Supporting Information

For

β -Stereoselective mannosylation using 2,6-lactones

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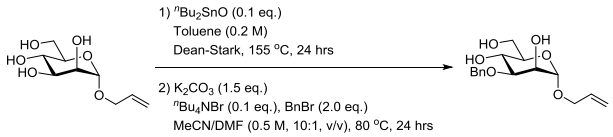
General Information

Analytical thin layer chromatography (TLC) was performed using Merck KGaA TLC 60F-254 plates (0.25 mm), and visualization was accomplished by 10 % sulfuric acid in EtOH or PMA (Phosphomolybdic acid), followed by heating or UV irradiation (254 nm). Specific rotations were measured on an automatic polarimeter with a path length of 50 mm in the solvent specified. Concentrations are given in g/100 mL. Optical rotations were measured on a JASCO P-2200 photoelectric polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Ltd. JNM-ECP400 series (400 MHz). Chemical shifts (δ) are reported in parts par million (ppm) downfield or upfield from tetramethylsilane (δ 0.00), $(CD_3)_2CO$ (δ 2.05) or $CHCl_3$ (δ 7.26), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). ^{13}C chemical shifts are reported in ppm downfield or upfield from $(CD_3)_2CO$ (δ 29.8, 206.3) and $CDCl_3$ (δ 77.36). High-resolution mass spectra (HRMS) were recorded on a JEOL Ltd. AccuTOFCS JIMS-T100CS with an electrospray ionization (ESI) source coupled. Silica-gel column chromatography was performed on FUJI SILYSIA CHEMICAL Ltd. Silica Gel PSQ60B 46-50 μm (spherical, neutral). HPLC analysis was performed JASCO 860-CO (Column Oven), JASCO

880-31 (Solvent Mixing Module), JASCO 880-50 (3-Line Degasser), JASCO 880-PU (Intelligent HPLC Pump), JASCO 875-UV (Intelligent UV/Vis Detector, 254 nm) and JASCO 807-IT (Integrator).

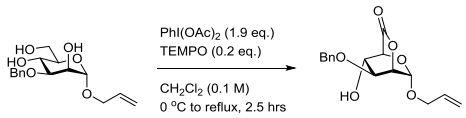
Scheme 2

Allyl 3-*O*-benzyl-α-D-mannopyranoside (2)



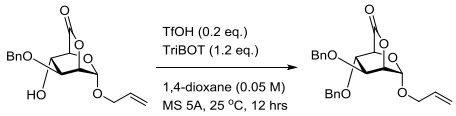
Under Ar atmosphere, to a solution of **1**[1] (6.38 g, 29.0 mmol) in toluene (145.0 ml) was added ^{n}Bu$_2$SnO (0.72 g, 2.90 mmol) at room temperature and the mixture was refluxed and stirred for 24 hrs. The mixture was cooled to room temperature and concentrated *in vacuo*. Under Ar atmosphere, to a solution of crude product in MeCN (52.7 ml) and DMF (5.3 ml) were added K_2CO_3 (6.01 g, 43.5 mmol) and ^{n}Bu$_4$NBr (0.93 g, 2.90 mmol) at room temperature. After stirring for 10 min, BnBr (6.94 ml, 58.0 mmol) was added and the reaction was stirred at 80 °C for 24 hrs. After the mixture was cooled to room temperature, it was firtrated through Slicagel pad and concentrated *in vacuo*. The residue was purified by flash column chromatography (50 g, Hexane → Hexane/EtOAc = 3/1 → Hexane/EtOAc = 1/1 → Hexane/EtOAc = 3/7), which gave the title compound **2** (3.65 g, 41%) in 2 steps as brown oil. The spectra of the obtained compound is identical to the reported ones.[2]

Allyl 3-*O*-benzyl-α-D-mannopyranurono-2,6-lactone (3)



Under Ar atmosphere, to a solution of **2** (387.0 mg, 1.25 mmol) and PhI(OAc)$_2$ (0.76 g, 2.37 mmol) in anhydrous CH_2Cl_2 (12.5 ml) was added TEMPO (39.1 mg, 250.0 μmol) at 0 °C. After stirring for 30 min, reaction temperature was raised to reflux and the mixture was stirred for 2 hrs. After the TLC analysis showed the completion of reaction, the reaction was quenched by 10% $Na_2S_2O_3$ aq. and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, Hexane → Hexane/EtOAc = 9/1 → Hexane/EtOAc = 4/1), which gave the title compound **3** as yellow oil (206.0 mg, 54%). R_f = 0.37 (Hexane/EtOAc = 2/1, v/v); $[\alpha]^{20}_D$ = +37.1 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39-7.26 (m, 5H, Ar-H), 5.87 (dddd, $J_{\beta,\gamma trans}$ = 14.8 Hz, $J_{\beta,\gamma cis}$ = 9.6 Hz, $J_{\beta,\alpha1}$ = 4.8 Hz, $J_{\beta,\alpha2}$ = 6.0 Hz, 1H, H-β), 5.28 (d, $J_{\beta,\gamma trans}$ = 14.8 Hz, 1H, H-γ_{trans}), 5.25 (d, $J_{\beta,\gamma cis}$ = 9.6 Hz, 1H, H-γ_{cis}), 5.19 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1), 4.78 (ddd, $J_{2,1}$ = 3.2 Hz, $J_{2,3}$ = 1.2 Hz, $J_{2,4}$ = 2.4 Hz, 1H, H-2), 4.64 & 4.59 (ABq, J = 11.6 Hz, 2H, $PhCH_2$), 4.37 (dd, $J_{4,2}$ = 2.4 Hz, $J_{4,5}$ = 0.8 Hz, 1H, H-4), 4.34 & 4.31 (dd, $J_{\alpha1,\alpha2}$ = 12.6 Hz, $J_{\alpha1,\beta}$ = 4.8 Hz, 1H, H-α1), 4.13 & 4.10 (dd, $J_{\alpha1,\alpha2}$ = 12.6 Hz, $J_{\alpha2,\beta}$ = 6.0 Hz, 1H, H-α2), 4.02 (d, $J_{3,2}$ = 1.2 Hz, 1H, H-3), 3.97 (d, $J_{5,4}$ = 0.8 Hz,1H, H-5), 3.00 (br , 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.5, 136.9, 132.8, 128.6, 128.2, 127.9, 119.0, 95.6, 75.8, 74.9, 74.1, 72.4, 70.8, 70.5; HRMS (ESI) Calcd for $C_{16}H_{18}O_6Na$ $[M+Na]^+$: 329.1001, found: 329.1010.

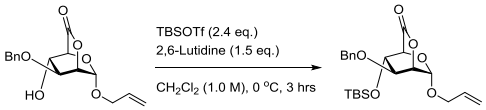
Allyl 3,4-di-*O*-benzyl-α-D-mannopyranurono-2,6-lactone (4a)



Under Ar atmosphere, to **3** (21.9 mg, 71.5 μmol), TriBOT (11.4 mg, 28.6 μmol) and activated 5 Å molecular sieves (150

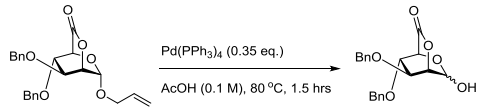
mg) was added anhydrous 1,4-dioxane (1.43 ml) at room temperature. After stirring for 30 min, TfOH (1.3 μl, 14.3 μmol) was added at room temperature, and the mixture was stirred for 12 hrs. The reaction was quenched by Et_3N, the mixture was filtrated through Celite pad and concentrated *in vacuo*. The residue was purified by open column chromatography (7 g, Hexane/EtOAc = 4/1), which gave the title compound **4a** (21.4 mg, 75%) as colorless oil. R_f = 0.57 (Hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = +28.2 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.31 (m, 10H, Ar-H), 5.89 (dddd, $J_{\beta,\gamma trans}$ = 17.2 Hz, $J_{\beta,\gamma cis}$ = 10.4 Hz, $J_{\beta,\alpha2}$ = 6.4 Hz, $J_{\beta,\alpha1}$ = 4.8 Hz, 1H, Hβ), 5.29 (d, $J_{\beta,\gamma trans}$ = 17.2 Hz, 1H, H-γ_{trans}), 5.22 (d, $J_{\beta,\gamma cis}$ = 10.4 Hz, 1H, H-γ_{cis}), 5.20-5.19 (m, 1H, H-1), 4.76 (s, 1H, H-2), 4.63 & 4.49 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.58 & 4.52 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.50 (s, 1H, H-5), 4.37 & 4.34 (dd, $J_{\alpha1,\alpha2}$ = 12.4 Hz, $J_{\alpha1,\beta}$ = 4.8 Hz, 1H, H-α1), 4.24 (s, 1H, H-4), 4.12 & 4.08 (dd, $J_{\alpha2,\alpha1}$ = 12.4 Hz, $J_{\alpha2,\beta}$ = 6.4 Hz, 1H, H-α2), 3.77 (s, 1H, H-3); ^{13}C NMR(100 MHz, $CDCl_3$, TMS) δ 168.4, 137.1, 133.4, 128.6, 128.2, 128.2, 128.0, 127.9, 118.2, 95.7, 79.6, 75.5, 74.7, 71.2, 71.1, 69.8; HRMS (ESI) Calcd for $C_{23}H_{24}NaO_6$ $[M+Na]^+$: 419.1471, found: 419.1465.

Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2,6-lactone (4b)



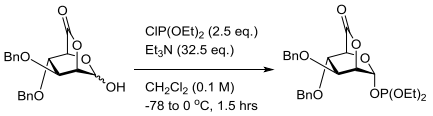
Under Ar atmosphere, to a solution of **3** (0.52 g, 1.7 mmol) and 2,6-lutidine (0.30 ml, 2.6 mmol) in anhydrous CH_2Cl_2 (1.7 ml) was added TBSOTf (0.94 ml, 4.0 mmol) at 0 °C and the mixture was stirred for 3 hrs. The mixture was poured into sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, Hexane → Hexane/EtOAc = 19/1), which gave the title compound **4b** as yellow oil (0.40 g, 95%). R_f = 0.67 (Hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = +15.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40-7.27 (5H, m), 5.89 (dddd, $J_{\beta,\gamma trans}$ = 17.2 Hz, $J_{\beta,\gamma cis}$ = 14.8 Hz, $J_{\beta,\alpha1}$ = 4.8 Hz, $J_{\beta,\alpha2}$ = 6.4 Hz, 1H, H-β), 5.12 (d, $J_{\gamma trans,\beta}$ = 17.2 Hz, 1H, H-γ_{trans}), 5.24 (d, $J_{\beta,\gamma cis}$ = 14.8 Hz, 1H, H-γ_{cis}), 5.08 (s, 1H, H-1), 4.70 (s, 1H, H-2), 4.62 & 4.57 (ABq, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.34 & 4.31 (dd, $J_{\alpha1,\alpha2}$ = 12.6 Hz, $J_{\alpha1,\beta}$ = 4.8 Hz, 1H, H-α1), 4.16 (s, 1H, H-4), 4.02 (s, 1H, H-3), 4.08 & 4.05 (dd, $J_{\alpha1,\alpha2}$ = 12.6 Hz, $J_{\alpha2,\beta}$ = 6.4 Hz, 1H, H-α2), 3.93 (s, 1H, H-5), 0.91 (s, 9H, $C(CH_3)_3$), 0.11 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.9, 137.2, 133.45, 128.6, 128.1, 127.9, 117.9, 95.4, 75.0, 74.9, 74.3, 71.2, 69.2, 25.7, 18.0, -4.6, -4.8; HRMS (ESI) Calcd for $C_{22}H_{32}O_6SiNa$ $[M+Na]^+$: 443.1866, found: 443.1873.

3,4-Di-*O*-benzyl-D-mannopyranurono-2,6-lactone (S1)



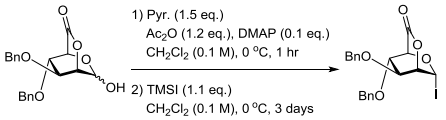
Under Ar atmosphere, to a solution of allyl glycoside **4a** (407.5 mg, 1.03 mmol) in AcOH (10.3 ml) was added $Pd(PPh_3)_4$ (416.6 mg, 360.0 μmol) at room temperature. The mixture was degassed, and then warmed up to 80 °C. The mixture was stirred for 1.5 hrs. The mixture was filtilated through Celite pad and concentrated *in vacuo*. The residue was purified by column chromatography (15 g, Hexane/EtOAc = 1/1), which gave the title compound **S1** (346.6 mg, 95%, mixture of α- and β-anomers) as yellow oil. R_f = 0.51 (Hexane/EtOAc = 1/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.30 (m, 20H, Ar-H), 5.40-5.39 (m, 0.3H), 5.18 (s, 0.7H), 4.76-4.73 (m, 1H), 4.63-4.62 (m, 5H), 4.19 (s, 0.4H), 3.77-3.76 (m, 1H), 3.64 (s, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.8, 136.6, 136.6, 128.8, 128.7, 128.7, 128.7, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.0, 91.3, 90.4, 79.1, 77.8, 77.4, 75.6, 73.8, 71.5, 71.5, 71.4, 71.1, 71.0, 70.9; HRMS (ESI) Calcd for $C_{20}H_{20}NaO_6$ $[M+Na]^+$: 379.1158, found: 379.1141.

3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diethyl phosphite (5aα)



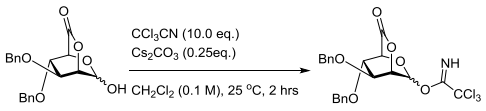
Under Ar atmosphere, to a solution of hemiacetal **S1** (109.0 mg, 0.31 mmol) and Et_3N (0.32 ml, 2.29 mmol) in anhydrous CH_2Cl_2 (3.06 ml) was added diethyl chlorophosphite (0.11 ml, 0.76 mmol) at -78 °C and the mixture was gradually warmed up to 0 °C, and stirred for 2 hrs. Et_3N (1.06 ml, 7.65 mmol) was added at 0 °C, and the mixture was extracted with ice-cooled CH_2Cl_2. The organic layer was washed with cold sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, Hexane/EtOAc = 9/1 → Hexane/EtOAc = 4/1 + 5% Et_3N), which gave the α-anomer **5aα** as colorless syrup (29.0 mg, 20%). R_f = 0.45 (Hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = -46.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36-7.29 (m, 10H, Ar-H), 5.61-5.59 (m, 1H, H-1), 4.75 (s, 1H, H-2), 4.64 & 4.48 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.59 & 4.52 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.54 (s, 1H, H-5), 3.95-3.86 (m, 4H, CH_2 ×2), 3.80 (s, 1H, H-4), 3.71 (s, 1H, H-3), 1.28-1.24 (m, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.1, 136.6, 136.6, 128.7, 128.7, 128.4, 128.3, 128.2, 128.0, 89.8, 89.7, 79.3, 77.6, 71.4, 71.1, 71.1, 59.1, 59.0, 58.9, 16.9, 16.9, 16.8, 16.8; HRMS (ESI) Calcd for $C_{24}H_{29}NaO_8P$ $[M+Na]^+$: 499.1498, found: 499.1485.

3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl iodide (5bα)



Under Ar atmosphere, to a solution of hemiacetal **S1** (61.0 mg, 171.2 μmol), Pyr. (20.7 μl, 256.8 μmol) and Ac_2O (19.4 μl, 205.4 μmol) in anhydrous CH_2Cl_2 (1.71 ml) was added DMAP (2.1 mg, 17.1 μmol) at 0 °C. The mixture was stirred for 1 hr. The reaction was quenched by water. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with water, 1 M $KHSO_4$ aq. and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Under Ar atmosphere, to a solution of the residue (66.9 mg) in anhydrous CH_2Cl_2 (1.71 ml) was added TMSI (26.7 μl, 188.3 μmol) at 0 °C and the mixture was stirred for 3 days. The mixture was co-evaporated with toluene for 3 times. The mixture was purified by open column chromatography (7 g, Hexane/EtOAc = 4/1), which gave the pure α-anomer **5bα** as brown syrup (18.4 mg, 23% in 2 steps) and anomeric mixture **5bαβ** as brown syrup (5.6 mg, 7% in 2 steps). For **5bα**: R_f = 0.43 (Hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = -149.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.29 (m, 10H, Ar-H), 6.68 (s, 1H, H-1), 4.90 (s, 1H, H-2), 4.59 & 4.50 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.59 & 4.46 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.46 (s, 1H, H-5), 3.86 (s, 1H, H-4), 3.78 (s, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 165.5, 136.3, 136.3, 128.8, 128.8, 128.6, 128.5, 128.2, 128.1, 80.2, 80.1, 71.6, 71.3, 71.2, 58.2; HRMS (ESI) Calcd for $C_{20}H_{19}INaO_5$ $[M+Na]^+$: 489.0175, found: 489.0157. For **5bαβ**: ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36-7.29 (m, 10H, Ar-H), 6.68-6.53 (m, 1H, H-1), 5.29 & 4.90 (m, 1H, H-2), 4.64-4.44 (m, 5H, H-5, $Ph2CH_2$ ×2), 4.40 & 3.86 (s, 1H, H-4), 3.80-3.77 (s, 1H, H-3)

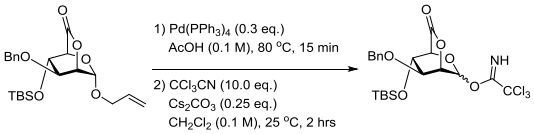
3,4-Di-*O*-benzyl-D-mannopyranurono-2,6-lactone-1-yl trichloroacetimidate (5c)



Under Ar atmosphere, to a solution of hemiacetal **S1** (98.4 mg, 196.0 μmol) and CCl_3CN (0.20 ml, 1.96 mmol) in anhydrous CH_2Cl_2 (1.96 ml) was added Cs_2CO_3 (17.3 mg, 49.1 μmol) at room temperature. After the TLC analysis showed the completion of reaction, the reaction mixture was filtrated through Celite pad and concentrated *in vacuo*. The residue was

purified by open column chromatography (7 g, Petroleum ether/$CHCl_3$ = 1/19), which gave the title compound **5cα** (31.2 mg, 32%) and **5cβ** (20.8 mg, 19%) in 2 steps as colorless oil, each. For **5cα**: Colorless oil, R_f = 0.29 (Petroleum ether/$CHCl_3$ = 1/9, v/v); $[\alpha]^{20}_D$ = +25.6 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.70 (s, 1H, NH), 7.36-7.28 (m, 10H, Ar-H), 6.39 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1), 5.00 (ddd, $J_{2,1}$ = 3.3 Hz, $J_{2,3}$ = 1.0 Hz, $J_{2,4}$ = 1.9 Hz, 1H, H-2), 4.65 (dd, $J_{5,3}$ = 1.9 Hz, $J_{5,4}$ = 0.8 Hz, 1H, H-5), 4.62 & 4.47 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.56 & 4.56 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.23 (dd, $J_{4,2}$ = 1.9 Hz, $J_{4,3}$ = 1.6 Hz, 1H, H-4), 3.84 (dd, $J_{3,4}$ = 4.6 Hz, $J_{3,5}$ = 1.9 Hz, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 167.4, 160.4, 136.7, 136.5, 128.7, 128.6, 128.6, 128.5, 128.4, 128.2, 128.0, 92.8, 78.9, 73.5, 73.4, 72.5, 71.2, 71.1; HRMS (ESI) Calcd for $C_{22}H_{20}Cl_3NO_6Na$ $[M+Na]^+$: 522.0254, found: 522.0226. For **5cβ**: Colorless oil, R_f = 0.52 (Petroleum ether/$CHCl_3$ = 1/9, v/v); $[\alpha]^{20}_D$ = -15.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.67 (s, 1H, NH), 7.37-7.30 (m, 10H, Ar-H), 6.30 (s, 1H, H-1), 5.10 (s, 1H, H-2), 4.66 & 4.49 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.65 (s, 1H, H-5), 4.62 & 4.54 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 3.85 (s, 1H, H-4), 3.80 (s, 1H, H-3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 167.2, 160.8, 136.4, 136.4, 128.8, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 93.5, 79.2, 77.2, 75.1, 71.7, 71.5, 71.2; HRMS (ESI) Calcd for $C_{22}H_{20}Cl_3NO_6Na$ $[M+Na]^+$: 522.0254, found: 522.0262. The NOE correlation observed between δ 6.30 and δ 3.80 confirmed the stereochemistry at C-1 to be β.

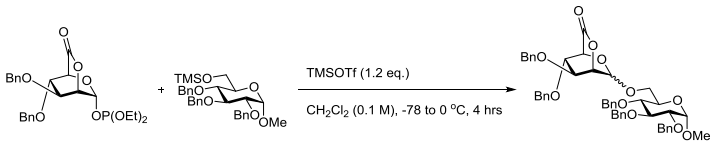
3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-D-mannopyranurono-2,6-lactone-1-yl trichloroacetimidate (5d)



Under Ar atmosphere, to a solution of **4b** (54.3 mg, 129.1 μmol) in AcOH (1.29 ml) was added $Pd(PPh_3)_4$ (44.8 mg, 38.7 μmol) at room temperature. The mixture was degassed, and then warmed to 80 °C. The mixture was stirred for 15 min. The mixture was filtilated through Celite pad and concentrated *in vacuo*. Under Ar atmosphere, to a solution of the crude product and CCl_3CN (0.13 ml, 1.29 mmol) in anhydrous CH_2Cl_2 (1.29 ml) was added Cs_2CO_3 (11.4 mg, 32.3 μmol) at room temperature. After the TLC analysis showed the completion of reaction, the reaction was filtrated through Celite pad and concentrated *in vacuo*. The residue was purified by open column chromatography (7 g, Hexane/CH_2Cl_2 = 3/7), which gave the title compound **5dα** (9.3 mg, 14% in 2 steps), **5dβ** (17.8 mg, 26% in 2 steps). For **5dα**: Colorless oil, R_f = 0.33 (Hexane/CH_2Cl_2 = 3/7, v/v); $[\alpha]^{20}_D$ = +54.5 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.67 (s, 1H, NH), 7.35-7.31 (m, 5H, Ar-H), 6.36 (m, 1H, H-1), 4.97 (s, 1H, H-2), 4.65 & 4.60 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.36 (s, 1H, H-5), 4.08 (s, 1H, H-4), 4.08 (s, 1H, H-3), 0.87 (s, 9H, $C(CH_3)_3$), 0.10 (s, 3H, $-CH_3$), 0.09 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 167.7, 160.6, 136.5, 128.7, 128.4, 128.3, 93.2, 76.1, 75.9, 74.2, 73.2, 71.3, 25.7, 18.0, -4.7, -4.8; HRMS (ESI) Calcd for $C_{21}H_{28}Cl_3NO_6SiNa$ $[M+Na]^+$: 546.0649, found: 546.0636. For **5dβ**: Colorless oil, R_f = 0.59 (Hexane/CH_2Cl_2 = 3/7, v/v); $[\alpha]^{20}_D$ = -11.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.66 (s, 1H, NH), 7.37-7.33 (m, 5H, Ar-H), 6.29 (s, 1H, H-1), 5.12 (s, 1H, H-2), 4.65 & 4.60 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.36 (s, 1H, H-5), 4.07 (s, 1H, H-4), 3.67 (s, 1H, H-3), 0.90 (s, 9H, $C(CH_3)_3$), 0.13 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 167.6, 160.8, 136.4, 128.7, 128.4, 128.0, 93.7, 79.7, 75.6, 74.4, 74.3, 71.4, 25.7, 18.0, -4.58, -4.79; HRMS (ESI) Calcd for $C_{21}H_{28}Cl_3NO_6SiNa$ $[M+Na]^+$: 546.0649, found: 546.0651. The NOE correlation observed between δ 6.29 and δ 3.67 confirmed the stereochemistry at C-1 to be β.

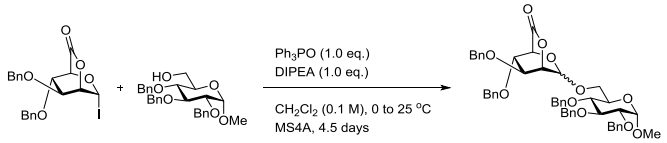
Table 1

Entry 1



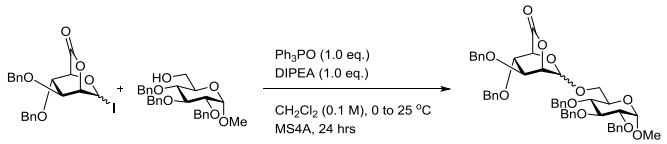
Under Ar atmosphere, to a glycosyl phosphite **5aα** (16.7 mg, 35.1 μmol) and trimethylsilylated acceptor **6a'**[3] (22.6 mg, 42.1 μmol) was added anhydrous CH_2Cl_2 (0.35 ml) at room temperature. After stirring for 30 min, TMSOTf (7.6 μl, 42.1 μmol) were added at -78 °C, and the mixture was stirred and warmed up to 0 °C over 4 hrs. The reaction was quenched by Et_3N at 0 °C and the mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, Hexane/EtOAc = 9/1 → Hexane/EtOAc = 17/3 → Hexane/EtOAc = 4/1). The ratio of α- and β-anomers was determined by NMR (25.5 mg, 52%, α:β = 1:9).

Entry 2



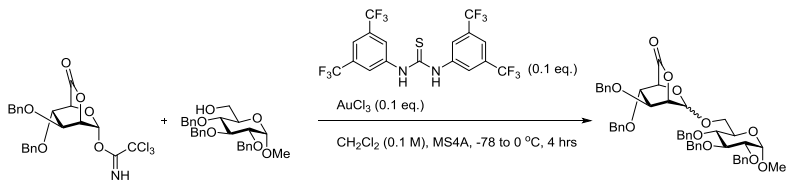
Under Ar atmosphere, to a glycosyl iodide **5bα** (16.0 mg, 36.7 μmol), glycosyl acceptor **6a**[4] (18.7 mg, 40.4 μmol) and activated 4 Å molecular sieves (30 mg) was added anhydrous CH_2Cl_2 (0.37 ml) at room temperature. After stirring for 30 min, Ph_3PO (10.2 mg, 36.7 μmol) and DIPEA (6.4 μl, 36.7 μmol) were added at 0 °C, and the mixture was stirred for 4.5 days. The reaction was diluted with 10 mL of CH_2Cl_2. The mixture was filtrated through Celite pad and the mixture concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, Hexane only → Hexane/EtOAc = 9/1 → Hexane/EtOAc = 17/3 → Hexane/EtOAc = 4/1), which gave the β-anomer (10.1 mg, 37%, β-only), and the α-anomer was not detected by ^{1}H NMR.

Entry 3



Under Ar atmosphere, to glycosyl iodide **5bαβ** (9.8 mg, 21.0 μmol, α:β = 2:1), glycosyl acceptor **6a** (10.7 mg, 23.1 μmol) and activated 4 Å molecular sieves (20 mg) was added anhydrous CH_2Cl_2 (0.21 ml) at room temperature. After stirring for 30 min, Ph_3PO (5.8 mg, 21.0 μmol) and DIPEA (3.7 μl, 21.0 μmol) were added at 0 °C. The mixture was stirred for 4.5 days. The reaction was diluted with 10 mL of CH_2Cl_2. The mixture was filtrated through Celite and concentrated *in vacuo*. The residue was purified by open column chromatography (7 g, Hexane/EtOAc = 7/3). The ratio of the α- and β-anomers was analyzed by ^{1}H NMR (3.0 mg, 37%, α:β = 1:2.3).

Entry 4, 5



Under Ar atmosphere, to glycosyl imidate **5cα** or **5cβ**, glycosyl acceptor **6a** (1.2 equiv. to **5c**) and activated 4 Å molecular sieves was added anhydrous CH_2Cl_2 (0.1 M to **5c**) at room temperature. After stirring for 30 min, gold (III) chloride and 1,3-bis[3,5-bis(trifluoromethyl)phenyl] thiourea were added at -78 °C. The mixture was stirred and warmed up to 0 °C over 4 hrs. The reaction was quenched by Et_3N at 0 °C and diluted with 10 mL of CH_2Cl_2. The mixture was filtrated through

Celite pad and concentrated *in vacuo*. The ratio of the α- and β-anomers was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 80/20; flow rate, 1.0 ml/min; t_R α-mannoside 13.400 min; t_R β-mannoside 12.258 min).

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aβ)

Colorless oil, R_f = 0.49 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +78.7 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.27 (m, 25H, Ar-H), 4.98 & 4.46 (ABq, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.85 & 4.48 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.78 & 4.62 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.77 & 4.53 (ABq, *J* = 12.4 Hz, 2H, $PhCH_2$), 4.76 (s, 1H, H-1'), 4.64 & 4.54 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.62 (s, 1H, H-2'), 4.55 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.45 (s, 1H, H-5'), 4.01-3.96 (m, 1H, H-6), 3.98 (dd, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.79-3.71 (m, 1H, H-5), 3.76 (s, 1H, H'-4), 3.59-3.54 (m, 1H, H-6), 3.55 (s, 1H, H'-3), 3.51 & 3.48 (dd, $J_{2,3}$ = 9.6 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.40 (d, $J_{4,3}$ = 9.6 Hz, 0.5H, H-4), 3.38-3.36 (m, 0.5H, H-4), 3.33 (s, 3H, $-OCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.2, 138.8, 138.4, 138.2, 136.7, 136.6, 128.7, 128.7, 128.5, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 97.9, 95.7, 82.1, 80.1, 79.6, 77.7, 77.6, 77.3, 76.5, 75.8, 74.8, 73.5, 71.4, 70.9, 70.9, 69.8, 67.2, 55.2; HRMS (ESI) Calcd for $C_{48}H_{50}O_{11}Na$ $[M+Na]^+$: 825.3251, found: 825.3225. The NOE correlation observed between δ 4.76 and δ 3.55 confirmed the stereochemistry at C-1 to be β.

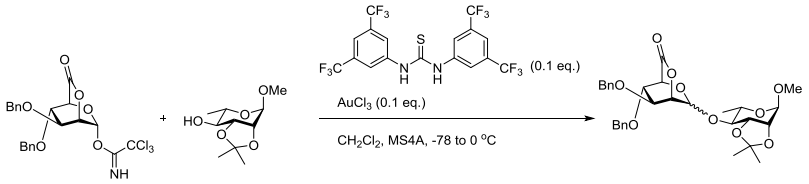
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aα)

α-anomer: Colorless oil, R_f = 0.43 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +4.1 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.39-7.13 (m, 25H, Ar-H), 5.22-5.21 (m, 1H, H-1'), 4.98 & 4.83 (ABq, *J* = 10.4 Hz, 2H, $PhCH_2$), 4.81 & 4.70 (ABq, *J* = 12.4 Hz, 2H, $PhCH_2$), 4.80 (s, 1H, H-2'), 4.67 (s, 2H, $PhCH_2$), 4.62 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.54 & 4.43 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.46 (s, 1H, H-5'), 4.40 & 4.32 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.27-4.23 (m, 1H, H-6), 4.18 (s, 1H, H-3'), 3.96 (dd, $J_{3,2}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.72-3.68 (m, 3H, H-4', H-5, H-6), 3.54-3.52 (m, 0.5H, H-4), 3.51 (d, $J_{4,3}$ = 9.2 Hz, 0.5H, H-4), 3.49 (dd, $J_{2,3}$ = 9.2 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.33 (s, 3H, $-OCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.2, 138.8, 138.4, 138.2, 136.8, 136.6, 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 98.3, 97.3, 82.0, 79.9, 79.5, 77.3, 76.0, 75.5, 75.2, 74.1, 73.4, 71.7, 71.2, 70.9, 69.7, 67.7, 55.3; HRMS (ESI) Calcd for $C_{48}H_{50}O_{11}Na$ $[M+Na]^+$: 825.3251, found: 825.3239.

Table 2

Under Ar atmosphere, to a glycosyl imidate **5cα** or **5dα**, the glycosyl acceptor listed in Table 2 (1.2 equiv. to **5cα** or **5dα**) and activated 4 Å molecular sieves was added anhydrous CH_2Cl_2 (0.1 M or 1.5 M to **5cα** or **5dα**) at room temperature. After stirring for 30 min, gold (III) chloride (0.1 equiv.) and 1,3-bis[3,5-bis(trifluoromethyl)phenyl] thiourea (0.1 equiv.) were added at -78 °C, and the mixture was stirred and gradually warmed up to 0 °C. The reaction was quenched by Et_3N at 0 °C and diluted with 10 mL of CH_2Cl_2. The mixture was filtrated through Celite pad and concentrated *in vacuo*. The residue was purified by column chromatography.

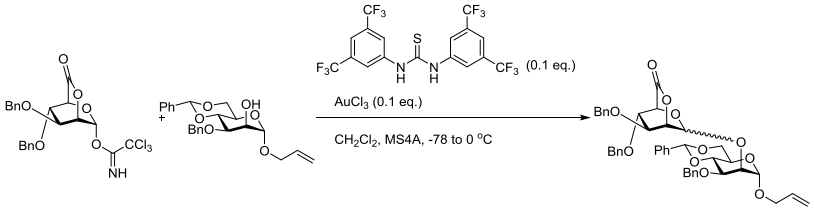
Methyl 2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bβ)



6b[5] was used as an acceptor. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). The ratio of α- and β-anomers was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 70/30; flow rate, 1.0 ml/min; t_R α-mannoside 8.847 min; t_R β-mannoside 9.388 min). For **7bβ**: Colorless oil, R_f = 0.57 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = -41.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.30 (m, 10H, Ar-H), 5.43-5.42 (m, 1H, H-1'), 4.85 (m, 2H, H-1, H-2'), 4.65 & 4.50 (ABq, J = 11.6 Hz, 2H, $PhCH_2$), 4.60 & 4.53 (ABq, J = 12.0 Hz, 2H, $PhCH_2$), 4.51 (s, 1H, H-5), 4.17 (d, $J_{3,4}$ = 5.6 Hz, 0.5H, H-3), 4.17-4.15 (m, 0.5H, H-3), 4.10 (d, $J_{2,3}$ = 5.6 Hz, 1H, H-2), 3.80 (s, 1H, H-4'), 3.70 (s, 1H, H-3'), 3.66-3.56 (m, 2H, H-4, H-5), 3.35 (s, 3H, $-OCH_3$), 1.53 (s, 3H, $-CH_3$), 1.34 (s, 3H, $-CH_3$), 1.23-1.21 (m, 3H, C-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.5, 136.8, 136.7, 128.7, 128.7, 128.4, 128.1, 127.9, 109.6, 97.9, 94.7, 79.8, 78.3, 78.2, 77.8, 77.3, 77.0, 76.2, 71.4, 71.1, 70.8, 63.9, 54.9, 28.1, 26.4, 17.4; HRMS (ESI) Calcd for $C_{34}H_{44}O_{12}Na$ $[M+Na]^+$: 579.2206, found: 579.2217. The NOE correlation observed between δ 5.43-5.42 and δ 3.70 confirmed the stereochemistry at C-1 to be β.

Allyl

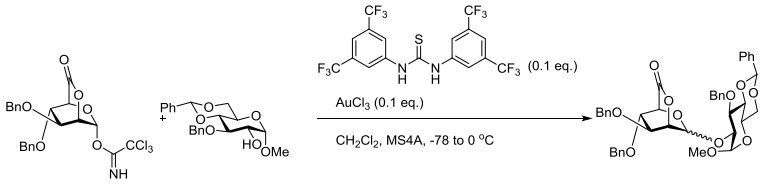
2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cβ)



6c[6] was used as an acceptor. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). The ratio of the α- and β-mixtures was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 80/20; flow rate, 1.0 ml/min; t_R α-mannoside 10.200 min; t_R β-mannoside 7.500 min). For **7cβ**: Colorless oil, R_f = 0.55 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = -14.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.28 (m, 20H, Ar-H), 5.91-5.81 (dddd, $J_{\beta,\gamma\text{-trans}}$ = 18.8 Hz, $J_{\beta,\gamma\text{-cis}}$ = 10.4 Hz, $J_{\beta,\alpha 2}$ = 5.6 Hz, $J_{\beta,\alpha 1}$ = 4.6 Hz, 1H, CH_β), 5.63 (s, 1H, PhCH), 5.26 (d, $J_{\gamma\text{-trans},\beta}$ = 18.8 Hz, 1H, H-γ_{trans}), 5.21 (d, $J_{\gamma\text{-cis},\beta}$ = 10.4 Hz, 1H, H-γ_{cis}), 5.18 (s, 1H, H-1'), 4.91 (s, 1H, H-2'), 4.86 (s, 1H, H-1), 4.76 & 4.70 (ABq, J = 12.2 Hz, 2H, $PhCH_2$), 4.62 & 4.47 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.55 & 4.45 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.45 (s, 1H, H-5'), 4.27 (s, 1H, H-2), 4.24-4.22 (m, 1H, H-6), 4.16 (dd, $J_{\alpha 1,\alpha 2}$ = 12.6 Hz, $J_{\alpha 1,\beta}$ = 4.6 Hz, 1H, H-α_1), 4.14-4.11 (m, 0.5H, H-4), 4.10 (d, $J_{4,3}$ = 9.2 Hz, 0.5H, H-4), 3.95 (d, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.94 (dd, $J_{\alpha 2,\alpha 1}$ = 12.6 Hz, $J_{\alpha 2,\beta}$ = 5.6 Hz, 1H, H-α_2), 3.86-3.80 (m, 2H, H-5, H-6), 3.79 (s, 1H, H-4'), 3.63 (s, 1H, H-3'); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 167.8, 138.7, 137.6, 136.6, 136.5, 133.4, 128.9, 128.7, 128.5, 128.3, 128.2, 128.2, 128.0, 127.6, 127.4, 126.1, 118.1, 101.5, 97.7, 93.8, 79.7, 78.6, 77.8, 77.3, 76.2, 74.4, 72.8, 72.3, 71.5, 71.1, 70.9, 68.8, 68.3, 64.3, 29.8; HRMS (ESI) Calcd for $C_{43}H_{44}O_{11}Na$ $[M+Na]^+$: 759.2781, found: 759.2753. The NOE correlation observed between δ 5.18 and δ 3.63 confirmed the stereochemistry at C-1 to be β.

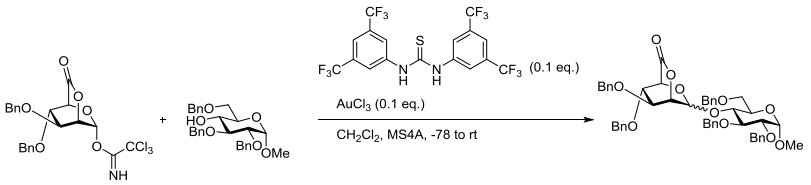
Methyl

2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dβ)



6d[7] was used as an acceptor. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). The ratio of α- and β-anomers was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 80/20; flow rate, 1.0 ml/min; t_R α-mannoside 6.804 min; t_R β-mannoside 6.292 min). For **7dβ**: Colorless oil, R_f = 0.35 (Hexane/EtOAc = 3:1, v/v); $[\alpha]^{20}_D$ = -21.5 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49-7.27 (m, 20H, Ar-H), 5.57 (s, 1H, PhCH), 5.18 (s, 1H, H-1'), 4.95 & 4.63 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.76 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.63 & 4.47 (ABq, J = 12.0 Hz, 2H, $PhCH_2$), 4.59 (s, 1H, H-2'), 4.48 & 4.39 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.45 (s, 1H, H-5'), 4.29 (dd, $J_{6,6}$ = 10.0 Hz, $J_{6,5}$ = 4.4 Hz, 1H, H-6), 4.04 (dd, $J_{2,3}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.86 (ddd, $J_{5,6}$ = 10.0 Hz, $J_{5,4}$ = 9.2 Hz, $J_{5,6}$ = 4.4 Hz, 1H, H-5), 3.78 (dd, $J_{2,3}$ = 9.2 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.75 (s, 1H, H-4'), 3.74 (dd, $J_{6,6}$ = 10.0 Hz, $J_{6,5}$ = 10.0 Hz, 1H, H-6), 3.60 (dd, $J_{4,3}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.47 (s, 1H, H-3'), 3.41 (s, 3H, $-OCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.1, 139.0, 137.4, 136.7, 136.5, 128.8, 128.7, 128.47, 128.2, 127.8, 126.1, 101.4, 100.3, 96.8, 82.5, 79.5, 78.7, 77.7, 77.6, 76.2, 75.3, 71.5, 71.1, 71.0, 69.1, 62.3, 55.8; HRMS (ESI) Calcd for $C_{41}H_{42}O_{11}Na$ $[M+Na]^+$: 733.2625, found: 733.2642. The NOE correlation observed between δ 5.18 and δ 3.47 confirmed the stereochemistry at C-1 to be β.

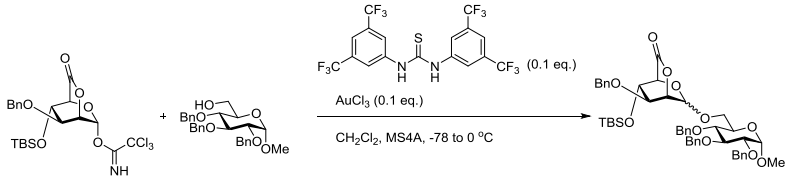
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eβ)



6e[8] was used as an acceptor. After getting the crude mixture, acetylation was performed for expediting purification by standard procedure using Ac_2O and DMAP in pyr./CH_2Cl_2. Under Ar, to a solution of residue in anhydrous CH_2Cl_2, anhydrous Pyr. and Ac_2O (1.0 equiv. to **6e**) was added DMAP (0.6 mg, 4.4 μmol) at 0 °C. After the TLC analysis showed the completion of acetylation, the mixture was extracted with CH_2Cl_2, and the organic layer was washed with water, 1 M $KHSO_4$ aq. and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (Hexane/EtOAc = 2/1). The mixture of α- and β-anomers was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 80/20; flow rate, 1.0 ml/min; t_R α-mannoside 12.521 min; t_R β-mannoside 10.554 min). For **7eβ**: Colorless oil, R_f = 0.32 (Hexane/Acetone = 7:3, v/v); $[\alpha]^{20}_D$ = -6.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40-7.16 (m, 25H, Ar-H), 5.24 (s, 1H, H-1'), 4.89 & 4.80 (ABq, J = 9.8 Hz, 2H, $PhCH_2$), 4.80 & 4.65 (ABq, J = 12.2 Hz, 2H, $PhCH_2$), 4.65 (s, 1H, H-2'), 4.62 & 4.45 (ABq, J = 11.2 Hz, 2H, $PhCH_2$), 4.59 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.58 & 4.38 (ABq, J = 11.4 Hz, 2H, $PhCH_2$), 4.46 (s, 1H, H-5'), 4.33 & 4.24 (ABq, J = 11.6 Hz, 2H, $PhCH_2$), 3.97 (dd, $J_{3,4}$ = 9.2 Hz, $J_{3,2}$ = 9.2 Hz, 1H, H-3), 3.84-3.81 (m, 0.5 H, H-4), 3.80 (d, $J_{4,3}$ = 9.2 Hz, 0.5H, H-4), 3.82-3.79 (m, 1H, H-6), 3.75-3.71 (m, 1H, H-5 & H-4'), 3.61-3.58 (m, 1H, H-6), 3.50 (dd, $J_{2,3}$ = 9.2, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.41 (s, 1H, H-3'), 3.37 (s, 3H, $-OCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.3, 138.4, 138.0, 137.8, 136.7, 136.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.7, 127.6, 98.3, 96.5, 80.8, 79.6, 79.3, 77.7, 76.1, 75.9, 75.3, 73.5, 73.4, 71.1, 70.9, 70.8, 69.2, 68.3, 55.3; HRMS (ESI) Calcd for $C_{48}H_{50}O_{11}Na$ $[M+Na]^+$: 825.3251, found: 825.3266. The NOE correlation observed between δ 5.24 and δ 3.41 confirmed the stereochemistry at C-1 to be β.

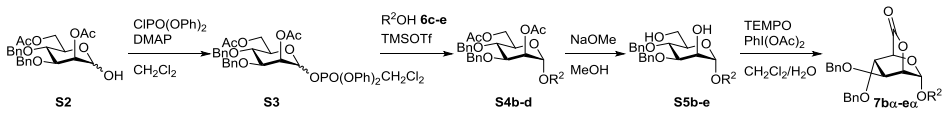
Methyl

2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-gluco pyranoside (7fα and β)



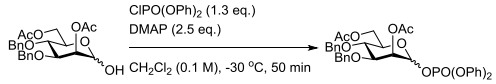
Glycosyl imidate **5dα** and glycosyl acceptor **6a** were used. The residue was purified by column chromatography (Hexane/EtOAc = 4/1 → 2/1). For **7fβ**: Colorless oil, R_f = 0.46 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = +18.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.27 (m, 20H, Ar-H), 4.99 & 4.80 (ABq, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.87 & 4.56 (ABq, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.78 & 4.65 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.73 (s, 1H, H-1'), 4.64 (s, 1H, H-2'), 4.60 & 4.55 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.57 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.17 (s, 1H, H-5'), 4.00 (d, $J_{3,2}$ = 9.6 Hz, 0.5H, H-3), 3.99-3.95 (m. 2.5H, H-3, H-4', H-6), 3.79-3.75 (m, 1H, H-5), 3.59-3.55 (m, 1H, H-6), 3.51 (dd, $J_{2,3}$ = 9.6 Hz, $J_{2,1}$ = 3.2 Hz, 1H, H-2), 3.42 (s, 1H, H-3'), 3.40-3.36 (m, 1H, H-4), 3.35 (s, 3H, -OCH_3), 0.90 (s, 9H, -$C(CH_3)_3$), 0.11 (s, 3H, -CH_3), 0.11 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.7, 138.8, 138.4, 138.2, 136.7, 128.7, 128.5, 128.5, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 97.9, 95.6, 82.1, 80.2, 80.1, 77.8, 77.3, 76.0, 75.8, 74.8, 74.5, 74.5, 73.5, 71.1, 69.8, 67.1, 55.2, 25.7, 18.1, -4.5, -4.8; HRMS (ESI) Calcd for $C_{47}H_{58}O_{11}SiNa$ $[M+Na]^+$: 849.3646, found: 849.3655. The NOE correlation observed between δ 4.73 and δ 3.42 confirmed the stereochemistry at C-1 to be β. For **7fα**: Colorless oil, R_f = 0.38 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = -12.4 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36-7.20 (m, 20H, Ar-H), 5.24-5.23 (m, 1H, H-1'), 4.99 & 4.83 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.81 & 4.69 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.78 & 4.55 (ABq, *J* = 10.4 Hz, 2H, $PhCH_2$), 4.73 (s, 1H, H-2'), 4.60 & 4.53 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.57 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1), 4.21 (s, 1H, H-5'), 4.06 (dd, $J_{6,6}$ = 11.6 Hz, $J_{6,5}$ = 3.6 Hz, 1H, H-6), 4.03 (s, 1H, H-3'), 3.99 (s, 1H, H-4'), 3.97 (dd, $J_{3,2}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.80 (dd, $J_{6,6}$ = 11.6 Hz, $J_{6,5}$ = 2.2 Hz, 1H, H-6), 3.69 (ddd, $J_{5,4}$ = 9.2 Hz, $J_{5,6}$ =3.6 Hz, $J_{5,6}$ = 2.2 Hz, 1H, H-5), 3.47 (dd, $J_{2,3}$ = 9.2 Hz, $J_{2,1}$ = 3.2 Hz, 1H, H-2), 3.44 (dd, $J_{4,3}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.32 (s, 3H, -OMe), 0.80 (s, 9H, -$C(CH_3)_3$), 0.03 (s, 3H, -CH_3), 0.03 (s, 3H, -CH_3);^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.7, 138.8, 138.2, 138.1, 136.9, 128.6, 128.6, 128.5, 128.5, 128.2, 128.1, 128.1, 128.0, 127.9, 127.7, 98.1, 97.1, 81.9, 80.0, 77.7, 77.3, 76.6, 75.9, 75.3, 75.3, 74.9, 74.7, 73.4, 71.1, 70.0, 67.4, 55.3, 25.7, 18.1, -4.6, -4.8; HRMS (ESI) Calcd for $C_{47}H_{58}O_{11}SiNa$ $[M+Na]^+$: 849.3646, found: 849.3635.

Scheme S1. Preparations of the authentic samples of the α-glycosides.



	S2	S3	7α
b	45.6 mg, 44%	22.0 mg, 78%	4.4 mg, 31%
c	34.0 mg, 27%	8.7 mg, 33%	26.9 mg, 69%
d	42.4 mg, 53%	25.9 mg, 75%	13.9 mg, 64%
e	Not isolated	12.0 mg, 10% in 2 steps.	9.2 mg, 77%

2,6-Di-*O*-acethyl-3,4-di-*O*-benzyl-D-mannopyranosyl diphenylphosphate (S3)

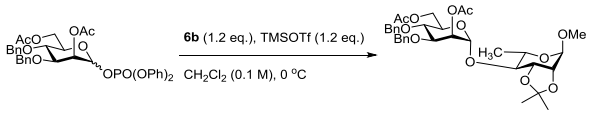


Under Ar atmosphere, to a solution of hemiacetal **S2**[9] (1.03 g, 2.31 mmol) in anhydrous CH_2Cl_2 (23.1 ml) was added diphenyl chlorophosphate (0.62 ml, 3.00 mmol) and DMAP (0.71 g, 5.78 mmol) at -30 °C and the mixture was stirred for 50 min. The reaction was quenched by clashed ice. The mixture was extracted with CH_2Cl_2. The combined organic layer was washed with sat. $NaHCO_3$ aq. brine and dried over Na_2SO_4. The extracted organic layer was concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, hexane → hexane/EtOAc = 7/3), which gave the title compound **S3** as yellow syrup (1.20 g, 81%, mixture of α- and β-anomers). R_f = 0.46 (Hexane/EtOAc = 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37-7.20 (m, 20H, Ar-H), 5.89-5.88 & 5.64 (m, 1H, H-1), 5.50-5.48 & 5.39 (m, 1H, H-2), 4.89-4.43 (m, 8H, $PhCH_2\times4$), 4.30-4.23 (m, 1H, H-5), 4.13-4.10 (m, 1H, H-4), 3.97-3.94 (m, 2H, H-3 & H-6), 3.79-3.63 (m, 1H, H-6), 2.16 & 2.12 (m, 3H, $-CH_3$), 2.00-1.95 (m, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.7, 169.8, 150.4, 137.7, 137.4, 130.0, 128.6, 128.2, 128.2, 128.1, 125.8, 120.5, 120.1, 96.8, 75.4, 73.2, 72.1, 72.0, 67.8, 67.7, 62.7, 20.9, 20.8; HRMS (ESI) Calcd for $C_{36}H_{37}NaO_{11}P$ $[M+Na]^+$: 699.1971, found: 699.1973.

