Efficient Synthesis of Methylene *exo*-Glycals: Another Use of Glycosylthiomethyl Chlorides

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General Information

Unless otherwise stated, all moisture-sensitive reactions were performed in oven-dried glassware under an argon atmosphere using dry solvents. Solvents were evaporated under reduced pressure while maintaining the water bath temperature below 40 °C. All reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F₂₅₄ coated on aluminium sheet and the compounds visualized by UV or by treatment with 8% H₂SO₄ in methanol followed by heating. Flash chromatography was performed with the indicated solvent system using 40-60 µm silica gel. Optical rotations were measured at 20 °C. CDCl₃ and tetramethylsilane was used as solvent and internal standard, respectively, for ¹H NMR (400 MHz) spectra. ¹³C NMR spectra were recorded at 100 MHz by using CDCl₃ as solvent and the signals were assigned with the aid of DEPT, HSQC. Yields refer to chromatographically pure compounds and are calculated based on reagents consumed.

Chloromethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (9). The reaction procedure was identical with that for **8**. Thiol **2** (160 mg, 0.29 mmol) yielded the title compound **9** (128 mg, 73%) as a colorless syrup: TLC *R_f* = 0.54 (cyclohexane/EtOAc, 4:1); [α]_D -35.6 (c 1.5 CHCl₃); ¹H NMR δ 7.30 (m, 20H, ArH), 4.97, 4.78 (AB peak, *J* = 11.6 Hz, 2H, H-1'), 4.96, 4.62 (AB peak, *J* = 11.6 Hz, 2H, PhCH₂), 4.82 (s, 2H, PhCH₂), 4.72 (AB peak, *J* = 12.0 Hz, 2H, PhCH₂), 4.68 (d, *J* = 9.6 Hz, 1H, H-1), 4.44 (AB peak, 2H, *J* = 11.6 Hz, PhCH₂), 3.98 (d, *J* = 2.4 Hz, 1H, H-4), 3.97 (t, *J* = 9.4 Hz, 1H, H-2), 3.66-3.58 (m, 4H, H-3, H-5, H-6); ¹³C NMR δ 138.8, 138.4, 138.2, 138.0, 128.7, 128.6, 128.55, 128.45, 128.3, 128.13, 128.07, 128.02, 127.9, 127.8 (aromatic carbons), 84.3 (C-3), 82.7 (C-1), 78.1 (C-2), 77.7 (C-5), 75.9, 74.8, 73.8 (3xPhCH₂), 73.7 (C-4), 73.0 (PhCH₂), 68.7 (C-6), 46.2 (C-1'); ESI-MS *m/z* 627.3 [M + Na]⁺, 643.3 [M + K]⁺;

ESI-HRMS calcd for $C_{35}H_{37}ClNaO_5S$ $[M + Na]^+$ 627.1948, found 627.1937.

Chloromethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio- β -D-glucopyranoside (10). The reaction procedure was identical with that for **8**. Thiol **3** (180 mg, 0.32 mmol) yielded the title compound **10** (167 mg, 86%) as a white amorphous solid: TLC R_f = 0.58 (cyclohexane/EtOAc, 4:1); $[\alpha]_D$ -82.0 (c 1.0 $CHCl_3$); 1H NMR δ 7.37-7.26 (m, 18H, ArH), 7.17 (m, 2H, ArH), 4.99, 4.80 (AB peak, J = 11.8 Hz, 2H, H-1'), 4.91, 4.85 (AB peak, J = 12.6 Hz, 2H, $PhCH_2$), 4.86, 4.76 (AB peak, J = 10.0 Hz, 2H, $PhCH_2$), 4.83, 4.58 (AB peak, J = 12.2 Hz, 2H, $PhCH_2$), 4.71 (d, J = 10.0 Hz, 1H, H-1), 4.61, 4.53 (AB peak, 2H, J = 12.2 Hz, $PhCH_2$), 3.75 (dd, J = 11.2, 2.4 Hz, 1H, H-6_a), 3.71 (m, 3H, H-6_b, H-3, H-4), 3.59 (t, J = 9.2 Hz, 1H, H-2), 3.53 (m, 1H, H-5); ^{13}C NMR δ 138.6, 138.3, 138.2, 137.9, 128.7, 128.63, 128.62, 128.60, 128.5, 128.15, 128.12, 128.02, 127.97, 127.96, 127.92, 127.88 (aromatic carbons), 86.8 (C-3), 82.3 (C-1), 81.4 (C-2), 79.5 (C-5), 77.9 (C-4), 76.0, 75.6, 75.3, 73.6 (4x $PhCH_2$), 68.9 (C-6), 46.1 (C-1'); ESI-MS m/z 627.2 $[M + Na]^+$, 643.3 $[M + K]^+$; ESI-HRMS calcd for $C_{35}H_{37}ClNaO_5S$ $[M + Na]^+$ 627.1948, found 627.1943.

Chloromethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio- α -D-mannopyranoside (11). The reaction procedure was identical with that for **8**. Thiol **4** (150 mg, 0.27 mmol) yielded the title compound **11** (114 mg, 70%) as a white amorphous solid: TLC R_f = 0.57 (cyclohexane/EtOAc, 4:1); $[\alpha]_D$ +65.5 (c 1.0 $CHCl_3$); 1H NMR δ 7.39-7.27 (m, 18H, ArH), 7.18 (m, 2H, ArH), 5.69 (br s, 1H, H-1), 4.88, 4.51 (AB peak, J = 10.8 Hz, 2H, $PhCH_2$), 4.85, 4.58 (AB peak, J = 11.8 Hz, 2H, H-1'), 4.76, 4.68 (AB peak, J = 12.4 Hz, 2H, $PhCH_2$), 4.65, 4.52 (AB peak, J = 12.0 Hz, 2H, $PhCH_2$), 4.55 (s, 2H, $PhCH_2$), 4.05 (t, J = 9.4 Hz, 1H, H-4), 3.97 (ddd-like, J = 9.6, 4.4, 1.2 Hz, 1H, H-5), 3.83 (dd-like, J = 3.2, 1.6 Hz, 1H, H-2), 3.79 (dd, J = 10.8, 4.8 Hz, 1H, H-6_a), 3.72 (m, 2H, H-6_b, H-3); ^{13}C NMR δ 138.5, 138.4, 138.2, 137.9, 128.7, 128.64, 128.56, 128.24, 128.20, 128.1, 128.0, 127.97, 127.89, 127.77 (aromatic carbons), 80.4 (C-1), 80.3 (C-3), 75.8 (C-2), 75.4 ($PhCH_2$),

75.0 (C-4), 73.7 (PhCH₂), 73.4 (C-5), 72.33, 72.27 (2xPhCH₂), 69.2 (C-6), 46.7 (C-1'); ESI-MS m/z 627.3 [M + Na]⁺; ESI-HRMS calcd for C₃₅H₃₇ClNaO₅S [M + Na]⁺ 627.1948, found 627.1943.

Chloromethyl 2,3,4-Tri-*O*-benzyl-1-thio- α -L-arabinopyranoside (12). The reaction procedure was identical with that for **8**. Thiol **5** (78 mg, 0.18 mmol) yielded the title compound **12** (62 mg, 71%) as a white amorphous solid: TLC R_f = 0.46 (cyclohexane/EtOAc, 4:1); [α]_D +56.8 (c 1.1 CHCl₃); ¹H NMR δ 7.32 (m, 15H, ArH), 5.12 (d, J = 4.4 Hz, 1H, H-1), 4.91, 4.67 (AB peak, J = 11.6 Hz, 2H, H-1'), 4.70, 4.62 (AB peak, J = 11.4 Hz, 2H, PhCH₂), 4.61 (s, 2H, PhCH₂), 4.59 (AB peak, J = 12.0 Hz, 2H, PhCH₂), 4.15 (dd, J = 11.6, 7.6 Hz, 1H, H-5_a), 3.86 (m, 2H, H-2, H-4), 3.72 (dd, J = 5.8, 3.0 Hz, H-3), 3.50 (dd, J = 11.6, 3.6 Hz, 1H, H-5_b); ¹³C NMR δ 138.4, 138.2, 137.9, 128.7, 128.61, 128.57, 128.2, 128.1, 128.0, 127.93, 127.92, 127.91 (aromatic carbons), 81.3 (C-1), 77.6 (C-2), 76.9 (C-3), 73.8 (PhCH₂), 72.7 (PhCH₂), 72.5 (C-4), 71.5 (PhCH₂), 62.3 (C-5), 47.7 (C-1'). ESI-MS m/z 507.3 [M + Na]⁺, 523.2 [M + K]⁺. ESI-HRMS calcd for C₂₇H₂₉ClNaO₄S [M + Na]⁺ 507.1373, found 507.1396.

Chloromethyl 2-*O*-Benzyl-3,4-*O*-isopropylidene-1-thio- α -L-arabinopyranoside (13). The reaction procedure was identical with that for **8**. Thiol **6** (118 mg, 0.40 mmol) yielded the title compound **13** (119 mg, 86%) as a colorless syrup: TLC R_f = 0.50 (cyclohexane/EtOAc, 3:1); [α]_D +34.2 (c 1.2 CHCl₃); ¹H NMR δ 7.40-7.28 (m, 5H, ArH), 4.97, 4.70 (AB peak, J = 11.6 Hz, 2H, H-1'), 4.88 (d, J = 8.0 Hz, 1H, H-1), 4.82, 4.73 (AB peak, J = 12.0 Hz, 2H, PhCH₂), 4.32 (dt, J = 6.0, 3.6 Hz, 1H, H-4), 4.26 (t, J = 6.0, 5.6 Hz, 1H, H-3), 4.15 (dd, J = 12.8, 3.6 Hz, 1H, H-5_a), 3.81 (dd, J = 12.8, 4.0 Hz, 1H, H-5_b) 3.64 (dd, J = 7.6, 5.6 Hz, 1H, H-2), 1.50, 1.38 (2s, 6H, 2Me); ¹³C NMR δ 137.7, 128.6, 128.4, 128.1 (aromatic carbons), 110.2 (Me₂C), 80.8 (C-1), 78.3

