Supporting Information

*Ortho-(Methyltosylaminoethynyl)benzyl Glycosides as New Glycosyl Donors for Latent-Active Glycosylation*

Xiaoping Chen, Dacheng Shen, Qiaoling Wang, You Yang and Biao Yu

*State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: byu@mail.sioc.ac.cn.*

*Shanghai Key Laboratory of New Drug Design, School of Pharmacy, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China*

Contents

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General information</td>
</tr>
<tr>
<td>2. Experimental details and characterization data of new compounds</td>
</tr>
<tr>
<td>3. References</td>
</tr>
<tr>
<td>4. NMR spectra of new compounds</td>
</tr>
</tbody>
</table>

1. **General information.** Commercial reagents were used without further purification unless specialized. Solvents were dried and redistilled prior to use in the usual way. Thin layer chromatographies (TLCs) were performed on precoated plates of Silica Gel HF254 (0.5 mm, Yantai, China). Flash column chromatography was performed on Silica Gel H (10-40 μ, Yantai, China). Optical rotations were determined with a Perkin-Elmer Model 241 MC polarimeter. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker AM 400 or Bruker AM 500 spectrometer with Me₄Si as the internal standard. Chemical shifts were recorded in δ values and J values were given in Hz. Mass spectra were obtained on an HP5989A or a VG Quatro mass spectrometer.
2. Experimental details and characterization data of new compounds

2.1. Ortho-Iodobenzyl 2,3,4,6-tetra-O-benzoyl-D-glucopyranoside (3a)

A mixture of 2a (10 g, 14.3 mmol), 2-iodobenzyl alcohol (4.0 g, 17.1 mmol), and 4Å MS in dry CH₂Cl₂ (100 mL) under argon atmosphere was stirred at room temperature for 30 minutes. TMSOTf (1.3 mL, 7.2 mmol) was injected to the mixture and the mixture was stirred at room temperature for another hour before it was quenched with Et₃N (5 mL). The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 4:1) to provide 3a as a colorless syrup (9.8 g, 85%, α/β = 1:20): [α]²⁵D = 5.6 (c 1.8, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.11–8.02 (m, 2 H), 7.96–7.89 (m, 4 H), 7.87–7.82 (m, 2 H), 7.74 (d, J = 7.9 Hz, 1 H), 7.61–7.47 (m, 3 H), 7.47–7.27 (m, 11 H), 7.10 (t, J = 7.5 Hz, 1 H), 6.93 (t, J = 7.6 Hz, 1 H), 5.90 (t, J = 9.6 Hz, 1 H), 5.70 (t, J = 9.7 Hz, 1 H), 5.65 (dd, J = 9.6, 8.0 Hz, 1 H), 4.93–4.86 (m, 2H), 4.76 (d, J = 13.2 Hz, 1 H), 4.69 (dd, J = 12.1, 2.9 Hz, 1 H), 4.54 (dd, J = 12.1, 5.8 Hz, 1 H), 4.24–4.17 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 165.8, 165.2, 165.1, 139.1, 139.0, 133.4, 133.2, 133.1, 130.2, 129.9, 129.8, 129.8, 129.7, 129.4, 129.1, 128.8, 128.7, 128.4, 128.3, 128.2, 99.6, 98.1, 97.8, 74.3, 72.9, 72.4, 71.8, 69.7, 63.2; HRMS (MALDI) m/z calcd for C₄₁H₃₃O₁₀INa [M+Na]⁺ 835.1011, found 835.0993.

2.2. Ortho-Iodobenzyl 2,3,4-tri-O-benzoyl-L-rhamnopyranoside (3b)

To a solution of 2b (291 mg, 0.50 mmol) and 2-iodobenzyl alcohol (141 mg, 0.60 mmol) in dry CH₂Cl₂ (5 mL) containing 4Å MS (400 mg) under the protection of
argon, was added TMSOTf (10 µL, 0.05 mmol) dropwise. The mixture was allowed to be stirred at ambient temperature for 2 h before it was quenched with Et₃N (1 mL). The mixture was filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1) to give 3b as a colorless foam (343 mg, 99%): [α]²⁵ D = 83.3 (c 0.9, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.11 (dd, J = 8.3, 1.4 Hz, 2 H), 7.97 (dd, J = 8.4, 1.4 Hz, 2 H), 7.85 (ddd, J = 17.6, 8.2, 1.4 Hz, 3 H), 7.64–7.53 (m, 2 H), 7.49 (td, J = 7.5, 5.9 Hz, 3 H), 7.47–7.29 (m, 4 H), 7.28–7.21 (m, 2 H), 7.04 (td, J = 7.7, 1.7 Hz, 1 H), 5.92 (dd, J = 10.1, 3.5 Hz, 1 H), 5.79 (dd, J = 3.5, 1.8 Hz, 1 H), 5.72 (t, J = 10.0 Hz, 1 H), 5.19 (d, J = 1.7 Hz, 1 H), 4.86 (d, J = 12.7 Hz, 1 H), 4.65 (d, J = 12.6 Hz, 1 H), 4.29 (dq, J = 9.8, 6.2 Hz, 1 H), 1.38 (d, J = 6.2 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 165.8, 165.6, 165.5, 139.4, 139.2, 133.5, 133.3, 133.1, 129.9, 129.8, 129.7, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.5, 128.4, 128.3, 98.0, 97.5, 73.9, 71.8, 70.8, 70.1, 67.2, 17.7; HRMS (ESI) m/z calcd for C₃₄H₃₃O₈NI [M+NH₄]+ 710.1245, found 710.1241.

