Supporting Information

for

Stereocontrolled Glycoside and Glycosyl Ester Synthesis. Neighboring Group Participation and Hydrogenolysis of 3-(2'-Benzyloxyphenyl)-3,3-dimethylpropanoates

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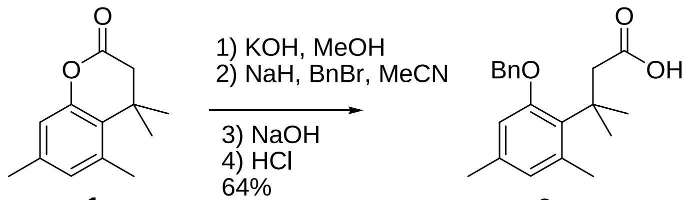
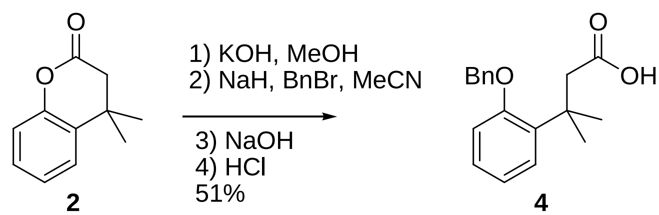
Table of Contents

Protecting Group Synthesis



1 **3**

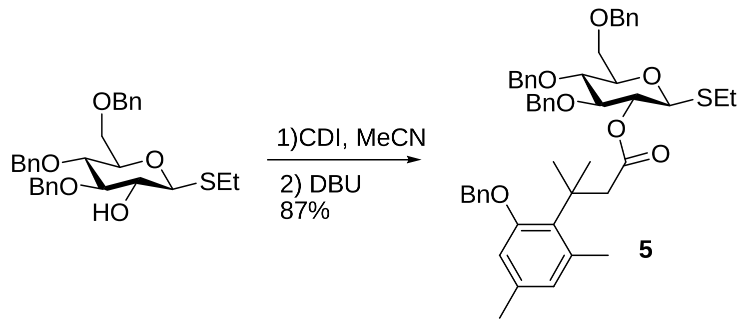
A solution of lactone **1** (5.10 g, 25 mmol) and KOH powder (1.46 g, 26 mmol) in MeOH (40 mL) was stirred for 3 h at room temperature. After removal of the solvent under vacuum, the residue was redissolved in dry MeCN (150 mL) and 60 % NaH dispersion in mineral oil (2.6 g, 60 mmol) was added at 0 °C. The resulting solution was stirred for 10 mins before benzyl bromide (7.1 mL, 60 mmol) was added. The reaction mixture was stirred overnight at room temperature before H_2O (25 mL) was dropped in at 0 °C. The resulting clear solution was stirred for 5 h, then was neutralized by addition of HCl. After removal of MeCN under reduced pressure, the water layer was extracted by CH_2Cl_2 3 times, and the combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give the acid **3**[1] (5.0 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.60 (s, 6H), 2.23 (s, 3H), 2.51 (s, 3H), 2.97 (s, 2H), 5.04 (s, 2H), 6.56 (s, 1H), 6.66 (s, 1H), 7.36-7.44 (m, 5H), 10.07 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.9, 25.7, 31.8(2 C), 39.6, 46.8, 70.9, 112.2, 127.6, 127.7(2C), 127.9, 128.6(2C), 130.0, 136.2, 137.2, 137.7, 158.2, 177.3.



2 **4**

Using the same procedure as for the synthesis of **3**, compound **4**[1] was obtained in 51% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.51 (s, 6H), 2.95 (s, 2H), 5.12 (s, 2H), 6.92-6.96 (m, 2H), 7.21 (t, J = 7.5Hz, 1H), 7.31 (d, J = 8.0Hz, 1H), 7.36 (d, J = 7.0Hz, 1H), 7.41 (t, J = 7.5Hz, 1H), 7.47 (d, J = 7.5Hz, 1H), 11.18 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.4(2C), 37.0, 44.7, 70.3, 112.4, 120.7, 127.5, 127.6, 127.7(2 C), 127.9, 128.7(2 C), 134.9,137.1, 157.2, 178.5.

Protection reactions[2]



5

Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-1-thio-*β*-D-glucopyranoside (5). A solution of 3'-(2"-benzyloxyphenyl)-3',3'-dimethylpropionic acid (2.72 g, 8.7 mmol) and 1,1′-carbonyl diimidazole (1.40 g, 8.7 mmol) in dry acetonitrile (20 mL) was stirred at 60 °C for 2 h under argon. After cooling to room temperature an acetonitrile solution of the alcohol (2.15 g, 4.3 mmol) was added followed by the addition of DBU (1.2 mL, 7.85 mmol). The resulting yellow solution then was stirred at 60 °C for 3 h before it was cooled to rt and diluted with EtOAc, then was washed with 1 N HCl, satd aq $NaHCO_3$, and brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (Hex:EtOAc/10:1) to afford donor **5** (3.0 g, 87%) as a colorless oil. $[\alpha]^{23}_D$ -18° (c, 1.65, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.5 Hz, 3H), 1.65 (s, 3H), 1.70 (s, 3H), 2.26 (s, 3H), 2.62 (s, 3H), 2.62-2.74 (m, 2H), 2.98 (d, *J* = 18.0 Hz, 1H), 2.33 (d, *J* = 18.0 Hz, 1H), 3.50 (m, 1H), 3.53 (t, *J* = 5.0Hz, 1H), 3.64 (t, *J* = 9.5 Hz, 1H), 3.74 (dd, *J* = 6.0, 11.0 Hz, 1H), 3.79 (dd, *J* = 2.0, 11.0 Hz, 1H), 4.25 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 4.52-4.55 (m, 2H), 4.59 (d, *J*= 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.93 (s, 2H), 5.07 (t, *J* = 9.5 Hz, 1H), 6.60 (s, 1H), 6.61 (s, 1H), 7.17-7.18 (m, 2H), 7.22-7.24 (m, 2H), 7.31-7.33 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.8, 20.9, 23.4, 25.9, 31.8, 32.0, 39.8, 47.3, 69.0, 70.8, 71.4, 73.5, 74.9, 75.2, 79.5, 83.3, 84.7, 112.2, 127.66-128.60 (21 C), 130.5, 135.9, 137.3, 137.8, 137.8, 138.0, 138.3, 158.2, 171.4; IR (film, cm^{-1}): 1744; ESI HRMS Calcd for $C_{49}H_{56}O_7SNa$, $[M+Na]^+$: 811.3645. Found 811.3679.

Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-1-thio-*β*-D-glucopyranoside (6) was prepared analogously to **5**. $[\alpha]^{21}_D$ -25.0° (c, 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.25 (s, *J* = 7.5 Hz, 3H), 1.53 (s, 3H), 1.58 (s, 3H), 2.61-2.72 (m, 2H), 2.86 (d, *J* = 15.0 Hz, 1H), 3.25 (d, *J* = 15.0 Hz, 1H), 3.43-3.47 (m, 2H), 3.62 (t, *J* = 9.5 Hz, 1H), 3.71 (dd, *J* = 4.5, 11.0 Hz, 1H), 3.76 (dd, *J* = 2.0, 11.0 Hz, 1H), 4.08 (d, *J* = 10.0 Hz, 1H), 4.50 (d, *J* = 11.0 Hz, 1H), 4.53 (d, *J* = 11.0 Hz, 1H), 4.59 (dd, *J* = 12.0, 26.5 Hz, 2H), 4.59 (d, *J* = 1.5 Hz, 1H), 4.73 (d, *J* = 11.0 Hz, 1H), 4.99 (t, *J* = 9.5 Hz, 1H), 5.02 (s, 2H), 6.91-6.96 (m, 2H), 7.16-7.22 (m, 5H), 7.28-7.39 (m, 17H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.8, 23.4, 28.4, 28.6, 37.1, 45.1, 69.0, 70.2, 71.3, 73.5, 75.0, 75.1, 79.4, 83.2, 84.6, 112.2, 120.6, 127.48-128.61

(23 C), 135.4, 137.0, 138.0, 138.2, 138.2, 157.2, 170.8; IR (film, cm^{-1}): 1738; ESI HRMS Calcd for $C_{47}H_{52}O_7SNa$ $[M+Na]^+$: 783.3326. Found: 783.3318.

Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-1-thio-*α*-D-mannopyranoside (7) was prepared analogously to **5**. $[\alpha]^{23}_{D}$ +49.9° (c, 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.25 (t, J = 8.0 Hz, 3H), 1.61(s, 3H), 1.62 (s, 3H), 2.22 (s, 3H), 2.51 (s, 3H), 2.51-2.60 (m, 2H), 3.04 (d, J = 15.0 Hz, 1H), 3.17 (d, J = 15.0 Hz, 1H), 3.63-3.69 (m, 2H), 3.74 (dd, J = 5.0, 12.0 Hz, 1H), 3.83 (dd, J = 3.0, 10.0 Hz, 1H), 4.11-4.14 (m, 1H), 4.42-4.51 (m, 3H), 4.59 (d, J = 11.0 Hz, 1H), 4.61 (d, J = 11.0 Hz, 1H), 4.83-4.86 (m, 2H), 4.03 (dd, J = 11.0, 28.0 Hz, 1H), 5.33 (m, 1H), 6.53 (s, 1H), 6.64 (s, 1H), 7.19 (m, 2H), 7.22-7.40 (m , 16H), 7.34-7.36 (m, 2H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.9, 20.9, 25.4, 25.8, 31.90, 31.94, 40.2, 47.6, 69.2, 69.7, 70.9, 71.5, 71.8, 73.3, 74.9, 75.1, 78.5, 82.5, 112.4, 127.18-128.96 (21 C), 130.2, 135.8, 137.56, 137.62, 138.0, 138.3, 138.5, 158.5, 172.0; IR (film, cm^{-1}): 1729; ESI HRMS Calcd for $C_{49}H_{56}O_7SNa$, $[M+Na]^+$: 811.3645. Found 811.3631.

General Glycosylation Procedure. A 0.5M solution of donor, acceptor (1.5 equiv) and 3 Å molecular sieves in dry CH_2Cl_2 was stirred at room temperature for 0.5 h under argon before it was cooled under argon to -40 °C. NIS (1 equiv) was then added followed by TfOH (0.3 equiv), and the resulting mixture was stirred for 15 min before it was filtered. The filtrate was washed by 20% $Na_2S_2O_3$ solution and brine. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (Hex:EtOAc/5-10: 1) to afford the glycosylation products.

General Deprotection Procedure. A 0.05M solution of the substrate and 20% mol Pd/C or $Pd(OH)_2/C$ in a mixture of MeOH/EtOAc (v/v, 5:1) were shaken in a Parr hydrogenator for 5 h under 3 atm of H_2. The reaction mixture was then filtered through Celite, and the filtrate was concentrated under reduced pressure. The residue was dissolved in H_2O, then was washed with EtOAc. Evaporation of the H_2O phase then gave the hydrogenolysis product.

1-Adamantanyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethyl-phenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (8). $[\alpha]^{18}_{D}$ +5.3° (c, 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.53-1.69 (m, 15H), 1.76 (d, *J* = 11.5 Hz,3H), 2.09 (br, 3H), 2.15 (s, 3H), 2.56 (s, 3H), 2.93 (d, *J* = 16.5 Hz, 1H), 3.15 (d, *J* = 16.0 Hz, 1H), 3.46-3.52 (m, 2H), 3.54-3.62 (m, 2H), 3.71 (dd, *J* = 1.5, 11.0 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.42 (d , *J* = 10.5 Hz, 1H), 4.46 (d, *J* = 11.0 Hz, 1H), 4.52-4.61 (m, 3H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 11.0 Hz, 1H), 4.90 (t, *J* = 9.0 Hz, 1H), 4.92 (d, *J* = 11.0 Hz, 1H), 6.51 (s, 1H), 6.54 (s, 1H), 7.10-7.20 (m, 4H), 7.20-7.40 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.8, 25.8, 30.7 (3 C), 31.8, 32.0, 36.2 (3 C), 39.6, 42.5 (3 C), 46.7, 69.4, 70.7, 73.4(2 C), 74.3, 74.8, 74.9, 77.9, 83.5, 94.1 ($^1J_{CH}$ = 158.6 Hz), 112.3, 127.5-128.5 (21 C), 130.5, 135.9, 137.3, 138.0, 138.1, 138.4 (2 C), 158.1, 170.9; IR (film, cm^{-1}): 1751; ESI HRMS Calcd for $C_{57}H_{66}O_8Na$ $[M+Na]^+$: 901.4650. Found 901.4667.

1-Adamantanyl *β*-D-glucopyranoside[3] (9). M.p. 221-223 °C; $[\alpha]^{20}_{D}$ -24.0° (c, 0.2, MeOH) [lit[3]: m.p. 222-223 °C, $[\alpha]^{24.5}_{D}$ -26.2° (c, 1.0, pyridine)]; ^{1}H NMR (500 MHz, MeOD) δ: 1.67 (t, *J* = 15.0 Hz, 6H), 1.80 (d, *J* = 11.0 Hz, 3H), 1.92 (d, *J* = 11.0 Hz, 3H), 2.13 (br, 3H), 3.11 (t, *J* = 8.0 Hz, 1H), 3.22-3.28 (m, 1H), 3.28 (t, *J* = 8.0 Hz, 1H), 3.36 (t, *J* = 8.0 Hz, 1H), 3.63 (dd, *J* = 5.0, 11.0 Hz, 1H), 3.81 (dd, *J* = 2.0, 11.0 Hz, 1H), 4.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 30.8 (3 C), 36.0 (3 C), 42.2 (3 C), 61.4, 70.4, 73.7, 74.7, 76.2, 76.7, 95.7; MS/ESI for $C_{16}H_{26}O_6Li$ $[M+Li\ ]^+$: 321.4.

Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (10) $[\alpha]^{17}_{D}$ -6.8° (c, 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.08 (d, *J* = 6.0 Hz, 3H), 1.21 (d, *J* = 6.0 Hz, 3H), 1.61 (s, 6H), 2.17 (s, 3H), 2.56 (s, 3H), 3.06 (d, *J* = 5.0 Hz, 2H), 3.41-3.48 (m, 1H), 3.51 (t, *J* = 7.5 Hz, 1H), 3.53 (t, *J* = 8.5 Hz, 1H), 3.63 (dd, *J* = 5.0, 11.0 Hz, 1H), 3.70 (dd, *J* = 2.0, 11.0 Hz, 1H), 3.85 (sp, *J* = 6.0 Hz, 1H), 4.28 (d, *J* = 11.0 Hz, 1H), 4.36 (d, *J* = 8.0 Hz, 1H), 4.39 (d, *J* = 11.0 Hz, 1H), 4.51 (dd, *J* = 11.0, 45.0 Hz, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.87 (s, 2H), 4.92 (d, *J* = 8.0 Hz, 1H), 6.54 (br, 2H), 7.10-7.20 (m, 4H), 7.20-7.30 (m, 8H), 7.30-7.40 (m, 8H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.8, 22.0, 23.5, 25.8, 31.7, 39.6, 46.9, 69.1, 70.7, 71.9, 73.2, 73.4, 74.5, 75.0, 75.1, 77.8, 83.3, 99.7 ($^1J_{CH}$ = 163.6 Hz), 112.3, 127.55-129.01(25 C), 135.9, 138.0, 138.3, 138.4, 158.1, 171.0; IR (film, cm^{-1}): 1749; ESI HRMS Calcd for $C_{50}H_{58}O_8Na$ $[M+Na]^+$: 809.4024. Found: 809.4034.

Isopropyl *β*-D-glucopyranoside[4] (11) Mp, 127-128°C; $[\alpha]^{23}_{D}$ -32.2° (c, 0.6, MeOH) [lit[4]: m.p. 126-127°C, $[\alpha]^{27}_{D}$ -35.5° (c, 0.5, H_2O)]; ^{1}H NMR (500 MHz, MeOD) δ: 1.19 (d, *J* = 6.0 Hz, 3H), 1.22 (d, *J* = 6.0 Hz, 3H), 3.13 (t, *J* = 9.0 Hz, 1H), 3.25-3.29 (m, 2H), 3.35 (t, *J* = 9.0 Hz, 1H), 3.66 (dd, *J* = 5.0, 11.0 Hz, 1H), 3.85 (d, *J* = 12.0 Hz, 1H), 4.01-4.05 (m, 1H), 4.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 20.7, 22.4, 61.4, 70.3, 71.2, 73.8, 76.4, 76.7, 101.2. MS/ESI for $C_9H_{18}O_6Li$ $[M+Li\ ]^+$: 229.2.

Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxyphenyl)-3',3'-dimethyl propanoyl]-*β*-D-glucopyranoside (12) $[\alpha]^{17}_{D}$ -11.2° (c, 1.2 , $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.10 (d, J = 6.0 Hz, 3H), 1.22 (d, J = 6.0 Hz, 3H), 1.508 (s, 3H), 1.514 (s, 3H), 2.93 (d, J = 15.0 Hz, 1H), 3.07 (d, J = 15.0 Hz, 1H), 3.43-3.47 (m, 2H), 3.57 (t, J = 8.0 Hz, 1H), 3.66 (dd, J = 5.0, 11.0 Hz, H), 3.73 (dd, J = 2.0, 11.0 Hz, 1H), 3.88 (sp, J = 6.0 Hz, 1H), 4.29 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 11.0 Hz, 1H), 4.49-4.52 (m, 2H), 4.58 (dd, J = 12.0, 24.0 Hz, 2H), 4.71 (d, J = 11.0 Hz, 1H), 4.92 (t, J = 8.0 Hz, 1H), 4.99 (s, 2H), 6.89-6.93 (m, 2H), 7.14-7.20 (m, 5H), 7.25-7.27 (m, 17H),; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.0, 23.6, 28.1, 36.9, 44.9, 69.1, 70.2, 71.7, 73.2, 73.5, 74.6, 74.9, 75.0, 77.8, 83.3, 99.6 ($^1J_{CH}$ = 158.6 Hz), 112.3, 120.7, 127.5-128.7 (23 C), 135.7, 137.0, 138.0, 138.29, 138.31, 157.1, 10.6; IR (film, cm^{-1}): 1739; ESI HRMS Calcd for $C_{48}H_{54}O_8Na$ $[M+Na]^+$: 781.3717. Found: 781.3691.

Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*α*-D-mannopyranoside (13) $[\alpha]^{23}_{D}$ +20.8° (c, 1.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.08 (d, J = 6.0 Hz, 3H), 1.15 (d, J = 6.0 Hz, 3H), 1.60 (s, 3H), 1.61 (s, 3H), 2.21 (s, 3H), 2.50 (s, 3H), 3.02 (d, J = 15.0 Hz, 1H), 3.16 (d, J = 15.0 Hz, 1H), 3.60 (t, J = 10.0 Hz, 1H), 3.66-3.73 (m, 2H), 3.81-3.85 (m, 2H), 3.91 (dd, J = 3.0, 9.0 Hz, 1H), 4.43 (d, J = 10.0 Hz, 1H), 4.46 (d, J = 10.0 Hz, 1H), 4.49-4.62 (m, 2H), 4.83 (d, J = 10.0 Hz, 1H), 5.02 (dd, J = 12.0, 26.0 Hz, 2H), 5.20-5.21 (m, 1H), 6.53 (s, 1H), 6.64 (s, 1H), 7.15-7.16 (m, 2H), 7.23-7.37 (m, 16H), 7.44-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.9, 21.4, 23.2, 25.8, 31.8, 31.9, 40.2, 47.6, 68.5, 69.3, 69.5, 70.9, 71.3, 71.4, 73.3, 74.8, 75.2, 78.3, 96.0 ($^1J_{CH}$ = 168.7 Hz), 112.4, 127.5-128.52(21 C), 130.2, 135.8, 137.56, 137.62, 138.37, 138.40, 138.5, 158.5, 172.2; IR (film, cm^{-1}): 1732; ESI HRMS Calcd for $C_{50}H_{58}O_8Na$ $[M+Na]^+$: 809.4024. Found: 809.4019.

Isopropyl *α*-D-mannopyranoside[5] (14) $[\alpha]^{25}_{D}$ +80.1° (c, 0.7, MeOH) [lit[5]: $[\alpha]^{31}_{D}$ +83° (c, 1.0, H_2O)]; ^1H NMR (500 MHz, MeOD) δ: 1.14 (d, J = 6.0 Hz, 3H), 1.20 (d, J = 6.0 Hz, 3H), 3.56-3.62 (m, 2H), 3.67-3.72 (m, 3H), 3.79 (d, J = 2.0 Hz, 1H), 3.96 (sp, J = 6.0 Hz, 1H), 4.86 (m, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 20.1, 22.2, 61.5, 67.3, 68.6, 77.2, 71.3, 73.2, 98.1.

Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (15) $[\alpha]^{18}_{D}$ -26.0° (c, 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ: 1.26 (d, J = 6.0 Hz, 3H), 1.29 (s, 3H), 1.45 (s, 3H), 1.58 (s, 3H), 1.61 (s, 3H), 2.17 (s, 3H), 2.55 (s, 3H), 2.99 (d, J = 16.0 Hz, 1H), 3.14 (d, J = 16.0 Hz, 1H), 3.37 (s, 3H), 3.38-3.43 (m, 2H), 3.50-3.55 (m, 2H), 3.59-3.72 (m, 5H), 4.01-4.05 (m, 2H), 4.27 (d, J = 11.0 Hz, 1H), 4.40 (d, J = 11.0 Hz, 1H), 4.49-4.54 (m, 2H), 4.60 (d, J = 12.5 Hz, 1H), 4.68 (d, J = 10.5 Hz, 1H), 4.83-4.94 (m, 3H), 6.52 (s, 1H), 6.53 (s, 1H), 7.10-7.35 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.6, 20.8, 25.7, 26.4, 27.9, 31.7, 31.9, 39.6, 46.8, 54.8, 64.1, 68.7, 70.7, 73.1, 73.5, 74.4, 74.9, 75.2, 76.0, 77.65, 77.73, 78.2, 83.2, 97.9 ($^1J_{CH}$ = 167.4 Hz), 99.1 ($^1J_{CH}$ = 168.7 Hz), 109.7, 112.3, 127.4-128.6 (21 C), 130.5, 135.9, 137.3, 137.8, 138.2, 138.3. 138.5, 158.1, 171.3; IR (film, cm^{-1}): 1749; ESI HRMS Calcd for $C_{57}H_{68}O_{12}Na$ $[M+Na]^+$: 967.4603. Found: 967.4604.

Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside[6] (16) $[\alpha]^{23}_D$ -61.3° (c, 0.4, MeOH); ^{1}H NMR (500 MHz, MeOD) δ: 1.26 (d, *J* = 6.0 Hz, 3H), 1.32 (s, 3H), 1.49 (s, 3H), 3.13 (t, *J* = 13.0 Hz, 1H), 3.18-3.22 (m, 1H), 3.30 (t, *J* = 9.0 Hz, 1H), 3.57 (s, 3H), 3.63-3.72 (m, 3H), 3.83 (dd, *J* = 4.0, 11.0 Hz, 1H), 4.09 (d, *J* = 5.0 Hz, 1H), 4.25 (t, *J* = 6.0 Hz, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.80 (s, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 16.6, 25.2, 26.9, 53.7, 61.4, 63.9, 70.3, 74.0, 75.9, 76.7, 76.8, 77.7, 78.1, 98.0, 100.9, 109.0; ESI HRMS Calcd for $C_{16}H_{28}O_{10}Na$ $[M+Na]^+$: 403.1575. Found: 403.1570.

Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L - rhamanopyranoside (17) $[\alpha]^{23}_D$ +25.1° (c, 1.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.15 (d, *J* = 6.0 Hz, 3H), 1.24 (s, 3H), 1.44 (s, 3H), 1.59 (s, 3H), 1.60 (s, 3H), 2.21 (s, 3H), 2.47 (s, 3H), 2.98 (d, *J* = 14.0 Hz, 1H), 3.22 (d, *J* = 7.5, 10.0 Hz, 1H), 3.34 (s, 3H), 3.54 (dd, *J* = 6.0, 10.0 Hz, 1H), 3.62 (dd, *J* = 1.5, 5.5 Hz, 1H), 3.82-3.85 (m, 2H), 3.92-3.97 (m, 2H), 4.02 (d, *J* = 6.0 Hz, 1H), 4.41-4.51 (m, 4H), 4.56-4.59 (m, 2H), 4.81-4.86 (m, 2H), 4.95 (d, *J* = 11.0 Hz, 1H), 5.05 (d, *J* = 11.0 Hz, 1H), 5.19-5.20 (m, 1H), 6.50 (s, 1H), 6.61 (s, 1H), 7.18-7.47 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.4, 21.0, 25.7, 26.4, 28.1, 31.9, 40.4, 47.4, 54.9, 64.8, 67.9, 68.7, 70.8, 71.3, 71.4, 73.4, 74.5, 75.3, 75.9, 77.3, 78.0, 80.5, 98.0 ($^1J_{CH}$ = 167.4 Hz), 98.7 ($^1J_{CH}$ = 171.2 Hz), 109.0, 112.4, 127.45-128.51 (22 C), 129.9, 135.9, 137.5, 137.6, 138.35, 138.43, 138.7, 58.5, 172.2; IR (film, cm^{-1}): 1730; ESI HRMS Calcd for $C_{57}H_{68}O_{12}Na$ $[M+Na]^+$: 967.4603. Found: 967.4593.

Methyl 4-*O*-α-D-mannopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (18) $[\alpha]^{23}_D$ +49.7° (c, 0.4, MeOH); ^{1}H NMR (500 MHz, MeOD) δ: 1.26 (d, *J* = 6.0 Hz, 3H), 1.31 (s, 3H), 1.50 (s, 3H), 3.34 (br, 2H), 3.36 (s, 3H), 3.61 (dd, *J* = 6.0, 10.0 Hz, 1H), 3.67 (dd, *J* = 3.5, 9.0 Hz, 1H), 3.74 (t, *J* = 9.0 Hz, 1H), 3.79 (br, 2H), 3.81-3.81 (m, 2H), 4.06 (t, *J* = 6.0 Hz, 1H), 4.11 (d, *J* = 6.0 Hz, 1H), 4.80 (br, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 16.5, 25.1, 27.0, 53.8, 61.1, 64.5, 66.7, 70.8, 71.1, 73.0, 75.9, 77.1, 81.1, 97.9, 101.5, 108.9; ESI HRMS Calcd for $C_{16}H_{28}O_{10}Na$ $[M+Na]^+$: 403.1575. Found: 403.1571.

Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (19) $[\alpha]^{18}_D$ +1.2° (c, 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.58 (s, 3H), 1.63 (s, 3H), 2.07 (s, 3H), 2.55 (s, 3H), 2.93 (d, *J* = 16.0 Hz, 1H), 3.32 (d, *J* = 16.5 Hz, 1H), 3.33 (s, 3H), 3.49-3.77 (m, 10H), 3.86 (dd, *J* = 3.0, 8.5 Hz, 1H), 4.14-4.17 (m, 1H), 4.18 (d, *J* = 11.0 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 4.38 (d, *J* = 11.0 Hz, 1H), 4.40 (d, *J* = 10.5 Hz, 1H), 4.43 (s, 2H), 4.47-4.51 (m, 2H), 4.53 (d, *J* =

3.0 Hz, 1H), 4.62 (d, J = 11.0 Hz, 1H), 4.66 (s, 1H), 4.79-4.89 (m, 3H), 5.06 (t, J = 8.0 Hz, 1H), 6.44 (s, 1H), 6.47 (s, 1H), 7.02-7.07 (m, 2H), 7.10-7.18 (m, 4H), 7.20-7.40 (m, 29H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.7, 25.8, 31.9, 32.1, 39.6, 46.8, 54.7, 69.6, 70.2, 70.7, 71.6, 73.15, 73.20, 73.4, 73.6, 74.0, 74.7, 74.9, 77.4, 77.8, 78.0, 83.4, 98.6 ($^1J_{CH}$ = 162.8 Hz), 99.9 ($^1J_{CH}$ = 156.4 Hz), 112.4, 127.3-128.5 (37 C), 130.5, 135.9, 137.4, 137.8, 137.9, 138.0, 138.4, 138.6, 138.7, 158.1, 171.1; IR (film, cm^{-1}): 1734; ESI HRMS Calcd for $C_{75}H_{82}O_{13}Na$ $[M+Na]^+$: 1213.5648. Found: 1213.5606.

Methyl 4-*O*-*β*-D-glucopyranosyl-(1→2)-α-D-mannopyranoside[7] (20) $[\alpha]^{15}_D$ +13.6° (c, 0.1, MeOH); ^{1}H NMR (500 MHz, D_2O) δ: 3.24 (dd, J = 8.0, 8.5 Hz, 1H), 3.31 (m, 1H), 3.33 (s, 3H), 3.40 (t, J = 8.0 Hz, 1H), 3.51-3.56 (m, 1H), 3.59 (t, J = 8.5 Hz, 1H), 3.63 (dd, J = 5.5, 7.5 Hz, 1H), 3.70-3.73 (m, 2H), 3.795 (t, J = 12.5 Hz, 1H), 3.799 (t, J = 12.0 Hz, 1H), 4.01 (dd, J = 1.5, 3.5 Hz, 1H), 4.40 (d, J = 8.0 Hz, 1H), 4.78 (d, J = 1.0 Hz, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 53.9, 60.6, 61.1, 67.1, 69.9, 70.3, 73.0, 76.2, 76.8, 78.1, 89.7, 99.4, 102.7.

Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (21) $[\alpha]^{18}_D$ +1.0° (c, 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.49 (s, 6H), 2.98 (d, J = 15.0 Hz, 1H), 3.13 (d, J = 15.0 Hz, 1H), 3.33 (s, 3H), 3.46-3.50 (m, 2H), 3.54-3.60 (m, 3H), 3.61-3.72 (m, 4H), 3.85 (dd, J = 3.0 8.0 Hz, 1H), 4.17 (t, J = 2.5 Hz, 1H), 4.33 (d, J = 11.0 Hz, 1H), 4.38-4.43 (m, 6H), 4.46-4.53 (m, 3H), 4.62-4.68 (m, 2H), 4.82 (dd, J = 5.0, 11.0 Hz, 1H), 4.95 (d, J = 4.0 Hz, 2H), 5.05 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 7.05-7.10 (m, 3H), 7.10-7.39 (m, 34H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.2, 28.5, 36.9, 44.9, 54.7, 69.5, 70.1, 70.2, 70.7, 71.6, 72.9, 73.1, 73.3, 73.5, 74.1, 74.7, 74.9, 77.5, 78.0, 83.2, 98.5 ($^1J_{CH}$ = 167.4 Hz), 99.6 ($^1J_{CH}$ = 163.7 Hz), 112.4, 120.7, 127.4-128.6(38C), 135.6, 137.2, 137.9, 138.0, 138.3, 138.5, 138.7, 137.1, 170.6; IR (film, cm^{-1}): 1740; ESI HRMS Calcd for $C_{73}H_{78}O_{13}Na$ $[M+Na]^+$: 1185.5335. Found 1185.5303.

Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→2)-α-D-mannopyranoside (22) $[\alpha]^{18}_D$ +8.2° (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.59 (s, 3H), 2.20 (s, 3H), 2.47 (s, 3H), 3.05 (d, J = 15.0 Hz, 1H), 3.15 (d, J = 15.0 Hz, 1H), 3.23 (s, 3H), 3.51 (t, J = 9.0 Hz, 1H), 3.68-3.78 (m, 6H), 3.85-3.91 (m, 3H), 3.92-3.96 (m, 1H), 4.34 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.0 Hz, 1H), 4.47-4.71 (m, 9H), 4.80-4.84 (m, 3H), 5.99 (dd, J = 11.5, 23.5 Hz, 1H), 5.44 (dd, J = 1.5, 3.5 Hz, 1H), 6.51 (s, 1H), 6.62 (s, 1H), 7.15-7.40 (m, 33H), 7.44 (d, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.9, 25.8, 31.8, 31.9, 40.1, 47.5, 54.7, 68.0, 69.4, 69.5, 70.9, 71.56, 71.62, 71.7, 71.9, 73.3, 74.6, 74.7, 75.0, 75.1, 75.2, 78.1, 79.6, 99.6 ($^1J_{CH}$ = 172.5 Hz), 100.0 ($^1J_{CH}$ = 173.7 Hz), 112.5, 127.4-128.5 (37 C), 130.4, 135.8, 137.5, 137.7, 138.27, 138.34, 138.4, 138.6, 158.5, 171.8; IR (film, cm^{-1}): 1732; ESI HRMS

Calcd for $C_{75}H_{82}O_{13}Na$ $[M+Na]^+$: 1213.5648. Found: 1213.5635.

Methyl 4-*O*-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside[8] (23) $[\alpha]^{19}_D$ +73.2° (c, 0.3, MeOH) [lit[8]: $[\alpha]_D$ +72.0° (c, 0.49, MeOH)]; ^{1}H NMR (500 MHz, MeOD) δ: 3.37 (s, 3H), 3.46 (m, 1H), 3.54-3.60 (m, 2H), 3.64-3.73 (m, 4H), 3.77 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.81-3.86 (m, 3H), 3.97 (br, 1H), 3.85 (m, 1H), 3.96 (s, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 53.8, 61.6, 61.7, 67.4, 67.6, 70.4, 70.7, 71.0, 73.1, 73.6, 79.0, 99.7, 102.9.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-α-D-glucopyranoside (24) Using 3 eq acceptor. $[\alpha]^{18}_D$ +8.2° (c, 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.50 (s, 3H), 1.59 (s, 3H), 2.17 (s, 3H), 2.52 (s, 3H), 2.70 (d, *J* = 11.5 Hz, 1H), 3.20 (d, *J* = 16.0 Hz, 1H), 3.26 (dd, *J* = 5.0, 9.0 Hz, 1H), 3.34 (s, 3H), 3.37 (t, *J* = 9.0 Hz, 1H), 3.40-3.47 (m, 2H), 3.48-3.59 (m, 3H), 3.62-3.69 (m, 2H), 3.84 (sp, *J* = 8.0 Hz, 2H), 4.30 (d, *J* = 12.5 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.38-4.45 (m, 4H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.54-4.60 (m, 3H), 4.63 (d, *J* = 11.0 Hz, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.87-4.93 (m, 2H), 5.02 (d, *J* = 11.5 Hz, 1H), 6.53 (s, 1H), 6.54 (s, 1H), 7.08-7.37 (m, 35H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.8, 25.8, 31.6, 31.9, 39.5, 46.5, 55.2, 68.0, 69.0, 69.9, 70.7, 73.3, 73.5, 73.6, 74.4, 74.7, 75.3, 75.4, 76.2, 77.8, 78.9, 80.2, 83.1, 98.4 ($^1J_{CH}$ = 171.2 Hz), 99.9 ($^1J_{CH}$ = 162.4 Hz), 112.3, 127.0-129.2 (36 C), 130.2, 136.0, 137.3, 137.8, 137.9, 138.1, 138.3, 138.4, 138.6, 139.6, 157.9, 170.8; IR (film, cm^{-1}): 1751; ESI HRMS Calcd for $C_{75}H_{82}O_{13}Na$ $[M+Na]^+$: 1213.5648. Found: 1213.5600.

Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranoside[9] (25) Mp, 143-145°C; $[\alpha]^{20}_D$ +96.5° (c, 0.4, H_2O) [lit[9]: m.p. 144-145°C, $[\alpha]^{16}_D$ +97.4° (c, 1.4, H_2O)]; ^{1}H NMR (500 MHz, D_2O) δ: 3.21(t, *J* = 8.5 Hz, 1H), 3.31 (t, *J* = 8.5 Hz, 1H), 3.32 (s, 3H), 3.36-3.42 (m, 2H), 3.50-3.57 (m, 2H), 3.60-3.70 (m, 3H), 3.74 (dd, *J* = 4.5, 12.5 Hz, 1H), 3.80-3.84 (m, 2H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.71 (m, 1H); ^{13}C NMR (125 MHz, D_2O) δ: 55.1, 59.9, 60.6, 69.5, 70.3, 71.0, 71.6, 73.2, 75.5, 76.0, 78.7, 99.0, 102.5.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)- α-D-glucopyranoside (26) $[\alpha]^{18}_D$ +8.4° (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.48 (s, 3H), 1.51 (s, 3H), 2.79 (d, *J* = 15.5 Hz, 1H), 3.07 (d, *J* = 15.0 Hz, 1H), 3.32 (dd, *J* = 3.5, 9.5 Hz, 1H), 3.38 (s, 3H), 3.41 (t, *J* = 13.0 Hz, 1H), 3.46-3.52 (m, 2H), 3.55-3.75 (m, 5H), 3.90 (sp, *J* = 8.0 Hz, 2H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.40-4.52 (m, 5H), 4.58-4.71 (m, 5H), 4.77 (d, *J* = 10.5 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.92-5.08 (m, 4H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.94 (t, *J* = 7.0 Hz, 1H), 7.14-7.40 (m, 37H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.0, 28.2, 36.9, 44.6, 55.3, 68.2, 69.0, 69.9, 70.2, 73.3, 73.4, 73.56, 73.64, 74.3, 74.7, 75.37, 75.43, 76.1, 77.9, 79.0, 80.3, 82.9, 98.5 ($^{1}J_{CH}$ = 173.7 Hz), 99.9 ($^{1}J_{CH}$ = 169.9 Hz), 112.5, 120.9, 127.1-128.7(37C), 135.3, 137.1, 137.9, 138.2, 138.3, 138.5, 138.6, 139.7, 157.0, 170.4; IR (cm^{-1}): 1749; ESI HRMS Calcd for $C_{73}H_{78}O_{13}Na$ [M+Na]$^{+}$: 1185.5335. Found: 1185.5291.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-α-D-glucopyranoside (27) $[\alpha]^{18}_{D}$ +21.0° (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.52 (s, 3H), 1.55 (s, 3H), 2.19 (s, 3H), 2.44 (s, 3H), 2.93 (d, *J* = 15.0 Hz, 2H), 3.14 (d, *J* = 15.0 Hz, 1H), 3.39 (s, 3H), 3.51-3.57 (m, 3H), 3.60 (dd, *J* = 5.0, 11.0 Hz, 1H), 3.68-3.81 (m, 5H), 3.84 (dd, *J* = 5.0, 9.5 Hz, 1H), 3.89 (t, *J* = 9.0 Hz, 1H), 4.33 (d, *J* = 11.5 Hz, 1H), 4.38-4.48 (m, 4H), 4.54-4.61 (m, 4H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 11.0 Hz, 1H), 4.91-4.99 (m, 3H), 5.26 (s, 1H), 5.40 (s, 1H), 6.50 (s, 1H), 6.58 (s, 1H), 7.17-7.52 (m, 35H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.9, 25.8, 31.5, 31.9, 39.9, 47.4, 55.3, 68.2, 69.3, 69.7, 70.9, 71.2, 72.5, 73.2, 73.3, 73.4, 74.4, 75.1, 75.2, 76.5, 77.3, 78.0, 80.1, 81.6, 97.8 ($^{1}J_{CH}$ = 167.4 Hz), 99.6 ($^{1}J_{CH}$ = 172.5 Hz), 99.9, 112.5, 127.3-128.6 (37 C), 130.6, 135.7, 137.5, 137.6, 138.0, 138.33, 138.36, 138.57, 138.62, 138.4, 171.5; IR (film, cm^{-1}): 1732; ESI HRMS Calcd for $C_{75}H_{82}O_{13}Na$ [M+Na]$^{+}$: 1213.5648. Found: 1213.5645.

Methyl 4-*O*-α-D-mannopyranosyl-(1→4)- α-D-glucopyranoside[10] (28) $[\alpha]^{19}_{D}$ +42.6° (c, 0.4, MeOH); ^{1}H NMR (500 MHz, MeOD) δ: 3.39 (m, 4H), 3.56-3.62 (m, 4H), 3.65-3.69 (m, 2H), 3.75 (t, *J* = 9.0 Hz, 1H), 3.76-3.78 (m, 2H), 3.86 (d, *J* = 10.0 Hz, 1H), 3.94 (br, 1H), 4.66 (d, *J* = 4.0 Hz, 1H), 5.33 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 54.2, 60.9, 61.6, 67.2, 70.8, 70.9, 71.1, 72.3, 74.16, 74.24, 75.9, 97.7, 101.4.

α-*tert*-Butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (29) $[\alpha]^{16}_{D}$ +22.1° (c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.44 (s, 9H), 1.46 (s, 9H), 1.60 (s, 6H), 1.80-1.90 (m, 1H), 2.10-2.20 (m, 1H), 2.21 (s, 3H), 2.26-2.45 (m, 2H), 2.49 (s, 3H), 3.11 (dd, *J* = 15.0, 33.0 Hz, 2H), 3.65-3.75 (m, 3H), 3.77-3.83 (m, 1H), 3.86 (dd, *J* = 4.0, 9.0 Hz, 1H), 4.16-4.22 (m, 1H), 4.44-4.52 (m, 3H), 4.59 (d, *J* = 13.5 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.83 (d, *J* = 10.5 Hz, 1H), 5.00 (dd, *J* = 11.5, 27.5 Hz, 2H), 5.10 (d, *J* = 8.0 Hz, 1H), 5.22-5.23 (m, 1H), 5.76 (s, 1H), 6.53 (s, 1H), 6.63 (s, 1H), 7.17-7.20 (m, 2H), 7.25-7.36 (m, 15H), 7.38 (t, *J* = 5.5 Hz, 2H), 7.46 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.9, 25.8, 28.0 (4 C), 28.3 (3 C), 30.2, 31.8, 31.9, 40.1, 47.5, 53.2, 66.7, 68.8, 70.9, 71.6, 73.4, 73.8, 73.9, 75.2, 77.6, 79.9, 82.4, 91.6 ($^{1}J_{CH}$ = 176.2 Hz), 112.3, 127.6-128.6(21 C), 129.9, 136.1, 137.46, 137.53, 137.9, 138.2, 138.3, 155.5, 158.4, 170.3, 171.2, 171.8; IR (film, cm^{-1}): 1733, 1716; ESI HRMS Calcd for $C_{61}H_{75}NO_{13}Na$ [M+Na]$^{+}$: 1052.5131. Found 1052.5125.

α-*tert*-butyl γ-α-D-mannopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (30) $[\alpha]^{20}_{D}$ +22.4° (c, 0.5, MeOH); ^{1}H NMR (500 MHz, MeOD) δ: 1.44 (s, 9H), 1.47 (s, 9H), 1.82-1.90 (m, 1H), 2.08-2.13 (m, 1H), 2.45-2.50 (m, 2H), 3.34 (s, 1H), 3.58-3.62 (m, 1H), 3.67-3.73 (m, 3H), 3.79-3.83 (m, 2H), 3.98-4.03 (m, 1H), 6.03 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 26.3, 26.9 (3 C), 27.3 (3 C), 28.0, 53.6, 61.3, 66.6, 69.7, 70.9, 75.7, 79.2, 81.5, 94.1, 156.5, 171.05, 171.68; ESI HRMS Calcd for $C_{20}H_{35}NO_{11}Na$ $[M+Na]^+$: 488.2103. Found: 488.2089.

α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (31) $[\alpha]^{18}_{D}$ +3.1° (c, 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.44 (s, 9H), 1.46 (s, 9H), 1.53 (s, 3H), 1.55 (s, 3H), 1.80-1.88 (m, 1H), 2.05-2.12 (m, 1H), 2.18 (s, 3H), 2.29-2.34 (m, 2H), 2.51 (s, 3H), 2.92 (d, *J* = 15.5 Hz, 1H), 3.10 (d, *J* = 15.5 Hz, 1H), 3.46 (t, *J* = 9.0 Hz, 1H), 3.53 (d, *J* = 10.0 Hz, 1H), 3.66-3.75 (m, 1H), 4.12-4.19 (m, 1H), 4.30 (d, *J* = 11.0 Hz, 1H), 4.41 (d, *J* = 11.0 Hz, 1H), 4.44 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 11.0 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.0 Hz, 1H), 4.85 (s, 2H), 5.02 (d, *J* = 8.5 Hz, 1H), 5.05 (t, *J* = 8.5 Hz, 1H), 5.49 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 6.54 (s, 1H), 7.05-7.10 (m, 2H), 7.11-7.16 (m, 2H), 7.19-7.38 (m, 16H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.8, 25.7, 27.6, 28.0 (4 C), 28.4 (3 C), 30.2, 31.7, 39.6, 47.0, 53.2, 68.1, 70.8, 71.6, 73.5, 74.6, 75.0, 75.5, 78.1, 79.8, 82.3, 83.0, 92.4 ($^{1}J_{CH}$ = 162.4 Hz), 112.2, 127.7-128.6 (21 C), 130.1, 136.1, 137.1, 137.6, 137.9, 138.1, 155.4, 158.1, 171.0 (2 C), 171.2; IR (film, cm^{-1}): 1740, 1716; ESI HRMS Calcd for $C_{61}H_{75}NO_{13}Na$ $[M+Na]^+$: 1052.5131. Found 1052.5181.

α-*tert*-butyl γ-*β*-D-glucopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (32) $[\alpha]^{18}_{D}$ -12.7° (c, 0.5, MeOD); ^{1}H NMR (500 MHz, MeOD) δ: 1.43 (s, 9H), 1.47 (s, 9H), 1.83-1.96 (m, 1H), 2.08-2.15 (m, 1H), 2.45-2.52 (m, 2H), 3.27-3.35 (m, 3H), 3.42 (t, *J* = 9.0 Hz, 1H), 3.67 (dd, *J* = 5.0, 12.0 Hz, 1H), 3.83 (dd, *J* = 2.0, 12.0 Hz, 1H), 3.99-4.04 (m, 1H), 5.49 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, MeOD) δ: 26.8 (3 C), 27.3 (3 C), 53.2, 61.0, 69.7, 72.6, 76.5, 77.4, 79.2, 81.4, 94.4, 156.8, 171.7 (2 C); ESI HRMS Calcd for $C_{20}H_{35}NO_{11}Na$ $[M+Na]^+$: 488.2108. Found: 488.2122.

α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (33) $[\alpha]^{18}_{D}$ -2.3 °(c, 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.43 (s, 3H), 1.45 (br, 12H), 1.47 (s, H), 1.82-1.90 (m, 1H), 2.08-2.15 (m, 1H), 2.31-2.35 (m, 2H), 2.79 (d, *J* = 14.5 Hz, 1H), 3.14 (d, *J* = 14.5 Hz, 1H), 3.40 (t, *J* = 9.0Hz, 1H), 3.50 (d, *J* = 9.5 Hz, 1H), 3.67-3.74 (m, 3H), 4.17-4.22 (m, 1H), 4.41 (d, *J* = 11.0 Hz, 1H), 4.45-4.53 (m, 3H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 10.5 Hz, 1H), 4.94-5.06 (m, 3H), 5.35 (d, *J* = 8.0 Hz, 1H), 6.88-6.93 (m, 2H), 7.09-7.11 (m, 2H), 7.16-7.26 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 27.6, 28.0(3 C), 28.2, 28.37 (3 C), 28.43, 30.1, 36.9, 44.9, 53.2, 68.0, 70.2, 71.5, 73.5, 74.8, 75.0, 75.5, 79.9, 82.3, 83.0, 92.3 ($^{1}J_{CH}$ = 167.4 Hz), 112.2, 120.8, 127.5-128.6 (23 C), 135.0, 136.9, 137.9, 138.0, 155.4, 157.1, 170.5, 171.2(2 C); IR (film, cm^{-1}): 1739, 1716; ESI HRMS Calcd for $C_{58}H_{71}NO_{13}Na$ $[M+Na]^+$:

1024.4818. Found 1024.4813.

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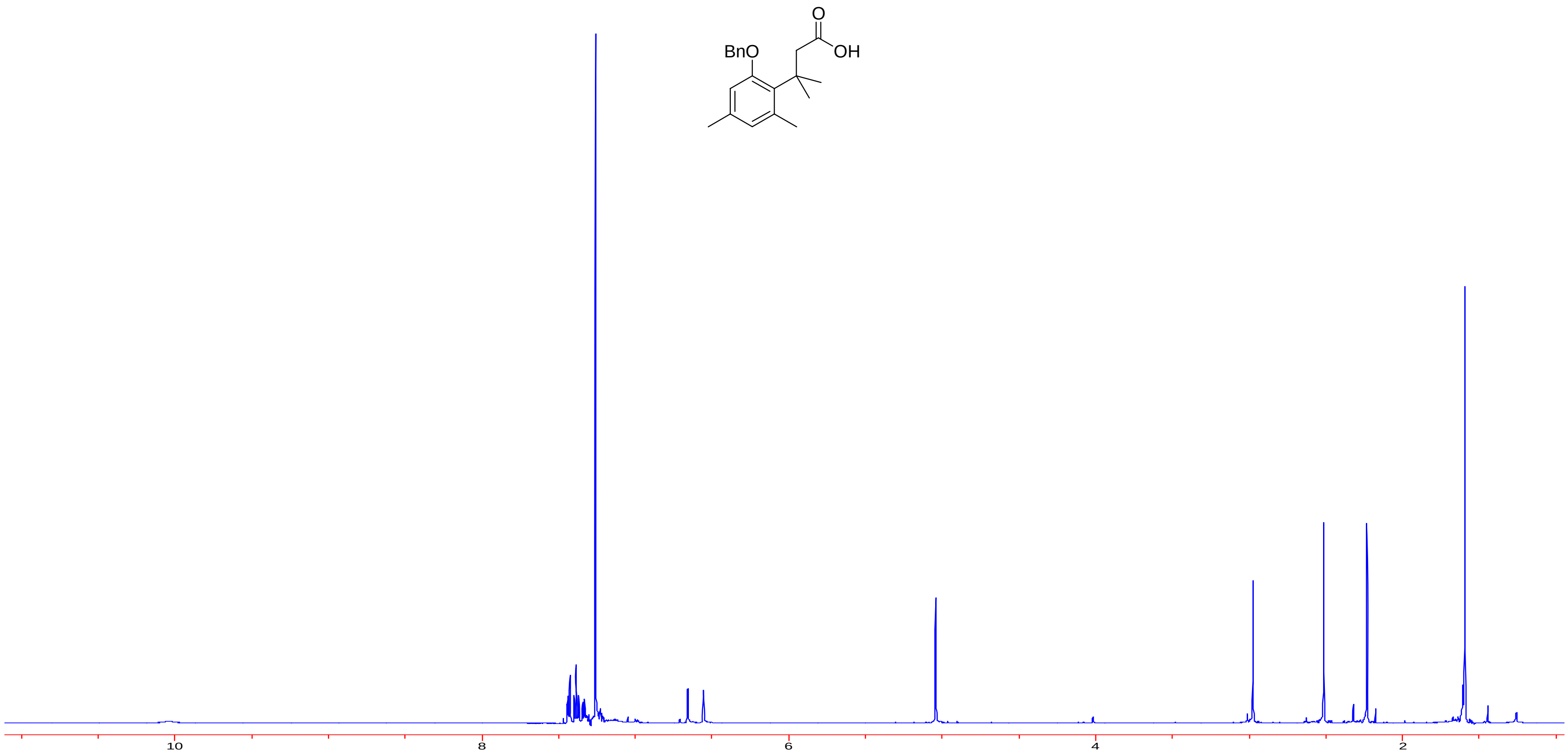
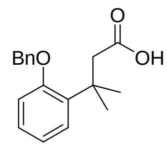
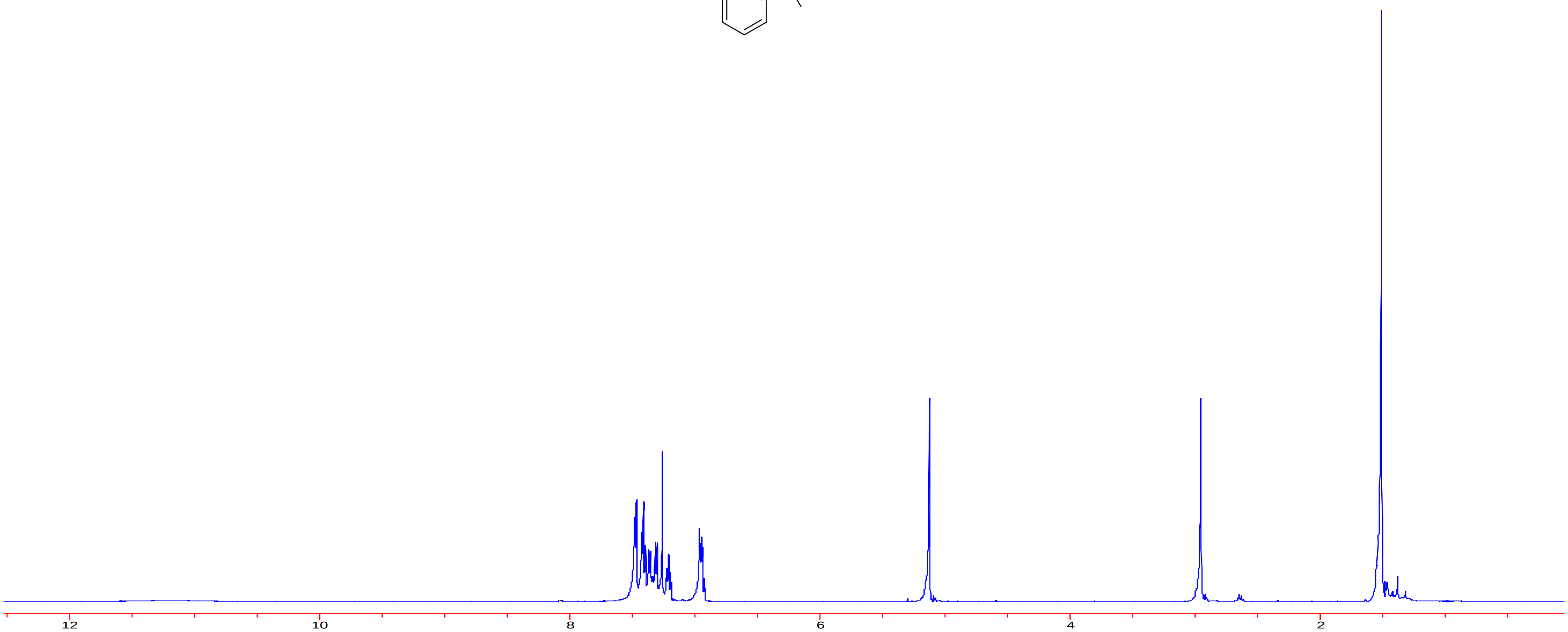
3-(2’-Benzyloxy-4’,6’-dimethylphenyl)-3,3-dimethylpropanoic acid (3)

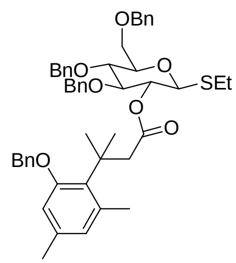


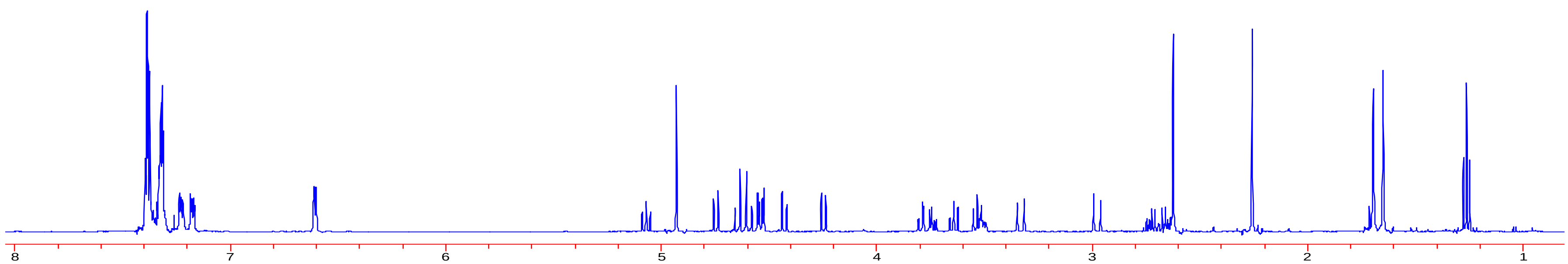
3-(2'-Benzyloxyphenyl)-3,3-dimethylpropanoic acid (4)



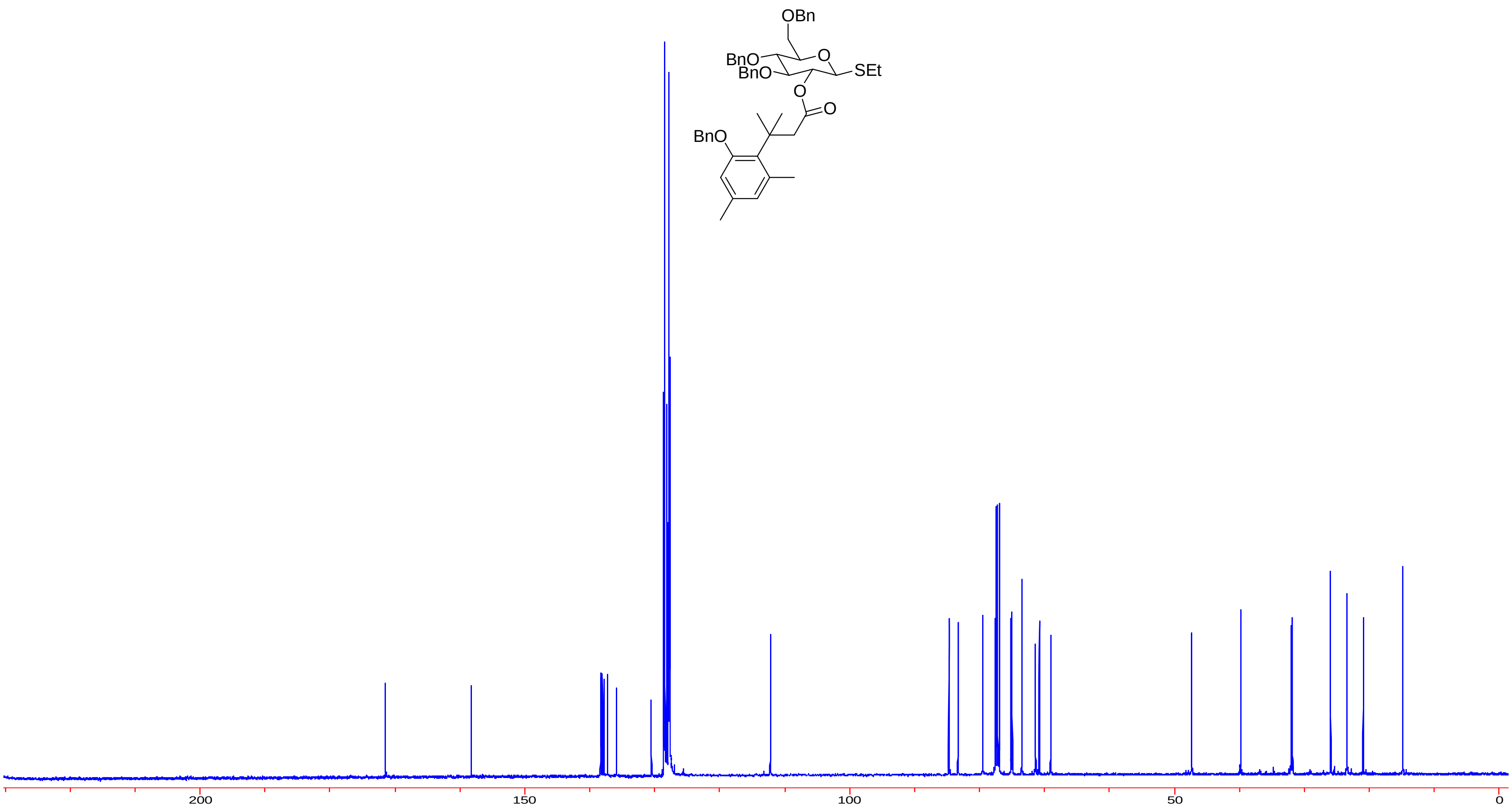


Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-1-thio-*β*-D-glucopyranoside(5)

