Supporting Information

C-Glycosidation of Unprotected Aldopentoses with Ketones Using Proline-Triethylamine as Catalyst

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General

For thin layer chromatography (TLC), Merck Silica gel 60 F254 aluminum sheets were used and compounds were visualized by treatment with a solution of p-anisaldehyde (3.7 mL), CH₃COOH (1.5 mL), and conc H₂SO₄ (5.0 mL) in EtOH (135 mL). Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh). ¹H NMR and ¹³C NMR were recorded on a Bruker Avance 400. Proton chemical shifts are given in ppm relative to tetramethylsilane (δ 0.00 ppm) in CDCl₃ or to the residual proton signals of the deuterated solvent in CDCl₃ (δ 7.26 ppm), in CD₃OD (δ 3.31 ppm), or in D₂O (δ 4.79 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl₃ (δ 77.0 ppm) or in CD₃OD (δ 49.0 ppm). High-resolution mass spectra were recorded on a Thermo Scientific LTQ Orbitrap ESI ion trap mass spectrometer.
1. Evaluations of Catalysts and Conditions for the Reactions to Afford 2

**General procedure for evaluations of catalysts and conditions**

To a mixture of carbohydrate (1.0 mmol) and acetone (20 mmol) in solvent (1.0 mL) was added catalyst (0.5 mmol) and additive (0.5 mmol) at room temperature (25 °C) and the mixture was stirred at the same temperature. Formation of the products was monitored by TLC analyses. The mixture was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH) to afford 2. Selected results are shown in Tables S1-S5.

**Table S1.** Reaction of 2-deoxy-D-ribose (1a) with acetone to afford 2a

<table>
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<tr>
<th>entry</th>
<th>catalyst</th>
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<th>solvent</th>
<th>time (h)</th>
<th>yield (%)</th>
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<td>-</td>
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<td>6</td>
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<td>H$_3$BO$_3$</td>
<td>2-PrOH</td>
<td>24</td>
<td><em>b</em></td>
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<tr>
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<td>Et$_3$N</td>
<td>2-PrOH</td>
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<td>78</td>
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$^a$H$_3$BO$_3$ (1.0 mmol) was used.  
$^b$Product 2 was not obtained and 1a was consumed.

**Table S2.** Reaction of D-ribose (1b) with acetone to afford 2b

<table>
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<tr>
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**Table S3.** Reaction of D-arabinose (1c) with acetone to afford 2c

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<td>35</td>
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<tr>
<td>6</td>
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$^a$H$_3$BO$_3$ (1.0 mmol) was used.
**Table S4.** Reaction of D-xylose (1d) with acetone to afford 2d

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**Table S5.** Reaction of D-lyxose (1e) with acetone to afford 2e

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<td>74</td>
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2. Reactions of 1 with Acetone to Afford 2 (Scheme 1)

**General Procedure**

To a mixture of carbohydrate (1.0 mmol) and acetone (20 mmol) in 2-PrOH (1.0 mL) was added L-proline (0.5 mmol) and Et<sub>3</sub>N (0.5 mmol) at room temperature (25 °C) and the mixture was stirred at the same temperature. Formation of the products was monitored by TLC analyses. The mixture was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to afford 2.

**Compound 2a-1**

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

Synthesized from 2-deoxy-D-ribose (1.11 mmol), flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 93:7), 152 mg, 78% (dr 3:2). R<sub>f</sub> 0.60 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 9:1). Pale yellow viscous oil. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ 4.53-4.41 (m, 1H), 4.25-4.16 (m, 1H), 3.83-3.72 (m, 1H), 3.60-3.47 (m, 2H), 2.90 (dd, J = 16.4 Hz, 8.0 Hz, 1H x 2/5), 2.76 (dd, J = 16.4 Hz, 7.6 Hz, 1H x 3/5), 2.75-2.68 (m, 1H x 2/5), 2.66 (dd, J = 16.4 Hz, 5.2 Hz, 1H x 3/5), 2.42-2.32 (m, 1H x 2/5), 2.17 (s, 3H), 2.03-1.95 (m, 1H x 3/5), 1.75-1.58 (m, 1H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD): δ 210.0, 209.9, 88.9, 87.3, 75.8, 75.7, 74.1, 73.5, 64.0, 63.4, 51.0, 50.1, 42.0, 41.4, 30.7, 30.6. ESI-HRMS: m/z calcd for C<sub>8</sub>H<sub>15</sub>O<sub>4</sub> [M+H]<sup>+</sup> 175.0965, found 175.0965.

