Supporting Information

Defining Oxyanion Reactivities in Base-promoted Glycosylations

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Proposed mechanism for base-promoted glycosylation on acceptors containing vicinal hydroxyl groups exemplary shown for the 4,6-diol 6

In the case of 6 deprotonation of one hydroxyl group resulted in the formation of compound 6a. Using a systematic study of the acidic behaviour ($K_e$) of partially methylated glucopyranosides 1 – 8 allowed to conclude that in such anionic species the negative charge was dispersed by hydrogen bonding from the unreacted hydroxyl group, i.e. stabilized by a mesomeric effect (6a$_1$ and 6a$_2$). In general it could be observed that adjacent hydroxyl groups of sugars exhibit a higher acidity relative to isolated ones. This suggests that diol and triol structures are likely to show hydrogen bonding.

Further deprotonation would lead to the proposed dianionic species 6b the formation of which was most likely hindered due to the incorporation of the unreacted hydrogen by dispersion of negative charge. Both disaccharides 15 and 16 were formed by nucleophilic attack of the sugar alkoholate 6a$_1$ and 6a$_2$ in $\beta$-position at the $\alpha$-glycosylchloride in a “SN$_2$-like” manner. The equilibrium between 6a$_1$ and 6a$_2$ is most likely shifted to structure 6a$_1$ in which the negative charge is located on the less basic oxyanion. Accordingly, O-6 acts mainly as a hydrogen-bond acceptor which enhances its reactivity.$^2$ Consequently, the 6-position exhibited a higher reactivity relative to the 4-position giving rise to a ratio of 1:4 for 15a and 16a. After monoglycosylation the presence of an excess of base and donor concentration leads to deprotonation of the remaining, now isolated hydroxyl groups of disaccharides 15a and 16a. Again, donor 9 was attacked in a “SN$_2$-like” manner resulting in the formation of trisaccharide 26, in which disaccharide 16a is the main reactant for a second glycosylation due to its excess.

Scheme 1: Proposed mechanism for base-promoted glycosylation
**Experimental:**

**General:**
All reagents were purchased from commercial sources and used as received. Sodium hydride (NaH) was purchased and used as 60% suspension in paraffine. Glycosylation reactions were conducted under an atmosphere of dry argon. Solvents for chromatography were distilled prior to use. Thin layer chromatography was performed on *Merck* silica gel 60 F254 plates. Column chromatography was performed on *Merck/Fluka* silica gel 60 (230 – 400 mesh). ¹H-NMR and ¹³C-NMR spectra were recorded on a *Bruker AMX-400* or *Bruker AV-400* spectrometers (400 MHz for ¹H, 101 MHz for ¹³C). Melting points were measured on a Apotec® melting point apparatus. Optical rotation were obtained using a Krüss Optronic P8000 polarimeter (c = [g 100cm⁻¹]). ESI HRMS were recorded on Thermo Finnigan MAT 95XL mass spectrometer.

Relative yields of disaccharide mixtures were determined by ¹H-NMR-integration of the anomeric or other well separated proton signals.

Partially methylated methyl α-D-glucopyranosides 1 – 8,³⁴ and methyl 3-O-benzyl-α-D-glucopyranoside (22) were synthesized applying standard protecting group chemistry (see Scheme 2).⁵⁶
Scheme 2: Synthesis of partially methylated methyl \( \alpha \)-D-glucopyranosides 1 – 8.

\( 9^7, 23^7, 8, 28^9, 34^{10} \) and \( 35^{10} \) were synthesized as described in the cited literature.

A) General procedure for methylation/benzylation:
The starting material (1 mmol) was dissolved in anhydrous \( \text{N}_2\text{N} \)-dimethylformamide (10 mL), treated with sodium hydride (2 – 2.5 eq. per OH group) at 0 °C and stirred for 1 h. Subsequently Mel/BnBr (2 – 2.5 eq. per OH group) was added at 0 °C, the mixture warmed to ambient temperature and stirred for 12 – 18 h. The reaction was quenched by addition of methanol (5 mL) and the solvents were removed under reduced pressure. The residue was taken up in \( \text{H}_2\text{O/DCM} \) 1:1 and the aqueous layer extracted twice with DCM. The organic phase was washed with brine, dried (\( \text{Na}_2\text{SO}_4 \)) and concentrated \textit{in vacuo}. The residue was purified by flash column chromatography (gradient petrol ether/ethyl acetate) to yield the corresponding methylated/benzylated derivatives \( 30^{11}, 33^{10}, 36^{16}, 40^{16}, 41, 42^{12}, 43 \) and 45.
B) General procedure for cleavage of the benzylidene group:
The 4,6-O-benzylidene protected derivative (1 mmol) was dissolved or suspended in distilled methanol (10 mL), treated with 0.5 mL H$_2$O and 1 mL 1 N HCl. The mixture was stirred for 3 h at 55 °C, neutralized by addition of NaHCO$_3$-solution. Solvents were evaporated \textit{in vacuo}, azeotroping with toluene, and the residue purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds 6$^{16}$, 7$^{16}$, 8, 22$^{13}$, 37$^{14}$ and 38$^{13}$.

C) General procedure for cleavage of the benzyl groups:
To a solution of the benzylated intermediate (1 mmol) in distilled methanol (20 mL) 30 mg Pd(10%)/C was added and the mixture stirred under an atmosphere of hydrogen at room temperature for 24 - 96 h. The catalyst was filtered off, the solvents evaporated \textit{in vacuo} and the residue purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds 1, 2, 3$^{16}$, and 5$^{16}$.

D) General procedure for tritylation:
To a solution of 1 mmol starting material in anhydrous pyridine (3 mL) Chlorotriphenylmethane (1.1 eq.) and catalytic amounts of 4-N,N-dimethylaminopyridine (DMAP) were added. The mixture was stirred at 60 °C for 72 h, evaporated \textit{in vacuo}, azeotroping with toluene and purified by flash silica gel chromatography (gradient petrol ether/ethyl acetate) to yield the compounds 29$^{15}$ and 39$^{16}$.

E) Standard procedure for base-promoted glycosylation:
The acceptor (0.1 mmol) was dissolved in anhydrous N,N-dimethylformamide (2.0 mL), treated with the specified amount of base (2 – 4 eq.) and stirred for 1 h. Subsequently the donor (2 – 4 eq.), dissolved in anhydrous N,N-dimethylformamide (2.0 mL), was added and the mixture stirred for 4 h. The reaction was quenched by addition of methanol (1 mL) and the solvents were removed under reduced pressure. The remaining syrup was taken up in pyridine and acetic anhydride (2:1 v/v, 6 mL) and stirred for 18 h. Pyridine was removed under reduced pressure and by codistilling with toluene. The remaining residue was purified using flash-column chromatography (eluent: petrol ether/ethyl acetate 2:1 to only ethylacetate) to give the disaccharide mixtures. The subsequent analysis of the disaccharide mixtures by $^1$H-NMR afforded their relative yields.
Characterization data for partially methylated methyl α-D-glucopyranosides 1 – 8 and donor 2,3,4,6-Tetra-O-methyl α-D-galactopyranosyl chloride (9).

Methyl 3,4,6-tri-O-methyl-α-D-glucopyranoside (1)

Prepared following procedure C. 1.12 g (3.44 mmol) 41, 110 mg Pd(10%)/C, 50 mL MeOH. Yield: 720 mg (3.05 mmol, 89%), colourless syrup, \( \left[ \alpha \right]_D^{23} = +179.0^\circ \) (c = 0.92 in CHCl₃), \( R_f \) (PE/EE 2:1, v/v) = 0.10, ESI HRMS for C₁₀H₂₀O₆ [M+Na⁺]: found 259.1162, calcd. 259.1152. \( ^1H\)-NMR (400 MHz, CDCl₃) \( \delta = 4.75 \) (d, \( ^3J_{1,2} = 4.0 \) Hz, 1H, H-1), 3.61-3.57 (m, 4H, H-5, H-6, H-2), 3.35 (dd, 1H, H-3), 3.19 (dd, \( ^3J_{3,4} = 9.1, ^3J_{4,5} = 9.1 \) Hz 1H, H-4), 3.65, 3.52, 3.41, 3.40 (OCH₃) ppm. \( ^13C\)-NMR (101 MHz, CDCl₃) \( \delta = 99.3 \) (C-1), 84.4 (C-3), 79.3 (C-4), 72.3 (C-2), 70.9 (C-6), 70.2 (C-5), 60.8, 60.2, 59.1, 55.2 (OCH₃) ppm.

Methyl 2,4,6-tri-O-methyl-α-D-glucopyranoside (2)

Prepared following procedure C. 1.44 g (4.41 mmol) 42, 117 mg Pd(10%)/C, 50 mL MeOH. Yield: 1.04 g (4.40 mmol, 99%) colourless syrup, \( \left[ \alpha \right]_D^{23} = +165.3^\circ \) (c = 0.19 in CHCl₃), \( R_f \) (ethyl acetate) = 0.17, ESI HRMS for C₁₀H₂₀O₆ [M+Na⁺]: found 259.1152, calcd. 259.1152. \( ^1H\)-NMR (400 MHz, CDCl₃) \( \delta = 4.89 \) (d, \( ^3J_{1,2} = 3.5 \) Hz, 1H, H-1), 3.91 (dd, \( ^3J_{2,3} = 9.4 \) Hz, \( ^3J_{3,4} = 9.2 \) Hz, 1H, H-3), 3.64 – 3.58 (m, 3H, H-5, H-6), 3.26 (dd, 1H, H-4), 3.21 (dd, 1H, H-2), 3.57, 3.49, 3.43, 3.41 (OCH₃) ppm. \( ^13C\)-NMR (101 MHz, CDCl₃) \( \delta = 96.8 \) (C-1), 81.3 (C-3), 79.1 (C-4), 72.3 (C-2), 70.9 (C-6), 70.2 (C-5), 60.5, 59.2, 58.4, 55.2 (OCH₃) ppm.

Methyl 2,3,6-tri-O-methyl-α-D-glucopyranoside (3)

Prepared following procedure C. 937 mg (2.87 mmol) 45, 220 mg Pd(10%)/C, 50 mL MeOH. Yield: 672 mg (2.84 mmol, 99%), colourless syrup, \( \left[ \alpha \right]_D^{23} = +128.0^\circ \) (c = 0.2, MeOH), Lit.\(^{16}\); \( \left[ \alpha \right]_D = +149.0^\circ \) (MeOH), \( R_f \) (PE/EE 2:1, v/v) = 0.05, ESI HRMS for C₁₀H₂₀O₆ [M+Na⁺]: found 259.1155, calcd. 259.1152. \( ^1H\)-NMR (400 MHz, CDCl₃) \( \delta = 4.86 \) (d, \( ^3J_{1,2} = 3.6 \) Hz, 1H, H-1), 3.71 (dd, \( ^3J_{4,5} = 9.2 \) Hz,
$^3J_{5,6a} = 4.1$ Hz, $^3J_{5,6b} = 3.6$ Hz, 1H, H-5), 3.67 – 3.60 (m, 2H, H-6), 3.52 (dd, $^3J_{3,4} = 9.4$ Hz, $^3J_{4,5} = 9.2$ Hz, 1H, H-4), 3.46 (dd, $^3J_{2,3} = 9.4$ Hz, $^3J_{3,4} = 9.4$ Hz, 1H, H-3), 3.26 (dd, $^3J_{1,2} = 3.6$ Hz, $^3J_{2,3} = 9.4$ Hz, 1H, H-2), 3.64, 3.50, 3.44, 3.42 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 97.6$ (C-1), 82.8 (C-3), 81.7 (C-2), 72.0 (C-6), 70.6 (C-4), 69.6 (C-5), 61.2, 59.4, 58.5, 55.2 (OCH$_3$) ppm.

**Methyl-2,3,4-tri-O-methyl-α-D-glucopyranosid (4)**

![Diagram of Methyl-2,3,4-tri-O-methyl-α-D-glucopyranosid (4)](image)

3.66 g (7.64 mmol) 36 were deprotected and purified by flash silica gel chromatography with 5% TfOH in chloroform as eluent.$^{17}$ Yield: 390 mg (1.65 mmol, 22%), colourless syrup, $[\alpha]_D^{23} = +158.0^\circ$ (c = 0.26, CHCl$_3$), $R_f$ (ethyl acetate) = 0.16, ESI HRMS for C$_{10}$H$_{20}$O$_6$ [M+Na$^+$]: found 259.1153, calcd. 259.1152.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 4.80$ (d, $^3J_{1,2} = 3.5$ Hz, 1H, H-1), 3.83 (dd, $^3J_{5,6a} = 2.1$ Hz, $^2J_{6a,6b} = 11.7$ Hz, 1H, H-6a), 3.74 (dd, $^3J_{5,6b} = 4.2$ Hz, $^2J_{6a,6b} = 11.7$ Hz, 1H, H-6b), 3.56 – 3.50 (m, 2H, H-3, H-5), 3.21 – 3.12 (m, 2H, H-2, H-4), 3.63, 3.56, 3.52, 3.40 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 97.5$ (C-1), 83.4 (C-3), 81.8 (C-2), 79.7 (C-4), 70.5 (C-5), 62.0 (C-6), 60.9, 60.6, 59.0, 55.2 (OCH$_3$) ppm.

