Electronic Supplementary Material (ESI) for Chemical Communications

Reducing the conformational flexibility of carbohydrates: Locking the 6-hydroxyl group by cyclopropanes

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Supporting Information

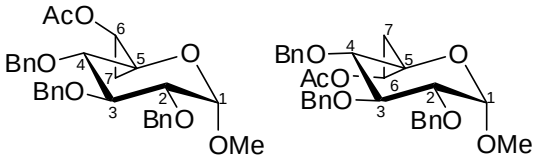
Table of contents

General Experimental.

All solvents were distilled before use unless otherwise stated. Dichloromethane (CH_2Cl_2), 1,2-dichloroethane ($ClCH_2CH_2Cl$) and toluene were distilled from $CaCl_2$ under a nitrogen atmosphere. Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated. Proton (^1H) and carbon (^{13}C) NMR spectra were recorded on a 300, 500 or 600 MHz instrument using the residual signals from $CHCl_3$, δ 7.26 ppm and δ 77.0 ppm, and methanol, δ 4.87 ppm and δ 49.2 ppm, as internal references for ^1H and ^{13}C, respectively. Assignments of the respective signals were made by the combination of H,H-COSY, HSQC, HMBC and NOESY experiments. ESI-HRMS mass spectrometry was carried out on a FTICR instrument. IR spectra were measured on a *JASCO* FT/IR-4100 spectrometer with a Pike GladiATR unit. Optical rotations were measured at 20 °C using a common optical rotation instrument.

^{1}H and ^{13}C NMR Spectra of Compounds 10-31

Compound 10 and 10a



10 **10a**

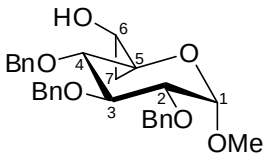
Enolether **8** (1.10 g, 2.18 mmol, 1.0 eq.) was azeotroped with toluene (2 x 8 mL) and then dried under reduced pressure for 1 h. 1,2-Dichloroethane (21 mL), diiodomethane (1.75 mL, 21.80 mmol, 10.0 eq.) and molecular sieves (4 Å) were added and the resulting reaction mixture was stirred for 15 min at room temperature. A solution of diethylzinc (1 M in hexane, 10.90 mL, 10.90 mmol, 5.0 eq.) was carefully added and the reaction mixture was stirred at 50 °C for 3 d. After filtration the reaction was stopped by adding saturated $NaHCO_3$ solution (35 mL) and diluted with dichloromethane (35 mL). After separation of the layers the aqueous phase was extracted with dichloromethane (2 x 35 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 6:1 → 5:1) afforded two diastereomers **10** and **10a** in a ratio of 12:1 (0.39 g, 35%) as colorless oils.

Analytical data of **10:** R_f: 0.38 (hexane/ethyl acetate, 4:1). $[\alpha]_D^{20}$ = –12.8° (c = 0.91, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.29 (dd, *J* = 9.2, 9.2 Hz, 1 H, 7-H), 1.61 (dd, *J* = 7.8, 5.6 Hz, 1 H, 7-H), 1.80 (s, 3 H, O(CO)C*H*$_3$), 3.36 (s, 3 H, OMe), 3.62 (dd, *J* = 9.0, 3.5 Hz, 1 H, 2-H), 3.78 (d, *J* = 8.0 Hz, 1 H, 4-H), 4.05 (dd, *J* = 8.7, 8.3 Hz, 1 H, 3-H), 4.16 (dd, *J* = 8.7, 5.5 Hz, 1 H, 6-H), 4.52–4.58 (m, 2 H, 1-H, CH_2Ph), 4.68 (d, *J* = 12.2 Hz, 1 H, CH_2Ph), 4.70 (d, *J* = 10.8 Hz, 1 H, CH_2Ph), 4.81 (d, *J* = 12.2 Hz, 1 H, CH_2Ph), 4.87 (d, *J* = 11.4 Hz, 1 H, CH_2Ph), 4.89 (d, *J* = 10.8 Hz, 1 H, CH_2Ph), 7.21–7.39 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 15.9 (C-7), 20.8 (O(CO)*C*H$_3$), 55.0 (C-6), 56.6 (OMe), 58.2 (C-5), 73.5, 73.7, 75.5 (CH_2Ph), 76.1 (C-4), 78.7 (C-2), 80.9 (C-3), 99.9 (C-1), 126.6, 127.2, 127.6, 127.8, 127.9, 128.0, 128.0, 128.2, 128.3, 128.4 ($Ph_{tert.}$), 138.1, 138.4, 138.5 ($Ph_{quart.}$), 171.1 (O(*C*O)CH$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2928, 2360, 1741, 1497, 1454. HRMS (ESI): *m/z* calcd for $C_{31}H_{34}O_7Na$: 541.21967; found: 541.21939.

Analytical data of **10a:** R_f: 0.28 (hexane/ethyl acetate, 4:1). $[\alpha]_D^{20}$ = 24.5° (c = 0.91, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.09 (dd, *J* = 7.8, 5.1 Hz, 1 H, 7-H), 1.14 (t, *J* = 7.8 Hz, 1 H, 7-H), 1.93 (s, 3 H, O(CO)C*H*$_3$), 3.39 (s, 3 H, OMe), 3.60 (dd, *J* = 7.6, 3.3 Hz, 1 H, 2-H), 3.71

(d, J = 7.6 Hz, 1 H, 4-H), 4.00 (t, J = 7.6 Hz, 1 H, 3-H), 4.24 (dd, J = 7.8, 5.1 Hz, 1 H, 6-H), 4.53 (d, J = 3.3 Hz, 1 H, 1-H), 4.61 (d, J = 11.7 Hz, 1 H, CH_2Ph), 4.66 (d, J = 12.1 Hz, 1 H, CH_2Ph), 4.70 (d, J = 12.1 Hz, 1 H, CH_2Ph), 4.76 (d, J = 12.1 Hz, 2 H, CH_2Ph), 4.80 (d, J = 11.6 Hz, 1 H, CH_2Ph), 7.23–7.36 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 14.7 (C-7), 20.8 (O(CO)CH_3), 55.6 (C-6), 56.6 (OMe), 57.7 (C-5), 73.6, 74.2, 74.6 (CH_2Ph), 77.8 (C-4), 78.8 (C-2), 79.2 (C-3), 100.2 (C-1), 127.2, 127.3, 127.5, 127.6, 127.6, 127.7, 127.9, 128.0, 128.1, 128.3, 128.3 ($Ph_{tert.}$), 138.4, 138.4, 138.5 ($Ph_{quart.}$), 171.0 (O(CO)CH_3). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3010, 2934, 1740, 1497, 1454. HRMS (ESI): *m/z* calcd for $C_{31}H_{34}O_7Na$: 541.2197; found: 541.2196.

Compound 12



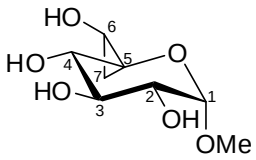
12

To a solution of **10** (0.057 g, 0.11 mmol, 1.0 eq.) in methanol (1.5 mL) and water (0.3 mL) was added potassium carbonate (0.017 g, 0.12 mmol, 1.1 eq.) and the reaction mixture was stirred at room temperature for 1 h. The reaction was stopped by addition of water (6 mL) and diluted with ethyl acetate (6 mL). After separation of the layers the aqueous phase was extracted with ethyl acetate (2 x 6 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 2:1 → 1:1) afforded **12** (0.040 g, 77%) as colorless oil.

R_f: 0.35 (hexane/ethyl acetate, 2:1). $[\alpha]_D^{20}$ = 29.5° (c = 0.19, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 1.11–1.16 (m, 2 H, 7-H), 2.34 (s_{br}, 1 H, OH), 3.36 (s, 3 H, OMe), 3.38–3.44 (m, 1 H, 6-H), 3.62 (dd, J = 6.3, 2.8 Hz, 1 H, 2-H), 3.69 (d, J = 5.9 Hz, 1 H, 4-H), 3.99 (t, J = 6.3 Hz, 1 H, 3-H), 4.55 (d, J = 11.0 Hz, 1 H, CH_2Ph), 4.57 (d, J = 2.8 Hz, 1 H, 1-H), 4.61 (d, J = 11.4 Hz, 1 H, CH_2Ph), 4.71 (d, J = 12.3 Hz, 1 H, CH_2Ph), 4.76 (d, J = 12.5 Hz, 1 H, CH_2Ph), 4.77 (d, J = 11.0 Hz, 1 H, CH_2Ph), 7.21–7.38 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.9 (C-7), 54.0 (C-6), 56.5 (OMe), 58.8 (C-5), 73.1, 73.6, 74.4 (CH_2Ph), 75.2 (C-4), 76.6 (C-2), 78.9 (C-3), 100.1 (C-1), 127.6, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.3, 128.4, 128.5 ($Ph_{tert.}$), 137.5, 137.9, 138.3 ($Ph_{quart.}$). IR (ATR):

$\tilde{\nu}$ (cm^{-1}) = 3412, 2913, 1498, 1454. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2093.

Compound 14

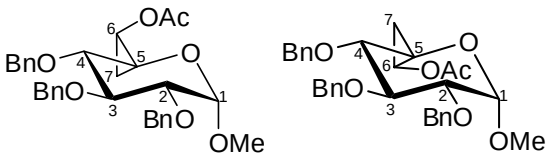


14

To a solution of **12** (9.0 mg, 0.019 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 0.5 mL) was added Pd/C (10 wt.% on activated carbon, 10 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 10:1) afforded **14** (3.9 mg, quant.) as a colorless oil.

R_f: 0.33 (dichloromethane/methanol, 7:1). $[\alpha]_D^{20}$ = 58.9° (c = 0.35, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ = 0.99 (dd, *J* = 7.6, 7.4 Hz, 1 H, 7-H), 1.11 (dd, *J* = 7.6, 4.7 Hz, 1 H, 7-H), 3.36 (s, 3 H, OMe), 3.48 (dd, *J* = 7.6, 4.7 Hz, 1 H, 6-H), 3.56 (dd, *J* = 6.7, 2.8 Hz, 1 H, 2-H), 3.74 (d, *J* = 6.7 Hz, 1 H, 4-H), 3.87 (dd, *J* = 6.7, 6.7 Hz, 1 H, 3-H), 4.66 (d, *J* = 2.8 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 17.8 (C-7), 54.2 (C-6), 56.8 (OMe), 60.8 (C-5), 70.8 (C-4), 72.5 (C-2), 72.8 (C-3), 102.0 (C-1). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3326, 2923, 2853, 2360, 2341, 1454. HRMS (ESI): *m/z* calcd for $C_8H_{14}O_6Na$: 229.0683; found: 229.0689.

Compound 11 and 11a



11 **11a**

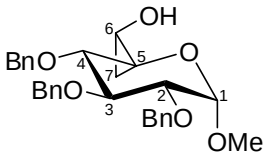
Enolether **9** (3.97 g, 7.87 mmol, 1.0 eq.) was azeotroped with toluene (2 x 5 mL) and then dried under reduced pressure for 1 h. 1,2-Dichloroethane (80 mL), diiodomethane (6.33 mL, 78.7 mmol, 10.0 eq.) and molecular sieves (4 Å) were added and the resulting reaction

mixture was stirred for 15 min at room temperature. A solution of diethylzinc (1 M in hexane, 39.3 mL, 39.3 mmol, 5.0 eq.) was carefully added and the reaction mixture was stirred at 50 °C for 2 d. After filtration the reaction was stopped by the addition of saturated $NaHCO_3$-solution (80 mL) and diluted with dichloromethane (80 mL). After separation of the layers the aqueous phase was extracted with dichloromethane (2 x 60 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 7:1 → 6:1) afforded two diastereoisomers **11** and **11b** in a ratio of 4.3:1 (2.61 g, 64%) as colorless foam.

Analytical data of **11:** R_f: 0.31 (hexane/ethyl acetate, 4:1). $[\alpha]_D^{20}$ = –15.0° (c = 0.34, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.94 (dd, *J* = 7.8, 4.7 Hz, 1 H, 7-H), 1.46 (t, *J* = 7.9 Hz, 1 H, 7-H), 2.06 (s, 3 H, O(CO)C*H*$_3$), 3.39 (s, 3 H, OMe), 3.61 (dd, *J* = 9.6, 3.9 Hz, 1 H, 2-H), 3.81 (d, *J* = 8.9 Hz, 1 H, 4-H), 3.87 (dd, *J* = 8.1, 4.5 Hz, 1 H, 6-H), 3.95 (t, *J* = 9.5 Hz, 1 H, 3-H), 4.59–4.67 (m, 3 H, 1-H, 2 x C*H*$_2$Ph), 4.78 (d, *J* = 10.9 Hz, 1 H, C*H*$_2$Ph), 4.82 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$Ph), 4.86 (d, *J* = 11.2 Hz, 1 H, C*H*$_2$Ph), 4.95 (d, *J* = 10.9 Hz, 1 H, C*H*$_2$Ph), 7.20–7.37 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 13.9 (C-7), 20.7 (O(CO)*C*H$_3$), 49.9 (C-6), 55.4 (C-5), 56.6 (OMe), 73.5, 75.2, 75.6 (C-3, 2 x *C*H$_2$Ph), 77.4 (C-4), 79.9 (C-2), 80.9 (C-3), 100.2 (C-1), 127.4, 127.5, 127.5, 127.8, 127.9, 128.0, 128.3, 128.4 (Ph$_{tert.}$), 137.9, 138.0, 138.5 (Ph$_{quart.}$), 171.4 (O(*C*O)CH$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3063, 3030, 2925, 1750, 1497, 1454. HRMS (ESI): *m/z* calcd for $C_{31}H_{34}O_7Na$: 541.2197; found: 541.2204.

Analytical data of **11b:** R_f: 0.27 (hexane/ethyl acetate, 4:1). $[\alpha]_D^{20}$ = 18.7° (c = 0.15, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.73 (dd, *J* = 7.7, 4.7 Hz, 1 H, 7-H), 1.11 (dd, *J* = 7.7, 7.7 Hz, 1 H, 7-H), 2.06 (s, 3 H, O(CO)C*H*$_3$), 3.49 (s, 3 H, OMe), 3.57 (dd, *J* = 9.4, 3.8 Hz, 1 H, 2-H), 3.66 (d, *J* = 9.4 Hz, 1 H, 4-H), 3.97 (t, *J* = 9.4 Hz, 1 H, 3-H), 4.39 (dd, *J* = 7.7, 4.7 Hz, 1 H, 6-H), 4.51 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.52 (d, *J* = 3.8 Hz, 1 H, 1-H), 4.65 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$Ph), 4.75 (d, *J* = 10.7 Hz, 1 H, C*H*$_2$Ph), 4.82 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$Ph), 4.83 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.93 (d, *J* = 10.7 Hz, 1 H, C*H*$_2$Ph), 7.17–7.37 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-7), 21.1 (O(CO)*C*H$_3$), 52.8 (C-6), 58.0 (C-5), 58.5 (OMe), 73.5, 75.3, 75.7 (*C*H$_2$Ph), 78.2 (C-4), 79.9 (C-2), 80.6 (C-3), 100.6 (C-1), 127.5, 127.6, 127.6, 127.9, 128.0, 128.3, 128.3, 128.4 (Ph$_{tert.}$), 137.8, 138.1, 138.5 (Ph$_{quart.}$), 170.8 (O(*C*O)CH$_3$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2940, 2864, 1727, 1612, 1513, 1453. HRMS (ESI): *m/z* calcd for $C_{31}H_{34}O_7Na$: 541.2197; found: 541.2197.

Compound 13

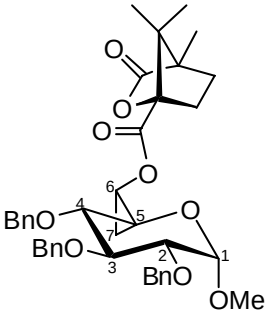


13

To a solution of **11** (0.059 g, 0.11 mmol, 1.0 eq.) in methanol (1.0 mL) and water (0.2 mL) was added potassium carbonate (0.018 g, 0.13 mmol, 1.1 eq.) and the reaction mixture was stirred at room temperature for 1 h. The reaction was stopped by addition of water (5.0 mL) and diluted with ethyl acetate (5.0 mL). After separation of the layers the water phase was extracted with ethyl acetate (2 x 5.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 2:1 $\rightarrow$ 1:1) afforded **13** (0.028 g, 55%) as colorless foam.

R_f: 0.47 (hexane/ethyl acetate, 1:1). $[\alpha]_D^{20}$ = 7.8° (c = 1.86, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.65 (dd, *J* = 7.6, 4.1 Hz, 1 H, 7-H), 1.24 (dd, *J* = 7.6, 7.6 Hz, 1 H, 7-H), 1.86 (bs, 1 H, OH), 3.28 (dd, *J* = 7.6, 4.1 Hz, 1 H, 6-H), 3.38 (s, 3 H, OMe), 3.59 (dd, *J* = 9.5, 4.0 Hz, 1 H, 2-H), 3.71 (d, *J* = 9.1 Hz, 1 H, 4-H), 3.95 (t, *J* = 9.5 Hz, 1 H, 3-H), 4.52 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.60 (d, *J* = 4.0 Hz, 1 H, 1-H), 4.65 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.75 (d, *J* = 10.9 Hz, 1 H, C*H*$_2$Ph), 4.83 (d, *J* = 11.5 Hz, 2 H, C*H*$_2$Ph), 4.52 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.94 (d, *J* = 10.6 Hz, 1 H, C*H*$_2$Ph), 7.16-7.38 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 16.2 (C-7), 47.7 (C-6), 55.6 (C-5), 56.8 (OMe), 73.6, 75.1, 75.8 (*C*H$_2$Ph), 77.3 (C-4), 80.2 (C-2), 81.1 (C-3), 100.3 (C-1), 127.5, 127.6, 127.6, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4 ($Ph_{tert.}$), 138.0, 138.1, 138.5 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3413, 2924, 1727, 1453. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2082.

Compound 33

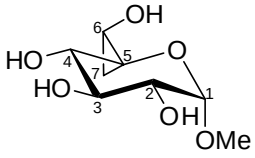


33

To a 0 °C cooled solution of **13** (0.10 g, 0.21 mmol, 1.0 eq.) in anhydrous dichloromethane (2.5 mL) was sequentially added 4-dimethylaminopyridine (0.0051 g, 0.042 mmol, 0.2 eq.), pyridine (0.034 mL, 0.033 g, 0.42 mmol, 2.0 eq.) and camphanic acid chloride (0.091 g, 0.42 mmol, 2.0 eq.). The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 16 h. The reaction was stopped by addition of methanol (1.0 mL) and diluted with ethyl acetate (10.0 mL) and water (10 mL). After separation of the layers the water phase was extracted with ethyl acetate (2 x 10.0 mL), the combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 4:1 → 3:1) afforded **33** (0.11 g, 80%) as colorless solid.

R_f: 0.33 (hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = 3.4° (c = 0.35, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.01 (dd, *J* = 7.8, 4.4 Hz, 1 H, 7-H), 1.03 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.51 (t, *J* = 7.8 Hz, 1 H, 7-H), 1.62–1.73 (m, 1 H), 1.85–2.08 (m, 2 H), 2.34–2.45 (m, 1 H), 3.36 (s, 3 H, OMe), 3.62 (dd, *J* = 9.3, 3.9 Hz, 1 H, 2-H), 3.86 (d, *J* = 9.1 Hz, 1 H, 4-H), 3.90–3.98 (m, 2 H, 3-H, 6-H), 4.54 (d, *J* = 3.9 Hz, 1 H, 1-H), 4.62 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.65 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.77 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$Ph), 4.81 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.89 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.95 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$Ph), 7.19–7.37 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 9.7 (CH_3), 13.7 (C-7), 16.4, 16.5 (CH_3), 29.0, 30.7 (CH_2), 50.6 (C-6), 54.2, 54.7, 55.1 ($C_{quart.}$), 56.7 (OMe), 73.6, 75.3, 75.6 (*C*H$_2$Ph), 77.4 (C-4), 80.0 (C-2), 80.9 (C-3), 90.9 ($C_{quart.}$), 100.3 (C-1), 127.5, 127.6, 127.7, 127.9, 127.9, 128.0, 128.4, 128.4, 128.5 ($Ph_{tert.}$), 138.0, 138.1, 138.7 ($Ph_{quart.}$), 168.0, 178.0 (C=O). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2962, 1775, 1760, 1497, 1450. HRMS (ESI): *m/z* calcd for $C_{39}H_{44}O_9Na$: 679.2878; found: 679.2875.

Compound 15



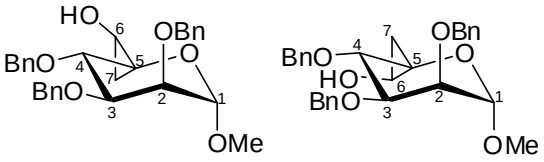
15

To a solution of **13** (0.010 g, 0.021 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 0.5 mL) was added Pd/C (10 wt.% on activated carbon, 10 mg) under an argon atmosphere. The argon atmosphere was exchanged

by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 8:1 → 6:1) afforded **15** (4.3 mg, quant.) as a colorless oil.

R_f: 0.35 (dichloromethane/methanol, 6:1). $[\alpha]_D^{20}$ = 118.4° (c = 1.34, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ = 0.69 (dd, *J* = 7.2, 4.5 Hz, 1 H, 7-H), 1.10 (dd, *J* = 7.2, 7.2 Hz, 1 H, 7-H), 3.28–3.33 (m, 1 H, 6-H), 3.44 (s, 3 H, OMe), 3.49–3.54 (m, 2 H, 2-H, 4-H), 3.65 (t, *J* = 8.3 Hz, 1 H, 3-H), 4.77 (d, *J* = 3.5 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 15.5 (C-7), 49.9 (C-6), 57.0 (OMe), 58.7 (C-5), 71.7, 73.5, 73.6 (C-2, C-3, C-4), 102.7 (C-1). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3318, 2924, 2360, 1446. HRMS (ESI): *m/z* calcd for $C_8H_{14}O_6Na$: 229.0683; found: 229.0690.

Compound 19 and 19a



19 **19a**

Enolether **17** (0.81 g, 1.61 mmol, 1.0 eq.) was azeotroped with toluene (2 x 8 mL) and then dried under reduced pressure for 1 h. 1,2-Dichloroethane (17 mL), diiodomethane (1.35 mL, 16.1 mmol, 10 eq.) and molecular sieves (4 Å) were added under an argon atmosphere and the resulting reaction mixture was stirred for 15 min at room temperature. A solution of diethylzinc (1 M in hexane, 8.03 mL, 8.03 mmol, 5 eq.) was slowly added and the reaction mixture was stirred at 50 °C for 2 d. After filtration the reaction was stopped by adding saturated $NaHCO_3$ solution (25 mL) and diluted with dichloromethane (50 mL). After separation of the layers the aqueous phase was extracted with dichloromethane (2 x 25 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 6:1) afforded two isomers of the crude product in a ratio of 2.5:1 (0.46 g, 55%) as colorless oils.

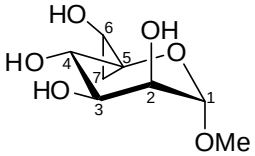
To a solution of the crude mixture (0.21 g, 0.40 mol, 1.0 eq.) in methanol (5.0 mL) and water (1.0 mL) potassium carbonate (0.061 g, 0.44 mol, 1.1 eq.) was added and the reaction mixture was stirred at room temperature for 1 h. The reaction was stopped by addition of water (15 mL) and diluted with ethyl acetate (20 mL). After separation of the layers the aqueous

phase was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 4:1 → 3:1) afforded two diastereomers **19** (103 mg, 54%) and **19a** (38 mg, 20%) as colorless oil.

Analytical data of **19:** R_f: 0.64 (hexane/ethyl acetate, 2:1). $[\alpha]_D^{20}$ = 19.6° (c = 0.52, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.93 (dd, *J* = 7.4, 4.3 Hz, 1 H, 7^b-H), 1.22 (t, *J* = 7.4 Hz, 1 H, 7^a-H), 3.03 (s_{br}, 1 H, OH), 3.35 (dd, *J* = 7.4, 4.3 Hz, 1 H, 6-H), 3.44–3.47 (m, 4 H, OMe, 4-H), 3.78 (dd, *J* = 8.1, 3.1 Hz, 1 H, 2-H), 3.97 (t, *J* = 3.1 Hz, 1 H, 3-H), 4.45 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.58 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.62 (d, *J* = 11.7 Hz, 1 H, C*H*$_2$Ph), 4.64 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$Ph), 4.78 (d, *J* = 8.1 Hz, 1 H, 1-H), 4.90 (d, *J* = 11.9 Hz, 1 H, C*H*$_2$Ph), 4.94 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 7.20–7.39 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 20.5 (C-7), 52.8 (C-6), 56.6 (OMe), 59.1 (C-5), 71.3, 73.9, 74.9 (*C*H$_2$Ph), 75.7 (C-4), 76.8 (C-2), 77.3 (C-3), 101.8 (C-1), 127.5, 127.6, 127.7, 127.7, 128.2, 128.2, 128.3, 128.3, 128.7 ($Ph_{tert.}$), 137.4, 138.0, 138.8 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3483, 2913, 2872, 1728, 1497. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2092.

Analytical data of **19a:** R_f: 0.39 (hexane/ethyl acetate, 2:1). $[\alpha]_D^{20}$ = 22.1° (c = 0.48, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.91 (dd, *J* = 7.5, 4.5 Hz, 1 H, 7-H), 0.99 (t, *J* = 7.5 Hz, 1 H, 7-H), 3.38 (s, 3 H, OMe), 3.56 (dd, *J* = 7.9, 4.5 Hz, 1 H, 6-H), 3.77 (dd, *J* = 6.0, 3.1 Hz, 1 H, 2-H), 3.79–3.84 (m, 1 H, 4-H), 3.95 (dd, *J* = 5.4, 3.1 Hz, 1 H, 3-H), 4.47 (d, *J* = 11.6 Hz, 1 H, C*H*$_2$Ph), 4.55–4.68 (m, 6 H, 1-H, C*H*$_2$Ph), 4.78 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 7.15–7.18 (m, 2 H, Ph-H), 7.25–7.36 (m, 13 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.6 (C-7), 54.0 (C-6), 56.3 (OMe), 58.9 (C-5), 72.9, 72.9, 73.3 (*C*H$_2$Ph), 76.5, 76.6 (C-2, C-4), 76.8 (C-3), 100.7 (C-1), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.3, 128.5 ($Ph_{tert.}$), 137.8, 138.4, 138.6 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3428, 2912, 2362, 1726, 1496, 1453. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2096.

Compound 21

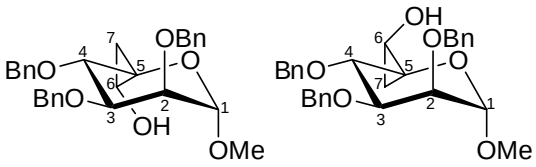


21

To a solution of **19** (11.0 mg, 0.023 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 1.0 mL) was added Pd/C (10 wt.% on activated carbon, 9 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 7:1) afforded **21** (4.7 mg, quant.) as a colorless oil.

R_f: 0.18 (dichloromethane/methanol, 7:1). $[\alpha]_D^{20}$ = 62.8° (c = 0.39, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ = 0.85 (dd, *J* = 7.4, 4.5 Hz, 1 H, 7-H), 0.99 (t, *J* = 7.4 Hz, 1 H, 7-H), 3.34 (s, 3 H, OMe), 3.45 (dd, *J* = 7.4, 4.5 Hz, 1 H, 6-H), 3.61–3.68 (m, 2 H, 2-H, 4-H), 3.94 (t, *J* = 3.5 Hz, 1 H, 3-H), 4.52–4.54 (m, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 19.1 (C-7), 55.2 (C-6), 57.0 (OMe), 62.2 (C-5), 69.4, 70.7 (C-2, C-4), 73.1 (C-3), 102.6 (C-1). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3350, 2921, 1650, 1447. HRMS (ESI): *m/z* calcd for $C_8H_{14}O_6Na$: 229.0683; found: 229.0693.

Compound 20 and 20a



20a **20**

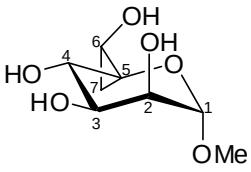
Enolether **18** (0.53 g, 1.05 mmol, 1.0 eq.) was azeotroped with toluene (2 x 5 mL) and then dried under reduced pressure for 1 h. 1,2-Dichloroethane (11 mL), diiodomethane (0.86 mL, 10.5 mmol, 10 eq.) and molecular sieves (4 Å) were added under an argon atmosphere and the resulting reaction mixture was stirred for 15 min at room temperature. A solution of diethylzinc (1 M in hexane, 5.25 mL, 5.25 mmol, 5 eq.) was slowly added and the reaction mixture was stirred at 50 °C for 2 d. After filtration the reaction was stopped by adding saturated $NaHCO_3$ solution (20 mL) and diluted with dichloromethane (40 mL). After separation of the layers the aqueous phase was extracted with dichloromethane (2 x 20 mL). The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 6:1) afforded two diastereomers **20a** and **20** in a ratio of 5:1 (0.26 g, 48%) as colorless oils.

To a solution of the crude mixture (0.26 g, 0.50 mmol, 1.0 eq.) in methanol (5.0 mL) and water (0.5 mL) was added potassium carbonate (0.076 g, 0.55 mol, 1.1 eq.) and the reaction mixture was stirred at room temperature for 1 h. The reaction was stopped by addition of water (15 mL) and diluted with ethyl acetate (25 mL). After separation of the layers the aqueous phase was extracted with ethyl acetate (2 x 25 mL). The combined organic layers were washed brine, dried over Na_2SO_4, filtrated and concentrated to dryness. Purification by column chromatography (SiO_2, pentane/ethyl acetate, 3.5:1 → 3:1 → 2:1) afforded two diastereomers **20a** (0.31 g, 13%) and **20** (0.11 g, 46%) as colorless foam.

Analytical data of **20a**: R_f: 0.23 (hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = 26.3° (c = 0.24, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.85 (dd, *J* = 7.4, 4.3 Hz, 1 H, 7-H), 0.94 (t, *J* = 7.4 Hz, 1 H, 7-H), 2.77 (d, *J* = 2.9 Hz, 1 H, OH), 3.42 (s, 3 H, OMe), 3.44–3.51 (m, 1 H, 6-H), 3.67 (d, *J* = 6.1 Hz, 1 H, 4-H), 3.79 (dd, *J* = 4.9, 3.0 Hz, 1 H, 2-H), 3.87 (dd, *J* = 6.1, 3.0 Hz, 1 H, 3-H), 4.47 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$Ph), 4.58–4.68 (m, 3 H, C*H*$_2$Ph), 4.72 (d, *J* = 4.9 Hz, 1 H, 1-H), 4.74 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 4.78 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 7.16–7.40 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.1 (C-7), 50.0 (C-6), 57.0 (OMe), 59.3 (C-5), 73.0, 73.0, 73.4 (*C*H$_2$Ph), 76.0 (C-2), 76.4 (C-4), 77.9 (C-3), 102.4 (C-1), 127.5, 127.7, 127.7, 127.9, 128.3, 128.4 (Ph$_{tert.}$), 138.0, 138.3, 138.4 (Ph$_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3442, 2907, 1497, 1454. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2083.

