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# Syntheses of a partially benzylated derivative of the anhydro-D-*altro*-heptulose found in *Coriaria japonica* A and of its analogs

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ABSTRACT

A partially benzylated derivative of anhydro-D-*altro*-heptulose found in *Coriaria japonica* A, which is a synthetically useful unit, was successfully synthesized from a D-mannose derivative by a novel synthetic approach involving the intramolecular O-ketopyranosylation reaction developed by us. This synthetic approach was also applicable to the preparation of its four analogs.



## 1. Introduction

Several anhydroketopyranoses having 6,8-dioxabicyclo[3.2.1]octane structures are found in natural products such as *Sedum spectabile*,[1] *Smallanthus sonchifolius*,[2] and *Coriaria japonica* A.[3] Coriariin, found in *C. japonica* A, has an anhydro-D-*altro*-heptulose **1** bound to a tannin via an ester linkage (Fig. 1). Its analogs have biologically important antitumor and antivirus activities.[3] Compound **1** is synthetically interesting because it has not only a unique anhydroketopyranose structure but also a rare D-altro-pyranose-ring configuration. Several synthetic approaches to **1** have been reported, such as enzymatic transketolization reaction of hydroxypyruvic acid with D-ribose,[4] molybdic acid treatment of 2-*C*-hydroxymethyl-allofuranose,[5] and radical intramolecular cyclization of a *C*-altropyranoside derivative via intramolecular hydrogen abstraction reaction.[6] Unfortunately, these methods require complicated processes or special compounds.

Our preliminary letter described the synthesis of a partially benzylated anhydro-D-*altro*-heptulose derivative **2**.[7] Compound **2** is a useful unit for synthesizing coriariin because it has a free hydroxyl function as a binding site with a tannin and its other hydroxyl functions are protected by benzyl groups. Our approach to **2** starts from a D-mannopyranose derivative and consists of the following key reaction steps: (1) steric inversion at the C-3 position from a D-mannopyranose derivative to a D-altro-pyranose derivative, (2) introduction of a vinyl group into the C-1 position of the altro-pyranose derivative to produce a 1-*C*-vinylated D-altro-pyranose derivative, (3) intramolecular O-glycosidation of the 1-*C*-vinylated D-altro-pyranose derivative to form the anhydroketopyranose structure, and (4) conversion of the vinyl group of the anhydroketopyranose into a hydroxymethyl group to produce the desired compound **2**. The third key reaction step is based on the

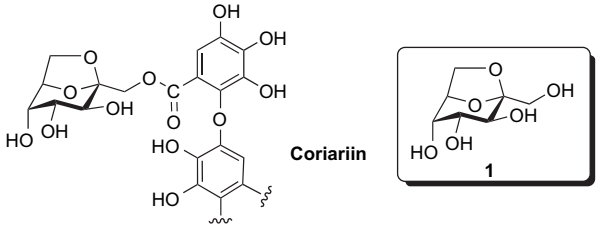


**Figure 1.**

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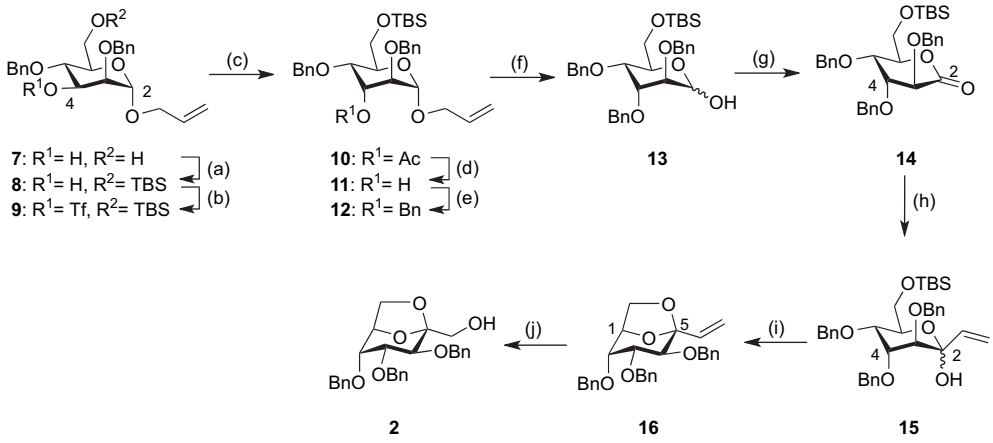


**Scheme 1.** Reagents and conditions: (a) TBSCl (2 equiv), imidazole (2 equiv), $CH_2Cl_2$, rt, 2 h, 88%; (b) $Tf_2O$ (1.5 equiv), pyridine, −20 °C to rt, 2.5 h, 93%; (c) CsOAc (2 equiv), 18-crown-6 (2 equiv), toluene, sonication, 30 °C, 24 h, 62%; (d) NaOMe, MeOH (cat.), rt, overnight, 95%; (e) BnBr (1.7 equiv), NaH (4 equiv), DMF, 0 °C to rt, overnight, 96%; (f) $PdCl_2$ (3 equiv), AcOH–AcONa buffer, sonication, 30 °C, 4 h, 87%; (g) DMSO, $Ac_2O$, rt, overnight, 99%; (h) vinylMgCl (1.2 equiv), $CeCl_3$ (1.2 equiv), toluene, −78 °C, 1 h, 62%; (i) TfOH (0.05 equiv), $CH_3CN$, 0 °C, 88%; (j) $O_3$, $Ph_3P$ (5 equiv), $CH_2Cl_2$, −78 °C, 45 min, then $NaBH_4$ (8 equiv), THF, 0 °C, 3 h, 72%.

intramolecular O-ketosylation reaction developed by us. It can efficiently convert ketopyranoses into anhydroketopyranoses having the 6,8-dioxabicyclo[3.2.1]octane structures.[8]

The above-mentioned synthetic method was expected to be applicable to the preparation of some analogs of **2**. We then utilized our method for the synthesis of the four compounds shown in Figure 1. The anhydro-D-*gluco*-heptulose **3** and the anhydro-D-*manno*-heptulose **4** are stereoisomeric analogs of **2**. The anhydro-D-*altro*-octulose **5** and the anhydro-D-*manno*-octulose **6** are analogs of **2** having a hydroxyethyl group at C-5. This paper describes in detail the synthetic approaches to **2** and its four analogs **3**–**6**.

## 2. Results and discussion

Our synthetic approach to **2** from **7**[9] is shown in Scheme 1. First, the conversion of **7** into **9** was investigated. A *tert*-butyldimethylsilyl (TBS) group was introduced into C-6 of **7** using TBSCl and imidazole in $CH_2Cl_2$. Introduction of a Tf group into C-3 was performed using $Tf_2O$ in pyridine. Steric inversion at C-3 of **9** into **10**, which is the first key reaction step, was successfully accomplished in 62% yield using AcOCs (2 equiv) in the presence of 18-crown-6 (2 equiv) in toluene at 30 °C for 24 h under ultrasonic conditions.[10] The altropyranoside structure of **10** was assigned by measurement of the $^1$H NMR spectrum. The signal of H-3 of **10** was observed at 5.33 ppm with a triplet peak ($J_{2,3}$=3.4 Hz, $J_{3,4}$=3.4 Hz), and its spin coupling constants indicated the dihedral angles of H-$2_{eq}$–H-$3_{eq}$ and H-$3_{eq}$–H-$4_{ax}$. These results supported the ring conformation of the altropyranoside.

Next, the conversion of **10** into the lactone **14** was investigated. Deprotection of the acetyl group of **10** using NaOMe in MeOH and subsequent introduction of the benzyl group to C-3 using NaH and benzyl bromide in DMF gave **12**. The allyl group of **12** was removed using $PdCl_2$ in AcOH–AcONa at 30 °C for 4 h under ultrasonic conditions.[11] Oxidation of **13** using dimethyl sulfoxide (DMSO) and $Ac_2O$[12] produced the desired **14**. Introduction of the vinyl group into C-1 of **14** to produce **15**, which is the second key reaction step, was successfully achieved in 62% yield using vinylmagnesium chloride (1.2 equiv) in toluene in the presence of $CeCl_3$[13] (1.2 equiv) at −78 °C for 1 h.

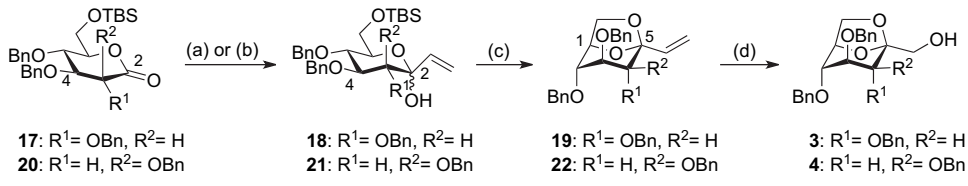
Intramolecular O-glycosidation of **15**, which is the third key reaction step, smoothly proceeded to afford the desired compound **16** in 88% yield using 5 mol% TfOH in the presence of $CaSO_4$ in $CH_3CN$ at 0 °C for 2 h. These are the same reaction conditions as those used in our previous study.[8] It is unnecessary to deprotect the TBS group at C-6 of **15** prior to the intramolecular O-glycosidation because the TBS group is removed under acidic conditions during the intramolecular O-glycosidation, as we reported previously.[8]

As the final key reaction step, the vinyl group of **16** was converted into a hydroxymethyl group to give the desired **2**. Compound **2** was obtained from **16** in 72% yield by ozone oxidation and treatment with triphenylphosphine (5 equiv) at −78 °C for 45 min, and subsequent reduction using $NaBH_4$[14] (8 equiv) at 0 °C for 3 h.

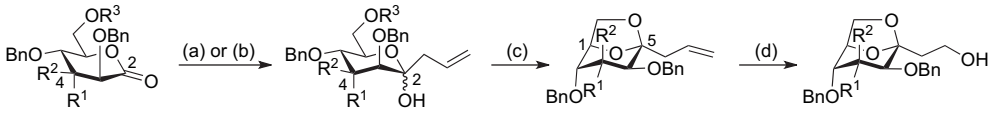
Next, the stereoisomers **3** and **4** were synthesized by the same synthetic approach, as shown in Scheme 2. The introduction of the vinyl group to the lactone **17** or **20** was performed efficiently using vinylmagnesium chloride. The intramolecular O-glycosidation of **18** or **21** to afford the ketopyranose **19** or **22** was accomplished in the presence of 5 mol% TfOH. The conversion of **19** or **22** into the desired **3** or **4** was successfully accomplished by ozone oxidation and subsequent reduction using $NaBH_4$.

The syntheses of the octulose analogs **5** and **6** were also examined, as shown in Scheme 3. The syntheses of **5** and **6** were successfully achieved from **14** or **25** by introduction of an allyl group to C-1 using allylmagnesium bromide, intramolecular O-glycosidation using 5 mol% TfOH, and conversion of terminal olefins to the hydroxyethyl group.

In summary, a partially benzylated anhydro-D-*altro*-heptulose derivative **2**, which is a synthetically useful unit for coriariin found in *C. japonica* A, was successfully synthesized from a D-mannose derivative by a novel synthetic approach involving the



**Scheme 2.** Reagents and conditions: (a) vinylMgCl (1.2 equiv), THF, −78 °C, 1 h, 80% (**18**); (b) vinylMgCl (1.5 equiv), $CeCl_3$ (1.5 equiv), toluene, −78 °C, 1 h, 64% (**21**); (c) TfOH (0.05 equiv), $CH_3CN$, 0 °C, 89% (**19**), 89% (**22**); (d) $O_3$, $Ph_3P$ (5 equiv), $CH_2Cl_2$, −78 °C, 45 min, then $NaBH_4$ (8 equiv), THF, 0 °C, 3 h, 73% (**3**), 77% (**4**).




**14**: $R^1$= OBn, $R^2$= H, $R^3$= TBS
**25**: $R^1$= H, $R^2$= OBn, $R^3$= Ac
**23**: $R^1$= OBn, $R^2$= H, $R^3$= TBS
**26**: $R^1$= H, $R^2$= OBn, $R^3$= H
**24**: $R^1$= OBn, $R^2$= H
**27**: $R^1$= H, $R^2$= OBn
**5**: $R^1$= OBn, $R^2$= H
**6**: $R^1$= H, $R^2$= OBn

**Scheme 3.** Reagents and conditions: (a) allylMgBr (1.2 equiv), THF, −78 °C, 1.5 h, 92% (**23**); (b) allylMgCl (2.4 equiv), THF, −78 °C, 2 h, 85% (**26**); (c) TfOH (0.05 equiv), $CH_3CN$, 0 °C, 99% (**24**), 87% (**27**); (d) $O_3$, $Ph_3P$ (5 equiv), $CH_2Cl_2$, −78 °C, 45 min, then $NaBH_4$ (3 equiv), THF, 0 °C, 3 h, 85% (**5**), 95% (**6**).

intramolecular O-ketopyranosylation reaction developed by us. This approach was also found to be applicable to the syntheses of the four analogs: anhydro-D-*gluco*-heptulose **3**, anhydro-D-*manno*-heptulose **4**, anhydro-D-*altro*-octulose **5**, and anhydro-D-*manno*-octulose **6**.

## 3. Experimental

### 3.1. General

$^1$H NMR and $^{13}$C NMR spectra were recorded on JEOL EX-400 and ECA-600 spectrometers in $CDCl_3$ using TMS as the internal standard. IR spectra were registered on a JASCCO FT/IR-460Plus spectrophotometer. Optical rotations were recorded on a JASCO DIP-360 digital polarimeter. High-resolution mass spectra (HRMS) were obtained on a Mariner spectrometer (PerSeptive Biosystems, Inc.). Preparative thin-layer chromatography (TLC) was performed on Merck silica gel 60$GF_{254}$. Column chromatography was conducted using silica gel 60 N (40–50 μm, Kanto Chemical Co., Inc.). All anhydrous solvents were purified according to standard methods.

#### *3.1.1. (2S,3S,4S,5R,6R)-2-Allyloxy-3,5-bisbenzyloxy-6-[(tert-butyldimethylsilyl)oxy]methyl-tetrahydropyran-4-ol (**8**)*

To a solution of **7** (365 mg, 0.91 mmol) and imidazole (148 mg, 2.2 mmol) in $CH_2Cl_2$ (10 mL) was added TBSCl (148 mg, 2.1 mmol) at rt. After stirring for 2 h, the reaction was then quenched by addition of a solution of ~30% citric acid (5 mL). The reaction mixture was extracted with $CH_2Cl_2$ (10 mL). After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:4) to give **8** (415.1 mg, 88% yield) as a colorless oil. $[\alpha]_D^{23}$ +27 (*c* 2.7, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 0.07 (3H, s, Si(C*H*$_3$)$_2$), 0.08 (3H, s, Si(C*H*$_3$)$_2$), 0.91 (9H, s, C(C*H*$_3$)$_3$), 2.35 (1H, d, *J*=9.6 Hz, O*H*), 3.57–3.60 (1H, m, H-6), 3.65 (1H, t, *J*=9.6 Hz, H-5), 3.74 (1H, dd, *J*=1.4, 3.4 Hz, H-3), 3.83–3.88 (2H, m, H-7), 3.92 (1H, dt, *J*=4.1, 9.6 Hz, H-4), 3.93 (1H, dd, *J*=6.2, 13.1 Hz, OC*Ha*HbCH=$CH_2$), 4.01 (1H, ddd, *J*=1.4, 5.5, 13.1 Hz, OCHa*Hb*CH=$CH_2$), 4.93 (1H, d, *J*=1.4 Hz, H-2), 5.16 (1H, dd, *J*=1.4, 10.3 Hz, $OCH_2CH$=C*Ha*Hb), 5.25 (1H, dd, *J*=1.4, 17.2 Hz, $OCH_2CH$=CHa*Hb*), 5.86 (1H, m, $OCH_2CH$=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.3 (Si(*C*H$_3$)$_2$), −5.1 (Si(*C*H$_3$)$_2$), 18.3 (*C*(CH$_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 62.6 (C-7), 67.6 ($OCH_2CH$=$CH_2$), 71.8 (C-4), 72.3 (C-6), 72.7 (*C*H$_2$Ph), 74.8 (*C*H$_2$Ph), 76.6 (C-5), 78.6 (C-3), 95.7 (C-2, $J_{C2-H2}$=167.6 Hz), 117.2 ($OCH_2CH$=*C*H$_2$), 133.8 ($OCH_2CH$=$CH_2$). HRMS (ESI): *m*/*z* calcd for $C_{29}H_{42}O_6Si\cdot Na^+$: 537.2643; found: 537.2690.

#### *3.1.2. (2S,3S,4S,5R,6R)-2-Allyloxy-3,5-bisbenzyloxy-6-[(tert-butyldimethylsilyl)oxy]methyl-4-trifuloromethanesulfonyloxy-tetrahydropyran (**9**)*

To a solution of **8** (110 mg, 0.21 mmol) in pyridine (2.5 mL), $Tf_2O$ (0.053 mL, 0.32 mmol) was added dropwise at −20 °C under Ar atmosphere, and the reaction temperature was then allowed to increase up to rt. After stirring for 2.5 h, the reaction was then quenched by addition of a satd $NaHCO_3$ solution. The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with a solution of ~30% citric acid, water, and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the organic solvent was filtered and evaporated under reduced pressure. The crude product was purified by flash silica gel column chromatography (ethyl acetate/hexane=1:2) to give **9** (167.8 mg, 93% yield) as a colorless oil. $[\alpha]_D^{23}$ +35 (*c* 2.6, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 0.069 (3H, s, (C*H*$_3$)$_2$Si), 0.073 (3H, s, (C*H*$_3$)$_2$Si), 0.89 (9H, s, (C*H*$_3$)$_3$C), 3.62 (1H, dd, *J*=2.8, 12.4 Hz, H-6), 3.49 (1H, d, *J*=11.7 Hz, OC*Ha*HbCH=$CH_2$), 3.88–3.93 (2H, m, Ha-7, OCHa*Hb*CH=$CH_2$), 3.97 (1H, dd, *J*=2.1, 2.7 Hz, H-3), 4.10 (1H, dd, *J*=5.5, 13.1 Hz, Hb-7), 4.19 (1H, t, *J*=9.6 Hz, H-5), 4.86 (1H, s, H-2), 5.16–5.23 (2H, m, $OCH_2CH$=C*H*$_2$), 5.27 (1H, dd, *J*=3.4, 9.6 Hz, H-4), 5.81 (1H, m, $OCH_2CH$=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si(*C*H$_3$)$_2$), −5.2 (Si(*C*H$_3$)$_2$), 18.2 (*C*(CH$_3$)$_3$), 25.8 (C(*C*H$_3$)$_3$), 61.8 ($OCH_2CH$=$CH_2$), 67.9 (C-7), 72.5 (C-5), 73.1 (C-6), 73.2 (*C*H$_2$Ph), 75.2 (*C*H$_2$Ph), 76.8 (C-3), 88.3 (C-4), 96.3 (C-2), 117.8 ($OCH_2CH$=*C*H$_2$), 133.2 ($OCH_2CH$=$CH_2$). HRMS (ESI): *m*/*z* calcd for $C_{30}H_{41}O_{8S}SSi\cdot Na^+$: 669.2136; found: 669.2142.

#### *3.1.3. (2S,3S,4R,5R,6R)-2-Allyloxy-3,5-bisbenzyloxy-6-[(tert-butyldimethylsilyl)oxy]methyl-tetrahydropyran-4-yl acetate (**10**)*

A toluene solution (25 mL) of **9** (134 mg, 0.21 mmol), 18-crown-6 (116 mg, 0.44 mmol), and cesium acetate (85 mg, 0.44 mmol) was sonicated at 30 °C for 24 h, and water (15 mL) was then added to the mixture. The reaction mixture was extracted with AcOEt (30 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:6) to give **10** (71.1 mg, 62% yield) as a colorless oil. $[\alpha]_D^{22}$ +63 (*c* 3.6, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 0.07 (3H, s, Si(C*H*$_3$)$_2$), 0.08 (3H, s, Si(C*H*$_3$)$_2$), 0.91 (9H, s, C(C*H*$_3$)$_3$), 2.01 (3H, s, C*H*$_3$CO), 3.71 (1H, dd, *J*=1.4, 3.4 Hz, H-3), 3.80 (1H, dd, *J*=5.5, 11.0 Hz, Ha-7), 3.88 (1H, dd, *J*=3.4, 8.9 Hz, H-5), 3.85–3.93 (2H, m, OC*Ha*HbCH=$CH_2$, Hb-7), 4.03 (1H, m, H-6), 4.23 (1H, m, OCHa*Hb*CH=$CH_2$), 4.80 (1H, d, *J*=1.4 Hz, H-2), 5.13 (1H, ddd, *J*=1.4, 3.4, 10.3 Hz, $OCH_2CH$=C*Ha*Hb), 5.13 (1H, ddd, *J*=1.4, 2.1, 18.6 Hz, $OCH_2CH$=CHa*Hb*), 5.33 (1H, t, *J*=3.4 Hz, H-4), 5.87 (1H, m, $OCH_2CH$=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si(*C*H$_3$)$_2$), −5.2 (Si(*C*H$_3$)$_2$), 18.2 (*C*(CH$_3$)$_3$), 21.0 (*C*H$_3$CO), 25.8 (C(*C*H$_3$)$_3$), 62.7 (C-7), 67.3 (C-4), 67.4 ($OCH_2CH$=$CH_2$), 68.9 (C-6), 70.7 (C-5), 71.5 (*C*H$_2$Ph), 72.4 (*C*H$_2$Ph), 75.6 (C-3), 97.5 (C-2, $J_{C2-H2}$=164.7 Hz), 116.3 ($OCH_2CH$=*C*H$_2$), 134.1 ($OCH_2CH$=$CH_2$), 170.7 (*C*H$_3$CO). HRMS (ESI): *m*/*z* calcd for $C_{31}H_{44}O_7Si\cdot Na^+$: 579.2749; found: 579.2795.

#### *3.1.4. (2S,3S,4R,5R,6R)-2-Allyloxy-3,5-bisbenzyloxy-6-[(tert-butyldimethylsilyl)oxy]methyl-tetrahydropyran-4-ol (**11**)*

To a solution of **10** (468 mg, 0.84 mmol) in MeOH (5 mL) was added two drops of a 28% sodium methoxide methanol solution at rt. After the reaction mixture was stirred overnight, the reaction was quenched by addition of water (5 mL). The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the organic solvent was filtered and evaporated under reduced pressure. The crude product was purified by flash silica gel column chromatography (ethyl acetate/hexane=1:4) to give **11** (413 mg, 95% yield) as a colorless oil. $[\alpha]_D^{23}$ +61 (*c* 3.0, $CHCl_3$).

$^1$H NMR ($CDCl_3$): $\delta$ 0.05 (3H, s, Si($CH_3$)$_2$), 0.08 (3H, s, Si($CH_3$)$_2$), 0.84 (9H, s, C($CH_3$)$_3$), 3.61 (1H, dd, $J$=1.4, 3.8 Hz, H-3), 3.71 (1H, dd, $J$=3.3, 9.5 Hz, H-5), 3.76 (1H, dd, $J$=5.7, 11.5 Hz, Ha-7), 3.83–3.85 (2H, m, H-6, Hb-7), 3.93 (1H, dtd, $J$=1.2, 6.2, 12.9 Hz, OC*Ha*HbCH=$CH_2$), 4.04–4.06 (1H, m, H-4), 4.16 (1H, dtd, $J$=1.4, 5.3, 12.9 Hz, OCHa*Hb*CH=$CH_2$), 4.82 (1H, d, $J$=0.2 Hz, H-2), 5.11 (1H, ddd, $J$=1.2, 2.6, 10.3 Hz, $OCH_2$CH=C*Ha*Hb), 5.18 (1H, ddd, $J$=1.5, 3.1, 17.2 Hz, $OCH_2$CH=CHa*Hb*), 5.81 (1H, m, $OCH_2$*C*H=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si($CH_3$)$_2$), −5.2 (Si($CH_3$)$_2$), 18.2 (*C*($CH_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 62.8 (C-7), 66.6 (C-4), 68.0 ($OCH_2$CH=$CH_2$), 68.2 (C-6), 71.2 (*C*$H_2$Ph), 71.9 (C-5), 72.1 (*C*$H_2$Ph), 76.6 (C-3), 97.3 (C-2, $J_{C2-H2}$=168.3 Hz), 117.9 ($OCH_2$CH=*C*$H_2$), 133.3 ($OCH_2$*C*H=$CH_2$). HRMS (ESI): $m/z$ calcd for $C_{29}H_{42}O_6Si\cdot Na^+$: 537.2643; found: 537.2657.

### 3.1.5. (2S,3S,4R,5R,6R)-2-Allyloxy-6-[(tert-butyldimethylsilyl)oxy]-methyl-3,4,5-trisbenzyloxy-tetrahydropyran (**12**)

To a solution of **11** (177 mg, 0.34 mmol) in anhydrous DMF (6 mL) was added NaH (33 mg, 1.4 mmol) at 0 °C. After the suspension was stirred for 40 min, benzyl bromide (0.07 mL, 0.58 mmol) was added dropwise over a 5-min period and stirred for 30 min; the reaction temperature was then allowed to warm to rt. The reaction mixture was stirred overnight, and 5 mL of MeOH was then added slowly to react with the excess NaH, and water (5 mL) was added to the reaction. The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:6) to give **12** (199 mg, 96% yield) as a colorless oil. $[\alpha]_D^{23}$ +55 (*c* 3.3, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 0.04 (6H, s, Si($CH_3$)$_2$), 0.89 (9H, s, C($CH_3$)$_3$), 3.74–3.83 (5H, m, H-3, H-7, H-4, H-5, or H-6), 3.98 (1H, dd, $J$=6.2, 13.1 Hz, OC*Ha*HbCH=$CH_2$), 4.09–4.12 (2H, m, H-4, H-5, or H-6), 4.26 (1H, dd, $J$=4.8, 13.1 Hz, OCHa*Hb*CH=$CH_2$), 4.83 (1H, d, $J$=0.7 Hz, H-2), 5.15 (1H, dd, $J$=1.4, 10.3 Hz, $OCH_2$CH=C*Ha*Hb), 5.29 (1H, dd, $J$=1.4, 19.2 Hz, $OCH_2$CH=CHa*Hb*), 5.91 (1H, m, $OCH_2$*C*H=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si($CH_3$)$_2$), −5.2 (Si($CH_3$)$_2$), 18.3 (*C*($CH_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 63.0 (C-7), 6.7.8 ($OCH_2$CH=$CH_2$), 70.2, 71.7 (*C*$H_2$Ph), 72.0 (*C*$H_2$Ph), 72.6 (*C*$H_2$Ph), 72.8, 74.3, 76.5, 98.6 (C-2, $J_{C2-H2}$=167.5 Hz), 116.7 ($OCH_2$CH=*C*$H_2$), 134.4 ($OCH_2$CH=$CH_2$). HRMS (ESI): $m/z$ calcd for $C_{36}H_{48}O_6Si\cdot Na^+$: 627.3112; found: 627.3154.

### 3.1.6. (3S,4R,5R,6R)-6-[(tert-Butyldimethylsilyl)oxy]methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-ol (**13**)

To a solution of AcOH (13.6 mL), water (0.68 mL), AcONa (448 mg), and **12** (199 mg, 0.33 mmol) was added $PdCl_2$ (180 mg, 1.01 mmol). After the reaction mixture was sonicated at 30 °C for 4 h, the mixture was filtered on a bed of Celite, and $NaHCO_3$ (5 g) was added to the solution. The reaction mixture was extracted with AcOEt, and the organic layer was washed with a satd $NaHCO_3$ and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:4) to give **13** (162 mg, 87% yield) as a colorless oil.

*α Form*. $^1$H NMR ($CDCl_3$): $\delta$ 0.07 (3H, s, ($CH_3$)$_2$Si), 0.09 (3H, s, ($CH_3$)$_2$Si), 0.91 (9H, s, ($CH_3$)$_3$C), 3.53 (1H, dd, $J$=2.1, 12.4 Hz, H-3), 3.59 (1H, d, $J$=4.1 Hz, H-5), 3.85–3.90 (2H, m, H-4, Ha-7), 3.99–4.03 (1H, m, H-6, Hb-7), 5.04–5.08 (1H, m, H-2). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.3 (Si(*C*$H_3$)$_2$), −5.0 (Si(*C*$H_3$)$_2$), 18.3 (*C*($CH_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 62.8 (C-7), 68.2 (C-6), 72.2 (*C*$H_2$Ph), 73.065 (*C*$H_2$Ph), 73.074 (*C*$H_2$Ph), 73.5 (C-4), 75.2 (C-5), 77.3 (C-3), 91.6 (C-2). *β Form*. $^1$H NMR ($CDCl_3$): $\delta$ 0.07 (3H, s, (Si*C*$H_3$)$_2$), 0.09 (3H, s, Si(*C*$H_3$)$_2$), 0.91 (9H, s, C(*C*$H_3$)$_3$), 3.47 (1H, t, $J$=2.1 Hz, H-3), 3.75 (1H, dd, $J$=2.1, 2.8 Hz, H-4), 3.85–3.90 (2H, m, H-5, Ha-7), 3.99–4.03 (2H, m, H-6, Hb-7), 5.06 (1H, d, $J$=2.1 Hz, H-2). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si(*C*$H_3$)$_2$), −5.1 (Si(*C*$H_3$)$_2$), 18.3 (*C*($CH_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 62.6 (C-7), 68.2 (C-6), 71.7 (*C*$H_2$Ph), 71.9 (C-4), 72.4 (*C*$H_2$Ph), 74.0 (*C*$H_2$Ph), 75.5 (C-5), 77.3 (C-3), 92.8 (C-2). HRMS (ESI): $m/z$ calcd for $C_{33}H_{44}O_6Si\cdot Na^+$: 587.2799; found: 587.2775.

### 3.1.7. (3S,4R,5R,6R)-6-[(tert-Butyldimethylsilyl)oxy]methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-one (**14**)

To a solution of **13** (70.3 mg, 0.124 mmol) in DMSO (3 mL) was added $Ac_2O$ (2 mL). After stirring overnight, cool water was added to the reaction mixture. The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude product was purified by a preparative flash silica gel column chromatography (ethyl acetate/hexane=1:6) to give **14** (69.8 mg, 99%) as a colorless oil. $[\alpha]_D^{23}$ −21 (*c* 1.4, $CHCl_3$). IR (neat): 3088, 3063, 3033, 2952, 2929, 2857, 1741, 1496, 1455, 1361, 1265, 1119, 1027, 837, 737, 699 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 0.08 (3H, s, Si($CH_3$)$_2$), 0.09 (3H, s, Si($CH_3$)$_2$), 0.91 (9H, s, C($CH_3$)$_3$), 3.86 (2H, d, $J$=3.2 Hz, H-7), 4.06 (1H, dd, $J$=2.7, 6.3 Hz, H-4), 4.23 (1H, dd, $J$=2.7, 6.3 Hz, H-5), 4.26 (1H, d, $J$=6.3 Hz, H-3), 4.57–4.59 (1H, m, H-6). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si(*C*$H_3$)$_2$), −5.2 (Si(*C*$H_3$)$_2$), 18.3 (*C*($CH_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 62.0 (C-7), 71.9 (C-5), 72.6 (*C*$H_2$Ph), 72.7 (*C*$H_2$Ph), 73.6 (*C*$H_2$Ph), 74.9 (C-4), 75.7 (C-3), 79.0 (C-6), 168.7 (C-2). HRMS (ESI): $m/z$ calcd for $C_{33}H_{42}O_6Si\cdot Na^+$: 585.2643; found: 585.2681.

### 3.1.8. (3S,4R,5R,6R)-6-[(tert-Butyldimethylsilyl)oxy]methyl-3,4,5-tris(benzyloxy)-2-vinyl-tetrahydropyran-2-ol (**15**)

To a solution of **14** (54.5 mg, 0.097 mmol) in toluene (3 mL), a 1.3 M THF solution of vinylmagnesium chloride (0.090 mL, 0.12 mmol) was added dropwise at −78 °C in the presence of dry $CeCl_3$ (30.6 mg, 0.12 mmol) under Ar atmosphere. After the resulting mixture was stirred at −78 °C for 1 h, the reaction was quenched by addition of water (5 mL). The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/toluene=1:19) to give **15** (35.1 mg, 62% yield) as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 0.08 (3H, s, Si($CH_3$)$_2$), 0.09 (3H, s, Si($CH_3$)$_2$), 0.91 (9H, s, C($CH_3$)$_3$), 3.33 (1H, d, $J$=3.4 Hz, H-3), 3.80 (1H, dd, $J$=2.1, 3.4 Hz, H-4), 3.89 (1H, d, $J$=11.0 Hz, Ha-7), 3.98–4.12 (3H, m, H-5, H-6, Hb-7), 5.22 (1H, dd, $J$=2.1, 11.0 Hz, CH=*Ha*Hb), 5.58 (1H, dd, $J$=2.1, 17.9 Hz, CH=Ha*Hb*), 5.98 (1H, m, C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.3 (Si($CH_3$)$_2$), −5.0 (Si($CH_3$)$_2$), 18.3 (*C*($CH_3$)$_3$), 5.9 (($CH_3$)$_3$C), 62.6 (C-7), 68.9 (C-5 or C-6), 71.2 (C-5 or C-6), 72.6 (*C*$H_2$Ph), 73.1 (*C*$H_2$Ph), 73.9 (*C*$H_2$Ph), 75.4 (C-4), 78.4 (C-3), 96.5 (C-2), 116.3 (CH=*C*$H_2$), 138.1 (*C*H=$CH_2$). HRMS (ESI): $m/z$ calcd for $C_{35}H_{46}O_6Si\cdot Na^+$: 613.2950; found: 613.2968.

### 3.1.9. (1R,2R,3R,4S,5R)-2,3,4-Tris(benzyloxy)-5-vinyl-6,8-dioxabicyclo[3.2.1]octane (**16**)

To a stirred solution of TfOH (0.25 μL, 0.0028 mmol) and dry $CaSO_4$ (35.3 mg) was added **15** (32.7 mg, 0.0554 mmol) in $CH_3CN$ (2 mL) at 0 °C under Ar atmosphere. After the resulting mixture was stirred for 2 h, the reaction was then quenched by addition of a satd $NaHCO_3$ solution (5 mL). The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water and a satd NaCl solution. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/benzene=1:10) to give **16** (22.3 mg, 88% yield) as amorphous crystals. $[\alpha]_D^{23}$ −66 (*c* 1.1, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 3.62 (1H, dd, $J$=0.7, 7.6 Hz, Ha-7), 3.66 (1H, dd, $J$=2.4, 3.6 Hz, H-2), 3.78–3.82 (2H, m, H-3, H-4), 3.80 (1H, dd, $J$=0.7, 6.9 Hz,

Hb-7), 4.59–4.65 (1H, m, H-1), 5.33 (1H, dd, *J*=2.1, 11.0 Hz, CH=C*Ha*Hb), 5.70 (1H, dd, *J*=2.1, 17.9 Hz, CH=CHa*Hb*), 6.10 (1H, dd, *J*=11.0, 17.2 Hz, C*H*=CH$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 66.1 (C-7), 72.1 (*C*H$_2$Ph), 72.7 (*C*H$_2$Ph), 74.7 (C-2), 75.2 (C-1), 75.3 (*C*H$_2$Ph), 78.5 (C-3), 82.9 (C-4), 106.7 (C-5), 118.3 (CH=*C*H$_2$), 133.0 (*C*H=CH$_2$). HRMS (ESI): *m*/*z* calcd for $C_{29}H_{30}O_5\cdot Na^+$: 481.1985; found: 481.1999.

### 3.1.10. (1R,2R,3R,4S,5R)-2,3,4-Tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane-5-methanol (**2**)

Ozone was bubbled through a stirred solution of **16** (21.7 mg, 0.047 mmol) in $CH_2Cl_2$ (5 mL) at −78 °C for 45 min. $Ph_3P$ (62.2 mg, 0.237 mmol) was added to the reaction mixture. The reaction temperature was then allowed to increase to rt, and the solvent was evaporated under reduced pressure. After the reaction mixture was dissolved in THF (4 mL), $NaBH_4$ (15.1 mg, 0.399 mmol) was added at 0 °C and stirred for 3 h. The reaction was then quenched by addition of a solution of ~30% citric acid (5 mL). The reaction mixture was extracted with AcOEt (5 mL), and the organic layer was washed with water and brine. After the organic layer was dried over anhydrous $Na_2SO_4$, the solvent was filtered and evaporated under reduced pressure. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=3:1) to give **2** (16.1 mg, 72% yield) as amorphous crystals. $[\alpha]_D^{23}$ −45 (*c* 0.8, $CHCl_3$). IR (KBr) 3486, 3087, 3063, 3031, 2962, 2904, 2871, 1496, 1454, 1371, 1358, 1241, 1146, 1090, 1079, 1044, 1017, 860, 831, 803, 747, 696 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 3.63 (1H, dd, *J*=0.7, 8.3 Hz, Ha-7), 3.67–3.68 (1H, m, H-2), 3.74–3.83 (4H, m, H-4, Hb-7, C*H*$_2$OH), 3.93 (1H, d, *J*=8.9 Hz, H-3), 4.57–4.63 (1H, m, H-1). $^{13}$C NMR ($CDCl_3$): $\delta$ 62.0 (*C*H$_2$OH), 66.6 (C-7), 72.1 (*C*H$_2$Ph), 72.5 (*C*H$_2$Ph), 74.6 (C-2), 75.2 (*C*H$_2$Ph), 75.5 (C-1), 78.9 (C-4), 79.8 (C-3), 107.9 (C-5). HRMS (ESI): *m*/*z* calcd for $C_{28}H_{30}O_6\cdot Na^+$: 485.1935; found: 485.1950.

### 3.1.11. (3R,4S,5R,6R)-6-[(tert-Butyldimethylsilyl)oxy]methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-one (**17**)

To a solution of (3*R*,4*S*,5*R*,6*R*)-6-[(*tert*-butyldimethylsilyl)oxy]-methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-ol[15] (197.2 mg, 0.349 mmol) in DMSO (3 mL) was added $Ac_2O$ (2 mL). The resulting mixture was stirred overnight. The remaining procedure was the same as that used for the preparation of **14**. The crude product was purified by preparative flash silica gel column chromatography (ethyl acetate/hexane=1:15) to give **17** (186.1 mg, 95% yield) as a colorless oil. $[\alpha]_D^{25}$ +70 (*c* 4.5, $CHCl_3$). IR (neat) 3064, 3031, 2952, 2928, 2856, 1757, 1455, 1362, 1097, 1074, 1028, 1007, 837, 779, 737, 697 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 0.06 (6H, s, Si(C*H*$_3$)$_2$), 0.88 (9H, s, C(C*H*$_3$)$_3$), 3.79 (1H, dd, *J*=2.8, 11.7 Hz, Ha-7), 3.87 (1H, dd, *J*=2.1, 11.7 Hz, Hb-7), 3.93 (1H, dd, *J*=6.9, 7.6 Hz, H-4), 3.97 (1H, dd, *J*=7.6, 8.2 Hz, H-5), 4.08 (1H, d, *J*=7.6 Hz, H-3), 4.30 (1H, m, H-6). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.5 (Si(*C*H$_3$)$_2$), −5.3 (Si(*C*H$_3$)$_2$), 18.2 (*C*(CH$_3$)$_3$), 25.8 (C(*C*H$_3$)$_3$), 61.6 (C-7), 73.9 (*C*H$_2$Ph), 74.0 (*C*H$_2$Ph), 74.2 (*C*H$_2$Ph), 75.7 (C-5), 77.7 (C-3), 79.4 (C-6), 81.0 (C-4), 169.6 (C-2). HRMS (ESI): *m*/*z* calcd for $C_{33}H_{42}O_6Si\cdot Na^+$: 585.2643; found: 585.2655.

### 3.1.12. (3R,4S,5R,6R)-6-tert-Butyldimethylsilyloxymethyl-3,4,5-tris(benzyloxy)-2-vinyl-tetrahydropyran-2-ol (**18**)

To a stirred solution of **17** (86.3 mg, 0.153 mmol) in tetrahydrofuran (2 mL), a 1.4 M THF solution of vinylmagnesium chloride (0.231 mL, 0.307 mmol) was added dropwise at −78 °C under Ar atmosphere. The resulting mixture was stirred at −78 °C for 3 h. The remaining procedure was the same as that used for the preparation of **15**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:4) to give **18** (72.7 mg, 80% yield) as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 0.07 (3H, s, Si(C*H*$_3$)$_2$), 0.08 (3H, s, Si(C*H*$_3$)$_2$), 0.85 (9H, s, C(C*H*$_3$)$_3$), 3.38 (1H, d, *J*=8.9 Hz, H-3), 3.77 (1H, dd, *J*=8.9, 9.6 Hz, H-5), 3.83 (1H, d, *J*=11.0 Hz, Ha-7), 3.88–3.90 (1H, m, H-6), 3.98 (1H, dd, *J*=8.9, 9.6 Hz, H-4), 3.98–4.00 (1H, m, Hb-7), 5.28 (1H, d, *J*=11.0 Hz, CH=C*Ha*Hb), 5.59 (1H, d, *J*=17.2 Hz, CH=CHa*Hb*), 5.96 (1H, dd, *J*=11.0, 17.2 Hz, C*H*=CH$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.3 (Si(*C*H$_3$)$_2$), −5.0 (Si(*C*H$_3$)$_2$), 18.3 (Si*C*(CH$_3$)$_3$), 25.9 (C(*C*H$_3$)$_3$), 61.8 (C-7), 72.7 (C-6), 75.0 (*C*H$_2$Ph), 75.7 (*C*H$_2$Ph), 75.8 (*C*H$_2$Ph), 77.7 (C-5), 83.1 (C-3), 83.3 (C-4), 96.4 (C-2), 116.8 (CH=*C*H$_2$), 138.9 (*C*H=CH$_2$). ESI-MS *m*/*z* calcd for $C_{29}H_{42}O_6Si\cdot Na^+$: 613.2956; found: 613.2972.

### 3.1.13. (1R,2R,3S,4R,5R)-2,3,4-Tris(benzyloxy)-5-vinyl-6,8-dioxabicyclo[3.2.1]octane (**19**)

To a stirred solution of TfOH (1.0 μL, 0.0113 mmol) was added **18** (136.1 mg, 0.231 mmol) in $CH_3CN$ (2 mL) at 0 °C in the presence of dry $CaSO_4$ (137.2 mg) under Ar atmosphere. The resulting mixture was stirred for 2 h. The remaining procedure was the same as that used for the preparation of **16**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:4) to give **19** (94.1 mg, 89% yield) as a colorless oil. $[\alpha]_D^{27}$ −12 (*c* 1.9, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 3.31 (1H, s, H-4), 3.33 (1H, s, H-2), 3.60 (1H, s, H-3), 3.79 (1H, dd, *J*=6.2, 6.9 Hz, Ha-7), 4.03 (1H, d, *J*=6.9 Hz, Hb-7), 4.67 (1H, br d, *J*=5.5 Hz, H-1), 5.30 (1H, dd, *J*=2.4, 10.8 Hz, CH=C*Ha*Hb), 5.66 (1H, dd, *J*=1.8, 17.4 Hz, CH=CHa*Hb*), 6.23 (1H, m, C*H*=CH$_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 65.5 (C-7), 71.0 (*C*H$_2$Ph), 71.6 (*C*H$_2$Ph), 72.6 (*C*H$_2$Ph), 74.6 (C-2), 75.6 (C-3), 75.7 (C-1), 77.6 (C-4), 105.4 (C-5), 117.6 (CH=*C*H$_2$), 134.0 (*C*H=CH$_2$). ESI-MS *m*/*z* calcd for $C_{29}H_{30}O_5Si\cdot Na^+$: 481.1985; found: 481.1941.

### 3.1.14. (1R,2R,3S,4R,5R)-2,3,4-Tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane-methanol (**3**)

Ozone was bubbled through a stirred solution of **19** (35.8 mg, 0.0781 mmol) in $CH_2Cl_2$ (5 mL) at −78 °C for 40 min. $Ph_3P$ (117.5 mg, 0.448 mmol) was added to the reaction mixture, and the reaction temperature was then allowed to increase to rt. After the solvent was evaporated under reduced pressure and tetrahydrofuran (4 mL) was added, $NaBH_4$ (25.2 mg, 0.666 mmol) was then added to the solution at 0 °C. The remaining procedure was the same as that used for the preparation of **2**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=3:1) to give **3** (26.5 mg, 73% yield) as a colorless oil. $[\alpha]_D^{27}$ −28 (*c* 1.3, $CHCl_3$). IR (neat) 3476, 3087, 3062, 3031, 2898, 1496, 1454, 1392, 1370, 1328, 1266, 1207, 1074, 1028, 938, 860, 737, 699 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 3.35 (1H, d, *J*=1.4 Hz, H-4), 3.42 (1H, s, H-2), 3.61 (1H, d, *J*=1.4 Hz, H-3), 3.71 (1H, dd, *J*=6.9, 11.7 Hz, C*Ha*HbOH), 3.76 (1H, dd, *J*=5.5, 6.9 Hz, Ha-7), 3.89 (1H, dd, *J*=6.2, 11.7 Hz, CHa*Hb*OH), 4.03 (1H, d, *J*=6.9 Hz, Hb-7), 4.67 (1H, br d, *J*=5.5 Hz, H-1). $^{13}$C NMR ($CDCl_3$): $\delta$ 62.8 (*C*H$_2$OH), 65.9 (C-7), 71.1 (*C*H$_2$Ph), 71.6 (*C*H$_2$Ph), 72.2 (*C*H$_2$Ph), 74.7 (C-2), 75.0 (C-4), 75.1 (C-3), 75.8 (C-1), 106.2 (C-5). ESI-MS *m*/*z* calcd for $C_{28}H_{30}O_6Si\cdot Na^+$: 485.1935; found: 485.1952.

### 3.1.15. (3S,4S,5R,6R)-6-[(tert-Butyldimethylsilyl)oxy]methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-one (**20**)

To a solution of (3*S*,4*S*,5*R*,6*R*)-6-[(*tert*-butyldimethylsilyl)oxy]-methyl-3,4,5-trisbenzyloxy-tetrahydropyran-2-ol (497.4 mg, 881 mmol) in DMSO (3 mL) was added $Ac_2O$ (2 mL). The resulting mixture was stirred overnight. The remaining procedure was the same as that used for the preparation of **14** to afford **20** (489.8 mg, 93% yield) as a colorless oil. $[\alpha]_{577}^{27}$ −9.6 (*c* 2.7, $CHCl_3$). IR (neat) 2952, 2927, 2855, 1772, 1471, 1455, 1254, 1107, 1028, 837, 779, 737, 698 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 0.50 (3H, s, Si(C*H*$_3$)$_2$), 0.52 (3H, s, Si(C*H*$_3$)$_2$), 0.87 (9H, s, C(C*H*$_3$)$_3$), 3.75 (1H, dd, *J*=4.8, 11.0 Hz, Ha-7), 3.78 (1H, dd, *J*=4.1, 11.0 Hz, Hb-7), 3.87 (1H, dd, *J*=2.1, 6.9 Hz, H-5), 4.05 (1H, dd, *J*=2.1, 2.8 Hz, H-4), 4.12 (1H, m, H-6), 4.35 (1H, d, *J*=2.1 Hz, H-3). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.43 (Si(*C*H$_3$)$_2$), −5.42 (Si(*C*H$_3$)$_2$), 18.2 (*C*(CH$_3$)$_3$), 25.8 (C(*C*H$_3$)$_3$), 62.5 (C-7), 71.8 (*C*H$_2$Ph), 72.8 (*C*H$_2$Ph), 72.8 (*C*H$_2$Ph), 75.2 (C-5), 75.8 (C-3), 76.7 (C-4), 80.0 (C-6), 169.4 (C-2). ESI-MS *m*/*z* calcd for $C_{33}H_{42}O_6Si\cdot Na^+$: 585.2643; found: 585.2648.

*3.1.16. (3S,4S,5R,6R)-6-tert-Butyldimethylsilyloxymethyl-3,4,5-tris(benzyloxy)-2-vinyl-tetrahydropyran-2-ol (**21**)*

To a stirred solution of **20** (86.3 mg, 0.153 mmol) in toluene (3 mL), a 1.3 M THF solution of vinylmagnesium chloride (0.231 mL, 0.307 mmol) was added dropwise at −78 °C in the presence of dry $CeCl_3$ (61.7 mg, 0.250 mmol) under Ar atmosphere. The resulting mixture was stirred at −78 °C for 1 h. The remaining procedure was the same as that used for the preparation of **15**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/benzene=1:9) to give **21** (70.5 mg, 64% yield) as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 0.03 (3H, s, Si($CH_3$)$_2$), 0.05 (3H, s, Si($CH_3$)$_2$), 0.87 (9H, s, C($CH_3$)$_3$), 3.73 (1H, d, $J$=2.8 Hz, H-3), 3.80–3.83 (2H, m, H-5, Ha-7), 3.93 (1H, dd, $J$=4.8, 11.7 Hz, Hb-7), 4.09–4.12 (2H, m, H-2, H-6), 5.19 (1H, dd, $J$=1.4, 11.0 Hz, CH=C*Ha*Hb), 5.47 (1H, dd, $J$=1.4, 17.2 Hz, CH=CHa*Hb*), 6.12 (1H, m, C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.4 (Si($CH_3$)$_2$), −5.1 (Si($CH_3$)$_2$), 18.2 (*C*($CH_3$)$_3$), 25.9 (C($CH_3$)$_3$), 62.6 (C-7), 72.4 ($CH_2$Ph), 73.9 (C-5), 74.58 ($CH_2$Ph), 74.61 (C-4), 75.1 ($CH_2$Ph), 79.2 (C-3), 81.2 (C-6), 97.4 (C-2), 115.6 (CH=$CH_2$), 140.6 (*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{29}H_{42}O_6Si\cdot Na^+$: 613.2956; found: 613.2985.

*3.1.17. (1R,2R,3S,4S,5R)-2,3,4-Tris(benzyloxy)-5-vinyl-6,8-dioxabicyclo[3.2.1]octane (**22**)*

To a stirred solution of TfOH (0.29 μL, 0.00328 mmol) was added **21** (38.1 mg, 0.0645 mmol) in $CH_3CN$ (2 mL) at 0 °C in the presence of dry $CaSO_4$ (49.4 mg) under Ar atmosphere. The resulting mixture was stirred for 1 h. The remaining procedure was the same as that used for the preparation of **16** to afford **22** (26.2 mg, 89% yield) as a colorless oil. $[\alpha]_D^{27}$ −28 (*c* 0.68, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 3.49 (1H, t, $J$=2.1 Hz, H-2), 3.34 (1H, d, $J$=5.5 Hz, H-4), 3.80 (1H, dt, $J$=2.1, 5.5 Hz, H-3), 3.86 (1H, dd, $J$=6.9, 6.2 Hz, Ha-7), 4.26 (1H, d, $J$=6.9 Hz, Hb-7), 4.54 (1H, br d, $J$=6.2 Hz, H-1), 5.33 (1H, dd, $J$=1.4, 11.0 Hz, CH=C*Ha*Hb), 5.71 (1H, dd, $J$=1.4, 17.2 Hz, CH=CHa*Hb*), 3.17 (1H, m, C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 65.8 (C-7), 71.3 ($CH_2$Ph), 72.3 ($CH_2$Ph), 73.3 ($CH_2$Ph), 74.9 (C-3), 75.3 (C-1), 76.6 (C-2), 77.2 (C-4), 105.9 (C-5), 117.7 (CH=$CH_2$), 133.8 (*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{29}H_{30}O_5SiNa^+$: 481.1985; found: 481.1985.

*3.1.18. (1R,2R,3S,4S,5R)-2,3,4-Tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane-5-methanol (**4**)*

Ozone was bubbled through a stirred solution of **22** (13.6 mg, 0.0297 mmol) in $CH_2Cl_2$ (5 mL) at −78 °C for 30 min. $Ph_3P$ (40.4 mg, 0.154 mmol) was added to the reaction mixture, and the reaction temperature was then allowed to increase to rt. After the solvent was evaporated under reduced pressure and tetrahydrofuran (4 mL) was added, $NaBH_4$ (11.1 mg, 0.293 mmol) was then added to the solution at 0 °C. The resulting mixture was stirred for 2.5 h. The remaining procedure was the same as that used for the preparation of **2**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=2:1) to give **4** (10.9 mg, 77% yield) as a colorless oil. $[\alpha]_D^{27}$ +15 (*c* 0.55, $CHCl_3$). IR (neat) 3476, 3063, 3032, 2921, 1496, 1454, 1366, 1329, 1266, 1213, 1093, 1027, 737, 700 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 3.51 (1H, t, $J$=2.1 Hz, H-2), 3.73 (1H, d, $J$=12.4 Hz, H-4), 3.77 (1H, ddd, $J$=0.7, 7.6 Hz, $J$=12.4 Hz, Ha-7), 3.82–3.84 (2H, m, C$H_2$OH), 3.92 (1H, dd, $J$=0.7, 3.4 Hz, H-3), 4.27 (1H, d, $J$=7.6 Hz, Hb-7), 4.54–4.56 (1H, m, H-1). $^{13}$C NMR ($CDCl_3$): $\delta$ 62.4 (*C*H$_2$OH), 66.4 (C-7), 71.4 (*C*H$_2$Ph), 71.6 (*C*H$_2$Ph), 73.3 (*C*H$_2$Ph), 74.2 (C-4), 74.3 (C-3), 75.4 (C-1), 76.4 (C-2), 106.9 (C-5). ESI-MS $m/z$ calcd for $C_{29}H_{30}O_5Si\cdot Na^+$: 485.1935; found: 485.1972.

*3.1.19. (3S,4R,5R,6R)-2-Allyl-[(6-tert-butyldimethylsilyl)oxy]-methyl-3,4,5-tris(benzyloxy)-tetrahydropyran-2-ol (**23**)*

To a stirred solution of **14** (81.9 mg, 0.146 mmol) in THF (3 mL), a 1.0 M diethyl ether solution of allylmagnesium bromide (0.175 mL, 0.175 mmol) was added dropwise at −78 °C under Ar atmosphere. The resulting mixture was stirred at −78 °C for 1.5 h. The remaining procedure was the same as that used for the preparation of **15**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:6) to give **23** (81.1 mg, 92% yield) as a colorless oil. $^1$H NMR ($CDCl_3$): $\delta$ 0.05 (3H, s, Si($CH_3$)$_2$), 0.06 (3H, s, Si($CH_3$)$_2$), 0.88 (9H, s, C($CH_3$)$_3$), 2.42–2.44 (2H, m, $CH_2$CH=$CH_2$), 3.33 (1H, d, $J$=3.6 Hz, H-3), 3.80 (1H, dd, $J$=2.4, 4.0 Hz, H-4), 3.80 (1H, d, $J$=11.3 Hz, Ha-7), 3.95–4.01 (3H, m, H-5, H-6, Hb-7), 5.04–5.07 (2H, m, $CH_2$CH=C$H_2$), 5.88 (1H, m, $CH_2$C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ −5.31 (Si(*C*H$_3$)$_2$), −5.26 (Si(*C*H$_3$)$_2$), 18.3 (Si*C*(CH$_3$)$_3$), 25.9 (SiC(*C*H$_3$)$_3$), 41.6 ($CH_2$CH=$CH_2$), 62.5 (C-7), 68.7 (C-6), 71.3 (C-5), 72.4 ($CH_2$Ph), 71.6 ($CH_2$Ph), 73.3 ($CH_2$Ph), 74.4 (C-4), 76.5 (C-3), 98.3 (C-2), 117.1 ($CH_2$CH=$CH_2$), 133.5 ($CH_2$*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{36}H_{48}O_6Si\cdot Na^+$: 627.3112; found: 627.3147.

*3.1.20. (1R,2R,3R,4S,5R)-5-Allyl-2,3,4-tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**24**)*

To a stirred solution of TfOH (0.58 μL, 0.066 mmol) was added **23** (81.1 mg, 0.134 mmol) in $CH_3CN$ (2 mL) at 0 °C in the presence of dry $CaSO_4$ (120.0 mg) under Ar atmosphere. The resulting mixture was stirred for 2 h. The remaining procedure was the same as that used for the preparation of **16**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:4) to give **24** (62.5 mg, 99% yield) as a colorless oil. $[\alpha]_D^{28}$ −66 (*c* 3.1, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 2.59 (1H, dd, $J$=8.2, 15.1 Hz, C*Ha*HbCH=$CH_2$), 2.72 (1H, dd, $J$=6.2, 15.8 Hz, CHa*Hb*CH=$CH_2$), 3.58 (1H, d, $J$=8.2 Hz, Ha-7), 3.66 (1H, s, H-2), 3.73 (1H, dd, $J$=6.2, 6.9 Hz, Hb-7), 3.78–3.81 (2H, m, H-4, H-3), 5.10–5.13 (2H, m, CHaHbCH=C$H_2$), 5.86 (1H, m, $CH_2$C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 37.2 (*C*H$_2$CH=CH$_2$), 66.3 (C-7), 71.8 (*C*H$_2$Ph), 72.3 (*C*H$_2$Ph), 74.4 (C-2), 75.0 (C-1), 75.2 (*C*H$_2$Ph), 79.0 (C-3 or C-4), 81.6 (C-3 or C-4), 108.8 (C-5), 118.4 ($CH_2$CH=$CH_2$), 131.8 ($CH_2$*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{30}H_{32}O_5\cdot Na^+$: 495.2142; found: 495.2106.

*3.1.21. (1R,2R,3R,4S,5R)-2,3,4-Tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane-5-ethanol (**5**)*

Ozone was bubbled through a stirred solution of **24** (31.6 mg, 0.0669 mmol) in $CH_2Cl_2$ (5 mL) at −78 °C for 30 min. $Ph_3P$ (93.0 mg, 0.355 mmol) was added to the reaction mixture, and the reaction temperature was then allowed to increase to rt. After the solvent was evaporated under reduced pressure and tetrahydrofuran (4 mL) was added, $NaBH_4$ (6.8 mg, 0.180 mmol) was then added to the solution at 0 °C. The resulting mixture was stirred for 3 h. The remaining procedure was the same as that used for the preparation of **2** to afford **5** (27.0 mg, 85% yield) as a colorless oil. $[\alpha]_D^{27}$ −5.6 (*c* 1.4, $CHCl_3$). IR (neat) 3475, 3088, 3063, 3033, 3009, 2968, 2891, 1497, 1454, 1398, 1370, 1361, 1265, 1208, 1142, 1098, 1048, 969, 941, 796, 734, 697 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.91 (1H, m, C*Ha*HbCH$_2$OH), 2.34 (1H, m, CHa*Hb*CH$_2$OH), 3.61 (1H, dd, $J$=0.7, 8.2 Hz, Ha-7), 3.67 (1H, dd, $J$=2.7, 4.1 Hz, H-2), 3.74–3.79 (5H, m, H-3, H-4, Hb-7, $CH_2$C$H_2$OH), 4.58–4.60 (1H, m, H-1). $^{13}$C NMR ($CDCl_3$): $\delta$ 34.2 (*C*H$_2$CH$_2$OH), 55.7 (CH$_2$*C*H$_2$OH), 66.4 (C-7), 72.1 (*C*H$_2$Ph), 72.4 (*C*H$_2$Ph), 74.4 (C-2), 75.1 (C-1), 75.5 (*C*H$_2$Ph), 798.6 (C-3 or C-4), 82.0 (C-3 or C-4), 109.9 (C-5). ESI-MS $m/z$ calcd for $C_{29}H_{32}O_6\cdot Na^+$: 499.2091; found: 499.2088.