2.3. Ortho-Iodobenzyl 2,3,4,6-tetra-O-benzyl-D-glucopyranoside (3c)

Compound 3a (2.0 g, 2.46 mmol) was treated with NaOMe (100 mg) in methanol (10 mL) for 2 h at room temperature. The mixture was neutralized with Amberlite IRA-120B(H⁺) resin and then concentrated. The syrupy residue was stirred with benzyl bromide (1.46 mL, 12.3 mmol) in dry DMF (15 mL) in the presence of 50% sodium hydride (0.78 g, 19.7 mmol) for 3 h at room temperature. After treatment with water, the mixture was diluted with CH₂Cl₂, washed with water, and concentrated. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 7:1) to afford 3c as a colorless oil (1.7 g, 91 % for two steps, α/β = 1:20). 3cα: [α]²⁵ D = 35.2 (c 1.1 CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (dd, J = 7.9, 0.9 Hz, 1 H), 7.55 (dd, J = 7.7, 1.2 Hz, 1 H), 7.38–7.22 (m, 20 H), 7.14 (m, 2 H), 6.97 (td, J = 7.7, 1.6 Hz, 1 H), 5.01 (d, J = 10.9 Hz, 1 H), 4.94 (d, J = 3.6 Hz, 1 H), 4.63 (m, 9 H), 4.07
(t, J = 9.3 Hz, 1 H), 3.85 (ddd, J = 10.0, 3.1, 2.2 Hz, 1 H), 3.76–3.59 (m, 4 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.9, 139.0 138.9, 138.3, 138.0, 129.2, 129.0, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 97.5, 96.7, 82.7, 82.1, 80.7, 80.2, 77.7, 75.7, 75.1, 73.5, 73.3, 73.2, 70.6, 68.4; HRMS (MALDI) m/z calcd for C$_{41}$H$_{41}$O$_6$INa [M+Na$^+$] 779.1840, found 779.1844. 3cβ: [α]$^{25}$ D = –4.1 (c 1.0 CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (dd, J = 7.9, 1.2 Hz, 1 H), 7.52 (dd, J = 7.8, 1.7 Hz, 1 H), 7.39–7.21 (m, 19 H), 7.17 (dd, J = 7.3, 2.2 Hz, 2 H), 6.98 (td, J = 7.6, 1.7 Hz, 1 H), 5.00 (d, J = 10.9 Hz, 1 H), 4.95 (d, J = 10.4 Hz, 1 H), 4.92 (d, J = 8.3 Hz, 1 H), 4.83 (d, J = 10.8 Hz, 1 H), 4.79 (d, J = 10.9 Hz, 1 H), 4.76–4.69 (m, 2 H), 4.64 (d, J = 12.2 Hz, 1 H), 4.59–4.51 (m, 3 H), 3.79 (dd, J = 10.9, 2.1 Hz, 1 H), 3.72 (dd, J = 10.8, 4.6 Hz, 1 H), 3.68–3.62 (m, 2 H), 3.60–3.53 (m, 1 H), 3.49 (ddt, J = 6.9, 4.6, 2.0 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.0, 139.2, 138.7, 138.4, 138.3, 138.2, 138.4, 138.2, 129.4, 129.2, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 102.6, 98.0, 84.9, 82.4, 77.9, 75.8, 75.2, 75.1, 75.1, 74.7, 73.6, 68.9; LRMS (ESI) m/z [M+Na$^+$] 779.2, found 779.6.

2.4. Ortho-Iodobenzyl 3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside (3d)

A mixture of 3,4,6-tri-O-acetyl-D-glucal (5.2 g, 19.1 mmol), the alcohol (9.0 g, 38.2 mmol), CeCl$_3$·7H$_2$O (10.6 g, 28.7 mmol), and NaI (4.3 g, 28.7 mmol) in acetonitrile (100 mL) was stirred at reflux temperature for 5 h; the reaction completed as monitored by TLC. The reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (2×15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 4:1) to afford glycoside 3d as a colorless oil (83%, α/β = 15:1): [α]$^{25}$ D = 71.0 (c 1.3 CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, J = 7.9, 1.0 Hz, 1 H), 7.44 (dd, J = 7.6, 1.5 Hz, 1 H), 7.37 (td, J = 7.6, 1.1 Hz, 1 H), 7.02 (td, J = 7.7, 1.7 Hz, 1 H), 5.39 (ddd, J = 11.6, 9.5, 5.4 Hz, 1 H),
5.12 (d, $J = 3.0$ Hz, 1 H), 5.03 (t, $J = 9.7$ Hz, 1 H), 4.69 (d, $J = 12.8$ Hz, 1 H), 4.48 (d, $J = 12.8$ Hz, 1 H), 4.31 (dd, $J = 12.7$, 5.3 Hz, 1 H), 4.09–4.01 (m, 2 H), 2.36 (ddd, $J = 13.0$, 5.4, 0.9 Hz, 1 H), 2.11 (s, 3 H), 2.04 (s, 3 H), 2.02 (s, 3 H), 1.90 (ddd, $J = 13.0$, 11.8, 3.8 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.7, 170.2, 169.9, 139.5, 139.2, 129.5, 128.8, 128.3, 97.8, 96.8, 73.3, 69.3, 69.1, 68.3, 62.34, 34.9, 21.0, 20.8, 20.7; HRMS (MALDI) $m/z$ calcd for C$_{19}$H$_{23}$O$_8$INa [M+Na]$^+$ 529.0330, found, 529.0326.

2.5. Preparation of the ortho-(methyldtosylaminoethyl)benzyl glycosides

General Sonogashira coupling procedure. A mixture of the ortho-iodobenzyl glycoside (3a-3d) (0.22 mmol), Ph$_3$P (24 mg, 0.08 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (32 mg, 0.04 mmol), and CuI (8.6 mg, 0.04 mmol) in DMF (2 mL) and iPr$_2$NH(4 mL) was deoxygenated, and a solution of ynamide 4 (187 mg, 0.88 mmol) in DMF (2 mL) was injected dropwise. After 5 h, the reaction was quenched with NH$_4$Cl and extracted with CH$_2$Cl$_2$ (3×15 mL). The organic phase was washed with brine and dried under Na$_2$SO$_4$. The volatiles were removed under reduce pressure. The residue was purified by column chromatography on silica gel to afford the desired glycoside (1a-1d).

Compound 1a$^{\beta}$/$\alpha$ (90% yield, $\alpha/\beta = 1:20$, a white solid). 1a$^{\beta}$: [$\alpha$]$^\circ_D = 50.7$ (c 1.1, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06–7.97 (m, 2 H), 7.92–7.86 (m, 4 H), 7.86–7.77 (m, 4 H), 7.57–7.20 (m, 12 H), 7.12 (td, $J = 7.6$, 1.2 Hz, 1 H), 7.02 (td, $J = 7.6$, 1.3 Hz, 1 H), 5.88 (t, $J = 9.6$ Hz, 1 H), 5.74 (t, $J = 9.7$ Hz, 1 H), 5.61 (dd, $J = 9.7$, 7.9 Hz, 1 H), 4.99 (d, $J = 13.3$ Hz, 1 H), 4.98 (d, $J = 8.0$ Hz, 1 H), 4.88 (d, $J = 13.3$ Hz, 1 H), 4.65 (dd, $J = 12.2$, 3.1 Hz, 1 H), 4.49 (dd, $J = 12.2$, 4.5 Hz, 1 H), 4.21 (ddd, $J =$
9.7, 4.3, 3.3 Hz, 1 H), 3.05 (s, 3 H), 2.40 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
166.1, 165.8, 165.1, 144.9, 138.0, 133.3, 133.3, 133.1, 133.1, 133.1, 131.2, 129.9, 129.8, 129.8, 129.7, 129.6, 129.3, 128.9, 128.8, 128.3, 128.2, 127.8, 127.7, 127.5, 121.4, 100.3, 88.5, 73.0, 72.2, 71.9, 69.6, 69.4, 66.7, 63.0, 39.1, 21.6; HRMS (MALDI) $m/z$ calcd for C$_{51}$H$_{43}$NO$_{12}$SNa $[M+Na]^+$ 916.2398, found 916.2392.