(C-2), 78.0 (C-3), 73.3 (PhCH₂), 72.7 (C-4), 65.2 (C-5), 46.4 (C-1'), 28.0, 26.3 (2xMe); ESI-MS m/z 383.3 [M + K]⁺. ESI-HRMS calcd for C₁₆H₂₁ClNaO₄S [M + Na]⁺ 367.0747, found 367.0752.

Chloromethyl 2,3-Di-O-benzyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (14). The reaction procedure was identical with that for **8**. Thiol **7** (96 mg, 0.21 mmol) yielded the title compound **14** (79 mg, 73%) as a colorless syrup: TLC R_f = 0.26 (cyclohexane/EtOAc, 3:1); [α]_D -78.6 (c 1.1 CHCl₃); ¹H NMR δ 7.56 (dd-like, J = 8.0, 2.0 Hz, 2H, ArH), 7.41-7.28 (m, 13H, ArH), 5.49 (s, 1H, PhCH), 4.98 (AB peak, J = 12.0 Hz, 2H, H-1'), 4.88 (s, 2H, PhCH₂), 4.75 (s, 2H, PhCH₂), 4.68 (d, J = 9.6 Hz, 1H, H-1), 4.31 (dd, J = 12.4, 1.2 Hz, 1H, H-6_a), 4.18 (d, J = 3.2 Hz, 1H, H-4), 4.09 (t, J = 9.4 Hz, 1H, H-2), 3.99 (dd, J = 12.4, 1.6 Hz, 1H, H-6_b), 3.63 (dd, J = 9.2, 3.6 Hz, 1H, H-3), 3.43 (s, 1H, H-5); ¹³C NMR δ 138.4, 138.3, 138.0, 129.3, 128.7, 128.6, 128.53, 128.48, 128.1, 128.0, 126.7 (aromatic carbons), 101.7 (PhCH), 82.0 (C-1), 81.4 (C-3), 77.0 (C-2), 75.9 (PhCH₂), 74.0 (C-4), 72.0 (PhCH₂), 70.3 (C-5), 69.5 (C-6), 45.8 (C-1'); ESI-MS m/z 535.3 [M + Na]⁺, 551.1 [M + K]⁺; ESI-HRMS calcd for C₂₈H₂₉ClNaO₅S [M + Na]⁺ 535.1322, found 535.1329.

2,3,4,6-Tetra-O-benzyl-β-D-galactopyranosyl chloromethyl sulfone (16). The reaction procedure was identical with that for **15**. Chloride **9** (120 mg, 0.20 mmol) yielded the title compound **16** (124 mg, 98%) as a white amorphous solid: TLC R_f = 0.38 (cyclohexane/EtOAc, 3:1); [α]_D -78.2 (c 1.2 CHCl₃); ¹H NMR δ 7.30 (m, 20H, ArH), 4.96, 4.61 (AB peak, J = 11.6 Hz, 2H, PhCH₂), 4.89 (AB peak, J = 12.0 Hz, 2H, PhCH₂), 4.72 (s, 2H, PhCH₂), 4.71, 4.36 (AB peak, J = 12.0 Hz, 2H, H-1'), 4.66 (d, J = 9.6 Hz, 1H, H-1), 4.48 (t, J = 9.6 Hz, 1H, H-2), 4.43 (AB peak, 2H, J = 11.6 Hz, PhCH₂), 3.93 (d, J = 2.0 Hz, 1H, H-4), 3.69 (dd, J = 9.6, 2.4 Hz, 1H, H-3), 3.67 (m, 1H, H-5), 3.61 (dd, J = 9.6, 6.0 Hz, 1H, H-6_a), 3.56 (dd, J = 9.6, 6.8 Hz, 1H, H-6_b); ¹³C NMR δ 138.4, 138.0, 137.8, 137.7, 128.9, 128.8, 128.7, 128.6, 128.5, 128.22, 128.19, 128.17,

128.15, 128.07, 127.9, 127.8 (aromatic carbons), 88.3 (C-1), 83.7 (C-3), 78.8 (C-5), 75.9, 74.8 (2xPhCH₂), 73.78 (C-2), 73.77, 73.15 (2xPhCH₂), 73.11 (C-4), 68.6 (C-6), 54.2 (C-1'); ESI-MS *m/z* 659.3 [M + Na]⁺, 675.3 [M + K]⁺; ESI-HRMS calcd for C₃₅H₃₇ClNaO₇S [M + Na]⁺ 659.1846, found 659.1850.