**Methyl-4,6-di-O-methyl-α-D-glucopyranoside (5)**

![Diagram of Methyl-4,6-di-O-methyl-α-D-glucopyranoside (5)](image)

Prepared following procedure C. 1.33 g (3.30 mmol) 40, 111 mg Pd(10%)/C, 50 mL MeOH. Yield: 704 mg (3.17 mmol, 96%), colourless syrup, $[\alpha]_D^{23} = +152.0^\circ$ (c = 1.00, CHCl$_3$), Lit.$^{16}$: $[\alpha]_D = +157.0^\circ$ (CHCl$_3$), $R_f$ (PE/EE 1:1, v/v) = 0.04, ESI HRMS for C$_9$H$_{18}$O$_6$ [M+Na$^+$]: found 245.0991, calcd. 245.0996. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 4.79$ (d, $^3J_{1,2} = 3.8$ Hz, 1H, H-1), 3.75 (dd, $^3J_{2,3} = 9.4$ Hz, $^3J_{3,4} = 9.2$ Hz, 1H, H-3), 3.64 – 3.58 (m, 3H, H-5, H-6), 3.55 (dd, $^3J_{1,2} = 3.8$ Hz, $^3J_{2,3} = 9.4$ Hz, 1H, H-2), 3.26 – 3.19 (dd, $^3J_{3,4} = 9.2$ Hz, $^3J_{4,5} = 9.2$ Hz, 1H, H-4), 3.57, 3.43, 3.42 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 99.1$ (C-1), 79.0 (C-4), 75.0 (C-3), 72.5 (C-2), 71.0 (C-6), 70.0 (C-5), 60.6, 59.2, 55.4 (OCH$_3$) ppm.
Methyl-2,3-di-O-methyl-α-D-glucopyranoside (6)

Prepared following procedure B. 2.00 g (6.44 mmol) 30, 40 mL MeOH, 4 mL H2O, 1 mL 1 N HCl. Yield: 1.40 g (6.32 mmol, 98%), white solid, $[\alpha]_D^{23} = +146.4^\circ$ (c = 1.0, H2O), Lit.16: $[\alpha]_D = +143^\circ$ (H2O), m.p.: 83 – 85 °C, Lit.16: m.p.: 83 – 85 °C, $R_f$ (ethyl acetate) = 0.12, ESI HRMS for C9H18O6 [M+Na+]: found 245.0990, calcd. 245.0996.

$^1$H-NMR (400 MHz, CDCl3) δ = 4.85 (d, $^3J_{1,2} = 3.6$ Hz, 1H, H-1), 3.86 (dd, $^3J_{5,6a} = 3.6$ Hz, $^2J_{6a,6b} = 12.0$ Hz, 1H, H-6a), 3.81 (dd, $^3J_{5,6b} = 4.2$ Hz, $^2J_{6a,6b} = 12.0$ Hz, 1H, H-6b), 3.70 – 3.61 (m, 1H, H-5), 3.55-3.44 (m, 2H, H-3, H-4), 3.23 (dd, $^3J_{1,2} = 3.6$, $^3J_{2,3} = 9.4$ Hz, 1H, H-2), 3.64, 3.50, 3.44 (OCH3) ppm.

$^{13}$C-NMR (101 MHz, CDCl3) δ = 97.6 (C-1), 82.7 (C-3), 82.0 (C-2), 70.7 (C-5), 70.6 (C-4), 62.6 (C-6), 61.2, 58.5, 55.3 (OCH3) ppm.

Methyl-2-O-methyl-α-D-glucopyranoside (7)

Prepared following procedure B. 1.07 g (3.61 mmol) 31, 30 mL MeOH, 2 mL H2O, 1 mL 1 N HCl. Yield: 712 mg (3.42 mmol, 95%), white solid, $[\alpha]_D^{23} = +139.0^\circ$ (c = 0.2, H2O), Lit.16: $[\alpha]_D = +155^\circ$ (H2O), m.p.: 144 – 145 °C, Lit.16: m.p.: 147 – 148 °C, $R_f$ (DCM/MeOH 9:1, v/v) = 0.15, ESI HRMS for C8H16O6 [M+Na+]: found 231.0844, calcd. 231.0839.

$^1$H-NMR (400 MHz, CDCl3) δ = 4.91 (d, $^3J_{1,2} = 3.5$ Hz, 1H, H-1), 3.91 – 3.80 (m, 3H, H-3, H-6), 3.69 - 3.56 (m, 2H, H-5, H-4), 3.17 (dd, $^3J_{1,2} = 3.5$ Hz, $^3J_{2,3} = 9.7$ Hz, 1H, H-2), 3.50, 3.44 (OCH3) ppm.

$^{13}$C-NMR (101 MHz, CDCl3) δ = 96.9 (C-1), 81.1 (C-2), 73.0 (C-3), 70.8 (C-4), 70.7 (C-5), 62.5 (C-6), 58.3, 55.3 (OCH3) ppm.

Methyl-3-O-methyl-α-D-glucopyranoside (8)

Prepared following procedure B. 1.35 g (4.56 mmol) 32, 30 mL MeOH, 2 mL H2O, 1 mL 1 N HCl. Yield: 876 mg (4.21 mmol, 92%), white solid, $[\alpha]_D^{23} = +146.0^\circ$ (c = 0.5, CHCl3), m.p.: 79 °C, $R_f$ (DCM/MeOH 9:1, v/v) = 0.18, ESI HRMS for C8H16O6 [M+Na+]: found 231.0833, calcd. 231.0839.

$^1$H-NMR (400 MHz, CDCl3) δ = 4.74 (d, $^3J_{1,2} = 3.8$ Hz, 1H, H-1), 3.87 (dd, $^3J_{5,6a} = 3.8$ Hz, $^2J_{6a,6b} = 11.7$ Hz, 1H, H-6a), 3.81 (dd, $^3J_{5,6b} = 4.6$ Hz, $^2J_{6a,6b} = 11.7$ Hz, 1H, H-6b), 3.69 – 3.62 (m, 1H, H-5), 3.62 – 3.55 (m, 1H, H-2), 3.55 – 3.48 (m, 1H, H-6b), 3.48 - 3.30 (m, 2H, H-3, H-4), 3.23 (dd, $^3J_{1,2} = 3.6$, $^3J_{2,3} = 9.4$ Hz, 1H, H-2), 3.64, 3.50, 3.44 (OCH3) ppm.
3.52 (dd, $^3J_{3,4} = 9.2$ Hz, $^3J_{4,5} = 9.5$ Hz, 1H, H-4), 3.34 (dd, $^3J_{2,3} = 9.2$ Hz, $^3J_{3,4} = 9.2$ Hz, 1H, H-3), 3.68, 3.44 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 99.6 (C-1), 84.2 (C-3), 72.8 (C-2), 70.9 (C-5), 70.2 (C-4), 62.5 (C-6), 60.9, 55.4 (OCH$_3$) ppm.

2,3,4,6-Tetra-0-methyl-\(\alpha\)-d-galactopyranosyl chloride (9)

Prepared as described in the literature. 7 516 mg (2.18 mmol) 2,3,4,6-Tetra-0-methyl \(\alpha\)-D-galactopyranose$^{18,19}$, 50 \(\mu\)L (0.64 mmol) abs. DMF, 500 \(\mu\)L (5.71 mmol) Oxalylichlorid, 10 mL abs. DCM, Yield: 511 mg (2.01 mmol, 92%), colourless oil, $[\alpha]^D_{23} = +203.3^\circ$ (c = 0.66, CHCl$_3$), $R_f$ (ethyl acetate) = 0.55, $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 6.28 (d, $^3J_{1,2} = 3.8$ Hz, 1H, H-1), 4.22 – 4.16 (m, 1H, H-5), 3.83 (dd, $^3J_{1,2} = 3.8$ Hz, $^3J_{2,3} = 9.9$ Hz, 1H, H-2), 3.77 (dd, $^3J_{3,4} = 2.5$ Hz, $^3J_{4,5} = 0.8$ Hz, 1H, H-4), 3.62 – 3.56 (m, 2H, H-3, H-6a), 3.56 – 3.50 (m, 1H, H-6b), 3.59, 3.55, 3.52, 3.41, (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 94.1 (C-1), 79.8 (C-3), 77.8 (C-2), 75.4 (C-4), 72.1 (C-5), 70.3 (C-6), 61.5, 59.2, 58.5, 58.4 (OCH$_3$) ppm.

Methyl 3,4,6-tri-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10), methyl 2,4,6-tri-O-methyl-3-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (11), methyl 2,3,6-tri-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12) and methyl 2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)

Prepared following procedure E. 25.3 mg (0.107 mmol) methyl 3,4,6-tri-O-methyl-α-D-glucopyranoside (1), 25.3 mg (0.107 mmol) methyl 2,4,6-tri-O-methyl-α-D-glucopyranoside (2), 25.2 mg (0.107 mmol) methyl 2,3,6-tri-O-methyl-α-D-glucopyranoside (3), 25.2 mg (0.107 mmol) methyl 2,3,4-tri-O-methyl-α-D-glucopyranoside (4), 34.2 mg (0.856, 2.0 eq.) NaH, 218 mg (0.857 mmol, 2.0 eq.) 2,3,4,6-tetra-O-methyl-α-D-galactopyranosyl chloride (9); Yield (10 – 13): 38.4 mg (0.0845 mmol, 20%), yellow syrup; Relative yield (10/11/12/13): 40:11:26:23; Rf (ethyl acetate) = 0.17; ESI HRMS for C20H38O11 [M+Na+]: found 477.2303, calcd. 477.2306; Disaccharides 10 and 12 were fully characterized by NMR-spectroscopy.

Methyl 3,4,6-tri-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10)

1H-NMR (400 MHz, CDCl3) δ = 4.82 (d, $3^3J_{1,2} = 2.8$ Hz, 1H, H-1), 4.39 (d, $3^3J_{1,2} = 7.8$ Hz, 1H, H-1’), 3.64 – 3.60 (m, 1H, H-4’), 3.60 – 3.50 (m, 6H, H-5, H-6a, H-6b, H-6a’, H-3, H-2), 3.48 – 3.42 (m, 2H, H-6b’, H-5’), 3.38 – 3.33 (m, 1H, H-2’), 3.23 – 3.16 (m, 1H, H-4), 3.13 (dd, $3^3J_{3,2} = 9.7$ Hz, $3^3J_{3,4} = 3.2$ Hz, 1H, H-3’), 3.63, 3.62, 3.55, 3.54, 3.52, 3.41, 3.36, 3.36 (OCH3) ppm; 13C-NMR (101 MHz, CDCl3) δ = 105.1 (C-1’), 99.7 (C-1), 84.2 (C-3’), 83.3 (C-3), 80.6 (C-2’), 80.0 (C-4), 79.6 (C-2), 74.9 (C-4’), 72.9 (C-5’), 71.1 (C-6), 70.7 (C-6’), 69.7 (C-5), 61.2, 60.8, 60.7, 60.4, 59.2, 59.1, 58.3, 55.1 (OCH3) ppm.

Methyl 2,3,6-tri-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12)
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 4.82$ (d, $^{3}J_{1,2} = 3.5$ Hz, 1H, H-1), 4.32 (d, $^{3}J_{1',2'} = 7.6$ Hz, 1H, H-1’), 3.77 (dd, $^{3}J_{6a,5} = 4.1$ Hz, $^{2}J_{6a,6b} = 10.4$ Hz, 1H, H-6a), 3.69 (ddd, $^{3}J_{5,4} = 9.8$ Hz, $^{3}J_{5,6a} = 4.1$ Hz, $^{3}J_{5,6b} = 1.6$ Hz, 1H, H-5), 3.68 – 3.65 (m, 1H, H-4’), 3.65 – 3.60 (m, 3H, H-6b, H-4, H-6a’), 3.57 - 3.52 (m, 2H, H-3, H-6b’), 3.50 – 3.46 (m, 1H, H-5’), 3.27 (dd, $^{3}J_{2',1'} = 7.6$ Hz, $^{3}J_{2',3'} = 9.8$ Hz, 1H, H-2’), 3.21 (dd, 1H, H-2), 3.14 (dd, $^{3}J_{3',2'} = 9.8$ Hz, $^{3}J_{3',4'} = 3.2$ Hz, 1H, H-3’), 3.59, 3.58, 3.56, 3.52, 3.51, 3.42, 3.40, 3.39 (OCH$_3$) ppm; $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 103.8$ (C-1’), 97.4 (C-1), 84.5 (C-3’), 81.7 (C-3), 81.5 (C-2), 81.0 (C-2’), 78.5 (C-4'), 74.4 (C-4’), 72.7 (C-5’), 70.5 (C-6), 69.7 (C-5), 61.2, 61.0, 60.9, 59.1, 59.0, 59.0, 58.0, 55.2 (OCH$_3$) ppm.

Methyl 3-O-acetyl-4,6-di-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14)

Prepared following procedure E. 52.3 mg (0.235 mmol) methyl 4,6-di-O-methyl-α-D-glucopyranoside (5), 28.5 mg (0.713, 3.0 eq.) NaH, 175 mg (0.687 mmol, 3.0 eq.) 2,3,4,6-tetra-O-methyl-α-D-galactopyranosyl chloride (9); Yield (14): 19.2 mg (0.0398 mmol, 17%), colourless syrup; $[\alpha]_{D}^{23} = +67.2^\circ$ (c = 0.06, in CHCl$_3$); $R_f$ (ethyl acetate) = 0.23; ESI HRMS for C$_{21}$H$_{38}$O$_{12}$ [M+Na$^+$]: found 505.2258, calcd. 505.2255.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 5.47$ (dd, $^{3}J_{3,2} = 9.8$ Hz, $^{3}J_{3,4} = 9.9$ Hz, 1H, H-3), 4.88 (d, $^{3}J_{1,2} = 3.4$ Hz, 1H, H-1), 4.20 (d, $^{3}J_{1',2'} = 7.8$ Hz, 1H, H-1’), 3.73 – 3.69 (m, 1H, H-5), 3.62 – 3.52 (m, 5H, H-4, H-4’, H-6, H-6a’), 3.45 – 3.33 (m, 3H, H-2, H-5’, H-6b’), 3.30 (dd, 1H, H-2’), 3.06 (dd, $^{3}J_{3',2'} = 9.8$ Hz, $^{3}J_{3',4'} = 3.1$ Hz, 1H, H-3’), 3.54, 3.50, 3.48, 3.41, 3.41, 3.36, 3.36 (OCH$_3$)$_2$, 2.11 (CH$_3$-OAc) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 169.9$ (C=O), 105.6 (C-1’), 99.6 (C-1), 84.1 (C-3’), 80.0 (C-2’), 78.6 (C-4), 77.8 (C-2), 74.9 (C-4’), 73.0 (C-5’), 72.8 (C-3), 70.8 (C-6), 70.7 (C-6’), 69.3 (C-5), 61.2, 61.0, 59.5, 59.2, 59.1, 58.3, 55.2 (OCH$_3$)$_2$, 21.1 (CH$_3$-OAc) ppm.