1aα: $\left[^{25}\text{D}\right] = 46.8$ (c 1.2, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98–7.93 (m, 2 H), 7.91–7.77 (m, 6 H), 7.74 (d, $J = 8.3$ Hz, 2 H), 7.50–7.19 (m, 12 H), 7.08 (td, $J = 7.6$, 1.0 Hz, 1 H), 6.99 (td, $J = 7.6$, 1.2 Hz, 1 H), 6.18 (t, $J = 9.9$ Hz, 1 H), 5.68 (t, $J = 9.9$ Hz, 1 H), 5.36–5.31 (m, 1 H), 5.28 (dd, $J = 10.2$, 3.7 Hz, 1 H), 4.86 (d, $J = 13.3$ Hz, 1 H), 4.70 (d, $J = 13.2$ Hz, 1 H), 4.50–4.40 (m, 2 H), 4.36 (dd, $J = 12.0$, 4.1 Hz, 1 H), 3.00(s, 3 H), 2.31(s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 165.8, 165.7, 165.3, 144.9, 138.1, 133.4, 133.1, 131.5, 129.9, 129.9, 129.7, 129.7, 129.2, 129.1, 128.9, 128.4, 128.4, 128.3, 127.9, 127.8, 127.6, 121.4, 95.7, 88.7, 71.9, 70.6, 69.4, 68.3, 68.1, 66.6, 62.8, 39.1, 21.6; HRMS (MALDI) $m/z$ calcd for C$_{51}$H$_{43}$NO$_{12}$SNa $[M+Na]^+$ 916.2398, found 916.2392.

1b

Compound 1b (90% yield, a white foam): $\left[^{25}\text{D}\right] = 79.9$ (c 1.1, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.09 (dd, $J = 8.3$, 1.4 Hz, 2 H), 7.96 (dd, $J = 8.3$, 1.4 Hz, 2 H), 7.89–7.78 (m, 4 H), 7.66–7.55 (m, 2 H), 7.54–7.46 (m, 3 H), 7.45–7.23 (m, 11 H), 5.88 (dd, $J = 10.1$, 3.4 Hz, 1 H), 5.73 (dd, $J = 3.5$, 1.8 Hz, 1 H), 5.69 (t, $J = 10.0$ Hz, 1 H), 5.11 (d, $J = 1.7$ Hz, 1 H), 4.94 (d, $J = 12.9$ Hz, 1 H), 4.77 (d, $J = 12.8$ Hz, 1 H), 4.24 (dq, $J = 9.8$, 6.3 Hz, 1 H), 3.21 (s, 3 H), 2.40 (s, 3 H), 1.34 (d, $J = 6.2$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.8, 165.5, 165.5, 144.9, 138.2, 133.4, 133.4, 133.3, 133.1, 131.7, 129.9, 129.9, 129.7, 129.7, 129.4, 129.3, 129.2, 128.6, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 121.5, 97.3, 88.6, 71.9, 70.8, 70.1, 68.0, 67.0, 66.7, 39.3, 21.6, 17.6; HRMS (ESI) $m/z$ calcd for C$_{44}$H$_{43}$N$_2$O$_{10}$S $[M+N\text{H}_4]^+$ 791.2633, found
Compound 1c (88% yield, α/β = 1:20, a colorless oil). 1cβ: [α]_{D}^{25} = 48.0 (c 1.0, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.56 (d, J = 7.3 Hz, 1 H), 7.42–7.19 (m, 19 H), 7.18–6.96 (m, 2 H), 5.00 (d, J = 10.7 Hz, 1 H), 4.98 (d, J = 2.3 Hz, 1 H), 4.85–4.41 (m, PhCH₂, 9 H), 4.07 (t, J = 9.3 Hz, 1 H), 3.86–3.80 (m, 1 H), 3.77–3.68 (m, 2 H), 3.60 (ddd, J = 12.6, 10.2, 2.7 Hz, 1 H), 3.10 (s, 3 H), 2.39 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 139.0, 138.9, 138.4, 138.3, 138.0, 133.4, 131.3, 129.9, 128.3, 128.3, 128.3, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.2, 121.3, 96.4, 88.5, 82.1, 80.1, 77.7, 75.6, 75.1, 73.4, 72.9, 70.5, 68.4, 67.3, 66.9, 39.2, 21.6; HRMS (MALDI) m/z calcd for C₅₁H₅₁NO₈SNa [M+Na]^+ 860.3228, found 860.3205.

1cα: [α]_{D}^{25} = 24.0 (c 0.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.87–7.74 (m, 2 H), 7.56–7.46 (m, 1 H), 7.38–7.21 (m, 19 H), 7.19–7.13 (m, 2 H), 5.05 (d, J = 12.9 Hz, 1 H), 4.93 (d, J = 4.8 Hz, 1 H), 4.91 (d, J = 4.9 Hz, 1 H), 4.85–4.46 (m, 8 H), 3.81–3.71 (m, 2 H), 3.71–3.59 (m, 2 H), 3.57–3.45 (m, 2 H), 3.08 (s, 3 H), 2.39 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 144.8, 139.0, 138.6, 138.4, 138.2, 133.3, 131.4, 129.9, 128.4, 128.3, 128.3, 127.9, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 121.4, 103.1, 88.4, 84.7, 82.4, 77.8, 75.7, 74.9, 73.4, 69.4, 68.8, 66.9, 39.2, 21.6; HRMS (MALDI) m/z calcd for C₅₁H₅₁NO₈SNa [M+Na]^+ 860.3228, found 860.3217.

Compound 1d (83% yield, a white solid): [α]_{D}^{25} = 91.9 (c 1.1, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.3 Hz, 2 H), 7.46–7.20 (m, 6 H), 5.37 (ddd, J = 11.6, 9.6, 5.4 Hz, 1 H), 5.10 (d, J = 2.7 Hz, 1 H), 5.03 (t, J = 9.8 Hz, 1 H), 4.76 (d, J = 12.7 Hz, 1 H), 4.64 (d, J = 12.6 Hz, 1 H), 4.31 (dd, J = 12.3, 4.2 Hz, 1 H), 4.07–3.94 (m, 1 H),
3.16 (s, 3 H), 2.45 (s, 3 H), 2.31 (dd, \( J = 13.0, 5.4 \) Hz, 1 H), 2.07 (s, 3 H), 2.02 (s, 3 H), 2.00 (s, 3 H), 1.86 (td, \( J = 13.0, 3.7 \) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.7, 170.2, 169.9, 144.8, 138.6, 133.3, 131.6, 129.9, 127.9, 127.8, 127.5, 121.6, 96.8, 88.4, 69.3, 69.1, 68.0, 67.9, 66.7, 62.2, 39.2, 35.0, 21.6, 21.0, 20.7, 20.7; HRMS (MALDI) \( m/z \) calcd for C\(_{29}\)H\(_{33}\)NO\(_{10}\)SNa [M+Na]\(^+\) 610.1717, found 610.1722.