Analytical data of **20:** R_f: 0.19 (hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = 35.2° (c = 0.52, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.71 (dd, *J* = 7.4, 4.2 Hz, 1 H, 7^a-H), 1.40 (t, *J* = 7.4 Hz, 1 H, 7^b-H), 3.23 (dd, *J* = 7.4, 4.2 Hz, 1 H, 6-H), 3.41 (s, 3 H, OMe), 3.59–3.65 (m, 1 H, 4-H), 3.81 (dd, *J* = 4.4, 3.0 Hz, 1 H, 2-H), 3.87 (dd, *J* = 6.9, 3.0 Hz, 1 H, 3-H), 4.50 (d, *J* = 11.7 Hz, 1 H, C*H*$_2$Ph), 4.60 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$Ph), 4.66 (d, *J* = 12.0 Hz, 2 H, C*H*$_2$Ph), 4.72 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 4.77 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 4.81 (d, *J* = 4.4 Hz, 1 H, 1-H), 7.16–7.37 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 16.2 (C-7), 50.1 (C-6, C-5), 56.3 (OMe), 57.1 (C-6, C-5), 72.8, 73.4, 73.4 (*C*H$_2$Ph), 75.7 (C-4), 76.2 (C-2), 78.2 (C-3), 101.7 (C-1), 127.6, 127.6, 127.6, 127.8, 128.3, 128.3, 128.3 (Ph$_{tert.}$), 138.2, 138.4, 138.4 (Ph$_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2926, 2106, 1722, 1453. HRMS (ESI): *m/z* calcd for $C_{29}H_{32}O_6Na$: 499.2091; found: 499.2085.

Compound 22

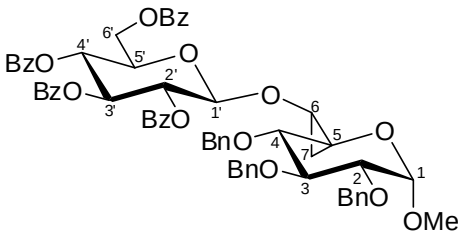


22

To a solution of **20** (14.0 mg, 0.029 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 1.0 mL) was added Pd/C (10 wt.% on activated carbon, 14 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 5:1) afforded **22** (4.1 mg, 69%) as a colorless oil.

R_f: 0.27 (dichloromethane/methanol, 7:1). $[\alpha]_D^{20}$ = 72.1° (c = 0.70, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ = 0.68 (dd, *J* = 7.3, 4.3 Hz, 1 H, 7-H), 0.93 (t, *J* = 7.3 Hz, 1 H, 7H), 3.29 (d, *J* = 5.2 Hz, 1 H, 4-H), 3.33 (dd, *J* = 7.3, 4.3 Hz, 1 H, 6-H), 3.45 (s, 3 H, OMe), 3.72 (dd, *J* = 6.2, 3.4 Hz, 1 H, 2-H), 3.88 (d, *J* = 5.2 Hz, 1 H, 3-H), 4.68 (d, *J* = 6.2 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 17.6 (C-7), 54.7 (C-6), 59.5 (OMe), 62.8 (C-5), 73.0 (C-2), 75.4, 75.4 (C-3, C-4), 105.7 (C-1). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3331, 2925, 2360, 1737, 1642. HRMS (ESI): *m/z* calcd for $C_8H_{14}O_6Na$: 229.0683; found: 229.0687.

Compound 24



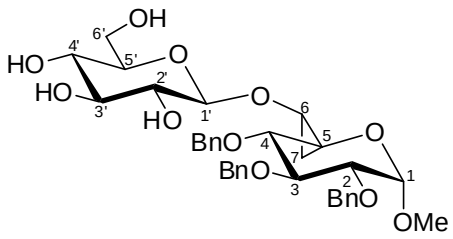
24

Glycosyl donor **23** (0.150 g, 0.206 mmol, 2.0 eq.) and glycosyl acceptor **14** (0.049 g, 0.103 mmol, 1.0 eq.) were azeotroped with toluene (2 x 3 mL) and then dried under reduced pressure for 1 h. Dichloromethane (3.0 mL) was added under an argon atmosphere and the solution was cooled to 0 °C. TMSOTf (2.9 µL, 0.015 mmol, 0.15 eq.) was added and stirred at 0 °C for 3 h. Pyridine (1.1 mL) was added and the solvents were removed under reduced

pressure. The residue was purified by column chromatography (SiO_2, pentane/ethyl acetate, 2:1 → 3:2) to afford **24** (0.077 g, 71%) as colorless foam.

R_f: 0.23 (hexane/ethyl acetate, 2:1). $[\alpha]_D^{20}$ = 9.7° (c = 0.3, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.8 Hz, 1 H, 7-H), 1.22–1.28 (m, 1 H, 7-H), 3.30 (s, 3 H, OMe), 3.50 (dd, *J* = 6.5, 2.5 Hz, 1 H, 2-H), 3.54 (d, *J* = 5.6 Hz, 1 H, 4-H), 3.68–3.74 (m, 1 H, 6-H), 3.83 (dd, *J* = 6.4, 5.6 Hz, 1 H, 3-H), 4.15–4.22 (m, 2 H, C*H*$_2$Ph, 5'-H), 4.34 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$Ph), 4.45–4.54 (m, 2 H, C*H*$_2$Ph, 6'-H), 4.55 (d, *J* = 2.5 Hz, 1 H, 1-H), 4.60 (s, 2 H, C*H*$_2$Ph), 4.65–4.75 (m, 2 H, C*H*$_2$Ph, 6'-H), 4.95 (d, *J* = 7.9 Hz, 1 H, 1'-H), 5.43 (dd, *J* = 9.6, 7.9 Hz, 1 H, 2'-H), 5.63 (t, *J* = 9.6 Hz, 1 H, 4'-H), 5.87 (t, *J* = 9.6 Hz, 1 H, 3'-H), 7.02–7.09 (m, 2 H, Ph-H), 7.14–7.53 (m, 25 H, Ph-H), 7.74–7.79 (m, 2 H, Ph-H), 7.85–7.95 (m, 4 H, Ph-H), 7.98–8.04 (m, 2 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 16.5 (C-7), 56.4 (OMe), 60.4 (C-5), 61.2 (C-6), 62.8 (C-6'), 69.4 (C-4'), 71.7 (C-2'), 72.5, 73.0, 73.1, 73.4, 73.5 (3 x *C*H$_2$Ph, C-3', C-5'), 74.6 (C-4), 77.1 (C-2), 77.8 (C-3), 100.0 (C-1), 101.3 (C-1'), 127.1, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.4, 128.5, 128.7, 128.8, 129.1, 129.6, 129.8, 129.8, 129.8 ($Ph_{tert.}$), 133.1, 133.2, 133.4, 133.5 ($Ph_{quart.(Bz)}$), 138.6, 138.7, 138.7 ($Ph_{quart.(Bn)}$), 164.7, 165.1, 165.8, 166.1 (O(*C*O)Ph). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2985, 2360, 1725, 1600. HRMS (ESI): *m/z* calcd for $C_{63}H_{58}O_{15}Na$: 1077.3668; found: 1077.3673.

Compound 25a

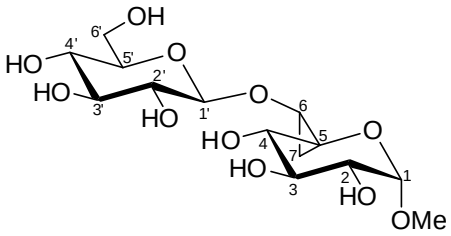


25a

Disaccharide **24** (0.028 g, 0.027 mmol, 1.0 eq.) was dissolved in methanol (0.5 mL) and treated under an argon atmosphere with a solution of NaOMe (5.25 M in methanol, 1.0 µL, 0.0053 mmol, 0.2 eq.). The reaction mixture was stirred for 7 h at room temperature. Amberlite acidic resin was added until the reaction mixture turned to pH 7. After filtration the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, dichloromethane/methanol, 20:1) afforded **25a** (0.016 g, 93%) as a colorless oil.

R_f: 0.23 (dichloromethane/methanol, 20:1). $[\alpha]_D^{20}$ = 17.2° (c = 0.69, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.10 (t, *J* = 7.6 Hz, 1 H, 7-H), 1.33 (dd, *J* = 7.6, 5.0 Hz, 1 H, 7-H), 3.13 (dd, *J* = 9.2, 7.4 Hz, 1 H, 2'-H), 3.25 (t, *J* = 9.3 Hz, 1 H), 3.29–3.35 (m, 2 H), 3.36 (s, 3 H, OMe), 3.59 (dd, *J* = 6.2, 2.4 Hz, 1 H, 2-H), 3.70 (dd, *J* = 11.9, 5.7 Hz, 1 H, 6'-H), 3.76 (dd, *J* = 7.6, 5.0 Hz, 1 H, 6-H), 3.87–3.95 (m, 3 H, 3-H, 6'-H), 4.36 (d, *J* = 7.4 Hz, 1 H, 1'-H), 4.56–4.69 (m, 5 H, C*H*$_2$Ph), 4.70 (d, *J* = 2.4 Hz, 1 H, 1-H), 4.78 (d, *J* = 11.2 Hz, 1 H, C*H*$_2$Ph), 7.20–7.35 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 17.0 (C-7), 56.9 (OMe), 61.4 (C-6), 61.8 (C-5), 62.8 (C-6'), 71.6 (C-4, C-3', C-4', C-5'), 74.2, 74.3, 74.8, 74.9 (3 x *C*H_2Ph, C-2'), 75.8, 78.0, 78.3 (C-4, C-3', C-4', C-5'), 78.8 (C-2), 79.3 (C-3), 101.1 (C-1), 104.2 (C-1'), 128.4, 128.7, 128.7, 128.9, 129.1, 129.2, 129.2, 129.3, 129.3 ($Ph_{tert.}$), 139.7, 139.7, 140.4 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3376, 2922, 2360, 1738, 1452. HRMS (ESI): *m/z* calcd for $C_{35}H_{42}O_{11}Na$: 661.2619; found: 661.2618.

Compound 25



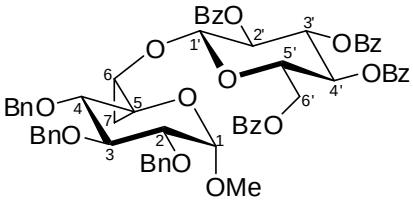
25

To a solution of disaccharide **25a** (12.0 mg, 0.018 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 1.0 mL) was added Pd/C (10 wt.% on activated carbon, 15 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 5:1) afforded **25** (6.6 mg, quant.) as a colorless oil.

R_f: 0.15 (dichloromethane/methanol, 5:1). $[\alpha]_D^{20}$ = -3.5° (c = 0.40, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.00 (t, *J* = 7.7 Hz, 1 H, 7-H), 1.40 (dd, *J* = 7.4, 4.8 Hz, 1 H, 7-H), 3.13 (dd, *J* = 9.1, 8.0 Hz, 1 H, 2'-H), 3.27–3.29 (m, 2 H, 5'-H, 4'-H), 3.32–3.35 (m, 4 H, 3'-H, OMe), 3.53 (dd, *J* = 8.5, 3.4 Hz, 1 H, 2-H), 3.69 (dd, *J* = 12.0, 5.1 Hz, 1 H, 6'-H), 3.80 (t, *J* = 7.7 Hz, 1 H, 3-H), 3.84–3.90 (m, 3 H, 4-H, 7-H, 6'-H), 4.25 (d, *J* = 8.0 Hz, 1 H, 1'-H), 4.63 (d, *J* = 3.4 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 15.4 (C-7), 56.9 (OMe),

59.6 (C-6), 61.4 (C-5), 62.6 (C-6'), 70.4 (C-4), 71.5 (C-5'), 72.2 (C-2), 73.4 (C-3), 74.6 (C-2'), 77.9, 78.3 (C-3', C-4'), 102.4 (C-1), 103.1 (C-1'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3341, 2923, 2361, 1738, 1366. HRMS (ESI): *m/z* calcd for $C_{14}H_{24}O_{11}Na$: 391.1211; found: 391.1205.

Compound 26



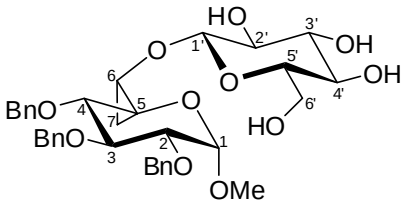
26

Glycosyl donor **23** (0.093 g, 0.13 mmol, 1.5 eq.) and glycosyl acceptor **15** (0.040 g, 0.084 mmol, 1.0 eq.) were azeotroped with toluene (2 x 2 mL) and then dried under reduced pressure for 1 h. Dichloromethane (1.5 mL) was added under an argon atmosphere and the solution was cooled to 0 °C. TMSOTf (2.4 µL, 0.013 mmol, 0.15 eq.) was added and stirred at 0 °C for 1 h. Pyridine (0.8 mL) was added and the solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, pentane/ethyl acetate, 4:1 → 3:1) to afford **26** (0.053 g, 60%) as colorless foam.

R_f: 0.25 (hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = 24.6° (c = 3.05, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.89 (dd, *J* = 7.5, 4.5 Hz, 1 H, 7-H), 1.27 (t, *J* = 7.8 Hz, 1 H, 7-H), 2.72 (s, 3 H, OMe), 3.47 (dd, *J* = 9.6, 3.8 Hz, 1 H, 2-H), 3.59 (dd, *J* = 8.0, 4.2 Hz, 1 H, 6-H), 3.66 (d, *J* = 9.0 Hz, 1 H, 4-H), 3.81 (t, *J* = 9.0 Hz, 1 H, 3-H), 4.04 (d, *J* = 3.8 Hz, 1 H, 1-H), 4.13 (m, 1 H, 5'-H), 4.42 (d, *J* = 11.3 Hz, 1 H, C*H*$_2$Ph), 4.49 (dd, *J* = 12.1, 5.1 Hz, 1 H, 6'-H), 4.55 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 4.60 (dd, *J* = 12.9, 3.7 Hz, 1 H, 6'-H), 4.67–4.72 (m, 3 H, C*H*$_2$Ph), 4.85 (d, *J* = 7.9 Hz, 1 H, 1'-H), 4.88 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$Ph), 5.48 (dd, *J* = 9.8, 8.0 Hz, 1 H, 2'-H), 5.64 (t, *J* = 9.8 Hz, 1 H, 4'-H), 5.90 (t, *J* = 9.7 Hz, 1 H, 3'-H), 7.12 (d, *J* = 6.8 Hz, 2 H, Ph-H), 7.21–7.49 (m, 25 H, Ph-H), 7.80 (d, *J* = 8.3 Hz, 2 H, Ph-H), 7.87 (d, *J* = 8.4 Hz, 2 H, Ph-H), 7.92 (d, *J* = 8.4 Hz, 2 H, Ph-H), 7.95 (d, *J* = 8.4 Hz, 2 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 14.1 (C-7), 52.9 (C-6), 55.7 (OMe), 55.9 (C-5), 63.2 (C-6'), 69.6 (C-4'), 71.6 (C-2'), 72.2 (C-5'), 72.7 (C-3'), 73.2, 74.9, 75.6 (*C*H$_2$Ph), 77.5 (C-4), 80.1 (C-2), 81.1 (C-3), 99.4 (C-1), 101.8 (C-1'), 127.7, 127.8, 127.9, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 129.5, 129.7, 129.7, 129.9 ($Ph_{tert.}$), 133.0, 133.1, 133.3 ($Ph_{quart.(Bz)}$), 137.8, 138.1, 138.6

($Ph_{quart.(Bn)}$), 164.6, 165.1, 165.7, 166.1 (O(*C*O)Ph). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2913, 1726, 1601, 1451. HRMS (ESI): *m/z* calcd for $C_{63}H_{58}O_{15}Na$: 1077.3668; found: 1077.3672.

Compound 27a

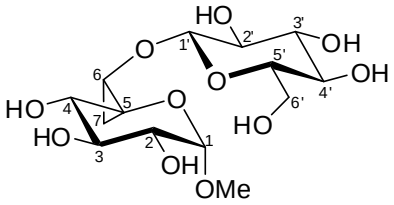


27a

Compound **26** (0.032 g, 0.030 mmol, 1.0 eq.) was dissolved in methanol (1.0 mL) and treated under an argon atmosphere with a solution of NaOMe (5.25 M in methanol, 1.1 µL, 0.0060 mmol, 0.2 eq.). The reaction mixture was stirred for 7 h at room temperature. Amberlite acidic resin was added until the reaction mixture turned to pH 7. After filtration the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, dichloromethane/methanol, 20:1) afforded **27a** (0.015 g, 78%) as a colorless oil.

R_f: 0.25 (dichloromethane/methanol, 20:1). $[\alpha]_D^{20}$ = 27.9° (c = 0.24, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.04 (dd, *J* = 7.4, 4.3 Hz, 1 H, 7-H), 1.22 (t, *J* = 7.4 Hz, 1 H, 7-H), 3.15 (dd, *J* = 9.0, 8.0 Hz, 1 H, 2'-H), 3.23–3.28 (m, 2 H, 4'-H, 5'-H), 3.33 (t, *J* = 9.0 Hz, 1 H, 3'-H), 3.40 (s, 3 H, OMe), 3.59 (dd, *J* = 7.9, 4.4 Hz, 1 H, 6-H), 3.64 (dd, *J* = 9.2, 3.7 Hz, 1 H, 2-H), 3.67 (dd, *J* = 11.9, 5.4 Hz, 1 H, 6'-H), 3.71 (d, *J* = 8.8 Hz, 1 H, 4-H), 3.83 (t, *J* = 9.2 Hz, 1 H, 3-H), 3.85 (dd, *J* = 12.0, 2.2 Hz, 1 H, 6'-H), 4.33 (d, *J* = 8.0 Hz, 1 H, 1'-H), 4.58 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$Ph), 4.67 (d, *J* = 11.9 Hz, 1 H, C*H*$_2$Ph), 4.71 (d, *J* = 10.9 Hz, 1 H, C*H*$_2$Ph), 4.73 (d, *J* = 11.6 Hz, 1 H, C*H*$_2$Ph), 4.76 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$Ph), 4.79 (d, *J* = 3.7 Hz, 1 H, 1-H), 4.84–4.86 (m, 1 H, C*H*$_2$Ph), 7.20–7.38 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 14.9 (C-7), 54.4 (C-6), 57.1 (C-5), 57.4 (OMe), 62.7 (C-6'), 71.5 (C-4', C-5'), 74.2 (*C*H$_2$Ph), 75.2 (C-2'), 76.0, 76.3 (*C*H$_2$Ph), 77.9 (C-3'), 78.1 (C-4', C-5), 78.8 (C-4), 81.4 (C-2), 81.7 (C-3), 101.2 (C-1), 105.0 (C-1'), 128.7, 128.8, 129.0, 129.0, 129.3, 129.3, 129.4, 129.5 ($Ph_{tert.}$), 139.5, 139.6, 140.0 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3411, 2926, 2340, 1739, 1452. HRMS (ESI): *m/z* calcd for $C_{35}H_{42}O_{11}Na$: 661.2619; found: 661.2619.

Compound 27

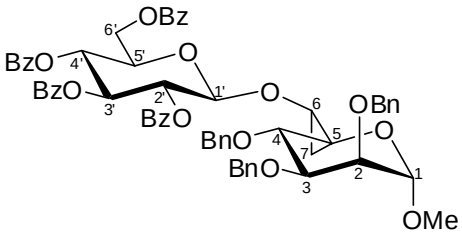


27

To a solution of disaccharide **27a** (8.2 mg, 0.013 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 0.5 mL) was added Pd/C (10 wt.% on activated carbon, 15 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (SiO_2, dichloromethane/methanol, 5:1) afforded **27** (4.7 mg, quant.) as a colorless oil.

R_f: 0.44 (dichloromethane/methanol, 5:1). $[\alpha]_D^{20}$ = 15.1° (c = 0.43, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ = 1.03 (dd, *J* = 7.3, 4.4 Hz, 1 H, 7-H), 1.21 (t, *J* = 7.5 Hz, 1 H, 7-H), 3.18 (dd, *J* = 8.9, 8.0 Hz, 1 H), 3.26–3.29 (m, 1 H), 3.33–3.35 (m, 1 H), 3.44 (s, 3 H, OMe), 3.51 (dd, *J* = 8.2, 3.7 Hz, 1 H, 2-H), 3.55–3.70 (m, 5 H), 3.87 (dd, *J* = 11.8, 1.2 Hz, 1 H, 6'-H), 4.44 (d, *J* = 7.8 Hz, 1 H, 1'-H), 4.77 (d, *J* = 3.7 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 14.4 (C-7), 54.4 (C-5, C-6), 57.1 (OMe), 58.5 (C-5, C-6), 62.7 (C-6'), 71.5, 71.7, 73.4, 73.6, 75.2, 77.9, 78.2 (C-2, C-3, C-4, C-2', C-3', C-4', C-5'), 102.9 (C-1), 104.9 (C-1'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3318, 2923, 2341, 1453. HRMS (ESI): *m/z* calcd for $C_{14}H_{24}O_{11}Na$: 391.1211; found: 391.1215.

Compound 28



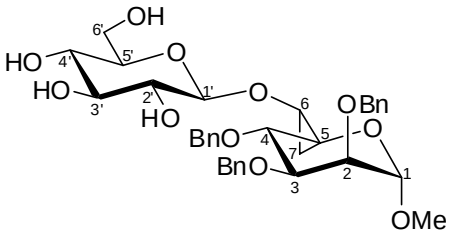
28

Glycosl donor **23** (0.27 g, 0.36 mmol, 2.0 eq.) and glycosyl acceptor **19** (0.085 g, 0.18 mmol, 1.0 eq.) were azeotroped with toluene (2 x 4 mL) and then dried under reduced pressure for 1 h. Dichloromethane (4.0 mL) was added under an argon atmosphere and the solution was

cooled to 0 °C. TMSOTf (5.2 µL, 0.027 mmol, 0.15 eq.) was added and stirred at 0 °C for 3 h. Pyridine (0.7 mL) was added and the solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, pentane/ethyl acetate, 2.5:1 → 2:1 → 1.5:1) and afforded **28** (0.14 g, 76%) as a colorless foam.

R_f: 0.31 (hexane/ethyl acetate, 3:2). $[\alpha]_D^{20}$ = 1.4° (c = 0.36, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): δ = 0.78 (dd, *J* = 7.1, 4.2 Hz, 1 H, 7-H), 1.15 (t, *J* = 7.1 Hz, 1 H, 7-H), 3.31 (d, *J* = 3.3 Hz, 1 H, 4-H), 3.39 (s, 3 H, OMe), 3.57 (dd, *J* = 8.1, 3.2 Hz, 1 H, 2-H), 3.65 (d, *J* = 11.5 Hz, 1 H, C*H*$_2$Ph), 3.69 (t, *J* = 3.2 Hz, 1 H, 3-H), 3.97 (dd, *J* = 6.9, 4.1 Hz, 1 H, 6-H), 4.00 (d, *J* = 11.5 Hz, 1 H, C*H*$_2$Ph), 4.18 (ddd, *J* = 9.9, 4.9, 3.4 Hz, 1 H, 5'-H), 4.30 (d, *J* = 13.1 Hz, 1 H, C*H*$_2$Ph), 4.41 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.54 (dd, *J* = 12.1, 4.9 Hz, 1 H, 6'-H), 4.63 (d, *J* = 11.9 Hz, 1 H, C*H*$_2$Ph), 4.65 (dd, *J* = 12.1, 3.4 Hz, 1 H, 6'-H), 4.82 (d, *J* = 13.1 Hz, 1 H, C*H*$_2$Ph), 4.85 (d, *J* = 8.1 Hz, 1 H, 1-H), 4.87 (d, *J* = 8.0 Hz, 1 H, 1'-H), 5.45 (dd, *J* = 9.8, 8.0 Hz, 1 H, 2'-H), 5.65 (t, *J* = 9.8 Hz, 1 H, 4'-H), 5.88 (t, *J* = 9.8 Hz, 1 H, 3'-H), 6.81–6.84 (m, 2 H, Ph-H), 7.11–7.54 (m, 25 H, Ph-H), 7.78–7.82 (m, 2 H, Ph-H), 7.86–7.89 (m, 2 H, Ph-H), 7.97–8.03 (m, 4 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 17.5 (C-7), 56.5 (OMe), 60.0 (C-6), 60.4 (C-5), 63.1 (C-6'), 69.7 (C-4'), 71.2 (*C*H$_2$Ph), 71.8 (C-2'), 72.2 (*C*H$_2$Ph), 72.4 (C-5'), 72.6 (*C*H$_2$Ph), 72.9 (C-3'), 74.6, 74.6 (C-3, C-4), 75.1 (C-2), 100.6 (C-1'), 100.9 (C-1), 127.2, 127.2, 127.2, 127.3, 127.7, 127.8, 127.8, 128.0, 128.1, 128.3, 128.4, 128.4, 128.7, 128.8, 129.0, 129.6, 129.7, 129.8, 129.8, 129.8 ($Ph_{tert.}$), 133.1, 133.3, 133.4, 133.7 ($Ph_{quart.(Bz)}$), 138.1, 138.7, 138.7 ($Ph_{quart.(Bn)}$), 164.7, 165.1, 165.8, 166.2 (O(*C*O)Ph). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2921, 1725, 1451, 1259. HRMS (ESI): *m/z* calcd for $C_{63}H_{58}O_{15}Na$: 1077.3668; found: 1077.3689.

Compound 29a



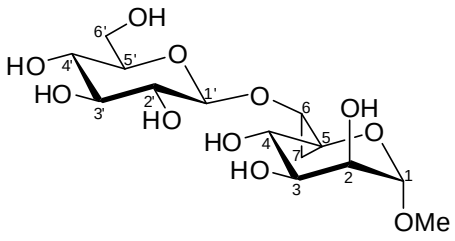
29a

Disaccharide **28** (0.067 g, 0.063 mmol, 1.0 eq.) was dissolved in methanol (1.0 mL) and treated under an argon atmosphere with a solution of NaOMe (5.25 M in methanol, 2.5 µL, 0.013 mmol, 0.2 eq.). The reaction mixture was stirred for 16 h at room temperature.

Amberlite acidic resin was added until the reaction mixture turned to pH 7. After filtration the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, dichloromethane/methanol, 20:1) afforded **29a** (0.031 g, 77%) as a colorless oil.

R_f: 0.29 (dichloromethane/methanol, 10:1). $[\alpha]_D^{20}$ = 1.8° (c = 1.24, DMF). ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.09 (t, *J* = 7.0 Hz, 1 H, 7-H), 1.12 (dd, *J* = 7.0, 4.5 Hz, 1 H, 7-H), 3.18 (dd, *J* = 9.1, 8.0 Hz, 1 H, 2'-H), 3.29 (dd, *J* = 9.5, 9.1 Hz, 1 H, 4'-H), 3.32–3.35 (m, 1 H, 5'-H), 3.38 (t, *J* = 9.1 Hz, 1 H, 3'-H), 3.44 (s, 3 H, OMe), 3.67 (dd, *J* = 8.0, 3.4 Hz, 1 H, 2-H), 3.71 (dd, *J* = 12.0, 5.9 Hz, 1 H, 6'-H), 3.86 (t, *J* = 3.4 Hz, 1 H, 3-H), 3.93 (dd, *J* = 12.0, 2.3 Hz, 1 H, 6'-H), 3.98 (d, *J* = 3.4 Hz, 1 H, 4-H), 4.03 (dd, *J* = 7.0, 4.5 Hz, 1 H, 6-H), 4.34 (d, *J* = 8.0 Hz, 1 H, 1'-H), 4.40 (d, *J* = 12.2 Hz, 1 H, C*H*$_2$Ph), 4.48 (d, *J* = 11.9 Hz, 2 H, C*H*$_2$Ph), 4.61 (d, *J* = 11.9 Hz, 1 H, C*H*$_2$Ph), 4.70 (d, *J* = 11.6 Hz, 1 H, C*H*$_2$Ph), 4.76 (d, *J* = 12.1 Hz, 1 H, C*H*$_2$Ph), 4.84 (d, *J* = 8.0 Hz, 1 H, 1-H), 7.24–7.34 (m, 13 H, Ph-H), 7.40–7.43 (m, 2 H, Ph-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 17.8 (C-7), 56.9 (OMe), 60.2 (C-6), 62.0 (C-5), 62.8 (C-6'), 71.5 (C-4'), 72.9, 73.4, 73.5 (*C*H$_2$Ph), 74.7 (C-2'), 75.2 (C-4), 76.4, 76.4 (C-2, C-3), 77.9 (C-5'), 78.4 (C-3'), 101.9 (C-1), 103.2 (C-1'), 128.4, 128.6, 128.6, 128.9, 129.1, 129.1, 129.2, 129.3, 129.3 (Ph$_{tert.}$), 139.5, 139.7, 139.7 (Ph$_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3387, 2924, 1655, 1496, 1387. HRMS (ESI): *m/z* calcd for $C_{35}H_{42}O_{11}Na$: 661.2619; found: 661.2609.

Compound 29

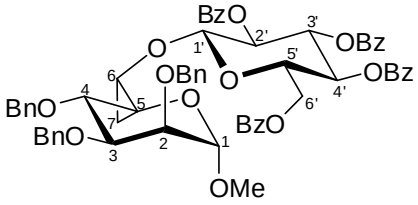


29

To a solution of disaccharide **29a** (0.016 g, 0.025 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 1.0 mL) was added Pd/C (10 wt.% on activated carbon, 10 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (Celite, dichloromethane/methanol, 4:1) afforded **29** (9.2 mg, quant.) as a colorless oil.

R_f: 0.16 (dichloromethane/methanol, 4:1). $[\alpha]_D^{20}$ = –11.4° (c = 0.49, MeOH). ^{1}H-NMR (300 MHz, CD_3OD): δ =1.01 (t, *J* = 7.3 Hz, 1 H, 7-H), 1.13 (dd, *J* = 7.3, 4.7 Hz, 1 H, 7-H), 3.16 (dd, *J* = 8.7, 8.0 Hz, 1 H, 2'-H), 3.27–3.36 (m, 3 H), 3.39 (s, 3 H, OMe), 3.69 (dd, *J* = 11.9, 5.2 Hz, 1 H, 6'-H), 3.76 (dd, *J* = 6.3, 3.3 Hz, 1 H, 2-H), 3.86–4.00 (m, 4 H, 6-H, 6'-H), 4.26 (d, *J* = 8.0 Hz, 1 H, 1'-H), 4.62 (d, *J* = 6.3 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 16.3 (C-7), 56.7 (OMe), 60.7 (C-6), 62.7, 62.7 (C-5, C-6'), 69.6 (C-3, C-4, C-3', C-4', C-5'), 70.2 (C-2), 71.6, 73.0 (C-3, C-4, C-3', C-4', C-5'), 74.6 (C-2'), 77.8, 78.2 (C-3, C-4, C-3', C-4', C-5'), 103.0 (C-1), 103.1 (C-1'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3311, 2923, 1645, 1444. HRMS (ESI): *m/z* calcd for $C_{14}H_{24}O_{11}Na$: 391.1211; found: 391.1206.

