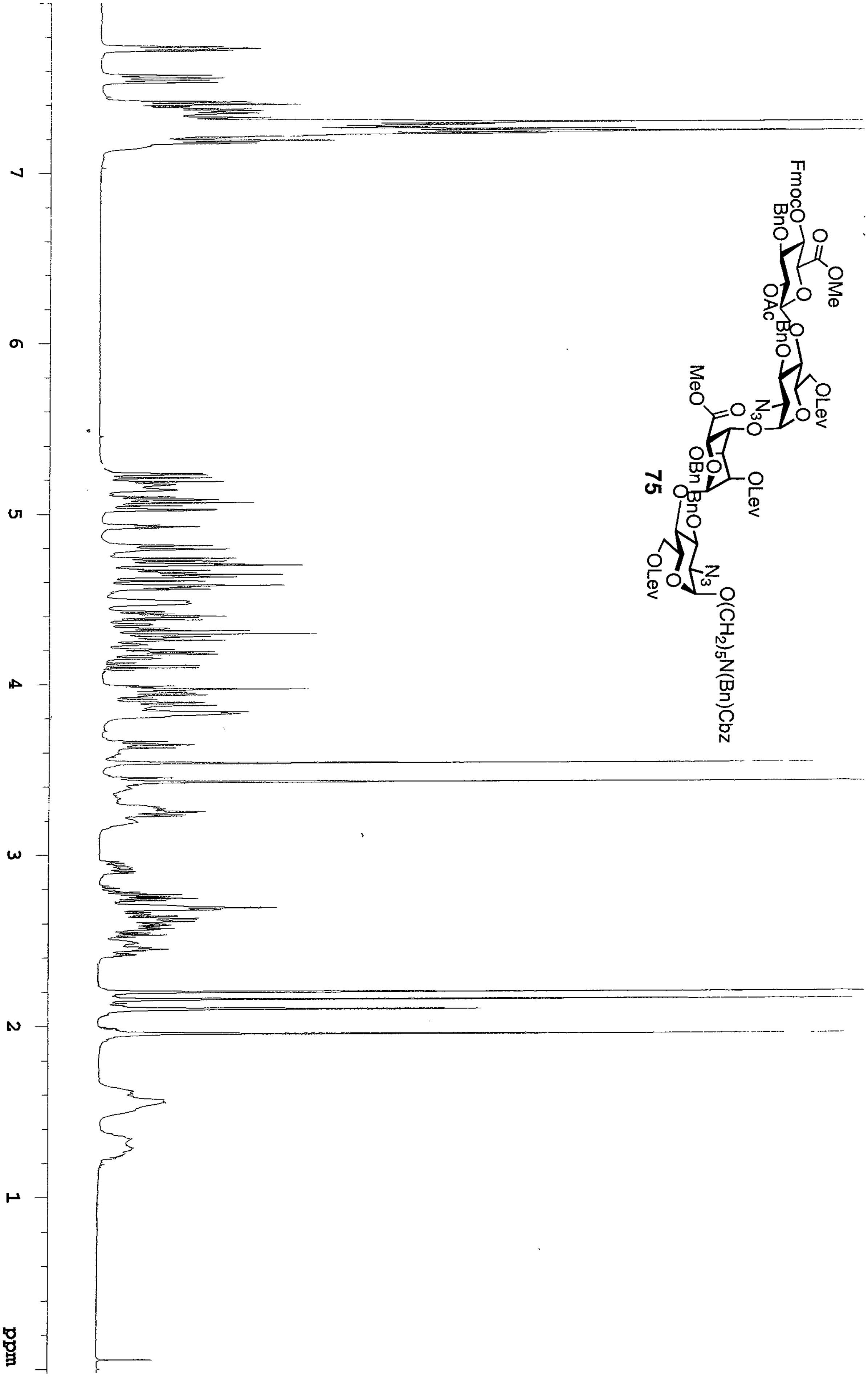

7
6
5
4
3
2
1
ppm
MeO
O
FmocO
OBn
O
OAc
BnO
O
OLev
N3
O
MeO
O
OLev
OBn
O
BnO
N3
O(CH2)5N(Bn)Cbz
O
OLev

74


200
180
160
140
120
100
80
60
40
20
ppm

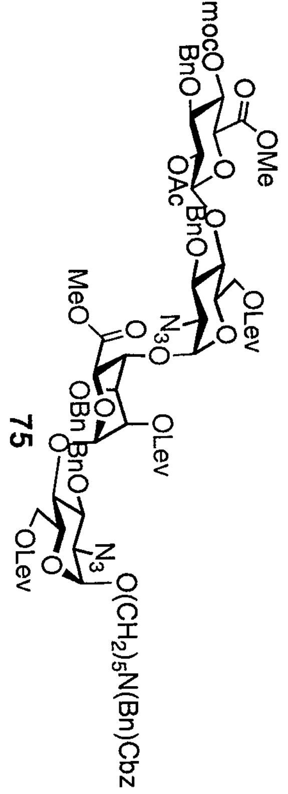

MeO
FmocO
O
OBn
BnO
OAc
O
OLev
N3
O
MeO
O
OLev
OBn
BnO
O
N3
O(CH2)5N(Bn)Cbz
OLev

74



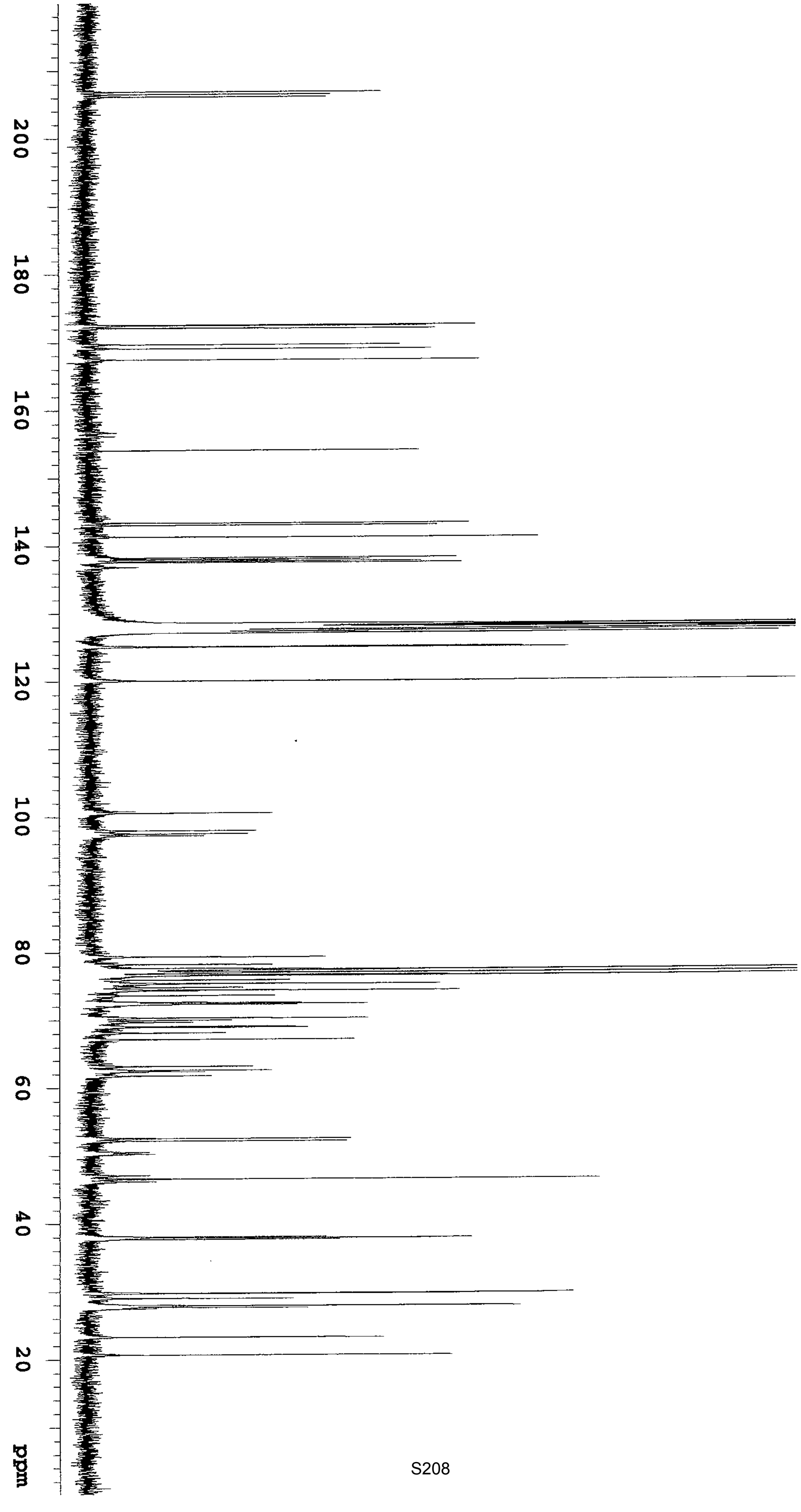
75

7
6
5
4
3
2
1
ppm
FmocO
BnO
OAc
OMe
O
BnO
OLev
N3
MeO
OBn
OLev
BnO
OLev
N3
O(CH2)5N(Bn)Cbz



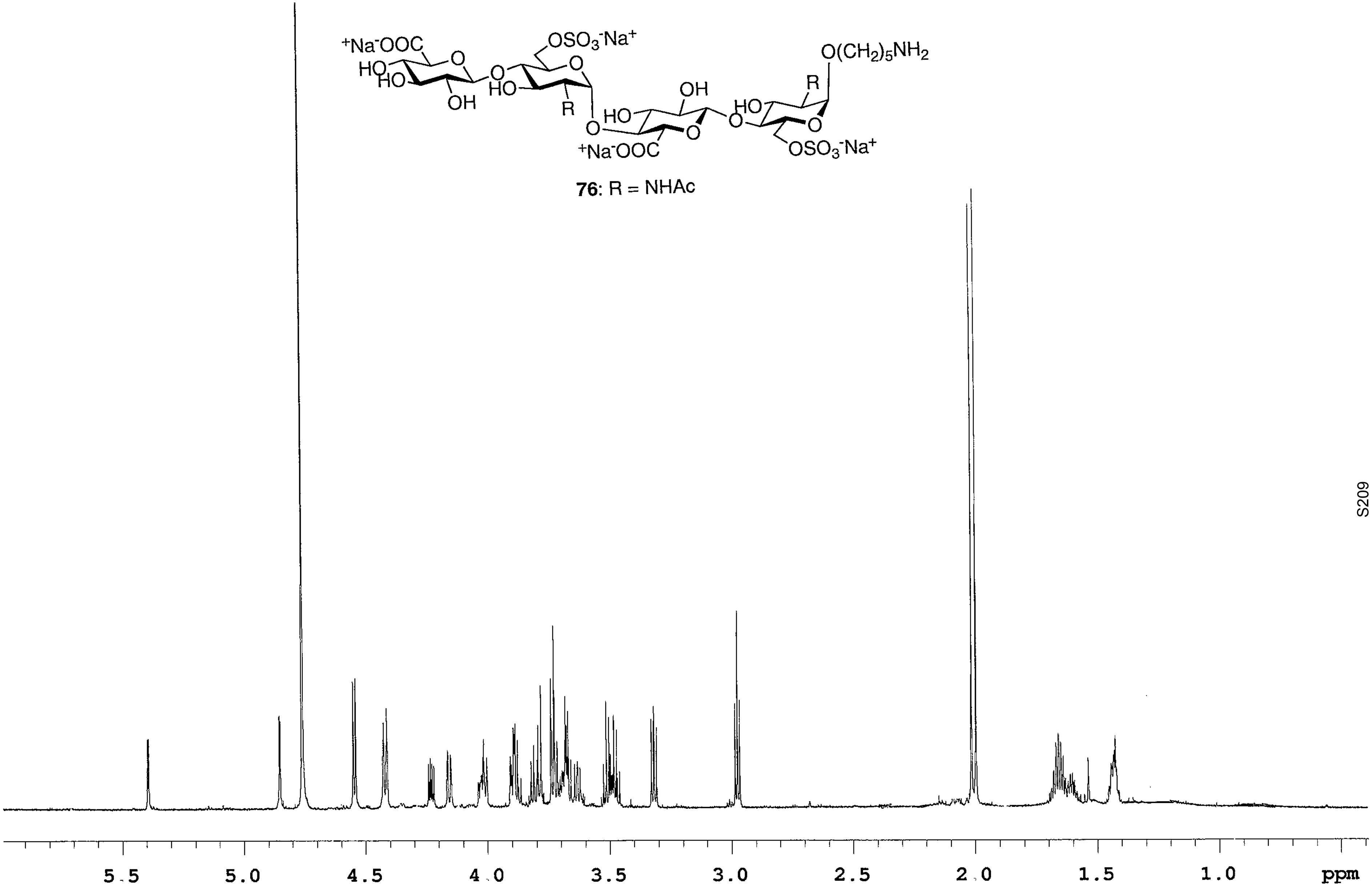
FmocO
BnO
O
OMe
O
OAc
BnO
O
BnO
OLev
O
N3
O
MeO
O
OBn
O
OLev
O
BnO
N3
O
OLev
O(CH2)5N(Bn)Cbz

75

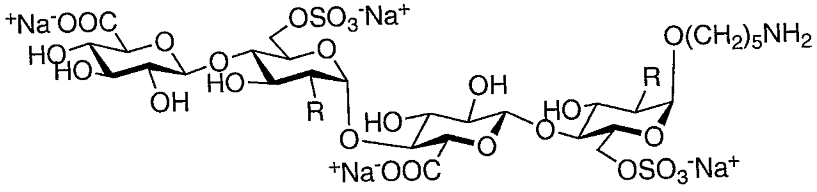


200
180
160
140
120
100
80
60
40
20
ppm

β-D-GlcA(1-4)-α-D-GlcNAc(6S)(1-4)-β-D-GlcA(1-4)-α-D-GlcNAc(6S)(1)-(CH$_2$)$_5$NH$_2$ (**76**)