Methyl 6-O-acetyl-2,3-di-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15), Methyl 4-O-acetyl-2,3-di-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16),
Prepared following procedure E. 51.6 mg (0.232 mmol) methyl 2,3-di-O-methyl-α-D-glucopyranoside (6), 24.0 mg (0.600, 2.6 eq.) NaH, 159 mg (0.624 mmol, 2.7 eq.) 2,3,4,6-tetra-O-methyl-α-D-galactopyranosyl chloride (9); Yield (15, 16): 69.4 mg (0.144 mmol, 62%), white solid; Relative yield (15/16): 20:80; $R_f$ (ethyl acetate) = 0.23; ESI HRMS for $C_{21}H_{38}O_{12}$ [M+Na$^+$]: found 505.2252, calcd. 505.2255.

Methyl 6-O-acetyl-2,3-di-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15)

$^1$H-NMR (400 MHz, CDCl$_3$) δ = 4.81 (d, $^3$J$_{1,2}$ = 3.8 Hz, 1H, H-1), 4.51 (dd, $^3$J$_{6a,5}$ = 1.9 Hz, $^2$J$_{6a,6b}$ = 12.0 Hz, 1H, H-6a), 4.34 (d, $^3$J$_{1',2'}$ = 7.9 Hz ,1H, H-1’), 4.29 (dd, $^3$J$_{6b,5}$ = 5.4 Hz, $^2$J$_{6b,6a}$ = 12.0 Hz, 1H, H-6b), 3.81 (ddd, $^3$J$_{5,4}$ = 9.8 Hz, $^3$J$_{5,6a}$ = 1.9 Hz, $^3$J$_{5,6b}$ = 5.4 Hz, 1H, H-5), 3.67 – 3.64 (m, 1H, H-4’), 3.64 – 3.46 (m, 5H, H-6a’, H-3’, H-4’, H-6b’, H-5’), 3.26 (dd, $^3$J$_{2',1'}$ = 7.9 Hz, $^3$J$_{2',3'}$ = 9.7 Hz, 1H, H-2’), 3.21 (dd, $^3$J$_{2,1}$ = 3.8 Hz, $^3$J$_{2,3}$ = 9.5 Hz, 1H, H-2), 3.14 (dd, $^3$J$_{5',2'}$ = 9.7 Hz, $^3$J$_{5',4'}$ = 3.0 Hz, 1H, H-3’), 3.60, 3.56, 3.56, 3.52, 3.52, 3.51, 3.42, 3.39 (OCH$_3$), 2.09 (CH$_3$-OAc) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) δ = 170.8 (C=O), 104.0 (C-1’), 97.2 (C-1), 84.9 (C-3’), 81.9 (C-3), 81.8 (C-2), 81.0 (C-2’), 79.3 (C-4), 74.3 (C-4’), 72.8 (C-5’), 70.4 (C-6’), 68.4 (C-5), 63.2 (C-6), 61.2, 61.2, 61.1, 59.1, 59.0, 57.9, 55.2 (OCH$_3$), 20.9 (CH$_3$-OAc) ppm.

Methyl 4-O-acetyl-2,3-di-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16)

$^1$H-NMR (400 MHz, CDCl$_3$) δ = 4.83 (d, $^3$J$_{1,2}$ = 3.6 Hz, 1H, H-1), 4.72 (dd, $^3$J$_{4,3}$ = 9.4 Hz, $^2$J$_{4,5}$ = 10.1 Hz, 1H, H-4), 4.27 (d, $^3$J$_{1',2'}$ = 7.6 Hz, 1H, H-1’), 3.93 – 3.84 (m, 2H, H-5, H-6a), 3.67 – 3.63 (m, 1H, H-4’), 3.63 – 3.44 (m, 5H, H-6a’, H-3, H-6b’, H-6b, H-5’), 3.30 (dd, $^3$J$_{2',1'}$ = 7.6 Hz, $^3$J$_{2',3'}$ = 9.8 Hz, 1H, H-2’), 3.27 (dd, $^3$J$_{2,1}$ = 3.6 Hz, $^3$J$_{2,3}$ = 9.7 Hz, 1H, H-2), 3.13 (dd, 1H, $^3$J$_{3',2'}$ = 9.8 Hz, $^3$J$_{3',4'}$ = 3.0 Hz, 1H, H-3’), 3.59, 3.56, 3.52, 3.52, 3.51, 3.43, 3.40 (OCH$_3$), 2.08 (CH$_3$-OAc) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) δ = 170.0 (C=O), 103.9 (C-1’), 97.1 (C-1), 83.6 (C-3’), 81.5 (C-2), 80.8 (C-3), 80.6 (C-2’), 74.6
Methyl 3,6-di-O-acetyl-2-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)

Methyl 3,4-di-O-acetyl-2-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)

Prepared following procedure E. 42.0 mg (0.202 mmol) methyl 2-O-methyl-α-D-glucopyranoside (7), 24.0 mg (0.600, 3.0 eq.) NaH, 160 mg (0.624 mmol, 3.0 eq.) 2,3,4,6-tetra-O-methyl-α-D-galactopyranosyl chloride (9); Yield (17, 18): 31.0 mg (0.0607 mmol, 30%), white solid; Relative yield (17/18): 39:61; Rf (ethyl acetate) = 0.26; ESI HRMS for C_{22}H_{38}O_{13} [M+Na+]: found 533.2211, calcd. 533.2205.

Methyl 3,6-di-O-acetyl-2-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)

\[ \text{H-NMR} \ (400 \text{ MHz, CDCl}_3) \delta = 5.35 \ (\text{dd}, \ ^3J_{3,2} = ^3J_{3,4} = 9.5 \text{ Hz, 1H, H-3}), 4.84 \ (\text{d}, \ ^3J_{1,2} = 3.5 \text{ Hz, 1H, H-1}), 4.53 \ (\text{dd}, \ ^3J_{\text{H6a,b}} = 2.0 \text{ Hz, } ^2J_{\text{H6a,b}} = 11.8 \text{ Hz, 1H, H-6a}), 4.30 \ (\text{dd}, \ ^3J_{\text{H6b,6a}} = 5.2 \text{ Hz, } ^2J_{\text{H6b,6a}} = 11.8 \text{ Hz, 1H, H-6b}), 4.10 \ (\text{d}, \ ^3J_{\text{H1-2'}} = 7.6 \text{ Hz, 1H, H-1'}), 3.92 – 3.84 \ (\text{m}, 1H, H-5'), 3.73 – 3.31 \ (\text{m}, 6H, H-4', H-6', H-5', H-2), 3.20 \ (\text{dd}, \ ^3J_{\text{H2',1'}} = 7.6 \text{ Hz, } ^3J_{\text{H2',3'}} = 9.7 \text{ Hz, 1H, H-2'}), 3.07 \ (\text{dd}, \ ^3J_{\text{H3',2'}} = 9.7 \text{ Hz, } ^3J_{\text{H3',4'}} = 3.2 \text{ Hz, 1H, H-3'}), 3.51, 3.50, 3.48, 3.41, 3.38 \ (\text{OCH}_3), 2.09, 2.07 \ (\text{CH}_3\text{-OAc}) \ \text{ppm.} \]

\[ \text{C-NMR} \ (101 \text{ MHz, CDCl}_3) \delta = 170.5, 169.8 \ (\text{C}=\text{O}, 103.4 \ (\text{C}=-\text{C'}), 97.2 \ (\text{C}-1), 84.3 \ (\text{C}=-\text{C'}), 80.5 \ (\text{C}-2'), 79.3 \ (\text{C}-2), 76.3 \ (\text{C}-4), 74.5 \ (\text{C}-4'), 73.1 \ (\text{C}-5'), 71.6 \ (\text{C}-3), 70.7 \ (\text{C}-6'), 68.6 \ (\text{C}-5), 62.4 \ (\text{C}-6), 61.0, 60.9, 59.0, 58.7, 58.2, 55.2 \ (\text{OCH}_3), 21.1, 20.8 \ (\text{CH}_3\text{-OAc}) \ \text{ppm.} \]

Methyl 3,4-di-O-acetyl-2-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)
**1H-NMR** (400 MHz, CDCl₃) δ = 5.36 (dd, J₃,₂ = J₃,₄ = 9.5 Hz, 1H, H-3), 4.87 (d, J₁,₂ = 3.5 Hz, 1H, H-1), 4.82 (dd, J₄,₃ = 9.5 Hz, J₄,₅ = 9.8 Hz, 1H, H-4), 4.24 (d, J₁',₂' = 7.5 Hz, 1H, H-1'), 4.00 – 3.93 (m, 1H, H-5), 3.88 (dd, J₄,a,₅ = 1.9 Hz, J₆,a,₆b = 10.9 Hz, 1H, H-6a), 3.73 – 3.31 (m, 6H, H-4', H-6', H-5', H-2), 3.58, 3.54, 3.51, 3.43, 3.43, 3.38 (OCH₃), 2.02, 1.99 (CH₃-OAc) ppm.

**13C-NMR** (101 MHz, CDCl₃) δ = 170.0, 170.0 (C=O), 103.9 (C-1'), 101.9 (C-1), 83.8 (C-3'), 80.6 (C-2'), 80.2 (C-3), 74.9 (C-4'), 72.9 (C-4), 70.8 (C-6'), 70.3 (C-5'), 67.3 (C-5), 61.1 (C-6), 59.1, 58.3, 55.2 (OCH₃), 20.8, 20.6 (CH₃-OAc) ppm.

**Methyl 4,6-di-O-acetyl-3-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (19),**

**Methyl 2,6-di-O-acetyl-3-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (20),**

**Methyl 2,4-di-O-acetyl-3-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (21)**

Prepared following procedure E. 40.5 mg (0.195 mmol) methyl 3-O-methyl-α-D-glucopyranoside (8), 75.7 mg (0.800, 4.0 eq.) NaH, 202 mg (0.793 mmol, 4.0 eq.) 2,3,4,6-tetra-O-methyl α-D-galactopyranosyl chloride (9); Yield (19 - 21): 39.7 mg (0.0778 mmol, 40%), white solid; Relative yield (19/20/21): 32:10:58; Rᵣ (ethyl acetate) = 0.30; ESI HRMS for C₂₂H₃₈O₁₃ [M+Na⁺]: found 533.2211, calcd. 533.2205. Disaccharide 21 was fully characterized by NMR-spectroscopy. Disaccharide 19 was characterized by 

**13C-NMR**-spectroscopy.

Methyl 4,6-di-O-acetyl-3-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (19)

![Diagram of 19](image)

**13C-NMR** (101 MHz, CDCl₃) δ = 170.7, 169.6 (C=O), 104.8 (C-1'), 99.6 (C-1), 84.1 (C-3'), 80.4 (C-2'), 80.2 (C-3), 78.7 (C-2), 74.9 (C-4'), 72.9 (C-4), 70.7 (C-6'), 70.3 (C-5'), 67.3 (C-5), 62.4 (C-6), 61.2, 60.7, 60.4, 59.1, 58.3, 55.3 (OCH₃), 20.8, 20.7 (CH₃-OAc) ppm.

Methyl 2,4-di-O-acetyl-3-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (21)
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 4.89 (d, $^3$J$_{1,2}$ = 3.8 Hz, 1H, H-1), 4.79 (dd, $^3$J$_{1,3}$ = 9.8 Hz, $^3$J$_{4,5}$ = 10.0 Hz, 1H, H-4), 4.77 (dd, $^3$J$_{4,3}$ = 3.8 Hz, $^3$J$_{2,3}$ = 10.0 Hz, 1H, H-2), 4.28 (d, $^3$J$_{1',2'}$ = 7.5 Hz, 1H, H-1'), 3.93 (dd, $^3$J$_{5,4}$ = 10.0 Hz, $^3$J$_{5,6a}$ = 1.5 Hz, $^3$J$_{5,6b}$ = 8.2 Hz, 1H, H-5), 3.87 (dd, $^3$J$_{6a,5}$ = 1.5 Hz, $^2$J$_{6a,6b}$ = 10.8 Hz, 1H, H-6a), 3.71 (dd, $^3$J$_{5,2}$ = 10.0 Hz, $^3$J$_{3,4}$ = 9.8 Hz, 1H, H-3), 3.67 – 3.64 (m, 1H, H-4'), 3.64 – 3.44 (m, 4H, H-6b, H-6', H-5'), 3.58, 3.56, 3.52, 3.45, 3.40, 3.39 (OCH$_3$), 2.14, 2.08 (CH$_3$-OAc) ppm.

