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Experimental Section

General Techniques. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF), toluene and diethyl ether (ether) were distilled from sodium-benzophenone, and methylene chloride (CH_2Cl_2) from calcium hydride. Anhydrous solvents were also obtained by passing them through commercially available alumina columns. Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reagents were purchased at highest commercial quality and used without further purification unless otherwise stated. Reactions were monitored by thin layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid or *p*-anisaldehyde solution and heat as developing agents. E. Merck silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25, 0.50 or 1 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker AMX-600 or AMX-500 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter. High resolution mass spectra (HRMS) were recorded on a VG ZAB-ZSE mass spectrometer under fast atom bombardment (FAB) conditions with NBA as the matrix. Melting points (m.p.) are uncorrected and were recorded on a Thomas Hoover Unimelt capillary melting point apparatus.

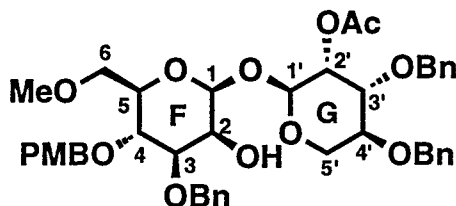
Typical procedure for the synthesis of disaccharides. Preparation of compound 7.

In a 50 mL Schlenk-tube were added diol **3** (91 mg, 0.20 mmole), (*n*-Bu)₂SnO (60 mg, 0.24 mmol) and anhydrous methanol (5 mL) and the mixture was brought to a gentle reflux under argon. After the solution turned clear, refluxing was continued for an additional 2 h, before cooling to ambient temperature and concentration under reduced pressure. The residue was azeotroped with benzene (2 mL) before addition of imidate **3** (85 mg, 0.13 mmol) in benzene (2 mL). Removal of the solvent under reduced pressure followed by further drying by azeotroping with benzene (3 x 2 mL) and finally applying high vacuum (1 mbar, 0.5 h) gave an amorphous residue which was dissolved in anhydrous ether (1.0 mL). The solution was cooled (0 °C) and TMSOTf in ether (0.13 mL, 0.5 M) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature and stirred until TLC analysis indicated complete disappearance of imidate **4** (ca 48 h). Triethylamine (0.2 mL) was added, followed by a saturated aqueous solution of NaHCO₃ (10 mL) and EtOAc (30 mL). The layers were separated and the organic phase was extracted with brine (5 mL), dried (MgSO₄), filtered, and concentrated *in vacuo*. Purification of the residual oil on silica gel (ether/hexanes, 1:2→1:1→2:1) afforded compounds **7** (81 mg, 66%) and **9** (17 mg, 9%).

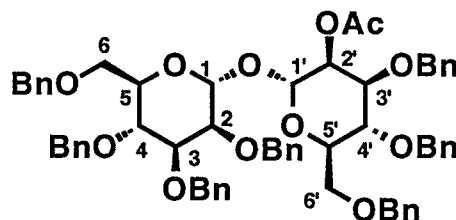
Typical procedure for the synthesis of trisaccharides. Preparation of compound 9.

The procedure as described above for the synthesis of disaccharides was followed, except for the use of 2.2 equiv of glycosyl fluoride **8** instead of trichloroacetimidate **4**. Yield of **9** (84%).

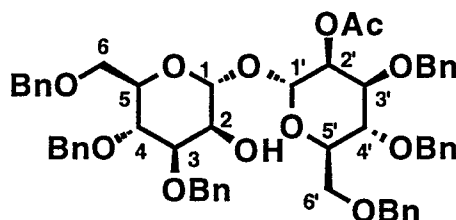
FG ring system 2



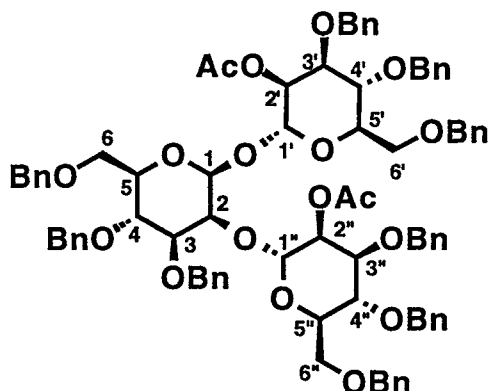
$R_f = 0.14$ (70% ether in hexanes); $[\alpha]_D^{20} -32.2$ ($c = 0.7$, CHCl_3); IR (film) ν_{max} 3477, 3031, 2922, 1746, 1613, 1513, 1456, 1371, 1304, 1242, 1105, 1048, 924, 820, 738, 699 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.39-7.26 (m, 15 H, ArH), 7.25 (d, $J = 8.9$ Hz, 2 H, ArH, PMB), 6.88 (d, $J = 8.8$ Hz, 2 H, ArH, PMB), 5.52 (dd, $J = 2.8, 2.7$ Hz, 1 H, H-2'), 5.19 (d, $J = 2.2$ Hz, 1 H, H-1'), 4.84-4.53 (m, 8 H, OCH_2Ar), 4.67 (s, 1 H, H-1), 4.06 (d, $J = 3.7$ Hz, 1 H, H-2), 3.92 (dd, $J = 9.3, 3.3$ Hz, 1 H, H-3'), 3.90 (dd, $J = 9.4, 9.4$ Hz, 1 H, H-4), 3.86 (ddd, $J = 9.6, 3.8, 2.8$ Hz, 1 H, H-4'), 3.81 (s, 3 H, ArOCH_3), 3.79 (dd, $J = 11.1, 5.5$ Hz, 1 H, H-6a), 3.63 (dd, $J = 11.1, 2.5$ Hz, 1 H, H-5'a), 3.60 (dd, $J = 11.1, 4.3$ Hz, 1 H, H-5'b), 3.56 (dd, $J = 9.2, 3.1$ Hz, 1 H, H-3), 3.52 (dd, $J = 10.8, 10.5$ Hz, 1 H, H-6b), 3.38 (s, 3 H, OCH_3), 3.35 (ddd, $J = 9.9, 4.3, 2.5$ Hz, 1 H, H-5), 2.12 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 169.8, 159.3, 138.3, 137.9, 137.7, 130.3, 129.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 113.8, 101.6, 94.8, 94.5, 81.2, 77.2, 77.0, 76.9, 76.8, 75.3, 74.8, 73.7, 73.7, 73.4, 71.9, 71.4, 71.1, 68.3, 68.1, 61.7, 59.3, 56.7, 55.2, 33.4, 29.6, 20.9; ^{13}C NMR (150 MHz, CDCl_3 ; proton coupled) δ 94.9 ($J_{\text{C,H}} = 168.8$ Hz), 94.6 ($J_{\text{C,H}} = 159.1$ Hz); HRMS (FAB), calcd for $\text{C}_{43}\text{H}_{50}\text{O}_{12}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 891.2357, found 891.2379.

