Efficient and Selective Removal of Methoxy Protecting Groups in Carbohydrates

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Supporting Information

Preparation of Substrates 8–13.

The preparation of compounds **7–11** and **13** was carried out according to literature procedures.⁵ The synthesis of compound **12** is described below.

Benzyl 2,3,6-Tri-*O*-methyl- β -D-glucopyranoside (12). To a solution of benzyl 4-*O*-(α -D-glucopyranosyl)- β -D-glucopyranoside (**33**)¹⁰ (770 mg, 1.78 mmol) (Scheme 5) in DMSO (10 mL) was added aqueous 50% NaOH (1 mL, 500 mg, 12.5 mmol) and MeI (1.16 mL, 2.64 g, 18.6 mmol) and the mixture was stirred at room temperature overnight. The reaction mixture was poured into H₂O and extracted with EtOAc. The organic layer was dried on Na₂SO₄, filtered and evaporated under vacuum. The residue was treated with 1M HCl in MeOH (35 mL, 35 mmol), and the reaction mixture was refluxed overnight; then it was poured into saturated aqueous NaHCO₃ and extracted with EtOAc. The organic layer was dried on Na₂SO₄ and concentrated under vacuum. The residue was purified by chromatography on silica gel (hexanes–EtOAc, 80:20) yielding methyl 2,3,4,6-tetra-*O*-methyl- α -D-glucopyranoside (**34**)¹¹ (129 mg, 29%), methyl 2,3,4,6-tetra-*O*-methyl- β -D-glucopyranoside (**35**)¹² (49 mg, 11%), and benzyl 2,3,6-tri-*O*-methyl- β -D-glucopyranoside (**12**) (186 mg, 33%): Syrup; [α]_D –20 (c = 0.2, CHCl₃); IR (CHCl₃) ν_{max} 3597, 3045, 3036 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) δ_{H} 2.78 (1H, br s), 3.11 (2H, m), 3.41 (1H, ddd, *J* = 3.6, 5.2, 9.1 Hz), 3.42 (3H, s), 3.50 (1H, m), 3.59 (3H, s), 3.63 (3H, s), 3.65 (1H, dd, *J* = 5.2,

10.4 Hz), 3.69 (1H, dd, *J* = 3.9, 10.4 Hz), 4.40 (1H, d, *J* = 7.6 Hz), 4.64 (1H, d, *J* = 12.0 Hz), 4.93 (1H, d, *J* = 12.0 Hz), 7.28–7.37 (5H, m); ¹³C NMR (125.7 MHz, CDCl₃) δ_{C} 59.6 (CH₃), 60.3 (CH₃), 60.8 (CH₃), 71.1 (CH₂), 71.2 (CH), 72.6 (CH₂), 73.8 (CH), 83.5 (CH), 85.7 (CH), 102.5 (CH), 127.6 (CH), 127.7 (2 $\times$ CH), 128.3 (2 $\times$ CH), 137.4 (C); MS *m/z* (rel intensity) 237 (*M*⁺ – H – MeOCH=CHOH, 1), 91 (PhCH₂, 100); HRMS calcd for C₁₃H₁₇O₄ 237.1127, found 237.1144. Anal. Calcd for C₁₆H₂₄O₆: C, 61.52; H, 7.74. Found: C, 61.46; H, 7.74.

Scheme 5. Synthesis of substrate **12**: methylation of compound **33** and cleavage of one glycosidic bond.

¹⁰Benzyl 4-*O*-(α -D-glucopyranosyl)- β -D-glucopyranoside (**33**): Hirooka, M.; Koto, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2893–2902.

¹¹Compound **34**: Lee, C. K.; Kim, E. J.; Lee, I.-S. H. *Carbohydr. Res.* **1998**, *309*, 243–250.

¹²Compound **35**: Cesane, P. D.; Duchaussoy, P.; Gross, B. *Synthesis* **1980**, 953–954.