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 170.1, 169.8 (C=O), 103.8 (C-1'), 96.5 (C-1), 83.6 (C-3'), 80.7 (C-2'), 78.5 (C-3), 74.6 (C-4'), 73.0 (C-2), 72.9 (C-4), 70.7 (C-5'), 70.5 (C-6'), 69.0 (C-5), 68.5 (C-6), 61.2, 60.7, 60.3, 59.2, 58.4, 55.1 (OCH$_3$), 21.0, 20.9 (CH$_3$-OAc) ppm.

Methyl 3-O-benzyl-2-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (24),
Methyl 3-O-benzyl-6-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

Prepared following procedure E. 100 mg (0.352 mmol) methyl 3-O-benzyl-α-D-glucopyranoside (22) was dissolved in 5 mL anhydrous N,N-dimethylformamide and treated with 42.0 mg (0.650 mmol, 3.0 eq.) NaH. The mixture was stirred for 1 h. Subsequently 500 mg (1.10 mmol, 3.1 eq.) 2,3,4-tri-O-benzyl-α-L-fucopyranosyl chloride (23), dissolved in 5 mL anhydrous N,N-dimethylformamide, was added and the mixture stirred for 20 h. The reaction was stopped with methanol and the solvents were removed under reduced pressure. The remaining syrup was purified using flash-column chromatography (eluent: petrol ether/ethyl acetate 2:1 → ethylacetate) to give 24 and 25 (119 mg, 0.170 mmol, 48%) white solid; Relative yield (24/25): 13:87.

Methyl 3-O-benzyl-2-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (24)

15.8 mg (0.0225 mmol, 6%), $[\alpha]_{D}^{23}$ = + 50.0° (c = 0.30, in CHCl$_3$); m.p. 150 °C; $R_f$ (ethyl acetate) = 0.50; ESI HRMS for C$_{41}$H$_{48}$O$_{10}$ [M+Na$^+$]: found 723.3133, calcd. 723.3140. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.40 – 7.12 (m, 20H, H$_{arom}$), 5.01 (d, $^2$J$_{A,A'}$ = 11.6 Hz, 1H, OCH$_3$-Ph-A), 4.98 (d, $^2$J$_{B,B'}$ = 11.8 Hz, 1H, OCH$_3$-Ph-B), 4.93 – 4.88 (m, 2H, OCH$_3$-Ph-A', C'), 4.90 (d, $^3$J$_{1,2}$ = 3.5 Hz, 1H, H-1), 4.77 (d, $^2$J$_{D,D'}$ = 11.8 Hz, 1H, H-2) ppm.
Hz, 1H, OCH$_3$Ph-D), 4.72 (d, $^2J_{D,D}$ = 11.8 Hz, 1H, OCH$_3$Ph-B), 4.59 (d, $J_{1,2'}$ = 7.8 Hz, 1H, H-1'), 4.49 (d, $^2J_{C,C}$ = 11.8 Hz, 1H, OCH$_3$Ph-C), 3.90 (dd, $^3J_{2,1'}$ = 7.8 Hz, $^3J_{2,3'}$ = 9.3 Hz, 1H, H-2'), 3.85 – 3.63 (m, 5H, H-3, H-6, H-2, H-5), 3.58 – 3.44 (m, 4H, H-4, H-3', H-4, H-5'), 3.43 (OCH$_3$), 1.17 (d, $^3J_{5,6'}$ = 6.3 Hz, 3H, H-6") ppm.

Methyl 3-O-benzyl-6-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

103 mg (0.147 mmol, 42%), $[a]_D^{23} = +37.6^\circ$ (c = 1.00, in CHCl$_3$); m.p. 146 °C; R$_f$ (ethyl acetate) = 0.56; ESI HRMS for C$_{41}$H$_{48}$O$_{10}$ [M+Na$^+$]: found 723.3133, calcd. 723.3140.

Methyl 2,3-di-O-methyl-4,6-di-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (26)

Trisaccharide isolated after base-promoted glycosylation of methyl 2,3-di-O-methyl-α-D-glucopyranoside (6). 4 – 24% yield as white solid; $[a]_D^{23} = +41.7^\circ$ (c = 0.23, in CHCl$_3$); R$_f$ (ethyl acetate) = 0.05; ESI HRMS for C$_{29}$H$_{54}$O$_{16}$ [M+Na$^+$]: found 681.3306, calcd. 681.3304.
$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 4.79 (d, $^3$$J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.35 (d, $^3$$J_{1',2'}$ = 7.6 Hz, 1H, H-1’), 4.29 (d, $^3$$J_{1'',2''}$ = 7.6 Hz, 1H, H-1’’), 4.27 – 4.22 (m, 1H, H-6a), 3.79 – 3.72 (m, 2H, H-5, H-6b), 3.67 – 3.56 (m, 10H, H-4$, H-4''$, H-3, H-4, H-6b$, H-6b''$, H-5$, H-5''$), 3.34 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’), 3.24 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’’), 3.19 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’), 3.13 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’’), 3.12 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’), 3.05 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’), 3.04 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’’), 3.03 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’), 3.02 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’’), 3.01 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’), 3.00 (dd, $^3$$J_{3',2'}$ = 8.8 Hz, $^3$$J_{3',4'}$ = 3.2 Hz, 1H, H-3’’), 3.34 (dd, $^3$$J_{2',1'}$ = 7.6 Hz, $^3$$J_{2',3'}$ = 9.8 Hz, 1H, H-2’), 3.05 – 3.01 (m, 2H, H-2, H-5), 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.52, 3.51, 3.40, 3.39, 3.38 (s, 3H, OCH$_3$) ppm.

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 103.9 (C-1’), 103.9 (C-1’’), 97.1 (C-1), 84.5 (C-3’), 83.8 (C-3’’), 81.8 (C-3), 81.5 (C-2), 81.1 (C-2’), 80.6 (C-2’’), 79.3 (C-4), 74.6 (C-4’), 74.5 (C-4’’), 72.8 (C-5’), 72.6 (C-5’’), 70.7 (C-6’), 70.4 (C-6’’), 69.6 (C-5), 68.1 (C-6), 61.2, 61.1, 61.1, 61.0, 60.9, 59.1, 59.1, 59.0, 58.1, 57.9, 55.1 (OC$_3$H$_9$) ppm.

Characterization data for donor 23 and intermediates 22, 28 – 45.

Methyl 3-$O$-benzyl-$\alpha$-d-glucopyranoside (22)$^{13}$

Prepared following procedure B. 2.00 g (5.37 mmol) 35, 50 mL MeOH, 4.0 mL H$_2$O, 1 mL 1 N HCl.
Yield: 1.40 g (4.92 mmol, 92%), white solid, $[\alpha]^D_{D}$ = + 102.5° (c = 0.2, CHCl$_3$), Lit.$^{13}$: $[\alpha]^D_{D}$ = + 90.3° (c = 0.66, CHCl$_3$), m.p.: 94 °C, Lit.$^{13}$: m.p.: 89 – 91 °C, $R_f$ (EE) = 0.23. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.41 – 7.29 (m, 5H, H arom.), 5.03 (d, 1H, OCH$_2$Ph-A), 4.76 (d, $^3$$J_{1,2}$ = 3.8 Hz, 1H, H-1), 4.73 (d, $^2$$J_{A,A'}$ = 11.5 Hz, 1H, OCH$_2$Ph-A’), 3.85 (dd, $^3$$J_{5,6a}$ = 3.6 Hz, $^2$$J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.78 (dd, $^3$$J_{5,6b}$ = 4.6 Hz, $^2$$J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.71 – 3.61 (m, 2H, H-2, H-5), 3.60 – 3.54 (m, 2H, H-3, H-4), 3.44 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 138.5 (C arom.), 128.7, 128.0, 128.0 (CH$_2$ arom.), 99.6 (C-1), 82.8 (C-3), 75.0 (OCH$_2$Ph-A), 72.9 (C-2), 70.9 (C-5), 70.3 (C-4), 62.6 (C-6), 55.4 (OCH$_3$) ppm.

2,3,4-tri-$O$-benzyl-$\alpha$-L-fucopyranosyl chloride (23)$^8$

Prepared as described in the literature.$^7$ 1.00 g (2.30 mmol) 2,3,4-tri-$O$-benzyl $\alpha$-L-fucopyranose, 53 µL (0.69 mmol) abs. DMF, 550 µL (6.44 mmol) oxalylchloride, 8 mL abs. DCM. Yield: 917 mg (2.02 mmol, 88%), colourless oil, $[\alpha]^D_{D}$ = - 180.0° (c = 0.2, CHCl$_3$), Lit.$^8$: $[\alpha]^D_{D}$ = - 169.0° (c = 1.0, CH$_2$Cl$_2$), $R_f$ (PE/EE
Methyl 4,6-O-benzylidene-α-D-glucopyranoside (28)\textsuperscript{9}

Prepared as described in the literature\textsuperscript{9}. 20.0 g (103 mmol) 27, 320 mL CH\textsubscript{3}CN, 28.0 mL (186 mmol) benzaldehyde dimethylacetal, 1.2 g (5.0 mmol) camphor-10-sulfonic acid. Yield: 23.1 g (82.0 mmol, 80%), white solid, [α\textsubscript{D}\textsuperscript{23}] = + 112.6° (c = 1.0, CHCl\textsubscript{3}), Lit.\textsuperscript{9}: [α\textsubscript{D}\textsuperscript{23}] = + 110° (c = 2.0, CHCl\textsubscript{3}), m.p.: 160 °C, Lit.\textsuperscript{9}: m.p.: 161 – 162 °C, R\textsubscript{f} (DCM/MeOH 9:1, v/v) = 0.45. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.53 – 7.47 (m, 2H, Harom.), 7.42-7.35 (m, 3H, H arom.), 5.54 (s, 1H, PhCHO\textsubscript{O}), 4.80 (d, J\textsubscript{1,2} = 4.0 Hz, 1H, H-1), 4.30 (dd, J\textsubscript{2,3} = 9.2 Hz, 2 J\textsubscript{6a,6b} = 9.7 Hz, 1H, H-6a), 3.94 (dd, 2 J\textsubscript{2,3} = 9.2 Hz, 2 J\textsubscript{3,4} = 9.3 Hz, 1H, H-3), 3.82 (ddd, 3 J\textsubscript{4,5} = 9.2 Hz, 3 J\textsubscript{5,6a} = 4.4 Hz, 3 J\textsubscript{5,6b} = 10.3 Hz, 1H, H-5), 3.75 (dd, 3 J\textsubscript{5,6b} = 10.3 Hz, 2 J\textsubscript{6a,6b} = 9.7 Hz, 1H, H-6b), 3.64 (dd, 3 J\textsubscript{1,2} = 4.0 Hz, 3 J\textsubscript{2,3} = 9.2 Hz, 1H, H-2), 3.50 (dd, 3 J\textsubscript{3,4} = 9.3 Hz, 3 J\textsubscript{4,5} = 9.2 Hz, 1H, H-4), 3.47 (OCH\textsubscript{3}) ppm, \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): δ = 137.1 (C arom.), 129.3, 128.3, 126.3 (C\textsubscript{H arom.}), 102.0 (PhCHO\textsubscript{O}), 99.7 (C-1), 80.8 (C-4), 72.9 (C-2), 71.9 (C-3), 68.9 (C-6), 62.4 (C-5), 55.6 (OCH\textsubscript{3}) ppm.

Methyl 6-O-triphenylmethyl-α-D-glucopyranoside (29)\textsuperscript{15}

Prepared following procedure D. 3.00 g (15.4 mmol) 27, 4.33 g (15.5 mmol) Chlorotriphenylmethane, 20 mg DMAP, 40 mL pyridine. Yield: 3.66 g (8.38 mmol, 54%), white solid, [α\textsubscript{D}\textsuperscript{23}] = + 53.6° (c = 0.56, CHCl\textsubscript{3}), m.p.: 134 °C, Lit.\textsuperscript{15}: m.p.: 151 – 152 °C, R\textsubscript{f} (EE) = 0.16, MALDI TOF MS for C\textsubscript{26}H\textsubscript{28}O\textsubscript{6} [M+Na\textsuperscript{+}]: found 459.0, calcld. 459.2. \textsuperscript{1}H-NMR (400 MHz, MeOD) δ = 4.71 (d, J\textsubscript{1,2} = 3.8 Hz, 1H, H-1), 3.75 (ddd, J\textsubscript{4,5} = 9.8 Hz, J\textsubscript{5,6a} = 1.7 Hz, J\textsubscript{5,6b} = 6.8 Hz, 1H, H-5), 3.59 (dd, J\textsubscript{2,3} = 9.3 Hz, J\textsubscript{3,4} = 9.0 Hz, 1H, H-3), 3.51 (OCH\textsubscript{3}), 3.45-3.36 (m, 2H, H-2, H-6a), 3.25 (dd, J\textsubscript{3,4} = 9.0 Hz, J\textsubscript{4,5} = 9.8 Hz, 1H, H-4),
3.22 (dd, $^3J_{5,6b} = 6.8$ Hz, $^2J_{6a,6b} = 9.8$ Hz, 1H, H-6b) ppm. $^{13}$C-NMR (101 MHz, MeOD) $\delta = 145.8$ (C$_{arom.}$), 130.1, 128.9, 128.2 (C$_{CH_{arom.}}$), 101.3 (C-1), 75.6 (C-3), 73.8 (C-2), 72.7 (C-5), 72.5 (C-4), 65.1 (C-6), 55.6 (OCH$_3$).

