Supporting Information

Synthesis of D-*glycero*-D-*manno*-heptose-1β,7-bisphosphate (HBP) from D-mannurono-2,6-lactone

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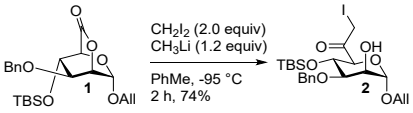
General Information

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 , ^{13}C and ^{31}P NMR spectra were recorded on a JEOL Ltd. JNM-ECP400 series (400 MHz). Chemical shifts (δ) are reported in parts per million (ppm) downfield or upfield from tetramethylsilane (δ 0.00), $CHCl_3$ (δ 7.26), or DHO (δ 4.79) 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 $CDCl_3$ (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).

Experimental procedure

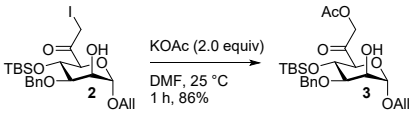
Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-7-deoxy-7-iodo-6-oxo-α-D-*manno*-heptopyranoside (2)



Under Ar atmosphere, to a solution of **1** (3.6 g, 8.6 mmol) in anhydrous PhMe (43 mL) was added CH_2I_2 (1.4 mL, 17 mmol) at 25 ºC. Then the mixture was cooled to -95 ºC and CH_3Li in Et_2O (1.2 M, 7.5 mL, 10 mmol) was added at -95 ºC and stirred for 2 h at -95 ºC. After the TLC analysis indicated the completion of reaction, the reaction was quenched with sat. NH_4Cl aq. (10 mL) and the mixture was poured to water (50 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel 30 g, hexane/EtOAc = 19/1→4/1, v/v), which gave the title compound **2** (3.6 g, 74%) as a yellow oil. R_f = 0.53 (hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = +35.6 (*c* 2.6, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.31 (m, 5H, Ar-H), 5.98-5.88 (m, 1H, H_β), 5.32 (dd, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, $J_{\gamma\ trans,\beta}$ = 17.2 Hz, 1H, $H_{\gamma\ trans}$), 5.25 (dd, $J_{\gamma\ cis,\gamma\ trans}$ = 1.6 Hz, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, 1H, $H_{\gamma\ cis}$), 4.96 (d, $J_{1,2}$ = 2.1 Hz, 1H, H-1), 4.63 & 4.57 (ABq, J = 11.2 Hz, 2H, $PhCH_2$), 4.46 (d, $J_{4,5}$ = 8.8 Hz, 1H, H-5), 4.30 (dd, $J_{\alpha,\alpha}$ = 12.0 Hz, $J_{\alpha,\beta}$ = 4.8 Hz, 1H, H_α), 4.14 (dd, $J_{4,5}$ =8.4 Hz, $J_{3,4}$ = 8.4 Hz, 1H, H-4), 4.07 (d, $J_{7,7}$ = 11.2 Hz, 1H, H-7), 4.06 (dd, $J_{\alpha,\alpha}$ = 12.0 Hz, $J_{\alpha,\beta}$ = 4.8 Hz, 1H, H_α), 3.97 (m, 1H, H-2), 3.96 (d, $J_{7,7}$ = 11.2 Hz, 1H, H-7), 3.70 (dd, $J_{3,4}$ = 8.4 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-3), 0.85 (s, 9H, $C(CH_3)_3$), 0.04 (s, 3H, $Si(CH_3)$), 0.01 (s, 3H, $Si(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$,

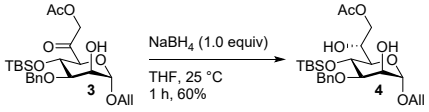
TMS) δ 198.4, 137.6, 133.5, 128.6, 128.1, 127.9, 118.2, 98.9, 80.1, 74.2, 71.8, 68.9, 68.4, 67.5, 26.0, 18.2, 5.0, -4.0, -4.6; HRMS (ESI) Calcd for $C_{23}H_{35}O_6ISiNa$ $[M+Na]^+$: 585.1139, found: 585.1163.

Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-oxo-α-D-*manno*-heptopyranoside (3)



Under Ar atmosphere, to a solution of **2** (5.1 g, 9.1 mmol) in anhydrous DMF (18 mL) was added KOAc (1.8 g, 18 mmol) at 25 ºC and stirred for 1 h at 25 ºC. After the TLC analysis indicated the completion of reaction, the mixture was poured to water (50 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with brine (50 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by flash column chromatography (silica gel 25 g, hexane/EtOAc - = 9/1→7/3, v/v), which gave the title compound **3** (3.8 g, 86%) as a yellow oil. R_f = 0.38 (hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = +31.0 (*c* 3.3, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.27-7.21 (m, 5H, Ar-H), 5.85-5.75 (m, 1H, H_β), 5.20 (dddd, $J_{\gamma\ trans,\beta}$ = 17.6 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.7 Hz, $J_{\gamma\ trans,\alpha}$ = 1.7 Hz, $J_{\gamma\ trans,\alpha}$ = 1.7 Hz, 1H, $H_{\gamma\ trans}$), 5.14 (dddd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.7 Hz, $J_{\gamma\ cis,\alpha}$ = 1.7 Hz, $J_{\gamma\ cis,\alpha}$ = 1.7 Hz, 1H, $H_{\gamma\ cis}$), 4.85 (s, 2H, H-7), 4.84 (d, $J_{1,2}$ = 2.4 Hz, 1H, H-1), 4.53 & 4.46 (ABq, *J* = 11.6 Hz, 2H, $PhCH_2$), 4.11 (dddd, $J_{\alpha,\alpha}$ = 12.9 Hz, $J_{\alpha,\beta}$ = 5.2 Hz, $J_{\alpha,\gamma}$ = 1.5 Hz, $J_{\alpha,\gamma}$ = 1.5 Hz, 1H, H_α), 4.04-4.03 (m, 2H, H-4&H-5), 3.92 (dddd, $J_{\alpha,\alpha}$ = 12.9 Hz, $J_{\alpha,\beta}$ = 6.1 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 3.86 (m, 1H, H-2), 3.60-3.57 (m, 1H, H-3), 2.06 (s, 3H, CH_3), 0.74 (s, 9H, $C(CH_3)_3$), -0.05 (s, 3H, $Si(CH_3)$), -0.09 (s, 3H, $Si(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 199.1, 170.1, 137.6, 133.4, 128.6, 128.0, 127.9, 118.0, 98.8, 79.9, 76.2, 71.8, 68.9, 67.8, 67.5, 66.4, 25.9, 20.5, 18.1, -4.1, -4.9; HRMS (ESI) Calcd for $C_{25}H_{38}O_8SiNa$ $[M+Na]^+$: 517.2228, found: 517.2236.

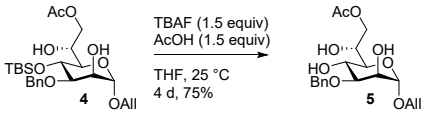
Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (4)



Under Ar atmosphere, to a solution of **3** (1.1 g, 2.2 mmol) in anhydrous THF (11 mL) was added $NaBH_4$ (85 mg, 2.2 mmol) at 0 ºC and warmed to 25 ºC. After stirring for 1 h, the mixture was poured to water (20 mL) and extracted with EtOAc (10 mL x 3). The organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 10 g, hexane/EtOAc = 2/1, v/v), which gave the title compound **4** (0.66 g, 60%) as a colorless viscous syrup. R_f = 0.28 (hexane/EtOAc = 2/1, v/v); $[\alpha]^{20}_D$ = +52.2 (*c* 1.5, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35-7.31 (m, 5H, Ar-H), 5.94-5.84 (m, 1H, H_β), 5.28

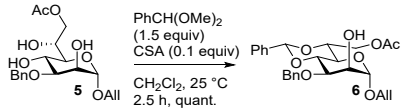
(dddd, $J_{\gamma\ trans,\beta}$ = 17.6 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, $J_{\gamma\ trans,\alpha}$ = 1.6 Hz, 1H, $H_{\gamma\ trans}$), 5.20 (dddd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.3 Hz, $J_{\gamma\ cis,\alpha}$ = 1.3 Hz, 1H, $H_{\gamma\ cis}$), 4.85 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1), 4.57 (s, 2H, $PhCH_2$), 4.34-4.24 (m, 2H, H-7), 4.19 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 3.4 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 4.12 (m, 1H, H-6), 3.98 (m, 1H, H-2), 3.96 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 6.4 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 3.88 (dd, $J_{4,5}$ = 8.7 Hz, $J_{3,4}$ = 8.7 Hz, 1H, H-4), 3.78 (dd, $J_{4,5}$ = 8.7 Hz, $J_{5,6}$ = 4.4 Hz, 1H, H-5), 3.65 (dd, $J_{3,4}$ = 8.7 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-3), 2.82 (d, J = 5.7 Hz, 1H, OH), 2.45 (s, 1H, OH), 2.06 (s, 3H, CH_3), 0.86 (s, 9H, $C(CH_3)_3$), 0.08 (s, 3H, $Si(CH_3)$), 0.05 (s, 3H, $Si(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 171.4, 137.6, 133.6, 128.6, 128.0, 127.8, 117.7, 98.4, 80.5, 73.2, 71.3, 70.0, 69.5, 68.2, 67.6, 64.9, 26.0, 21.0, 18.3, -3.5, -4.7; HRMS (ESI) Calcd for $C_{25}H_{40}O_8SiNa$ $[M+Na]^+$:519.2384, found: 519.2360.

Allyl 7-*O*-acetyl-3-*O*-benzyl-α-D-*glycero*-D-*manno*-heptopyranoside (5)



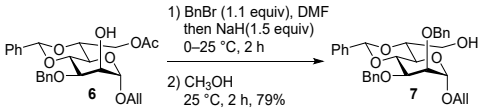
Under Ar atmosphere, to a solution of **4** (0.17 g, 0.33 mmol) in anhydrous THF (1.5 mL) was added AcOH (28 μL, 0.49 mmol) and TBAF in THF (0.49 mL, 0.49 mmol) at 25 ºC. After stirring for 4 days, the mixture was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 3 g, hexane/EtOAc = 1/1→1/2, v/v), which gave the title compound **5** (95 mg, 75%) as a colorless viscous syrup. R_f = 0.12 (hexane/EtOAc = 1/1, v/v); $[\alpha]^{20}_D$ = +54.3 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38-7.35 (m, 5H, Ar-H), 5.93-5.83 (m, 1H, H_β), 5.28 (dddd, $J_{\gamma\ trans,\beta}$ = 17.2 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, $J_{\gamma\ trans,\alpha}$ = 1.6 Hz, 1H, $H_{\gamma\ trans}$), 5.22 (dddd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.2 Hz, $J_{\gamma\ cis,\alpha}$ = 1.2 Hz, $J_{\gamma\ cis,\alpha}$ = 1.2 Hz, 1H, $H_{\gamma\ cis}$), 4.89 (d, $J_{1,2}$ = 1.2 Hz, 1H, H-1), 4.72 & 4.67 (ABq, J = 11.3 Hz, 2H, $PhCH_2$), 4.39 (dd, $J_{7,7}$ = 12.0 Hz, $J_{6,7}$ = 2.8 Hz, 1H, H-7), 4.37 (dd, $J_{7,7}$ = 12.0 Hz, $J_{6,7}$ = 5.6 Hz, 1H, H-7), 4.17 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 5.0 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, 1H, H_α), 4.11-4.07 (m, 1H, H-6), 4.04-4.01 (m, 2H, H-2&H-5), 3.96 (dddd, $J_{\alpha,\alpha}$ = 13.2 Hz, $J_{\alpha,\beta}$ = 6.4 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, 1H, H_α), 3.74 (dd, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 3.6 Hz, 1H, H-3), 3.65 (dd, $J_{4,5}$ = 9.4 Hz, $J_{3,4}$ = 9.4 Hz, 1H, H-4), 3.36 (d, J = 3.6 Hz, 1H, OH), 3.05 (d, J = 2.0 Hz, 1H, OH), 2.40 (d, J = 2.4 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 171.6, 137.7, 133.5, 128.6, 128.2, 128.1, 117.6, 98.6, 79.5, 72.7, 72.4, 70.2, 68.7, 68.1, 67.9, 65.7, 21.0; HRMS (ESI) Calcd for $C_{19}H_{26}O_8Na$ $[M+Na]^+$: 405.1519, found: 405.1522.

Allyl 7-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (6)



Under Ar atmosphere, to a solution of **5** (95 mg, 0.25 mmol) in anhydrous CH_2Cl_2 (1.0 mL) was added $PhCH(OMe)_2$ (56 μL, 0.37 mmol) and CSA (5.8 mg, 25 μmol) at 25 ºC. Then the mixture was stirred for 2.5 h. After the TLC analysis indicated the completion of reaction, the reaction was quenched with Et_3N (0.1 mL) and the mixture was poured to water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 6 g, hexane/EtOAc = 2/1, v/v), which gave the title compound **6** (0.11 g, quant.) as a white foam. R_f= 0.52 (hexane/EtOAc = 1/1, v/v); $[\alpha]^{20}_D$ = +56.7 (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53-7.50 (m, 10H, Ar-H), 5.93-5.83 (m, 1H, H_β), 5.72 (s, 1H, PhCH), 5.28 (dd, $J_{\gamma\ trans,\beta}$ = 17.2 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, 1H, $H_{\gamma\ trans}$), 5.22 (dd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.6 Hz , 1H, $H_{\gamma\ cis}$), 4.89 (d, $J_{1,2}$ = 1.1 Hz, 1H, H-1), 4.86 & 4.71 (ABq, J = 12.0 Hz, 2H, $ArCH_2$), 4.45 (dd, $J_{7,7}$ = 12.0 Hz, $J_{6,7}$ = 3.2 Hz, 1H, H-7), 4.26 (dd, $J_{7,7}$ = 12.0 Hz, $J_{6,7}$ = 5.4 Hz, 1H, H-7), 4.15 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.14-4.07 (m, 2H, H-6 & H_α), 4.02 (dd, $J_{1,2}$ = 1.1 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.97-3.92 (m, 1H, H_α), 3.95 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.74 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5), 2.88 (s, 1H, OH), 2.06 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.9, 138.0, 137.3, 133.3, 129.0, 128.5, 128.3, 128.0, 127.9, 126.2, 117.8, 101.2, 99.1, 78.0, 77.5, 77.1, 76.8, 75.8, 73.2, 69.9, 68.0, 64.0, 62.9, 20.9; HRMS (ESI) Calcd for $C_{26}H_{30}O_8Na$ $[M+Na]^+$:493.1832, found: 493.1819.

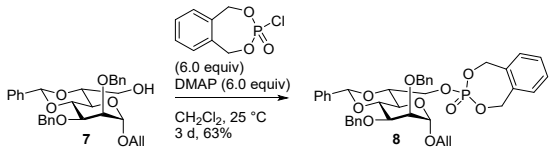
Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (7)



Under Ar atmosphere, to a solution of **6** (68 mg, 0.14 mmol) in anhydrous DMF (1.0 mL) was added BnBr (19 μL, 0.16 mmol) at 0 ºC and stirred for 10 min. Then NaH (9.1 mg, 0.21 mmol, purity 55%) was added at 0 ºC and warmed to 25 ºC and stirred for 2 h at 25 ºC. After the TLC analysis indicated the completion of reaction, the reaction was quenched with MeOH (0.5 mL). After stirring for 2 h, the mixture was poured to water (10 mL) and extracted with EtOAc (5 mL x 3). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 5 g, hexane/EtOAc = 2/1, v/v), which gave the title compound **7** (57 mg, 79%) as a colorless viscous syrup. R_f= 0.33 (hexane/EtOAc = 3/1, v/v) ; $[\alpha]^{20}_D$ = +53.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52-7.50 (m, 2H, Ar-H), 7.40-7.26 (m, 13H, Ar-H), 5.89-5.79 (m, 1H, H_β), 5.76 (s, 1H, PhCH), 5.22 (dddd, $J_{\gamma\ trans,\beta}$ = 17.2 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, $J_{\gamma\ trans,\alpha}$ = 1.6 Hz, $J_{\gamma\ trans,\alpha}$ = 1.6 Hz, 1H, $H_{\gamma\ trans}$), 5.17 (dddd, $J_{\gamma\ cis,\beta}$ = 11.6 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.3 Hz, $J_{\gamma\ cis,\alpha}$ = 1.3 Hz, $J_{\gamma\ cis,\alpha}$ = 1.3 Hz, 1H, $H_{\gamma\ cis}$), 4.85 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1), 4.82 & 4.73 (ABq, J = 12.2 Hz, 2H, $ArCH_2$), 4.81 & 4.65 (ABq, J = 12.2 Hz, 2H, $ArCH_2$), 4.29 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.14 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 5.2 Hz, $J_{\alpha,\gamma}$ = 1.4 Hz, $J_{\alpha,\gamma}$ = 1.4 Hz, 1H, H_α), 4.01-3.97

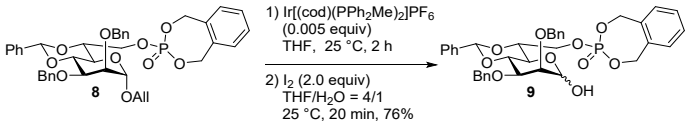
(m, 1H, H-6), 3.98 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.95-3.91 (m, 1H, H-7), 3.92 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 6.2 Hz, $J_{\alpha,\gamma}$ = 1.3 Hz, $J_{\alpha,\gamma}$ = 1.3 Hz, 1H, H_α), 3.86 (dd, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.82-3.76 (m, 1H, H-7), 3.75 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5), 1.92 (t, J = 6.6 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.7, 138.1, 137.5, 133.4, 129.0, 128.4, 128.3, 128.28, 128.20, 127.8, 127.6, 127.5, 126.2, 117.8, 101.1, 98.4, 78.8, 78.1, 76.6, 76.2, 73.7, 73.2, 67.9, 64.6, 62.0; HRMS (ESI) Calcd for $C_{31}H_{34}O_7Na$ $[M+Na]^+$: 541.2196, found: 541.2194.

(Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl *o*-xylenyl phosphate (8)



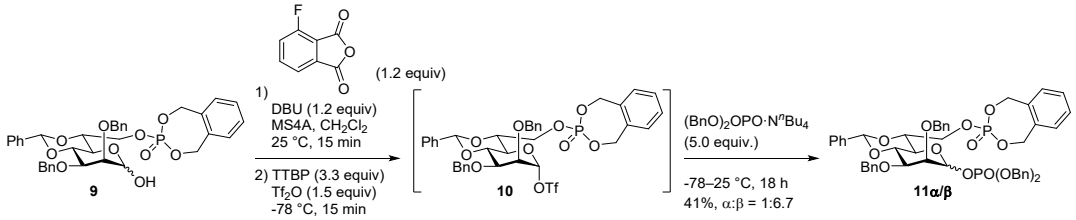
Under Ar atmosphere, to a solution of **7** (40 mg, 77 μmol) in anhydrous CH_2Cl_2 (1.5 mL) were added XylPOCl (0.10 g, 0.46 mmol) and DMAP (56 mg, 0.46 mmol) at 25 ºC. After stirring for 3 days, the mixture was poured to water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 7 g, hexane/EtOAc = 2/1→1/1, v/v), which gave the title compound **8** (34 mg, 63%) as a white foam and **7** was recovered (13 mg, 32%). R_f = 0.40 (hexane/EtOAc = 1/1, v/v); $[\alpha]^{20}_D$ = +20.6 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.50-7.48 (m, 2H, Ar-H), 7.38-7.26 (m, 16H, Ar-H), 7.23-7.17 (m, 1H, Ar-H), 5.86-5.77 (m, 1H, H_β), 5.77 (s, 1H, PhCH), 5.29-5.11 (m, 2H, $ArCH_2$), 5.07-4.89 (m, 2H, $ArCH_2$), 5.22 (d, $J_{\gamma\ cis,\beta}$ = 17.6 Hz, 1H, $H_{\gamma\ trans}$), 5.14 (d, $J_{\gamma\ cis,\beta}$ = 10.8 Hz , 1H, $H_{\gamma\ cis}$) 4.85 (s, 1H, H-1), 4.82 & 4.73 (ABq, J = 12.0 Hz, 2H, $ArCH_2$), 4.81 & 4.64 (ABq, J = 12.0 Hz, 2H, $ArCH_2$), 4.50 (ddd, $J_{6,7}$ = 6.0 Hz, $J_{7,7}$ = 12.8 Hz, $J_{H,P}$ = 1.6 Hz, 1H, H-7), 4.40 (dd, $J_{6,7}$ = 5.6 Hz, $J_{7,7}$ = 12.8 Hz, 1H, H-7), 4.31 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.18-4.13 (m, 2H, H-6 & H_α), 3.99 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.92 (dd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 6.0 Hz, 1H, H_α), 3.86 (dd, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.75 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.6, 138.0, 137.4, 135.5, 135.3, 133.3, 129.2, 129.1, 129.0, 128.9, 128.5, 128.3, 128.2, 128.1, 127.9, 127.6, 127.5, 126.1, 117.5, 101.0, 98.4, 78.2, 77.3, 77.2, 77.1, 76.5, 76.2, 73.7, 73.2, 68.7, 68.0, 65.8, 64.1; ^{31}P NMR (161 MHz, $CDCl_3$) δ −0.7; HRMS (ESI) Calcd for $C_{39}H_{41}O_{10}PNa$ $[M+Na]^+$:723.2329, found: 723.2312.