### 2.6. General procedure for the glycosylation

![Diagram of glycosylation reaction](image)

To a solution of the donor (1a-1d) (0.12 mmol), acceptor (5a-5f) (0.10 mmol), and 4Å MS (100 mg) in dry CH\(_2\)Cl\(_2\) (2 mL) under the protection of argon, was added TMSOTf (1.85 \( \mu \)L, 0.01 mmol). The mixture was allowed to be stirred at ambient temperature for 2 h before it was quenched with Et\(_3\)N (10 mL). The mixture was filtered and concentrated in vacuo. The residue was purified with silica gel column chromatography to afford glycoside 6.

6aa\(^1\) (91% yield, \( \beta \) only)

![Image of 6aa](image)

6ab\(^2\) (91% yield, \( \beta \) only)

![Image of 6ab](image)
6ac$^3$ (98% yield, β only)

![Diagram](image)

6ad (94% yield, β only; a white solid): $[\alpha]^{25}_D = 5.8 \, (c \, 1.8, \text{CHCl}_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96–7.90 (m, 2 H), 7.90–7.85 (m, 2 H), 7.85–7.81 (m, 2 H), 7.78–7.71 (m, 2 H), 7.47–7.37 (m, 3 H), 7.34–7.24 (m, 7 H), 7.22–7.15 (m, 2 H), 5.85 (t, $J = 9.6$ Hz, 1 H), 5.48 (t, $J = 9.7$ Hz, 1 H), 5.42 (dd, $J = 9.7$, 8.0 Hz, 1 H), 5.05 (d, $J = 7.9$ Hz, 1 H), 4.51 (dd, $J = 11.9$, 3.0 Hz, 1 H), 4.41 (dd, $J = 11.9$, 7.1 Hz, 1 H), 4.11 (ddd, $J = 10.0$, 7.1, 3.1 Hz, 1 H), 1.93 (s, 3 H), 1.74 (d, $J = 11.3$ Hz, 3 H), 1.57 (d, $J = 11.4$ Hz, 3 H), 1.43 (dd, $J = 29.1$, 12.1 Hz, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.0, 165.3, 164.9, 133.4, 133.1, 133.0, 129.8, 129.7, 129.6, 129.6, 129.5, 128.9, 128.8, 128.3, 128.2, 128.2, 94.3, 75.9, 73.2, 72.0, 71.9, 70.3, 63.6, 42.3, 36.0, 30.5; HRMS (MALDI) $m/z$ calcd for C$_{44}$H$_{42}$O$_{10}$Na [M+Na]$^+$ 753.2670, found 753.2669.

![Diagram](image)

6af$^4$ (62% yield, β only)

7 (34% yield, β only; a white solid): $[\alpha]^{25}_D = -11.7 \, (c \, 1.5, \text{CHCl}_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10–8.03 (m, 2 H), 7.89 (dt, $J = 8.4$, 1.4 Hz, 4 H), 7.85–7.79 (m, 2 H), 7.60–7.17 (m, 14 H), 7.16–7.03 (m, 2 H), 5.84 (t, $J = 9.6$ Hz, 1 H), 5.77–5.64 (m, 2 H), 5.59 (dd, $J = 9.7$, 7.9 Hz, 1 H), 5.07–4.90 (m, 3 H), 4.86–4.73 (m, 2 H), 4.66 (dd, $J = 12.1$, 3.1 Hz, 1 H), 4.52 (dd, $J = 12.1$, 5.3 Hz, 1 H), 4.18–4.07 (m, 1 H), 3.98 (t, $J$
= 6.6 Hz, 2 H), 3.59 (d, $J = 15.6$ Hz, 1 H), 3.36 (d, $J = 15.6$ Hz, 1 H), 2.06–1.93 (m, 2 H), 1.69–1.55 (m, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.2, 166.1, 165.8, 165.2, 165.0, 137.3, 134.7, 133.5, 133.4, 133.2, 133.1, 130.6, 129.8, 129.8, 129.7, 129.6, 129.1, 128.8, 128.6, 128.4, 128.3, 128.3, 127.3, 115.3, 98.9, 72.9, 72.2, 71.7, 69.7, 68.6, 64.2, 63.1, 37.9, 29.9, 27.6; HRMS (ESI) $m/z$ calcd for C$_{48}$H$_{44}$O$_{12}$Na [M+Na]$^+$ 835.2725, found 835.2746.

![Diagram of molecule](image1)

6ba (90% yield, $\alpha$ only; a colorless syrup): $[\alpha]^{25}_D = 43.7$ (c 1.1, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.14–8.08 (m, 2 H), 7.99 (d, $J = 7.6$ Hz, 2 H), 7.83 (d, $J = 7.6$ Hz, 2 H), 7.65–7.58 (m, 1 H), 7.51 (dt, $J = 12.7$, 7.8 Hz, 3 H), 7.41 (dt, $J = 15.6$, 7.7 Hz, 3 H), 7.29–7.23 (m, 2 H), 5.87 (dd, $J = 10.1$, 3.4 Hz, 1 H), 5.71–5.60 (m, 2 H), 5.39 (d, $J = 5.0$ Hz, 1 H), 5.18 (s, 1 H), 4.28 (dq, $J = 12.5$, 6.4 Hz, 1 H), 3.60 (tt, $J = 11.0$, 4.7 Hz, 1 H), 2.44 (ddd, $J = 13.0$, 5.2, 2.1 Hz, 1 H), 2.03 (dt, $J = 13.1$, 3.4 Hz, 2 H), 1.98 (s, 2 H), 1.98–1.68 (m, 3 H), 1.64–1.43 (m, 5 H), 1.35 (d, $J = 6.4$ Hz, 5 H), 1.33–1.22 (m, 1 H), 1.23–1.08 (m, 3 H), 1.07 (s, 3 H), 1.07–0.96 (m, 2 H), 0.99–0.91 (m, 4 H), 0.88 (dd, $J = 6.7$, 2.1 Hz, 6 H), 0.70 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 165.8, 165.7, 165.5, 140.2, 133.4, 133.2, 133.0, 129.9, 129.7, 129.7, 129.5, 129.4, 129.3, 128.5, 128.4, 122.2, 95.8, 78.0, 77.3, 72.1, 71.5, 70.1, 66.7, 56.8, 56.2, 50.2, 42.3, 39.8, 39.5, 38.5, 37.3, 36.7, 36.2, 35.8, 32.0, 31.9, 29.5, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 17.7, 11.9; HRMS (ESI) $m/z$ calcd for C$_{54}$H$_{72}$NO$_8$ [M+NH$_4^+$] $^+$ 862.5252, found 862.5250.

