Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Stereoselective oxidative *O*-glycosylation of disarmed glycosyl iodides with alcohols using PIDA as the promoter

Maria A. Boulogeorgou, Alexandros Toskas, John K. Gallos,* Christos I. Stathakis*

Department of Chemistry, Aristotle University of Thessaloniki, University Campus, Thessaloniki, 541 24, Greece

E mail: cstathakis@chem.auth.gr; igallos@chem.auth.gr*

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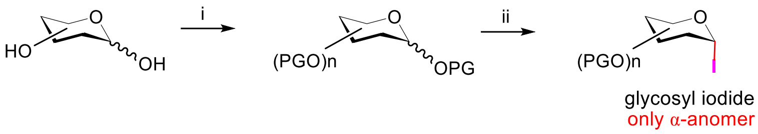
General Experimental Details. All reagents are commercially available and were used without further purification. Solvents were dried by standard methods. The progress of reactions was checked by thin layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and Seebach or anisaldehyde solution as developing agent. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Melting points were determined with a Koffler hot-stage microscope. HRMS spectra were recorded on a Bruker® Maxis Impact QTOF spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz and 126 MHz respectively using Agilent 500 spectrometer. Chemical shift values are referenced against residual protons in the deuterated solvents. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets. Optical rotations were recorded on a Perkin-Elmer Model 343 polarimeter at 589 nm.

Detailed synthetic procedures and analytical data

I. Protection of D-sugars and formation of glycosyl iodides.

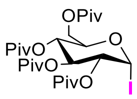


i. **PG = Piv**: Pivaloyl-chloride, DMAP, pyridine, 0°C to r.t. or
PG = Ac: Acetic anhydride, pyridine, 0°C to r.t
ii. I_2, Et_3SiH, DCM, r.t., 1h reflux

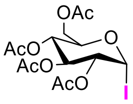
Scheme S1. General route of synthesis of glycosyl iodides.

Penta-*O*-acyl-D-glycosylpyranosides were synthesized according to reported procedures.[1,2,3]

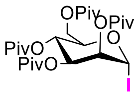
General procedure for the synthesis of 2,3,4,6-tetra-*O*-acylglycosyl iodides. Et_3SiH (1.4 equiv.) was added at 0°C, to a solution of penta-*O*-acyl-D-glycosylpyranoside (1.0 equiv.) in dry dichloromethane, containing I_2 (1.4 equiv.). The resulting mixture was stirred at the same temperature for 20 minutes, then warmed at 40°C for 1 hour. A solution of $Na_2S_2O_3$ (20% w/v) was added portionwise to the mixture until discoloration, which was, then extracted with dichloromethane twice. The combined organic layers were dried over Na_2SO_4, filtered, volatiles were evaporated off and the residue was chromatographed on a silica gel column with cyclohexane:EtOAc as the eluting solvents to give glycosyl iodides.



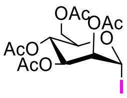
2,3,4,6-tetra-O-pivaloylglucosyl iodide 1a: *Rf* = 0.7 [cyclohexane:EtOAc (5:1)]. Yield 98% as a solid. m.p. = 140-142°C. $[a]^{25}_D$ = +172 (c = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, J = 4.4 Hz, 1H), 5.53 (t, J = 9.7 Hz, 1H), 5.23 (t, J = 9.7 Hz, 1H), 4.21 (dd, J = 9.8, 4.4 Hz, 1H), 4.17 (d, J = 3.2 Hz, 2H), 4.06 (dt, J = 10.2, 3.2 Hz, 1H), 1.22 (s, 9H), 1.20 (s, 9H), 1.18 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.83, 177.05, 176.68, 176.39, 75.40, 73.34, 71.09, 70.41, 66.28, 60.79, 38.87, 38.79, 38.70, 38.55, 27.14, 27.08, 27.03. The spectroscopic data are in good agreement with the reported ones.[2,3]



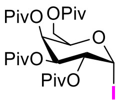
2,3,4,6-tetra-O-acetylglucosyl iodide 1b: *Rf* = 0.65 [cyclohexane:EtOAc (1:1)]. Yield 92% as a solid. m.p. = 108-109^{o}C, $[a]^{25}_{D}$ = +234 (c = 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 4.3 Hz, 1H), 5.47 (t, *J* = 9.6 Hz, 1H), 5.18 (t, *J* = 9.9 Hz, 1H), 4.34 (dd, *J* = 12.7, 4.1 Hz, 1H), 4.21 (dd, *J* = 9.9, 4.3 Hz, 1H), 4.12 (dd, *J* = 12.7, 2.1 Hz, 1H), 4.08 – 4.04 (td, J = 10.0, 4.1, 1.8 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.46, 169.80, 169.55, 169.43, 74.86, 72.91, 71.69, 70.25, 66.87, 60.83, 20.80, 20.64, 20.59, 20.53. The spectroscopic data are in good agreement with the reported ones.[4]



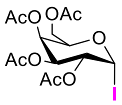
2,3,4,6-tetra-O-pivaloylmannosyl iodide 5a: *Rf* = 0.7 [cyclohexane:EtOAc (5:1)]. Yield 38% as an oil (purified through a short silica pad and used directly to the next step). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (s, 1H), 5.82 (dd, *J* = 10.3, 3.2 Hz, 1H), 5.58 (t, J = 10.2 Hz, 1H), 5.48 (dd, J = 3.2, 1.56 Hz, 1H), 4.24 (dd, *J* = 12.7, 3.4 Hz, 1H), 4.13 (dd, J = 12.7, 1.8 Hz, 1H), 4.0 - 3.97 (m, 1H), 2.26 (s, 9H), 2.23 (s, 9H), 2.19 (s, 9H), 2.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.84, 177.10, 176.59, 176.51, 75.62, 73.21, 68.95, 67.10, 64.37, 60.83, 38.90, 38.88, 38.85, 38.75, 27.07, 27.06, 27.04.



2,3,4,6-tetra-O-acetylmannosyl iodide 5b: *Rf* = 0.65 [cyclohexane:EtOAc (1:1)]. Yield 85% as an oil (not stable enough). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (s, 1H), 5.79 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.47 (dd, *J* = 3.4, 1.4 Hz, 1H), 5.38 (t, *J* = 10.2 Hz, 1H), 4.35 (dd, *J* = 12.6, 5.0 Hz, 1H), 4.14 (dd, J = 12.4, 2.1 Hz, 1H), 3.96 (ddd, *J* = 10.3, 5.0, 2.1 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.34, 21.44, 21.53, 62.03, 66.10, 66.90, 69.30, 74.03, 76.04, 170.23, 170.41, 171.20. The spectroscopic data are in good agreement with the reported ones.[5]

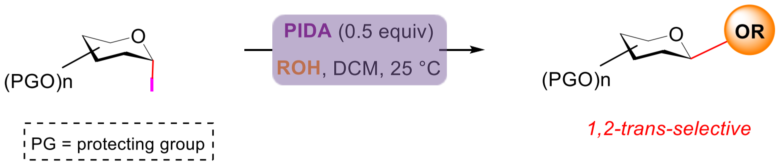


2,3,4,6-tetra-O-pivaloylgalactosyl iodide 6a: *Rf* = 0.7 [cyclohexane:EtOAc (5:1)]. Yield 48% as an oil (not stable enough). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 4.2 Hz, 1H), 5.53 (d, *J* = 3.2 Hz, 1H), 5.41 (dd, J = 10.2, 3.2 Hz, 1H), 4.39 (dd, J = 10.4, 4.2 Hz, 1H), 4.29 (t, J = 6.7 Hz, 1H), 4.16 – 4.09 (m, 2H), 1.23 (s, 9H), 1.20 (s, 9H), 1.19 (s, 9H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.77, 177.20, 176.93, 176.65, 75.39, 74.26, 69.96, 67.45, 66.28, 60.45, 39.04, 38.75, 38.62, 38.50, 27.15, 27.13, 27.07, 27.05. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{43}INaO_9^+$: 649.1844, Found: 649.1852.



2,3,4,6-tetra-O-acetylgalactosyl iodide 6b: *Rf* = 0.65 [cyclohexane:EtOAc (1:1)]. Yield 87% as an oil (not stable enough). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 4.1 Hz, 1H), 5.49 (d, *J* = 2.1 Hz, 1H), 5.29 (dd, *J* = 10.6, 3.1 Hz, 1H), 4.36 (dd, *J* = 10.5, 4.3 Hz, 1H), 4.25 – 4.19 (m, 2H), 4.13 – 4.09 (m, 1H), 2.15 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H) 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.44, 170.02, 169.99, 169.88, 75.31, 73.75, 69.87, 67.64, 66.70, 60.77, 21.05, 20.76, 20.70. The spectroscopic data are in good agreement with the reported ones.[4]

II. Target glycosides.



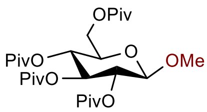
Scheme S2. General route of synthesis of target glycosides.

General procedure for the synthesis of *O*-glycosides. PIDA (0.5 equiv.) was added to a solution of 2,3,4,6-tetra-*O*-acyl-glycosyl iodide (1.0 equiv.) in dry dichloromethane, containing the corresponding alcohol (1.5 equiv.). The resulting mixture was stirred for 1-6 hours at room temperature, under argon atmosphere and light protection. The reactions were monitored by TLC. Upon completion, a solution of $Na_2S_2O_3$ (20% w/v) was added portionwise to the mixture until discoloration, which was, then extracted with dichloromethane twice. The combined organic layers were dried over Na_2SO_4, filtered, volatiles were evaporated off and the residue chromatographed on a silica gel column with cyclohexane:EtOAc as the eluting solvents.

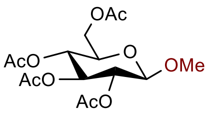
Reactions were, typically, performed on 50 mg scale. Yields refer to isolated products.

Pivaloyl-protected *O*-glycosides: Purification by flash column chromatography on silica gel using cyclohexane:EtOAc (12:1) afforded products as white semi-solids or solids.

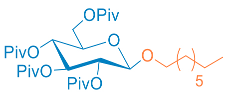
Acetyl-protected *O*-glycosides: Purification by flash column chromatography on silica gel using cyclohexane:EtOAc (4:1) afforded products as white semi-solids or solids.



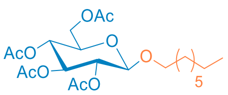
2,3,4,6-tetra-O-pivaloyl-1-O-methyl-β-D-glucopyranoside 2aa: *Rf* = 0.65 [cyclohexane:EtOAc (5:1)]. Yield 97% as a solid, m.p. = 100-102°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (t, *J* = 9.5 Hz, 1H), 5.10 (t, *J* = 9.7 Hz, 1H), 4.98 (dd, *J* = 9.6, 8.1 Hz, 1H), 4.39 (d, *J* = 8.0 Hz, 1H), 4.21 (dd, *J* = 12.2, 1.7 Hz, 1H), 4.05 (dd, *J* = 12.2, 5.7 Hz, 1H), 3.71 (ddd, *J* = 9.9, 5.7, 1.7 Hz, 1H), 3.43 (s, 3H), 1.22 (s, 9H), 1.15 (s, 18H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.99, 177.13, 176.52, 176.36, 102.10, 72.22, 72.08, 70.99, 67.98, 61.90, 56.95, 38.80, 38.68, 38.65, 38.63, 27.06, 27.03, 26.97, 26.93. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{47}O_{10}^+$: 531.3164, Found: 531.3159.



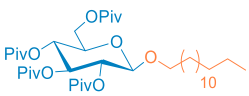
2,3,4,6-tetra-O-acetyl-1-O-methyl-β-D-glucopyranoside 2ba: *Rf* = 0.6 [cyclohexane:EtOAc (1:1)]. Yield 86% as a solid, m.p. = 99-101°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (t, *J* = 9.5 Hz, 1H), 5.07 (t, *J* = 9.7 Hz, 1H), 4.94 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 4.24 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.12 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.67 (ddd, *J* = 10.0, 4.6, 2.4 Hz, 1H), 3.49 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 170.22, 169.35, 169.34, 101.57, 72.83, 71.74, 71.20, 68.38, 61.87, 56.99, 20.69, 20.66, 20.56, 20.55. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{23}O_{10}^+$: 363.1286, Found: 363.1283. The spectroscopic data are in good agreement with the reported ones.[6]



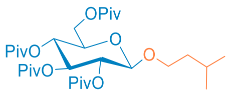
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-β-D-glucopyranoside 2ab: yield 62%, as a solid. m.p. = 61-64°C, $[a]^{25}_D$ = -7.28 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (t, J = 9.5 Hz, 1H), 5.09 (t, J = 9.7 Hz, 1H), 5.00 (dd, J = 9.5, 8.0 Hz, 1H), 4.49 (d, J = 8.0 Hz, 1H), 4.21 (dd, J = 12.2, 1.8 Hz, 1H), 4.05 (dd, J = 12.2, 6.0 Hz, 1H), 3.81 (dt, J = 9.4, 6.6 Hz, 1H), 3.71 (ddd, J = 10.0, 6.0, 1.8 Hz, 1H), 3.43 (dt, J = 9.4, 6.6 Hz, 1H), 1.56-1.51 (m, 4H), 1.23-1.28 (m, 8H), 1.25 (s, 9H), 1.22 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.06, 177.21, 176.46, 176.41, 100.99, 72.28, 72.18, 71.18, 69.92, 68.18, 62.07, 38.84, 38.73, 38.68, 31.76, 29.51, 29.30, 29.17, 27.12, 27.08, 27.06, 27.02, 25.92, 22.61, 14.05. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{61}O_{10}^+$: 629.4259, Found: 629.4267.



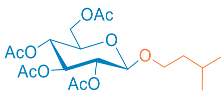
2,3,4,6-tetra-O-acetyl-1-O-(octyl)-β-D-glucopyranoside 2bb: yield 72%, as a solid. m.p. = 61-63°C, $[a]^{25}_D$ = -12,7 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (t, *J* = 9.5 Hz, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 4.98 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.26 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.88 – 3.84 (m, 1H), 3.68 (ddd, *J* = 10.0, 4.7, 2.4 Hz, 1H), 3.49 – 3.44 (m, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.58 – 1.52 (m, 2H), 1.28 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.68, 170.31, 169.38, 169.25, 100.81, 72.87, 71.71, 71.34, 70.23, 68.48, 61.99, 31.77, 29.36, 29.24, 29.22, 25.78, 22.62, 20.72, 20.62, 20.61, 20.58, 14.06. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{37}O_{10}^+$: 461.2381, Found: 461.2374. The spectroscopic data are in good agreement with the reported ones.[7]



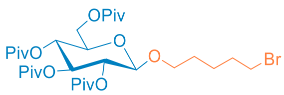
2,3,4,6-tetra-O-pivaloyl-1-O-(tetradecyl)-β-D-glucopyranoside 2ac: yield 59%, as a solid. m.p. = 50-52°C, $[a]^{25}_D$ = -7.28 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (t, J = 9.5 Hz, 1H), 5.09 (t, J = 9.7 Hz, 1H), 5.00 (dd, J = 9.5, 8.1 Hz, 1H), 4.49 (d, J = 8.0 Hz, 1H), 4.21 (dd, J = 12.2, 1.7 Hz, 1H), 4.05 (dd, J = 12.2, 6.0 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.71 (ddd, J = 10.0, 6.0, 1.7 Hz, 1H), 3.46 – 3.41 (m, 1H), 1.57 - 1.51 (m, 2H), 1.24 (m, 22H), 1.22 (s, 9H), 1.15 (s, 18H), 1.11 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.06, 177.21, 176.46, 176.40, 100.99, 72.28, 72.19, 71.18, 69.93, 68.18, 62.07, 38.84, 38.73, 38.68, 31.90, 29.66, 29.64, 29.63, 29.57, 29.54, 29.52, 29.36, 29.33, 27.12, 27.08, 27.07, 27.02, 25.93, 22.67, 14.09. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{36}H_{65}O_{10}^+$: 657.4572, Found: 657.4582.



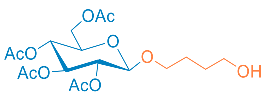
2,3,4,6-tetra-O-pivaloyl-1-O-(isopentyl)-β-D-glucopyranoside 2ad: yield 57%, as a solid. m.p. = 75-78°C, $[a]^{25}_{D}$ = -5.6 (c = 0.72, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (t, *J* = 9.5 Hz, 1H), 5.09 (t, *J* = 9.7 Hz, 1H), 5.00 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.22 (dd, *J* = 12.2, 1.6 Hz, 1H), 4.04 (dd, *J* = 12.2, 6.0 Hz, 1H), 3.85 (dt, *J* = 9.5, 6.8 Hz, 1H), 3.70 (ddd, *J* = 11.8, 6.0, 1.6 Hz, 1H), 3.47 (dt, *J* = 9.5, 6.8 Hz, 1H), 1.65 (dt, *J* = 20.2, 6.7 Hz, 1H), 1.48 – 1.40 (m, 2H), 1.22 (s, 9H), 1.15 (s, 18H), 1.11 (s, 9H), 0.87 (dd, *J* = 6.6, 2.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.20, 176.47, 176.41, 100.94, 72.29, 72.18, 71.19, 68.21, 68.13, 62.08, 38.84, 38.73, 38.68, 38.23, 27.12, 27.08, 27.05, 27.03, 24.67, 22.50, 22.40. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{54}NaO_{10}^+$: 609.3609, Found: 609.3615.



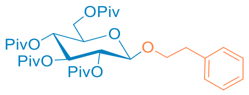
2,3,4,6-tetra-O-acetyl-1-O-(isopentyl)-β-D-glucopyranoside 2bc: yield 60%, as a semi-solid. $[a]^{25}_{D}$ = -15.1 (c = 0.72, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (t, J = 9.5 Hz, 1H), 5.08 (t, J = 9.7 Hz, 1H), 4.98 (dd, J = 9.5, 8.0 Hz, 1H), 4.48 (d, J = 8.0 Hz, 1H), 4.26 (dd, J = 12.3, 4.7 Hz, 1H), 4.13 (dd, J = 12.2, 2.1 Hz, 1H), 3.90 (dt, J = 9.7, 6.4 Hz, 1H), 3.69 (ddd, J = 10.0, 4.7, 2.1 Hz, 1H), 3.50 (dt, J = 9.6, 6.9 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.66 (dt, J = 20.3, 6.8 Hz, 1H), 1.50 (td, J = 13.7, 6.9 Hz, 1H), 1.41 (dt, J = 13.6, 6.6 Hz, 1H), 0.88 (dd, J = 6.6, 3.8 Hz, 6H). ^{13}C NMR (126 MHz, cdcl$_3$) δ 170.66, 170.30, 169.37, 169.24, 100.83, 72.86, 71.71, 71.33, 68.58, 68.49, 62.00, 38.04, 24.73, 22.58, 22.23, 20.72, 20.61, 20.60, 20.58. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{30}NaO_{10}^+$: 441.1731, Found: 441.1723.



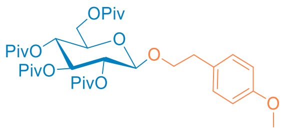
2,3,4,6-tetra-O-pivaloyl-1-O-(5-bromopentyl)-β-D-glucopyranoside 2ae: yield 55%, as a solid. m.p. = 59-62°C, $[a]^{25}_{D}$ = -10.9 (c = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (t, J = 9.5 Hz, 1H), 5.10 (t, J = 9.7 Hz, 1H), 5.01 (dd, J = 9.5, 8.0 Hz, 1H), 4.49 (d, J = 8.0 Hz, 1H), 4.22 (dd, J = 12.2, 1.9 Hz, 1H), 4.07 (dd, J = 12.2, 5.9 Hz, 1H), 3.84 (dt, J = 9.4, 6.3 Hz, 1H), 3.73 – 3.7 (m, 1H), 3.46 (dt, J = 9.5, 6.5 Hz, 1H), 3.38 (td, J = 6.7, 1.3 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.61 - 1.56 (m, 2H), 1.50 – 1.44 (m, 2H), 1.22 (s, 9H), 1.16 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.04, 177.20, 176.46, 176.43, 101.00, 72.24, 72.22, 71.14, 69.41, 68.10, 62.00, 38.85, 38.74, 38.70, 38.69, 33.48, 32.41, 28.70, 27.12, 27.10, 27.08, 27.03, 24.68. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{53}BrNaO_{10}^+$: 687.2714, Found: 687.2716.



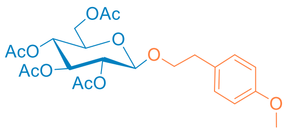
2,3,4,6-tetra-O-acetyl-1-O-(4-hydroxybutyl)-β-D-glucopyranoside 2bd: yield 71%, as a solid. m.p. = 69-71°C, $[a]^{25}_{D}$ = -14.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (t, *J* = 9.5 Hz, 1H), 5.06 (t, *J* = 9.7 Hz, 1H), 4.96 (dd, J = 9.5, 8.0 Hz, 1H), 4.48 (d, *J* = 8.0 Hz, 1H), 4.23 (dd, *J* = 12.2, 4.6 Hz, 1H), 4.12 (dd, *J* = 12.2, 1.9 Hz, 1H), 3.90 (dt, *J* = 9.7, 5.8 Hz, 1H), 3.67 (ddd, *J* = 9.9, 4.6, 2.1 Hz, 1H), 3.61 (t, *J* = 6.1 Hz, 2H), 3.51 (dt, *J* = 9.6, 6.1 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.68 – 1.56 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.70, 170.27, 169.39, 100.72, 72.80, 71.73, 71.27, 69.96, 68.37, 62.23, 61.87, 29.24, 25.81, 20.72, 20.63, 20.59, 20.57. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{28}NaO_{11}^+$: 443.1524, Found: 443.1519. The spectroscopic data are in good agreement with the reported ones.[8]



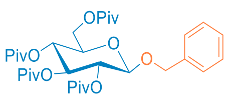
2,3,4,6-tetra-O-pivaloyl-1-O-(phenethyl)-β-D-glucopyranoside 2af: yield 57%, as a solid. m.p. = 63-65°C, $[a]^{25}_{D}$ = -5.45 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 5.30 (t, J = 9.5 Hz, 1H), 5.11 (t, J = 9.7 Hz, 1H), 5.03 (dd, J = 9.5, 8.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 4.22 (dd, 12.2, 1.8 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.73 – 3.66 (m, 2H), 2.88 (td, J = 7.3, 3.0 Hz, 2H), 1.21 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H), 1.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.19, 176.44, 176.39, 138.08, 128.86, 128.38, 126.33, 100.99, 72.29, 72.22, 71.06, 70.48, 68.06, 62.00, 38.84, 38.73, 38.68, 38.63, 36.16, 27.12, 27.09, 27.02, 26.96. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{53}O_{10}^+$: 621.3633, Found: 621.3636.



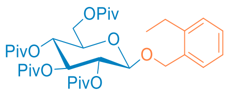
2,3,4,6-tetra-O-pivaloyl-1-O-(4-methoxy-phenethyl)-β-D-glucopyranoside 2ag: yield 32%, as a solid. m.p. = 83-88°C, $[a]^{25}_{D}$ = -10.1 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.30 (t, J = 9.5 Hz, 1H), 5.10 (t, J = 9.7 Hz, 1H), 5.02 (dd, J = 9.5, 8 Hz, 1H), 4.52 (d, J = 8.0 Hz, 1H), 4.21 (dd, J = 12.2, 1.6 Hz, 1H), 4.05 (dd, J = 12.2, 5.8 Hz, 1H), 4.01 - 3.97 (m, 1H), 3.77 (s, 3H), 3.71 (ddd, 10.0, 5.8, 1.6 Hz, 1H), 3.66-3.61 (m, 1H), 2.83 – 2.79 (m, 2H), 1.29 (s, 9H), 1.15 (s, 9H), 1.10 (s, 9H), 1.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.19, 176.44, 176.39, 158.14, 130.13, 129.81, 113.82, 101.02, 72.28, 72.22, 71.07, 70.78, 68.07, 62.01, 55.22, 38.84, 38.73, 38.68, 38.63, 35.26, 27.12, 27.09, 27.02, 26.96. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{35}H_{55}O_{11}^+$: 651.3739, Found: 651.3733.



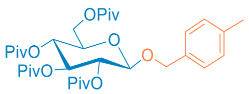
2,3,4,6-tetra-O-acetyl-1-O-(4-methoxy-phenethyl)-β-D-glucopyranoside 2be: yield 58%, as a semi-solid. $[a]^{25}_{D}$ = -22.7 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 5.17 (t, J = 9.5 Hz, 1H), 5.08 (t, J = 9.7 Hz, 1H), 4.98 (dd, J = 9.5, 8.0 Hz, 1H), 4.48 (d, J = 8.0 Hz, 1H), 4.25 (dd, J = 12.2, 4.7 Hz, 1H), 4.14 – 4.07 (m, 2H), 3.77 (s, 3H), 3.66 (ddd, J = 10.2, 4.7, 2.3 Hz, 1H), 3.64 – 3.60 (m, 1H), 2.82 (m, 2H), 2.08 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.66, 170.26, 169.37, 169.24, 158.11, 130.42, 129.87, 113.74, 100.76, 72.79, 71.77, 71.14, 70.92, 68.42, 61.94, 55.23, 35.02, 20.73, 20.59, 20.57, 20.57. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{31}O_{11}^+$: 483.1861, Found: 483.1853.



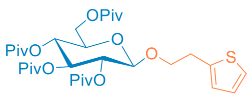
2,3,4,6-tetra-O-pivaloyl-1-O-(benzyl)-β-D-glucopyranoside 2ah: yield 59%, as a solid. m.p. = 109-111°C, $[a]^{25}_{D}$ = -25.4 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 5H), 5.29 (t, *J* = 9.5 Hz, 1H), 5.14 – 5.08 (m, 2H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.58 (dd, *J* = 18.2, 10.0 Hz, 2H), 4.25 (dd, *J* = 12.2, 1.8 Hz, 1H), 4.07 (dd, *J* = 12.2, 5.9 Hz, 1H), 3.71 (ddd, *J* = 10.0, 5.9, 1.8 Hz, 1H), 1.25 (s, 9H), 1.15 (s, 9H), 1.11 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.08, 177.18, 176.49, 176.45, 136.41, 128.38, 128.06, 128.01, 99.14, 72.30, 72.28, 71.10, 70.33, 68.15, 62.07, 38.88, 38.74, 38.68, 38.68, 27.13, 27.06, 27.02. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{50}NaO_{10}^+$: 629.3296, Found: 629.3293. The spectroscopic data are in good agreement with the reported ones.[9]



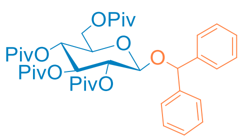
2,3,4,6-tetra-O-pivaloyl-1-O-(2-ethylbenzyl)-β-D-glucopyranoside 2ai: yield 51%, as a semi-solid. $[a]^{25}_D$ = -3.78 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.21 (dd, *J* = 7.5, 1.9 Hz, 2H), 5.18 (t, J = 9.5 Hz, 1H), 5.11 – 5.06 (m, 2H), 4.64 (t, *J* = 6.8 Hz, 2H), 4.35 (d, *J* = 8.0 Hz, 1H), 4.25 (dd, *J* = 12.1, 1.8 Hz, 1H), 3.99 (dd, *J* = 12.1, 6.2 Hz, 1H), 3.55 (ddd, *J* = 10.0, 6.2, 1.8 Hz, 1H), 1.90 – 1.84 (m, 1H), 1.73 – 1.67 (m, 1H), 1.27 (s, 9H), 1.12 (s, 18H), 1.09 (s, 9H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.13, 176.51, 176.42, 140.20, 128.33, 127.99, 127.27, 97.32, 80.56, 72.57, 72.04, 71.42, 68.40, 62.20, 38.86, 38.71, 38.68, 38.65, 30.28, 27.17, 27.14, 27.01, 9.85. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{54}NaO_{10}^+$: 657.3609, Found: 657.3601.



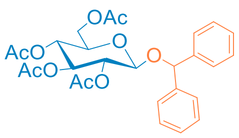
2,3,4,6-tetra-O-pivaloyl-1-O-(4-methylbenzyl)-β-D-glucopyranoside 2aj: yield 52%, as a solid. m.p. = 79-82°C, $[a]^{25}_D$ = -9.8 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.17-7.12 (m, 4H), 5.27 (t, J = 9.5 Hz, 1H), 5.13 – 5.07 (m, 2H), 4.80 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 12.1 Hz, 1H), 4.52 (d, J = 8.0 Hz, 1H), 4.25 (dd, J = 12.2, 1.8 Hz, 1H), 4.07 (dd, J = 12.2, 6.0 Hz, 1H), 3.69 (ddd, J = 10.0, 6.0, 1.8 Hz, 1H), 2.35 (s, 3H), 1.25 (s, 9H), 1.14 (s, 9H), 1.11 (s, 9H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.08, 177.17, 176.47, 176.45, 137.82, 133.25, 129.05, 128.26, 98.80, 72.31, 72.26, 71.09, 70.11, 68.19, 62.12, 38.88, 38.73, 38.68, 38.67, 27.14, 27.13, 27.07, 27.02, 21.16. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{52}NaO_{10}^+$: 643.3453, Found: 643.3458.



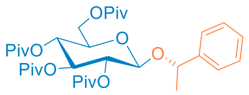
2,3,4,6-tera-O-pivaloyl-1-O-(2-thiopheneethyl)-β-D-glucopyranoside 2ak: yield 51%, as a solid. m.p. = 61-65°C, $[a]^{25}_D$ = -3.2 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, J = 4.1, 0.9 Hz, 1H), 6.91 (dd, J = 4.1, 3.4 Hz, 1H), 6.82 (d, J = 3.4 Hz, 1H), 5.31 (t, J = 9.5 Hz, 1H), 5.11 (t, J = 9.7 Hz, 1H), 5.04 (dd, J = 9.5, 8.0 Hz, 1H), 4.56 (d, J = 8.0 Hz, 1H), 4.22 (dd, J = 12.2, 1.8 Hz, 1H), 4.06 (m, 2H), 3.73 (m, 2H), 3.09 (t, J = 7.1 Hz, 2H), 1.22 (s, 9H), 1.15 (s, 9H), 1.11 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.06, 177.19, 176.44, 176.41, 140.09, 126.83, 125.38, 123.65, 100.99, 72.29, 72.20, 71.08, 70.15, 68.05, 61.98, 38.85, 38.74, 38.69, 38.66, 30.31, 27.12, 27.10, 27.03, 26.98. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{51}O_{10}S^+$: 627.3197, Found: 627.3192.



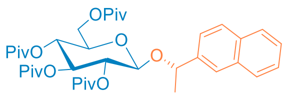
2,3,4,6-tetra-O-pivaloyl-1-O-(diphenyl-carbinyl)-β-D-glucopyranoside 2al: yield 28%, as a semi-solid. $[a]^{25}_D$ = -6 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 8H), 7.23 – 7.20 (m, 2H), 5.90 (s, 1H), 5.24 – 5.23 (m, 2H), 5.13 – 5.10 (m, 1H), 4.50 (d, J = 8.0, Hz, 1H), 4.24 (dd, J = 12.1, 1.8 Hz, 1H), 4.04 (dd, J = 12.1, 5.6 Hz, 1H), 3.63 – 3.59 (m, 1H), 1.26 (s, 9H), 1.14 (s, 9H), 1.13 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.15, 176.47, 176.44, 141.40, 128.58, 128.34, 128.27, 128.10, 127.16, 126.31, 97.11, 79.80, 72.46, 72.22, 71.39, 68.21, 62.13, 38.87, 38.73, 38.72, 38.68, 29.68, 27.21, 27.17, 27.14, 27.01. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{55}O_{10}^+$: 683.3790, Found: 683.3787.



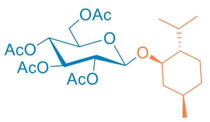
2,3,4,6-tetra-O-acetyl-1-O-(diphenyl-carbinyl)-β-D-glucopyranoside 2bf: yield 41%, as a semi-solid. $[a]^{25}_D$ = -17.6 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 10H), 5.38 (s, 1H), 5.18 – 5.05 (m, 3H), 4.50 (d, J = 8.0 Hz, 1H), 4.24 (dd, J = 12.2, 4.6 Hz, 1H), 4.16 (dd, J = 12.2, 2.6 Hz, 1H), 3.61 – 3.58 (m, 1H), 2.10 (s, 3H), 2.02 (s, 3H), 2.00 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 170.24, 169.36, 169.20, 141.22, 140.08, 128.61, 128.29, 128.19, 127.83, 127.35, 126.47, 97.80, 80.99, 72.82, 71.77, 71.37, 68.50, 61.98, 20.73, 20.66, 20.60, 20.56. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{31}O_{10}^+$: 515.1912, Found: 515.1921. The spectroscopic data are in good agreement with the reported ones.[10]



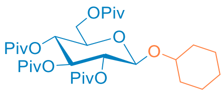
2,3,4,6-tetra-O-pivaloyl-1-O-(1-phenylethyl)-β-D-glucopyranoside 2am: yield 50%, as a solid. m.p. = 69-71°C, $[a]^{25}_D$ = -2.7 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 5H), 5.33 (t, *J* = 9.5 Hz, 1H), 5.11-5.08 (m, 2H), 4.82 (q, *J* = 6.5 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 4.08 (dd, *J* = 12.1, 1.7 Hz, 1H), 3.96 (dd, *J* = 12.2, 5.6 Hz, 1H), 3.65 (ddd, *J* = 10.1, 5.6, 1.7 Hz, 1H), 1.44 (d, *J* = 6.5 Hz, 3H), 1.19 (s, 9H), 1.18 (s, 9H), 1.14 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.03, 177.24, 176.40, 176.36, 142.71, 128.13, 127.40, 126.01, 99.06, 76.67, 72.41, 72.16, 71.44, 68.06, 61.91, 38.80, 38.73, 38.72, 38.69, 27.18, 27.14, 27.06, 27.02, 22.14. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{53}O_{10}^+$: 621.3633, Found: 621.3631.



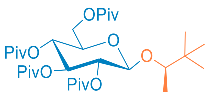
2,3,4,6-tetra-O-pivaloyl-1-O-(naphthyl)-β-D-glucopyranoside 2an: yield 48%, as a solid. m.p. = 91-93°C, $[a]^{25}_D$ = -7.5 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 4H), 7.47 - 7.45 (m, 3H), 5.34 (t, J = 9.5 Hz, 1H), 5.16 – 5.08 (m, 2H), 4.97 (q, J = 6.2 Hz, 1H), 4.77 (d, J = 8.0 Hz, 1H), 4.05 (d, J = 12.0 Hz, 1H), 3.93 (dd, J = 12.0, 5.4 Hz, 1H), 3.64 (dd, J = 9.5, 5.1 Hz, 1H), 1.52 (d, J = 6.2 Hz, 3H), 1.21 (s, 9H), 1.13 (s, 9H), 1.12 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.28, 176.45, 176.43, 140.12, 133.07, 132.87, 127.96, 127.89, 127.61, 126.00, 125.78, 124.57, 124.46, 99.24, 72.38, 72.19, 71.46, 67.98, 61.84, 38.77, 38.75, 38.72, 38.71, 29.70, 27.22, 27.15, 27.02, 26.99, 22.25. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{38}H_{55}O_{10}^+$: 671.3790, Found: 671.3793.



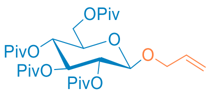
2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-β-D-glucopyranoside 2bg: yield 63%, as a solid. m.p. = 127-130°C, $[a]^{25}_D$ = -27.2 (c = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.20 (t, J = 9.5 Hz, 1H), 5.05 (t, J = 9.7 Hz, 1H), 4.93 (dd, J = 9.5, 8.0 Hz, 1H), 4.55 (d, J = 8.0 Hz, 1H), 4.19 (dd, J = 12.1, 5.6 Hz, 1H), 4.12 (dd, J = 12.1, 2.6 Hz, 1H), 3.67 (ddd, J = 10.0, 5.6, 2.6 Hz, 1H), 3.38 (td, J = 10.7, 4.3 Hz, 1H), 2.23 (ddd, J = 14.0, 7.0, 2.7 Hz, 1H), 2.06 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H), 1.94 (m, 1H), 1.65 – 1.61 (m, 2H), 1.26 – 1.18 (m, 2H), 0.99 – 0.96 (m, 1H), 0.91 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H), 0.82 (m, 1H), 0.73 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.63, 170.35, 169.43, 169.28, 98.72, 79.03, 73.04, 71.53, 71.47, 68.91, 62.49, 47.41, 40.78, 34.18, 31.44, 24.98, 22.95, 22.24, 20.85, 20.70, 20.67, 20.64, 20.61, 15.41. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{39}O_{10}^+$: 487.2538, Found: 487.2544.



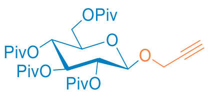
2,3,4,6-tetra-O-pivaloyl-1-O-(cyclohexyl)-β-D-glucopyranoside 2ao: yield 52%, as a solid. m.p. = 124-129°C, $[a]^{25}_D$ = -9.09 (c = 0.5, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.31 (t, J = 9.5 Hz, 1H), 5.07 (t, J = 9.7 Hz, 1H), 4.99 (dd, J = 9.5, 8.0 Hz, 1H), 4.61 (d, J = 8.0 Hz, 1H), 4.20 (dd, J = 12.1, 1.9 Hz, 1H), 4.00 (dd, J = 12.1, 6.8 Hz, 1H), 3.71 (ddd, 10.0, 6.8, 1.9 Hz, 1H), 3.58 - 3.53 (m, 1H), 1.91 – 1.88 (m, 1H), 1.80 – 1.77 (m, 1H), 1.69 - 1.72 (m, 2H), 1.52 – 1.32 (m, 3H), 1.29 – 1.22 (m, 3H), 1.21 (s, 9H), 1.15 (s, 18H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.05, 177.21, 176.55, 176.33, 99.51, 78.13, 72.40, 72.04, 71.38, 68.44, 62.36, 38.80, 38.74, 38.67, 38.66, 33.45, 31.87, 27.14, 27.13, 27.06, 27.03, 25.44, 23.92, 23.91. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{54}NaO_{10}^+$: 621.3609, Found: 621.3612.



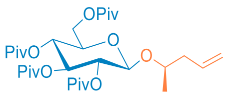
2,3,4,6-tetra-O-pivaloyl-1-O-(3,3-dimethyl-2-butyl)-β-D-glucopyranoside 2ap: yield 47%, as a solid. m.p. = 98-105°C, $[a]^{25}_D$ = -6.3 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.31 (t, J = 9.5 Hz, 1H), 5.09 (t, J = 9.7 Hz, 1H), 5.00 (dd, J = 9.6, 8.0 Hz, 1H), 4.57 (dd, J = 18.3, 7.9 Hz, 1H), 4.24 (ddd, J = 12.0, 6.7, 1.9 Hz, 1H), 3.98 (ddd, J = 12.0, 6.1, 4.0 Hz, 1H), 3.71 (ddd, 10.0, 6.8, 1.9 Hz, 1H), 3.46 (q, J = 6.3 Hz, 0.5H), 3.29 (q, J = 6.4 Hz, 0.5H), 1.22 (s, 9H), 1.15 (s, 18H), 1.14 (s, 3H), 1.11 (s, 9H), 0.83 (d, J = 6.6 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.07, 177.21, 176.60, 176.51, 101.94, 85.01, 79.90, 72.42, 72.05, 71.79, 68.60, 62.21, 38.81, 38.75, 38.69, 38.65, 27.18, 27.14, 27.09, 27.05, 16.78, 13.44. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{56}NaO_{10}^+$: 623.3766, Found: 623.3760.



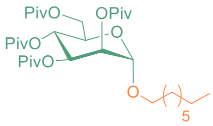
2,3,4,6-tetra-O-pivaloyl-1-O-(allyl)-β-D-glucopyranoside 2aq: yield 40%, as a solid. m.p. = 91-95°C, $[a]^{25}_D$ = -20.2 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 22.3, 10.9, 5.8 Hz, 1H), 5.31 (t, *J* = 9.5 Hz, 1H), 5.21 (dd, *J* = 26.7, 13.8 Hz, 2H), 5.11 – 5.02 (m, 2H), 4.55 (d, *J* = 8.0 Hz, 1H), 4.31 (dd, *J* = 12.7, 4.8 Hz, 1H), 4.22 (d, *J* = 11.9 Hz, 1H), 4.05 (dd, *J* = 12.3, 6.0 Hz, 2H), 3.71 (dd, *J* = 9.9, 5.4 Hz, 1H), 1.22 (s, 9H), 1.14 (s, 18H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.08, 177.21, 176.49, 176.46, 133.23, 118.00, 99.69, 72.26, 72.15, 71.00, 70.05, 68.06, 62.04. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{49}O_{10}^+$: 557.3320, Found: 557.3327.



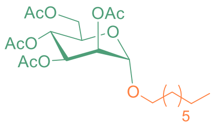
2,3,4,6-tetra-O-pivaloyl-1-O-(propargyl)-β-D-glucopyranoside 2ar: yield 39%, as a solid. m.p. = 74-79°C, $[a]^{25}_D$ = -12.6 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.35 (t, *J* = 9.5 Hz, 1H), 5.10 (t, *J* = 9.7 Hz, 1H), 5.03 (t, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 8.1 Hz, 1H), 4.34 (t, *J* = 2.8 Hz, 2H), 4.21 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.03 (dd, *J* = 12.3, 5.8 Hz, 1H), 3.76 (td, *J* = 10.8, 5.4, 1.5 Hz, 1H), 2.42 (t, *J* = 2.2 Hz, 1H), 1.21 (s, 9H), 1.15 (s, 9H), 1.14 (s, 9H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.08, 177.18, 176.69, 176.45, 97.98, 78.03, 75.48, 72.35, 72.05, 70.67, 67.98, 63.67, 61.84, 55.47, 38.85, 38.74, 38.72, 38.69, 27.10, 27.06, 27.04, 27.01. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{47}O_{10}^+$: 555.3164, Found: 555.3158.



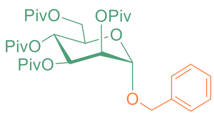
2,3,4,6-tetra-O-pivaloyl-1-O-(4-pentenyl)-β-D-glucopyranoside 2as: yield 26%, as a solid. m.p. = 89-92°C, $[a]^{25}_{D}$ = -13.2 (c = 0.72, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72 (dq, *J* = 10.2, 7.1 Hz, 1H), 5.31 (t, *J* = 9.5 Hz, 1H), 5.08 – 4.99 (m, 4H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.22 (dd, *J* = 12.1, 1.2 Hz, 1H), 4.00 (dd, *J* = 12.1, 6.6 Hz, 1H), 3.78 – 3.70 (m, 2H), 2.33 – 2.28 (m, 1H), 2.16 – 2.10 (m, 1H), 1.21 (s, 9H), 1.16 (s, 9H), 1.15 (s, 9H), 1.12 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.08, 177.21, 176.55, 176.34, 134.17, 117.42, 100.12, 76.25, 72.40, 72.09, 71.42, 68.33, 62.27, 40.89, 38.81, 38.75, 38.69, 38.69, 27.16, 27.14, 27.09, 27.04, 20.94. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{31}H_{53}O_{10}^+$: 585.3633, Found: 585.3637.



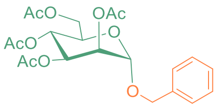
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-a-D-mannopyranoside 7aa: yield 42%, as a semi-solid. $[a]^{25}_{D}$ = +15.1 (c = 0.72, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (t, *J* = 10.1 Hz, 1H), 5.38 (dd, *J* = 10.2, 3.2 Hz, 1H), 5.23 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.75 (d, *J* = 1.6 Hz, 1H), 4.19 (dd, *J* = 12.3, 4.4 Hz, 1H), 4.13 (dd, *J* = 12.4, 1.8 Hz, 1H), 4.04 – 4.01 (m, 1H), 3.68 (dt, *J* = 9.5, 6.7 Hz, 1H), 3.43 (dt, J = 9.7, 6.8 Hz, 1H), 1.63 – 1.57 (m, 2H), 1.31 - 1.28 (m, 10H), 1.26 (s, 9H), 1.24 (s, 9H), 1.16 (s, 9H), 1.12 (s, 9H), 0.90 – 0.87 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.11, 177.19, 177.17, 176.72, 97.70, 69.59, 69.45, 68.80, 68.41, 65.24, 62.09, 38.89, 38.88, 38.79, 38.74, 31.81, 29.33, 29.29, 29.22, 27.13, 27.08, 27.06, 26.07, 22.65, 14.10. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{61}O_{10}^+$: 629.4259, Found: 629.4252.