2,3,4,6-Tetra-*O*-benzyl- β -D-glucopyranosyl chloromethyl sulfone (17). The reaction procedure was identical with that for **15**. Chloride **10** (135 mg, 0.22 mmol) yielded the title compound **17** (142 mg, 100%) as a white amorphous solid: TLC *R_f* = 0.40 (cyclohexane/EtOAc, 3:1); [α]_D -57.5 (c 1.6 CHCl₃); ¹H NMR δ 7.37-7.27 (m, 18H, ArH), 7.17 (m, 2H, ArH), 4.94, 4.79 (AB peak, *J* = 9.8 Hz, 2H, PhCH₂), 4.93, 4.88 (AB peak, *J* = 11.2 Hz, 2H, PhCH₂), 4.81, 4.59 (AB peak, *J* = 10.8 Hz, 2H, PhCH₂), 4.74, 4.35 (AB peak, *J* = 12.2 Hz, 2H, H-1'), 4.71 (d, *J* = 9.6 Hz, 1H, H-1), 4.56, 4.51 (AB peak, 2H, *J* = 11.4 Hz, PhCH₂), 4.11 (t, *J* = 9.0 Hz, 1H, H-2), 3.80 (t, *J* = 8.8 Hz, 1H, H-3), 3.69 (m, 2H, H-6), 3.66 (t, *J* = 8.8 Hz, 1H, H-4), 3.58 (ddd, *J* = 9.6, 4.0, 2.4 Hz, 1H, H-5); ¹³C NMR δ 138.2, 138.0, 137.8, 137.4, 128.8, 128.75, 128.71, 128.69, 128.66, 128.3, 128.2, 128.1, 127.93, 127.85 (aromatic carbons), 87.3 (C-1), 86.2 (C-3), 80.2 (C-5), 77.1 (C-4), 77.0 (C-2), 76.1, 75.7, 75.4, 73.5 (4xPhCH₂), 68.6 (C-6), 54.3 (C-1'); ESI-MS *m/z* 659.3 [M + Na]⁺, 675.2 [M + K]⁺; ESI-HRMS calcd for C₃₅H₃₇ClNaO₇S [M + Na]⁺ 659.1846, found 659.1876.

2,3,4,6-Tetra-*O*-benzyl- α -D-mannopyranosyl chloromethyl sulfone (18). The reaction procedure was identical with that for **15**. Chloride **11** (112 mg, 0.185 mmol) yielded the title compound **18** (108 mg, 92%) as a white amorphous solid: TLC *R_f* = 0.39 (cyclohexane/EtOAc, 4:1); [α]_D +56.8 (c 1.1 CHCl₃); ¹H NMR δ 7.39-7.26 (m, 18H, ArH), 7.13 (dd-like, *J* = 7.2, 2.4 Hz, 2H, ArH), 5.26 (d, *J* = 3.6 Hz, 1H, H-1), 4.87, 4.26 (AB peak, *J* = 12.4 Hz, 2H, H-1'), 4.69, 4.64 (AB peak, *J* = 11.6 Hz, 2H, PhCH₂), 4.67, 4.38 (AB peak, *J* = 11.4 Hz, 2H, PhCH₂), 4.60 (s,

2H, PhCH₂), 4.58, 4.48 (AB peak, $J = 11.8$ Hz, 2H, PhCH₂), 4.44 (t, $J = 3.6, 3.2$ Hz, 1H, H-2), 4.31 (ddd, $J = 8.8, 5.6, 2.4$ Hz, 1H, H-5), 4.01 (dd, $J = 7.2, 3.2$ Hz, 1H, H-3), 3.84 (dd, $J = 9.2, 7.2$ Hz, 1H, H-4), 3.66 (dd, $J = 10.8, 2.4$ Hz, 1H, H-6_a), 3.61 (dd, $J = 10.8, 5.6$ Hz, 1H, H-6_b); ¹³C NMR δ 138.1, 138.0, 137.2, 128.8, 128.7, 128.65, 128.62, 128.4, 128.2, 128.13, 128.08, 128.05, 127.95, 127.92 (aromatic carbons), 86.2 (C-1), 78.4 (C-3), 76.6 (C-5), 74.3 (C-4), 74.2, 73.54, 73.52, 73.1 (4xPhCH₂), 71.1 (C-2), 69.5 (C-6), 53.2 (C-1'); ESI-MS m/z 659.4 [M + Na]⁺; ESI-HRMS calcd for C₃₅H₃₇ClNaO₇S [M + Na]⁺ 659.1846, found 659.1833.