Sequential Protecting Group Transformation–Hydrolysis (from substrates **8**, **9**, and **12** to products **28**, **31**, and **32**, respectively). **General Procedure.** A solution of the substrate (0.2 mmol) in dry dichloromethane (4 mL), placed in a pyrex round bottom flask under nitrogen, was treated with (diacetoxyiodo)benzene (DIB) (97 mg, 0.3 mmol) and iodine (51 mg, 0.2 mmol). The reaction mixture was irradiated with two tungsten-filament lamps for 1 h at 22–25 °C. Then the solvent was evaporated under vacuum, and glacial acetic acid (25 μ L, 0.5 mmol) and trifluoroacetic anhydride (38 μ L, 0.5 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to reach room temperature (1 h) and stirred for other 2 h. Afterwards the reagents were removed under vacuum and the residue was treated with 4% NaOH (MeOH–H₂O, 9:1, 0.5 mL). After stirring at room temperature for 1 h, the reaction mixture was poured into water, neutralized with aqueous 5% HCl and extracted with EtOAc. The organic layer was dried (Na₂SO₄), evaporated under vacuum and the resulting residue was purified by chromatography on silica gel (hexanes–EtOAc).

Methyl 2,3-Di-*O*-methyl-4,6-*O*-methylene- α -D-galactopyranoside (14): ¹H NMR (500 MHz, C₆D₆) δ 3.05 (1H, br s), 3.13 (3H, s), 3.23 (1H, dd, J = 1.8, 12.1 Hz), 3.29 (3H, s), 3.30 (3H, s), 3.54 (1H, d, J = 3.6 Hz), 3.59 (1H, dd, J = 3.5, 10.0 Hz), 3.89 (1H, dd, J = 3.5, 10.0 Hz), 3.90 (1H, d, J = 12.2 Hz), 4.31 (1H, d, J = 6.2 Hz), 4.79 (1H, d, J = 3.5 Hz), 5.07 (1H, d, J = 6.2 Hz); ¹³C NMR (100.6 MHz, C₆D₆) δ 55.2 (CH₃), 56.9 (CH₃), 58.8 (CH₃), 63.7 (CH), 68.9 (CH₂), 73.2 (CH), 77.8 (CH), 77.9 (CH), 93.3 (CH₂), 99.4 (CH). MS m/z (rel intensity) 234 (M^+ , 2), 75 (C₃H₆O₂ + H, 100); HRMS calcd for C₁₀H₁₈O₆ 234.1103, found 234.1084. Anal. Calcd for C₁₀H₁₈O₆: C, 51.27; H, 7.75. Found: C, 51.34; H, 7.81.

Methyl 2,3-Di-*O*-methyl-4-*O*-(methylacetate)- α -D-galactopyranoside (15): Compound **15** could not be totally purified from its mixture with the major product **14**: ¹H NMR (500 MHz, C₆D₆) δ 1.65 (3H, s), 3.13 (3H, s), 3.21 (3H, s), 3.26 (3H, s), 3.51 (1H, m), 3.71 (2H, m), 3.80 (2H, m), 4.03 (1H, d, J = 2.9 Hz), 4.73 (1H, d, J = 3.5 Hz), 5.34 (1H, d, J = 6.1 Hz), 5.36 (1H, d, J = 6.1 Hz); ¹³C NMR (100.6 MHz, C₆D₆) δ 16.4 (CH₃), 55.0 (CH₃), 55.2 (CH₃), 58.2 (CH₃), 61.1 (CH), 70.3 (CH₂), 75.6 (CH), 78.8 (CH), 80.0 (CH), 88.9 (CH₂), 98.5 (CH), 167.4 (C).

Methyl 2,3-Di-*O*-methyl-4,6-*O*-methylene- β -D-galactopyranoside (16): ¹H NMR (500 MHz, CDCl₃) δ 3.20 (1H, dd, J = 3.7, 9.6 Hz), 3.34 (1H, d, J = 1.2 Hz), 3.42 (1H, dd, J = 7.8, 9.6 Hz), 3.51 (3H, s), 3.55 (3H, s), 3.59 (3H, s), 3.82 (1H, dd, J = 1.5, 12.3 Hz), 4.03 (1H, d, J = 3.6 Hz), 4.18 (1H, d, J = 12.2 Hz), 4.19 (1H, d, J = 7.7 Hz), 4.73 (1H, d, J = 6.3 Hz), 5.19 (1H, d, J = 6.3 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 56.8 (CH₃), 58.1 (CH₃), 60.8 (CH₃), 67.0 (CH), 68.6 (CH₂), 72.5 (CH), 79.6 (CH), 81.3 (CH), 93.5 (CH₂), 104.3 (CH). MS m/z (rel intensity)

234 (M^+ , 1), 75 (MeOCH=CHOH + H, 100); HRMS calcd for C₁₀H₁₈O₆ 234.1103, found 234.1118. Anal. Calcd for C₁₀H₁₈O₆: C, 51.27; H, 7.75. Found: C, 51.43; H, 7.74.