**Compound 2a-2**

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{O} & \quad \text{OH}
\end{align*}
\]

Obtained with 2a-1, 19.5 mg, 10%. R<sub>f</sub> 0.64 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1). Pale yellow viscous oil. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ 4.19-4.10 (m, 1H), 4.01 (brs, 1H), 3.68-3.46 (m, 3H), 2.57 (dd, J = 15.6 Hz, 8.6 Hz, 1H), 2.47 (dd, J = 15.6 Hz, 4.4 Hz, 1H), 2.15 (s, 3H), 1.87-1.80 (m, 1H), 1.58-1.49 (m, 1H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD): δ 209.99, 209.91, 69.15, 69.14, 68.6, 68.0, 67.1, 50.0, 49.9, 38.86, 38.84, 30.6, 30.5. ESI-HRMS: m/z calcd for C<sub>8</sub>H<sub>15</sub>O<sub>4</sub> [M+H]<sup>+</sup> 175.0965, found 175.0964.
Compound 2b (2b-1 and 2b-2)

Synthesized from D-ribose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 92:8), 173 mg, 67% ($2b$-1:2b-2 = 7:3). $R_f$ 0.51 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): peaks of 2b-1 major isomer extracted from the spectrum: $\delta$ 4.83-4.79 (m, 1H), 4.15-4.08 (m, 1H), 3.97-3.93 (m, 1H), 3.82-3.77 (m, 1H), 3.72-3.68 (m, 1H), 3.58 (dd, $J$ = 4.6 Hz, 11.2 Hz, 1H), 2.84 (d, $J$ = 6.4 Hz, 1H), 2.79-2.64 (m, 1H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD): peaks of 2b-1 major isomer extracted from the spectrum: $\delta$ 210.0, 86.4, 79.9, 76.3, 72.6, 63.5, 48.2, 30.6. ESI-HRMS: $m/z$ calc'd for C$_8$H$_{14}$O$_5$Na [M+Na]$^+$ 213.0733, found 213.0735.

Compound 2c (2c-1, 2c-2, and 2c-3)

Synthesized from D-arabinose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 9:1), 200 mg, 79% (2c-1:2c-2:2c-3 = 5:3:2). $R_f$ 0.50 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): peaks of 2c-1 major isomer extracted from the spectrum: $\delta$ 4.51-4.45 (m, 1H), 3.98-3.94 (m, 1H), 3.84-3.79 (m, 1H), 3.75-3.71 (m, 1H), 3.66-3.63 (m, 1H), 3.61-3.55 (m, 1H), 2.82 (dd, $J$ = 6.8 Hz, 1.6 Hz, 1H), 2.79 (dd, $J$ = 7.6 Hz, 2.4 Hz, 1H), 2.19 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD): peaks of 2c-1 major isomer extracted from the spectrum: $\delta$ 209.9, 87.3, 84.8, 80.4, 78.8, 63.6, 43.8, 30.5. ESI-HRMS: $m/z$ calc'd for C$_8$H$_{14}$O$_5$Na [M+Na]$^+$ 213.0733, found 213.0736.

Compound 2c-3

Purified from the mixture of 2c-1, 2c-2, and 2c-3, flash column chromatography (CH$_2$Cl$_2$/MeOH = 95:5). $R_f$ 0.65 (CH$_2$Cl$_2$/MeOH = 95:5). Colorless solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.88 (dd, $J$ = 6.4 Hz, 5.2 Hz, 1H), 4.56 (dd, $J$ = 5.0 Hz, 1.0 Hz, 1H), 4.31 (d, $J$ = 7.2 Hz, 1H), 4.14-4.10 (m, 1H), 3.90-3.82 (m, 2H), 2.22 (d, $J$ = 14.4 Hz, 1H), 2.21 (d, $J$ = 9.2 Hz, 1H), 1.93 (dd, $J$ = 14.4 Hz, 6.8 Hz, 1H), 1.48 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 107.9, 87.0, 83.4, 80.1, 78.6, 68.5, 43.1, 24.6. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.86 (dd, $J$ = 6.4 Hz, 5.2 Hz, 1H), 4.48 (dd, $J$ = 5.2 Hz, 1.2 Hz, 1H), 4.18 (s, 1H), 4.08-4.05 (m, 1H), 3.85-3.77 (m, 2H), 2.18 (d, $J$ = 14.0 Hz, 1H), 1.94 (dd, $J$ = 14.0 Hz, 6.4 Hz, 1H), 1.42 (s, 3H). $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ 109.4, 88.6, 84.7, 81.6, 79.6, 70.0, 44.3, 25.0. ESI-HRMS: $m/z$ calc'd for C$_8$H$_{13}$O$_4$ [M+H]$^+$ 173.0808, found 173.0808.