2,3,4-Tri-*O*-benzyl- α -L-arabinopyranosyl chloromethyl sulfone (19). The reaction procedure was identical with that for **15**. Chloride **12** (60 mg, 0.12 mmol) yielded the title compound **19** (59 mg, 95%) as a white amorphous solid: TLC $R_f = 0.46$ (cyclohexane/EtOAc, 4:1); [α]_D +56.8 (c 1.1 CHCl₃); ¹H NMR δ 7.35 (m, 15H, ArH), 4.86 (s, 2H, PhCH₂), 4.74, 4.37 (AB peak, $J = 12.0$ Hz, 2H, H-1'), 4.69 (AB peak, $J = 12.4$ Hz, 2H, PhCH₂), 4.66 (d, $J = 8.4$ Hz, 1H, H-1), 4.63 (AB peak, $J = 12.0$ Hz, 2H, PhCH₂), 4.48 (t, $J = 8.6$ Hz, 1H, H-2), 4.24 (dd, $J = 12.4, 3.2$ Hz, 1H, H-5_a), 3.76 (m, 1H, H-4), 3.68 (dd, $J = 8.6, 3.0$ Hz, H-3), 3.43 (dd, $J = 12.6, 1.4$ Hz, 1H, H-5_b); ¹³C NMR δ 138.0, 137.9, 137.7, 128.8, 128.71, 128.69, 128.65, 128.2, 128.11, 128.09, 127.99 (aromatic carbons), 88.0 (C-1), 80.6 (C-3), 75.6 (PhCH₂), 73.3 (C-2), 72.4 (PhCH₂), 71.9 (C-4), 71.7 (PhCH₂), 67.7 (C-5), 54.4 (C-1'); ESI-MS m/z 539.1 [M + Na]⁺, 555.1 [M + K]⁺; ESI-HRMS calcd for C₂₇H₂₉ClNaO₆S [M + Na]⁺ 539.1271, found 539.1287.

2-*O*-Benzyl-3,4-*O*-isopropylidene- α -L-arabinopyranosyl chloromethyl sulfone (20). The reaction procedure was identical with that for **15**. Chloride **13** (98 mg, 0.28 mmol) yielded the title compound **20** (107 mg, 100%) as a white amorphous solid: TLC $R_f = 0.21$ (cyclohexane/EtOAc, 3:1); [α]_D +47.2 (c 1.1 CHCl₃); ¹H NMR δ 7.44-7.27 (m, 5H, ArH), 4.87, 4.76 (AB peak, $J = 11.2$ Hz, 2H, PhCH₂), 4.78, 4.39 (AB peak, $J = 12.0$ Hz, 2H, H-1'), 4.71 (d, J

= 8.8 Hz, 1H, H-1), 4.38 (t, J = 6.8, 6.4 Hz, 1H, H-3), 4.33 (m, 1H, H-4), 4.20 (dd, J = 12.8, 4.0 Hz, 1H, H-5_a), 4.19 (dd, J = 8.8, 6.4 Hz, 1H, H-2), 3.92 (dd, J = 12.8, 4.0 Hz, 1H, H-5_b) 1.54, 1.38 (2s, 6H, 2Me); ^{13}C NMR δ 137.3, 128.63, 128.62, 128.3 (aromatic carbons), 110.7 (Me₂C), 86.6 (C-1), 78.2 (C-3), 74.1 (C-2), 74.0 (PhCH₂), 72.2 (C-4), 67.2 (C-5), 54.1 (C-1'), 27.6, 25.8 (2xMe); ESI-MS m/z 415.2 [M + K]⁺. ESI-HRMS calcd for C₁₆H₂₁ClNaO₆S [M + Na]⁺ 399.0645, found 399.0631.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- β -D-galactopyranosyl chloromethyl sulfone (21). The reaction procedure was identical with that for **15**. Chloride **14** (70 mg, 0.14 mmol) yielded the title compound **21** (74 mg, 100%) as a white amorphous solid: TLC R_f = 0.21 (cyclohexane/EtOAc, 2:1); $[\alpha]_D$ -26.6 (c 1.2 CHCl₃); ^1H NMR δ 7.54 (dd-like, J = 8.0, 2.0 Hz, 2H, ArH), 7.42-7.28 (m, 13H, ArH), 5.46 (s, 1H, PhCH), 4.91 (s, 2H, PhCH₂), 4.83, 4.48 (AB peak, J = 12.4 Hz, 2H, H-1'), 4.75 (AB peak, J = 12.4 Hz, 2H, PhCH₂), 4.73 (d, J = 9.2 Hz, 1H, H-1), 4.53 (t, J = 9.6 Hz, 1H, H-2), 4.28 (dd, J = 12.8, 1.6 Hz, 1H, H-6_a), 4.12 (d, J = 3.6 Hz, 1H, H-4), 3.98 (dd, J = 12.8, 1.6 Hz, 1H, H-6_b), 3.73 (dd, J = 9.6, 3.6 Hz, 1H, H-3), 3.46 (d-like, J = 0.8 Hz, 1H, H-5); ^{13}C NMR δ 137.9, 137.8, 137.6, 129.6, 128.9, 128.8, 128.61, 128.60, 128.3, 128.2, 128.0, 126.7 (aromatic carbons), 101.8 (PhCH), 88.4 (C-1), 80.7 (C-3), 76.0 (PhCH₂), 73.2 (C-4), 73.0 (C-2), 72.2 (PhCH₂), 71.0 (C-5), 68.9 (C-6), 54.2 (C-1'); ESI-MS m/z 567.3 [M + Na]⁺, 583.3 [M + K]⁺; ESI-HRMS calcd for C₂₈H₂₉ClNaO₇S [M + Na]⁺ 567.1220, found 567.1208.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-galactopyranose (23).¹ The reaction procedure was identical with that for **22**. Sulfone **16** (117 mg, 0.18 mmol) yielded the title compound **23** (86 mg, 87%) as a colorless syrup: TLC R_f = 0.65 (cyclohexane/EtOAc, 3:1); ^1H NMR δ 7.29 (m, 20H, ArH), 4.92, 4.60 (AB peak, J = 11.6 Hz, 2H, PhCH₂), 4.78, 4.71 (AB peak,

