Solving the Convergence Problem in the Synthesis of Triantennary *N*-Glycan Relevant to Prostate-Specific Membrane Antigen (PSMA)

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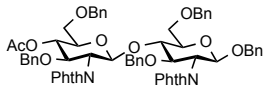
Experimental Section

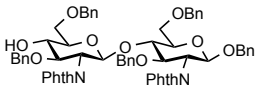
General Procedures: All reactions were carried out under dry Ar in an oven-dried glassware. CH_2Cl_2 was freshly distilled over CaH_2 and THF was filtered through a column of activated alumina prior to use. Anhydrous methanol was purchased from Aldrich. NIS was recrystallized from 1,4-dioxane/CCl_4 and was kept in dark. Ammonia was condensed (-78 ^oC) into a flask, dried with Na and then distilled into the reaction flask. All other reagents were used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 500/600 MHz instruments and are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. The residual solvent reference peaks were used from published literature.[1] IR measurements were performed on Jasco ATR FT/IR-6100 instrument and optical rotations were measured on JASCO P-2000 and are reported as average of five data points. TLC analyses were performed on Merck TLC plates and visualizations were performed with UV light and/or Hanessian stain and/or sulfuric acid stain (5% H_2SO_4 in MeOH). Preparative purifications were performed using Silcacycle silica using HPLC grade solvents.



4

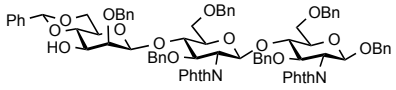
Benzyl 4-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (4). A mixture of **2** (12.1 g, 21.0 mmol) and **3** (14.7 g, 25.2 mmol) was azeotropically dried with PhMe (3x) and then on high vacuum for 1 h. This mixture was dissolved in anh. CH_2Cl_2 (210 mL), freshly activated 4Å MS (20 g) were added and the mixture was stirred at rt for 1 h, cooled to -50 ^oC, NIS (4.96 g, 22.0 mmol) was added followed by AgOTf (2.70 g, 10.5 mmol). The reaction mixture was allowed to warm up to -20 ^oC, stirred at this temp. for 14 h, quenched with Et_3N, filtered through pad of Celite, washed with sat. $Na_2S_2O_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 2:1) afforded **4** (23.0 g, >99%) as a clear oil: $[\alpha]_D^{24}$ +17.4 (c 1.0, $CHCl_3$); IR (ATR) 3032, 2880, 1775, 1709, 1387 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.89 (br s, 1 H), 7.80-7.67 (br m, 6 H), 7.53-7.51 (br m, 1 H), 7.39-7.33 (m, 8 H), 7.31-7.27 (m, 1 H), 7.21-7.17 (m, 1 H), 7.08-7.06 (m, 1 H), 7.03-6.92 (m, 11 H), 6.86-6.84 (m, 3 H), 5.37 (d, *J* = 8.3 Hz, 1 H), 5.18 (t, *J* = 9.2 Hz, 1 H), 4.98 (d, *J* = 7.9 Hz, 1 H), 4.85 (d, *J* = 12.5 Hz, 1 H), 4.71 (d, *J* = 12.4 Hz, 1 H), 4.63 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 11.7 Hz, 1 H), 4.54 (d, *J* = 10.9 Hz, 1 H), 4.52-4.57 (m, 4 H), 4.39 (d, *J* = 12.4 Hz, 1 H), 4.35 (d, *J* = 12.1 Hz, 1 H), 4.31 (dd, *J* = 10.7, 8.4 Hz, 1 H), 4.28-4.15 (m, 3 H), 3.61-3.55 (m, 3 H), 3.49 (dd, *J* = 10.9, 5.9 Hz, 1 H), 3.45 (dd, *J* = 10.3, 3.9 Hz, 1 H),

3.34 (dd, *J* = 9.3, 2.6 Hz, 1 H), 1.95 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 167.6, 138.6, 138.4, 138.2, 137.8, 137.2, 134.3, 134.1, 133.5, 131.7, 128.4 (4), 128.3, 128.1, (2), 127.9, 127.8, 127.7, 127.6, 127.5, 127.4 (2), 127.3, 126.9, 123.2, 87.1, 76.9, 76.6, 76.2, 74.5, 74.4, 73.9, 73.6, 73.4, 72.7 (2), 70.5, 69.4, 68.1, 56.3, 55.7, 20.9; HRMS (ESI) calc for $C_{65}H_{60}N_2O_{14}Na$ (M+Na) 1115.3942, found 1115.3954.



5

Benzyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (5). A solution of **4** (23.0 g, 21.0 mmol) in anh. THF (100 mL) and MeOH (100 mL) was treated with a solution of NaOMe (42.0 mL, 42 mmol, 0.5 M in MeOH) and stirred at rt for 1 h. This mixture was quenched with DOWEX-50WX8, filtered, and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 2:1 to 1:1) afforded **5** (20.1 g, 91%) as a clear oil: $[\alpha]_D^{24}$ -8.52 (c 1.0, $CHCl_3$), IR (ATR) 3474. 2874, 1775, 1710, 1387, 1070 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 6.8 Hz, 1 H), 7.77 (app. t, *J* = 5.0 Hz, 2 H), 7.73 (br s, 2 H), 7.67 (br s, 2 H), 7.41-7.33 (m, 10 H), 7.08-7.06 (m, 4 H), 7.02-6.99 (m, 6 H), 6.98-6.96 (m, 3 H), 6.86-6.83 (m, 3 H), 5.34 (d, *J* = 8.34 Hz, 1 H), 4.98 (d, *J* = 8.4 Hz, 1 H), 4.81 (t, *J* = 11.8 Hz, 2 H), 4.72 (d, *J* = 12.4 Hz, 1 H), 4.57-4.54 (m, 2 H), 4.53 (br s, 3 H), 4.51-4.47 (m, 1 H), 4.39 (d, *J* = 12.4 Hz, 1 H), 4.28 (dd, *J* = 10.8, 8.4 Hz, 1 H), 4.22-4.13 (m, 4 H), 3.84 (t, *J* = 8.4 Hz, 1 H), 3.73 (dd, *J* = 9.9, 4.3 Hz, 1 H), 3.59-3.56 (m, 2 H), 3.47 (dd, *J* = 10.9, 3.8 Hz, 1 H), 3.43-3.39 (m, 1 H), 3.33 (dd, *J* = 9.7, 2.5 Hz, 1 H), 3.11 (d, *J* = 1.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 167.6, 138.6, 138.4, 138.3, 137.5, 137.2, 134.0, 133.8, 133.5, 131.7, 131.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9 (2), 127.7 (2), 127.5, 127.4, 127.3, 126.6, 123.6, 123.1, 97.1, 96.9, 78.3, 76.5, 75.5, 74.5, 74.3, 74.1, 73.7, 72.7 (2), 71.0, 70.5, 68.2, 65.1, 55.7; HRMS (ESI) calc for $C_{63}H_{58}N_2O_{13}Na$ (M+Na) 1073.3837, found 1073.3833.

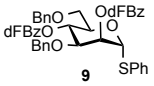


8

Benzyl 2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (8). A solution of mannose sulfoxide **6** (5.28 g, 8.94 mmol) and DTBMP (7.46 g, 29.9 mmol) was azeotropically dried with PhMe (3 x 10 mL) and then on high vacuum for 2 h. Freshly activated 4Å MS (10 g) were added and the mixture was dissolved in anh. CH_2Cl_2 (59.0 mL). After 1 h at rt, this mixture was cooled to -78 ^{o}C, Tf_2O (1.51 mL, 8.99 mmol) was added, the mixture was allowed to

warm up to -60 °C over 25 min, cooled to -78 °C and a cold (-78 °C) solution of acceptor **5** (6.30 g, 5.99 mmol) in CH_2Cl_2 (59.0 mL) was introduced *via* cannula. The mixture was stirred at -78 °C for 12 h, quenched with Et_3N, filtered through a pad of Celite, washed with EtOAc, and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1 to 2:1 and PhMe:EtOAc, 4:1) afforded trisaccharide (8.0 g, 89%) as a white foam: MS (ESI) *m/z* calc for $C_{91}H_{86}N_2O_{19}Na$ (M+Na) 1533.57, found 1534.57.

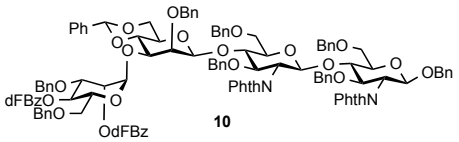
A mixture of trisaccharide (13.0 g) was dissolved in CH_2Cl_2 (194 mL), cooled to 0 °C, pH 7 phosphate buffer (10 mL) was added, and the mixture treated with DDQ (2.37 g, 10.4 mmol). After 4 h, additional portion of DDQ (1.58 g, 6.96 mmol) was added, the mixture was stirred for 1 h, quenched with sat. $NaHCO_3$, extracted with EtOAc and the combined organic layers were washed with water, brine, dried (MgSO4), and concentrated. Purification by chrom. on SiO_2 (PhMe:EtOAc, 3:1) afforded **8** (5.57 g, 56%) as a clear oil: $[\alpha]_D^{24}$ -3.70 (c 1.0, $CHCl_3$); IR (ATR) 3398, 2871, 1713, 1453, 1387 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.4 Hz, 1 H), 7.66-7.56 (m, 7 H), 7.37-7.36 (m, 2 H), 7.32-7.16 (m, 18 H), 6.98-6.95 (m, 1 H), 6.92-6.85 (m, 8 H), 6.81-6.80 (m, 3 H), 6.69-6.68 (m, 3 H), 5.34 (s, 1 H), 5.21 (d, *J* = 7.8 Hz, 1 H), 4.93 (d, *J* = 11.6 Hz, 1 H), 4.88 (d, *J* = 8.3 Hz, 1 H), 4.82 (d, *J* = 12.2 Hz, 1 H), 4.76 (d, *J* = 12.8 Hz, 1 H), 4.63-4.58 (m, 3 H), 4.52 (d, *J* = 12.1 Hz, 1 H), 4.47-4.42 (m, 3 H), 4.38 (d, *J* = 12.1 Hz, 1 H), 4.31 (d, *J* = 11.9 Hz, 2 H), 4.19-4.12 (m, 4 H), 4.07-4.01 (m, 3 H), 3.64-3.56 (m, 3 H), 3.51-3.47 (m, 2 H), 3.42-3.56 (m, 3 H), 3.25-3.23 (m, 1 H), 3.12 (d, *J* = 9.9 Hz, 1 H), 3.04 (dt, *J* = 9.6, 4.8 Hz, 1 H), 2.24 (d, *J* = 8.6 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 167.6, 138.8, 1386, 138.5, 138.2, 137.7, 137.2 (2), 134.0, 133.8, 133.4, 131.7, 131.4, 129.0, 128.6, 128.5, 128.2 (2), 128.0 (3), 127.9 (3), 127.8 (2), 127.5 (2), 127.4, 127.3, 126.9, 126.8, 126.3, 123.6, 123.1, 101.9, 97.1, 97.0, 79.4, 79.1, 79.0, 77.1, 76.5, 75.8, 75.7, 74.6 (2), 74.5, 74.3, 73.4, 72.6, 70.9, 70.5, 68.4, 68.2, 67.8, 66.8, 56.5, 55.7; HRMS (ESI) calc for $C_{83}H_{78}N_2O_{18}Na$ (M+Na) 1413.5147, found 1413.5082.



9

Thiophenyl 3,6-di-*O*-benzyl-2,4-di-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranoside (9). A solution of thiophenyl 3,6-di-*O*-benzyl-α-D-mannopyranoside[2] (3.20 g, 7.08 mmol) in anh. pyridine (25.0 mL) was treated with 2,5-diflurorobenzoyl chloride (2.64 mL, 21.2 mmol) and stirred at rt for 12 h. The reaction mixture was quenched with sat. $NaHCO_3$, extracted with EtOAc and the combined organic layers were washed with water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **9** (4.21 g, 81%) as a clear oil: $[\alpha]_D^{20}$ +28.1 (c 1.0, $CHCl_3$), IR (ATR) 3076, 2872, 1739, 1723, 1428, 1185 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (ddd, *J* = 8.4, 5.3, 3.3 Hz, 1 H), 7.47-7.44 (m, 2 H), 7.36 (ddd, *J* = 13.0, 5.8, 3.4 Hz, 1 H), 7.20-7.06 (m, 15 H), 7.01 (td, *J* = 9.3, 4.2

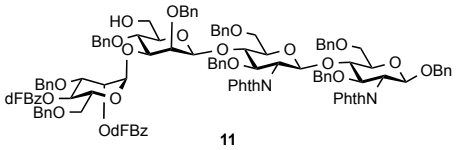
Hz, 2 H), 5.79 (dd, *J* = 2.0, 2.6 Hz, 1 H), 5.68 (t, *J* = 9.9 Hz, 1 H), 5.58 (d, *J* = 1.5 Hz, 1 H), 4.62 (d, *J* = 12.3 Hz, 1 H), 4.52 (ddd, *J* = 8.9, 5.1, 3.5 Hz, 1 H), 4.47 (d, *J* = 11.7 Hz, 1 H), 4.42 (d, *J* = 12.3 Hz, 1 H), 4.39 (d, *J* = 11.8 Hz, 1 H), 3.96 (dd, *J* = 9.6, 3.0 Hz, 1 H), 3.64 (qd, *J* = 10.9, 5.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 162.0, 159.3 (2), 158.9 (3), 158.8, 157.3, 156.9 (2), 137.8, 137.0, 132.9, 132.0 (2), 131.9, 131.3, 129.7, 129.4, 129.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.4, 121.9, 121.8, 121.6, 121.5, 121.4, 121.3, 121.2, 119.3 (3), 119.2, 119.0, 118.9 (2), 118.8, 118.7, 118.6, 118.5, 118.4 (2), 118.3, 118.2 (3), 118.1, 86.0, 74.8, 73.5, 71.5, 71.0, 70.9, 69.3, 69.1; HRMS (ESI) calc for $C_{40}H_{32}O_7SF_4Na$ (M+Na) 755.1703, found 755.1720.



10

Benzyl [3,6-di-*O*-benzyl-2,4-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranosyl-(1→3)]-2-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (10). A mixture of **8** (1.59 g, 1.09 mmol) and **9** (1.59 g, 2.17 mmol) was azeotropically dried with PhMe (3 x 10 mL) and under high vacuum for 2 h. This mixture was dissolved in anh. CH_2Cl_2 (21.7 mL), freshly activated 3Å MS (1.0 g) were added and after 1 h at rt, this mixture was cooled to -50 ^{o}C, NIS (0.488 g, 2.17 mmol) was added followed by AgOTf (0.139 g, 0.54 mmol). The mixture was allowed to warm up to -20 ^{o}C, stirred at this temp. for 12 h, quenched with Et_3N, filtered through a pad of Celite and the organic layer was washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (PhMe:EtOAc, 3:1) afforded **10** (1.97 g, 90%) as a clear oil: $[\alpha]_D^{24}$ -69.9 (c 1.0, $CHCl_3$); IR (ATR) 3033, 2873, 1773, 1718, 1496, 1386, 1082 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 7.73-7.70 (m, 5 H), 7.65 (br s, 1 H), 7.21-7.49 (m, 2 H), 7.44 (d, *J* = 7.3 Hz, 3 H), 7.39-7.38 (m, 10 H), 7.24-7.16 (m, 7 H), 7.14-7.05 (m, 7 H), 7.00 (dd, *J* = 7.6, 2.5 Hz, 2 H), 6.94-6.86 (m, 8 H), 6.85-6.83 (m, 3 H), 6.80-6.78 (m, 1 H), 6.75-6.68 (m, 3 H), 6.49-6.45 (m, 1 H), 6.40-6.36 (m, 2 H), 6.32 (dt, *J* = 9.3, 4.3 Hz, 1 H), 6.24 (t, *J* = 2.2 Hz, 1 H), 6.16 (t, *J* = 10.0 Hz, 1 H), 5.73 (d, *J* = 8.0 Hz, 1 H), 5.71 (d, *J* = 1.5 Hz, 1 H), 5.33 (d, *J* = 12.2 Hz, 1 H), 5.30 (s, 1 H), 5.23 (d, *J* = 8.5 Hz, 1 H), 5.16 (d, *J* = 11.5 Hz, 1 H), 5.11 (d, *J* = 11.8 Hz, 1 H), 4.84 (d, *J* = 12.9 Hz, 1 H), 4.81-4.73 (m, 5 H), 4.67-4.64 (m, 2 H), 4.63-4.52 (m, 5 H), 4.53-4.546 (m, 4 H), 4.44-4.36 (m, 5 H), 4.34-4.26 (m, 3 H), 4.14 (d, *J* = 3.2 Hz, 1 H), 4.03 (dd, *J* = 10.3, 4.7 Hz, 1 H), 3.93 (dd, *J* = 10.1, 2.8 Hz, 1 H), 3.83 (d, *J* = 4.4 Hz, 2 H), 3.64-3.58 (m, 2 H), 3.45 (d, *J* = 11.3, 2.7 Hz, 1 H), 3.38 (d, *J* = 9.8 Hz, 1 H), 3.27 (d, *J* = 10.2 Hz, 1 H), 3.11 (dt, *J* = 9.5, 4.8 Hz, 1 H), 2.93 (dd, *J* = 9.8, 8.3 Hz, 1 H); ^{13}C NMR (150 MHz, C_6D_6) δ 162.5, 159.0, 157.4, 157.3, 139.8, 139.5, 139.3 139.2,

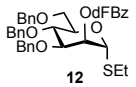
138.5, 138.4, 138.2, 138.1 (2), 133.2, 132.3, 129.0, 128.9 (2), 128.8, 128.7 (2), 128.6 (2), 128.5, 128.4 (2), 128.3 (2), 128.1, 128.0, 127.8 (2), 127.7 (2), 127.6 (2), 127.5, 127.2, 127.1, 126.6, 123.1, 118.6 (2), 118.5, 118.4 (2), 118.3 (2), 101.8, 101.4, 99.6, 97.9, 97.8, 79.4, 79.1, 78.5, 77.9, 77.7, 77.1, 76.5, 76.2, 75.7, 75.3, 75.9, 74.8, 73.7, 73.4 73.2, 71.6, 70.6, 70.5, 70.4, 69.8, 68.6, 68.5, 67.7, 67.5, 57.3, 56.6; HRMS (ESI) calc for $C_{117}H_{104}N_2O_{25}F_4Na$ (M+Na) 2035.6762, found 2035.6793.



11

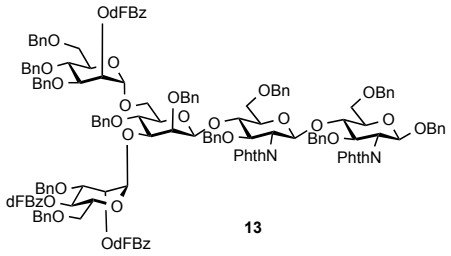
Benzyl [3,6-di-*O*-benzyl-2,4-di-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (11). Benzylidene acetal **10** (1.30 g, 0.645 mmol) was azeotropically dried with PhMe (3 x 5 mL) and then on high vacuum for 1 h. This compound was cooled to 0 ^oC, a solution of BH_3·THF (6.54 mL, 6.54 mmol, 1.0 M in THF) was added followed by a solution of *n*-Bu_2BOTf (1.94 mL, 1.94 mmol, 1.0 M in CH_2Cl_2). The reaction mixture was stirred at 0 ^oC for 4 h, quenched with Et_3N, MeOH was introduced and the volatiles were removed *in vacuo*. The crude mixture was concentrated from MeOH two more times and purified by chromatography on SiO_2 (PhMe:EtOAc, 3:1) to afford **11** (1.14 g, 88%) as a clear film: $[\alpha]_D^{20}$ -25.4 (c 1.0, $CHCl_3$); IR (ATR) 2926, 2870, 1713, 1496, 1389, 1268, 1074 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.1 Hz, 1 H), 7.65-7.63 (m, 2 H), 7.60 (br s, 2 H), 7.56-7.53 (m, 3 H), 7.34 (d, *J* = 7.4 Hz, 2 H), 7.26-7.18 (m, 13 H), 7.16-7.10 (m, 13 H), 7.06-7.00 (m, 6 H), 6.98-6.94 (m, 3 H), 6.91-6.81 (m, 11 H), 6.65-6.63 (m, 3 H), 5.60 (s, 1 H), 5.54 (t, *J* = 9.9 Hz, 1 H), 5.22 (s, 1 H), 5.21 (d, *J* = 8.2 Hz, 1 H), 4.95 (d, *J* = 12.2 Hz, 1 H), 4.88 (s, 1 H), 4.86 (d, *J* = 5.0 Hz, 1 H), 4.76 (d, *J* = 13.0 Hz, 1 H), 4.72 (d, *J* = 12.1 Hz, 1 H), 4.66 (d, *J* = 11.1 Hz, 1 H), 4.61 (d, *J* = 12.4 Hz, 1 H), 4.52 (d, *J* = 12.1 Hz, 2 H), 4.47 (d, *J* = 11.5 Hz, 2 H), 4.44-4.38 (m, 5 H), 4.31 (d, *J* = 11.8 Hz, 2 H), 4.28 (dd, *J* = 5.9, 4.4 Hz, 2 H), 4.23-4.09 (m, 4 H), 4.06-4.03 (m, 2 H), 3.99 (dd, *J* = 9.4, 3.1 Hz, 1 H), 3.97 (dd, *J* = 14.6, 8.8 Hz, 1 H), 3.83 (d, *J* = 2.8 Hz, 1 H), 3.77 (t, *J* = 9.5 Hz, 1 H), 3.58-3.55 (m, 1 H), 3.54-3.50 (m, 3 H), 3.47 (d, *J* = 10.5 Hz, 2 H), 3.36 (dd, *J* = 11.0, 3.8 Hz, 1 H), 3.33-3.31 (m, 2 H), 3.23 (dd, *J* = 9.7, 2.5 Hz, 1 H), 3.13 (d, *J* = 9.9 Hz, 1 H), 2.99 (ddd, *J* = 9.1, 4.6, 2.3 Hz, 1 H), 1.55 (t, *J* = 7.0 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 162.2, 162.0, 158.8, 157.1, 138.9, 138.7 (2), 138.5, 137.8, 137.7, 137.6, 137.3, 137.2, 134.1, 133.9, 133.5, 131.7, 128.0, 128.5, 128.3 (2), 128.2, 128.1 (3), 128.0, 127.9 (2), 127.8, 127.7 (3), 127.6, 127.5 (2), 127.4, 127.3, 127.1 (2), 126.9, 126.8, 123.8, 123.1, 118.7, 118.5 (2), 118.4 (2), 118.3, 118.2 (2), 118.1, 100.9, 99.7, 97.2, 97.1, 82.0, 78.5, 78.4, 77.0, 76.7, 76.0, 75.5, 75.2, 74.8, 74.6, 74.5, 74.3 (2), 73.6, 73.2,

72.8, 71.5, 70.8, 70.5, 69.5, 69.4, 69.2, 68.2, 67.5, 62.0, 56.5, 55.8; HRMS (ESI) calc for $C_{117}H_{106}N_2O_{25}F_4Na$ (M+Na) 2037.6919, found 2037.7015.



12

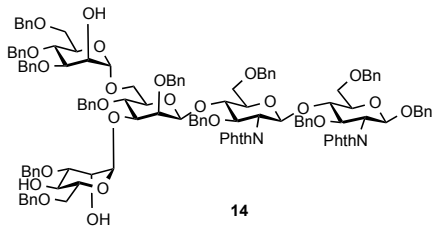
Thioethyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranoside (12). A solution of thioethyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[2] (1.54 g, 3.11 mmol) in anh. pyridine (10.0 mL) was treated with 2,5-difluorobenzoyl chloride (0.77 mL, 6.22 mmol) and stirred at rt for 2 h. This mixture was quenched with sat. $NaHCO_3$, diluted with EtOAc and the organic layer was washed with water, sat. $CuSO_4$, sat. $NaHCO_3$, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **12** (1.59 g, 81%) as a clear oil: $[\alpha]_D^{20}$ +35.0 (c 1.0, $CHCl_3$); IR (ATR) 3031, 2871, 1736, 1718, 1496, 1270, 1098 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.63-7.60 (m, 1 H), 7.32-7.13 (m, 14 H), 7.11-7.08 (m, 2 H), 7.03 (dt, *J* = 9.3, 4.2 Hz, 1 H), 5.59 (s, 1 H), 5.36 (s, 1 H), 4.77 (d, *J* = 10.8 Hz, 1 H), 4.67 (d, *J* = 11.4 Hz, 1 H) 4.63 (d, *J* = 12.2 Hz, 1 H), 4.50 (d, *J* = 11.4 Hz, 1 H), 4.41 (app. t, *J* = 12.4 Hz, 2 H), 4.12 (dd, *J* = 9.6, 2.0 Hz, 1 H), 4.00 (t, *J* = 9.5 Hz, 1 H), 3.92 (dd, *J* = 9.3, 2.9 Hz, 1 H), 3.78 (dd, *J* = 10.8, 4.0 Hz, 1 H), 3.06 (d, *J* = 10.7 Hz, 1 H), 2.64-2.50 (m, 2 H), 1.21 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (3), 162.2, 159.3 (2), 158.9 (2), 157.3 (2), 157.0 (2), 138.2 (2), 137.6, 129.0, 128.4, 128.3, 128.2 (2), 128.1, 127.9, 127.7, 127.6, 127.5, 125.3, 121.6 (2), 121.5, 121.4, 119.4 (3), 119.3, 118.6, 118.5, 118.4, 118.3, 82.8, 78.5, 75.2, 74.5, 73.3, 71.9, 71.8, 71.7, 68.7, 25.6, 14.9; HRMS (ESI) calc for $C_{36}H_{36}O_6SF_2Na$ (M+Na) 657.2098, found 657.2109.



13

Benzyl [3,6-di-*O*-benzyl-2,4-di-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-*O*-(2,5-difluorobenzoyl)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13). A mixture of **12** (0.410 g, 0.644 mmol) and **11** (0.650 g, 0.322 mmol) was azeotropically dried with PhMe (3x) and then on high vacuum for 1 h. This mixture was dissolved in anh. CH_2Cl_2 (8.1 mL), freshly activated 4Å MS (0.50 g) were added and after 1 h at rt, this mixture was cooled to -20 °C, NIS (0.152 g, 0.676 mmol) was added, followed by

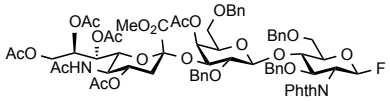
AgOTf (41.0 mg, 0.160 mmol). The reaction mixture was stirred at -20 °C for 12 h, quenched with Et_3N, filtered through a pad of Celite, washed with sat. $Na_2S_2O_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (PhMe:EtOAc, 3:1) afforded **13** (0.748 g, 90%) as a white foam: $[\alpha]_D^{24}$ -16.8 (c 1.0, $CHCl_3$), IR (ATR) 2923, 2870, 1716, 1495, 1269 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.67 d, *J* = 7.14 Hz, 2 H), 7.58 (t, *J* = 7.14 Hz, 1 H), 7.43 (d, *J* = 7.14 Hz, 1 H), 7.39 (d, *J* = 7.5 Hz, 2 H), 7.33-7.31 (m, 1 H), 7.27-7.22 (m, 2 H), 7.21-7.06 (m, 38 H), 7.04-6.97 (m, 8 H), 6.96-6.92 (m, 3 H), 6.89-6.85 (m, 4 H), 6.82-6.79 (m, 3 H), 6.76-6.75 (m, 2 H), 6.64-6.59 (m, 3 H), 6.51-6.46 (m, 3 H), 5.56 (br s, 1 H), 5.59 (t, J = 9.81 Hz, 1 H), 5.48 (br s, 1 H), 5.21 (s, 1 H), 5.12 (d, *J* = 8.04 Hz, 1 H), 5.04 (d, *J* = 12.1 Hz, 1 H), 4.94 (d, *J* = 1.3 Hz, 1 H) 4.84 (d, *J* = 8.5 Hz, 1 H), 4.80 (d, *J* = 13.1 Hz, 1 H), 4.78 (d, *J* = 12.1 Hz, 1 H), 4.71 (t, *J* = 14.0 Hz, 1 H), 4.62 (d, *J* = 11.3 Hz, 1 H), 4.59-4.53 (m, 3 H), 4.48 (d, *J* = 12.1 Hz, 2 H), 4.45 (d, *J* = 8.3 Hz, 1 H), 4.44-4.39 (m, 6 H), 4.38-3.35 (m, 4 H), 4.32 (dd, *J* = 5.6, 3.3 Hz, 2 H), 4.30 (d, *J* = 3.1 Hz, 1 H), 4.25 (d, *J* = 12.4 Hz, 1 H), 4.21 (d, *J* = 11.4 Hz, 1 H), 4.13-4.10 (m, 2 H), 4.09-4.04 (m, 4 H), 4.01-3.97 (m, 2 H), 3.93 (d, *J* = 9.6 Hz, 1 H), 3.89-3.87 (m, 2 H), 3.84 (d, *J* = 9.4 Hz, 1 H), 3.82-3.79 (m, 1 H), 3.69 (d, *J* = 10.7 Hz, 1 H), 3.63-6.58 (m, 2 H), 3.56-3.53 (m, 2 H), 3.51-3.48 (m, 3 H), 3.40 (d, *J* = 10.2 Hz, 1 H), 3.33-3.31 (m, 1 H), 3.28 (dd, *J* = 10.8, 3.8 Hz, 1 H), 3.17 (dd, *J* = 9.5, 2.5 Hz, 1 H), 3.10 (d, *J* = 9.4 Hz, 1 H), 3.04 (d, *J* = 9.8 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 167.5, 167.3, 162.0, 161.6, 159.1, 158.8, 158.7, 158.6, 158.5, 157.4, 157.3, 157.1 (2), 157.0 (3), 156.9 (2), 138.9, 138.6, 138.5, 138.4 (3), 137.8 (2), 137.7, 137.5, 137.3, 137.1, 133.6, 133.4, 133.3, 131.6, 131.4, 128.5, 128.4, 128.3 (3), 128.2, 128.1 (3), 128.0 (3), 127.8, 127.7, 127.6, 127.4 (2), 127.3, 127.2 (3), 123.4, 123.0, 121.7, 121.6, 121.5 (2), 121.3, 121.2, 121.1 (2), 121.0, 120.9, 120.8, 119.4 (3), 119.3 (2), 119.2 (2), 119.1 (2), 119.0, 118.9, 118.6, 118.5, 118.4 (2), 118.3 (2), 118.2 (2), 101.9, 99.7, 98.0, 97.0 (2), 82.2, 80.0, 78.2, 77.4, 76.5, 75.8, 75.1, 75.0, 74.8, 74.6, 74.5, 74.4 (2), 74.3, 74.1 (2), 73.6, 73.2, 73.0, 72.6, 72.0, 71.5, 70.8, 70.4, 69.4, 69.3, 69.2, 68.7, 68.0, 67.5, 66.4, 56.5, 55.7; HRMS (ESI) calc for $C_{151}H_{136}N_2O_{31}F_6Na$ (M+Na) 2609.8929, found 2609.8945.



14

Benzyl [3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-Benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (14). A solution of **13** (0.748 g, 0.289 mmol) in anh. CH_2Cl_2 (4.0 mL) and MeOH (6.0 mL) was treated with NaOMe

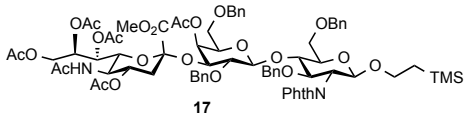
(0.867 mL, 0.433 mmol, 0.5 M in MeOH) and stirred at rt for 1 h 30 min. The mixture was quenched with DOWEX-50WX8, filtered, and concentrated. Purification by chrom. on SiO_2 (PhMe:EtOAc, 3:1) afforded **14** (0.520 g, 83%) as a clear oil: $[\alpha]_D^{24}$ +11.6 (c 1.0, $CHCl_3$); IR (ATR) 3475, 3031, 2917, 2873, 1777, 1718, 1496, 1452, 1386, 1075 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1 H), 7.74-7.71 (m, 2 H), 7.678-7.59 (m, 3 H), 7.48 (d, *J* = 7.5 Hz, 1 H), 7.35-7.18 (m, 40 H), 7.14-7.13 (m, 2 H), 7.08-7.7.06 (m, 1 H), 7.03-6.97 (m, 6 H), 6.89-6.87 (d, *J* = 6.9 Hz, 1 H), 6.76-6.72 (m, 6 H), 5.29-5.27 (m, 1 H), 5.17 (s, 1 H), 5.07 (d, *J* = 11.9 Hz, 1 H), 5.02-4.96 (m, 3 H), 4.85 (t, *J* = 13.4 Hz, 1 H), 4.77 (d, *J* = 10.9 Hz, 1 H), 4.72 (d, *J* = 12.4 Hz, 1 H), 4.67-4.63 (m, 4 H), 4.61-4.58 (m, 1 H), 4.56-4.49 (m, 8 H), 4.46 (d, *J* = 6.7 Hz, 1 H), 4.43-4.33 (m, 5 H), 4.22-4.19 (m, 4 H), 4.16-4.14 (m, 1 H), 4.12-4.09 (m, 1 H), 3.97-3.89 (m, 6 H), 3.85 (dd, *J* = 11.8, 3.3 Hz, 1 H), 3.82-3.71 (m, 7 H), 3.65-3.52 (m, 5 H), 3.47-3.43 (m, 2 H), 3.33-3.32 (m, 1 H), 3.22-3.20 (m, 2 H), 2.41 (s, 1 H), 2.29 (s, 1 H), 2.09 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 139.1, 138.9, 138.6, 138.4, 138.3, 138.0 (2), 137.9, 137.8, 137.7, 137.2, 128.6 (3), 128.5, 128.4, 128.3, 128.2 (4), 128.1, 128.0, 127.9 (2), 127.8 (5), 127.7, 127.6 (2), 127.5 (2), 127.4 (3), 127.3 (2), 127.2, 126.8 (2), 101.6 (2), 99.8, 97.0, 81.7, 79.6, 79.3, 79.2, 78.5, 76.6, 75.9, 75.0, 74.8 (2), 74.7, 74.5, 74.4, 74.3, 74.1, 73.7, 73.3, 73.1, 72.7, 72.1, 71.5, 71.4, 71.2, 70.5, 70.4, 68.8, 68.1, 68.0, 67.7, 56.5, 55.7; HRMS (ESI) calc for $C_{130}H_{130}N_2O_{28}Na$ (M+Na) 2189.8708, found 2189.8740.



16

Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl fluoride (16). A solution of **15** (0.659 g, 0.474 mmol) in anh. CH_2Cl_2 (2.90 mL) was cooled to 0 °C, treated with NBS (0.127g, 0.565 mmol) and HF/pyridine (0.173 mL, 70% HF/pyridine). After 20 min this mixture was poured into water, extracted (3x) with EtOAc and the combined organic layers were washed with water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (PhMe:Acetone, 1:1) afforded **16** (0.582 g, 91%, 5:1 mixture of anomers) as a white foam: $[\alpha]_D^{24}$ +16.1 (c 1.0, $CHCl_3$); IR (ATR) 2873, 1745, 1718, 1387, 1370, 1225, 1121, 1075 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ (major anomer) 7.84-7.80 (m, 5 H), 7.53 (d, *J* = 7.4 Hz, 2 H), 7.46-7.42 (m, 2 H), 7.42-7.27 (m, 9 H), 7.02-6.97 (m, 3 H), 6.93 (q, *J* = 7.3 Hz, 3 H), 6.13 (d, *J* = 9.8 Hz, 1 H), 5.89 (dd, *J* = 54.1, 7.9 Hz, 1 H), 5.57 (ddd, *J* = 8.3, 5.4, 2.9 Hz, 1 H), 5.32 (dd, *J* = 8.3, 2.3 Hz, 1 H), 5.17 (d, *J* = 3.2 Hz, 1 H), 4.97 (d, *J* = 12.1 Hz, 1 H), 4.95-4.89 (m, 1 H), 4.77 (d, *J* = 11.9 Hz, 1 H), 4.73 (d, *J* = 7.6 Hz, 1 H), 4.71-4.56 (m, 3 H), 4.55-4.48 (m, 2 H), 4.43 (d, *J* = 11.6 Hz, 1 H), 4.38 (d, *J* = 11.8 Hz, 1 H), 4.33 (dd, *J* = 12.5, 2.9 Hz, 1 H), 4.27 (dd, *J* = 10.8, 8.8 Hz, 1 H), 4.17-4.04 (m, 4 H), 3.88-3.86 (m, 2 H),

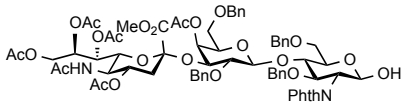
3.83 (s, 3 H), 3.80-3.76 (m, 2 H), 3.70-3.66 (m, 1 H), 3.64-3.57 (m, 1 H), 3.53-3.48 (m, 1 H), 3.43 (d, *J* = 6.3 Hz, 1 H), 2.58 (dd, *J* = 12.5, 4.7 Hz, 1 H), 2.07 (s, 3 H), 1.97 (s, 3 H), 1.96 (s, 3 H), 1.95 (s, 3 H), 1.91 (s, 3 H), 1.84 (dd, *J* = 11.1, 8.8 Hz, 1 H), 1.79 (s, 3 H); ^{13}C NMR (150 MHz, CD_3CN) δ (major anomer) 178.0 170.0, 169.6, 169.5, 169.4, 167.8, 167.5, 139.1, 138.2, 138.1, 134.2, 131.0, 129.2, 128.1, 128.0, 127.9 (2), 127.7 (3), 127.6 (2), 127.4, 127.3 (2), 127.2 (2), 127.1 (2), 127.0 (2), 123.0, 105.4, 104.0, 101.6, 97.3, 78.7, 75.8, 73.8, 73.0, 72.5, 72.3, 71.6, 69.2, 68.8, 68.2, 67.8, 67.4, 67.1, 61.7, 52.3, 48.1, 36.7, 21.9, 20.2, 19.8 (2), 19.7, 19.5; HRMS (ESI) calc for $C_{70}H_{77}N_2O_{24}FNa$ (M+Na) 1371.4748, found 1371.4799.



17

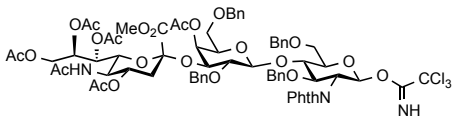
Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-((2-trimethylsilyl)ethyl)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17). A mixture of **15** (0.260 g, 0.186 mmol) and 2-(trimethylsilyl)ethanol (0.054 mL, 0.374 mmol) was dissolved in anhydrous CH_2Cl_2 (3.72 mL) and 4Å MS (0.10 g) were added. After 1 h at rt, this mixture was cooled to -50 ^{o}C, NIS (0.0631 g, 0.280 mmol) was added, followed by AgOTf (0.0238 g, 0.0925 mmol). The reaction mixture was allowed to warm up to -25 ^{o}C, stirred at this temp. for 2 h, quenched with Et_3N, warmed up to rt, filtered through a pad of Celite, washed with sat. $Na_2S_2O_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (PhMe:EtOAc, 1:2.5) afforded **17** (0.253 g, 94%) as an off-white foam: $[\alpha]_D^{24}$ +8.7 (c 1.0, $CHCl_3$); IR (ATR) 2951, 2860, 1743, 1716, 1385, 1365, 1226 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (br s, 1 H), 7.84 (br s, 3 H), 7.64 (d, *J* = 7.4 Hz, 2 H), 7.58-7.52 (m, 3 H), 7.51-7.38 (m, 10 H), 7.16 (dd, *J* = 7.1, 1.5 Hz, 2 H), 7.09-7.01 (m, 3 H), 5.76 (ddd, *J* = 10.9, 5.2, 2.6 Hz, 1 H), 5.57-5.48 (m, 1 H), 5.29 (d, *J* = 10.2, Hz, 1 H), 5.26 (d, *J* = 11.3 Hz, 1 H), 5.21 (d, *J* = 3.4 Hz, 1 H), 5.14 (d, *J* = 12.4 Hz, 1 H), 5.09 (ddd, *J* = 11.9, 10.6, 4.7 Hz, 1 H), 5.02 (d, *J* = 12.1 Hz, 1 H), 491 (br s, 1 H), 4.89 (d, *J* = 3.4 Hz, 1 H), 4.78-4.73 (m, 1 H), 4.69 (dd, *J* = 9.5, 3.4 Hz, 2 H), 4.59 (d, *J* = 11.8 Hz, 1 H), 4.49 (dd, *J* = 12.7, 2.6 Hz, 1 H), 4.46-4.42 (m, 2 H), 4.36-4.33 (m, 1 H), 4.29 (d, *J* = 10.9 Hz, 1 H), 4.24-4.19 (m, 2 H), 4.07-4.03 (m, 1 H), 3.99 (s, 3 H), 3.98-3.96 (m, 1 H), 3.94-3.88 (m, 3 H), 3.69-3.66 (m, 2 H), 3.65-3.62 (m, 1 H), 3.62-3.58 (m, 1 H), 3.52 (dd, *J* = 10.0, 5.8 Hz, 1 H), 3.42 (dd, *J* = 10.0, 7.0 Hz, 1 H), 2.76 (dd, *J* = 12.5, 4.6 Hz, 1 H), 2.25 (s, 3 H), 2.19 (t, *J* = 2.0 Hz, 1 H), 2.18 (s, 3 H), 2.14 (s, 3 H), 2.12 (s, 3 H), 2.03 (s, 3 H), 2.00 (s, 3 H), 0.97-0.92 (m, 1 H), 0.90-0.85 (m, 1 H), 0.00 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.5, 170.3, 169.9, 169.8, 167.9, 139.2, 138.9, 138.6, 138.2, 128.3 (3), 128.2, 128.1 (2), 127.8, 127.7, 127.6 (3), 127.4 (2), 127.3 (2), 127.2 (2), 126.9, 102.2, 97.6, 97.3, 79.3, 77.6, 75.1, 75.0, 73.9,

73.6, 73.2, 72.8, 72.3, 71.6, 69.5, 68.8, 68.5, 68.3, 68.0, 67.1, 66.5, 62.0, 55.7, 53.0, 49.2, 37.5, 23.2, 21.2, 20.8, 20.7, 20.6, 20.5, 17.7, -1.6; IR (ATR); HRMS (ESI) calc for $C_{75}H_{90}N_2O_{25}SiNa$ (M+Na) 1469.5500, found 1469.5471.