(2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl-*o*-xylenyl phosphate (9)



Under Ar atmosphere, to $Ir[(cod)(PPh_2Me)_2]PF_6$ (0.20 mg, 0.21 μmol) was added anhydrous THF (0.50 mL) at 25 °C. The mixture was degassed under sonication, and the atmosphere was replaced with H_2 at the temperature. After observing the color change of the solution from yellow to colorless, the atmosphere was replaced with Ar. The solution was then transferred to a solution of **8** (29 mg, 42 μmol) in anhydrous THF (0.50 mL), and the mixture was stirred for 2 h, before being concentrated *in vacuo*. Upon confirmation of complete migration of the double bond *via* ^{1}H NMR spectroscopy, the mixture was diluted with THF/H_2O = 4/1 (0.50 mL) and I_2 (21 mg, 83 μmol) was added. After stirring for 20 min, the TLC analysis indicated the completion of reaction. The reaction was quenched with 10% $Na_2S_2O_3$ aq. (2 mL) and the mixture was poured to water (5 mL) and extracted with EtOAc (2 mL x 3). The organic layer was washed with brine (5 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 4 g, CH_3Cl/EtOAc = 9/1, v/v), yielding the title compound **9** (21 mg, 76%) as a white foam. R_f = 0.25 (hexane/EtOAc = 1/2, v/v); $[\alpha]^{20}_D$ = -3.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53-7.51 (m, 2H, Ar-H), 7.39-7.25 (m, 17H, Ar-H), 5.74 (s, 1H, PhCH), 5.36-5.30 (m, 1H, $ArCH_2$), 5.26-5.20 (m, 1H, $ArCH_2$), 5.24 (s, 1H, H-1), 5.06-4.97 (m, 2H, $ArCH_2$), 4.80 & 4.73 (ABq, J = 12.4 Hz, 2H, $PhCH_2$), 4.79 & 4.64 (ABq, J = 12.2 Hz, 2H, $ArCH_2$), 4.64-4.58 (m, 1H, H-7), 4.37-4.31 (m, 1H, H-7), 4.31 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.12 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5), 4.09 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 4.08-4.05 (m, 1H, H-6), 3.89 (dd, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ138.7, 138.2, 137.5, 135.3, 135.2, 129.4, 129.2, 129.1, 129.0, 128.4, 128.3, 128.2, 127.7, 127.59, 127.53, 126.3, 101.4, 94.5, 78.2, 77.3, 76.9, 76.8, 76.6, 76.5, 73.7, 73.1, 69.1, 68.7, 65.5, 63.0 ; ^{31}P NMR (161 MHz, $CDCl_3$) δ –1.0; HRMS (ESI) Calcd for $C_{36}H_{37}O_{10}PNa$ $[M+Na]^+$:683.2016, found: 683.2006.

1-Bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11α) and 1-bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-β-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11β)



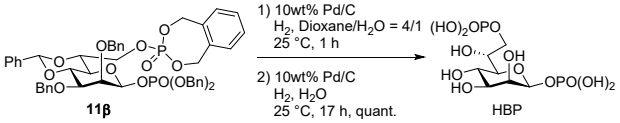
Under Ar atmosphere, to a solution of **9** (29 mg, 44 μmol), 3-fluorophthalic anhydride (8.8 mg, 53 μmol) and MS4A (100 mg) in anhydrous CH_2Cl_2 (0.8 mL) was added DBU (7.9 μL, 53 μmol) at 25 ºC and stirred for 15 min. Then TTBP (36 mg, 0.15 mmol) was added at 25 ºC and the mixture was cooled to -78 ºC. After that, to the mixture was added Tf_2O (11 μl, 66 μmol) at -78 ºC and stirred at 15 min. $PO(OBn)_2O•N^nBu_4$ (0.11 g, 0.22 mmol) in CH_2Cl_2 (0.4 mL) was added at -78 ºC and the mixture was warmed to 25 ºC. After the TLC analysis indicated the completion of reaction, the reaction was quenched with sat. $NaHCO_3$ aq. (2 mL). The mixture was filtrated with celite pad, and poured to water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 14 g, $CHCl_3$/acetone/PhMe = 4/1/1, v/v), which gave the title compound **11α** (2.2 mg, 5.3%) and **11β** (14mg, 35%) both as white solid.

11α: R_f = 0.53 ($CHCl_3$/acetone/PhMe = 4/1/1, v/v); $[\alpha]^{20}_D$ = +21.5 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51-7.48 (m, 2H, Ar-H), 7.35-7.28 (m, 25H, Ar-H), 7.16-7.14 (m, 2H, Ar-H), 5.73 (s, 1H, PhCH), 5.59 (dd, $J_{1,2}$ = 2.0 Hz, $J_{H,P}$ = 6.4 Hz, 1H, H-1), 5.18 (dd, $^2J_{H,H}$ = 12.5 Hz, $J_{H,P}$ = 13.5 Hz, 1H, $ArCH_2$), 5.14 (dd, $^2J_{H,H}$ = 13.5 Hz, $J_{H,P}$ = 13.5 Hz, 1H, $ArCH_2$), 5.00 (dd, $^2J_{H,H}$ = 13.5 Hz, $J_{H,P}$ = 9.6 Hz, 1H, $ArCH_2$), 4.98 (d, $J_{H,P}$ = 9.6 Hz, 2H, $ArCH_2$), 4.95 (dd, $^2J_{H,H}$ = 13.5 Hz, $J_{H,P}$ = 10.2 Hz, 1H, $ArCH_2$), 4.92 (d, $J_{H,P}$ = 9.2 Hz, 2H, $ArCH_2$), 4.73 & 4.55 (ABq, J = 12.4 Hz, 2H, $ArCH_2$), 4.70 & 4.61 (ABq, J = 11.6 Hz, 2H, $ArCH_2$), 4.45 (ddd, $J_{6,7}$ = 2.1 Hz, $J_{7,7}$ = 11.6 Hz, $J_{H,P}$ = 7.3 Hz, 1H, H-7), 4.27 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.19 (ddd, $J_{6,7}$ = 6.0 Hz, $J_{7,7}$ = 11.6 Hz, $J_{H,P}$ = 6.6 Hz, 1H, H-7), 4.15-4.10 (m, 1H, H-6), 3.83 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.73 (d, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.72 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.3, 137.5, 137.1, 135.49, 135.43, 129.1, 129.08, 129.01, 128.9, 128.89, 128.81, 128.79, 128.73, 128.5, 128.4, 128.3, 128.19, 128.14, 128.0, 127.7, 127.5, 126.1, 101.0, 96.7, 77.2, 76.9, 76.0, 75.9, 75.1, 73.8, 73.2, 69.8, 69.7, 68.6, 66.2, 66.1; ^{31}P NMR (161 MHz, $CDCl_3$) δ –0.5, –2.3; HRMS (ESI) Calcd for $C_{50}H_{50}O_{13}P_2Na$ $[M+Na]^+$:943.2618, found: 943.2601.

11β: R_f = 0.48 ($CHCl_3$/acetone/PhMe = 4/1/1, v/v); $[\alpha]^{20}_D$ = -12.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.51-7.48 (m, 2H, Ar-H), 7.38-7.27 (m, 25H, Ar-H), 7.20-7.15 (m, 2H, Ar-H), 5.71 (s, 1H, PhCH), 5.20 (d, $J_{H,P}$ = 7.6 Hz, 1H, H-1), 5.16 & 5.03 (ABq, J = 13.2 Hz, 2H, $ArCH_2$), 5.13 & 4.99 (ABq, J = 13.6 Hz, 2H, $ArCH_2$), 5.10 & 5.05 (ABq, J = 12.0 Hz, 2H, $ArCH_2$), 5.08 & 5.00 (ABq, J = 8.4 Hz, 2H, $ArCH_2$), 4.78 (s, 2H, $ArCH_2$), 4.71 & 4.59 (ABq, J = 12.0 Hz, $ArCH_2$), 4.41 (ddd, $J_{6,7}$ = 6.8 Hz, $J_{7,7}$ = 10.8 Hz, $J_{H,P}$ = 1.5 Hz, 1H, H-7), 4.26 (m, 1H, H-7), 4.23 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 4.13 (m, 1H, H-6), 3.85 (d, $J_{2,3}$ = 1.6 Hz, 1H, H-2), 3.58 (dd, $J_{2,3}$ = 1.6 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.26 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 9.6 Hz, 1H, H-5) ; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 138.0, 137.0, 135.6, 135.5, 135.4, 129.0, 128.99, 128.94, 128.74, 128.72, 128.70, 128.49, 128.41, 128.3, 128.2, 127.9, 127.86, 127.81, 127.6, 126.2, 101.1, 97.1, 77.2, 75.4, 72.9, 69.96, 69.90, 69.7, 69

.6, 68.66, 68.60, 68.0, 65.9, 65.8; ^{31}P NMR (161 MHz, $CDCl_3$) δ –0.1, –2.2; HRMS (ESI) Calcd for $C_{50}H_{50}O_{13}P_2Na$ $[M+Na]^+$:943.2618, found: 943.2612.

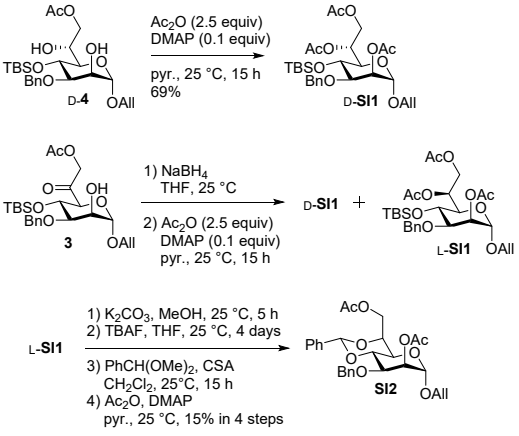
1,7-*O*-Bisphosphoryl-β-D-*glycero*-D-*manno*-heptopyranose (HBP)



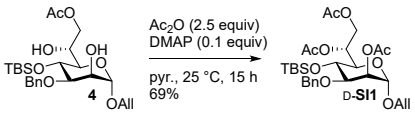
A mixture of **11β** (5.3 mg, 5.8 μmol) and 10% (w/w) Pd/C (2.1 mg) in 1,4-dioxane/H_2O (1.0 mL, 4:1) was stirred at 25 ºC under H_2 (1 atm). After stirring for 1 h, the mixture was filtered through celite pad. The filtrate was concentrated under reduced pressure. A mixture of **11β'** and 10% (w/w) Pd/C (2.6 mg) in H_2O (2.0 mL) was stirred at 25 ºC under H_2 (1 atm). After stirring for 17 h at this temperature, the mixture was filtered through celite pad. The filtrate was concentrated under reduced pressure, which gave the HBP (2.1 mg, quant.) as white solid. $[\alpha]^{20}_D$ = +3.8 (*c* 0.1, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.12 (d, $J_{H,P}$ = 8.8 Hz, 1H, H-1), 4.19-4.15 (m, 1H, H-6), 4.10-4.04 (m, 1H, H-7), 4.01-3.92 (m, 2H, H-2 & H-7), 3.73 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 3.66 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.50 (d, $J_{4,5}$ = 9.6 Hz, 1H, H-5); ^{13}C NMR (100 MHz, D_2O) δ 95.7, 76.8, 72.9, 70.9, 70.7, 67.1, 65.6; ^{31}P NMR (161 MHz, D_2O) δ 4.7, 3.1; HRMS (ESI) Calcd for $C_7H_{15}O_{13}P_2$ $[M-H]^-$: 368.9993, found: 369.0022.

Experiments concerning 4'

The reduction of ketone **3** yielded the desired D-glycero adduct D-**4**, isolable along with a challenging-to-isolate mixture of diastereomer L-**4** and products of acetyl migrations D/L-**4'**. Immediately post-reduction, an acetylation experiment resulted in two products, revealing acetyl group migration. The one not matching acetylated D-**4**, assumed to be L-**SI1**, was converted to L-**SI2** through deprotection, benzylidene formation, and acetylation. Indeed, $^3J_{H5\text{-}H6}$ indicated a gauche conformation at 3.6 Hz. The D-**SI1**:L-**SI1** ratio confirmed the stereoselectivity of the reduction reaction as D-**4**:L-**4** = 9:1.

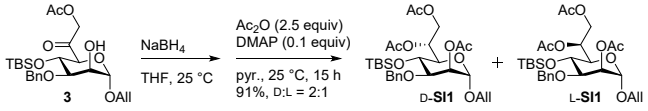


Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (D-SI1)



Under Ar atmosphere, to a solution of **4** (70 mg, 0.14 mmol) in anhydrous pyr. (0.70 mL) were added Ac_2O (33 μL, 0.35 mmol) and DMAP (2.0 mg, 14 μmol) at 25 ºC and stirred for 15 h. After the TLC analysis indicated the completion of reaction, the mixture was poured to water (5 mL) and extracted with EtOAc (5 mL x 3). The organic layer was washed with 10% citric acid aq. (10 mL) and brine (10 ml), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 5 g, hexane/EtOAc = 3/1, v/v), which gave the title compound D-**SI1** (56 mg, 70%) as colorless syrup. R_f = 50 (hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = +54.9 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32-7.24 (m, 5H, Ar-H), 5.94-5.84 (m, 1H, H_β), 5.60 (ddd, $J_{5,6}$ = 0.8 Hz, $J_{6,7}$ = 2.8 Hz, $J_{6,7}$ = 8.4 Hz, 1H, H-6), 5.32 (dd, $J_{1,2}$ = 1.6 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 5.27 (dddd, $J_{\gamma\ trans,\beta}$ = 17.6 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.6 Hz, $J_{\gamma\ trans,\alpha}$ = 1.6 Hz, 1H, $H_{\gamma\ trans}$), 5.22 (dddd, $J_{\gamma\ cis,\beta}$ = 10.5 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.4 Hz, $J_{\gamma\ cis,\alpha}$ = 1.4 Hz, $J_{\gamma\ cis,\alpha}$ = 1.4 Hz, 1H, $H_{\gamma\ cis}$), 4.79 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1), 4.63 & 4.40 (ABq, *J* = 11.1 Hz, 2H, $ArCH_2$), 4.42 (dd, $J_{6,7}$ = 2.8 Hz, $J_{7,7}$ = 12.3 Hz, 1H, H-7), 4.29 (dd, $J_{6,7}$ = 8.4 Hz, $J_{7,7}$ = 12.3 Hz, 1H, H-7), 4.14 (dddd, $J_{\alpha,\alpha}$ = 12.2 Hz, $J_{\alpha,\beta}$ = 5.3 Hz, $J_{\alpha,\gamma}$ = 1.8 Hz, $J_{\alpha,\gamma}$ = 1.8 Hz, 1H, H_α), 3.97 (dddd, $J_{\alpha,\alpha}$ = 12.2 Hz, $J_{\alpha,\beta}$ = 6.2 Hz, $J_{\alpha,\gamma}$ = 1.4 Hz, $J_{\alpha,\gamma}$ = 1.4 Hz, 1H, H_α), 3.84 (dd, $J_{3,4}$ = 9.7 Hz, $J_{4,5}$ = 9.7 Hz, 1H, H-4), 3.82 (m, 1H, H-5), 3.69 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.7 Hz, 1H, H-3), 2.10 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 0.88 (s, 9H, $C(CH_3)_3$), 0.07 (s, 3H, $Si(CH_3)$), -0.01 (s, 3H, $Si(CH_3)$) ; ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.8, 170.2, 169.9, 137.7, 133.3, 128.2, 127.8, 127.6, 117.9, 96.8, 78.2, 73.8, 70.9, 70.4, 68.28, 68 .21, 67.9, 62.1, 25.9, 21.04, 21.02, 20.8, 18.3, –3.7, –5.0 ; HRMS (ESI) Calcd for $C_{29}H_{44}O_{10}SiNa$ $[M+Na]^+$:603.2595, found: 603.2604.

Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-L-*glycero*-D-*manno*-heptopyranoside (L-**SI1**)

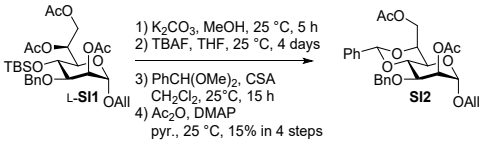


Reduction of **3** (3.3 g, 6.6 mmol) gave **4** (1.3 g, 39%) and residue (0.42 g). Under Ar atmosphere, to a solution of the residue in anhydrous pyr. (4.0 mL) were added Ac_2O (0.20 mL, 2.1 mmol) and DMAP (9.7 mg, 85 μmol) at 25 ºC and stirred for 15 h. After the TLC analysis indicated the completion of reaction, the mixture was poured to water (10 mL) and extracted with EtOAc (5 mL x 3). The organic

layer was washed with 10% citric acid aq. (20 ml), brine (20 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 15 g, hexane/EtOAc = 4/1, v/v), which gave the title compound D-**SI1** (0.30 g, 61%) as a colorless syrup and compound L-**SI1** (0.15 g, 30%) as white solid.

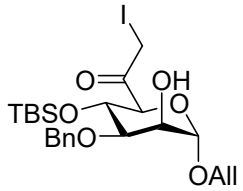
L-**SI1**: R_f= 0.31 (hexane/EtOAc = 4/1, v/v); $[\alpha]^{20}_D$ = +12.1 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32-7.25 (m, 5H, Ar-H), 5.92-5.82 (m, 1H, H_β), 5.36 (d, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 5.37-5.32 (m, 1H, H–6), 5.28 (dddd, $J_{\gamma\ trans,\beta}$ = 17.0 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.3 Hz, $J_{\gamma\ trans,\alpha}$ = 1.3 Hz, $J_{\gamma\ trans,\alpha}$ = 1.3 Hz, 1H, $H_{\gamma\ trans}$), 5.22 (dddd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.3 Hz, $J_{\gamma\ cis,\alpha}$ = 1.3 Hz, $J_{\gamma\ cis,\alpha}$ = 1.3 Hz, 1H, $H_{\gamma\ cis}$), 4.92 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1), 4.64 & 4.40 (ABq, *J* = 11.2 Hz, 2H, $ArCH_2$), 4.27 (d, $J_{6,7}$ = 4.3, 2H, H-7), 4.14 (dddd, $J_{\alpha,\alpha}$ = 13.0 Hz, $J_{\alpha,\beta}$ = 5.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 3.96 (dddd, $J_{\alpha,\alpha}$ = 13.0 Hz, $J_{\alpha,\beta}$ = 6.4 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 3.87 (dd, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.80-3.78 (m, 1H, H-5), 3.75 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 2.12 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 0.84 (s, 9H, $C(CH_3)_3$), -0.02 (s, 6H, $Si(CH_3)$); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 170.2, 170.1, 137.7, 132.2, 128.2, 127.8, 127.6, 118.1, 96.8, 78.0, 71.0, 70.6, 68.9, 68.5, 67.6, 67.0, 61.5, 26.0, 21.04, 21.00, 20.8, 18.3, -3.3, -5.4; HRMS (ESI) Calcd for $C_{29}H_{44}O_{10}SiNa$ $[M+Na]^+$:603.2595, found:603.2600.