$J = 11.6$ Hz, 2H, PhCH_2), 4.74 (AB peak, $J = 12.0$ Hz, 2H, PhCH_2), 4.72 (d, $J = 1.6$ Hz, 1H, $\text{H-1}'_a$), 4.71 (d, $J = 1.2$ Hz, 1H, $\text{H-1}'_b$), 4.48 (AB peak, 2H, $J = 12.0$ Hz, PhCH_2), 4.37 (dt-like, $J = 8.8, 1.2$ Hz, 1H, H-2), 4.05 (t, $J = 2.4$ Hz, 1H, H-4), 3.82 (td, $J = 6.2, 1.6$ Hz, 1H, H-5), 3.70 (dd, $J = 9.6, 6.0$ Hz, 1H, H-6_a), 3.66 (dd, $J = 8.8, 2.8$ Hz, 1H, H-3), 3.62 (dd, $J = 9.6, 6.8$ Hz, 1H, H-6_b); ^{13}C NMR δ 157.6 (C-1), 138.72, 138.71, 138.4, 138.2, 128.64, 128.60, 128.59, 128.49, 128.2, 128.15, 128.12, 128.0, 127.9, 127.83, 127.80, 127.7 (aromatic carbons), 95.3 (C-1'), 82.3 (C-3), 78.6 (C-5), 77.1 (C-2), 74.7 (C-4), 74.6, 74.0, 73.7, 73.2 (4x PhCH_2), 68.8 (C-6); ESI-MS m/z 559.3 $[\text{M} + \text{Na}]^+$, 575.2 $[\text{M} + \text{K}]^+$; ESI-HRMS calcd for $\text{C}_{35}\text{H}_{36}\text{NaO}_5$ $[\text{M} + \text{Na}]^+$ 559.2460, found 559.2435.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-glucopyranose (24).^{1,2} The reaction procedure was identical with that for **22**. Sulfone **17** (96 mg, 0.15 mmol) yielded the title compound **24** (70 mg, 87%) as a white amorphous solid: TLC $R_f = 0.65$ (cyclohexane/EtOAc, 3:1); ^1H NMR δ 7.37-7.22 (m, 18H, ArH), 7.14 (m, 2H, ArH), 4.86, 4.72 (AB peak, $J = 11.2$ Hz, 2H, PhCH_2), 4.78, 4.51 (AB peak, $J = 10.6$ Hz, 2H, PhCH_2), 4.77, 4.65 (AB peak, $J = 12.0$ Hz, 2H, PhCH_2), 4.76 (d, $J = 1.6$ Hz, 1H, $\text{H-1}'_a$), 4.63, 4.53 (AB peak, 2H, $J = 11.2$ Hz, PhCH_2), 4.62 (s, 1H, $\text{H-1}'_b$), 3.96 (dt, $J = 7.6, 0.8$ Hz, 1H, H-2), 3.75 (m, 4H, H-4, H-5, H-6), 3.70 (t, $J = 7.2$ Hz, 1H, H-3); ^{13}C NMR δ 156.6 (C-1), 138.6, 138.32, 138.26, 138.1, 128.7, 128.63, 128.59, 128.57, 128.15, 128.12, 128.09, 128.02, 127.93, 127.91, 127.88 (aromatic carbons), 95.0 (C-1'), 84.9 (C-3), 79.2 (C-2), 78.8 (C-4), 77.8 (C-5), 74.72, 74.66, 73.8, 73.0 (4x PhCH_2), 69.0 (C-6); ESI-MS m/z 559.4 $[\text{M} + \text{Na}]^+$, 575.3 $[\text{M} + \text{K}]^+$; ESI-HRMS calcd for $\text{C}_{35}\text{H}_{36}\text{NaO}_5$ $[\text{M} + \text{Na}]^+$ 559.2460, found 559.2471.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-methylidene-D-mannopyranose (25).¹ The reaction procedure was identical with that for **22**. Sulfone **18** (89 mg, 0.14 mmol) yielded the title