18

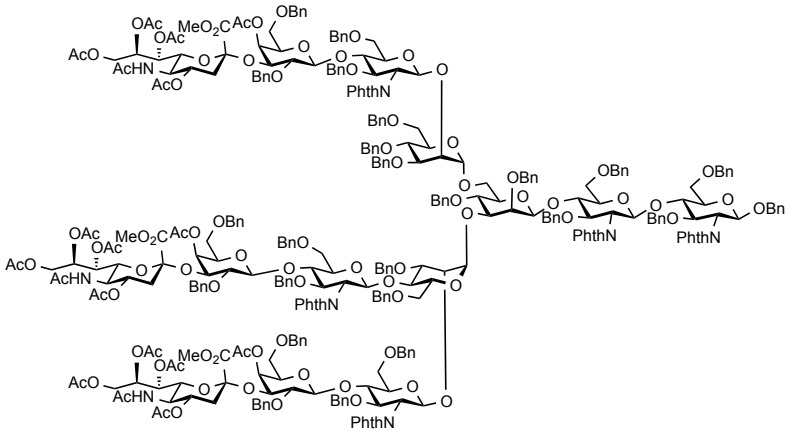
Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18). A solution of **17** (0.200 g, 0.138 mmol) in CH_2Cl_2 (1.50 mL) was cooled to 0 ^oC, treated with TFA (0.420 mL) and stirred at this temp. for 5 h. The reaction mixture was concentrated and purification by chrom. on SiO_2 (PhMe:EtOAc, 1:2.5) afforded **18** (0.125 g, 67%, 7.7:1 mixture of anomers) as a white foam: $[\alpha]_D^{24}$ +15.0 (c 1.0, $CHCl_3$), IR (ATR) 3388, 2873, 1743.3, 1713, 1369, 1222 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.4 Hz, 2 H), 7.50 (d, *J* = 7.4 Hz, 2 H), 7.40-7.36 (m, 5 H), 7.30-7.20 (m, 7 H), 7.1407.09 (m, 2 H), 6.87-6.74 (m, 6 H), 5.98-5.94 (m, 1 H), 5.6405.58 (m, 1 H), 5.50 (dd, *J* = 8.4, 2.6 Hz, 1 H), 5.46 (d, *J* = 3.3 Hz, 1 H), 5.24 (d, *J* = 11.9 Hz, 1 H), 5.12 (d, *J* = 7.6 Hz, 1 H), 5.03 (d, *J* = 12.4 Hz, 1 H), 5.00-4.94 (m, 2 H), 4.88-4.86 (m, 1 H), 4.78-4.72 (m, 3 H), 4.65-4.54 (m, 3 H), 4.47-4.42 (m, 2 H), 4.41-4.36 (m, 1 H), 4.35-4.31 (m, 1 H), 4.23 (d, *J* = 12.0 Hz, 1 H), 4.21 (d, *J* = 10.4 Hz, 1 H), 4.11 (t, *J* = 6.6 Hz, 1 H), 4.00 (dd, *J* = 10.8, 4.4 Hz, 1 H), 3.91 (d, *J* = 9.6 Hz, 1 H), 3.85-3.81 (m, 1 H), 3.79 (s, 3 H), 3.70-3.63 (m, 2 H), 3.42-3.27 (m, 2 H), 2.84 (dd, *J* = 12.4, 4.6 Hz, 1 H), 2.09 (s, 3 H), 1.92 (t, *J* = 5.0 Hz, 1 H), 1.90 (s, 3 H), 1.78 (s, 3 H), 1.78 (s, 3 H), 1.68 (s, 3 H), 1.65 (s, 3 H), 1.64 (s, 3 H); ^{13}C NMR (150 MHz, C_6D_6) δ 170.3 (2), 170.0, 169.9, 169.8, 168.9, 139.8 (2), 139.3, 139.0, 138.9, 133.4, 132.2, 130.1, 129.2, 128.8, 128.5 (2), 127.7, 127.2, 127.1, 123.2, 103.0, 97.8, 93.6, 80.3, 78.2, 77.8, 75.9, 75.8, 74.4, 74.1, 73.4, 72.8, 72.2, 69.7, 69.3, 69.2, 68.9, 68.2, 67.2, 62.6, 58.2, 53.1, 49.0, 38.4, 23.1, 21.3, 20.8, 20.5, 20.4 (2); HRMS (ESI) calc for $C_{70}H_{78}N_2O_{25}Na$ (M+Na) 1369.4791, found 1369.4839.



19

Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (19). A solution of **18** (0.125 g, 0.0927 mmol)

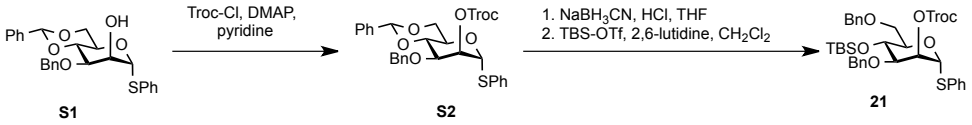
in anh. CH_2Cl_2 (1.0 mL) was cooled to 0 ^oC and treated with CCl_3CN (0.046 mL, 0.464 mmol) and DBU (0.0139 mL, 0.0927 mmol). After 2 h at 0 ^oC, the volatiles were removed *in vacuo* and the residual material was purified by chrom. on SiO_2 (PhMe:Acetone, 1:1) to afford crude **19** (0.120 g, 87%) as a light-yellow oil. This material was taken immediately to the next step. ^1H NMR (600 MHz, $CDCl_3$) δ (representative signals) 5.86-5.84 (m, 1 H), 3.68 (s, 3 H), 3.56 (dd, J = 10.7, 2.6 Hz, 1 H), 2.73 (dd, J = 12.5, 4.7 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (representative signals) 170.2, 170.0 (2), 169.9 (2), 169.2, 168.6, 161.0, 102.7, 97.5, 94.6; HRMS (ESI) calc for $C_{72}H_{78}N_3O_{25}Cl_3Na$ (M+Na) 1512.3888, found 1512.3929.



Benzyl [2,4-bis[methyl [5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]]-3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)]-[2-[methyl [5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)]-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20). Table 1, entry 4. A mixture of **14** (0.0278 g, 0.0128 mmol) and **15** (0.214 g, 0.154 mmol) was dried overnight over P_2O_5 and dissolved in anh. CH_2Cl_2 (0.32 mL), freshly activated 3Å MS (50 mg) were added. After 1 h at rt, this mixture was cooled to -20 ^oC, NIS (0.0432 g, 0.0192 mmol) was added, followed by AgOTf (9.6 mg, 0.0375 mmol). The reaction mixture was stirred at -20 ^oC for 24 h, quenched at this temp. with Et_3N, filtered through a pad of Celite, washed with sat. $Na_2S_2O_3$, water brine, dried ($MgSO_4$), and concentrated. Repeated purification by gravity filtration on LH-20 (CH_2Cl_2:MeOH, 1:1), chromatography on SiO_2 (PhMe:MeCN, 1:2) and BioGel S-X1 (PhMe:Acetone 1:1) and afforded **20** (16.9 mg, 21%) as a white powder.

Synthesis from **27**. A mixture of acceptor **27** (0.0287 g, 0.00821 mmol) and donor **15** (0.114 g, 0.0821 mmol) was azeotropically dried with PhMe (3 x 2 mL) and then on high vacuum for 3 h. This mixture was dissolved in anh CH_2Cl_2 (0.21 mL), freshly activated 3Å MS (0.10 g) were added and after 1 h at rt, this mixture was cooled to -20 ^oC, NIS (0.0369 g, 0.164 mmol) was added, followed by AgOTf (2.1 mg). After 22 h, additional portion of AgOTf (5.0 mg) was added and the mixture was stirred at -20 ^oC for total 36 h. The reaction mixture was quenched with Et_3N, filtered though a pad of Celite, washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom on SiO_2 (PhMe:MeCN, 1:2) and LH-20 (MeOH:CH_2Cl_2, 1:1) afforded **20** (0.0251 g, 50%) as a clear oil: $[\alpha]_D^{24}$ -0.10 (c 1.0, $CHCl_3$); IR (ATR) 2925, 1743, 1713, 1453, 1388, 1369, 1208 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.64 (ddq, *J* = 8.0, 5.8, 2.6 Hz, 4 H), 7.61-7.52 (m, 7 H), 7.52-7.27 (m, 37 H), 7.23 (q, *J* = 7.4 Hz, 10 H), 7.20-7.13 (m, 48 H), 7.10 (dd, *J* = 12.4, 5.7 Hz, 9 H), 7.03 (d, *J* = 7.2 Hz, 2 H), 7.02-6.96 (m, 4 H), 6.93 (dt, *J* = 5.7, 2.8 Hz, 2 H), 6.91-6.83 (m, 8 H), 6.83-6.69 (m, 11 H), 6.68-6.66 (m, 1 H), 5.95 (d, *J* = 5.6 Hz, 3 H), 5.88-5.79 (m, 1 H), 5.76-5.74 (m, 2 H), 5.58-5.55 (m, 3 H), 5.54-5.41 (m, 6 H), 5.30-5.11 (m, 8 H), 5.08 (dd, *J* = 9.2, 5.9 Hz, 3 H), 5.05-4.98 (m, 3 H), 4.90-4.97 (m, 10 H), 4.84-4.56 (m, 25 H), 4.56-4.50 (m, 5 H), 4.46 (dd, *J* = 11.9, 7.4 Hz, 5 H), 4.39-4.33 (m, 8 H), 4.33-4.24 (m, 10 H), 4.14-4.00 (m, 10 H), 3.97-3.89 (m, 4 H), 3.89-3.82 (m, 6 H), 3.79 (s, 6 H), 3.77 (s, 3 H), 3.73-3.63 (m, 5 H), 3.58-3.41 (m, 10 H), 3.41-3.22 (m, 12 H), 3.22-3.04 (m, 5 H), 2.99-2.88 (m, 4 H), 2.87-2.70 (m, 3 H), 2.11 (s, 6 H), 2.08 (s, 6 H), 1.98-1.93 (m, 6 H), 1.93-1.87 (m, 6 H), 1.83-1.80 (m, 3 H), 1.80 (s, 3 H), 1.78 (s, 3 H), 1.75-1.70 (m, 1 H), 1.69 (s, 3 H), 1.68 (s, 3 H), 1.65 (s, 3 H), 1.63 (s, 6 H), 1.62 (s, 6 H); ^{13}C NMR (150 MHz, C_6D_6) δ 170.71, 170.69, 170.58, 170.56, 170.44, 170.41, 170.39, 170.37, 170.36, 170.31, 170.28, 170.25, 170.23, 170.20, 170.18, 170.16, 170.14, 170.12, 170.08, 170.06, 170.04, 170.01, 169.97, 169.95, 169.93, 169.91, 169.89, 169.83, 169.82, 169.78, 169.74, 169.69, 169.54, 169.50, 169.48, 169.45, 169.43, 169.40, 169.12, 169.09, 169.06, 168.99, 168.98, 168.96, 168.93, 168.90, 168.88, 168.86, 168.83, 168.81, 168.77, 168.76, 168.66, 168.64, 168.31, 168.29, 168.27, 168.25, 167.85, 167.84, 167.82, 167.80, 167.77, 167.74, 167.72, 167.69, 167.64, 167.62, 167.60, 167.58, 167.55, 167.52, 167.49, 167.48, 166.78, 139.89, 139.84, 139.79, 139.76, 139.74, 139.70, 139.68, 139.67, 139.63, 139.58, 139.57, 139.54, 139.53, 139.51, 139.50, 139.49, 139.47, 139.43, 139.39, 139.37, 139.35, 139.32, 139.30, 139.25, 139.22, 139.19, 139.16, 139.14, 139.10, 139.07, 139.05, 139.02, 138.99, 138.98, 138.97, 138.91, 138.85, 138.82, 138.80, 138.78, 138.70, 138.68, 138.05, 138.03, 138.02, 133.51, 133.49, 133.45, 133.43, 133.39, 133.36, 133.34, 133.33, 133.31, 133.28, 133.26, 133.25, 133.24, 133.22, 133.21, 133.18, 133.13, 133.10, 133.08, 132.35, 132.30, 132.27, 132.22, 132.21, 132.19, 132.18, 132.15, 130.77, 130.75, 130.74, 130.72, 130.21, 130.14, 130.13, 130.11, 130.09, 129.31, 129.29, 129.27, 129.26, 129.20, 129.18, 129.16, 129.14, 129.05, 129.01, 128.84, 128.77, 128.71, 128.68, 128.65, 128.62, 128.60, 128.57, 128.53, 128.52, 128.50, 128.49, 128.45, 128.43, 128.40, 128.28, 128.26, 128.10, 128.07, 128.06, 127.94, 127.90, 127.87, 127.74, 127.70, 127.67,

127.65, 127.62, 127.61, 127.59, 127.57, 127.54, 127.50, 127.49, 127.47, 127.44, 127.41, 127.39, 127.38, 127.34, 127.32, 127.28, 127.26, 127.20, 127.18, 127.15, 127.09, 127.07, 127.06, 127.03, 127.00, 126.96, 126.93, 126.91, 126.86, 126.84, 126.83, 126.81, 126.79, 126.78, 126.76, 126.73, 126.69, 126.69, 126.63, 126.61, 126.59, 126.56, 126.53, 126.50, 126.48, 126.46, 126.44, 126.43, 126.41, 126.40, 126.36, 126.34, 126.31, 126.30, 126.28, 126.26, 103.30, 102.81, 102.78, 101.75, 101.70, 100.27, 99.95, 99.87, 99.54, 99.25, 98.37, 97.88, 97.77, 97.66, 80.09, 79.78, 77.87, 77.45, 77.44, 77.42, 77.40, 77.37, 77.35, 77.33, 77.31, 77.29, 77.27, 77.24, 77.21, 77.18, 77.17, 77.15, 77.13, 77.11, 76.50, 76.01, 75.44, 75.39, 75.35, 75.31, 75.26, 75.18, 75.14, 75.13, 75.12, 74.92, 74.90, 74.87, 74.85, 74.83, 74.77, 74.73, 74.70, 74.66, 74.61, 74.60, 74.30, 74.28, 74.13, 74.10, 74.06, 74.02, 73.92, 73.87, 73.84, 73.83, 73.82, 73.80, 73.76, 73.75, 73.63, 73.62, 73.60, 73.59, 73.50, 73.45, 73.40, 73.34, 73.31, 73.29, 73.25, 73.23, 73.18, 73.14, 73.13, 73.08, 73.06, 73.03, 72.97, 72.94, 72.92, 72.90, 72.82, 72.80, 72.79, 72.74, 72.72, 72.70, 72.68, 72.62, 72.60, 72.58, 72.51, 72.48, 72.01, 71.99, 71.97, 71.92, 70.29, 70.27, 69.66, 69.64, 69.62, 69.59, 69.57, 69.55, 69.53, 69.51, 69.49, 69.21, 69.12, 69.09, 69.07, 69.04, 68.72, 68.39, 68.06, 67.98, 67.96, 67.28, 67.27, 67.25, 67.14, 67.12, 67.11, 67.07, 66.10, 66.09, 65.78, 65.73, 62.59, 62.57, 62.54, 62.52, 62.51, 57.25, 57.23, 56.50, 56.48, 56.35, 53.03, 53.02, 52.99, 52.97, 52.95, 48.94, 48.94, 48.88, 48.85, 48.84, 48.81, 48.79, 39.11, 38.65, 38.39, 38.37, 38.33, 38.30, 38.27, 38.24, 38.20, 36.88, 36.78, 36.37, 35.57, 34.62, 33.36, 32.76, 32.29, 32.27, 32.25, 32.23, 32.20, 31.71, 31.31, 30.74, 30.28, 30.19, 30.15, 30.13, 30.09, 30.04, 30.03, 30.01, 29.99, 29.95, 29.93, 29.92, 29.89, 29.88, 29.85, 29.84, 29.78, 29.76, 29.75, 29.74, 29.72, 29.70, 29.68, 29.66, 29.62, 29.59, 29.58, 29.56, 29.54, 29.52, 29.49, 29.46, 29.44, 29.43, 29.40, 29.39, 29.37, 29.35, 29.32, 29.31, 29.29, 29.23, 29.21, 28.96, 28.83, 28.82, 27.67, 27.64, 27.63, 27.61, 27.59, 27.57, 27.55, 27.10, 27.09, 27.06, 26.61, 26.48, 25.90, 25.89, 25.63, 24.07, 23.35, 23.30, 23.08, 23.05, 23.02, 22.97, 22.95, 22.92, 22.90, 22.83, 22.82, 22.66, 22.63, 21.32, 21.29, 21.26, 21.23, 21.21, 20.84, 20.82, 20.81, 20.77, 20.74, 20.72, 20.57, 20.54, 20.52, 20.50, 20.47, 20.42, 20.41, 20.39, 20.34, 20.33, 20.31, 20.27, 20.25, 20.23, 20.20, 19.62, 19.31; MS-ESI *m/z* calc for $C_{340}H_{358}N_8O_{100}Na_2$ 3099.15 $(M+2Na)^{2+}$, $C_{340}H_{358}N_8O_{100}Na_3$ 2073.77 $(M+3Na)^{3+}$, found 3101.44, 2075.35.

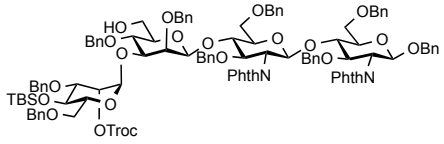


S1 **S2** **21**

Thiophenyl 3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranoside (S2). A solution of thiophenyl 3-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-mannopyranoside[2] (**S1**, 0.727 g, 1.61 mmol) in anh. pyridine (20.0 mL) was treated with Troc-Cl (0.653 mL, 4.83 mmol) and DMAP (0.0780 g, 0.644 mmol) and stirred at rt for 24 h. This mixture was quenched with sat. NH_4Cl, diluted with EtOAc and the organic layer was washed with water, 10% $CuSO_4$, brine,

dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **S2** (0.806 g, 80%) as a clear oil: $[\alpha]_D^{24}$ +60.4 (c 0.5, $CHCl_3$), IR (ATR) 2868, 1762, 1379, 1246, 1102 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.44 (m, 2 H), 7.39-7.38 (m, 2 H), 7.34-7.24 (m, 11 H), 5.60 (s, 1 H), 5.50 (s, 1 H), 5.42 (d, *J* = 3.1 Hz, 1 H), 4.74-4.65 (m, 4 H), 4.30 (app. quintet, *J* = 5.0 Hz, 1 H), 4.17 (dd, *J* = 8.6, 4.8 Hz, 1 H), 4.12 (d, *J* = 9.6 Hz, 1 H), 3.98 (dd, *J* = 9.8, 3.2 Hz, 1 H), 3.83 (t, *J* = 10.3 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 139.1, 138.7, 133.6, 130.7, 130.5, 129.8, 129.7, 129.3, 129.1, 127.5, 103.1, 88.1, 79.8, 78.0, 75.5, 74.1, 69.7, 66.7; HRMS (ESI) calc for $C_{29}H_{27}O_7SCl_3Na$ (M+Na) 647.0441, found 647.0436.

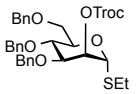
Thiophenyl 3,6-di-*O*-benzyl-4-*O*-(*t*-butyldimethylsilyl)-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranoside (21). A solution of **S2** (0.526 g, 0.840 mmol) in anh. THF (10.0 mL) was cooled to 0 ^oC, $NaBH_3CN$ (0.265 g, 4.20 mmol) was added, followed by a solution of HCl in Et_2O (4.20 mL, 8.40 mmol, 2.0 M). After 4 h, the mixture was quenched with sat. $NaHCO_3$, diluted with EtOAc and the organic layer was washed with water, brine, dried ($MgSO_4$), and concentrated. The crude material was dissolved in anh. CH_2Cl_2 (10.0 mL), 2,6-lutidine (0.0970 mL, 8.40 mmol) was added and the reaction mixture was cooled to 0 ^oC. TBSOTf (0.578 mL, 2.52 mmol) was introduced *via* syringe and the mixture was stirred at 0 ^oC for 3 h, carefully quenched with sat. $NaHCO_3$, diluted with EtOAc and the organic layer was washed with water (3x), brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 6:1) afforded **21** (0.370 g, 60%) as a clear oil: $[\alpha]_D^{24}$ +66.7 (c 1.0, $CHCl_3$); IR (ATR) 2856, 1741, 1722, 1362, 1105 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.35-7.30 (m, 8 H), 7.29-7.22 (m, 5 H), 5.58 (d, *J* = 1.4 Hz, 1 H), 5.40 (dd, *J* = 2.8, 1.8 Hz, 1 H), 4.74-4.68 (m, 3 H), 4.58 (s, 2 H), 4.56 (d, *J* = 11.6 Hz, 1 H), 4.35 (ddd, *J* = 8.7, 6.3, 1.6 Hz, 1 H), 4.00 (t, *J* = 9.3 Hz, 1 H), 3.83 (dd, *J* = 10.8, 1.9 Hz, 1 H), 3.77 (dd, *J* = 10.8, 6.4 Hz, 1 H), 3.73 (dd, *J* = 8.9, 3.0 Hz, 1 H), 0.84 (s, 9 H), 0.02 (s, 3 H), 0.00 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 138.3, 137.4, 133.3, 132.3, 129.1, 128.2, 127.9, 127.7 (2), 127.5, 127.4, 94.3, 85.7, 78.5, 76.9, 74.9, 74.1, 73.2, 71.5, 69.4, 68.0, 25.9, 18.1, -3.9, -5.0; HRMS (ESI) calc for $C_{35}H_{43}O_7SCl_3SiNa$ (M+Na) 763.1462, found 763.1458.



22

Benzyl [3,6-di-*O*-benzyl-4-*O*-(*t*-butyldimethylsilyl)-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→3)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-

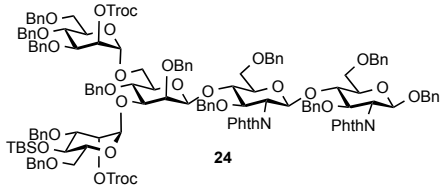
phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (22). A mixture of **21** (0.150 g, 0.203 mmol) and acceptor **8** (0.188 g, 0.135 mmol) was azeotropically dried with PhMe and then on high vacuum for 1 h. This mixture was dissolved in anh. CH_2Cl_2 (2.5 mL), freshly activated 3Å MS (0.30 g) were added and after 1 h, the mixture was cooled to -20 ^oC, NIS (0.0607 g, 0.270 mmol) was added, followed by a solution of TfOH (0.20 mL, 10% w/v in CH_2Cl_2). The reaction mixture was stirred at -20 ^oC for 2 h, quenched with Et_3N, filtered, washed with sat. $NaHCO_3$, sat. $Na_2S_2O_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 2:1) afforded crude tetrasaccharide (0.185 g, 68%). This material was cooled to 0 ^oC, a solution of BH_3·THF (0.91 mL, 0.91 mmol 1.0 M in THF) was added, followed by a solution of *n*-Bu_2BOTf (0.30 mL, 0.30 mmol, 1.0 M in CH_2Cl_2). After 4 h at this temperature, the mixture was quenched with Et_3N, and methanol was added. The volatiles were removed *in vacuo* and the mixture was concentrated from methanol two more times. The crude oil was purified by chrom. on SiO_2 (Hexanes:EtOAc, 3:1 to 2:1 to 1:1) to afford **22** (0.146 g, 53%) as a clear oil: $[\alpha]_D^{24}$ -5.5 (c 1.0, $CHCl_3$); IR (ATR) 2863, 1775, 1716, 1388 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.0 Hz, 1 H), 7.78-7.77 (m, 2 H), 7.74 (br s, 2 H), 7.68 (br s, 2 H), 7.49 (d, *J* = 7.4, 3 H), 7.42-7.23 (m, 28 H), 7.25-7.23 (m, 1 H), 7.10-7.08 (m, 1 H), 7.05-7.00 (m, 5 H), 6.98-6.95 (m, 6 H), 6.79-6.76 (m, 3 H), 5.34 (d, *J* = 8.2 Hz, 1 H), 5.39-5.25 (m, 2 H), 5.10 (m, *J* = 12.0 Hz, 1 H), 5.03 (d, *J* = 12.2 Hz, 1 H), 5.00 (d, *J* = 8.3 Hz, 1 H), 4.89 (d, *J* = 12.0, 8.3 Hz, 2 H), 4.73 (dd, *J* = 12.4, 7.3 Hz, 2 H), 4.71 (d, *J* = 2.4 Hz, 2 H), 4.69-4.62 (m, 3 H), 4.59-4.51 (m, 5 H), 4.49-4.40 (m, 3 H), 4.49-4.45 (m, 3 H), 4.39-4.32 (m, 1 H), 4.30-4.22 (m, 3 H), 4.20-4.17 (m, 1 H), 4.09 (t, *J* = 8.8 Hz, 1 H), 4.00 (t, *J* = 8.2 Hz, 1 H), 3.90 (t, *J* = 9.0 Hz, 1 H), 3.84 (t, *J* = 9.6 Hz, 1 H), 3.80-3.77 (m, 2 H), 3.70-3.64 (m, 4 H), 3.61 (d, *J* = 10.2 Hz, 1 H), 3.51-3.42 (m, 3 H), 3.37 (dd, *J* = 9.7, 3.1 Hz, 1 H), 3.27 (d, *J* = 9.8 Hz, 1 H), 3.11 (ddd, *J* = 7.5, 4.8, 2.5 Hz, 1 H), 0.82 (s, 9 H), 0.00 (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 167.6, 153.5, 138.9, 138.6, 138.4, 138.0, 137.8, 137.6, 137.1, 133.4, 131.6, 128.5, 128.4 (2), 128.3 (2), 128.2, 128.1 (2), 128.0 (2), 127.9, 127.8, 127.7 (2), 127.6 (3), 127.5 (2), 127.4 (2), 127.3 (2), 127.0 (2), 126.8, 123.7, 123.1, 100.8, 99.3, 97.1 (2), 94.2, 81.2, 78.4, 78.2, 77.8, 76.9 (2), 76.6, 75.4, 75.0, 74.8 (2), 74.7 (2), 74.5, 74.4, 74.3, 73.9, 73.4 (2), 73.1, 72.7, 71.5, 70.4, 69.7, 68.1, 67.8, 67.4, 61.9, 56.5, 55.7, 25.9, 18.0, -4.0, -5.1; HRMS (ESI) calc for $C_{112}H_{117}N_2O_{25}SiCl_3Na$ (M+Na) 2045.6678, found 2045.6676.



23

Thioethyl 3,4,6-tri-*O*-benzyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranoside (23). A solution of thioethyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[2] (0.440 g, 0.890 mmol) in anh. CH_2Cl_2

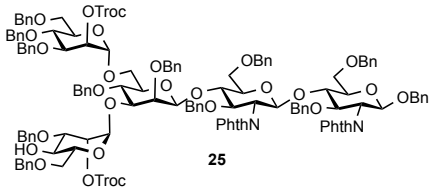
(5.0 mL) was treated with anh. pyridine (0.36 mL) and Troc-Cl (0.37 mL). After 2 h at rt, the mixture was quenched with sat. NH_4Cl, extracted (3 x 20 mL) with EtOAc and the combined organic layers were washed with water, sat. $CuSO_4$, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 6:1 to 4:1) afforded **23** (0.510 g, 86%) as a clear oil: $[\alpha]_D^{22}$ +56.5 (c 1.0, $CHCl_3$); IR (ATR) 2953, 2929, 1761, 1247, 1100 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ 7.34-7.25 (m, 13 H), 7.22-7.20 (m, 2 H), 5.43 (d, *J* = 1.1 Hz, 1 H), 5.23 (dd, *J* = 3.2, 1.6 Hz, 1 H), 4.67 (d, *J* = 11.5 Hz, 1 H), 4.55 (t, *J* = 11.5 Hz, 2 H), 4.52 (d, *J* = 11.0 Hz, 1 H), 4.46 (d, *J* = 11.9 Hz, 1 H), 4.04 (ddd, *J* = 9.8, 4.4, 1.6 Hz, 1 H), 3.85 (dd, *J* = 9.4, 3.3 Hz, 1 H), 3.77 (d, *J* = 9.7 Hz, 1 H), 3.75 (d, *J* = 4.6 Hz, 1 H), 3.73 (d, *J* = 4.5 Hz, 1 H), 3.63 (dd, *J* = 11.0, 1.7 Hz, 1 H), 2.65 (dq, *J* = 13.1, 7.4 Hz, 1 H), 2.58 (dq, *J* = 13.1, 7.4 Hz, 1 H), 1.24 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (150 MHz, CD_3CN) δ 154.3, 139.6, 139.4, 138.9, 129.3, 129.2, 129.1, 129.0, 128.8 (2), 128.6, 128.5, 95.4, 82.3, 79.1, 77.6, 76.6, 75.8, 75.3, 73.9, 72.7, 72.5, 69.7, 26.0, 15.2; HRMS (ESI) calc for $C_{32}H_{35}O_7SCl_3Na$ (M+Na) 691.1067, found 691.1055.



24

Benzyl [3,6-di-*O*-benzyl-4-*O*-(*t*-butyldimethylsilyl)-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24). A mixture of **23** (0.0965 g, 0.144 mmol) and **21** (0.146 g, 0.0721 mmol) was azeotropically dried with PhMe (3 x 5 mL) and then on high vacuum for 1 h. This mixture was dissolved in anh. CH_2Cl_2 (1.80 mL), freshly activated 3Å MS (0.10 g) were added and after 1 h at rt, the reaction mixture was cooled to -20 ^oC, NIS (0.0486 g, 0.216 mmol) was added, followed by AgOTf (9.30 mg, 0.0361 mmol). After 3 h at -20 ^oC, the reaction was quenched with Et_3N, filtered through a pad of Celite, washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 3:1 to 2:1) afforded **24** (0.147 g, 78%) as a clear oil: $[\alpha]_D^{22}$ +7.2 (c 1.0, $CHCl_3$); IR (ATR) 3063, 2864, 1763, 1716, 1389, 1250, 1076 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ 7.84-7.76 (m, 4 H), 7.69-7.65 (m, 2 H), 7.55-7.53 (m, 2 H), 7.45-7.24 (m, 40 H), 7.21-7.17 (m, 3 H), 7.15-7.11 (m, 1 H), 7.06-7.03 (m, 3 H), 7.01-7.00 (m, 3 H), 6.96-6.92 (m, 4 H), 6.89-6.86 (m, 1 H), 6.84-6.77 (m, 4 H), 6.75-6.73 (m, 1 H), 5.49 (br s, 1 H), 5.35-5.30 (m, 1 H), 5.25-5.17 (m, 2 H), 5.14 (dd, *J* = 3.1, 1.9 Hz, 1 H), 5.00 (dd, *J* = 10.3, 8.7 Hz, 1 H), 4.90-4.82 (m, 5 H), 4.80-4.76 (m, 1 H), 4.74-4.69 (m, 2 H), 4.68-

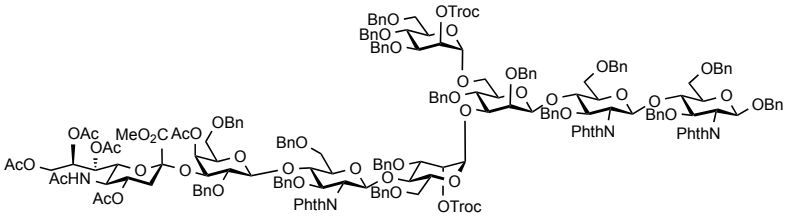
4.63 (m, 3 H), 4.62-4.57 (m, 6 H), 4.54-4.47 (m, 5 H), 4.46-4.39 (m, 5 H), 4.31 (d, *J* = 11.3 Hz, 1 H), 4.26 (dd, *J* = 10.6, 8.5 Hz, 1 H), 4.19 (dd, *J* = 7.4, 1.0 Hz, 1 H), 4.16-4.09 (m, 4 H), 4.07-4.02 (m, 2 H), 3.96-3.91 (m, 2 H), 3.88-3.83 (m, 3 H), 3.80-3.75 (m, 3 H), 3.74-3.70 (m, 4 H), 3.64-3.61 (m, 3 H), 3.56-3.53 (m, 2 H), 3.42 (dd, *J* = 10.9, 3.8 Hz, 1 H), 3.36-3.34 (m, 1 H), 3.30-3.27 (m, 1 H), 0.84 (s, 9 H), 0.04 (s, 3 H), 0.00 (s, 3 H); ^{13}C NMR (150 MHz, CD_3CN) δ 167.3, 152.9, 152.8, 138.3, 138.1, 137.6, 137.0, 133.8, 131.0, 128.1 (2), 128.0 (4), 127.9 (2), 127.8 (2), 127.6 (3), 127.5 (2), 127.4, 127.3 (2), 127.2, 127.1, 127.0, 126.9, 126.8, 122.7, 98.3, 96.9, 94.0 (2), 78.2, 77.7, 76.6, 76.4, 76.3, 76.1, 76.0, 74.4, 74.1, 74.0, 73.9, 73.8, 73.6, 73.3, 73.2, 72.9, 72.7, 72.6, 72.5, 72.4, 72.0, 70.8, 70.7, 70.2, 67.2, 64.6, 55.4, 25.0, 17.4, -4.2; HRMS (ESI) calc for $C_{142}H_{146}N_2O_{32}Cl_6SiNa$ (M+Na) 2651.7657, found 2651.7622.



25

Benzyl [3,6-di-*O*-benzyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (25). A solution of **24** (0.140 g, 0.0531 mmol) in anh. THF (1.0 mL) and pyridine (0.50 mL) was treated with HF/pyridine (0.50 mL, 70% in pyridine) and stirred at rt for 44 h. The reaction mixture was quenched with sat. $NaHCO_3$, extracted with EtOAc and the combined organic layers were washed with water, sat. $CuSO_4$, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 2:1 to 1:1) afforded **25** (0.0776 g, 58%) as a clear oil: $[\alpha]_D^{22}$ +5.9 (c 1.0, $CHCl_3$); IR (ATR) 3476, 3030, 2925, 2871, 1763, 1714, 1388, 1250, 1075 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.1 Hz, 1 H), 7.62 (t, *J* = 7.0 Hz, 1 H), 7.56-7.51 (m, 4 H), 7.45 (d, *J* = 6.9 Hz, 1 H), 7.39-7.34 (m, 3 H), 7.25-7.11 (m, 41 H), 7.09-7.05 (m, 2 H), 7.00-6.99 (m, 1 H), 6.97-6.94 (m, 1 H), 6.91-6.83 (m, 5 H), 6.80-6.78 (m, 2 H), 6.73-6.69 (m, 1 H), 6.66-6.56 (m, 4 H), 6.51 (t, *J* = 7.5 Hz, 1 H), 519 (br s, 1 H), 5.15-5.13 (m, 2 H), 5.07-5.06 (d, *J* = 1.9 Hz, 1 H), 4.99-4.95 (m, 1 H), 4.88-4.81 (m, 2 H), 4.76-4.67 (m, 4 H), 4.64-4.57 (m, 4 H), 4.54-4.48 (m, 3 H), 4.45-4.30 (m, 12 H), 4.28-4.24 (m, 3 H), 4.21-4.19 (m, 1 H), 4.12-3.96 (m, 6 H), 3.87-3.71 (m, 9 H), 3.61-3.48 (m, 5 H), 3.44-3.40 (m, 2 H), 3.37-3.27 (m, 2 H), 3.19-3.17 (m, 1 H), 3.05 (d, *J* = 9.5 Hz, 1 H); ^{13}C NMR (150 MHz, CD_3CN) δ 167.3, 153.0, 139.1, 138.4, 138.3 (2), 138.2, 137.8, 137.0, 133.8, 131.0, 128.2, 128.1, 128.0 (3), 127.9 (3), 127.8, 127.7 (2), 127.6 (4), 127.5 (3), 127.4 (2), 127.3 (2), 127.1 (2), 127.0, 126.9 (2), 126.8 (2), 126.7, 122.7, 99.1, 96.9 (2), 96.3, 93.9, 76.9, 76.3, 76.1 (2), 75.9, 75.6, 75.5, 75.1, 74.4,

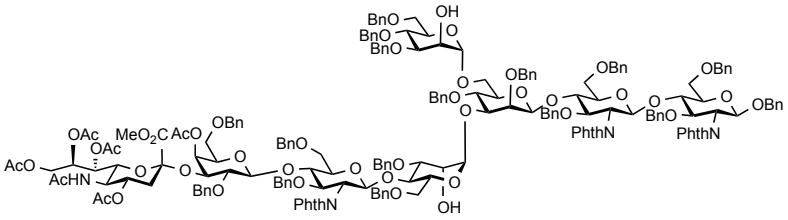
74.3, 74.2, 74.0, 73.9, 73.8, 73.6, 73.3, 73.0, 72.9, 72.8 (2), 72.7, 72.6, 72.5, 72.4, 72.0, 71.6, 71.5, 71.2, 70.8, 70.2, 68.8, 68.3, 67.8, 66.1, 56.1, 55.4; HRMS (ESI) calc for $C_{138}H_{132}N_2O_{32}Cl_6Na$ (M+Na) 2537.6792, found 2537.6879.



26

Benzyl [3,6-di-*O*-benzyl-4-(methyl [5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-2-*O*-((2,2,2-trichloroethoxy)carbonyl)-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (26). A mixture of acceptor **25** (0.0440 g, 0.0175 mmol) and donor **15** (0.122 g, 0.0875 mmol) was azeotropically dried with PhMe (3 x 5 mL) and then on high vacuum for 12 h. This mixture was dissolved in distilled CH_2Cl_2 (0.35 mL), freshly activated 3Å MS (0.10 g) were added and after 1 h at rt, this mixture was cooled to -20 ^oC, NIS (0.0295 g, 0.131 mmol) was added, followed by AgOTf (0.0225 g, 0.0175 mmol). After 36 h at this temperature, the reaction mixture was quenched with Et_3N, filtered through a pad of Celite, and the combined organic layers were washed with sat. $Na_2S_2O_3$, sat. $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (EtOAc then PhMe:MeCN, 2:1 to 1:1) afforded **26** (0.0402 g, 60%) as a clear oil: $[\alpha]_D^{24}$ +10.7 (c 1.0, $CHCl_3$); IR (ATR) 2874, 1745, 1715, 1388, 1224, 1040 cm^{-1}; ^1H NMR (600 MHz, CD_3CN) δ 7.85-7.75 (m, 5 H), 7.72 (s, 4 H), 7.64 (s, 3 H), 7.45 (dd, *J* = 7.5, 5.5 Hz, 2 H), 7.42-7.37 (m, 3 H), 7.37-7.31 (m, 14 H), 7.31-7.24 (m, 23 H), 7.24-7.20 (m, 9 H), 7.20-7.16 (m, 6 H), 7.16-7.08 (m, 6 H), 7.02 (dd, *J* = 8.3, 7.1 Hz, 2 H), 7.00 – 6.96 (m, 3 H), 6.94-6.87 (m, 5 H), 6.87-6.83 (m, 1 H), 6.83-6.79 (m, 2 H), 6.79-6.77 (m, 1 H), 6.77-6.72 (m, 2 H), 6.70 (dd, *J* = 8.5, 6.6 Hz, 1 H), 6.08 (d, *J* = 9.9 Hz, 1 H), 5.51 (ddd, *J* = 8.2, 5.4, 2.8 Hz, 1 H), 5.46 (t, *J* = 8.7 Hz, 1 H), 5.29 (dd, *J* = 8.1, 2.1 Hz, 1 H), 5.26 (d, *J* = 8.4 Hz, 1 H), 5.12 (dd, *J* = 8.3, 2.8 Hz, 1 H), 5.10-5.03 (m, 1 H), 4.95-4.91 (m, 2 H), 4.91-4.85 (m, 2 H), 4.85-4.80 (m, 1 H), 4.80-4.77 (m, 1 H), 4.75 (d, *J* = 9.0 Hz, 1 H), 4.74-4.71 (m, 2 H), 4.69 (ddd, *J* = 11.3, 5.1, 3.4 Hz, 1 H), 4.64 (ddd, *J* = 11.9, 5.0, 3.7 Hz, 3 H), 4.60 (d, *J* = 4.2 Hz, 1 H), 4.59-4.53 (m, 3 H), 4.50 (ddd, *J* = 11.3, 7.0, 3.1 Hz, 4 H), 4.47-4.40 (m, 6 H), 4.40-4.33 (m, 4 H), 4.33-4.27 (m, 2 H), 4.25 (d, *J* = 12.8 Hz, 1 H), 4.23-

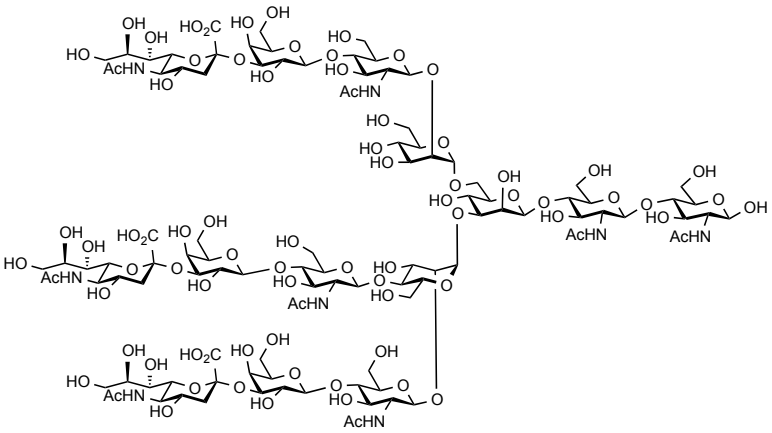
4.19 (m, 1 H), 4.19-4.16 (m, 1 H), 4.16-4.11 (m, 2 H), 4.11-4.08 (m, 1 H), 4.07 (t, *J* = 5.4 Hz, 2 H), 4.06-3.98 (m, 3 H), 3.97-3.89 (m, 3 H), 3.83 (ddd, *J* = 12.0, 8.6, 2.9 Hz, 2 H), 3.80 (s, 3 H), 3.78-3.70 (m, 2 H), 3.67 (d, *J* = 3.4 Hz, 1 H), 3.66-3.58 (m, 4 H), 3.58-3.47 (m, 4 H), 3.47-3.34 (m, 4 H), 3.32 (d, *J* = 7.8 Hz, 1 H), 3.22-3.15 (m, 1 H), 2.50 (dd, *J* = 12.5, 4.4 Hz, 1 H), 2.04 (s, 3 H), 1.99 (d, *J* = 7.4 Hz, 1 H), 1.95 (s, 3 H), 1.93 (s, 3 H), 1.92 (s, 3 H), 1.89 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR (150 MHz, CD_3CN) δ 178.0 (2), 169.6, 169.5, 169.4 (2), 169.2, 167.8, 167.3 (2), 152.8, 139.0, 138.8, 138.4, 138.3 (2), 138.1, 138.0 (2), 137.9, 137.4, 137.0, 133.8, 131.0, 128.6, 128.1 (2), 128.0 (5), 127.9, 127.9 (4), 127.8, 127.8 (3), 127.7, 127.6 (4), 127.5 (3), 127.4 (2), 127.3 (3), 127.2 (3), 127.1 (2), 127.0 (4), 126.9 (2), 126.7, 126.5, 126.4, 124.9, 122.9, 122.7, 101.5, 101.1, 98.3, 98.1, 97.4, 96.9, 96.6, 94.1, 94.0, 93.9, 78.3, 77.9, 76.6, 76.2, 76.1, 75.9, 74.8, 74.3, 74.3, 74.2, 74.0, 74.0, 73.9, 73.8, 73.7, 73.5, 72.9, 72.5 (3), 72.3, 72.0, 71.7, 71.1, 70.7, 70.2, 69.2, 69.0, 68.4, 67.9, 67.1, 66.1, 61.6, 55.4, 52.2, 48.1, 36.5, 29.0, 21.8, 20.2, 20.1, 19.8, 19.8, 19.7, 19.5; MS-ESI *m/z* calc for $C_{206}H_{208}Cl_6N_4O_{56}Na$ $(M+Na)^+$ 3866.16, found 3868.85; $C_{206}H_{208}Cl_6N_4O_{56}Na_2$ $(M+2Na)^{2+}$ calc 1944.58, found 1947.06.



