Automated Synthesis of a Protected *N*-linked Glycoprotein Core Pentasaccharide

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Supplementary Material

General Methods. All chemicals used were reagent grade and used as supplied except where noted. Trimethylsilyl trifluoromethanesulfonate (TMSOTf) was purchased from Acros Chemicals. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), and tetrahydrofuran (THF) were purchased from J.T. Baker (Cycletainer ™) and passed through neutral alumina columns prior to use. Toluene was purchased from J.T. Baker (Cycletainer ™) and passed through a neutral alumina column and a copper (II) oxide column prior to use. Pyridine and acetonitrile were refluxed over calcium hydride and distilled prior to use. Analytical thin-layer chromatography was performed on E. Merck silica column 60 F_{254} places (0.25 mm). Compounds were visualized by dipping the plates in a cerium sulfate-ammonium molybdate solution followed by heating. Liquid column chromatography was performed using forced flow of the indicated solvent on Silicycle 230-400 mesh (60 Å pore diameter) silica gel. Optical rotation was recorded on a Perkin-Elmer 241 polarimeter using a sodium lamp (589 l) at 24°C. IR spectra were obtained on a Perkin-Elmer System 2000 series FTIR spectrometer. ^{1}H NMR spectra were obtained on a Bruker (400 MHz) or a Varian VXR-500 (500 MHz) and are reported in parts per million (d) relative to $CHCl_3$ (7.27 ppm). Coupling constants (*J*) are reported in Hertz. ^{13}C NMR

spectra were obtained on a Bruker (100 MHz) or a Varian VXR-500 (125 MHz) and are reported in d relative to $CDCl_3$ (77.23 ppm) as an internal reference. High-resolution mass spectrometry was performed on a Bruker DALTONICS APEX II, 3 Tesla, FT-ICR-MS.

***tert*-Butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranoside 6.** Differentially protected glucosamine **5**[11] (5.5 g, 8.9 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to 0°C. Triethylsilane (8.5 mL, 53.5 mmol) was added and the resulting mixture was stirred for 10 min. Trifluoromethanesulfonic acid (3.4 mL, 44.5 mmol) and trifluoromethanesulfonic acid anhydride (1.3 mL, 8.9 mmol) were added simultaneously to the cooled solution and the mixture was stirred at 0°C for 30 min. The solution was warmed slowly to room temperature over a period of 1 h. The reaction mixture was poured into a saturated aqueous solution of Na_2CO_3. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the organic layer was dried over $NaSO_4$, filtered, and solvents removed *in vacuo.* Purification by flash silica column chromatography (10%Æ25% EtOAc/hexanes) afforded **6** as an oil (3.47 g, 63% yield). $[a]^{24}_D$: -13.4° (*c* 1.8, CH_2Cl_2); IR (thin film) 2929, 2858, 1692, 1529, 1070, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.40-7.27 (m, 10H), 6.99 (d, *J* = 8.1 Hz, 1H), 5.05 (d, *J* = 7.8 Hz, 1H), 4.83-4.76 (m, 2H), 4.64-4.57 (m, 2H), 3.95 (dd, *J* = 8.6, 10.5 Hz, 1H), 3.76-3.71 (m, 3H), 3.62-3.55 (m, 2H), 2.92 (s, 1H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) d 161.9, 138.2, 137.8, 128.7, 128.6, 128.2, 128.0, 128.0, 127.8, 94.9, 92.7, 79.8, 74.4, 74.0, 73.8, 73.3, 70.7, 60.1, 25.8, 18.0, -4.0, -5.0; ESI MS *m/z* (M^+ + Na^+) calcd 640.1426, found 640.1400.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-α-D-glucopyranosyl trichloroacetimidate 2. A solution of **6** (1.06 g, 1.71 mmol) in CH_2Cl_2 (20 mL) was cooled to 0°C. Acetic anhydride (0.24 mL, 2.57 mmol) was added and the resulting solution was stirred for 5 min. Dimethylaminopyridine (314 mg, 2.57 mmol) was added and the reaction was allowed to warm slowly to room temperature while stirring overnight. The mixture was diluted with CH_2Cl_2 (30 mL) and the organic layer was washed with 5% HCl (2 x 30 mL). The organic layer was dried over Na_2SO_4, filtered, and solvents removed in vacuo to afford *tert*-butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-acetyl-2-trichloroacetimido-β-D-glucopyranoside (1.13 g, 99%). $[\alpha]^{24}_D$: +9.0° (*c* 1.7, CH_2Cl_2); IR (thin film) 3354, 1715, 1527, 1249, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 10H), 7.12 (d, *J* = 7.7 Hz, 1H), 5.20 (d, *J* = 7.8 Hz, 1H), 5.09 (γ t, *J* = 9.4 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.54 (s, 2H), 4.29 (γ t, *J* = 10.3 Hz, 3H), 3.71-3.69 (m, 1H), 3.58-3.52 (m, 1H), 1.89 (s, 3H), 0.92 (s, 9H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 169.9, 161.9, 138.0, 137.8, 128.6, 128.4, 128.0, 127.8, 127.8, 94.3, 92.7, 77.4, 74.1, 73.6, 73.4, 71.8, 69.8, 60.8, 25.8, 21.0, 18.0, -4.0, -5.1; ESI MS *m/z* (M^+ + Na^+) calcd 682.1532, found 682.1543.

A solution *tert*-butyldimethylsilyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-acetyl-2-trichloroacetimido-β-D-glucopyranoside (1.13 g, 1.71 mmol) in THF (18 mL) was cooled to 0°C. Acetic acid (0.15 mL, 2.68 mmol) and then tetrabutylammonium fluoride (1.0 M in THF, 2.68 mL, 2.68 mmol) were added to the cooled solution. The reaction mixture was allowed to warm slowly to room temperature while stirring overnight. The reaction mixture was diluted with EtOAc and washed with $NaHCO_3$ (2 x 30 mL) and H_2O (1 x 30

mL). The organic layer was dried over Na_2SO_4, filtered, and solvents removed *in vacuo*. The crude material (887 mg, 1.62 mmol) was dissolved in CH_2Cl_2 (16 mL) and trichloroacetonitrile (4 mL). After stirring for 5 min, DBU (49 mL, 0.32 mmol) was added and the reaction mixture was allowed to stir for 1.5 h. The reaction mixture was passed through a silica plug, washed with EtOAc and solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **2** (942 mg, 76% two steps, 95:5 a:b). IR (thin film) 1747, 1722, 1678, 1514,1226, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 8.79 (s, 1H), 7.37-7.27 (m, 10H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.49 (d, *J* = 3.5 Hz, 1H), 5.41 (Yt, *J* = 9.7 Hz, 1H), 4.70-4.64 (m, 2H), 4.57-4.45 (m, 3H), 4.10-4.02 (m, 2H), 3.63-3.55 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) d 169.3, 161.8, 159.9, 137.6, 137.0, 128.8, 128.4, 128.4, 128.3, 128.1, 127.8, 94.3, 92.1, 90.7, 76.0, 73.6, 73.0, 72.1, 69.9, 68.4, 53.5, 20.9; ESI MS *m/z* (M^+ + Na^+) calcd 710.9763, found 710.9762.

***tert*-Butyldimethylsilyl 3-*O*-acetyl-2-*O*-benzyl-4,6-*O*-benzylidene-b-D-mannopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranoside 8.** Phenyl sulfoxide **7** (1.50 g, 2.56 mmol) and **6** (2.53 g, 4.09 mmol) were coevaporated separately (important!) with toluene (3 x 10 mL) and dried under vacuum overnight. Sulfoxide **7** was dissolved in CH_2Cl_2 (26 mL) and cooled to -78°C. Di-*t*-butyl pyridine (1.15 mL, 5.12 mmol) was added to the cooled solution and stirred for 10 min. Triflic anhydride (474 mL, 2.82 mmol) was added and the mixture was stirred for 5 min, during which time the colorless mixture turned orange. A solution of **6** in CH_2Cl_2 (10 mL) was slowly added to the reaction mixture via cannula and the reaction was stirred at -78°C for 1 h. The reaction was quenched with saturated $NaHCO_3$ (20 mL)

and diluted with CH_2Cl_2 (30 mL). The organic layer was were washed with $NaHCO_3$ (2 x 30 mL), dried over Na_2SO_4, filtered, and solvents removed *in vacuo*. Purification by flash silica column chromatography (100% toluene Æ 25% EtOAc/toluene) afforded *tert*-butyldimethylsilyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-b-D-mannopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranoside (1.77 g, 68%). $[a]^{24}_D$: -25.7° (*c* 3.1, CH_2Cl_2); IR (thin film) 3322, 2861, 1691, 1531, 1089 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.51-7.18 (m, 22H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.87-6.85 (m, 2H), 5.54 (s, 1H), 5.19 (d, *J* = 7.7 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 2.6 Hz, 2H), 4.68-4.45 (m, 6H), 4.14-4.06 (m, 3H), 3.99 (Yt, *J* = 8.7 Hz, 1H), 3.80 (s, 3H) 3.79-3.77 (m, 1H), 3.68-3.39 (m, 6H), 3.16-3.15 (m, 1H), 2.37 (s, 1H), 0.90 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) d 161.8, 159.3, 138.7, 138.6, 138.0, 137.8, 130.7, 129.3, 129.2, 129.1, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.1, 127.9, 127.8, 126.3, 125.5, 113.9, 101.9, 101.5, 94.4, 92.7, 78.8, 78.3, 78.0, 77.4, 77.3, 75.2, 75.1, 74.8, 73.8, 72.5, 68.9, 68.7, 67.6, 60.7, 55.5, 25.9, 18.1, -4.0, -4.9; ESI MS *m/z* ($M^+ + Na^+$) calcd 1100.3312, found 1100.3278.