Compound 2d (2d-1 and 2d-2)

Synthesized from D-xylose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 92:8), 207 mg, 80% (2d-1:2d-2 = 2:3). $R_f$ 0.51 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): peaks of 2d-2...
major isomer (α-isomer) extracted from the spectrum: δ 4.98-4.94 (m, 1H), 4.49 (d, J = 4.2 Hz, 1H), 4.10 (d, J = 3.2 Hz, 1H), 3.94 (ddd, J = 6.4 Hz, 4.8 Hz, 3.2 Hz, 1H), 3.81 (dd, J = 11.2 Hz, 4.8 Hz, 1H), 3.72 (dd, J = 11.2 Hz, 6.4 Hz, 1H), 2.30 (dd, J = 14.0 Hz, 7.6 Hz, 1H), 1.89 (dd, J = 14.0 Hz, 3.4 Hz, 1H), 1.48 (s, 3H). 13C NMR (100 MHz, CD3OD): peaks of 2d-2 major isomer (α-isomer) extracted from the spectrum: δ 107.7, 89.2, 83.8, 83.1, 82.1, 76.3, 61.3, 46.9, 26.9. ESI-HRMS: m/z calcd for C8H15O3 [M+H]+ 191.0914, found 191.0917.

**Compound 2d-3**

Purified from stored 2d, column chromatography (CH2Cl2/MeOH = 92:8). Rf 0.51 (CH2Cl2/MeOH = 9:1). Colorless viscous oil. 1H NMR (400 MHz, CD3OD): peaks of 2d-3 major isomer (β-isomer) extracted from the spectrum: δ 3.81 (dd, J = 10.8 Hz, 5.6 Hz, 1H), 3.57 (td, J = 9.4 Hz, 2.8 Hz, 1H), 3.44 (ddd, J = 10.8 Hz, 9.4 Hz, 5.6 Hz, 1H), 3.27 (t, J = 9.4 Hz, 1H), 3.15 (t, J = 10.8 Hz, 1H), 3.05 (t, J = 9.4 Hz, 1H), 2.88 (dd, J = 16.0 Hz, 2.8 Hz, 1H), 2.54 (dd, J = 16.0 Hz, 9.4 Hz, 1H), 2.17 (s, 3H). 13C NMR (100 MHz, CD3OD): peaks of 2d-3 major isomer (β-isomer) extracted from the spectrum: δ 210.1, 79.8, 78.3, 75.2, 71.6, 71.1, 47.3, 30.7. ESI-HRMS: m/z calcd for C8H15O3 [M+H]+ 191.0914, found 191.0900.

**Compound 2e**

Synthesized from d-lyxose, flash column chromatography (CH2Cl2/MeOH = 92:8), 192 mg, 74% (dr 2:1). Rf 0.52 (CH2Cl2/MeOH = 9:1). Pale yellow viscous oil. 1H NMR (400 MHz, CD3OD): δ 3.97 (td, J = 9.6 Hz, 3.2 Hz, 1H x 2/3), 3.88-3.79 (m, 2H), 3.78-3.70 (m, 1H x 2/3), 3.69-3.66 (m, 1H x 2/3), 3.60-3.58 (m, 1H x 1/3), 3.57-3.55 (m, 1H x 1/3), 3.54 (dd, J = 10.0 Hz, 3.2 Hz, 1H x 2/3), 3.41 (dd, J = 9.6 Hz, 3.2 Hz, 1H x 1/3), 3.08 (t, J = 10.6 Hz, 1H x 1/3), 2.86 (dd, J = 16.8 Hz, 8.0 Hz, 1H x 1/3), 2.84 (dd, J = 15.8 Hz, 3.2 Hz, 1H x 2/3), 2.66 (dd, J = 16.8 Hz, 4.8 Hz, 1H x 1/3), 2.56 (dd, J = 15.8 Hz, 9.4 Hz, 1H x 2/3), 2.18 (s, 3H x 2/3), 2.16 (s, 3H x 1/3). 13C NMR (100 MHz, CD3OD): δ 210.8, 209.5, 76.6, 76.5, 73.8, 72.3, 71.8, 71.5, 71.3, 69.8, 68.2, 68.1, 47.6, 45.8, 30.7, 30.6. ESI-HRMS: m/z calcd for C8H15O3 [M+H]+ 191.0914, found 191.0916.