Compound 30



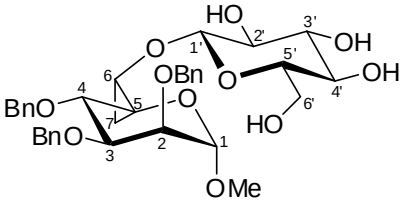
30

Glycosyl donor **23** (0.208 g, 0.281 mmol, 1.5 eq.) and glycosyl acceptor **20** (0.089 g, 0.187 mmol, 1.0 eq.) were azeotroped with toluene (2 x 2 mL) and then dried under reduced pressure for 1 h. Dichloromethane (3 mL) was added under an argon atmosphere and the solution was cooled to 0 °C. TMSOTf (2.5 µL, 3.1 mg, 0.014 mmol, 0.075 eq.) was added and stirred at 0 °C for 3 h. Pyridine (0.5 mL) was added and the solvents were removed under reduced pressure. The residue was purified by column chromatography (SiO_2, pentane/ethyl acetate, 4:1 → 3:1) to afford **30** (0.118 g, 60%) as a colorless foam.

R_f: 0.29 (hexane/ethyl acetate, 3:1). $[\alpha]_D^{20}$ = 27.5° (c = 0.08, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.92 (dd, *J* = 7.6, 4.2 Hz, 1 H, 7-H), 1.12 (t, *J* = 7.6 Hz, 1 H, 7-H), 2.74 (s, 3 H, OMe), 3.61 (dd, *J* = 7.6, 4.2 Hz, 1 H, 6-H), 3.68 (m_c, 1 H, 2-H), 3.70–3.79 (m, 2 H, 3-H, 4-H), 3.92 (m_c, 1 H, 5'-H), 4.36 (d, *J* = 3.7 Hz, 1 H, 1-H), 4.38–4.77 (m, 8 H, 6'-H, 6'-H, 6 x C*H*$_2$Ph), 4.98 (d, *J* = 7.9 Hz, 1 H, 1'-H), 5.50 (dd, *J* = 9.8, 7.9 Hz, 1 H, 2'-H), 5.63 (t, *J* = 9.8 Hz, 1 H, 4'-H), 5.88 (t, *J* = 9.8 Hz, 1 H, 3'-H), 7.09–7.53 (m, 27 H, Ph-H), 7.76–8.01 (m, 8 H, Ph-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 14.3 (C-7), 54.9 (C-5), 55.4 (OMe), 57.0 (C-6), 63.2 (C-6'), 69.6 (C-4'), 71.9 (C-2'), 72.1 (C-5'), 72.8, 72.9 (C-3', *C*H$_2$Ph), 73.1, 73.6 (*C*H$_2$Ph), 75.6 (C-3, C-4), 76.4 (C-2), 78.7 (C-3, C-4), 100.9 (C-1), 101.3 (C-1'), 127.6, 127.6,

127.7, 127.7, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.9, 129.5, 129.6, 129.6, 129.7, 129.8, 130.0 ($Ph_{tert.}$), 133.0, 133.0, 133.1, 133.4 ($Ph_{quart.(Bz)}$), 138.1, 138.6, 138.6 ($Ph_{quart.(Bn)}$), 164.9, 165.2, 165.8, 166.1 (O(*C*O)Ph). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2194, 1956, 1721, 1600, 1584, 1451. HRMS (ESI): *m/z* calcd for $C_{63}H_{58}O_{15}Na$: 1077.3668; found: 1077.3685.

Compound 31a

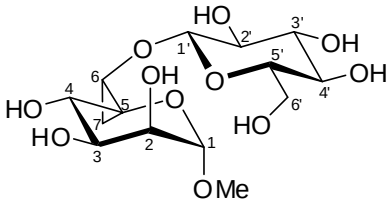


31a

Compound **30** (0.16 g, 0.15 mmol, 1.0 eq.) was dissolved in methanol (1.5 mL) and treated under an argon atmosphere with a solution of NaOMe (5.25 M in methanol, 5.7 µL, 0.030 mmol, 0.2 eq.). The reaction mixture was stirred for 16 h at room temperature. Amberlite acidic resin was added until the reaction mixture turned to pH 7. After filtration the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, dichloromethane/methanol, 10:1) afforded **31a** (0.090 g, 94%) as a colorless oil.

R_f: 0.38 (dichloromethane/methanol, 10:1). $[\alpha]_D^{20}$ = 6.0° (c = 0.35, DMF). ^{1}H-NMR (600 MHz, CD_3OD): δ = 0.96 (t, *J* = 7.6 Hz, 1 H, 7-H), 1.04 (dd, *J* = 7.6, 4.8 Hz, 1 H, 7-H), 2.98 (m_c, 1 H, 5'-H), 3.15 (dd, *J* = 9.2, 8.0 Hz, 1 H, 2'-H), 3.19 (m_c, 1 H, 4-H), 3.24 (t, *J* = 9.0 Hz, 1 H, 4'-H), 3.28–3.31 (m, 1 H, 3'-H), 3.51 (s, 3 H, OMe), 3.58–3.64 (m, 2 H, 6-H, 6'-H), 3.68 (dd, *J* = 6.8, 3.1 Hz, 1 H, 2-H), 3.76 (dd, *J* = 12.1, 2.3 Hz, 1 H, 6'-H), 3.86 (dd, *J* = 4.9, 3.1 Hz, 1 H, 3-H), 4.44–4.51 (m, 3 H, 1'-H, 2 x C*H*$_2$Ph), 4.56–4.63 (m, 3 H, C*H*$_2$Ph), 4.70 (d, *J* = 11.8 Hz, 1 H, C*H*$_2$Ph), 4.94 (d, *J* = 6.8 Hz, 1 H, 1-H), 7.15–7.36 (m, 15 H, Ph-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 14.8 (C-7), 57.2 (OMe), 58.6 (C-5), 58.9 (C-6), 62.7 (C-6'), 71.5 (C-4'), 73.5, 73.9, 74.1 (*C*H$_2$Ph), 75.2 (C-2'), 77.3 (C-2), 77.7, 77.8, 78.0 (C-3, C-4, C-5'), 102.5 (C-1), 104.4 (C-1'), 128.8, 128.8, 129.0, 129.0, 129.2, 129.3, 129.3, 129.4, 129.4, 129.5 ($Ph_{tert.}$), 139.6, 139.7, 139.8 ($Ph_{quart.}$). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3364, 2923, 1733, 1660, 1454. HRMS (ESI): *m/z* calcd for $C_{35}H_{42}O_{11}Na$: 661.2619; found: 661.2615.

Compound 31



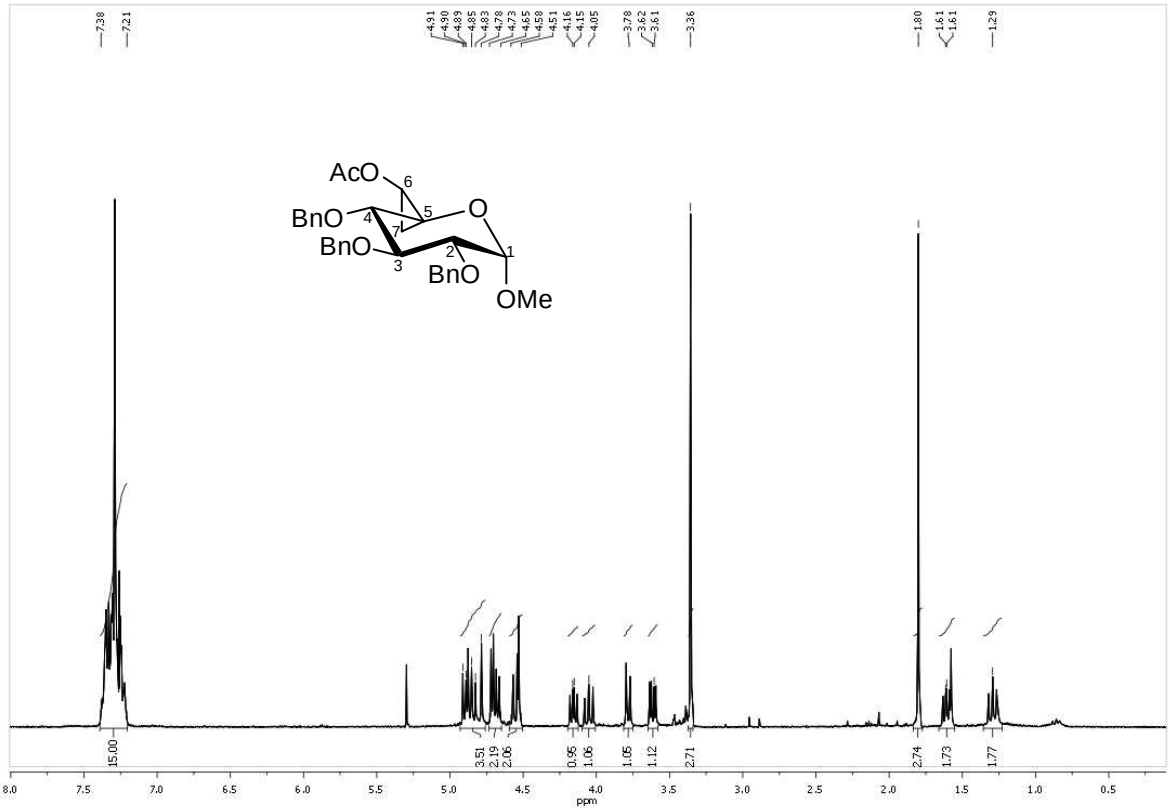
31

To a solution of disaccharide **31a** (0.032 g, 0.050 mmol, 1.0 eq.) in a mixture of methanol/dichloromethane/ethyl acetate (3:1:1, 1.5 mL) was added Pd/C (10 wt.% on activated carbon, 15 mg) under an argon atmosphere. The argon atmosphere was exchanged by a hydrogen atmosphere and the reaction mixture was stirred for 3 h at room temperature. Purification by column chromatography (Celite, dichloromethane/methanol, 4:1) afforded **31** (0.018 g, 98%) as a colorless oil.

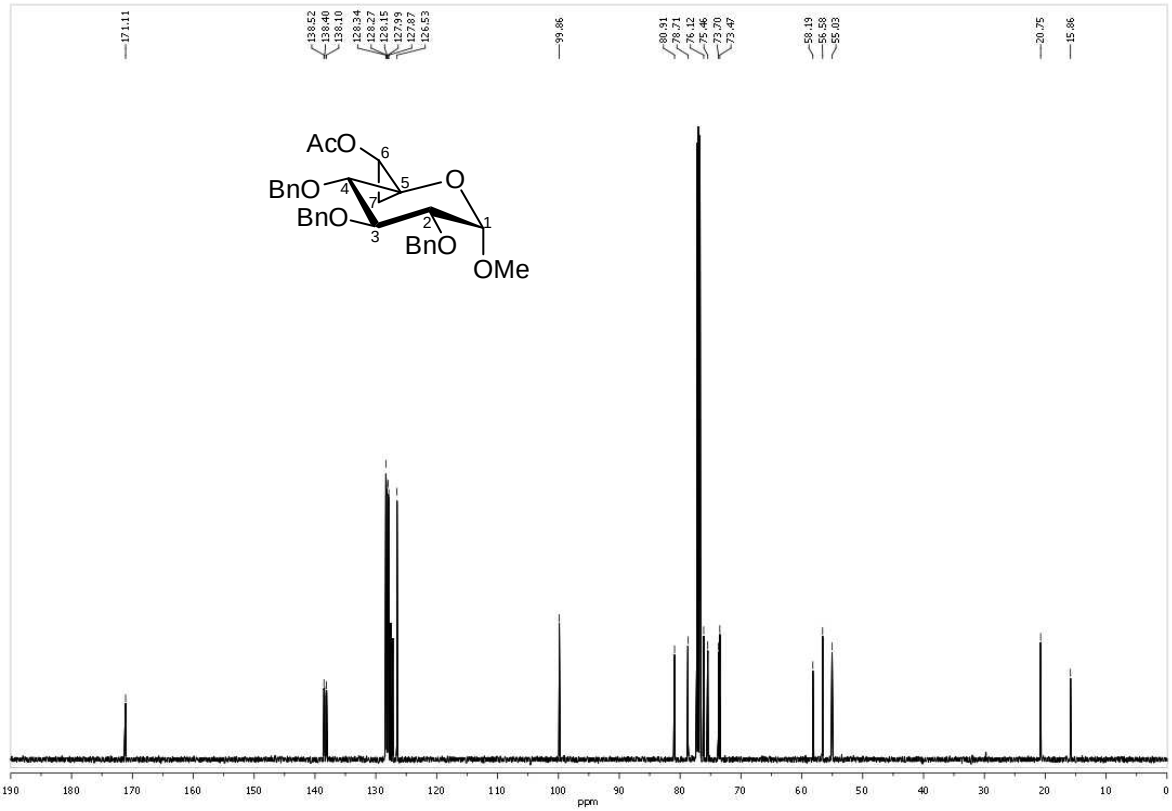
R_f: 0.21 (dichloromethane/methanol, 4:1). $[\alpha]_D^{20}$ = 14.3° (c = 0.70, MeOH). ^{1}H-NMR (600 MHz, CD_3OD): δ = 1.03–1.09 (m, 2 H, 7-H, 7-H), 3.20 (dd, *J* = 9.1, 8.0 Hz, 1 H, 2'-H), 3.26–3.32 (m, 2 H, 4-H, 4'-H), 3.40 (t, *J* = 9.1 Hz, 1 H, 3'-H), 3.45–3.50 (m, 4 H, OMe, 5'-H), 3.65–3.71 (m, 2 H, 6'-H, 6-H), 3.78 (dd, *J* = 5.3, 3.4 Hz, 1 H, 2-H), 3.85–3.90 (m, 2 H, 3-H, 6'-H), 4.57 (d, *J* = 8.0 Hz, 1 H, 1'-H), 4.75 (5, *J* = 5.3 Hz, 1 H, 1-H). ^{13}C-NMR (125 MHz, CD_3OD): δ = 14.1 (C-7), 57.0 (C-OMe), 57.9 (C-6), 59.8 (C-5), 62.8 (C-6'), 70.9 (C-2), 71.6 (C-4, C-4'), 71.9 (C-5'), 72.5 (C-3), 75.2 (C-2), 78.0 (C-3'), 78.1 (C-4, C-4'), 103.6 (C-1), 104.8 (C-1'). IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3321, 2923, 1702, 1601, 1449. HRMS (ESI): *m/z* calcd for $C_{14}H_{24}O_{11}Na$: 391.1211; found: 391.1213.

^{1}H and ^{13}C NMR Spectra of Compound 10-33

Compound 10

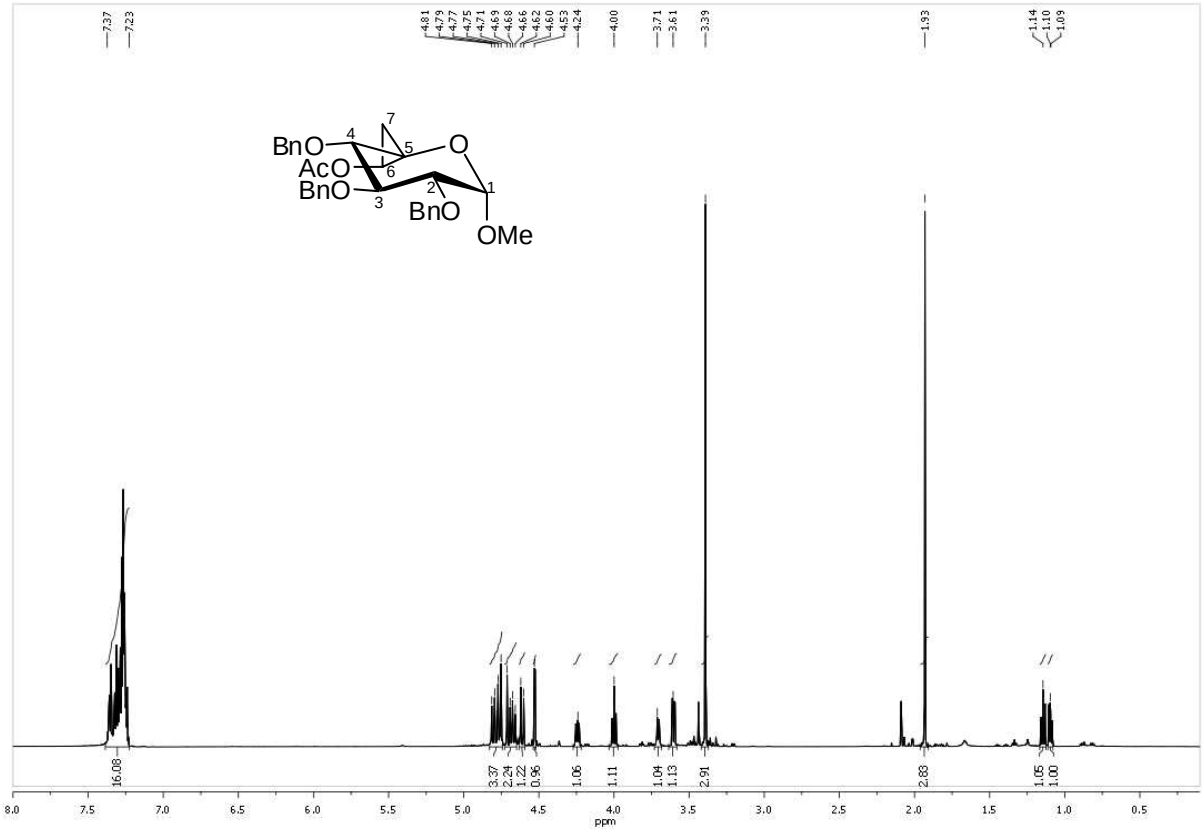


^{1}H NMR ($CDCl_3$, 300 MHz)

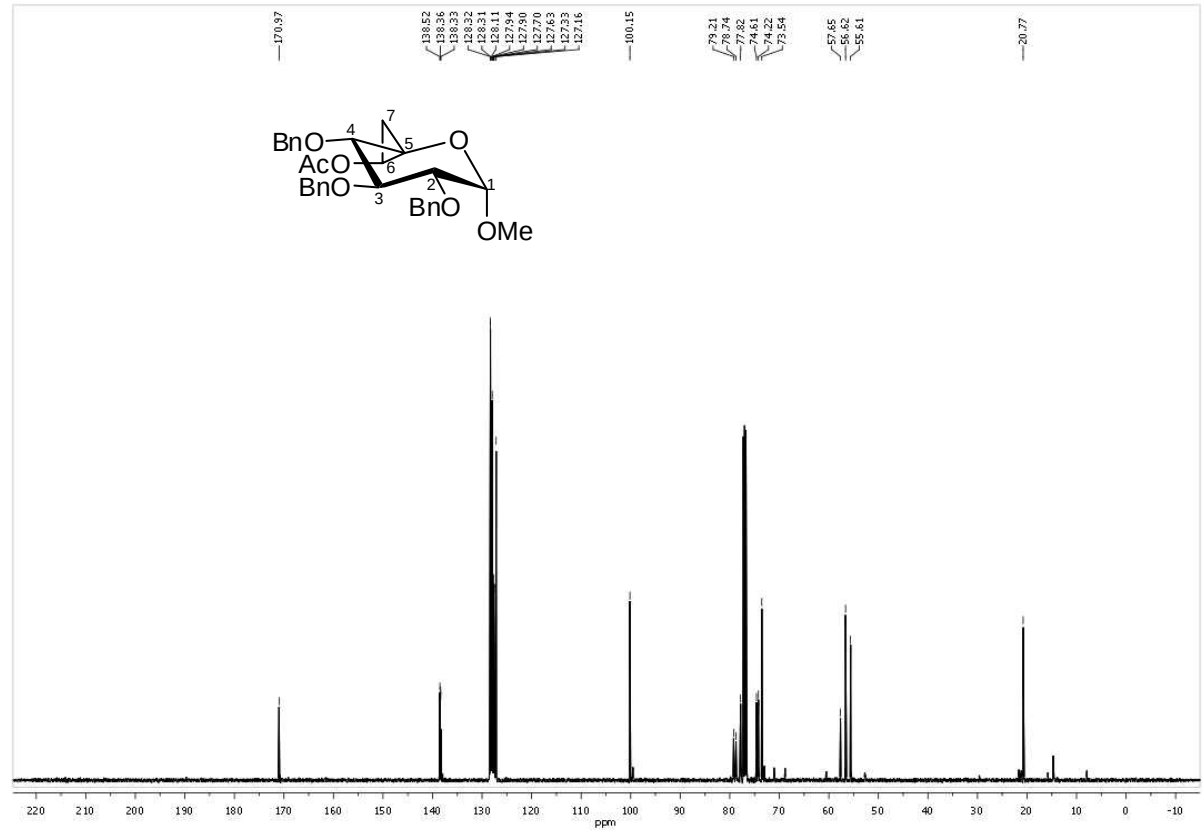


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 10a

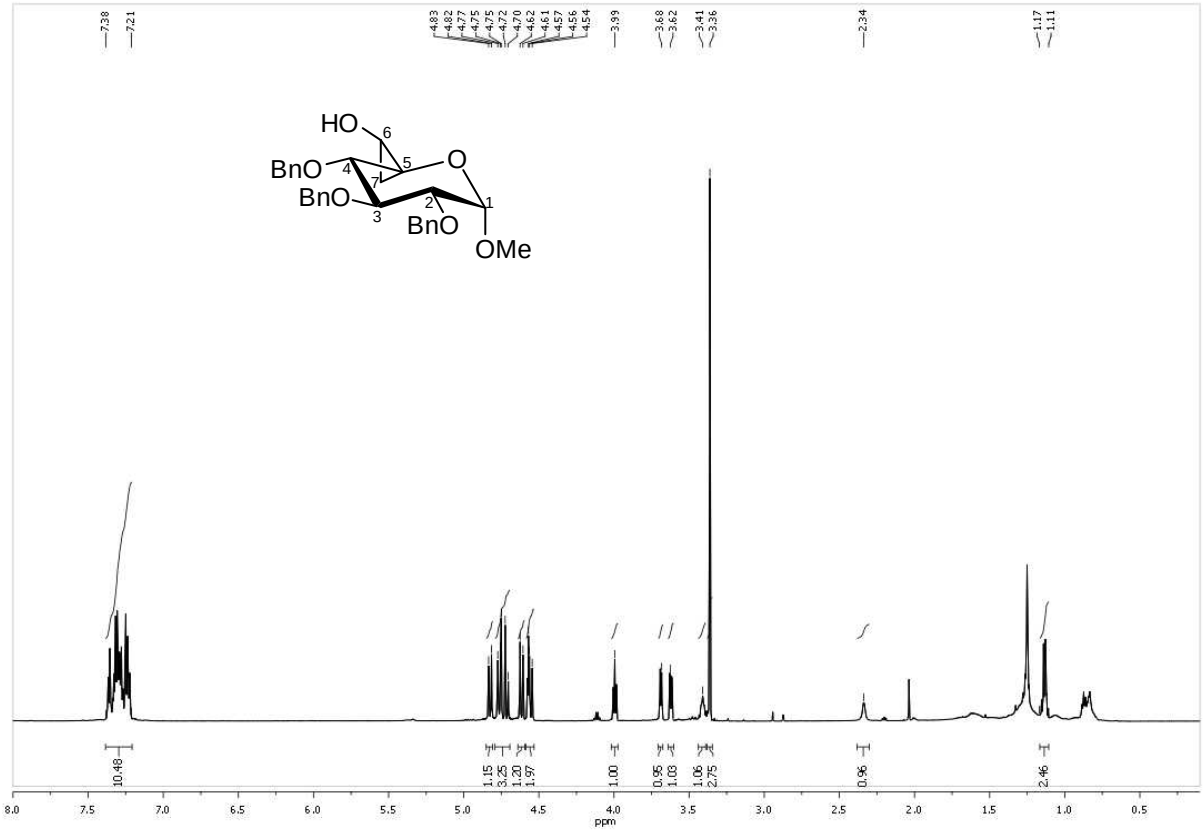


^{1}H NMR ($CDCl_3$, 600 MHz)

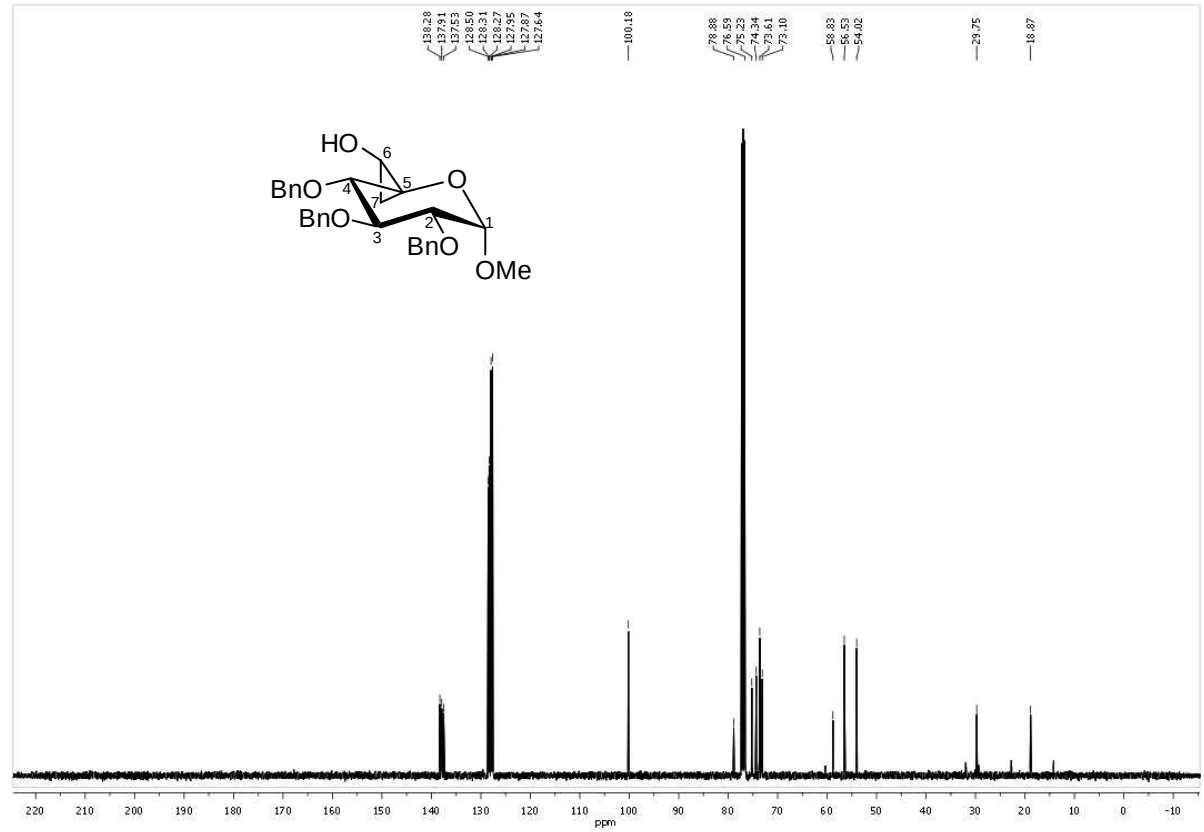


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 12

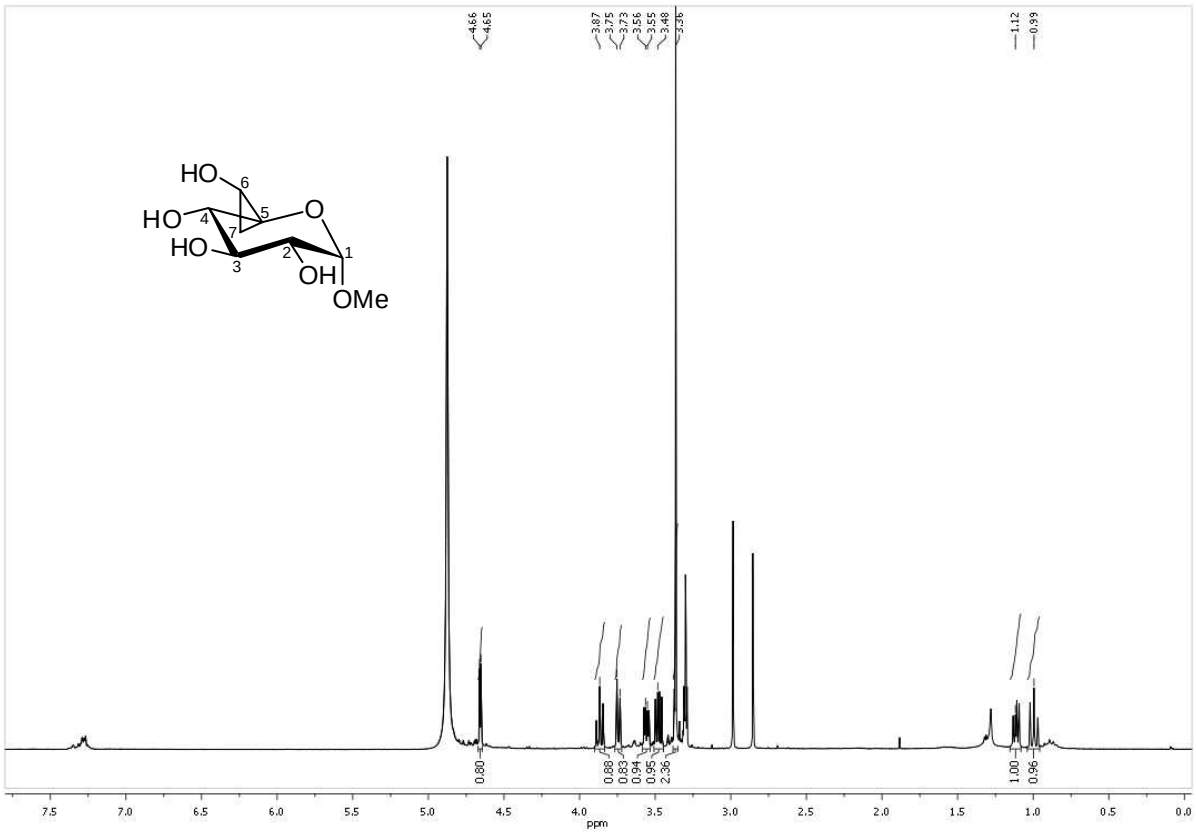


^{1}H NMR ($CDCl_3$, 600 MHz)