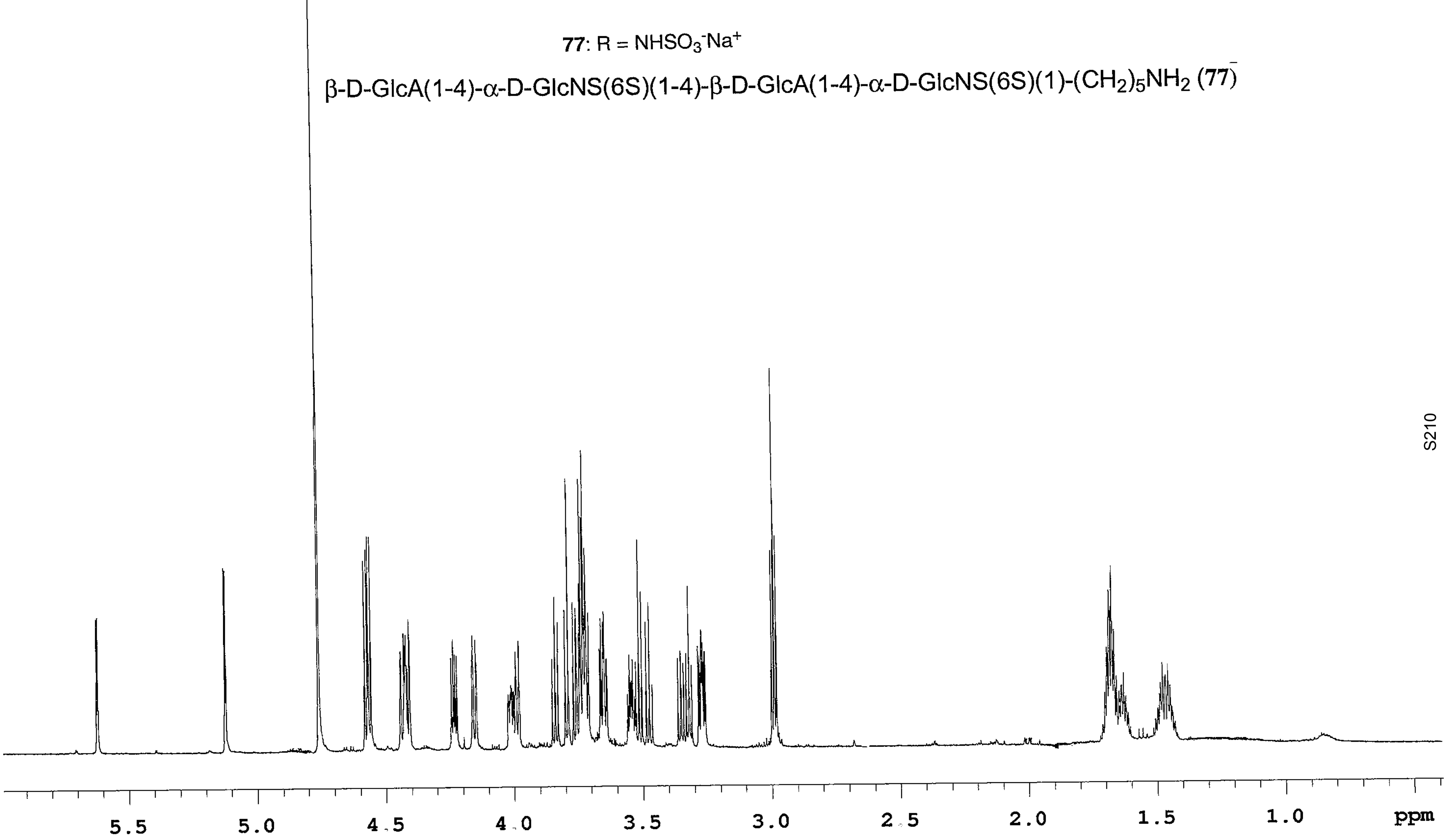


76: R = NHAc

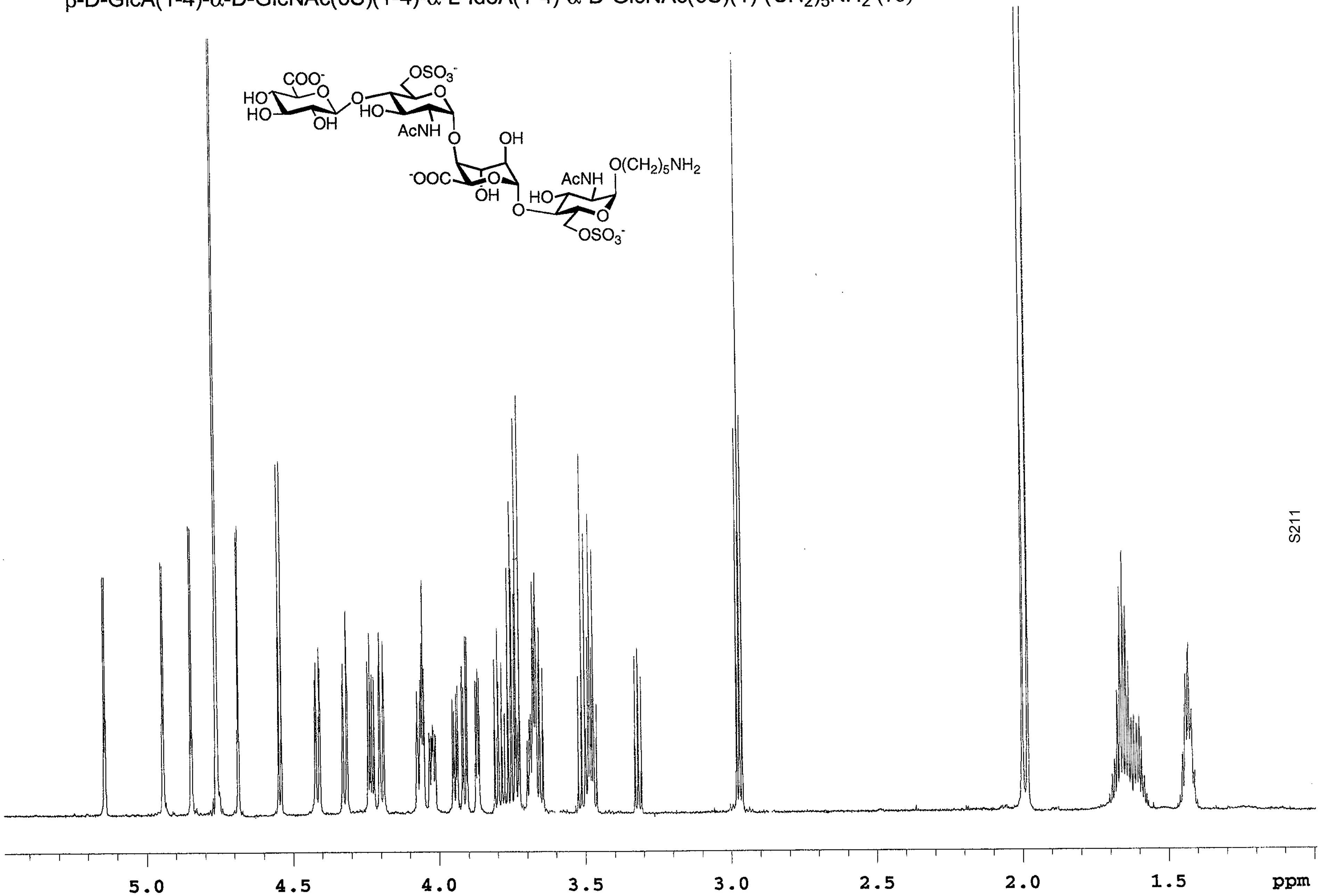


77: R = $NHSO_3^-Na^+$

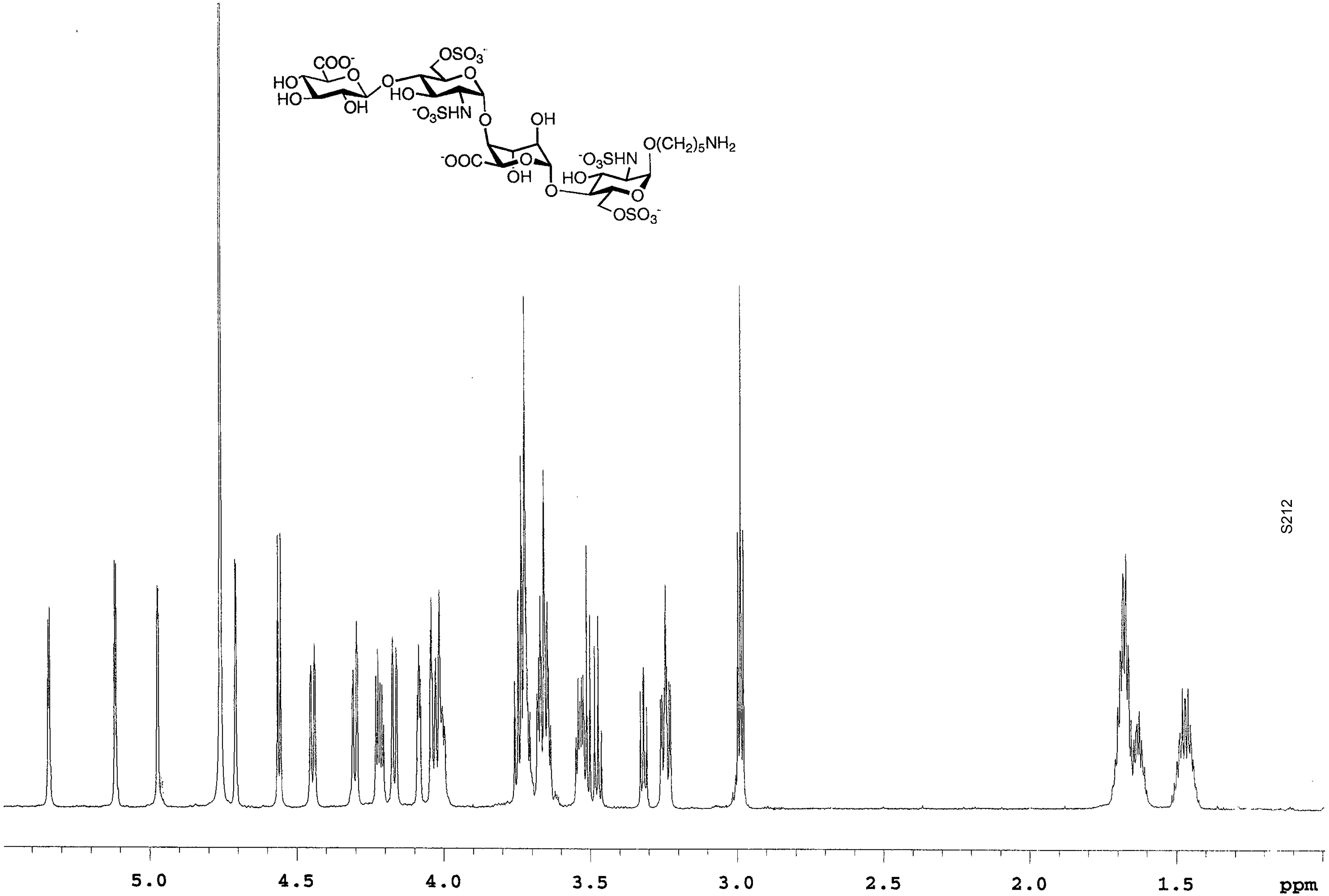
β-D-GlcA(1-4)-α-D-GlcNS(6S)(1-4)-β-D-GlcA(1-4)-α-D-GlcNS(6S)(1)-$(CH_2)_5NH_2$ (77)



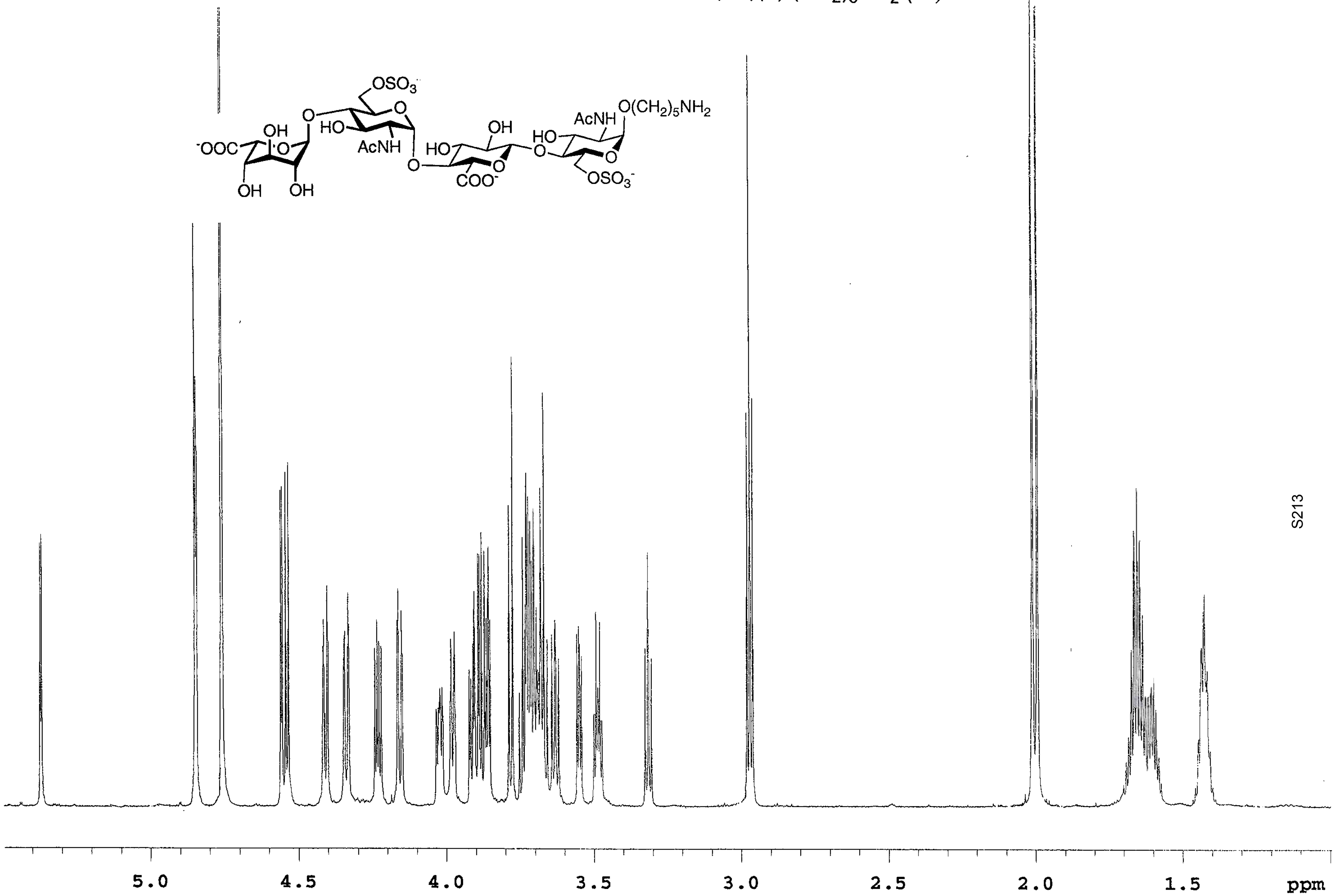
β-D-GlcA(1-4)-α-D-GlcNAc(6S)(1-4)-α-L-IdoA(1-4)-α-D-GlcNAc(6S)(1)-$(CH_2)_5NH_2$ (**78**)



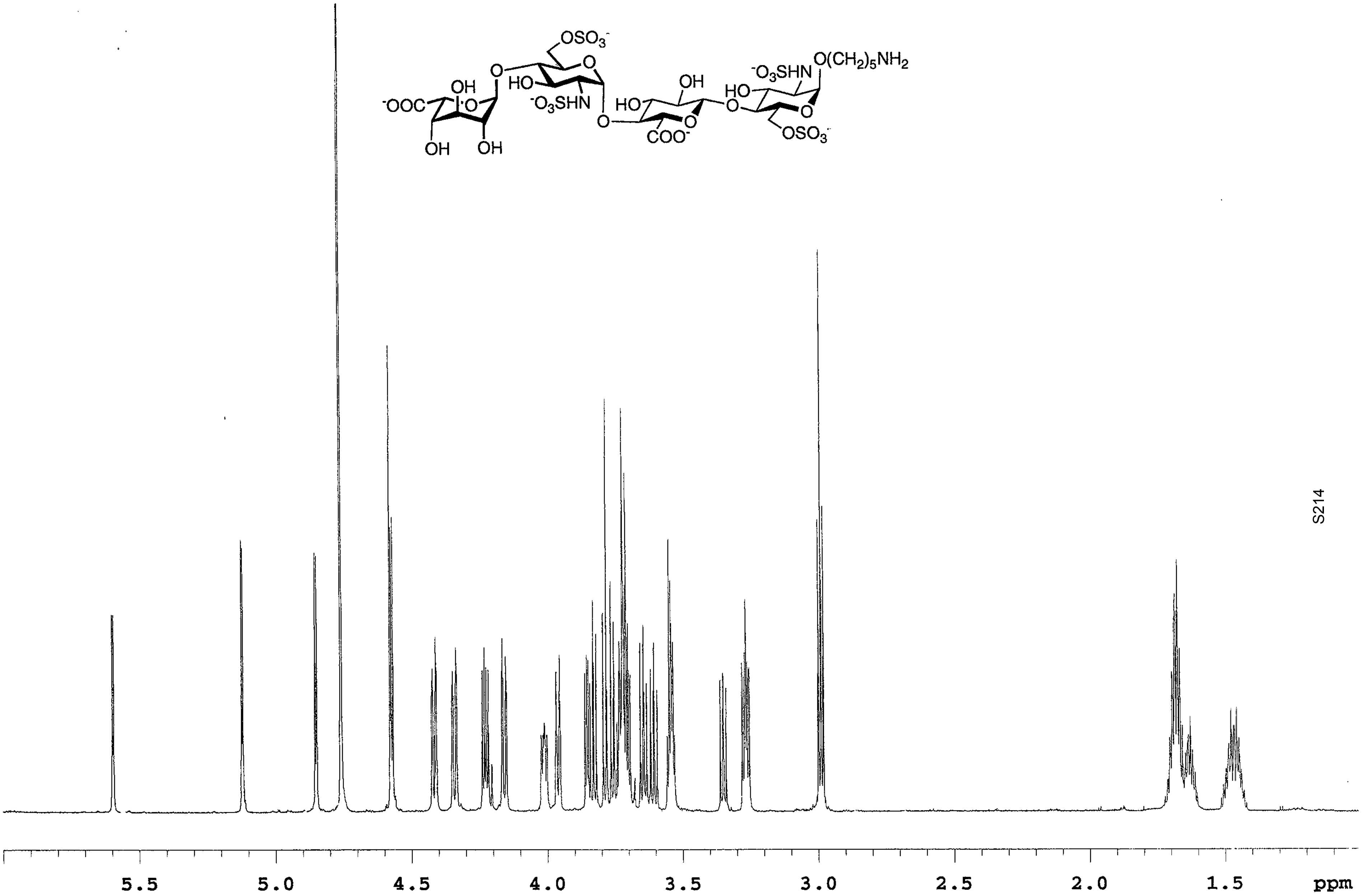
β-D-GlcA(1-4)-α-D-GlcNS(6S)(1-4)-α-L-IdoA(1-4)-α-D-GlcNS(6S)(1)-$(CH_2)_5NH_2$ (**79**)