3. Reactions of 1 with Ketones to Afford C-Glycosides 3–10 (Table 1)

**General Procedure**

To a mixture of carbohydrate (1.0 mmol) and ketone (20 mmol) in 2-PrOH (1.0 mL) was added L-proline (0.5 mmol) and Et3N (0.5 mmol) at room temperature (25 °C) and the mixture was stirred at the same temperature. Formation of the products was monitored by TLC analyses. The mixture was purified by flash column chromatography (CH2Cl2/MeOH) to afford the C-glycosidation product.
**Compound 3**

![Structure](image)

Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 128 mg, 61% (dr 3:2). Rₐ 0.61 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 4.54-4.42 (m, 1H), 4.26-4.13 (m, 1H), 3.83-3.70 (m, 1H), 3.60-3.46 (m, 2H), 2.89 (dd, J = 16.2 Hz, 7.8 Hz, 1H x 2/5), 2.75 (dd, J = 16.2 Hz, 7.4 Hz, 1H x 3/5), 2.70-2.65 (m, 1H x 2/5), 2.65 (dd, J = 16.0 Hz, 5.2 Hz, 1H x 3/5), 2.52 (q, J = 7.2 Hz, 2H), 2.37 (dt, J = 12.8 Hz, 6.4 Hz, 1H x 2/5), 1.99 (dd, J = 12.8 Hz, 5.2 Hz, 1H x 3/5), 1.75-1.57 (m, 1H), 1.01 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CD₃OD): δ 212.7, 212.3, 88.9, 87.3, 75.9, 75.8, 74.1, 73.5, 64.0, 63.4, 49.8, 49.0, 42.0, 41.5, 37.5, 37.3, 7.9. ESI-HRMS: m/z calcd for C₉H₁₅O₄ [M+H]^+ 189.1121, found 189.1121.

**Compound 4**

![Structure](image)

Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 93.5 mg, 48% (dr 3:2). Rₐ 0.62 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 4.53-4.42 (m, 1H), 4.26-4.17 (m, 1H), 4.14 (s, 2H), 3.85-3.72 (m, 1H), 3.60-3.47 (m, 2H), 3.39 (s, 3H), 2.89 (dd, J = 16.0 Hz, 7.6 Hz, 1H x 2/5), 2.74 (dd, J = 16.0 Hz, 7.6 Hz, 1H x 3/5), 2.68-2.52 (m, 1H), 2.43-2.33 (m, 1H x 2/5), 2.00 (dd, J = 12.8 Hz, 5.2 Hz, 1H x 3/5), 1.78-1.61 (m, 1H). ¹³C NMR (100 MHz, CD₃OD): δ 209.1, 208.8, 88.9, 87.4, 78.89, 78.83, 75.6, 74.1, 73.5, 63.9, 63.4, 59.5, 46.5, 45.5, 42.0, 41.4. ESI-HRMS: m/z calcd for C₉H₁₅O₅ [M+H]^+ 205.1075, found 205.1075.

**Compound 5**

![Structure](image)

Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 150 mg, 49% (dr 3:2). Rₐ 0.63 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 4.52-4.41 (m, 1H), 4.26-4.16 (m, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.83-3.71 (m, 1H), 3.60-3.46 (m, 2H), 2.88 (dd, J = 16.0 Hz, 7.6 Hz, 1H x 1/3), 2.74 (dd, J = 16.0 Hz, 7.6 Hz, 1H x 2/3), 2.67 (dd, J = 16.0 Hz, 5.2 Hz, 1H x 1/3), 2.63 (dd, J = 16.0 Hz, 5.2 Hz, 1H x 2/3), 2.60-2.52 (m, 2H), 2.41-2.33 (m, 1H x 1/3), 2.32 (t, J = 7.4 Hz, 2H), 2.02-1.94 (m, 1H x 2/3), 1.83 (quintet, J = 7.2 Hz, 2H), 1.75-1.58 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CD₃OD): δ 211.3, 210.9, 175.2, 88.9, 87.3, 75.9, 75.8, 74.1, 73.5, 64.0, 63.4, 61.6, 50.2, 43.2, 43.1, 42.0, 41.5, 34.2, 19.9, 14.6. ESI-HRMS: m/z calcd for C₁₃H₂₃O₆ [M+H]^+ 275.1489, found 275.1498.