Methyl 2,3-Di-*O*-methyl-4-*O*-(methylacetate)- β -D-galactopyranoside (17): IR (film) 3518, 1735 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.10 (3H, s), 3.16 (1H, dd, J = 3.0, 9.7 Hz), 3.30 (1H, dd, J = 7.7, 9.6 Hz), 3.46 (1H, dd, J = 6.3, 6.5 Hz), 3.53 (3H, s), 3.54 (3H, s), 3.58 (3H, s), 3.68 (1H, dd, J = 6.6, 11.4 Hz), 3.78 (1H, dd, J = 6.5, 11.4 Hz), 4.17 (1H, d, J = 4.1 Hz), 4.18 (1H, d, J = 7.4 Hz), 5.35 (1H, d, J = 6.1 Hz), 5.38 (1H, d, J = 6.1 Hz); ¹³C NMR (100.6 MHz, CDCl₃) δ 19.6 (CH₃), 56.9 (CH₃), 59.0 (CH₃), 60.4 (CH₃), 60.8 (CH₂), 73.6 (2 $\times$ CH), 80.7 (CH), 83.4 (CH), 89.9 (CH₂), 104.7 (CH), 169.9 (C). MS m/z (rel intensity) 234 (M^+ – MeCO₂H, 2), 75 (C₃H₆O₂ + H, 100); HRMS calcd for C₁₀H₁₈O₆ 234.1103, found 234.1091. Anal. Calcd for C₁₂H₂₂O₈: C, 48.97; H, 7.53. Found: C, 49.14; H, 7.33.

Benzyl 2,3-Di-*O*-methyl-4,6-*O*-methylene- α -D-glucopyranoside (18): IR (CHCl₃) 3090, 3067 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.22 (1H, dd, J = 9.4, 9.7 Hz), 3.25 (1H, dd, J = 3.8, 9.4 Hz), 3.39 (1H, dd, J = 10.5, 10.5 Hz), 3.41 (3H, s), 3.63 (3H, s), 3.65 (1H, dd, J = 9.3, 9.4 Hz), 3.73 (1H, ddd, J = 4.9, 10.0, 10.0 Hz), 4.01 (1H, dd, J = 4.9, 10.2 Hz), 4.60 (1H, d, J = 6.3 Hz), 4.62 (1H, d, J = 12.2 Hz), 4.73 (1H, d, J = 12.2 Hz), 4.98 (1H, d, J = 3.8 Hz), 5.06 (1H, d, J = 6.3 Hz), 7.31 (1H, dd, J = 7.1, 7.1 Hz), 7.37 (2H, dd, J = 7.1, 7.6 Hz), 7.39 (2H, d, J = 7.0 Hz); ¹³C NMR (125.7 MHz, CDCl₃) δ 58.6 (CH₃), 61.0 (CH₃), 62.7 (CH), 68.7 (CH₂), 69.5 (CH₂), 79.5 (CH), 81.6 (CH), 81.7 (CH), 93.7 (CH₂), 95.8 (CH), 128.0 (CH), 128.3 (2 $\times$ CH), 128.4 (2 $\times$ CH), 136.9 (C). MS m/z (rel intensity) 219 (M^+ – PhCH₂, 2), 91 (PhCH₂, 100); HRMS calcd for C₉H₁₅O₆ 219.0869, found 219.0938. Anal. Calcd for C₁₆H₂₂O₆: C, 61.92; H, 7.15. Found: C, 61.87; H, 7.11.