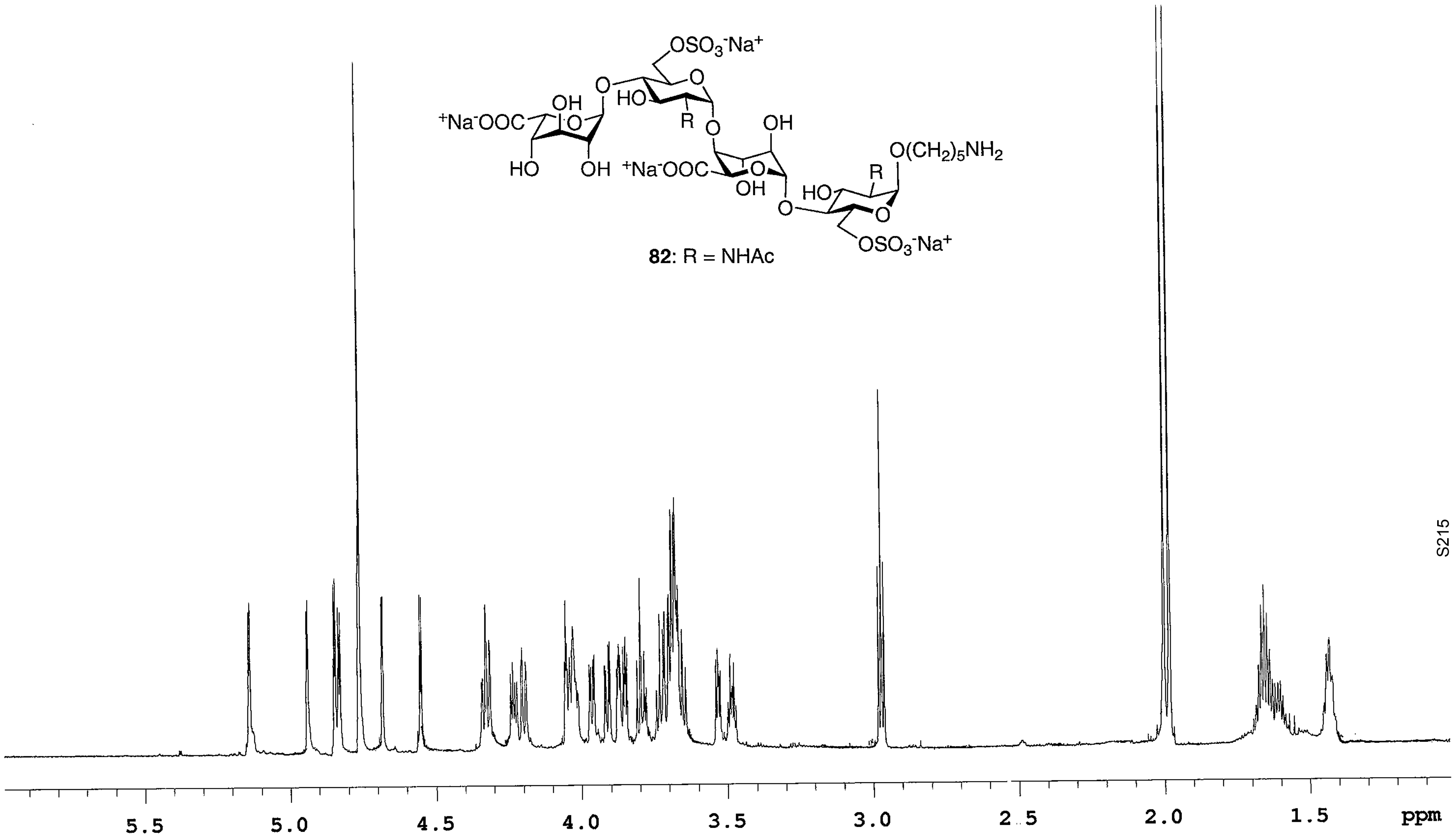
α-L-IdoA(1-4)-α-D-GlcNAc(6S)(1-4)-β-D-GlcA(1-4)-α-D-GlcNAc(6S)(1)-$(CH_2)_5NH_2$ (**80**)



α-L-IdoA(1-4)-α-D-GlcNS(6S)(1-4)-β-D-GlcA(1-4)-α-D-GlcNS(6S)(1)-$(CH_2)_5NH_2$ (**81**)

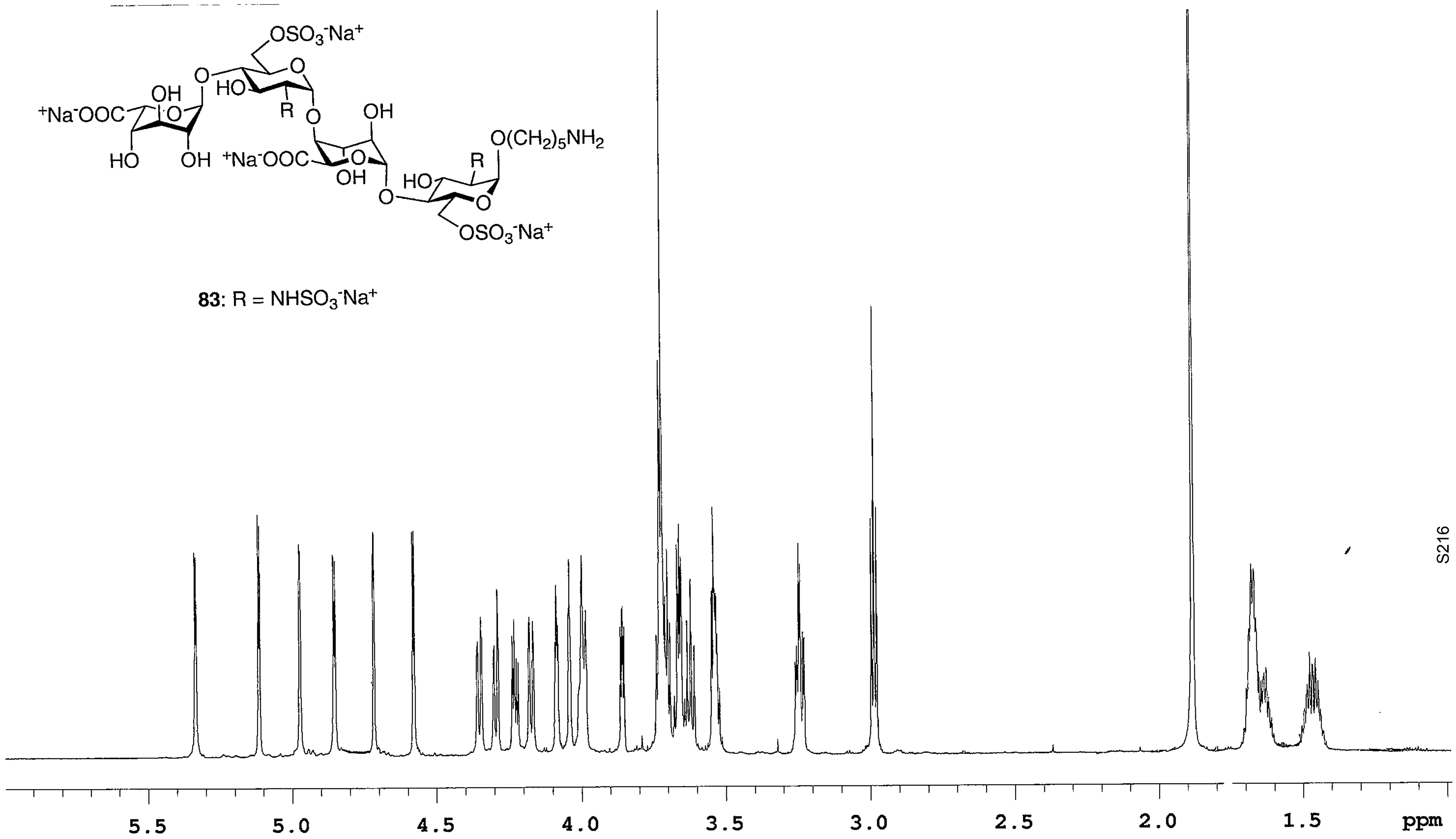


α-L-IdoA(1-4)-α-D-GlcNAc(6S)(1-4)-α-L-IdoA(1-4)-α-D-GlcNAc(6S)(1)-$(CH_2)_5NH_2$ (82)



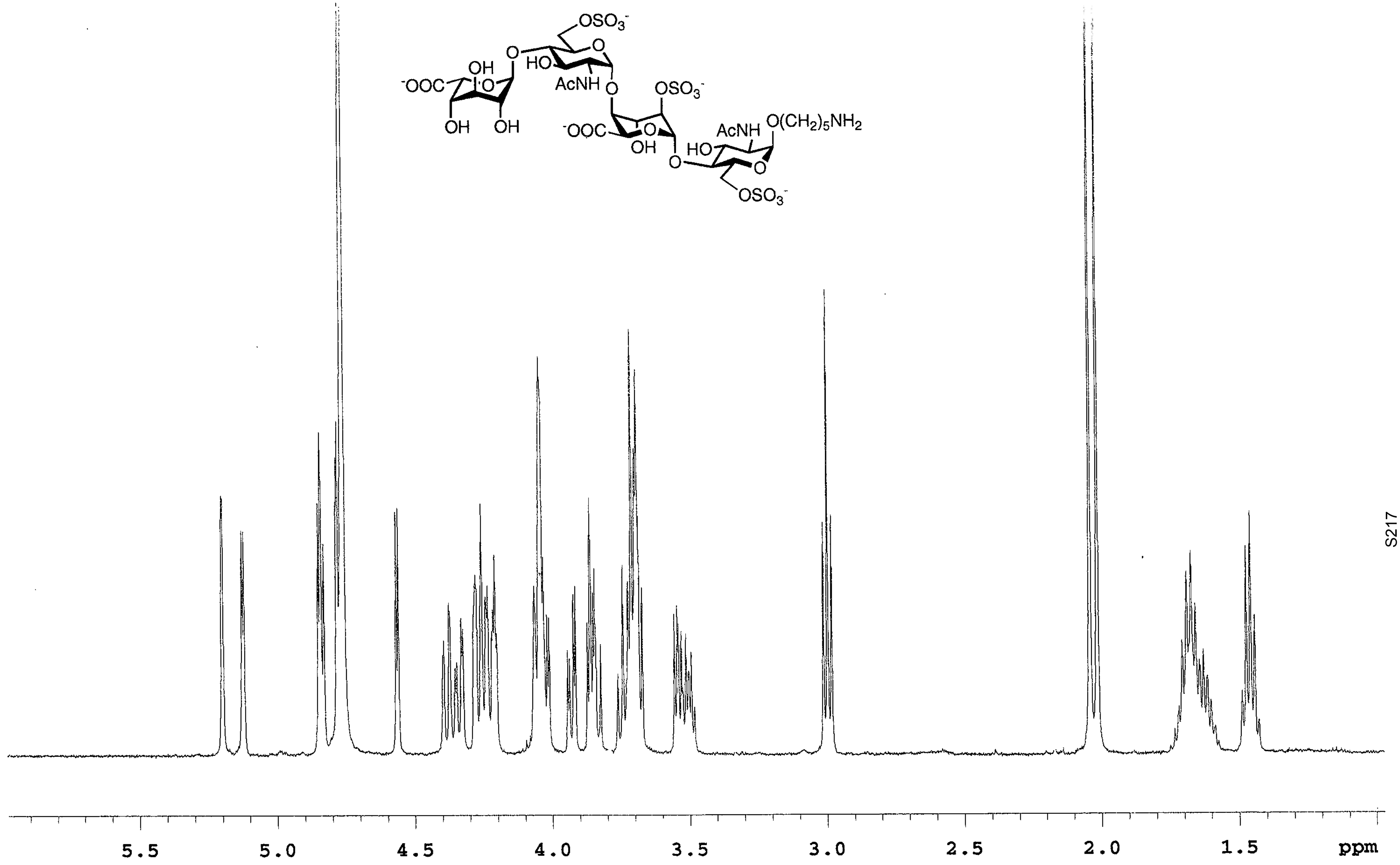
82: R = NHAc

α-L-IdoA(1-4)-α-D-GlcNS(6S)(1-4)-α-L-IdoA(1-4)-α-D-GlcNS(6S)(1)-$(CH_2)_5NH_2$

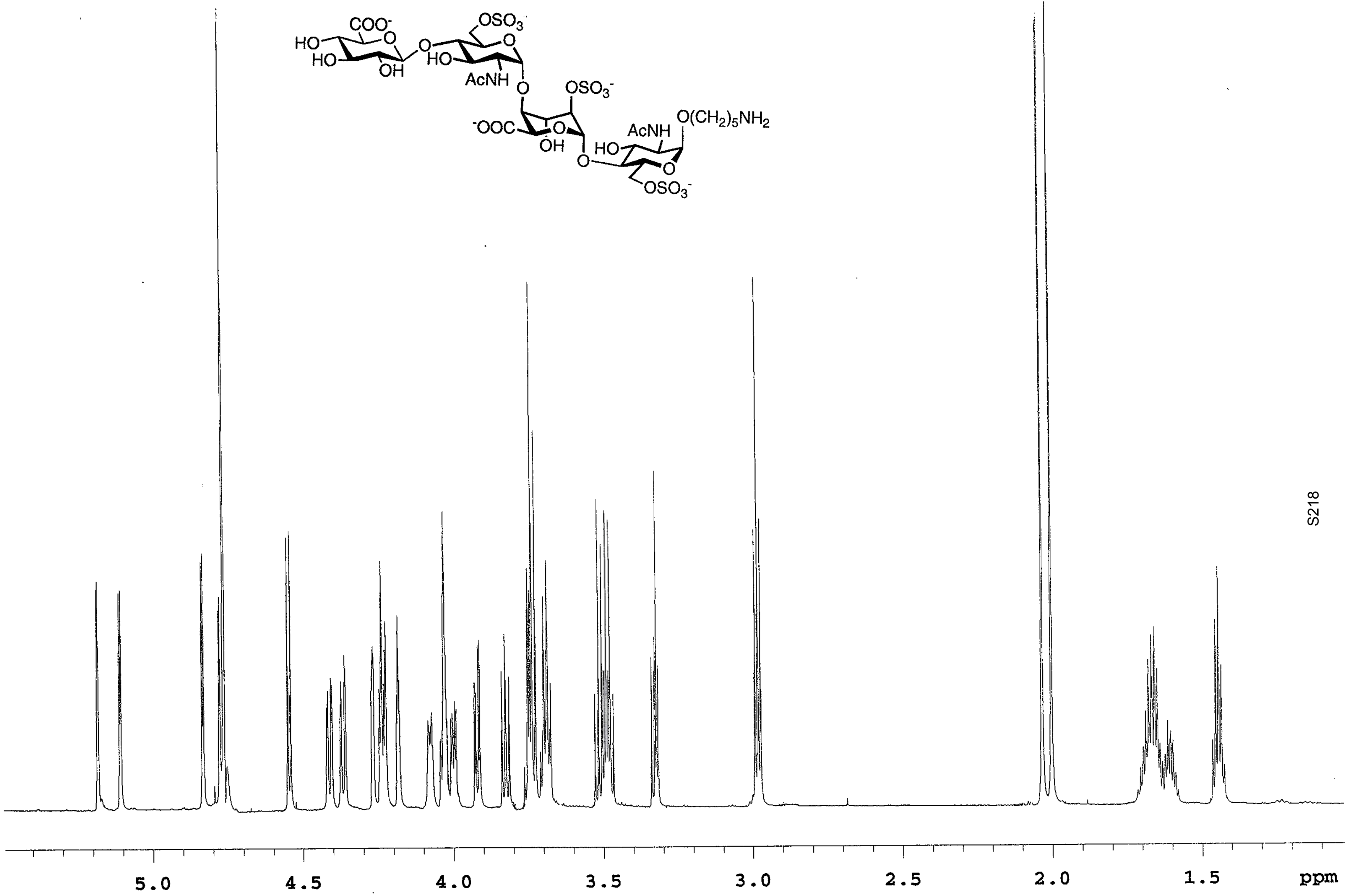


83: R = $NHSO_3^-Na^+$

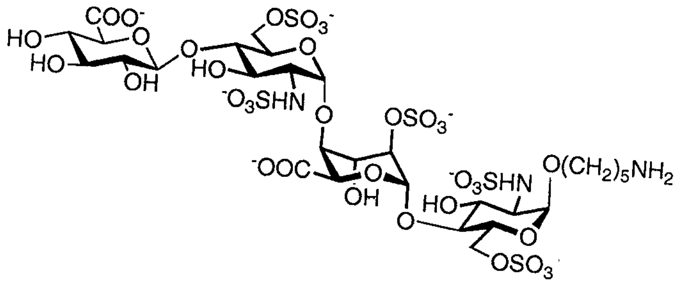
α-L-IdoA(1-4)-α-D-GlcNAc(6S)(1-4)-α-L-IdoA(2S)(1-4)-α-D-GlcNAc(6S)(1)-(CH$_2$)$_5$NH$_2$ (**84**)