Procedure for the reactions from S3 to S4

Under Ar atmosphere, to a glycosyl phosphate **S3** and glycosyl acceptor **6b-d** (1.2 equiv. to **S3**) was added anhydrous CH_2Cl_2 (0.1 M to **S3**) at room temperature. After stirring for 15 min, TMSOTf (1.2 equiv. to **S3**) were added at 0 °C and the mixture was stirred. After the TLC analysis showed the completion of reaction, the reaction was quenched by Et_3N at 0 °C. The mixture was poured to water, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography, which gave the title compound **S4**.

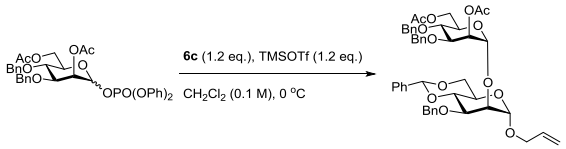
Methyl 2,3-*O*-isopropylidene-4-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S4b)



6b was used as an acceptor. The residue was purified by flash column chromatography (Hexane/EtOAc = 9/1 → Hexane/EtOAc = 4/1 → Hexane/EtOAc = 7/3). Colorless oil; R_f = 0.46 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +4.5 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34-7.29 (m, 10H, Ar-H), 5.31 (dd, $J_{2',1'}$ = 1.6 Hz, $J_{2',3'}$ = 3.2 Hz, 1H, H-2'), 4.96 (d, $J_{1',2'}$ = 1.6 Hz, 1H, H-1'), 4.90 & 4.55 (ABq, J = 10.4 Hz, 2H, $PhCH_2$), 4.83 (s, 1H, H-1), 4.70 & 4.56 (ABq, J = 11.2 Hz, 2H, $PhCH_2$), 4.52 (dd, $J_{6'6'}$ = 12.0 Hz, $J_{6'5'}$ = 2.4 Hz, 1H, H-6'), 4.22 (dd, $J_{6'6'}$ = 12.0 Hz, $J_{6'5'}$ = 2.0 Hz, 1H, H-6'), 4.16 (ddd, $J_{5'6'}$ = 9.6 Hz, $J_{5'6'}$ = 2.4 Hz, $J_{5'6'}$ = 2.0 Hz, 1H, H-5'), 4.08 (d, J = 5.6 Hz, 1H, H-2), 4.02 (dd, $J_{3,2}$ = 5.6 Hz, $J_{3,4}$ = 7.2 Hz,1H, H-3), 3.98 (dd, $J_{3'2'}$ = 3.2 Hz, $J_{3'4'}$ = 9.6 Hz, 1H, H-3'), 3.89 (dd, $J_{4'3'}$ = 9.6 Hz, $J_{4'5'}$ = 9.6 Hz, 1H, H-4'), 3.67-3.60 (m, 1H, H-5), 3.36 (s, 3H, $-OCH_3$), 3.34 (dd, $J_{4,3}$ = 7.2 Hz, 0.5H, H-4), 3.33-3.32 (m, 0.5H, H-4), 2.16 (s, 3H, -OAc), 2.07 (s, 3H, -OAc), 1.51 (s, 3H, -CH3), 1.30 (s, 3H, -CH3), 1.28-1.27 (m, 3H, C-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.9, 170.6, 138.1, 137.9, 128.5, 128.3, 128.1, 128.0, 127.9, 109.3, 98.5, 98.0, 81.2, 78.1, 76.7, 76.0, 75.4, 73.7, 71.9, 69.6, 68.8, 64.6, 63.0, 54.9, 28.2, 26.4, 21.2, 21.0, 17.5; HRMS (ESI) Calcd for $C_{30}H_{40}O_{10}$ $[M+Na]^+$: 667.2731, found: 667.2748.

Allyl

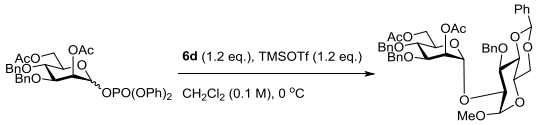
2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S4c)



6c was used as an acceptor. The residue was purified column chromatography (Hexane/EtOAc = 13/7). Colorless oil; R_f = 0.53 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = +20.5 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51-7.27 (m, 20H, Ar-H), 5.86 (dddd, $J_{\beta,\gamma trans}$ = 17.2 Hz, $J_{\beta,\gamma cis}$ = 10.4 Hz, $J_{\beta,\alpha 2}$ = 5.6 Hz, $J_{\beta,\alpha 1}$ = 4.8 Hz, 1H, H-β), 5.64 (s, 1H, PhCH), 5.59 (s, 1H, H-2'), 5.25 (d, $J_{\gamma trans,\beta}$ = 17.2 Hz, 1H, H-γ_{trans}), 5.20 (d, $J_{\gamma cis,\beta}$ = 10.4 Hz, 1H, H-γ_{cis}), 5.12 (s, 1H, H-1'), 4.90 & 4.54 (ABq, *J* = 10.4 Hz, 2H, $PhCH_2$), 4.86 & 4.65 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.83 (s, 1H, H-1), 4.78 & 4.56 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.36-4.28 (m, 2H, H-6', H-6'), 4.15 (dd, $J_{\alpha 1,\alpha 2}$ = 12.8 Hz, $J_{\alpha 1,\beta}$ = 4.8 Hz, 1H, H-α1), 4.07-4.05 (m, 1H, H-3'), 4.03 (m, 2H, H-2, H-5), 3.99-3.97 (m, 3H, H-4, H-5, H-α1), 3.84-3.80 (m, 2H, H-3, H-6), 3.75-3.70 (m 1H, H-4'), 2.13 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.8, 169.9, 138.5, 137.9, 137.9, 137.6, 133.4, 129.0, 128.5, 128.4, 128.3, 128.3, 128.1, 127.9, 127.6, 127.5, 126.1, 117.8, 101.6, 100.0, 99.0, 79.2, 78.0, 77.4, 76.6, 75.7, 75.5, 74.2, 73.2, 71.9, 70.3, 68.8, 68.3, 68.2, 64.0, 63.6, 21.1, 20.9; HRMS (ESI) Calcd for $C_{47}H_{52}O_{13}$ $[M+Na]^+$: 847.3306, found: 847.3314.

Methyl

2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S4d)

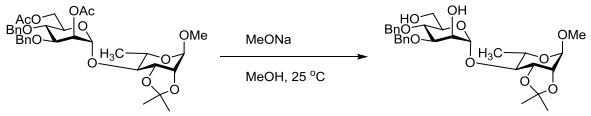


6d was used as an acceptor. The residue was purified by column chromatography (Hexane/EtOAc = 13/7). Colorless oil; R_f = 0.49 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +28.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50-7.05 (m, 20H, Ar-H), 5.44 (dd, $J_{2',3'}$ = 3.6, $J_{2',1'}$ = 1.6 Hz, 1H, H-2'), 4.95 (d, $J_{1',2'}$ = 1.6 Hz, 1H, H-1'), 4.92 & 4.54 (ABq, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.86 (d, *J* = 3.6 Hz, 1H, H-1), 4.79 & 4.64 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.72 & 4.54 (ABq, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.32-4.29 (m, 1H, H-6), 4.19-4.13 (m, 3H, H-6', H-6', H-5'), 4.05 (dd, $J_{3',4'}$ = 9.2, $J_{3',2'}$ =3.6 Hz, 1H, H-3'), 3.96-3.94 (m, 0.5H, H-4), 3.92 (d, $J_{4,3}$ = 9.2 Hz, 0.5H, H-4), 3.88-3.81 (m, 1H, H-5), 3.83 (dd, $J_{2,3}$ = 9.2 Hz, $J_{2,1}$ = 3.6 Hz, 1H, H-2), 3.79-3.73 (m, 2H, H-4' & H-6), 3.64 (dd, $J_{3,2}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.46 (s, 3H, $-OCH_3$), 2.16 (s, 3H, -OAc), 2.03 (s, 3H, -OAc); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.7, 170.4, 138.4, 137.9, 137.8, 137.4, 128.4, 128.1, 127.9, 127.7, 126.0, 101.4, 97.2, 94.8, 82.4, 78.0, 75.6, 75.2, 74.2, 73.8, 71.9, 69.9, 69.1, 68.8, 63.0, 62.3, 55.5, 21.2, 20.9; HRMS (ESI) Calcd for $C_{45}H_{50}O_{13}$ $[M+Na]^+$: 821.3149, found: 821.3153.

Procedure for the reactions from S4 to S5

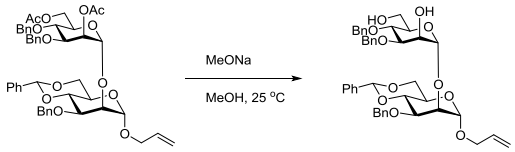
To **S4b-d** was added 0.1 M solution of MeONa in MeOH (1.0 equiv. to **S4**) at room temperature and the mixture was stirred for 30 min. To the mixture was added protonic ion-exchanger resin, AMBERLYST 15 (H^+), until the pH of the mixture became about 7. The resin was removed by filtration through a cotton pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography to give **S5**.

Methyl 2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S5b)



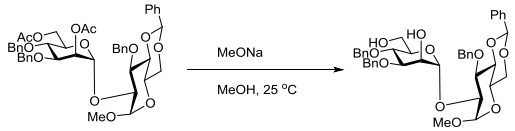
S4b was employed. The residue was purified by column chromatography (Hexane/EtOAc = 7/13). Colorless oil; R_f = 0.69 ($CHCl_3$/MeOH = 9:1, v/v); $[\alpha]^{20}_D$ = +21.4 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.29 (m, 10H, Ar-H), 4.94 (s, 1H, H-1'), 4.86 & 4.62 (ABq, *J* = 11.2 Hz, 2H, $PhCH_2$), 4.84 (s, 1H, H-1), 4.72 & 4.62 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.10-4.07 (m, 2H, H-2 & H-3), 3.99 (br, 1H, H-2'), 3.94-3.93 (m, 1H, H-5'), 3.87-3.84 (m, 2H, H-3' & H-6'), 3.75-3.71 (m, 2H, H-4' & H-6'), 3.66-3.59 (m, 1H, H-5), 3.36 (s, 1H, -OMe), 3.31-3.29 (m, 1H, H-4), 2.76 (br, 1H, -OH), 2.56 (s, 1H, -OH), 1.52 (s, 3H, -CH3), 1.31 (s, 3H, -CH3), 1.26-1.24 (m, 3H, C-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.2, 137.8, 128.7, 128.5, 128.2, 128.1, 128.1, 128.0, 109.3, 100.8, 98.0, 83.0, 80.0, 75.9, 75.2, 74.6, 72.4, 72.4, 68.8, 64.3, 62.3, 54.9, 28.0, 26.2, 17.6, 14.3; HRMS (ESI) Calcd for $C_{34}H_{44}O_{12}$ $[M+Na]^+$: 583.2519, found: 583.2505.

Allyl 2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S5c)



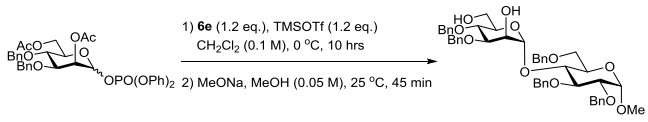
S4c was employed. The residue was purified by column chromatography (Hexane/EtOAc = 1/1). Colorless oil; R_f = 0.55 (Hexane/EtOAc = 1:2, v/v); $[\alpha]^{20}_D$ = +32.9 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.27 (m, 20H, Ar-H), 5.86 (dddd, $J_{\beta,\gamma trans}$ = 17.2 Hz, $J_{\beta,\gamma cis}$ = 10.4 Hz, $J_{\beta,\alpha1}$ = 4.8 Hz, $J_{\beta,\alpha2}$ = 4.6 Hz, 1H, H-β), 5.62 (s, 1H, PhCH), 5.25 (d, $J_{\gamma trans,\beta}$ = 17.2 Hz, 1H, H-γ_{trans}), 5.20 (d, $J_{\gamma cis,\beta}$ = 10.4 Hz, 1H, H-γ_{cis}), 5.16 (s, 1H, H-1'), 4.88 & 4.65 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.86 (d, *J* = 1.6 Hz, H-1), 4.83 & 4.68 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.73 (s, 2H, $PhCH_2$), 4.26-4.20 (m, 2H, H-2', H-3), 4.13 (dd, $J_{\alpha1,\alpha2}$ = 12.8 Hz, $J_{\alpha1,\beta}$ = 4.8 Hz, 1H, H-α1), 4.04-4.00 (m, 3H, H-2, H-5, H-6), 3.97-3.92 (m, 1H, H-3'), 3.94 (dd, $J_{\alpha2,\alpha1}$ = 12.8 Hz, $J_{\alpha2,\beta}$ = 4.6 Hz, 1H, H-α2), 3.86-3.83 (m, 1H, H-4'), 3.81-3.73 (m, 5H, H-4, H-6, H-5', H-6', H-6'), 2.52 (br, 1H, -OH), 1.98 (br, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.4, 138.1, 137.9, 137.6, 129.0, 128.6, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.6, 127.6, 126.1, 117.8, 101.6, 98.9, 79.7, 79.1, 77.3, 75.9, 75.4, 74.2, 73.3, 72.2, 72.2, 68.9, 68.4, 68.1, 64.1, 62.1; HRMS (ESI) Calcd for $C_{43}H_{48}O_{11}$ $[M+Na]^+$: 763.3094, found: 763.3089.

Methyl 2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S5d)



S4d was employed. The residue was purified by column chromatography (Hexane/EtOAc = 1/4). Colorless oil; R_f = 0.55 (Hexane/EtOAc = 1/4, v/v); $[\alpha]^{20}_D$ = +23.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.49-7.07 (m, 20H, Ar-H), 5.58 (s, 1H, PhCH), 5.02 (s, 1H, H-1'), 4.90-4.87 (m, 1H, H-1), 4.89 & 4.65 (ABq, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.81 & 4.67 (ABq, *J* = 10.6 Hz, 2H, $PhCH_2$), 4.71 (s, 2H, $PhCH_2$), 4.32-4.28 (m, 1H, H-6), 4.17 (s, 1H, H-2'), 4.00-3.81 (m, 7H, H-3', H-5', H-6', H-6', H-2, H-3, H-6), 3.77-3.64 (m, 3H, H-4', H-4, H-5), 3.44 (s, 3H, -OCH_3), 2.63 (br, 1H, -OH), 1.69 (br, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.7, 137.9, 137.9, 137.4, 129.0, 128.7, 128.6, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 126.0, 101.3, 97.1, 96.1, 82.3, 79.9, 76.9, 75.7, 75.1, 73.8, 73.7, 72.2, 71.7, 69.1, 68.6, 62.4, 61.6, 55.4; HRMS (ESI) Calcd for $C_{41}H_{46}O_{11}$ $[M+Na]^+$: 737.2938, found: 737.2950.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)- α-D-glucopyranoside (S5e)



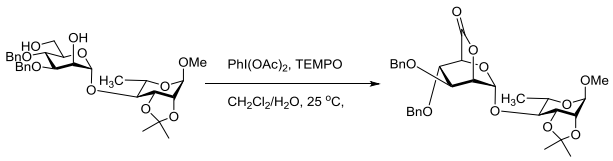
Under Ar atmosphere, to a glycosyl phosphate **S3** (100.1 mg, 155.2 μmol) and glycosyl acceptor **6e** (79.3 mg, 186.3 μmol) was added anhydrous CH_2Cl_2 (1.55 ml) at room temperature. After stirring for 15 min, TMSOTf (28.0 μl, 155.2 μmol) were added at 0 °C and the mixture was stirred for 30 min. After the TLC analysis showed the completion of reaction, the reaction was quenched by Et_3N at 0 °C. The mixture was poured to water, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. To the crude product was added 0.05 M MeONa in MeOH (3.0 ml) at room temperature and the mixture was stirred for 45 min. To the mixture was added protonic ion-exchanger resin, AMBERLYST 15 (H^+), until the pH of the mixture became about 7. The resin was removed by filtration through a cotton pad, and the filtrate was concentrated *in vacuo*. The residue was purified by open column chromatography (7 g, Hexane/EtOAc = 1/1 → Hexane/EtOAc = 2/3) to afford **S5e** as colorless oil (12.0 mg, 10% in 2 steps.). R_f = 0.27 (Hexane/EtOAc = 1:1, v/v); $[\alpha]^{20}_D$ = +36.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33-7.30 (m, 25H, Ar-H), 5.31 (s, 1H, H-1'), 5.04-5.01 (m, 1H), 4.86-4.83 (m, 1H), 4.75-4.72 (m ,1H), 4.61-4.51 (m, 9H), 3.88-3.84 (m, 2H), 3.76-3.62 (m, 10H), 3.55-3.51 (m, 1H), 3.39 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.5, 138.3, 138.1, 138.0, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 127.8, 127.8, 127.6, 127.6, 101.3, 97.8, 81.8, 80.3, 79.7, 75.6, 75.2, 74.0, 73.6, 73.3, 72.7, 72.1, 69.8, 69.0, 68.9, 62.1, 55.4; HRMS (ESI) Calcd for $C_{48}H_{54}O_{11}$ $[M+Na]^+$: 829.3564, found: 829.3588.

Procedure for the reaction from S5 to 7

To **S5b-e** and $PhI(OAc)_2$ (3.5 equiv. to **S5**) in CH_2Cl_2 and H_2O (0.1 M to **S5**, 2/1, v/v) was added TEMPO (0.2 equiv. to **S5**) at room temperature and the mixture was stirred. After the TLC analysis showed the completion of reaction, the reaction was quenched by 10% $Na_2S_2O_3$ aq. and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography, which gave the title compound **7αb-e**.

Methyl

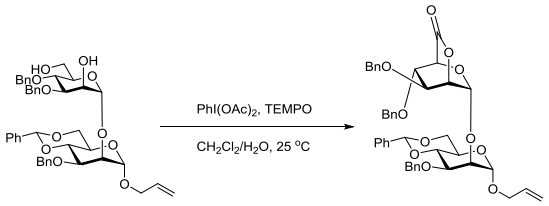
2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bα)



S5b was used. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). Colorless oil, R_f = 0.57 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +7.1 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.29 (m, 10H, Ar-H), 5.43-5.42 (m, 1H, H-1'), 4.83 (s, 1H, H-1), 4.69 (s, 1H, H-2'), 4.67 & 4.49 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.58 (s, 1H, H-5'), 4.55 & 4.51 (ABq, J = 11.8 Hz, 2H, $PhCH_2$), 4.35 (dd, $J_{3,2}$ = 6.0 Hz, $J_{3,4}$ = 6.8 Hz, 1H, H-3), 4.14 (s, 1H, H-3'), 4.09 (d, $J_{2,3}$ = 6.0 Hz, 1H, H-2), 3.69-3.61 (m, 1H, H-5), 3.37 (s, 1H, -OCH_3), 3.35-3.34 (m, 0.5H, H-4), 3.34 (d, $J_{4,3}$ = 6.8 Hz, 0.5H, H-4), 1.53 (s, 3H, -CH_3), 1.35 (s, 3H, -CH_3), 1.16-1.15 (m, 3H, C-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.3, 137.1, 137.0, 128.6, 128.6, 128.2, 128.1, 127.9, 109.5, 98.2, 96.8, 83.2, 79.7, 77.3, 76.7, 75.8, 75.4, 74.1, 71.6, 71.1, 71.0, 63.8, 55.0, 28.1, 26.3, 17.8; HRMS (ESI) Calcd for $C_{34}H_{44}O_{12}Na$ $[M+Na]^+$: 579.2206, found: 579.2215.

Allyl

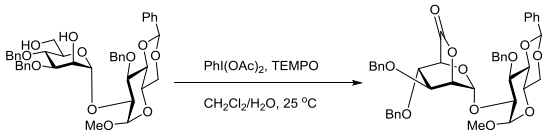
2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene--α-D-mannopyranoside (7cα)



S5c was used. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). Colorless oil; R_f = 0.66 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +30.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.30 (m, 20H, Ar-H), 5.87 (dddd, $J_{\beta,\gamma\,trans}$ = 19.2 Hz, $J_{\beta,\gamma\,cis}$ = 11.2 Hz, $J_{\beta,\alpha1}$ = 6.0 Hz, $J_{\beta,\alpha2}$ = 5.2 Hz, 1H, H-β), 5.60 (s, 1H, PhCH), 5.47-5.46 (s, 1H, H-1'), 5.17 (d, $J_{\gamma\,trans,\beta}$ = 19.2 Hz, 1H, H-γ_{trans}), 5.13 (d, $J_{\gamma\,cis,\beta}$ = 11.2 Hz, 1H, H-γ_{cis}), 4.92 (s, 1H, H-2'), 4.88 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1), 4.83 & 4.68 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.61 & 4.50 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.56 & 4.47 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.49 (s, 1H, H-5'), 4.25-4.22 (m, 1H, H-6), 4.18-4.17 (m, 0.5H, H-2), 4.17 (d, $J_{2,1}$ = 1.6 Hz, 0.5H, H-2), 3.99-3.92 (m, 3H, H-3, H-4, H-α1), 3.81-3.72 (m, 3H, H-3', H-5, H-6), 3.67 (dd, $J_{\alpha1,\alpha2}$ = 12.8 Hz, $J_{\alpha1,\beta}$ = 6.0 Hz, 1H, H-α1); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.4, 138.2, 137.6, 137.1, 137.0, 133.7, 129.0, 128.6, 128.6, 128.3, 128.2, 128.2, 128.0, 127.9, 127.7, 126.1, 117.4, 101.6, 99.5, 96.9, 79.7, 79.4, 77.3, 75.9, 75.4, 74.8, 73.8, 73.6, 71.6, 71.3, 70.9, 69.0, 68.2, 63.8; HRMS (ESI) Calcd for $C_{43}H_{44}O_{11}Na$ $[M+Na]^+$: 759.2781, found: 759.2775.

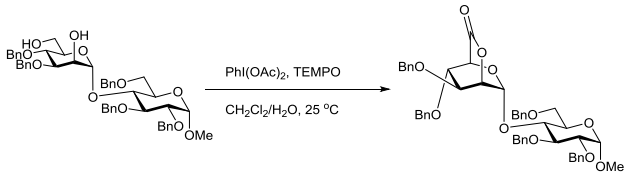
Methyl

2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene--α-D-glucopyranoside (7dα)



S5d was used. The residue was purified by column chromatography (Hexane/EtOAc = 7/3). Colorless oil; R_f = 0.16 (Hexane/EtOAc = 3:1, v/v); $[\alpha]^{20}_D$ = +21.5 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.45-7.21 (m, 20H, Ar-H), 5.55 (s, 1H, PhCH), 5.34 (d, $J_{1',2'}$ = 2.8 Hz, 1H, H-1'), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.78 & 4.71 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.77 (d, $J_{2',1'}$ = 3.6 Hz, 1H, H-2'), 4.53 & 4.46 (ABq, *J* = 12.2 Hz, 2H, $PhCH_2$), 4.51 (s, 1H, H-5'), 4.48 & 4.41 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.31 (s, 1H, H-3'), 4.29 (dd, $J_{6,6}$ = 10.0 Hz, $J_{6,5}$ = 4.4 Hz, 1H, H-6), 4.06(dd, $J_{3,2}$ = 9.2, $J_{2,1}$ = 3.6 Hz, H-2), 3.93 (dd, $J_{3,2}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz,1H, H-3), 3.81 (ddd, $J_{5,6}$ = 10.0 Hz, $J_{5,4}$ = 9.2 Hz, $J_{5,6}$ = 4.4 Hz, 1H, H-5), 3.75 (dd, $J_{6,6}$ = 10.0, $J_{6,5}$ = 4.4 Hz, 1H, H-6), 3.60 (dd, $J_{4,3}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.42 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.1, 138.9, 137.4, 137.0, 136.9, 128.6, 128.2, 128.2, 128.0, 127.5, 126.1, 101.4, 97.8, 94.3, 81.5, 79.4, 77.3, 77.0, 76.9, 75.9, 75.0, 74.2, 71.9, 71.0, 71.0, 69.0, 62.5, 55.3; HRMS (ESI) Calcd for $C_{41}H_{42}O_{11}Na$ $[M+Na]^+$: 733.2625, found: 733.2642.

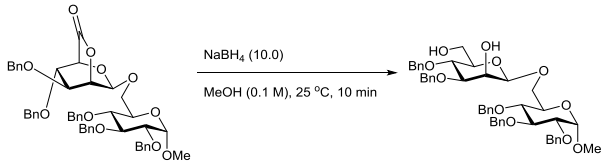
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)- α-D-glucopyranoside (7eα)



S5e was used. The residue was purified by column chromatography (Hexane/EtOAc = 3/1). Colorless oil; R_f = 0.64 (Hexane/EtOAc = 2:1, v/v); $[\alpha]^{20}_D$ = +33.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40-7.22 (m, 25H, Ar-H), 5.41-5.40 (m, 1H, H-1'), 4.99 & 4.60 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.75 & 4.64 (ABq, *J* = 10.6 Hz, 2H, $PhCH_2$), 4.62 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.72 & 4.62 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.53 & 4.37 (ABq, *J* = 12.2 Hz, 2H, $PhCH_2$), 4.45 & 4.36 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.40 & 4.31 (ABq, *J* = 12.2 Hz, 2H, $PhCH_2$), 4.35 (s, 1H, H-5'), 4.07 (s, 1H, H-2'), 4.02 (s, 1H, H-3'), 3.87 (d, $J_{3,2}$ = 9.2 Hz, 0.5H, H-3), 3.86-3.84 (m, 0.5 H, H-3), 3.80-3.75 (m, 2H, H-4 & H-6), 3.68 (s, 1H, H-4'), 3.65-3.60 (m, 2H, H-5 & H-6), 3.53 (dd, $J_{2,3}$ = 9.2, $J_{2,1}$ =3.6 Hz, 1H, H-2), 3.39 (s, 3H, -OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.3, 138.5, 138.5, 137.9, 137.1, 136.7, 128.8, 128.6, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 127.5, 97.9, 97.9, 81.2, 80.1, 79.8, 76.4, 75.6, 74.9, 74.4, 73.4, 73.3, 71.6, 71.3, 71.0, 69.5, 68.3, 55.4; HRMS (ESI) Calcd for $C_{48}H_{54}O_{11}Na$ $[M+Na]^+$: 825.3251, found: 825.3241.

Scheme 3

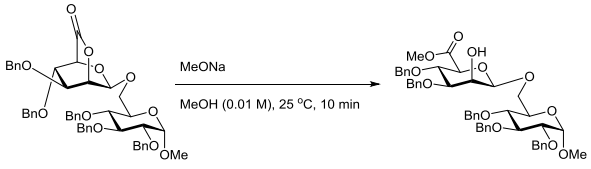
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranoyl)-α-D-glucopyranoside (8)



To a solution of **7aβ** (12.1 mg, 12.6 μmol) in MeOH (0.15 ml) was added $NaBH_4$ (5.7 mg, 150.7 μmol) at room temperature and the mixture was stirred for 10 min. After the TLC analysis showed the completion of reaction, the mixture was poured to water, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (10 g, Hexane/EtOAc = 1/2), which gave the title compound **8** as colorless oil (9.9 mg, 82%). R_f = 0.44 (Hexane/EtOAc = 1/3, v/v); $[\alpha]^{20}_D$ = +21.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.22 (m, 25H, Ar-H), 5.00 & 4.81 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.91 & 4.63 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.86 & 4.55 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.78 & 4.65 (ABq, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.73 & 4.68 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.55 (s, 1H, H-1'), 4.14 (s, 1H, H-1), 4.02-3.97 (m, 2H, H-3', H-6), 3.92-3.91 (m, 1H, H-2), 3.85-3.80 (m, 2H, H-3, H-5), 3.78-3.69 (m, 3H, H-5', H-6, H-6), 3.58-3.54 (m, 1H, H-6'), 3.53-3.44 (m, 3H, H-3, H-2', H-4'), 3.34 (s, 3H, -OCH_3), 3.24-3.20 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.8, 138.4, 138.2, 138.1, 137.8, 128.6, 128.6, 128.5, 128.2, 128.0, 128.0, 128.0, 127.9, 127.7, 100.1, 100.0, 98.0, 82.2, 81.2, 79.9, 77.3, 75.8, 75.4, 75.3, 74.8, 74.2, 73.5, 71.6, 69.9, 68.3, 68.3, 62.3, 55.3; HRMS (ESI) Calcd for $C_{48}H_{54}O_{11}Na$ $[M+Na]^+$: 829.3564, found: 829.3549.

Methyl

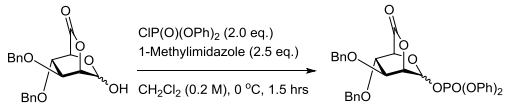
2,3,4-tri-*O*-benzyl-6-*O*-(methyl(3',4'-di-*O*-benzyl-β-D-mannopyranosyl)uronate)-α-D-glucopyranoside (9)



To **7aβ** (10.0 mg, 12.5 μmol) was added 0.01 M solution of MeONa in MeOH (1.25 ml) at room temperature and the mixture was stirred for 10 min. To the mixture was added protonic ion-exchanger resin, AMBERLYST 15 (H^+), until the pH of the mixture became about 7. The resin was removed by filtration through a cotton pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (7 g, Hexane/EtOAc = 1/1), which gave the title compound **9** as colorless oil (7.9 mg, 76%). R_f = 0.47 (Hexane/EtOAc = 1/1, v/v); $[\alpha]^{20}_D$ = +13.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.23 (m, 25H, Ar-H), 4.99 & 4.81 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.86 & 4.53 (ABq, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.84 & 4.62 (ABq, *J* = 11.0 Hz, 2H, $PhCH_2$), 4.78 & 4.62 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.73 & 4.68 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.54 (d, $J_{1'2'}$ = 3.6 Hz, 1H, H-1'), 4.17-4.13 (m, 1H, H-4), 4.14 (s, 1H, H-1), 4.09-4.06 (m, 1H, H-6), 3.98 (dd, $J_{3'2'}$ = 9.6 Hz, $J_{3'4'}$ = 9.6 Hz, 1H, H-3'), 3.89 (s, 1H, H-2), 3.76-3.73 (m, 2H, H-5, H-5'), 3.68 (s, 3H, $COOCH_3$), 3.53-3.50 (m, 1H, H-6), 3.49 (dd, $J_{2'3'}$ = 9.6 Hz, $J_{2'1'}$ = 3.6 Hz, 1H, H-2'), 3.49-3.48 (m, 1H, H-3), 3.40-3.38 (m, 0.5H, H-4'), 3.37 (d, $J_{4'3'}$ = 9.6 Hz, 1H, H-4'), 3.31 (s, 3H, $-OCH_3$), 2.45 (br, 1H, -OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 168.8, 138.8, 138.4, 138.1, 138.0, 137.8, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 100.4, 97.9, 82.2, 80.0, 79.9, 77.6, 77.3, 75.8, 75.3, 75.1, 74.8, 74.6, 73.5, 71.7, 69.8, 68.5, 68.0, 55.2, 52.5; HRMS (ESI) Calcd for $C_{49}H_{54}O_{12}Na$ $[M+Na]^+$: 857.3513, found: 857.3493.

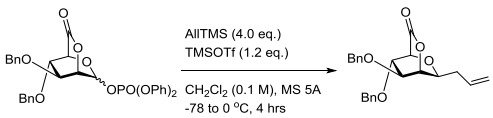
Table 3

3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diphenylphosphate (10)



Under Ar atmosphere, to a solution of hemiacetal **S1** (81 mg, 0.23 mmol) and 1-methylimidazole (50 μl, 0.57 mmol) in anhydrous CH_2Cl_2 (1.1 ml) was added diphenyl chlorophosphate (90 μl, 0.46 mmol) at 0 °C and the mixture was stirred for 1.5 hrs. The reaction was quenched by clashed ice. The mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (10 g, hexane → hexane/EtOAc = 4/1), which gave the title compound **10** as colorless syrup (0.11 g, 83%). For the α-anomer: R_f = 0.62 (Hexane/EtOAc = 2/1, v/v); $[\alpha]^{20}_D$ = -41.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.44-7.27 & 7.25-7.24 (m, 20H, Ar-H), 6.26-6.25 (m, 1H, H-1), 5.22 (s, 1H, H-2), 4.76 (s, 1H, H-5), 4.75 & 4.66 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.73 & 4.65 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.06 (s, 1H, H-3), 3.91 (s, 1H, H-4); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 167.2, 150.6, 150.5, 150.5, 137.6, 137.6, 130.1, 130.0, 128.4, 128.4, 128.2, 128.0, 128.0, 127.9, 125.7, 125.7, 94.6, 94.6, 79.2, 77.3, 76.6, 76.5, 71.8, 70.9; HRMS (ESI) Calcd for $C_{32}H_{29}NaO_9P$ $[M+Na]^+$: 611.1447, found: 611.1459. For **5bαβ**: ^{1}H NMR (400 MHz, $(CD_3)_2CO$, TMS) δ 7.44-7.24 (m, 20H, Ar-H), 6.25-6.21 (m, 1H, H-1), 5.22 & 5.15 (m, 1H, H-2), 4.81-4.55 (m, 5H, H-5, $Ph2CH_2\times2$), 4.20 & 4.06 (m, 1H, H-3), 3.95 & 3.91 (m, 1H, H-4).

Procedures for Table 3



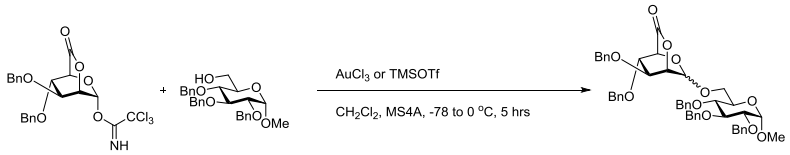
Under Ar atmosphere, to donor **10α** or **10αβ**, AllTMS (4.0 equiv. to **10**) and activated 5 Å molecular sieves was added anhydrous CH_2Cl_2 (0.46 ml) at room temperature. After stirring for 30 min, TMSOTf (1.2 equiv. to **10**) were added at -78 °C. The mixture was stirred and warmed up to 0 °C over 4 hrs. The reaction was quenched by Et_3N at 0 °C. The mixture was filtrated through Celite pad and concentrated *in vacuo*. The residue was diluted with CH_2Cl_2, and the solution was washed

with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*, which gave the title compound **11** as colorless oil without further purification.

3-(3',4'-Di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1-yl)propene (11)

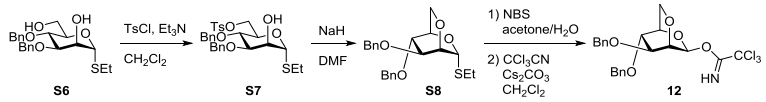
R_f = 0.60 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = -11.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.29 (m, 10H, Ar-H), 5.78-5.67 (dddd, $J_{\beta,\gamma trans}$ = 18.0 Hz, $J_{\beta,\gamma cis}$ = 9.6 Hz, $J_{\beta,\alpha1}$ = 8.0 Hz, $J_{\beta,\alpha2}$ = 7.6 Hz, 1H, Hβ), 5.17 (d, $J_{\beta,\gamma trans}$ = 18.0 Hz, 1H, H-γ_{trans}), 5.16 (d, $J_{\beta,\gamma cis}$ = 9.6 Hz, 1H, H-γ_{cis}), 4.67 (s, 1H, H-2), 4.65 & 4.49 (ABq, *J* = 12.6 Hz, 2H, $PhCH_2$), 4.65 & 4.48 (ABq, *J* = 12.0 Hz, 2H, $PhCH_2$), 4.46 (s, 1H, H-5), 3.90 (dd, $J_{H\text{-}1,\alpha1}$ = 6.8 Hz, $J_{H\text{-}1,\alpha2}$ = 6.4 Hz, 1H, H-1), 3.82 (s, 1H, H-4), 3.63 (s, 1H, H-3), 2.49-2.42 & 2.36-2.29 (ddd, $J_{\alpha1,\alpha2}$ = 13.2 Hz, $J_{\alpha1,\beta}$ = 8.0 Hz, $J_{\alpha2,\beta}$ = 7.6 Hz, $J_{H\text{-}1,\alpha1}$ = 6.8 Hz, $J_{H\text{-}1,\alpha2}$ = 6.4 Hz, 2H, $H_{\alpha1,\alpha2}$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.0, 136.8, 136.7, 132.1, 128.7, 128.2, 128.0, 119.5, 79.6, 78.9, 75.4, 72.0, 71.2, 70.7, 36.3; HRMS (ESI) Calcd for $C_{23}H_{24}NaO_5$ $[M+Na]^+$: 403.1521, found: 403.1523. The NOE correlation observed between δ 3.90 and δ 3.63 confirmed the stereochemistry at C-1 to be β.

Table 4

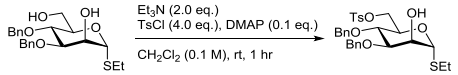


Under Ar atmosphere, to glycosyl imidate **5cα**, glycosyl acceptor **6a** (1.2 equiv. to **5cα**) and activated 4 Å molecular sieves in the presence or absence of 1,3-bis[3,5-bis(trifluoromethyl) phenyl]thiourea (0.1 equiv. to **5cα**) was added anhydrous CH_2Cl_2 at room temperature. After stirring for 30 min, gold (III) chloride or TMSOTf (0.1 equiv. to **5cα**) was added at -78 °C. The mixture was stirred and warmed up to 0 °C over 5 hrs. The reaction was quenched by Et_3N at 0 °C and diluted with 10 mL of CH_2Cl_2. The diluted solution was filtrated through Celite pad and the filtrate was concentrated *in vacuo*. The reaction mixture was analyzed by HPLC (column, Mightysil, RP-18 MS 150-4.6 (5 μm); eluent, CH_3CN/H_2O = 80/20; flow rate, 1.0 ml/min; t_R α-mannoside 13.400 min; t_R β-mannoside 12.258 min).

Scheme S2. Preparations of 2,6-anhydro sugar **12**.



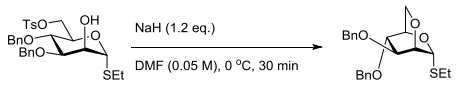
Ethyl 1-thio-3,4-di-*O*-benzyl-6-*O*-tosyl-α-D-mannopyranoside (S7)



Under Ar atmosphere, to a solution of **S6**[10] (47.1 mg, 116.4 μmol), TsCl (88.8 mg, 465.7 μmol) in anhydrous CH_2Cl_2 (1.16 ml) was added Et_3N (32.3 μl, 232.9 μmol) and DMAP (1.4 mg, 11.6 μmol) at room temperature. The mixture was stirred for 1 hr. The mixture was poured into sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography (7 g, hexane/EtOAc = 2/1), which gave the title compound **S7** as colorless oil (48.0 mg, 74%). R_f = 0.33 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = +25.1 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78-7.76 (m, 2H, Ar-H), 7.32-7.20 (m, 12H, Ar-H), 5.25 (d, $J_{1,2}$ = 1.2 Hz, 1H, H-1), 4.83 & 4.48 (ABq, *J* = 10.8 Hz, 2H, $PhCH_2$), 4.66 & 4.62 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.28-4.22 (m, 2H, H-6. H-6), 4.20-4.16 (m, 1H, H-5), 4.04 (dd, $J_{2,1}$ = 1.2 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.79 (dd, $J_{3,2}$

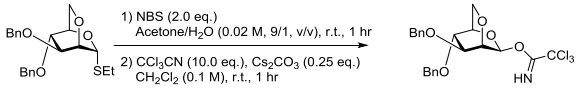
= 3.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 3.74 (d, $J_{4,3}$ = 9.2 Hz, 0.5H, H-4), 3.73-3.70 (m, 0.5H, H-4), 2.63 (m, 1H, -OH), 2.60-2.42 (m, 2H, CH_2), 2.41(s, 3H, -CH_3), 1.24-1.20 (m, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.8, 137.9, 137.5, 133.0, 129.8, 128.7, 128.5, 128.2, 128.1, 128.1, 128.0, 83.3, 80.4, 75.2, 73.8, 72.1, 69.8, 69.7, 68.9, 24.9, 21.7, 14.8; HRMS (ESI) Calcd for $C_{29}H_{34}NaO_7S_2$ $[M+Na]^+$: 581.1644, found: 581.1642.

Ethyl 1-thio-3,4-di-*O*-benzyl-2,6-anhydro-α-D-mannopyranoside (S8)



Under Ar atmosphere, to a solution of **S7** (23.4 mg, 41.9 μmol) in anhydrous DMF (0.84 ml) was added NaH (2.2 mg, 50.3 μmol, 55%) at 0 °C and the mixture was stirred for 30 min. The reaction was quenched by MeOH (1.0 ml). The mixture was poured to water, and extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (7 g, Hexane/EtOAc = 3/1), which gave the title compound **S8** as colorless oil (12.1 mg, 75%). R_f = 0.44 (Hexane/EtOAc = 2/1, v/v); $[\alpha]^{20}_D$ = +5.6 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37-7.28 (m, 10H, Ar-H), 5.46-5.45 (m, 1H, H-1), 4.63 & 4.51 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.63 & 4.57 (ABq, *J* = 12.4 Hz, 2H, $PhCH_2$), 4.20-4.17 (m, 0.5H, H-6), 4.18 (d, $J_{6,6}$ = 10.0 Hz, 0.5H, H-6), 4.07 (s, 1H, H-2), 4.04-4.03 (m , 2H, H-3, H-5), 3.85 (d, $J_{6,6}$ = 10.0 Hz, 1H, H-6), 3.66 (s, 1H, H-4), 2.74 (q, *J* = 7.2 Hz, 2H, CH_2), 1.32 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 137.9, 137.7, 128.5, 128.5, 128.2, 128.1, 128.0, 127.8, 83.6, 80.8, 79.2, 71.0, 70.6, 70.4, 69.6, 67.1, 26.5, 15.4; HRMS (ESI) Calcd for $C_{22}H_{26}NaO_4S$ $[M+Na]^+$: 409.1450, found: 409.1453.

3,4-Di-*O*-benzyl-2,6-anhydro-β-D-mannopyranosyl trichloroacetimidate (12)



To a solution of **S8** (78.7 mg, 196.4 μmol) in acetone (42.4 ml) and H_2O (4.7 ml) was added NBS (0.34 g, 1.88 mmol) at room temperature and the mixture was stirred for 1 hr. After the TLC analysis showed the completion of reaction, the reaction was quenched by 10% $Na_2S_2O_3$ aq. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Under Ar atmosphere, to a solution of the crude product and CCl_3CN (0.94 ml, 9.42 mmol) in anhydrous CH_2Cl_2 (9.4 ml) was added Cs_2CO_3 (83.1 mg, 235.6 μmol) at room temperature. After the TLC analysis showed the completion of reaction, the reaction mixture was filtrated through Celite pad. The filtrate was concentrated *in vacuo*. The residue was purified by open column chromatography (20 g, Hexane/EtOAc = 3/1), which gave the title compound **12** (84.5 mg, 18% in 2 steps) as colorless oil. R_f = 0.38 (Hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = +43.2 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.56 (s, 1H, -NH), 7.37-7.31 (m, 10H, Ar-H), 6.17 (s, 1H, H-1), 4.69 & 4.58 (ABq, *J* = 11.8 Hz, 2H, $PhCH_2$), 4.66 & 4.55 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.31 (s, 1H, H-2), 4.23 (s, 1H, H-5), 3.91-3.89 (m, 1H, H-6), 3.82 (s, 1H, H-4), 3.79 (s, 1H, H-3), 3.34 (s, 3H, -OMe), 3.24-3.20 (m, 1H, H-4); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 161.1, 137.5, 137.4, 128.7, 128.6, 128.6, 128.1, 128.1, 97.5, 80.9, 80.1, 71.1, 70.9, 69.9, 68.0, 67.0; HRMS (ESI) Calcd for $C_{22}H_{22}Cl_3NNaO_5$ $[M+Na]^+$: 508.0461, found: 508.0475. The NOE correlation observed between δ 6.17 and δ 3.79 confirmed the stereochemistry at C-1 to be β.