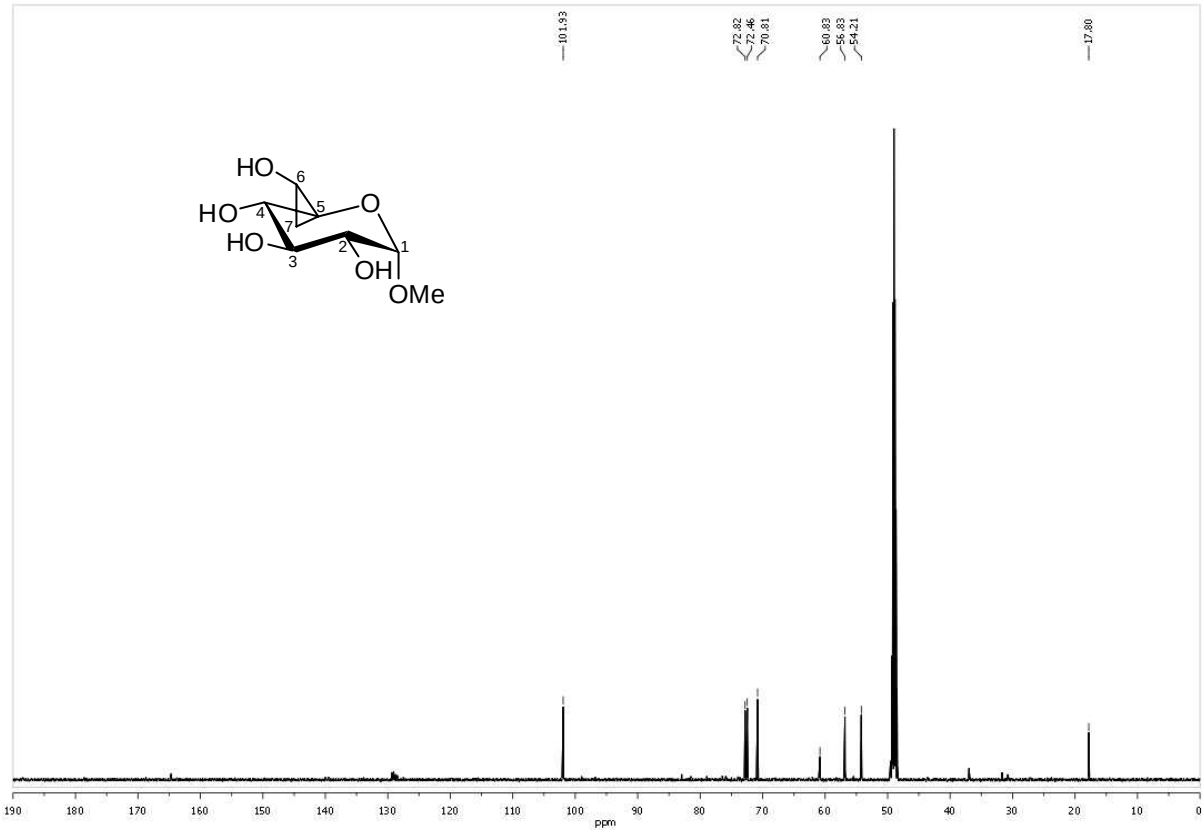


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 14

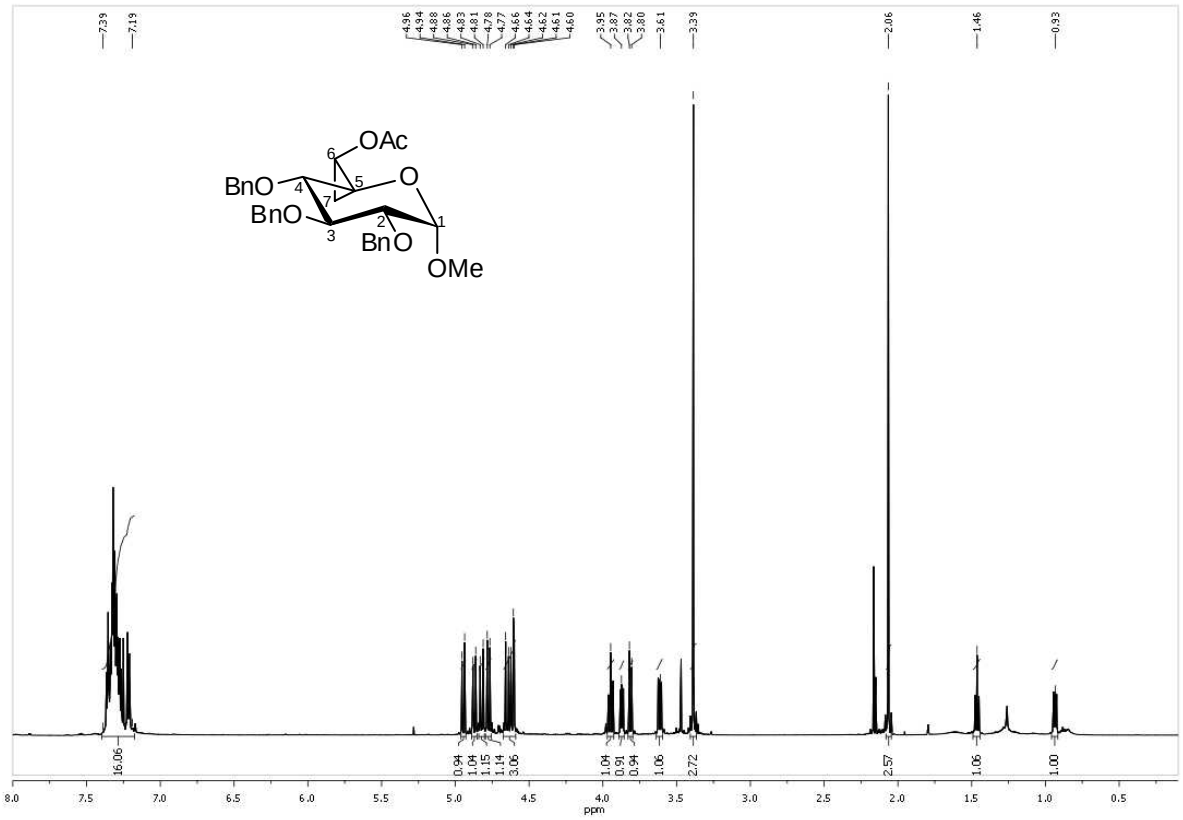


^{1}H NMR (CD_3OD, 300 MHz)

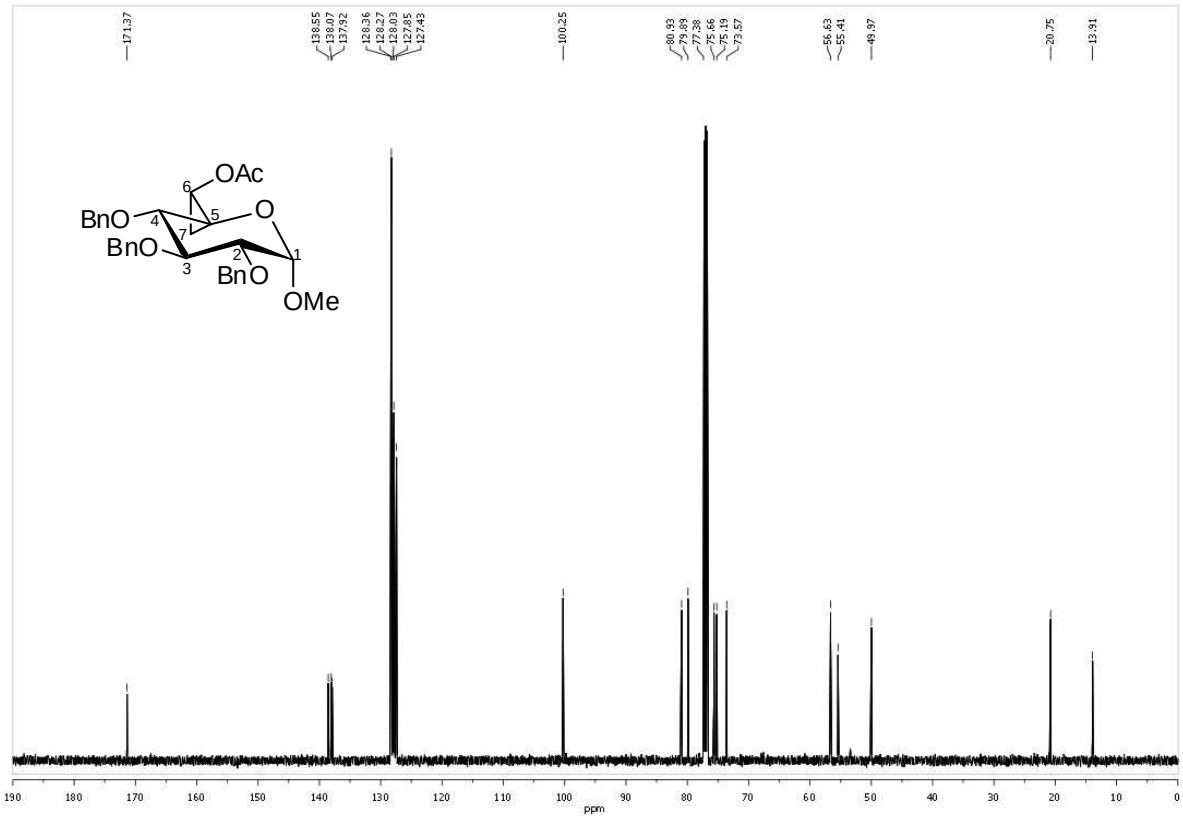


^{13}C NMR (CD_3OD, 125 MHz)

Compound 11

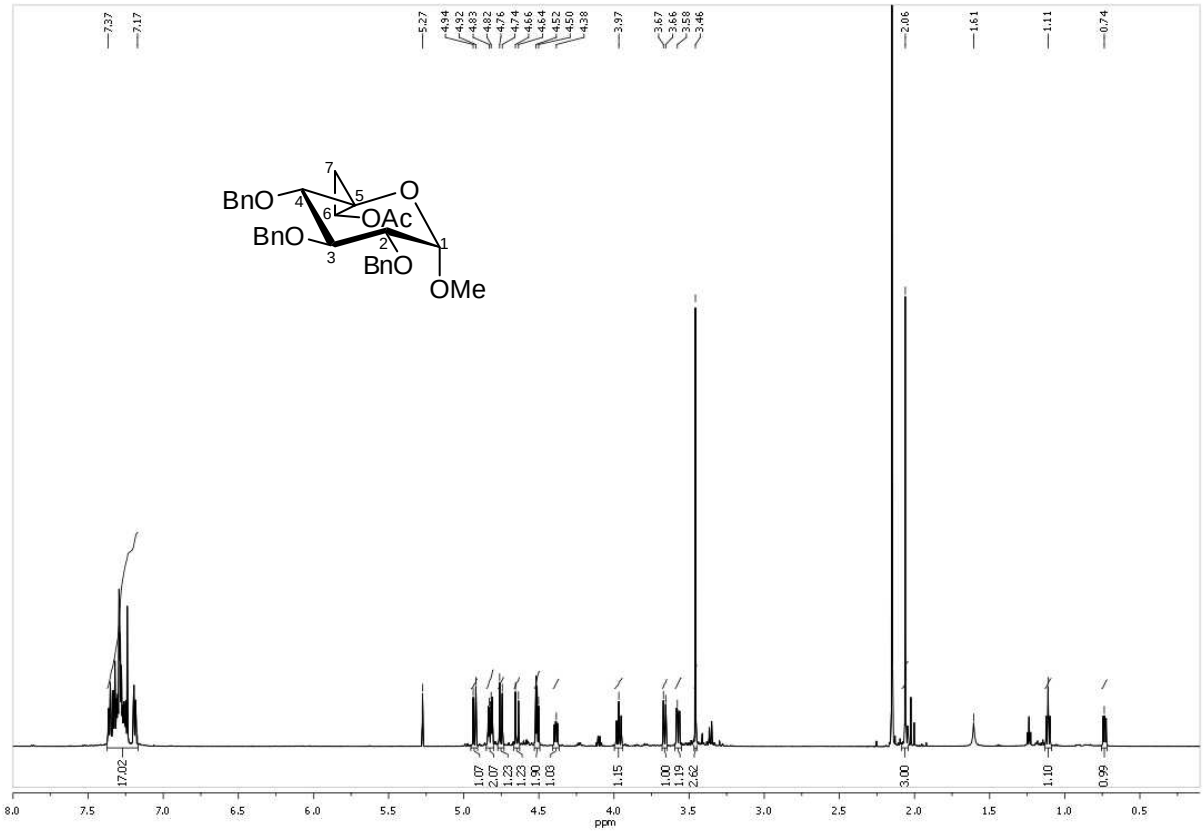


^{1}H NMR ($CDCl_3$, 600 MHz)

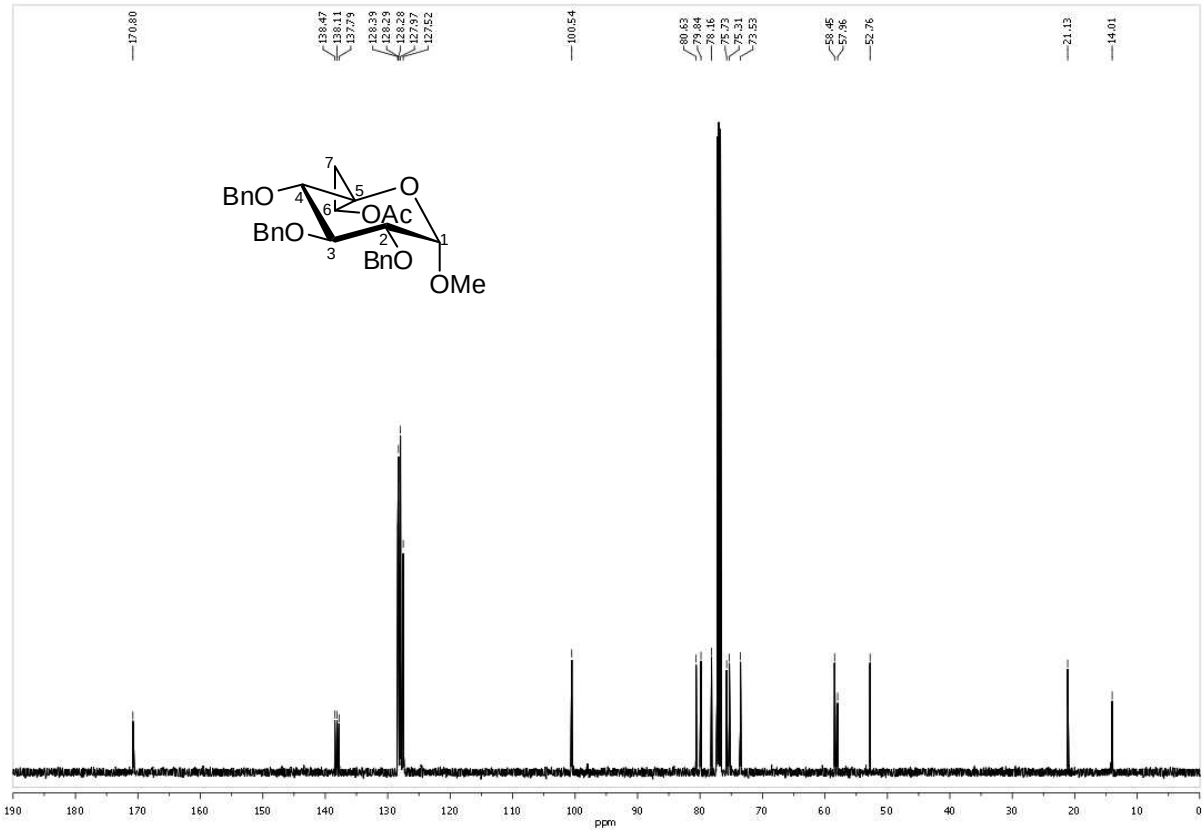


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 11a

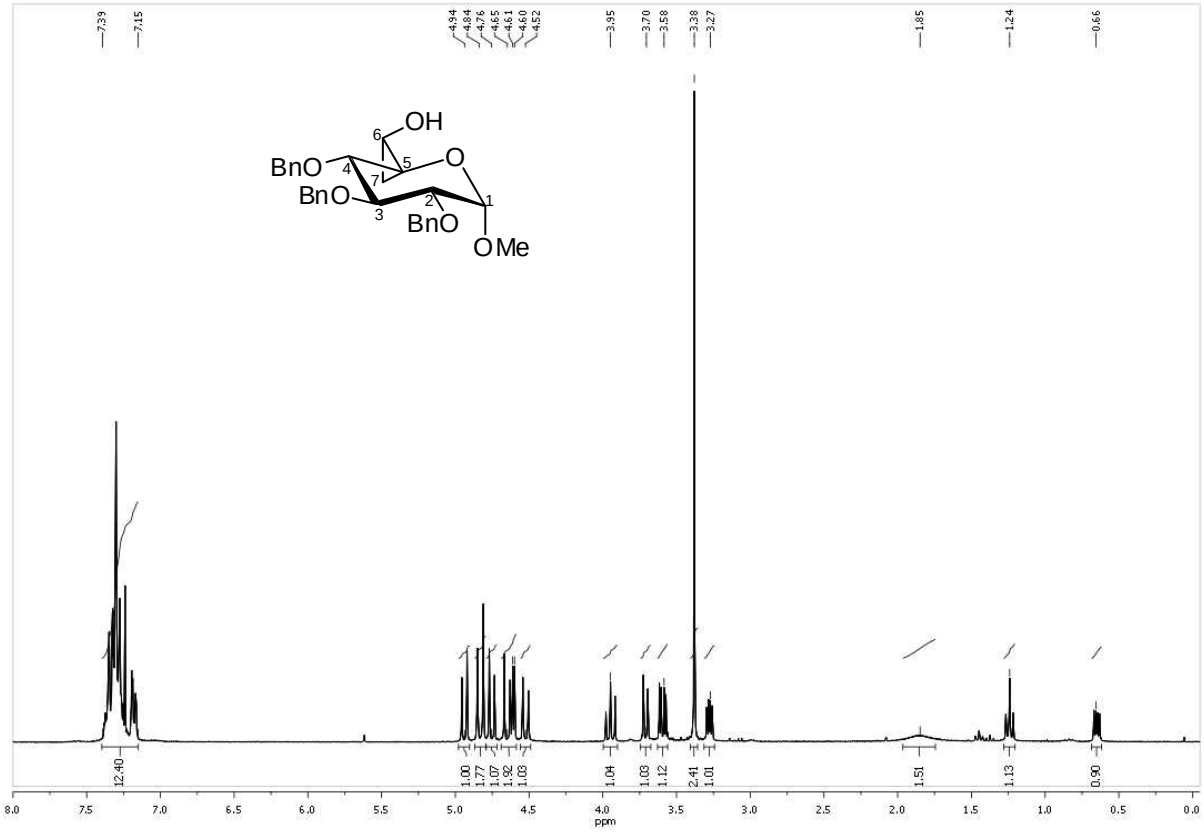


^{1}H NMR ($CDCl_3$, 600 MHz)

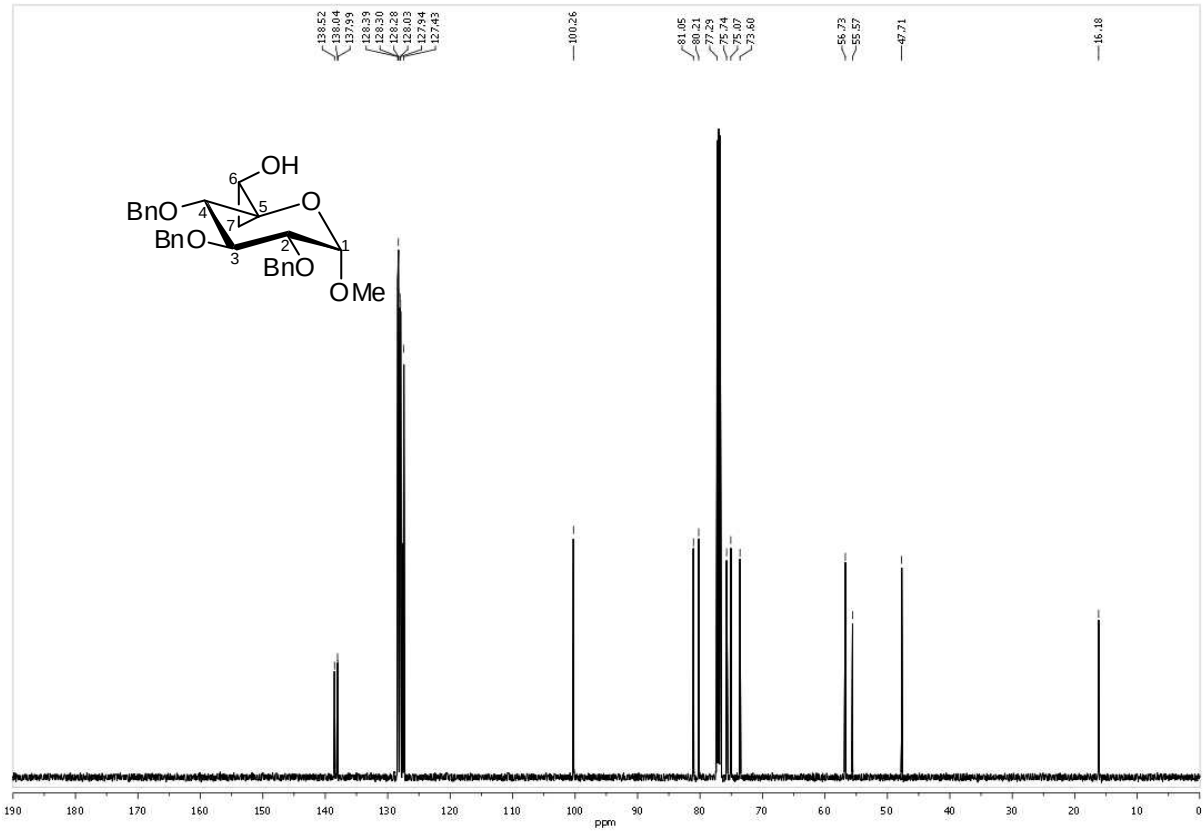


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 13

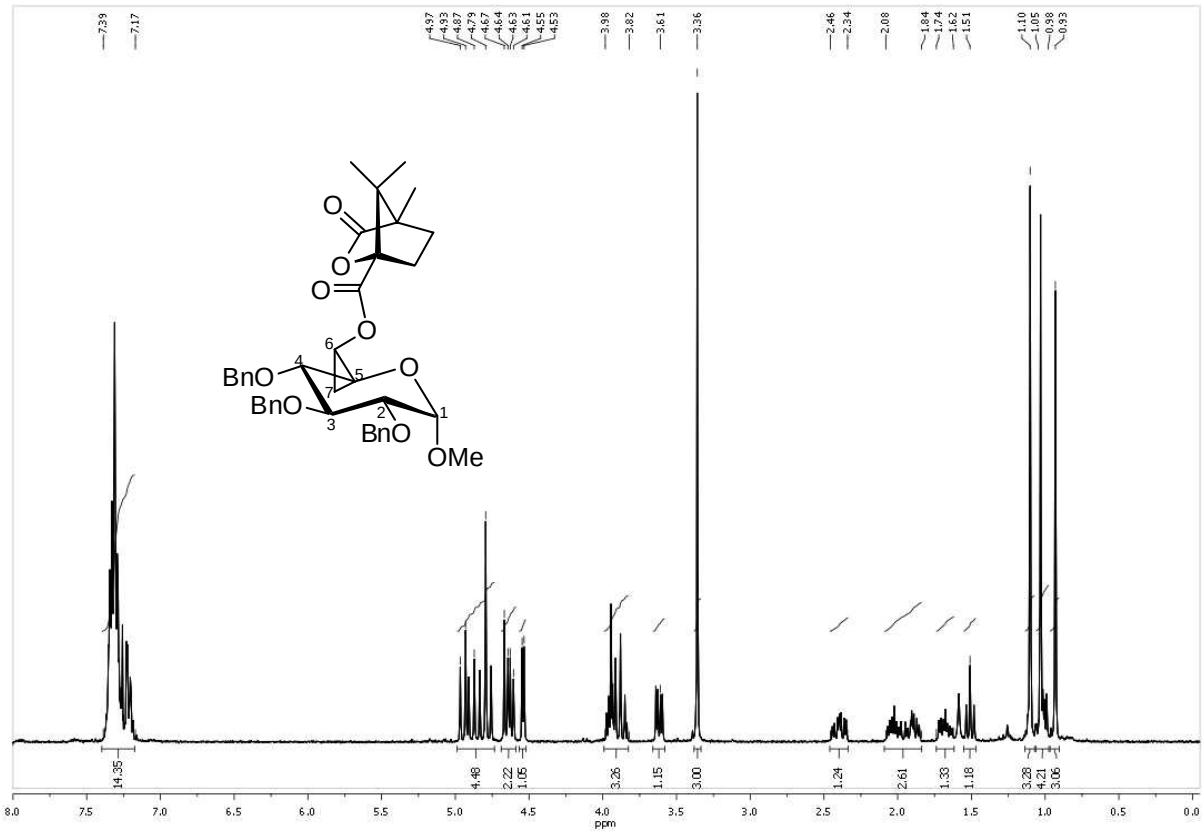


^{1}H NMR ($CDCl_3$, 300 MHz)

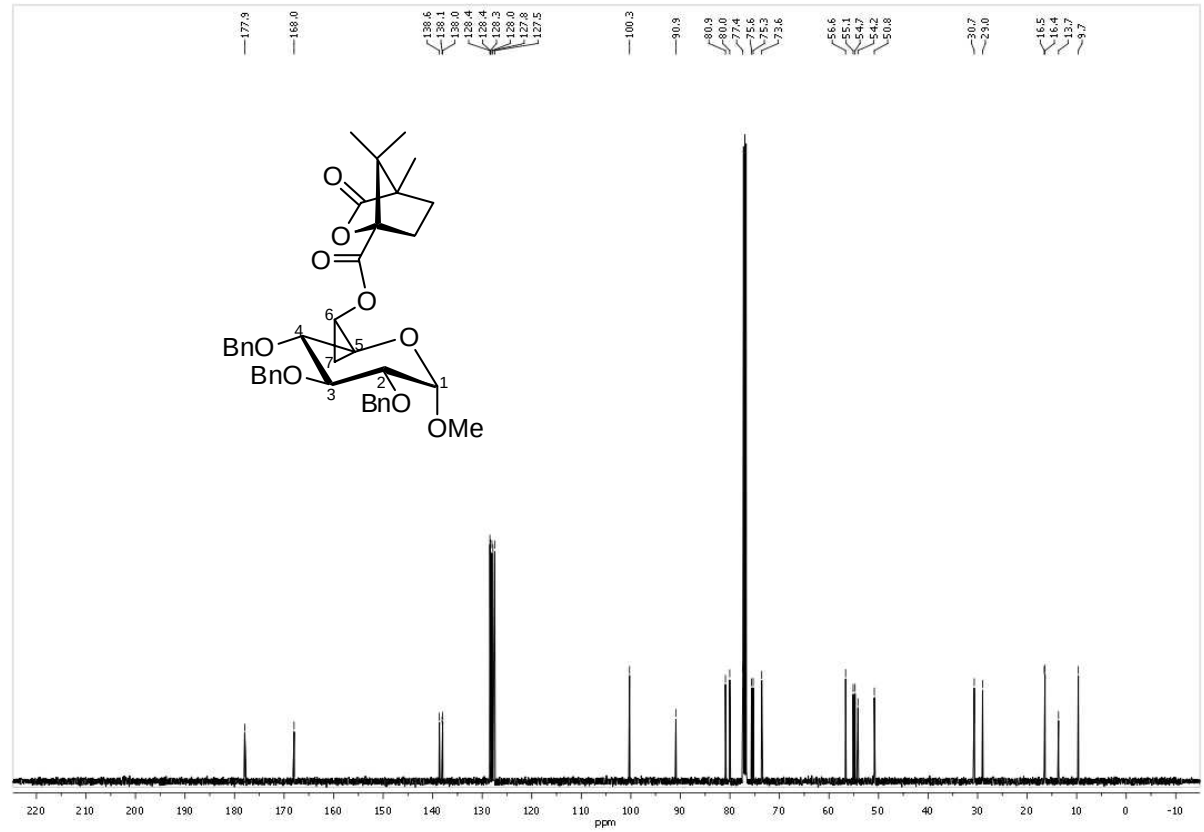


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 33

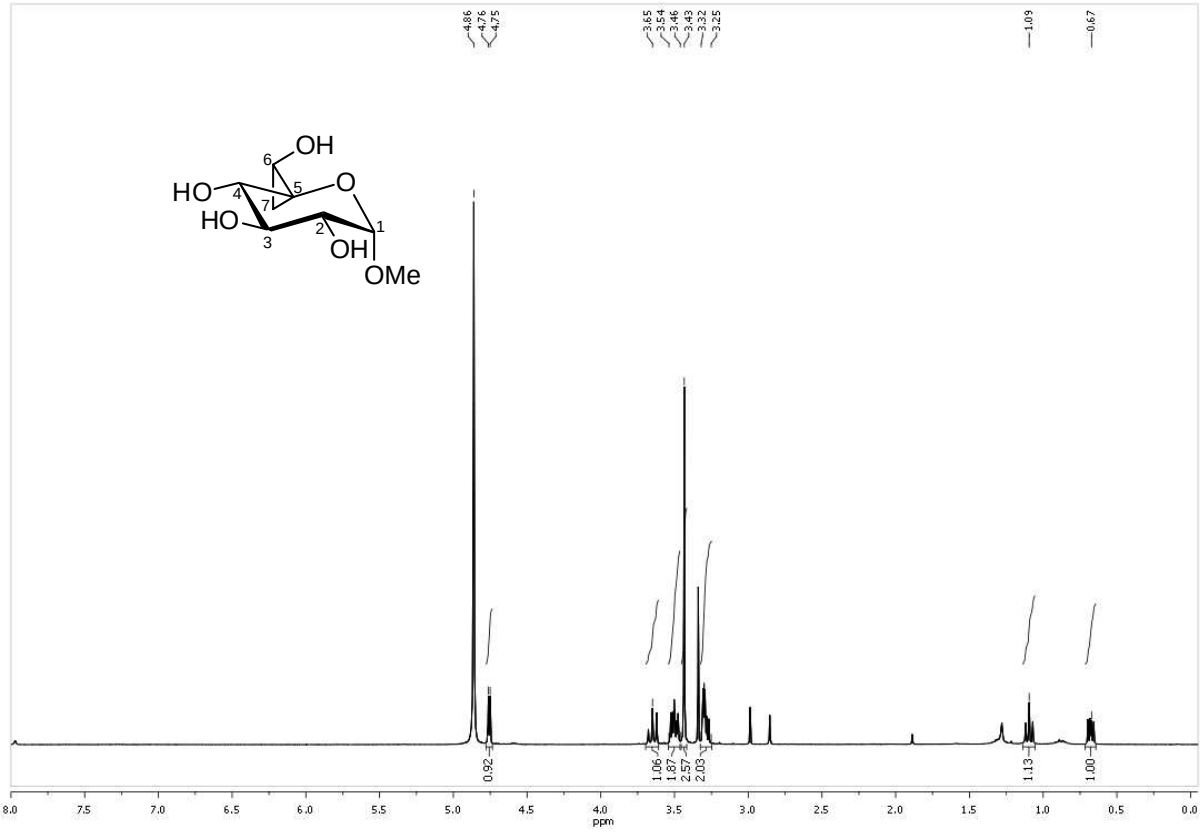


^{1}H NMR ($CDCl_3$, 300 MHz)