Disaccharide 5

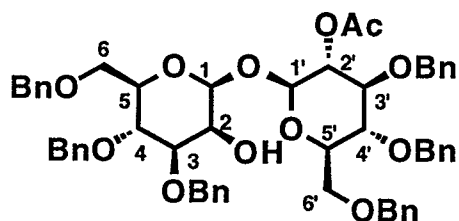
$R_f = 0.38$ (60% ether in hexanes); $[\alpha]_D^{20} +31.6$ ($c = 0.9$, CHCl_3); IR (film) ν_{max} 3030, 2920, 1732, 1453, 1366, 1234, 1099, 1025, 826, 741, 698 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.38-7.20 (m, 30 H, ArH), 5.26 (dd, $J = 3.2, 1.9$ Hz, 1 H, H-2'), 5.19 (d, $J = 1.7$ Hz, 1 H, H-1), 5.14 (d, $J = 1.5$ Hz, 1 H, H-1'), 4.91-4.49 (m, 14 H, OCH_2Ar), 4.09 (dd, $J = 9.9, 9.8$ Hz, 1 H, H-4'), 3.88 (dd, $J = 9.9, 9.8$ Hz, 1 H, H-4), 3.86-3.83 (m, 2 H, H-6a, H-6'a), 3.80 (dd, $J = 9.3, 3.2$ Hz, 1 H, H-3'), 3.78 (ddd, $J = 10.0, 4.1, 1.6$ Hz, 1 H, H-5'), 3.73-3.71 (m, 2 H, H-6b, H-6'b), 3.62 (dd, $J = 2.3, 1.6$ Hz, 1 H, H-2), 3.59 (dd, $J = 10.7, 1.6$ Hz, 1 H, H-3), 3.55 (ddd, $J = 10.0, 4.4, 1.5$ Hz, 1 H, H-5), 2.13 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.2, 138.3, 138.2, 138.2, 138.1, 138.0, 137.9, 137.7, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.5, 93.2, 93.1, 79.4, 77.7, 75.3, 75.2, 74.4, 74.0, 74.0, 73.5, 73.3, 72.5, 72.3, 72.1, 71.8, 68.6, 68.5, 68.2, 21.0; ^{13}C NMR (150 MHz, CDCl_3 ; proton coupled) δ 93.2 ($J_{\text{C,H}} = 174.1$ Hz), 93.1 ($J_{\text{C,H}} = 175.1$ Hz); HRMS (FAB), calcd for $\text{C}_{63}\text{H}_{66}\text{O}_{12}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1147.3609, found 1147.3678.

Disaccharide 7

$R_f = 0.15$ (60% ether in hexanes); $[\alpha]_D^{20} +29.4$ ($c = 0.49$, CHCl_3); IR (neat) ν_{max} 3467, 3030, 2918, 2864, 1742, 1496, 1453, 1368, 1237, 1103, 1051, 911, 738, 698 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.38-7.17 (m, 30 H, ArH), 5.40 (dd, $J = 3.1, 1.8$ Hz, 1 H, H-2'), 5.17 (d, $J = 1.6$ Hz, 1 H, H-1'), 4.89-4.32 (m, 12 H, OCH_2Ar), 4.68 (s, 1 H, H-1), 4.14 (bd, $J = 10.3$ Hz, 1 H, H-5'), 4.12 (d, $J = 3.0$ Hz, 1 H, H-2), 4.07 (dd, $J = 9.7, 3.2$ Hz, 1 H, H-3'), 3.98 (dd, $J = 9.9, 9.8$ Hz, 1 H, H-4'), 3.87 (dd, $J = 9.8, 9.4$ Hz, 1 H, H-4), 3.70 (dd, $J = 10.9, 3.0$ Hz, 1 H, H-6'a), 3.65 (d, $J = 2.6$ Hz, 2 H, H-6), 3.60 (dd, $J = 11.0, 2.5$ Hz, 1 H, H-6'b), 3.56 (dd, $J = 9.3, 2.9$ Hz, 1 H, H-3), 3.42 (dt, $J = 9.8, 2.7$ Hz, 1 H, H-5), 2.15 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.5, 138.6, 138.2, 138.1, 137.9, 137.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.5, 127.4, 99.2, 98.0, 81.3, 77.8, 75.5, 75.1, 74.9, 74.0, 73.7, 73.3, 73.2, 72.2, 72.1, 71.5, 68.9, 68.6, 68.2, 21.1; ^{13}C NMR (150 MHz, CDCl_3 ; proton coupled) δ 99.2 ($J_{\text{C,H}} = 156.9$ Hz), 98.0 ($J_{\text{C,H}} = 171.3$ Hz); HRMS (FAB), calcd for $\text{C}_{56}\text{H}_{60}\text{O}_{12}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1057.3139, found 1057.3111.