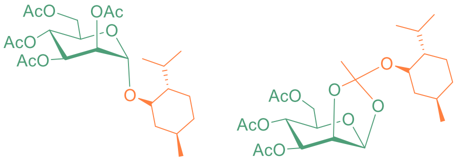
2,3,4,6-tetra-O-acetyl-1-O-(octyl)-a-D-mannopyranoside 7ba: yield 20%, as a semi-solid. $[a]^{25}_{D}$ = +53.4 (c = 1.43, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (dd, *J* = 10.0, 3.2 Hz, 1H), 5.27 (t, *J* = 10.0 Hz, 1H), 5.23 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.78 (s, 1H), 4.27 (dd, *J* = 12.2, 5.3 Hz, 1H), 4.10 (dd, *J* = 12.2, 2.2 Hz, 1H), 4.00 – 3.96 (m, 1H), 3.69 – 3.63 (m, 1H), 3.46 – 3.42 (m, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.61 – 1.58 (m, 2H), 1.31 – 1.25 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.62, 170.07, 169.86, 169.72, 97.55, 69.73, 69.14, 68.55, 68.36, 66.28, 62.52, 31.78, 29.67, 29.28, 29.24, 29.16, 26.05, 22.61, 20.89, 20.71, 20.69, 20.68, 14.06. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{37}O_{10}^+$: 461.2381, Found: 461.2383.



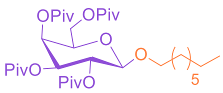
2,3,4,6-tetra-O-pivaloyl-1-O-(benzyl)-a-D-mannopyranoside 7ab: yield 44%, as solid and was obtained *as a mixture with peracylated α-anomer (1:1)*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 5H), 5.54 (t, *J* = 10.3 Hz, 1H), 5.35 (dd, *J* = 9.9, 3.0 Hz, 1H), 5.29 (dt, *J* = 16.0, 4.7, 1.9 Hz, 1H), 4.87 (s broad, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.17 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.15 – 4.11 (m, 1H), 4.06 (m, 1H), 1.26 (s, 9H), 1.25 (s, 9H), 1.15 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.00, 177.36, 176.77, 176.56, 136.46, 128.55, 128.09, 127.79, 97.15, 71.19, 69.45, 69.35, 68.17, 64.46, 61.67, 39.13, 38.90, 38.84, 38.82, 38.74, 27.16, 27.11, 27.08, 27.04.



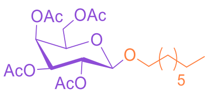
2,3,4,6-tetra-O-acetyl-1-O-(benzyl)-α-D-mannopyranoside 7bb: yield 45%, as a semi-solid. $[\alpha]^{25}_D$ = +68.1 (c = 0.72, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 5.38 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.29 – 5.27 (m, 2H), 4.89 (d, *J* = 1.6 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.27 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.04 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.00 (ddd, *J* = 10.0, 5.1, 2.4 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.62, 169.99, 169.85, 169.70, 136.20, 128.57, 128.23, 128.17, 96.74, 69.79, 69.59, 69.14, 68.64, 66.15, 62.40, 20.87, 20.75, 20.68, 20.66. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_{10}^+$: 461.1418, Found: 461.1411. The spectroscopic data are in good agreement with the reported ones.[10]



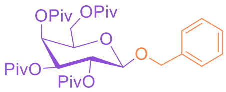
2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-α-D-mannopyranoside 7bc: yield 46%, as a semi-solid were obtained and *as a mixture with ortho-ester **7bd** the main product (4:1)*. ^1H NMR (500 MHz, $CDCl_3$) δ 5.47 (d, *J* = 2.3 Hz, 1H), 5.36 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.28 (t, *J* = 9.8 Hz, 1H), 5.23 (t, *J* = 10.0 Hz, 1H), 5.15 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.11 (dd, *J* = 9.9, 4.0 Hz, 1H), 4.88 (d, *J* = 1.6 Hz, 1H), 4.56 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.25 – 4.19 (m, 2H), 4.15 – 4.09 (m, 2H), 3.64 (ddd, *J* = 9.7, 4.9, 2.6 Hz, 1H), 3.41 (td, *J* = 10.6, 4.3 Hz, 1H), 3.38 – 3.32 (m, 1H), 2.14 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.74 (s, 3H), 1.63 – 1.59 (m, 3H), 1.18 – 1.14 (m, 1H), 1.03 (dd, *J* = 23.4, 12.4 Hz, 2H), 0.96 – 0.89 (m, 4H), 0.85 – 0.87 (m, 6H), 0.82 - 0.75 (m, 2H), 0.70 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.61, 170.30, 170.14, 169.91, 169.76, 169.34, 124.94, 99.16, 97.09, 82.66, 75.77, 73.53, 71.10, 70.89, 70.14, 69.03, 68.58, 66.51, 65.43, 62.80, 62.24, 48.29, 48.16, 43.49, 42.63, 34.25, 34.14, 31.84, 31.60, 26.12, 25.78, 25.19, 23.22, 23.11, 22.29, 21.16, 20.93, 20.90, 20.72, 20.68, 20.67, 20.65, 16.18, 15.61.



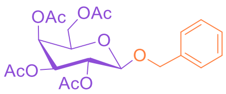
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-β-D-galactopyranoside 8aa: yield 58%, as a semi-solid. $[\alpha]^{25}_D$ = -8.9 (c = 1.43, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.39 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.21 (dd, *J* = 10.5, 7.9 Hz, 1H), 5.10 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.49 (d, *J* = 7.9 Hz, 1H), 4.18 (dd, *J* = 11.0, 6.7 Hz, 1H), 4.02 (dd, *J* = 11.0, 7.1 Hz, 1H), 3.95 (t, *J* = 6.9 Hz, 1H), 3.84 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.44 (dt, *J* = 9.5, 7.0 Hz, 1H), 1.60 – 1.54 (m, 2H), 1.27 – 1.25 (m, 19H), 1.17 (s, 9H), 1.16 (s, 9H), 1.11 (s, 9H), 0.87 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.86, 177.32, 176.94, 176.62, 101.41, 71.07, 70.90, 70.08, 68.78, 66.82, 61.22, 39.04, 38.73, 38.69, 31.76, 29.52, 29.33, 29.17, 27.14, 27.09, 27.07, 27.05, 25.93, 22.60, 14.05. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{61}O_{10}^+$: 629.4259, Found: 629.4253.



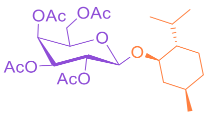
2,3,4,6-tetra-O-acetyl-1-O-(octyl)-β-D-galactopyranoside 8ba: yield 60%, as a semi-solid. $[\alpha]^{25}_D$ = -13.9 (c = 1.43, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.37 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.19 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.00 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.44 (d, *J* = 8.0 Hz, 1H), 4.17 (dd, *J* = 11.2, 6.5 Hz, 1H), 4.12 (dd, *J* = 11.2, 2.1 Hz, 1H), 3.90 – 3.85 (m, 2H), 3.46 (dt, *J* = 9.6, 6.9 Hz, 1H), 2.13 (s, 3H), 2.03 (s, 6H), 1.97 (s, 3H), 1.60 – 1.52 (m, 2H), 1.24 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H). [3]C NMR (126 MHz, $CDCl_3$) δ 170.36, 170.25, 170.16, 169.31, 101.33, 70.95, 70.53, 70.26, 68.92, 67.05, 61.25, 31.77, 29.37, 29.24, 29.21, 25.77, 22.61, 21.01, 20.71, 20.64, 20.57, 14.16, 14.05. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{37}O_{10}^+$: 461.2381, Found: 461.2389. The spectroscopic data are in good agreement with the reported ones.[11]



2,3,4,6-tetra-O-pivaloyl-1-O-(benzyl)-β-D-galactopyranoside 8ab: yield 45%, as a solid. m.p. = 87-91°C, $[a]^{25}_D$ = -15.3 (c = 1.43, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.35 - 5.28 (m, 5H), 5.40 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.30 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.08 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.88 (d, *J* = 11.9 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.57 (d, J = 8.0 Hz, 1H), 4.21 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.05 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.96 (td, *J* = 6.8, 0.9 Hz, 1H), 1.27 (s, 9H), 1.20 (s, 9H), 1.11 (s, 9H), 1.10 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.87, 177.29, 176.93, 176.68, 136.50, 128.36, 128.04, 127.98, 99.69, 71.04, 70.48, 68.70, 66.84, 61.31, 39.06, 38.73, 27.15, 27.08, 27.08, 27.07. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{50}NaO_{10}^+$: 629.3296, Found: 629.3291. The spectroscopic data are in good agreement with the reported ones.[12]

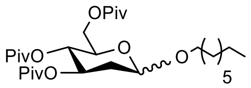


2,3,4,6-tetra-O-acetyl-1-O-(benzyl)-β-D-galactopyranoside 8bb: yield 52%, as a semi-solid. $[a]^{25}_D$ = -27.6 (c = 1.71, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 5H), 5.37 (d, *J* = 3.4 Hz, 1H), 5.27 (dd, *J* = 10.4, 8.0 Hz, 1H), 4.98 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.90 (d, *J* = 12.3 Hz, 1H), 4.62 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 4.20 (dd, *J* = 11.6, 6.2 Hz, 1H), 4.15 (dd, J = 11.6, 6.2 Hz, 1H), 3.88 (t, *J* = 6.7 Hz, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.35, 170.23, 170.09, 169.37, 136.69, 128.43, 127.97, 127.72, 99.77, 70.89, 70.70, 70.68, 68.83, 67.04, 61.30, 20.71, 20.66, 20.64, 20.55. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}NaO_{10}^+$: 461.1418, Found: 461.1423. The spectroscopic data are in good agreement with the reported ones.[12]

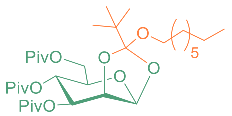


2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-β-D-galactopyranoside 8bc: yield 56%, as a semi-solid. $[a]^{25}_D$ = -24.4 (c = 1.71, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.12 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.01 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.47 (d, *J* = 7.9 Hz, 1H), 4.14 (dd, *J* = 11.2, 6.8 Hz, 1H), 4.07 (dd, *J* = 11.2, 6.6 Hz, 1H), 3.86 (td, *J* = 6.6, 1.0 Hz, 1H), 3.36 (td, *J* = 10.7, 4.3 Hz, 1H), 2.29 – 2.26 (m, 1H), 2.15 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.64 – 1.61 (m, 2H), 1.25 – 1.18 (m, 2H), 0.99 – 0.92 (m, 1H), 0.90 (d, J = 6.8 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.83 – 0.77 (m, 2H), 0.72 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.44, 170.37, 170.19, 169.36, 99.70, 79.58, 71.14, 70.41, 69.08, 67.19, 61.56, 47.39, 41.04, 34.16, 31.44, 24.82, 22.84, 22.24, 20.93, 20.82, 20.71, 20.64, 20.60, 15.35. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{39}O_{10}^+$: 487.2538, Found: 487.2544.

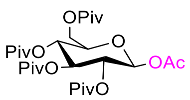
III. Results from mechanistic studies and Side-products.



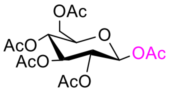
3,4,6-tri-O-pivaloyl-2-deoxy-1-O-(octyl)-D-glucopyranoside (α:β = 1.4:1) 10a: *Rf* = 0.7 [cyclohexane:EtOAc (5:1)]. Yield 59%, as a semi-solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ for *α-glucoside*: 5.29 (ddd, *J* = 11.5, 9.6, 5.4 Hz, 1H), 5.02 (t, J = 10 Hz, 1H), 4.91 (d, *J* = 3.2 Hz, 1H), 4.12 (dd, *J* = 11.8, 1.8 Hz, 1H), 4.10 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.97 (ddd, *J* = 10.0, 5.3, 2.0 Hz, 1H), 3.65 - 3.60 (m, 1H), 3.34 (dt, *J* = 9.6, 6.7 Hz, 1H), 2.22 (dd, *J* = 13.0, 5.3 Hz, 1H), 1.76 (td, *J* = 11.8, 3.6 Hz, 1H), 1.60 - 1.55 (m, 2H), 1.34 – 1.28 (m, 10H), 1.22 (s, 9H), 1.16 (s, 9H), 1.13 (s, 9H), 0.89 – 0.87 (m, 3H), for *β-glucoside:* 5.02 – 4.96 (m, 2H), 4.54 (dd, *J* = 9.6, 1.9 Hz, 1H), 4.19 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.08 – 4.05 (m, 1H), 3.85 (dt, *J* = 9.4, 6.7 Hz, 1H), 3.65 - 3.60 (m, 1H), 3.43 (dt, *J* = 9.4, 6.8 Hz, 1H), 2.31 – 2.27 (m, 1H), 1.68 (dt, *J* = 18.1, 7.8 Hz, 1H), 1.59 - 1.54 (m, 2H), 1.34 – 1.23 (m, 10H), 1.21 (s, 9H), 1.16 (s, 9H), 1.13 (s, 9H), 0.89 – 0.86 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ for *α-glucoside*: 178.11, 177.48, 176.85, 96.74, 68.96, 68.84, 68.22, 67.66, 62.59, 38.84, 38.76, 38.64, 35.18, 31.81, 29.69, 29.38, 29.25, 27.15, 27.08, 27.06, 26.18, 22.64, 14.09, for *β-glucoside:* 178.15, 177.62, 176.82, 99.35, 72.26, 70.44, 69.68, 68.62, 62.63, 38.82, 38.76, 38.67, 36.24, 31.79, 29.51, 29.32, 29.22, 27.10, 27.05, 27.00, 25.97, 22.63, 14.09. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{52}NaO_8^+$: 551.3554, Found: 551.3551.



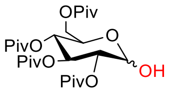
Ortho-ester of pivaloyl mannose 7ac: *Rf* = 0.65 [cyclohexane:EtOAc (5:1)]. Yield 24%, as a semi-solid. $[a]^{25}_D$ = -10 (c = 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (d, *J* = 3.0 Hz, 1H), 5.48 (t, *J* = 10.0 Hz, 1H), 4.95 (dd, *J* = 9.9, 5.1 Hz, 1H), 4.79 (dd, *J* = 5.1, 3.0 Hz, 1H), 4.23 (dd, *J* = 12.5, 3.5 Hz, 1H), 4.08 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.62 (ddd, *J* = 10.0, 3.4, 1.7 Hz, 1H), 3.45 – 3.41 (m, 1H), 3.35 (dd, *J* = 10.6, 4.0 Hz, 1H), 1.52 – 1.48 (m, 2H), 1.30 – 1.24 (m, 10H), 1.20 (s, 9H), 1.18 (s, 9H), 1.14 (s, 9H), 1.08 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.27, 178.02, 176.20, 127.99, 97.41, 75.85, 72.06, 70.46, 64.42, 62.57, 61.72, 39.44, 38.91, 38.80, 38.72, 31.79, 29.59, 29.22, 29.13, 27.06, 26.98, 26.95, 26.05, 25.76, 22.62, 14.07. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{61}O_{10}^+$: 629.4259, Found: 629.4246.



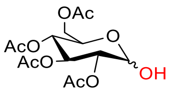
2,3,4,6-tetra-O-pivaloyl-1-O-acetyl-β-D-glucopyranoside 4a: *Rf* = 0.62 [cyclohexane:EtOAc (5:1)]. Solid. m.p. = 155-157ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (d, *J* = 8.4 Hz, 1H), 5.36 (t, *J* = 9.5 Hz, 1H), 5.18 (td, *J* = 9.8, 4.7 Hz, 2H), 4.18 (dd, *J* = 12.5, 1.8 Hz, 1H), 4.11 (dd, *J* = 12.5, 5.1 Hz, 1H), 3.87 (ddd, *J* = 10.2, 5.1, 1.8 Hz, 1H), 2.08 (s, 3H), 1.22 (s, 9H), 1.15 (s, 9H), 1.13 (s, 9H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.00, 177.03, 176.45, 176.34, 168.78, 91.85, 73.20, 72.08, 70.02, 67.37, 61.41, 38.85, 38.75, 38.75, 38.70, 29.67, 27.10, 27.05, 27.00, 26.93, 20.62. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{47}O_{11}^+$: 559.3113, Found: 559.3118. The spectroscopic data are in good agreement with the reported ones.[13]



2,3,4,6-tetra-O-acetyl-1-O-acetyl-β-D-glucopyranoside 4b: *Rf* = 0.55 [cyclohexane:EtOAc (1:1)]. Solid. m.p. = 97-99°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 (d, *J* = 8.3 Hz, 1H), 5.25 (t, *J* = 9.4 Hz, 1H), 5.15 – 5.13 (m, 2H), 4.29 (dd, *J* = 12.5, 4.5 Hz, 1H), 4.13 (dd, J = 12.5, 2.1 Hz, 1H), 3.84 (ddd, *J* = 10.0, 4.5, 2.2 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.57, 170.06, 169.35, 169.21, 168.92, 91.67, 72.77, 72.70, 70.20, 67.73, 61.42, 20.79, 20.68, 20.54, 20.53. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{16}H_{23}O_{11}^+$: 391.1235, Found: 391.1233. The spectroscopic data are in good agreement with the reported ones.[14]



2,3,4,6-tetra-O-pivaloyl-α,β-D-glucopyranoside 3a: α/β: 2/1; *Rf* = 0.3 [cyclohexane:EtOAc (5:1)]. Solid. m.p. = 183-185°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (α) 5.61 (t, J = 9.8 Hz, 1H), 5.45 (t, J = 2.9 Hz, 1H), 5.15 (t, J = 10.0 Hz, 1H), 4.83 (dd, J = 10.1, 3.7 Hz, 1H), 4.27 (ddd, J = 10.0, 4.8, 1.8 Hz, 1H), 4.23 - 4.16 (m, 1H), 4.07 (dd, J = 12.5, 4.2, 1H), 1.23 (s, 9H), 1.18 (s, 9H), 1.15 (s, 9H), 1.13 (s, 9H); (β) 5.36 (t, J = 9.6 Hz, 1H), 5.28 - 5.14 (m, 1H), 4.90 (dd, J = 9.7, 8.1 Hz, 1H), 4.72 (d, J = 8.1 Hz, 1H), 4.22 - 4.17 (m, 1H), 4.13 - 4.07 (m, 1H), 3.76 (dd, J = 10.2, 4.5, 1.8 Hz, 1H), 1.23 (s, 9H), 1.18 (s, 9H), 1.15 (s, 9H), 1.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (α) 90.13, 71.57, 69.49, 67.79, 67.67, 61.73; (β) 96.15, 73.56, 72.72, 71.69, 67.85, 61.81. The spectroscopic data are in good agreement with the reported ones.[14]



2,3,4,6-tetra-O-acetyl-α,β-D-glucopyranoside 3b: α/β: 2/1; *Rf* = 0.3 [cyclohexane:EtOAc (1:1)]. Solid. m.p. = 107-109°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (α) 5.53 (t, *J* = 9.8 Hz, 1H), 5.46 (t, *J* = 3.1 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.92 - 4.89 (m, 1H), 4.29 - 4.22 (m, 2H), 4.13 (dd, *J* = 12.3, 1.8 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H); (β) 5.25 (t, *J* = 9.4 Hz, 1H), 5.10 - 5.07 (m, 1H), 4.88 (dd, *J* = 9.4, 8.4 Hz, 1H), 4.74 (d, *J* = 8.4 Hz, 1H), 4.29 - 4.22 (m, 1H), 4.17 - 4.14 (m, 1H), 3.75 (ddd, *J* = 10.3, 4.8, 2.2 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (α) 90.32, 71.18,69.96, 68.60, 67.41, 62.08; (β) 95.73, 73.39, 72.28, 72.23, 68.55, 62.08. The spectroscopic data are in good agreement with the reported ones.[14]

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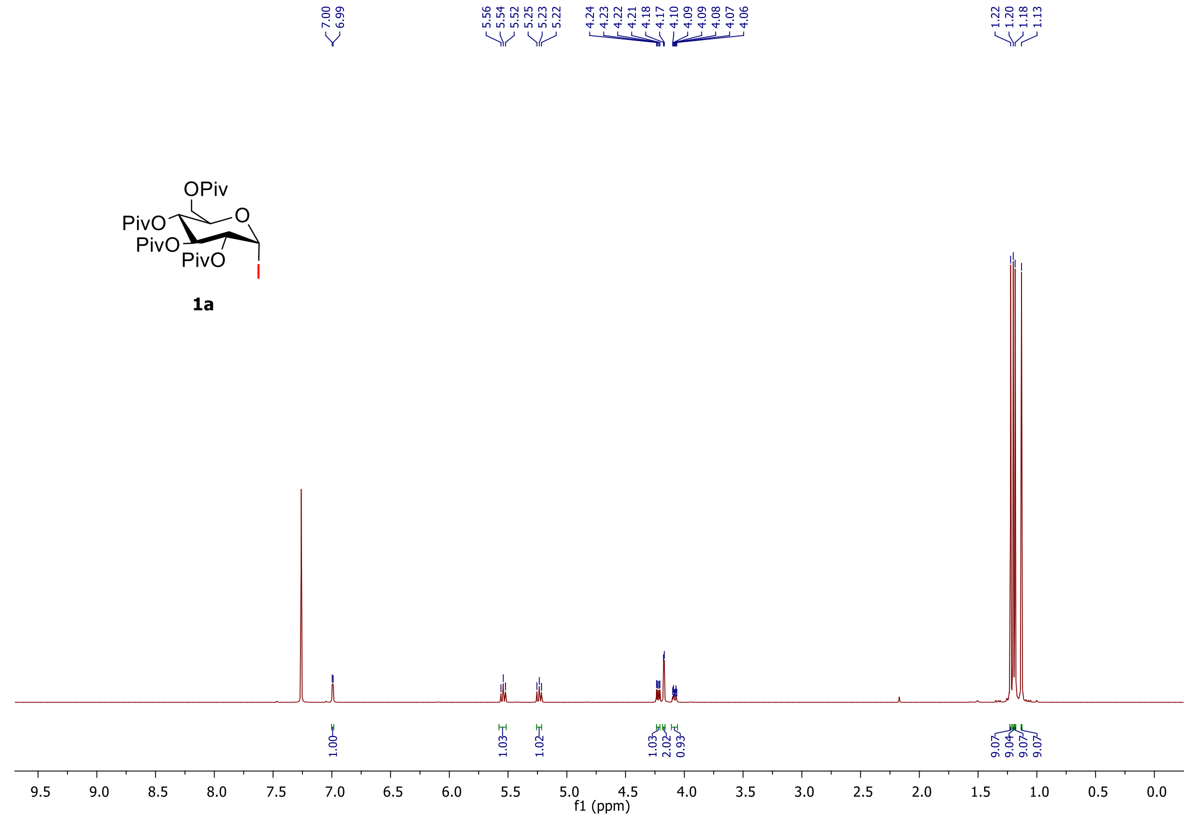
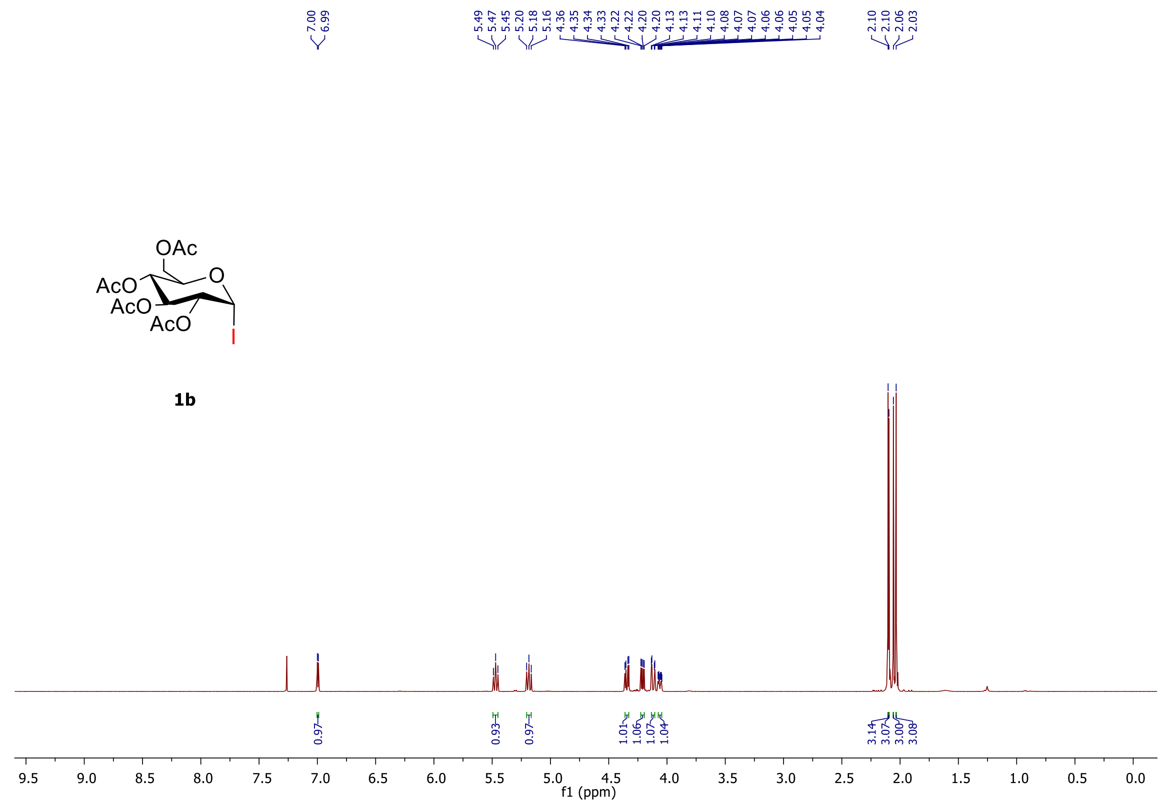
Copies of ¹H NMR and ¹³C NMR

2,3,4,6-tetra-O-pivaloylglucosyl iodide 1a:



2,3,4,6-tetra-O-acetylglucosyl iodide 1b:



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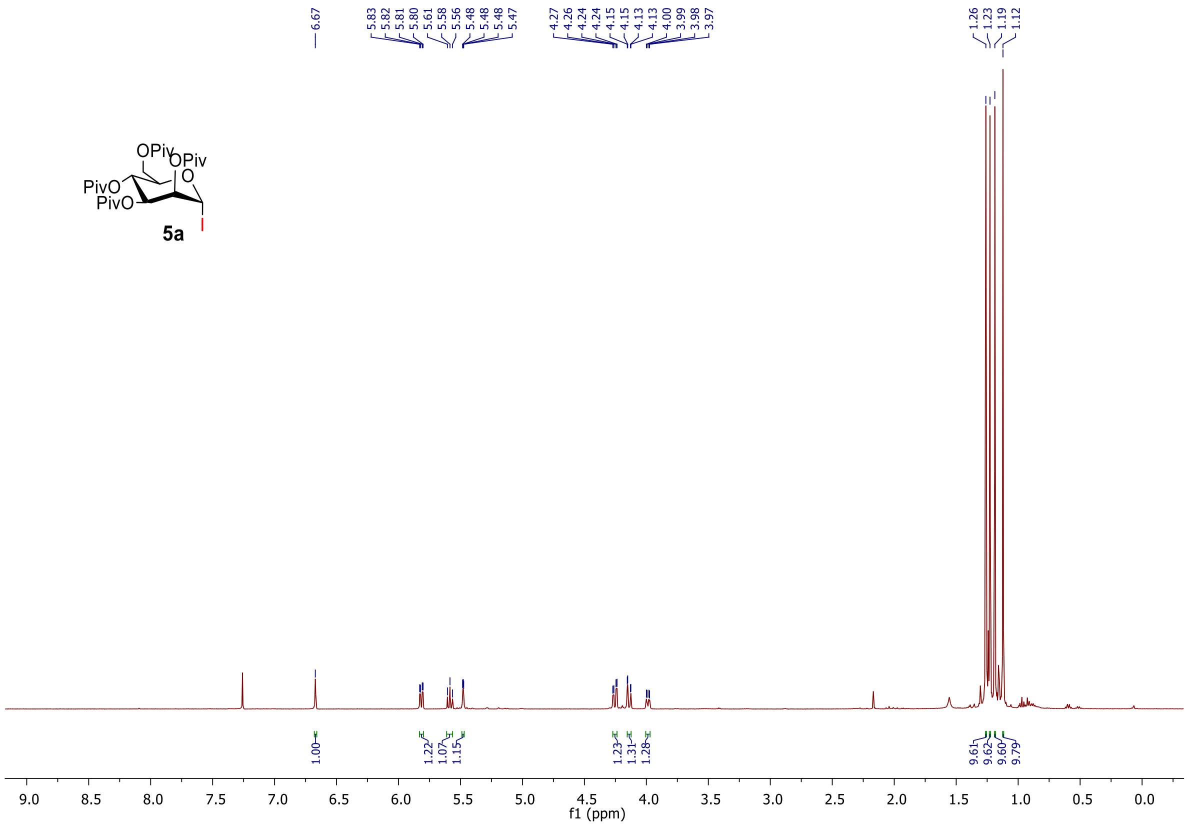

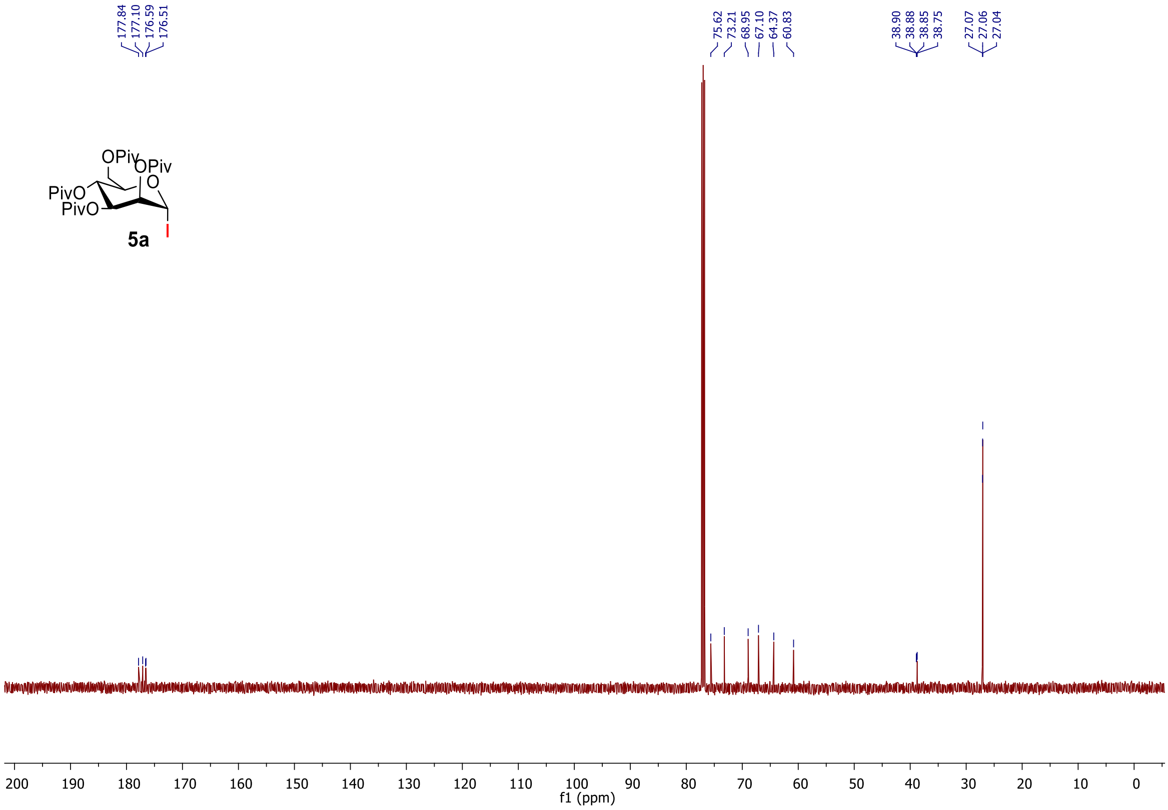

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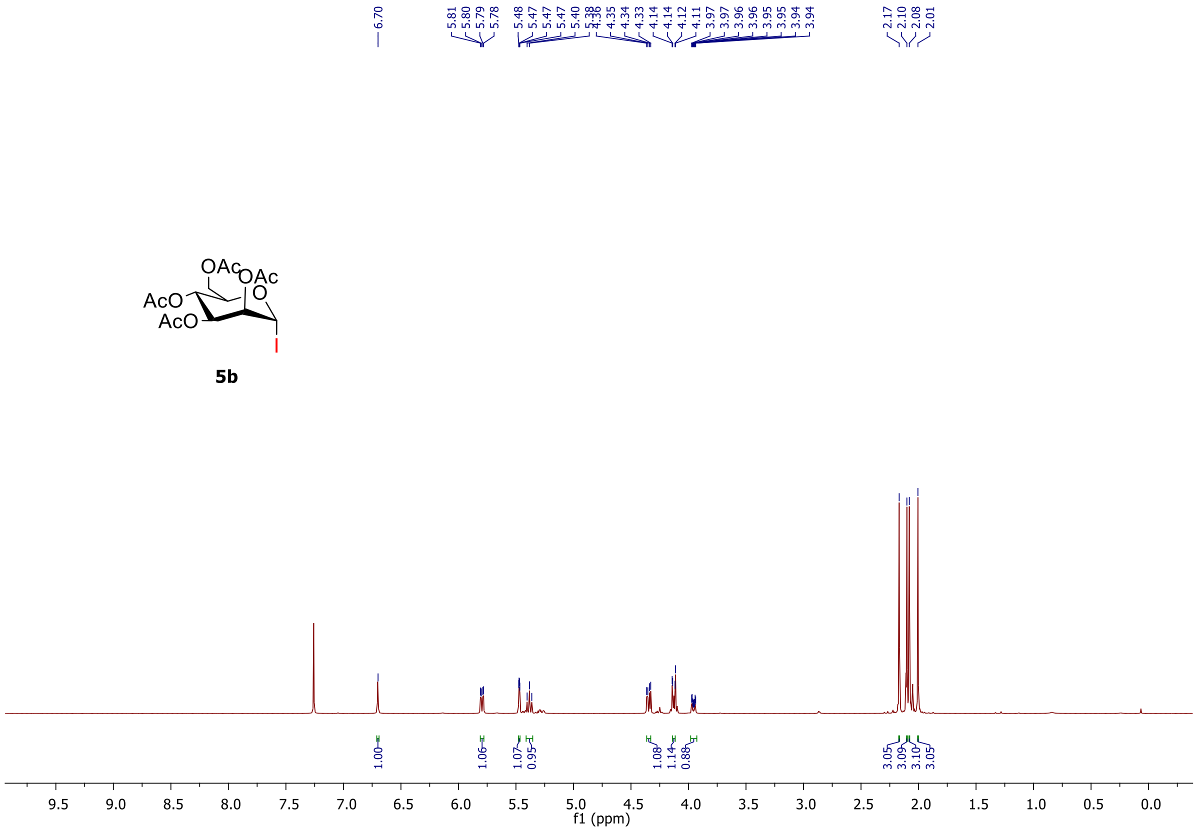

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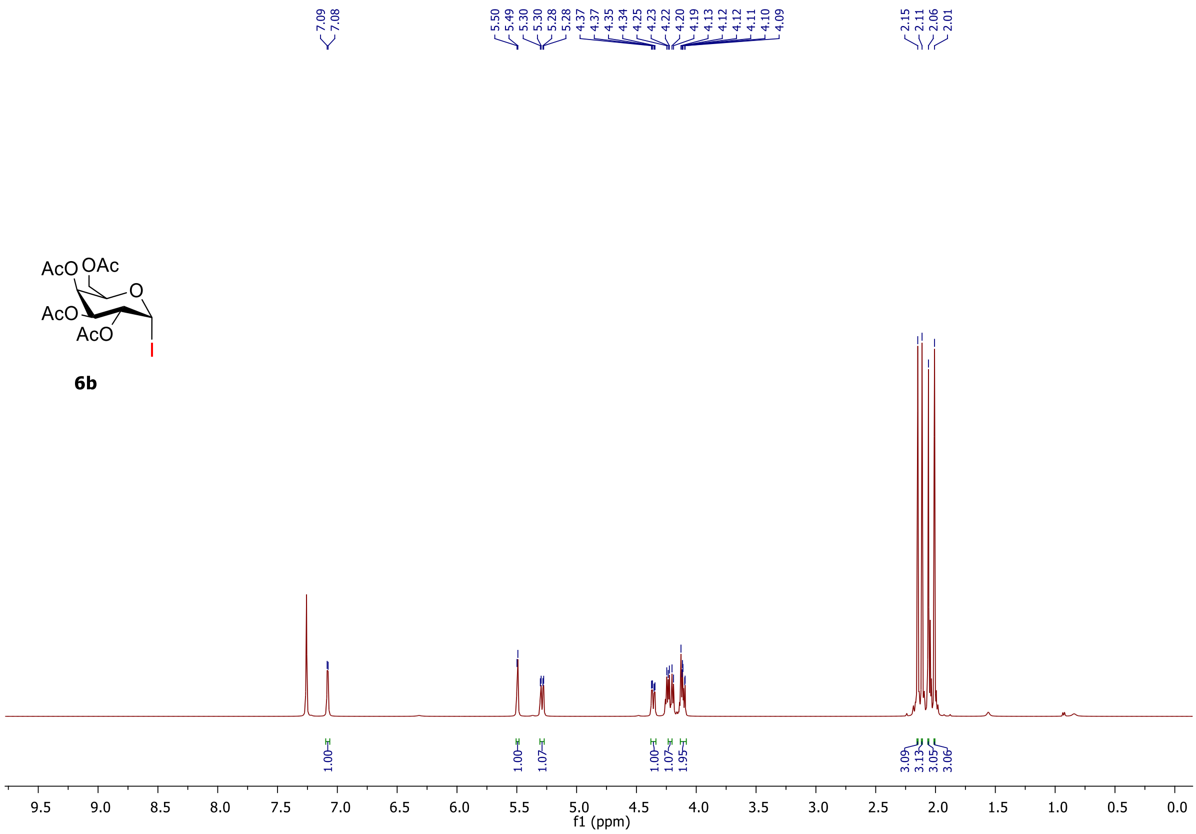

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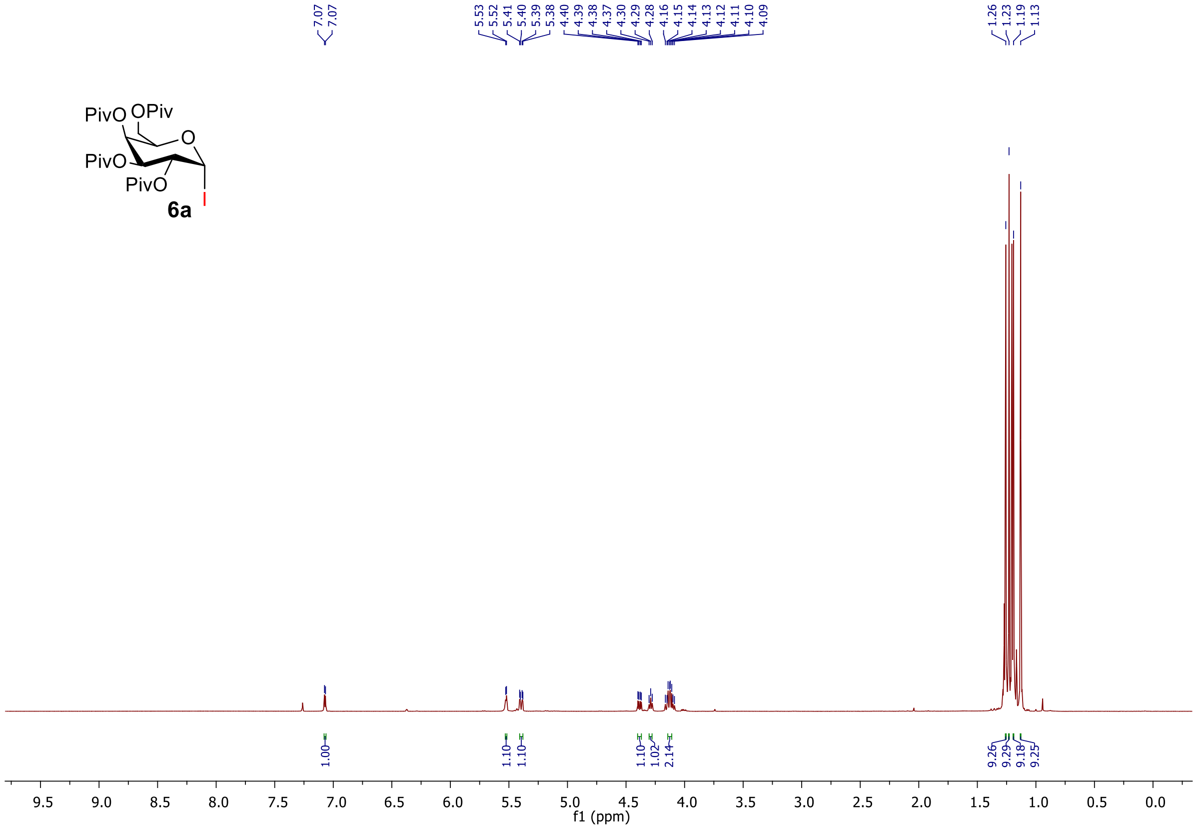
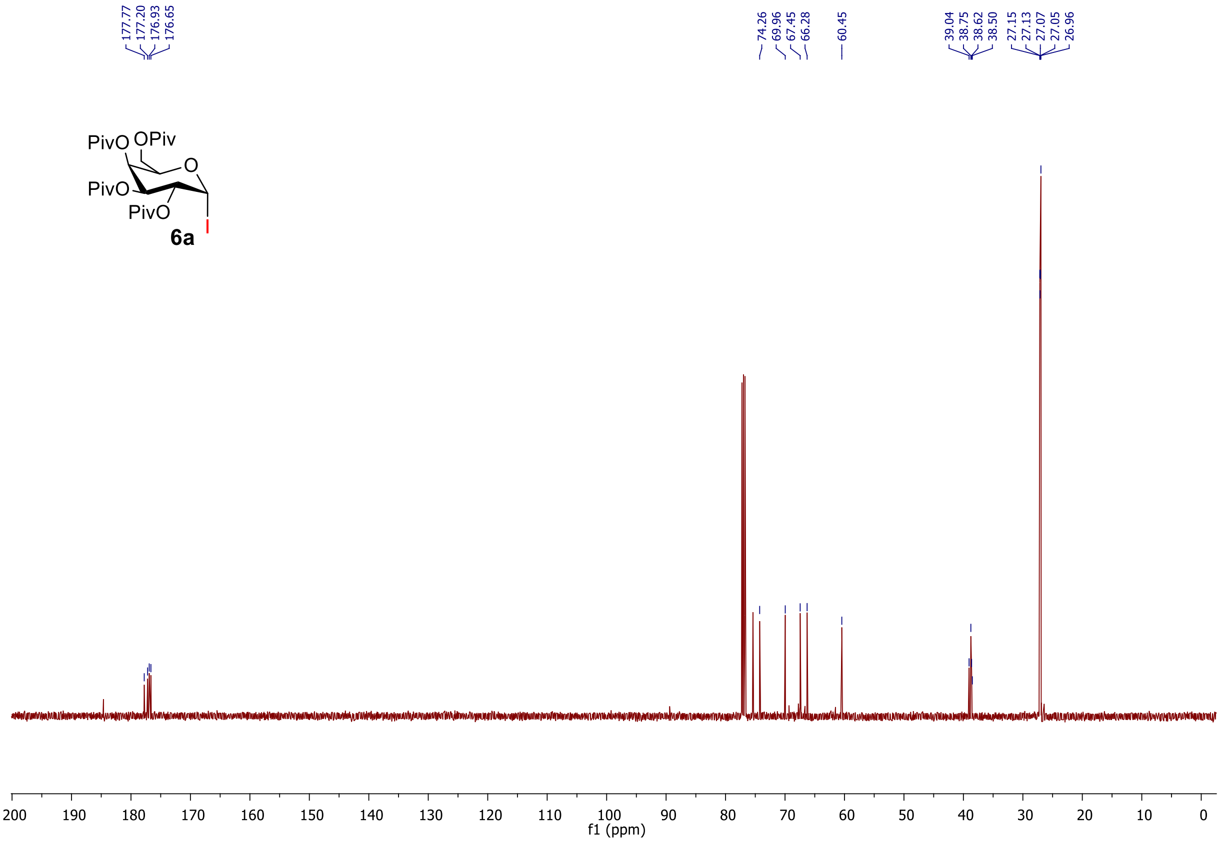
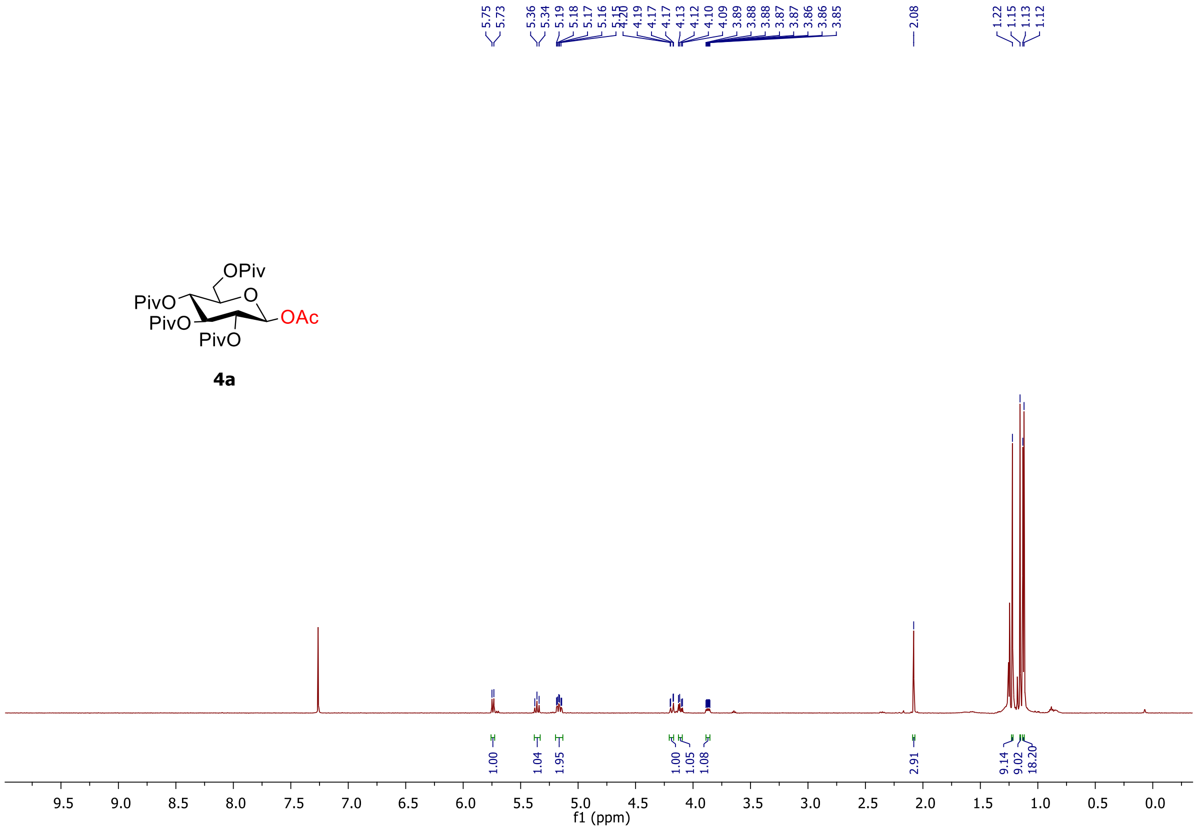