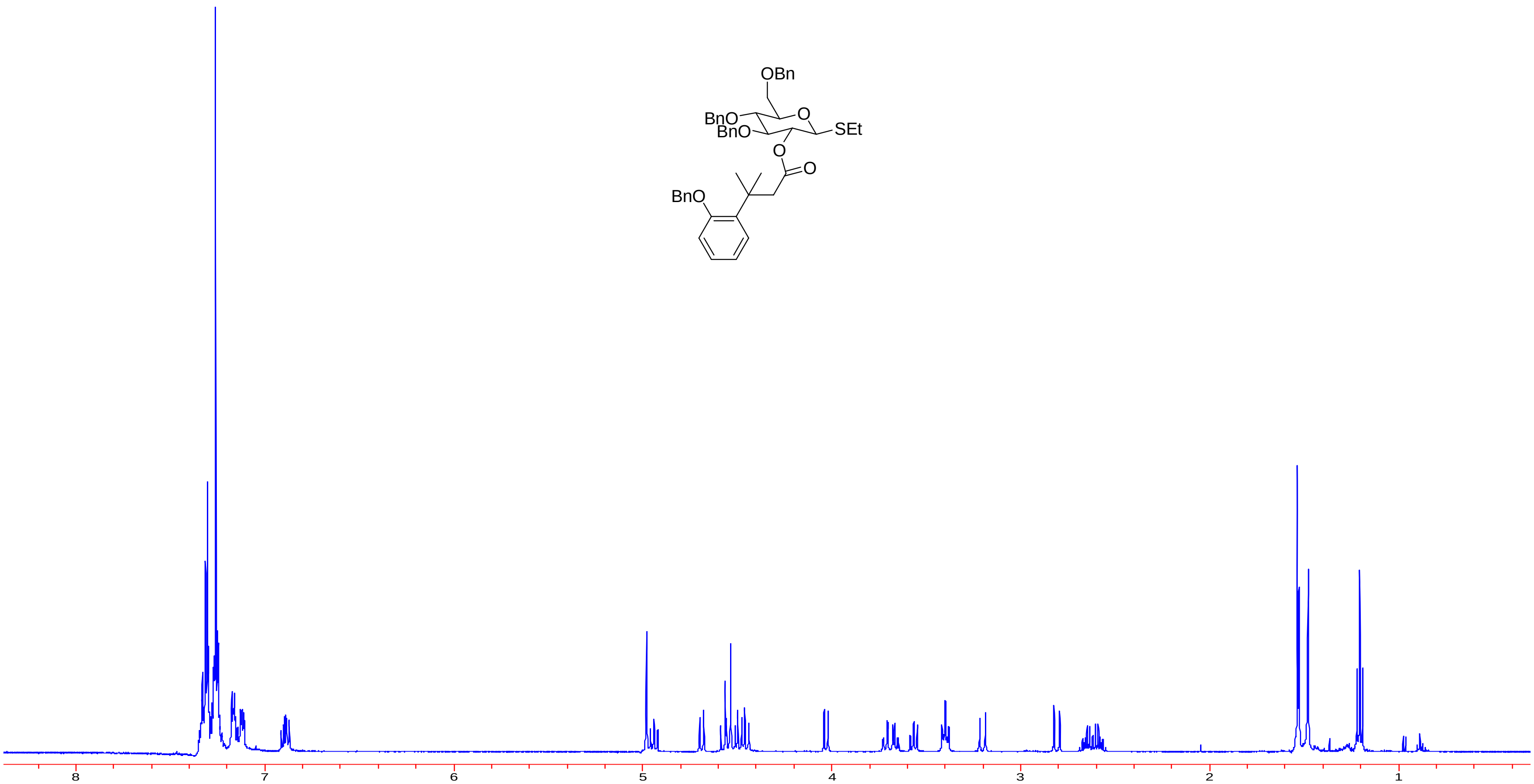




Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-1-thio-*β*-D-glucopyranoside (5)



Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-1-thio-*β*-D-glucopyranoside (6)



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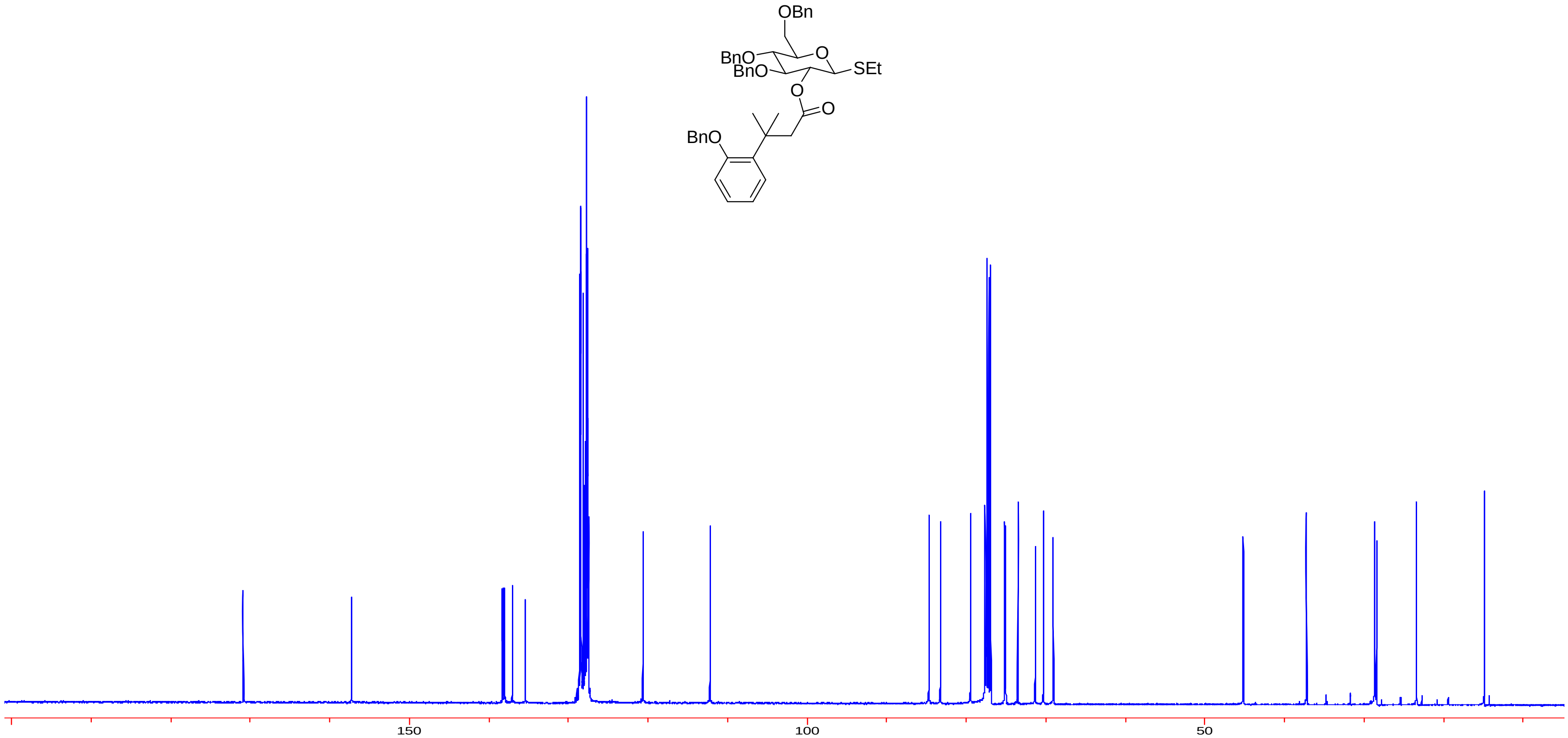
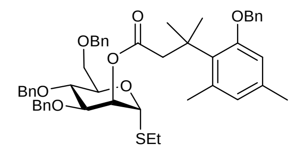
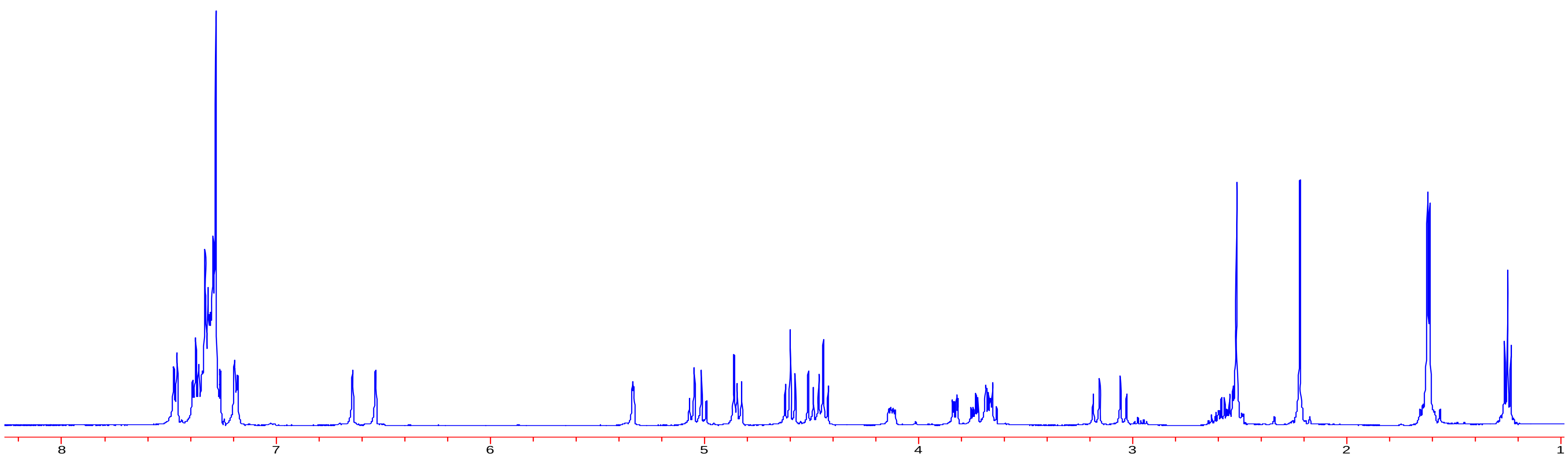
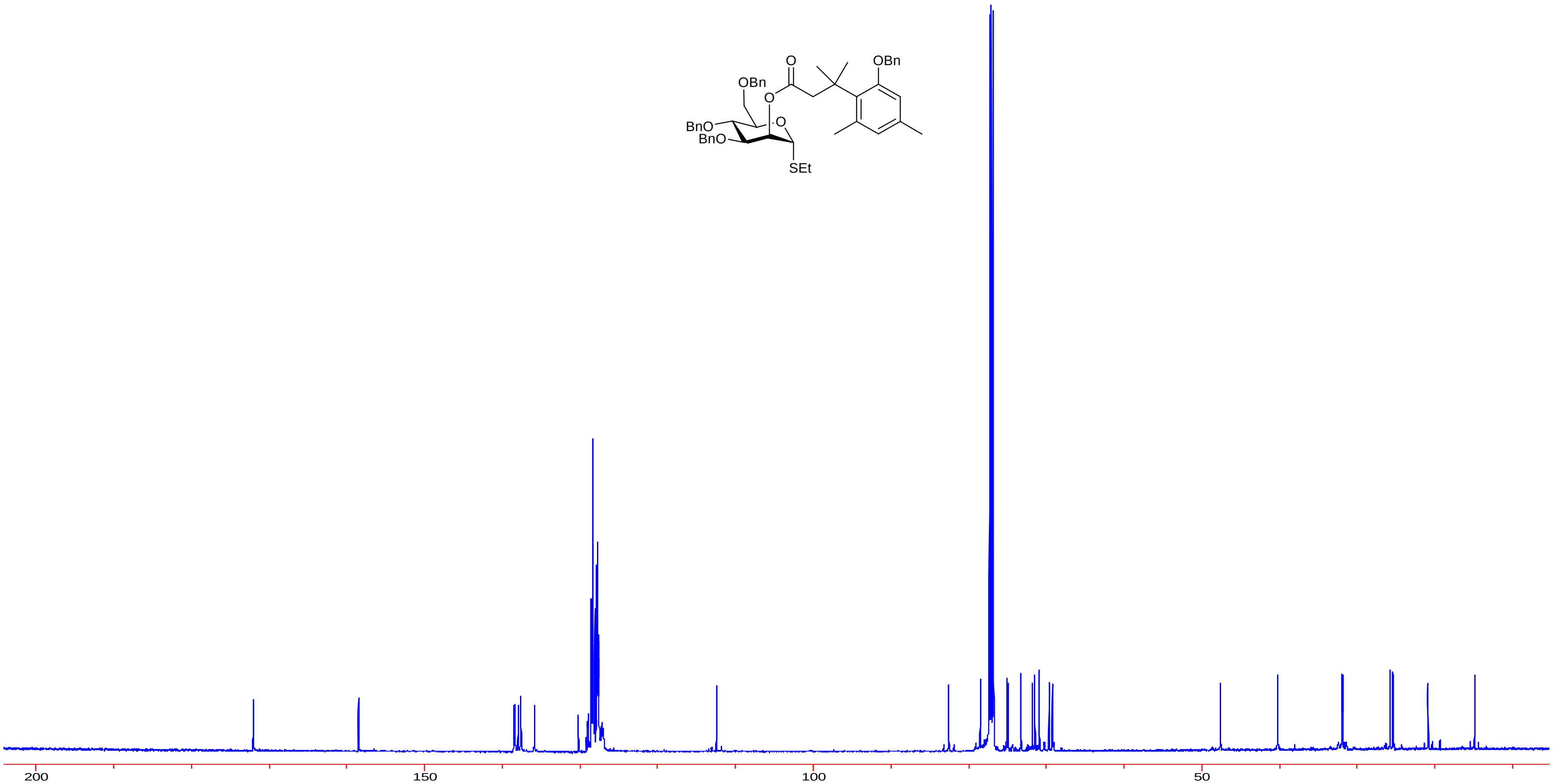


Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3’-(2”-benzyloxy-4”,6”-dimethylphenyl)-3’,3’-dimethylpropanoyl]-1-thio-*α*-D-mannopyranoside (7)

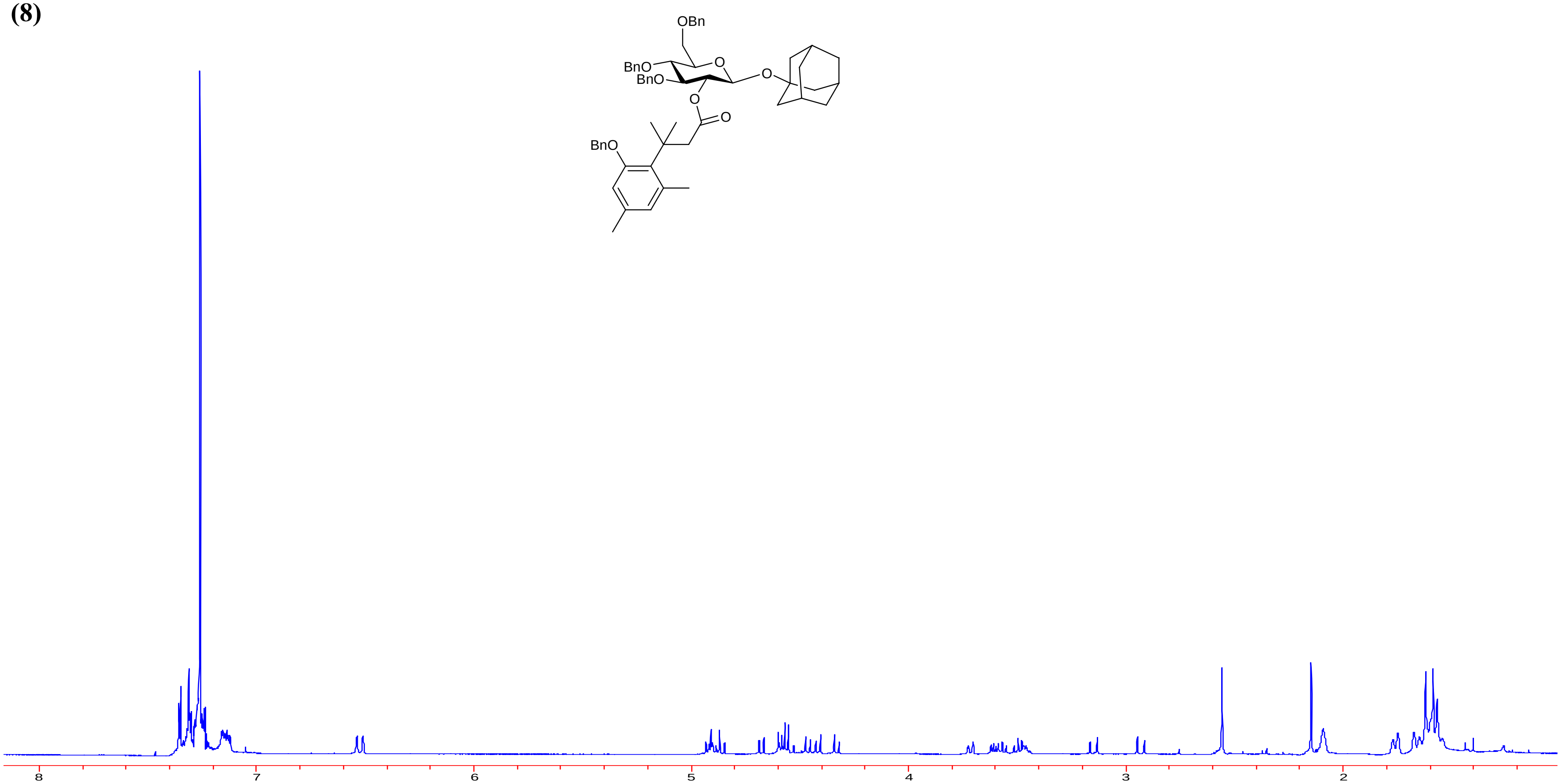




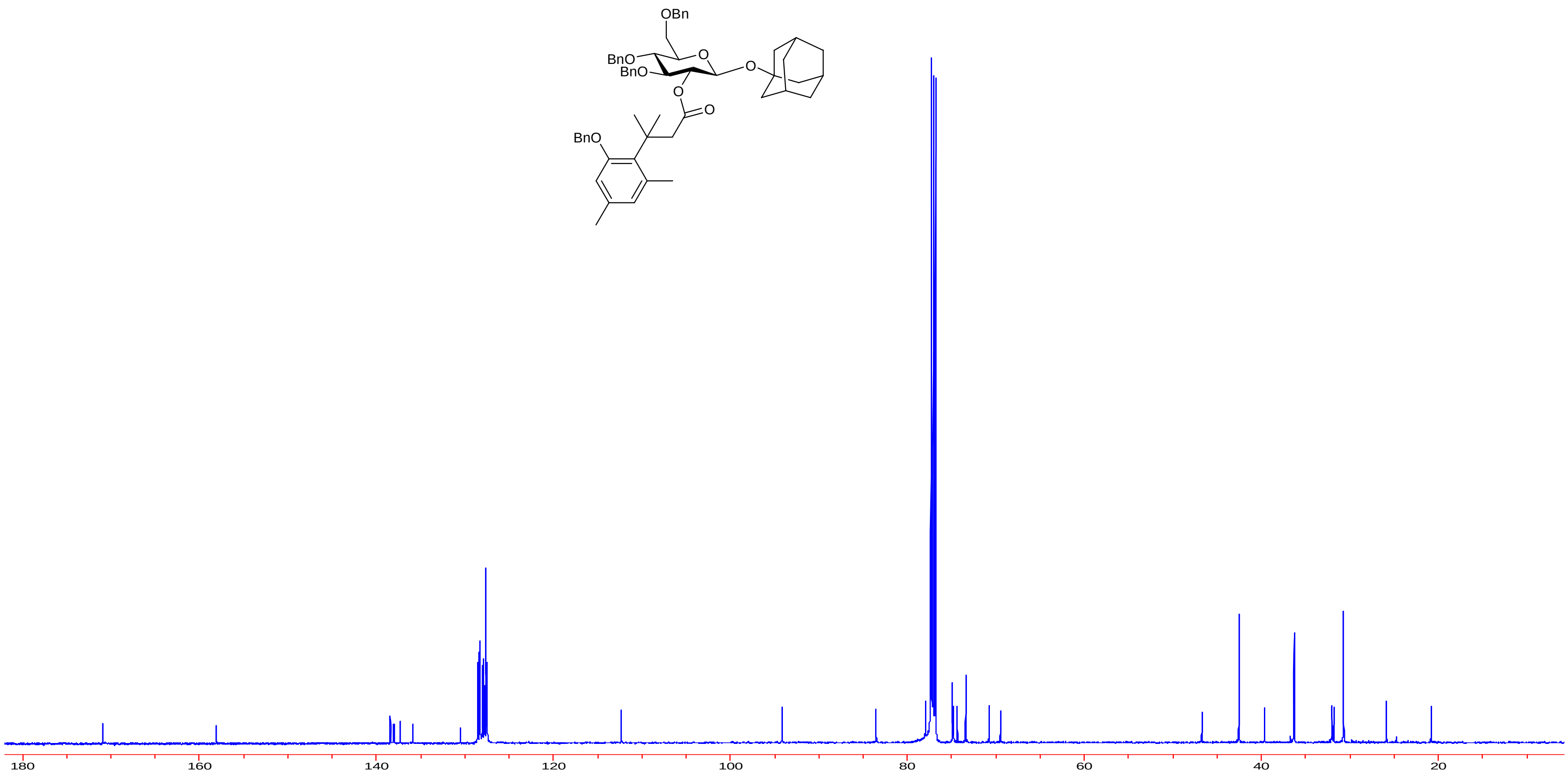
Ethyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-1-thio-*α*-D-mannopyranoside (7)



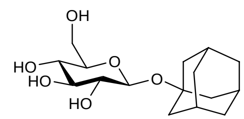
1-Adamantanyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (8)

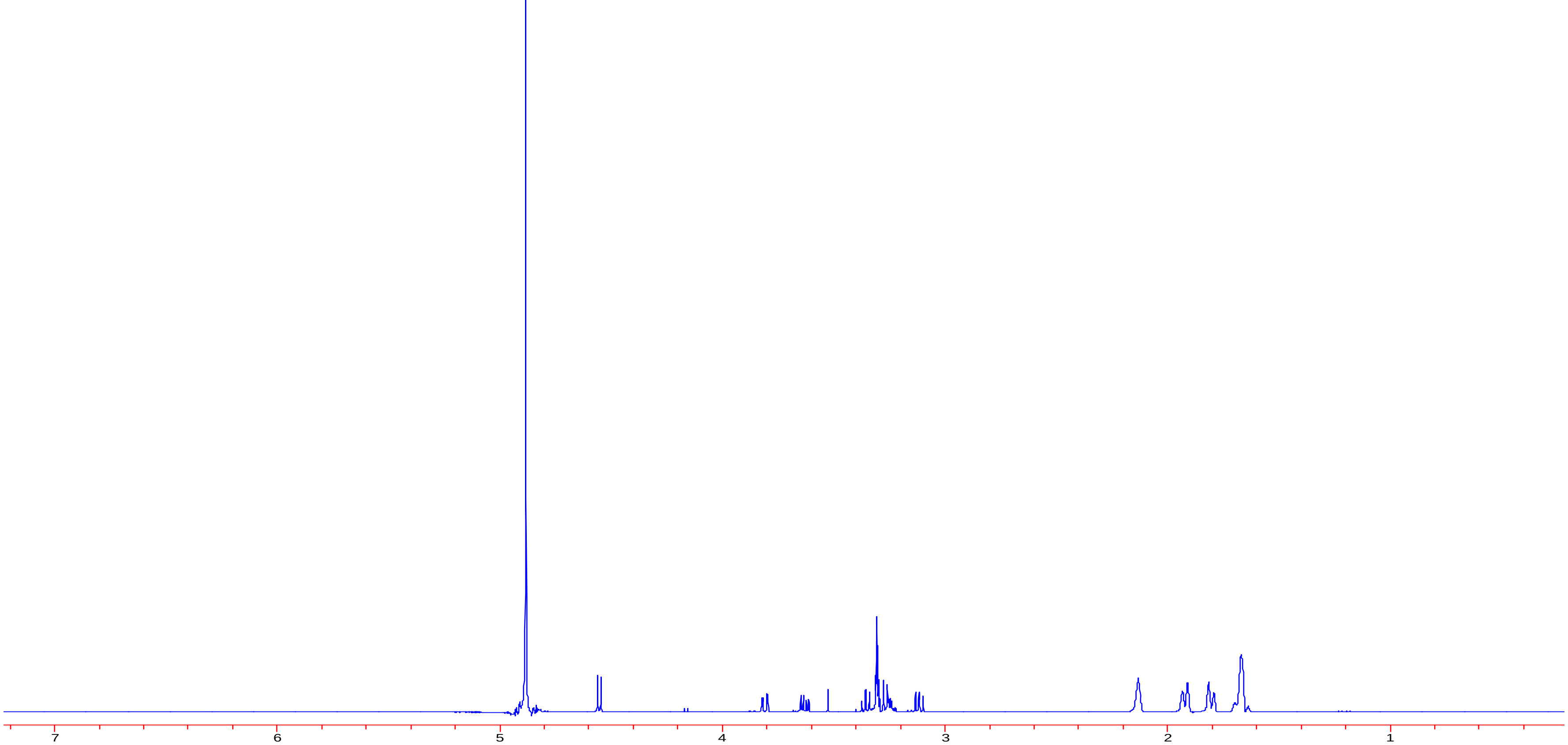


1-Adamantanyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (8)

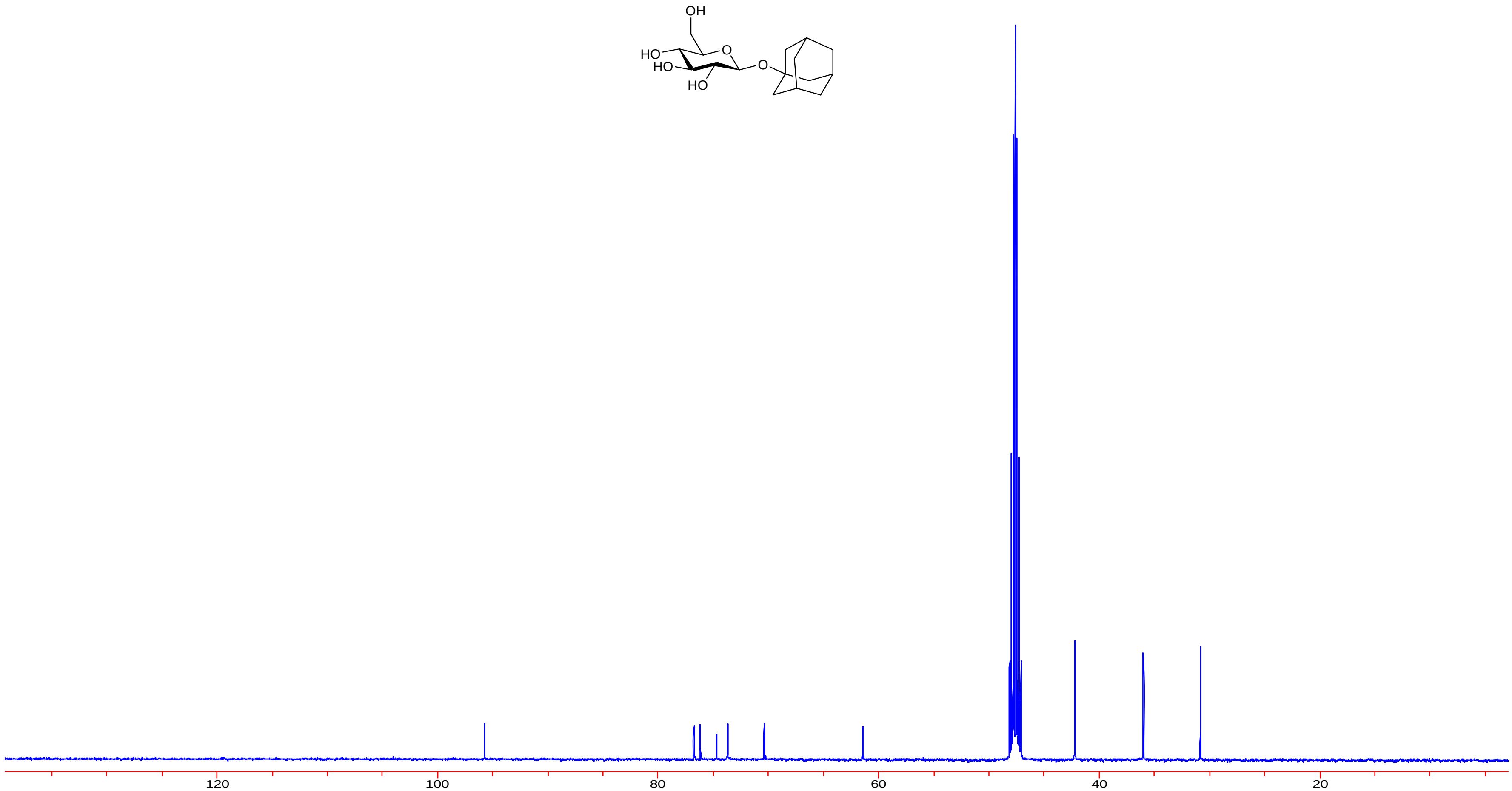


1-Adamantanyl *β*-D-glucopyranoside (9)

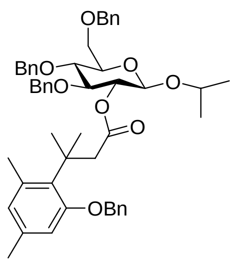


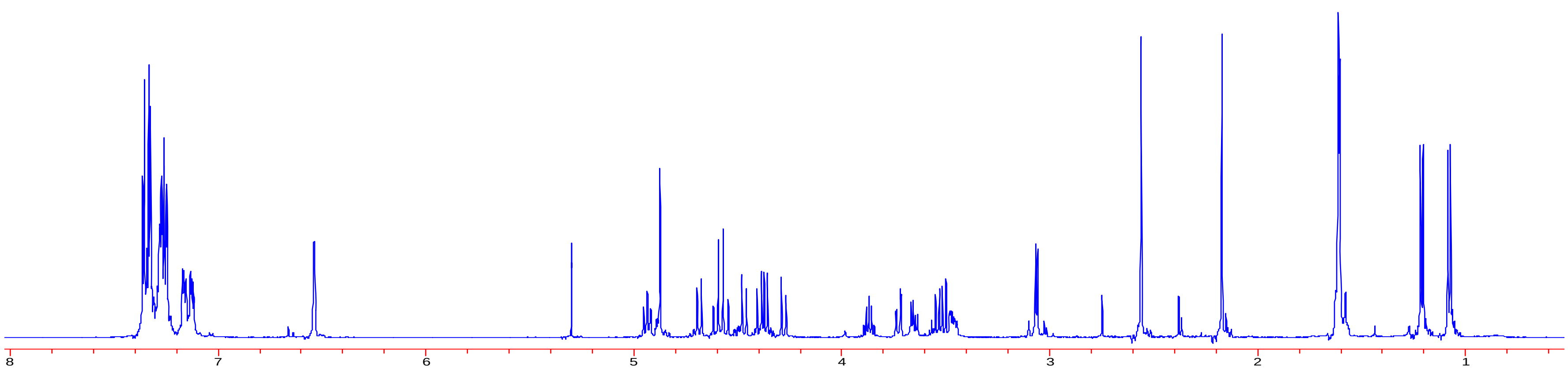


1-Adamantanyl *β*-D-glucopyranoside (9)