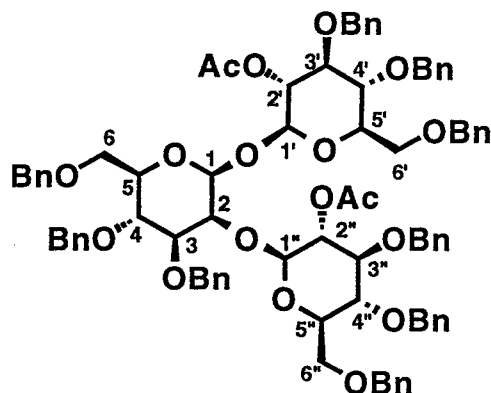
Trisaccharide 9

$R_f = 0.11$ (60% ether in hexanes); $[\alpha]_D^{20} +21.8$ ($c = 1.71$, CHCl_3); IR (film) ν_{max} 3031, 2864, 1743, 1496, 1454, 1368, 1236, 1110, 912, 739, 698 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.02 (m, 45 H, ArH), 5.69 (dd, $J = 3.3, 1.8$ Hz, 1 H, H-2'), 5.43 (s, 1 H, H-2''), 5.38 (s, 1 H, H-1'), 5.12 (s, 1 H, H-1''), 4.92-4.27 (m, 14 H, OCH_2Ar), 4.64 (s, 1 H, H-1), 4.35 (d, $J = 1.6$ Hz, 1 H, H-2), 4.32 (bd, $J = 10.4$ Hz, 1 H, H-5'), 4.16 (dd, $J = 9.6, 3.4$ Hz, 1 H, H-3'), 4.00 (dd, $J = 9.7, 9.4$ Hz, 1 H, H-4''), 3.93 (dd, $J = 10.0, 9.9$ Hz, 1 H, H-4'), 3.89-3.82 (m, 3 H, H-3'', H-4, H-6'a), 3.73-3.66 (m, 5 H, H-3, H-6, H-6'b, H-6''), 3.49 (ddd, $J = 9.9, 5.6, 1.9$ Hz, 1 H, H-5), 2.17 (s, 3 H, C(O)CH_3), 2.13 (s, 3 H, C(O)CH_3); ^{13}C NMR (150 MHz, CDCl_3) δ 170.2, 170.1, 138.5, 138.4, 138.2, 138.2, 138.0, 138.0, 137.9, 137.6, 128.3, 128.3, 128.2, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.4, 127.4, 127.1, 127.0, 98.9, 98.7, 98.2, 82.4, 78.6, 78.6, 75.7, 75.1, 75.0, 74.8, 74.2, 73.8, 73.8, 73.3, 73.1, 72.1, 72.0, 71.8, 71.8, 71.5, 71.5, 69.3, 68.6, 68.5, 68.2, 68.1, 21.1, 21.0; ^{13}C NMR (150 MHz, CDCl_3 ; proton coupled) δ 98.9 ($J_{\text{C,H}} = 177.5$ Hz), 98.7 ($J_{\text{C,H}} = 151.2$ Hz), 98.2 ($J_{\text{C,H}} = 170.5$ Hz); HRMS (FAB), calcd for $\text{C}_{85}\text{H}_{90}\text{O}_{18}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1532.5182, found 1532.5122.

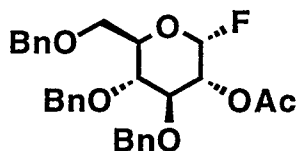
Disaccharide 11

$R_f = 0.24$ (70% ether in hexanes); $[\alpha]_D^{20} -2.1$ ($c = 1.1$, CHCl_3); IR (film) ν_{max} 3025, 2868, 1746, 1366, 1234, 1066 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.36-7.19 (m, 30 H, ArH), 5.05 (dd, $J = 9.2, 7.9$ Hz, 1 H, H-2'), 4.84 (d, $J = 7.8$ Hz, 1 H, H-1'), 4.78 (s, 1 H, H-1), 4.84-4.53 (m, 12 H, OCH_2Ar), 4.17 (d, $J = 3.0$ Hz, 1 H, H-2), 3.96 (dd, $J = 9.5, 9.4$ Hz, 1 H, H-4), 3.78 (dd, $J = 11.0, 1.9$ Hz, 1 H, H-6'a), 3.75-3.73 (m, 5 H, H-3', H-4', H-6, H-6'b), 3.57 (dd, $J = 9.1, 3.1$ Hz, 1 H, H-3), 3.53 (m, 1 H, H-5'), 3.44 (ddd, $J = 9.7, 4.9, 1.8$ Hz, 1 H, H-5), 1.96 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.6, 138.2, 138.1, 138.0, 137.8, 137.7, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.2, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.5, 127.5, 127.5, 96.6, 95.4, 82.4, 80.8, 77.4, 75.2, 75.2, 75.0, 74.9, 74.9, 73.9, 73.4, 73.2, 73.1, 70.9, 68.9, 68.4, 67.7, 20.9; HRMS (FAB), calcd for $\text{C}_{56}\text{H}_{60}\text{O}_{12}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1057.3139, found 1057.3108.

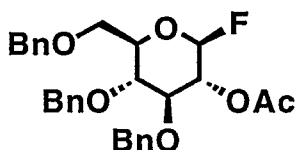
Trisaccharide 12



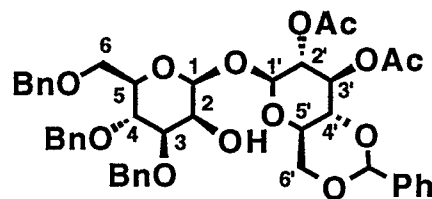
$R_f = 0.49$ (70% ether in hexane); $[\alpha]_D^{20} -19.0$ ($c = 0.3$, CHCl_3); IR (film) ν_{max} 3029, 2920, 1746, 1454, 1365, 1233, 1058, 739, 697 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.32–7.14 (m, 45 H, ArH), 5.09 (dd, $J = 8.0, 3.3$ Hz, 1 H, H-2' or H-2''), 5.07 (dd, $J = 8.0, 2.9$ Hz, 1 H, H-2' or H-2''), 4.85 (d, $J = 7.8$ Hz, 1 H, H-1' or H-1''), 4.78 (d, $J = 7.9$ Hz, 1 H, H-1' or H-1''), 4.94–4.45 (m, 18 H, OCH_2Ar), 4.59 (s, 1 H, H-1), 4.40 (d, $J = 2.7$ Hz, 1 H, H-2), 3.87 (dd, $J = 9.6, 8.9$ Hz, 1 H, H-3' or H-3''), 3.77–3.52 (m, 11 H, H-3' or H-3'', H-4, H-4', H-4'', H-5' or H-5'', H-6, H-6', H-6''), 3.48 (dd, $J = 9.4, 2.9$ Hz, 1 H, H-3), 3.44 (ddd, $J = 9.9, 3.7, 2.3$ Hz, 1 H, H-5), 3.41 (ddd, $J = 9.8, 7.2, 2.2$ Hz, 1 H, H-5' or H-5''), 1.9 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 1.89 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 169.7, 169.4, 138.9, 138.6, 138.3, 138.2, 138.2, 137.9, 137.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 127.4, 127.4, 127.3, 99.6, 95.5, 95.1, 93.6, 83.1, 82.4, 80.0, 78.6, 77.6, 75.7, 75.1, 75.1, 74.9, 74.7, 74.7, 74.4, 74.3, 73.8, 73.5, 73.4, 72.9, 70.2, 69.6, 69.4, 68.1, 21.3, 21.2; HRMS (FAB), calcd for $\text{C}_{85}\text{H}_{90}\text{O}_{18}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1531.5182, found 1531.5254.