To a stirring solution of *tert*-butyldimethylsilyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-b-D-mannopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranoside (1.0 g, 0.93 mmol) in CH_2Cl_2 (4.5 mL) and H_2O (0.5 mL) was added 2,3-dichloro-5,6-dicyanobenzoquinone (252 mg, 1.11 mmol). After stirring for 45 min, the reaction mixture was diluted with CH_2Cl_2 (45 mL). The organic layer was washed with $NaHCO_3$ (2 x 25 mL), H_2O (1 x 25 mL), dried over Na_2SO_3, filtered and solvents removed *in vacuo*. Purification by flash silica column chromatography (20% EtOAc/hexanes) gave a white solid. The solid (743 mg, 0.77

mmol) was dissolved in CH_2Cl_2 (8 mL) and cooled to 0°C. Acetic anhydride (147 mL, 1.55 mmol) was added and stirred for 5 min. Dimethylaminopyridine (114 mg, 0.93 mmol) was added and the stirring mixture was warmed slowly to room temperature over 2 h. The reaction was diluted with CH_2Cl_2 (15 mL) and washed with 5% HCl (2 x 15 mL), H_2O (1 x 15 mL), $NaHCO_3$ (2 x 15 mL). The organic layer was dried over Na_2SO_4, filtered, and solvents removed in vacuo. Purification by flash silica column chromatography (33% EtOAc/hexanes) afforded **8** (771 mg, 79% for two steps). $[a]^{24}_D$: -45.0° (*c* = 0.7, CH_2Cl_2); IR (thin film) 3339, 2858, 1738, 1691, 1092, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 7.47-7.28 (m, 20H), 6.99 (d, *J* = 7.5 Hz, 1H), 5.48 (s, 1H), 5.22 (d, *J* = 7.7 Hz, 1H), 5.11 (d, *J* =10.4 Hz, 1H), 4.87-4.82 (m, 2H), 4.74-4.50 (m, 5H), 4.18-4.02 (m, 5H), 3.71 (dq, *J* = 2.3, 5.6 Hz, 2H), 3.57-3.52 (m, 2H), 3.41-3.38 (m, 1H), 3.23-3.22 (m, 1H), 1.99 (s, 3H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) d 170.6, 161.8, 138.7, 138.2, 137.9, 137.4, 129.3, 128.8, 128.5, 128.4, 128.4, 128.4, 128.2, 128.2, 128.0, 128.0, 127.8, 126.4, 101.9, 101.3, 94.4, 92.7, 78.1, 77.3, 76.5, 75.9, 75.7, 75.1, 74.8, 73.8, 72.6, 68.8, 68.6, 67.5, 60.8, 25.8, 21.22, 18.1, -4.0, -4.9; ESI MS m/z ($M^+ + Na^+$) calcd 1022.2843, found 1022.2807.

***tert*-Butyldimethylsilyl 3,6-di-*O*-acetyl-2,4-di-*O*-benzyl-b-D-mannopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranoside 9.** To a solution of **8** (213 mg, 0.213 mmol) in CH_2Cl_2 (2 mL) were added freshly dried 4Å molecular sieves (750 mg). After stirring for 1h, the mixture was cooled to -78°C. Triethylsilane (102 mL, 0.64 mmol) was added and the resulting solution was stirred for 5 min. Dichlorophenylborane (83 mL, 0.64 mmol) was added and the mixture was stirred for 30 min at -78°C. The reaction was quenched with the addition of triethylamine (0.4 mL)

and methanol (0.4 mL) and diluted with CH_2Cl_2 (20 mL). The organic layer was washed with $NaHCO_3$ (2 x 20 mL), H_2O (1 x 20 mL), dried over Na_2SO_4, filtered, and solvents removed in vacuo. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded a white solid. The solid (170 mg, 0.17 mmol) was dissolved in CH_2Cl_2 (2 mL) and cooled to 0°C. Acetic anhydride (32 mL, 0.34 mmol) was added and stirred for 5 min. Dimethylaminopyridine (25 mg, 0.20 mmol) was added and the stirring mixture was warmed slowly to room temperature over 2.5 h. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with 5% HCl (2 x 15 mL), H_2O (1 x 15 mL), and $NaHCO_3$ (2 x 15 mL). The organic layer was dried over Na_2SO_4, filtered, and the solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **9** (163 mg, 82% two steps). $[\alpha]^{24}_D$: -23.5° (*c* 1.0, CH_2Cl_2); IR (thin film) 3342, 2858, 1742, 1691, 1234, 1073 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, 20H), 6.93 (d, *J* = 7.5 Hz, 1H), 5.15-5.11 (m, 2H), 4.86-4.49 (m, 9H), 4.25-4.08 (m, 4H), 3.94 (d, *J* = 3.0 Hz, 1H), 3.85 (Yt, *J* = 9.7 Hz, 1H), 3.74 (dd, *J* = 2.7, 11.1 Hz, 1H), 3.66 (dd, *J* = 3.4, 11.1 Hz, 1H), 3.54-3.37 (m, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 0.89 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 171.0, 170.4, 161.8, 139.0, 138.5, 138.0, 128.7, 128.7, 128.5, 128.4, 128.1, 128.1, 127.9, 127.9, 127.6, 100.8, 94.5, 92.7, 77.9, 77.7, 77.4, 76.2, 75.9, 75.1, 74.9, 74.3, 73.8, 73.6, 73.3, 68.9, 63.6, 60.4, 25.8, 21.2, 20.9, 18.1, -4.0 -4.9; ESI MS m/z (M^+ + Na^+) calcd 1066.3105, found 1066.3124.

3,6-Di-*O*-acetyl-2,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-α-D-glucopyranosyl trichloroacetimidate 4. A solution of **9** (330 g, 0.31 mmol) in THF (3 mL) was cooled to 0°C. Acetic acid (27 mL, 0.47

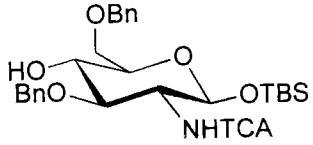
mmol) and then tetrabutylammonium fluoride (1.0 M in THF, 470 mL, 0.47 mmol) were added to the cooled solution. The reaction mixture was allowed to warm slowly to room temperature while stirring for 3 h. The reaction mixture was diluted with EtOAc and washed with $NaHCO_3$ (2 x 10 mL) and H_2O (1 x 10 mL). The organic layer was then dried over Na_2SO_4, filtered, and solvents removed in vacuo. The crude material (294 mg, 0.31 mmol) was dissolved in CH_2Cl_2 (3 mL) and trichloroacetonitrile (0.3 mL) and cooled to 0°C. After stirring for 5 min, DBU (9.3 mL, 0.062 mmol) was added and the reaction mixture was allowed to stir for 1.5 h. The reaction mixture was passed through a silica plug, washed with EtOAc and the solvents removed *in vacuo*. Purification by flash silica column chromatography (25% EtOAc/hexanes) afforded **4** (298 mg, 89%, 95:5 a:b). IR (thin film) 1739, 1513, 1234, 1076, 1028 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d 8.71 (s, 1H), 7.43-7.26 (m, 20H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 11.9 Hz, 1H), 4.87 (d, *J* = 12.1 Hz, 1H), 4.77-4.66 (m, 6H), 4.59-4.50 (m, 2H), 4.30-4.22 (m, 4H), 3.95-3.86 (m, 4H), 3.70 (s, 2H), 3.38-3.35 (m, 1H), 1.97 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) d 170.9, 170.3, 162.0, 160.1, 138.4, 138.4, 137.9, 137.5, 128.8, 128.7, 128.7, 128.6, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 100.6, 94.5, 92.1, 91.0, 76.7, 76.2, 75.8, 75.7, 75.0, 74.8, 73.9, 73.8, 73.7, 73.4, 73.1, 67.9, 63.1, 54.1, 21.1, 20.8; ESI MS m/z (M^+ + Na^+) calcd 1095.1336, found 1095.1343.