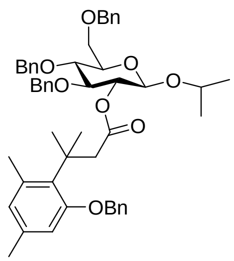


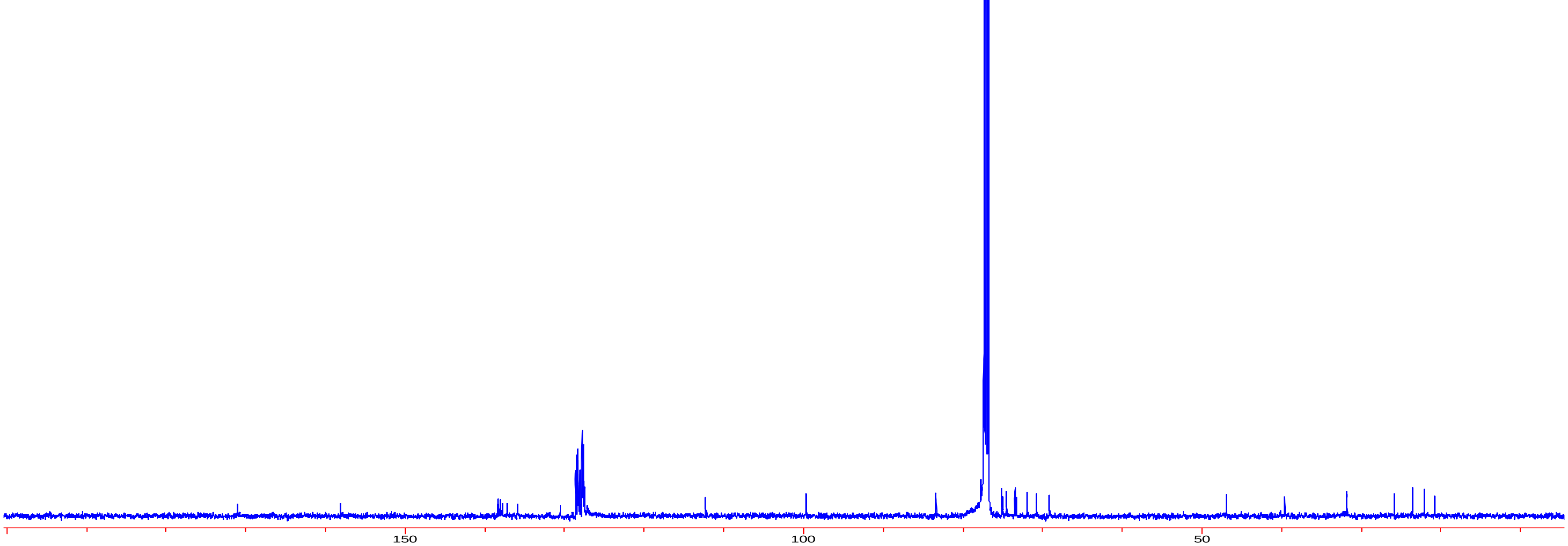
Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (10)



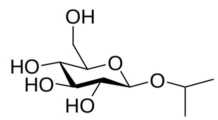


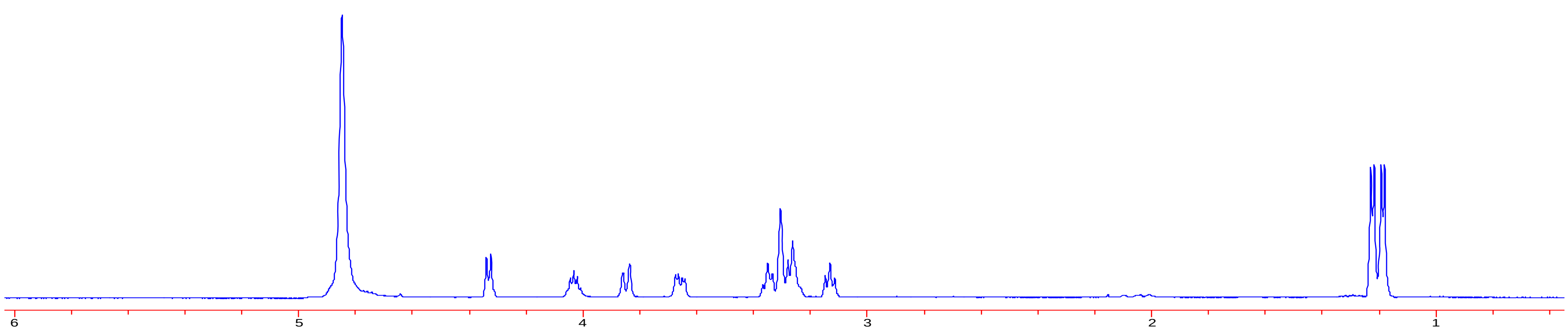
Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (10)



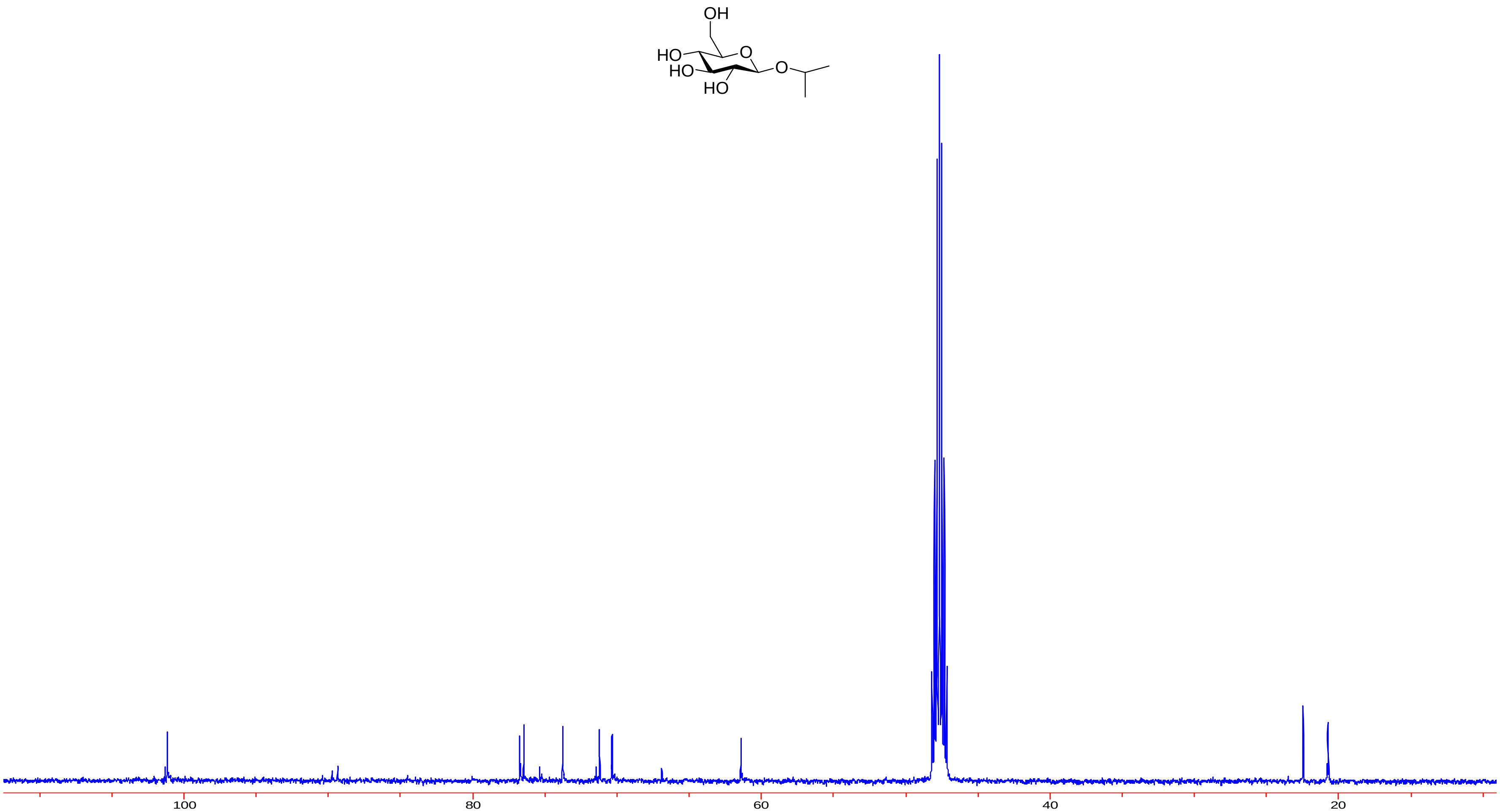


Isopropyl *β*-D-glucopyranoside (11)

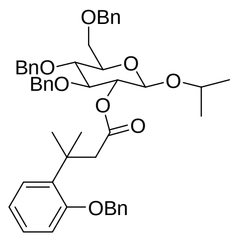


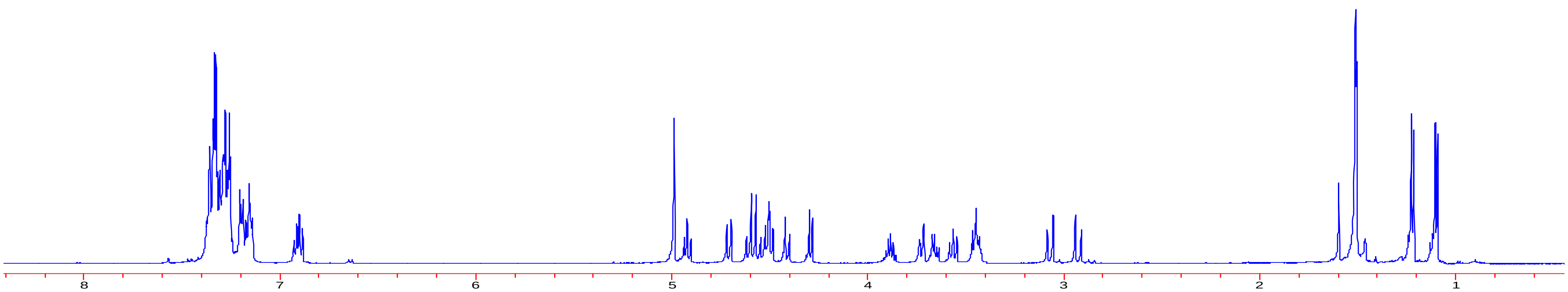


Isopropyl *β*-D-glucopyranoside (11)



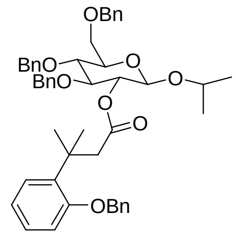
Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (12)

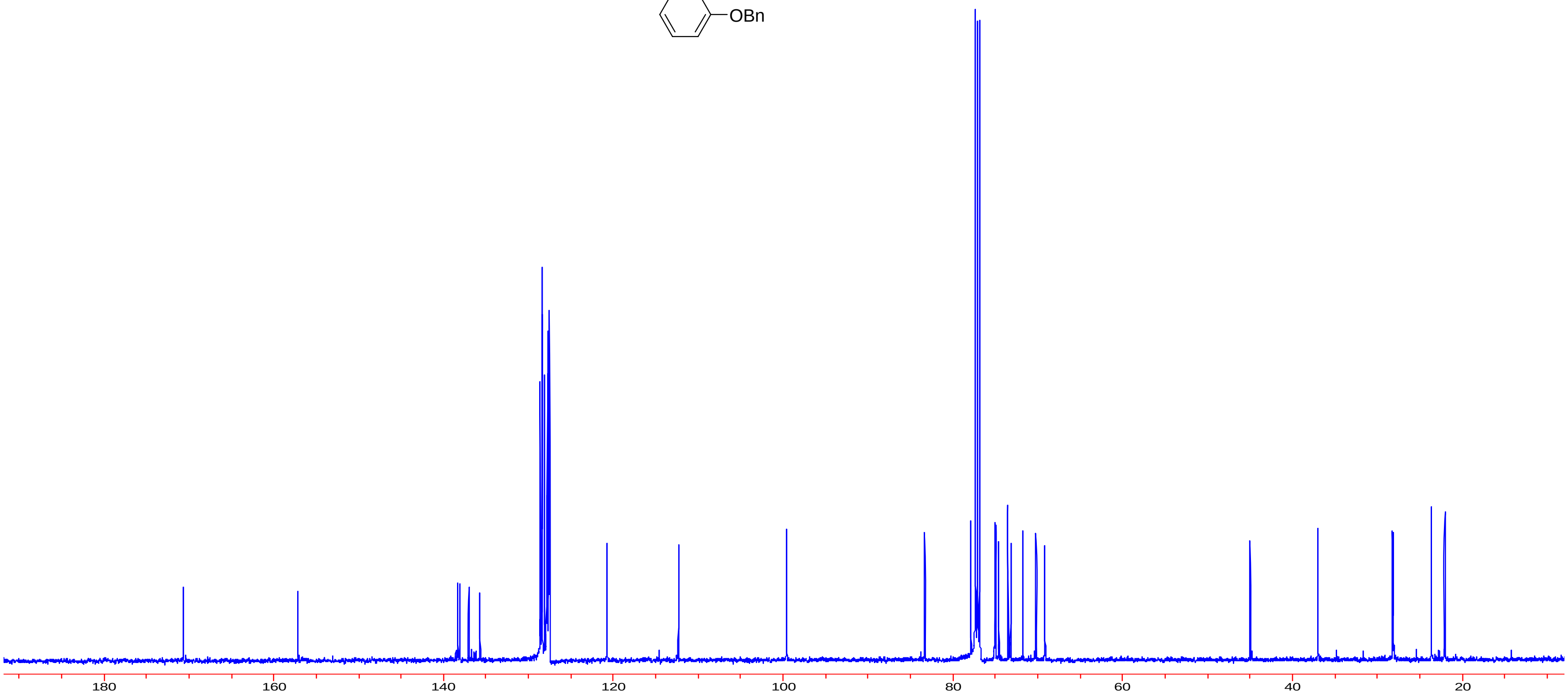




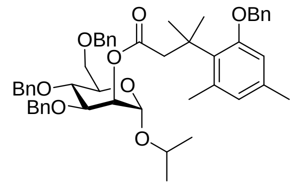
Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranoside (12)

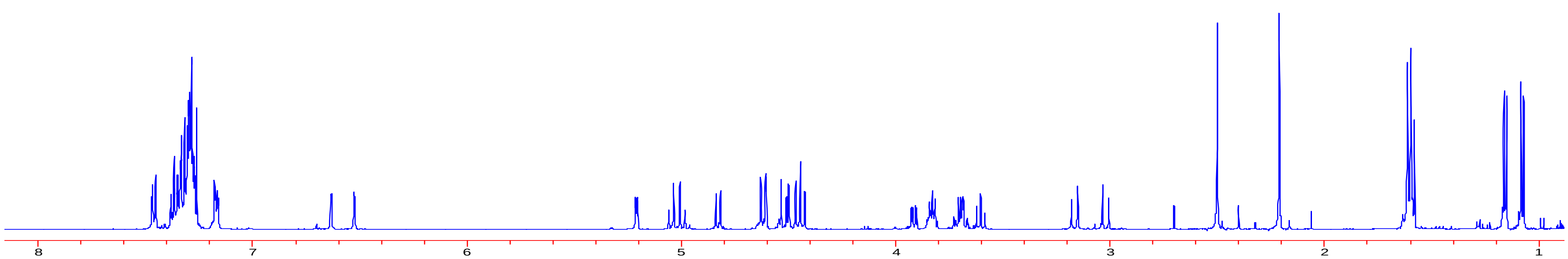
Isopropyl



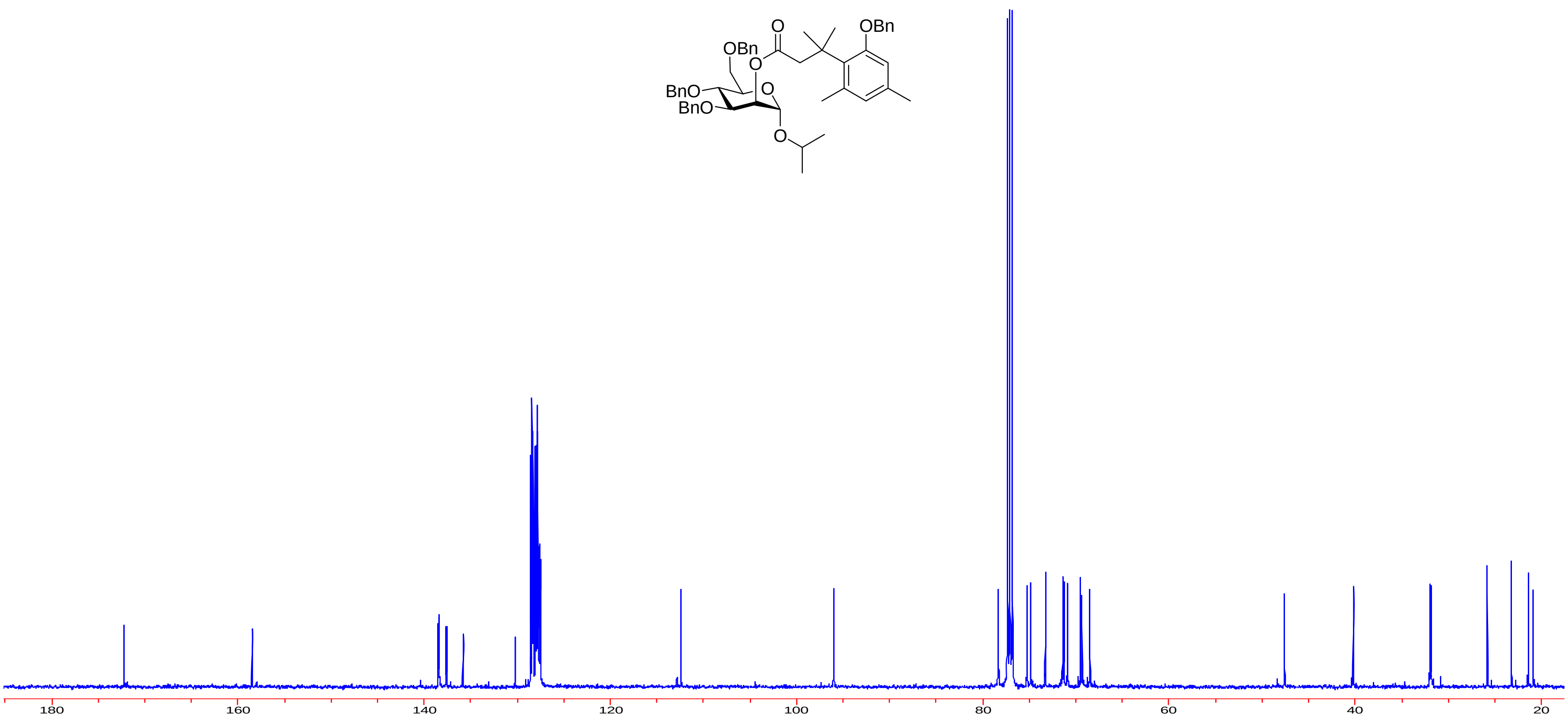


3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*α*-D-mannopyranoside (13)

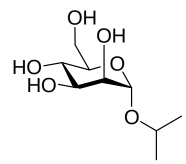


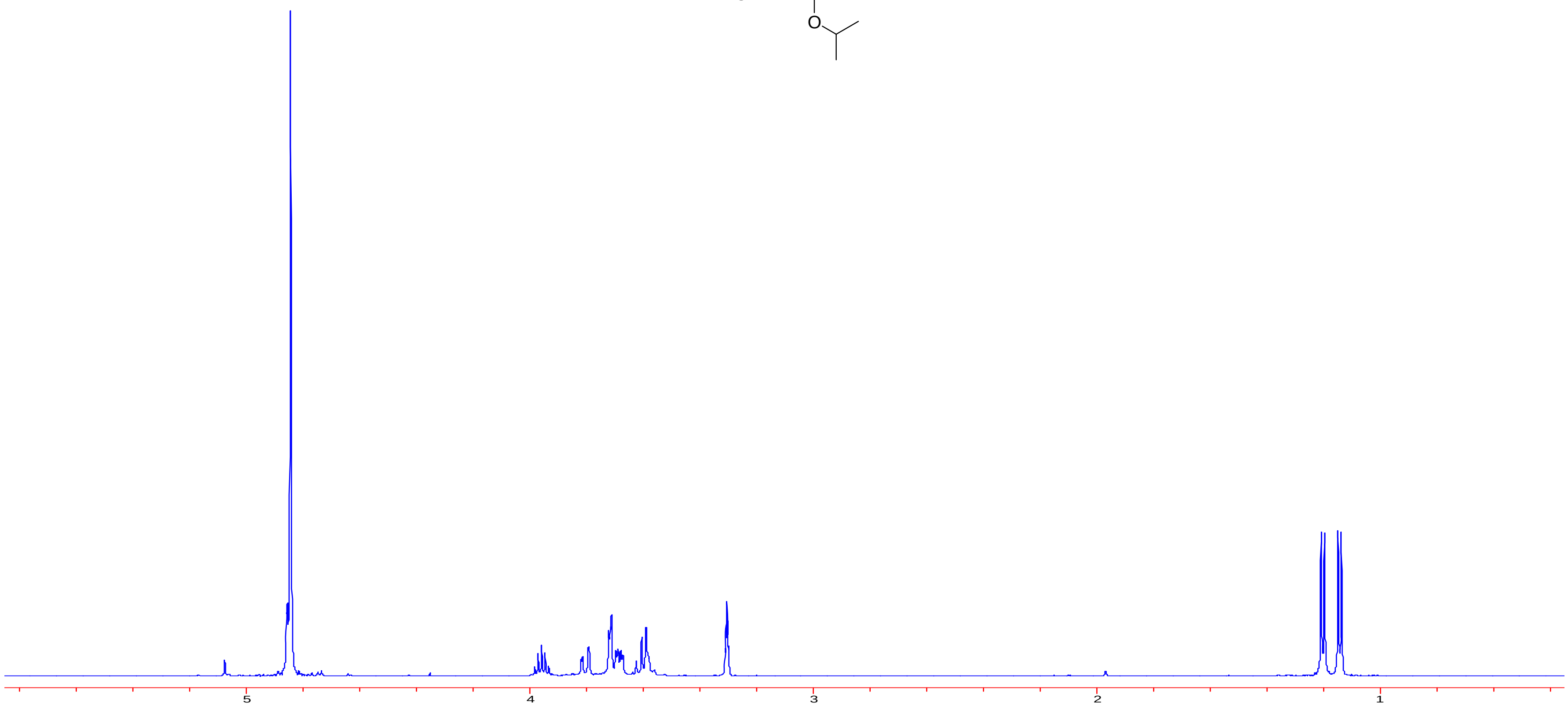


Isopropyl 3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*α*-D-mannopyranoside (13)

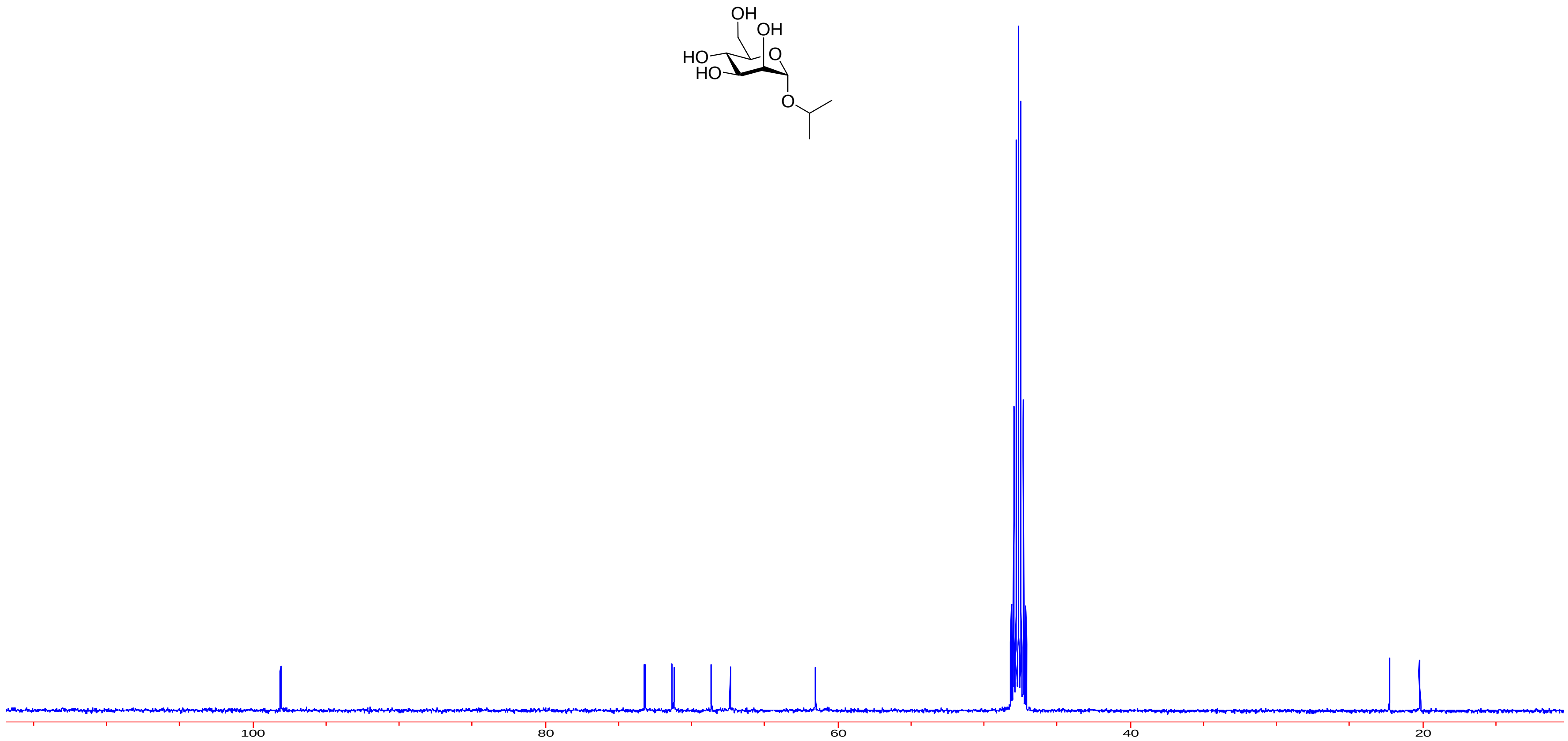


Isopropyl α-D-mannopyranoside (14)

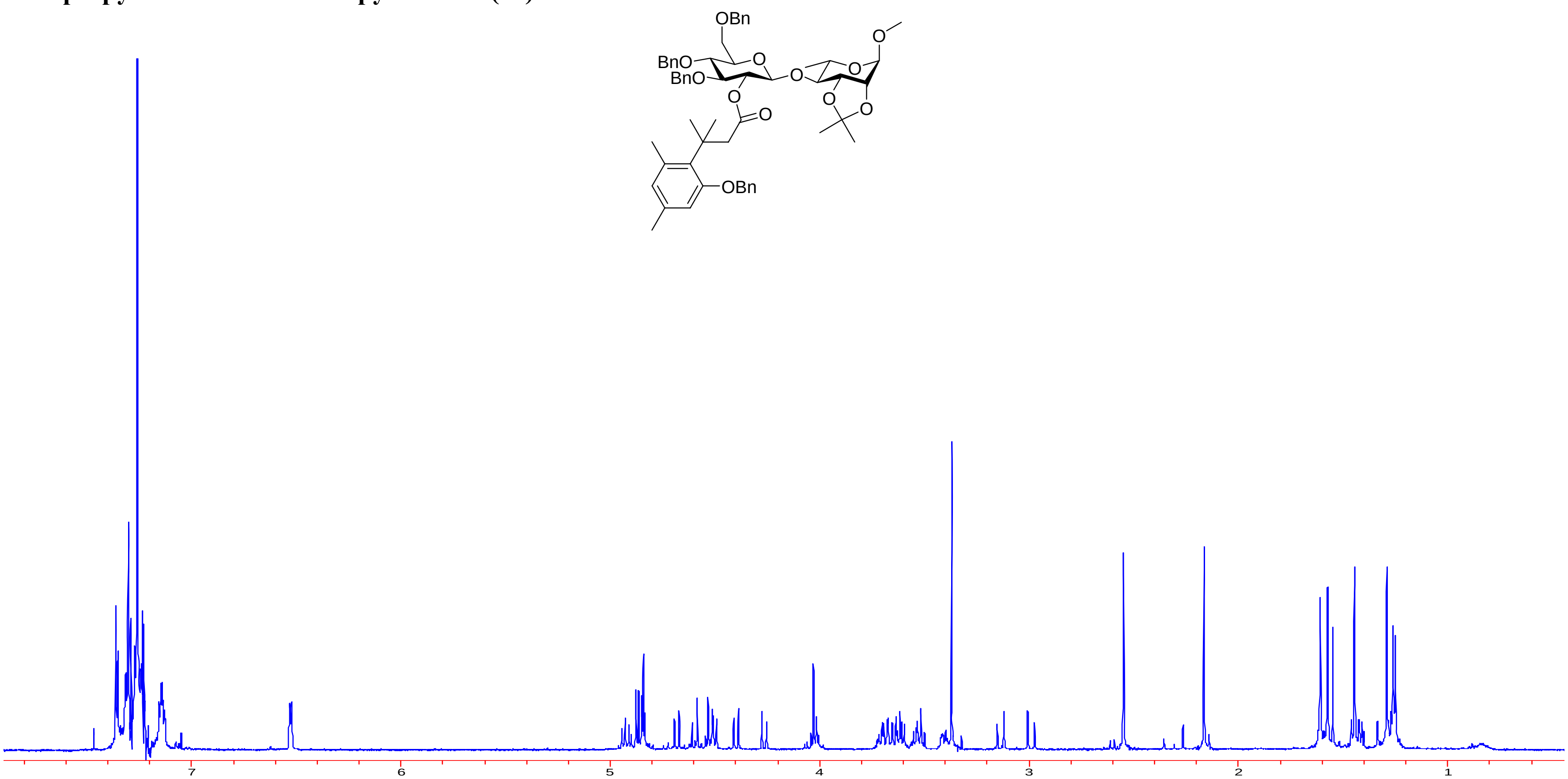




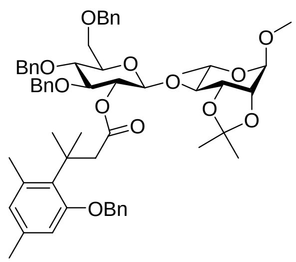
Isopropyl *α*-D-mannopyranoside (14)