Fluoride 13 α 

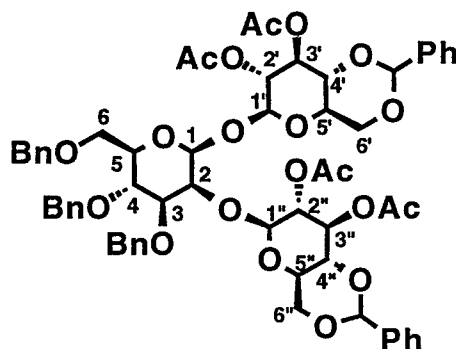
$R_f = 0.54$ (50% ether in hexanes); $[\alpha]_D^{20} +50.6$ ($c = 1.47$, CHCl_3); IR (film) ν_{max} 2923, 1746, 1454, 1366, 1231, 1162, 1060 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.33-7.14 (m, 15 H, ArH), 5.71 (dd, $J = 53.9, 2.7$ Hz, 1 H, H-1), 4.9 (ddd, $J = 24.9, 9.9, 2.7$ Hz, 1 H, H-2), 4.84-4.50 (m, 6 H, OCH_2Ar), 3.68 (dd, $J = 9.6, 9.6$ Hz, 1 H, H-3), 3.96 (ddd, $J = 10.0, 3.5, 1.9$ Hz, 1 H, H-5), 3.81 (dd, $J = 9.6, 9.6$ Hz, 1 H, H-4), 3.77 (dd, $J = 11.0, 3.5$ Hz, 1 H, H-6a), 3.68 (dd, $J = 11.0, 1.9$ Hz, 1 H, H-6b), 2.03 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.2, 138.2, 137.8, 137.7, 128.4, 128.4, 127.9, 127.9, 127.8, 127.8, 127.6, 105.4, 103.9, 79.4, 76.7, 75.5, 75.3, 73.5, 72.9, 72.9, 72.8, 67.7, 20.7; HRMS (FAB), calcd for $\text{C}_{29}\text{H}_{31}\text{O}_6\text{FNa}$ ($\text{M}+\text{Na}^+$): 517.2002, found 517.2018.

Fluoride 13 β 

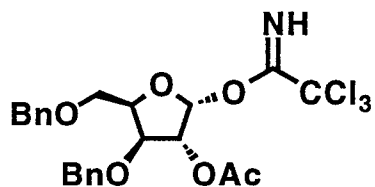
m.p. 49-50 $^{\circ}\text{C}$ (ether/ hexanes); $R_f = 0.52$ (50% ether in hexanes); $[\alpha]_D^{20} +15.5$ ($c = 2.19$, CHCl_3); IR (film) ν_{max} 3025, 2873, 1750, 1454, 1368, 1228, 1106 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.16 (m, 15 H, ArH), 5.26 (dd, $J = 54.0, 6.3$ Hz, 1 H, H-1), 5.11 (ddd, $J = 11.0, 8.2, 6.5$ Hz, 1 H, H-2), 4.78-4.53 (m, 6 H, OCH_2Ar), 3.85 (dd, $J = 9.3, 9.2$ Hz, 1 H, H-3), 3.77-3.66 (m, 3 H, H-4, H-5, H-6), 2.02 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 169.3, 137.7, 137.5, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 107.5, 105.8, 81.5, 81.5, 76.6, 74.8, 74.3, 73.5, 72.5, 72.3, 68.3, 20.7; HRMS (FAB), calcd for $\text{C}_{29}\text{H}_{31}\text{O}_6\text{FNa}$ ($\text{M}+\text{Na}^+$): 517.2002, found 517.2014.

Disaccharide 15

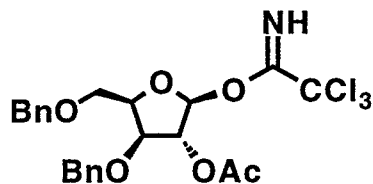
m.p. 74-75 °C (ether/ hexanes); $R_f = 0.13$ (70% ether in hexanes); $[\alpha]_D^{20} -25.7$ ($c = 0.43$, CHCl_3); IR (film) ν_{max} 3541, 3032, 2868, 1750, 1496, 1454, 1372, 1239, 1073, 911, 800, 735, 699 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.43-7.24 (m, 20 H, ArH), 5.50 (s, 1 H, PhCH), 5.40 (dd, $J = 9.5, 9.4$ Hz, 1 H, H-3'), 5.03 (dd, $J = 9.2, 8.0$ Hz, 1 H, H-2'), 5.00 (d, $J = 7.9$ Hz, 1 H, H-1'), 4.73 (d, $J = 0.6$ Hz, 1 H, H-1), 4.91, 4.57 (AB, $J = 11.1$ Hz, 2 H, CH_2Ar), 4.77, 4.65 (AB, $J = 12.3$ Hz, 2 H, CH_2Ar), 4.61, 4.55 (AB, $J = 12.3$ Hz, 2 H, CH_2Ar), 4.35 (dd, $J = 10.5, 5.0$ Hz, 1 H, H-6'a), 4.11 (d, $J = 2.8$ Hz, 1 H, H-2), 3.95 (dd, $J = 9.4, 9.4$ Hz, 1 H, H-4), 3.78 (dd, $J = 10.8, 2.1$ Hz, 1 H, H-6a), 3.77 (dd, $J = 10.3, 10.2$ Hz, 1 H, H-6'b), 3.73 (dd, $J = 10.9, 4.9$ Hz, 1 H, H-6b), 3.69 (dd, $J = 9.6, 9.5$ Hz, 1 H, H-4'), 3.56 (dd, $J = 9.2, 3.0$ Hz, 1 H, H-3), 3.53 (ddd, $J = 9.8, 9.8, 4.9$ Hz, 1 H, H-5'), 3.46 (ddd, $J = 9.5, 4.9, 2.0$ Hz, 1 H, H-5), 2.07 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 2.00 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.7, 169.9, 138.2, 138.1, 137.8, 136.7, 129.1, 128.4, 128.4, 128.2, 128.1, 127.8, 127.8, 127.7, 127.6, 126.1, 101.5, 97.2, 95.9, 80.9, 78.3, 75.4, 75.2, 73.8, 73.8, 73.4, 71.9, 71.2, 71.1, 68.9, 68.4, 67.8, 66.4, 20.7; HRMS (FAB), calcd for $\text{C}_{44}\text{H}_{48}\text{O}_{13}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 917.2149, found 917.2170.