References

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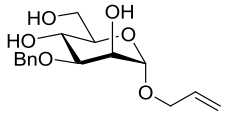
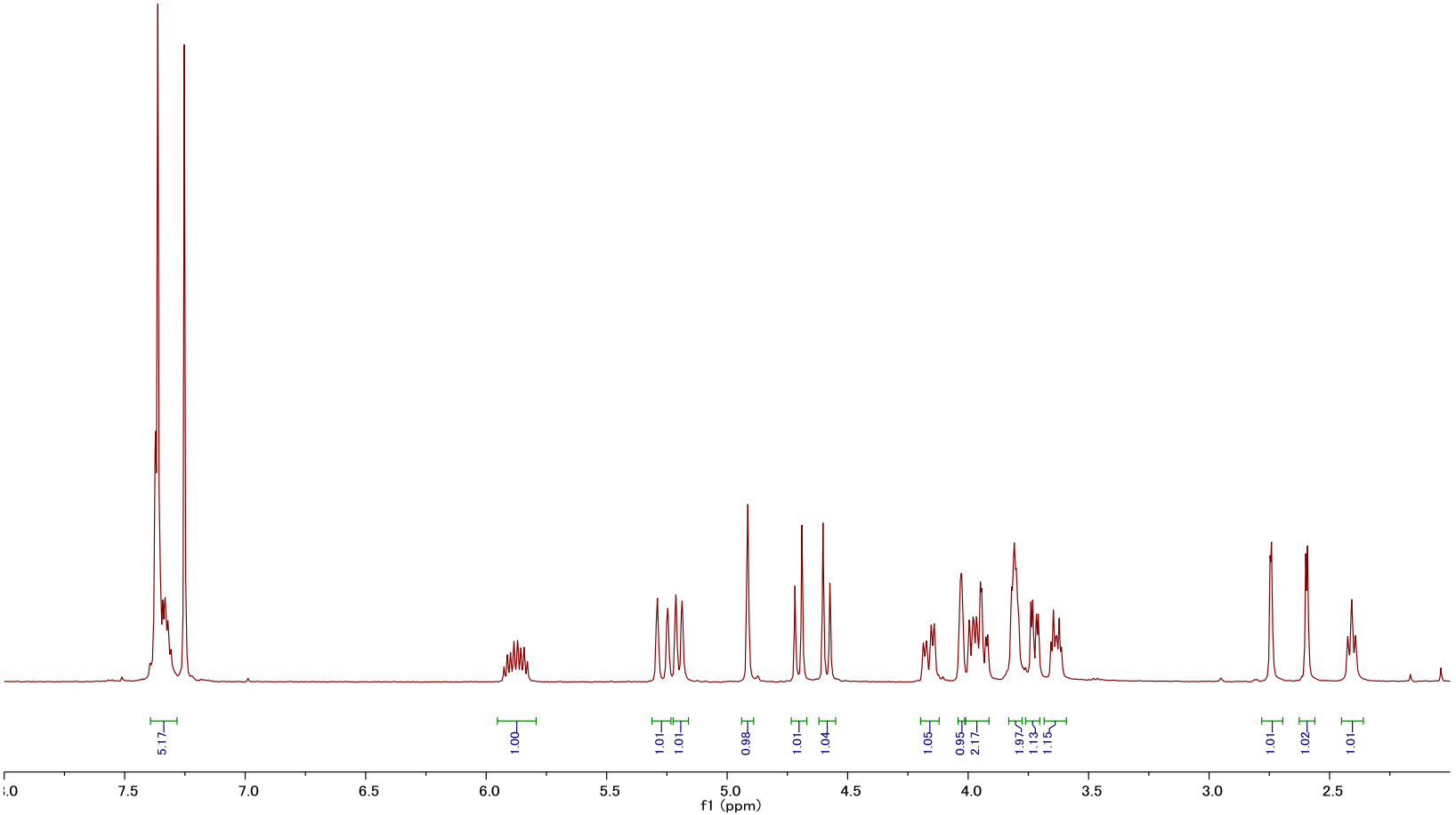
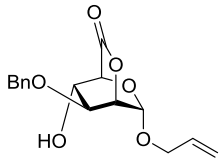
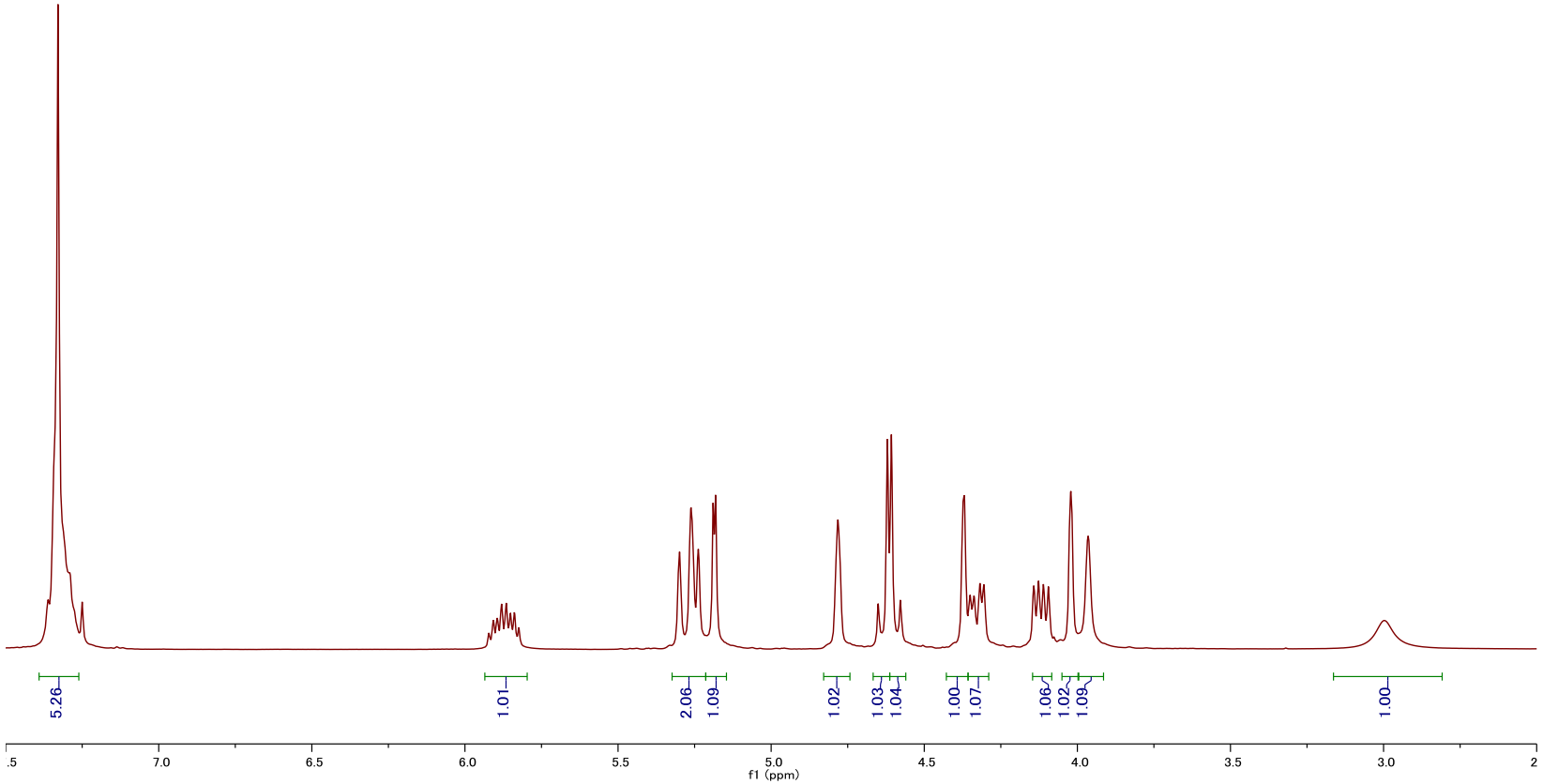
Allyl 3-*O*-benzyl-α-D-mannopyranoside (2) [2] ^{1}H NMR (400 MHz, $CDCl_3$)



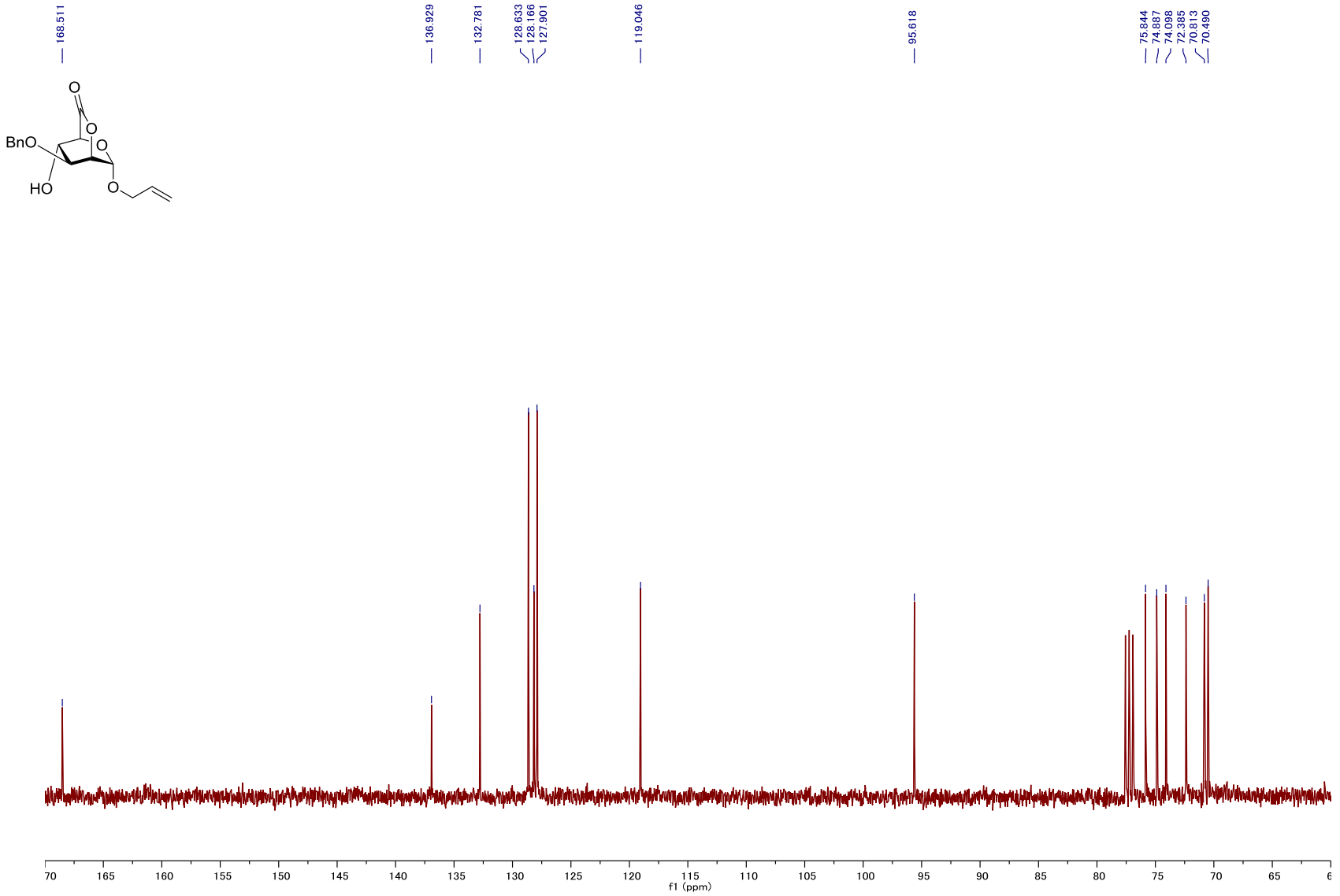


Allyl 3-*O*-benzyl-α-D-mannopyranurono-2,6-lactone (3) ^{1}H NMR (400 MHz, $CDCl_3$)

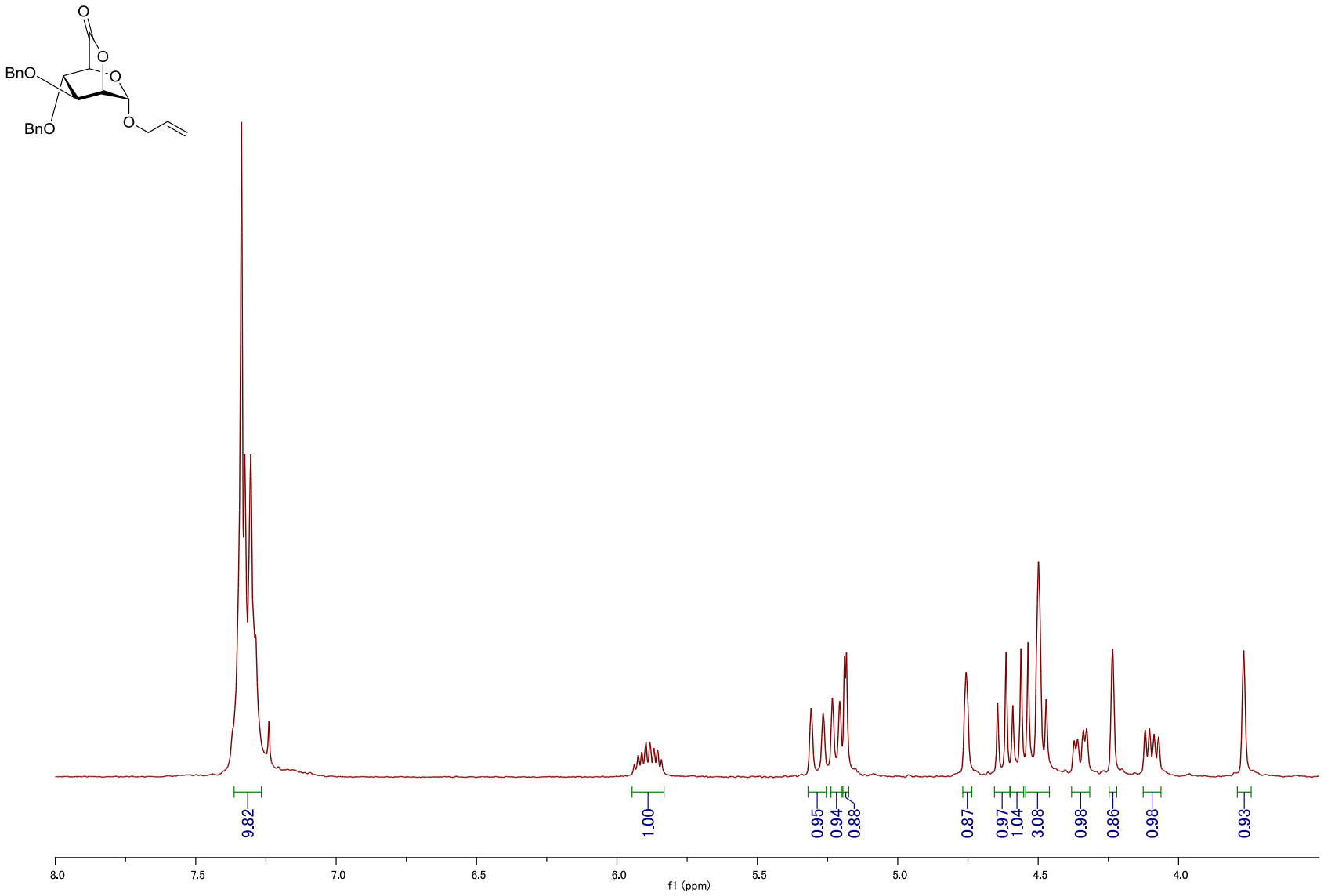




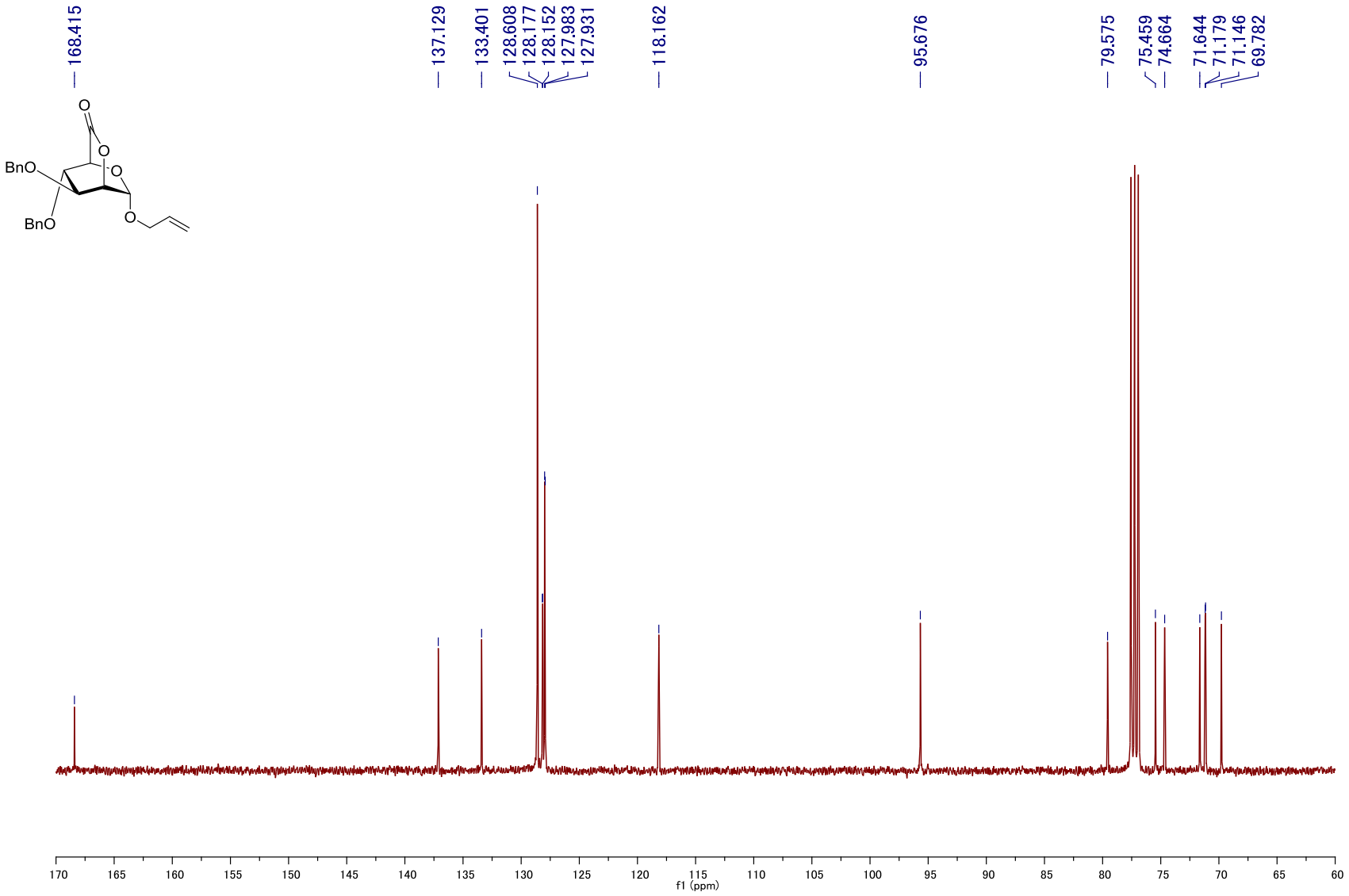
Allyl 3-*O*-benzyl-α-D-mannopyranurono-2,6-lactone (3) ^{13}C NMR (100 MHz, $CDCl_3$)



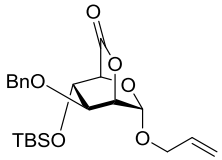
Allyl 3,4-di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton (4a) ^{1}H NMR (400 MHz, $CDCl_3$)

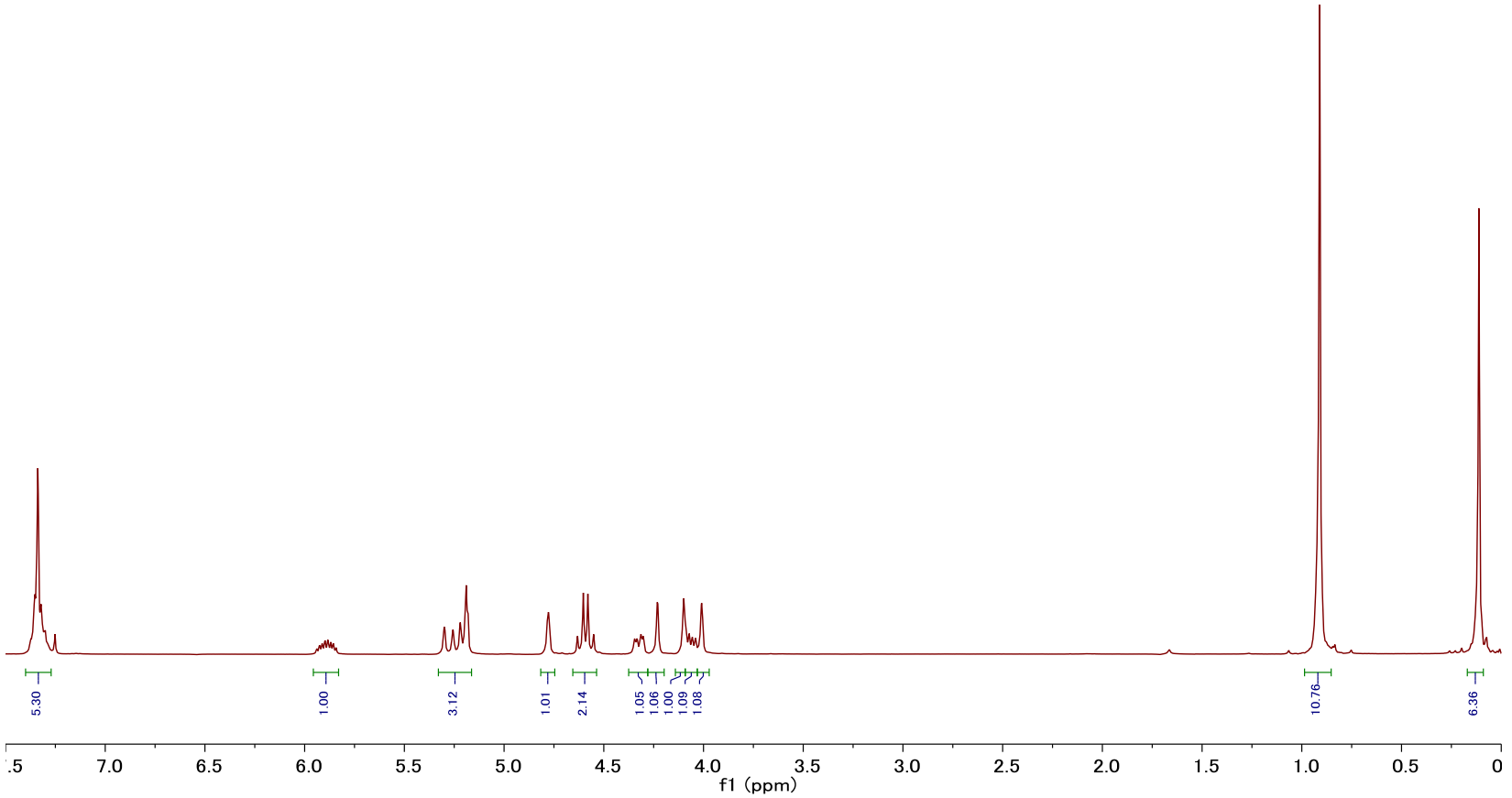


Allyl 3,4-di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton (4a) ^{13}C NMR (100 MHz, $CDCl_3$)

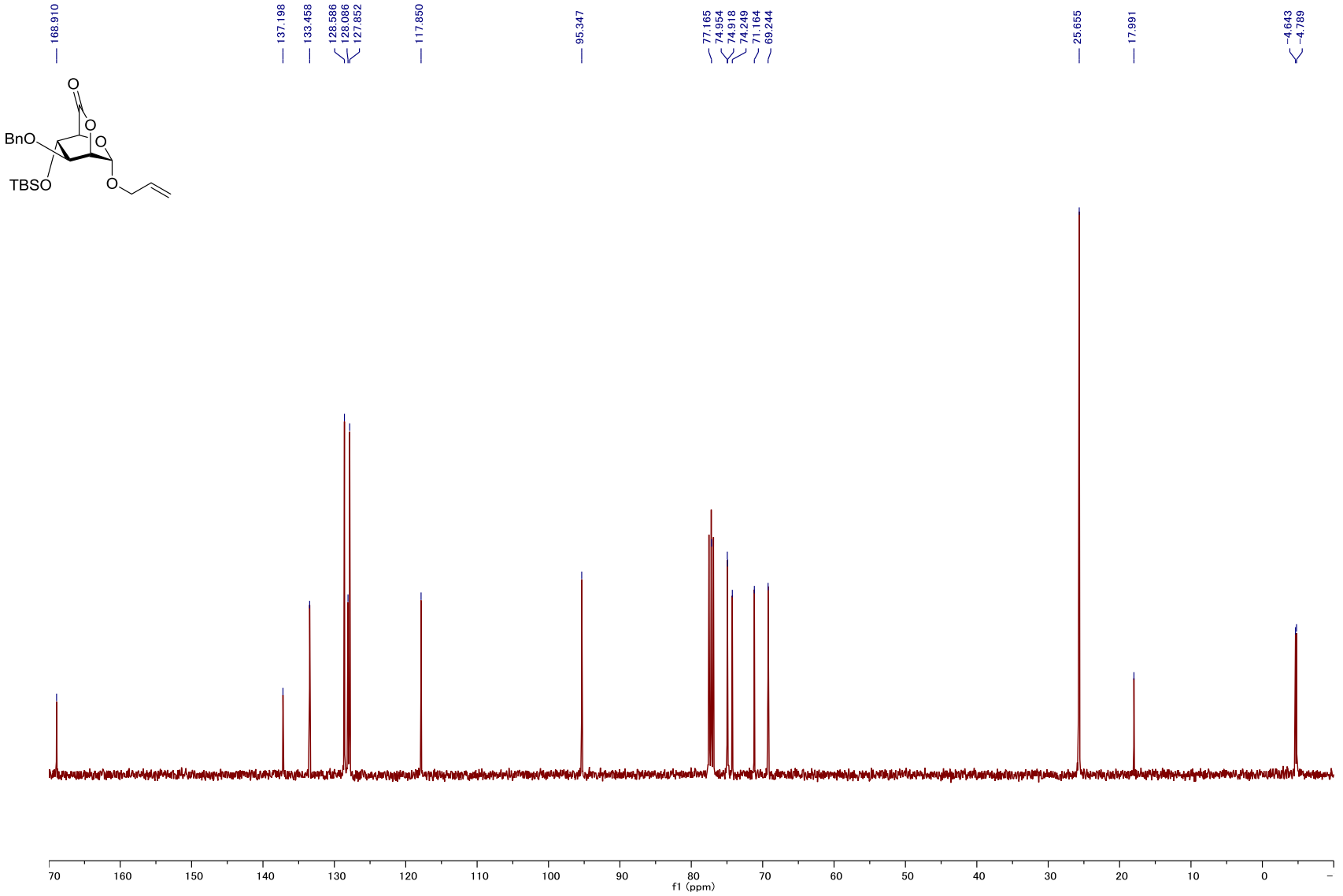


Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2,6-lactone (4b) ^{1}H NMR (400 MHz, $CDCl_3$)

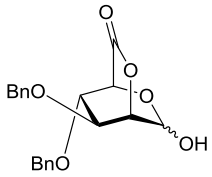


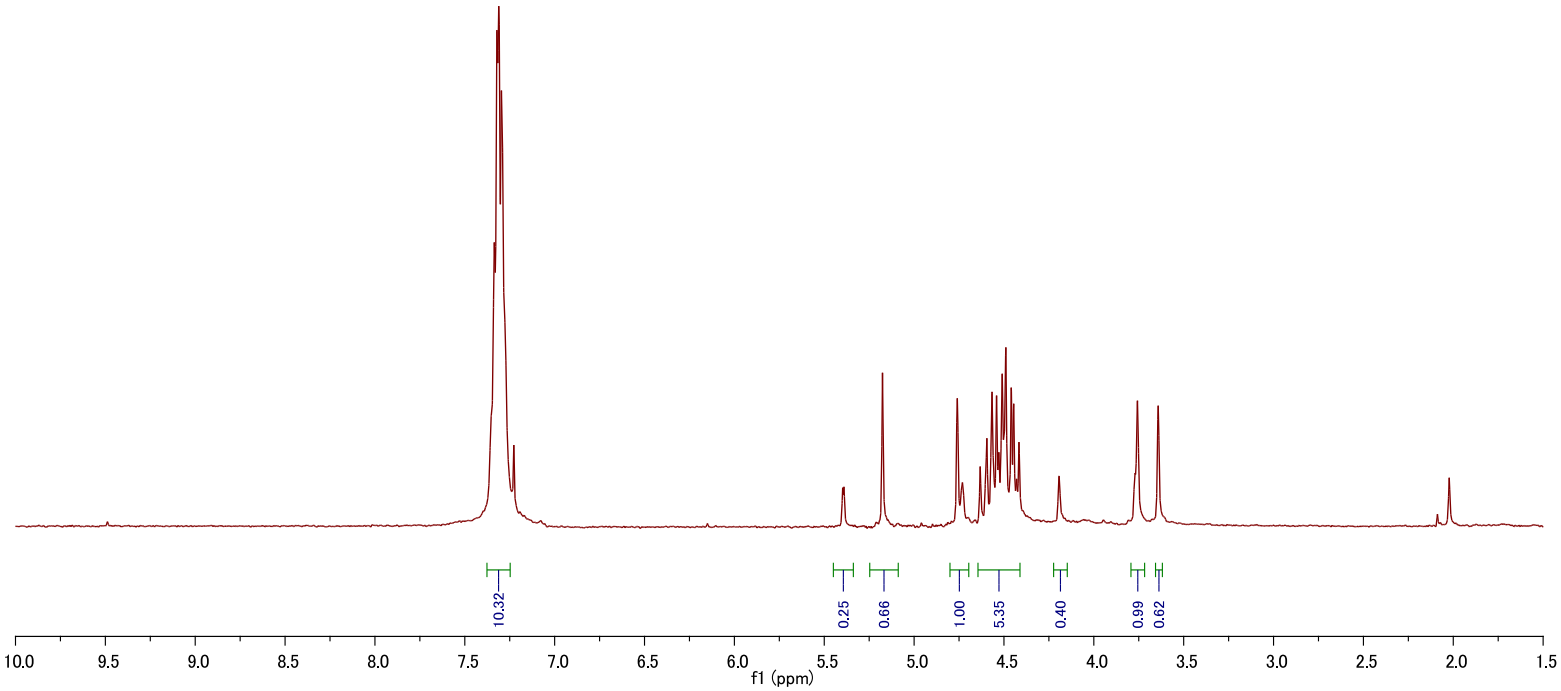


Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2,6-lactone (4b) ^{13}C NMR (100 MHz, $CDCl_3$)

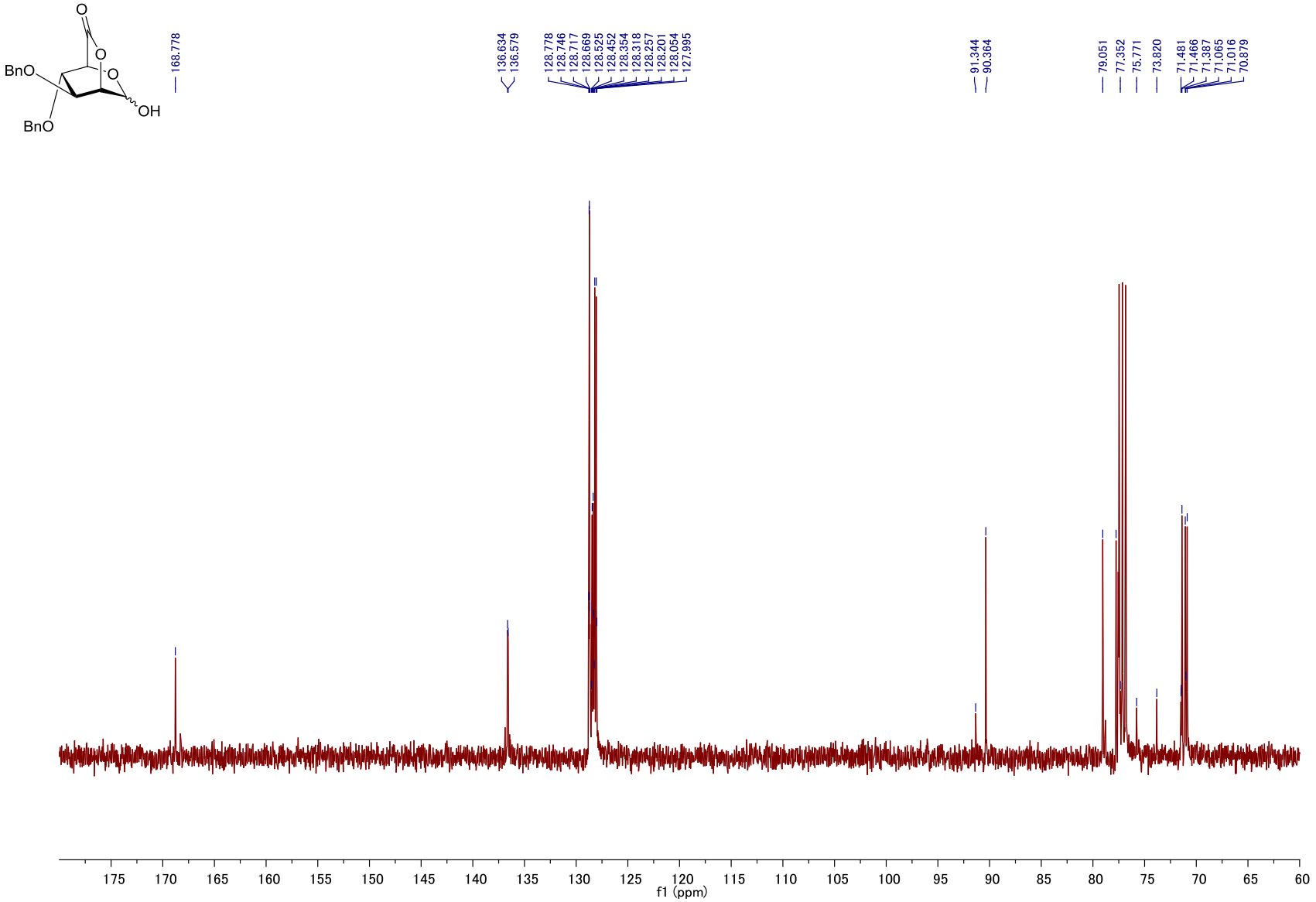


3,4-Di-*O*-benzyl-D-mannopyranurono-2,6-lactone (S1) ^{1}H NMR (400 MHz, $CDCl_3$)

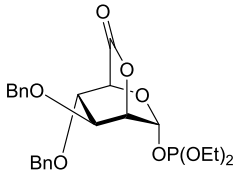


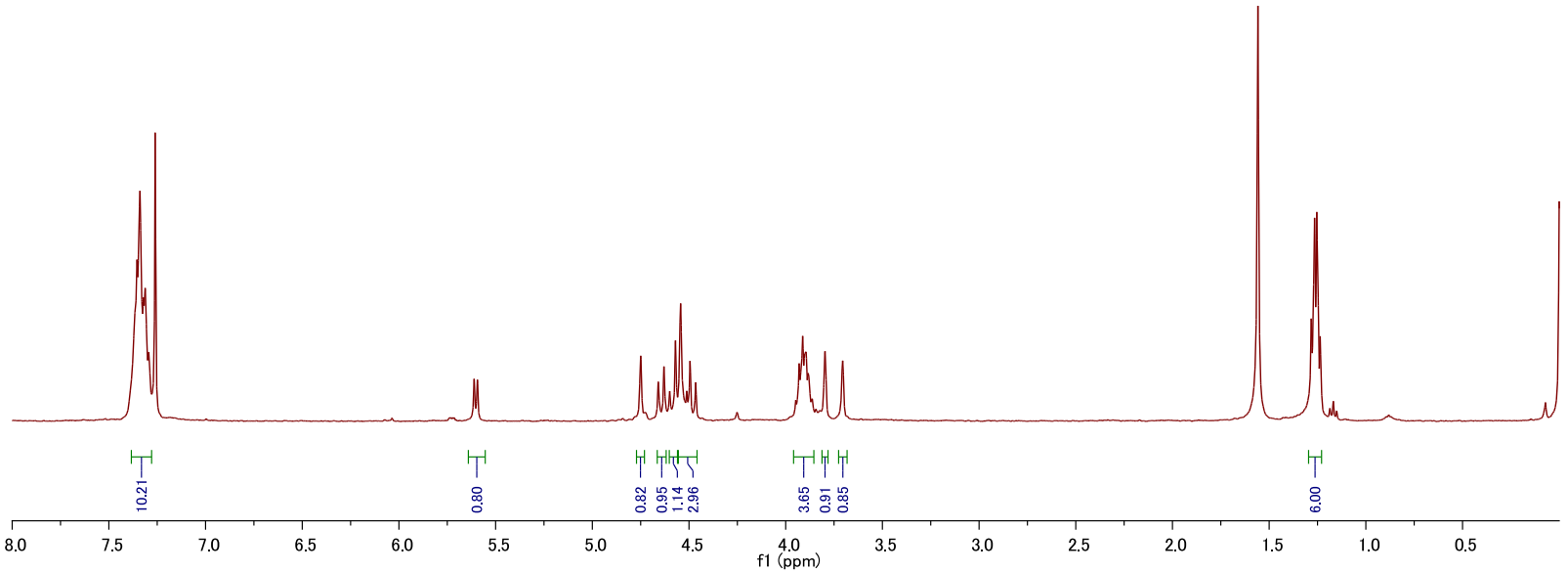


3,4-Di-*O*-benzyl-D-mannopyranurono-2,6-lactone (S1) ^{13}C NMR (100 MHz, $CDCl_3$)

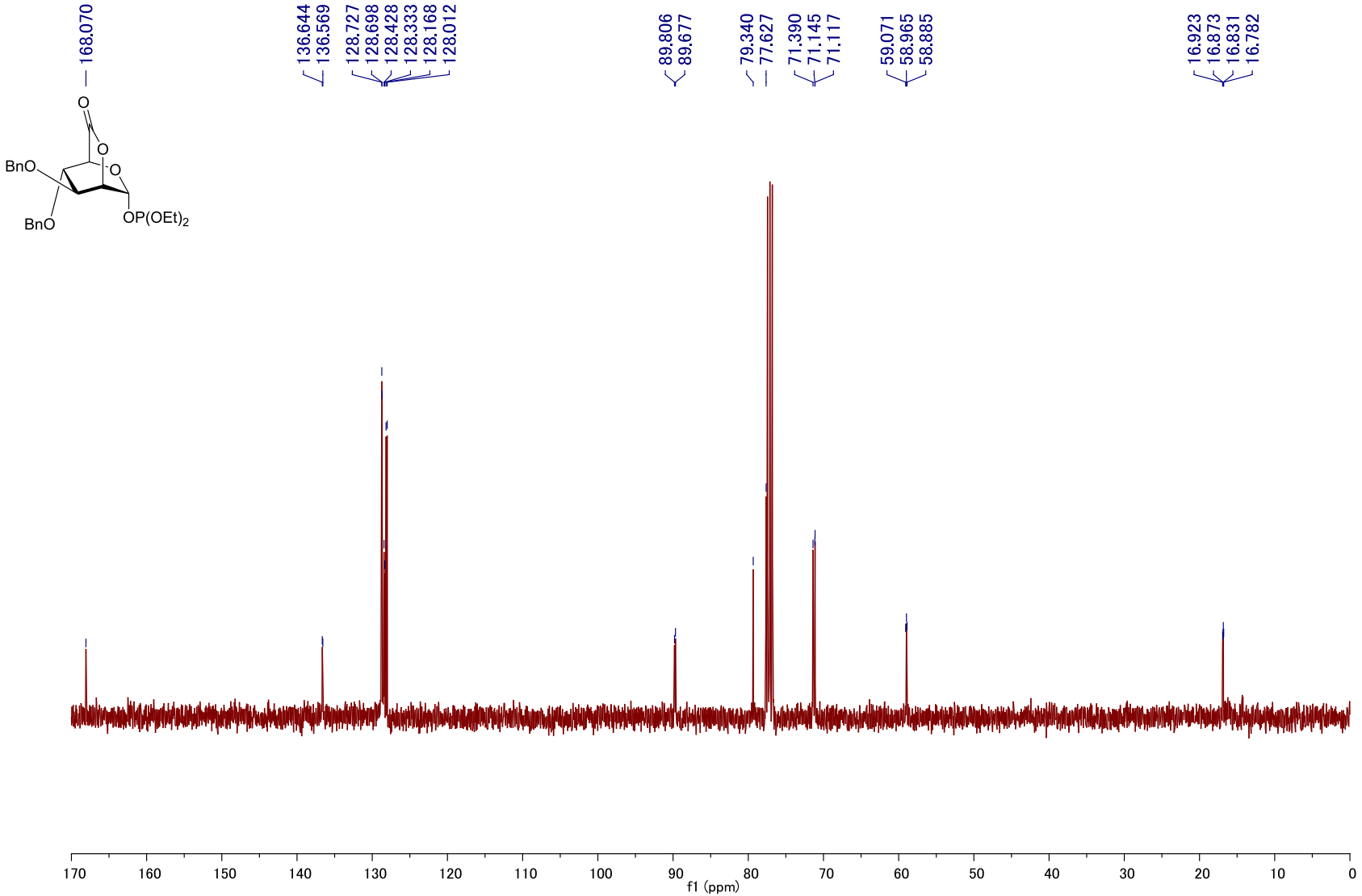


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diethylphosphite (5a) ^{1}H NMR (400 MHz, $CDCl_3$)

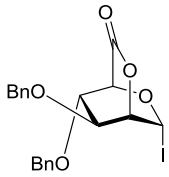


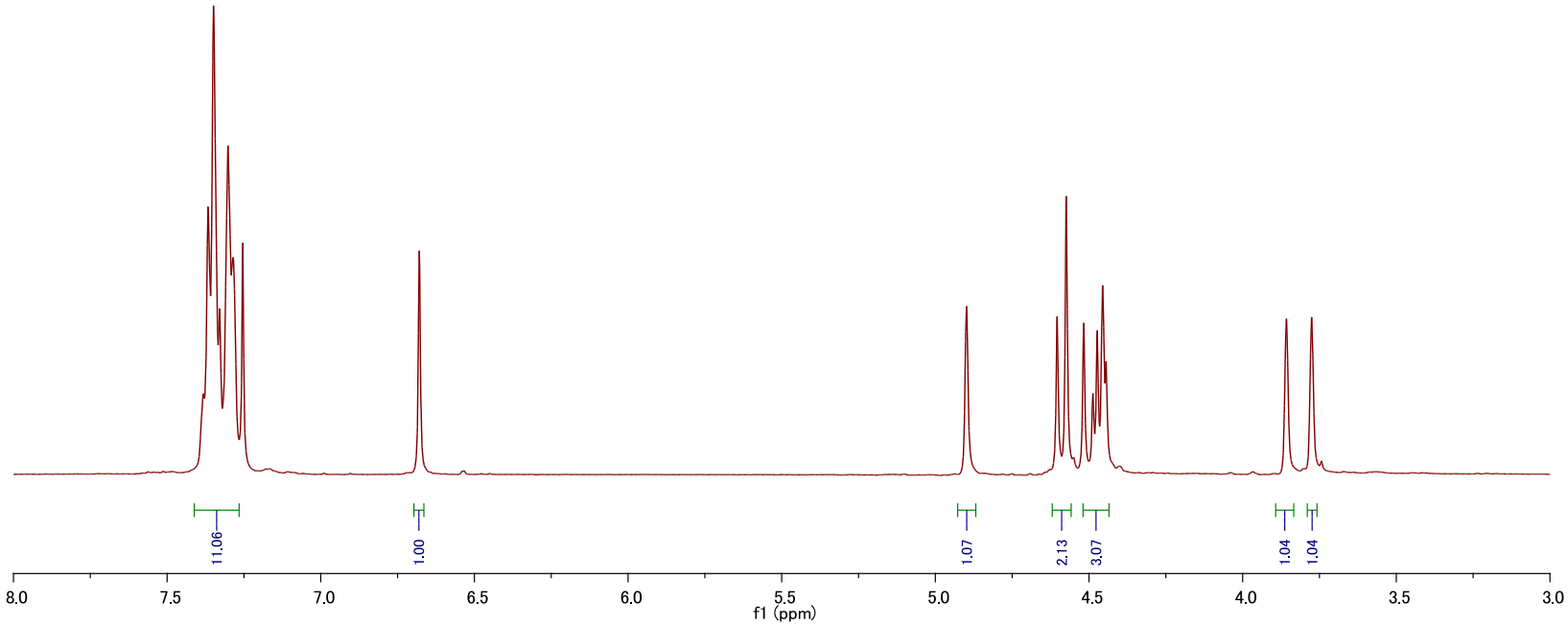


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diethylphosphite (5a) ^{13}C NMR (100 MHz, $CDCl_3$)

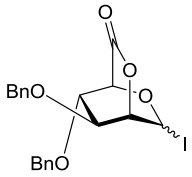


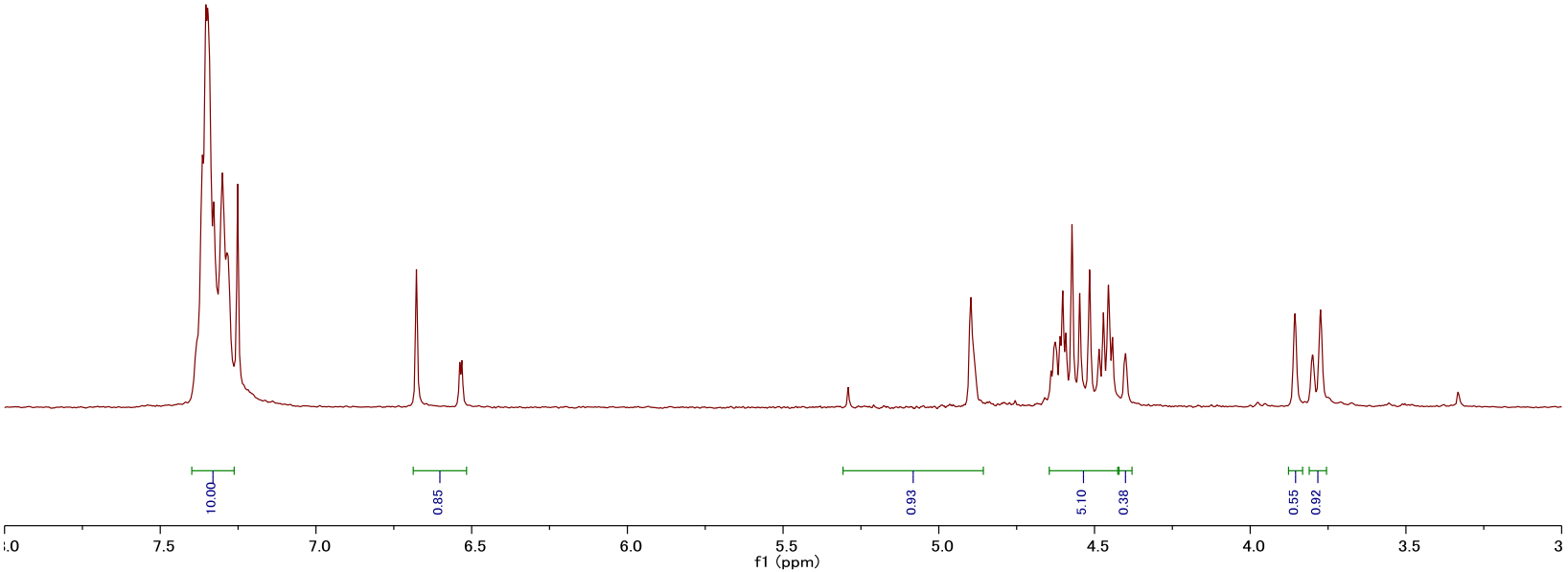
3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl iodide (5bα) ^{1}H NMR (400 MHz, $CDCl_3$)



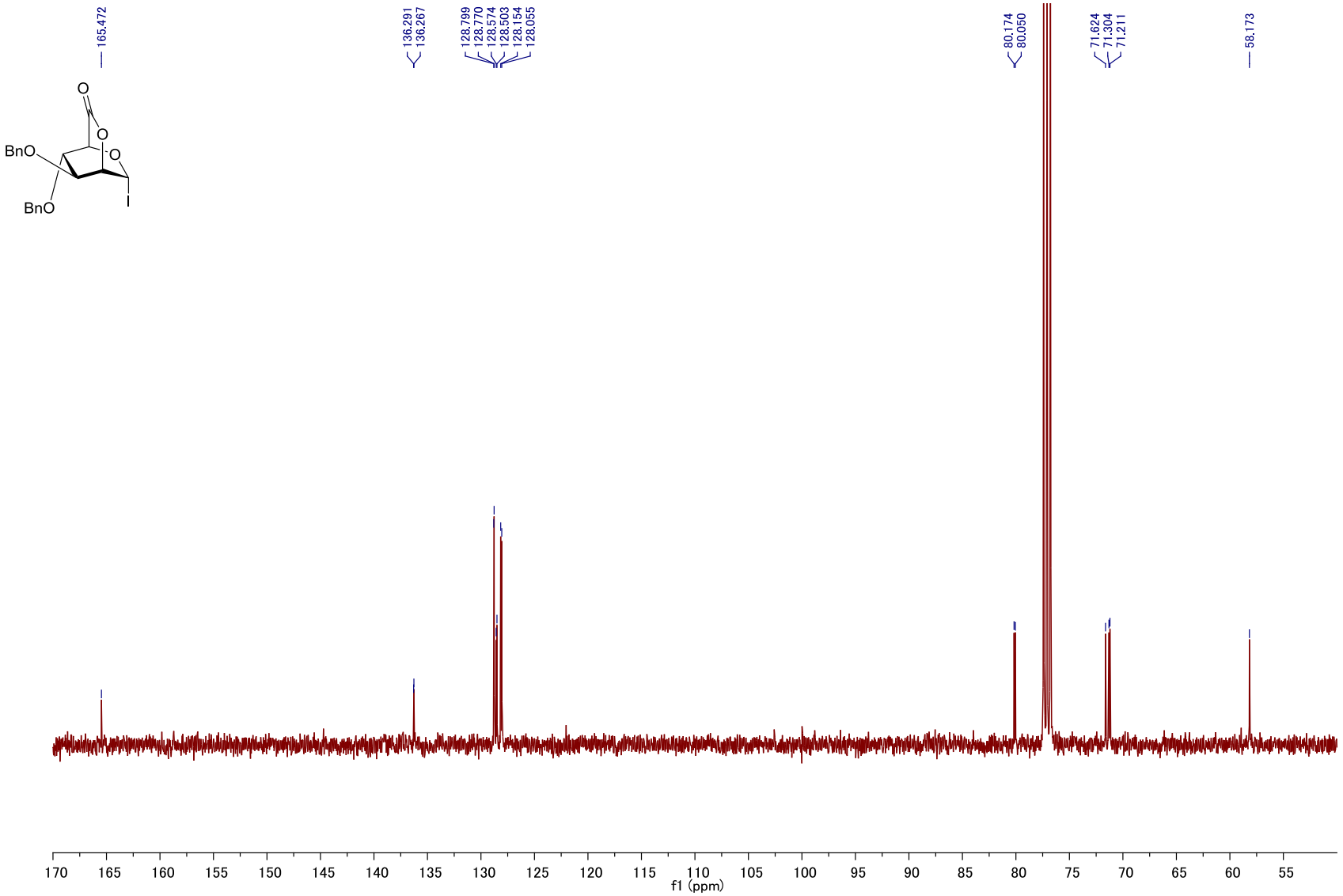


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl iodide (5bαβ) ^{1}H NMR (400 MHz, $CDCl_3$)

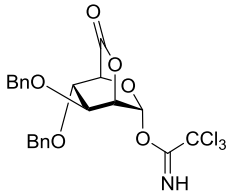


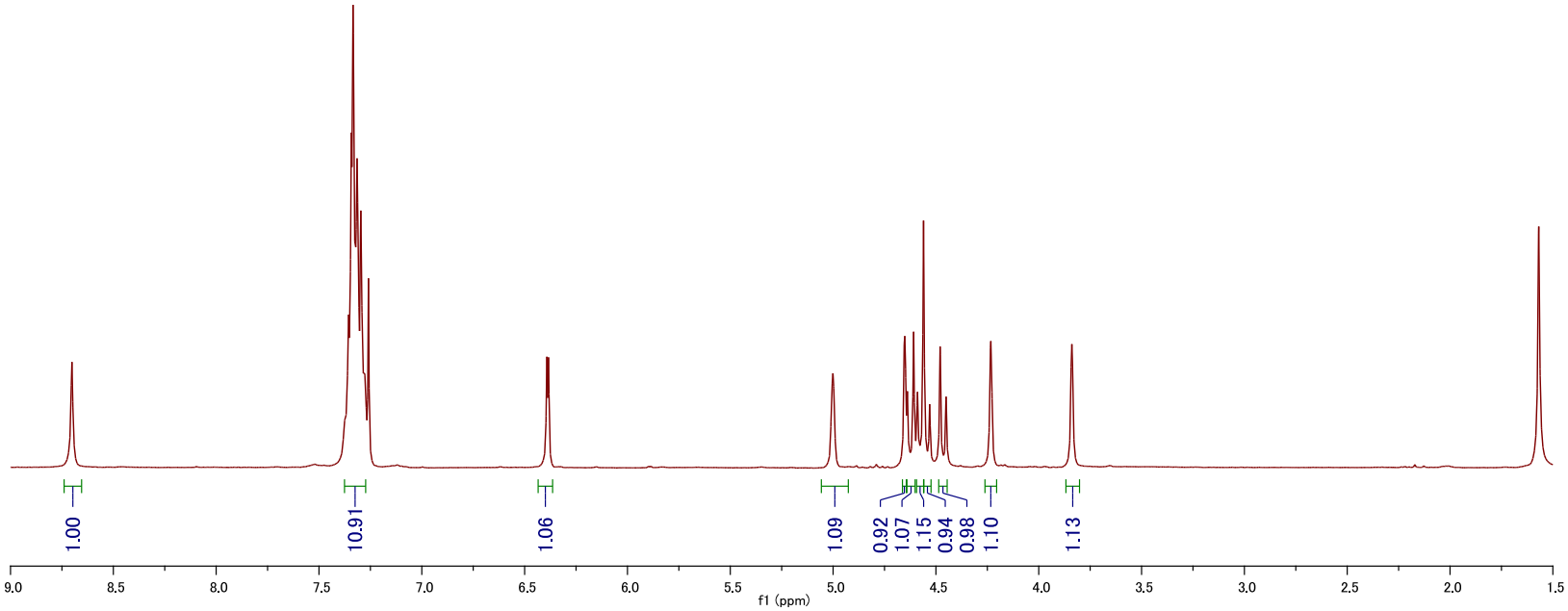


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl iodide (5b) ^{13}C NMR (100 MHz, $CDCl_3$)

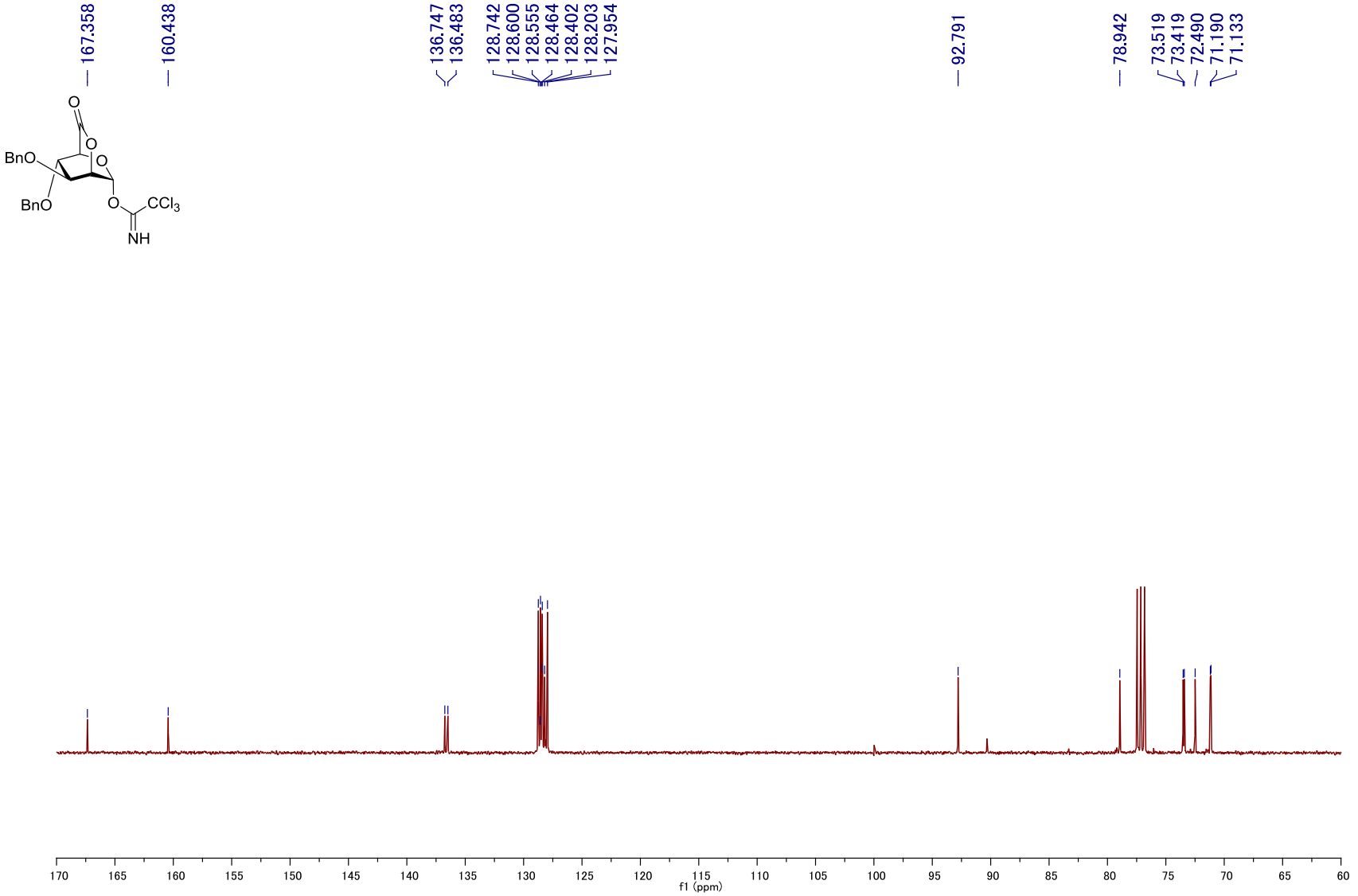


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5cα) ^{1}H NMR (400 MHz, $CDCl_3$)