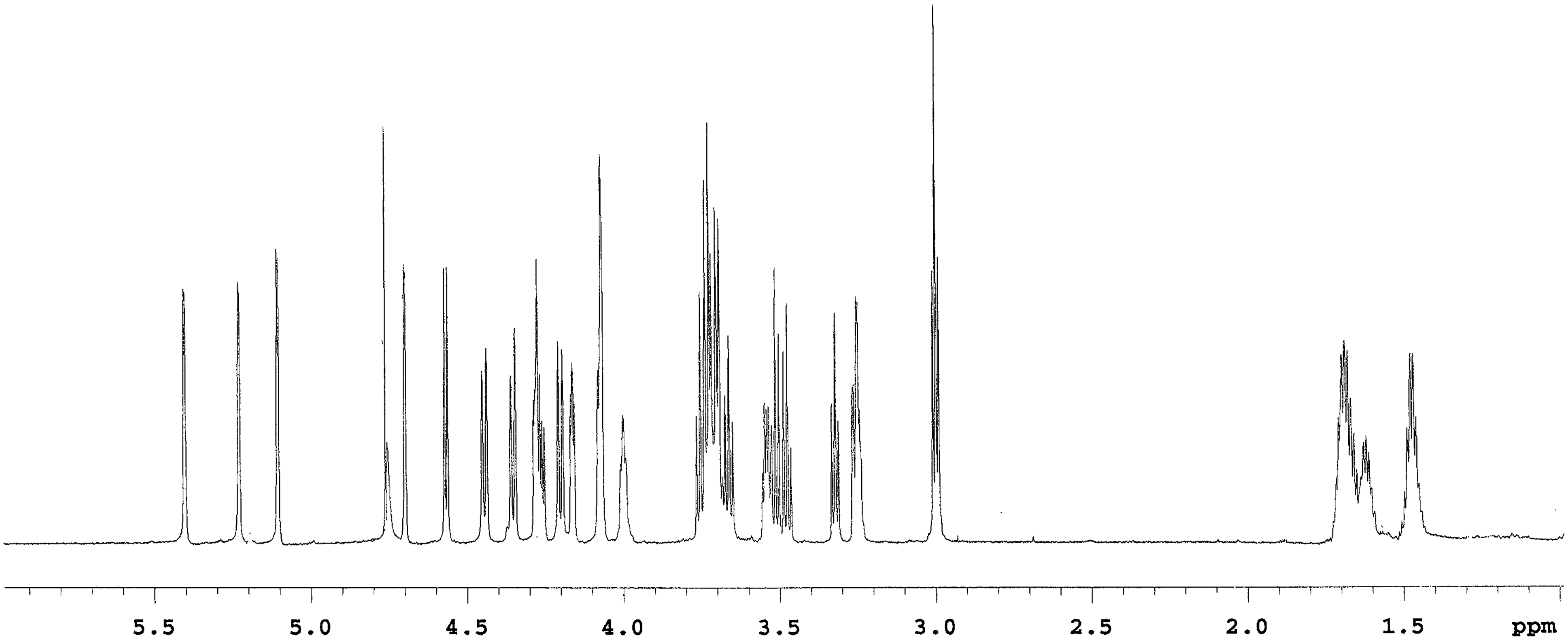


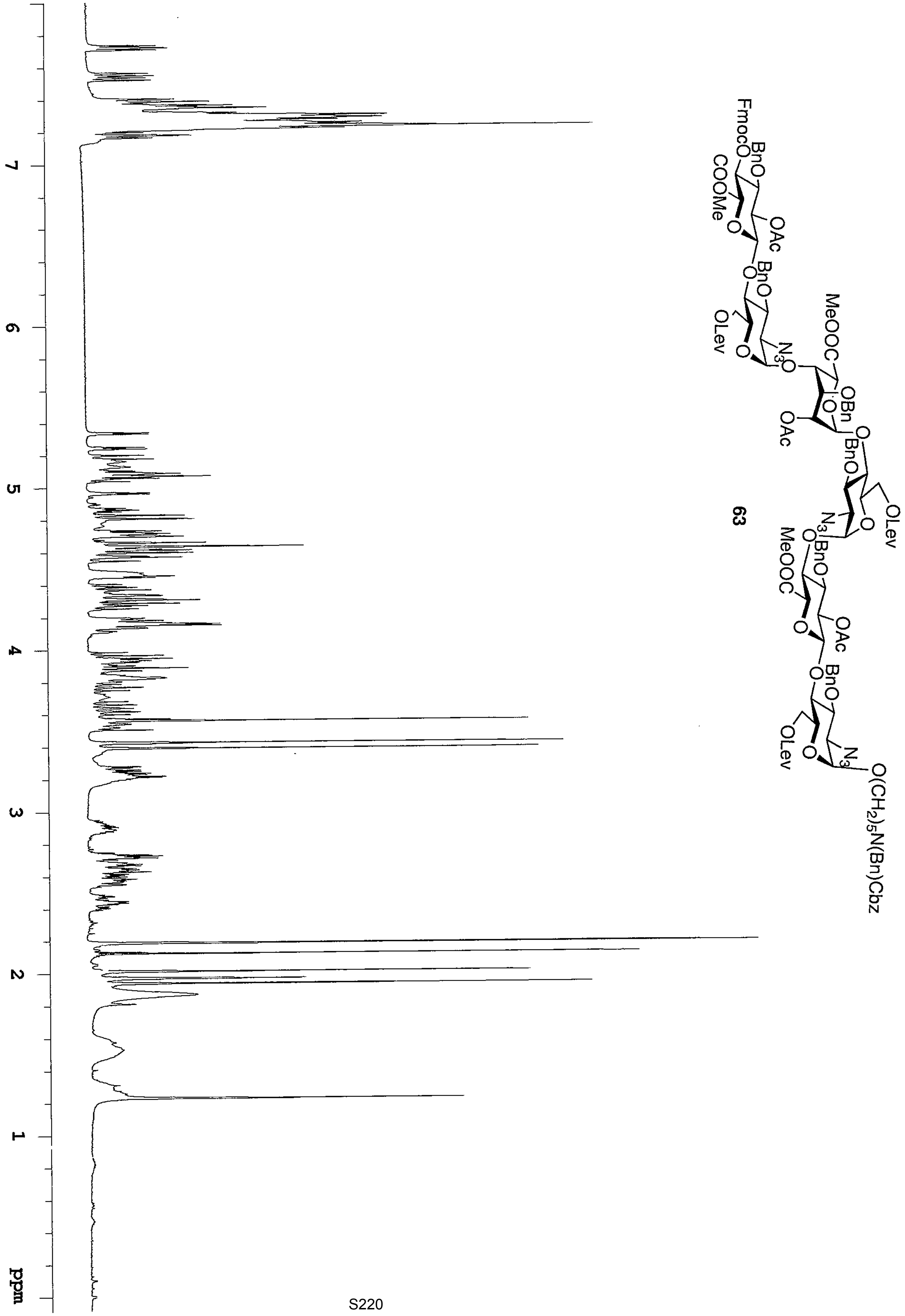
β-D-GlcA(1-4)-α-D-GlcNAc(6S)(1-4)-α-L-IdoA(2S)(1-4)-α-D-GlcNAc(6S)(1)-$(CH_2)_5NH_2$ (**85**)



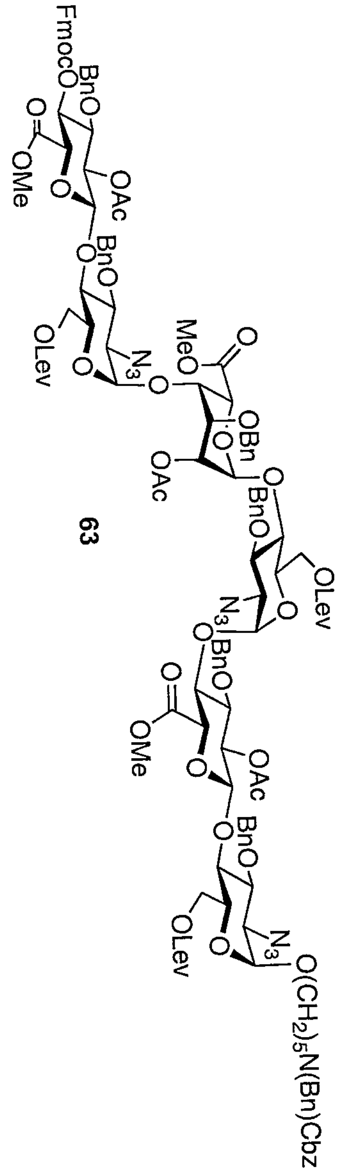
β-D-GlcA(1-4)-α-D-GlcNS(6S)(1-4)-α-L-IdoA(2S)(1-4)-α-D-GlcNS(6S)(1)-$(CH_2)_5NH_2$ (**86**)



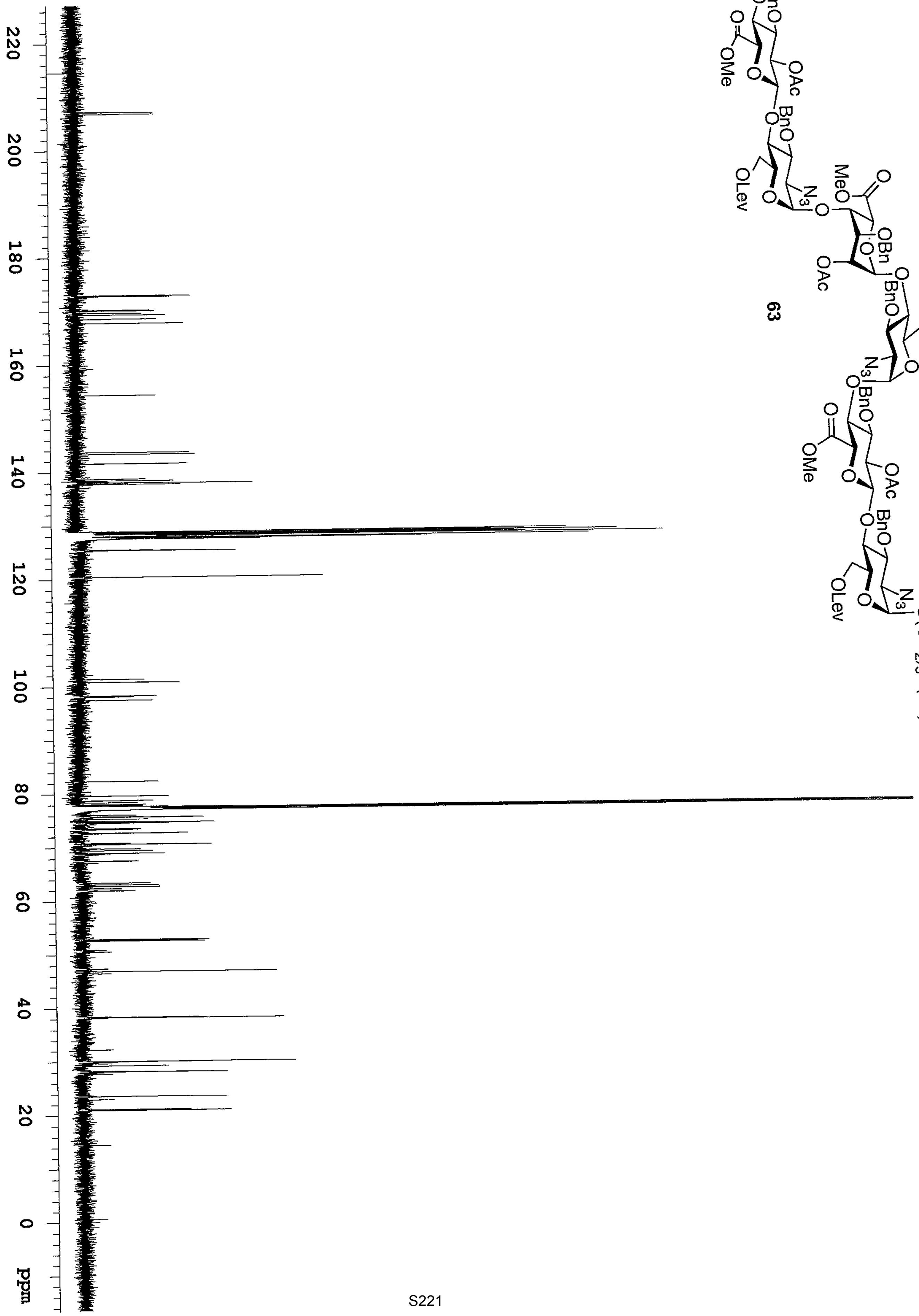


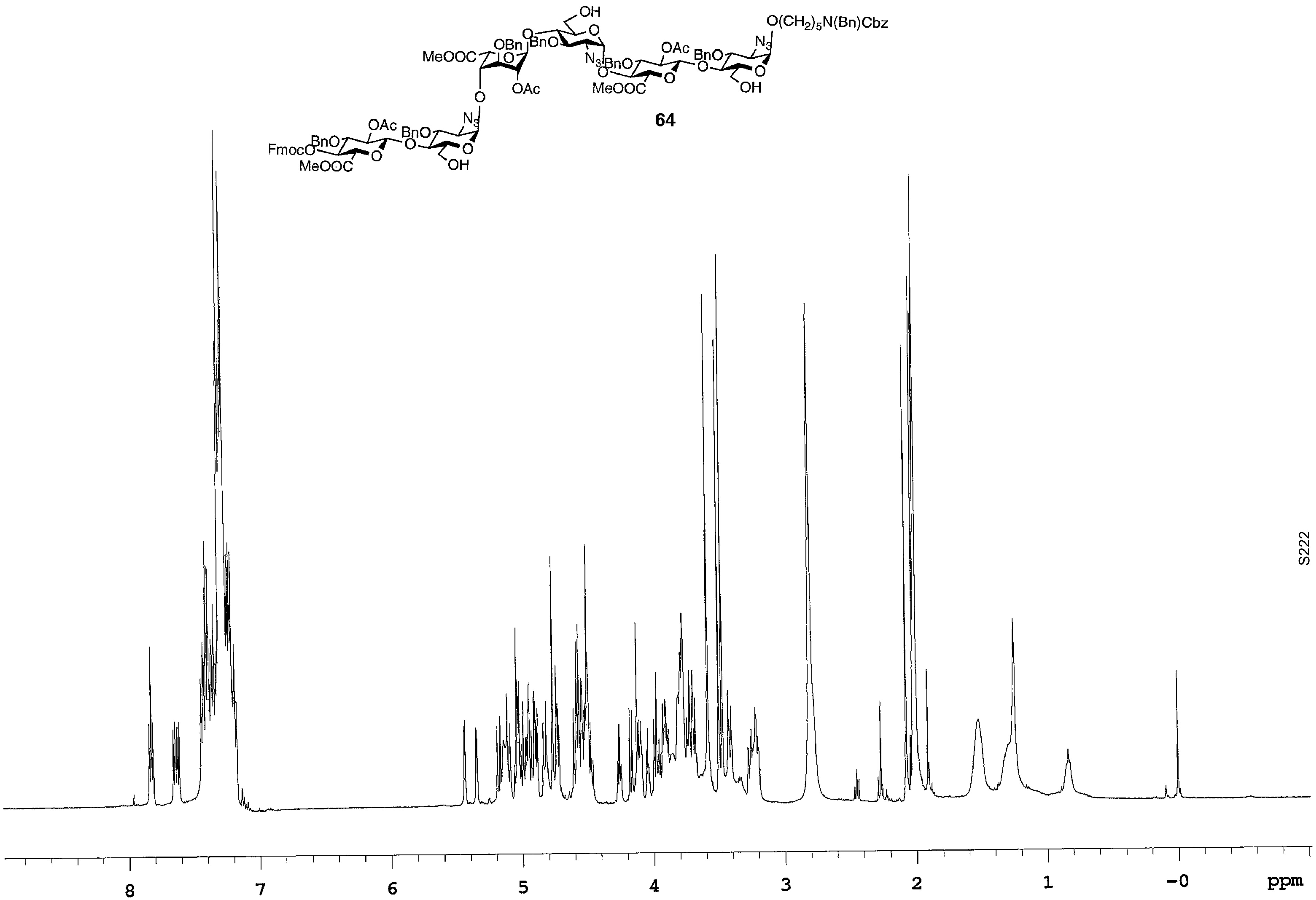

FmocO
BnO
COOMe
OAc
BnO
OLev
N3
MeOOC
OBn
OAc
BnO
OLev
N3
MeOOC
BnO
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz
7
6
5
4
3
2
1
ppm