Trisaccharide 16

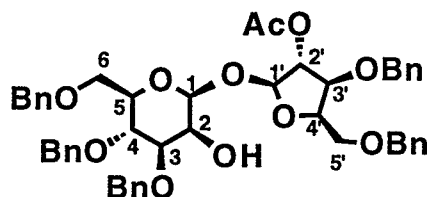
m.p. 97-98 °C (ether/ hexanes); $R_f = 0.36$ (70% ether in hexanes); $[\alpha]_D^{20} -70.0$ ($c = 1.2$, CHCl_3); IR (film) ν_{max} 3033, 2871, 1751, 1497, 1454, 1372, 1316, 1236, 1068, 912, 802, 739, 700 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.44-7.26 (m, 25 H, ArH), 5.50 (s, 6 H, 2 x PhCH), 5.50 (t, $J = 9.8, 9.2$ Hz, 1 H, H-3''), 5.40 (t, $J = 9.9, 9.8$ Hz, 1 H, H-3'), 5.15 (dd, $J = 9.8, 8.1$ Hz, 1 H, H-2'), 5.14 (dd, $J = 9.2, 8.3$ Hz, 1 H, H-2''), 5.11 (d, $J = 8.0$ Hz, 1 H, H-1''), 5.01 (d, $J = 8.2$ Hz, 1 H, H-1'), 4.80 (s, 1 H, H-1), 4.92, 4.49 (AB, $J = 11.2$ Hz, 2 H, CH_2Ar), 4.75, 4.58 (AB, $J = 12.2$ Hz, 2 H, CH_2Ar), 4.55, 4.50 (AB, $J = 12.5$ Hz, 2 H, CH_2Ar), 4.41 (dd, $J = 10.5, 5.0$ Hz, 1 H, H-6'a or H-6''a), 4.37 (dd, $J = 10.8, 5.1$ Hz, 1 H, H-6'a or H-6''a), 4.30 (d, $J = 2.9$ Hz, 1 H, H-2), 3.83 (dd, $J = 10.5, 10.4$ Hz, 1 H, H-4''), 3.75 (dd, $J = 10.5, 10.4$ Hz, 1 H, H-4'), 3.74-3.68 (m, 4 H, H-6, H-6'b, H-6''b), 3.61 (dd, $J = 9.6, 9.6$ Hz, 1 H, H-4), 3.56-3.53 (m, 2 H, H-5', H-5''), 3.52 (dd, $J = 9.3, 2.8$ Hz, 1 H, H-3), 3.47 (ddd, $J = 9.6, 5.5, 1.9$ Hz, 1 H, H-5); ^{13}C NMR (150 MHz, CDCl_3) δ 170.4, 169.9, 169.9, 169.6, 138.2, 137.9, 137.8, 136.9, 136.6, 129.1, 129.0, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 126.2, 126.1, 101.5, 99.7, 95.5, 94.8, 80.4, 78.9, 78.3, 75.7, 75.2, 74.3, 73.1, 72.4, 71.7, 71.3, 71.1, 71.1, 70.7, 69.7, 68.6, 68.3, 66.2, 65.7, 20.9, 20.7; HRMS (FAB), calcd for $\text{C}_{61}\text{H}_{66}\text{O}_{20}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1251.3202, found 1251.3258.

Imidate 18 α 

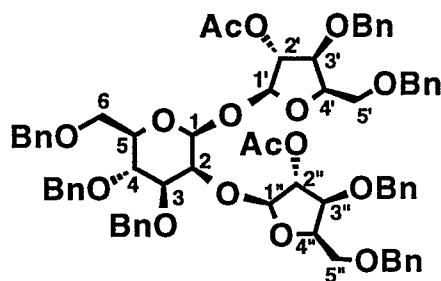
R_f = 0.49 (60% ether in hexanes); IR (film) $\nu_{\max}$ 3031, 2868, 1747, 1620, 1452, 1369, 1299, 1228, 1066, 884, 832, 797, 739, 698, 645 cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 8.41 (s, 1 H, NH), 7.22-7.06 (m, 10 H, ArH), 6.97 (d, J = 4.6 Hz, 1 H, H-1), 5.52 (dd, J = 5.1, 4.6 Hz, 1 H, H-2), 4.53 (dt, J = 5.6, 5.1 Hz, 1 H, H-4), 4.41, 4.29 (AB, J = 11.5 Hz, 2 H, OCH_2Ar), 4.28 (s, 2 H, OCH_2Ar), 4.25 (dd, J = 6.0, 5.1 Hz, 1 H, H-3), 3.72 (dd, J = 10.3, 5.2 Hz, 1 H, H-5a), 3.61 (dd, J = 10.3, 5.1 Hz, 1 H, H-5b), 1.63 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 170.5, 161.8, 139.0, 138.4, 129.3, 129.2, 128.8, 128.6, 128.5, 128.5, 98.2, 80.6, 79.3, 78.0, 74.4, 73.5, 68.8, 30.6, 21.4.

Imidate 18 β 

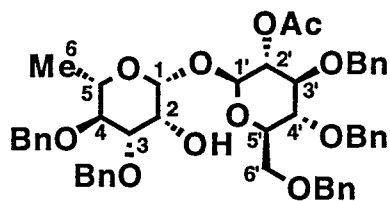
R_f = 0.27 (60% ether in hexanes); IR (film) $\nu_{\max}$ 3031, 2868, 1747, 1670, 1452, 1369, 1299, 1228, 1066, 843, 832, 797, 739, 698, 645 cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 8.41 (s, 1 H, NH), 7.30-7.05 (m, 10 H, ArH), 6.59 (s, 1 H, H-1), 5.57 (s, 1 H, H-2), 4.67, 4.42 (AB, J = 12.0 Hz, 2 H, OCH_2Ar), 4.60 (dt, J = 6.0, 5.6 Hz, 1 H, H-4), 4.40, 4.33 (AB, J = 11.8 Hz, 2 H, OCH_2Ar), 3.98 (dd, J = 10.0, 5.6 Hz, 1 H, H-5a), 3.91 (dd, J = 10.0, 5.5 Hz, 1 H, H-5b), 3.84 (d, J = 5.3 Hz, 1 H, H-3), 1.46 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 161.8, 129.2, 129.2, 129.2, 128.6, 128.5, 128.5, 128.4, 104.1, 84.0, 80.9, 79.6, 74.3, 72.8, 69.6, 21.7.