**Methyl 4,6-O-benzylidene-2,3-di-O-methyl-\(\alpha\)-d-glucopyranoside (30)**

![Image](image)

Prepared following procedure A. 6.0 g (21 mmol) 28, 3.8 g (96 mmol) NaH, 6.0 mL (96 mmol) MeI, 50 mL DMF. Yield: 6.29 g (20.3 mmol, 97%), white solid, $[\alpha]_{D}^{23} = + 95.1$° (c = 1.0, CHCl$_3$), Lit.11: $[\alpha]_{D}^{23} = + 97.9$° (c = 1.5, acetone), m.p.: 123 – 124 °C, Lit.11: m.p.: 121 – 122 °C, $R_f$ (PE/EE 1:1, v/v) = 0.30

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 7.53 – 7.49$ (m, 2H, H$_{arom.}$), 7.41-7.33 (m, 3H, H$_{arom.}$), 5.55 (s, 1H, PhCH$_{OO}$), 4.87 (d, $^3J_{1,2} = 3.7$ Hz, 1H, H-1), 4.30 (dd, $^3J_{5,6a} = 4.6$ Hz, $^2J_{6a,6b} = 9.9$ Hz, 1H, H-6a), 3.83 (ddd, $^3J_{4,5} = 9.4$ Hz, $^3J_{5,6a} = 4.6$ Hz, $^3J_{5,6b} = 10.2$ Hz, 1H, H-5), 3.74 (dd, $^3J_{5,6b} = 10.2$ Hz, $^2J_{6a,6b} = 9.9$ Hz 1H, H-6b), 3.70 (dd, $^3J_{2,3} = 9.2$ Hz, $^3J_{3,4} = 9.4$ Hz, 1H, H-3), 3.52 (dd, $^3J_{3,4} = 9.4$ Hz, $^3J_{4,5} = 9.4$ Hz, 1H, H-4), 3.31 (dd, $^3J_{1,2} = 3.7$ Hz, $^3J_{2,3} = 9.2$ Hz, 1H, H-2), 3.64, 3.56, 3.46 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta = 137.3$ (C$_{arom.}$), 128.9, 128.2, 126.1 (C$_{CH_{arom.}}$), 101.4 (PhCHO), 98.4 (C-1), 82.1 (C-4), 81.4 (C-2), 79.8 (C-3), 69.1 (C-6), 62.2 (C-5), 61.0, 59.3, 55.3 (OCH$_3$) ppm.

**Methyl 4,6-O-benzylidene-2-O-methyl-\(\alpha\)-d-glucopyranoside (31) and Methyl 4,6-O-benzylidene-3-O-methyl-\(\alpha\)-d-glucopyranoside (32).**

Prepared following procedure A with substoichiometric amounts of base and methylating agent, 9.40 g (33.3 mmol) 28, 1.24 g NaH (31.0 mmol, 0.9 eq), 2.80 mL (45.0 mmol) MeI, 100 mL DMF.

Methyl 4,6-O-benzylidene-2-O-methyl-\(\alpha\)-d-glucopyranoside (31).

Yield: 1.51 g (5.10 mmol, 16 %), white solid, $[\alpha]_{D}^{20} = + 100.2$° (c = 0.5, CHCl$_3$), m.p.: 165 – 166 °C, $R_f$ (PE/EE 1:1, v/v) = 0.14, ESI HRMS for C$_{15}$H$_{20}$O$_6$ [M+Na$^+$]: found 319.1147, calcd. 319.1152. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta = 7.53 – 7.46$ (m, 2H, H$_{arom.}$), 7.40 – 7.32 (m, 3H, H$_{arom.}$), 5.54 (s, 1H, PhCHO), 4.92 (d, $^3J_{1,2} = 3.5$ Hz, 1H, H-1), 4.29 (dd, $^3J_{5,6a} = 4.6$ Hz, $^2J_{6a,6b} = 9.9$ Hz, 1H, H-6a), 4.10 (dd, $^3J_{2,3} = 9.4$ Hz, $^3J_{3,4} = 9.2$ Hz, 1H, H-3), 3.83 (ddd, $^3J_{4,5} = 9.4$ Hz, $^3J_{5,6a} = 4.6$ Hz, $^3J_{5,6b} = 10.4$ Hz, 1H, H-5), 3.74 (dd, $^3J_{5,6b} = 10.4$ Hz, $^2J_{6a,6b} = 9.9$ Hz, 1H, H-6b), 3.52 (dd, $^3J_{3,4} = 9.2$ Hz, $^3J_{4,5} = 9.4$ Hz, 1H, H-4), 3.54, 3.46
(OCH$_3$)$_3$, 3.31 (dd, $^3$J$_{1,2}$ = 3.5 Hz, $^3$J$_{2,3}$ = 9.4 Hz, 1H, H-2) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 137.2 (C$_{arom}$), 129.4, 128.5, 126.5 (CH$_{arom}$), 102.2 (PhCHO), 97.9 (C-1), 81.8 (C-2), 81.4 (C-4), 70.4 (C-3), 69.1 (C-6), 62.2 (C-5), 58.9, 55.5 (OCH$_3$) ppm.

Methyl 4,6-O-benzylidene-3-O-methyl-\(\alpha\)-D-glucopyranoside (32).

Yield: 2.08 g (7.02 mmol, 23 %), white solid, $\left[\alpha\right]_{D}^{20} = + 123.0 ^\circ$ (c = 1.0, CHCl$_3$), m.p.: 143 – 145 °C, $R_f$ (PE/EE 1:1, v/v) = 0.18, ESI HRMS for C$_{13}$H$_{20}$O$_6$ [M+Na$^+$]: found 319.1153, calcd. 319.1152. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.52 – 7.45 (m, 2H, H$_{arom}$), 7.41 – 7.33 (m, 3H, H$_{arom}$), 5.55 (s, 1H, PhCHO), 4.93 (d, $^2$J$_{A,A'}$ = 11.3 Hz, 1H, OCH$_2$Ph-A), 4.87 (d, $^2$J$_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B), 4.85 (d, $^2$J$_{A,A'}$ = 11.3 Hz, 1H, OCH$_2$Ph-A’), 4.71 (d, $^2$J$_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B’), 4.61 (d, $^3$J$_{1,2}$ = 3.8 Hz, 1H, H-1), 4.28 (dd, $^3$J$_{5,6a}$ = 4.7 Hz, 2$^2$J$_{6a,6b}$ = 10.1 Hz, 1H, H-6a), 4.06 (dd, $^3$J$_{2,3}$ = 9.4 Hz, $^3$J$_{3,4}$ = 9.4 Hz, 1H, H-3), 3.72 (dd, $^3$J$_{5,6b}$ = 10.1 Hz, $^2$J$_{6a,6b}$ = 10.1 Hz, 1H, H-6b), 3.62 (dd, $^3$J$_{3,4}$ = 9.4 Hz, $^3$J$_{4,5}$ = 9.4 Hz, 1H, H-4), 3.57 (dd, $^3$J$_{1,2}$ = 3.8 Hz, $^3$J$_{2,3}$ = 9.4 Hz, 1H, H-2), 3.42 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 138.8, 138.2, 137.4 (C$_{arom}$), 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.0 (CH$_{arom}$), 101.3 (PhCHO), 99.3 (C-1), 82.2 (C-4), 79.2 (C-2), 78.6 (C-3), 75.3 (OCH$_2$Ph-A), 73.8 (OCH$_2$Ph-B), 69.1 (C-6), 62.3 (C-5), 55.3 (OCH$_3$) ppm.

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-\(\alpha\)-D-glucopyranoside (33)

Prepared following procedure A. 8.0 g (28 mmol) 28, 3.2 g (80 mmol) NaH, 9.4 mL (80 mmol) BnBr, 80 mL DMF. Yield: 11.4 g (24.7 mmol, 87%), white solid, $\left[\alpha\right]_{D}^{23} = - 31.5^\circ$ (c = 1.0, CHCl$_3$), Lit.$^{10}$: $\left[\alpha\right]_{D}^{23} = -32^\circ$ (CHCl$_3$), m.p. = 98 – 99 °C, $R_f$ (PE/EE 3:1, v/v) = 0.39. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.52 – 7.48 (m, 2H, H$_{arom}$), 7.43-7.26 (m, 13H, H$_{arom}$), 5.56 (s, 1H, PhCHO), 4.93 (d, $^2$J$_{A,A'}$ = 11.3 Hz, 1H, OCH$_2$Ph-A), 4.87 (d, $^2$J$_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B), 4.85 (d, $^2$J$_{A,A'}$ = 11.3 Hz, 1H, OCH$_2$Ph-A’), 4.71 (d, $^2$J$_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B’), 4.61 (d, $^3$J$_{1,2}$ = 3.8 Hz, 1H, H-1), 4.28 (dd, $^3$J$_{5,6a}$ = 4.7 Hz, $^2$J$_{6a,6b}$ = 10.1 Hz, 1H, H-6a), 4.06 (dd, $^3$J$_{2,3}$ = 9.4 Hz, $^3$J$_{3,4}$ = 9.4 Hz, 1H, H-3), 3.84 (ddd, $^3$J$_{4,5}$ = 9.4 Hz, $^3$J$_{5,6a}$ = 4.7 Hz, $^3$J$_{5,6b}$ = 10.1 Hz, 1H, H-5), 3.72 (dd, $^3$J$_{5,6b}$ = 10.1 Hz, $^2$J$_{6a,6b}$ = 10.1 Hz, 1H, H-6b), 3.62 (dd, $^3$J$_{3,4}$ = 9.4 Hz, $^3$J$_{4,5}$ = 9.4 Hz, 1H, H-4), 3.57 (dd, $^3$J$_{1,2}$ = 3.8 Hz, $^3$J$_{2,3}$ = 9.4 Hz, 1H, H-2), 3.42 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 138.8, 138.2, 137.4 (C$_{arom}$), 128.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 126.0 (CH$_{arom}$), 101.3 (PhCHO), 99.3 (C-1), 82.2 (C-4), 79.2 (C-2), 78.6 (C-3), 75.3 (OCH$_2$Ph-A), 73.8 (OCH$_2$Ph-B), 69.1 (C-6), 62.3 (C-5), 55.3 (OCH$_3$) ppm.
Methyl 2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (34)\textsuperscript{10} and Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (35)\textsuperscript{10}

Prepared as described in the literature\textsuperscript{10}. 5.00 g (17.7 mmol) 28, 1.20 g (3.50 mmol) tetrabutylammonium hydrogensulfate, 300 mL DCM, 3.6 mL (30.3 mmol) benzyl bromide, 25 mL aq. NaOH solution (5%).

Methyl 2-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (34)\textsuperscript{10}

Yield: 3.69 g (9.91 mmol, 56 %), white solid, $[\alpha]_D^{23} = + 33.8 \, ^\circ$ (c = 0.5, CHCl$_3$), Lit.\textsuperscript{10}: $[\alpha]_D^{23} = + 35 \, ^\circ$ (CHCl$_3$), m.p. = 129 – 130 °C, Lit.: m.p. = 131 – 132 °C, $R_f$ (PE/EE 2:1, v/v) = 0.27. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.52 – 7.46 (m, 2H, Harom.), 7.39 – 7.29 (m, 8H, Harom.), 5.52 (s, 1H, PhCHOO), 4.79 (d, $^2$J$_{A,A'}$ = 12.2 Hz, 1H, OCH$_2$Ph-A), 4.71 (d, $^2$J$_{A,A'}$ = 12.2 Hz, 1H, OCH$_3$Ph-A'), 4.62 (d, $^3$J$_{1,2}$ = 3.6 Hz, 1H, H-1), 4.26 (dd, $^2$J$_{5,6a}$ = 4.8 Hz, $^2$J$_{6a,6b}$ = 10.0 Hz, 1H, H-6a), 4.16 (dd, $^2$J$_{2,3}$ = 9.2 Hz, $^2$J$_{3,4}$ = 9.4 Hz, 1H, H-3), 3.82 (ddd, $^3$J$_{4,5}$ = 9.7 Hz, $^2$J$_{5,6a}$ = 4.8 Hz, $^3$J$_{5,6b}$ = 10.1 Hz, 1H, H-5), 3.70 (dd, $^3$J$_{5,6b}$ = 10.1 Hz, $^3$J$_{6a,6b}$ = 10.0 Hz, 1H, H-6b), 3.50 (dd, $^3$J$_{3,4}$ = 9.4 Hz, $^3$J$_{4,5}$ = 9.7 Hz, 1H, H-4), 3.47 (dd, $^3$J$_{1,2}$ = 3.6 Hz, $^3$J$_{2,3}$ = 9.2 Hz, 1H, H-2), 3.38 (OCH$_3$) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ = 137.9, 137.1 (C arom.), 129.2, 128.6, 128.4, 128.2, 127.9, 127.7, 127.6, 126.3 (CH$_2$Ph), 73.4 (OCH$_3$Ph), 70.3 (C-3), 69.0 (C-6), 62.0 (C-5), 55.4 (OCH$_3$) ppm.

Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-glucopyranoside (35)\textsuperscript{10}

Yield: 1.58 g (4.25 mmol, 24 %), white solid, $[\alpha]_D^{23} = + 82.6 \, ^\circ$ (c = 0.5, CHCl$_3$), Lit.\textsuperscript{10}: $[\alpha]_D^{23} = + 78 \, ^\circ$ (CHCl$_3$), m.p. = 184 °C, Lit.: m.p. = 187 – 188 °C, $R_f$ (PE/EE 2:1, v/v) = 0.16. $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.52 – 7.47 (m, 2H, Harom.), 7.42 – 7.26 (m, 8H, Harom.), 5.57 (s, 1H, PhCHOO), 4.96 (d, $^2$J$_{A,A'}$ = 11.7 Hz, 1H, OCH$_2$Ph-A), 4.81 (d, $^3$J$_{1,2}$ = 4.1 Hz, 1H, H-1), 4.80 (d, $^2$J$_{A,A'}$ = 11.7 Hz, 1H, OCH$_2$Ph-A'), 4.30 (dd, $^3$J$_{5,6a}$ = 4.4 Hz, $^2$J$_{6a,6b}$ = 9.9 Hz, 1H, H-6a), 3.84 (ddd, $^3$J$_{4,5}$ = 9.2 Hz, $^3$J$_{5,6a}$ = 4.4 Hz, $^3$J$_{5,6b}$ = 10.2 Hz, 1H, H-5), 3.83 (dd, $^3$J$_{2,3}$ = 9.1 Hz, $^3$J$_{3,4}$ = 9.1 Hz, 1H, H-3), 3.76 (dd, $^3$J$_{5,6b}$ = 10.2, $^2$J$_{6a,6b}$ = 9.9 Hz, 1H, H-6b), 3.77 – 3.70 (m, 1H, H-2), 3.65 (dd, $^3$J$_{3,4}$ = 9.1 Hz, $^3$J$_{4,5}$ = 9.2 Hz, 1H, H-4), 3.45 (OCH$_3$) ppm.