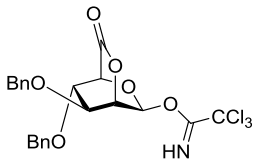


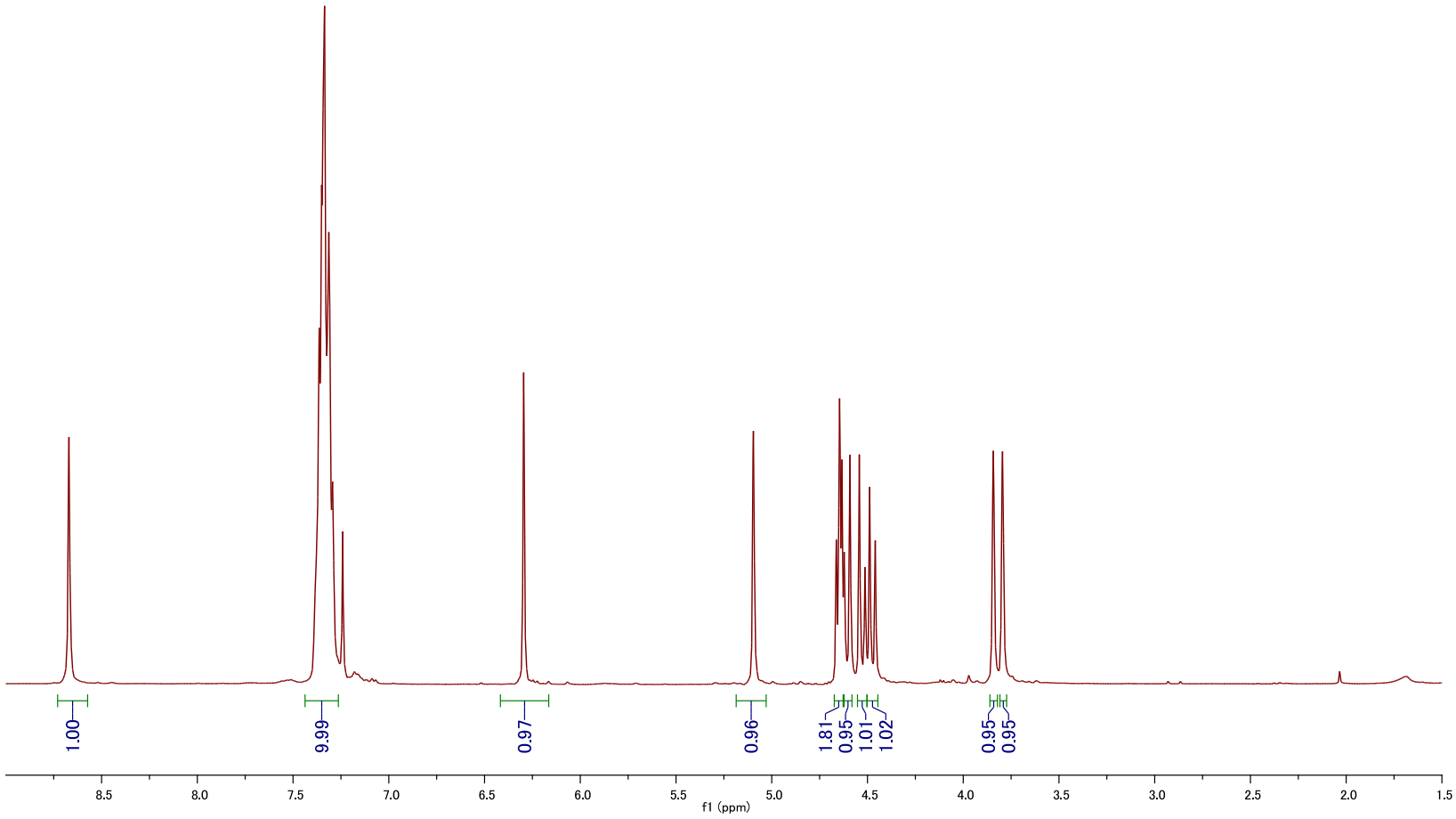


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5cα) ^{13}C NMR (100 MHz, $CDCl_3$)

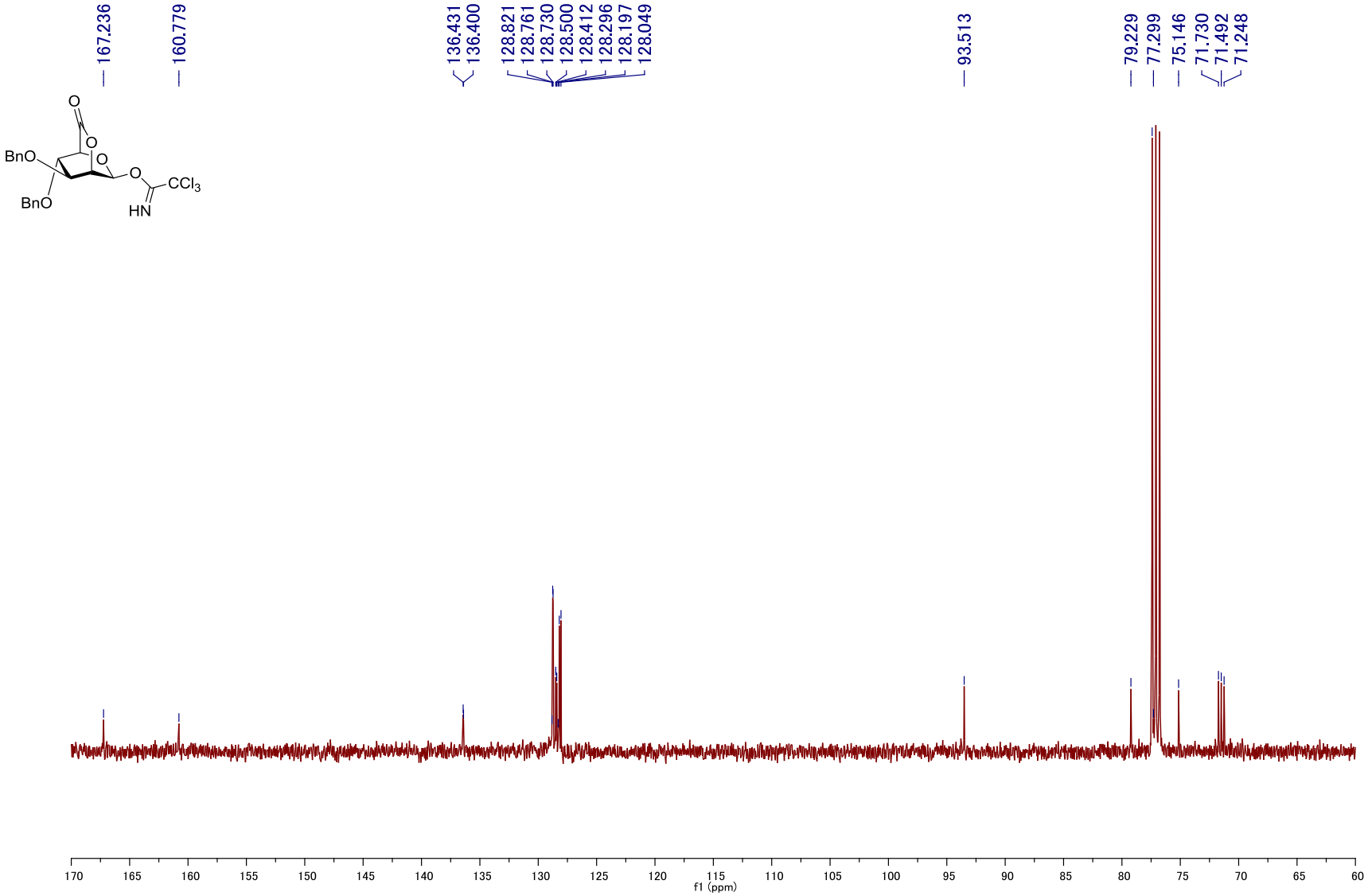


3,4-Di-*O*-benzyl-β-D-mannopyranurono-2,6-lactone-1-yl trichloroacetimidate (5cβ) ^{1}H NMR (400 MHz, $CDCl_3$)

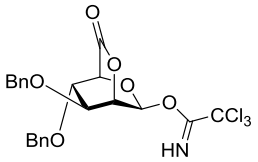


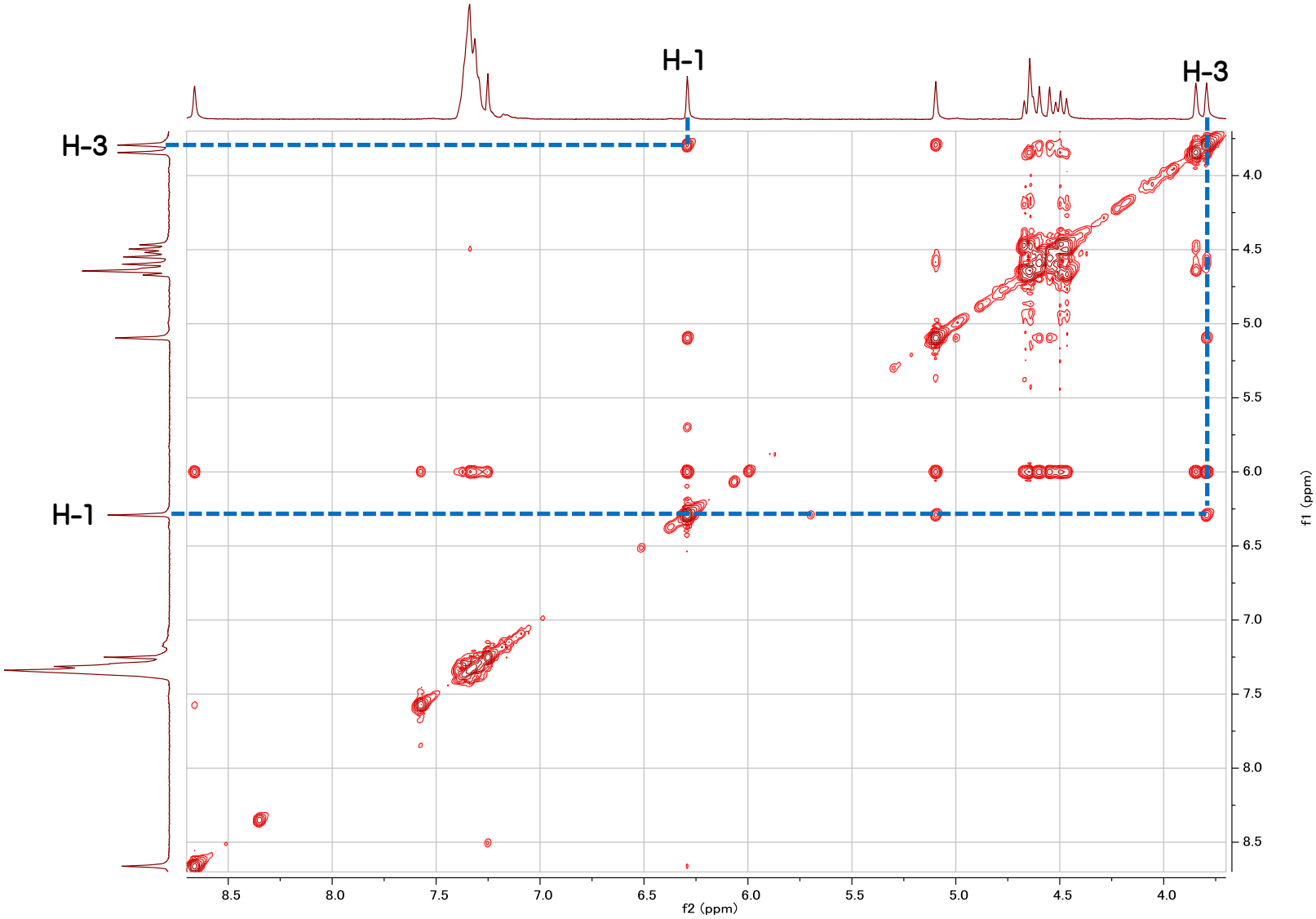


3,4-Di-*O*-benzyl-β-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5cα) ^{13}C NMR (100 MHz, $CDCl_3$)

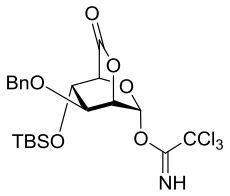


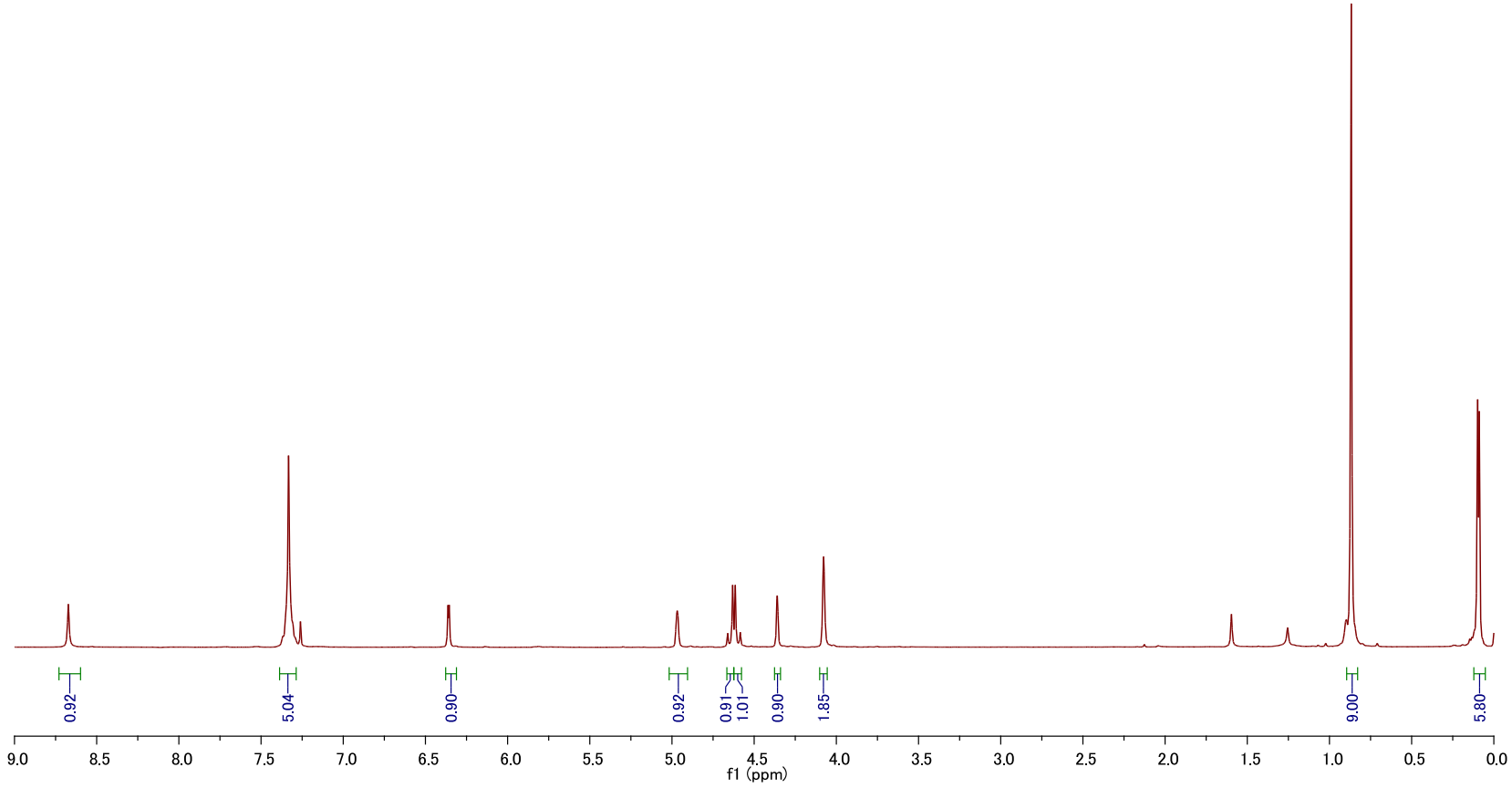
3,4-Di-*O*-benzyl-β-D-mannopyranurono-2,6-lactone-1-yl trichloroacetimidate (5cβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)



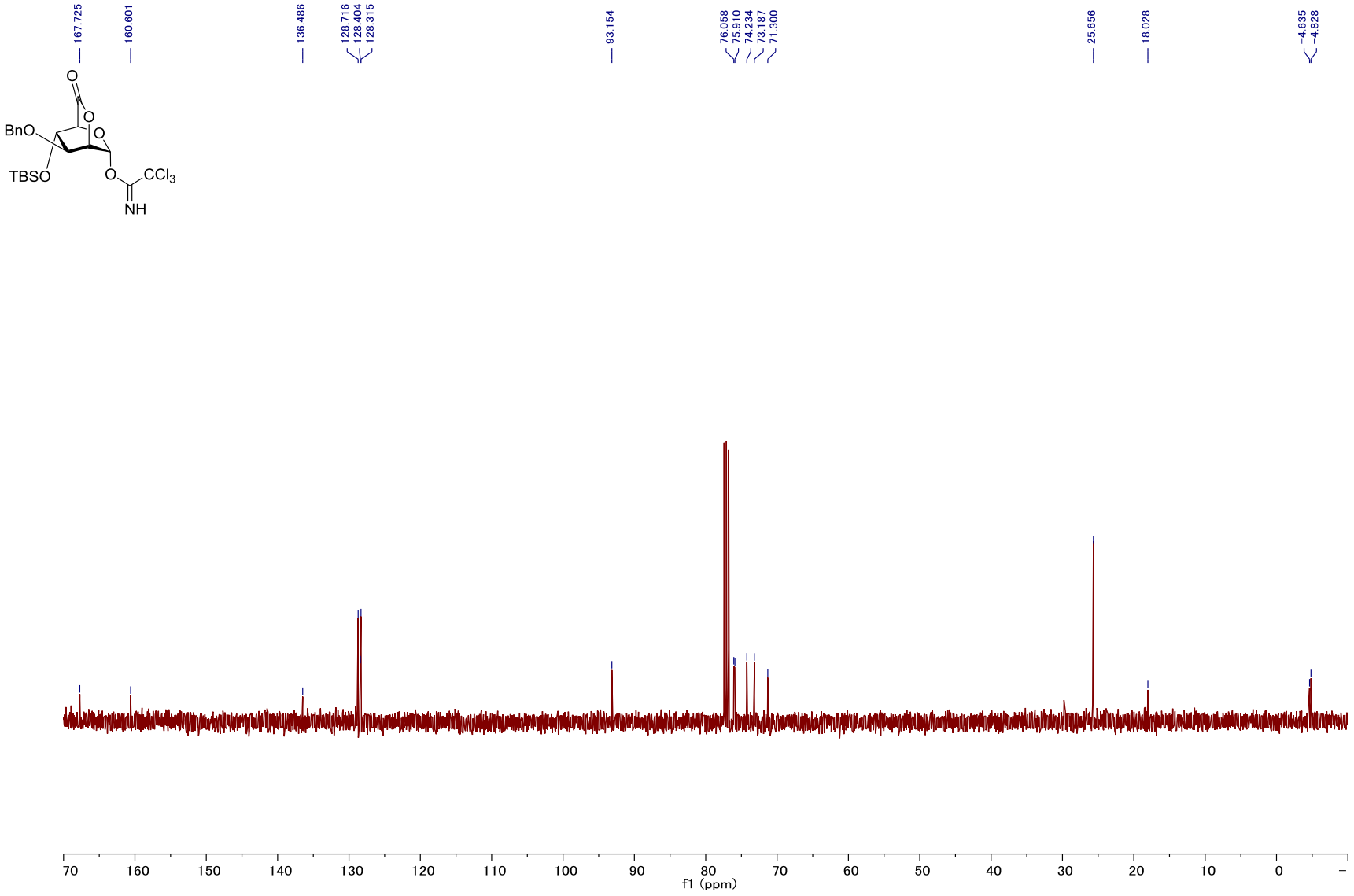


3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5dα) ^{1}H NMR (400 MHz, $CDCl_3$)

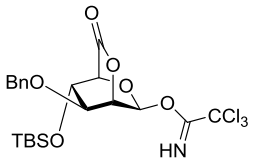


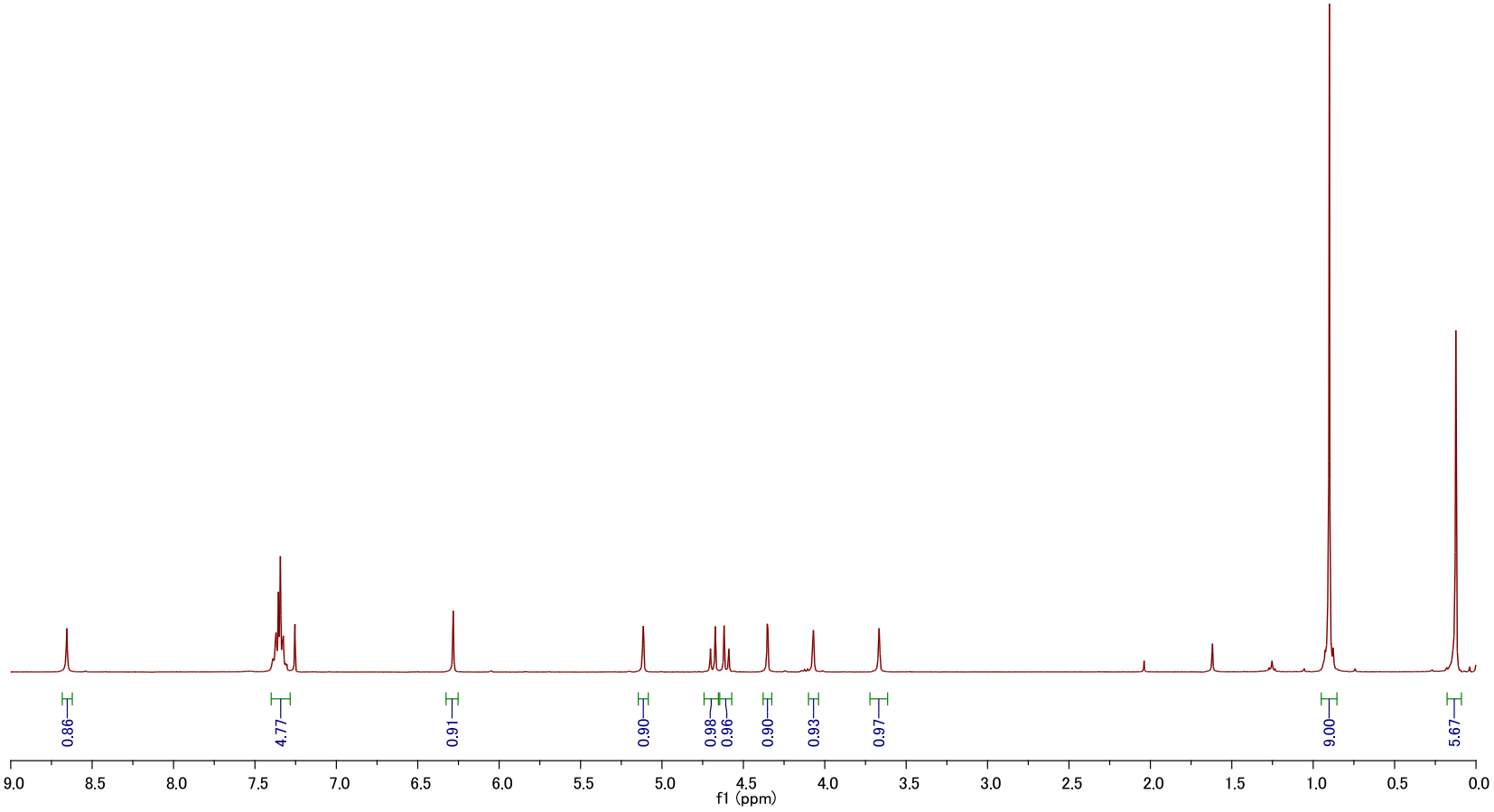


3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5dα) ^{13}C NMR (100 MHz, $CDCl_3$)

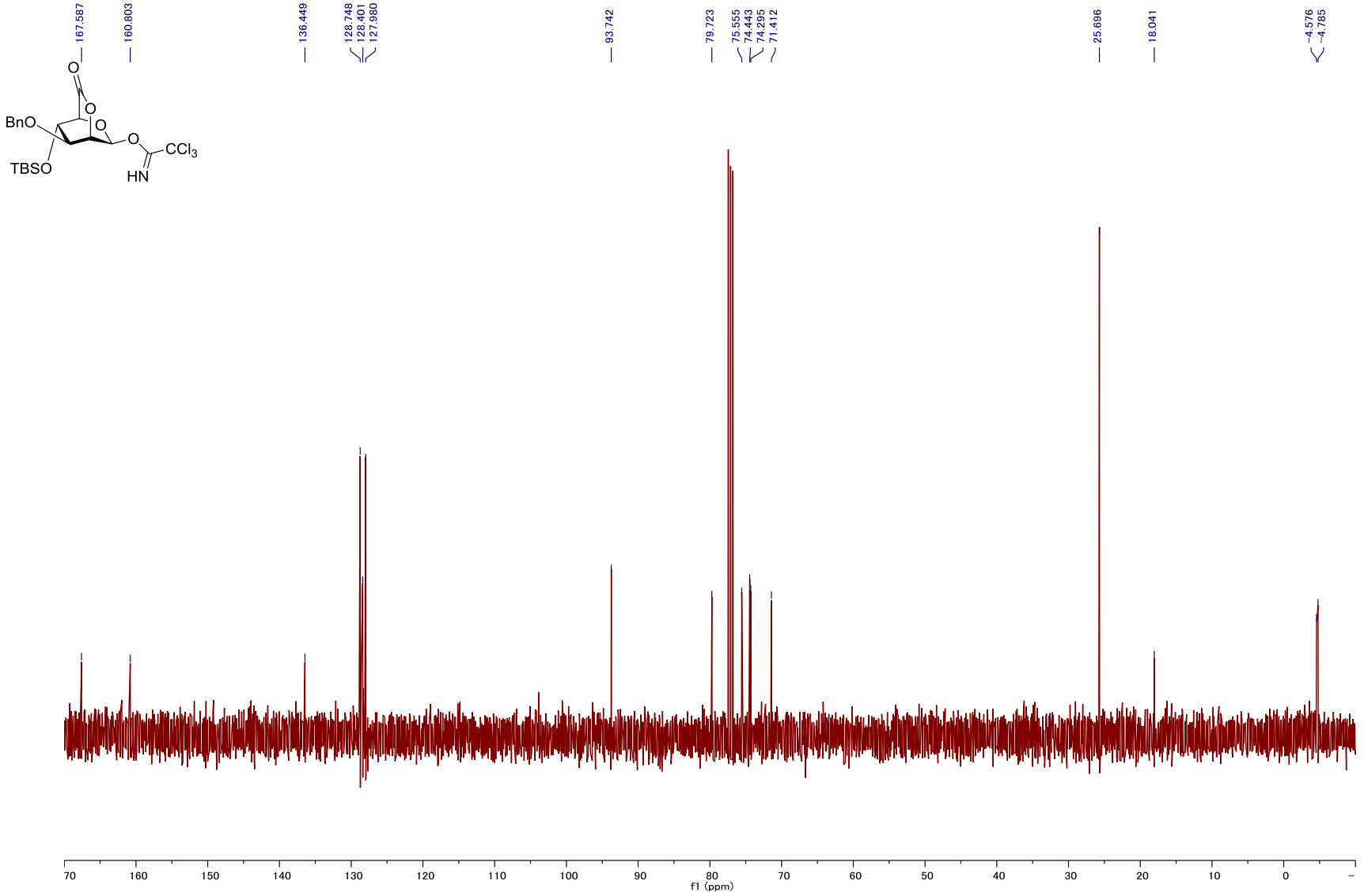


3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5dβ) ^{1}H NMR (400 MHz, $CDCl_3$)

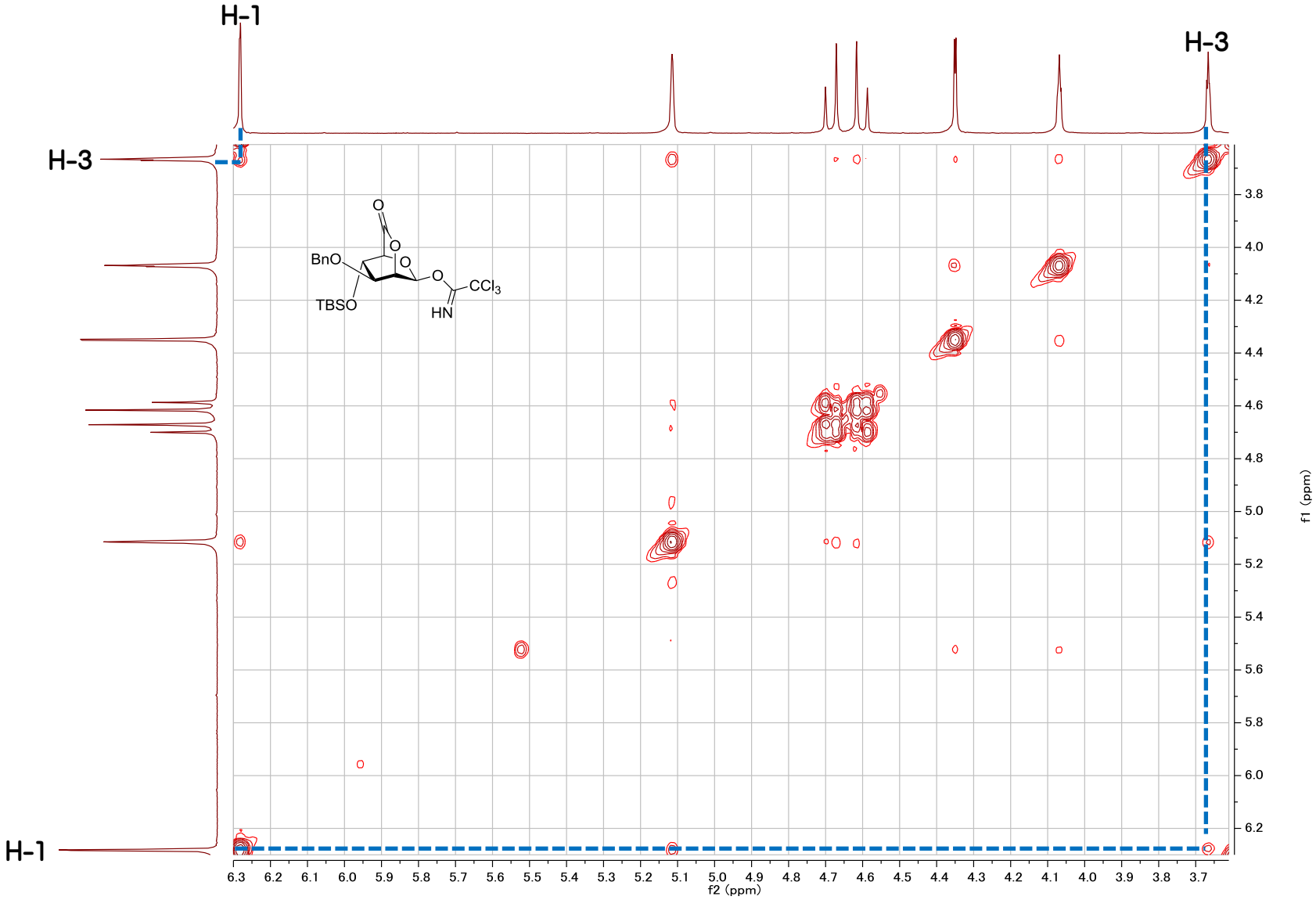




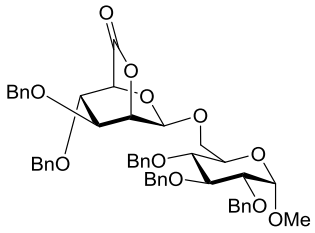
3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5dβ) ^{13}C NMR (100 MHz, $CDCl_3$)

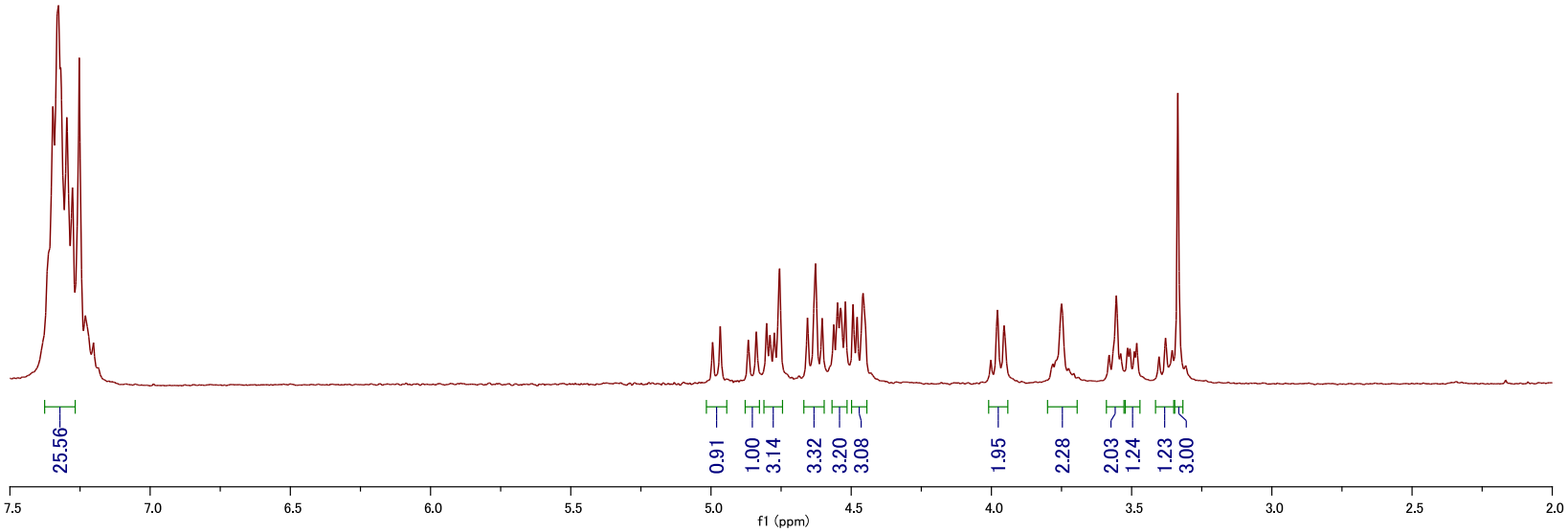


3-*O*-Benzyl-4-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2,6-lactone-1-yl-trichloroacetimidate (5dβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)

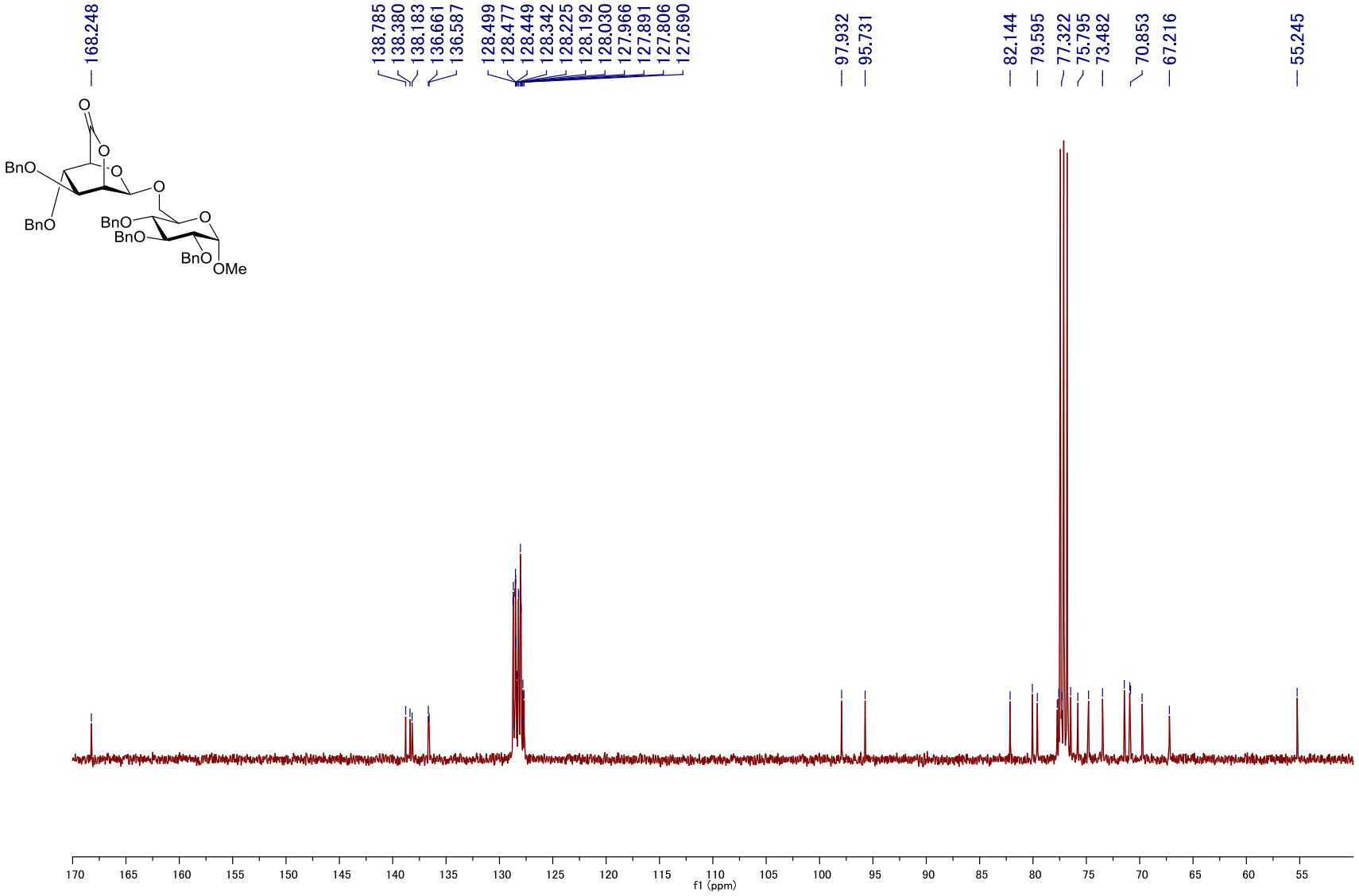


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aβ) ^{1}H NMR (400 MHz, $CDCl_3$)

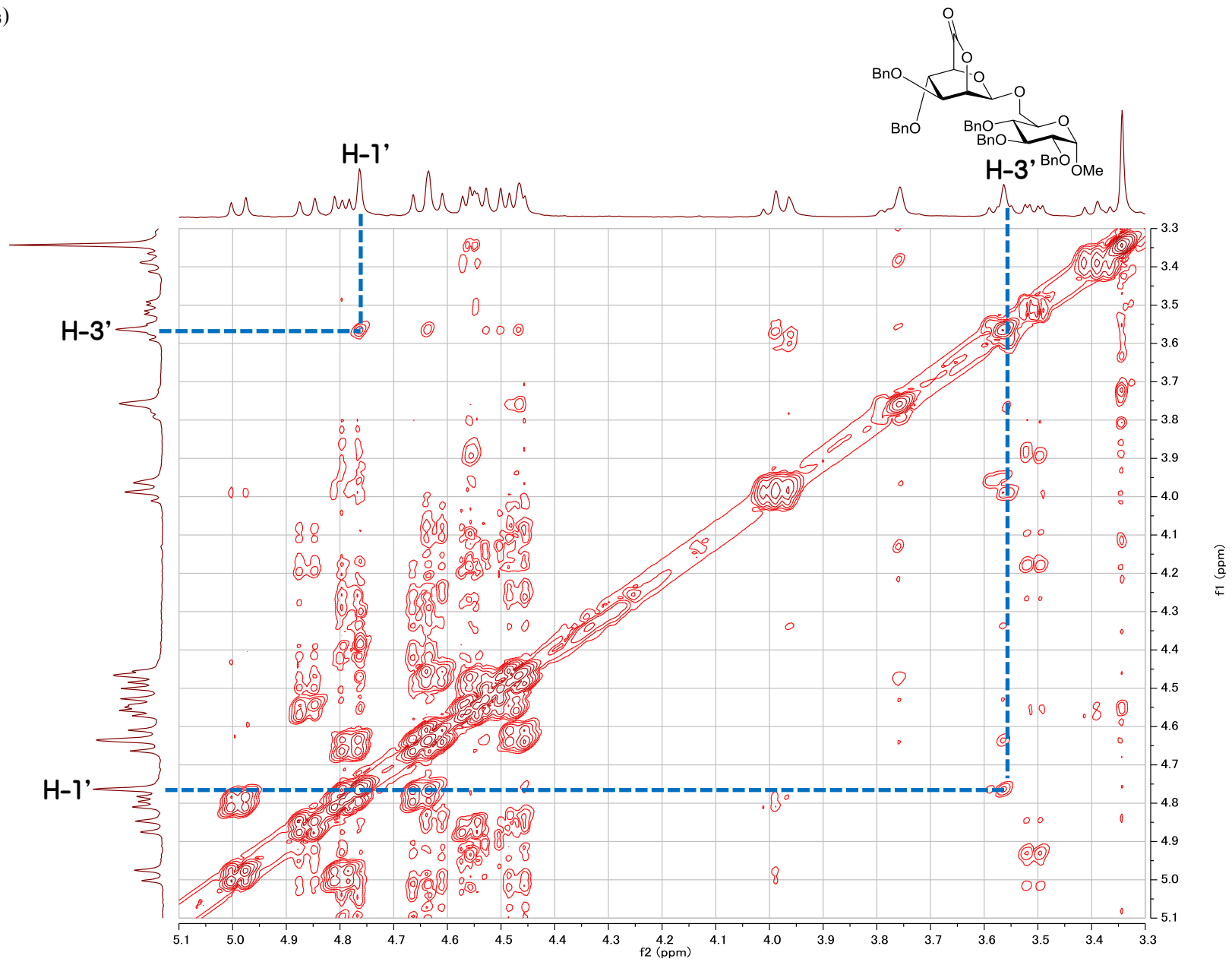




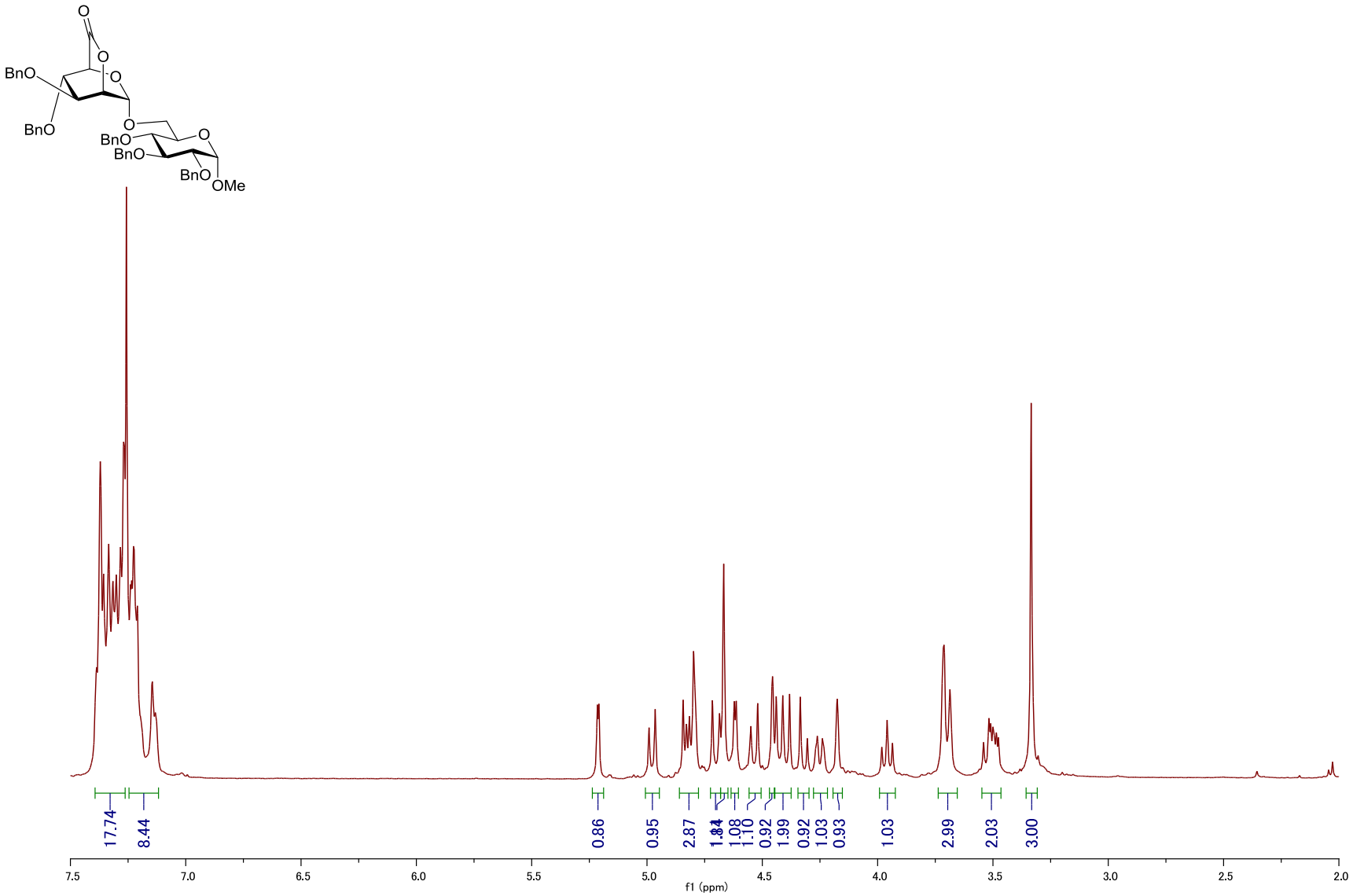
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aβ) ^{13}C NMR (100 MHz, $CDCl_3$)



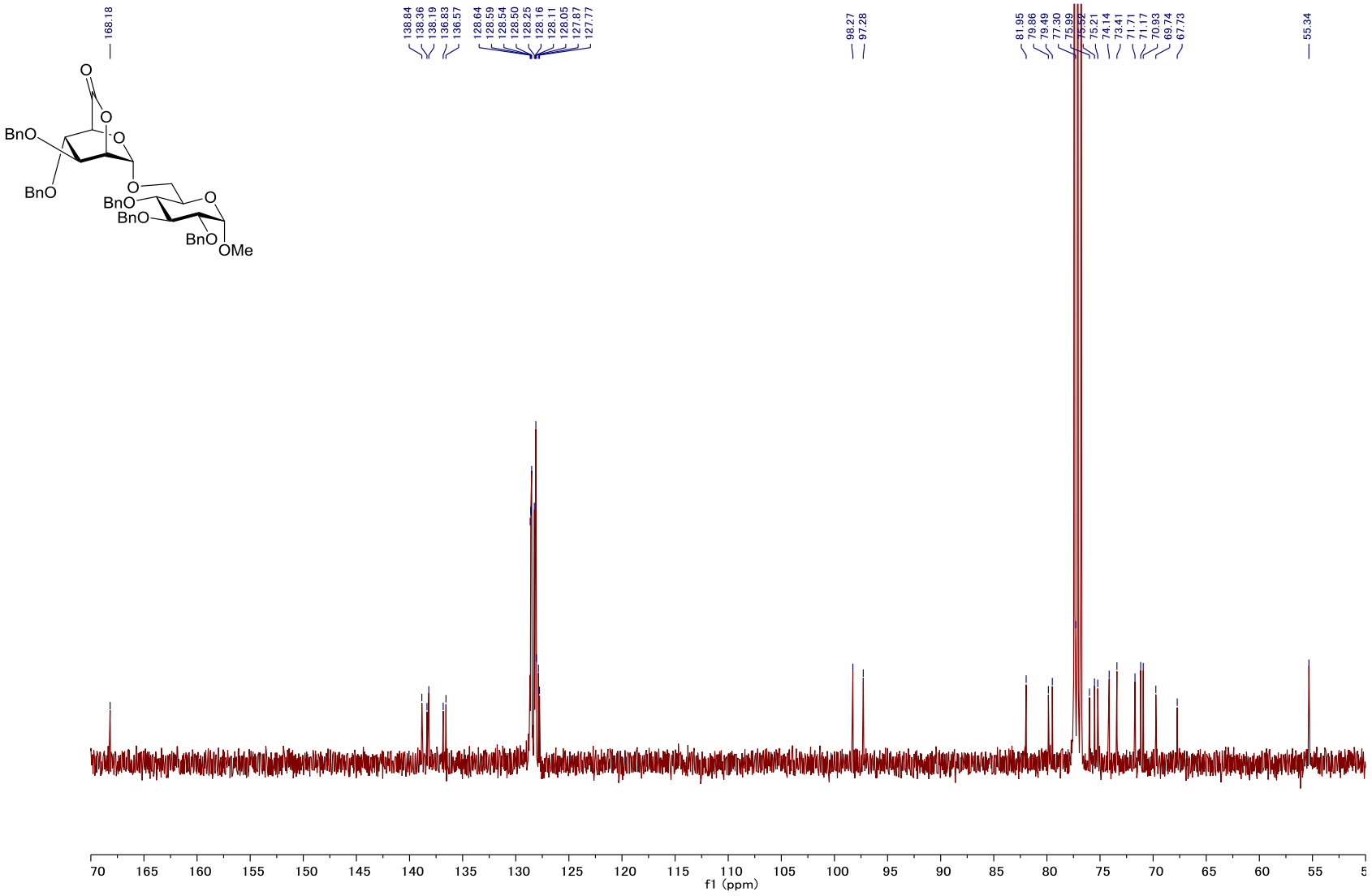
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)