Disaccharide 19

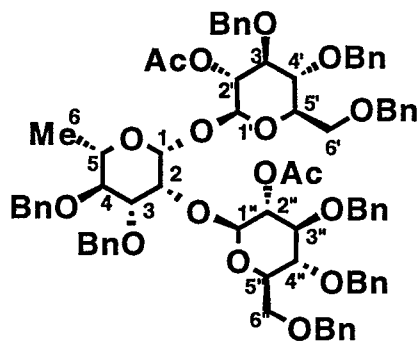
$R_f = 0.16$ (70% ether in hexanes); $[\alpha]_D^{20} -54.9$ ($c = 0.8$, CHCl_3); IR (film) ν_{max} 3495, 3029, 2866, 2359, 1742, 1496, 1453, 1369, 1233, 1097, 1046, 739, 697 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.37-7.19 (m, 25 H, ArH), 5.52 (s, 1 H, H-1'), 5.35 (s, 1 H, H-2'), 4.81 (d, $J = 0.7$ Hz, 1 H, H-1), 4.90-4.51 (m, 10 H, OCH_2Ar), 4.45 (dt, $J = 7.4$, 4.9 Hz, 1 H, H-4'), 4.06 (bs, 1 H, H-2), 3.95 (d, $J = 5.1$ Hz, 1 H, H-3'), 3.93 (dd, $J = 9.3$, 9.0 Hz, 1 H, H-4), 3.77-3.70 (m, 4 H, H-5', H-6), 3.57 (dd, $J = 9.0$, 3.1 Hz, 1 H, H-3), 3.47 (ddd, $J = 9.4$, 3.3, 2.9 Hz, 1 H, H-5), 2.06 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 169.5, 138.2, 138.2, 138.0, 137.9, 137.6, 128.4, 128.3, 128.3, 128.3, 128.2, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.5, 102.6, 95.3, 81.6, 81.2, 80.4, 79.7, 75.2, 75.0, 73.9, 73.4, 73.3, 71.6, 71.3, 69.2, 68.9, 68.2, 65.8, 20.8; HRMS (FAB), calcd for $\text{C}_{48}\text{H}_{52}\text{O}_{11}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 937.2564, found 937.2597.

Trisaccharide 20

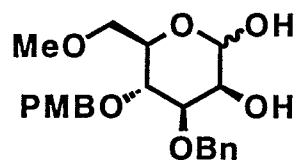
$R_f = 0.48$ (70% ether in hexanes); $[\alpha]_D^{20} -104.2$ ($c = 0.9$, CHCl_3); IR (film) ν_{max} 3030, 2865, 1742, 1496, 1453, 1369, 1234, 1050, 738, 697 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.39-7.11 (m, 35 H, ArH), 5.65 (s, 1 H, H-1' or H-1''), 5.52 (s, 1 H, H-1' or H-1''), 5.40 (s, 1 H, H-2' or H-2''), 5.31 (s, 1 H, H-2' or H-2''), 4.79 (s, 1 H, H-1), 4.91-4.78 (m, 14 H, OCH_2Ar), 4.45 (dt, $J = 7.5, 5.4$ Hz, 1 H, H-4' or H-4''), 4.36 (m, 1 H, H-4' or H-4''), 4.23 (d, $J = 3.0$ Hz, 1 H, H-2), 3.91 (d, $J = 5.1$ Hz, 2 H, H-3', H-3''), 3.79-3.67 (m, 7 H, H-4, H-6, H-5', H-5''), 3.51 (dd, $J = 9.3, 2.9$ Hz, 1 H, H-3), 3.45 (ddd, $J = 9.7, 5.3, 1.8$ Hz, 1 H, H-5), 2.07 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 1.99 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3) δ 169.7, 169.7, 138.7, 138.5, 138.4, 138.4, 138.3, 138.0, 137.5, 128.4, 128.4, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 127.4, 127.4, 127.3, 127.2, 127.1, 106.4, 102.0, 99.5, 95.9, 81.7, 81.2, 80.8, 80.6, 80.1, 79.8, 79.8, 75.5, 75.0, 74.3, 73.3, 73.2, 73.0, 72.4, 71.3, 71.2, 70.1, 69.5, 69.2, 20.9, 20.8; HRMS (FAB), calcd for $\text{C}_{69}\text{H}_{74}\text{O}_{16}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1291.4031, found 1291.4135.

Disaccharide 23

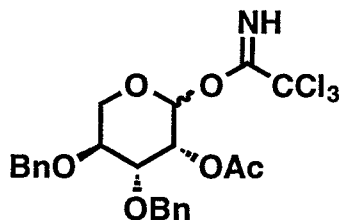
m.p. 165-166 °C (ether/ hexanes); $R_f = 0.21$ (70% ether in hexanes); $[\alpha]_D^{20} +19.9$ ($c = 0.56$, CHCl_3); IR (film) ν_{max} 3546, 3031, 2903, 1744, 1452, 1365, 1231, 1071, 740, 695 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.34-7.26 (m, 25 H, ArH), 5.05 (dd, $J = 9.3$, 8.0 Hz, 1 H, H-2'), 4.96-4.54 (m, 10 H, OCH_2Ar), 4.81 (d, $J = 8.0$ Hz, 1 H, H-1'), 4.60 (s, 1 H, H-1), 4.05 (d, 2.7 H, H-2), 3.74 (dd, $J = 10.8$, 1.9 Hz, 1 H, H-6'a), 3.68-3.64 (m, 3 H, H-3', H-4', H-6'b), 3.57 (m, 1 H, H-5'), 3.56 (dd, $J = 9.2$, 9.2 Hz, 1 H, H-4), 3.49 (dd, $J = 9.1$, 3.0 Hz, 1 H, H-3), 3.34 (dq, $J = 9.2$, 6.2 Hz, 1 H, H-5), 2.90 (bs, 1 H, OH), 1.95 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$), 1.34 (d, $J = 6.1$ Hz, 3 H, H-6); ^{13}C NMR (150 MHz, CDCl_3) δ 169.4, 138.3, 138.0, 137.9, 137.8, 137.7, 128.4, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 98.1, 97.8, 82.9, 81.0, 79.2, 77.8, 75.4, 75.4, 75.1, 75.0, 73.4, 72.9, 71.2, 68.6, 68.4, 20.9, 17.9; HRMS (FAB), calcd for $\text{C}_{49}\text{H}_{54}\text{O}_{11}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 951.2735, found 951.2720.