![Diagram of molecule](image2)

6bb$^5$ (95% yield, $\alpha$ only)
6be (88% yield, α only)

6bd (91% yield, α only; a colorless syrup): [α]$_D^{25}$ = 56.5 (c 1.3, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.15–8.09 (m, 2 H), 8.03–7.97 (m, 2 H), 7.87–7.81 (m, 2 H), 7.65–7.57 (m, 1 H), 7.56–7.36 (m, 7 H), 7.30–7.23 (m, 1 H), 5.91 (dd, $J$ = 10.1, 3.3 Hz, 1 H), 5.66 (t, $J$ = 10.0 Hz, 1 H), 5.50–5.42 (m, 2 H), 4.38 (dq, $J$ = 9.8, 6.3 Hz, 1 H), 2.20 (p, $J$ = 3.1 Hz, 3 H), 1.97–1.87 (m, 7 H), 1.66 (d, $J$ = 3.7 Hz, 6 H), 1.57 (s, 1 H), 1.35–1.24 (m, 4 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 165.9, 165.8, 165.6, 133.3, 133.2, 133.0, 129.9, 129.7, 129.7, 129.6, 129.5, 129.4, 128.5, 128.4, 128.2, 90.7, 75.6, 72.7, 72.3, 70.2, 66.2, 42.3, 36.2, 30.7, 17.7; HRMS (ESI) m/z calcd for C$_{37}$H$_{42}$NO$_8$ [M+NH$_4$]$^+$ 628.2905, found 628.2906.

6ca (95% yield, α/β = 1:1)

6cb (93% yield, α/β = 1.5:1)
6ce\(^9\) (85\% yield, \(\alpha/\beta = 1.2:1\))

6cd (89\% yield, \(\alpha/\beta = 1.2:1\); a colorless oil): \([\alpha]^{25}_D = 44.7 \ (c \ 1.5, \text{CHCl}_3); \ ^1\text{H NMR (400 MHz, CDCl}_3) \ \delta 7.41–7.20 \ (m, 18 \text{ H}), 7.18–7.10 \ (m, 2 \text{ H}), 5.28 \ (d, J = 3.6 \text{ Hz, 1 H}), 4.98 \ (d, J = 10.9 \text{ Hz, 1 H}), 4.87–4.42 \ (m, 7 \text{ H}), 4.04–3.96 \ (m, 2 \text{ H}), 3.76 \ (dd, J = 10.5, 3.6 \text{ Hz, 1 H}), 3.69–3.58 \ (m, 2 \text{ H}), 3.53 \ (dd, J = 9.7, 3.7 \text{ Hz, 1 H}), 2.13 \ (s, 3 \text{ H}), 1.83 \ (q, J = 11.6 \text{ Hz, 6 H}), 1.68–1.52 \ (m, 6 \text{ H}); \ ^{13}\text{C NMR (100 MHz, CDCl}_3) \ \delta 139.1, 138.4, 138.3, 138.1, 128.3, 128.3, 128.3, 128.1, 127.9, 127.9, 127.7, 127.6, 127.6, 127.4, 89.8, 82.1, 80.1, 78.2, 75.5, 75.1, 74.5, 73.4, 72.8, 69.7, 68.8, 42.4, 36.3, 30.6; HRMS (MALDI) \ m/z \ \text{calcd for C}_{44}\text{H}_{50}\text{O}_6\text{Na} \ [\text{M}+\text{Na}]^+ \ 697.3500, \ \text{found 697.3496.}"

6ed (89\% yield, \(\alpha/\beta = 1.2:1\); a colorless oil): \([\alpha]^{25}_D = 7.8 \ (c \ 1.6, \text{CHCl}_3); \ ^1\text{H NMR (400 MHz, CDCl}_3) \ \delta 7.38–7.23 \ (m, 18 \text{ H}), 7.22–7.16 \ (m, 2 \text{ H}), 5.00 \ (d, J = 11.0 \text{ Hz, 1 H}), 4.91 \ (d, J = 10.9 \text{ Hz, 1 H}), 4.82 \ (d, J = 10.9 \text{ Hz, 1 H}), 4.77 \ (d, J = 10.9 \text{ Hz, 1 H}), 4.71 \ (d, J = 7.5 \text{ Hz, 1 H}), 4.69 \ (d, J = 4.3 \text{ Hz, 1 H}), 4.61–4.50 \ (m, 3 \text{ H}), 3.73 \ (dd, J = 10.6, 1.6 \text{ Hz, 1 H}), 3.68–3.58 \ (m, 2 \text{ H}), 3.55–3.39 \ (m, 3 \text{ H}), 2.15 \ (s, 3 \text{ H}), 1.94 \ (d, J = 11.6 \text{ Hz, 3 H}), 1.83 \ (d, J = 11.6 \text{ Hz, 1 H}), 1.69–1.53 \ (m, 6 \text{ H}); \ ^{13}\text{C NMR (100 MHz, CDCl}_3) \ \delta 138.7, 138.6, 138.4, 138.2, 128.3, 128.3, 128.3, 128.3, 128.2, 127.9, 127.9, 127.7, 127.6, 127.5, 127.4, 85.1, 82.3, 78.2, 75.7, 75.3, 74.9, 74.6, 73.4, 69.5, 42.8, 36.3, 30.7; HRMS (MALDI) \ m/z \ \text{calcd for C}_{44}\text{H}_{50}\text{O}_6\text{Na} \ [\text{M}+\text{Na}]^+ \ 697.3500, \ \text{found 697.3479.}"

S12
6da\textsuperscript{10} (98% yield, \(\alpha/\beta = 1.8:1\))

6db\textsuperscript{11} (99% yield, \(\alpha/\beta = 2.5:1\))

6dc\textsuperscript{11} (83% yield, \(\alpha/\beta = 10:1\))

6dd (89% yield, \(\alpha/\beta = 3:1\); a colorless oil). \(6\text{dd}\alpha\): \([\alpha]_{D}^{25} = 114.6 (c 1.1, \text{CHCl}_3)\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 5.50–5.31 (m, 2 \text{H}), 4.96 (t, J = 9.8 \text{ Hz}, 1 \text{H}), 4.30 (dd, J = 12.1, 4.8 \text{ Hz}, 1 \text{H}), 4.19 (ddd, J = 10.1, 4.8, 2.2 \text{ Hz}, 1 \text{H}), 4.02 (dd, J = 12.0, 2.2 \text{ Hz}, 1 \text{H}), 2.14 (s, 3 \text{H}), 2.08 (s, 3 \text{H}), 2.04 (s, 3 \text{H}), 2.00 (s, 3 \text{H}), 1.88–1.74 (m, 6 \text{H}), 1.62 (dd, \(J = 21.5, 12.4 \text{ Hz}, 6 \text{H})\); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)) \(\delta 170.8, 170.3, 170.0, 90.1, 74.6, 69.9, 69.4, 67.4, 62.6, 42.4, 36.5, 36.2, 30.6, 29.7, 21.0, 20.7\); HRMS (MALDI) \(m/z\) calcd for C\(_{44}\)H\(_{50}\)O\(_6\)Na \([\text{M+Na}]^{+}\) 447.1989, found 447.1989.