**Compound 6**

![Structure](image)

Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 75 mg, 31% (dr 3:2). Rₐ 0.64 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 4.53-4.41 (m, 1H), 4.25-4.14 (m,
Compound 7

Synthesized from 2-deoxy-d-ribose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 94:6), 140 mg, 40% (dr 3:2). R$_f$ 0.62 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.566 (s, 1H x 3/5), 4.562 (s, 1H x 2/5), 4.54-4.51 (m, 1H), 4.24-4.17 (m, 1H), 3.80 (dt, J = 4.8 Hz, 4.4 Hz, 1H x 2/5), 3.74 (td, J = 4.8 Hz, 2.8 Hz, 1H x 3/5), 3.60-3.46 (m, 2H), 3.40 (s, 6H), 3.06 (dd, J = 17.2 Hz, 7.2 Hz, 1H x 2/5), 2.93 (dd, J = 17.2 Hz, 7.2 Hz, 1H x 3/5), 2.78 (dd, J = 17.2 Hz, 5.6 Hz, 1H x 2/5), 2.74 (dd, J = 17.2 Hz, 6.0 Hz, 1H x 3/5), 2.42-2.33 (m, 1H x 2/5), 2.01 (dd, J = 13.2 Hz, 5.4 Hz, 2.0 Hz, 1H x 3/5), 1.74-1.59 (m, 1H). $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ 205.8, 205.4, 105.29, 105.27, 88.8, 87.2, 75.36, 75.32, 74.1, 73.6, 64.0, 63.4, 55.3, 55.2, 45.5, 44.6, 42.0, 41.4. ESI-HRMS: m/z calcd for C$_{10}$H$_{18}$O$_6$Na [M+Na]$^+$ 257.0996, found 257.0995.

Compound 8 (8-1 and 8-2)$^2$

Synthesized from d-arabinose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 9:1), 143 mg, 70% (8-1:8-2 = 2:3). R$_f$ 0.52 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.90-4.80 (m, 1H x 3/5), 4.48 (d, J = 4.8 Hz, 1H x 3/5), 4.20-4.14 (m, 2H x 2/5), 4.10-4.06 (m, 1H x 3/5), 3.99-3.93 (m, 1H x 2/5), 3.87 (dd, J = 13.4 Hz, 3.0 Hz, 1H x 3/5), 3.83-3.76 (m, 3H x 2/5), 3.66 (dd, J = 12.0 Hz, 3.4 Hz, 1H x 2/5), 3.60 (dd, J = 12.0 Hz, 5.2 Hz, 1H x 2/5), 2.85-2.70 (m, 2H x 2/5), 2.59-2.47 (m, 2H x 2/5), 2.11 (d, J = 14.4 Hz, 1H x 3/5), 1.91 (dd, J = 14.4 Hz, 6.6 Hz, 1H x 3/5), 1.80-1.59 (m, 2H x 3/5), 1.01 (t, J = 7.2 Hz, 3H x 2/5), 0.91 (t, J = 7.4 Hz, 3H x 3/5). $^{13}$C NMR (100 MHz, CD$_3$OD): $\delta$ 212.5, 111.6, 88.4, 85.4, 84.7, 82.3, 81.1, 80.7, 79.7, 78.7, 70.1, 63.4, 47.1, 42.0, 37.5, 32.1, 9.2, 7.9. ESI-HRMS: m/z calcd for C$_9$H$_{17}$O$_5$ [M+H]$^+$ 205.1071, found 205.1073.

Compound 9 (9-1 and 9-2)$^2$

Synthesized from d-arabinose, flash column chromatography (CH$_2$Cl$_2$/MeOH = 9:1); 9-1, 50 mg, 17%, R$_f$ 0.48 (CH$_2$Cl$_2$/MeOH = 9:1); 9-2, 141 mg, 48%, R$_f$ 0.57 (CH$_2$Cl$_2$/MeOH = 9:1).