Benzyl 2,3-Di-*O*-methyl-4,6-*O*-methylene- β -D-glucopyranoside (19): IR (CHCl₃) 3090, 3063 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.12 (1H, dd, J = 7.8, 8.1 Hz), 3.23–3.30 (3H, m), 3.48 (1H, dd, J = 9.8, 10.2 Hz), 3.60 (3H, s), 3.61 (3H, s), 4.20 (1H, dd, J = 4.3, 10.6 Hz), 4.48 (1H, d, J = 7.6 Hz), 4.60 (1H, d, J = 6.3 Hz), 4.64 (1H, d, J = 12.0 Hz), 4.89 (1H, d, J = 11.8 Hz), 5.05 (1H, d, J = 6.3 Hz), 7.28–7.36 (5H, m); ¹³C NMR (125.7 MHz, CDCl₃) δ 60.8 (CH₃), 60.9 (CH₃), 66.2 (CH), 68.5 (CH₂), 71.3 (CH₂), 80.7 (CH), 82.5 (CH), 84.2 (CH), 93.6 (CH₂), 102.9 (CH), 127.8 (2 $\times$ CH), 127.9 (CH), 128.4 (2 $\times$ CH), 137.1 (C). MS m/z (rel intensity) 219 (M^+ – PhCH₂, <1), 91 (PhCH₂, 100); HRMS calcd for C₉H₁₅O₆ 219.0869, found 219.0891. Anal. Calcd for C₁₆H₂₂O₆: C, 61.92; H, 7.15. Found: C, 62.17; H, 6.82.

Methyl 2,6-Di-*O*-methyl-3-*O*-(methylacetate)- β -D-glucopyranoside (20): IR (film) 3518, 1742 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.10 (3H, s), 3.01 (1H, dd, J

= 8.2, 8.3 Hz), 3.41 (1H, m), 3.42 (3H, s), 3.53 (3H, s), 3.54 (3H, s), 3.55 (1H, m), 3.64 (1H, dd, J = 5.1, 10.3 Hz), 3.68 (1H, dd, J = 3.8, 10.4 Hz), 4.19 (1H, d, J = 7.8 Hz), 5.38 (1H, d, J = 6.0 Hz), 5.46 (1H, d, J = 6.0 Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 21.1 (CH_3), 57.0 (CH_3), 59.6 (CH_3), 60.6 (CH_3), 70.5 (CH), 72.6 (CH_2), 73.8 (CH), 82.5 (CH), 84.3 (CH), 89.9 (CH_2), 104.4 (CH), 170.7 (C). MS m/z (rel intensity) 234 ($\text{M}^+ - \text{MeCO}_2\text{H}$, <1), 74 ($\text{C}_3\text{H}_6\text{O}_2$, 100); HRMS calcd for $\text{C}_{10}\text{H}_{18}\text{O}_6$, 234.1103, found 234.1053. Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_8$: C, 48.97; H, 7.53. Found: C, 49.29; H, 7.84.

Benzyl 2,6-Di-*O*-methyl-3-*O*-(methylacetate)- β -D-glucopyranoside (22): IR (film) 3592, 1739 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.10 (3H, s), 3.11 (1H, dd, J = 8.0, 8.8 Hz), 3.40 (1H, m), 3.42 (3H, s), 3.50 (1H, dd, J = 8.8, 9.2 Hz), 3.54 (1H, dd, J = 7.5, 9.0 Hz), 3.56 (3H, s), 3.65 (1H, dd, J = 5.1, 10.5 Hz), 3.70 (1H, dd, J = 3.7, 10.4 Hz), 4.40 (1H, d, J = 7.8 Hz), 4.63 (1H, d, J = 11.9 Hz), 4.93 (1H, d, J = 11.9 Hz), 5.38 (1H, d, J = 6.1 Hz), 5.45 (1H, d, J = 6.0 Hz), 7.35-7.42 (5H, m); ^{13}C NMR (100.6 MHz, CDCl_3) δ 30.0 (CH_3), 60.0 (CH_3), 61.1 (CH_3), 70.8 (CH), 71.4 (CH_2), 73.8 (CH_2), 74.3 (CH), 83.0 (CH), 84.7 (CH), 90.3 (CH_2), 102.8 (CH), 128.1 (2 $\times$ CH), 128.2 (CH), 128.8 (2 $\times$ CH), 137.7 (C) 164.8 (C). MS m/z (rel intensity) 295 ($\text{M}^+ - \text{H} - \text{MeOCH}_2\text{CHO}$, <1), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{O}_6$, 295.1182, found 219.1191. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}_8$: C, 58.37; H, 7.08. Found: C, 58.07; H, 7.43.