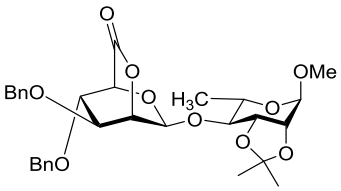
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aα) ^{1}H NMR (400 MHz, $CDCl_3$)

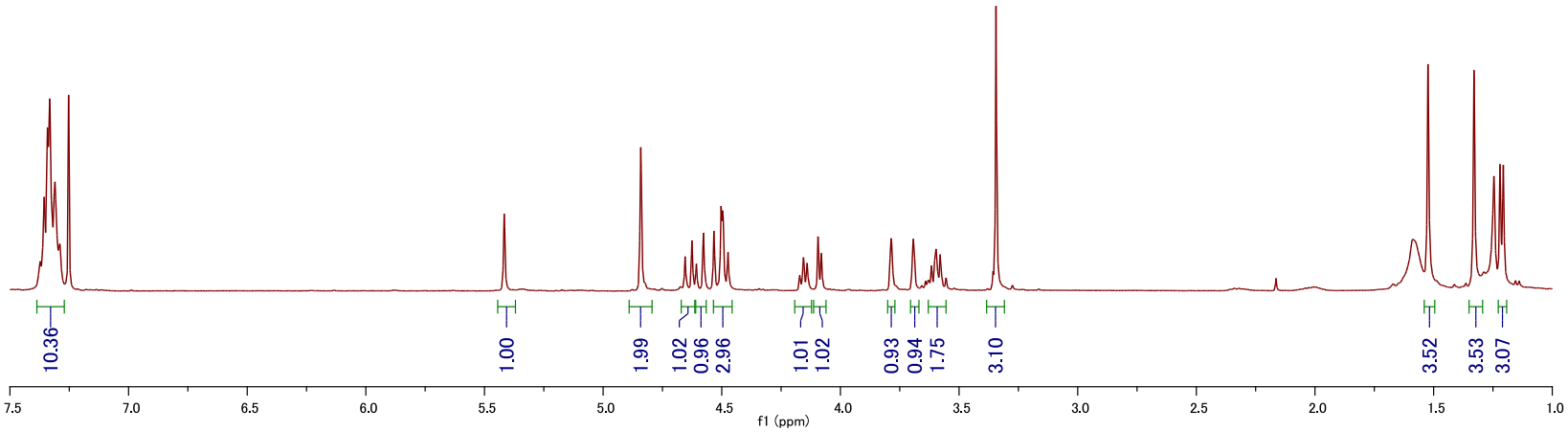


Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7aα) ^{13}C NMR (100 MHz, $CDCl_3$)



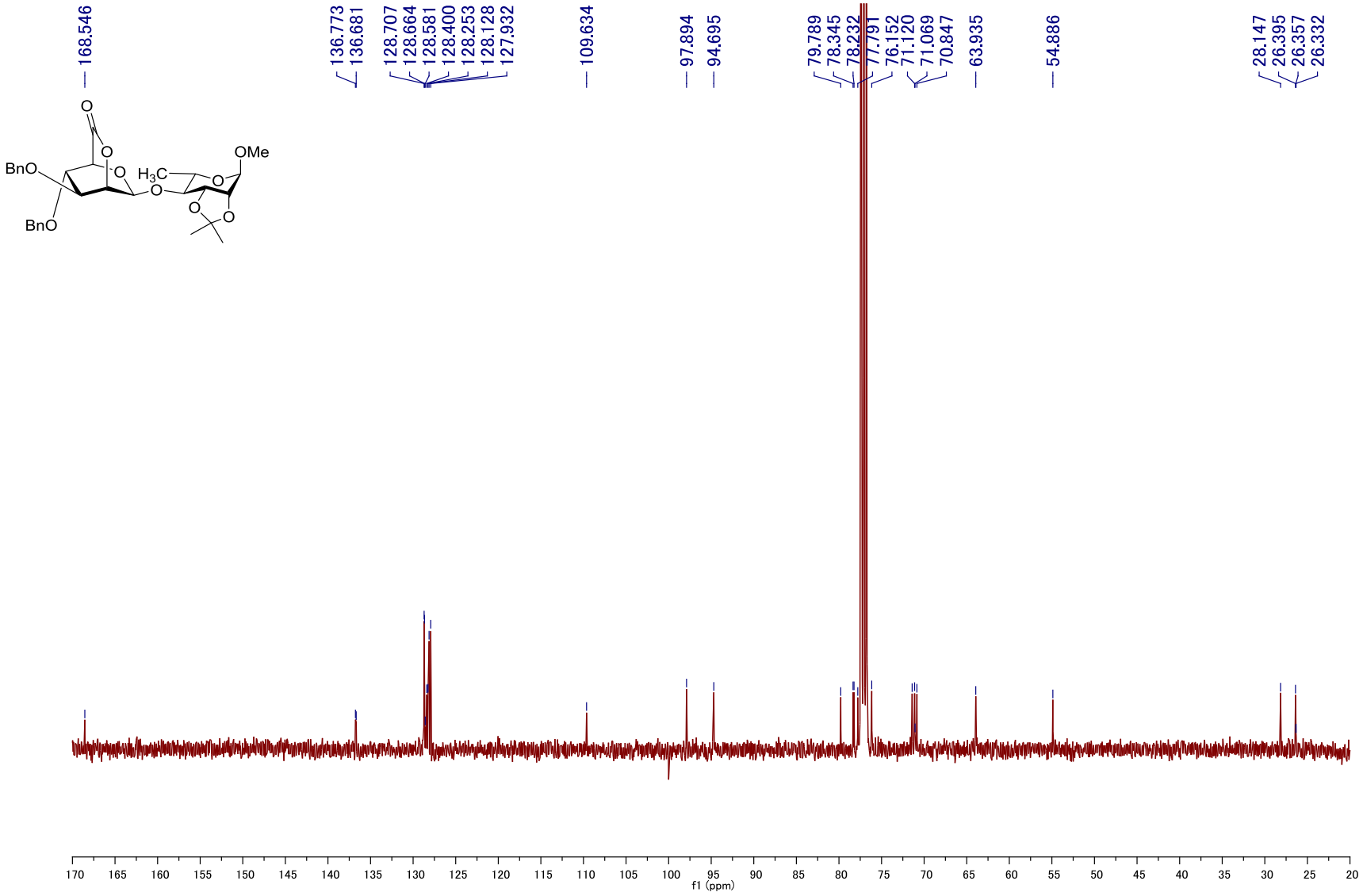
Methyl 2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bβ) ^{1}H NMR (400 MHz, $CDCl_3$)



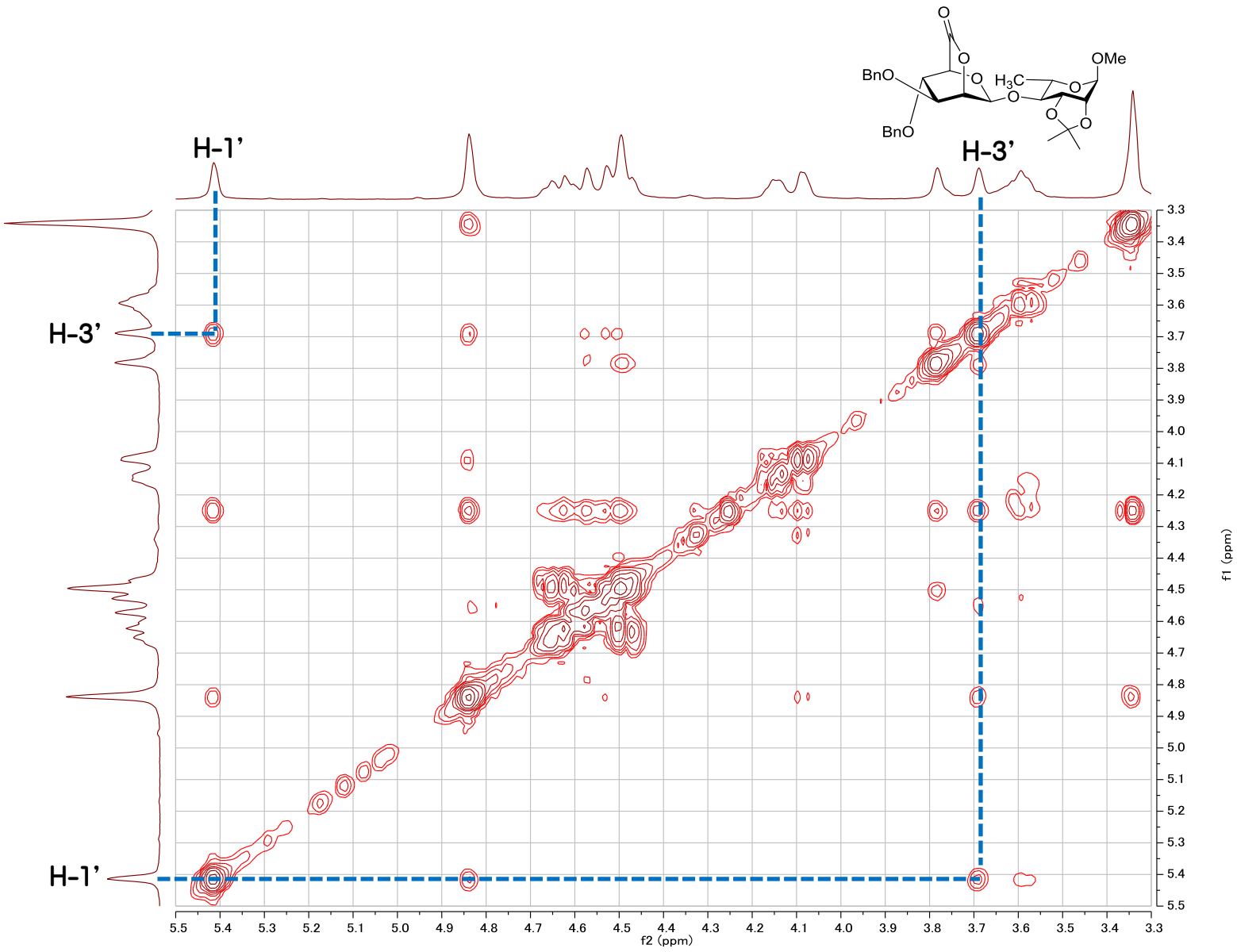


Methyl

2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bβ) ^{13}C NMR (100 MHz, $CDCl_3$)

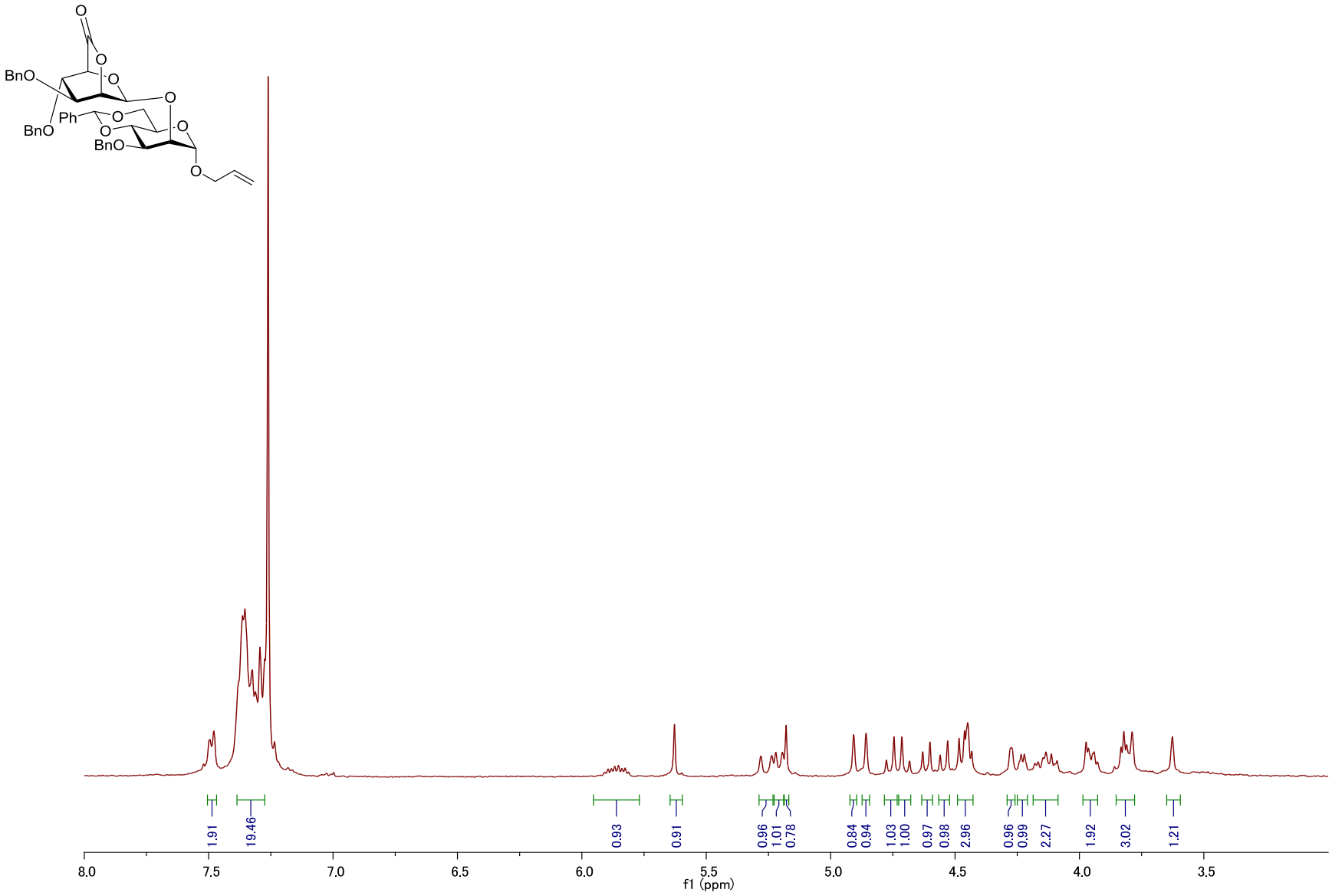


Methyl 2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)



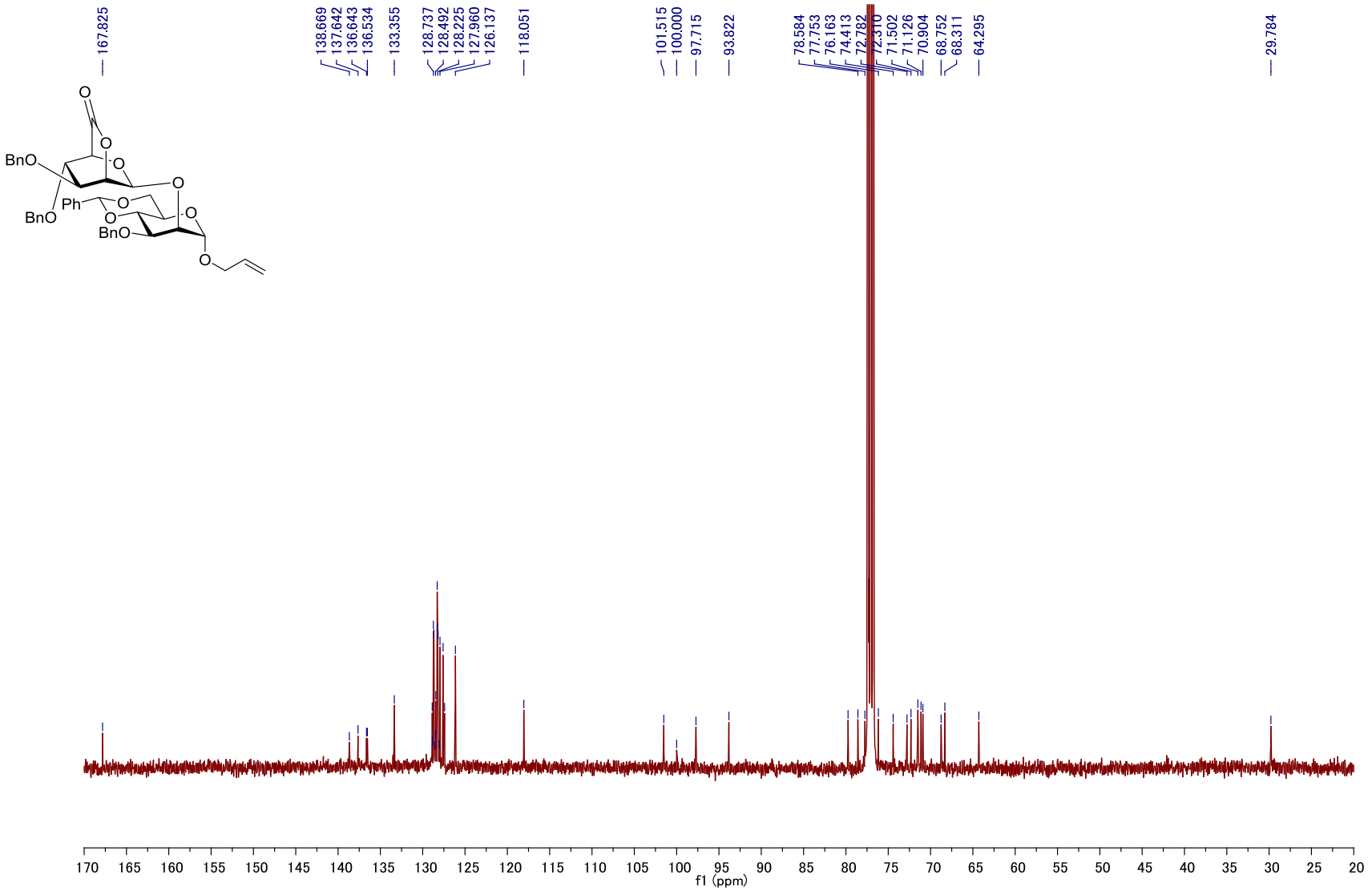
Allyl

2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cβ) ^{1}H NMR (400 MHz, $CDCl_3$)

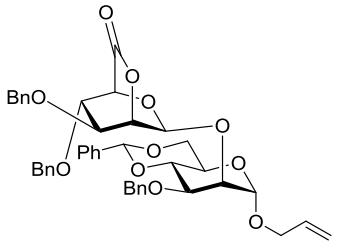


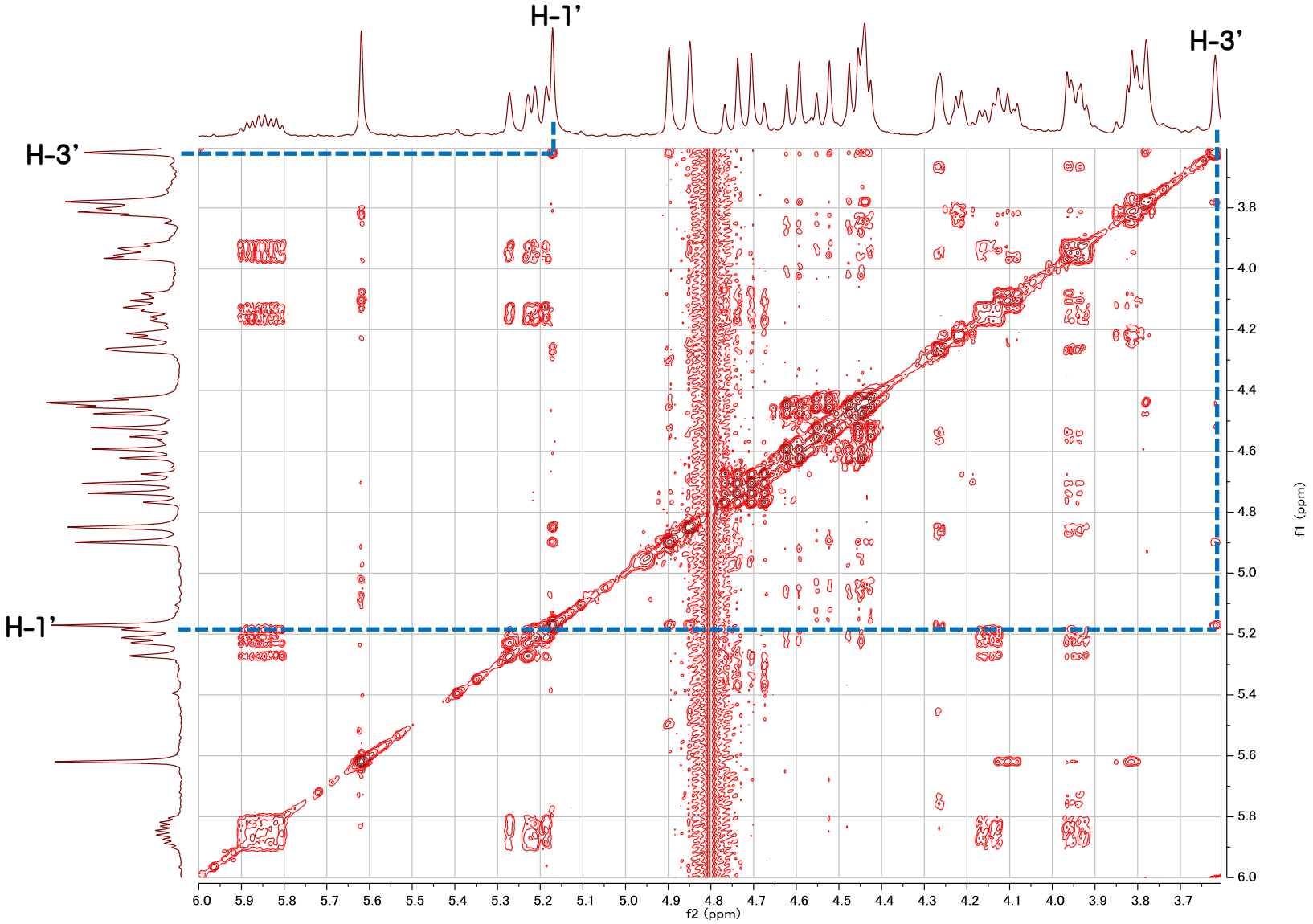
Allyl

2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cβ) ^{13}C NMR (100 MHz, $CDCl_3$)



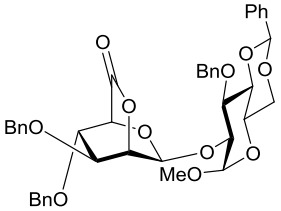
Allyl 2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)

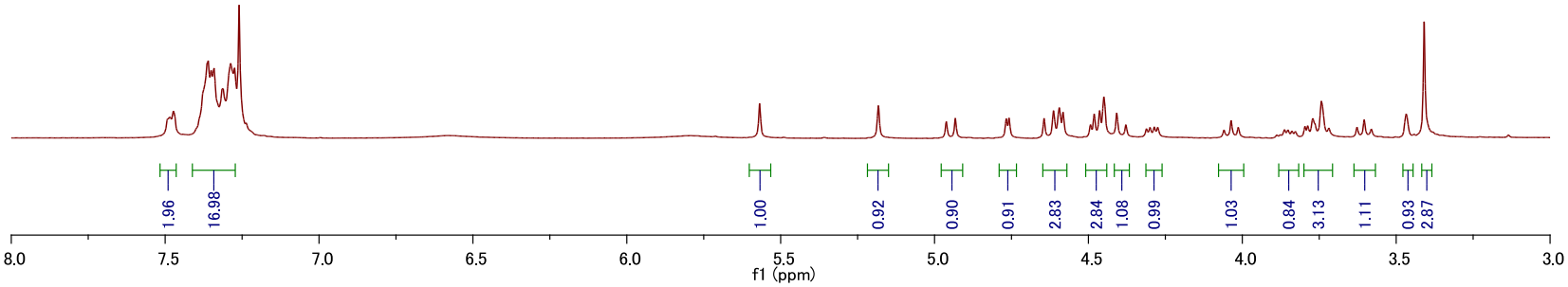




Methyl

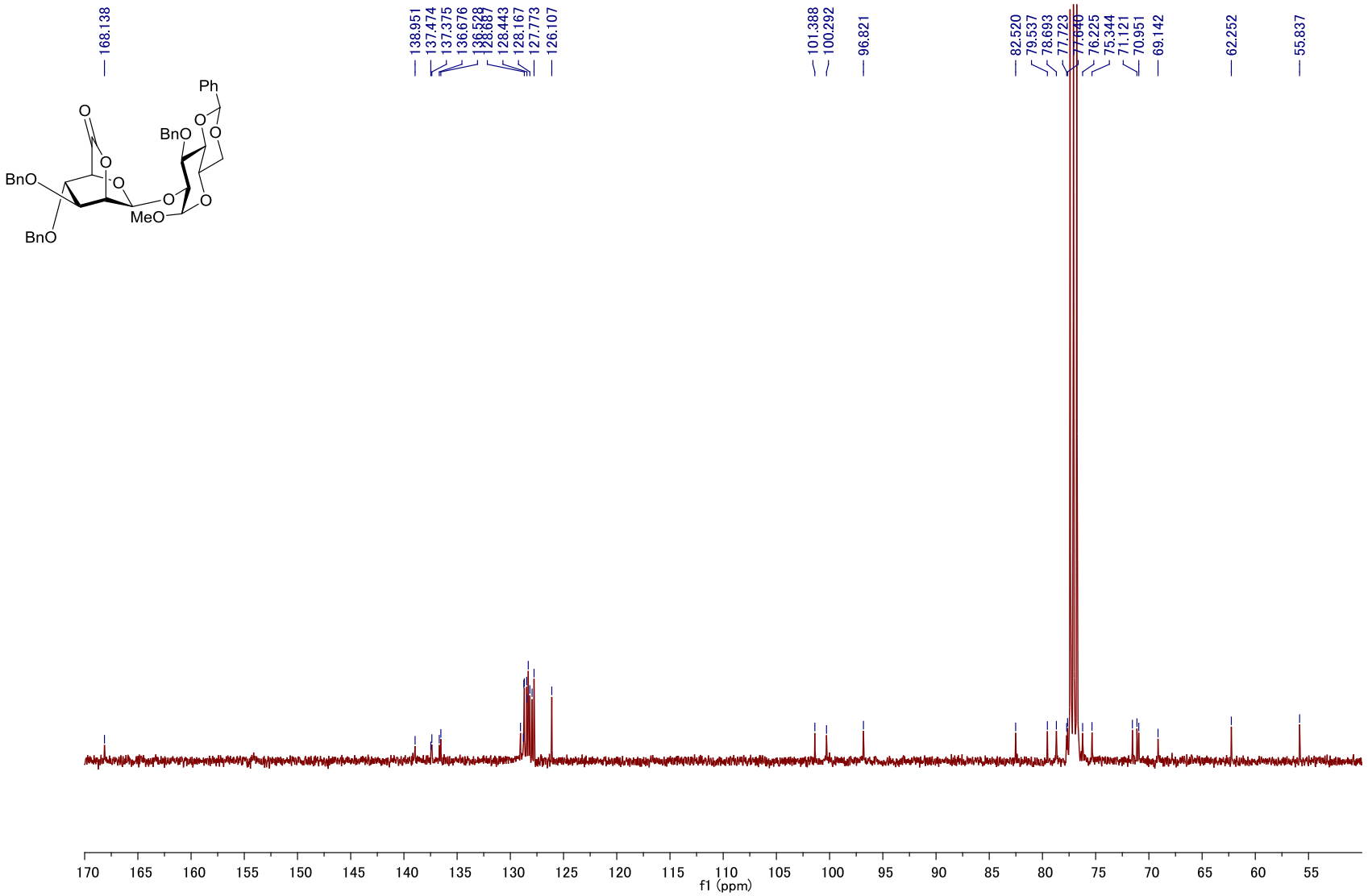
2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dβ) ^{1}H NMR (400 MHz, $CDCl_3$)



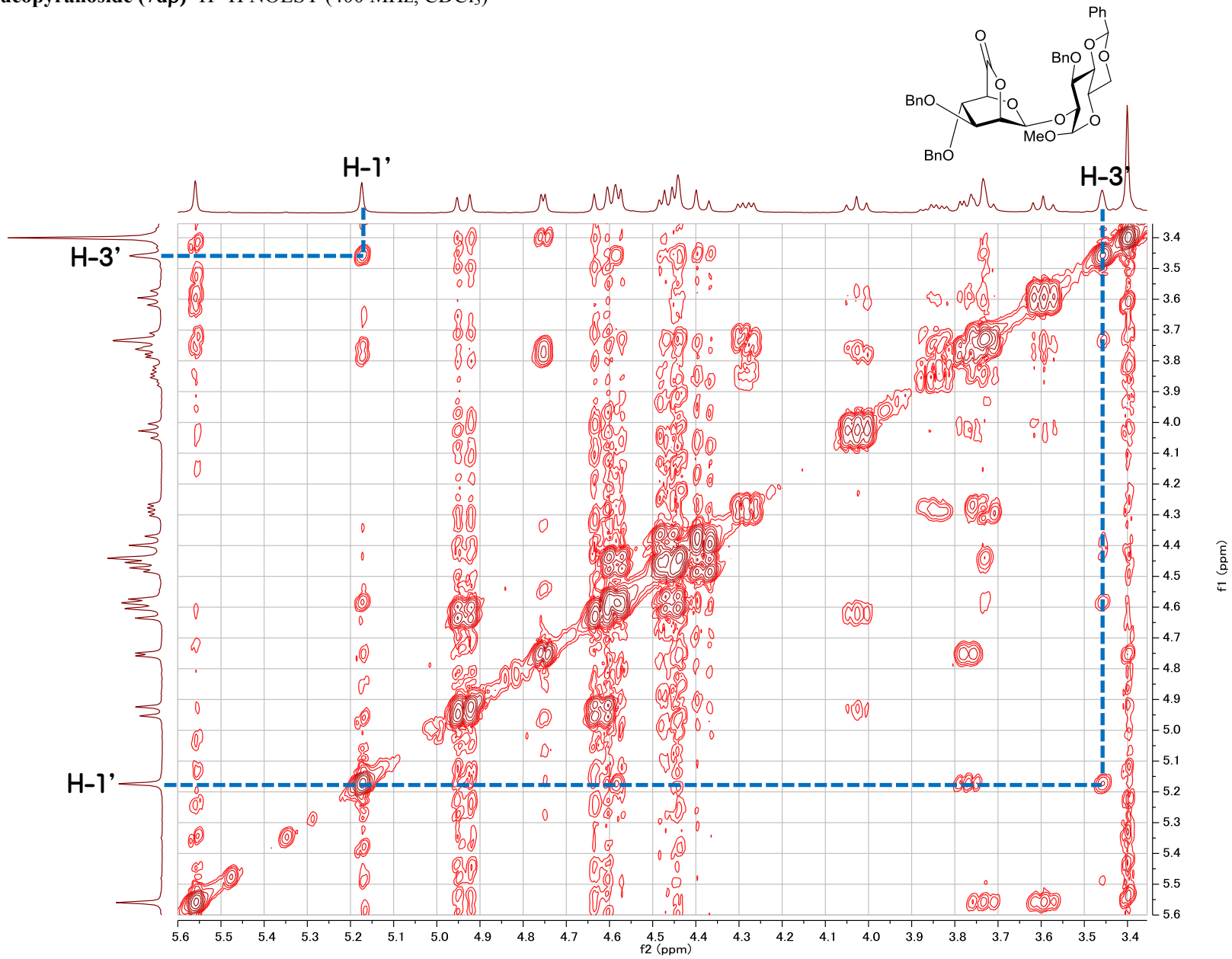


Methyl

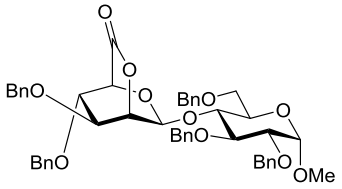
2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dβ) ^{13}C NMR (100 MHz, $CDCl_3$)

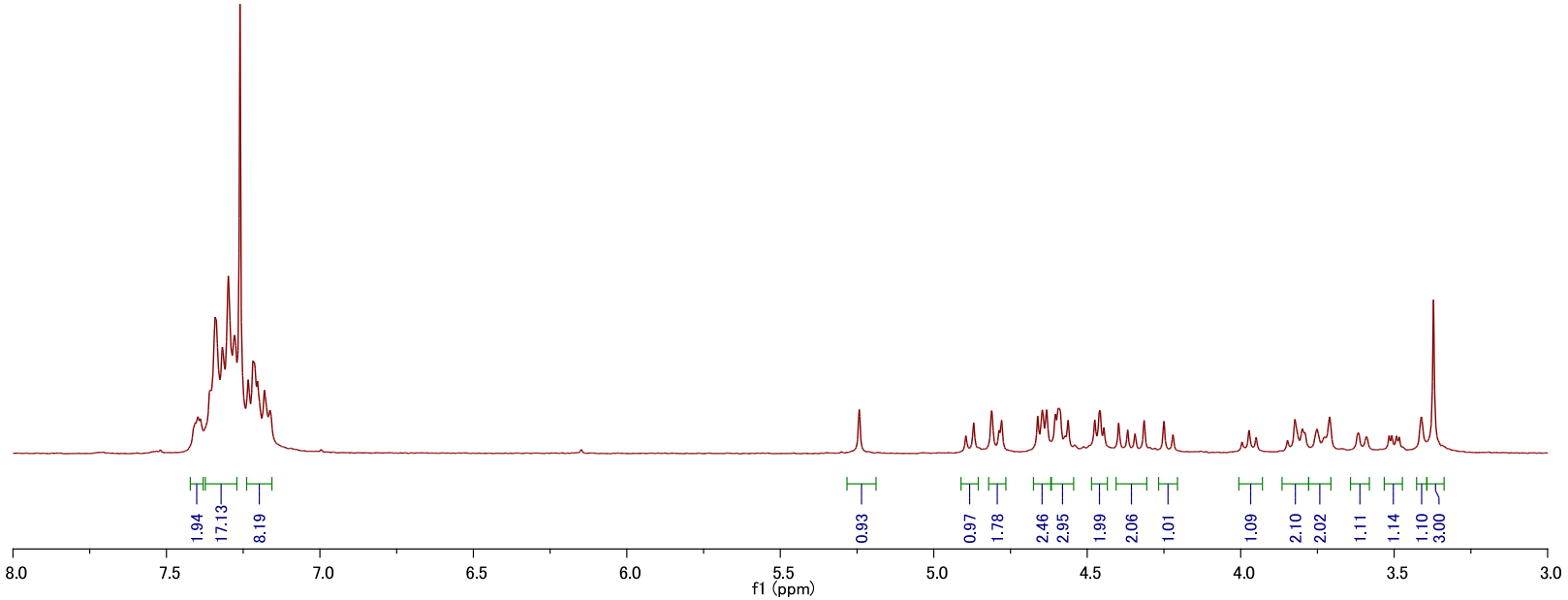


Methyl 2-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)

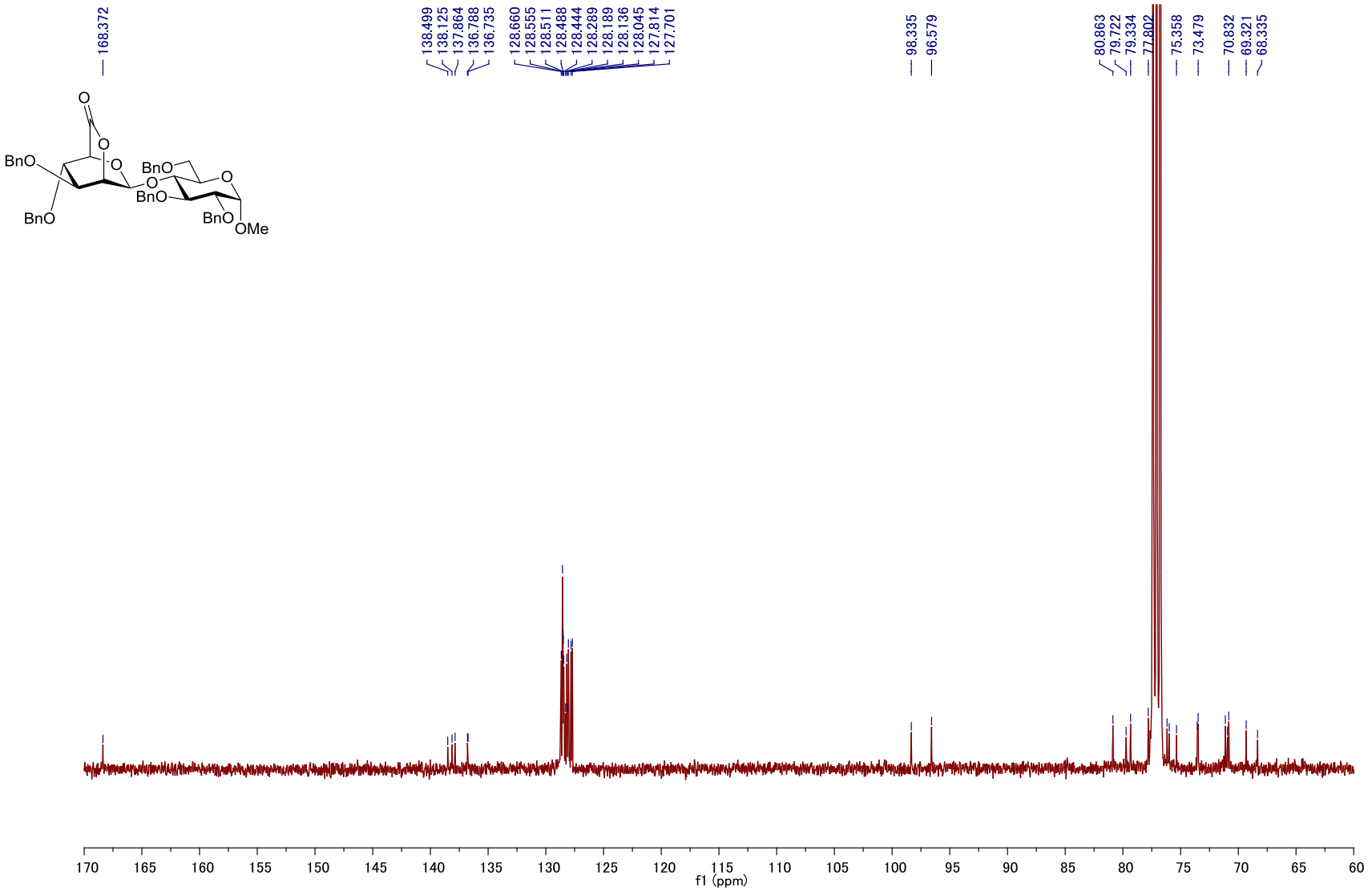


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eβ) ^{1}H NMR (400 MHz, $CDCl_3$)

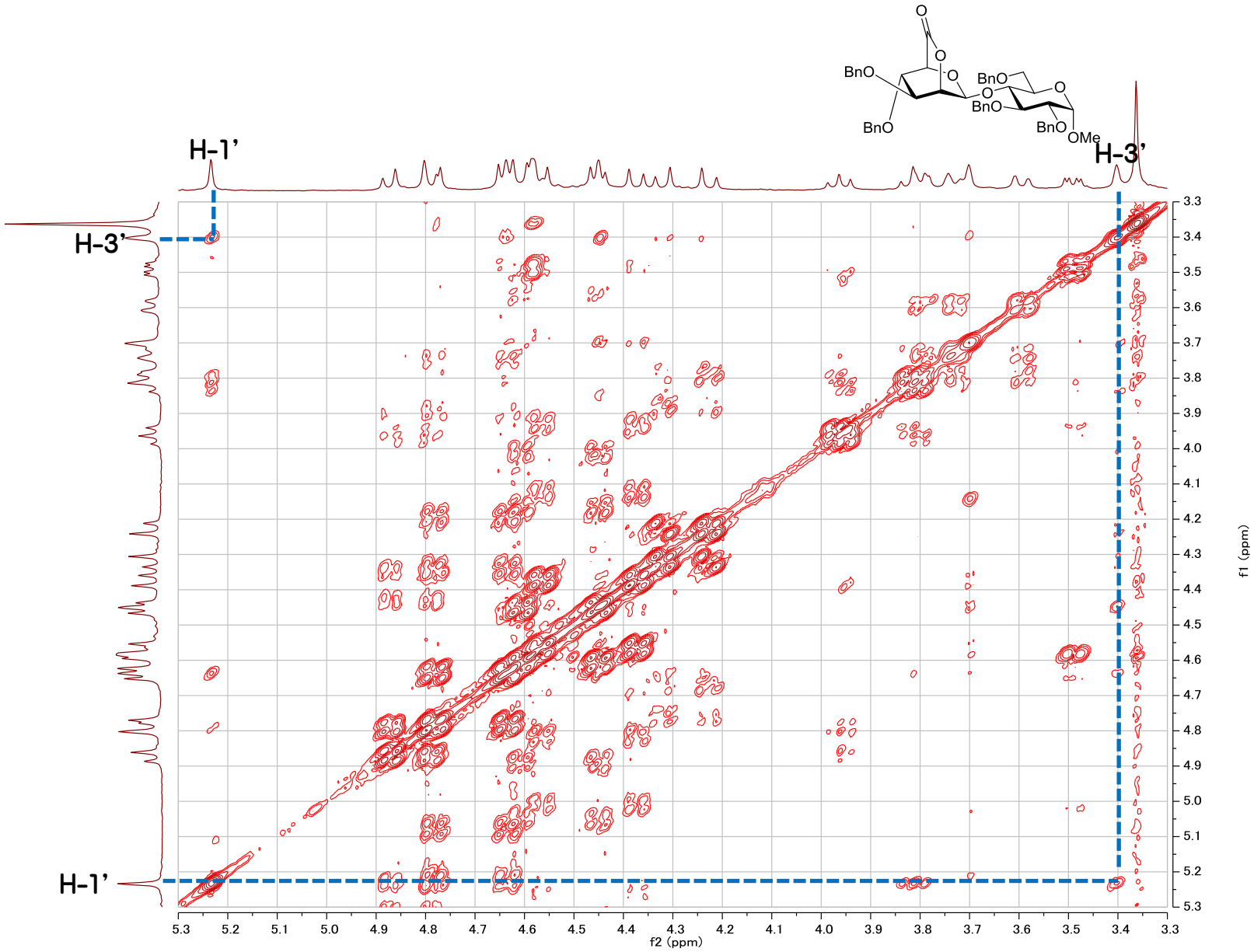




Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eβ) ^{13}C NMR (100 MHz, $CDCl_3$)

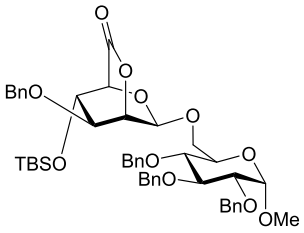


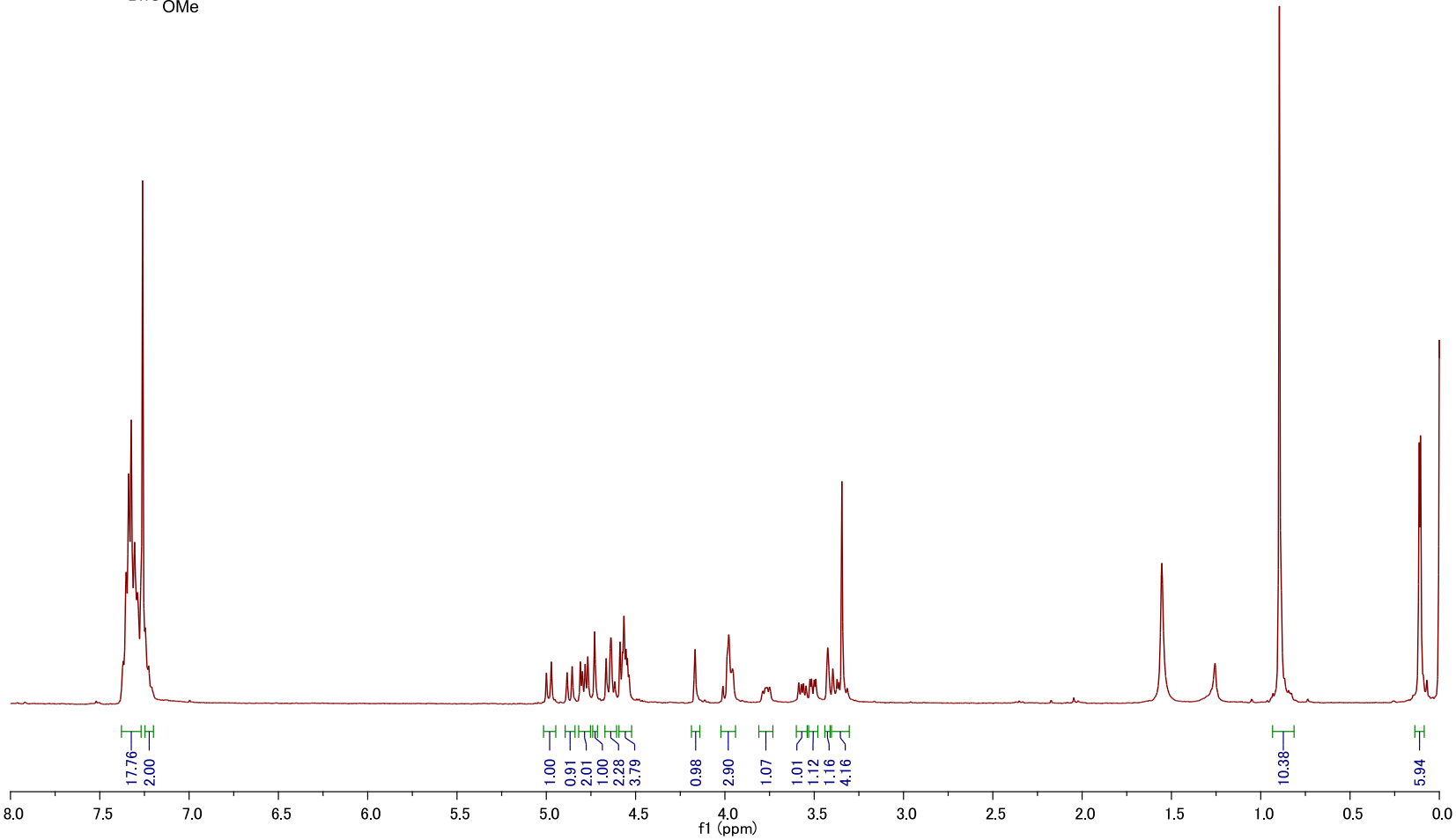
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)



Methyl

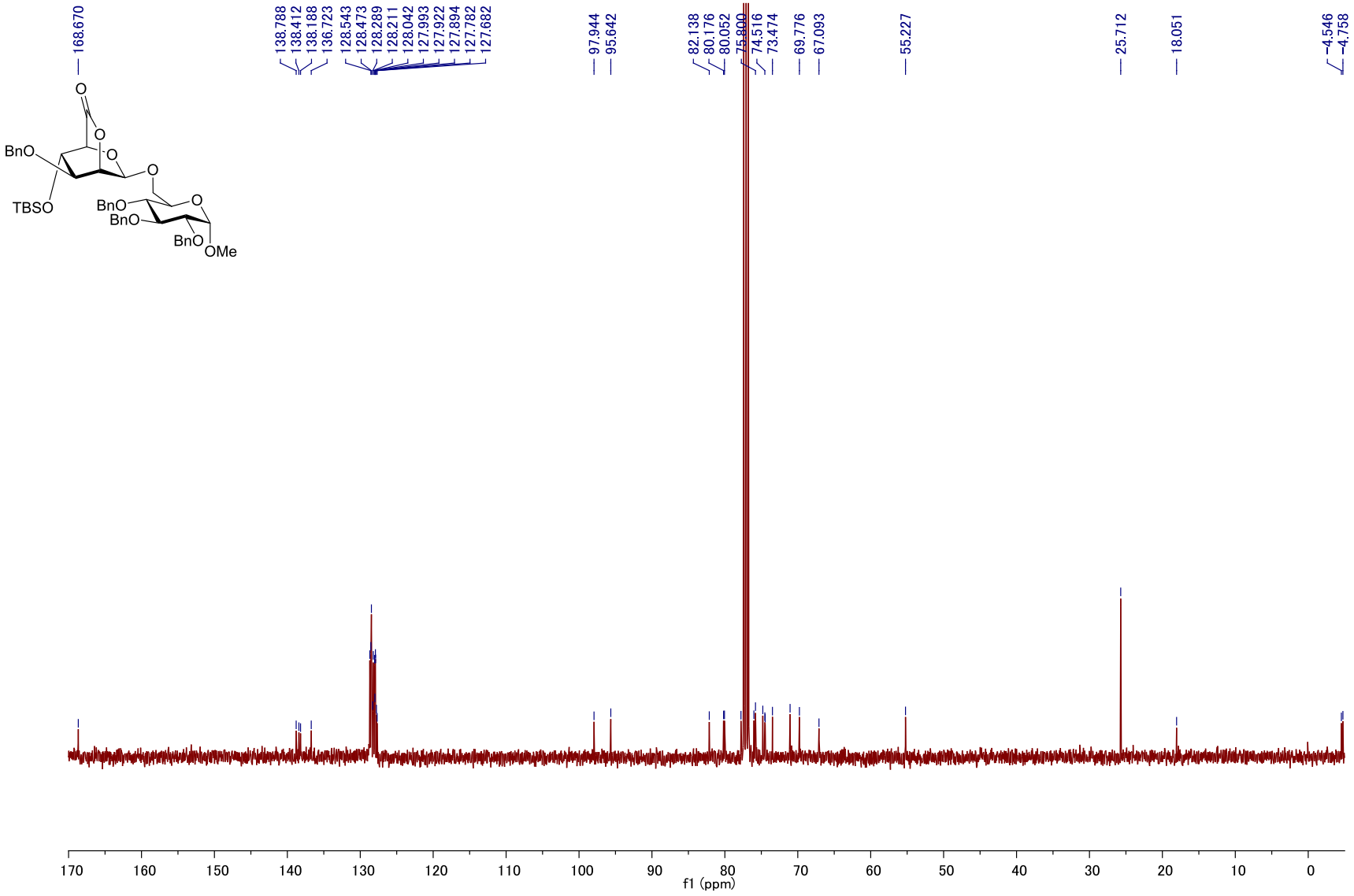
2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7fβ) ^{1}H NMR (400 MHz, $CDCl_3$)