\(6\text{dd}\beta\): \([\alpha]_{D}^{25} = -14.7 (c 0.6, \text{CHCl}_3)\); \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)) \(\delta 5.03 (ddd, J = 11.6, 9.3, 5.3 \text{ Hz}, 1 \text{H}), 4.93 (t, J = 9.6 \text{ Hz}, 1 \text{H}), 4.86 (dd, J = 9.7, 2.0 \text{ Hz}, 1 \text{H}), 4.25 (dd, J = 12.0, 5.9 \text{ Hz}, 1 \text{H}), 4.07 (dd, J = 12.0, 2.5 \text{ Hz}, 1 \text{H}), 3.60 (ddd, J = 9.6, 5.9, 2.6 \text{ Hz}, 1 \text{H}), 2.20–2.10 (m, 4 \text{H}), 2.06 (s, 3 \text{H}), 2.03 (s, 3 \text{H}), 2.02 (s, 3 \text{H}), 1.79 (dt, J
= 11.9, 6.8 Hz, 6 H), 1.63 (q, J = 12.5 Hz, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 170.4, 169.8, 92.5, 75.3, 71.7, 71.1, 69.4, 62.9, 42.4, 37.5, 36.2, 30.7, 29.7, 20.9, 20.8, 20.7; HRMS (MALDI) m/z calcd for C₄₄H₅₀O₆Na [M+Na]+ 447.1989, found 447.1987.

2.7. Synthesis of Ortho-iodobenzyl

2,3,4-tri-0-benzoyl-6-0-tert-butyldiphenylsilyl-β-D-glucopyranoside (S3)

Compound 3a (2.0 g, 2.46 mmol) was treated with sodium methoxide (100 mg) in methanol (10 mL) for 2 h at room temperature. The mixture was neutralized with Amberlite IRA-120B(H⁺) resin and then concentrated to give S1. To a solution of S1 (2.1 g, 5.3 mmol) and imidazole (805 mg, 10.6 mmol) in DMF (50 mL), was added dropwise a solution of tert-butyldiphenylchlorosilane (1.5 mL, 7.9 mmol). After the reaction mixture was stirred overnight at ambient temperature, the mixture was concentrated to afford a yellowish oily foam S2. To a solution of S2 in pyridine (10 mL) was added benzoyl chloride (2.8 mL, 21.2 mmol). The reaction mixture was stirred at ambient temperature and monitored by TLC. Quantitative conversion of the starting material to a single product was observed after 6 h. The mixture was cooled using an ice-bath, quenched by addition of MeOH (5 mL), and extracted with CH₂Cl₂ (3×30 mL). The organic phase was washed with brine, dried over sodium sulfate, and evaporated to dryness. The residue was purified by silica gel column chromatography (hexane/ethyl acetate, 10:1) to give S3 (88% for three steps) as a white solid: [α]²⁵ᵋ = −10.2 (c 5.3, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.98 (dd, J = 8.3, 1.2 Hz, 2 H), 7.89 (ddd, J = 8.5, 5.7, 1.2 Hz, 4 H), 7.79 (dd, J = 7.9, 1.1 Hz, 1 H), 7.75 (dd, J = 8.0, 1.4 Hz, 2 H), 7.65 (dd, J = 8.0, 1.3 Hz, 2 H), 7.58–7.49 (m, 2 H),
7.47–7.29 (m, 12 H), 7.25 (t, J = 7.4 Hz, 2 H), 7.17 (td, J = 7.6, 1.1 Hz, 1 H), 6.96 (td, J = 7.7, 1.6 Hz, 1 H), 5.88 (t, J = 9.6 Hz, 1 H), 5.74 (t, J = 9.3 Hz, 1 H), 5.67 (dd, J = 9.7, 7.9 Hz, 1 H), 4.98 (d, J = 13.3 Hz, 1 H), 4.92 (d, J = 7.9 Hz, 1 H), 4.78 (d, J = 13.3 Hz, 1 H), 3.96–3.90 (m, 3 H), 1.10 (s, 9 H); 13C NMR (125 MHz, CDCl3) δ 165.9, 165.1, 164.9, 139.3, 139.0, 135.6, 135.5, 133.2, 133.1, 133.0, 133.0, 129.8, 129.7, 129.6, 129.6, 129.4, 129.3, 129.2, 128.9, 128.9, 128.3, 128.2, 128.2, 127.7, 127.6, 99.8, 97.5, 75.2, 74.2, 73.3, 72.8, 72.0, 69.2, 62.6, 26.7, 19.2; HRMS (MALDI) m/z calcd for C30H27O9SiNa [M+Na]^+ 969.1926, found 969.1941.

2.8. Ortho-Iodobenzyl 2,3,4-tri-O-benzoyl-β-D-glucopyranoside (8)

To a solution of S3 (283 mg, 0.3 mmol) in THF (3 mL) was added HF·pyridine (0.3 mL) at 0°C. After being stirred at room temperature for 8 h under nitrogen, the reaction mixture was evaporated under vacuum. The residue was dissolved in CH2Cl2 and washed with sat. NaHCO3, H2O, and brine, respectively. The organic layer was dried (Na2SO4) and concentrated. The residue was chromatographed on silica gel (hexane/ethyl acetate, 5:1) to afford 8 (88%) as a white solid: [α]25°D = –14.7 (c 2.0, CHCl3); 1H NMR (500 MHz, CDCl3) δ 7.95 (td, J = 8.4, 1.2 Hz, 4 H), 7.86 (dd, J = 8.4, 1.3 Hz, 2 H), 7.76 (dd, J = 7.9, 1.1 Hz, 1 H), 7.56–7.48 (m, 2 H), 7.45–7.36 (m, 5 H), 7.34–7.27 (m, 3 H), 7.15 (td, J = 7.5, 1.1 Hz, 1 H), 6.95 (td, J = 7.7, 1.7 Hz, 1 H), 5.94 (t, J = 9.7 Hz, 1 H), 5.64 (dd, J = 9.8, 7.9 Hz, 1 H), 5.56 (t, J = 9.7 Hz, 1 H), 4.93 (d, J = 13.2 Hz, 1 H), 4.92 (d, J = 7.9 Hz, 1 H), 4.78 (d, J = 13.2 Hz, 1 H), 3.93 (dd, J = 12.6, 1.8 Hz, 1 H), 3.84 (ddd, J = 9.7, 4.3, 2.1 Hz, 1 H), 3.79 (dd, J = 12.6, 4.4 Hz, 1 H), 2.64 (brs, 1 H); 13C NMR (125 MHz, CHCl3) δ 166.0, 165.8, 165.0, 139.1, 139.1, 133.6, 133.2, 133.2, 129.9, 129.8, 129.7, 129.4, 129.2, 129.1, 128.5, 128.5, 128.5, 128.3, 128.2, 99.9, 97.8, 74.7, 74.6, 72.7, 71.8, 69.8, 61.3; HRMS (MALDI) m/z calcd for C34H29O9INa [M+Na]^+ 731.0749, found 731.0761.
2.9. Disaccharide 9