$^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$ = 138.6, 137.5 (C arom.), 129.1, 128.6, 128.4, 128.2, 127.9, 126.2 (CH$_2$Ph),
Methyl 2,3,4-tri-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (36)$^{16}$

Prepared following procedure A. 3.54 g (8.11 mmol) 29, 1.85 g (46.3 mmol) NaH, 2.9 mL (80 mmol) MeI, 80 mL DMF. Yield: 3.74 g (7.82 mmol, 97%), white solid, $\alpha^{23}_{D} = + 90.4^\circ$ (c = 0.88, CHCl$_3$), Lit.$^{16}$: $\alpha^{23}_{D} = + 88.9^\circ$ (Aceton), m.p. = 105 – 112 °C, $R_f$ (PE/EE 3:1, v/v) = 0.16, MALDI TOF MS for C$_{29}$H$_{34}$O$_{6}$ [M+Na$^+$]: found 501.0, calcd. 501.2.

$^1$H-NMR (400 MHz, MeOD) $\delta$ = 7.51 – 7.45 (m, 6H, H$_{\text{arom}}$), 7.33 – 7.26 (m, 6H, H$_{\text{arom}}$), 7.26 – 7.20 (m, 3H, H$_{\text{arom}}$), 4.95 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.60 – 3.55 (m, 1H, H-5), 3.41 – 3.34 (m, 2H, H-3, H-6a), 3.30 – 3.22 (m, 2H, H-2, H-4), 3.11 (dd, $^3J_{5,6b}$ = 4.8 Hz, $^2J_{6a,6b}$ = 10.0 Hz, 1H, H-6b), 3.56, 3.50, 3.44, 3.26 (OCH$_3$) ppm.

$^{13}$C-NMR (101 MHz, MeOD) $\delta$ = 145.6 (C$_{\text{arom}}$), 130.7, 128.9, 128.3 (C$_{\text{arom}}$), 98.7 (C-1), 85.0 (C-3), 83.2 (C-2), 81.4 (C-4), 71.6 (C-5), 63.9 (C-6), 61.2, 60.9, 59.0, 55.5 (OCH$_3$).

Methyl 2,3-di-O-benzyl-α-D-glucopyranoside (37)$^{14}$

Prepared following procedure B. 2.07 g (4.48 mmol) 33, 50 mL MeOH, 5.0 mL H$_2$O, 1 mL 1 N HCl. Yield: 1.62 g (4.32 mmol, 96%), white solid, $\alpha^{23}_{D} = + 14.9^\circ$ (c = 1.01, CHCl$_3$), Lit.$^{14}$: $\alpha^{23}_{D} = + 18.8^\circ$ (c = 1.0, CHCl$_3$), m.p. = 72 – 75 °C, Lit.$^{14}$. m.p. = 75 – 76 °C, $R_f$ (PE/EE 2:1, v/v) = 0.05, MALDI TOF MS for C$_{21}$H$_{26}$O$_{6}$ [M+Na$^+$]: found 397.6, calcd. 397.2.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.41 – 7.28 (m, 10H, H$_{\text{arom}}$), 5.04 (d, $^2J_{A,A'}$ = 11.6 Hz, 1H, OCH$_2$Ph-A), 4.78 (d, $^2J_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B), 4.71 (d, $^2J_{A,A'}$ = 11.6 Hz, 1H, OCH$_2$Ph-A$'$), 4.67 (d, $^2J_{B,B'}$ = 12.1 Hz, 1H, OCH$_2$Ph-B$'$), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.81 (dd, $^3J_{5,6a}$ = 3.8 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6a), 3.80 (dd, $^3J_{3,4}$ = 9.4 Hz, $^3J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.75 (dd, $^3J_{5,6b}$ = 4.6 Hz, $^2J_{6a,6b}$ = 11.7 Hz, 1H, H-6b), 3.63 (ddd, $^3J_{4,5}$ = 9.7 Hz, $^3J_{5,6a}$ = 3.8 Hz, $^3J_{5,6b}$ = 4.6 Hz, 1H, H-5), 3.52 (dd, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 9.7 Hz, 1H, H-4), 3.51 (dd, $^3J_{1,2}$ = 3.6 Hz, $^3J_{2,3}$ = 9.4 Hz, 1H, H-2), 3.39 (s, 3H, OCH$_3$) ppm.

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 138.7, 137.9 (C$_{\text{arom}}$), 128.6, 128.5, 128.1, 128.0, 128.0, 127.9 (C$_{\text{arom}}$), 98.2 (C-1), 81.3 (C-3), 79.8 (C-2), 75.4 (OCH$_2$Ph-A), 73.1 (OCH$_2$Ph-B), 70.6 (C-5), 70.4 (C-4), 62.4 (C-6), 55.2 (OCH$_3$) ppm.
Methyl 2-\textit{O}-benzyl-\textit{\alpha}-\textit{D}-glucopyranoside (38): Prepared following procedure B. 1.49 g (4.03 mmol) 34, 50 mL MeOH, 4.0 mL H₂O, 1 mL 1 N HCl. Yield: 1.09 g (3.83 mmol, 95%), white solid, \([\alpha]_{D}^{23} = + 85.2^\circ \) \((c = 1.0, \text{CHCl}_3)\), Lit.: \([\alpha]_{D}^{23} = + 86.8^\circ \) \((c = 1.1, \text{CHCl}_3)\), m.p. = 120 °C, Lit.: m.p. = 120 °C, \(R_f\) (EE) = 0.17. \(^1\text{H}-\text{NMR} \) (400 MHz, CDCl₃) \(\delta = 7.38 – 7.29\) (m, 5H, H arom.), 4.70 (d, \(\text{J}_{A,A'} = 12.2\) Hz, 1H, OCH₂Ph-A), 4.66 (d, \(\text{J}_{A,A'} = 12.2\) Hz, 1H, OCH₂Ph-A'), 4.61 (d, \(\text{J}_{1,2} = 3.6\) Hz, 1H, H-1), 3.91 (dd, \(\text{J}_{2,3} = 9.7\) Hz, \(\text{J}_{3,4} = 8.8\) Hz, 1H, H-3), 3.84 (dd, \(\text{J}_{5,6a} = 3.6\) Hz, \(\text{J}_{6a,6b} = 11.7\) Hz, 1H, H-6a), 3.79 (dd, \(\text{J}_{5,6b} = 4.1\) Hz, \(\text{J}_{6a,6b} = 11.7\) Hz, 1H, H-6b), 3.62 (ddd, \(\text{J}_{4,5} = 9.7\) Hz, \(\text{J}_{5,6a} = 3.6\) Hz, \(\text{J}_{5,6b} = 4.1\) Hz, 1H, H-5), 3.55 (ddd, \(\text{J}_{3,4} = 8.8\) Hz, \(\text{J}_{4,5} = 9.7\) Hz, 1H, H-4), 3.35 (OCH₃), 3.34 (dd, \(\text{J}_{1,2} = 3.6\) Hz, \(\text{J}_{2,3} = 9.7\) Hz, 1H, H-2) ppm. \(^{13}\text{C}-\text{NMR} \) (101 MHz, CDCl₃) \(\delta = 137.8\) (C arom.), 128.6, 128.2, 128.1 (C₃H₉a), 97.7 (C-1), 79.3 (C-2), 73.0 (OCH₂Ph-A), 72.9 (C-3), 70.6 (C-4), 70.6 (C-5), 62.3 (C-6), 55.3 (OCH₃) ppm.

Methyl 2,3-di-\textit{O}-methyl-6-\textit{O}-triphenylmethyl-\textit{\alpha}-\textit{D}-glucopyranoside (39): Prepared following procedure D. 2.08 g (9.36 mmol) 6, 2.65 g (9.51 mmol) Chlorotriphenylmethane, 20 mg DMAP, 25 mL pyridine. Yield: 3.52 g (7.58 mmol, 81%), white solid, \([\alpha]_{D}^{23} = + 66.2^\circ \) \((c = 1.0, \text{CHCl}_3)\), Lit.: \([\alpha]_{D}^{23} = + 66.4^\circ \) \((\text{CHCl}_3)\), m.p.: 174 °C, Lit.: m.p. = 169 – 170 °C, \(R_f\) (PE/EE 2:1, v/v) = 0.14, MALDI TOF MS for C₂₈H₃₂O₆ [M+Na⁺]: found 487.1, calcd. 487.2. \(^1\text{H}-\text{NMR} \) (400 MHz, CDCl₃) \(\delta = 7.49 – 7.44\) (m, 6H, Harom.), 7.34 – 7.21 (m, 9H, Harom.), 4.87 (d, \(\text{J}_{1,2} = 3.6\) Hz, 1H, H-1), 3.70 (ddd, \(\text{J}_{4,5} = 9.4\) Hz, \(\text{J}_{5,6a} = 4.1\) Hz, \(\text{J}_{5,6b} = 5.1\) Hz, 1H, H-5), 3.52 (ddd, \(\text{J}_{5,6a} = 8.9\) Hz, \(\text{J}_{4,5} = 9.4\) Hz, \(\text{J}_{4,0} = 2.3\) Hz, 1H, H-4), 3.44 (dd, \(\text{J}_{2,3} = 9.4\) Hz, \(\text{J}_{3,4} = 8.9\) Hz, 1H, H-3), 3.39 (dd, \(\text{J}_{5,6a} = 4.1\) Hz, \(\text{J}_{5,6b} = 4.1\) Hz, \(\text{J}_{6a,6b} = 9.9\) Hz, 1H, H-6a), 3.35 (dd, \(\text{J}_{5,6b} = 5.1\) Hz, \(\text{J}_{6a,6b} = 9.9\) Hz, 1H, H-6b), 3.25 (dd, \(\text{J}_{1,2} = 3.6\) Hz, \(\text{J}_{2,3} = 9.4\) Hz, 1H, H-2), 3.63, 3.51, 3.45 (OCH₃), 2.52 (d, \(\text{J}_{4,0} = 2.3\) Hz, 1H, OH) ppm. \(^{13}\text{C}-\text{NMR} \) (101 MHz, CDCl₃) \(\delta = 143.8\) (C arom.), 128.7, 127.9, 127.1 (C₃H₉a), 97.3 (C-1), 87.0 (Ph₃CO), 82.8 (C-3), 81.7 (C-2), 71.9 (C-4), 69.8 (C-5), 64.1 (C-6), 61.2, 58.6, 55.1 (OCH₃) ppm.

Methyl 2,3-di-\textit{O}-benzyl-4,6-di-\textit{O}-methyl-\textit{\alpha}-\textit{D}-glucopyranoside (40):
Prepared following procedure A. 1.35 g (3.61 mmol) NaH, 0.9 mL (14.5 mmol) MeI, 40 mL DMF. Yield: 1.36 g (3.37 mmol, 93%), colourless syrup, $\left[\alpha\right]_D^{23} = + 30.6^\circ$ (c = 0.5, CHCl$_3$), Lit.$^{16}$: $\left[\alpha\right]_D^{23} = + 32.9^\circ$ (CHCl$_3$), $R_f$ (PE/EE 2:1, v/v) = 0.35, MALDI TOF MS for C$_{23}$H$_{30}$O$_6$ [M+Na$^+$]: found 426.2, calcd. 425.2.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.42 – 7.25 (m, 10H, H arom.), 4.94 (d, $^2J_{A,A'} = 11.1$ Hz, 1H, OCH$_2$Ph-A), 4.82 (d, $^2J_{A,A'} = 11.1$ Hz, 1H, OCH$_2$Ph-A$'$), 4.79 (d, $^2J_{B,B'} = 12.4$ Hz, 1H, OCH$_2$Ph-B), 4.64 (d, $^2J_{B,B'} = 12.4$ Hz, 1H, OCH$_2$Ph-B$'$), 4.58 (d, $^3J_{1,2} = 3.6$ Hz, 1H, H-1), 4.36 (dd, $^3J_{2,3} = 9.7$ Hz, $^3J_{3,4} = 9.4$ Hz, 1H, H-2), 3.64 – 3.55 (m, 3H, H-5, H-6), 3.50 (dd, $^3J_{1,2} = 3.6$ Hz, $^3J_{2,3} = 9.7$ Hz, 1H, H-2), 3.28 (dd, $^3J_{3,4} = 9.4$ Hz, $^3J_{4,5} = 9.4$ Hz, 1H, H-4), 3.54, 3.40, 3.38 (OCH$_3$) ppm.

$^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 139.0, 138.2 (C arom.), 128.4, 128.3, 128.1, 127.9, 127.8, 127.5 (CH$_{arom}$), 98.3 (C-1), 81.9 (C-3), 79.6 (C-2), 79.5 (C-4), 75.6 (OCH$_2$Ph-A), 73.4 (OCH$_2$Ph-B), 71.1 (C-6), 69.9 (C-5), 60.6, 59.2, 55.2 (OCH$_3$) ppm.