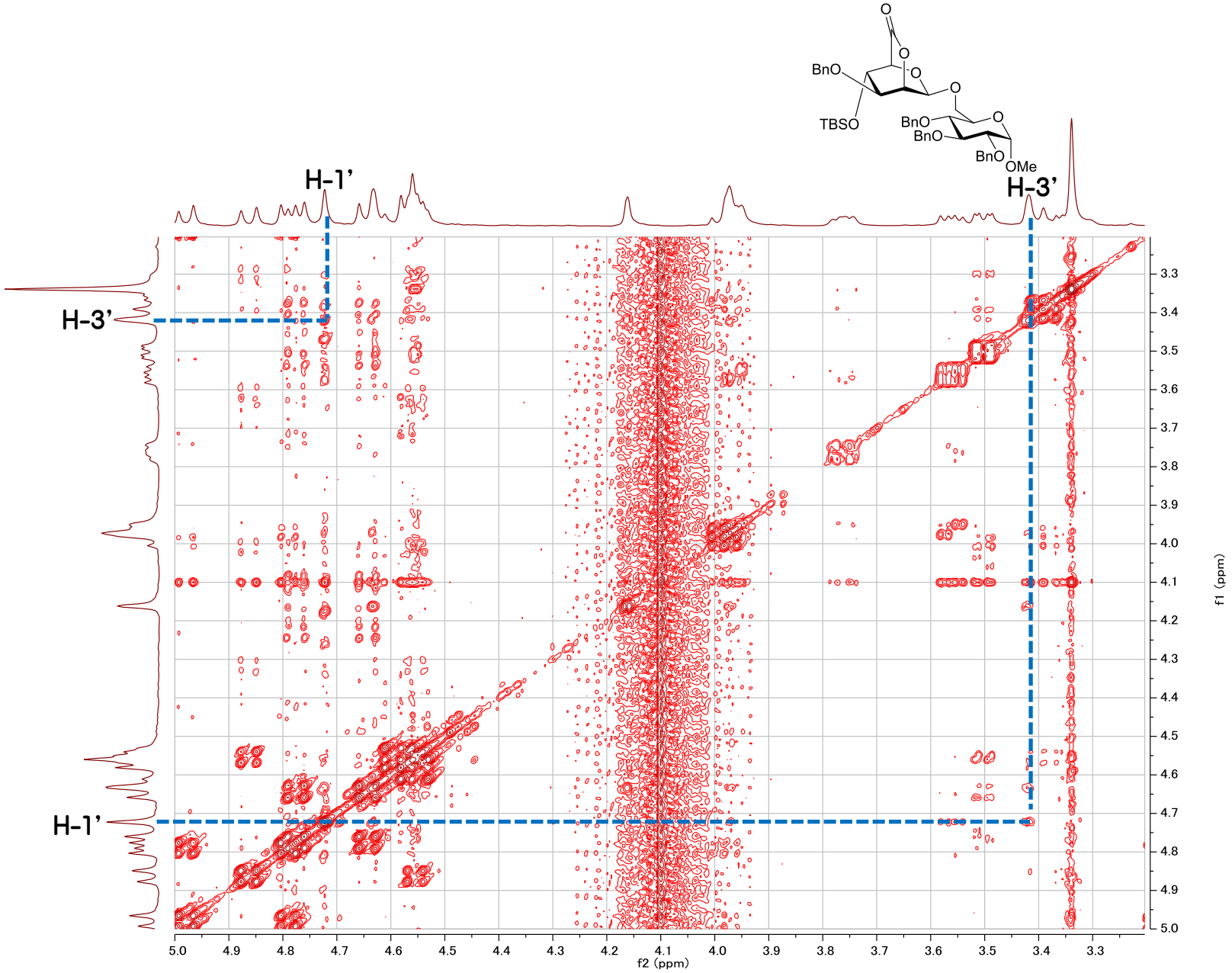


Methyl

2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7fβ) ^{13}C NMR (100 MHz, $CDCl_3$)

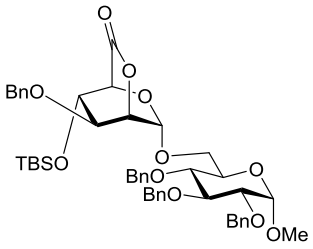


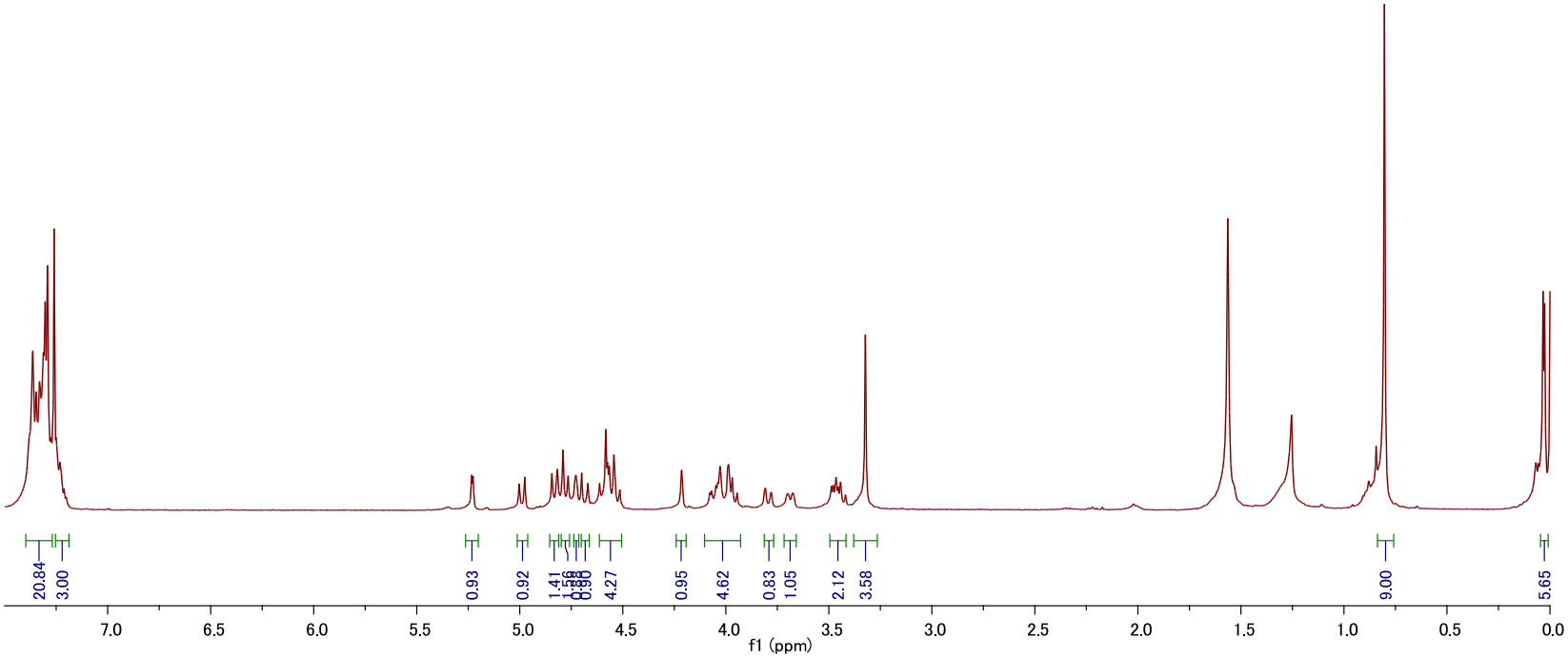
Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7fβ) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)



Methyl

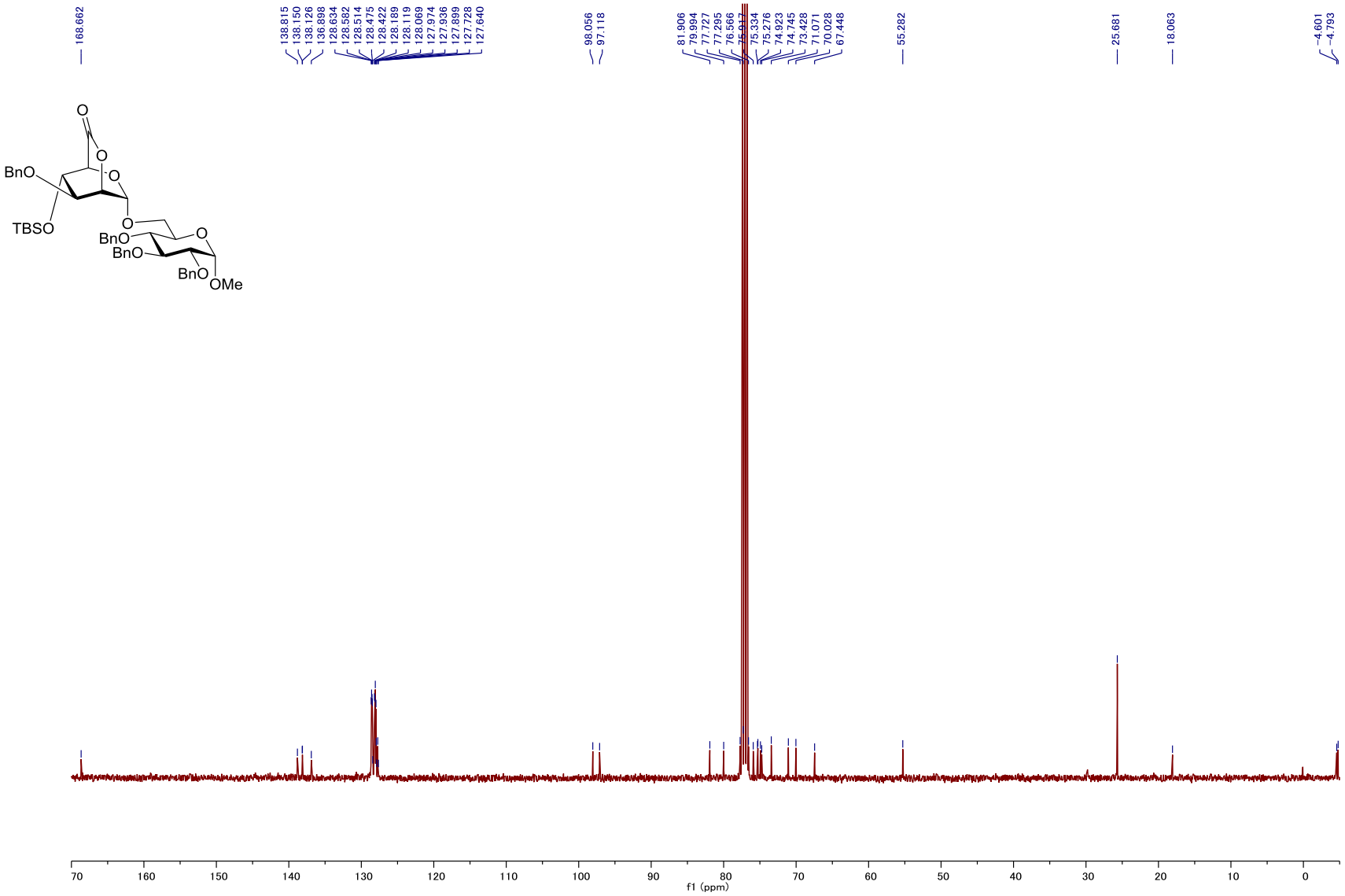
2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7fα) ^{1}H NMR (400 MHz, $CDCl_3$)



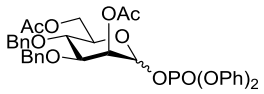


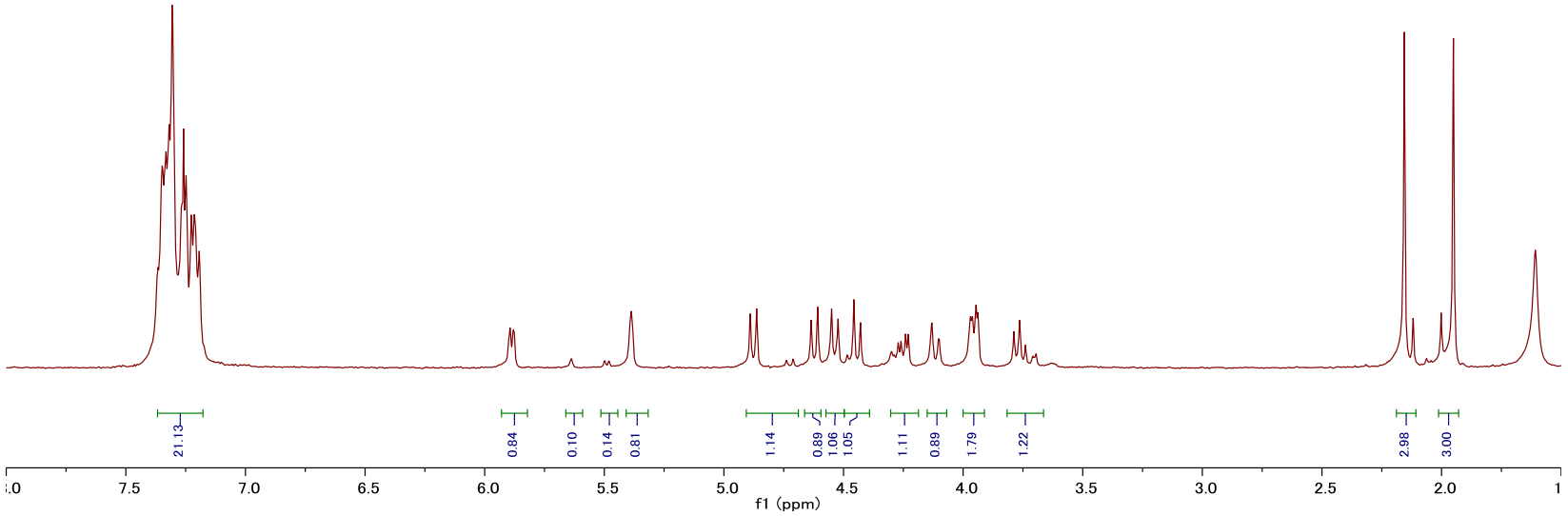
Methyl

2,3,4-tri-*O*-benzyl-6-*O*-(3'-di-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7fα) ^{13}C NMR (100 MHz, $CDCl_3$)

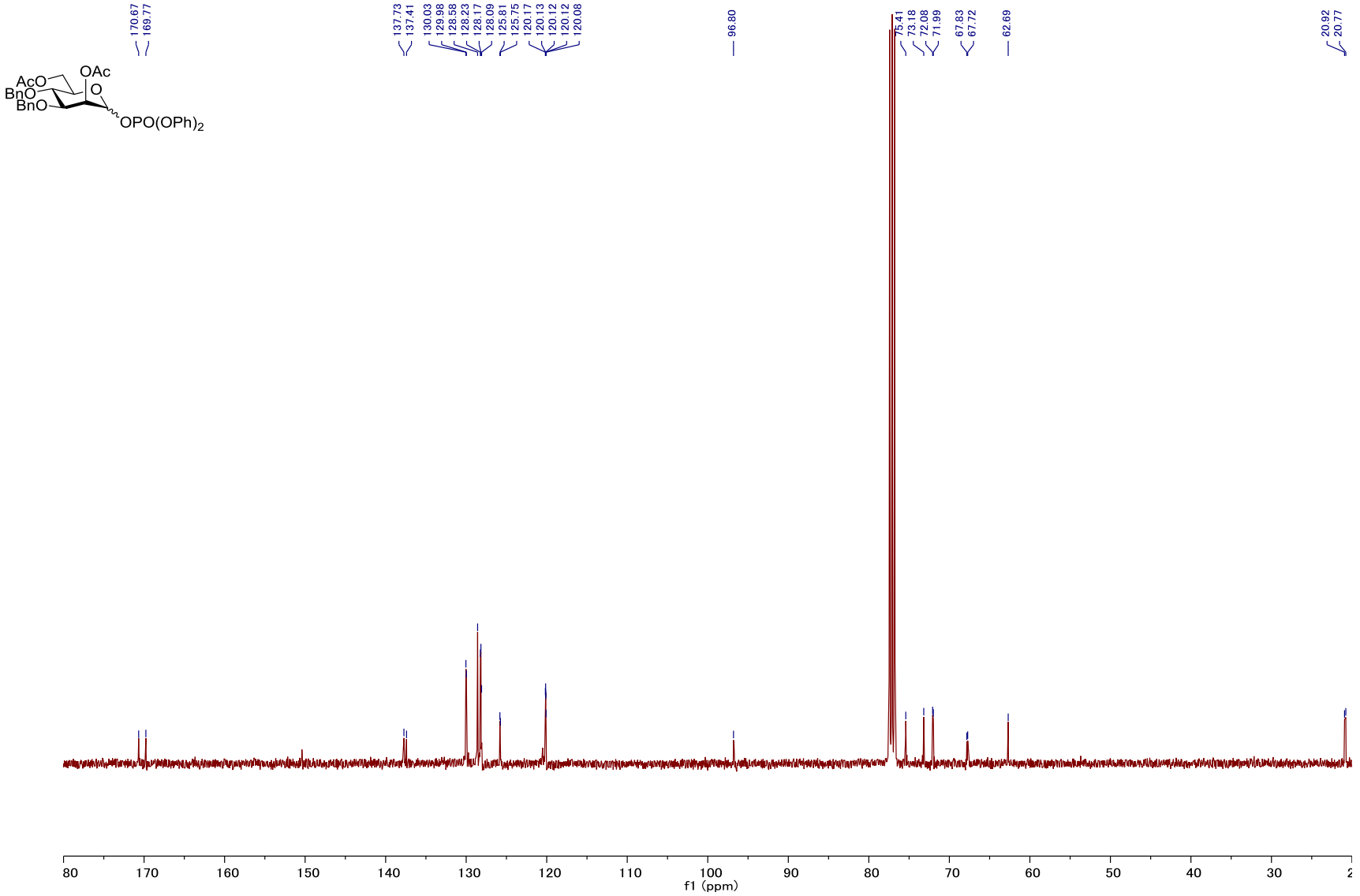


2,6-Di-*O*-acethyl-3,4-di-*O*-benzyl-D-mannopyranosyl diphenylphosphate (S3) ^{1}H NMR (400 MHz, $CDCl_3$)



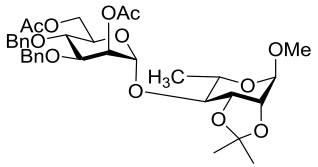


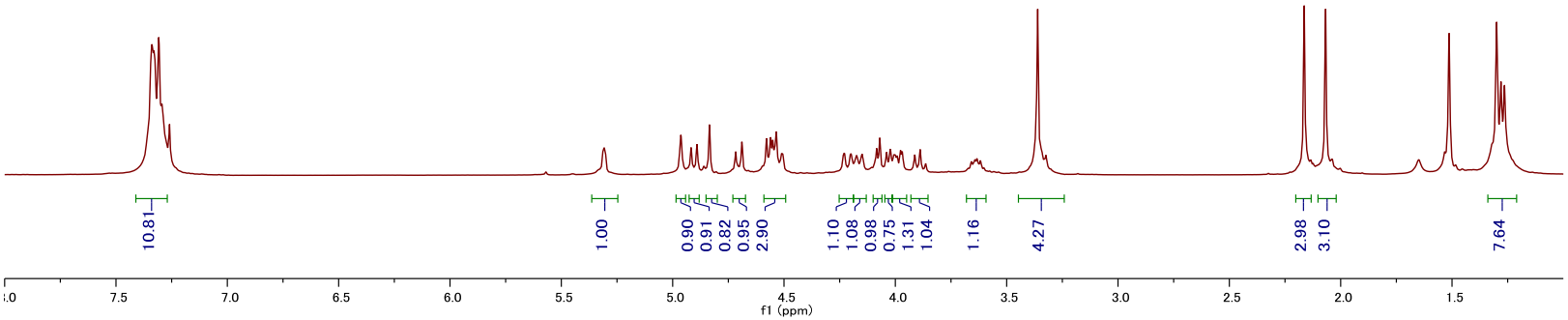
2,6-Di-*O*-acethyl-3,4-di-*O*-benzyl-D-mannopyranosyl diphenylphosphate (S3) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

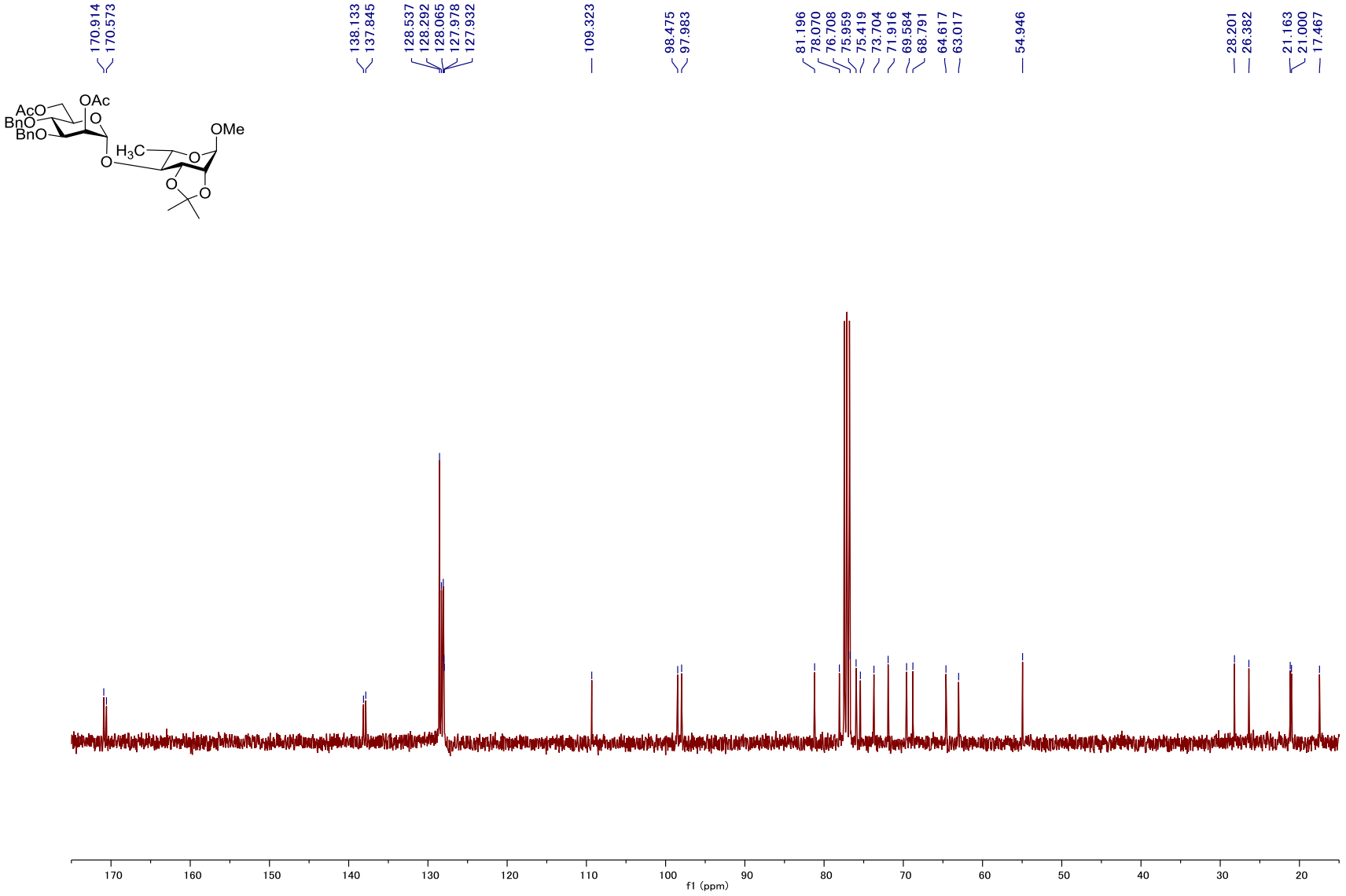
2,3-*O*-isopropylidene-4-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S4b) ^{1}H NMR (400 MHz, $CDCl_3$)





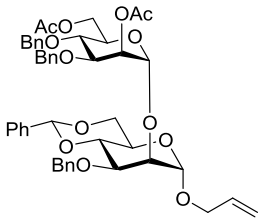
Methyl

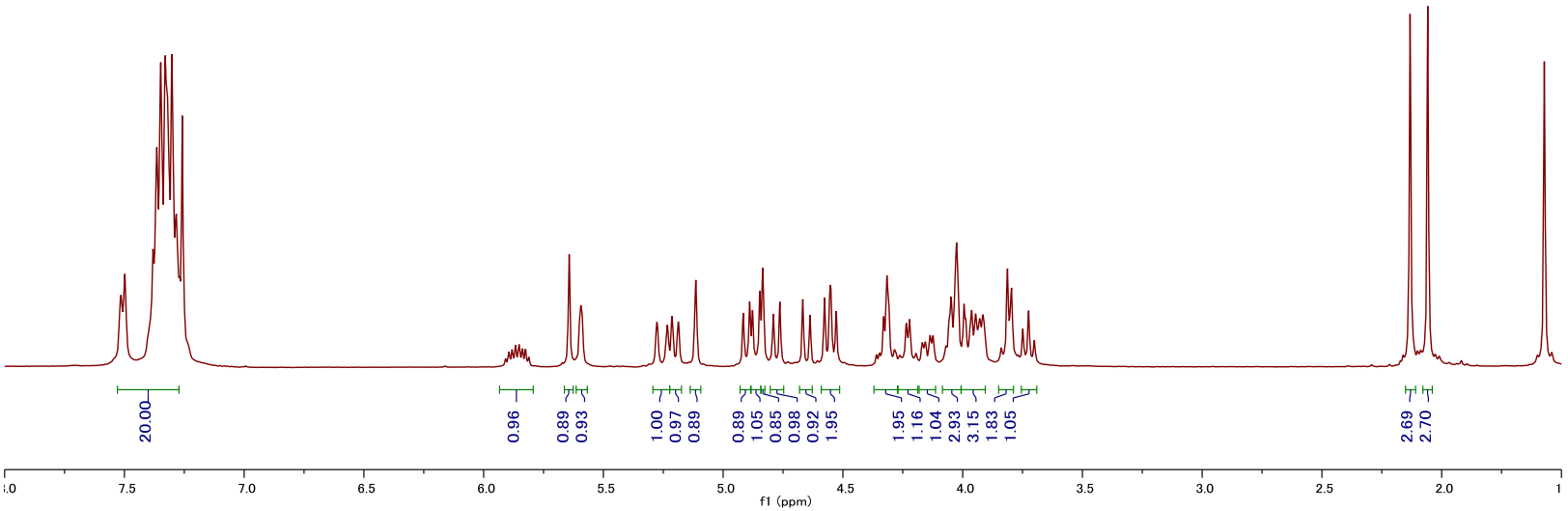
2,3-*O*-isopropylidene-4-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S4b) ^{13}C NMR (100 MHz, $CDCl_3$)



Allyl

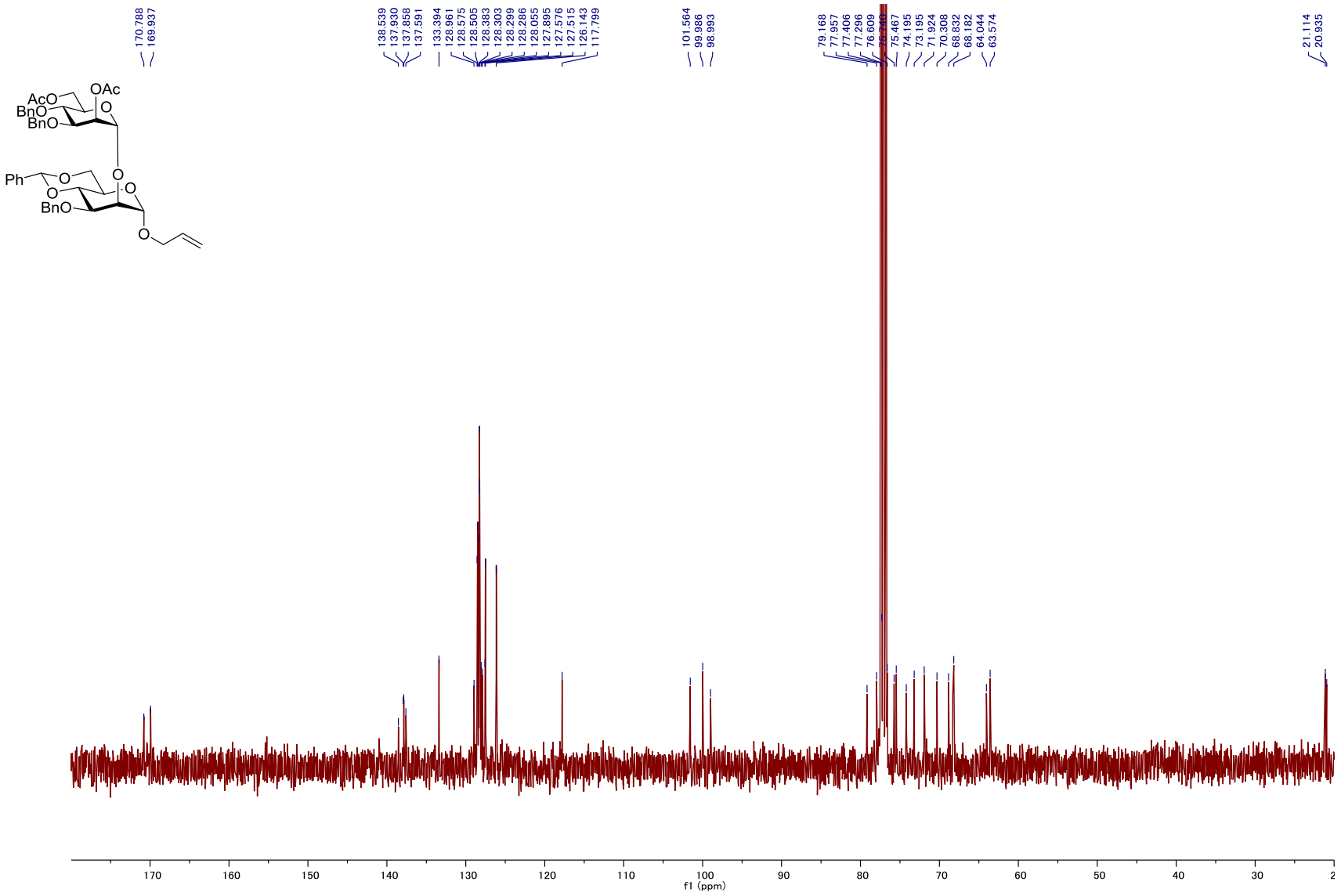
2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S4c) ^{1}H NMR (400 MHz, $CDCl_3$)





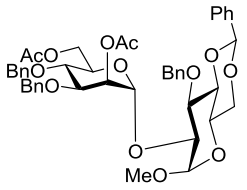
Allyl

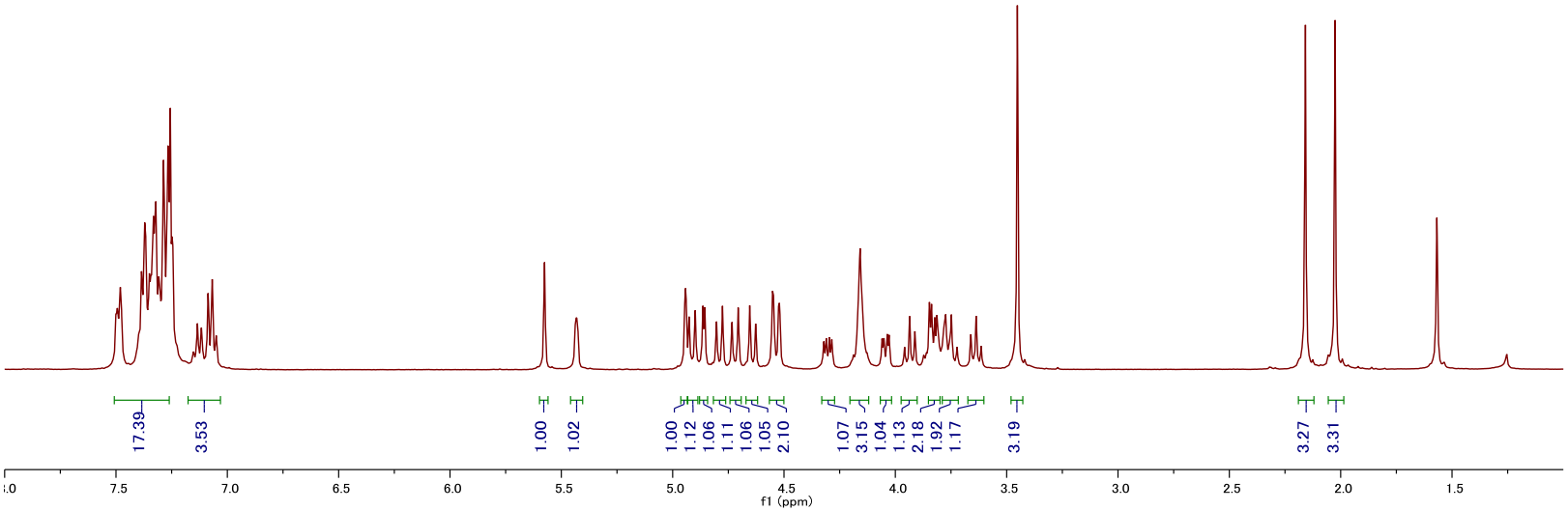
2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S4c) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

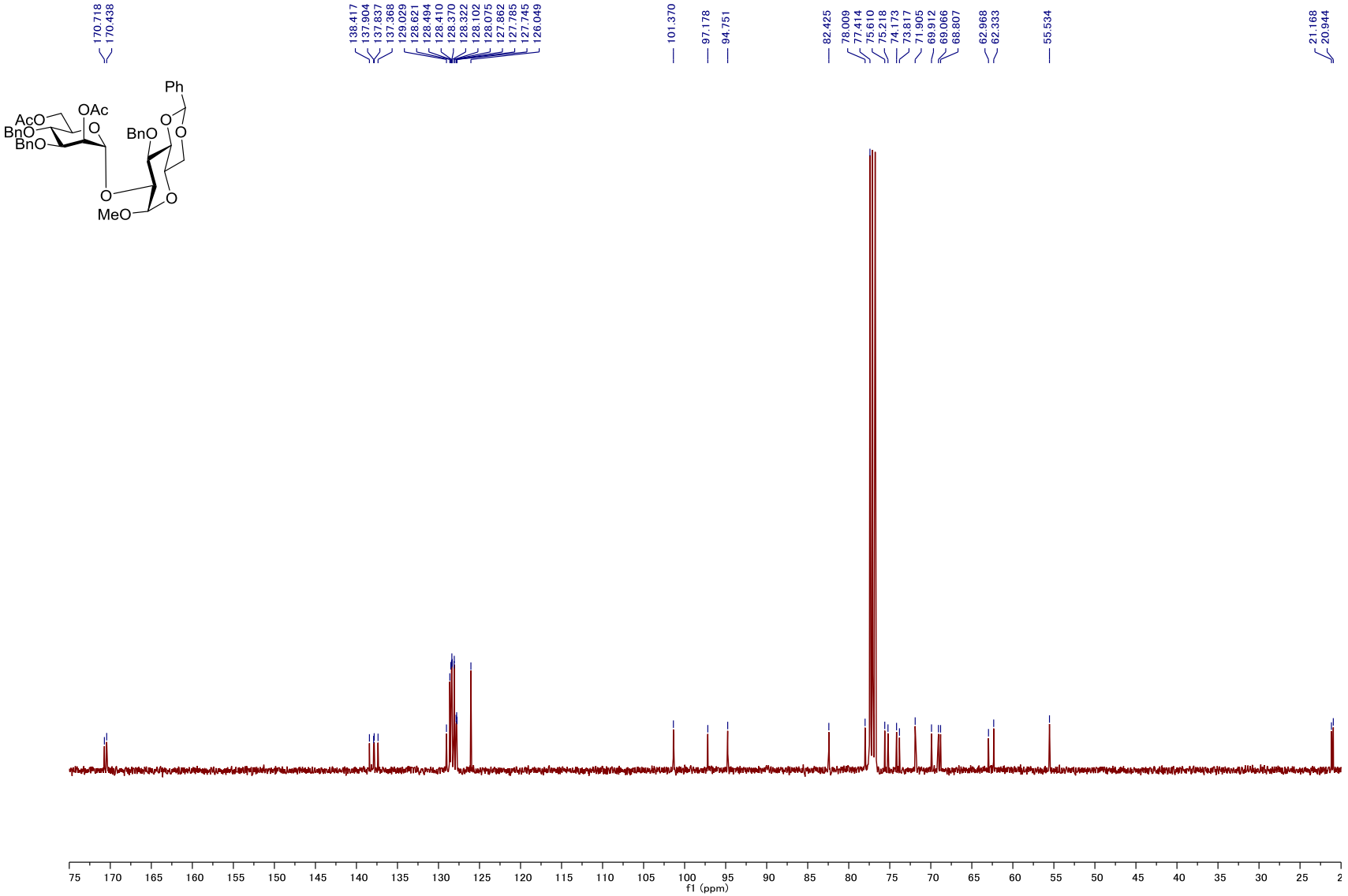
2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S4d) ^{1}H NMR (400 MHz, $CDCl_3$)





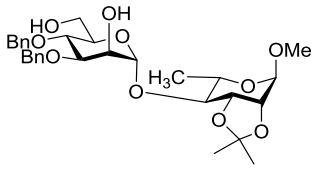
Methyl

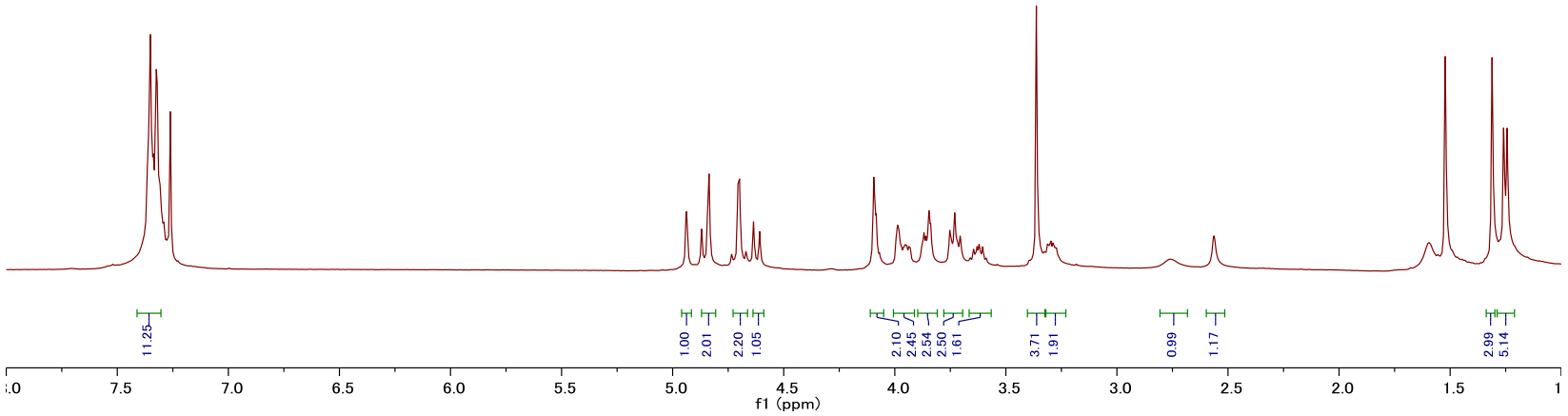
2-*O*-(2',6'-di-*O*-acetyl-3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S4d) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

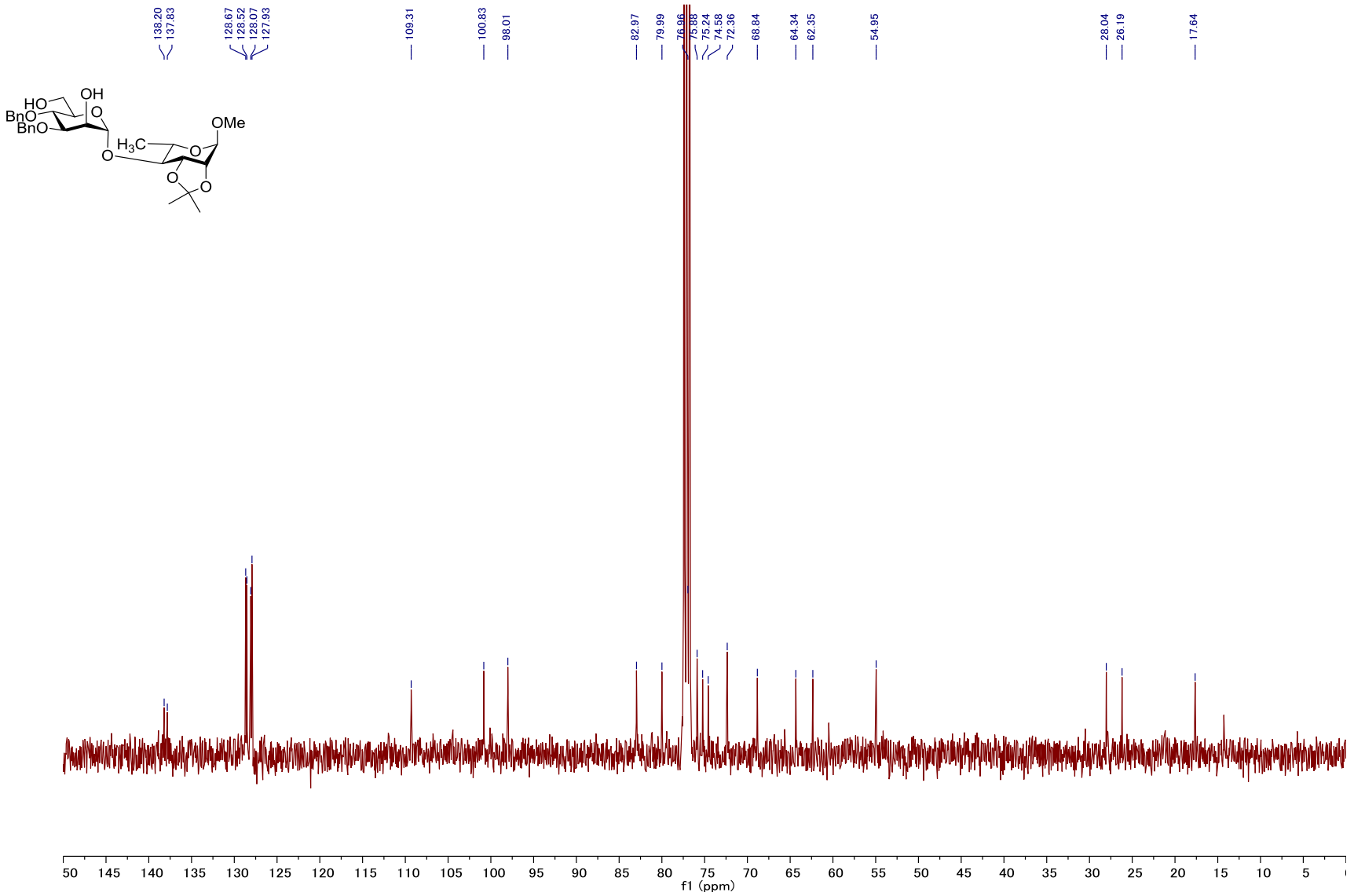
2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S5b) ^{1}H NMR (400 MHz, $CDCl_3$)





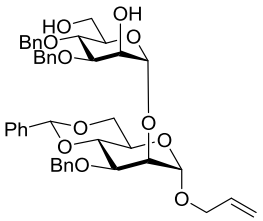
Methyl

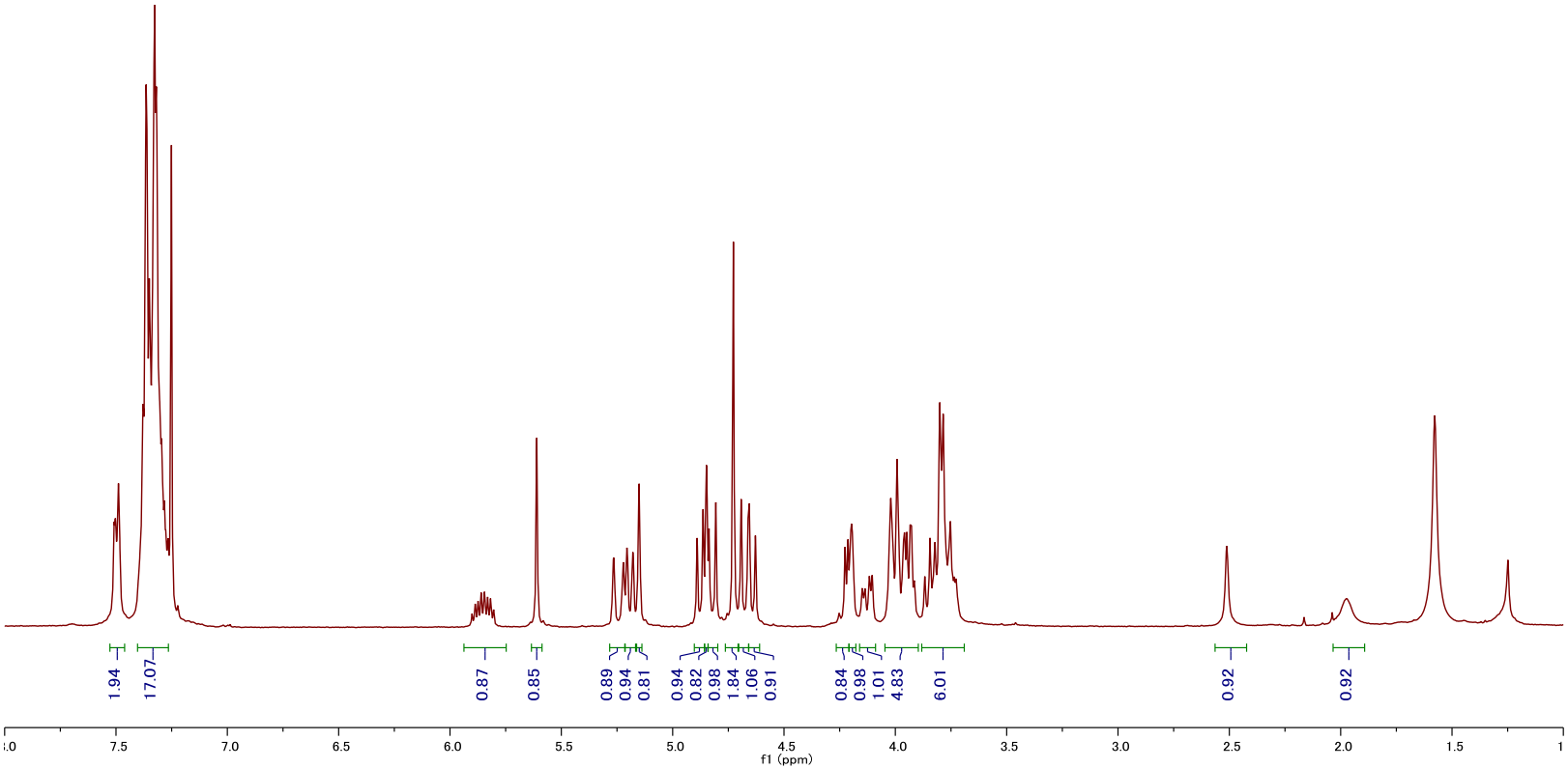
2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-L-rhamnopyranoside (S5b) ^{13}C NMR (100 MHz, $CDCl_3$)



Allyl

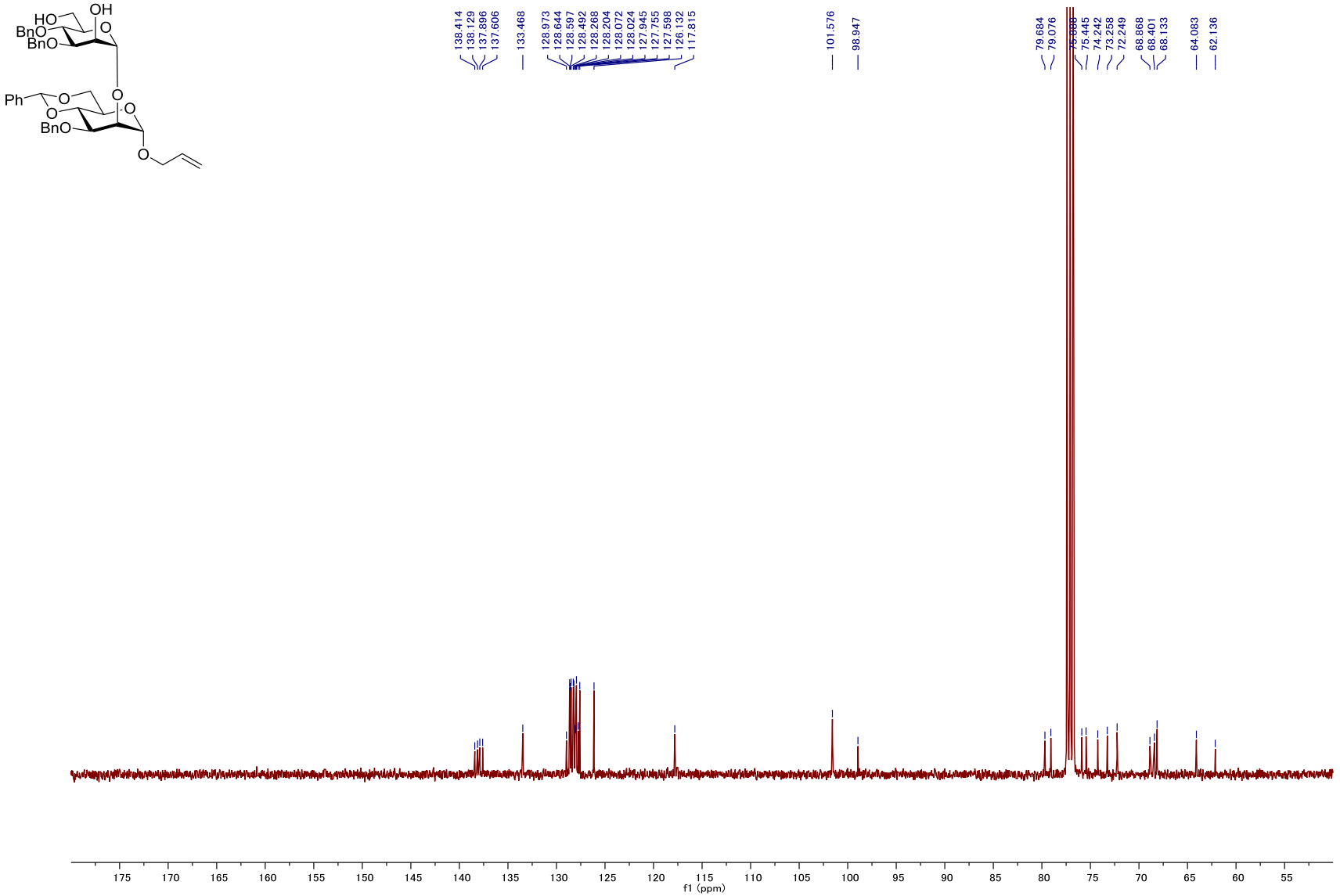
2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S5c) ^{1}H NMR (400 MHz, $CDCl_3$)