Trisaccharide 24

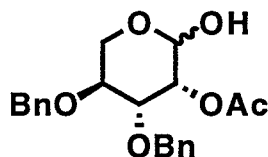
$R_f = 0.2$ (60% ether in hexanes); $[\alpha]_D^{20} +9.2$ ($c = 0.4$, CHCl_3); IR (film) ν_{max} 3029, 2866, 1741, 1453, 1365, 1235, 1064, 826, 739, 697 cm^{-1} ; ^1H NMR (600 MHz, CHCl_3) δ 7.34-7.16 (m, 40 H, ArH), 5.03 (dd, $J = 9.1, 7.9$ Hz, 1 H, H-2' or H-2''), 5.01 (dd, $J = 9.0, 8.1$ Hz, 1 H, H-2' or H-2''), 4.80 (d, $J = 7.8$ Hz, 1 H, H-1' or H-1''), 4.75 (d, $J = 8.9$ Hz, 1 H, H-1' or H-1''), 4.79-4.45 (m, 16 H, OCH_2Ar), 4.59 (s, 1 H, H-1), 4.16 (bs, 1 H, H-2), 3.74 (bd, $J = 11.5$ Hz, 1 H, H-6'a or H-6''a), 3.70 (dd, $J = 11.5, 5.2$ Hz, 1 H, H-6'a or H-6''a), 3.66-3.61 (m, 5 H, H-3' or H-3'', H-4', H-4'', H-6'b, H-6''b), 3.58 (dd, $J = 9.3, 9.3$ Hz, 1 H, H-3' or H-3''), 3.47-3.43 (m, 3 H, H-3, H-5', H-5''), 3.37 (dd, $J = 9.0, 9.0$ Hz, 1 H, H-4), 3.31 (dq, $J = 8.9, 2.7$ Hz, 1 H, H-5), 1.96 (s, 3 H, C(O)CH_3), 1.86 (s, 3 H, C(O)CH_3), 1.59 (d, $J = 2.4$ Hz, 3 H, H-6); ^{13}C NMR (125 MHz, CDCl_3) δ 169.6, 169.3, 138.6, 138.3, 138.2, 138.1, 138.0, 137.9, 128.4, 128.4, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 101.0, 98.0, 95.6, 83.1, 83.0, 82.6, 80.0, 78.0, 77.8, 76.8, 75.5, 75.3, 75.0, 74.9, 74.2, 73.8, 73.5, 73.2, 72.5, 72.3, 72.3, 69.1, 68.7, 21.1, 21.0, 17.9; HRMS (FAB), calcd for $\text{C}_{78}\text{H}_{84}\text{O}_{17}\text{Cs}$ ($\text{M}+\text{Cs}^+$): 1425.4763, found 1425.4860.

F ring diol 25

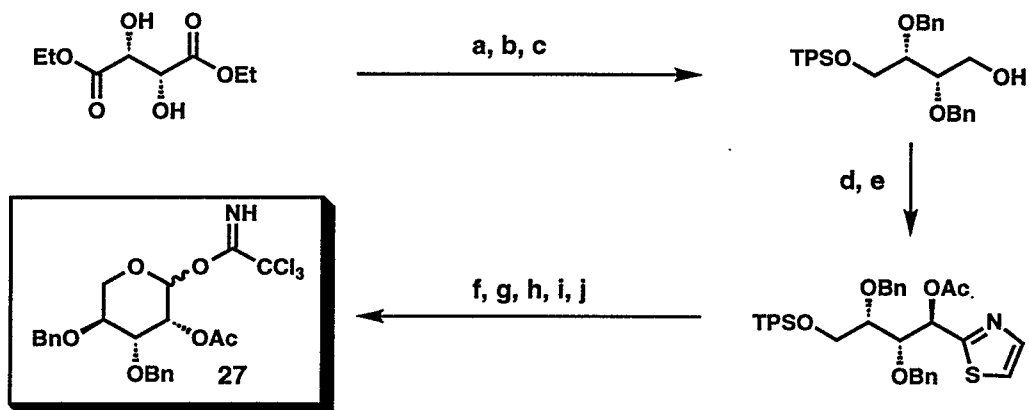
$R_f = 0.12$ (80% ether in hexanes); $[\alpha]_D^{20} +16.7$ ($c = 3.17$, CHCl_3); IR (film) ν_{max} 3419, 2924, 1613, 1513, 1457, 1249, 1090 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.34 (m, 5 H, ArH), 7.23 (d, $J = 8.8$ Hz, 2 H, ArH, PMB), 6.87 (d, $J = 8.7$ Hz, 2 H, ArH, PMB), 5.30 (s, 1 H, H-1), 4.80, 4.52 (AB, $J = 10.8$ Hz, 2 H, OCH_2Ar), 4.73 (s, 2 H, OCH_2Ar), 4.06 (d, $J = 1.6$ Hz, 1 H, H-2), 4.03 (m, 1 H, H-5), 3.94 (dd, $J = 9.4$ Hz, 3.3 H, 1 H, H-3), 3.80 (s, 3 H, ArOCH_3), 3.71 (dd, $J = 9.9, 9.7$ Hz, 1 H, H-4), 3.60-3.58 (m, 2 H, H-6), 3.35 (s, 3 H, OCH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 159.2, 137.8, 130.3, 129.6, 129.5, 128.5, 128.4, 127.9, 127.8, 127.7, 113.7, 113.7, 94.0, 93.8, 81.4, 79.6, 74.7, 74.7, 74.3, 74.0, 73.3, 71.9, 71.8, 71.7, 71.1, 70.4, 68.9, 68.4, 59.0, 59.0, 55.2; HRMS (FAB), calcd for $\text{C}_{22}\text{H}_{28}\text{O}_7\text{Cs}$ ($\text{M}+\text{Cs}^+$): 537.0889, found 537.0909.

Imidate 27

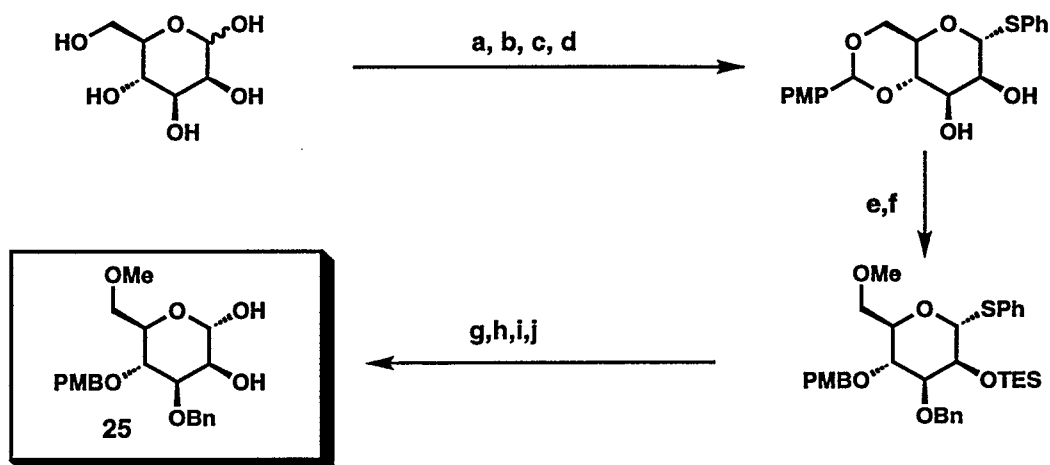
$R_f = 0.55$ (70% ether in hexanes); $[\alpha]_D^{20} -20.2$ ($c = 1.3$, CHCl_3); IR (film) ν_{max} 3336, 3032, 2921, 1746, 1672, 1496, 1367, 1231, 1069, 795, 737 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.69 (s, 0.9 H, $\text{NH}\alpha$), 8.60 (s, 0.1 H, $\text{NH}\beta$), 7.37-7.30 (m, 10 H, ArH), 7.26 (s, 0.1 H, H-1 β), 6.17 (d, $J = 3.3$ Hz, 0.9 H, H-1 α), 5.60 (dd, $J = 3.1$, 3.1 Hz, 0.9 H, H-2 α), 5.55 (d, $J = 3.0$ Hz, 0.1 H, H-2 β), 4.83, 4.66 (AB, $J = 11.5$ Hz, 2 H, OCH_2Ar), 4.75, 4.64 (AB, $J = 11.4$ Hz, 2 H, OCH_2Ar), 3.99-3.93 (m, 3 H, H-3, H-4, H-5a), 3.75 (m, 1 H, H-5b), 2.17, 2.13 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 169.9, 160.1, 138.1, 137.5, 128.4, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 95.1, 77.3, 77.0, 76.7, 76.4, 73.7, 73.4, 72.6, 72.3, 67.7, 67.3, 63.4, 20.9.