**Methyl 2-O-benzyl-3,4,6-tri-O-methyl-α-D-glucopyranoside (41)**

Prepared following procedure A. 1.06 g (3.73 mmol) NaH, 1.4 mL (22 mmol) MeI, 40 mL DMF. Yield: 1.12 g (3.44 mmol, 92%), colourless syrup, $\left[\alpha\right]_D^{23} = + 129.0^\circ$ (c = 0.84, CHCl$_3$), $R_f$ (PE/EE 2:1, v/v) = 0.27, ESI HRMS for C$_{17}$H$_{26}$O$_6$ [M+Na$^+$]: found 349.1596, calcd. 349.1622.

$^1$H-NMR (400 MHz, CDCl$_3$) $\delta$ = 7.39 – 7.25 (m, 5H, H arom.), 4.79 (d, $^2J_{A,A'} = 12.2$ Hz, 1H, OCH$_2$Ph-A), 4.63 (d, $^2J_{A,A'} = 12.2$ Hz, 1H, OCH$_2$Ph-A$'$), 4.55 (d, $^3J_{1,2} = 3.6$ Hz, 1H, H-1), 3.60 – 3.52 (m, 4H, H-3, H-5, H-6), 3.39 (dd, $^3J_{1,2} = 3.6$ Hz, $^3J_{2,3} = 9.7$ Hz, 1H, H-2), 3.18 (dd, $^3J_{3,4} = 9.0$ Hz, $^3J_{4,5} = 8.8$ Hz, 1H, H-4), 3.67, 3.54, 3.40, 3.36 (OCH$_3$) ppm. $^{13}$C-NMR (101 MHz, CDCl$_3$) $\delta$ = 138.3 (C$_{arom}$), 128.4, 128.2, 127.8 (CH$_{arom}$), 98.3 (C-1), 83.6 (C-3), 79.4 (C-2), 79.4 (C-2), 73.3 (OCH$_2$Ph-A), 71.1 (C-6), 69.8 (C-5), 61.0, 60.4, 59.2, 55.2 (OCH$_3$) ppm.

**Methyl 3-O-benzyl-2,4,6-tri-O-methyl-α-D-glucopyranoside (42)**

![Methyl 3-O-benzyl-2,4,6-tri-O-methyl-α-D-glucopyranoside (42)](image_url)
Prepared following procedure A. 1.32 g (4.64 mmol) 22, 1.16 mg (29.0 mmol) NaH, 1.70 mL (27.4 mmol) MeI, 50 mL DMF. Yield: 1.47 g (4.50 mmol, 97%), colourless syrup, \([\alpha]_D^{23} = + 102.0^\circ (c = 0.2, \text{CHCl}_3)\), Lit.\(^{12}\): \([\alpha] = + 133.0^\circ (c = 0.47, \text{CHCl}_3)\), \(R_t\) (PE/EE 1:1, v/v) = 0.37. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.43 – 7.26 (m, 5H, \text{Harom.}), 4.89 (d, ^2J_{A,A’} = 11.0 \text{ Hz}, 1H, \text{OCH}_2\text{Ph-A}), 4.86 (d, ^3J_{1,2} = 3.6 \text{ Hz}, 1H, H-1), 4.79 (d, ^2J_{A,A’} = 11.0 \text{ Hz}, 1H, \text{OCH}_2\text{Ph-A’}), 3.80 (dd, ^3J_{1,2} = 3.6 \text{ Hz}, ^3J_{2,3} = 9.7 \text{ Hz}, 1H, H-2), 3.29 (dd, ^3J_{3,4} = 9.3 \text{ Hz}, ^3J_{4,5} = 9.3 \text{ Hz}, \text{OCH}_3)\) ppm.

13C-NMR (101 MHz, CDCl\(_3\)) \(\delta = 139.0 (\text{Carom.}), 128.3, 127.9, 127.4 (\text{CHarom.}), 97.6 (C-1), 82.0 (C-2), 81.9 (C-3), 79.3 (C-4), 75.4 (\text{OCH}_2\text{Ph-A}), 71.1 (C-6), 70.0 (C-5), 60.7, 59.2, 59.2, 55.2 (\text{OCH}_3)\) ppm.

**Methyl 4-O-benzyl-2,3-di-O-methyl-6-O-triphenylmethyl-\(\alpha\)-\(\text{D}\)-glucopyranoside (43).**

Prepared following procedure A. 3.46 g (7.45 mmol) 6, 653 mg (15.2 mmol) NaH, 2.0 mL (17 mmol) BnBr, 40 mL DMF. Yield: 3.84 g (6.93 mmol, 93%), white solid, \([\alpha]_D^{23} = + 117.6^\circ (c = 0.5, \text{CHCl}_3)\), m.p.: 57 °C, \(R_t\) (PE/EE 5:1, v/v) = 0.13, ESI HRMS for C\(_{35}\)H\(_{38}\)O\(_6\) [M+Na+] found 577.2553, calcd. 577.2561. \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.52 – 7.47 (m, 6H, \text{Harom.}), 7.32 – 7.18 (m, 12H, \text{Harom.}), 6.97 – 6.92 (m, 2H, H-2, H-5, H-6), 4.95 (d, ^3J_{1,2} = 3.6 \text{ Hz}, 1H, H-1), 4.67 (d, ^2J_{A,A’} = 10.4 \text{ Hz}, 1H, \text{OCH}_2\text{Ph-A}), 4.30 (d, ^2J_{A,A’} = 10.4 \text{ Hz}, 1H, \text{OCH}_2\text{Ph-A’}), 3.77 (ddd, ^3J_{4,5} = 9.4 \text{ Hz}, ^3J_{5,6a} = 1.8 \text{ Hz}, ^3J_{5,6b} = 4.8 \text{ Hz}, 1H, H-5), 3.60 (dd, ^3J_{2,3} = 9.2 \text{ Hz}, ^3J_{3,4} = 8.9 \text{ Hz}, 1H, H-3), 3.56 (dd, ^3J_{3,4} = 8.9 \text{ Hz}, ^3J_{4,5} = 9.4 \text{ Hz}, 1H, H-4), 3.50 (dd, ^3J_{5,6a} = 1.8 \text{ Hz}, ^2J_{6a,6b} = 10.2 \text{ Hz}, 1H, H-6a), 3.34 (dd, ^3J_{1,2} = 3.6 \text{ Hz}, ^3J_{2,3} = 9.2 \text{ Hz}, 1H, H-2), 3.20 (dd, ^3J_{5,6b} = 4.8 \text{ Hz}, ^2J_{6a,6b} = 10.2 \text{ Hz}, 1H, H-6b), 3.65, 3.59, 3.47 (\text{OCH}_3)\) ppm. 13C-NMR (101 MHz, CDCl\(_3\)) \(\delta = 144.0, 138.1 (\text{Carom.}), 128.8, 128.2, 128.1, 127.9, 127.8, 127.6, 126.9 (\text{CHarom.}), 97.3 (C-1), 86.3 (\text{Ph}_3\text{CO}), 83.9 (C-3), 82.2 (C-2), 78.2 (C-4), 74.9 (\text{OCH}_2\text{Ph-A}), 70.2 (C-5), 62.6 (C-6), 61.1, 59.0, 54.9 (\text{OCH}_3)\) ppm.

**Methyl 4-O-benzyl-2,3-di-O-methyl-\(\alpha\)-\(\text{D}\)-glucopyranoside (44).**

2.86 g (5.17 mmol) 43 was stirred in 15 mL trifluoroacetic acid (90%) for 5 min. The mixture was diluted with DCM, neutralized by washing with sat. NaHCO\(_3\), dried and concentrated in vacuo. The residue was purified by flash column chromatography (gradient petrol ether/ethyl acetate). Yield: 1.27 g (4.08 mmol, 79%), white solid, \([\alpha]_D^{23} = + 151.8^\circ (c = 0.5, \text{CHCl}_3)\), m.p.: 98 °C, \(R_t\) (PE/EE 1:1, v/v) = 0.12, ESI HRMS
for C\textsubscript{16}H\textsubscript{24}O\textsubscript{6} [M+Na\textsuperscript{+}]: found 335.1465, calcd. 335.1458. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.40 - 7.28\) (m, 5H, H\textsubscript{arom.}), 4.89 (d, \(^2J\text{A,A'} = 11.1\) Hz, 1H, OCH\textsubscript{2}Ph-A), 4.83 (d, \(^3J\text{1,2} = 3.6\) Hz, 1H, H-1), 4.66 (d, \(^2J\text{A,A'} = 11.1\) Hz, 1H, OCH\textsubscript{2}Ph-A'), 3.80 (dd, \(^3J\text{5,6a} = 2.8\) Hz, \(^2J\text{6a,6b} = 11.8\) Hz, 1H, H-6a), 3.71 (dd, \(^3J\text{5,6b} = 4.1\) Hz, \(^2J\text{6a,6b} = 11.8\) Hz, 1H, H-6b), 3.64 (dd, \(^3J\text{2,3} = 9.4\) Hz, \(^3J\text{3,4} = 9.1\) Hz, 1H, H-3), 3.63 (ddd, \(^3J\text{4,5} = 9.9\) Hz, \(^3J\text{5,6a} = 2.8\) Hz, \(^3J\text{5,6b} = 2.0\) Hz, 1H, H-5), 3.44 (dd, \(^3J\text{3,4} = 9.1\) Hz, \(^3J\text{4,5} = 9.9\) Hz, 1H, H-4), 3.22 (dd, \(^3J\text{1,2} = 3.6\) Hz, \(^3J\text{2,3} = 9.4\) Hz, 1H, H-2), 3.66, 3.55, 3.41 (OCH\textsubscript{3}) ppm. \textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 138.2\) (C\textsubscript{arom.}), 128.5, 128.1, 127.9, (C\textsubscript{arom.}), 97.5 (C-1), 83.7 (C-3), 82.1 (C-2), 77.4 (C-4), 74.9 (OCH\textsubscript{2}Ph-A), 70.6 (C-5), 61.9 (C-6), 61.1, 59.0, 55.1 (OCH\textsubscript{3}) ppm.

**Methyl 4-O-benzyl-2,3,6-tri-O-methyl-\(\alpha\)-d-glucopyranoside (45)**

Prepared following procedure A. 1.27 g (4.08 mmol) 44, 326 mg (8.16 mmol) NaH, 0.51 mL (8.2 mmol) Mel 50 mL DMF. Yield: 1.31 g (4.03 mmol, 98%), colourless syrup, \([\alpha]_{D}^{23} = +158.4^\circ\) (c = 0.5, CHCl\textsubscript{3}), \(R_f\) (PE/EE 1:1, v/v) = 0.34, ESI HRMS for C\textsubscript{17}H\textsubscript{26}O\textsubscript{6} [M+Na\textsuperscript{+}]: found 349.1618, calcd. 349.1622. \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}) \(\delta = 7.40 - 7.28\) (m, 5H, H\textsubscript{arom.}), 4.87 (d, \(^2J\text{A,A'} = 11.1\) Hz, 1H, OCH\textsubscript{2}Ph-A), 4.65 (d, \(^3J\text{1,2} = 3.6\) Hz, 1H, H-1), 4.62 (d, \(^2J\text{A,A'} = 11.1\) Hz, 1H, OCH\textsubscript{2}Ph-A'), 3.68 (ddd, \(^3J\text{4,5} = 9.9\) Hz, \(^3J\text{5,6a} = 3.6\) Hz, \(^3J\text{5,6b} = 2.0\) Hz, 1H, H-5), 3.62 (dd, \(^3J\text{2,3} = 9.4\) Hz, \(^3J\text{3,4} = 8.9\) Hz, 1H, H-3), 3.62 (dd, \(^3J\text{5,6a} = 3.6\) Hz, \(^2J\text{6a,6b} = 10.4\) Hz, 1H, H-6a), 3.56 (dd, \(^3J\text{5,6b} = 2.0\) Hz, \(^2J\text{6a,6b} = 10.4\) Hz, 1H, H-6b), 3.51 (dd, \(^3J\text{3,4} = 8.9\) Hz, \(^3J\text{4,5} = 9.9\) Hz, 1H, H-4), 3.26 (dd, \(^3J\text{1,2} = 3.6\) Hz, \(^3J\text{2,3} = 9.4\) Hz, 1H, H-2), 3.65, 3.53, 3.42, 3.37 (OCH\textsubscript{3}) ppm. \textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}) \(\delta = 138.4\) (C\textsubscript{arom.}), 128.4, 128.0, 127.7 (C\textsubscript{arom.}), 97.6 (C-1), 83.7 (C-3), 81.9 (C-2), 77.5 (C-4), 75.0 (OCH\textsubscript{2}Ph-A), 70.9 (C-6), 69.8 (C-5), 61.1, 59.2, 59.0, 55.1 (OCH\textsubscript{3}) ppm.
Methyl 3,4,6-tri-\(\text{O}\)-methyl-\(\alpha\)-D-glucopyranoside (1)

\[ \text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3) \]
Methyl 3,4,6-tri-O-methyl-α-D-glucopyranoside (1)

$\text{^{13}C-NMR (101 MHz, CDCl}_3\text{)}$

Chemical Shift (ppm)
Methyl 2,4,6-tri-\(\text{O}\)-methyl-\(\alpha\)-d-glucopyranoside (2)

\(\text{\(^1\text{H-NMR (400 MHz, CDCl}_3\)}\)

S-32
Methyl 2,4,6-tri-O-methyl-α-D-glucopyranoside (2)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 2,3,6-tri-O-methyl-α-D-glucopyranoside (3)

\[(\text{HO})_3\text{C}_6\text{H}_3\text{O}(\text{Me})_3\text{C}^\text{O}\]