27

Benzyl [3,6-di-*O*-benzyl-4-(methyl [5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3)-2,6-di-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranosyl-(1→3)]-[3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27). A solution of **26** (0.0370 g, 0.00960 mmol) in anh. THF (1.0 mL) was treated with AcOH (0.50 mL) and nano-Zn (12.5 mg, 1.91 mmol). After 20 min of stirring at rt, the mixture was filtered through a pad of Celite, concentrated and purified by chrom. on SiO_2 (PhMe:MeCN, 1:1) to provide **27** (28.7 mg, 85%) as a clear oil: ^{1}H NMR (600 MHz, CD_3CN) δ 7.66 (dd, *J* = 5.5, 2.8 Hz, 2 H), 7.59 (s, 3 H), 7.56-7.48 (m, 4 H), 7.38-7.33 (m, 2 H), 7.29 (t, *J* = 7.6 Hz, 3 H), 7.26-7.20 (m, 12 H), 7.20-7.04 (m, 41 H), 7.04-6.94 (m, 7 H), 6.94-6.84 (m, 6 H), 6.84-6.75 (m, 6 H), 6.75-6.64 (m, 4 H), 6.61 (dd, *J* = 9.2, 6.4 Hz, 1 H), 5.98 (d, *J* = 9.9 Hz, 1 H), 5.41 (ddd, *J* = 8.5, 5.6, 2.9 Hz, 1 H), 5.18 (dd, *J* = 8.0, 2.3 Hz, 1 H), 5.15 (d, *J* = 8.9 Hz, 1 H), 4.88-4.66 (m, 9 H), 4.66-4.50 (m, 6 H), 4.50-4.41 (m, 7 H), 4.41-4.22 (m, 20 H), 4.22-4.13 (m, 4 H), 4.13-4.00 (m, 4 H), 4.00-3.85 (m, 8 H), 3.76-3.71 (m, 2 H), 3.68 (s, 3 H),

3.68-3.65 (m, 1 H), 3.64-3.58 (m, 3 H), 3.58-3.46 (m, 6 H), 3.46-3.33 (m, 7 H), 3.33-3.16 (m, 8 H), 3.12-2.96 (m, 3 H), 2.42-2.35 (m, 1 H), 1.93 (s, 3 H), 1.89 (s, 1 H), 1.84 (s, 3 H), 1.82-1.80 (m, 6 H), 1.78 (d, *J* = 2.3 Hz, 3 H), 1.66 (s, 3 H); MS-ESI *m/z* calc for $C_{200}H_{206}N_4O_{52}Na_2$ $(M+2Na)^{2+}$ 1771.88, found 1772.34.



1

[2,4-Bis[5-acetamido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-α-D-mannopyranosyl-(1→3)]-[2-[5-acetamido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylate]-(2→3)-β-D-galactopyranosyl-(1→4)]-2-acetamido-2-deoxy-β-D-glucopyranosyl]-α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-D-glucopyranoside (1). A solution of **20** (30.0 mg, 0.00487 mmol) in anh. CH_2Cl_2 (1.1 mL) and MeOH (1.1 mL) was treated at rt with NaOMe (0.25 mL, 0.125 mmol, 0.5 M in MeOH) and stirred at rt for 12 h. The reaction mixture was cooled to 0 ^oC, H_2O (0.21 mL) was introduced and the mixture was allowed to warm up to rt, stirred at this temp. for 8 h, cooled to 0 ^oC and quenched with DOWEX-MAC3 resin until pH was adjusted to 6. The mixture was then filtered and concentrated to provide triacid: ESI *m/z* calc for $(M+3Cl)^{3-}$ 1861.7, found 1864.8.

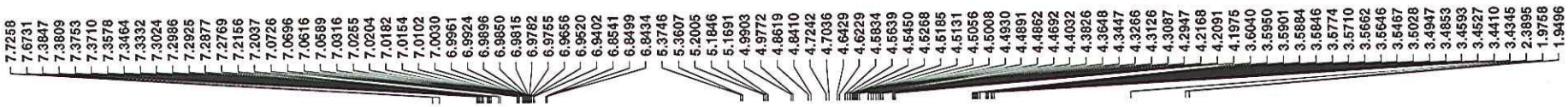
The crude mixture was dissolved in PhMe (0.50 mL), *n*-BuOH (4.3 mL), and 1,2-ethylenediamine (2.3 mL) and heated at 90 ^oC for 12 h. The volatiles were remove *in vacuo* and the crude material was dissolved in PhMe (1.0 mL), heated at 90 ^oC for 24 and concentrated to provide triamine: ESI *m/z* calc for $(M-H+Cl)^{2-}$ 2432.1, $(M-3H)^{3-}$ 1609.0, found 2427.2, 1610.1.

The crude mixture from above was dissolved in MeOH (1.40 mL), Et_3N (0.140 mL) was added and Ac_2O (89.6 μL) was introduced *via* syringe. After 2 h at rt, this mixture was loaded directly onto column packed with Sephadex LH-20, eluted with MeOH/CH_2Cl_2 (1:1), and concentrated to afford **28** as a clear, colorless oil: ESI *m/z* calc for $(M-2H)^{2-}$ 2519.1, $(M-3H)^{3-}$ 1679.0, found 2520.5, 1679.9.

A three-neck flask equipped with a Dewar condenser was cooled to -78 ^{o}C, charged with pre-dried (Na) liquid ammonia (10.0 mL), anhydrous THF (0.50 mL), and sodium was added (0.108 g). The mixture was stirred for ca. 1 h and a suspension of crude oligosaccharide in THF (0.50 + 0.50 mL) was added to the blue solution. After 6 h at -78 ^{o}C, this mixture was quenched with NH_4Cl (0.250 g), allowed to warp up to rt and the volatiles were removed overnight by a stream of nitrogen. This mixture was dissolved in water and purified by gravity filtration on BioGel P2 to provide **1** (1.5 mg, 11%) as a white solid: ^{1}H NMR (500 MHz, CD_3OD) δ representative signals 2.77-2.73 (m, 3 H), 1.92-1.91 (m, 6 H), 1.73-1.68 (m, 9 H), 1.64-1.62 (m, 6 H); ESI *m/z* calc for $C_{109}H_{176}N_8O_{80}Cl$ $(M+Cl-2H)^{3-}$ 970.67, found 970.04.

References:

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010,** *29*, 2176.
2. Dudkin, V. Y.; Miller, J. S.; Dudkina, A. S.; Antczak, C.; Scheinberg, D. A.; Danishefsky, S. J., *J. Am. Chem. Soc.* **2008,** *130*, 13598.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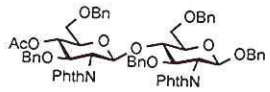
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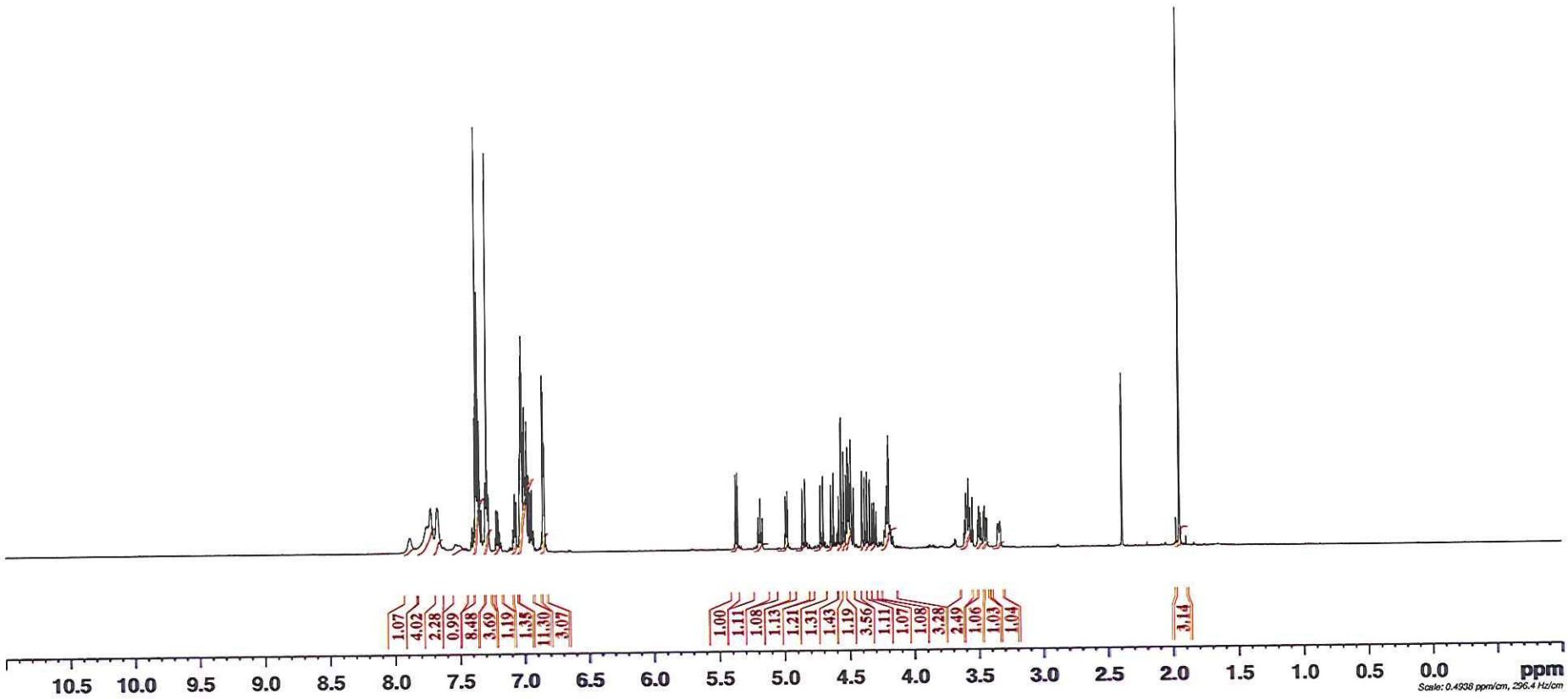
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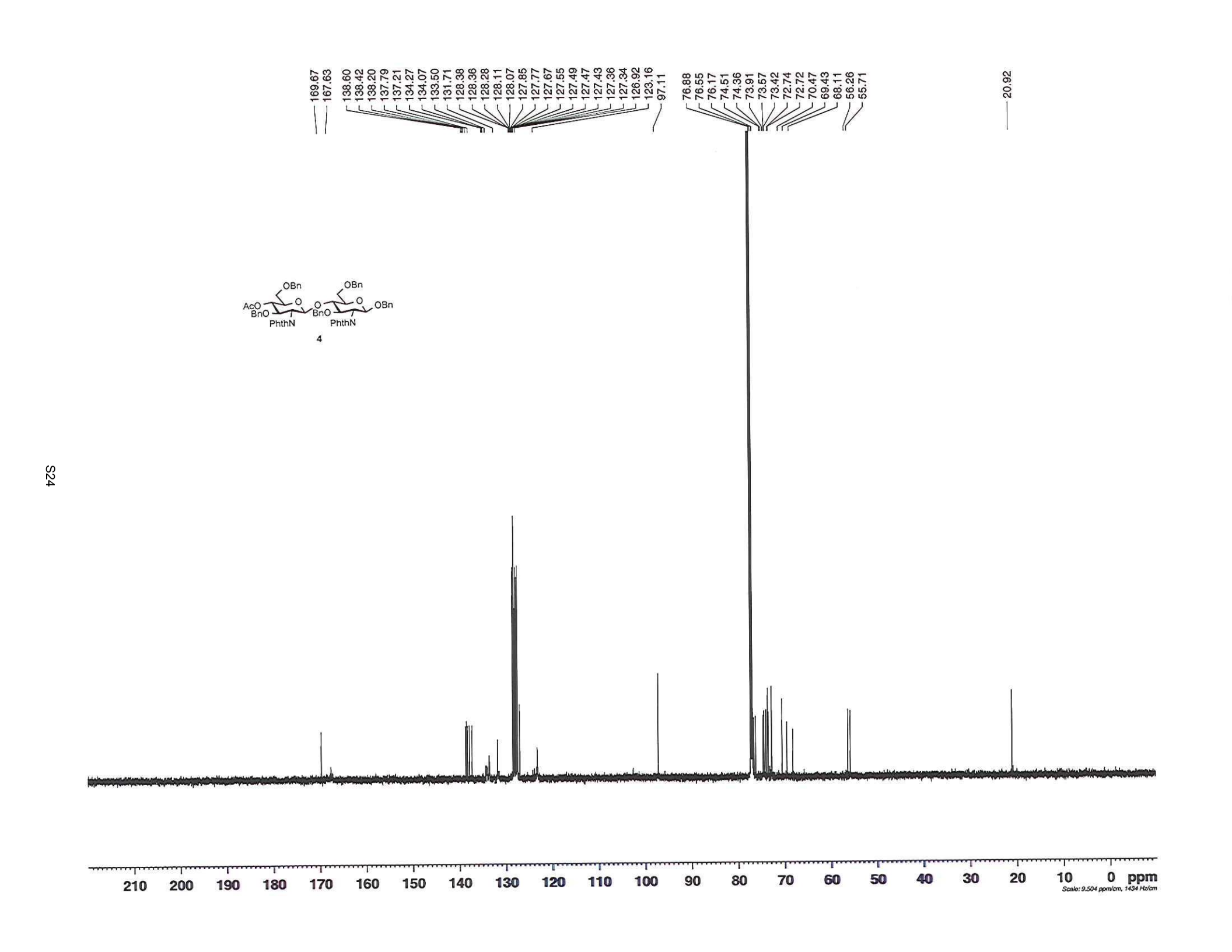
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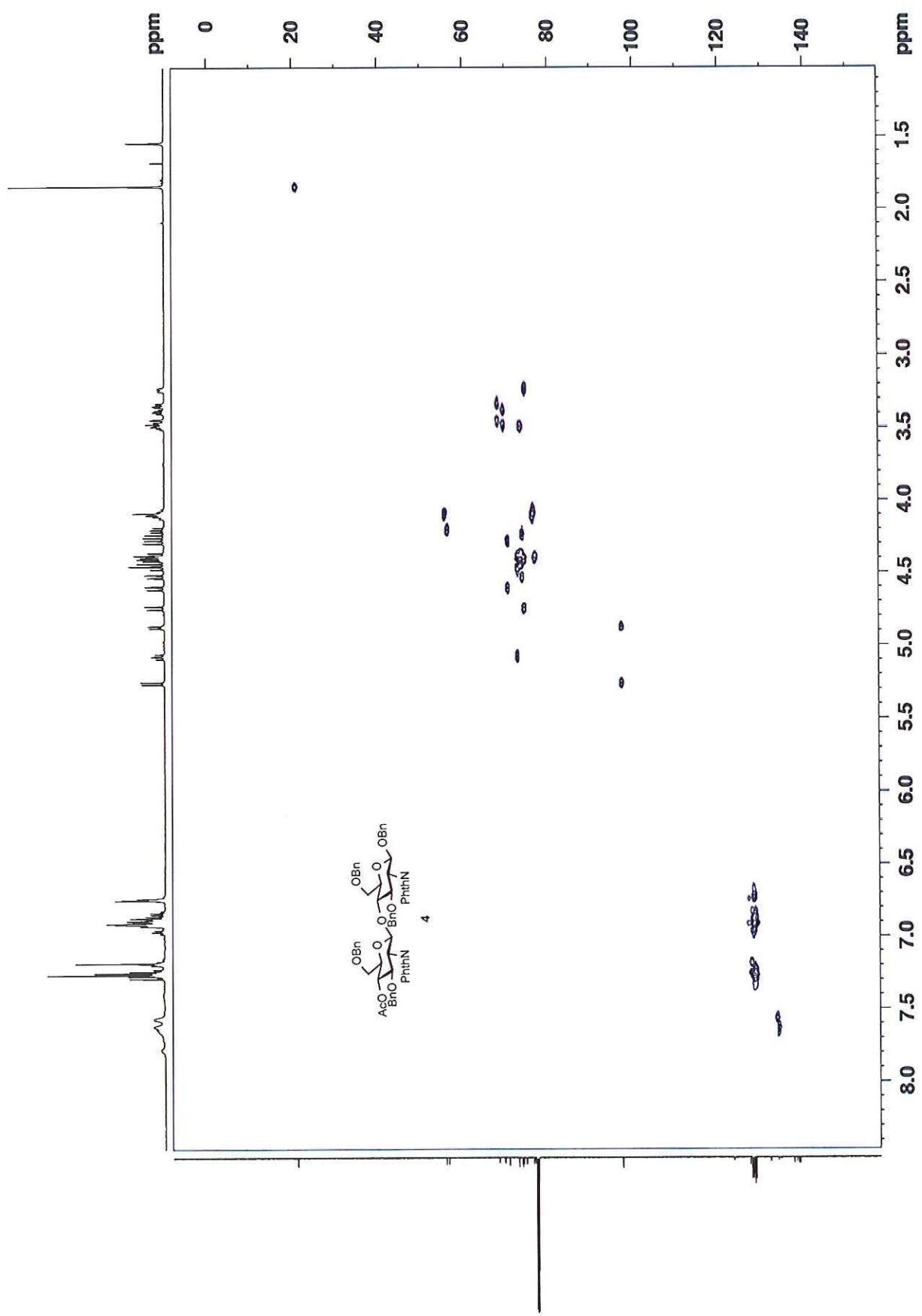
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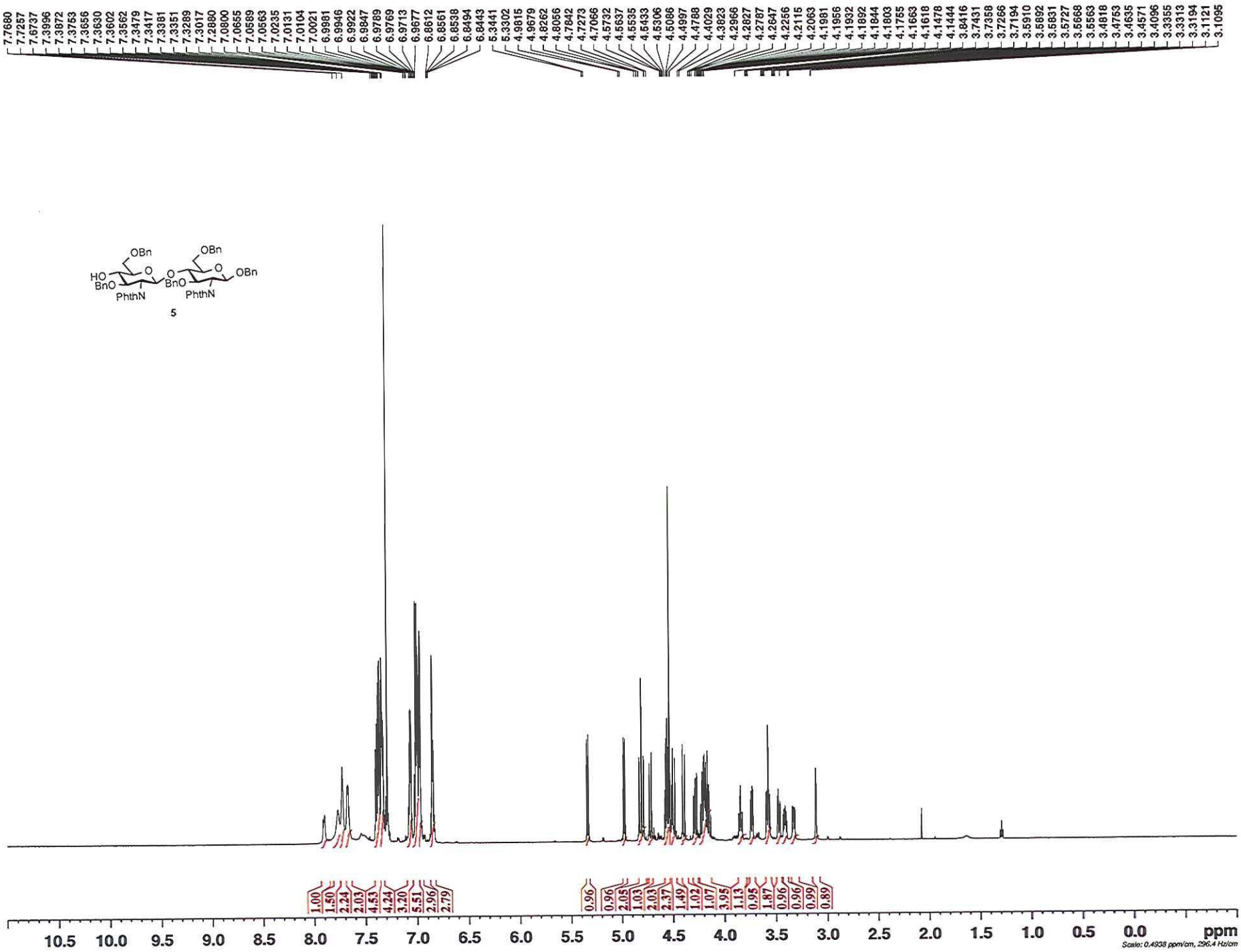
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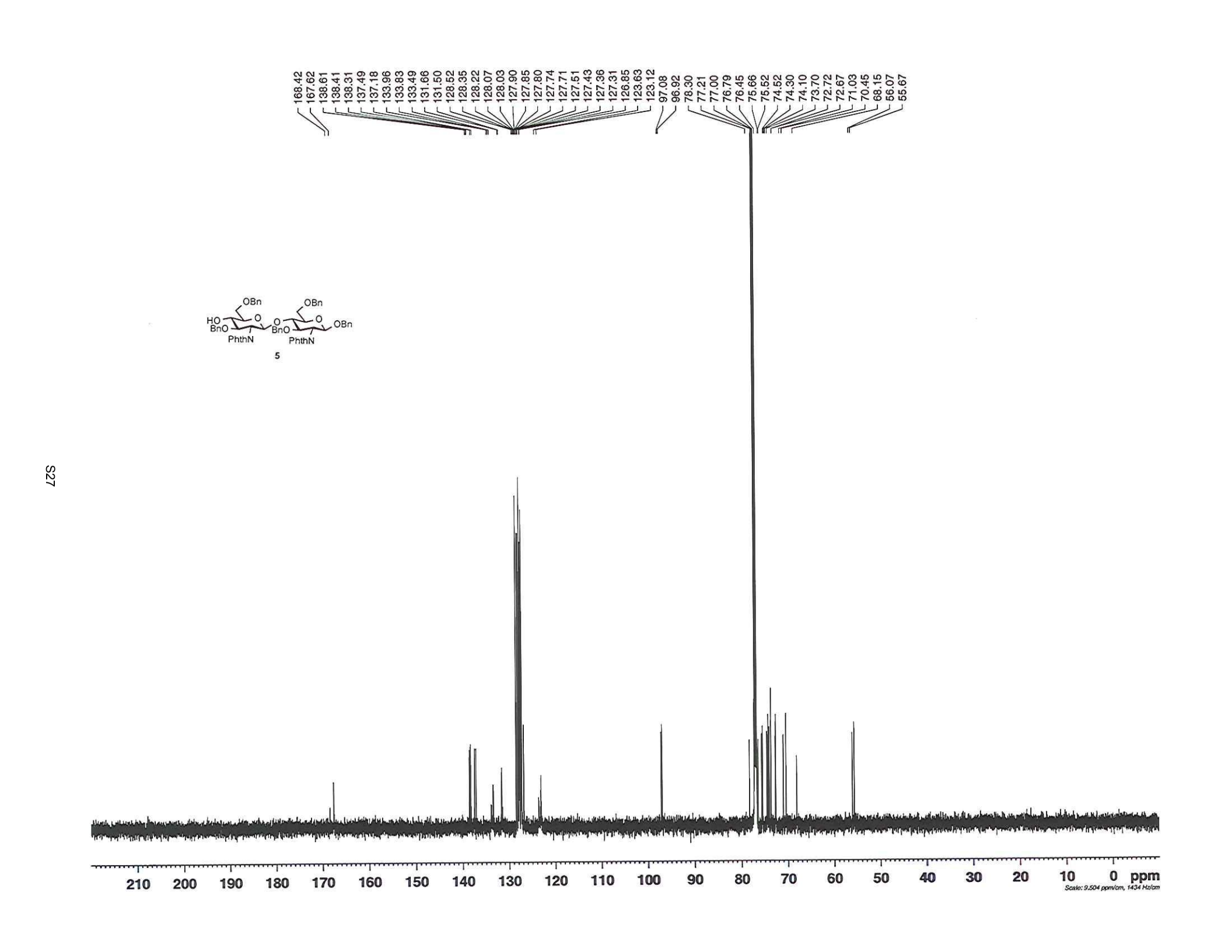
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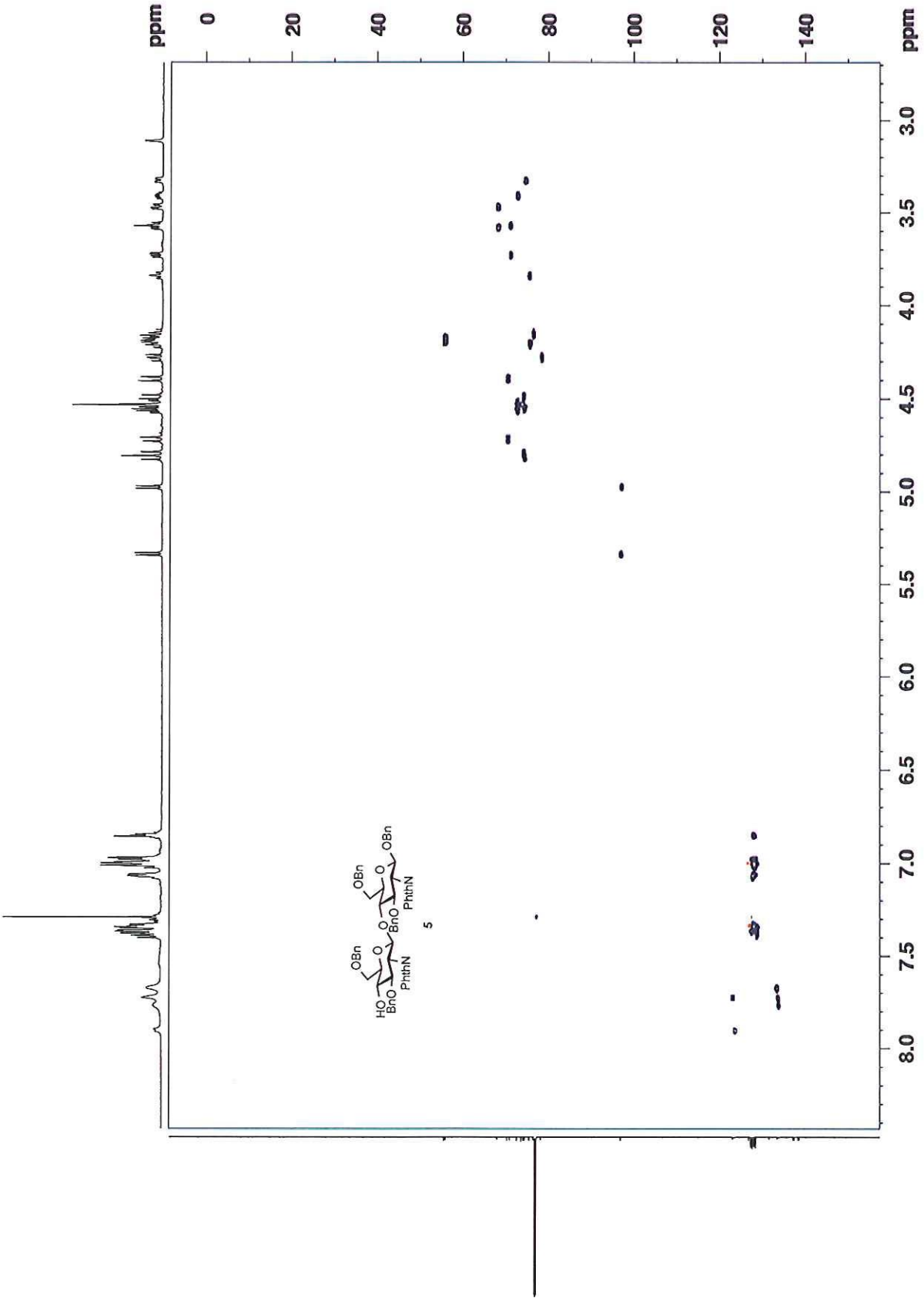
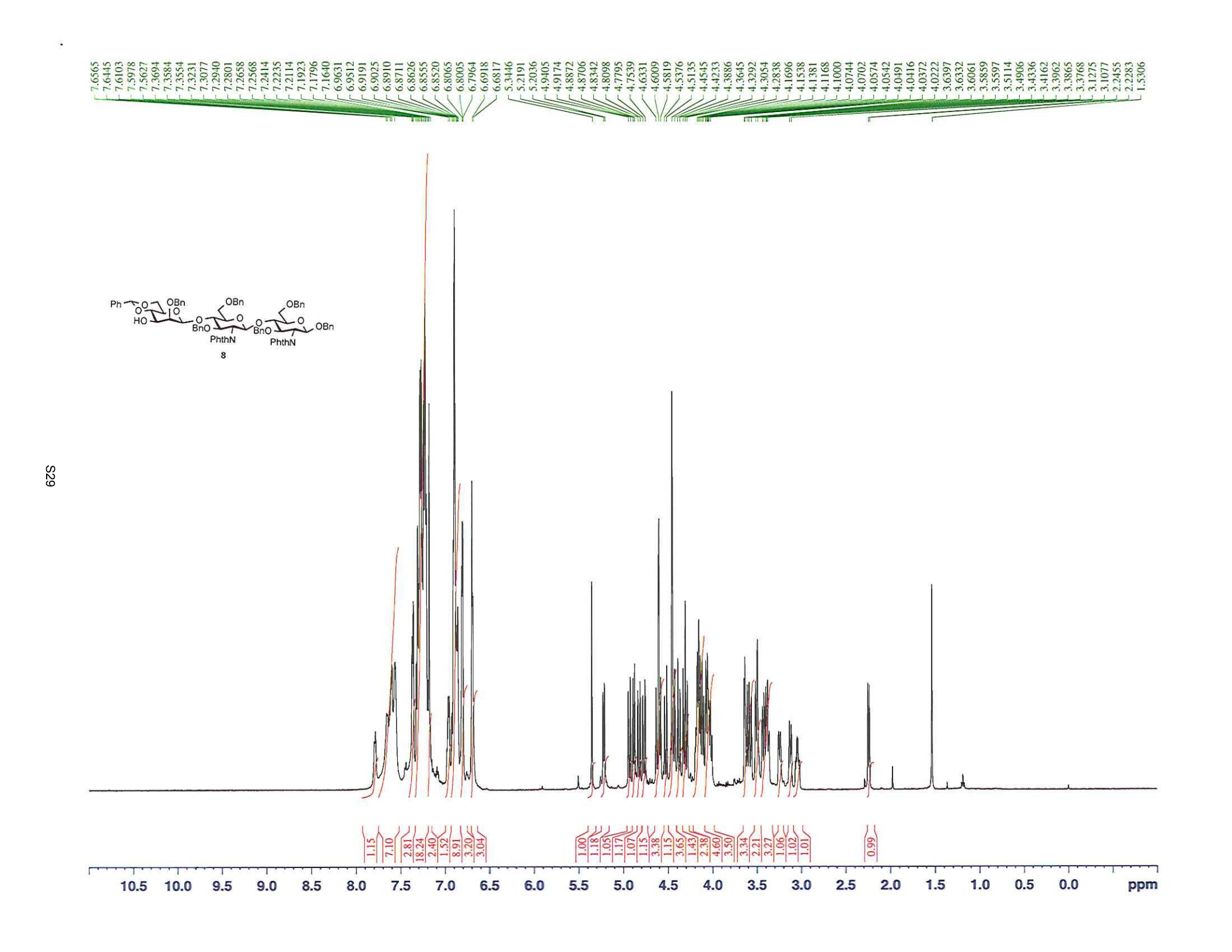
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.504 ppm/cm, 1434 Hz/cm


ppm
0
20
40
60
80
100
120
140
ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
OBn
HO
BnO
O
PhthN
OBn
O
BnO
O
PhthN
OBn
5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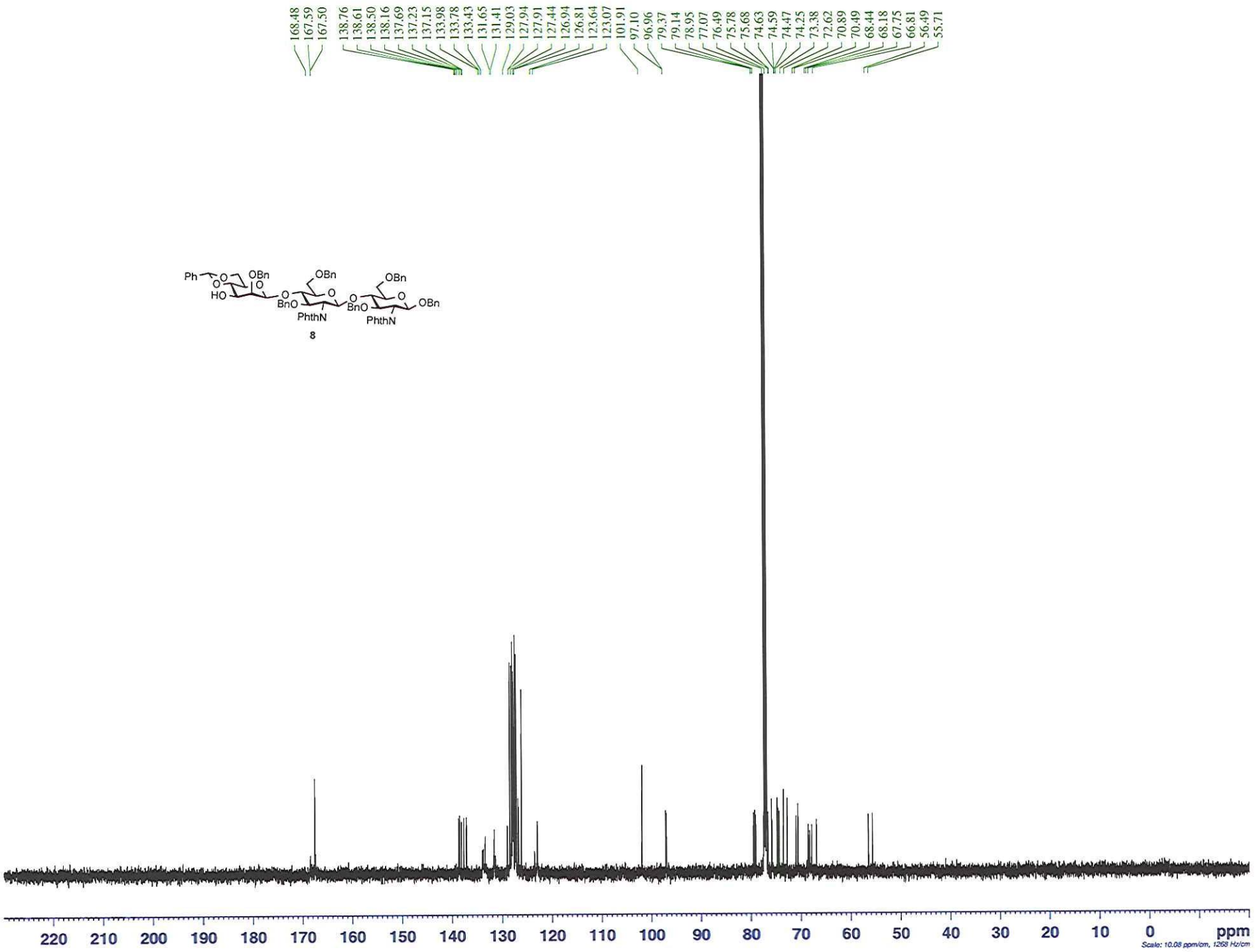
7.6445
7.6103
7.5978
7.5627
7.3694
7.3584
7.3554
7.3231
7.3077
7.2940
7.2801
7.2658
7.2568
7.2414
7.2235
7.2114
7.1923
7.1796
7.1640
6.9631
6.9512
6.9191
6.9025
6.8910
6.8711
6.8626
6.8555
6.8520
6.8065
6.8005
6.7964
6.6918
6.6817
5.3446
5.2191
5.2036
4.9405
4.9174
4.8872
4.8706
4.8342
4.8098
4.7795
4.7539
4.6331
4.6009
4.5819
4.5376
4.5135
4.4545
4.4233
4.3886
4.3645
4.3292
4.3054
4.2838
4.1696
4.1538
4.1381
4.1168
4.1000
4.0744
4.0702
4.0574
4.0542
4.0491
4.0416
4.0372
4.0222
3.6397
3.6332
3.6061
3.5859
3.5597
3.5114
3.4906
3.4336
3.4162
3.3962
3.3865
3.3768
3.1275
3.1077
2.2455
2.2283
1.5306
Ph
O
OBn
HO
O
BnO
PhthN
OBn
O
O
BnO
PhthN
OBn
O
OBn
8
1.15
7.10
2.81
18.24
2.40
1.52
8.91
3.20
3.04
1.00
1.18
1.05
1.17
1.07
1.15
3.38
1.15
3.65
1.43
2.38
4.60
3.50
3.34
2.21
3.27
1.06
1.02
1.01
0.99
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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167.59
167.50
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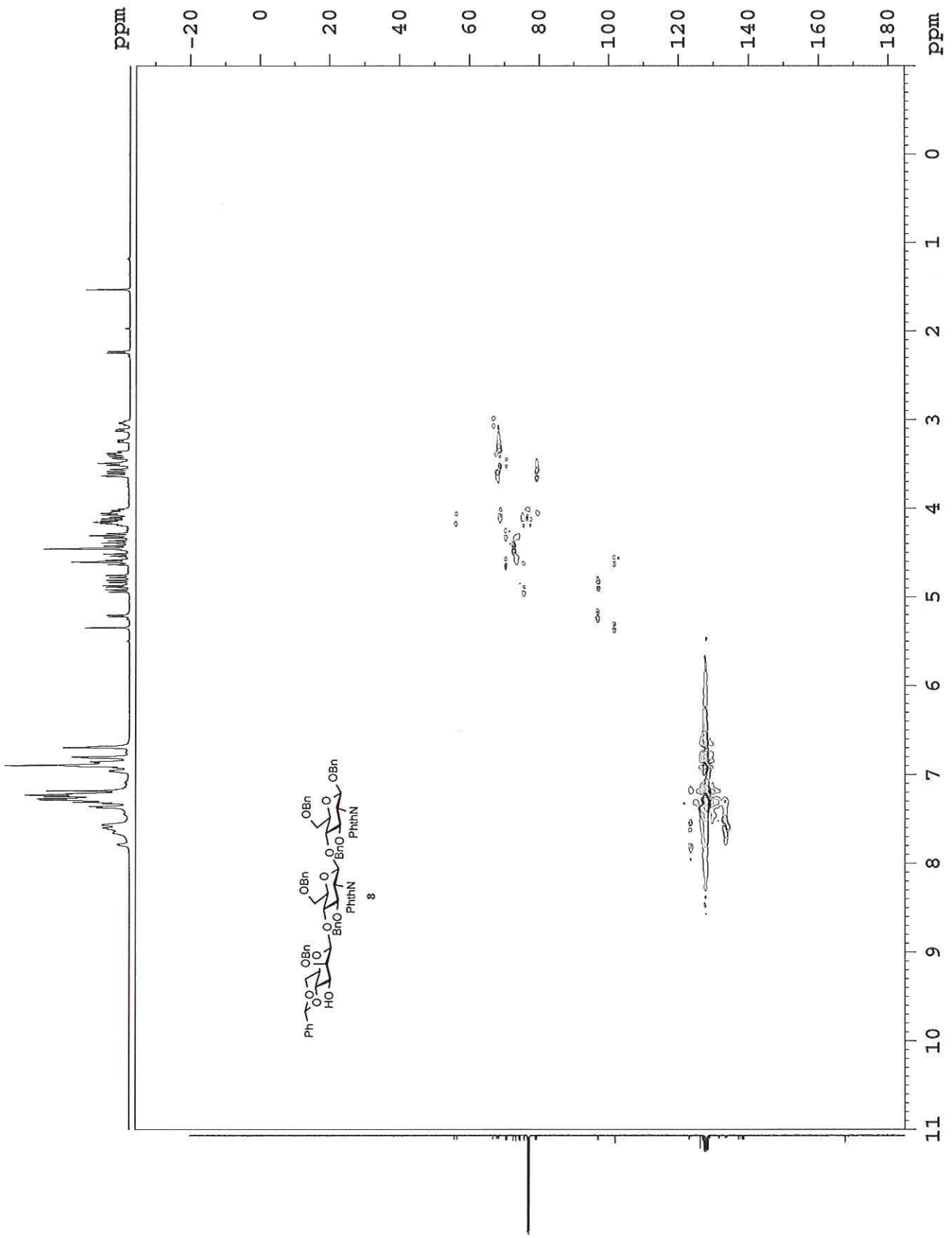
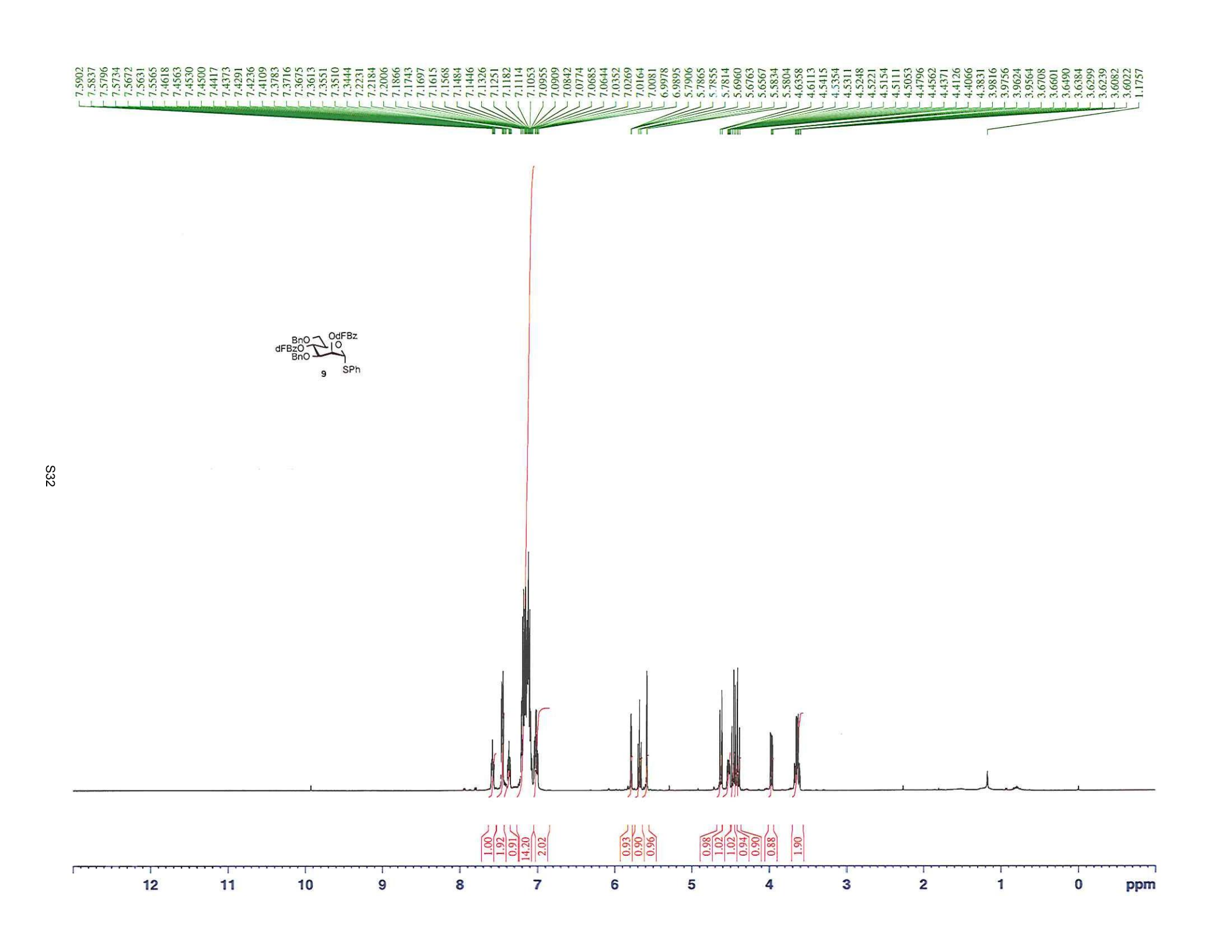
138.61
138.50
138.16
137.69
137.23
137.15
133.98
133.78
133.43
131.65
131.41
129.03
127.94
127.91
127.44
126.94
126.81
123.64
123.07
101.91
97.10
96.96
79.37
79.14
78.95
77.07
76.49
75.78
75.68
74.63
74.59
74.47
74.25
73.38
72.62
70.89
70.49
68.44
68.18
67.75
66.81
56.49
55.71
Ph
HO
OBn
BnO
PhthN
8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 10.08 ppm/cm, 1268 Hz/cm