***n*-Pentenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-a-D-mannopyranosyl-(1Æ3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-a-D-mannopyranosyl-(1Æ6)]-2,4-di-*O*-benzyl-b-D-mannopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-glucopyranosyl-(1Æ4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetimido-b-D-**

glucopyranoside 1. Glycosylated resin from automated synthesis was dried *in vacuo* for 18 h over phosphorous pentoxide and transferred into a solid-phase round bottom flask with glass frit. The resin was swelled with 5 ml CH_2Cl_2, purged with an atmosphere of ethylene followed by the addition of 10 mol % Grubbs' catalyst (bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride. The reaction mixture was stirred for 24 h under an atmosphere of ethylene, an additional 10 mol% Grubbs' catalyst was added, and the reaction was allowed to stir an additional 24 h under an atmosphere of ethylene. Triethylamine (100 equiv.) and tris hydroxymethylphosphine (50 equiv.) were added, and the mixture stirred 2 h at room temperature. The reaction was diluted in CH_2Cl_2 and washed 3 times with water. The aqueous fractions were washed with additional CH_2Cl_2. The organic fractions were combined, dried over $MgSO_4$, filtered, and dried to yield adark oil.

The crude product was analyzed by HPLC (Waters Nova-pak" silica column (3.9 x 150 mm) with EtOAc/hexanes as the mobile phase), monitoring at 260 nm. A portion of the crude product was purified by semi-preparative HPLC using a Waters prep Nova-pak" silica column (7.8 x 300 mm) with a gradient of EtOAc/hexanes. Semi-preparative HPLC yielded 3 mg of **1** that corresponded to **1** made by solution phase synthesis. IR (thin film) 2867, 1746, 1711, 1693, 1235, 1077 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) d 7.41-7.08 (m, 60H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 5.80-5.72 (m, 1H), 5.48-5.46 (m, 1H), 5.37-5.35 (m, 1H), 5.14-4.27 (m, 31H), 4.42-3.14 (m, 30H), 2.14-2.06 (m, 5H), 1.98 (s, 3H), 1.68-1.63 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) d 170.3, 170.3, 161.9, 161.8, 138.9, 138.8, 138.7, 138.7, 138.6, 138.5, 138.5, 138.2, 138.2, 138.2, 138.0, 137.9, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5 128.4, 128.4, 128.3,

128.2, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.3, 115.1, 101.5, 99.8, 99.7, 99.0, 97.8, 92.7, 81.2, 78.5, 78.2, 78.1, 77.5, 77.2, 77.0, 75.5, 75.3, 75.2, 75.0, 75.0, 74.9, 74.5, 74.5, 74.4, 74.3, 74.2, 73.6, 73.5, 73.5, 72.5, 72.0, 71.7, 71.6, 71.5, 69.4, 69.2, 68.8, 68.6, 68.5, 66.7, 58.2, 57.4, 30.2, 29.9, 28.9, 28.9, 21.3, 21.2, 21.2; ESI MS m/z ($M^+ + Na^+$) calcd 2369.7303, found 2369.7401.



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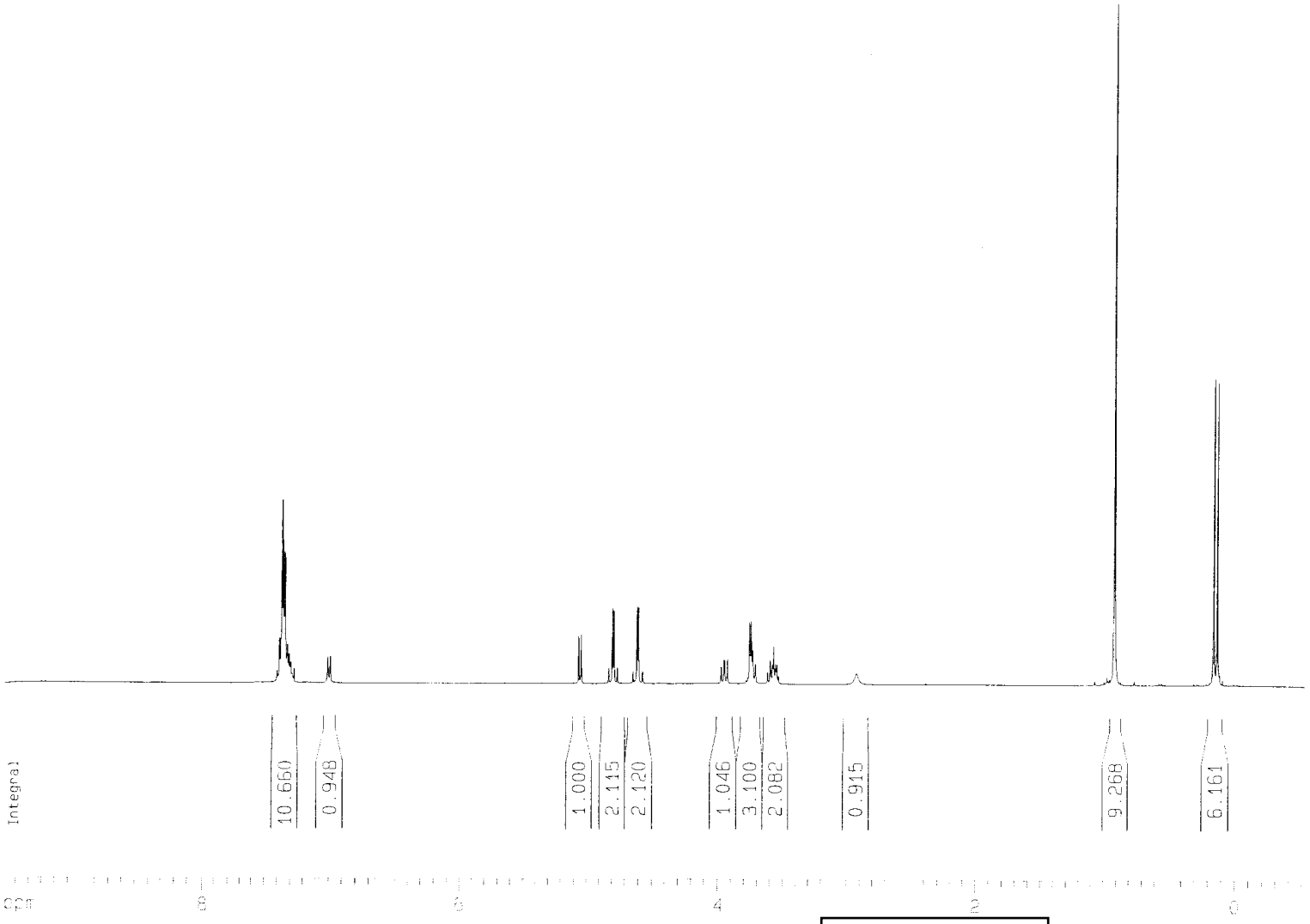


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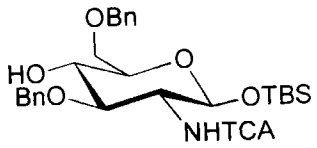

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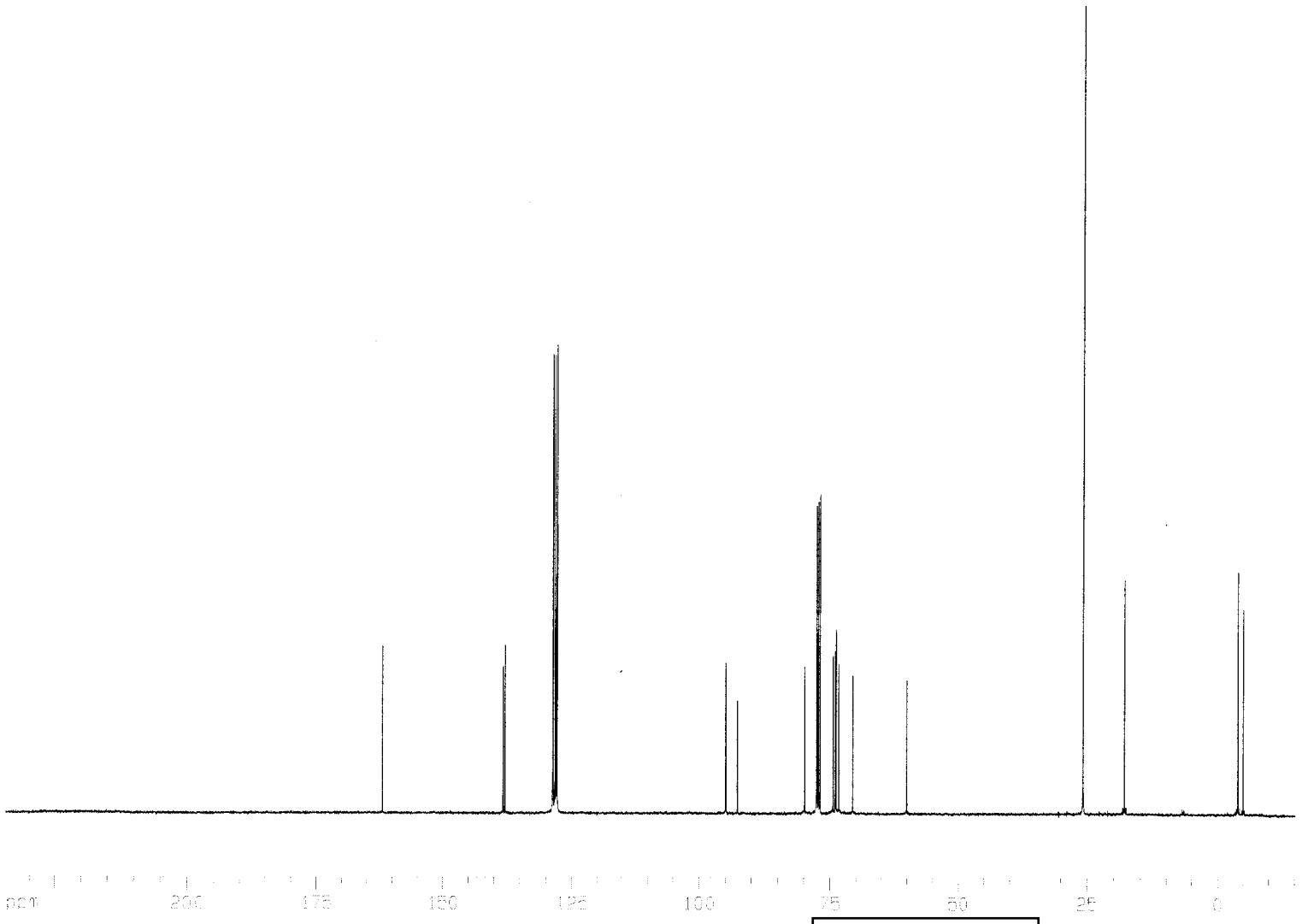
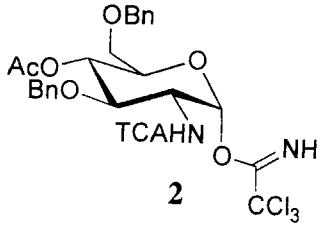
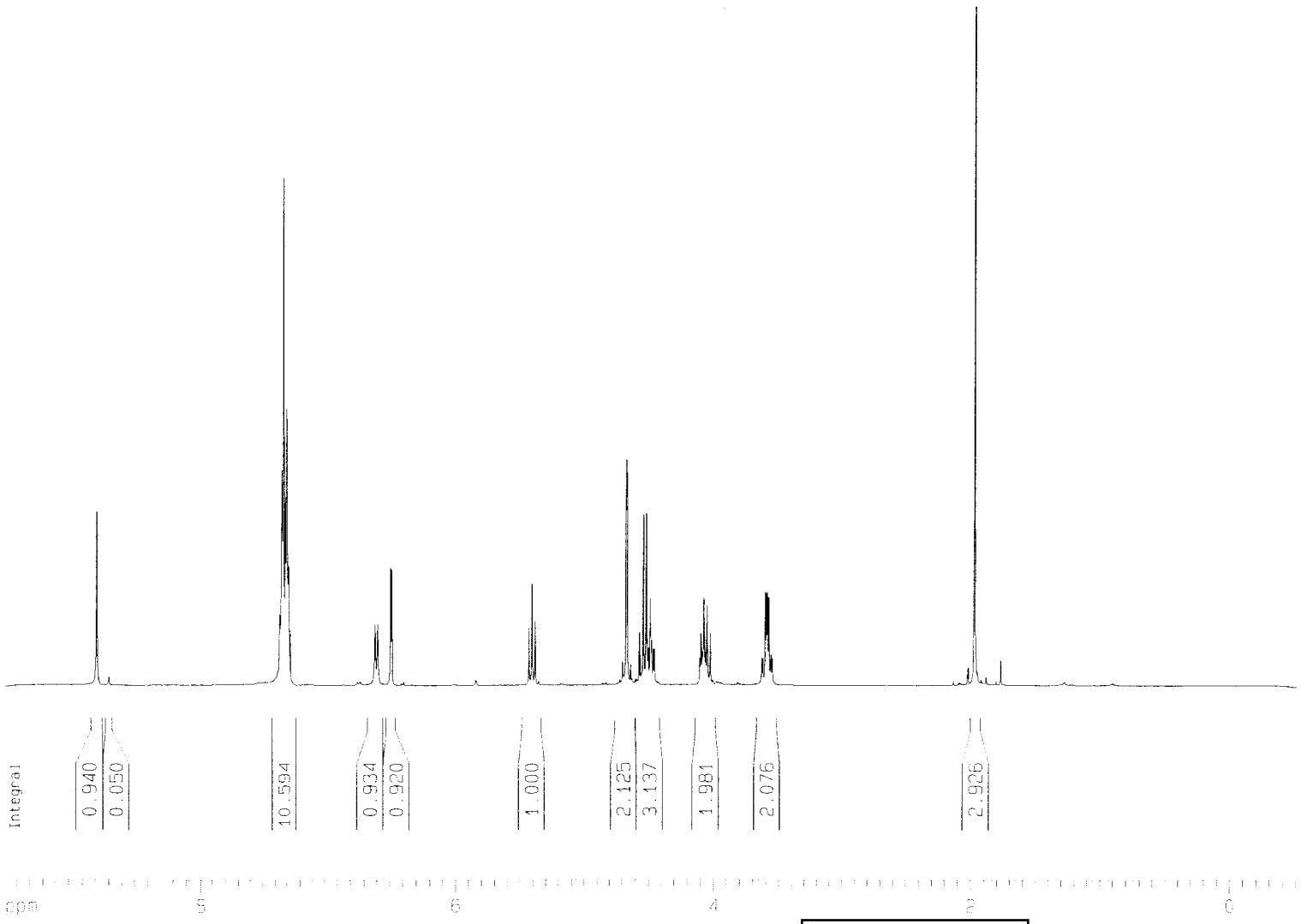



```
Current Data Parameters
NAME      ERS-III-238C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030105
Time                21.16
INSTRUM             spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG              14596.5
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                15.25 usec
PL1               3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2            107.50 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127614 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
F1P              234.536 ppm
F1             23597.30 Hz
F2P              -15.190 ppm
F2             -1528.33 Hz
PPMCM           12.48630 ppm/cm
HZCM          1256.28137 Hz/cm
```

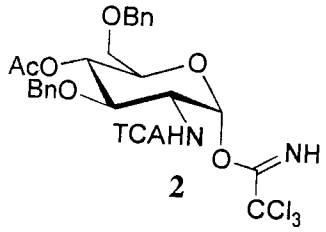
12



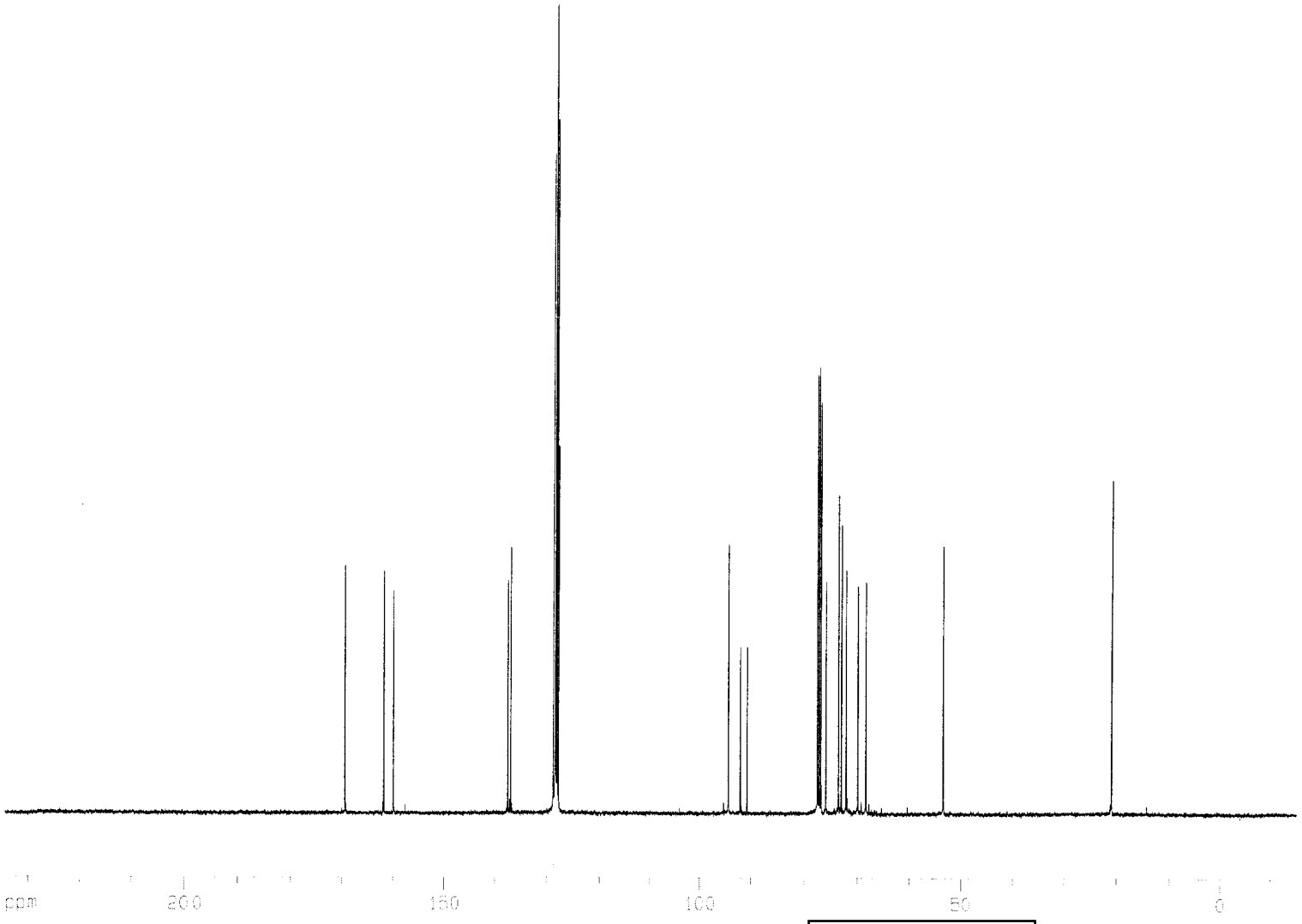
2



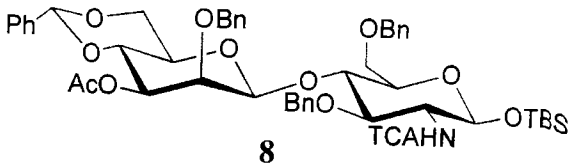

```
Current Data Parameters
NAME        ERS-IV-027z3
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20030120
Time              20.56
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               40062
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          4006.410 Hz
FIDRES       0.100005 Hz
AQ           4.9997878 sec
RG                50.8
DW             124.800 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1               7.90 usec
PL1              0.00 dB
SFO1       400.1318006 MHz

F2 - Processing parameters
SI                32768
SF         400.1300056 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00

1D NMR plot parameters
CX              20.00 cm
F1P              9.492 ppm
F1            3798.19 Hz
F2P             -0.520 ppm
F2            -208.23 Hz
PPMCM         0.50064 ppm/cm
HZCM        200.32053 Hz/cm
```



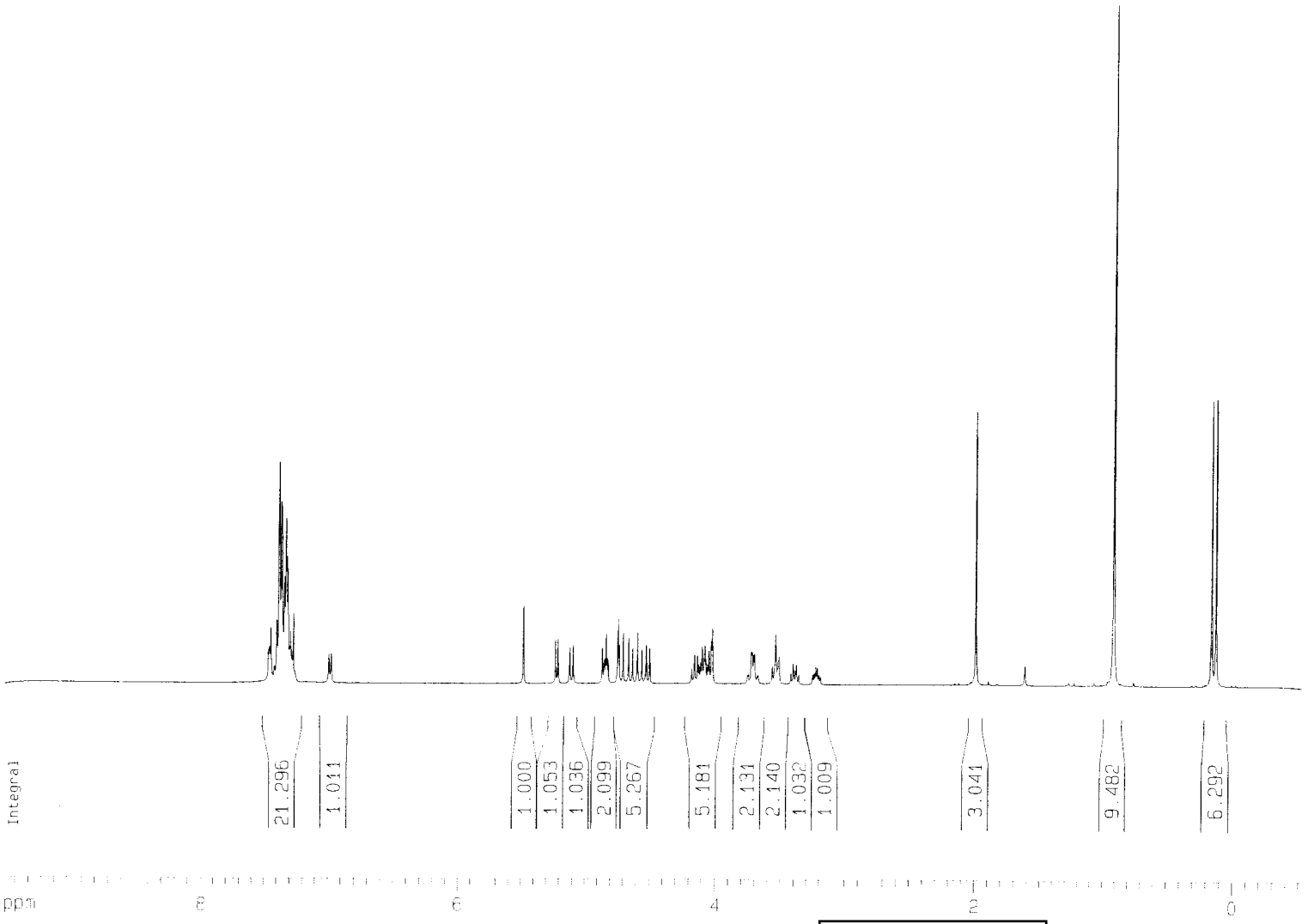
2



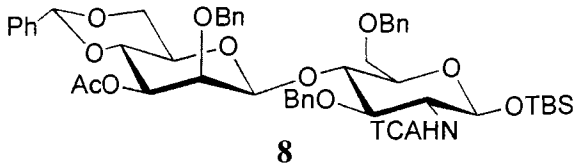

```
Current Data Parameters
NAME       ERS-IV-027C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20030119
Time               18.24
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG                 2048
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1               13C
P1               15.25 usec
PL1               3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2           107.50 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127691 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40

1D NMP plot parameters
CX               20.00 cm
F1P             234.459 ppm
F1              23589.62 Hz
F2P             -15.267 ppm
F2              -1536.01 Hz
PPMCM           12.48630 ppm/cm
HZCM          1256.28137 Hz/cm
```



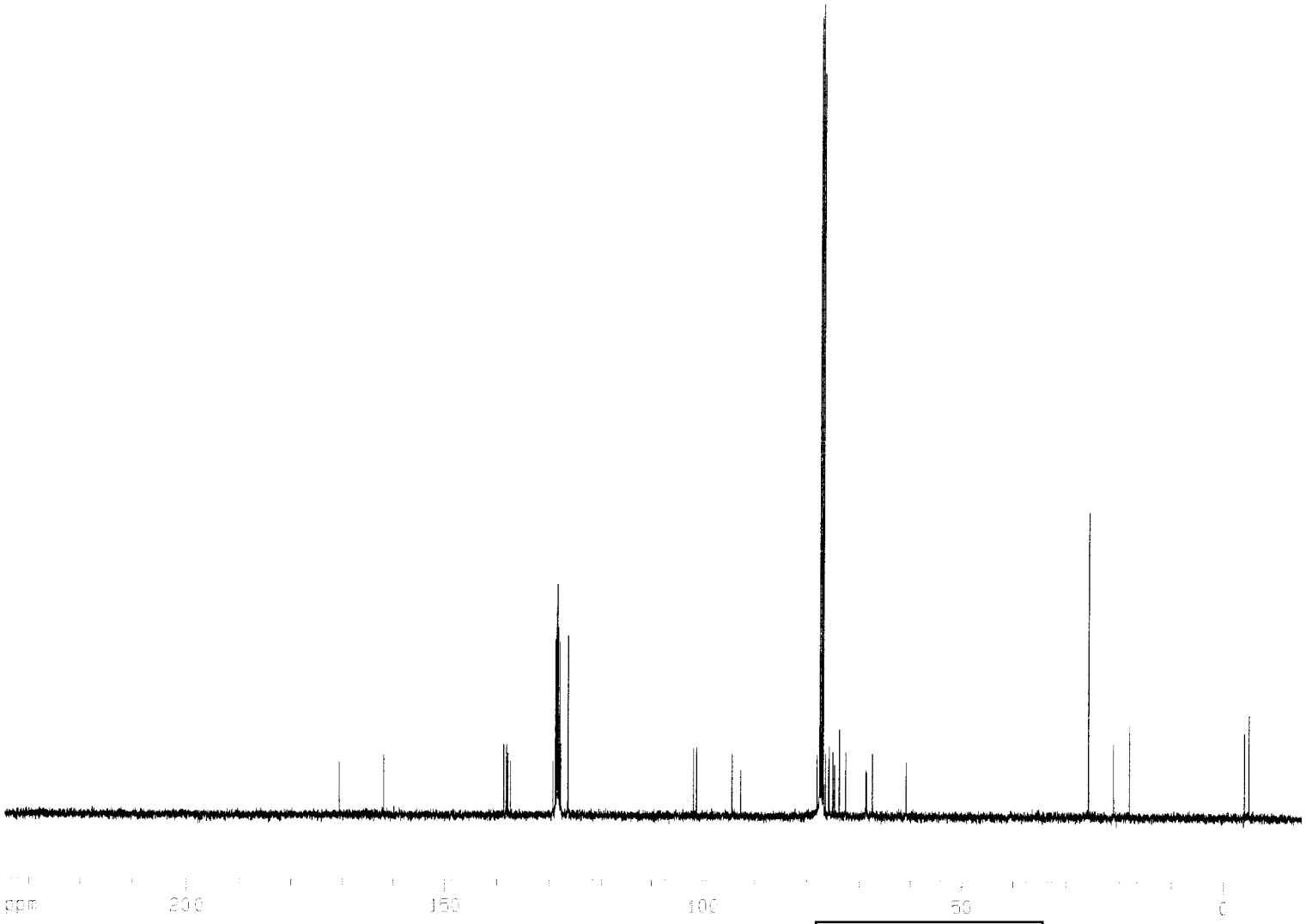
8



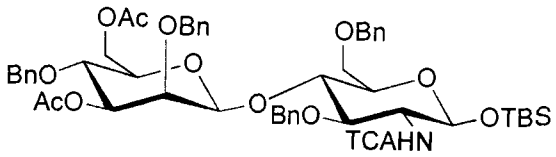

```
Current Data Parameters
NAME      ERS-III-242dry
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20021028
Time               16.02
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG            zg30
TD                40062
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           4006.410 Hz
FIDRES        0.100005 Hz
AQ            4.9997878 sec
RG                 80.6
DW              124.800 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1318006 MHz

F2 - Processing parameters
SI                32768
SF          400.1300060 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC                1.00

1D NMR plot parameters
CX               20.00 cm
F1P               9.491 ppm
F1             3797.82 Hz
F2P              -0.521 ppm
F2             -208.59 Hz
PPMCM         0.50064 ppm/cm
HZCM         200.32053 Hz/cm
```



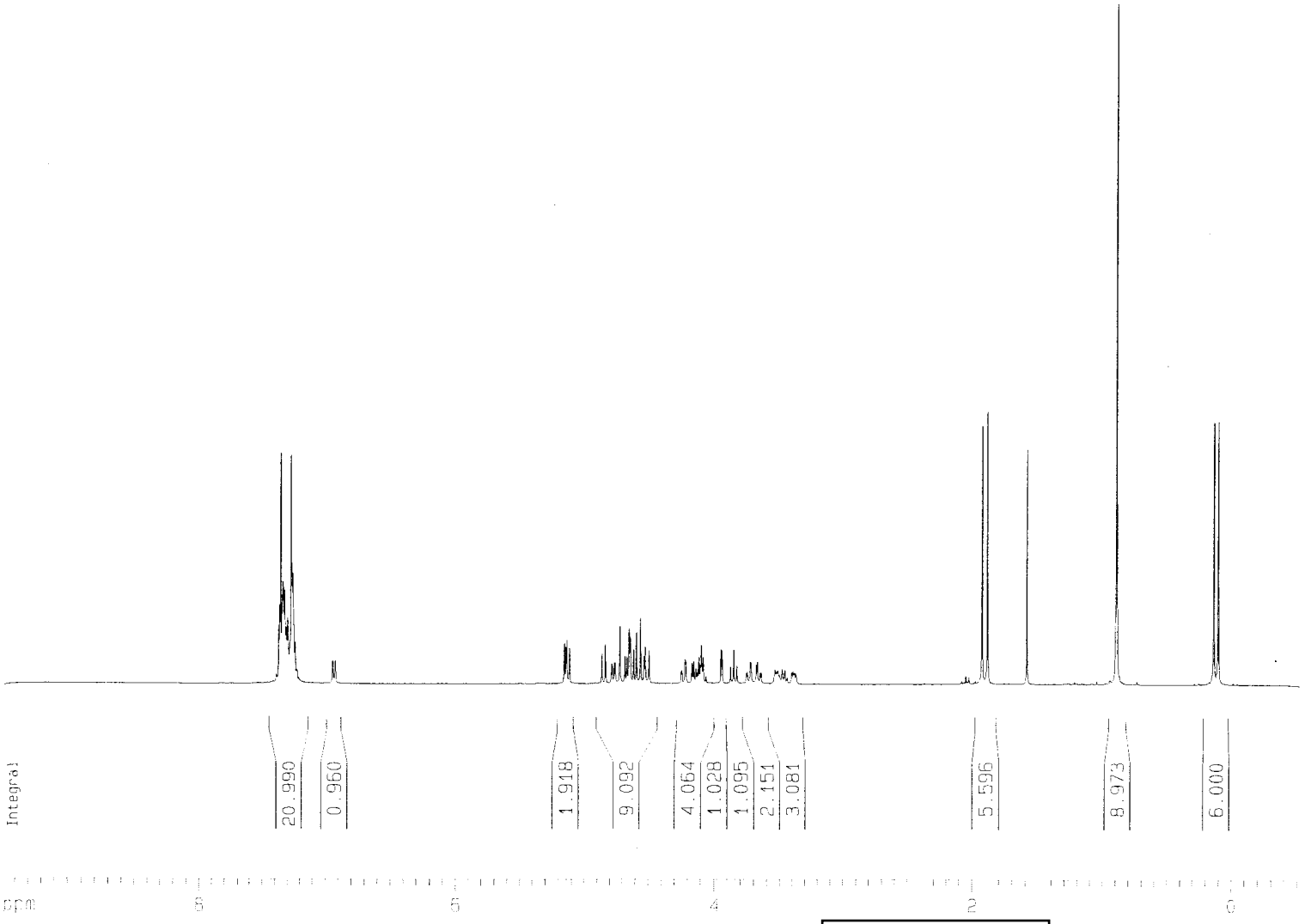
8



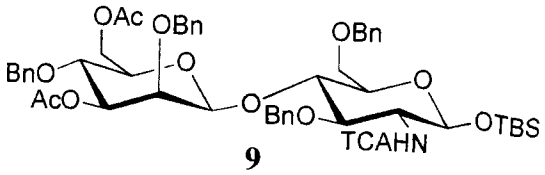

```
Current Data Parameters
NAME      ERS-III-242c13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20021026
Time               16.48
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  655
DS                    4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                16384
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2            107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127530 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              234.620 ppm
F1               23605.72 Hz
F2P              -15.106 ppm
F2               -1519.90 Hz
PPMCM            12.48630 ppm/cm
HZCM          1256.28137 Hz/cm
```