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 2,3,6-tri-O-methyl-α-D-glucopyranoside (3)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 2,3,4-tri-O-methyl-α-D-glucopyranoside (4)

1H-NMR (400 MHz, CDCl₃)
Methyl 2,3,4-tri-O-methyl-α-D-glucopyranoside (4)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4,6-di-\(\text{O}\)-methyl-\(\alpha\)-D-glucopyranoside (5)

\[
\begin{align*}
\text{MeO} & \quad \text{OMe} \\
\text{HO} & \quad \text{HO} \\
\text{HO} & \quad \text{OMe}
\end{align*}
\]

\(^1\text{H-NMR (400 MHz, CDCl}_3\))
Methyl 4,6-di-O-methyl-α-D-glucopyranoside (5)

\[
\text{\textsuperscript{13}C-NMR (101 MHz, CDCl}_3)\]

![NMR Spectrogram](image-url)
Methyl 2,3-di-\(O\)-methyl-\(\alpha\)-D-glucopyranoside (6)

\[ ^1H\text{-NMR (400 MHz, CDCl}_3\]
Methyl 2,3-di-\(O\)-methyl-\(\alpha\)-D-glucopyranoside (6)

\( ^{13} \text{C-NMR} \ (101 \text{ MHz, CDCl}_3) \)
Methyl 2-\textit{O}-methyl-\textalpha-D-glucopyranoside (7)

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{chart.png}
\caption{\textit{1}H-NMR (400 MHz, CDCl$_3$)}
\end{figure}
Methyl 2-\(\text{O}\)-methyl-\(\alpha\)-\(\text{d}\)-glucopyranoside (7)

\[ \text{Chemical Shift (ppm)} \]

\( ^{13}\text{C-NMR (101 MHz, CDCl}_3\)
Methyl 3-\textit{O}-methyl-\textit{\alpha}-\textit{D}-glucopyranoside (8)

\[ \text{\textit{\alpha}} \ 	ext{\textit{D}-glucopyranoside} \]

\[ \text{\textit{\alpha}} \ 	ext{\textit{D}-glucopyranoside} \]

\[ \text{\textit{\alpha}} \ 	ext{\textit{D}-glucopyranoside} \]

$^1$H-NMR (400 MHz, CDCl$_3$)

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Methyl 3-O-methyl-α-D-glucopyranoside (8)

$\text{\textsuperscript{13}C-NMR (101 MHz, CDCl}_3\text{)}$
2,3,4,6-Tetra-O-methyl α-D-galactopyranosyl chloride (9)

$^1$H-NMR (400 MHz, CDCl$_3$)
2,3,4,6-Tetra-O-methyl α-D-galactopyranosyl chloride (9)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 3,4,6-tri-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10)
Methyl 2,4,6-tri-O-methyl-3-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (11)
Methyl 2,3,6-tri-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12)
Methyl 2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 3,4,6-tri-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (10)
Methyl 2,4,6-tri-O-methyl-3-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (11)
Methyl 2,3,6-tri-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (12)
Methyl 2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (13)

\(^{13}\text{C-NMR (101 MHz, CDCl}_3\)}}
Methyl 3-O-acetyl-4,6-di-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 3-O-acetyl-4,6-di-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (14)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 6-O-acetyl-2,3-di-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15)
Methyl 4-O-acetyl-2,3-di-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16)

\[ \text{1H-NMR (400 MHz, CDCl}_3\text{)} \]
Methyl 6-O-acetyl-2,3-di-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (15)
Methyl 4-O-acetyl-2,3-di-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (16)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 3,6-di-O-acetyl-2-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)
Methyl 3,4-di-O-acetyl-2-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 3,6-di-O-acetyl-2-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (17)
Methyl 3,4-di-O-acetyl-2-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (18)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4,6-di-\textit{O}-acetyl-3-\textit{O}-methyl-2-\textit{O}-(2,3,4,6-tetra-\textit{O}-methyl-\textit{\beta}-\textit{D}-galactopyranosyl)-\textit{\alpha}-\textit{D}-glucopyranoside (19)
Methyl 2,6-di-\textit{O}-acetyl-3-\textit{O}-methyl-4-\textit{O}-(2,3,4,6-tetra-\textit{O}-methyl-\textit{\beta}-\textit{D}-galactopyranosyl)-\textit{\alpha}-\textit{D}-glucopyranoside (20)
Methyl 2,4-di-\textit{O}-acetyl-3-\textit{O}-methyl-6-\textit{O}-(2,3,4,6-tetra-\textit{O}-methyl-\textit{\beta}-\textit{D}-galactopyranosyl)-\textit{\alpha}-\textit{D}-glucopyranoside (21)

\begin{align*}
\text{(19)} & \quad \text{AcO} \quad \text{MeO} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{MeO} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{OMe} \\
\text{(20) 20} & \quad \text{MeO} \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{OMe} \\
\text{(21) 21} & \quad \text{MeO} \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe} \\
\text{AcO} & \quad \text{OMe}
\end{align*}

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 4,6-di-O-acetyl-3-O-methyl-2-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (19)
Methyl 2,6-di-O-acetyl-3-O-methyl-4-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (20)
Methyl 2,4-di-O-acetyl-3-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (21)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 3-\(O\)-benzyl-\(\alpha\)-d-glucopyranoside (22)

\[\text{\(1^1\)H-NMR (400 MHz, CDCl}\_3)\]

![NMR spectrum of Methyl 3-\(O\)-benzyl-\(\alpha\)-d-glucopyranoside (22)]
Methyl 3-O-benzyl-α-D-glucopyranoside (22)

\[ \text{\textsuperscript{13}C-NMR (101 MHz, CDCl}_3) \]

Chemical Shift (ppm)
2,3,4-Tri-O-benzyl-α-L-fucopyranosyl chloride (23)

\[ \text{Chemical Shift (ppm)} \]

\(^1\)H-NMR (400 MHz, CDCl\textsubscript{3})
2,3,4-Tri-O-benzyl-α-L-fucopyranosyl chloride (23)

\[
\begin{align*}
\text{13C-NMR (101 MHz, CDCl}_3\text{)}
\end{align*}
\]
Methyl 3-\(O\)-benzyl-2-\(O\)-(2,3,4-tri-\(O\)-benzyl-\(\beta\)-L-fucopyranosyl)-\(\alpha\)-D-glucopyranoside (24)

\[
\begin{align*}
\text{1H-NMR (400 MHz, CDCl}_3)\end{align*}
\]
Methyl 3-<i>O</i>-benzyl-2-<i>O</i>-(2,3,4-tri-<i>O</i>-benzyl-<i>β</i>-<i>L</i>-fucopyranosyl)-<i>α</i>-<i>D</i>-glucopyranoside (24)

<sup>13</sup>C-NMR (101 MHz, CDCl<sub>3</sub>)
Methyl 3-O-benzyl-2-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 3-O-benzyl-2-O-(2,3,4-tri-O-benzyl-β-L-fucopyranosyl)-α-D-glucopyranoside (25)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 2,3-di-O-methyl-4,6-di-O-(2,3,4,6-tetra-O-methyl-β-D-galactopyranosyl)-α-D-glucopyranoside (26)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 2,3-di-\textit{O}-methyl-4,6-di-\textit{O}-\(\text{2,3,4,6-tetra-\textit{O}-methyl-}\beta\text{-d-galactopyranosyl}\)-\(\alpha\text{-d-glucopyranoside}\) (26)

\(^{13}\text{C-\textit{NMR}}\) (101 MHz, CDCl\(_3\))
Methyl 4,6-\textit{O}\textendash benzylidene\textit{\textalpha}{\textit{D}}-\textit{glucopyranoside (28)}

\[\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3)\]

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Methyl 4,6-O-benzylidene-\(\alpha\)-D-glucopyranoside (28)

\[ \text{\(^{13}\)C-NMR (101 MHz, CDCl}_3\)} \]
Methyl 6-O-triphenylmethyl-α-D-glucopyranoside (29)

$^1$H-NMR (400 MHz, MeOD)
Methyl 6-O-triphenylmethyl-$\alpha$-D-glucopyranoside (29)

$^{13}$C-NMR (400 MHz, MeOD)
Methyl 4,6-O-benzylidene-2,3-di-O-methyl-α-D-glucopyranoside (30)

\[ \text{1H-NMR (400 MHz, CDCl}_3\text{)} \]
Methyl 4,6-O-benzylidene-2,3-di-O-methyl-α-D-glucopyranoside (30)

\[\text{13}^\text{C}-\text{NMR (101 MHz, CDCl}_3\text{)}\]
Methyl 4,6-O-benzylidene-2-O-methyl-α-D-glucopyranoside (31)

\[
\begin{align*}
\text{31} \\
\end{align*}
\]

\( ^1H \text{-NMR (400 MHz, CDCl}_3 \text{)} \)
Methyl 4,6-O-benzylidene-2-O-methyl-α-D-glucopyranoside (31)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4,6-O-benzylidene-3-O-methyl-α-D-glucopyranoside (32)

\[ \text{\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3})} \]
Methyl 4,6-O-benzylidene-3-O-methyl-α-D-glucopyranoside (32)

$\text{Ph} \quad \text{Me} \quad \text{OMe} \quad \text{H}_2\text{O} \quad \text{OMe}$

$^1\text{C}-\text{NMR (101 MHz, CDCl}_3)$
Methyl 4,6-\textit{O}-benzylidene-2,3-di-\textit{O}-benzyl-\textalpha{}-D-glucopyranoside (33)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 4,6-\textit{O}-benzyldene-2,3-di-\textit{O}-benzyl-\textalpha-\textit{D}-glucopyranoside (33)

\begin{equation}
13\text{C-NMR (101 MHz, CDCl}_3\text{)}
\end{equation}
Methyl 4,6-\textit{O}-benzylidene-2-\textit{O}-benzyl-\textalpha-D-glucopyranoside (34)

\textsuperscript{1}H-NMR (400 MHz, CDCl$_3$)
Methyl 4,6-\(O\)-benzylidene-2-\(O\)-benzyl-\(\alpha\)-\(D\)-glucopyranoside (34)

\(^{13}\)C-NMR (101 MHz, CDCl₃)
Methyl 4,6-O-benzylidene-3-O-benzyl-α-D-glucopyranoside (35)

$^{1}$H-NMR (400 MHz, CDCl$_3$)
Methyl 4,6-O-benzylidene-3-O-benzyl-α-D-glucopyranoside (35)

\[
\begin{align*}
35
\end{align*}
\]

\[ ^{13}\text{H-NMR (101 MHz, CDCl}_{3}) \]
Methyl 2,3,4-tri-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (36)

\[ \text{\textsuperscript{1}H-NMR (400 MHz, MeOD)} \]
Methyl 2,3,4-tri-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (36)

$^{13}$C-NMR (101 MHz, MeOD)
Methyl 2,3-di-O-benzyl-α-D-glucopyranoside (37)

$^1$H-NMR (400 MHz, CDCl$_3$)

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Methyl 2,3-di-O-benzyl-α-D-glucopyranoside (37)

\[ \text{\textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}) \hspace{1cm} \includegraphics{methyl_di_0_benzyl_alpha_d_glucopyranoside_37}} \]
Methyl 2-O-benzyl-α-D-glucopyranoside (38)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 2-\textit{O}-benzyl-\textit{\alpha}-\textit{D}-glucopyranoside (38)

\begin{center}
\includegraphics[width=1\textwidth]{s89.png}
\end{center}

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 2,3-di-O-methyl-6-O-triphenylmethyl-\(\alpha\)-D-glucopyranoside (39)

\[\text{\textsuperscript{1}H-NMR (400 MHz, CDCl}_3\text{)}\]

Chemical Shift (ppm)
Methyl 2,3-di-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (39)

\[ \text{Structural formula} \]

$^{13}$C-NMR (101 MHz, CDCl$_3$)

![NMR spectrum image](image-url)
Methyl 2,3-di-O-benzyl-4,6-di-O-methyl-α-D-glucopyranoside (40)

\[ ^1 \text{H-NMR (400 MHz, CDCl}_3 \text{)} \]

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Methyl 2,3-di-O-benzyl-4,6-di-O-methyl-α-D-glucopyranoside (40)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 2-O-benzyl-3,4,6-tri-O-methyl-α-D-glucopyranoside (41)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 2-\textit{O}-benzyl-3,4,6-tri-\textit{O}-methyl-\textalpha-\textit{D}-glucopyranoside (41)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 3-\textit{O}-benzyl-2,4,6-tri-\textit{O}-methyl-\textalpha{D}-glucopyranoside (42)

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3})
Methyl 3-O-benzyl-2,4,6-tri-O-methyl-α-D-glucopyranoside (42)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4-O-benzyl-2,3-di-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (43)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 4-O-benzyl-2,3-di-O-methyl-6-O-triphenylmethyl-α-D-glucopyranoside (43)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4-\(O\)-benzyl-2,3-di-\(O\)-methyl-\(\alpha\)-d-glucopyranoside (44)

\(^1\)H-NMR (400 MHz, CDCl₃)
Methyl 4-O-benzyl-2,3-di-O-methyl-α-D-glucopyranoside (44)

${}^{13}$C-NMR (101 MHz, CDCl$_3$)
Methyl 4-O-benzyl-2,3,6-tri-O-methyl-α-D-glucopyranoside (45)

$^1$H-NMR (400 MHz, CDCl$_3$)
Methyl 4-O-benzyl-2,3,6-tri-O-methyl-α-D-glucopyranoside (45)

$^{13}$C-NMR (101 MHz, CDCl$_3$)
References: