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 (CH₂Cl₂/MeOH) to afford **2**. Selected results are shown in Tables S1-S5.

entry	catalyst	additive	solvent	time (h)	yield	l (%)
					2a-1	2a-2
1	L-proline	-	DMF	48	70	8
2	D-proline	-	DMSO	48	65	9
3	L-proline	-	DMSO	48	60	8
4	L-proline	-	MeOH	24	65	10
5	pyrrolidine	-	MeOH	24	40	5
6	pyrrolidine	H ₃ BO ₃ ^a	2-PrOH	24	_b	_b
7	L-proline	Et ₃ N	2-PrOH	24	78	10

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

^a H₃BO₃ (1.0 mmol) was used. ^b Product **2** was not obtained and **1a** was consumed.

Table S2.	Table S2. Reaction of D-ribose (1b) with acetone to afford 2b										
entry	catalyst additive solvent time (h) yield (%										
					2b-1 and 2b-2						
1	L-proline	-	DMSO	48	30						
2	L-proline	Et ₃ N	2-PrOH	24	67						

Table S3. Reaction of D-arabinose (1c) with acetone to afford 2c

entry	catalyst	additive	solvent	time (h)	yield (%)
					2c-1, 2c-2, and 2c-3
1	L-proline	-	DMF	48	15
2	L-proline	-	DMSO	72	70
3	D-proline	-	DMSO	72	66
4	pyrrolidine	CH ₃ COOH	MeOH	20	75
5	pyrrolidine	H ₃ BO ₃ ^a	2-PrOH	120	35
6	pyrrolidine	H ₃ BO ₃ ^a	DMSO	120	36
7	L-proline	Et ₃ N	2-PrOH	24	79

^a H₃BO₃ (1.0 mmol) was used.

entry	catalyst	additive	solvent	time (h)	yield (%)
					2d-1 and 2d-2
1	L-proline	-	DMSO	48	50
2	L-proline	Et ₃ N	2-PrOH	24	80

Table S4. Reaction of D-xylose (1d) with acetone to afford 2d

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

entry	catalyst	additive	solvent	time (h)	yield (%)
					2e
1	L-proline	-	DMSO	48	32
2	L-proline	Et ₃ N	2-PrOH	24	74

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 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 **2**.

Compound 2a-1



Synthesized from 2-deoxy-D-ribose (1.11 mmol), flash column chromatography (CH₂Cl₂/MeOH = 93:7), 152 mg, 78% (dr 3:2). R_f 0.60 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): 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). ¹³C NMR (100 MHz, CD₃OD): 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 C₈H₁₅O₄ [M+H]⁺ 175.0965, found 175.0965.

Compound 2a-2



Obtained with **2a-1**, 19.5 mg, 10%. R_f 0.64 (CH₂Cl₂/MeOH 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): 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). ¹³C NMR (100 MHz, CD₃OD): 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 C₈H₁₅O₄ [M+H]⁺ 175.0965, found 175.0964.

Compound 2b (2b-1 and 2b-2)^{1,2,3}



Synthesized from D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 92:8), 173 mg, 67% (**2b-1:2b-2** = 7:3). R_f 0.51 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): peaks of **2b-1**

major isomer extracted from the spectrum: δ 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). ¹³C NMR (100 MHz, CD₃OD): peaks of **2b-1** major isomer extracted from the spectrum: δ 210.0, 86.4, 79.9, 76.3, 72.6, 63.5, 48.2, 30.6. ESI-HRMS: *m/z* calcd for C₈H₁₄O₅Na [M+Na]⁺ 213.0733, found 213.0735.

Compound 2c (2c-1, 2c-2, and 2c-3)¹



Synthesized from D-arabinose, flash column chromatography (CH₂Cl₂/MeOH = 9:1), 200 mg, 79% (**2c-1:2c-2:2c-3** = 5:3:2). R_f 0.50 (CH₂Cl₂/MeOH = 9:1). Pale

yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): peaks of **2c-1** major isomer extracted from the spectrum: δ 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). ¹³C NMR (100 MHz, CD₃OD): peaks of **2c-1** major isomer extracted from the spectrum: δ 209.9, 87.3, 84.8, 80.4, 78.8, 63.6, 43.8, 30.5. ESI-HRMS: *m*/*z* calcd for C₈H₁₄O₅Na [M+Na]⁺ 213.0733, found 213.0736.

Compound 2c-3¹



Purified from the mixture of **2c-1**, **2c-2**, and **2c-3**, flash column chromatography (CH₂Cl₂/MeOH = 95:5). R_f 0.65 (CH₂Cl₂/MeOH = 95:5). Colorless solid. ¹H NMR (400 MHz, CDCl₃): δ 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). ¹³C NMR (100 MHz, CDCl₃): δ 107.9, 87.0, 83.4, 80.1, 78.6, 68.5, 43.1, 24.6. ¹H NMR (400 MHz, CD₃OD): δ 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). ¹³C NMR (100 MHz, CD₃OD): δ 109.4, 88.6, 84.7, 81.6, 79.6, 70.0, 44.3, 25.0. ESI-HRMS: m/z calcd for C₈H₁₃O₄ [M+H]⁺ 173.0808, found 173.0808.

Compound 2d $(2d-1 \text{ and } 2d-2)^1$



Synthesized from D-xylose, flash column chromatography (CH₂Cl₂/MeOH = 92:8), 207 mg, 80% (**2d-1:2d-2** = 2:3). R_f 0.51 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): 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 C₈H₁₅O₅ [M+H]⁺ 191.0914, found 191.0917.

Compound 2d-3



Purified from stored **2d**, column chromatography (CH₂Cl₂/MeOH = 92:8). R_f 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 C₈H₁₅O₅ [M+H]⁺ 191.0914, found 191.0900.



2d-3 major isomer (β -isomer)

Compound 2e



Synthesized from D-lyxose, flash column chromatography (CH₂Cl₂/MeOH = 92:8), 192 mg, 74% (dr 2:1). R_f 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 C₈H₁₅O₅ [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 3²



Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 128 mg, 61% (dr 3:2). R_f 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 C₉H₁₇O₄ [M+H]⁺ 189.1121, found 189.1121.

Compound 4²



Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 93.5 mg, 48% (dr 3:2). R_f 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 C₉H₁₇O₅ [M+H]⁺ 205.1071, found 205.1075.

Compound 5



Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 150 mg, 49% (dr 3:2). R_f 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



Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 75 mg, 31% (dr 3:2). R_f 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,

1H), 3.83-3.71 (m, 1H), 3.60-3.47 (m, 2H), 2.89 (dd, J = 16.4 Hz, 7.6 Hz, 1H x 1/3), 2.75 (dd, J = 16.0 Hz, 7.6 Hz, 1H x 2/3), 2.68 (dd, J = 16.4 Hz, 5.6 Hz, 1H x 1/3), 2.63 (dd, J = 16.0 Hz, 5.2 Hz, 1H x 2/3), 2.54-2.46 (m, 2H), 2.37 (dt, J = 12.8 Hz, 7.8 Hz, 1H x 1/3), 2.03-1.94 (m, 1H x 2/3), 1.74-1.58 (m, 1H), 1.53 (quin, J = 7.6 Hz, 2H), 1.32 (sextet, J = 7.6 Hz, 2H), 0.91 (t, J = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CD₃OD): δ 212.3, 212.0, 88.9, 87.3, 75.9, 75.8, 74.1, 73.5, 64.0, 63.4, 50.1, 44.1, 43.9, 42.0, 41.5, 26.9, 26.8, 23.4, 14.3. ESI-HRMS: *m/z* calcd for C₁₁H₂₁O₄ [M+H]⁺ 217.1434, found 217.1436.

Compound 7



Synthesized from 2-deoxy-D-ribose, flash column chromatography (CH₂Cl₂/MeOH = 94:6), 140 mg, 40% (dr 3:2). R_f 0.62 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 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 (ddd, J = 13.2 Hz, 5.4 Hz, 2.0 Hz, 1H x 3/5), 1.74-1.59 (m, 1H). ¹³C NMR (100 MHz, CD₃OD): δ 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 C₁₀H₁₈O₆Na [M+Na]⁺ 257.0996, found 257.0995.

Compound 8 (8-1 and 8-2)²



Synthesized from D-arabinose, flash column chromatography (CH₂Cl₂/MeOH = 9:1), 143 mg, 70% (8-1:8-2 = 2:3). R_f 0.52 (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 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). ¹³C NMR (100 MHz, CD₃OD): δ 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 C₉H₁₇O₅ [M+H]⁺ 205.1071, found 205.1073.

Compound 9 $(9-1 \text{ and } 9-2)^2$

Synthesized from D-arabinose, flash column chromatography ($CH_2Cl_2/MeOH = 9:1$); **9-1**, 50 mg, 17%, Rf 0.48 ($CH_2Cl_2/MeOH = 9:1$); **9-2**, 141 mg, 48%, R_f 0.57 ($CH_2Cl_2/MeOH = 9:1$).

Compound 9-1²



 $R_f 0.48$ (CH₂Cl₂/MeOH = 9:1). Pale yellow viscous oil. ¹H NMR (400 MHz, CD₃OD): δ 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 9-2²



R_f 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



Synthesized from D-arabinose, flash column chromatography (CH₂Cl₂/MeOH = 93:7), 100 mg, 30%. R_f 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 3/5), 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 Darabinose, 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.⁴ The mixture was purified by flash column chromatography (CH₂Cl₂/MeOH 9:1) to give **11-1**, R_f 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_f 0.54 (CH₂Cl₂/MeOH 9:1). Colorless oil. ¹H NMR (400 MHz, CD₃OD): 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). ¹³C NMR (100 MHz, CD₃OD): 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 C₁₁H₂₀O₅Na [M+Na]⁺ 255.1203, found 255.1201.

Compound 11-2



R_f 0.50 (CH₂Cl₂/MeOH 9:1). Colorless oil. ¹H NMR (400 MHz, CD₃OD): 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). ¹³C

NMR (100 MHz, CD₃OD): 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 C₁₁H₂₀O₅Na [M+Na]⁺ 255.1203, found 255.1203.

5. References

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- (4) Chan, T. H.; Yang, Y. J. Am. Chem. Soc., 1999, 121, 3228.



















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	-108.35 -91.68.34 -91.62.14 -91.62.484.34 -90.07 -77.19.17 -77.192 -63.59.84 -63.59.84 -63.59.81 -49.79 -49.79 -49.357 -49.357 -48.793 -48.722 -48.722 -48.722 -48.51	Current Data Parameters NAME EJ2015-06-29 EXPNO 16 PROCNO 1
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$HO \underbrace{O}_{HO} \underbrace{HO}_{OH} \underbrace{O}_{HO} \underbrace{O}_{OH}$ 11-1	135.44		687.10 87.09 80.05 80.05	79.93	63.52	48.94	- 47.98 - 40.25 - 40.04 - 27.31 - 27.31			Current Dai NAME EXPNO PROCNO F2 - Acqui: Date_ Time INSTRUM PROBHD 5 PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0 E E TE D1 D11 TD0 SF01 NUC1 P1 PLW1 E SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW12 F12 SF SF NUC2 CPDPRG[2 PCPD2 PLW12 F12 SF SF WDW SSB 0 LB GB 0 PC	ta Parameters EJ2015-04-16 7 1 sition Parameters 20150416 10.57 spect mm PABO BB/ 2gpg30 65536 MeOD 1024 4 24038.461 Hz 0.366798 Hz 1.3631488 sec 195.88 20.800 use 6.50 use 299.3 K 2.0000000 sec 0.03000000 sec 0.03000000 sec 1 HANNEL f1 ======== 100.6228293 MHz 13C 10.00 use 70.0000000 W HANNEL f2 ======= 400.1316005 MHz 1H waltz16 8.0000000 W 0.28125000 W 0.28125000 W ssing parameters 32768 100.6126468 MHz EM 1.00 Hz 1.40
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