compound **25** (61 mg, 81%) as a colorless syrup: TLC R_f = 0.54 (cyclohexane/EtOAc, 4:1); ^1H NMR δ 7.41-7.25 (m, 18H, ArH), 7.18 (m, 2H, ArH), 4.92, 4.53 (AB peak, J = 11.0 Hz, 2H, PhCH_2), 4.83 (s, 1H, H-1'_a), 4.77, 4.43 (AB peak, J = 12.4 Hz, 2H, PhCH_2), 4.67, 4.57 (AB peak, J = 12.2 Hz, 2H, PhCH_2), 4.62, 4.55 (AB peak, 2H, J = 11.8 Hz, PhCH_2), 4.37 (s, 1H, H-1'_b), 4.17 (t, J = 9.2 Hz, 1H, H-4), 4.07 (d, J = 3.2 Hz, 1H, H-2), 3.79 (m, 2H, H-6), 3.66 (dd, J = 9.2, 3.2 Hz, 1H, H-3), 3.62 (m, 1H, H-5); ^{13}C NMR δ 155.1 (C-1), 138.6, 138.5, 138.4, 138.2, 128.59, 128.57, 128.56, 128.4, 128.2, 128.1, 128.0, 127.99, 127.88, 127.84, 127.78 (aromatic carbons), 99.9 (C-1'), 81.7 (C-3), 80.4 (C-5), 75.3 (PhCH_2), 74.3 (C-4), 73.8 (C-2), 73.7, 71.6 (2x PhCH_2), 69.61 (C-6), 69.56 (PhCH_2); ESI-MS m/z 537.4 [$\text{M} + \text{H}$]⁺, 559.4 [$\text{M} + \text{Na}$]⁺, 575.3 [$\text{M} + \text{K}$]⁺; ESI-HRMS calcd for $\text{C}_{35}\text{H}_{37}\text{O}_5$ [$\text{M} + \text{H}$]⁺ 537.2641, found 537.2616.

2,3,4-Tri-*O*-benzyl-1-deoxy-1-methylidene-L-arabinopyranose (26). The reaction procedure was identical with that for **22**. Sulfone **19** (49 mg, 95 μmol) yielded the title compound **26** (35 mg, 89%) as a colorless syrup.: TLC R_f = 0.57 (cyclohexane/EtOAc, 3:1); $[\alpha]_D^{+25}$ +162.5 (c 1.1 CHCl_3); ^1H NMR δ 7.30 (m, 15H, ArH), 4.77 (s, 1H, H-1'_a), 4.69 (AB peak, J = 12.0 Hz, 2H, PhCH_2), 4.68, 4.49 (AB peak, J = 11.6 Hz, 2H, PhCH_2), 4.64 (AB peak, J = 12.4 Hz, 2H, PhCH_2), 4.50 (s, 1H, H-1'_b), 4.10 (d, J = 6.0 Hz, 1H, H-2), 4.03 (m, 2H, H-4, H-5_a), 3.83 (dd, J = 6.0, 2.4 Hz, 1H, H-3), 3.78 (m, 1H, H-5_b); ^{13}C NMR δ 156.0 (C-1), 138.7, 138.4, 138.3, 128.64, 128.62, 128.56, 128.0, 127.94, 127.90, 127.87, 127.83 (aromatic carbons), 98.1 (C-1'), 77.1 (C-3), 76.4 (C-2), 72.8 (C-4), 72.7, 71.8, 71.6 (3x PhCH_2), 67.1 (C-5); ESI-MS m/z 417.3 [$\text{M} + \text{H}$]⁺, 439.4 [$\text{M} + \text{Na}$]⁺; ESI-HRMS calcd for $\text{C}_{27}\text{H}_{29}\text{O}_4$ [$\text{M} + \text{H}$]⁺ 417.2066, found 417.2060.

2-*O*-benzyl-3,4-*O*-isopropylidene-1-deoxy-1-methylidene-L-arabinopyranose (27). The reaction procedure was identical with that for **22**. Sulfone **20** (75 mg, 0.20 mmol) yielded the title compound **27** (52 mg, 94%) as a colorless syrup.: TLC R_f = 0.70 (cyclohexane/EtOAc, 3:1);