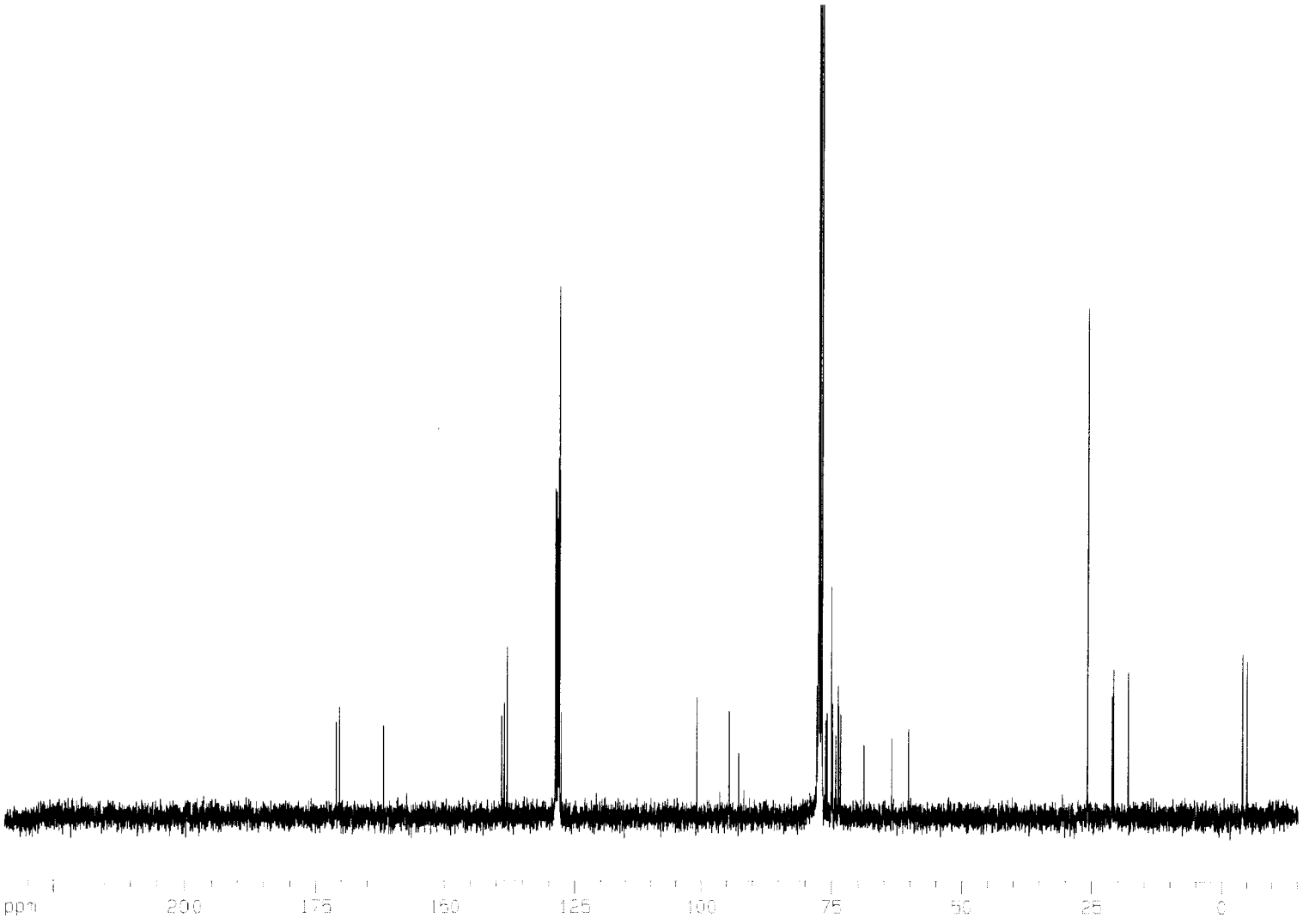
9



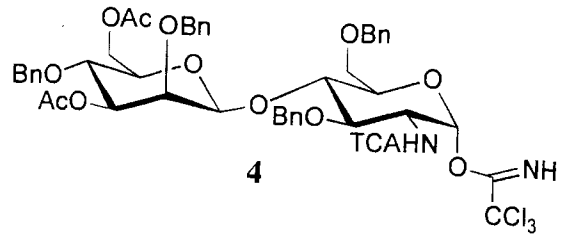

```
Current Data Parameters
NAME          ERS-III-165
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20020903
Time              21.38
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               40062
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.100005 Hz
AQ            4.9997878 sec
RG                143.7
DW              124.800 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SFO1        400.1318006 MHz

F2 - Processing parameters
SI                32768
SF          400.1300057 MHz
WDW                EM
SSB                 0
LB              0.30 Hz
GB                  0
PC              1.00

1D NMR plot parameters
CX              20.00 cm
F1P             9.492 ppm
F1             3798.06 Hz
F2P             -0.521 ppm
F2             -208.35 Hz
PPMCM         0.50064 ppm/cm
HZCM         200.32053 Hz/cm
```



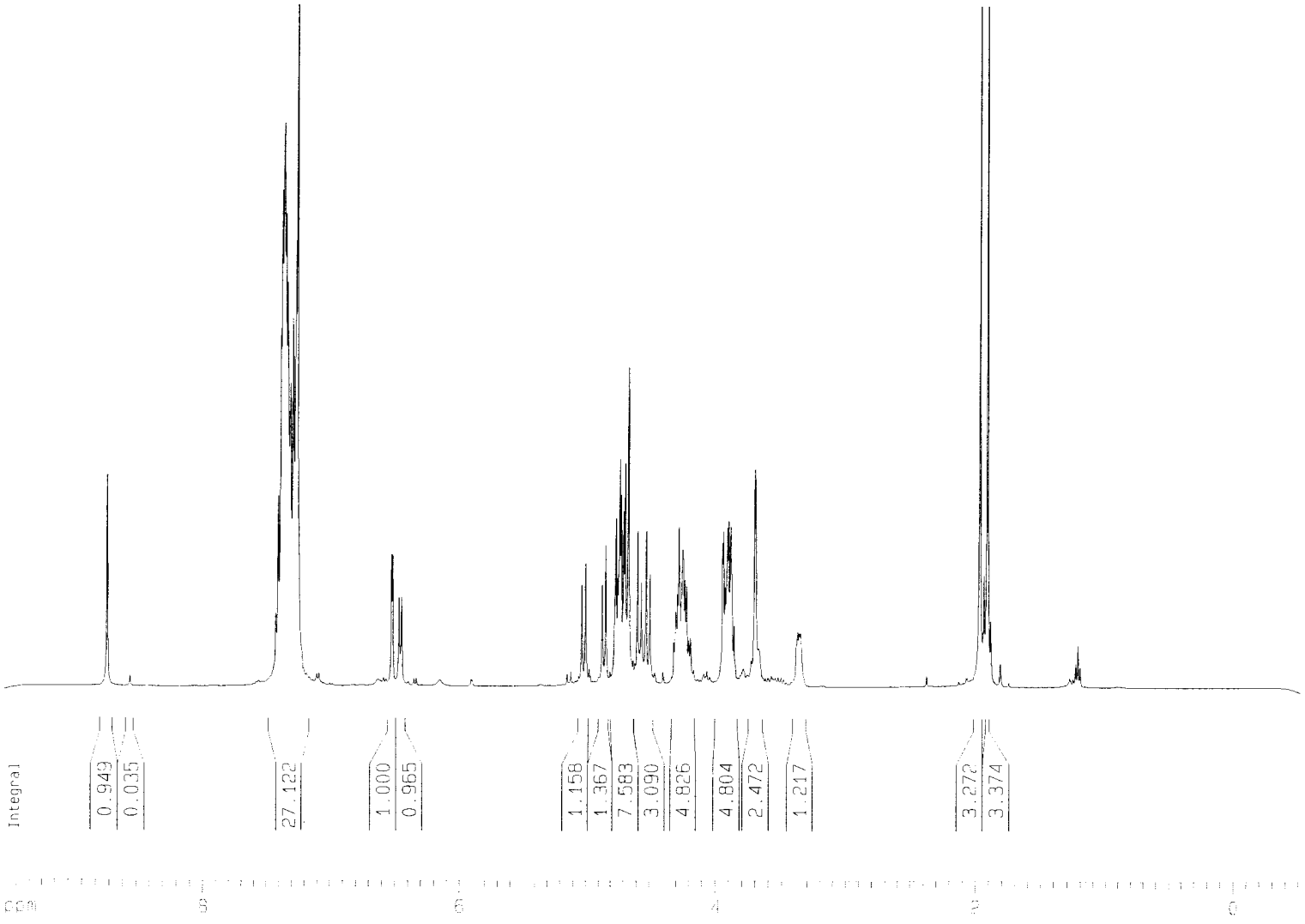
9



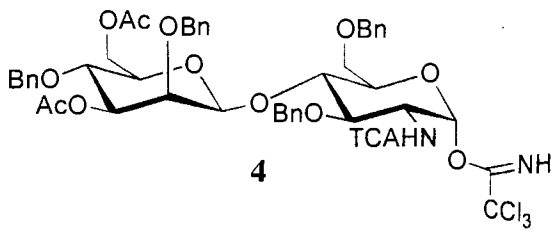

```
Current Data Parameters
NAME      ERS-III-166c13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20020904
Time                2.15
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 6502
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2           107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127492 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
F1P              234.658 ppm
F1               23609.56 Hz
F2P              -15.068 ppm
F2               -1516.07 Hz
PPMCM            12.48630 ppm/cm
HZCM          1256.28137 Hz/cm
```