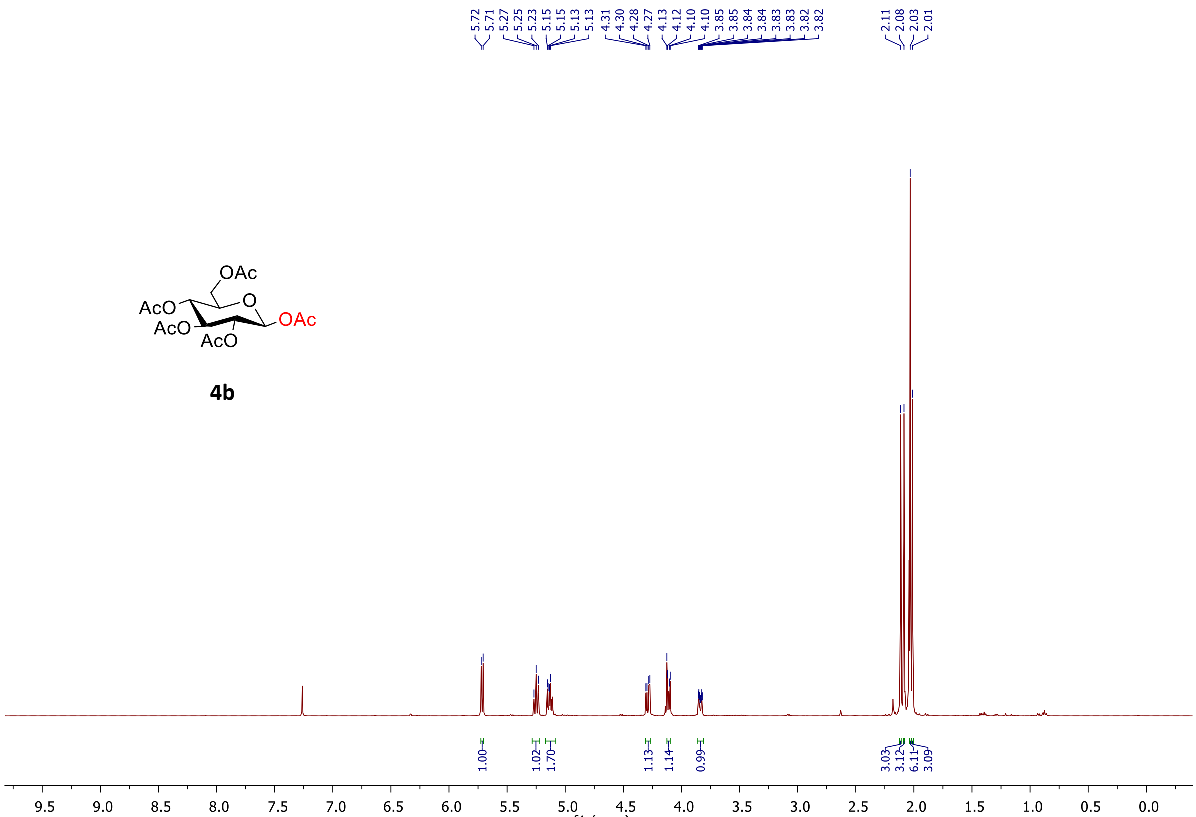


***2,3,4,6-tetra-O-pivaloyl-1-O-acetyl-β-D-glucopyranoside 4a*:**



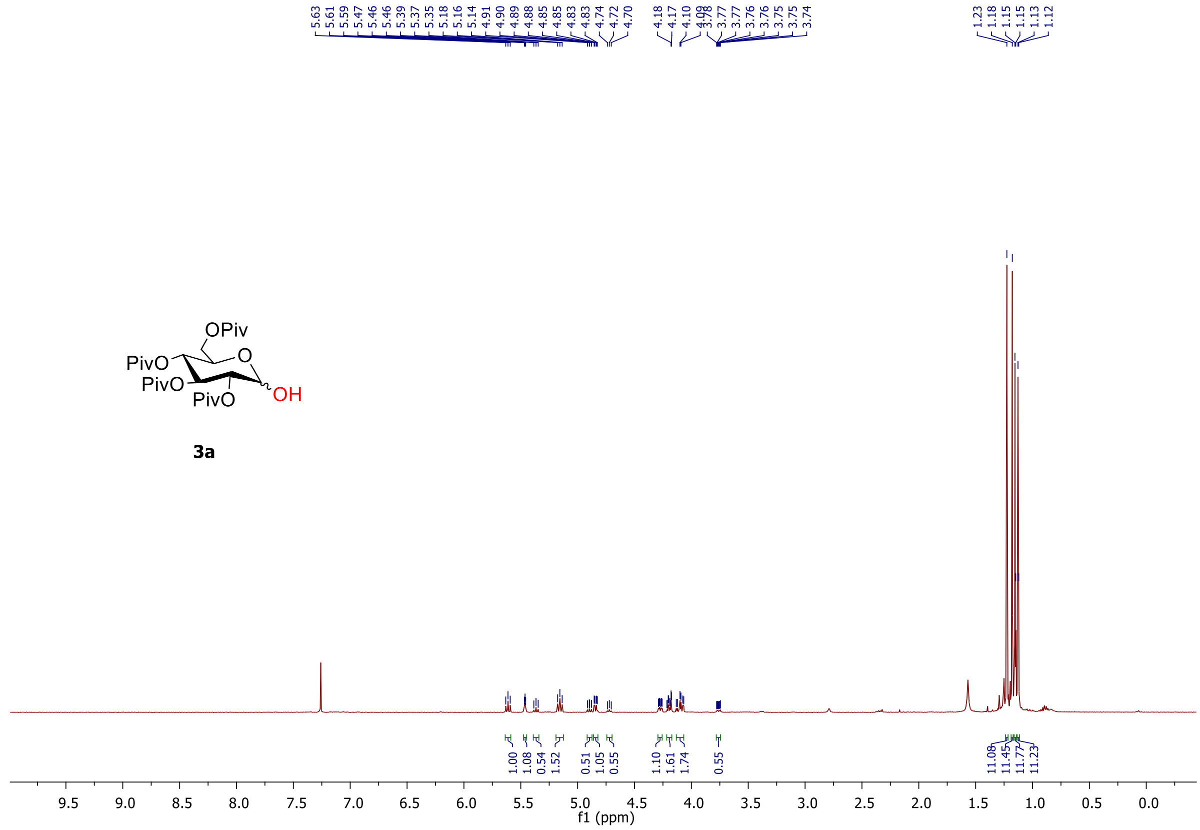
4a

***2,3,4,6-tetra-O-acetyl-1-O-acetyl-β-D-glucopyranoside 4b*:**

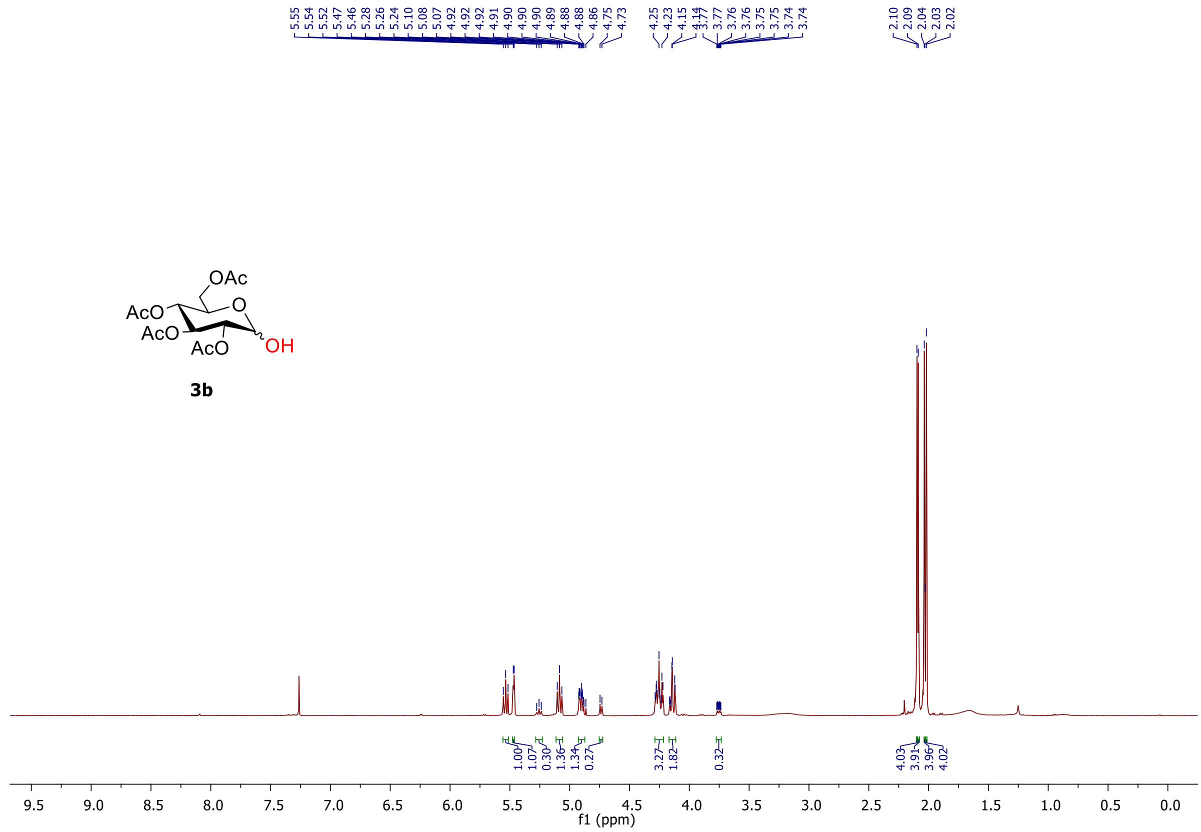


4b

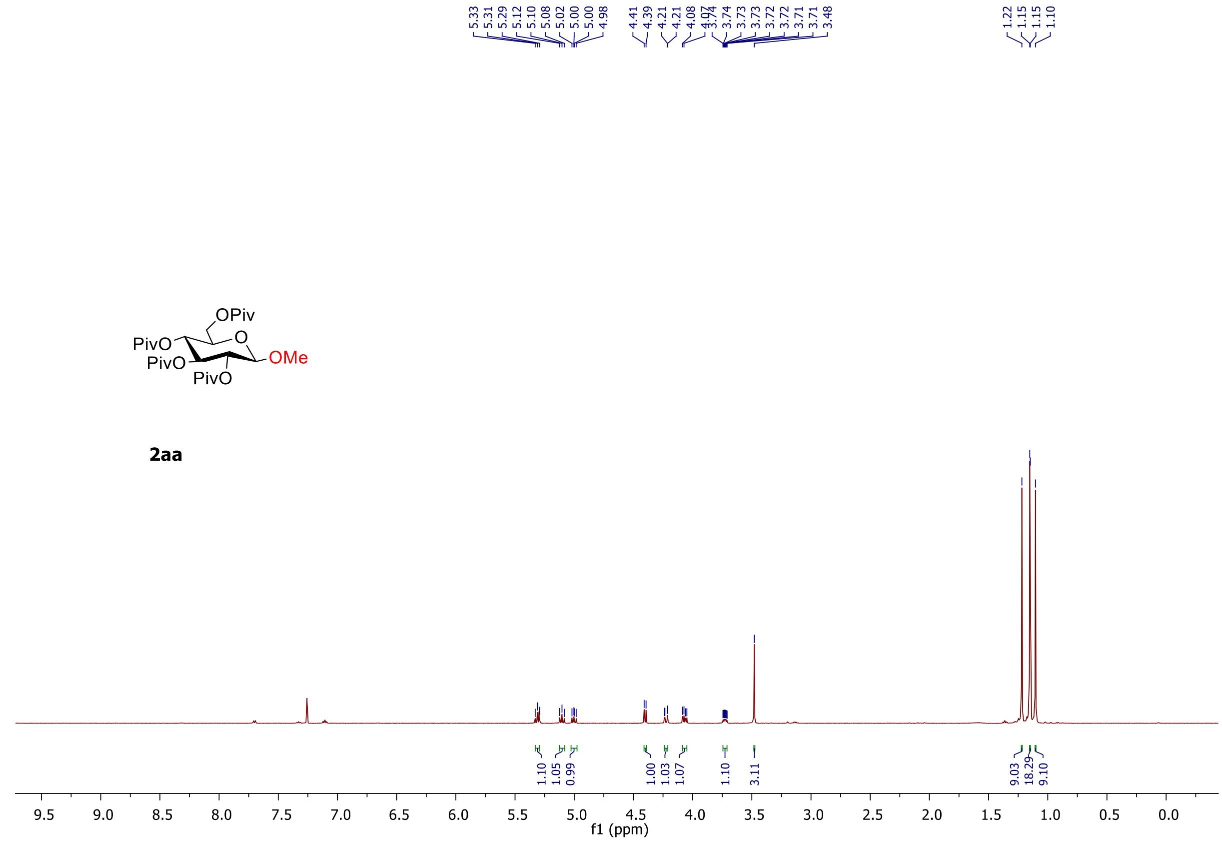
2,3,4,6-tetra-O-pivaloyl-α,β-D-glucopyranoside (α/β: 2/1) ***3a:***

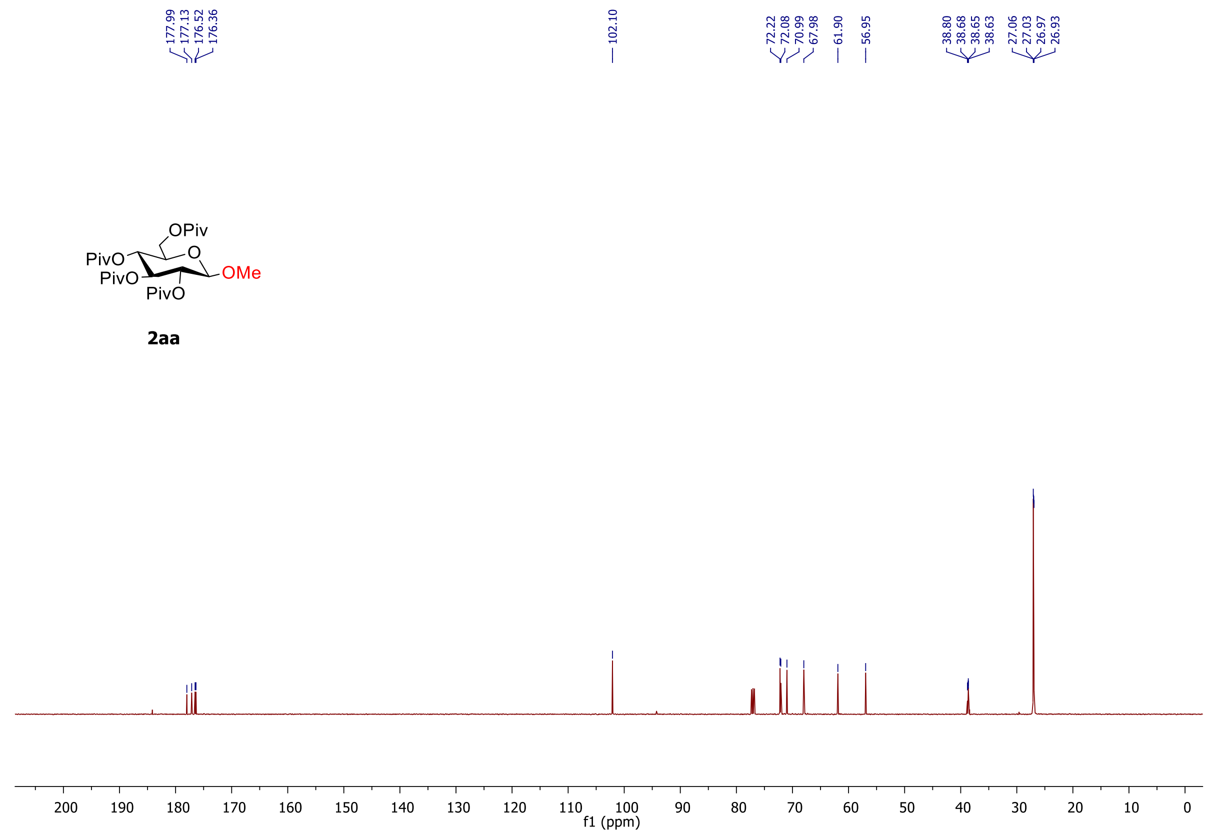


2,3,4,6-tetra-O-acetyl-α,β-D-glucopyranoside (α/β: 3/1) ***3b:***

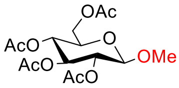


***2,3,4,6-tetra-O-pivaloyl-1-O-methyl-β-D-glucopyranoside 2aa*:**

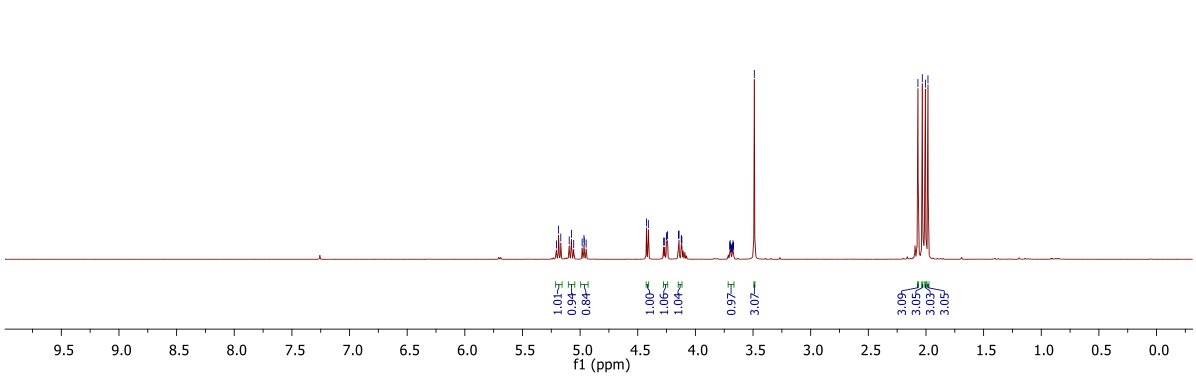


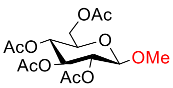


2,3,4,6-tetra-O-acetyl-1-O-methyl-β-D-glucopyranoside 2ba:

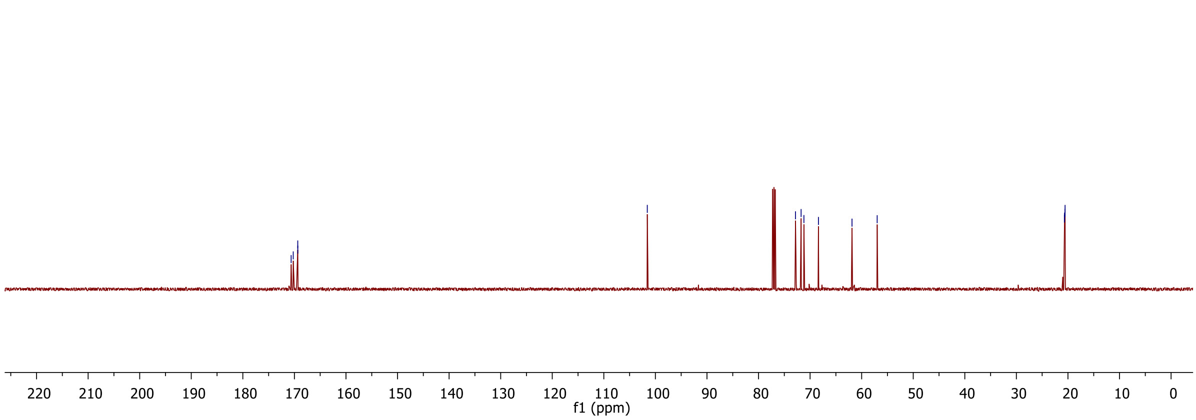


2ba

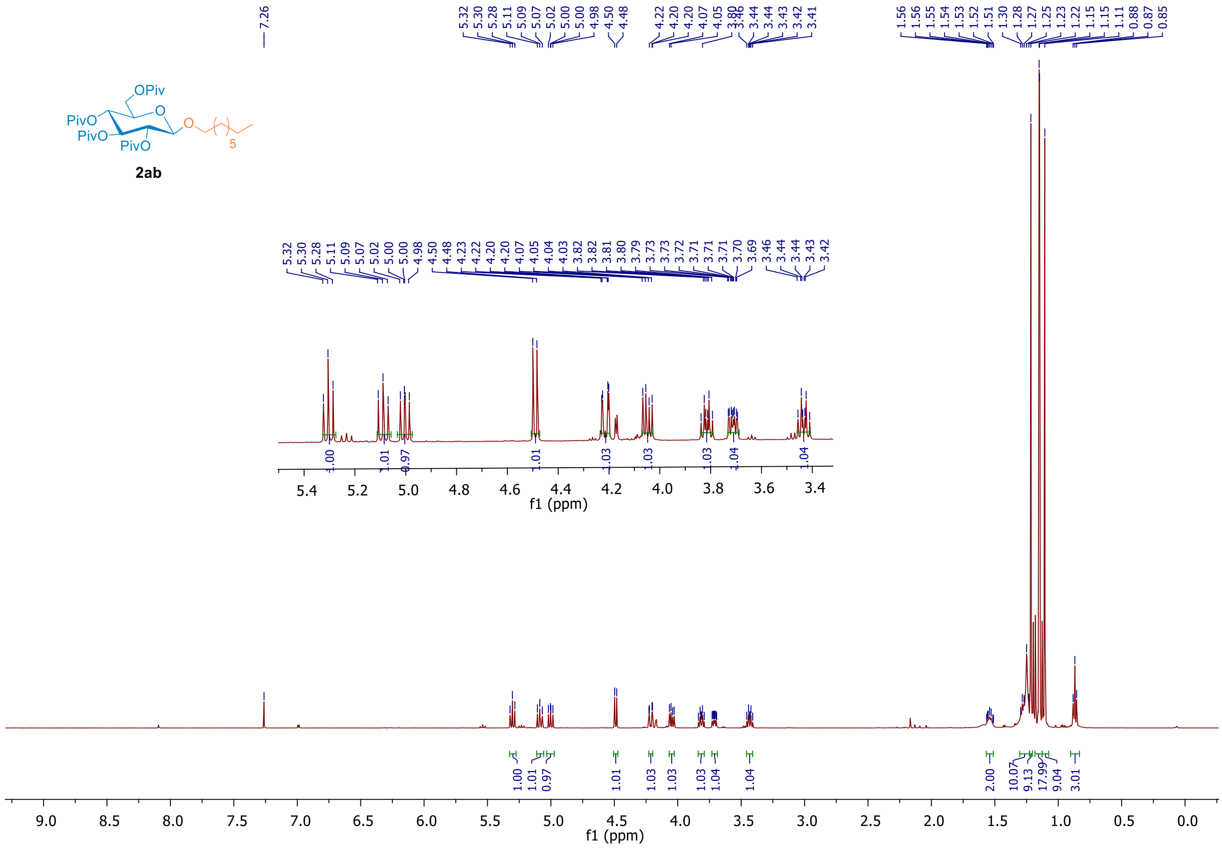


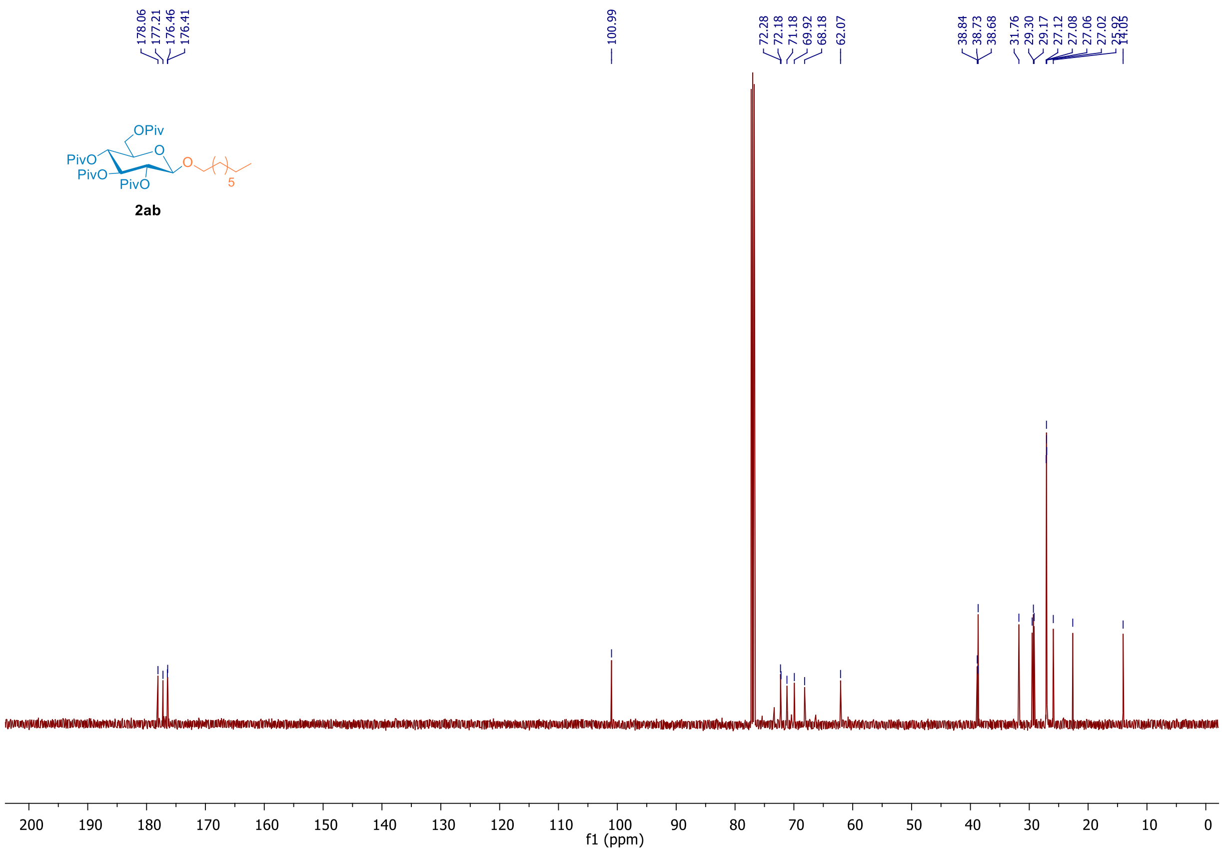


2ba

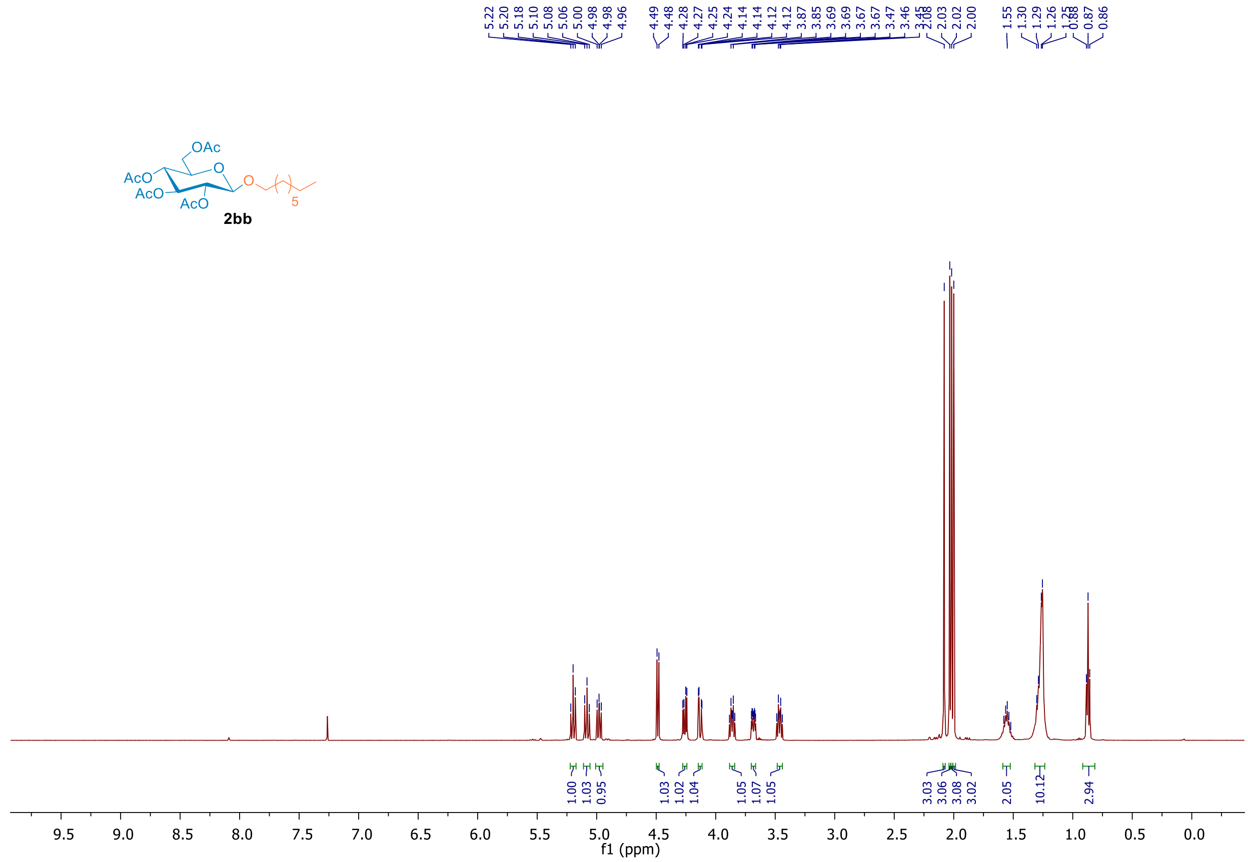


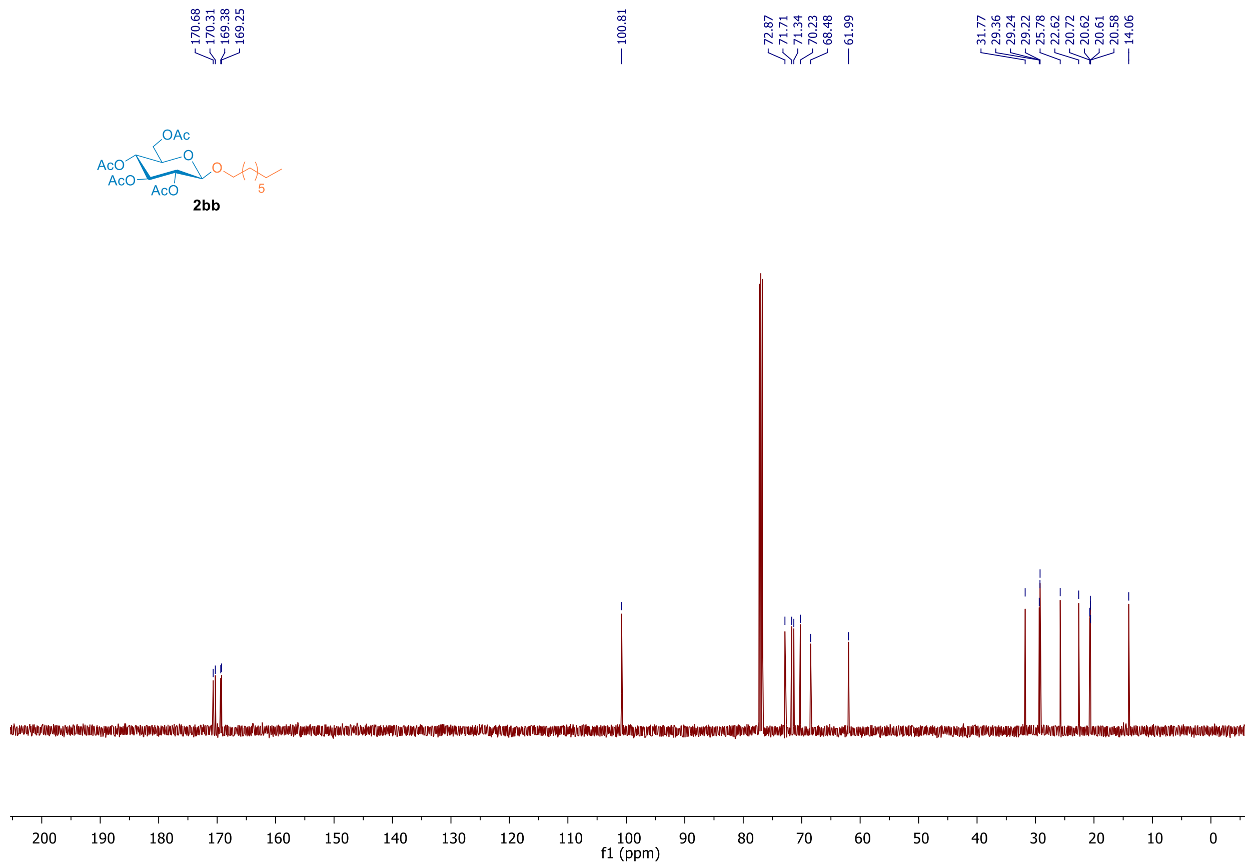
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-β-D-glucopyranoside 2ab:



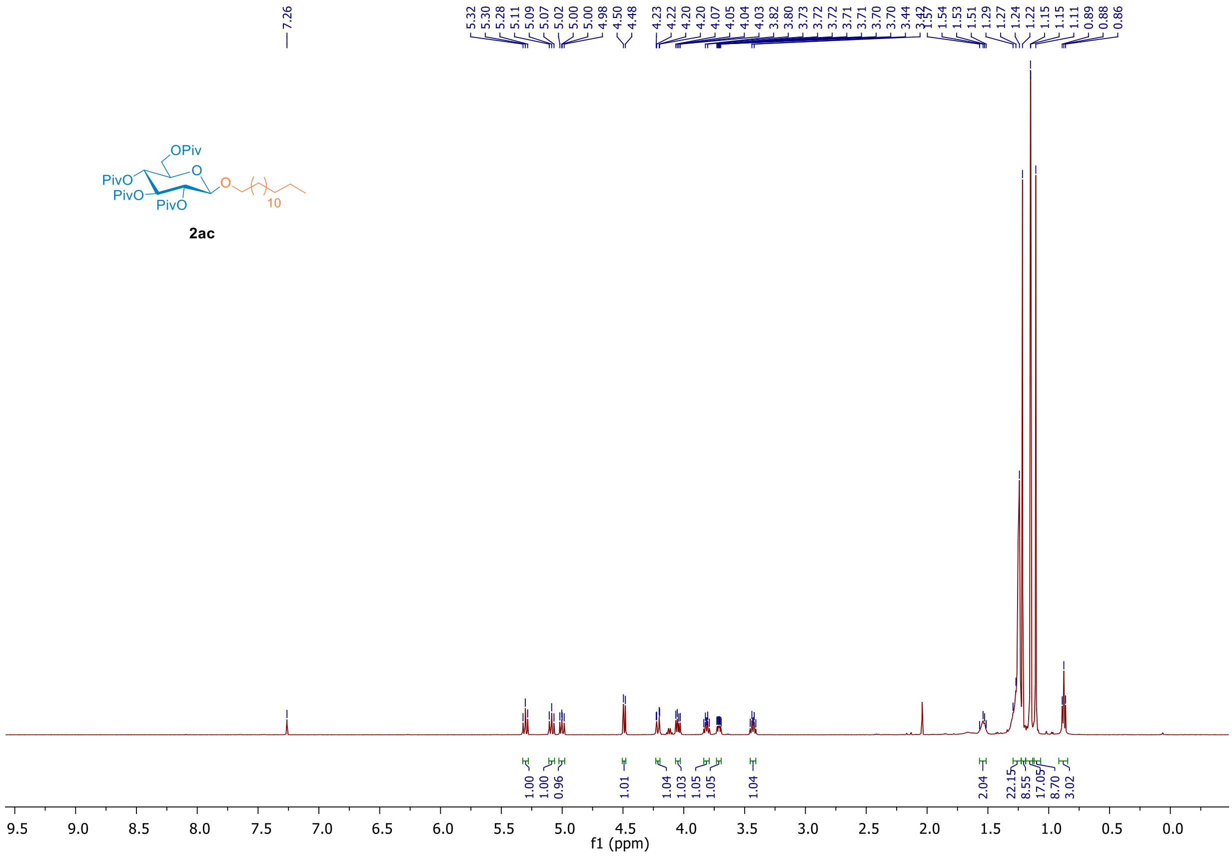


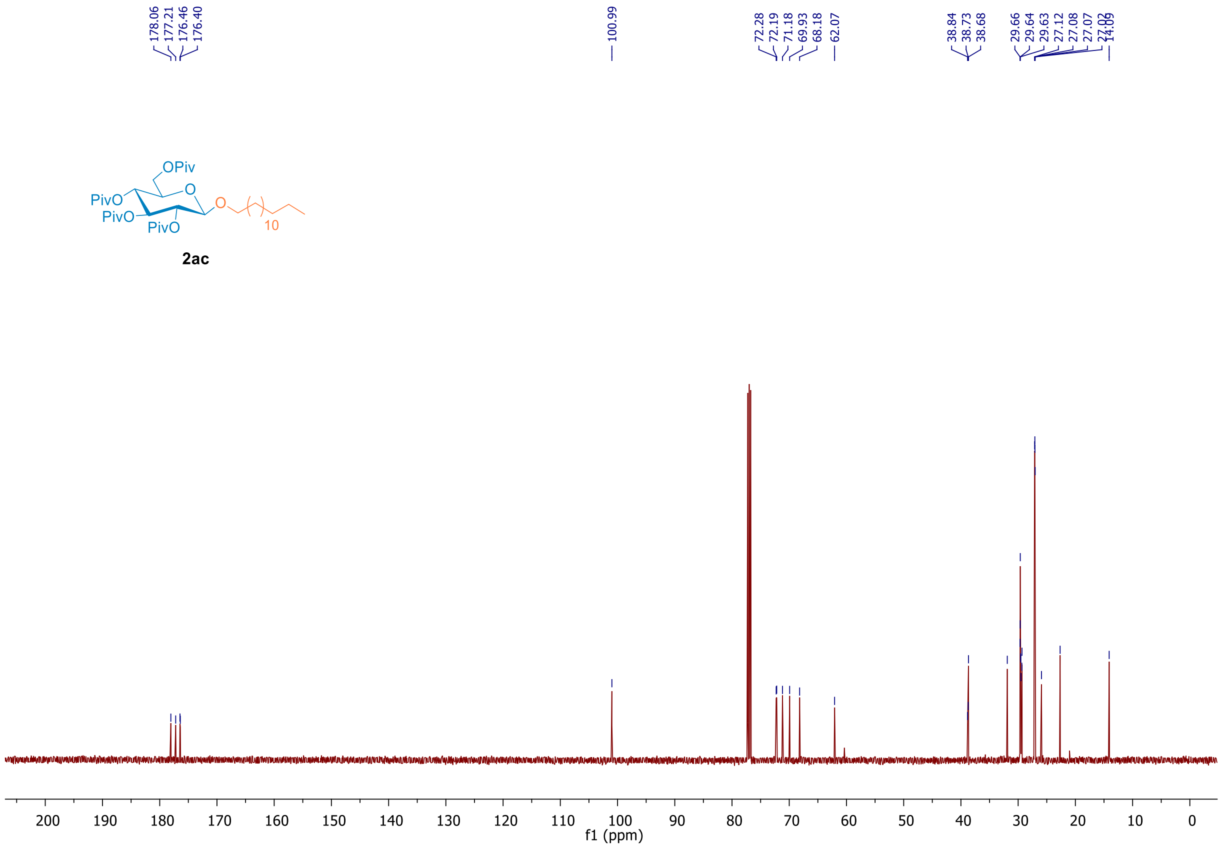
2,3,4,6-tetra-O-acetyl-1-O-(octyl)-β-D-glucopyranoside 2bb:



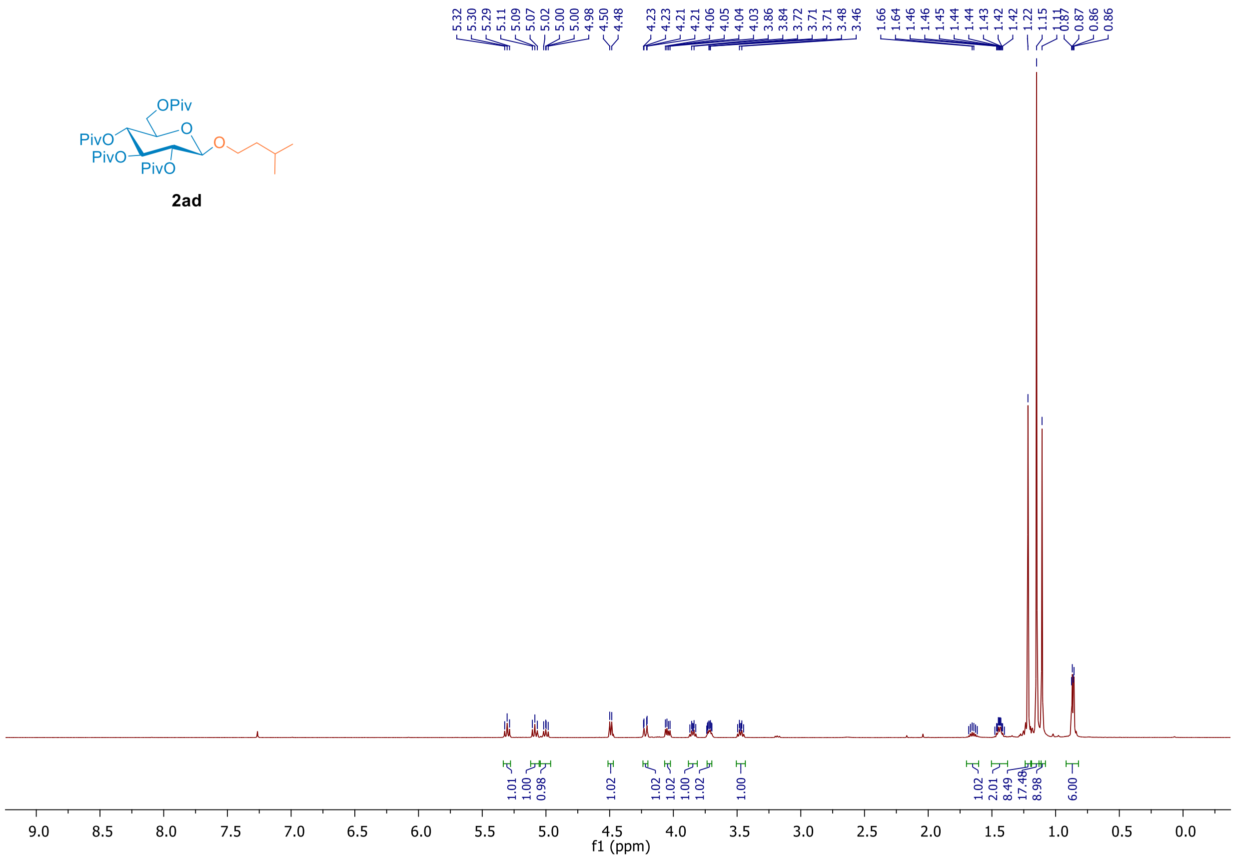


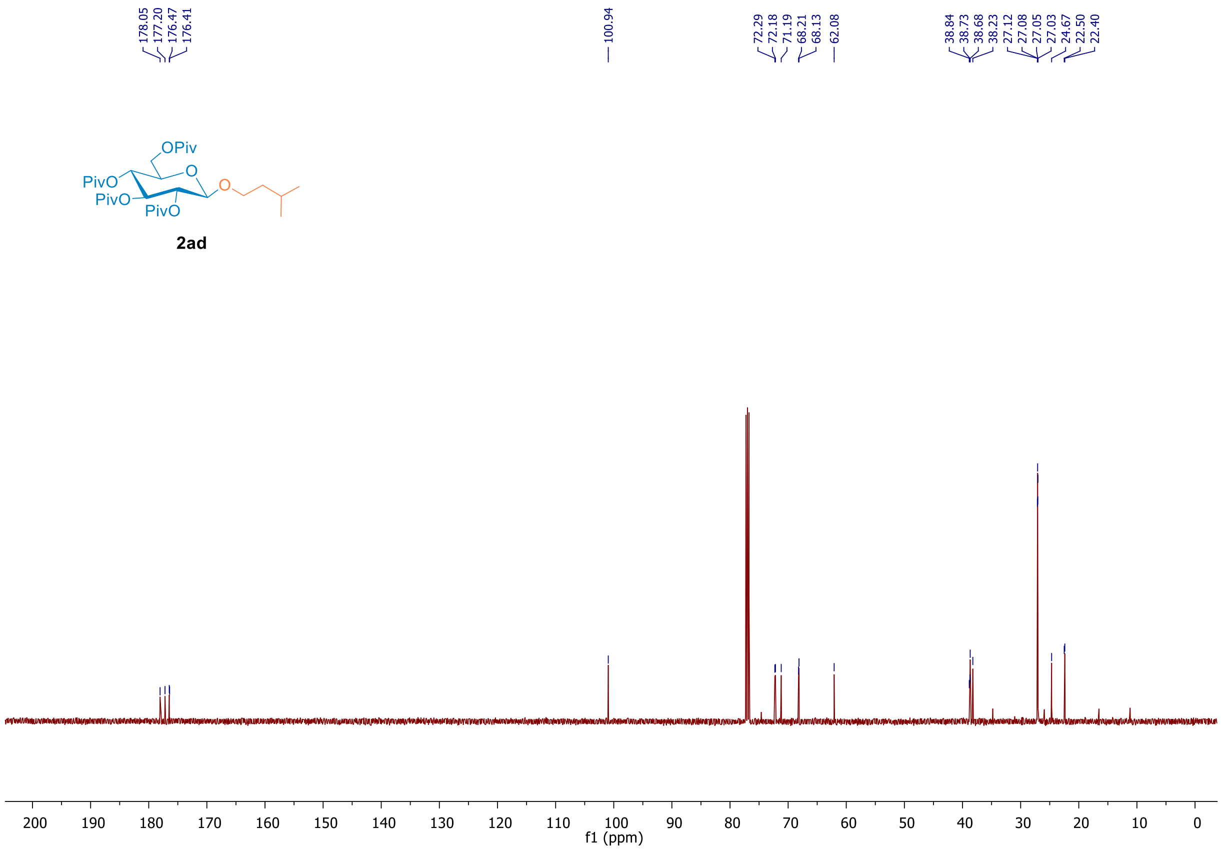
2,3,4,6-tetra-O-pivaloyl-1-O-(tetradecyl)-β-D-glucopyranoside 2ac:



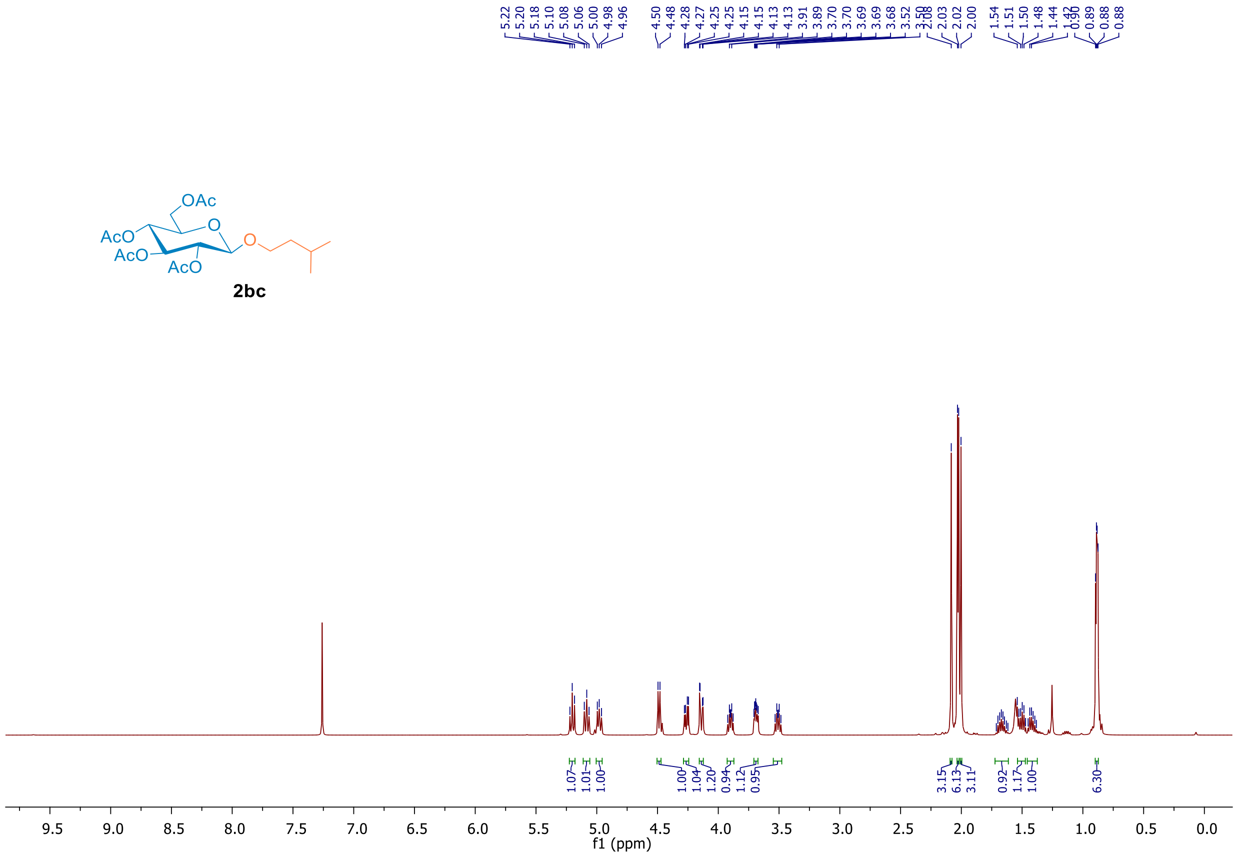


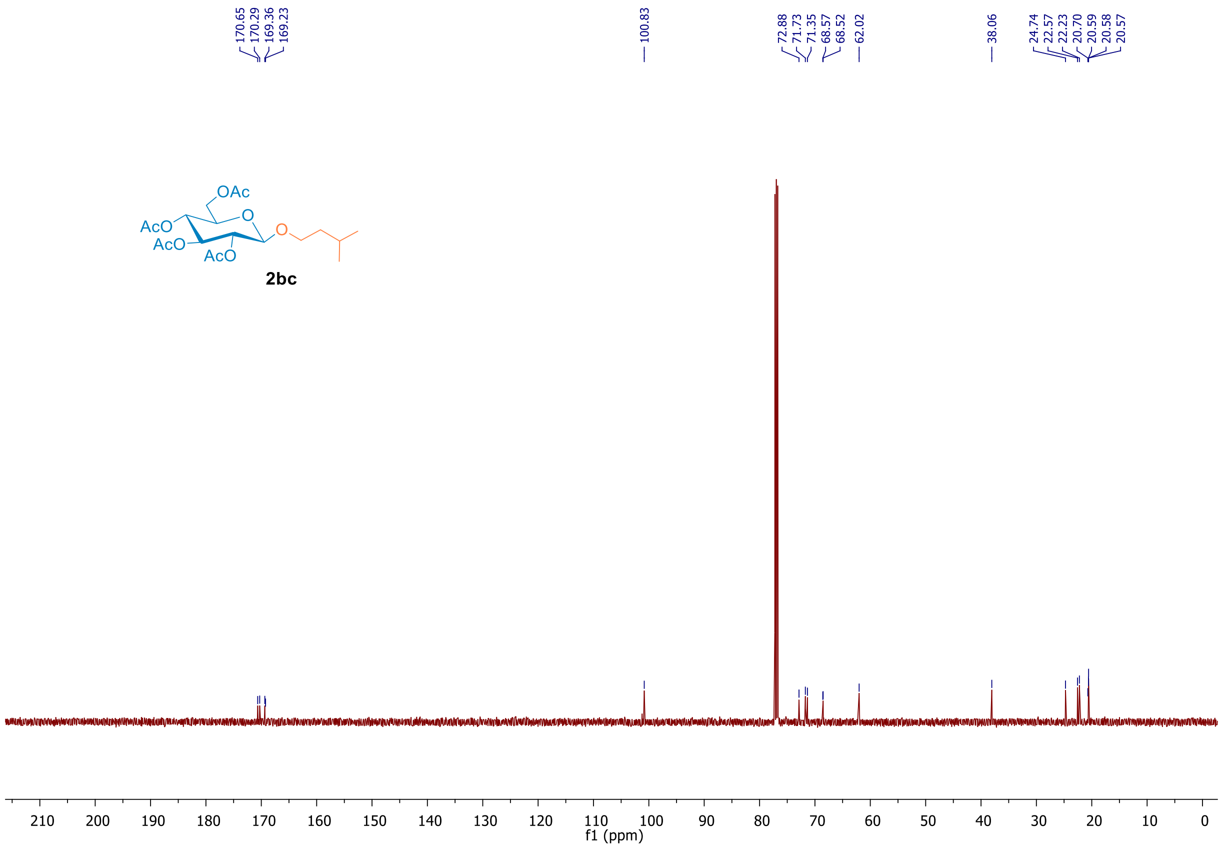
2,3,4,6-tetra-O-pivaloyl-1-O-(isopentyl)-β-D-glucopyranoside 2ad:



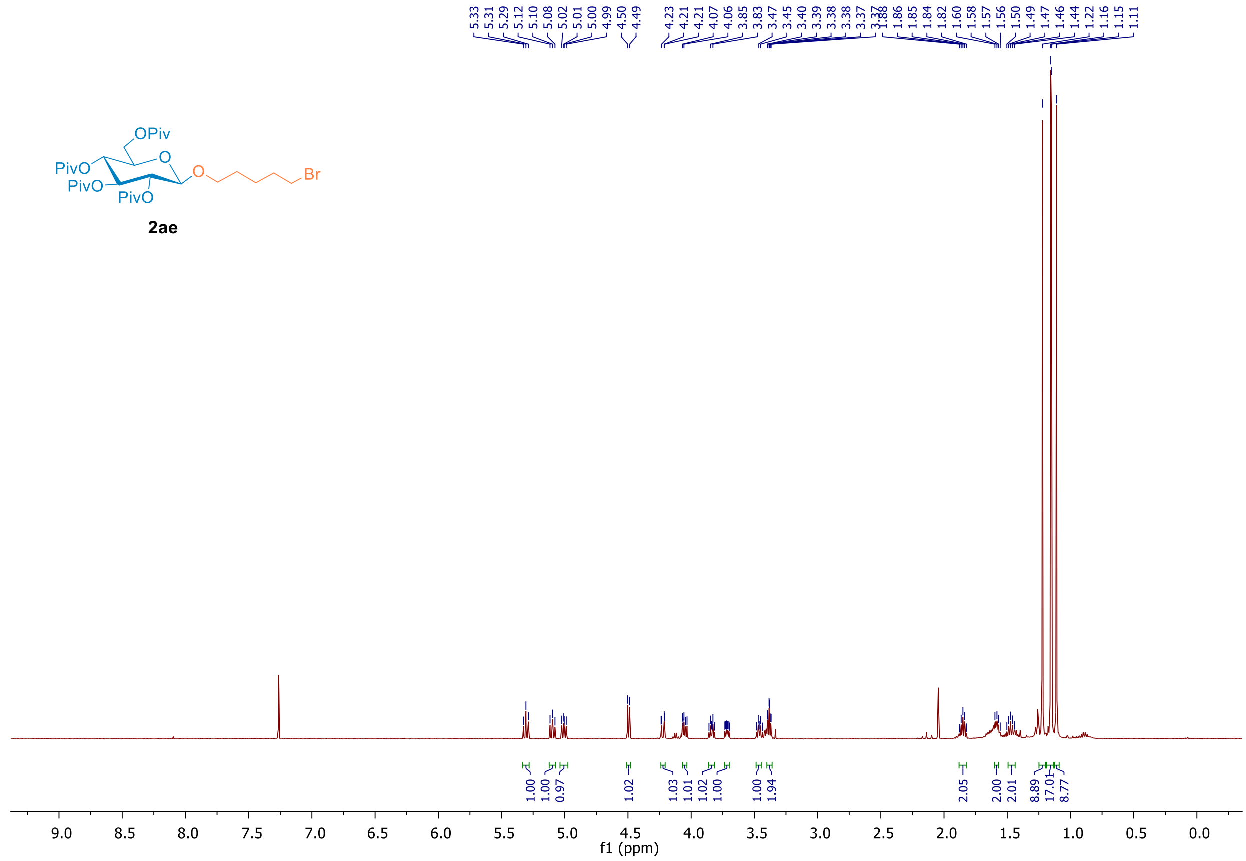


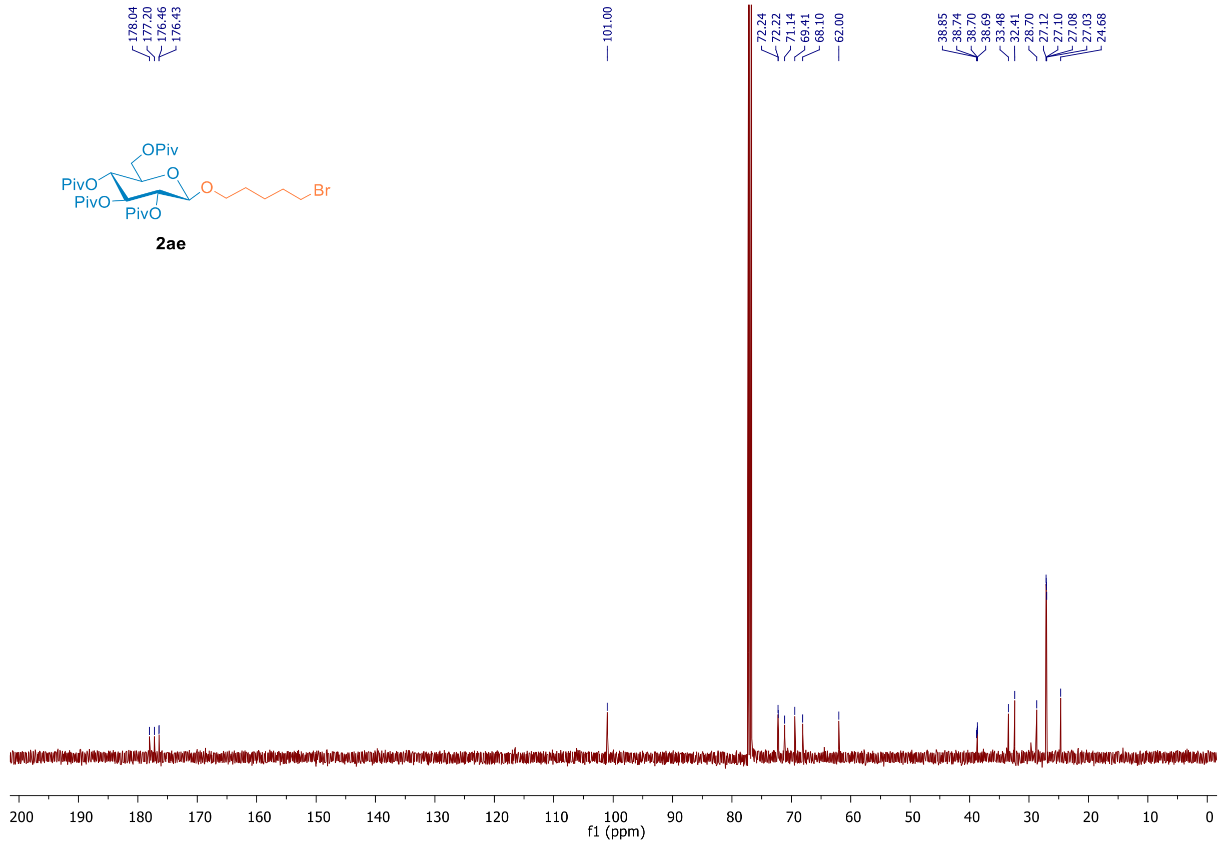
2,3,4,6-tetra-O-acetyl-1-O-(isopentyl)-β-D-glucopyranoside 2bc:



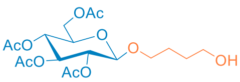


2,3,4,6-tetra-O-pivaloyl-1-O-(5-bromopentyl)-β-D-glucopyranoside 2ae:

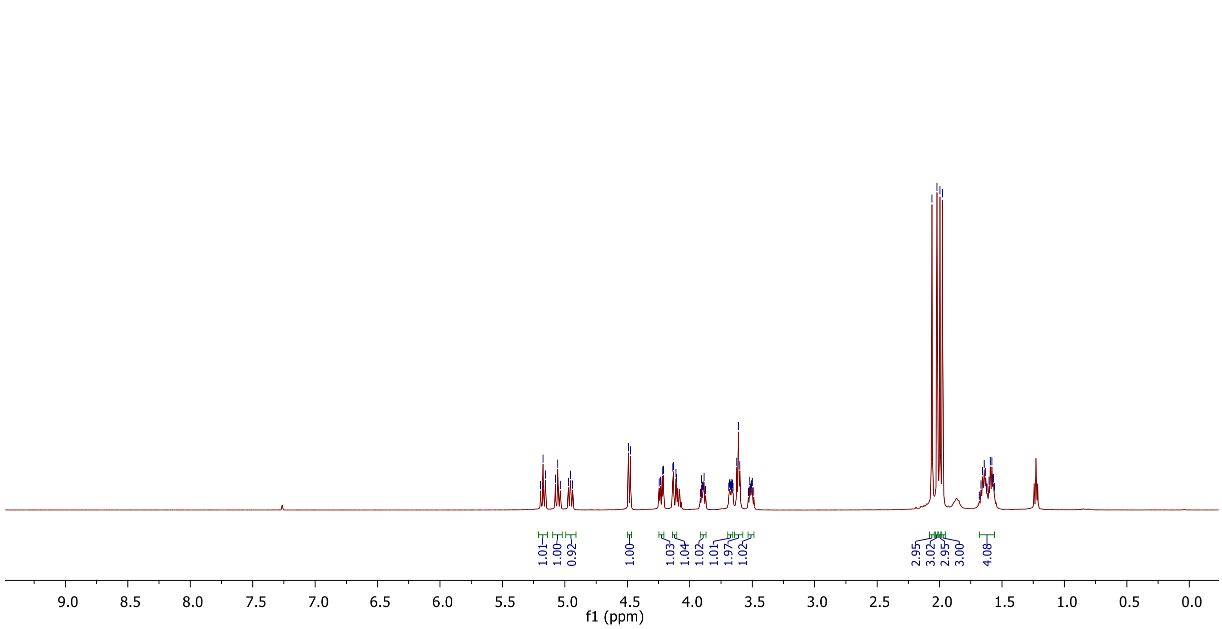


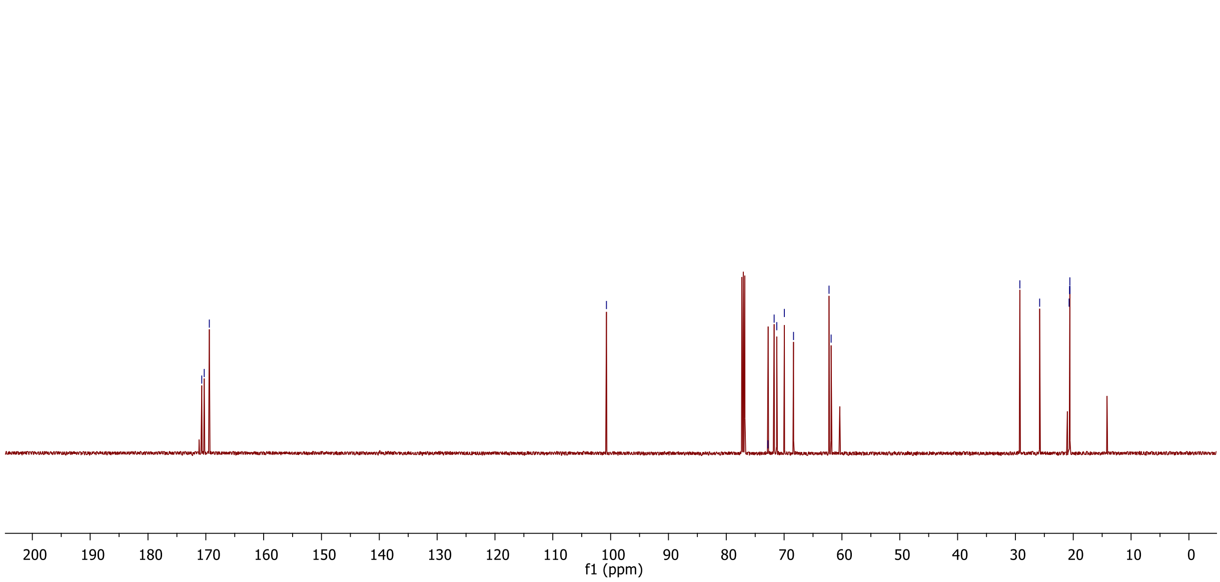


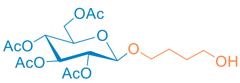
2,3,4,6-tetra-O-acetyl-1-O-(4-hydroxybutyl)-β-D-glucopyranoside 2bd:



2bd







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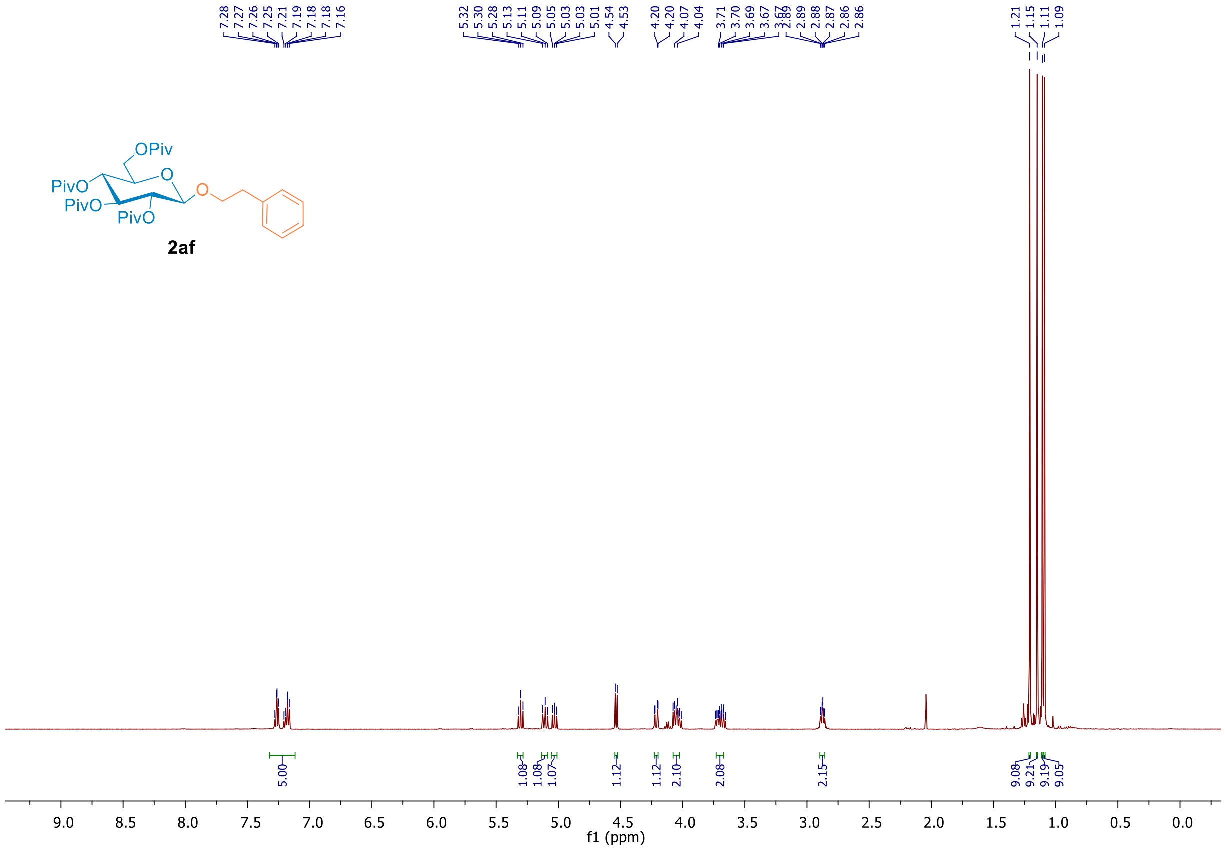
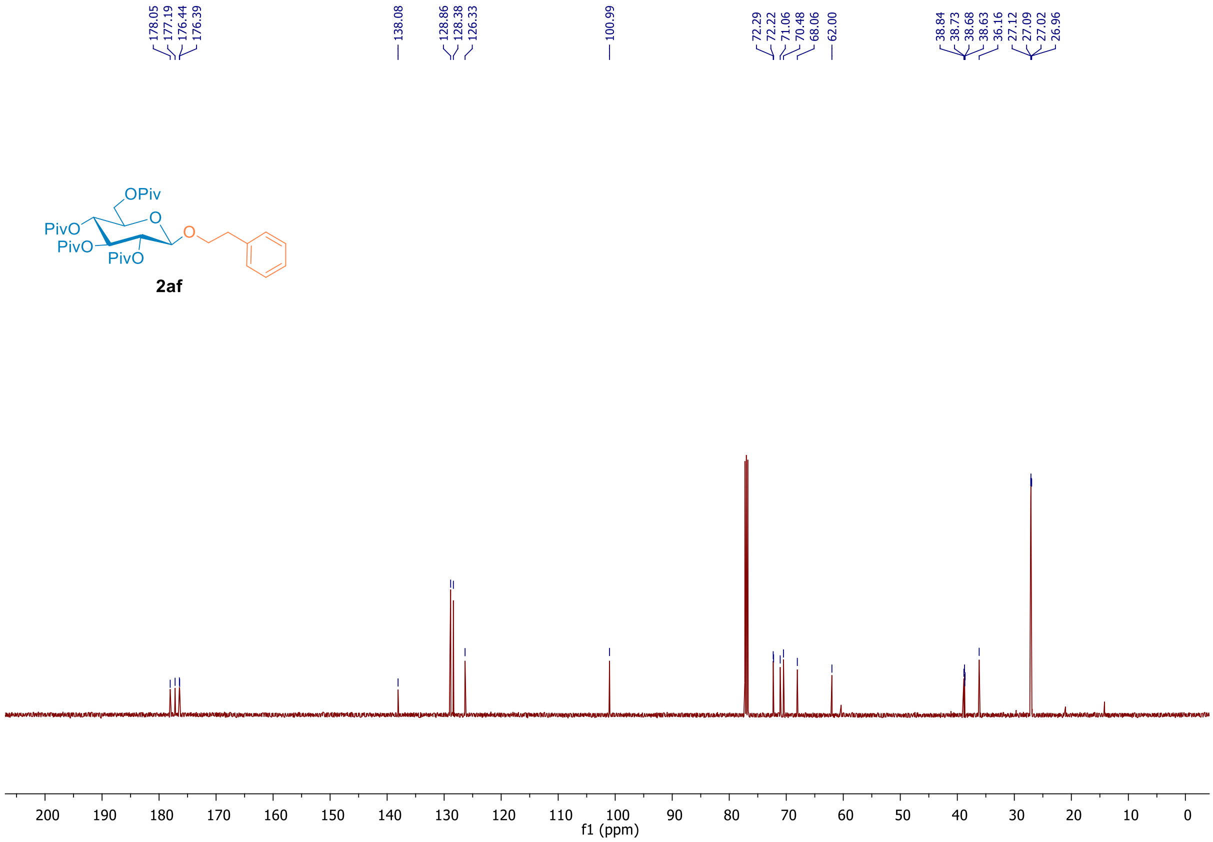
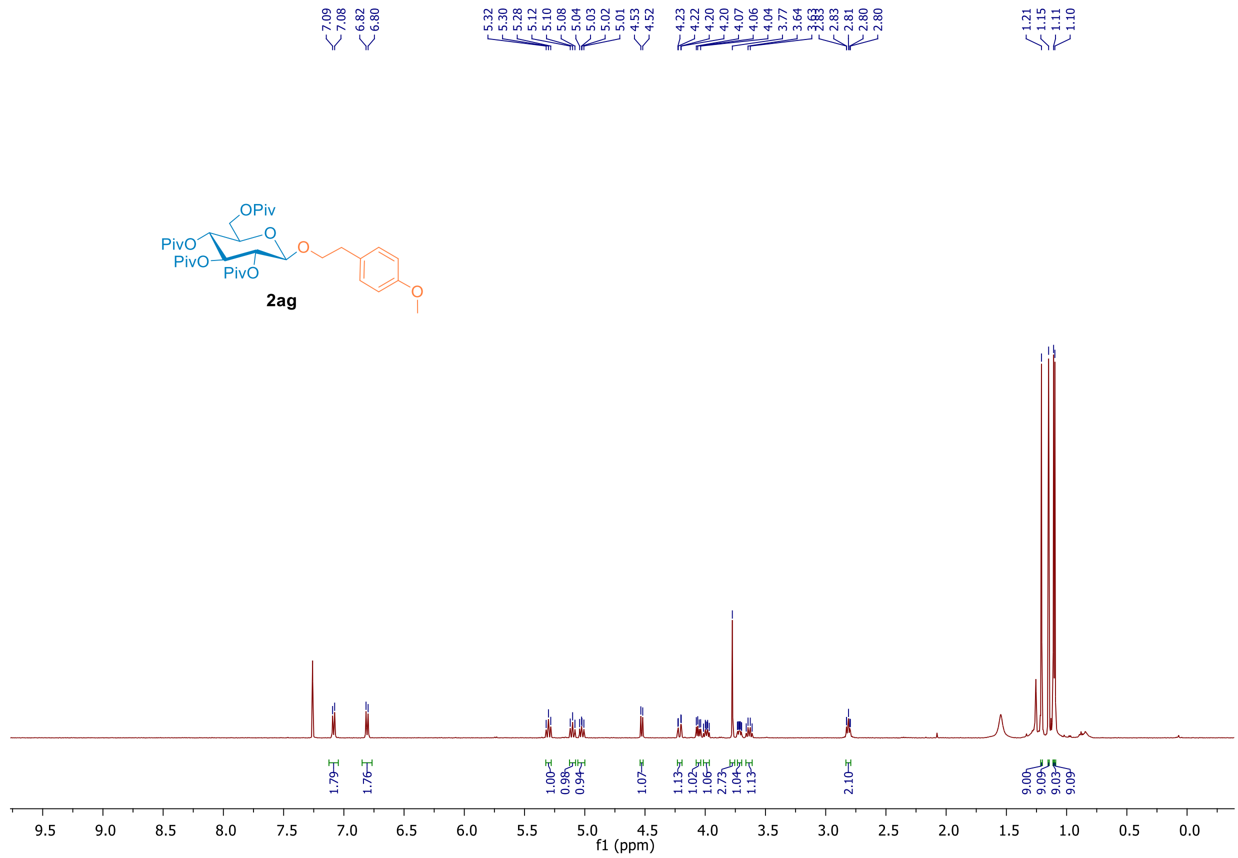
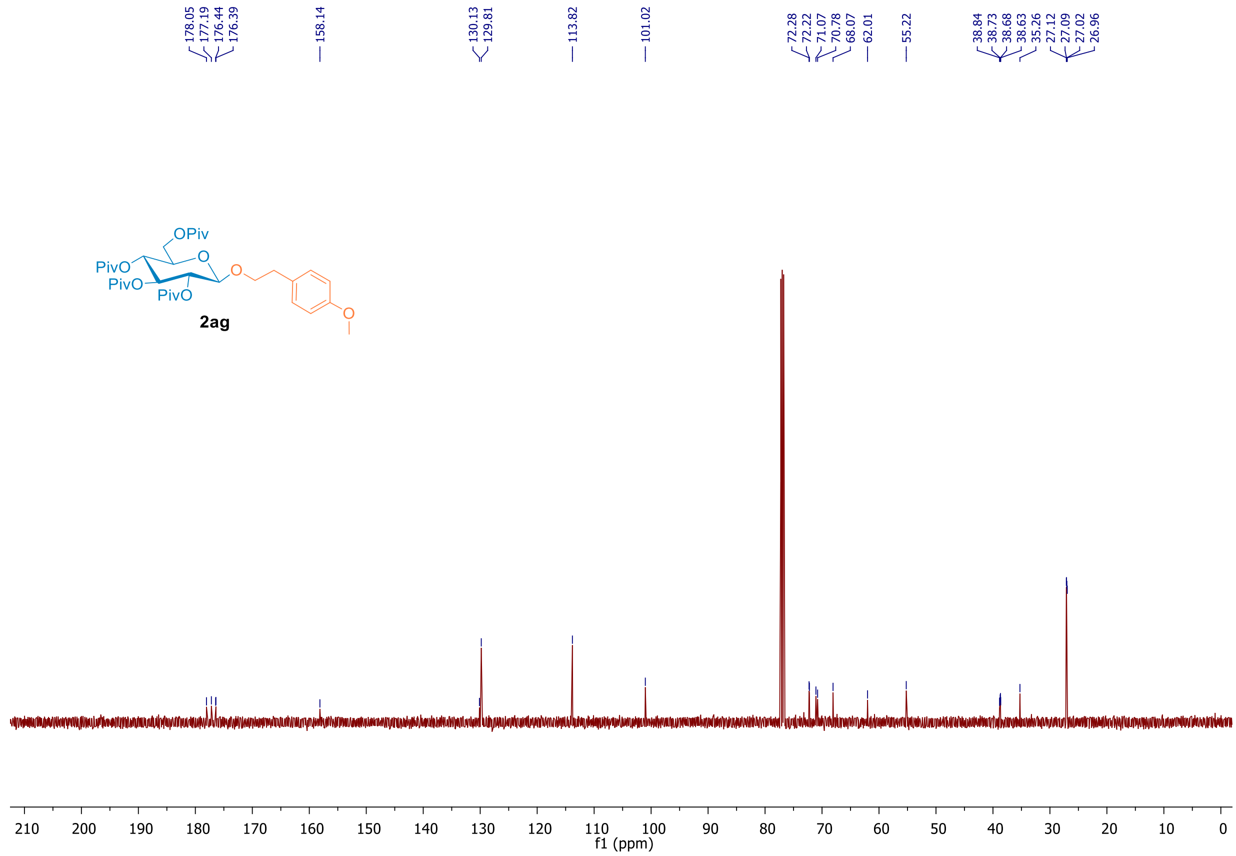
2,3,4,6-tetra-O-pivaloyl-1-O-(phenethyl)-β-D-glucopyranoside 2af:



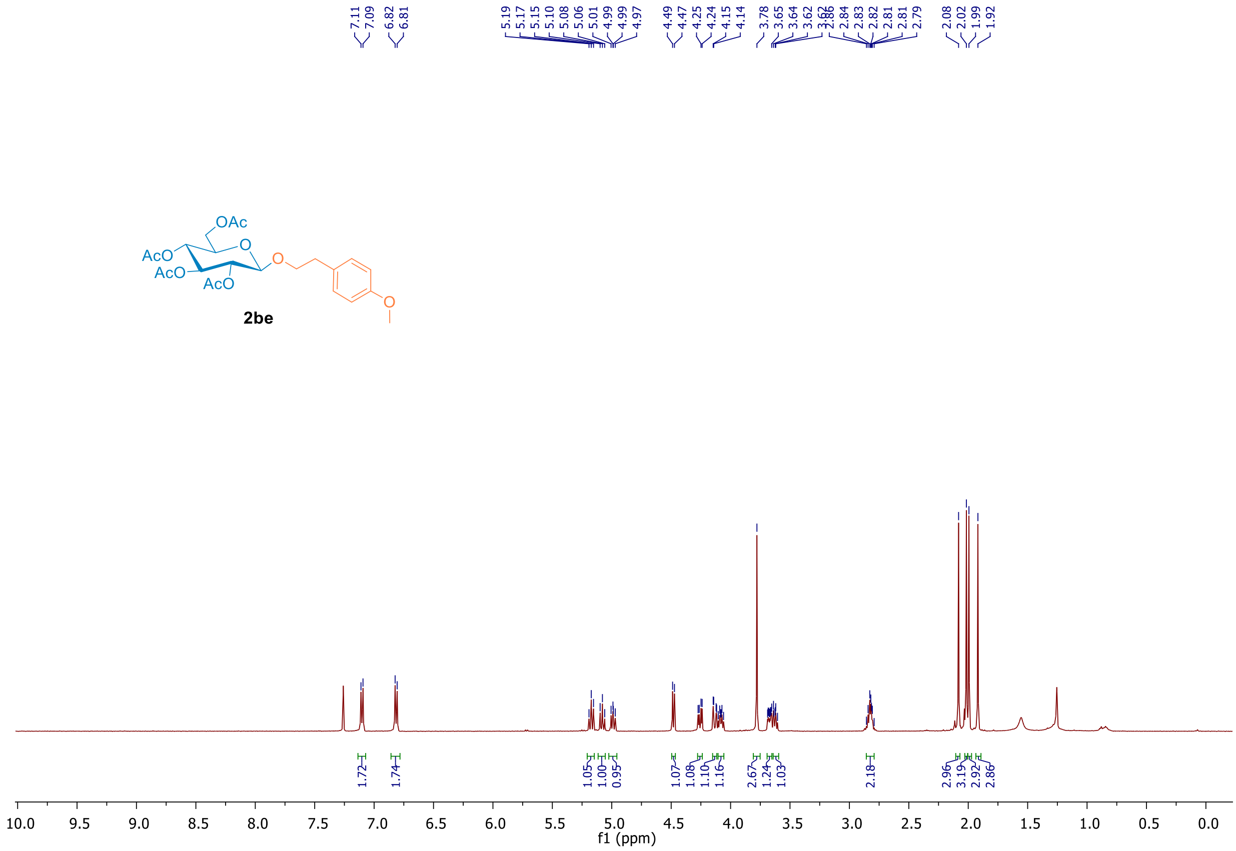


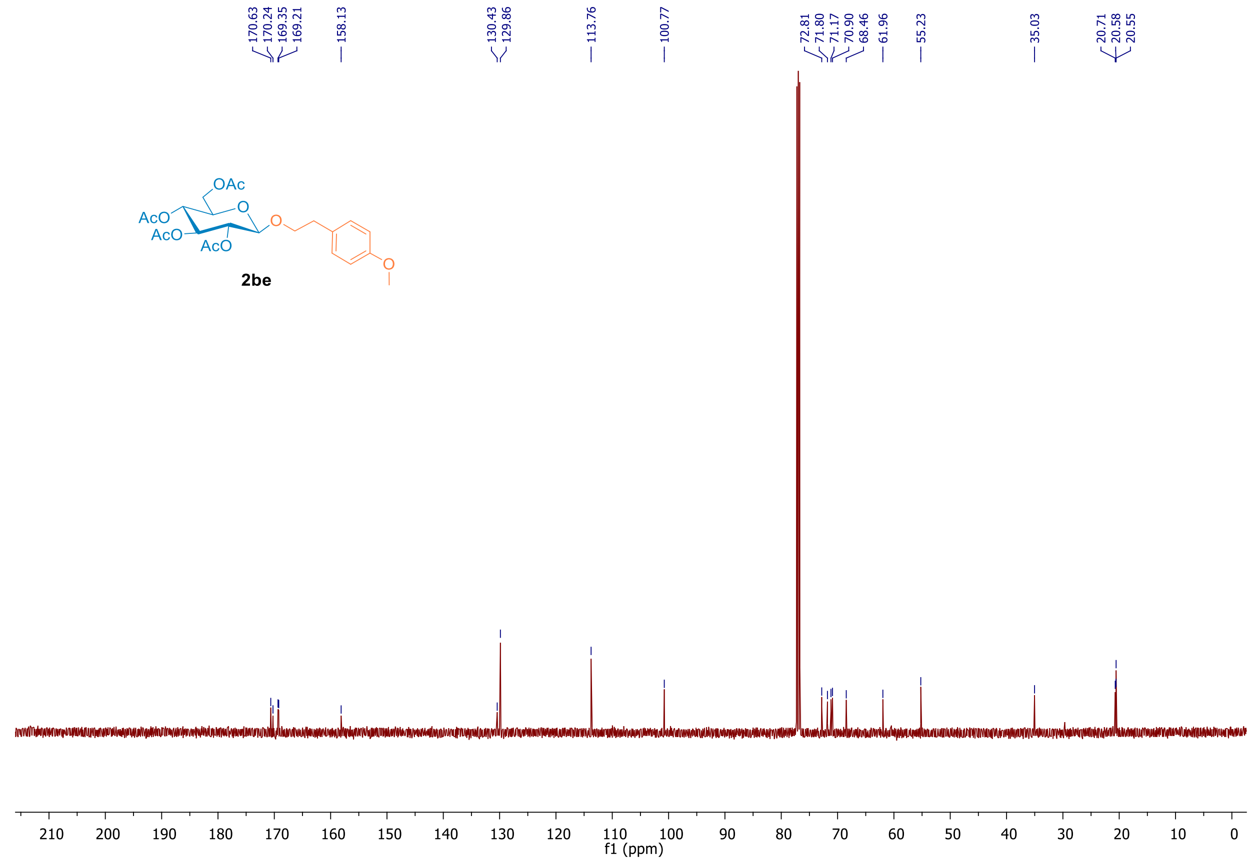
2,3,4,6-tetra-O-pivaloyl-1-O-(4-methoxy-phenethyl)-β-D-glucopyranoside 2ag:



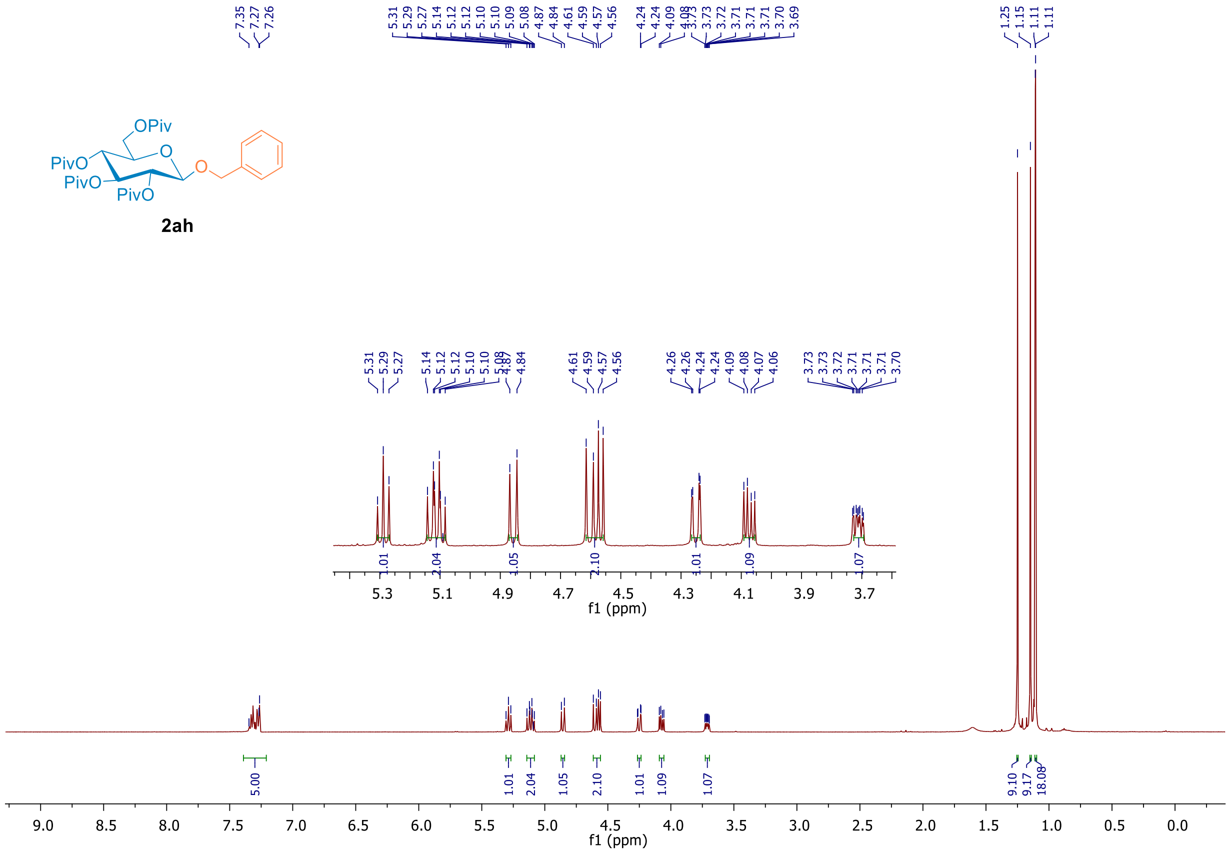


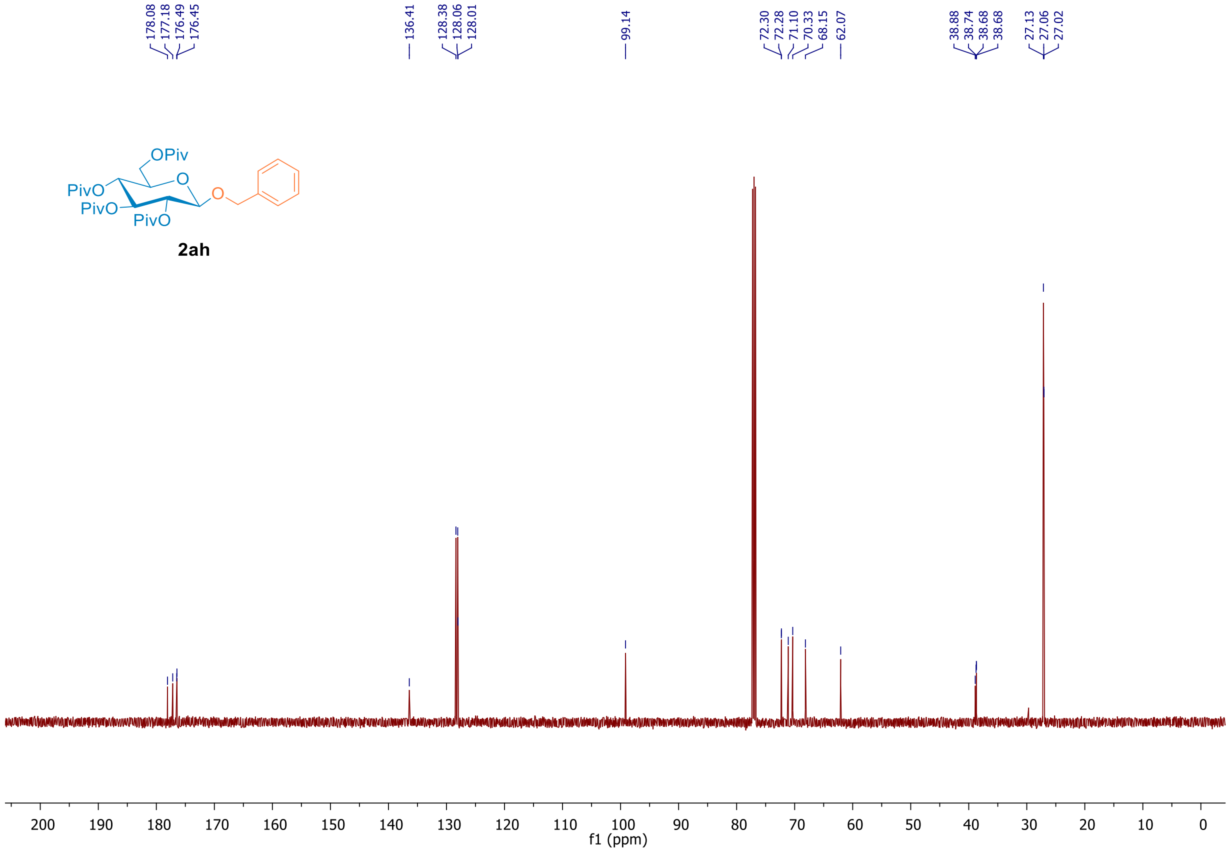
2,3,4,6-tetra-O-acetyl-1-O-(4-methoxy-phenethyl)-β-D-glucopyranoside 2be:



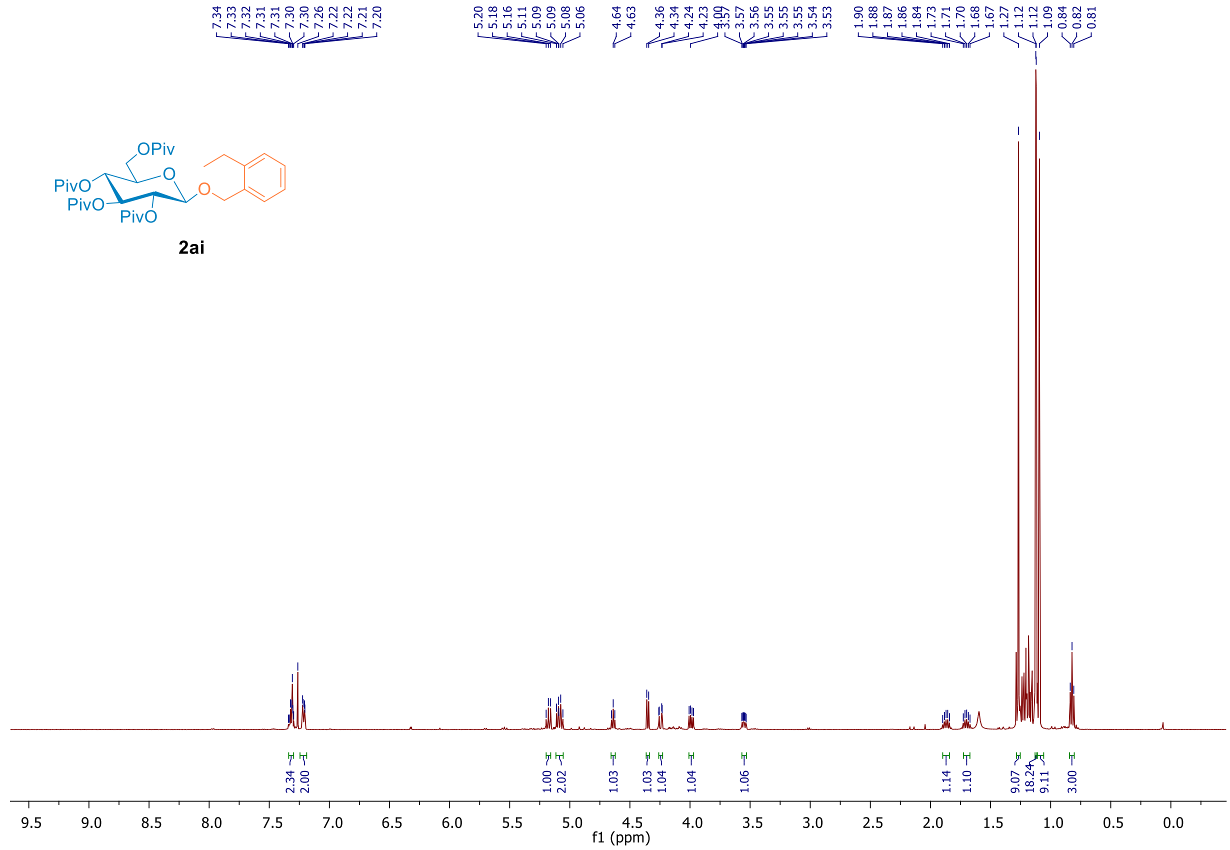


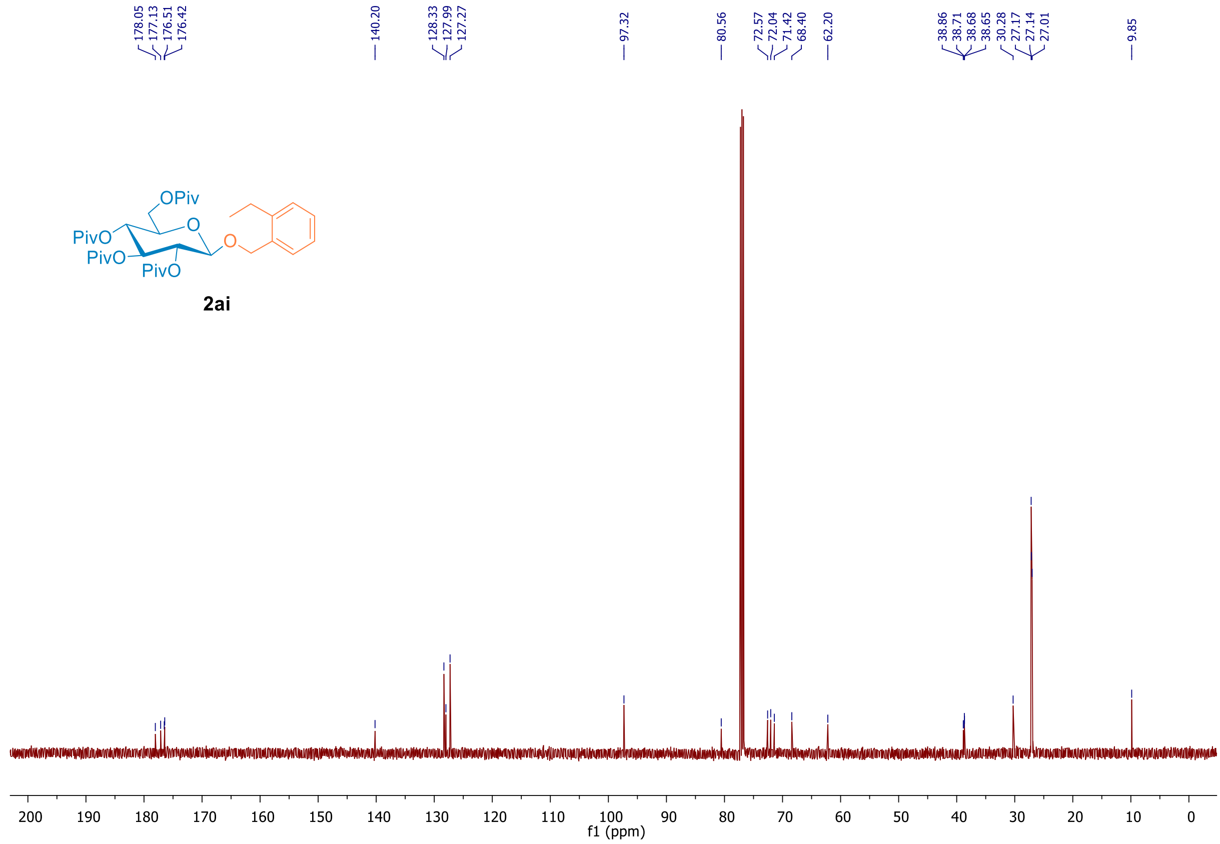
2,3,4,6-tetra-O-pivaloyl-1-O-(benzyl)-β-D-glucopyranoside 2ah:



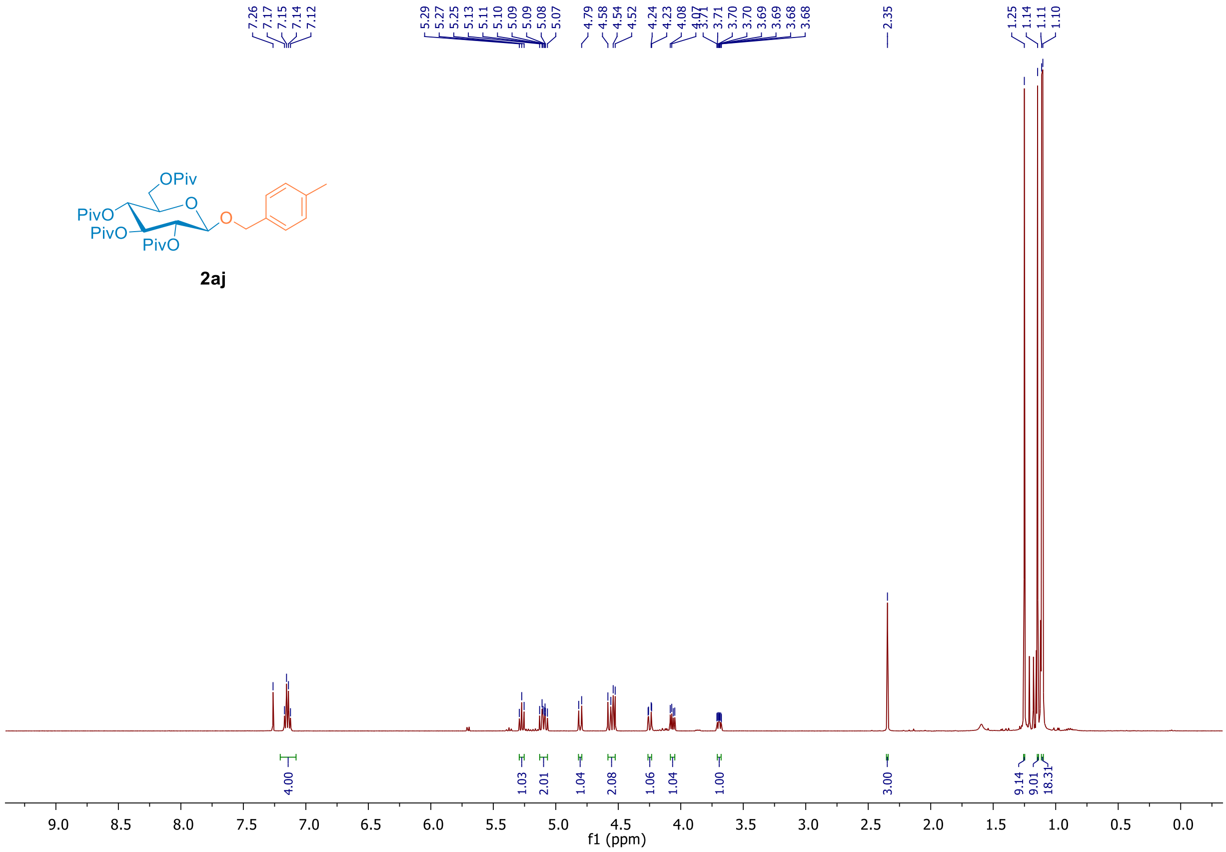


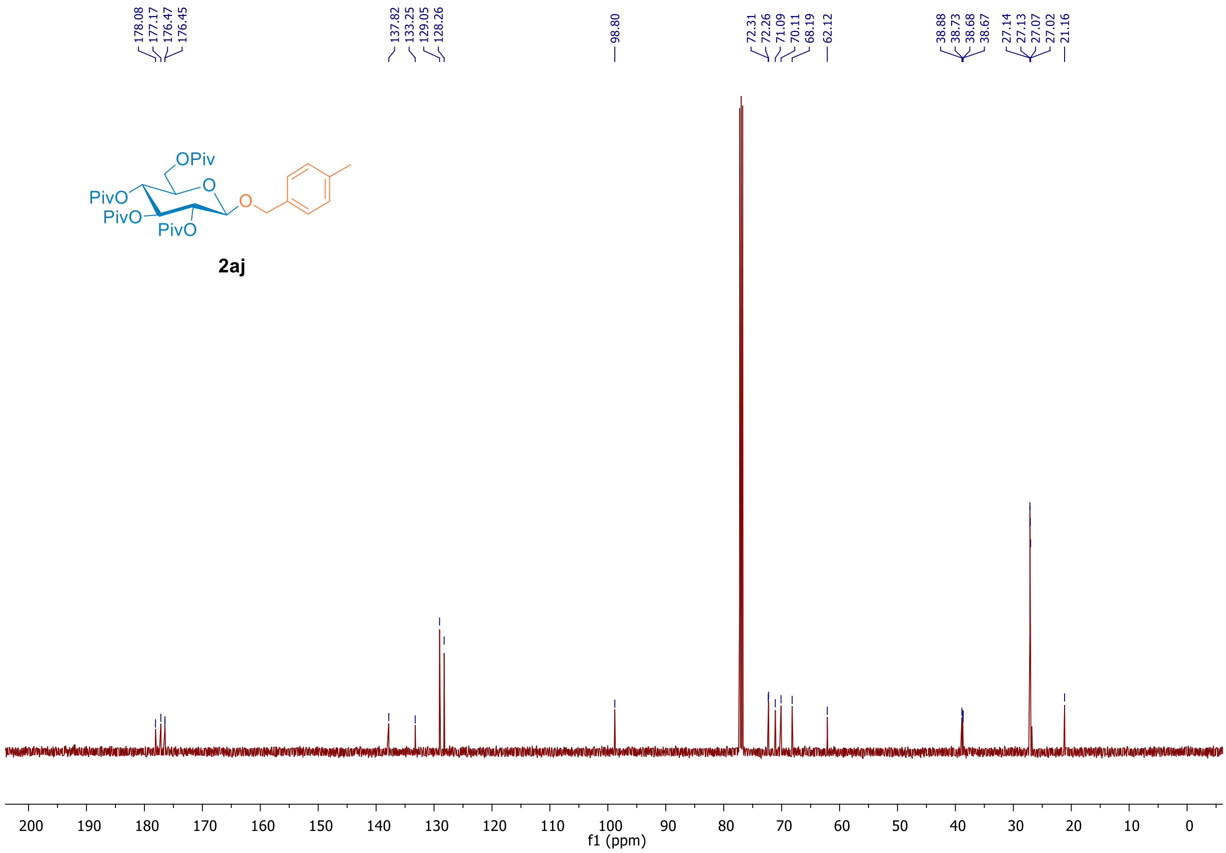
2,3,4,6-tetra-O-pivaloyl-1-O-(2-ethylbenzyl)-β-D-glucopyranoside 2ai:



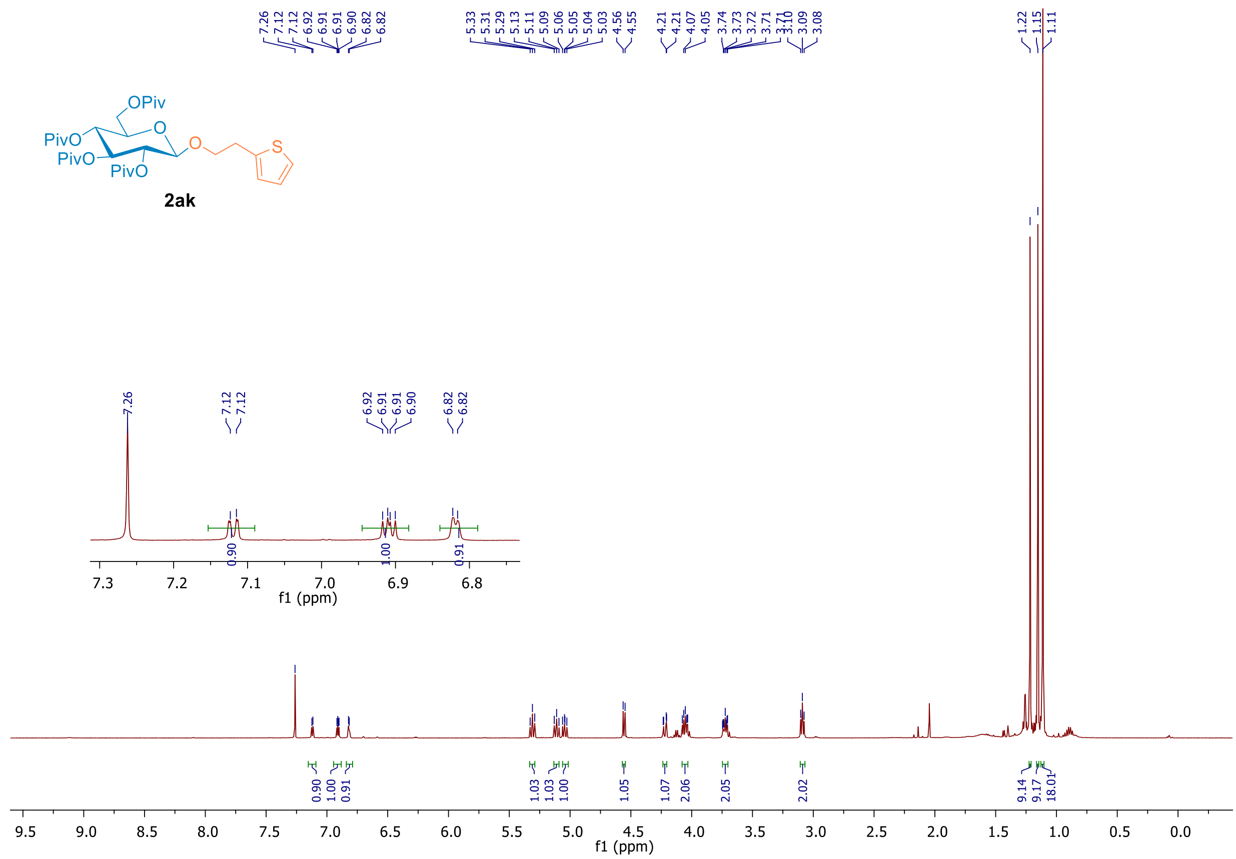


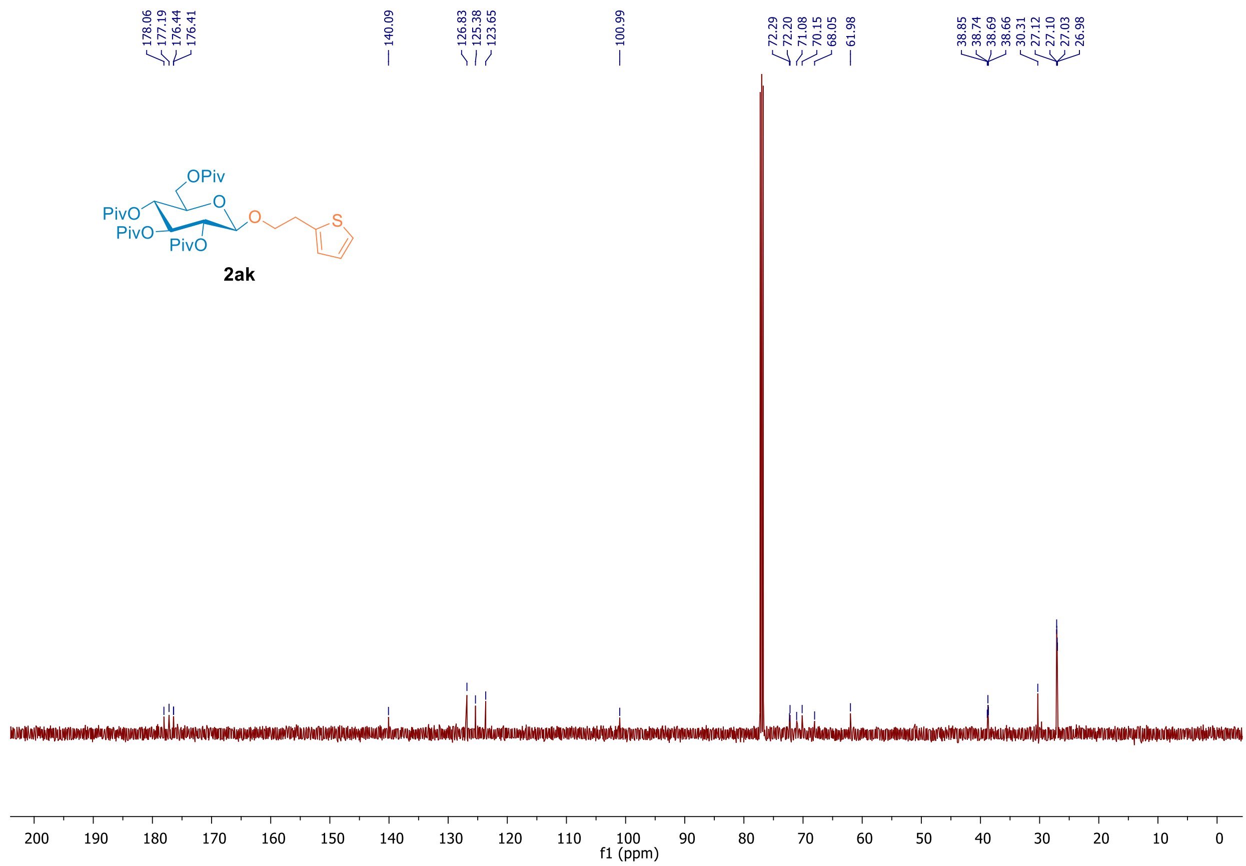
2,3,4,6-tetra-O-pivaloyl-1-O-(4-methylbenzyl)-β-D-glucopyranoside 2aj:



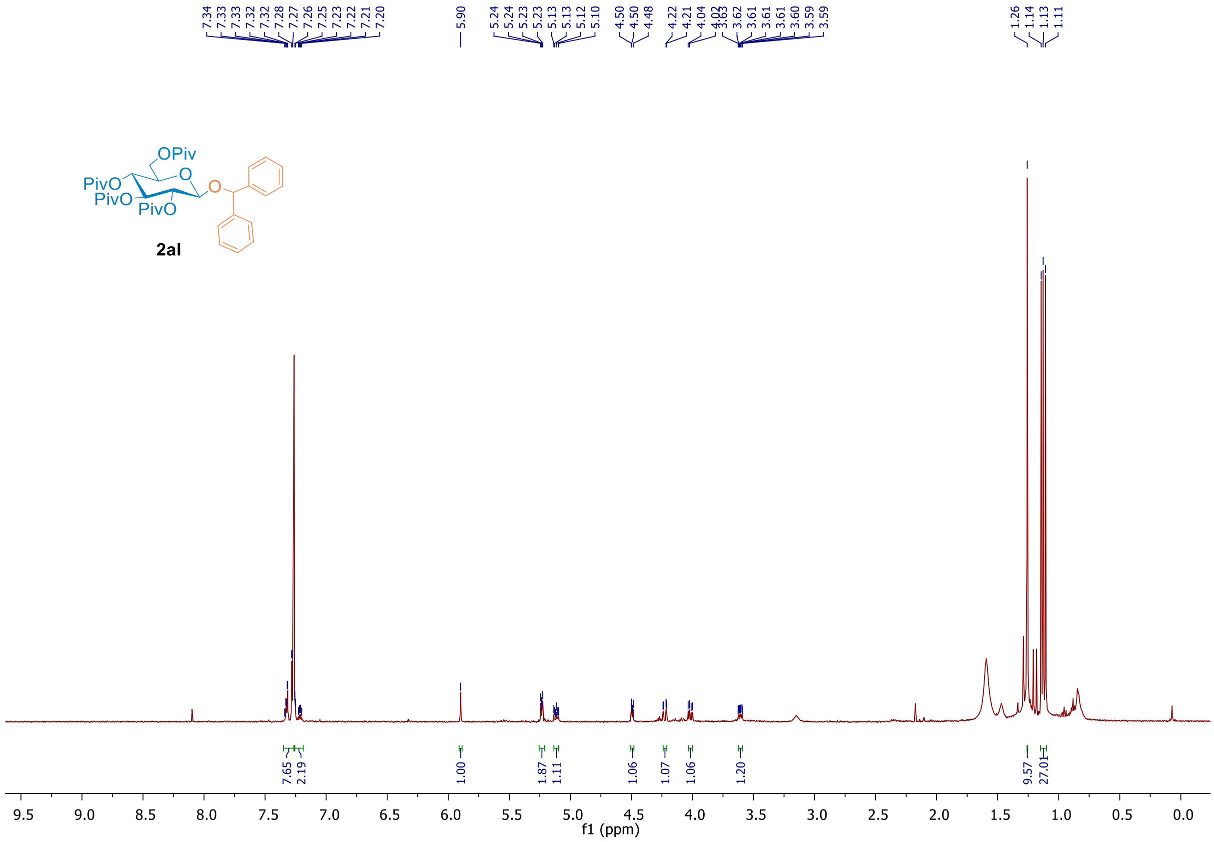


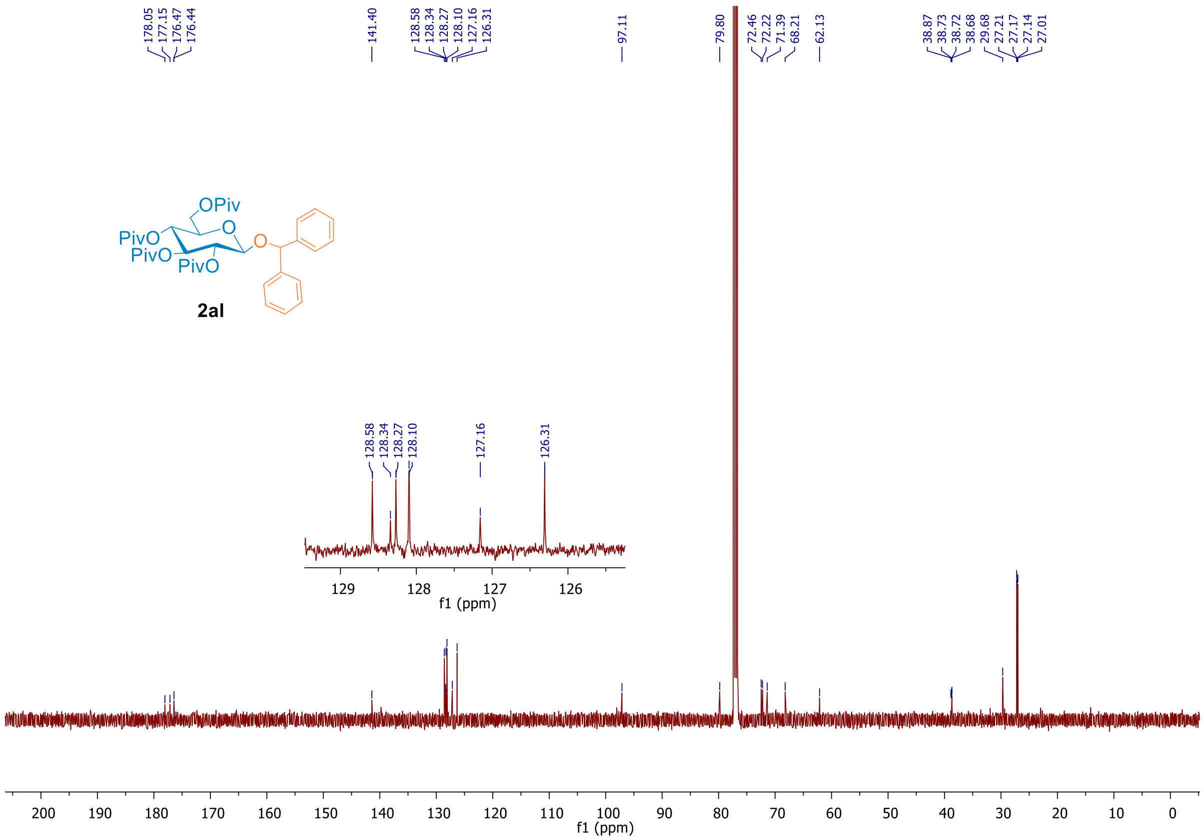
2,3,4,6-tera-O-pivaloyl-1-O-(2-thiopheneethyl)-β-D-glucopyranoside 2ak:



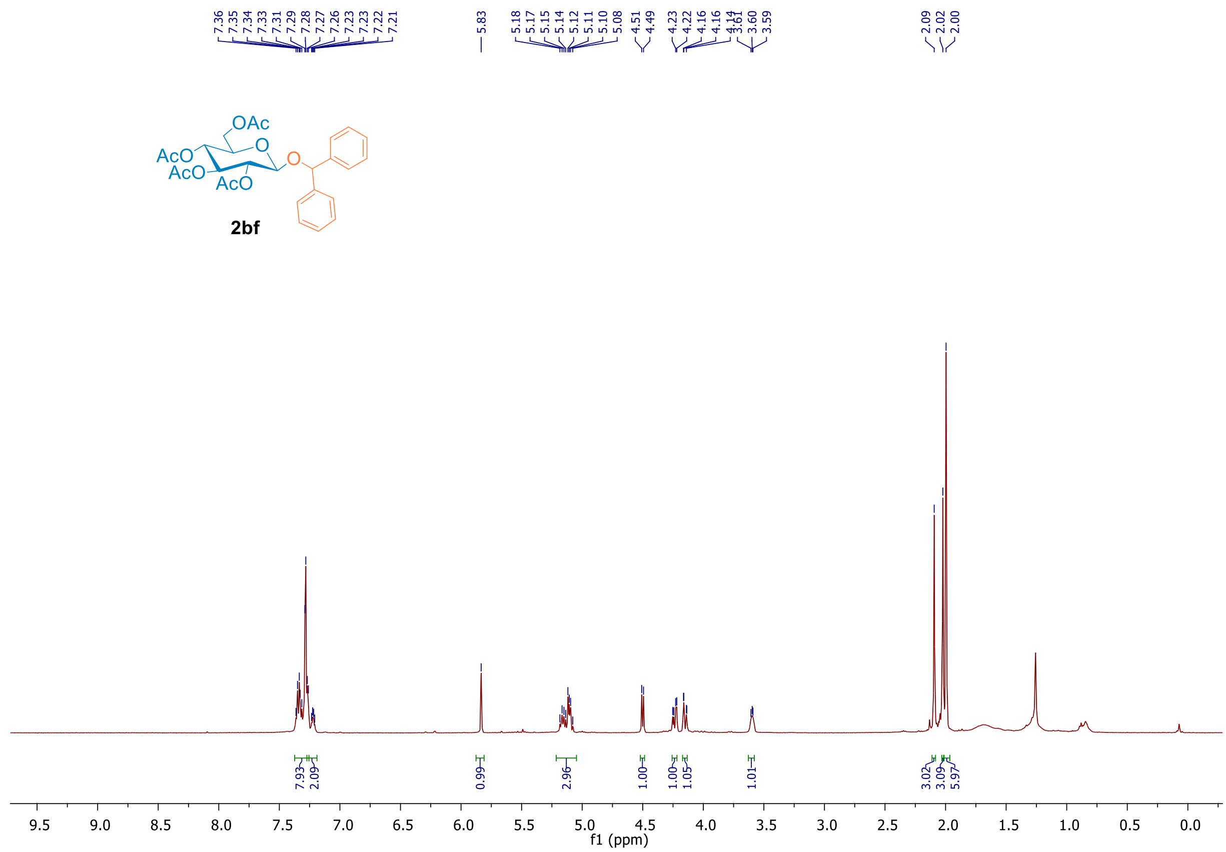


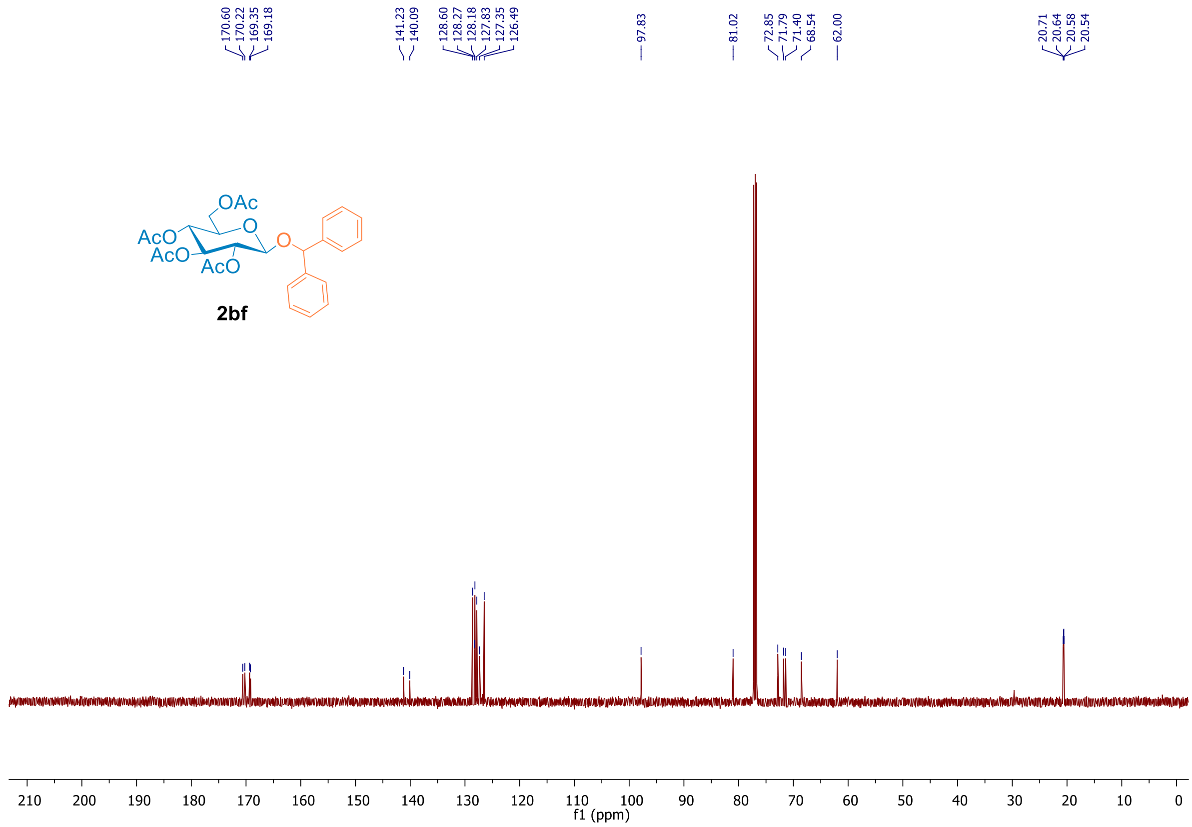
2,3,4,6-tetra-O-pivaloyl-1-O-(diphenyl-carbinyl)-β-D-glucopyranoside 2al:



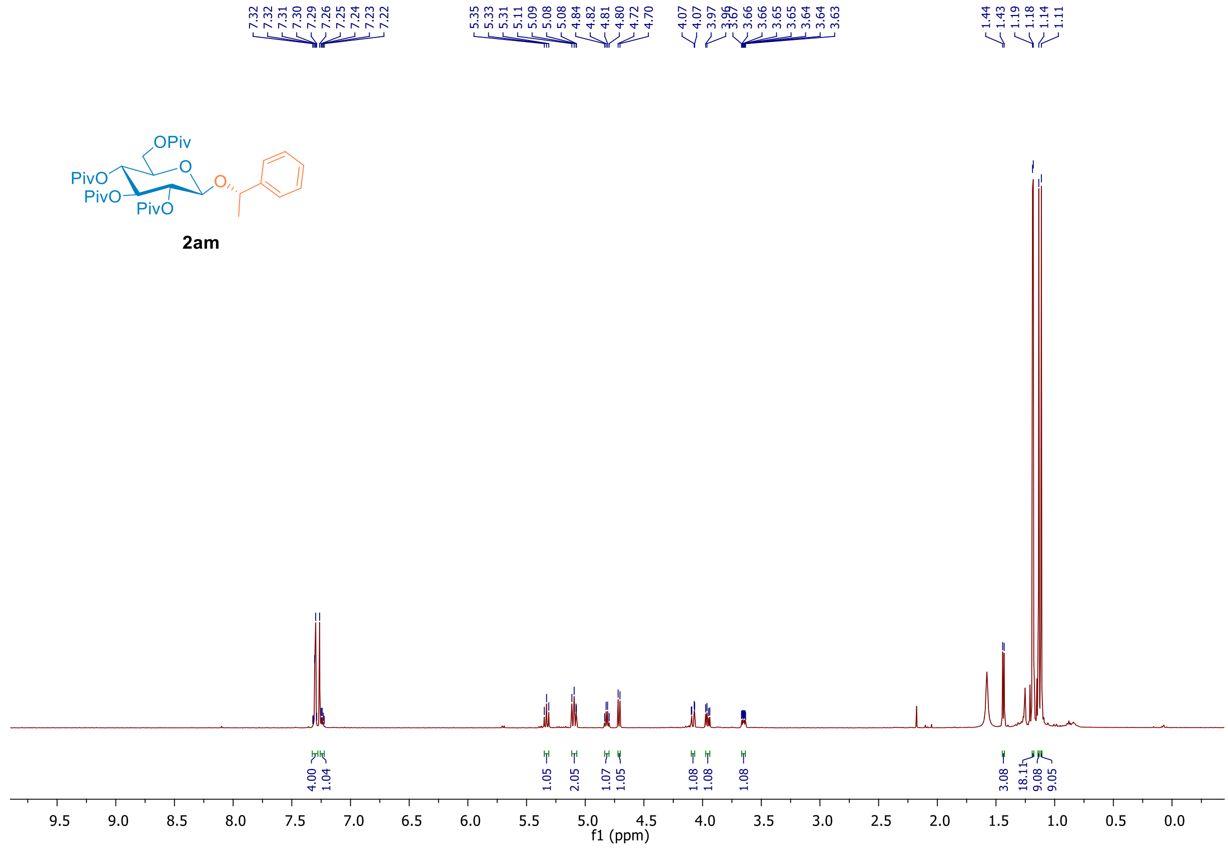


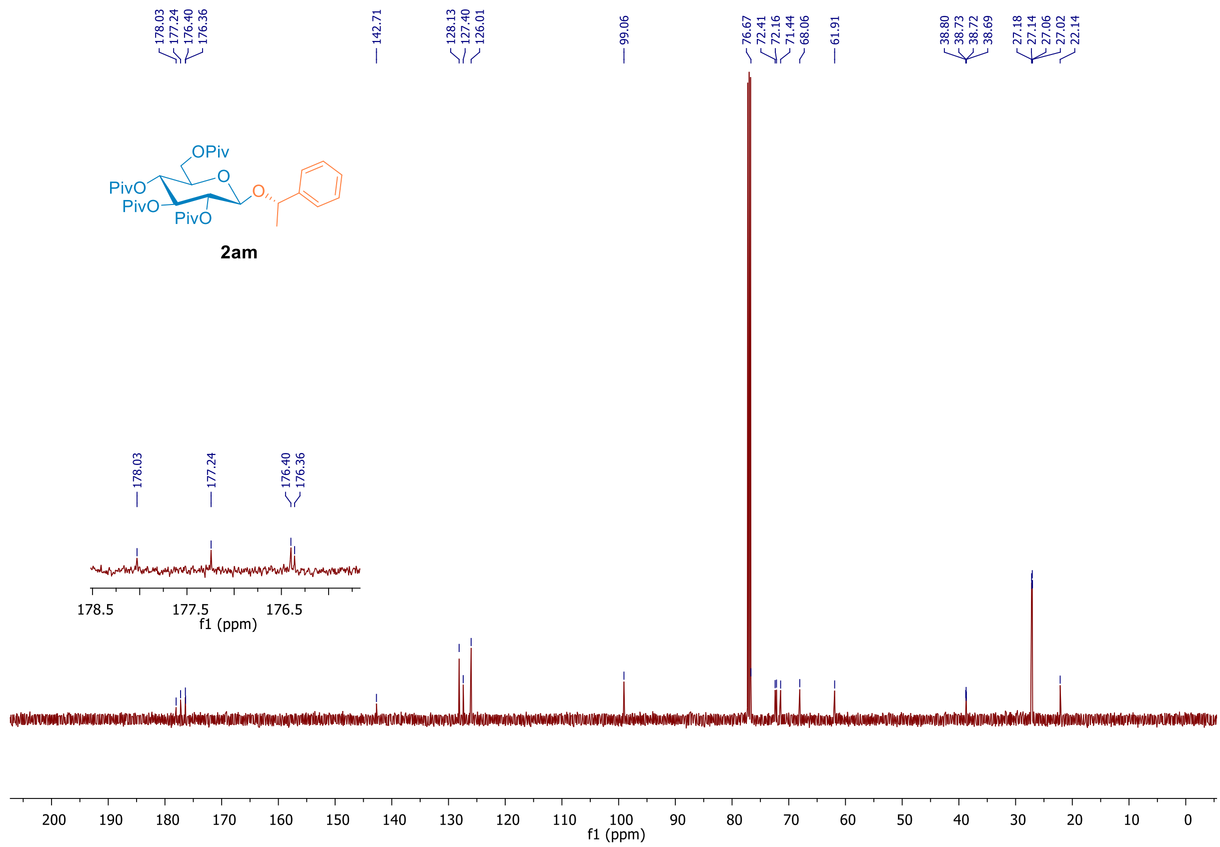
2,3,4,6-tetra-O-acetyl-1-O-(diphenyl-carbinyl)-β-D-glucopyranoside 2bf:



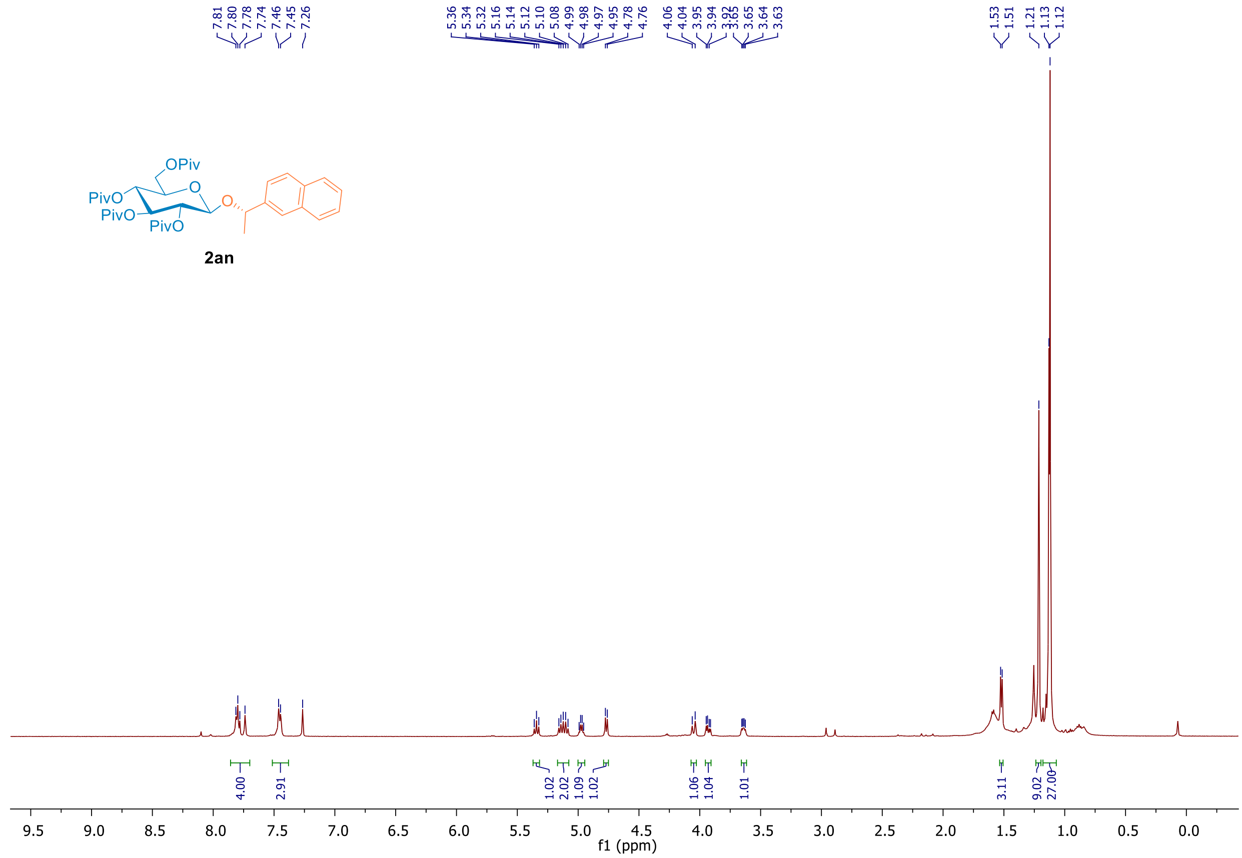


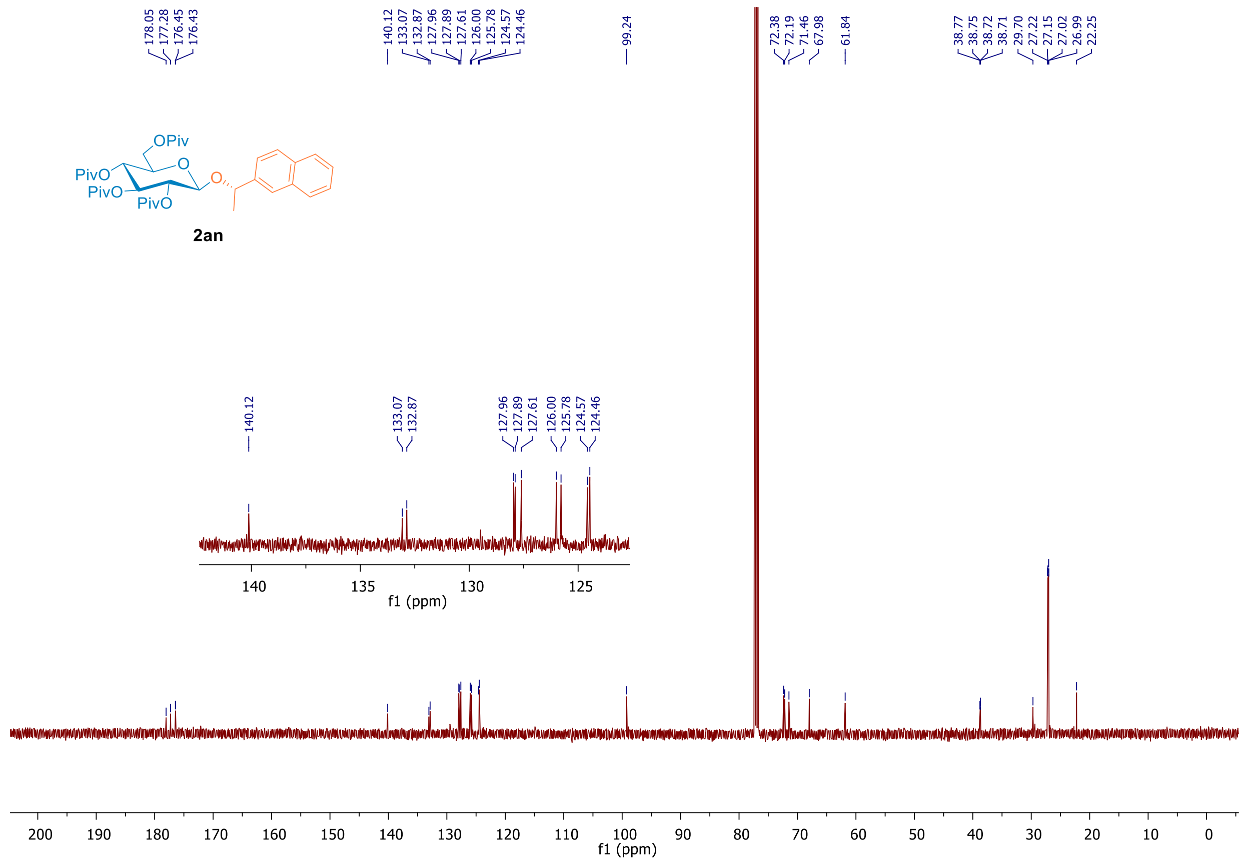
2,3,4,6-tetra-O-pivaloyl-1-O-(1-phenylethyl)-β-D-glucopyranoside 2am:



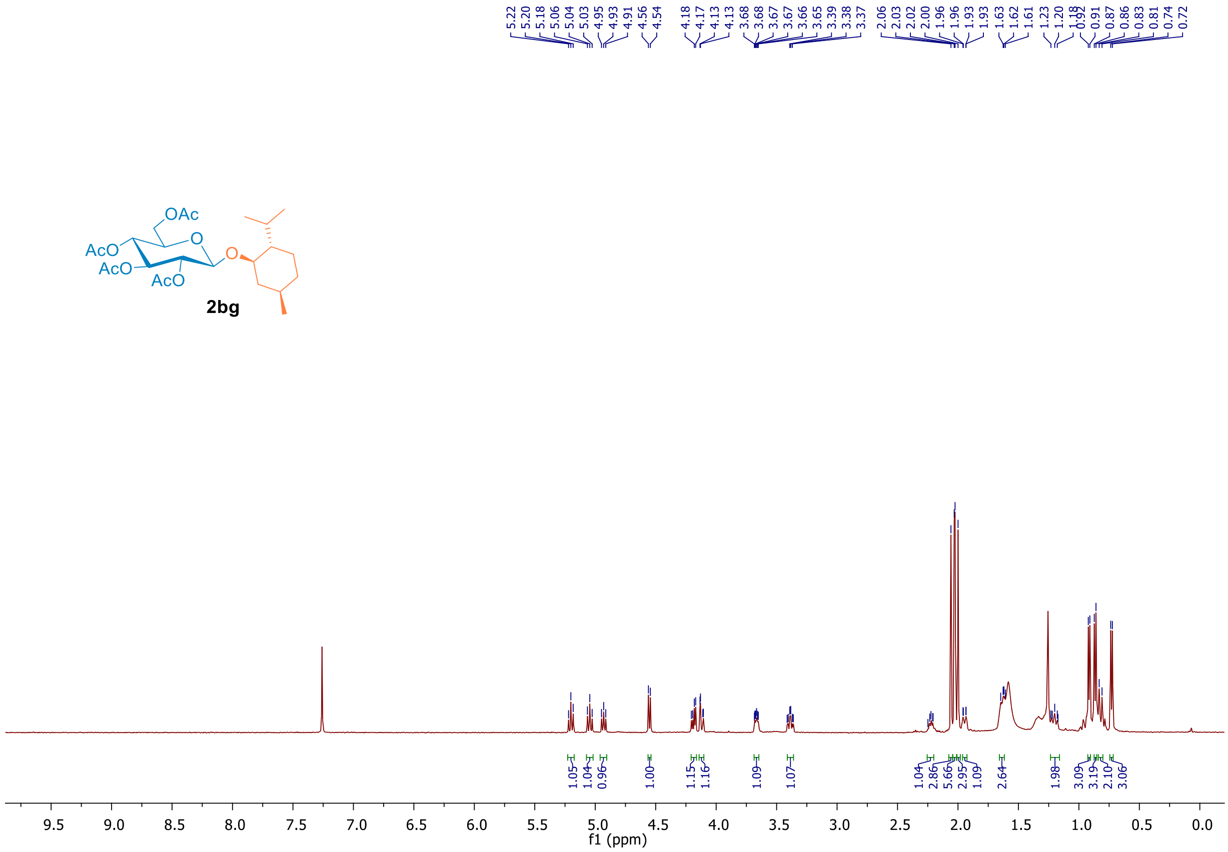


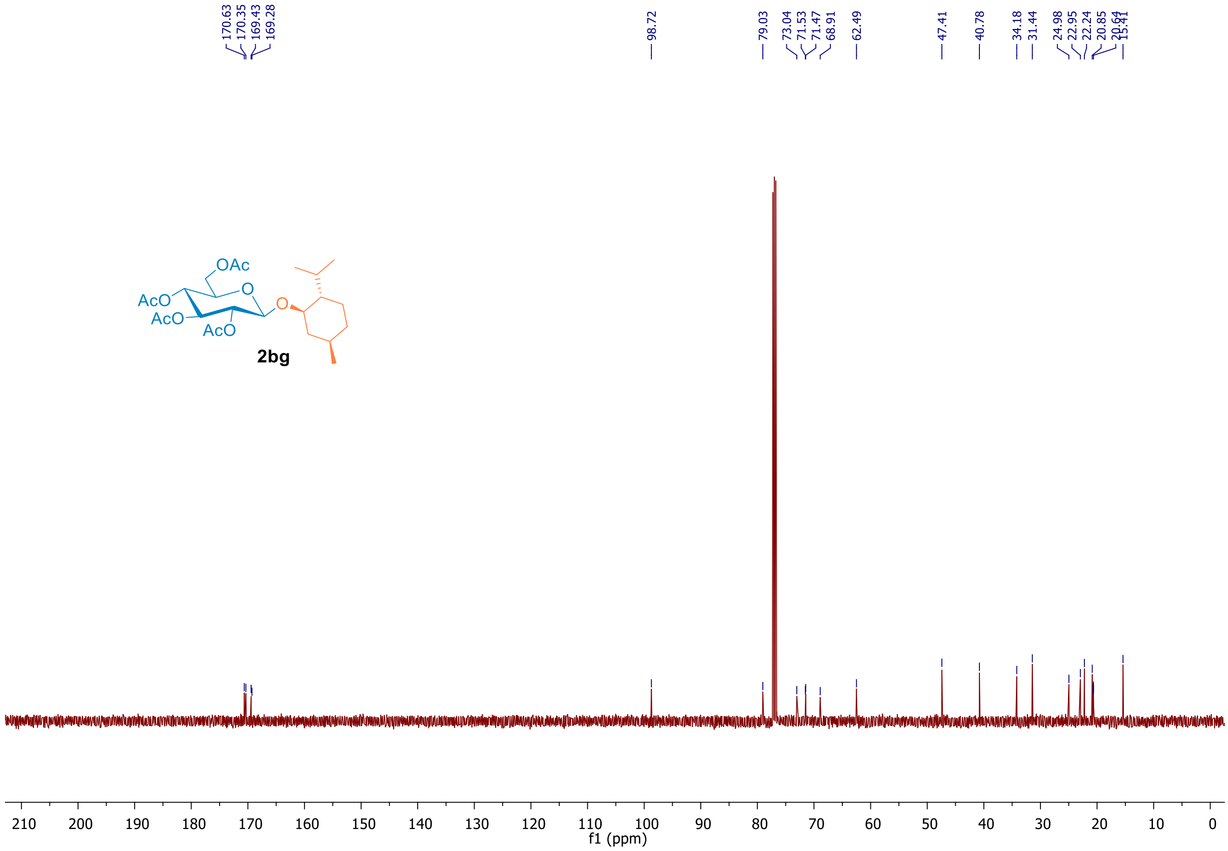
2,3,4,6-tetra-O-pivaloyl-1-O-(naphthyl)-β-D-glucopyranoside 2an:



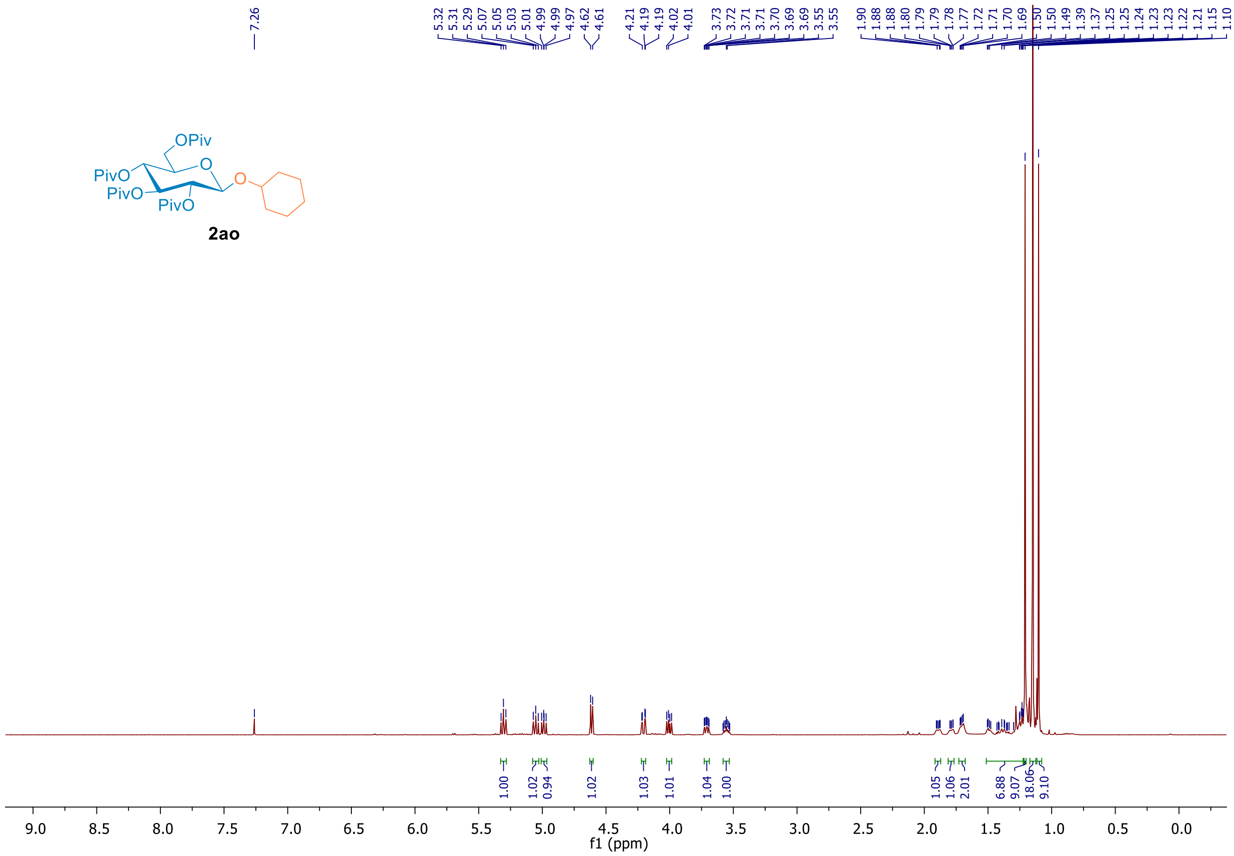


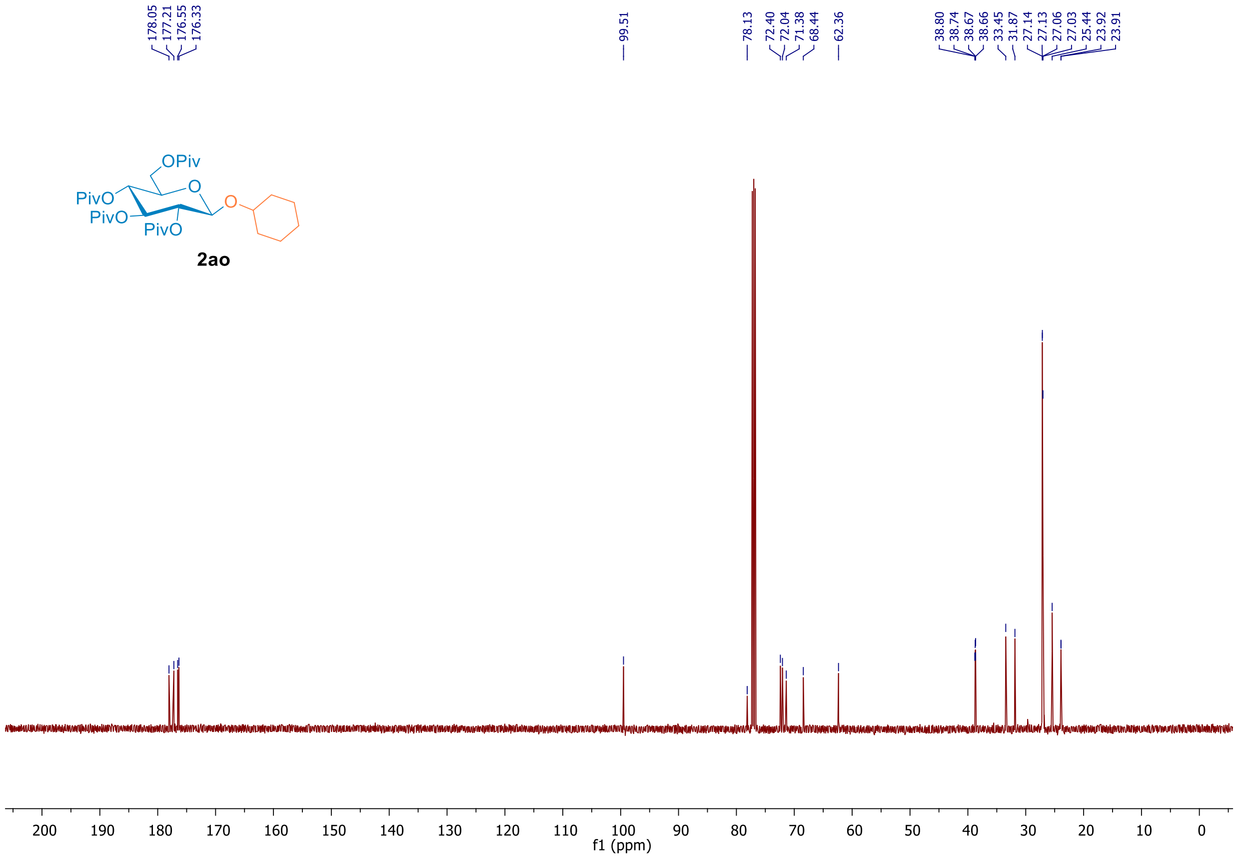
2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-β-D-glucopyranoside 2bg:



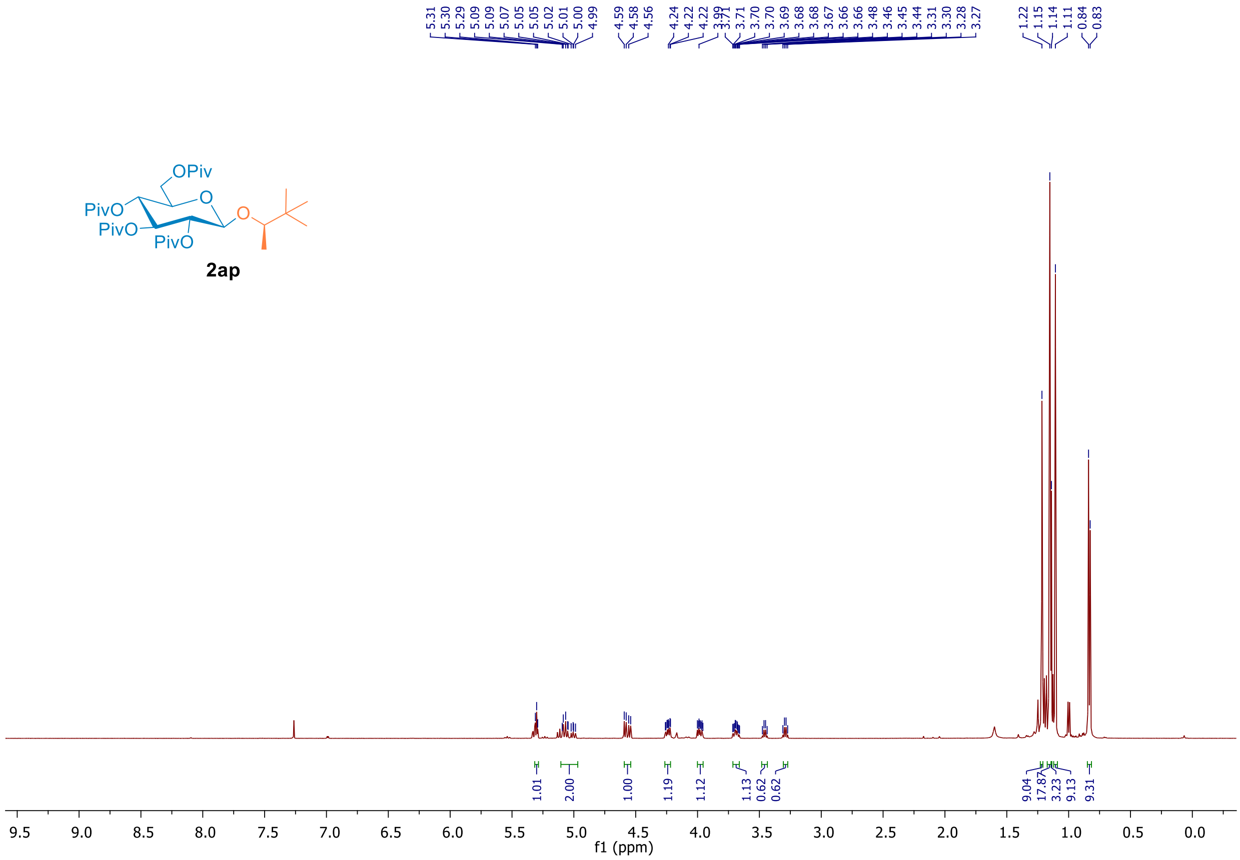


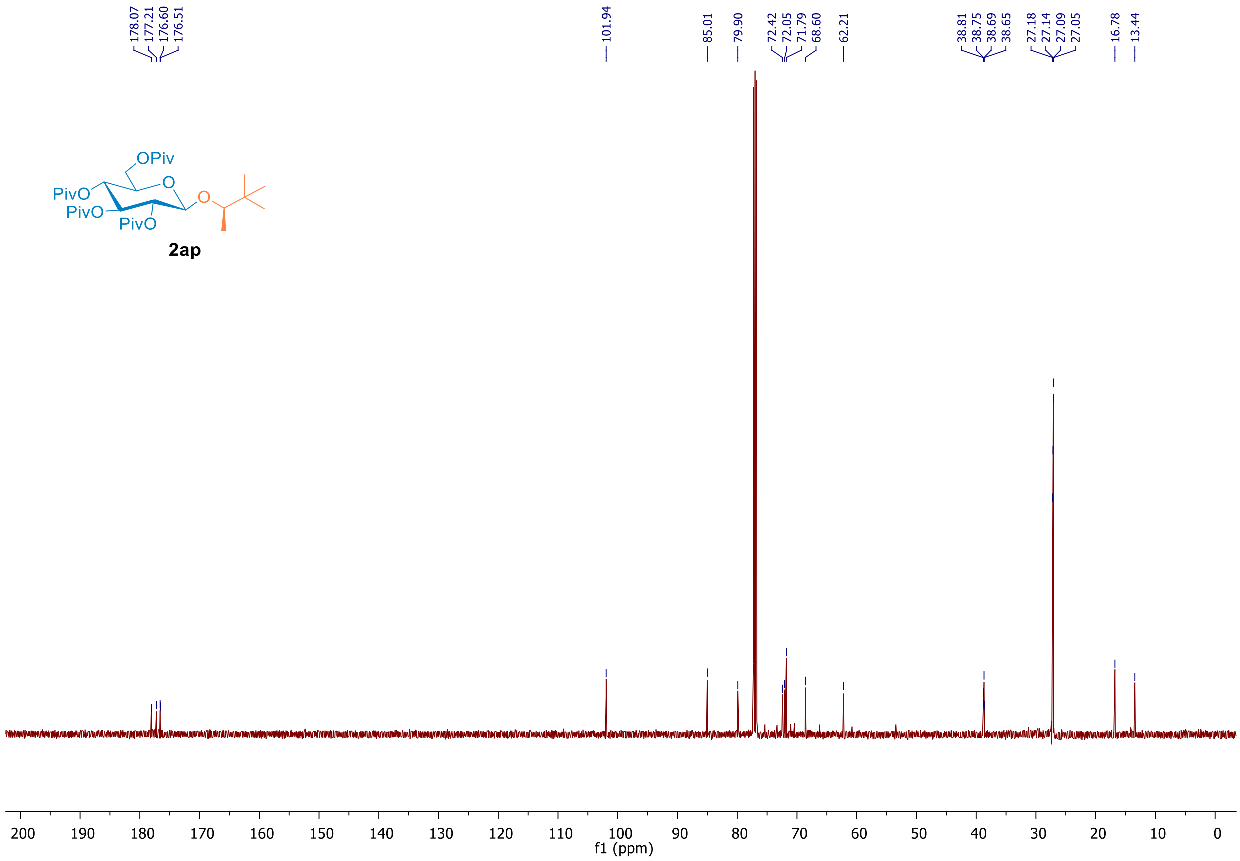
2,3,4,6-tetra-O-pivaloyl-1-O-(cyclohexyl)-β-D-glucopyranoside 2ao:



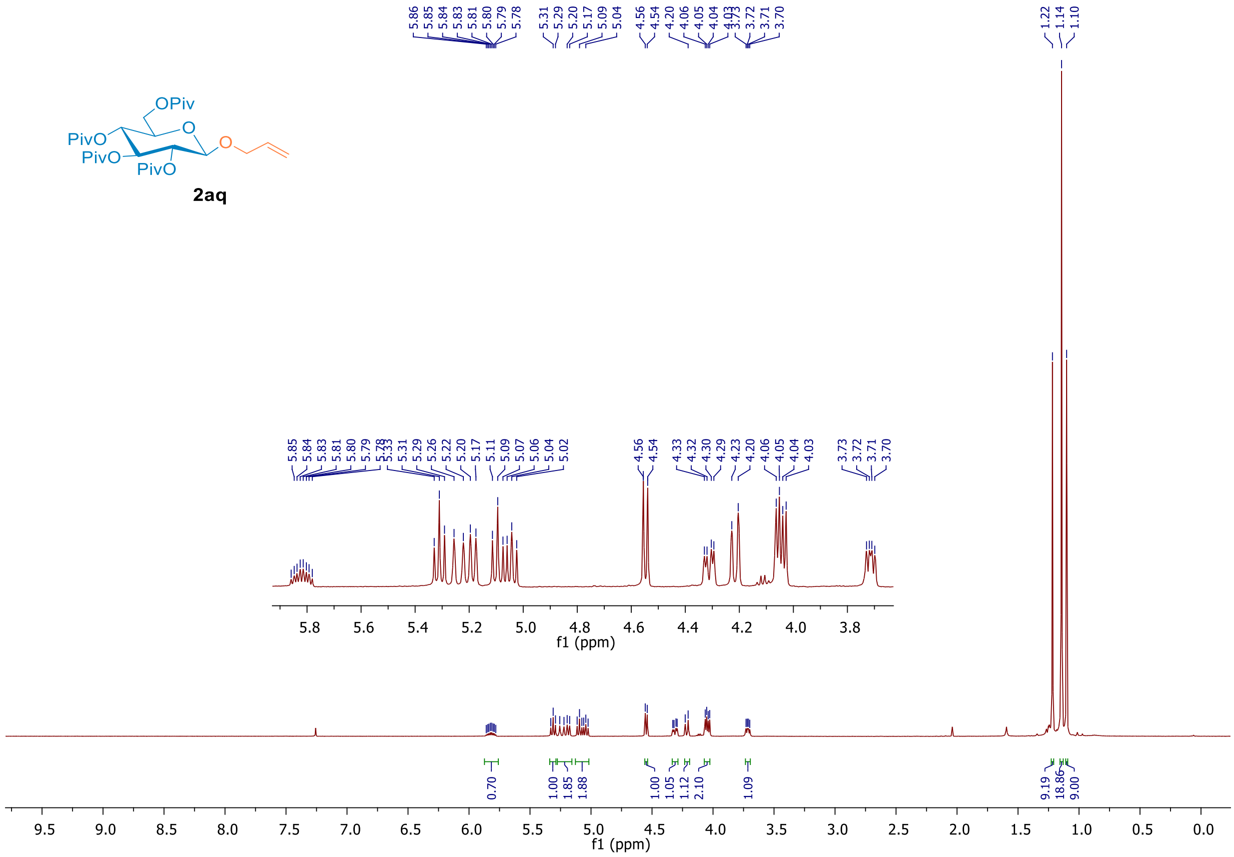


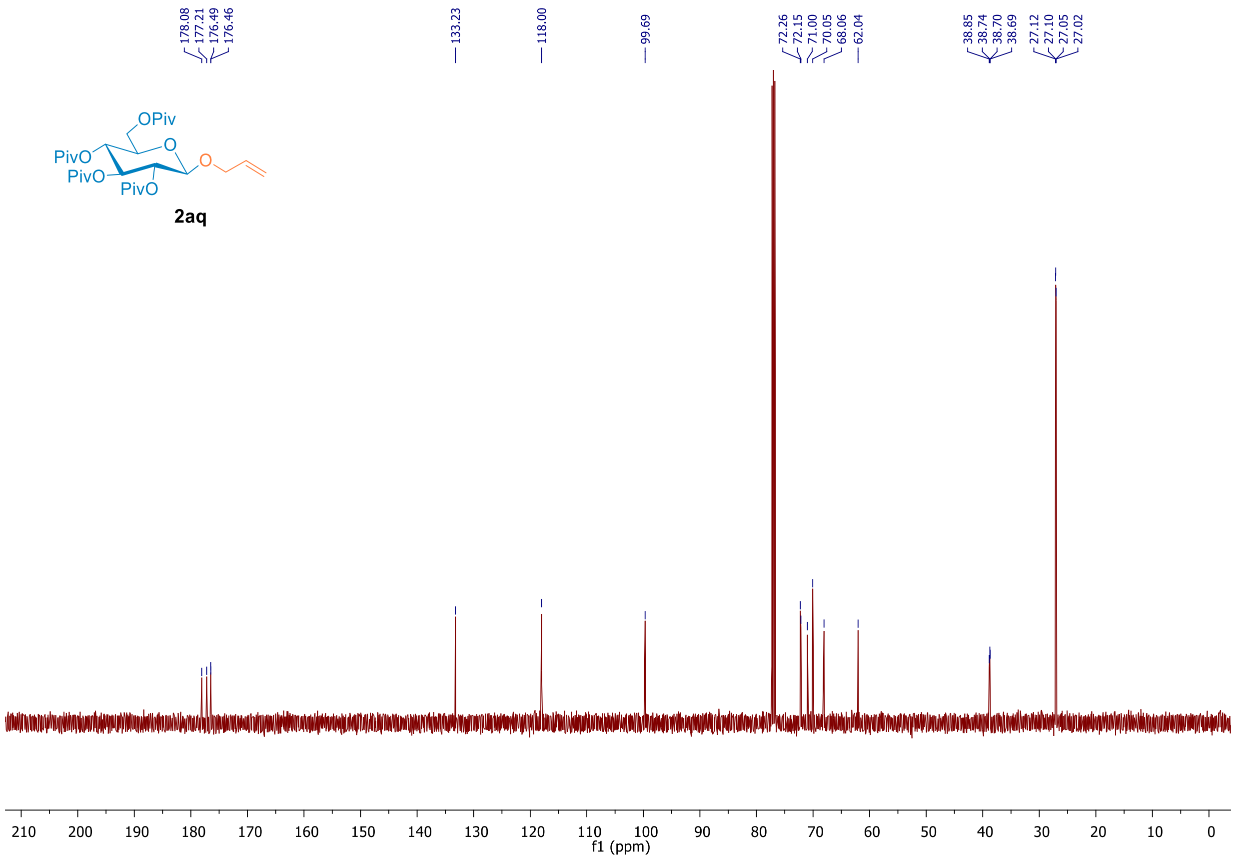
2,3,4,6-tetra-O-pivaloyl-1-O-(3,3-dimethyl-2-butyl)-β-D-glucopyranoside 2ap:



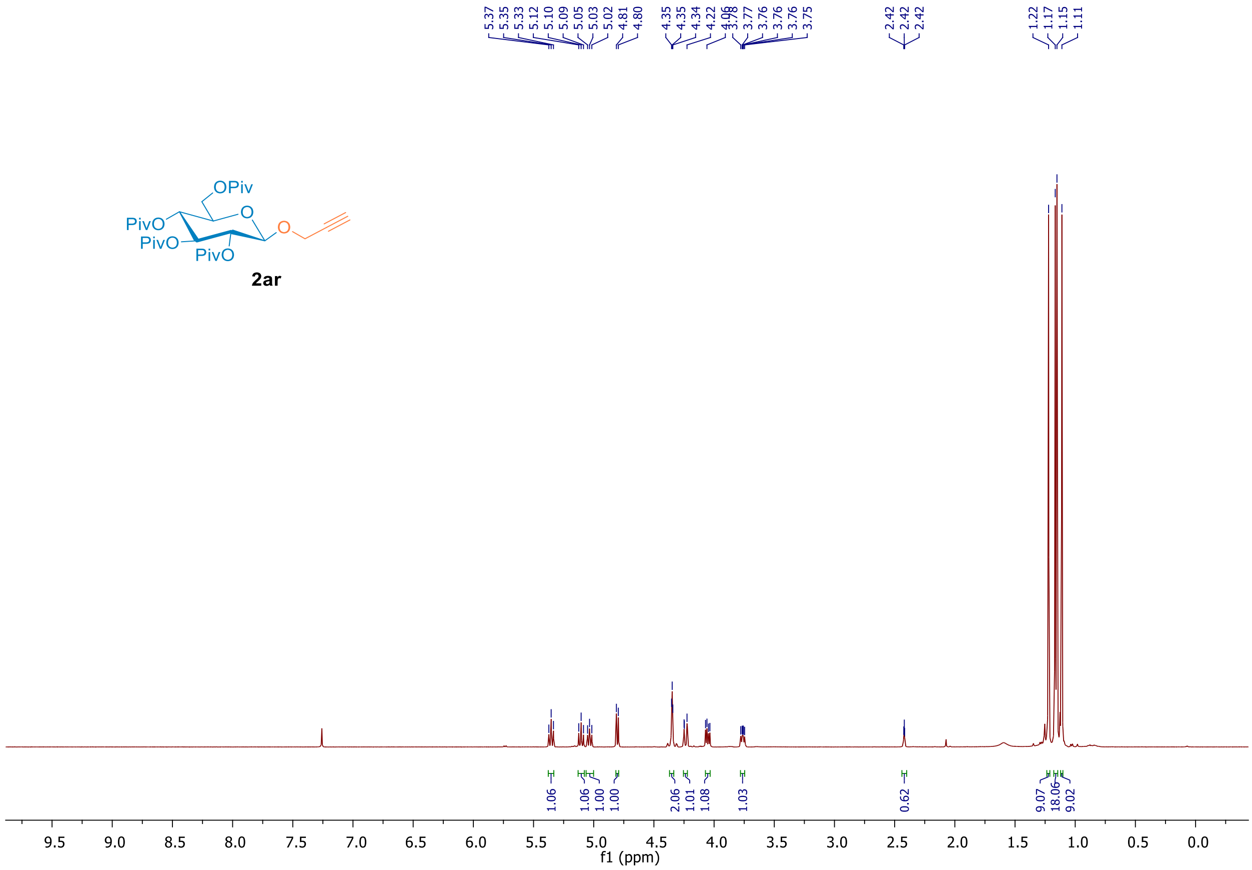


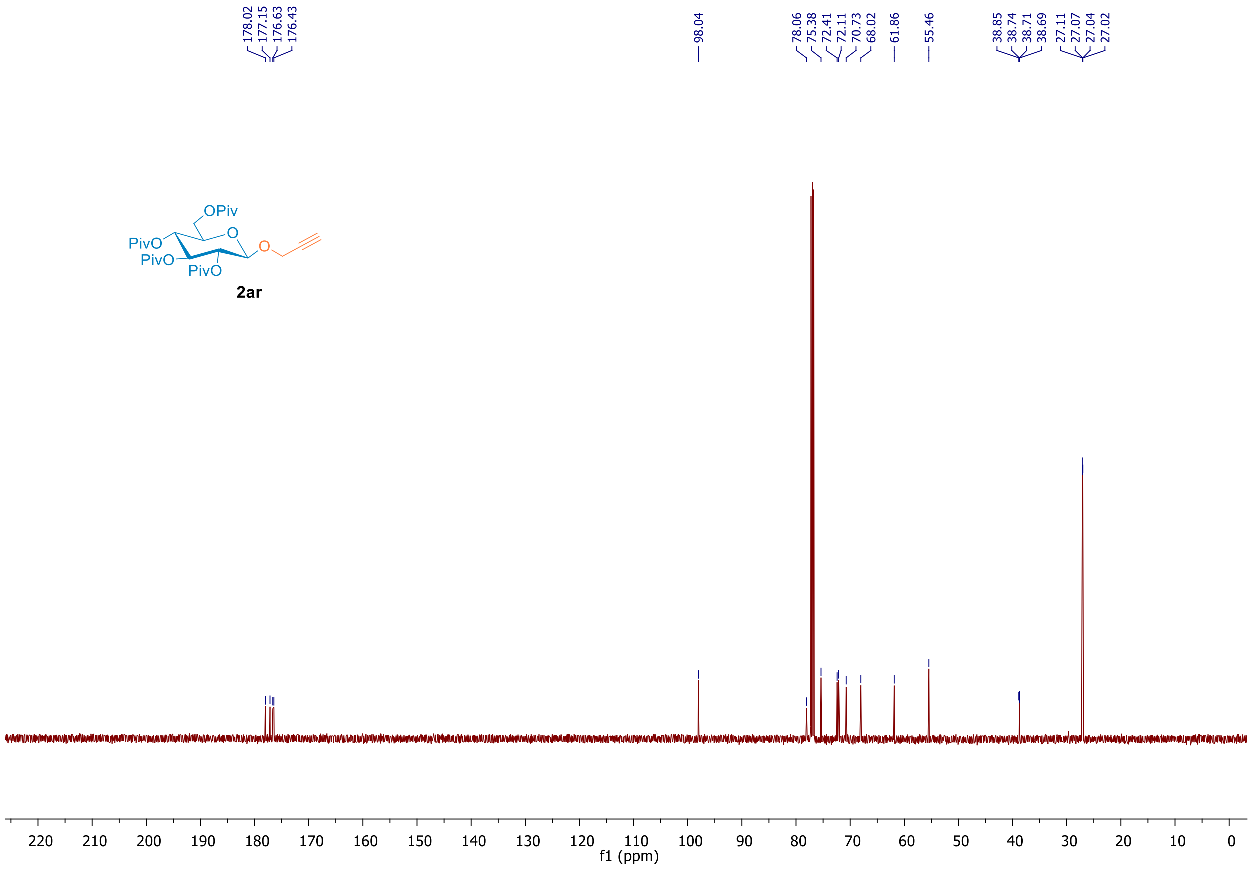
2,3,4,6-tetra-O-pivaloyl-1-O-(allyl)-β-D-glucopyranoside 2aq:



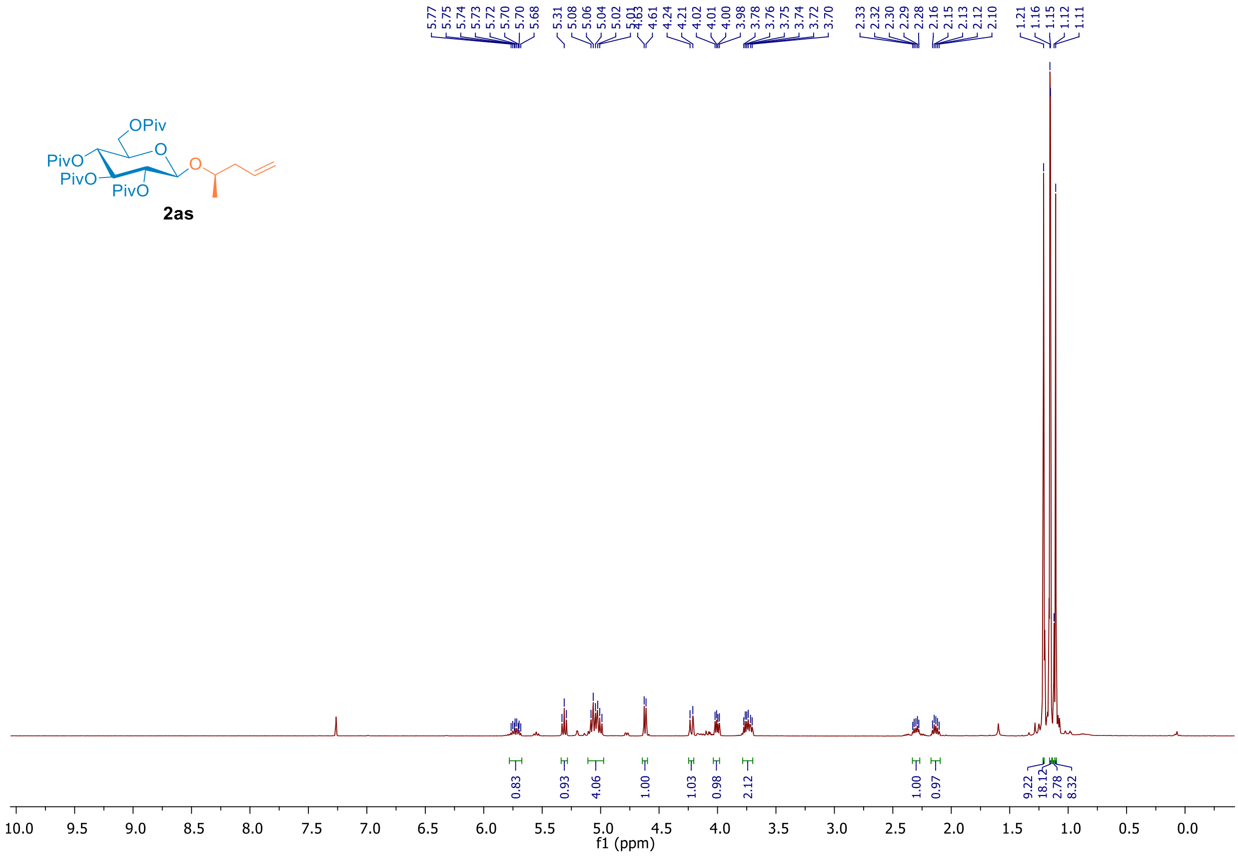


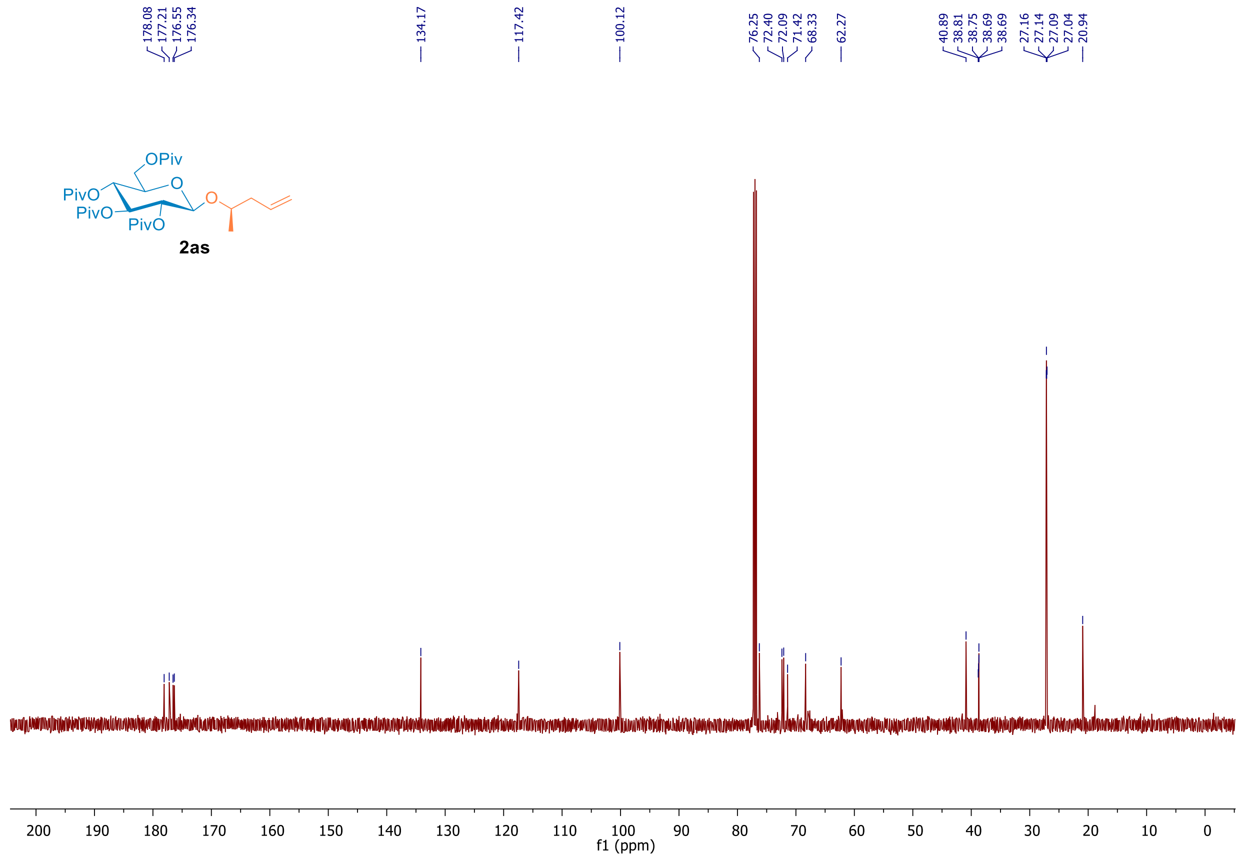
2,3,4,6-tetra-O-pivaloyl-1-O-(propargyl)-β-D-glucopyranoside 2ar:



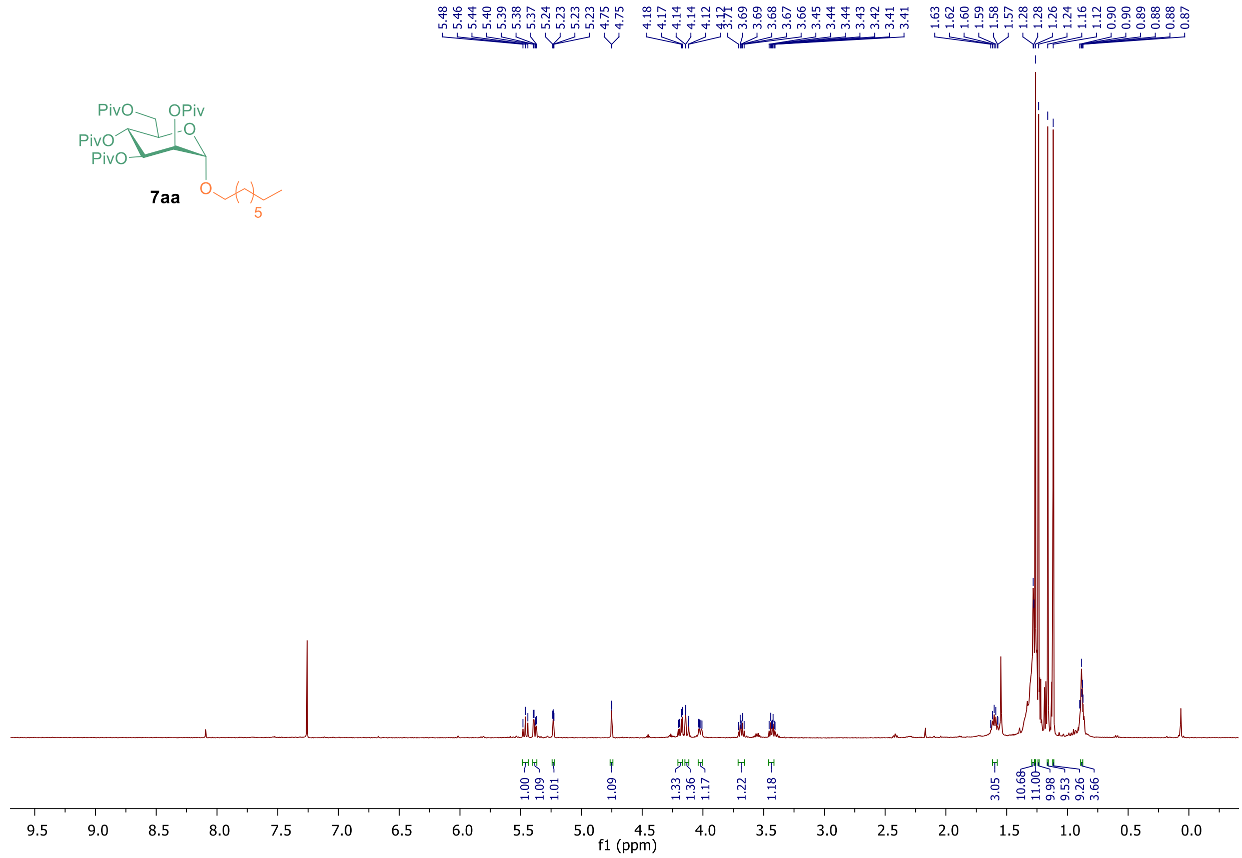


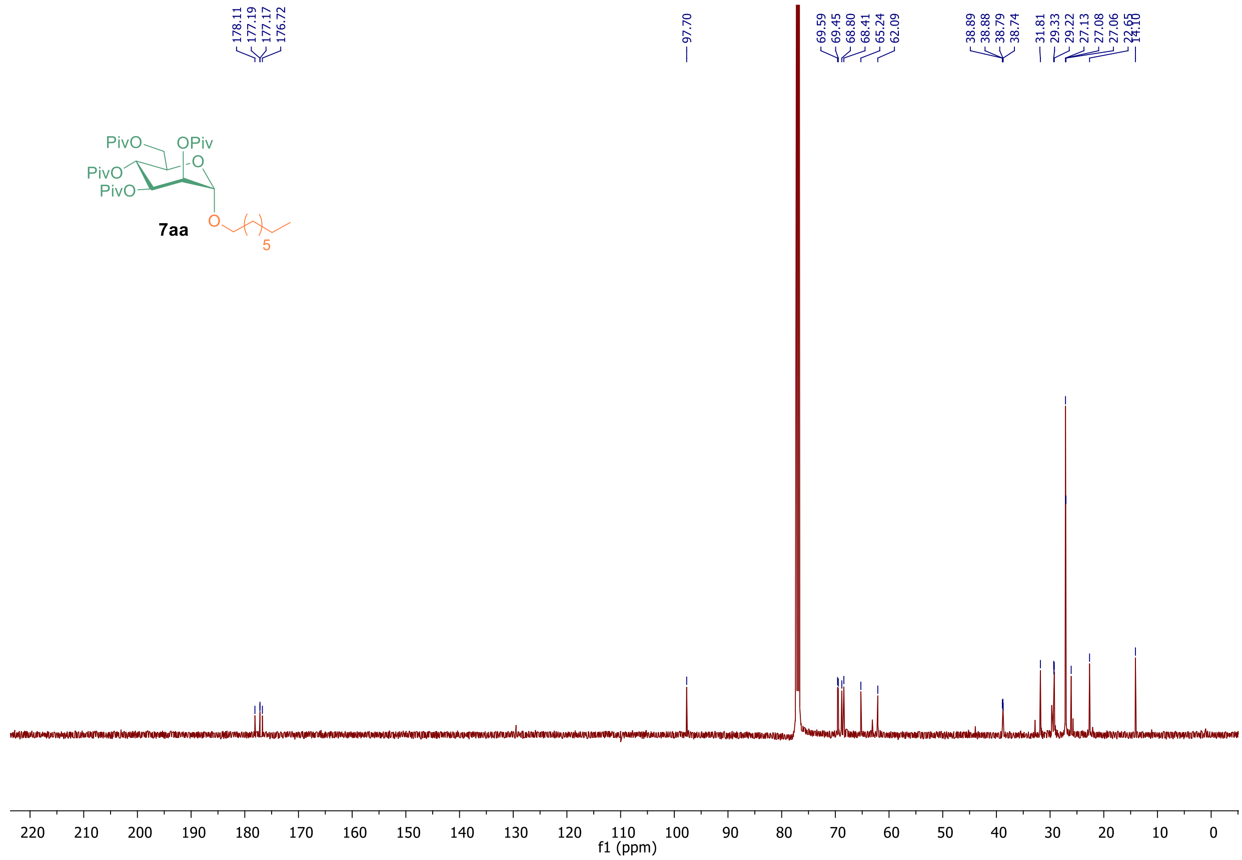
2,3,4,6-tetra-O-pivaloyl-1-O-(4-pentenyl)-β-D-glucopyranoside 2as:



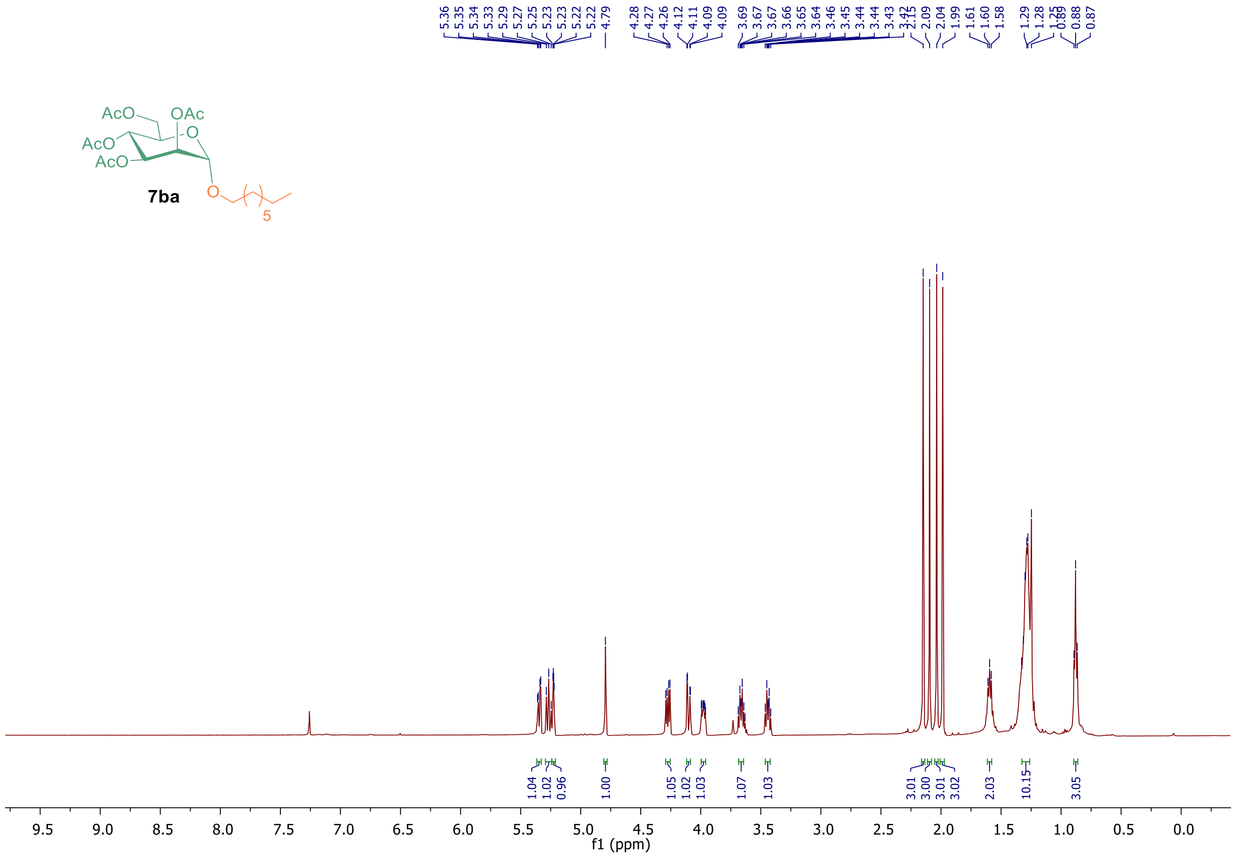


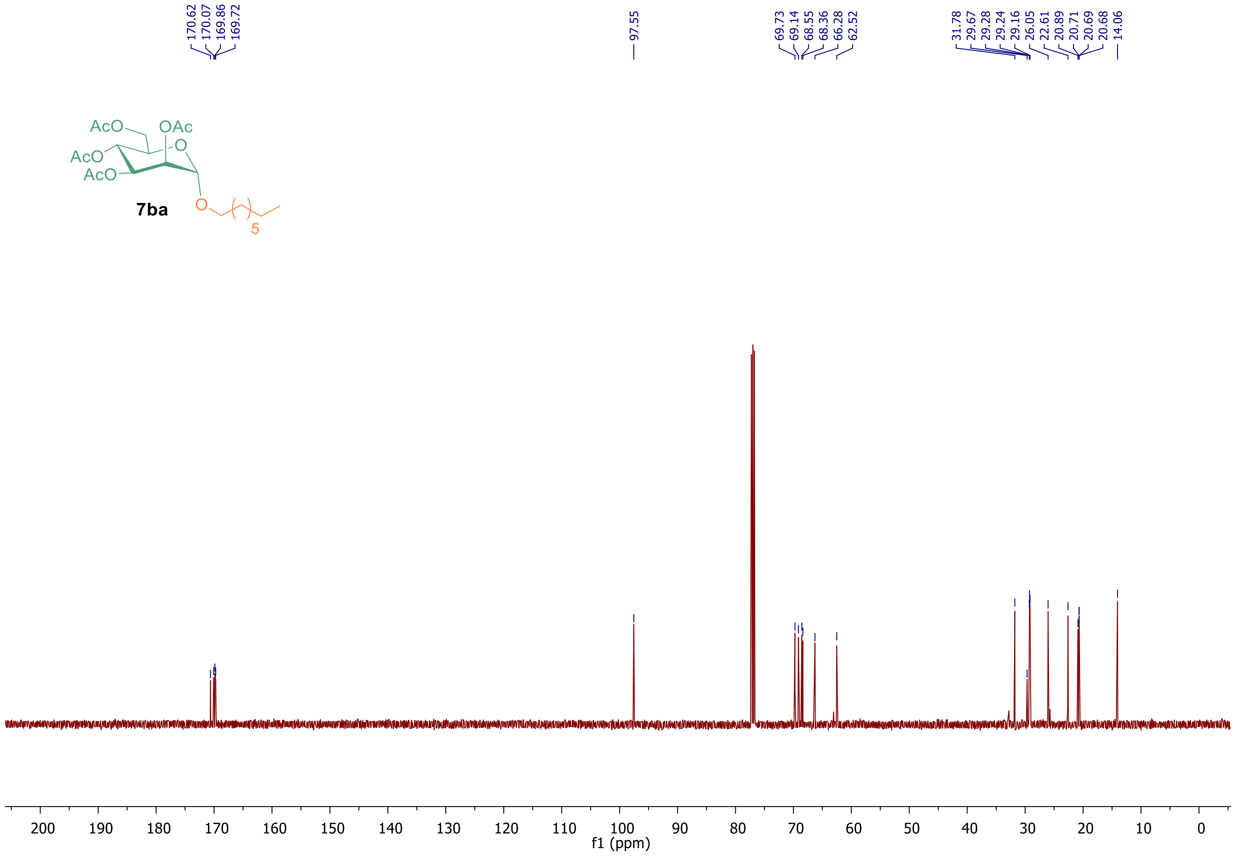
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-a-D-mannopyranoside 7aa:





2,3,4,6-tetra-O-acetyl-1-O-(octyl)-a-D-mannopyranoside 7ba:





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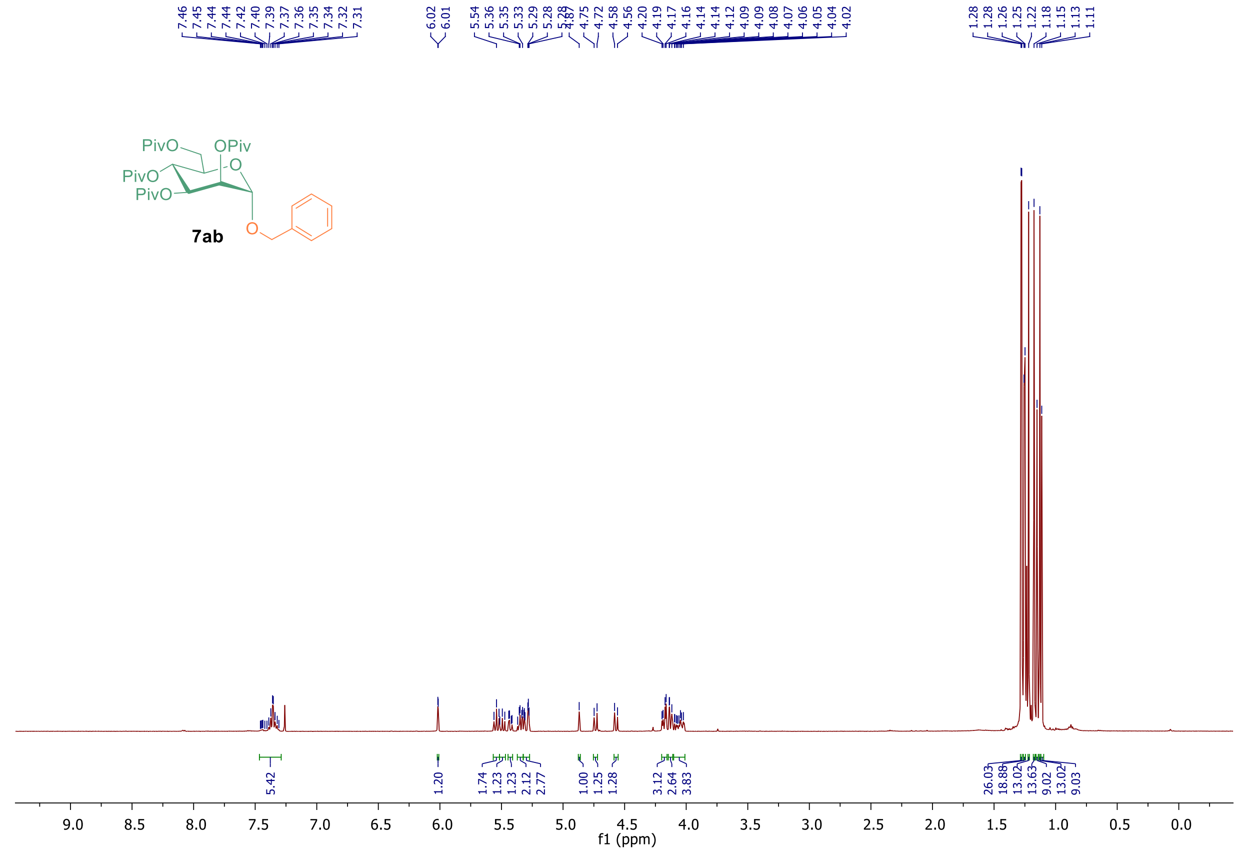
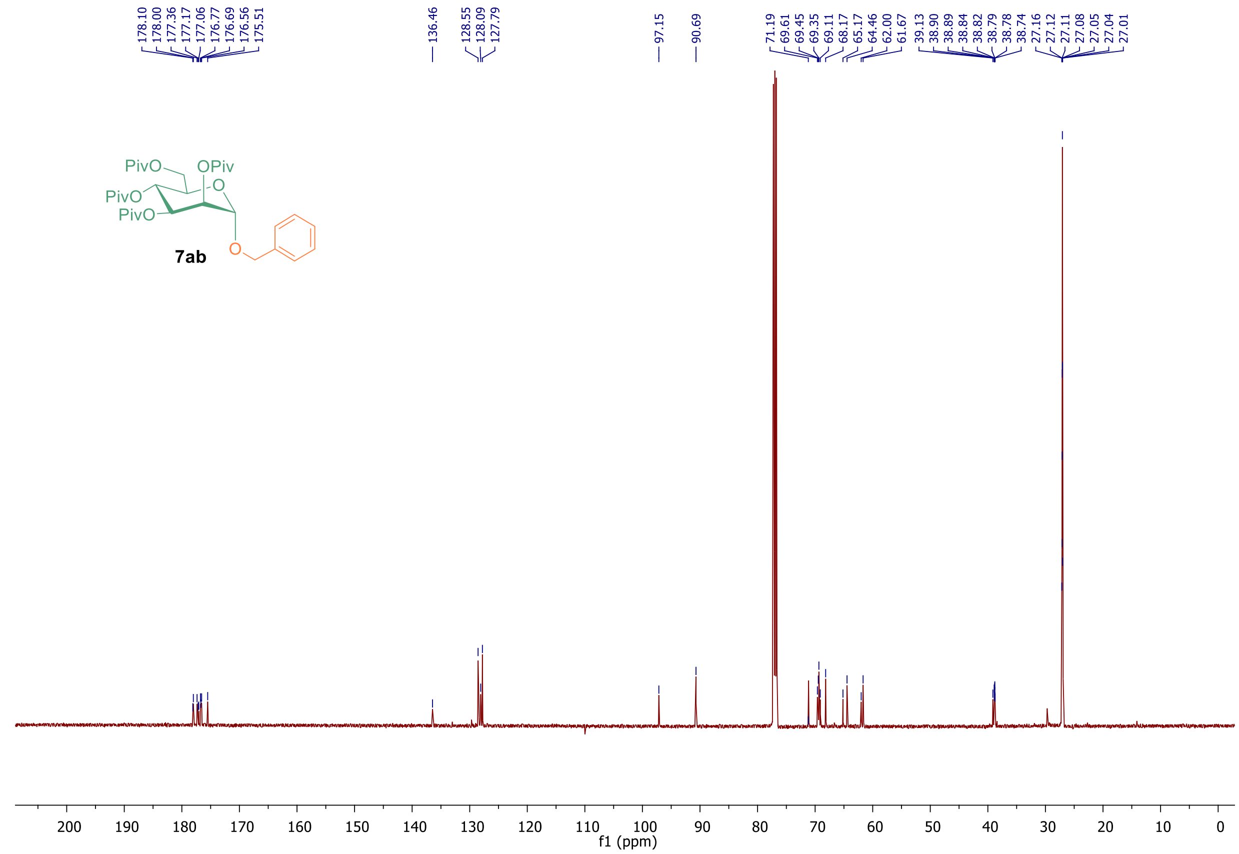
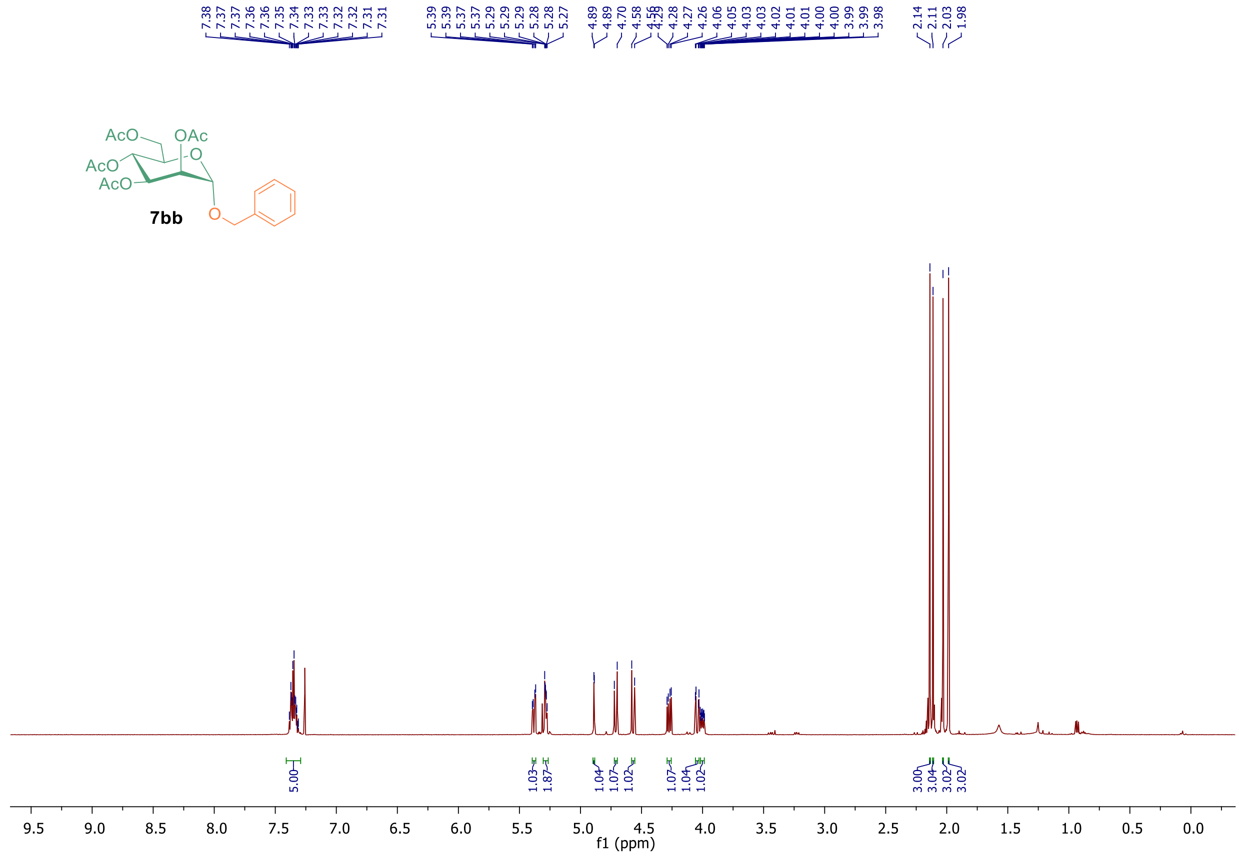
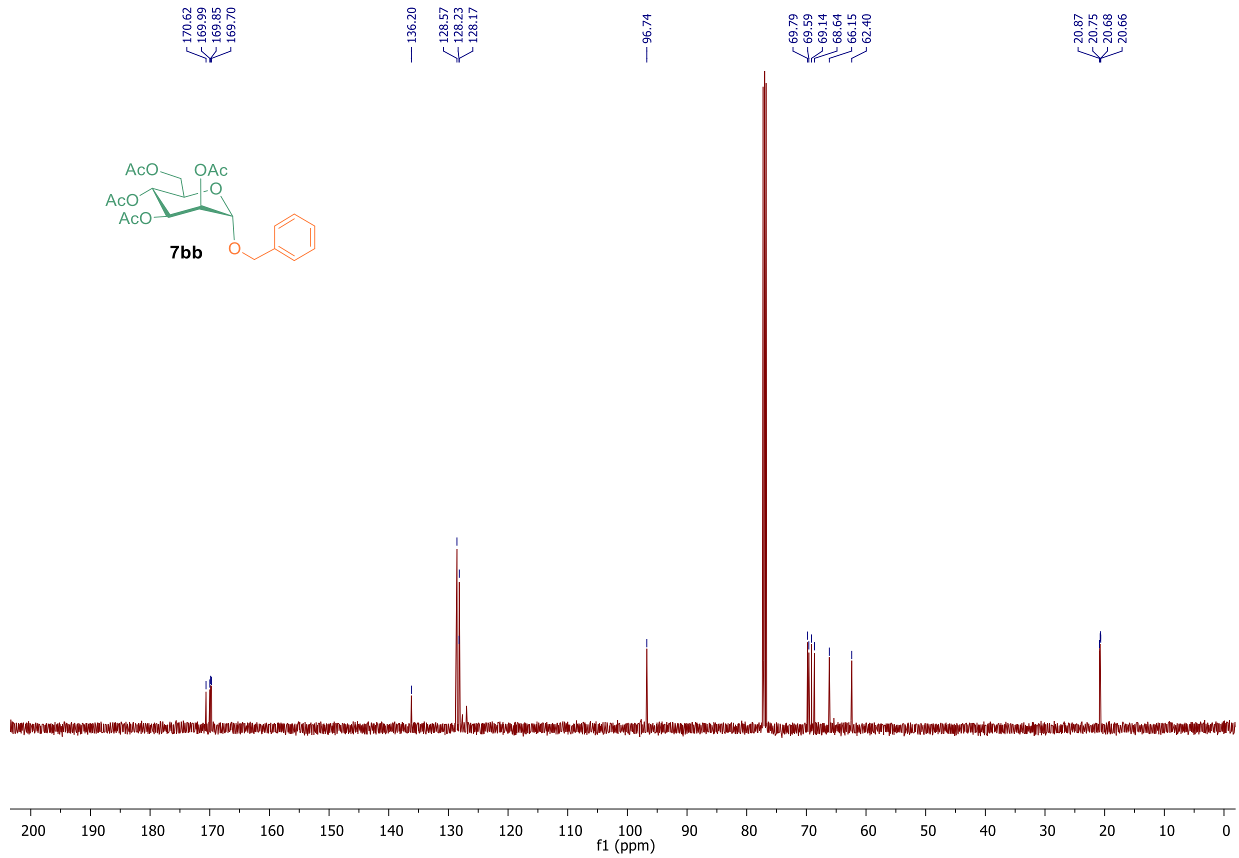


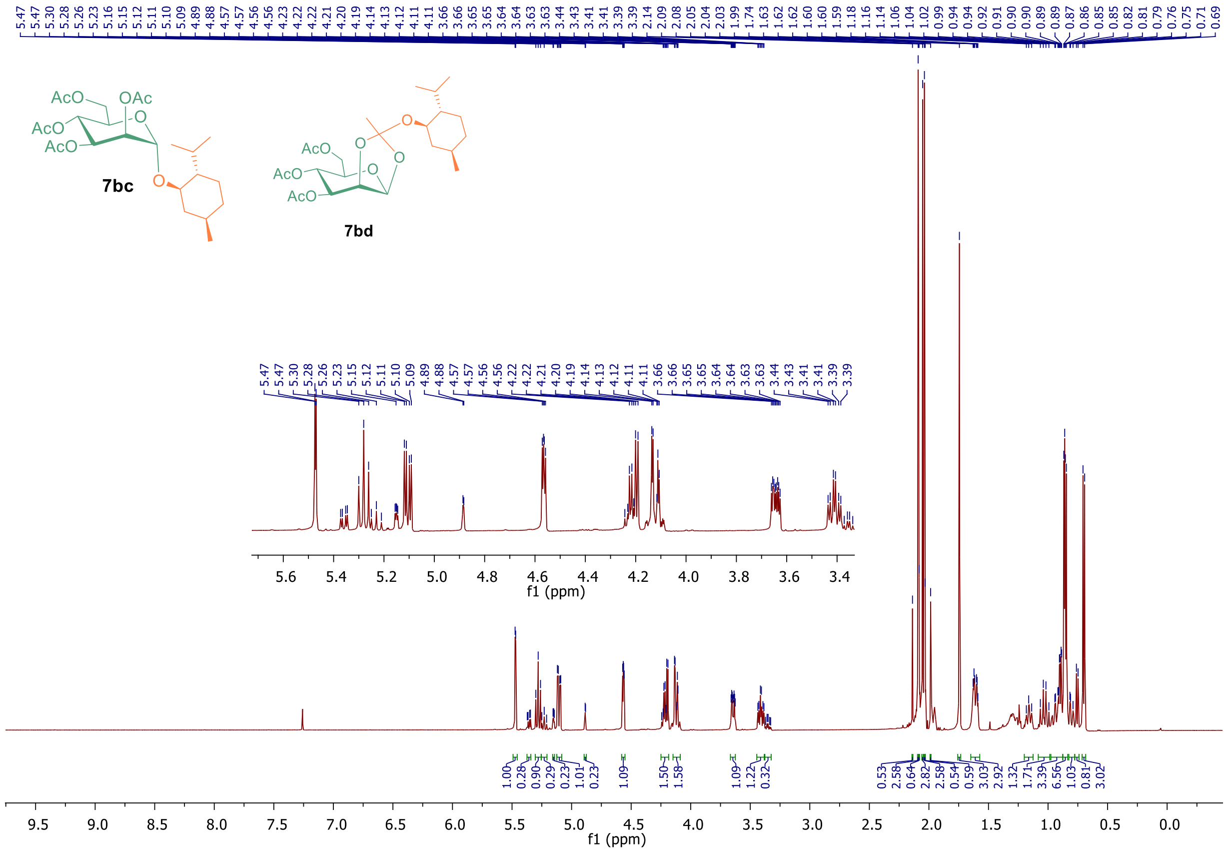


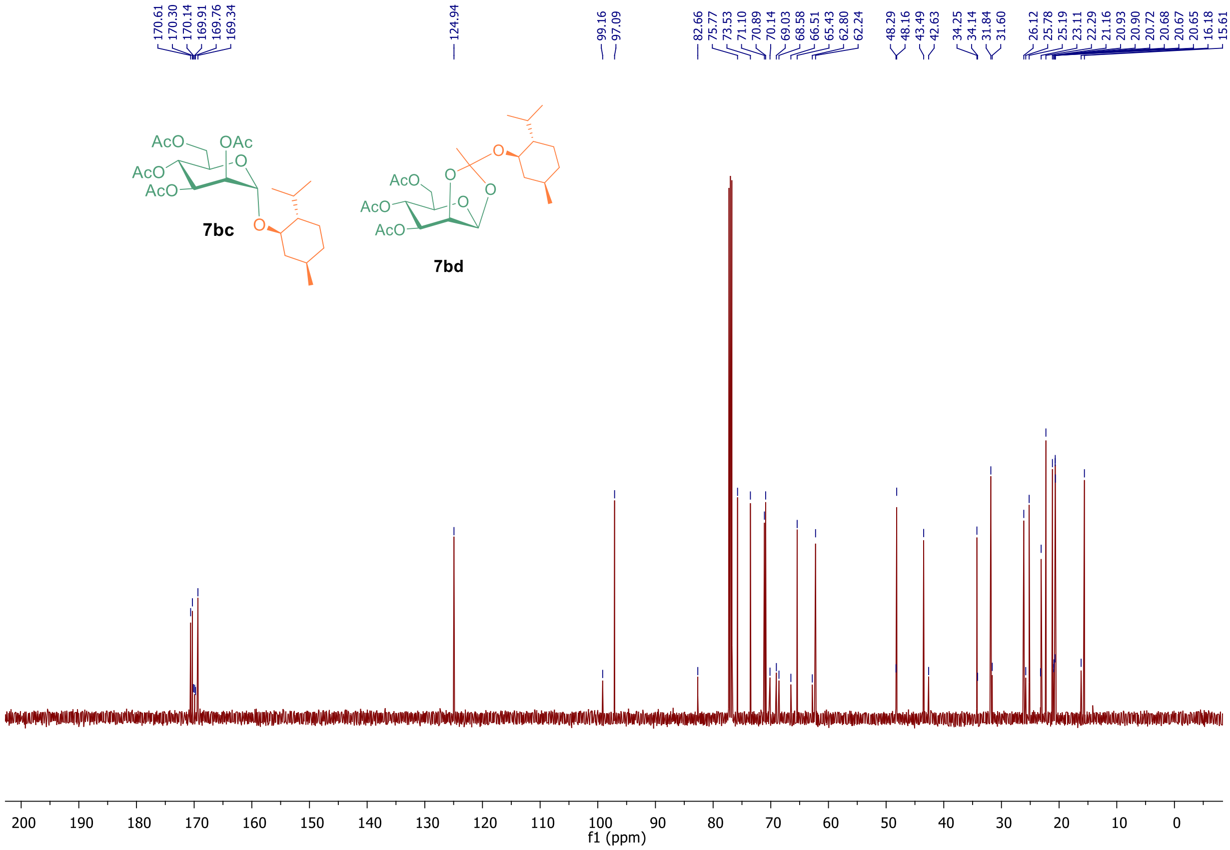
2,3,4,6-tetra-O-acetyl-1-O-(benzyl)-a-D-mannopyranoside 7bb:



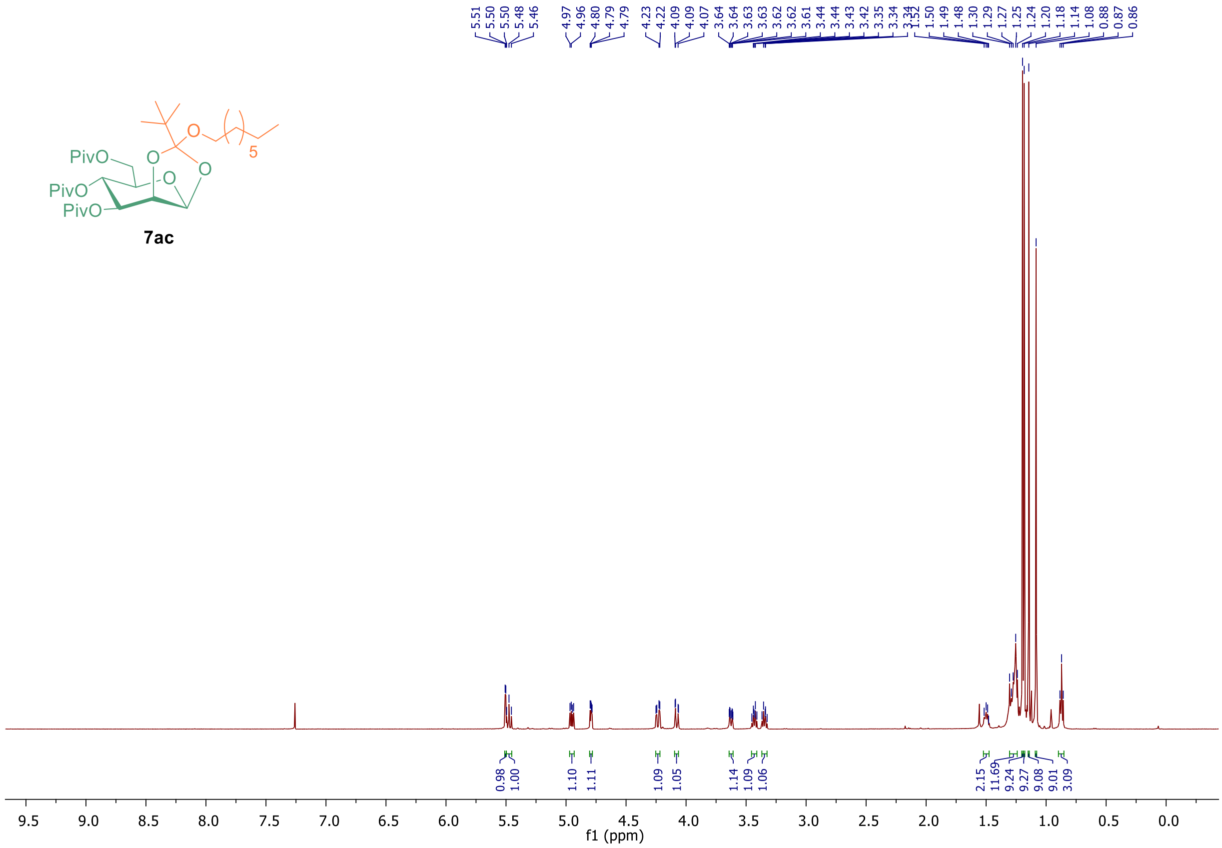


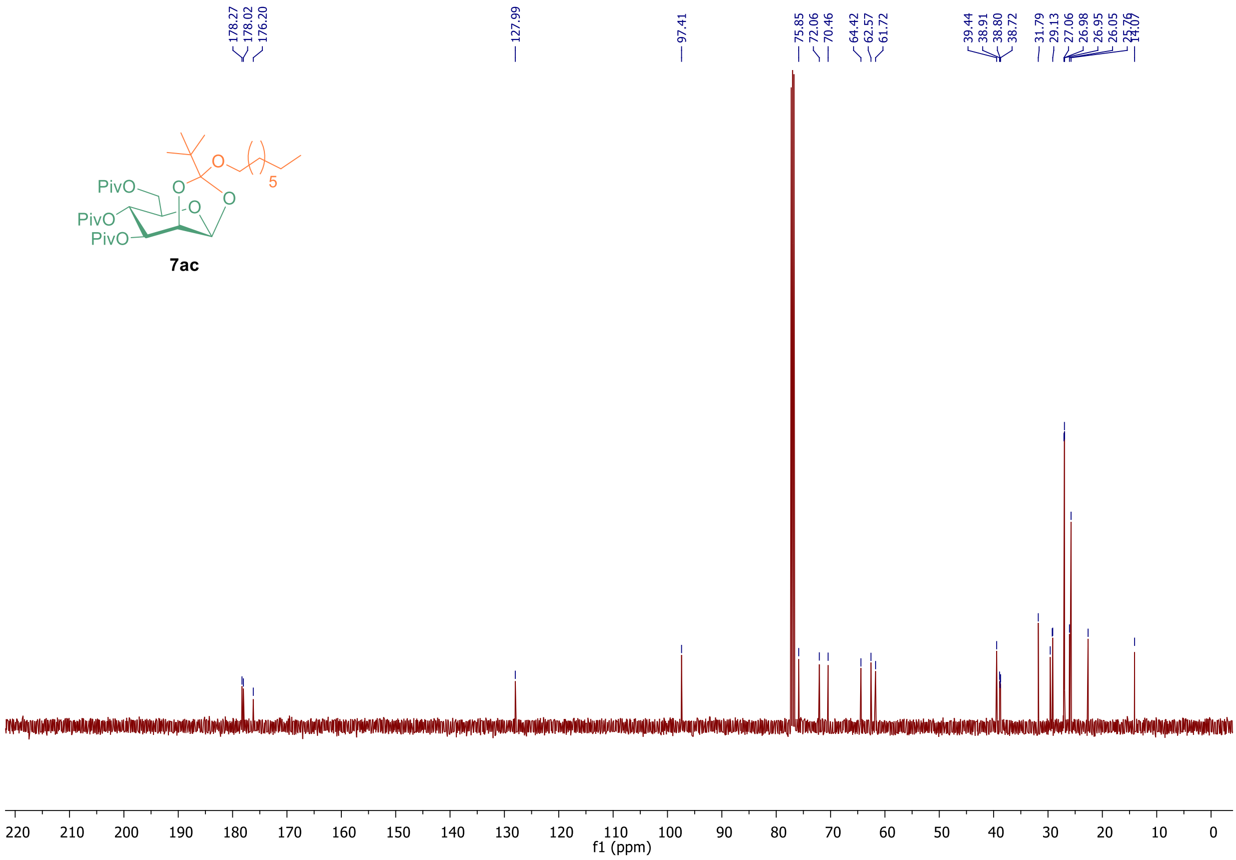
2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-a-D-mannopyranoside 7bc** with ortho-ester **7bd:



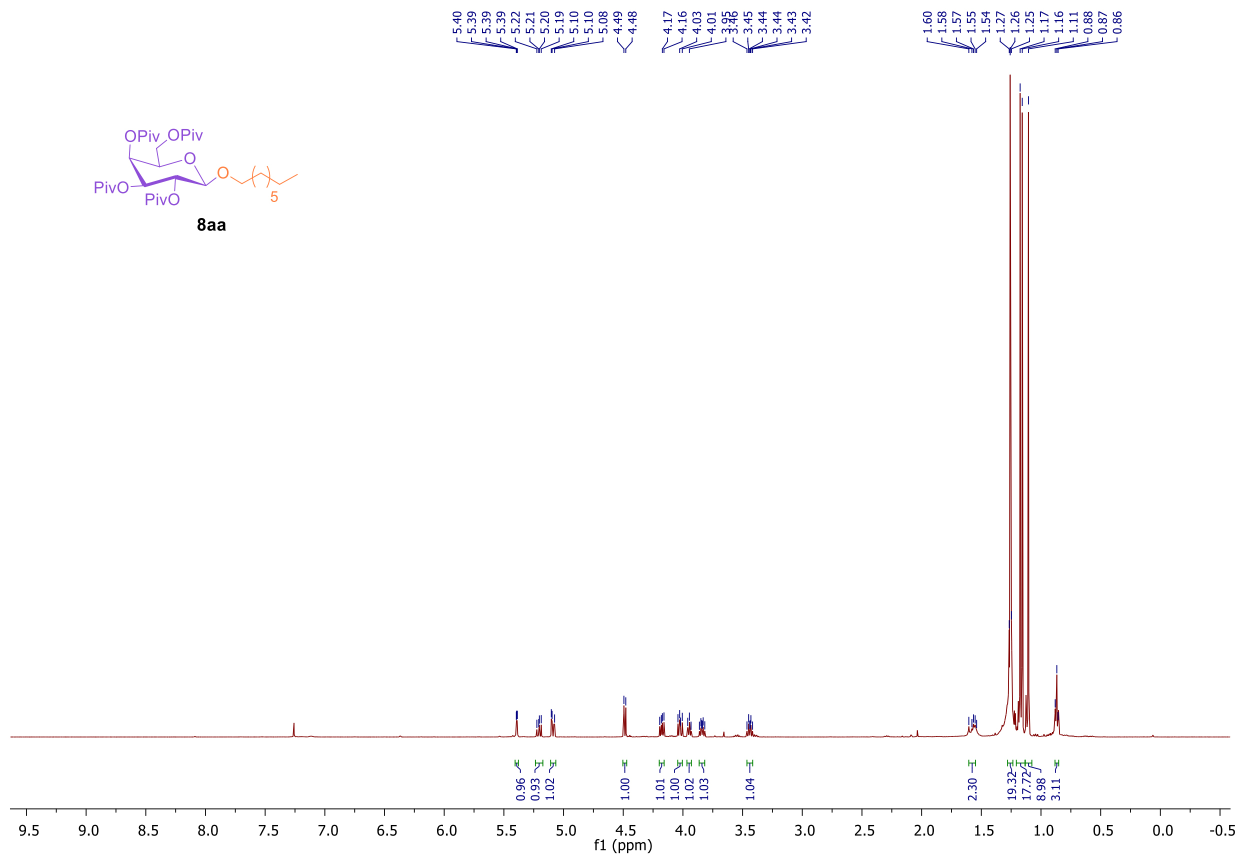


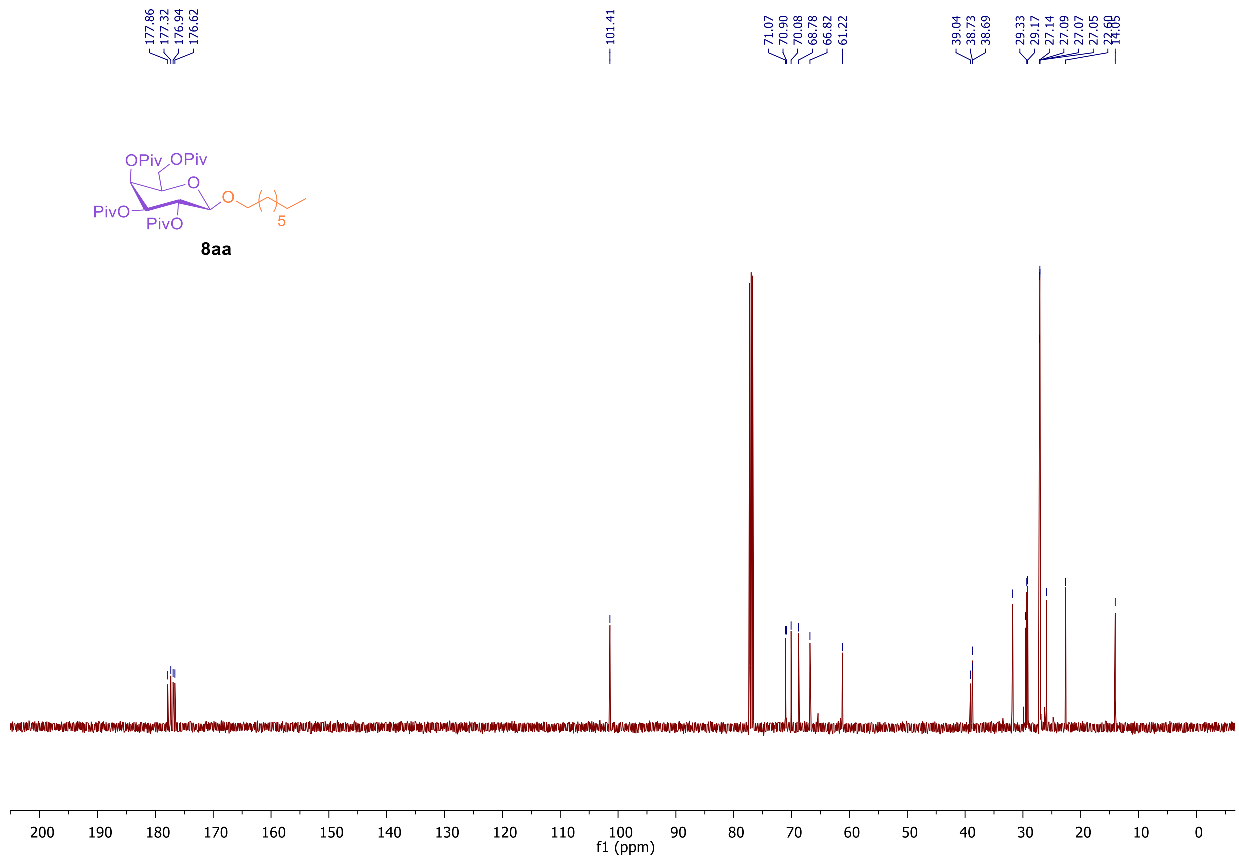
Ortho-ester of pivaloyl mannose 7ac:



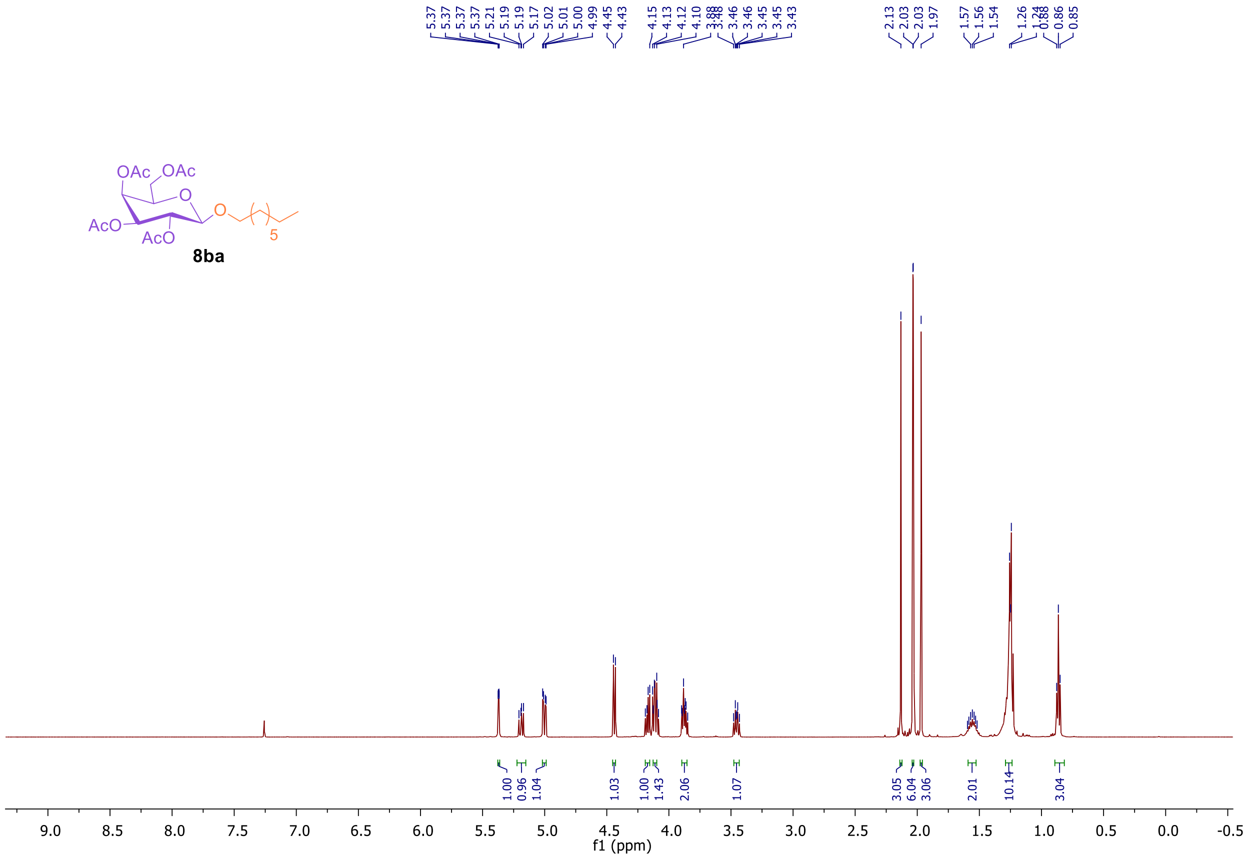


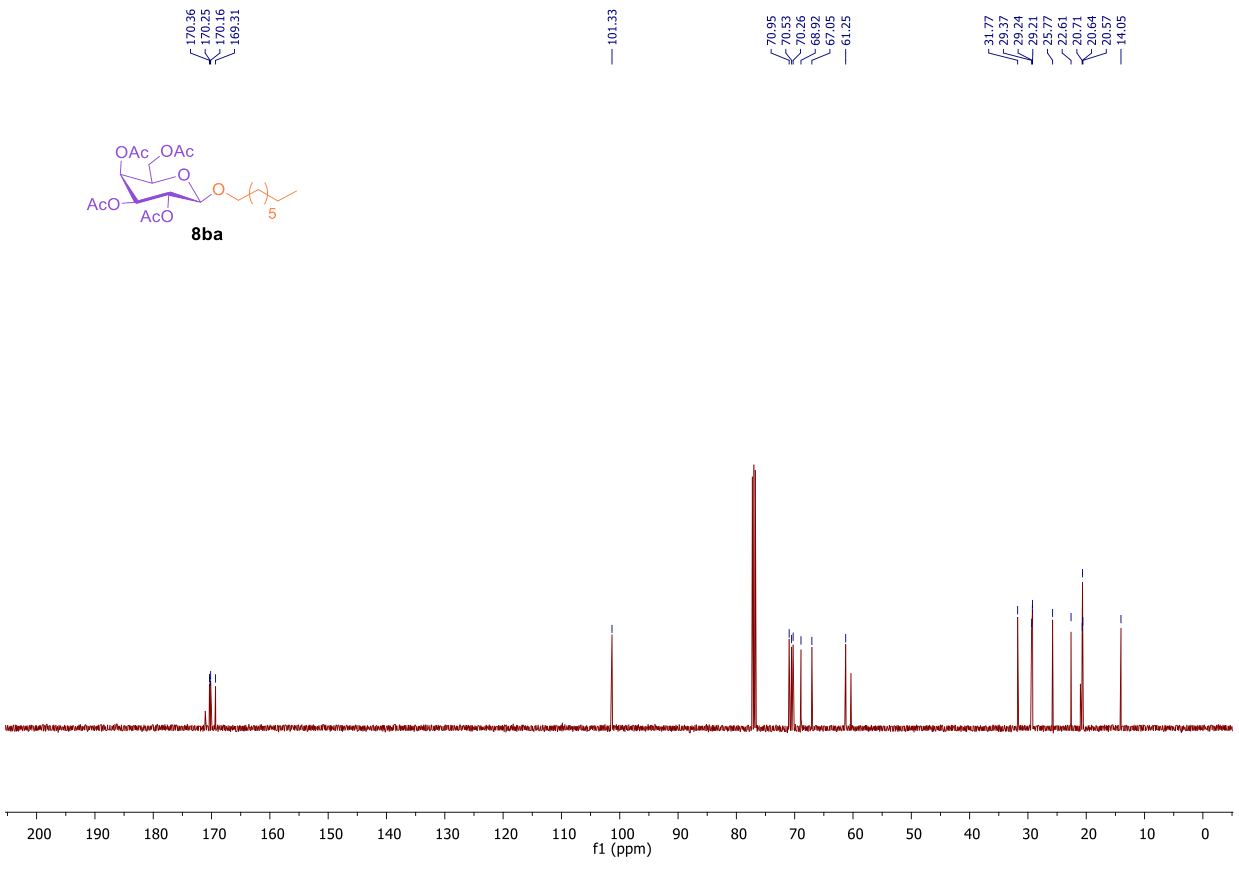
2,3,4,6-tetra-O-pivaloyl-1-O-(octyl)-β-D-galactopyranoside 8aa:



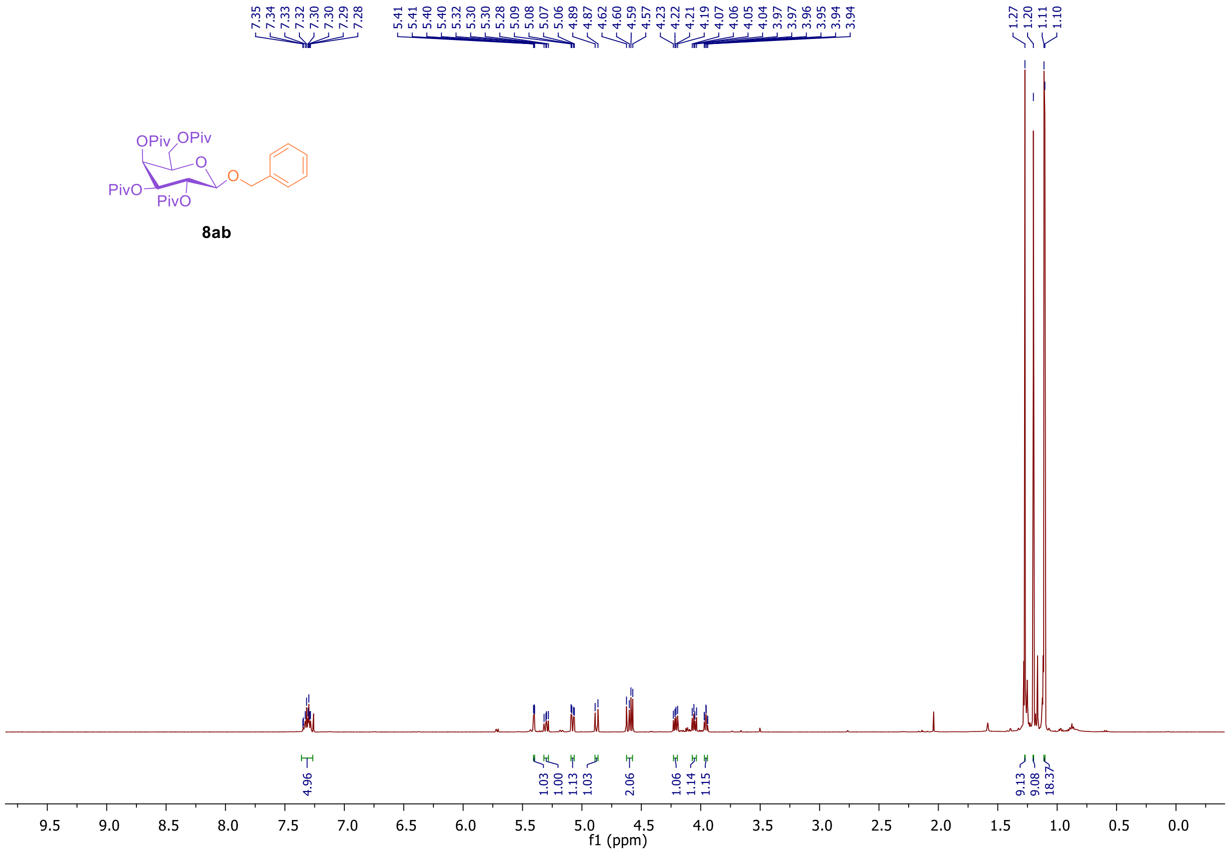


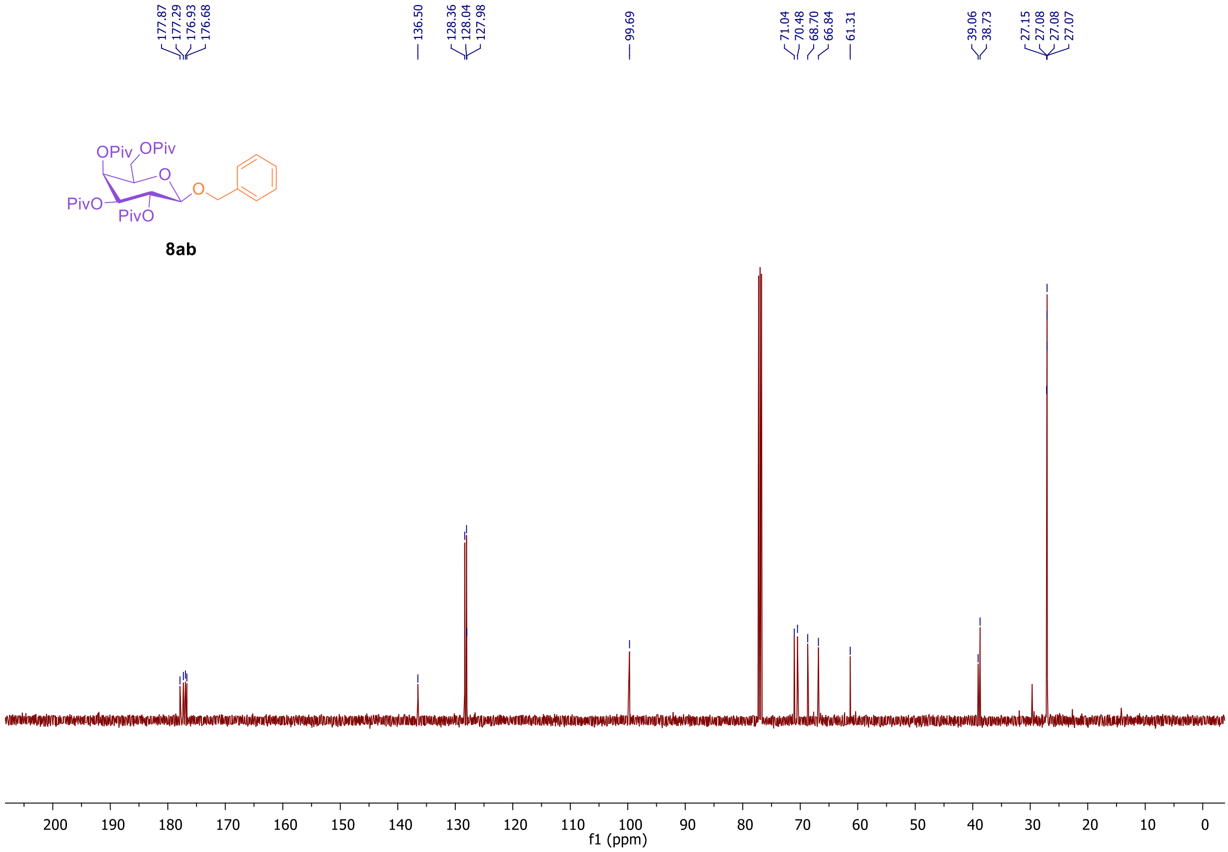
2,3,4,6-tetra-O-acetyl-1-O-(octyl)-β-D-galactopyranoside 8ba:





2,3,4,6-tetra-O-pivaloyl-1-O-(benzyl)-β-D-galactopyranoside 8ab:





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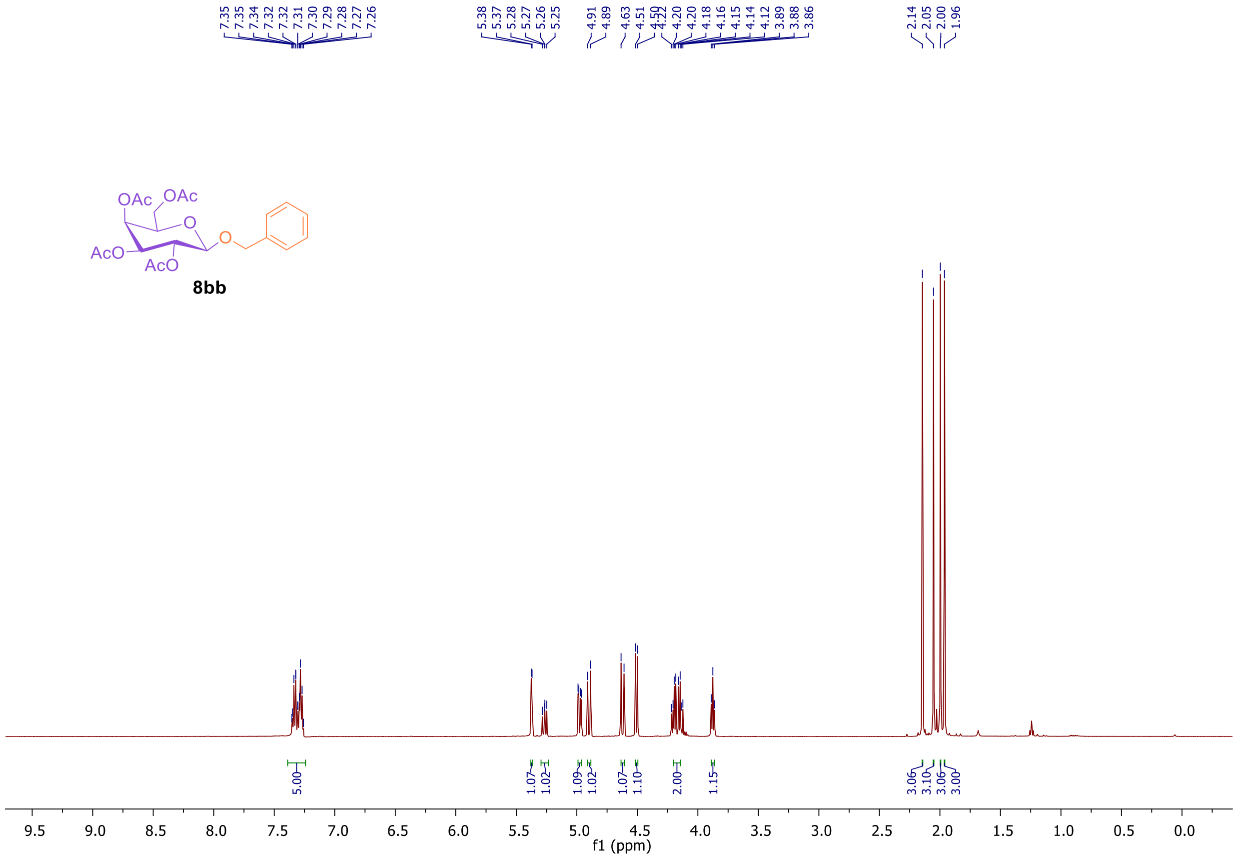
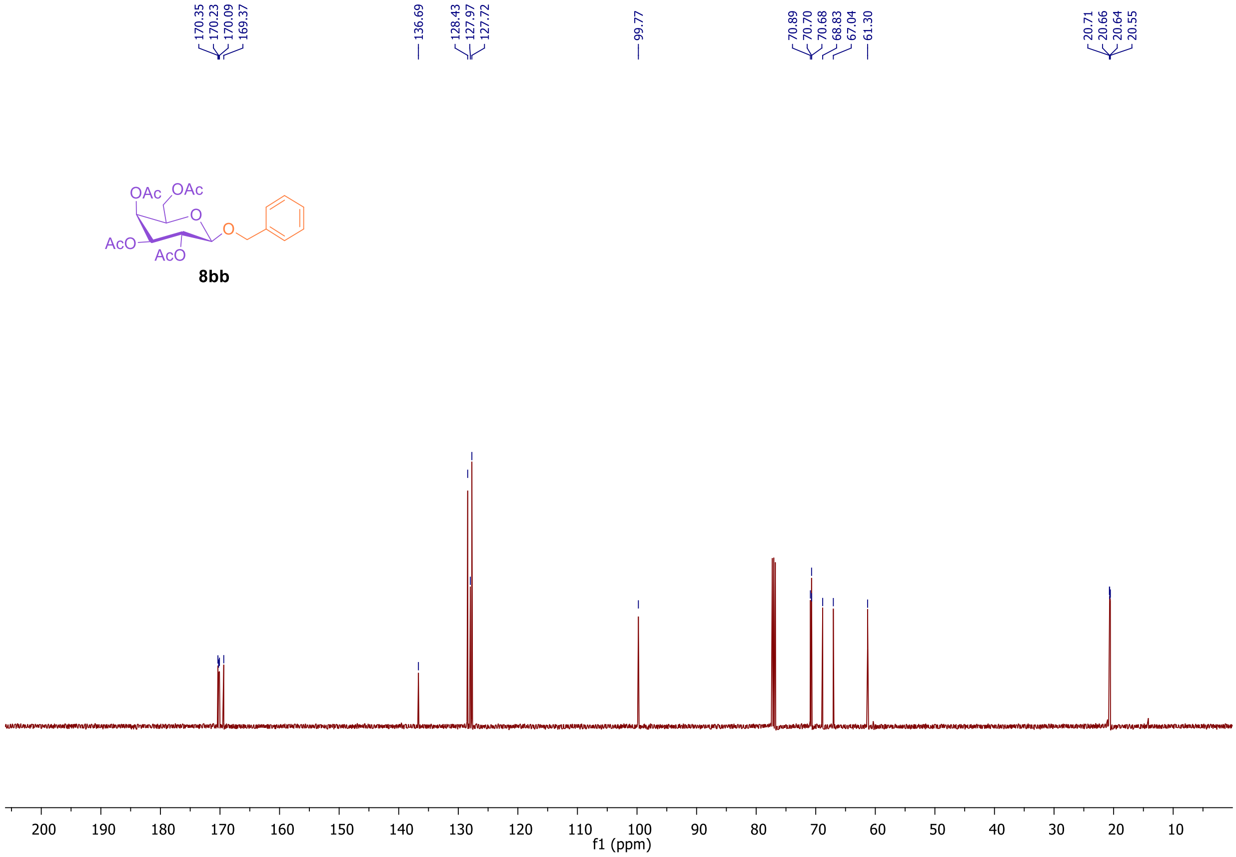
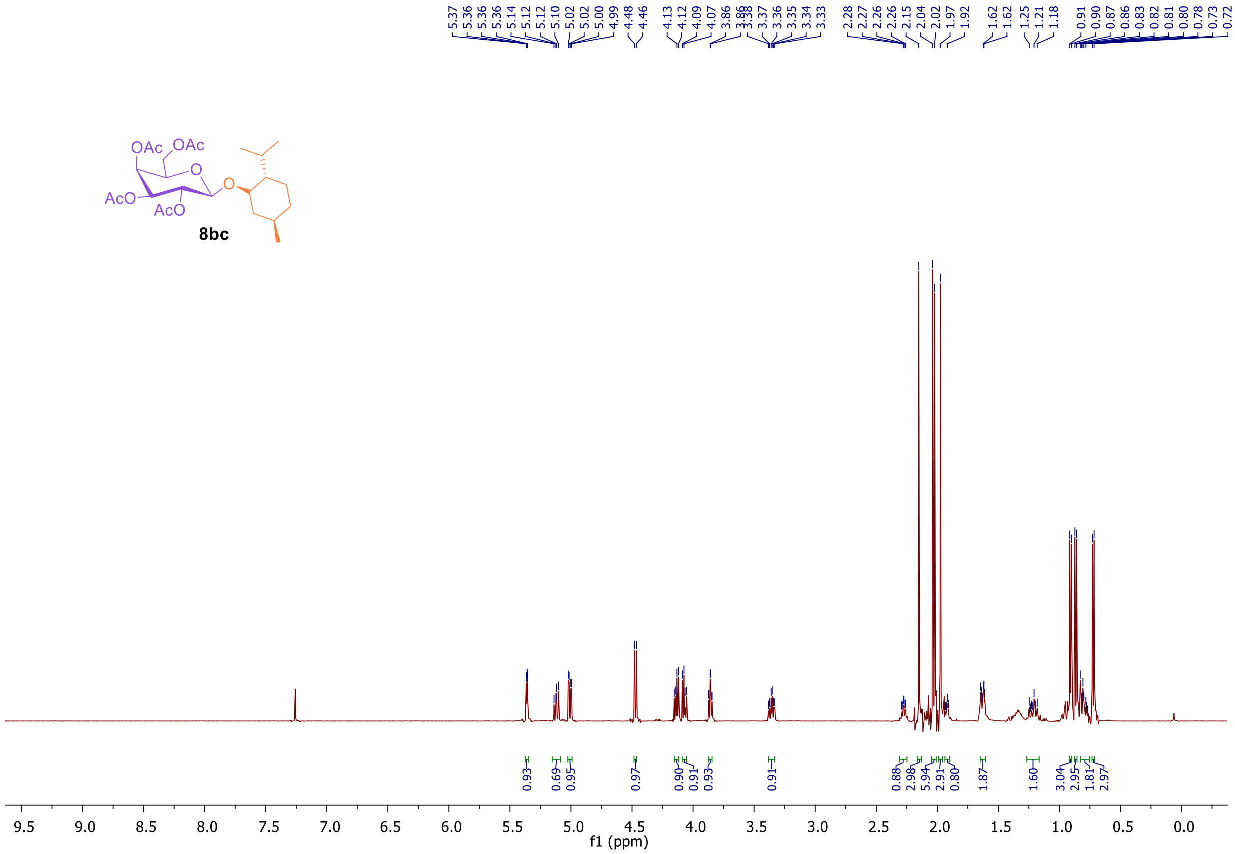
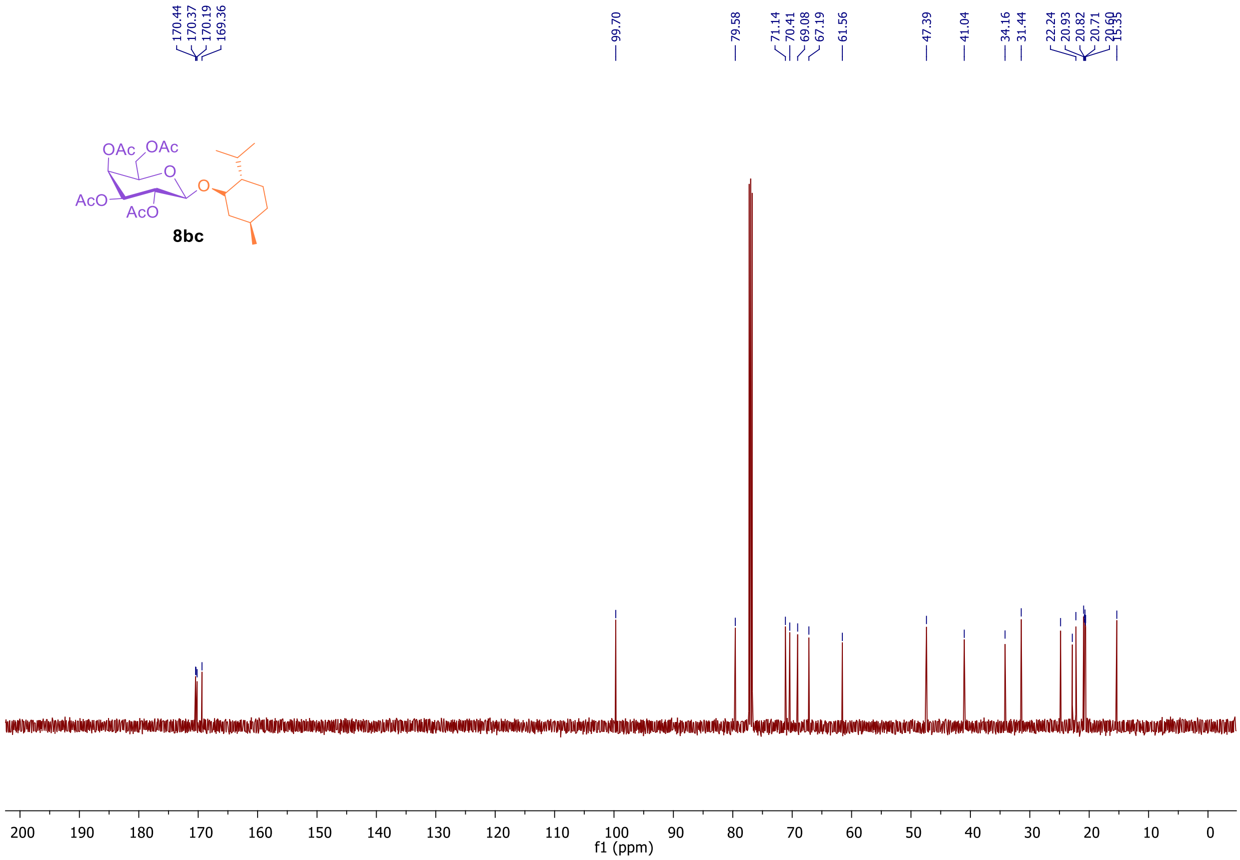


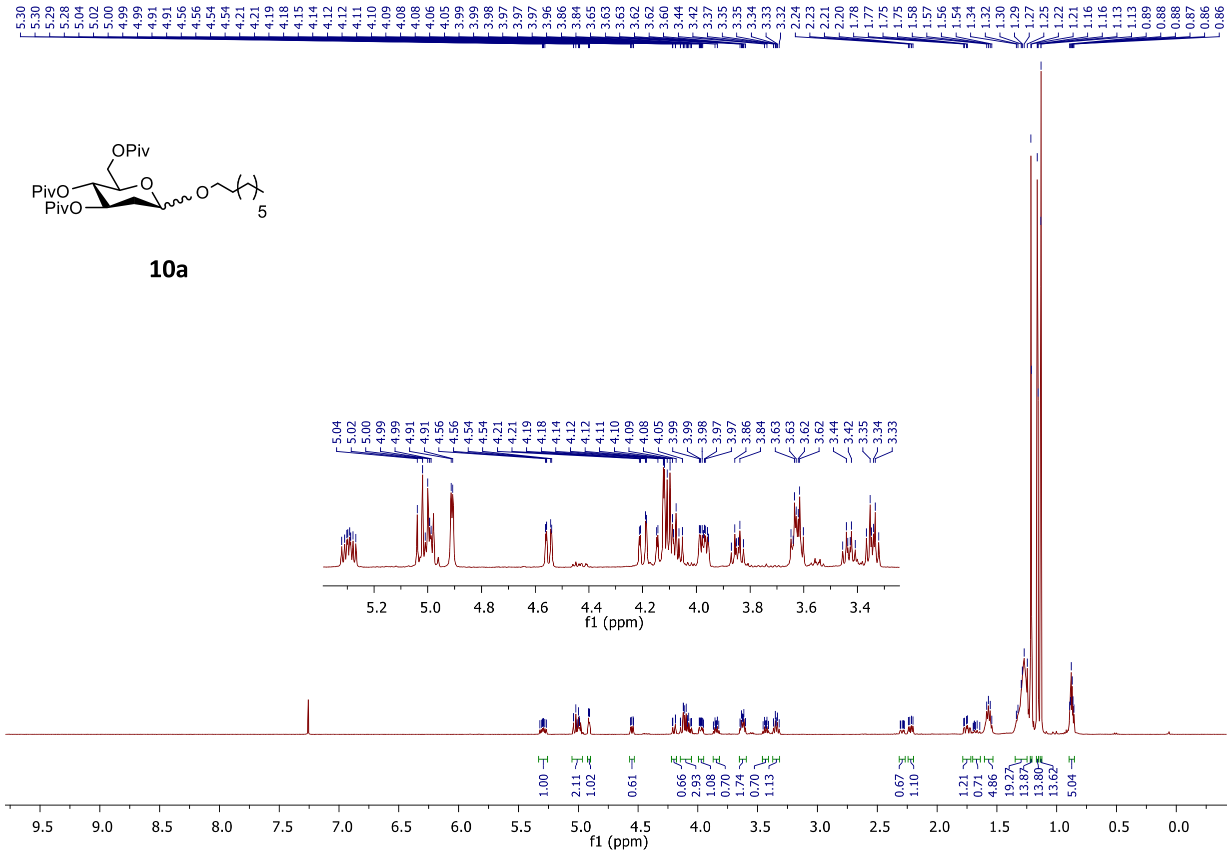


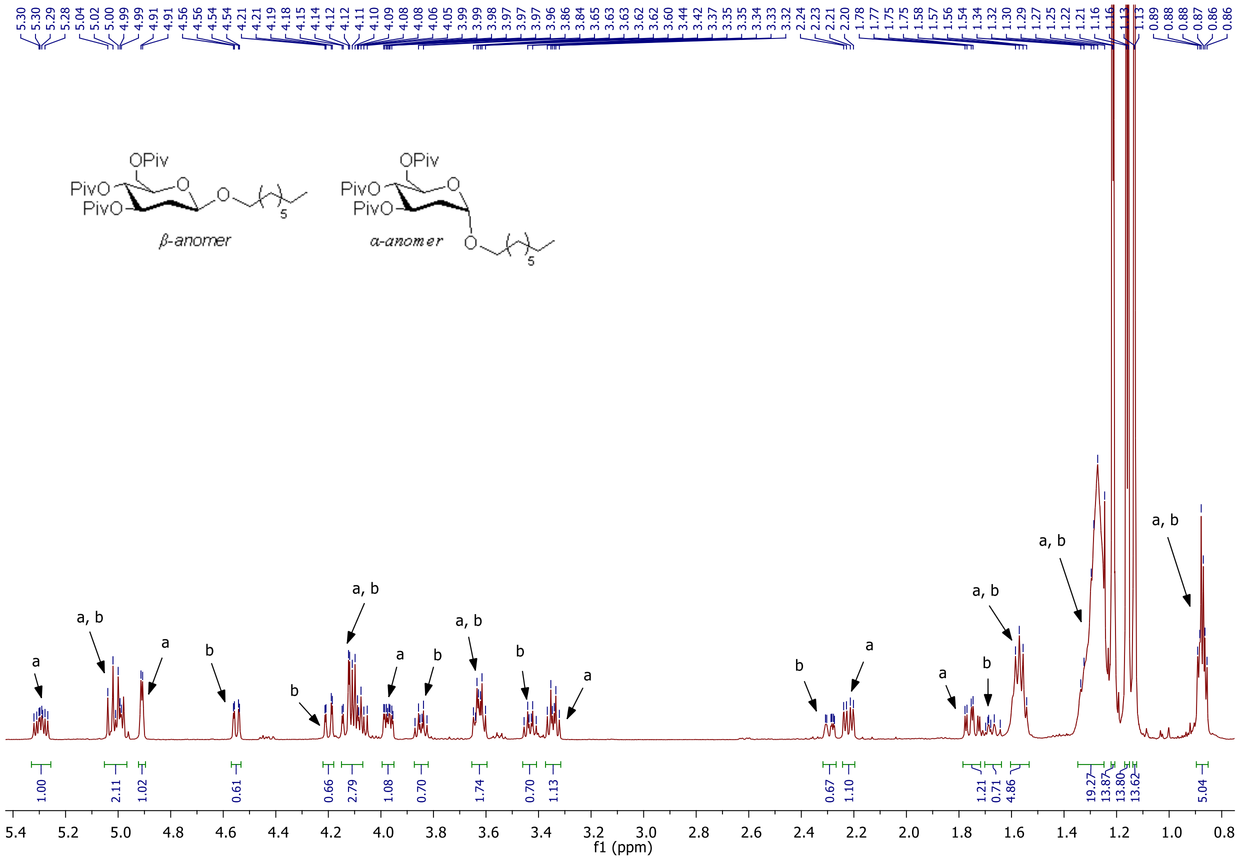
2,3,4,6-tetra-O-acetyl-1-O-(menthyl)-β-D-galactopyranoside 8bc:

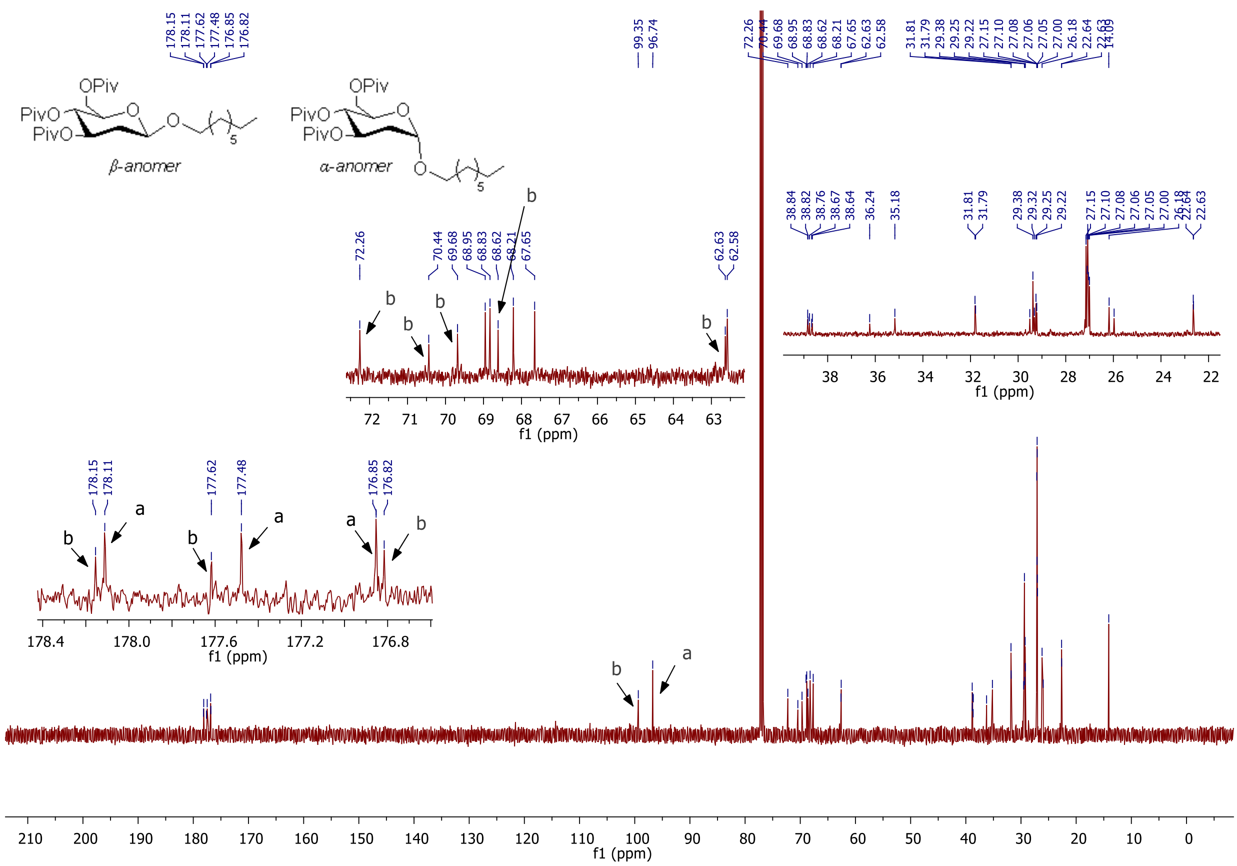




3,4,6-tri-O-pivaloyl-2-deoxy-1-O-(octyl)-α,β-D-glucopyranoside 10a:






OPiv
PivO
PivO
β-anomer
α-anomer
f1 (ppm)

Pure *α-D-glucopyranoside 10a:*