Compound 9-1$^2$

R$_f$ 0.48 (CH$_2$Cl$_2$/MeOH = 9:1). Pale yellow viscous oil. $^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.20-4.15 (m, 1H), 4.15 (s, 2H),
3.96 (t, J = 5.4 Hz, 1H), 3.84-3.80 (m, 2H), 3.67 (dd, J = 12.0 Hz, 3.6 Hz, 1H), 3.59 (dd, J = 12.0 Hz, 5.2 Hz, 1H), 3.39 (s, 3H), 2.80 (dd, J = 15.8 Hz, 8.4 Hz, 1H), 2.71 (dd, J = 15.8 Hz, 4.4 Hz, 1H). 13C NMR (100 MHz, CD3OD): δ 209.0, 85.4, 82.3, 80.5, 78.9, 78.6, 63.3, 59.6, 43.7. ESI-HRMS: m/z calcd for C9H16O6Na [M+Na]+ 243.0839, found 243.0844.

**Compound 9-2**

![Compound 9-2](image)

Rf 0.57 (CH2Cl2/MeOH = 9:1). Pale yellow viscous oil. 1H NMR (400 MHz, CD3OD): δ 4.77 (ddd, J = 5.6 Hz, 4.2 Hz, 1.6 Hz, 1H x 1/2), 4.71 (dd, J = 5.0 Hz, 4.4 Hz, 1H x 1/2), 4.52 (dd, J = 4.2 Hz, 0.8 Hz, 1H x 1/2), 4.45 (dd, J = 4.4 Hz, 0.8 Hz, 1H x 1/2), 4.22 (d, J = 4.8 Hz, 1H x 1/2), 4.06 (d, J = 4.4 Hz, 1H x 1/2), 3.84-3.74 (m, 3H x 1/2), 3.72-3.65 (m, 1H), 3.60 (dd, J = 11.6 Hz, 6.0 Hz, 1H x 1/2), 3.42 (d, J = 8.0 Hz, 2H x 1/2), 3.39 (s, 3H x 1/2), 3.38 (s, 3H x 1/2), 3.36 (d, J = 0.8 Hz, 2H x 1/2), 2.27 (dd, J = 14.4 Hz, 1.6 Hz, 1H x 1/2), 2.24 (dd, J = 14.4 Hz, 5.0 Hz, 1H x 1/2), 2.11 (dd, J = 14.4 Hz, 5.6 Hz, 1H x 1/2), 2.09 (d, J = 14.4 Hz, 1H). 13C NMR (100 MHz, CD3OD): δ 108.3, 108.1, 94.3, 91.6, 90.0, 89.1, 84.3, 84.1, 79.1, 77.9, 77.6, 77.1, 63.5, 62.4, 59.84, 59.81, 43.2, 41.7. ESI-HRMS: m/z calcd for C9H16O6Na [M+Na]+ 243.0839, found 243.0843.

**Compound 10**

![Compound 10](image)

Synthesized from d-arabinose, flash column chromatography (CH2Cl2/MeOH = 93:7), 100 mg, 30%. Rf 0.57 (CH2Cl2/MeOH = 9:1). Pale yellow viscous oil. 1H NMR (400 MHz, CD3OD): δ 4.77 (ddd, J = 6.4 Hz, 4.4 Hz, 2.0 Hz, 1H x 2/5), 4.66 (dd, J = 5.6 Hz, 4.0 Hz, 1H x 3/5), 4.52 (dd, J = 4.4 Hz, 0.8 Hz, 1H x 2/5), 4.39 (dd, J = 4.0 Hz, 0.8 Hz, 1H x 3/5), 4.23 (s, 1H x 2/5), 4.19 (d, J = 5.2 Hz, 1H x 3/5), 4.12 (s, 1H x 3/5), 4.08 (d, J = 4.4 Hz, 1H x 2/5), 3.84-3.75 (m, 3H x 2/5), 3.73-3.64 (m, 2H x 3/5), 3.61 (dd, J = 11.6 Hz, 6.0 Hz, 1H x 3/5), 3.50 (s, 3H x 2/5), 3.49 (s, 3H x 3/5), 3.47 (s, 3H x 2/5), 3.46 (s, 3H x 3/5), 3.40 (d, J = 0.8 Hz, 1H x 3/5), 2.30 (dd, J = 14.4 Hz, 5.6 Hz, 1H x 1/2), 2.27 (dd, J = 14.4 Hz, 2.0 Hz, 1H x 2/5), 2.06 (dd, J = 14.4 Hz, 6.4 Hz, 1H x 2/5), 2.00 (d, J = 14.4 Hz, 1H x 3/5). 13C NMR (100 MHz, CD3OD): δ 109.4, 109.3, 108.4, 107.7, 94.2, 91.8, 90.1, 89.5, 83.9, 83.8, 78.9, 77.7, 63.5, 62.8, 57.88, 57.81, 57.3, 57.0, 42.2, 40.0. ESI-HRMS: m/z calcd for C10H18O7Na [M+Na]+ 273.0945, found 273.0943.