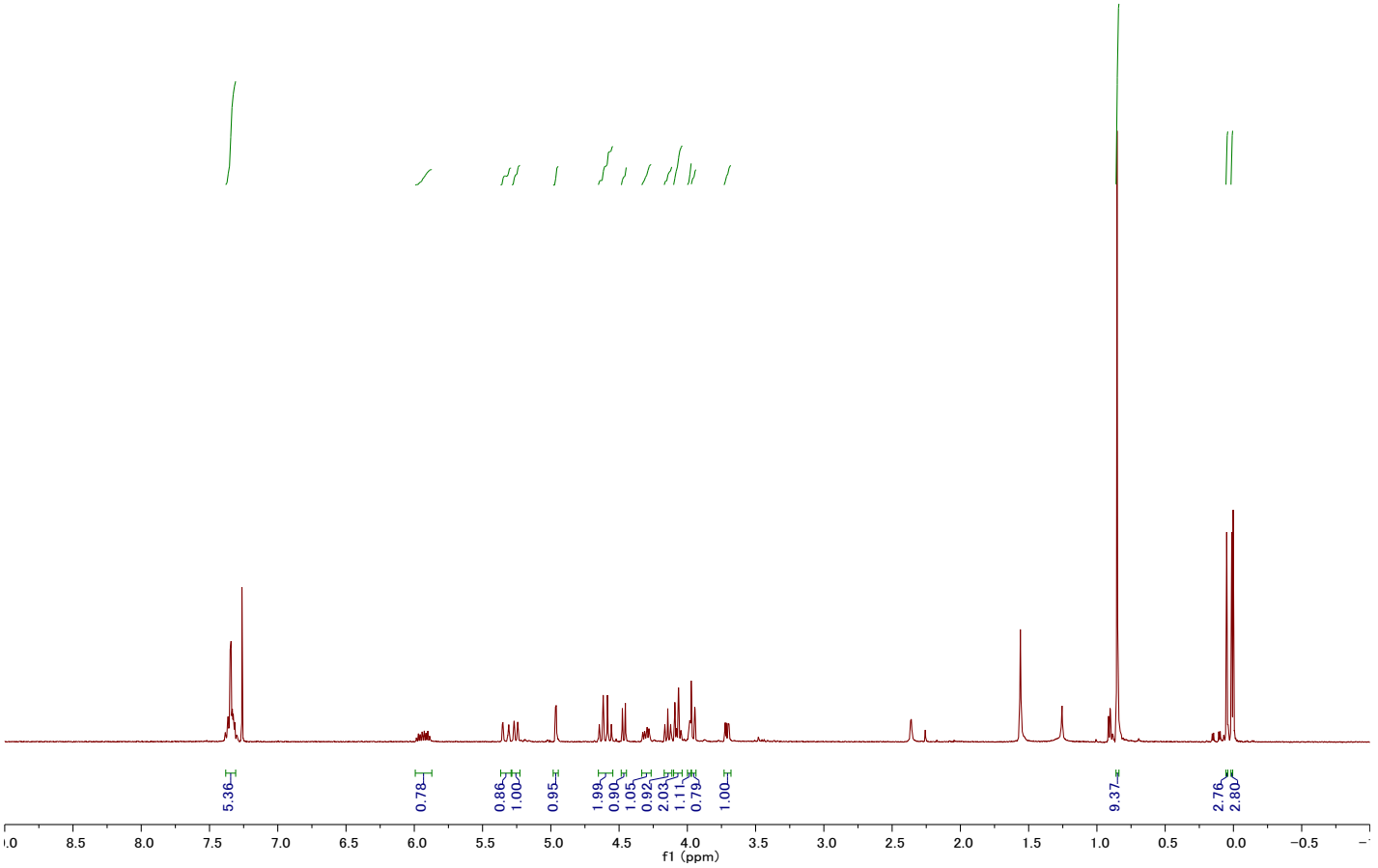
Allyl 2,7-diacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-*glycero*-D-*manno*-heptopyranoside (SI2)



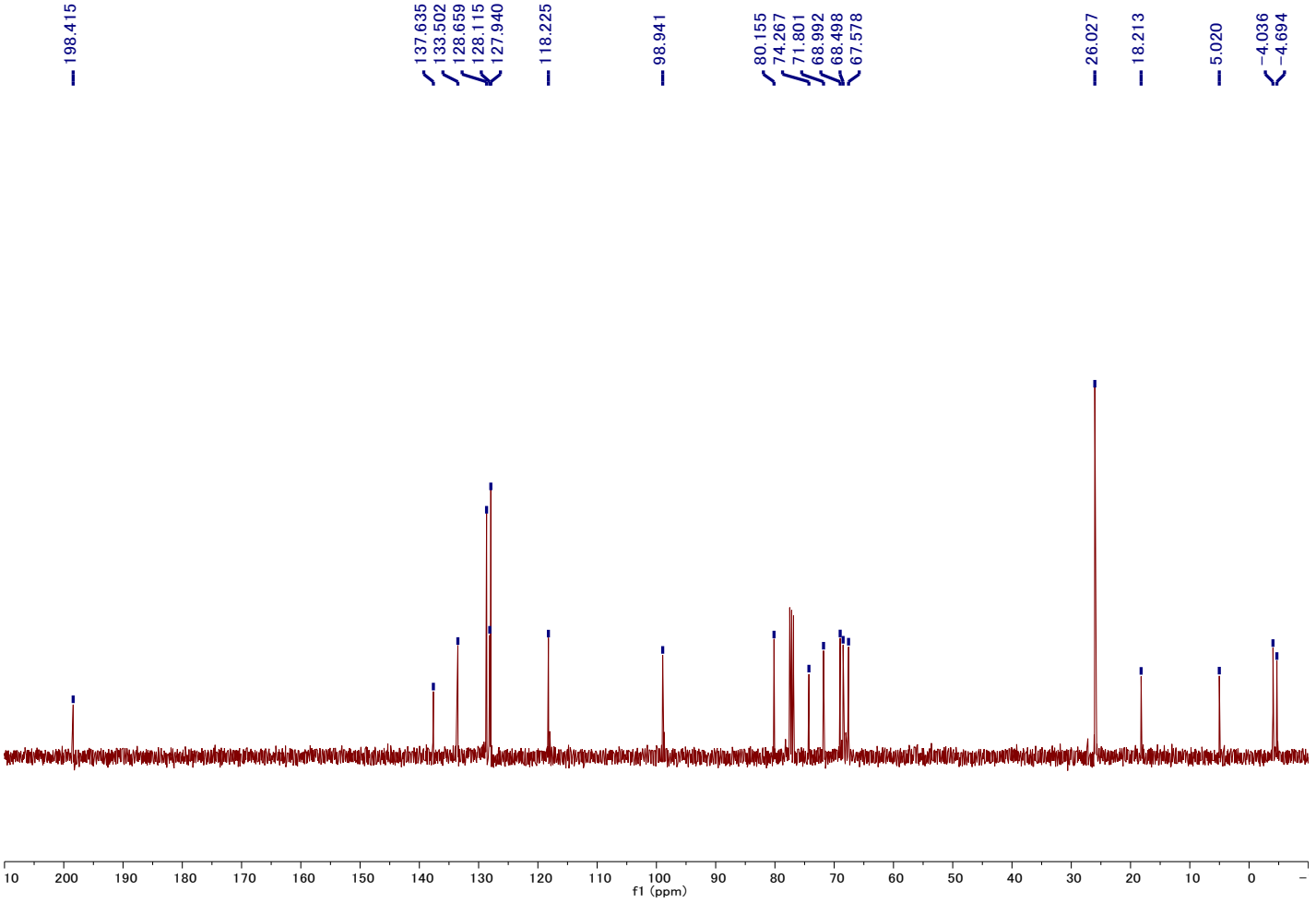
Under Ar atmosphere, to a solution of L-**SI1** (89 mg, 0.15 mmol) in anhydrous MeOH (1.0 mL) was added K_2CO_3 (4.2 mg, 30 μmol) at 25 ºC and stirred for 4 h. After the TLC analysis indicated the completion of reaction, the mixture was concentrated *in vacuo*, to give a yellow oily residue, which was used without further purification. Under Ar atmosphere, to a solution of the residue in anhydrous THF (0.50 mL) was added TBAF (2.0 mL, 0.20 mmol) at 25 ºC and stirred for 4 days. After the TLC analysis indicated the completion of reaction, the mixture was concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography ($CHCl_3$/MeOH = 9/1, v/v), to give a colorless oily residue. Deprotection of TBS and acetyl groups was confirmed by ^{1}H NMR. Under Ar atmosphere, to a solution of the residue in anhydrous CH_2Cl_2 (0.50 mL) were added $PHCH(OMe)_2$ (46 μL, 0.31 mmol) and CSA (9.0 mg, 38 μmol) at 25 ºC and stirred for 15 h. After the TLC analysis indicated the completion of reaction, the reaction was quenched with Et_3N (0.2 mL) and the mixture was poured to water (5 mL) and extracted with CH_2Cl_2 (5 mL x 3). The organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 4 g, hexane/EtOAc = 1/1, v/v), to give a colorless syrupy residue. Under Ar atmosphere, to a solution of the residue in anhydrous pyr. (0.25 mL) were added Ac_2O (7 μL, 77 μmol) and DMAP (0.6 mg, 5 μmol) at 25 ºC and stirred for 15 h. After the TLC analysis indicated the completion of reaction, the mixture was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel 3 g, hexane/EtOAc = 3/1, v/v), which gave the title compound **SI2** (12 mg, 15% in 4 steps) as colorless syrup. R_f = 0.38 (hexane/EtOAc = 3/1, v/v); $[\alpha]^{20}_D$ = -1.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.47-7.44 (m, 2H, Ar-H), 7.38-7.26 (m, 8H, Ar-H), 5.98 (s, 1H, PhCH), 5.94-5.84 (m, 1H, H_β), 5.48 (dd, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 5.37 (dd, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 3.6 Hz, 1H, H-2), 5.29 (dddd, $J_{\gamma\ trans,\beta}$ = 17.6 Hz, $J_{\gamma\ trans,\gamma\ cis}$ = 1.2 Hz, $J_{\gamma\ trans,\alpha}$ = 1.2 Hz, $J_{\gamma\ trans,\alpha}$ = 1.2 Hz, 1H, $H_{\gamma\ trans}$), 5.24 (dddd, $J_{\gamma\ cis,\beta}$ = 10.4 Hz, $J_{\gamma\ cis,\gamma\ trans}$ = 1.2 Hz, $J_{\gamma\ cis,\alpha}$ = 1.2 Hz, $J_{\gamma\ cis,\alpha}$ = 1.2 Hz, 1H, $H_{\gamma\ cis}$), 4.94 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 4.66 & 4.42 (ABq, *J* = 12.0 Hz, 2H, $ArCH_2$), 4.31 (ddd, $J_{5,6}$ = 3.6 Hz, $J_{6,7}$ = 6.8 Hz, $J_{6,7}$ = 6.8 Hz, 1H, H-6), 4.18 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 5.2 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, $J_{\alpha,\gamma}$ = 1.6 Hz, 1H, H_α), 4.13 (dd, $J_{6,7}$ = 6.8 Hz, $J_{7,7}$ = 6.8 Hz, 1H, H-7), 4.03 (dddd, $J_{\alpha,\alpha}$ = 12.8 Hz, $J_{\alpha,\beta}$ = 6.0 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, $J_{\alpha,\gamma}$ = 1.2 Hz, 1H, H_α), 3.97 (dd, $J_{6,7}$ = 6.8 Hz, $J_{7,7}$ = 6.8 Hz, 1H, H-7), 3.89 (dd, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, 1H, H-3), 3.76 (dd, $J_{4,5}$ = 9.6 Hz, $J_{5,6}$ = 3.6 Hz, 1H, H-5), 2.14 (s, 3H, CH_3), 1.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.5, 169.4, 138.0, 137.9, 133.2, 129.1, 128.4, 128.3, 127.7, 126.5, 117.9, 104.4, 97.0, 77.2, 74.9, 74.2, 71.2, 70.3, 68.6, 68.28, 68.21, 66.2, 21.1, 21.0; HRMS (ESI) Calcd for $C_{28}H_{32}O_9Na$ $[M+Na]^+$: 535.1944, found: 535.1927.

Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-7-deoxy-7-iodo-6-oxo-α-D-*manno*-heptopyranoside (2) ^{1}H NMR (400 MHz, $CDCl_3$)

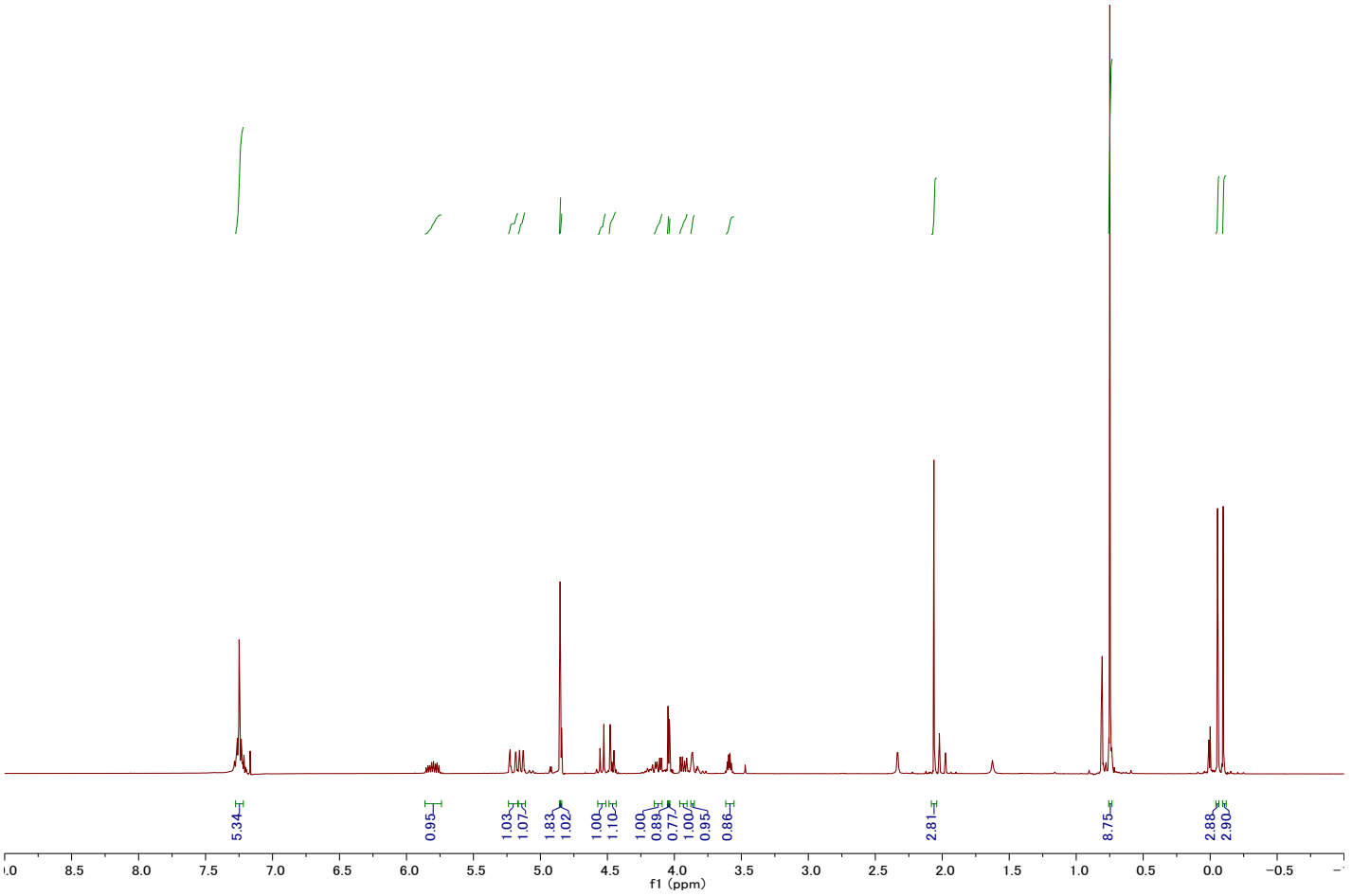


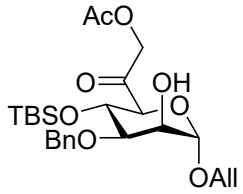


Allyl 3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-7-deoxy-7-iodo-6-oxo-α-D-*manno*-heptopyranoside (2) ^{13}C NMR (100 MHz, $CDCl_3$)

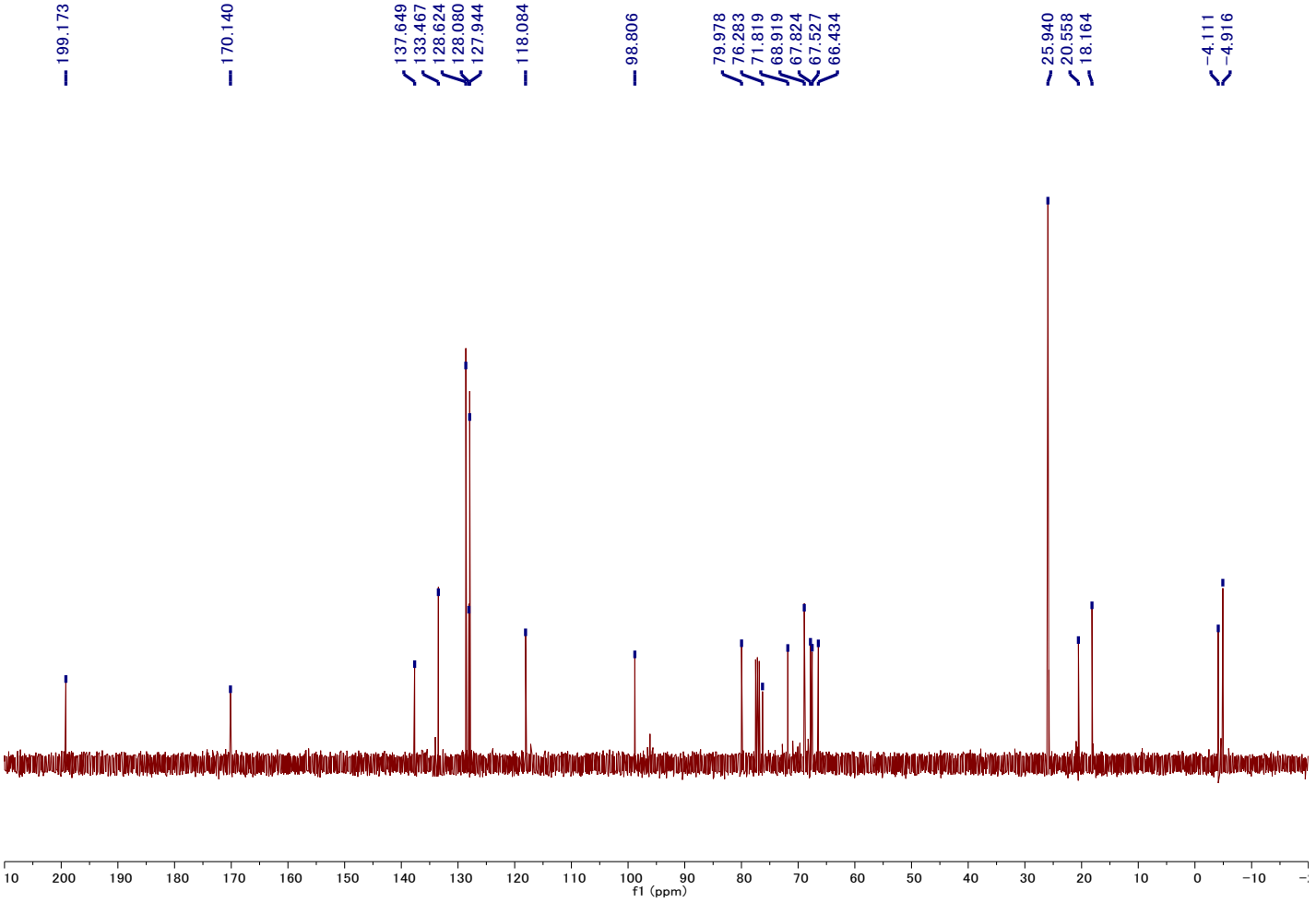


Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-oxo-α-D-*manno*-heptopyranoside (3) ^{1}H NMR (400 MHz, $CDCl_3$)

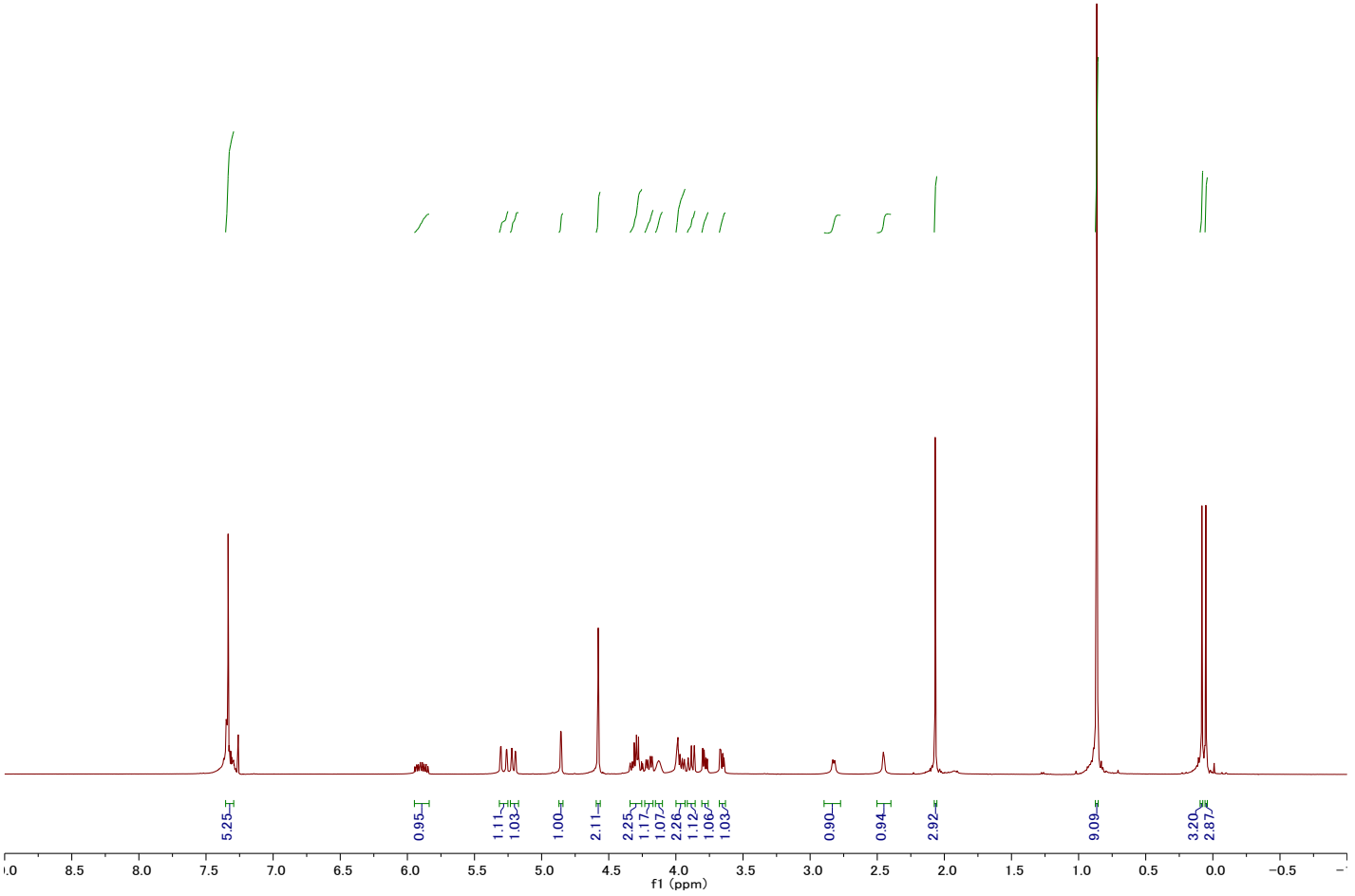


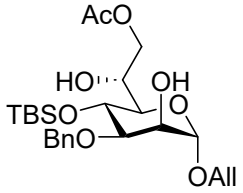


Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-oxo-α-D-*manno*-heptopyranoside (3) ^{13}C NMR (100 MHz, $CDCl_3$)