Benzyl 2,6-Di-*O*-methyl-3,4-*O*-methylene- β -D-glucopyranoside (23): IR (neat) 3095, 3067 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.49 (1H, m), 3.43 (3H, s), 3.51 (1H, m), 3.53 (1H, m), 3.61 (3H, s), 3.65 (1H, dd, J = 3.8, 8.4 Hz), 4.13 (1H, m), 4.35 (1H, dd, J = 4.5, 4.5 Hz), 4.67 (1H, d, J = 11.9 Hz), 4.81 (1H, d, J = 7.6 Hz), 4.94 (1H, d, J = 11.9 Hz), 4.97 (1H, s), 5.23 (1H, s), 7.27-7.38 (5H, m); ^{13}C NMR (125.7 MHz, CDCl_3) δ 59.4 (CH_3), 59.6 (CH_3), 70.7 (CH_2), 71.7 (CH), 71.9 (CH_2), 73.1 (CH), 75.8 (CH), 77.7 (CH), 95.7 (CH_2), 99.8 (CH), 127.6 (CH), 127.7 (2 $\times$ CH), 128.3 (2 $\times$ CH), 137.3 (C). MS m/z (rel intensity) 267 ($\text{M}^+ - \text{H} - \text{CH}_2=\text{CO}$, 3), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{O}_5$, 267.1232, found 267.1227. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_6$: C, 61.92; H, 7.15. Found: C, 62.27; H, 7.46.

Methyl 4-*O*-Methyl-3-*O*-(methylacetate)- β -L-rhamnopyranoside (24): IR (film) 3580, 1740 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.31 (3H, d, J = 6.3 Hz), 2.10 (3H, s), 3.12 (1H, dd, J = 9.4, 9.4 Hz), 3.35 (3H, s), 3.50 (3H, s), 3.60 (1H, dddd, J = 6.2, 6.3, 6.4, 9.6 Hz), 3.82 (1H, dd, J = 3.4, 9.3 Hz), 3.95 (1H, dd, J = 1.6, 3.3 Hz), 4.65 (1H, br s), 5.31 (1H, d, J = 6.3 Hz), 5.46 (1H, d, J = 6.2 Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 17.7 (CH_3), 21.1 (CH_3), 54.8 (CH_3), 61.0 (CH_3), 67.3 (CH), 70.1 (CH), 80.6 (CH), 81.4 (CH), 88.7 (CH_2), 100.0 (CH), 170.4 (C). MS m/z (rel intensity) 204 ($\text{M}^+ - \text{MeCO}_2\text{H}$, 1), 72 (100); HRMS calcd for $\text{C}_9\text{H}_{16}\text{O}_5$,

204.0998, found 204.0963. Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_7$: C, 49.99; H, 7.63. Found: C, 49.67; H, 7.98.

Methyl 4-*O*-Methyl-2,3-*O*-methylene- β -L-rhamnopyranoside (25): Compound **25** could not be totally purified from its mixture with the major product **24**: ^1H NMR (500 MHz, CDCl_3) δ 1.26 (3H, d, J = 6.3 Hz), 2.75 (1H, dd, J = 9.3, 9.3 Hz), 3.40 (3H, s), 3.51 (3H, s), 3.58 (2H, m), 3.72 (1H, dd, J = 9.3, 9.2 Hz), 4.67 (1H, d, J = 3.9 Hz), 5.40 (1H, d, J = 6.3 Hz), 5.49 (1H, d, J = 6.3 Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 17.6 (CH_3), 55.1 (CH_3), 60.9 (CH_3), 66.7 (CH), 72.1 (CH), 82.9 (CH), 84.7 (CH), 89.6 (CH_2), 99.0 (CH).

Methyl 6-*O*-Acetyl-2,3-di-*O*-methyl-4-*O*-(methylacetate)- β -D-galactopyranoside (26): IR (CHCl_3) 1740 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.08 (3H, s), 2.09 (3H, s), 3.13 (1H, dd, J = 3.0, 9.6 Hz), 3.30 (1H, dd, J = 7.6, 9.6 Hz), 3.52 (3H, s), 3.54 (3H, s), 3.56 (1H, dd, J = 6.3, 6.6 Hz), 3.57 (3H, s), 4.11 (1H, d, J = 2.9 Hz), 4.15 (1H, d, J = 7.6 Hz), 4.17 (1H, dd, J = 6.3, 11.2 Hz), 4.25 (1H, dd, J = 6.4, 11.2 Hz), 5.34 (1H, d, J = 6.4 Hz), 5.42 (1H, d, J = 6.4 Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 20.8 (CH_3), 21.0 (CH_3), 56.8 (CH_3), 59.0 (CH_3), 60.8 (CH_3), 62.7 (CH_2), 71.1 (CH), 73.2 (CH), 80.4 (CH), 83.2 (CH), 89.0 (CH_2), 104.5 (CH), 170.6 (C), 170.8 (C). MS m/z (rel intensity) 277 ($\text{M}^+ - \text{MeCO}_2$, 1), 88 ($\text{MeOCH}=\text{CHOMe}$, 100); HRMS calcd for $\text{C}_{12}\text{H}_{21}\text{O}_7$, 277.1287, found 277.1236. Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{O}_9$: C, 50.00; H, 7.19. Found: C, 50.09; H, 7.22.