4. Transformation of 2c to 11 (Scheme 2)

**Procedure of Allylation**

To a solution of 2c (a mixture of 2c-1, 2c-2, and 2c-3 obtained C-glycosidation reaction of D-arabinose, 200 mg, 1.05 mmol) in DMF (1.8 mL)-H2O (0.2 mL), allyl bromide (1.00 g, 8.42 mmol) and In (484 mg, 4.21 mmol) were added at room temperature (25 °C), and the mixture was stirred at the same temperature for 24 h. The mixture was purified by flash column chromatography (CH2Cl2/MeOH 9:1) to give 11-1, Rf 0.54 (CH2Cl2/MeOH 9:1), 117 mg, 48% and 11-2, Rf 0.50 (CH2Cl2/MeOH 9:1), 97.7 mg, 40%.
**Compound 11-1**

R<sub>f</sub> 0.54 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1). Colorless oil. ^1^H NMR (400 MHz, CD<sub>3</sub>OD): δ 5.95-5.80 (m, 1H), 5.12-5.04 (m, 2H), 4.25-4.17 (m, 1H), 3.97-3.93 (m, 1H), 3.88-3.84 (m, 1H), 3.79-3.73 (m, 1H), 3.69 (dd, J = 3.6 Hz, 11.6 Hz, 1H), 3.63 (dd, J = 5.2 Hz, 11.6 Hz, 1H), 2.35-2.23 (m, 2H), 1.89-1.75 (m, 2H), 1.21 (s, 3H x 1/2), 1.20 (s, 3H x 1/2). ^13^C NMR (100 MHz, CD<sub>3</sub>OD): δ 135.44, 135.41, 118.38, 118.34, 87.1, 87.0, 80.0, 79.95, 79.93, 79.4, 72.7, 72.6, 63.5, 48.3, 47.9, 40.2, 40.0, 27.3, 26.9. ESI-HRMS: m/z calcd for C<sub>11</sub>H<sub>20</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup> 255.1203, found 255.1201.

**Compound 11-2**

R<sub>f</sub> 0.50 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1). Colorless oil. ^1^H NMR (400 MHz, CD<sub>3</sub>OD): δ 5.95-5.78 (m, 1H), 5.11-5.02 (m, 2H), 4.04-3.97 (m, 1H), 3.96-3.88 (m, 1H), 3.88-3.76 (m, 1H), 3.76-3.49 (m, 3H), 2.35-2.22 (m, 2H), 1.86-1.72 (m, 2H), 1.25-1.13 (m, 3H). ^13^C NMR (100 MHz, CD<sub>3</sub>OD): δ (major isomer of 11-2) 135.8, 118.3, 84.7, 83.6, 80.7, 78.5, 73.1, 63.5, 48.1, 45.8, 27.2. ESI-HRMS: m/z calcd for C<sub>11</sub>H<sub>20</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup> 255.1203, found 255.1203.

### 5. References

2a-1

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PROCNO 1

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PULPROG zgpg30
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DW 20.800 usec
DE 6.50 usec
TE 299.3 K
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D11 0.03000000 sec
TD0 1

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======== CHANNEL f2 ========
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NUC2 1H
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PLW13 0.28125000 W

F2 - Processing parameters
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Current Data Parameters
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EXPO   13
PROCNO  1

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DS  2
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RG  31.13
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DE  6.50 usec
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TI  1.00000000 sec
TDO  1

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P1  15.00 usec
PLWL  8.0000000 W

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Current Data Parameters
NAME Ed2015-06-29
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 15.32
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TD0 1

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PLW1 8.00000000 W

F2 - Processing parameters
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LB 0.30 Hz
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FC 1.00
CD$_3$OD

2c-3