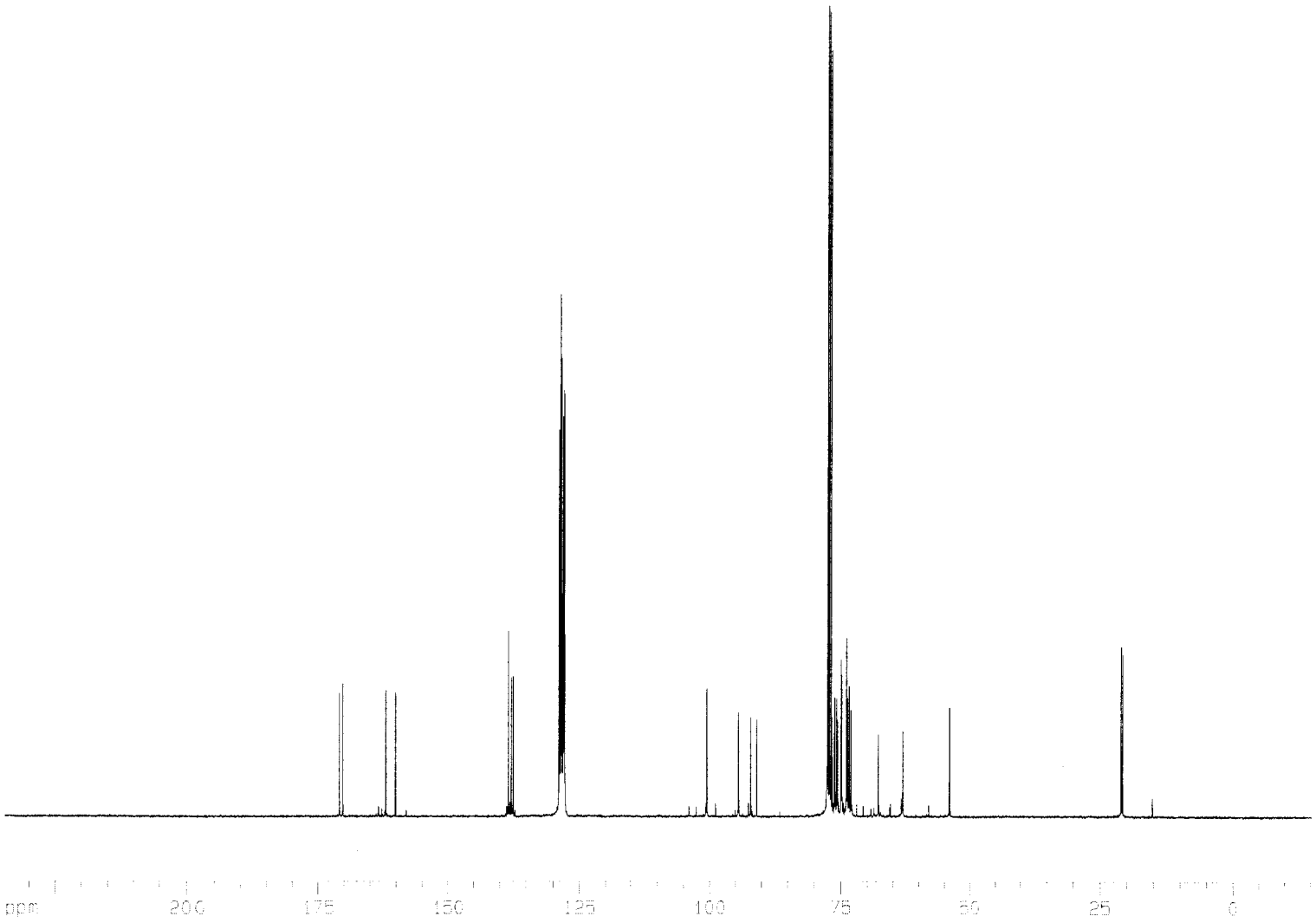
4



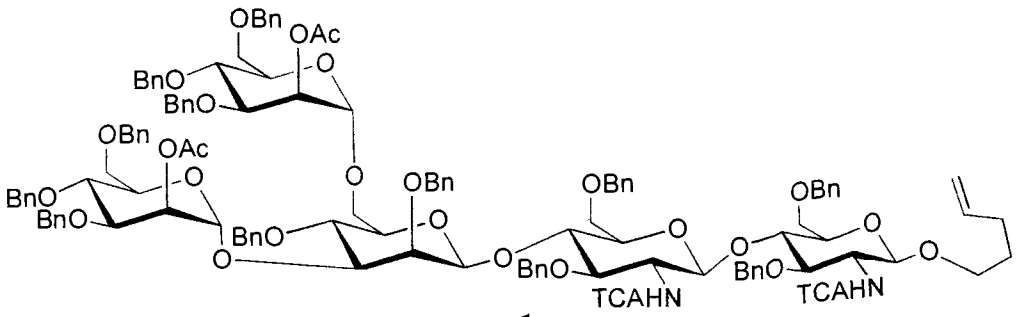

```
Current Data Parameters
NAME        ERS-III-176zz
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20030122
Time               4.07
INSTRUM           spect
PROBHD     5mm BBO BB-1
PULPROG           zg30
TD               40062
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           4006.410 Hz
FIDRES        0.100005 Hz
AQ            4.9997878 sec
RG                40.3
DW             124.800 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ============
NUC1                1H
P1                7.90 usec
PL1               0.00 dB
SF01        400.1318006 MHz

F2 - Processing parameters
SI                32768
SF          400.1300055 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               9.493 ppm
F1              3798.31 Hz
F2P              -0.520 ppm
F2              -208.10 Hz
PPMCM          0.50064 ppm/cm
HZCM          200.32053 Hz/cm
```



4




```
Current Data Parameters
NAME      ERS-III-176C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20030122
Time               14.43
INSTRUM            spect
PROBHD     5mm BBO BB-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                11498
DS                    4
SWH           25125.629 Hz
FIDRES         0.383387 Hz
AQ            1.3042164 sec
RG                 4096
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                15.25 usec
PL1                3.00 dB
SFO1         100.6237959 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2            107.50 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127607 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               234.543 ppm
F1              23598.06 Hz
F2P               -15.183 ppm
F2              -1527.57 Hz
PPMCM             12.48630 ppm/cm
HZCM            1256.28137 Hz/cm
```


OBn
OAc
BnO
BnO
OBn
OAc
BnO
BnO
O
BnO
O
OBn
O
O
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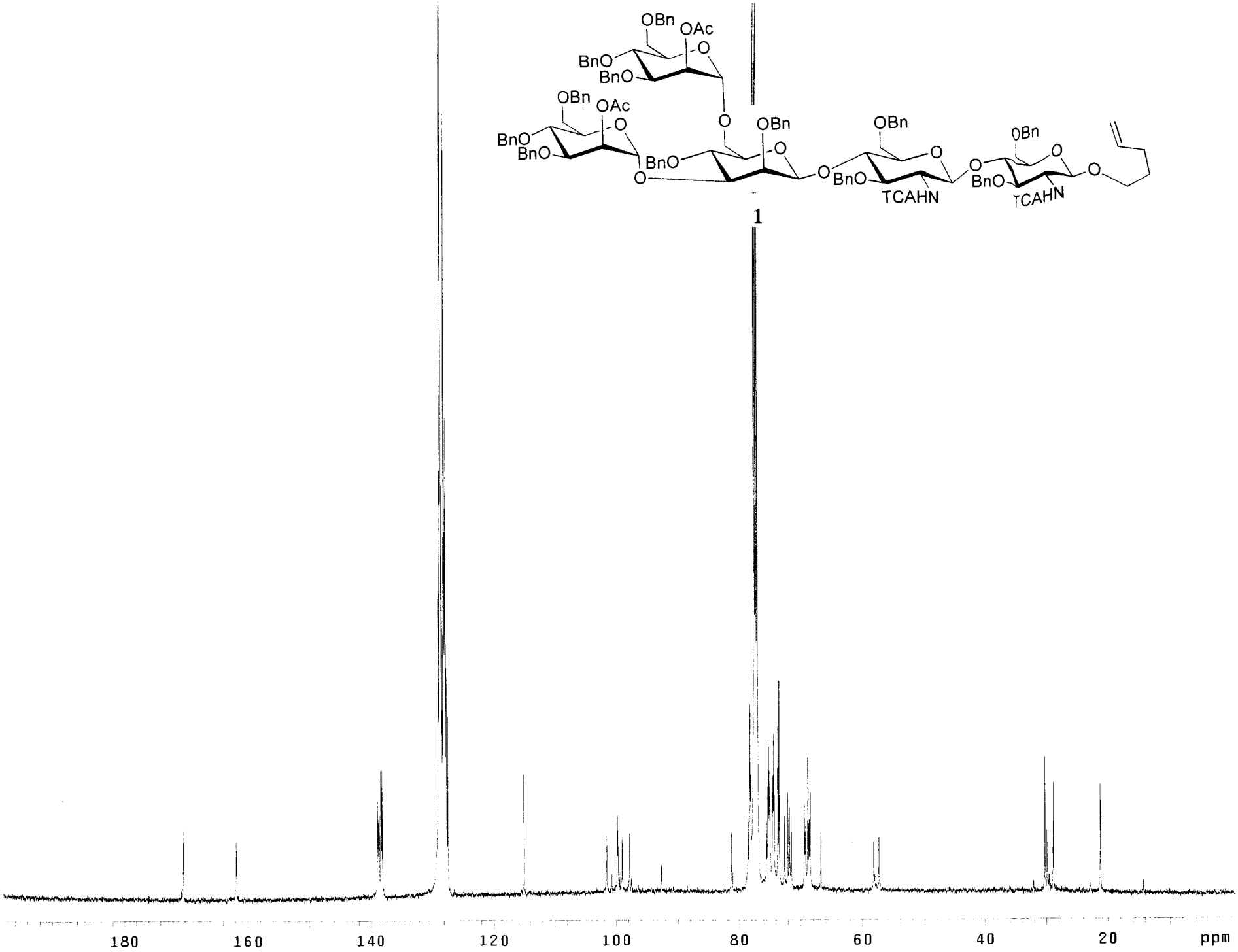
TCAHN
OBn
O
O
BnO
TCAHN
OBn
O
O

1

8
7
6
5
4
3
2
1
ppm


OBn
OAc
BnO
BnO
O
OBn
BnO
BnO
BnO
TCAHN
TCAHN
1
180
160
140
120
100
80
60
40
20
ppm