$[\alpha]_D +52.0$ (c 1.3 CHCl_3); ^1H NMR δ 7.33 (m, 5H, ArH), 4.72, 4.43 (AB peak, $J = 11.8$ Hz, 2H, PhCH_2), 4.63 (d, $J = 0.8$ Hz, 1H, $\text{H-1}'_a$), 4.45 (dd, $J = 7.6, 2.4$ Hz, 1H, H-3), 4.40 (m, 1H, H-4), 4.39 (dd, $J = 12.4, 1.2$ Hz, 1H, H-5_a), 4.15 (d, $J = 0.8$ Hz, 1H, $\text{H-1}'_b$), 4.09 (dd, $J = 12.4, 1.6$ Hz, 1H, H-5_b), 3.90 (d, $J = 2.4$ Hz, 1H, H-2), 1.47, 1.33 (2s, 6H, 2Me); ^{13}C NMR δ 152.1 (C-1), 137.8, 128.7, 128.3, 128.1 (aromatic carbons), 110.0 (Me_2C), 93.6 (C-1'), 75.7 (C-2), 73.7 (C-3), 72.7 (C-4), 70.0 (PhCH_2), 64.1 (C-5), 26.5, 24.6 (2xMe); ESI-MS m/z 299.6 $[\text{M} + \text{Na}]^+$. ESI-HRMS calcd for $\text{C}_{16}\text{H}_{21}\text{O}_4$ $[\text{M} + \text{H}]^+$ 277.1440, found 277.1426.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-methylidene-D-galactopyranose (28). The reaction procedure was identical with that for **22**. Sulfone **21** (52 mg, 95 μmol) yielded the title compound **28** (36 mg, 86%) as a white amorphous solid: TLC $R_f = 0.53$ (cyclohexane/EtOAc, 2:1); $[\alpha]_D +86.3$ (c 1.2 CHCl_3); ^1H NMR δ 7.55 (dd-like, $J = 7.6, 2.0$ Hz, 2H, ArH), 7.40-7.28 (m, 13H, ArH), 5.52 (s, 1H, PhCH), 4.85, 4.77 (AB peak, $J = 10.8$ Hz, 2H, PhCH_2), 4.83, 4.76 (AB peak, $J = 12.4$ Hz, 2H, PhCH_2), 4.81 (s, 1H, $\text{H-1}'_a$), 4.75 (s, 1H, $\text{H-1}'_b$), 4.48 (d, $J = 9.6$ Hz, 1H, H-2), 4.35 (dd, $J = 12.4, 1.6$ Hz, 1H, H-6_a), 4.23 (d, $J = 2.4$ Hz, 1H, H-4), 3.99 (dd, $J = 12.8, 1.6$ Hz, 1H, H-6_b), 3.64 (dd, $J = 9.8, 3.4$ Hz, 1H, H-3), 3.47 (d, $J = 0.8$ Hz, 1H, H-5); ^{13}C NMR δ 158.5 (C-1), 138.6, 138.5, 137.9, 129.3, 128.62, 128.61, 128.4, 128.11, 127.97, 127.94, 127.90, 126.7 (aromatic carbons), 101.5 (PhCH), 94.9 (C-1'), 80.3 (C-3), 76.4 (C-2), 74.9 (C-4), 74.7, 72.4 (2x PhCH_2), 71.4 (C-5), 69.7 (C-6); ESI-MS m/z 445.3 $[\text{M} + \text{H}]^+$, 467.2 $[\text{M} + \text{Na}]^+$, 483.2 $[\text{M} + \text{K}]^+$; ESI-HRMS calcd for $\text{C}_{28}\text{H}_{29}\text{O}_5$ $[\text{M} + \text{H}]^+$ 445.2015, found 445.2001.

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^1H NMR spectrum of compound 8

^{13}C NMR spectrum of compound 8

¹H NMR spectrum of compound 9

¹³C NMR spectrum of compound 9

^1H NMR spectrum of compound 10

^{13}C NMR spectrum of compound 10

^1H NMR spectrum of compound 11

^{13}C NMR spectrum of compound 11

^1H NMR spectrum of compound 12

^{13}C NMR spectrum of compound 12

^1H NMR spectrum of compound 13

^{13}C NMR spectrum of compound 13

^1H NMR spectrum of compound 14

^{13}C NMR spectrum of compound 14

¹H NMR spectrum of compound 15

^{13}C NMR spectrum of compound 15

^1H NMR spectrum of compound 16

^{13}C NMR spectrum of compound 16

^1H NMR spectrum of compound 17

^{13}C NMR spectrum of compound 17

¹H NMR spectrum of compound 18

¹³C NMR spectrum of compound 18

^1H NMR spectrum of compound 19

^{13}C NMR spectrum of compound 19

^1H NMR spectrum of compound 20

^{13}C NMR spectrum of compound 20

^1H NMR spectrum of compound 22

¹³C NMR spectrum of compound 22

¹H NMR spectrum of compound 23

^{13}C NMR spectrum of compound 23

^1H NMR spectrum of compound 24

^{13}C NMR spectrum of compound 24

^1H NMR spectrum of compound 25

^{13}C NMR spectrum of compound 25

^1H NMR spectrum of compound 26

^{13}C NMR spectrum of compound 26

^1H NMR spectrum of compound 27

^{13}C NMR spectrum of compound 27

^1H NMR spectrum of compound 28

^{13}C NMR spectrum of compound 28