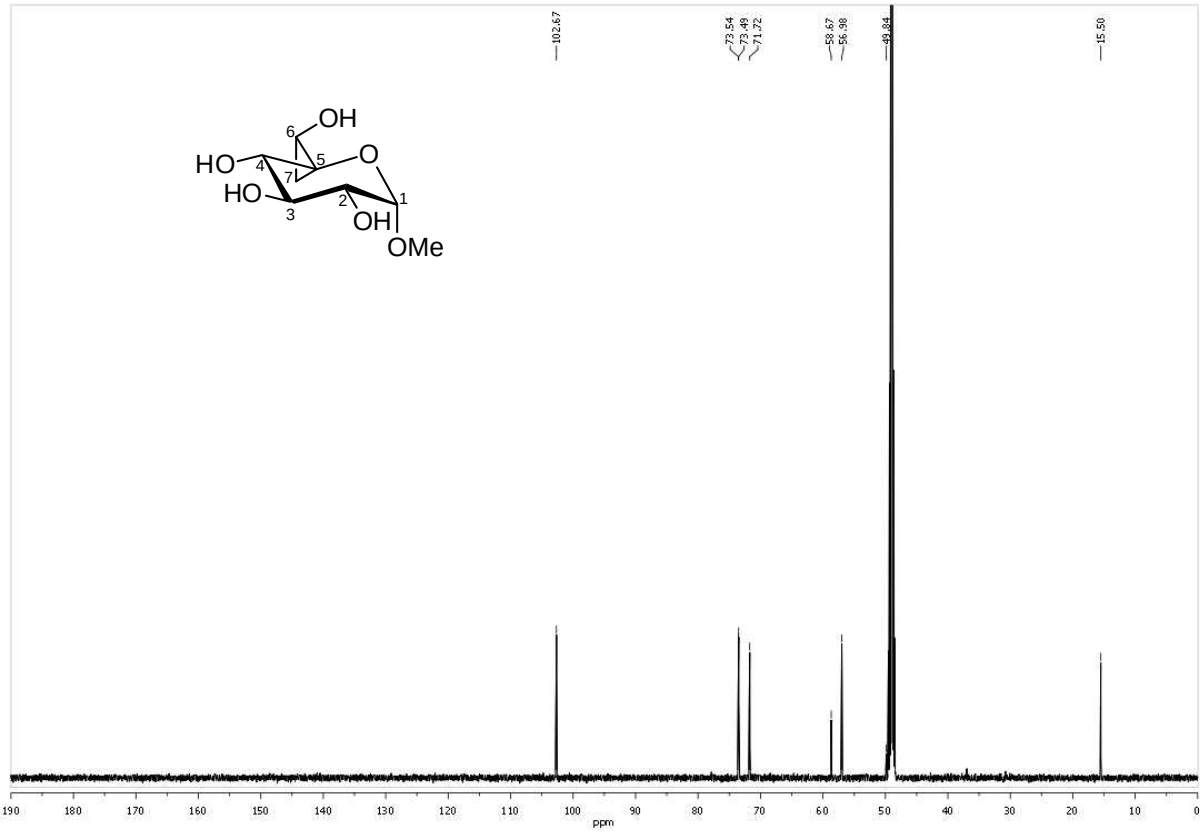


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 15

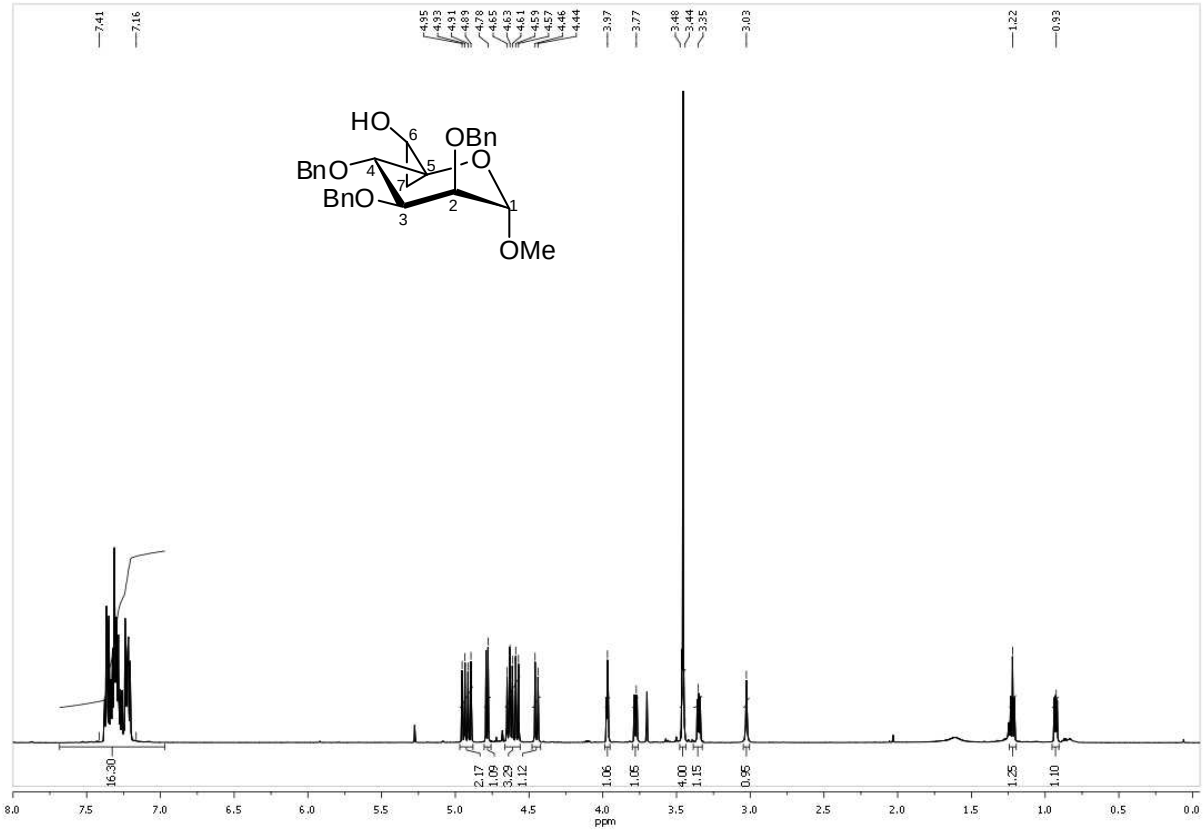


^{1}H NMR (CD_3OD, 300 MHz)

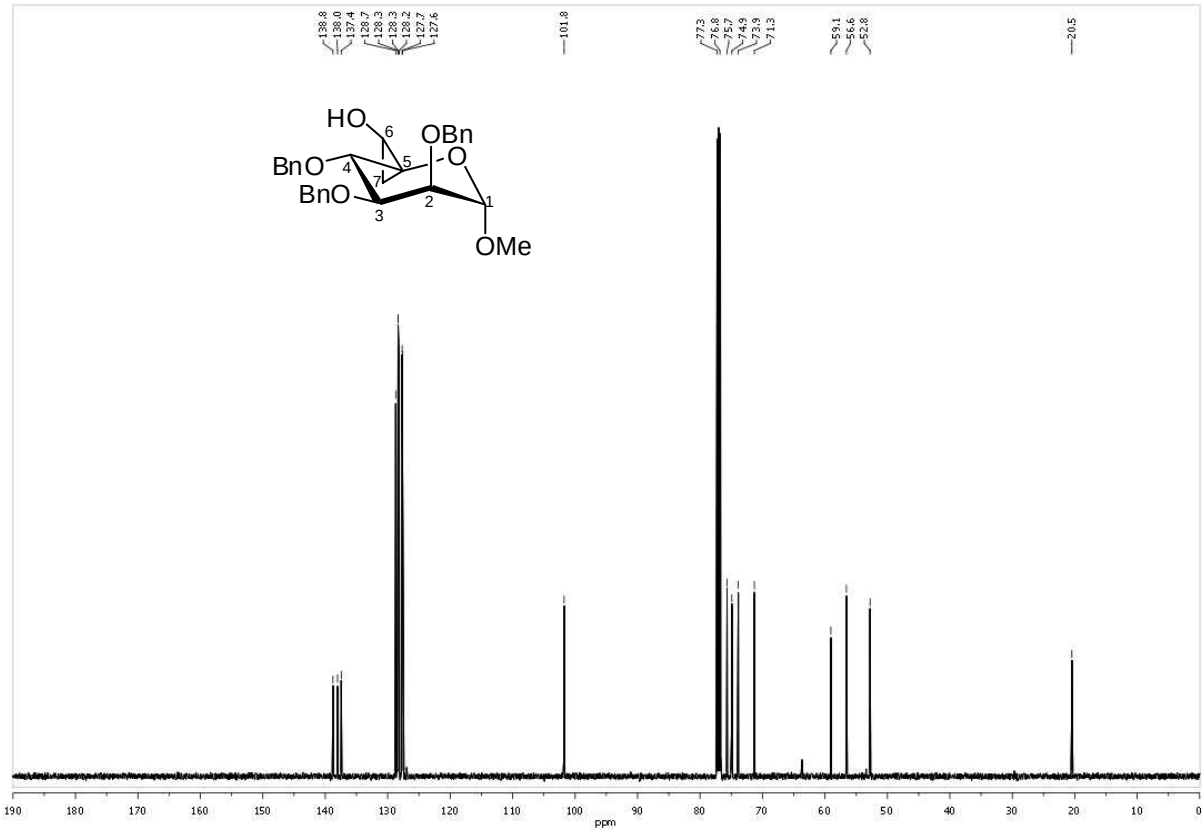


^{13}C NMR (CD_3OD, 125 MHz)

Compound 19

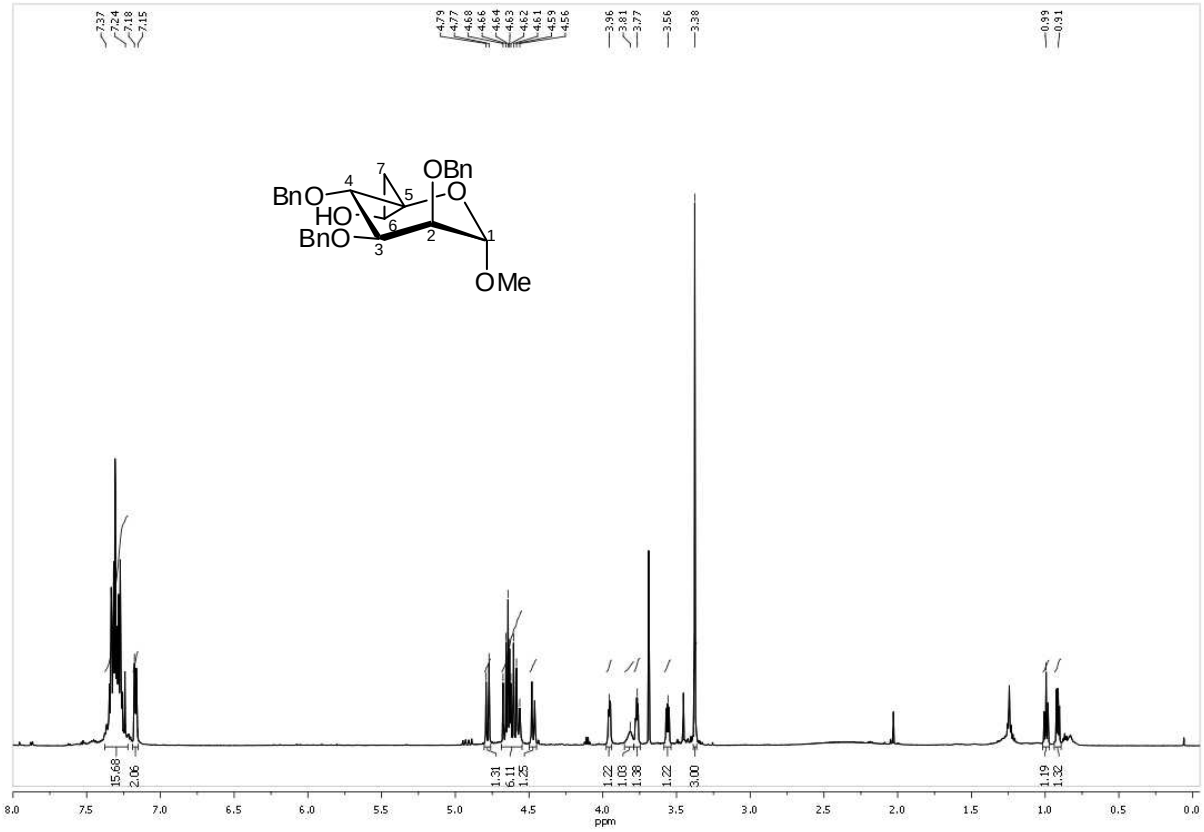


^{1}H NMR ($CDCl_3$, 600 MHz)

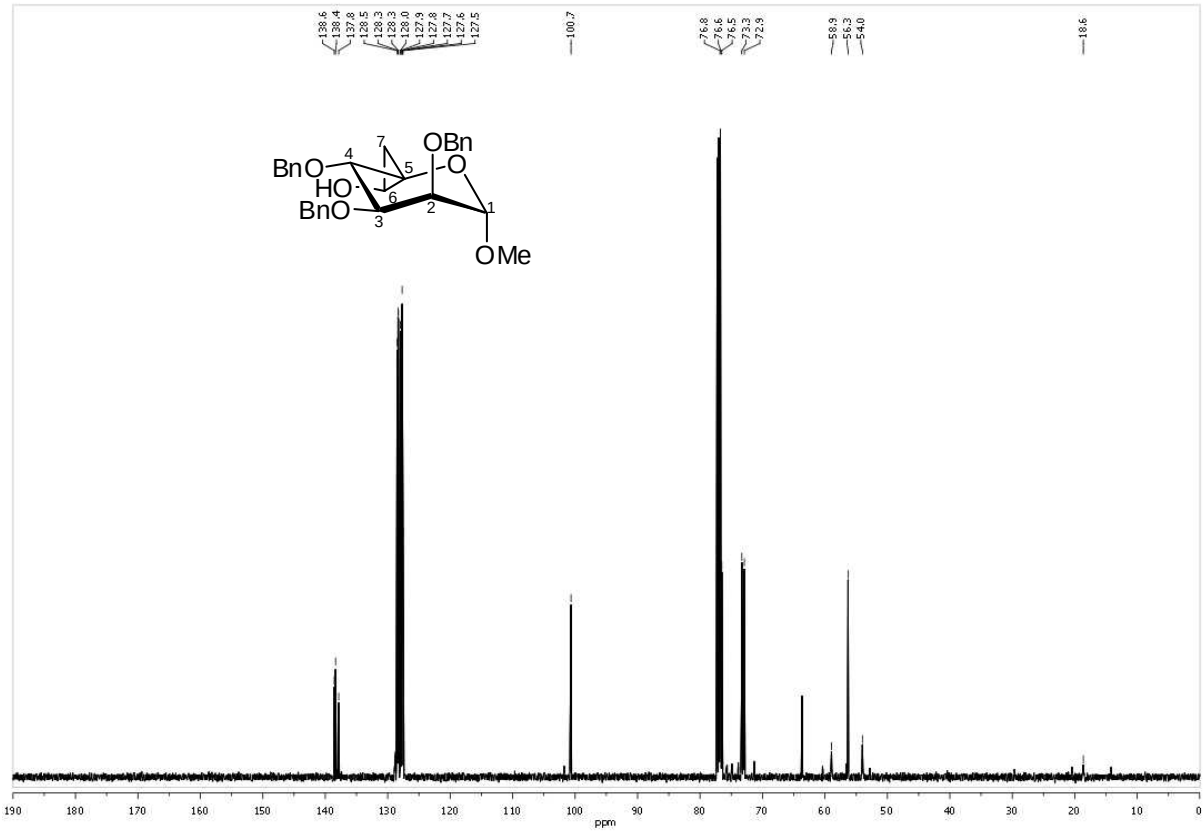


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 19a

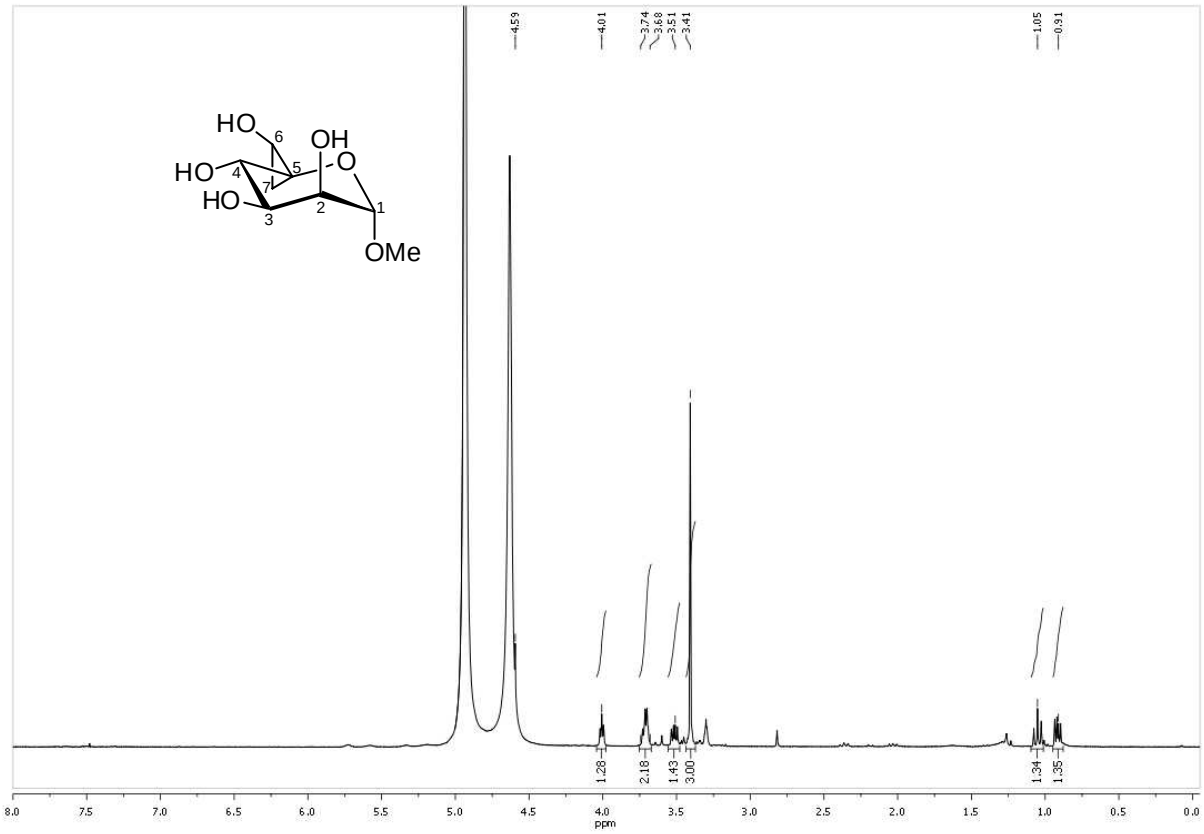


^{1}H NMR ($CDCl_3$, 600 MHz)

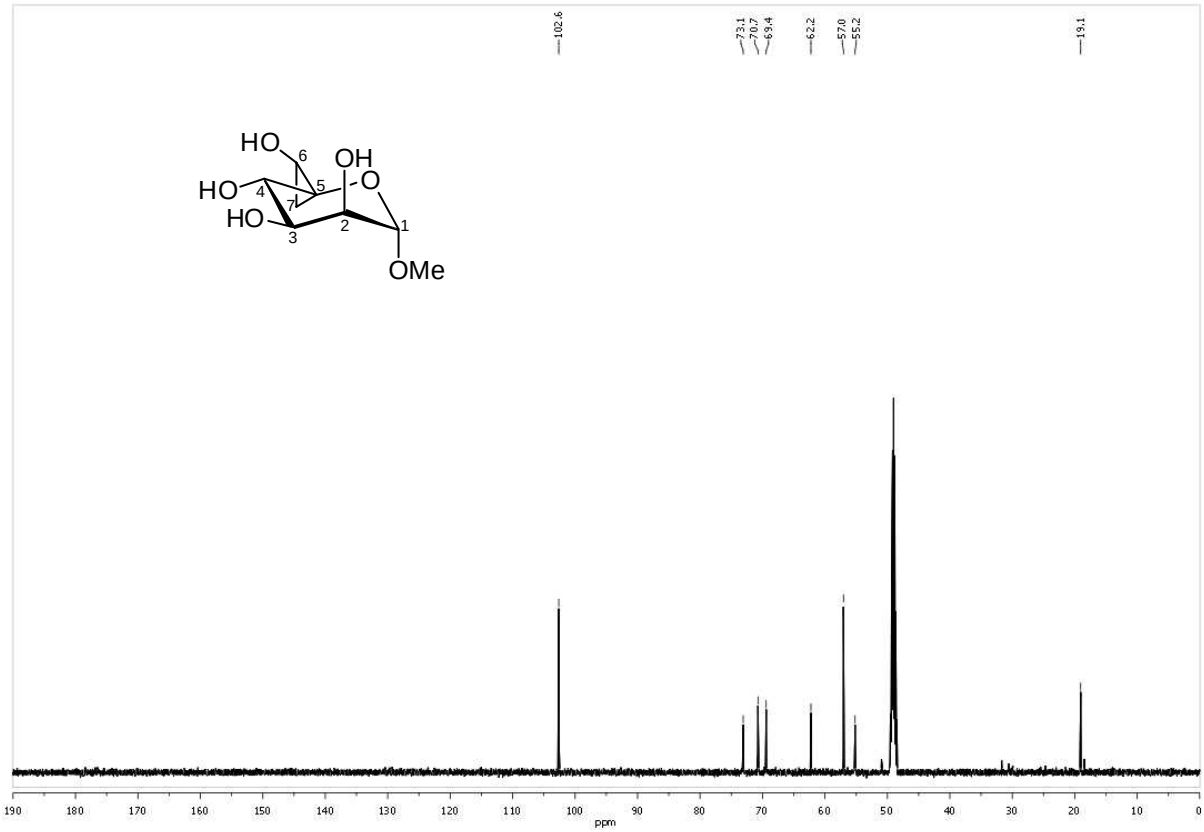


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 21

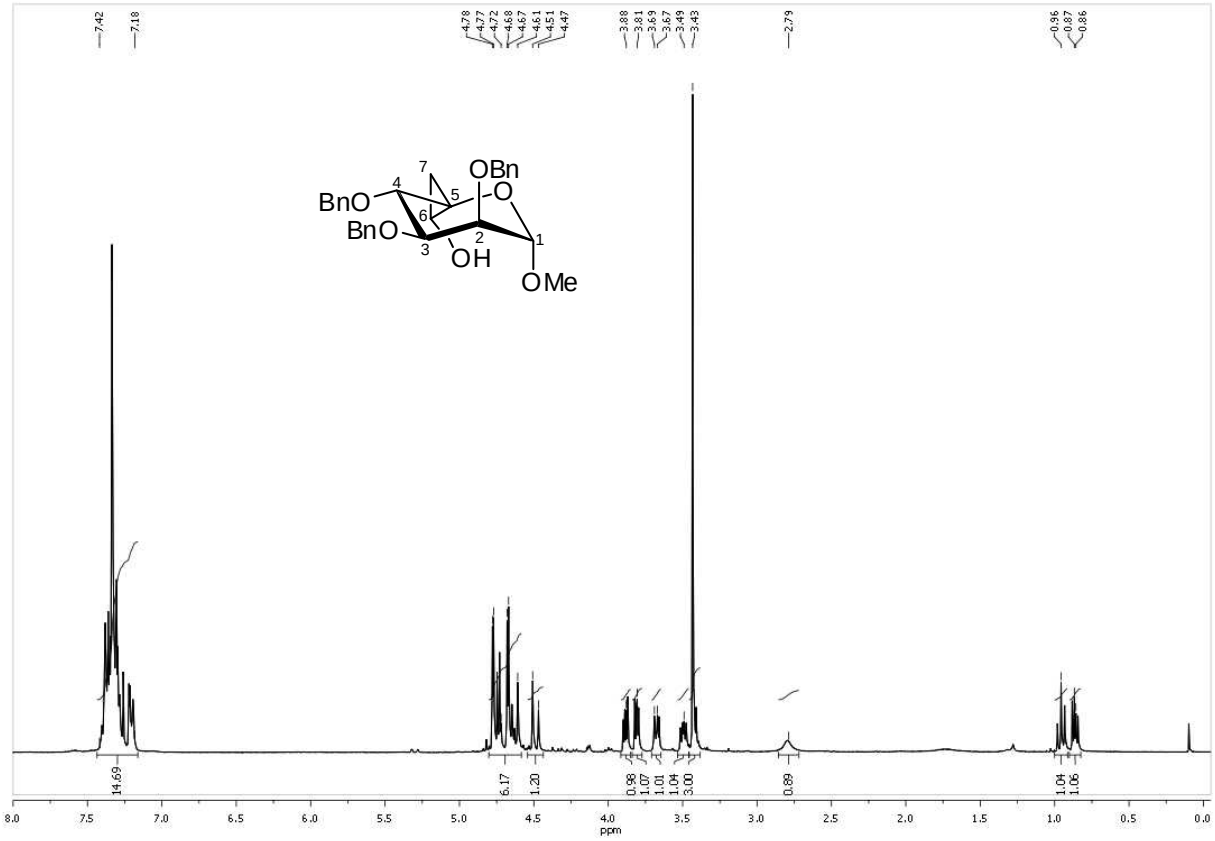


^{1}H NMR (CD_3OD, 300 MHz)

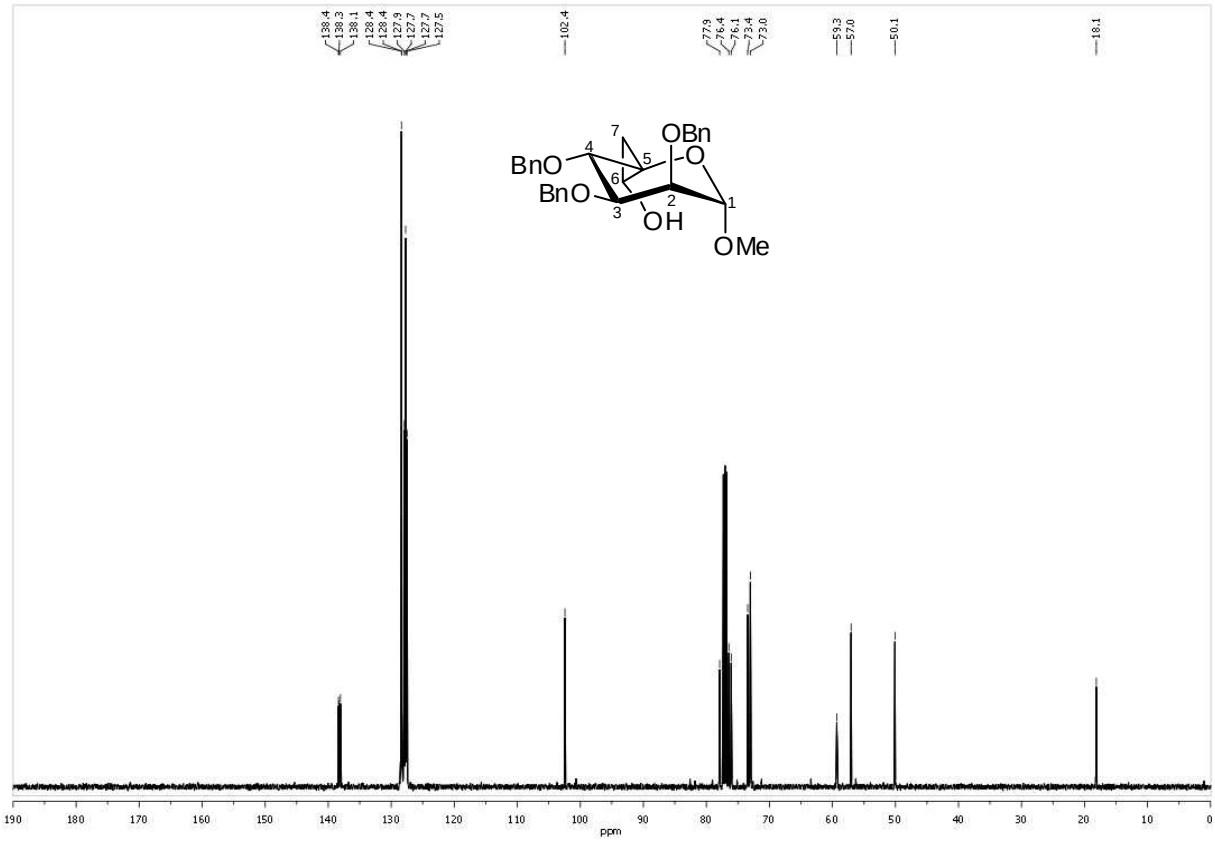


^{13}C NMR (CD_3OD, 125 MHz)

Compound 20a

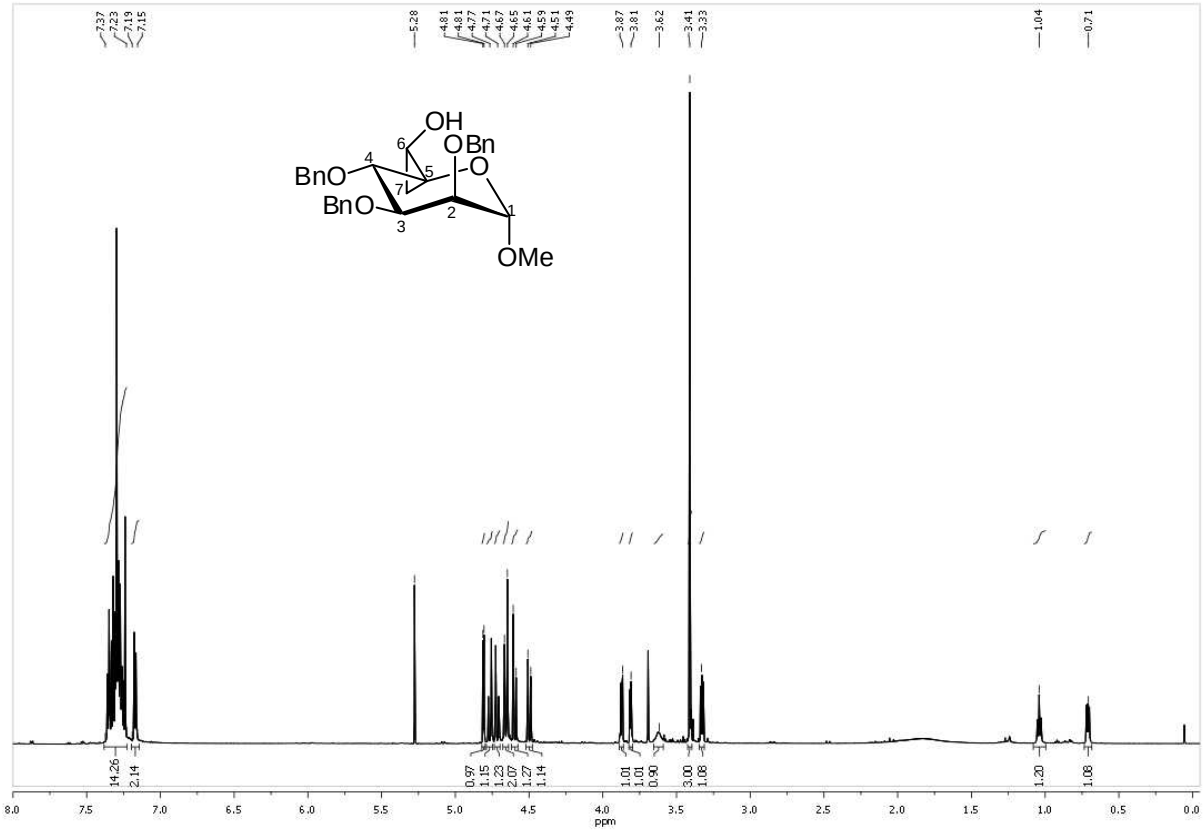


^{1}H NMR ($CDCl_3$, 300 MHz)