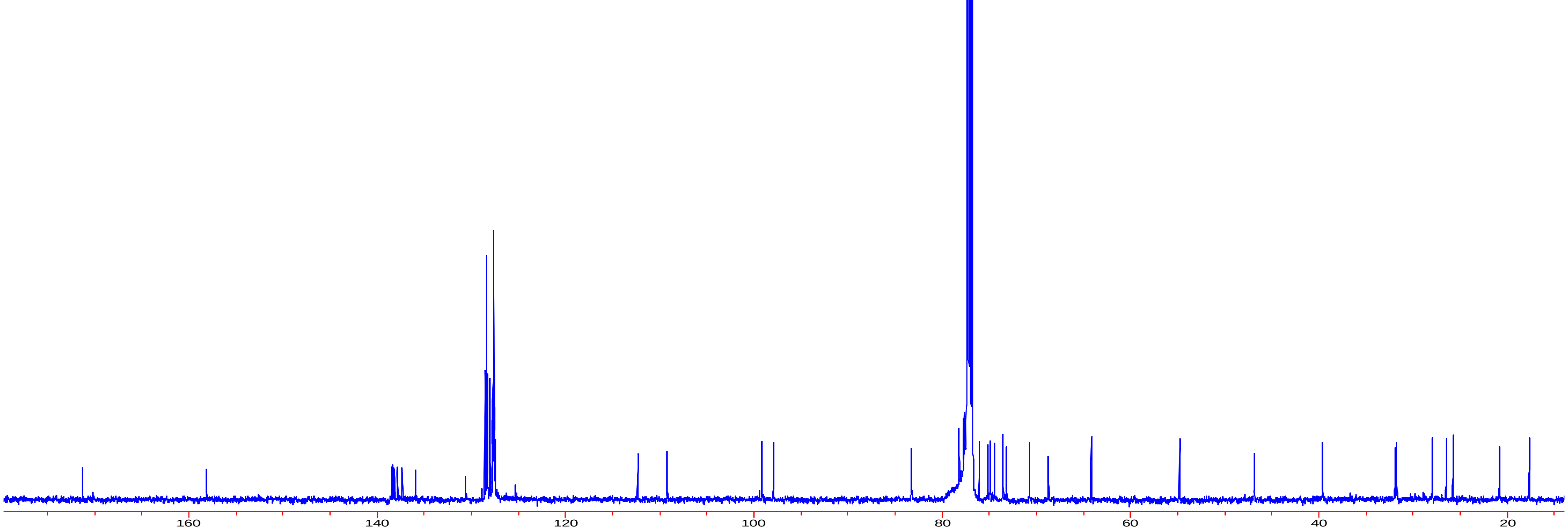


Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (15)

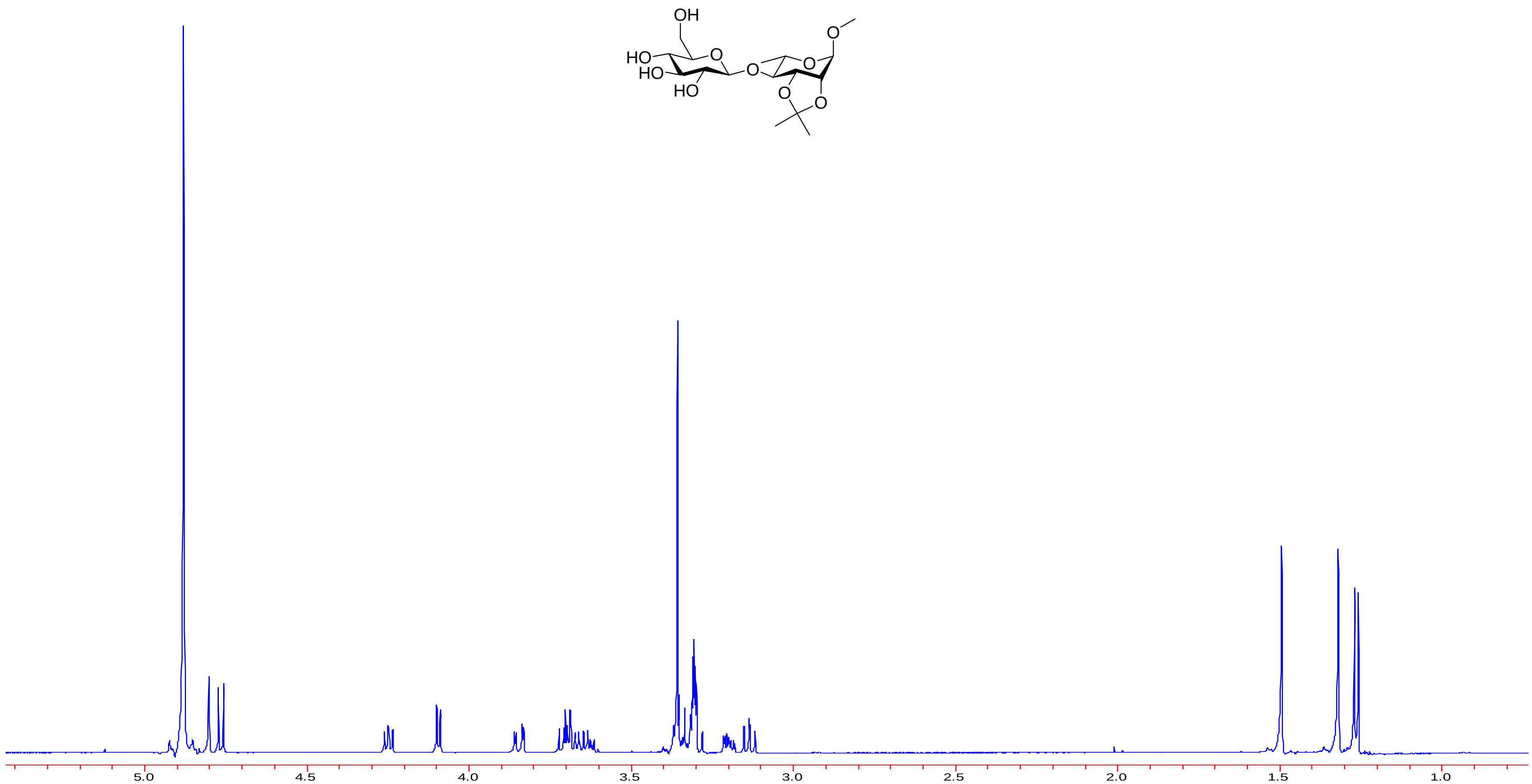


Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (15)

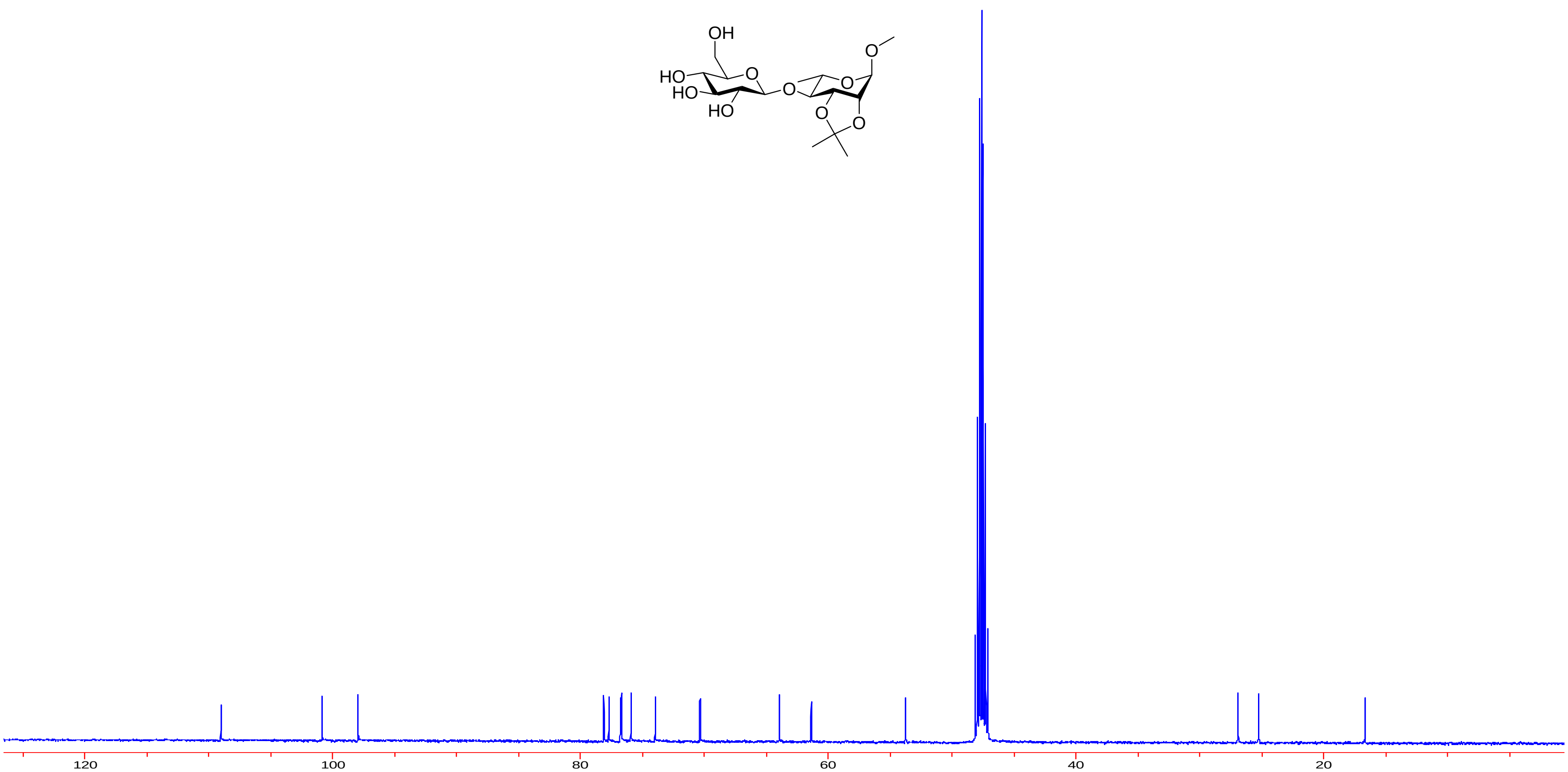




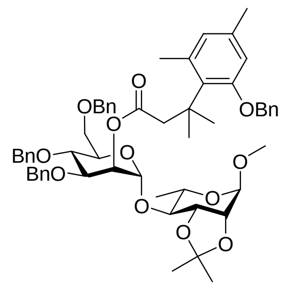
Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (16)

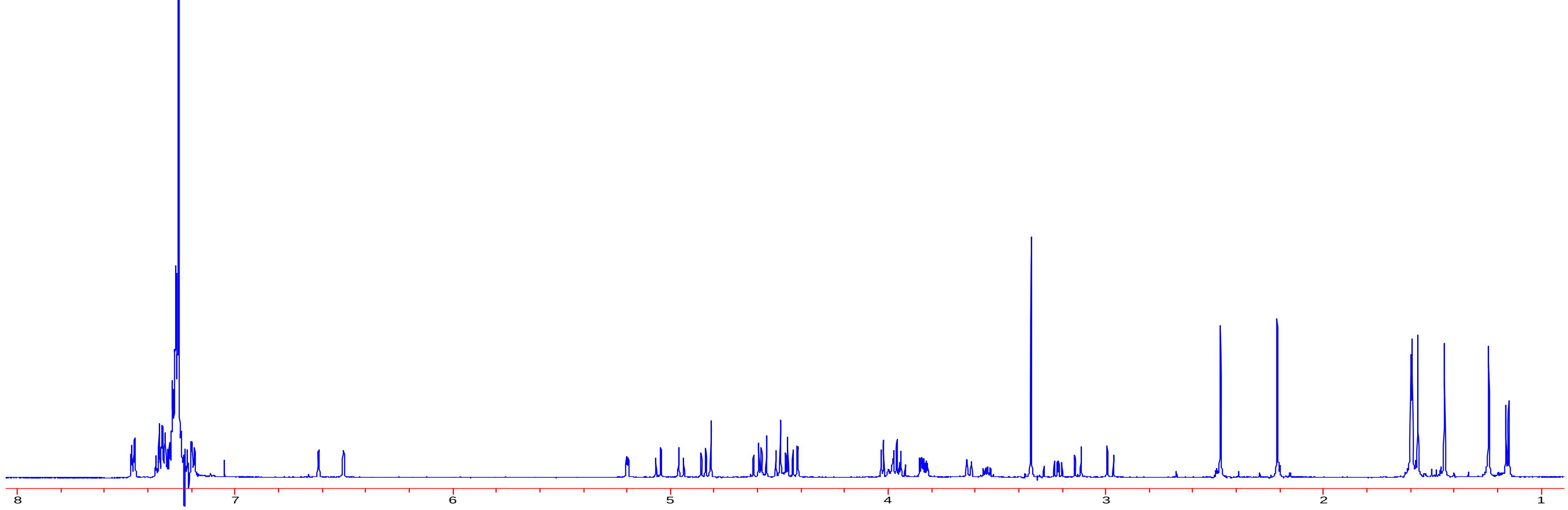


Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (16)

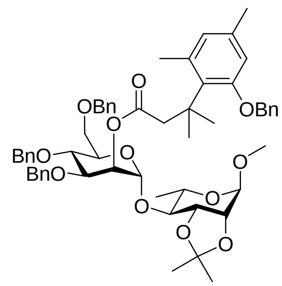


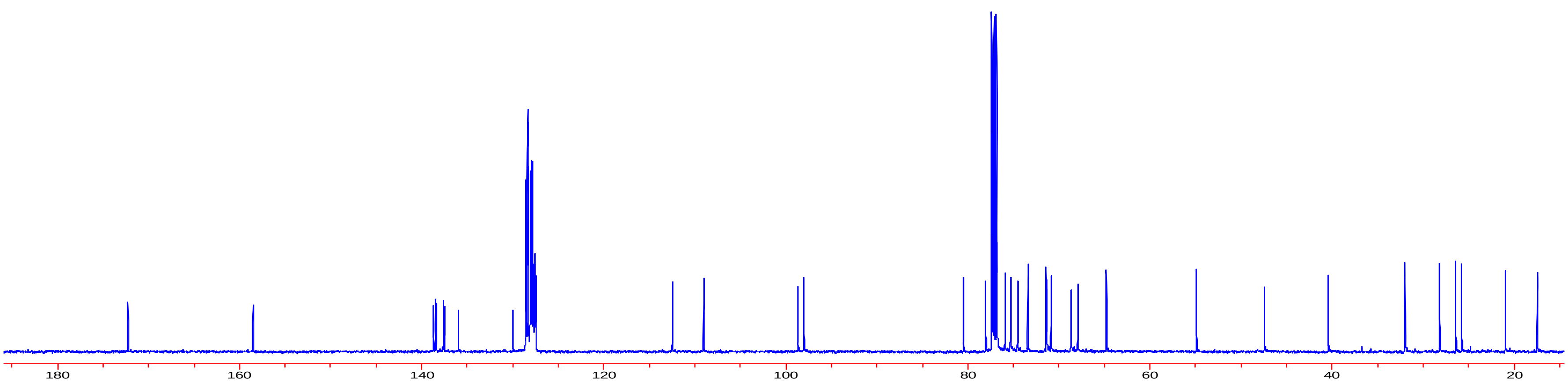
Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (17)



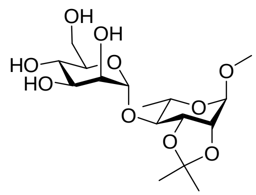


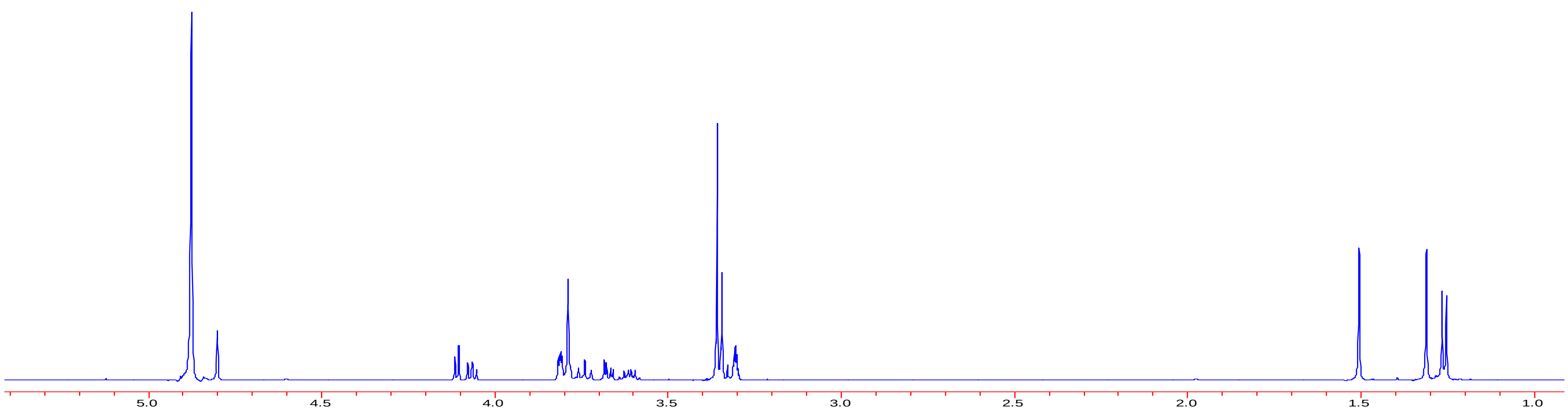
Methyl 4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (17)



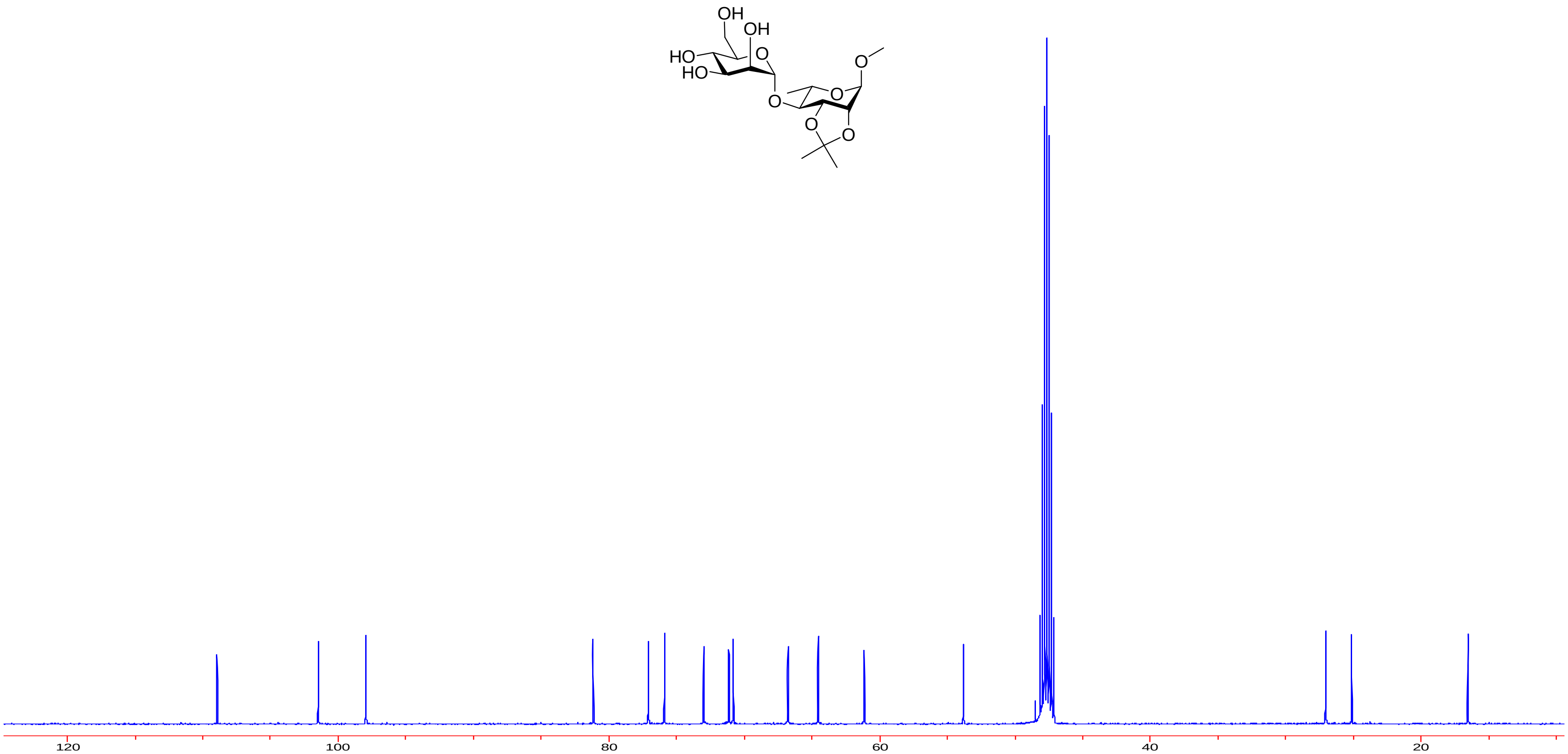


Methyl 4-*O*-α-D-mannopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (18)

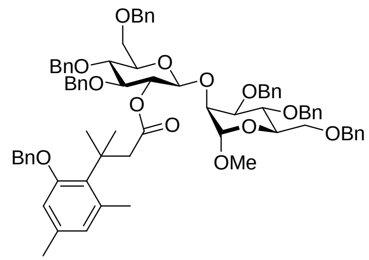


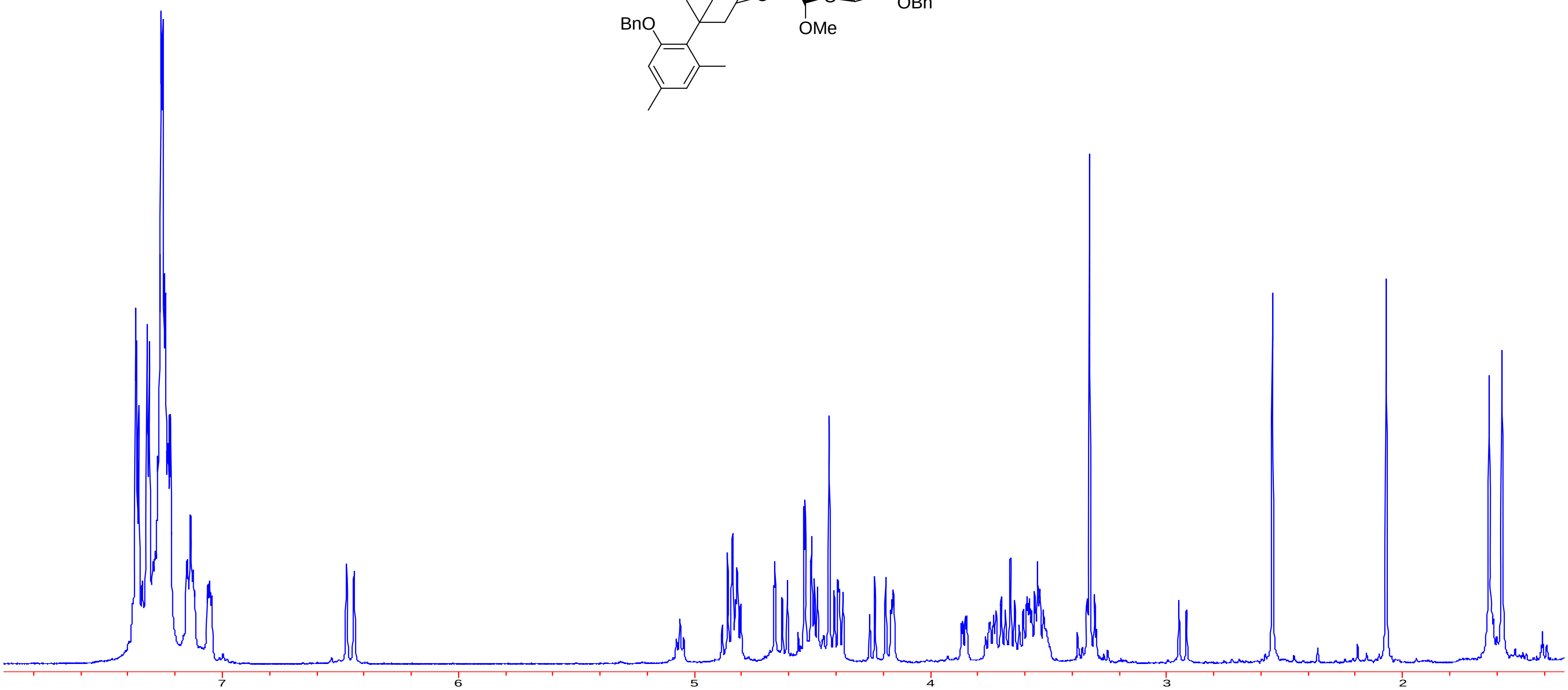


Methyl 4-*O*-α-D-mannopyranosyl-(1→4)-2,3-*O*-isopropylidene-α-L-rhamanopyranoside (18)

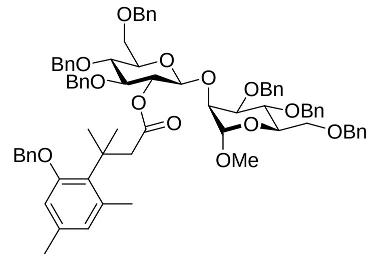


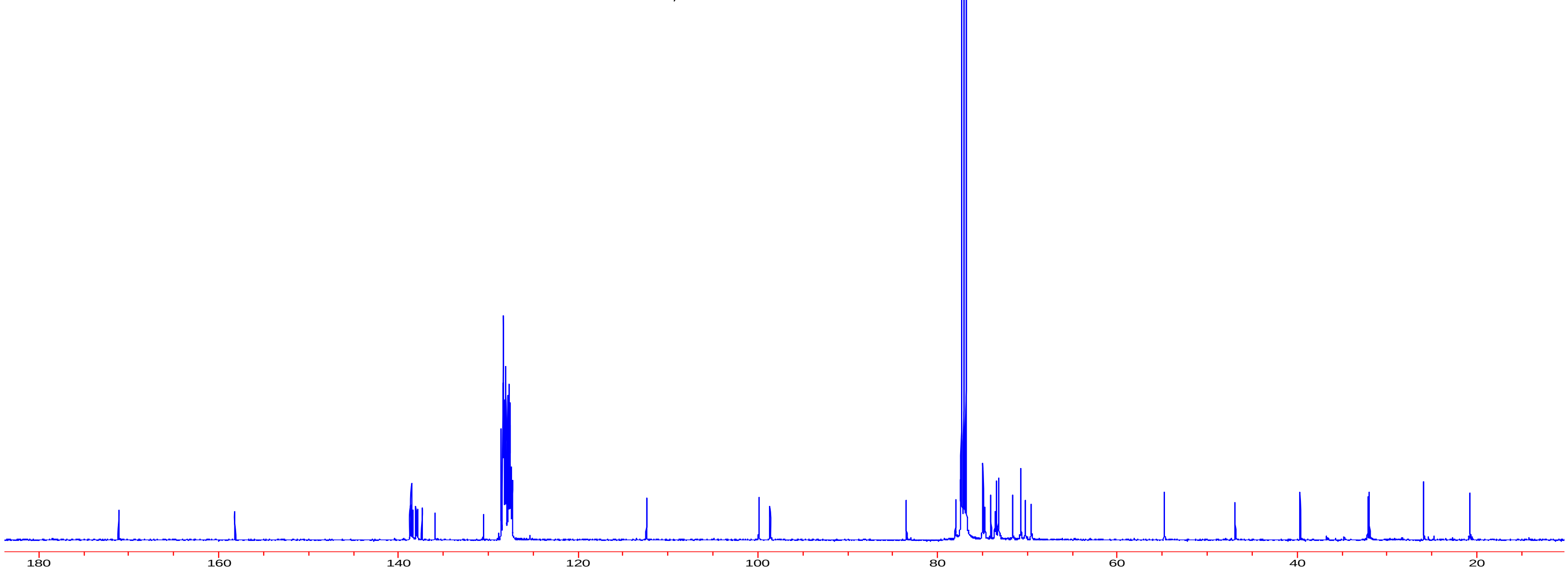
Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (19)



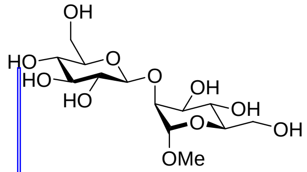


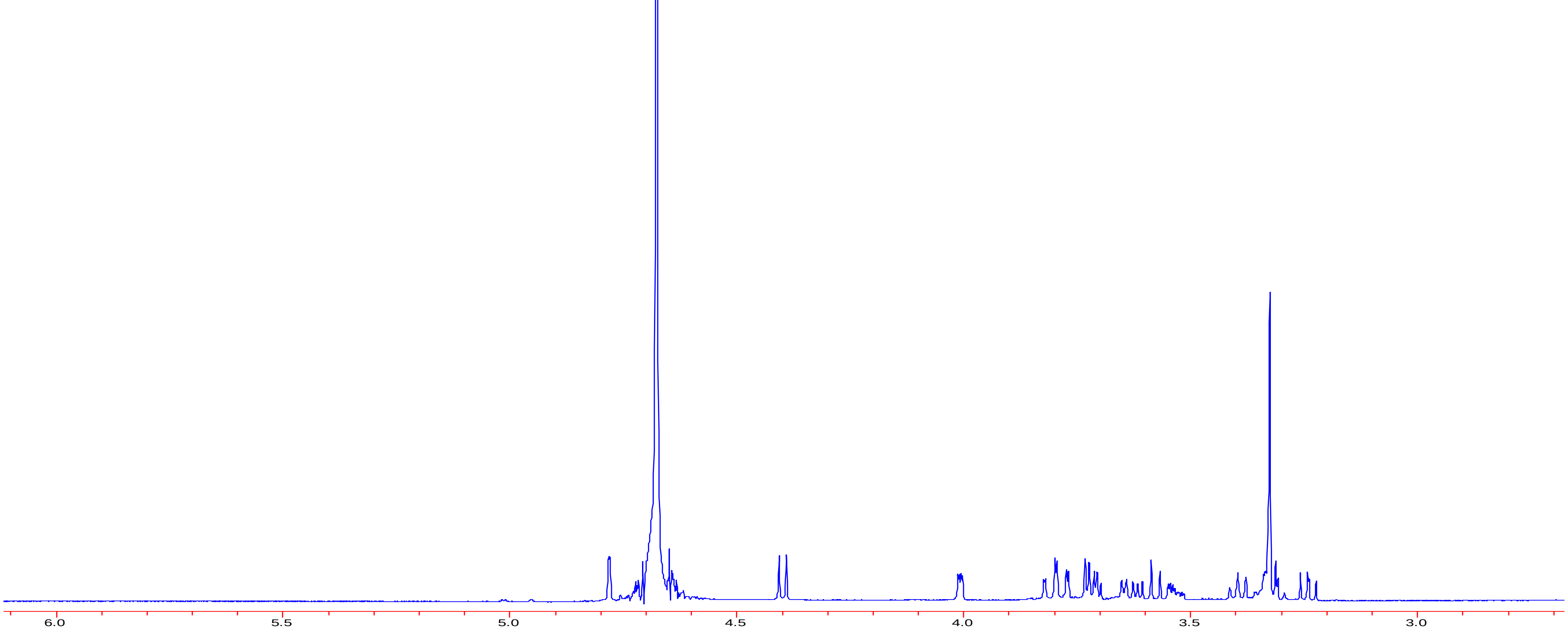
Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (19)