Methyl 6-*O*-Acetyl-2,3-di-*O*-methyl- β -D-galactopyranoside (27): IR (film) 3570, 1740 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.09 (3H, s), 3.17 (1H, dd, J = 3.2, 9.3 Hz), 3.24 (1H, dd, J = 7.7, 9.2 Hz), 3.51 (3H, s), 3.54 (3H, s), 3.57 (3H, s), 3.59 (1H, dd, J = 5.8, 6.8 Hz), 3.99 (1H, d, J = 3.2 Hz), 4.16 (1H, d, J = 7.5 Hz), 4.34 (2H, d, J = 6.2 Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 20.9 (CH_3), 56.8 (CH_3), 57.9 (CH_3), 60.8 (CH_3), 63.0 (CH_2), 65.5 (CH), 71.7 (CH), 80.1 (CH), 82.5 (CH), 104.3 (CH), 170.8 (C). MS m/z (rel intensity) 247 ($\text{M}^+ - \text{OH}$, <1), 88 ($\text{MeOCH}=\text{CHOMe}$, 100); HRMS calcd for $\text{C}_{11}\text{H}_{19}\text{O}_6$, 247.1182, found 247.1196. Anal. Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_7$: C, 49.99; H, 7.63. Found: C, 50.13; H, 7.52.

Benzyl 6-*O*-Acetyl-2,3-di-*O*-methyl-4-*O*-(methylacetate)- α -D-glucopyranoside (29): IR (CHCl_3) 3091, 3067, 1740 cm^{-1} ; ^1H NMR (500 Mz, CDCl_3) δ 2.08 (3H, s), 2.10 (3H, s), 3.21 (1H, dd, J = 3.7, 9.2 Hz), 3.41 (3H, s), 3.55 (1H, dd, J = 8.5, 8.8 Hz), 3.58 (1H, dd, J = 8.0, 8.5 Hz), 3.60 (3H, s), 3.78 (1H, ddd, J = 3.5, 3.7, 9.4 Hz), 4.15 (1H, dd, J = 3.8, 12.4 Hz), 4.17 (1H, dd, J = 4.0, 12.5 Hz), 4.59 (1H, d, J = 12.1 Hz), 4.70 (1H, d, J = 12.2 Hz), 4.98 (1H, d, J = 3.7 Hz), 5.33 (1H, d, J = 6.3 Hz), 5.42 (1H, d, J = 6.3 Hz), 7.30 (1H, dd, J = 6.9, 7.0 Hz), 7.34 (2H, dd, J = 7.0, 7.6 Hz), 7.37 (2H, d, J = 7.0 Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 20.8 (CH_3), 20.9 (CH_3), 58.4 (CH_3), 61.2 (CH_3), 62.8 (CH_2), 68.1 (CH), 69.2 (CH_2), 77.5 (CH), 81.7 (CH), 82.5 (CH), 89.2 (CH_2),

94.9 (CH), 128.0 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 136.8 (C), 170.5 (C), 170.8 (C). MS m/z (rel intensity) 353 ($M^+ - \text{MeCO}_2$, <1), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{O}_7$ 353.1600, found 353.1588. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_9$: C, 58.24; H, 6.84. Found: C, 58.19; H, 6.99.