ppm
-20
0
20
40
60
80
100
120
140
160
180
ppm
0
1
2
3
4
5
6
7
8
9
10
11
Ph
HO
OBn
BnO
PhthN
8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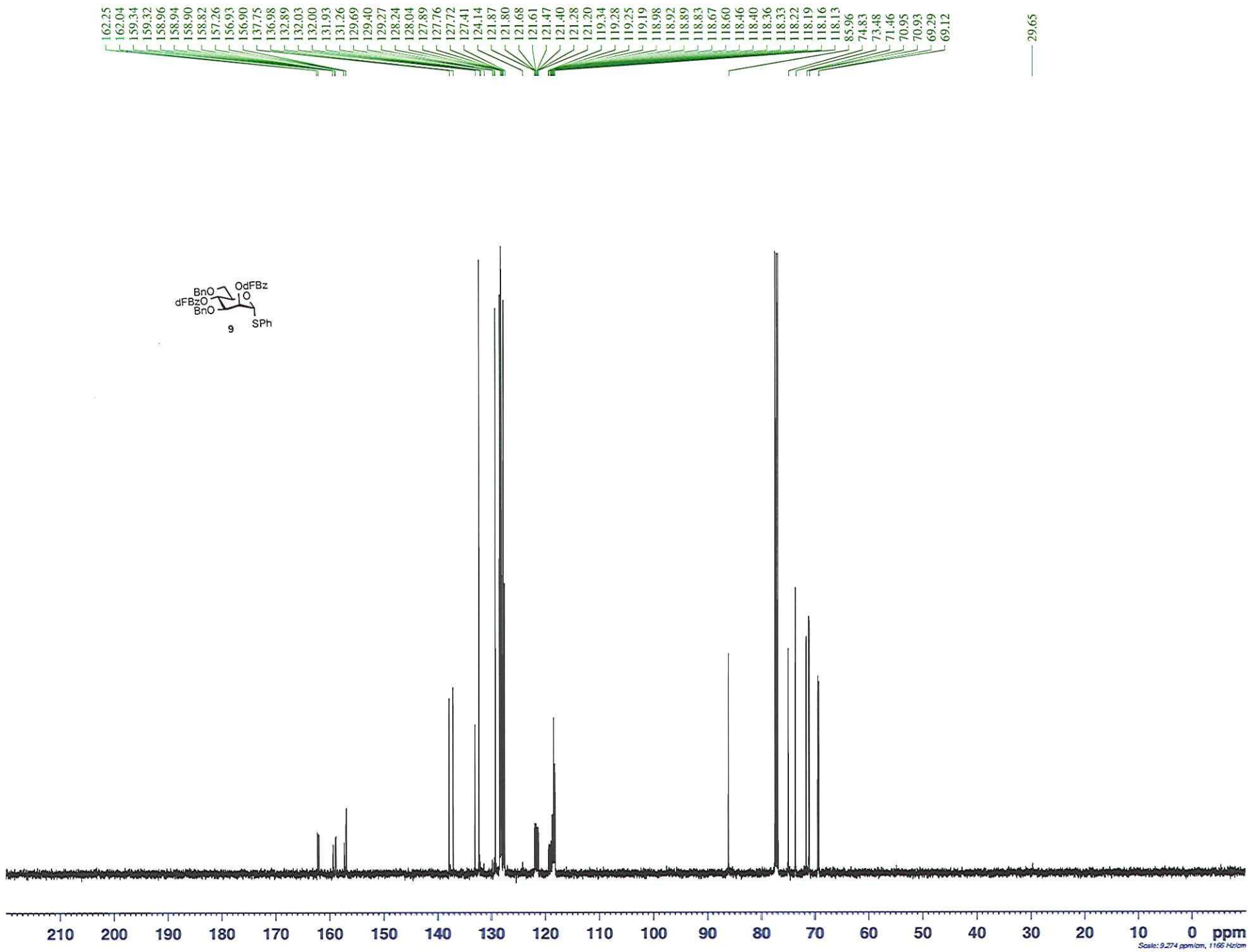
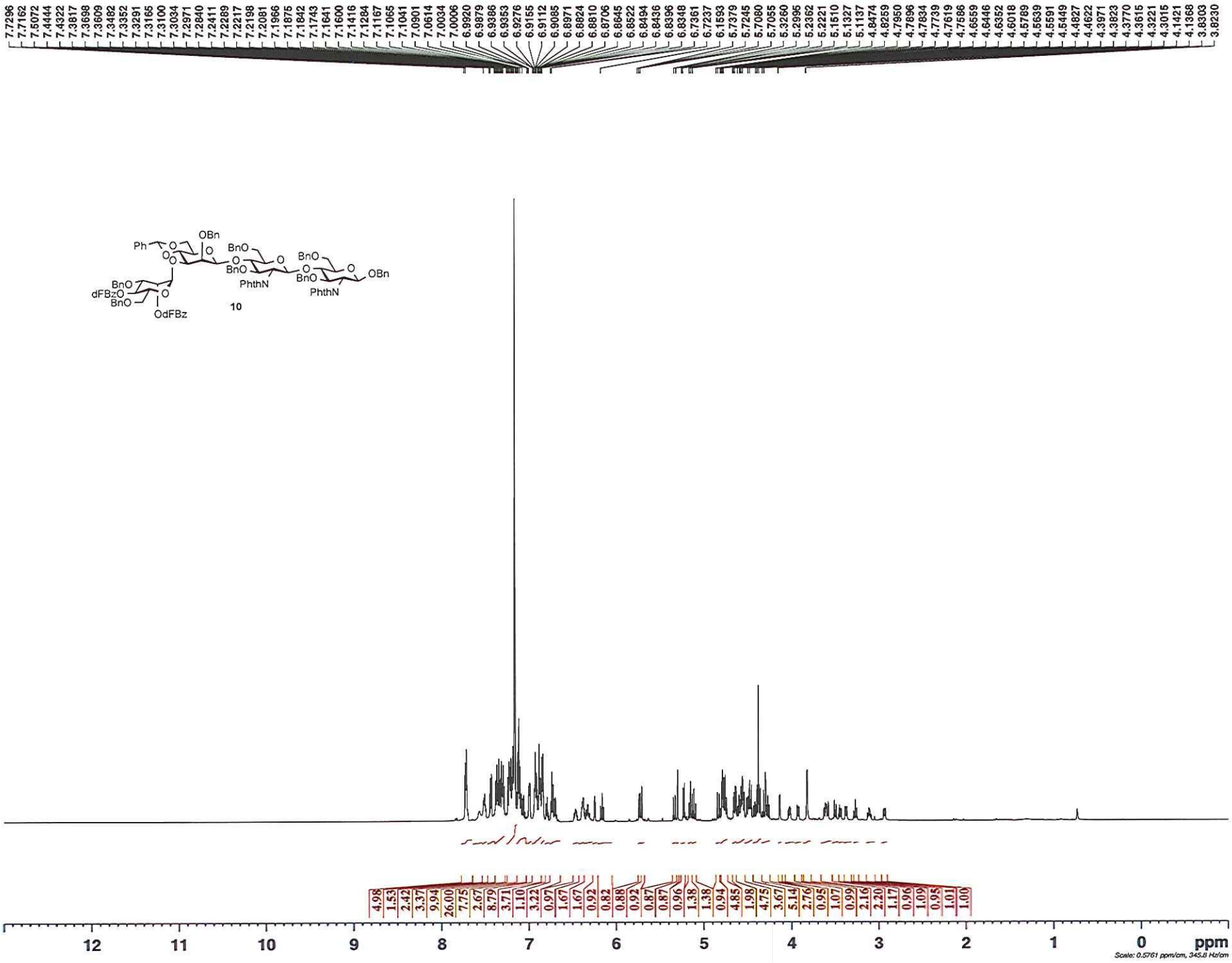
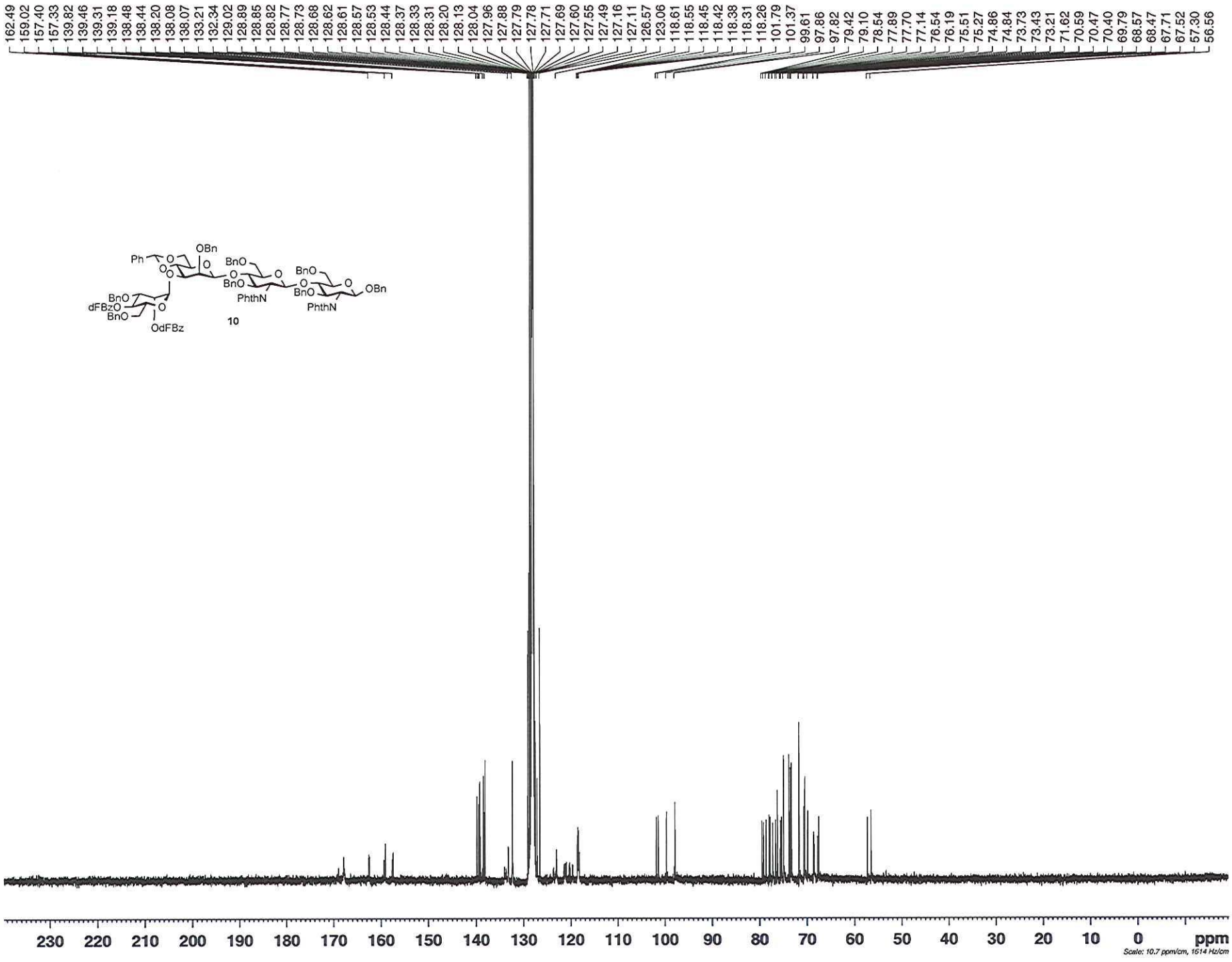
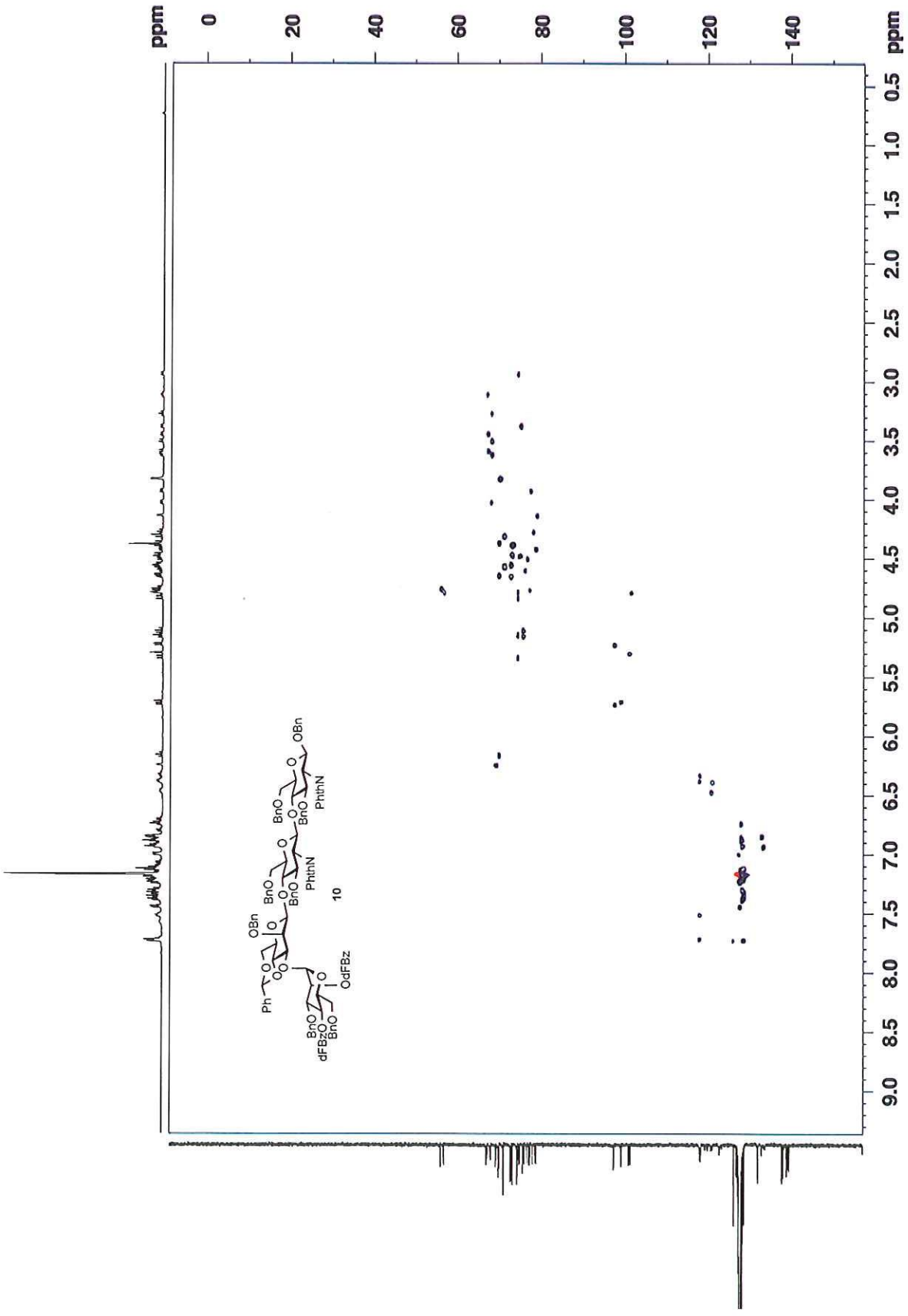
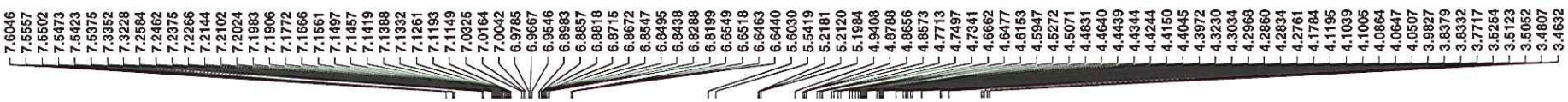
7.5796
7.5734
7.5672
7.5631
7.5565
7.4618
7.4563
7.4530
7.4500
7.4417
7.4373
7.4291
7.4236
7.4109
7.3783
7.3716
7.3675
7.3613
7.3551
7.3510
7.3444
7.2231
7.2184
7.2006
7.1866
7.1743
7.1697
7.1615
7.1568
7.1484
7.1446
7.1326
7.1251
7.1182
7.1114
7.1053
7.0955
7.0909
7.0842
7.0774
7.0685
7.0644
7.0352
7.0269
7.0164
7.0081
6.9978
6.9895
5.7906
5.7865
5.7855
5.7814
5.6960
5.6763
5.6567
5.5834
5.5804
4.6358
4.6113
4.5415
4.5354
4.5311
4.5248
4.5221
4.5154
4.5111
4.5053
4.4796
4.4562
4.4371
4.4126
4.4066
4.3831
3.9816
3.9756
3.9624
3.9564
3.6708
3.6601
3.6490
3.6384
3.6299
3.6239
3.6082
3.6022
1.1757
BnO
dFBzO
BnO
OdFBz
O
SPh
9
1.00
1.92
0.91
14.20
2.02
0.93
0.90
0.96
0.98
1.02
1.02
0.94
0.90
0.88
1.90
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


162.25
162.04
159.34
159.32
158.96
158.94
158.90
158.82
157.26
156.93
156.90
137.75
136.98
132.89
132.03
132.00
131.93
131.26
129.69
129.40
129.27
128.24
128.04
127.89
127.76
127.72
127.41
124.14
121.87
121.80
121.68
121.61
121.47
121.40
121.28
121.20
119.34
119.28
119.25
119.19
118.98
118.92
118.89
118.83
118.67
118.60
118.46
118.40
118.36
118.33
118.22
118.19
118.16
118.13
85.96
74.83
73.48
71.46
70.95
70.93
69.29
69.12
29.65
BnO
OdFBz
dFBzO
BnO
SPh
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.274 ppm/cm, 1166 Hz/cm


7.7296 7.7162 7.5072 7.4444 7.4322 7.3817 7.3698 7.3609 7.3482 7.3352 7.3291 7.3165 7.3100 7.3034 7.2971 7.2840 7.2411 7.2289 7.2217 7.2198 7.2081 7.1966 7.1875 7.1842 7.1743 7.1641 7.1600 7.1416 7.1284 7.1167 7.1065 7.1041 7.0901 7.0614 7.0034 7.0006 6.9920 6.9879 6.9386 6.9353 6.9276 6.9155 6.9112 6.9085 6.8971 6.8824 6.8810 6.8706 6.8645 6.8522 6.8494 6.8436 6.8396 6.8348 6.7361 6.7237 6.1593 5.7379 5.7245 5.7080 5.7055 5.3260 5.2995 5.2362 5.2221 5.1510 5.1327 5.1137 4.8474 4.8259 4.7950 4.7896 4.7834 4.7739 4.7619 4.7586 4.6559 4.6446 4.6352 4.6018 4.5789 4.5639 4.5591 4.5449 4.4827 4.4622 4.3971 4.3823 4.3770 4.3615 4.3221 4.3015 4.1421 4.1368 3.8303 3.8230
Ph
OBn
BnO
BnO
BnO
BnO
BnO
OBn
PhthN
PhthN
dFBzO
BnO
OdFBz
10
4.98 1.53 2.42 3.37 9.94 26.00 7.75 2.67 8.79 3.71 1.10 3.22 0.97 1.67 1.67 0.92 0.82 0.88 0.92 0.87 0.87 0.96 1.38 1.38 0.94 4.85 1.98 4.75 3.67 5.14 2.76 0.95 1.07 0.99 2.16 2.20 1.17 0.96 1.09 0.95 1.01 1.00
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
Scale: 0.5761 ppm/cm, 345.8 Hz/cm


162.49
159.02
157.40
157.33
139.82
139.46
139.31
139.18
138.48
138.44
138.20
138.08
138.07
133.21
132.34
129.02
128.89
128.85
128.82
128.77
128.73
128.68
128.62
128.61
128.57
128.53
128.44
128.37
128.33
128.31
128.20
128.13
128.04
127.96
127.88
127.79
127.78
127.71
127.69
127.60
127.55
127.49
127.16
127.11
126.57
123.06
118.61
118.55
118.45
118.42
118.38
118.31
118.26
101.79
101.37
99.61
97.86
97.82
79.42
79.10
78.54
77.89
77.70
77.14
76.54
76.19
75.51
75.27
74.86
74.84
73.73
73.43
73.21
71.62
70.59
70.47
70.40
69.79
68.57
68.47
67.71
67.52
57.30
56.56
Ph
OBn
BnO
BnO
PhthN
BnO
BnO
BnO
OBn
PhthN
dFBzO
BnO
OdFBz
10
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 10.7 ppm/cm, 1614 Hz/cm


ppm
0
20
40
60
80
100
120
140
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
Ph
OBn
BnO
BnO
PhthN
BnO
BnO
PhthN
BnO
BnO
OBn
PhthN
dFBzO
BnO
OdFBz
10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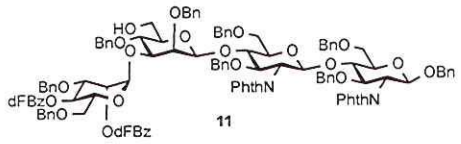
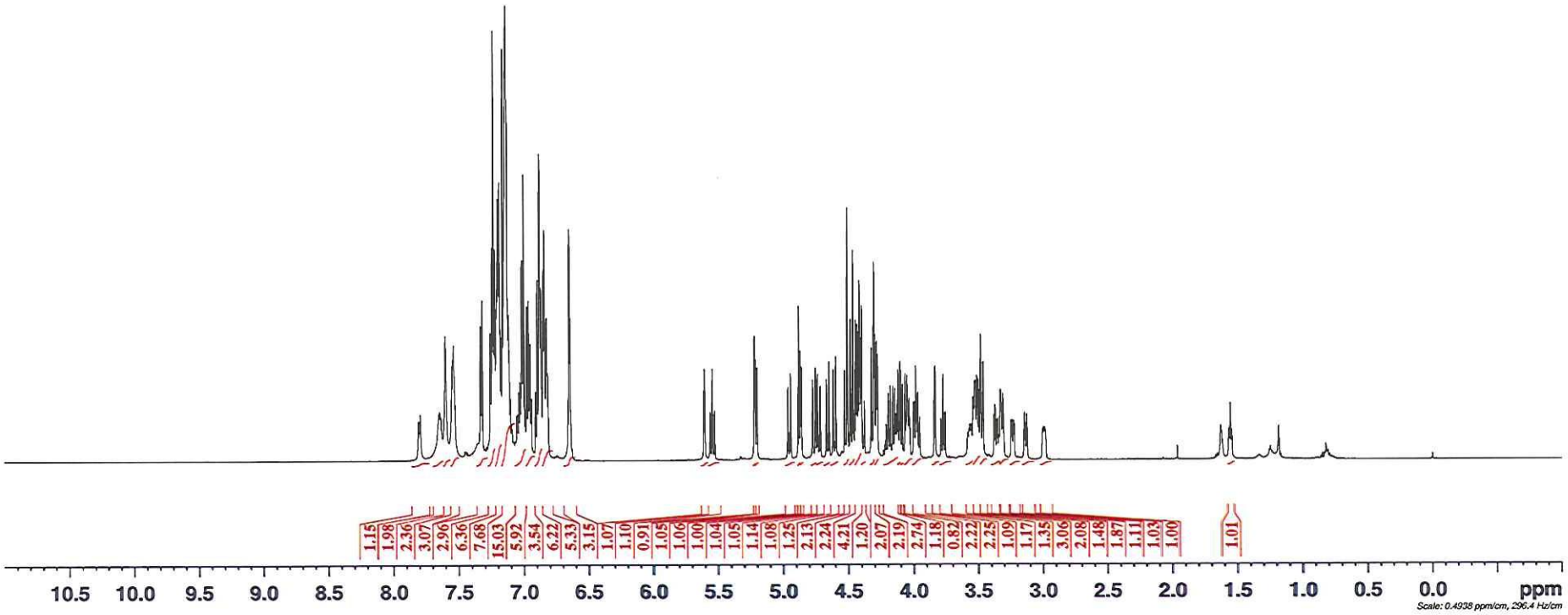
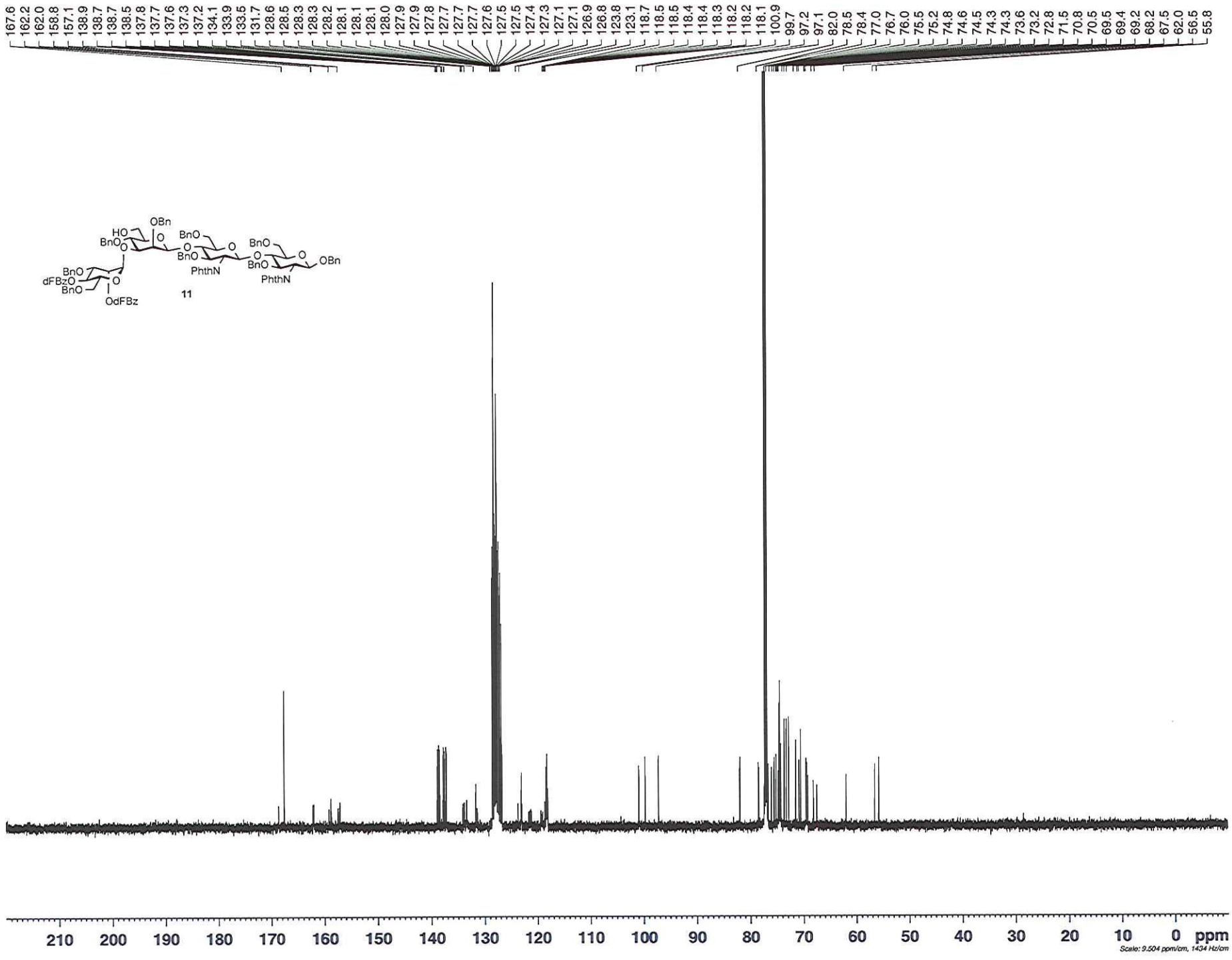
7.5557
7.5502
7.5473
7.5423
7.5375
7.3352
7.3228
7.2584
7.2462
7.2375
7.2266
7.2144
7.2102
7.2024
7.1983
7.1906
7.1772
7.1666
7.1661
7.1497
7.1457
7.1419
7.1388
7.1332
7.1261
7.1193
7.1149
7.0325
7.0164
7.0042
6.9785
6.9667
6.9546
6.8983
6.8857
6.8818
6.8715
6.8672
6.8547
6.8495
6.8438
6.8288
6.8199
6.6549
6.6518
6.6463
6.6440
5.6030
5.5419
5.2181
5.2120
5.1984
4.9408
4.8788
4.8656
4.8573
4.7713
4.7497
4.7341
4.6662
4.6477
4.6153
4.5947
4.5272
4.5071
4.4831
4.4640
4.4439
4.4344
4.4244
4.4150
4.4045
4.3972
4.3230
4.3034
4.2968
4.2860
4.2834
4.2761
4.1784
4.1195
4.1039
4.1005
4.0864
4.0647
4.0507
3.9827
3.8379
3.8332
3.7717
3.5254
3.5123
3.5052
3.4807
3.4632


OBn
HO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
dFBzO
BnO
OdFBz
PhthN
PhthN
OBn

11


1.15
1.98
2.36
3.07
2.96
6.36
7.68
15.03
5.92
3.54
6.22
5.33
3.15
1.07
1.10
0.91
1.05
1.06
1.00
1.04
1.05
1.14
1.08
1.25
2.13
2.24
4.21
1.20
2.07
2.19
2.74
1.18
0.82
2.22
2.25
1.09
1.17
1.35
3.06
2.08
1.48
1.87
1.11
1.03
1.00
1.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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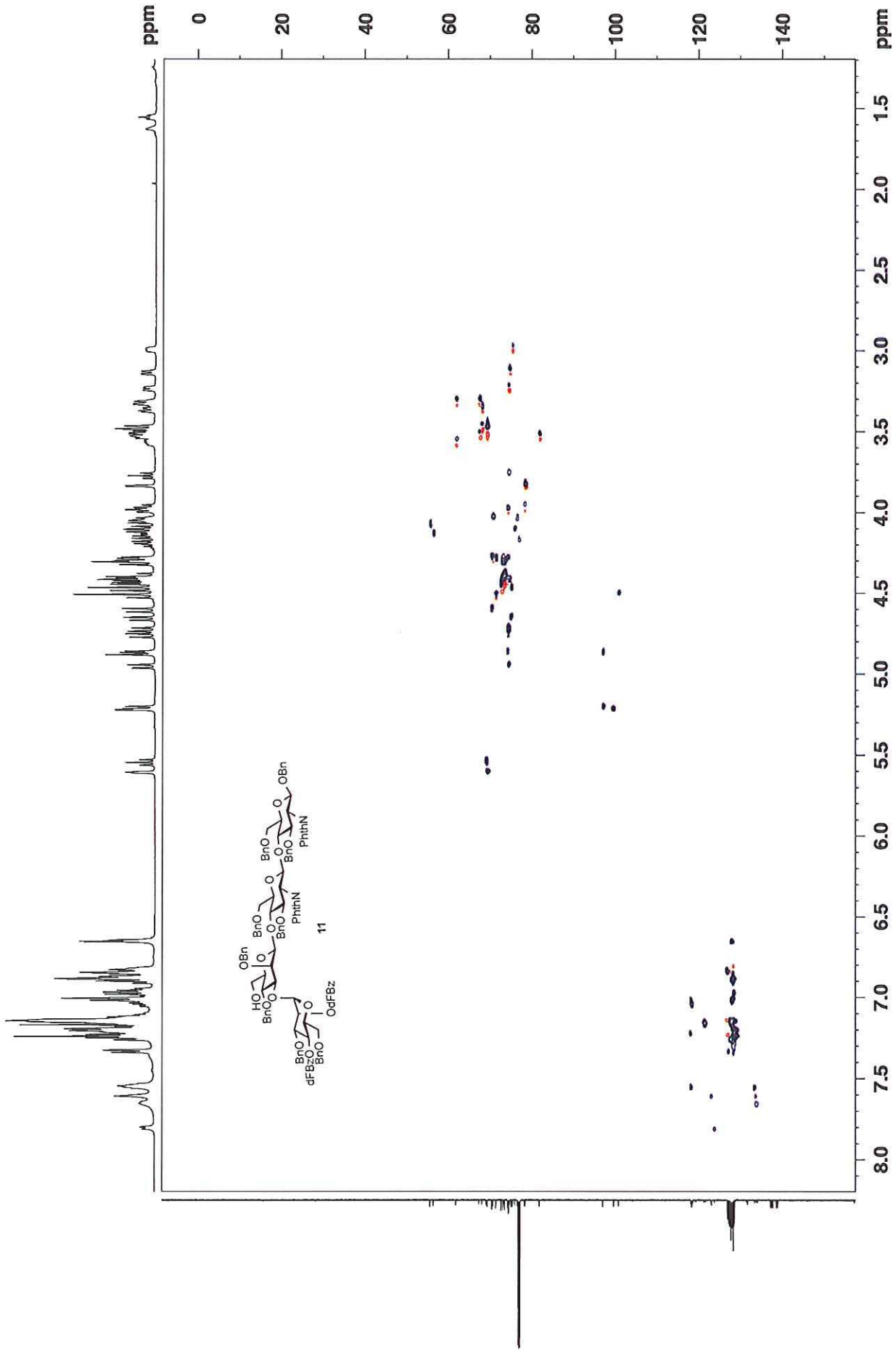
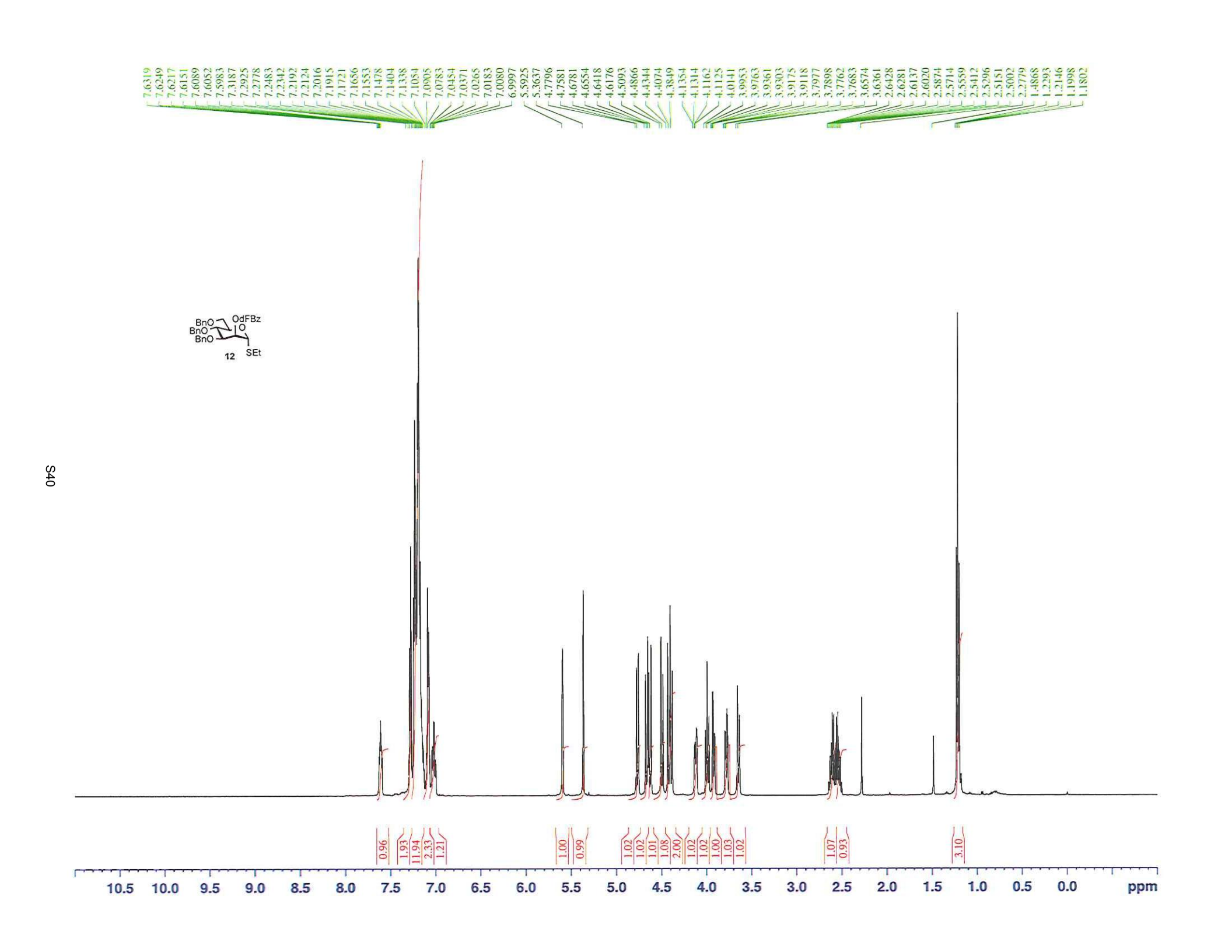
157.1
138.9
138.7
138.7
138.5
137.8
137.7
137.6
137.3
137.2
134.1
133.9
133.5
131.7
128.6
128.5
128.3
128.3
128.2
128.1
128.1
128.1
128.0
127.9
127.9
127.8
127.7
127.7
127.7
127.6
127.5
127.5
127.4
127.3
127.1
127.1
126.9
126.8
123.8
123.1
118.7
118.5
118.5
118.4
118.4
118.3
118.2
118.2
118.1
100.9
99.7
97.2
97.1
82.0
78.5
78.4
77.0
76.7
76.0
75.5
75.2
74.8
74.6
74.5
74.3
74.3
73.6
73.2
72.8
71.5
70.8
70.5
69.5
69.4
69.2
68.2
67.5
62.0
56.5
55.8
HO
OBn
BnO
BnO
BnO
BnO
BnO
BnO
BnO
BnO
dFBzO
BnO
OdFBz
PhthN
PhthN
OBn
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.504 ppm/cm, 1434 Hz/cm


ppm
0
20
40
60
80
100
120
140
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
HO
BnO
OBn
O
BnO
BnO
O
O
PhthN
BnO
BnO
O
O
PhthN
BnO
BnO
O
O
OBn
BnO
dFBzO
BnO
O
OdFBz
11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7.6217
7.6151
7.6089
7.6052
7.5983
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7.2925
7.2778
7.2483
7.2342
7.2192
7.2124
7.2016
7.1915
7.1721
7.1656
7.1553
7.1478
7.1404
7.1338
7.1054
7.0905
7.0783
7.0454
7.0371
7.0265
7.0183
7.0080
6.9997
5.5925
5.3637
4.7796
4.7581
4.6781
4.6554
4.6418
4.6176
4.5093
4.4866
4.4344
4.4074
4.3849
4.1354
4.1314
4.1162
4.1125
4.0141
3.9953
3.9763
3.9361
3.9303
3.9175
3.9118
3.7977
3.7898
3.7762
3.7683
3.6574
3.6361
2.6428
2.6281
2.6137
2.6020
2.5874
2.5714
2.5559
2.5412
2.5296
2.5151
2.5002
2.2779
1.4868
1.2293
1.2146
1.1998
1.1802
BnO
BnO
BnO
OdFBz
O
SEt
12
0.96
1.93
11.94
2.33
1.21
1.00
0.99
1.02
1.02
1.01
1.08
2.00
1.02
1.02
1.00
1.03
1.02
1.07
0.93
3.10
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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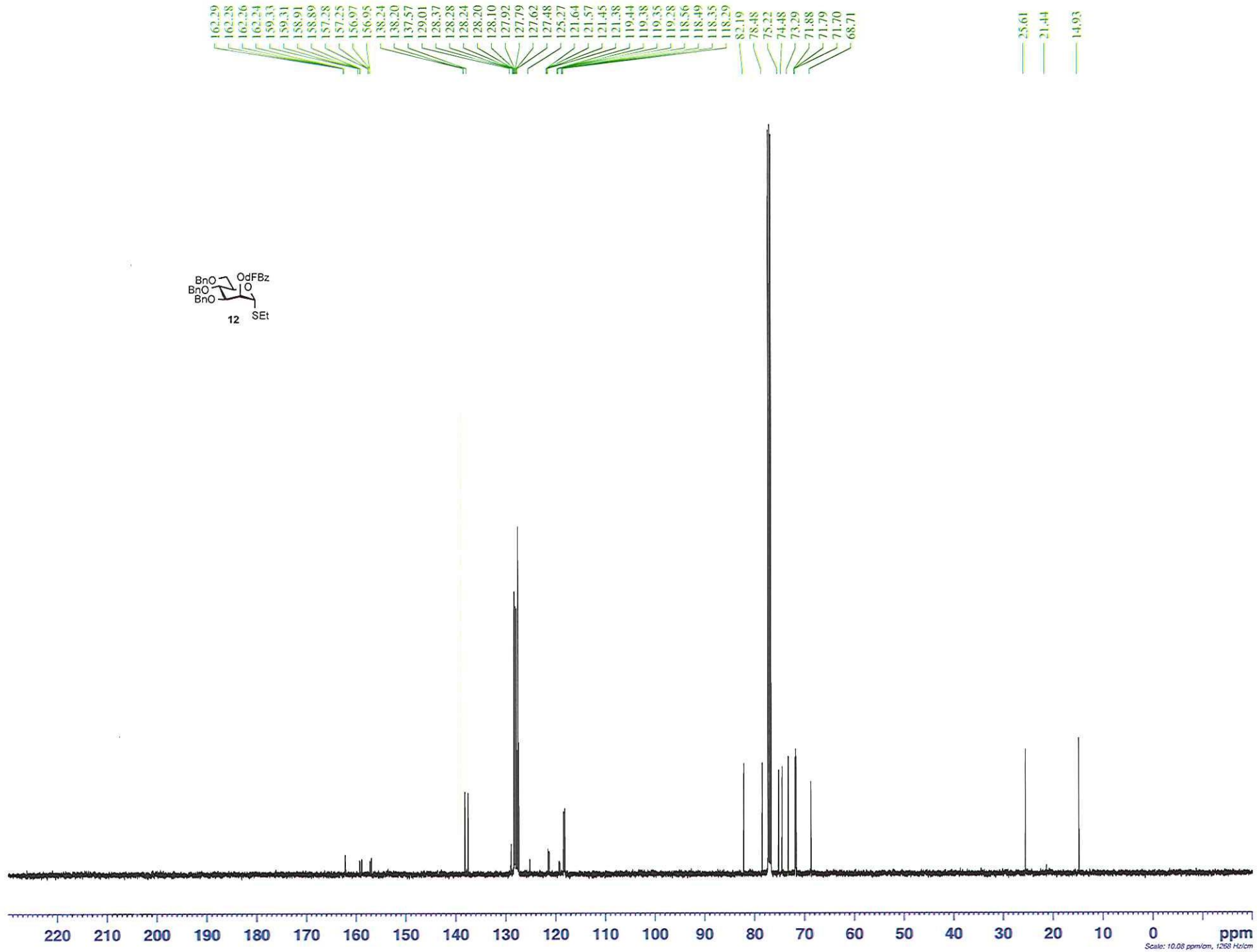
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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138.20
137.57
129.01
128.37
128.28
128.24
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128.10
127.92
127.79
127.62
127.48
125.27
121.64
121.57
121.45
121.38
119.44
119.38
119.35
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118.35
118.29
82.19
78.48
75.22
74.48
73.29
71.88
71.79
71.70
68.71
25.61
21.44
14.93
BnO
BnO
BnO
OdFBz
O
SEt
12
220
210
200
190
180
170
160
150
140
130
120
110
100
90
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70
60
50
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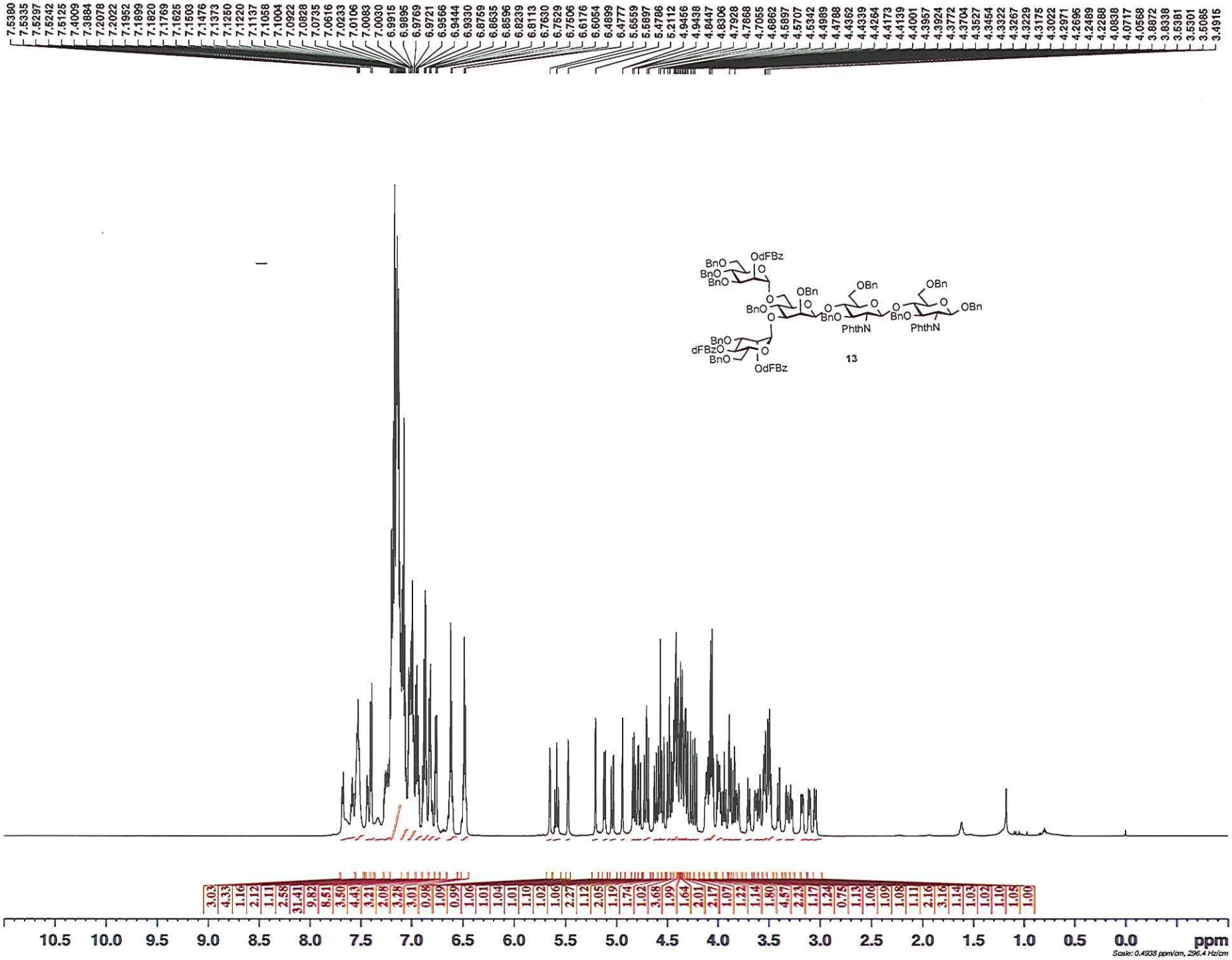
30
20
10
0
ppm
Scale: 10.08 ppm/cm, 1268 Hz/cm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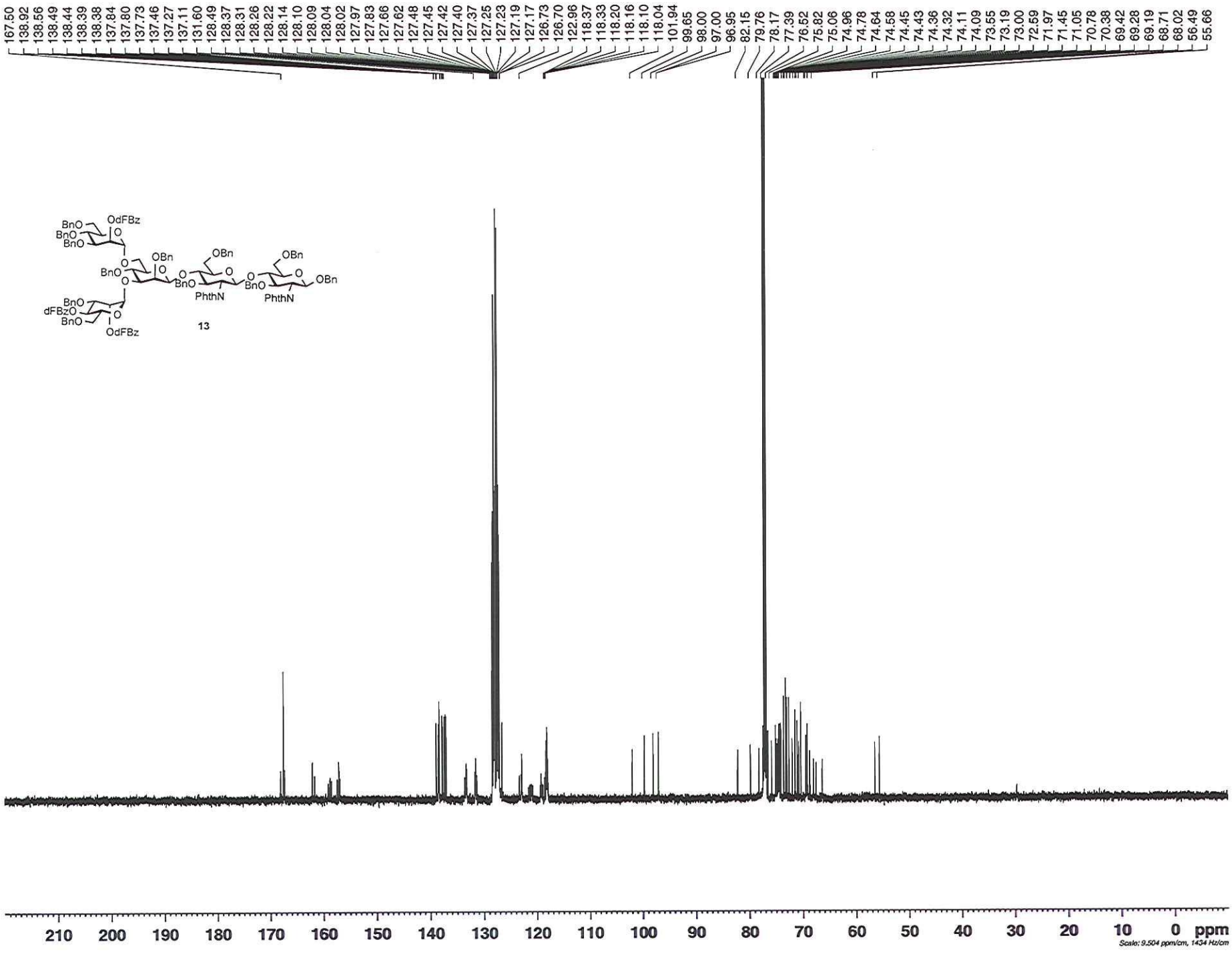
BnO
BnO
BnO
OdFBz
O
OBn
PhthN
dFBzO
13
3.03 4.33 1.16 2.12 1.11 2.58 31.41 9.82 8.51 3.50 4.43 3.21 2.05 3.28 3.01 0.98 1.09 0.99 1.06 1.01 1.04 1.01 1.10 1.02 1.06 2.27 1.12 2.05 1.19 1.74 1.02 3.68 1.99 1.64 2.01 2.17 1.07 1.22 1.14 1.80 4.57 2.23 1.17 1.24 0.75 1.13 1.06 1.09 1.08 1.11 2.16 3.16 1.14 1.03 1.02 1.10 1.05 1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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138.56
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137.46
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137.11
131.60
128.49
128.37
128.31
128.26
128.22
128.14
128.10
128.09
128.04
128.02
127.97
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127.40
127.37
127.25
127.23
127.19
127.17
126.73
126.70
122.96
118.37
118.33
118.20
118.16
118.10
118.04
101.94
99.65
98.00
97.00
96.95
82.15
79.76
78.17
77.39
76.52
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75.06
74.96
74.78
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74.58
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74.11
74.09
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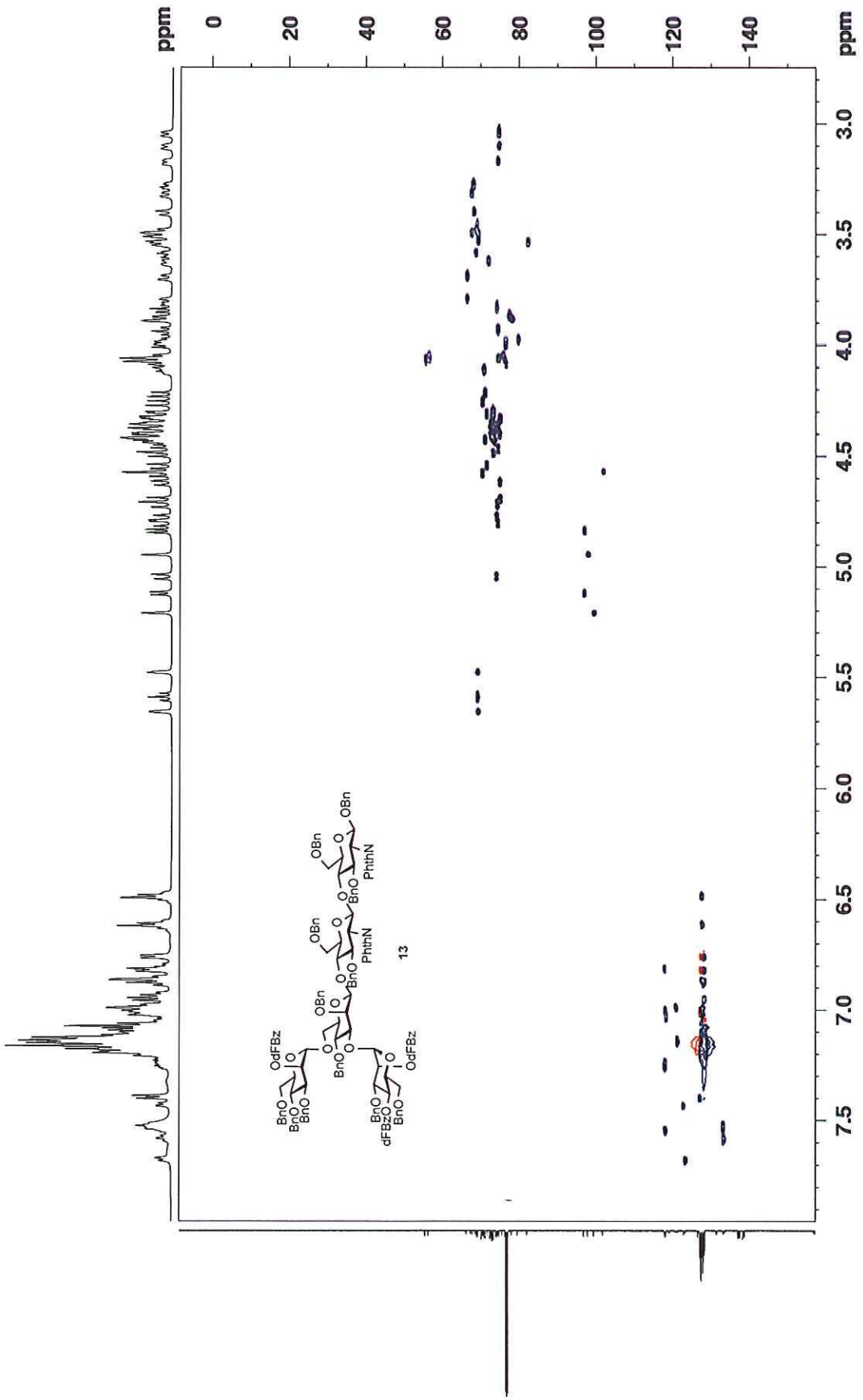
73.19
73.00
72.59
71.97
71.45
71.05
70.78
70.38
69.42
69.28
69.19
68.71
68.02
56.49
55.66
BnO
OdFBz
BnO
BnO
O
OBn
OBn
OBn
BnO
O
O
O
O
O
O
BnO
BnO
BnO
PhthN
BnO
PhthN
OBn
BnO
dFBzO
BnO
O
OdFBz
13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.504 ppm/cm, 1434 Hz/cm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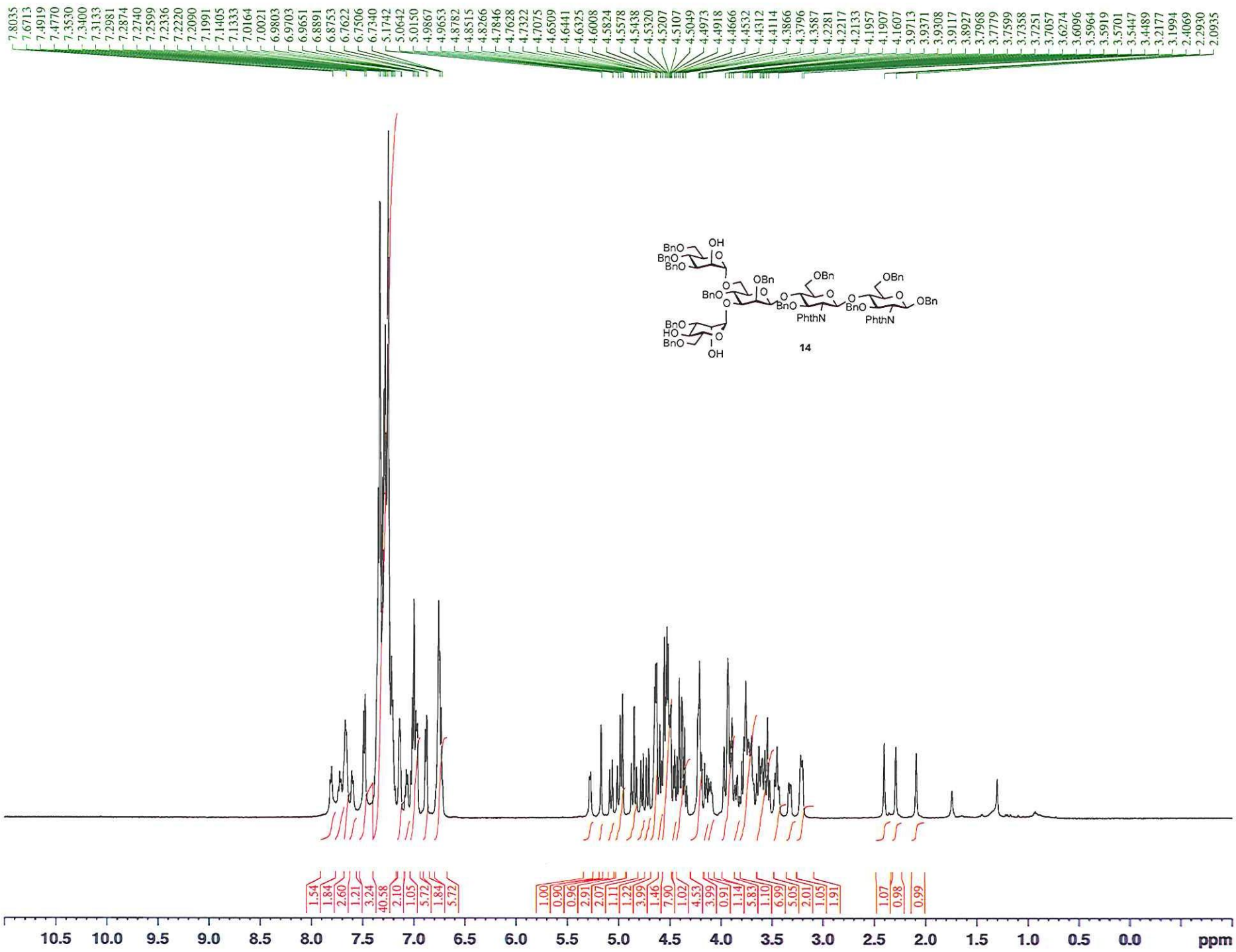
20
40
60
80
100
120
140
ppm
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
BnO
OdFBz
OBn
PhthN
13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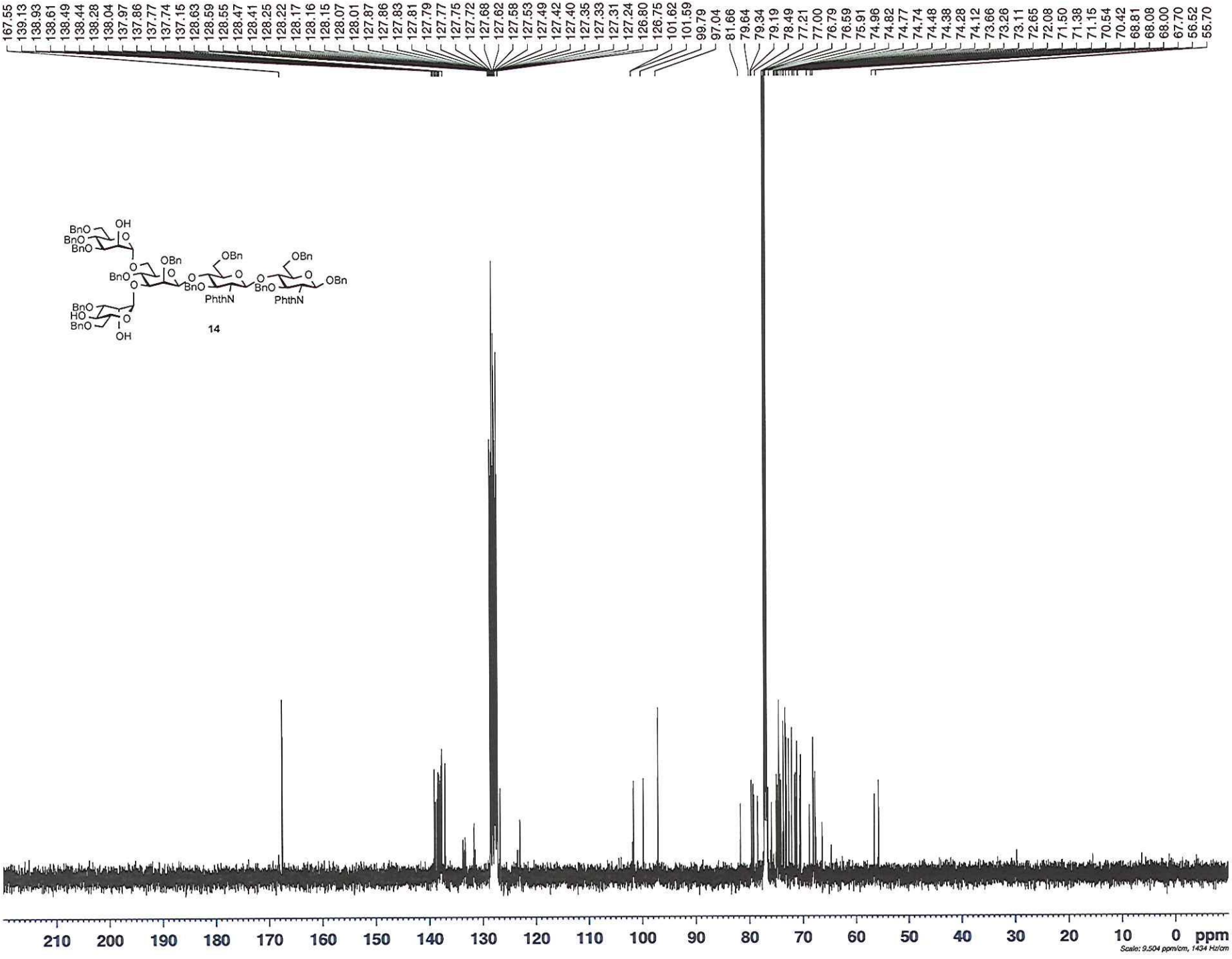
BnO OH BnO BnO OBn OBn OBn BnO BnO BnO PhthN BnO PhthN OBn BnO HO BnO OH
14
1.54 1.84 2.60 1.21 3.24 40.58 2.10 1.05 5.72 1.84 5.72
1.00 0.90 0.96 2.91 2.07 1.11 1.22 3.99 1.46 7.90 1.02 4.53 3.99 0.91 1.14 5.83 1.10 6.99 5.05 2.01 1.05 1.91
1.07 0.98 0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm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128.59
128.55
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128.41
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128.22
128.17
128.16
128.15
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128.01
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127.86
127.83
127.81
127.79
127.77
127.75
127.72
127.68
127.62
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127.49
127.42
127.40
127.35
127.33
127.31
127.24
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126.75
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101.59
99.79
97.04
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72.08
71.50
71.38
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70.54
70.42
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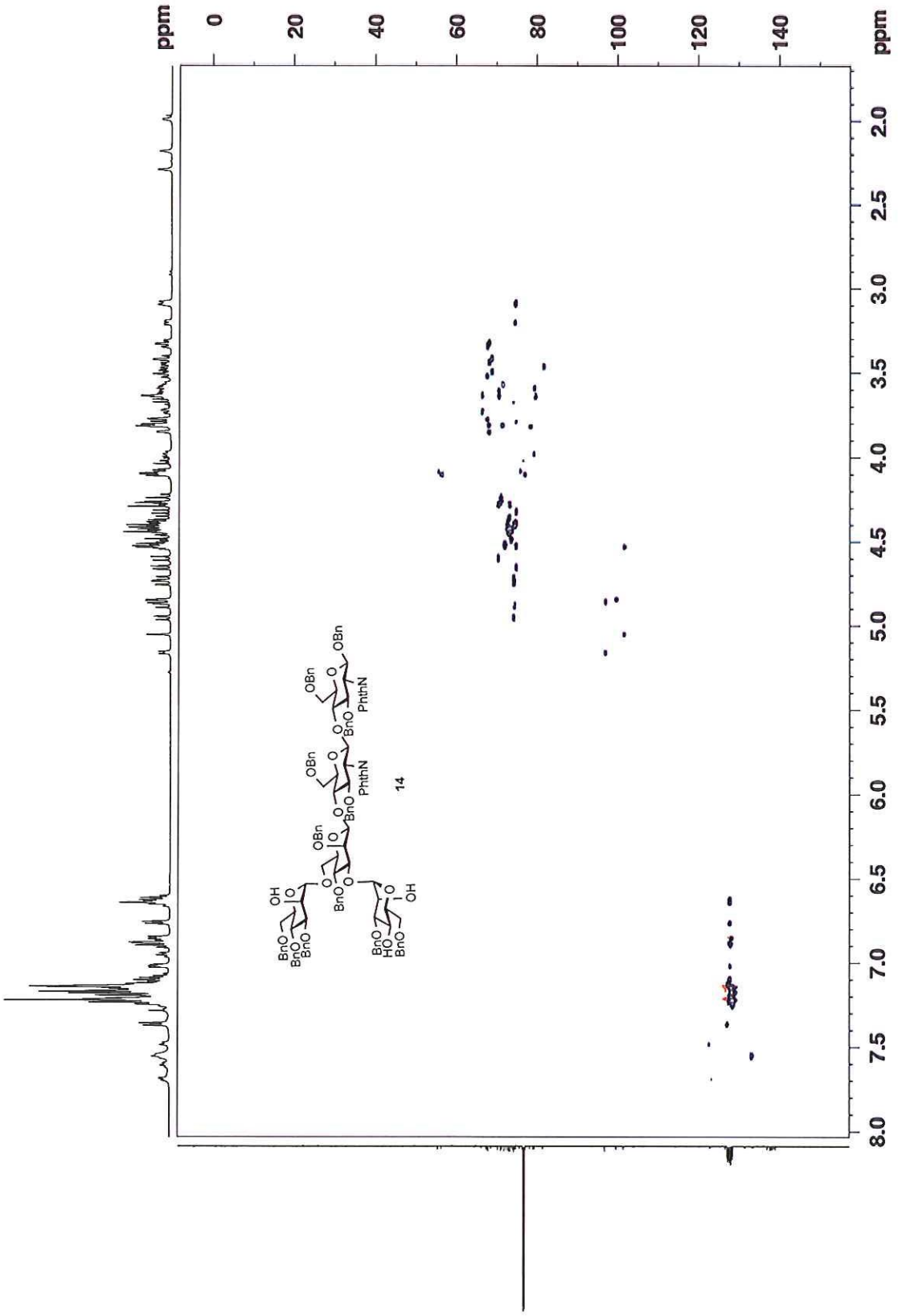
68.08
68.00
67.70
56.52
55.70
BnO
OH
BnO
O
BnO
OBn
O
BnO
O
O
BnO
OBn
O
BnO
PhthN
O
BnO
OBn
O
BnO
PhthN
OBn
BnO
HO
BnO
O
OH
14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.504 ppm/cm, 1434 Hz/cm


ppm
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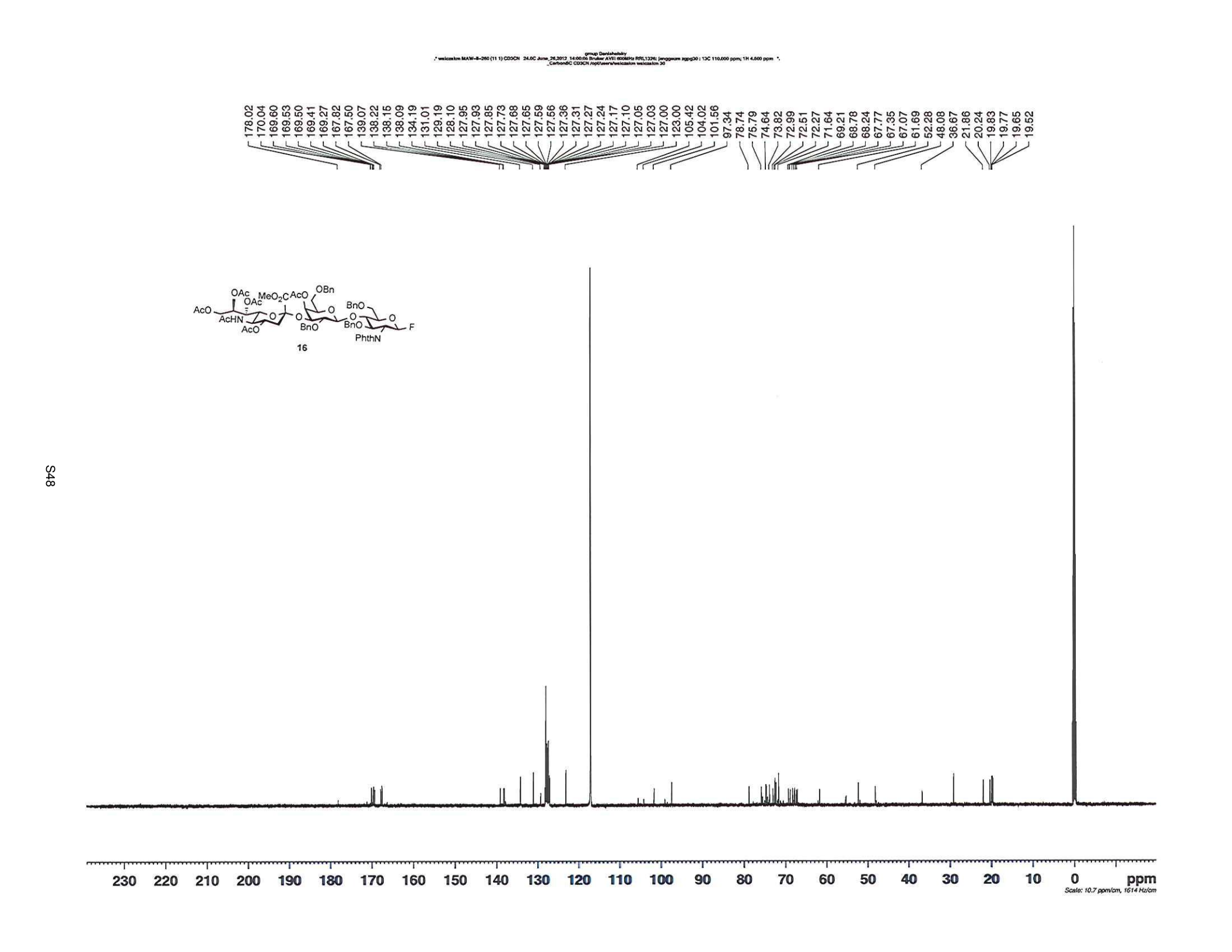
20
40
60
80
100
120
140
ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
14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169.41
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167.82
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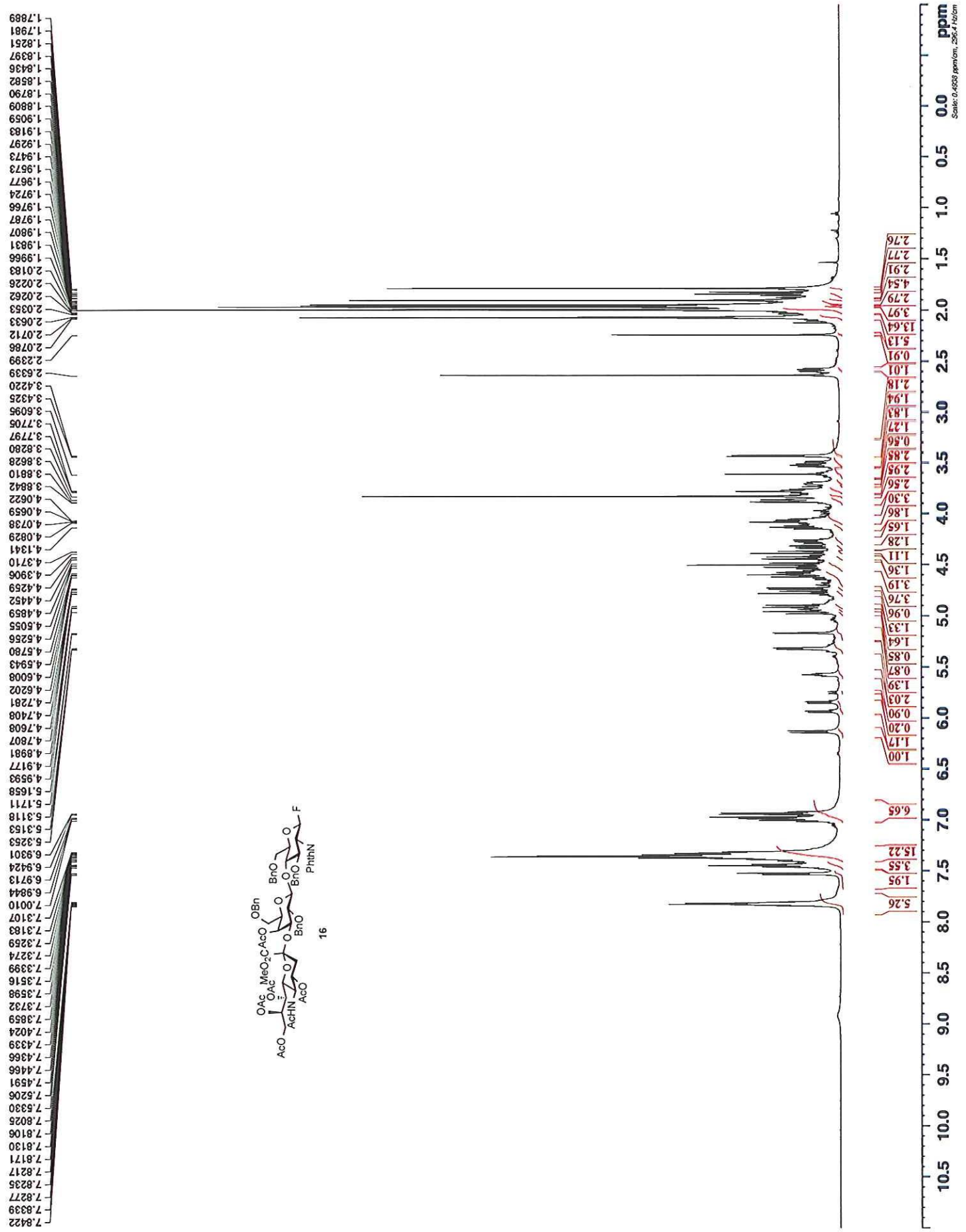
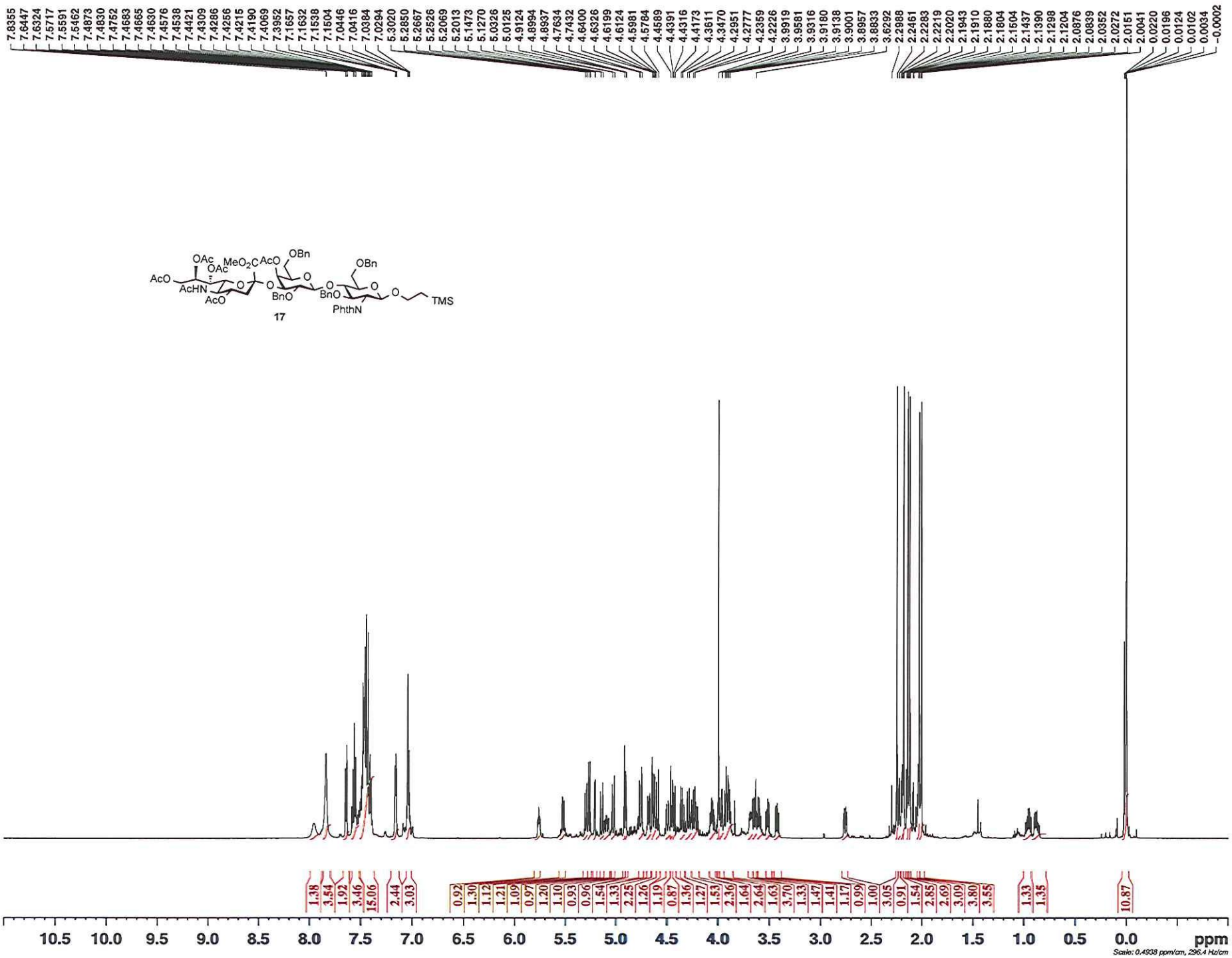
139.07
138.22
138.15
138.09
134.19
131.01
129.19
128.10
127.95
127.93
127.85
127.73
127.68
127.65
127.59
127.56
127.36
127.31
127.27
127.24
127.17
127.10
127.05
127.03
127.00
123.00
105.42
104.02
101.56
97.34
78.74
75.79
74.64
73.82
72.99
72.51
72.27
71.64
69.21
68.78
68.24
67.77
67.35
67.07
61.69
52.28
48.08
36.67
21.86
20.24
19.83
19.77
19.65
19.52
OAc
OAc
MeO2C
AcO
OBn
AcO
AcHN
AcO
BnO
BnO
BnO
PhthN
F
16
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 10.7 ppm/cm, 1614 Hz/cm