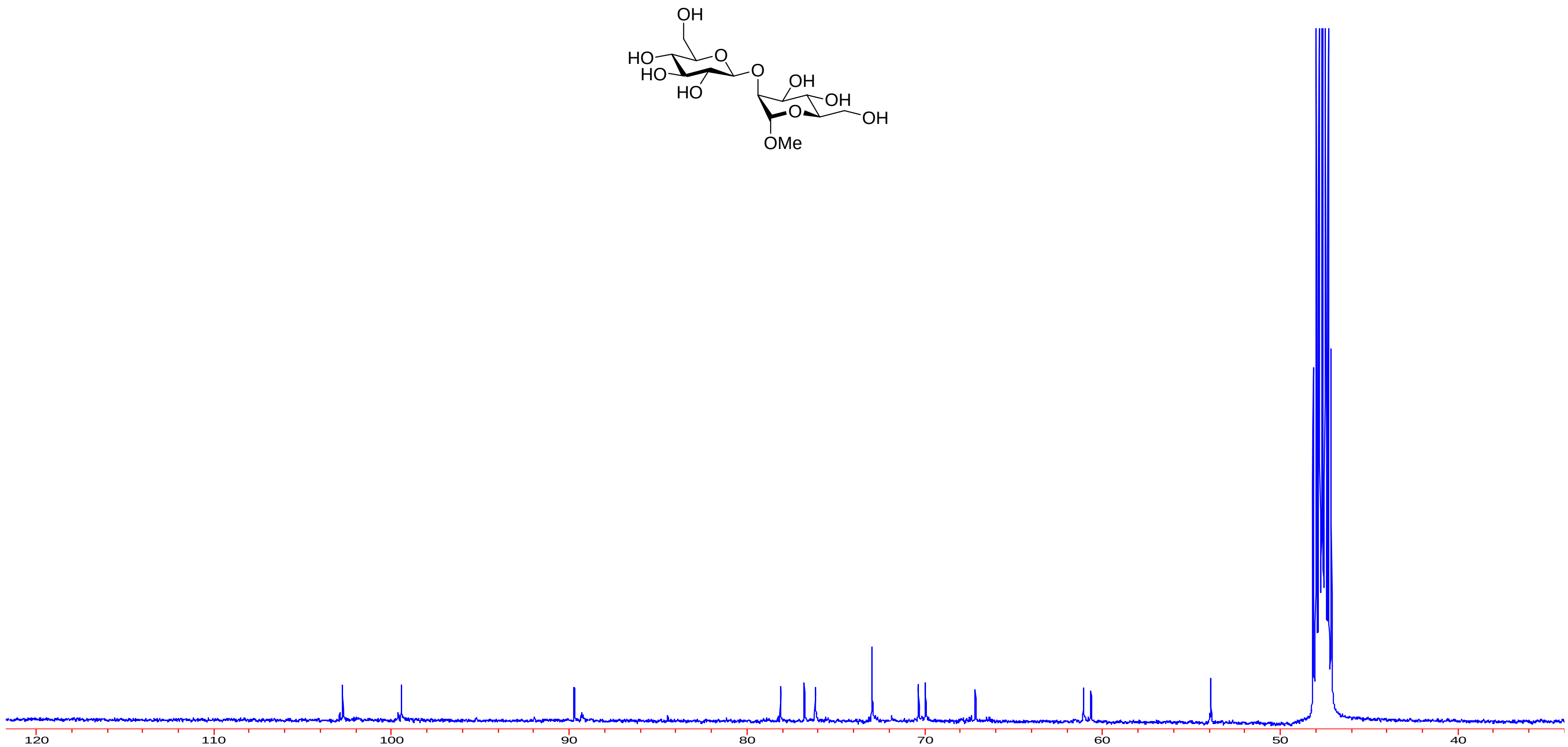


Methyl 4-*O*-*β*-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (20, D_2O)

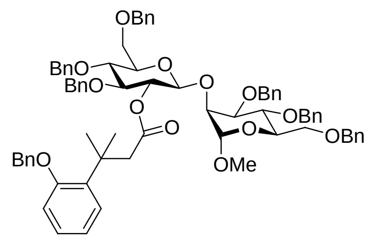


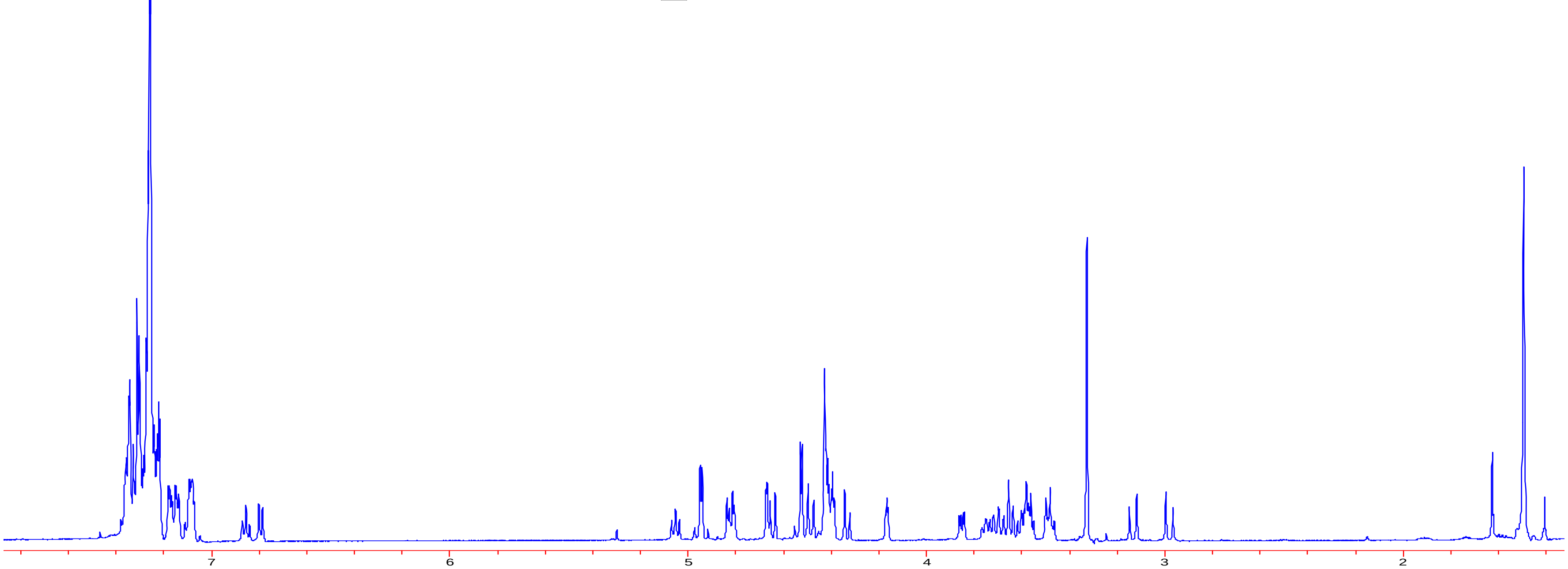


Methyl 4-*O*-*β*-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (20, MeOD)

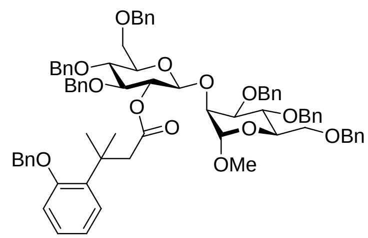


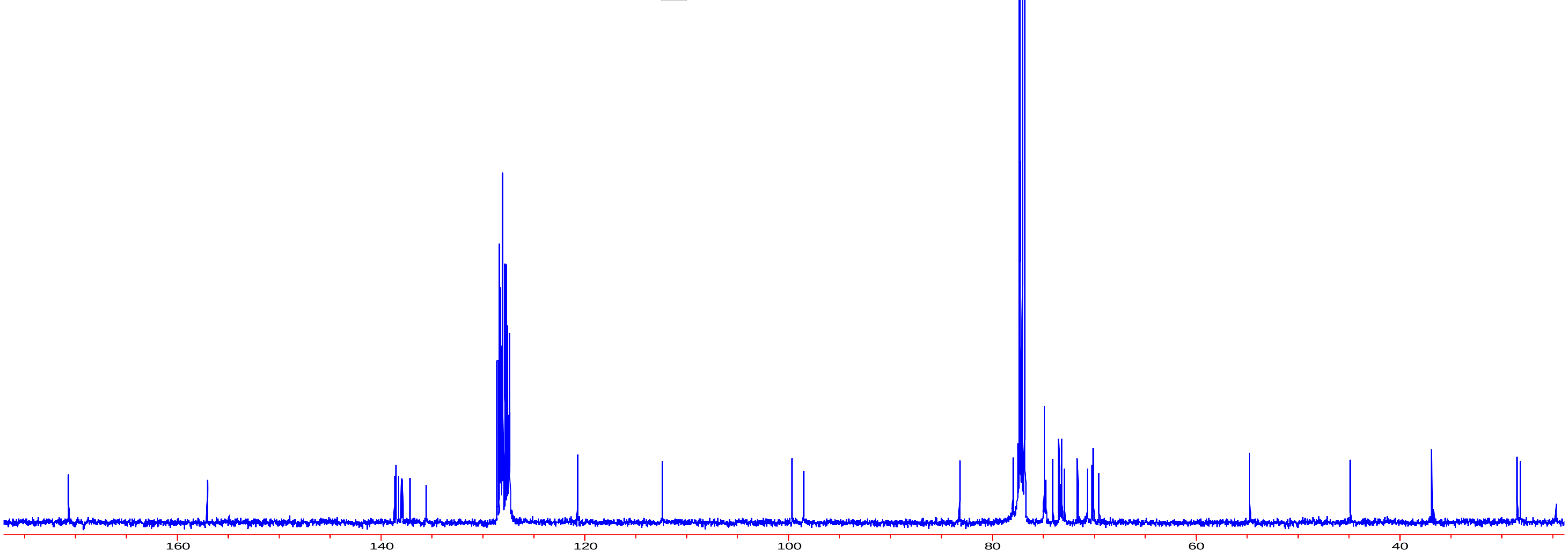
Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (21)



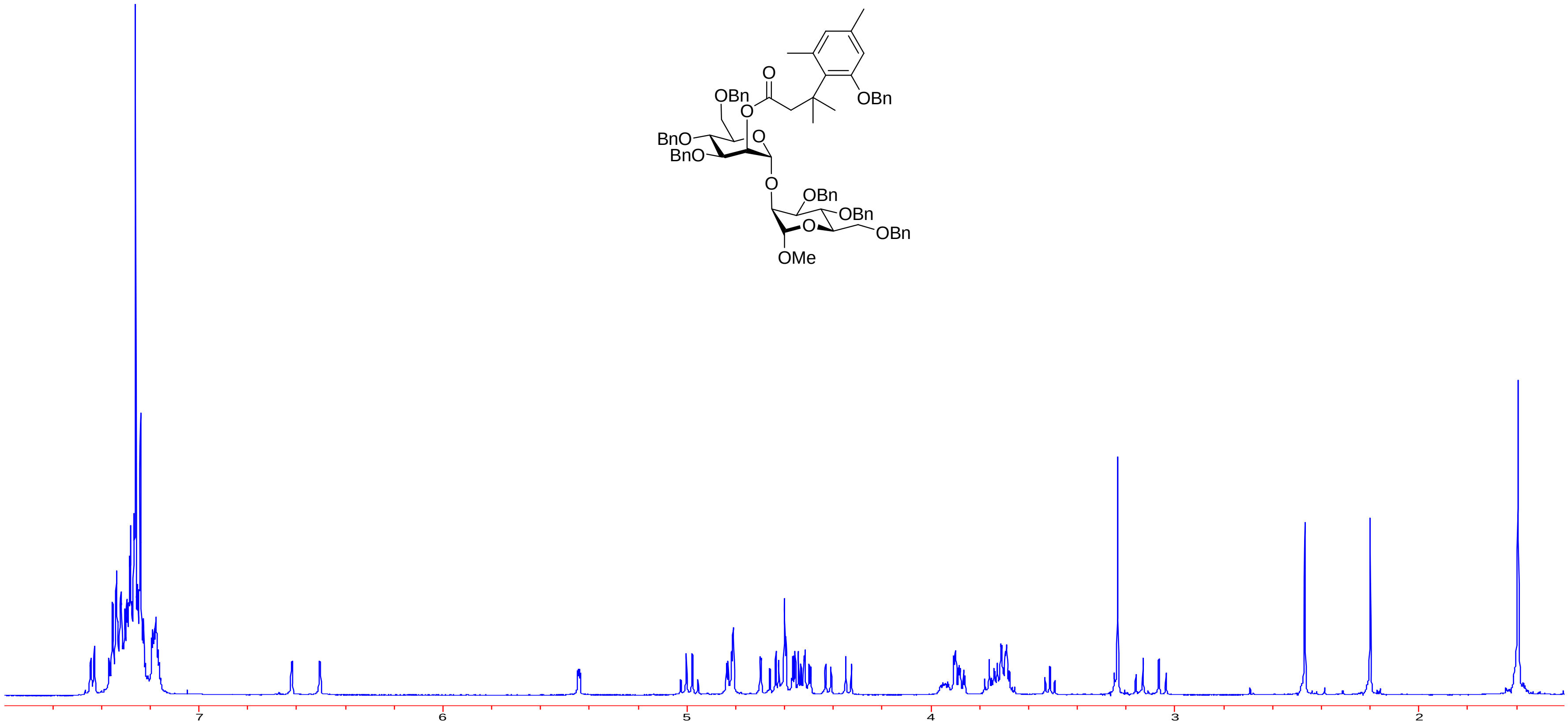


Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→2)-α-D-mannopyranoside (21)

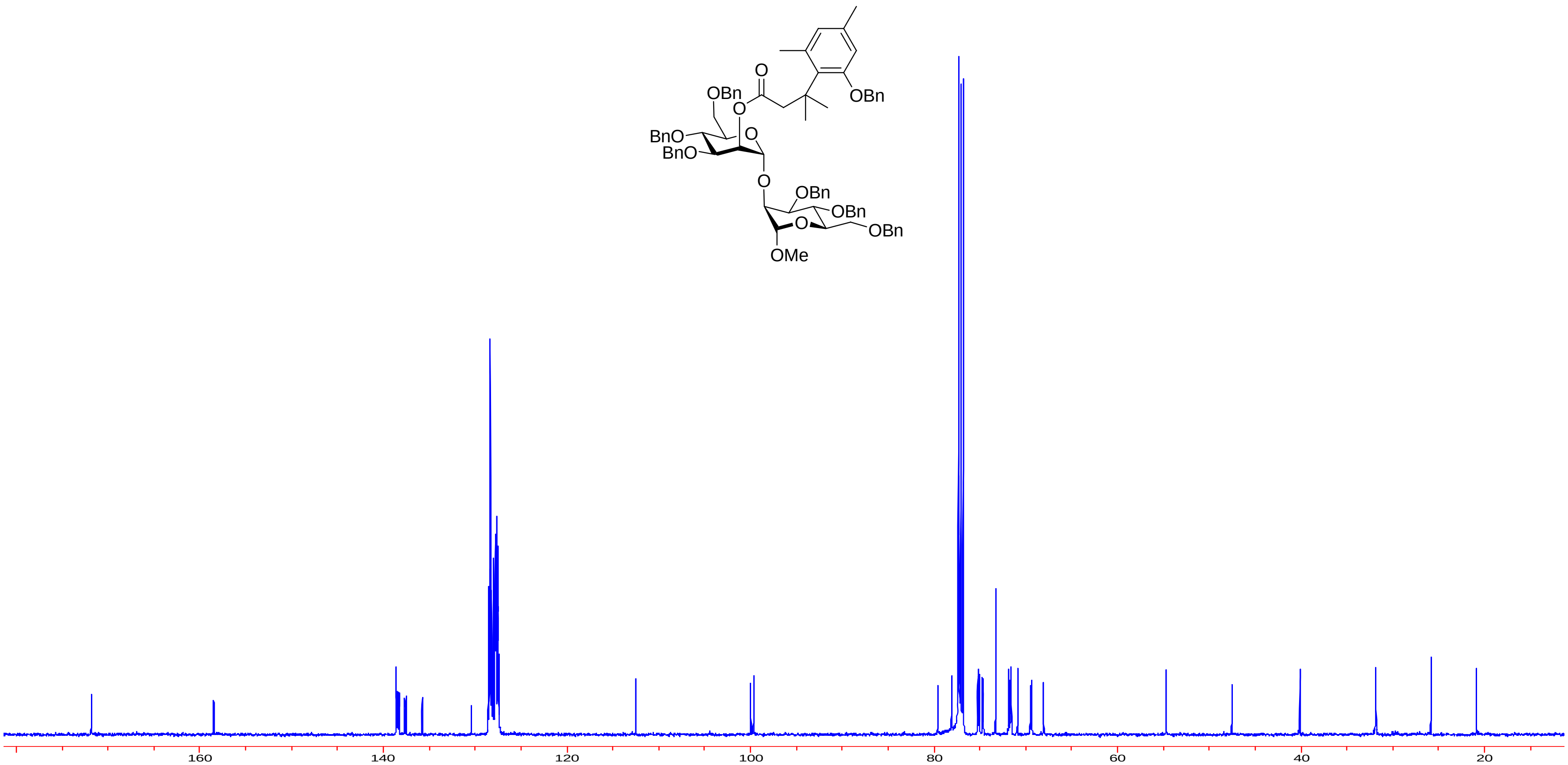




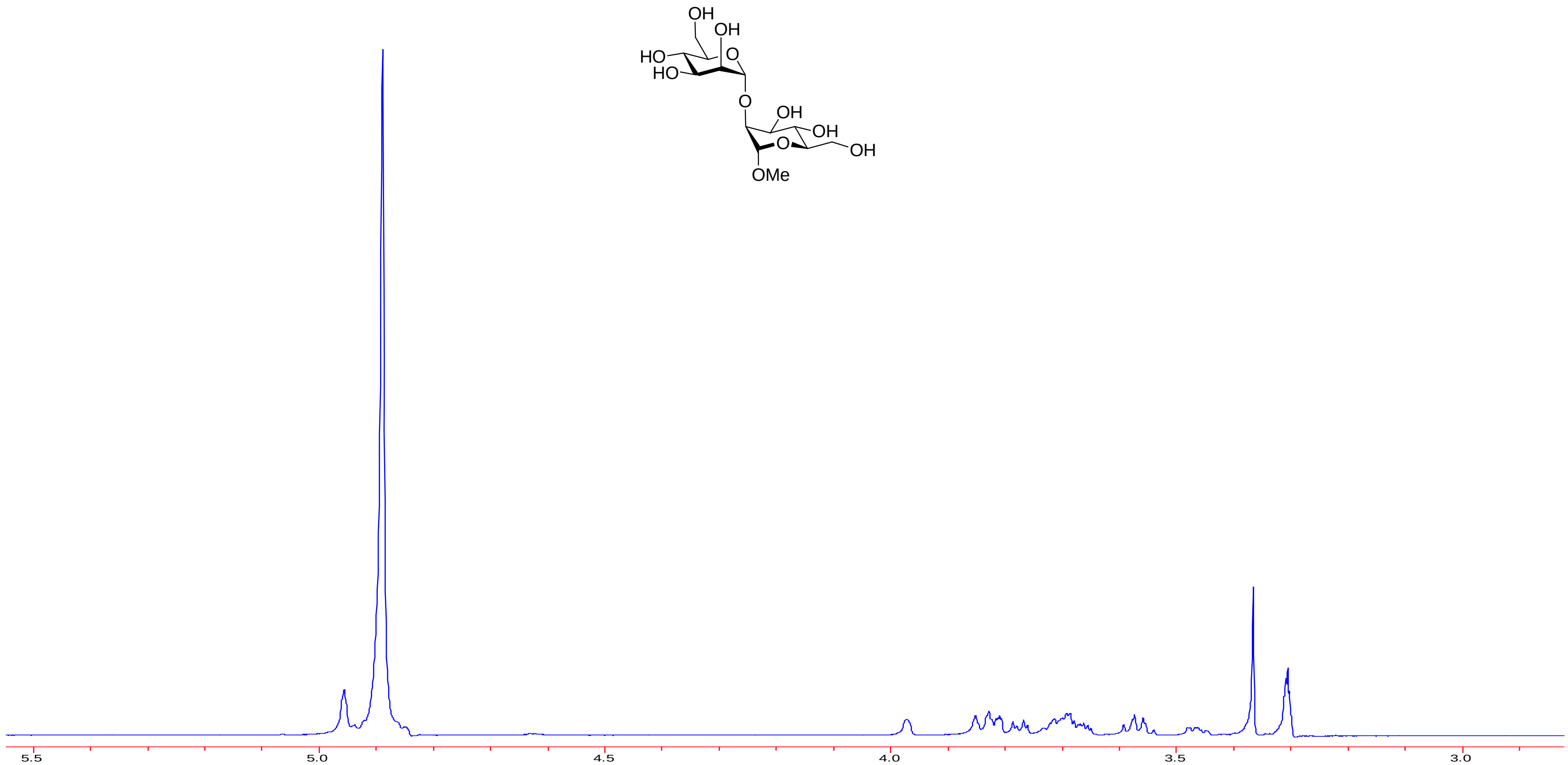
Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→2)-α-D-mannopyranoside (22)



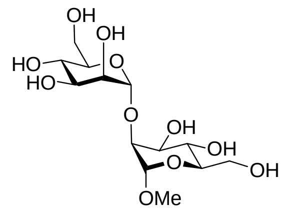
Methyl 3,4,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→2)-α-D-mannopyranoside (22)

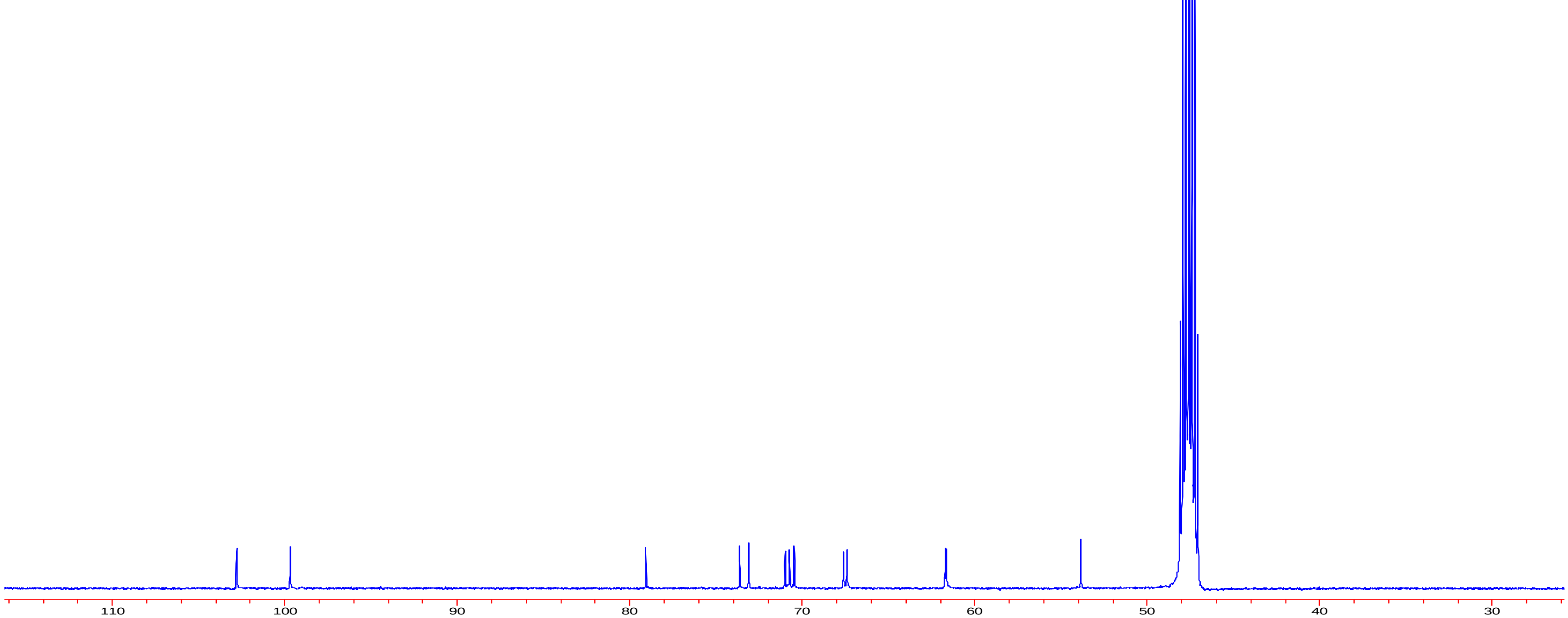


Methyl 4-*O*-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (23)

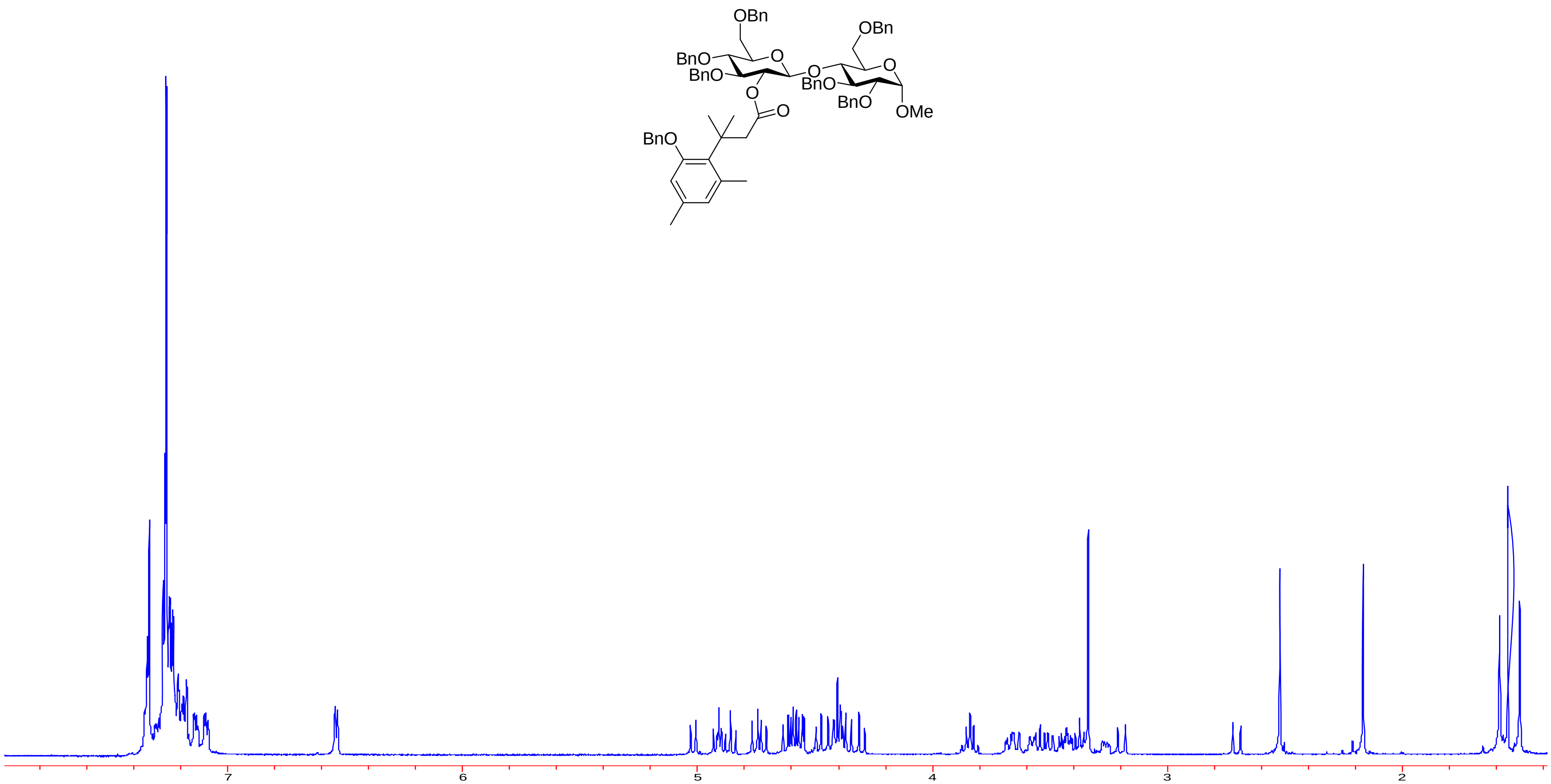


Methyl 4-*O*-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside (23)

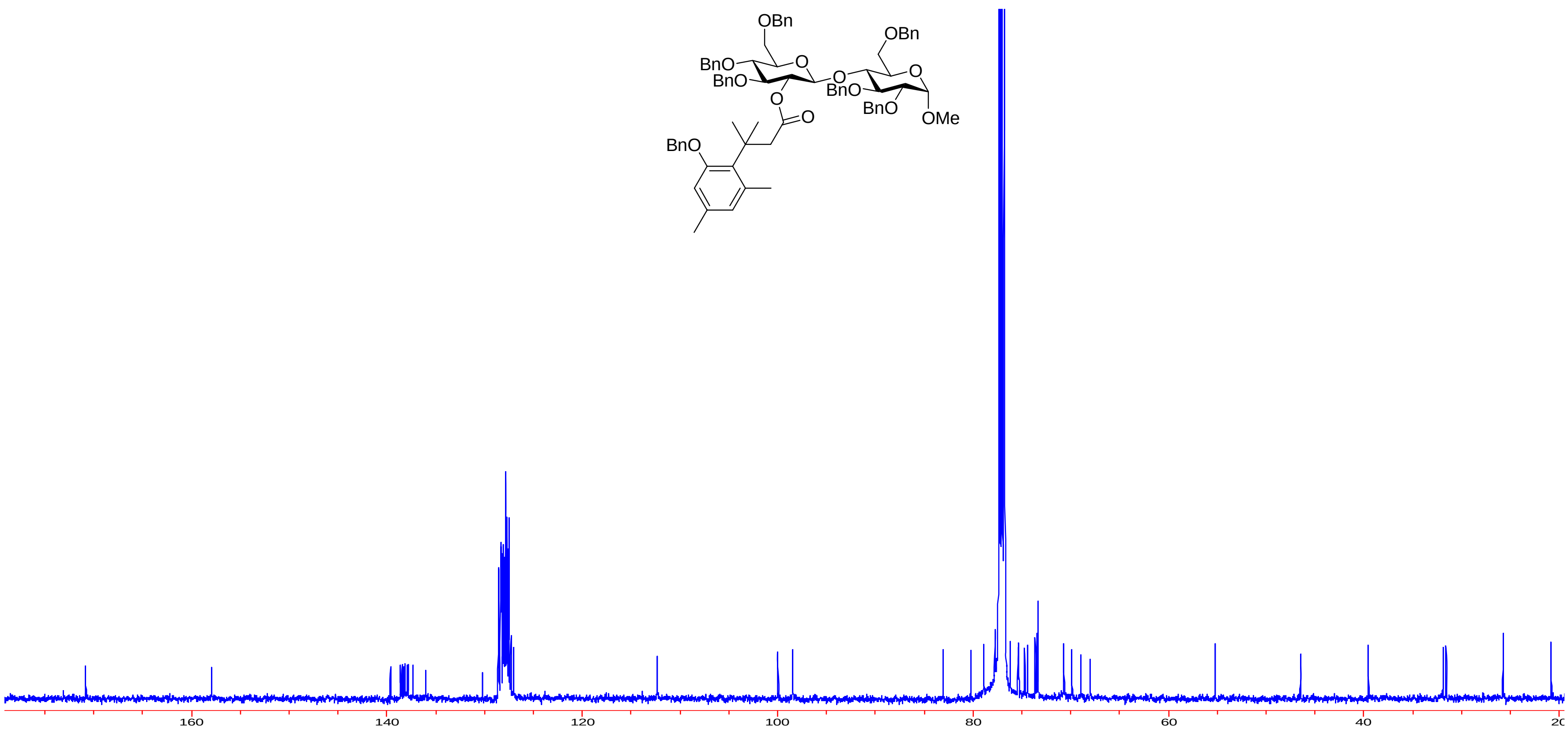




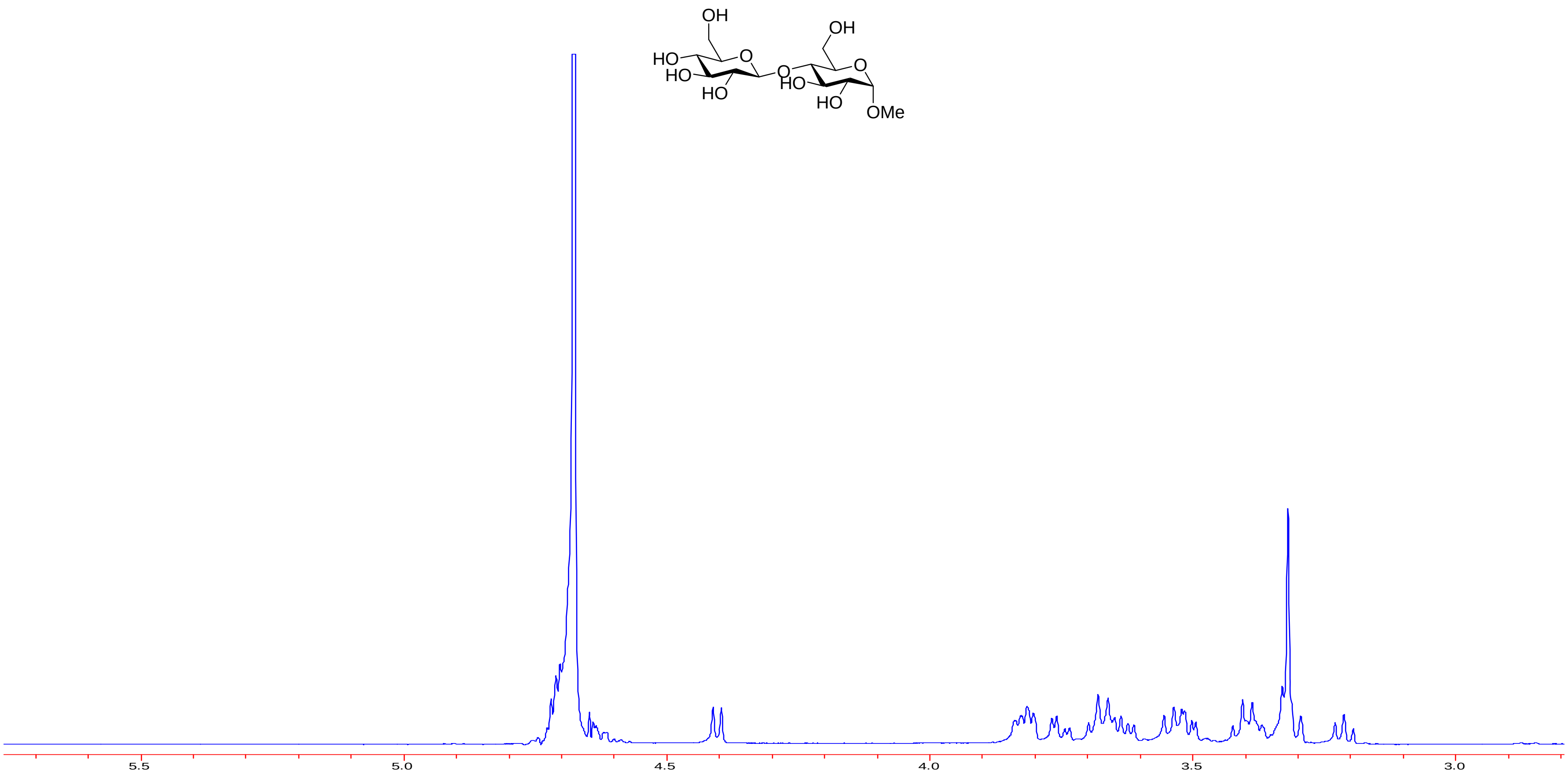
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3’-(2”-benzyloxy-4”,6”-dimethylphenyl)-3’,3’-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-α-D-glucopyranoside (24)



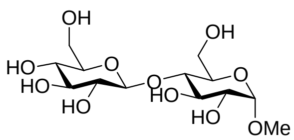
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)- α-D-glucopyranoside (24)

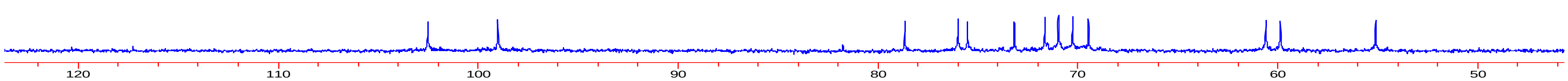


Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranoside (25, D_2O)

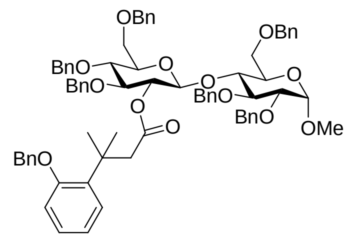


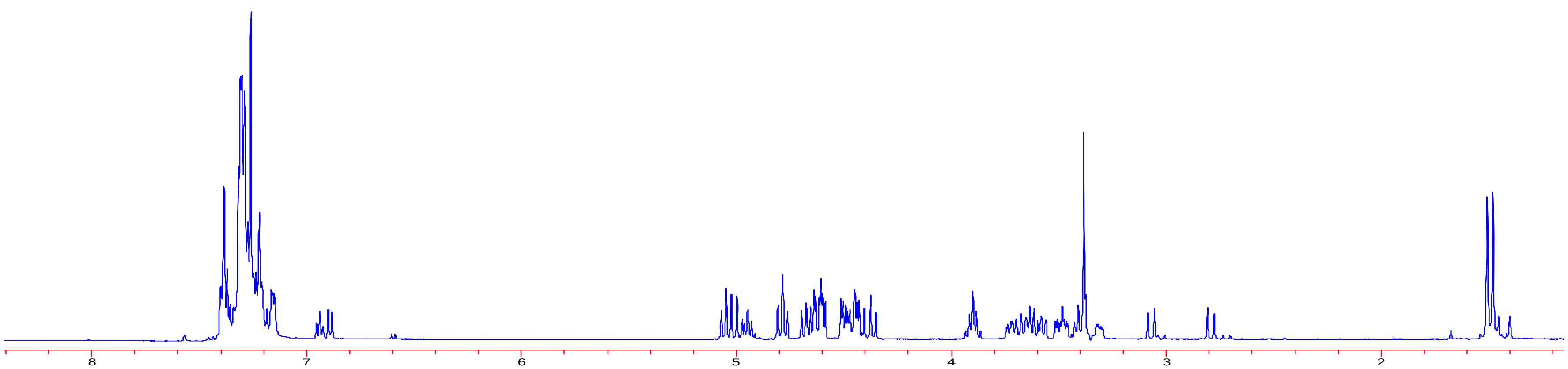
Methyl 4-*O*-*β*-D-glucopyranosyl-(1→4)-*α*-D-glucopyranoside (25, D_2O)



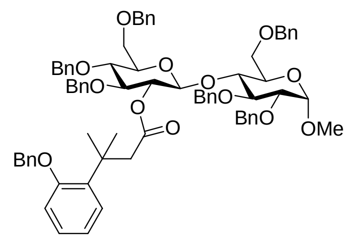


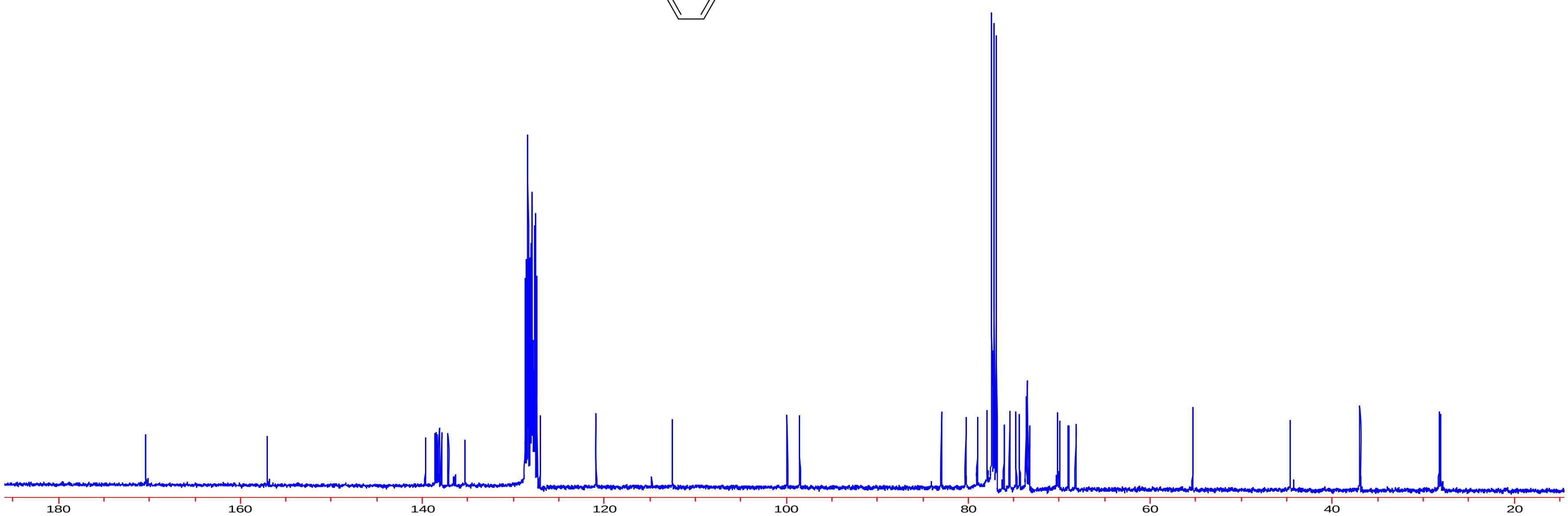
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-α-D-glucopyranoside (26)



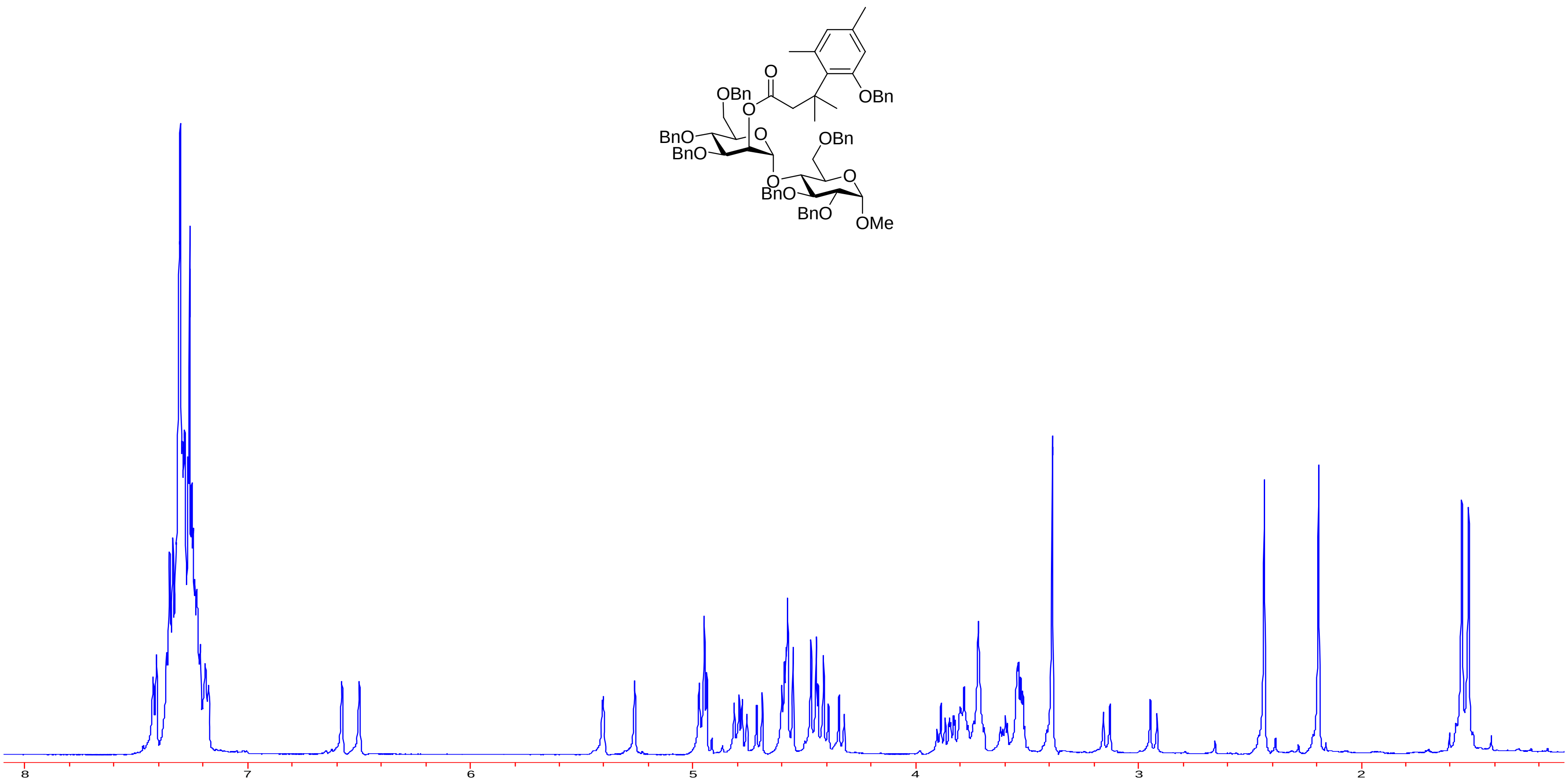


Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-(1→4)-*α*-D-glucopyranoside (26)

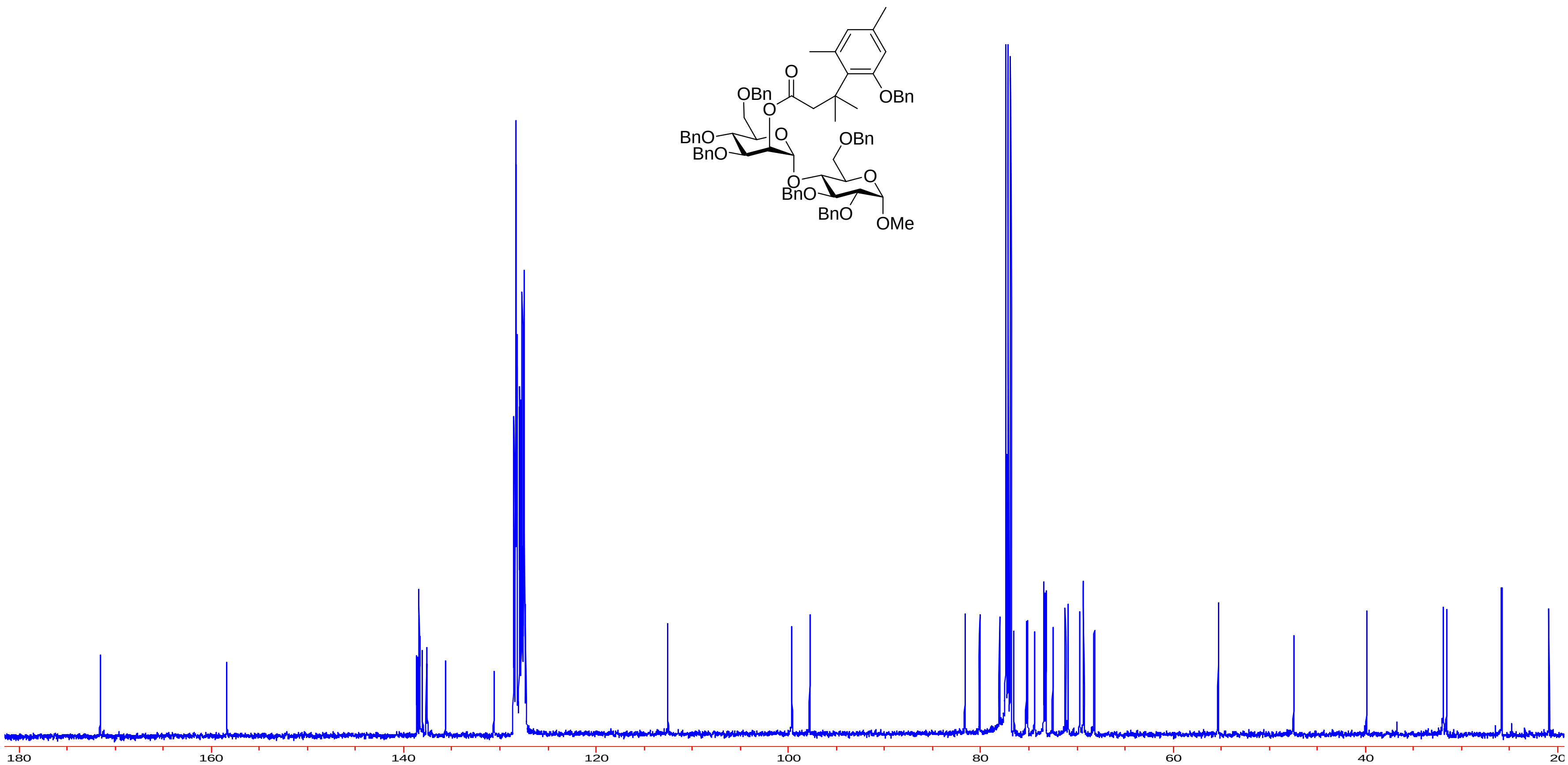




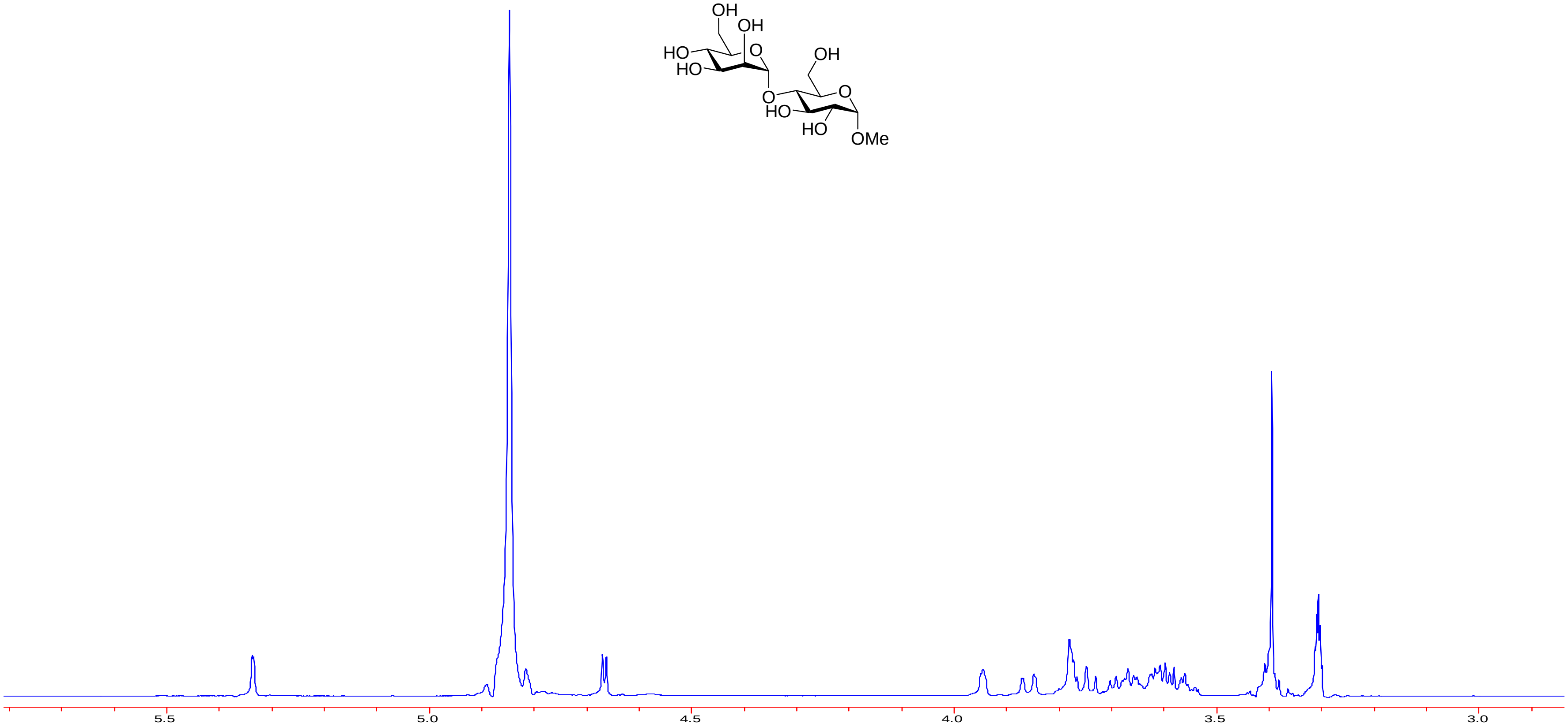
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-α-D-glucopyranoside (27)



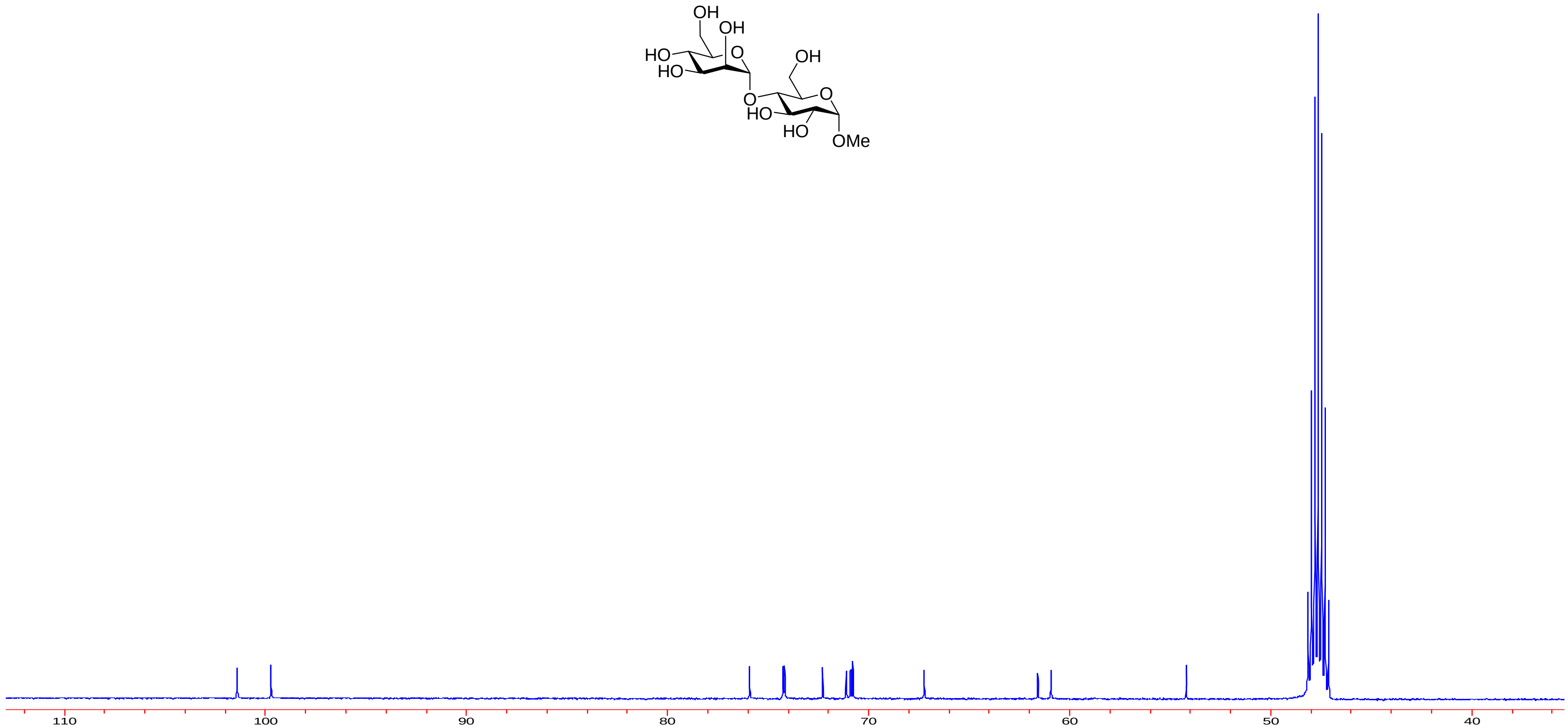
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-(1→4)-α-D-glucopyranoside (27)



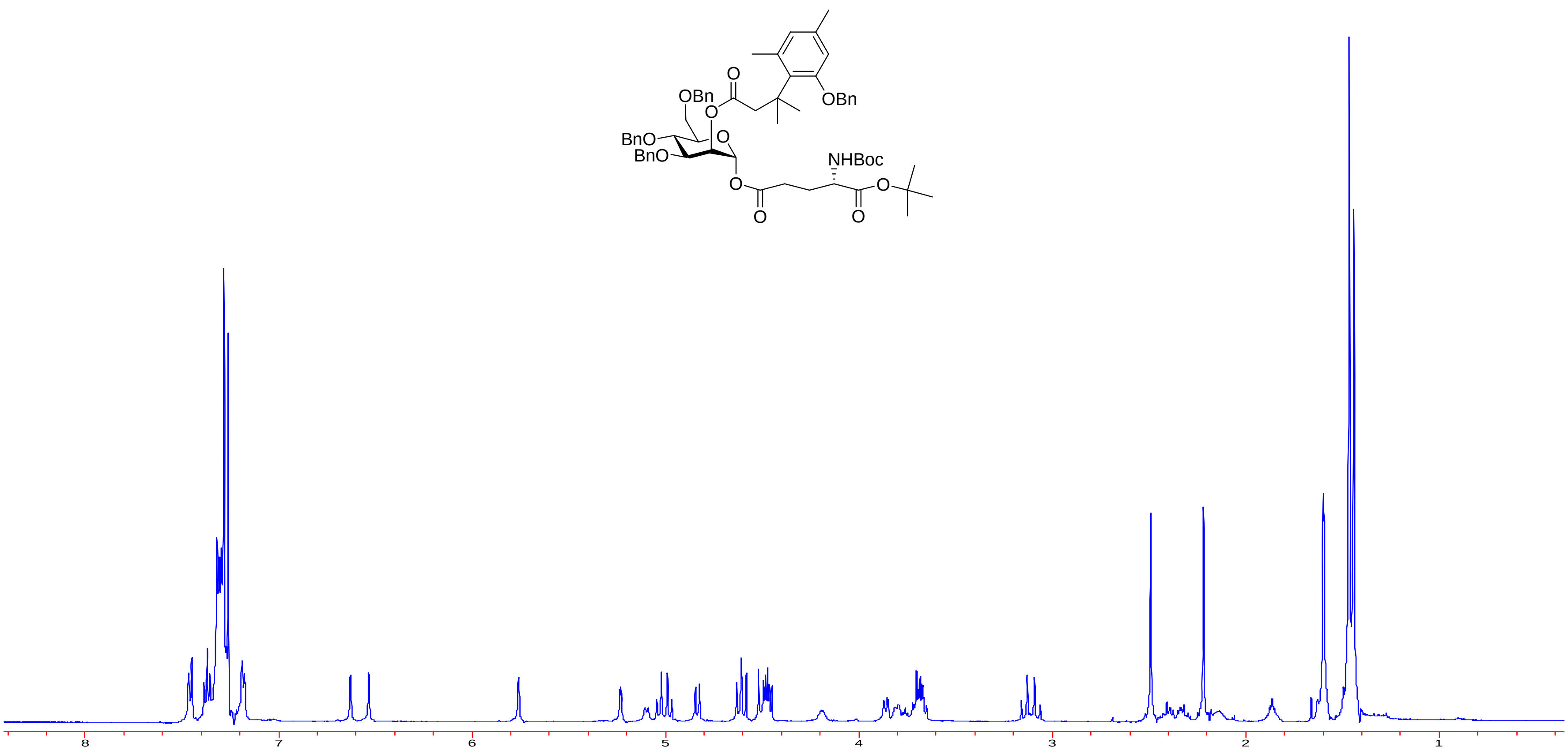
Methyl 4-*O*-α-D-mannopyranosyl-(1→4)-α-D-glucopyranoside (28, MeOD)