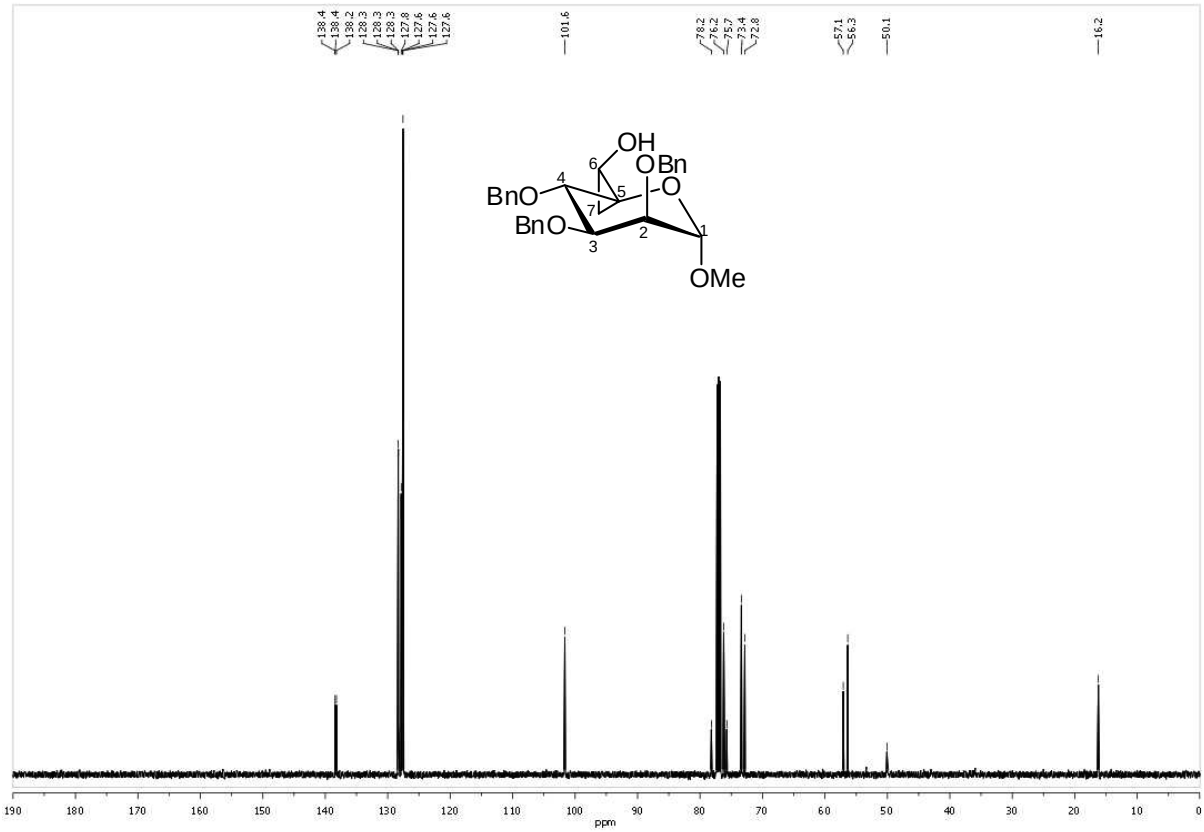


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 20

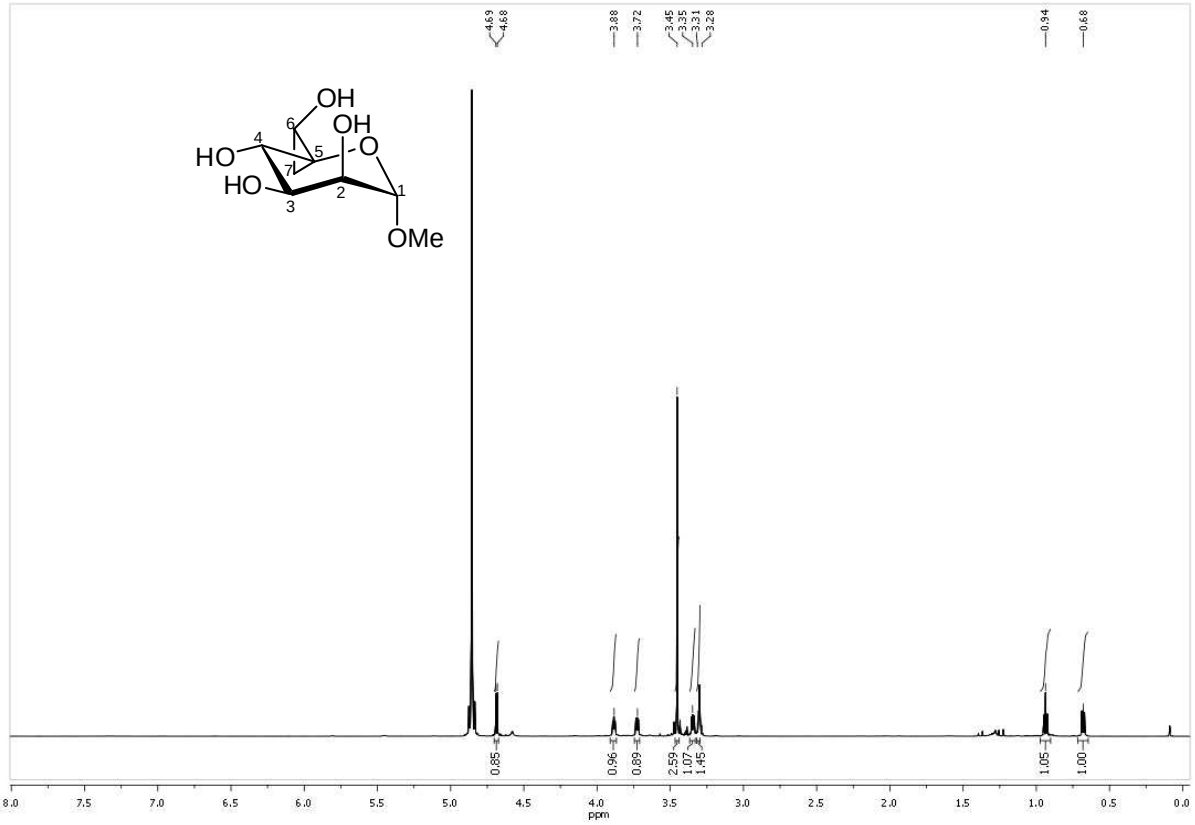


^{1}H NMR ($CDCl_3$, 600 MHz)

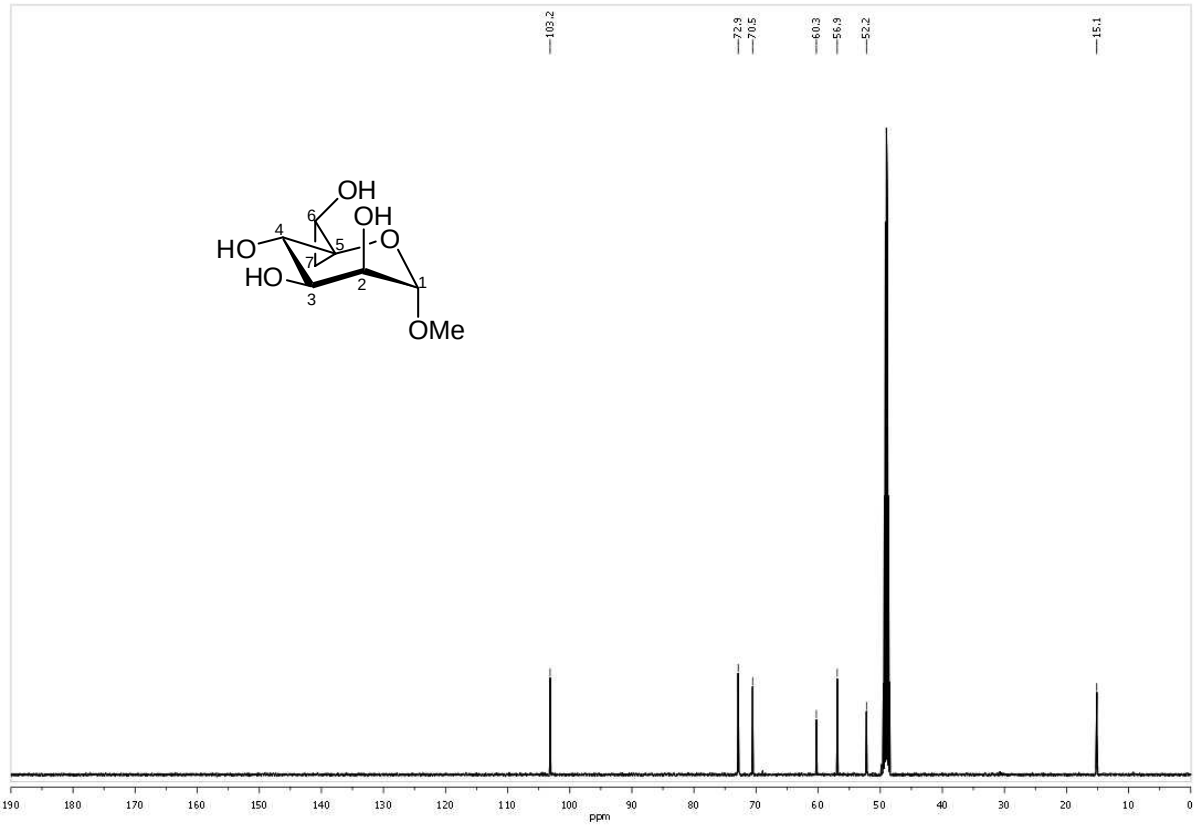


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 22

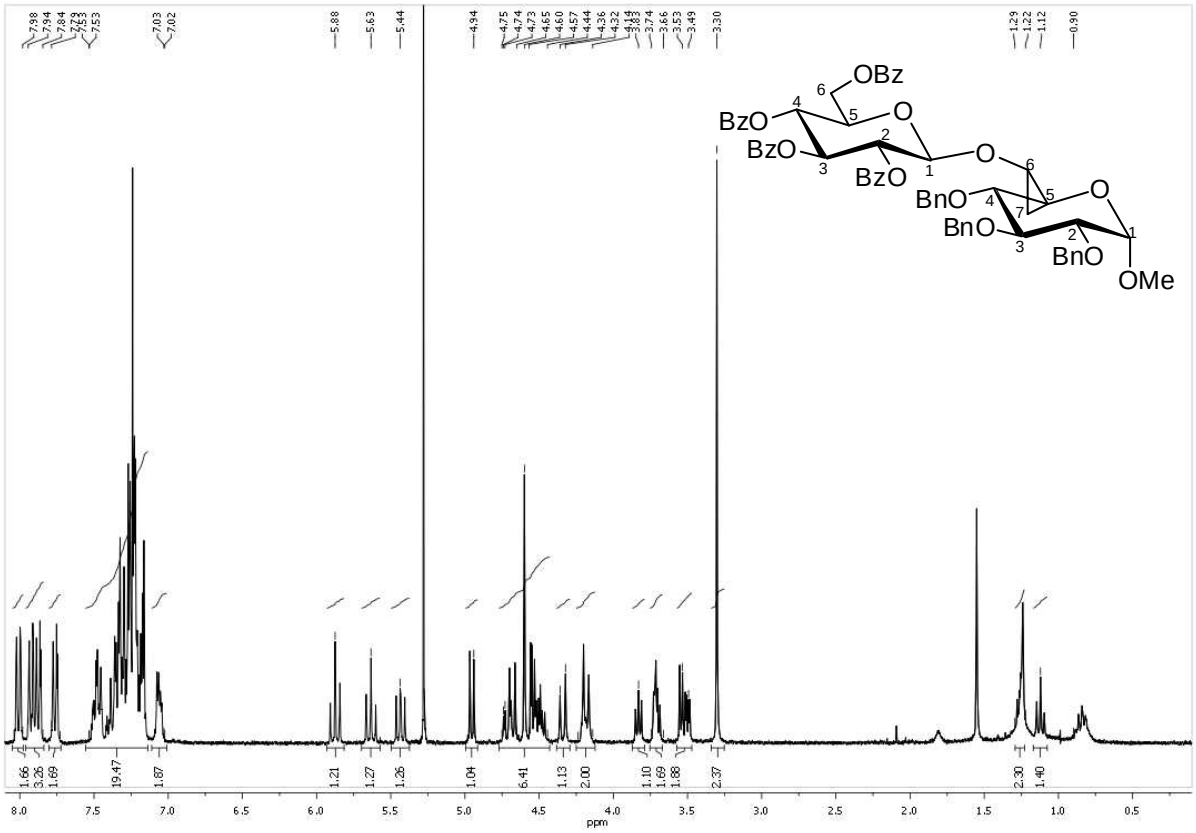


^{1}H NMR (CD_3OD, 600 MHz)

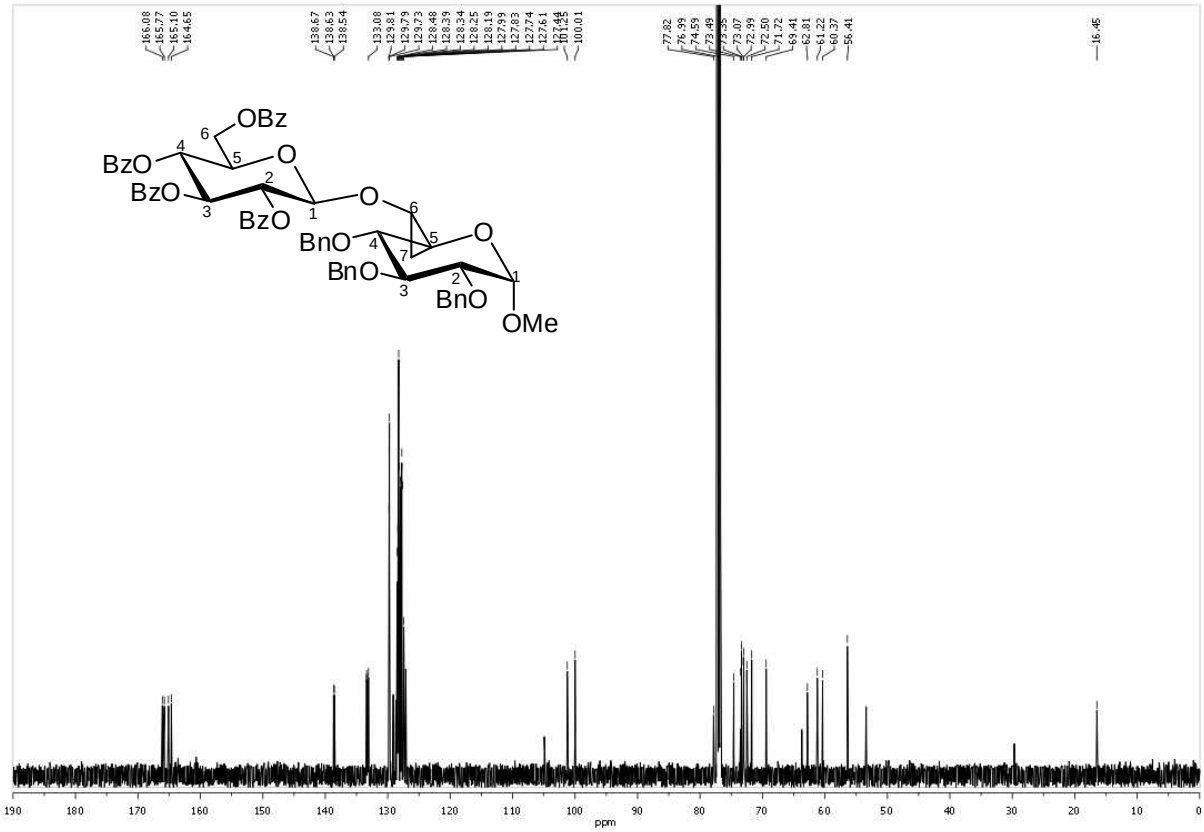


^{13}C NMR (CD_3OD, 125 MHz)

Compound 24

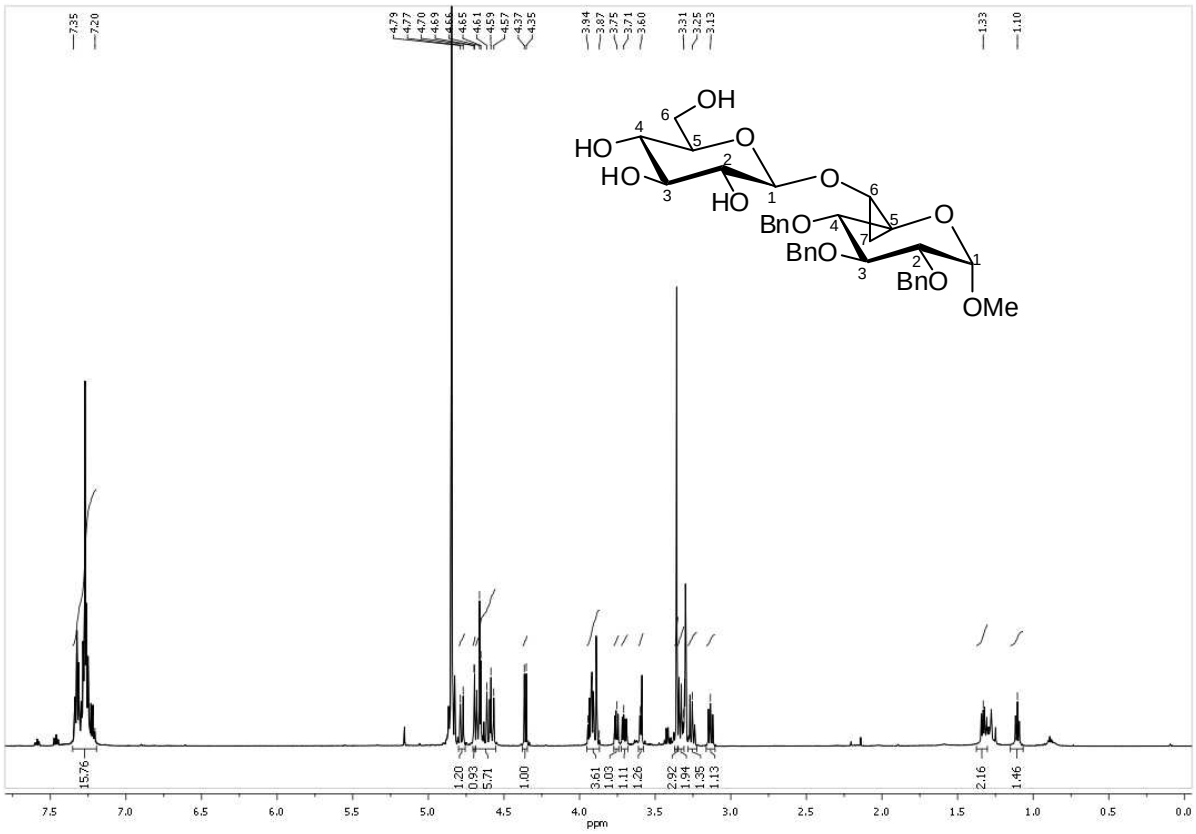


^{1}H NMR ($CDCl_3$, 300 MHz)

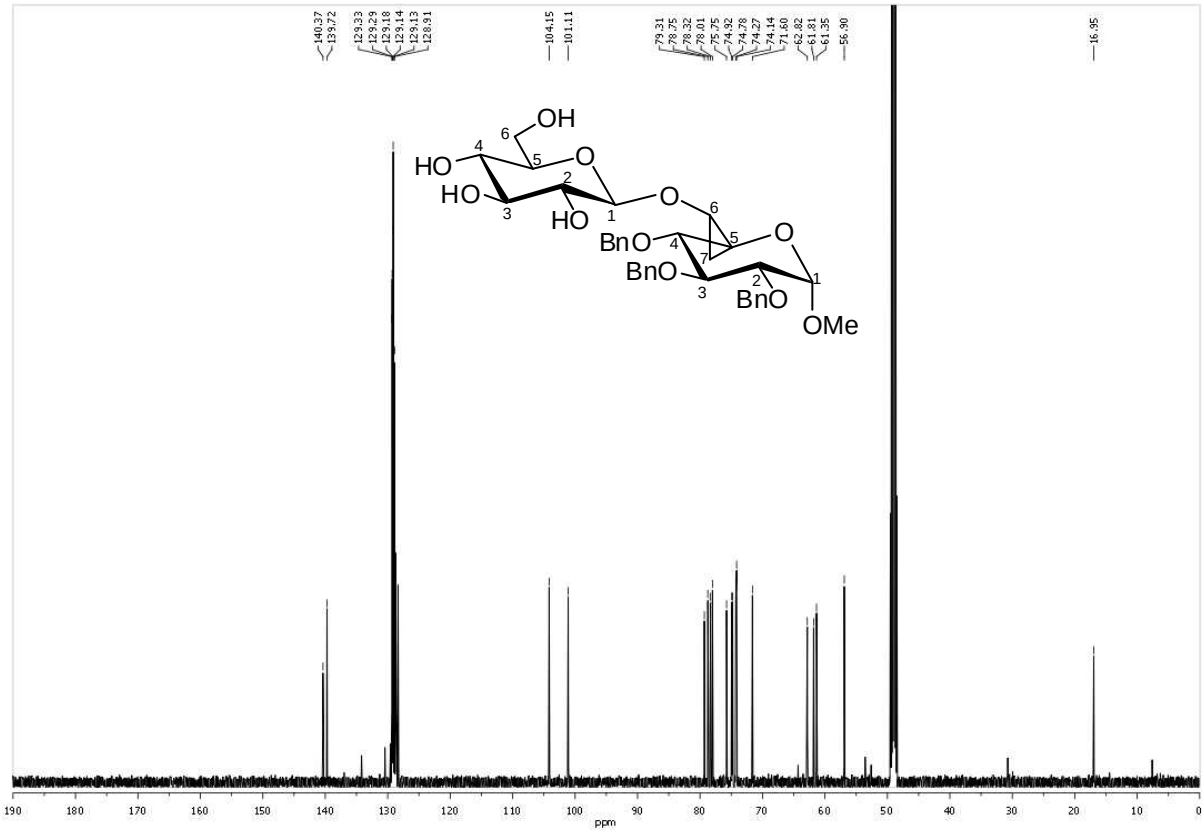


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 25a

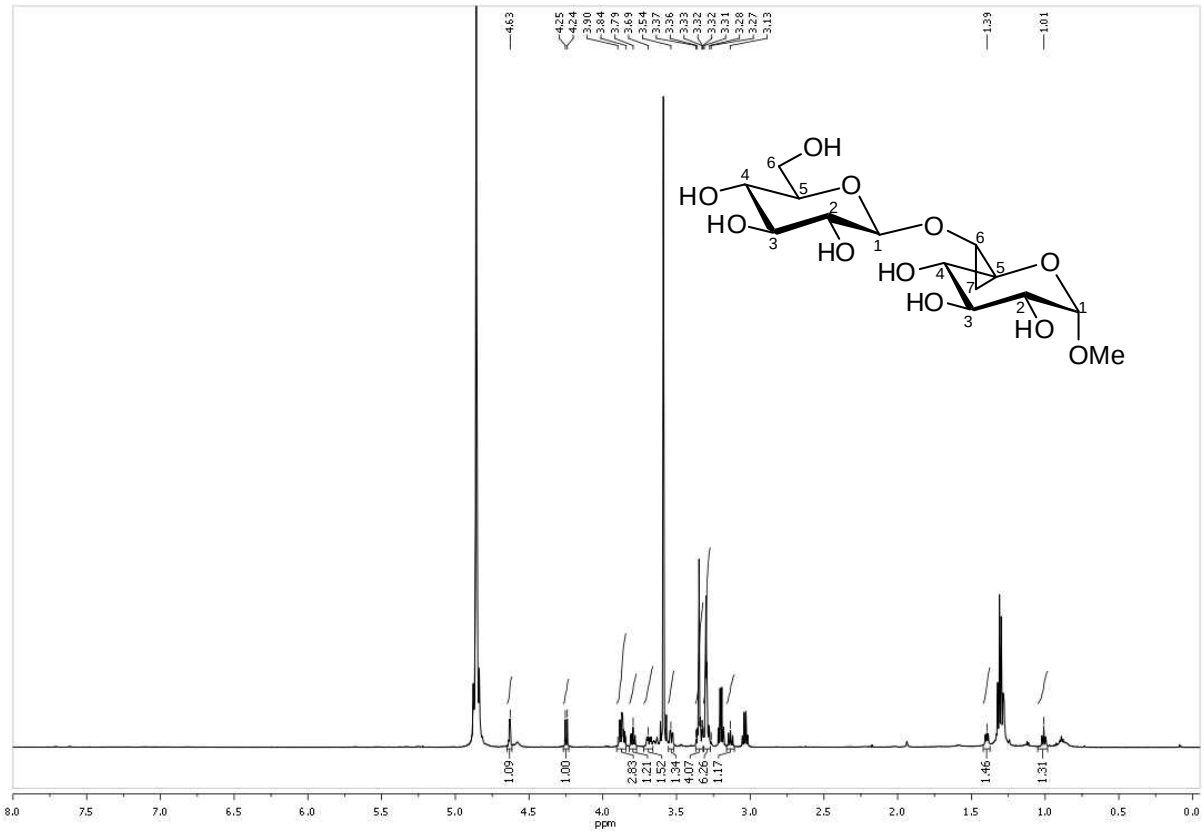


^{1}H NMR (CD_3OD, 600 MHz)

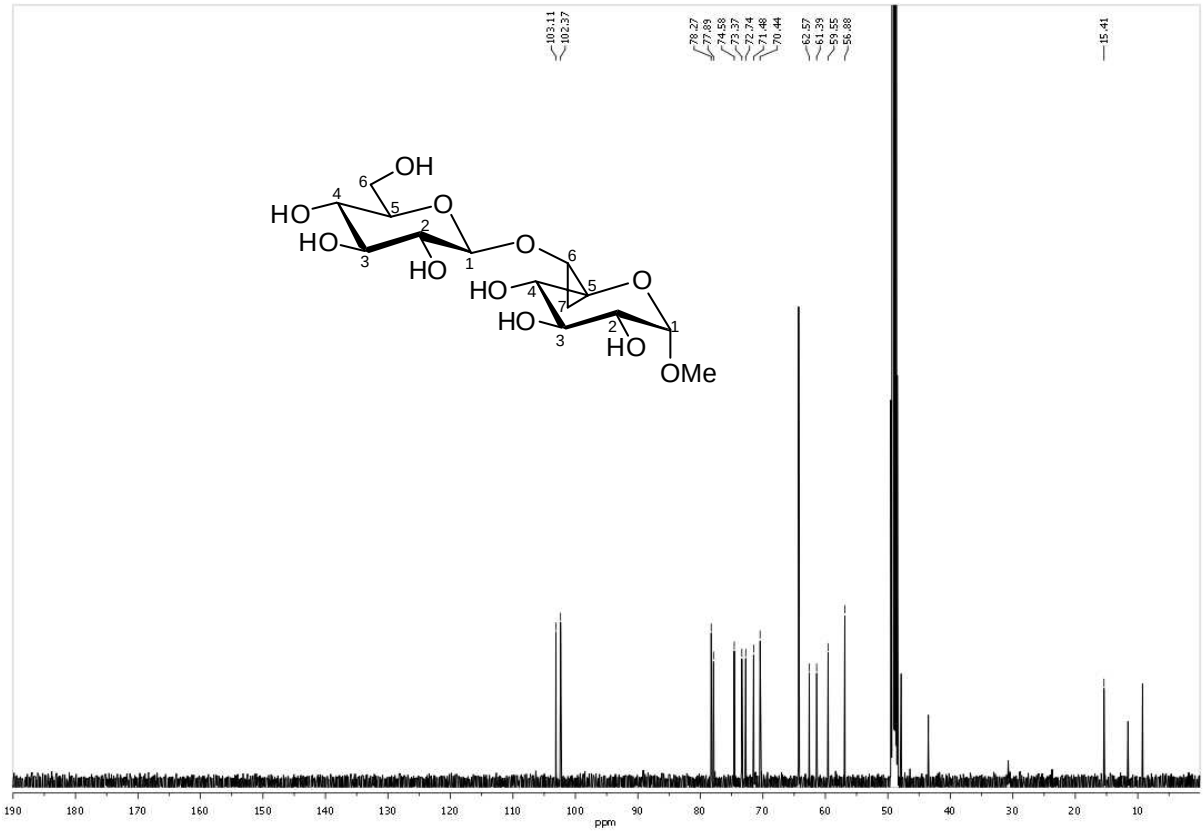


^{13}C NMR (CD_3OD, 125 MHz)

Compound 25

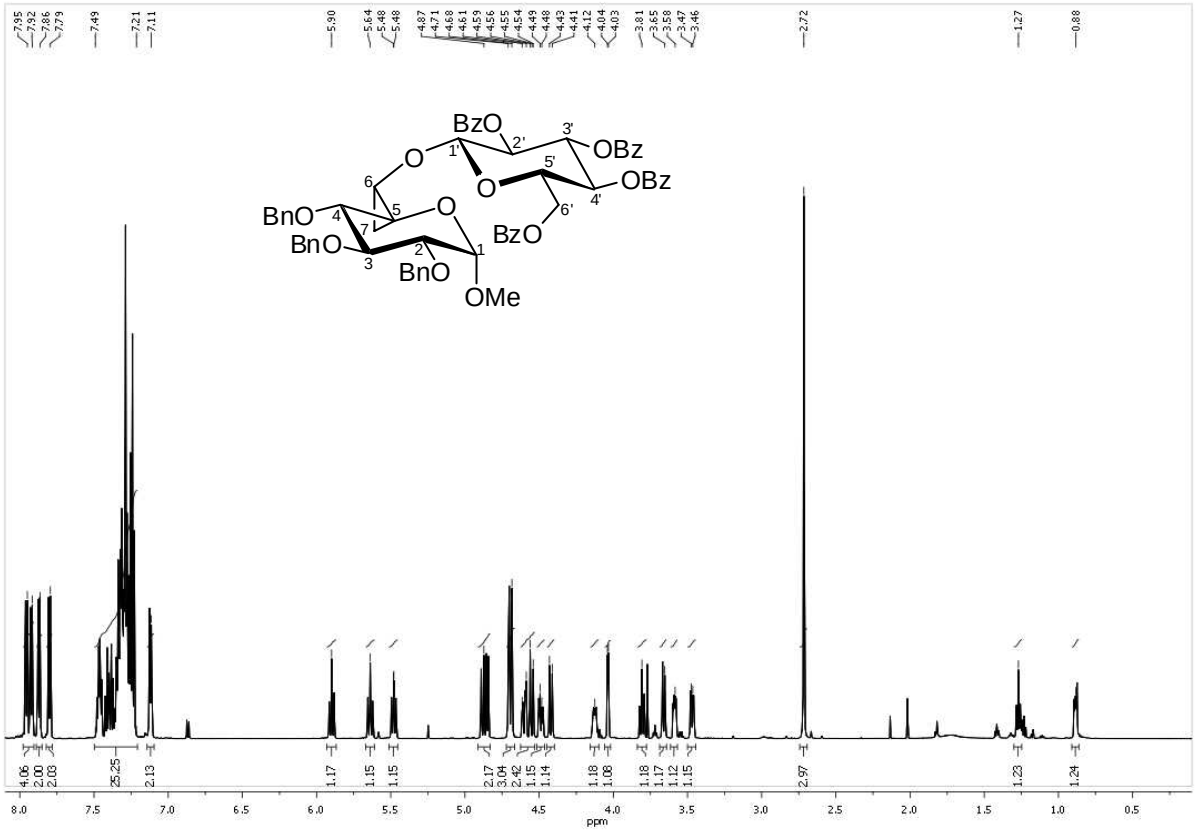


^{1}H NMR (CD_3OD, 600 MHz)