The general glycosylation procedure was applied to provide 9 (97% yield, β only) as a white solid: \([\alpha]_{D}^{25} = -18.4 (c 0.9, \text{CHCl}_3)\); \(\text{H NMR (400 MHz, CDCl}_3\) \(\delta 8.04–7.94 (m, 4 \text{ H}), 7.93–7.71 (m, 11 \text{ H}), 7.57–7.45 (m, 4 \text{ H}), 7.44–7.38 (m, 5 \text{ H}), 7.33 (dd, \(J = 13.8, 7.2 \text{ Hz, } 6 \text{ H}), 7.29–7.23 (m, 6 \text{ H}), 7.23–7.16 (m, 1 \text{ H}), 7.15 (td, \(J = 7.5, 1.1 \text{ Hz, } 1 \text{ H}), 6.93 (td, \(J = 7.6, 1.8 \text{ Hz, } 1 \text{ H}), 5.92 (t, \(J = 9.6 \text{ Hz, } 1 \text{ H}), 5.77 (t, \(J = 9.6 \text{ Hz, } 1 \text{ H}), 5.63 (t, \(J = 9.7 \text{ Hz, } 1 \text{ H}), 5.55 (dd, \(J = 9.8, 7.9 \text{ Hz, } 1 \text{ H}), 5.48 (dd, \(J = 9.8, 7.9 \text{ Hz, } 1 \text{ H}), 5.33 (t, \(J = 9.6 \text{ Hz, } 1 \text{ H}), 5.05 (d, \(J = 7.9 \text{ Hz, } 1 \text{ H}), 4.72 (d, \(J = 7.9 \text{ Hz, } 1 \text{ H}), 4.69 (d, \(J = 12.9 \text{ Hz, } 1 \text{ H}), 4.59 (dd, \(J = 12.2, 3.1 \text{ Hz, } 1 \text{ H}), 4.48–4.37 (m, 2 \text{ H}), 4.15–4.05 (m, 2 \text{ H}), 4.05–3.98 (m, 1 \text{ H}), 3.94 (dd, \(J = 11.2, 7.5 \text{ Hz, } 1 \text{ H}); \(\text{C NMR (100 MHz, CDCl}_3\) \(\delta 166.1, 165.7, 165.7, 165.4, 165.2, 165.0, 139.2, 138.9, 133.5, 133.4, 133.1, 129.9, 129.8, 129.8, 129.5, 129.5, 129.4, 129.2, 128.8, 128.7, 128.4, 128.4, 128.3, 128.2, 128.1, 101.1, 99.5, 98.2, 74.3, 72.9, 72.8, 72.3, 71.9, 71.7, 69.8, 69.62, 68.2, 63.0; \(\text{HRMS (MALDI) m/z calced for C}_{68}\text{H}_{55}\text{O}_{18}\text{INa [M+Na]}^+ 1309.2325, found 1309.2318.}

2.10. Disaccharide donor 10

The general Sonogashira procedure was applied to provide 10 (88% yield) as a white solid: \([\alpha]_{D}^{25} = -4.2 (c 3.2, \text{CHCl}_3)\); \(\text{H NMR (400 MHz, CDCl}_3\) \(\delta 8.01–7.96 (m, 2 \text{ H}), 7.96–7.92 (m, 2 \text{ H}), 7.91–7.87 (m, 2 \text{ H}), 7.78 (ddd, \(J = 16.4, 13.2, 5.1 \text{ Hz, } 10 \text{ H}), 7.57–7.12 (m, 26 \text{ H}), 7.09 (td, \(J = 7.4, 1.3 \text{ Hz, } 1 \text{ H}), 5.85 (t, \(J = 9.6 \text{ Hz, } 1 \text{ H}), 5.73 (t, \(J = 9.6 \text{ Hz, } 1 \text{ H}), 5.59 (t, \(J = 9.7 \text{ Hz, } 1 \text{ H}), 5.51 (dd, \(J = 9.7, 7.9 \text{ Hz, } 1 \text{ H}), 5.42 (dd, \(J = 9.7, 7.9 \text{ Hz, } 1 \text{ H}), 5.35 (t, \(J = 9.7 \text{ Hz, } 1 \text{ H}), 4.94 (d, \(J = 7.8 \text{ Hz, } 1 \text{ H}), 4.78–4.69 (m,
2 H), 4.55 (d, J = 13.2 Hz, 1 H), 4.38 (dd, J = 12.2, 5.0 Hz, 1 H), 4.17–4.08 (m, 1 H), 4.05–3.97 (m, 2 H), 3.86 (dd, J = 11.4, 6.9 Hz, 1 H), 3.04 (s, 3 H), 2.43 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.0, 165.7, 165.6, 165.3, 165.1, 165.1, 165.0, 144.8, 138.0, 133.4, 133.1, 133.1, 133.0, 131.4, 129.9, 129.8, 129.8, 129.7, 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.5, 128.4, 128.2, 128.2, 128.1, 127.8, 127.6, 121.9, 101.2, 99.7, 88.4, 73.8, 73.0, 72.9, 72.1, 71.8, 71.7, 69.9, 69.6, 69.2, 68.4, 66.7, 63.0, 39.0, 21.6; HRMS (MALDI) \(m/z\) calcd for C\(_{78}\)H\(_{65}\)NO\(_20\)SNa [M+Na]+ 1390.3713, found 1390.3712.

2.11. Disaccharides 11

![Diagram](image)

The general glycosylation procedure was applied to provide 11 (87% yield, \(\beta\) only) as a white solid: \([\alpha]^{25}_D = 5.6\) (c 1.1, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06–7.99 (m, 2 H), 7.97–7.90 (m, 4 H), 7.89–7.76 (m, 8 H), 7.58–7.26 (m, 21 H), 5.83 (t, J = 8.7 Hz, 1 H), 5.78 (t, J = 8.8 Hz, 1 H), 5.59 (t, J = 9.6 Hz, 1 H), 5.48 (dd, J = 9.7, 7.8 Hz, 1 H), 5.37 (dd, J = 9.8, 7.9 Hz, 1 H), 5.31 (t, J = 9.5 Hz, 1 H), 5.23 (d, J = 4.8 Hz, 1 H), 5.04 (d, J = 7.8 Hz, 1 H), 4.79 (d, J = 7.9 Hz, 1 H), 4.58 (dd, J = 12.1, 3.1 Hz, 1 H), 4.41 (dd, J = 12.2, 5.1 Hz, 1 H), 4.08 (dd, J = 9.6, 5.0, 3.3 Hz, 1 H), 4.04–3.91 (m, 3 H), 3.52–3.40 (m, 1 H), 0.66 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.0, 165.7, 165.6, 165.4, 165.1, 165.1, 165.0, 140.4, 133.4, 133.1, 133.1, 129.8, 129.8, 129.7, 129.7, 129.6, 129.5, 129.3, 128.9, 128.8, 128.4, 128.4, 128.3, 128.2, 128.2, 121.9, 100.9, 100.2, 80.6, 74.2, 72.9, 72.4, 72.1, 71.8, 69.9, 69.6, 68.1, 63.0, 56.7, 56.2, 49.9, 42.3, 39.8, 39.5, 39.0, 37.1, 36.6, 36.2, 35.7, 31.9, 31.8, 29.7, 28.2, 28.0, 24.3, 23.8, 22.8, 22.5, 21.1, 19.2, 18.7, 11.8; HRMS (MALDI) \(m/z\) calcd for C\(_{88}\)H\(_{94}\)O\(_{18}\)Na [M+Na]+ 1461.6332, found 1461.6348.

2.12. Trisaccharides 12
The general glycosylation procedure was applied to provide 12 (86% yield, β only) as a white solid: $[\alpha]_{D}^{25} = 5.9$ (c 1.5, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 7.3$ Hz, 4 H), 7.95–7.89 (m, 2 H), 7.83–7.70 (m, 8 H), 7.63 (d, $J = 7.1$ Hz, 2 H), 7.57–7.09 (m, 34 H), 5.82 (t, $J = 9.8$ Hz, 1 H), 5.55 (t, $J = 9.6$ Hz, 1 H), 5.50 (t, $J = 9.8$ Hz, 1 H), 5.39 (td, $J = 10.1$, 8.0 Hz, 2 H), 5.31 (t, $J = 9.8$ Hz, 1 H), 5.24 (d, $J = 8.0$ Hz, 1 H), 5.15 (d, $J = 11.7$ Hz, 1 H), 5.10 (d, $J = 11.7$ Hz, 1 H), 4.92 (d, $J = 11.7$ Hz, 1 H), 4.87 (d, $J = 11.7$ Hz, 1 H), 4.73 (d, $J = 3.3$ Hz, 1 H), 4.68 (d, $J = 8.0$ Hz, 1 H), 4.17 (dd, $J = 12.2$, 3.0 Hz, 2 H), 4.04–3.81 (m, 7 H), 3.68 (ddd, $J = 9.8$, 5.8, 2.7 Hz, 1 H), 3.58 (dd, $J = 9.6$, 2.1 Hz, 1 H), 3.50 (dd, $J = 10.5$, 4.0 Hz, 1 H), 3.40–3.22 (m, 5 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.1, 165.6, 165.5, 165.5, 165.3, 164.9, 164.7, 139.7, 138.9, 137.7, 133.5, 133.2, 133.2, 133.2, 133.1, 133.0, 132.9, 132.9, 130.2, 129.8, 129.7, 129.6, 129.6, 128.9, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.6, 100.1, 99.8, 96.9, 81.5, 80.2, 76.8, 76.5, 76.4, 74.7, 73.7, 73.2, 72.9, 72.2, 71.1, 70.0, 69.6, 55.3; HRMS (ESI) m/z calcd for C$_{89}$H$_{68}$O$_{23}$Na [M+Na]$^+$ 1539.4983, found 1539.4962.

2.13. Trisaccharides 13

The general glycosylation procedure was applied to provide 13 (97% yield, β only) as a white solid: $[\alpha]_{D}^{25} = -29.1$ (c 0.6, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08–7.98 (m, 4 H), 7.99–7.68 (m, 18 H), 7.59–7.30 (m, 22 H), 7.29–7.08 (m, 9 H), 6.91 (td, $J = 7.7$, 1.7 Hz, 1 H), 6.12 (t, $J = 9.7$ Hz, 1 H), 5.84 (t, $J = 9.6$ Hz, 1 H), 5.75–5.61 (m, 2 H), 5.55 (t, $J = 8.3$ Hz, 1 H), 5.51 (dd, $J = 8.5$, 6.5 Hz, 1 H), 5.25 (dd, $J = 9.7$, 7.8 Hz, 1 H), 5.15–5.03 (m, 2 H), 4.81–4.73 (m, 2 H), 4.66 (d, $J = 7.8$ Hz, 1 H), 4.61 (dd, $J = 12.1$, 3.0 Hz, 1 H), 4.52 (d, $J = 13.0$ Hz, 1 H), 4.46 (dd, $J = 12.1$, 5.4 Hz, 1 H),
4.35–4.29 (m, 1 H), 4.07 (dd, $J = 11.2, 3.3$ Hz, 1 H), 3.98 (d, $J = 10.2$ Hz, 1 H), 3.94–3.79 (m, 3 H), 3.70 (dd, $J = 11.2, 5.9$ Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.1, 165.7, 165.7, 165.5, 165.4, 165.3, 165.2, 165.0, 164.9, 139.1, 139.0, 133.4, 133.2, 133.1, 133.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.7, 129.6, 129.5, 129.4, 129.3, 129.1, 128.9, 128.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 101.4, 100.7, 99.9, 97.9, 74.4, 74.2, 73.6, 72.9, 72.8, 72.7, 72.3, 72.1, 71.9, 71.8, 70.7, 69.7, 68.6, 68.3, 63.2; HRMS (MALDI) $m/z$ calcd for C$_{95}$H$_{78}$O$_{26}$INa [M+Na]$^+$ 1784.3718, found 1784.3700.

2.14. 1H-isochromene D

![Chemical Structure](image)

**Compound D:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70–7.62 (m, 2 H), 7.23–7.19 (m, 2 H), 7.15 (td, $J = 7.5, 1.3$ Hz, 1 H), 7.07 (td, $J = 7.4, 1.3$ Hz, 1 H), 6.97–6.89 (m, 2 H), 5.77 (s, 1 H), 4.94 (s, 2 H), 3.03 (s, 3 H), 2.34 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.0, 144.0, 135.6, 132.0, 129.7, 128.4, 127.9, 127.4, 126.6, 123.9, 123.8, 98.6, 70.0, 36.3, 21.7; HRMS (ESI) $m/z$ calcd for C$_{17}$H$_{17}$NO$_3$SNa [M+Na]$^+$ 338.0821, found 338.0826.

3. References