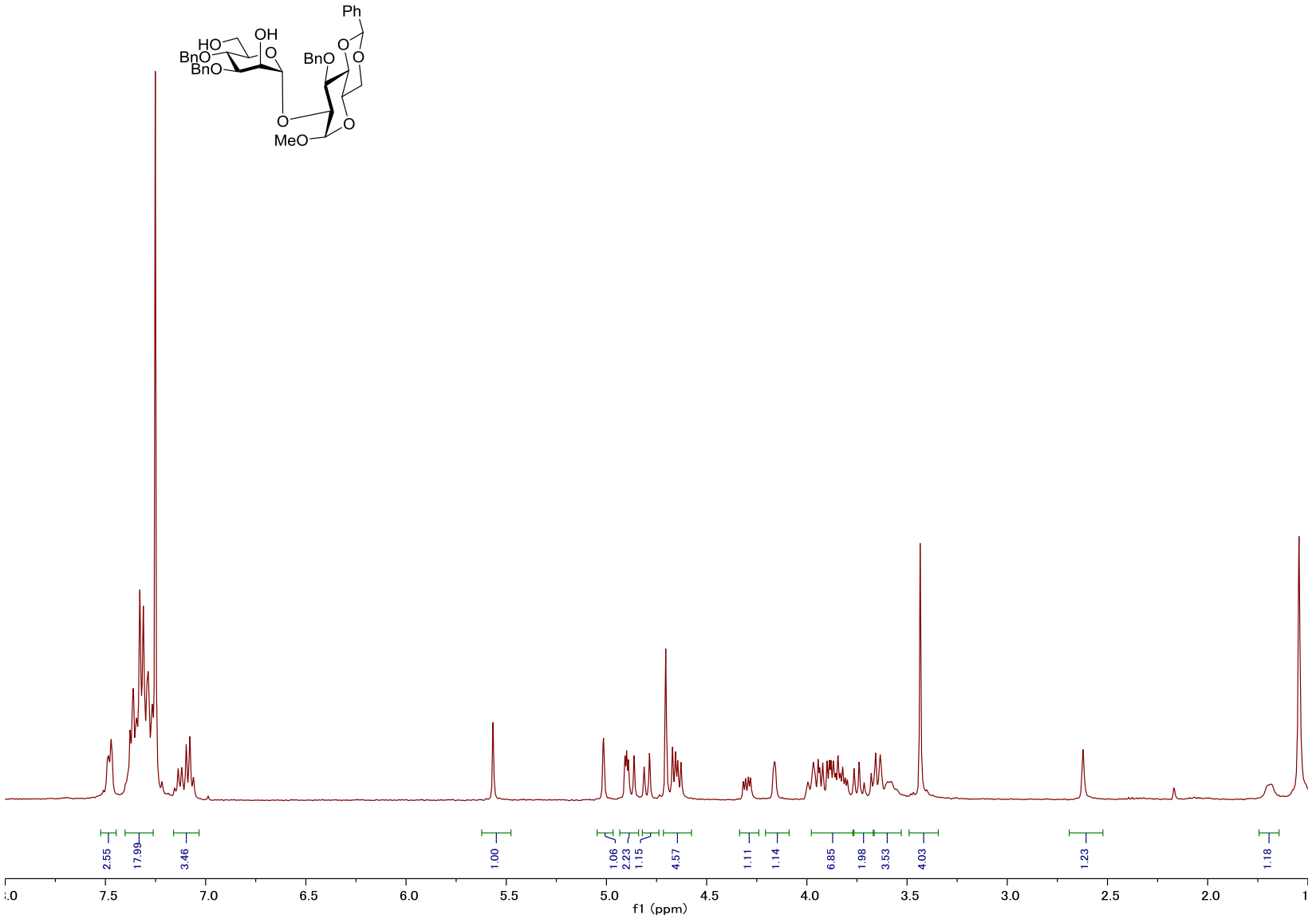
Allyl

2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (S5c) ^{13}C NMR (100 MHz, $CDCl_3$)



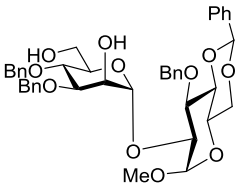
Methyl

2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S5d) ^{1}H NMR (400 MHz, $CDCl_3$)



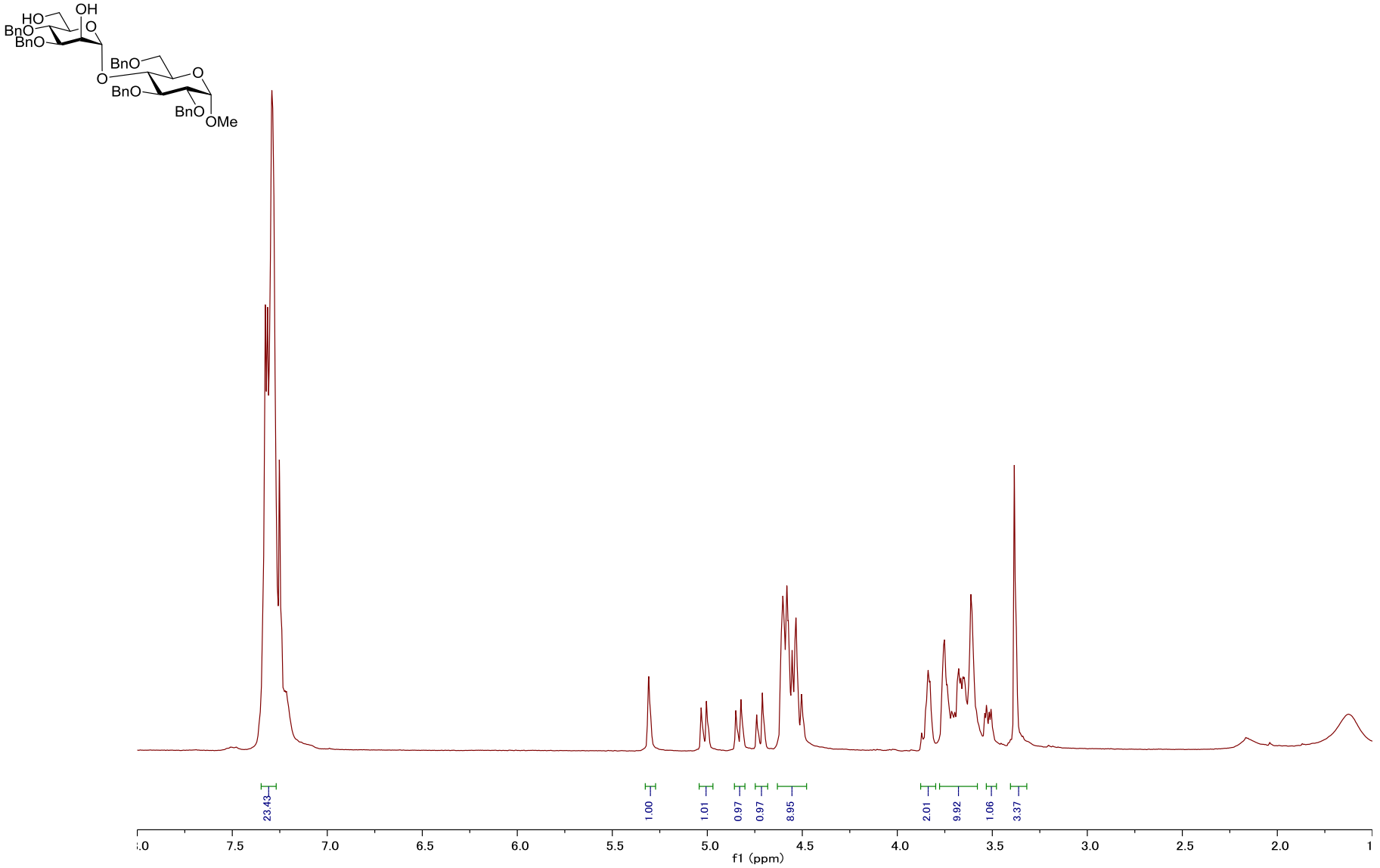
Methyl

2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (S5d) ^{13}C NMR (100 MHz, $CDCl_3$)



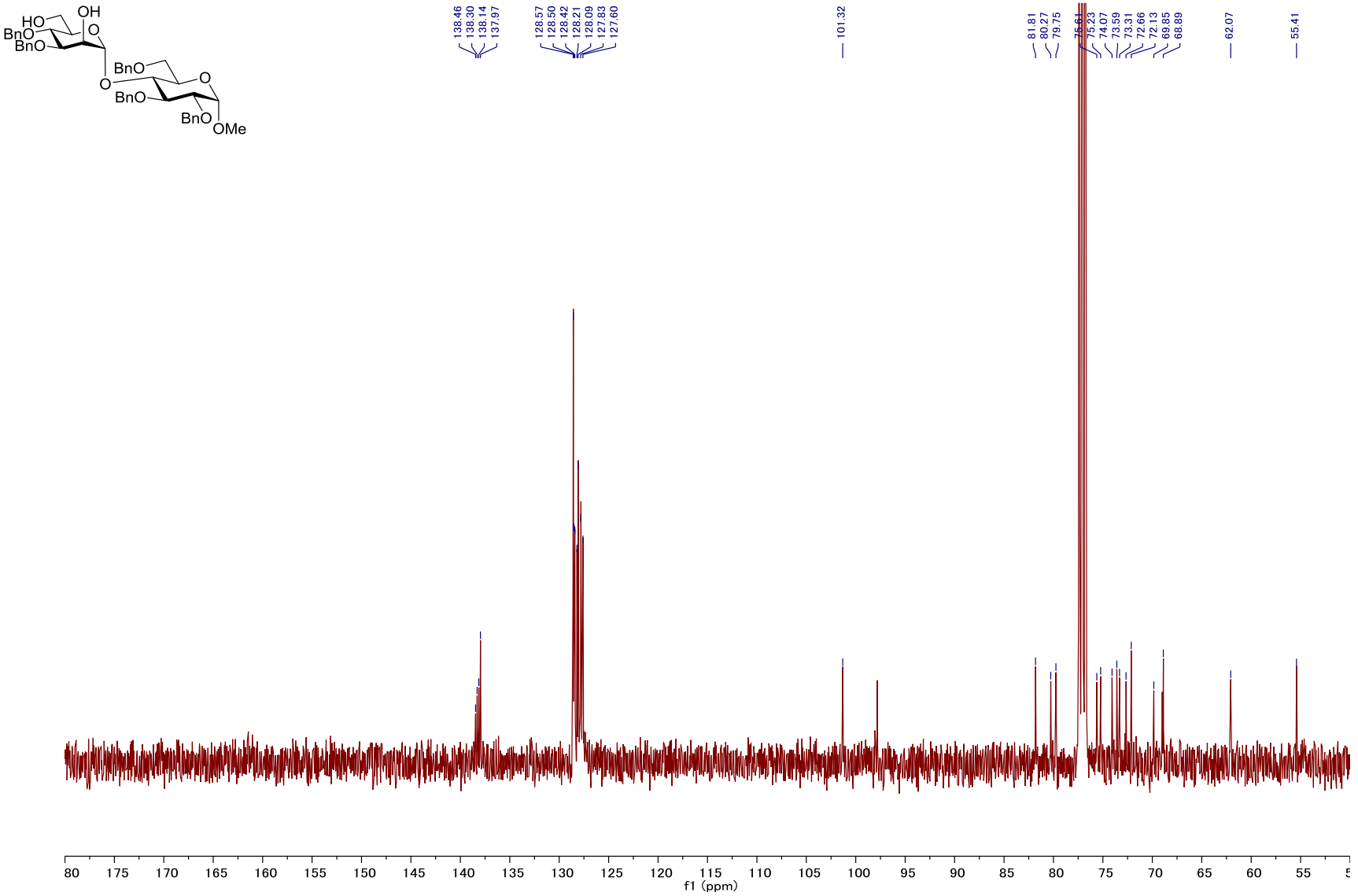
Methyl

2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-glucopyranoside (S5e) ^{1}H NMR (400 MHz, $CDCl_3$)



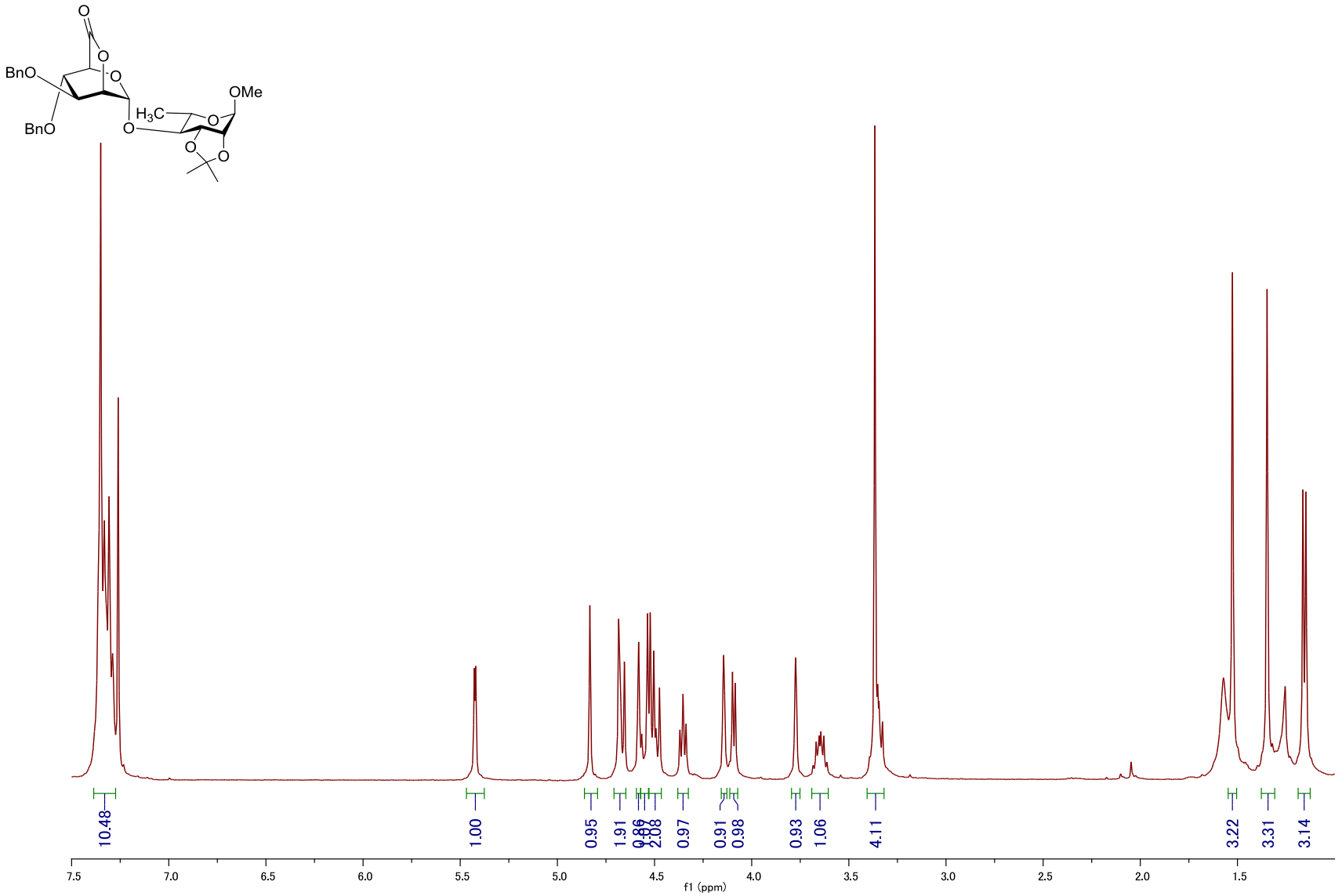
Methyl

2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranosyl)-α-D-glucopyranoside (S5e) ^{13}C NMR (100 MHz, $CDCl_3$)



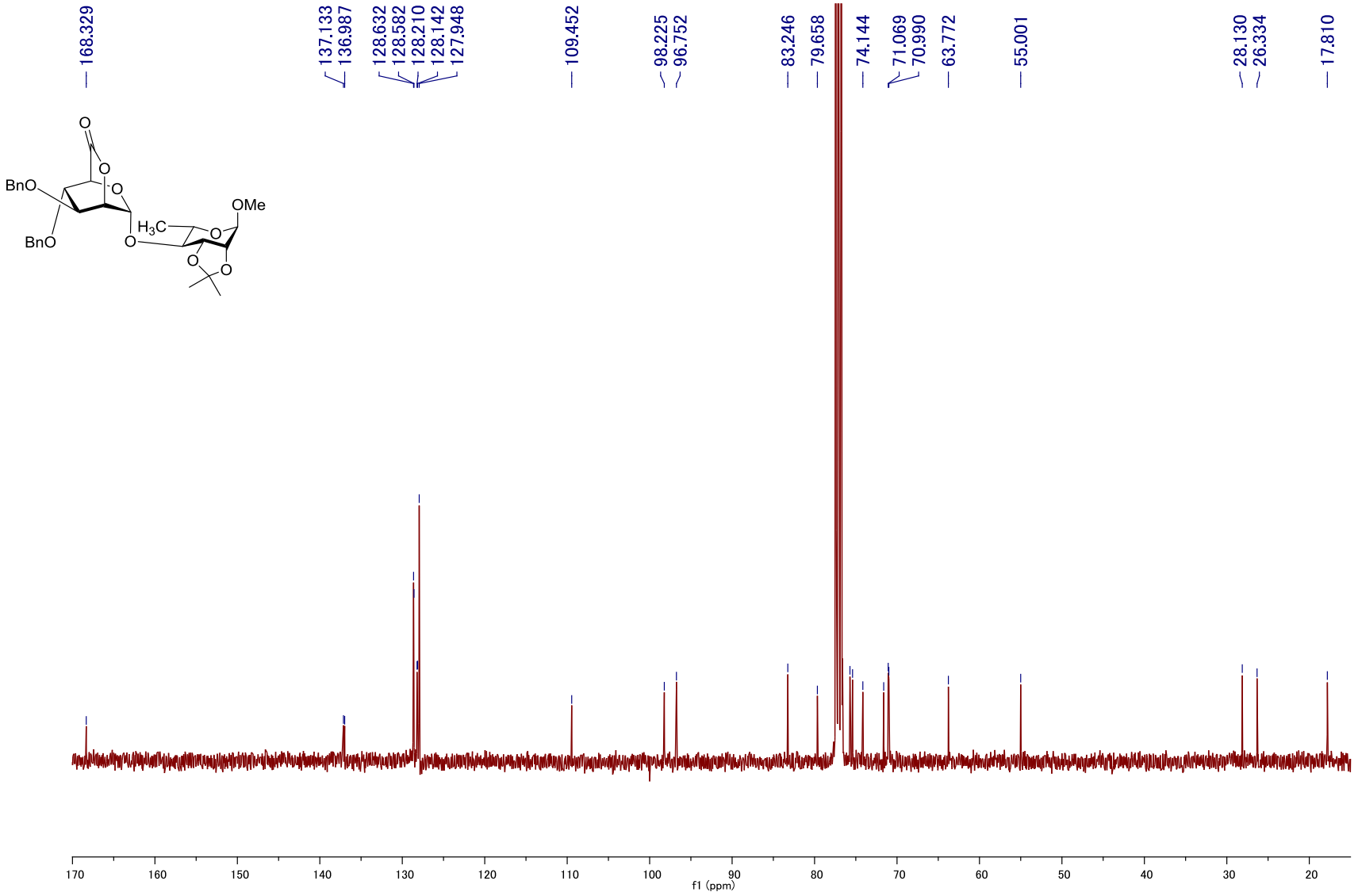
Methyl

2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bα) ^{1}H NMR (400 MHz,



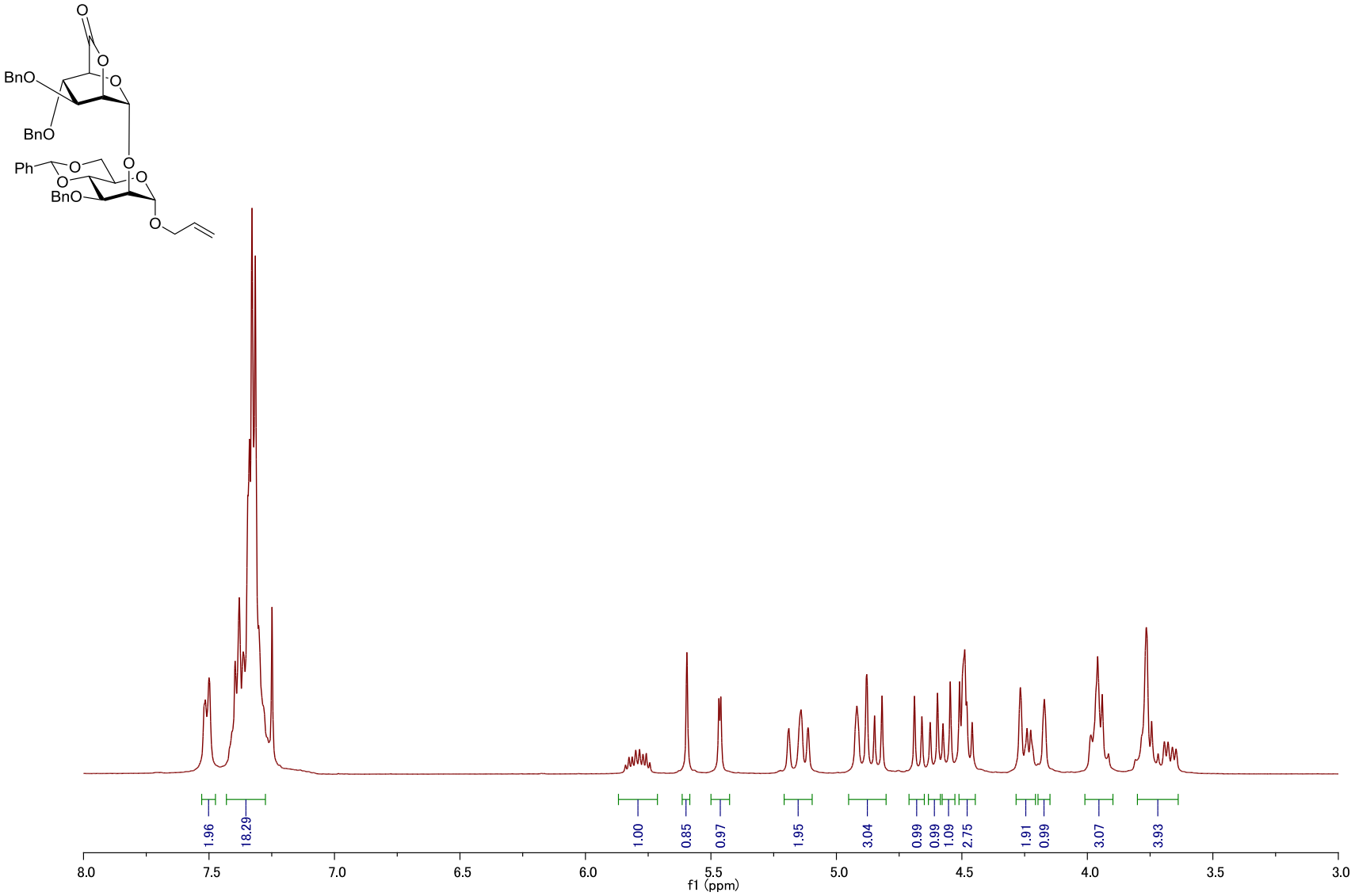
Methyl

2,3-*O*-isopropylidene-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-L-rhamnopyranoside (7bα) ^{13}C NMR (100 MHz,



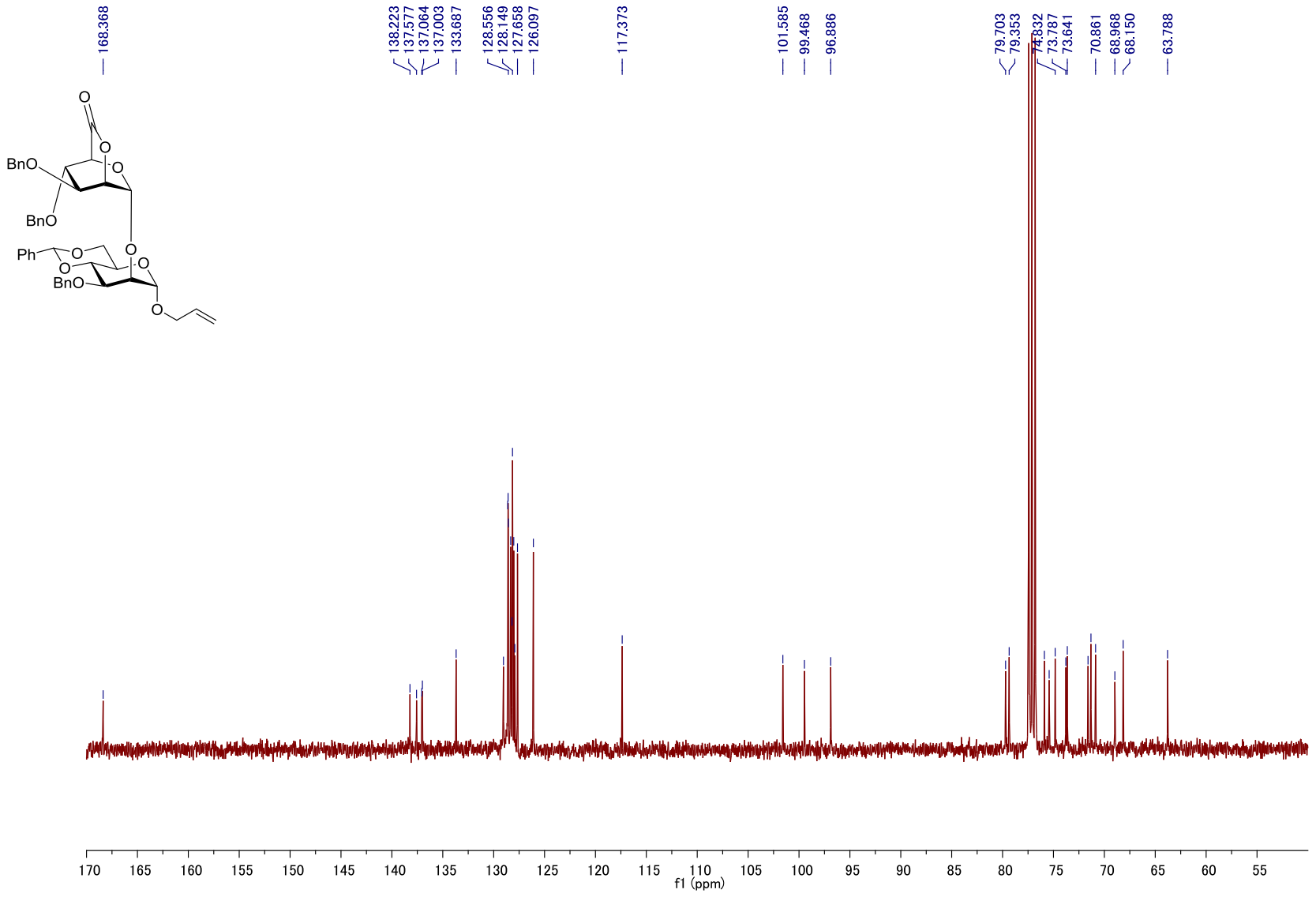
Allyl

2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cα) ^{1}H NMR (400 MHz, $CDCl_3$)



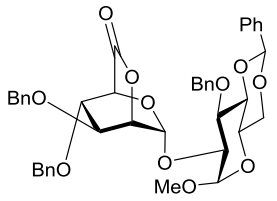
Allyl

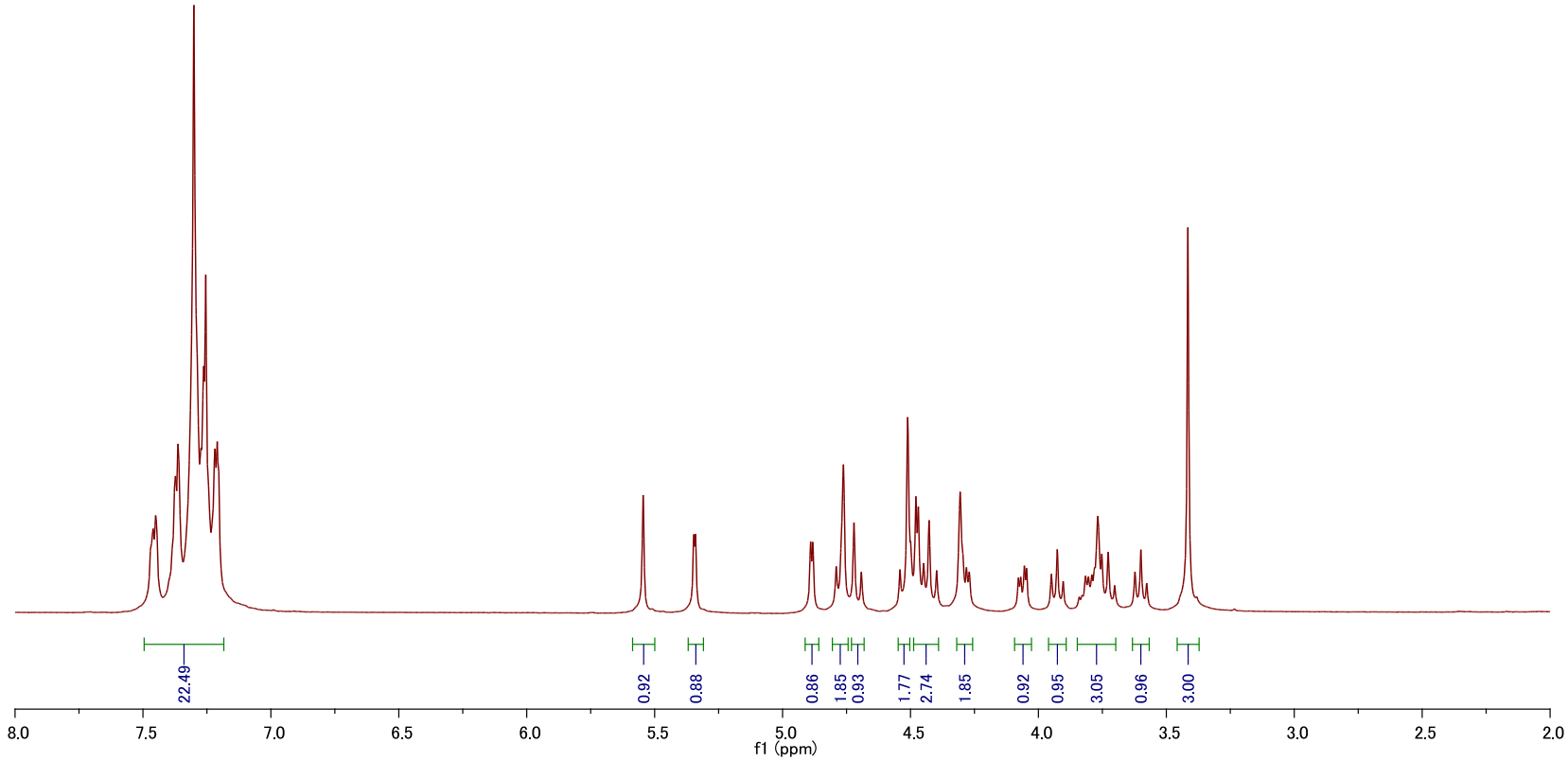
2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (7cα) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

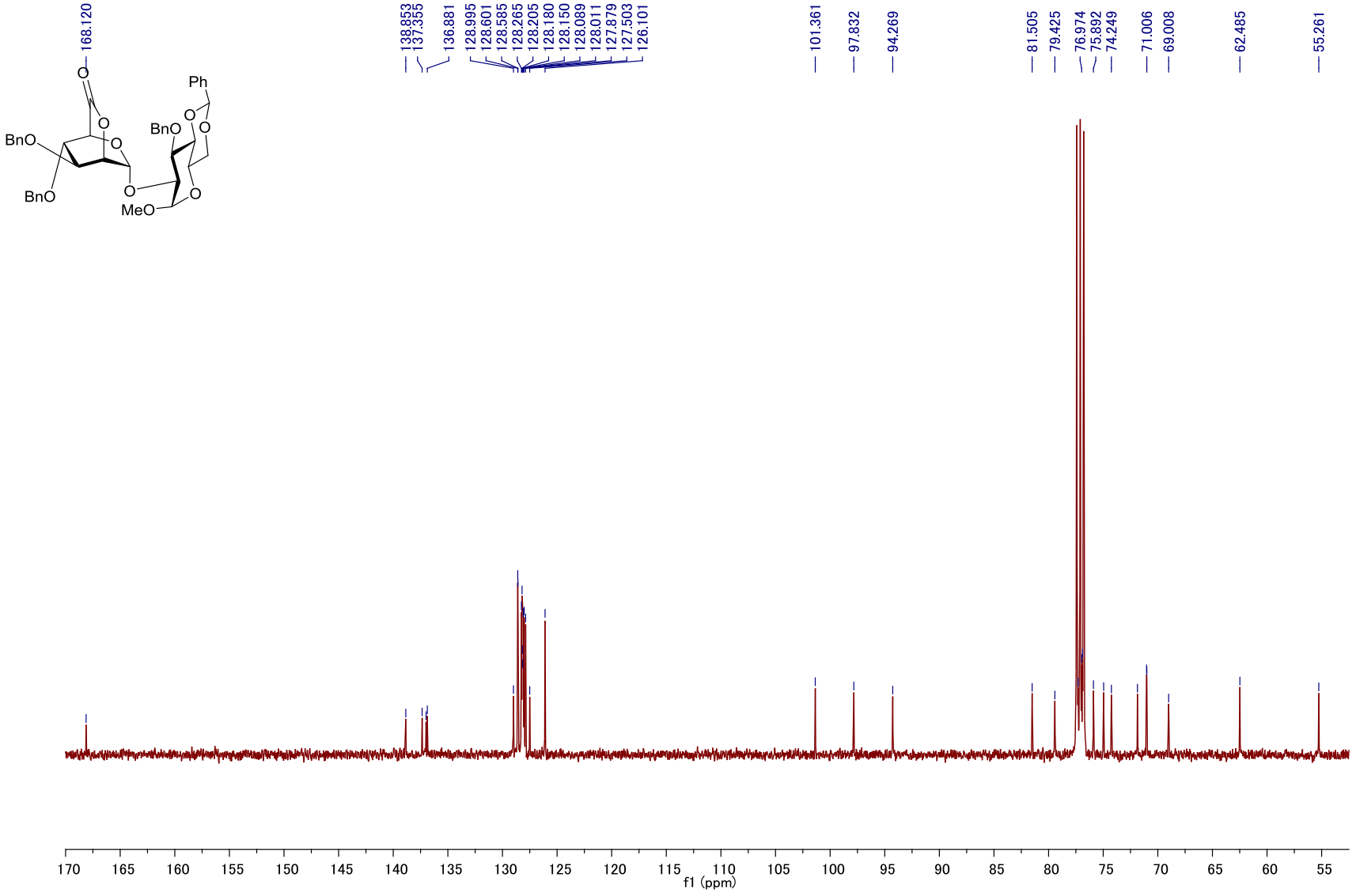
2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dα) ^{1}H NMR (400 MHz, $CDCl_3$)





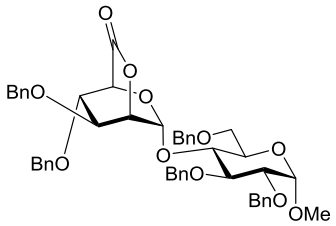
Methyl

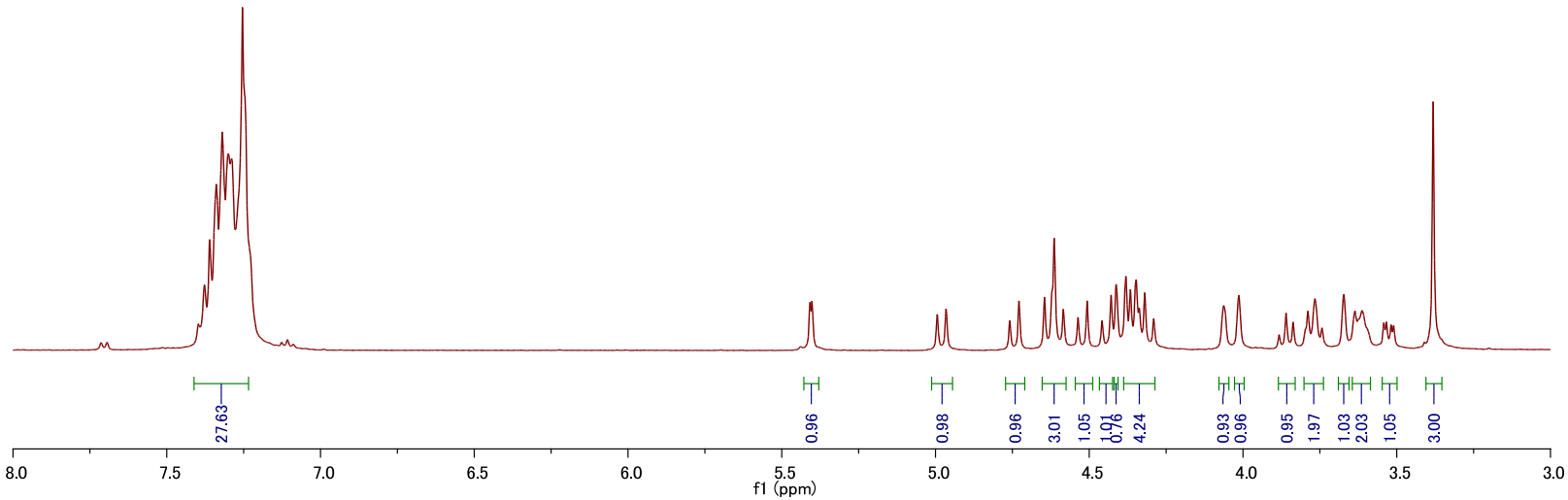
2-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (7dα) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

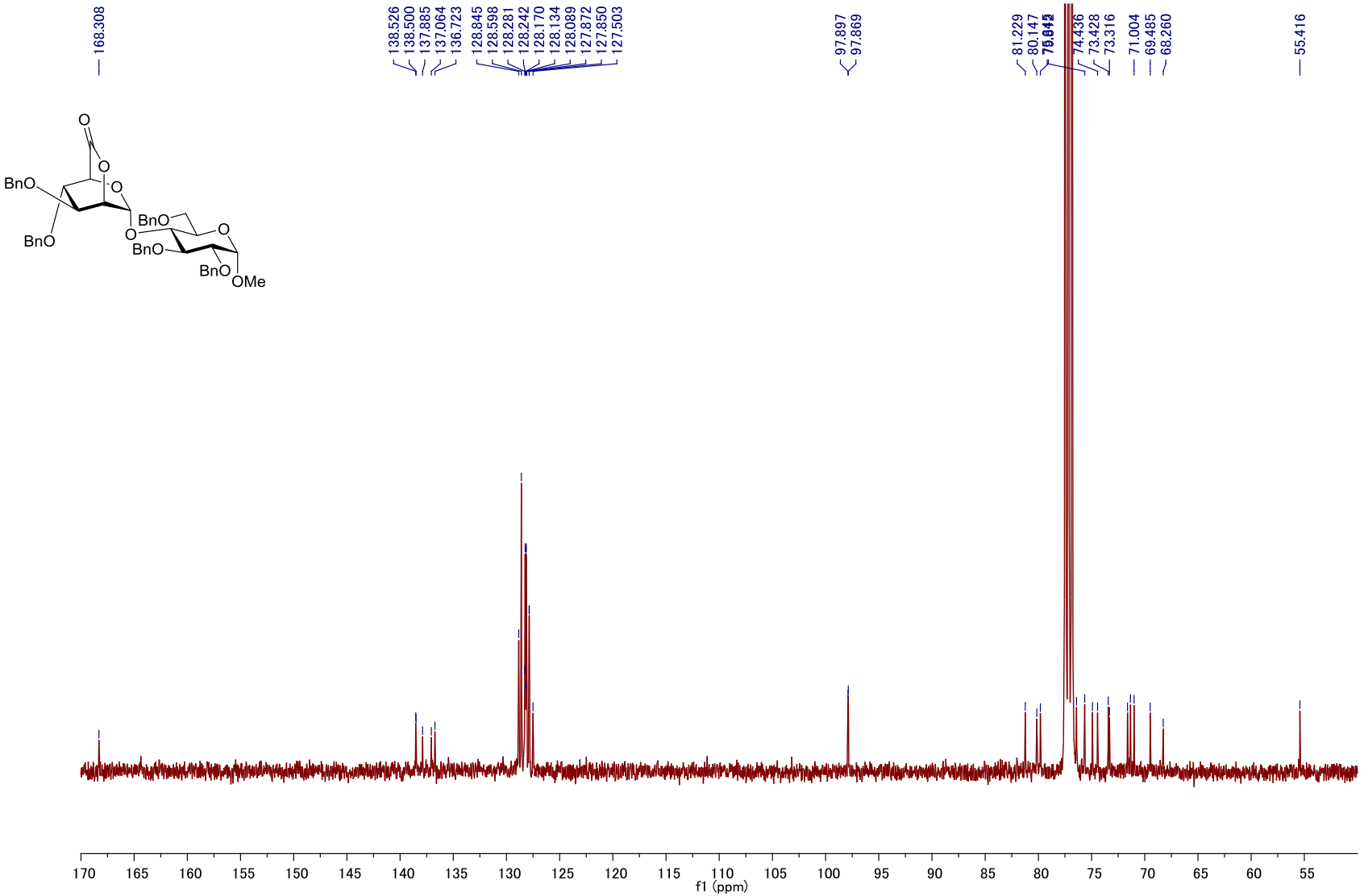
2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eα) ^{1}H NMR (400 MHz, $CDCl_3$)





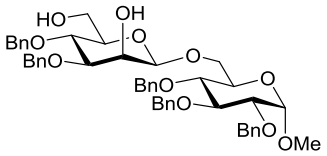
Methyl

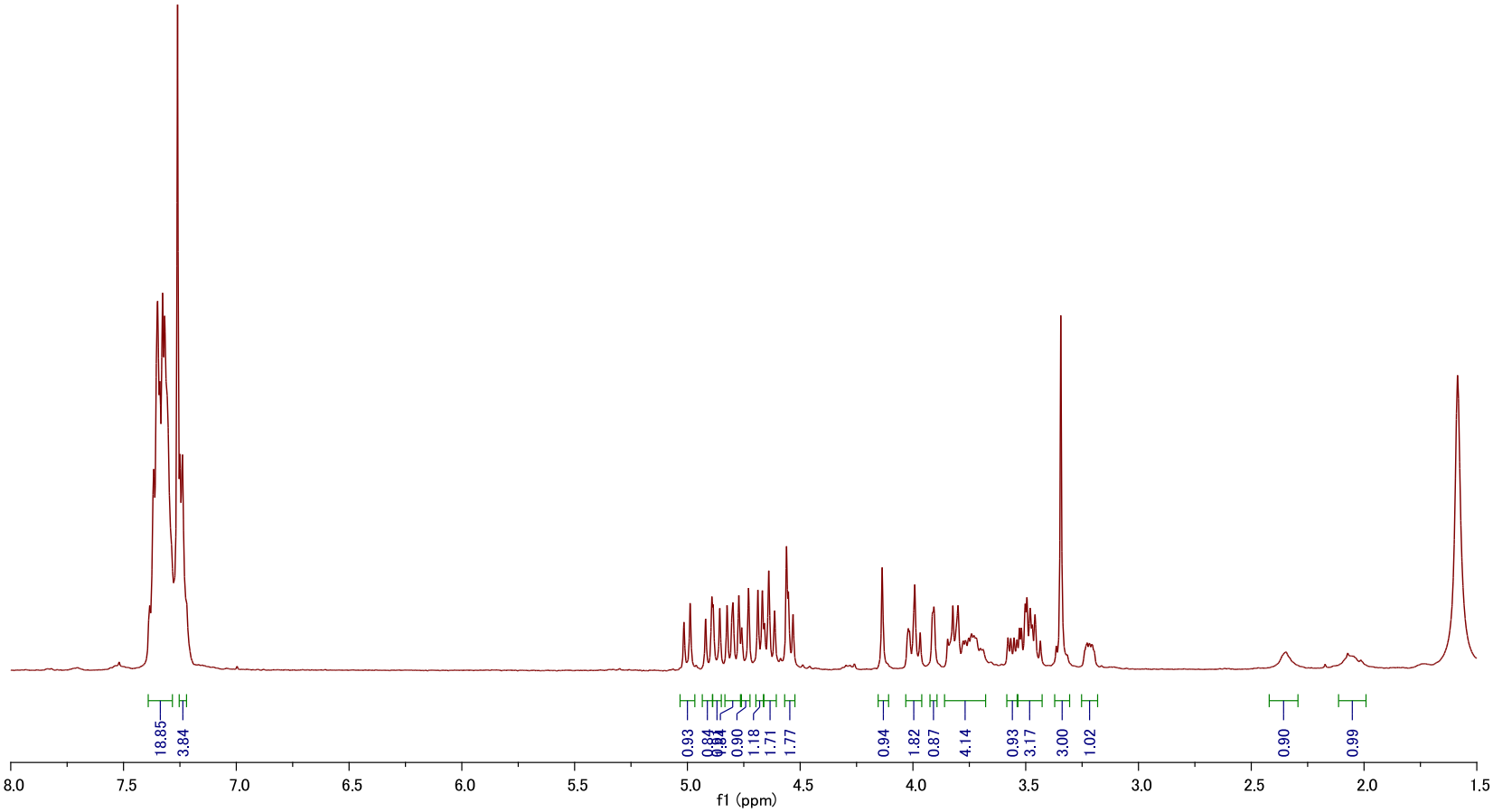
2,3,6-tri-*O*-benzyl-4-*O*-(3',4'-di-*O*-benzyl-α-D-mannopyranurono-2',6'-lacton-1'-yl)-α-D-glucopyranoside (7eα) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

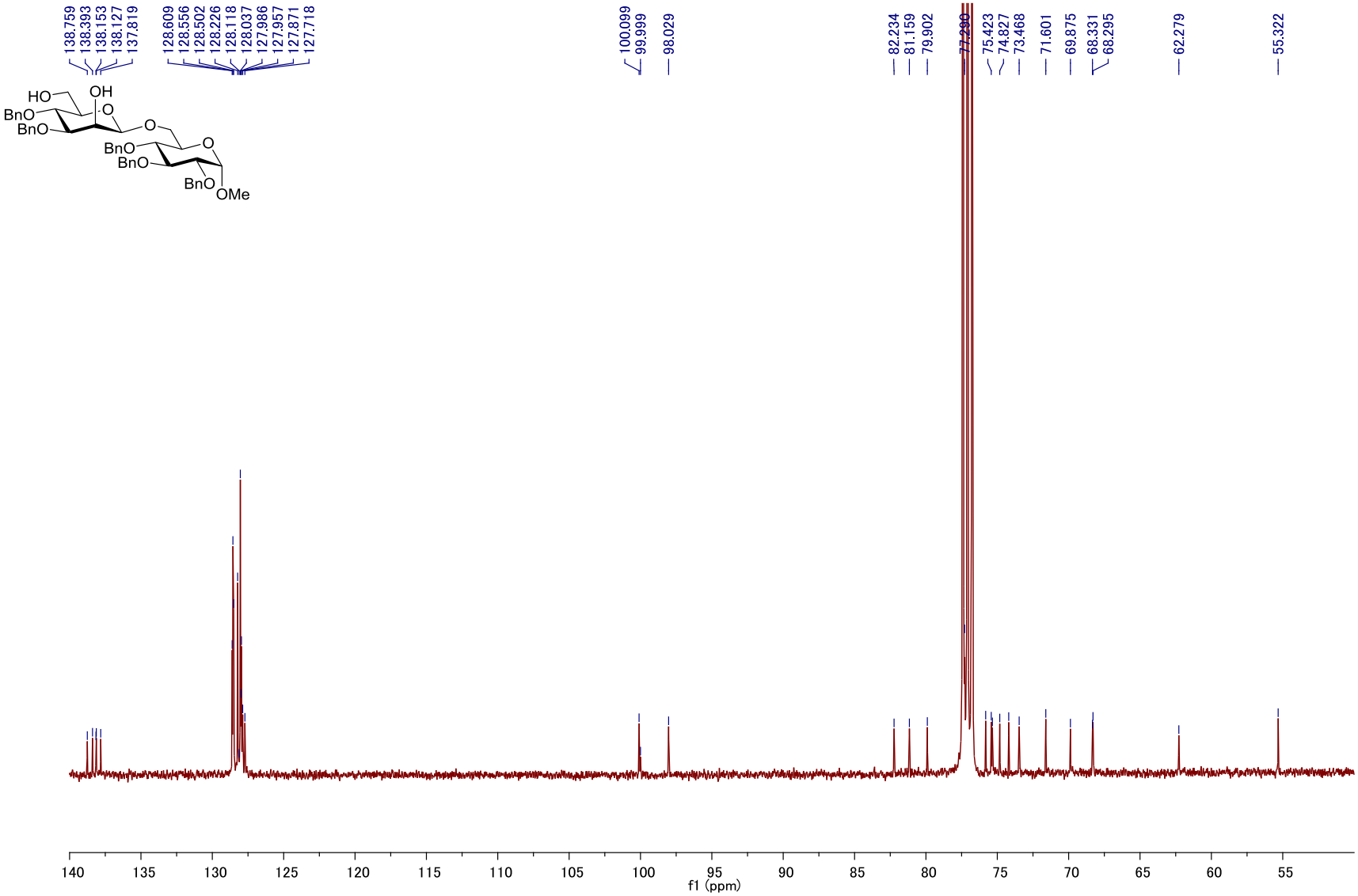
2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranoyl)-α-D-glucopyranoside (8) ^{1}H NMR (400 MHz, $CDCl_3$)