63


FmocO
BnO
OAc
OMe
BnO
OLev
N3
MeO
OBn
OAc
BnO
OLev
N3
BnO
OMe
OAc
BnO
OLev
N3
O(CH2)5N(Bn)Cbz

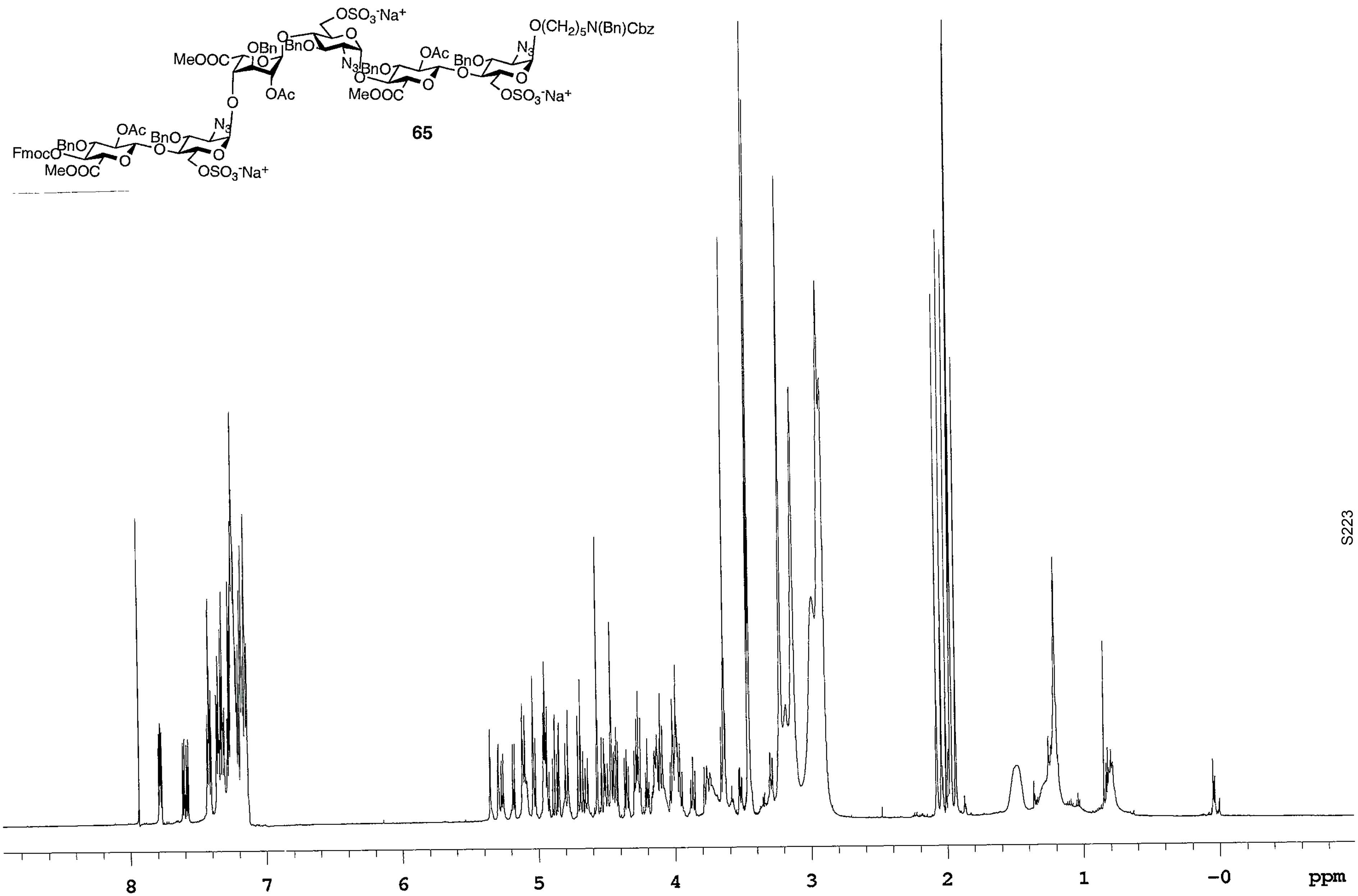
63


220
200
180
160
140
120
100
80
60
40
20
0
ppm



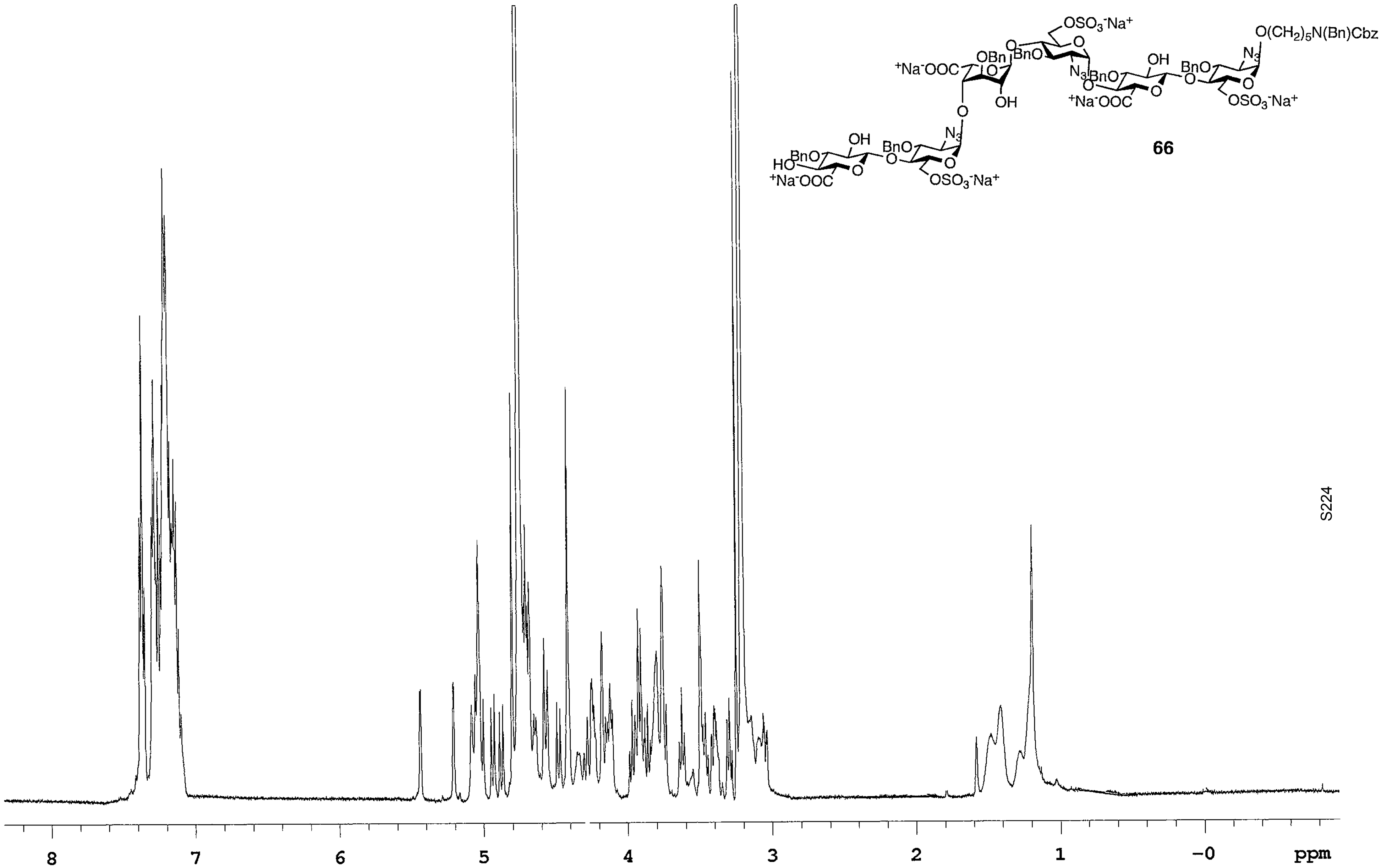
64

FmocO
BnO
MeOOC
OAc
BnO
OH
N3
O
MeOOC
OBn
OAc
BnO
OH
N3
BnO
MeOOC
OAc
BnO
OH
N3
O(CH2)5N(Bn)Cbz
8
7
6
5
4
3
2
1
-0
ppm

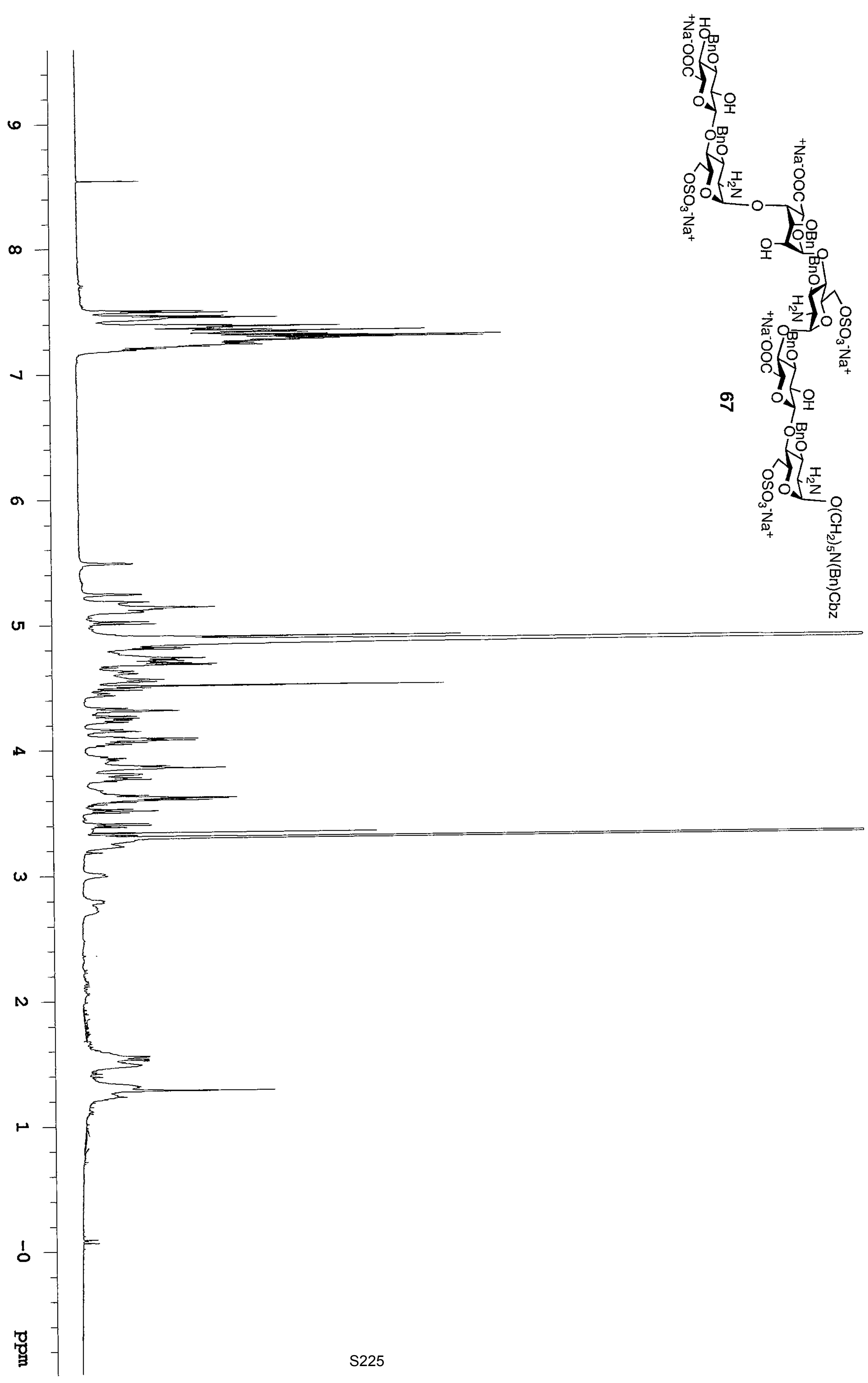


OSO3-Na+
O(CH2)5N(Bn)Cbz
MeOOC
OBn
BnO
N3
OAc
BnO
MeOOC
OSO3-Na+
FmocO
BnO
OAc
N3
8
7
6
5
4
3
2
1
-0
ppm