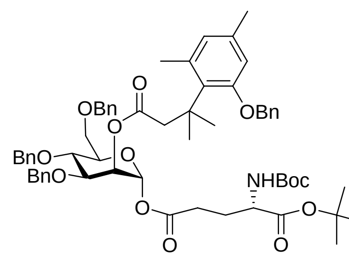
Methyl 4-*O*-α-D-mannopyranosyl-(1→4)-α-D-glucopyranoside (28, MeOD)

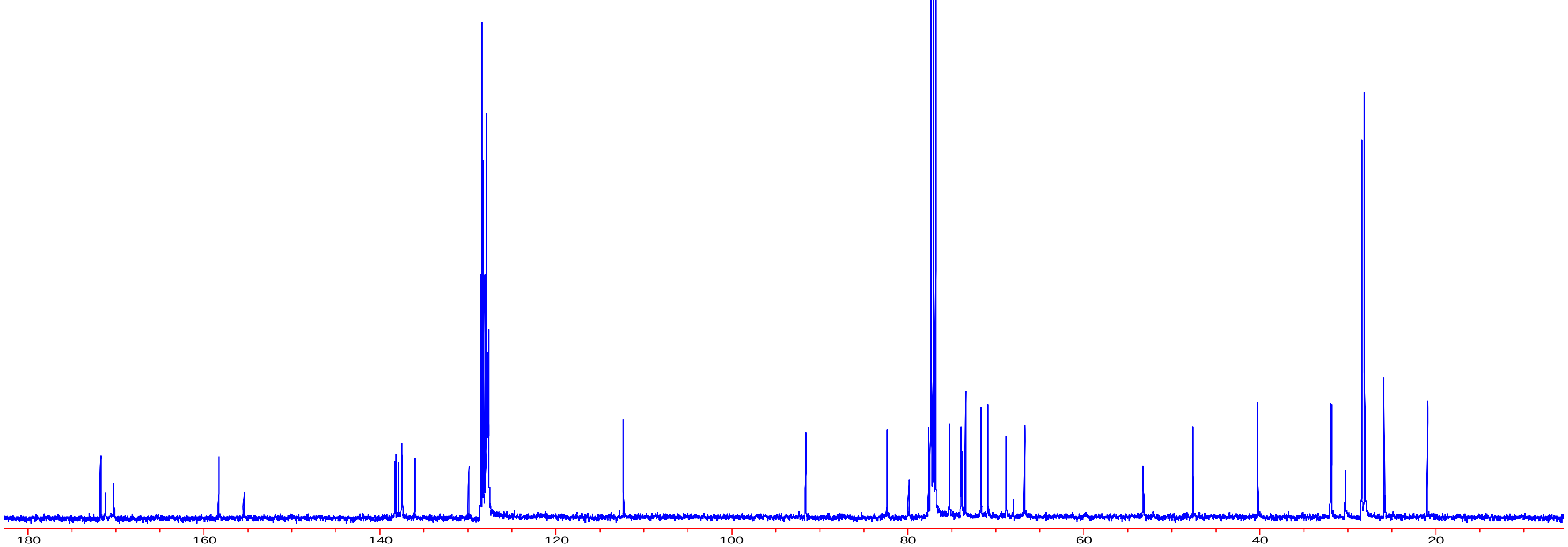


α-*tert*-Butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3’-(2”-benzyloxy-4”,6”-dimethylphenyl)- 3’,3’-dimethylpropanoyl]-α-D-mannopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (29)

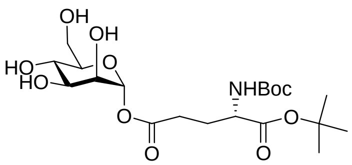


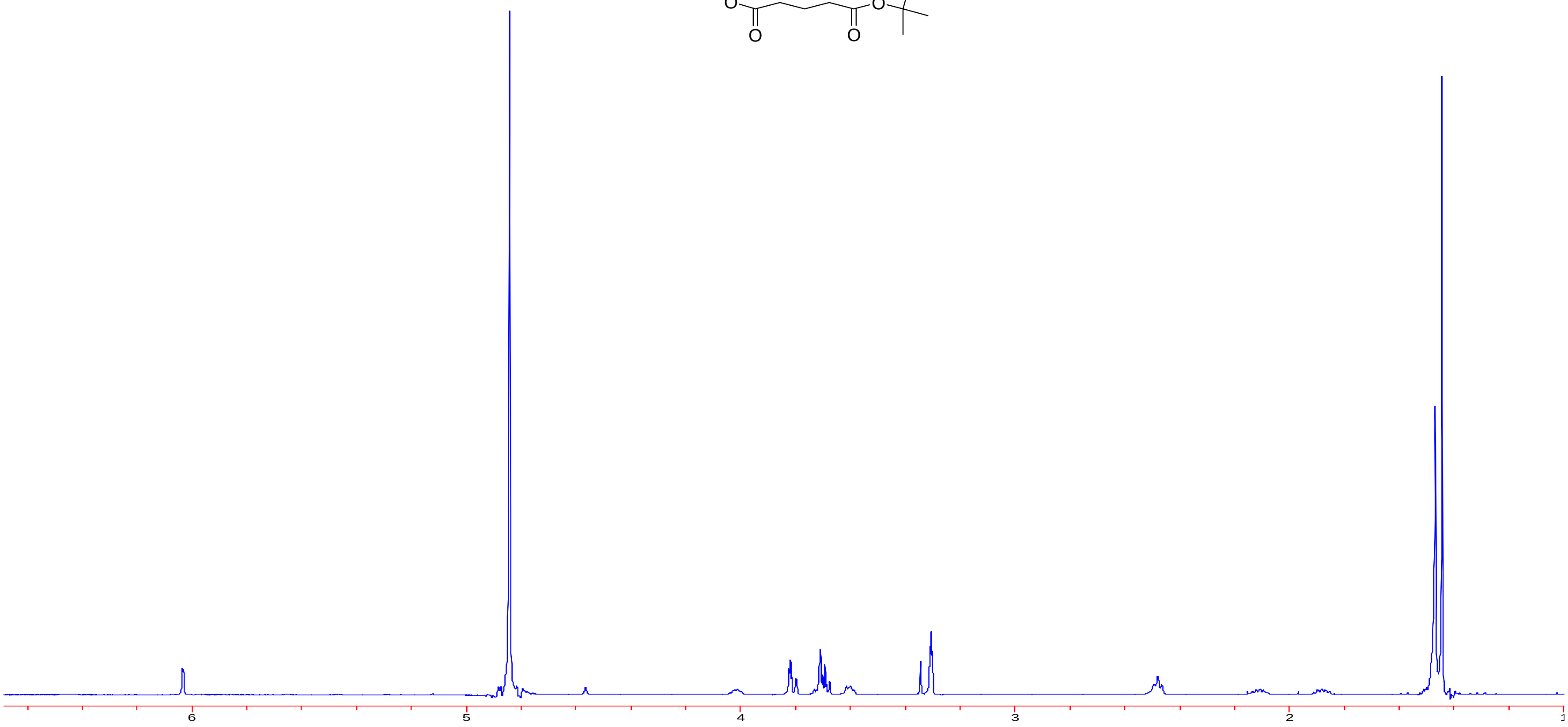
α-*tert*-Butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2"-benzyloxy-4",6"-dimethylphenyl)- 3',3'-dimethylpropanoyl]-α-D-mannopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (29)



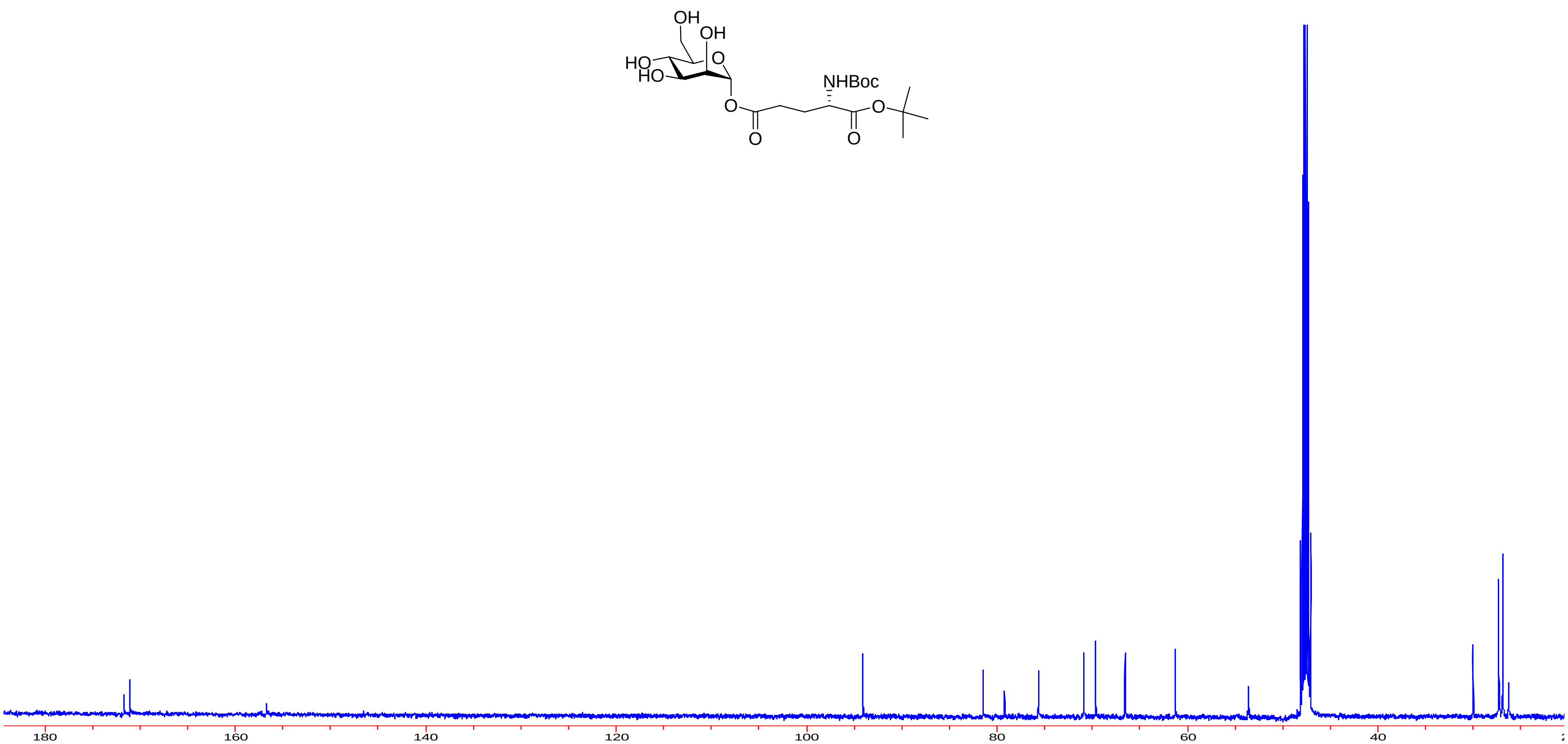


α-*tert*-butyl γ-α-D-mannopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (30)

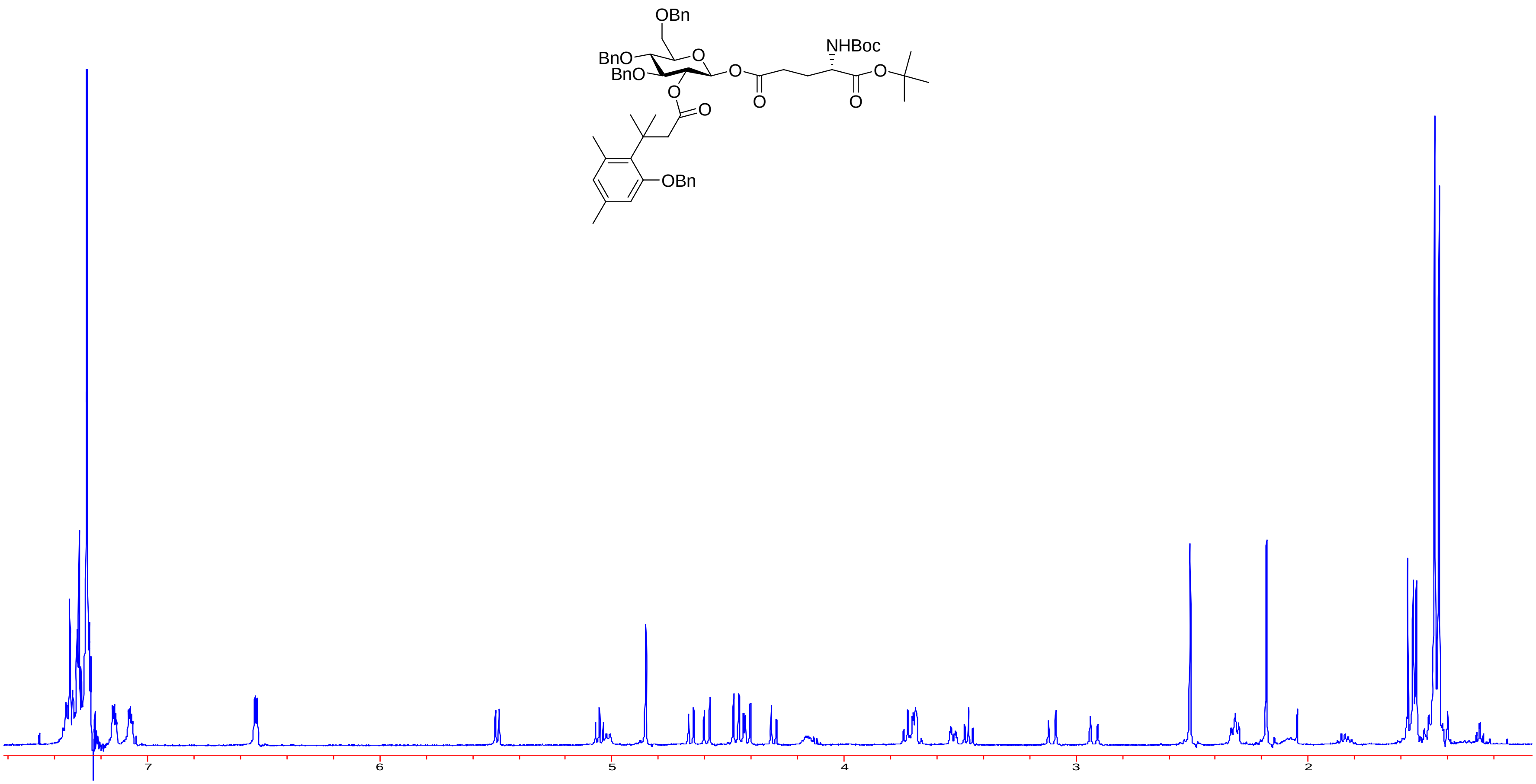




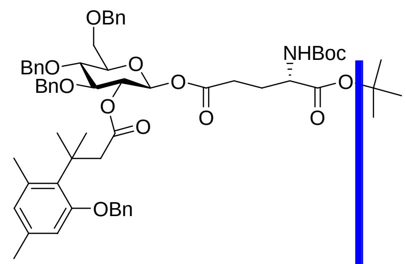
α-*tert*-butyl γ-α-D-mannopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (30)

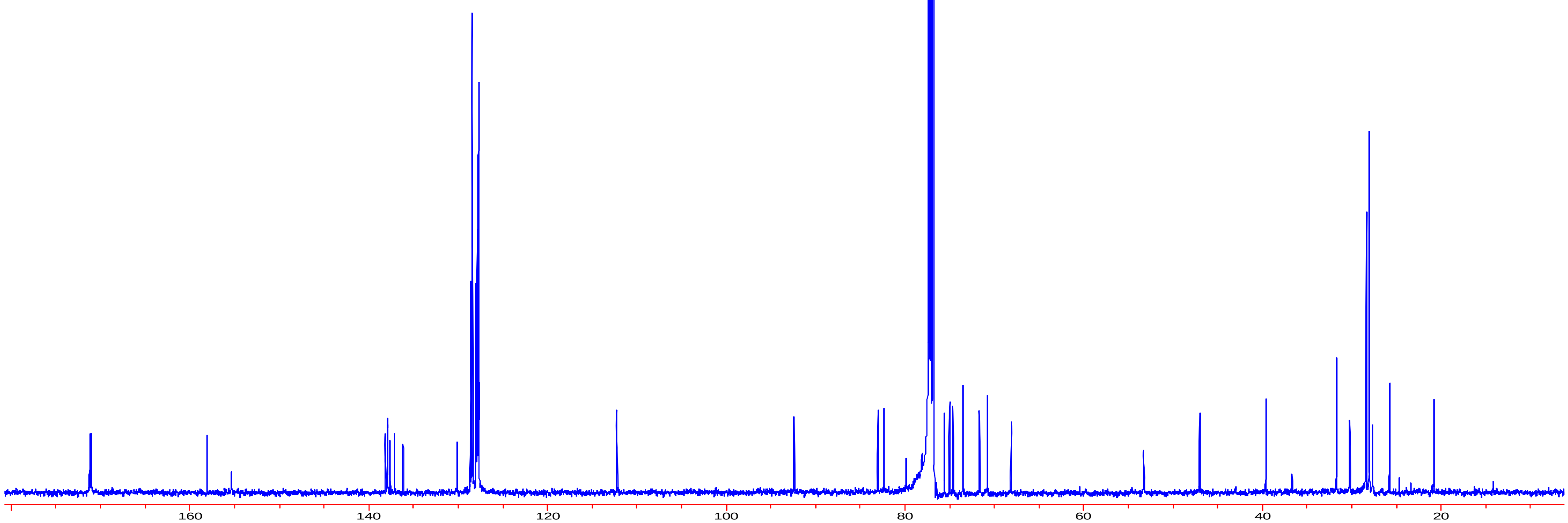


α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (31)

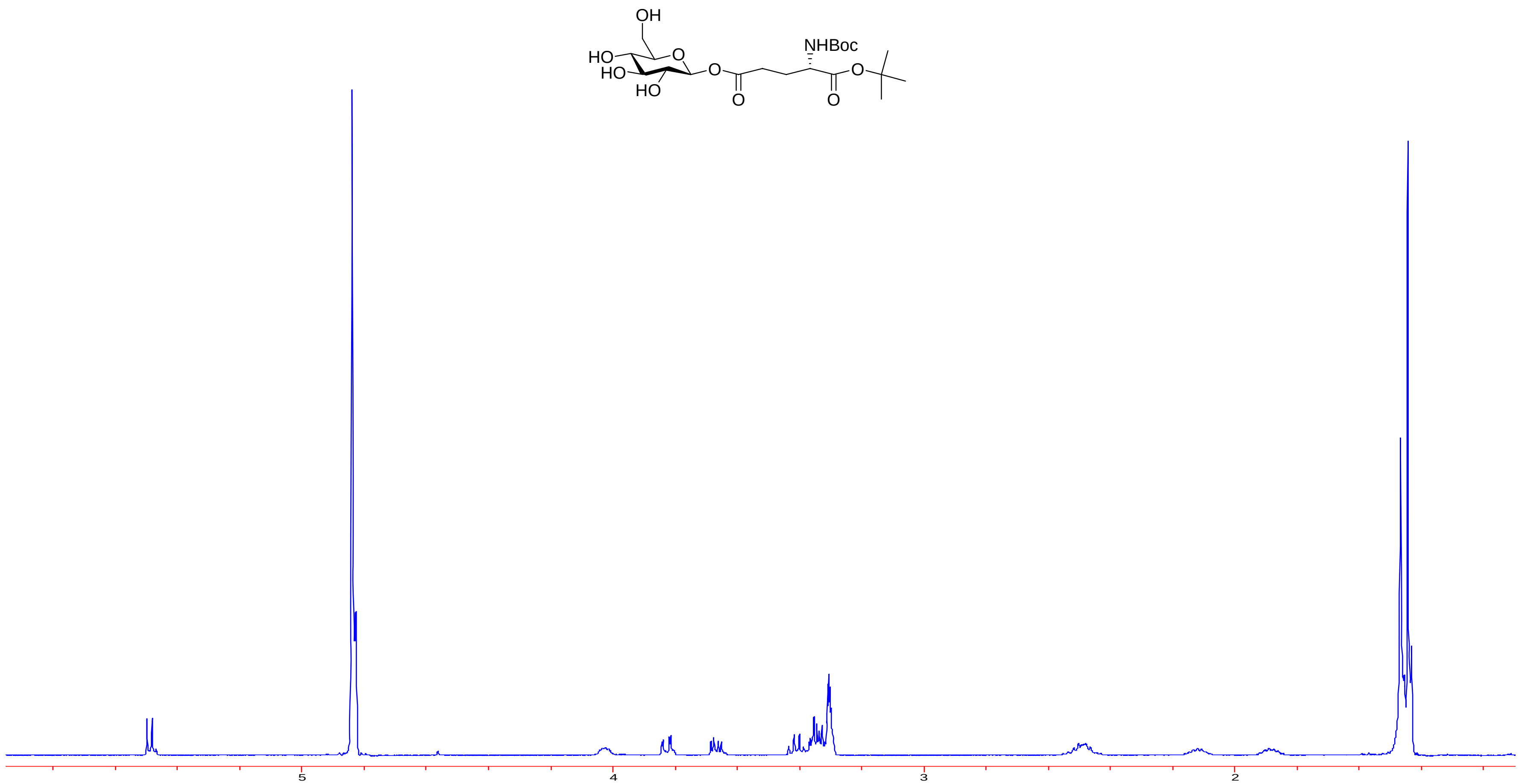


α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxy-4'',6''-dimethylphenyl)-3',3'-dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (31)

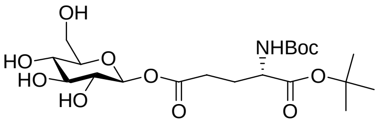


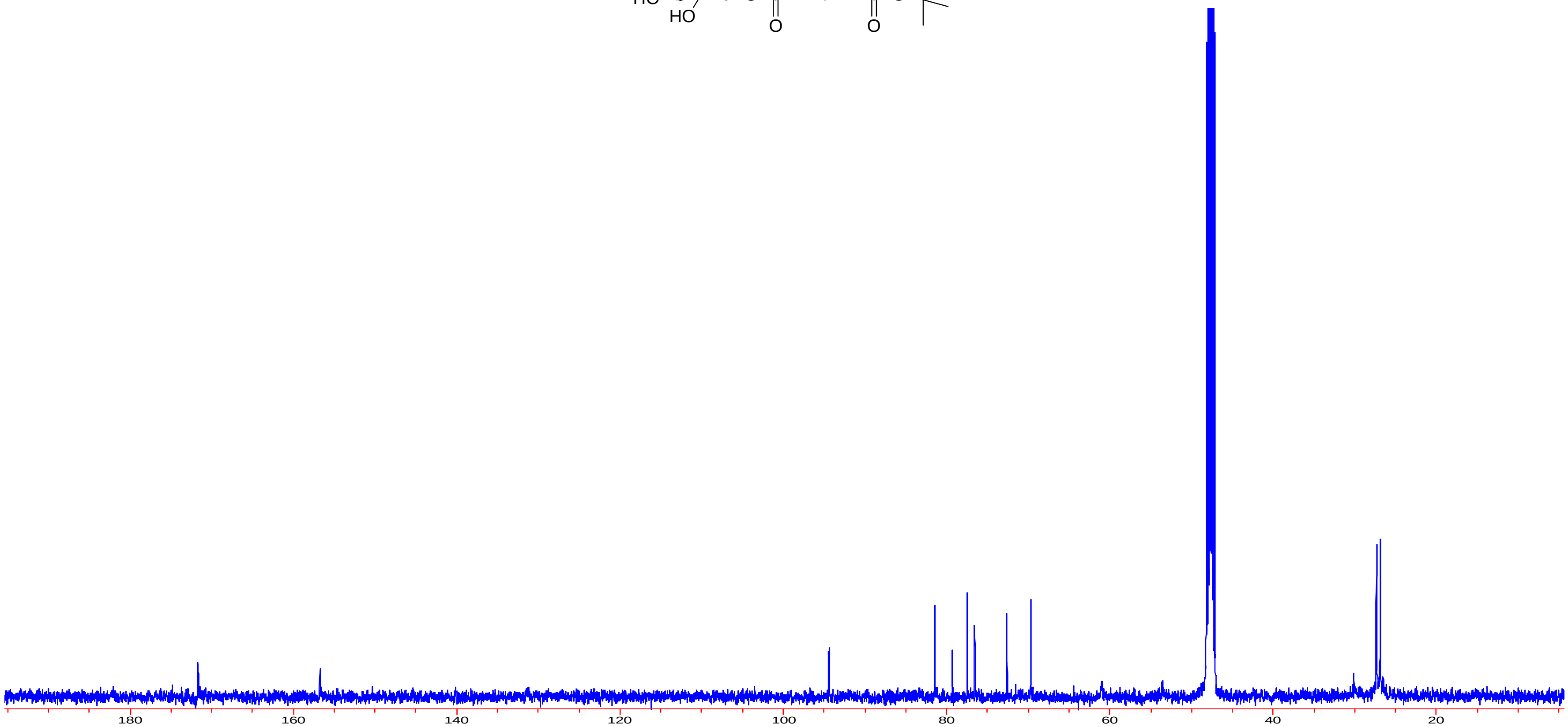


α-*tert*-butyl γ-*β*-D-glucopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (32)

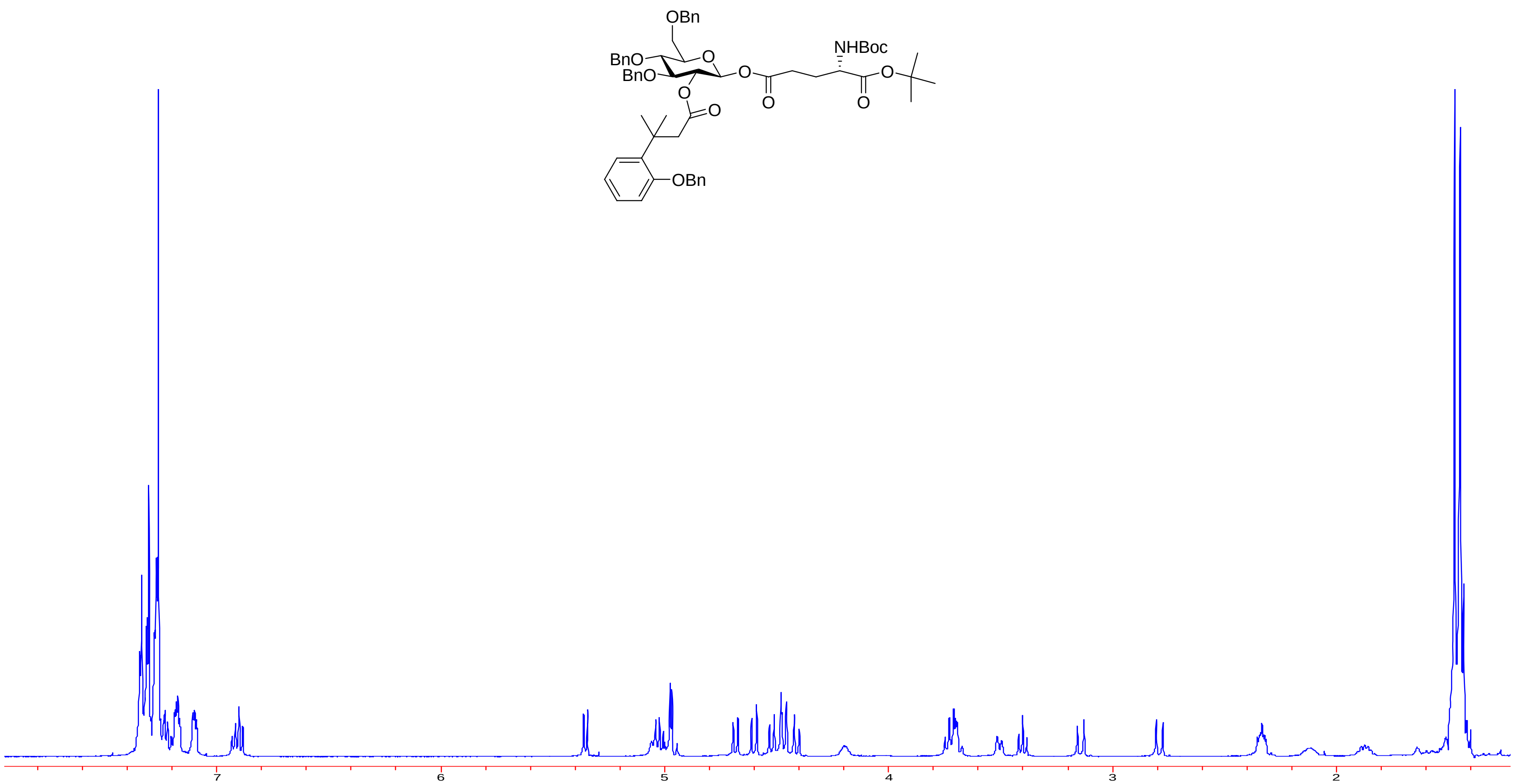


α-*tert*-butyl γ-*β*-D-glucopyranosyl-*N*-*tert*-butyloxycarbonyl-L-glutamate (32)





α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3’-(2”-benzyloxyphenyl)-3’,3’- dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (33)



α-*tert*-butyl γ-{3,4,6-tri-*O*-benzyl-2-*O*-[3'-(2''-benzyloxyphenyl)-3',3'- dimethylpropanoyl]-*β*-D-glucopyranosyl}-*N*-*tert*-butyloxycarbonyl-L-glutamate (33)