*3.1.22. (3S,4S,5R,6R)-2-Allyl-6-hydroxymethyl-3,4,5-tris(benzyloxy)-tetrahydropyran-2-ol (**26**) and (2R,3R,4S,5S)-6-allyl-6-hydroxy-3,4,5-tris(benzyloxy)-tetrahydropyran-2-ylmethyl acetate (6-O-acetyl-1-C-allyl-2,3,4-tri-O-benzyl-D-mannopyranose)*

To a stirred solution of **25**[16] (36.1 mg, 0.0736 mmol) in THF (2 mL), a 1.0 M diethyl ether solution of allylmagnesium bromide (0.177 mL, 0.177 mmol) was added dropwise at −78 °C under Ar atmosphere. The resulting mixture was stirred at −78 °C for 1 h. The remaining procedure was the same as that used for the preparation of **15**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:1) to give **26** (30.6 mg, 85% yield) as a colorless oil and the intermediate, (2*R*,3*R*,4*S*,5*S*)-6-allyl-6-

hydroxy-3,4,5-tris(benzyloxy)-tetrahydropyran-2-ylmethyl acetate (3.6 mg, 9% yield), as a colorless oil. Compound **26**: $^1$H NMR ($CDCl_3$): $\delta$ 2.19 (1H, dd, $J$=9.6, 13.8 Hz, C*Ha*HbCH=$CH_2$), 2.74 (1H, dd, $J$=4.8, 13.8 Hz, CHa*Hb*CH=$CH_2$), 3.70–3.73 (1H, m, Ha-7), 3.74 (1H, d, $J$=2.7 Hz, H-3), 3.77–3.81 (2H, m, H-6, Hb-7), 3.98 (1H, t, $J$=9.6 Hz, H-5), 4.15 (1H, dd, $J$=1.4, 9.6 Hz, H-4), 5.15 (1H, d, $J$=17.2 Hz, $CH_2$CH=C*Ha*Hb), 5.47 (1H, d, $J$=10.3 Hz, $CH_2$CH=CHa*Hb*), 5.79 (1H, m, $CH_2$C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 42.4 (*C*$H_2$CH=$CH_2$), 62.4 (C-7), 72.7 (*C*$H_2$Ph), 72.8 (C-6), 74.7 (*C*$H_2$Ph), 75.0 (C-5), 75.1 (*C*$H_2$Ph), 78.7 (C-3), 81.7 (C-4), 97.9 (C-2), 121.3 ($CH_2$CH=*C*$H_2$), 131.4 ($CH_2$*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{30}H_{34}O_6\cdot Na^+$: 513.2248; found: 513.2260.

*3.1.22.1. (2R,3R,4S,5S)-6-Allyl-6-hydroxy-3,4,5-tris(benzyloxy)-tetrahydropyran-2-ylmethyl acetate (6-O-acetyl-1-C-allyl-2,3,4-tri-O-benzyl-D-mannopyranose).* $^1$H NMR ($CDCl_3$): $\delta$ 2.03 (3H, s, CO*C*$H_3$), 2.18 (1H, dd, $J$=9.6, 13.7 Hz, C*Ha*HbCH=$CH_2$), 2.77 (1H, dd, $J$=4.8, 13.7 Hz, CHa*Hb*CH=$CH_2$), 3.75 (1H, d, $J$=2.7 Hz, H-5), 3.91 (1H, t, $J$=9.6 Hz, H-3), 3.91–3.99 (1H, m, H-2), 4.15 (1H, dd, $J$=2.9, 8.9 Hz, H-4), 4.23 (1H, $J$=4.8, 12.3 Hz, C*Ha*HbOAc), 4.32 (1H, dd, $J$=2.1, 11.7 Hz, CHa*Hb*OAc), 5.15 (1H, d, $J$=17.2 Hz, $CH_2$CH=C*Ha*Hb), 5.25 (1H, d, $J$=10.3 Hz, $CH_2$CH=CHa*Hb*), 5.80 (1H, m, $CH_2$C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 20.9 (CO*C*$H_3$), 42.4 (*C*$H_2$CH=$CH_2$), 63.9 (*C*$H_2$OAc), 70.8 (C-2), 72.6 (*C*$H_2$Ph), 74.5 (C-3), 74.9 (*C*$H_2$Ph), 75.1 (*C*$H_2$Ph), 77.5 (C-5), 81.8 (C-4), 97.8 (C-6), 121.2 ($CH_2$CH=*C*$H_2$), 132.0 ($CH_2$*C*H=$CH_2$), 171.0 (*C*OCH$_3$). ESI-MS $m/z$ calcd for $C_{32}H_{36}O_7\cdot Na^+$: 555.2353; found: 555.2356.

*3.1.23. (1R,2R,3S,4S,5R)-5-Allyl-2,3,4-tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane (**27**)*

To a stirred solution of TfOH (1.20 μL, 0.0126 mmol) was added **26** (123.7 mg, 0.252 mmol) in $CH_3CN$ (2 mL) at 0 °C in the presence of dry $CaSO_4$ (158.1 mg) under Ar atmosphere. The resulting mixture was stirred for 1.5 h. The remaining procedure was the same as that used for the preparation of **16**. The crude mixture was separated by preparative TLC (silica gel ethyl acetate/hexane=1:3) to give **27** (103.8 mg, 87% yield) as a colorless oil. $[\alpha]_D^{27}$ −13 (*c* 5.2, $CHCl_3$). $^1$H NMR ($CDCl_3$): $\delta$ 2.60 (1H, dd, $J$=8.2, 14.4 Hz, C*Ha*HbCH=$CH_2$), 2.79 (1H, dd, $J$=6.2, 14.4 Hz, CHa*Hb*CH=$CH_2$), 3.49 (1H, s, H-2), 3.58 (1H, d, $J$=4.8 Hz, H-4), 3.76 (1H, dd, $J$=6.2, 6.9 Hz, Ha-7), 3.82 (1H, d, $J$=4.8 Hz, H-3), 4.19 (1H, d, $J$=6.9 Hz, Hb-7), 4.50–4.52 (1H, m, H-1), 5.09 (1H, d, $J$=10.3 Hz, $CH_2$CH=C*Ha*Hb), 5.13 (1H, d, $J$=17.2 Hz, $CH_2$CH=CHa*Hb*), 5.87 (1H, m, $CH_2$C*H*=$CH_2$). $^{13}$C NMR ($CDCl_3$): $\delta$ 37.8 (*C*$H_2$CH=$CH_2$), 66.0 (C-7), 71.2 (*C*$H_2$Ph), 71.4 (*C*$H_2$Ph), 73.0 (*C*$H_2$Ph), 74.2 (C-3), 75.0 (C-1), 76.1 (C-2), 76.2 (C-4), 107.7 (C-5), 118.1 ($CH_2$CH=*C*$H_2$), 132.1 ($CH_2$*C*H=$CH_2$). ESI-MS $m/z$ calcd for $C_{30}H_{32}O_5\cdot Na^+$: 495.2142; found: 495.2182.

*3.1.24. (1R,2R,3S,4S,5R)-2,3,4-Tris(benzyloxy)-6,8-dioxabicyclo[3.2.1]octane-5-ethanol (**6**)*

Ozone was bubbled through a stirred solution of **27** (51.4 mg, 0.109 mmol) in $CH_2Cl_2$ (5 mL) at −78 °C for 30 min. $Ph_3P$ (85.0 mg, 0.324 mmol) was added to the reaction mixture, and the reaction temperature was then allowed to increase to rt. After the solvent was evaporated under reduced pressure and tetrahydrofuran (4 mL) was added, $NaBH_4$ (12.1 mg, 0.320 mmol) was then added to the solution at 0 °C. The resulting mixture was stirred for 1 h. The remaining procedure was the same as that used for the preparation of **2** to afford **6** (49.2 mg, 95% yield) as a colorless oil. $[\alpha]_D^{27}$ −5.7 (*c* 2.5, $CHCl_3$). IR (neat) 3522, 3087, 3062, 3031, 2893, 1496, 1454, 1398, 1367, 1331, 1266, 1208, 1076, 1027, 735, 699 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 1.85 (1H, ddd, $J$=2.7, 6.2, 15.1 Hz, C*Ha*HbC$H_2$OH), 2.47 (1H, ddd, $J$=2.8, 7.5, 15.1 Hz, CHa*Hb*C$H_2$OH), 3.51 (1H, s, H-2), 3.53 (1H, d, $J$=5.5 Hz, H-4), 3.77–3.83 (3H, m, Ha-7, C$H_2$C$H_2$OH), 3.82 (1H, d, $J$=6.2 Hz, H-3), 4.26 (1H, d, $J$=7.6 Hz, Hb-7), 4.47–4.55 (1H, m, H-1). $^{13}$C NMR ($CDCl_3$): $\delta$ 34.6 (*C*$H_2$CH$_2$OH), 57.7 (CH$_2$*C*$H_2$OH), 66.0 (C-7), 71.4 (*C*$H_2$Ph), 71.6 (*C*$H_2$Ph), 73.2 (*C*$H_2$Ph), 73.8 (C-3), 75.0 (C-1), 76.1 (C-2), 76.5 (C-4), 108.9 (C-5). ESI-MS $m/z$ calcd for $C_{29}H_{32}O_6\cdot Na^+$: 499.2091; found: 499.2091.

## References and notes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