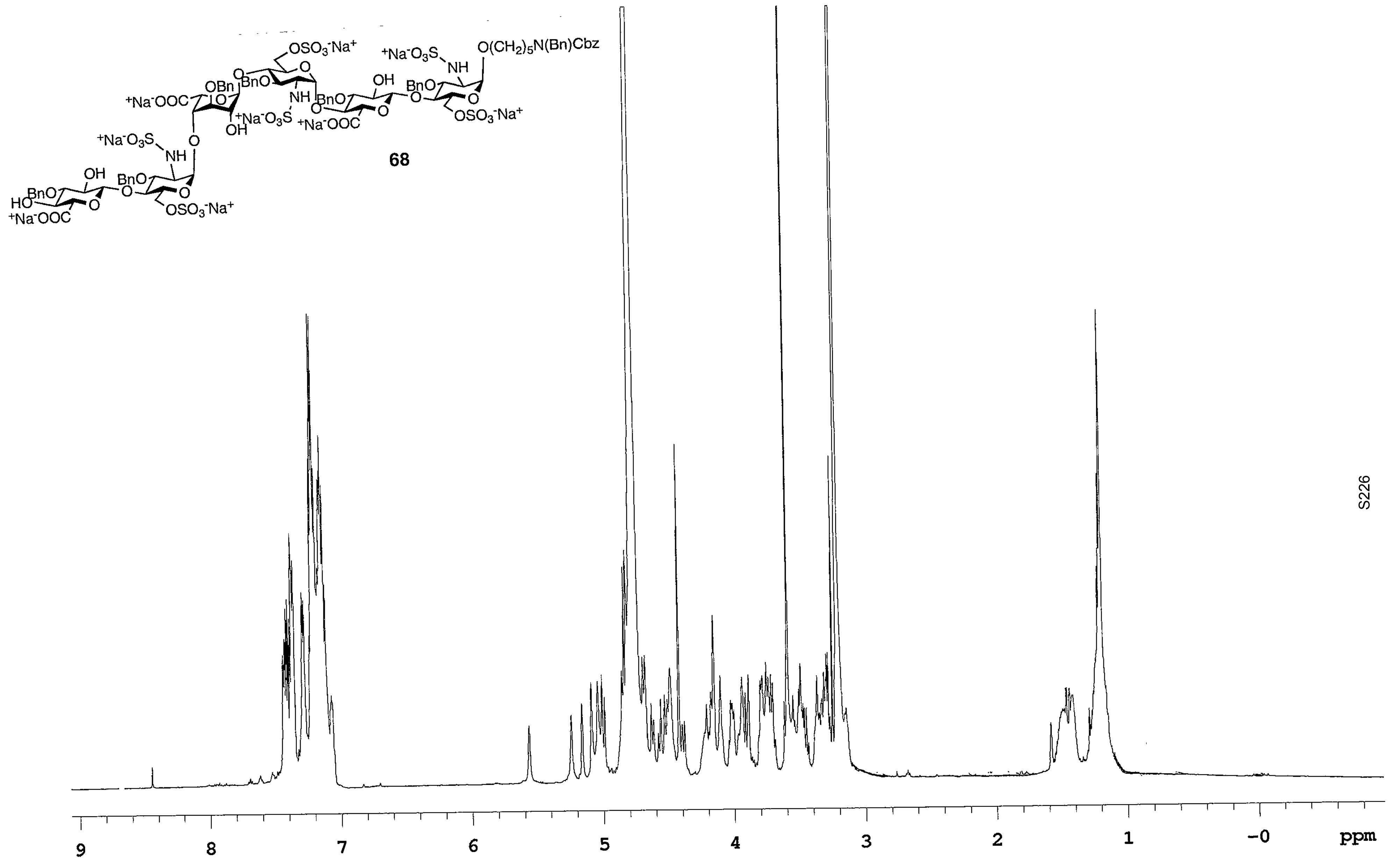
65



66

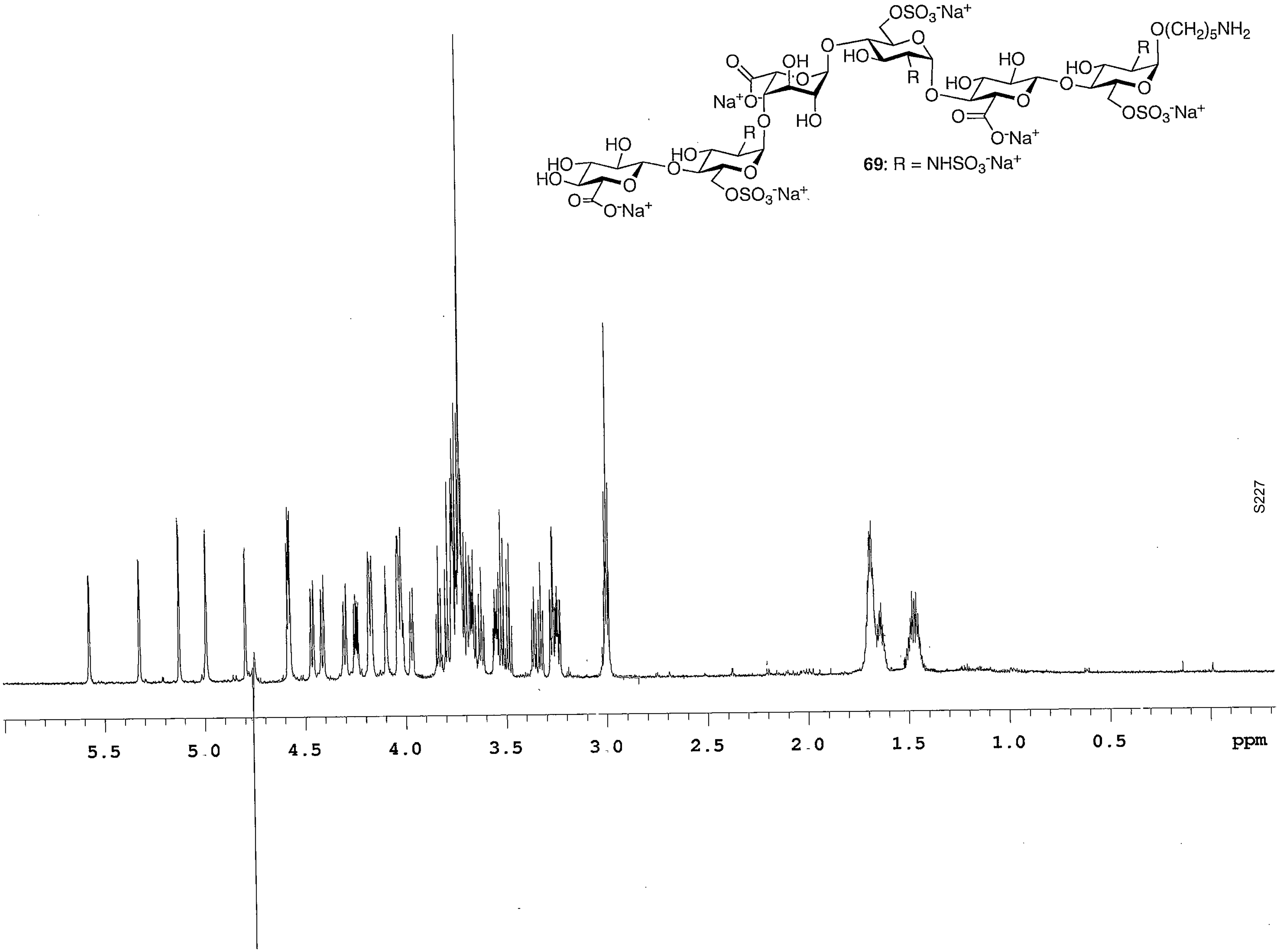

⁺Na⁻OOC
HO
BnO
OH
O
BnO
H₂N
OSO₃⁻Na⁺
OBn
OH
OSO₃⁻Na⁺
H₂N
O(CH₂)₅N(Bn)Cbz
9
8
7
6
5
4
3
2
1
−0
ppm

67



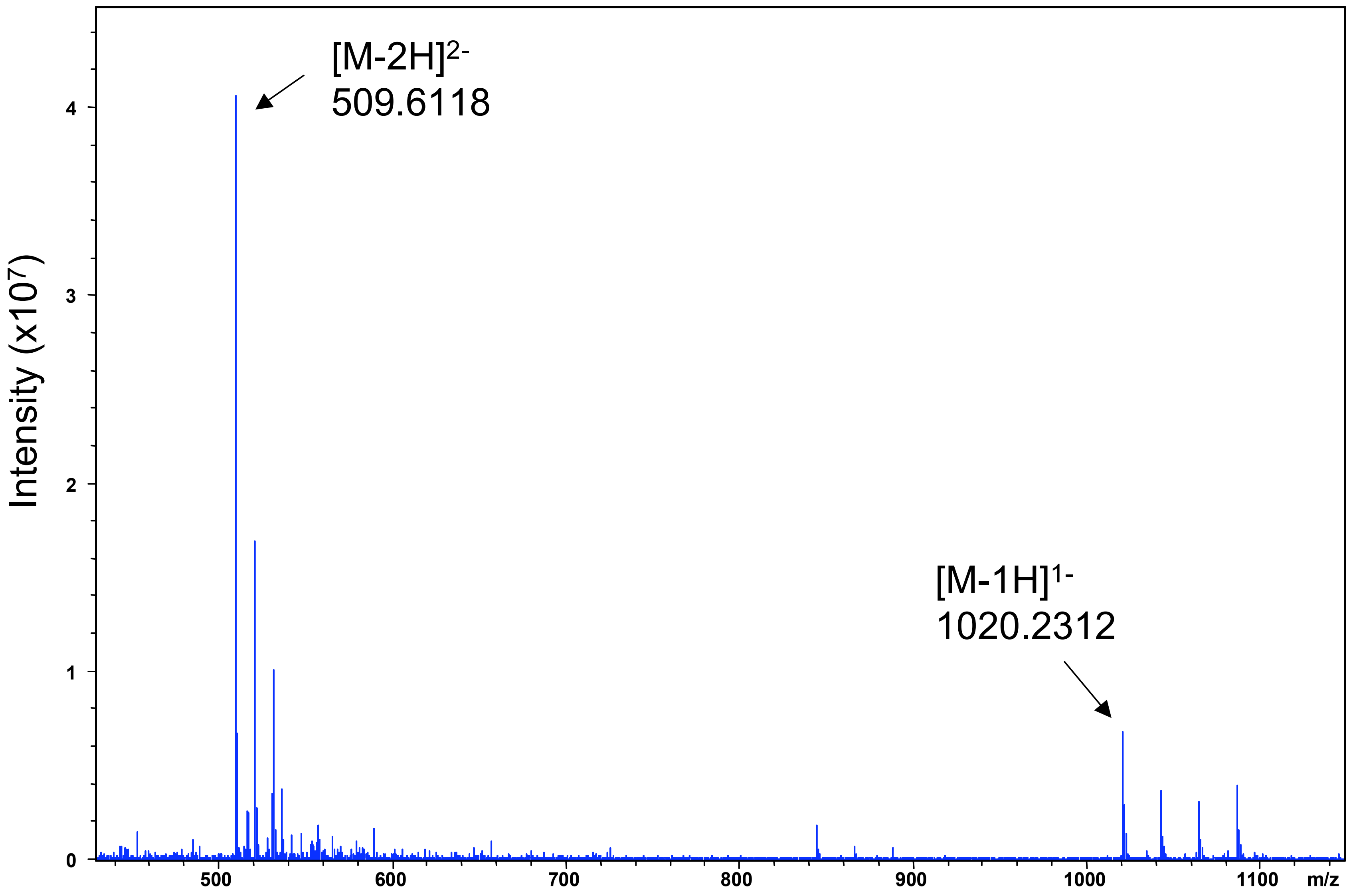
+Na-O3S
NH
O(CH2)5N(Bn)Cbz
OSO3-Na+
OBn
BnO
+Na-OOC
OH
NH
BnO
HO
OH
9
8
7
6
5
4
3
2
1
-0
ppm

68

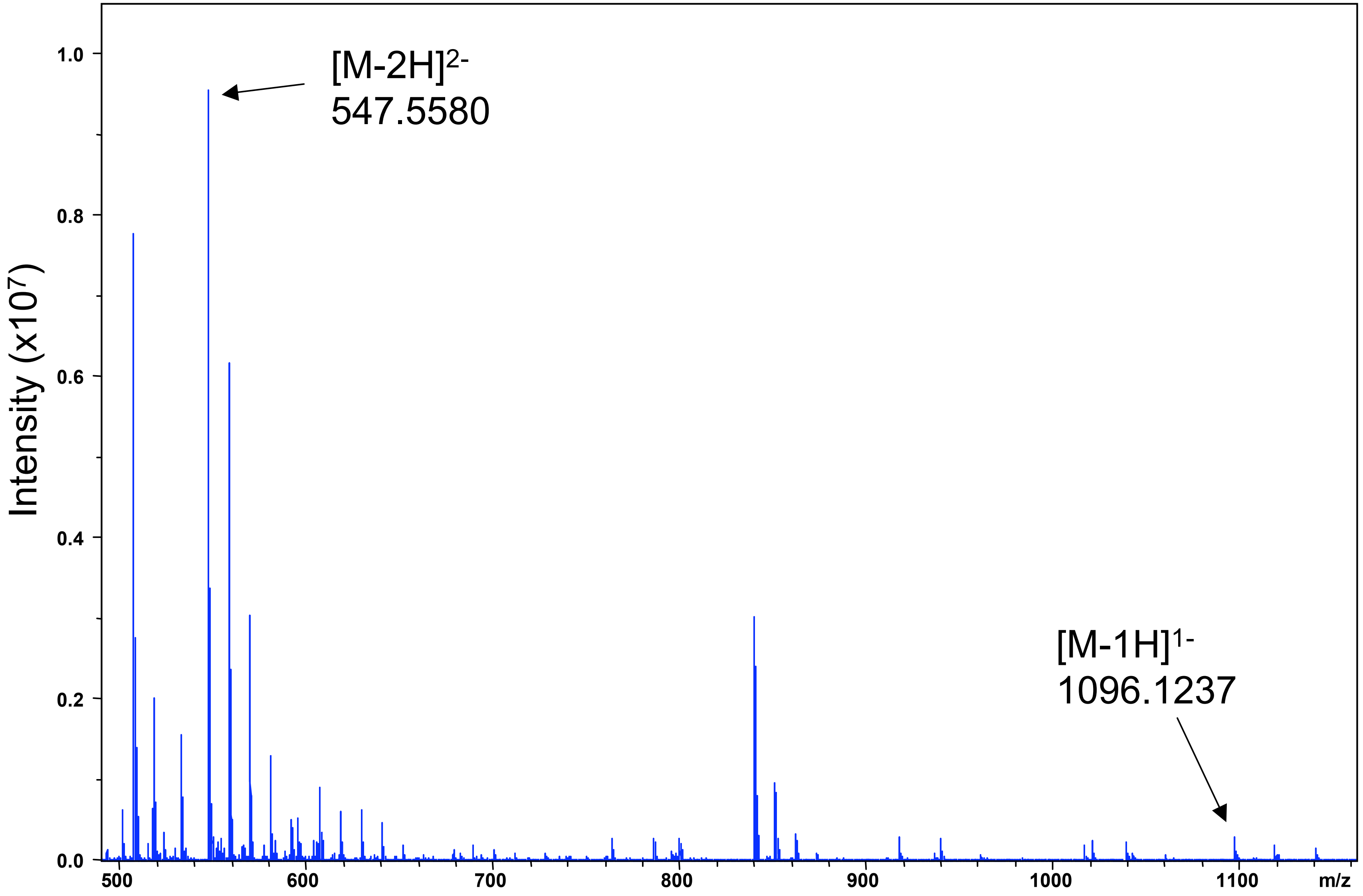


69: R = $NHSO_3^-Na^+$

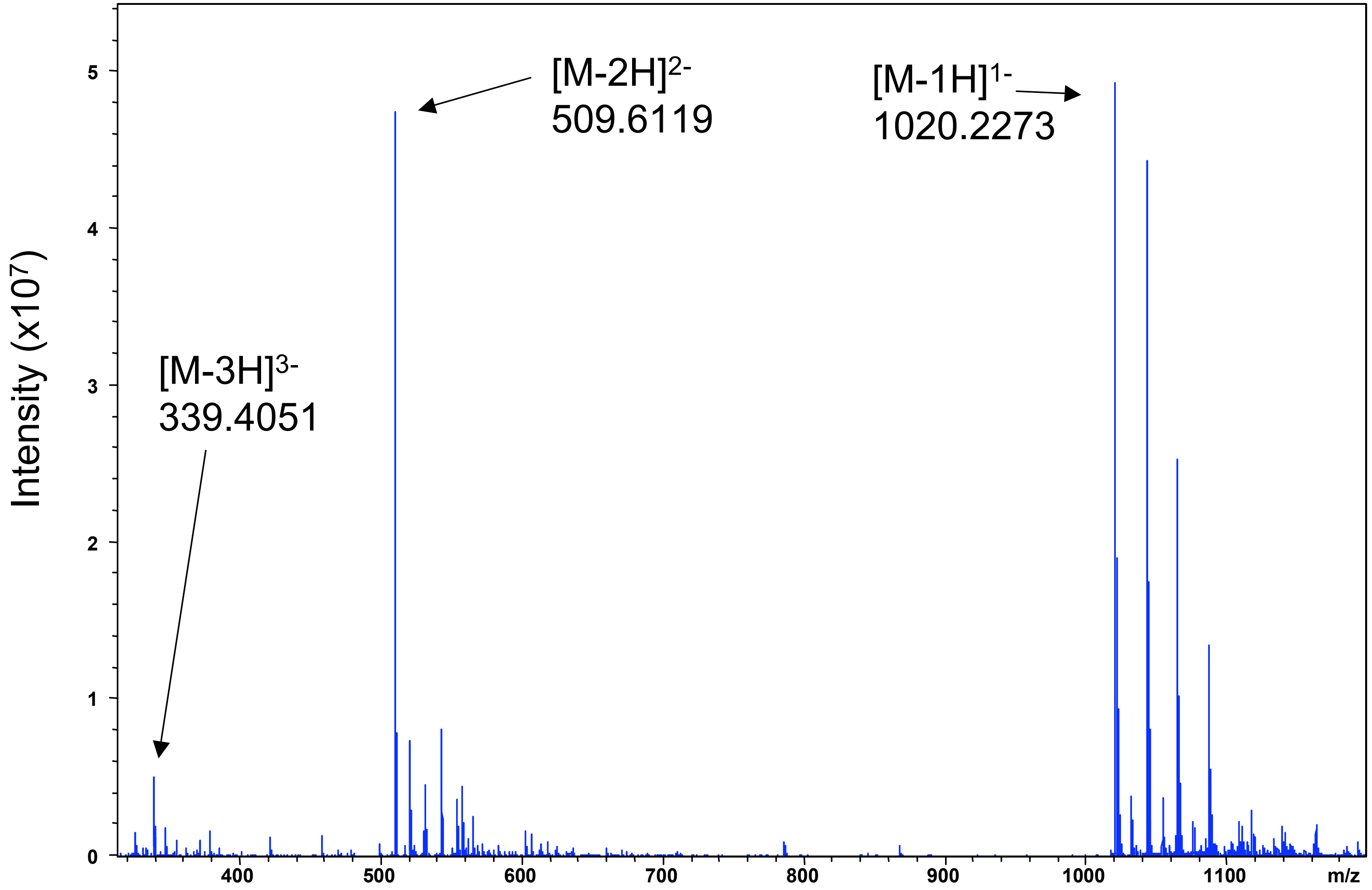
76


[M-2H]$^{2-}$
509.6118
[M-1H]$^{1-}$
1020.2312
Intensity (x10^7)
0
1
2
3
4
500
600
700
800
900
1000
1100
m/z