Benzyl 6-*O*-Acetyl-2,3-di-*O*-methyl- α -D-glucopyranoside (30): IR (CHCl_3) 3595, 3090, 3066, 1736 cm^{-1} ; ^1H NMR (500 Mz, CDCl_3) δ 2.11 (3H, s), 3.22 (1H, dd, $J = 3.7, 9.5$ Hz), 3.38 (1H, dd, $J = 9.3, 9.6$ Hz), 3.39 (3H, s), 3.52 (1H, dd, $J = 9.2, 9.2$ Hz), 3.65 (3H, s), 3.78 (1H, ddd, $J = 2.3, 4.5, 10.9$ Hz), 4.14 (1H, dd, $J = 2.2, 12.2$ Hz), 4.41 (1H, dd, $J = 4.5, 12.1$ Hz), 4.62 (1H, d, $J = 12.2$ Hz), 4.73 (1H, d, $J = 12.2$ Hz), 5.01 (1H, d, $J = 3.7$ Hz), 7.30 (1H, d, $J = 7.1, 7.1$ Hz), 7.35 (2H, dd, $J = 7.0, 7.6$ Hz), 7.40 (2H, d, $J = 7.0$ Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 20.8 (CH_3), 58.1 (CH_3), 61.3 (CH_3), 63.2 (CH_2), 69.5 (CH_2), 69.6 (CH), 70.0 (CH), 81.6 (CH), 82.3 (CH), 95.1 (CH), 128.0 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 136.9 (C), 171.4 (C). MS m/z (rel intensity) 341 ($M^+ + \text{H}$, <1), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}_7$ 341.1600, found 341.1568. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_7$: C, 59.99; H, 7.11. Found: C, 59.75; H, 7.37.

Benzyl 2,3-Di-*O*-methyl- α -D-glucopyranoside (31): IR (film) 3593, 3090, 3067 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 3.21 (1H, dd, $J = 3.5, 9.3$ Hz), 3.39 (3H, s), 3.51 (1H, dd, $J = 9.3, 9.6$ Hz), 3.53 (1H, dd, $J = 9.2, 9.2$ Hz), 3.64 (3H, s), 3.67 (1H, ddd, $J = 3.7, 3.9, 9.4$ Hz), 3.76 (1H, dd, $J = 3.7, 11.9$ Hz), 3.78 (1H, dd, $J = 3.9, 11.9$ Hz), 4.61 (1H, d, $J = 12.2$ Hz), 4.74 (1H, d, $J = 12.2$ Hz), 5.00 (1H, d, $J = 3.7$ Hz), 7.30 (1H, dd, $J = 7.0, 7.2$ Hz), 7.35 (2H, d, $J = 7.1, 7.6$ Hz), 7.39 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (125.7 MHz, CDCl_3) δ 58.0 (CH_3), 61.2 (CH_3), 62.3 (CH_2), 69.3 (CH_2), 70.4 (CH), 71.0 (CH), 81.8 (CH), 82.6 (CH), 95.0 (CH), 128.0 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 137.0 (C). MS m/z (rel intensity) 280 ($M^+ - \text{H}_2\text{O}$, <1), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5$ 280.1311, found 280.1297. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_6$: C, 60.39; H, 7.43. Found: C, 60.33; H, 7.68.

Benzyl 2,6-Di-*O*-methyl- β -D-glucopyranoside (32): IR (CHCl_3) 3592, 3461 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.93 (1H, br s), 3.06 (1H, dd, $J = 7.8, 8.9$ Hz), 3.40 (1H, m), 3.43 (3H, s), 3.49 (1H, m), 3.57 (1H, dd, $J = 8.5, 10.0$ Hz), 3.61 (3H, s), 3.69 (2H, d, $J = 4.7$ Hz), 4.43 (1H, d, $J = 7.8$ Hz), 4.63 (1H, d, $J = 11.9$ Hz), 4.93 (1H, d, $J = 11.9$ Hz), 7.34–7.44 (5H, m); ^{13}C NMR (100.6 MHz, CDCl_3) δ 59.6 (CH_3), 60.7 (CH_3), 71.0 (CH_2), 71.3 (CH), 72.7 (CH_2), 73.8 (CH), 76.2 (CH), 82.8 (CH), 102.3 (CH), 127.8 (3 × CH), 128.4 (2 × CH), 137.3 (C). MS m/z (rel intensity) 235 ($M^+ - \text{MeOH} - \text{MeO}$, <1), 91 (PhCH_2 , 100); HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4$ 235.0970, found 235.0975. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_6$: C, 60.39; H, 7.43. Found: C, 60.46; H, 7.49.

^1H and ^{13}C NMR spectra for compounds **12**, **14–20**, **22–27**, and **29–33**.