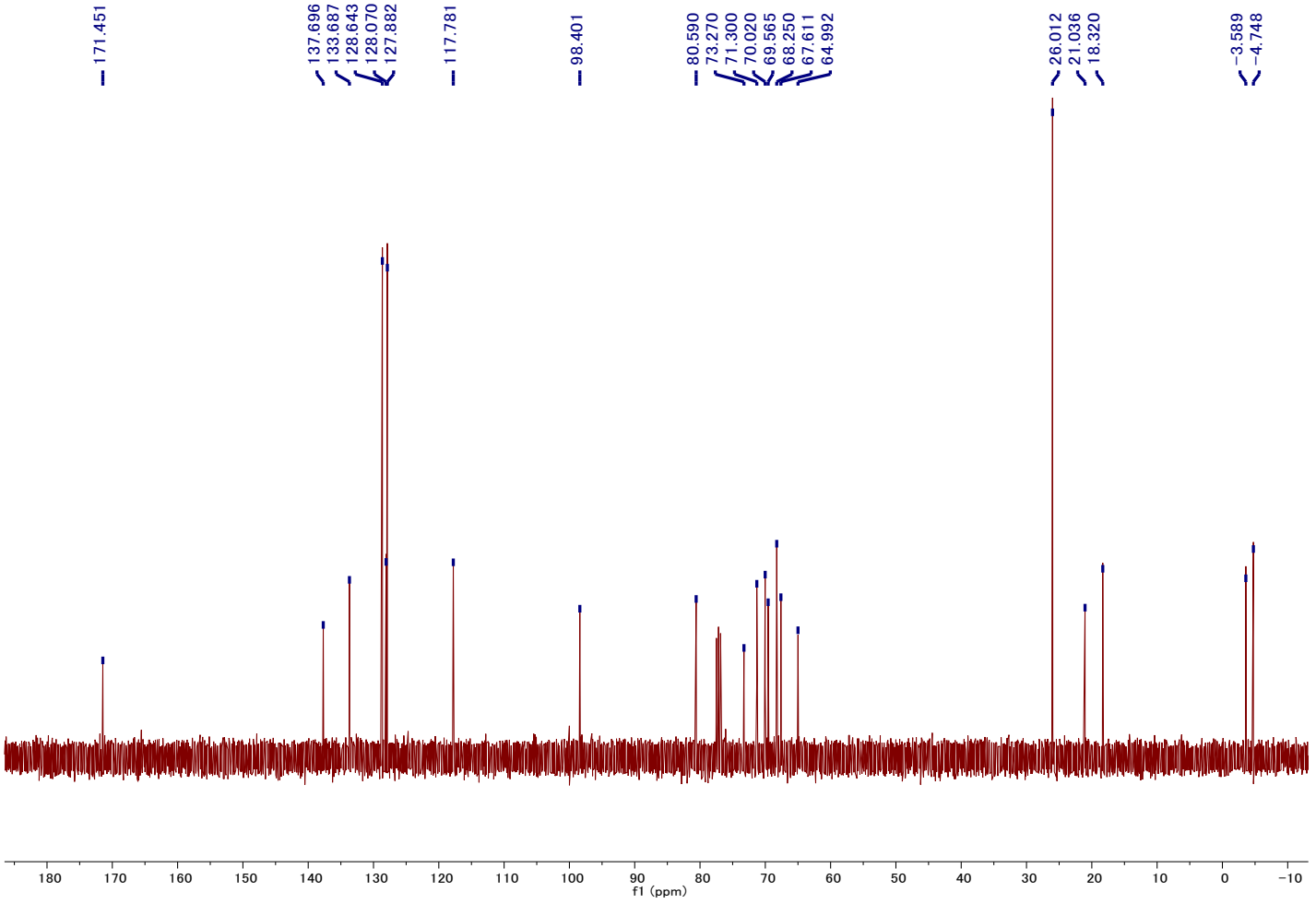


Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (4) ^{1}H NMR (400 MHz, $CDCl_3$)

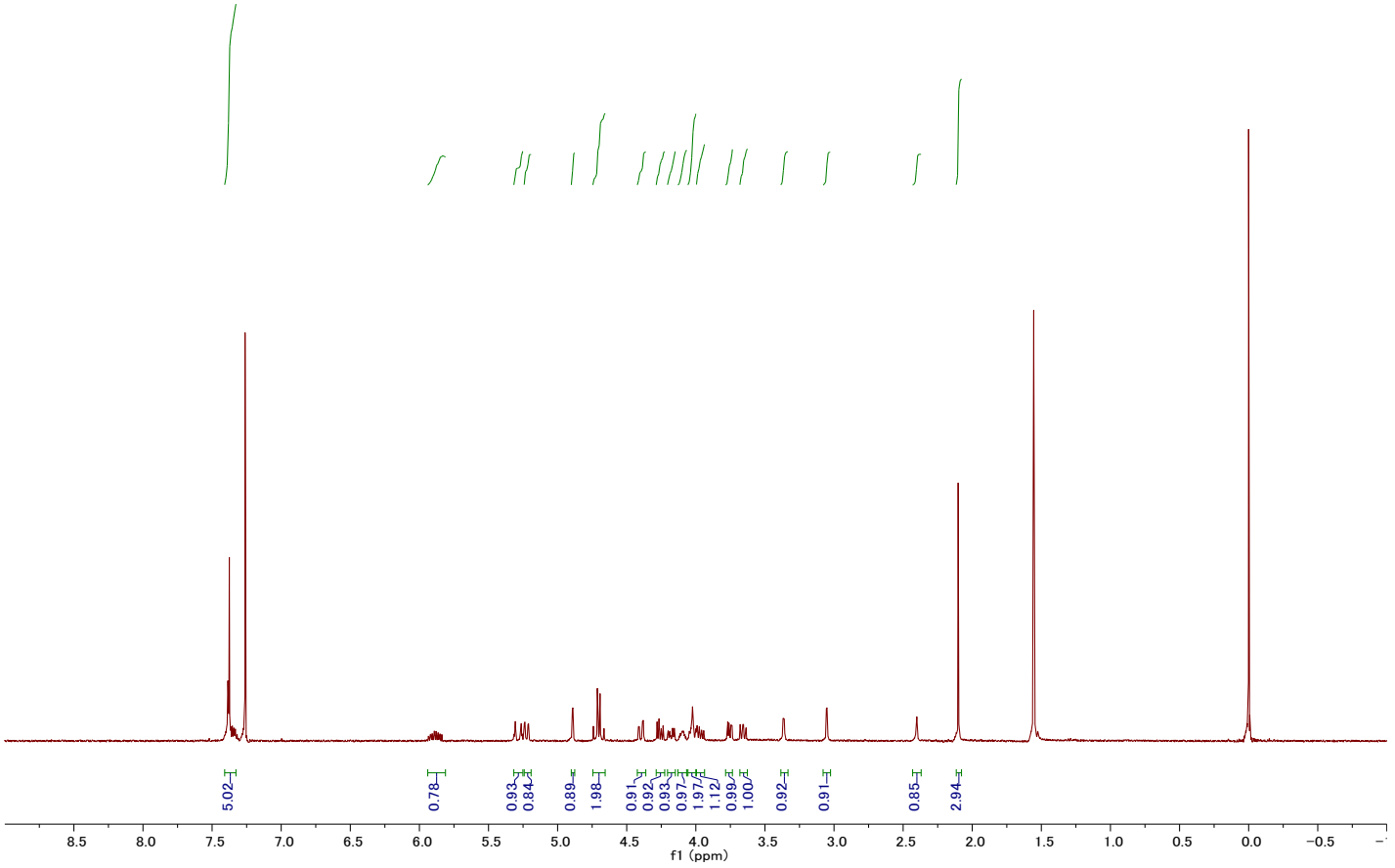


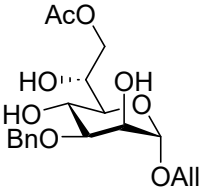


Allyl 7-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (4) ^{13}C NMR (100 MHz, $CDCl_3$)

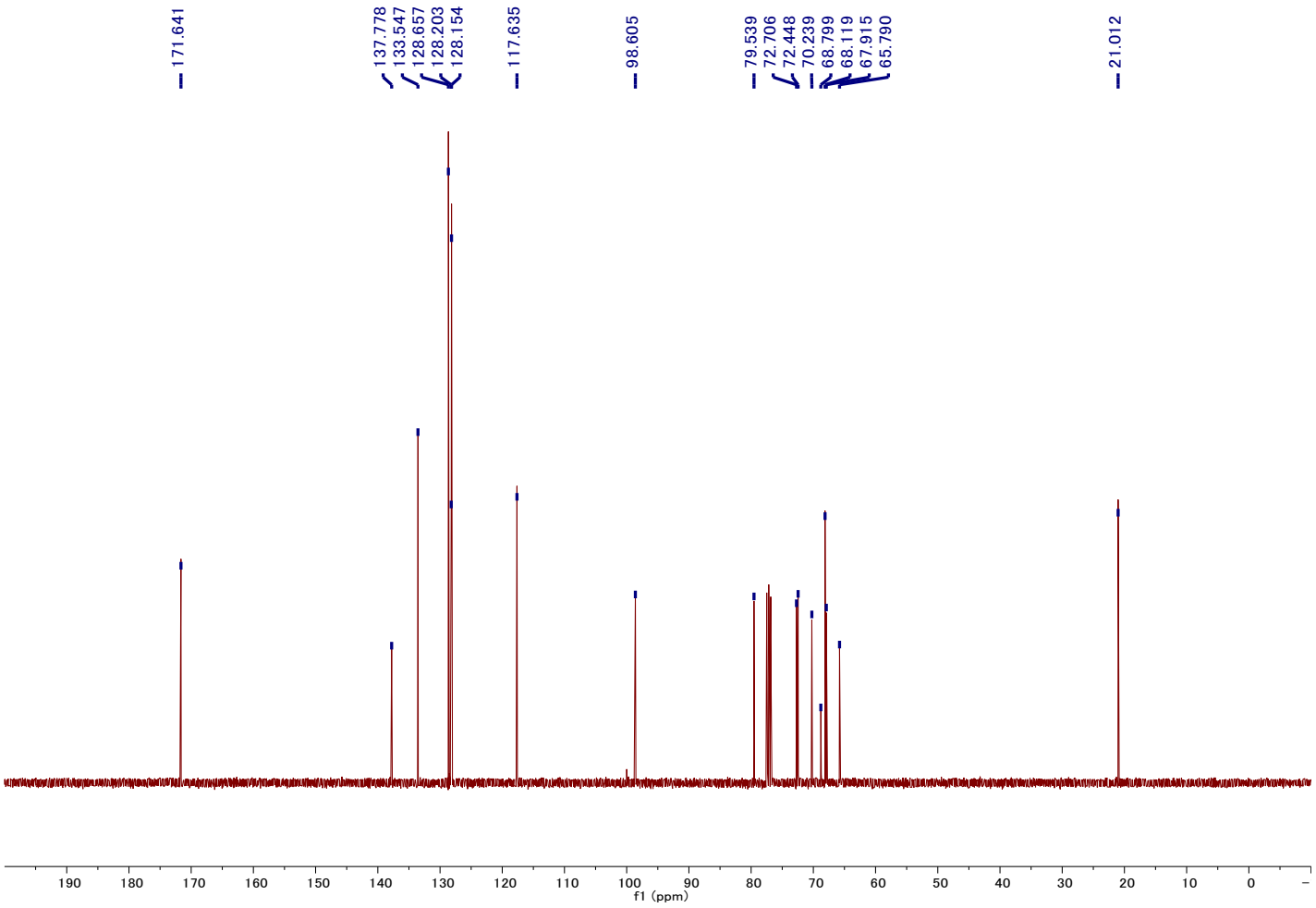


Allyl 7-*O*-acetyl-3-*O*-benzyl-α-D-*glycero*-D-*manno*-heptopyranoside (5) ^{1}H NMR (400 MHz, $CDCl_3$)

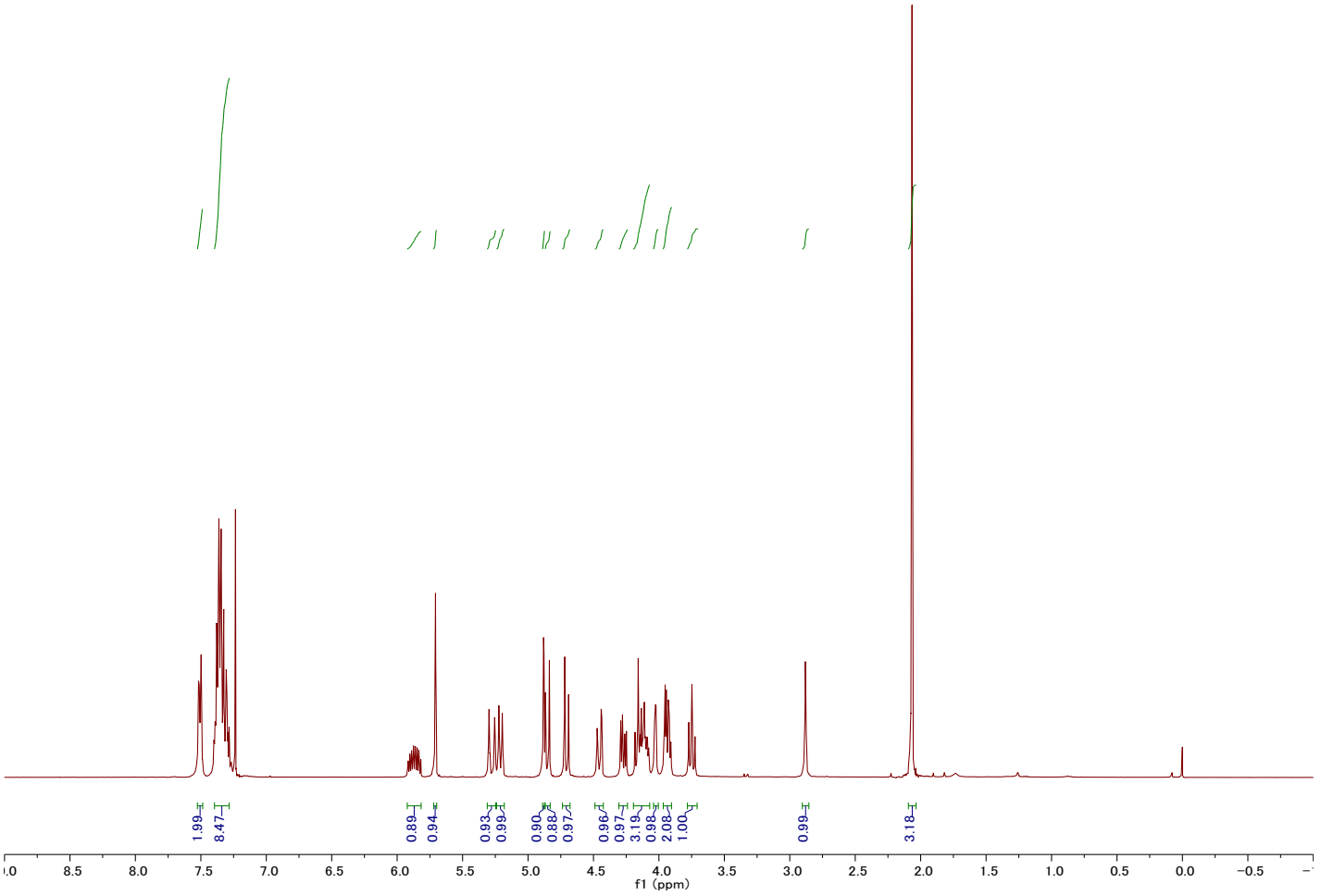


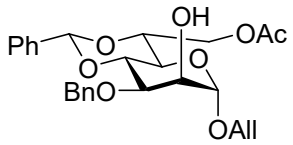


Allyl 7-*O*-acetyl-3-*O*-benzyl-α-D-*glycero*-D-*manno*-heptopyranoside (5) ^{13}C NMR (100 MHz, $CDCl_3$)

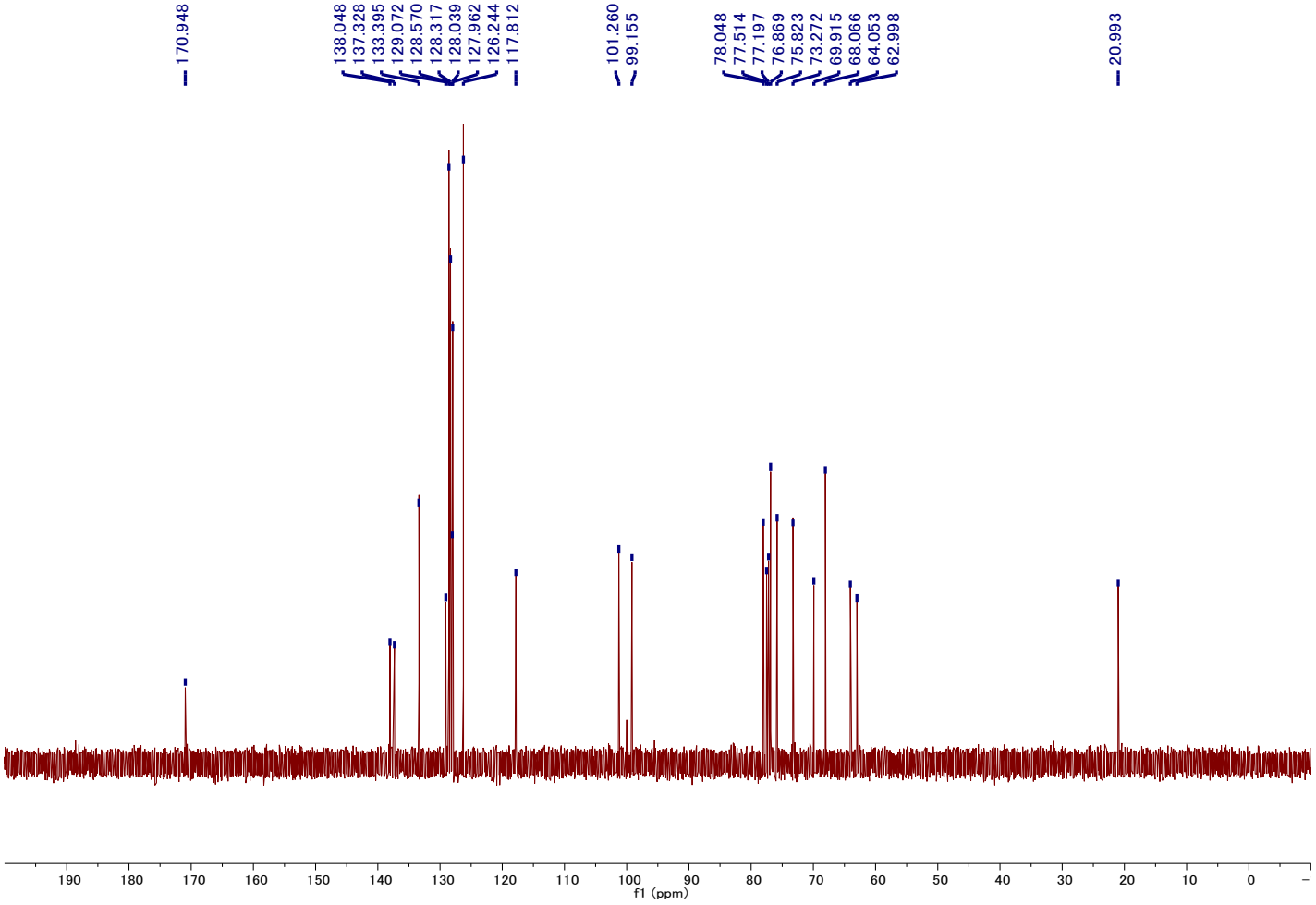


Allyl 7-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (6) ^{1}H NMR (400 MHz, $CDCl_3$)

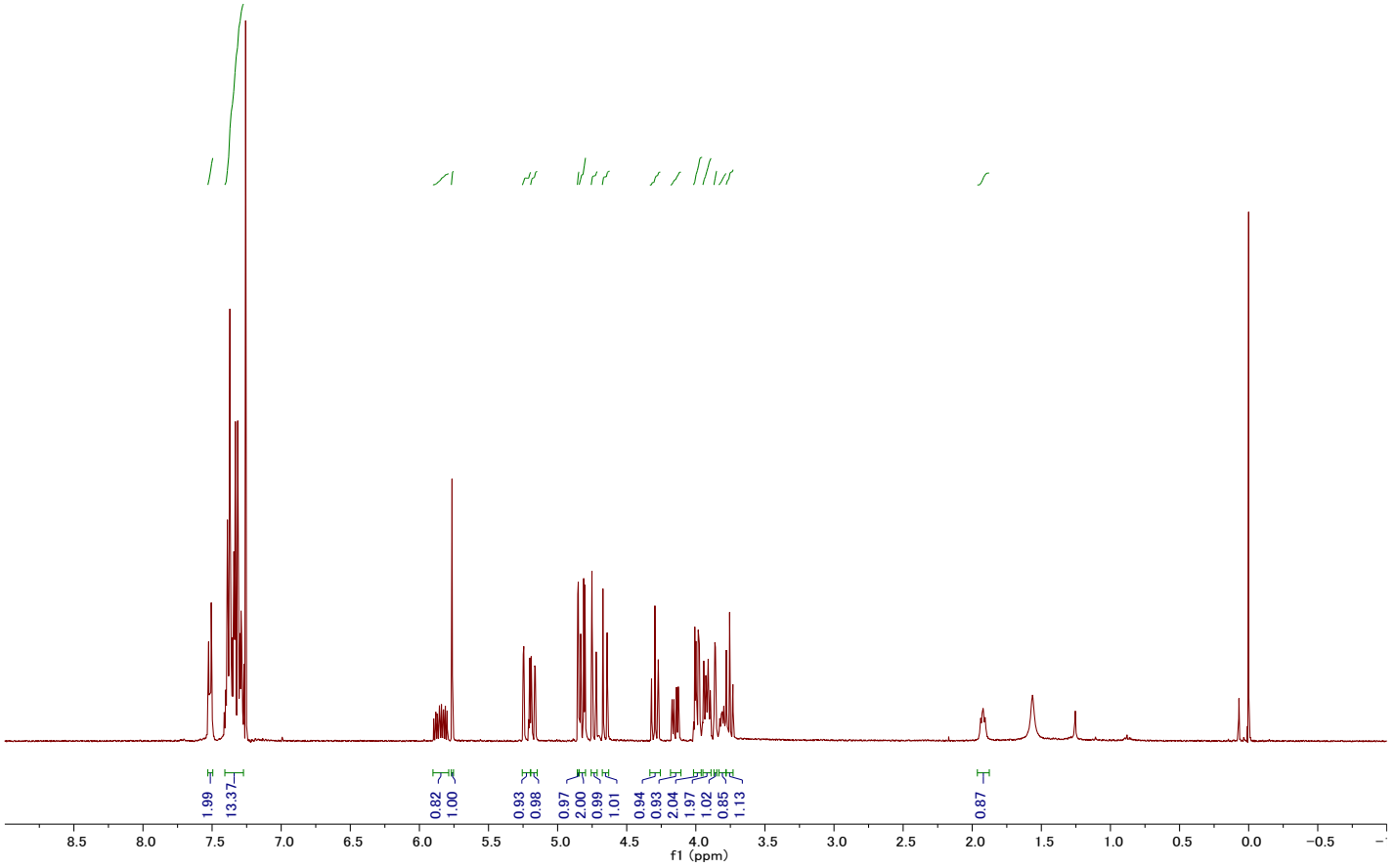


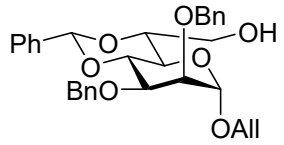


Allyl 7-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (6) ^{13}C NMR (100 MHz, $CDCl_3$)

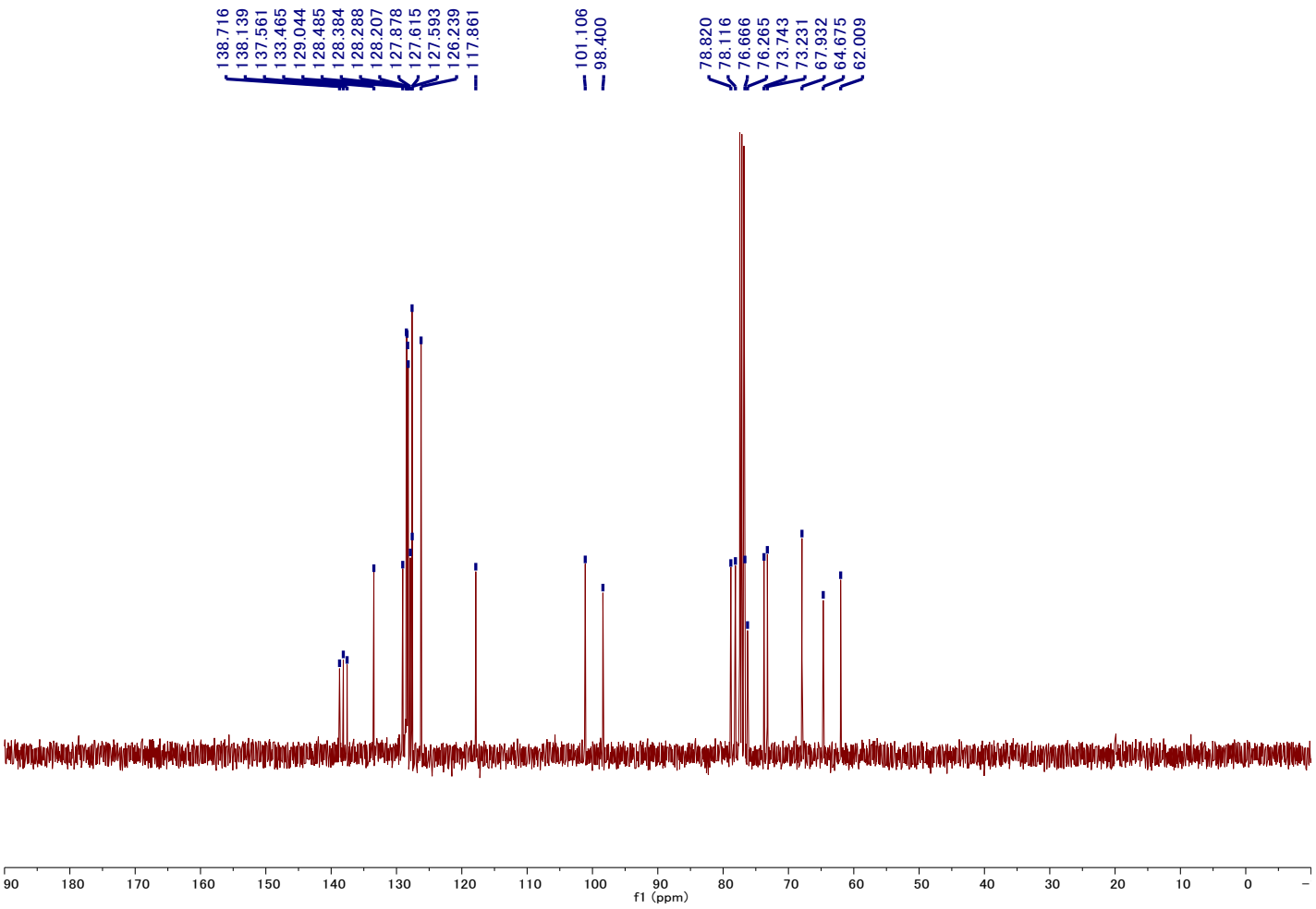


Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (7) ^{1}H NMR (400 MHz, $CDCl_3$)

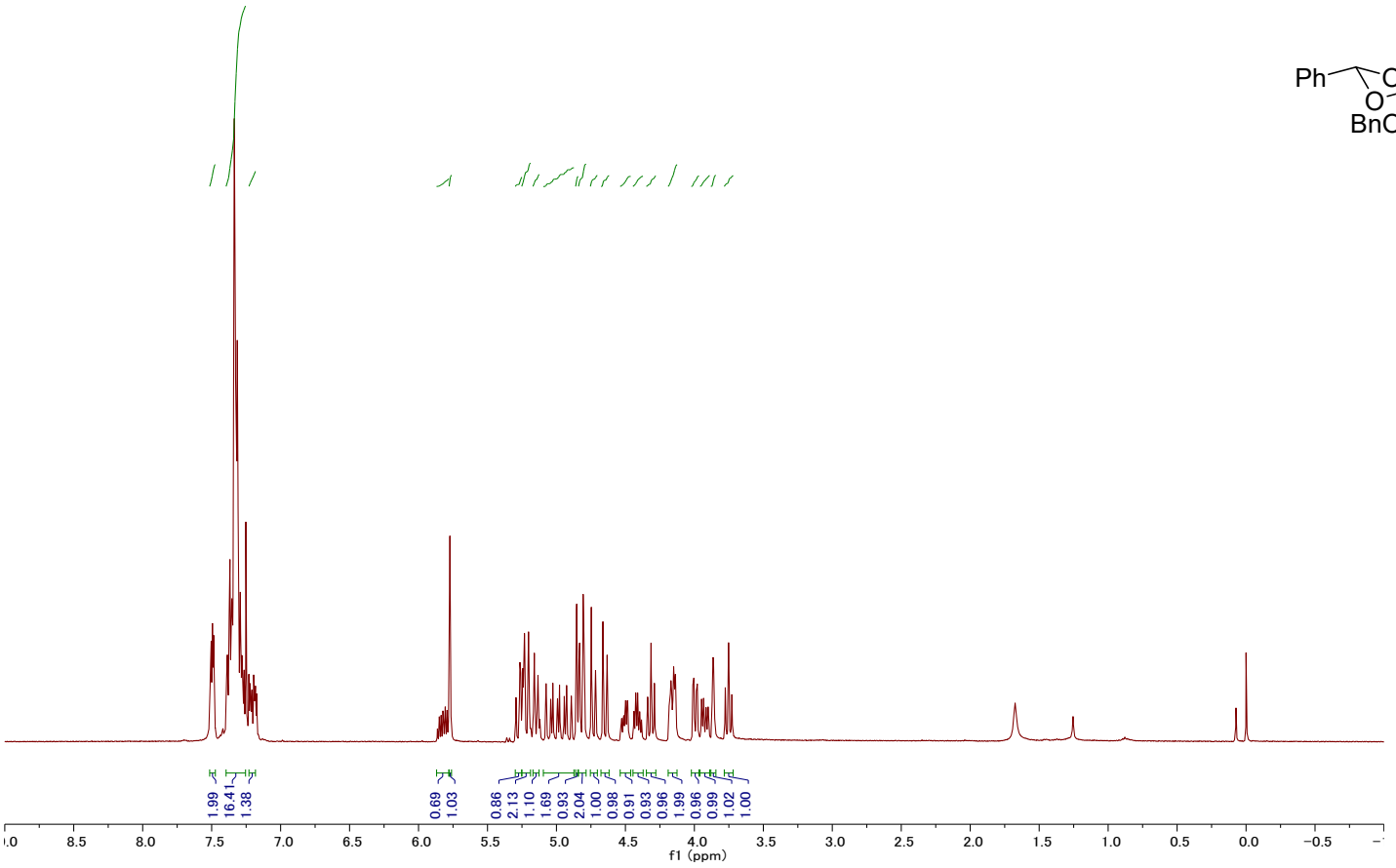


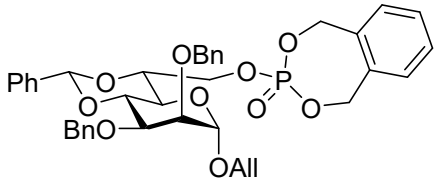


Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside (7) ^{13}C NMR (100 MHz, $CDCl_3$)

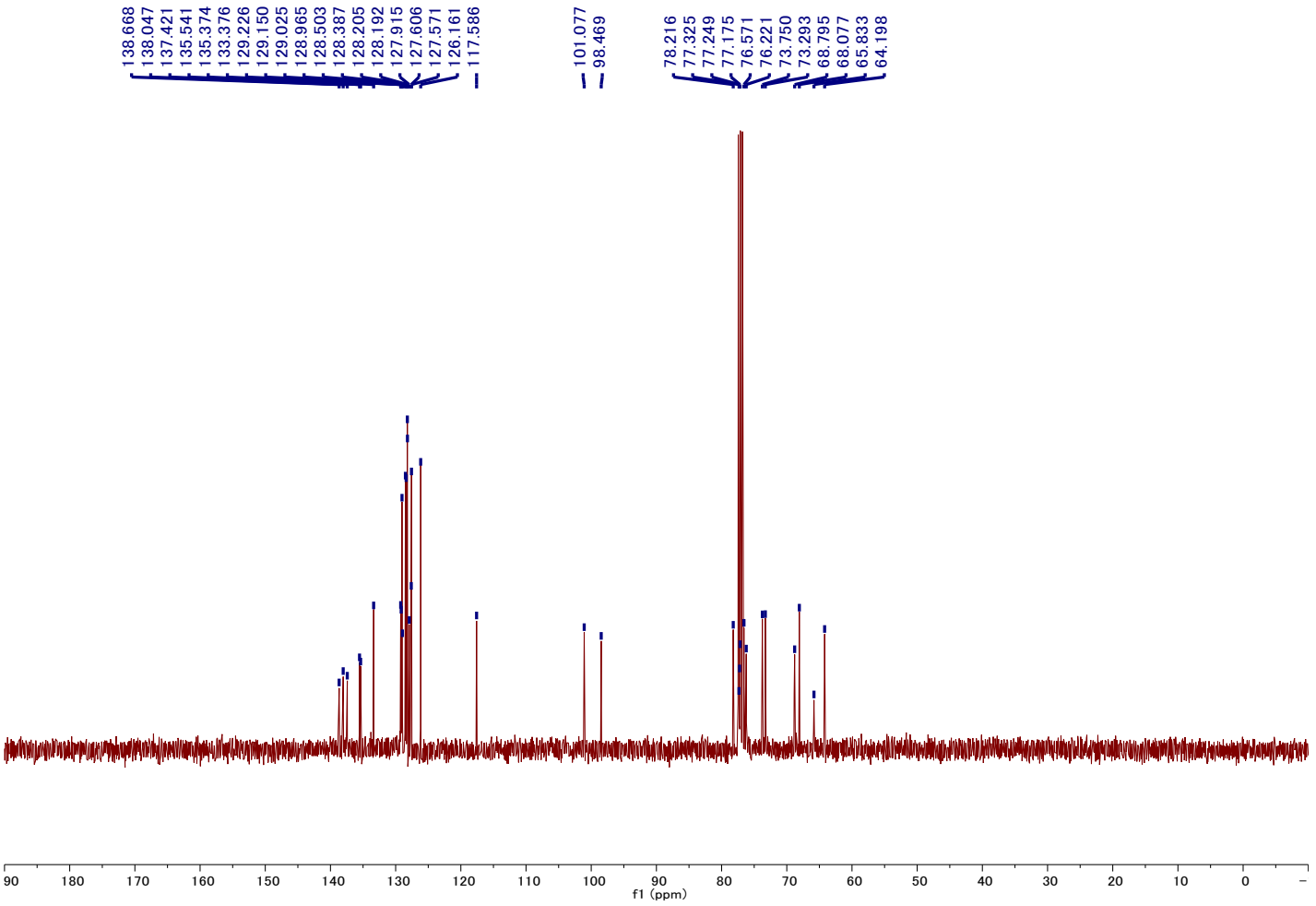


(Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl *o*-xylenyl phosphate (8) ^{1}H NMR (400 MHz, $CDCl_3$)

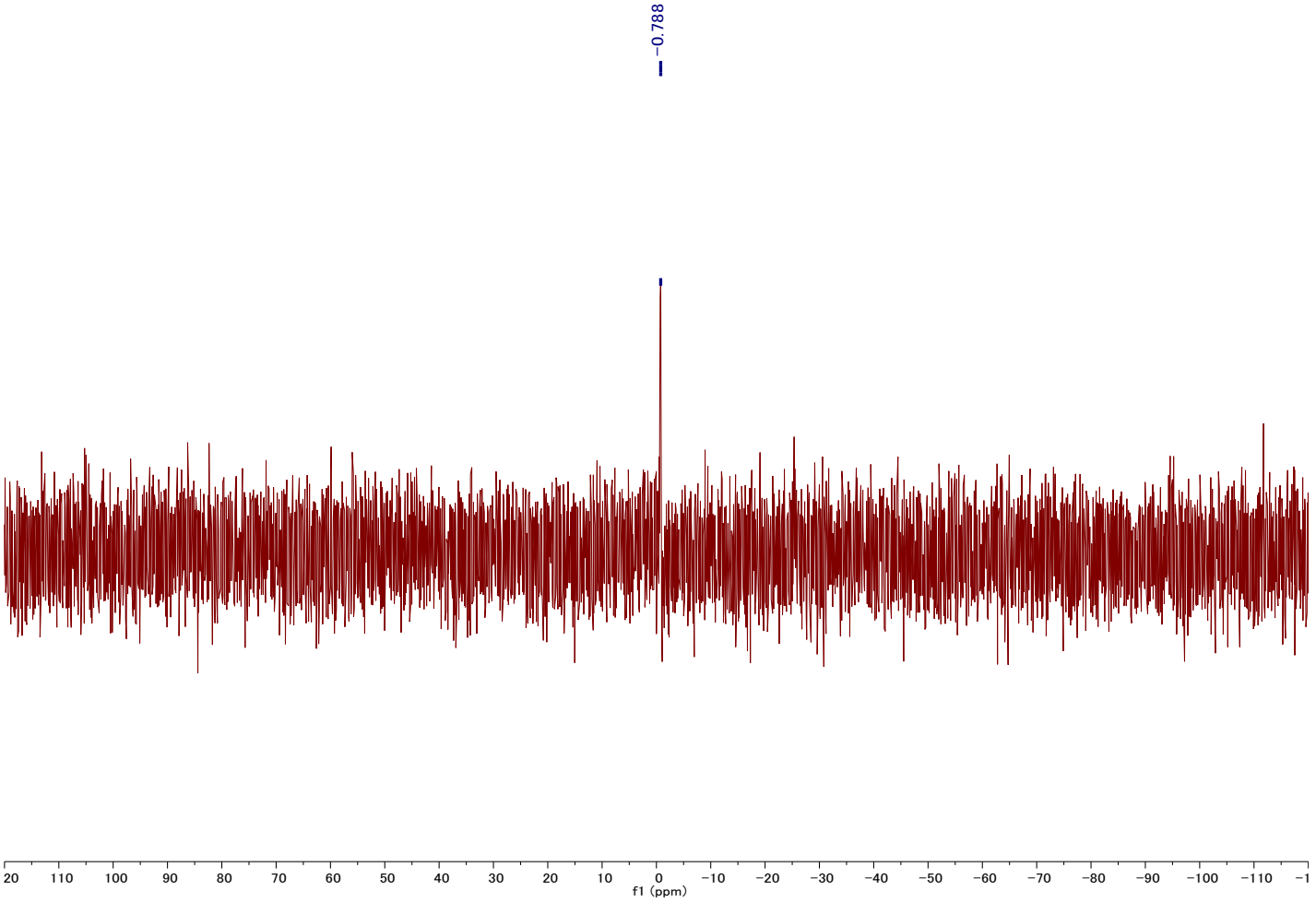




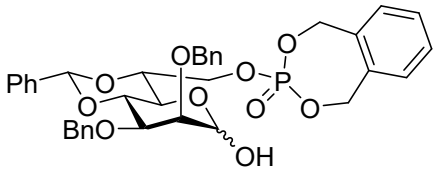
(Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl *o*-xylenyl phosphate (8) ^{13}C NMR (100 MHz, $CDCl_3$)

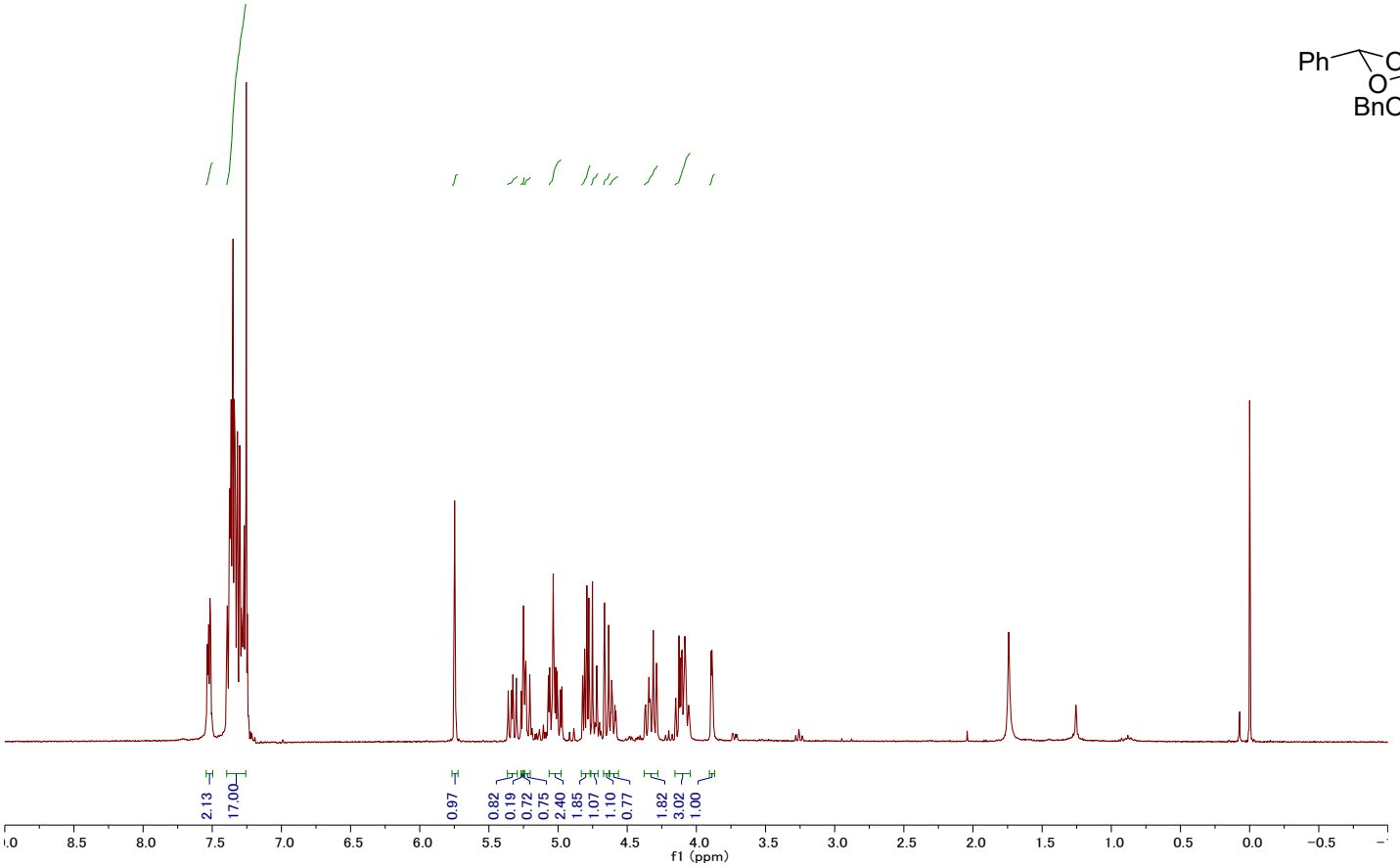


(Allyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl *o*-xylenyl phosphate (8) ^{31}P NMR (161 MHz, $CDCl_3$)

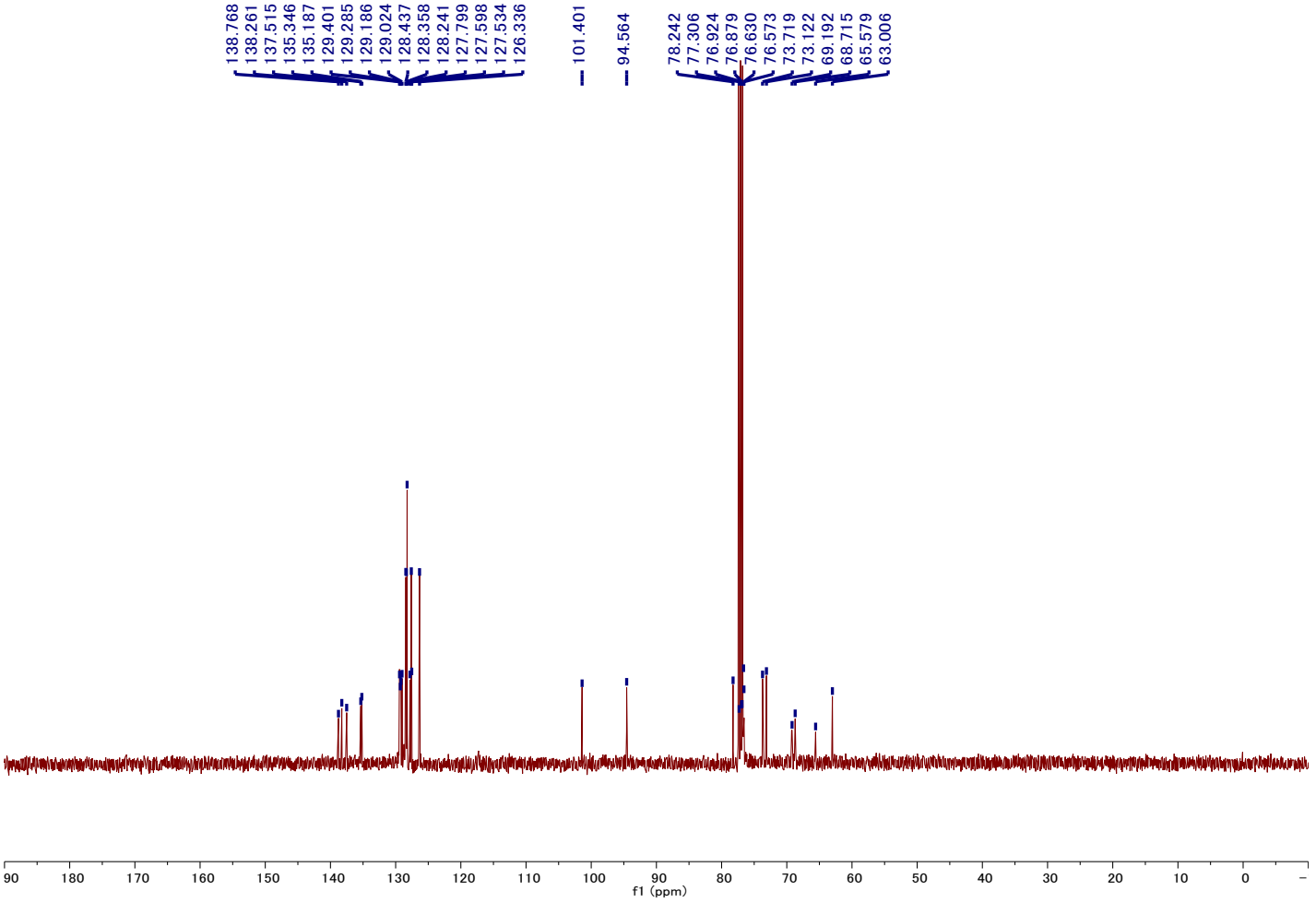


(2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl-*o*-xylenyl phosphate (9) ^{1}H NMR (400 MHz, $CDCl_3$)

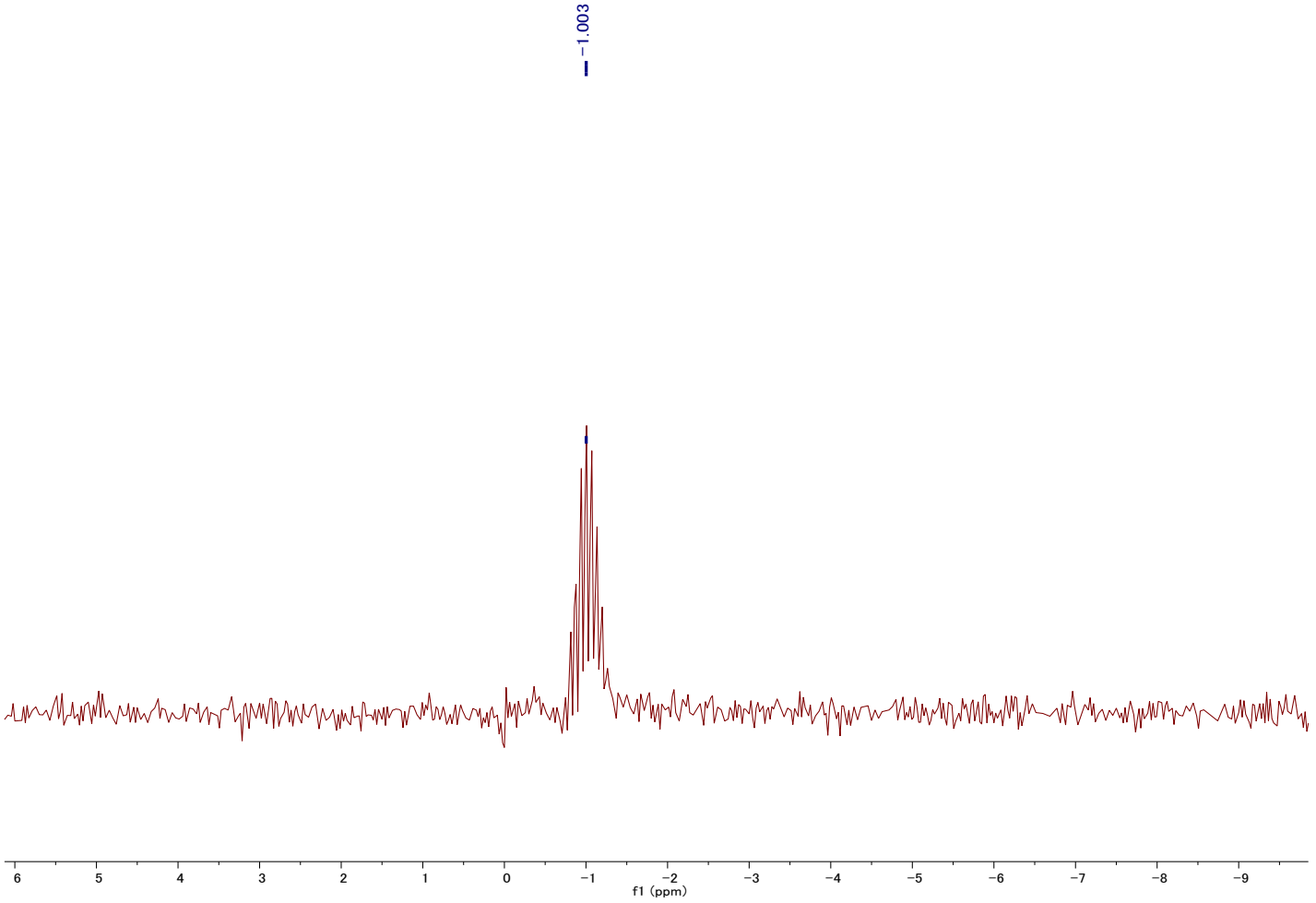




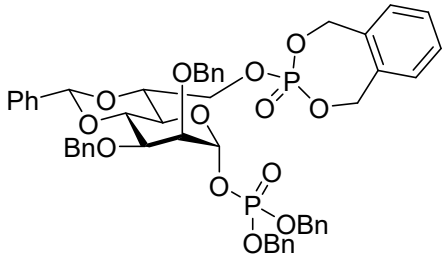
(2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl-*o*-xylenyl phosphate (9) ^{13}C NMR (100 MHz, $CDCl_3$)

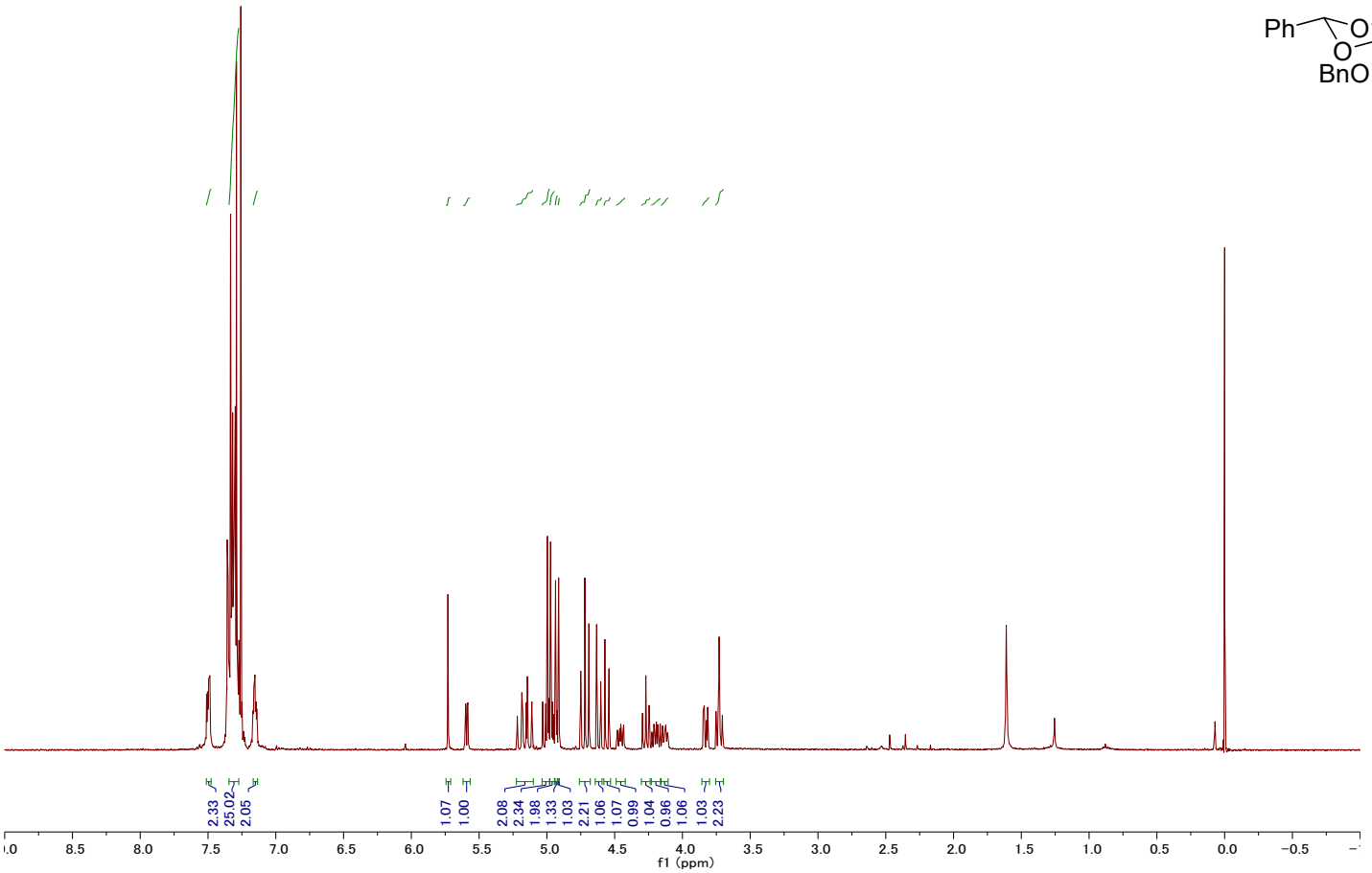


(2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranoside)-7-yl-*o*-xylenyl phosphate (9) ^{31}P NMR (161 MHz, $CDCl_3$)

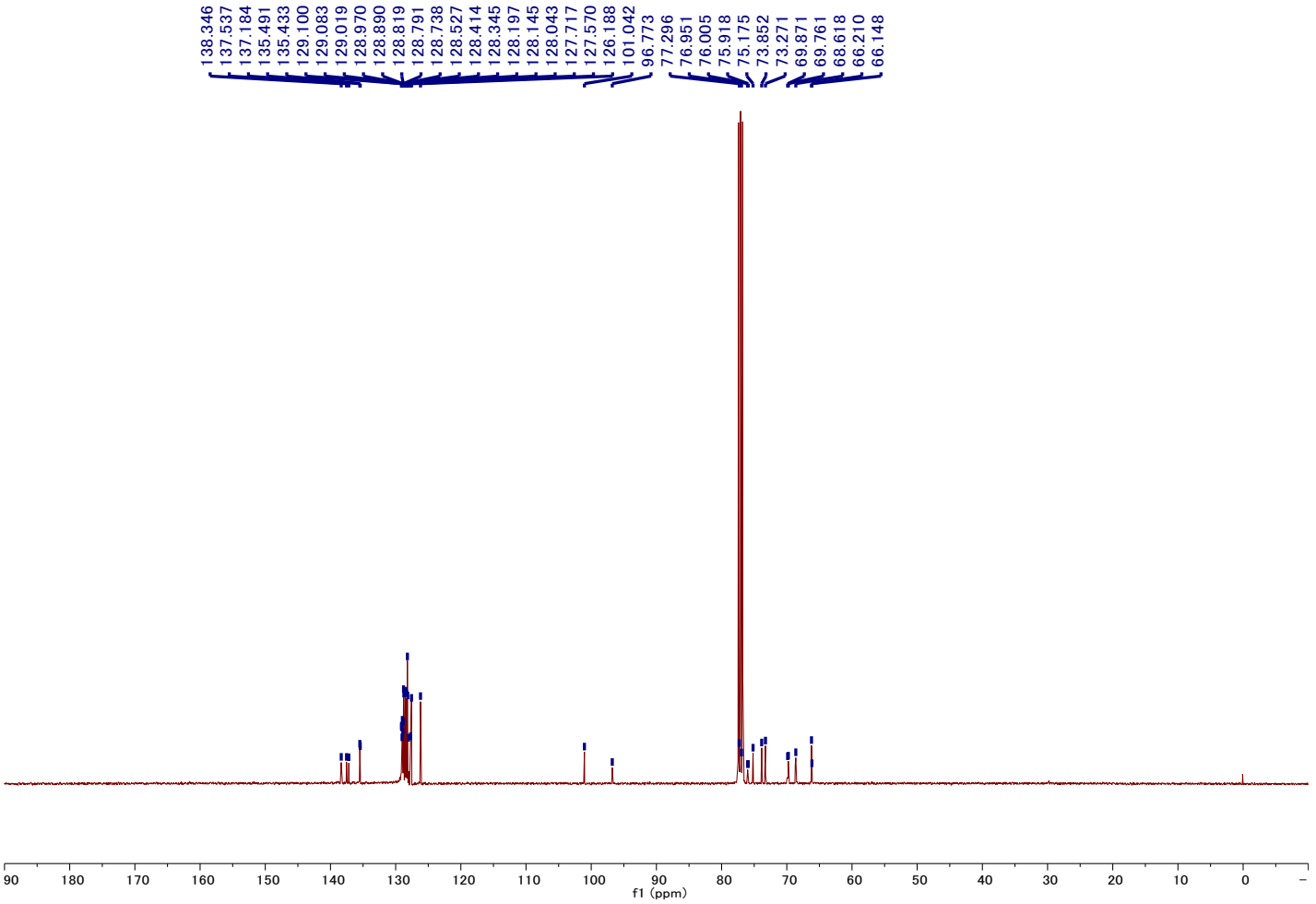


1-Bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11α) ^{1}H NMR (400 MHz, $CDCl_3$)

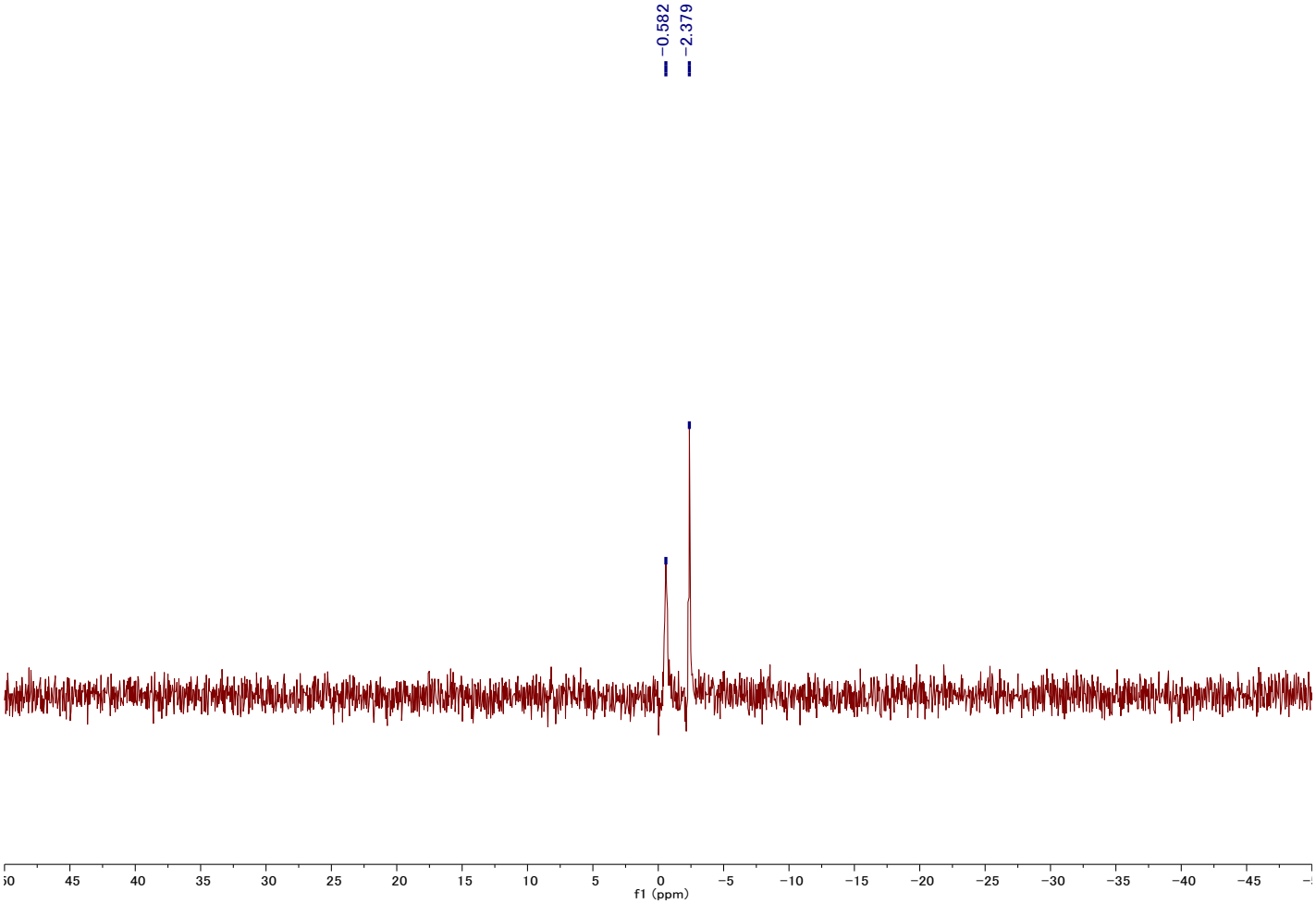




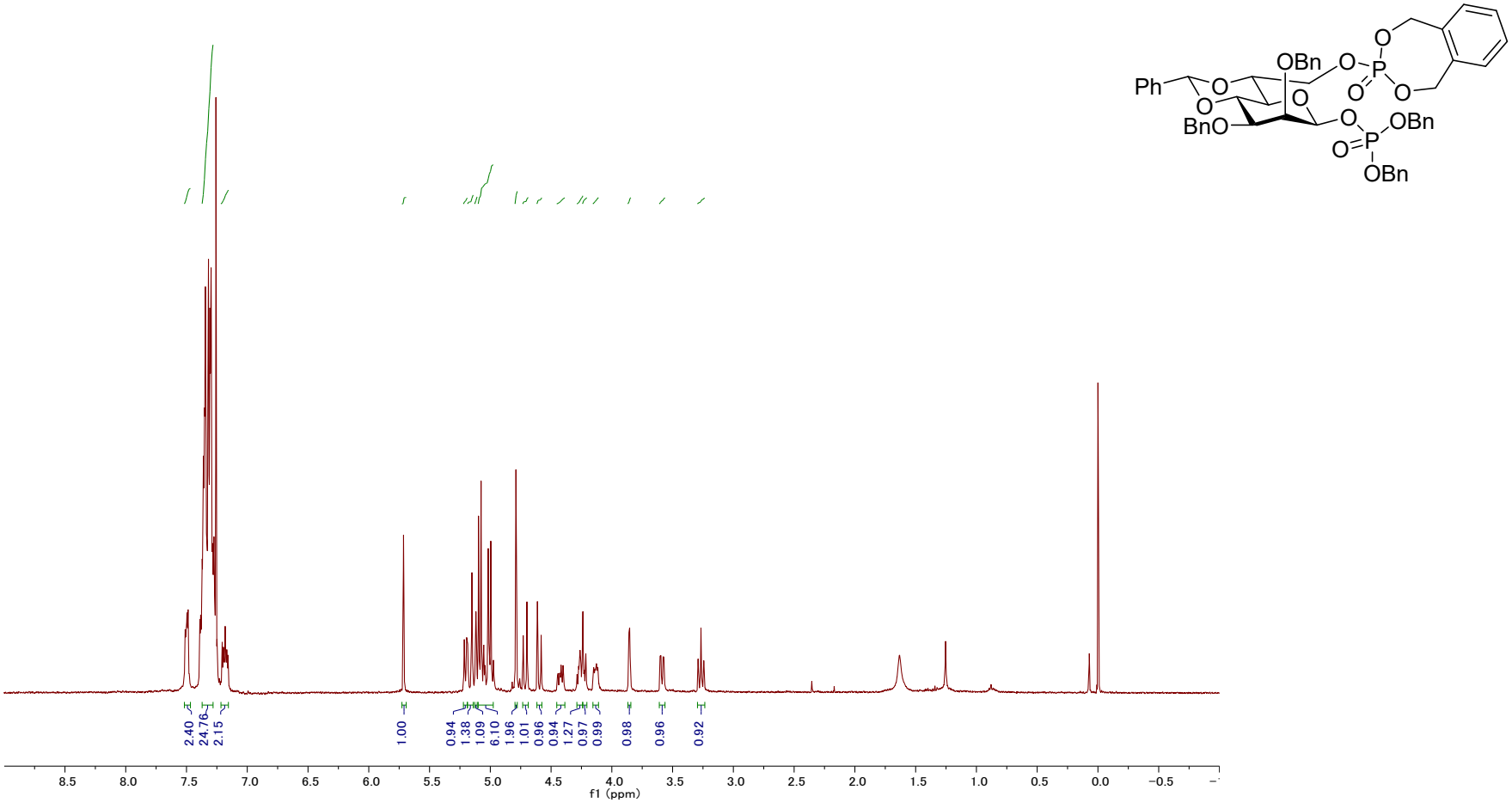
1-Bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11α) ^{13}C NMR (100 MHz, $CDCl_3$)



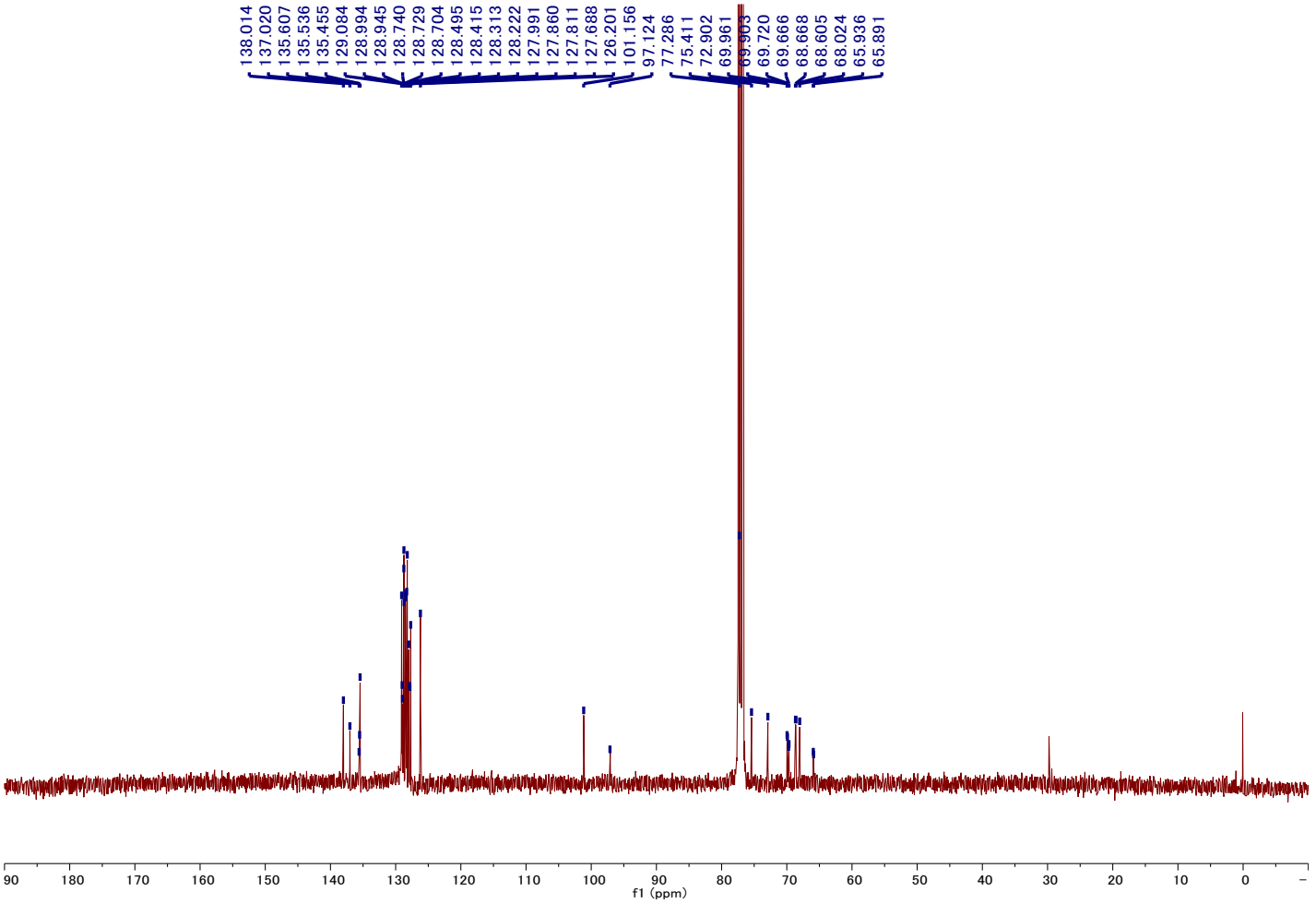
1-Bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11α) ^{31}P NMR (161 MHz, $CDCl_3$)



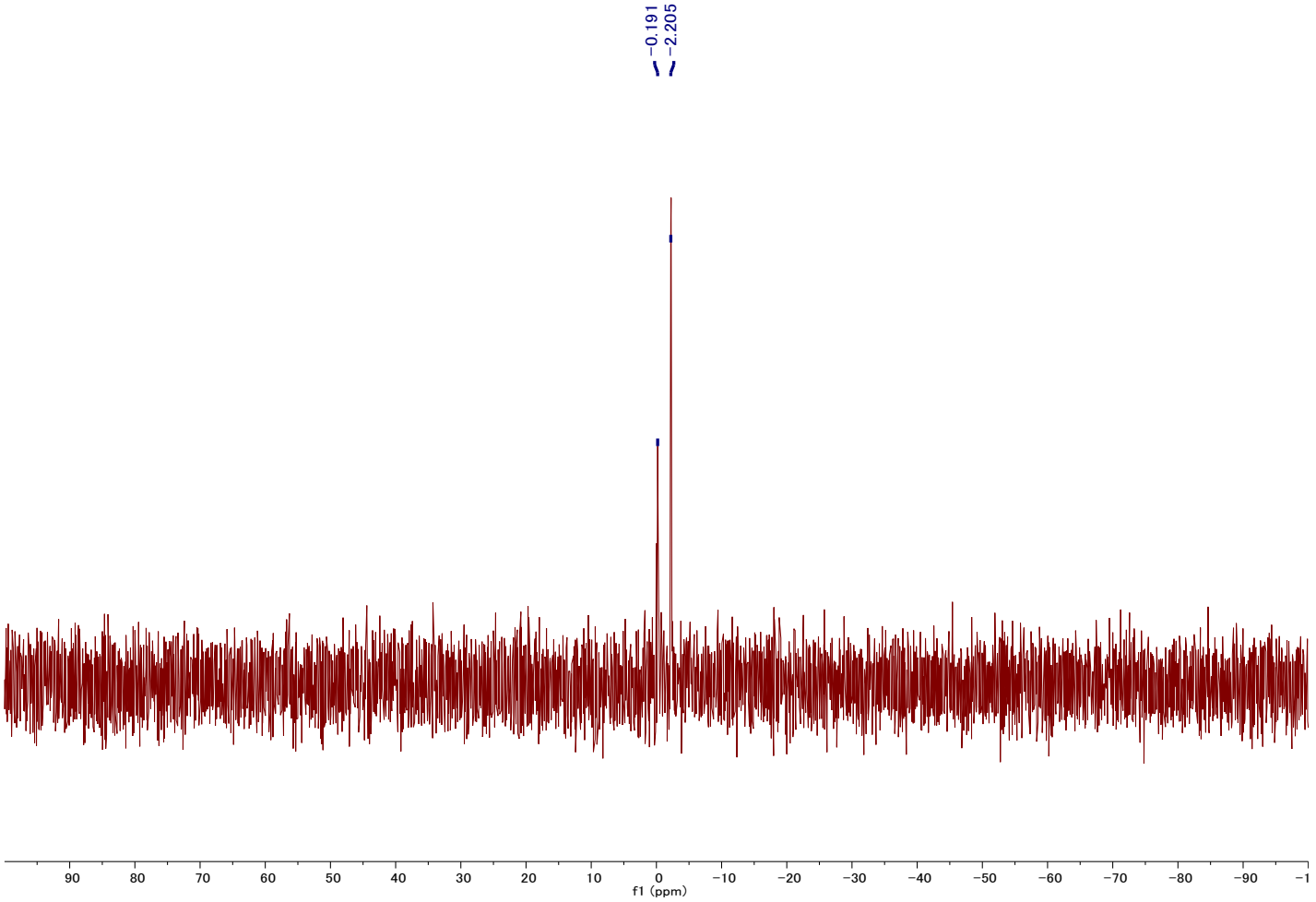
1-bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-β-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11β) ^{1}H NMR (400 MHz, $CDCl_3$)



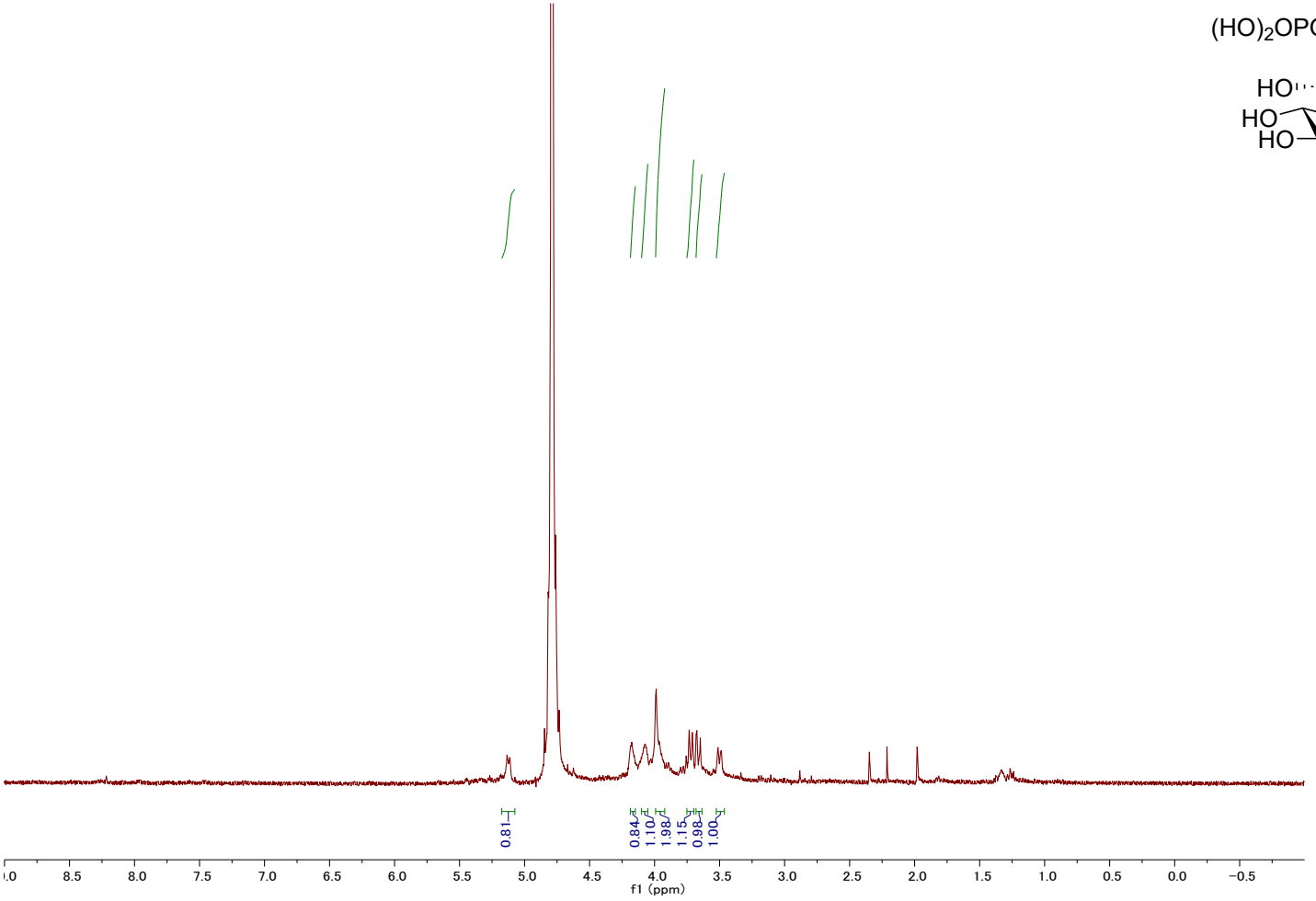
1-bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-β-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11β) ^{13}C NMR (100 MHz, $CDCl_3$)

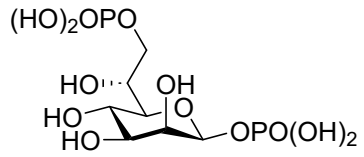


1-bis(benzyloxy)phosphoryl-2,3-*O*-dibenzyl-4,6-*O*-benzylidene-β-D-*glycero*-D-*manno*-heptopyranos-7-yl *o*-xylenyl phosphate (11β) ^{31}P NMR (161 MHz, $CDCl_3$)

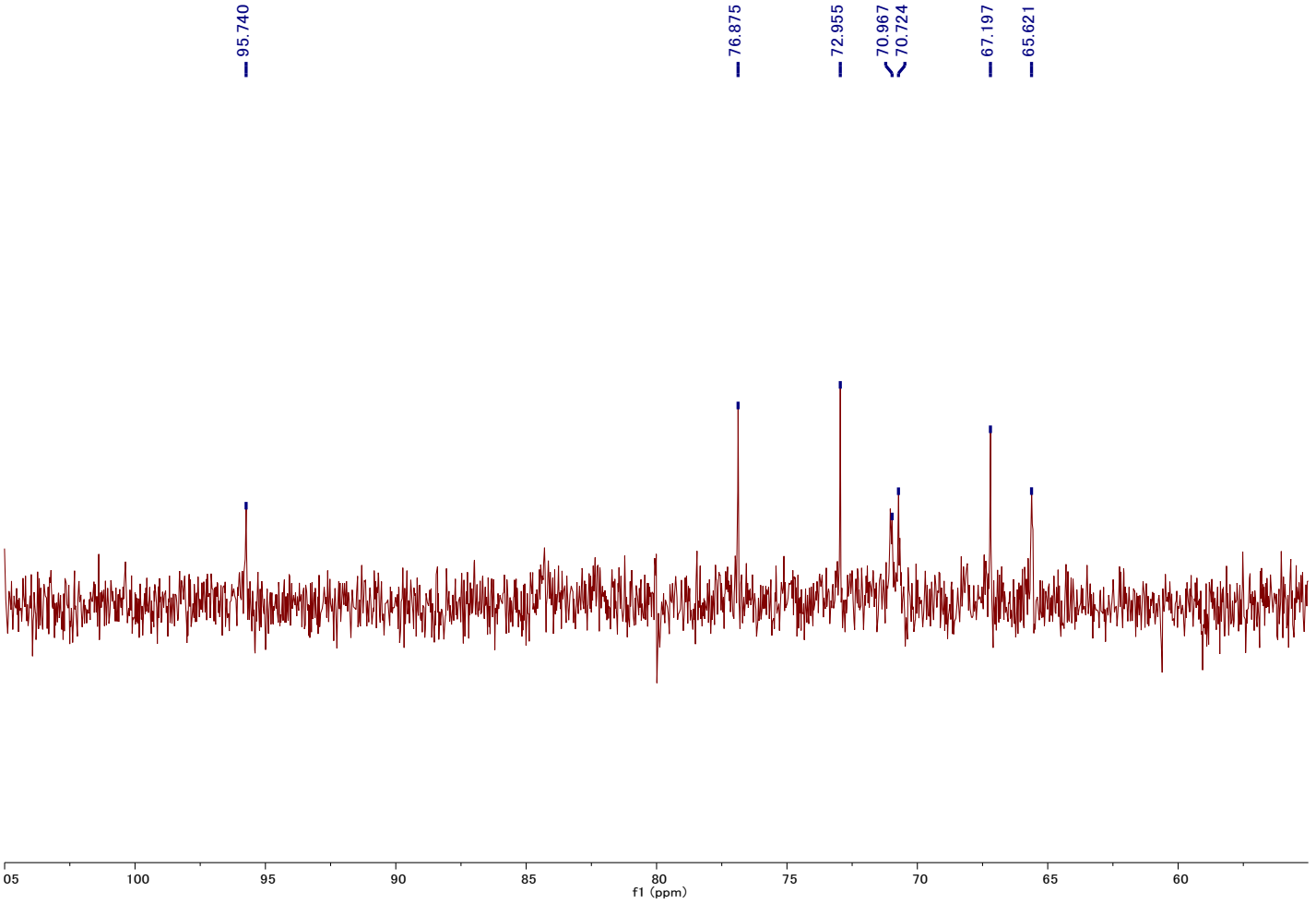


1,7-*O*-Bisphosphoryl-β-D-*glycero*-D-*manno*-heptopyranose (HBP) ^{1}H NMR (400 MHz, D_2O)

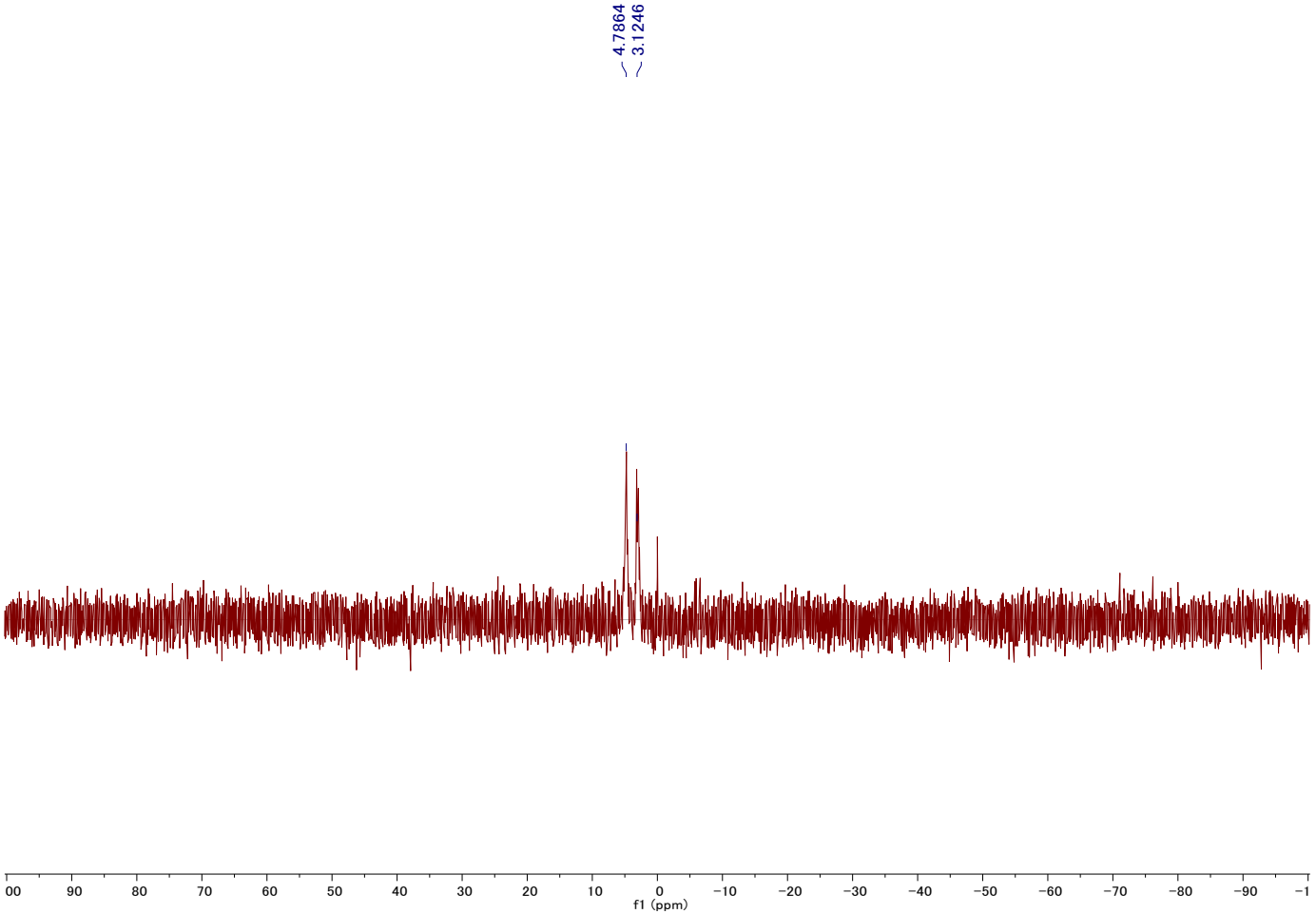




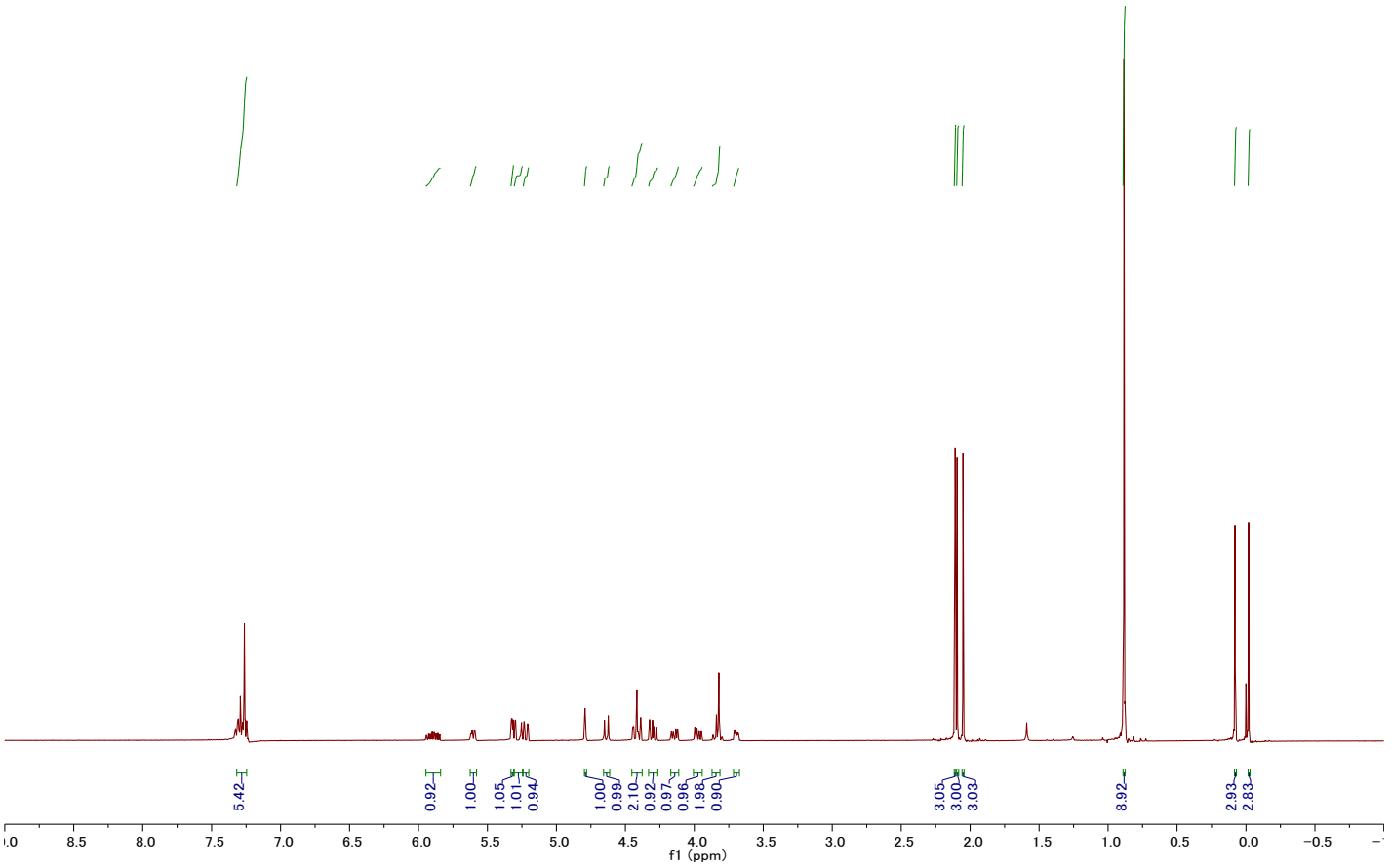
1,7-*O*-Bisphosphoryl-β-D-*glycero*-D-*manno*-heptopyranose (HBP) ^{13}C NMR (100 MHz, D_2O)

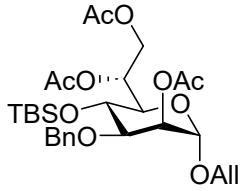


1,7-*O*-Bisphosphoryl-β-D-*glycero*-D-*manno*-heptopyranose (HBP) ^{31}P NMR (161 MHz, D_2O)

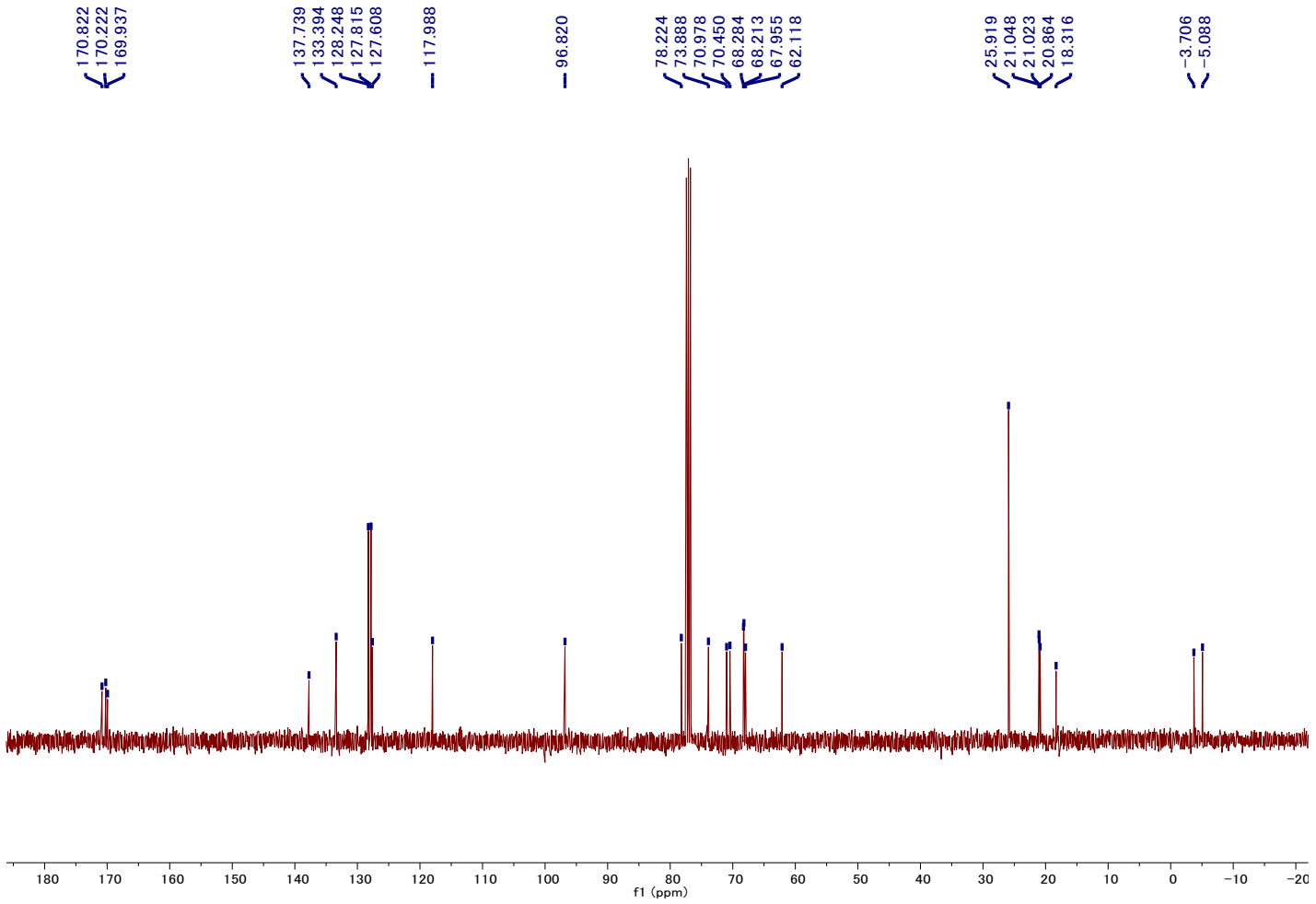


Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (D-SI1) ^{1}H NMR (400 MHz, $CDCl_3$)

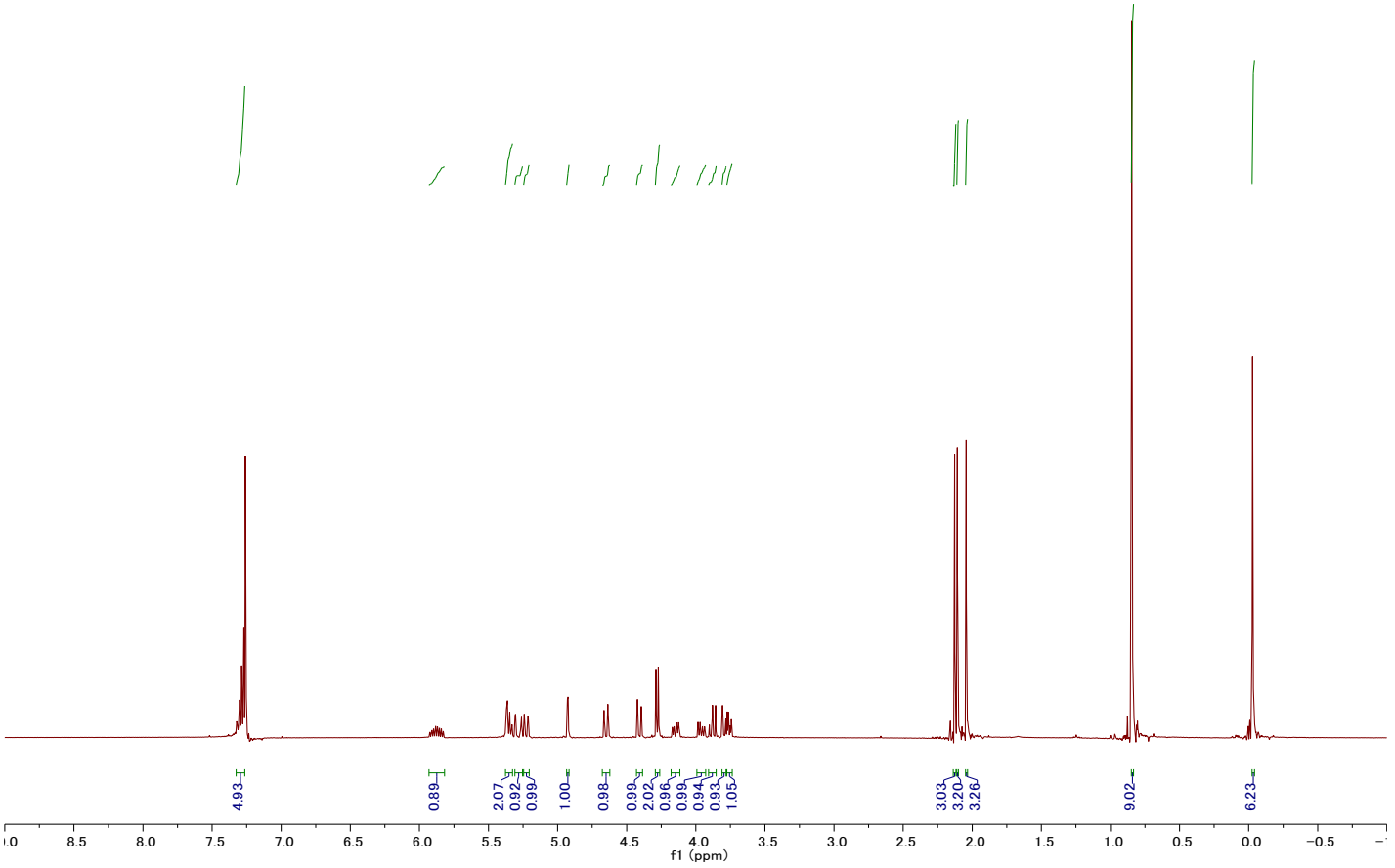


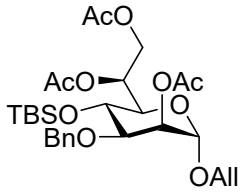


Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-D-*glycero*-D-*manno*-heptopyranoside (D-SI1) ^{13}C NMR (100 MHz, $CDCl_3$)

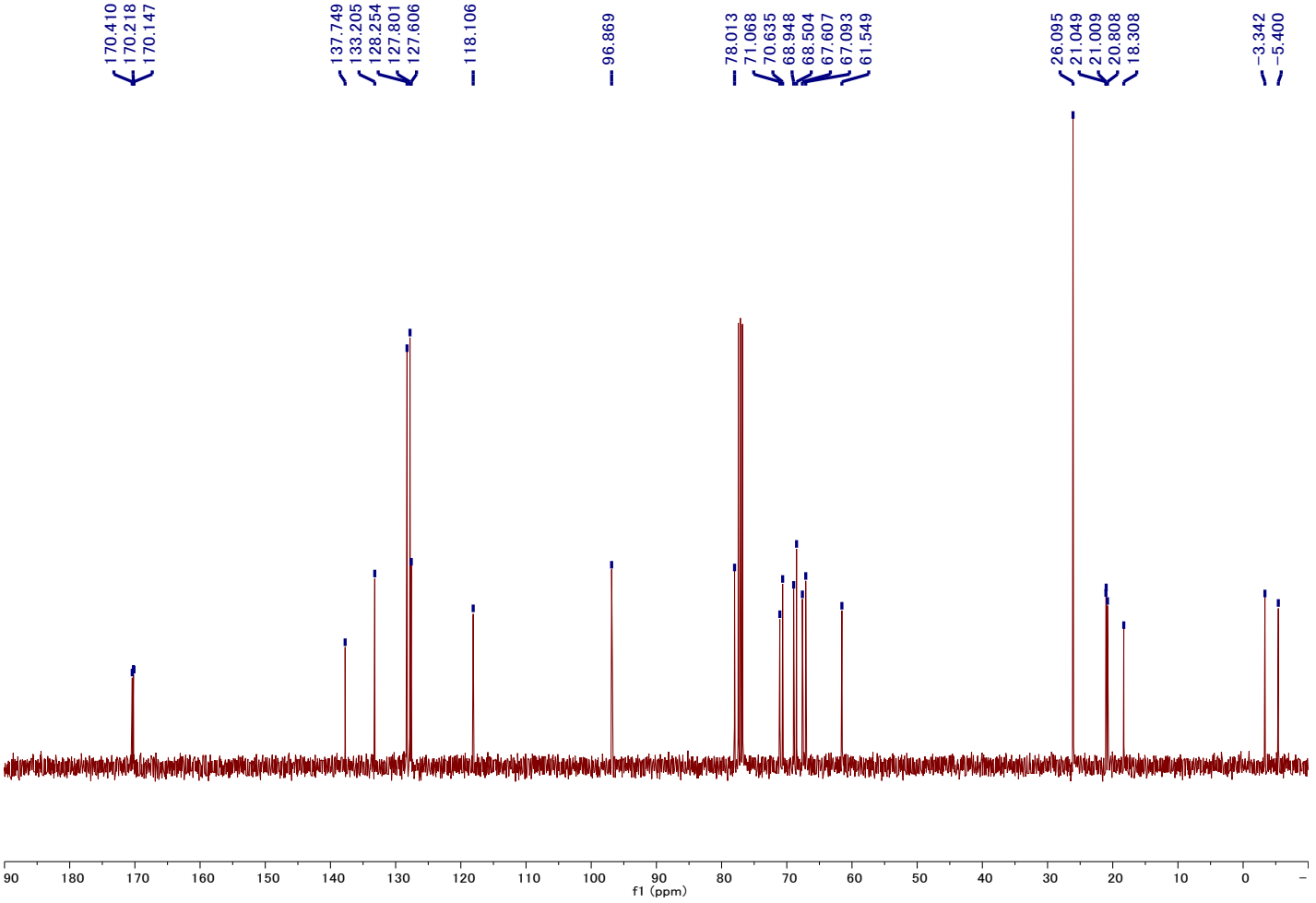


Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-L-*glycero*-D-*manno*-heptopyranoside (L-**SI1**) ^{1}H NMR (400 MHz, $CDCl_3$)

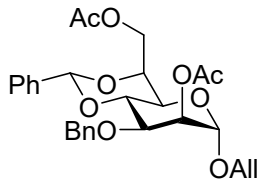


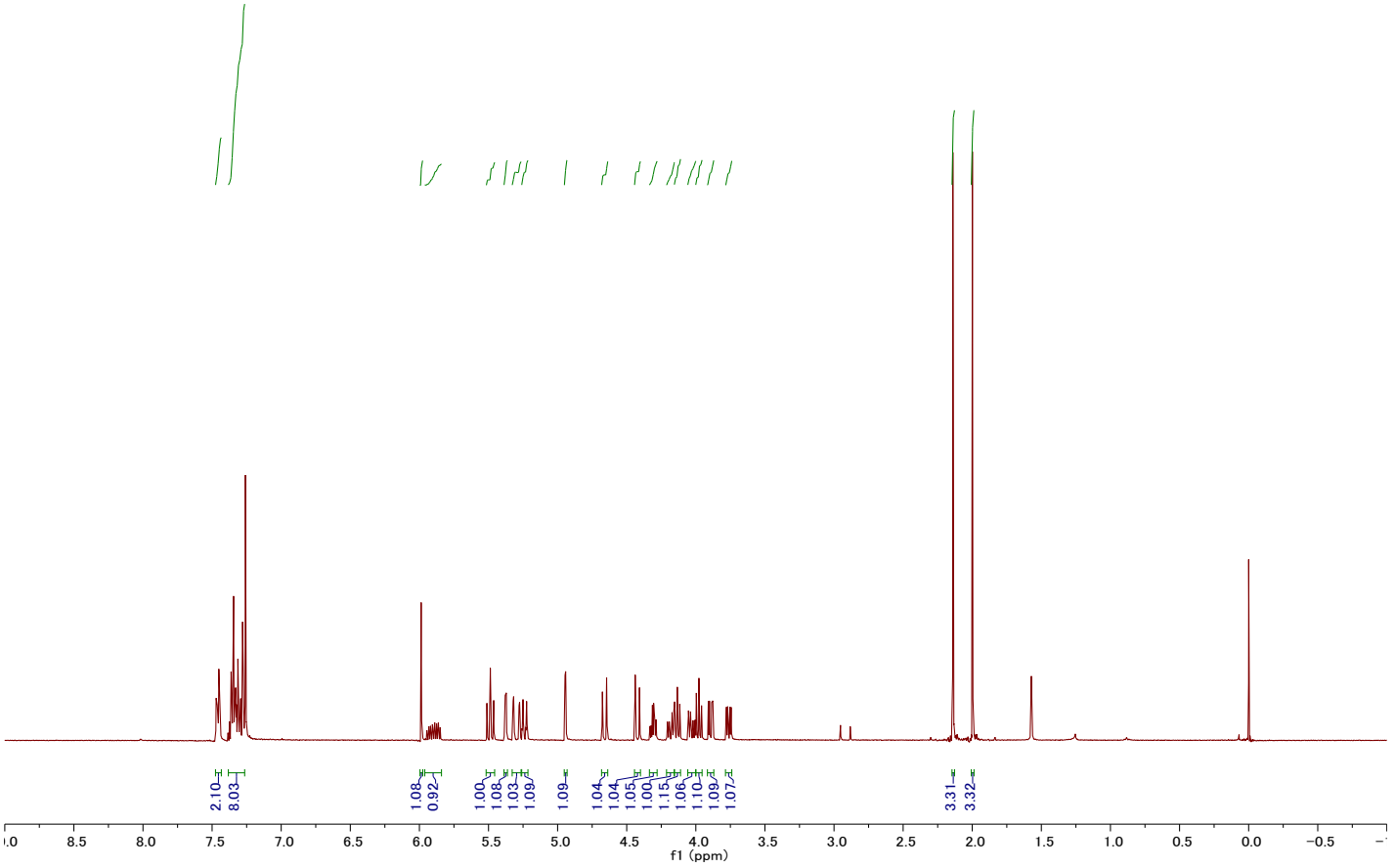


Allyl 2,6,7-*O*-triacetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α-L-*glycero*-D-*manno*-heptopyranoside (L-**SI1**) ^{13}C NMR (100 MHz, $CDCl_3$)



Allyl 2,7-diacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-*glycero*-D-*manno*-heptopyranoside (SI2) ^{1}H NMR (400 MHz, $CDCl_3$)





Allyl 2,7-diacetyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-L-*glycero*-D-*manno*-heptopyranoside (SI2) ^{13}C NMR (100 MHz, $CDCl_3$)