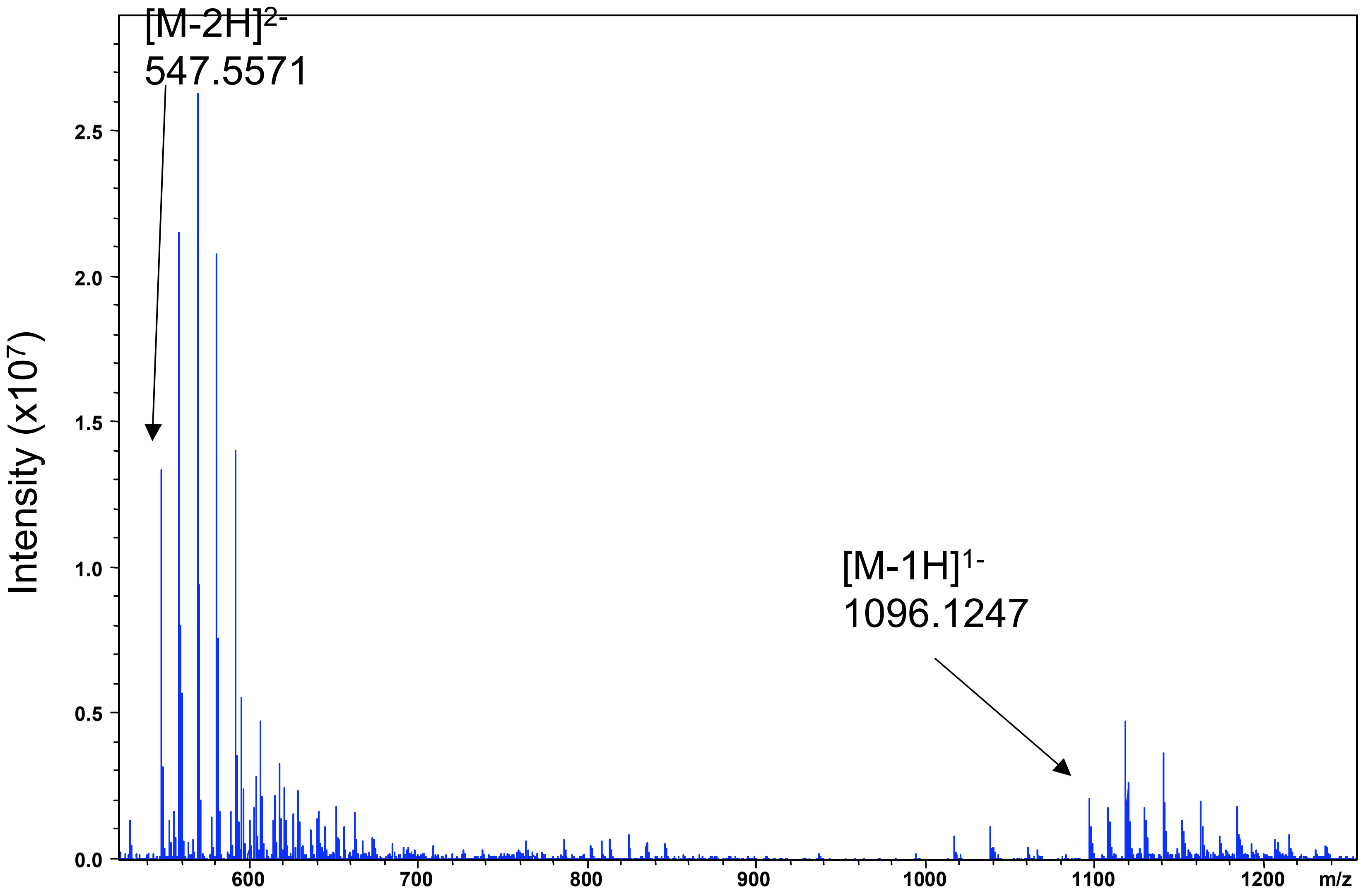
77


[M-2H]$^{2-}$
547.5580
[M-1H]$^{1-}$
1096.1237
Intensity (x10^{7})
0.0
0.2
0.4
0.6
0.8
1.0
500
600
700
800
900
1000
1100
m/z

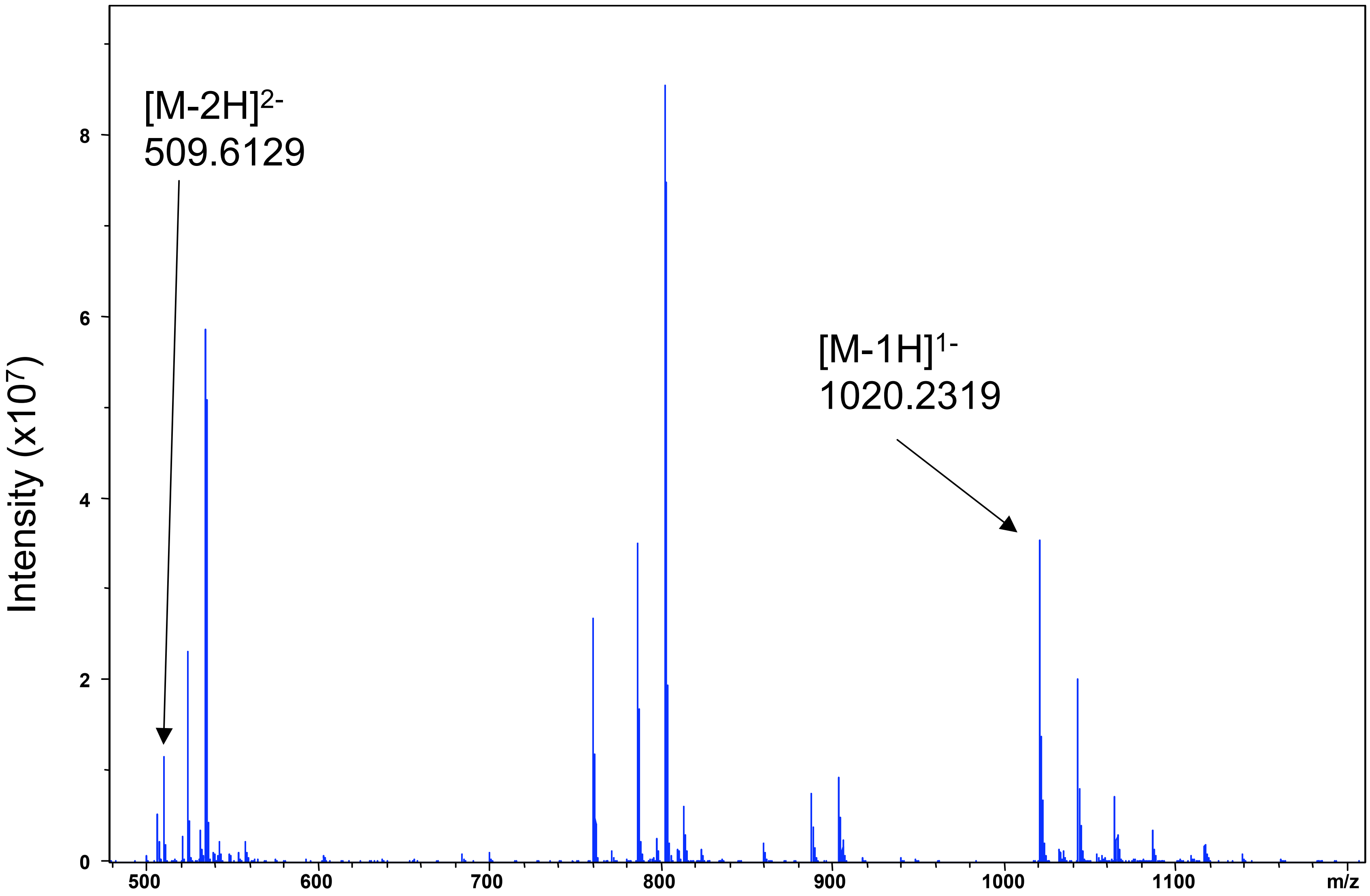
78


[M-3H]$^{3-}$
339.4051
[M-2H]$^{2-}$
509.6119
[M-1H]$^{1-}$
1020.2273
Intensity (x10^7)
0
1
2
3
4
5
400
500
600
700
800
900
1000
1100
m/z

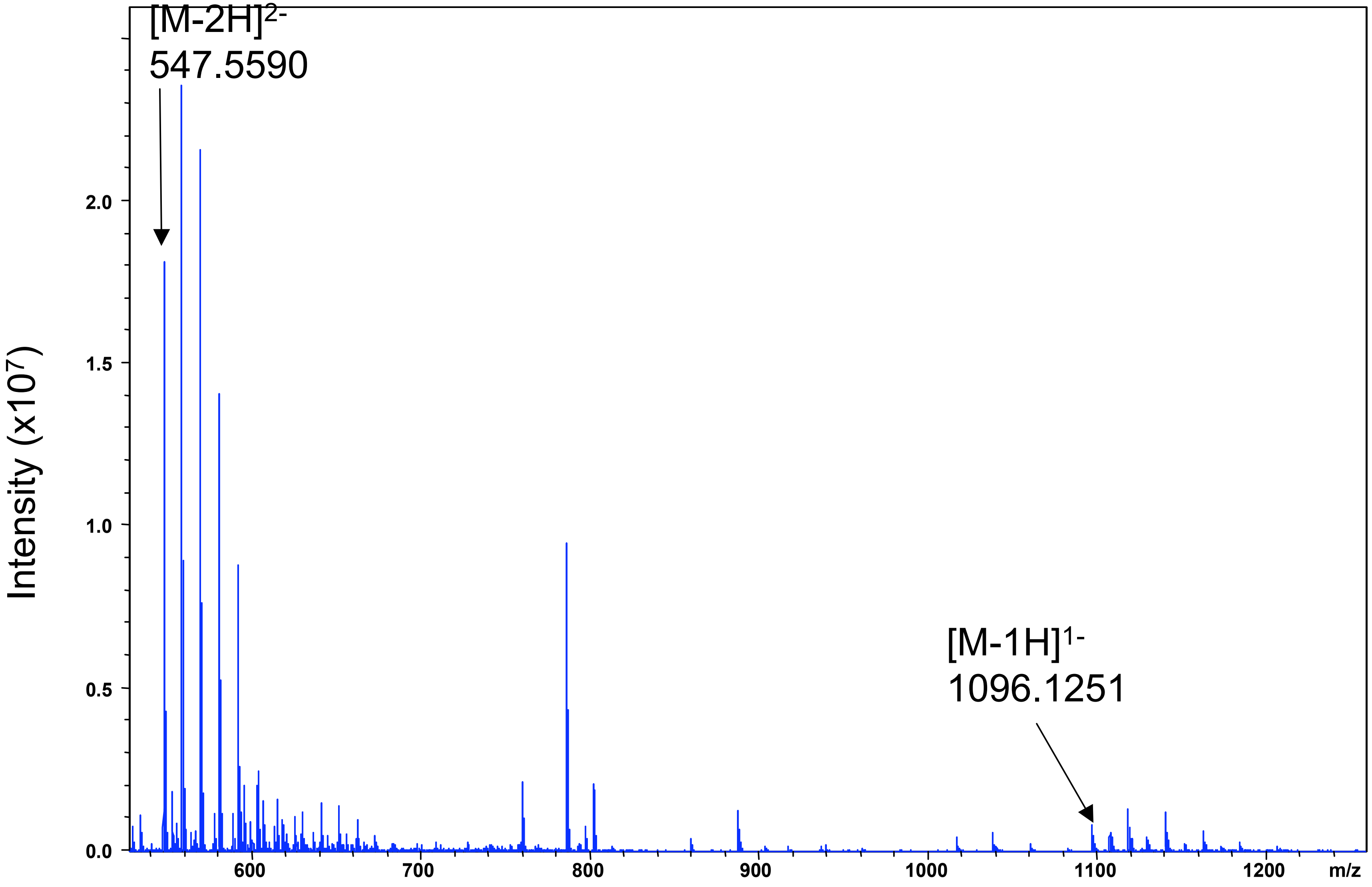
79


[M-2H]$^{2-}$
547.5571
[M-1H]$^{1-}$
1096.1247
Intensity (x10^{7})
0.0
0.5
1.0
1.5
2.0
2.5
600
700
800
900
1000
1100
1200
m/z

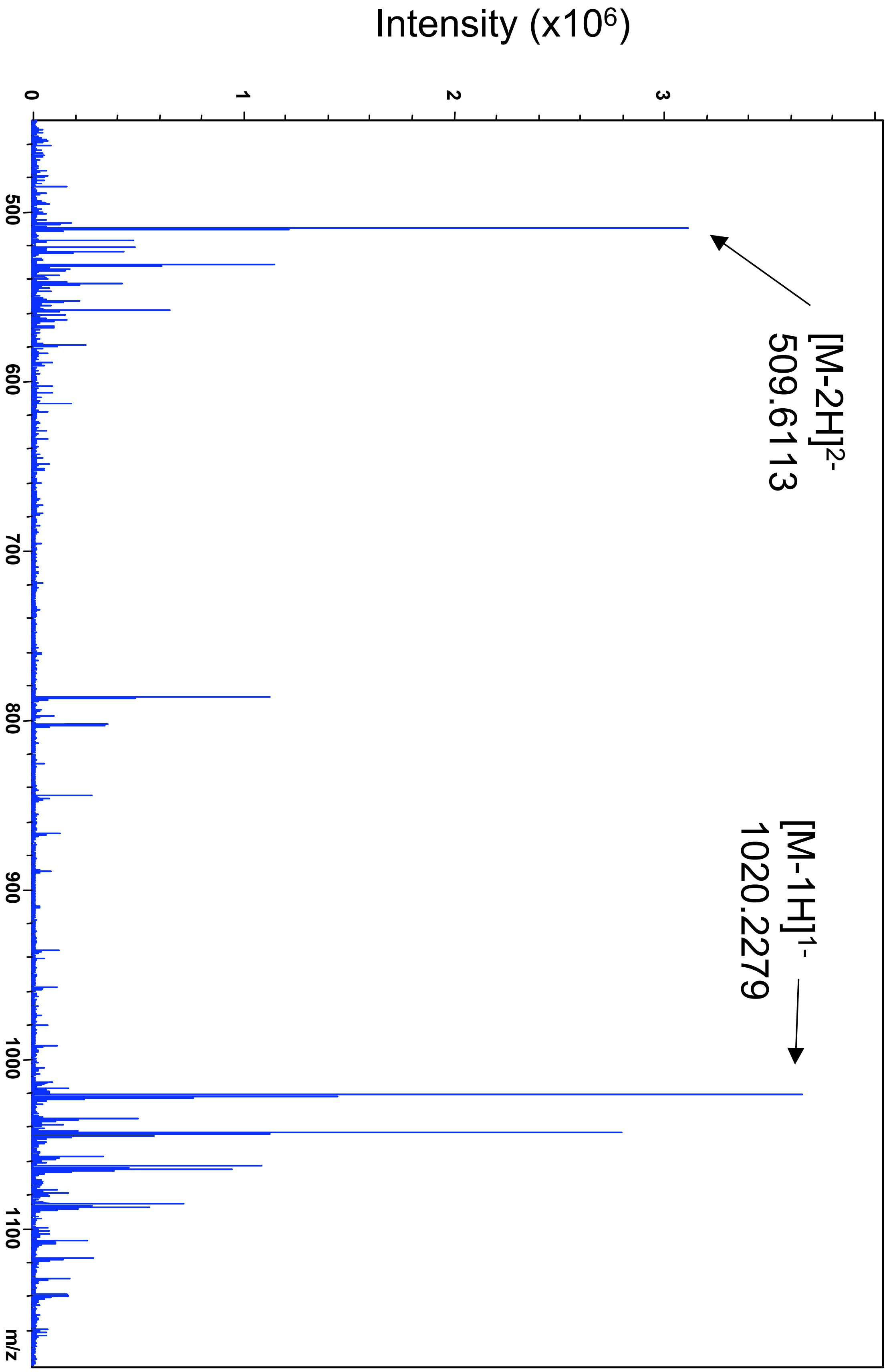
80


[M-2H]$^{2-}$
509.6129
[M-1H]$^{1-}$
1020.2319
Intensity (x10^7)
0
2
4
6
8
500
600
700
800
900
1000
1100
m/z