G ring lactol 28

$R_f = 0.30$ (70% ether in hexanes); $[\alpha]_D^{20} +1.5$ ($c = 2.5$, CHCl_3); IR (film) ν_{max} 3393, 3063, 3029, 2933, 1741, 1454, 1372, 1238, 1067, 932, 886, 853, 744, 689 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.26 (m, 10 H, ArH), 5.26 (dd, $J = 3.5$, 3.5 Hz, 0.75 H, H-2 α), 5.22 (dd, $J = 3.1$, 3.1 Hz, 0.25 H, H-2 β), 5.11 (d, $J = 2.1$ Hz, 0.25 H, H-1 β), 5.07 (d, $J = 3.7$ Hz, 0.75 H, H-1 α), 4.73-4.57 (m, 4 H, OCH_2Ar), 3.96 (dd, $J = 7.6$, 3.2 Hz, 1 H, H-3), 3.82-3.75 (m, 2 H, H-4, H-5a), 3.63 (dd, $J = 12.8$, 3.2 Hz, 1 H, H-5b), 2.12 (s, 3 H, $\text{C}(\text{O})\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 170.1, 138.2, 137.9, 137.5, 136.7, 128.6, 128.4, 128.3, 128.3, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 92.7, 92.3, 76.4, 76.0, 74.1, 73.7, 73.6, 72.9, 72.3, 71.5, 70.3, 68.1, 61.6, 57.7, 21.0, 20.9; HRMS (FAB), calcd for $\text{C}_{21}\text{H}_{24}\text{O}_6\text{Na}$ ($\text{M}+\text{Na}^+$): 395.1471, found 395.1483.



Scheme 1. Synthesis of imidate 27. Reagents and conditions: (a) 1.93 equiv of NaH, 1.93 equiv of BnBr, cat. 18-crown-6, 0.02 equiv of *n*-Bu₄NI, THF, 0 → 25 °C, 3 h, 77%; (b) 1.7 equiv of LAH, Et₂O, reflux, 4 h, 90%; (c) 1.0 equiv of NaH, 1.0 equiv of TPSCl, THF, 0 → 25 °C, 3 h, 88%; (d) 2.0 equiv of (COCl)₂, 3.0 equiv of DMSO, CH₂Cl₂, -78 °C; then 4.0 equiv of Et₃N, -78 → -45 °C; then 3.0 equiv of TMS-thiazole, -45 → 25 °C, 18 h, 1:1 mixture of diastereomers, 90%; (e) 1.2 equiv of Ac₂O, 1.5 equiv of Et₃N, CH₂Cl₂, 0 → 25 °C, 2 h, 95%; (f) 1.3 equiv of MeOTf, 4 Å MS, MeCN, 25 °C, 15 min; (g) 2.2 equiv of NaBH₄, MeOH, 25 °C, 15 min, 76%; (h) 8.0 equiv of CuO, 1.0 equiv of CuCl₂·2H₂O, MeCN:H₂O, 25 °C, 15 min; (i) 1.3 equiv of *n*-Bu₄NF, THF, 25 °C, 5 h, 69% over 4 steps; (j) 20 equiv of Cl₃CCN, 1 dr. DBU, CH₂Cl₂, -20 °C, 10 min, 94%. LAH = lithium aluminum hydride; TPSCl = *t*-BuPh₂SiCl; TMS = Me₃Si; MeOTf = CH₃OSO₂CF₃; DBU = 1,8-diazobicyclo[5.4.0]undec-7-ene.



Scheme 2. Synthesis of acceptor 25. Reagents and conditions: (a) 6.0 equiv of Ac_2O , 8.0 equiv of Et_3N , 4-DMAP, CH_2Cl_2 , $0 \rightarrow 25^\circ\text{C}$, 24 h, 96%; (b) 1.2 equiv of PhSH , 2.0 equiv of $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , 0°C , 4 h, 73%; (c) 1.0 equiv of NaOMe , MeOH , 0.5 h; (d) 1.5 equiv of $p\text{-(MeO)PhCH(OMe)}_2$, CSA, DMF, 4 h, 40% over two steps; (e) 1.5 equiv of $n\text{-Bu}_2\text{SnO}$, PhMe , reflux, 3 h; then 1.05 equiv of BnBr , 1.0 equiv of $n\text{-Bu}_4\text{NBr}$, 80°C , 2 h, 82%; (f) 1.5 equiv of TESOTf , 3.0 equiv of 2,6-lutidine, -78°C , 3 h, 98%; (g) 5.0 equiv of DIBAL, CH_2Cl_2 , -78°C , 2.4:1 mixture of regioisomers, 76%; (h) 3.0 equiv of NaH , 2.0 equiv of MeI , THF, $0 \rightarrow 25^\circ\text{C}$, 90%; (i) 1.1 equiv of $n\text{-Bu}_4\text{NF}$, THF, 0°C , 69%; (j) 2.0 equiv of NBS , acetone: H_2O , 94%. 4-DMAP = 4-dimethylaminopyridine; CSA = camphorsulfonic acid; $\text{TESOTf} = \text{Et}_3\text{SiOSO}_2\text{CF}_3$; DIBAL = diisobutyl aluminum hydride, NBS = N-bromosuccinimide; BnBr = benzyl bromide.