16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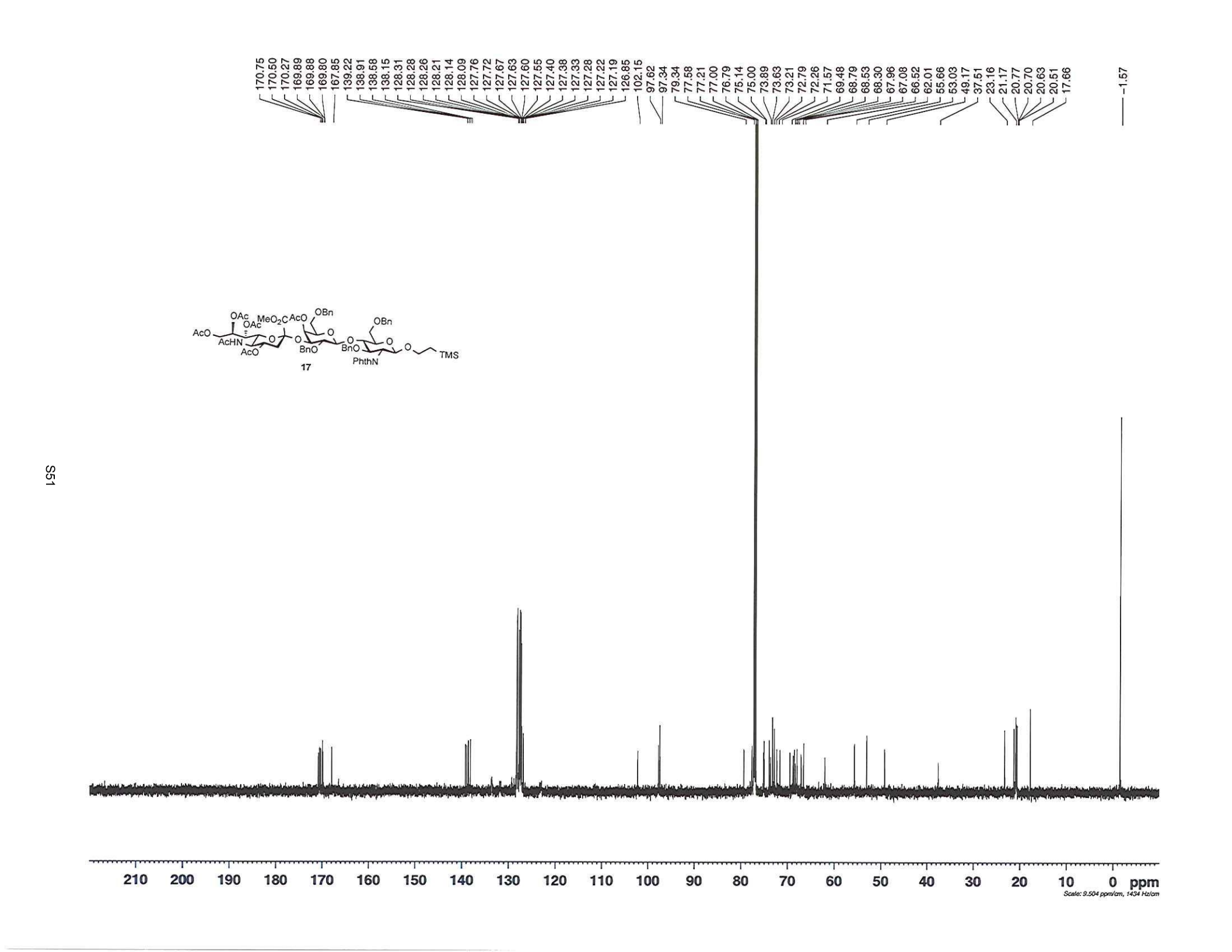
AcO
OAc
OAc
AcHN
AcO
MeO2C
AcO
OBn
BnO
O
O
BnO
OBn
O
O
PhthN
TMS
17
1.38 3.54 1.92 3.46 15.06 2.44 3.03 0.92 1.30 1.12 1.21 1.09 0.97 1.20 1.10 0.93 0.96 1.54 1.33 2.25 1.26 1.19 0.87 1.36 1.27 1.53 2.36 1.64 2.64 1.63 3.70 1.33 1.47 1.41 1.17 0.99 1.00 3.05 0.91 1.54 2.85 2.69 3.09 3.80 3.55 1.33 1.35 10.87
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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169.80
167.85
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138.58
138.15
128.31
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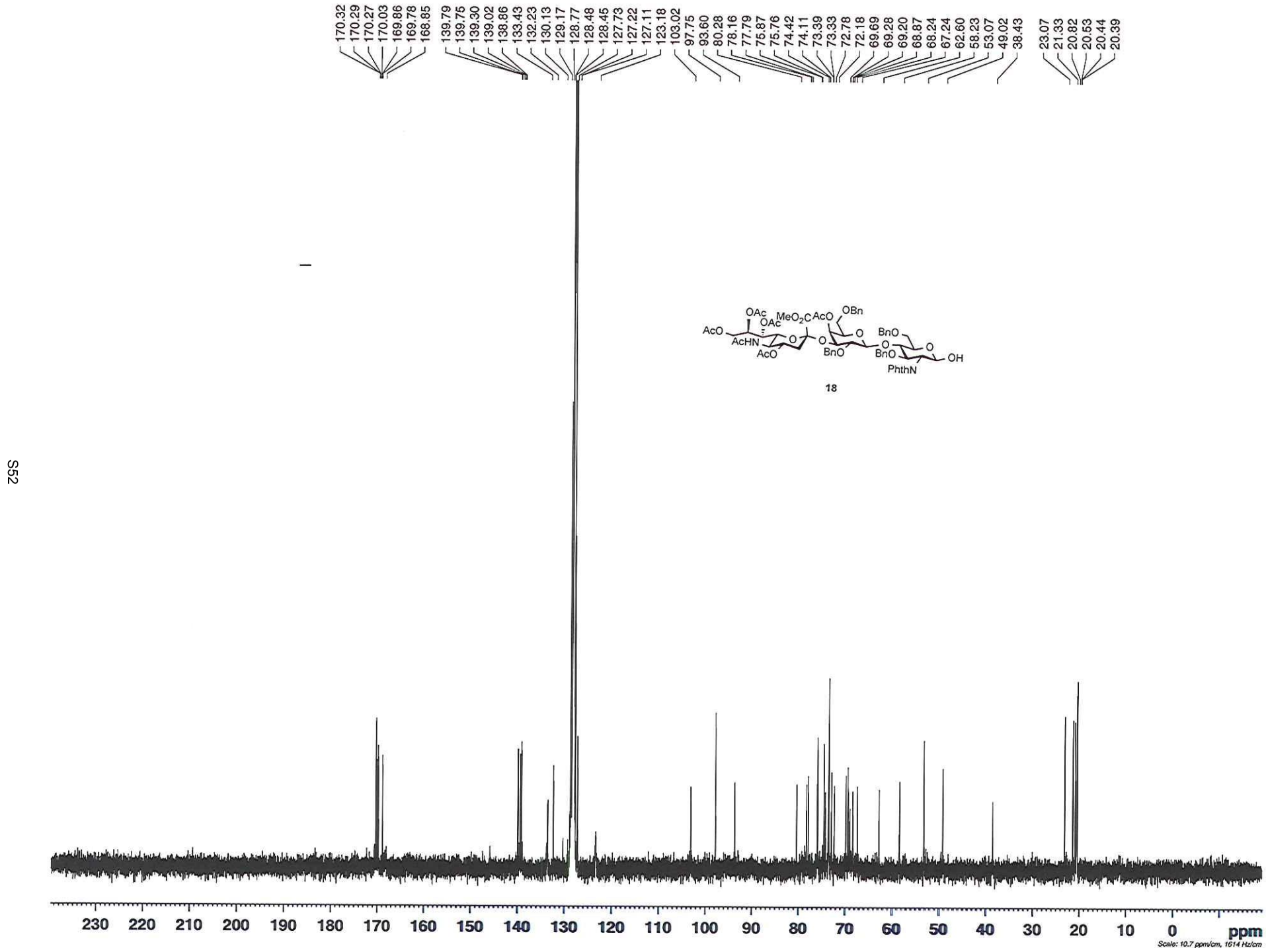
128.26
128.21
128.14
128.09
127.76
127.72
127.67
127.63
127.60
127.55
127.40
127.38
127.33
127.28
127.22
127.19
126.85
102.15
97.62
97.34
79.34
77.58
77.21
77.00
76.79
75.14
75.00
73.89
73.63
73.21
72.79
72.26
71.57
69.48
68.79
68.53
68.30
67.96
67.08
66.52
62.01
55.66
53.03
49.17
37.51
23.16
21.17
20.77
20.70
20.63
20.51
17.66
-1.57
OAc
OAc
MeO2C
AcO
OBn
OBn
AcO
AcHN
AcO
BnO
BnO
PhthN
TMS
17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.504 ppm/cm, 1434 Hz/cm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168.85
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139.75
139.30
139.02
138.86
133.43
132.23
130.13
129.17
128.77
128.48
128.45
127.73
127.22
127.11
123.18
103.02
97.75
93.60
80.28
78.16
77.79
75.87
75.76
74.42
74.11
73.39
73.33
72.78
72.18
69.69
69.28
69.20
68.87
68.24
67.24
62.60
58.23
53.07
49.02
38.43
23.07
21.33
20.82
20.53
20.44
20.39
OAc
OAc
MeO2C
AcO
OBn
AcO
AcHN
AcO
BnO
BnO
BnO
PhthN
OH
18
230
220
210
200
190
180
170
160
150
140
130
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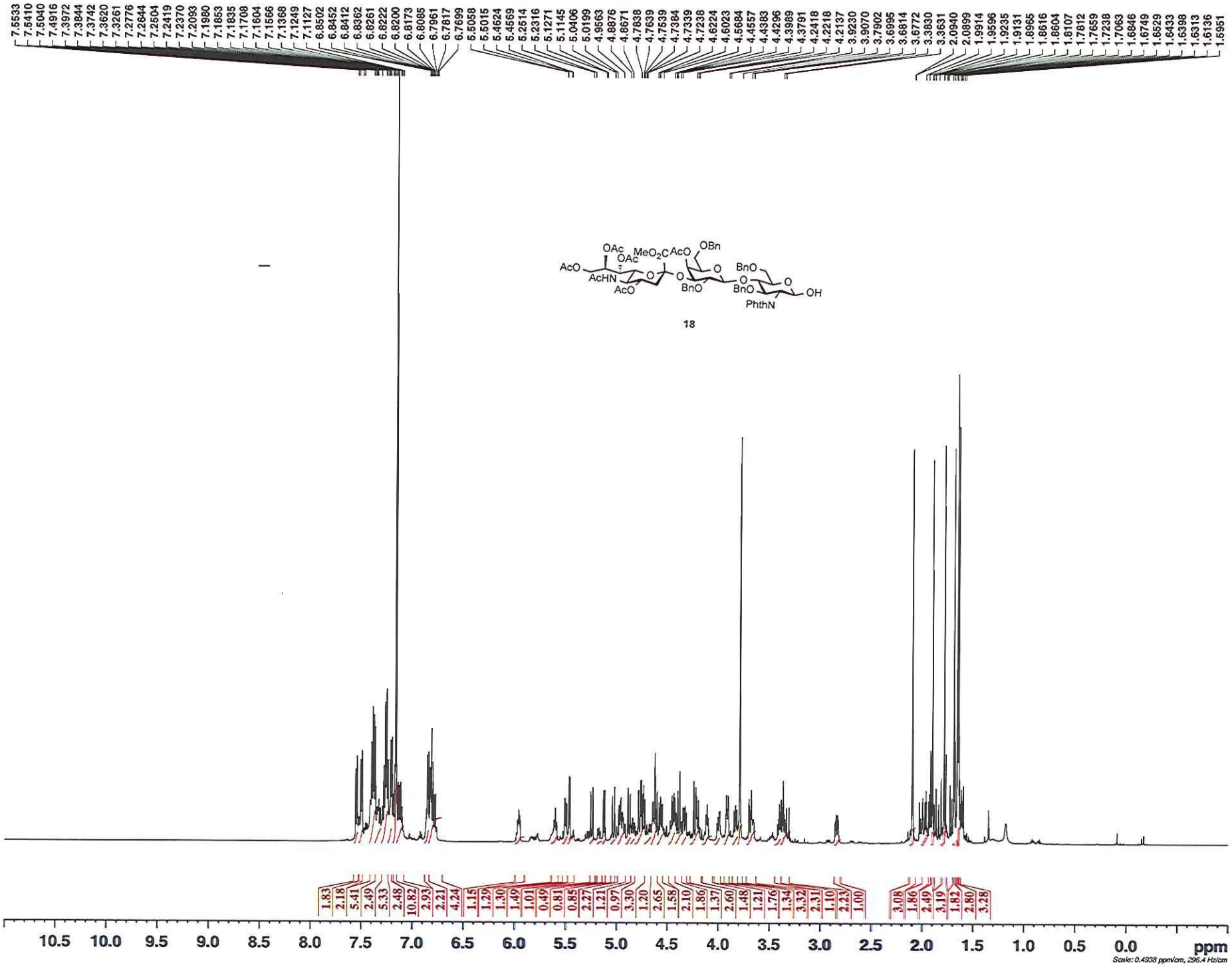
80
70
60
50
40
30
20
10
0
ppm
Scale: 10.7 ppm/cm, 1614 Hz/cm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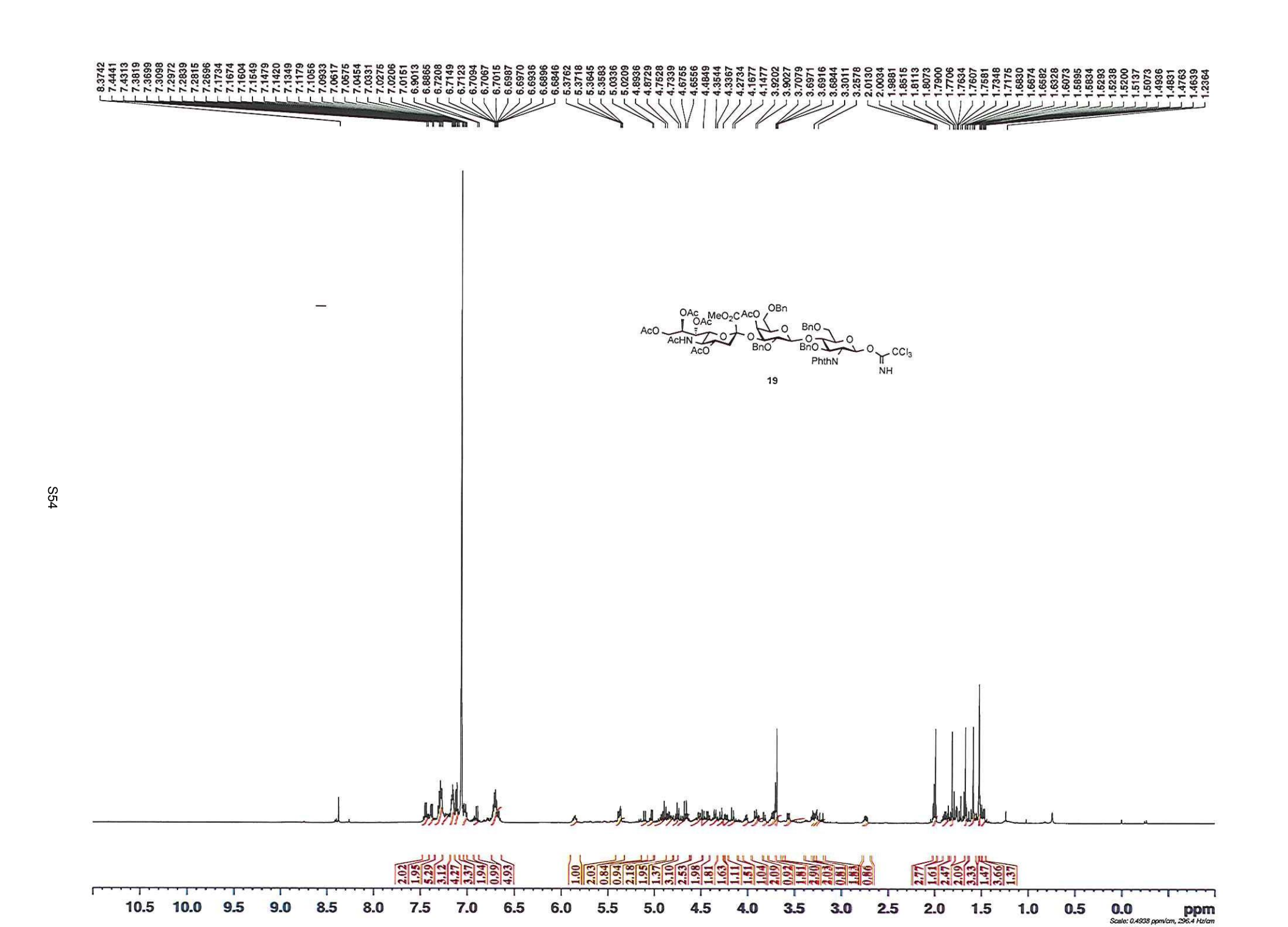
5.5058 5.5015 5.4624 5.4569 5.2514 5.2316 5.1271 5.1145 5.0406 5.0199 4.9563 4.8876 4.8671 4.7838 4.7639 4.7539 4.7384 4.7339 4.7238 4.6224 4.6023 4.5684 4.4557 4.4383 4.4296 4.3989 4.3791 4.2418 4.2218 4.2137 3.9230 3.9070 3.7902 3.6995 3.6814 3.6772 3.3830 3.3631 2.0940 2.0899 1.9914 1.9596 1.9235 1.9131 1.8965 1.8616 1.8604 1.8107 1.7812 1.7659 1.7238 1.7063 1.6846 1.6749 1.6529 1.6433 1.6398 1.6313 1.6136 1.5951
OAc OAc MeO2C AcO OBn
AcO AcHN AcO BnO BnO BnO OH PhthN
18
1.83 2.18 5.41 2.49 5.33 2.48 10.82 2.93 2.21 4.24 1.15 1.29 1.30 1.49 1.01 0.49 0.81 0.85 2.27 1.21 0.97 3.30 1.20 2.65 1.58 2.10 1.86 1.37 2.60 1.48 1.21 1.76 1.34 3.32 2.31 1.10 2.23 1.00 3.08 1.86 2.49 3.19 1.82 2.80 3.28
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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7.2815
7.2696
7.1734
7.1674
7.1604
7.1549
7.1479
7.1420
7.1349
7.1179
7.1056
7.0933
7.0617
7.0575
7.0454
7.0331
7.0275
7.0206
7.0151
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6.8865
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6.6970
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6.6846
5.3762
5.3718
5.3645
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5.0336
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4.7528
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4.6556
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4.3544
4.3367
4.2734
4.1677
4.1477
3.9202
3.9027
3.7079
3.6971
3.6916
3.6844
3.3011
3.2578
2.0130
2.0034
1.9881
1.8515
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1.8073
1.7900
1.7706
1.7634
1.7607
1.7581
1.7348
1.7175
1.6830
1.6674
1.6582
1.6328
1.6073
1.5895
1.5834
1.5293
1.5238
1.5200
1.5137
1.5073
1.4936
1.4831
1.4763
1.4639
1.2364
OAc
OAc
MeO2C
AcO
OBn
AcO
AcHN
AcO
BnO
BnO
BnO
PhthN
CCl3
NH
19
2.02
1.95
5.29
3.12
4.27
3.37
1.94
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4.93
1.00
2.03
0.84
0.94
2.18
1.95
1.37
3.10
2.53
1.98
1.81
1.63
1.11
1.51
1.04
2.09
0.92
1.81
2.90
2.03
0.81
1.83
0.86
2.77
1.61
2.47
2.09
3.33
1.47
3.66
1.37
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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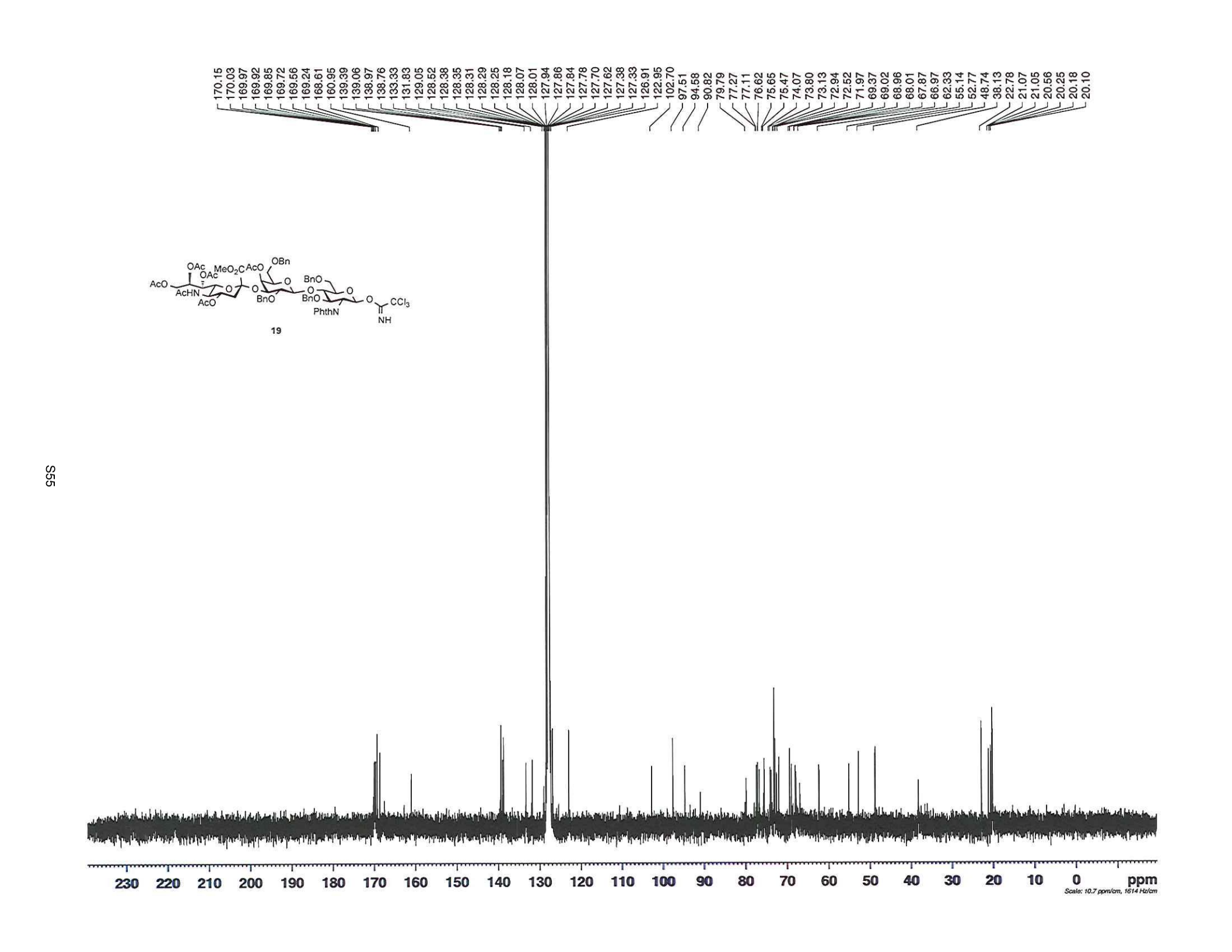
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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133.33
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129.05
128.52
128.38
128.35
128.31
128.29
128.25
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79.79
77.27
77.11
76.62
75.65
75.47
74.07
73.80
73.13
72.94
72.52
71.97
69.37
69.02
68.96
68.01
67.87
66.97
62.33
55.14
52.77
48.74
38.13
22.78
21.07
21.05
20.56
20.25
20.18
20.10
OAc
OAc
MeO2C
AcO
OBn
AcO
AcHN
AcO
BnO
BnO
BnO
PhthN
CCl3
NH
19
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
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30
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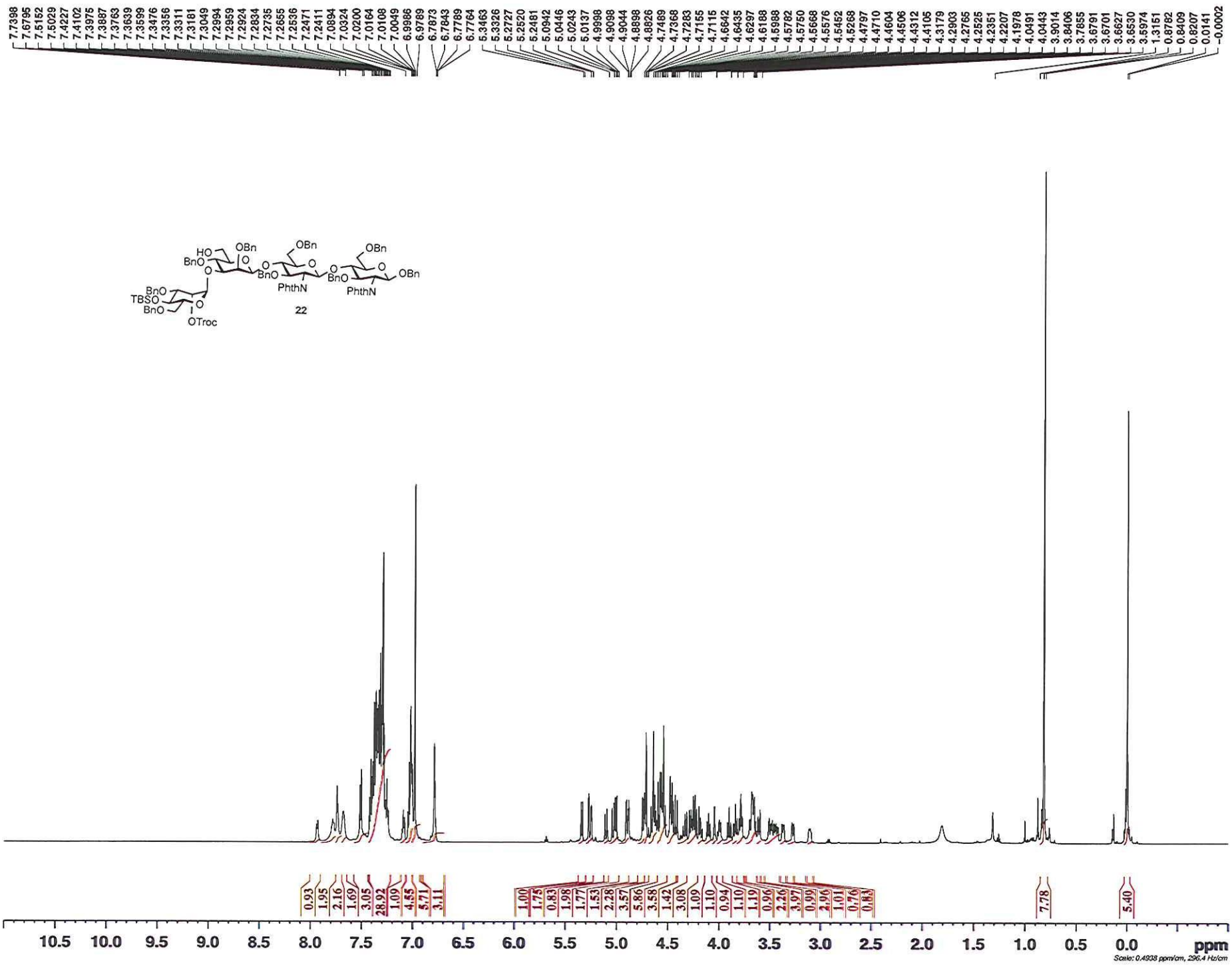
10
0
ppm
Scale: 10.7 ppm/cm, 1614 Hz/cm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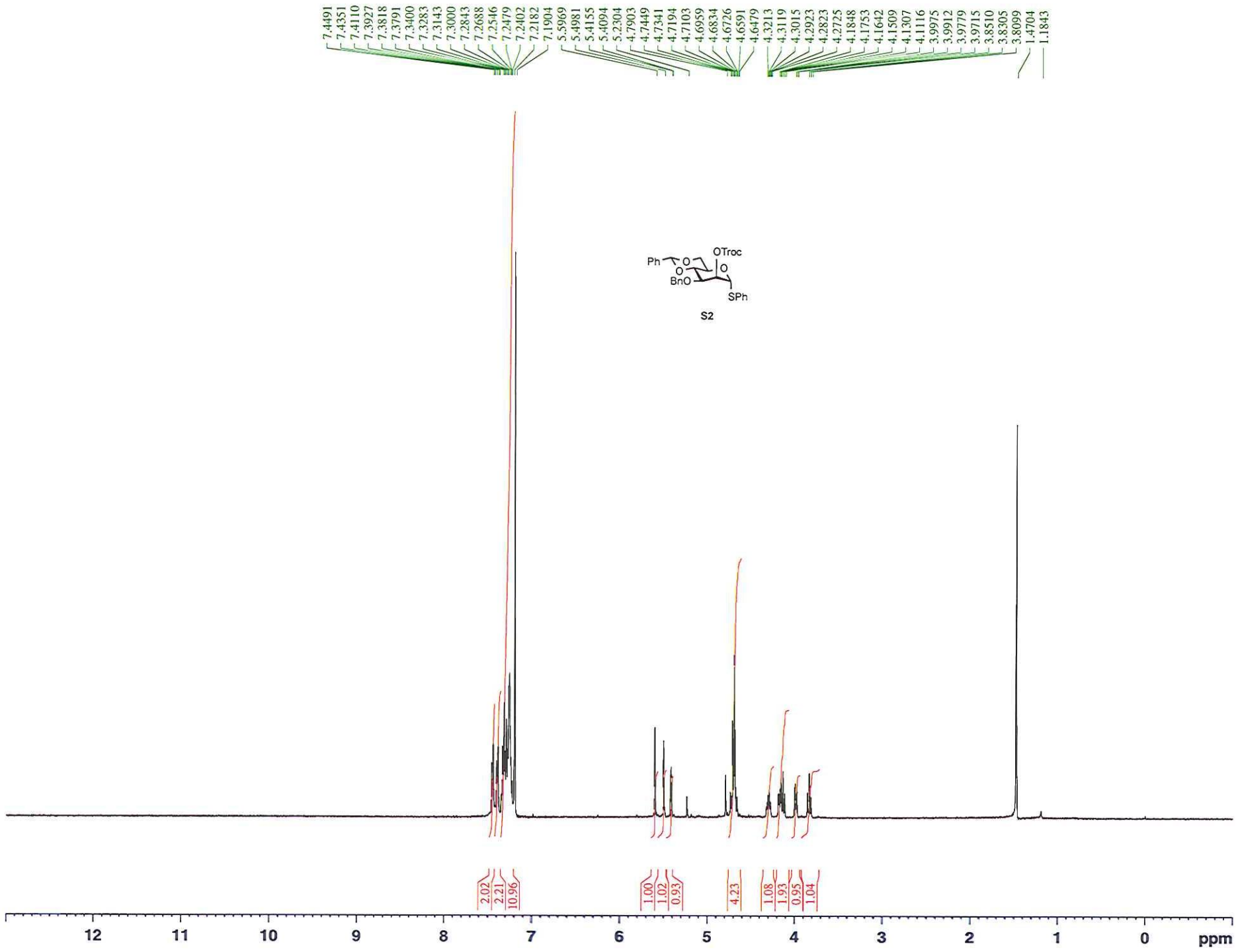
5.3463 5.3326 5.2727 5.2520 5.2481 5.0942 5.0446 5.0243 5.0137 4.9998 4.9098 4.9044 4.8898 4.8826 4.7489 4.7368 4.7283 4.7155 4.7115 4.6642 4.6435 4.6297 4.6188 4.5988 4.5782 4.5750 4.5668 4.5576 4.5452 4.5268 4.4797 4.4710 4.4604 4.4506 4.4312 4.4105 4.3179 4.2903 4.2765 4.2525 4.2351 4.2207 4.1978 4.0491 4.0443 3.9014 3.8406 3.7855 3.6791 3.6701 3.6627 3.6530 3.5974 1.3151 0.8782 0.8409 0.8207 0.0141 -0.0002
HO
OBn
OBn
OBn
BnO
BnO
BnO
BnO
PhthN
PhthN
OBn
BnO
TBSO
BnO
OTroc
22
0.93 1.95 2.16 1.69 3.05 28.92 1.09 4.55 5.71 3.11
1.00 1.75 0.83 1.98 1.77 1.53 2.28 3.57 5.86 3.58 1.42 3.08 1.09 1.10 0.94 1.10 1.19 0.96 2.26 3.97 0.99 2.96 1.01 0.76 0.83
7.78
5.40
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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7.3143
7.3000
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7.2688
7.2546
7.2479
7.2402
7.2182
7.1904
5.5969
5.4981
5.4155
5.4094
5.2304
4.7903
4.7449
4.7341
4.7194
4.7103
4.6959
4.6834
4.6726
4.6591
4.6479
4.3213
4.3119
4.3015
4.2923
4.2823
4.2725
4.1848
4.1753
4.1642
4.1509
4.1307
4.1116
3.9975
3.9912
3.9779
3.9715
3.8510
3.8305
3.8099
1.4704
1.1843
Ph
O
O
BnO
OTroc
O
SPh
S2
2.02
2.21
10.96
1.00
1.02
0.93
4.23
1.08
1.93
0.95
1.04
12
11
10
9
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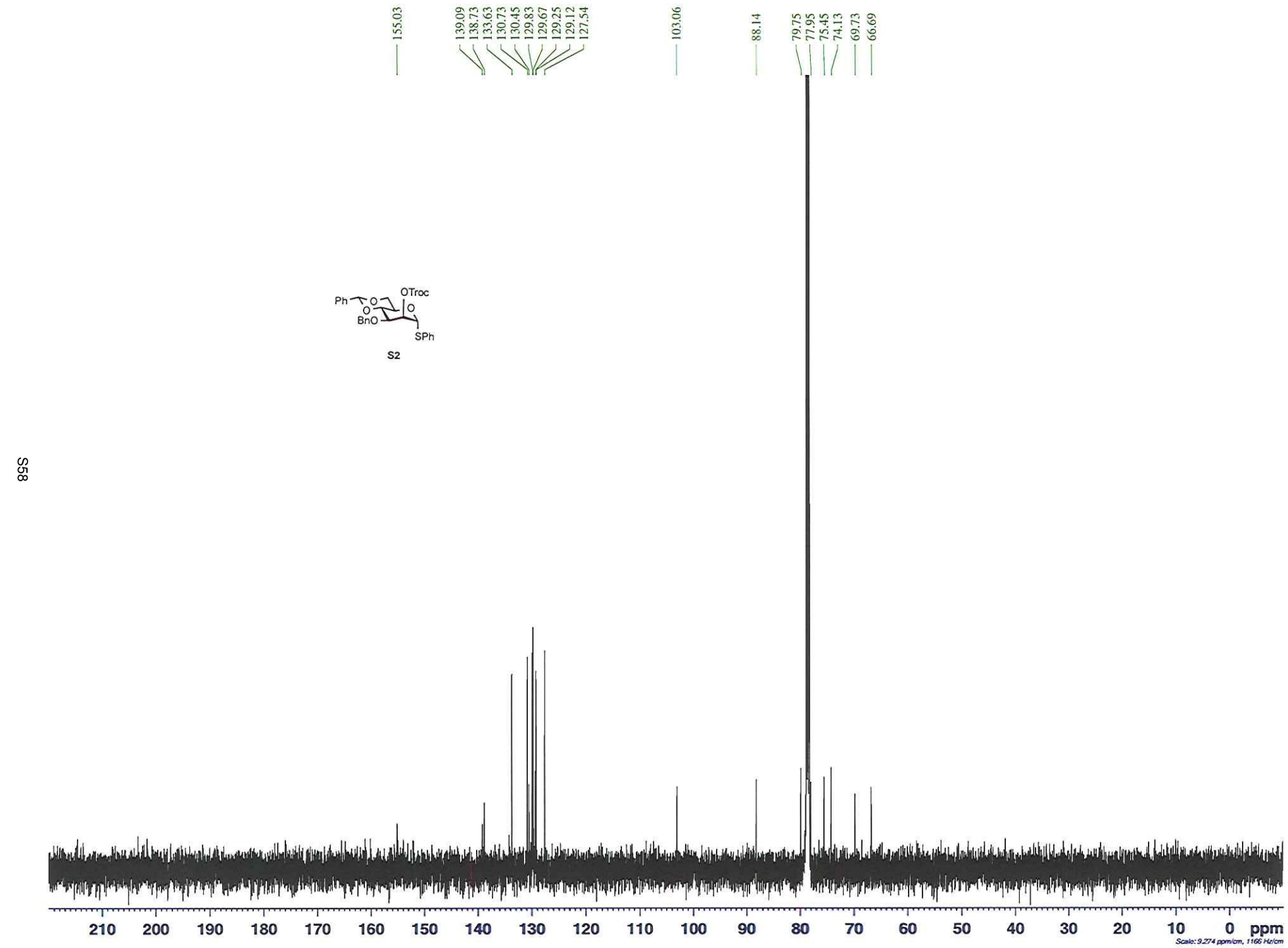
7
6
5
4
3
2
1
0
ppm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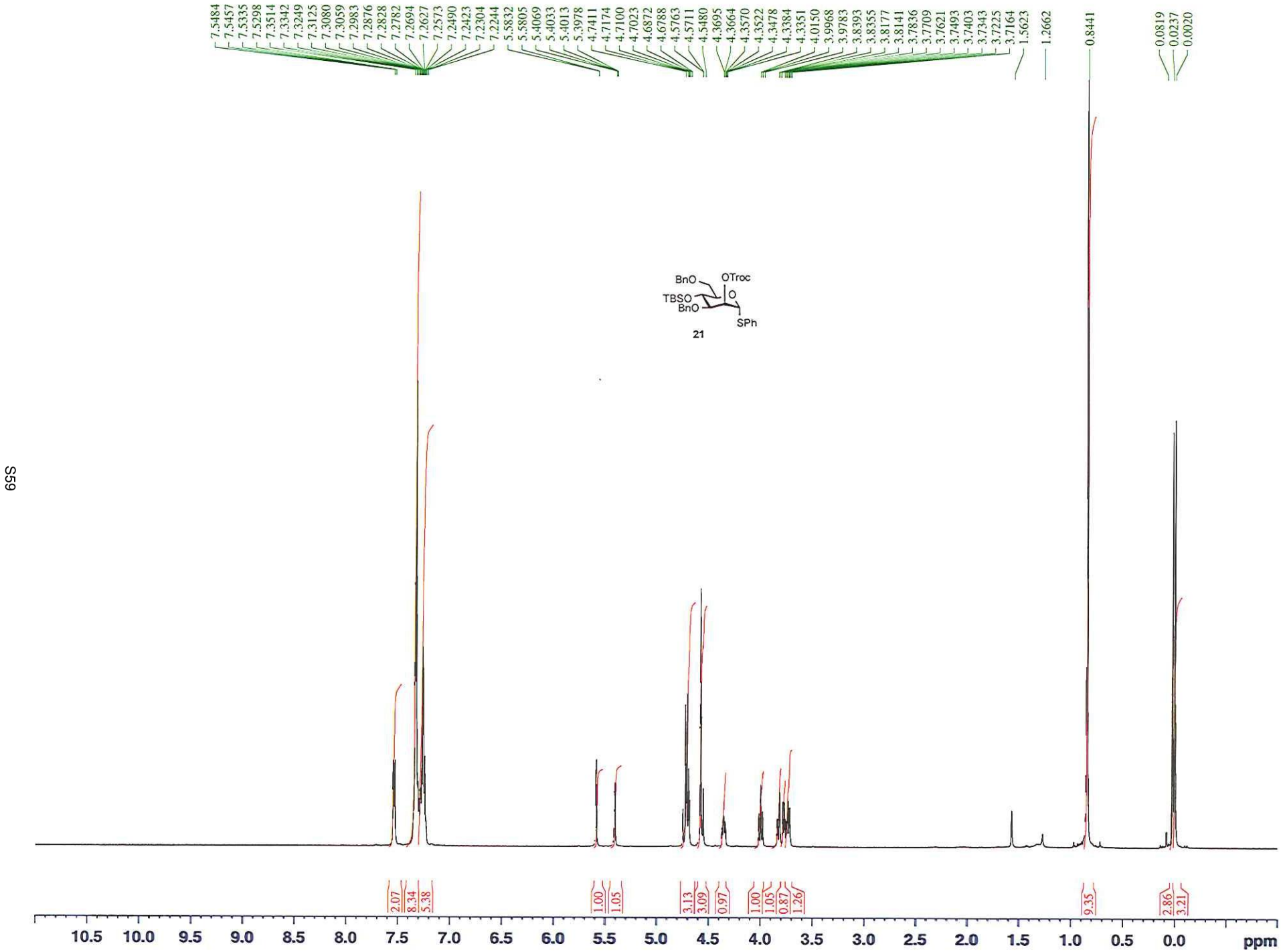
139.09
138.73
133.63
130.73
130.45
129.83
129.67
129.25
129.12
127.54
103.06
88.14
79.75
77.95
75.45
74.13
69.73
66.69
Ph
O
O
BnO
OTroc
O
SPh
S2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.274 ppm/cm, 1166 Hz/cm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7.3249
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7.3080
7.3059
7.2983
7.2876
7.2828
7.2782
7.2694
7.2627
7.2573
7.2490
7.2423
7.2304
7.2244
5.5832
5.5805
5.4069
5.4033
5.4013
5.3978
4.7411
4.7174
4.7100
4.7023
4.6872
4.6788
4.5763
4.5711
4.5480
4.3695
4.3664
4.3570
4.3522
4.3478
4.3384
4.3351
4.0150
3.9968
3.9783
3.8393
3.8355
3.8177
3.8141
3.7836
3.7709
3.7621
3.7493
3.7403
3.7343
3.7225
3.7164
1.5623
1.2662
0.8441
0.0819
0.0237
0.0020
BnO
OTroc
TBSO
BnO
O
SPh
21
2.07
8.34
5.38
1.00
1.05
3.13
3.09
0.97
1.00
1.05
0.87
1.26
9.35
2.86
3.21
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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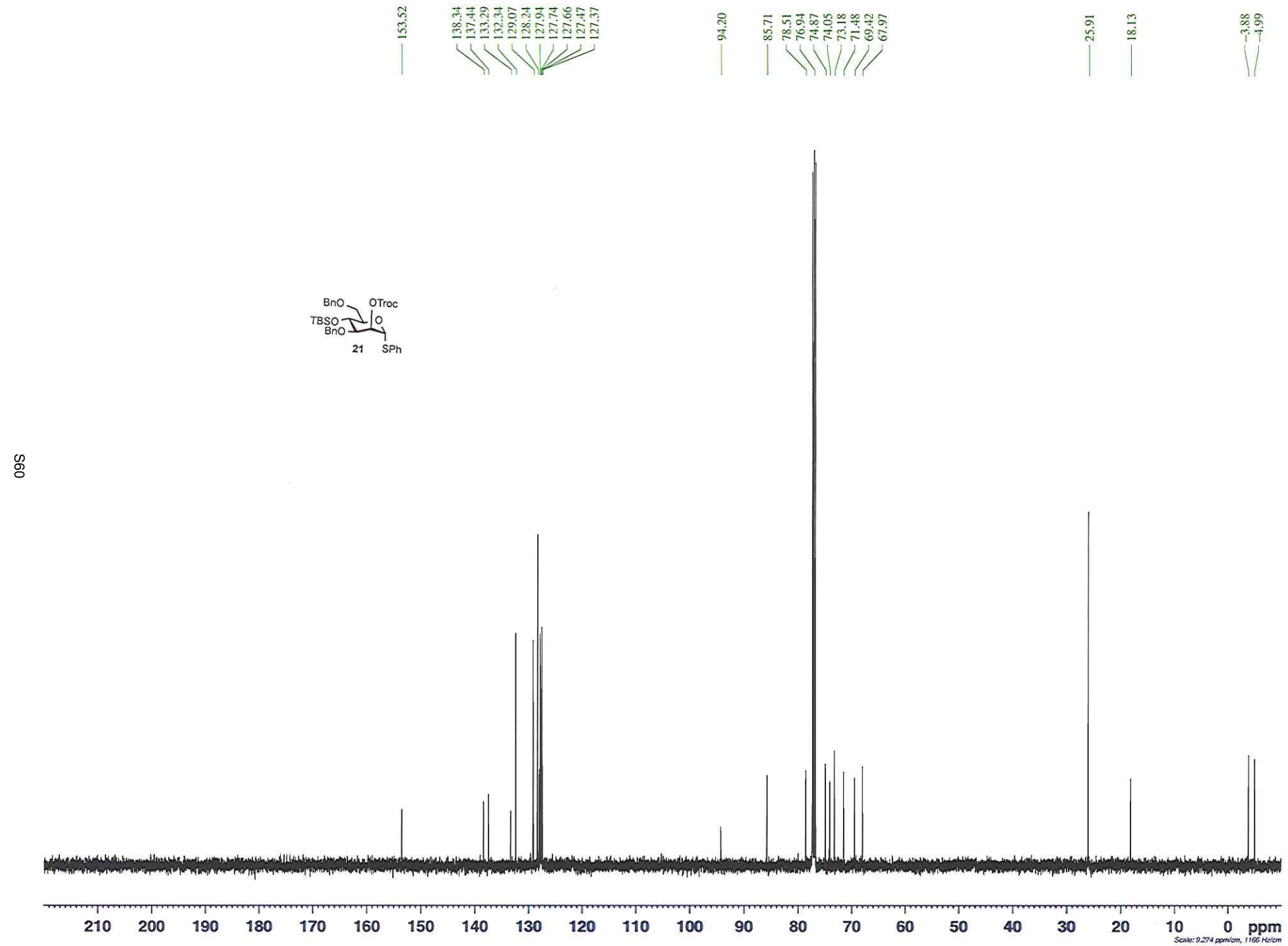
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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129.07
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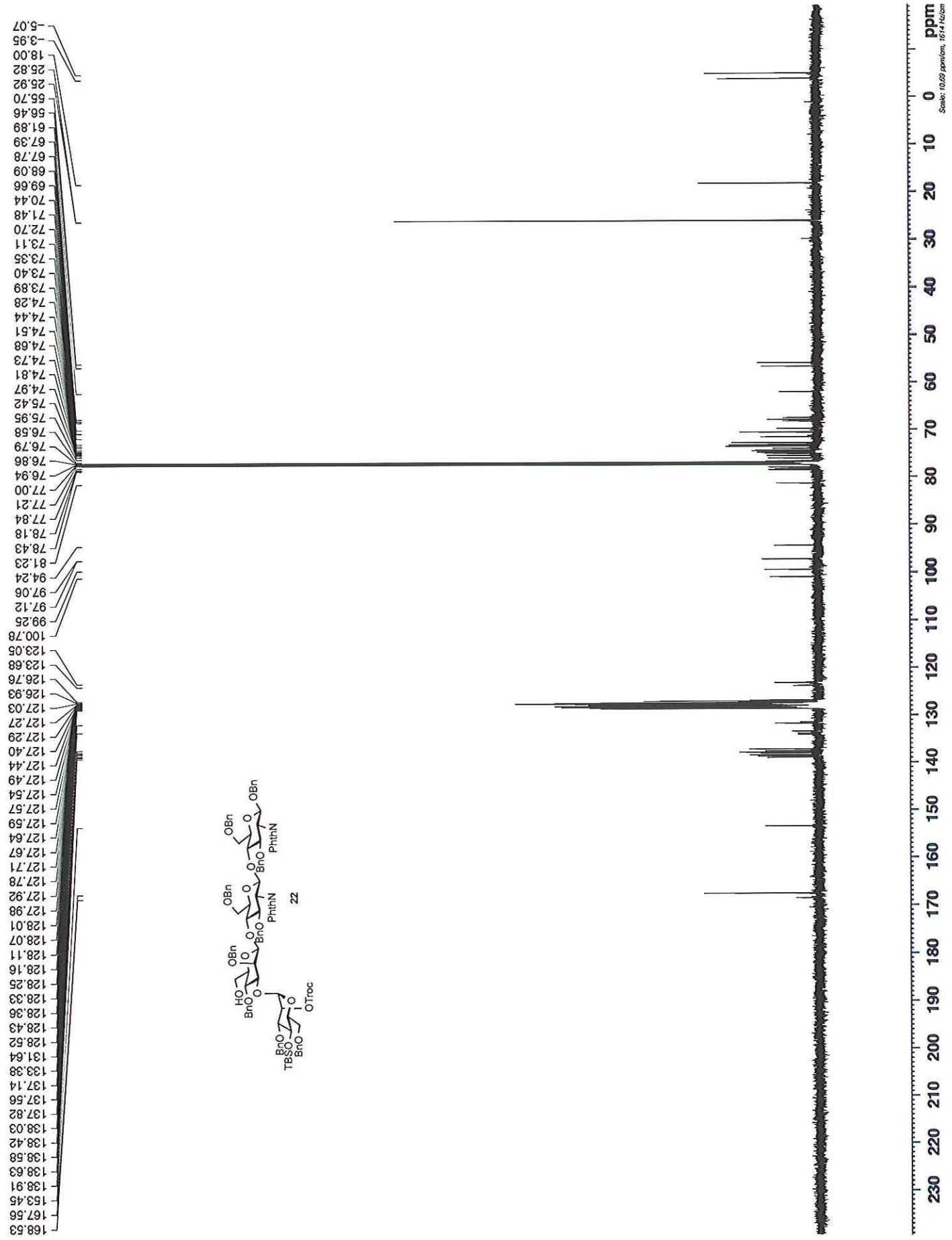
127.94
127.74
127.66
127.47
127.37
94.20
85.71
78.51
76.94
74.87
74.05
73.18
71.48
69.42
67.97
25.91
18.13
-3.88
-4.99
BnO
OTroc
TBSO
O
BnO
21
SPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 9.274 ppm/cm, 1166 Hz/cm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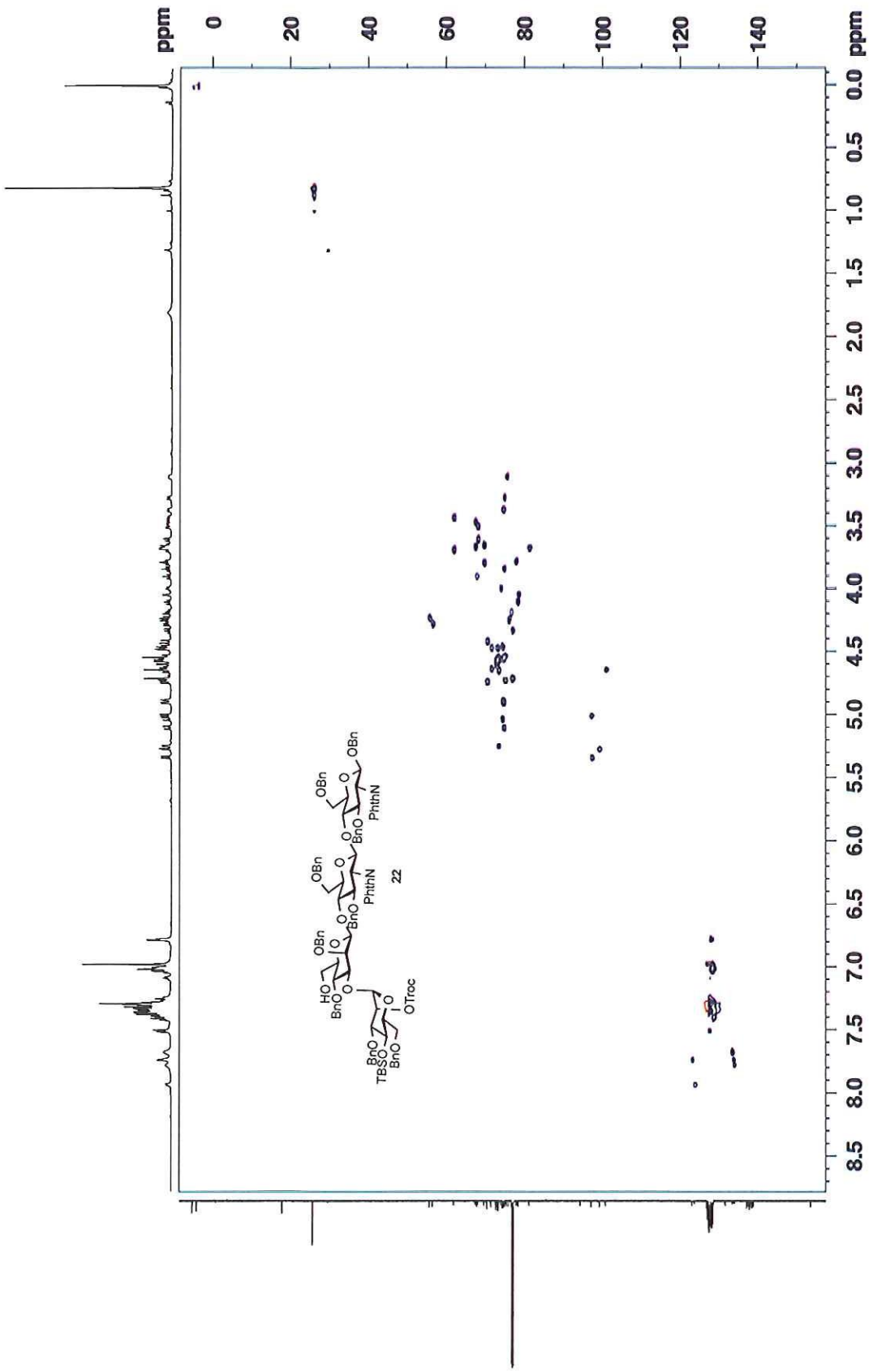
70.44
71.48
72.70
73.11
73.35
73.40
73.89
74.28
74.44
74.51
74.68
74.73
74.81
74.97
75.42
75.95
76.58
76.79
76.86
76.94
77.00
77.21
77.84
78.18
78.43
81.23
94.24
97.06
97.12
99.25
100.78
123.05
123.68
126.76
126.93
127.03
127.27
127.29
127.40
127.44
127.49
127.54
127.57
127.59
127.64
127.67
127.71
127.78
127.92
127.98
128.01
128.07
128.11
128.16
128.25
128.33
128.36
128.43
128.52
131.64
133.38
137.14
137.56
137.82
138.03
138.42
138.58
138.63
138.91
153.45
167.56
168.53
22
ppm
Scale: 10.69 ppm/cm, 1614 Hz/cm


ppm
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60
80
100
120
140
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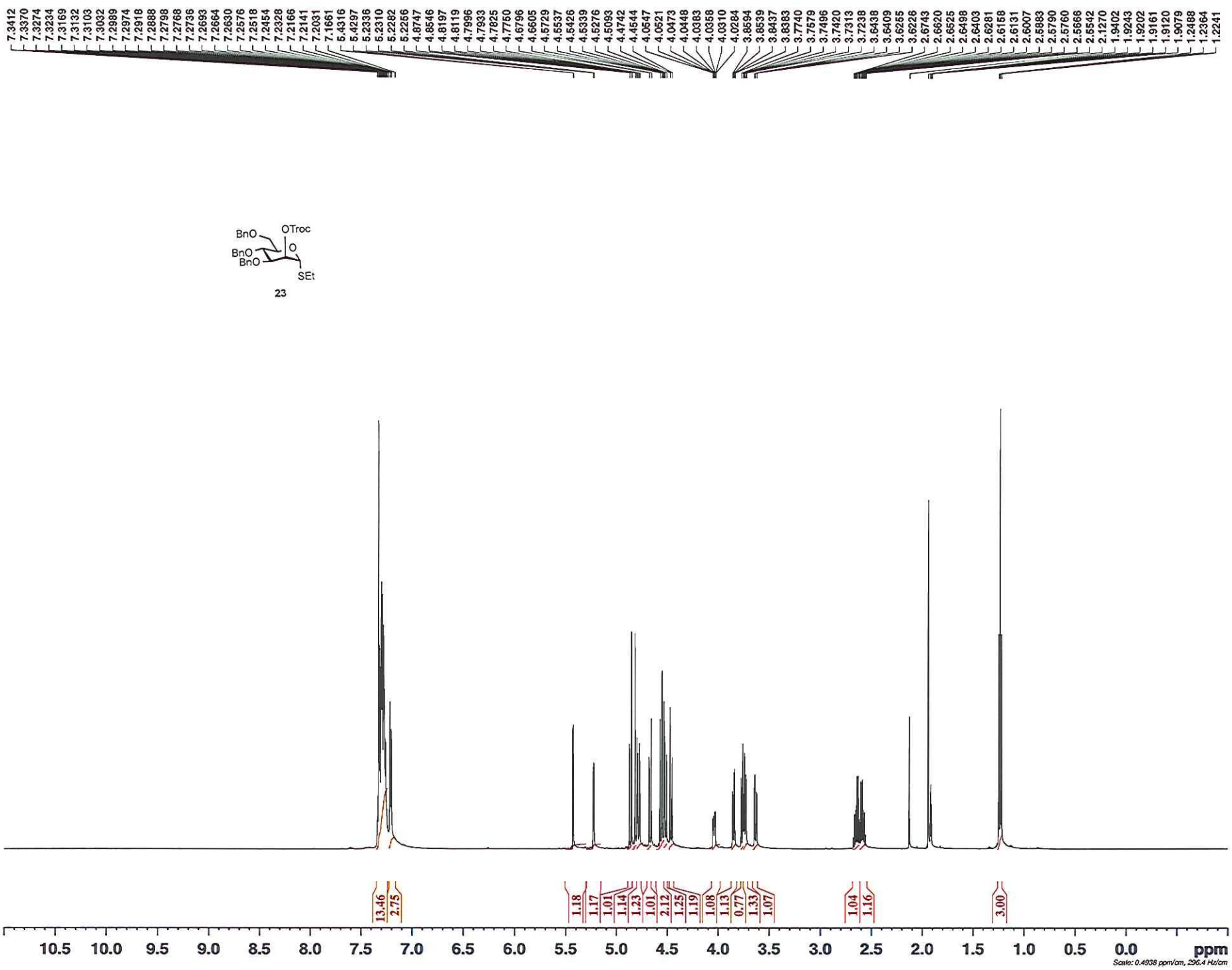
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
22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7.2768
7.2736
7.2693
7.2664
7.2630
7.2576
7.2518
7.2454
7.2328
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5.2336
5.2310
5.2282
5.2256
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4.8197
4.8119
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4.7933
4.7825
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4.6796
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4.5537
4.5426
4.5339
4.5276
4.5093
4.4742
4.4544
4.0547
4.0521
4.0473
4.0448
4.0383
4.0358
4.0310
4.0284
3.8594
3.8539
3.8437
3.8383
3.7740
3.7579
3.7496
3.7420
3.7313
3.7238
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3.6409
3.6255
3.6226
2.6743
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2.6525
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2.6403
2.6281
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2.6131
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2.5760
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2.5542
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1.9202
1.9161
1.9120
1.9079
1.2488
1.2364
1.2241
BnO
OTroc
BnO
BnO
O
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2.75
1.18
1.17
1.01
1.14
1.23
1.01
2.12
1.25
1.19
1.08
1.13
0.77
1.33
1.07
1.04
1.16
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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0.0
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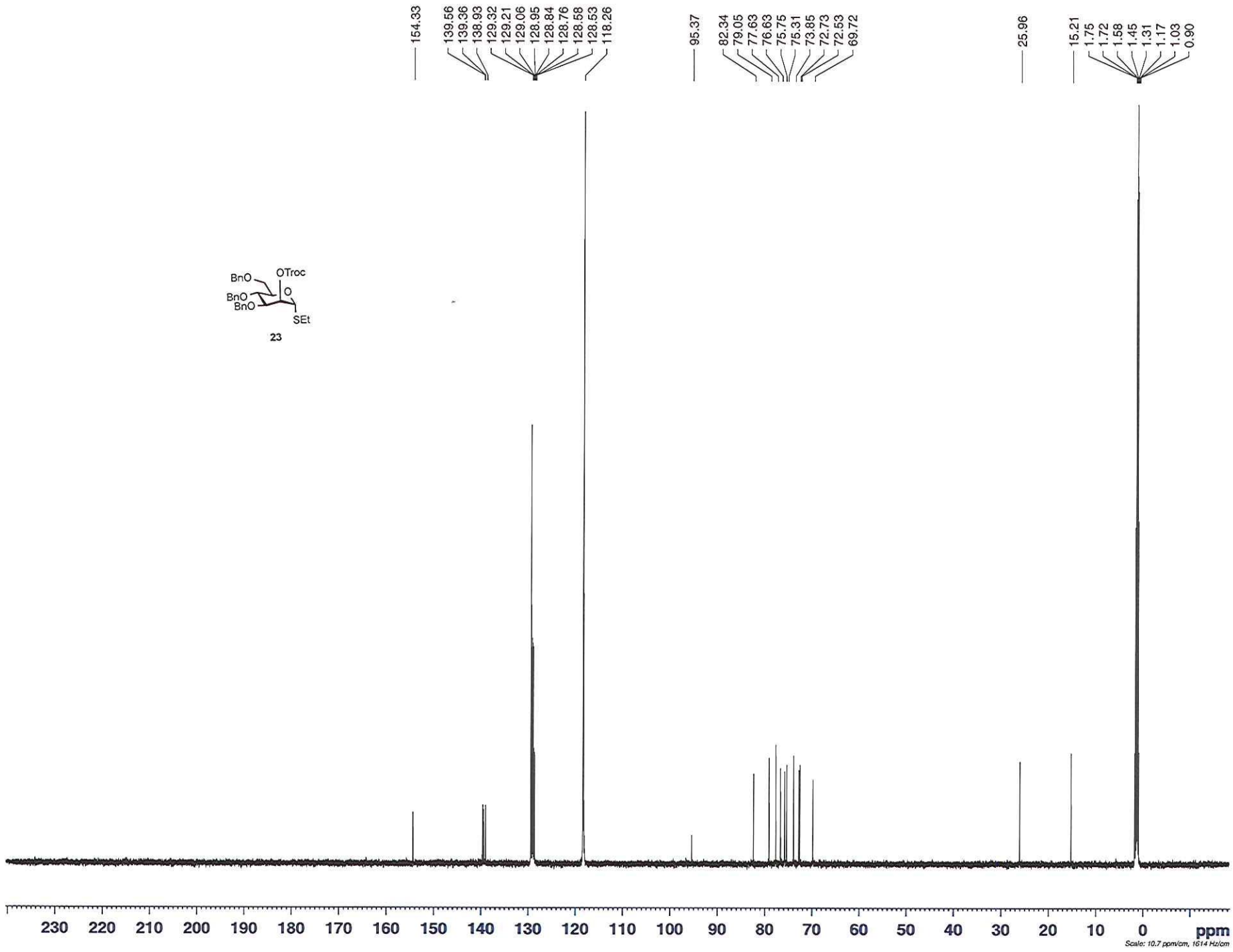
Scale: 0.4938 ppm/cm, 296.4 Hz/cm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128.58
128.53
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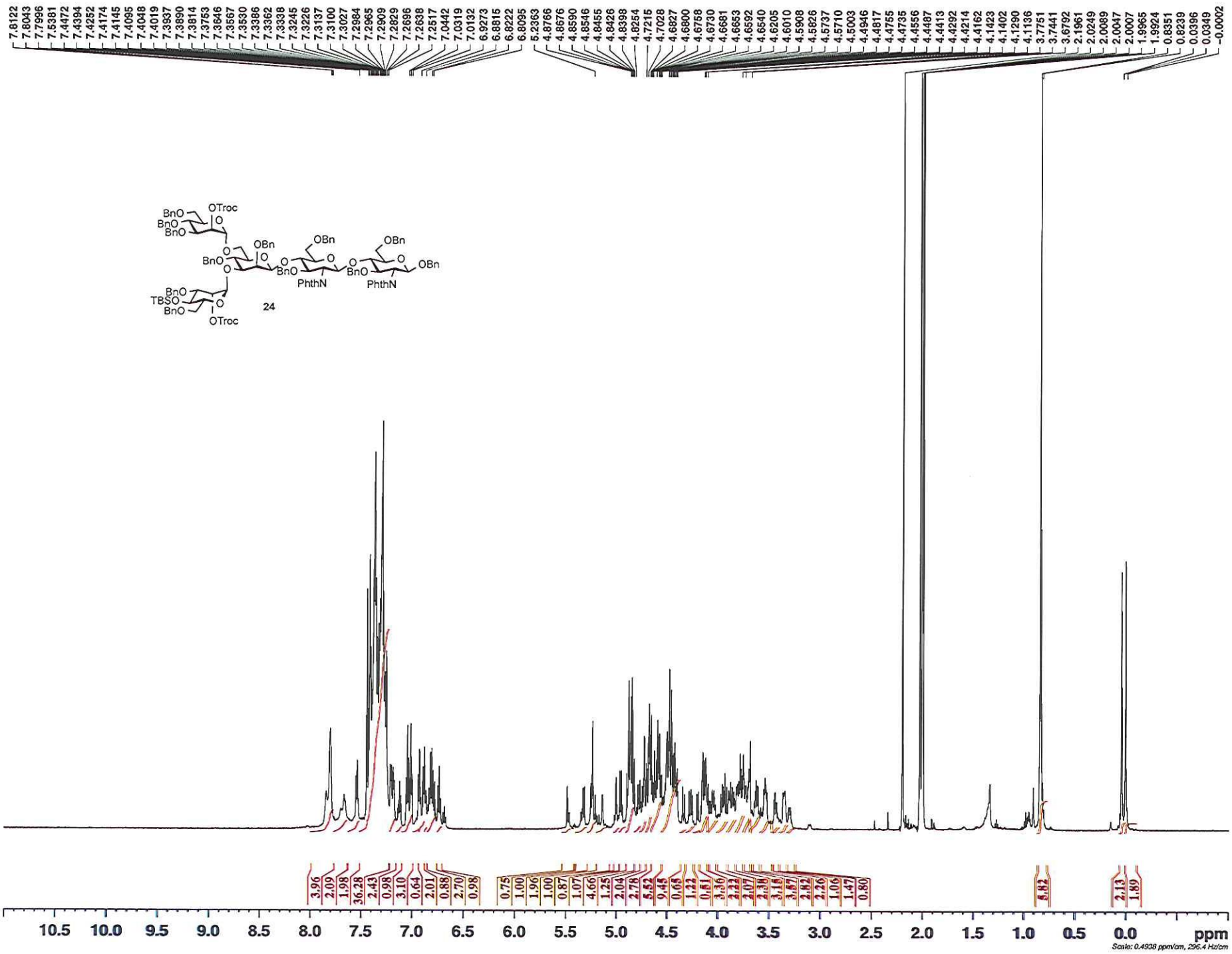
95.37
82.34
79.05
77.63
76.63
75.75
75.31
73.85
72.73
72.53
69.72
25.96
15.21
1.75
1.72
1.58
1.45
1.31
1.17
1.03
0.90
BnO
OTroc
BnO
O
BnO
SEt
23
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Scale: 10.7 ppm/cm, 1614 Hz/cm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7.3338
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7.2638
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2.0047
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0.8239
0.0396
0.0349
-0.0002
BnO
OTroc
BnO
BnO
OBn
OBn
OBn
BnO
BnO
BnO
PhthN
PhthN
BnO
TBSO
BnO
OTroc
24
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2.09
1.98
36.28
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0.98
3.10
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2.01
0.88
2.70
0.98
0.75
1.00
1.96
1.00
0.87
1.07
4.66
1.25
2.04
2.78
5.52
9.45
0.68
1.22
0.81
3.36
2.22
2.07
2.31
3.16
3.87
2.02
2.26
1.06
1.47
0.80
8.82
2.13
1.69
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
0.5
0.0
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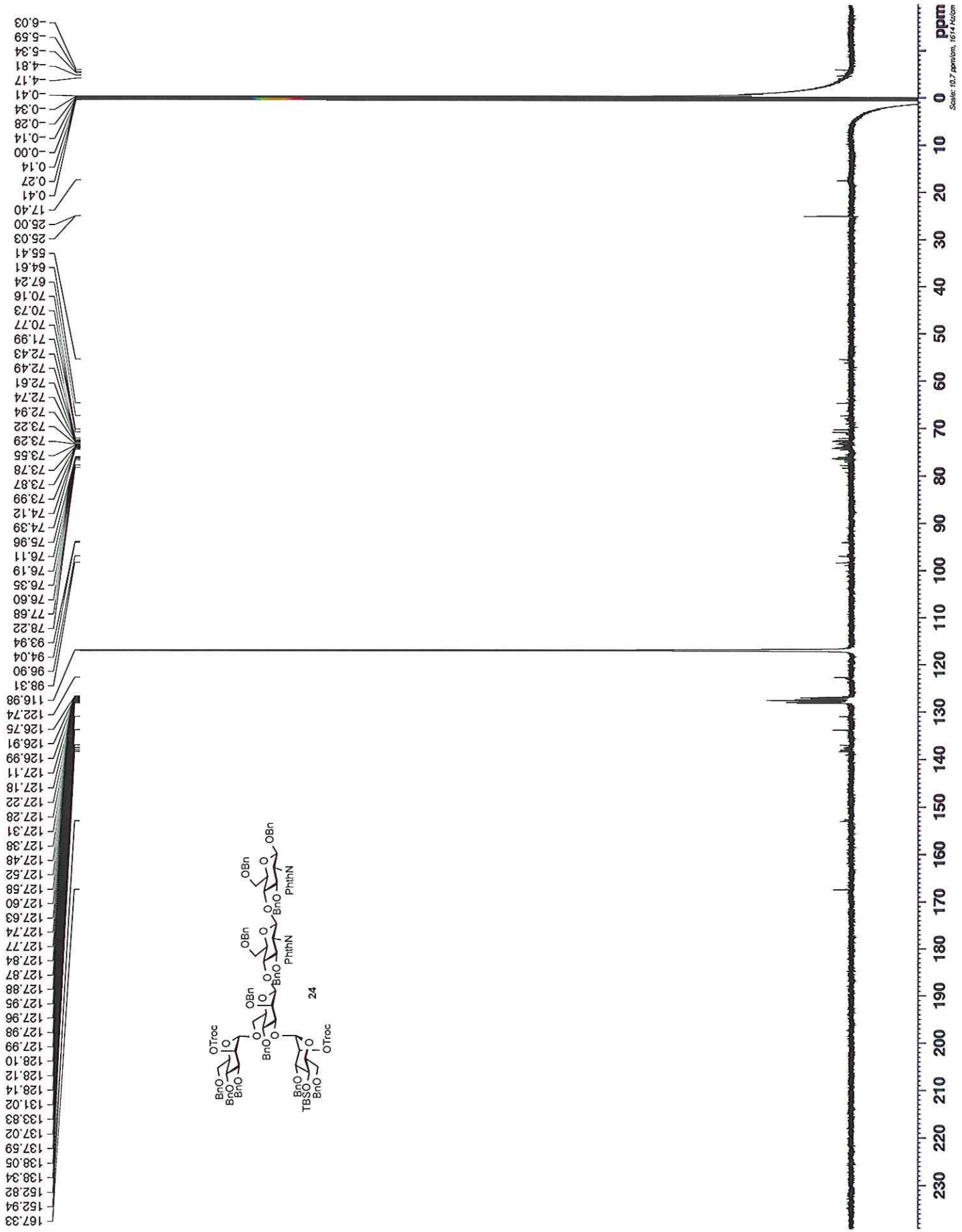
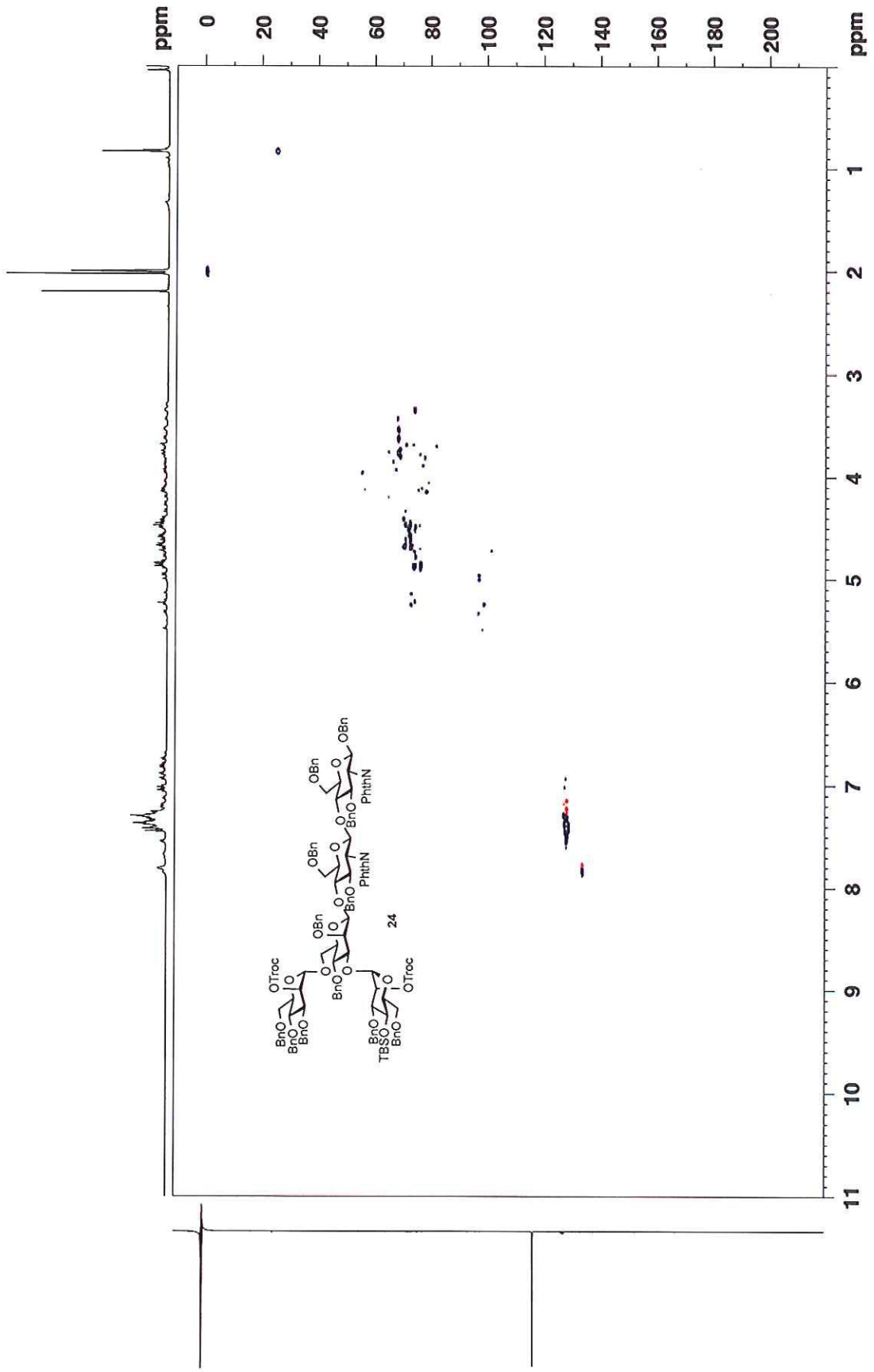
Scale: 0.4938 ppm/cm, 296.4 Hz/cm


24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140
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180
200
ppm
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4
5
6
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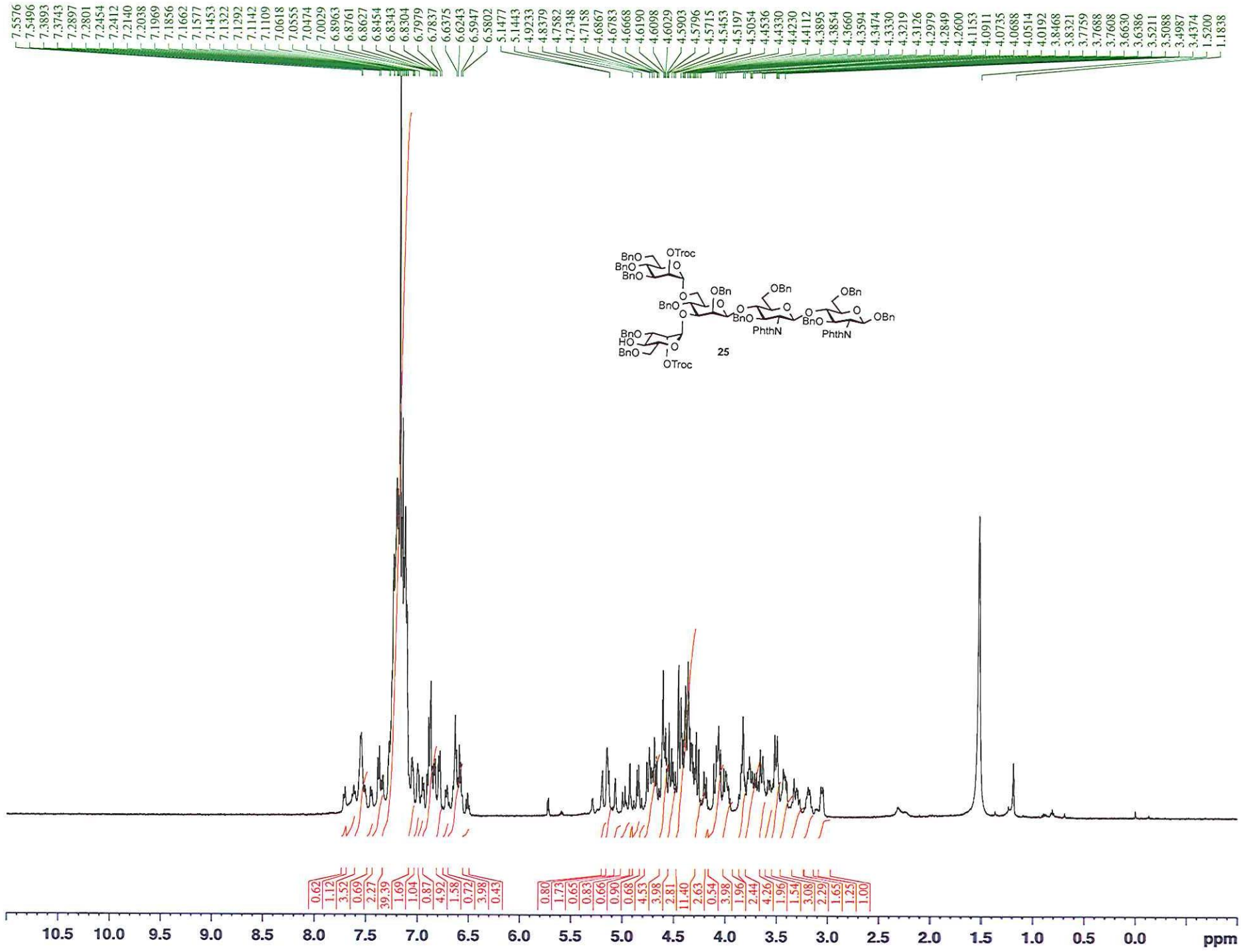
10
11
OTroc
BnO
BnO
BnO
OBn
BnO
BnO
OBn
PhthN
BnO
OBn
PhthN
BnO
OBn
24
BnO
TBSO
BnO
OTroc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7.0555
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6.7837
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6.6243
6.5947
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4.5903
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4.4536
4.4330
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4.4112
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4.3330
4.3219
4.3126
4.2979
4.2849
4.2600
4.1153
4.0911
4.0735
4.0688
4.0514
4.0192
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3.7759
3.7688
3.7608
3.6630
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3.5211
3.5088
3.4987
3.4374
1.5200
1.1838
BnO
OTroc
BnO
BnO
OBn
BnO
OBn
OBn
BnO
BnO
OBn
PhthN
PhthN
BnO
HO
BnO
OTroc
25
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1.12
3.52
0.69
2.27
39.39
1.69
1.04
0.87
4.92
1.58
0.72
3.98
0.43
0.80
1.73
0.65
0.83
0.66
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0.68
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3.98
2.81
11.40
2.63
0.54
3.98
1.96
2.44
4.26
1.96
1.54
3.08
2.29
1.65
1.25
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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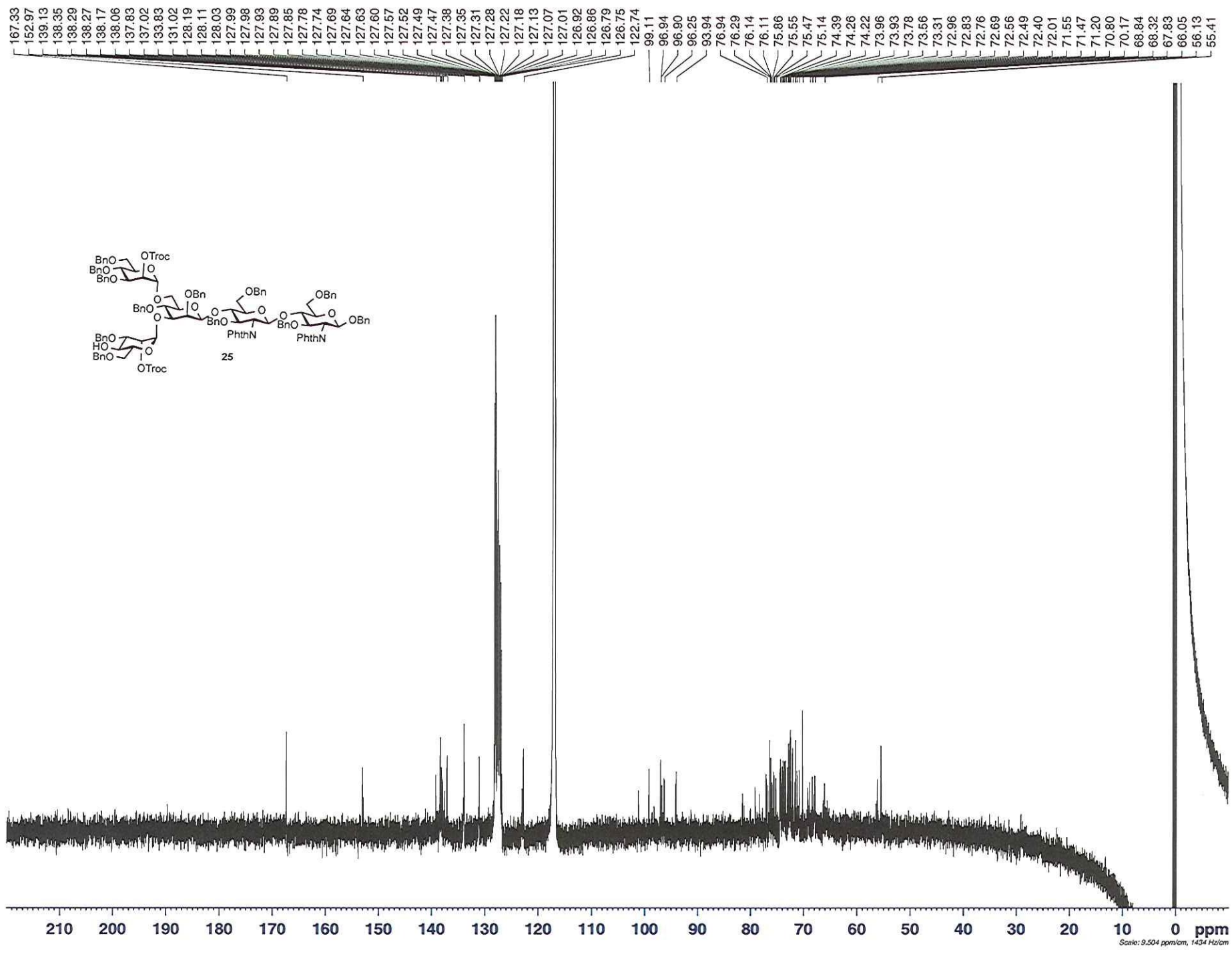
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128.11
128.03
127.99
127.98
127.93
127.89
127.85
127.78
127.74
127.69
127.64
127.63
127.60
127.57
127.52
127.49
127.47
127.38
127.35
127.31
127.28
127.22
127.18
127.13
127.07
127.01
126.92
126.86
126.79
126.75
122.74
99.11
96.94
96.90
96.25
93.94
76.94
76.29
76.14
76.11
75.86
75.55
75.47
75.14
74.39
74.26
74.22
73.96
73.93
73.78
73.56
73.31
72.96
72.83
72.76
72.69
72.56
72.49
72.40
72.01
71.55
71.47
71.20
70.80
70.17
68.84
68.32
67.83
66.05
56.13
55.41
BnO
OTroc
BnO
BnO
O
OBn
BnO
O
O
BnO
PhthN
OBn
BnO
PhthN
OBn
OBn
BnO
HO
BnO
O
OTroc
25
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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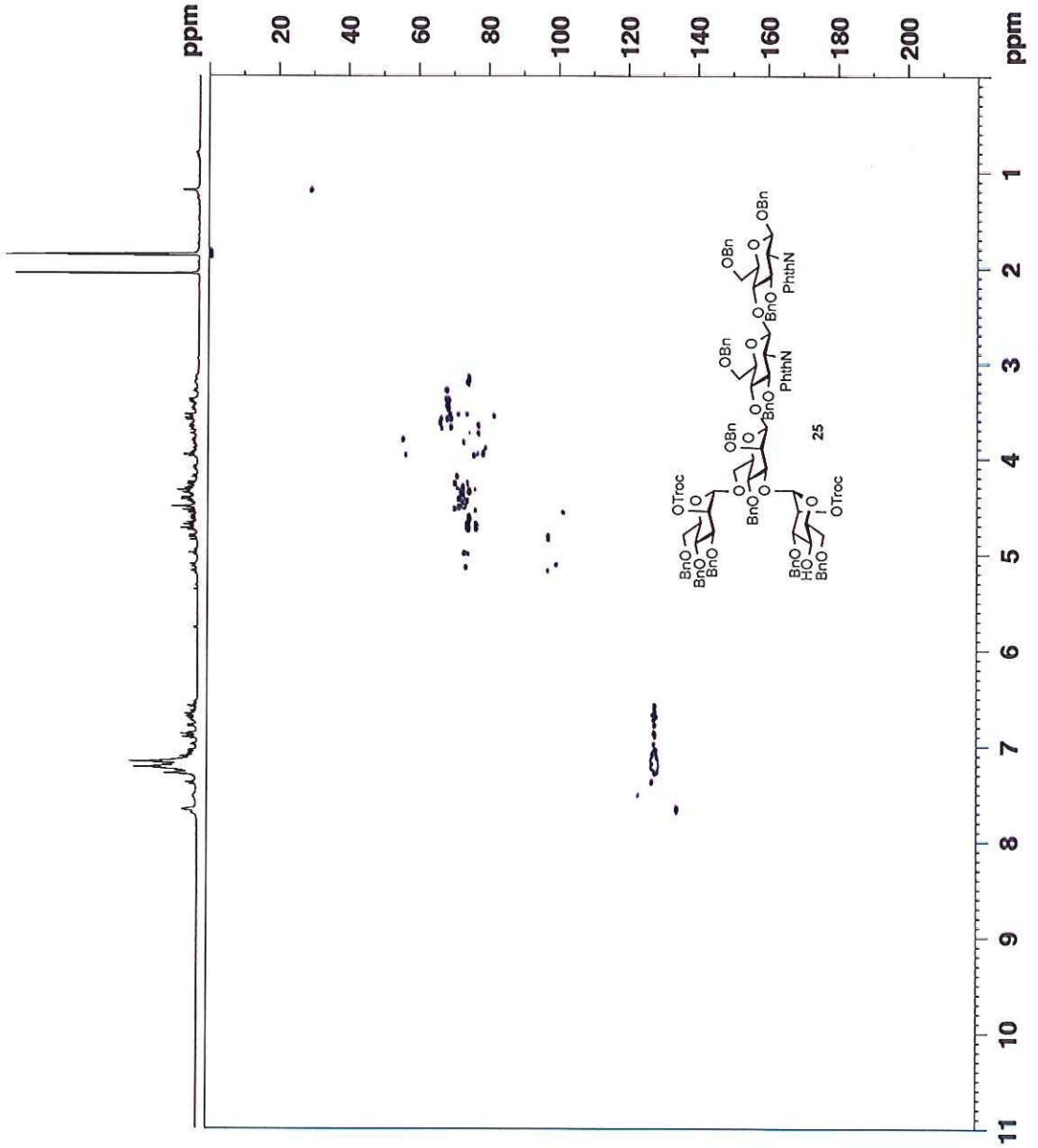
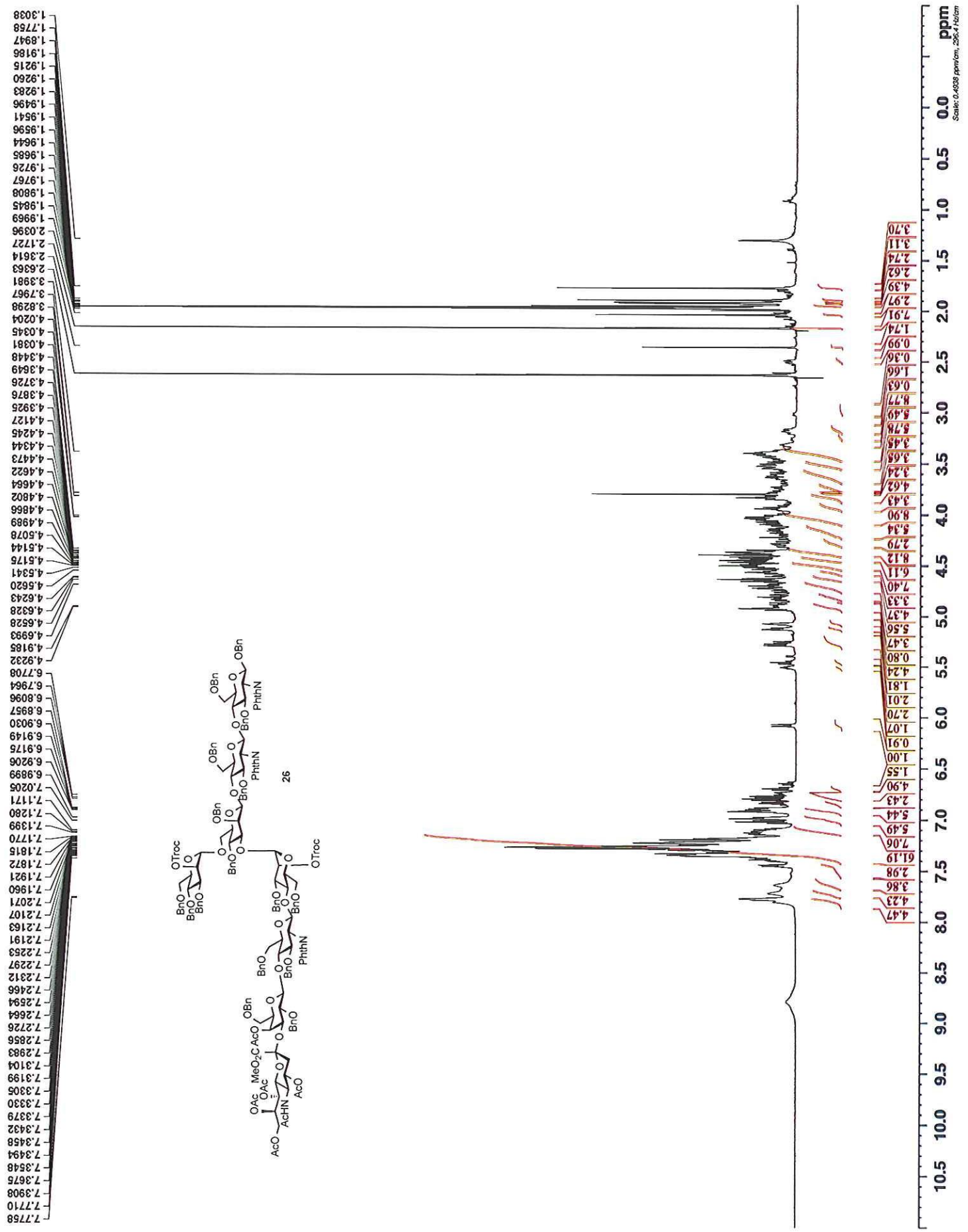
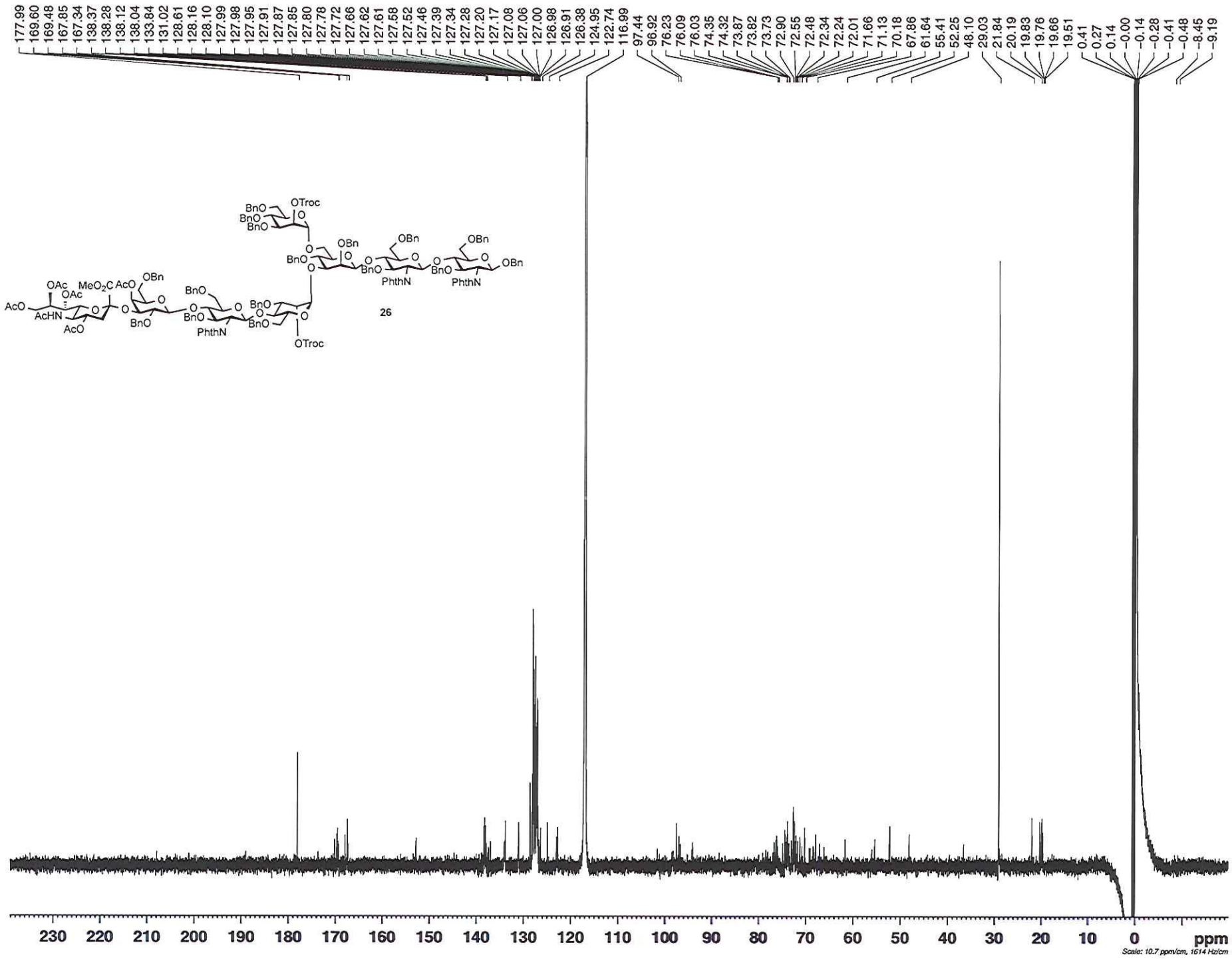

ppm
20
40
60
80
100
120
140
160
180
200
ppm
1
2
3
4
5
6
7
8
9
10
11
OTroc
BnO
BnO
BnO
OBn
BnO
O
25
OBn
PhthN
BnO
OBn
PhthN
BnO
OBn
BnO
HO
BnO
OTroc