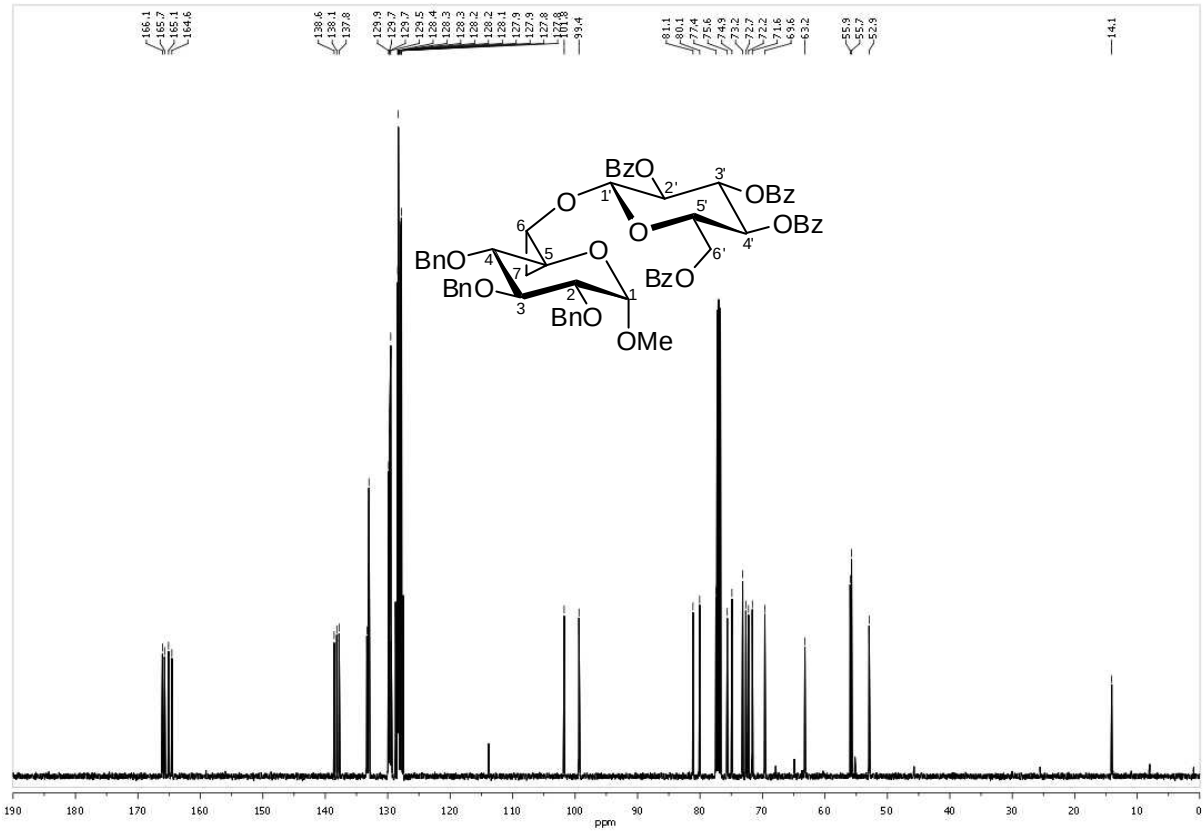


^{13}C NMR (CD_3OD, 125 MHz)

Compound 26

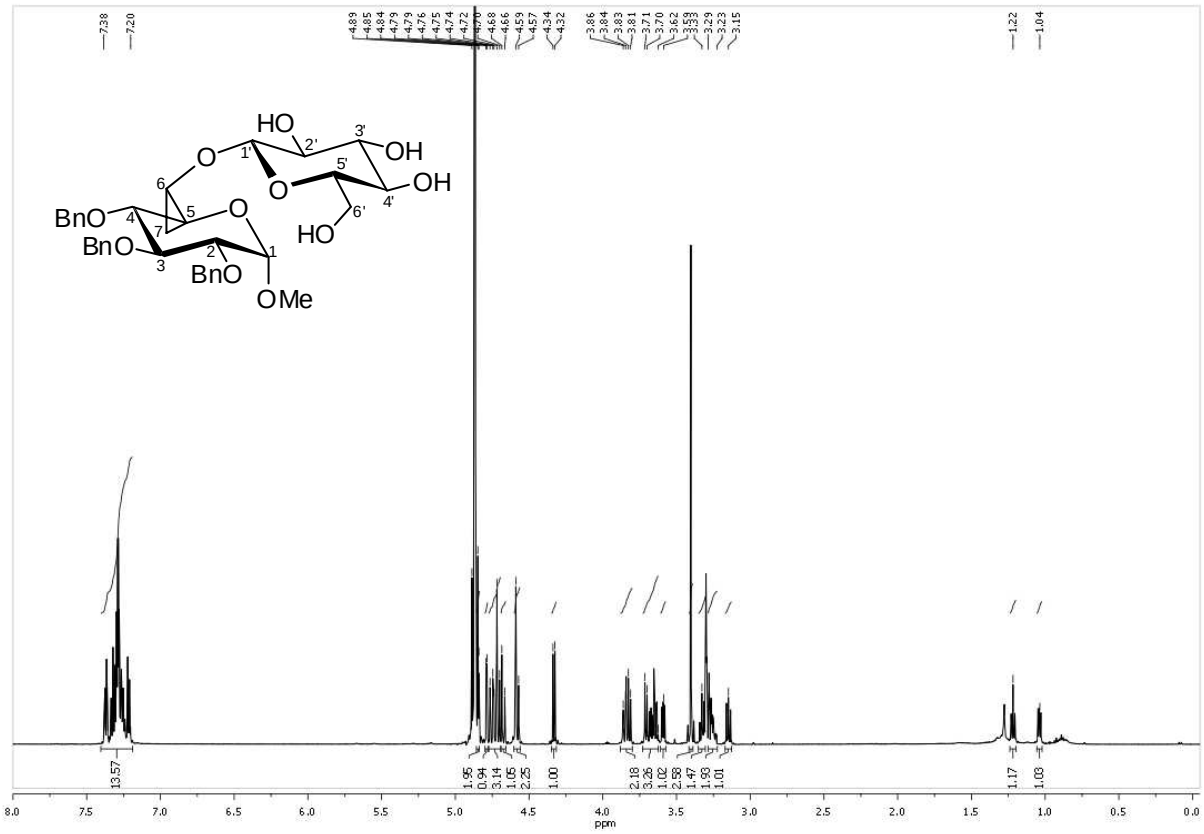


^{1}H NMR ($CDCl_3$, 600 MHz)

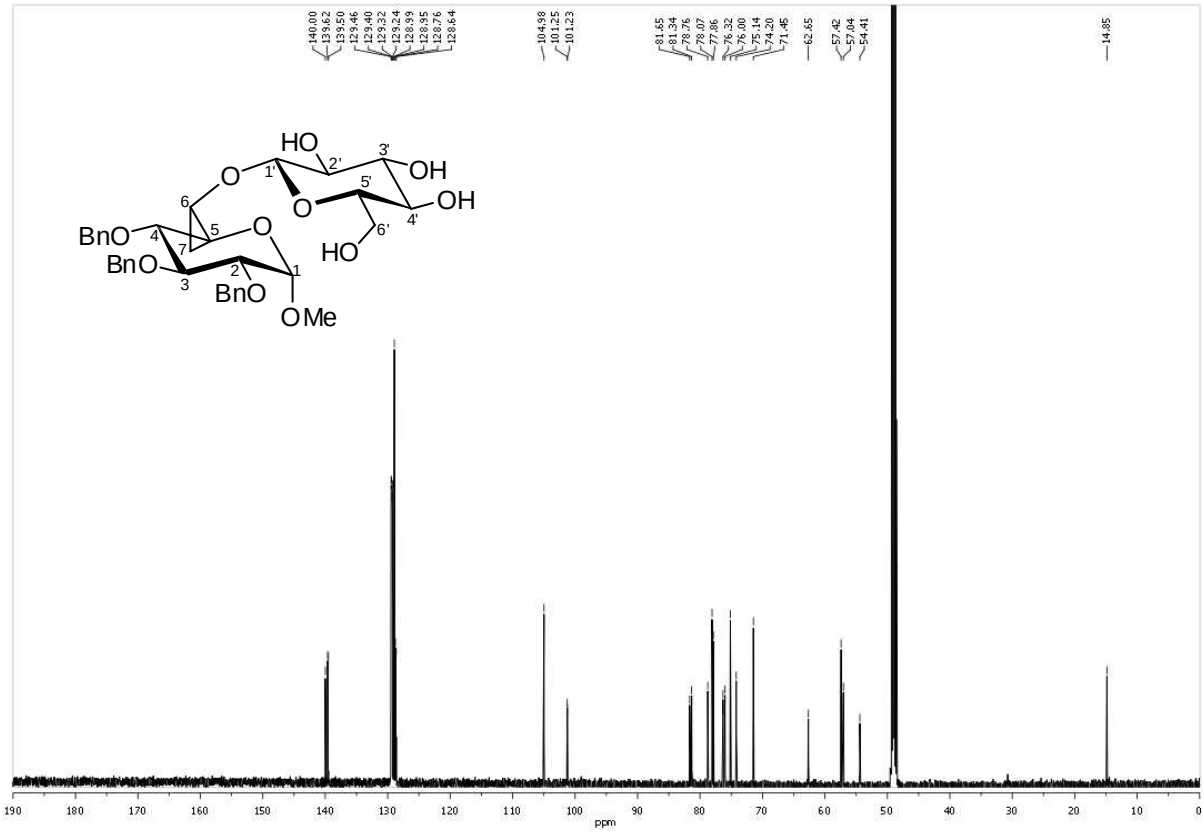


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 27a

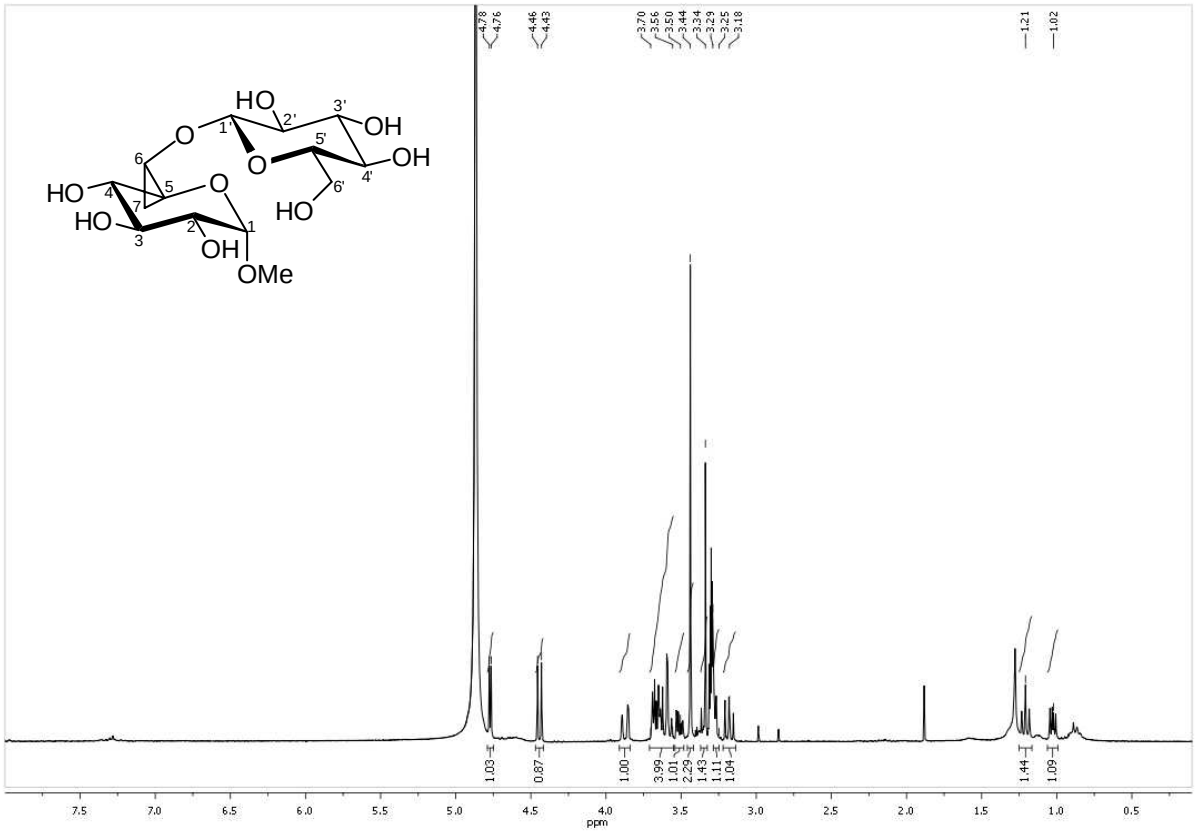


^{1}H NMR (CD_3OD, 600 MHz)

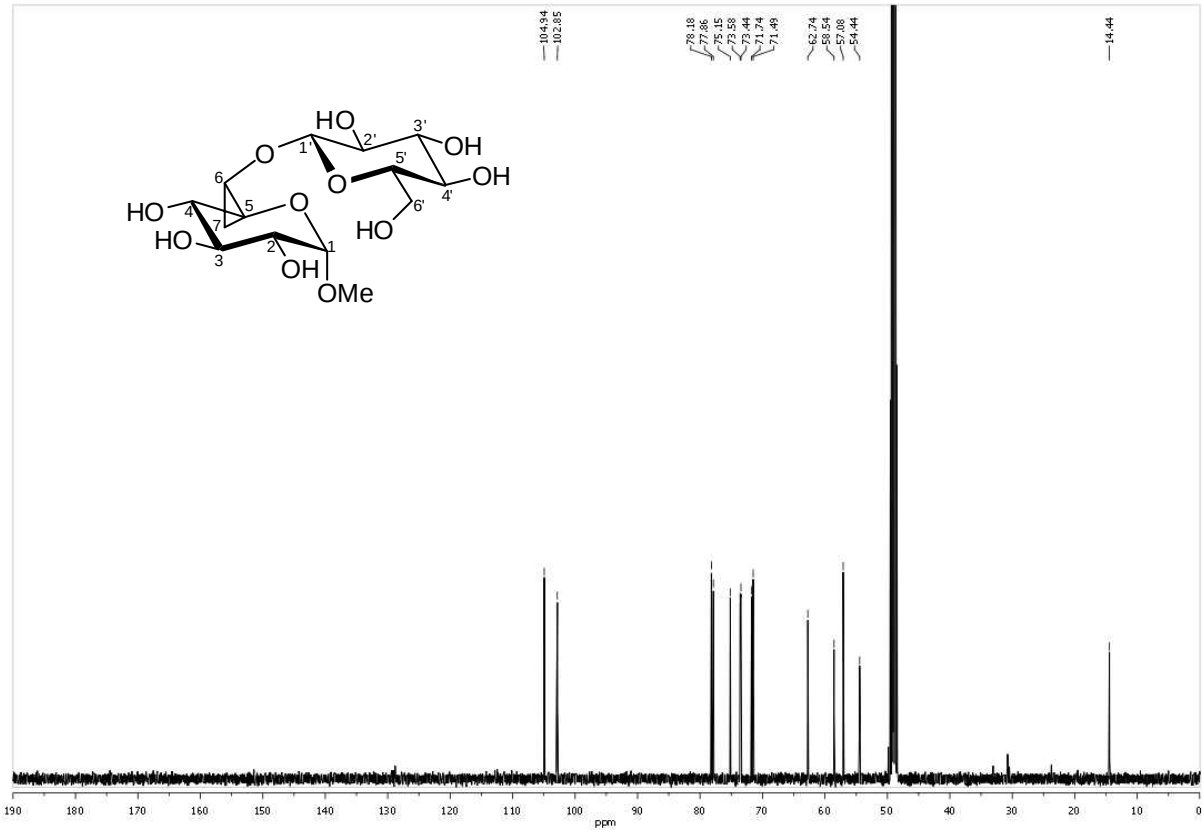


^{13}C NMR (CD_3OD, 125 MHz)

Compound 27

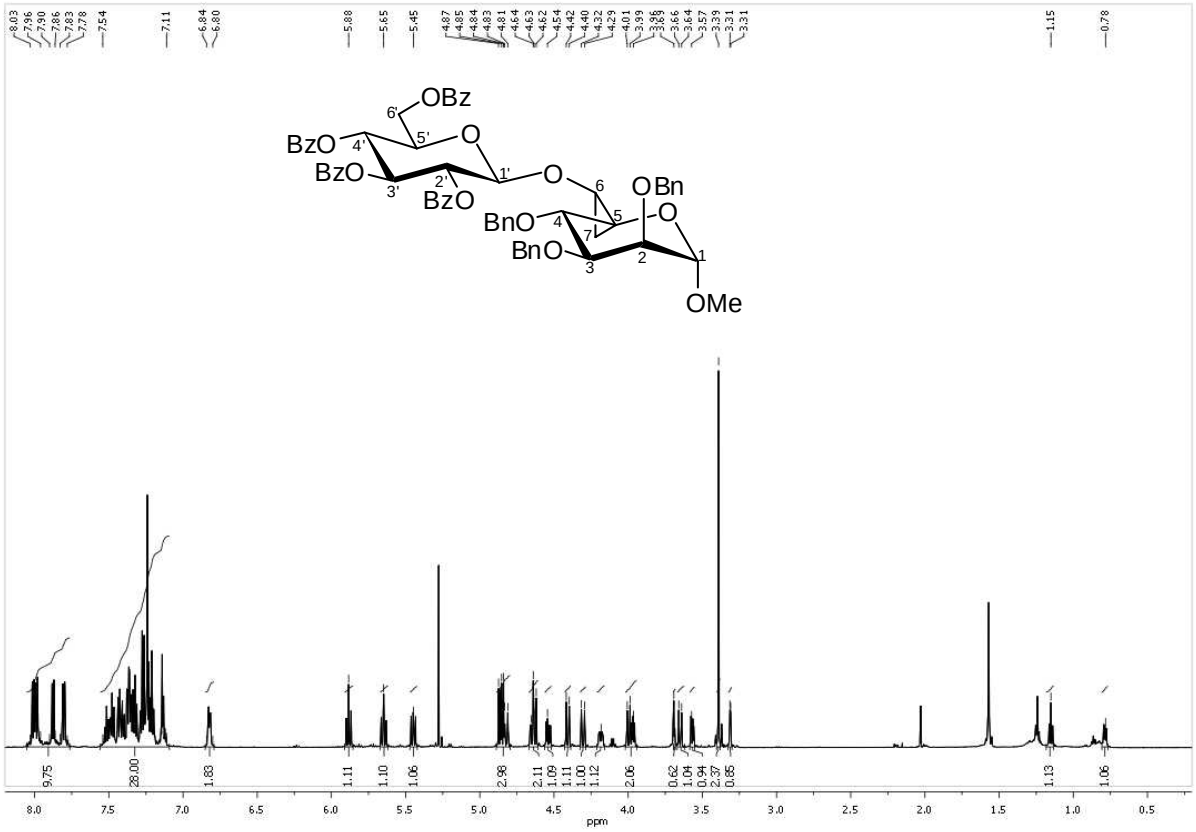


^{1}H NMR (CD_3OD, 300 MHz)

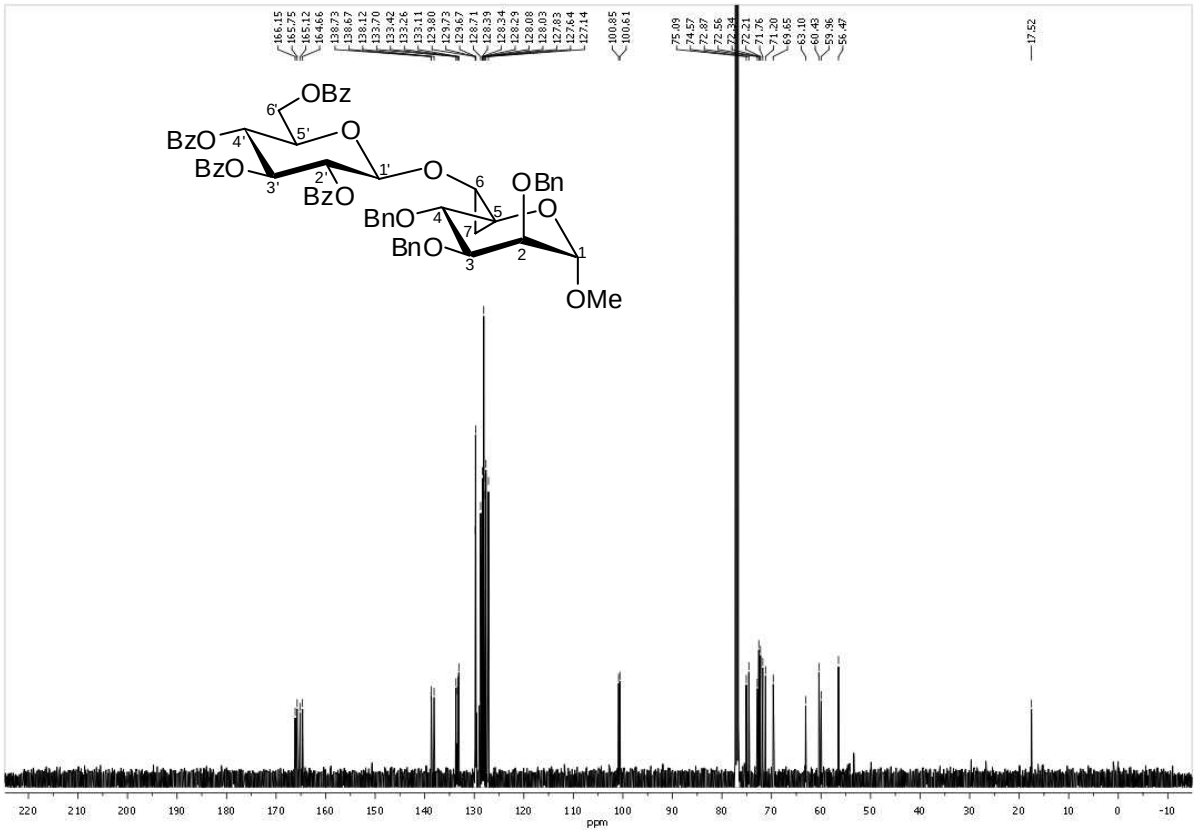


^{13}C NMR (CD_3OD, 125 MHz)

Compound 28

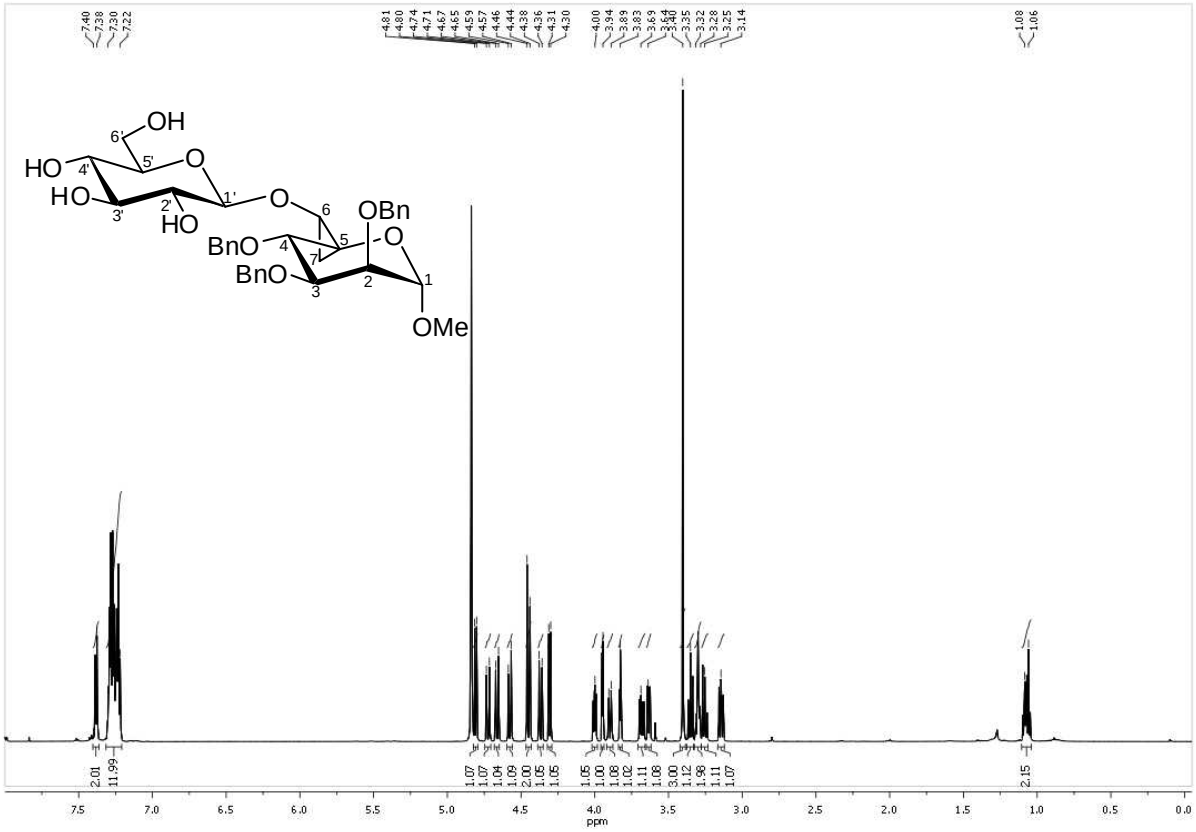


^{1}H NMR ($CDCl_3$, 600 MHz)

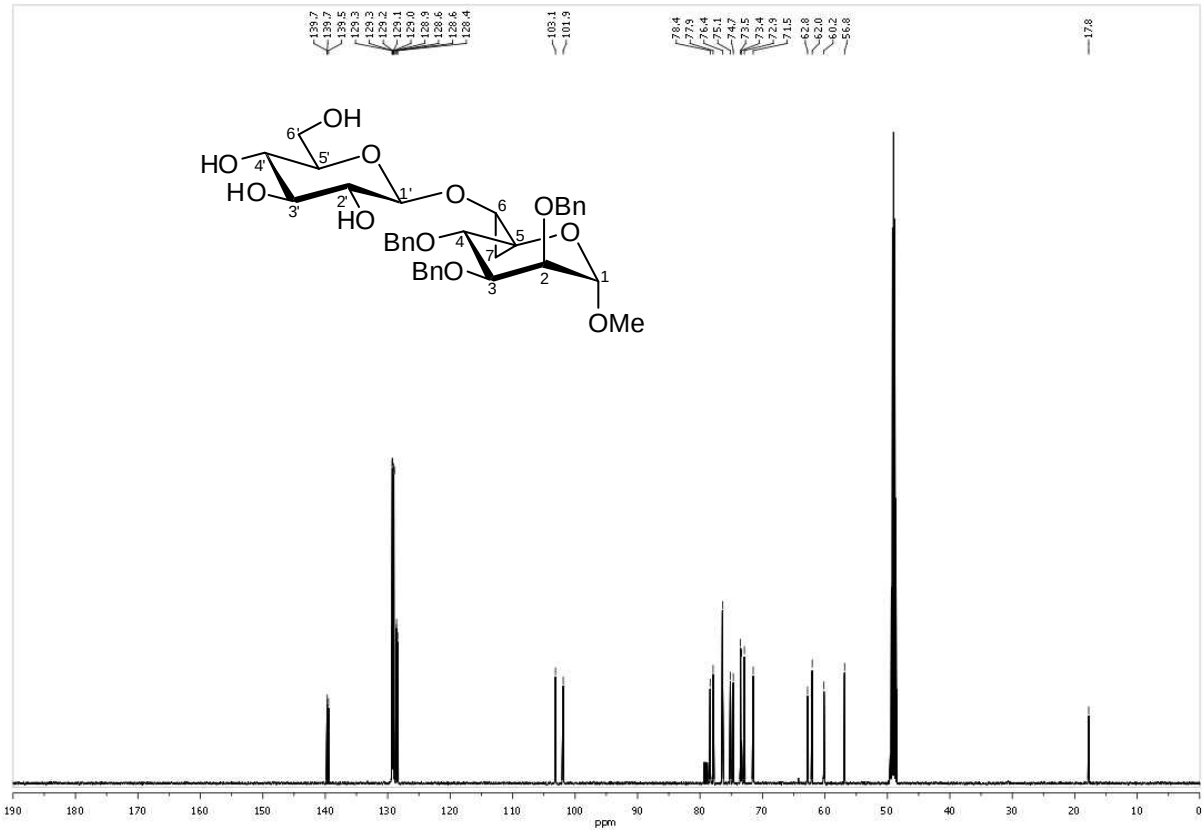


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 29a

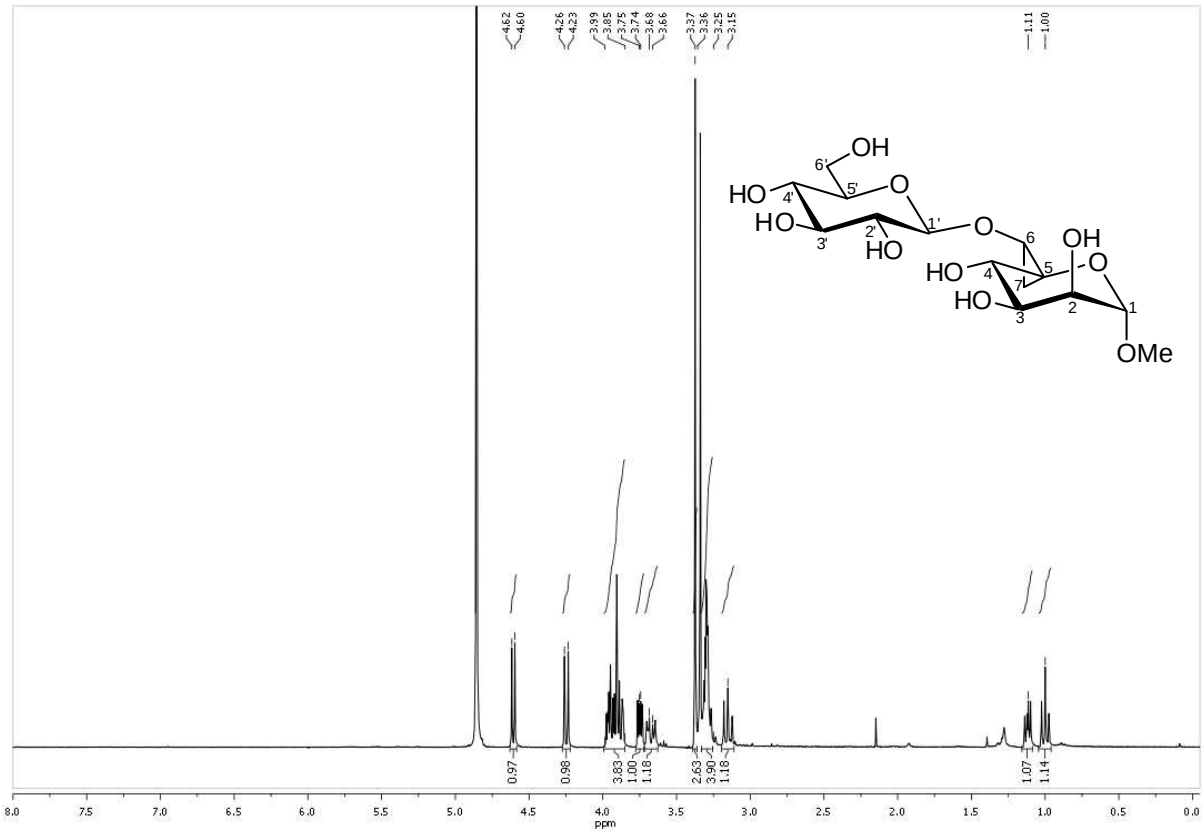


^{1}H NMR (CD_3OD, 600 MHz)