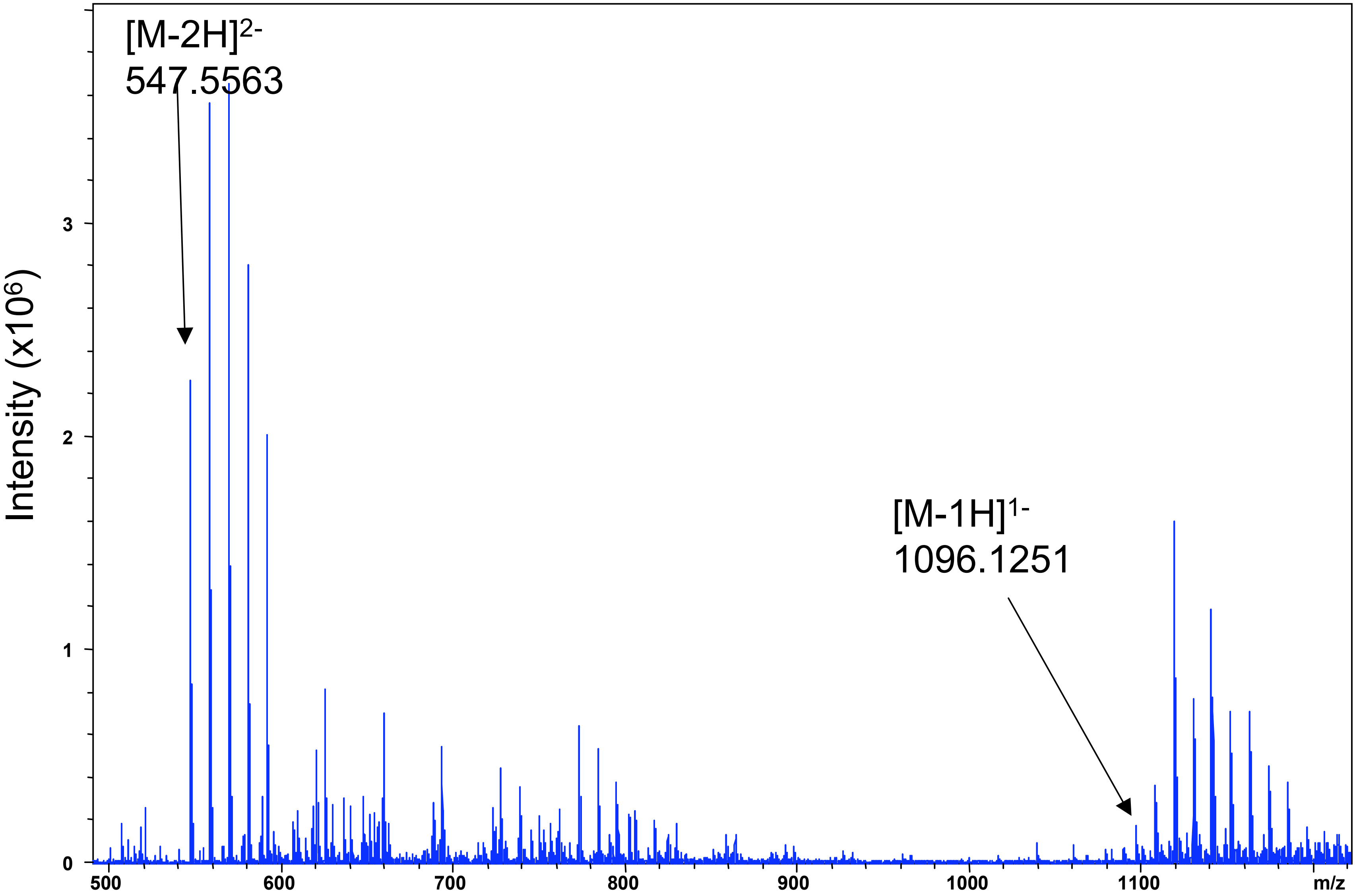
81


[M-2H]$^{2-}$
547.5590
[M-1H]$^{1-}$
1096.1251
Intensity (x10^{7})
0.0
0.5
1.0
1.5
2.0
600
700
800
900
1000
1100
1200
m/z

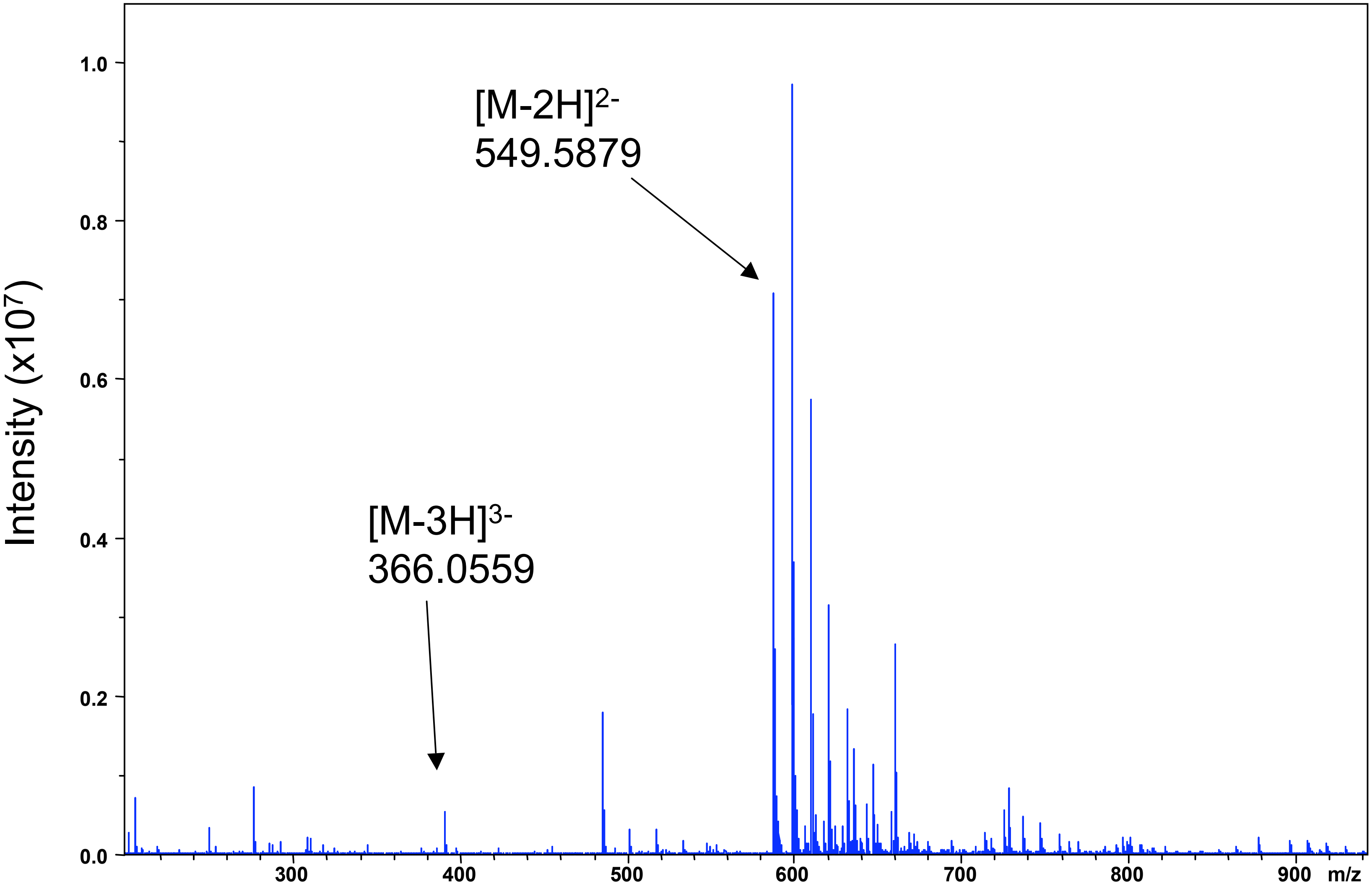
82


Intensity (x10^6)
0
1
2
3
500
600
700
800
900
1000
1100
m/z
[M-2H]$^{2-}$
509.6113
[M-1H]$^{1-}$
1020.2279

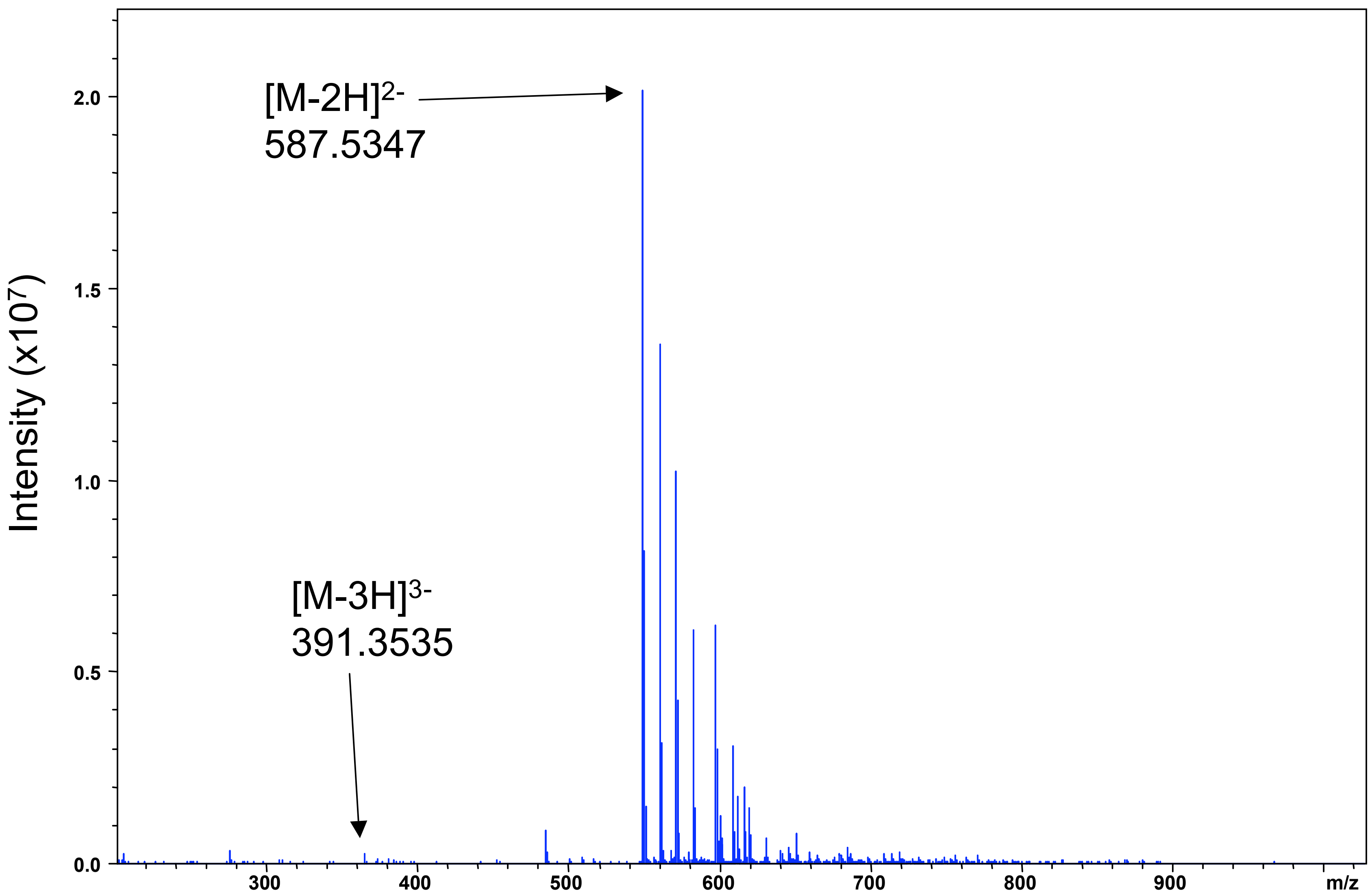
83


[M-2H]$^{2-}$
547.5563
[M-1H]$^{1-}$
1096.1251
Intensity (x10^6)
0
1
2
3
500
600
700
800
900
1000
1100
m/z

85

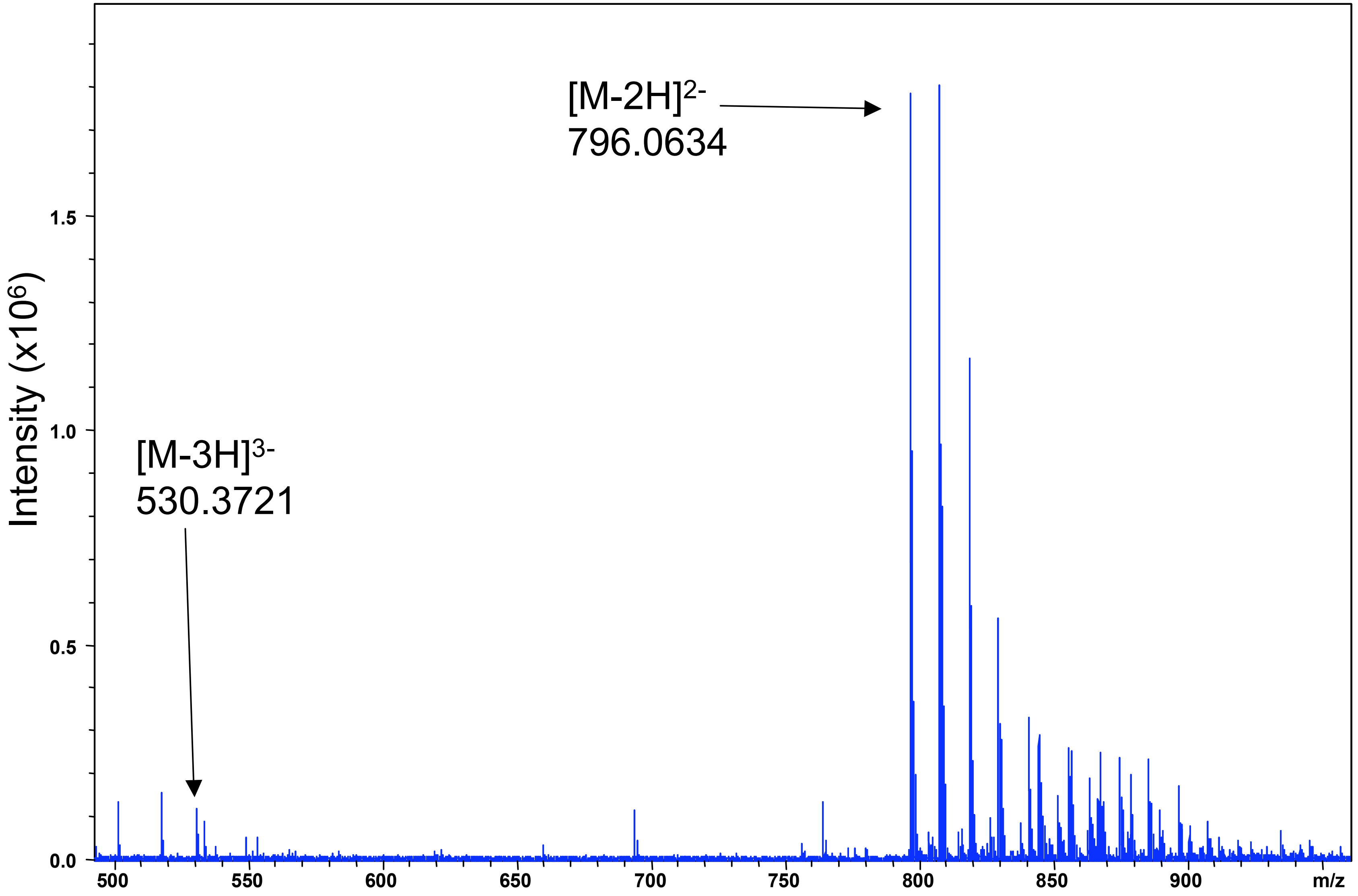

[M-2H]$^{2-}$
549.5879
[M-3H]$^{3-}$
366.0559
Intensity (x10^{7})
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900
m/z

86



Intensity (x10^7)
0.0
0.5
1.0
1.5
2.0
300
400
500
600
700
800
900
m/z
[M-2H]$^{2-}$
587.5347
[M-3H]$^{3-}$
391.3535

69


[M-2H]$^{2-}$
796.0634
[M-3H]$^{3-}$
530.3721
Intensity (x10^{6})
0.0
0.5
1.0
1.5
500
550
600
650
700
750
800
850
900
m/z