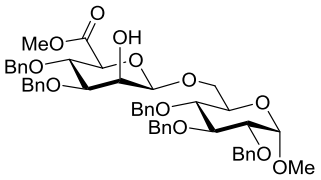
Methyl

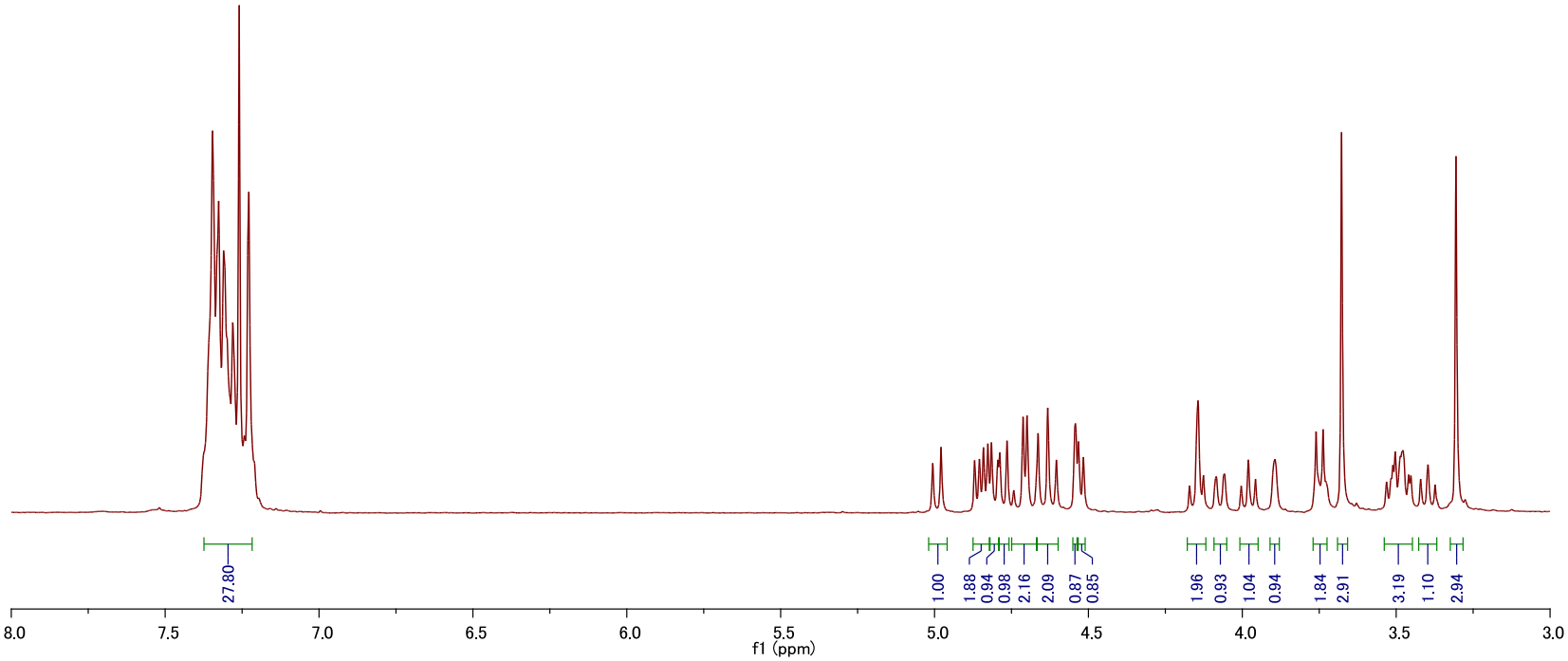
2,3,4-tri-*O*-benzyl-6-*O*-(3',4'-di-*O*-benzyl-β-D-mannopyranoyl)-α-D-glucopyranoside (8) ^{13}C NMR (100 MHz, $CDCl_3$)



Methyl

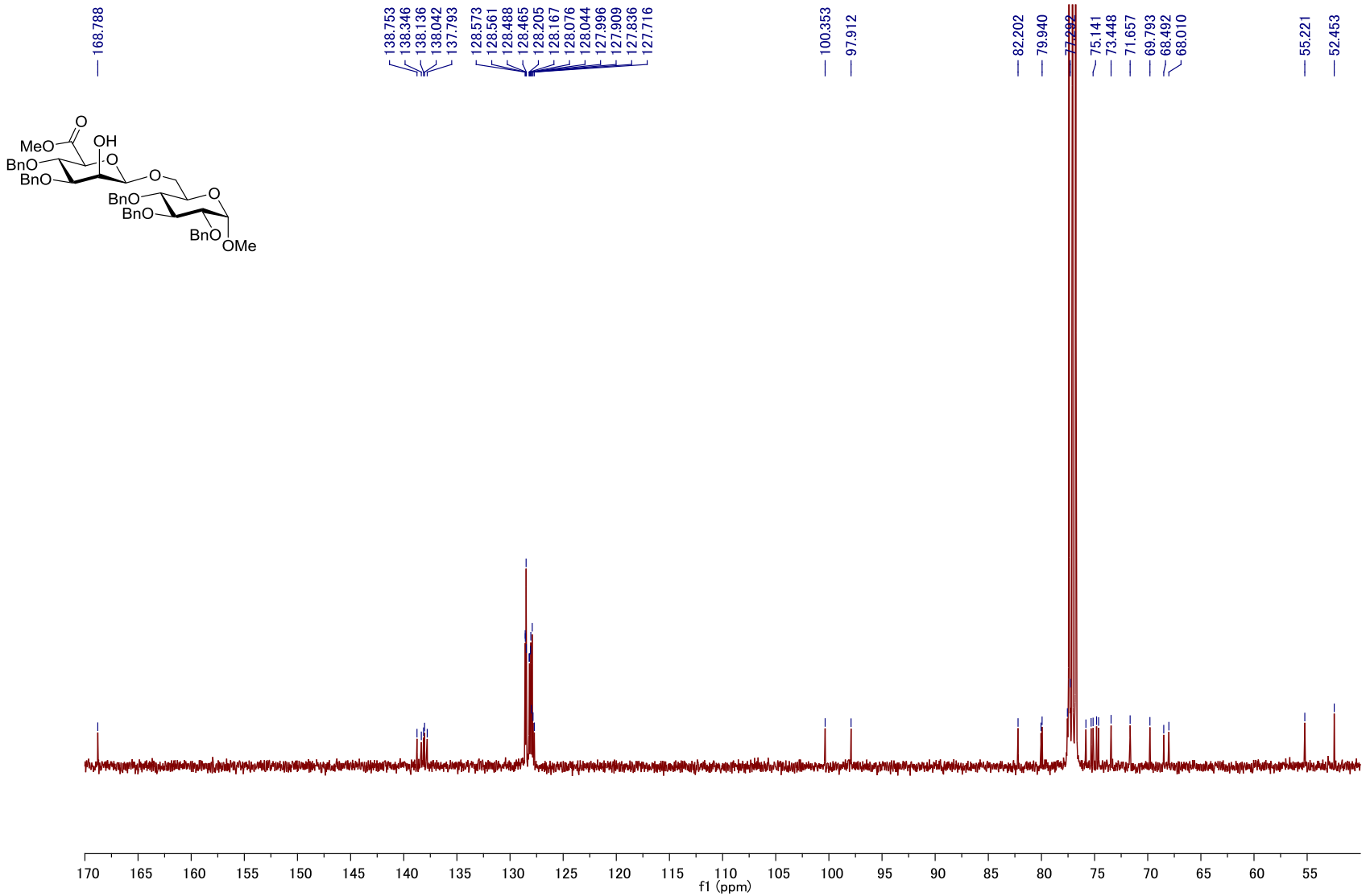
2,3,4-Tri-*O*-benzyl-6-*O*-(methyl (3',4'-di-*O*-benzyl-β-D-mannopyranosyl) uronate)-α-D-glucopyranoside (9) ^{1}H NMR (400 MHz, $CDCl_3$)



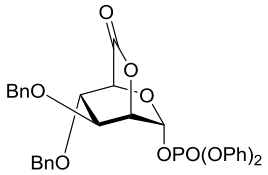


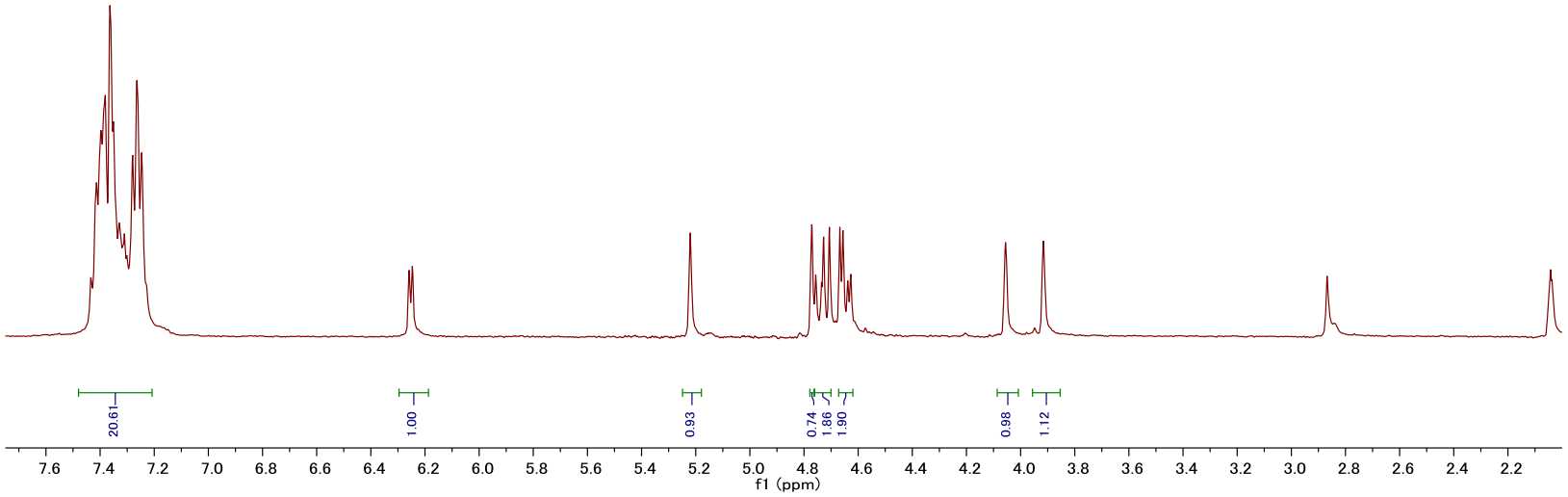
Methyl

2,3,4-Tri-*O*-benzyl-6-*O*-(methyl (3',4'-di-*O*-benzyl-β-D-mannopyranosyl) uronate)-α-D-glucopyranoside (9) ^{13}C NMR (100 MHz, $CDCl_3$)

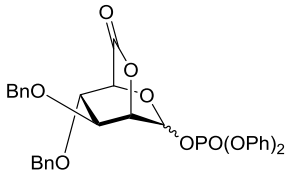


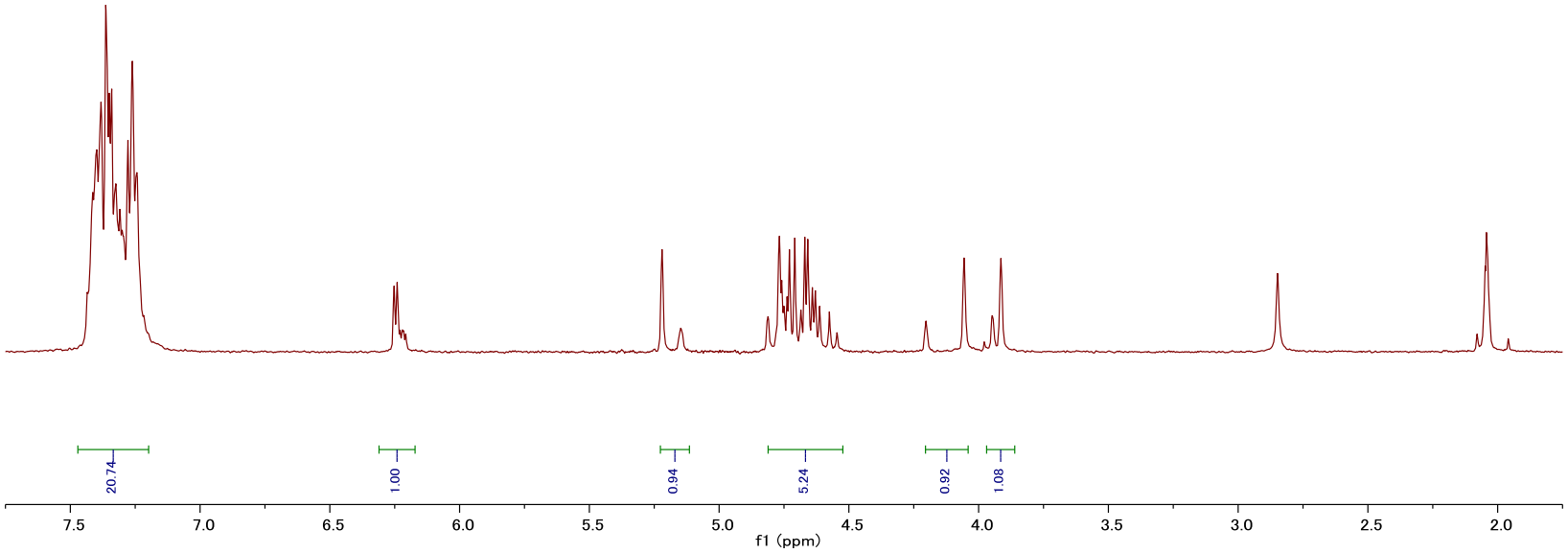
3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diphenylphosphate (10α) ^{1}H NMR (400 MHz, $(CD_3)_2CO$)



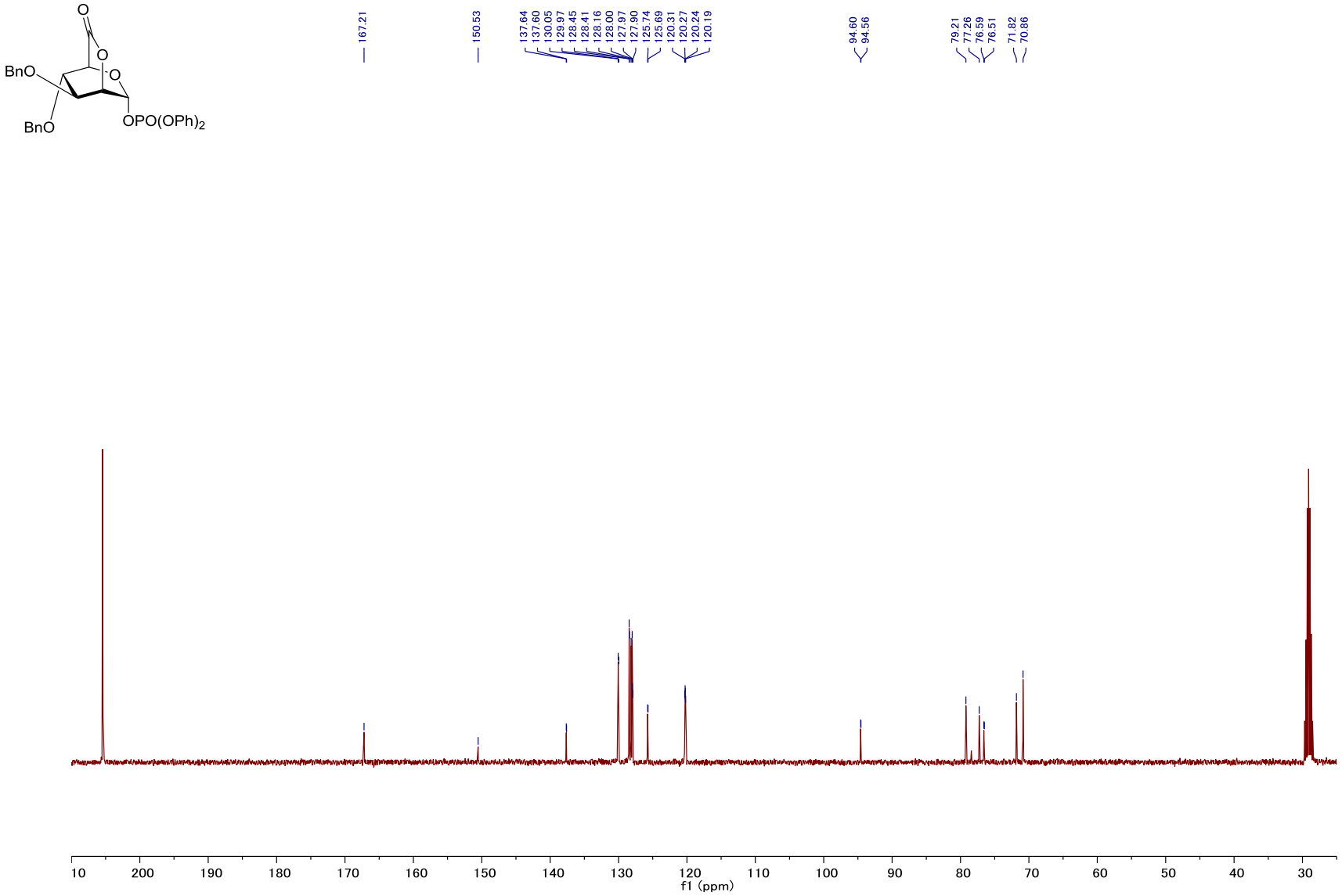


3,4-Di-*O*-benzyl-D-mannopyranurono-2,6-lacton-1-yl diphenylphosphate (10αβ) ^{1}H NMR (400 MHz, $(CD_3)_2CO$)

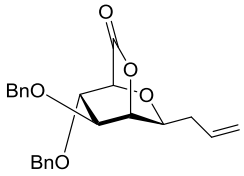


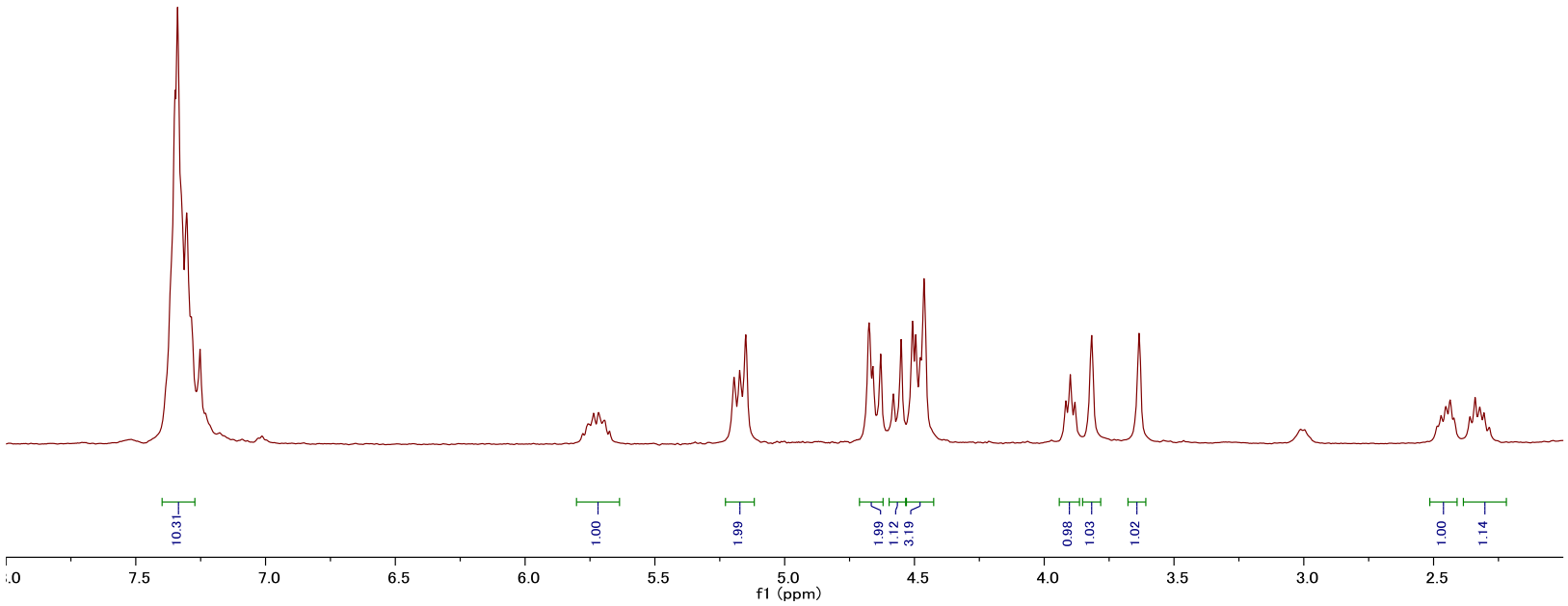


3,4-Di-*O*-benzyl-α-D-mannopyranurono-2,6-lacton-1-yl diphenylphosphate (10α) ^{13}C NMR (100 MHz, $(CD_3)_2CO$)

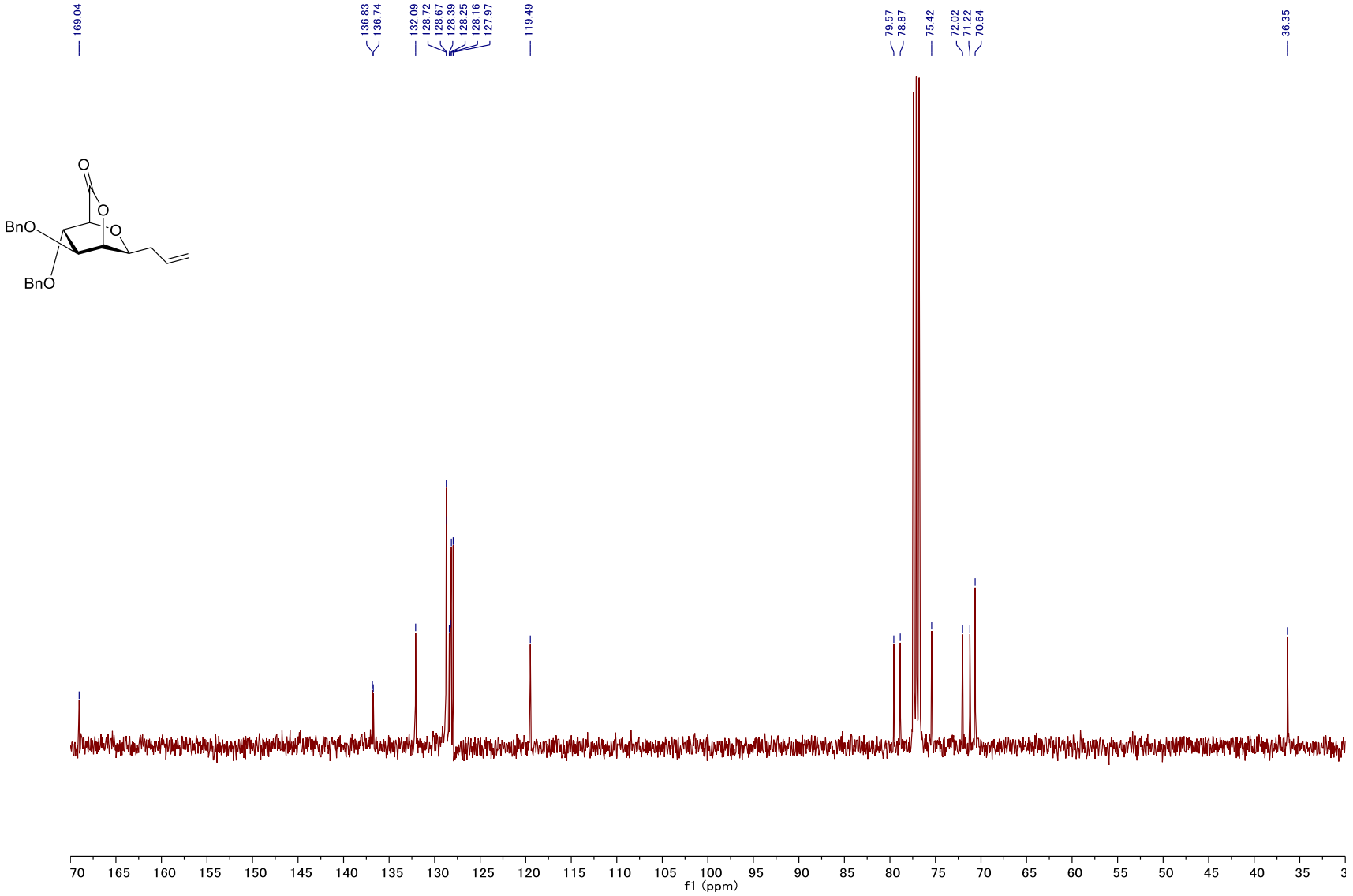


3-(3',4'-Di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)propene (11) ^{1}H NMR (400 MHz, $CDCl_3$)

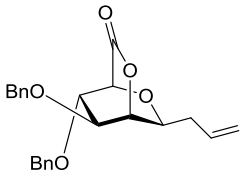


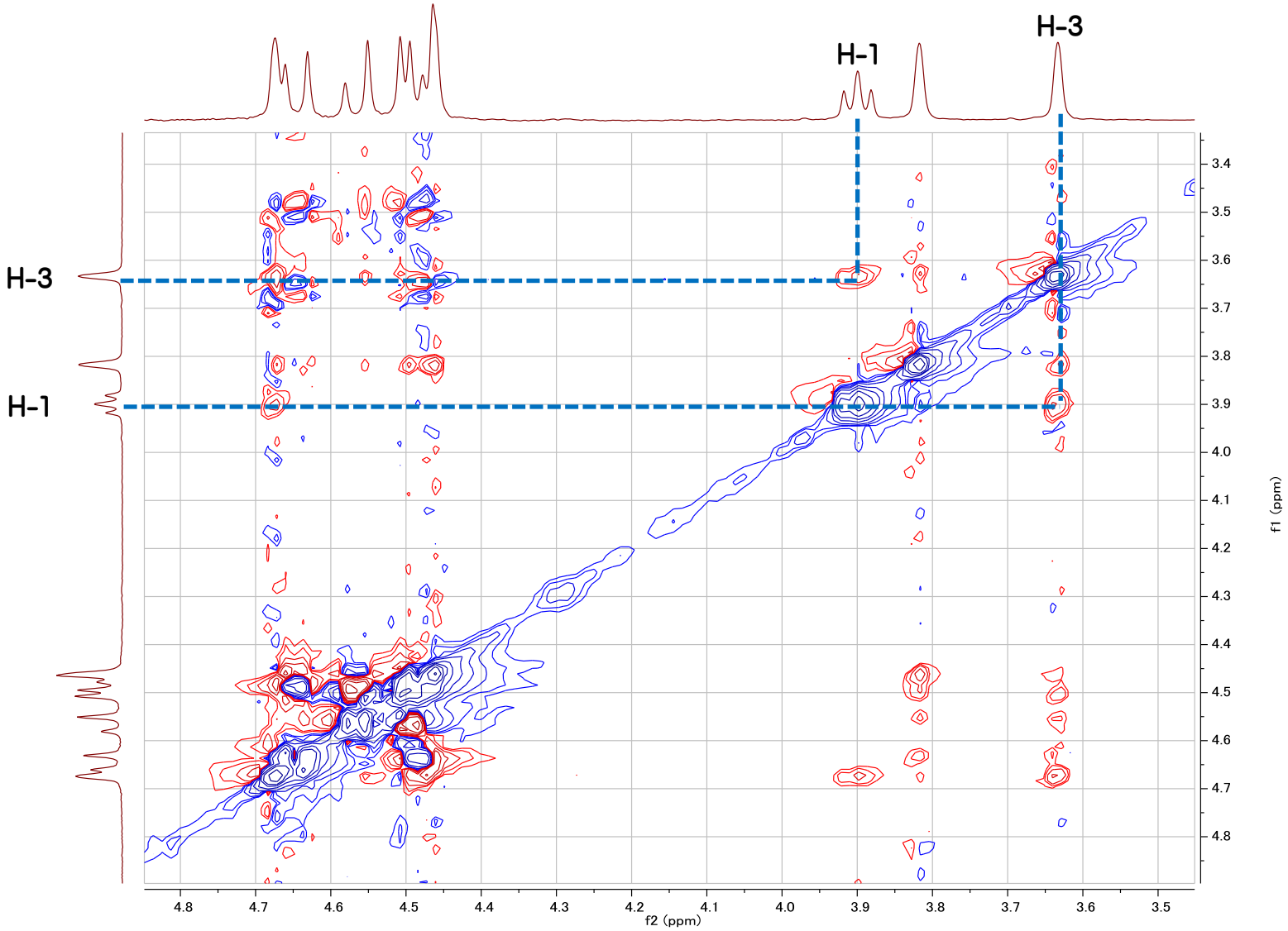


3-(3',4'-Di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)propene (11) ^{13}C NMR (100 MHz, $CDCl_3$)



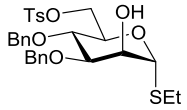
3-(3',4'-Di-*O*-benzyl-β-D-mannopyranurono-2',6'-lacton-1'-yl)propene (11) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)

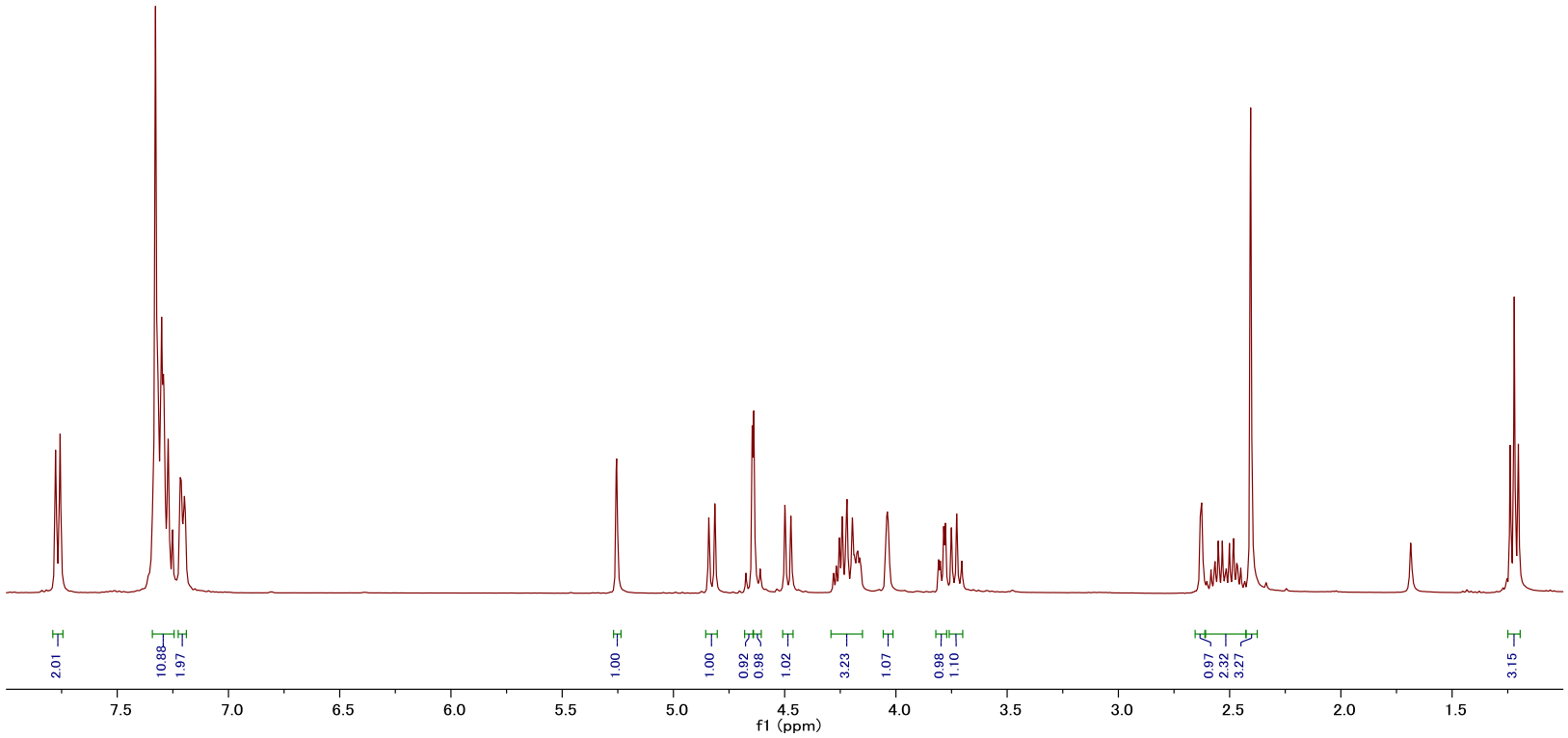




Ethyl

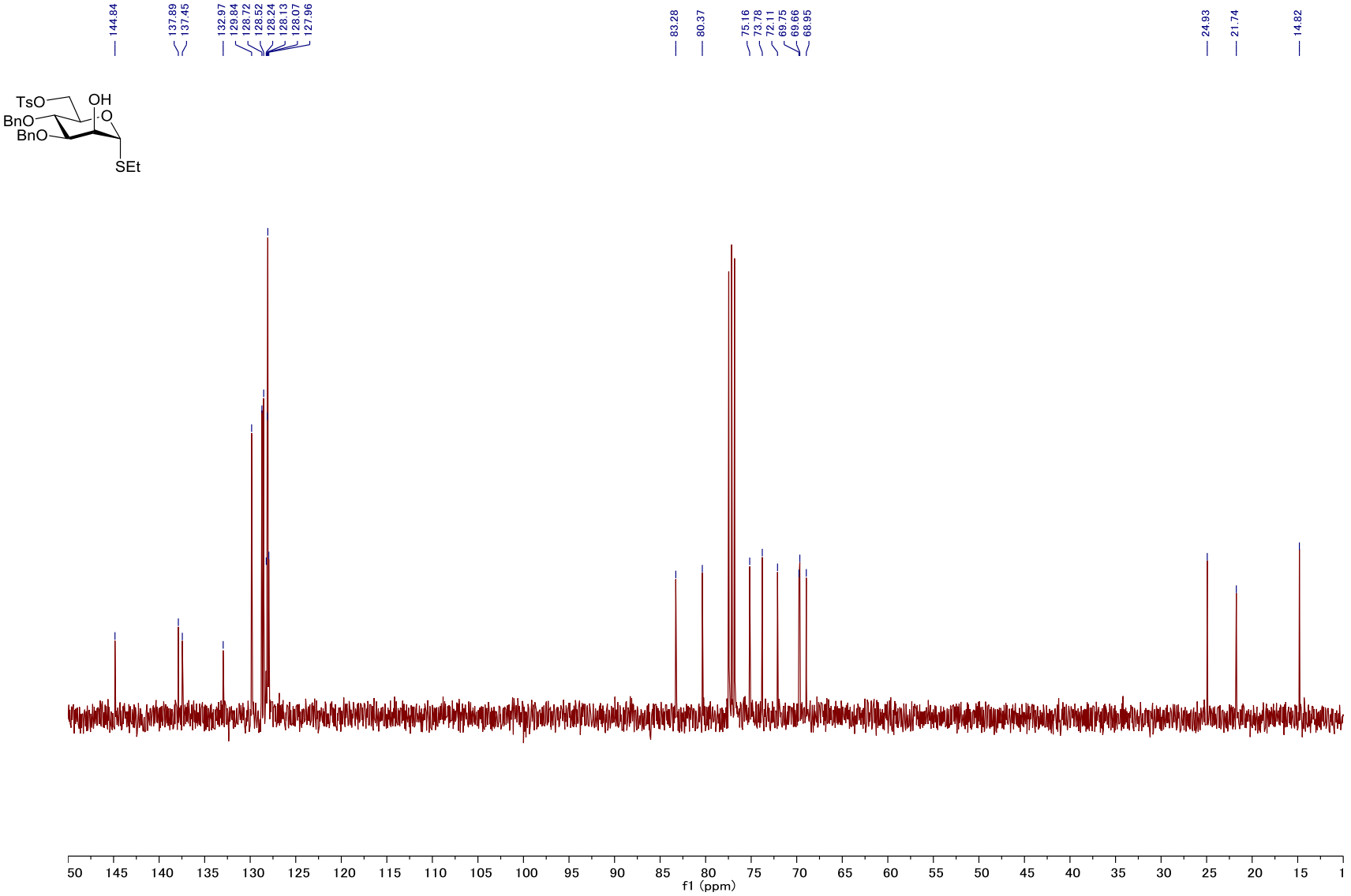
1-thio-3,4-di-*O*-benzyl-6-*O*-tosyl-α-D-mannopyranoside (S7) ^{1}H NMR (400 MHz, $CDCl_3$)





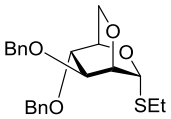
Ethyl

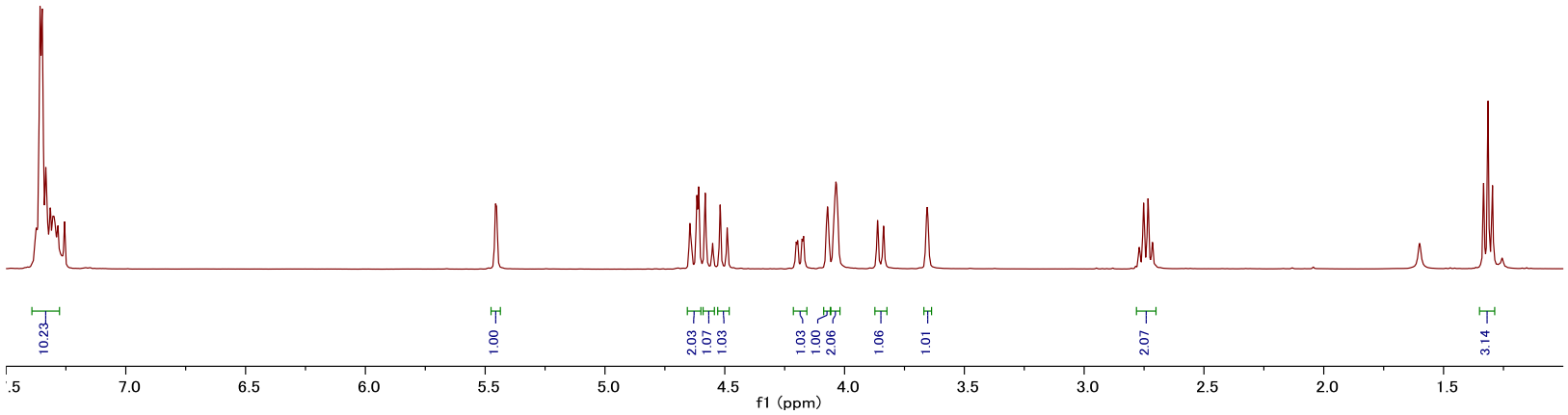
1-thio-3,4-di-*O*-benzyl-6-*O*-tosyl-α-D-mannopyranoside (S7) ^{13}C NMR (100 MHz, $CDCl_3$)



Ethyl

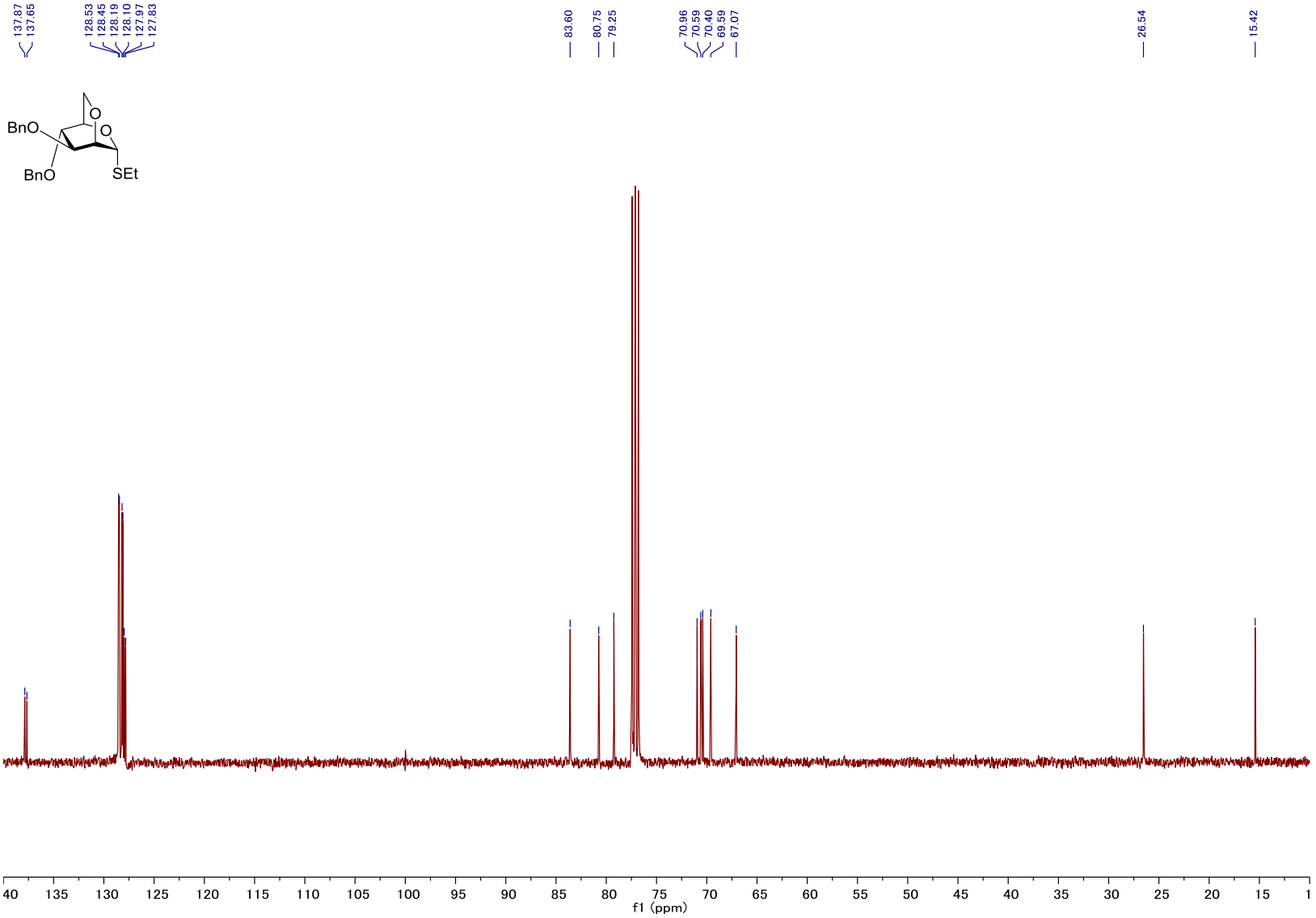
1-thio-3,4-di-*O*-benzyl-2,6-anhydro-α-D-mannopyranoside (S8) ^{1}H NMR (400 MHz, $CDCl_3$)



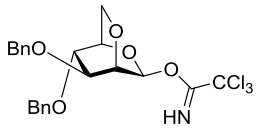


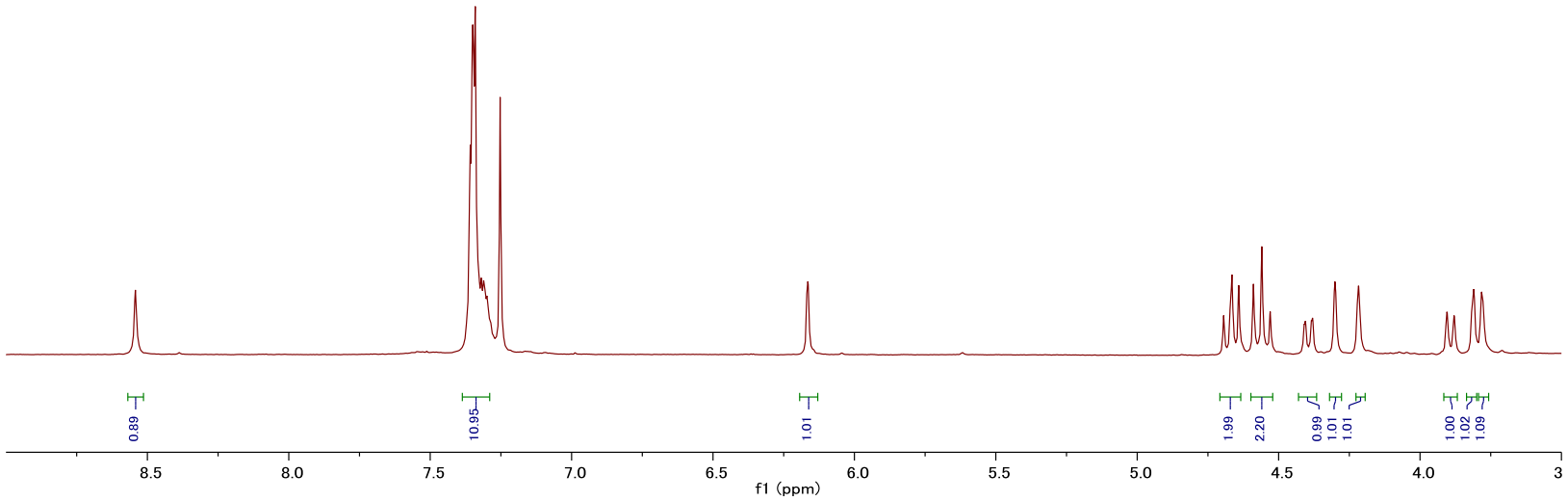
Ethyl

1-thio-3,4-di-*O*-benzyl-2,6-anhydro-α-D-mannopyranoside (S8) ^{13}C NMR (100 MHz, $CDCl_3$)

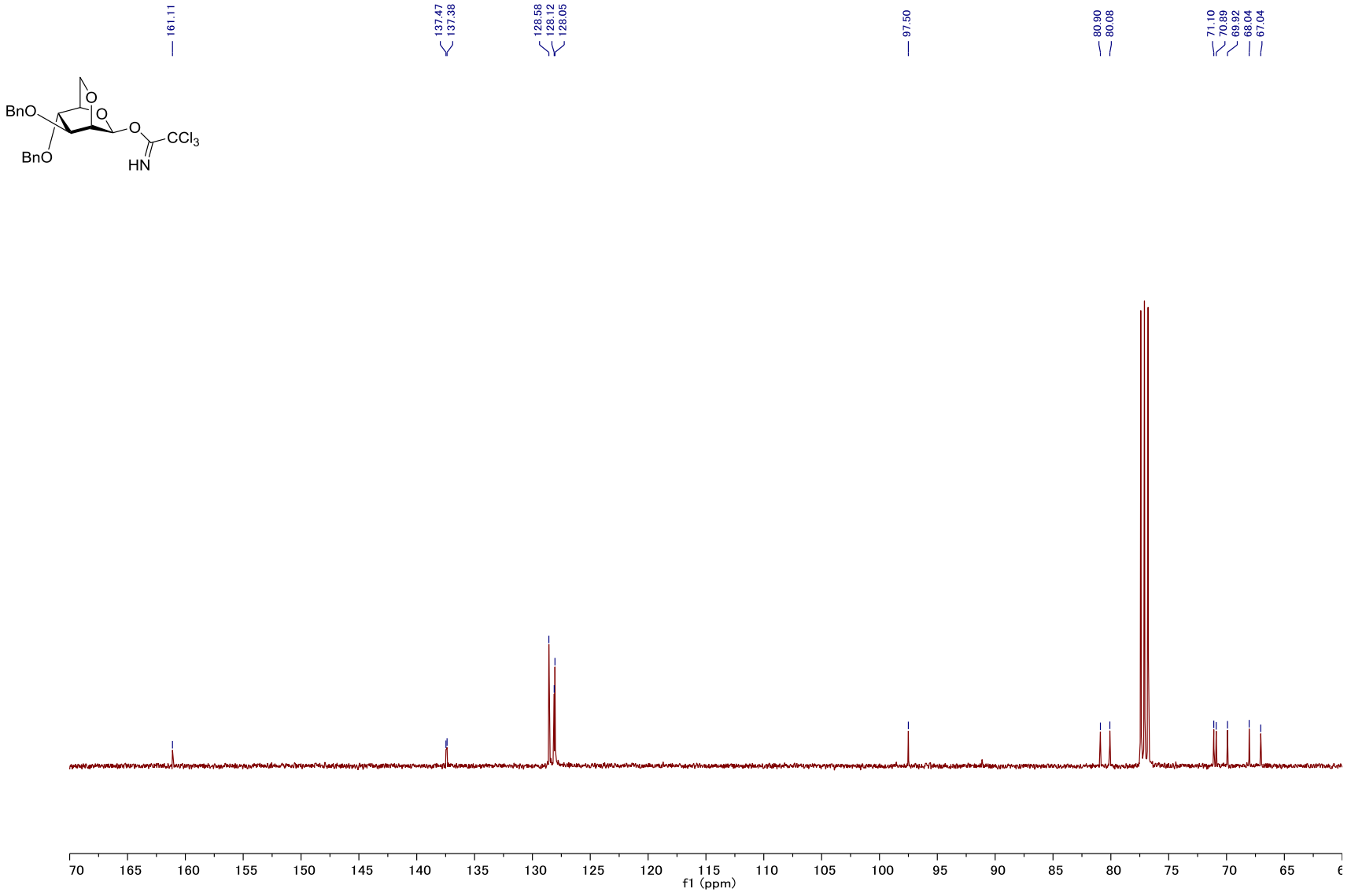


3,4-Di-*O*-benzyl-2,6-anhydro-β-D-mannopyranosyl trichloroacetimidate (12) ^{1}H NMR (400 MHz, $CDCl_3$)





3,4-Di-*O*-benzyl-2,6-anhydro-β--D-mannopyranosyl trichloroacetimidate (12) ^{13}C NMR (100 MHz, $CDCl_3$)



3,4-Di-*O*-benzyl-2,6-anhydro-β--D-mannopyranosyl trichloroacetimidate (12) ^{1}H-^{1}H NOESY (400 MHz, $CDCl_3$)