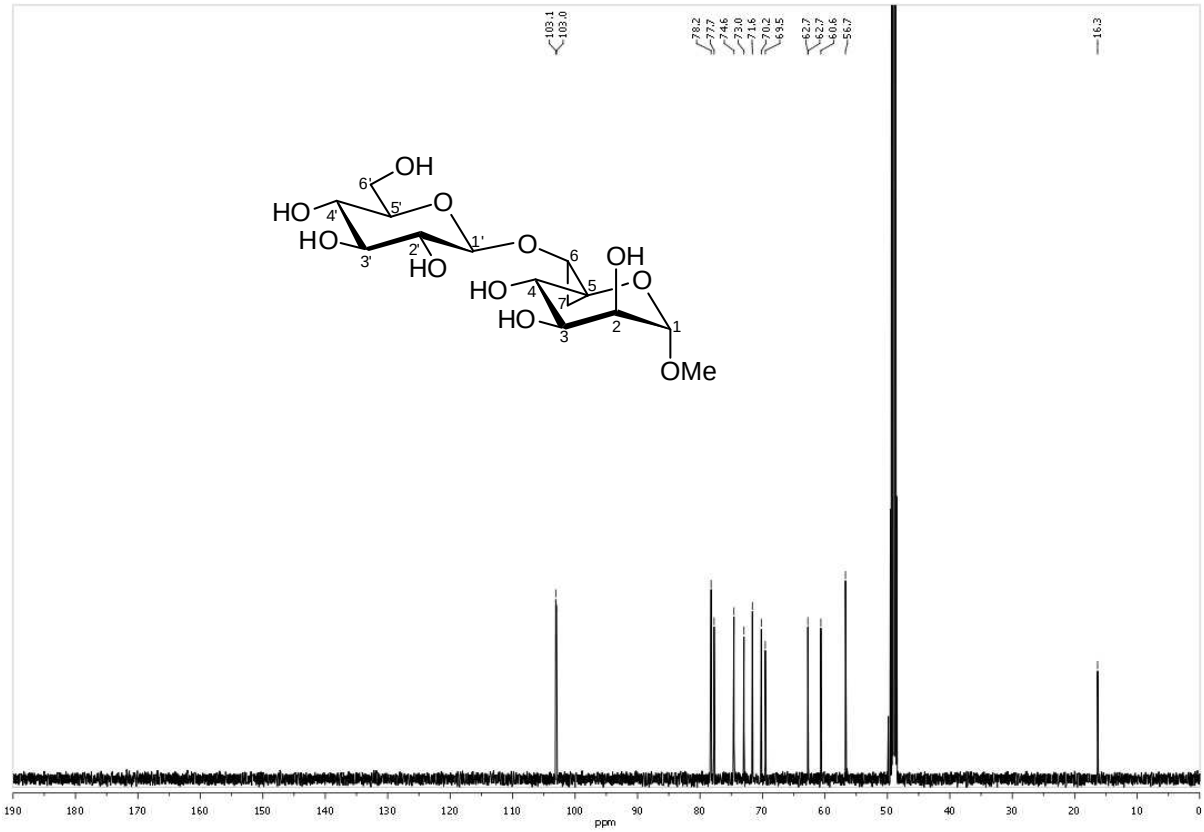


^{13}C NMR (CD_3OD, 125 MHz)

Compound 29

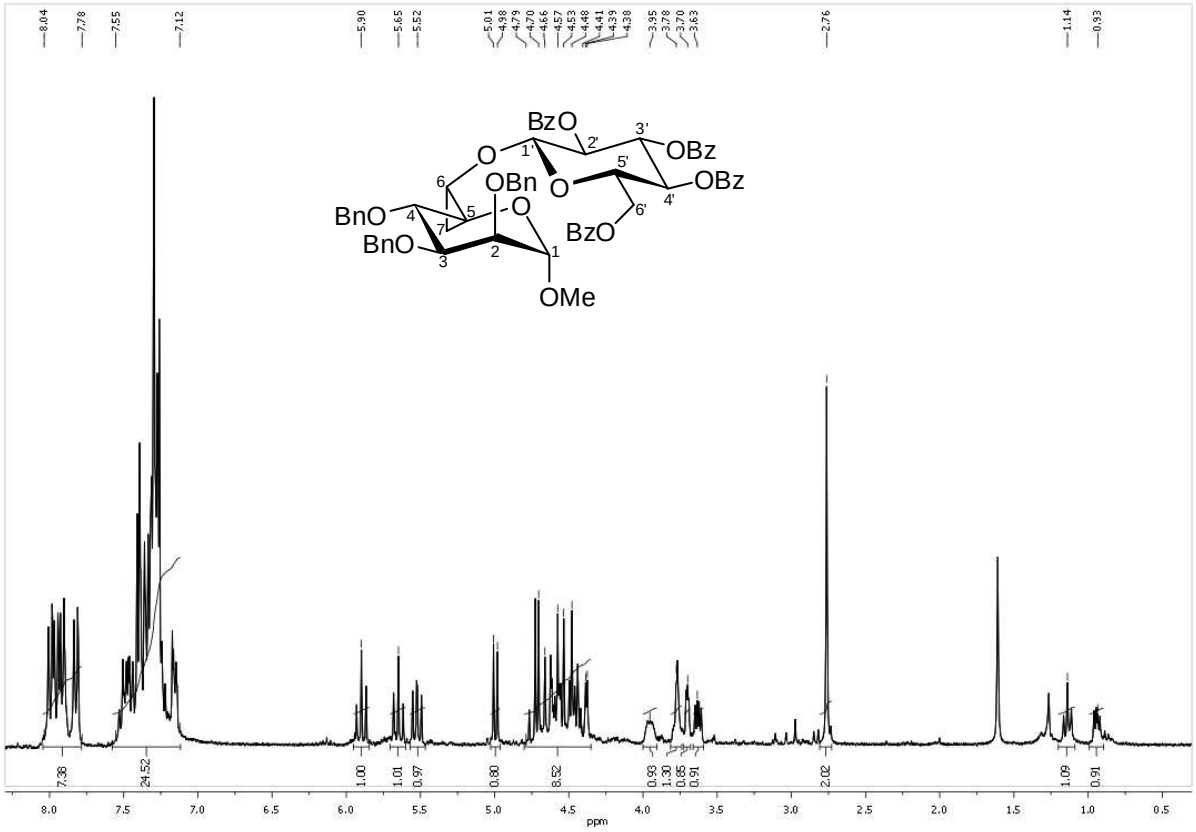


^{1}H NMR (CD_3OD, 300 MHz)

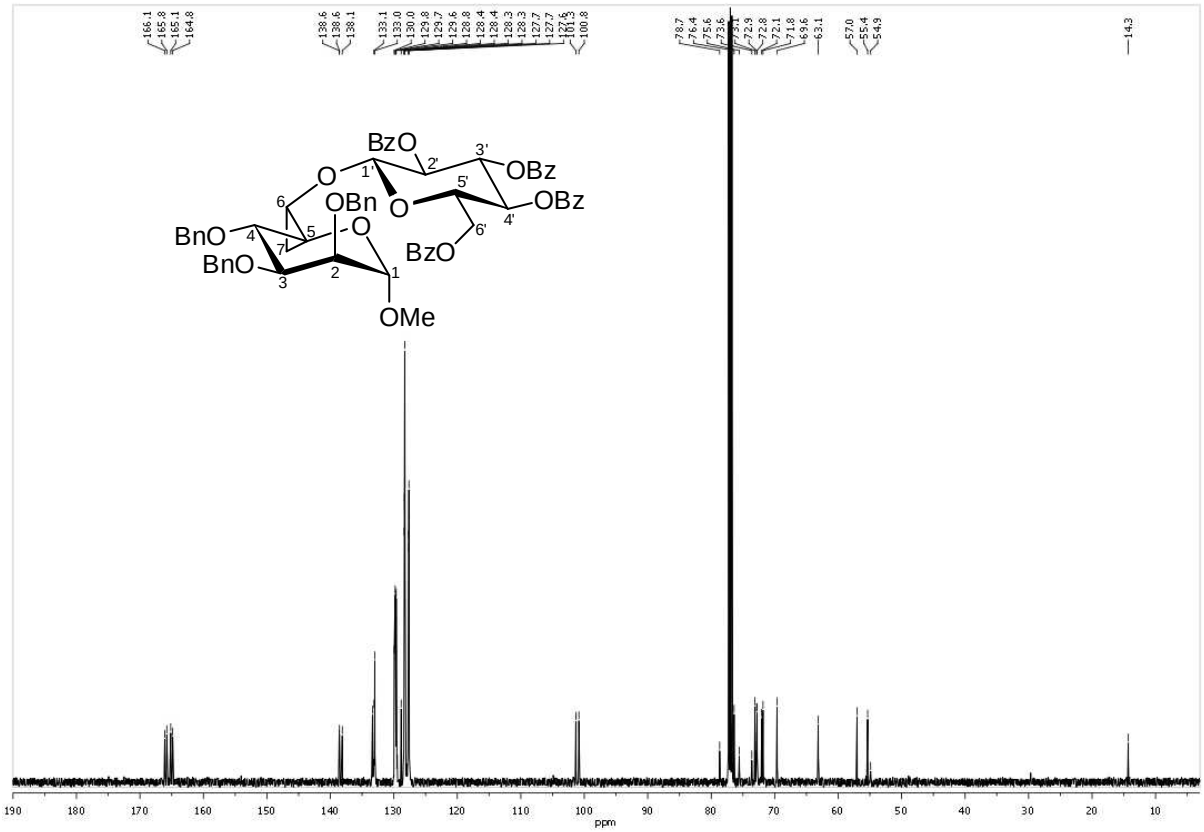


^{13}C NMR (CD_3OD, 125 MHz)

Compound 30

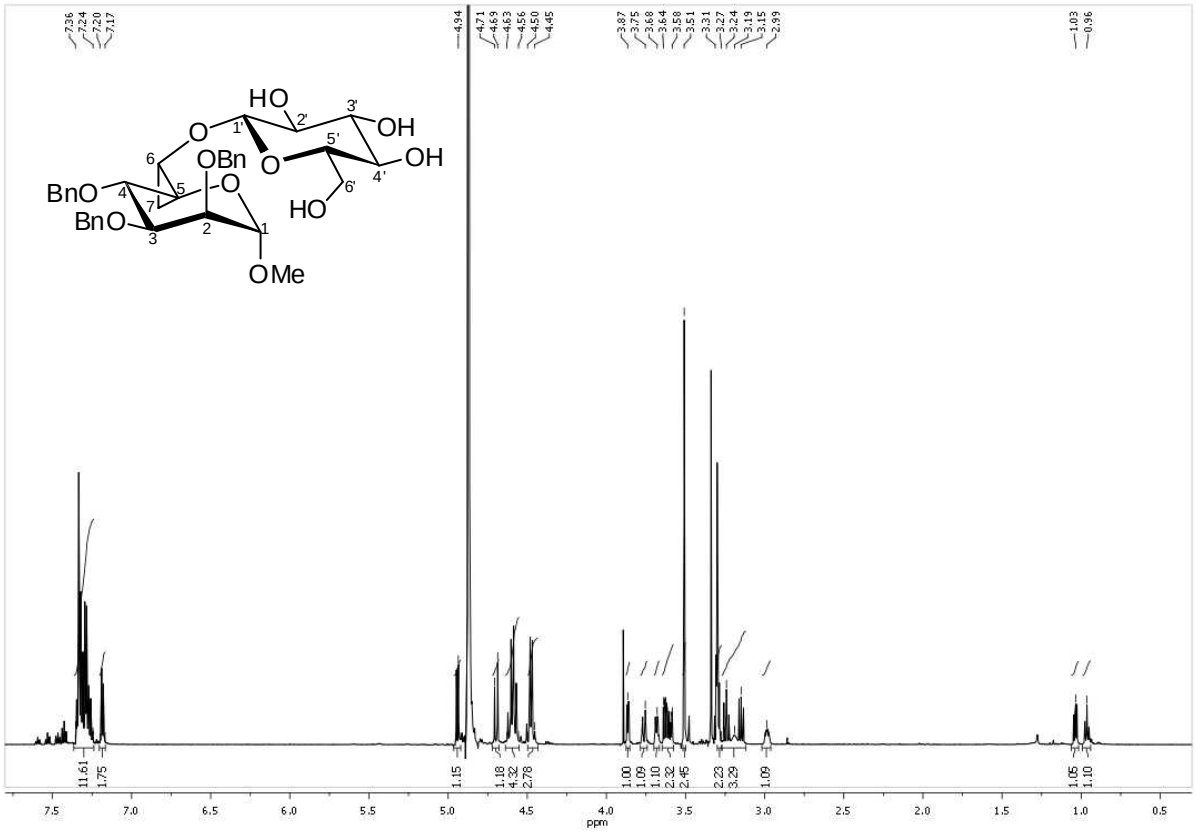


^{1}H NMR ($CDCl_3$, 300 MHz)

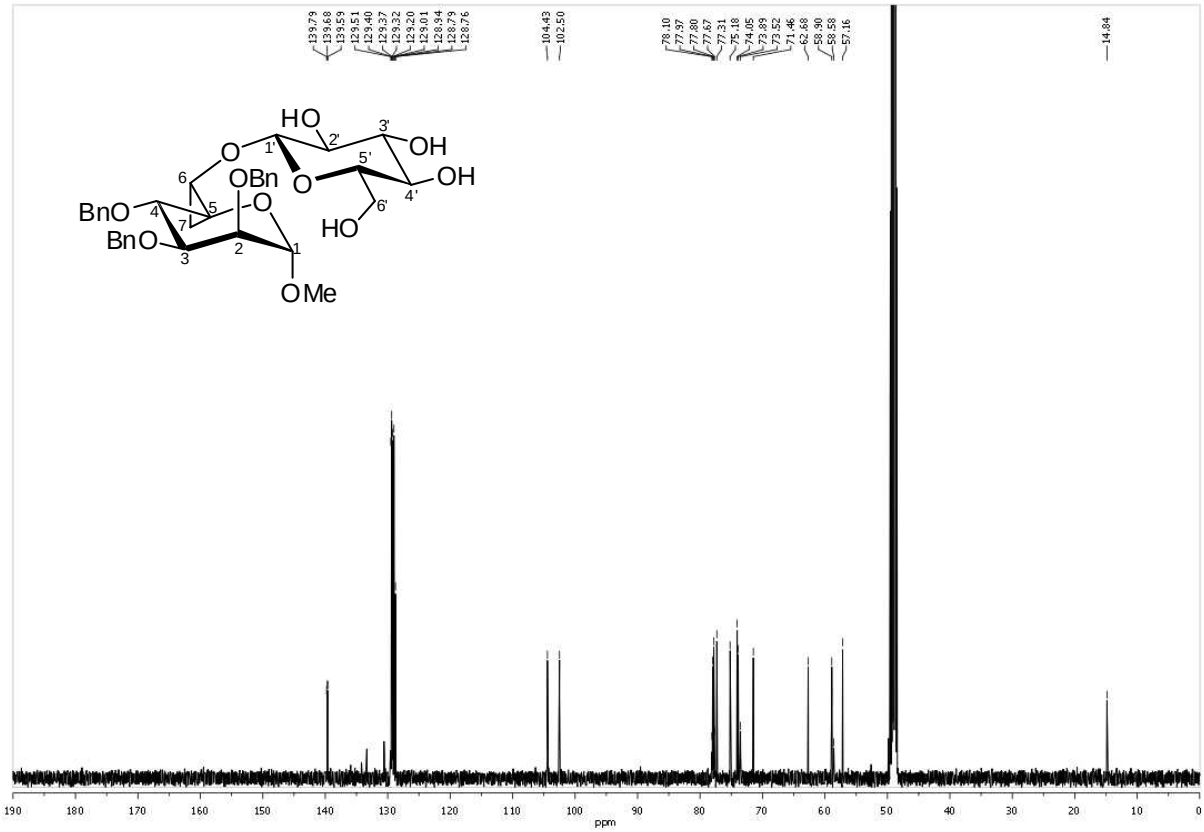


^{13}C NMR ($CDCl_3$, 125 MHz)

Compound 31a

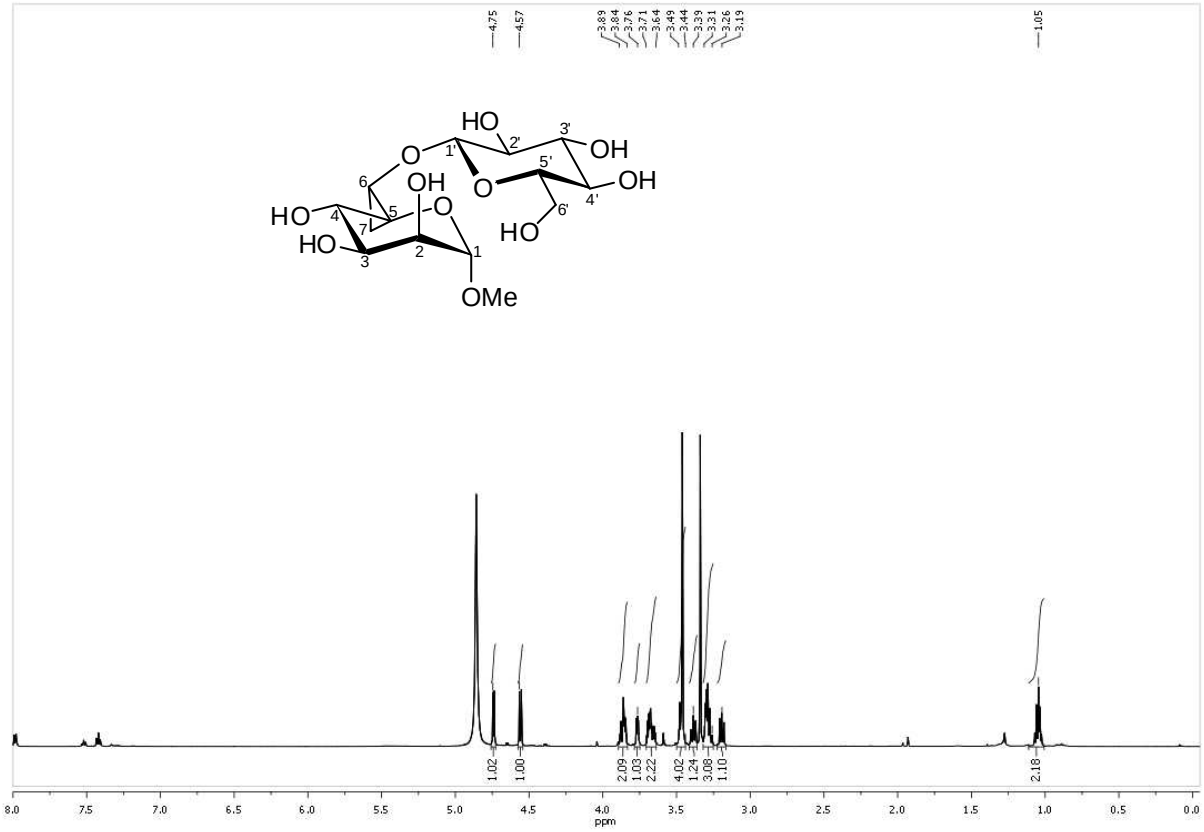


^{1}H NMR (CD_3OD, 600 MHz)

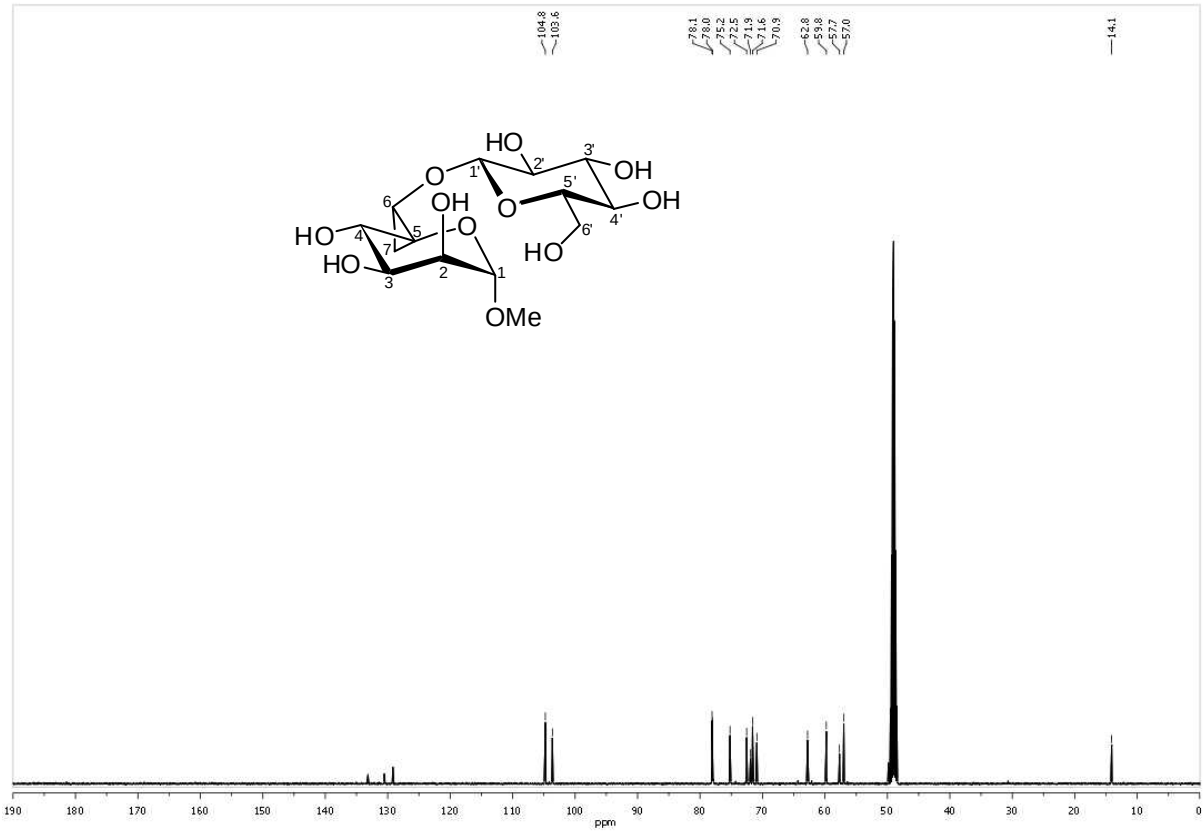


^{13}C NMR (CD_3OD, 125 MHz)

Compound 31

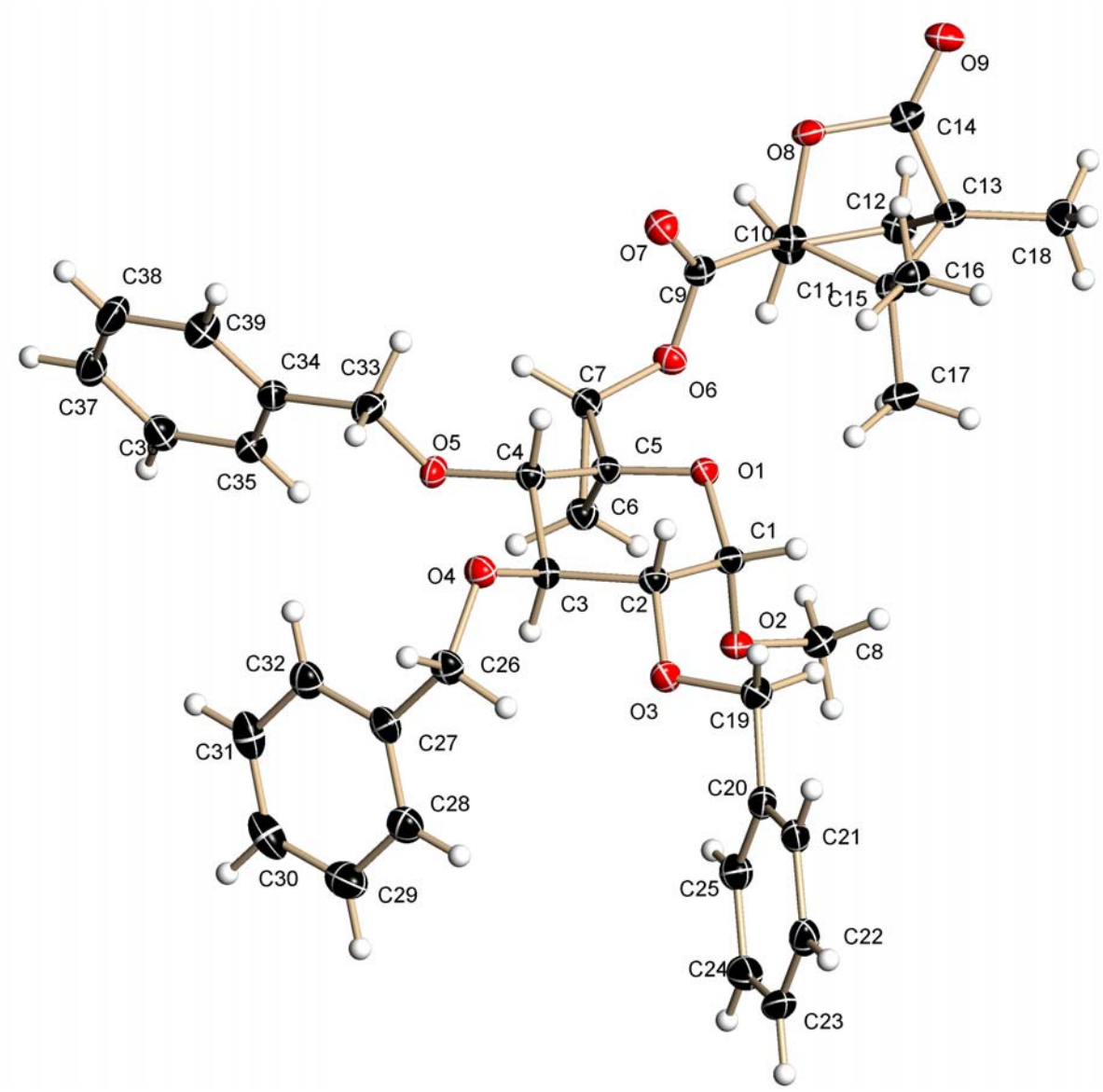


^{1}H NMR (CD_3OD, 600 MHz)



^{13}C NMR (CD_3OD, 125 MHz)

X-ray data for compound 33



Single crystal X-ray structure of **33** with ellipsoid at 50% probability level.

Table 1. Crystal data and structure refinement **33**.

CCDC no	832491
Empirical formula	$C_{39}H_{44}O_9$
Formula weight	656.74
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 6.249(2) Å
	b = 16.225(3) Å β= 91.93(2)°.
	c = 16.620(3) Å
Volume	1684.1(7) Å^3

Z	2
Density (calculated)	1.295 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	700
Crystal size	0.20 x 0.06 x 0.06 mm
Theta range for data collection	1.23 to 27.65°.
Index ranges	-8<=h<=8, -21<=k<=21, -21<=l<=21
Reflections collected	39222
Independent reflections	4052 [R(int) = 0.0459]
Completeness to theta = 27.65°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9897 and 0.9408
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4052 / 1 / 438
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	*R*1 = 0.0310, *wR*2 = 0.0732
R indices (all data)	*R*1 = 0.0348, *wR*2 = 0.0760
Extinction coefficient	0.0079(11)
Largest diff. peak and hole	0.198 and -0.156 $e.Å^{-3}$

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: p21

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=6.249(2) b=16.225(3) c=16.620(3)
alpha=90 beta=91.93(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1684.2(7)	1684.1(7)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C39 H44 O9	C39 H44 O9
Sum formula	C39 H44 O9	C39 H44 O9
Mr	656.74	656.74
Dx,g cm-3	1.295	1.295
Z	2	2
Mu (mm-1)	0.091	0.091
F000	700.0	700.0
F000'	700.37	
h,k,lmax	8,21,21	8,21,21
Nref	4064[7850]	4052
Tmin,Tmax	0.993,0.995	0.941,0.990
Tmin'	0.982	

Correction method= MULTI-SCAN

Data completeness= 1.00/0.52 Theta(max)= 27.650

R(reflections)= 0.0310(3761) wR2(reflections)= 0.0760(4052)

S = 1.042 Npar= 438

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel pairs is correct. If it is not, please give the correct count in the _publ_section_exptl_refinement section of the submitted CIF.
From the CIF: _diffrn_reflns_theta_max 27.65

```
          From the CIF: _reflns_number_total              4052
          Count of symmetry unique reflns         4064
          Completeness (_total/calc)             99.70%
          TEST3: Check Friedels for noncentro structure
          Estimate of Friedel pairs measured         0
          Fraction of Friedel pairs measured     0.000
          Are heavy atom types Z>Si present          no
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF ....          ?
PLAT791_ALERT_4_G Note: The Model has Chirality at C1     (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C2     (Verify)          R
PLAT791_ALERT_4_G Note: The Model has Chirality at C3     (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C4     (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C5     (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C7     (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C10    (Verify)          S
PLAT791_ALERT_4_G Note: The Model has Chirality at C13    (Verify)          R
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   0 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   9 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 27/06/2011; check.def file version of 27/06/2011

Datablock: p21 - ellipsoid plot