26
ppm
Scale:0.4038 ppm/cm, 296.4 Hz/cm


177.99
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169.48
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138.12
138.04
133.84
131.02
128.61
128.16
128.10
127.99
127.98
127.95
127.91
127.87
127.85
127.80
127.78
127.72
127.66
127.62
127.61
127.58
127.52
127.46
127.39
127.34
127.28
127.20
127.17
127.08
127.06
127.00
126.98
126.91
126.38
124.95
122.74
116.99
97.44
96.92
76.23
76.09
76.03
74.35
74.32
73.87
73.82
73.73
72.90
72.55
72.48
72.34
72.24
72.01
71.66
71.13
70.18
67.86
61.64
55.41
52.25
48.10
29.03
21.84
20.19
19.83
19.76
19.66
19.51
0.41
0.27
0.14
-0.00
-0.14
-0.28
-0.41
-0.48
-8.45
-9.19
26
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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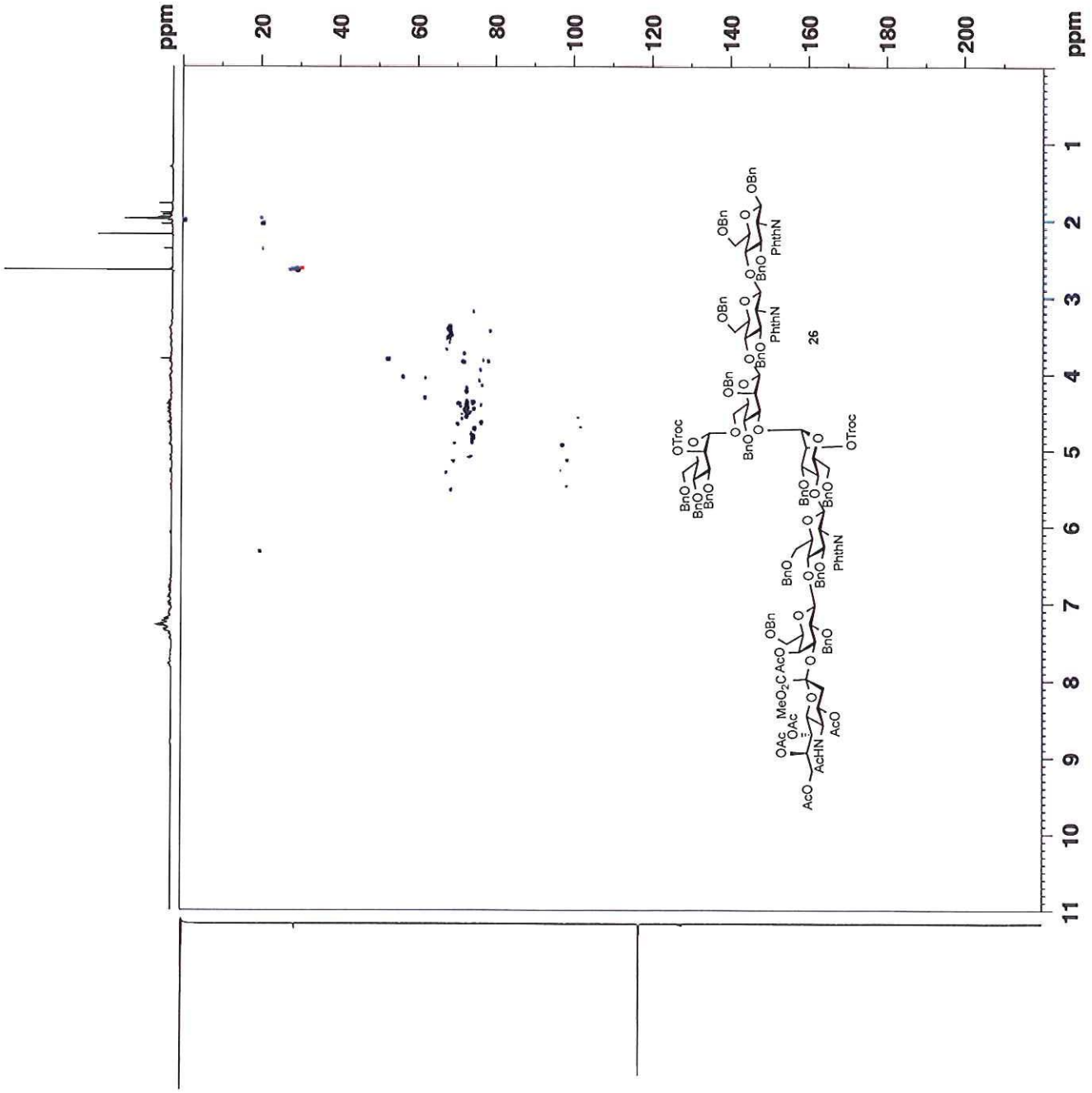
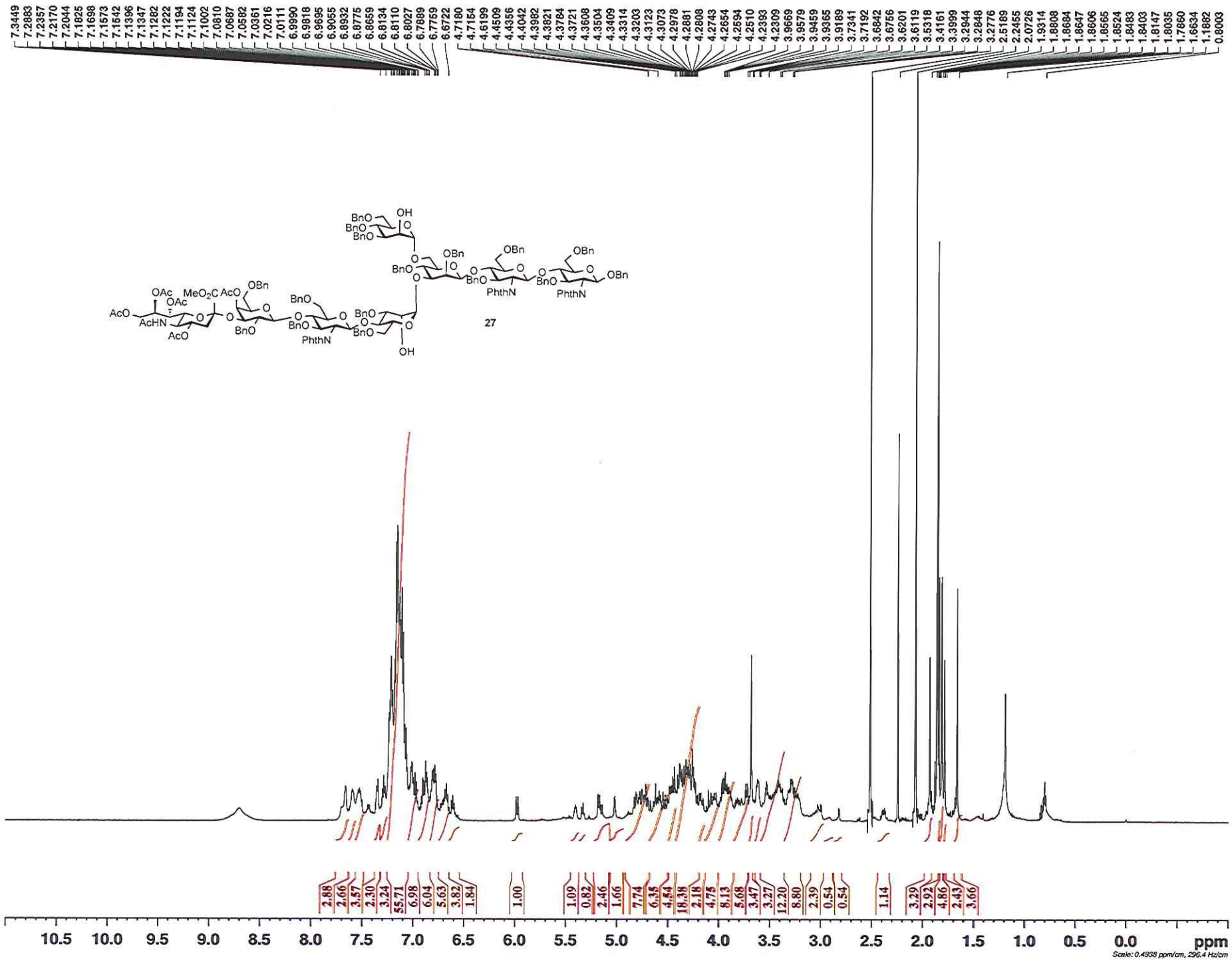
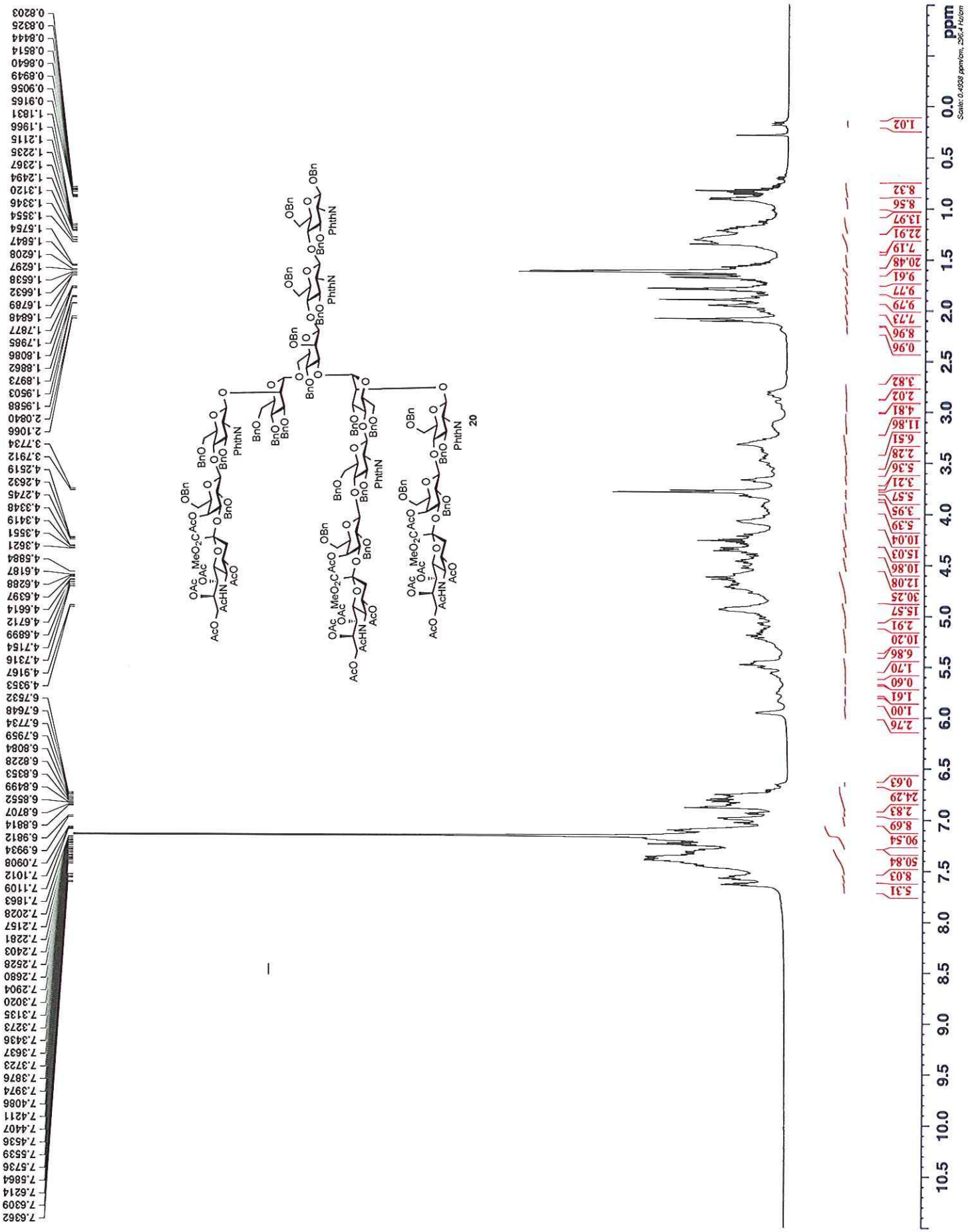
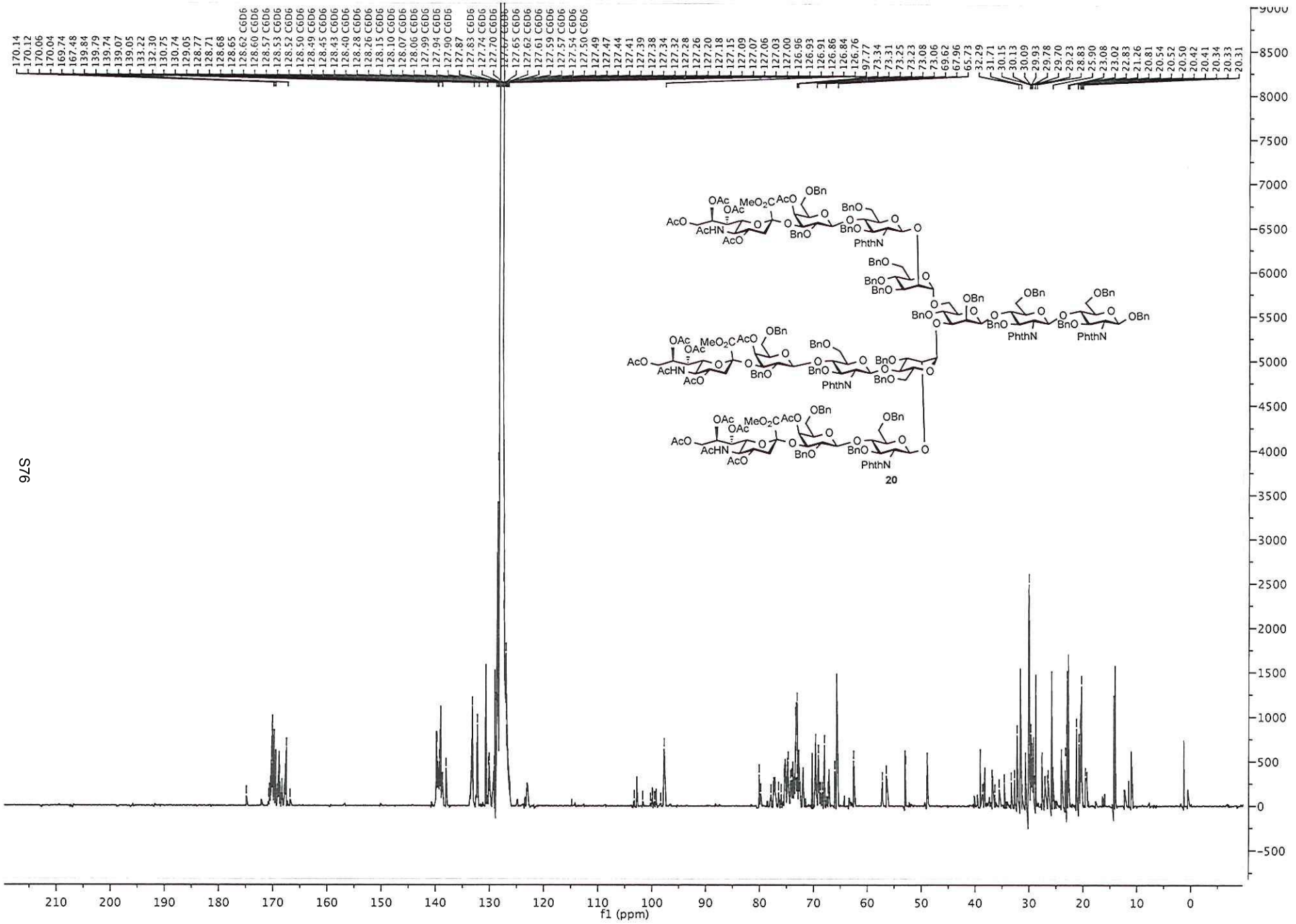
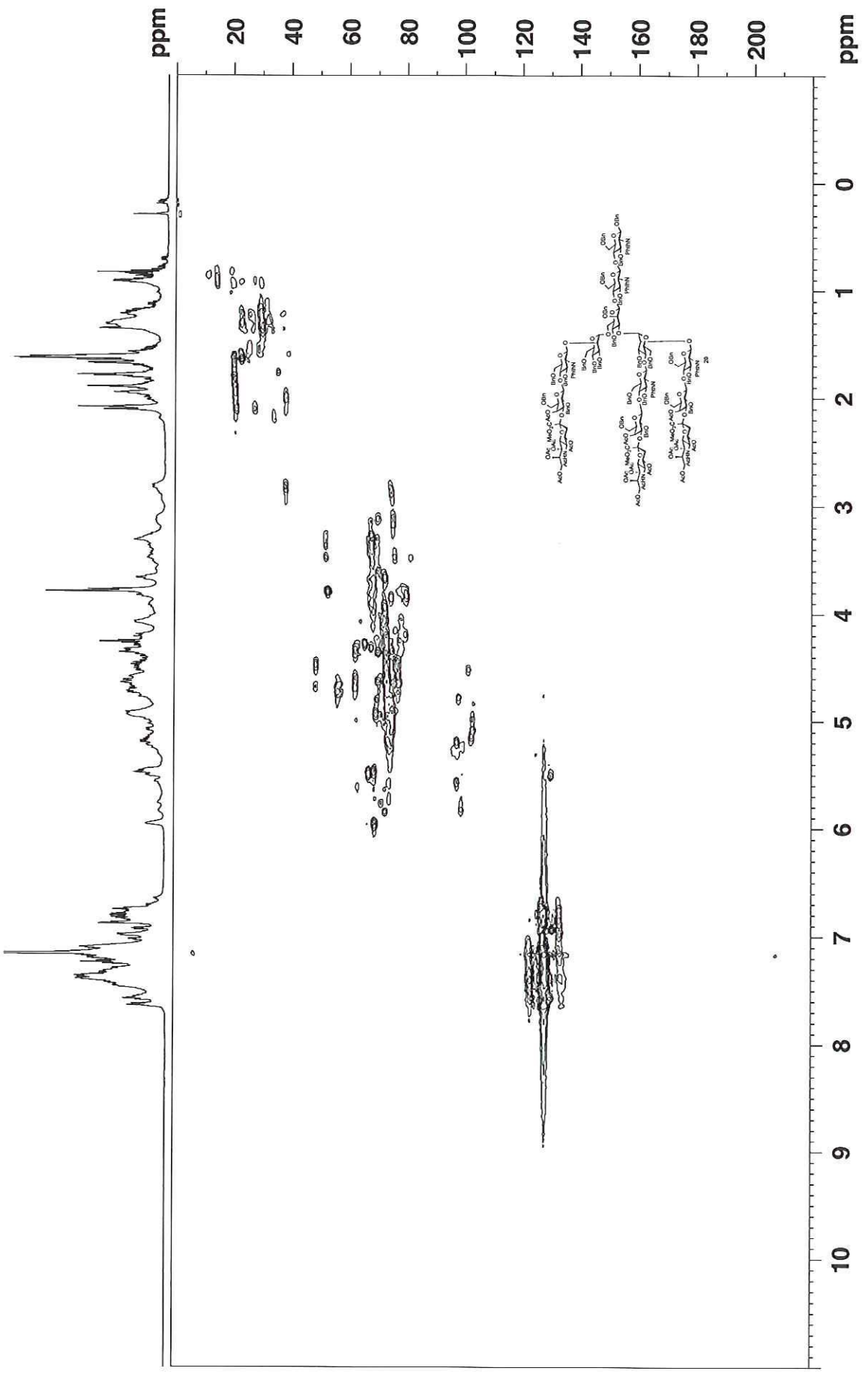
Scale: 10.7 ppm/cm, 1614 Hz/cm


ppm
20
40
60
80
100
120
140
160
180
200
ppm
1
2
3
4
5
6
7
8
9
10
11
26


27
ppm
Scale: 0.4938 ppm/cm, 296.4 Hz/cm




f1 (ppm)
20


ppm
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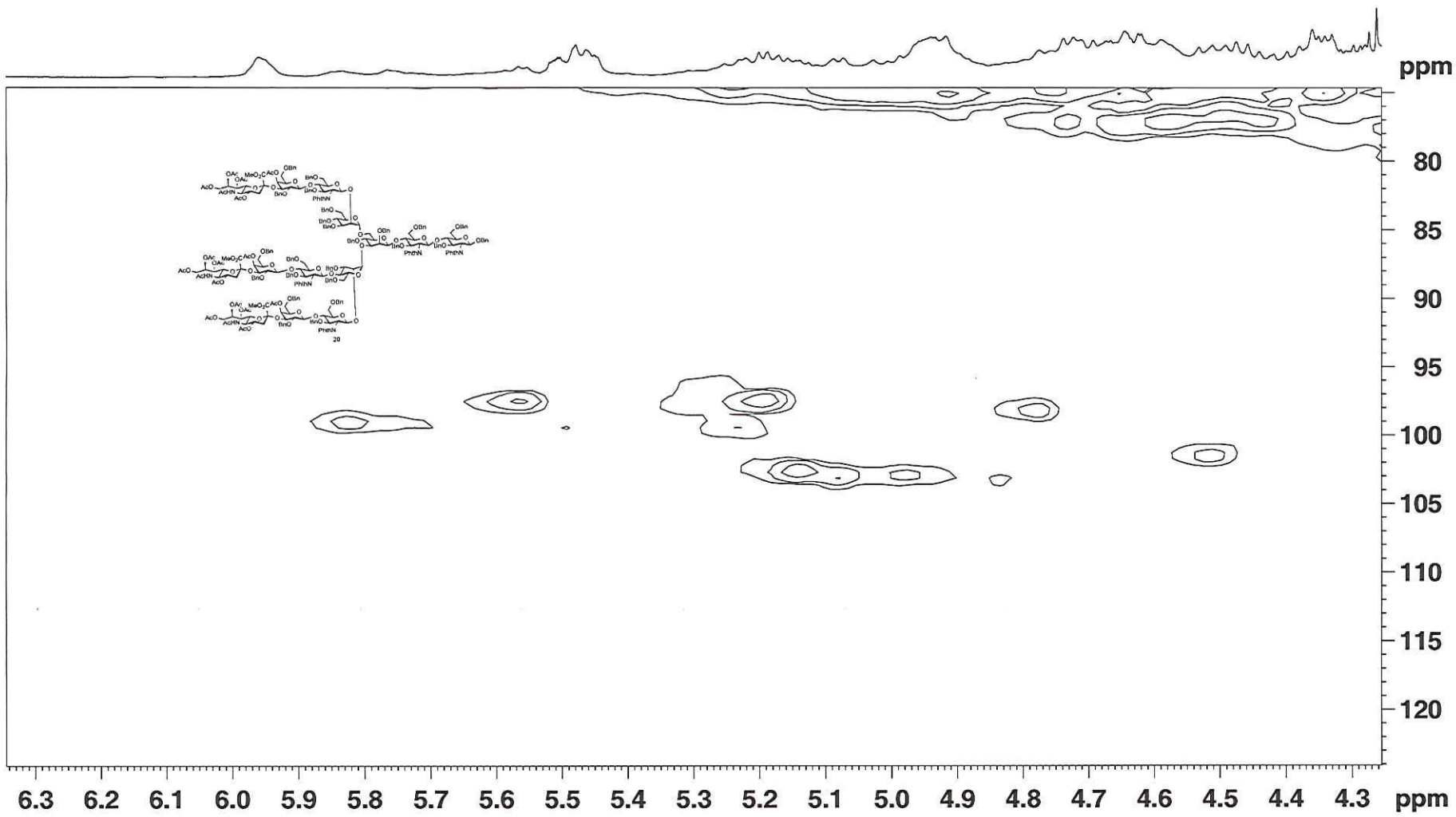
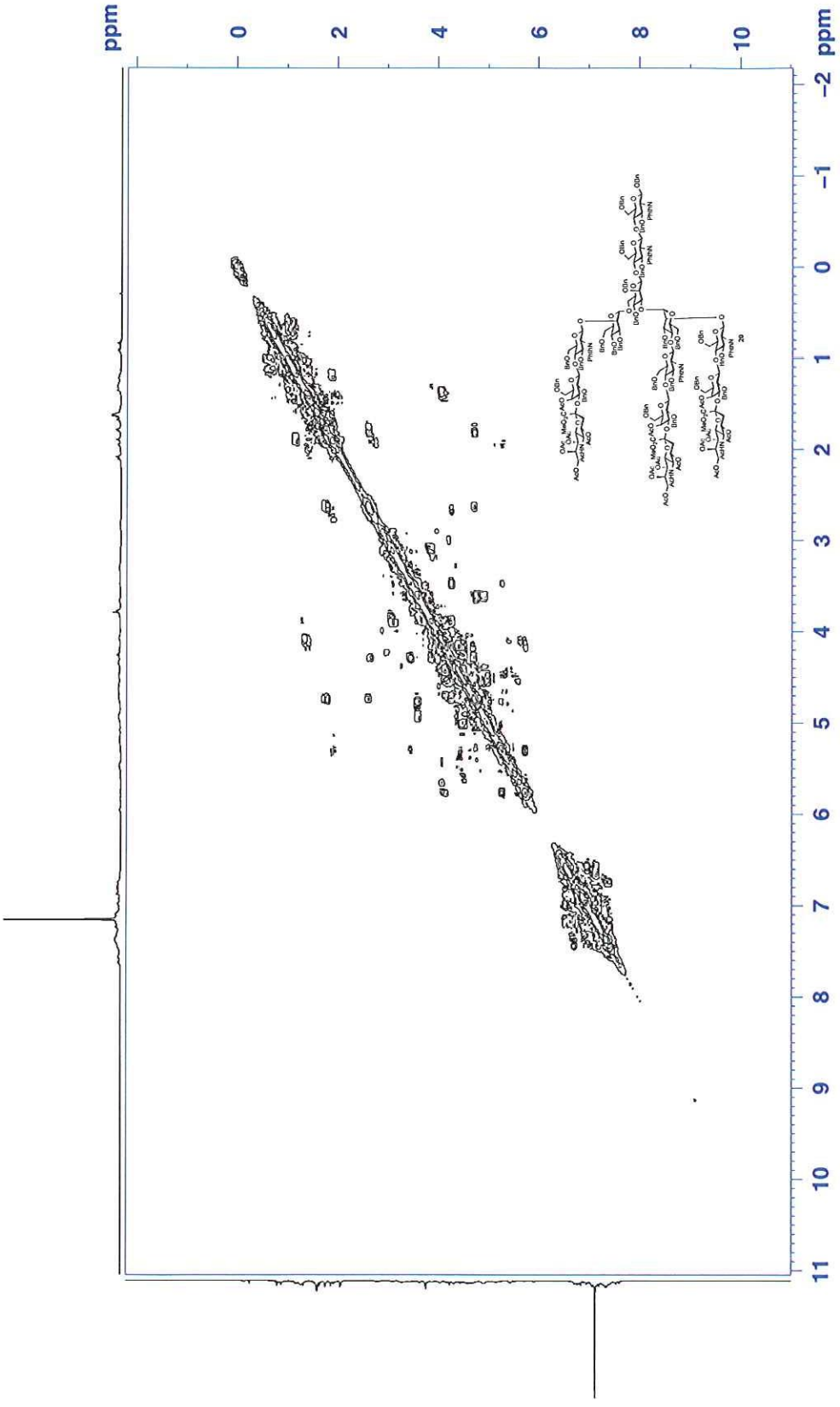
40
60
80
100
120
140
160
180
200
ppm
0
1
2
3
4
5
6
7
8
9
10


ppm
80
85
90
95
100
105
110
115
120
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
ppm


ppm
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6
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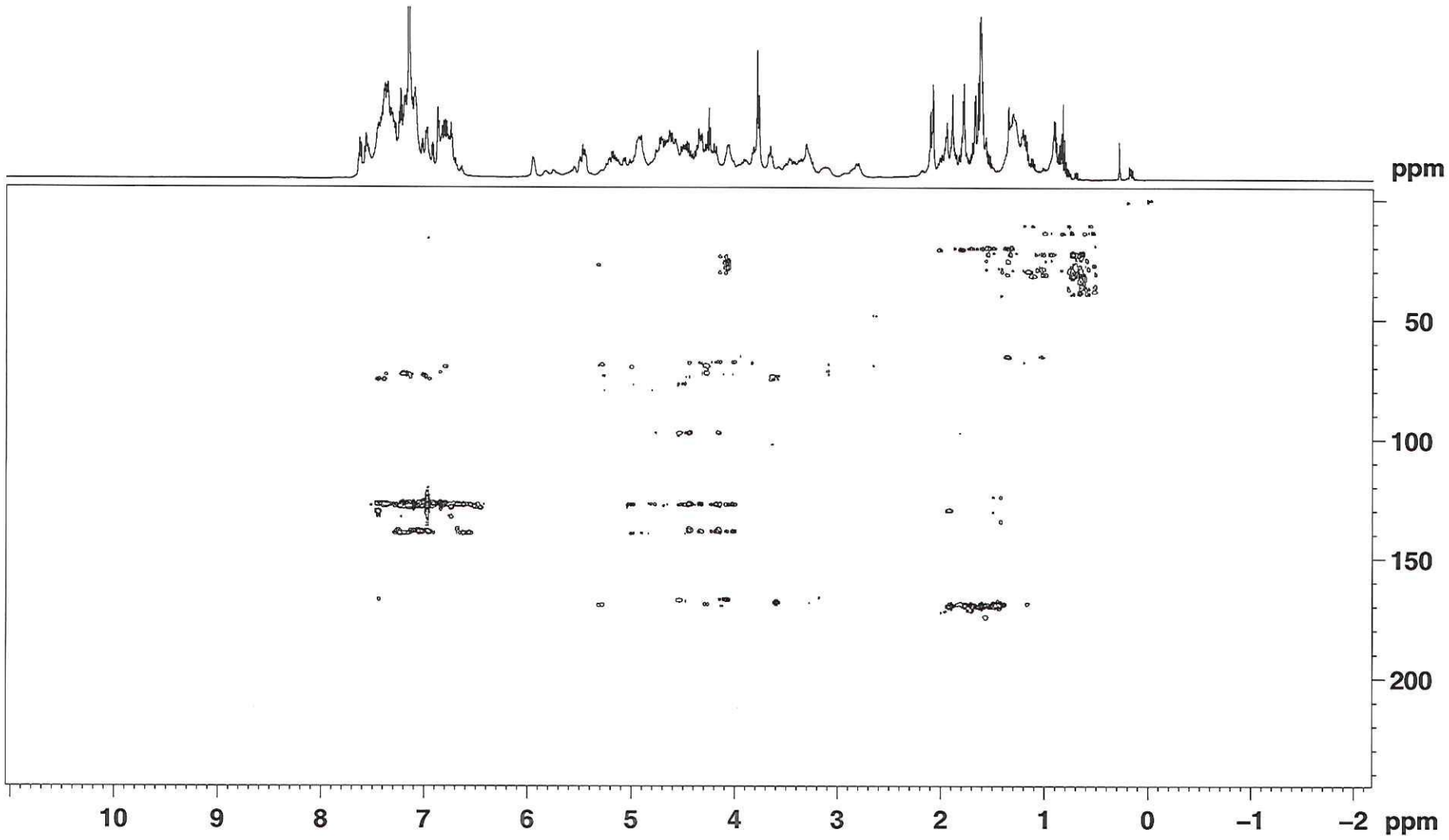
10
ppm
−2
−1
0
1
2
3
4
5
6
7
8
9
10
11


ppm
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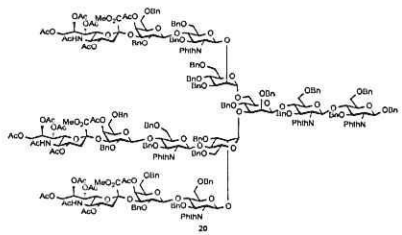
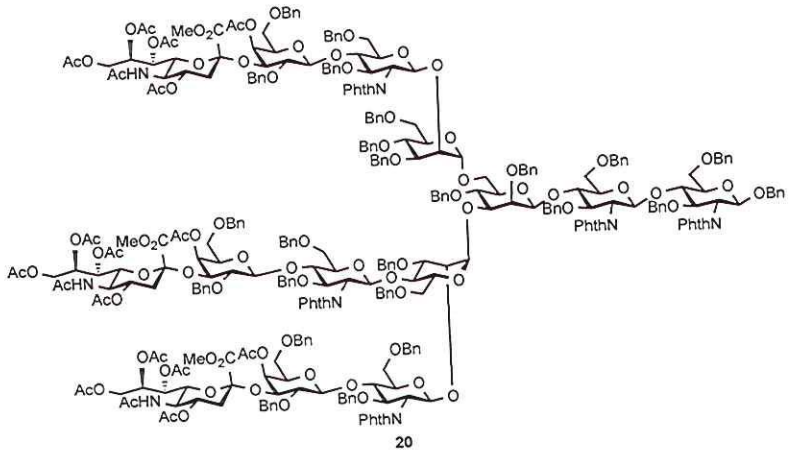
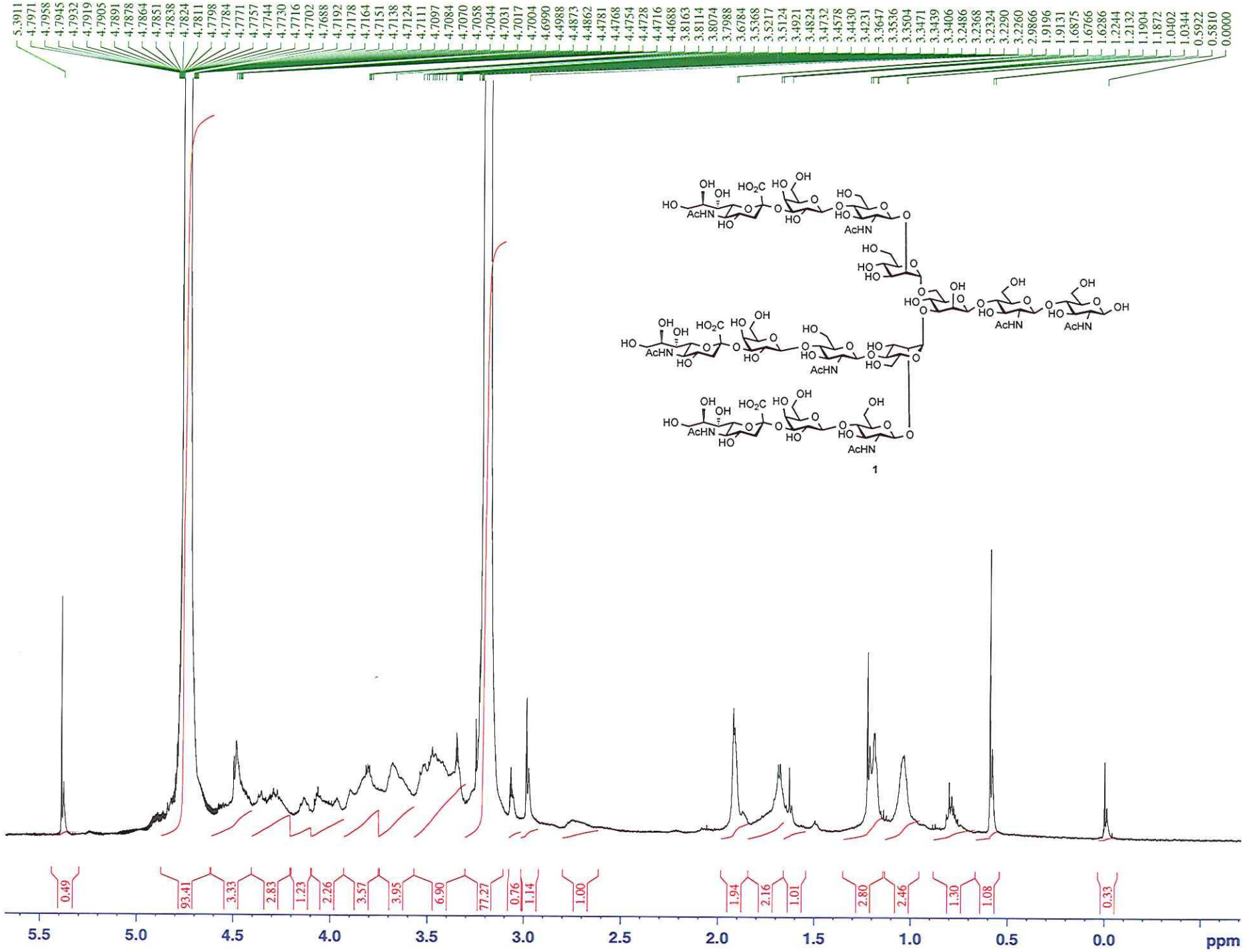
100
150
200
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm



MAW-IV-131-FR18 28 (0.471) Cm (3:32)

Scan ES+
6.71e6

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4.7838
4.7824
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4.7798
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4.7757
4.7744
4.7730
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4.7702
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4.7192
4.7178
4.7164
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4.7084
4.7070
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4.7044
4.7031
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4.7004
4.6990
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4.4768
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4.4728
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4.4688
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3.8114
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3.5368
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3.5124
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3.2260
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1.6766
1.6286
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1.1904
1.1872
1.0402
1.0344
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AcHN
1
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2.26
3.57
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6.90
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0.76
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1.08
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm